Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information

Toward designing neoteric acidic deep eutectic solvents: An innovative, low-cost and environment-friendly strategy in fast and facile production of 5-hydroxymethylfurfural

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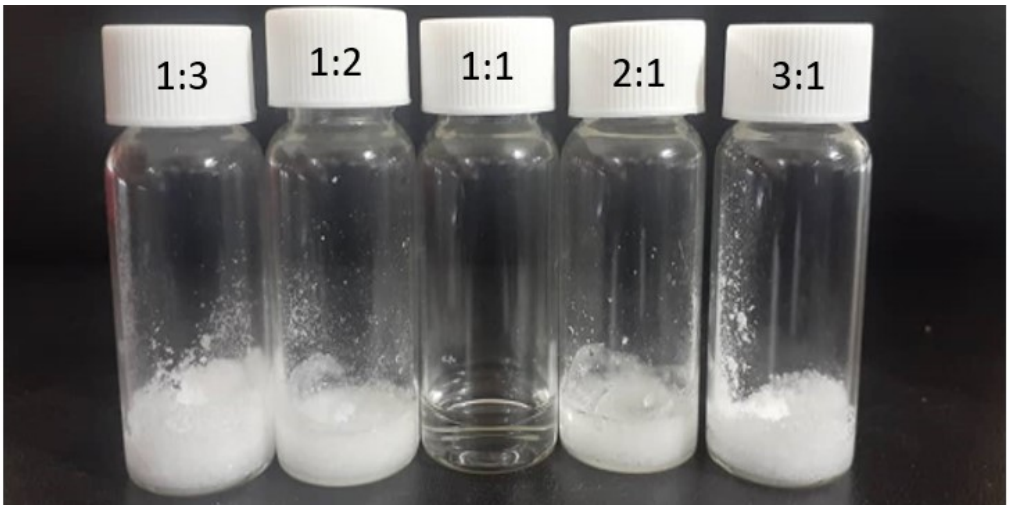

Fig. S1. The appearance of Oxalic:Malonic mixtures of different molar ratios at 363.15K.

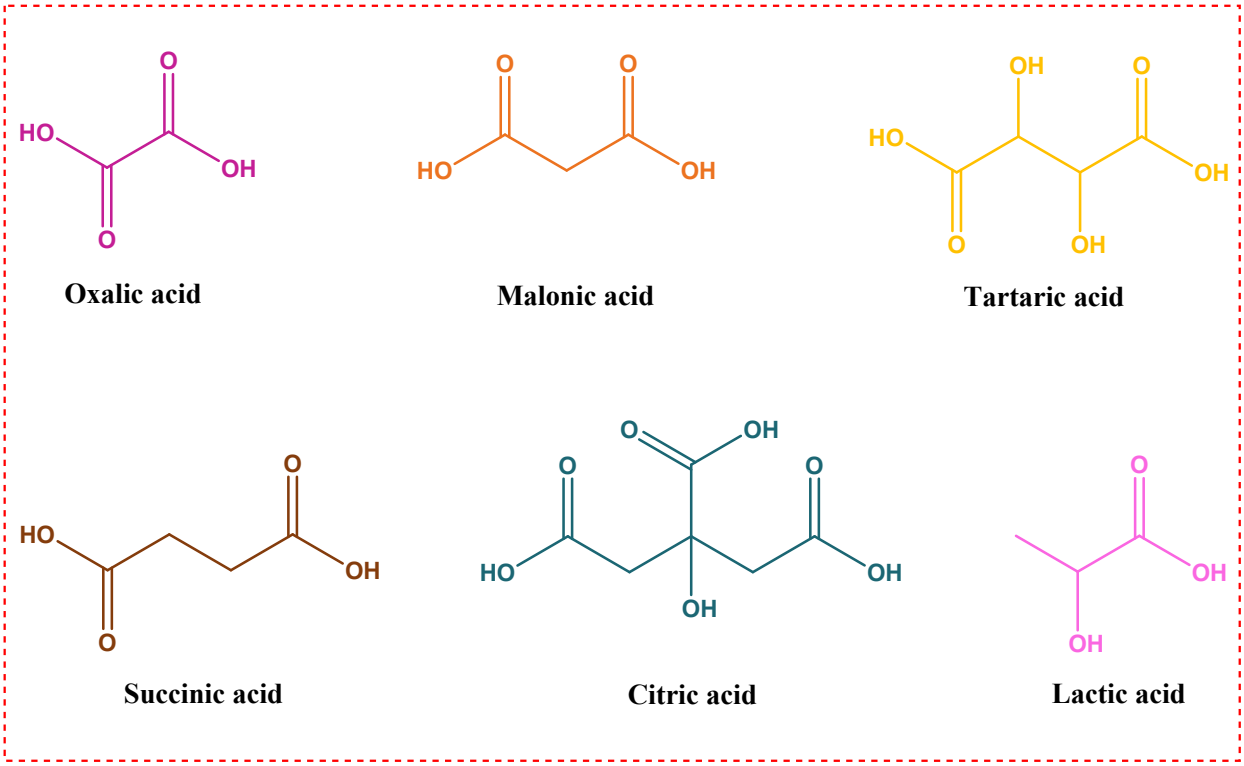

Fig. S2. Structural formula of carboxylic acids used in this work.

1.1. General procedure for the synthesis of 5-HMF

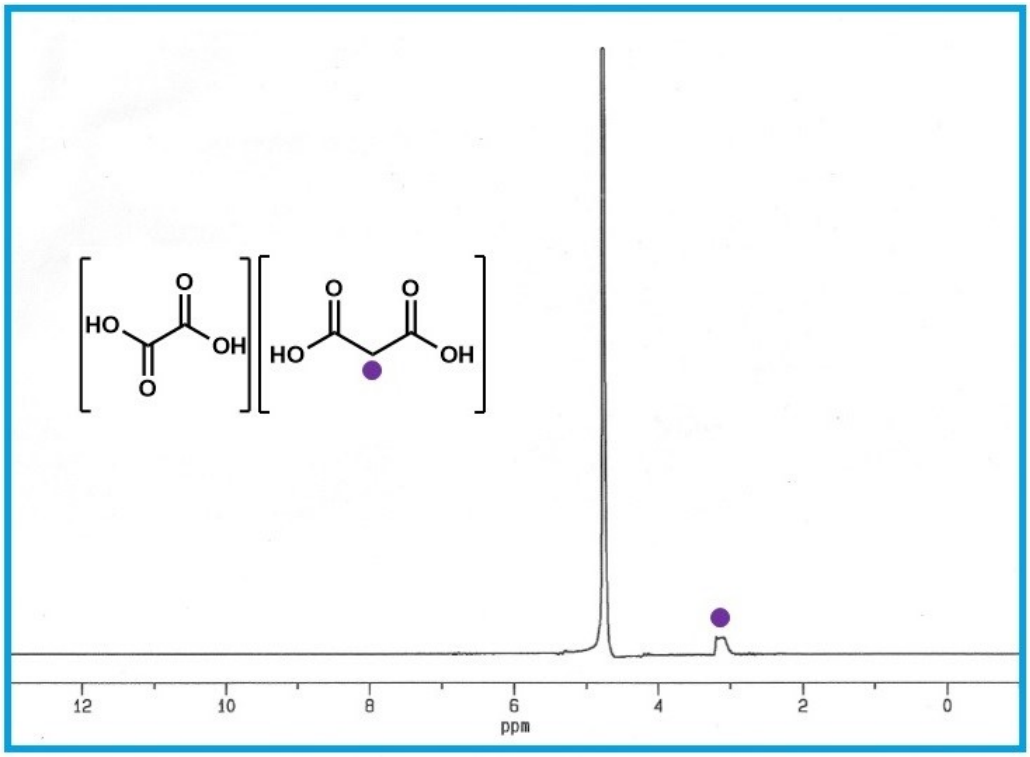

Fig. S3. ^{1}H NMR spectrum of Oxalic:Malonic in D_2O.

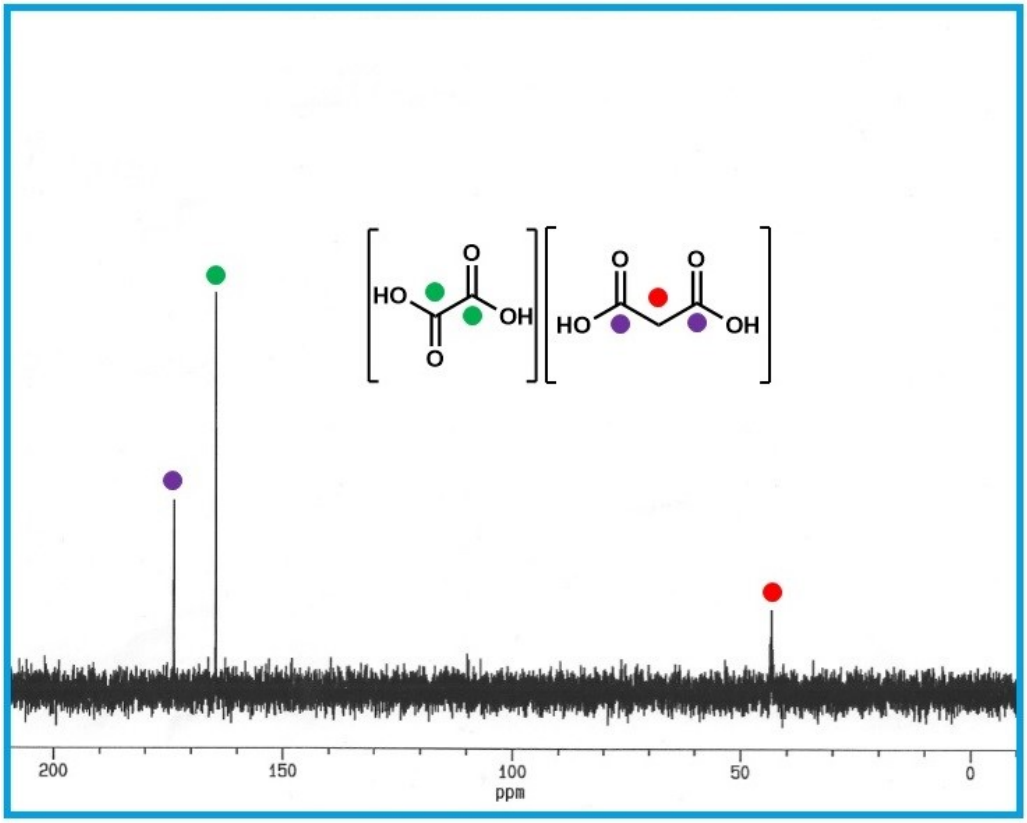

Fig. S4. ^{13}C NMR spectrum of Oxalic:Malonic in D_2O.

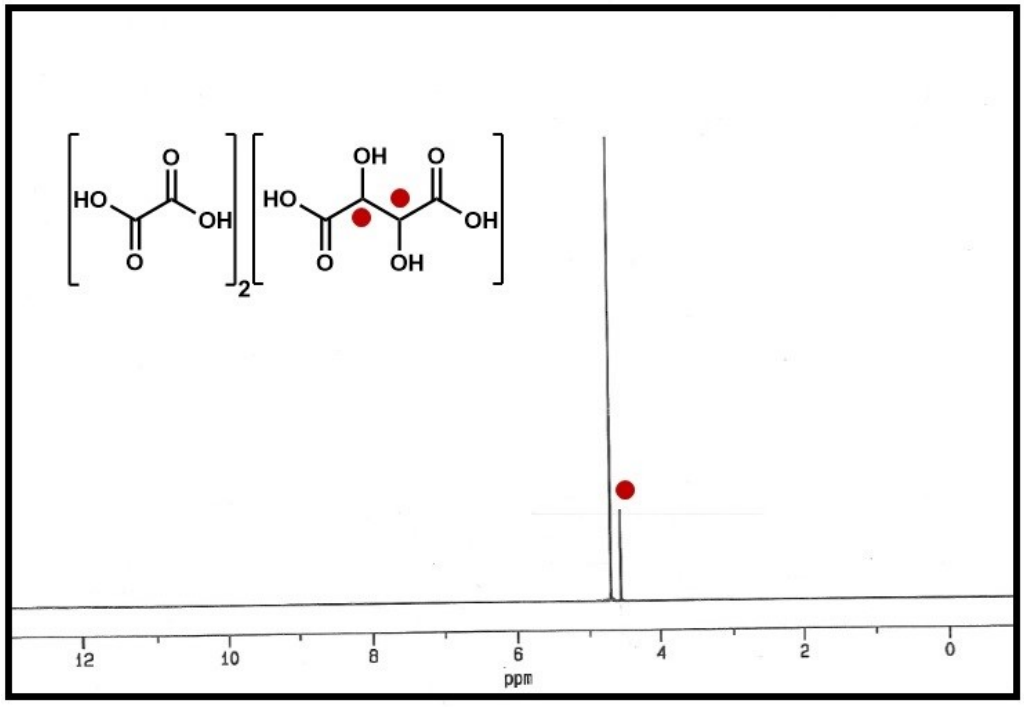

Fig. S5. ^{1}H NMR spectrum of Oxalic:Tartaric in D_2O.

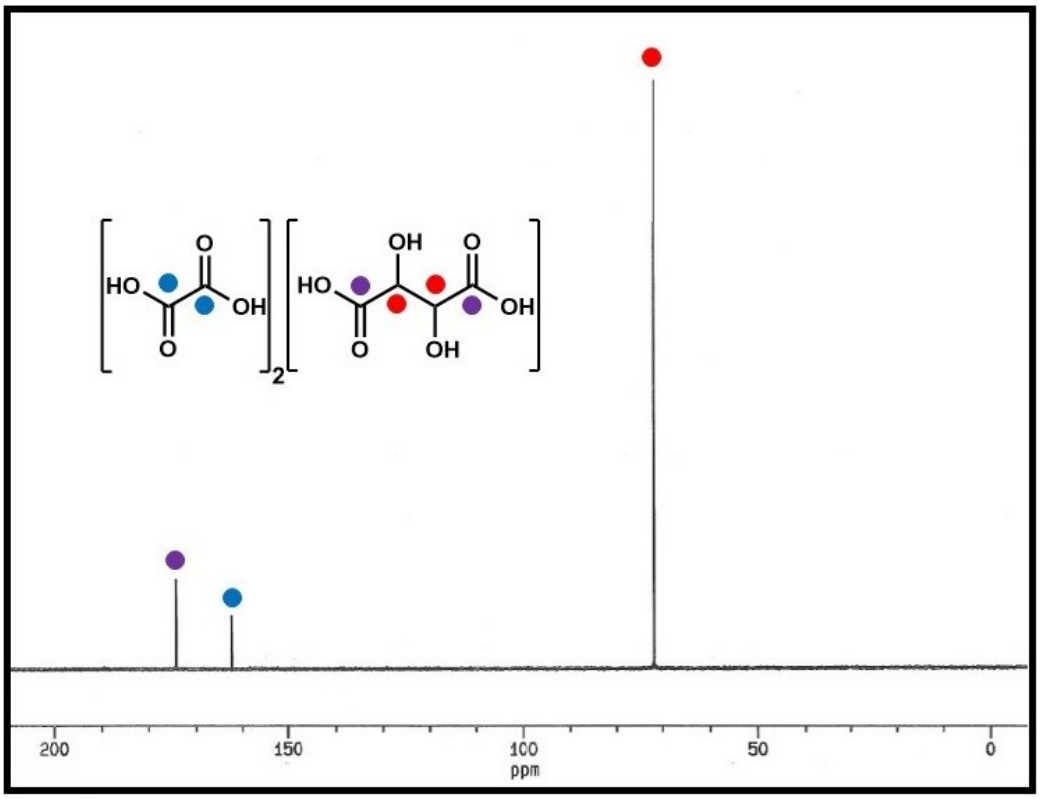

Fig. S6. ^{13}C NMR spectrum of Oxalic:Tartaric in D_2O.

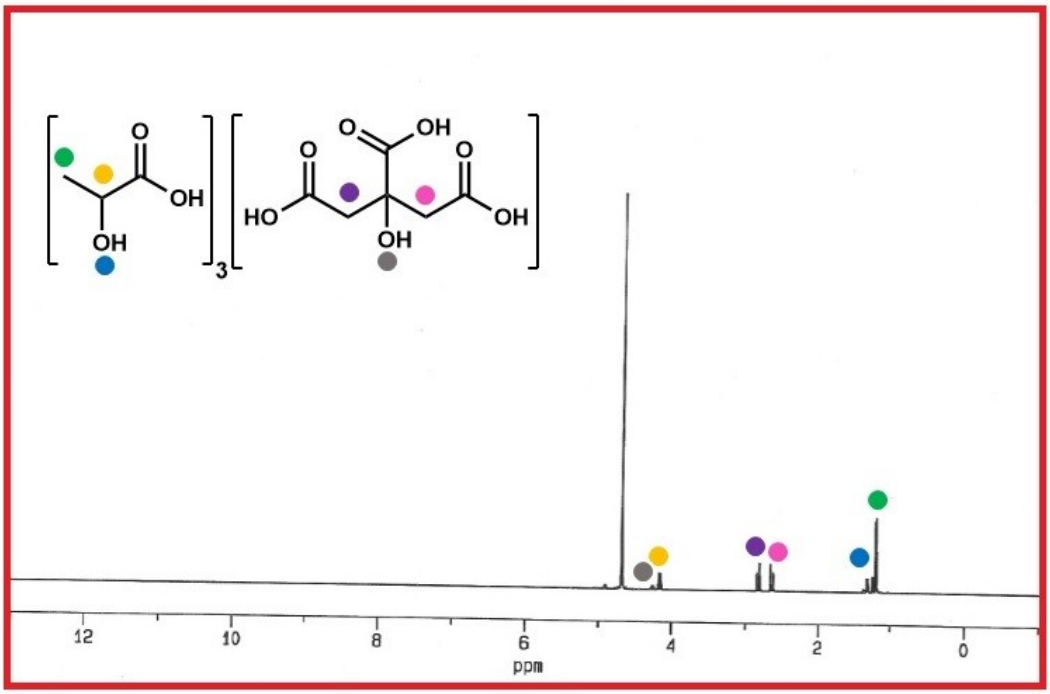

Fig. S7. ^{1}H NMR spectrum of Citric:Lactic in D_2O.

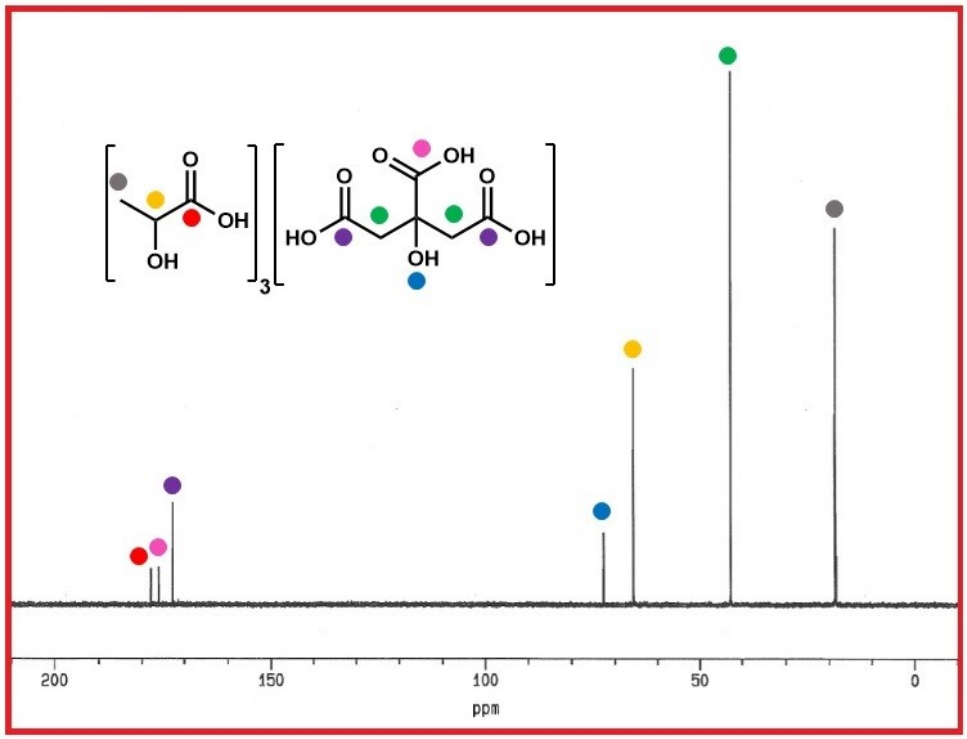

Fig. S8. ^{13}C NMR spectrum of Citric:Lactic in D_2O.

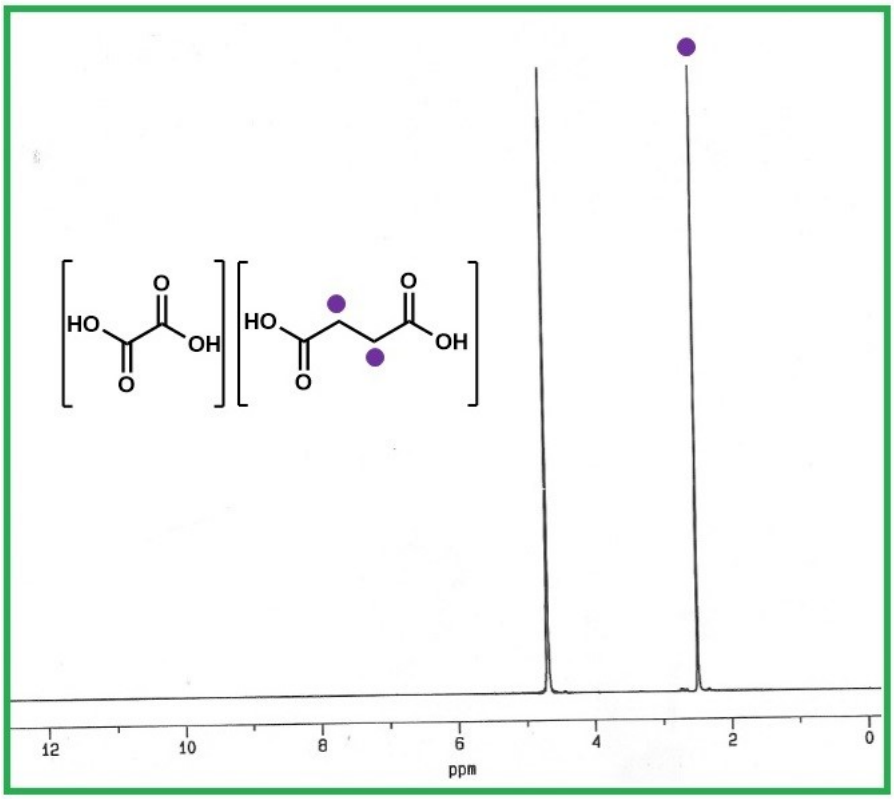

Fig. S9. ^{1}H NMR spectrum of Oxalic:Succinic in D_2O.

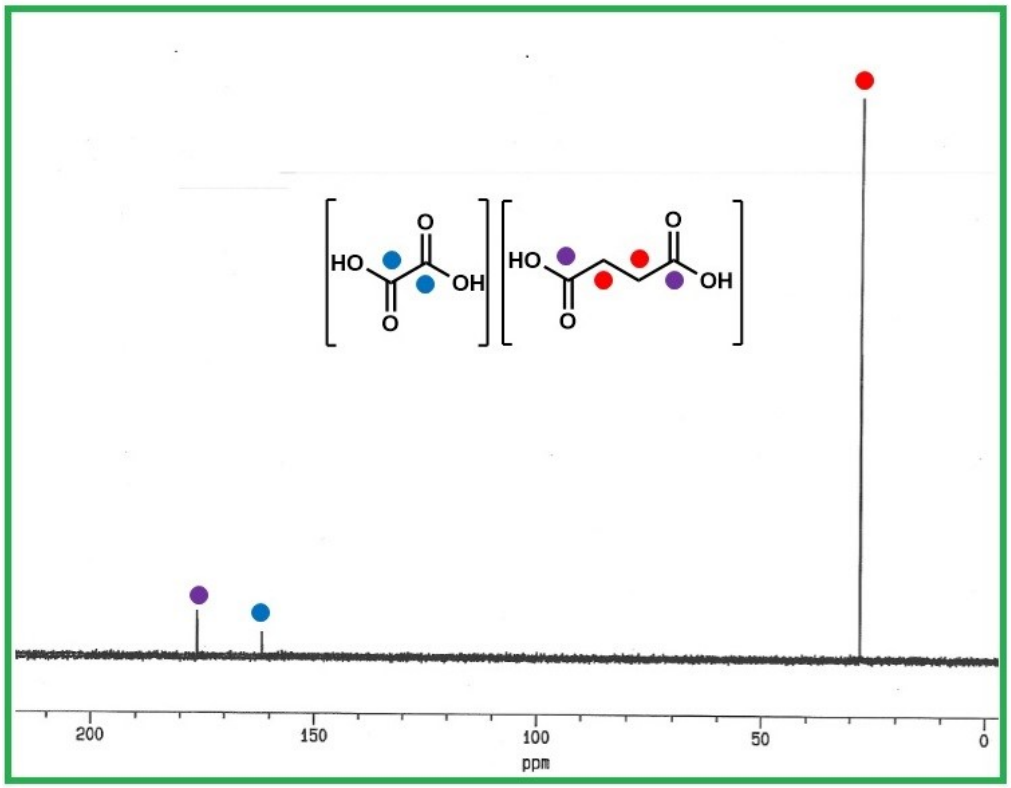

Fig. S10. ^{13}C NMR spectrum of Oxalic:Succinic in D_2O.

Due to the acidic nature of the prepared NADESs, they could provide the dual function of both reaction media and catalysts for the dehydration of fructose into 5-HMF. Initially, in order to find more efficient NADES as catalyst and solvent for 5-HMF production, the prepared acidic NADESs were tested in the dehydration of fructose under identical reaction conditions.

The suggested mechanism illustrates that all NADESs were very effective for the conversion of fructose to 5-HMF, affording 5-HMF in excellent yields. Significantly, the reactions were rapid and completed in very short spans of time. This phenomenon can be attributed to the dual roles of NADESs as catalysts and solvents which effectively facilitated and simplified the reaction. All of the fructose dehydration experiments were performed in 10 mL round bottom flasks ware with stopper. For each reaction, 75 mg of fructose was dissolved in 3 mL of solvent. The mixture was heated to a desired temperature using an oil bath for a given reaction time under magnetic stirring. After the completion of reaction, ethyl acetate (10 mL) was added to the mixture in order to extract

5-HMF. After evaporation of the solvent, the residue was subjected to silica gel column chromatography (ethyl acetate-hexane, 1:9) to obtain the pure 5-HMF. The isolated 5-HMF was analyzed by HPLC, 1H and 13C NMR spectroscopies. The 5-HMF yield was determined from this Eq.:

5-HMF yield (%) = [mol of isolated 5-HMF/mol of initial fructose] × 100

4. Characterization of 5-HMF

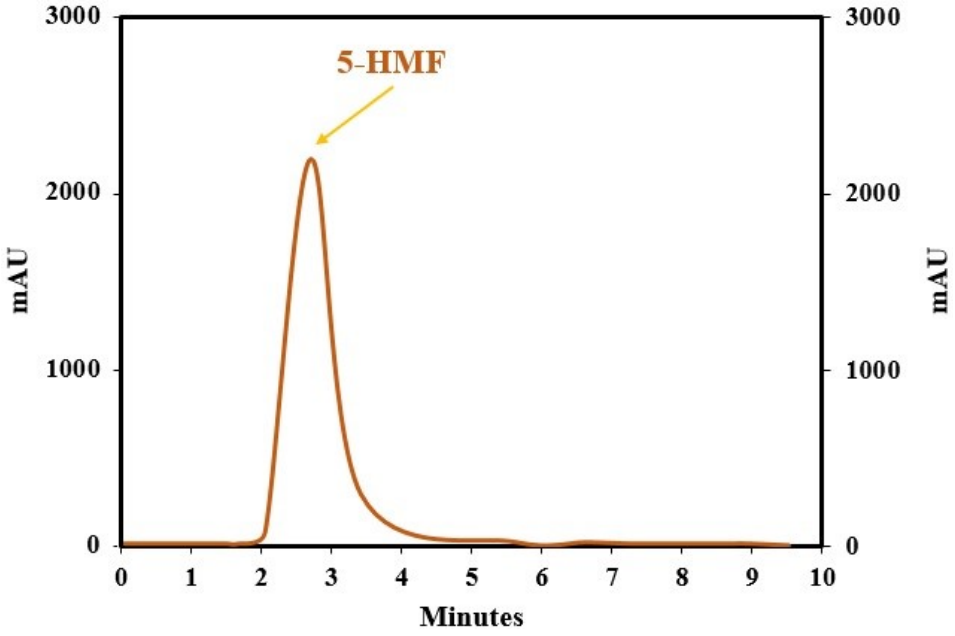

Fig. S11. HPLC analysis result of the isolated 5-HMF.

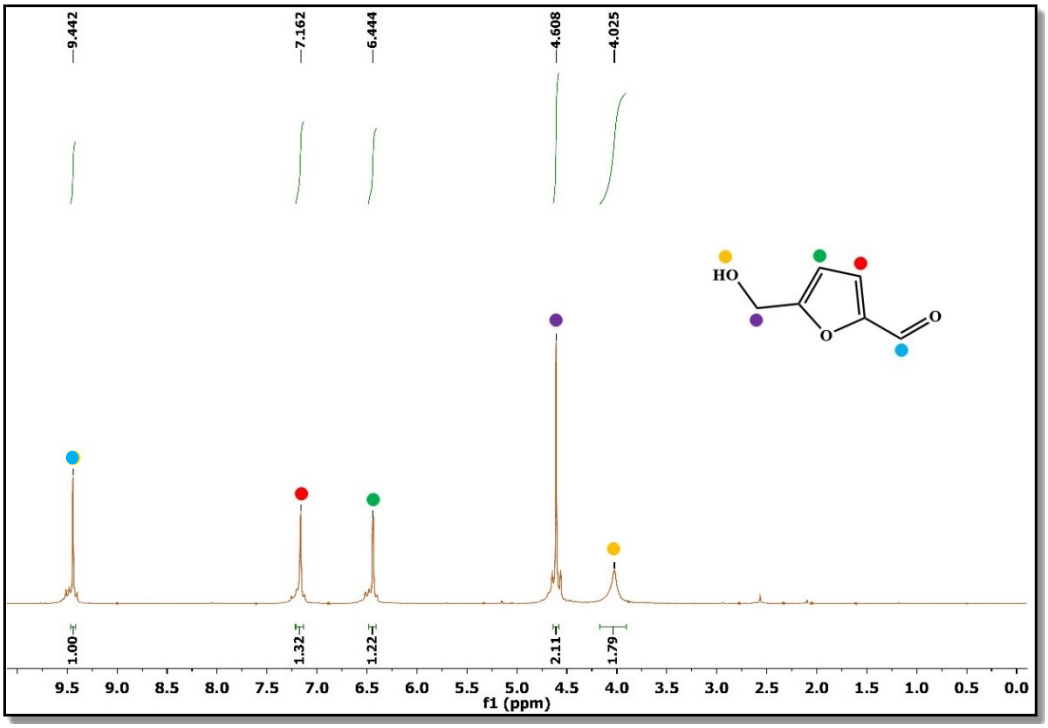

Fig. S12. ^{1}H NMR spectrum of the isolated 5-HMF in $CDCl_3$.

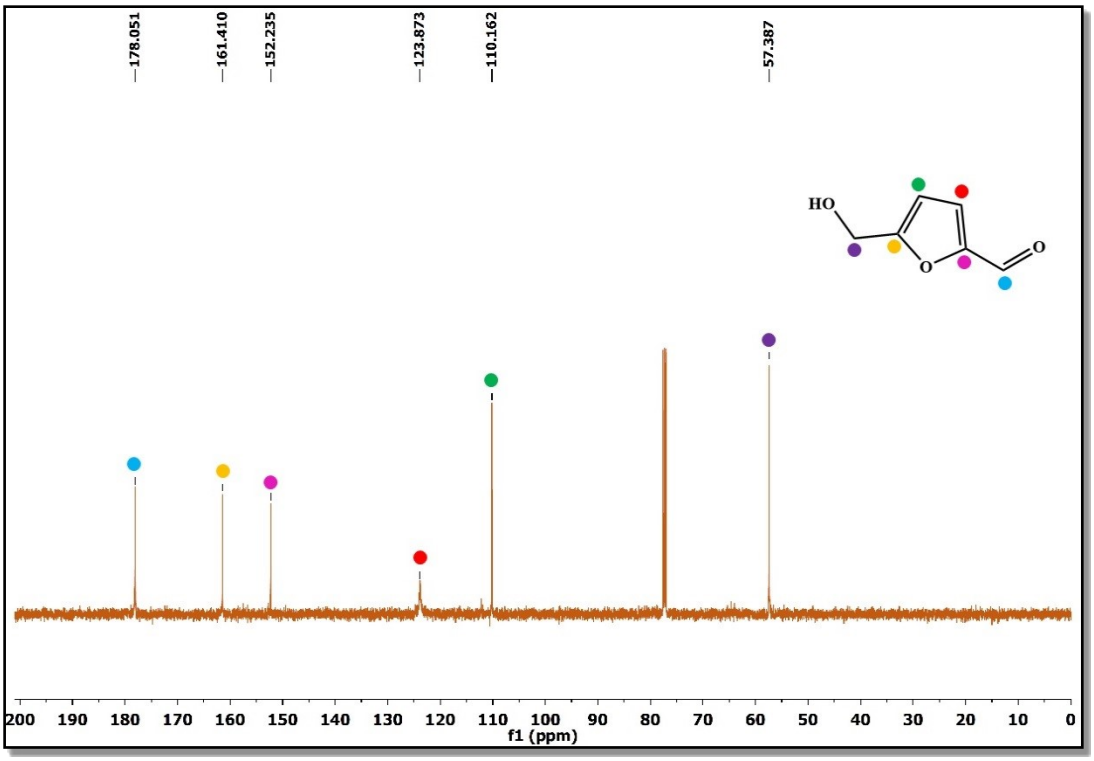

Fig. S13. ^{13}C NMR spectrum of the isolated 5-HMF in $CDCl_3$.

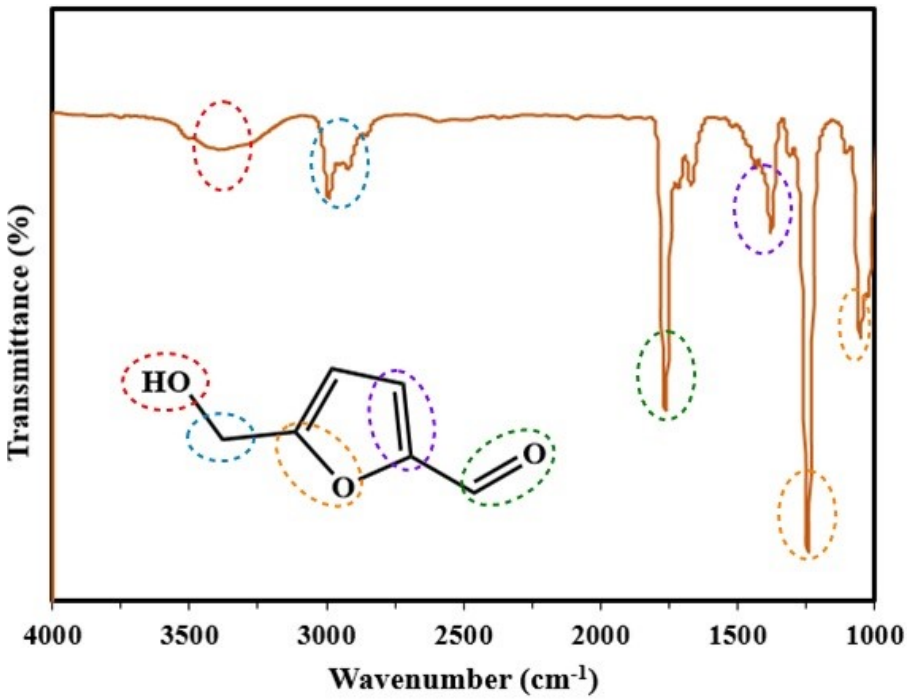

Fig. S14. FT-IR spectrum of the isolated 5-HMF.

5. Characterization of recycled NADES

It is critical to recover and reuse chemical to decrease the production cost and environmental impact in view of industrial application and green chemistry. Therefore, we decided to examine the recyclability of Oxalic:Malonic in the dehydration of fructose into 5-HMF.

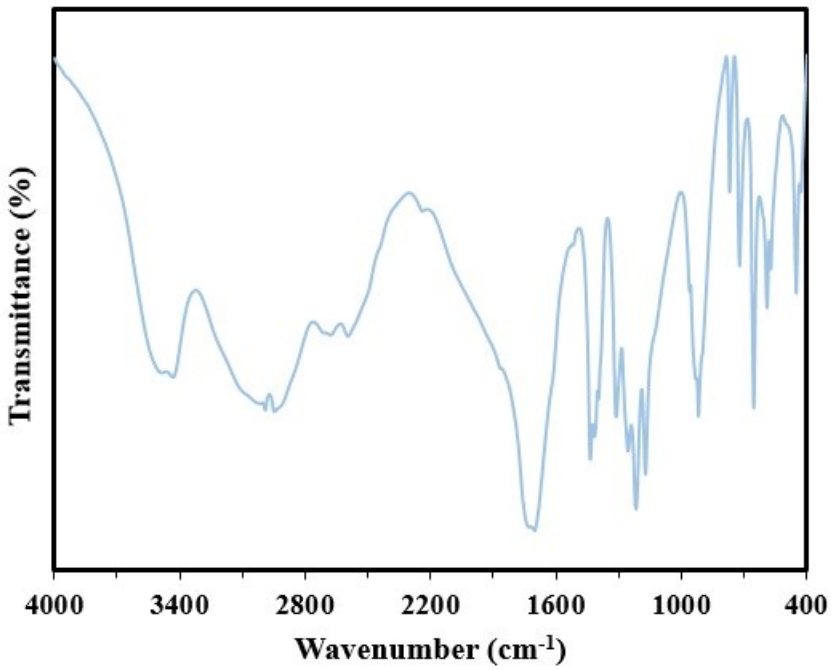

Fig. S15. FT-IR spectrum of the reused NADES (Oxalic:Malonic).

Fig. S16. ^{1}H NMR spectrum of the reused NADES (Oxalic:Malonic) in D_2O.

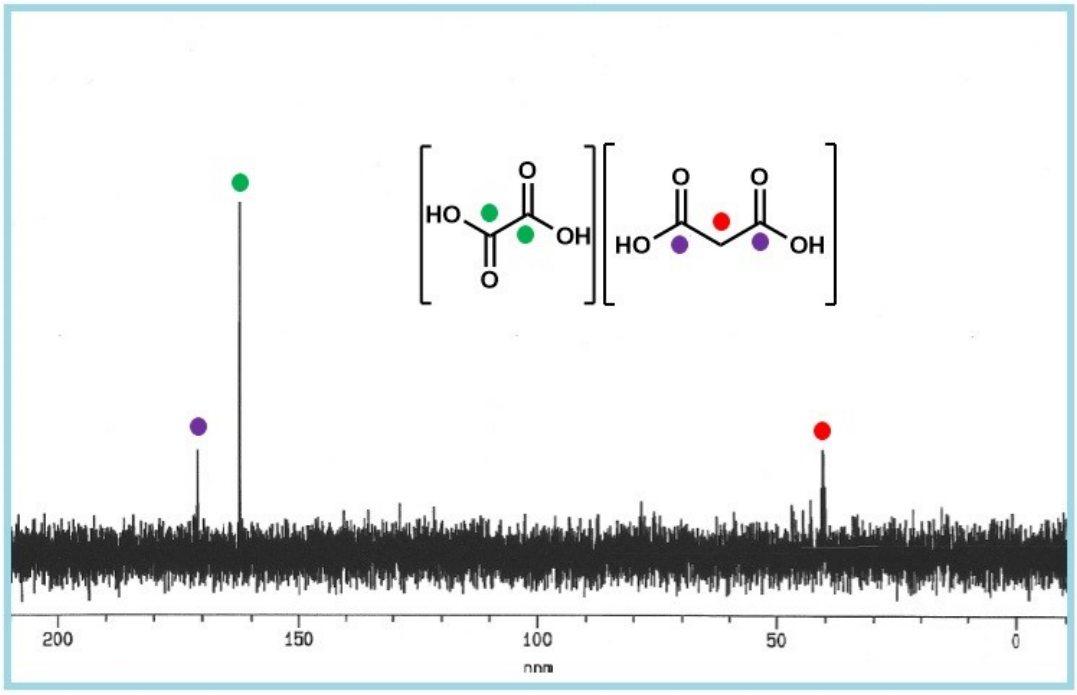

Fig. S17. ^{13}C NMR spectrum of the reused NADES (Oxalic:Malonic) in D_2O.

Calculation of the green chemistry metrics for the synthesis of 5-HMF from fructose in the presence of Oxalic:Malonic

Table S1. Calculation of the green chemistry metrics.

1	**Atom economy**	
	Atom Economy = (Exact molecular mass of 5-HMF / Exact Molecular mass of fructose) × 100%	= 126.11/180.16 × 100% AE = **70%**
2	**Reaction mass efficiency**	
	Reaction Mass Efficiency = (Mass of 5-HMF / Mass of fructose) × 100	= (0.05/ 0.07) × 100 RME = **71%**
3	**E-factor**	
	E-Factor = Amount of waste/ Amount of product	Total amount of reactant = 0.07 mg Amount of final product = 0.05 mg Amount of waste = (Total amount of reactant – amount of final product) = (0.07-0.05) mg = 0.02 mg E-factor = (0.02 /0.05) = **0.4**
4	**Ecoscale**	
	Ecoscale = (100 – Sum of individual penalties)	Ecoscale = 100–11.5 = **88.5**

Table S2. Calculation of the penalty points for the Ecoscale calculation

Calculation of penalty points		
	Parameters	Penalty points
1	**Reaction Yield**	
	Yield = 97%	1.5
2	**Price of reaction components (to obtain 0.4 mmol of final product)**	
	Fructose	0
	Oxalic acid	0
	Malonic acid	0
	Ethyl acetate	0
3	**Safety**	
	Fructose	0
	Oxalic acid	0
	Malonic acid	0
	Ethyl acetate (T)	5
4	**Technical setup**	
	Common setup	0
5	**Temperature/Time**	
	Heating, < 1 h	2
6	**Work and Purification**	
	Liquid-liquid extraction	3
	Total penalty points	**11.5**