Supporting Online Material for

Sulphanilic Acid as a Recyclable Bifunctional Organocatalyst in Selective Conversion of Lignocellulosic Biomass to 5-HMF

Hamid M. Mirzaei,[1] Babak Karimi,[*1]

[1]Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P.O. Box 45195-1159, Gava Zang, Zanjan 45137-66731, Iran.

To whom correspondence should be addressed, E-mail: karimi@iasbs.ac.ir

This PDF file includes:
Materials and Methods

Sulphanilic Acid as a Bifunctional Organocatalyst in Selective Conversion of Lignocellulosic Biomass to 5-HMF

Hamid M. Mirzaei,[1] Babak Karimi,[*1]

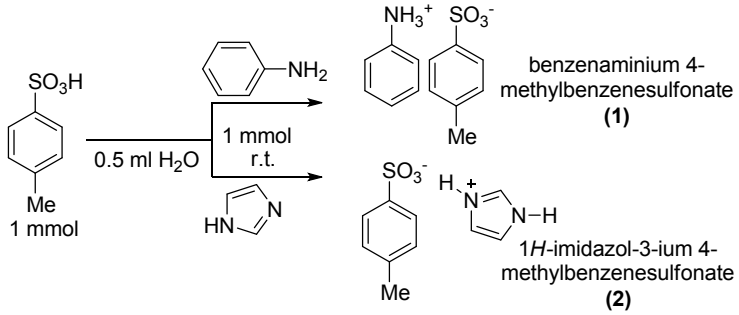
[1]Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P.O. Box 45195-1159, Gava Zang, Zanjan 45137-66731, Iran.

Materials and Methods

Carbohydrates such as Fructose, glucose and cellulose were purchased from Sigma-Aldrich and other biomass feedstock (straw and Barley husk) were prepared from the region. Reagents and solvents obtained from Aldrich and were used without further purification. Methyl isobutylketone (MIBK) was prepared from Daejung Company and used without purification. Thermal analyzes were conducted from room temperature to 600 ˚C using a NETZSCH analyzer (Germany). Reaction samples were analyzed using KNAUER High Performance Liquid Chromatography (HPLC) system equipped with UV K-2600 and RI K-2301 refractive index detectors. Portions of the aqueous (20 µL) and organic phases (50 µL in 1 ml CH_3OH) were analyzed. Sugar disappearance was monitored with an Eurokat *H C-54-1181H* column, using H_2SO_4 (5 mM) as the mobile phase at a flow rate of 1 $mlmin^{-1}$ and a column temperature of 303 K. HMF was quantified in the aqueous and organic phases with a Nucleosil-100 C18 column, using a 7:3 v/v (water: CH_3CN) gradient at a flow rate of 0.6 $mlmin^{-1}$ and a column temperature of 303 K using a UV detector (282 nm). It was assumed that the volume changes are negligible after the dehydration reaction for all experiments. Carbohydrates conversion was calculated as moles of hexose or pentose reacted per mole of carbohydrate fed based on external standard. Also, HMF yield was calculated as moles of HMF produced based on HMF external standard. Conversions of cellulose, straw, and Barley husk were determined according to the wt% of consumed substrate. For this means, after completion of the reaction, the unreacted substrate was filtered, thoroughly washed and dried to constant weight.

Preparation of organic salts

Salt formation is very simple in which an acid reacts with a base. In this regard, 1.1 mmol aniline or imidazole, 1 mmol *p*-toluenesulfonic acid, and 0.5 ml water were put into a 10 ml flask at ambient temperature and the reaction was easily terminated after 30 min. The prepared salt was filtered off and thoroughly washed with ethyl acetate for three times in order to remove any unreacted acid and/or base. The purity of the prepared salts was easily verified using NMR spectroscopy (>99% isolated yield).



Scheme S1. Preparation of organic salts through organic acid-base reaction at room temperature.

Lignocellulosic material constituents

The lignocellulosic materials were first oven dried at 80 ºC for 1 h before the reaction. After drying, the material was simply cut in small pieces (size: 5 mm) and used for thermal gravimetric analysis and reactions. In order to assess the cellulose, hemicellulose, and lignin content of lignocellulosic materials, TG analyzes were performed under nitrogen and oxygen atmosphere from 25 to 600 ºC using Netzsch apparatus, Germany (Table S1).

Table S1. Lignocellulosic biomass content*

Entry	Substrate	Cellulose content		Hemicellulose content		Lignin (%)
		%	mmol Glucose†	%	mmol pentose‡	
1	Straw	32	0.10	27	0.10	28
2	Barley husk	27	0.08	14	0.05	25

* Cellulose, hemicellulose, and lignin amounts were calculated according to thermal gravimetric analysis. † The amount of glucose unit in 50 mg substrate using $M_{glucose\ unit}$=162.14 $gmol^{-1}$. ‡ The amount of pentose unit in 50 mg substrate using $M_{pentose\ unit}$=132.12 $gmol^{-1}$.

For 50 mg lignocellulosic straw material, 16 mg cellulose was estimated to be present in this substrate through TG analysis. As the hexose unit molecular weight is 162.14, thus this case contains roughly 0.1 mmol glucose units. For the other Barley husk lignocellulosic material, glucose monomer is estimated to be 0.083 mmol for 50 mg substrate. Also, to determine the pentose unit, here we used hemicellulose as the source of pentose sugars with molecular weight of 132.12 g/mol. For straw lignocellulosic material, pentose unit has been calculated to be 0.1 mmol and for Barley husk, it has been measured to be 0.053 mmol.[1]

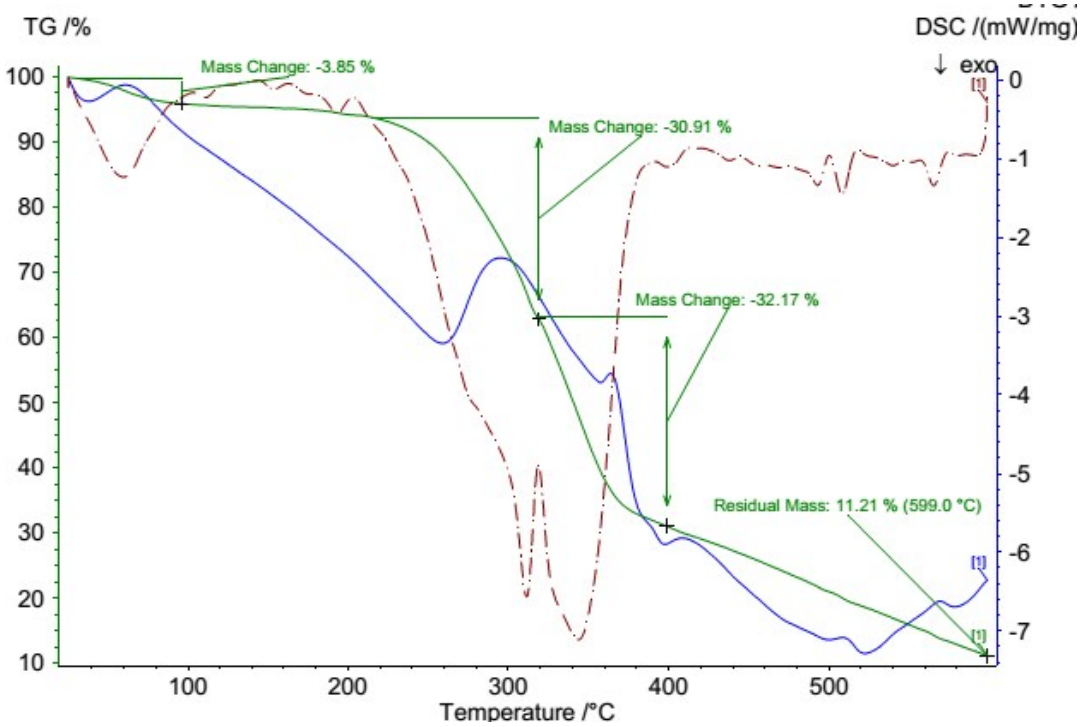


Figure S1. Thermal gravimetric analysis of straw under nitrogen atmosphere.

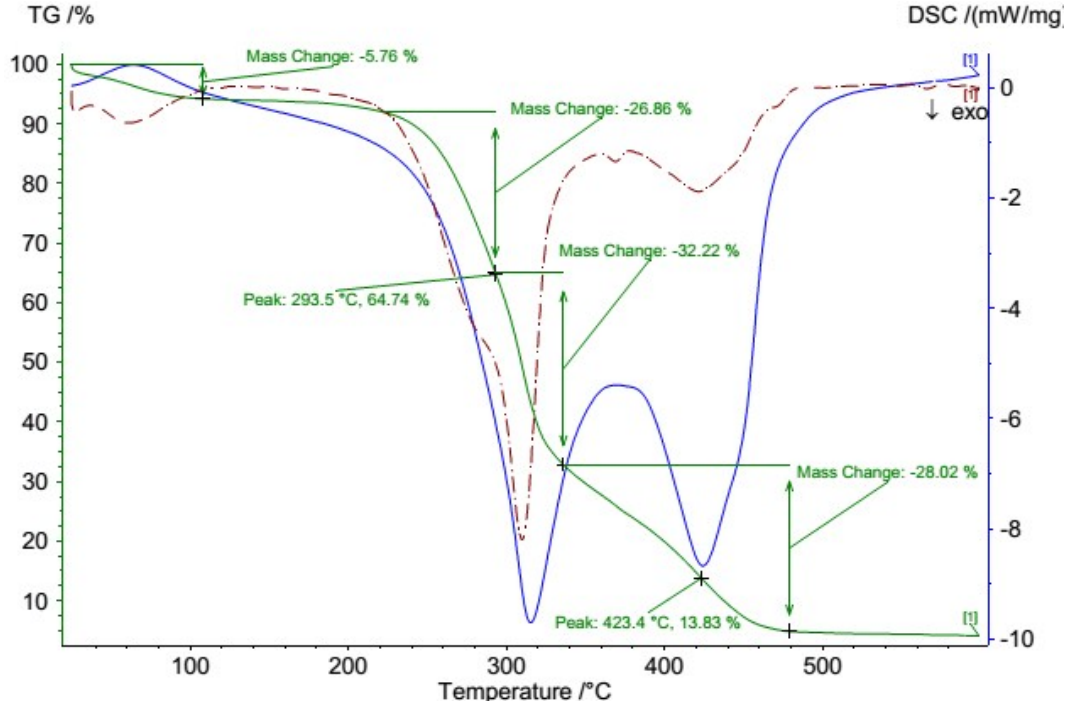


Figure S2. Thermal gravimetric analysis of straw under oxygen atmosphere.

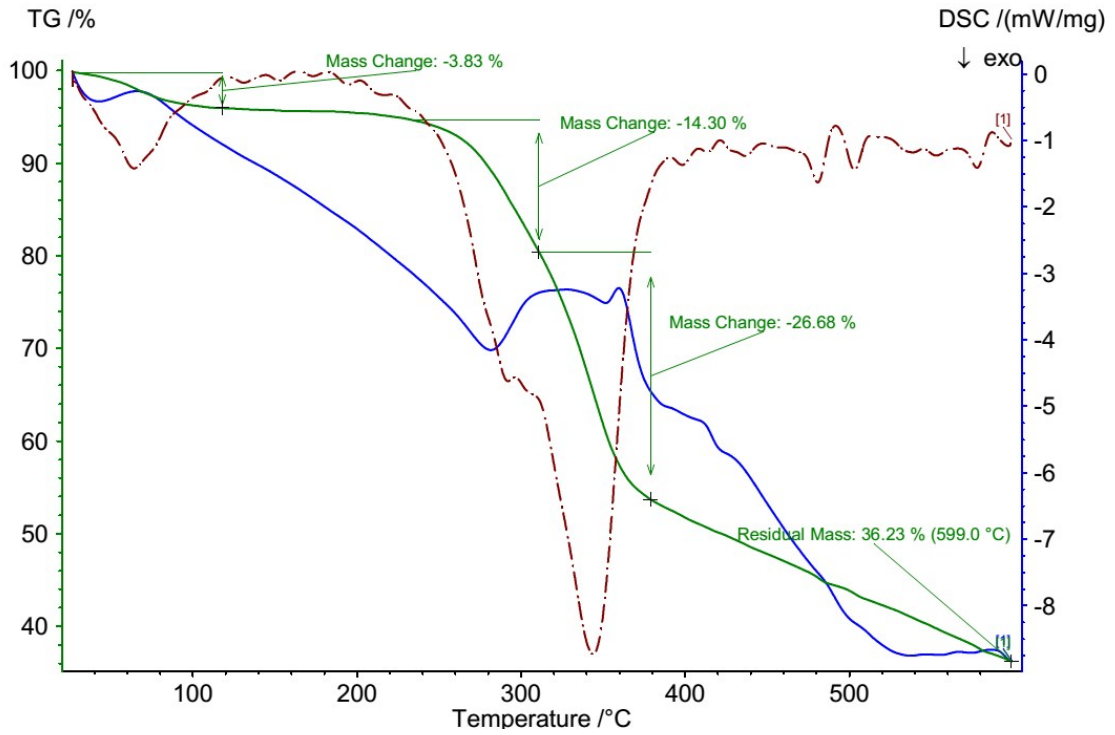


Figure S3. Thermal gravimetric analysis of Barley husk under nitrogen atmosphere.

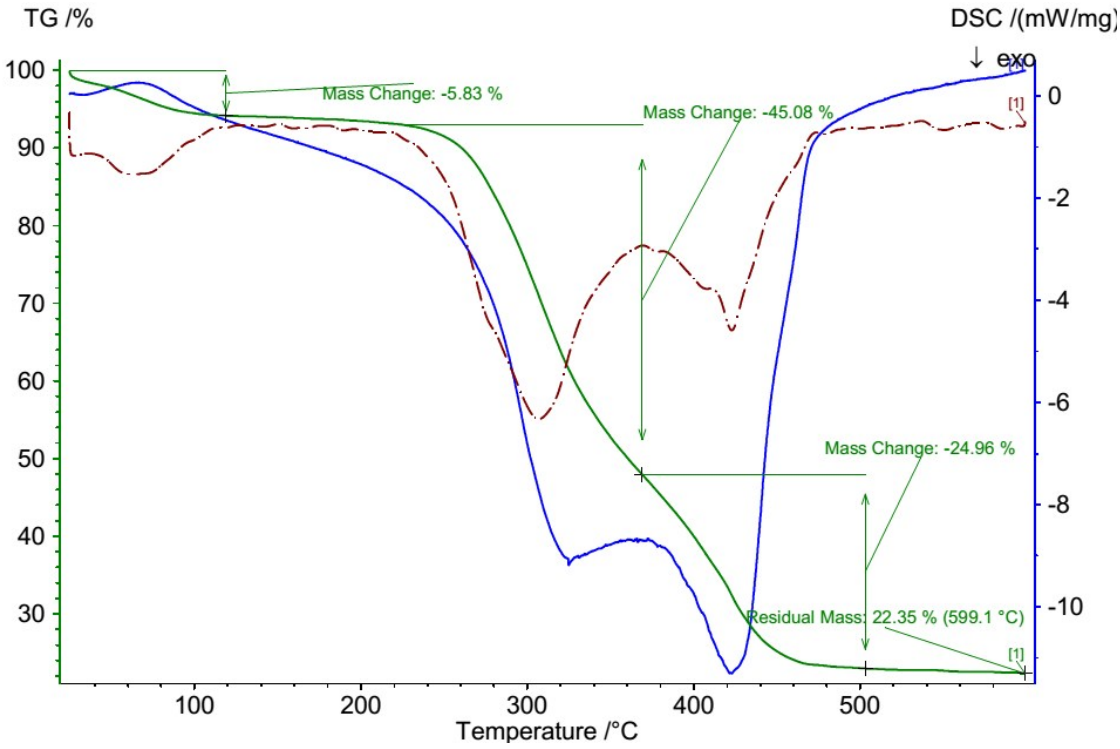
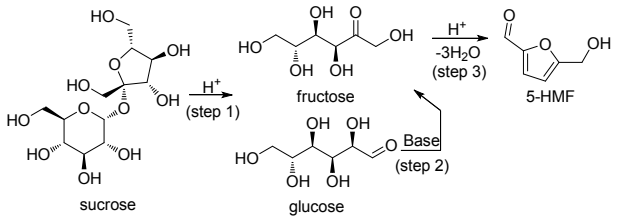


Figure S4. Thermal gravimetric analysis of Barley husk under oxygen atmosphere.



Scheme S2. Three-step hydrolysis, isomerization, and dehydration of sucrose into 5-HMF.

Figure S5. Biomass straw (A) and Barley husk (B) prepared from the region.

A Typical Procedure for Conversion of Glucose into 5-HMF

In a 25 mL home-designed high pressure Teflon-lined reactor (Figure S6), a mixture of glucose (0.28 mmol), catalyst (12-48 mol%), and (3 ml) biphasic solvent comprising H_2O, DMSO | 2-butanol, MIBK (0.3, 0.7 | 0.6, 1.4) (ml) was prepared. The sealed reactor was then immersed in an oil bath at 150 °C. After the indicated time in Table 1; 5-HMF yields in aqueous (aq) and organic (org) phases were determined based on HPLC analyzes

Figure S6. The home-designed reactor for 5-HMF production.

Table S2. Investigation of different salts as acid-base catalysts in the carbohydrates dehydration reaction into 5-HMF.[a]

Entry	Substrate (mmol)	Catalyst (mol %)	Time (min)	Conversion (%)	5-HMF yield (%) (aq)	5-HMF yield (%) (org)	Total 5-HMF (%)	Levulinic acid
1	Glucose (0.28)	$(NH_4)_2SO_4$ (12)	30	64	1	4	5	-
2	Glucose (0.28)	$(NH_4)_2SO_4$ (12)	60	73	2	10	12	-
3	Glucose (0.28)	$(NH_4)_2HPO_4$ (12)	60	83	6	22	28	-
4	Glucose (0.28)	NH_4NO_3 (12)	60	79	2	13	15	-
5	Glucose (0.28)	NH_4CO_2H (12)	60	80	3	14	17	-
6	Glucose (0.28)	SDBS (12)	60	-	nd	4	4	-
7	Glucose (0.28)	CTAB (12)	60	-	nd	6	6	-
8	Glucose (0.28)	NaCl (12)	60	-	nd	1	1	-
9	Glucose (0.28)	**1** (12)	60	80	15	33	48	1
10	Glucose (0.28)	**2** (12)	60	71	4	7	11	-
11	Glucose (0.28)	**3** (12)	15	79	5	38	43	1
12	Glucose (0.28)	**3** (12)	30	84	9	53	62	1
13	Glucose (0.28)	**3** (12)	45	92	8	55	63	1
14	Glucose (0.28)	**3** (12)	60	92	11	57	68	1
15	Glucose (0.28)	**3** (12)	75	94	8	56	64	1
16	Glucose (0.28)	**3** (12)	90	95	7	55	62	1
17	Glucose (0.28)	**3** (24)	60	98	12	66	78	1
18[b]	Glucose (0.28)	**3** (24)	60	80	3	13	16	1
19	Fructose (0.28)	**3** (24)	15	94	11	73	84	1
20	Sucrose (0.28)	**3** (24)	60	100	14	70	84	1
21[c]	Cellulose (0.31)	**3** (24)	60	67	10	27	37	1
22[c]	Cellulose (0.15)	**3** (48)	60	83	13	39	52	1
23[c, d]	Cellulose (0.15)	**3** (48)	60	82	11	36	47	1
24[c, e]	Cellulose (0.15)	**3** (48)	60	89	5	10	15	1

[a] Reactions were performed using a reaction volume of (3 mL) biphasic H_2O, DMSO | 2-butanol, MIBK (0.3, 0.7 | 0.6, 1.4) (ml), at 150 °C; 5-HMF yields in aqueous (aq) and organic (org) phases were determined based on HPLC analyses. [b] Solvent system was 3 mL H_2O | MIBK (1/2). [c] 5-HMF yield is relative to the moles of glucose units reacted. [d] Reaction was performed at 165 °C. [e] Reaction was performed at 180 °C.

Carbon balance:

The Carbon balance for one experiment (Table 1, Entry 17) was estimated as follow:

0.28 mmol (Glucose)= 1.68 mmol Glucose Carbon=20.16 mg Glucose Carbon

78% * 0.28 mmol Glucose= 0.22 mmol HMF= 15.73 mg HMF Carbon

1% * 0.28 mmol Glucose= 0.003 mmol LA= 0.17 mg LA Carbon

Total products Carbon= 15.73+ 0.17= 15.90

Carbon Balance= (15.90/20.16) * 100= 79%

A Typical Procedure for Conversion of Cellulose into 5-HMF

In a 25 mL home-designed high pressure Teflon-lined reactor (Figure S6), 50 mg (0.31 mmol) cellulose without any pretreatment and Sulphanilic acid (24 mol%) was added into 3 mL biphasic solvent (please see previous procedure) and the reaction was conducted under optimized conditions indicated in entry 17, Table 1 of the manuscript. After 60 min, the reaction was quenched and unreacted cellulose was filtered off. This residue was thoroughly washed with deionized water and

oven-dried. The reaction conversion was easily calculated according to the weight of cellulose consumed during the reaction. In this manner, 67% of cellulose converted and 37% 5-HMF was produced as determined by HPLC analysis (Table 1, entry 21).

A Typical Procedure for Conversion of Untreated Lignocellulose Biomass into 5-HMF

In a 25 mL home-designed high pressure Teflon-lined reactor (Figure S6), 25 mg of each oven-dried substrate of either Barely husk or Straw without any pretreatment was added into 3 mL biphasic solvent (please see previous procedure) and the reaction was conducted under optimized conditions indicated in entry 17, Table 1 of the manuscript. After 60 min, the reaction was quenched and unreacted materials was filtered off. This residue was thoroughly washed with deionized water and oven-dried. The reaction conversion was easily calculated according to the weight of biomass residue consumed during the reaction. In this context, both straw and barley husk in the same reaction conditions produced furfural in 50 and 41% yields and HMF in 41% yield, respectively (Table 2, entries 1-2) as determined by independent HPLC analysis (Table 1, entry 21).

Catalyst Durability in glucose conversion

For catalytic system durability, after completion of the reaction the organic phase was simply separated from aqueous phase by decantation and for another run; 50 mg glucose and fresh organic phase [2-butanol (0.6 mL) and MIBK (1.4 mL)] were added into the aqueous phase containing the catalyst. After completion of the reaction, the procedures were repeated up to 5 cycles with negligible decrease in HMF yield in each cycle.

NMR and HPLC analysis data

(a) benzenaminium 4-methylbenzenesulfonate

^{1}H-NMR (400 MHz; *d*-DMSO): 2.31 (s, 3H), 7.135 (m, 2H), 7.15-7.53 (m, 7H), 9.9 (brs, 1H); ^{13}C-NMR (100 MHz, *d*-DMSO): 146.5, 139.2, 133.2, 131.1, 129.5, 129.3, 126.8, 124.2, 22.1

(b) *1H*-imidazol-3-ium 4-methylbenzenesulfonate

^{1}H-NMR (400 MHz; *d*-DMSO): 2.30 (s, 3H), 7.12 (d, *J*=8.0, 2H), 7.50 (d, *J*=7.6, 2H), 7.70 (s, 2H), 9.11 (s, 2H), 14.2 (bs, 1H); ^{13}C-NMR (100 MHz, *d*-DMSO): 146.1, 139.6, 135.7, 129.6, 126.8, 120.7, 22.1

(c) 5-hydroxymethylfurfural (5-HMF)

^{1}H-NMR (400 MHz; $CDCl_3$): 3.42 (s, 1OH), 4,71 (s, 2H), 6.53 (s, 1H), 7.24 (s, 1H), 9.56 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 177.8, 160.8, 152.3, 123.1, 110.0, 57.6; IR (neat): 618, 775, 812, 1024, 1193, 1281, 1399, 1522, 1670, 2849, 3387

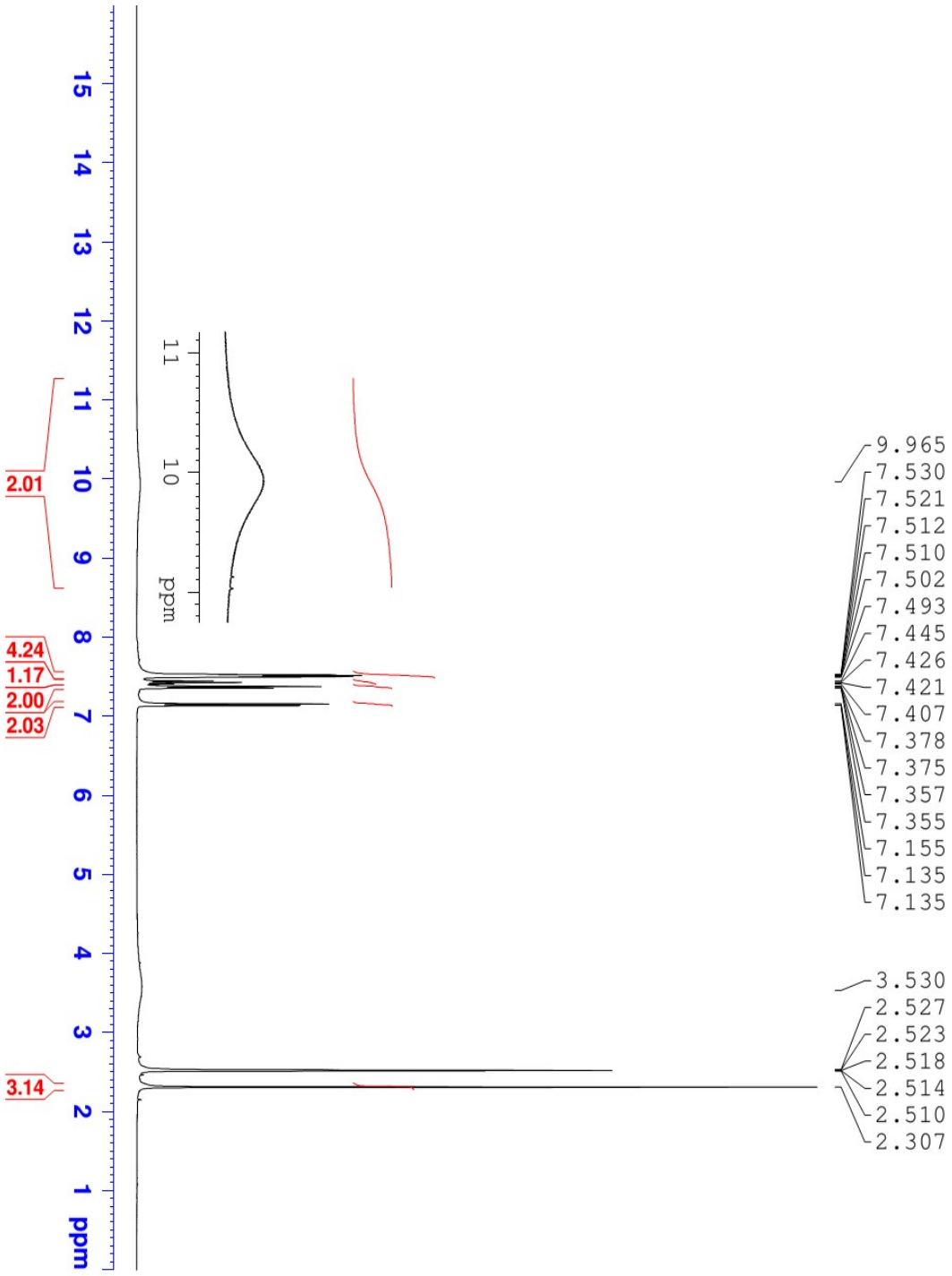


Figure S7. [1]HNMR of benzenaminium 4-methylbenzenesulfonate in d_6-DMSO.

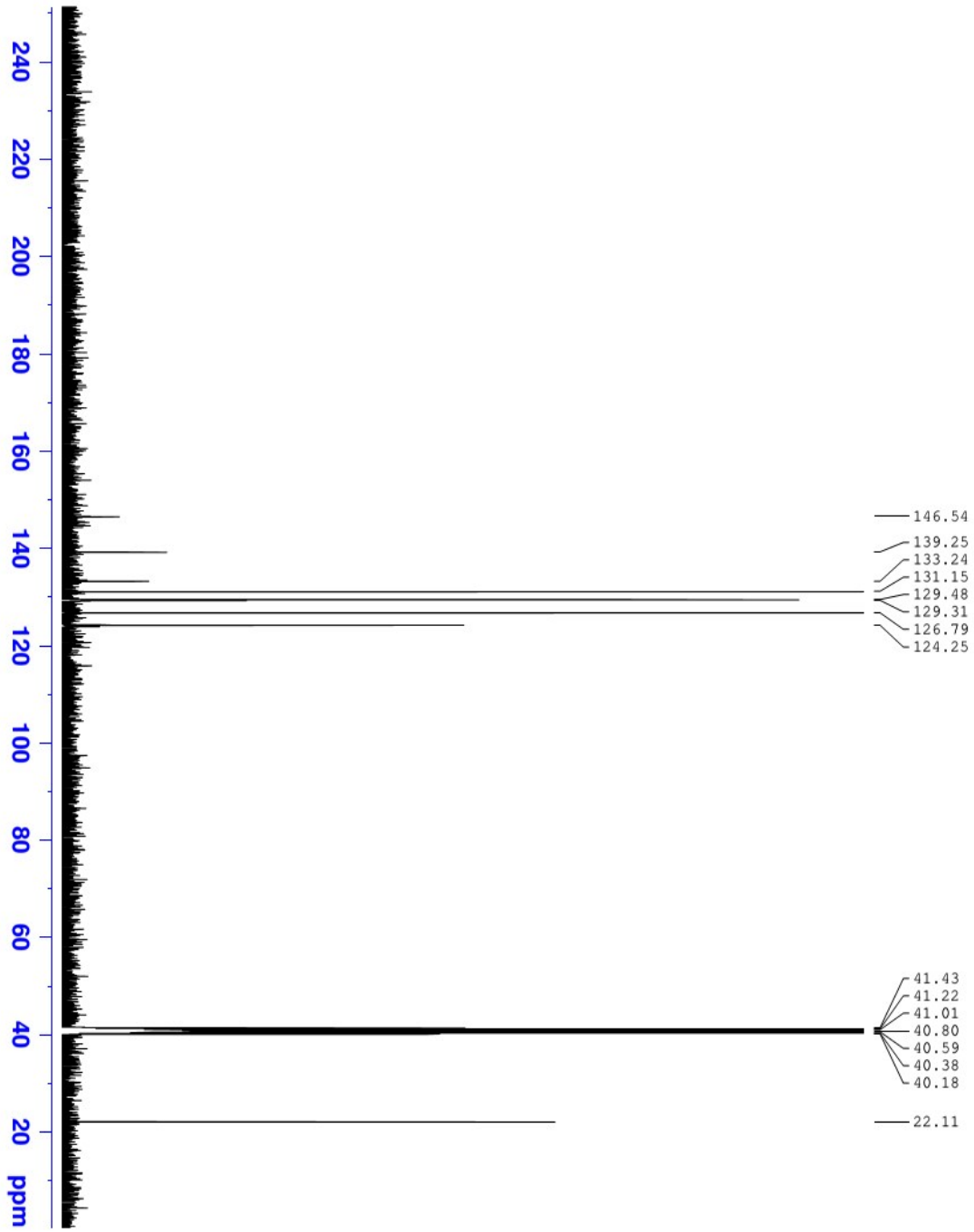


Figure S8. ^{13}CNMR of benzenaminium 4-methylbenzenesulfonate in d_6-DMSO.

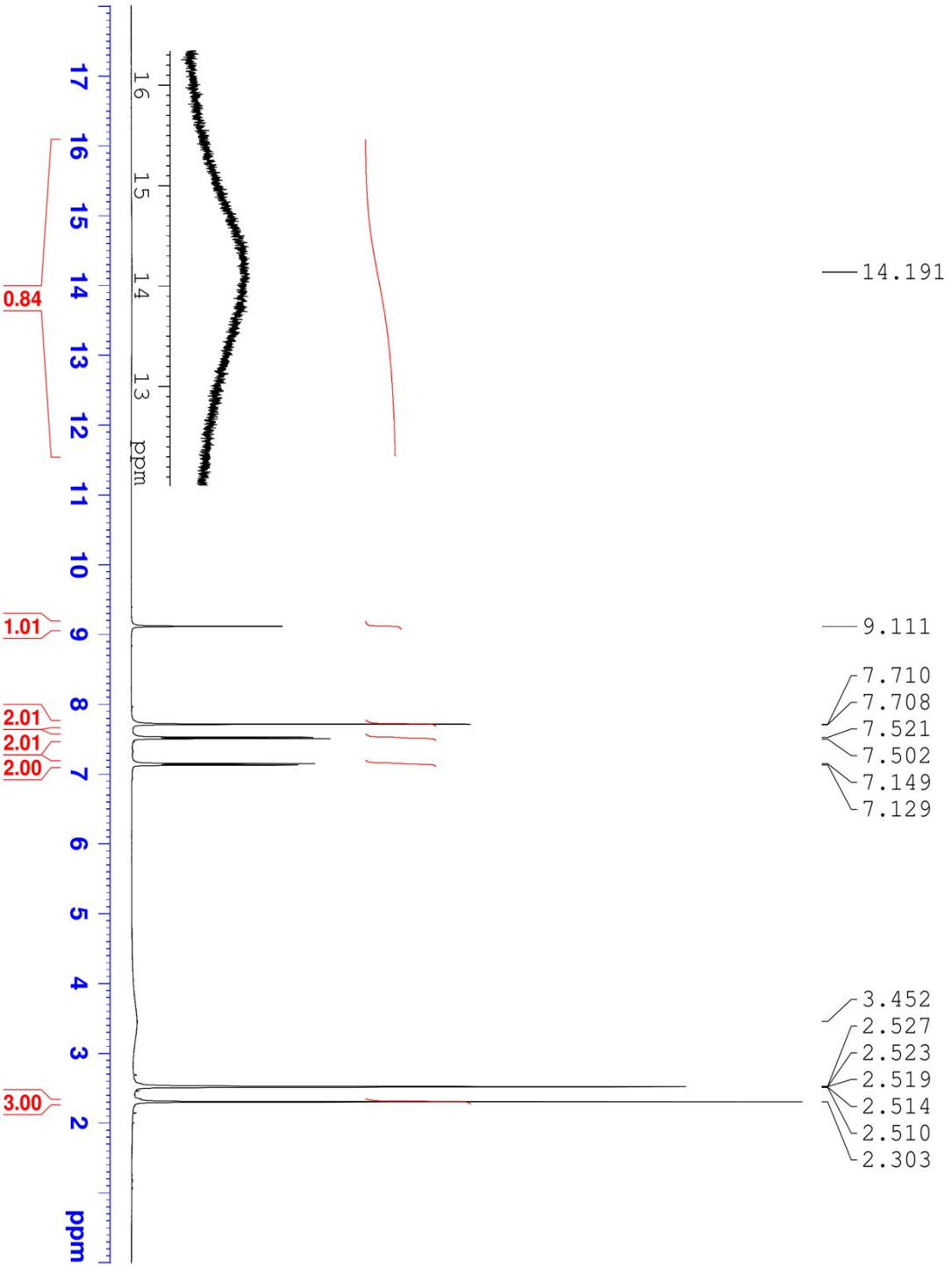


Figure S9. [1]HNMR of *1H*-imidazol-3-ium 4-methylbenzenesulfonate in d_6-DMSO.

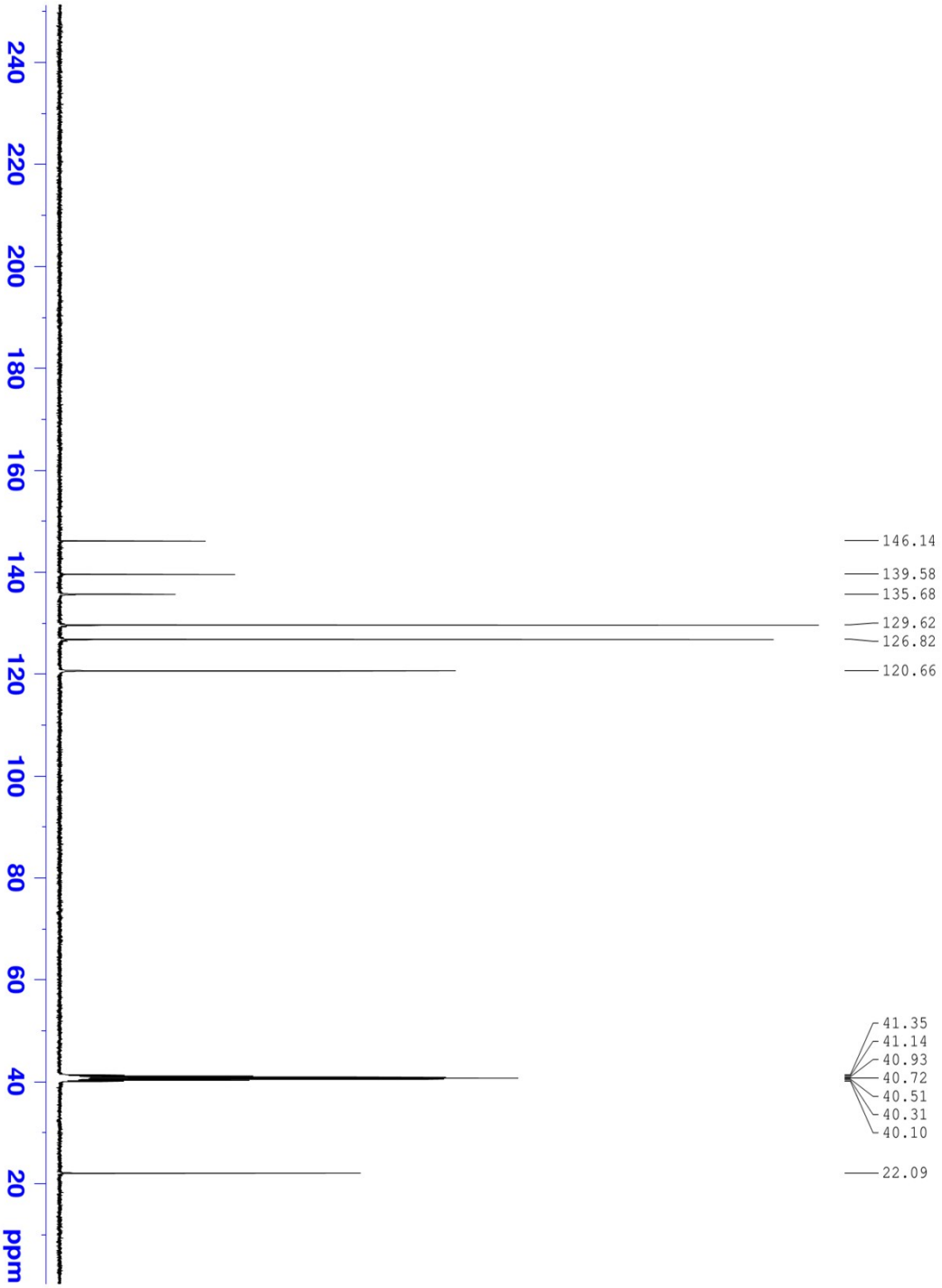


Figure S10. ^{13}CNMR of *1H*-imidazol-3-ium 4-methylbenzenesulfonate in d_6-DMSO.

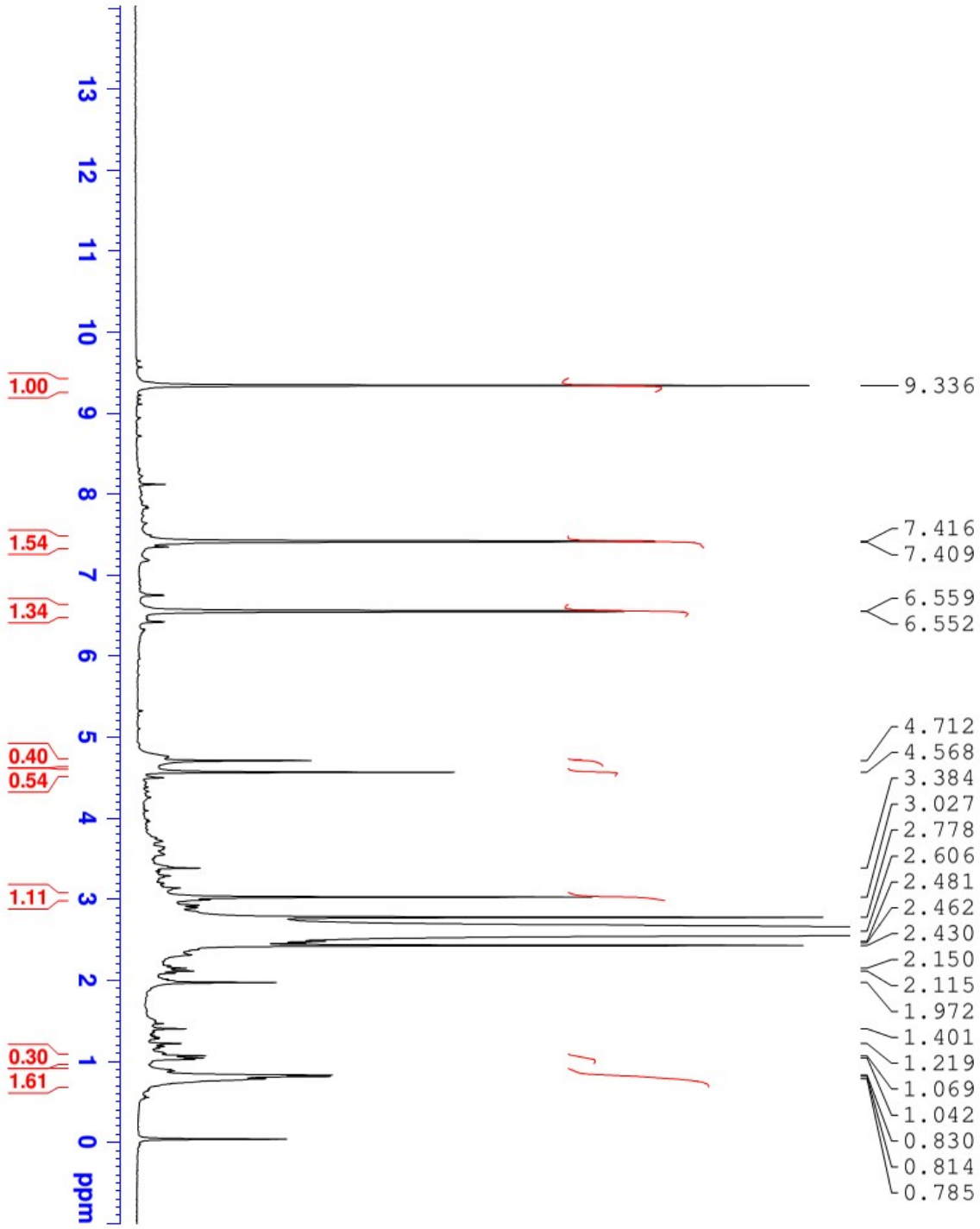


Figure S11. [1]HNMR of crude 5-HMF from cellulose in d_6-DMSO.

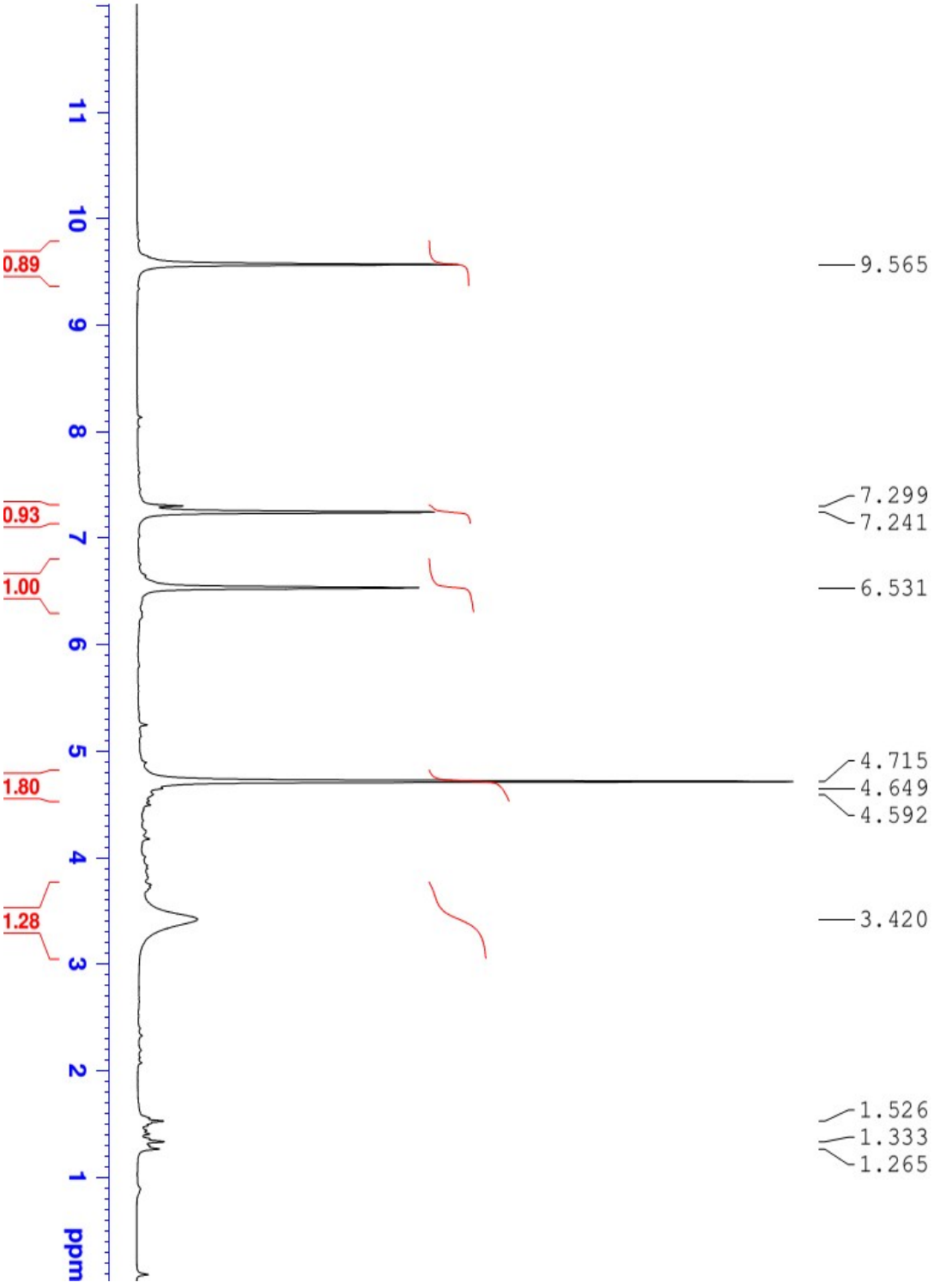


Figure S12. ^{1}HNMR spectra of isolated 5-HMF in $CDCl_3$.

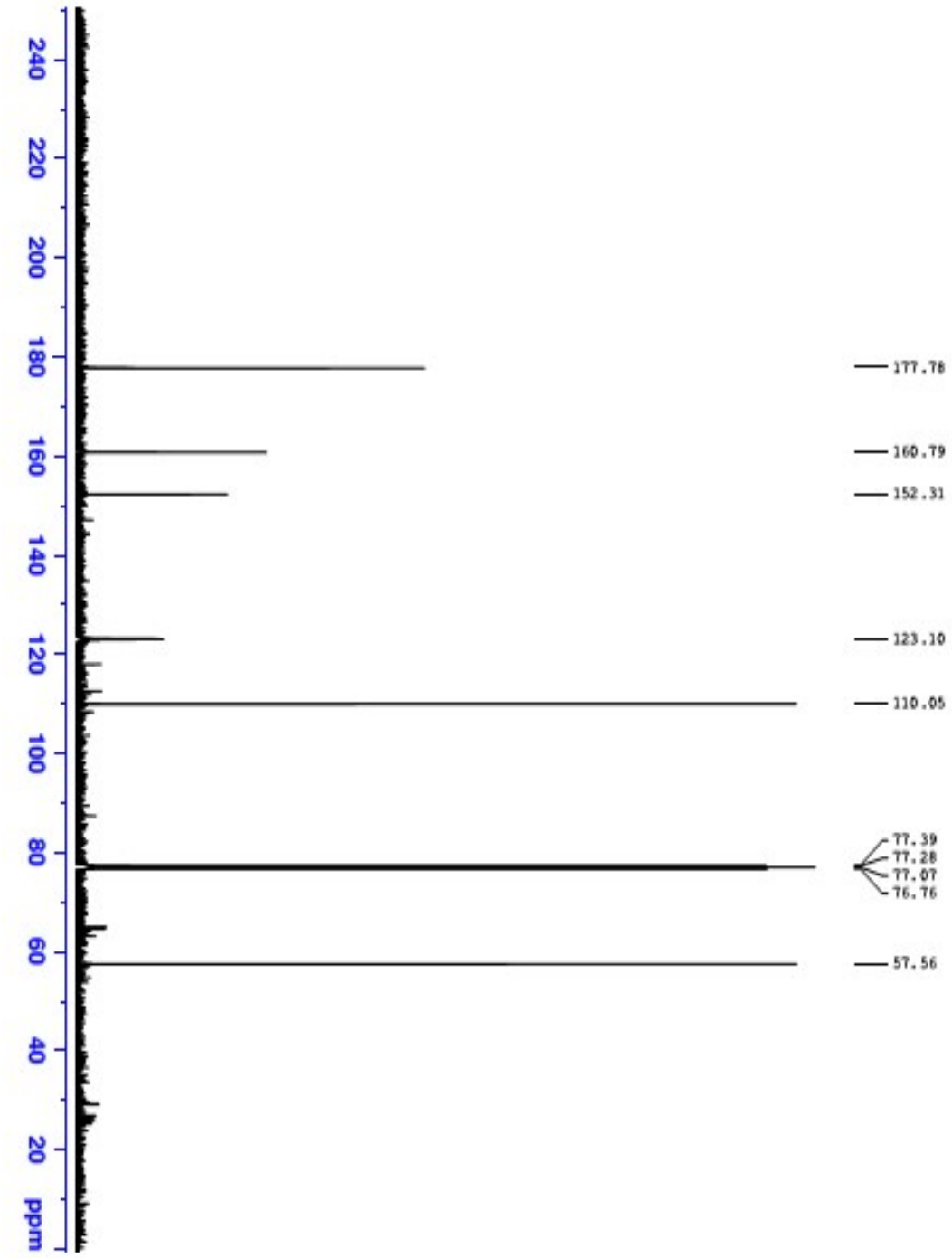


Figure S13. ^{13}CNMR spectra of 5-HMF in $CDCl_3$.

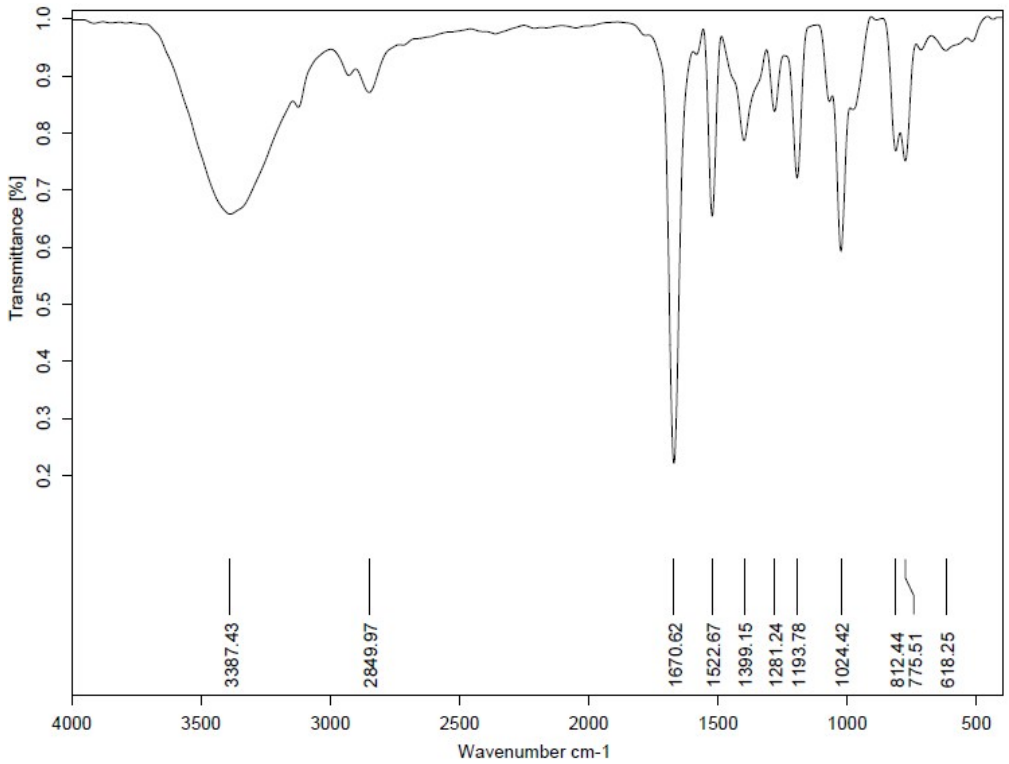


Figure S14. IR spectra of 5-HMF.

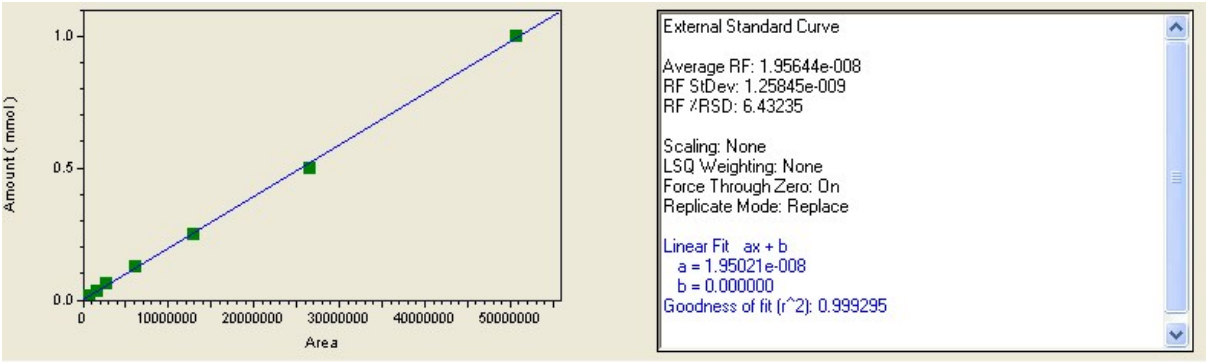


Figure S15. Standard calibration curve using different standard solution of 5-HMF.

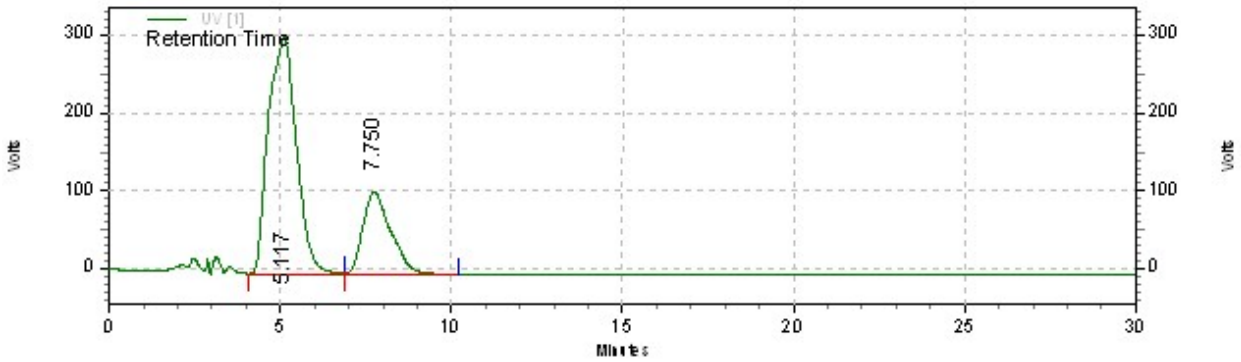


Figure S16. Cellulose dehydration products in MIBK phase; retention times (5-HMF=5.12 min, MIBK=7.75 min).

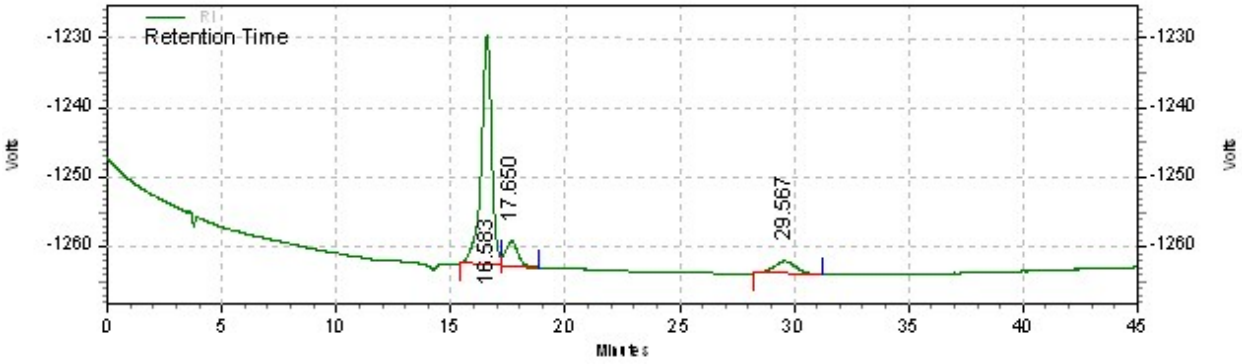


Figure S17. RID cellulose dehydration results in aqueous phase; retention time (glucose= 16.6 min).

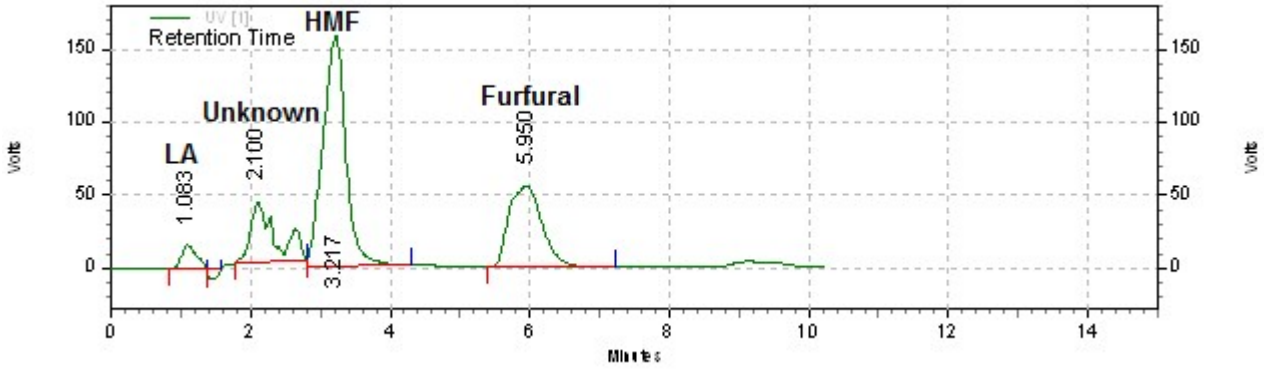


Figure S18. Straw dehydration products in organic phase; retention times (levulinic acid (LA)=1.1 min, HMF =3.22 min, Furfural=5.9 min).

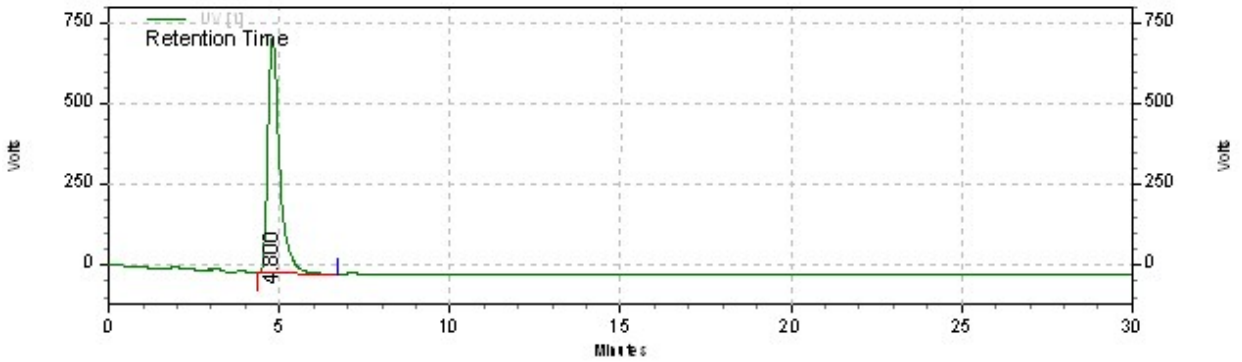


Figure S19. Fructose dehydration product in organic phase diluted in MeOH; retention time (5-HMF= 4.8 min).

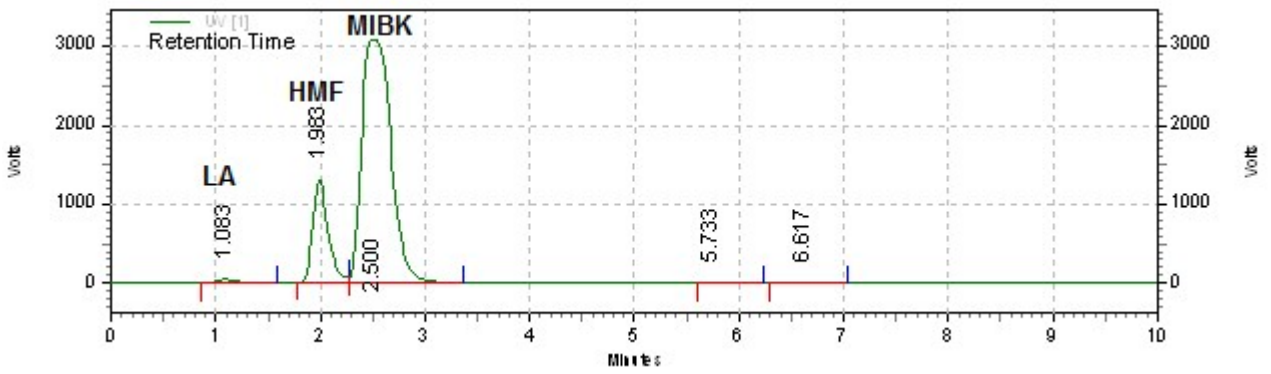


Figure S20. Fructose dehydration product in organic phase diluted in MIBK; retention times (Levulinic acid (LA)=1.1 min, 5-HMF≈ 2 min, MIBK=2.5 min); LA<1%.

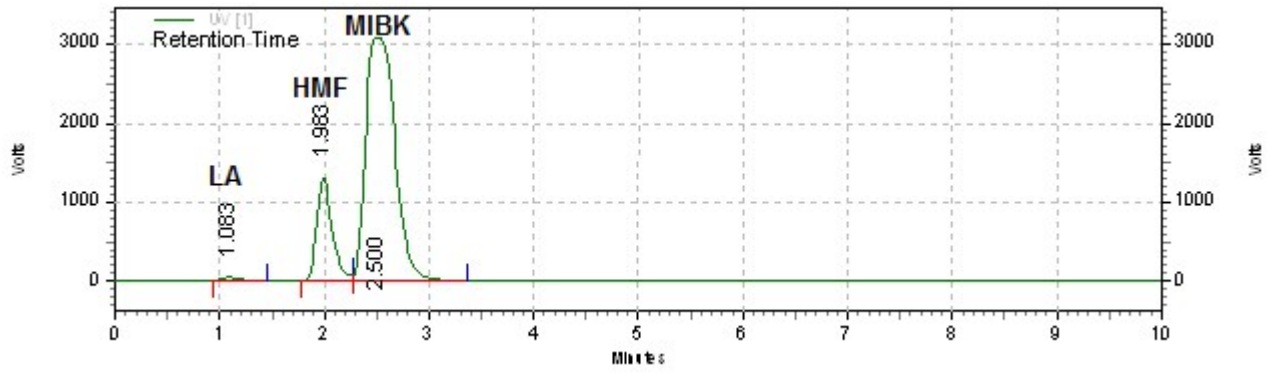


Figure S21. Glucose dehydration product in organic phase diluted in MIBK; LA<1%.

References

1. J. B. Binder, R. T. Raines, Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals. *J. Am. Chem. Soc.* **131**, 1979-1985 (2009)