Supplementary Material for

Catalytic strategy for conversion of fructose to organic dyes, polymers, and liquid fuels

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Tables and Figures

Table S1. Analysis of major products (HMF, HA, formic acid) from fructose dehydration after distillation of dehydrated and decolorized solution (Dehydration conditions: 9.1 wt% fructose in acetone/water (75/25, v/v) solvent with 124 mM HCl at 393 K, 40 min; Decolorization conditions: 4.1 wt% activated carbon addition at 298 K, 30 min; Distillation conditions: 50 mbar, 298 K)

	Collected chemical fraction in top product (%)	Collected chemical fraction in bottom product (%)	Chemical formation (+) & degradation (-) after distillation (%)
HMF	0.4	90	-9.6
HA	0	87	-13
Formic acid	9	105	+14

Table S2. Mass and energy balances (basis: 10000 $kg \cdot h^{-1}$ of fructose feedstock) based on process block-flow diagram in Fig. 6.

Process section	**Stream number**	**Mass flow (tonne/h)**	**Pressure (bar)**	**Temp (° C)**	**Energy requirement (MW)**
HMF production	1	10	1	25	Electricity: 0.04 Heating: 10.37 Cooling water: 0.07
	2	1.1	1	25	
	3	0.3	1	25	
	4	5.8	1	25	
	5	103.7	10	120	
	6	86.5	0.035	20	

Solvent recovery	7	0.9	1	51.3	Electricity: 4.53 $\times 10^{-3}$
	8	21.6	1	25	Heating: 11.11
	9	37.9	0.035	20	Refrigeration: 21.84
HAH production	10	33.4	1	25	Electricity: 1.16 $\times 10^{-3}$
	11	0.3	1	25	Heating: 0.94
	12	0.9	1	25	Cooling water: 2.38
	13	72.5	1	35	
HAH purification	14	284.2	1	27.4	Heating: 1.38
	15	216.4	1	25	
	16	0.6	1	25	
	17	5.3	1	27.4	

Table S3. Energy requirements before and after heat integration.

Energy required (MW)	Before	After
Heating	30	23.8
Cooling	30.5	24.3

Table S4. Summary of estimated capital costs of the proposed approach.

Process section	Capital cost (MM$)	Equipment	Installed equipment cost ($)	Reference
HMF production	1.1	R-1	630,782	(*2*)
		Miscellaneous	425,198	Aspen Plus
Solvent recovery	4.4	S-1	184,490	Aspen Plus
		S-2	580,006	(*2*)
		S-3	499,059	Aspen Plus
		E-1	175,563	Aspen Plus
		E-2	2,793,495	Aspen Plus
		Miscellaneous	150,695	Aspen Plus
HAH production	0.4	R-2	338,300	(*2*)
		Miscellaneous	104,360	Aspen Plus
HAH purification	3.8	S-4	2,927,143	(*2*)
		S-5	829,628	(*2*)
OSBL*	3.9	-	-	-

Total installed cost	13.6	-	-	-
Total capital investment	30.3	-	-	-

*OSBL (outside battery limits of the plant) consists of infrastructure costs for on-site storage, utilities, and on-site storage. It is taken to be 40% of the inside battery limits (ISBL) equipment costs.

Table S5. Summary of operating costs.

Raw material	Total cost (MM$/year)
Fructose	56.46
Acetone	12.23
HCl	3.25
Water	0.98
NaOH	6.48
Steam	1.28
Cooling water	0.01
Refrigerant	1.7
Electricity	0.02
Wastewater treatment	1.55
Total variable operating costs	84.27
Total fixed operating costs	1.79

Table S6. Economic parameters and assumptions.

Fructose price ($/ton) [a]	650
Acetone price ($/ton) [b]	950
33% HCL price ($/ton) [b]	150
NaOH price ($/ton) [b]	850
Water ($/ton) [c]	0.4
Low pressure steam ($/kJ) [d]	1.89e-06
Activated carbon ($/kg) [e]	1.48
Cooling water ($/kJ) [d]	2.12e-07
-25^{o} C Refrigerant ($/kJ) [d]	2.73e-06
Electricity price ($/kWh) [f]	0.0693
Wastewater treatment cost ($/ton) [g]	0.57
Ash disposal ($/ton)	37.93
Plant operating hours per year [c]	7880

Plant life (year) [c]	30
Internal rate of return (%) [c]	10
Plant depreciation (year) [c]	7
Loan terms [c]	10-year loan at 8% APR
Construction time (year) [c]	3
First 12 months' expenditure [c]	8
Next 12 months' expenditure [c]	60
Last 12 months' expenditure [c]	32
Federal tax rate (%) [c]	21
Financing (% of equity) [c]	40
Start-up time (month) [c]	6
Revenue during start-up (%) [c]	50
Variable operating costs during start-up (%) [c]	75
Fixed operating costs during start-up (%) [c]	100

[a] Taken from Motagamwala et al. (*3*).

[b] Taken from ICIS news (*4*–*6*).

[c] Taken from Davis et al. (*2*).

[d] Estimated based on Aspen Process Economic Analyzer (V10 Aspen Technology).

[e] Taken from a report by USGS (*7*).

[f] Taken from EIA (*8*).

[g] Taken from a report by IWW (*9*).

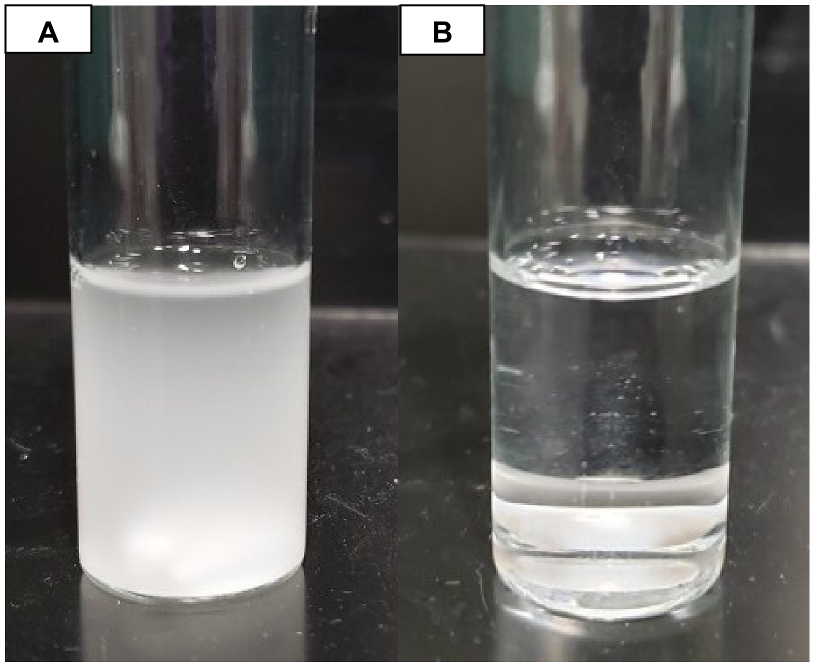


Fig. S1. (**A**) 8.5 wt% fructose (emulsion phase), (**B**) 8.3 wt% fructose (homogeneous phase) in acetone/water (80/20, v/v) solvent at 298 K.

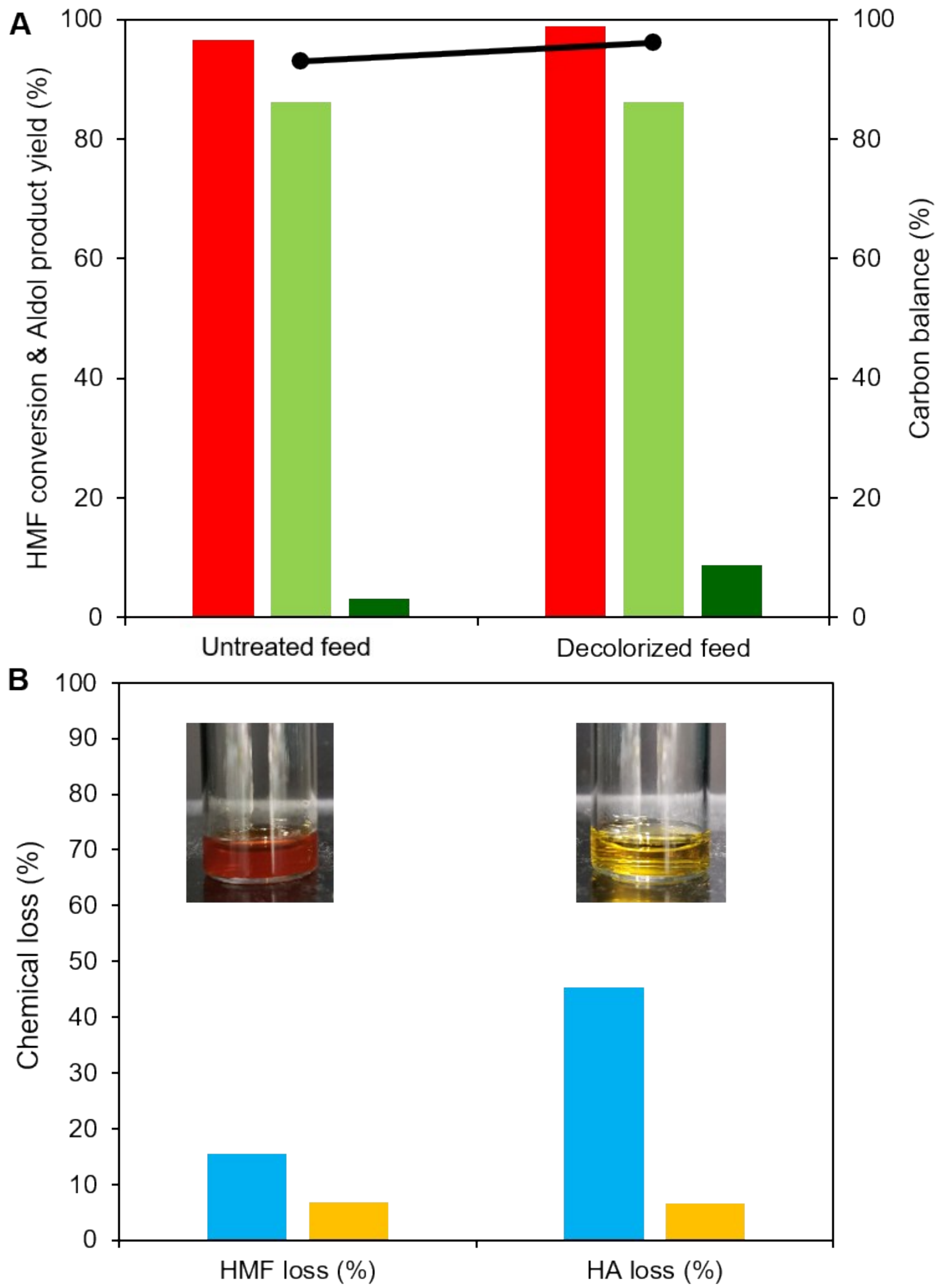


Fig.S2. (**A**) HMF conversion (Red bar) and aldol product yield (HAH: Light green bar, HA: Dark green bar), and carbon balance (Black dot) of 'Untreated feed' and 'Decolorized feed' for aldol condensation of fructose-derived HMF and acetone (Reaction conditions: $\frac{HMF}{Acetone + HA}$ (mol) = 2.6, 0.17 M NaOH, at 308K, 50 min for decolorized feed; $\frac{HMF}{Acetone + HA}$ (mol) = 2.5, 0.21 M NaOH, at 308 K, 60 min for pure feed), (**B**) Chemical loss after distillation with decolorization (Light blue bar) and after distillation without decolorization (Yellow bar). Inset images represent the color of HMF solution before (left) and after (right) the decolorization.

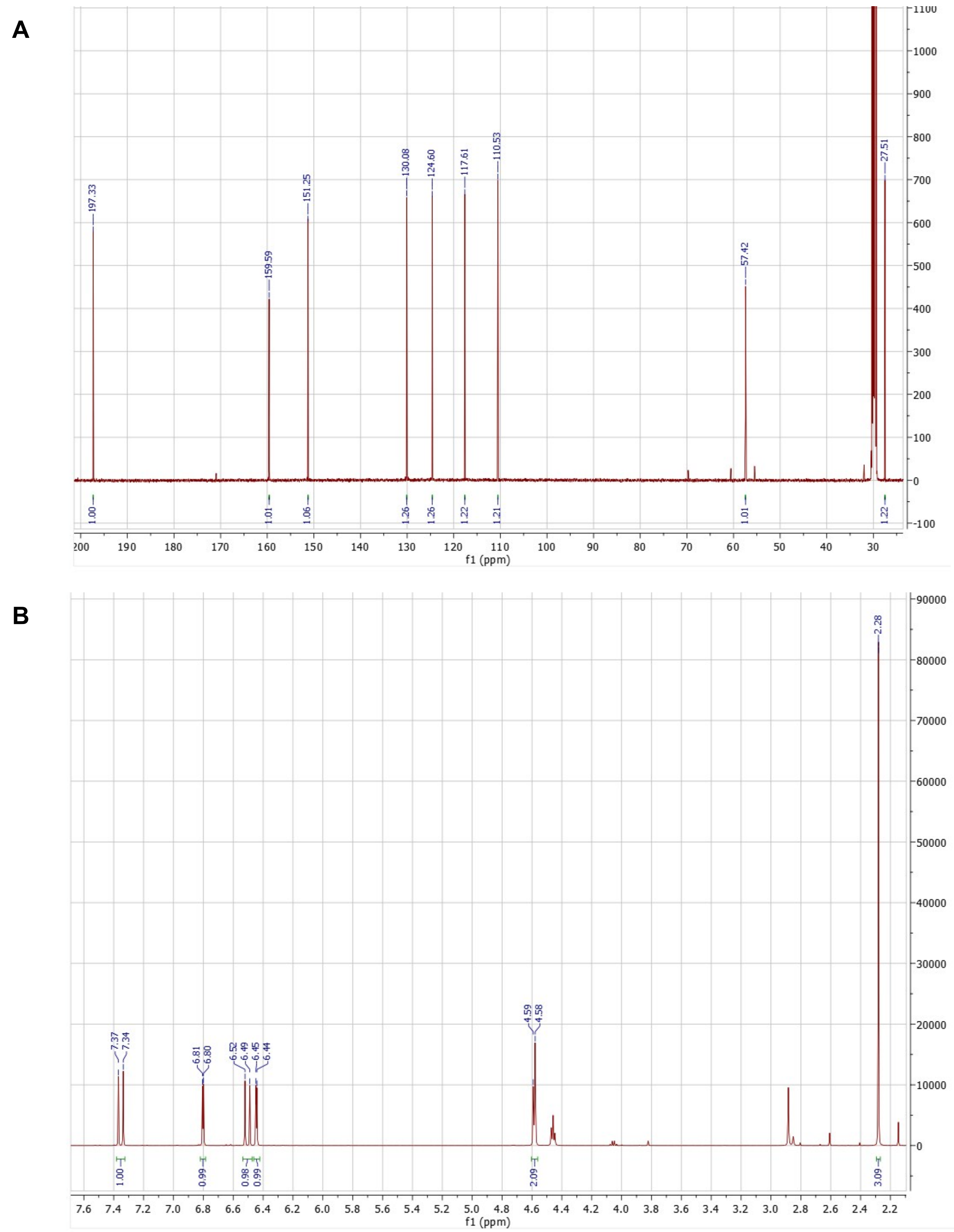


Fig.S3. (**A**) ^{13}C quantitative NMR spectrum of HA (126 MHz, Acetone) δ: 197.33 (1C), 159.59 (1C), 151.25 (1C), 130.08 (1C), 124.60 (1C), 117.61 (1C), 110.53 (1C), 57.42 (1C), 27.51 (1C) ppm. (**B**) ^{1}H standard NMR spectrum of HA (500 MHz, Acetone) δ: 7.37-7.34 (1H), 6.81-6.80 (1H), 6.52-6.49 (1H), 6.45-6.44 (1H), 4.59-4.58 (2H), 2.28 (3H) ppm.

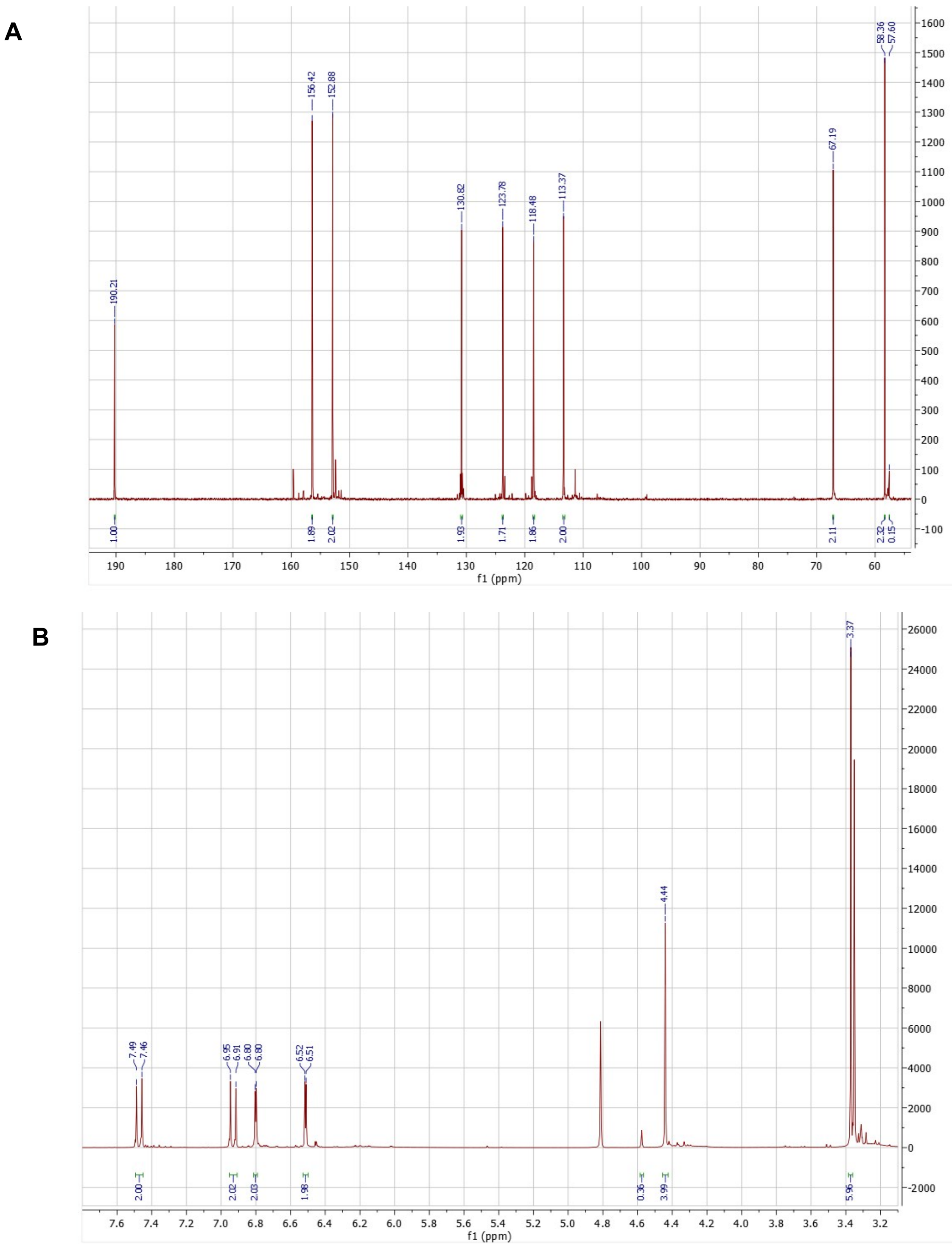
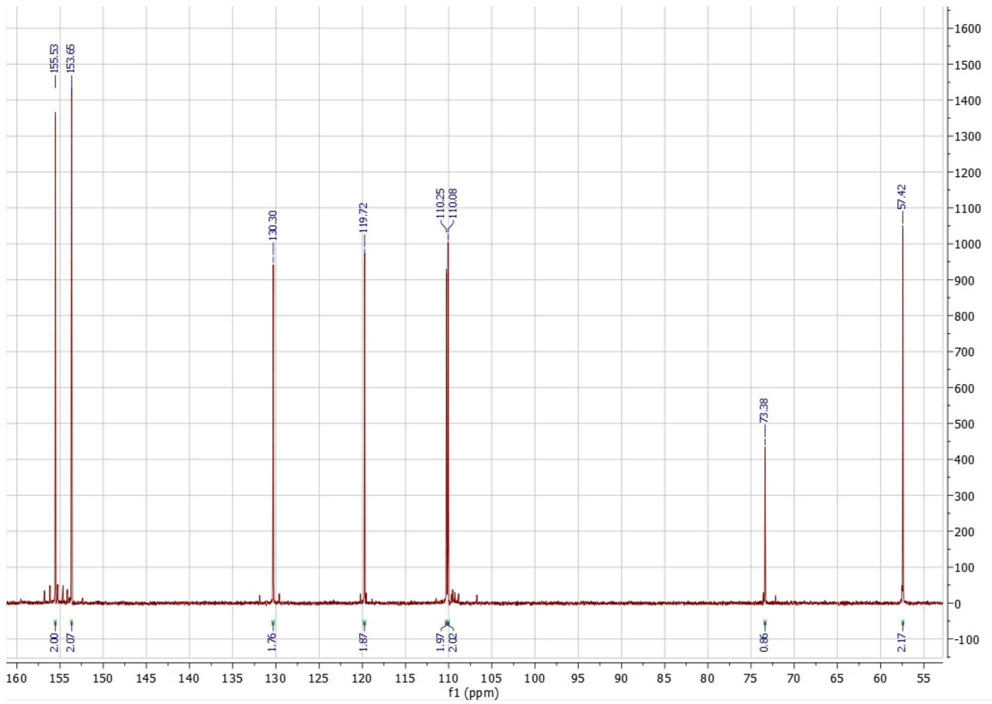


Fig.S4. (**A**) ^{13}C quantitative NMR spectrum of etherified HAH (126 MHz, MeOD) δ: 190.21 (1C), 156.42 (2C), 152.88 (2C), 130.82 (2C), 123.78 (2C), 118.48 (2C), 113.37 (2C), 67.19 (2C), 58.36 (2C) ppm. (**B**) ^{1}H standard NMR spectrum of etherified HAH (500 MHz, MeOD) δ: 7.49-7.46 (m,2H), 6.95-6.91 (m,2H), 6.80 (d,2H), 6.52 (d,2H), 4.44 (s,4H), 3.37 (s,6H) ppm. $C_{17}H_{18}O_5$ $[M+H]^+$ calculated: 303.1227, measured: 303.1224 (Error: 1.0 ppm).

A



B

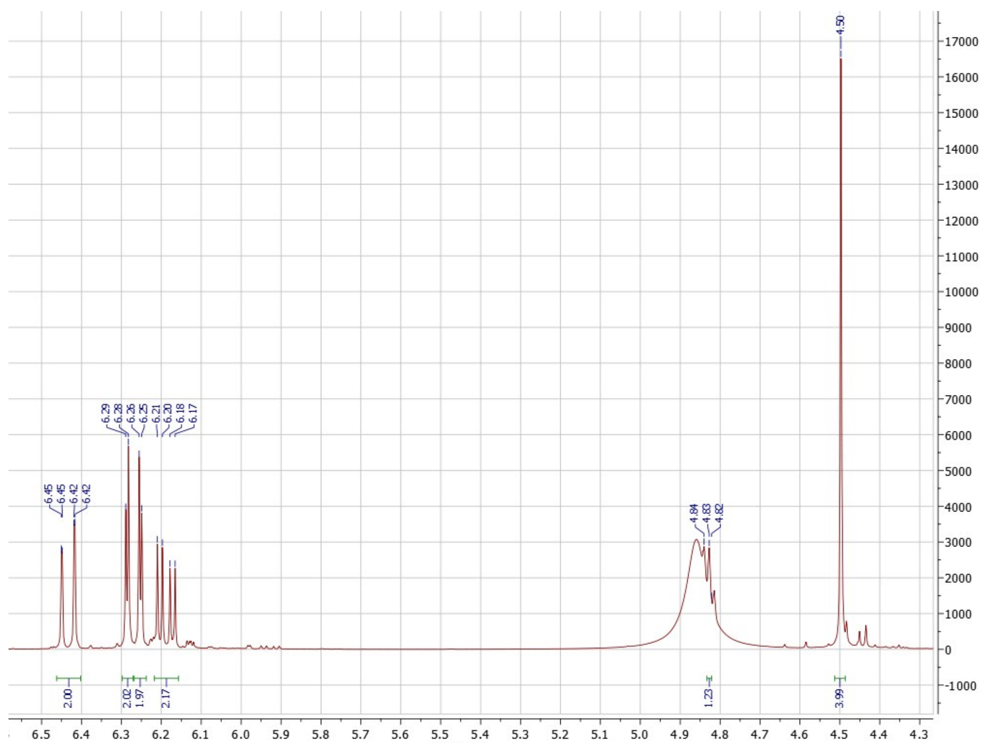


Fig.S5. (**A**) ^{13}C quantitative NMR spectrum of selectively reduced HAH (126 MHz, MeOD) δ: 155.53 (2C), 153.65 (2C), 130.30 (2C), 119.72 (2C), 110.25 (2C), 110.08 (2C), 73.38 (1C), 57.42 (2C) ppm. (**B**) ^{1}H standard NMR spectrum of selectively reduced HAH (500 MHz, MeOD) δ: 6.45 (d,1H), 6.42 (d,1H), 6.29 (d,2H), 6.26

(d,2H), 6.21 (d,1H), 6.18 (d,1H), 4.83 (t,1H), 4.50 (s,4H) ppm. $C_{15}H_{16}O_5$ $[M+Na]^+$ calculated: 299.0890, measured: 299.0889 (Error: 0.3 ppm).

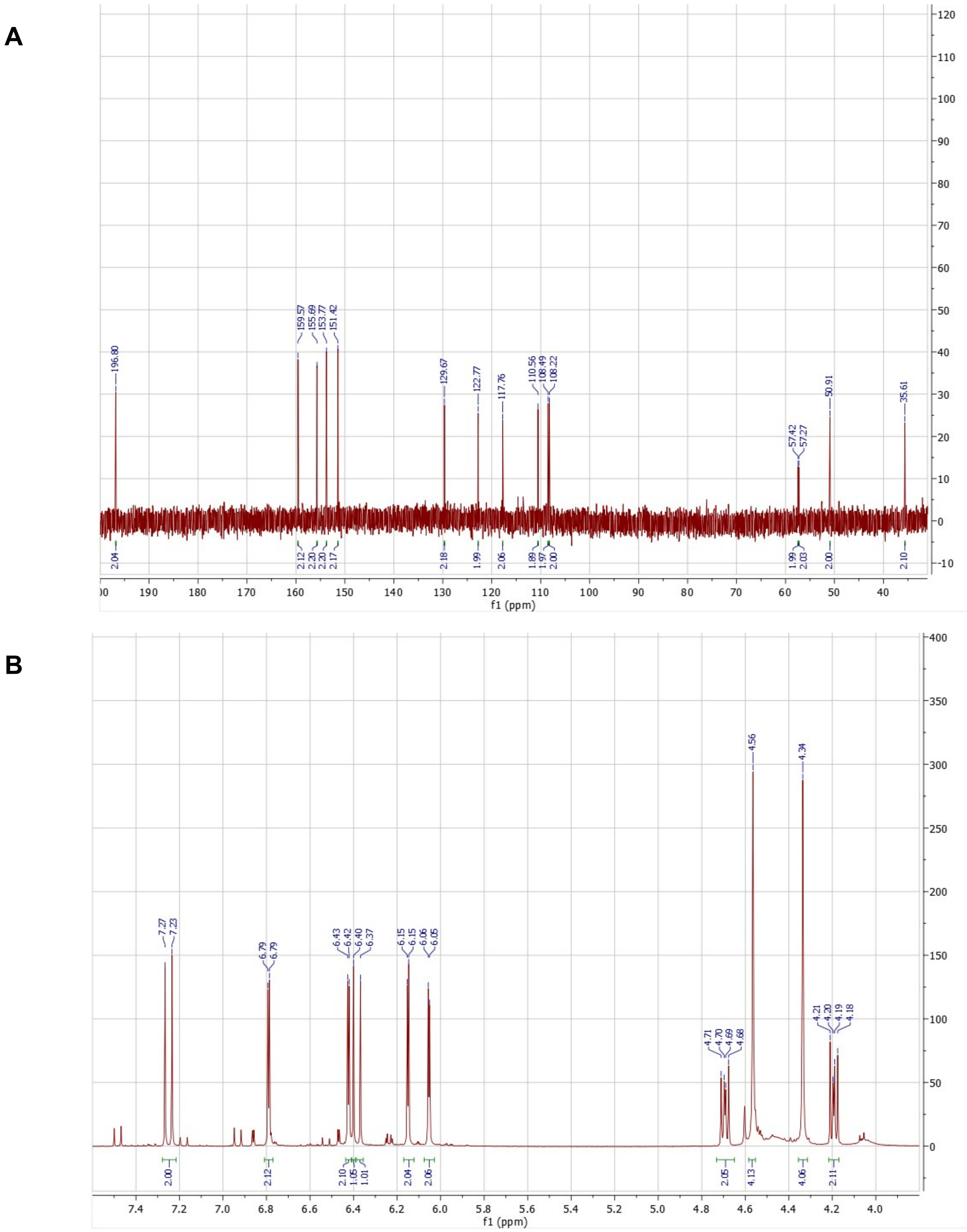


Fig.S6. (**A**) ^{13}C quantitative NMR spectrum of selectively reduced HAH (126 MHz, Acetone-d_6) δ: 196.80 (2C), 159.57 (2C), 155.69 (2C), 153.77 (2C), 151.42 (2C), 129.67 (2C), 122.77 (2C), 117.76 (2C), 110.56 (2C), 108.49 (2C), 108.22 (2C), 57.42 (2C), 57.27 (2C), 50.91 (2C), 35.61 (2C) ppm. (**B**) ^1H standard NMR spectrum of selectively reduced HAH (500 MHz, Acetone-d_6) δ: 7.27-7.23 (2H), 6.79 (d, 2H), 6.43 (d, 2H), 6.40 (s,1H), 6.37 (s,1H), 6.15 (d,2H), 6.05 (d,2H), 4.70 (dd,2H), 4.56 (s,4H), 4.34 (s,4H), 4.20 (dd,2H) ppm. $C_{30}H_{28}O_{10}$ $[M+Na]^+$ calculated: 571.1575, measured: 571.1567 (Error: 1.4 ppm).

A

B

C

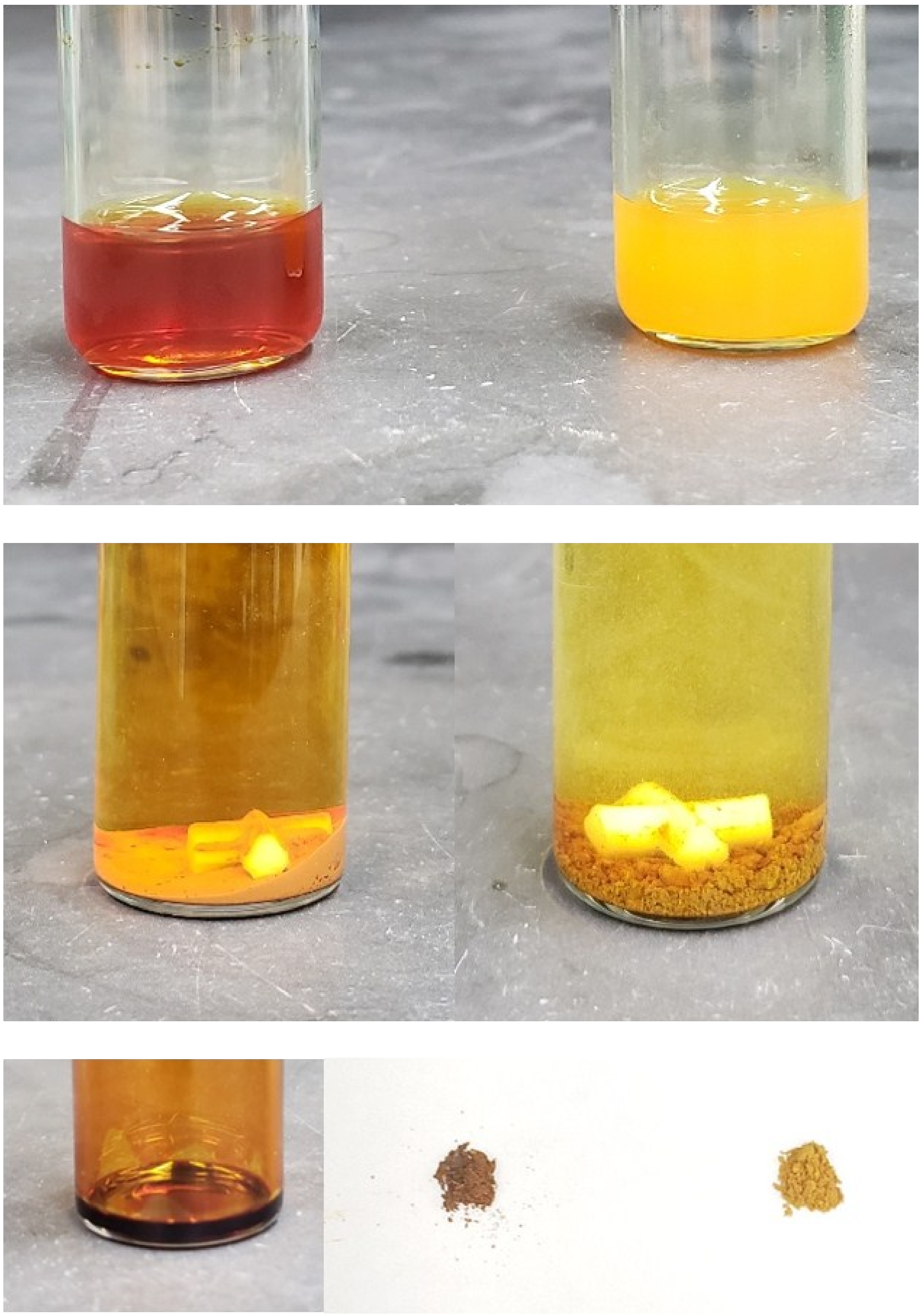


Fig.S7. (**A**) The color of the solution before (right) and after (left) the etherification, (**B**) The color of the solution before (right) and after (left) the dimerization, (C) Dried samples of etherified HAH, HAH dimer, and HAH at room temperature (from left to right, etherified HAH, HAH dimer, and HAH, respectively).

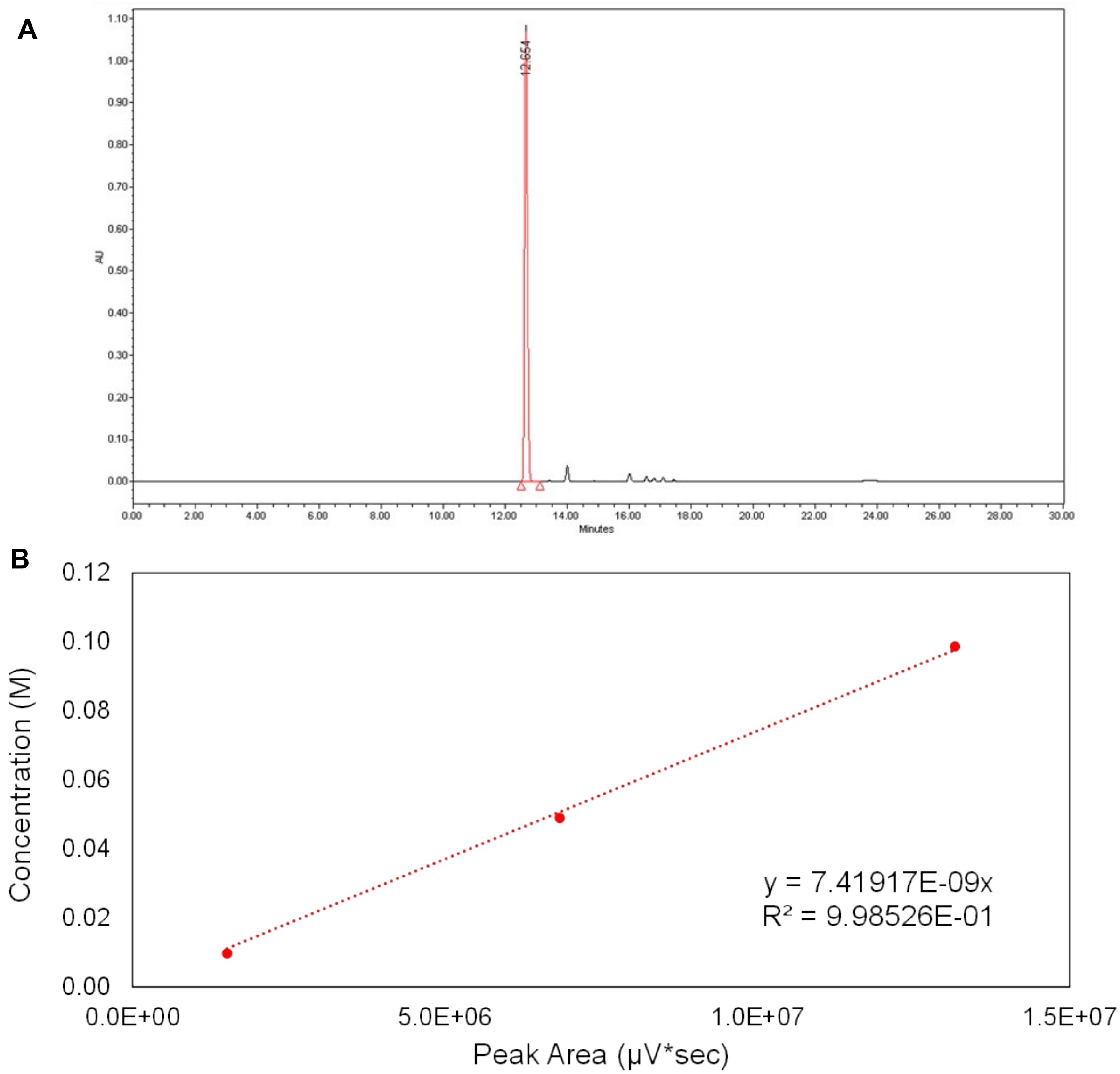


Fig.S8. (**A**) Retention time (12.654 min) of 0.05 M purified HA in methanol solvent by HPLC analysis (UV wavelength of detector: 390 nm), (**B**) HPLC calibration curve for HA qualification.

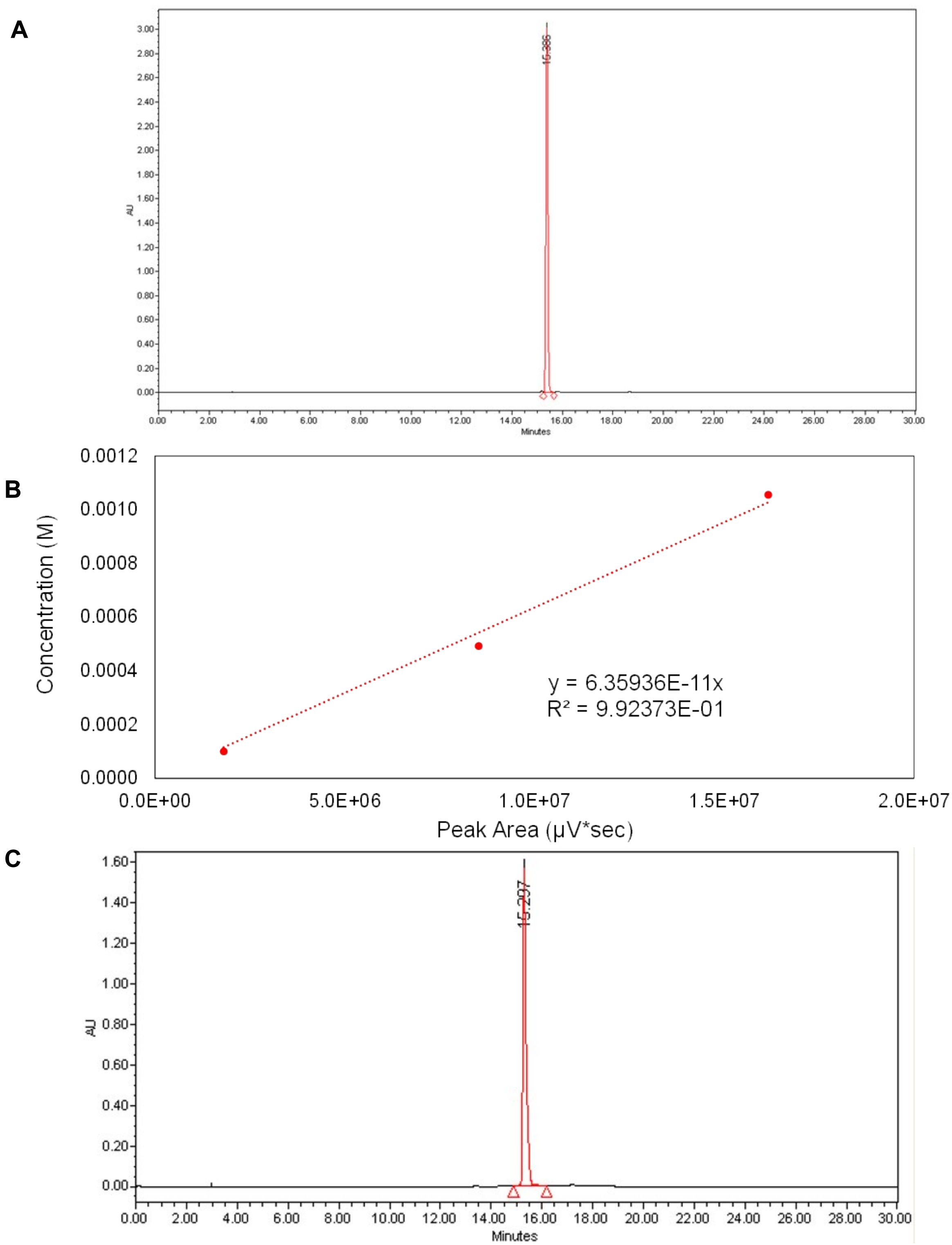


Fig. S9. (**A**) Retention time (15.386 min) of 0.001 M purified HAH in methanol solvent by HPLC analysis (UV wavelength of detector: 390 nm), (**B**) HPLC calibration curve for HAH qualification, (**C**) Purity analysis of 0.001 M fructose-derived HAH in methanol solvent (UV wavelength of detector: 390 nm).

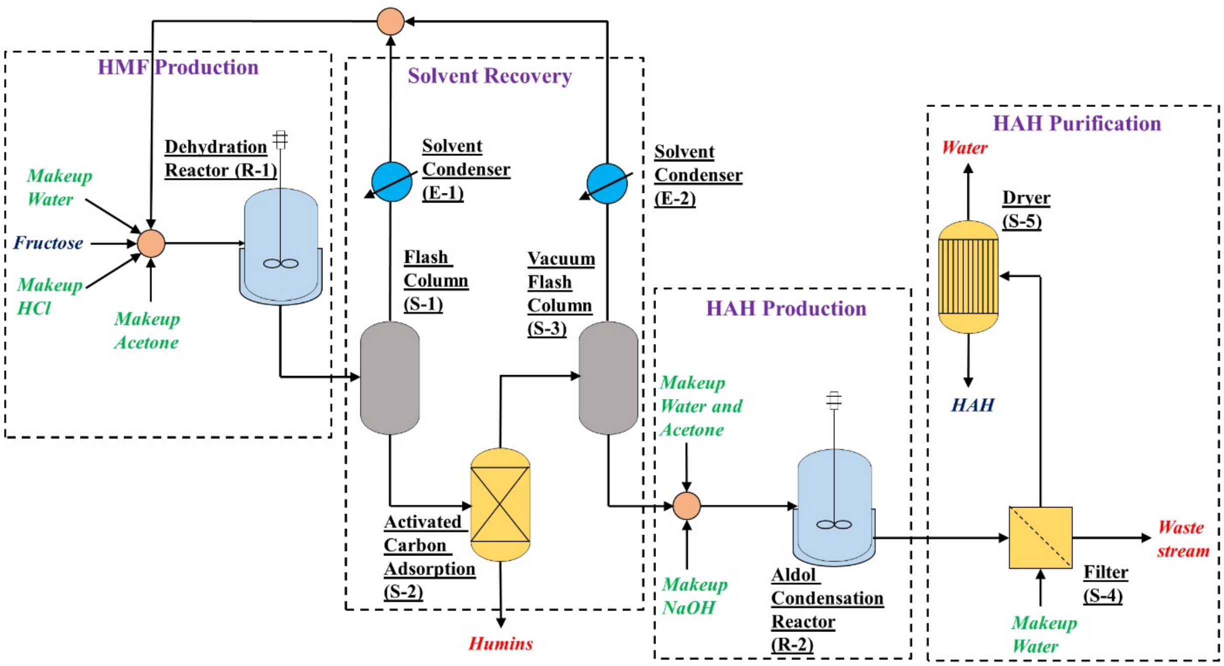


Fig. S10. Overview of the process flow diagram.

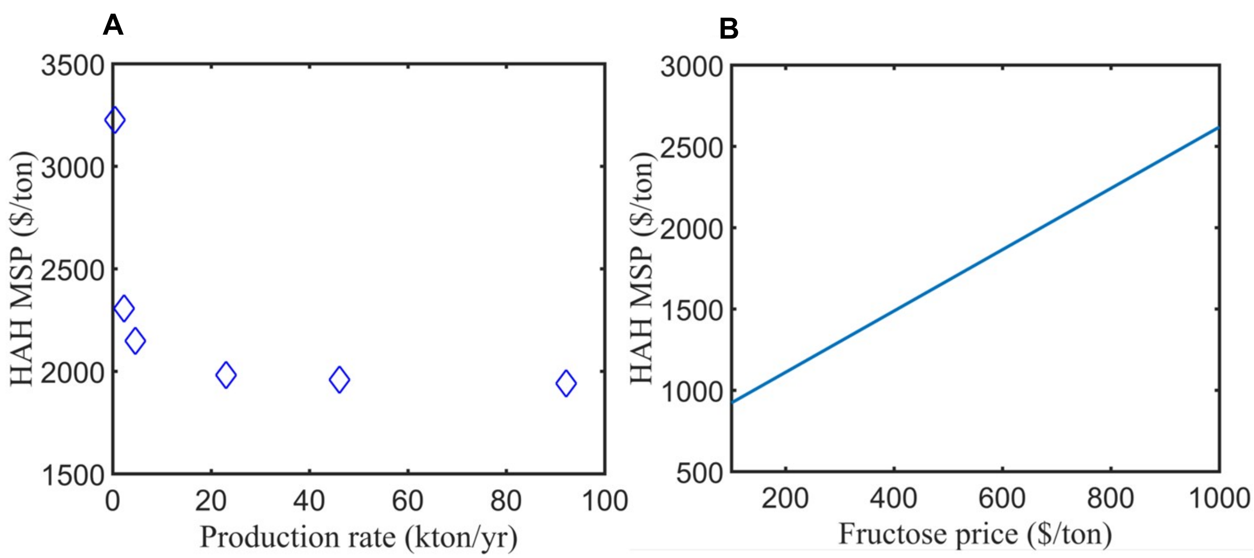


Fig. S11. Illustration of variation of HAH minimum selling price (MSP) as a function of (A) production rate of HAH and (B) fructose price. The annual production of high fructose corn syrup is 8.1 million tons (*10*), which suggests that orders of magnitude more fructose is available to meet the production capacity considered in Fig. (A).

References

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