Supporting Information

Catalytic Value Addition of Glycerol to Lactic Acid by Chromium Chloride and its Corresponding Pincer Complex

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1.X-Ray Analysis

Justification of alert observed in the check_cif file of **5a**.

ALERT level A
The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4523

Author Response

This error arises due to the weak diffraction of the crystal even when the crystal data was collected up to 0.78 Å resolution owing to the small size. Multiple attempts were made but crystal diffracted weakly. Multiple attempts to crystallise was also unsuccessful.

Table S1. Crystal structure and refinement parameters of 5a

Empirical formula	$C_{19}H_{15}Cl_3CrN_3$
Formula weight	443.70
Temperature/K	296.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.800(6)
b/Å	8.357(3)
c/Å	16.344(6)
α/°	90
β/°	103.866(10)
γ/°	90
Volume/Å^3	2095.2(12)
Z	4
ρ_{calc}g/cm^3	1.464
μ/mm^{-1}	0.942
F(000)	940.0
Crystal size/mm^3	0.18 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.112 to 37.506
Index ranges	-14 ≤ h ≤ 14, -7 ≤ k ≤ 7, -14 ≤ l ≤ 14
Reflections collected	24605
Independent reflections	1615 [R_{int} = 0.1150, R_{sigma} = 0.0500]
Data/restraints/parameters	1615/225/235
Goodness-of-fit on F^2	1.223
Final R indexes [I>=2σ (I)]	R_1 = 0.0761, wR_2 = 0.1220
Final R indexes [all data]	R_1 = 0.1029, wR_2 = 0.1337
Largest diff. peak/hole / e Å^{-3}	0.36/-0.30

2. Representative GC Spectra

GC analysis (TCD detection) was performed on a Agilent 7820-GC instrument fitted with Agilent Front SS7 inlet N2 HP-PLOT Q column (30 m length x 530 µm x 40 µm ID) using the following method:

Agilent 7820-GC Detector TCD

starting temperature 40 °C

Oven temperature 70 °C

Time at starting temp: 0 min

Hold time = 5 min

Ramp : 40 °C/min up to 250 °C

Flow rate (carrier): 25 mL/min (N2)

Split ratio: 195

Inlet temperature: 40 °C

Detector temperature: TCD: 250 °C

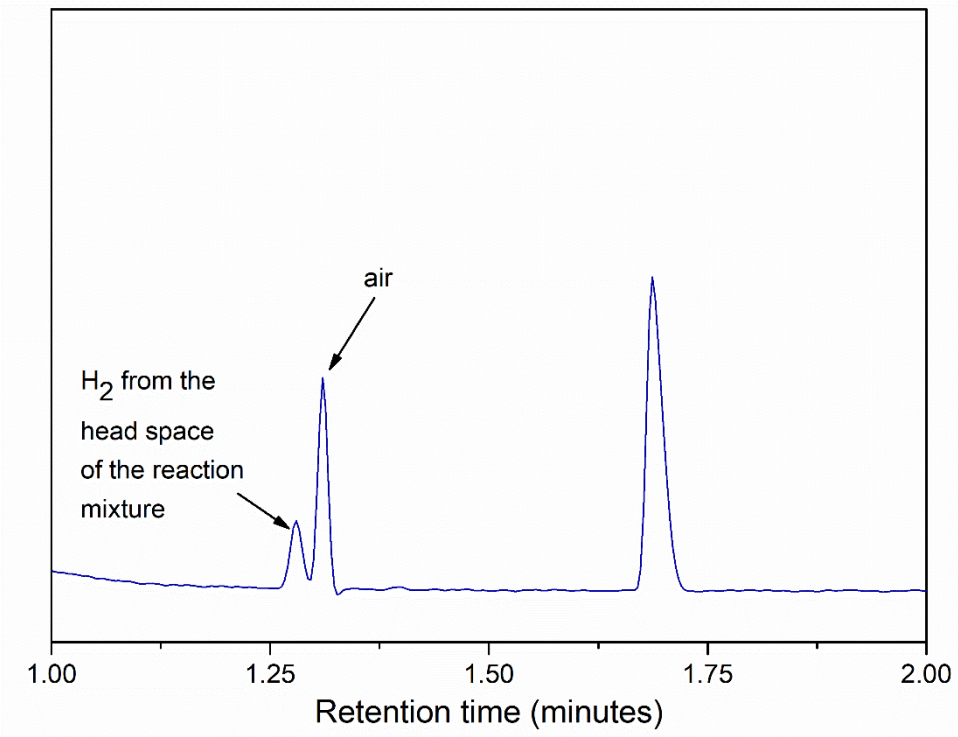

Figure S1a. GC data of the head space of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalent KOH, at 160 °C. (entry 4, Table 1).

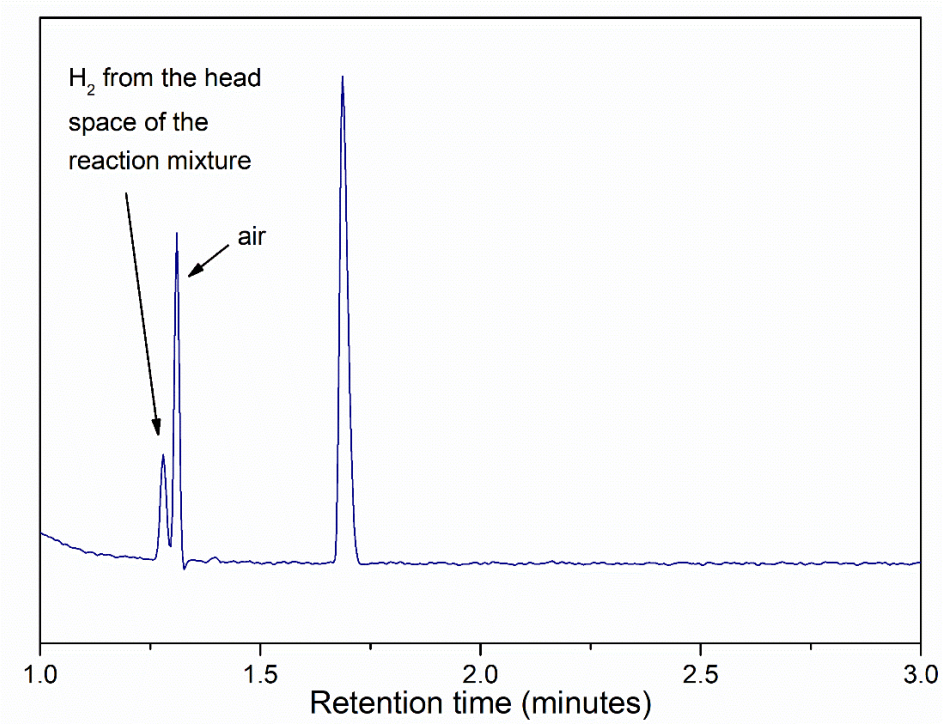

Figure S1b. GC data of the head space of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalent NaOH, at 160 °C. (entry 28, Table 1).

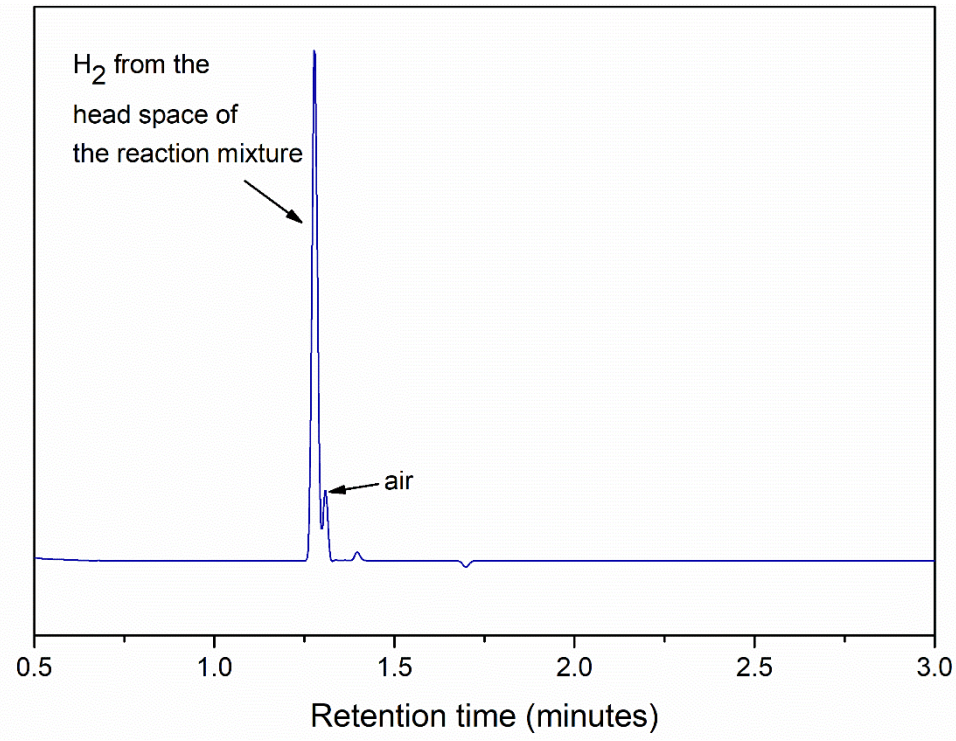

Figure S1c. GC data of the head space of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.75 mol% **5b**, 1.1 equivalent NaOH, at 160 °C. (entry 31, Table 1).

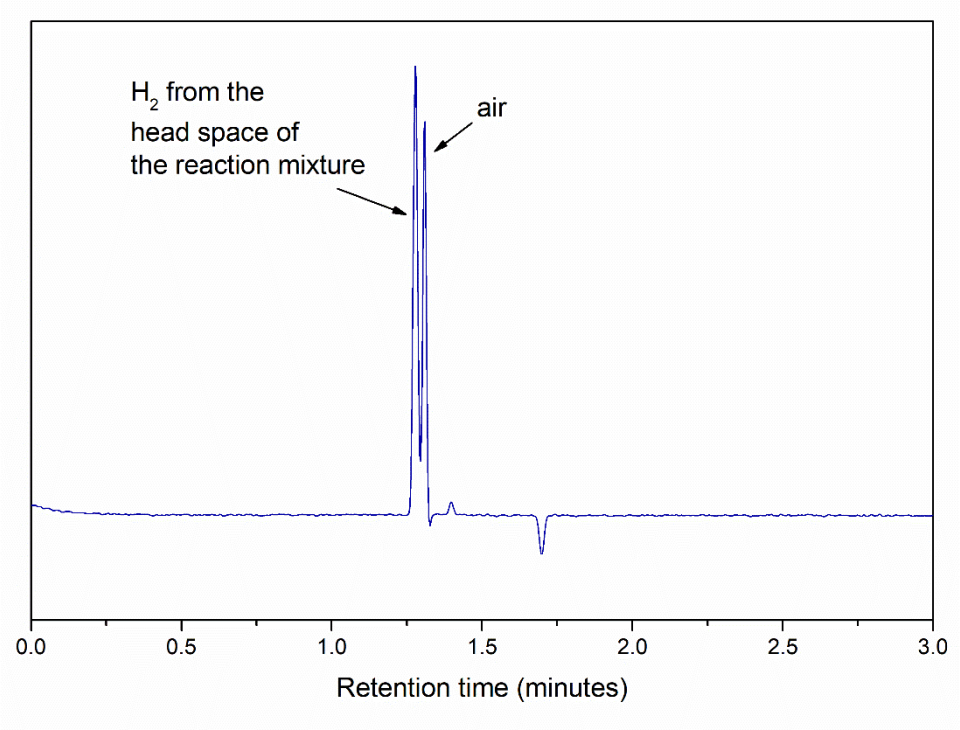

Figure S1d. GC data of the head space of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.25 mol% **5b**, 1.1 equivalent NaOH, at 160 °C. (entry 32, Table 1).

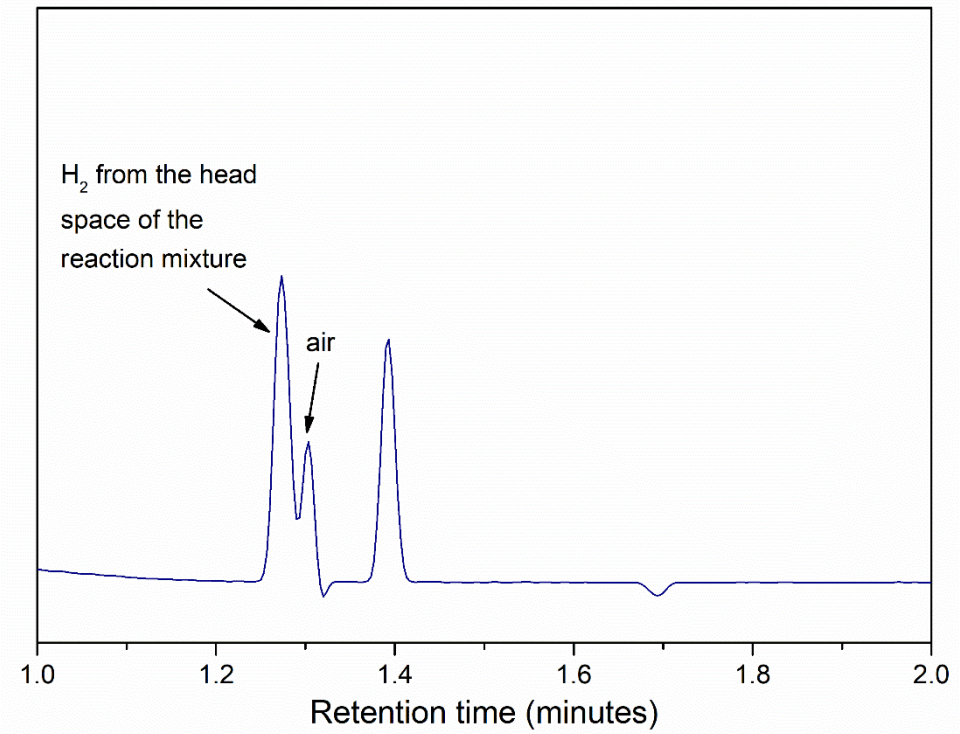

Figure S1e. GC data of the head space of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.05 mol% **5b**, 1.1 equivalent NaOH, at 160 °C. (entry 33, Table 1).

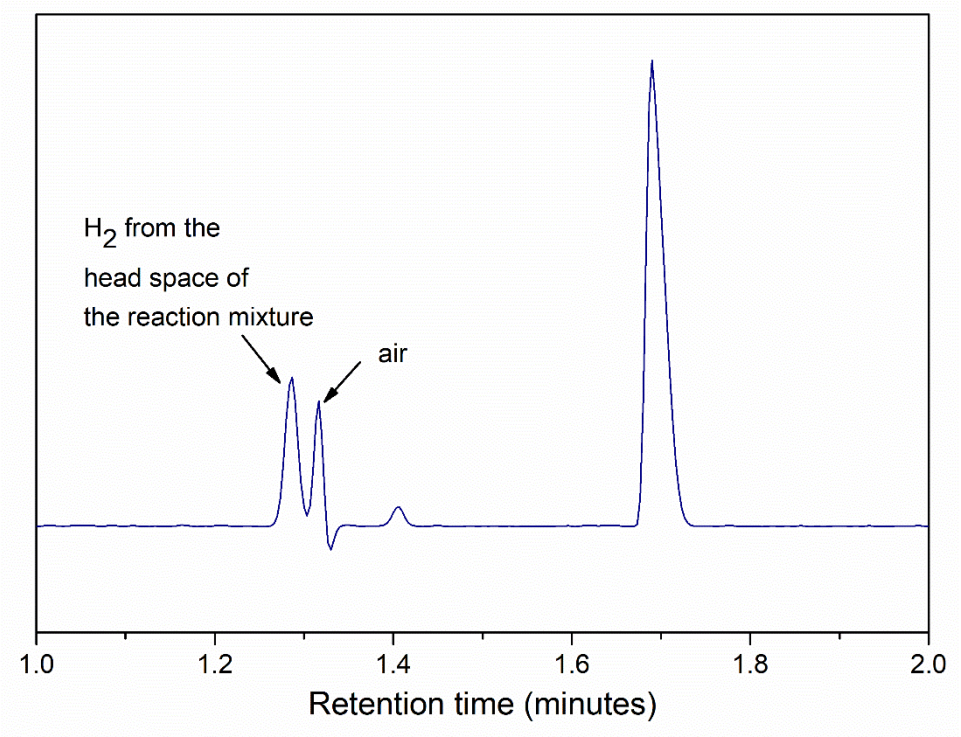

Figure S1f. GC data of the head space of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.005 mol% **5b**, 1.1 equivalent NaOH, at 160 °C. (entry 34, Table 1).

3. HRMS simulation

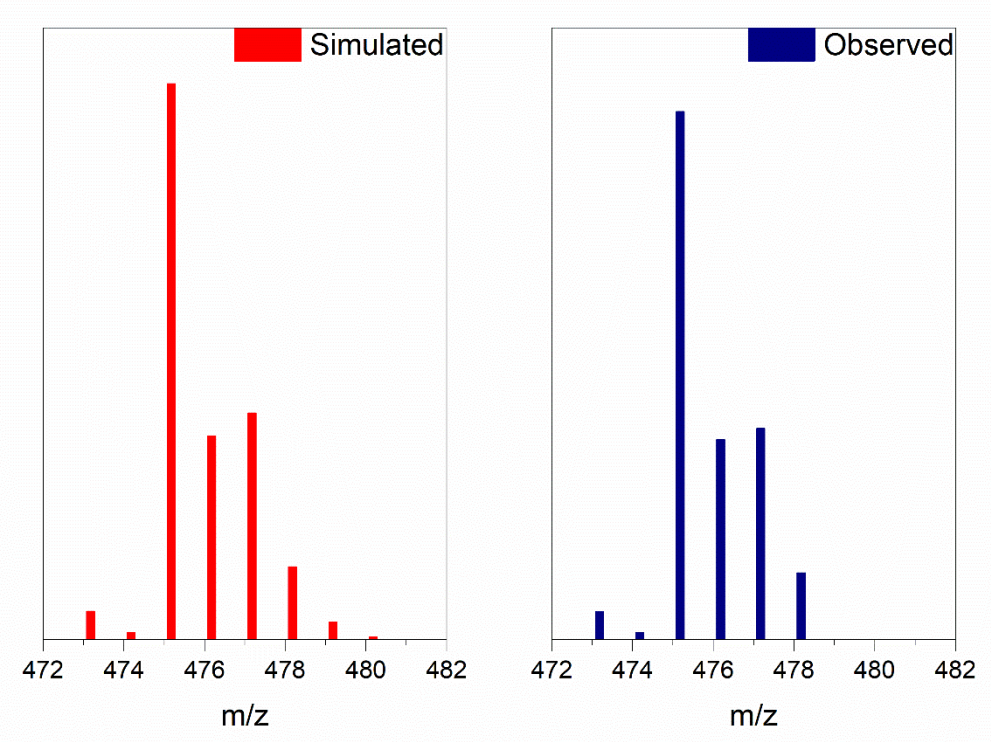

Figure S2a: HRMS(ESI) expanded spectrum of m/z 475.3254 : Simulated (red) and observed (blue).

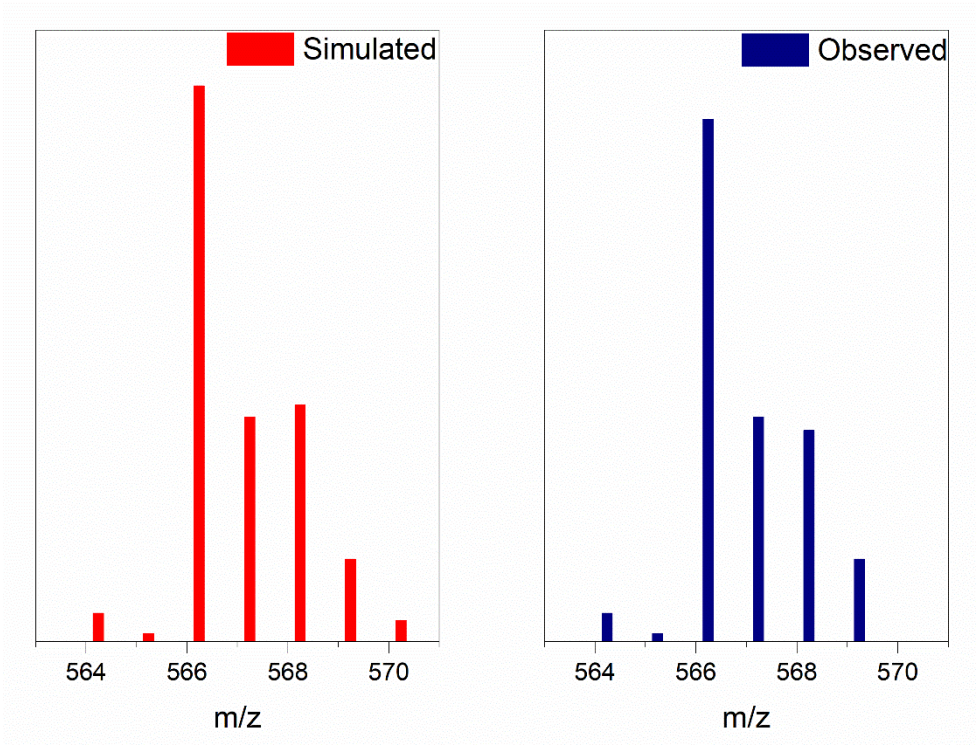

Figure S2b: HRMS(ESI) expanded spectrum of m/z 566.8870: Simulated (red) and observed (blue).

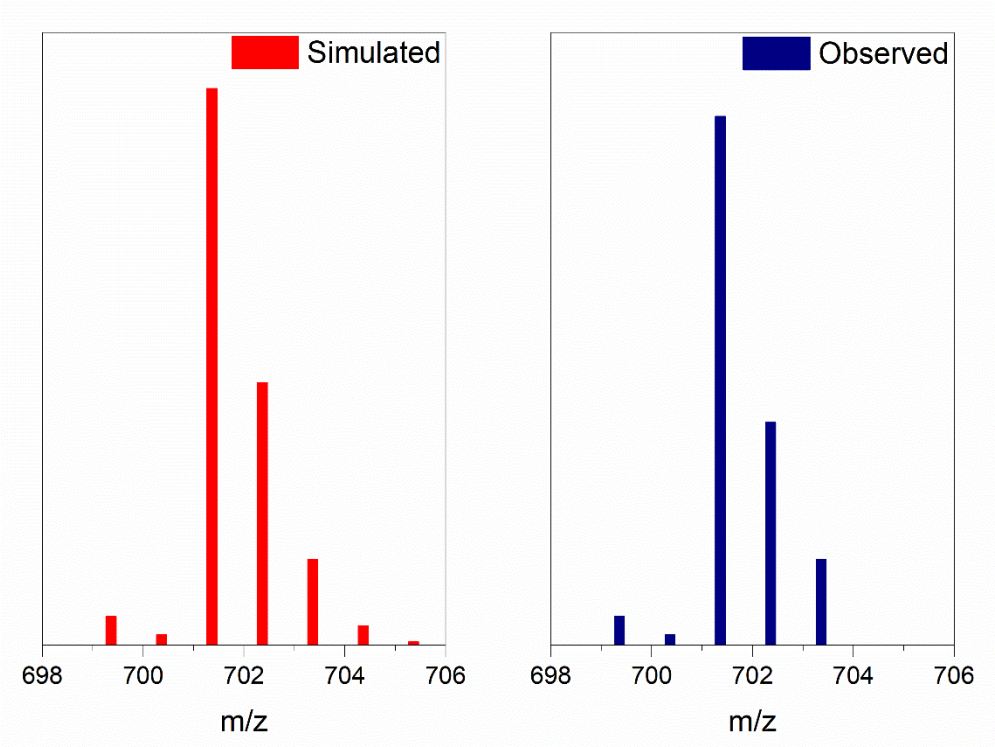

Figure S2c: HRMS(ESI) expanded spectrum of m/z 701.4891: Simulated (red) and observed (blue).

4. NMR spectra of crude reaction mixture

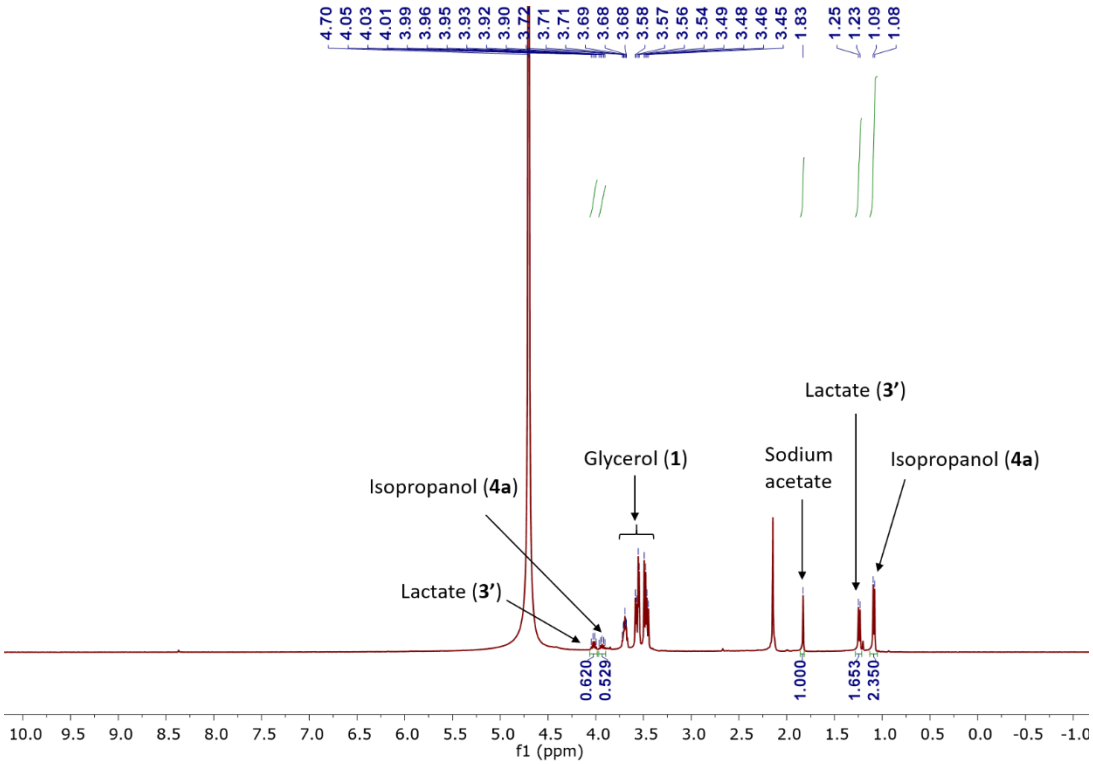

Figure S3: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 0.5 equivalents KOH, at 160 °C. (entry 1, Table 1).

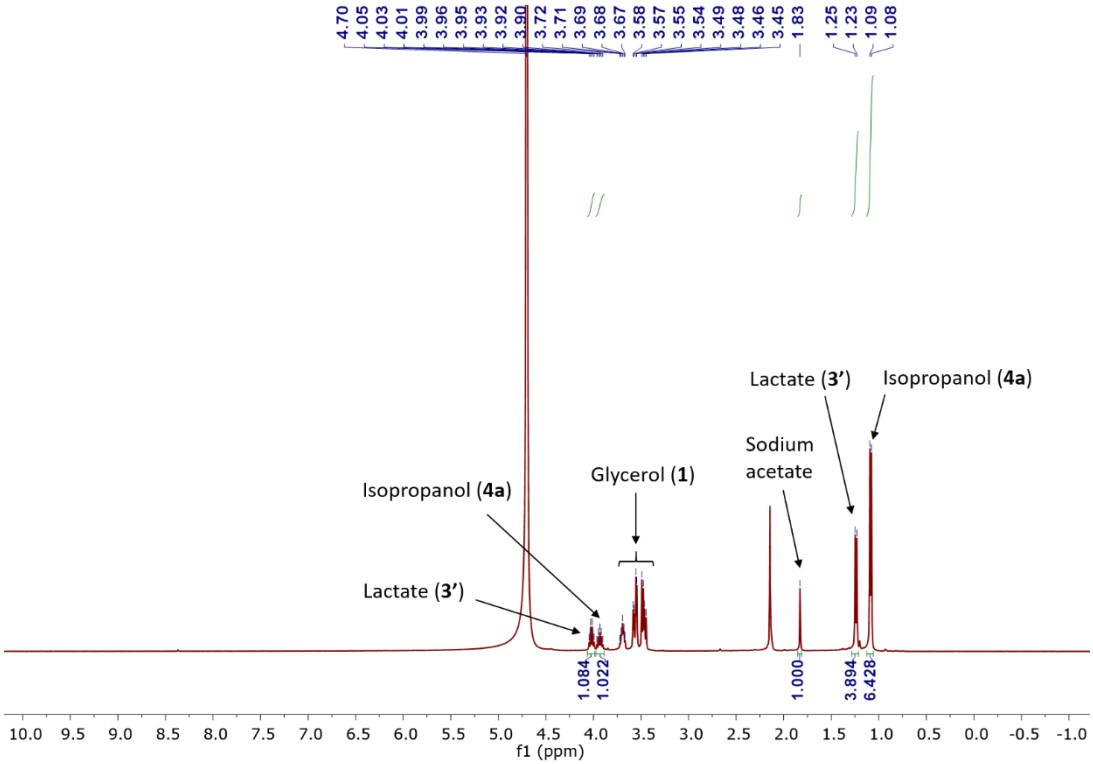

Figure S4: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 0.75 equivalents KOH, at 160 °C. (entry 2, Table 1).

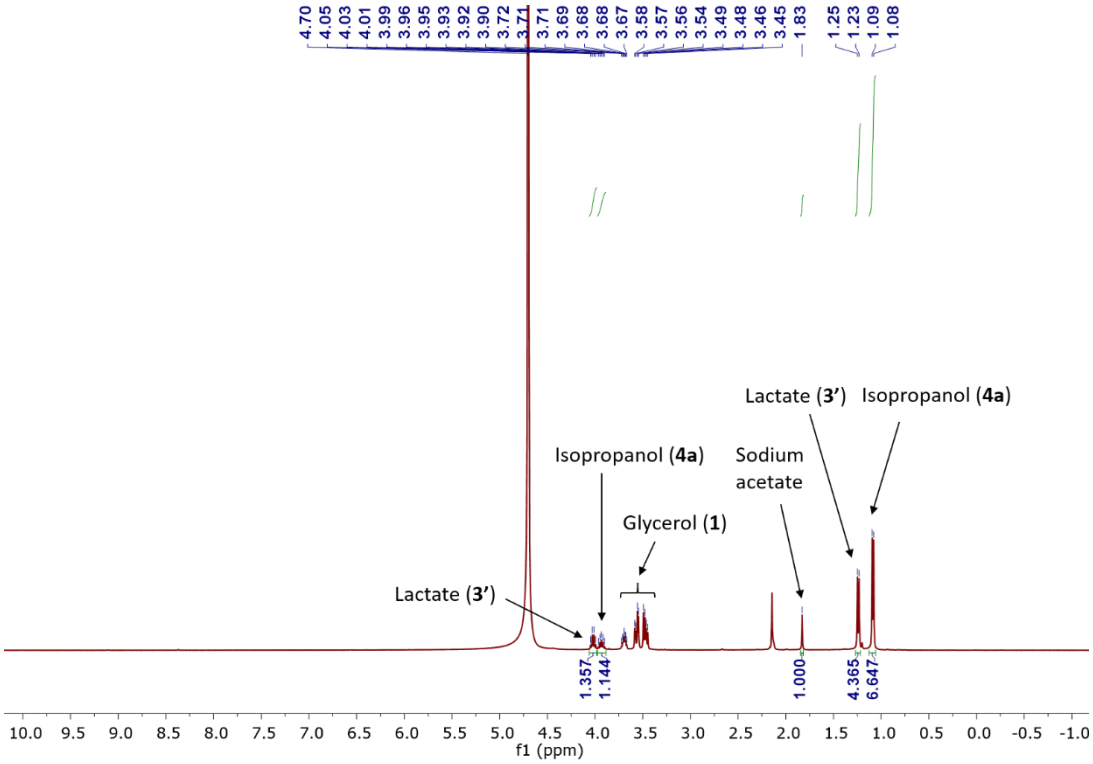

Figure S5: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1 equivalent KOH, at 160 °C. (entry 3, Table 1).

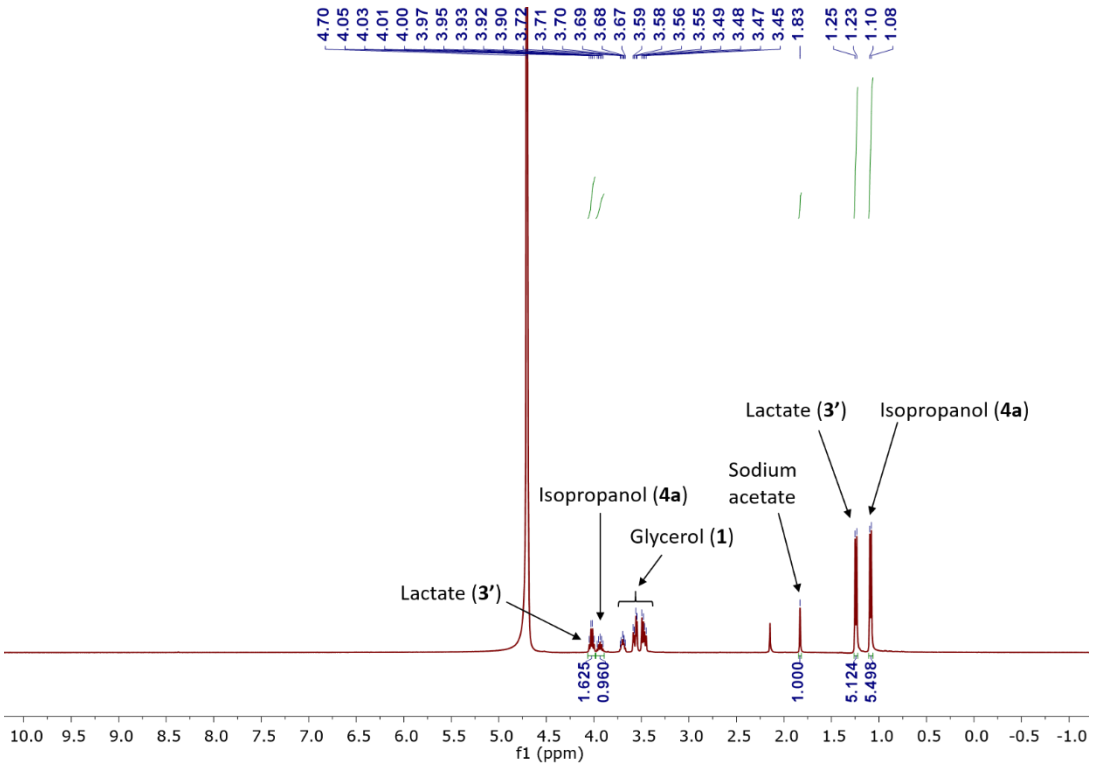

Figure S6: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 4, Table 1).

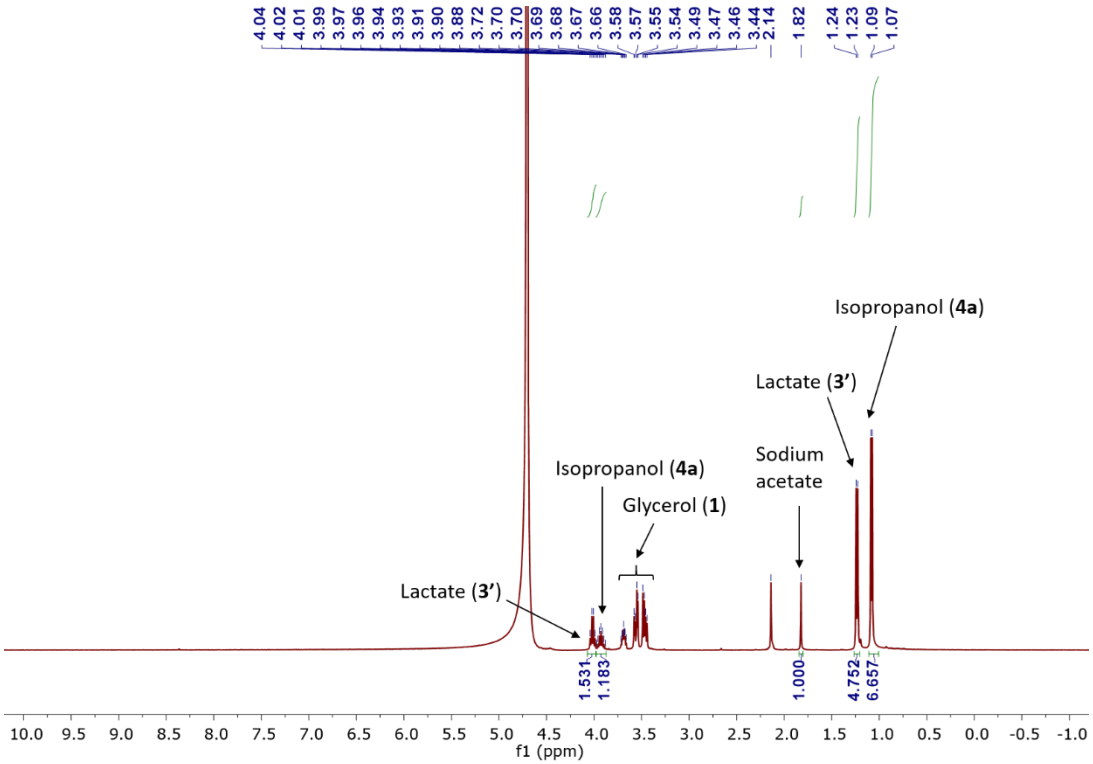

Figure S7: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.2 equivalents KOH, at 160 °C. (entry 5, Table 1).

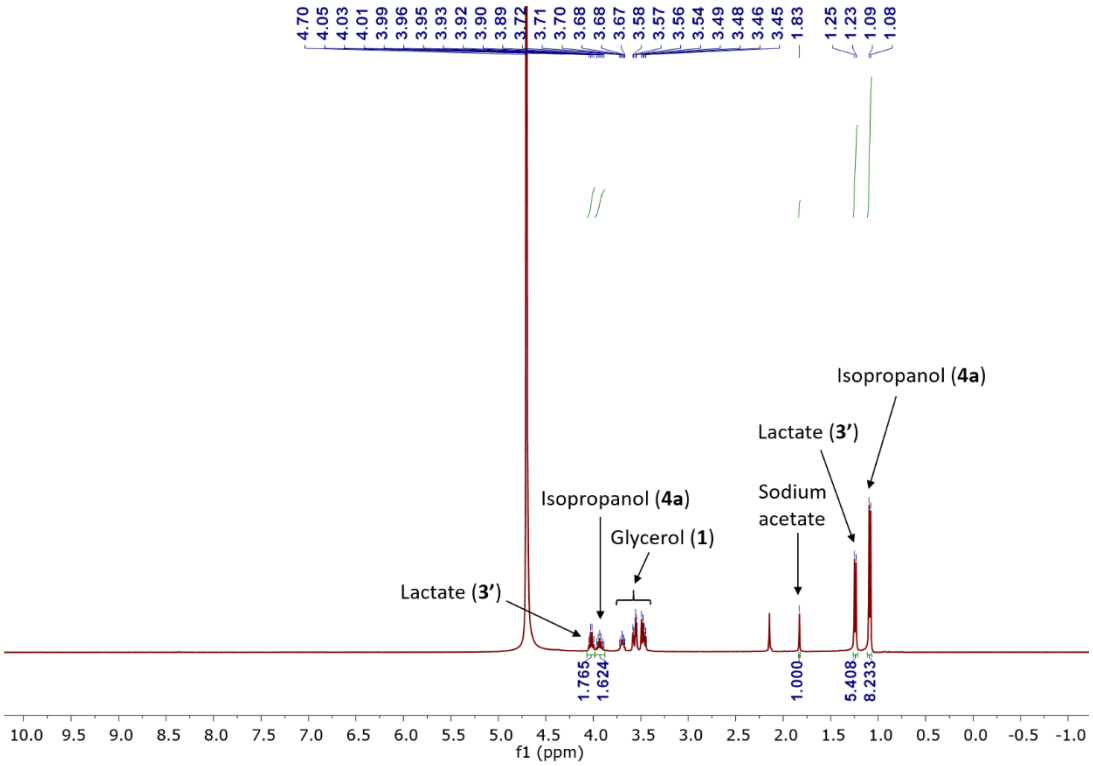

Figure S8: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.3 equivalents KOH, at 160 °C. (entry 6, Table 1).

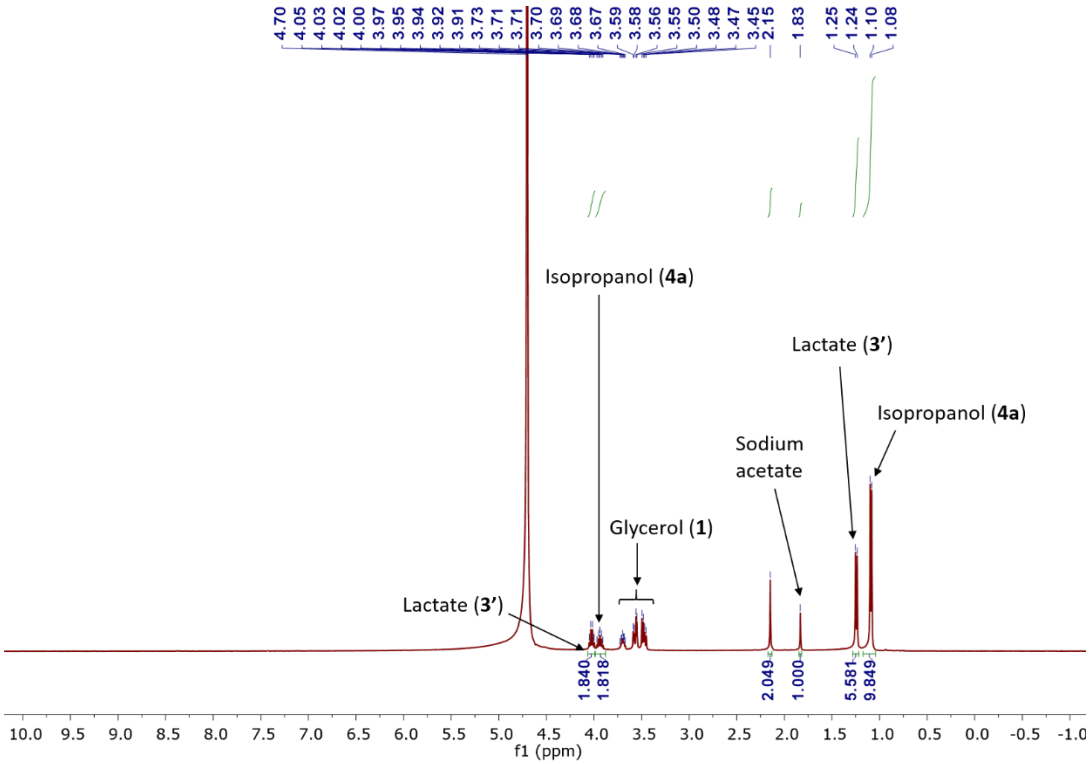

Figure S9: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.75 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 7, Table 1).

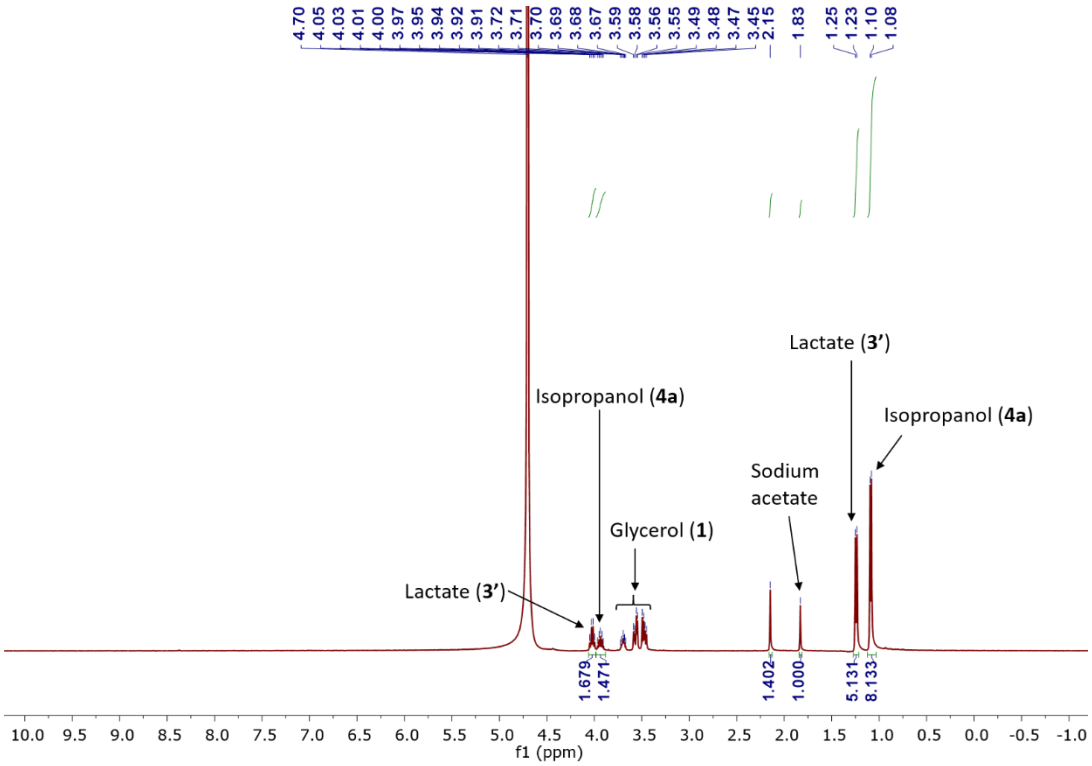

Figure S10: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.25 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 8, Table 1).

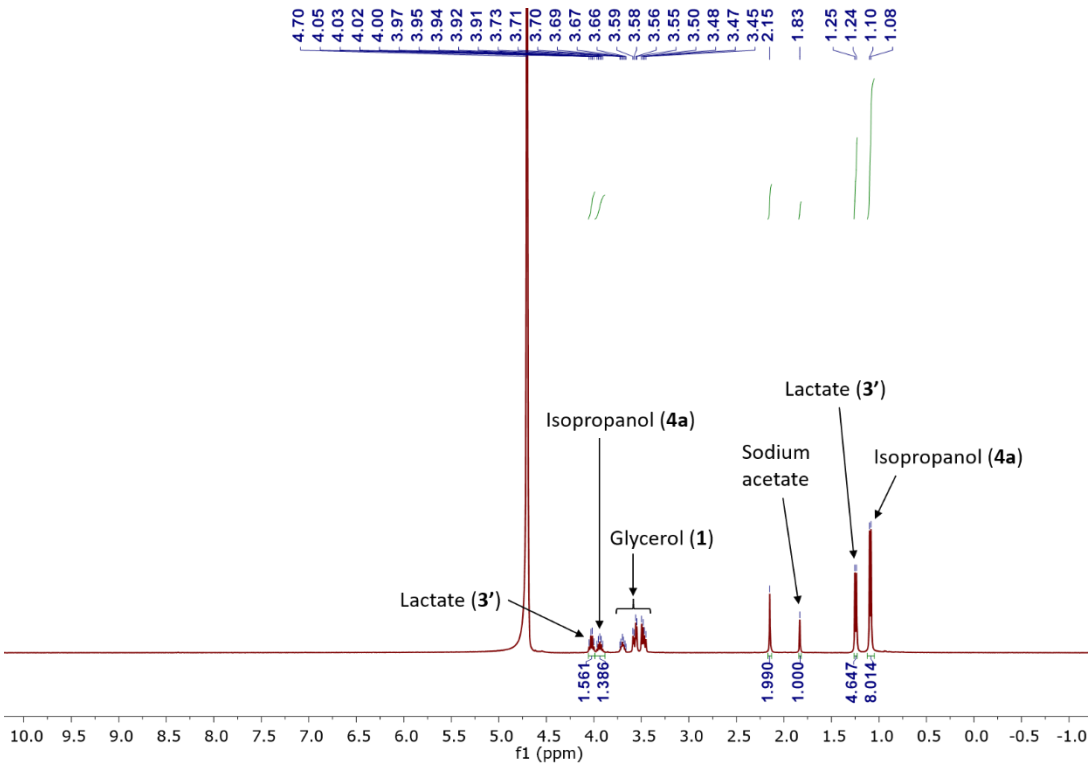

Figure S11: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.1 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 9, Table 1).

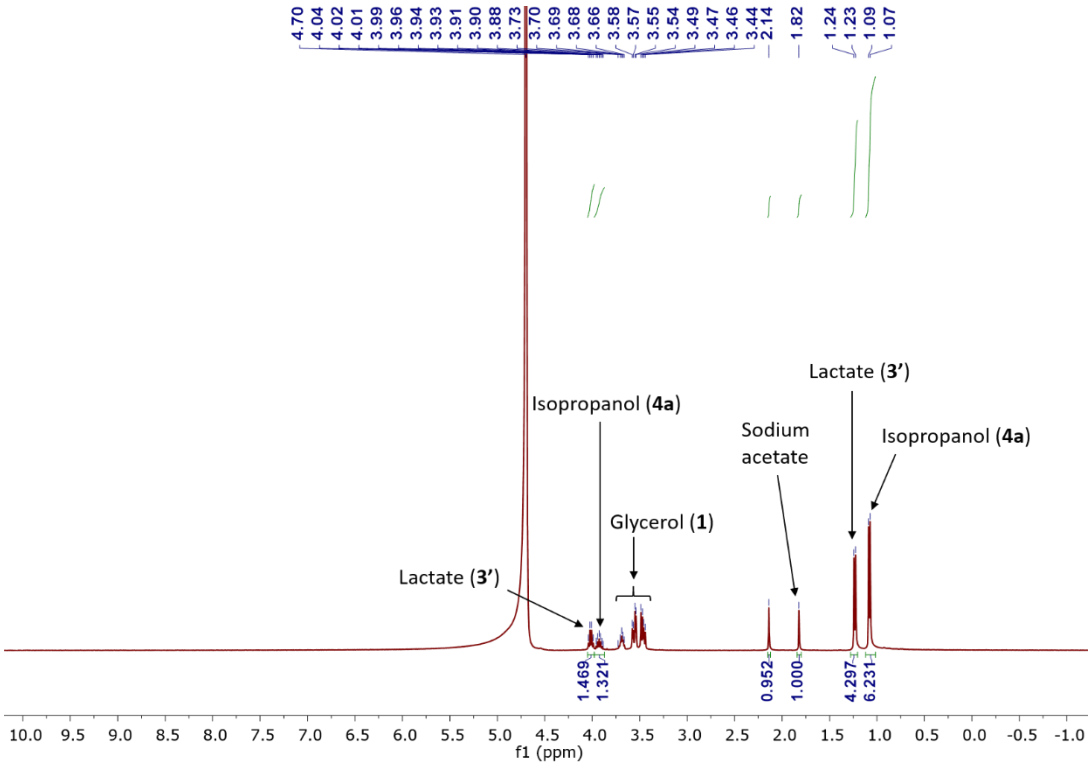

Figure S12: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.075 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 10, Table 1).

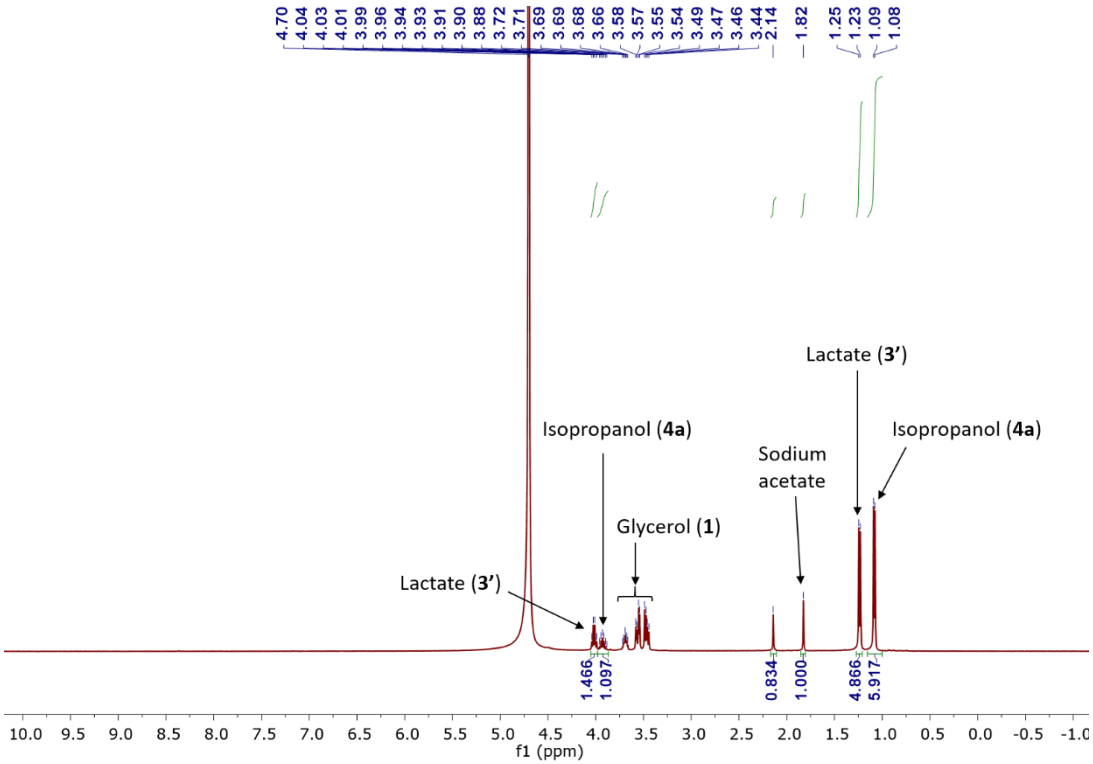

Figure S13: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.05 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 11, Table 1).

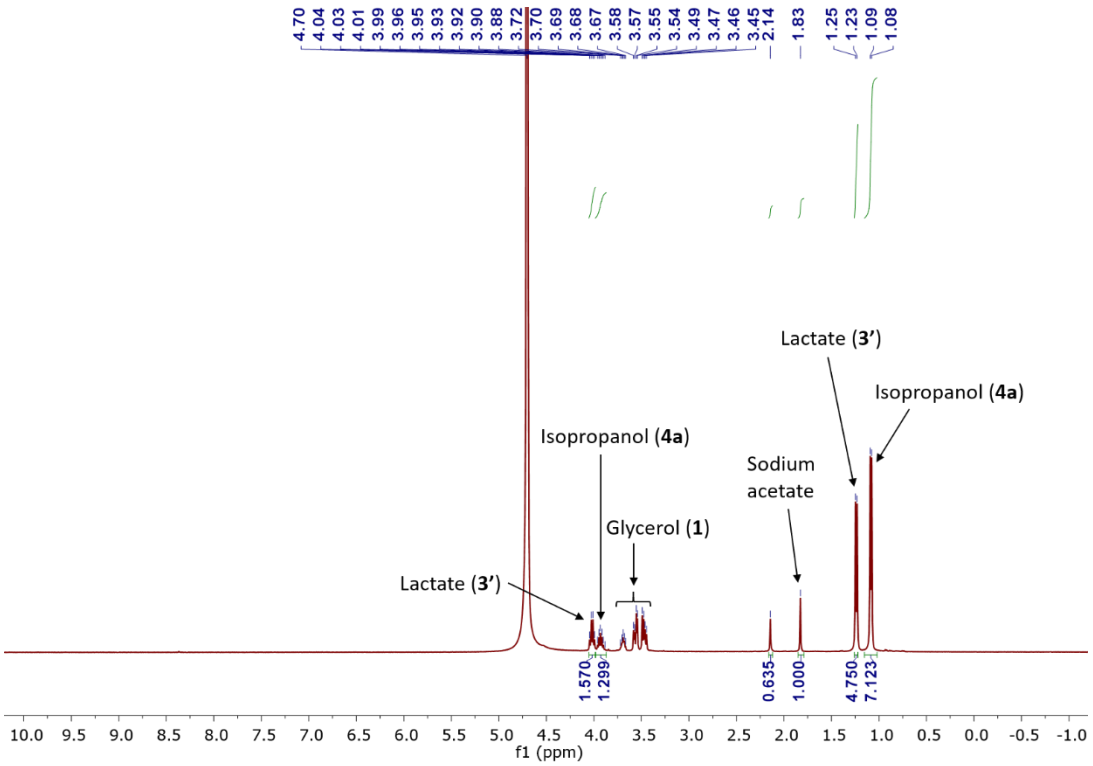

Figure S14: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.025 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 12, Table 1).

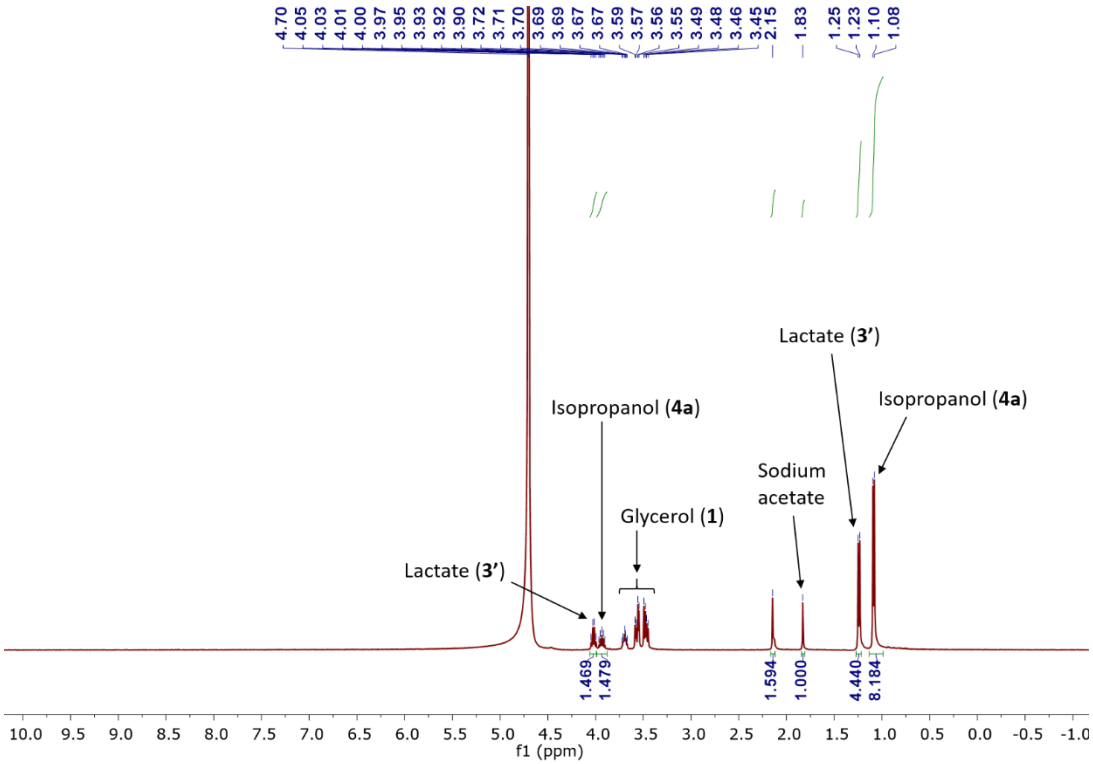

Figure S15: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.01 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 13, Table 1).

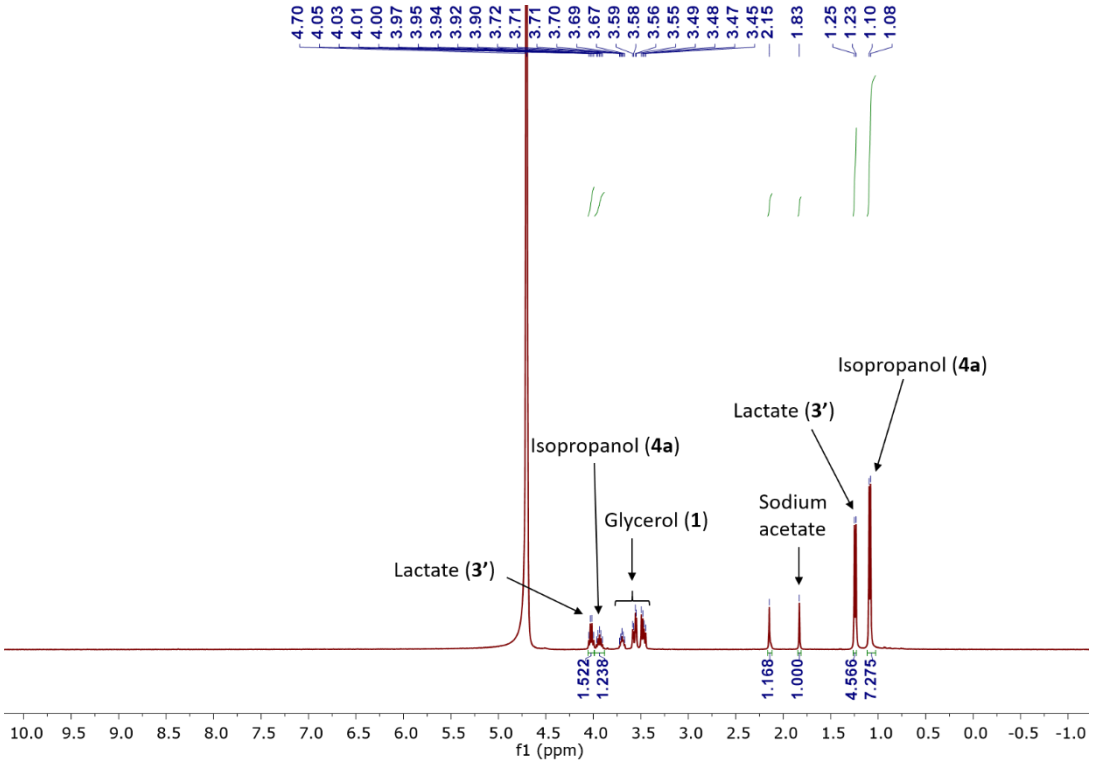

Figure S16: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.0075 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 14, Table 1).

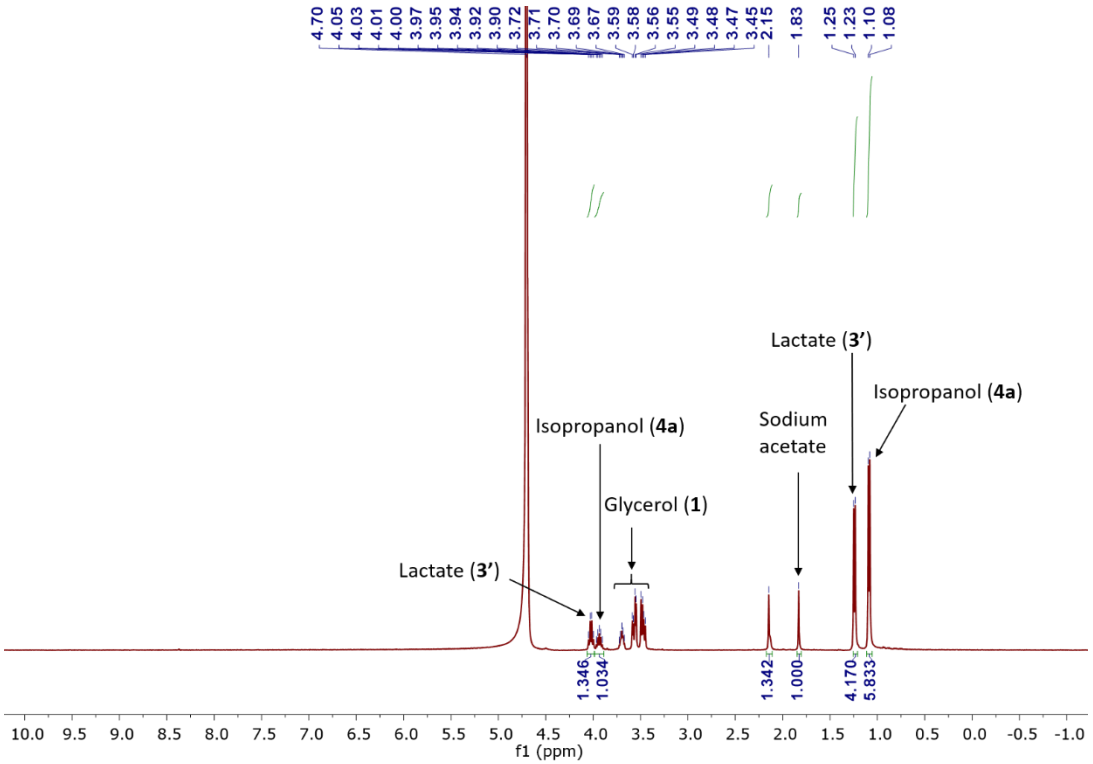

Figure S17: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.005 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, at 160 °C. (entry 15, Table 1).

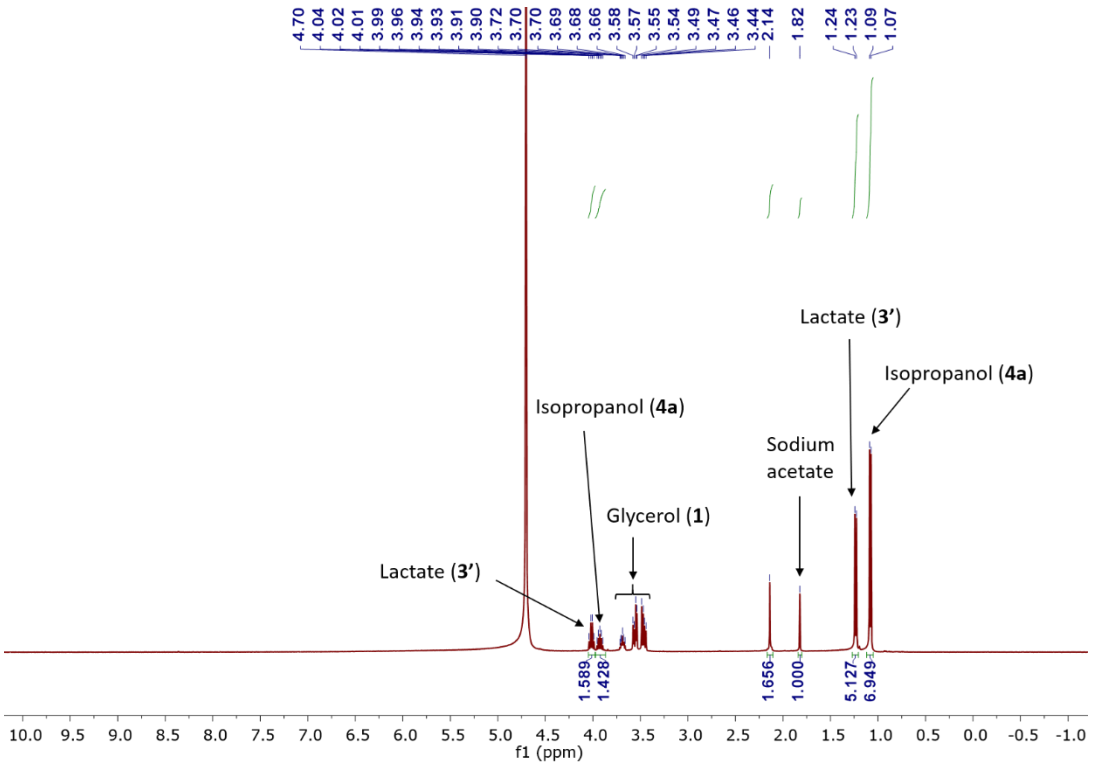

Figure S18: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.0025 mol% $CrCl_3.6H_2O$, 1.1 equivalents KOH, 1.5 equivalents acetone, at 160 °C. (entry 17, Table 1).

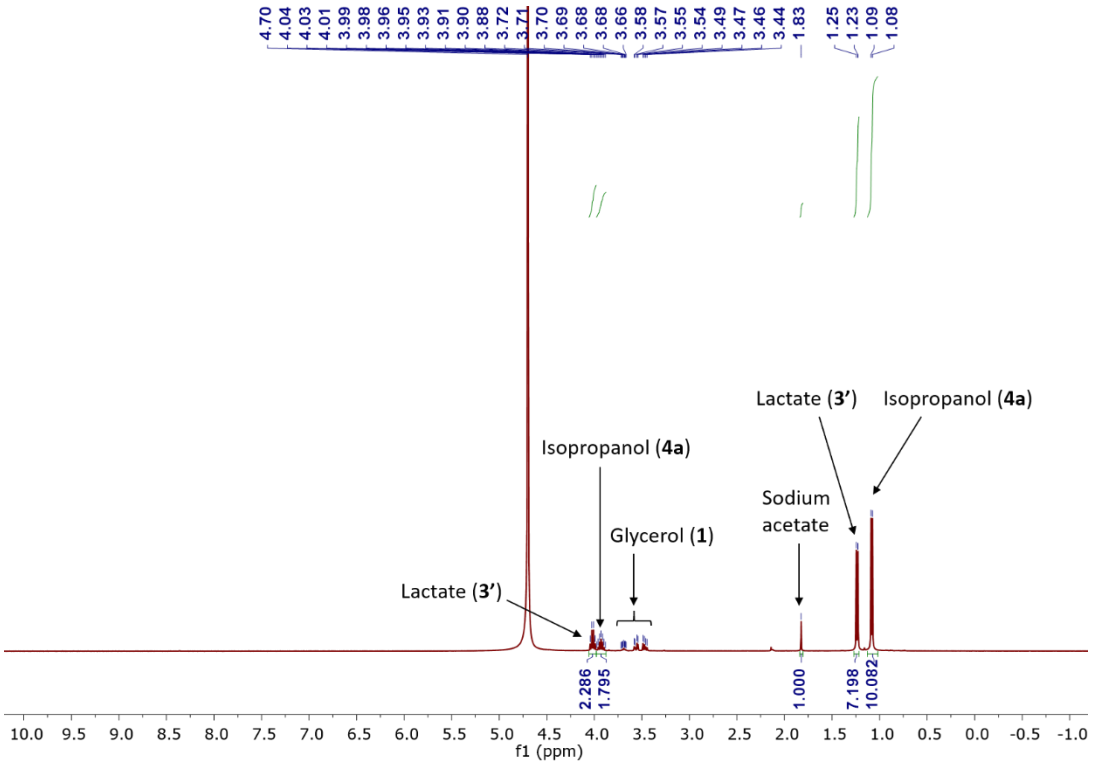

Figure S19: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents NaOH, at 160 °C. (entry 18, Table 1).

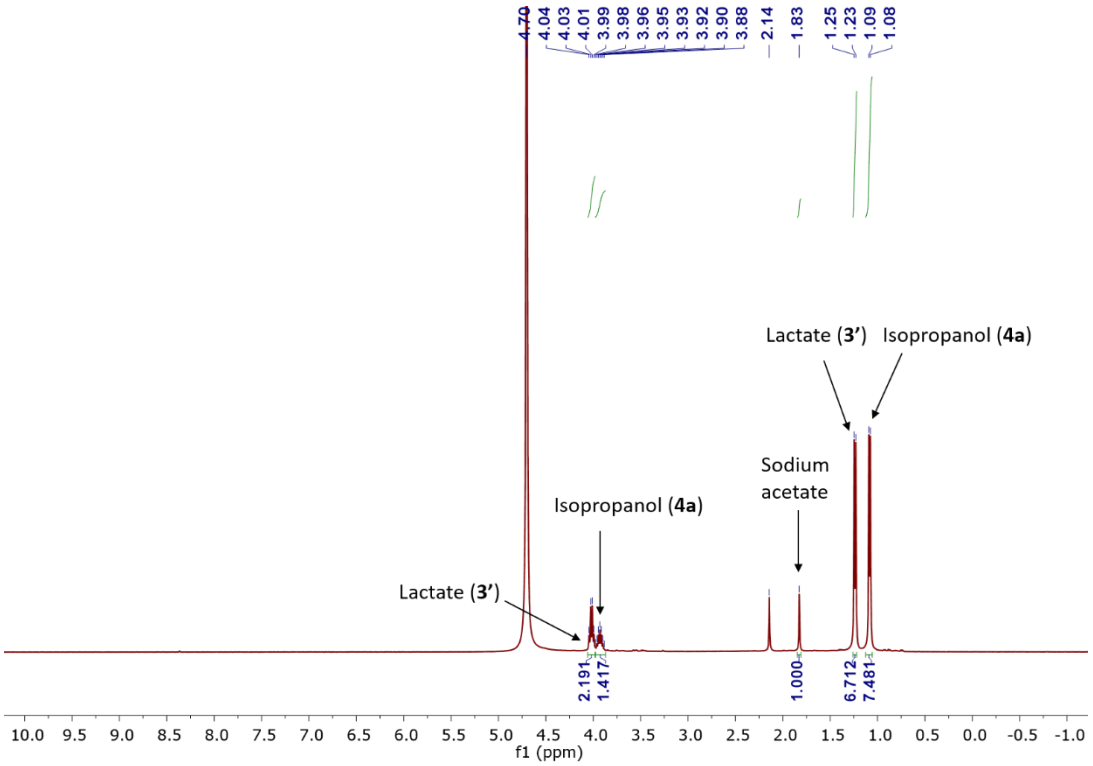

Figure S20: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents NaOH, 1.5 equivalents acetone (**2a**), at 160 °C. (entry 19, Table 1).

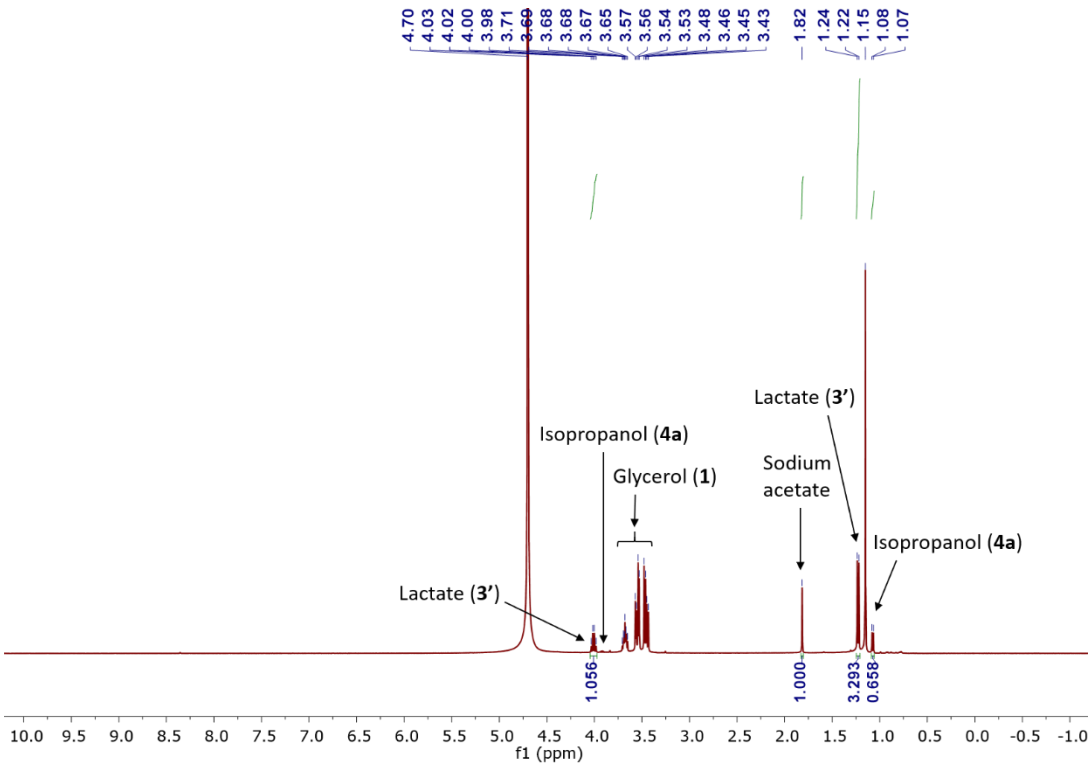

Figure S21: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents NaO^tBu, at 160 °C. (entry 20, Table 1).

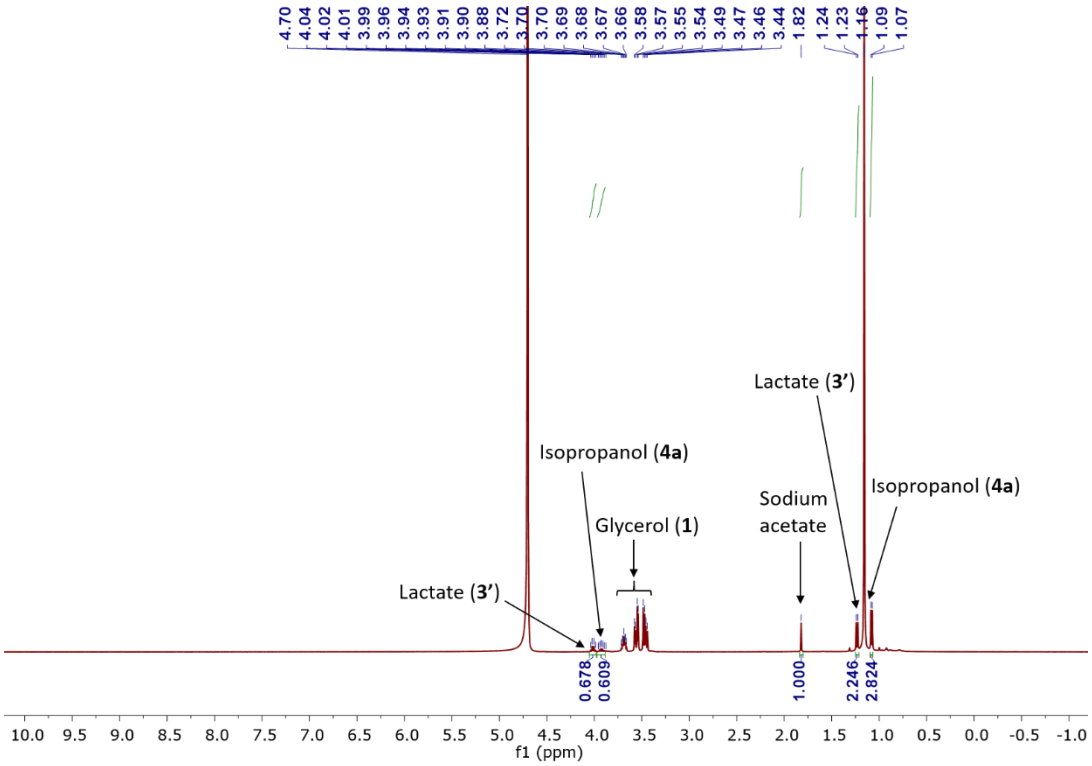

Figure S22: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents KO^tBu, at 160 °C. (entry 21, Table 1).

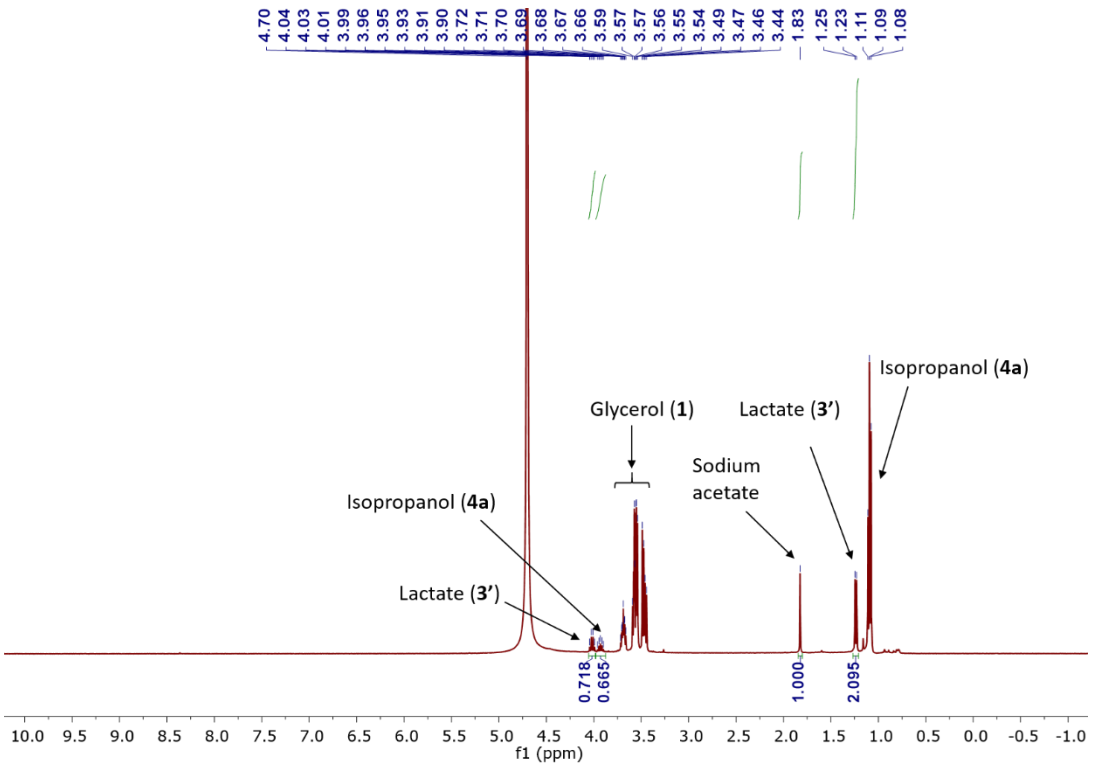

Figure S23: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents NaOEt, at 160 °C. (entry 22, Table 1).

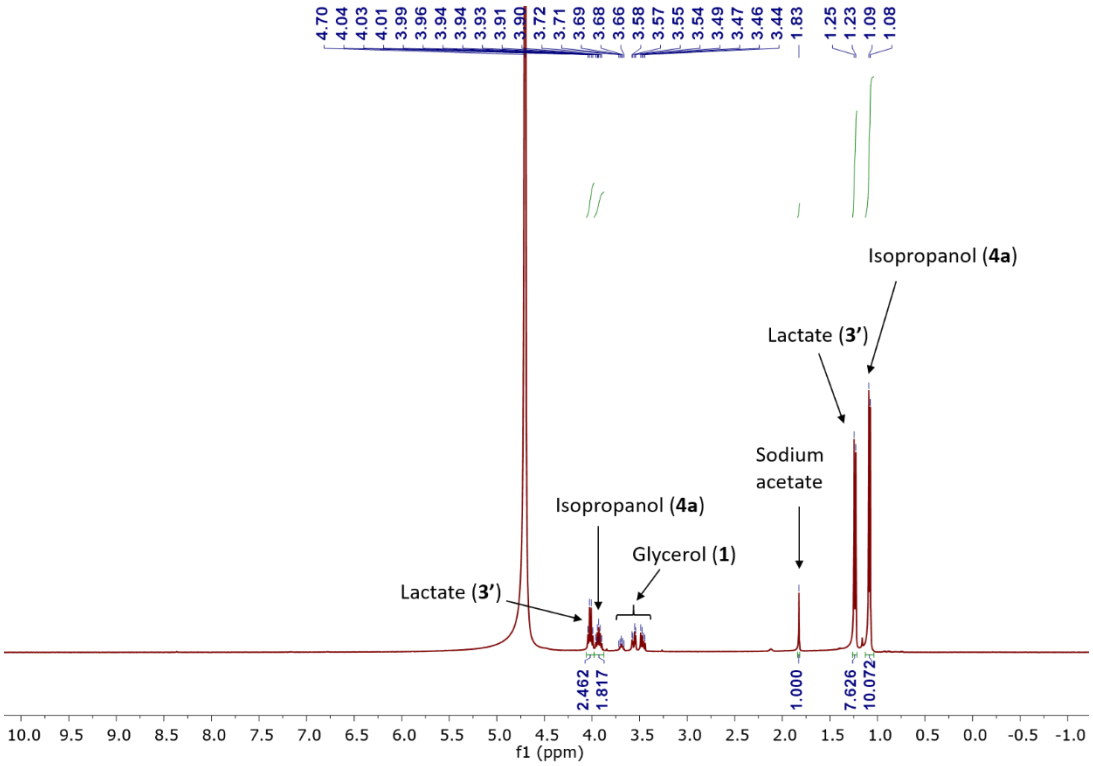

Figure S24: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5a**, 1.1 equivalents NaOH, at 160 °C. (entry 27, Table 1).

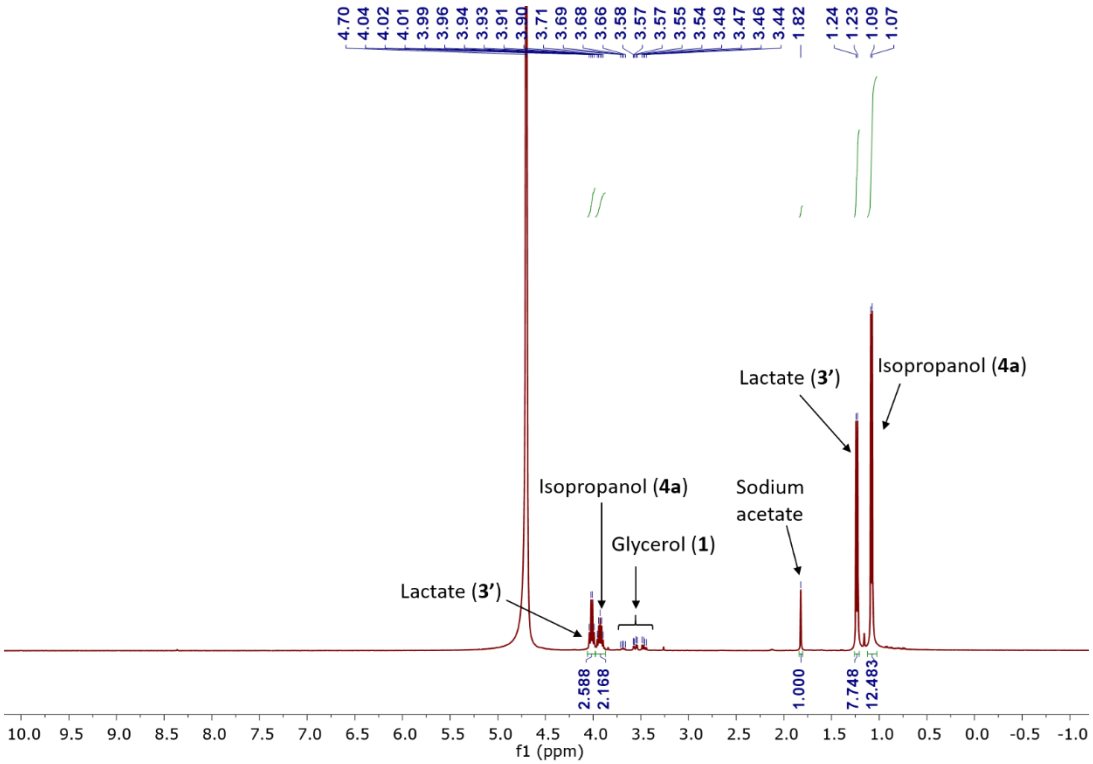

Figure S25: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, at 160 °C. (entry 28, Table 1).

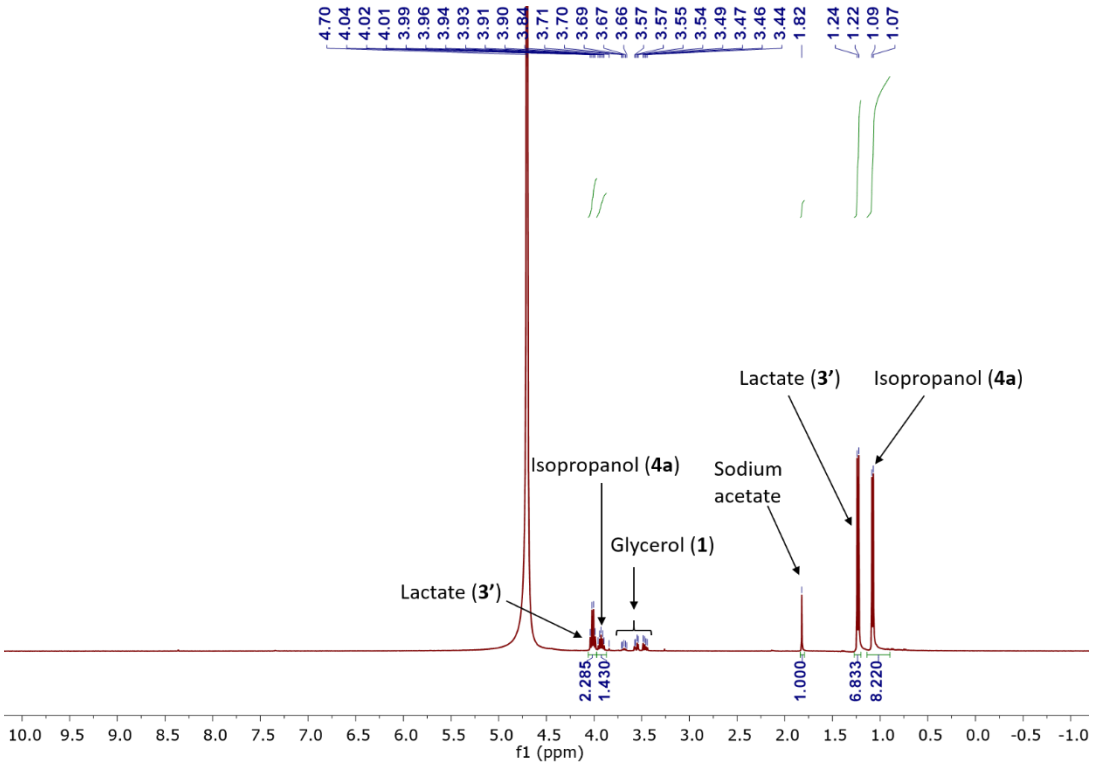

Figure S26: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5c**, 1.1 equivalents NaOH, at 160 °C. (entry 29, Table 1).

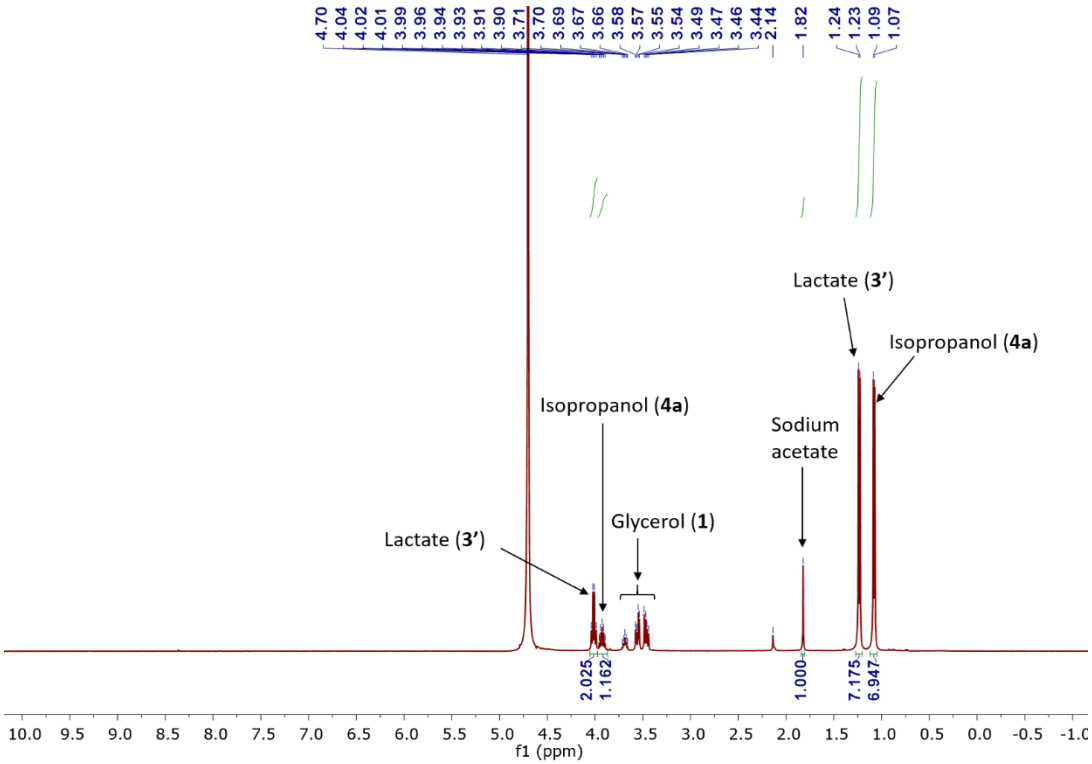

Figure S27: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5d**, 1.1 equivalents NaOH, at 160 °C. (entry 30, Table 1).

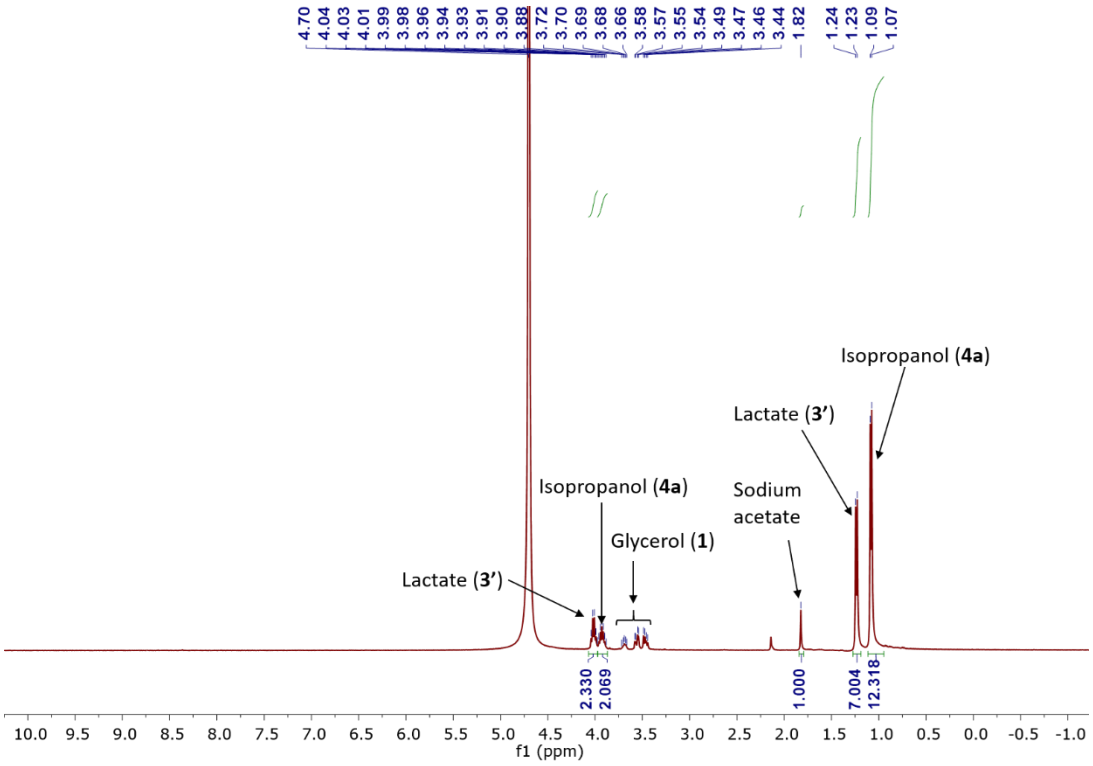

Figure S28: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.75 mol% **5b**, 1.1 equivalents NaOH, at 160 °C. (entry 31, Table 1).

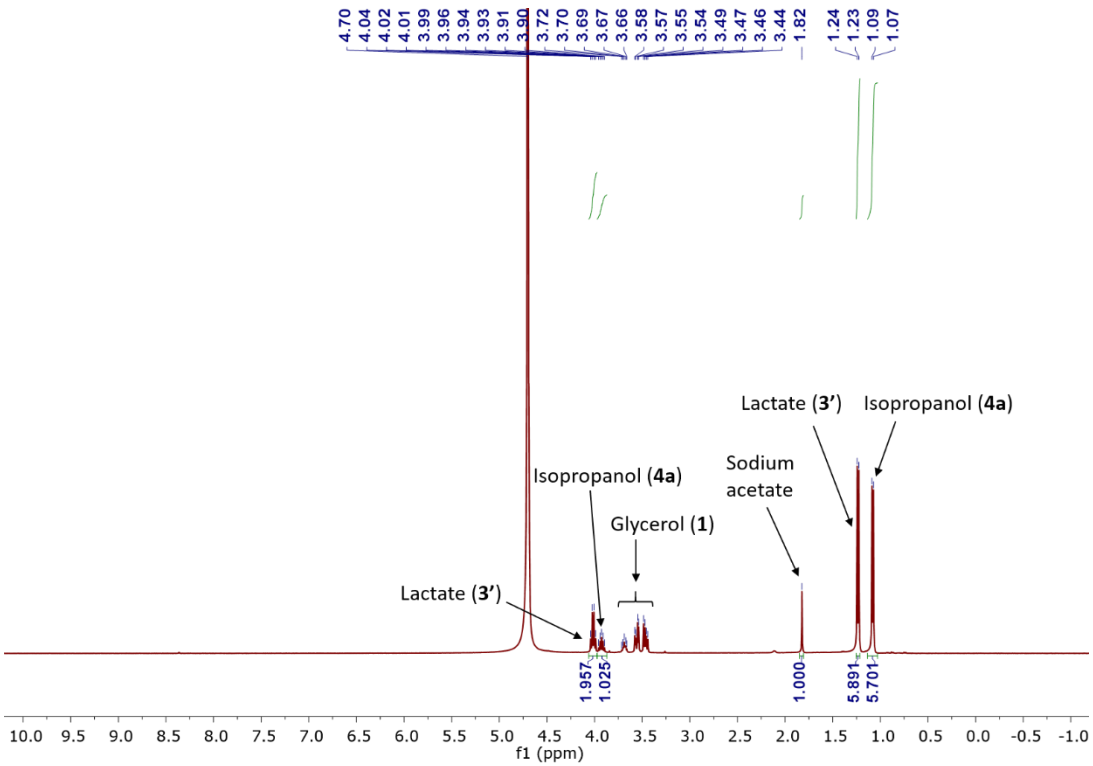

Figure S29: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.25 mol% **5b**, 1.1 equivalents NaOH, at 160 °C. (entry 32, Table 1).

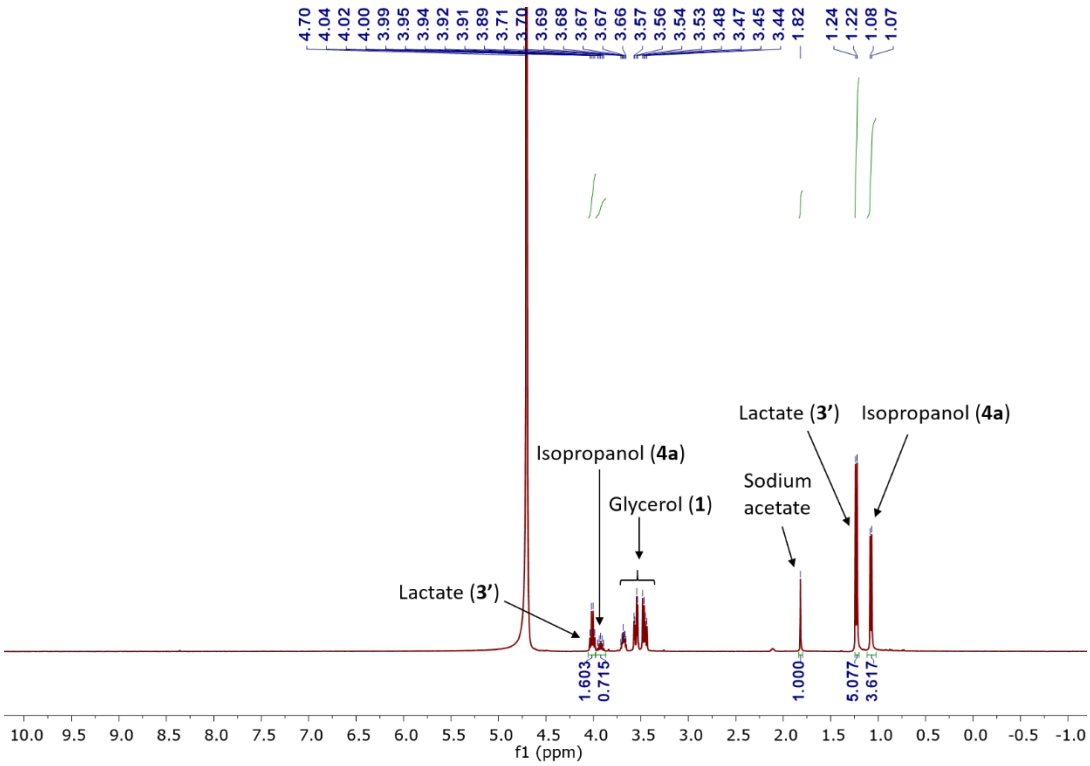

Figure S30: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.05 mol% **5b**, 1.1 equivalents NaOH, at 160 °C. (entry 33, Table 1).

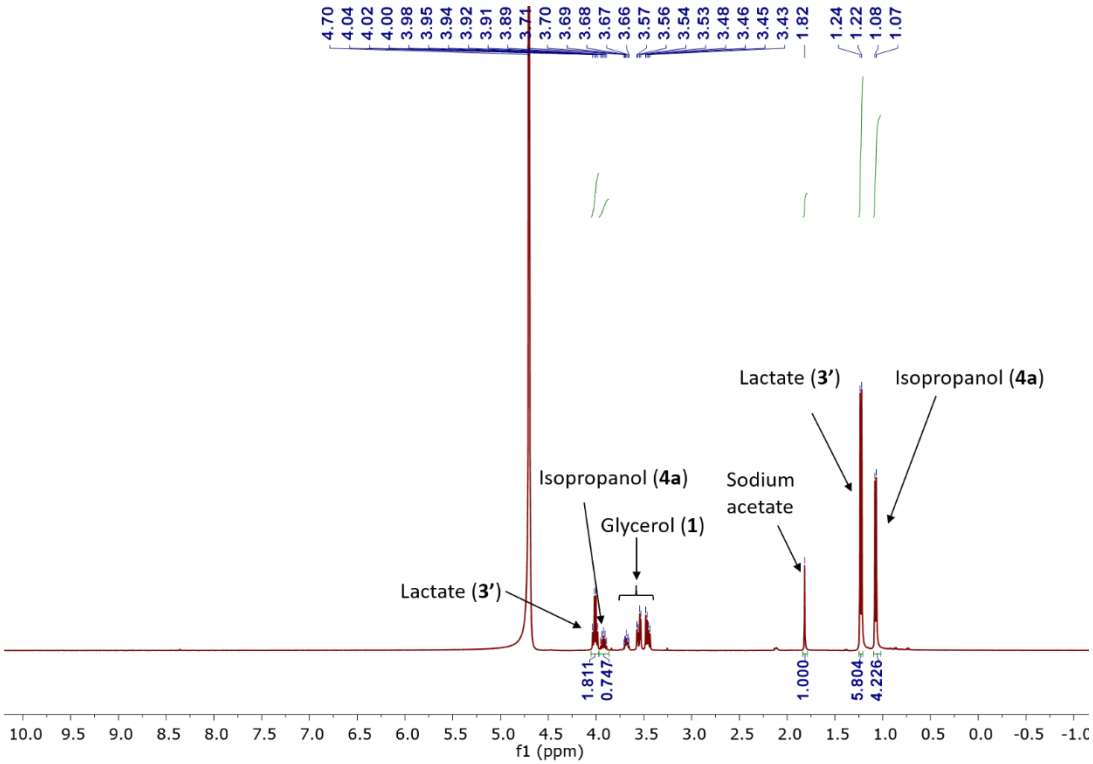

Figure S31: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.005 mol% **5b**, 1.1 equivalents NaOH, at 160 °C. (entry 34, Table 1).

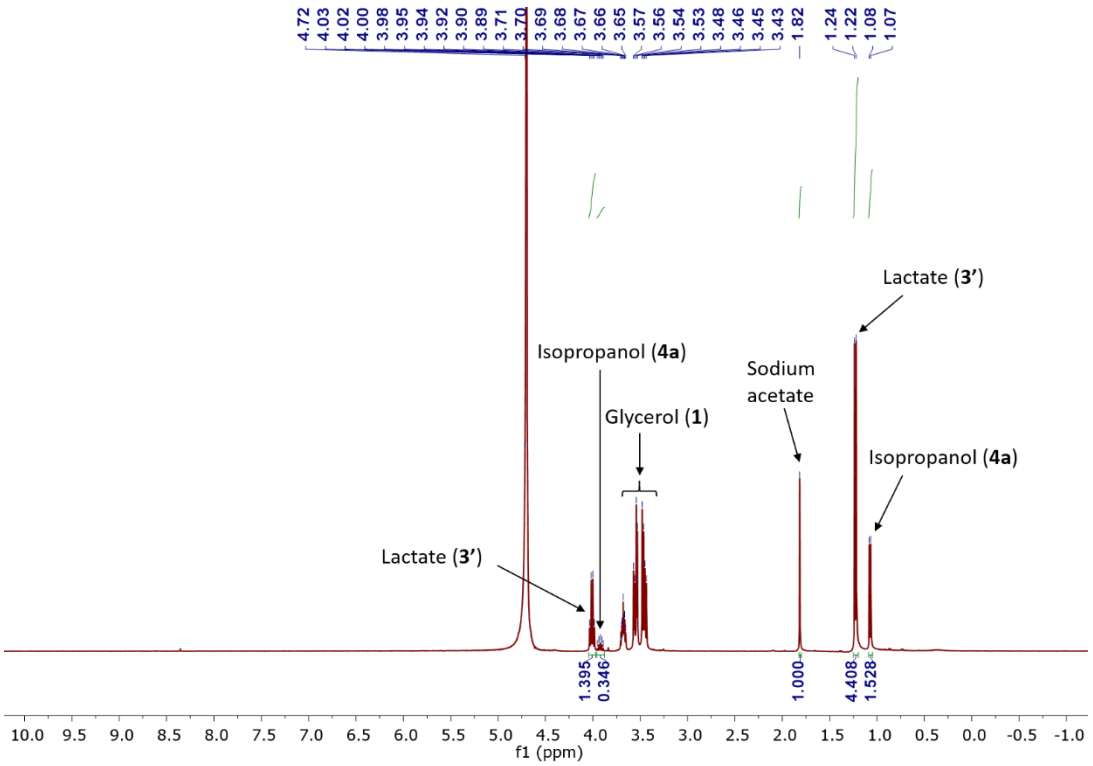

Figure S32: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.00125 mol% **5b**, 1.1 equivalents NaOH, at 160 °C. (entry 35, Table 1).

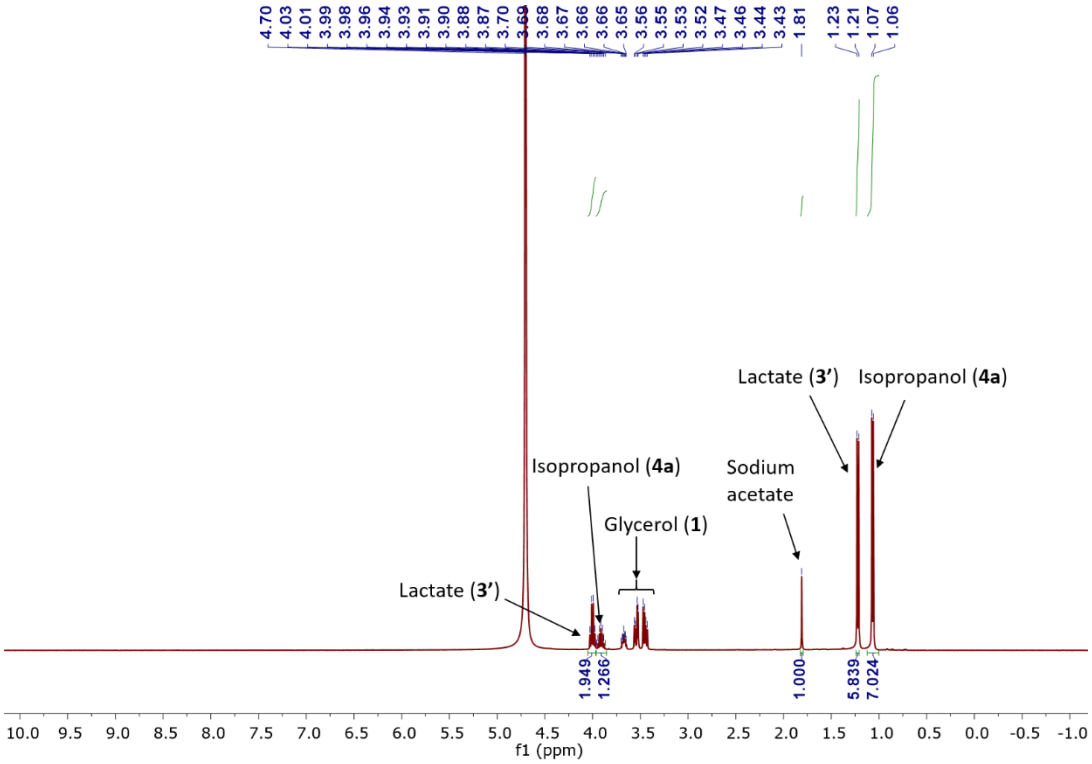

Figure S33: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, at 140 °C. (entry 36, Table 1).

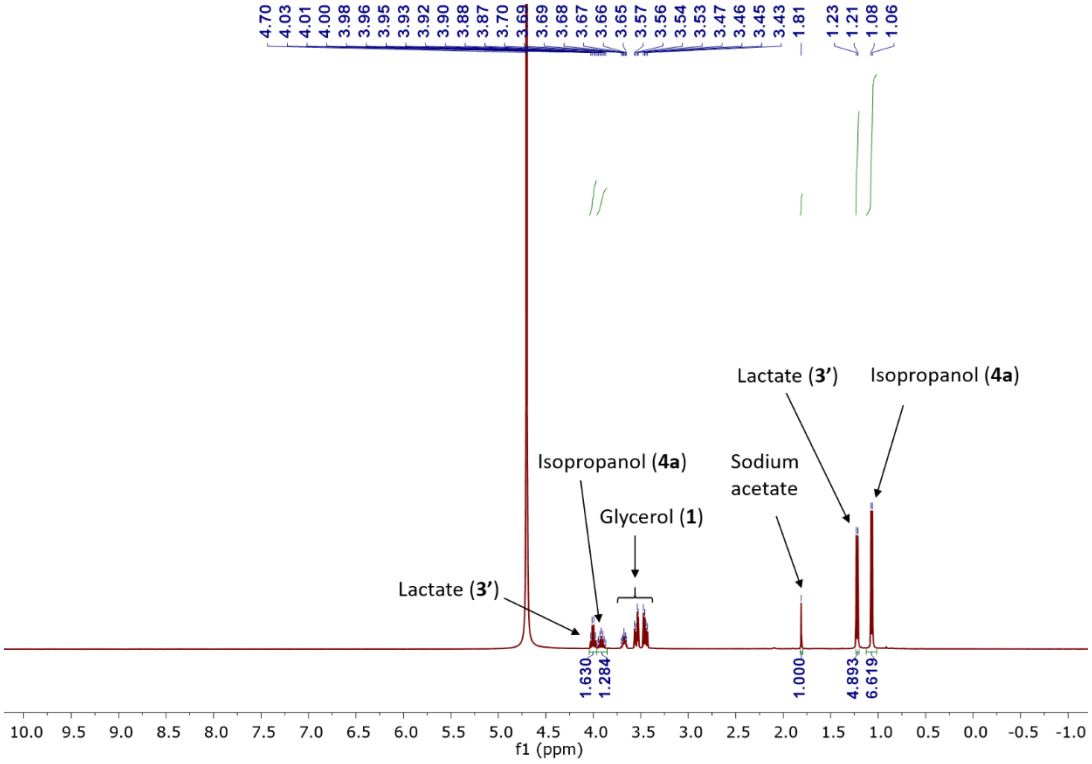

Figure S34: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, at 120 °C. (entry 37, Table 1).

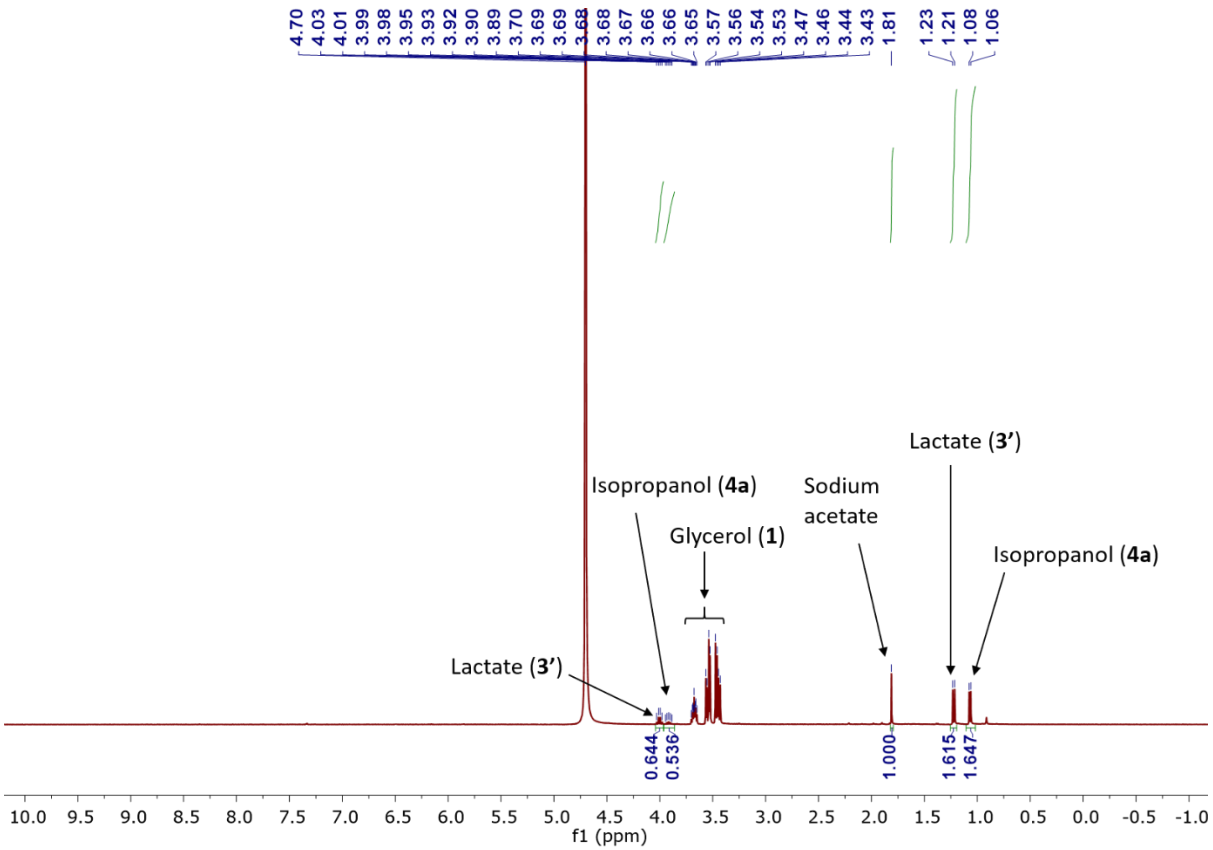

Figure S35: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, at 100 °C. (entry 38, Table 1).

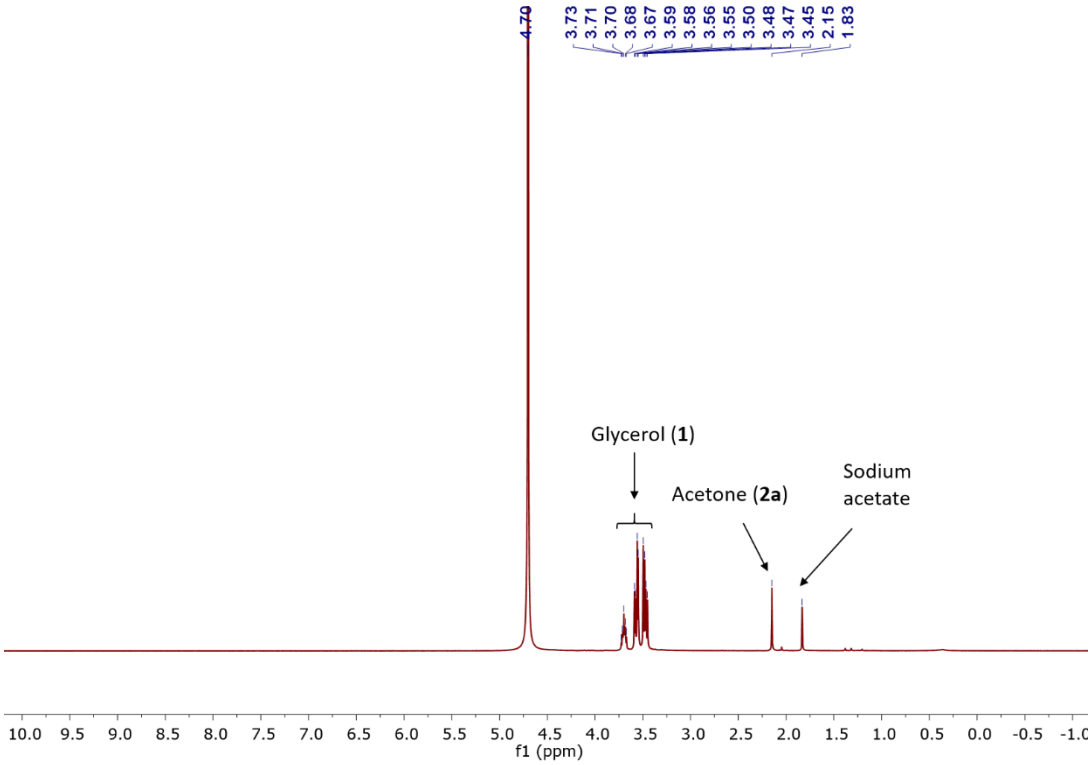

Figure S36: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, in presence of **2a**. (entry 2, Table 2).

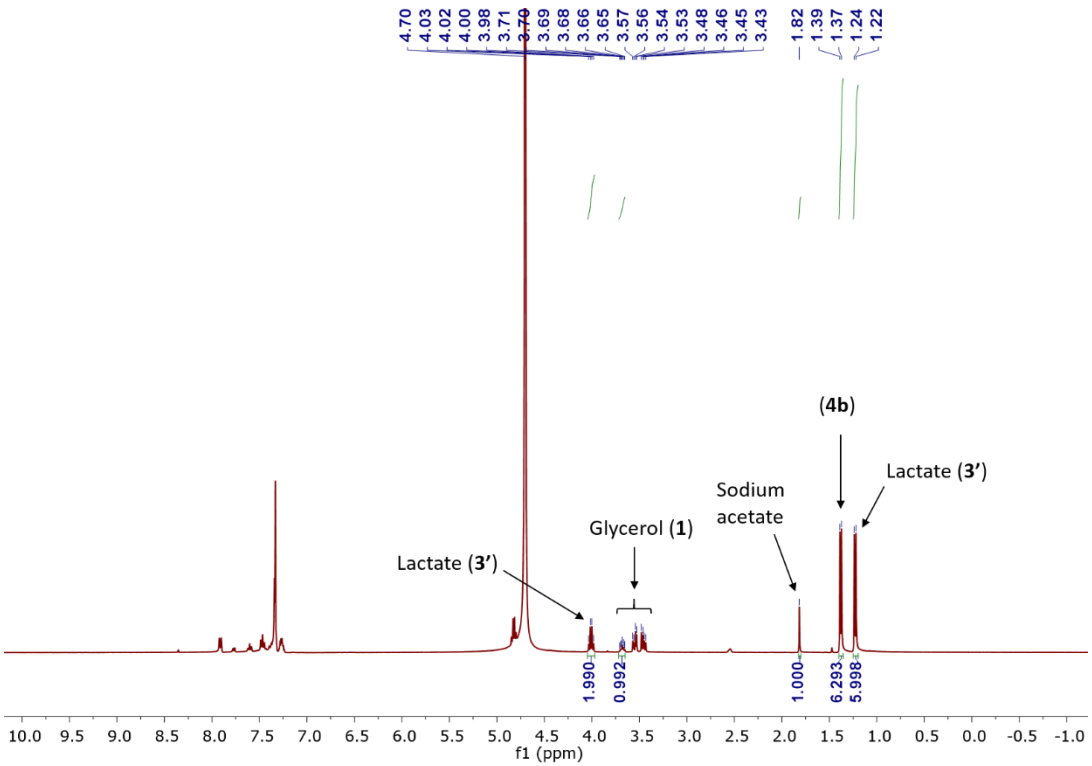

Figure S37: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2b**. (entry 4, Table 2).

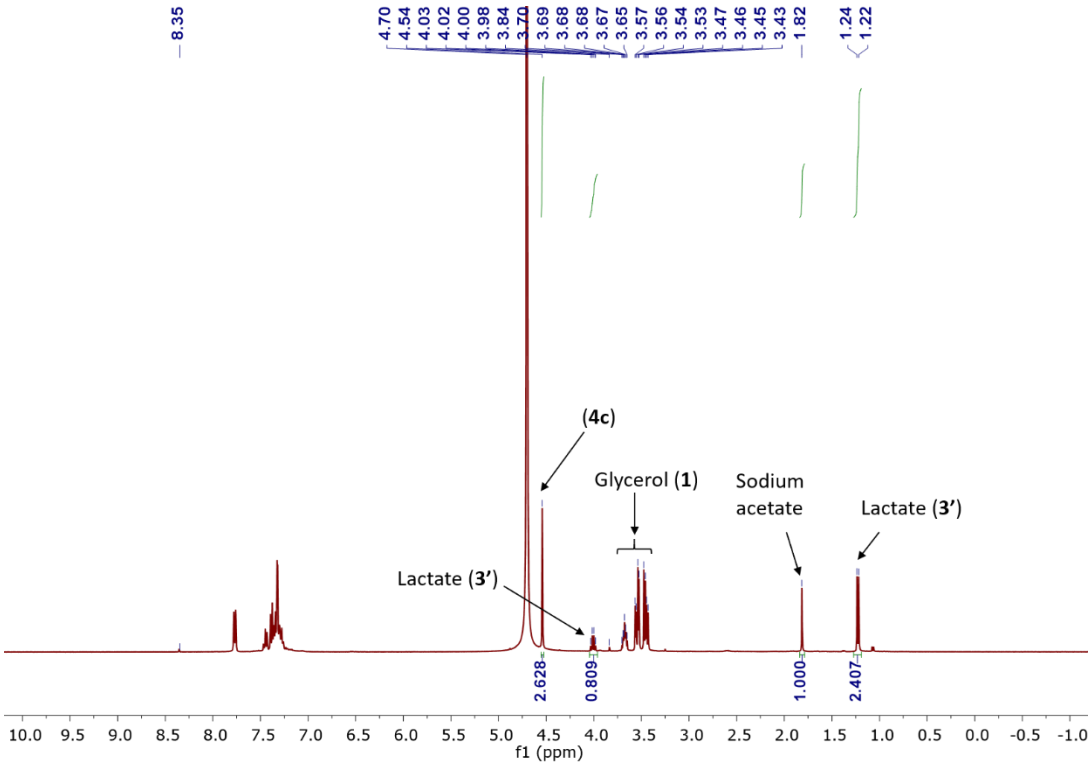

Figure S38: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2c**. (entry 5, Table 2).

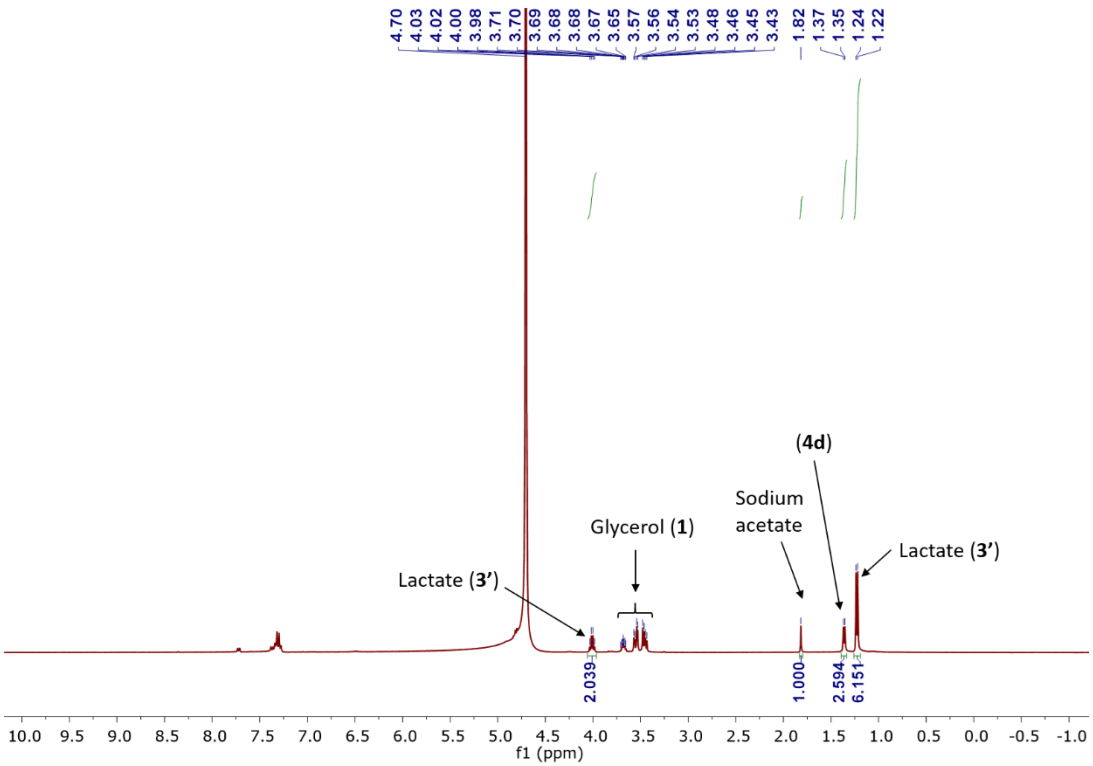

Figure S39: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2d**. (entry 6, Table 2).

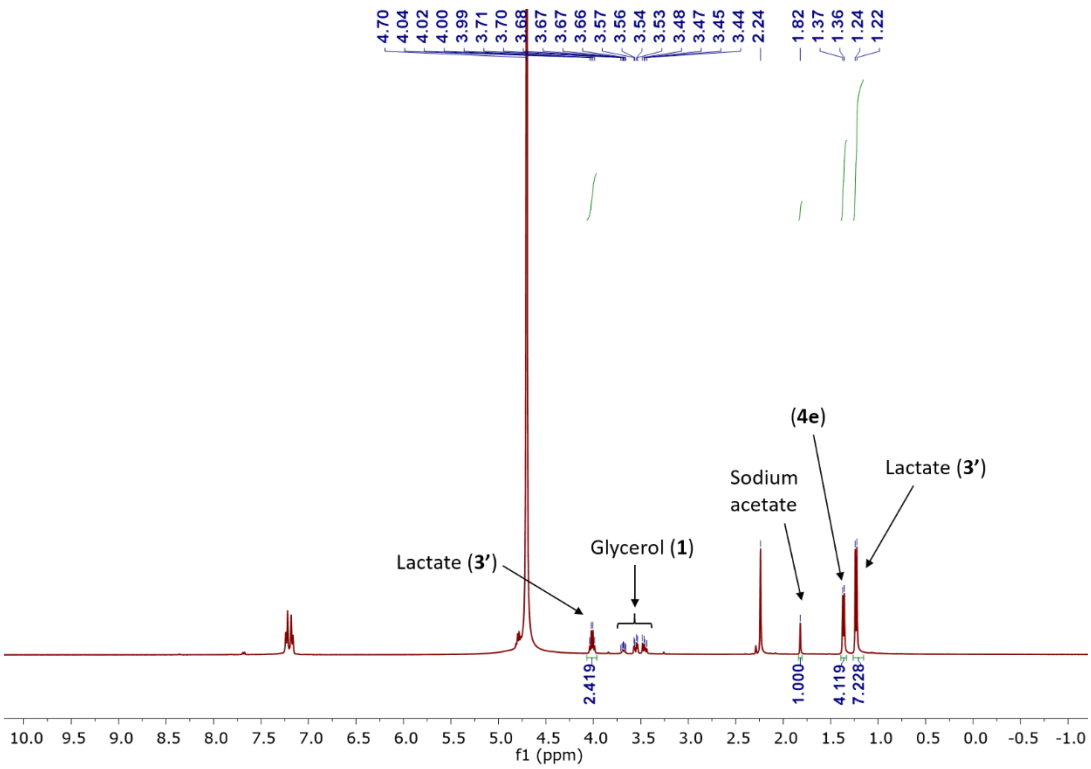

Figure S40: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2e**. (entry 7, Table 2).

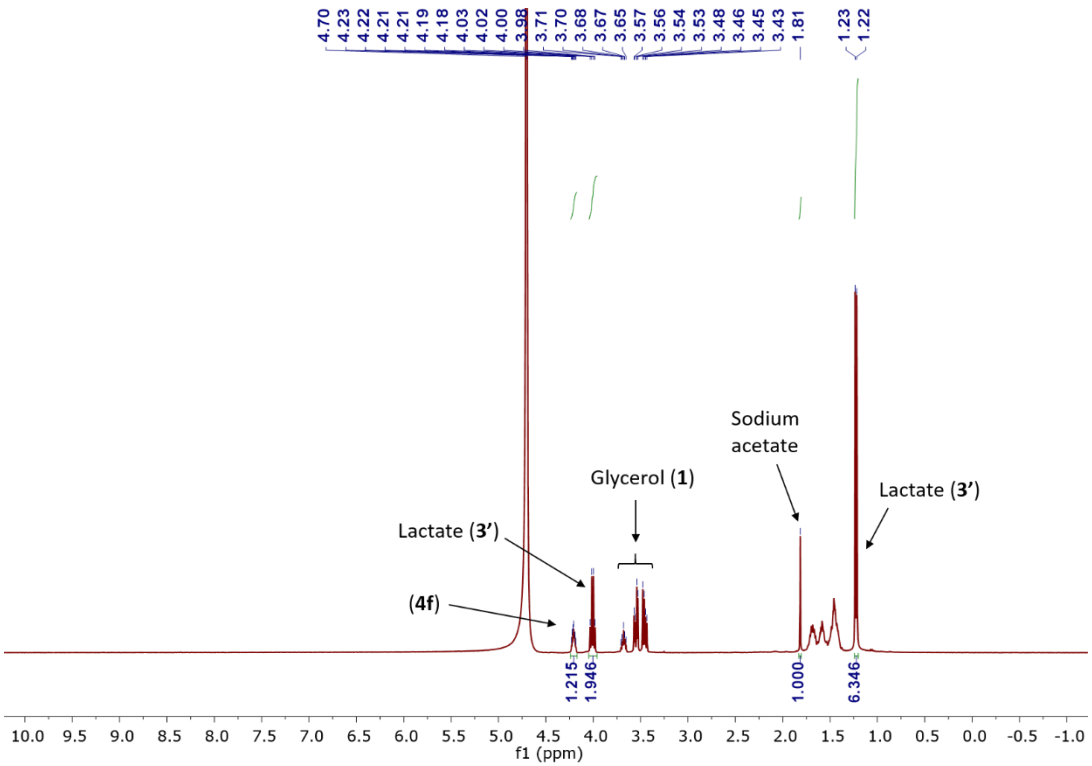

Figure S41: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2f**. (entry 8, Table 2).

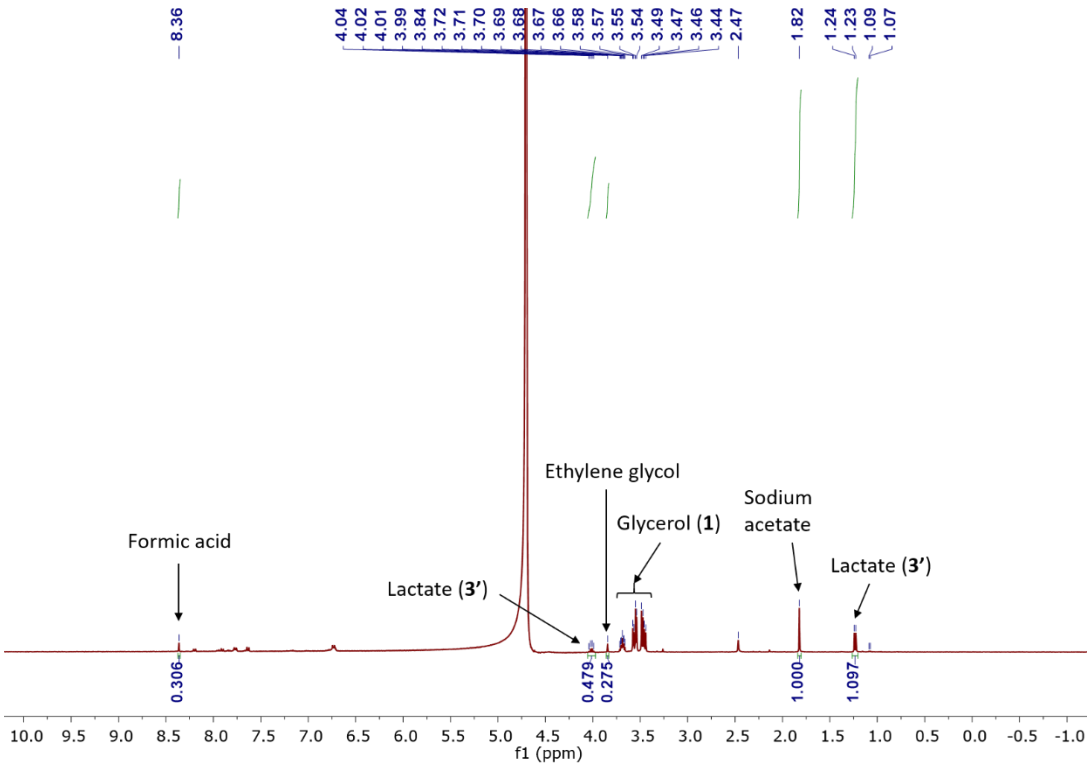

Figure S42: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2g**. (entry 9, Table 2).

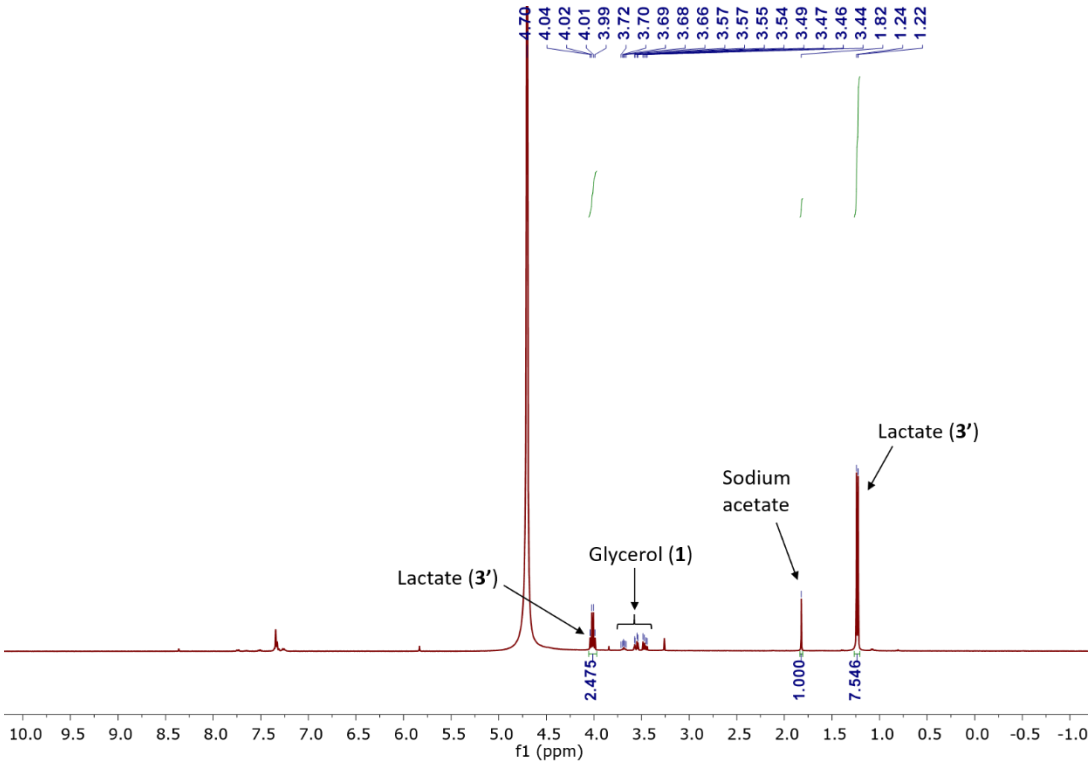

Figure S43a: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2h** in D_2O. (entry 10, Table 2).

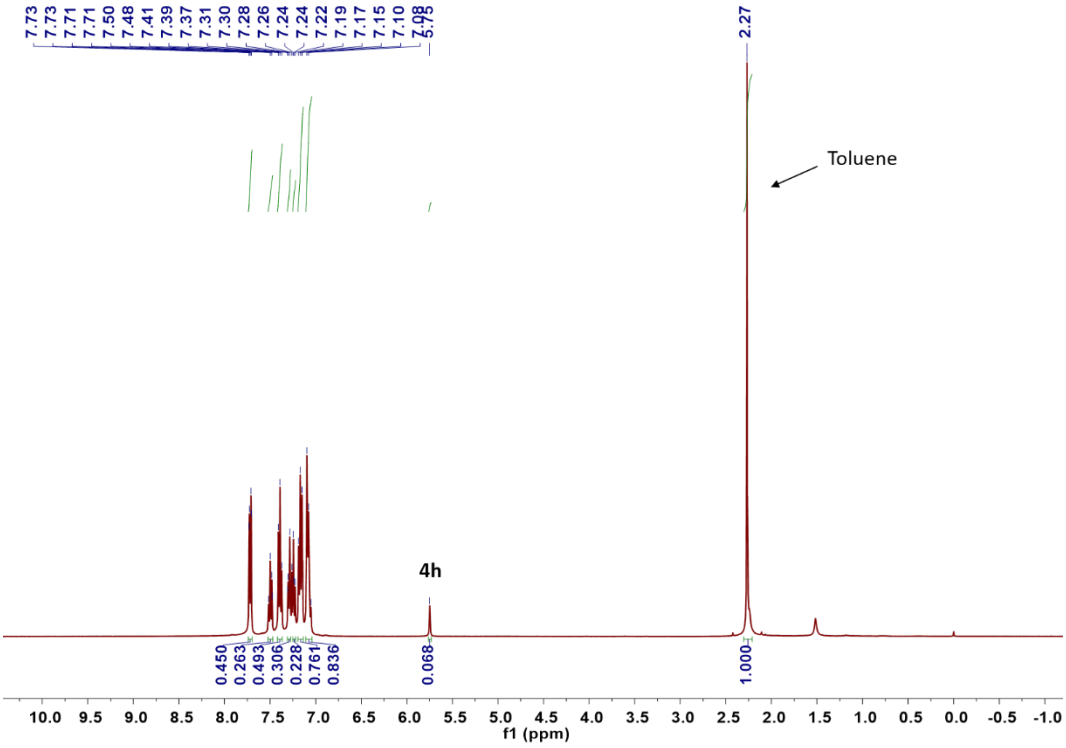

Figure S43b: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2h** in $CDCl_3$. (entry 10, Table 2).

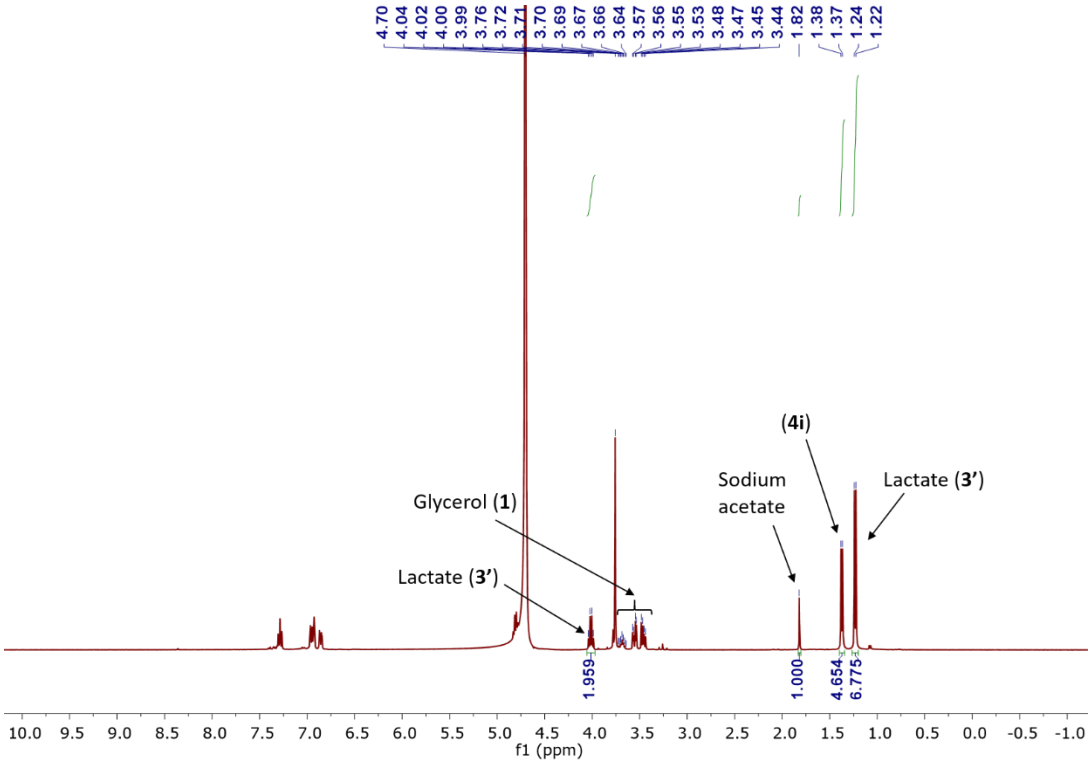

Figure S44: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2i**. (entry 11, Table 2).

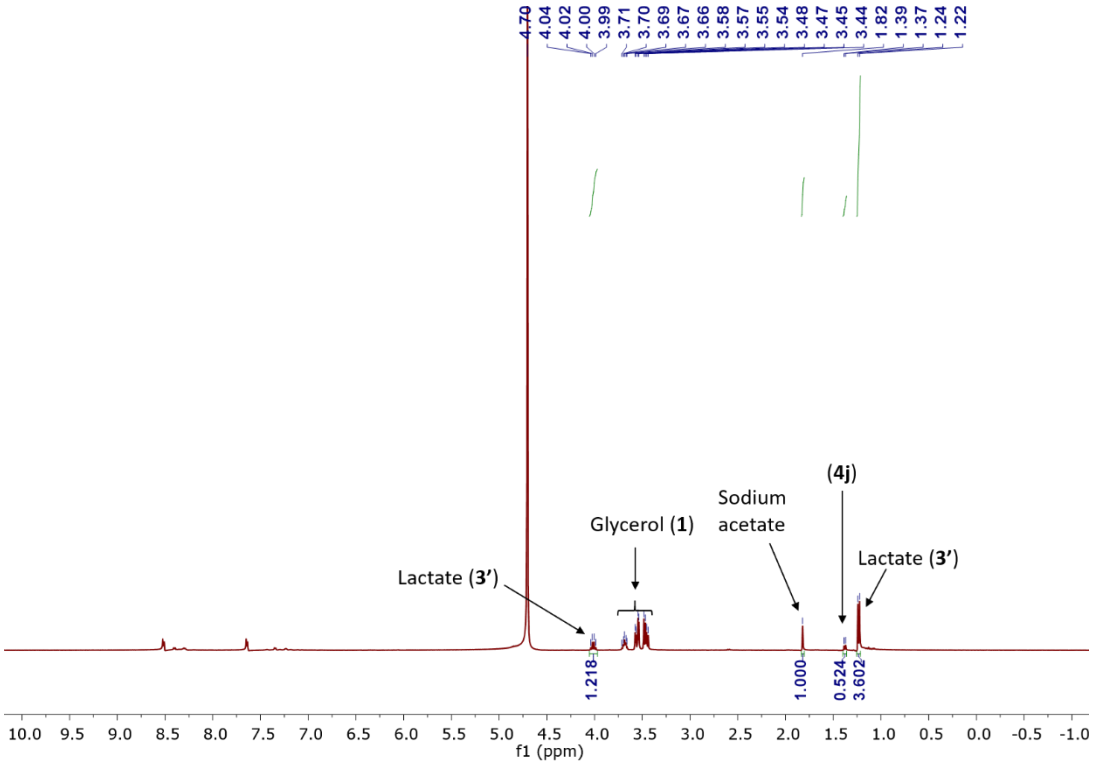

Figure S45: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2j**. (entry 12, Table 2).

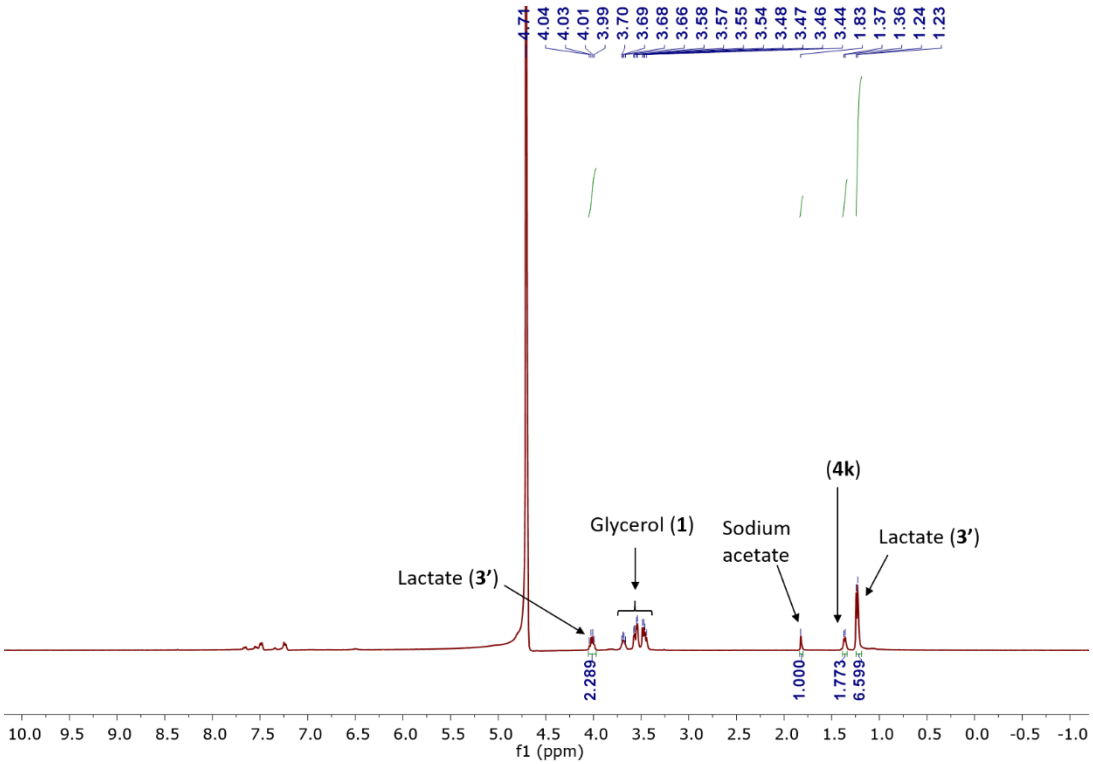

Figure S46: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2k**. (entry 13, Table 2).

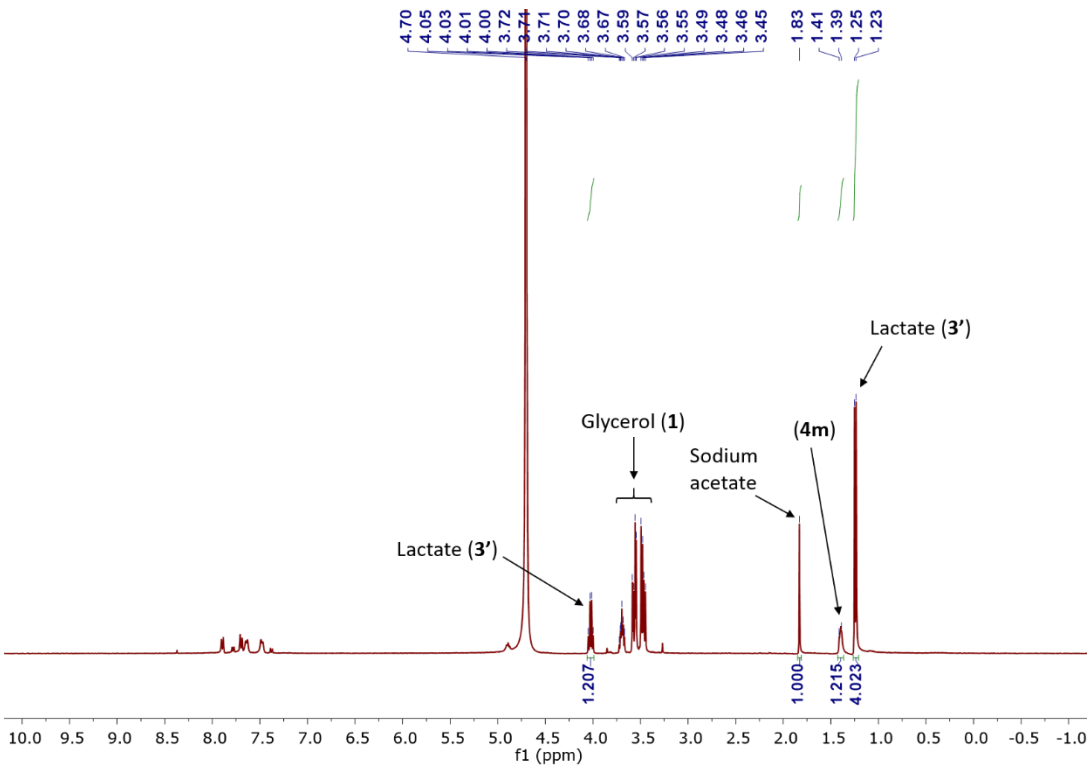

Figure S47: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2m**. (entry 15, Table 2).

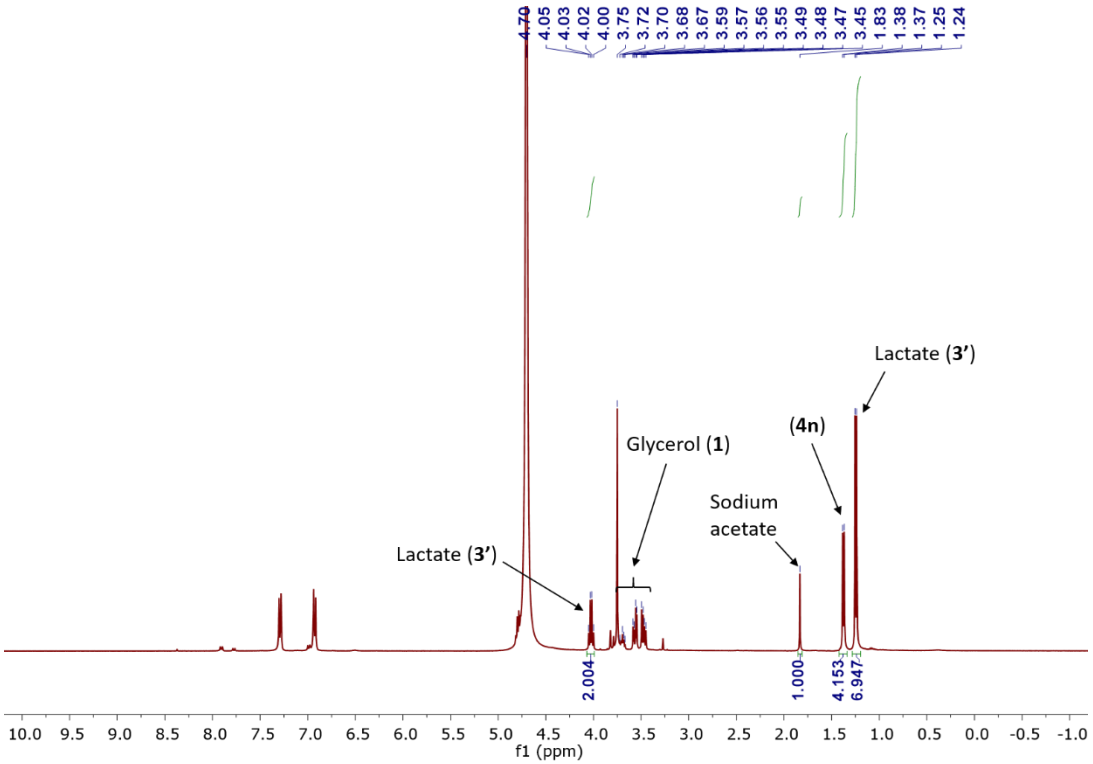

Figure S48: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2n**. (entry 16, Table 2).

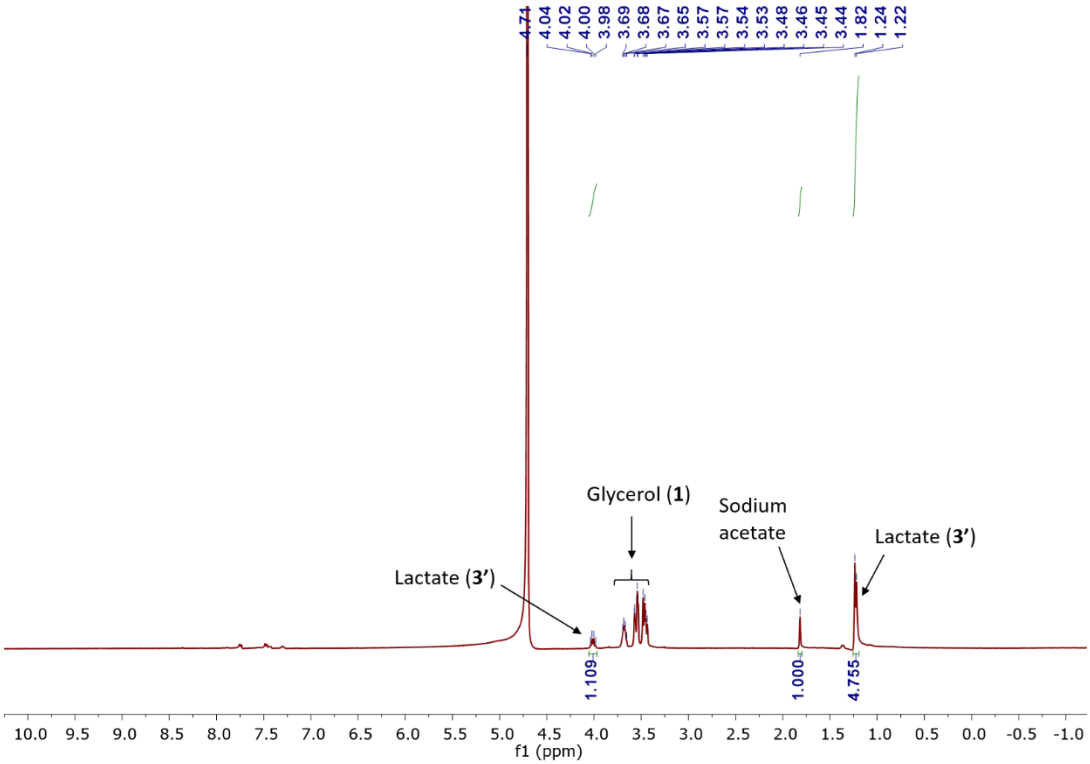

Figure S49: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2o**. (entry 17, Table 2).

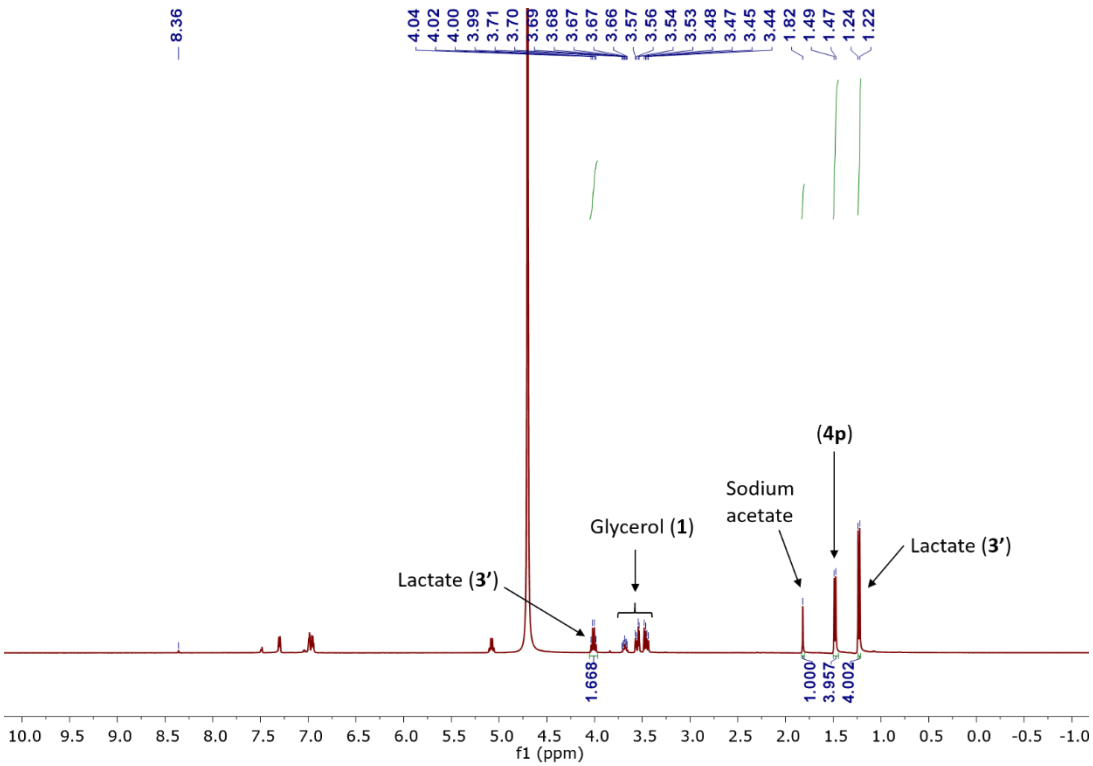

Figure S50: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2p**. (entry 18, Table 2).

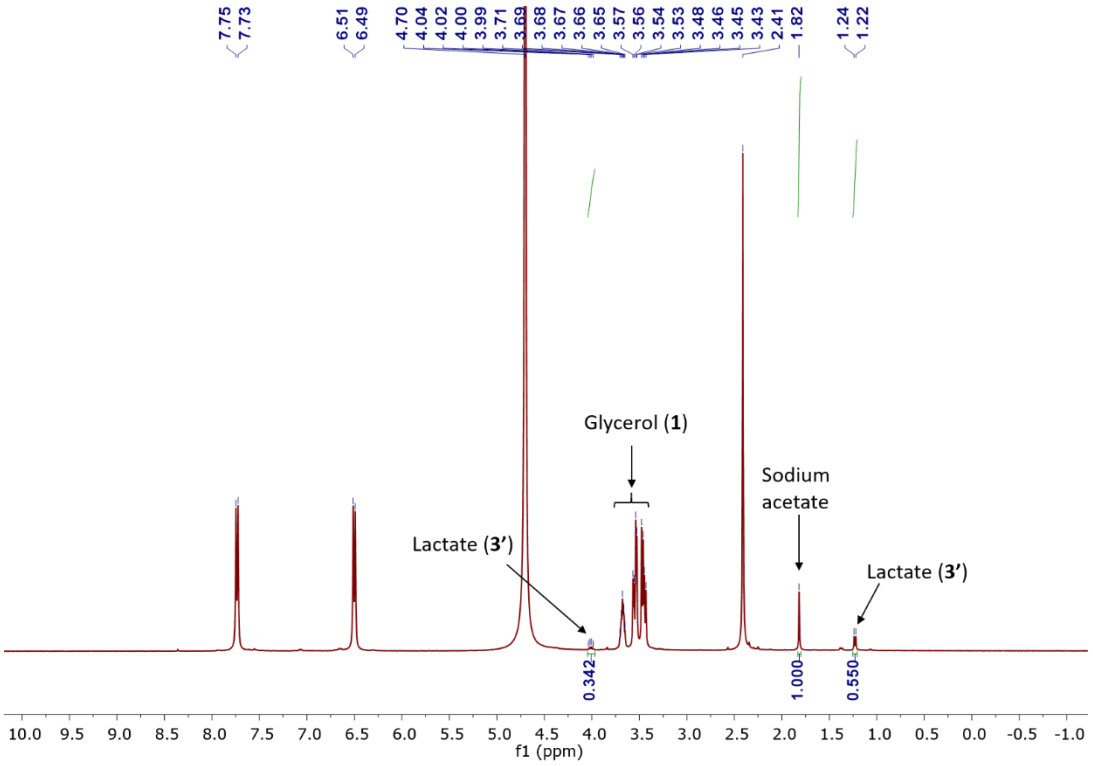

Figure S51: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of **2q**. (entry 19, Table 2).

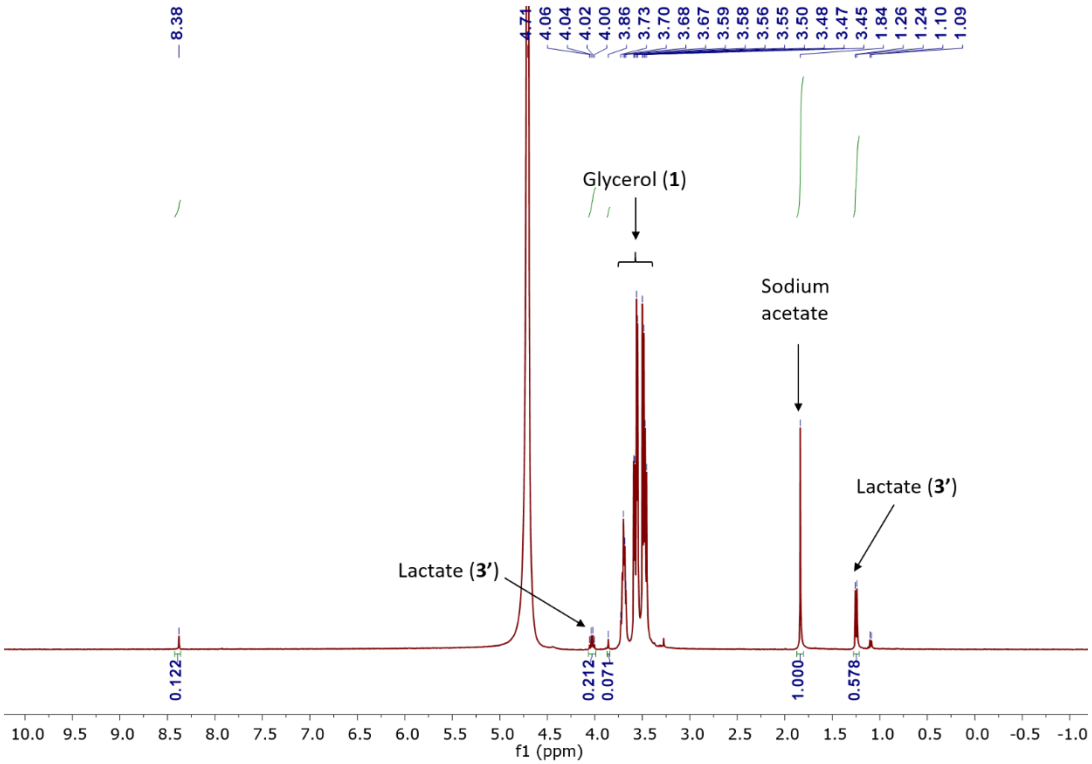

Figure S52: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in absence of any acceptor. (entry 20, Table 2).

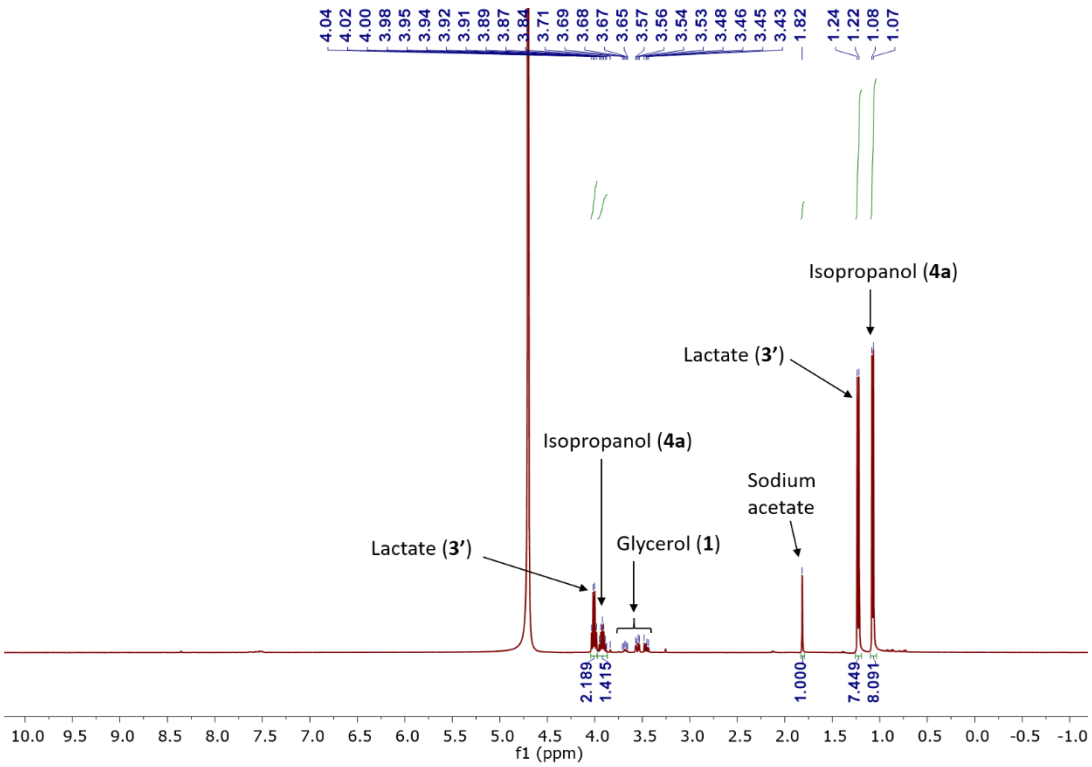

Figure S53: ^{1}H NMR spectra of glycerol (1) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents NaOH, in presence of 5 mol% PPh_3. (equation 3, Scheme 1).

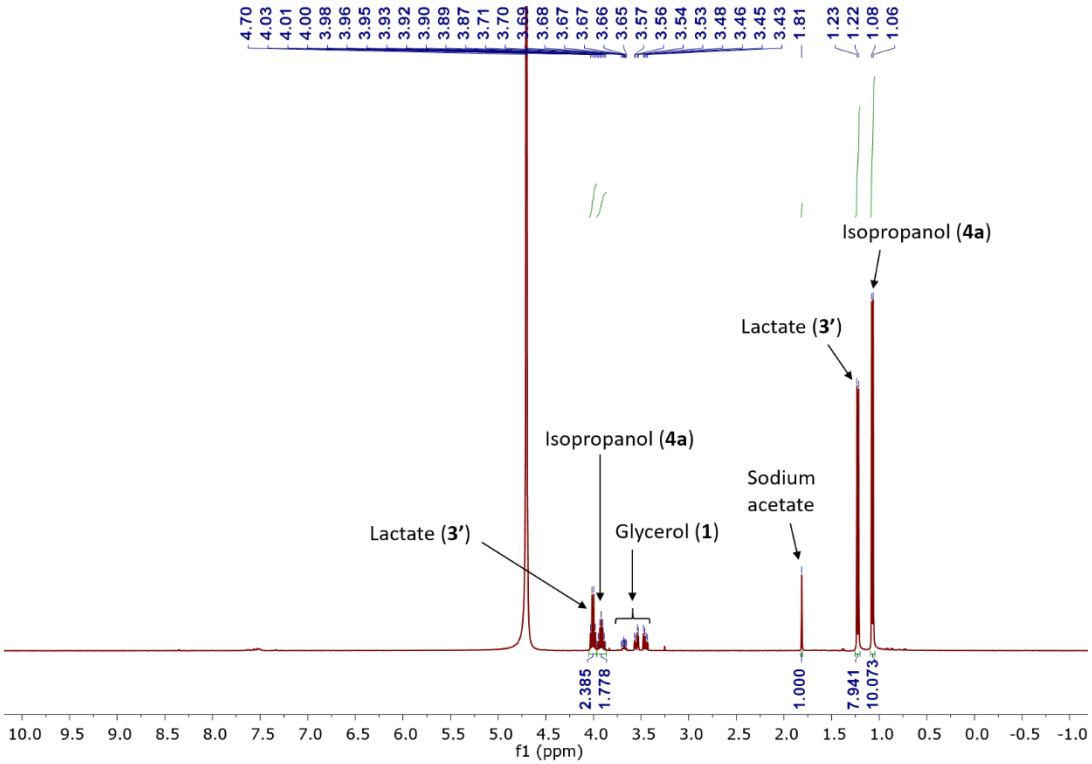

Figure S54: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of 5 mol% PPh_3. (equation 4, Scheme 1).

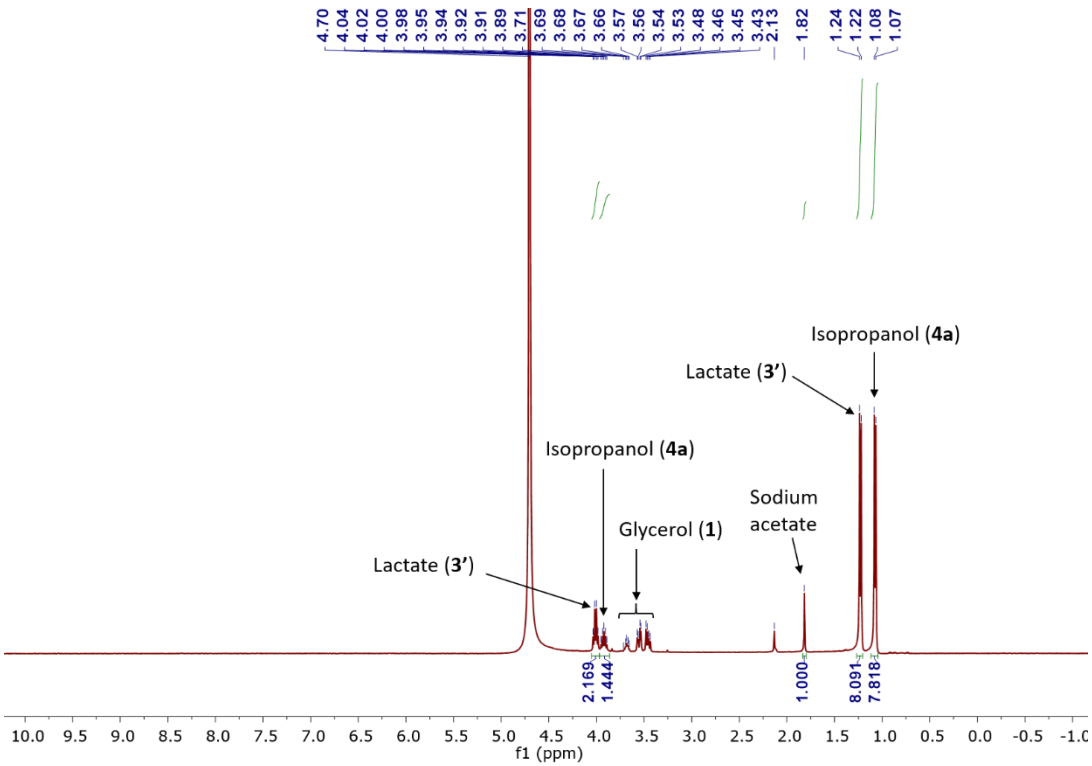

Figure S55: [1]H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% $CrCl_3.6H_2O$, 1.1 equivalents NaOH, in presence of 5 mol% CS_2. (equation 5, Scheme 1).

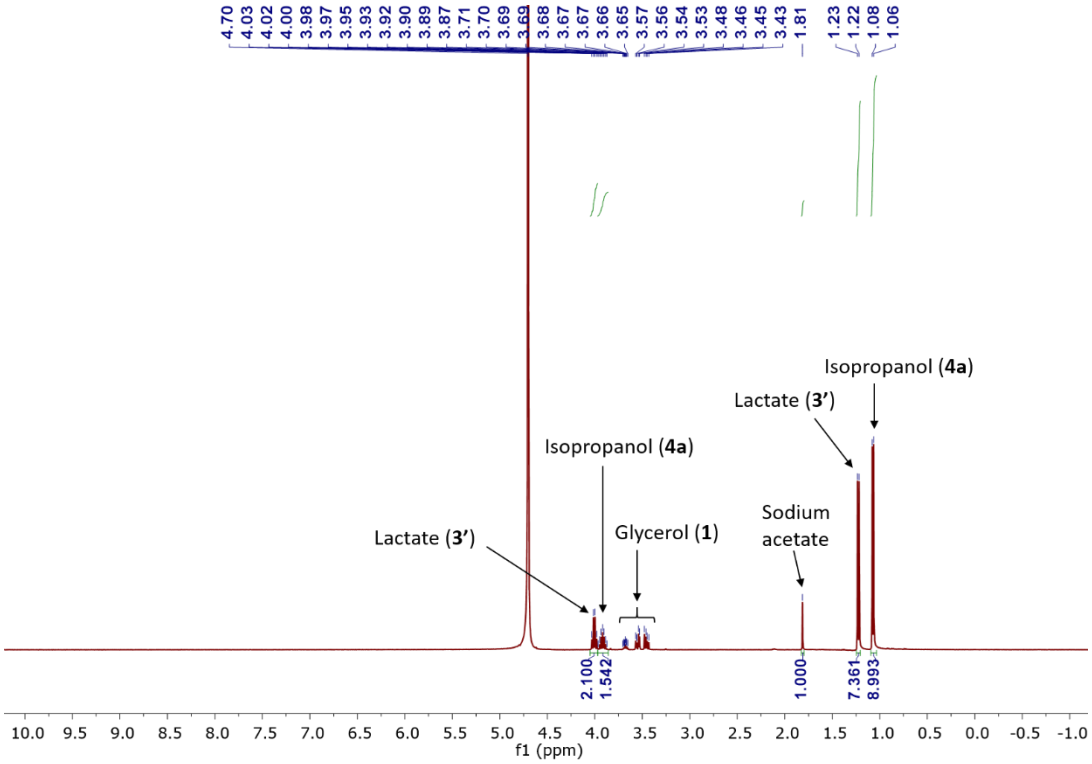

Figure S56: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of 5 mol% CS_2. (equation 6, Scheme 1).

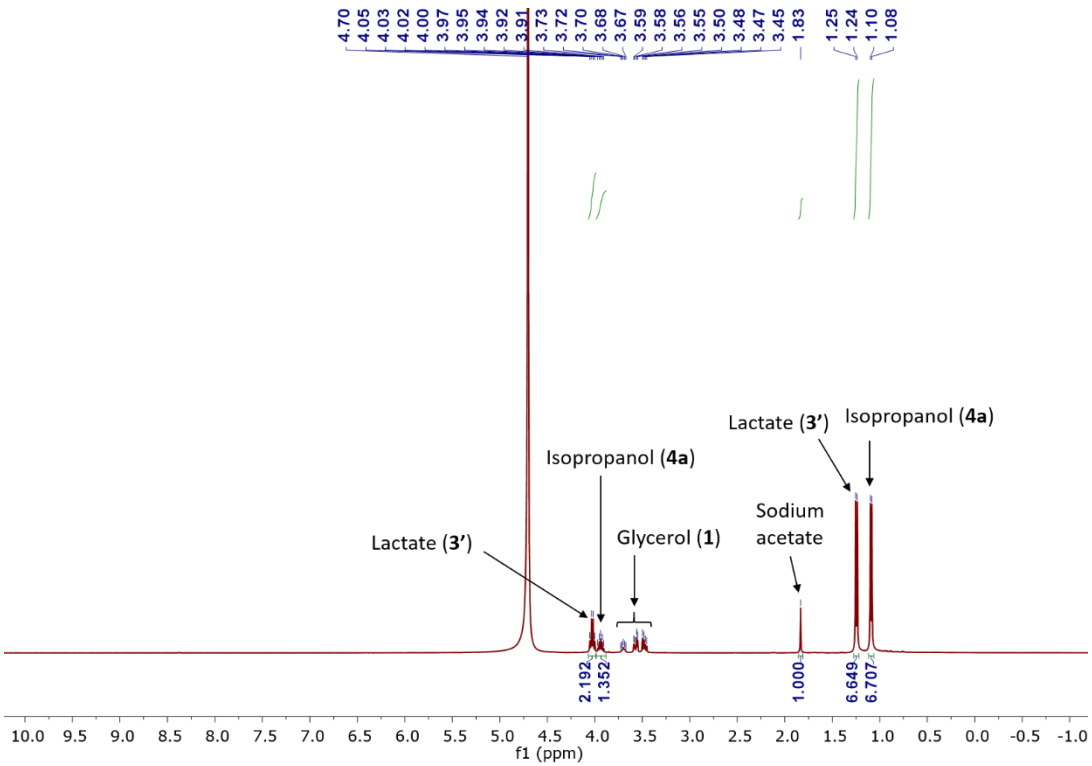

Figure S57: ^{1}H NMR spectra of glycerol (**1**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in presence of Hg (excess). (equation 7, Scheme 1).

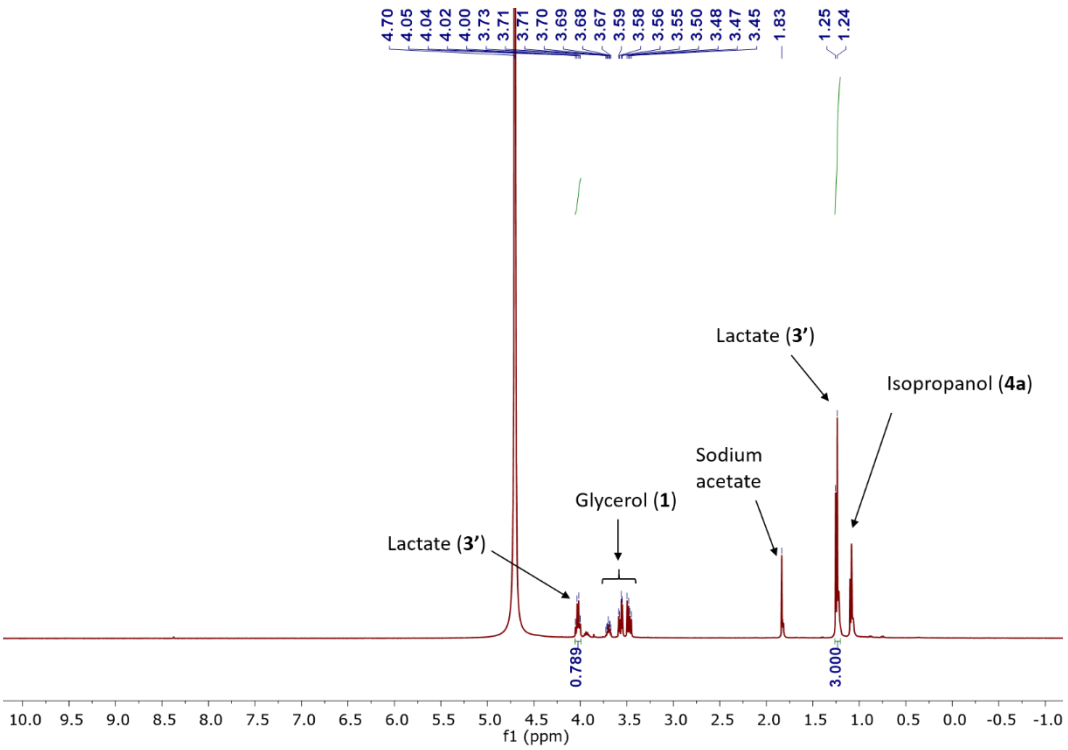

Figure S58a: ^{1}H NMR spectra of a mixture of glycerol (**1**) and glycerol-D8 (**1c**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH. (equation 10, Scheme 1).

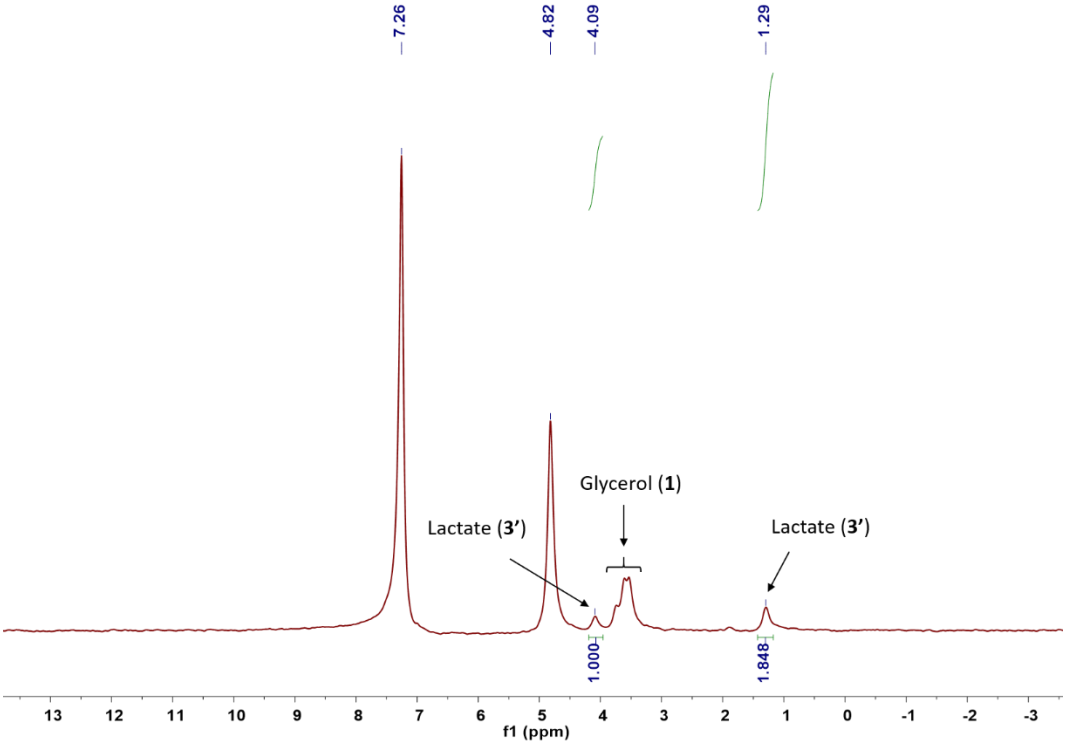

Figure S58b: ^{2}H NMR spectra of a mixture of glycerol (**1**) and glycerol-D8 (**1c**) transfer dehydrogenation to lactate catalyzed by 0.5 mol% **5b**, 1.1 equivalents NaOH, in water using $CDCl_3$ lock. (equation 10, Scheme 1).

5. Kinetic study

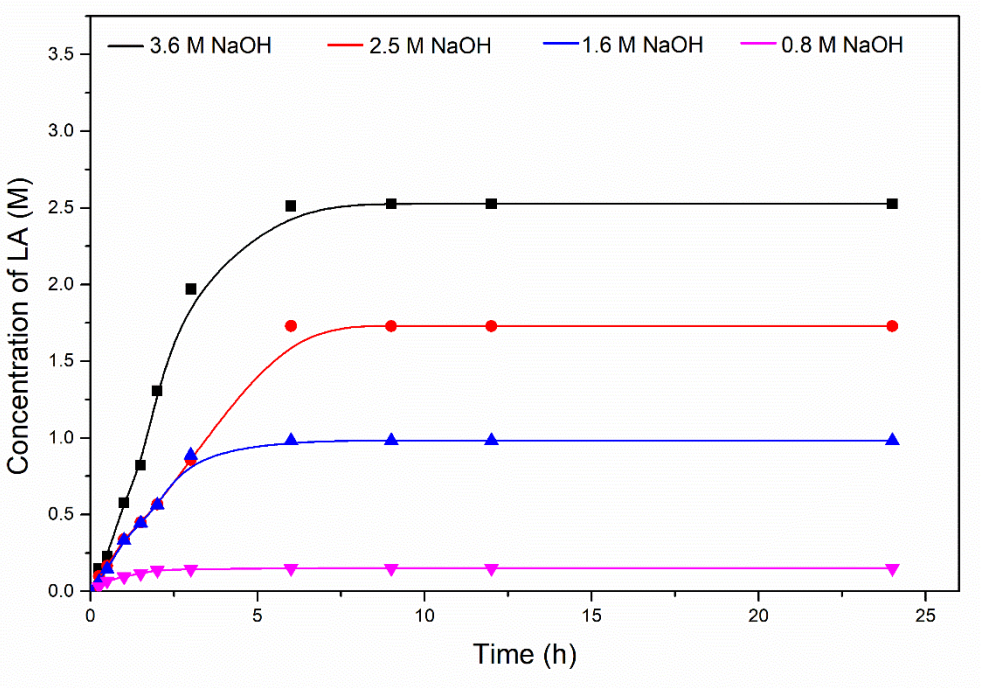

Figure S59. Time-profile of transfer dehydrogenation of glycerol in open vessel using glycerol (0.460 g, 5 mmol, 3.3 M), **5b** (0.0114 g, 0.025 mmol, 0.016 M), acetophenone (1.2 g, 10 mmol, 6.6 M), at 160 °C, in presence of NaOH (0.05-0.22 g, 1.25-5.5 mmol, 0.8-3.6 M).