Electronic Supplementary Information for

Iridium(NHC)-Catalyzed Sustainable Transfer Hydrogenation of CO_2 and Inorganic Carbonates

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I. Experimental procedure

General Procedure. Commercially available reagents were received from Sigma Aldrich and TCI. Catalysts **1**, **1′**, **2**, **2′**, **3**, and **3′** were prepared as described in the literature.[1] Low resolution mass spectra were obtained with a magnetic sector-electric sector double focusing mass analyzer equipment. Gas chromatograph (GC) (YL6500 GC, YOUNGLIN) equipped with a column (60/80 Carboxen-1000, 1.5 ft.) was operated at an Ar carrier gas flow rate of 30 sccm. X-ray structure was obtained by Rigaku R-axis Rapid S diffractometer. pH was measured by pH meter (Starter 3100, Ohaus corporation) at 25 °C.

Catalytic procedure of transfer hydrogenation of CO_2.

CO_2 (5 bar), KOH (40 mmol), H_2O (1.0 ml), catalysts (0.35 ppm based on the amount of iridium ion), and glycerol (21.1 mmol) were added into an autoclave. The mixture was heated at 200 °C for 20 h. Then, the reaction mixture was cooled down to ambient temperature, and diluted with H_2O. The amount of formate and lactate (mmol) were calculated by ^1H NMR spectroscopy in D_2O using isonicotinic acid as an internal standard. The reactions were run three times, and the average numbers of mmol were used. The ‘mmol’ of each product was divided by ‘mmol’ of catalysts to give TONs. The resulting TONs are divided by the reaction time (h) to afford TOFs.

Catalytic procedure of transfer hydrogenation of inorganic carbonate.

Inorganic carbonate (K_2CO_3, $KHCO_3$, and Na_2CO_3, 40 mmol), H_2O (2.0 ml), catalysts (0.35 ppm based on the iridium ion concentration), and glycerol (42.3 mmol) were added into an autoclave. In case of Cs_2CO_3, H_2O (3 ml) was used for stirring. The mixture was heated at 200 °C for 20 h. Then, the reaction mixture was cooled down to ambient temperature, and diluted with H_2O. The amount of formate and lactate (mmol) were calculated by ^1H NMR spectroscopy in D_2O using isonicotinic acid as an internal standard. The reactions were run three times, and the average numbers of mmol were used. The ‘mmol’ of each product was divided by mmol of catalysts to give TONs. The resulting TONs are divided by the reaction time (h) to afford TOFs.

[1] Cheong, Y.-J.; Sung, K.; Kim, J.-A.; Kim, Y. K.; Jang, H.-Y. Highly efficient iridium-catalyzed production of hydrogen and lactate from glycerol: rapid hydrogen evolution by bimetallic iridium catalysts. *Eur. J. Inorg. Chem.* **2020**, 4064-4068.

II. NMR spectra of carbonate

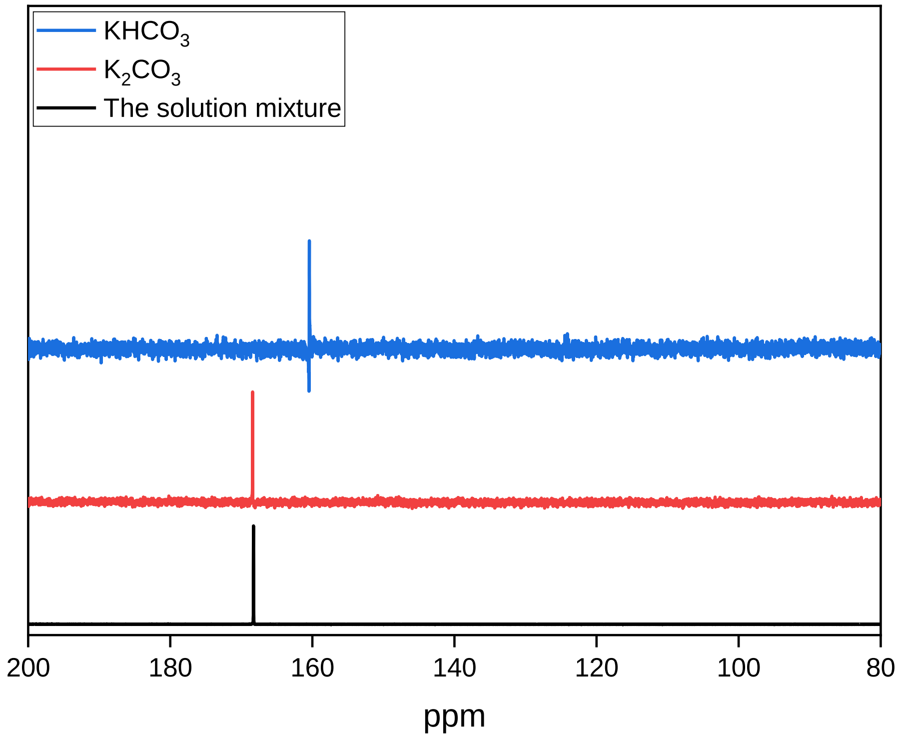


Figure S1. [13]C NMR spectrum of the mixture of CO_2 (5 bar) and KOH in glycerol (line black), $KHCO_3$ (Line Blue) and K_2CO_3 (Line Red).

III. Residual gas analysis

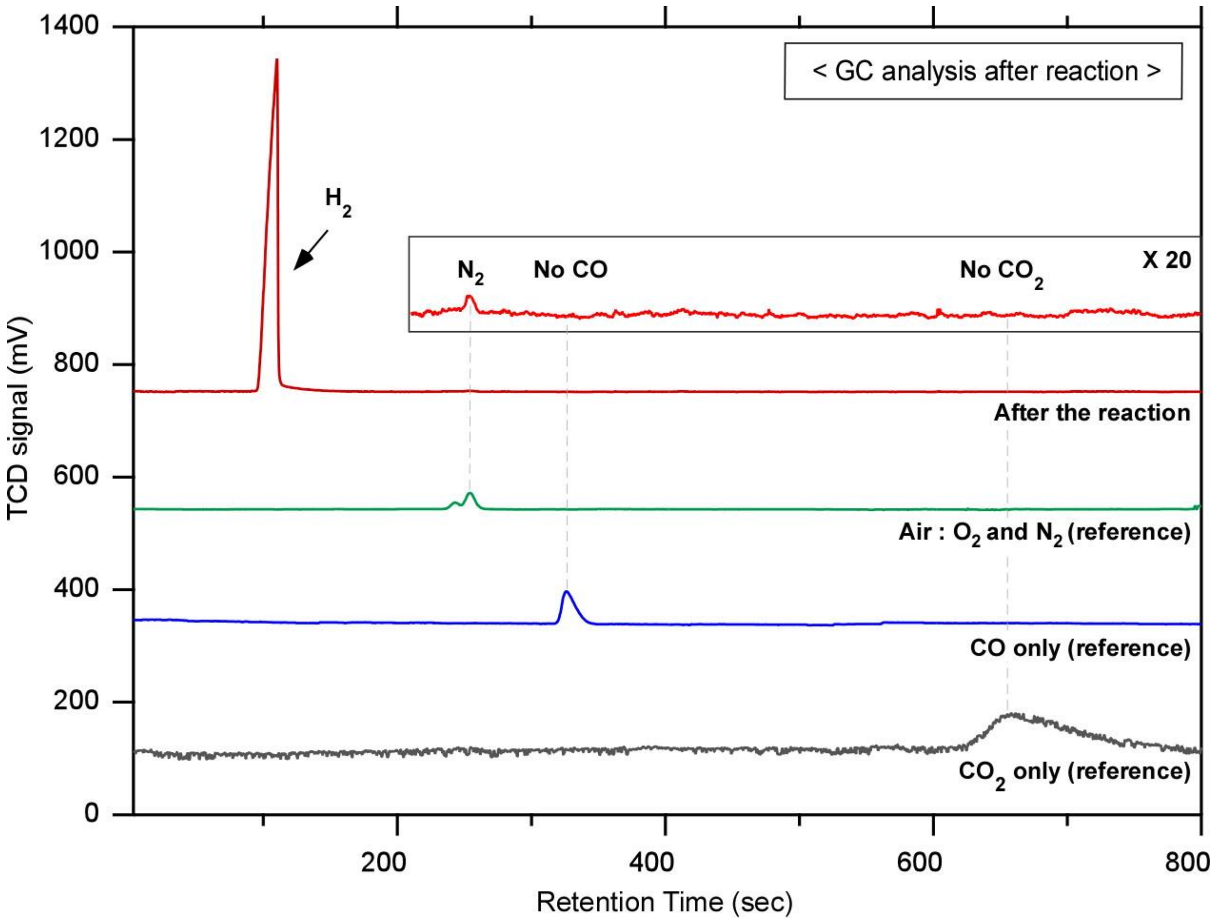
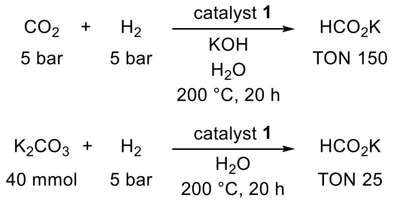


Figure S2. The GC (gas chromatography) spectrum of the gas obtained from the reaction of CO_2 and glycerol (Table 1, entry 6). Only H_2 generated by dehydrogenation of glycerol was identified and CO_2 was not detected.

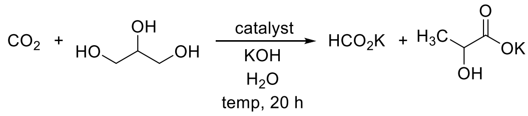
IV. Ir(NHC)-catalyzed hydrogenation of CO_2 and K_2CO_3



Scheme S1 The hydrogenation reaction of CO_2 and K_2CO_3. The pressure of H_2 (5 bar) was determined based on the observed H_2 pressure of transfer hydrogenation using glycerol. The reaction of CO_2 and H_2 was run with catalysts **1** (3.5×10^{-4} mol%), and the hydrogenation reaction of K_2CO_3 was run with catalysts **1** (7.5×10^{-4} mol%).

V. Transfer hydrogenation results including yields

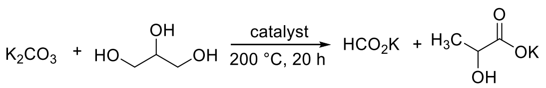
Table S1. Transfer hydrogenation of CO_2 in glycerol



entry	catalyst (mol%)	CO_2 (bar)	KOH (mmol)	temp (°C)	formate (TON, TOF h^{-1})	lactate (TON, TOF h^{-1})	lactate (%)
1	**1** (3.5*10^{-4})	5	20	180	3,360, 168	3,900, 195	1.3
2	**1** (3.5*10^{-4})	5	40	180	1,490, 74.5	23,800, 1,190	7.9
3	**1** (3.5*10^{-4})	5	40	200	15,800, 790	73,900, 3,700	24.5
4	**1** (3.5*10^{-4})	1	40	200	2,110, 106	104,000, 5,200	34.6
5	**1** (3.5*10^{-4})	10	40	200	12,700, 635	14,400, 720	4.7
6	**1** (3.5*10^{-5})	5	40	200	200,000, **10,000**	875,000, **43,800**	29.0
7	**1'** (1.75*10^{-5})[a]	5	40	200	77,400, **3,870**	534,000, **26,700**	17.7
8	**2** (3.5*10^{-5})	5	40	200	176,000, **8,800**	753,000, **37,700**	25.0
9	**2'** (1.75*10^{-5})[a]	5	40	200	70,400,**3,520**	548,000, **27,400**	16.2
10	**3** (3.5*10^{-5})	5	40	200	174,000, **8,700**	683,000, **34,200**	22.8
11	**3'** (1.75*10^{-5})[a]	5	40	200	103,000, **5,150**	414,000, **20,700**	13.7
12	**1** (3.5*10^{-5})	5	--	200	--	--	--
13	--	5	40	200	0.06 mmol	0.4 mmol	2.0

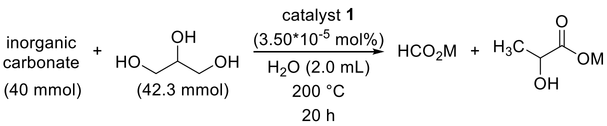
The mixture of catalysts, CO_2, KOH, and H_2O (1.0 ml) in glycerol (21.1 mmol) was heated at indicated temperature for 20 h. [a]Catalysts **1'**, **2'** and **3'** have two iridium ions in the molecule.

Table S2. Transfer hydrogenation of K_2CO_3 in glycerol



entry	catalyst (mol%)	formate (TON, TOF h^{-1})	formate (%)	lactate (TON, TOF h^{-1})	lactate (%)
1	**1** (3.50*10^{-5})	203,000, **10,150**	7.6	414,000, **20,700**	15
2	**1'** (1.75*10^{-5})[a]	163,000, **8,150**	6.1	357,000, **17,850**	12
3	**2** (3.50*10^{-5})	149,000, **7,450**	5.6	315,000, **15,800**	11
4	**2'** (1.75*10^{-5})[a]	178,000, **8,900**	6.7	342,000,**17,100**	12
5	**3** (3.50*10^{-5})	164,000, **8,200**	6.1	326,000, **16,300**	12
6	**3'** (1.75*10^{-5})[a]	195,000, **9,750**	7.3	400,000, **20,000**	14

The mixture of catalysts, K_2CO_3 (40 mmol), and glycerol (42.3 mmol) in H_2O (2 mL) was heated at 200 °C for 20 h. [a]Catalysts **1'**, **2'** and **3'** have two iridium ions in the molecule.



inorganic carbonate	pH	formate (TON, TOF h^{-1})	formate (%)	lactate (TON, TOF h^{-1})	lactate (%)
K_2CO_3	12.0	203,000, **10,150**	7.6	414,000, **20,700**	14.5
$KHCO_3$	8.6	54,000, **2,700**	2.0	57,300, **2,870**	2.0
Na_2CO_3	11.3	14,500, **725**	0.5	53,100, **2,660**	1.9
Cs_2CO_3[a]	12.0	145,000, **7,250**	5.4	191,000, **9,600**	6.8

[a]H_2O (3 mL) was added.

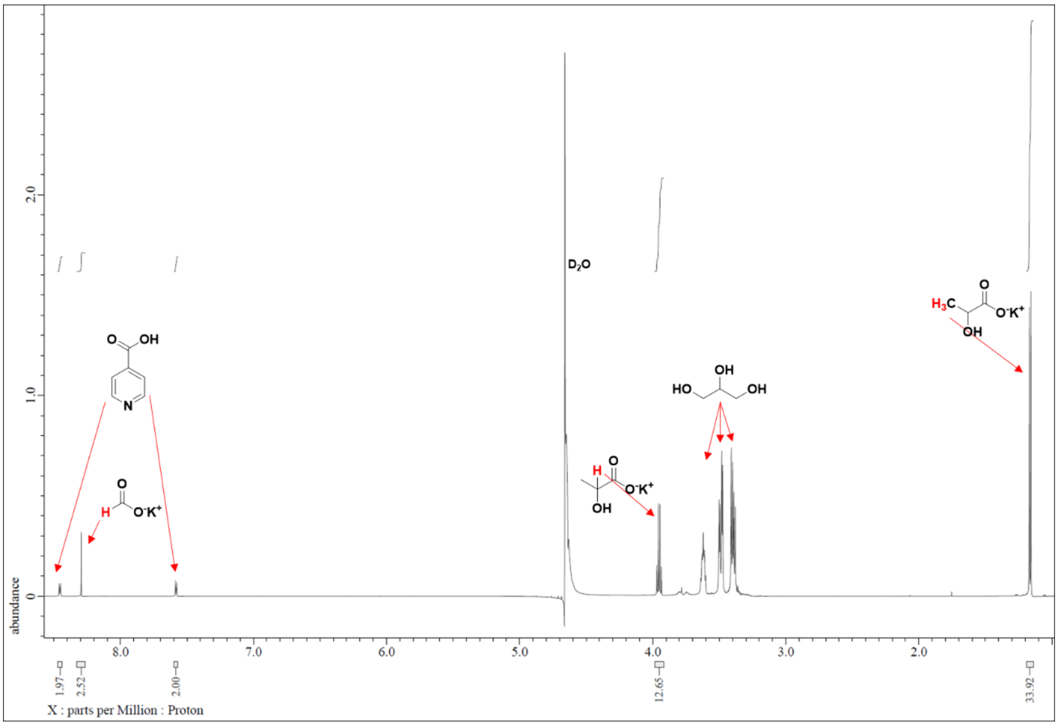
Scheme S2 Transfer hydrogenation of inorganic carbonate in glycerol

VI. Representative ^{1}H spectra of the reaction mixtures

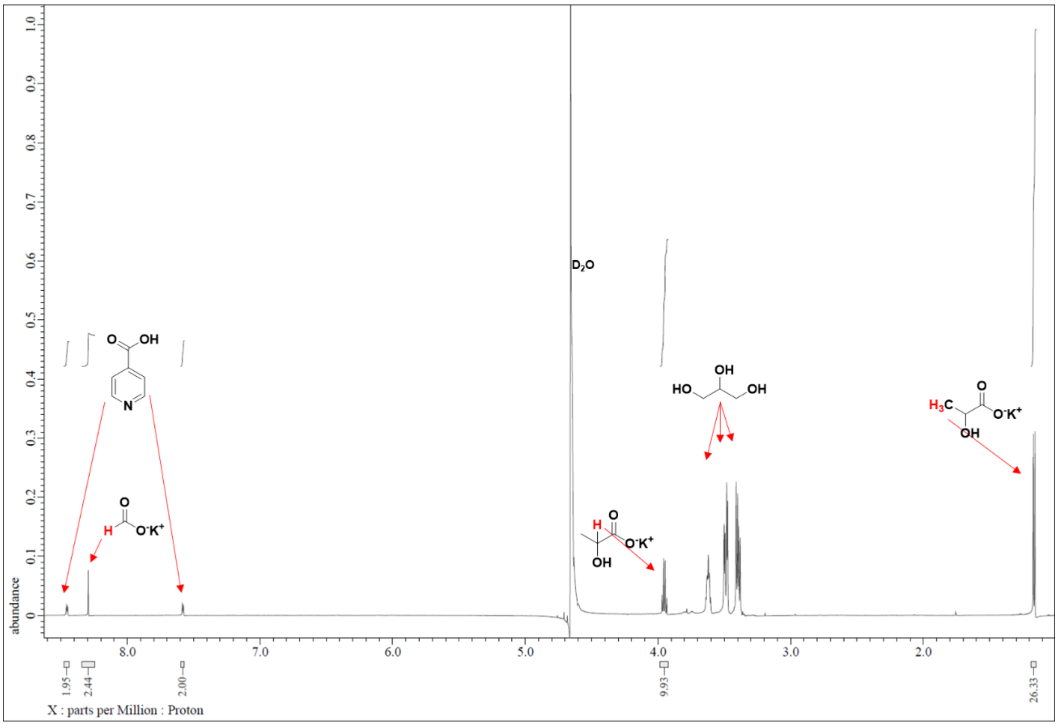
Determination of yields of formate and lactate by ^{1}H NMR

The reaction mixture was diluted with H_2O (total volume is 40 ml). Isonicotinic acid (70 mg, 0.57 mmol) as an internal standard was added to the diluted solution. The 0.45 ml of the diluted solution and 0.15 ml of D_2O were mixed for NMR analysis. The moles of the products were calculated by integration values of the signature peak of each product based on moles of the internal standard.

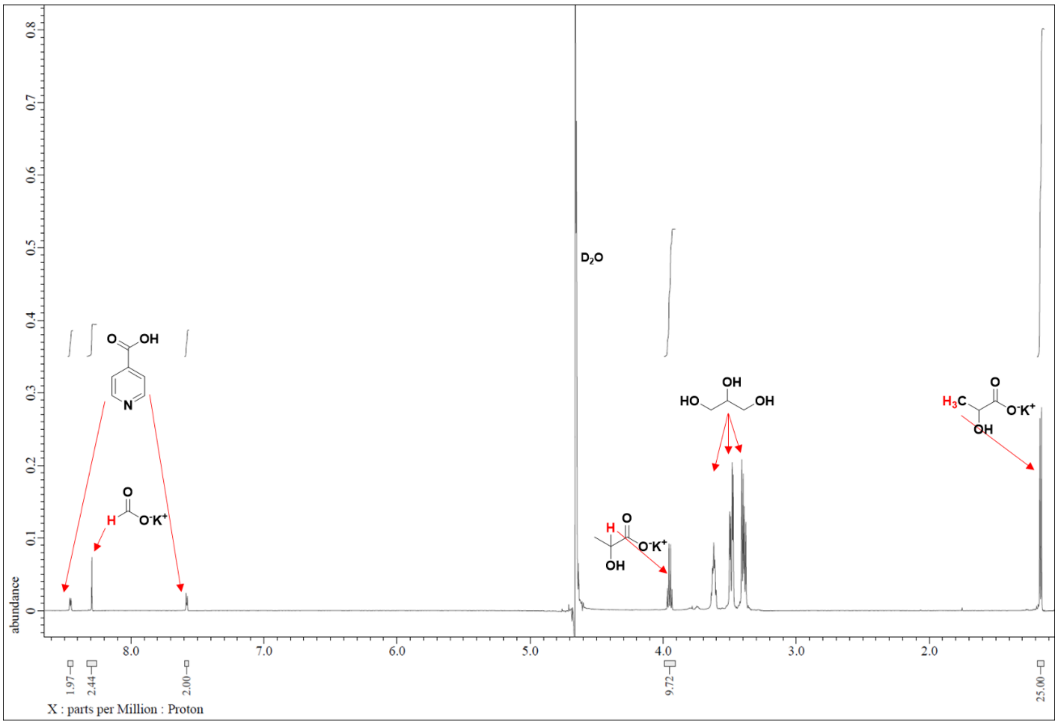
Entry 6 of Table 1 (formate TON_{avg} = 200,000, lactate TON_{avg} = 875,000)



Formate TON = 205,000, lactate TON = 1,030,000

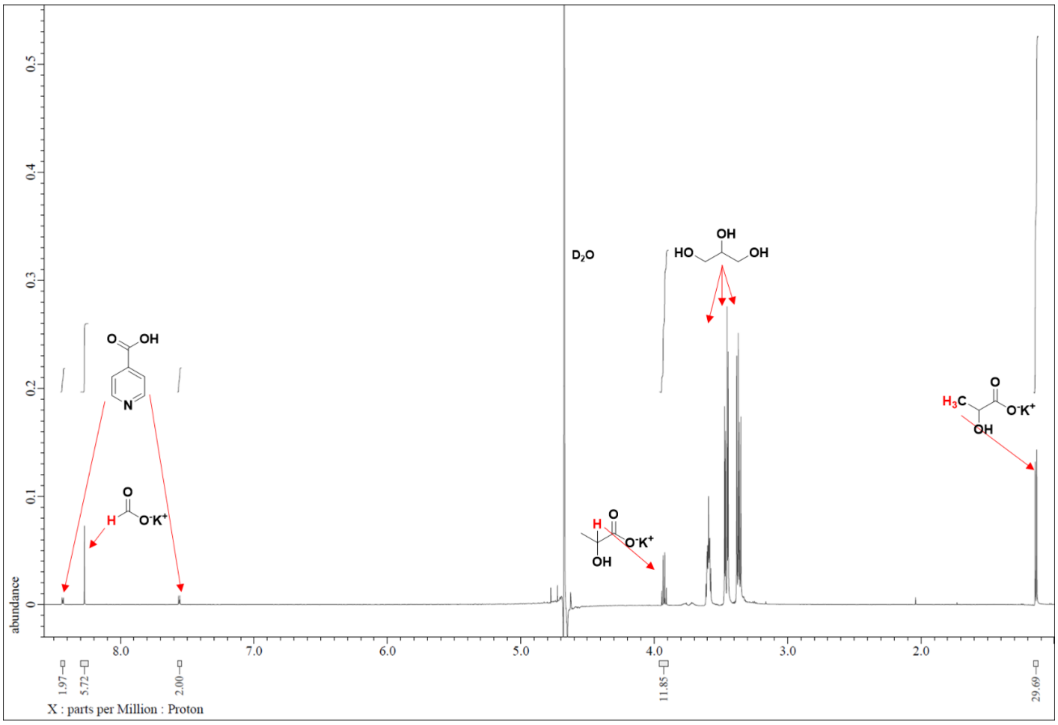


Formate TON = 198,000, lactate TON = 807,000

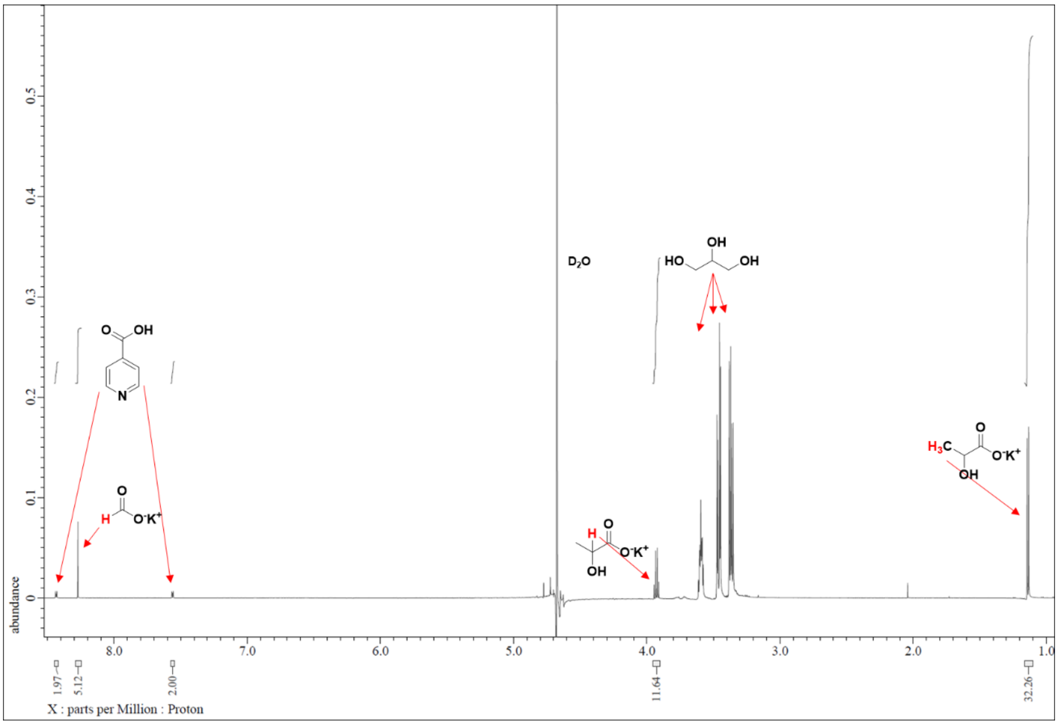


Formate TON = 198,000, lactate TON = 790,000

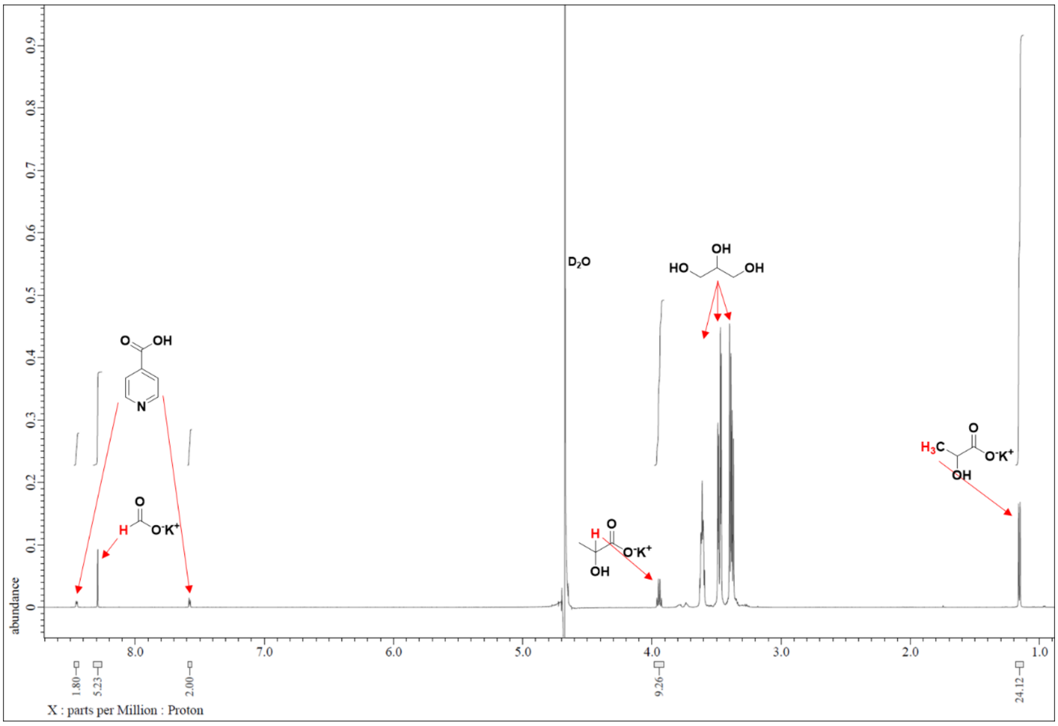
Entry 1 of Table 2 (formate TON_{avg} = 203,000, lactate TON_{avg} = 414,000)



Formate TON = 217,000, lactate TON = 449,000

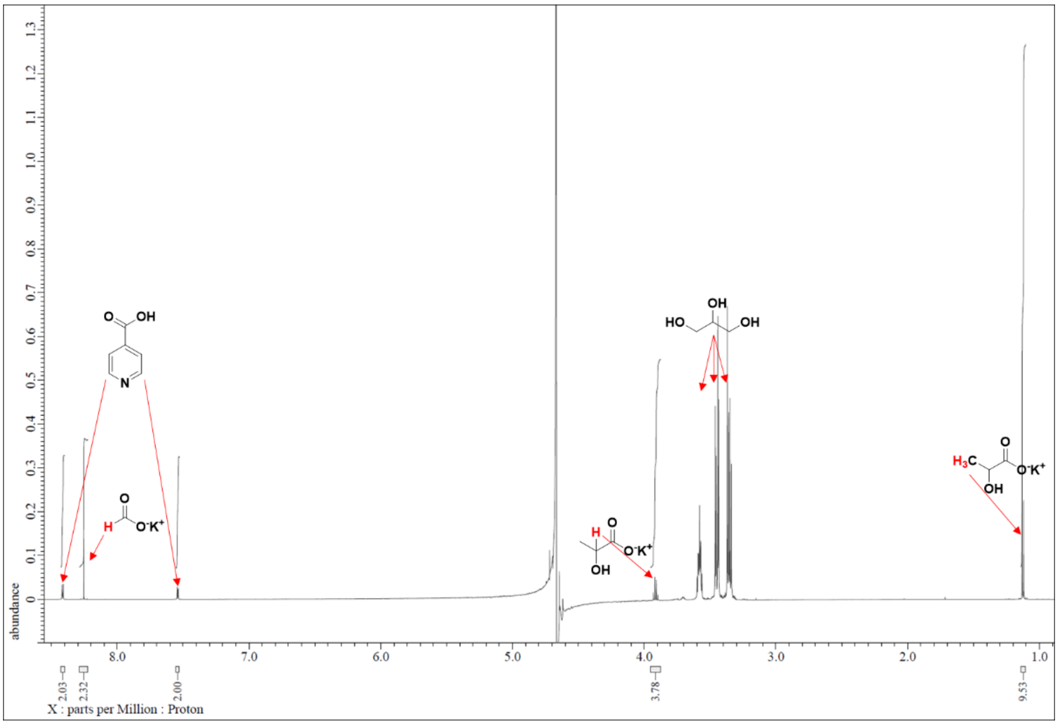


Formate TON = 194,000, lactate TON = 357,000

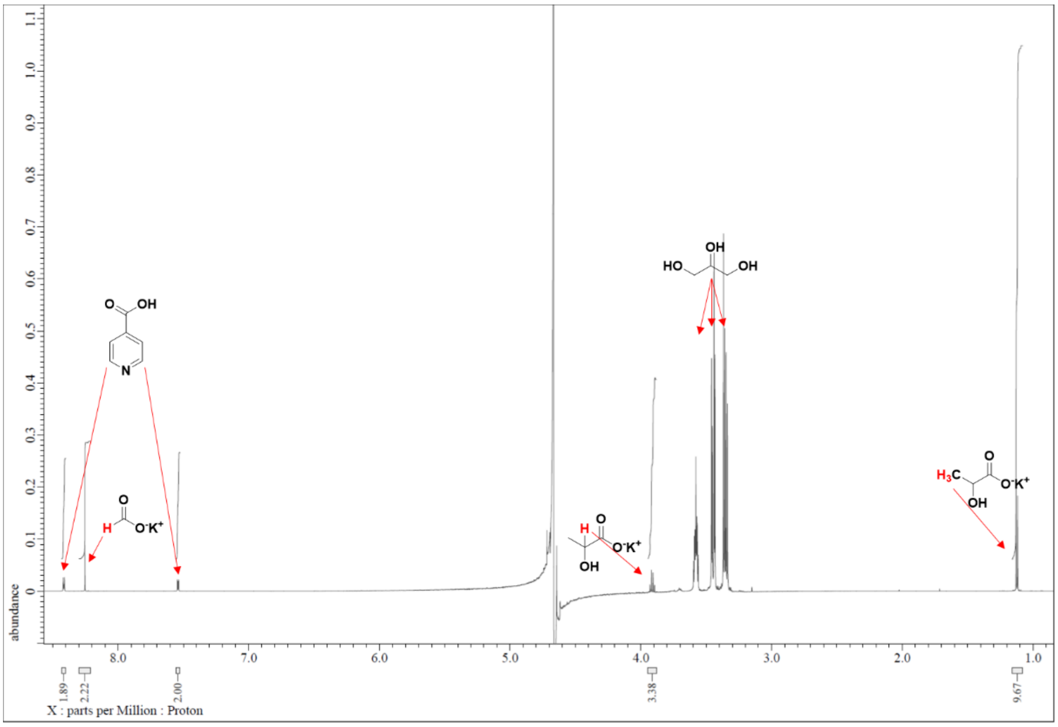


Formate TON = 198,000, lactate TON = 351,000

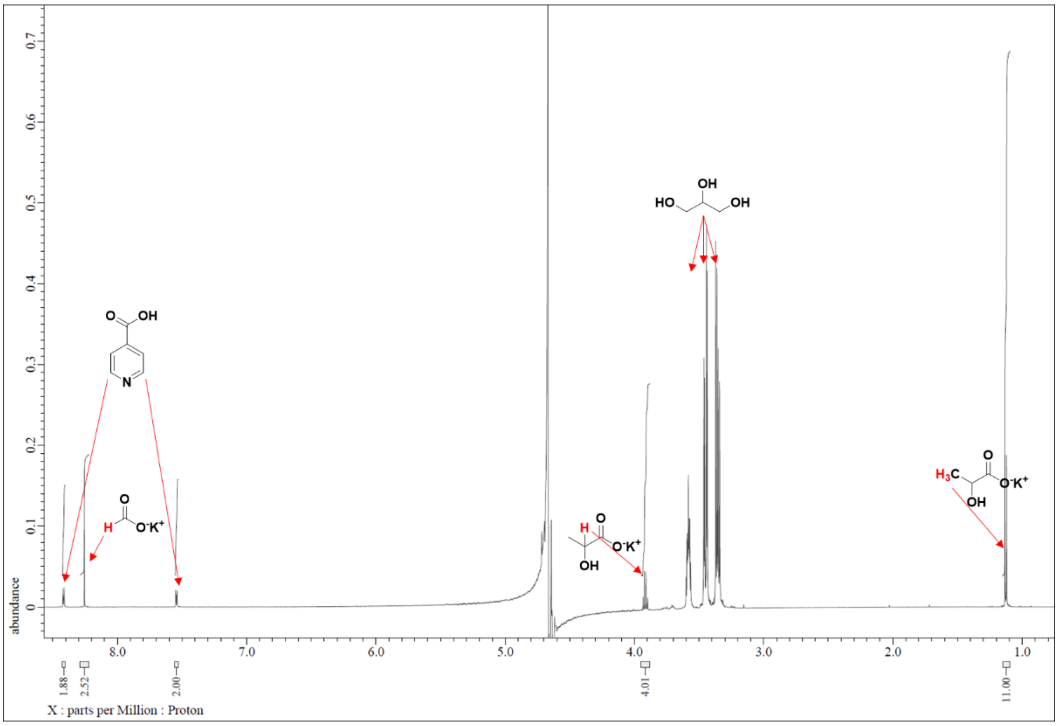
Entry 2 of Table 3 (formate TON_{avg} = 191,000, lactate TON_{avg} = 302,000)



Formate TON = 188,000, lactate TON = 307,000



Formate TON = 180,000, lactate TON = 275,000



Formate TON = 205,000, lactate TON = 326,000