Supplementary Materials

Production of alkyl levulinates from carbohydrate-derived chemical intermediates using phosphotungstic acid supported on humin-derived activated carbon (PTA/HAC) as a recyclable heterogeneous acid catalyst

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Characterization of 20%PTA/HAC−500 catalyst

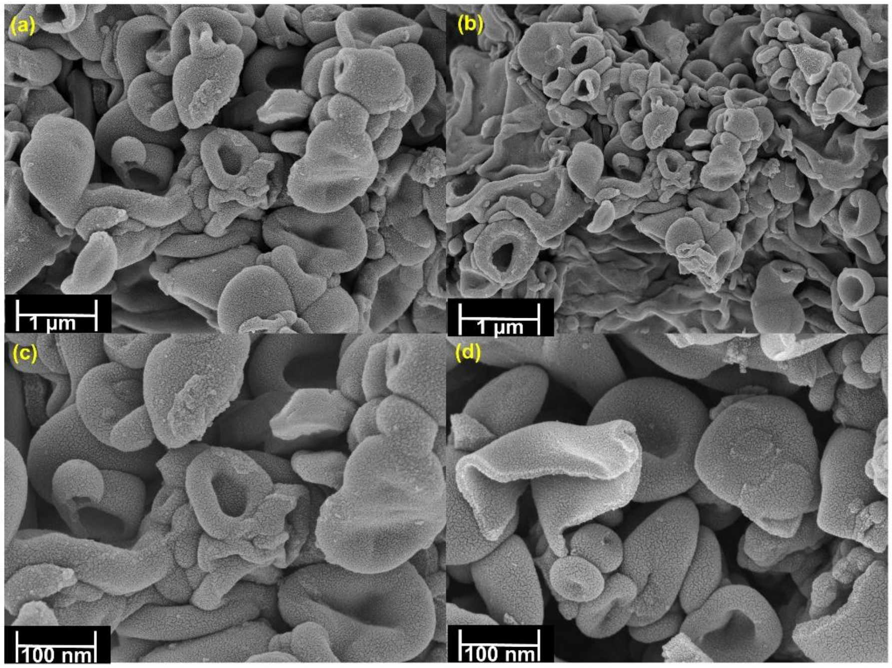

Figure S1. FESEM images of 20%PTA/HAC−500.

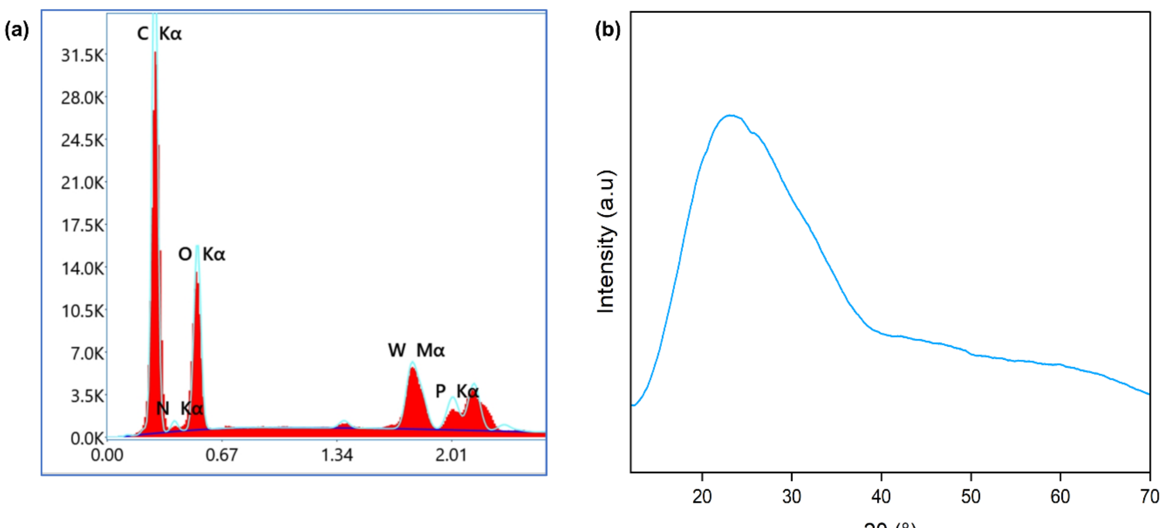

Figure S2. (a) EDAX pattern, and (b) PXRD pattern of 20%PTA/HAC−500.

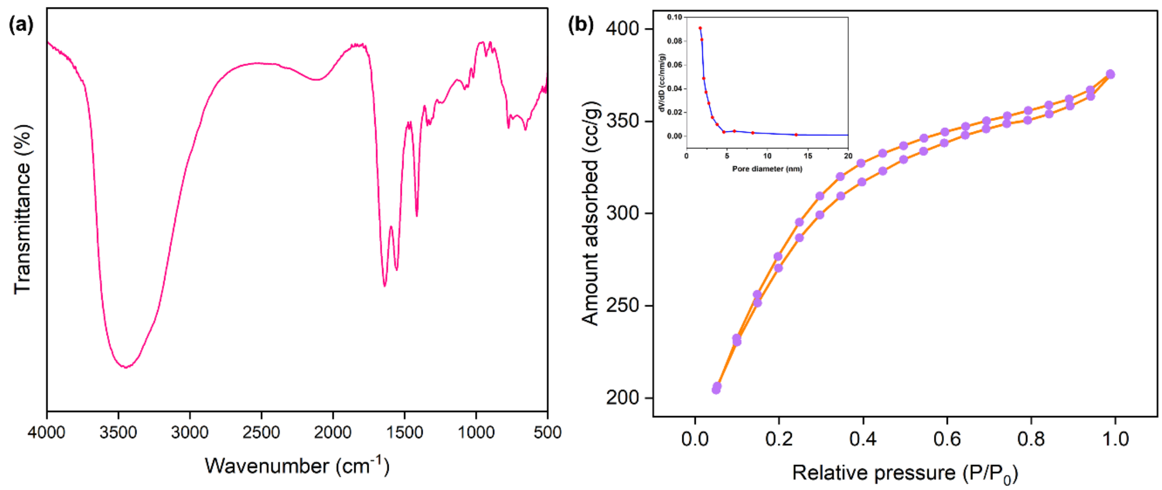

Figure S3. (a) IR spectrum, and (b) N_2 adsorption isotherm, and BJH pore size distribution curve (inset) of 20%PTA/HAC−500.

Characterization of synthesized alkyl levulinates

Methyl levulinate (ML): ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 3.60 (s, 3H), 2.69 (t, 2H, *J*=6.8 Hz), 2.50 (t, 2H, *J*=6.4 Hz), 2.12 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 205.7, 172.2, 50.8, 36.9, 28.8, 26.7; FTIR (ATR, cm^{-1}): 2955, 2852, 1712, 1157.

Ethyl levulinate (EL): ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 4.05 (q, 2H, *J*=7.2 Hz), 2.68 (t, 2H, *J*=6.4 Hz), 2.49 (t, 2H, *J*=6.4 Hz), 2.12 (s, 3H), 1.18 (t, 3H, *J*=7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz, δ ppm): 205.7, 171.7, 59.5, 36.8, 28.8, 27.0, 13.08; FTIR (ATR, cm^{-1}): 2981, 2929, 1718, 1096.

Propyl levulinate (PL): ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 3.95 (t, 2H, *J*=6.4 Hz), 2.68 (t, 2H, *J*=6.4 Hz), 2.49 (t, 2H, *J*=6.4 Hz), 2.11 (s, 3H), 1.57 (m, 2H), 0.86 (t, 3H, *J*=6.0 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz, δ ppm): 206.6, 172.7, 66.1, 37.8, 29.7, 27.9, 21.8, 10.2; FTIR (ATR, cm^{-1}): 2965, 2880, 1719, 1156.

Butyl levulinate (BL): ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 4.04 (t, 2H, *J*=6.8 Hz), 2.72 (t, 2H, *J*=6.8 Hz), 2.54 (t, 2H, *J*=6.8 Hz), 2.16 (s, 3H), 1.57 (m, 2H), 1.35 (m, 2H), 0.90 (t, 3H, *J*=7.6 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz, δ ppm): 206.7, 172.9, 64.6, 38.0, 30.6, 29.9, 28.0, 19.1, 13.7; FTIR (ATR, cm^{-1}): 2961, 2875, 1717, 1069.

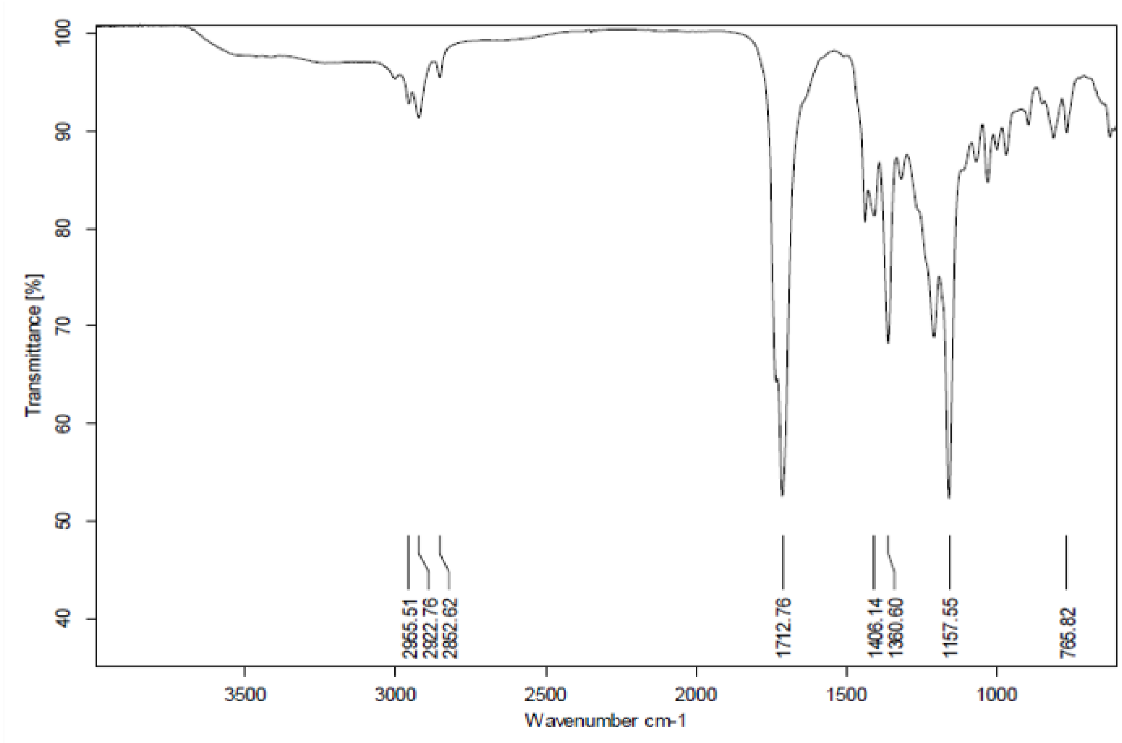

Figure S4. The FTIR spectrum of methyl levulinate.

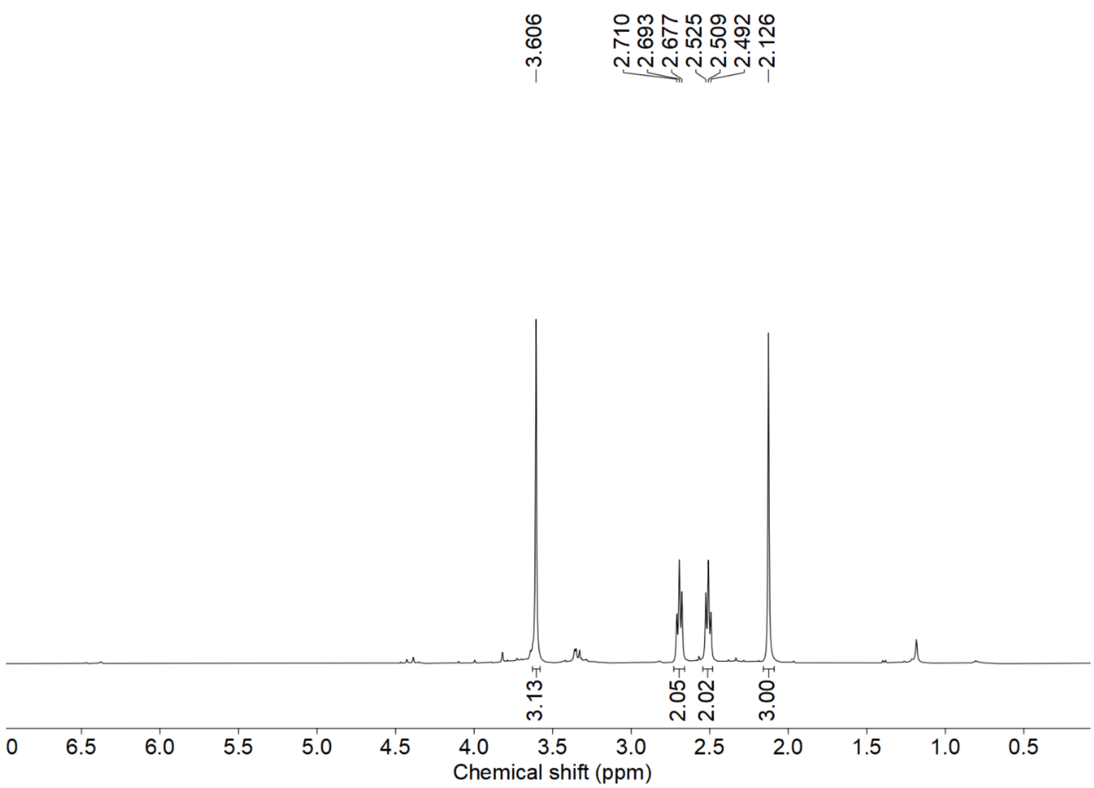

Figure S5. The ^{1}H-NMR spectrum of methyl levulinate.

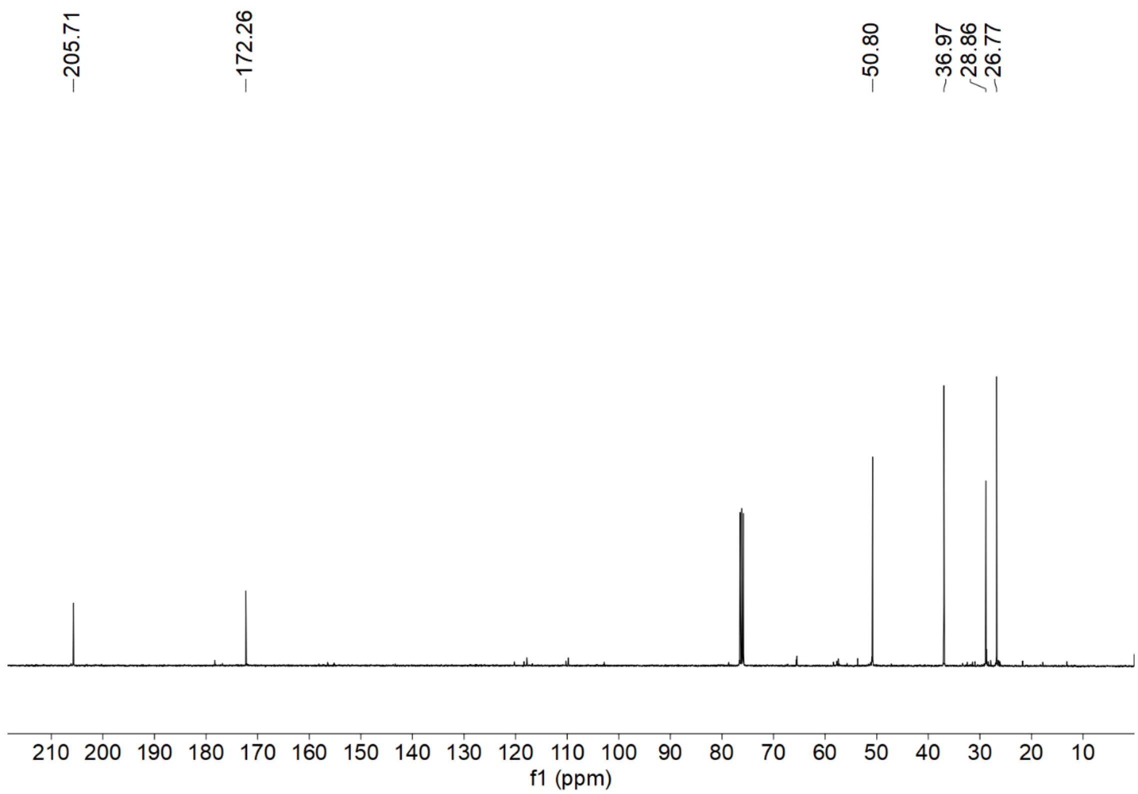

Figure S6. The ^{13}C-NMR spectrum of methyl levulinate.

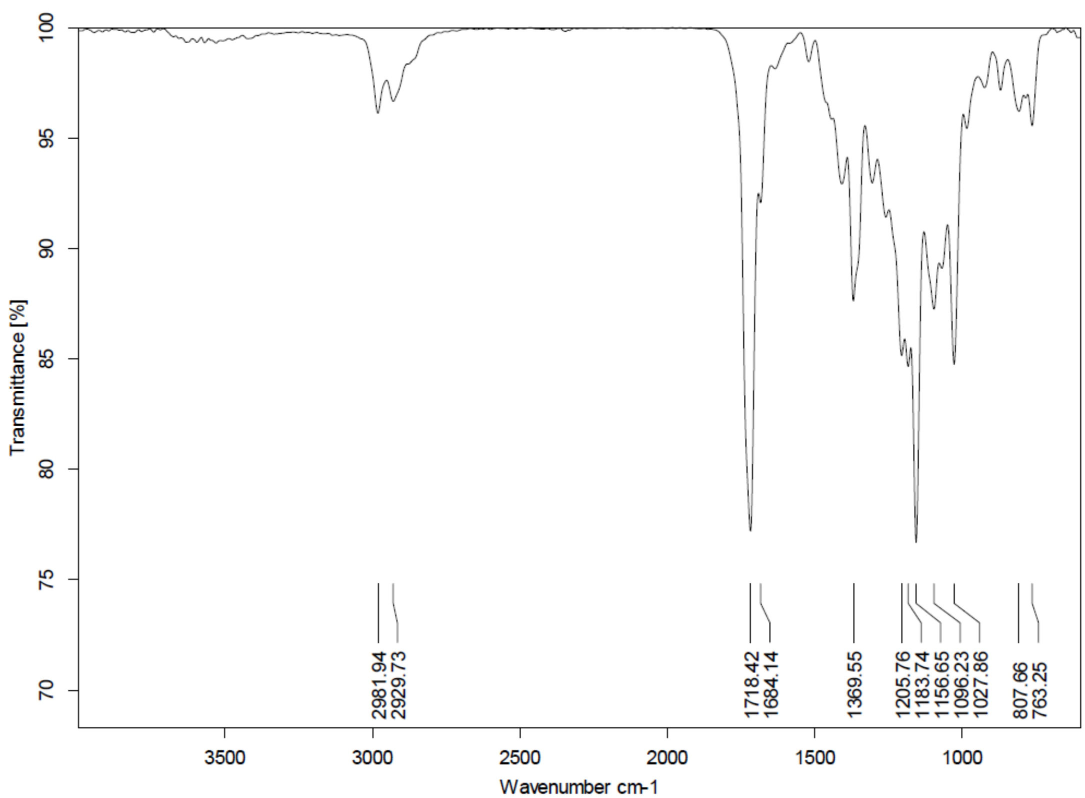

Figure S7. The FTIR spectrum of ethyl levulinate.

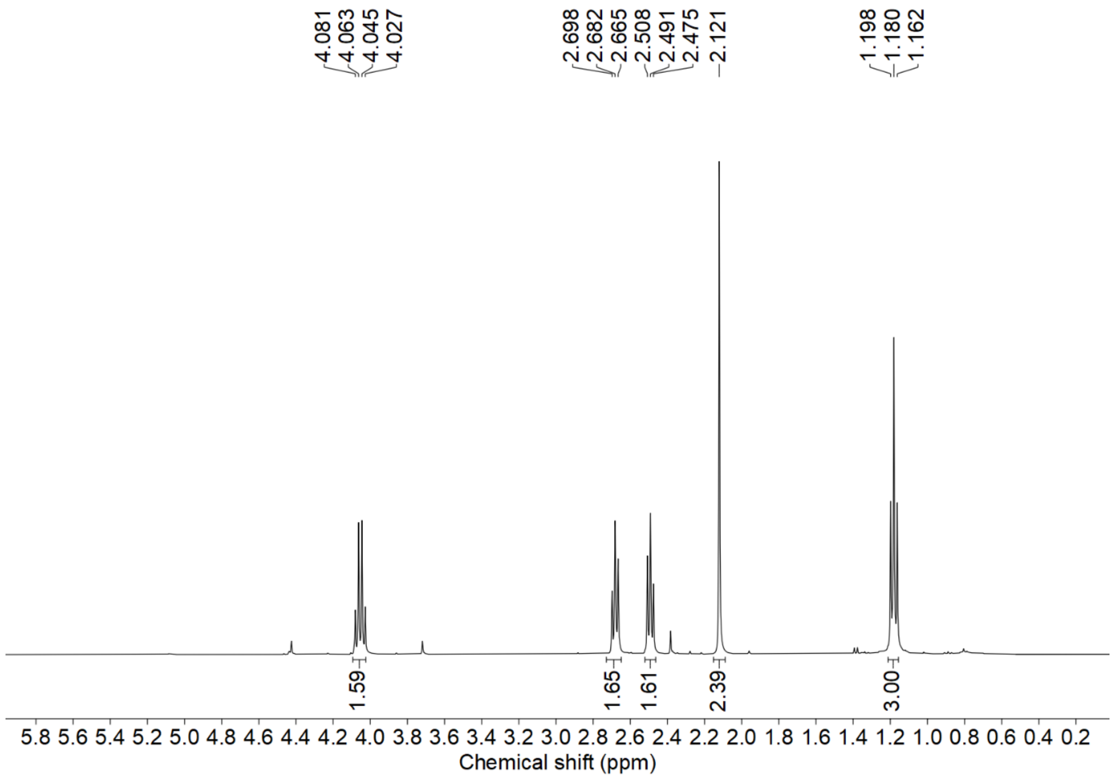

Figure S8. The ^{1}H-NMR spectrum of ethyl levulinate.

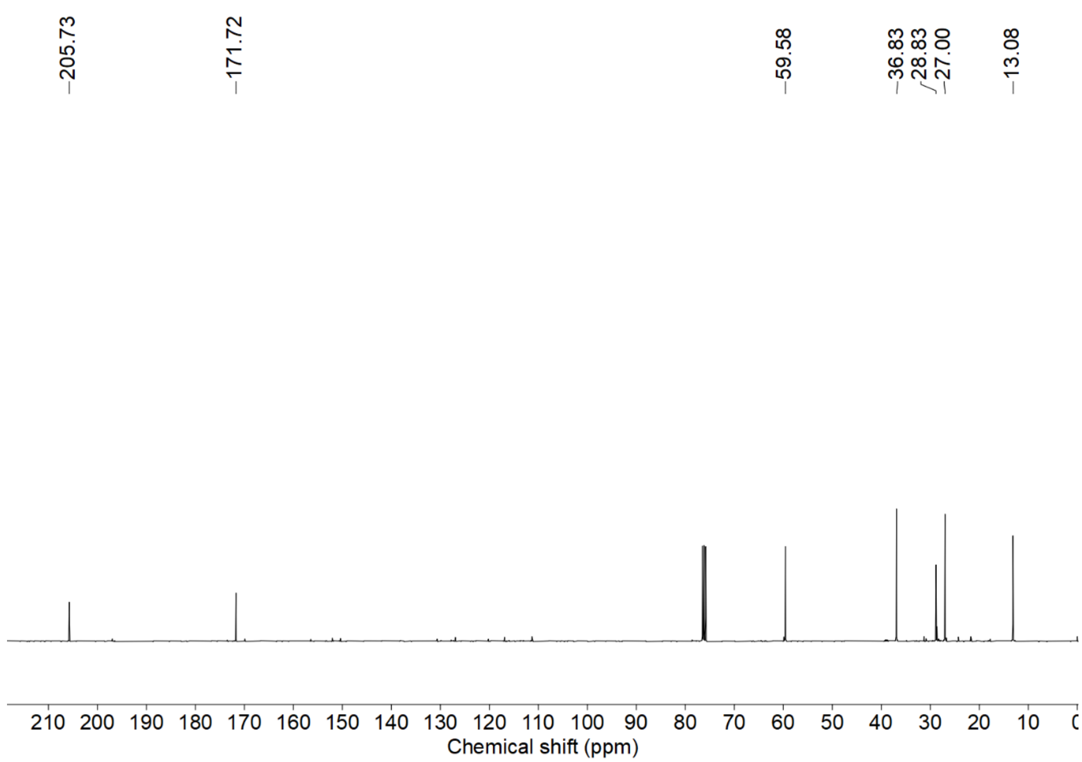

Figure S9. The ^{13}C-NMR spectrum of ethyl levulinate.

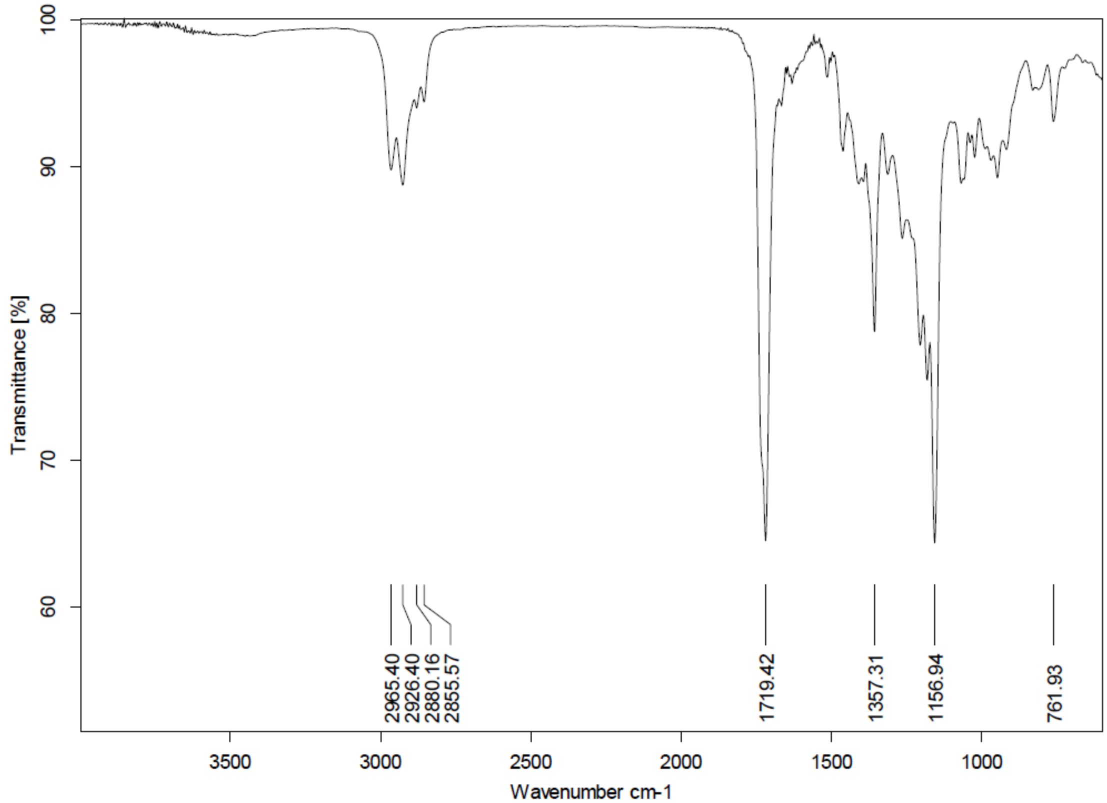

Figure S10. The FTIR spectrum of propyl levulinate.

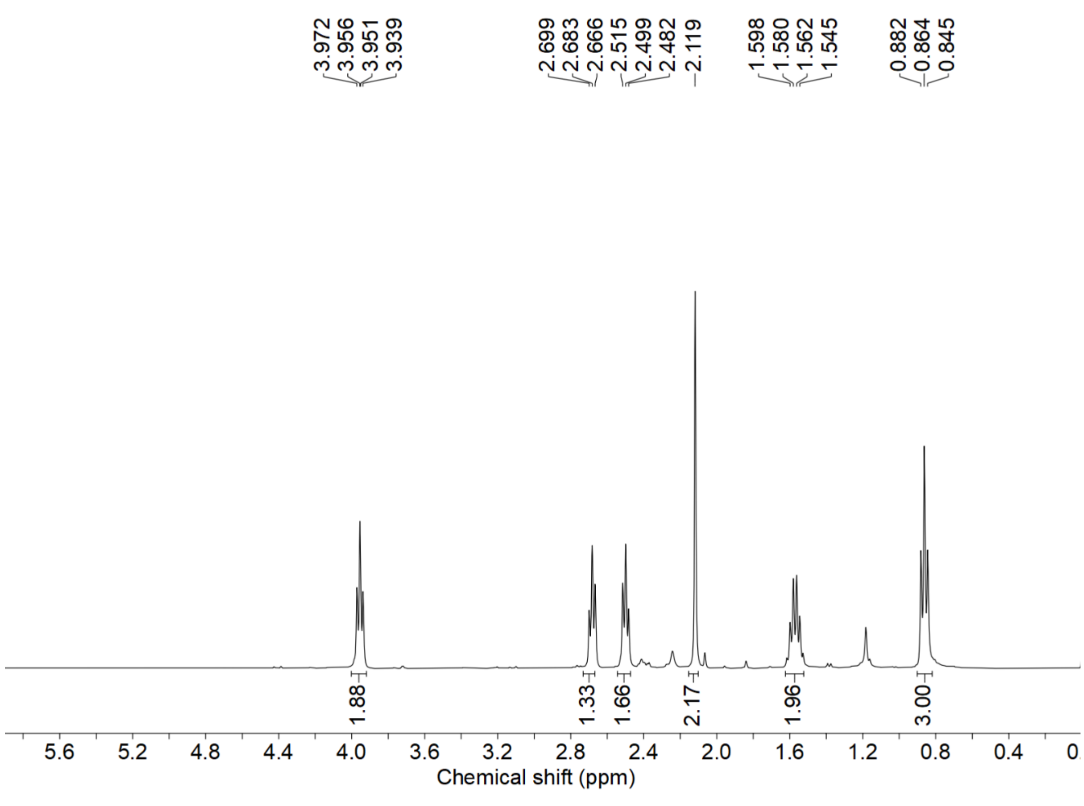

Figure S11. The ^{1}H-NMR spectrum of propyl levulinate.

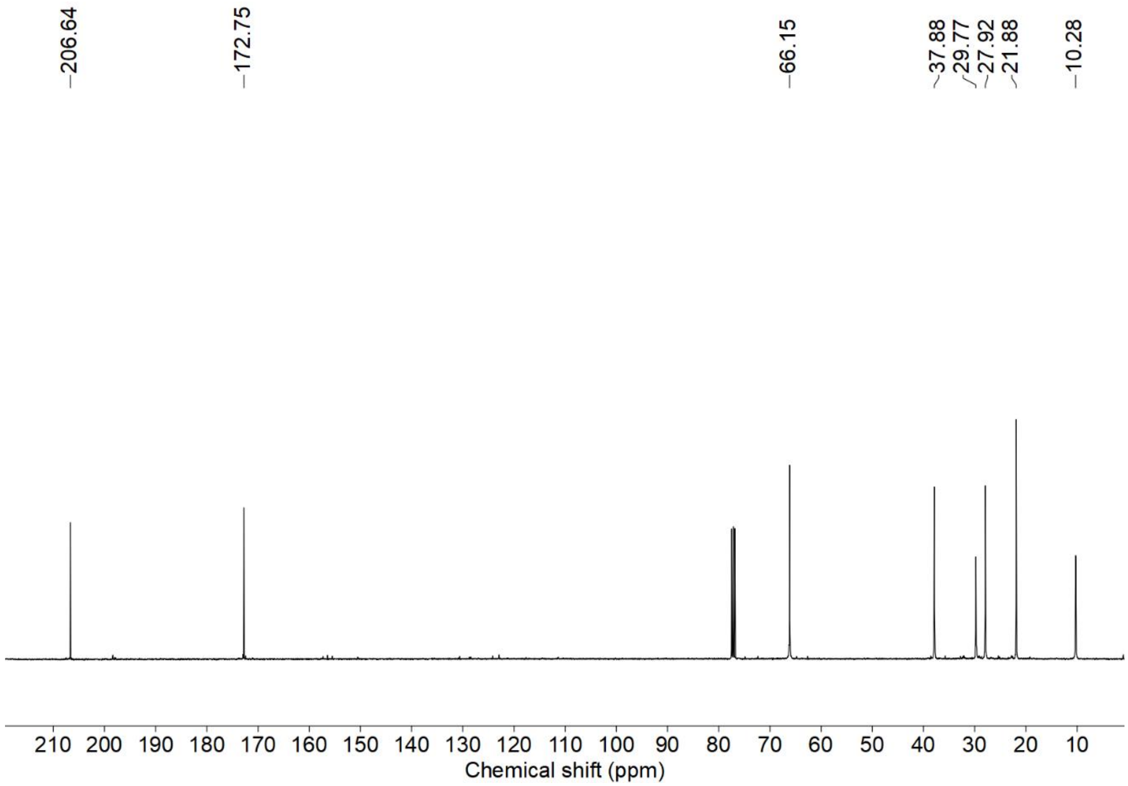

Figure S12. The ^{13}C-NMR spectrum of propyl levulinate.

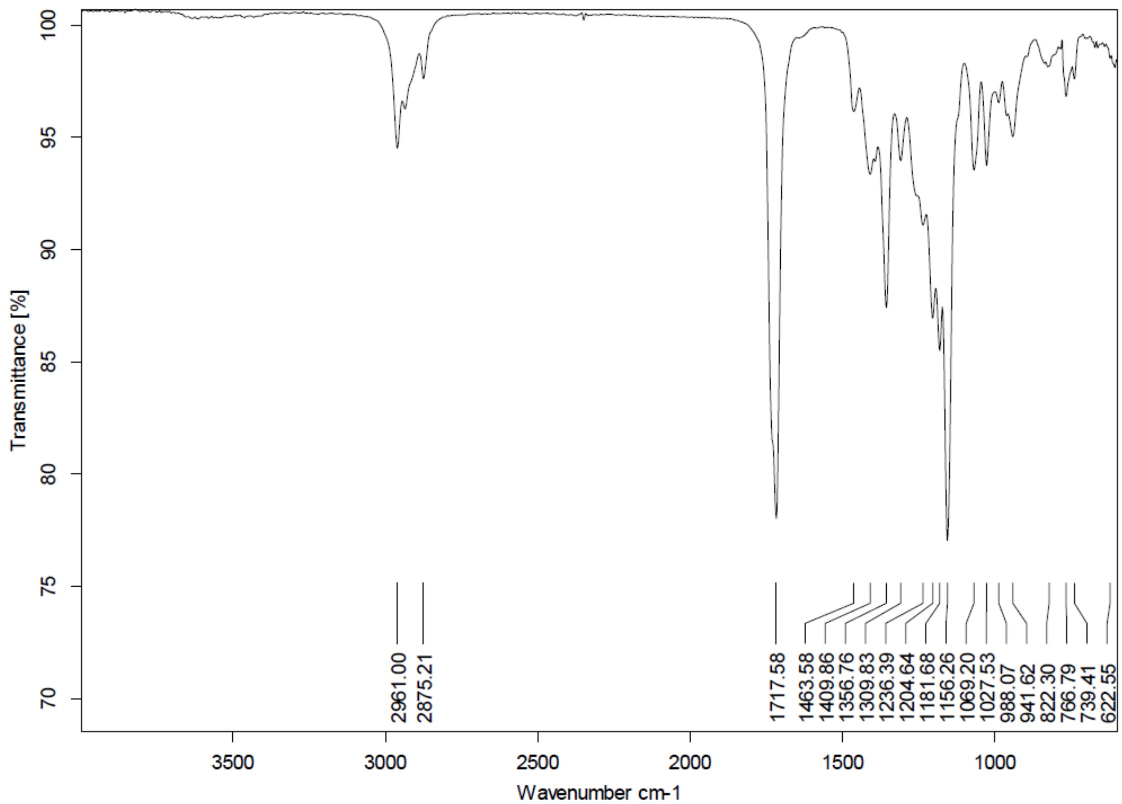

Figure S13. The FTIR spectrum of butyl levulinate.

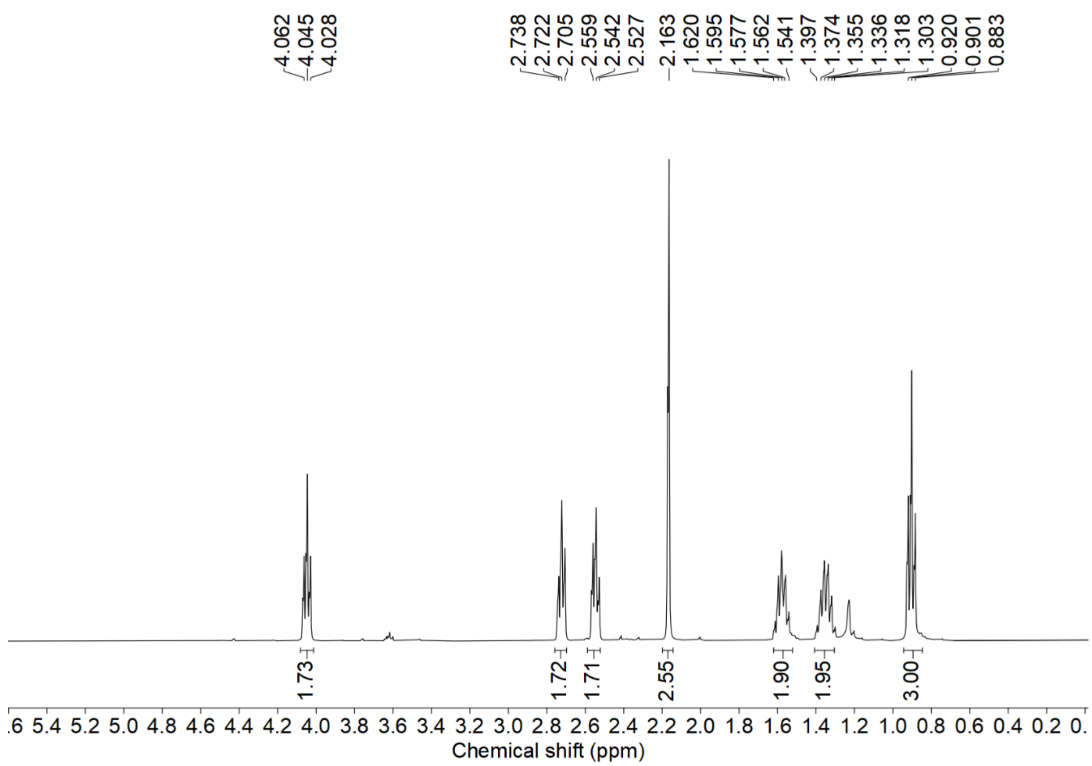

Figure S14. The ^{1}H-NMR spectrum of butyl levulinate.

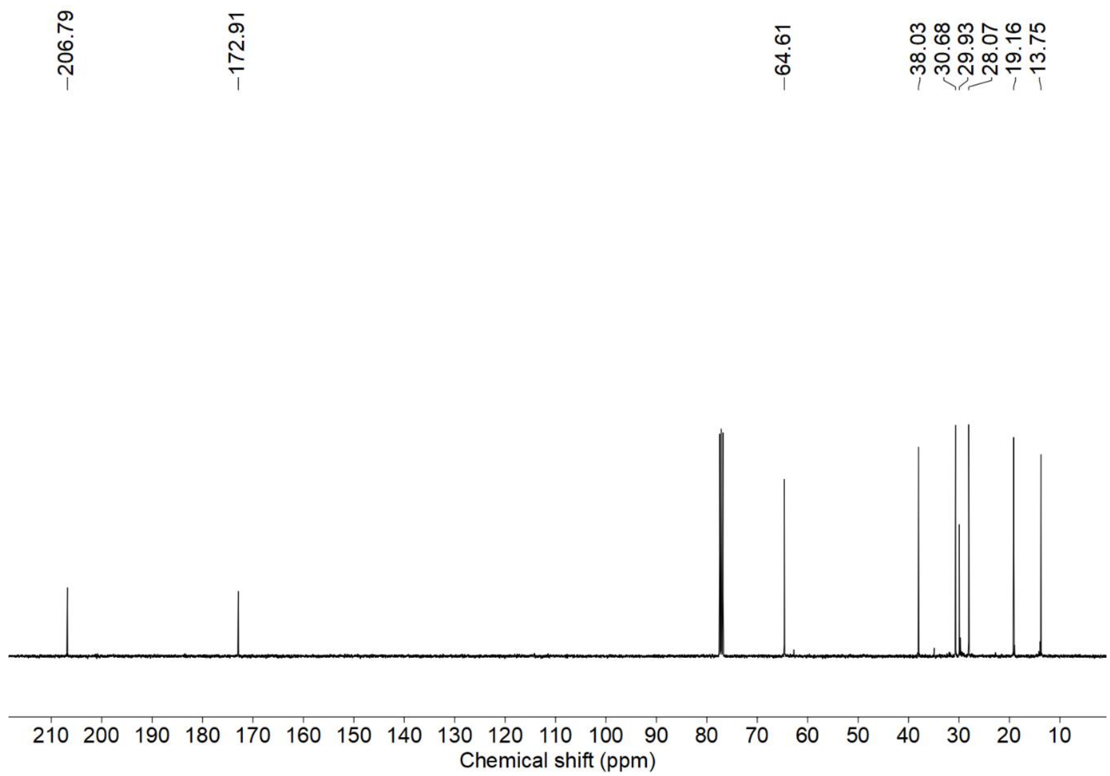

Figure S15. The ^{13}C-NMR spectrum of butyl levulinate.

Recyclability of 20%PTA/HAC−600 catalyst

The recyclability of 20%PTA/HAC−600 was studied for the conversion of LA to EL under optimized reaction conditions (150 °C, 7 h, 25 wt.% catalyst, and 5 mL ethanol). After the reaction, the volatiles (e.g., water, and ethanol) were removed from the mixture under reduced pressure. The catalyst was centrifuged and washed with chloroform. The catalyst was dried for 110 °C for 5 h before the next catalytic cycle. The catalyst was successfully recycled for four consecutive cycles with modest EL selectivity. Leaching of PTA from the HAC support was responsible for the drop in the yield of EL in the consecutive cycles.

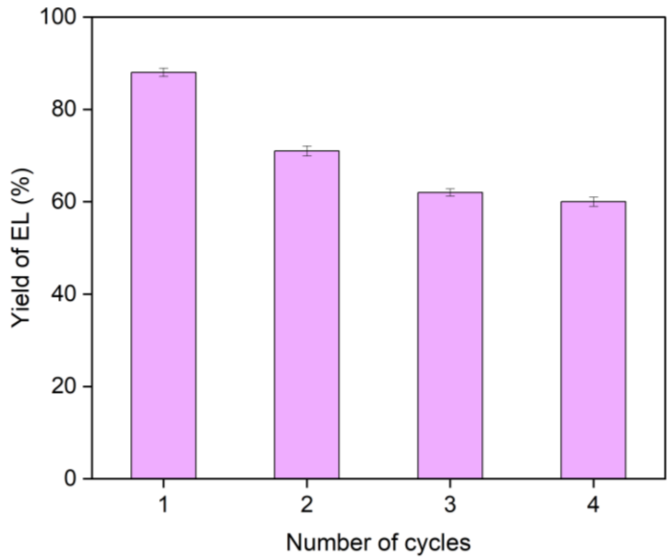

Figure S16. Catalyst recyclability test for the conversion of LA to EL. [Reaction conditions: LA (0.5 g, 4.30 mmol), ethanol (5 mL), 150 °C, 7 h, and 25 wt.% catalyst, 0.125 g].

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