

Electronic Supplementary Information for

**Iridium(triNHC)-Catalyzed Sustainable Transfer Hydrogenation of Glycerol Carbonate
without Exogeneous Reductants**

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I. Experimental Procedures

General Procedure. The $[\text{Ir}(\text{COD})\text{Cl}]_2$ was used as received from Strem chemicals, Inc. All commercially available reagent were obtained from Sigma Aldrich and TCI. Catalyst A, B, C and D was prepared as described in the literature procedures.¹ Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a JEOL Resonance ECZ600R (600 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of a singlet peak at 2.50 ppm for DMSO- d_6 . Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a JEOL Resonance ECZ600R (151 MHz). Chemical shift are reported in delta (δ) units, parts per million (ppm) relative to the center of a multiplet peak at 39.52 ppm for DMSO- d_6 . High resolution mass spectra were obtained with a magnetic sector-electric sector double focusing mass analyzer equipment. Melting points of the compounds were checked in open capillary and were uncorrected. Elemental analyses were performed by Flash 2000 (Thermo Scientific).

Synthetic Procedure for the catalyst E

1,1'-(1,4-Phenylene)bis(3-benzyl-1*H*-imidazol-3-ium) bromide (0.2 mmol, 1 equiv.) and Ag_2O (0.24 mmol, 1.2 equiv.) were dissolved in MeOH. The reaction mixture was stirred for 3 hours at room temperature. Then, the mixture was filtered with celite and filtrate was evaporated under vacuo. The residue, $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.2 mmol, 1 equiv.) and KPF_6 (0.5 mmol, 2.5 equiv.) were dissolved in MeCN. The reaction mixture was stirred for another 3 hours at room temperature under N_2 atmosphere. Then, the mixture was filtered with celite and filtrate was evaporated under vacuo. The catalyst E was obtained with 30 % yield as yellow solid.

Synthetic Procedure for the catalyst F

1-Phenyl-3-(pyridine-2-ylmethyl)-1*H*-imidazol-3-ium bromide (0.35 mmol, 1 equiv.) and Ag_2O (0.175 mmol, 0.5 equiv.) was dissolved in CH_2Cl_2 (0.05 M) under N_2 atmosphere. The reaction mixture was stirred for 2 hours at room temperature. Then, the mixture was filtered with celite. $[\text{IrCp}^*\text{Cl}_2]_2$ (0.175 mmol, 0.5 equiv.) and KPF_6 (0.7 mmol, 2.01 equiv.) were added to this residue and stirred for another 2 hours at room temperature under N_2 atmosphere. The reaction mixture was filtered with celite and wash with CH_2Cl_2 . The filtrate was evaporated and dried under vacuo. The catalyst F was obtained with 88 % yield as yellow solid.

Catalytic procedure

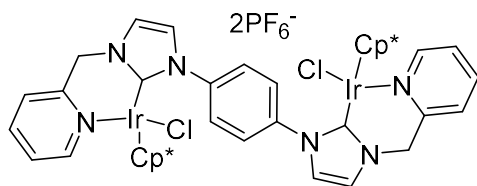
The catalyst (monometallic complexes 1 μmol and bimetallic complexes 0.5 μmol), glycerol carbonate (10.6 mmol), $\text{CsOH}\cdot\text{H}_2\text{O}$ (21.2 mmol) and NMP (10 ml) were put into an autoclave. The mixture was stirred at 200 $^\circ\text{C}$ for 20 hours. Then, the reaction mixture was cooled down to ambient temperature, and diluted with H_2O . The TONs of formates and lactates were calculated by ^1H NMR spectroscopy in D_2O using isonicotinic acid as an internal standard. The mole numbers of each product were calculated by comparing ^1H NMR integration values of the internal standard. Then, the mole numbers of each product were divided by the mole numbers of iridium ions to afford TONs.

¹ (a) Cheong, Y.-J.; Sung, K.; Kim, J.; Kim, Y. K.; and Jang, H.-Y. *Eur. J. Inorg. Chem.* **2020**, 4064. (b) Cheong, Y.-J.; Sung, K.; Park, S.; Jung, J.; and Jang, H. -Y. *ACS Sustainable Chem. Eng.* **2020**, 8, 6972. (c) Sharninghausen, L. S.; Campos, J.; Manas, M. G.; Crabtree, R. H. *Nat Commun* **2014**, 5, 5084.

Gas analysis

Gaseous products were analyzed using a Shimadzu Nexis GC-2030 gas chromatograph equipped with a barrier discharge ionization detector. The measurement of a gas-phase sample generated a chromatogram consisting of peaks associated with H₂, air (i.e., O₂ and N₂), and CO₂. Areas of these peaks were integrated by the instrument software, followed by conversion to the moles by taking into account the calibration constant for each species. In the case of CO₂, the peak contribution of CO₂ present in the air was removed from the total peak of CO₂ measured due to the reaction performed in the ambient conditions. The number of moles of product in the sampled volume for the measurement was multiplied by the ratio of the headspace volume to the sampled volume to yield the actual amount of product in the headspace.

II. Spectral data of E and F



Catalyst E

¹H NMR (DMSO-d₆, 600 MHz) δ 8.88 (d, *J* = 4.8 Hz, 2H), 8.18-8.15 (m, 6H), 7.91 (d, *J* = 2.1 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 2.1 Hz, 2H), 7.63 (t, *J* = 6.2 Hz, 2H), 5.76 (d, *J* = 15.8 Hz, 2H), 4.89 (d, *J* = 15.1 Hz, 2H), 1.40 (s, 30H)

¹³C NMR (DMSO-d₆, 151 MHz) δ 157.0, 154.8, 154.4, 140.7, 139.1, 127.7, 126.7, 125.2, 125.2, 123.4, 91.0, 54.2, 8.7

HRMS *m/z* (FAB, [M-PF₆]⁺) : calcd for C₄₄H₅₀N₆Cl₂Ir₂PF₆ 1263.2375, found 1263.2377

EA calculated for C₄₄H₅₀N₆Ir₂Cl₂P₂F₁₂ (wt 1408.19) C, 37.529; H, 3.579; N, 5.968 found C, 37.2819; H, 3.7631; N, 6.6047

Mp decomposed at 300 °C

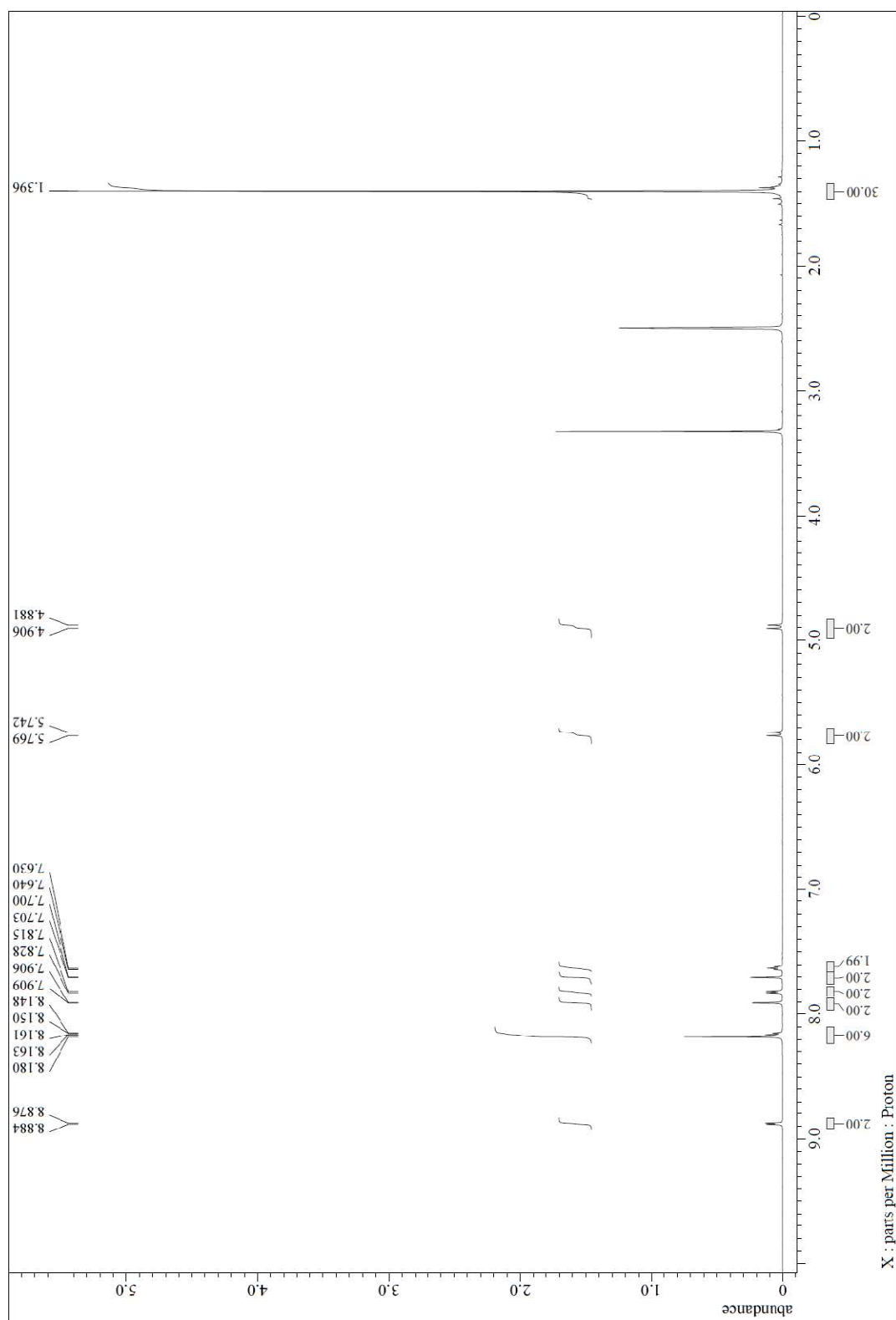


Figure S1. ^1H NMR spectra of catalyst **E**

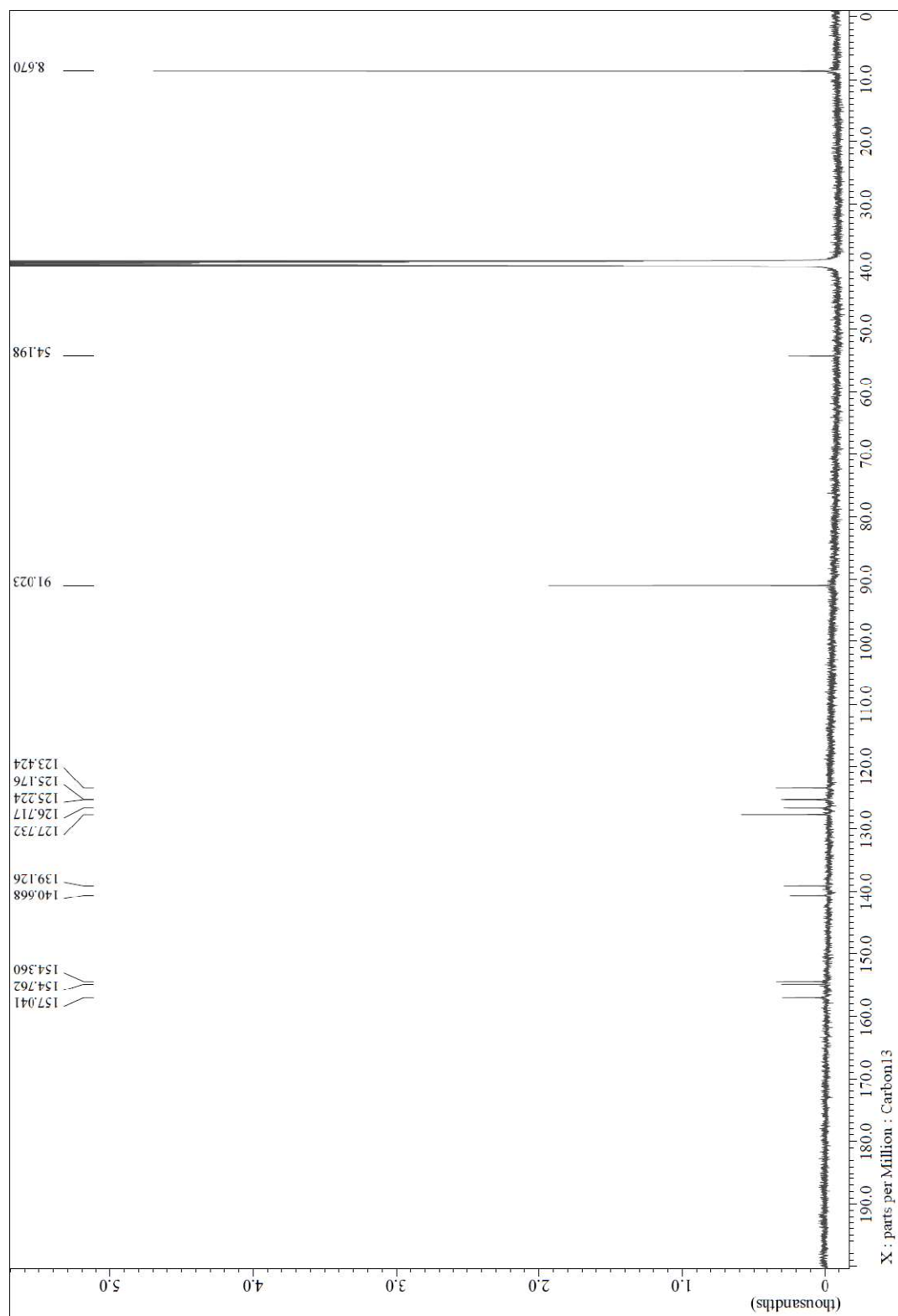
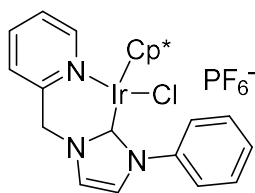


Figure S2. ^{13}C NMR spectra of catalyst **E**



Catalyst F

¹H NMR (DMSO-*d*₆, 600 MHz) δ 8.88 (dd, *J* = 5.5, 1.4 Hz, 1H), 8.14 (td, *J* = 7.9, 1.5 Hz, 1H), 7.96 (m, 2H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.62-7.60 (m, 1H), 7.57-7.53 (m, 3H), 5.72 (d, *J* = 15.8 Hz, 1H), 4.87 (d, *J* = 15.8 Hz, 1H), 1.32 (s, 15H)

¹³C NMR (DMSO-*d*₆, 151 MHz) δ 157.1, 154.4, 140.5, 138.8, 129.1, 128.8, 127.7, 126.6, 125.3, 125.0, 123.0, 90.8, 54.0, 8.5

HRMS *m/z* (FAB, [M-PF₆]⁺) : calcd for C₂₅H₂₈N₃ClIr 598.1601, found 598.1604

EA calculated for C₂₅H₂₈N₃IrClPF₆ (wt 743.152) C, 40.406; H, 3.798; N, 5.654 found C, 40.3011; H, 3.7075; N, 5.7049

Mp decomposed at 185 °C

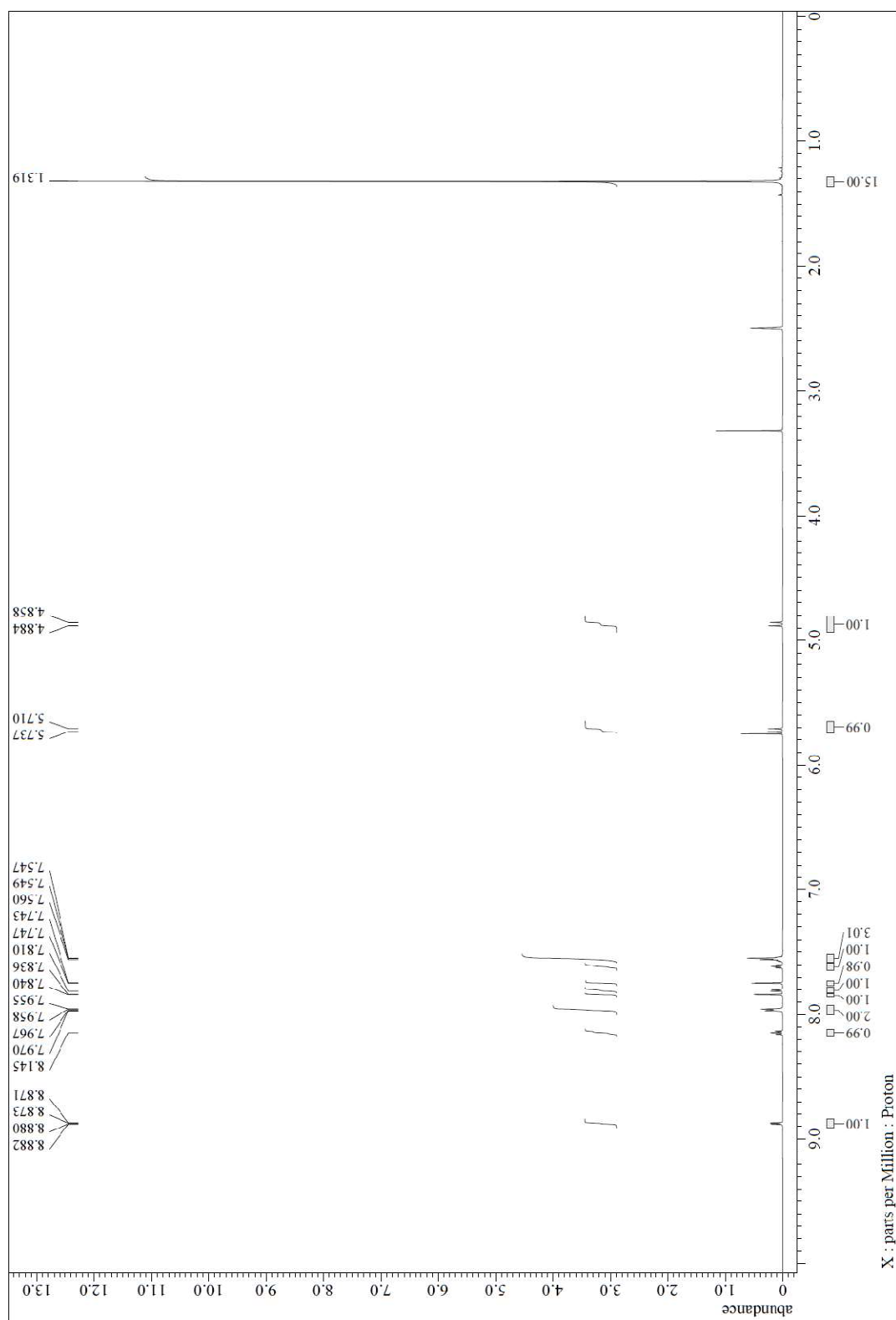


Figure S3. ^1H NMR spectra of catalyst **F**

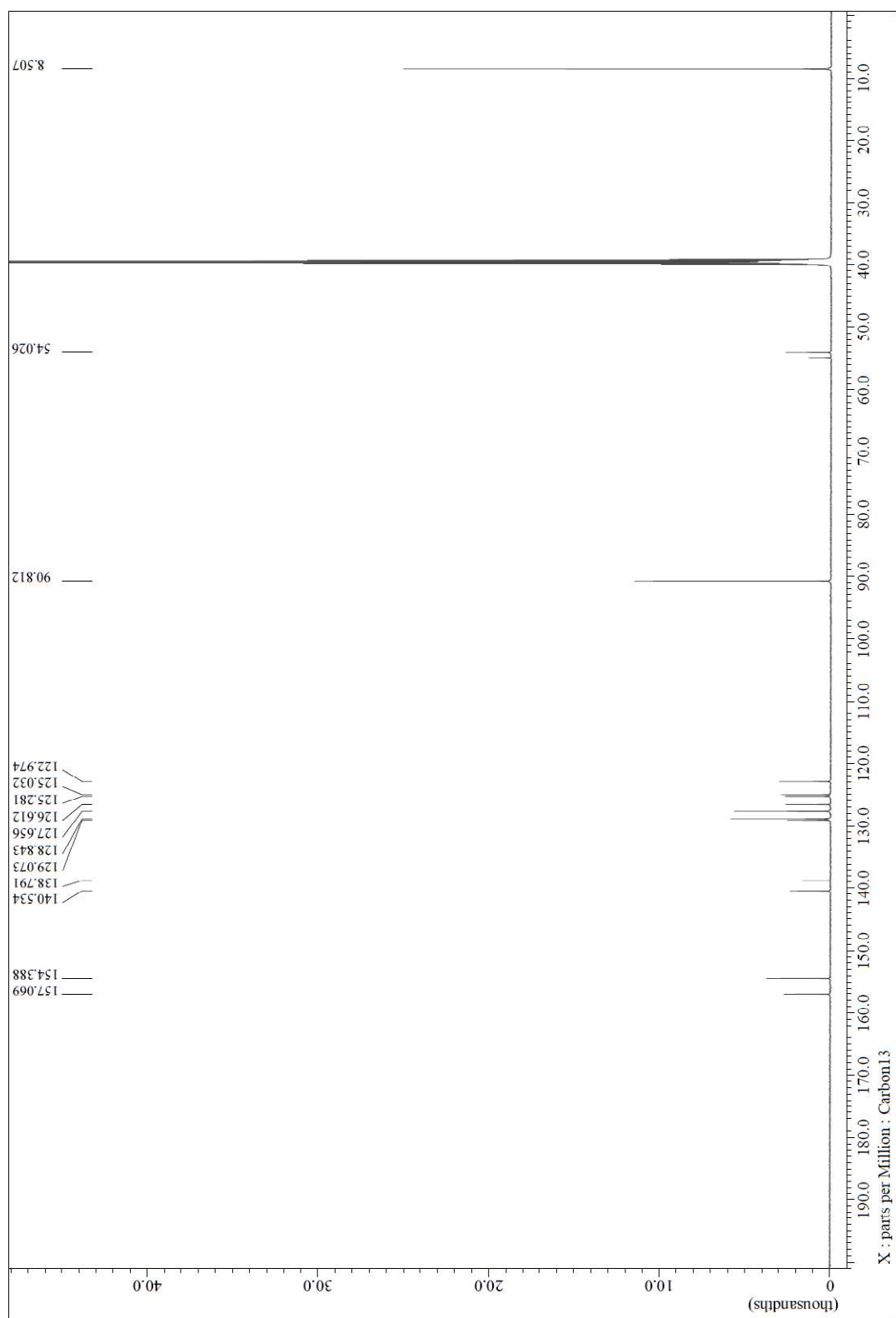
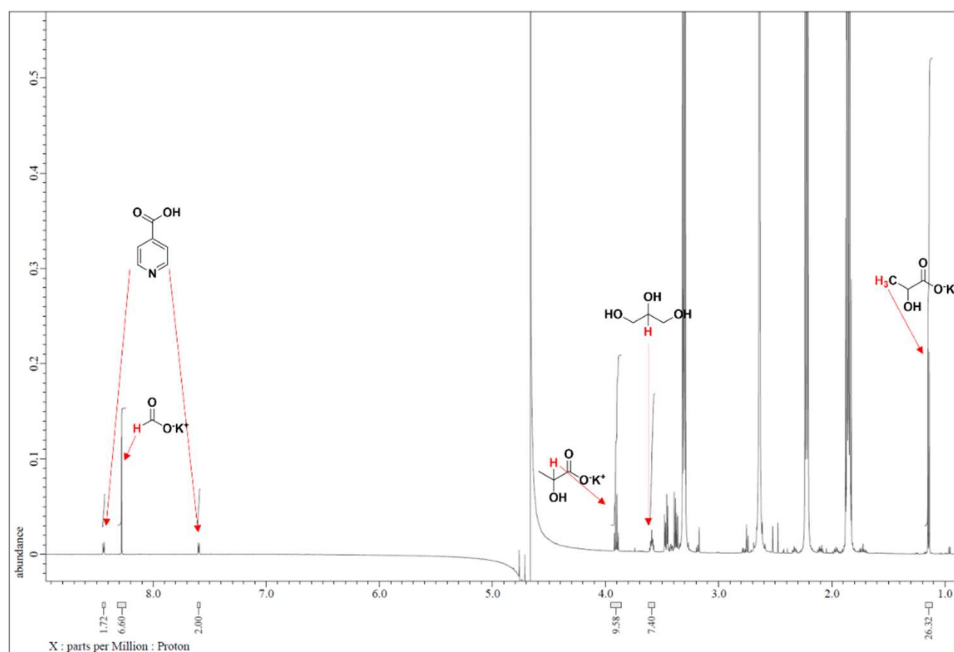


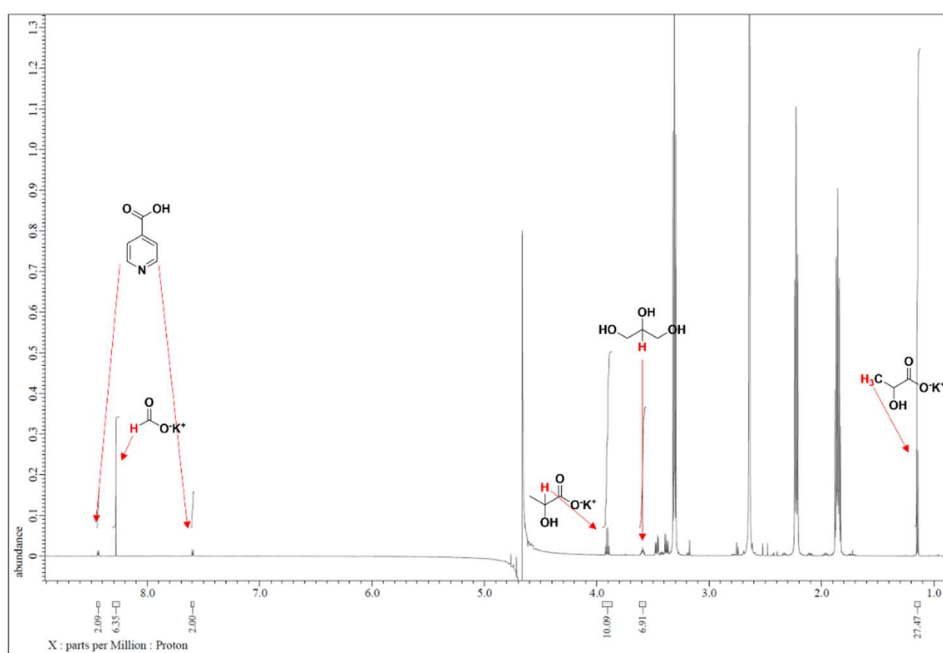
Figure S4. ^{13}C NMR spectra of catalyst **F**

III. ^1H NMR spectra of the reaction mixtures

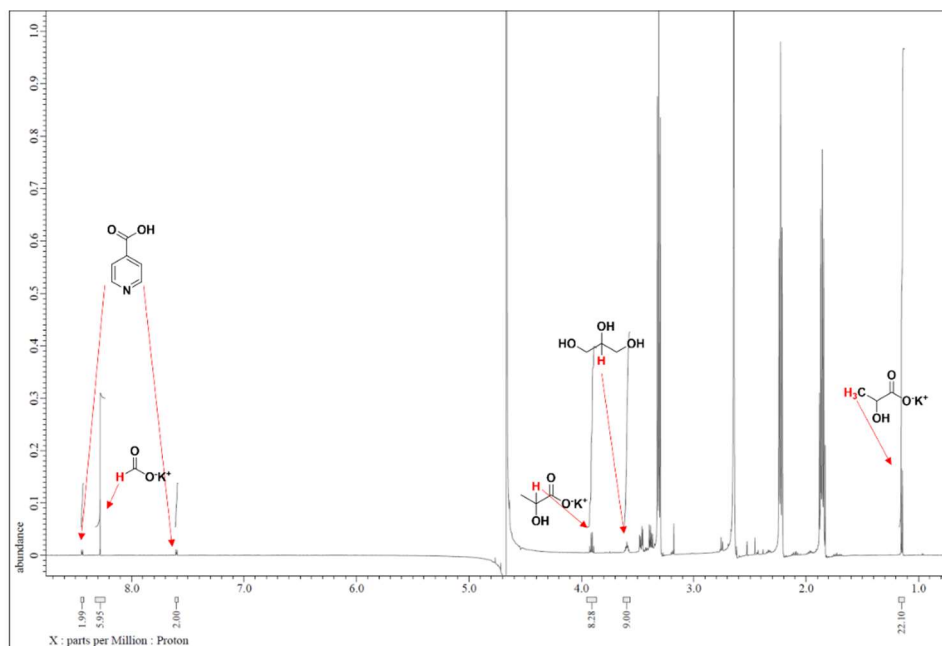
Entry 2 of Table 1 (Formate $\text{TONs}_{\text{avg}} = 3,600$, Lactate $\text{TONs}_{\text{avg}} = 5,300$)



Formate $\text{TONs} = 3,753$, Lactate $\text{TONs} = 5,447$

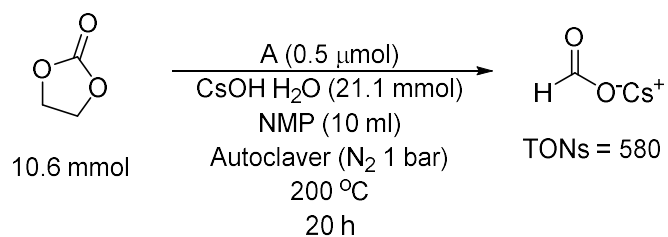


Formate $\text{TONs} = 3,611$, Lactate $\text{TONs} = 5,737$

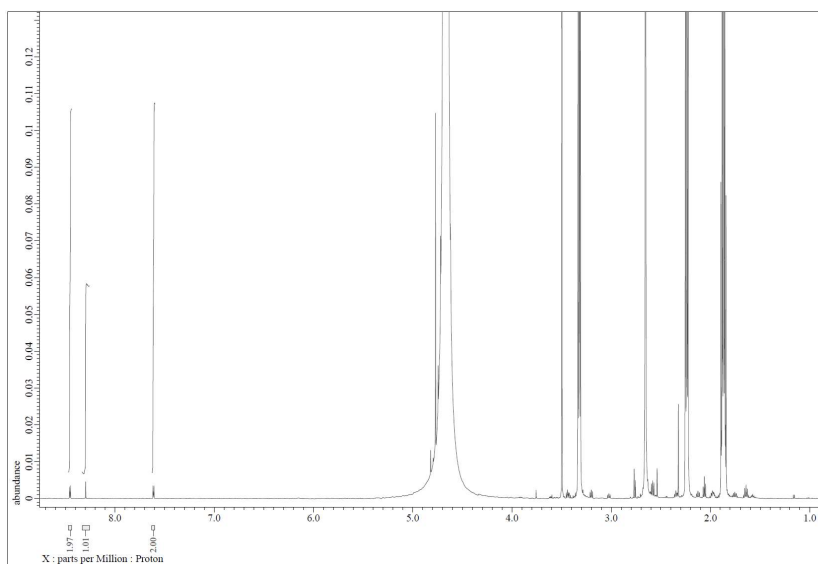


Formate TONs = 3,383, Lactate TONs = 4,708

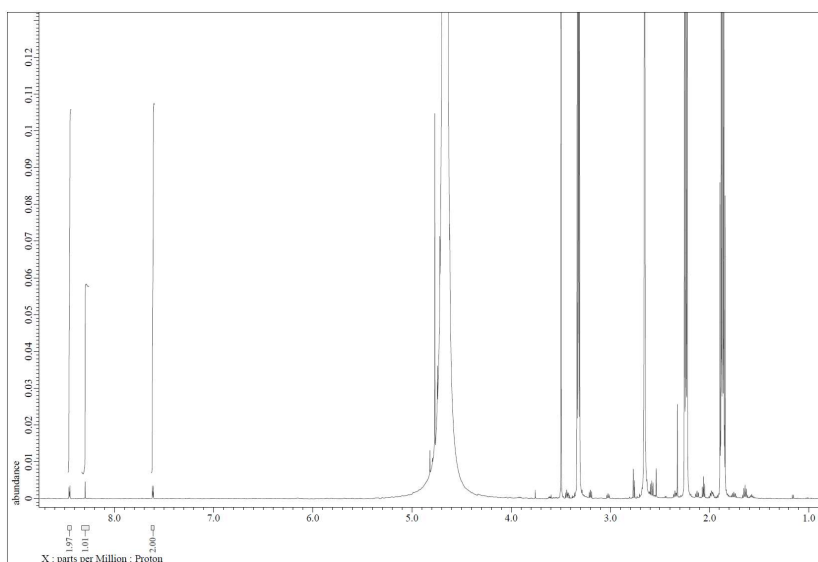
Figure S5. ^1H NMR spectra of Entry 2 (Table 1) indicating the signature peak of each species (three repeated runs)



Scheme S1. The reaction of ethylene carbonate

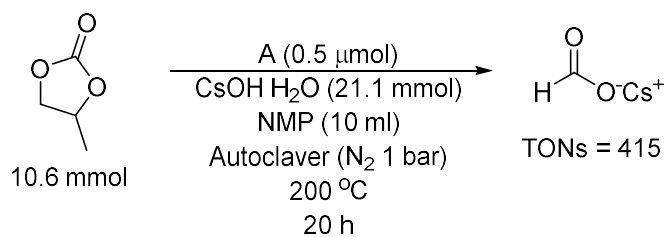


Formate TONs = 586

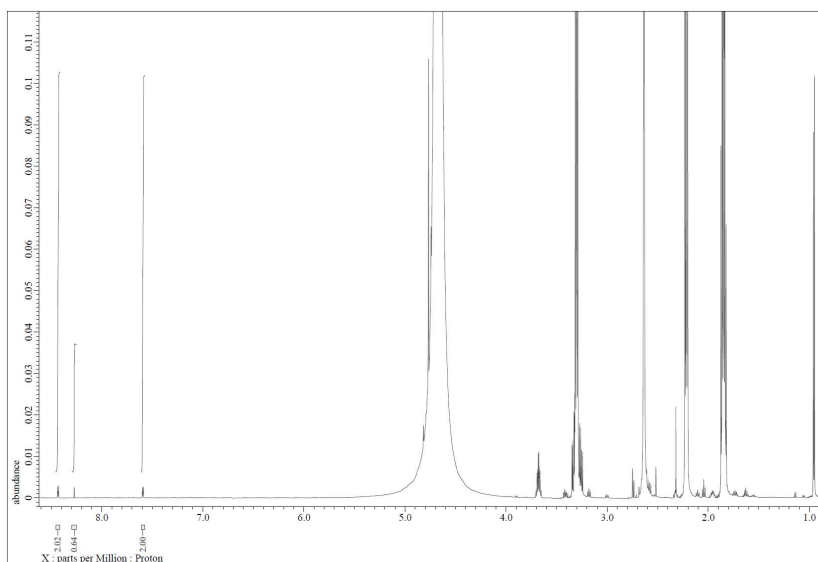


Formate TONs = 574

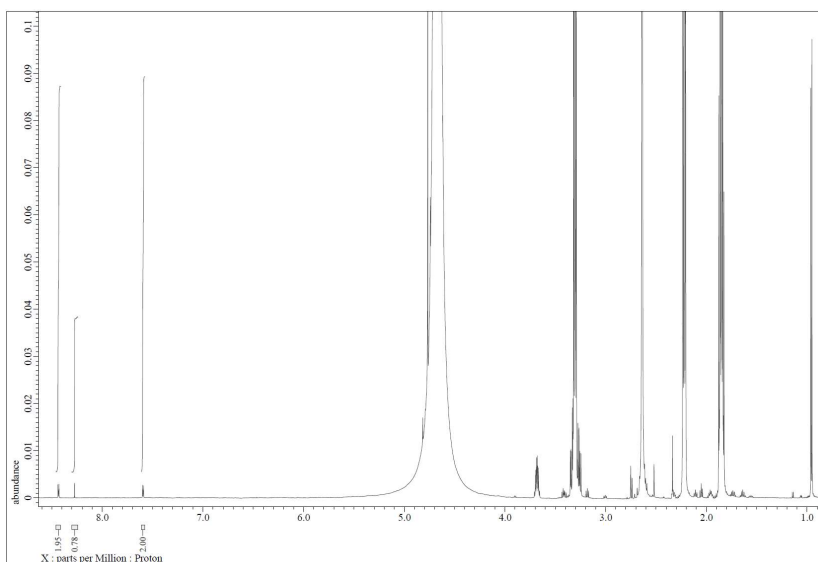
Figure S6. ¹H NMR spectra of the reaction mixture using ethylene glycol (two repeated runs)



Scheme S2. The reaction of propylene carbonate



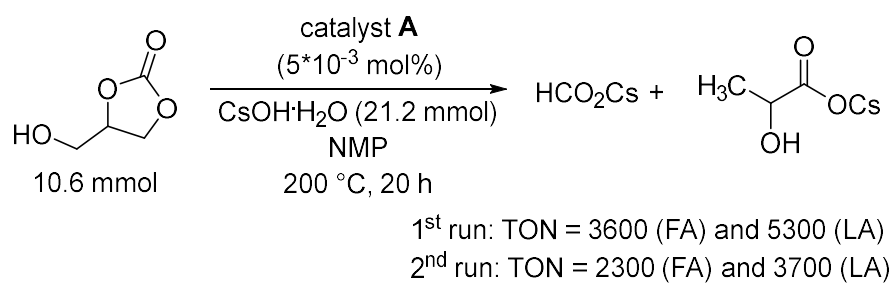
Formate TONs = 387



Formates TONs = 444

Figure S7. ¹H NMR spectra of the reaction mixture using propylene glycol (two repeated runs)

IV. Accumulation experiments



Scheme S3. Accumulation experiments of GC and OH⁻

V. Data of Transfer hydrogenation of glycerol carbonate

Table S1. Transfer hydrogenation of glycerol carbonate

entry	catalyst (mol%)	base (equiv.)	solvent	formate (TON, yield)	lactate (TON, yield)
1	A ($2.5 \cdot 10^{-3}$)	CsOH (2)	NMP	6,500, 31%	9,600, 45%
2	A ($5 \cdot 10^{-3}$)	CsOH (2)	NMP	3,600, 34%	5,300, 50%
3	A ($1 \cdot 10^{-2}$)	CsOH (2)	NMP	980, 19%	1,900, 35%
4	A ($5 \cdot 10^{-3}$)	CsOH (2)	H ₂ O	21, 0.2%	89, 0.8%
5	A ($5 \cdot 10^{-3}$)	KOH (2)	NMP	12, 0.1%	65, 0.6%
6	A ($5 \cdot 10^{-3}$)	NaOH (2)	NMP	160, 1.5%	130, 1.3%
7	A ($5 \cdot 10^{-3}$)	CsOH (3)	NMP	930, 8.8%	4800, 46%
8	A ($5 \cdot 10^{-3}$)	--	NMP	--	--
9	--	CsOH (2)	NMP	--	--
10	B ($1 \cdot 10^{-2}$)	CsOH (2)	NMP	2,400, 23%	3,600, 34%
11	B ($5 \cdot 10^{-3}$)	CsOH (2)	NMP	5,200, 25%	7,400, 35%
12	C ($1 \cdot 10^{-2}$)	CsOH (2)	NMP	2,600, 24%	4,200, 40%
13	D ($1 \cdot 10^{-2}$)	CsOH (2)	NMP	2,100, 20%	3,400, 32%
14	E ($5 \cdot 10^{-3}$)	CsOH (2)	NMP	580, 5.4%	2,400, 22%
15	F ($1 \cdot 10^{-2}$)	CsOH (2)	NMP	310, 3.0%	1,700, 16%

The mixture of catalysts, glycerol carbonate (10.6 mmol), and base in NMP (10 mL) was heated at 200 °C for 20 h. Catalysts **A** and **E** have two iridium ions in the molecule. CsOH is a monohydrate form.

VI. Mass spectra of the reaction mixture using deuterated glycerol

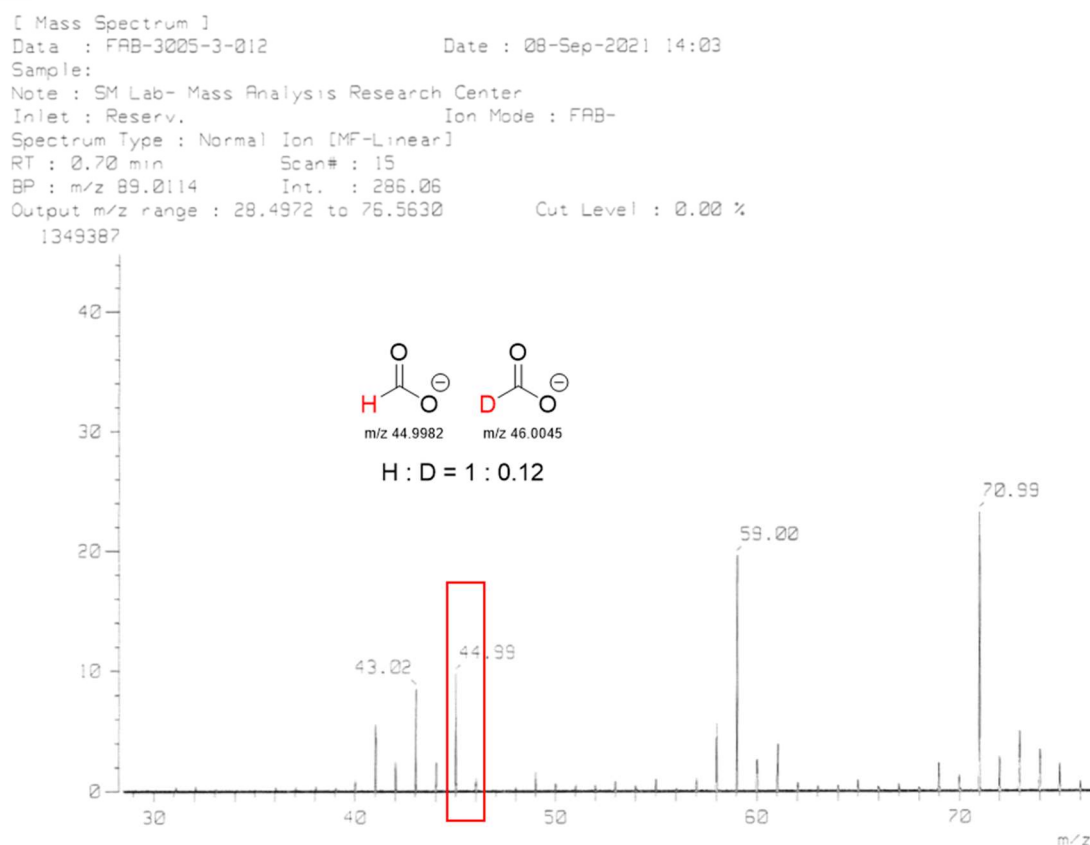
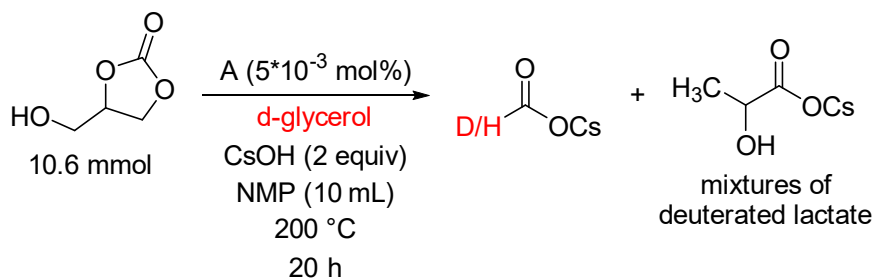


Figure S8. Mass spectrum of the reaction mixture involving *d*-glycerol

VII. ^{13}C NMR analysis of the mixture of glycerol carbonate and CsOH

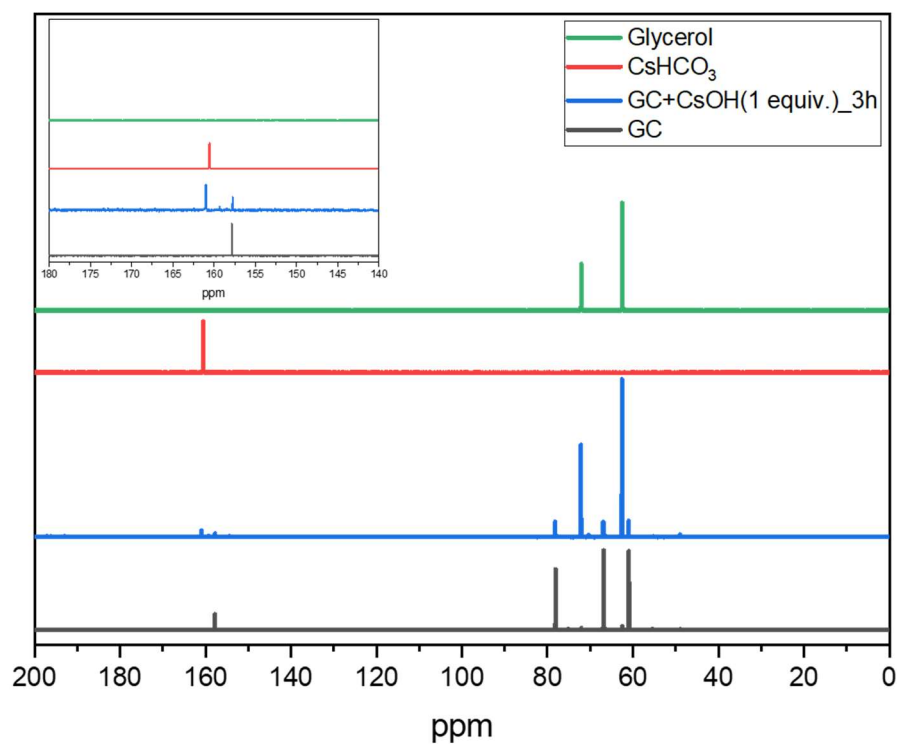


Figure S9. ^{13}C NMR spectra; glycerol (green), CsHCO_3 (red), the mixture of glycerol carbonate(GC) and CsOH (blue) and GC (black).

VIII. ^1H NMR spectra of reactants and the reaction mixture

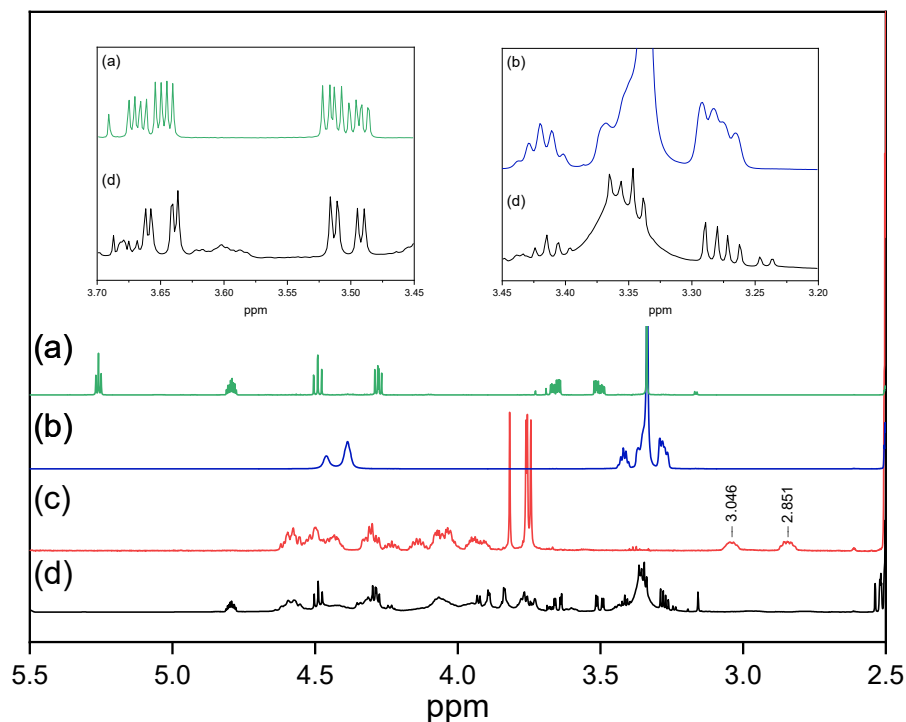


Figure S10. ^1H NMR spectra in DMSO-d_6 ; (a) glycerol carbonate (green), (b) glycerol (blue), (c) catalyst **A** (red), and (d) the mixture of glycerol carbonate (1 equiv), CsOH (2 equiv), catalyst **A** (0.5 equiv) (black).

Comments: The ^1H NMR spectrum of the mixture of catalyst **A**, glycerol carbonate, and CsOH (Figure S10(d)) shows the disappearance of cyclooctadiene (COD) peaks (3.046 ppm and 2.851 ppm of ^1H NMR of catalyst **A**), indicating the dissociation of COD from catalyst **A** during the reaction. Other peaks corresponding to COD are overlapped with other peaks of reactants. We also observed glycerol dissociated from glycerol carbonate in the mixture (d). However, it is challenging whether the glycerol is coordinated with iridium ions because the peak position and the splitting patterns of glycerol (b) and glycerol from the mixture (d) are similar.