Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2020

Supplementary information

5-Hydroxymethylfurfural from fructose: An efficient continuous process in water-dimethyl carbonate biphasic system with high yield product recovery

Mahmoud Sayed, [a] Niklas Warlin,[b] Christian Hulteberg,[c] Ian Munslow, [d] Stefan Lundmark, [d] Oleg Pajalic, [d] Per Tunå,[c] Baozhong Zhang,[b] Sang-Hyun Pyo[a] and Rajni Hatti-Kaul[a*]

[a]*Division of Biotechnology, Department of Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden*
[b]*Center of Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden*
[c]*Department of Chemical Engineering, Lund University, P.O. Box 124, SE-22100 Lund, Sweden*

[d]*Perstorp AB, Innovation, Perstorp Industrial Park, 284 80 Perstorp, Sweden*

*Corresponding author

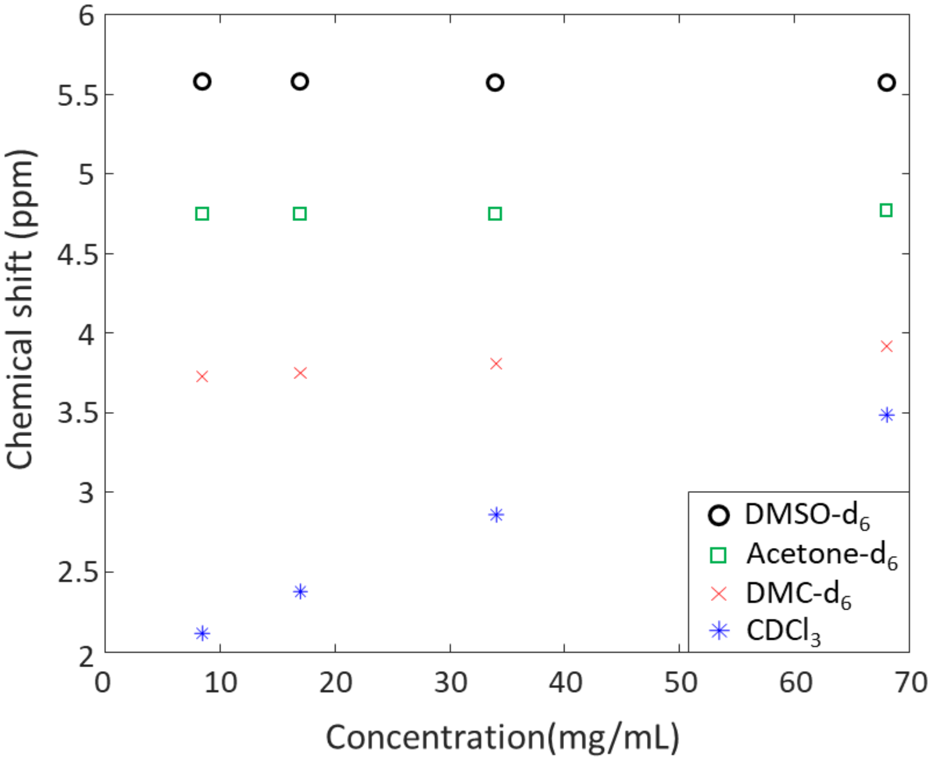

Figure S1. 5-HMF concentration dependence of the chemical shift of the –OH proton in 5-HMF in DMSO-d_6, acetone-d_6, DMC-d_6 and $CDCl_3$.

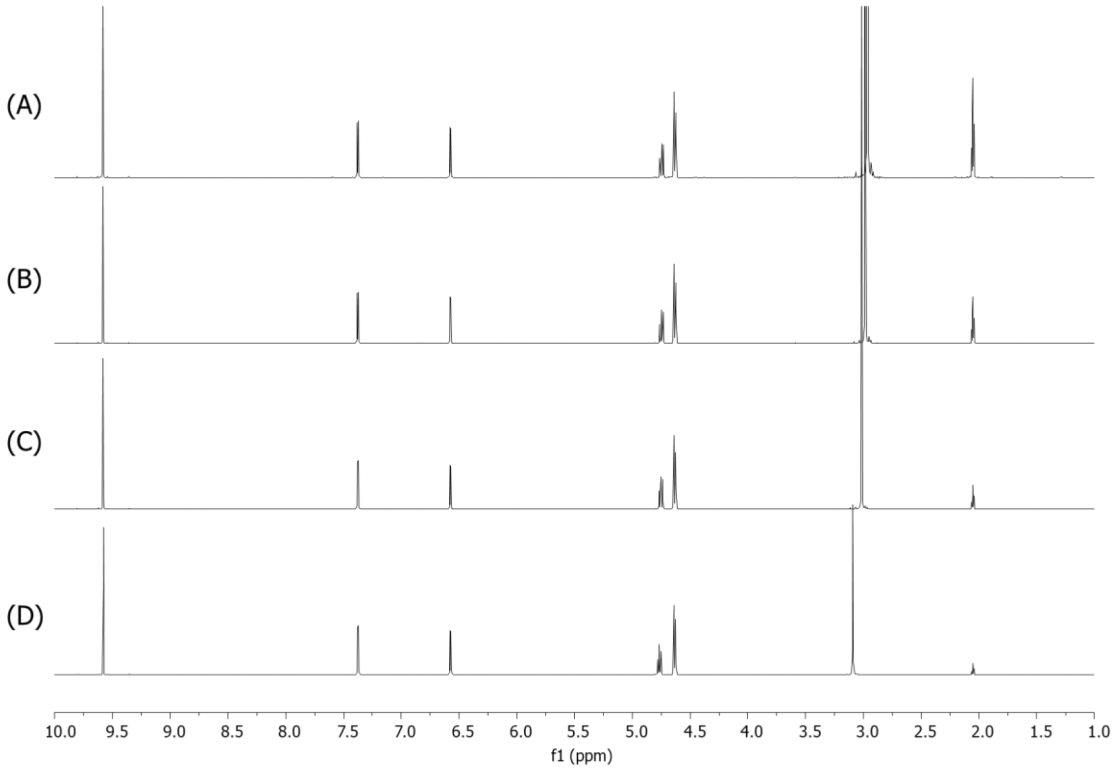

Fig S2. ^{1}H-NMR spectra of HMF in different concentrations dissolved in acetone-d_6. (A) = 8.5 mg/mL, (B) = 17 mg/mL, (C) = 34 mg/mL and (D) = 68 mg/mL.

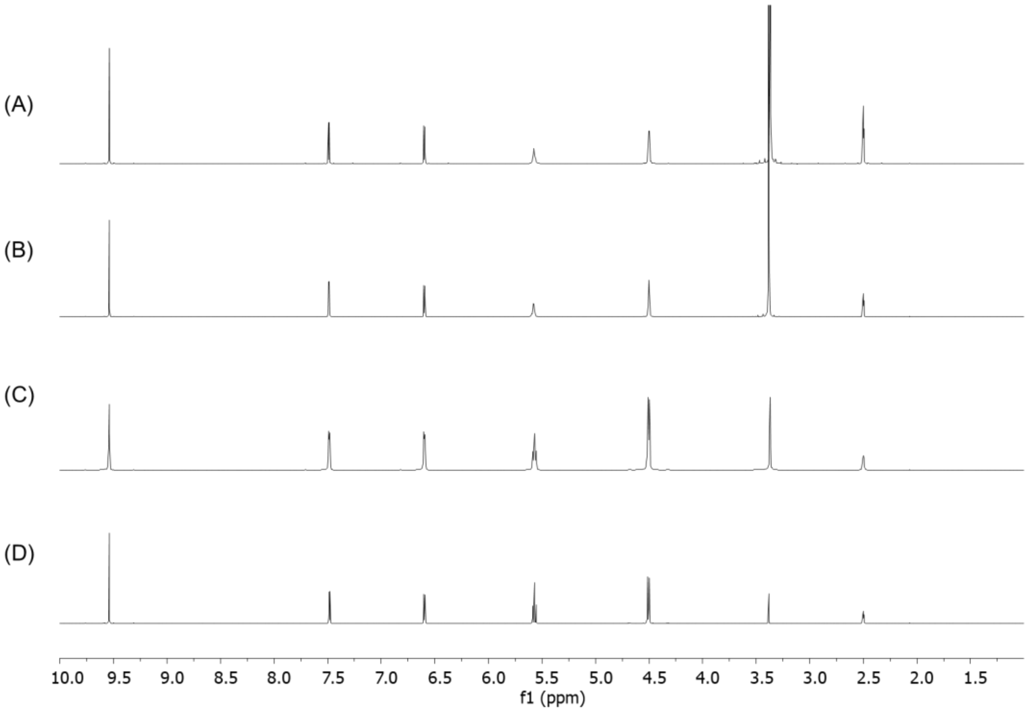

Fig S3. ^{1}H-NMR spectra of 5-HMF in different concentrations dissolved in DMSO-d_6. (A) = 8.5 mg/mL, (B) = 17 mg/mL, (C) = 34 mg/mL and (D) = 68 mg/mL

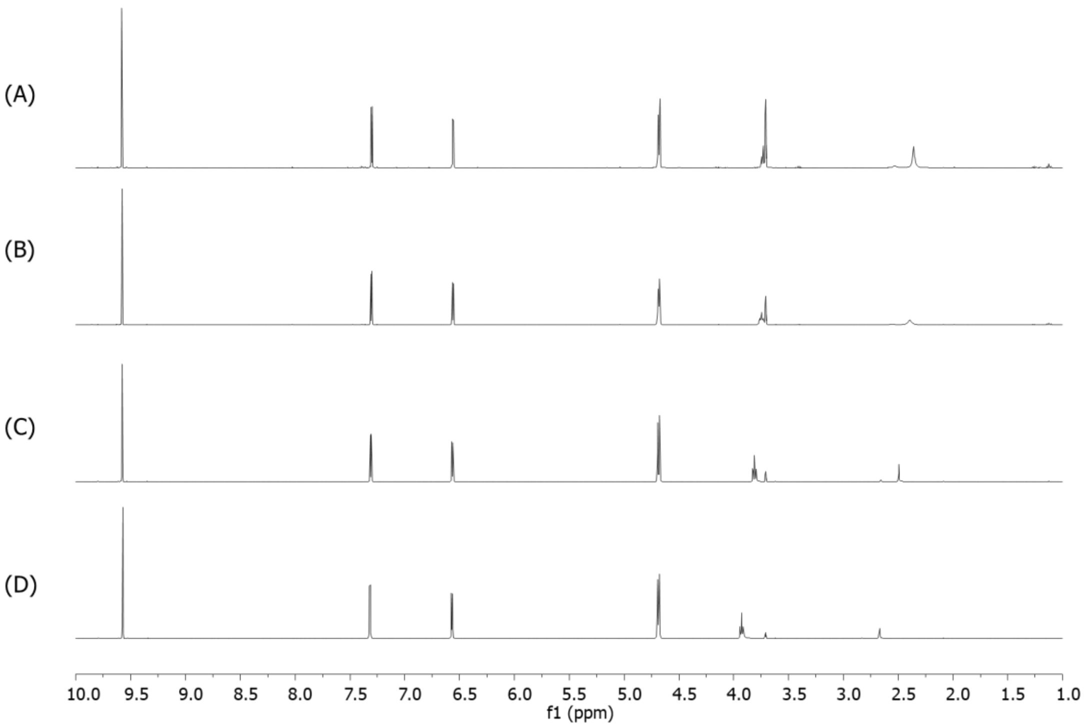

Fig S4. ^{1}H-NMR spectra of 5-HMF at different concentrations dissolved in dimethyl carbonate-d_6. (A) = 8.5 mg/mL, (B) = 17 mg/mL, (C) = 34 mg/mL and (D) = 68 mg/mL.

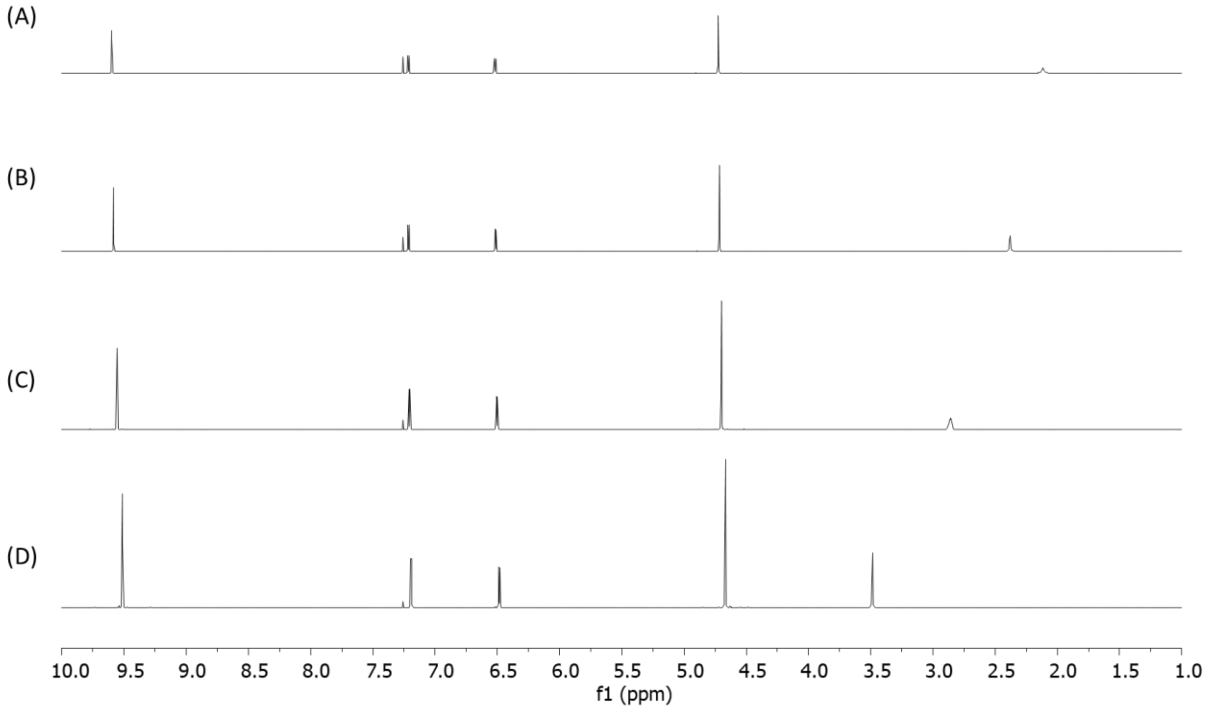

Fig S5. ^{1}H-NMR spectra of 5-HMF in different concentrations dissolved in $CDCl_3$. (A) = 8.5 mg/mL, (B= 17 mg/mL, (C) = 34 mg/mL and (D) = 68 mg/mL.

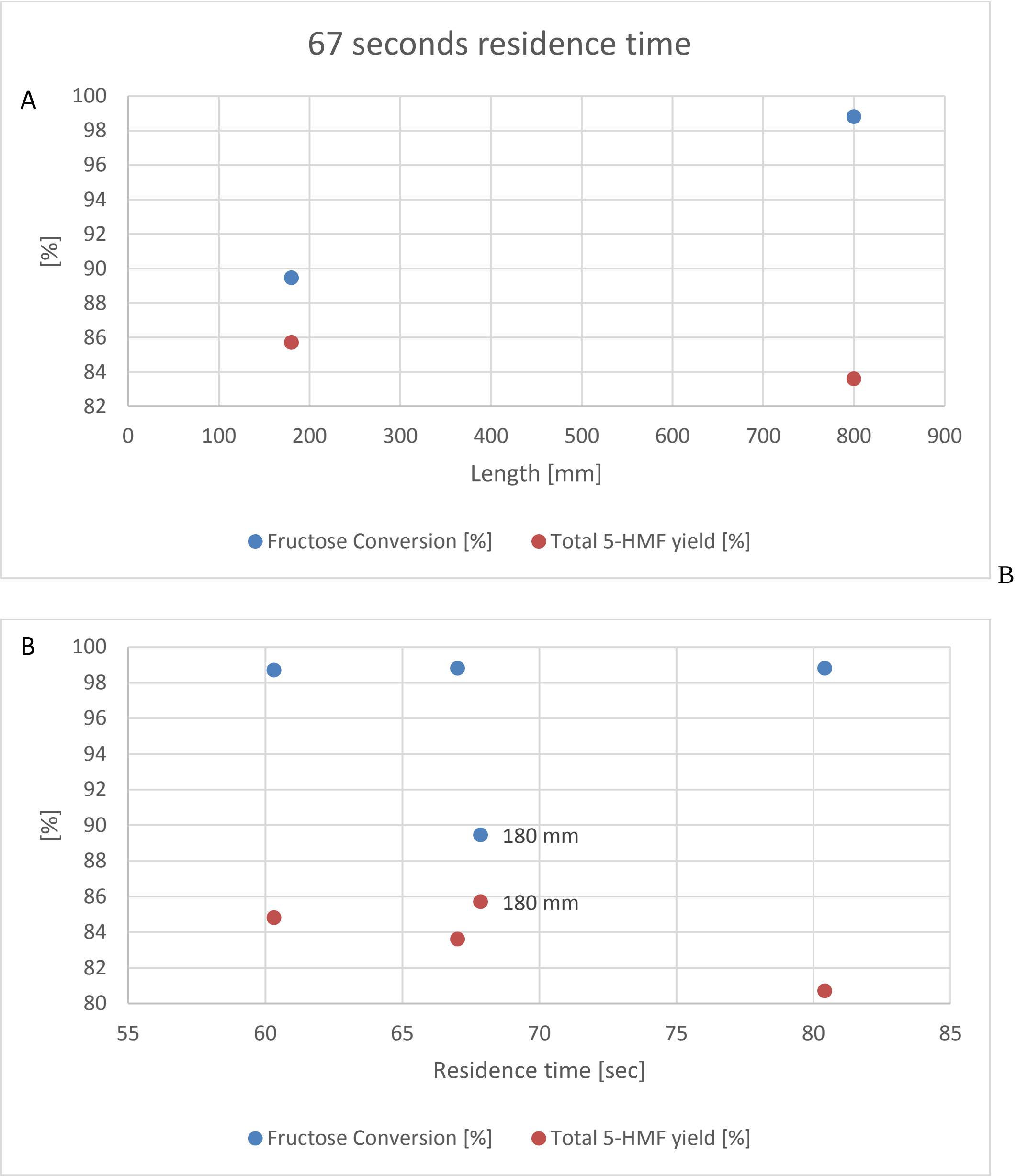

Fig. S6. 5-HMF space-time yield and fructose conversion at different (A) reactor lengths, and (B) residence times.

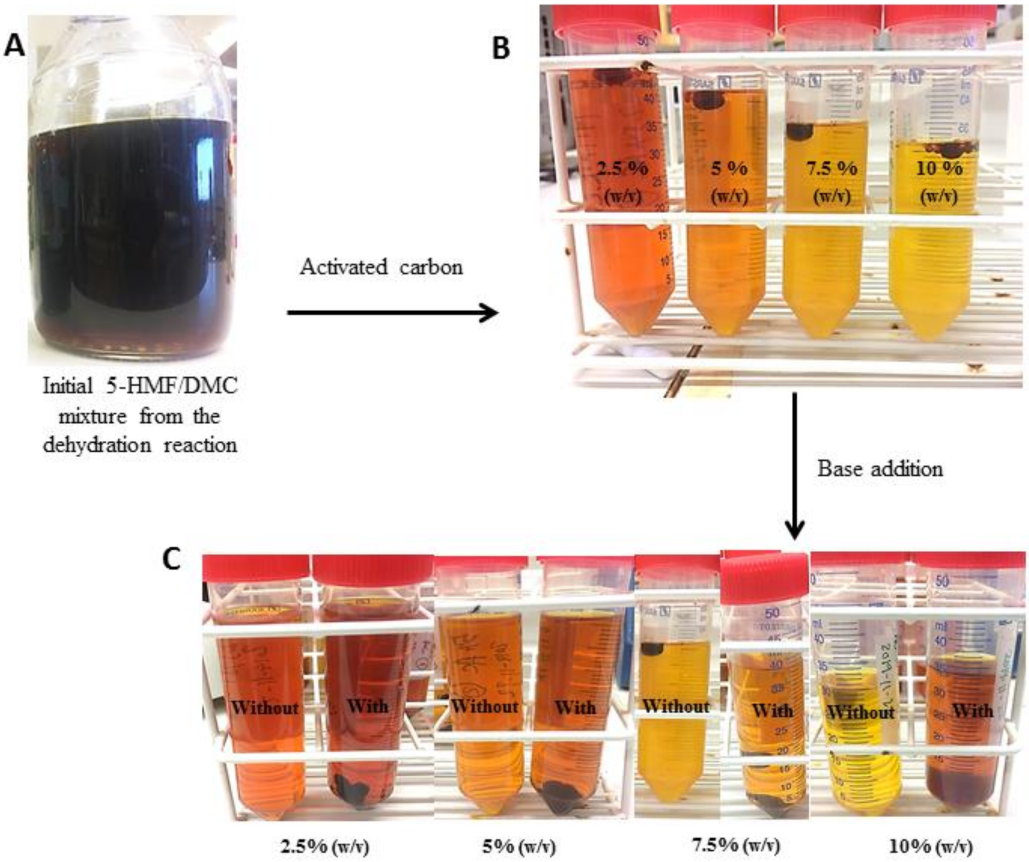

Fig. S7. Pretreatment steps for 5-HMF purification from the organic phase (A) through adding different concentrations of activated carbon (AC), (B) followed by adding 2 wt% NaOH to samples pretreated with 2.5, 5 and 7.5% AC, and 2% Na_2CO_3 to the one pretreated with 10% AC. Tubes without the base are shown for comparison.

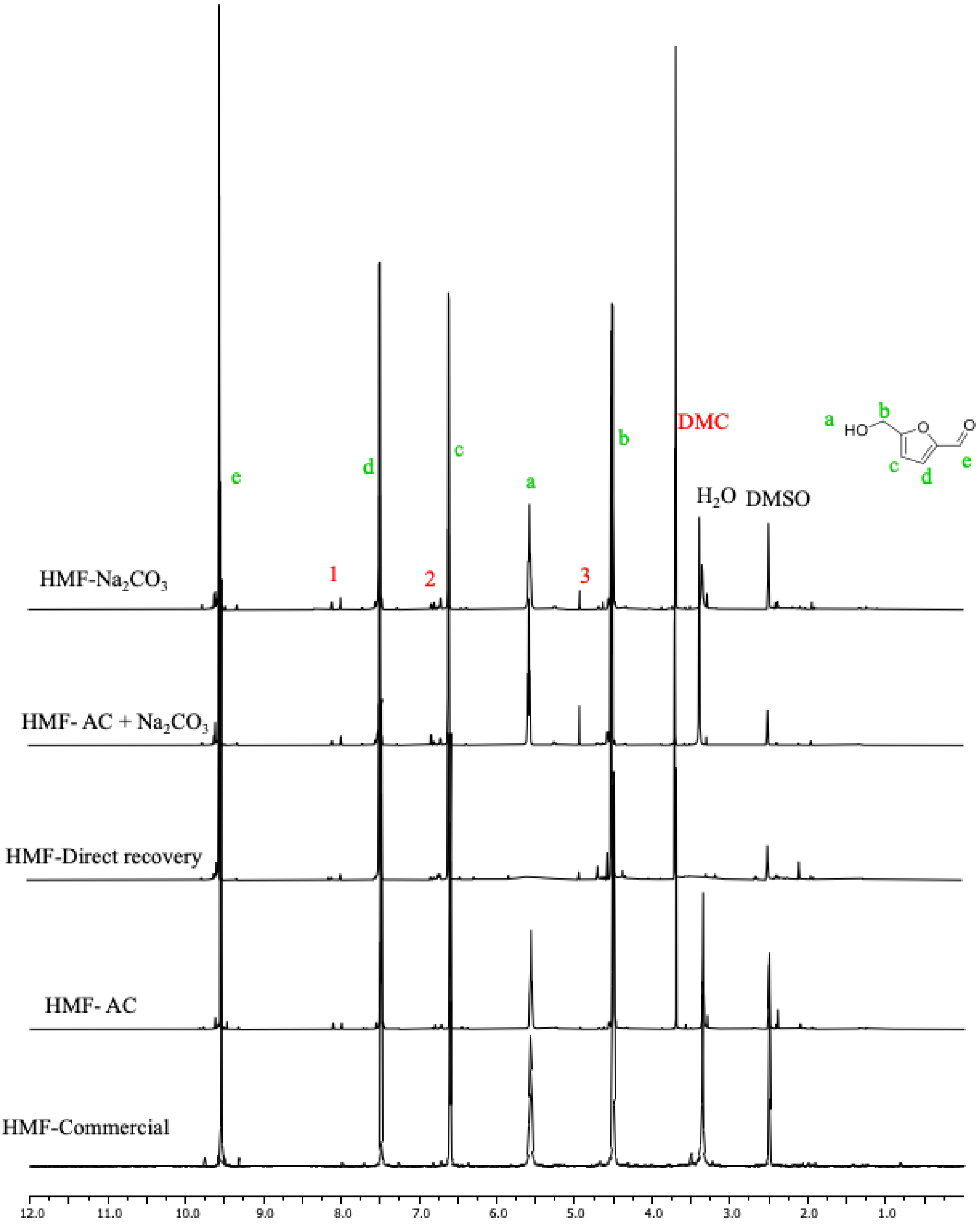

Figure S8. ^{1}H-NMR spectra of 5-HMF samples purified from the solvent phase of the biphasic system by direct solvent removal by rotary evaporation, treatment with activated carbon, and activated carbon and sodium carbonate, respectively, prior to solvent removal. NMR spectrum of the commercial 5-HMF sample is shown for comparison.

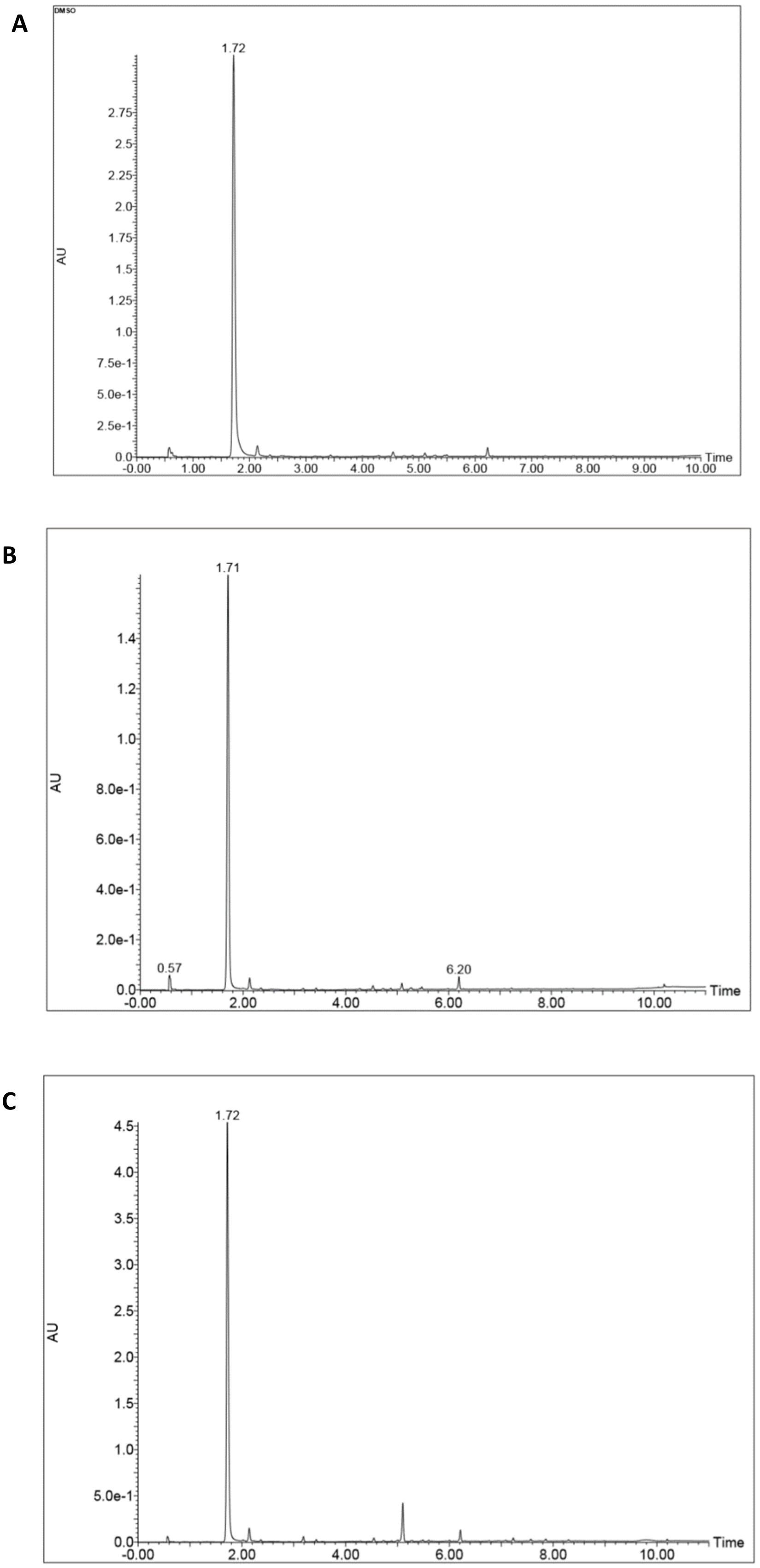

Figure S9. ULC Chromatograms of 5-HMF purified by direct evaporation of DMC and kept at -20 °C (A), and at room temperature for 24 h (B) and 72h (C).

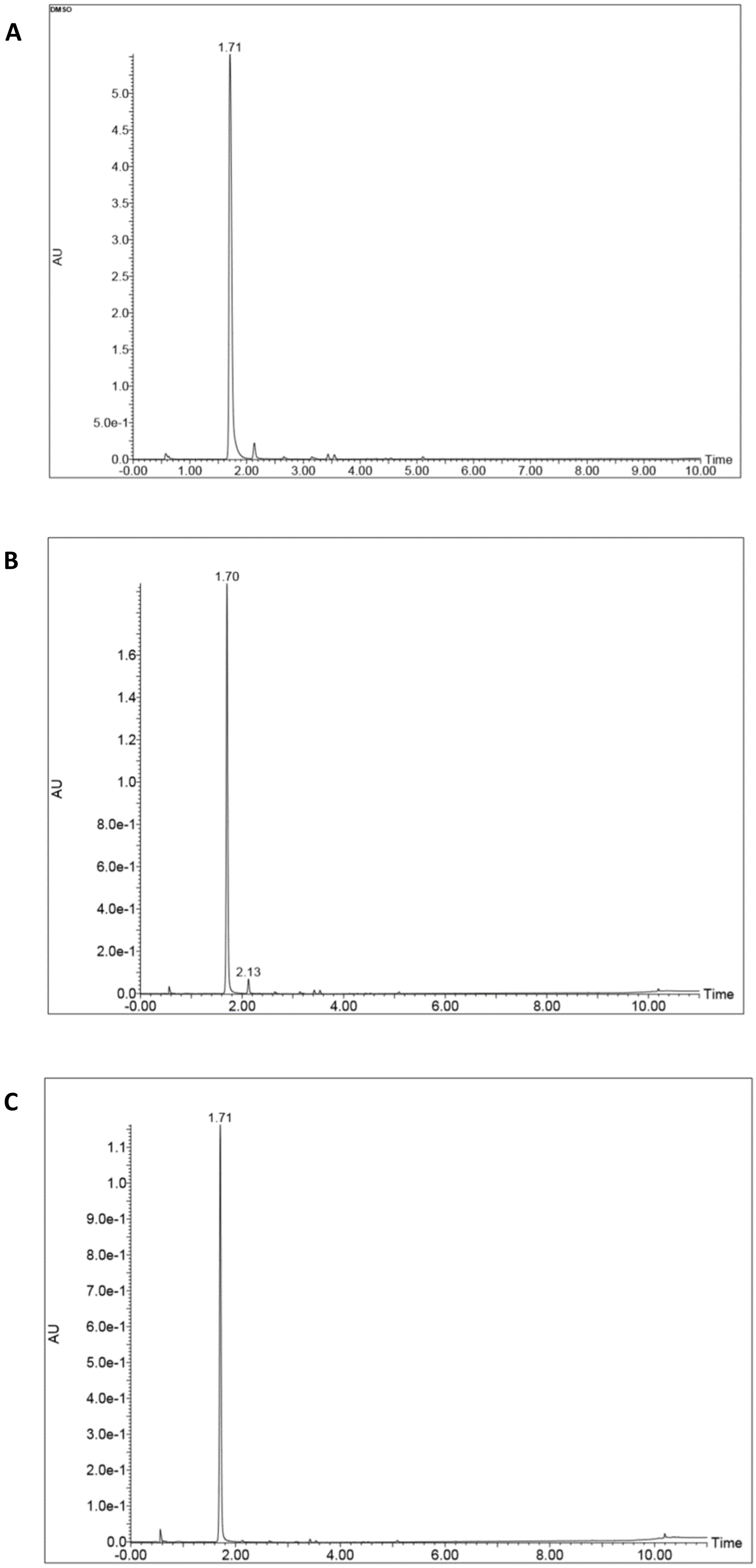

Figure S10. ULC Chromatograms of 5-HMF purified using activated carbon and kept at (A) -20 °C, and at room temperature for (B) 24 h and (C) 72 h respectively.

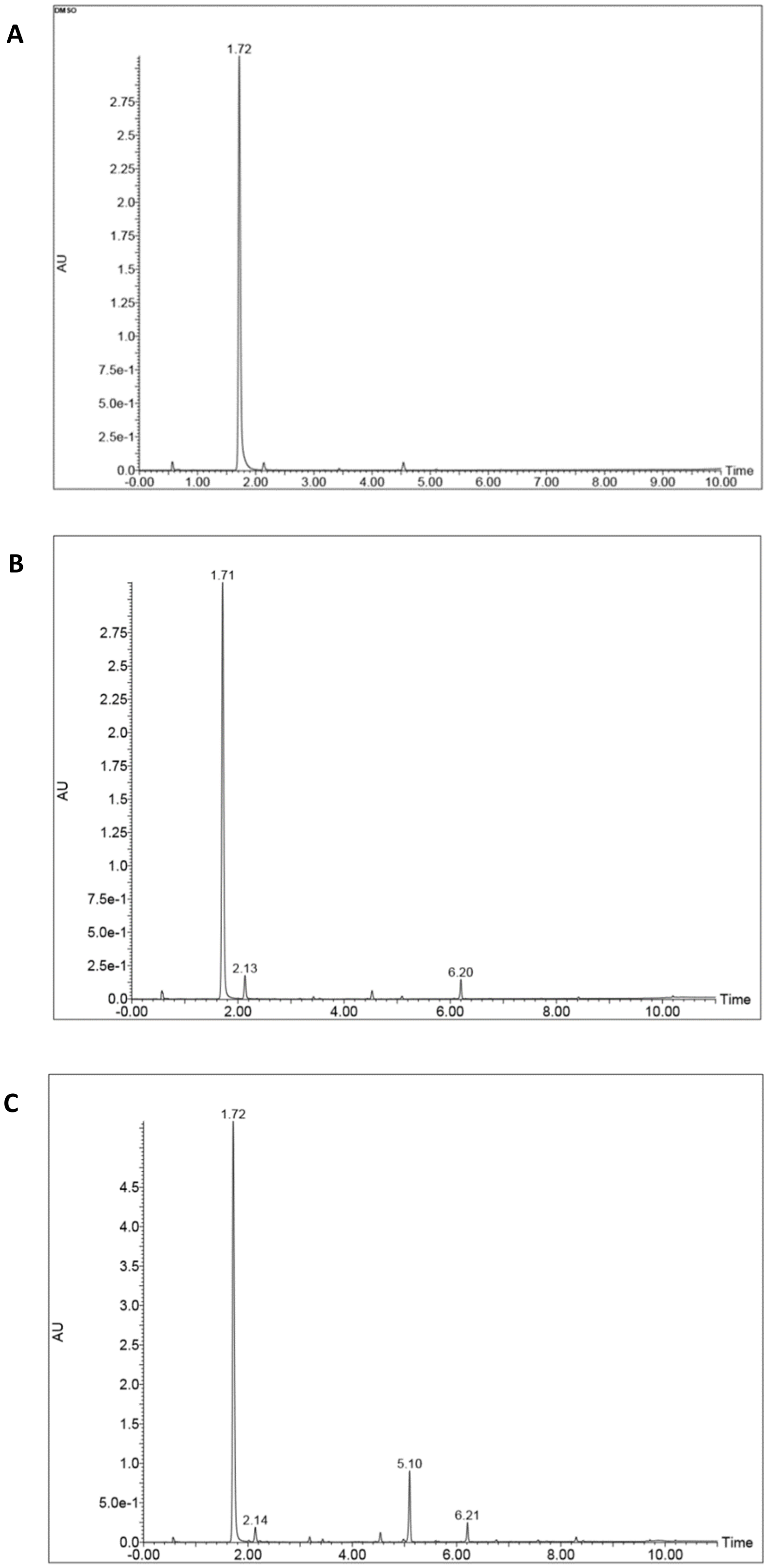

Figure S11. ULC Chromatograms of 5-HMF purified using activated carbon and Na_2CO_3 and kept at (A) -20 °C, and at room temperature for (B) 24 h and (C) 72 h, respectively.

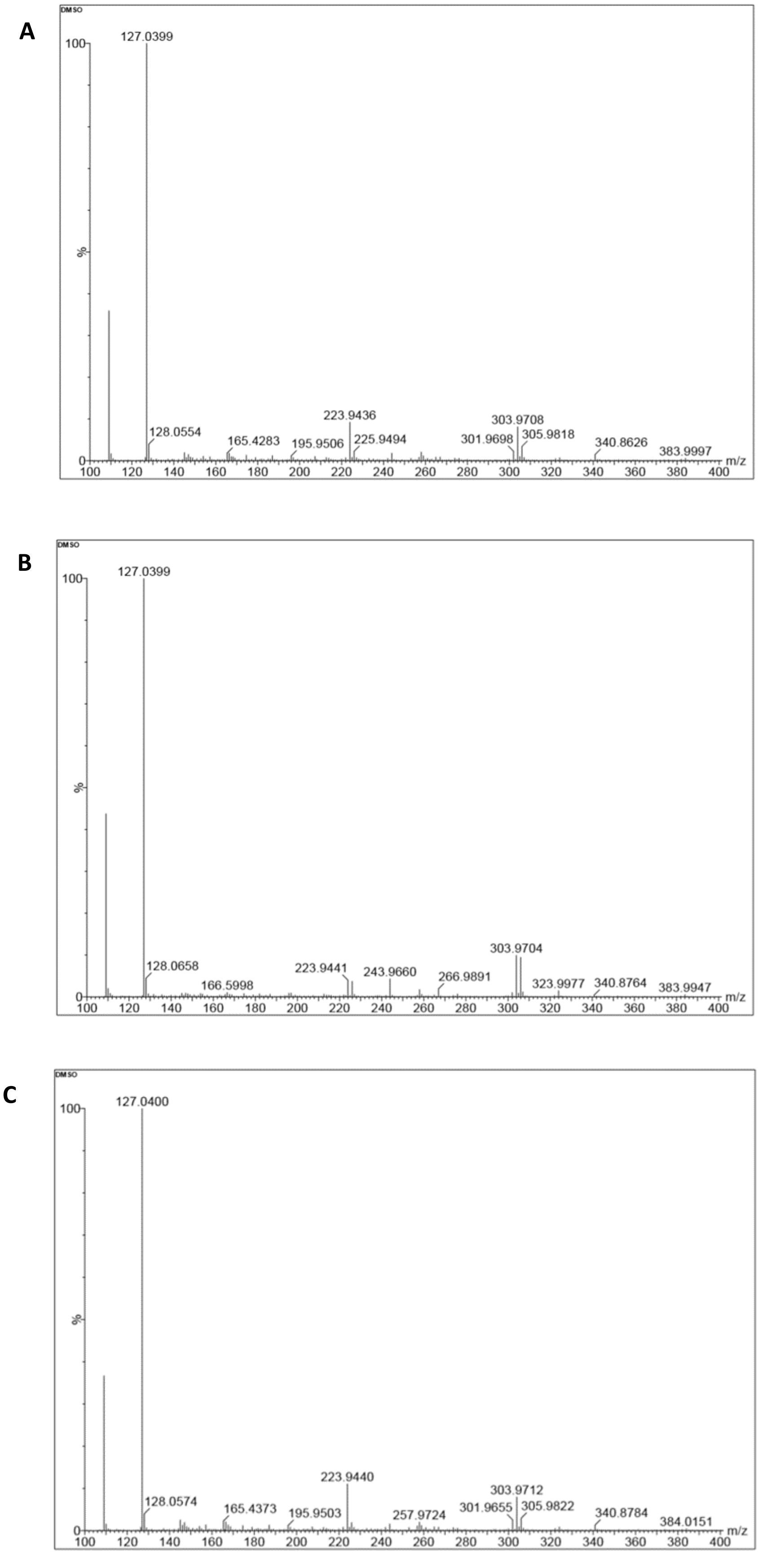

Figure S12. Mass spectrum of 5-HMF purified using (**A**) direct evaporation of organic solvent, (**B**) prior treatment with activated carbon, and (**C**) with activated carbon and Na_2CO_3, respectively.

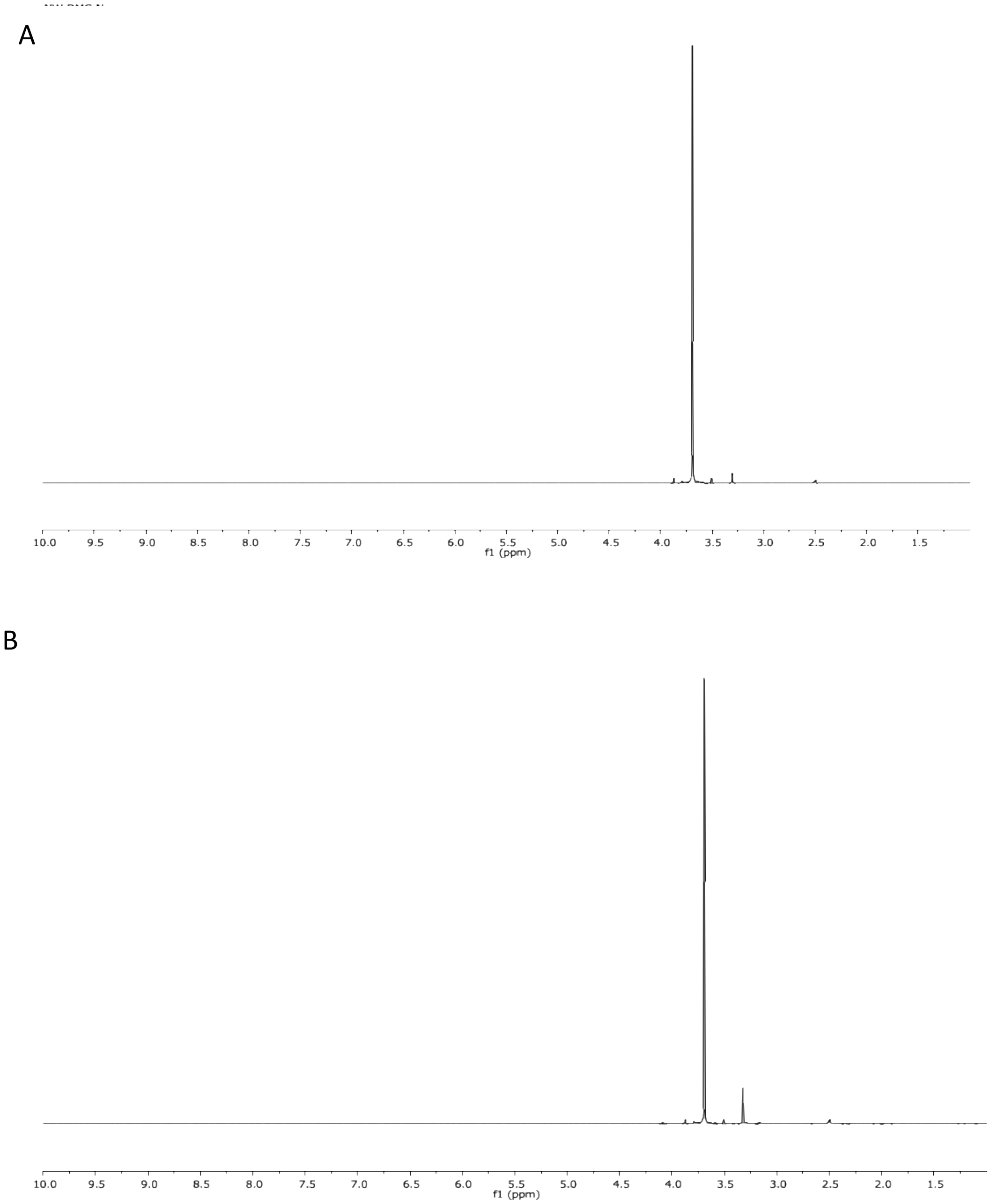

Fig. S13. ^{1}H-NMR spectra of (A) commercial DMC, and (B) the recovered DMC from the 5-HMF production process

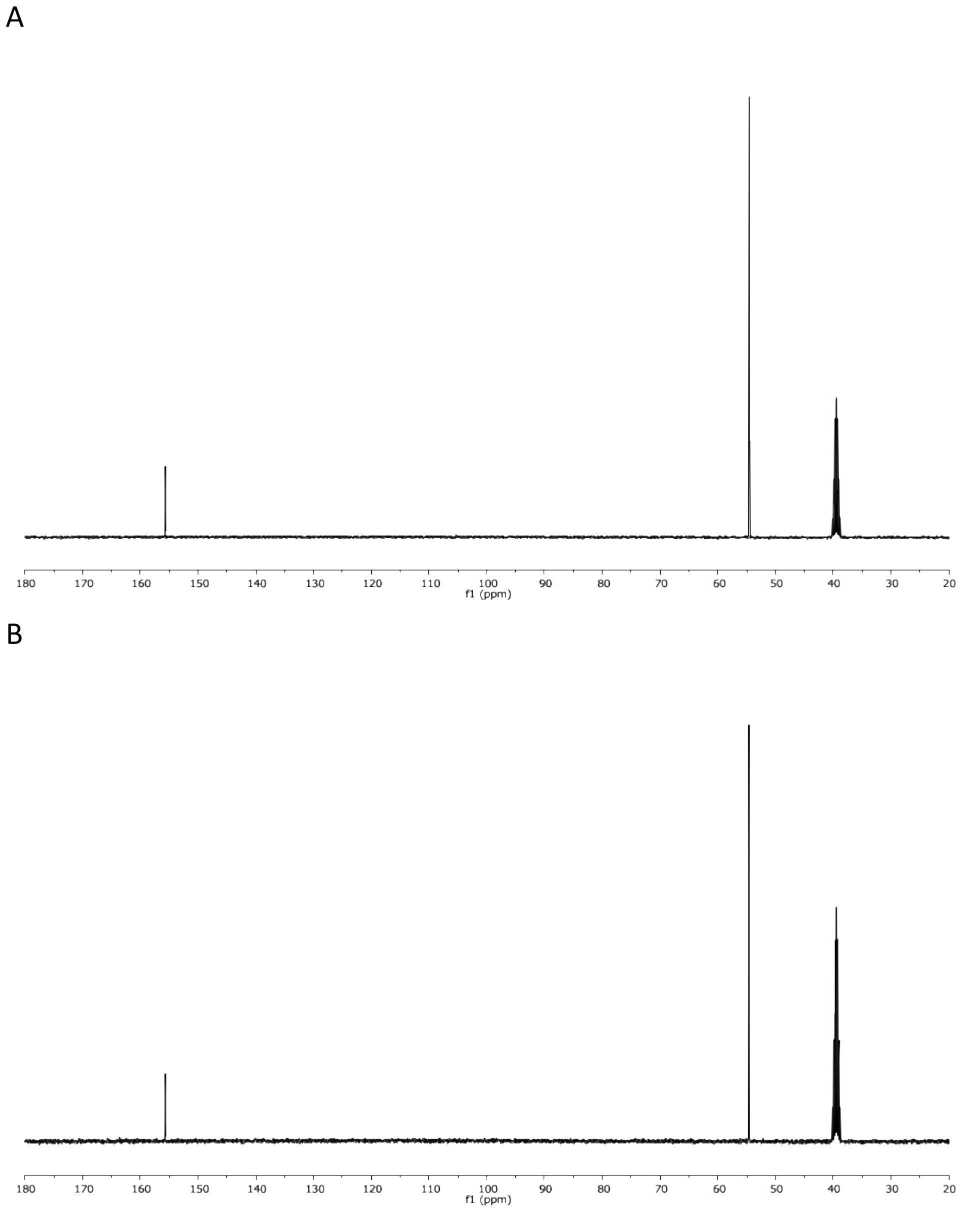

Fig. S14. ^{13}C-NMR spectra of (A) commercial DMC, and (B) the recovered DMC from the 5-HMF production process

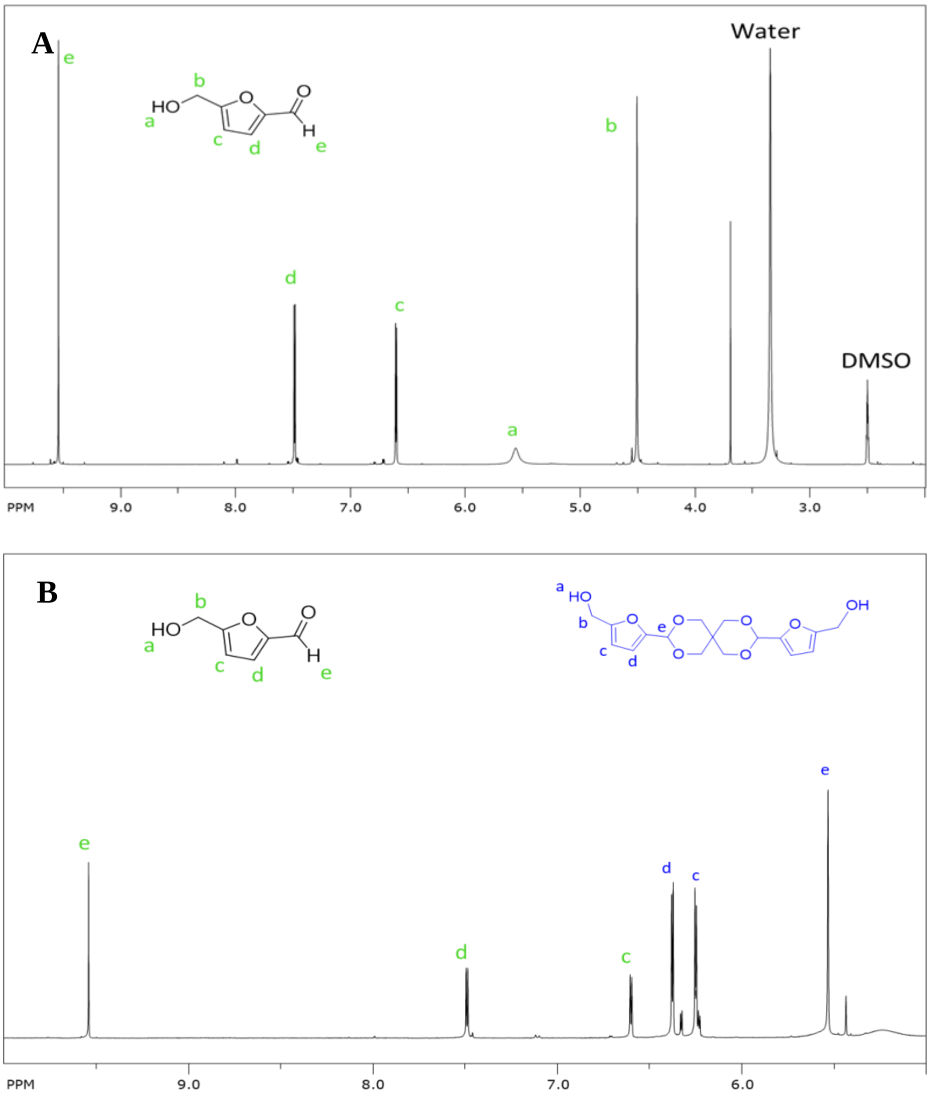

Fig. S15. ^{1}H-NMR spectra of (A) the purified 5-HMF, and (B) the spirocyclic diol product obtained by the reaction of 5-HMF with pentaerythritol.

Table S1. Comparison of 5-HMF production from fructose in this study with previous reports in biphasic systems using homogeneous or heterogeneous acid catalysts

Fructose (wt%)	Biphasic system	Catalyst, concentration	Temp (°C)	Reaction time (min)	Fructose conversion (%)	5-HMF yield (wt%)	Reference
30	Dioxane-H_2O (86.5:13.5 w/w)	HCl, 0.04 wt%	180	4	83.7	40	1
10	Water-MIBK (1:3 v/v)	HCl, 0.25 M	140	15	100	52	2
50	Water-DMSO-MIBK-2-butanol (8:2:21:9 w/w)	HCl, 0.25 M	180	3	91	47	3
10	Water-DMSO-MIBK-2-butanol (5:5:14:6 w/w)	HCl, pH 1	170	4	95	64	4
30*	**Water-DMC (1:3)**	**HCl, 0.2 M**	**200**	**1**	**96**	**87.2**	**This study**
30*	**Water-DMC (1:3)**	**HCl, 0.2 M**	**180**	**1**	**95**	**74.4**	**This study**
30	Water-DMSO-MIBK- 2-butanol (8:2:21:9 w/w)	H_2SO_4, 0.25 M	180	3	85	42	3
30	Water-MIBK-2-butanol (10:21:9 w/w)	H_3PO_4, 0.25 M	180	3	65	30	3
20	Water-MIBK (10:90 v/v)	SPC 108 0.61 * 10-^{3} (meq.H^{+}/mol fructose)	88	900	84	39	5
20	Water-MIBK (10:90 v/v)	Spherosil S 0.15 * 10-^{3} (meq. H^{+}/mol fructose)	88	900	100	34	5
20	Water-MIBK (10:90 v/v)	Lewatitt SPC 118, 0.61*10-^{3} (meq. H^{+}/mol fructose)	88	900	85	39	6
20	Water-MIBK (10:90 v/v)	Spherosil S ion exchange resin 0.125*10-3 (meq. H+/mol fructose)	88	900	100	34	6
10	Water-DMSO-PVP-MIBK-2-butanol	Ion-exchange resin, 10 wt%	90	480-960	76	41	3

	(56:14:30:210:90 w/w)						
30	Water-DMSO-PVP-MIBK-2-butanol (56:14:30:210:90 w/w)	Ion-exchange resin, 30 wt%	90	480-960	83	38	3
30	Water-MIBK	Niobium phosphate, 30 wt%	180	480-960	62	32	3
30	Water-MIBK (1:4 v/v)	$B(OH)_3$, 9 wt%; $MgCl_2$, 39 wt%	150	45	81	52	7
10	Water-MIBK (1:5 v/v)	Silicoalumino-phosphate (SAPO)-44, 2.9 wt%	175	60	89	55	8
9	Water-MIBK (1:3 v/v)	$Ag_3PW_{12}O_{40}$, 0.3 wt%	120	60	83	54	9
9	Water-MIBK (1:3 v/v)	$H_3PW_{12}O_{40}$, 0.27 wt%	120	60	86	31	9
3.5	Water-MIBK (1:1 v/v)	SiO_2/H-MOR zeolites, 0.7 wt%	165	300	75	33	10
2.4	Water-Benzonitrile (1:9 v/v)	Lewatit SPC 108, 2 wt%	89	300	82	41.6	1

*Fructose concentration was 30 wt% in the aqueous phase.

Table S2. The peak positions of 5-HMF carbonyl (C=O) and hydroxyl (O-H) groups in different solvents obtained from FTIR analysis.

Solvent	Peak positions	
	5-HMF carbonyl (C=O)	5-HMF hydroxyl (O-H)
H_2O	1657.54	3330.25*
1-Butanol	1670.42	3339.82*
DMSO	1671.52	3285.17
MIBK	1677,61	3428.63
GVL	1674.17	3447.36
DMC	1678	3501.24

* The peak positions of both 5-HMF hydroxyl group and solvent hydroxyl groups

Table S3. 5-HMF concentration dependence of the chemical shift of the hydroxyl (O-H) proton in 5-HMF in different deuterated solvents by ^{1}H-NMR spectroscopy.

Concentration (mg/mL)	**8.5**	**17**	**34**	**68**
DMSO-d_6	5.58	5.58	5.57	5.57
Acetone-d_6	4.75	4.75	4.75	4.77
DMC-d_6	3.73	3.75	3.81	3.92
$CDCl_3$	2.12	2.38	2.86	3.49

References

1. Mukherjee, M.-J. Dumont and V. Raghavan, *Biomass and Bioenergy*, 2015, 72, 143-183.
2. M. Brasholz, K. Von Kaenel, C. H. Hornung, S. Saubern and J. Tsanaktsidis, *Green Chem.*, 2011, 13, 1114-1117.
3. Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, 312, 1933-1937.
4. J. N. Chheda, Y. Román-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, 9, 342-350.
5. D. Mercadier, L. Rigal, A. Gaset and J. P. Gorrichon, *J. Chem. Technol. Biot.*, 1981, 31, 489-496.
6. L. Rigal, A. Gaset and J. P. Gorrichon, *Ind. Eng. Chem. Prod. Res. Dev.*, 1981, 20, 719-721.
7. T. S. Hansen, J. Mielby and A. Riisager, *Green Chem.*, 2011, 13, 109-114.
8. P. Bhaumik and P. L. Dhepe, *RSC Adv.*, 2013, 3, 17156-17165.
9. C. Fan, H. Guan, H. Zhang, J. Wang, S. Wang and X. Wang, *Biomass Bioenerg.*, 2011, 35, 2659-2665.
10. V. Ordomsky, J. Van der Schaaf, J. Schouten and T. Nijhuis, *J. Catal.*, 2012, 287, 68-75.