Preparation of catalysts

The Pd/C, Ru/C, Rh/C and Pt/C catalysts with a metal loading of 5wt.% were prepared by the incipient wetness impregnation of activated carbon with aqueous solutions of $PdCl_2$, $RuCl_3$, $RhCl_3$ and H_2PtCl_6. After being kept at room temperature for 12 h, the catalysts were dried at 393 K for 12 h and reduced at 623 K for 2 h in a 5% H_2/Ar flow. After cooling to room temperature, the catalysts were passivated by 1% O_2/Ar flow for 6 h.

The hydroxyapatite (HAP) loaded metal catalysts (denoted as M/HAP, M = Ni, Ru, Pd, Pt) used in the hydrodeoxygenation (HDO) process were prepared by deposition-precipitation (DP) method. Taking Ni/HAP for example, 2.0 g HAP was vigorously stirred in 30 mL aqueous solution of $Ni(NO_3)_2$ for 0.5 h at room temperature. Subsequently, the pH of resultant slurry was slowly adjusted to about 8.0 with $NH_3 \cdot H_2O$ solution. The mixture was stirred for another 2 h. Finally, the solid was separated by filtration and thoroughly washed with deionized water (to remove the NO_3^-). The resultant solid material was dried at 393 K for 12 h and reduced in a 20% H_2/Ar flow at 573 K for 3 h. After being cooled down to room temperature in hydrogen flow, the Ni/HAP catalyst was passivated by 1% O_2/Ar for 6 h. Analogously, the Ru/HAP, Pd/HAP and Pt/HAP catalysts were prepared by the method, using $RuCl_3$, $PdCl_2$ and H_2PtCl_6 as the precursors. To facilitate the comparison, the theoretical metal contents in the investigated HDO catalysts were fixed at 2wt.%.

Characterization of catalysts

The specific Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) of the catalysts were measured by N_2-physisorption that was carried out at 77 K with an ASAP 2010 apparatus. Before each measurement, the acidic resin was evacuated at 373 K for 6 h.

The amounts of acid sites on the surfaces of acidic resins were measured with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System by NH_3-chemisorption. To do this, the catalyst was put into the quartz tube, pretreated with He flow at 393 K for 30 min. After the baseline was stable, NH_3 was injected in a pulse mode until the saturation. The amounts of acid sites on the surfaces of acidic resins were calculated base on the consumption of NH_3.

General experimental details for NMR and GC-MS analysis

^{1}H NMR and ^{13}C NMR spectra of the products from the HAA reaction of MFA and 2-MF were recorded at room temperature in CDCl$_3$ on Bruker AVANCE III 400 MHz instrument. The chemical shifts for ^{1}H NMR were recorded in ppm downfield using the peak of CDCl$_3$ (7.26 ppm) as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of CDCl$_3$ (77.16 ppm) as the internal standard.

GC-MS analysis of the products was carried out by a Varian Corp 450GC/320MS which was equipped with a HP-5 capillary column.
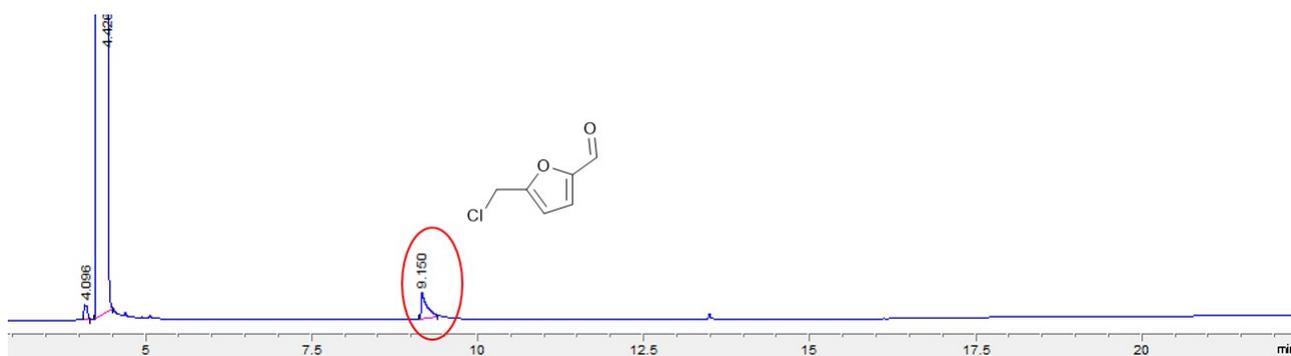
Figure S1. Gas chromatogram of the product obtained from the conversion of cellulose in the first-stage. Reaction conditions: 473 K, 1 MPa N_2, 400 rpm, 6 h; 1.5 g cellulose, 3 g NaCl, 10 mL H_2O, 20 mL organic solvent were used in the test.
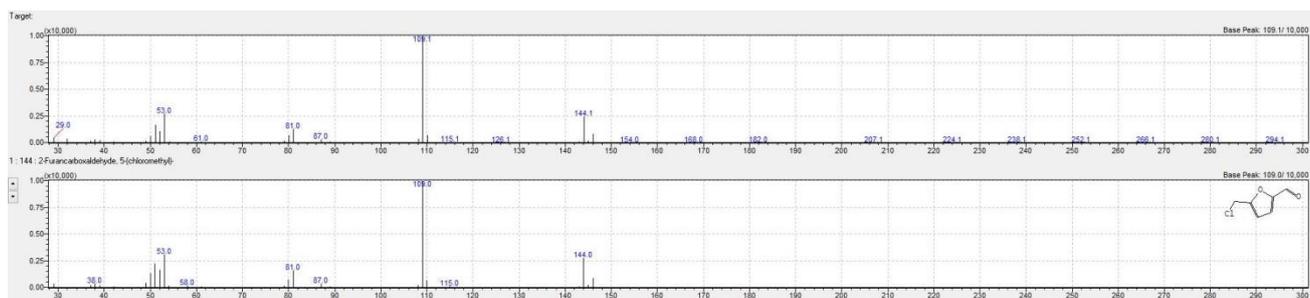
Figure S2. Mass spectrogram of the chloromethylfurfural obtained from the conversion of cellulose in the first-stage.
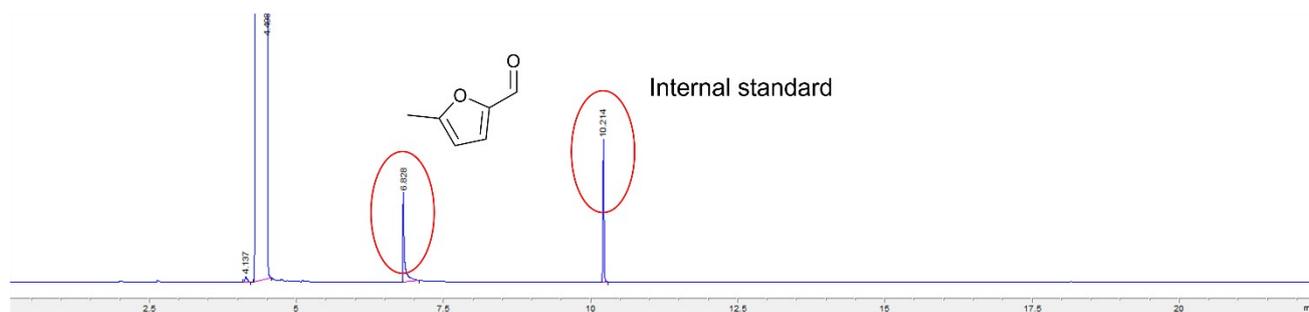
Figure S3. Gas chromatogram of the product obtained from the conversion of cellulose by the two-stage process. Reaction conditions: First stage: 473 K, 1 MPa N_2, 400 rpm, 6 h; 0.3 g cellulose, 3 g NaCl, 10 mL H_2O, 20 mL organic solvent were used in each test. Second stage: 303 K, 2 MPa H_2, 400 rpm, 2 h; the organic phase product from the first stage and 0.03 g Pd/C were used in each test.
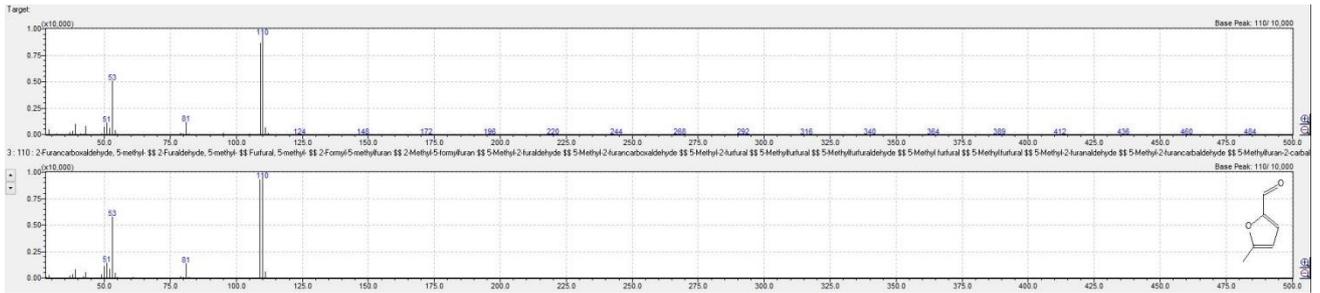
Figure S4. Mass spectrogram of the 5-methylfurfural (MFA) obtained from the two-stage conversion of cellulose.
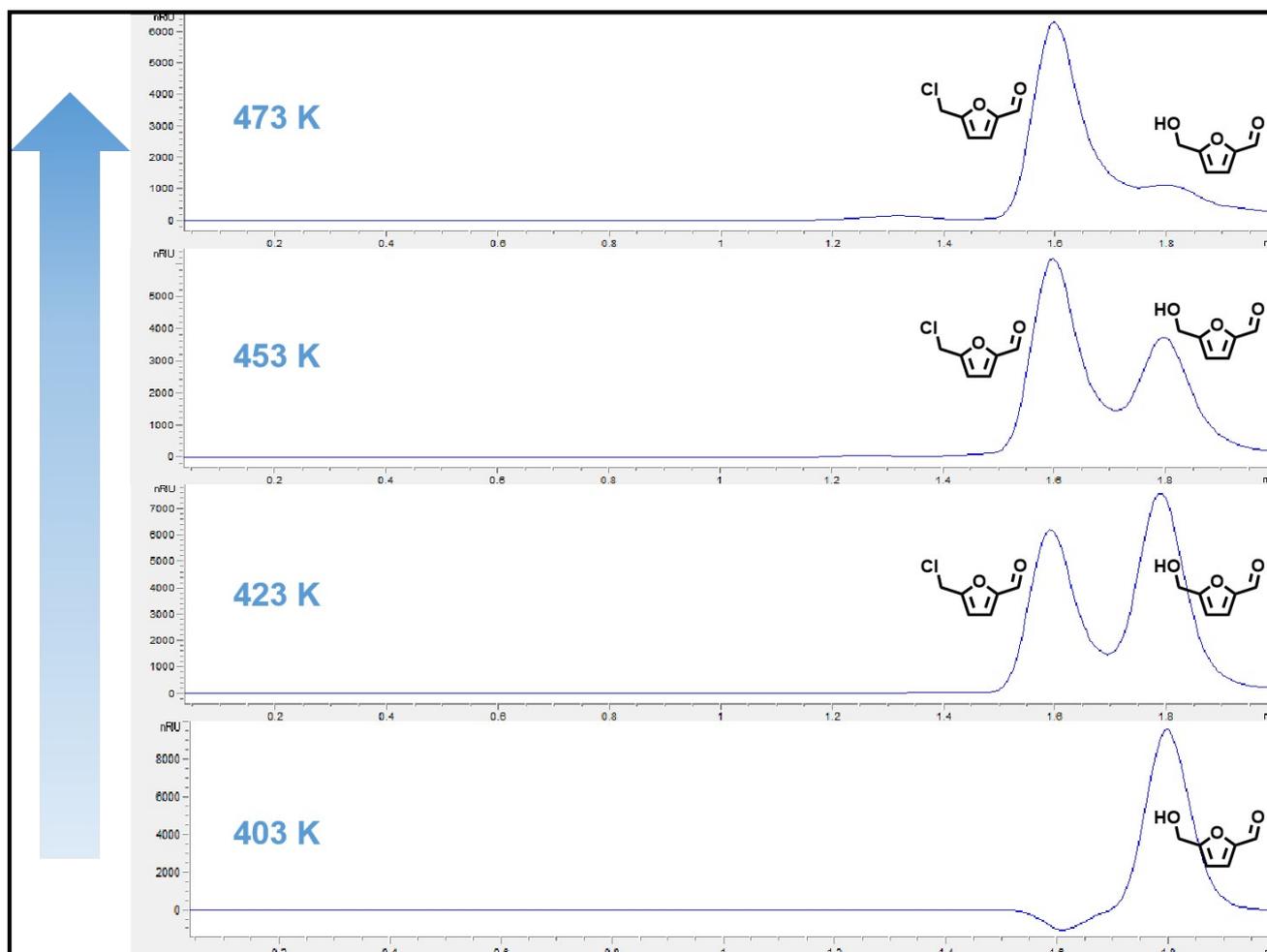
Figure S5. HPLC chromatograms of the products obtained from the conversion of cellulose at different reaction temperatures. Reaction conditions: 1 MPa N_2, 400 rpm, 6 h; 0.3 g cellulose, 3 g NaCl, 10 mL H_2O, 20 mL organic solvent were used in each test.
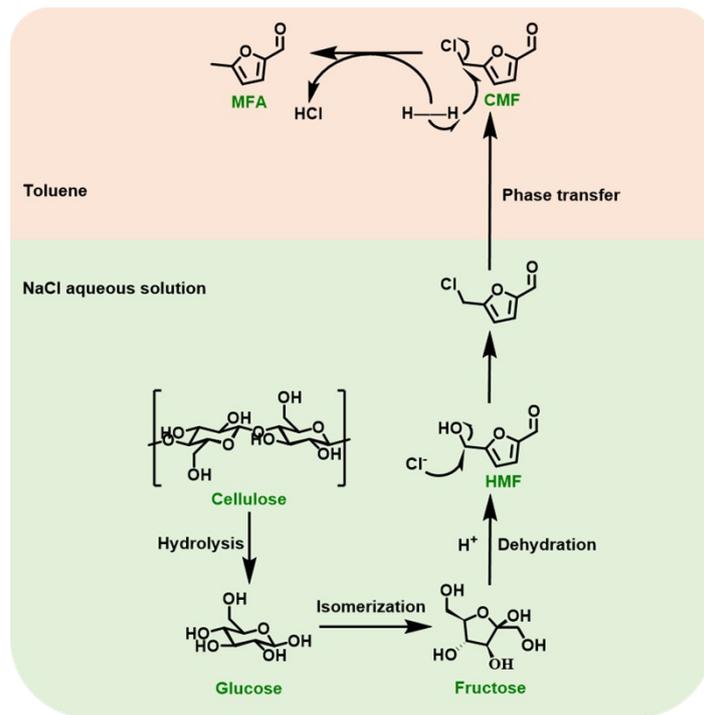
Figure S6. Reaction pathway for the synthesis of MFA from cellulose.
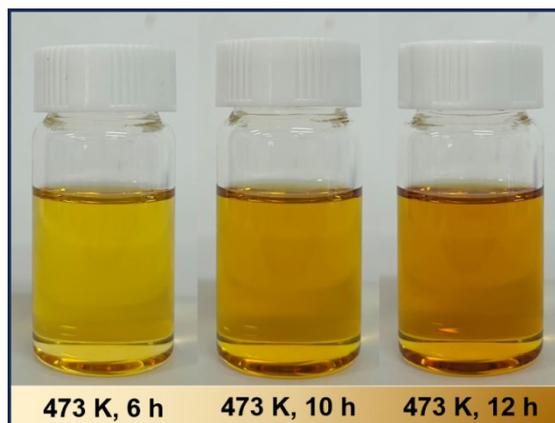
Figure S7. Photo of the products obtained from the conversion of cellulose at different reaction times. Reaction conditions: 473 K, 1 MPa N_2, 400 rpm; 0.3 g cellulose, 3 g NaCl, 10 mL H_2O, 20 mL organic solvent were used in each test.
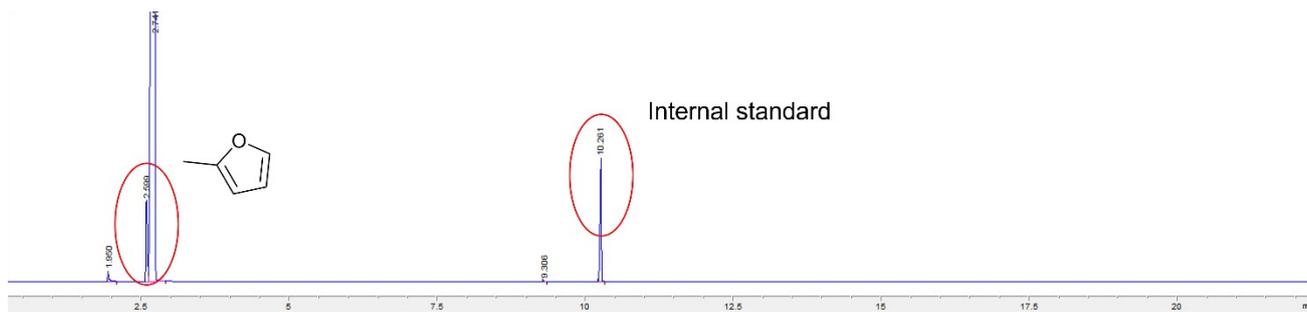
Figure S8. Gas chromatogram of the product obtained from decarbonylation of MFA. Reaction conditions: 443 K, 4 h, 400 rpm; 1 mmol MFA, 0.05 g Pd/C and 5 mL ethyl acetate were used in the test.
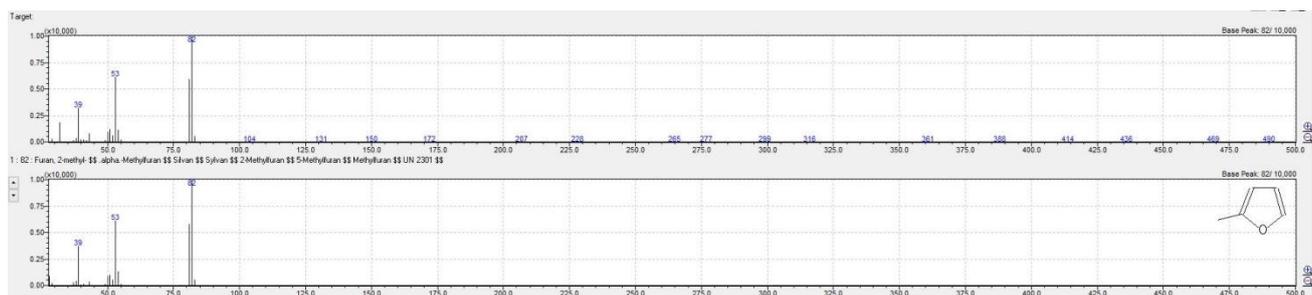
Figure S9. Mass spectrogram of the 2-methylfuran (2-MF) obtained from the decarbonylation of MFA.
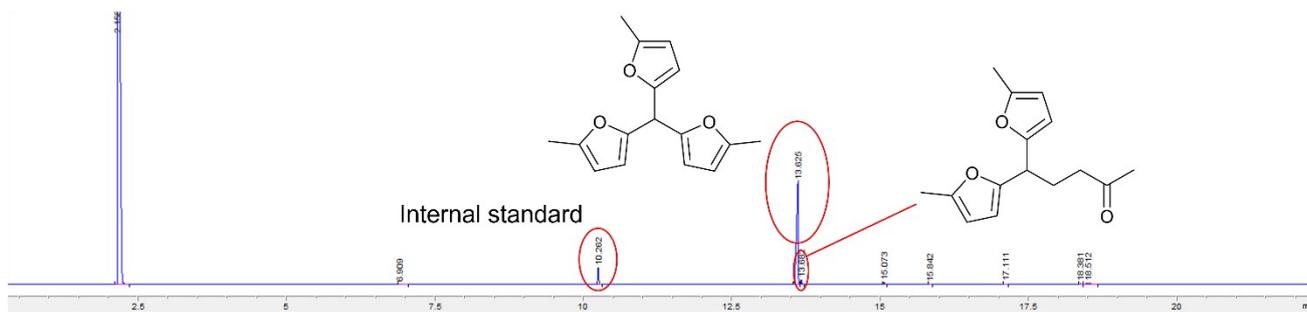
Figure S10. Gas chromatogram of the product obtained from HAA of MFA and 2-MF. Reaction conditions: 333 K, 400 rpm, 4 h; 5 mmol MFA, 10 mmol 2-MF and 0.09 g Nafion resin were used for each test.
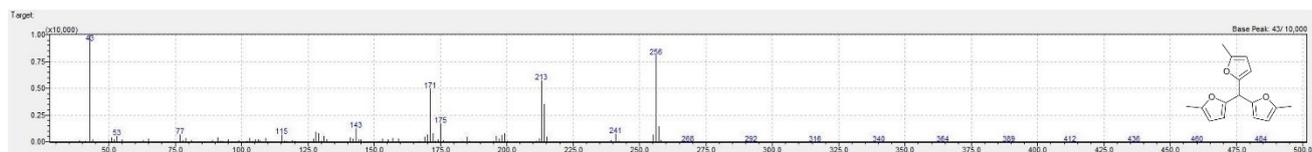
Figure S11. Mass spectrogram of the TMFM obtained from the HAA reaction of MFA and 2-MF.

¹H NMR (400 MHz, CDCl₃)
δ 6.00, 5.92, 5.40, 2.28.

¹³C NMR (101 MHz, CDCl₃)
δ 150.36, 149.65, 106.74, 105.16, 38.10, 12.56.
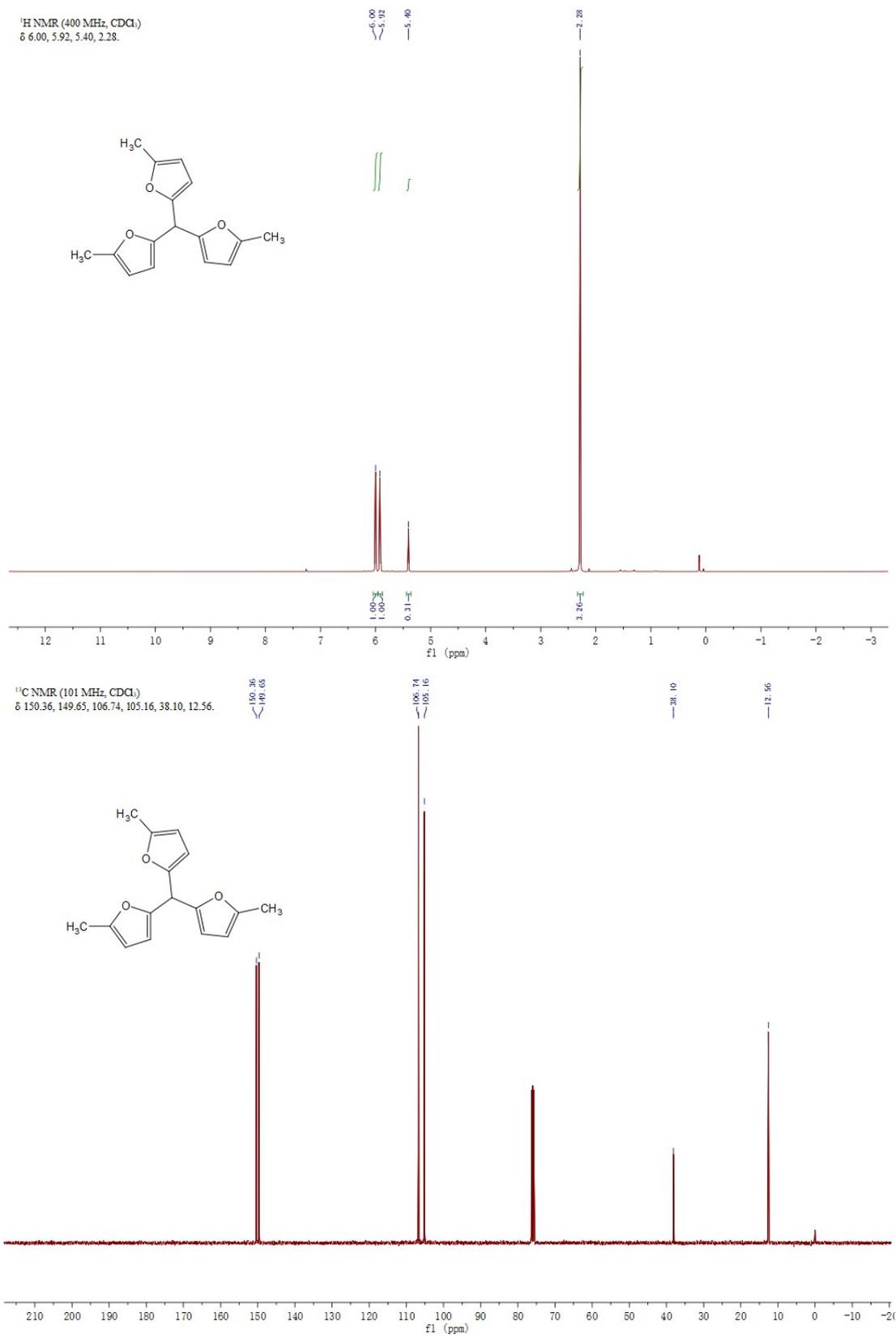
Figure S12. ¹H-NMR and ¹³C-NMR spectra of the TMFM obtained from the HAA reaction of MFA and 2-MF.
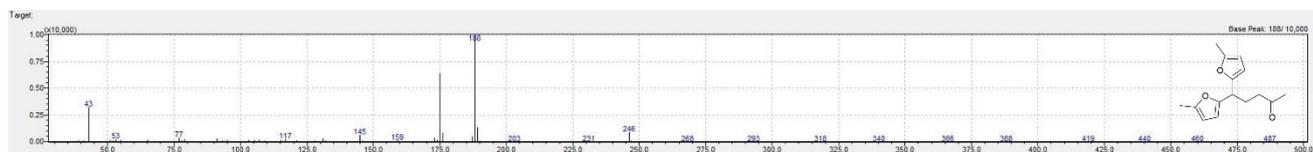
Figure S13. Mass spectrogram of the BMFPO generated during the HAA reaction of MFA and 2-MF.
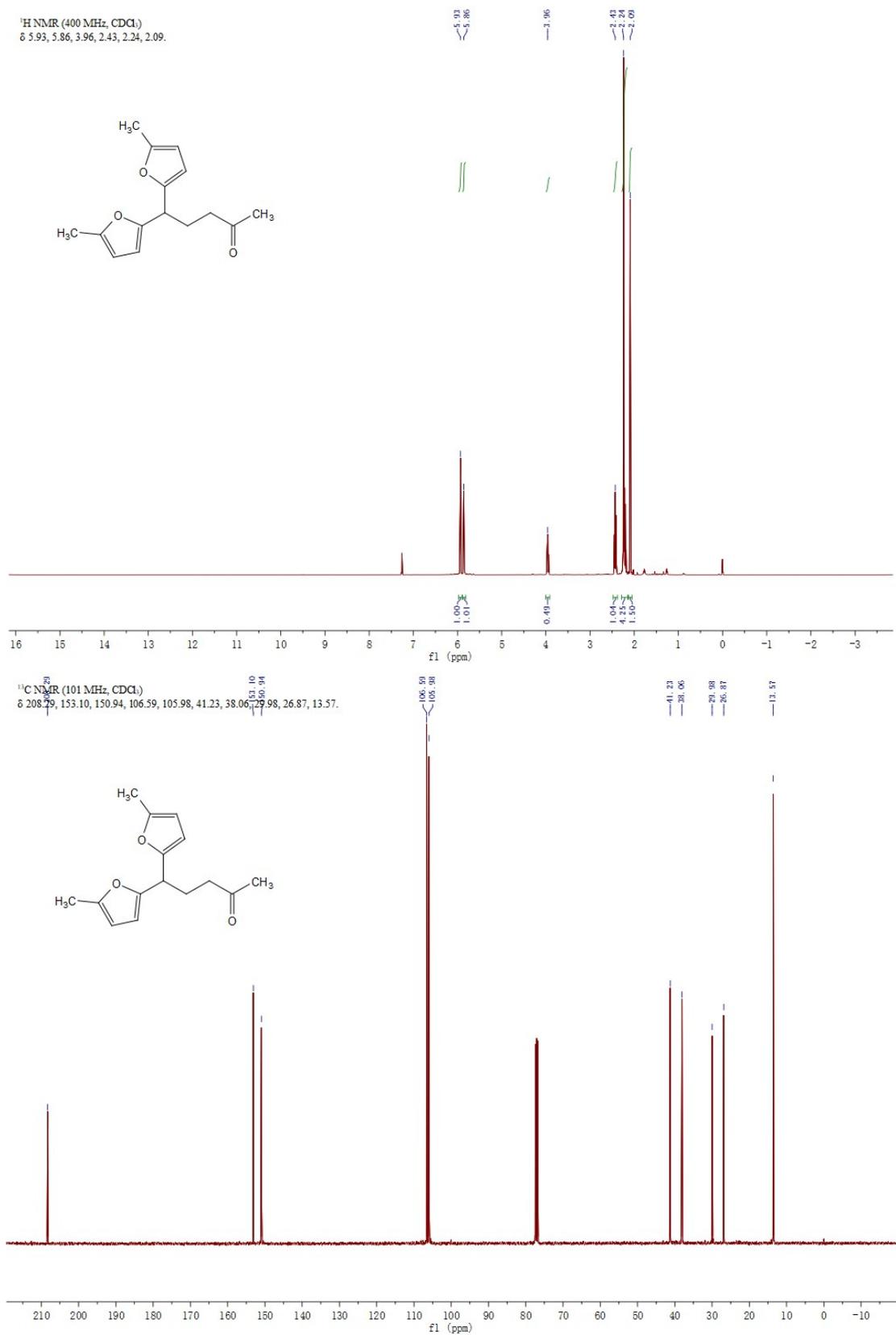
Figure S14. ^{1}H-NMR and ^{13}C-NMR spectra of the BMFPO generated during the HAA reaction of MFA and 2-MF.
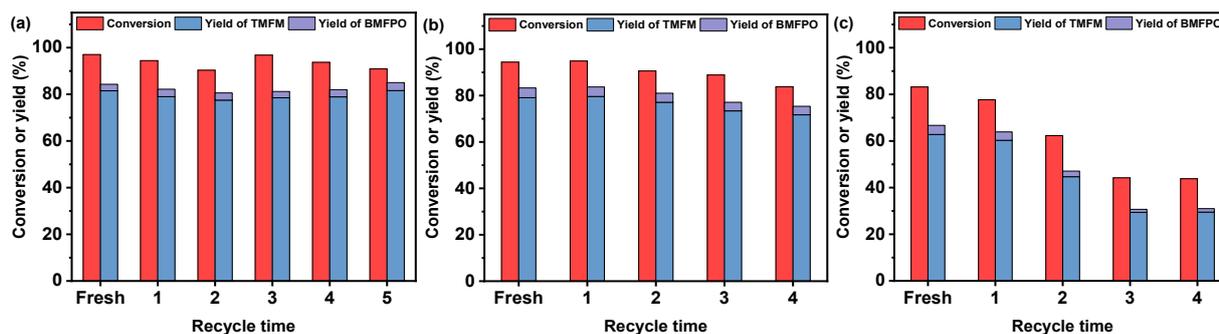
Figure S15. Conversion of 2-MF and the yields of TMFM and BMFPO over Nafion (a), Amberlyst-15 (b) and Amberlyst-36 (c) resins as the function of recycle time. Reaction conditions: 333 K, 400 rpm, 2 h; 5 mmol MFA, 10 mmol 2-MF, 0.09 g catalyst were used for each test.
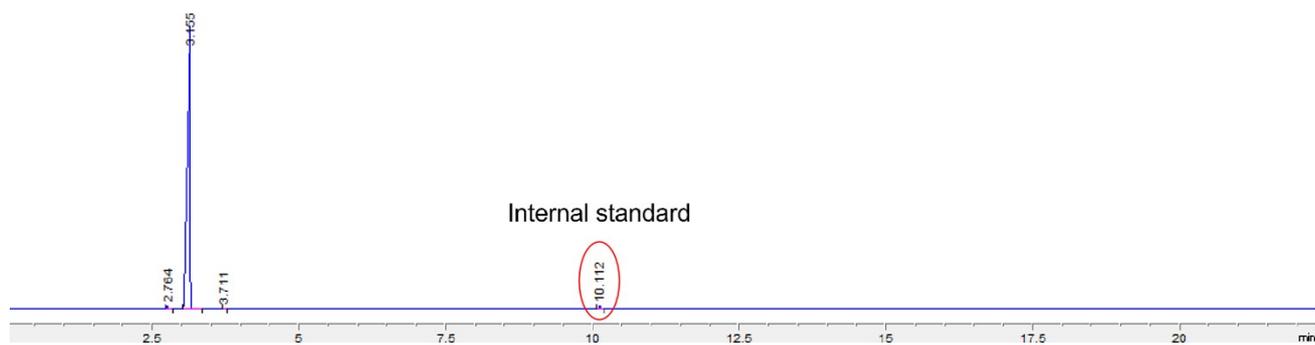
Figure S16. Gas chromatogram of blank control experiment for HDO. Reaction conditions: 493 K, 4 MPa H$_2$, 500 rpm, 24 h; 30 mL cyclohexane, 0.1 g Ni/HAP and 0.1 g H-ZSM-5 were used for the test.
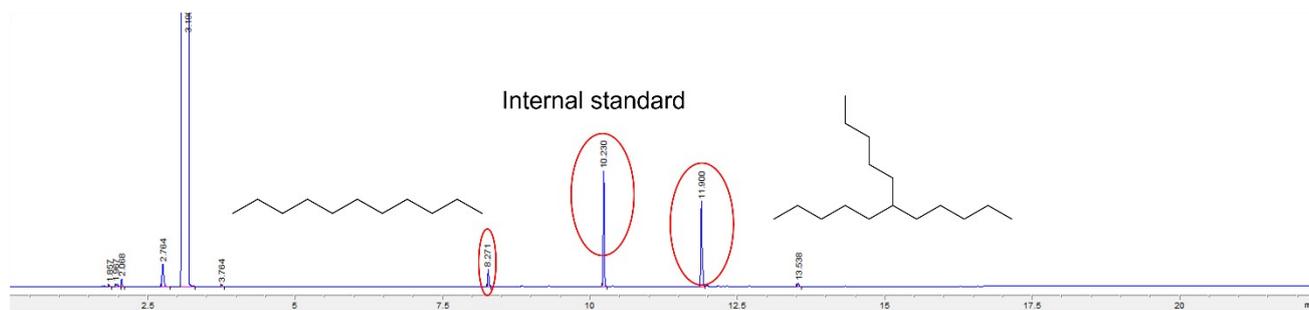
Figure S17. Gas chromatogram of the product obtained from HDO of TMFM. Reaction conditions: 453 K, 4 MPa H₂, 500 rpm, 24 h; 0.1 g TMFM, 30 mL cyclohexane, 0.1 g Ni/HAP and 0.1 g H-ZSM-5 were used for the test.

Figure S18. Mass spectrogram of the C$_{16}$ alkane obtained from HDO of TMFM.
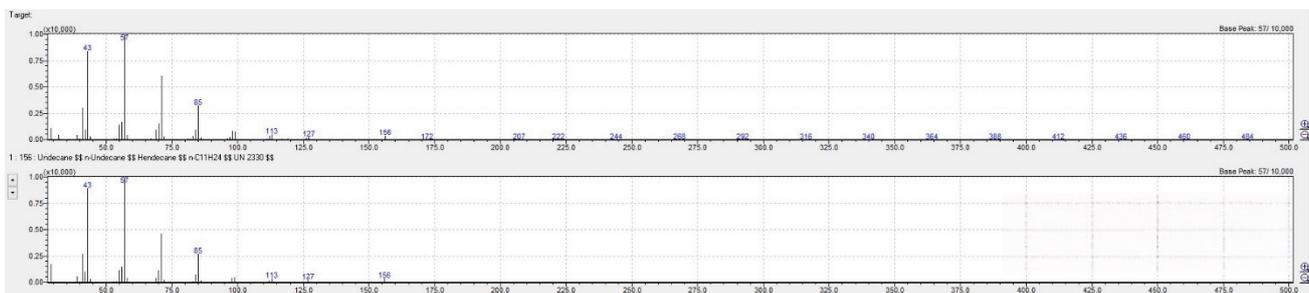
Figure S19. Mass spectrogram of the C$_{11}$ alkane obtained from HDO of TMFM.

Table S1. Comparison of the different routes for the synthesis of jet fuel range alkanes with cellulose.

Previous works:

		Main products	Overall yield	Reference
Route 1: Cellulose — Step 1: Hydrolysis/dehydration, H₂SO₄, 423 K, 4 h — Step 2: Reduction, RuRe/C, 423 K, 0.5 MPa H₂ — Step 3: Decarboxilation, SiO₂/Al₂O₃, 648 K + CO₂ — Step 4: Oligomerization, Amberlyst-70, 443 K → C₈-C₂₀ Branched alkenes		C₈-C₂₀ Alkanes	36%	1
Route 2: Cellulose — Step 1: Hydrolysis/dehydration, H₂SO₄, 423 K — Step 2: Dehydration, K10, 438 K, 6.5 KPa — Step 3: Dimerization, K₂CO₃, 343 K — Step 4: Oligomerization, Ir-ReOₓ/SiO₂, 493 K, 5.4 MPa, 7 h		C₇-C₁₀ Alkanes	47%	2,3
Route 3: Cellulose — Step 1: Hydrolysis/dehydration, HCl, 473 K, 10 min — Step 2: Dehydration, H-ZSM-5/SiO₂, 403 K, 0.01 MPa — Step 3: C-C bond formation, K₂CO₃, 353 K, 3.5 min — Step 4: Hydrodeoxygenation, Pd/C, 573 K, 5 MPa H₂ → C₆-C₁₅ Branched alkenes		C₆-C₁₅ Alkanes	43%	4
Route 4: Cellulose — Step 1: Hydrolysis/dehydration, H₂SO₄, 423 K — Step 2: Dehydration, K10, 438 K, 6.5 KPa — Step 3: Dimerization, K₂CO₃, 343 K — Step 4: Hydrodecarboxylation, Pd/γ-Al₂O₃, 573 K, 1 MPa H₂ (Minor product)		C₆-C₉ Alkanes	35%	2,3,5
Route 5: Hemicellulose — Step 1: Steam stripping, 428 K-438 K; Cellulose — Step 2: Hydrolysis/dehydration, 458 K-463 K — Step 3: Cross condensation, NaOH, 333 K — Step 4: Hydrodecarboxylation, Ru/Al₂O₃, 608-623 K, 0.013 h⁻¹ H₂ → C₈-C₁₅ Paraffins		C₈-C₁₅ Paraffins	25%	6
Route 6: Cellulose — Step 1: Hydrogenolysis, HCl + Pd/C, H₂, 373 K — Step 2: Aldol condensation/hydrogenation/hydrodeoxygenation, Cu₂Ni/MgO-p + Ni/H-Beta, H₂, 473 K		C₁₂ Alkanes	48%	7

This work:

		Main products	Overall yield
Route 7: Cellulose — Step 1: Cascade hydrolysis/isomerization/dehydration/chlorination, Toluene/NaCl aqueous solution — Hydrodechlorination at room temperature, Pd/C, H₂ — Step 2: Decarbonylation, Pd/C, 443 K — Step 3: Hydroxyalkylation/alkylation (HAA), Nafion, 333 K — Step 4: Hydrodeoxygenation, Ni/HAP + H-ZSM-5, 493 K → C₁₁ and C₁₆ Branched alkenes		C₁₁ and C₁₆ Alkanes	54%

References

1. S. Murat Sen, C. A. Henao, D. J. Braden, J. A. Dumesic and C. T. Maravelias, *Chem. Eng. Sci.,* 2012, **67**, 57-67.

2. B. Girisuta, L. P. B. M. Janssen and H. J. Heeres, *Ind. Eng. Chem. Res.*, 2007, **46**, 1696-1708.

3. M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem., Int. Ed.*, 2014, **53**, 1854-1857.

4. J. Xin, S. Zhang, D. Yan, O. Ayodele, X. Lu and J. Wang, *Green Chem.*, 2014, **16**, 3589-3595.

5. F. Chang, S. Dutta and M. Mascal, *ChemCatChem*, 2017, **9**, 2622-2626.

6. Y. Liu, L. Chen, Y. Chen, X. Zhang, J. Liu, Q. Liu, Y. Li, C. Wang, Q. Zhang and L. Ma, *Bioresour. Technol.*, 2023, **372**, 128653.

7. Y. Liu, G. Li, Y. Hu, A. Wang, F. Lu, J.-J. Zou, Y. Cong, N. Li and T. Zhang, *Joule*, 2019, *3*, 1028-1036.