Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Synthesis of biomass-derived feedstocks for the polymers and fuels industries from 5-(hydroxymethyl)furfural (HMF) and acetone

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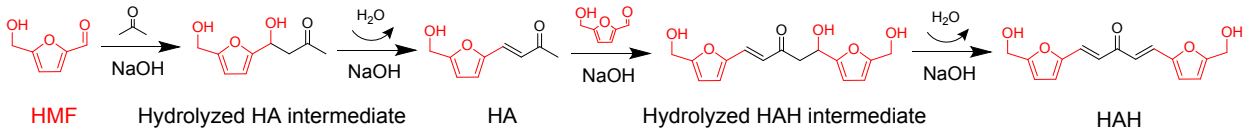
General information

^{1}H NMR and ^{13}C NMR spectra were obtained by using Brucker Avance-500 spectrometer. TMS (δ: 0 ppm) was used as a reference. Accurate mass measurements were acquired using a Thermo Q Exactive Plus (Electrospray ionization-quadrupole-ion trap methods).



Scheme S1. Reaction scheme showing the reactant, hydrolysed intermediates and products formed during base catalysed aldol condensation of HMF and acetone.

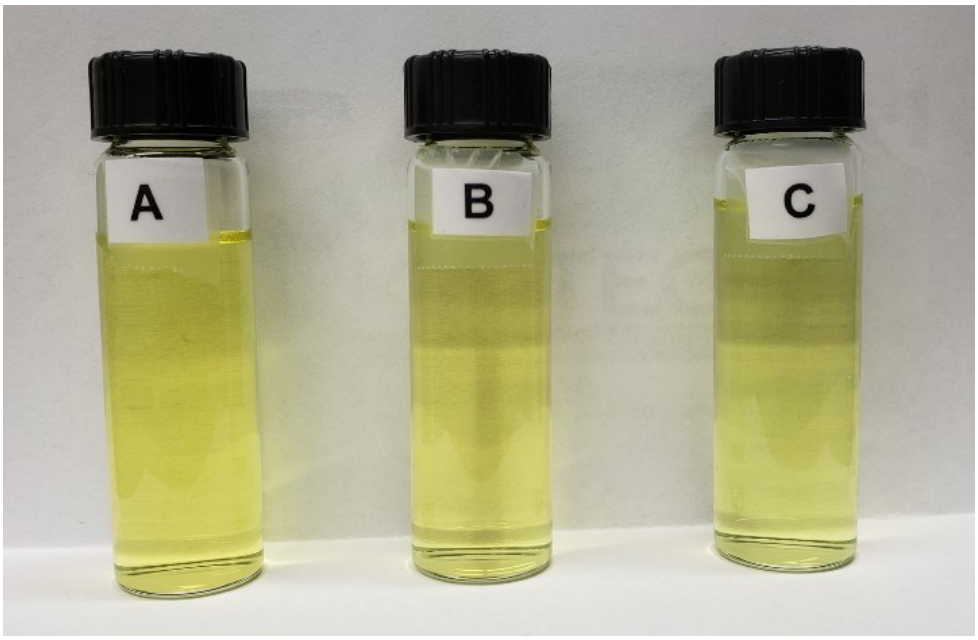


Figure S1. Color of diluted HAH solutions (Different amount of purified HAH was dissolved in methanol solvent). Concentration of sample **A**, **B**, and **C** was 0.037 wt % (= 1.1 mM), 0.017 wt % (= 0.5 mM), and 0.003 wt % (= 0.1 mM), respectively.

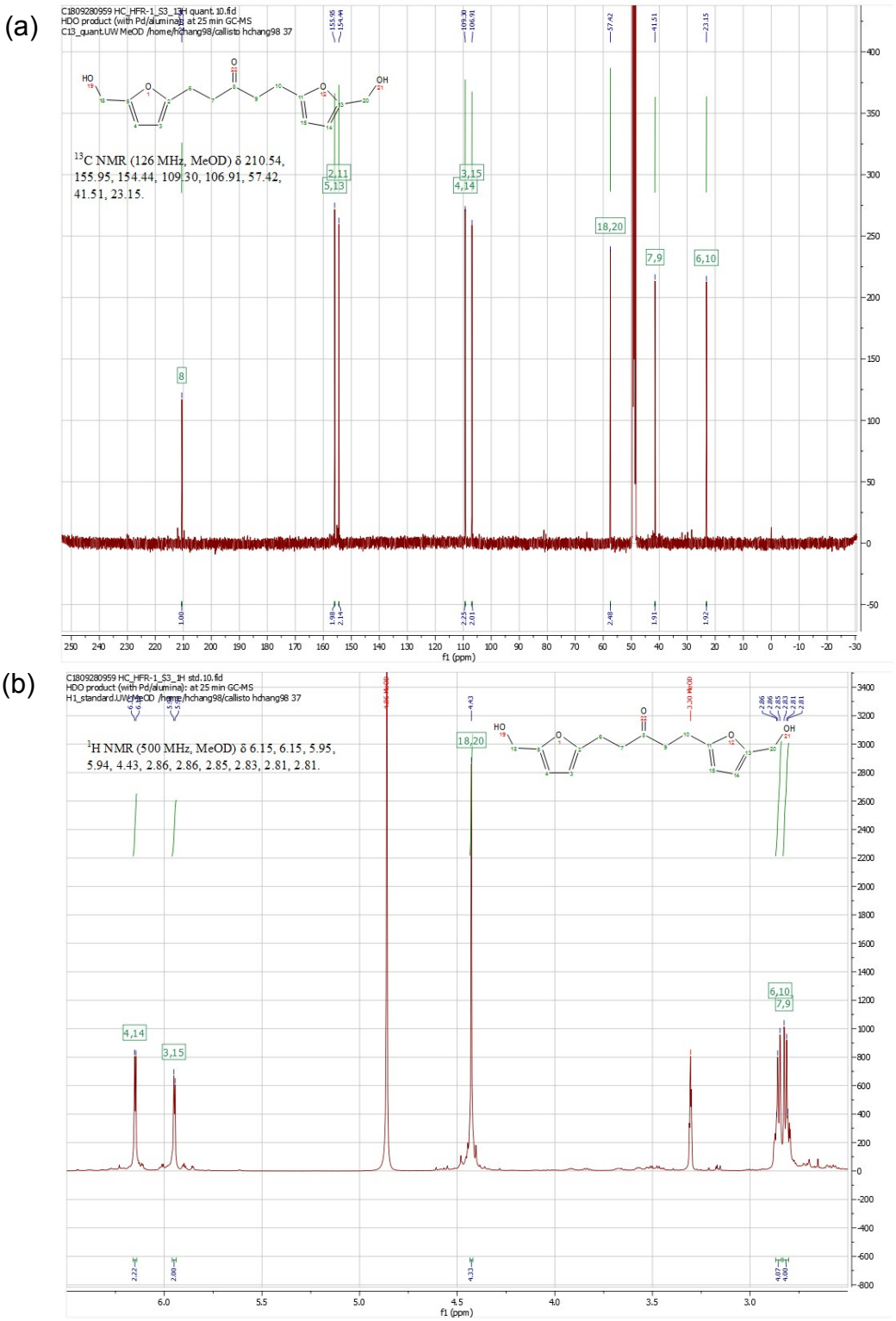
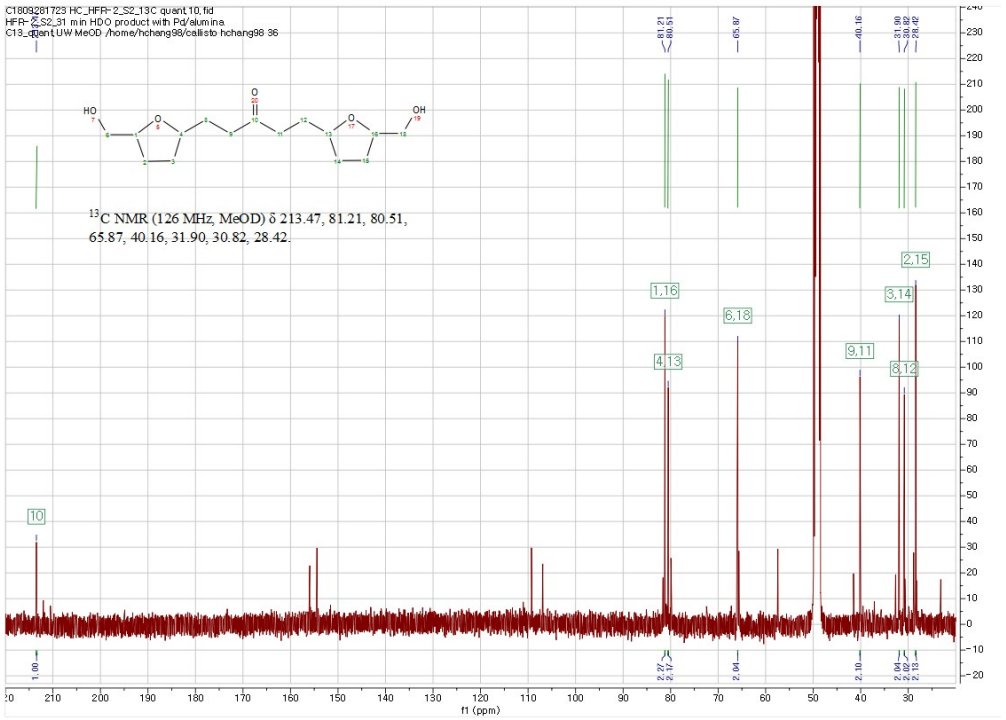


Figure S2. (a) ^{13}C quantitative NMR spectra of **3** (126 MHz, MeOD) δ: 210.54, 155.95, 154.44, 109.30, 106.91, 57.42, 41.51, 23.15 ppm. (b) ^{1}H standard NMR spectra of **3** (500 MHz, MeOD) δ: 6.15, 5.95, 4.43, 2.87-2.84, 2.83-2.80 ppm.

(a)



(b)

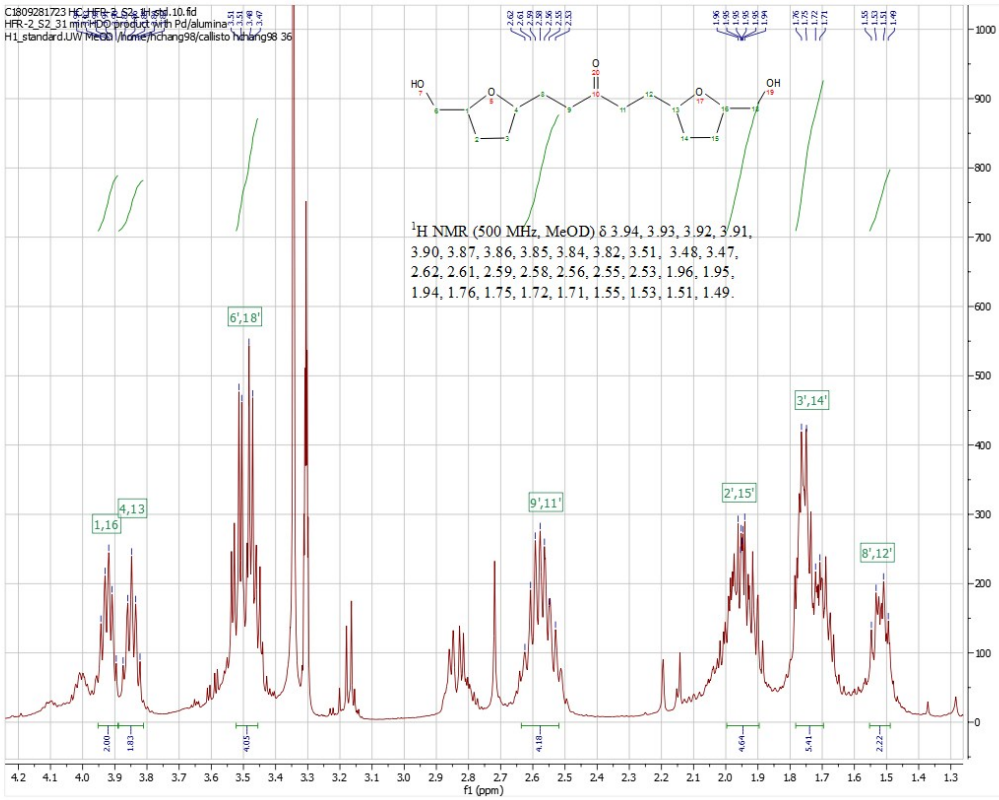


Figure S3. (a) ^{13}C quantitative NMR spectra of **4** (126 MHz, MeOD) δ: 213.47, 81.21, 80.51, 65.87, 40.16, 31.90, 30.82, 28.42 ppm. (b) ^{1}H standard NMR spectra of **4** (500 MHz, MeOD) δ: 3.96-3.88, 3.87-3.82, 3.51-3.47, 2.65-2.53, 1.99-1.89, 1.77-1.70, 1.56-1.49 ppm. HRMS (ESI) m/z calculated for **4**, $C_{15}H_{26}O_5$ $[M+H]^+$, 287.1853; measured, 287.1853.

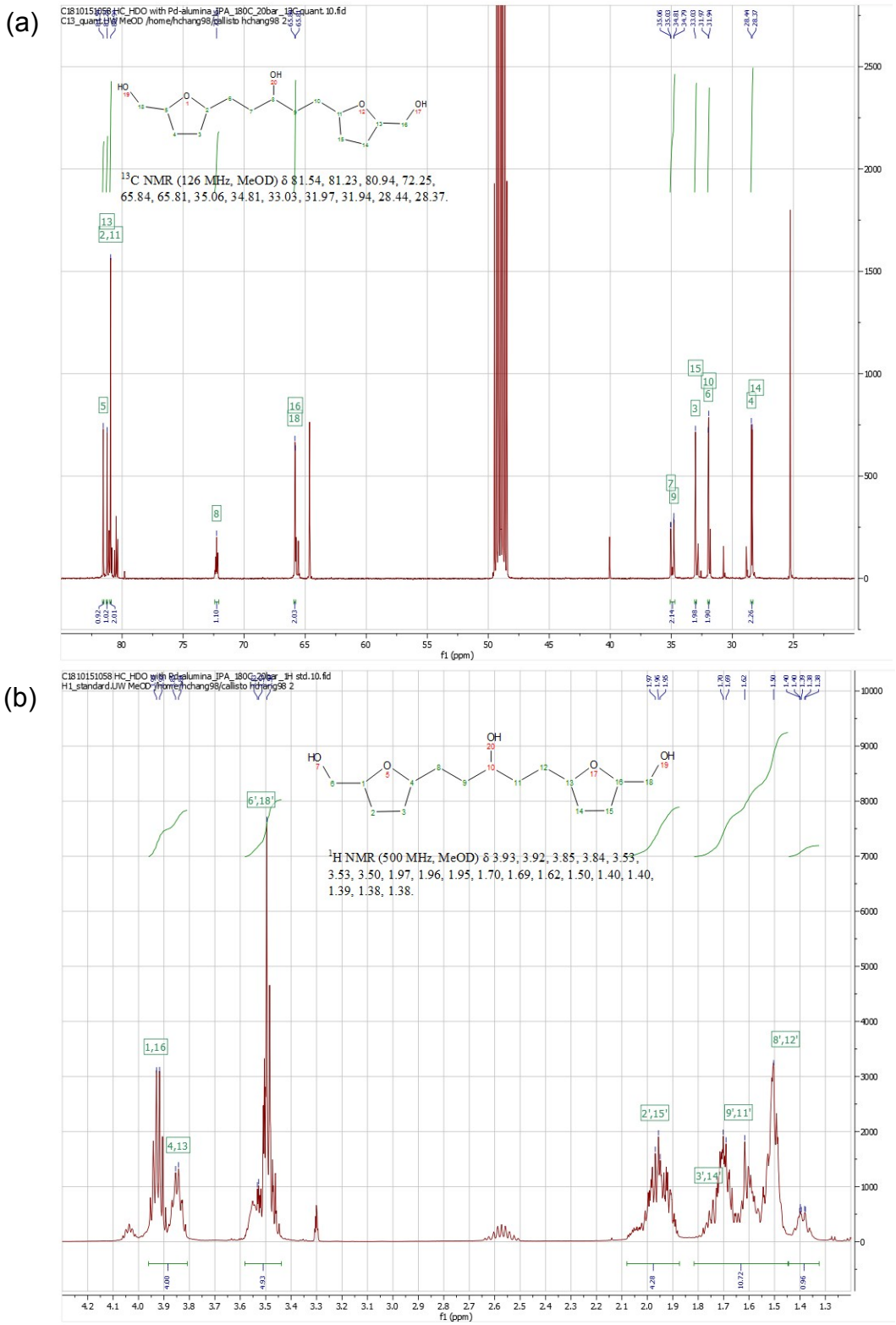
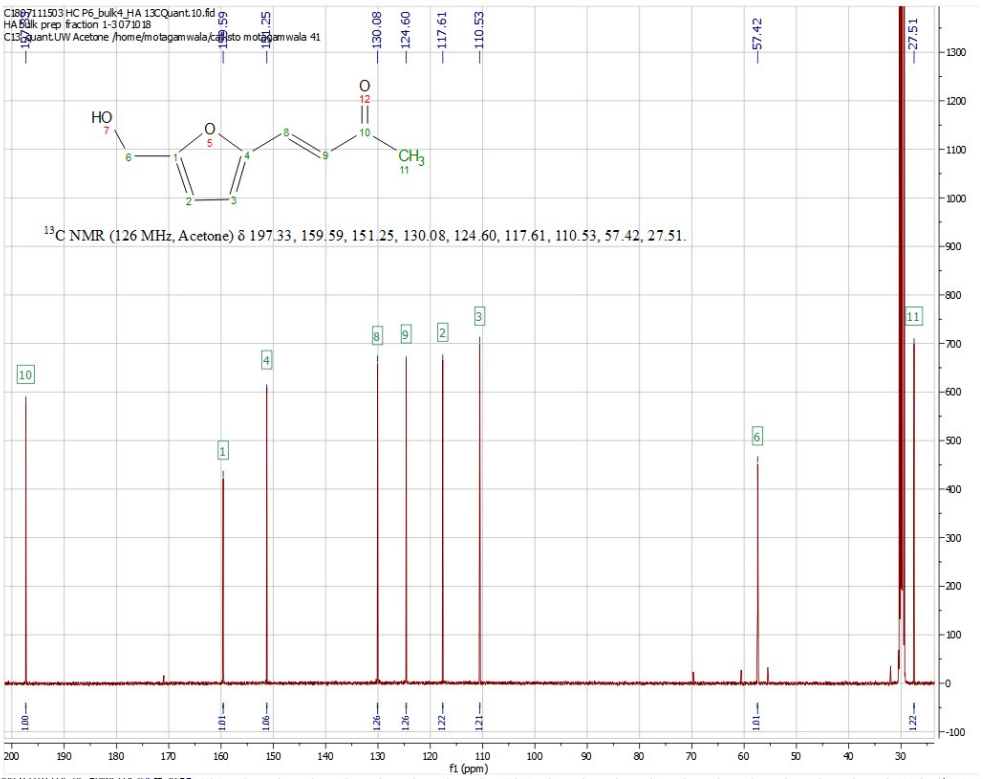


Figure S4. (a) ^{13}C quantitative NMR spectra of **5** (126 MHz, MeOD) δ: 81.54, 81.23, 80.94, 72.25, 65.84, 65.81, 35.06, 34.81, 33.03, 31.97, 31.94, 28.44, 28.37 ppm. (b) ^{1}H standard NMR spectra of **5** (500 MHz, MeOD) δ: 4.00-3.93, 3.92-3.84, 3.59-3.45, 2.09-1.89, 1.79-1.45, 1.44-1.34 ppm. HRMS (ESI) m/z calculated for **5**, C15H28O5 [M+H]+, 289.2010; measured, 289.2006.

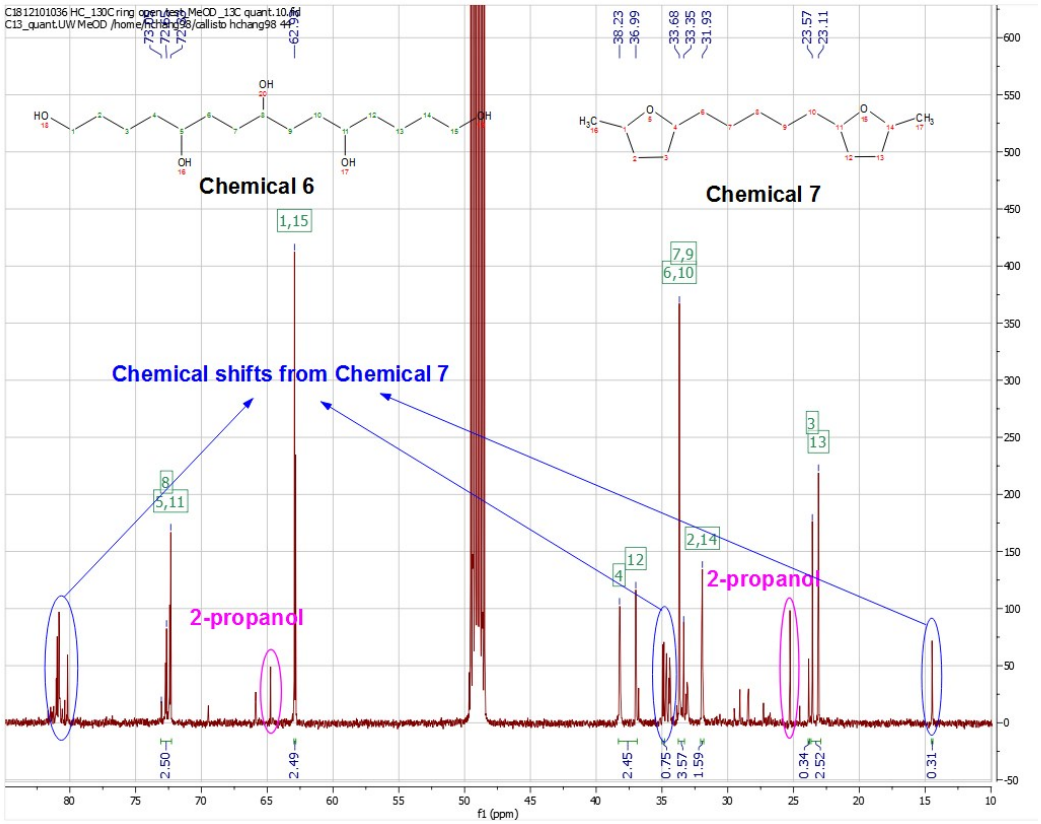
(a)



(b)

Figure S5. (a) ^{13}C quantitative NMR spectra of **1** (HA) (126 MHz, Acetone) δ: 197.33, 159.59, 151.25, 130.08, 124.60, 117.61, 110.53, 57.42, 27.51 ppm. (b) ^{1}H standard NMR spectra of **1** (HA) (500 MHz, Acetone) δ: 7.37-7.34, 6.81-6.80, 6.52-6.49, 6.45-6.44, 4.59-4.58, 2.28 ppm.

(a)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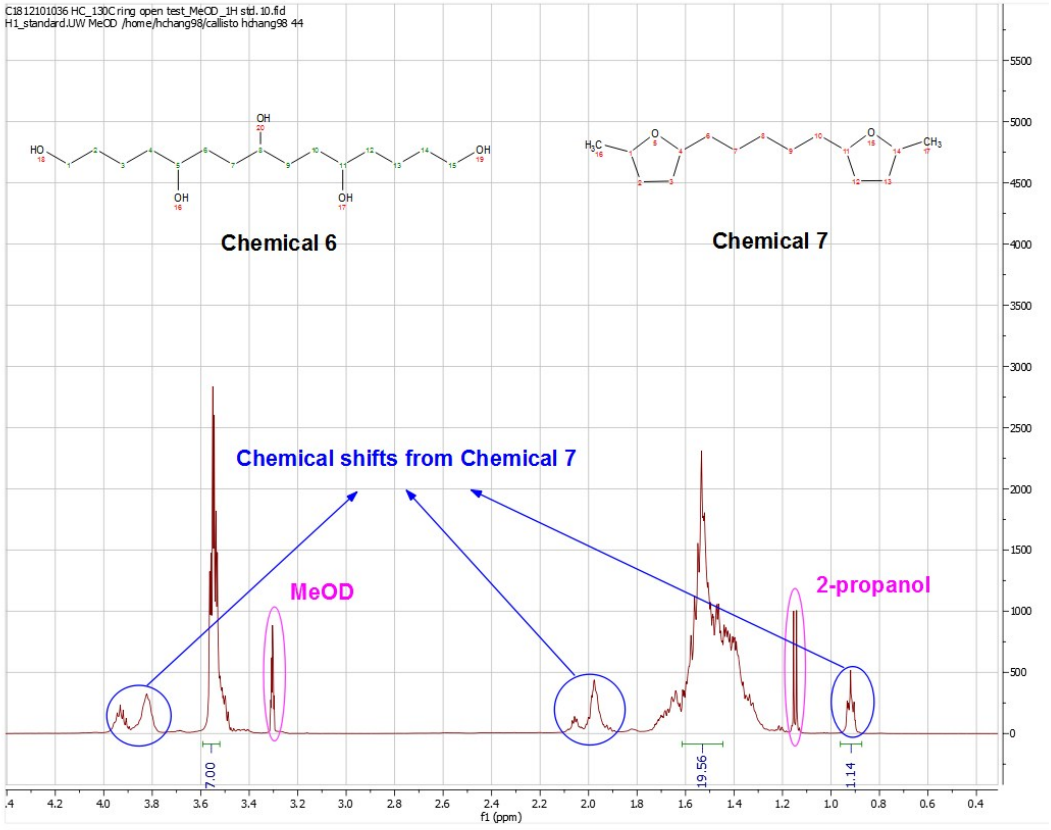
Chemical 7
Chemical shifts from Chemical 7
2-propanol
2-propanol
f1 (ppm)

(b)


Chemical 6
Chemical 7
Chemical shifts from Chemical 7
MeOD
2-propanol
f1 (ppm)

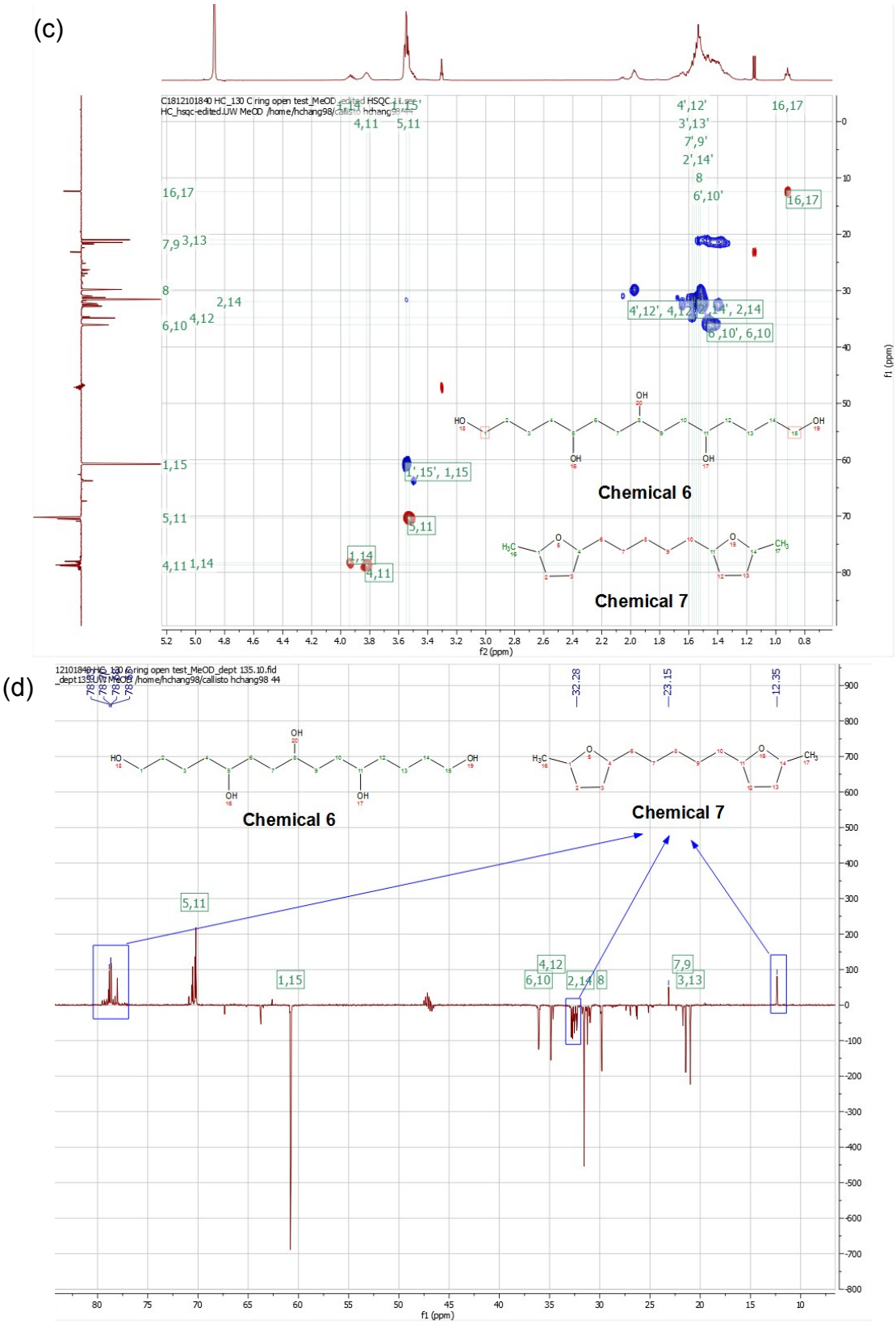


Figure S6. (a) ^{13}C quantitative NMR spectra of **6** and **7** mixture, (b) ^{1}H standard NMR spectra of **6** and **7** mixture, (c) 2D HSQC NMR spectra of **6** and **7** mixture (Blue: $=CH_2$, Red: $-CH_3$, $\equiv CH$), (d) ^{13}C DEPT-135 NMR spectra of **6** and **7** mixture (Negative peaks: $=CH_2$, Positive peaks: $-CH_3$, $\equiv CH$). UHPLC-QTOF m/z calculated for **6**, $C_{15}H_{32}O_5$ $[M\text{-}H]^-$, 291.2177; measured, 291.2176. HRMS (ESI) m/z calculated for **7**, $C_{15}H_{28}O_2$ $[M+H]^+$, 241.2162; measured, 241.2160.

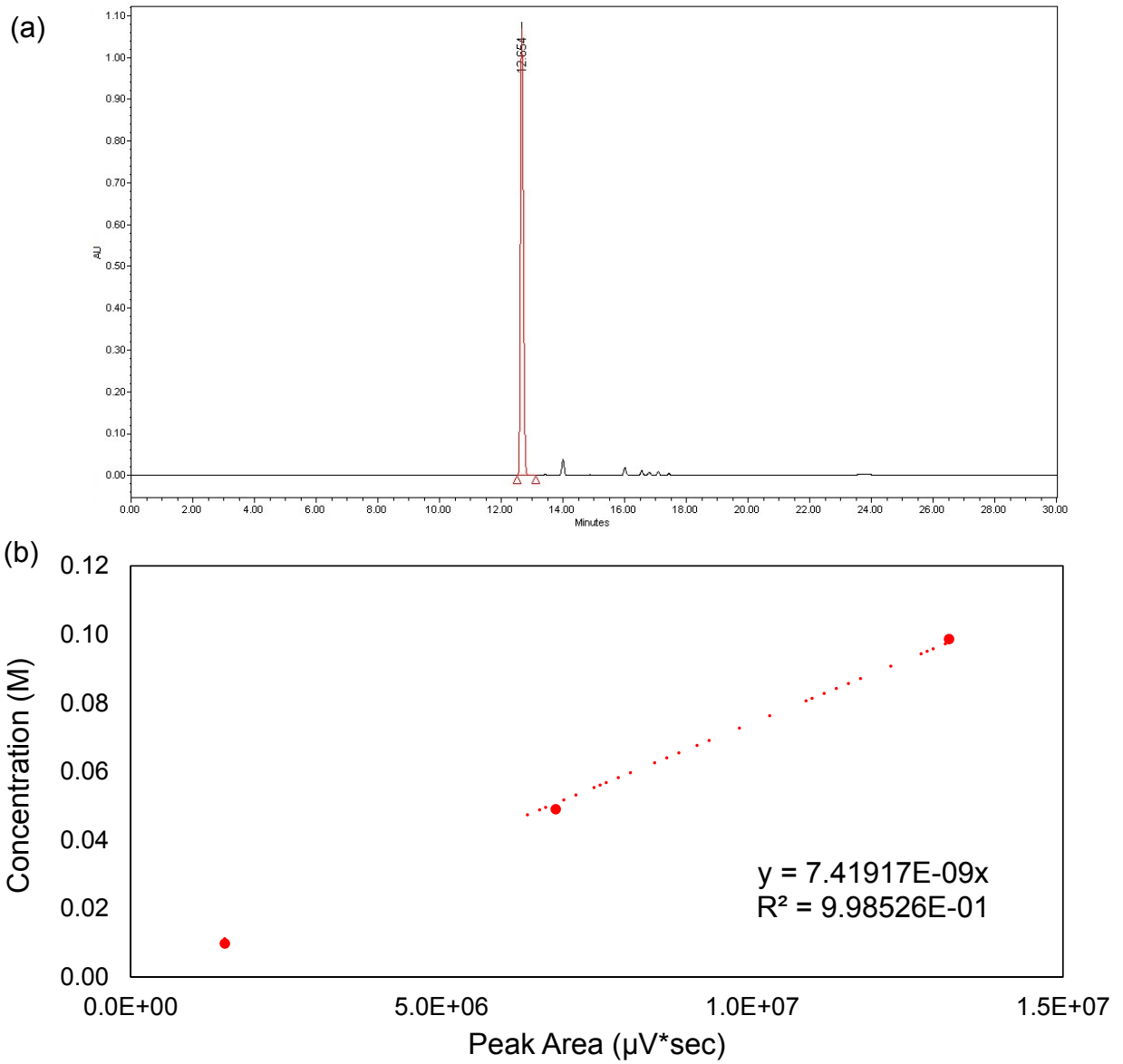


Figure S7. (a) Retention time (12.654 min) of 0.05 M purified HA in methanol solvent by HPLC analysis (UV wavelength of detector: 390 nm), (b) HPLC calibration curve for HA qualification.

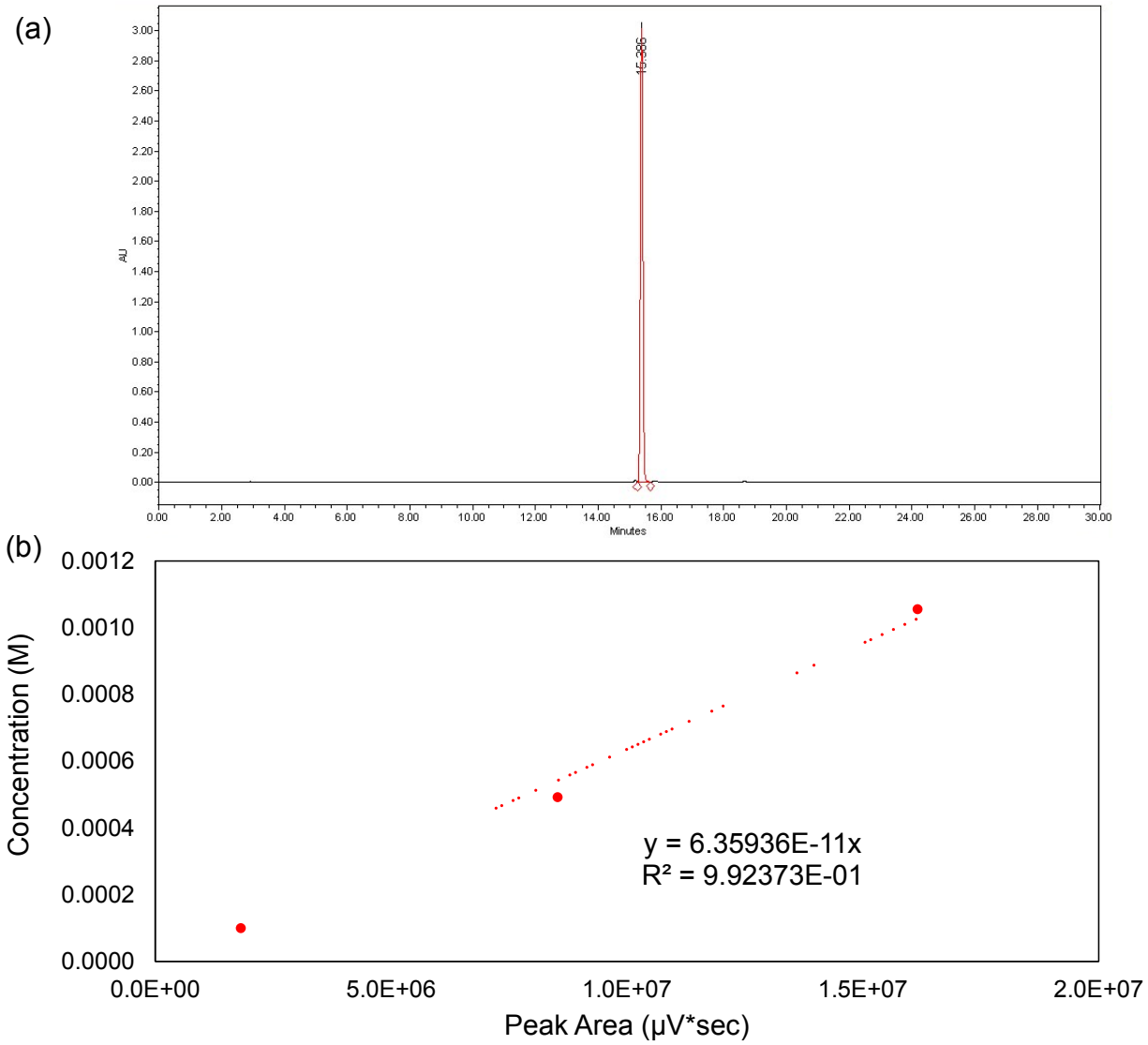


Figure S8. (a) Retention time (15.386 min) of 0.001 M purified HAH in methanol solvent by HPLC analysis (UV wavelength of detector: 390 nm), (b) HPLC calibration curve for HAH qualification.

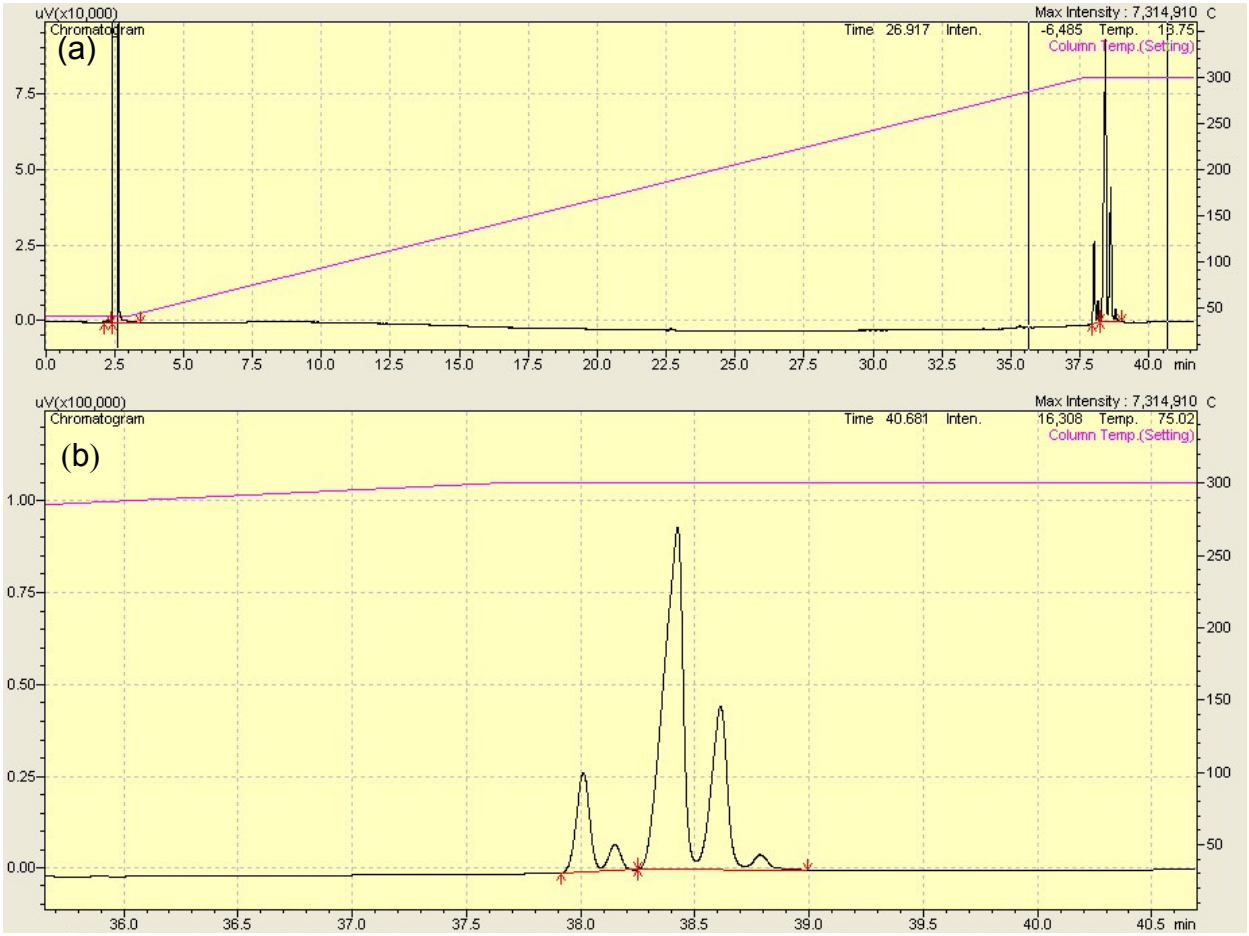


Figure S9. (a) As-synthesized product solution after hydrogenation of HAH (2) over Pd/Al_2O_3 (Molar ratio of 5/4 = 5.70) by GC-FID analysis. (Retention time of 2-propanol solvent: 2.5 min, Retention time of 4 and 5: around 38-39 min), (b) Zoomed-in image from 35.5 to 40.5 min retention time (First two peaks represents 4 and following three peaks represents 5). Peak splits in (b) were induced from stereo-centered carbons of 4 and 5.

Figure S10. (a) As-synthesized product solution after ring-opening and hydrodeoxygenation of 4 and 5 over Pt-WO_x/TiO_2 at 433 K by GC-FID with pentadecane ECN analysis. (Molar ratio of 7/6 = 1.43). (Retention time of 2-propanol solvent: 2.5 min, Retention time of pentadecane: 19.6 min, Retention time of 7: around 31.8-32.5 min, Retention time of 6: around 36.9-37.5 min), (b) Zoomed-in image from 31.5 to 40.0 min retention time (First five peaks represents 7 and following three peaks represents 6). Peak splits in (b) were induced from stereo-centered carbons of 4 and 5.

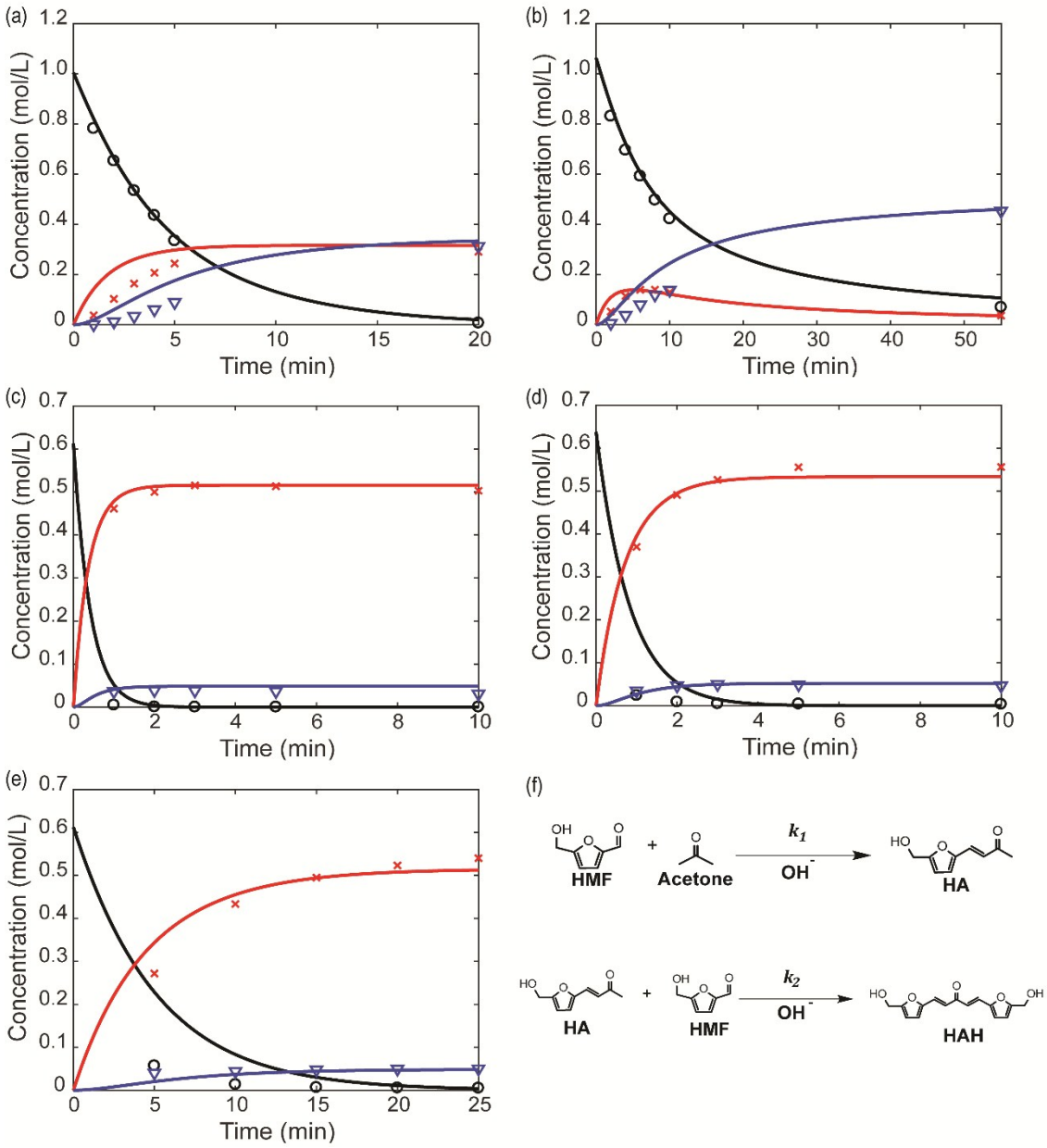


Figure S11. Experimental data and kinetic model (Concentration trajectories) for aldol condensation of HMF and acetone in batch reactor at 308 K. Solid lines are kinetic model and points describe experimental data (Black: HMF, Red: HA, Blue: HAH) (a) [NaOH] = 0.10 M, [HMF] = 1.00 M, [Ac] = 1.20 M; (b) [NaOH] = 0.11 M, [HMF] = 1.06 M, [Ac] = 0.53 M; (c) [NaOH] = 0.24 M, [HMF] = 0.61 M, [Ac] = 6.08 M; (d) [NaOH] = 0.12 M, [HMF] = 0.64 M, [Ac] = 6.08 M; (e) [NaOH] = 0.02 M, [HMF] = 0.61 M, [Ac] = 6.07 M. (f) Two step reaction pathways for the base-catalyzed aldol condensation of HMF and acetone.