Supporting Information

A Catalytic Approach for Dehydrogenative Upgradation of Crude Glycerol to Lactate and Hydrogen Generation

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1. General information

The experiments were conducted within an atmosphere of purified nitrogen, either within an N_2-filled glovebox or employing the standard Schlenk technique unless explicitly mentioned otherwise. All chemicals procured from commercial suppliers were of analytical grade and were utilized without further purification. Crude glycerol was collected from industrial sources, and the percentage of glycerol and methanol content was analyzed by NMR spectroscopy. Soyabean oil purchased from local supermarket. Solvents underwent drying procedures as outlined in the literature. Nitrogen gas degassing was performed to eliminate dissolved oxygen in the solvent. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on 400 MHz FT-NMR Bruker AVANCE NEO Ascend 400 spectrometer. The chemical shift values of all the spectra were reported with reference to the residual proton of the deuterated solvent (4.79 ppm D_2O and 7.26 ppm $CDCl_3$). Mass spectra were recorded on Xevo G2-XS QT of Quadrupole Time of Flight Mass spectrometer waters. The evolved gas was analyzed on TRACE 1610 gas chromatography (TCD, CARBOXEN™ 1000 column, Ar carrier gas flow, Thermo Scientific). Complex **1** was synthesized by following the literature reports.[1]

Equations used for the Calculation:

From ^1H NMR (fig. S21), 0.073 mL crude glycerol contains 0.3-0.32 mmol of glycerol

So, 0.235 mL of crude glycerol will contain ~1 mmol of glycerol

For Table S1:

% of lactate formation from glycerol

$$= \frac{mmol\ of\ lactate\ determined\ from\ 1H\ NMR}{mmol\ of\ glycerol\ feed\ initially} \times 100 \qquad -(S1)$$

% of glycolate formation from glycerol

$$= \frac{mmol\ of\ glycolate\ determined\ from\ 1H\ NMR}{mmol\ of\ glycerol\ feed\ initially} \times 100 \qquad -(S2)$$

For Table S2:

% of lactate formation from mixture of ethylene glycol and methanol

$$= \frac{mmol\ of\ lactate\ determined\ from\ 1H\ NMR}{mmol\ of\ ethylene\ glycol\ feed\ initially} \times 100 \qquad -(S3)$$

% of glycolate formation from mixture of ethylene glycol and methanol

$$= \frac{mmol\ of\ glycolate\ determined\ from\ 1H\ NMR}{mmol\ of\ ethylene\ glycol\ feed\ initially} \times 100 \qquad -(S4)$$

For Table S3:

% of lactate formation from mixture of glycerol, ethylene glycol, and methanol

$$= \frac{mmol\ of\ lactate\ determined\ from\ 1H\ NMR}{mmol\ of\ glycerol\ feed\ initially\ +\ mmol\ of\ ethylene\ glycol\ feed}\ X\ 100 \qquad -(S5)$$

% of glycolate formation from mixture of glycerol, ethylene glycol and methanol

$$= \frac{mmol\ of\ glycolate\ determined\ from\ 1H\ NMR}{mmol\ of\ ethylene\ glycol\ feed\ initially} \times 100 \qquad -(S6)$$

% of formate formation from mixture of glycerol, ethylene glycol and methanol

$$= \frac{mmol\ of\ formate\ determined\ from\ 1H\ NMR}{mmol\ of\ methanol\ feed\ initially} \times 100 \qquad -(S7)$$

% Carbon balance

$$= \frac{\begin{array}{c}3 \times mmol\ of\ unreacted\ glycerol + 2 \times mmol\ of\ unreacted\ ethylene\ glycol + mmol\ of\ unreacted\ methanol \\ +3 \times mmol\ of\ lactate\ formatiom + 2 \times mmol\ of\ glycolate\ formation + mmol\ of\ formate\ formation\end{array}}{3 \times mmol\ of\ glycerol\ feed\ initially\ +\ 2 \times mmol\ of\ ethylene\ glycol\ feed\ initially\ +\ mmol\ of\ methanol\ feed\ initially}$$
$$\times 100 \qquad -(S8)$$

For soyabean oil:

After hydrolysis, 891.5 mg of soyabean oil produces ~1.17 mmol of glycerol as determined from ^{1}H NMR (fig. S52)

% of lactate formation from soyabean oil

$$= \frac{mmol\ of\ lactate\ determined\ from\ 1H\ NMR}{mmol\ of\ glycerol\ as\ determined\ from\ hydrolysis\ of\ soyabean\ oil} \times 100 \qquad -(S9)$$

[**]In Tables S2 and S3, the yield of formate was calculated considering the methanol initially fed, although a minimal formate can also be contributed from glycerol and ethylene glycol by C-C bond cleavage.

2. General procedure for the conversion of glycerol to lactate catalyzed by 1

A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirrer bar, **1** (1 mol%), KOH (in mmol), ^{t}BuOH (1 mL), and glycerol (1 mmol) were added under a nitrogen atmosphere. The tube was closed properly, and the mixture was placed in a preheated oil bath at 120 °C for 24 hours. Upon completion of the mentioned period, the reaction mixture was cooled to room temperature, and the purity of the gas was analyzed by GC-TCD analysis by taking the sample from the headspace of the reaction tube. The side arm was connected to a gas measuring system (inverted burette containing KOH solution) to collect the evolved hydrogen gas. The solvent was evaporated under vacuum, and the residue was redissolved in 3-4 mL of water. The reaction yield was determined following equations S1 and S2 by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D_2O.
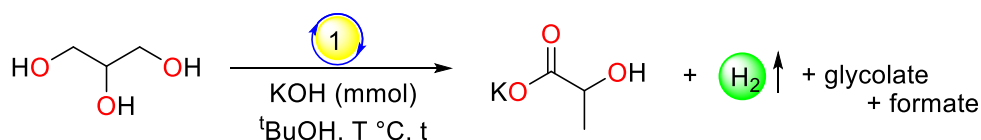
Table S1. Dehydrogenation of glycerol catalyzed by **1** to produce lactate[a]

Entry	KOH in mmol	Temp (°C) /Time (h)	Glycerol Conv%	Lactate yield%[b]	Glycolate yield%[b]	Formate mmol (yield%)[c]	H$_2$ in mL (mmol)	CB
1[§]	1.5	120/ 24	76	73	3	0.01 (1)	16 (0.71)	99
2	1.5	120/ 48	100	73	5	0.02 (2)	28 (1.24)	77
3	1.5	100/48	63	61	2	0	14 (0.62)	99
4[§]	1.5	140/24	87	63	6	0.01 (1)	30 (1.33)	80
5[§]	1.0	120/ 24	62	53	3	0.02 (2)	14 (0.62)	94
6[§]	0.5	120/ 24	46	42	2	0	11 (0.49)	97
7[d]	1.5	120/ 24	69	69	0	0	14 (0.62)	-
8[e]	1.5	120/ 24	4	-	-	-	-	-

[a] glycerol (1 mmol), KOH (in mmol), **1** (1 mol%), ^{t}BuOH (1 mL), 120 °C, 24 h, [b] % yield of lactate was determined by using equation S1. [c] %yield of glycolate (C2) and formate (C1) was calculated considering 1 equiv. of each will be produced from 1 equiv. of glycerol. [d] Crude glycerol was used (0.235 mL). [e] in the absence of catalyst **1**. [§]Reactions are repeated for 2 times, and an average of results is reported with an error limit of 5%. CB (carbon balance) was determined using the equation S8.

3. General procedure for synthesis of lactate from ethylene glycol and methanol mixture catalyzed by 1

A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar was charged with **1** (1 mol%), KOH (in mmol), MeOH (in mmol), ^{t}BuOH (1 mL), and ethylene glycol (1 mmol) under nitrogen atmosphere. The tube was closed properly, and the mixture was placed in a preheated oil bath at 120 °C for the mentioned period (in hours). Upon completion of the reaction, the mixture was cooled to room temperature, and the gas was analyzed by GC-TCD by taking the sample from the headspace of the reaction tube. The side arm was connected to a gas measuring system (inverted burette containing KOH solution) to collect the evolved hydrogen gas. The reaction mixture was dissolved in 3-4 mL of water. The yield and conversion of the reaction were determined following equations S3 and S4 by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D$_2$O.
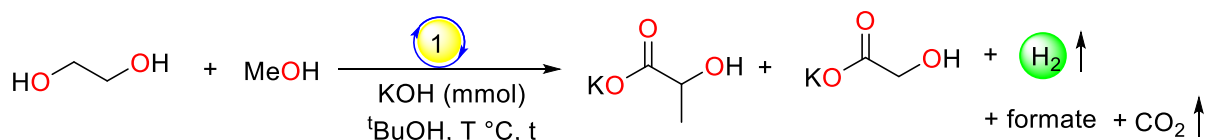
Table S2. Dehydrogenative coupling of ethylene glycol and methanol to lactate catalyzed by **1**[a]

Entry	KOH in mmol	t (h)	EG conv%	MeOH conv%	Lactate yield%[b]	glycolate yield%[b]	Formate yield%	H$_2$ in mL (mmol)	CB
1[§]	2.5	24	77	13	52	24	2.6	38 (1.69)	99
2	2.5	48	98	18	53	40	3	59 (2.62)	95
3[§]	3.5	48	98	19	67	31	5	55 (2.44)	99
4[c]	3.5	48	1	-	-	-	-	-	-

[a] Ethylene glycol (1 mmol), MeOH (5 mmol), **1** (1 mol%), ^{t}BuOH (1 mL), KOH (in mmol), 120 °C, 24 h, [b] % yield of lactate and glycolate were determined following the equation S3 and S4. [c] in the absence of catalyst **1**. [§]Reactions are repeated 2 times, and an average of results is reported with an error limit of 6%. CB (carbon balance was determined by using equation S8)

4. General procedure for the synthesis of lactate from a mixture of glycerol, ethylene glycol, and methanol catalyzed by 1

A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, **1** (1 mol%), Base (in mmol), MeOH (in mmol), solvent (1 mL), ethylene glycol (1 mmol), and glycerol (1 mmol) were added under nitrogen atmosphere. The tube was closed, and the mixture was placed in a preheated oil bath at 120 °C for the mentioned period (in hours). Upon completion of the reaction, the mixture was cooled to room temperature, and the gas was analyzed by GC-TCD by taking the sample from the headspace of the reaction tube and the gas volume was measured by inverted burette technique KOH solution. The reaction mixture was dissolved in 3-4 mL of water. The yield and conversion of the reaction were determined following equations S5, S6, and S7 by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D$_2$O.

Table S3. Lactate formation from a mixture of glycerol, ethylene glycol, and methanol catalyzed by **1**[a]
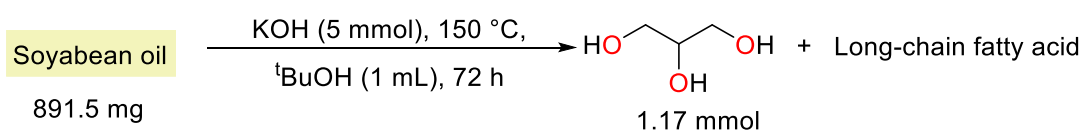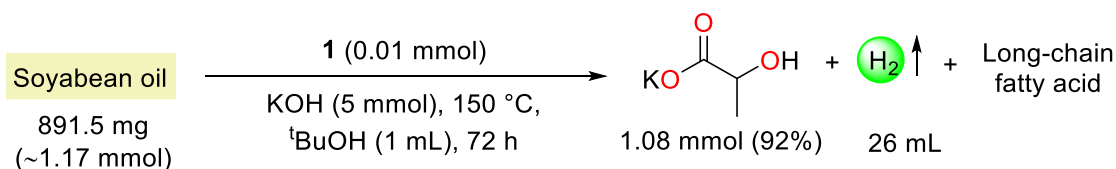
Entry	KOH in mmol	t (h)	Gly conv%	EG conv%	MeOH conv%	Lactate yield % (mmol)[b]	Glycolate yield%[b]	Formate yield%[b]	H$_2$ in mL (mmol)	CB
1[§]	2.5	24	47	51	9	43 (0.86)	10	1	36 (1.6)	99
2[§]	3.5	24	54	69	16	52 (1.04)	18	4	54 (2.4)	99

3	4.5	24	55	71	14	51 (1.02)	24	3	53 (2.35)	99
4	3.5	48	60	85	14	60 (1.2)	25	2	56 (2.49)	>99
5§	3.5	72	75	91	17	72 (1.44)	22	3	65 (2.89)	>99
6[c, §]	-	72	74	84	37	70 (1.4)	18	9	87 (3.87)	93
7[d]	-	72	26	63	27	31 (0.62)	25	4	58 (2.58)	92
8[e]	3.5	72	68	93	18	69 (1.38)	23	2	63 (2.8)	99
9[f]	3.5	72	-	-	17	30 (0.6)	39	1	40 (1.78)	-
10[g]	3.5	72	83	100	28	78 (1.56)	22	-	86 (3.82)	92
11[h, §]	3.5	72	76	95	53	62 (1.24)	43	14	56 (2.49)	>99
12i	3.5	72	-	-	-	-	-	-	2 (0.09)	-
13[j]	3.5	72	68	91	20	70 (1.4)	18	3	64 (2.85)	99
14[k]	3.5	72	40	45	10	36 (0.72)	10	1	38 (1.69)	98
15[l]	3.5	72	28	73	11	25 (0.5)	15	4	70 (3.11)	92
16[m, §]	3.5	72	100	100	-	80 (1.60)	13	-	73 (3.25)	-
17[n]	35	72	94	96		53 (1.06)	10	-	540 (24.01)	-
18[o]	105	120	92	98		61 (36.56)	22		1680 (74.67)	-

[a] glycerol (1 mmol), ethylene glycol (1 mmol), MeOH (5 mmol), **1** (1 mol%), KOH (in mmol), ^{t}BuOH (1 mL), 120 °C, 24 h. [b] lactate, glycolate, and formate yield were calculated from ^{1}H NMR using 2,6-lutidine as an internal standard following equations S5, S6, and S7. [c] NaOH (3.5 mmol) as a base, [d] CsOH. H_2O (3.5 mmol) as a base. [e] ^{t}AmOH was used as solvent, [f] dioxane was used as solvent due to solvent interference conversion of glycerol, and ethylene glycol was not mentioned. [g] at 140 °C, [h] methanol 1 mmol. [i] in the absence of catalyst **1**, [j] with 0.5 mol% of catalyst **1** loading, [k] 0.1 mol% of catalyst **1** loading, [l] neat reaction condition, [m], 0.235 mL of crude glycerol was used without any additional methanol, and the reaction solvent was reduced before water was added. [n] scale up the reaction with crude glycerol (2.35 mL), EG (10 mmol), **1** (0.5 mol%). [o] Scale up the reaction with crude glycerol (7 mL, 30 mmol), EG (30 mmol), **1** (0.5 mol%), and the reaction solvent was reduced before water was added. §Reactions are repeated 2 times, and an average of results is reported with an error limit of 6%. CB (carbon balance was determined by using equation S8)

5. Hydrolysis of soyabean oil (triglycerides) to glycerol

A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, KOH (5 mmol), ^{t}BuOH (1 mL), and soyabean oil (891.5 mg) were added. The tube was closed, and the mixture was placed in a preheated oil bath at 150 °C for 72 hours. Upon completion of the reaction, the mixture was cooled to room temperature, and the reaction mixture was dissolved in 3-4 mL of water. The glycerol yield was determined by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D_2O and also analyzed by mass spectrometry (Figure S55, S56).

Soyabean oil
891.5 mg

KOH (5 mmol), 150 °C,
^{t}BuOH (1 mL), 72 h

HO—CH₂—CH(OH)—CH₂—OH + Long-chain fatty acid

1.17 mmol

6. Lactate synthesis from soyabean oil in the presence of catalyst 1

A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, **1** (0.01 mmol), KOH (5 mmol), ^{t}BuOH (1 mL), and soyabean oil (891.5 mg) were added under nitrogen atmosphere. The tube was closed, and the mixture was placed in a preheated oil bath at 150 °C for 72 hours. Upon completion of the reaction, the mixture was cooled to room temperature, and the gas volume was measured by the inverted burette technique KOH solution. The reaction mixture was dissolved in 3-4 mL of water. The yield and conversion of the reaction were determined by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D_2O following equation S9, and the reaction mixture was also subjected to mass analysis (Figure S57, S58).

Soyabean oil
891.5 mg
(~1.17 mmol)

1 (0.01 mmol)

KOH (5 mmol), 150 °C,
^{t}BuOH (1 mL), 72 h

KO—C(=O)—CH(CH₃)—OH + H₂↑ + Long-chain fatty acid

1.08 mmol (92%)   26 mL

7. Comparing the rates of ethylene glycol and methanol dehydrogenation catalyzed by 1

KOH (3.5 equivalent w.r.t substrate), catalyst **1** (1 mol%), and degassed ^{t}BuOH (2 mL) were added sequentially to a 100 mL sealed tube with a side arm charged with a magnetic bar in an N_2-filled glove box. The mixture was stirred for 5 minutes, followed by adding 2 mmol of the substrate (ethylene glycol or methanol). The tube was sealed properly and placed in a preheated oil bath at 120 °C. After each 10-minute interval, the gas was measured through an inverted burette system containing an aqueous KOH solution (To reduce solvent vapor interference, the tube was cooled for a while before each gas collection). The rate of ethylene glycol and methanol dehydrogenation was compared by the amount of gas that evolved during 1 h of reaction. Upon completion of time, the solvent was reduced, and the residue was dissolved in 3-4 mL of water. The yield of glycolate and formate was calculated using 2,6-lutidine (1 mmol) as an internal standard in D_2O.
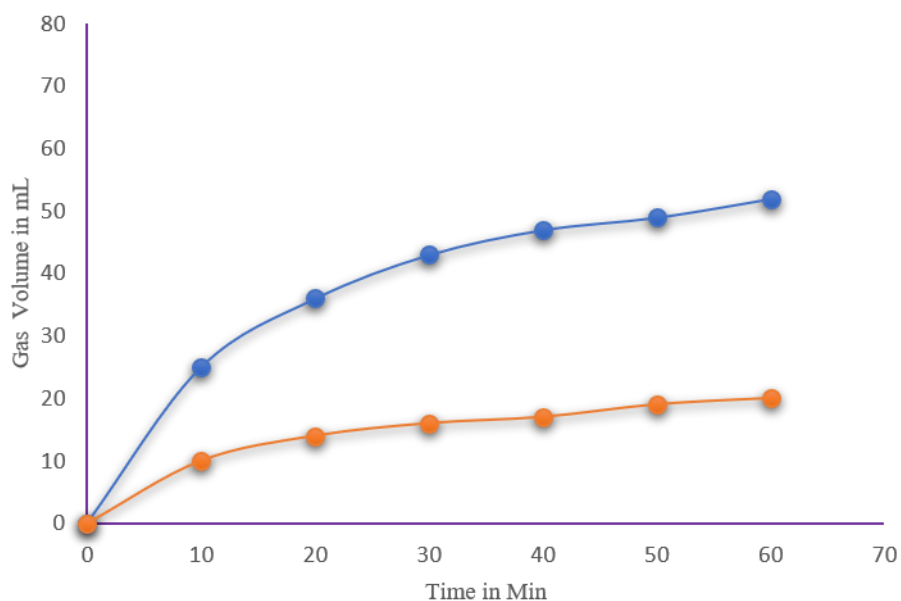
Figure S1. Time course plot for catalyst **1** catalyzed hydrogen evolution during dehydrogenation of ethylene glycol (blue) and methanol (orange).
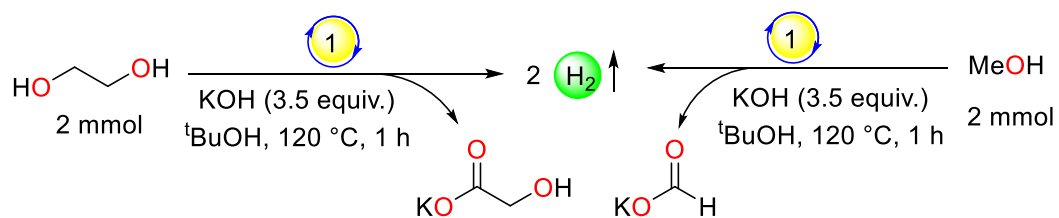
Table S4. Gas volume measured during dehydrogenation of ethylene glycol and methanol

Time in min	From EG	From methanol
10	25	10
20	36	14
30	43	16
40	47	17
50	49	19
60	52	20
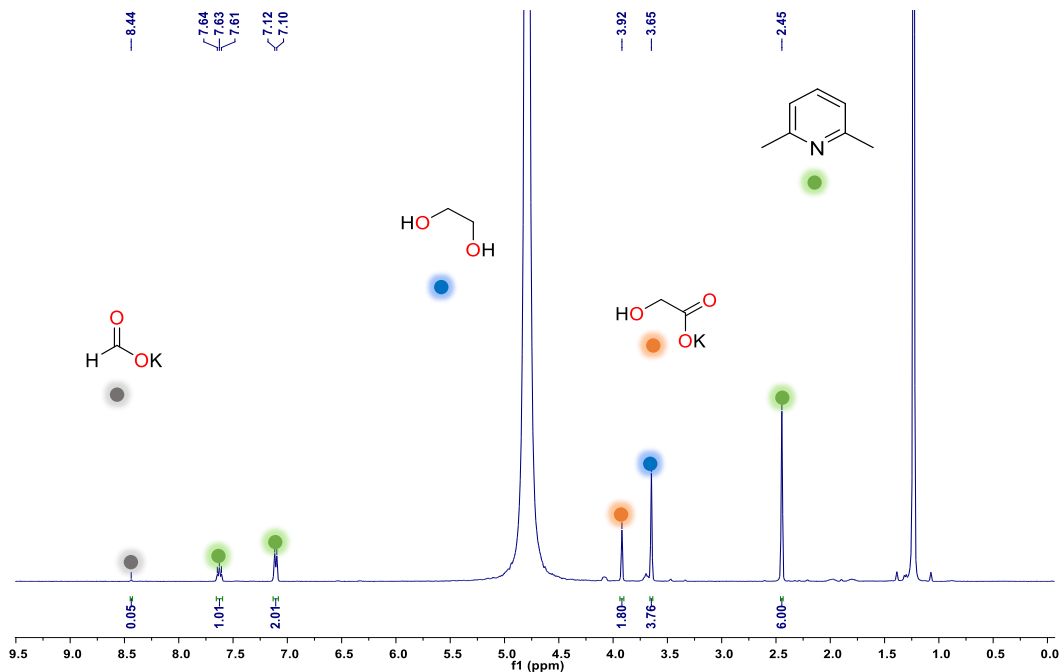
Figure S2. ^{1}H NMR spectrum of ethylene glycol dehydrogenation catalyzed by **1** after 1 h of reaction in D$_2$O.
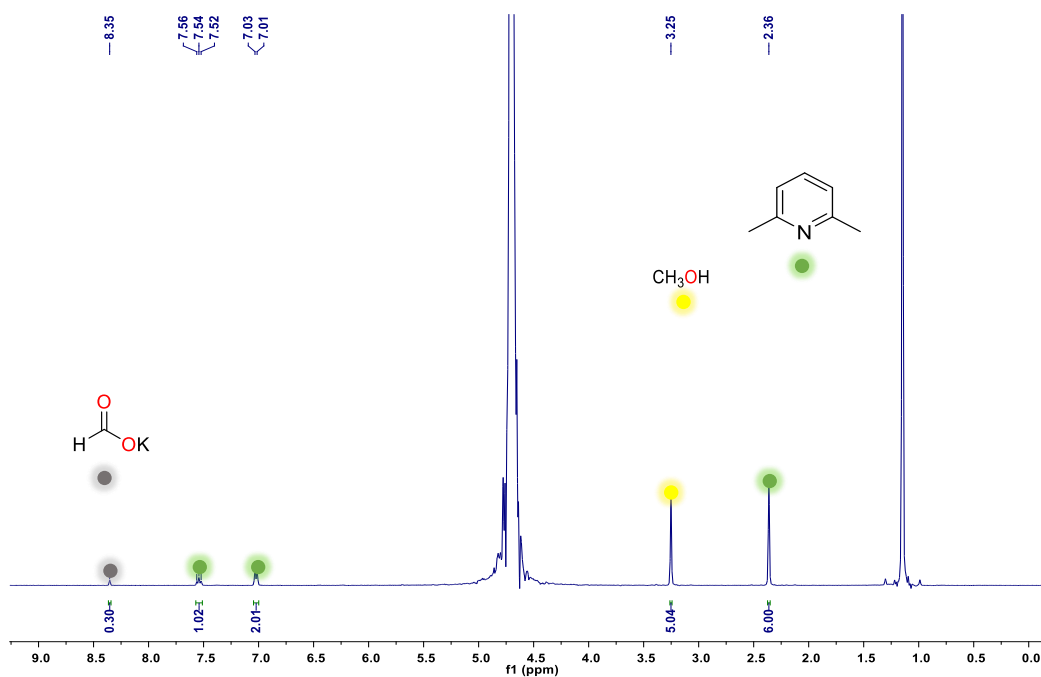
Figure S3. ^{1}H NMR spectrum of methanol dehydrogenation catalyzed by **1** after 1 h of reaction in D$_2$O.

8. GC-TCD spectra of evolved gas
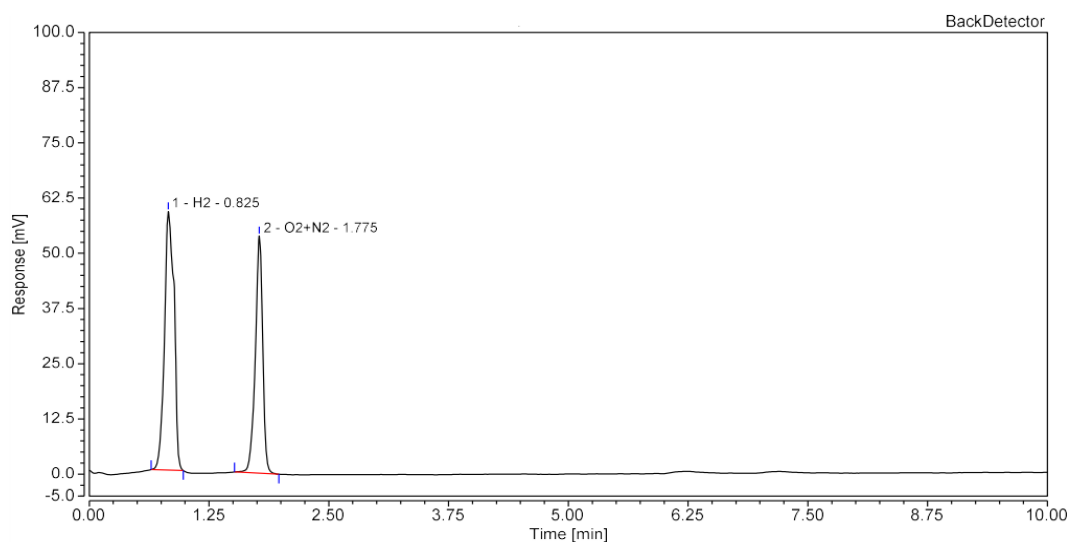
Figure S4. GC-TCD analysis of hydrogen gas evolved from the dehydrogenation of glycerol (Table S1, entry 1). A large $N_2 + O_2$ peak was observed due to the presence of N_2 in a 100 mL of reaction tube.
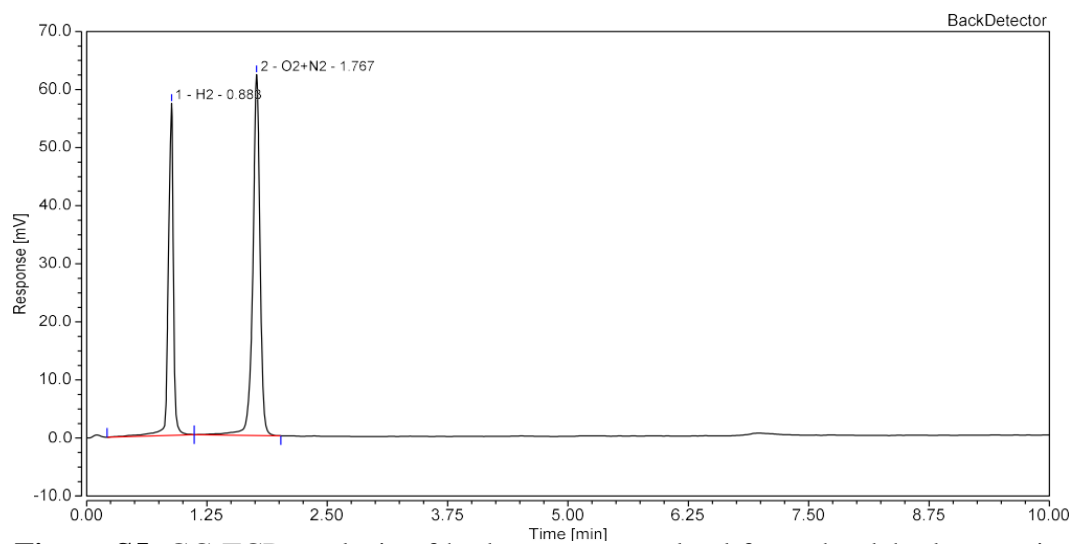
Figure S5. GC-TCD analysis of hydrogen gas evolved from the dehydrogenation of crude glycerol (Table S1, entry 7).
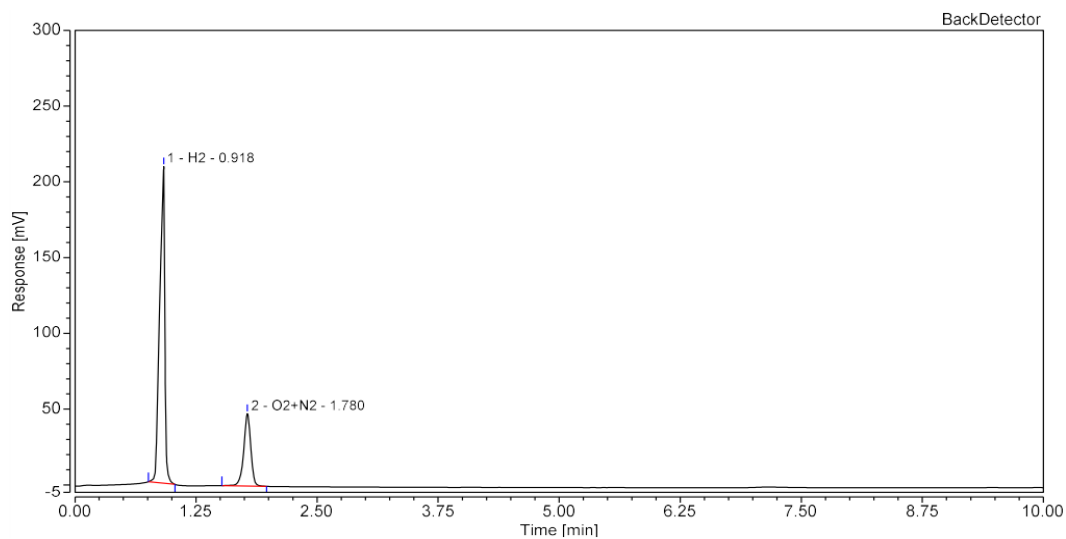
Figure S6. GC-TCD analysis of hydrogen gas evolved from dehydrogenation of the mixture of glycerol, ethylene glycol, and methanol (Table S3, entry 5).
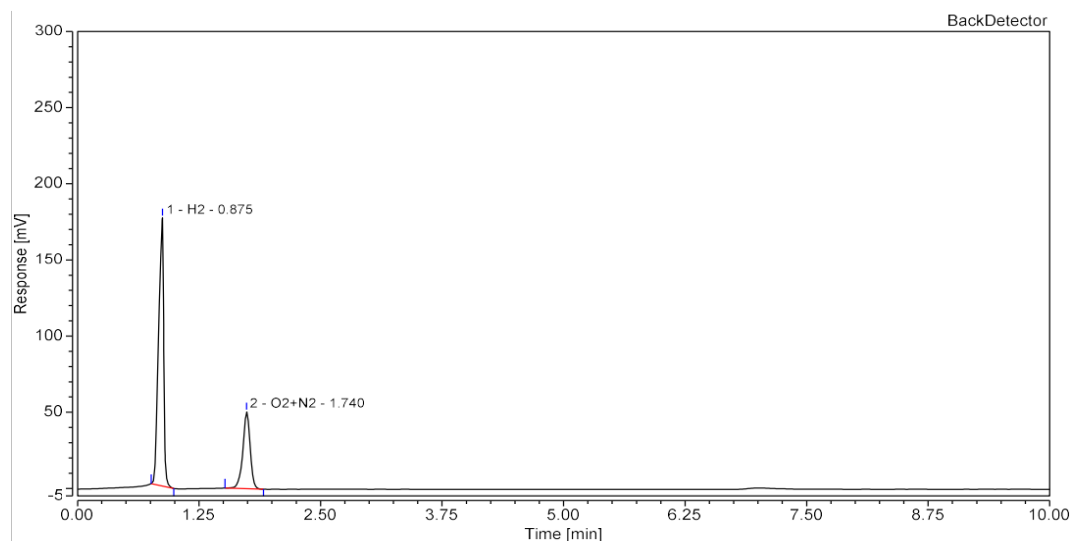
Figure S7. GC-TCD analysis of hydrogen gas evolved from dehydrogenation of the mixture of crude glycerol, and ethylene glycol (Table S3, entry 13)

9. Control mechanistic experiments

a. Mercury experiment

100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, **1** (1 mol%), KOH (3.5 mmol), MeOH (5 mmol), ^{t}BuOH (1 mL), ethylene glycol (1 mmol), and glycerol (1 mmol) were added under nitrogen atmosphere. The Hg (100 mol%) was added into the tube, and the tube was properly closed. The mixture was placed in a preheated oil bath at 120 $^\circ$C for 72 hours. Upon completion of the reaction, the mixture was cooled to room temperature, and gas was measured. Then, the solvent was evaporated under the vacuum. The residue was redissolved in 3-4 mL of water, and the yield of the reaction was determined by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D_2O.
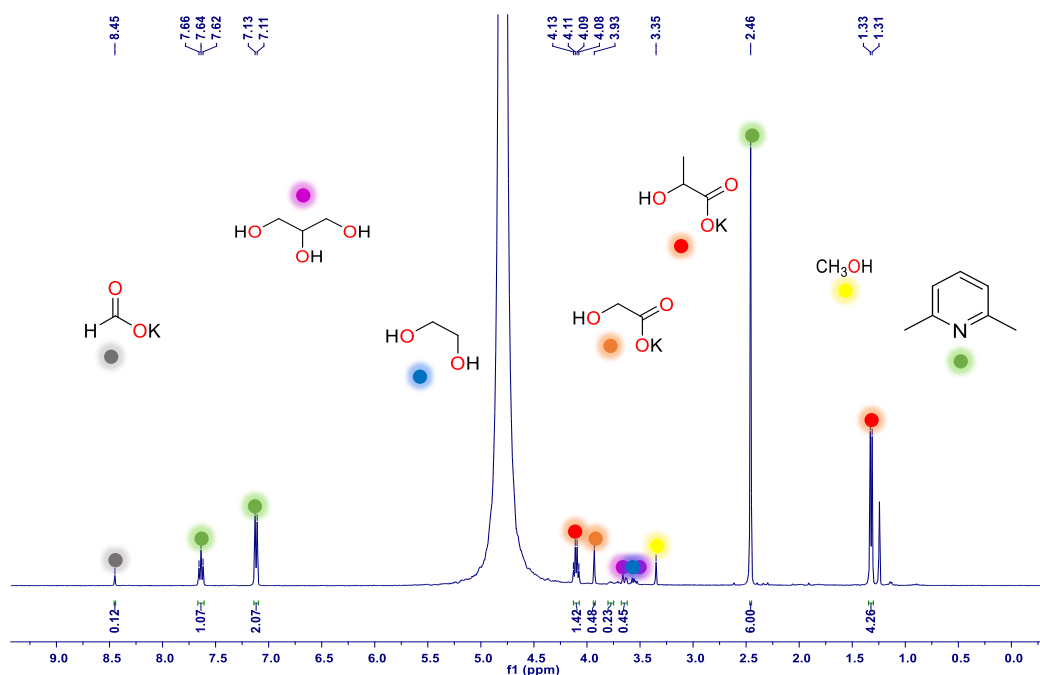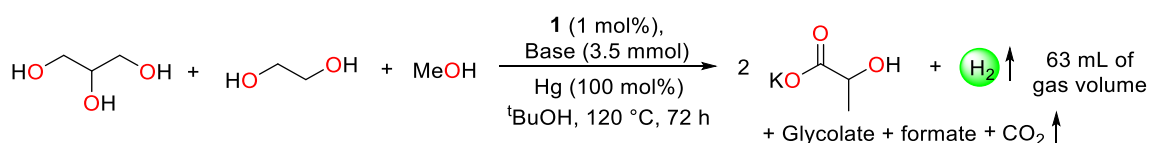
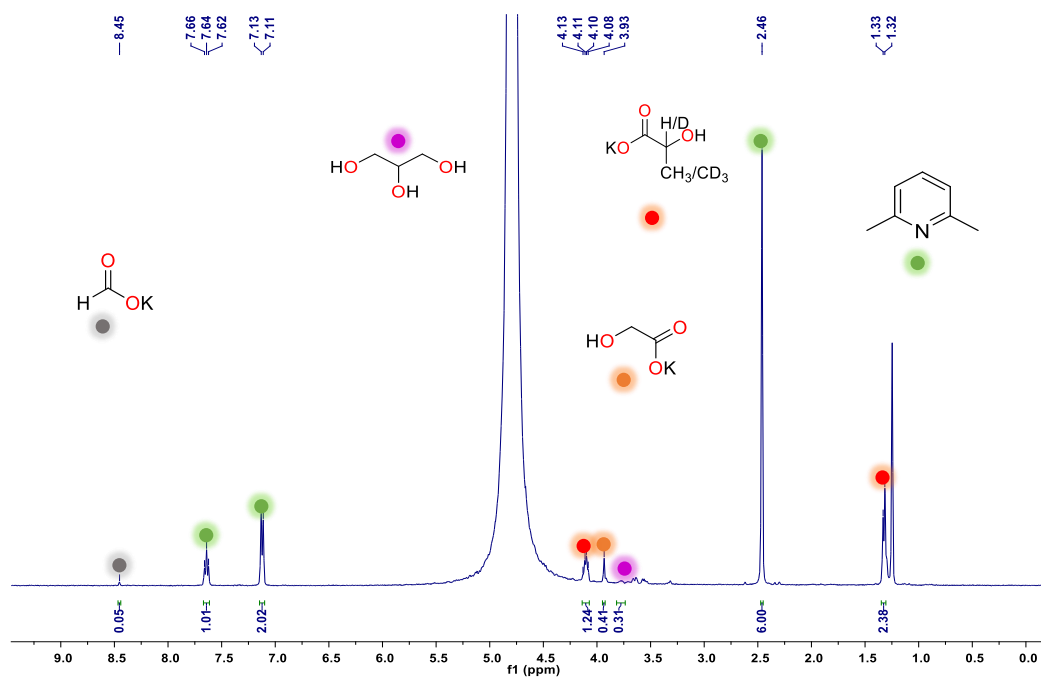**Figure S8**. ^{1}H NMR spectrum of lactate production from glycerol, ethylene glycol, and methanol mixture catalyzed by **1** in the presence of 100 mol% of Hg in D_2O.

b. Rearrangement of dihydroxyacetone to lactate

A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, KOH (1.5 mmol), ^{t}BuOH (1 mL), and dihydroxyacetone (1 mmol) was added under a nitrogen atmosphere. The tube was closed, and the mixture was placed in a preheated oil bath at 120 $^\circ$C for 2 h. Upon completion of the reaction, the mixture was cooled to room temperature. The reaction mixture was dissolved in 3-4 mL of water, and the yield of the reaction was determined by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D_2O.
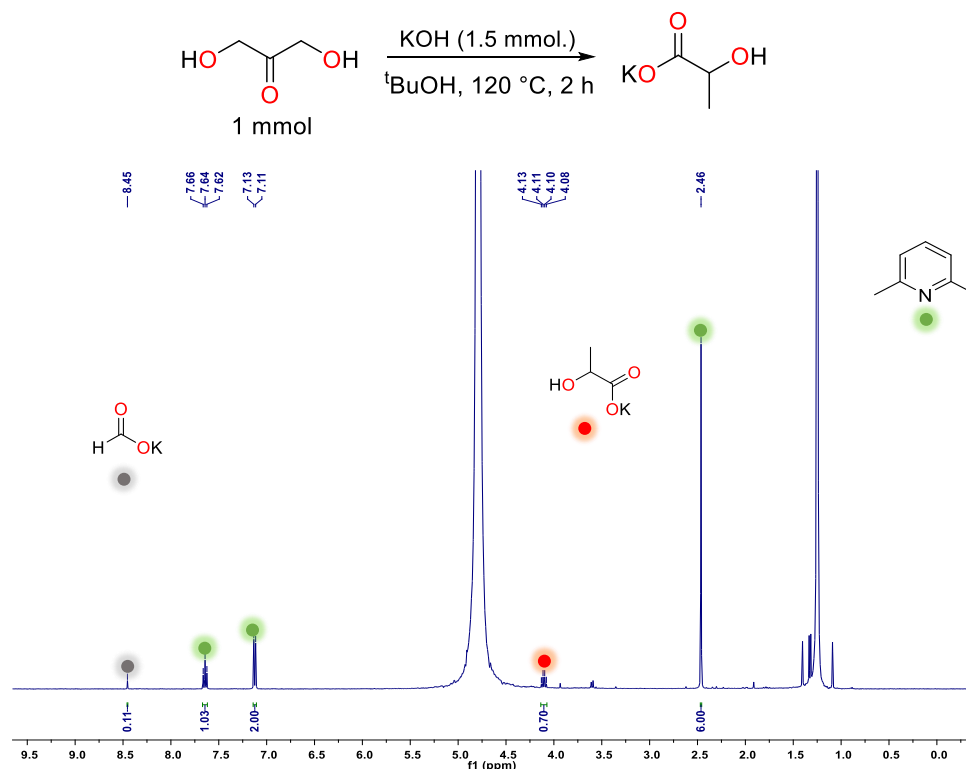
Figure S9. ^{1}H NMR spectrum of reaction of dihydroxyacetone in the presence of KOH to lactate in D_2O.

c. Identification of formaldehyde as intermediate

Following the general reaction process for the synthesis of lactate from ethylene glycol and methanol mixture, a reaction was performed using paraformaldehyde (5 mmol) as C1 source instead of methanol with **1** (1 mol%), KOH (3.5 mmol) in ^{t}BuOH (1 mL) at 120 °C for 48 h.
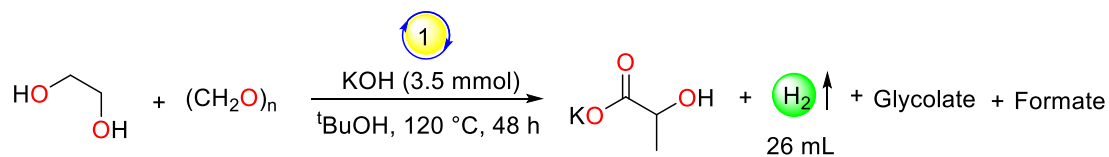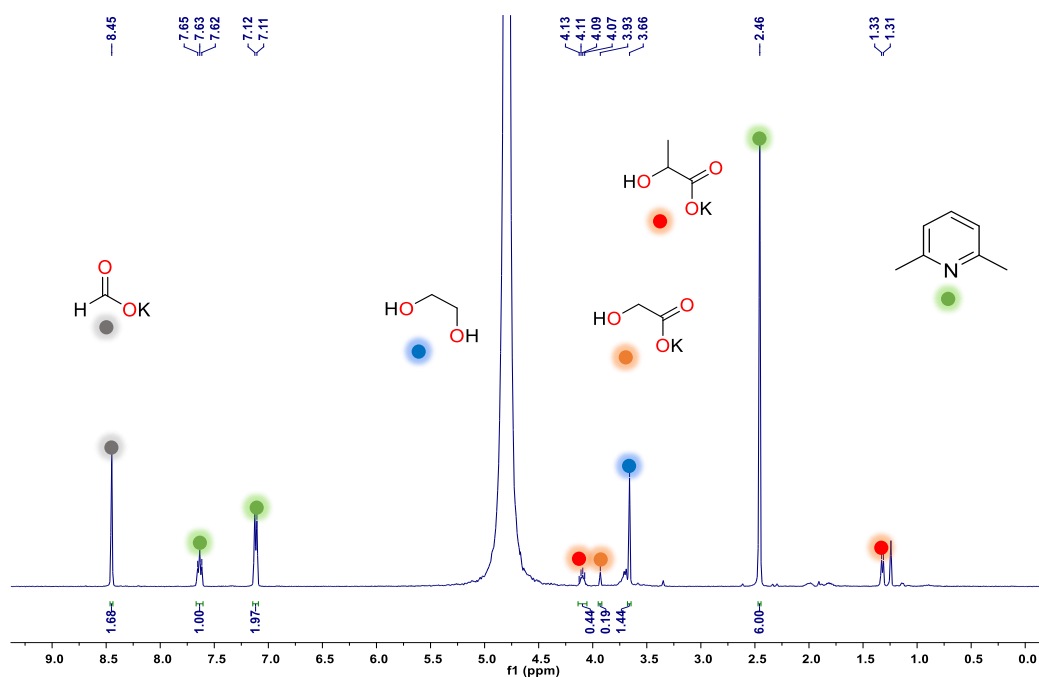
Figure S10. ^{1}H NMR spectrum of reaction of ethylene glycol with paraformaldehyde to lactate in D$_2$O.

d. Identification of glycolic acid not as intermediate
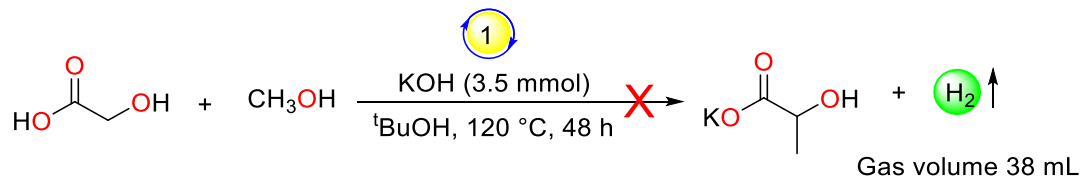
A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, **1** (1 mol%), KOH (3.5 mmol), CH$_3$OH (5 mmol), ^{t}BuOH (1 mL), and glycolic acid (1 mmol) were added under nitrogen atmosphere. The tube was closed, and the mixture was placed in a preheated oil bath at 120 $^\circ$C for 48 h. Upon completion of the reaction, the mixture was cooled to room temperature, evolved gas was measured, and the solvent was evaporated under vacuum. The residue was redissolved in 3-4 mL of water, and the yield of the reaction was determined by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D$_2$O.

Figure S11. ^{1}H NMR spectrum of reaction of glycolic acid with methanol to lactate in D$_2$O.

e. Reaction of glyoxal with methanol in the presence of catalyst 1

A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, **1** (1 mol%), KOH (3.5 mmol), CH$_3$OH (5 mmol), [t]BuOH (1 mL), and glyoxal (1 mmol) were added under nitrogen atmosphere. The tube was closed, and the mixture was placed in a preheated oil bath at 120 °C for 48 h. Upon completion of the reaction, the mixture was cooled to room temperature, and evolved gas volume was measured. The reaction mixture was dissolved in 3-4 mL of water, and the yield of the reaction was determined by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D$_2$O.

Figure S12. ^{1}H NMR spectrum of reaction of glycolic acid with methanol to lactate in D_2O.

f. H/D exchange experiment
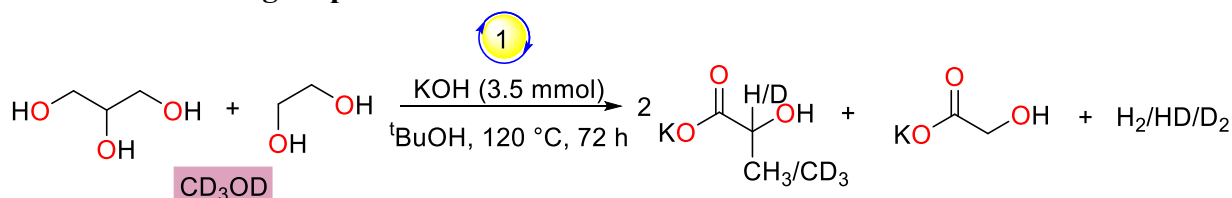
A 100 mL sealed tube with a side arm equipped with Teflon coated magnetic stirring bar, **1** (1 mol%), KOH (3.5 mmol), CD_3OD (5 mmol), ^tBuOH (1 mL), ethylene glycol (1 mmol), and glycerol (1 mmol) were added under nitrogen atmosphere. The tube was closed, and the mixture was placed in a preheated oil bath at 120 $^\circ$C for 72 h. Upon completion of the reaction, the mixture was cooled to room temperature, and the solvent was evaporated under vacuum. The residue was redissolved in 3-4 mL of water and the yield of the reaction was determined by ^{1}H NMR using 2,6-lutidine (1 mmol) as an internal standard in D_2O and ^{2}D NMR was taken in H_2O.

Figure S13. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol, and CD$_3$OD mixture catalyzed by **1** in D$_2$O.
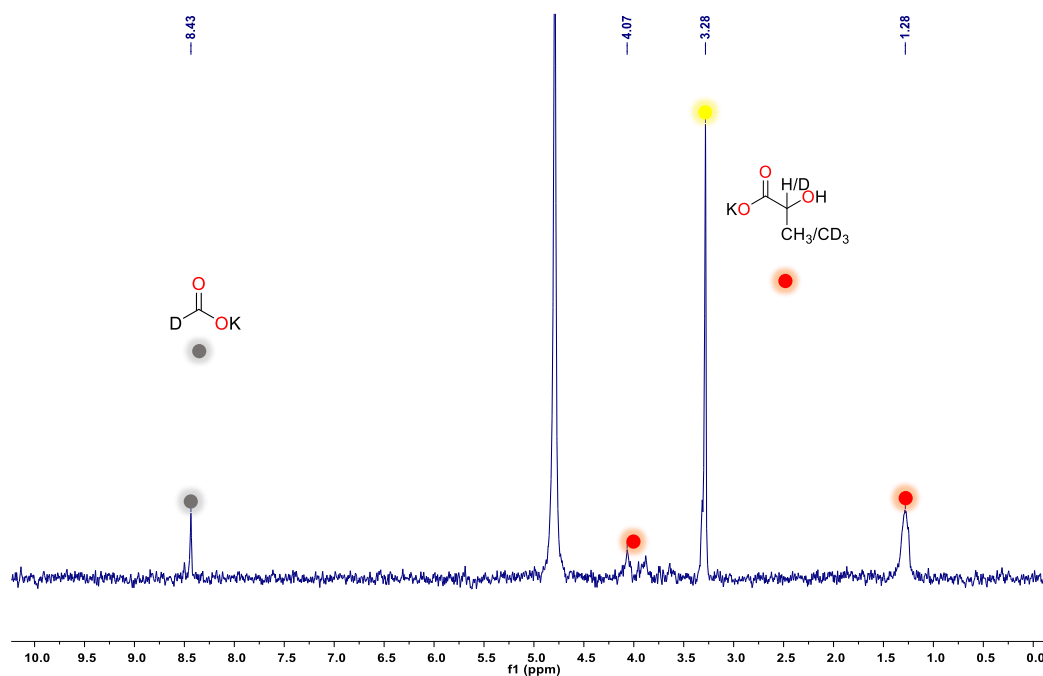
Figure S14. [2]D NMR spectrum of lactate formation from glycerol, ethylene glycol and CD$_3$OD mixture catalyzed by **1** in H$_2$O.

g. Treatment of lactic acid with 1 monitored by NMR

In an oven-dried NMR tube, **1a** was generated in situ by treatment of NEt$_3$ (0.02 mmol) with complex **1** (5.5 mg, 0.008 mmol) in CDCl$_3$. The solution was treated with 90% lactic acid for 3 hours at room temperature. The reaction was monitored by ^{31}P NMR and the mixture was also analyzed by HRMS.
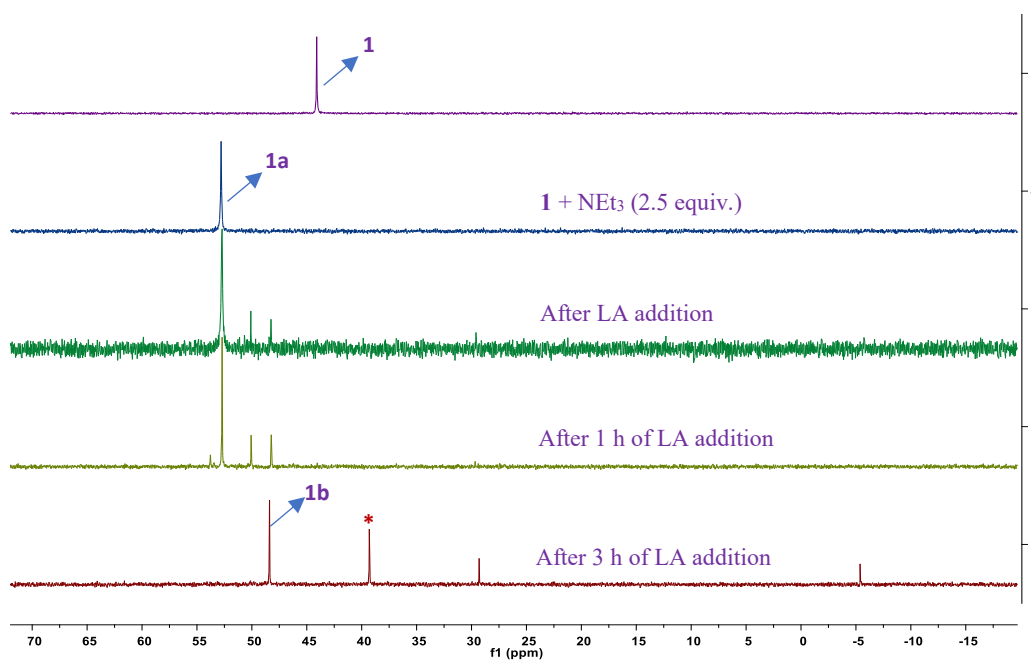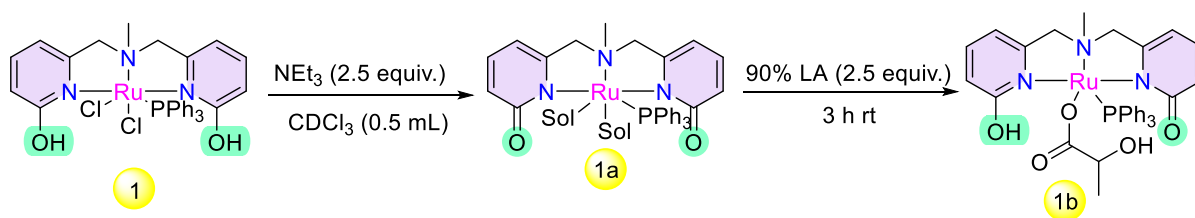
Figure S15. ^{31}P NMR spectra monitoring the reaction of lactic acid with **1.** * unidentified species.
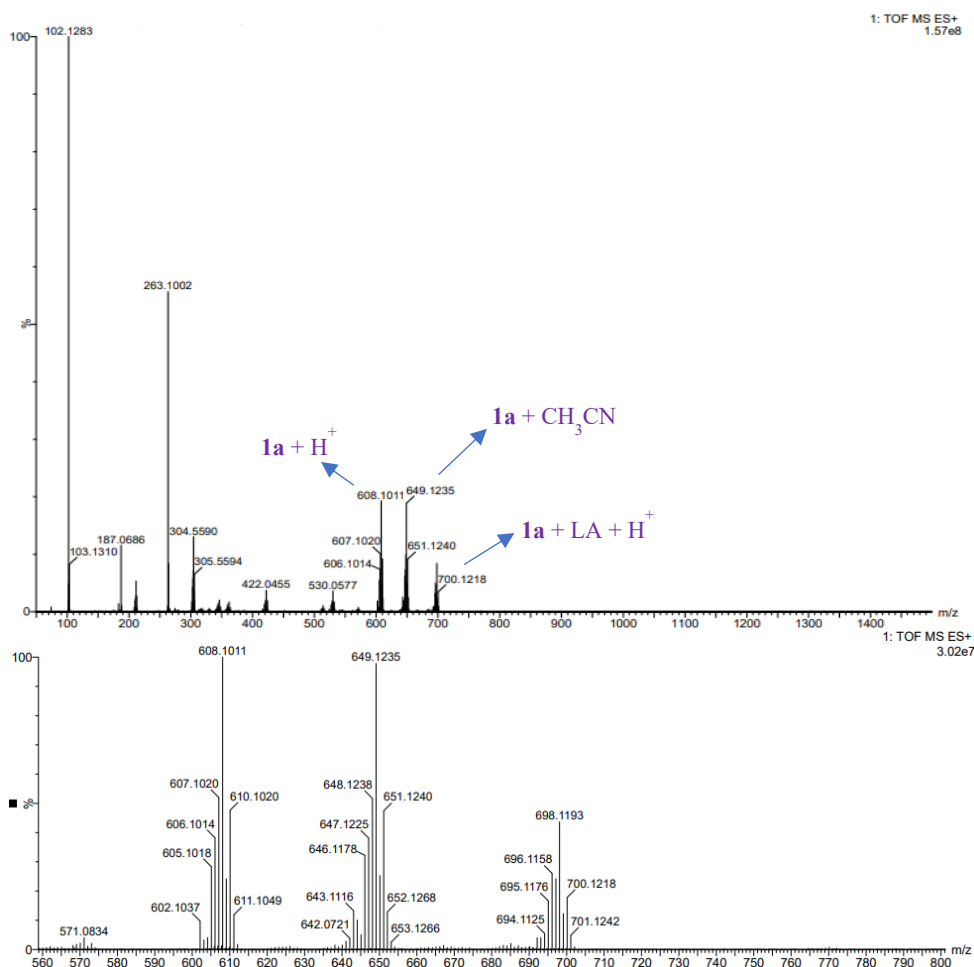
Figure S16. HRMS of reaction of lactic acid with catalyst **1** in presence

h. Treatment of dihydroxyacetone with 1 monitored by NMR

In an oven-dried NMR tube, catalyst **1** (5.5 mg, 0.008 mmol) was taken and dissolved in 0.5 mL of CDCl$_3$. Sequentially, NEt$_3$ (0.02 mmol) was added to generate **1a**. Dihydroxyacetone (0.04 mmol) and KOH (0.04 mmol) were added to the tube. The tube was sealed properly and placed in a preheated oil bath at 120 °C for 5 min. The whole experiment was monitored by recording ^{31}P NMR spectra.
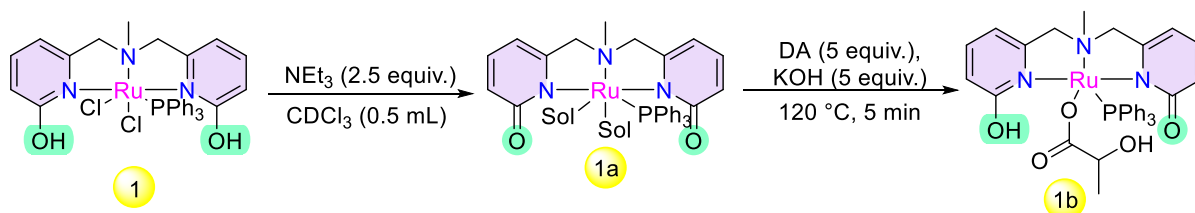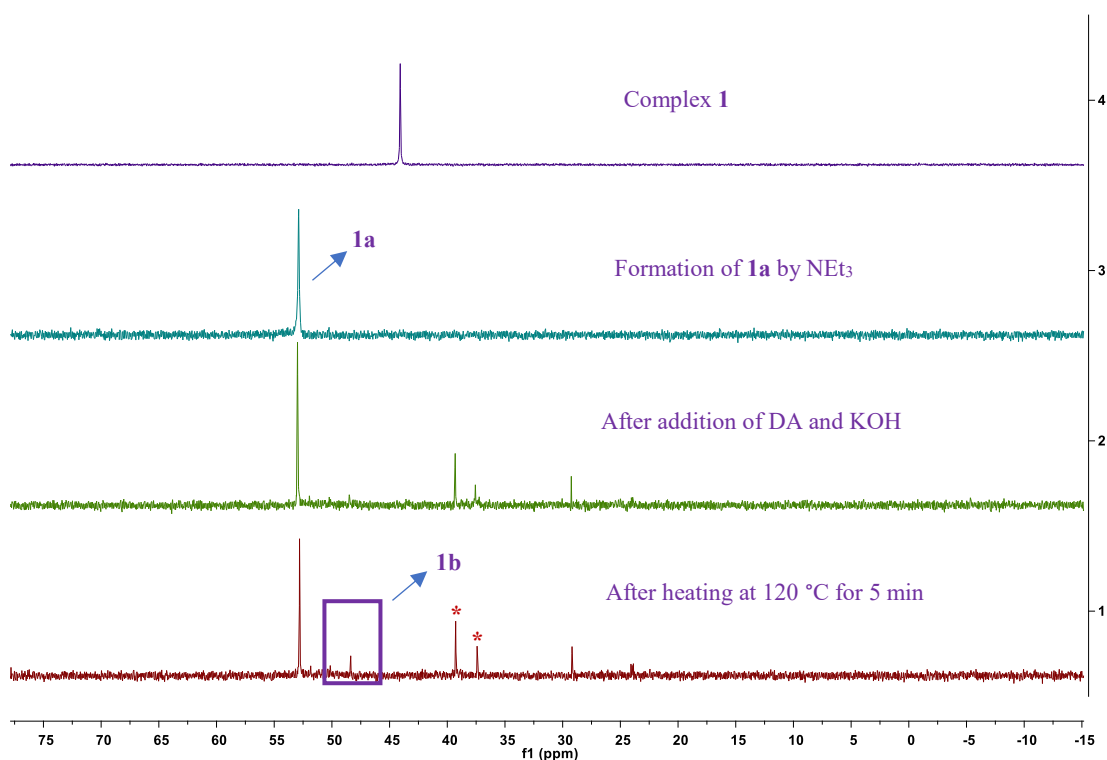
Figure S17. ^{31}P NMR spectra monitoring the reaction of dihydroxyacetone with **1.**
* unidentified species.

i. Treatment of glycerol with 1 monitored by NMR

In an oven-dried NMR tube, catalyst **1** (5.5 mg, 0.008 mmol) was taken and dissolved in 0.5 mL of CDCl$_3$. Sequentially, KOH (0.04 mmol) and glycerol (0.04 mmol) were added to the tube. The tube was sealed properly and placed in a preheated oil bath at 120 °C for 5 min. The whole experiment was monitored by recording ^{31}P NMR spectra.
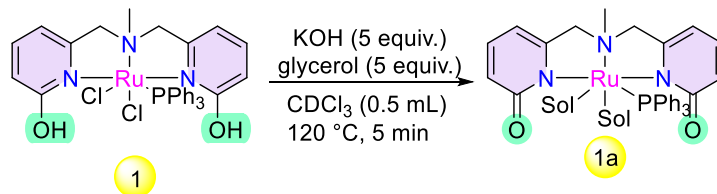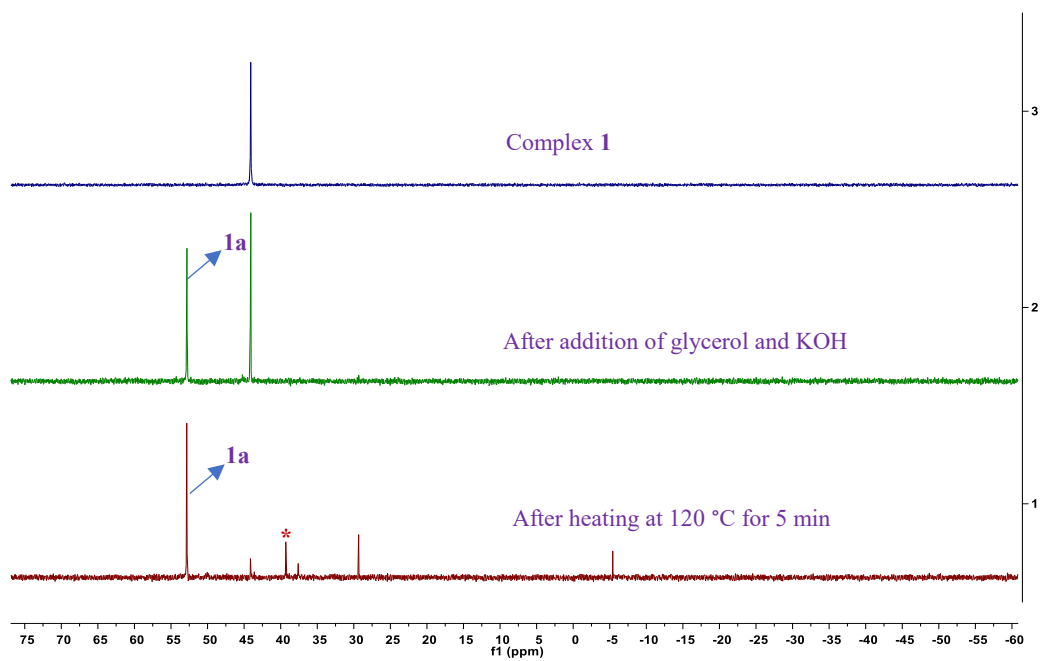
Figure S18. ^{31}P NMR spectra monitoring the reaction of glycerol with **1**. *** ** unidentified species.

10. Proposed reaction pathway

A **Proposed mechanism for dehydrogenation of alcohol substrate catalyzed by 1**

B **Possible dehydrogenative coupling and rearrangement mechanism for lactic acid formation**

Figure S19. Proposed reaction mechanism catalyzed by **1**

11. Homogeneous catalyst reported for lactate acid formation from a) glycerol[2–15] b) ethylene glycol and methanol[16–18]

A Lactic acid synthesis from Glycerol
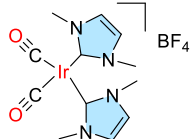
Crabtree (2014)
0.007 mol%,
KOH (1.1 equiv.),
Neat glycerol,
115 °C, 90 h,
Yield = 91%,
Selectivity > 95%
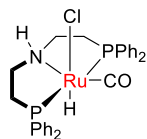
Beller (2015)
0.00025 mol%,
NaOH (1.1 equiv.),
Glycerol/NMP,
140 °C, 24 h,
Yield = 67%,
Selectivity = 67%
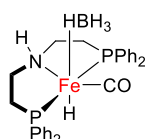
Hazari (2015)
0.02 mol%,
NaOH (1.0 equiv.),
Glycerol/NMP,
140 °C, 3 h,
Yield = 24%,
Selectivity = 83%
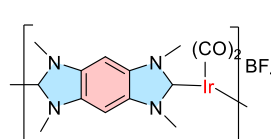
Tu (2015)
2.5 mol%,
KOH (1.1 equiv.),
Glycerol/Water,
115 °C, 36 h,
Yield = 92%,
Selectivity = 99%
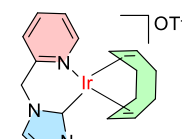
Williams (2016)
0.002 mol%,
KOH (1.0 equiv.),
Neat glycerol,
145 °C, 32 days,
Yield = 90%,
Selectivity = 100%
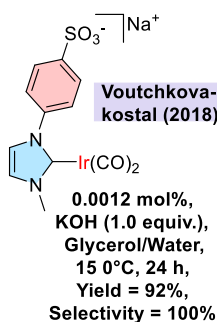
Voutchkova-kostal (2018)
0.0012 mol%,
KOH (1.0 equiv.),
Glycerol/Water,
15 0°C, 24 h,
Yield = 92%,
Selectivity = 100%
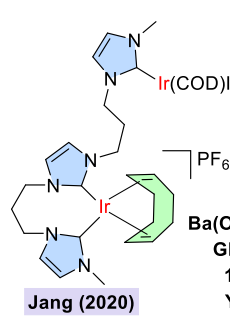
Jang (2020)
7 ppm,
Ba(OH)$_2$ (0.4 equiv.),
Glycerol/Water,
180 °C, 20 h,
Yield = 81%,
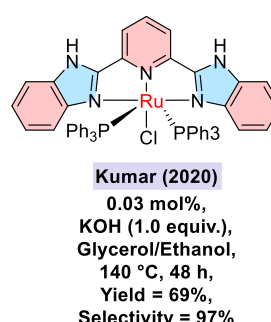
Kumar (2020)
0.03 mol%,
KOH (1.0 equiv.),
Glycerol/Ethanol,
140 °C, 48 h,
Yield = 69%,
Selectivity = 97%
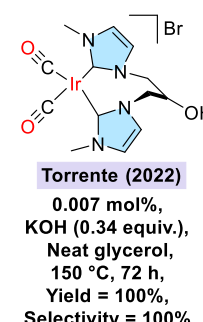
Torrente (2022)
0.007 mol%,
KOH (0.34 equiv.),
Neat glycerol,
150 °C, 72 h,
Yield = 100%,
Selectivity = 100%
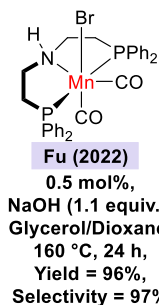
Fu (2022)
0.5 mol%,
NaOH (1.1 equiv.),
Glycerol/Dioxane,
160 °C, 24 h,
Yield = 96%,
Selectivity = 97%
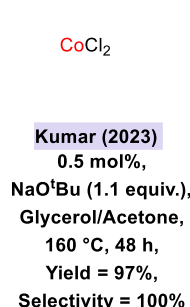
Kumar (2023)
0.5 mol%,
NaO^{t}Bu (1.1 equiv.),
Glycerol/Acetone,
160 °C, 48 h,
Yield = 97%,
Selectivity = 100%
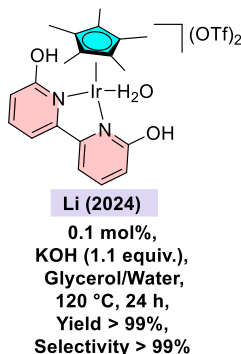
Li (2024)
0.1 mol%,
KOH (1.1 equiv.),
Glycerol/Water,
120 °C, 24 h,
Yield > 99%,
Selectivity > 99%
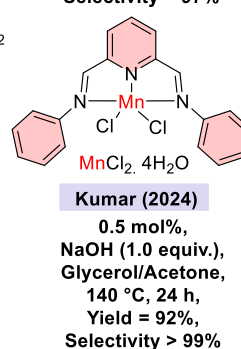
Kumar (2024)
0.5 mol%,
NaOH (1.0 equiv.),
Glycerol/Acetone,
140 °C, 24 h,
Yield = 92%,
Selectivity > 99%
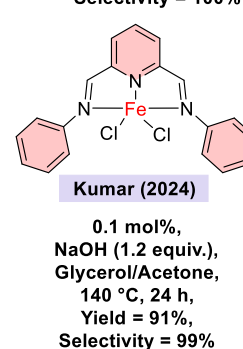
Kumar (2024)
0.1 mol%,
NaOH (1.2 equiv.),
Glycerol/Acetone,
140 °C, 24 h,
Yield = 91%,
Selectivity = 99%

B Lactic acid synthesis from Ethylene glycol and methanol
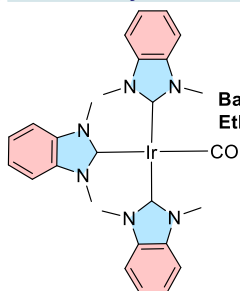
Tu (2020)
500 ppm,
Ba(OH)$_2$.8H$_2$O (1.2 equiv.),
Ethylene glycol/Methanol,
140 °C, 1 h,
Yield = 100%,
Selectivity >99%
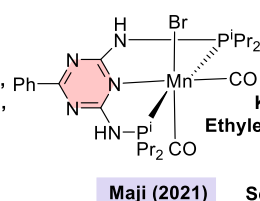
Maji (2021)
0.03 mol%,
KOH (5 equiv.),
Ethylene glycol/Methanol,
140 °C, 3 h,
Yield = 99%,
Selectivity = 99%
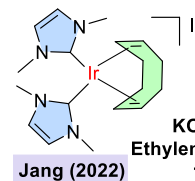
Jang (2022)
0.05 mol%,
KOH (1.5 equiv.),
Ethylene glycol/Methanol,
180 °C, 16 h,
Yield = 72%,

Figure S20. Previous homogeneous catalysts for lactate synthesis from a) glycerol b) from ethylene glycol and methanol
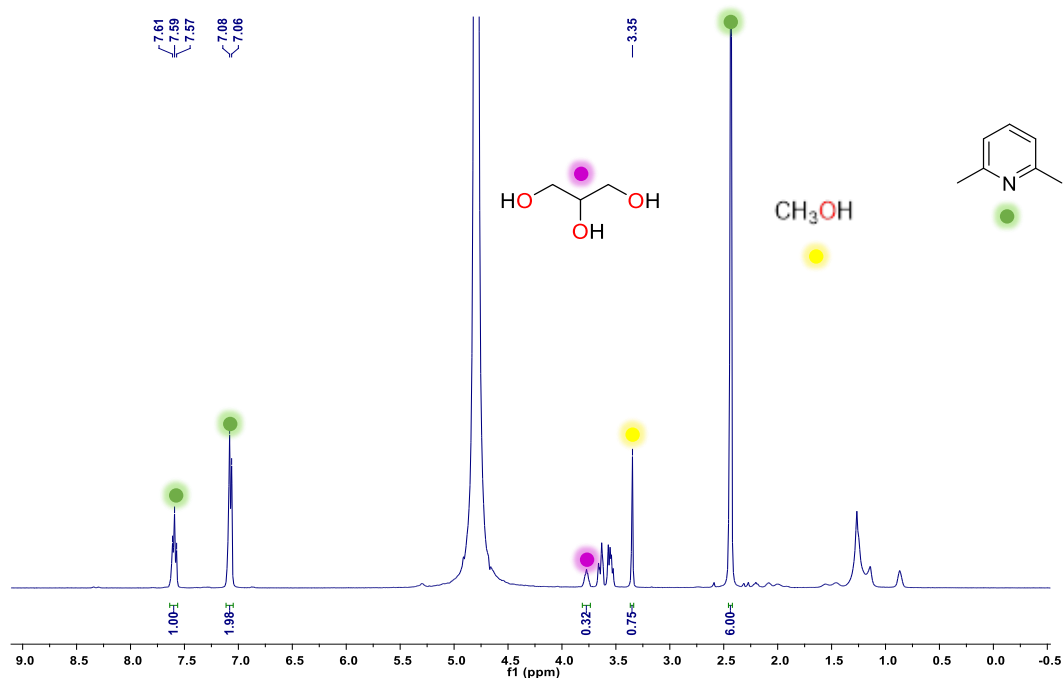
12.   Some representative spectra

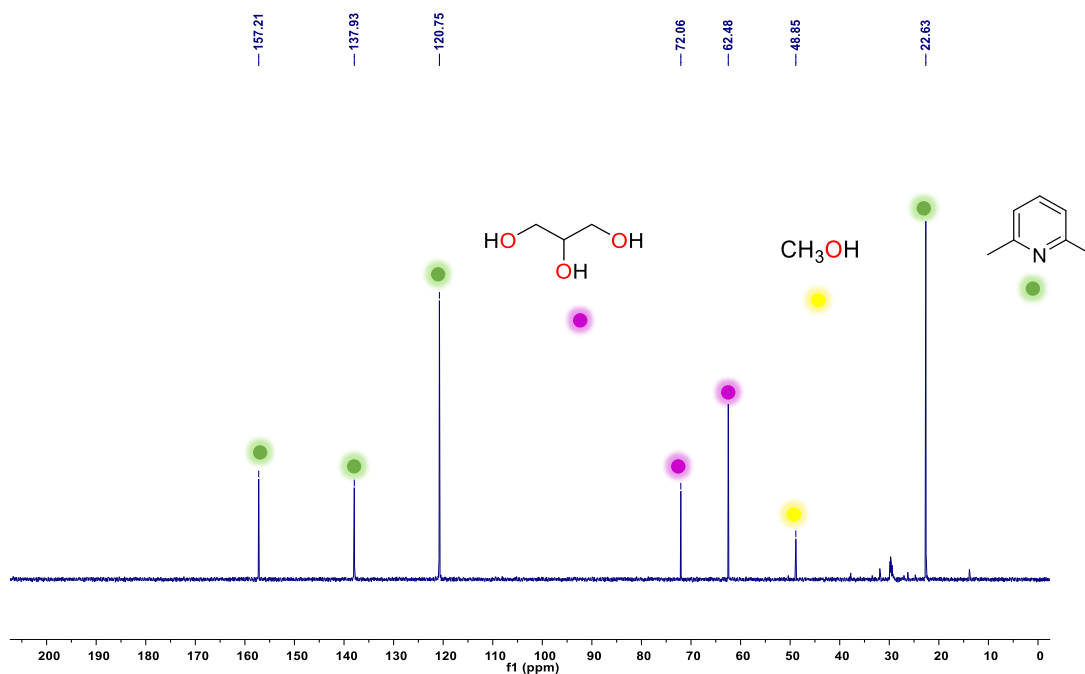**Figure S21.** ^{1}H NMR spectrum of crude glycerol in D$_2$O

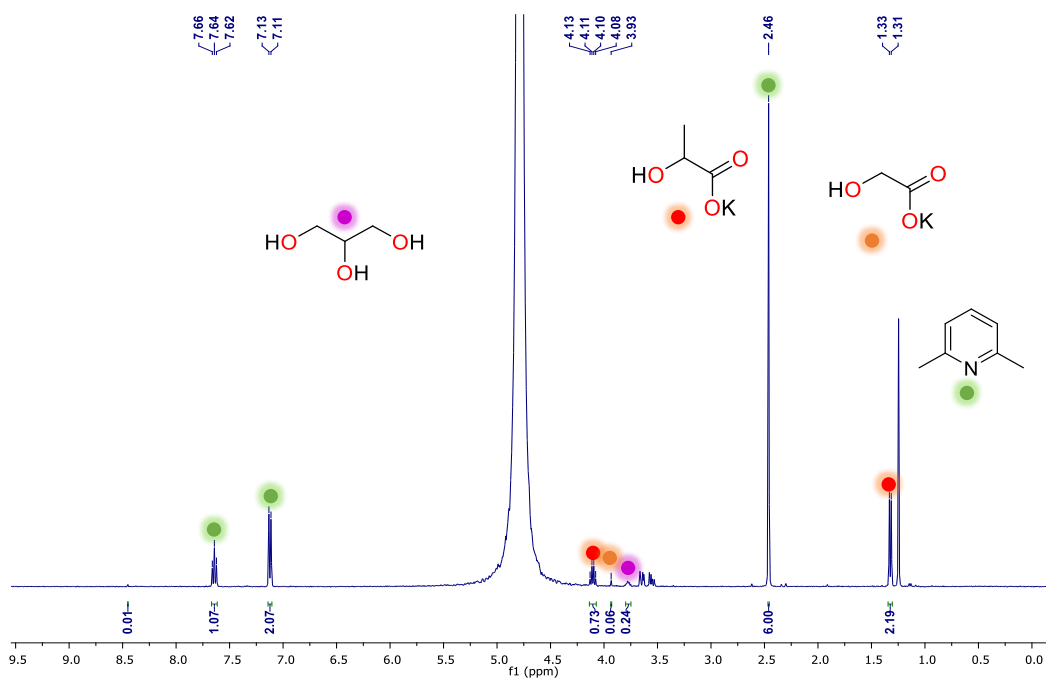**Figure S22.** ^{13}C NMR spectrum of crude glycerol in D$_2$O

Figure S23. ^{1}H NMR spectrum of glycerol to lactate formation in D$_2$O catalyzed by **1**, KOH (1.5 mmol), and ^{t}BuOH (1 mL) at 120 °C for 24 h (Table S1, entry 1).
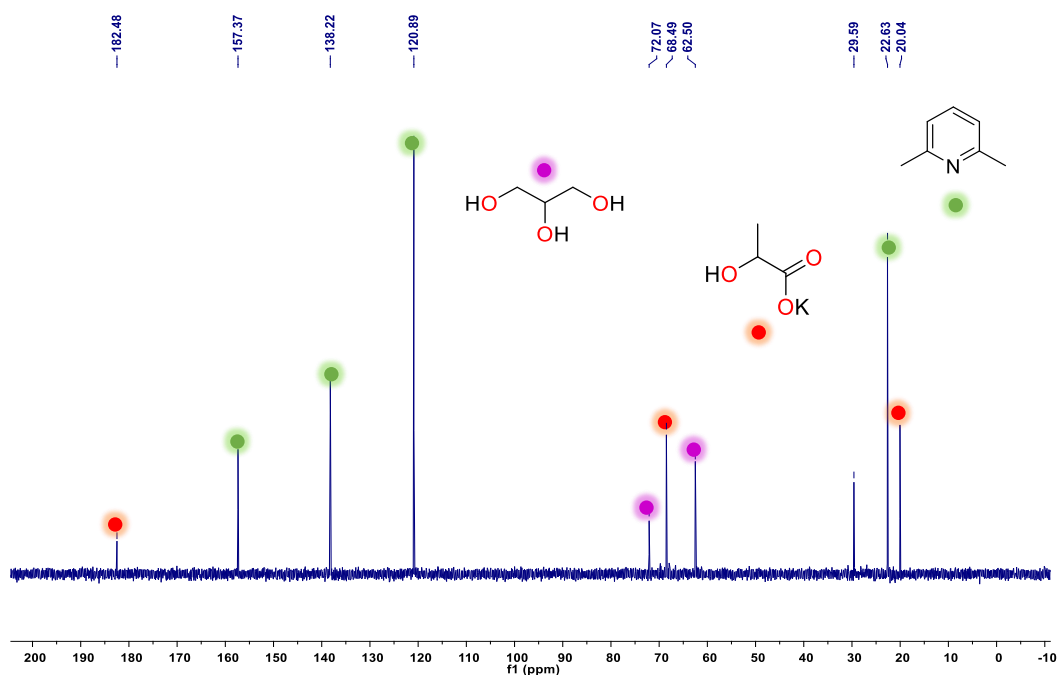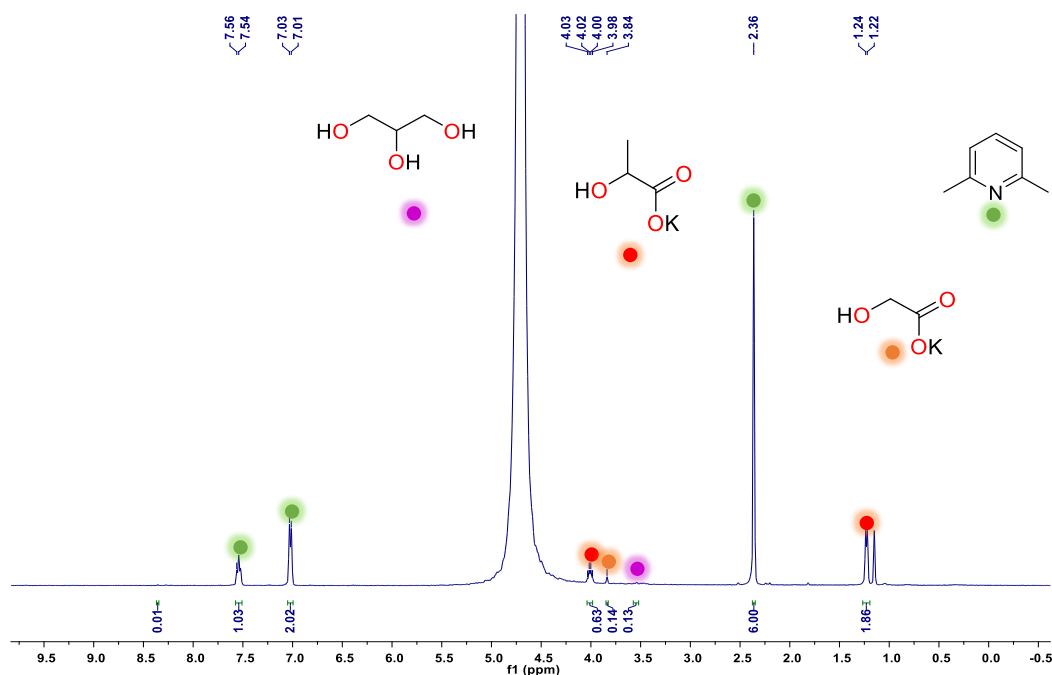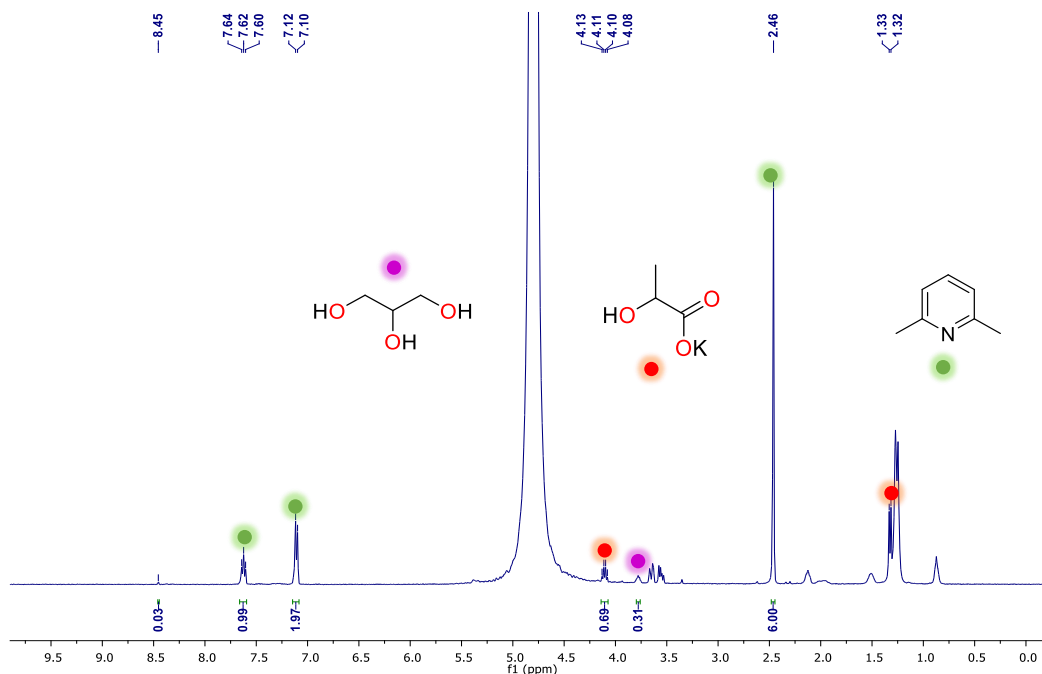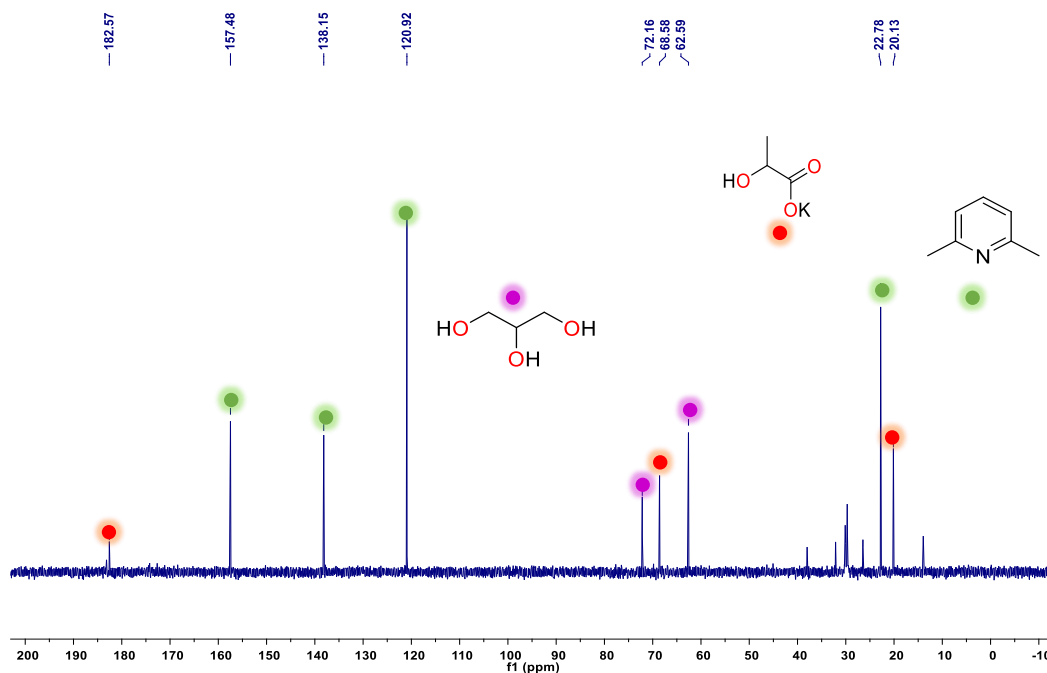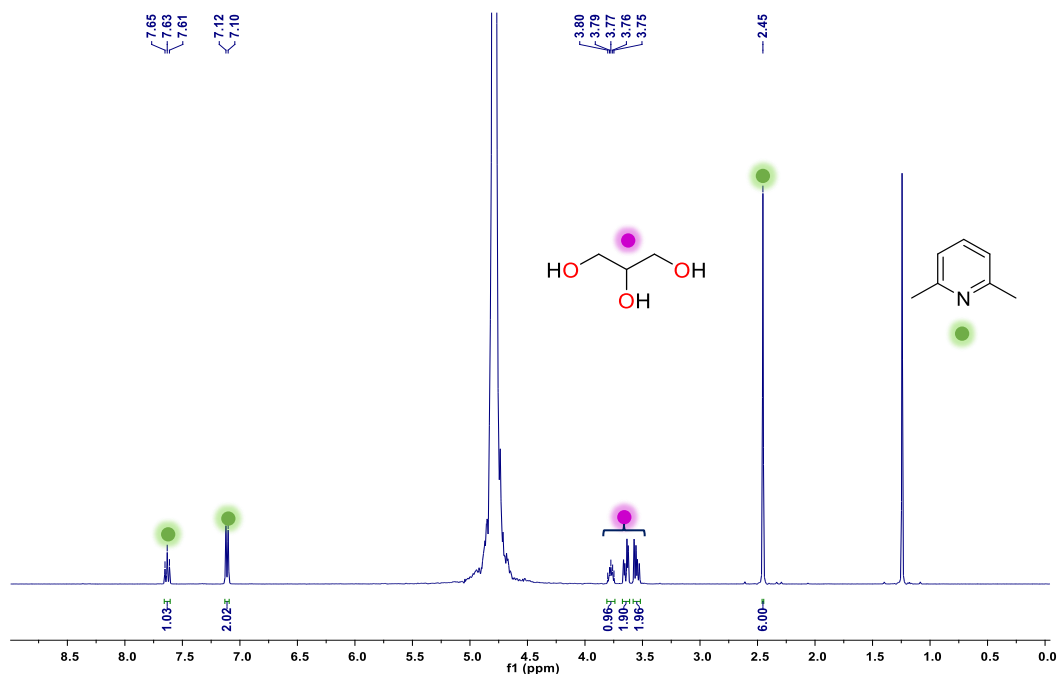

Figure S24. ^{13}C NMR spectrum of glycerol to lactate formation in D$_2$O catalyzed by **1**, KOH (1.5 mmol), and ^{t}BuOH (1 mL) at 120 °C for 24 h (Table S1, entry 1).

Figure S25. ^{1}H NMR spectrum of glycerol to lactate formation in D_2O catalyzed by **1** KOH (1.5 mmol), and [t]BuOH (1 mL) at 140 °C for 24 h (Table S1, entry 4).

Figure S26. ^{1}H NMR spectrum of crude glycerol to lactate formation in D_2O catalyzed by **1** KOH (1.5 mmol), and [t]BuOH (1 mL) at 120 °C for 24 h (Table S1, entry 7).

Figure S27. ^{13}C NMR spectrum of crude glycerol to lactate formation in D_2O catalyzed by **1**(1 mol%), KOH (1.5 mmol), and ^tBuOH (1 mL) at 120 °C for 24 h (Table S1, entry 7).

Figure S28. ^1H NMR spectrum in D_2O of glycerol to lactate conversion in the absence of catalyst **1**, KOH (1.5 mmol), and ^tBuOH (1 mL) at 120 °C for 24 h. (Table S1, entry 8).
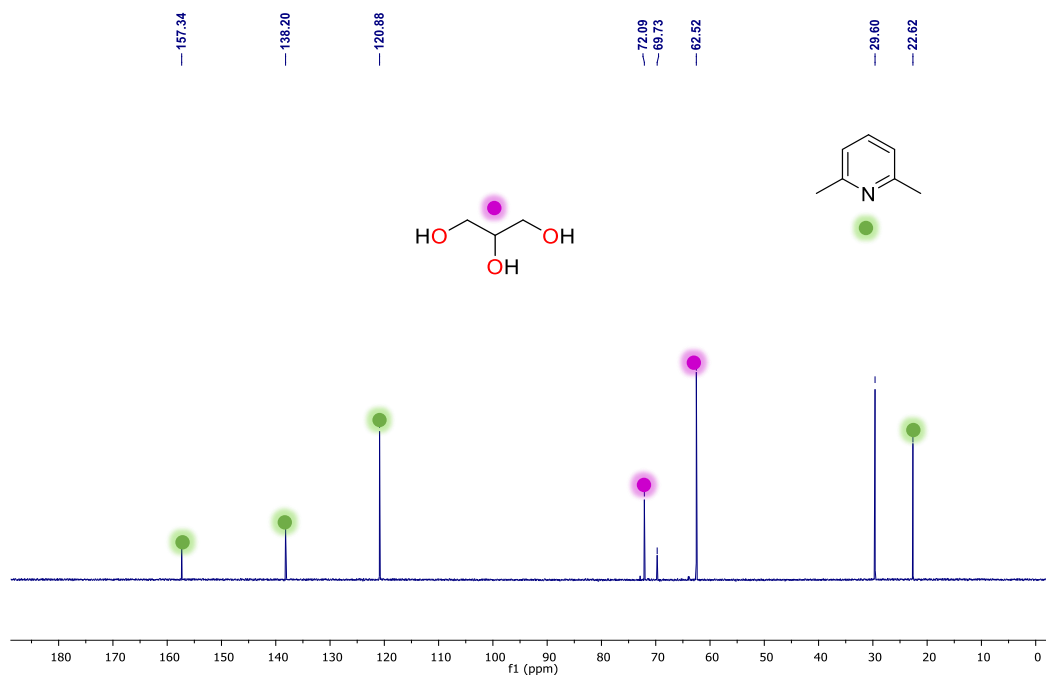
Figure S29. ^{13}C NMR spectrum in D_2O of glycerol to lactate conversion in the absence of catalyst **1**, KOH (1.5 mmol), and ^{t}BuOH (1 mL) at 120 °C for 24 h. (Table S1, entry 8).
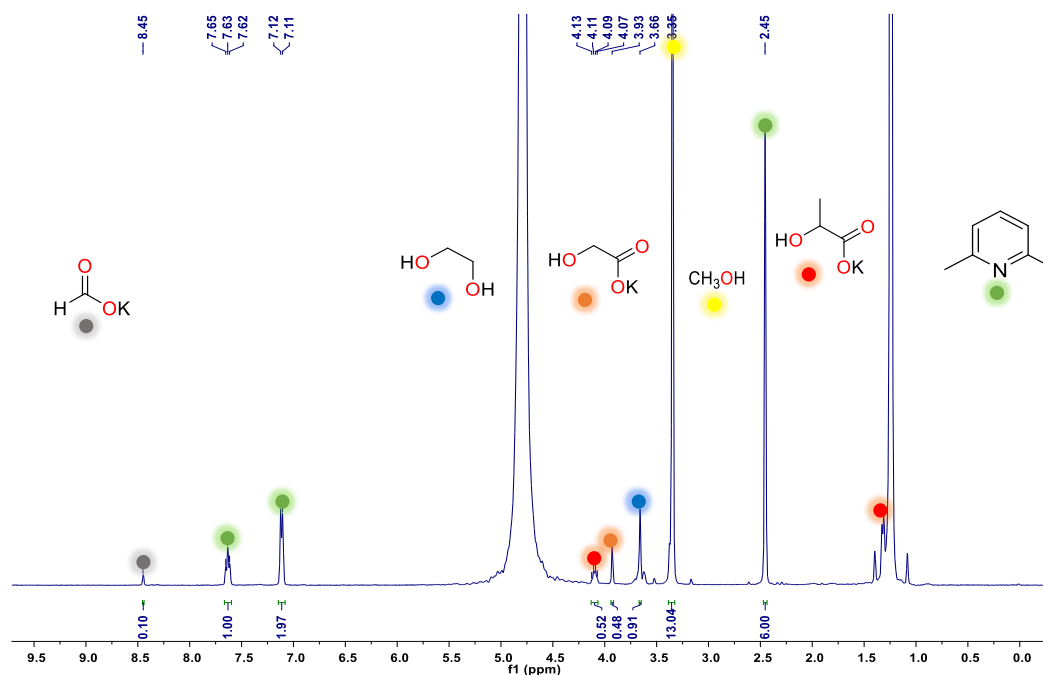
Figure S30. ^{1}H NMR spectrum of lactate formation from ethylene glycol and methanol mixture catalyzed by **1** (1 mol%), KOH (2.5 mmol) at 120 °C for 24 h (Table S2, entry 1)
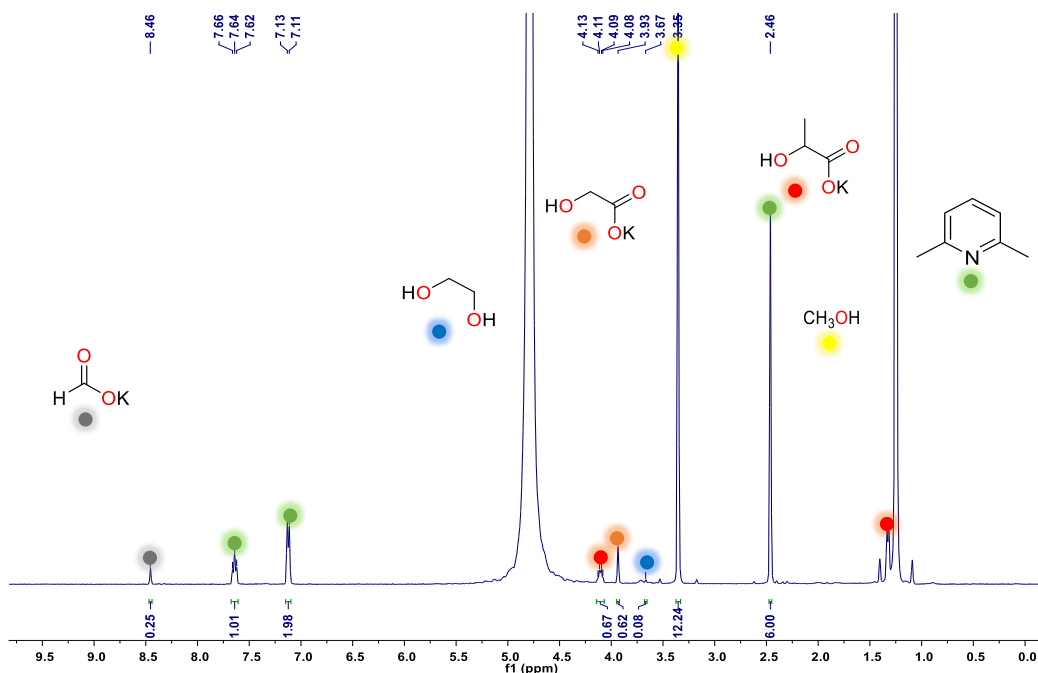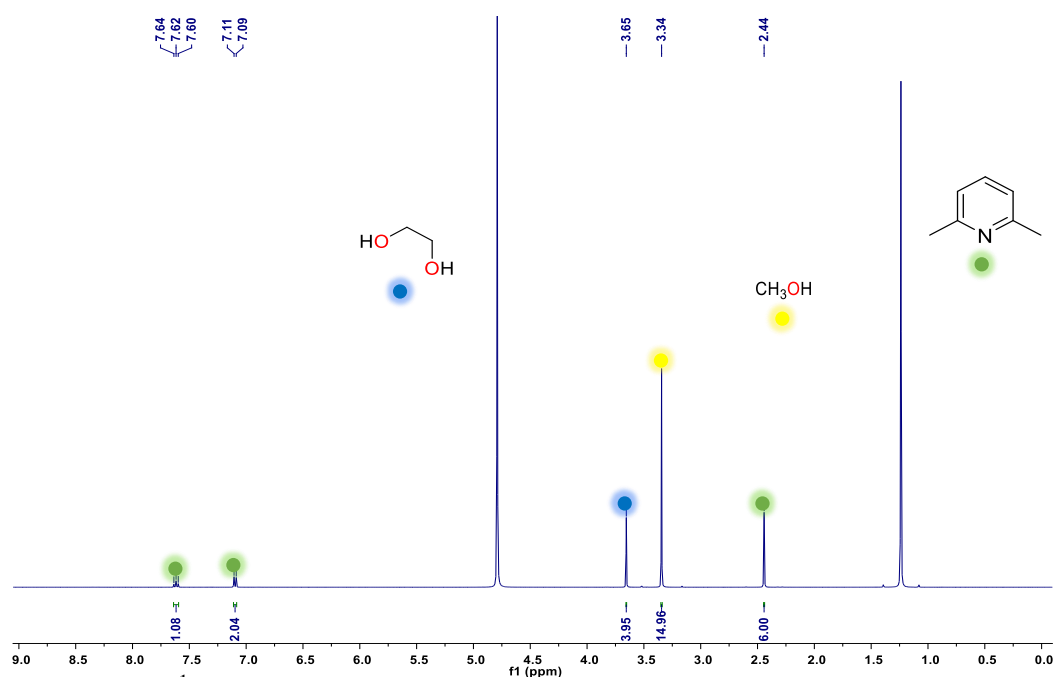
Figure S31. ^{1}H NMR spectrum of lactate formation from ethylene glycol and methanol mixture catalyzed by **1** (1 mol%), KOH (3.5 mmol) at 120 °C for 48 h (Table S2, entry 3)
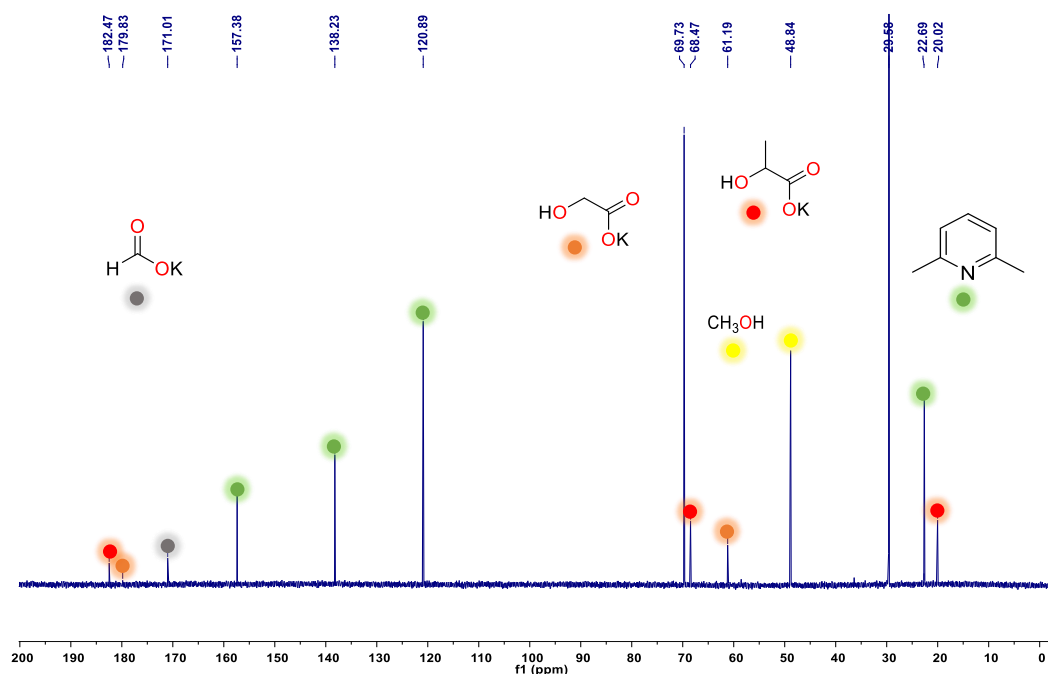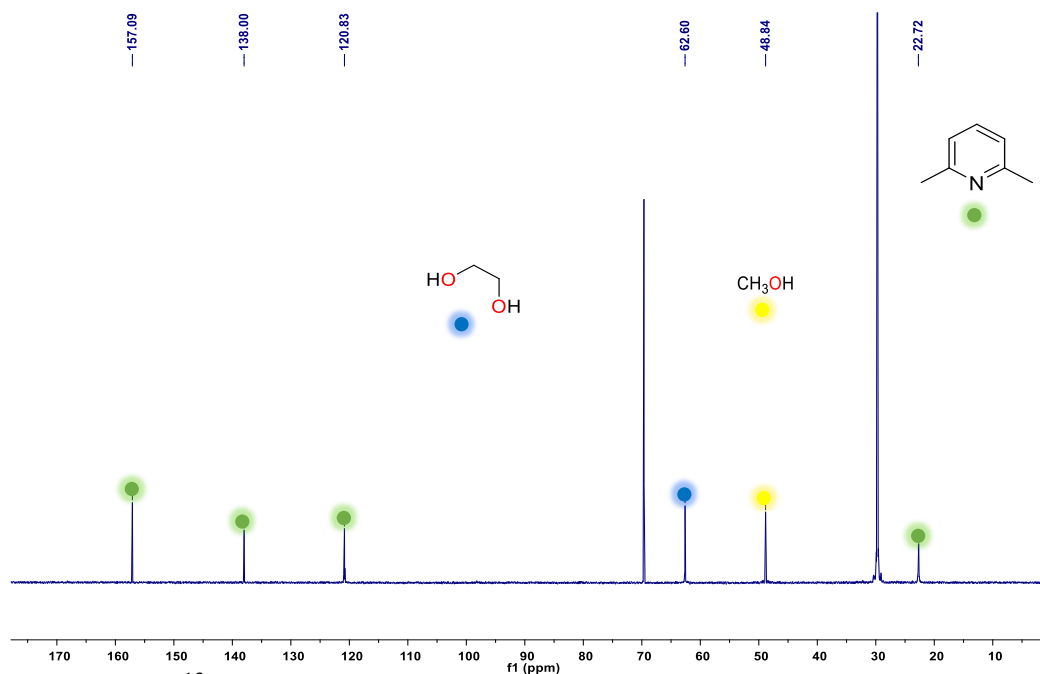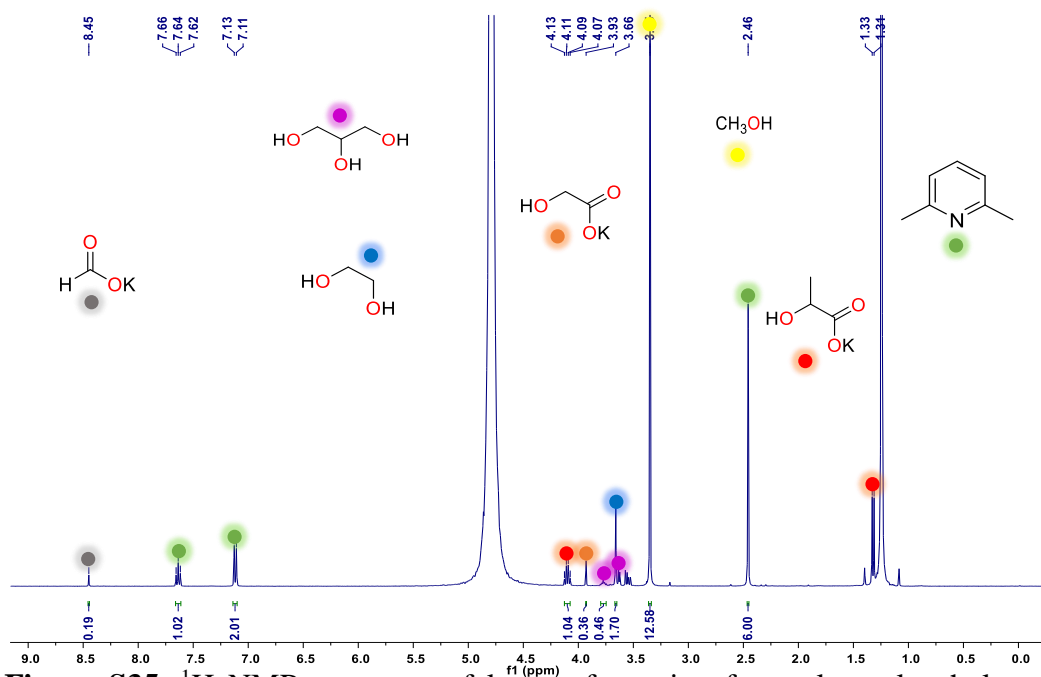

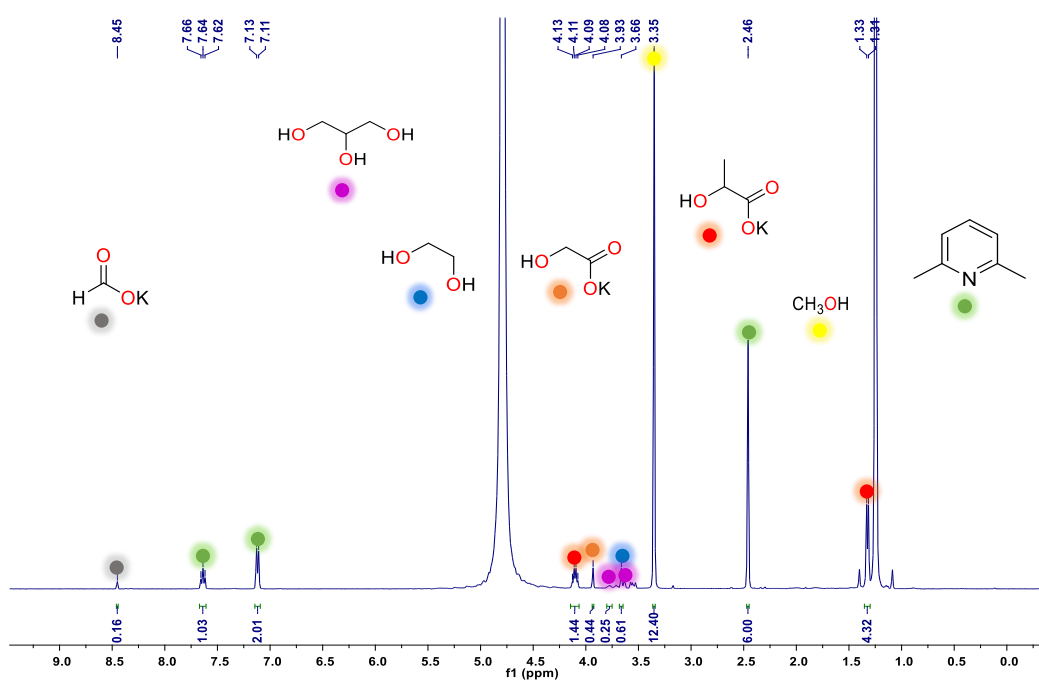**Figure S32.** ^{13}C NMR spectrum of lactate formation from ethylene glycol and methanol mixture catalyzed by **1** (1 mol%), KOH (3.5 mmol) at 120 °C for 48 h (Table S2, entry 3)

Figure S33. ^{1}H NMR spectrum of lactate formation from ethylene glycol and methanol mixture in absence of **1**, KOH (3.5 mmol) at 120 °C for 48 h (Table S2, entry 4)

Figure S34. ^{13}C NMR spectrum of lactate formation from ethylene glycol and methanol mixture in absence of **1**, KOH (3.5 mmol) at 120 °C for 48 h (Table S2, entry 4)
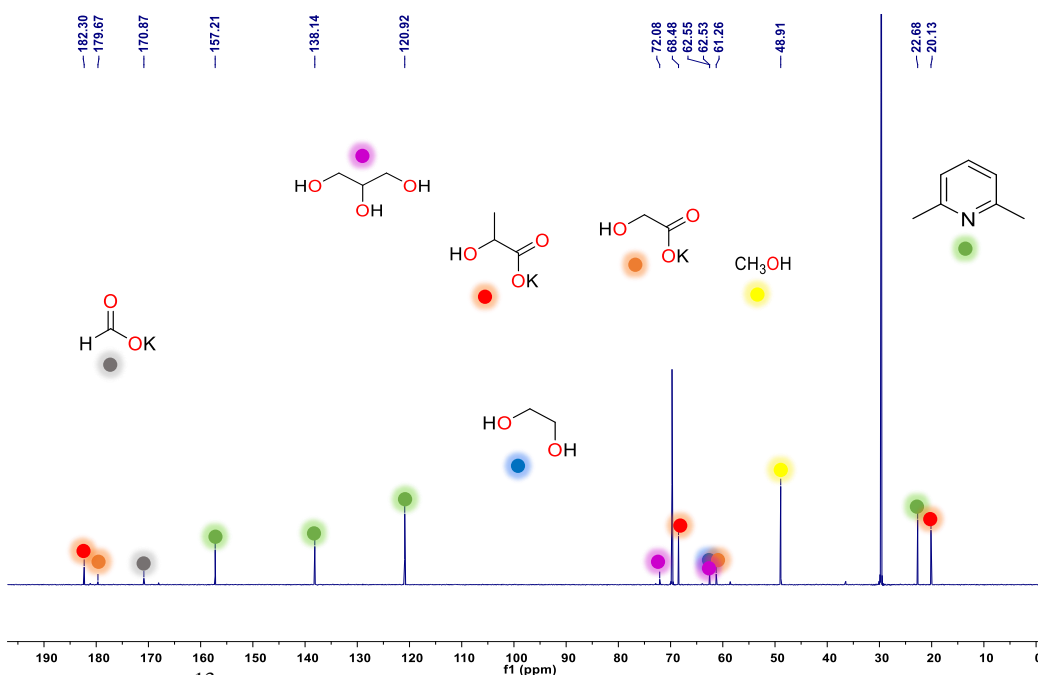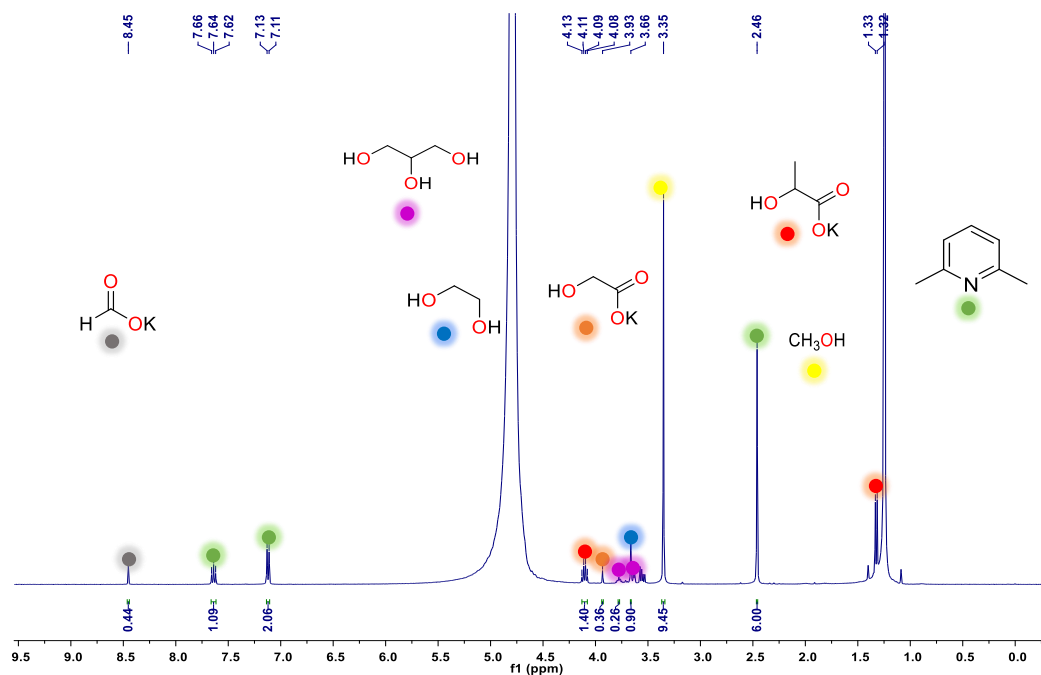
Figure S35. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture catalyzed by **1** (1 mol%), KOH (3.5 mmol), in ^{t}BuOH at 120 °C for 24 h (Table S3, entry 2). Both EG and glycerol proton coexist at 3.66 ppm

Figure S36. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture catalyzed by **1**(1 mol%), KOH (3.5 mmol), in ^{t}BuOH at 120 °C for 72 h (Table S3, entry 5).
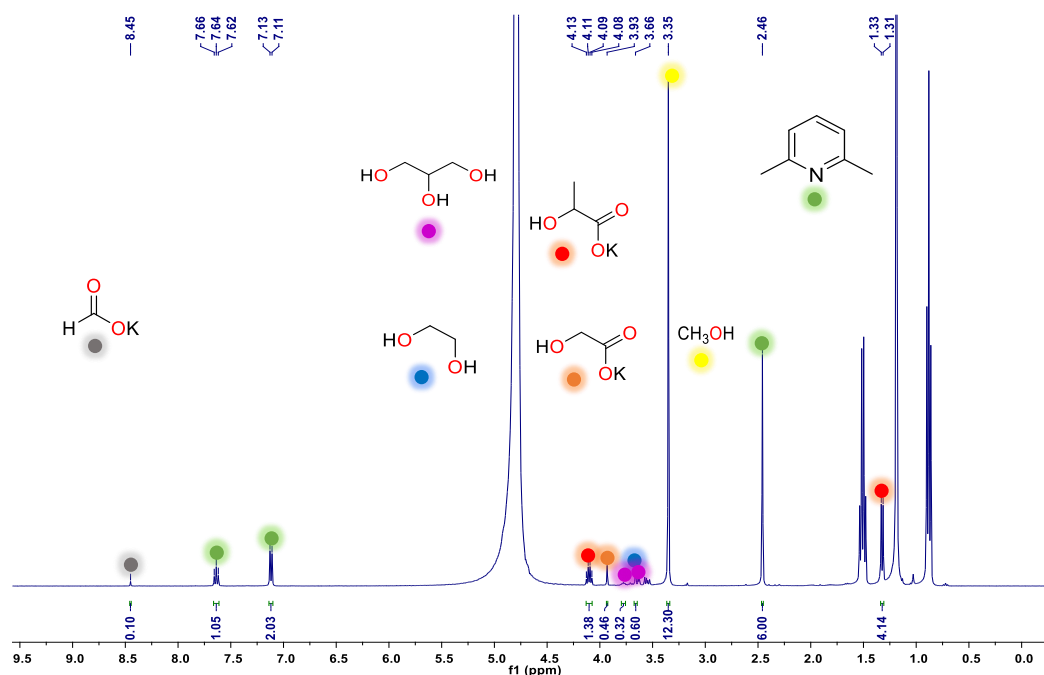
Figure S37. ^{13}C NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture catalyzed by **1**(1 mol%), KOH (3.5 mmol), in ^{t}BuOH at 120 °C for 72 h (Table S3, entry 5).
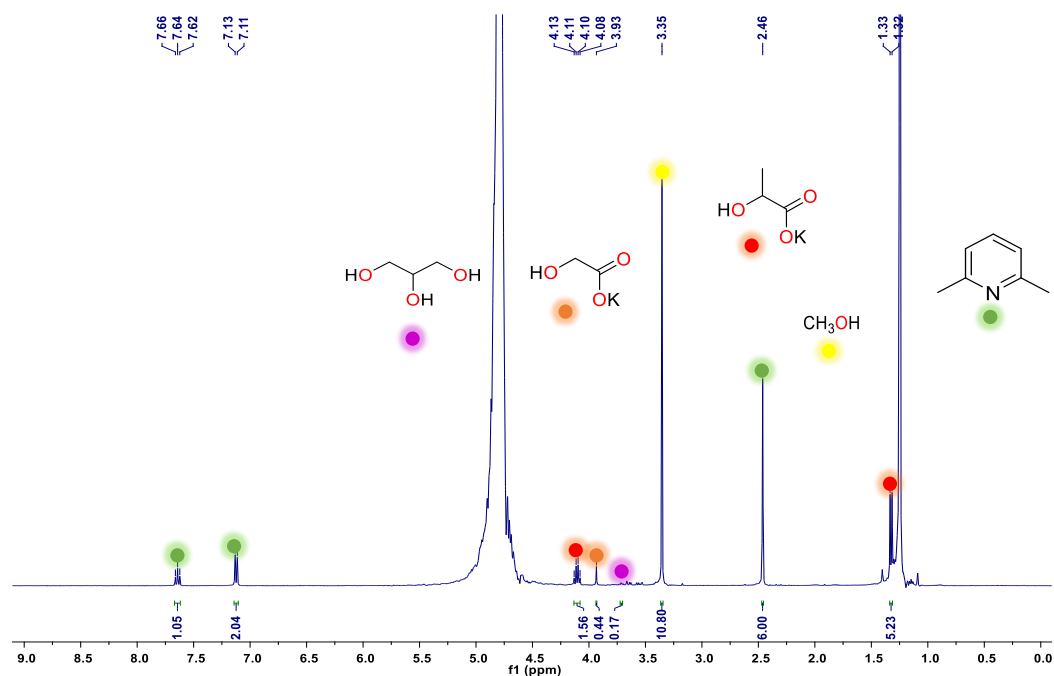

Figure S38. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture catalyzed by **1**(1 mol%), NaOH (3.5 mmol), in ^{t}BuOH at 120 °C for 72 h (Table S3, entry 6).
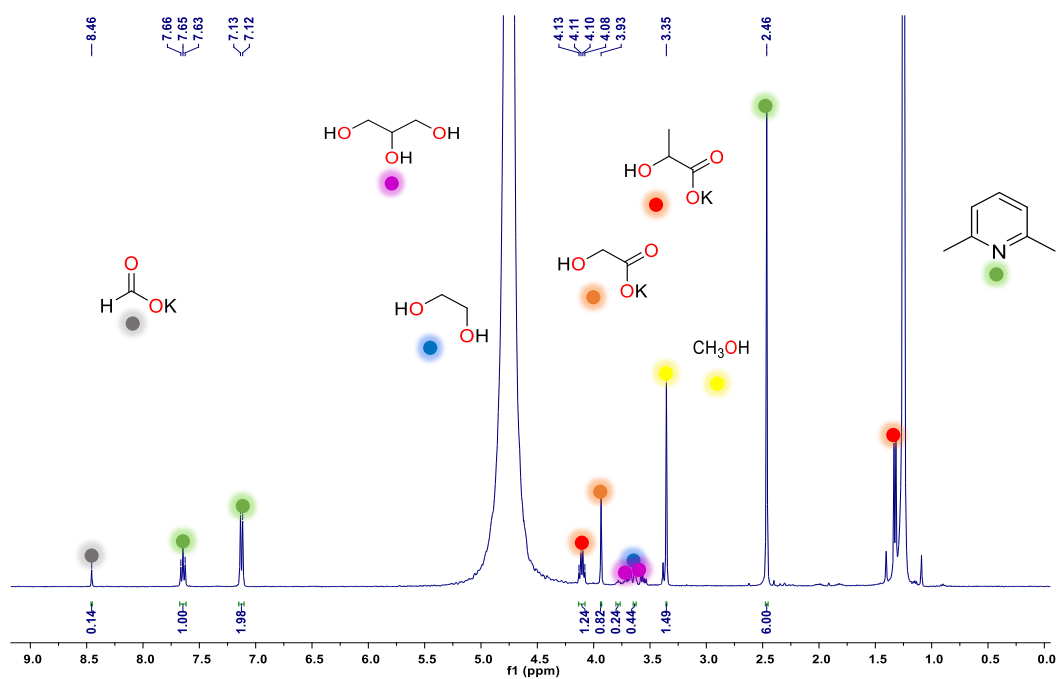
Figure S39. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture catalyzed by **1**(1 mol%), KOH (3.5 mmol), in [t]AmOH at 120 °C for 72 h (Table S3, entry 8).

Figure S40. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture catalyzed by **1**(1 mol%), KOH (3.5 mmol), in [t]BuOH at 140 °C for 72 h (Table S3, entry 10).

Figure S41. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture catalyzed by **1**(1 mol%), KOH (3.5 mmol), in [t]BuOH at 120 °C for 72 h (Table S3, entry 11).
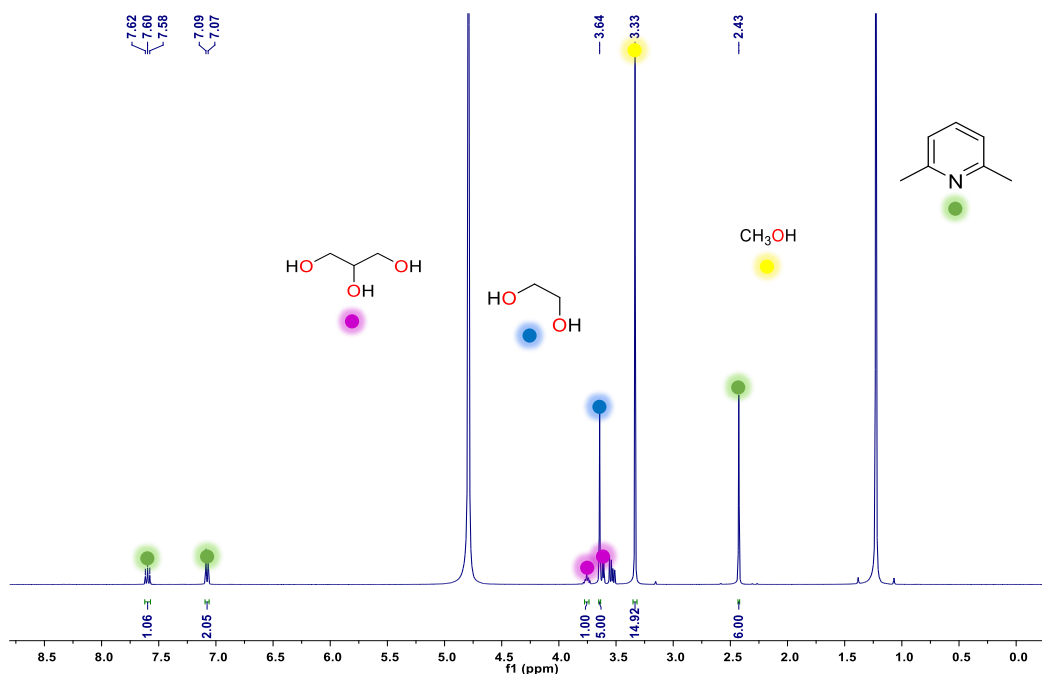

Figure S42. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture in absence of catalyst **1**, KOH (3.5 mmol) at 120 °C for 72 h (Table S3, entry 12).
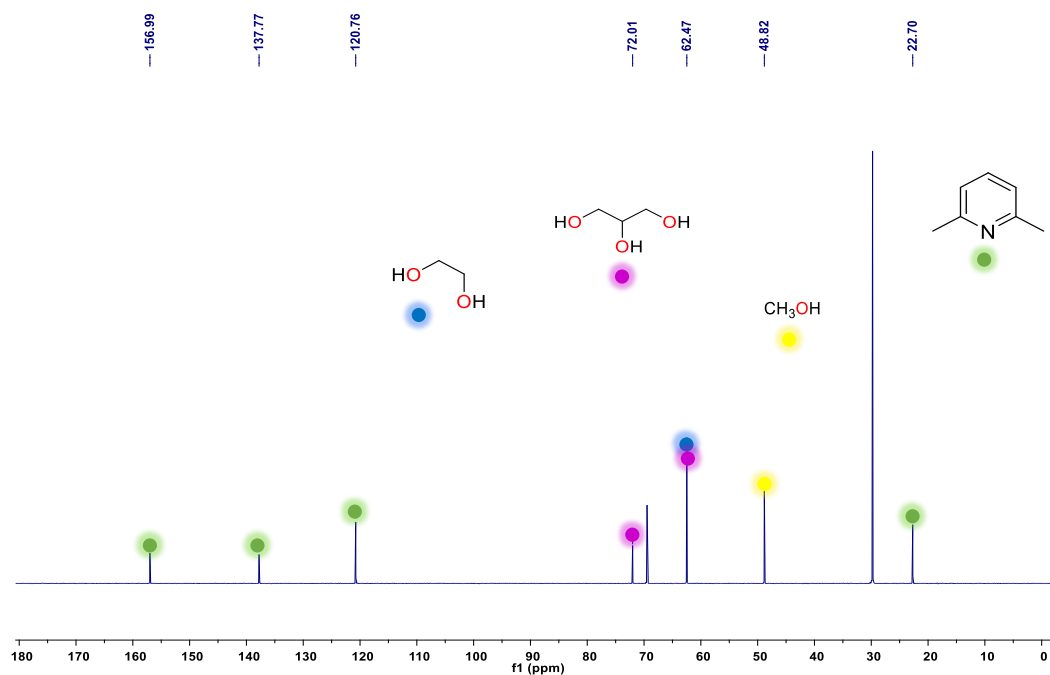
Figure S43. ^{13}C NMR spectrum of lactate formation from glycerol, ethylene glycol and methanol mixture in absence of catalyst **1**, KOH (3.5 mmol) at 120 ℃ for 72 h (Table S3, entry 12).

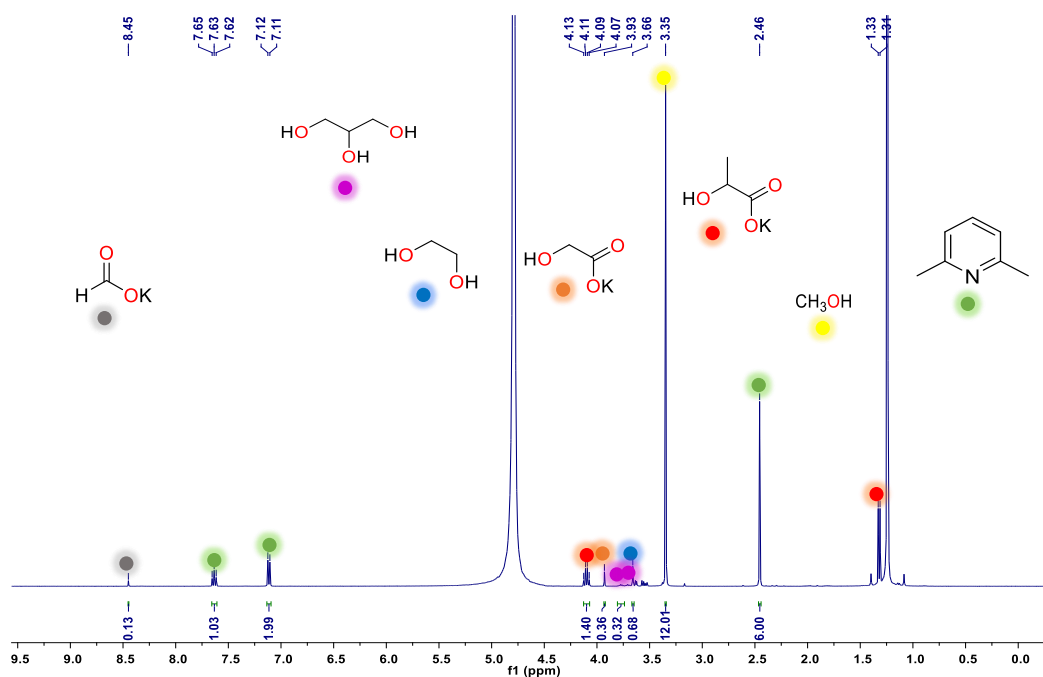

Figure S44. ^1H NMR spectrum of lactate formation from glycerol, ethylene glycol, and methanol mixture catalyzed by **1**(0.5 mol%), KOH (3.5 mmol), in ^tBuOH at 120 ℃ for 72 h (Table S3, entry 13).
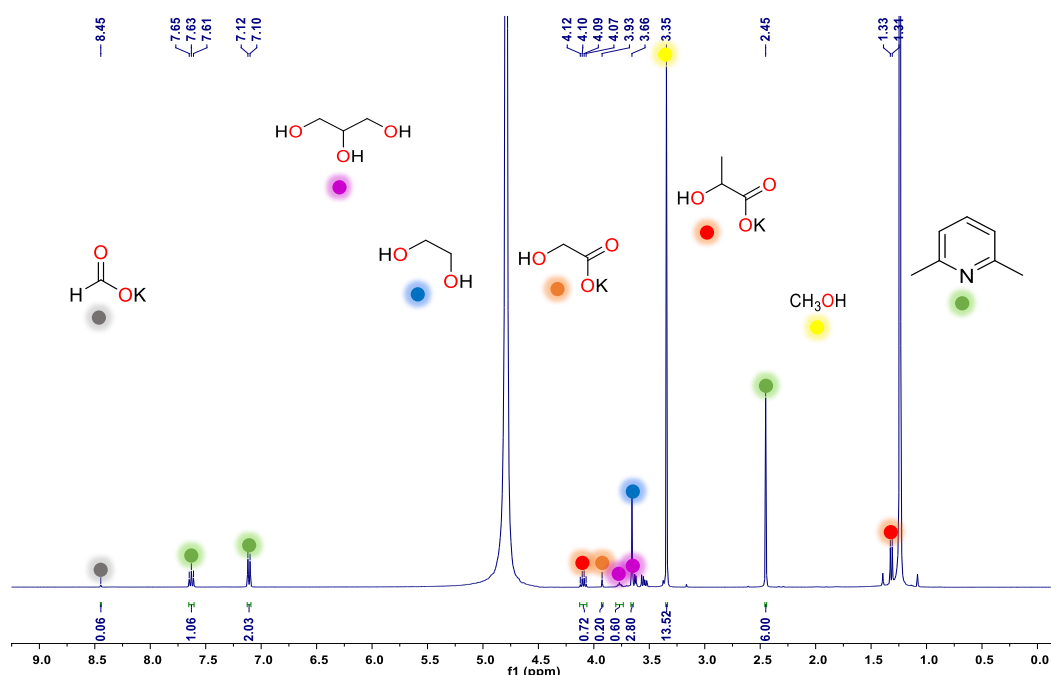
Figure S45. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol, and methanol mixture catalyzed by **1**(0.1 mol%), KOH (3.5 mmol), in ^{t}BuOH at 120 °C for 72 h (Table S3, entry 14).
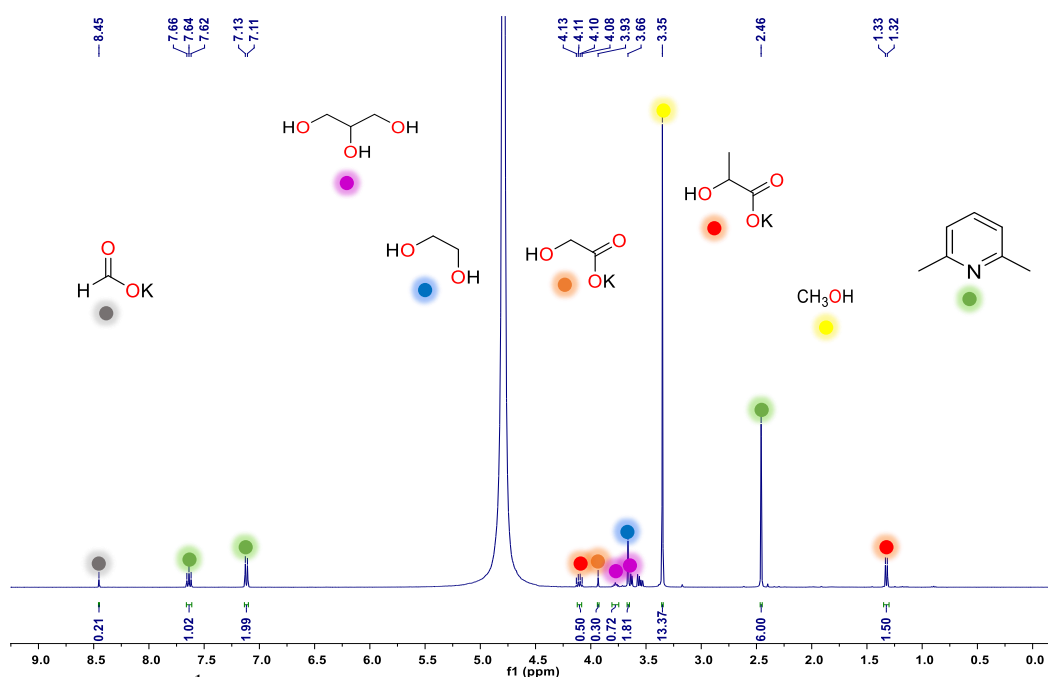

Figure S46. ^{1}H NMR spectrum of lactate formation from glycerol, ethylene glycol, and methanol mixture catalyzed by **1**(1 mol%), KOH (3.5 mmol), in neat at 120 °C for 72 h (Table S3, entry 15).
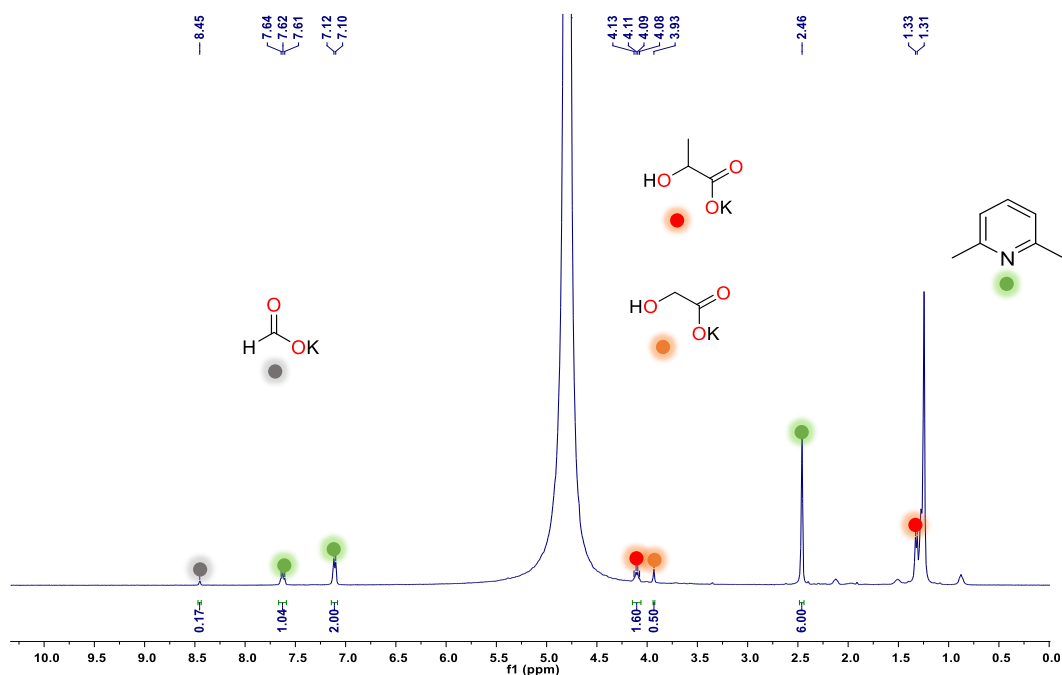
Figure S47. ^{1}H NMR spectrum of lactate formation from mixture of crude glycerol and ethylene glycol catalyzed by **1** (1 mol%), KOH (3.5 mmol) at 120 °C for 72 h (Table S3, entry 16)

Figure S48. ^{13}C NMR spectrum of lactate formation from mixture of crude glycerol and ethylene glycol catalyzed by **1** (1 mol%), KOH (3.5 mmol) at 120 °C for 72 h (Table S3, entry 16)
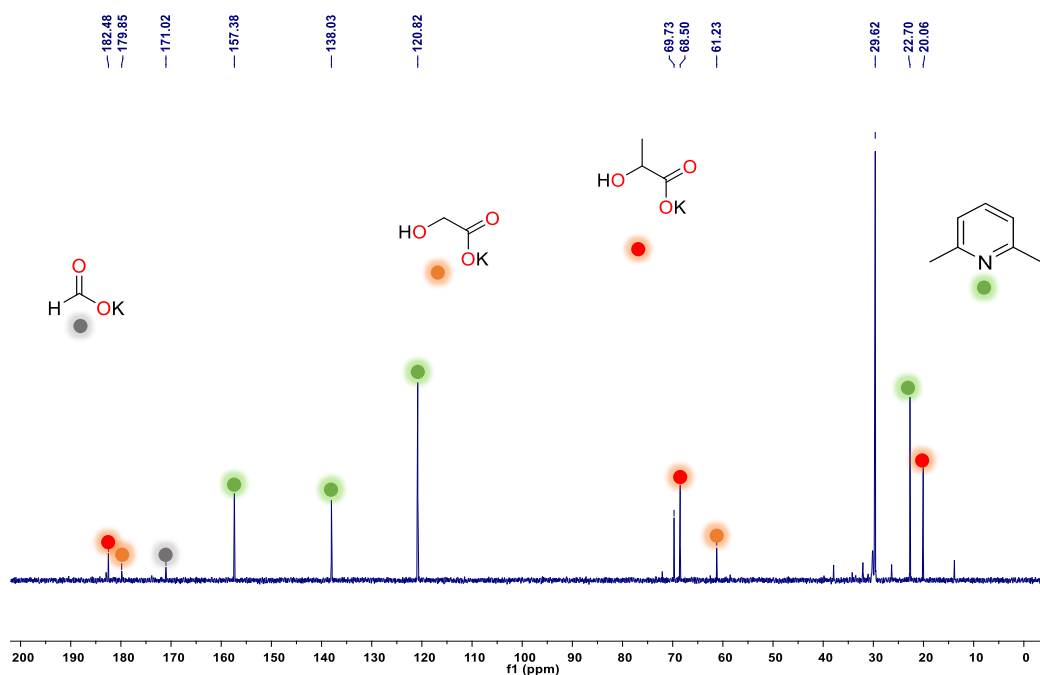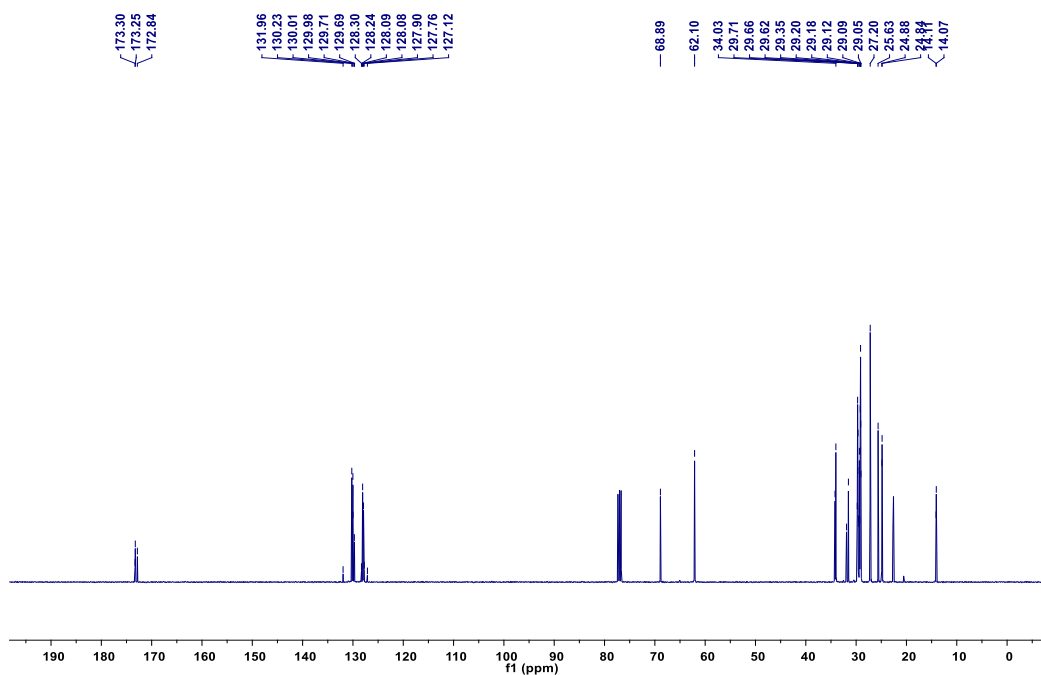
Figure S49. ^{1}H NMR spectrum of scale-up reaction of crude glycerol and ethylene glycol mixture to lactate formation catalyzed by **1** in D_2O (Table S3, entry 18). Reaction conditions: 7 mL crude glycerol (30 mmol), EG (30 mmol), KOH (105 mmol), and ^tBuOH (10 mL) at 120 °C for 72 h.

Figure S50. ^{1}H NMR spectrum of soyabean oil in $CDCl_3$.

Figure S51. ^{13}C NMR spectrum of soyabean oil in $CDCl_3$.
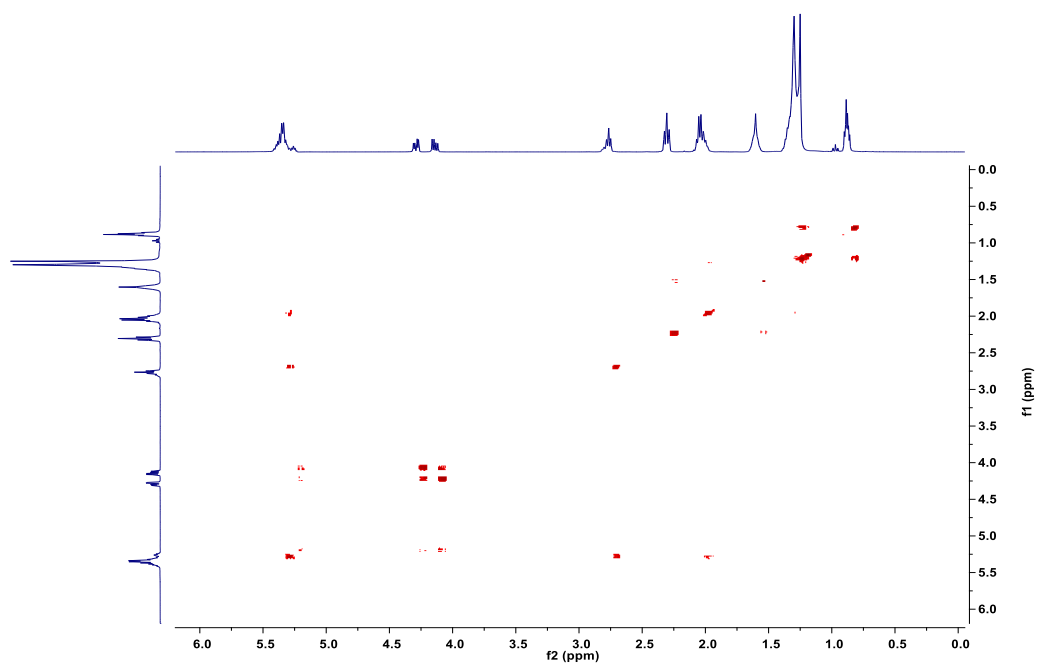
Figure S52. COSY NMR spectrum of soyabean oil in $CDCl_3$.
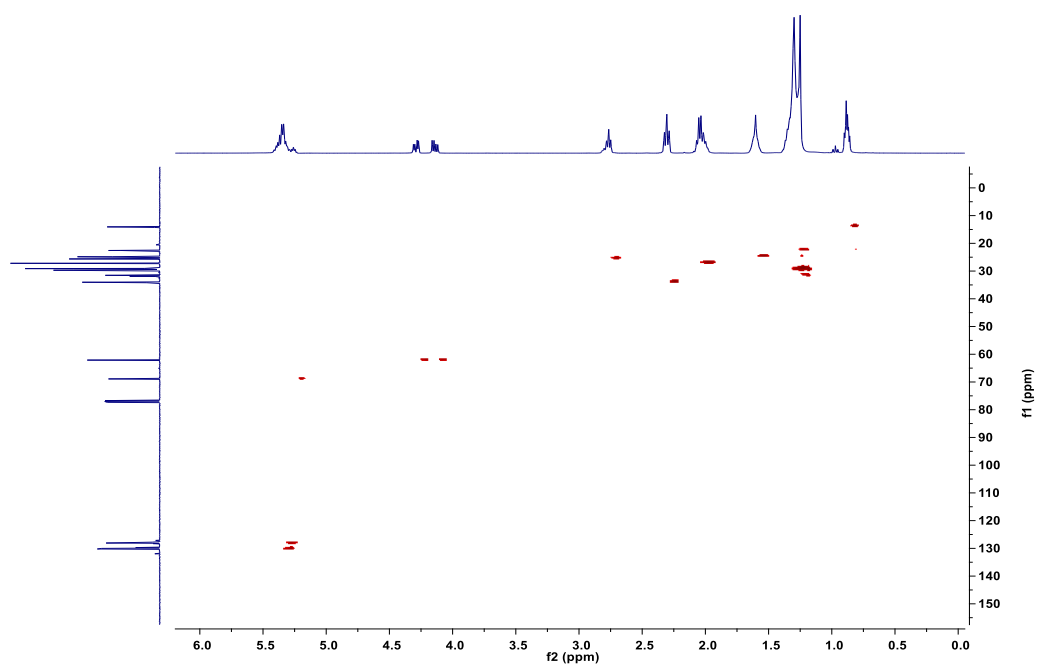
Figure S53. HSQC NMR spectrum of soyabean oil in CDCl$_3$.
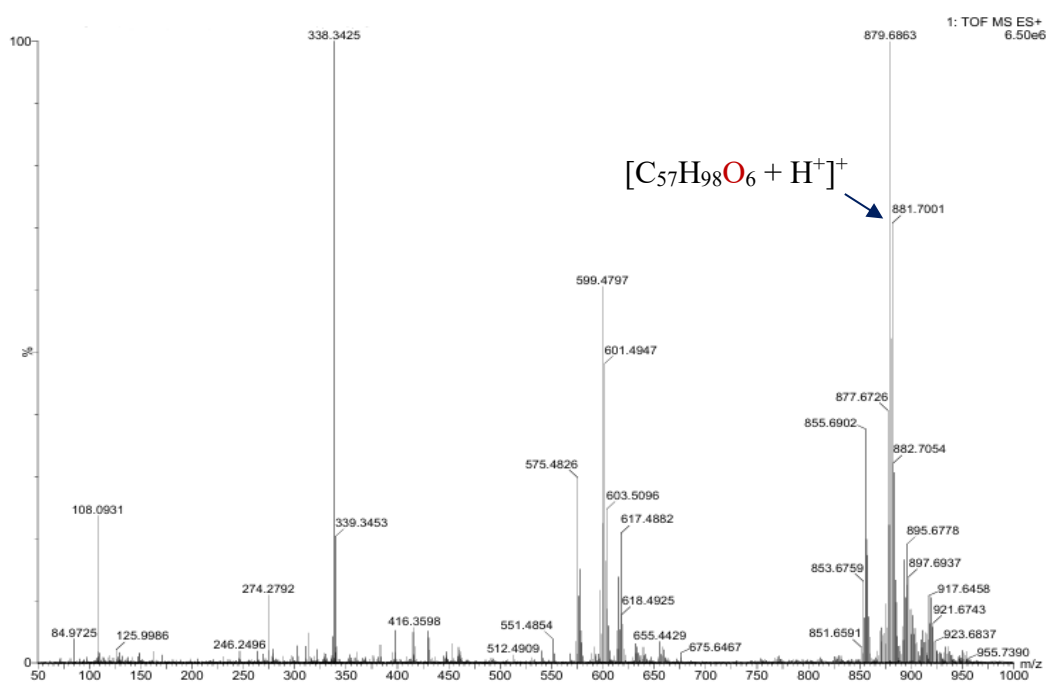

$[C_{57}H_{98}O_6 + H^+]^+$

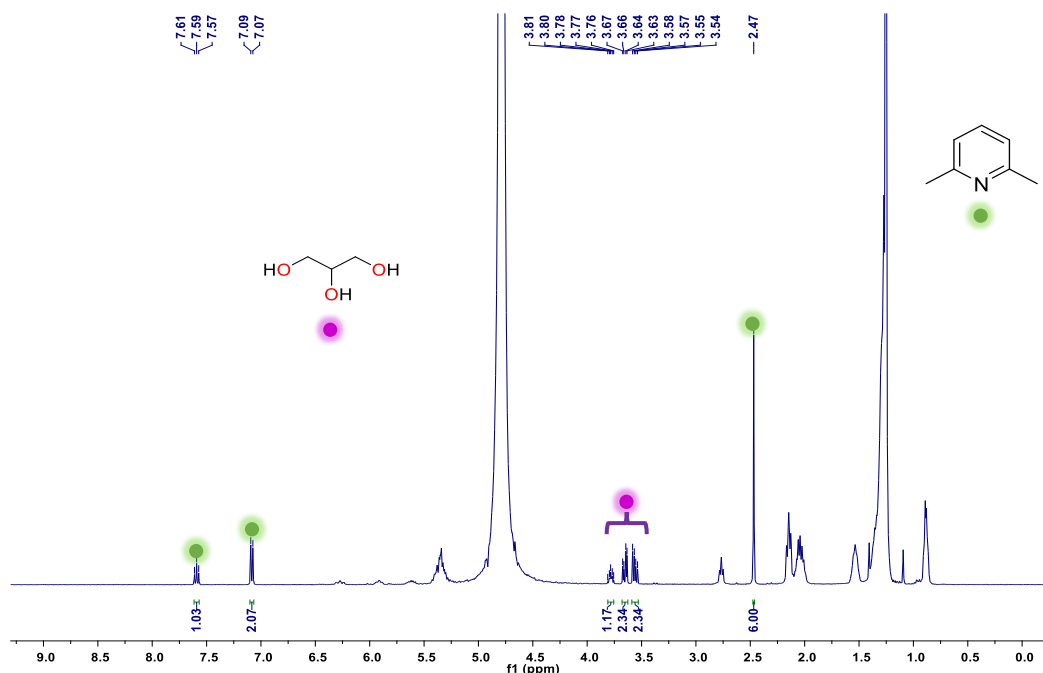**Figure S54.** +ve region HRMS data of soyabean oil

Figure S55. ^{1}H NMR spectrum of reaction of soyabean oil hydrolysis in the presence of KOH in D$_2$O. Reaction conditions: soyabean oil (891.5 mg), KOH (5 mmol), and ^{t}BuOH (1 mL) at 150 °C for 72 h.
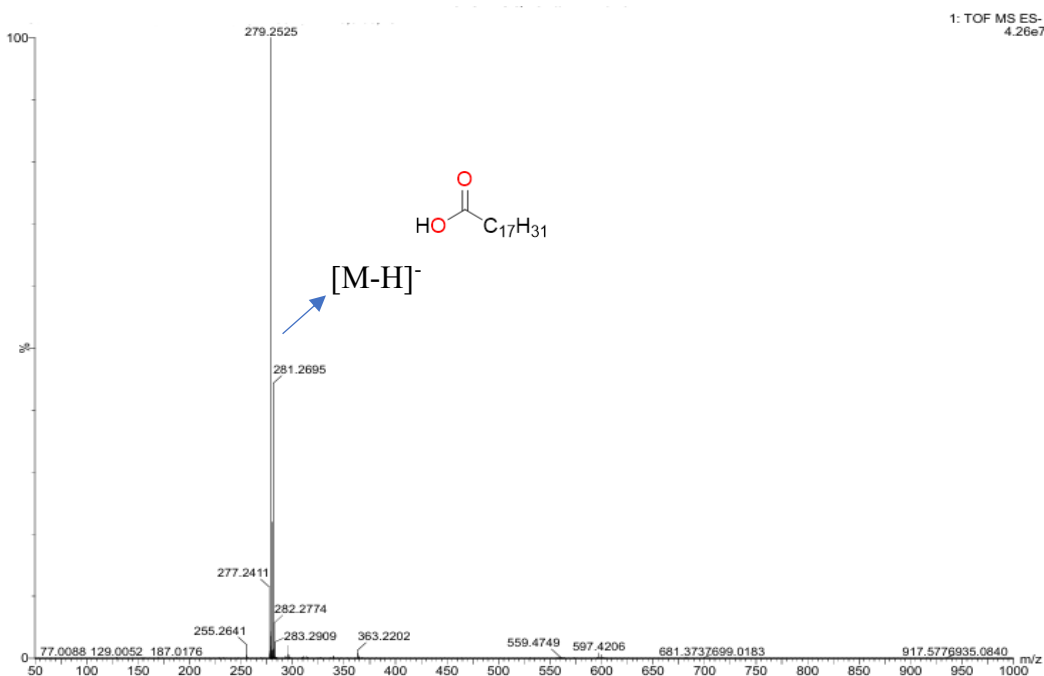

Figure S56. -ve region HRMS data of base-catalyzed hydrolysis of soyabean oil to glycerol and long-chain fatty acid. Reaction conditions: soyabean oil (891.5 mg, ~1.17 mmol), KOH (5 mmol), and ^{t}BuOH (1 mL) at 150 °C for 72
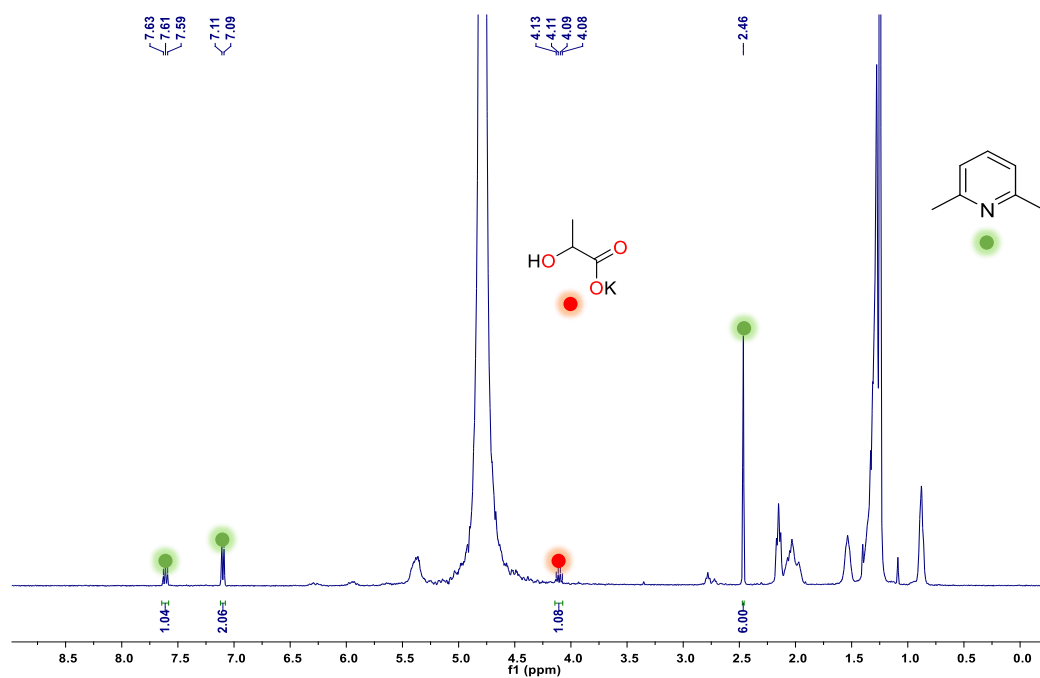
Figure S57. ^{1}H NMR spectrum of reaction of soyabean oil to lactate formation catalyzed by **1** in D$_2$O. Reaction conditions: 891.5 mg of soyabean oil (~1.17 mmol), **1** (0.01 mmol), KOH (5 mmol), and ^{t}BuOH (1 mL) at 150 °C for 72 h.
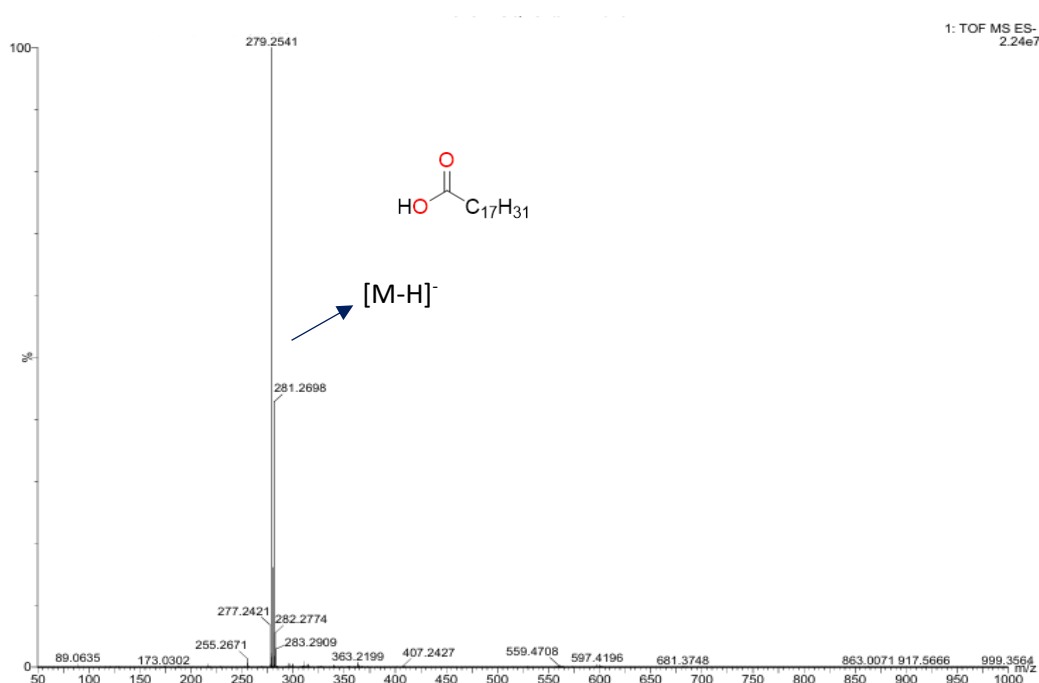

Figure S58. -ve region HRMS data of reaction of soyabean oil to lactate formation catalyzed by **1**. Reaction conditions: soyabean oil (891.5 mg, ~1.17 mmol), **1** (0.01 mmol), KOH (5 mmol), and ^{t}BuOH (1 mL) at 150 °C for 72 h.

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