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Supporting information

Practical DMSO-promoted selective hydrolysis–oxidation of lignocellulosic biomass to formic acid attributed to hydrogen bonds

Yan-Jun Guo,[1] Shi-Jun Li,[2] Yuan-Li Sun,[1] Lei Wang,[3] Wen-Min Zhang,[1] Ping Zhang,[1,4] Yu Lan[2]** and Yang Li[1]*

[1]Center for Organic Chemistry of Frontier Institute of Science and Technology and State Key Laboratory of Multi-phase Flow in Power Engineering, Xi' an Jiaotong University, Xi' an 710054, China,

[2]College of Chemistry, Zhengzhou University, Zhengzhou 450052, China

[3]Institute of Pulp and Paper Technology, Hubei University of Technology, Wuhan 430068, China

[4]College of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang 712000, China

*Correspondence: liyang79@mail.xjtu.edu.cn

**Correspondence: lanyu@zzu.edu.cn

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General Information

Materials

The wheat straw and the lignin were obtained from Institute of Pulp and Paper Technology, Hubei University of Technology, China. The wheat straw was milled into powder (200 mesh) before use. The analysis results are shown in Tables S1. The lignin [milled wood lignin (MWL), C%=58.73%] was obtained from wheat straw by Bjorkman method.[1] Microcrystalline cellulose (96%, 25 μm) was purchased from Aladdin Reagent Inc. (Shanghai, China). Xylan and xylose were purchased from Adamas Reagent Co., Ltd. (Shanghai, China). Glucose and sodium metavanadate ($NaVO_3$, AR) were purchased from Energy Chemical. All reagents were of analytical grade and were used without further purification.

Hydrolysis–oxidation of various substrates

The $NaVO_3$–H_2SO_4 solution was prepared by $NaVO_3$ (4 mol%, 271 mg), 0.7 wt% H_2SO_4 aqueous solution (100 mL) and stirred at room temperature until all the $NaVO_3$ was dissolved. Various substrates (containing 6 mmol of C-atoms), $NaVO_3$–H_2SO_4 solution (10 mL) and DMSO or sulfolane (1 v%, 100 μL) were added to a quartz inner charged with a stirring bar. Meanwhile the sleeves of the autoclave (Fig. S2, A) were preheated for 10–15 minute. The quartz lining was put into the autoclave (50 mL, 2.4 cm inner diameter). Then the autoclave was charged with oxygen (3 MPa). The mixture was stirred at a rate of 1,000 rpm and heated to 160 °C (inner temperature, ±0.5 °C) at a heating rate of 10–15 °C min^{-1} in about 10–15 min. Then the reaction mixture was stirred at 160 °C (inner temperature, ±0.5 °C) for the indicated time (3 hours for wheat straw, polysaccharides and lignin, 20 min for saccharides, 10 min for intermediates). The autoclave was cooled by water to room temperature and the pressure was released carefully after finish the reaction. Produced gas was collected in the gas collection bag, CH_4 was added as an internal standard for the detection of GC yield of CO_2. 1,4-Dioxane was added as an internal standard to the liquid phase for detection of ^{1}H NMR yield of HCO_2H.

Recycling experiments of formic acid production from biomass

Step 1: wheat straw (containing 0.94 g or 9.4 g of C-atoms in polysaccharides) and $NaVO_3$ (81.3 mg for 0.94 g, 813 mg for 9.4 g) were added to an erlenmeyer flask inner (150 mL) for 0.94 g, an quartz inner (1 L) for 9.4 g) charged with a stirring bar. Then added 0.7% H_2SO_4 aqueous solution (30.0 mL/0.94 g) and DMSO (1 v%). Stir vigorously until completely dissolved. The quartz inner was put in an autoclave (Fig. S2, B for 0.94 g, and Fig. S2, C for 9.4 g), and fill with oxygen (3 MPa). Then the reaction mixture was stirred at 160 °C (inner temperature, ± 0.5 °C) for 3 hours. After the reaction, the autoclave was cooled to room temperature under running water. Next, the gas in the autoclave was released and the quartz inner was taken out, and 1, 4-dioxane (192.5 μL/0.94 g) as internal standard for the detection of ^{1}H NMR yield of HCO_2H.

Step 2: The liquid of reaction mixture after reaction in step 1 was treated by evaporation in vacuo to afford the remained [V]–cat. and H_2SO_4.

Step 3: Deionized water (30 mL/22 mmol) and DMSO (1 v%) was added to the collected mixture of the [V] and H_2SO_4 and transferred to the inner. It is then stirred and heated (90 °C) for a period of time (10 min for 0.94 g; 30 min for 9.4 g reaction).

Step 4: Next, wheat straw (containing 0.94 g or 9.4 g) was added to the inner charged with a stirring bar and repeat step 1.

Influence of different components of wheat straw on recycling experiments

The $NaVO_3$–H_2SO_4 solution was prepared by $NaVO_3$ (4 mol%, 271 mg), 0.7 wt% H_2SO_4 aqueous solution (100 mL) and stirred at room temperature until all the $NaVO_3$ was dissolved.

Step 1: Various substrate (containing 6 mmol of C-atoms), $NaVO_3$–H_2SO_4 solution (10 mL) and DMSO (1 v%, 100 μL) were added to a quartz inner charged with a stirring bar. Meanwhile the sleeves of the autoclave (Fig. S2, A) were preheated for 10–15 minute. The quartz inner was put in the autoclave, and fill with oxygen (3 MPa). Then the reaction mixture was stirred at 160 °C (inner temperature, ± 0.5 °C) for 3 hours (glucose for 20 min). After the reaction, the autoclave was cooled to room temperature under running water. Next, the gas in the autoclave was released and the quartz inner was taken out, and 1, 4-dioxane (18 mmol, 64 μL) as internal standard for the detection of ^{1}H NMR yield of HCO_2H.

Step 2: The liquid of reaction mixture after reaction in step 1 was treated by evaporation in vacuo and left V–cat and H_2SO_4.

Step 3: Deionized water (10 mL) and DMSO (1 v%) was added to the collected mixture of the [V] and H_2SO_4 and transferred to the inner. It is then stirred for 10 min (heating at 90 °C for 10 min for E).

Step 4: Next, glucose (containing 6 mmol of C-atoms, 180 mg) was added to the inner charged with a stirring bar and repeat step 1.

Detection of oxidation of glycolaldehyde to glyoxal

Glycolaldehyde-dimer (containing 6 mmol of C-atoms, 182 mg), $NaVO_3$–H_2SO_4 solution (10 mL), DMSO (1 v%, 100 μL) and 1,2-diaminobenzene (1 mmol, 108 mg) were added to a quartz inner charged with a stirring bar. Meanwhile the sleeves of the autoclave (Fig. S2, A) were preheated for 10–15 minute. The quartz inner was put in the autoclave, and fill with oxygen (3 MPa). Then the reaction mixture was stirred at 160 °C (inner temperature, ± 0.5 °C) for 10 min. After the reaction, the autoclave was cooled to room temperature by water. Next, the gas in the autoclave was released and the quartz inner was taken out, and detected quinoxaline by ^{1}H NMR.

Time–resolved glucose conversion detected by HPLC

Glucose (containing 6 mmol of C-atoms, 180 mg), $NaVO_3$–H_2SO_4 solution (10 mL) and DMSO (1 v%, 100 μL) were added to a quartz inner charged with a stirring bar. Meanwhile the sleeves of the autoclave (Fig. S2, A) were preheated for 10–15 minute. The quartz inner was put in the autoclave, and fill with oxygen (3 MPa). Then the reaction mixture was stirred at 160 °C (inner temperature, ± 0.5 °C) for 0, 5, 10, 15, 20 min, respectively. After the reaction, the autoclave was cooled to room temperature by water. Next, the gas in the autoclave was released and the quartz inner was taken out, and filtered with the syringe–driven filter (0.22 μm), and detected by HPLC.

IR detection in Fig. 6

Various substrates (glycolaldehyde-dimer, glucose, glyoxal containing 6 mmol of C-atoms) were dissolved in water (1 mL) and DMSO (0.1 mL) for infrared test. The mixed sample was prepared by mixing the required solution with the same volume, and then for infrared test. Especially, glyoxal (aq.)

and DMSO (aq.) needed to be mixed for more than 2 h before test. All the experiments were performed for two times with the constant data.

Analysis of products

The elemental analysis for C% were performed on Elementar Vario MICRO cube apparatus. The components (water extracts, cellulose, hemicellulose and lignin) of wheat straw were analyzed according to NREL/TP-510-42618 method.[2] Analytical gas chromatography (GC) spectra were carried out on a SHIMDZU GC-2014ATF/SPL (TDX-01 60/80 mesh, 2.0 mm × 3.2 mm × 2.1 mm-FID, TCD permanent gases, N_2 carrier gas). The liquid samples were analyzed by HPLC (Agilent 1260) and NMR (Bruker Avance-400) in the solvents indicated. The HPLC were determined by a Sugar-H (7.8 × 300 mm, 5 μm) column and a RID detector (40 °C) using pH=2 H_2SO_4 solution as eluent. The ^{1}H NMR yields of HCO_2H after hydrolysis–oxidation were determined by using 1,4-dioxane as an internal standard. Chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm., D_2O resonance in the ^{1}H NMR spectrum as 4.79 ppm, $(CD_3)_2SO$ resonance in the ^{1}H NMR spectrum as 2.50 ppm., ^{51}V NMR spectrums were determined relative to $VOCl_3$ as external standard. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Attenuated Total Refraction-Fourier transform infrared (ATR-FTIR) spectra were obtained at room temperature using a Bruker ALPHA II. The spectra were recorded in the range of 4000–600 cm^{-1}. Element analysis for C% were performed on Elementar Vario MICRO cube apparatus. The hydrolysis–oxidization reactions were conducted in a Wattcas autoclave.

Computational details

All the calculations in this study were performed using the Gaussian 16 program package.[3] The All the geometries were optimized at the M06-2X[4]/6-31G(d, p) level, and the solvent effect was utilized the polarizable continuum model using integral equation formalism model (IEFPCM) in hexane solvent.[5]All the optimized stationary points had been identified as minima (zero imaginary frequencies) and transition states (one imaginary frequency), via the vibrational analysis. The solution-translational entropy correction has been calculated with THERMO program.[6]

Table S1. Components of the wheat straw[a]

 Wheat straw	H_2O /%	Glucose /%	Xylose /%	Galactose /%	Arabinose /%	Mannose /%	Cellulose /%	Hemicellulose /%	Lignin /%	Others /%	Element /% (C)
	6.36	40.00	21.50	0.04	0.16	0.62	40.00	22.32	23.24	8.08	43.84

[a]Wheat straw was prepared into 200 mesh. The components were analyzed according to NREL/TP-510-42618 method.[2] Cellulose contents were calculated based on the carbon content of glucose. Hemicellulose contents were calculated based on the carbon content of xylose, galactose, arabinose and mannose.

Calculation of the contribution of each component to the product (HCO_2H and CO_2)

Contribution = yield of product × mol fraction of the component in wheat straw

$$\textbf{C mol fraction of the component} = \frac{\mathbf{wt}_{component}\% \times \mathbf{C}_{component}\% \times \frac{m_{wheat\ straw\ (g)}}{12.01\ g/mol}}{\mathbf{C}_{wheat\ straw}\% \times \frac{m_{wheat\ straw\ (g)}}{12.01\ g/mol}} = \frac{\mathbf{wt}_{component}\% \times \mathbf{C}_{component}\%}{\mathbf{C}_{wheat\ straw}\%}$$

$C_{cellulose}\% = \frac{12.01\ g/mol\ \times 6}{162.14\ g/mol} = 44.44\%$

$C_{mol\ fraction\ of\ cellulose}\% = \frac{40.00\%\ \times 44.44\%}{43.84\%} = 40.55\%$

$C_{xylan}\% = \frac{12.01\ g/mol\ \times 5}{132.12\ g/mol} = 45.45\%$ (xylan was chosen as a model substrate of hemicellulose)

$C_{mol\ fraction\ of\ xylan}\% = \frac{22.32\% \times 45.45\%}{43.84\%} = 23.13\%$

$C_{lignin}\% = 58.73\%$ (detected by element analysis)

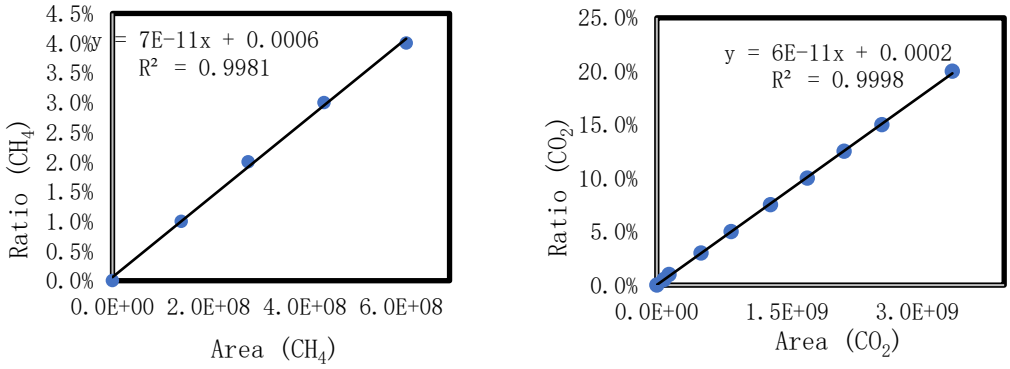
$C_{mol\ fraction\ of\ lignin}\% = \frac{23.24\% \times 58.73\%}{43.84\%} = 31.13\%$

Calculation the contents of CO_2. Produced gas was collected in the gas collection bag, CH_4 was added as an internal standard for the detection of GC yield of CO_2.

$Yield_{CO2}\%\ ^{a} = \frac{n_{CH4} \times C_{CO2}}{C_{CH4} \times 6\ \text{mmol C}} = \frac{V_{CH4}}{V_m} \times \frac{C_{CO2}}{C_{CH4} \times 6\ \text{mmol C}}$

[a] V_{CH4} = 20 mL, V_m = 24.041 L (20 °C)

Standard deviation (S) $= \sqrt{\frac{\sum_{i=1}^{n}(S_i - \bar{S})^2}{n}}$



A. **B.**

Fig. S1. The standard curve for the calculation of the contents of CH_4 (A) and CO_2 (B). CH_4 (20 μL, 40 μL, 60 μL, 80 μL) were injected into GC, respectively. These amounts of CH_4 were corresponding to the ratio of CH_4 (1%, 2%, 3% and 4%, respectively, the standard injection volume was 2 mL). The standard–curve was made by Ratio (CH_4)/Area (CH_4). The standard–curve for CO_2 calculation was made by the same method. CO_2 (10 μL, 20 μL, 60 μL, 100 μL, 150 μL, 200 μL, 250 μL, 300 μL, 400 μL) were injected into GC, respectively. These amounts of CO_2 were corresponding to the ratio of CH_4 (0.5%, 1%, 3%, 5%, 7.5%, 10%, 12.5%, 15% and 20%, respectively, the standard injection volume was 2 mL). The standard–curve was made by Ratio (CO_2)/Area (CO_2).

A. **B.** **C.**

Fig. S2. The pictures of the hydrolysis–oxidation procedure. A. autoclave for 50 mL; B. autoclave for 500 mL; C. autoclave for 1 L.

Table S2. Recycling Experiment

Entry[a]	Conditions			HCO_2H yield %[b] (Times)				
	substrates[c]	DMSO	Preheating	1	2	3	4	5
1	Wheat straw 1 gram–scale	—	—	55	34	35	29	29
2	Wheat straw 1 gram–scale	√	—	52	39	—	—	—
3	Wheat straw 1 gram–scale	√	10 min	52	54	—	—	—
4	Wheat straw 10 gram–scale	√	30 min	53	53	54	53	55
5	Wheat straw 1 gram–scale	√	10 min	53	0[d]	—	—	—

[a]Reaction conditions: substrate (including 0.94 g or 9.4 g), 0.7 wt% H_2SO_4 aqueous solution (30 mL/0.94 g), DMSO (1 v%), $NaVO_3$ (81.3 mg for 0.94 g, 813 mg for 9.4 g), O_2 (3.0 MPa), 160 °C, 3 h. [b]Yields of HCO_2H were determined by ^1H NMR with 1,4-dioxane as an internal standard. [c]The components were analyzed according to NREL/TP-510-42618 method.[2] The wheat straw was prepared into 200 mesh, carbon content was determined by elemental analysis as 43.84%. [d]To exclude the increased HCO_2H from oxidation of DMSO, no substrate was added in the second recycle.

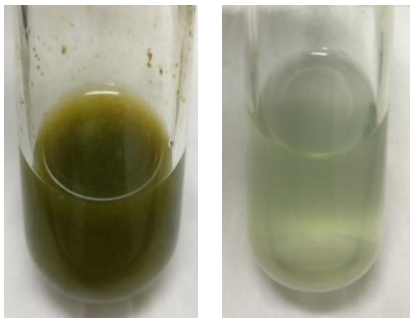
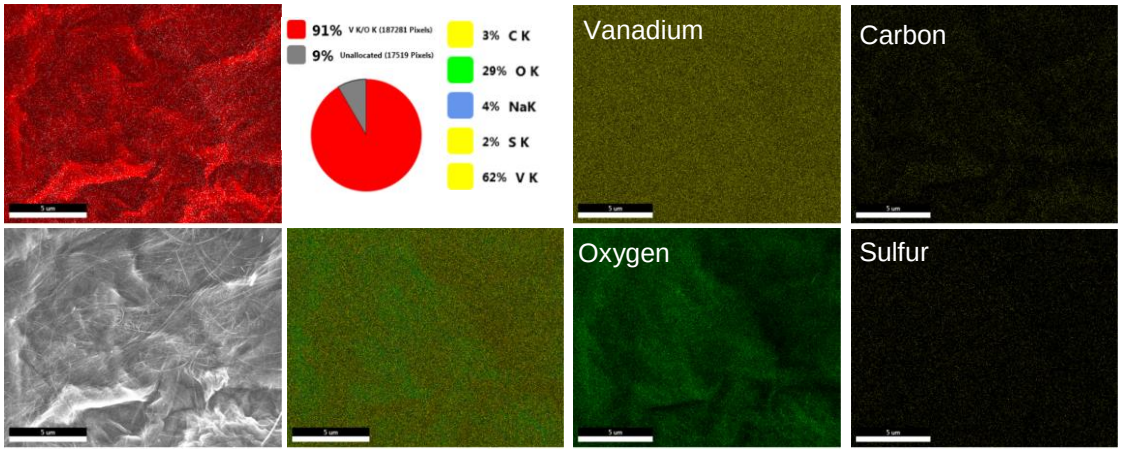


Fig. S3. The picture after the reaction with wheat straw. Without DMSO (left), with DMSO (right).

(A)



(B)

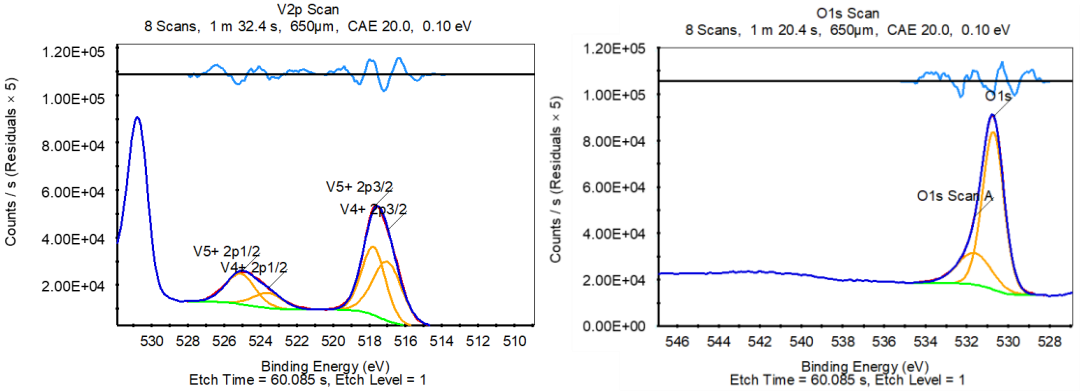


Fig. S4. EDX (A) and XPS (B) of dark green flocculation (VO_2). (A) SEM–EDX mapping results of elemental distribution for V, C, O and S elements of the dark green flocculation (VO_2). (B) V 2p (a) and O 1s (b) of XPS spectra of the dark green flocculation (VO_2).

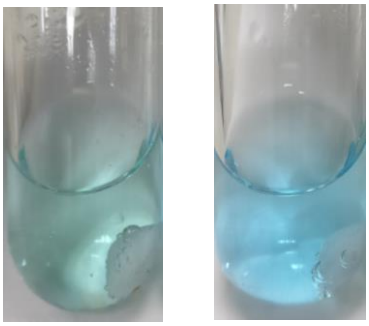
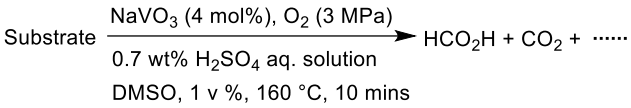
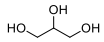


Fig. S5. The picture after the reaction with glucose. With sulfolane (left) and with DMSO (right).

Table S3. Investigation of possible intermediates



Entry[a]	Substrate	Conv.%[b]	HCO_2H%[b]	CO_2%[c]	Others%[b,d]
1		5	/	3	—
2[g]		16	—	<1	—
3		3	3	<1	—
4		7	3	2	CH_2O: 2
5		15	5	2	CH_2O: 4 AA: 5
6[f]		/[d]	5	<1	/
7		—	—	—	—
8		>99	6	91	CH_2O: 16
9		89	7	47	CH_2O: 8 AA: 16 MGO: 10
10		97	28	12	CH_2O: 7 AA: 50
11		74	17	34	CH_2O: 34
12		>99	54	46	CH_2O: 9
13[g]		>99	25	72	—

[a]Reaction conditions: substrate (including 6 mmol C-atoms), 0.7 wt% H_2SO_4 aqueous solution (10 mL), DMSO (100 μL, 1 v %), $NaVO_3$ (27.1 mg, 4 mol%), O_2 (3.0 MPa), 160 °C, 10 min. Reported as an average of two experiments with an error bar less than 4%. AA = acetic acid, MGO = methylglyoxal. [b]Conversion (Conv.) yields of HCO_2H, AA, and CH_2O were determined by ^1H NMR spectroscopy with 1,4-dioxane as an internal standard. [c]Yields of CO_2 were determined using GC with CH_4 as an internal standard. [d]Part of CH_2O was produced by oxidation of DMSO, which was proved by the experiments with ^{13}C-DMSO (See Fig. S6). [e]Higher conversion of CH_3OH than the total yield of substrate products should be attributed to volatilization. [f]37 wt% CH_2O aqueous solution was used. [g]Without DMSO.

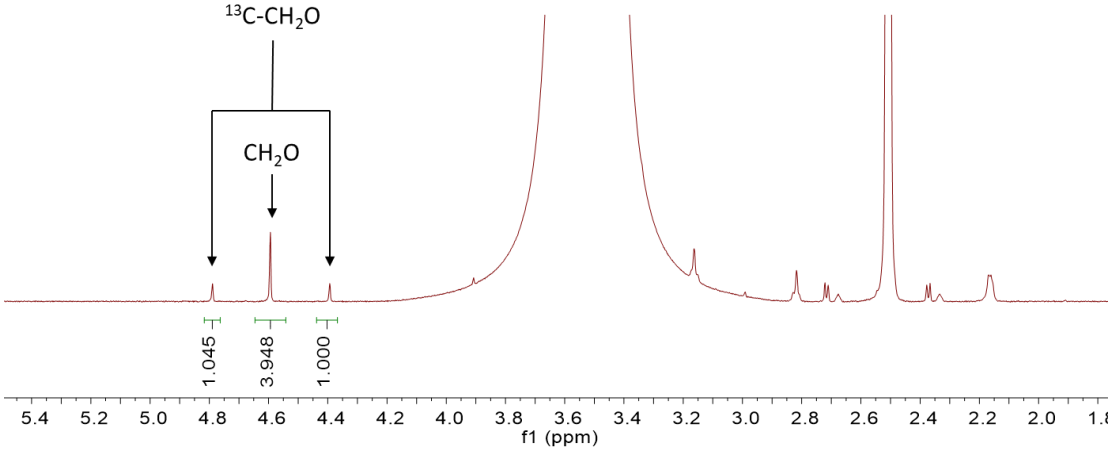


Fig. S6. ^{1}H NMR analysis of the reaction mixture after the hydrolysis–oxidation of glyoxal. To prove the part of CH_2O (CH_2O is existed as $CH_2(OH)_2$ in aqueous solution) was produced by the oxidation of DMSO, ^{13}C-DMSO was used. Base on the integration of the indicated peaks, CH_2O from substrate and from DMSO was determined as 2:1 in this reaction. The CH_2O is different with different substrates.

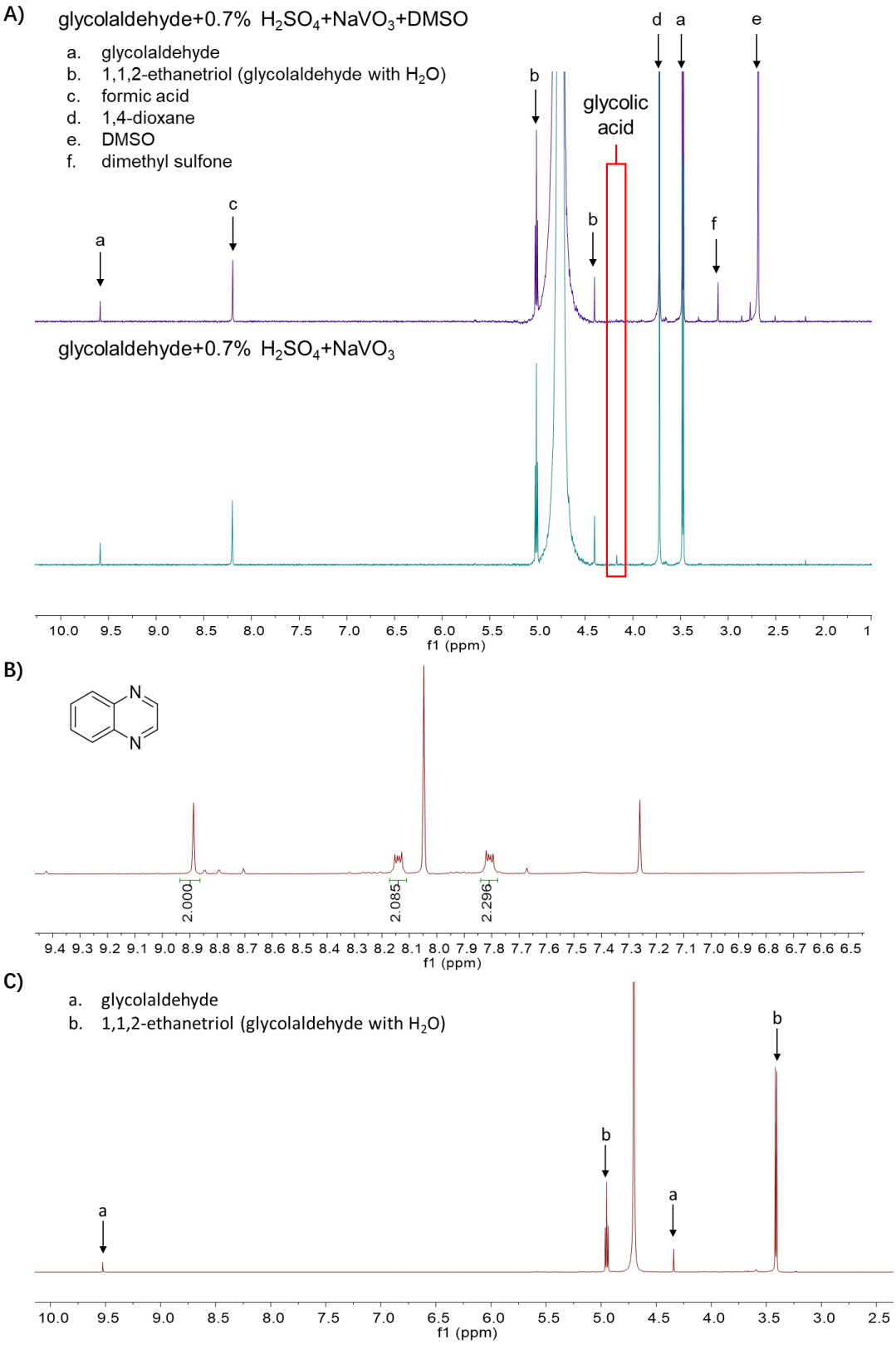
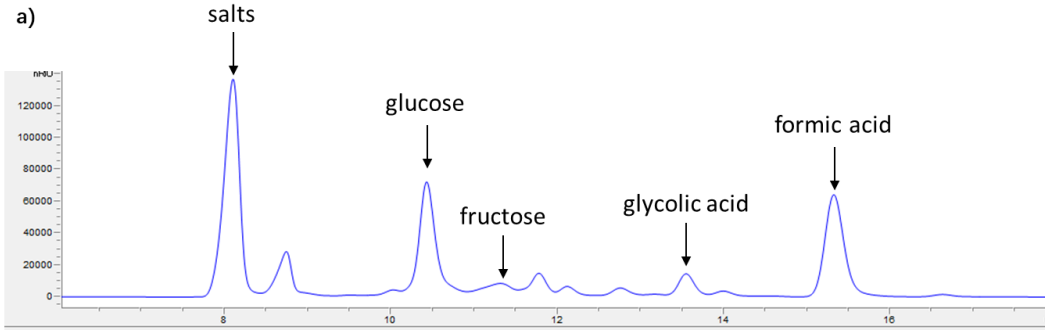
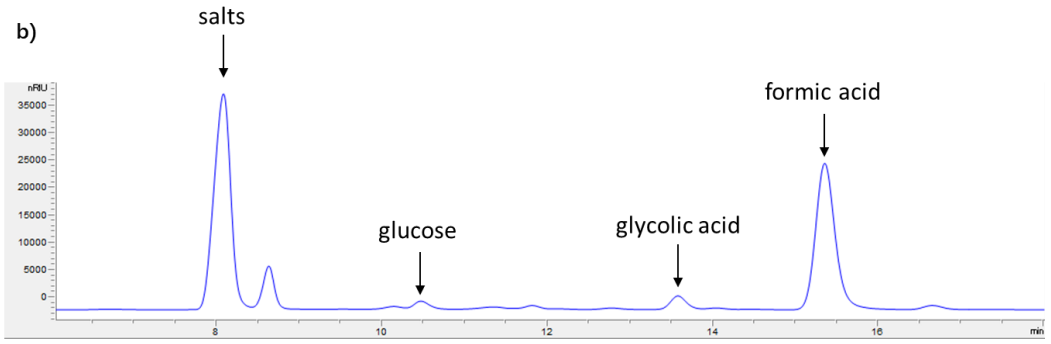
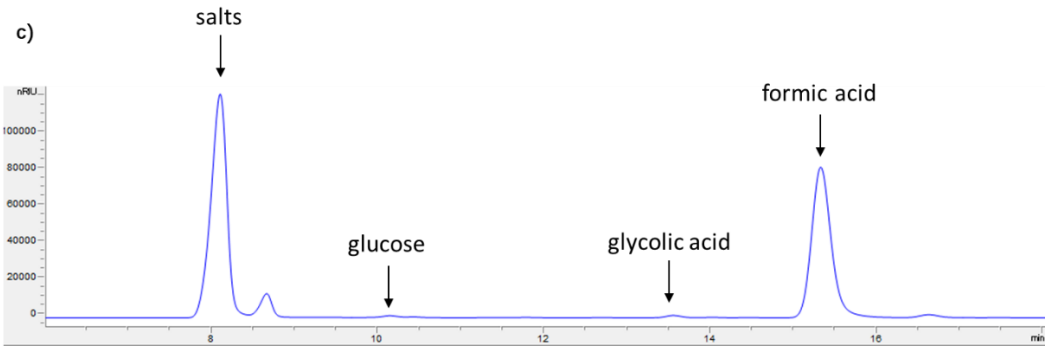
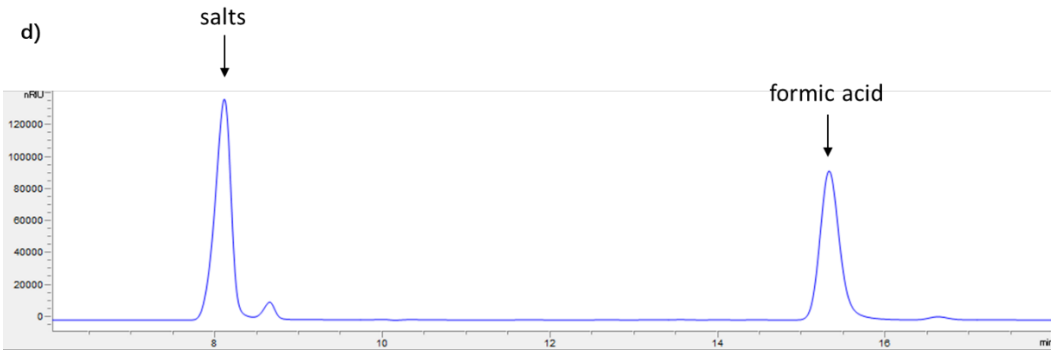


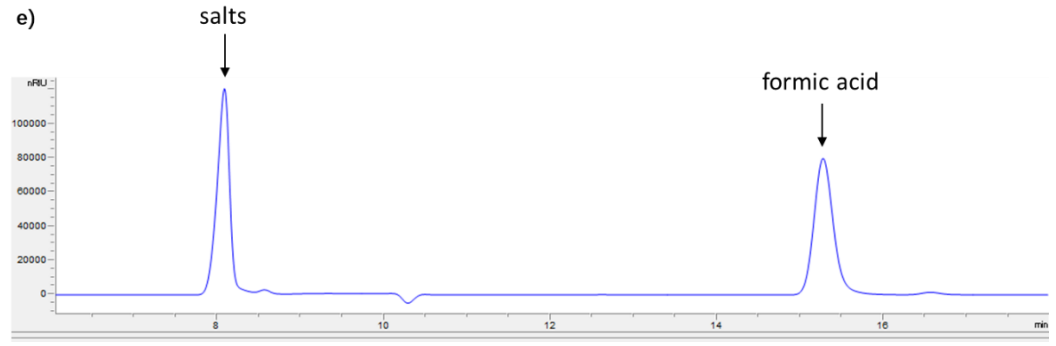
Fig. S7. ^{1}H NMR analysis of mixture after oxidation step of glycolaldehyde. A) ^{1}H NMR analysis of mixture after oxidation of glycolaldehyde with or without DMSO. B) ^{1}H NMR analysis of quinoxaline after oxidation of glycolaldehyde with DMSO and 1,2-diaminobenzene. C) ^{1}H NMR analysis of commercial glycolaldehyde-dimer solutions in the reaction concentration (major formed 1,1,2-ethanetriol and glycolaldehyde).

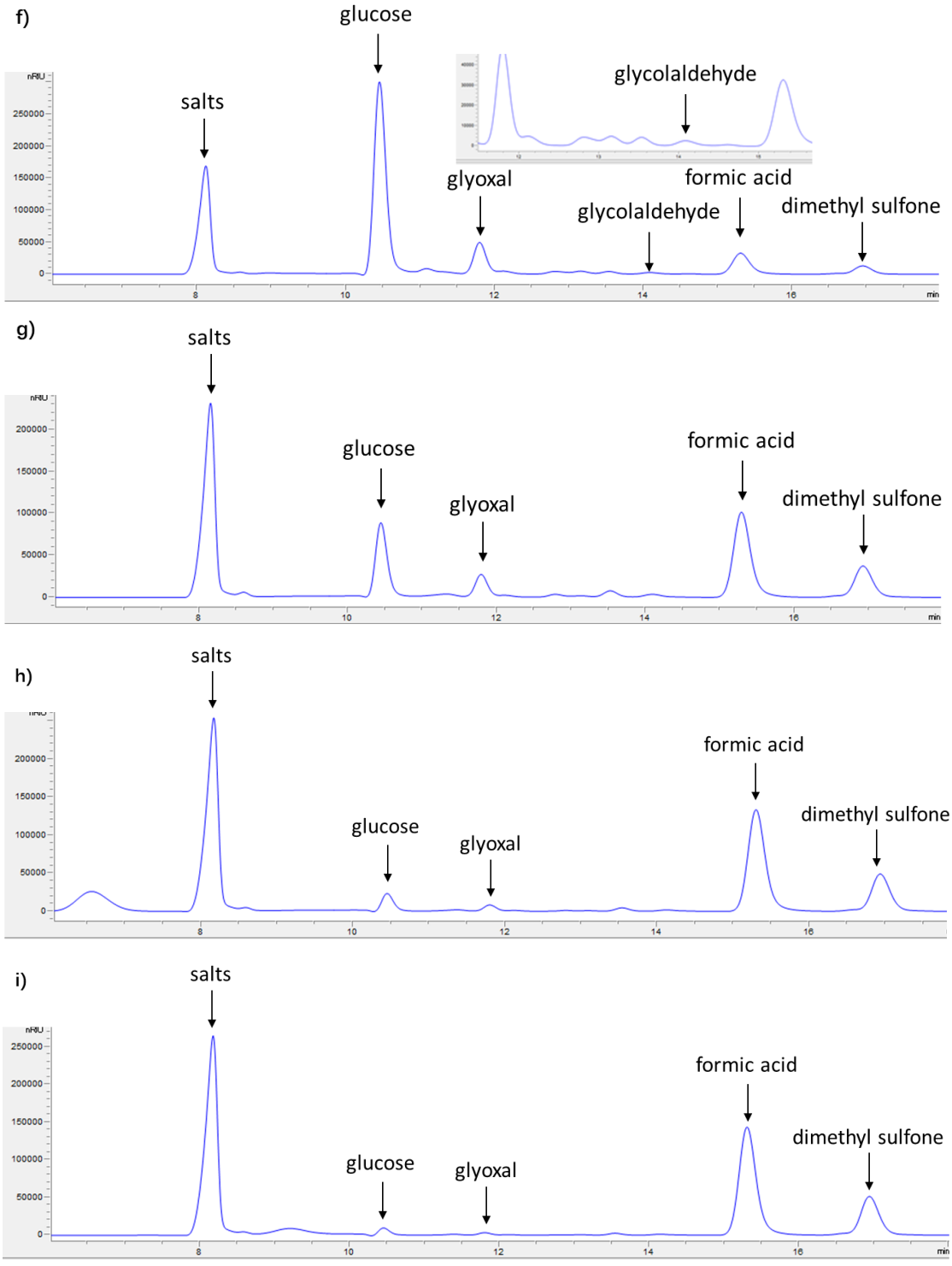

a)
salts
glucose
fructose
glycolic acid
formic acid


b)
salts
glucose
glycolic acid
formic acid


c)
salts
glucose
glycolic acid
formic acid


d)
salts
formic acid


e)
salts
formic acid


f)
glucose
salts
glycolaldehyde
glyoxal
formic acid
glycolaldehyde
dimethyl sulfone
g)
salts
glucose
glyoxal
formic acid
dimethyl sulfone
h)
salts
formic acid
glucose
glyoxal
dimethyl sulfone
i)
salts
formic acid
glucose
glyoxal
dimethyl sulfone

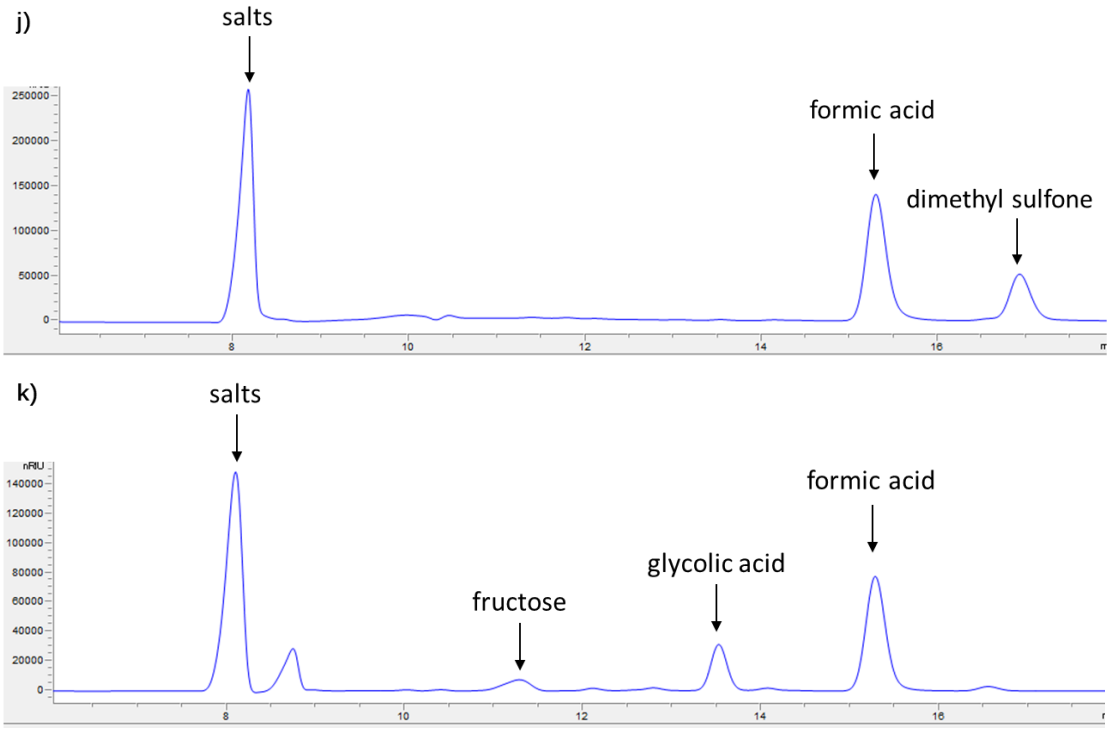


Fig. S8. HPLC analysis of mixture after the hydrolysis–oxidation step glucose and fructose. a)–e) glucose–without DMSO–0 min, 5 min, 10 min, 15 min to 20 min, respectively; f)–j) glucose–with DMSO–0 min, 5 min, 10 min, 15 min to 20 min, respectively; k) fructose–without DMSO–0 min.

Table S4. The Gibbs free energy for the species.

Species	G(a.u.)	Species	G(a.u.)
H_2O	-76.36863	DMSO	-553.02534
1	-228.90604	2	-305.28523
3	-858.31467	4	-858.31526
5	-858.31746	6	-227.71364
7	-380.48523	8	-933.51973
9	-763.11006	10	-1316.1435
11	-1316.1472	12	-381.66581
13	-456.86126	14	-839.48983

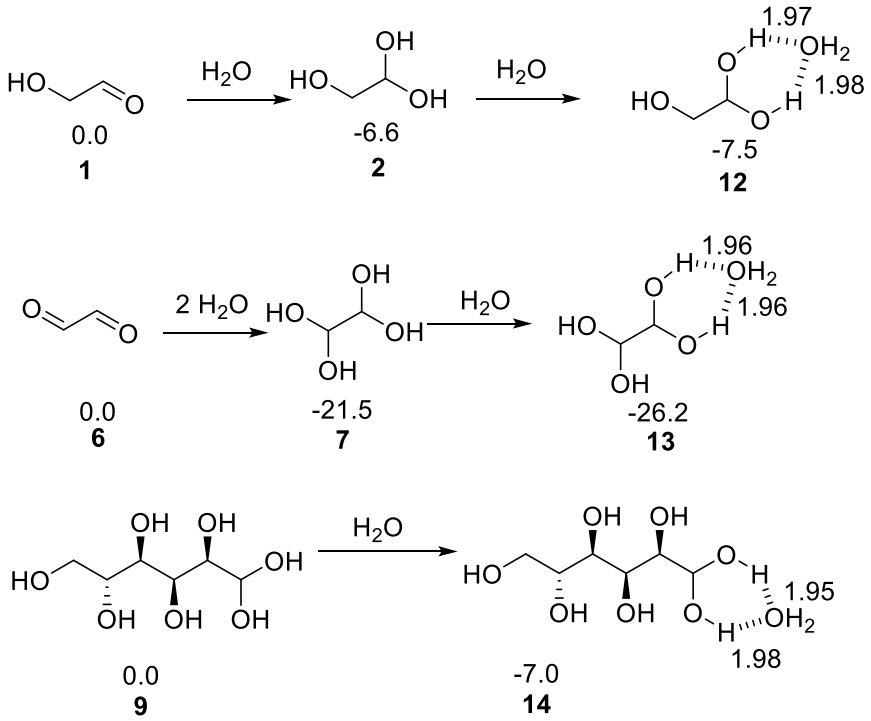


Fig. S9. The possible hydrogen bond for the water and substrates.

The ΔG shows the combination for the water and substrate **1, 6** and **9** would be weaker than that of DMSO, which would affect the further transformation.

Table S5. The coordination for the species.

H_2O			
O	-0.49458	0.43260	-0.02420
H	0.47107	0.48302	-0.02420
H	-0.76940	1.35970	-0.02420
1			
C	-0.13919	1.32815	-0.00264
O	1.06927	1.33171	-0.08403
H	-0.71236	0.39007	0.07979
C	-0.92031	2.61735	-0.01059

DMSO			
S	-0.06464	-0.00382	-0.03825
O	1.45252	-0.05029	-0.01534
C	-0.52965	1.74170	0.02803
H	-1.61104	1.83487	-0.09492
H	-0.23486	2.12101	1.00770
H	0.00007	2.28386	-0.75921
C	-0.56466	-0.28967	-1.75171
H	-0.29352	-1.31608	-2.00369

H	-1.63381	2.57562	-0.84654
H	-1.51575	2.65784	0.91325
O	-0.06825	3.72347	-0.11940
H	0.83451	3.35999	-0.16316
2			
C	-0.18443	1.31726	-0.08878
O	1.04335	1.52816	0.57333
C	-0.93109	2.63548	0.00696
H	-1.86405	2.57743	-0.55787
H	-1.17289	2.80487	1.06700
O	-0.15643	3.68238	-0.53287
H	0.72344	3.57954	-0.13440
H	0.00329	1.05608	-1.13877
H	1.70529	0.91129	0.22934
O	-0.97551	0.34934	0.53771
H	-0.61137	-0.52601	0.33956
4			
C	-1.84973	0.76916	0.55549
O	-2.67839	-0.04815	1.34775
C	-1.93315	0.21005	-0.85088
H	-1.36650	0.83945	-1.54138
H	-1.48223	-0.79321	-0.83921
O	-3.27548	0.18038	-1.28785
H	-3.77366	-0.20677	-0.54932
H	-2.23873	1.80052	0.57157
H	-2.70879	0.37470	2.22702
O	-0.51462	0.73910	0.96976
H	-0.54504	0.99531	1.91564
S	-1.57706	2.85002	3.94321
O	-1.55587	1.40709	3.41468
C	0.09167	3.14487	4.55410
H	0.18003	4.18822	4.86335
H	0.24191	2.48855	5.41220
H	0.80963	2.90787	3.76550
C	-1.49499	3.90257	2.48217
H	-2.46291	3.84840	1.98187
H	-1.29450	4.93126	2.78882
H	-0.70534	3.52771	1.82477
6			
C	-0.36072	-0.43155	-0.00460
O	0.84408	-0.40824	-0.00460
H	-0.95673	-1.36126	-0.00460
C	-1.16511	0.86184	-0.00460
O	-2.36991	0.83854	-0.00460

H	-1.64541	-0.15928	-1.84199
H	-0.03235	0.40935	-2.40157
3			
C	-0.33761	-0.68052	0.18830
O	-0.77846	0.55535	0.70280
C	0.80639	-0.38734	-0.76752
H	1.14008	-1.33628	-1.19899
H	0.40438	0.23510	-1.58028
O	1.89217	0.22413	-0.12153
H	1.69879	1.18970	-0.10133
H	0.00913	-1.31950	1.01241
H	-1.31896	0.39606	1.49120
O	-1.33067	-1.32875	-0.56074
H	-1.97558	-1.72179	0.04543
S	0.45276	3.23577	1.12665
O	1.21297	2.85322	-0.14879
C	1.23397	2.29504	2.45301
H	0.78189	2.56992	3.40840
H	1.05160	1.24418	2.22645
H	2.30625	2.50538	2.45259
C	1.10630	4.85577	1.58142
H	0.76428	5.57078	0.83168
H	0.72029	5.13629	2.56406
H	2.19770	4.80980	1.58883
5			
C	-2.03324	-0.36040	-0.19760
O	-1.39308	-0.88512	0.93961
C	-2.28100	1.13946	-0.09641
H	-2.98993	1.42901	-0.87793
H	-2.74425	1.33549	0.88227
O	-1.10902	1.89732	-0.29859
H	-0.41288	1.57635	0.31084
H	-1.42191	-0.55532	-1.09930
H	-0.51125	-0.46223	1.02968
O	-3.28302	-0.97566	-0.29785
H	-3.13128	-1.93209	-0.24899
S	1.78525	0.15191	-0.35725
O	0.96284	0.52408	0.89635
C	3.50062	0.26054	0.17704
H	4.14456	-0.13485	-0.61098
H	3.72271	1.31481	0.34638
H	3.61478	-0.30744	1.10257
C	1.66041	-1.64292	-0.46549
H	0.60824	-1.88228	-0.63339

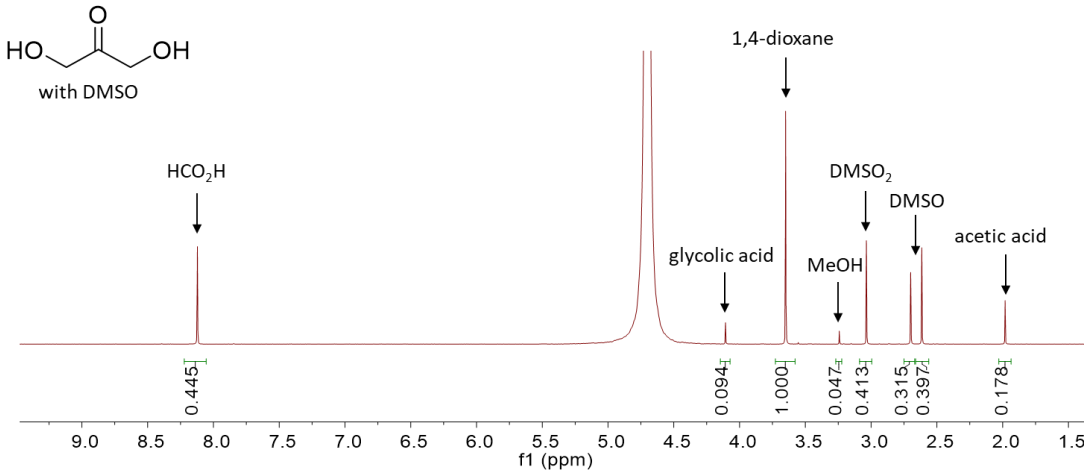
H	-0.56911	1.79155	-0.00460
7			
C	-0.32308	-0.41644	-0.06481
O	1.03197	-0.11547	-0.18743
C	-1.09991	0.89577	0.02580
O	-2.47032	0.61358	0.07973
H	-0.93128	1.50711	-0.86246
H	-0.68108	-1.00897	-0.91526
H	-2.57523	-0.09364	0.73956
H	1.50452	-0.91185	-0.47188
O	-0.65614	1.63811	1.12687
H	-0.54058	1.01032	1.86057
O	-0.63016	-1.07064	1.15026
H	-0.39991	-2.00926	1.09058
9			
C	-4.13469	-1.50230	-0.01696
C	-2.60796	-1.57946	-0.09177
C	-2.14499	-2.61503	-1.10501
C	-6.10588	-0.47622	1.16906
C	-4.61984	-0.83267	1.27072
H	-2.22224	-0.59891	-0.40989
H	-4.46489	-0.87463	-0.85291
H	-6.66533	-1.38534	0.92403
H	-4.05221	0.10853	1.39067
H	-2.40607	-3.61600	-0.73860
O	-4.46044	-1.66593	2.39975
H	-3.53693	-1.97023	2.38075
O	-4.73527	-2.78567	-0.09906
H	-4.67873	-3.04763	-1.03154
O	-2.79989	-2.34150	-2.31530
O	-0.74885	-2.48216	-1.18657
H	-0.35878	-3.32975	-1.44607
O	-2.06722	-1.92899	1.17341
H	-1.11718	-2.08292	1.04131
C	-6.62898	0.09145	2.47755
H	-6.45931	-0.63673	3.27824
H	-6.05881	1.00349	2.72353
O	-8.00497	0.38048	2.31028
H	-8.34255	0.69979	3.15869
H	-2.59043	-3.04506	-2.94867
O	-6.32656	0.41560	0.08952
H	-5.94568	1.27415	0.33371
11			
C	0.70604	-0.00811	0.46216
H	2.26480	-1.99611	-1.30327
H	1.99752	-2.08004	0.47698
8			
C	1.66147	-0.00535	0.28144
O	1.65582	-1.04021	-0.66387
C	3.12126	0.20266	0.68798
H	3.22476	1.13444	1.25774
O	3.55044	-0.89655	1.45346
H	2.74889	-1.25839	1.87067
H	1.26186	0.91878	-0.16234
H	0.72905	-1.13047	-0.96025
O	0.95346	-0.34791	1.44265
H	0.07208	-0.64500	1.12426
S	-2.22316	-0.03777	-0.59318
O	-1.05444	-0.98390	-0.26729
C	-3.40677	-0.29075	0.74072
H	-4.23134	0.41541	0.62380
H	-3.77631	-1.31317	0.65274
H	-2.90247	-0.14993	1.69960
C	-1.65705	1.60684	-0.11795
H	-0.94463	1.94268	-0.87274
H	-2.51070	2.28665	-0.08643
H	-1.17359	1.53860	0.86067
O	3.91833	0.33558	-0.44395
H	3.64454	-0.38574	-1.03791
10			
C	0.72801	-0.49534	0.20937
C	2.08450	0.18380	0.42516
C	3.05749	-0.73500	1.14272
C	-1.66161	-0.19866	-0.53352
C	-0.39643	0.51113	-0.04238
H	2.51203	0.43216	-0.55790
H	0.82216	-1.10720	-0.69579
H	-1.94703	-0.94880	0.21147
H	-0.05513	1.19577	-0.84101
H	2.72155	-0.85840	2.18318
O	-0.74426	1.23034	1.12313
H	0.09096	1.57550	1.48399
O	0.35515	-1.30753	1.31120
H	0.94734	-2.07686	1.27954
O	3.06798	-1.97839	0.49078
O	4.30752	-0.09419	1.12956
H	4.89441	-0.67719	1.65566
O	1.93749	1.36547	1.20171

C	2.15687	0.29352	0.06852
C	3.14658	-0.43430	0.99847
C	-1.72692	0.17193	-0.17705
C	-0.29974	0.62019	-0.50739
H	2.32431	-0.09415	-0.94781
H	0.57205	-1.09921	0.39031
H	-1.94196	0.44954	0.86006
H	-0.05354	0.24936	-1.52067
H	2.80315	-1.46441	1.13528
O	-0.28289	2.03253	-0.47176
H	0.64247	2.29573	-0.31611
O	0.40374	0.45527	1.76324
H	1.22145	0.38947	2.28907
O	4.43508	-0.52022	0.46343
O	3.13897	0.15604	2.28396
H	3.47001	1.06952	2.17713
O	2.32989	1.70034	0.11538
H	3.28113	1.93879	0.15242
C	-2.73924	0.84571	-1.08753
H	-2.61069	1.93177	-1.02230
H	-2.53843	0.54276	-2.12948
O	-4.03526	0.44451	-0.68028
H	-4.67546	0.93327	-1.21601
H	4.83943	0.36913	0.50268
O	-1.83717	-1.24076	-0.23065
H	-1.75491	-1.50803	-1.15993
S	5.69012	3.38983	1.04201
O	4.80207	2.12565	1.03895
C	6.32120	3.51441	-0.63804
H	6.86167	4.45740	-0.74301
H	7.00153	2.67593	-0.79214
H	5.48429	3.46181	-1.33783
C	4.52727	4.76127	0.99317
H	3.96758	4.74242	1.92917
H	5.08701	5.69540	0.91257
H	3.85368	4.63515	0.14239
14			
C	-1.38371	-0.11543	0.05464
C	-0.24808	0.71949	-0.54636
C	1.06088	0.49659	0.19216
C	-3.86452	-0.56605	0.06180
C	-2.76528	0.43510	-0.30486
H	-0.10361	0.41235	-1.59315
H	-1.30875	-1.11696	-0.38536
H	2.83139	1.66950	1.42954
C	-2.80825	0.78050	-0.71651
H	-2.98238	1.30985	0.22660
H	-2.52072	1.52760	-1.47606
O	-3.94797	0.04820	-1.12852
H	-4.68827	0.66804	-1.18909
H	3.73678	-2.51348	0.96537
O	-1.39966	-0.91929	-1.72588
H	-1.26488	-0.27340	-2.43746
S	6.60502	-2.78161	0.95117
O	5.42280	-2.47217	1.89108
C	6.02669	-2.40064	-0.71552
H	6.88023	-2.42787	-1.39600
H	5.30116	-3.16517	-0.99768
H	5.54883	-1.41835	-0.70308
C	7.72905	-1.38563	1.14034
H	8.07986	-1.39147	2.17314
H	8.57251	-1.51105	0.45858
H	7.19082	-0.45907	0.92464
12			
C	1.62670	-0.07205	0.23698
O	1.68475	-0.97657	-0.84116
C	3.06729	0.22595	0.60559
H	3.10616	0.99761	1.37819
H	3.50661	-0.69825	1.01014
O	3.77637	0.69687	-0.52045
H	3.53957	0.08945	-1.24061
H	1.11907	0.84901	-0.08999
H	0.76988	-1.06422	-1.16608
O	0.99093	-0.60964	1.35930
H	0.06187	-0.73735	1.09351
O	-1.08235	-0.86420	-0.52060
H	-1.66092	-1.63682	-0.60201
H	-1.62782	-0.11286	-0.79636
13			
C	0.64328	0.31308	-0.09161
O	0.78241	1.65871	0.26890
C	-0.83629	0.04591	-0.32793
H	-1.37957	0.24034	0.60793
O	-1.25922	0.91987	-1.33916
H	-2.22687	0.90252	-1.37343
H	1.18770	0.10873	-1.02892
H	1.74183	1.80005	0.36689
O	1.07434	-0.55291	0.92053

H	-3.79297	-0.77773	1.13376
H	-2.78752	0.58358	-1.40037
H	0.97525	0.92570	1.20161
O	-3.05467	1.64062	0.37364
H	-2.28765	2.22161	0.22711
O	-1.29693	-0.19587	1.46853
H	-0.53673	-0.77219	1.65102
O	1.29506	-0.88364	0.27336
O	2.04499	1.18806	-0.52987
H	2.84228	1.18439	0.03119
O	-0.55702	2.10583	-0.48844
H	0.25972	2.58392	-0.70865
C	-5.24320	-0.00448	-0.24055
H	-5.36132	0.95191	0.28068
H	-5.31912	0.18859	-1.32420
O	-6.20669	-0.95466	0.17701
H	-7.08147	-0.56568	0.03881
H	2.12498	-0.97589	0.77982
O	-3.65233	-1.80589	-0.59188
H	-3.82040	-1.67376	-1.53853
O	3.67210	0.02603	1.40994
H	3.74671	0.27591	2.34286
H	4.54062	-0.33345	1.17549
H	2.03087	-0.38771	1.00904
O	3.45876	0.89905	0.64669
O	-0.96223	-1.29886	-0.70327
H	-1.88370	-1.56913	-0.58101
H	4.08843	0.76548	-0.07704
H	3.99734	1.18253	1.40019

Selected ^{1}H NMR and Gas Chromatography (GC) spectra for the experiments in Table 2. The data are shown from one experiment, there are small differences with the average data.

a)



b)

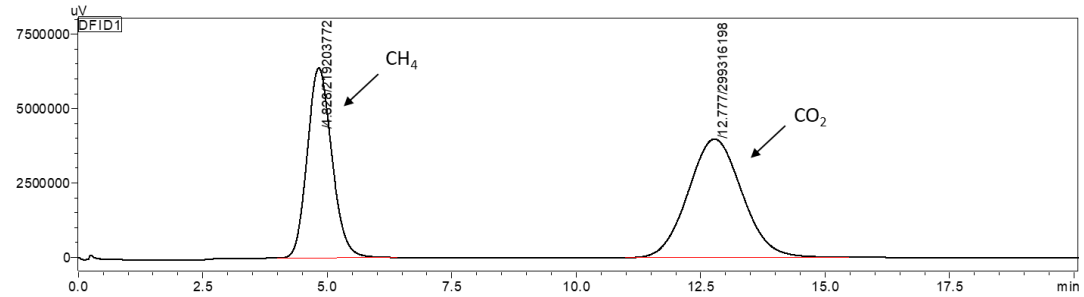
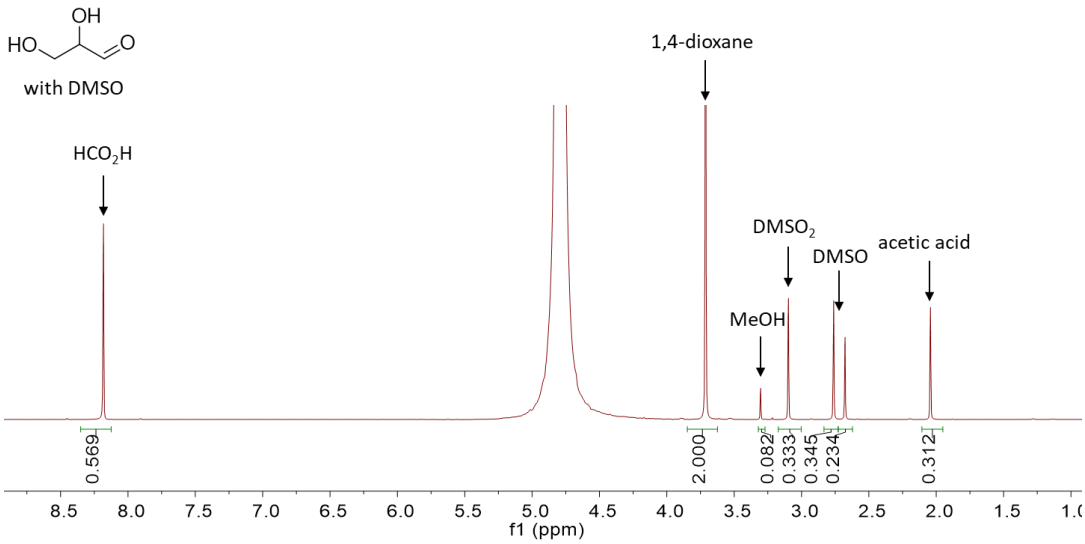


Fig. S10. ^{1}H NMR (a) and GC (b) spectra of 1,3-dioxyacetone with DMSO sample (Table 2, entry 1).

a)



b)

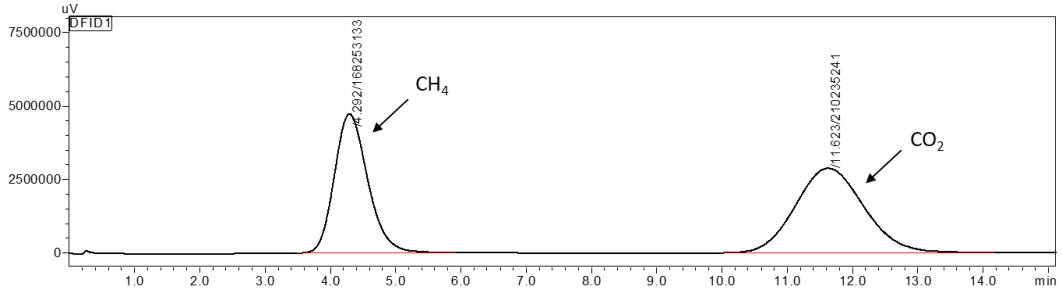
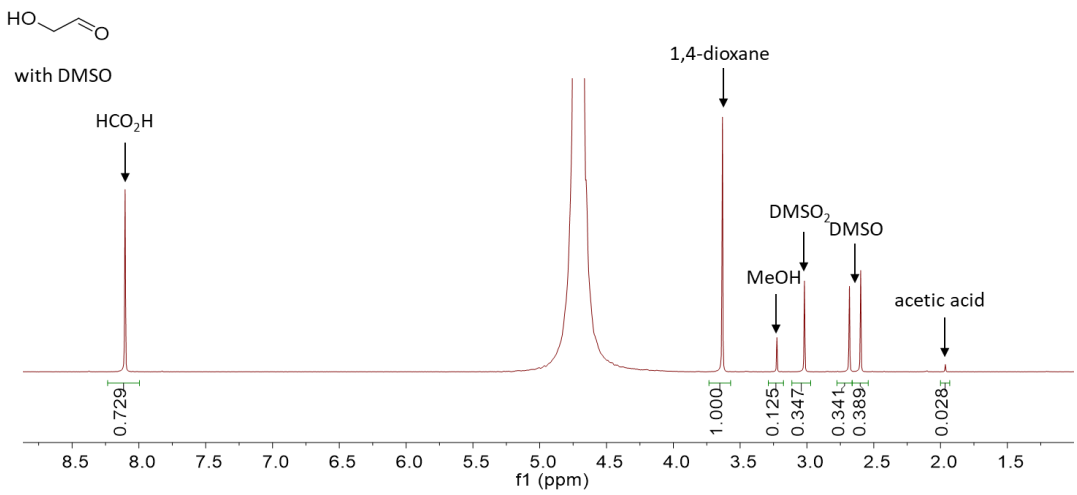


Fig. S11. ^{1}H NMR (a) and GC (b) spectra of glyceraldehyde with DMSO sample (Table 2, entry 2).

a)



b)

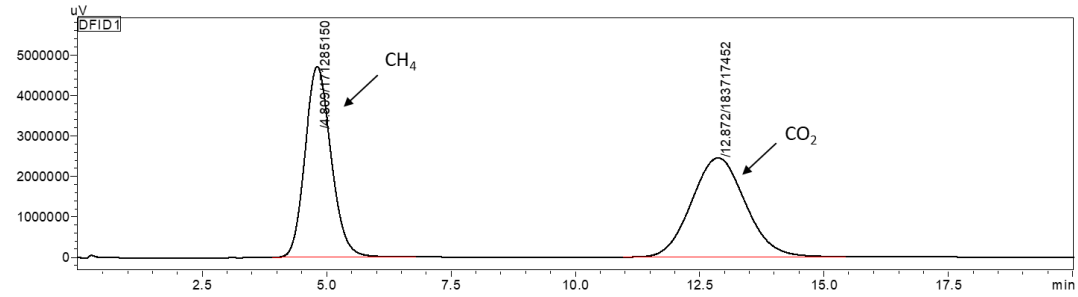
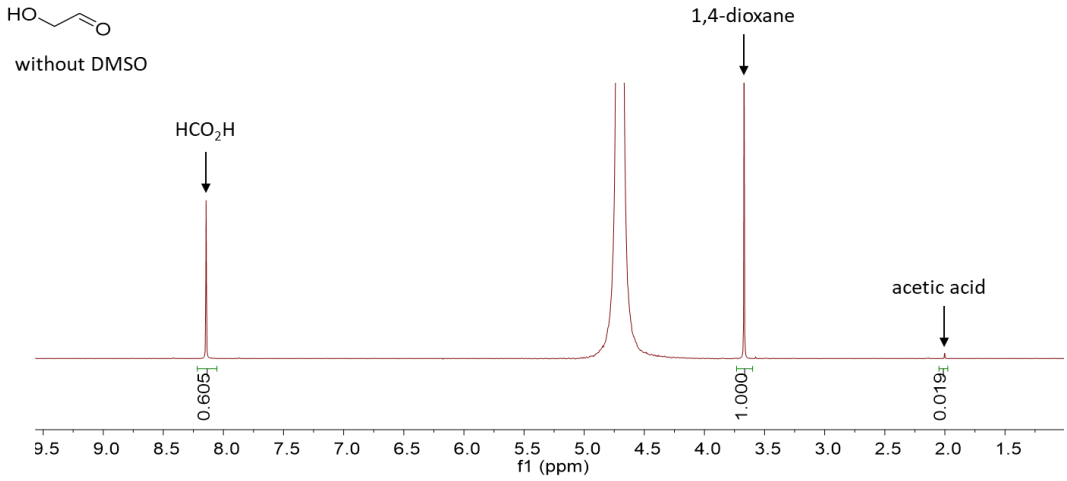


Fig. S12. ^{1}H NMR (a) and GC (b) spectra of glycolaldehyde with DMSO sample (Table 2, entry 3).

a)



b)

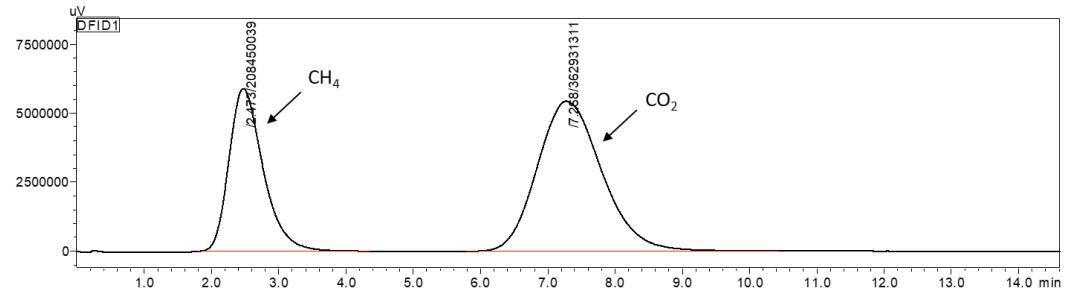
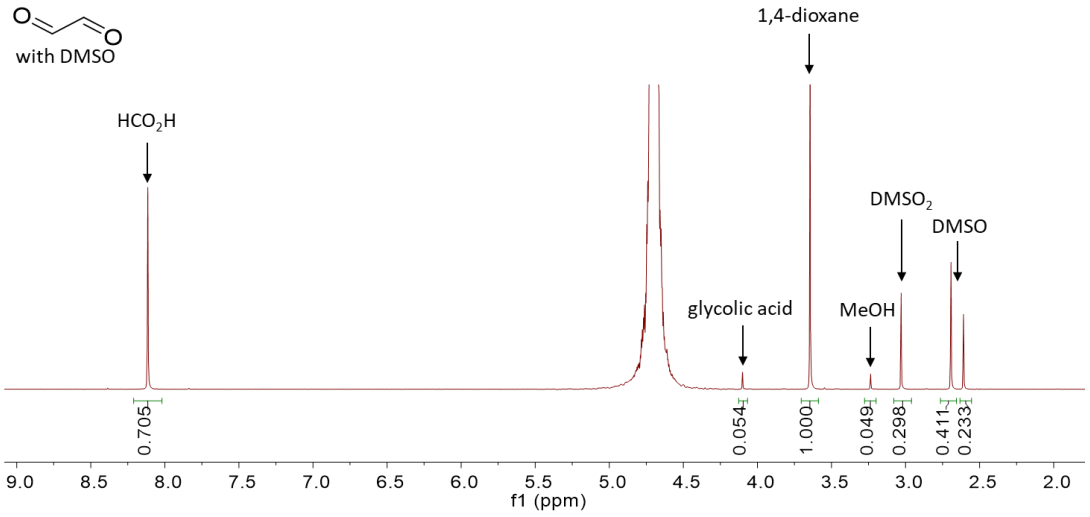


Fig. S13. ^{1}H NMR (a) and GC (b) spectra of glycolaldehyde without DMSO sample (Table 2, entry 4).

a)



b)

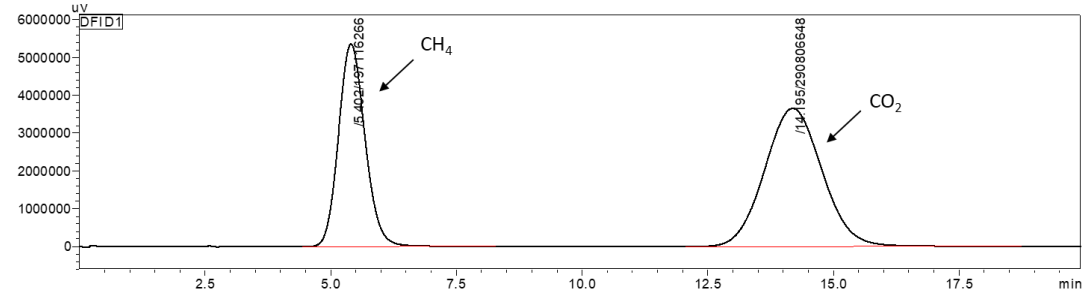
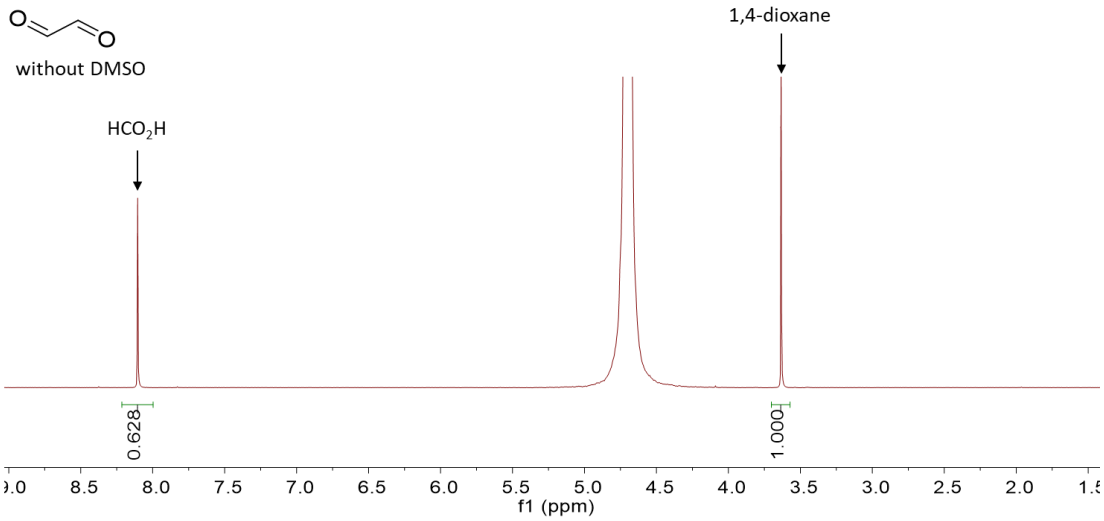


Fig. S14. ^{1}H NMR (a) and GC (b) spectra of glyoxal with DMSO sample (Table 2, entry 5).

a)



b)

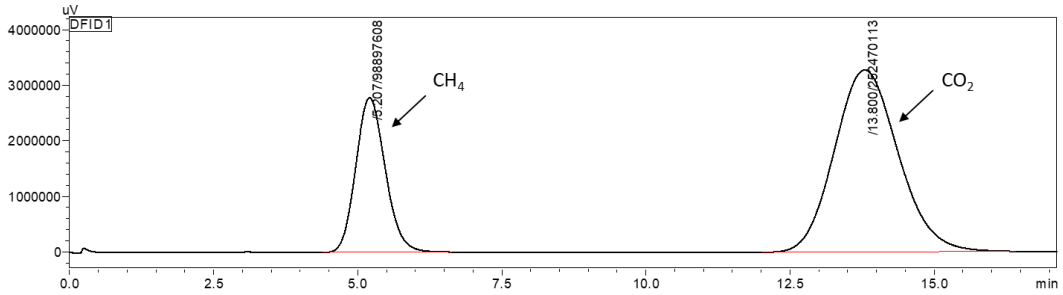
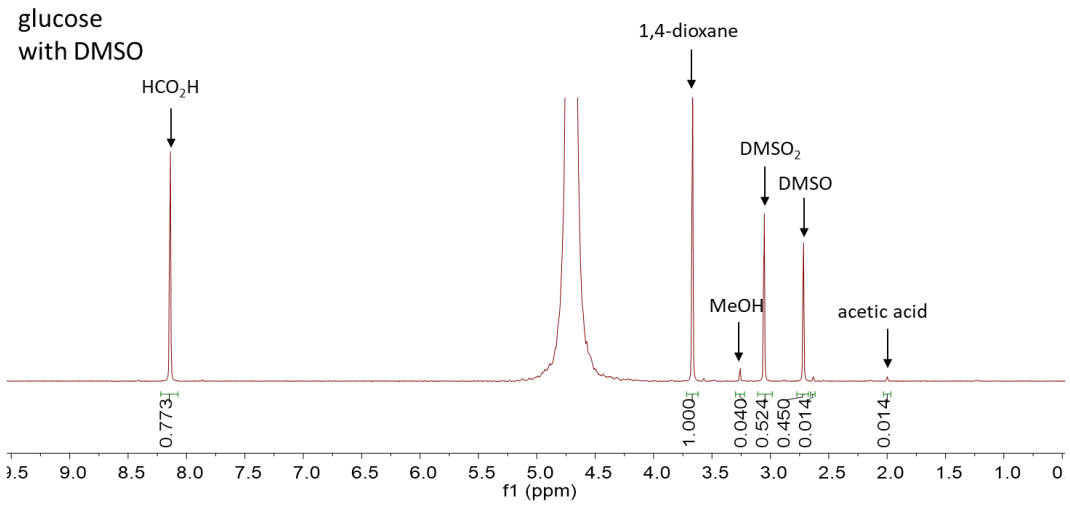


Fig. S15. ^{1}H NMR (a) and GC (b) spectra of glyoxal without DMSO sample (Table 2, entry 6).

a)



b)

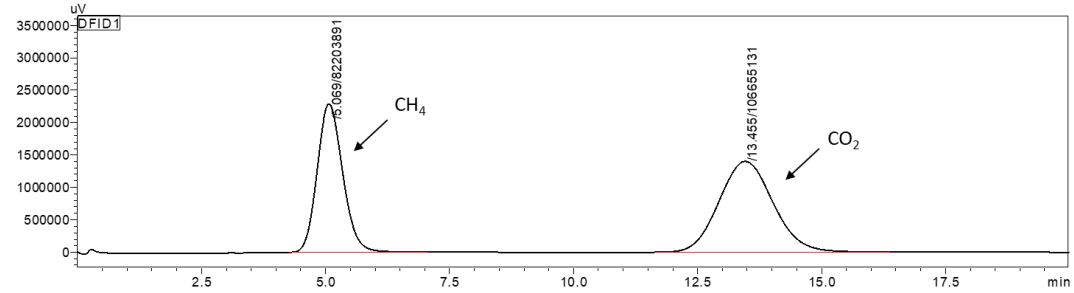
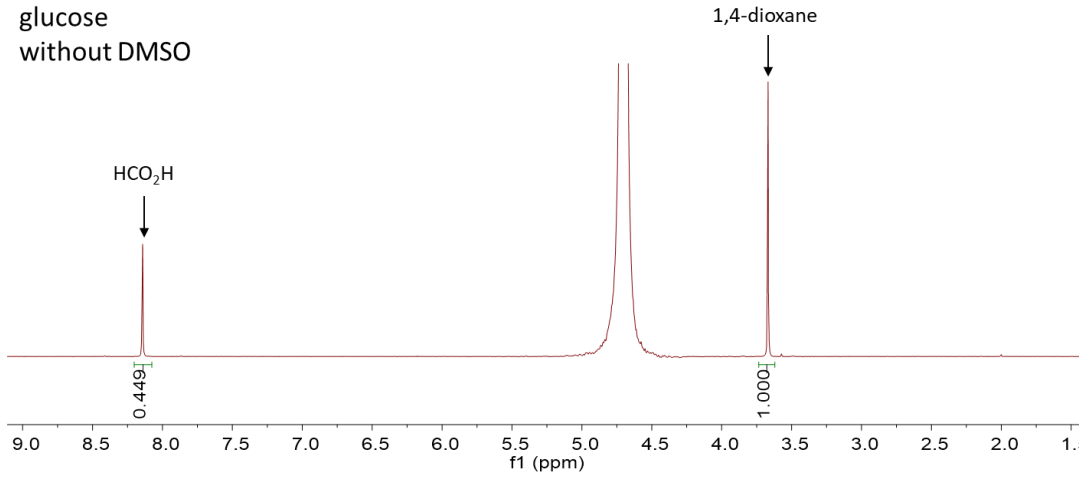


Fig. S16. ^{1}H NMR (a) and GC (b) spectra of glucose with DMSO sample (Table 2, entry 7).

a)



b)

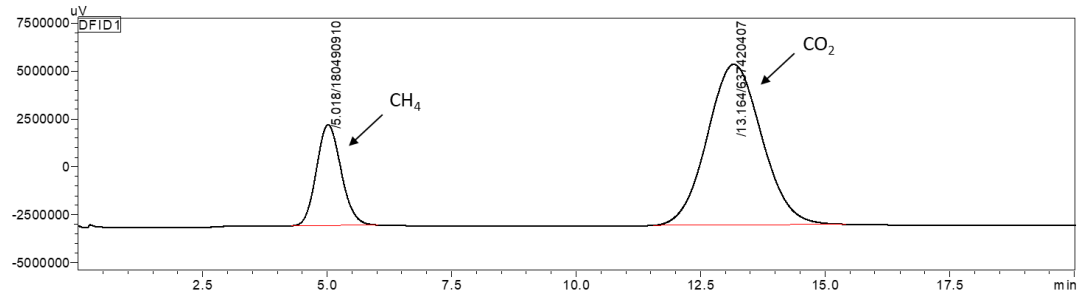
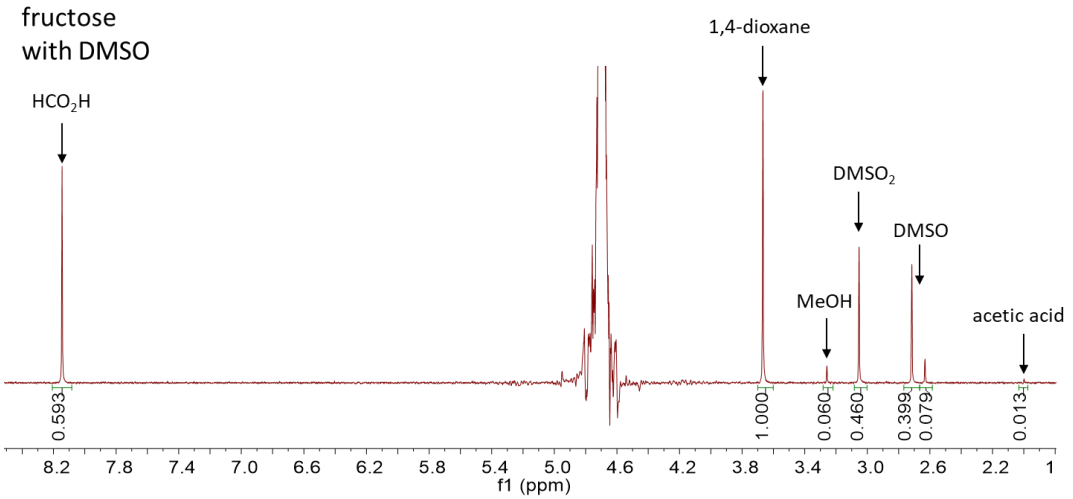


Fig. S17. ^{1}H NMR (a) and GC (b) spectra of glucose without DMSO sample (Table 2, entry 8).

a)



b)

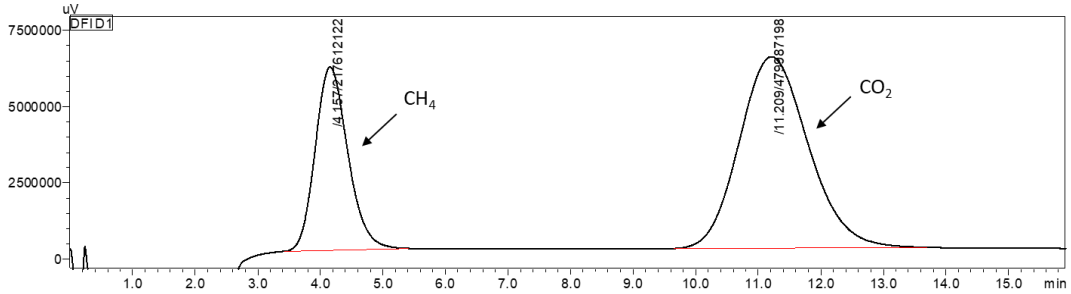
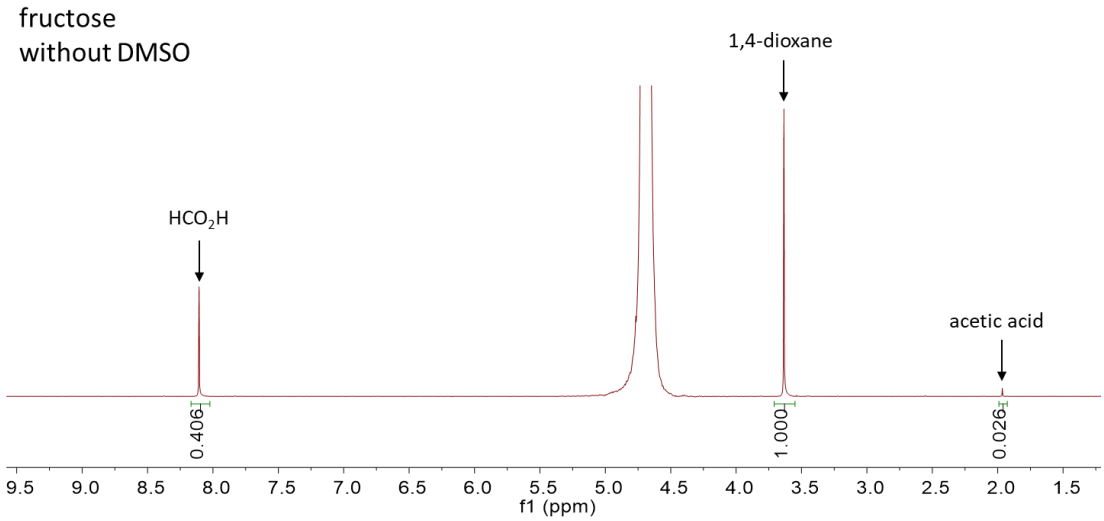


Fig. S18. ^{1}H NMR (a) and GC (b) spectra of fructose with DMSO sample (Table 2, entry 9).

a)



b)

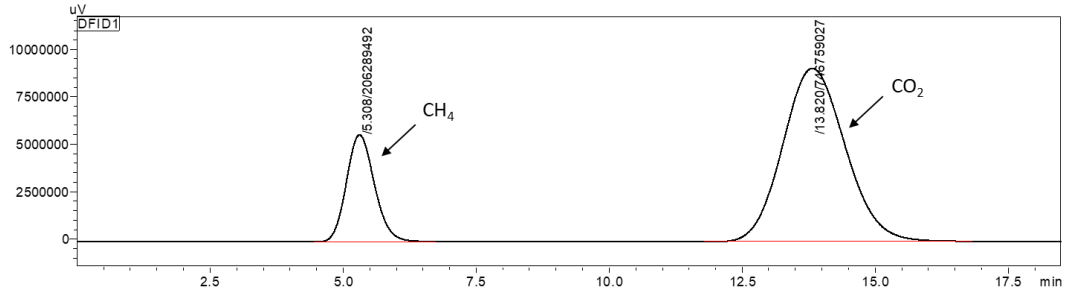


Fig. S19. ^{1}H NMR (a) and GC (b) spectra of fructose without DMSO sample (Table 2, entry 10).

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