Supporting Information

Efficient net transfer-dehydrogenation of glycerol: NNN pincer-Mn and manganese chloride as a catalyst unlocks the effortless production of lactic acid and isopropanol

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Table of Contents		**Page**
1.	**XRD Analysis**	S2-S4
2.	**Magnetic Moment Studies**	S5
3.	**HRMS Simulation**	S5-S15
4.	**GC Analysis**	S15-S17
5.	**Kinetic Studies**	S18
6.	**NMR Spectra**	S19-44

1. X-ray Analysis

Table S1. Crystal data and refinement parameter of 6a and 6b

Complex	6a	6b
Empirical formula	$C_{16}H_{25}Cl_4MnN_3$	$C_{13}H_{19}Cl_2MnN_3$
Formula weight	456.13	343.15
Temperature/K	296(2)	295.00
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	9.8115(11)	11.2911(13)
b/Å	14.4759(15)	12.0182(14)
c/Å	16.0170(18)	12.2882(15)
α/°	90	90
β/°	102.785(3)	104.003(3)
γ/°	90	90
Volume/Å^3	2218.5(4)	1617.9(3)
Z	4	4
ρ_{calc}g/cm^3	1.366	1.409
μ/mm^{-1}	1.080	1.136
F(000)	940.0	708.0
Crystal size/mm^3	0.36 × 0.28 × 0.23	0.33 × 0.28 × 0.21
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.256 to 52.788	4.398 to 54.248
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-20 \le l \le 20$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-15 \le l \le 15$
Reflections collected	38668	40218
Independent reflections	4520 [R_{int} = 0.0343, R_{sigma} = 0.0211]	3560 [R_{int} = 0.0396, R_{sigma} = 0.0201]
Data/restraints/parameters	4520/154/264	3560/24/188
Goodness-of-fit on F^2	1.073	1.114
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.0880	R_1 = 0.0409, wR_2 = 0.0824
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.0978	R_1 = 0.0580, wR_2 = 0.0925
Largest diff. peak/hole / e Å^{-3}	0.41/-0.34	0.28/-0.34

Table S2. Selected bond lengths and bond angles around metal (Mn) centre

Complex	6a	Complex	6b
Mn–N (Å) (Pyridine)	2.185(2)	Mn–N (Å) (Pyridine)	2.191(2)
Mn–N (imine) (Å)	2.391(2), 2.396(2)	Mn–N (imine) (Å)	2.332(3), 2.368(2)
Mn–Cl (Å)	2.3337(9), 2.3595(8)	Mn–Cl (Å)	2.3394(8), 2.3464(9)
(Imine)N-Mn-N(Imine) (°)	142.16(8)	(Imine)N-Mn-N(Imine) (°)	141.94(8)
(Imine)N-Mn-N(pyridine) (°)	71.48(8), 71.23(7)	(Imine)N-Mn-N(pyridine) (°)	71.42(9), 71.05(8)

Table S3. Crystal data and refinement parameter of 6c and 6d

Complex	6c	6d
Empirical formula	$C_{19}H_{26}Cl_2MnN_3$	$C_{19}H_{15}Cl_2MnN_3$
Formula weight	422.27	411.18
Temperature/K	298.00	296.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
a/Å	7.7457(18)	7.6526(10)
b/Å	15.224(4)	17.402(2)
c/Å	17.898(4)	13.8792(17)
α/°	90	90
β/°	100.367(6)	98.775(4)
γ/°	90	90
Volume/$Å^3$	2076.1(8)	1826.7(4)
Z	4	4
$\rho_{calc}g/cm^3$	1.351	1.495
μ/mm^{-1}	0.900	1.021
F(000)	880.0	836.0
Crystal size/mm^3	0.32 × 0.24 × 0.21	0.36 × 0.28 × 0.24
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.346 to 51.274	5.544 to 50.812
Index ranges	-9 ≤ h ≤ 9, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21	-9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -16 ≤ l ≤ 16
Reflections collected	48767	21648
Independent reflections	3913 [R_{int} = 0.0300, R_{sigma} = 0.0137]	1691 [R_{int} = 0.0381, R_{sigma} = 0.0212]
Data/restraints/parameters	3913/15/281	1691/0/115
Goodness-of-fit on F^2	1.061	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0846	R_1 = 0.0353, wR_2 = 0.0670
Final R indexes [all data]	R_1 = 0.0464, wR_2 = 0.0948	R_1 = 0.0453, wR_2 = 0.0718
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.26	0.35/-0.35

Table S4. Selected bond lengths and bond angles around metal (Mn) centre

Complex	6c	Complex	6d
Mn–N (Å) (Pyridine)	2.1991(18)	Mn–N (Å) (Pyridine)	2.194(3)
Mn–N (imine) (Å)	2.3618(18), 2.412(2)	Mn–N (imine) (Å)	2.359(2), 2.359(2)
Mn–Cl (Å)	2.3346(9), 2.3400(8)	Mn–Cl (Å)	2.3324(8), 2.3325(7)
(Imine)N-Mn-N(Imine) (°)	141.85(7)	(Imine)N-Mn-N(Imine) (°)	142.04(10)
(Imine)N-Mn-N(pyridine) (°)	71.60(6), 70.26(7)	(Imine)N-Mn-N(pyridine) (°)	71.02(5), 71.02(5)

2. Magnetic Moment Studies

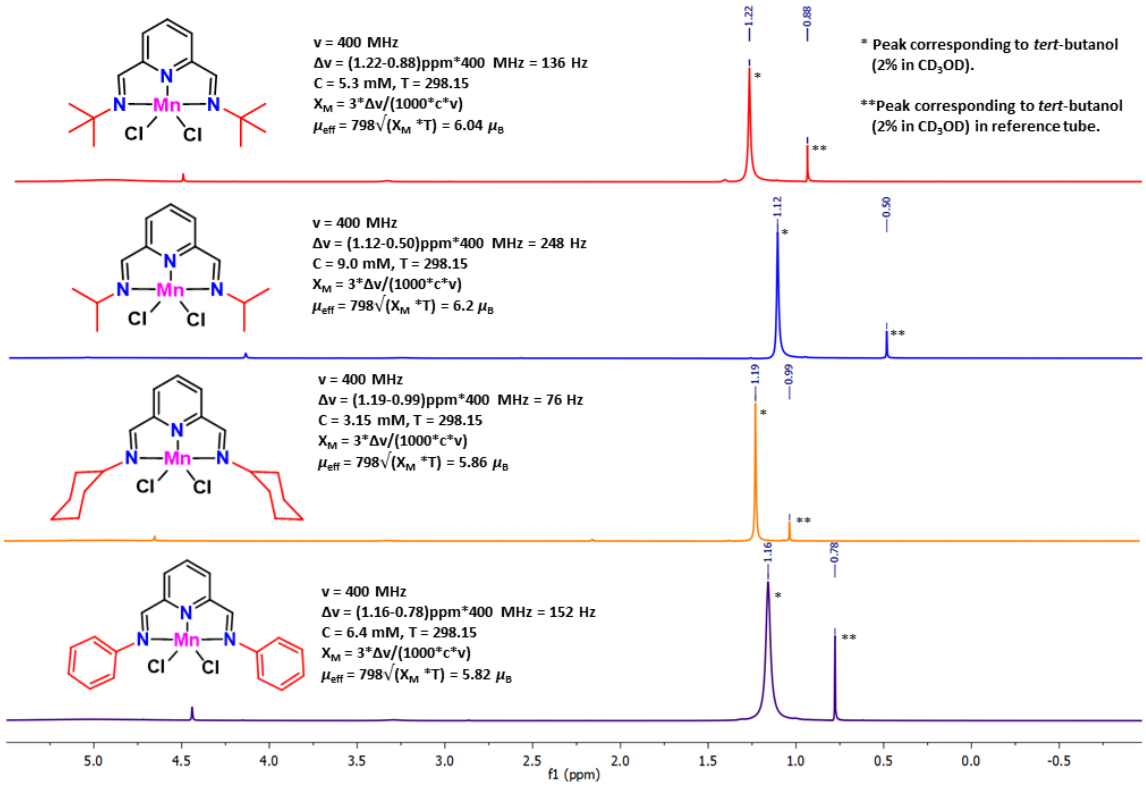

Figure S1. Determination of magnetic of ^{R2}NNNMnCl$_2$ complexes using Evan's method in CD_3OD.

3. HRMS analysis

3.1 HRMS analysis of 6a

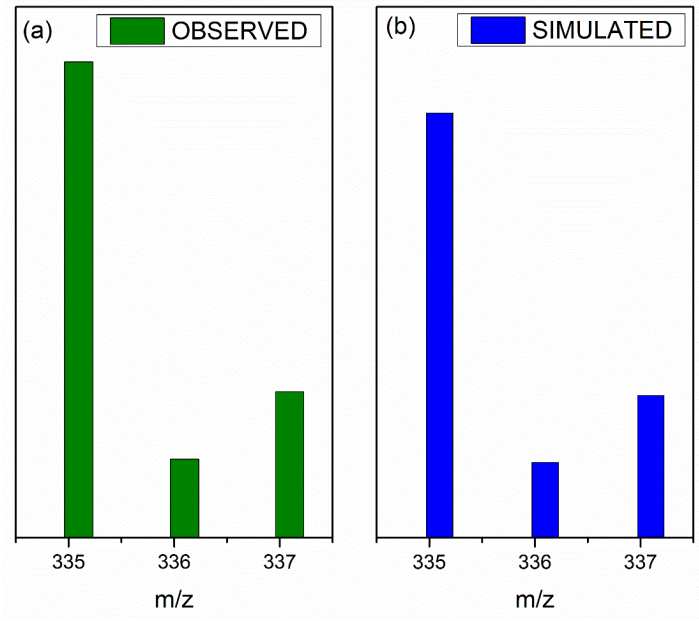

Figure S2. HRMS(ESI) analysis of **6a** at m/z value (a) 335.0952 (b) 335.0961

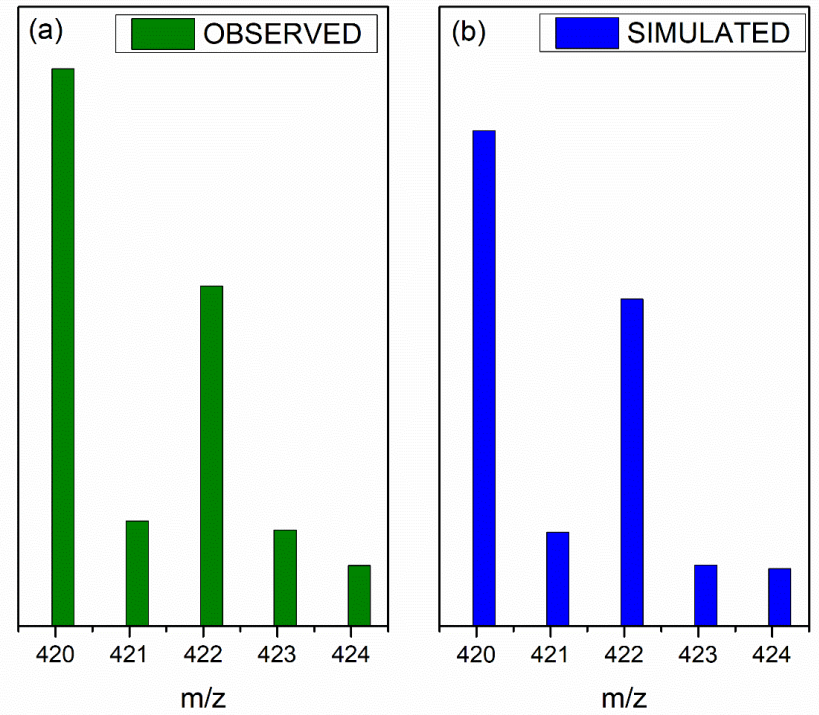

Figure S3. HRMS(ESI) analysis of **6a** at m/z value (a) 420.1035 (b) 420.1017.

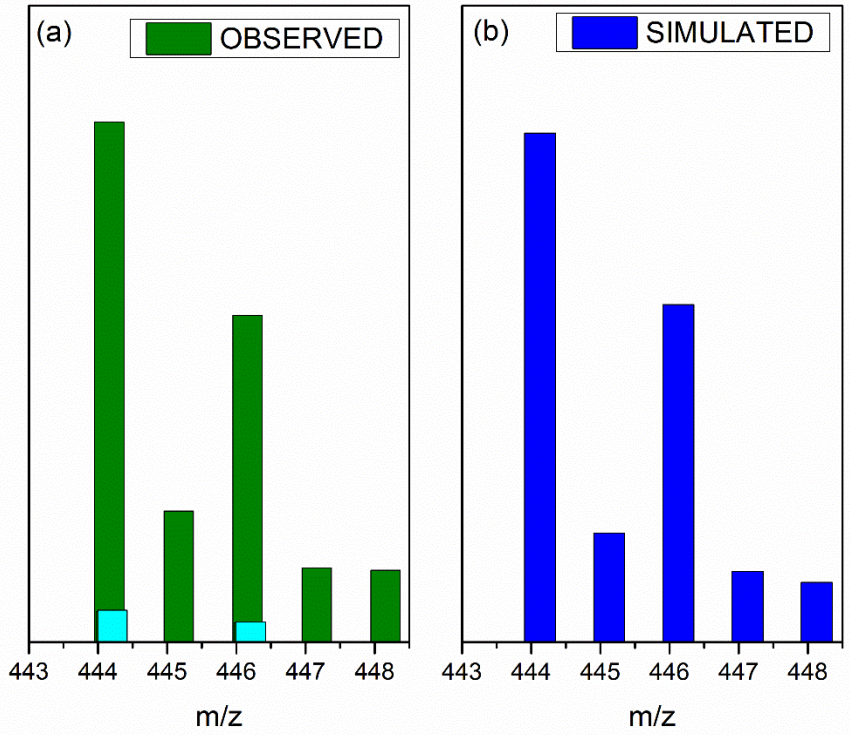

Figure S4. HRMS(ESI) analysis of **6a** at m/z value (a) 444.1613 (b) 444.1255.

3.2 HRMS analysis of 6b

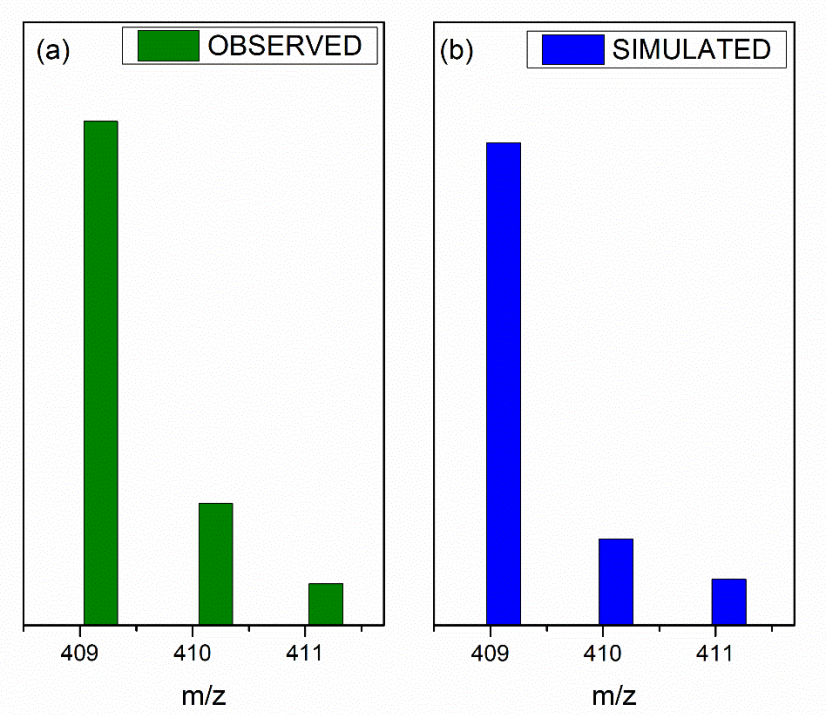

Figure S5. HRMS(ESI) analysis of **6b** at m/z value (a) 409.1851 (b) 409.1176.

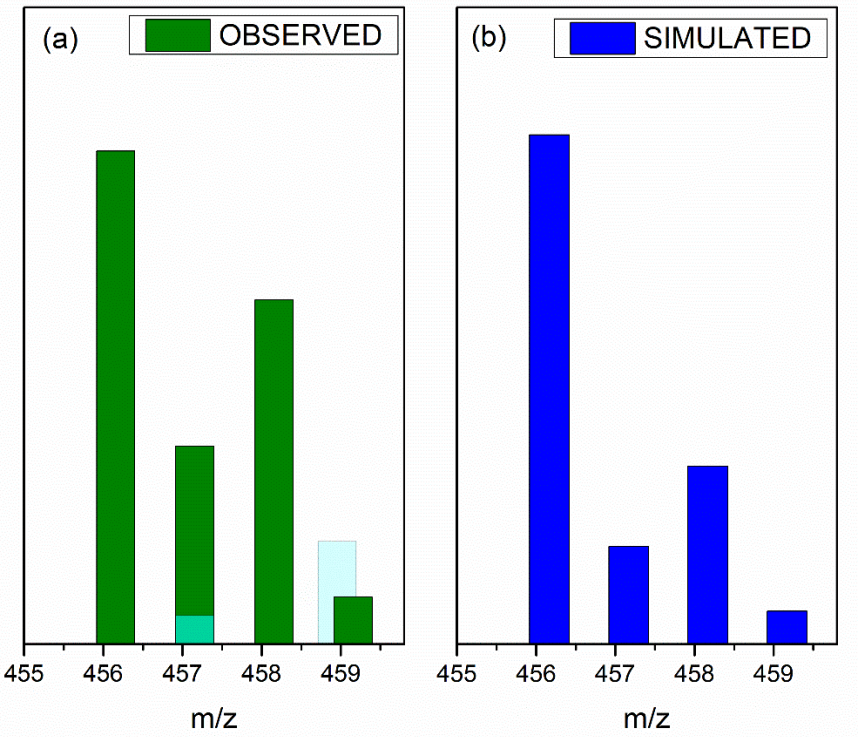

Figure S6. HRMS(ESI) analysis of **6b** at m/z value (a) 456.1558 (b) 456.1673.

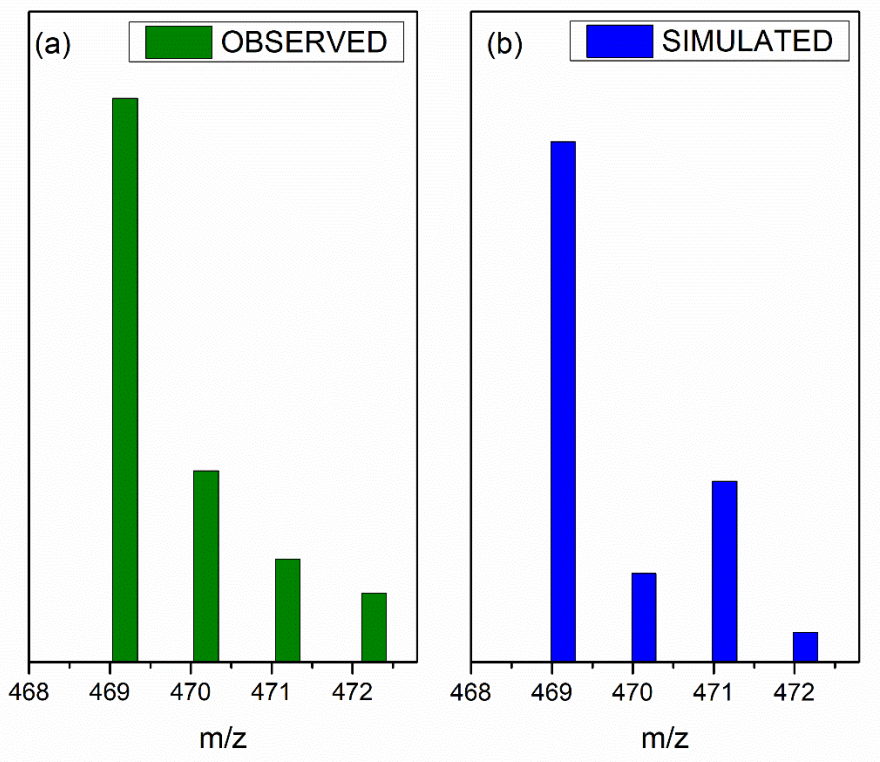

Figure S7. HRMS(ESI) analysis of **6b** at m/z value (a) 469.1875 (b) 469.1363.

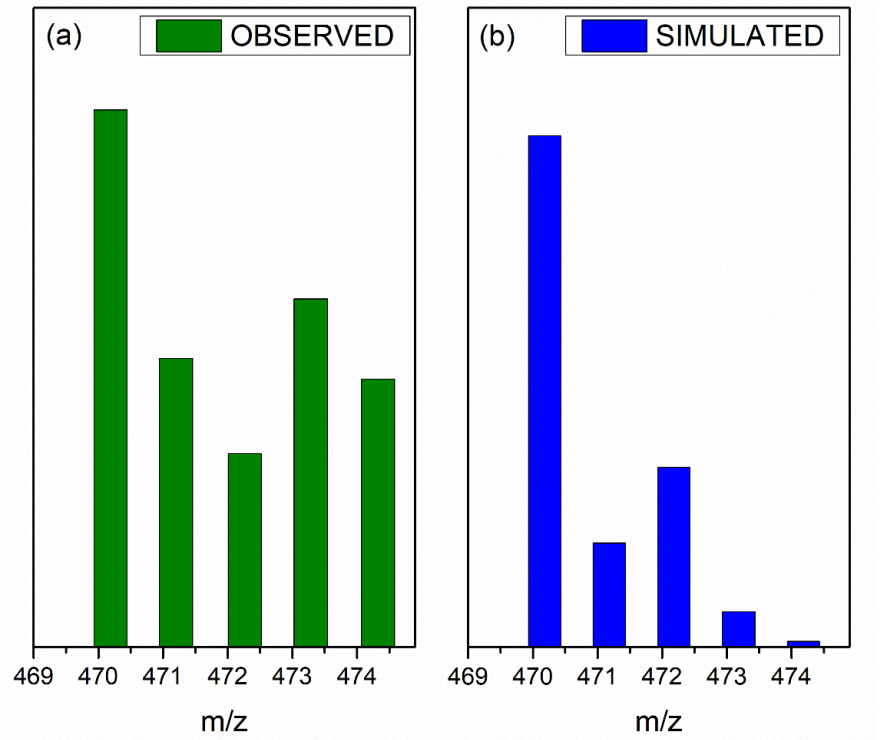

Figure S8. HRMS(ESI) analysis of **6b** at m/z value (a) 470.1889 (b) 470.1830.

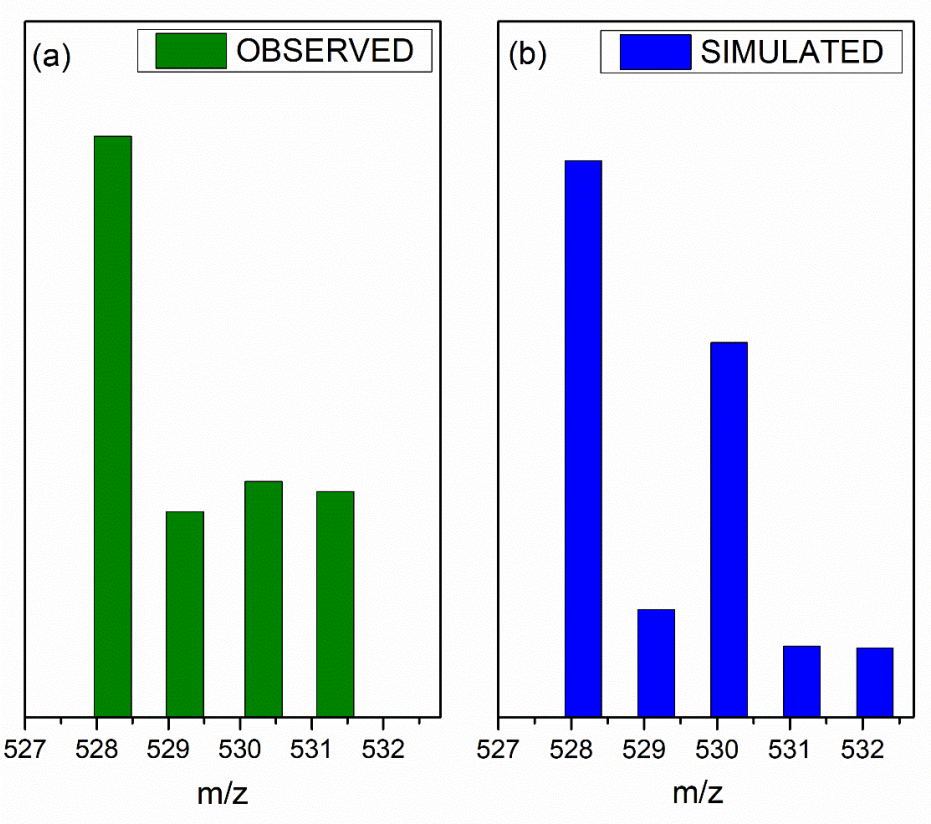

Figure S9. HRMS(ESI) analysis of **6b** at m/z value (a) 528.2246 (b) 528.1651.

3.3 HRMS analysis of 6c

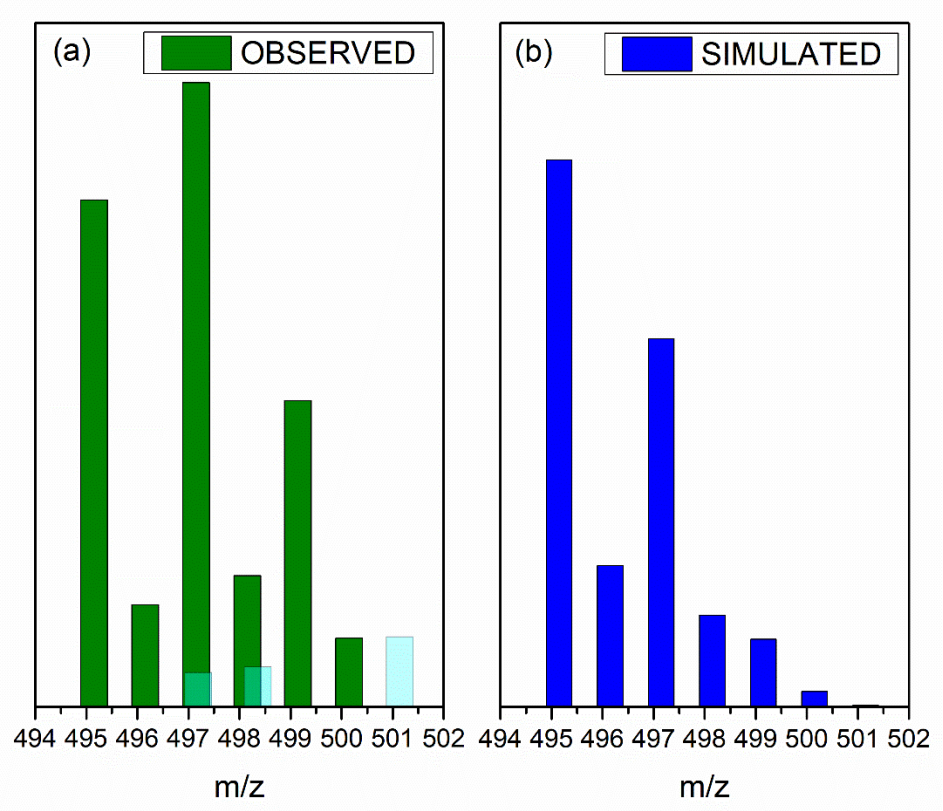

Figure S10. HRMS(ESI) analysis of **6c** at m/z value (a) 495.1508 (b) 495.1490.

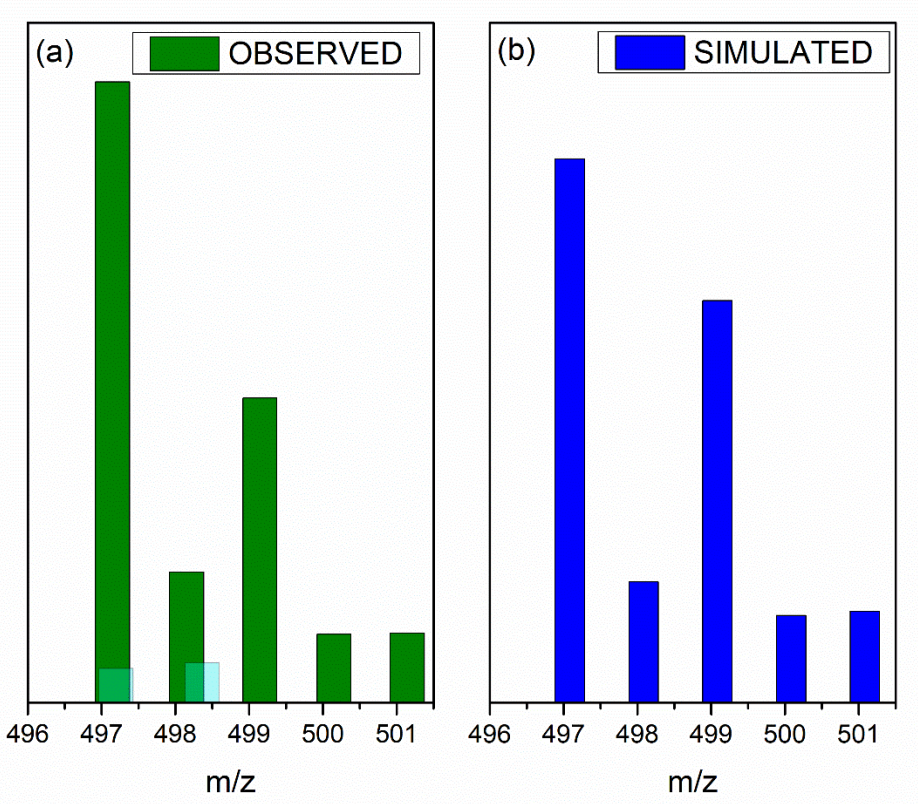

Figure S11. HRMS(ESI) analysis of **6c** at m/z value (a) 497.1478 (b) 497.0811.

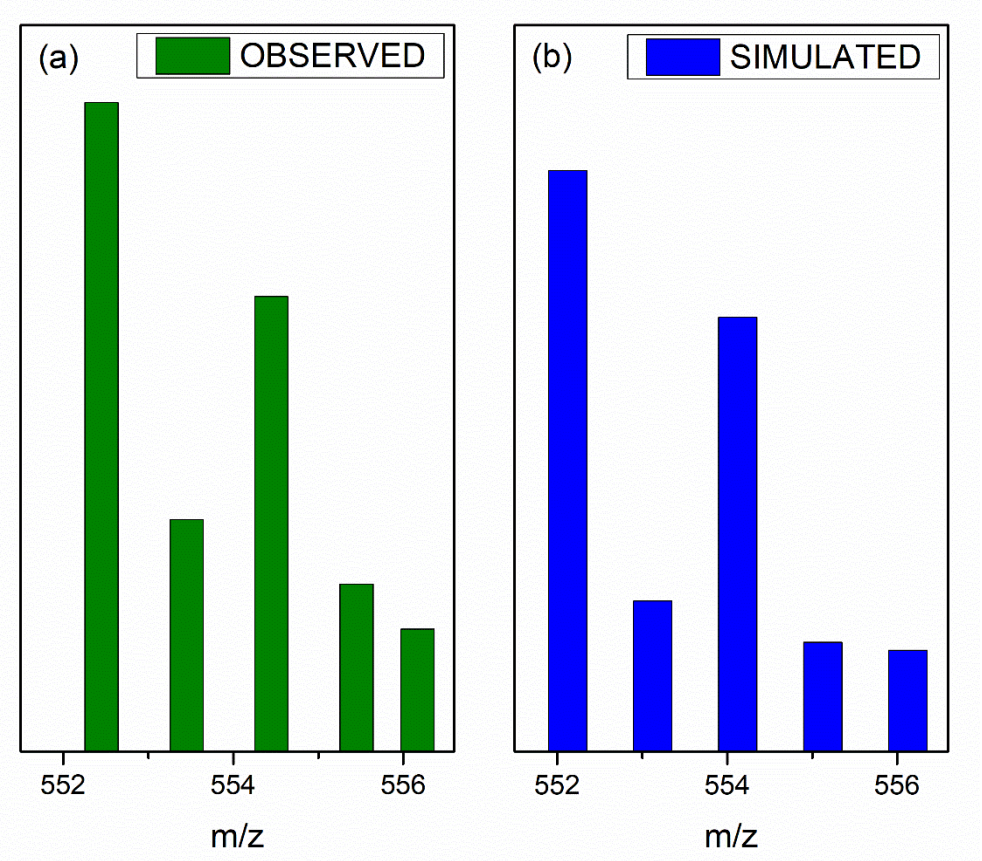

Figure S12. HRMS(ESI) analysis of **6c** at m/z value (a) 522.4487 (b) 522.1698.

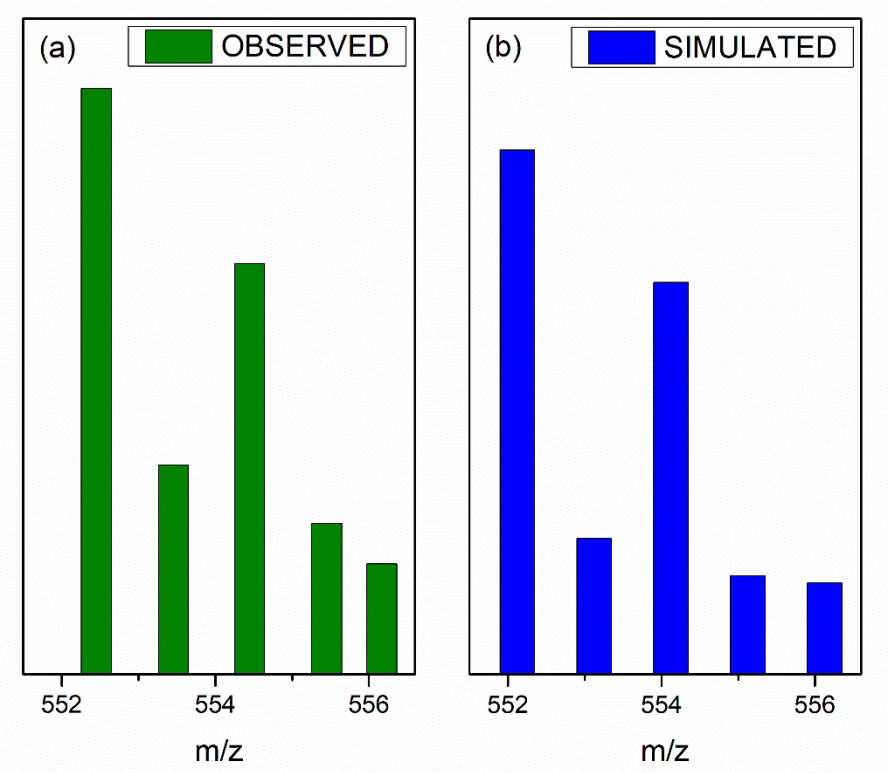

Figure S13. HRMS(ESI) analysis of **6c** at m/z value (a) 552.4487 (b) 552.1233.

3.4 HRMS analysis of 6d

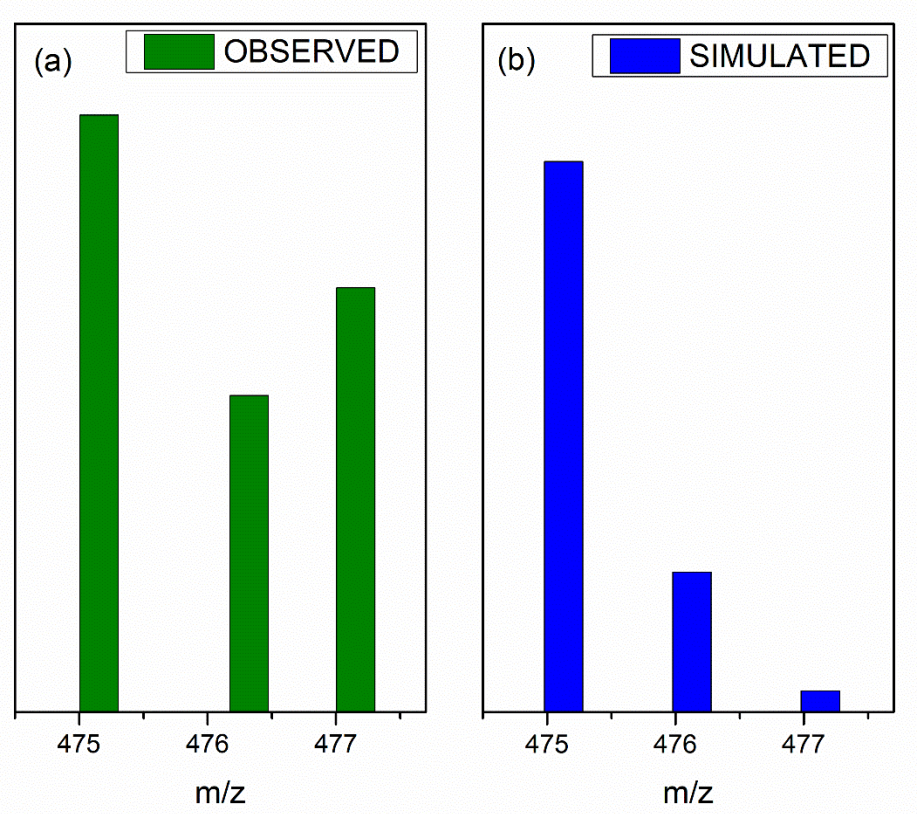

Figure S14. HRMS(ESI) analysis of **6d** at m/z value (a) 475.3258 (b) 475.1280.

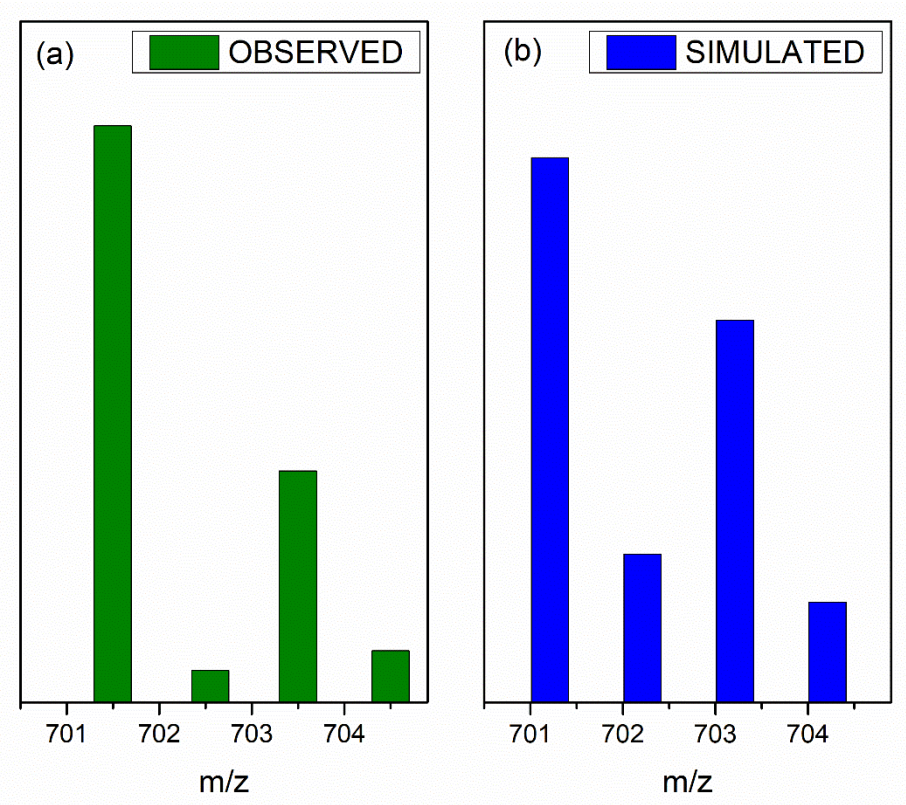

Figure S15. HRMS(ESI) analysis of **6d** at m/z value (a) 701.4941 (b) 701.2101.

3.5 HRMS analysis of reaction mixture

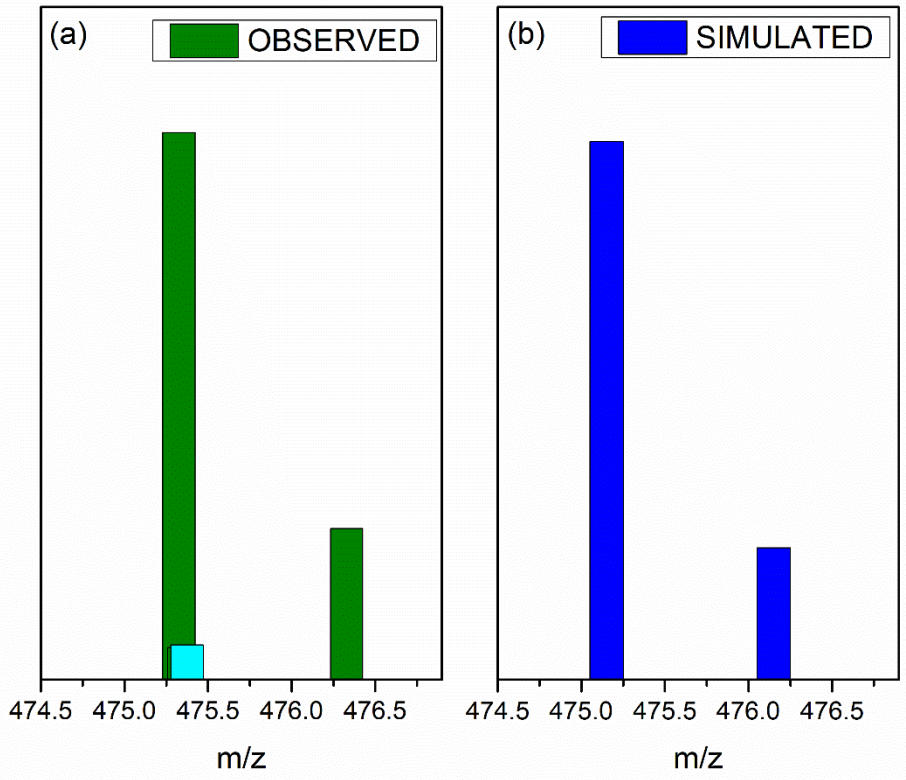

Figure S16. HRMS(ESI) analysis of reaction mixture at t =0h at m/z value (a) 475.3260 (b) 475.1515.

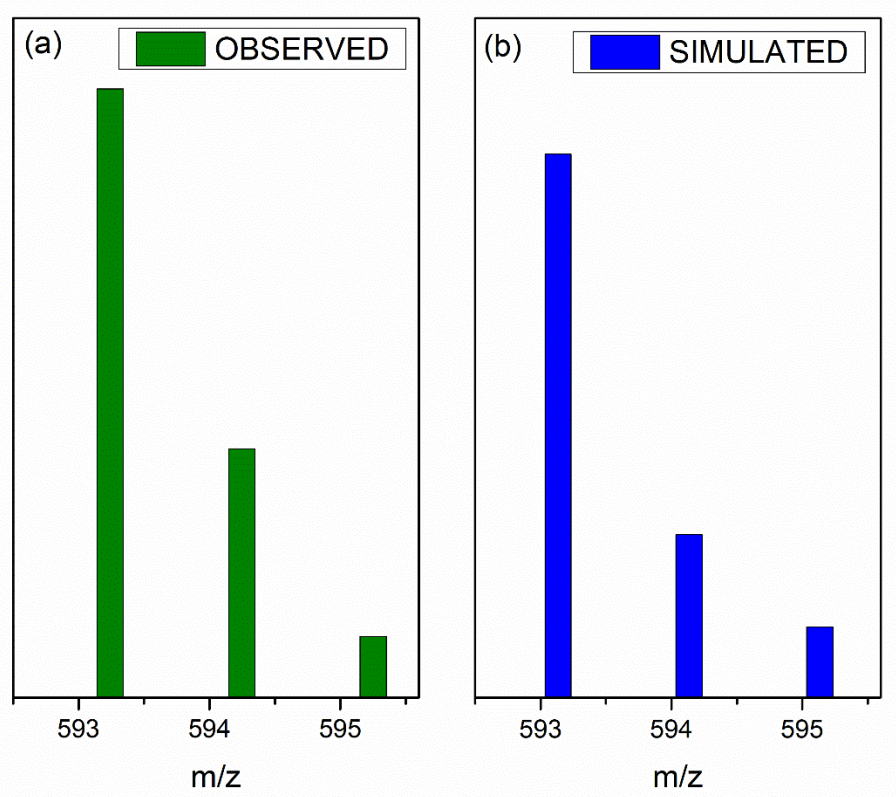

Figure S17. HRMS(ESI) analysis of reaction mixture at t =0h at m/z value (a) 593.2429 (b) 593.1336.

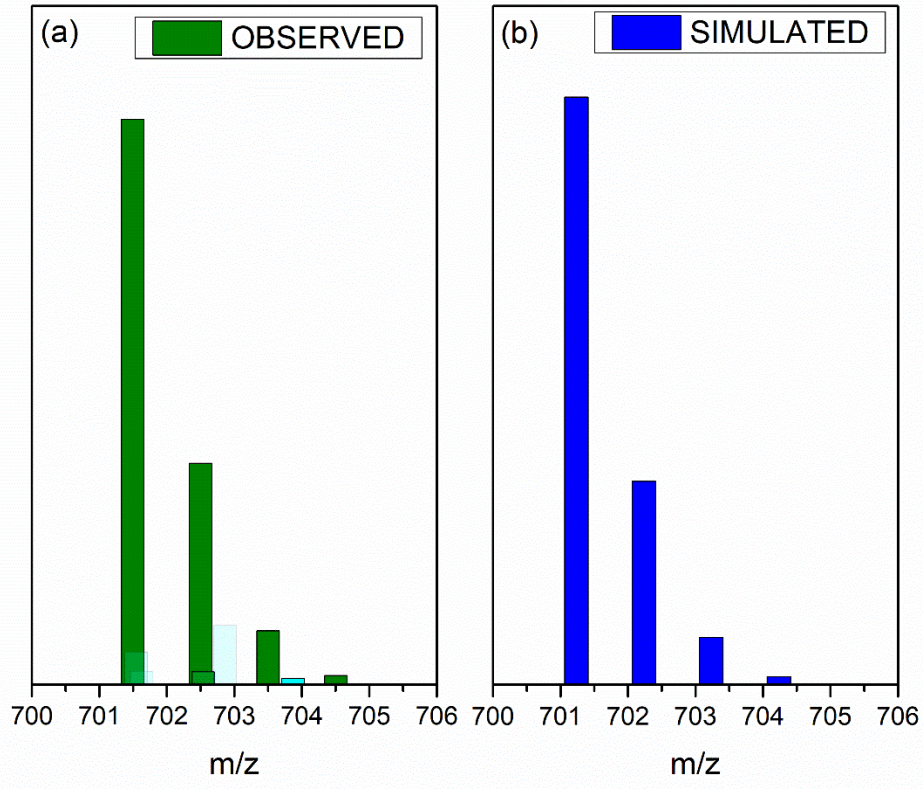

Figure S18. HRMS(ESI) analysis of reaction mixture at t =0h at m/z value (a) 701.4939 (b) 701.2332.

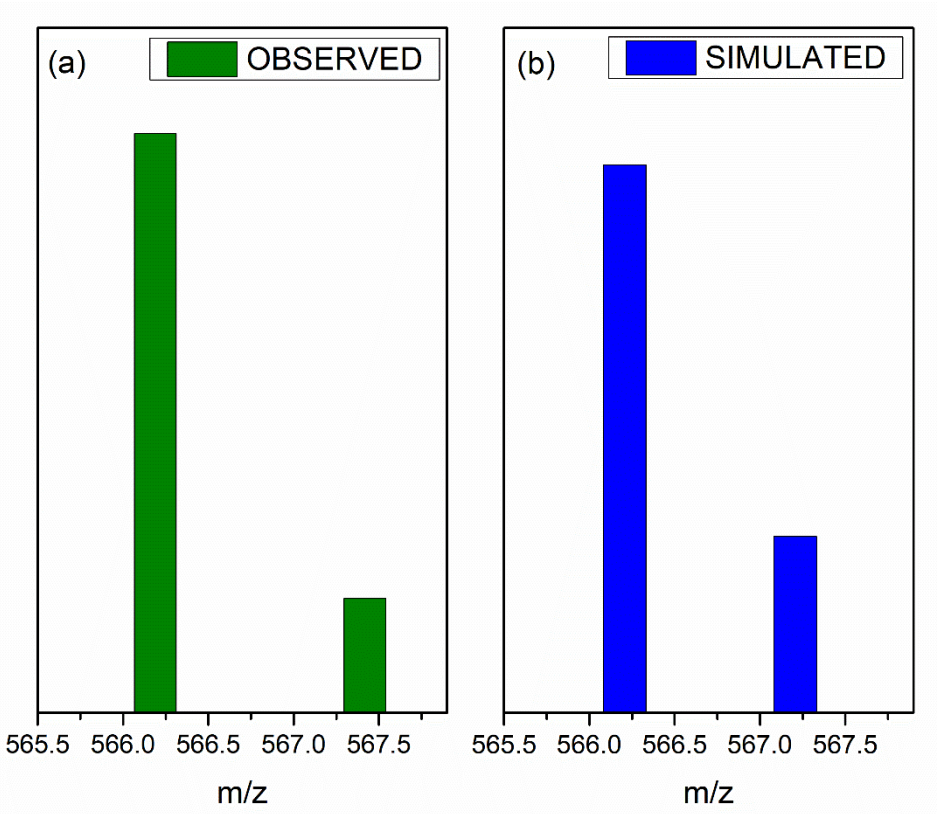

Figure S19. HRMS(ESI) analysis of reaction mixture at t =1h at m/z value (a) 566.8893 (b) 566.2063.

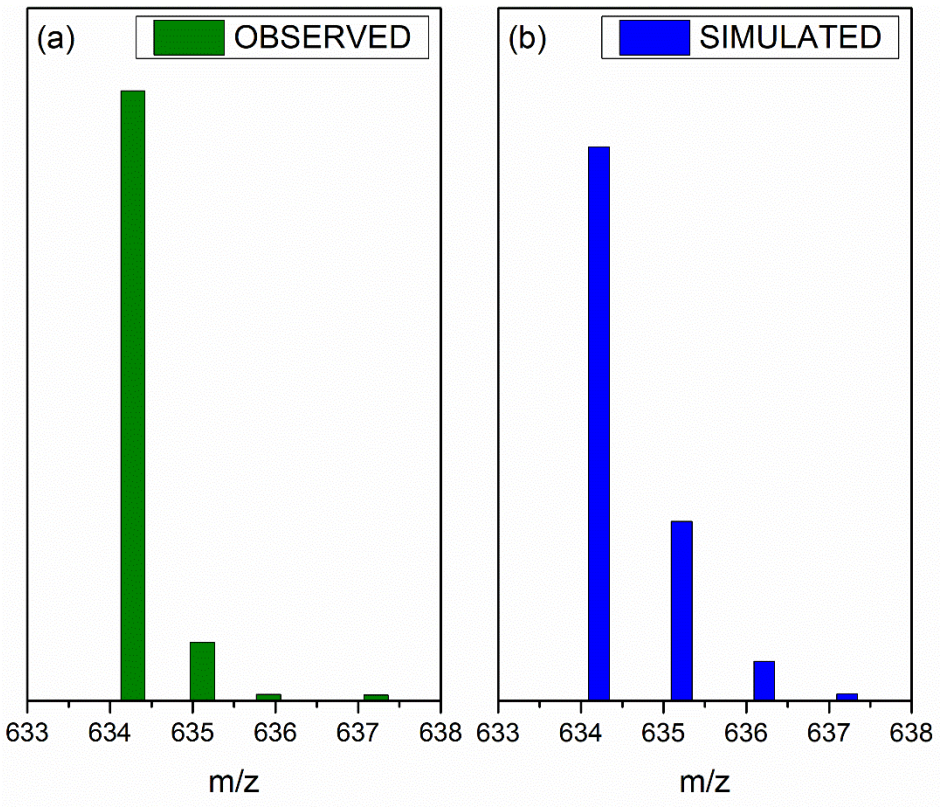

Figure S20. HRMS(ESI) analysis of reaction mixture at t =1h at m/z value (a) 634.8765 (b) 634.2172.

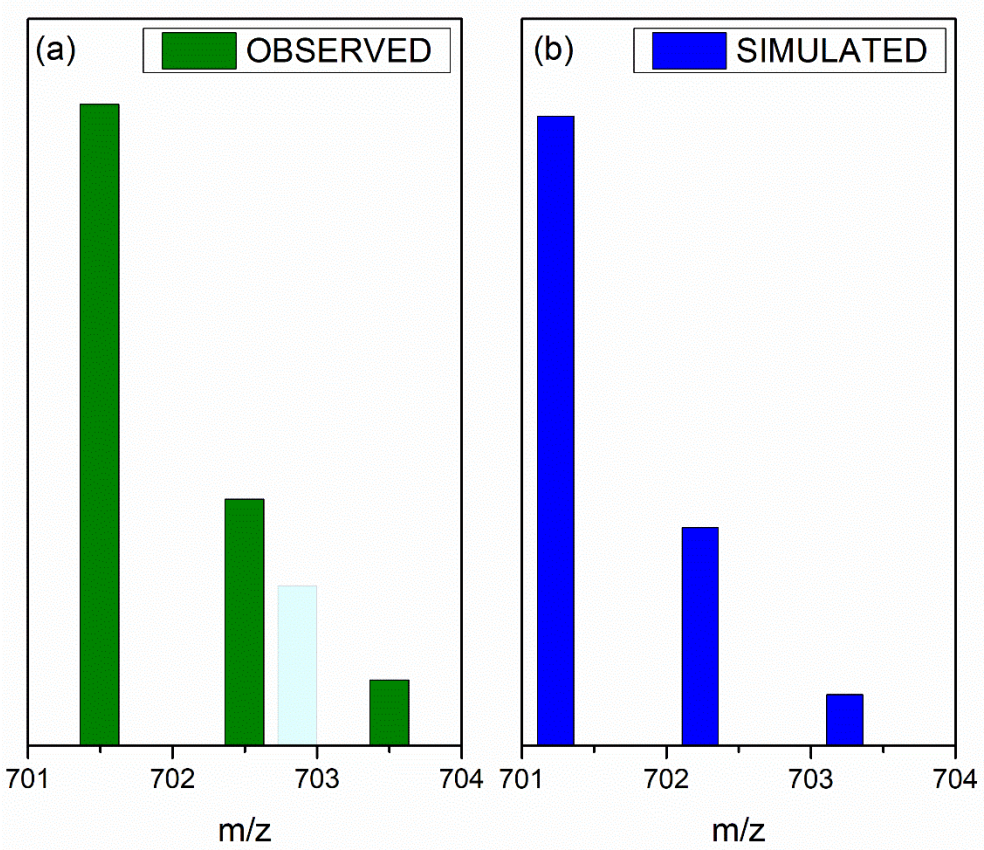

Figure S21. HRMS(ESI) analysis of reaction mixture at t =1h at m/z value (a) 701.4939 (b) 701.2332.

4. GC analysis

GC analysis (TCD detection) was performed on an Agilent 7820-GC instrument fitted with Agilent Front SSZ Inlet N_2 HP-PLOT Q column (30 m length x 530 µm x 40 µm) using the following method:

Agilent 7820-GC back detector TCD

Oven temperature: 50 °C

Time at starting temp: 0 min

Hold time = 10 min

Inlet temperature: 100 °C

Detector temperature (TCD): 250 °C

Detector temperature (FID): 300 °C

Flow rate (carrier): 5 mL/min (N_2)

Split ratio: 10

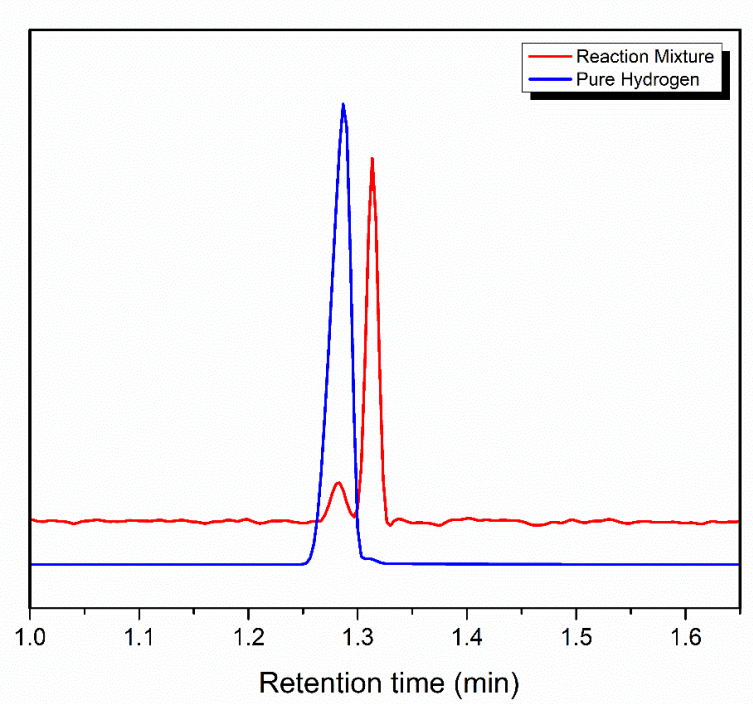

Figure S22. Evidence for H_2 evolution in the transfer dehydrogenation of glycerol **7** using acetophenone **8a** as acceptor**,** catalyzed by **6d** (0.5 mol%) and NaOH (1 equivalent) at 140 ^{o}C via GC analysis. (Entry 1, Table 2)

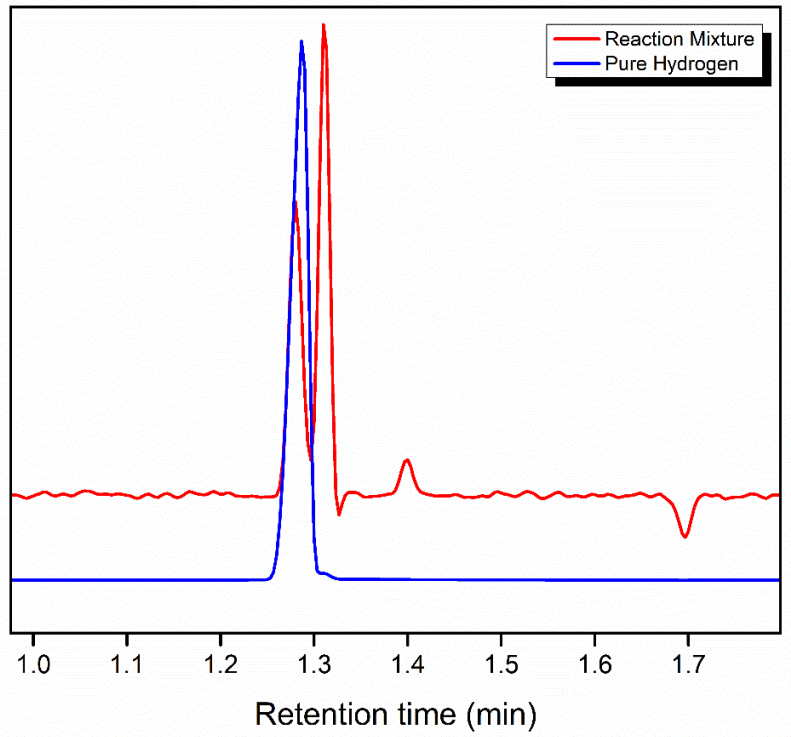

Figure S23. Evidence for H_2 evolution in the transfer dehydrogenation of glycerol **7** using 4-Bromoacetophenone **8f** as acceptor**,** catalyzed by **6d** (0.5 mol%) and NaOH (1 equivalent) at 140 ^{o}C via GC analysis. (Entry 6, Table 2)

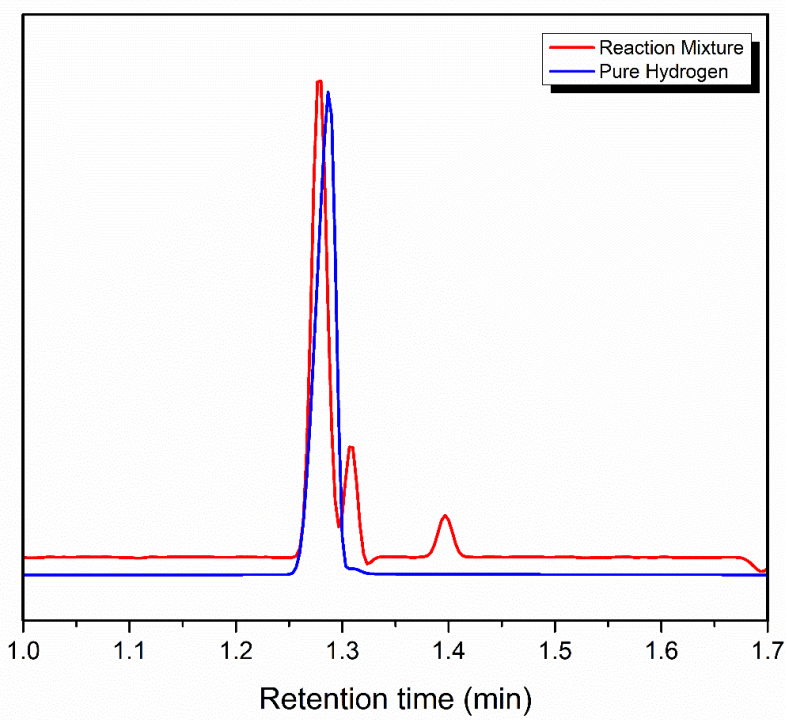

Figure S24. Evidence for H_2 evolution in the transfer dehydrogenation of glycerol **7** using 4-acetylpyridine **8j** as acceptor**,** catalyzed by **6d** (0.5 mol%) and NaOH (1 equivalent) at 140 °C via GC analysis. (Entry 10, Table 2)

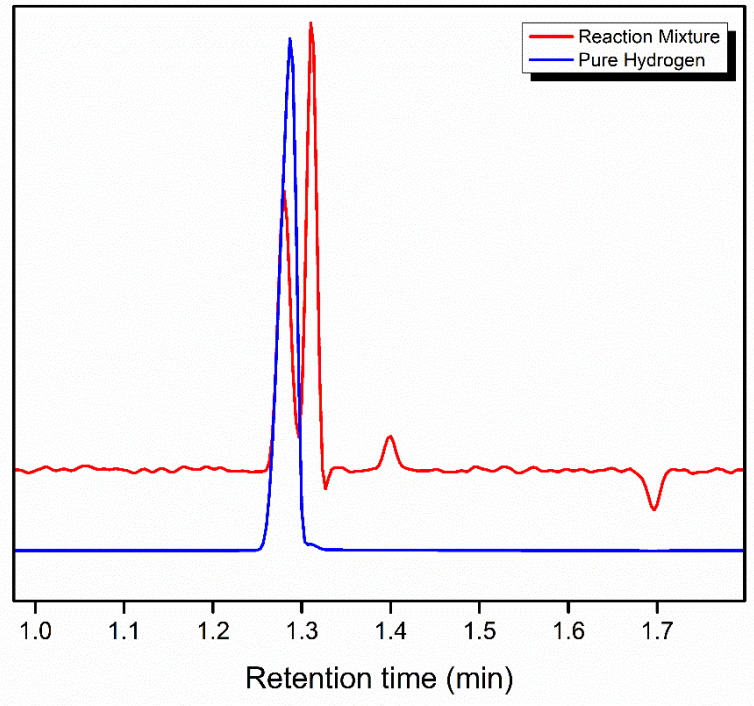

Figure S24. Evidence for H_2 evolution in the transfer dehydrogenation of glycerol **7** using 4-*tert*-butylacetophenone **8l** as acceptor**,** catalyzed by **6d** (0.5 mol%) and NaOH (1 equivalent) at 140 °C via GC analysis. (Entry 12, Table 2)

5. Kinetic studies

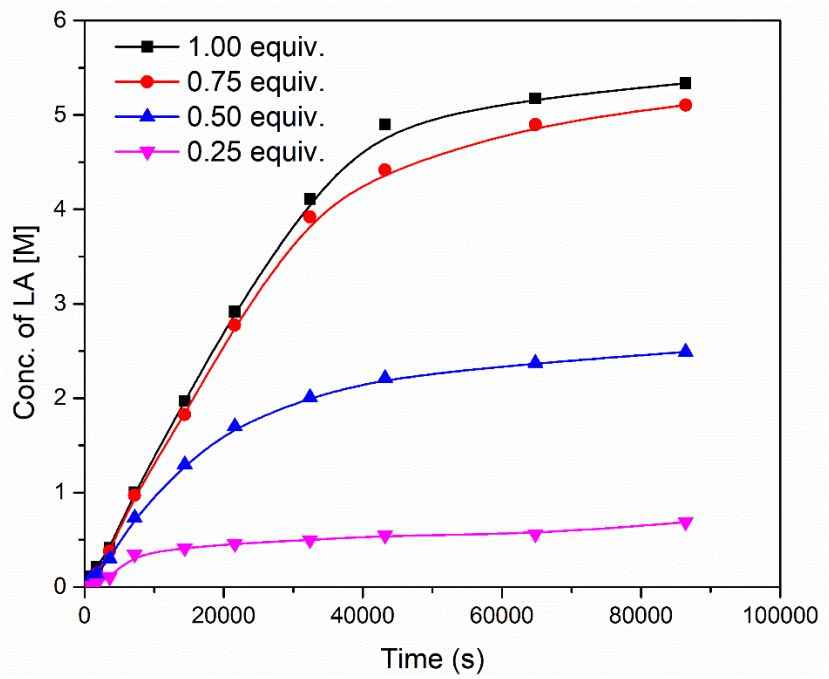

Figure S26. Time profile of formation of LA with concentration of NaOH (Reaction condition: Glycerol (**7**) (0.460 g, 5.0 mmol), **8** (372 µL, 5 mmol), NaOH (0.050 g (1.25 mmol), 0.100 (2.5 mmol), 0.150 g (3.75 mmol), 0.200 g (5.0 mmol) and **6d** (0.010 g, 0.025 mmol) at 140 °C for 24 h in closed-vessel condition.

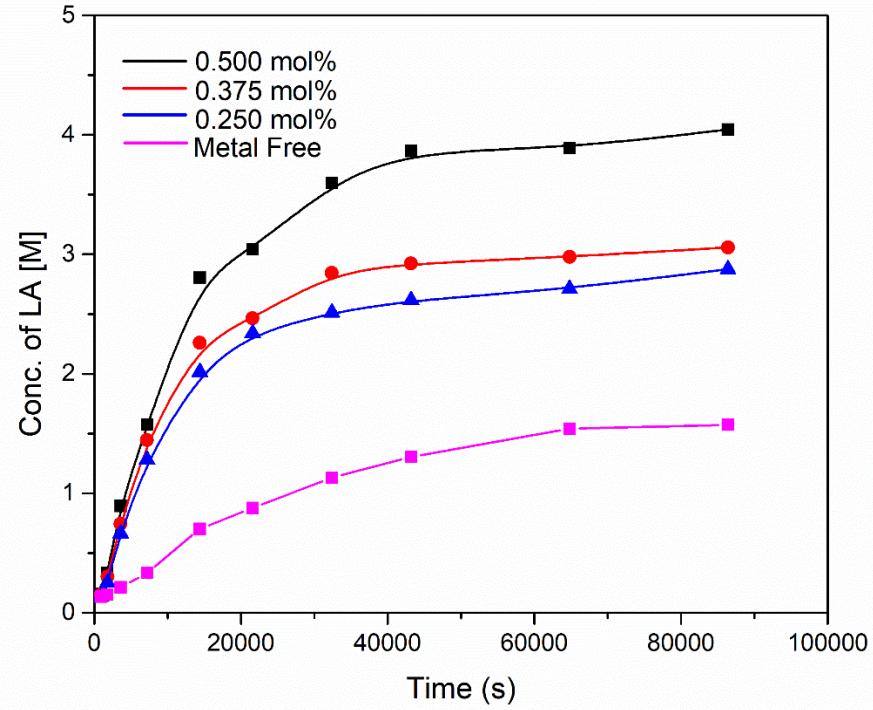

Figure S27. Time profile of formation of LA with concentration of **6d** (Reaction condition: Glycerol (**7**) (0.460 g, 5.0 mmol), **8** (372 µL, 5 mmol), 100 µL of water, NaOH (0.200 g (5.0 mmol) and **6d** (0.010 g, 0.025 mmol), (0.007 g, 0.018 mmol), (0.005 g, 0.0125mmol) and in metal free condition at 140 °C for 24 h in closed-vessel condition.

6. NMR Spectra

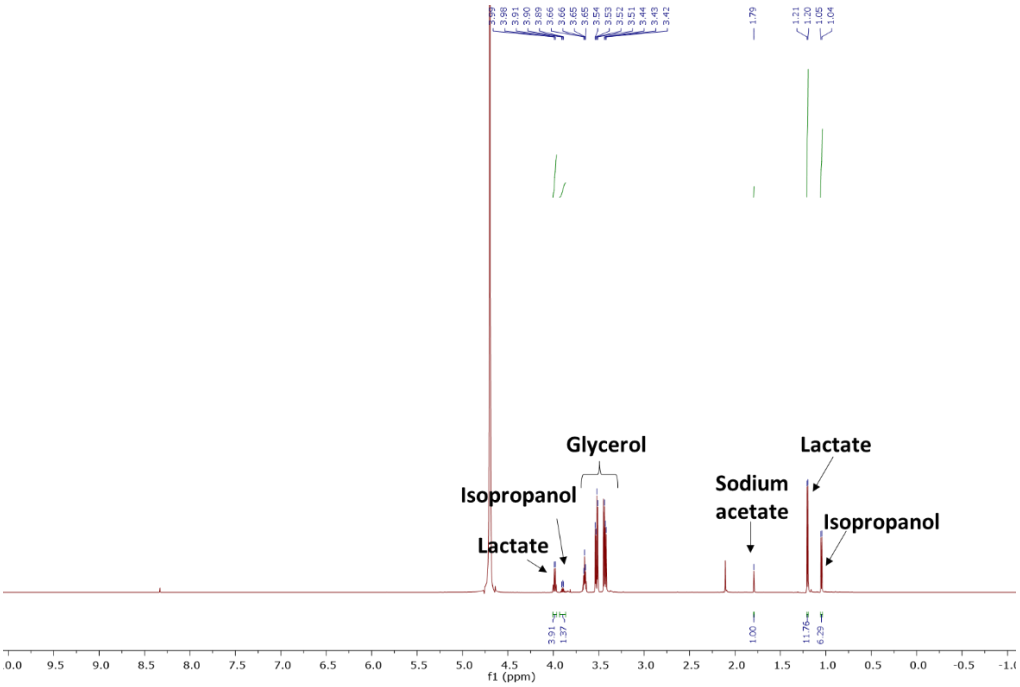

Figure S28. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), KOH (1 equiv.) at 140 ºC in D_2O. (Entry 1, Table 1)

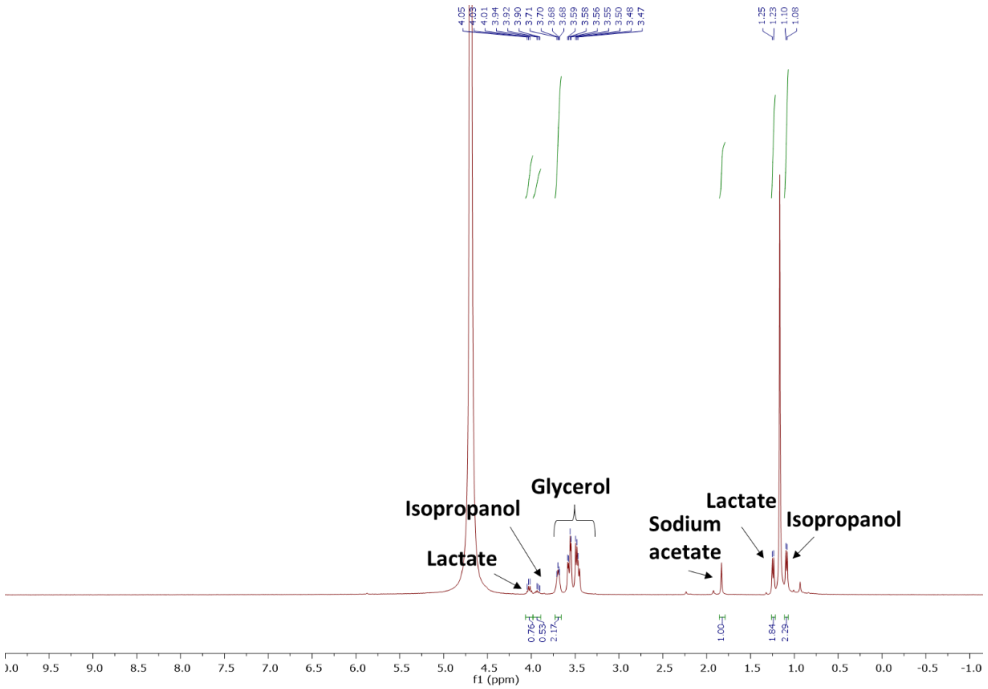

Figure S29. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaO^tBu (1 equiv.) at 140 ºC in D_2O. (Entry 2, Table 1)

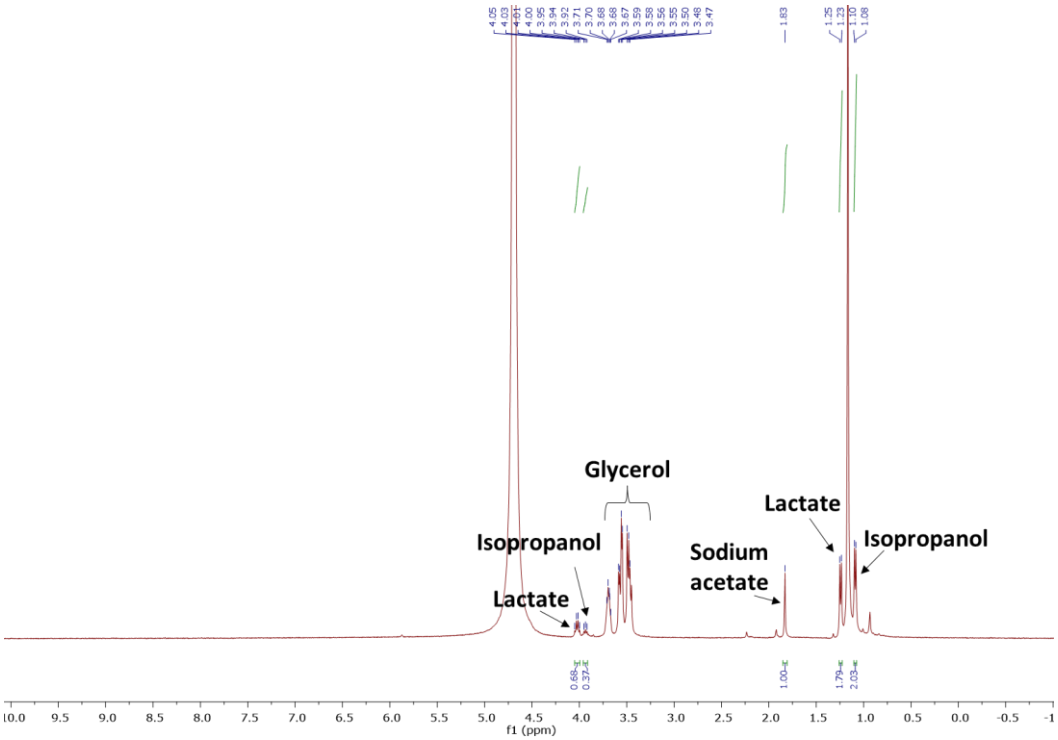

Figure S30. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), KO^{t}Bu (1 equiv.) at 140 ºC in D_2O. (Entry3, Table 1)

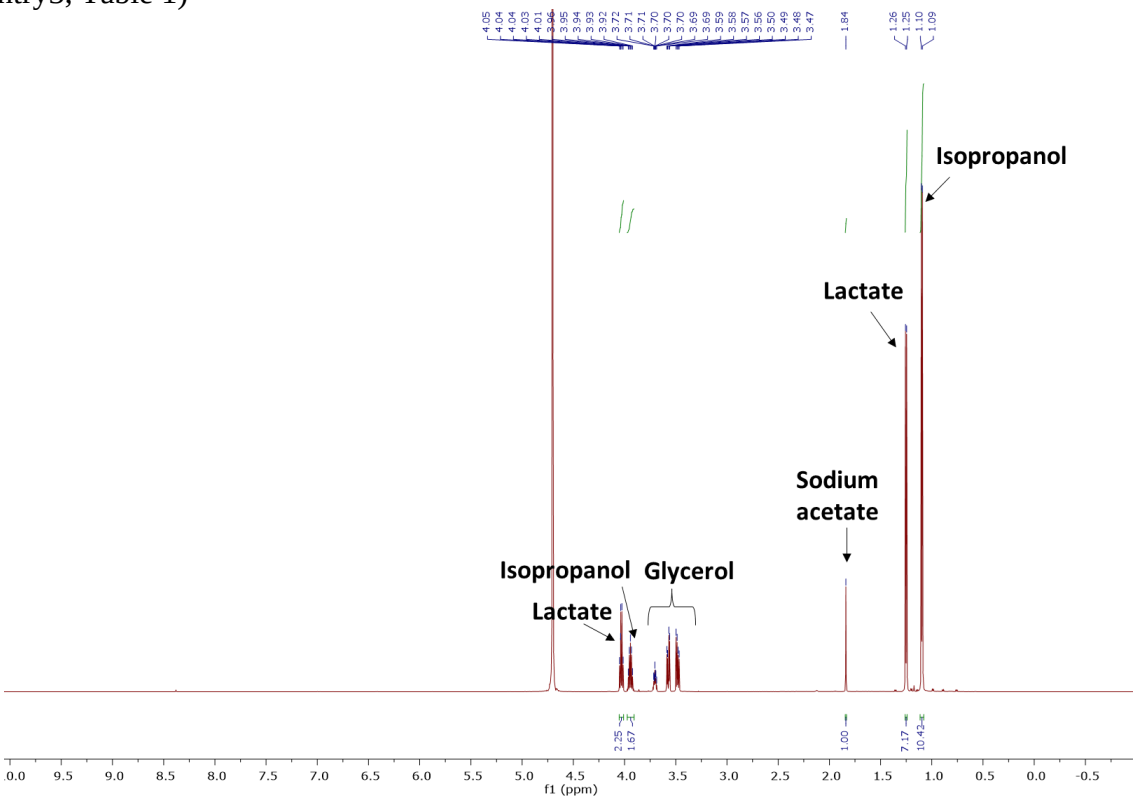

Figure S31. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 4, Table 1)

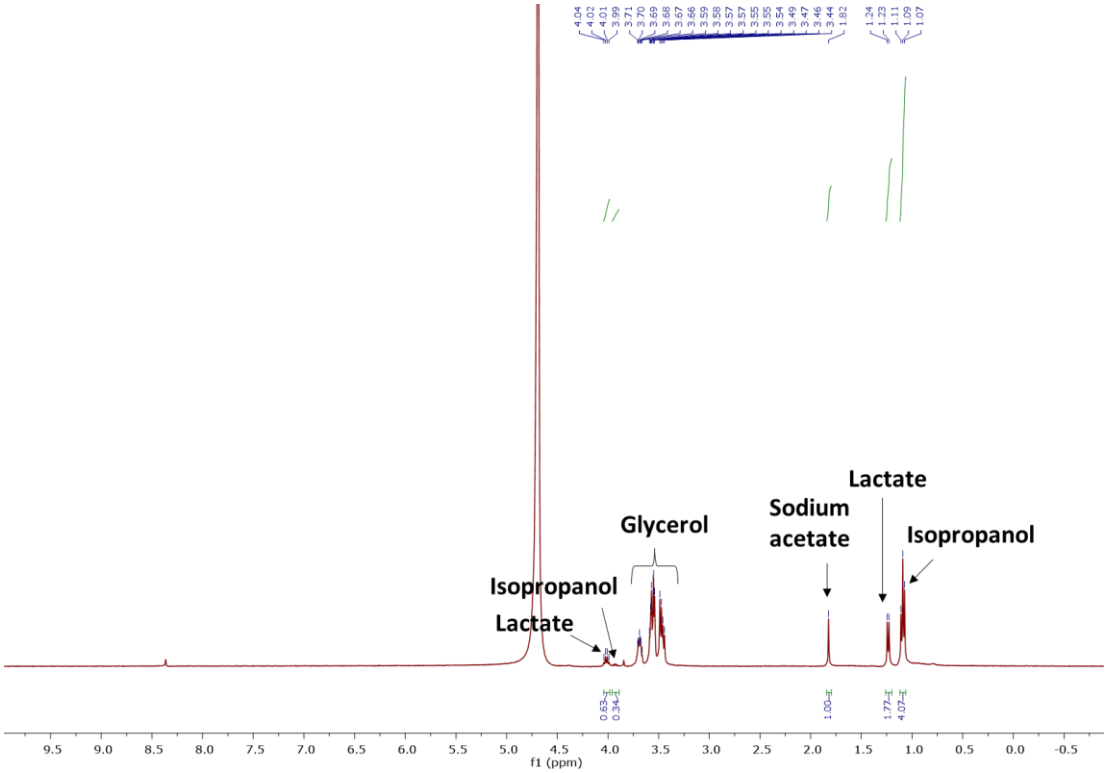

Figure S32. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOEt (1 equiv.) at 140 ºC in D_2O. (Entry 8, Table 1)

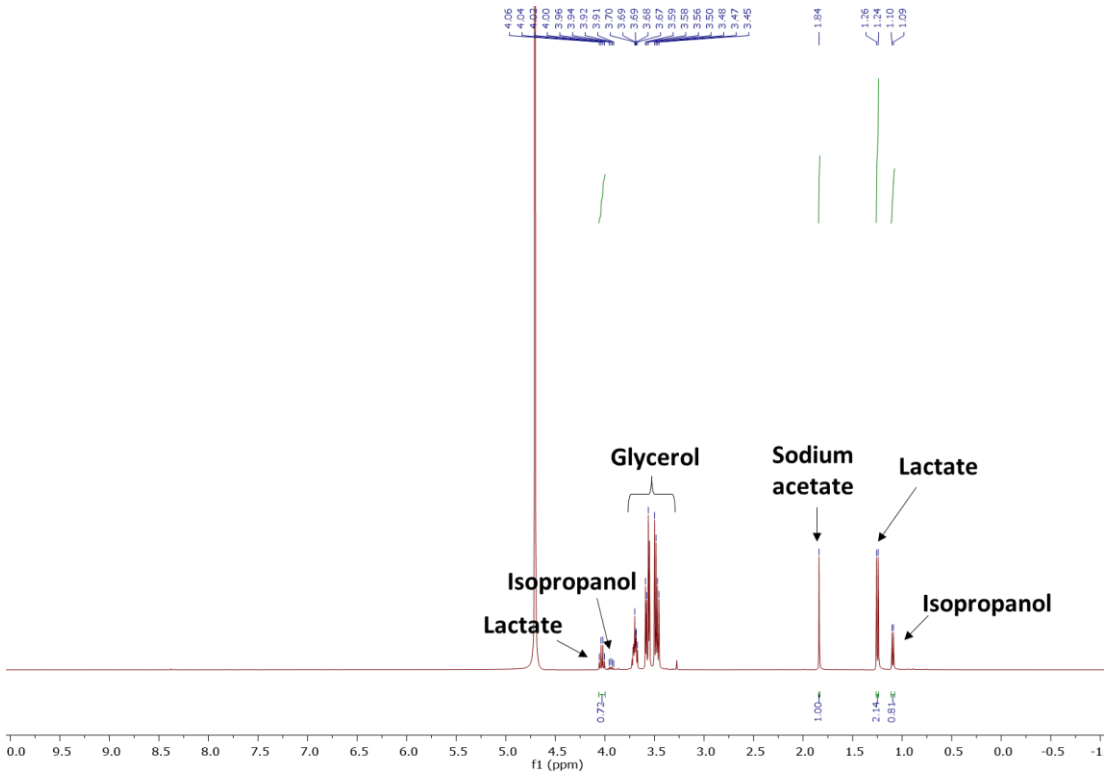

Figure S33. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, in metal free condition, NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 9, Table 1)

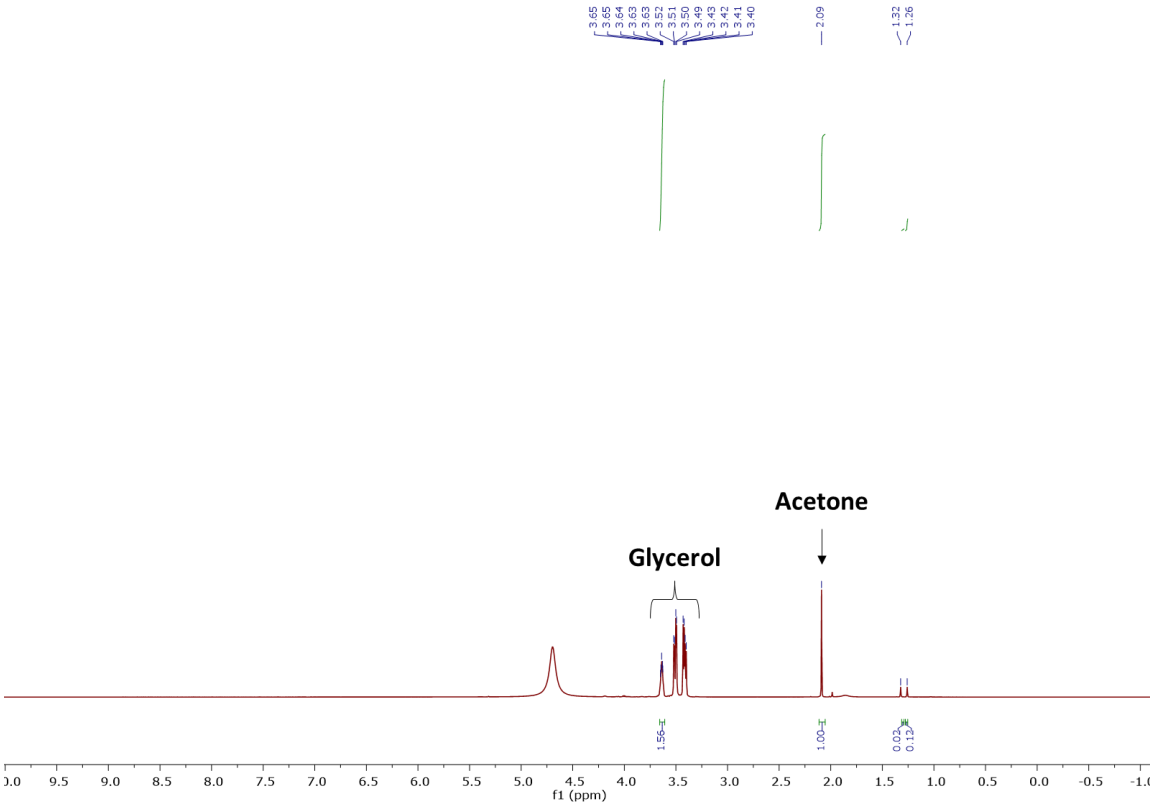

Figure S34. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), in base free condition at 140 ºC in D_2O. (Entry 10, Table 1)

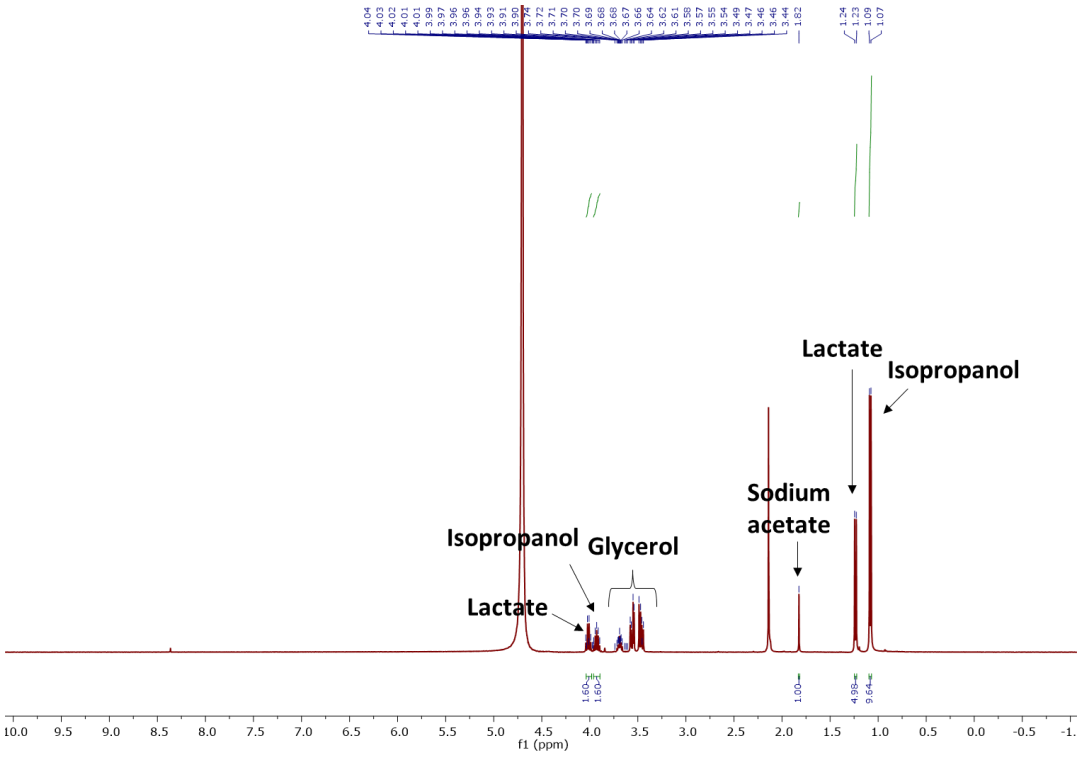

Figure S35. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (0.75 equiv.) at 140 ºC in D_2O. (Entry 11, Table 1)

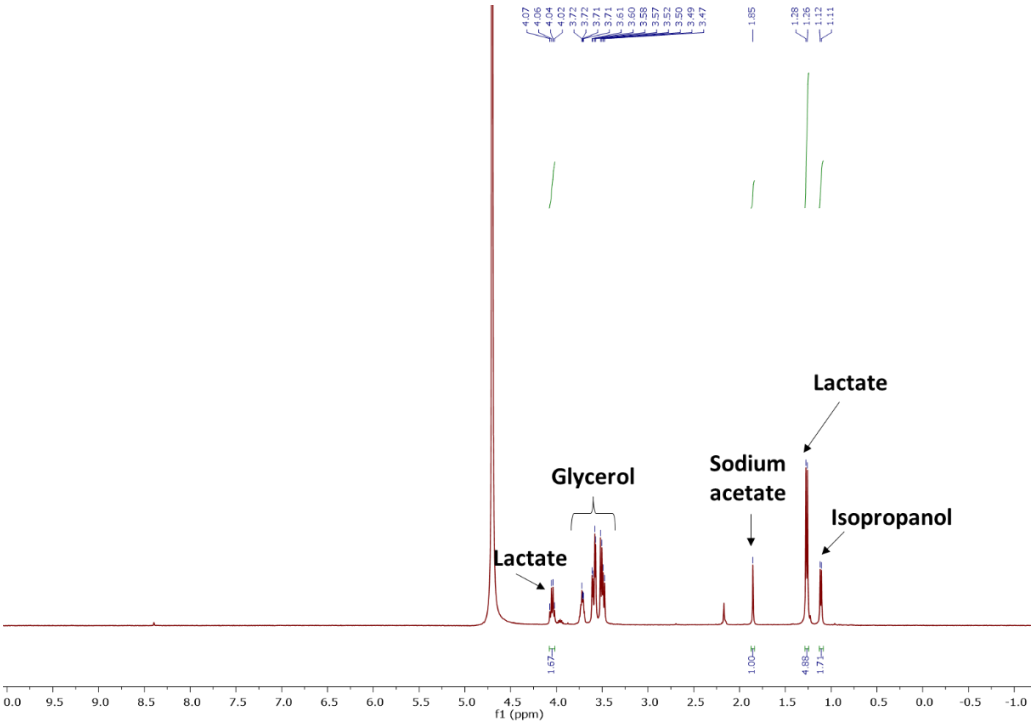

Figure S36. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (0.5 equiv.) at 140 ºC in D_2O. (Entry 12, Table 1)

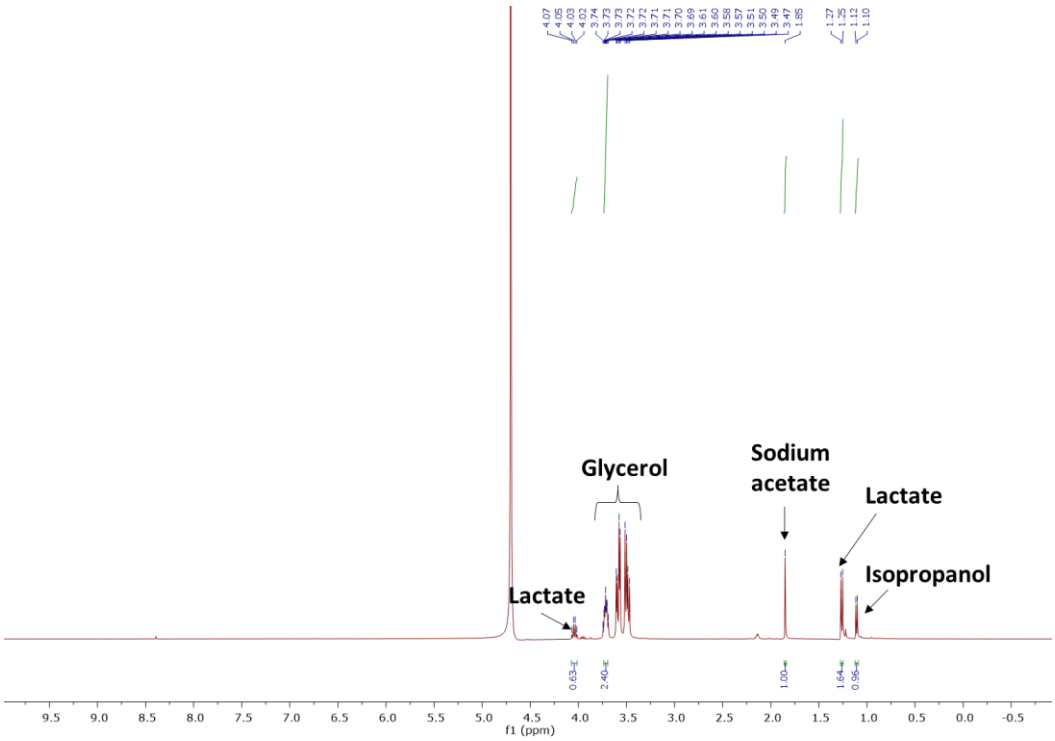

Figure S37. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (0.25 equiv.) at 140 ºC in D_2O. (Entry 13, Table 1)

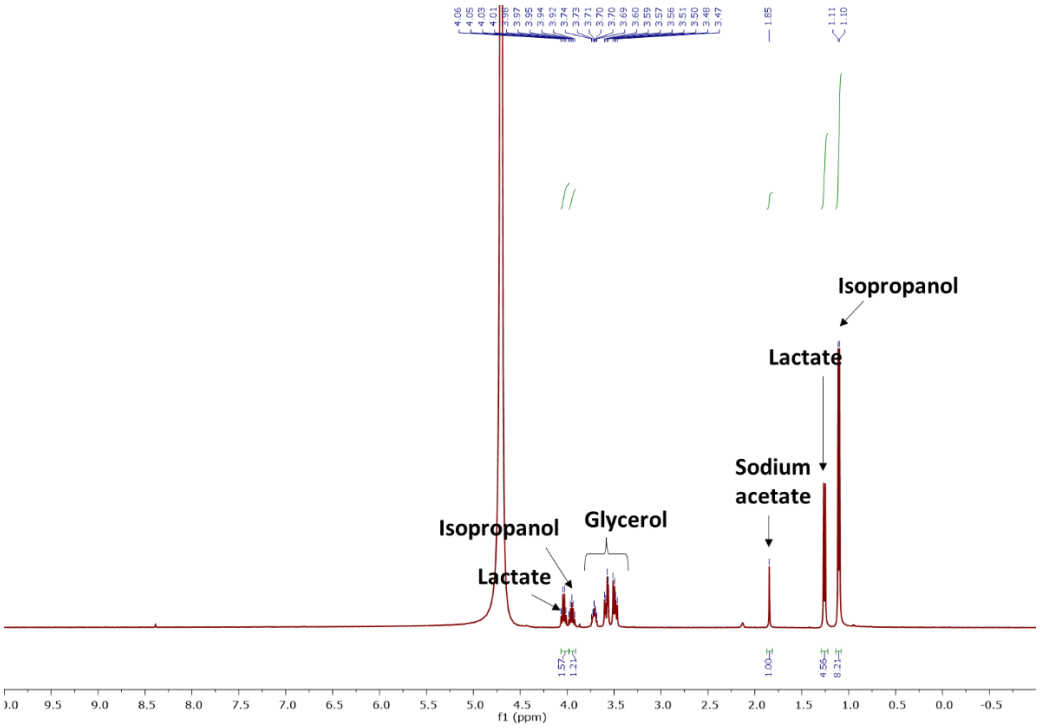

Figure S38. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.25 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 14, Table 1)

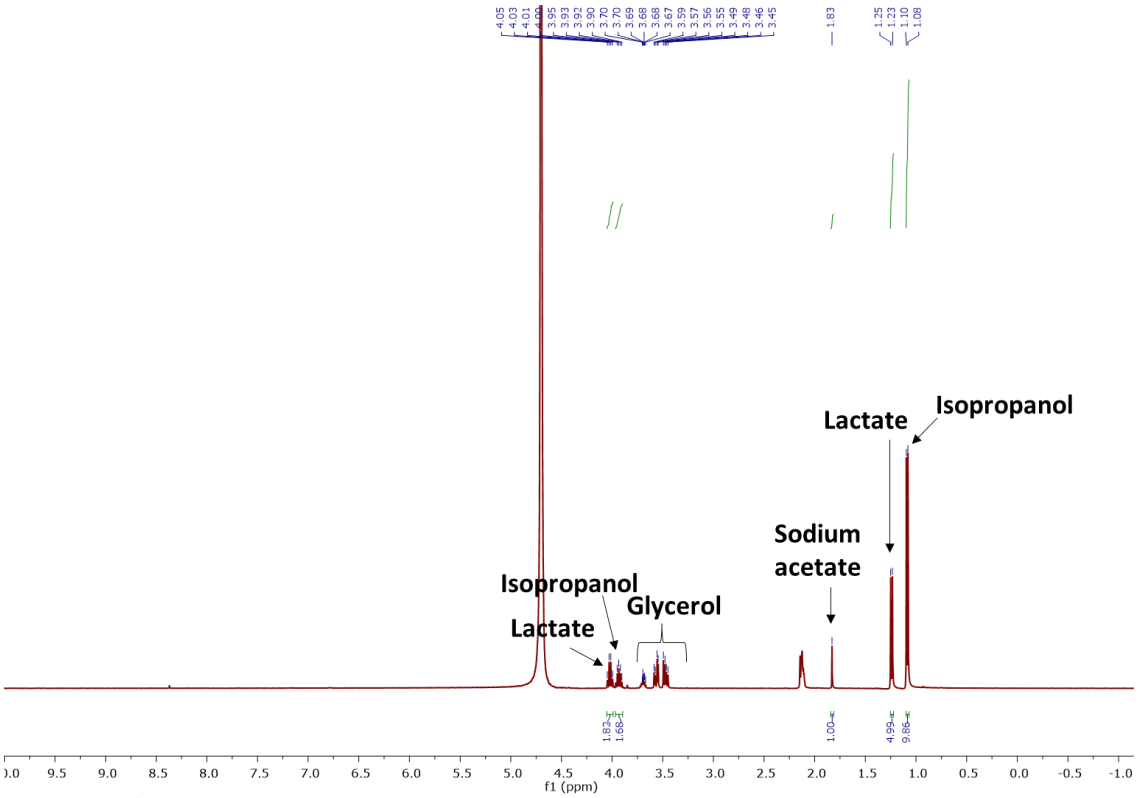

Figure S39. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.125 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 15, Table 1)

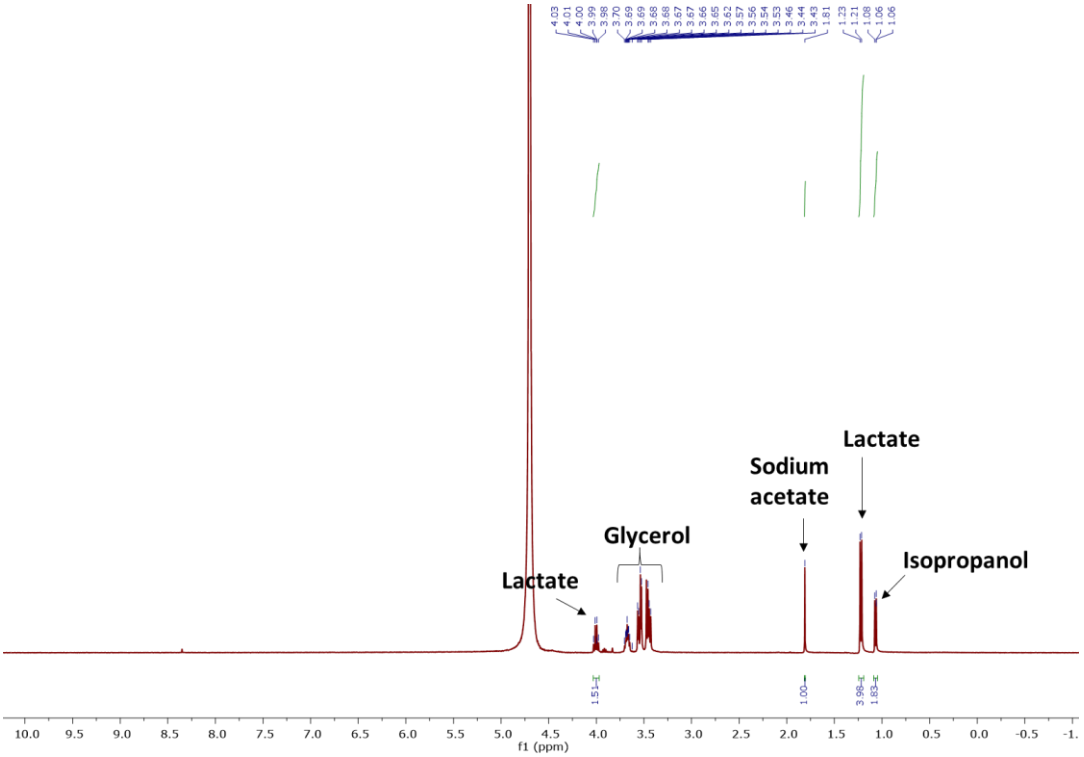

Figure S40. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.0625 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 16, Table 1)

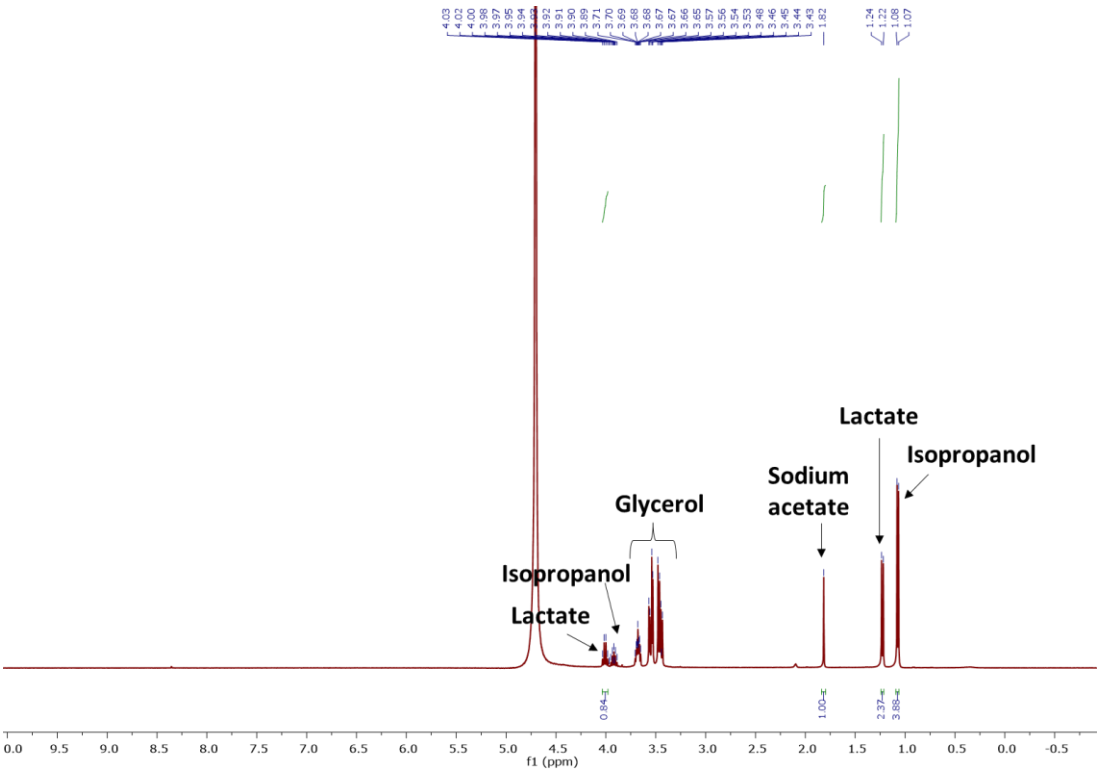

Figure S41. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 120 ºC in D_2O. (Entry 17, Table 1)

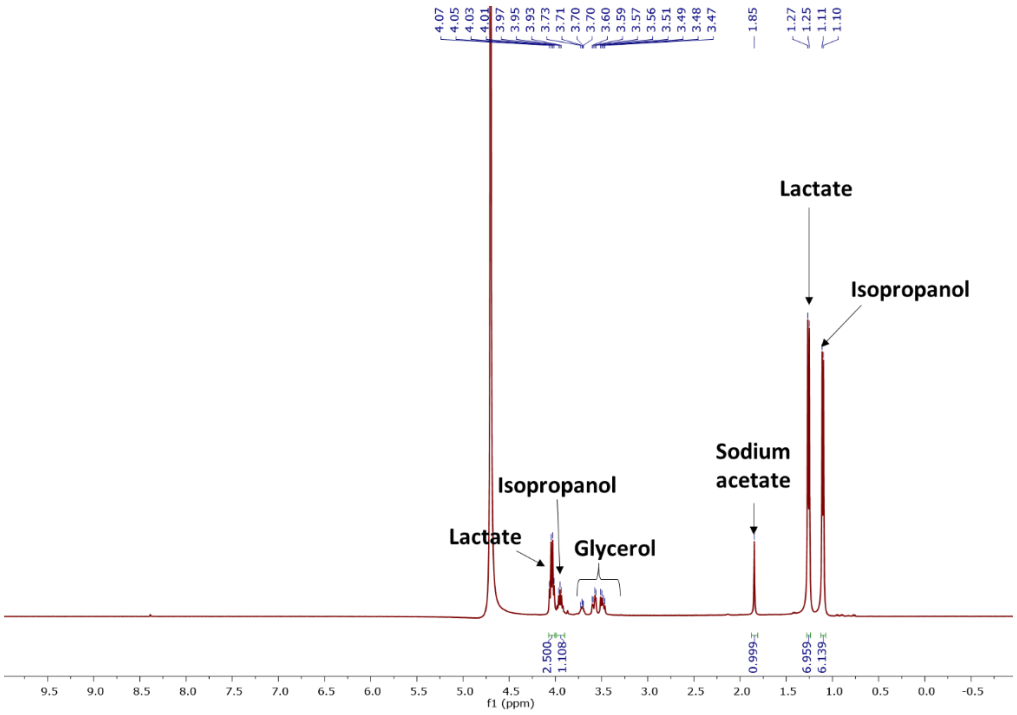

Figure S42. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 160 ºC in D_2O. (Entry 18, Table 1)

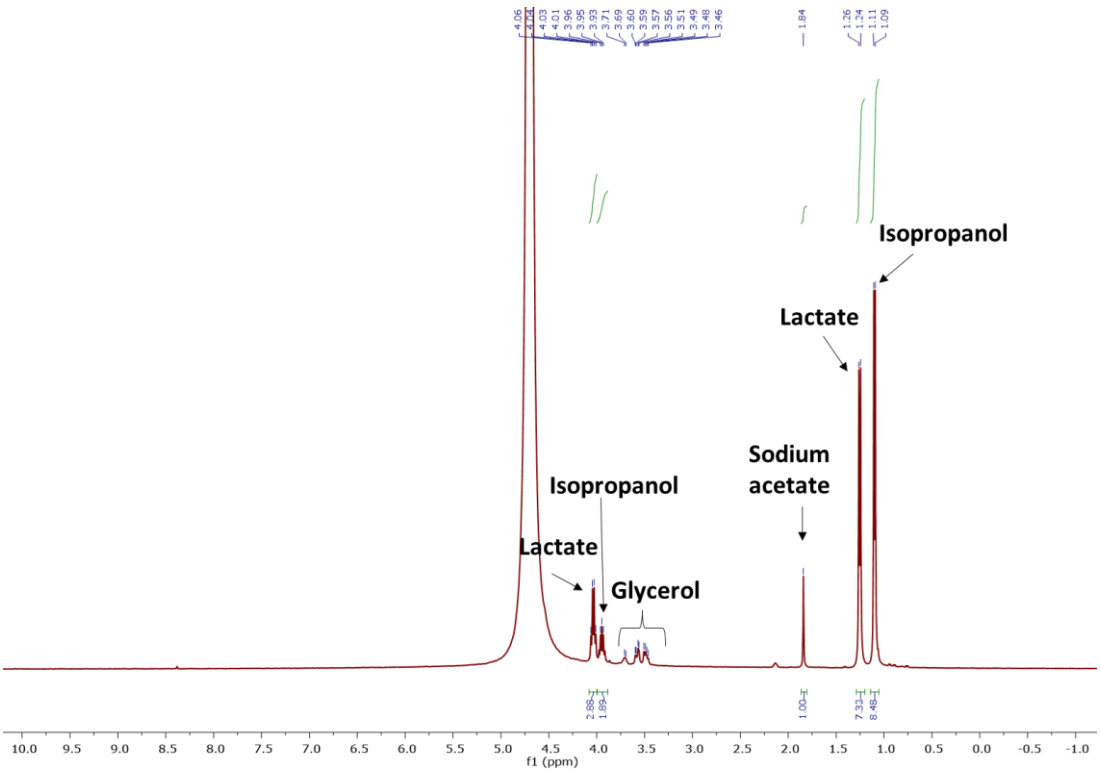

Figure S43. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by **6a** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 20, Table 1)

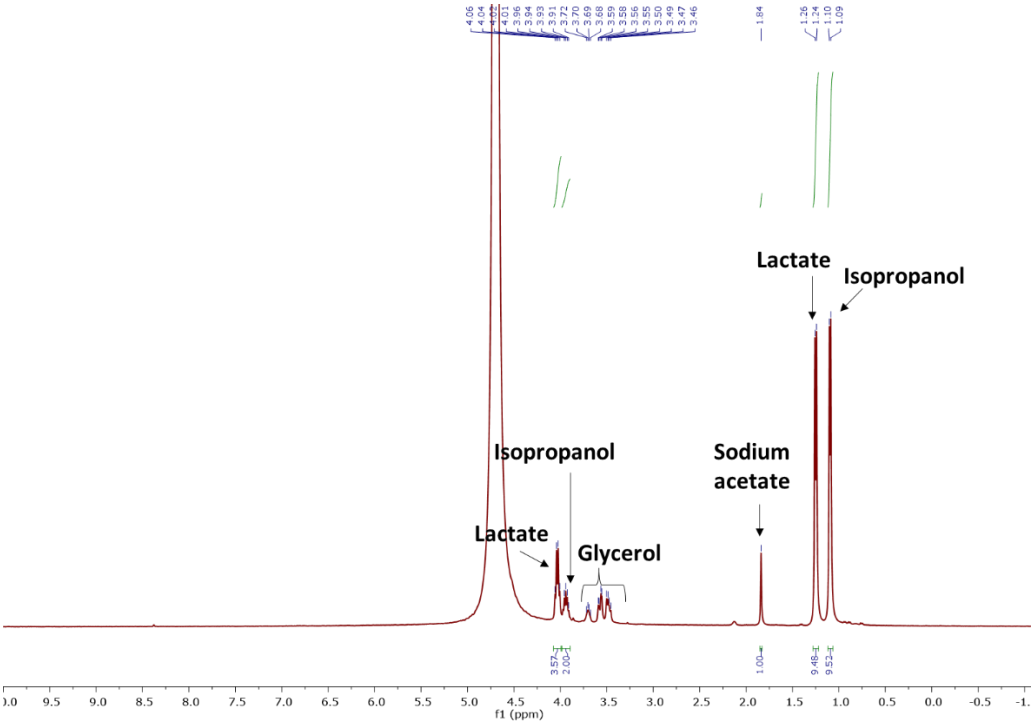

Figure S44. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by **6b** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 21, Table 1)

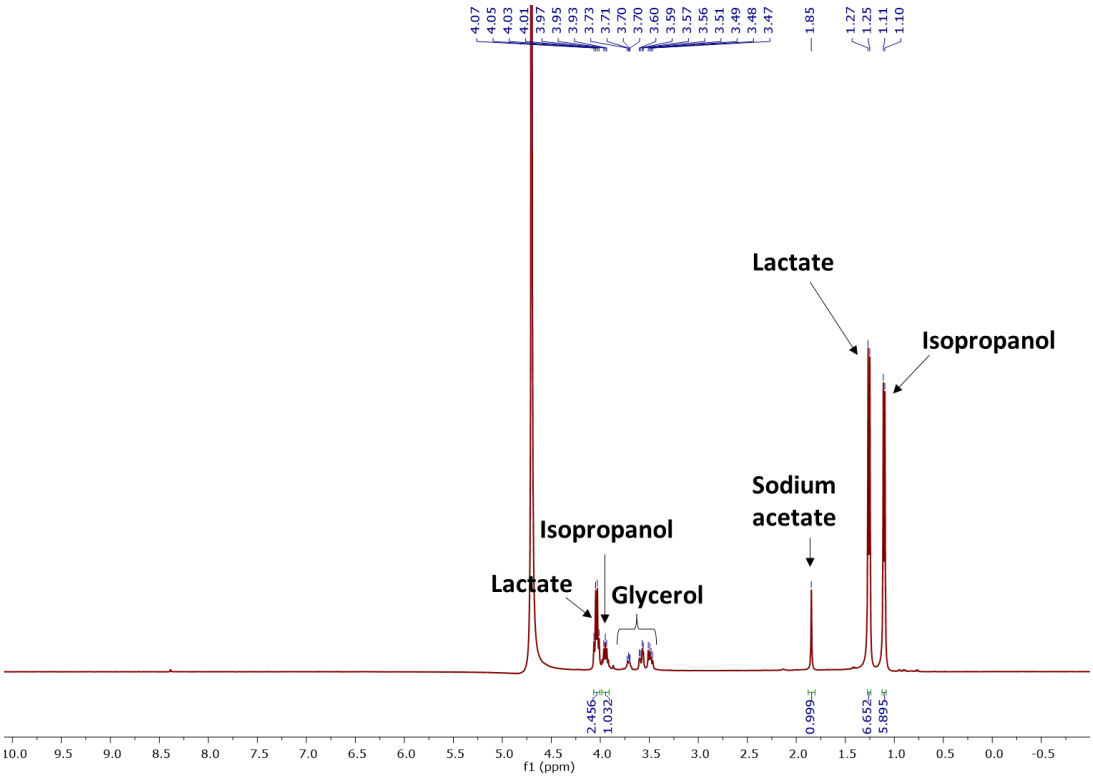

Figure S45. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by **6c** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 22, Table 1)

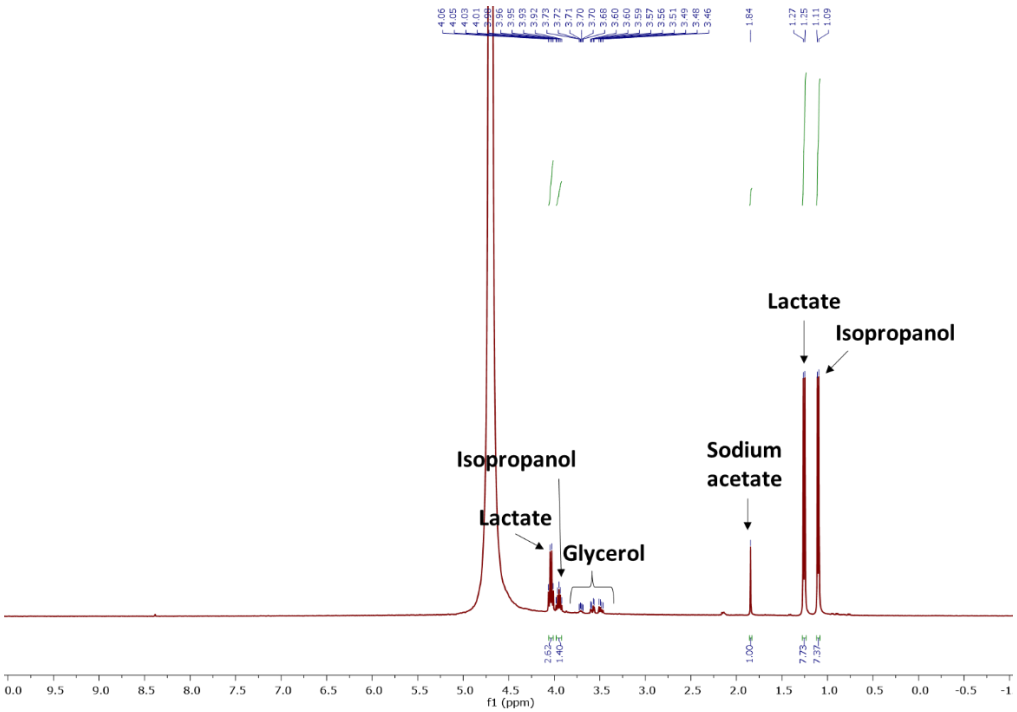

Figure S46. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetone (**8**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 23, Table 1)

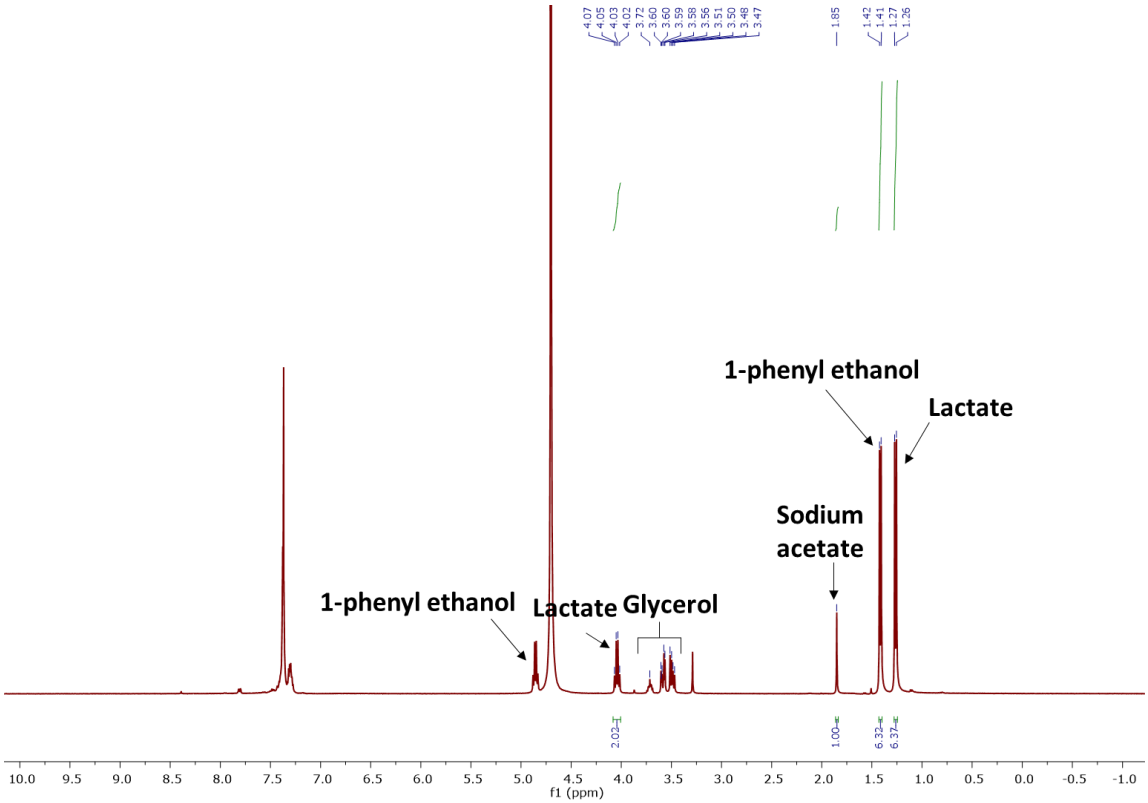

Figure S47. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetophenone (**8a**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 1, Table 2)

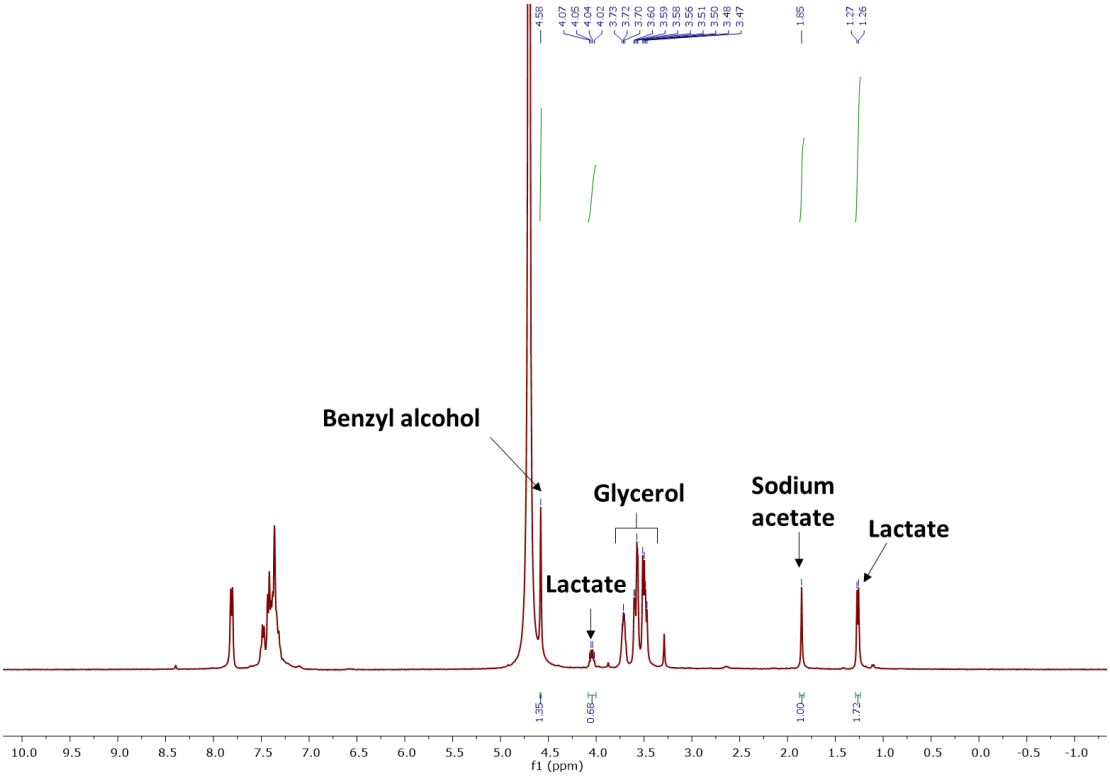

Figure S48. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using benzaldehyde (**8b**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 2, Table 2)

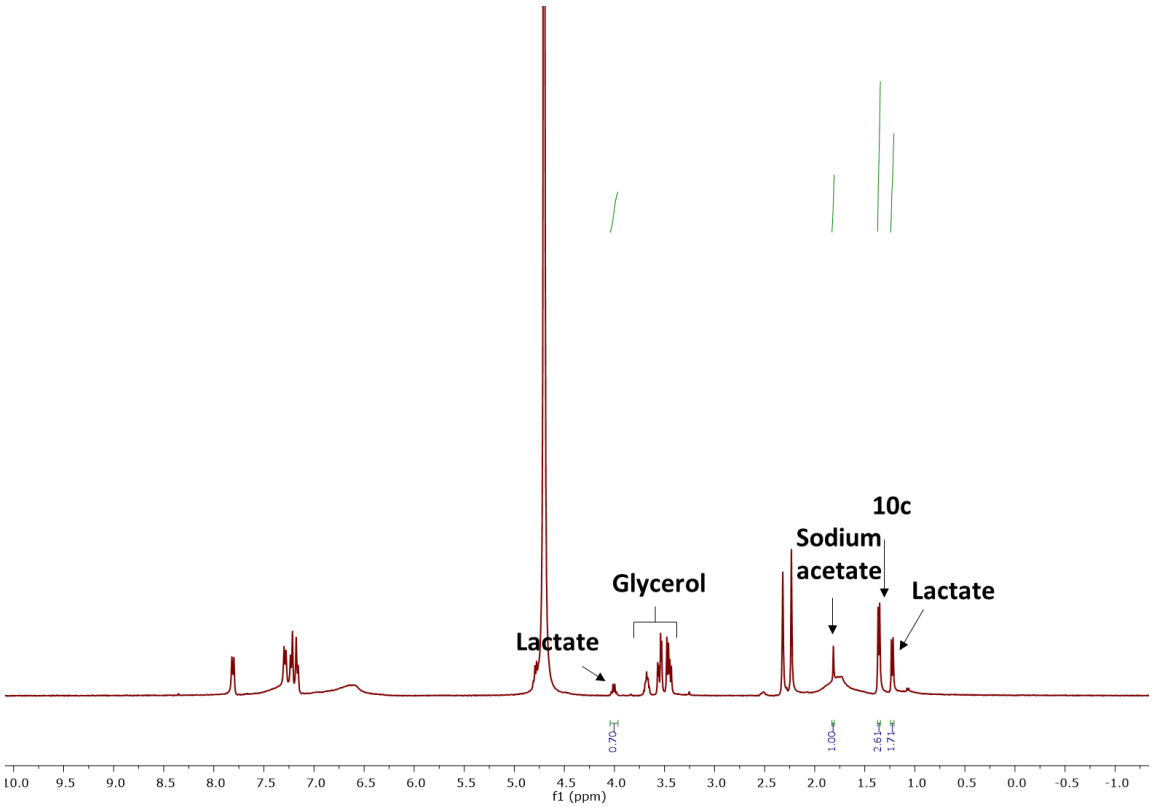

Figure S49. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-methyl acetophenone (**8c**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 3, Table 2)

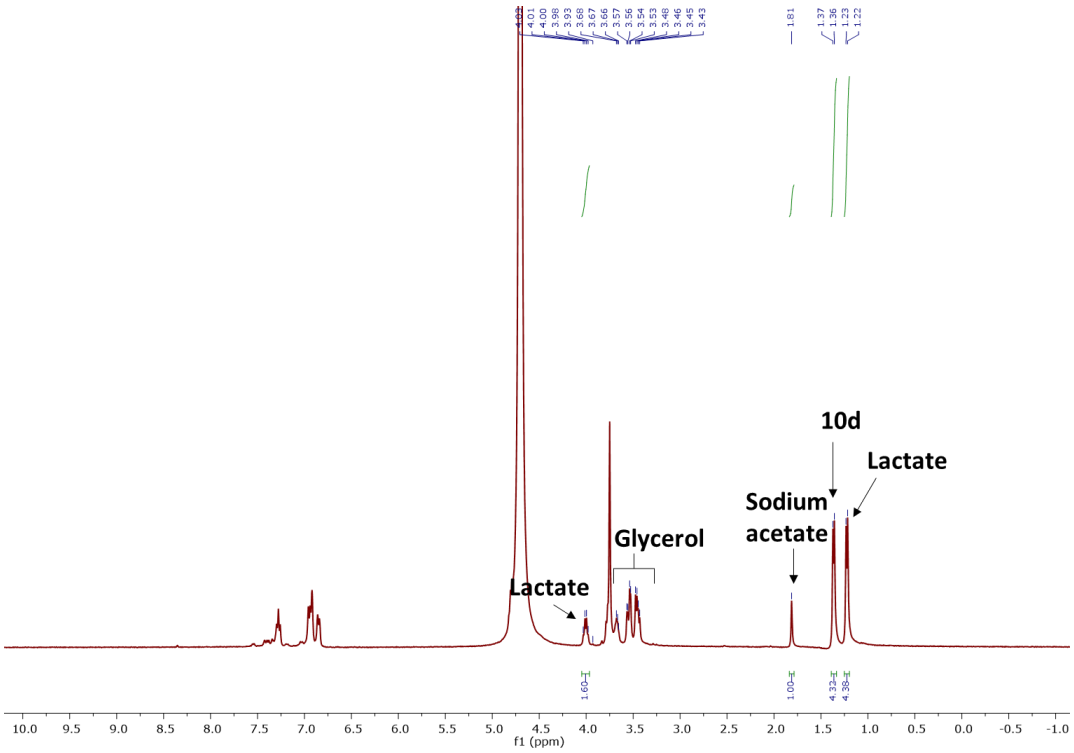

Figure S50. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 3-methoxy acetophenone (**8d**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 4, Table 2)

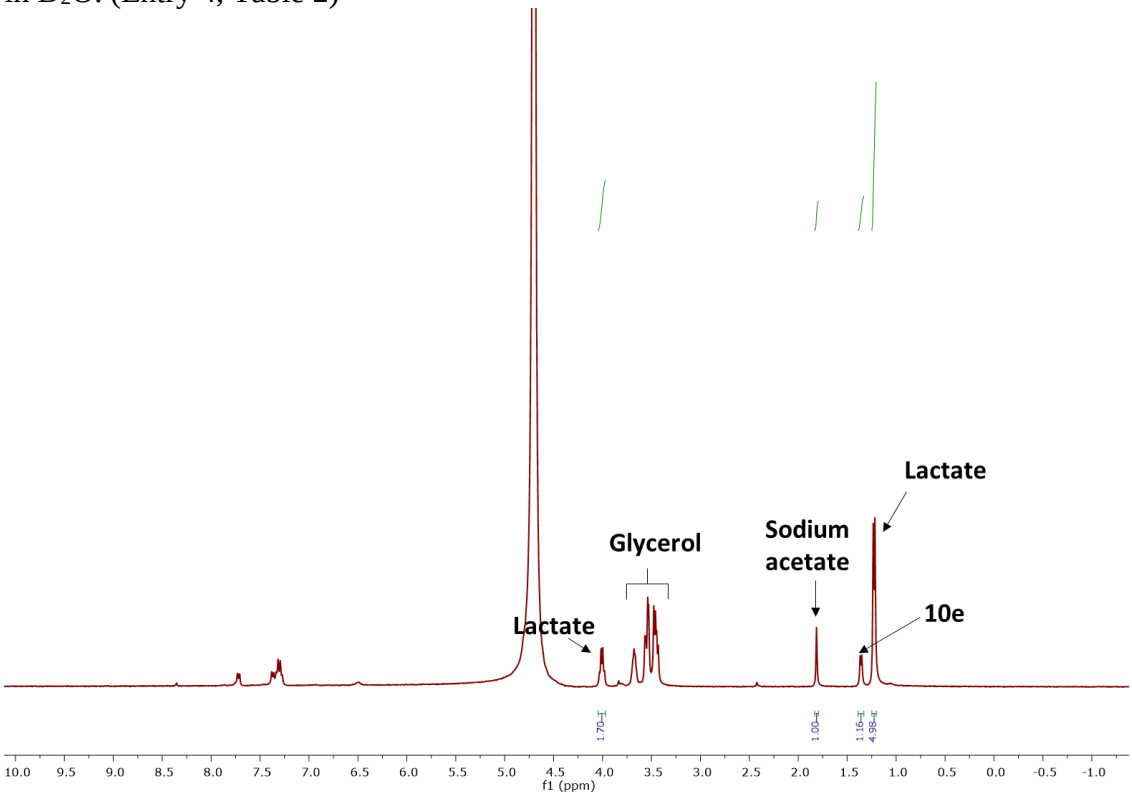

Figure S51. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-chloro acetophenone (**8e**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 5, Table 2)

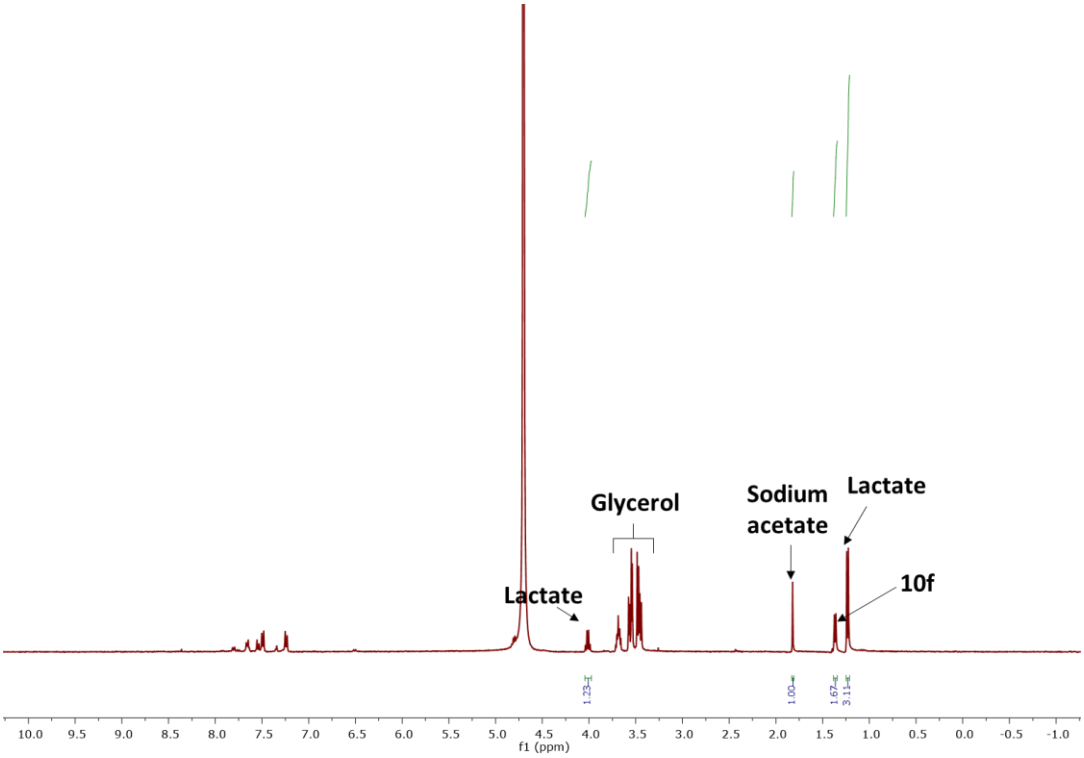

Figure S52. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-bromo acetophenone (**8f**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 6, Table 2)

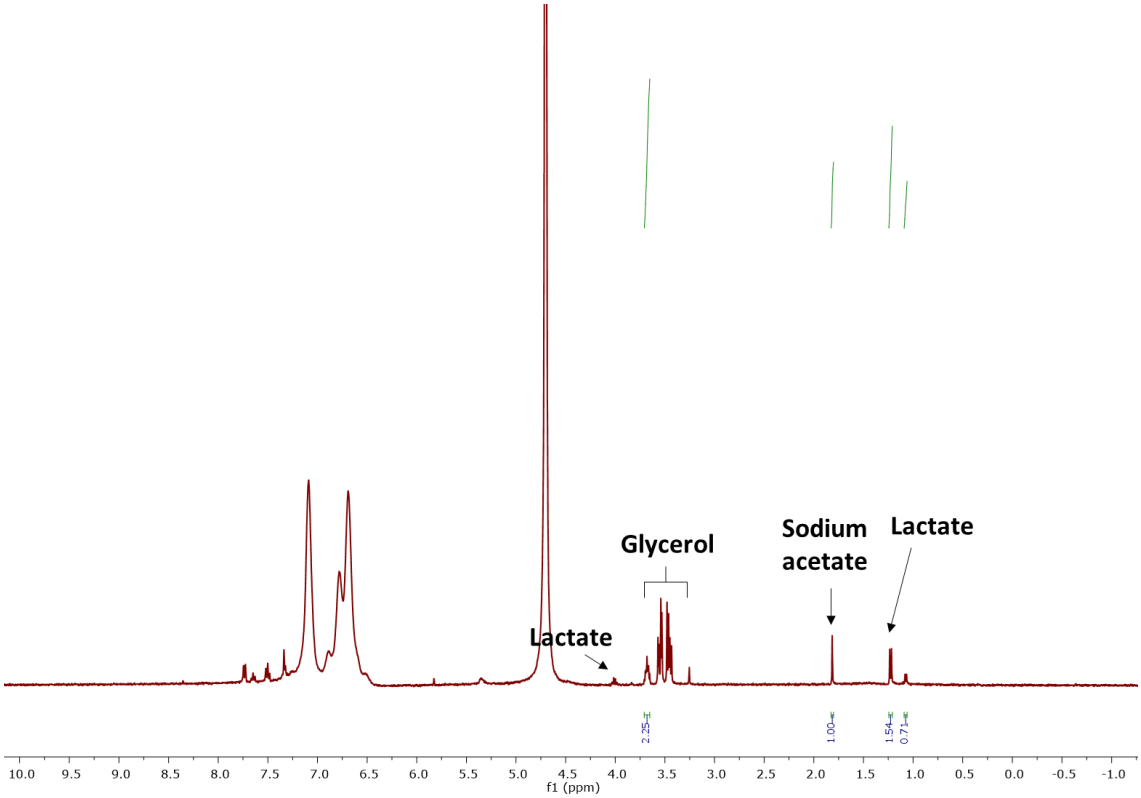

Figure S53.^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using benzophenone (**8h**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 8, Table 2)

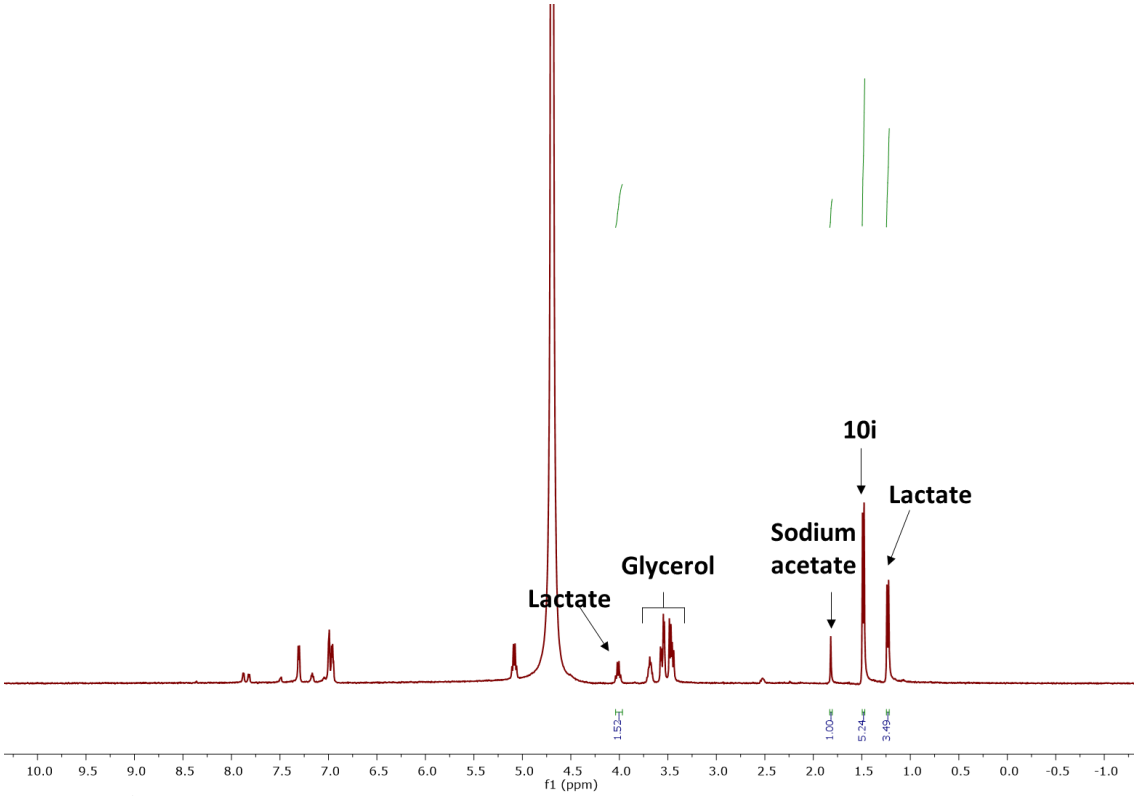

Figure S54.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 2-acetyl thiophene (**8i**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 9, Table 2)

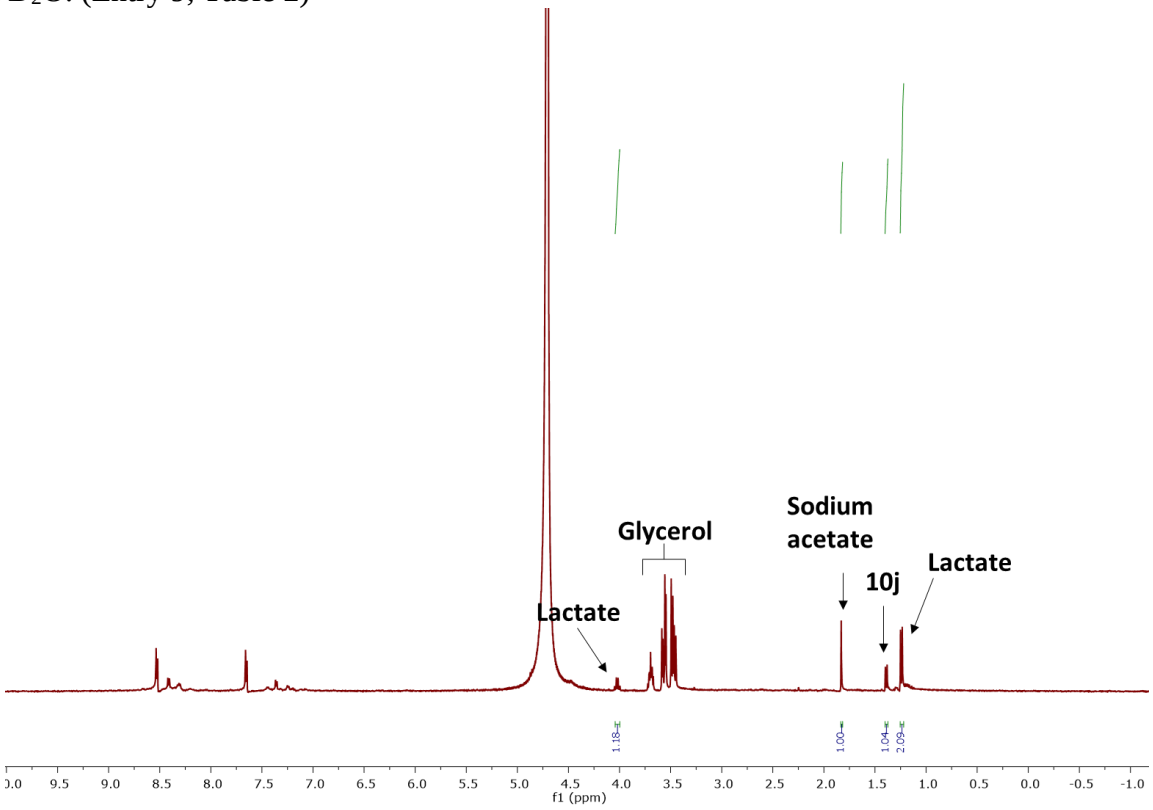

Figure S55.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-acetyl pyridine (**8j**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 10, Table 2)

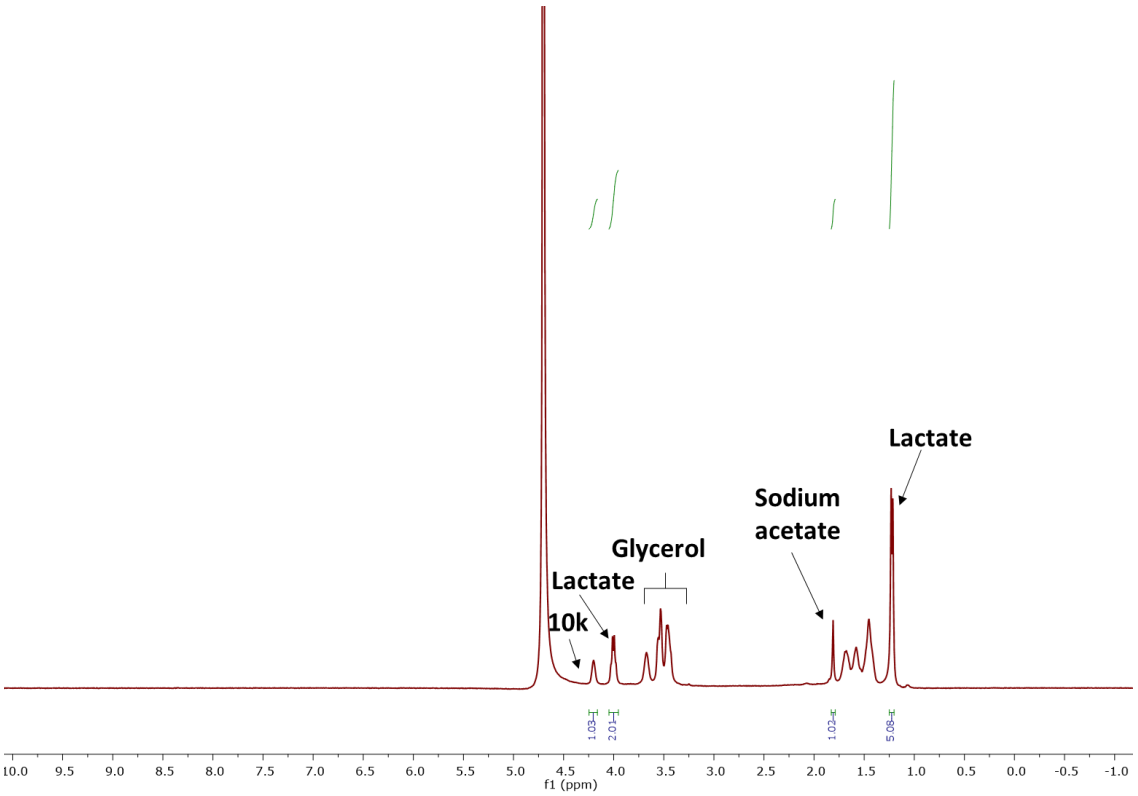

Figure S56. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using cyclopentanone (**8k**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 11, Table 2)

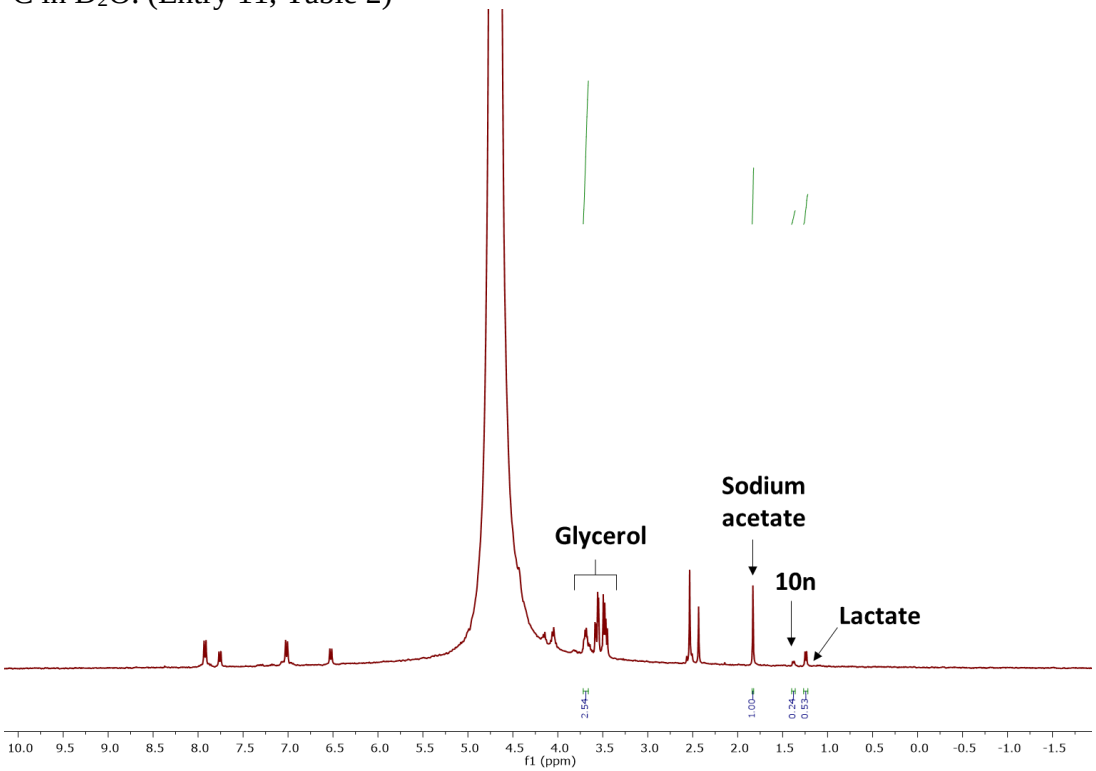

Figure S57. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-Fluoro acetophenone (**8n**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 14, Table 2)

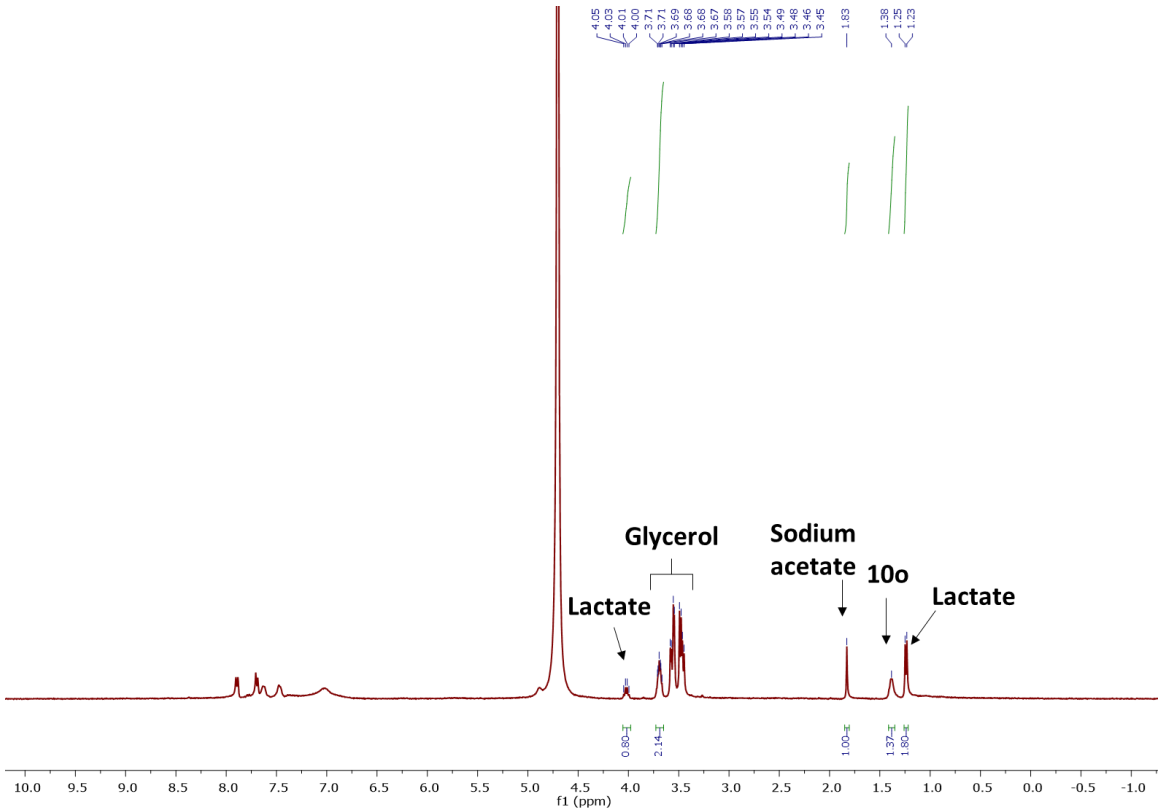

Figure S58. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-trifluoromethyl acetophenone (**8o**) as acceptor, catalyzed by $MnCl_2.4H_2O$ (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 15, Table 2)

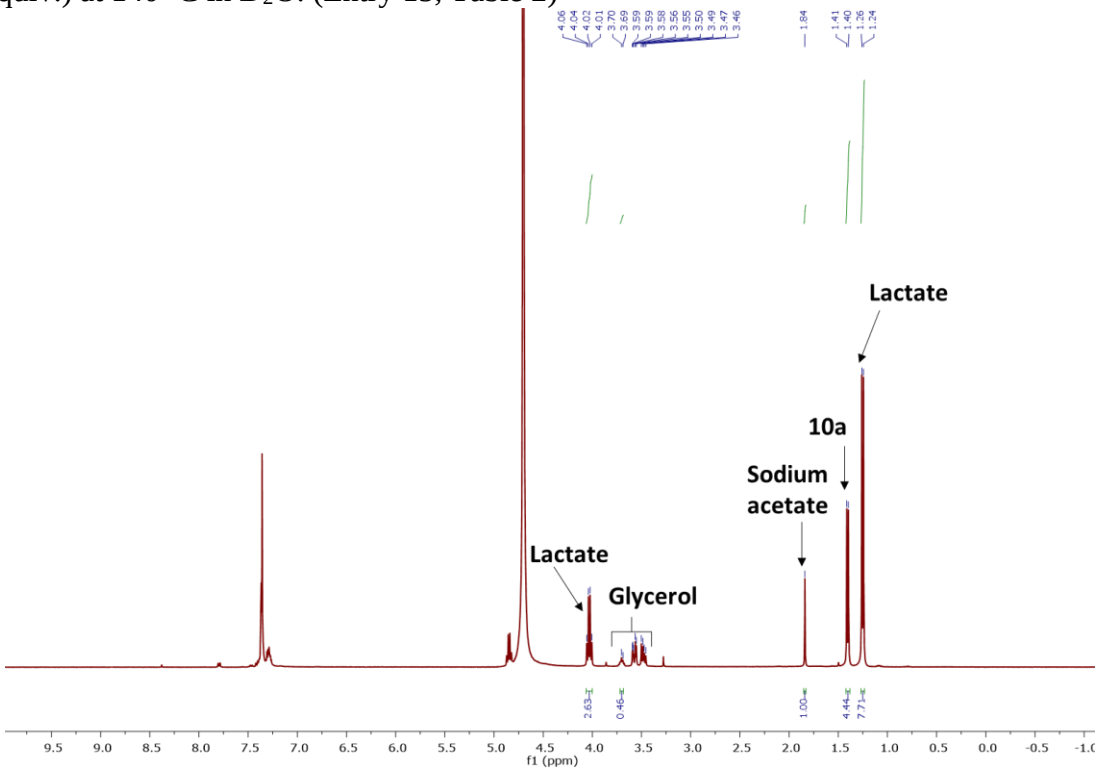

Figure S59. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using acetophenone (**8a**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 1, Table 2)

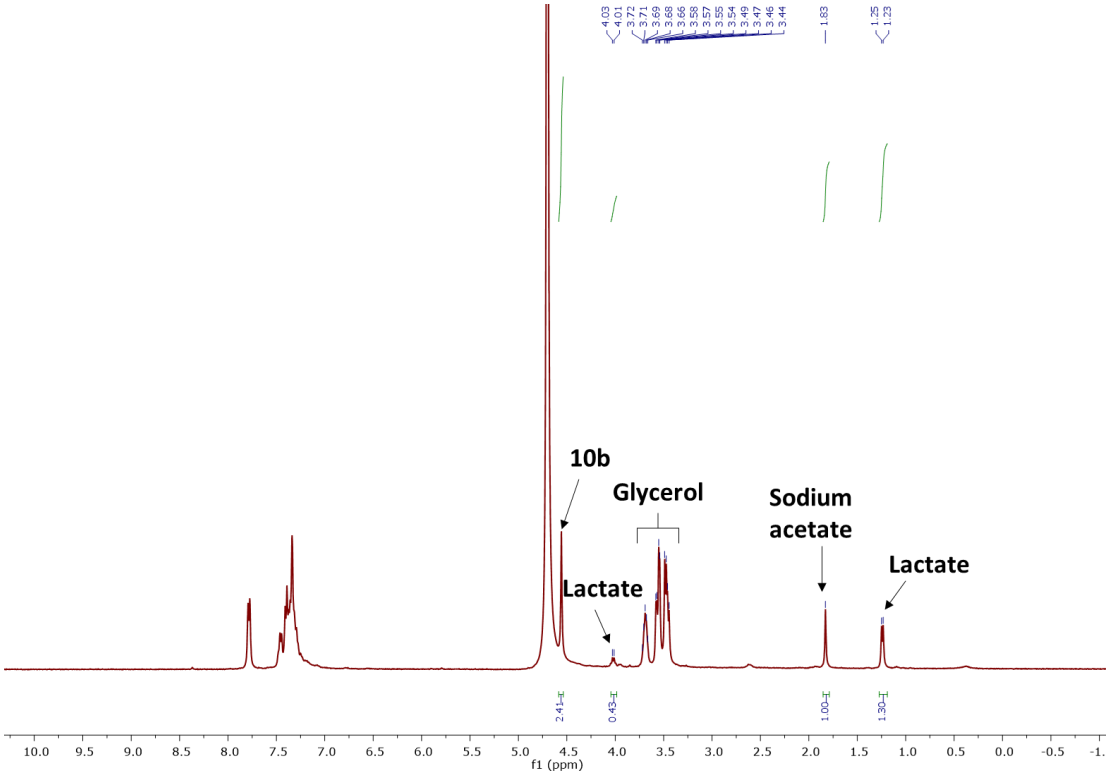

Figure S60. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using benzaldehyde (**8b**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 2, Table 2)

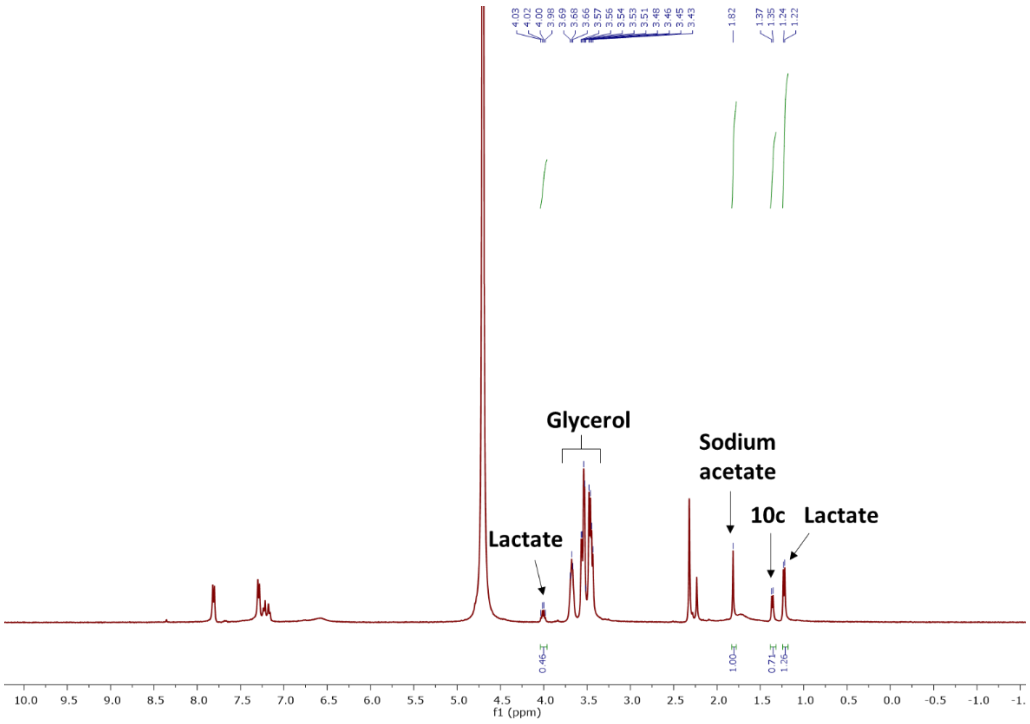

Figure S61. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-methyl acetophenone (**8c**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 3, Table 2)

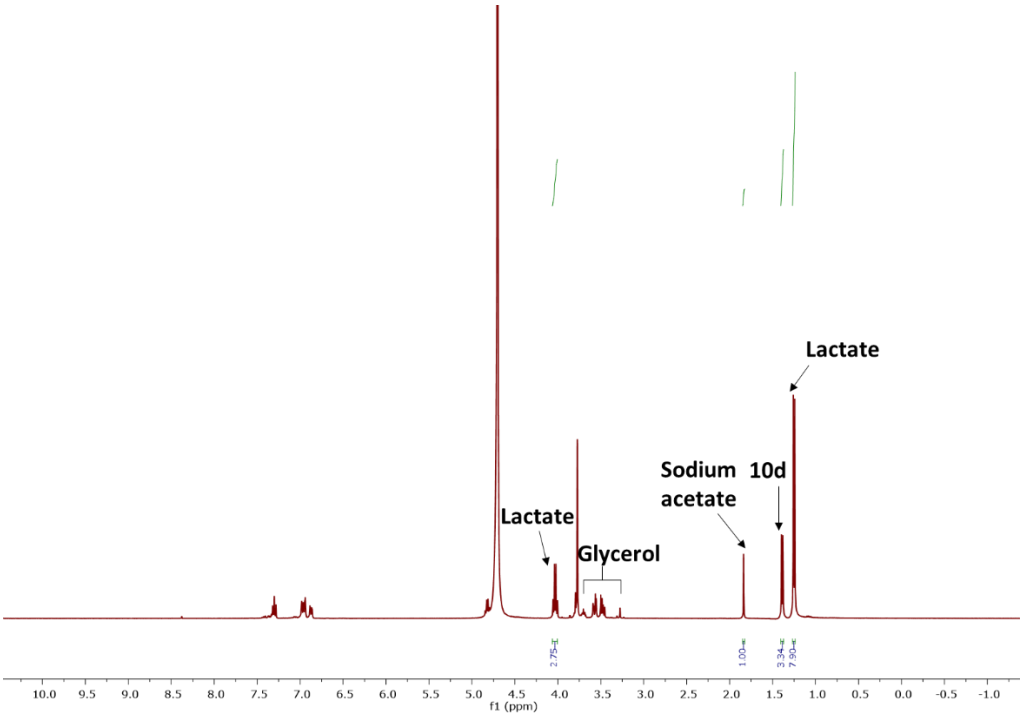

Figure S62.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 3-methoxy acetophenone (**8d**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 4, Table 2)

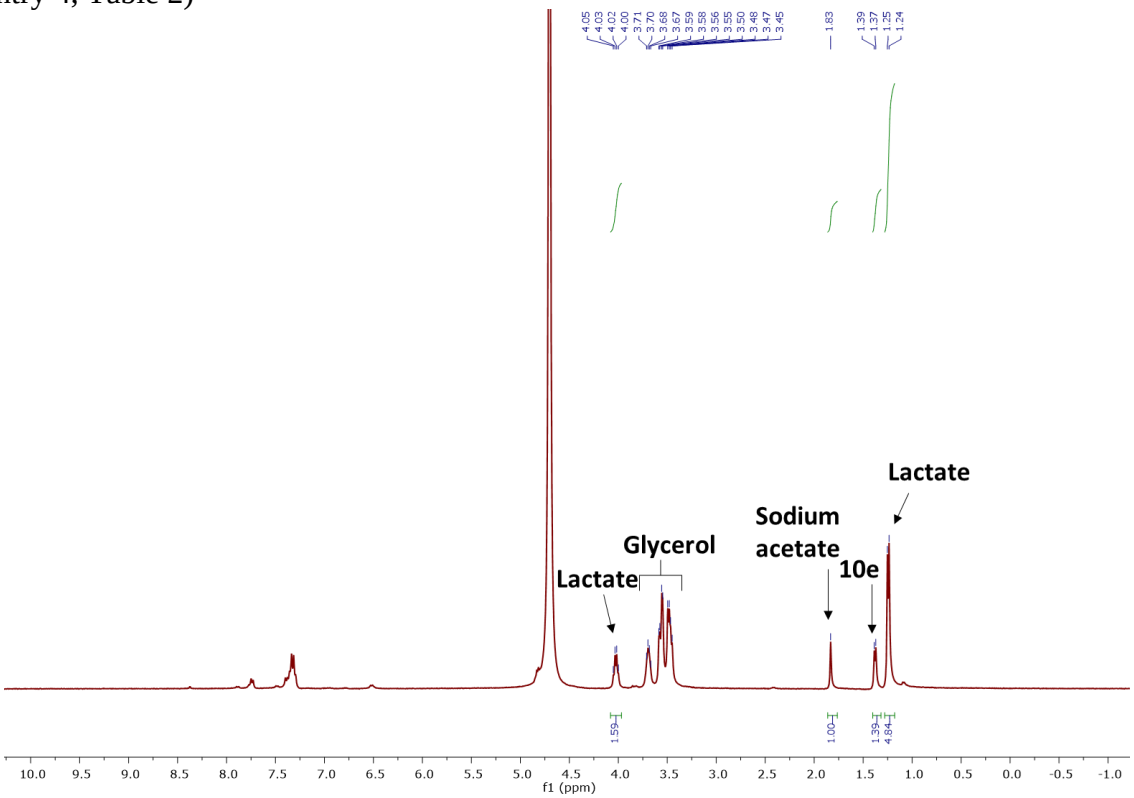

Figure S63.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-chloro acetophenone (**8e**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 5, Table 2)

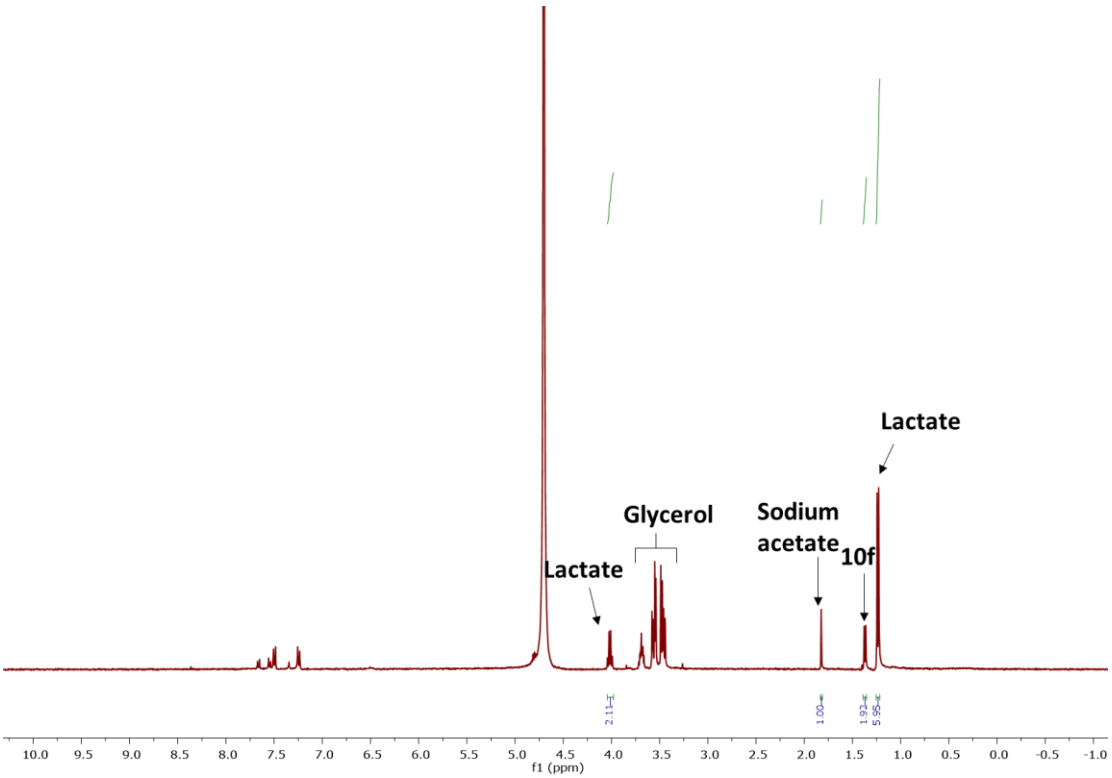

Figure S64.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-bromo acetophenone (**8f**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 6, Table 2)

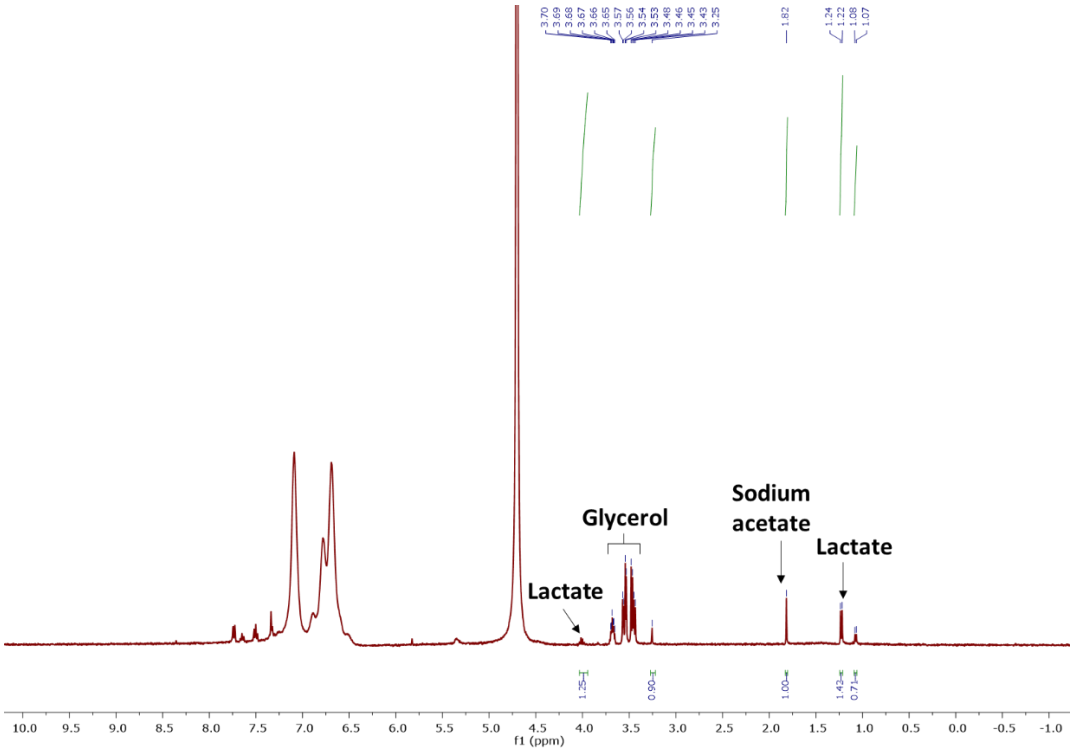

Figure S65.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using benzophenone (**8h**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 8, Table 2)

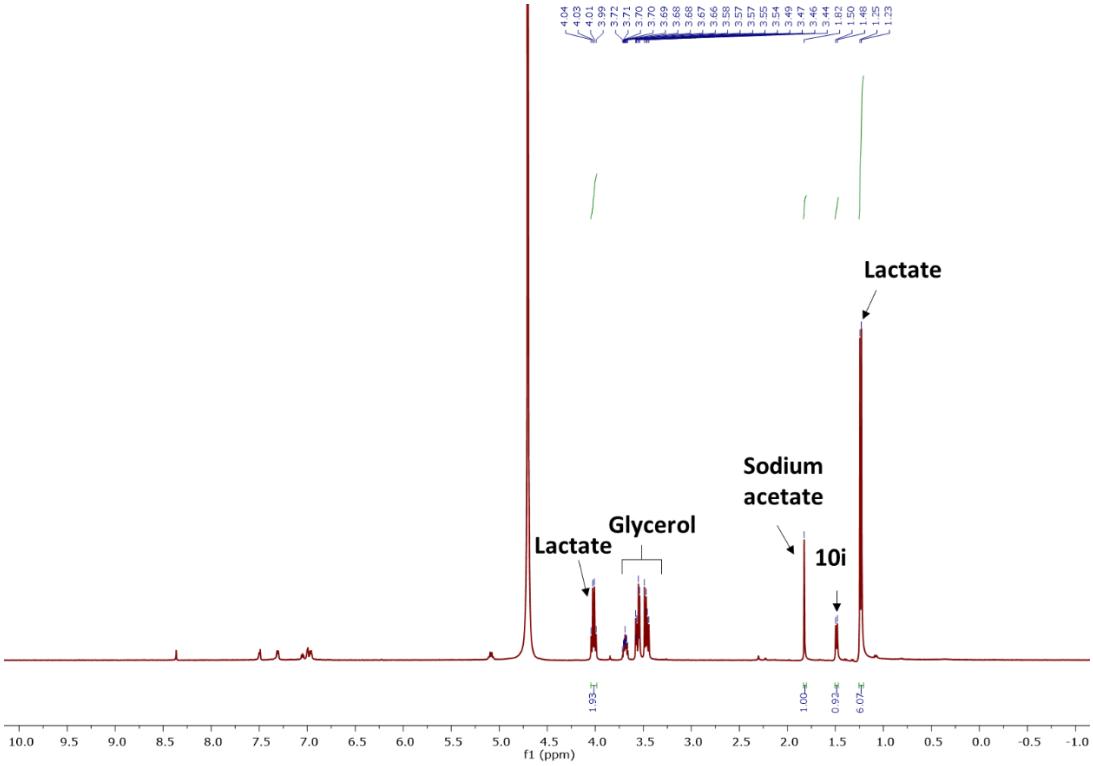

Figure S66. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 2-acetyl thiophene (**8i**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 9, Table 2)

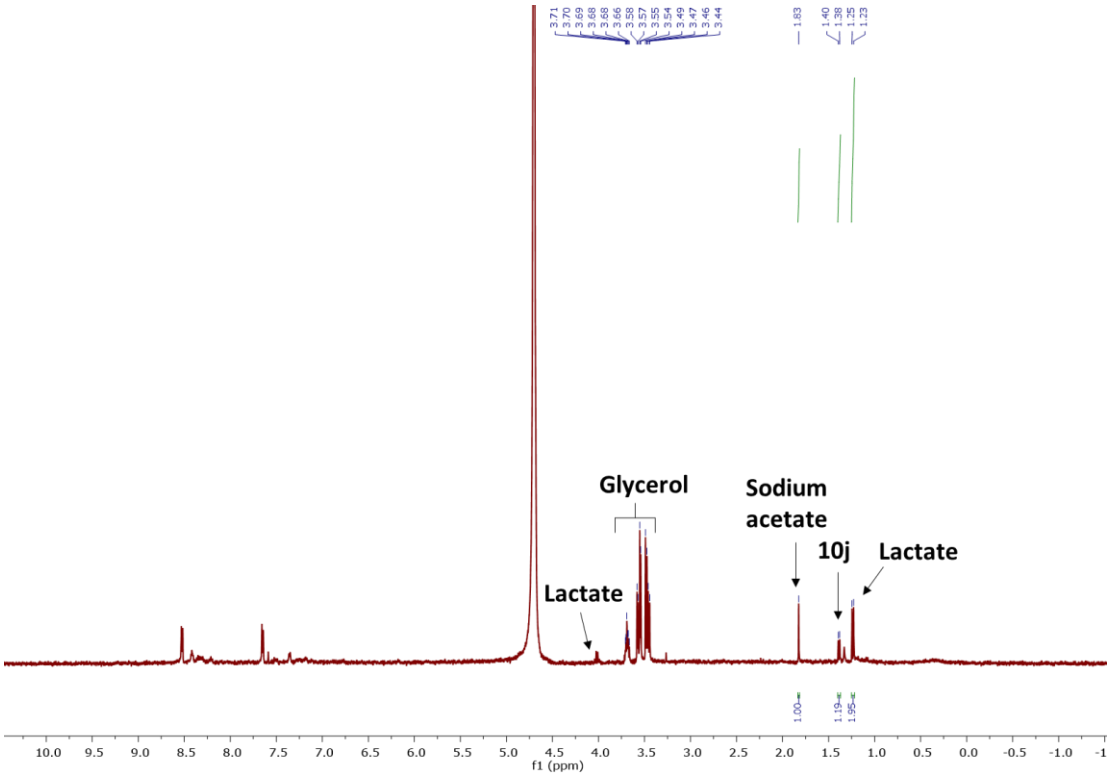

Figure S67. ^{1}H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-acetyl pyridine (**8j**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 10, Table 2)

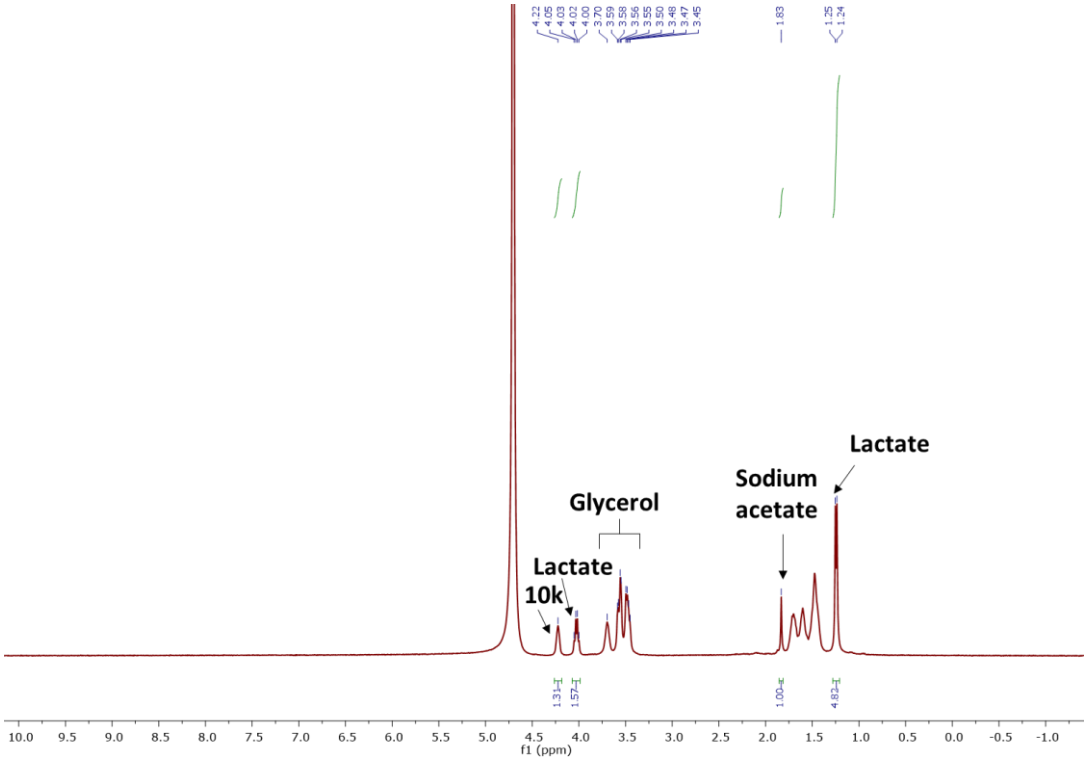

Figure S68.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using cyclopentanone (**8k**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 11, Table 2)

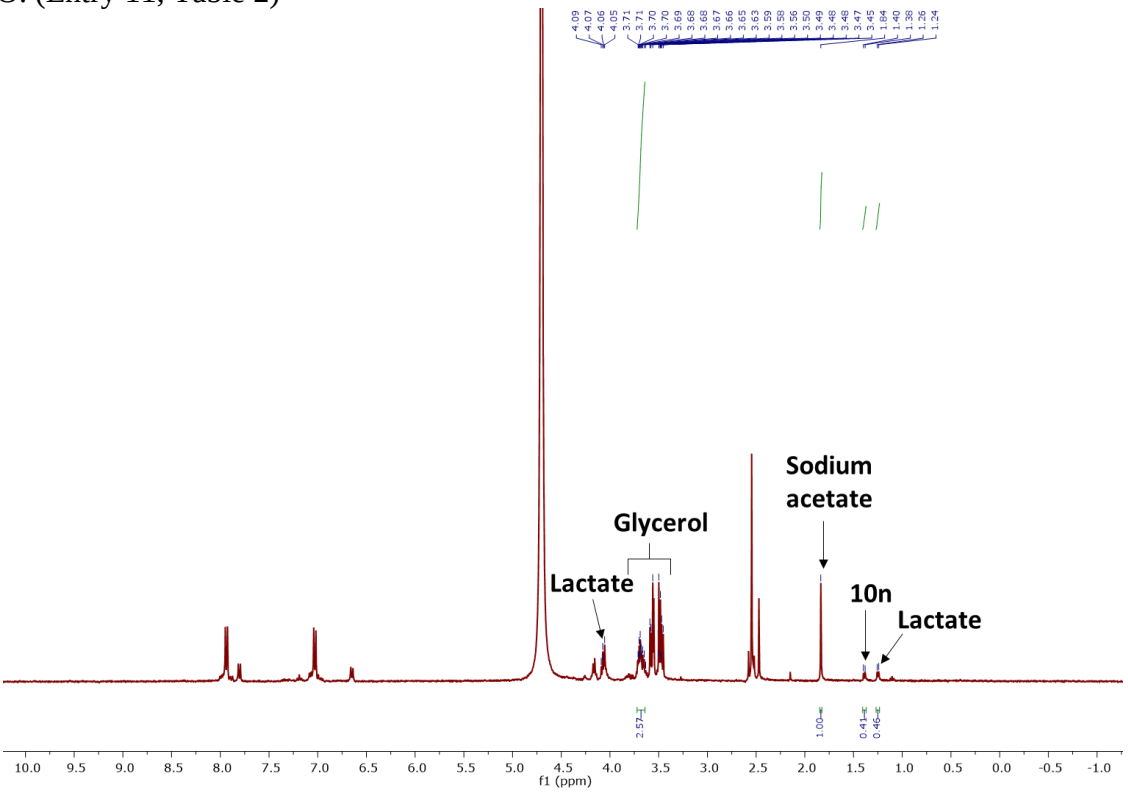

Figure S69.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-fluoro acetophenone (**8n**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 14, Table 2)

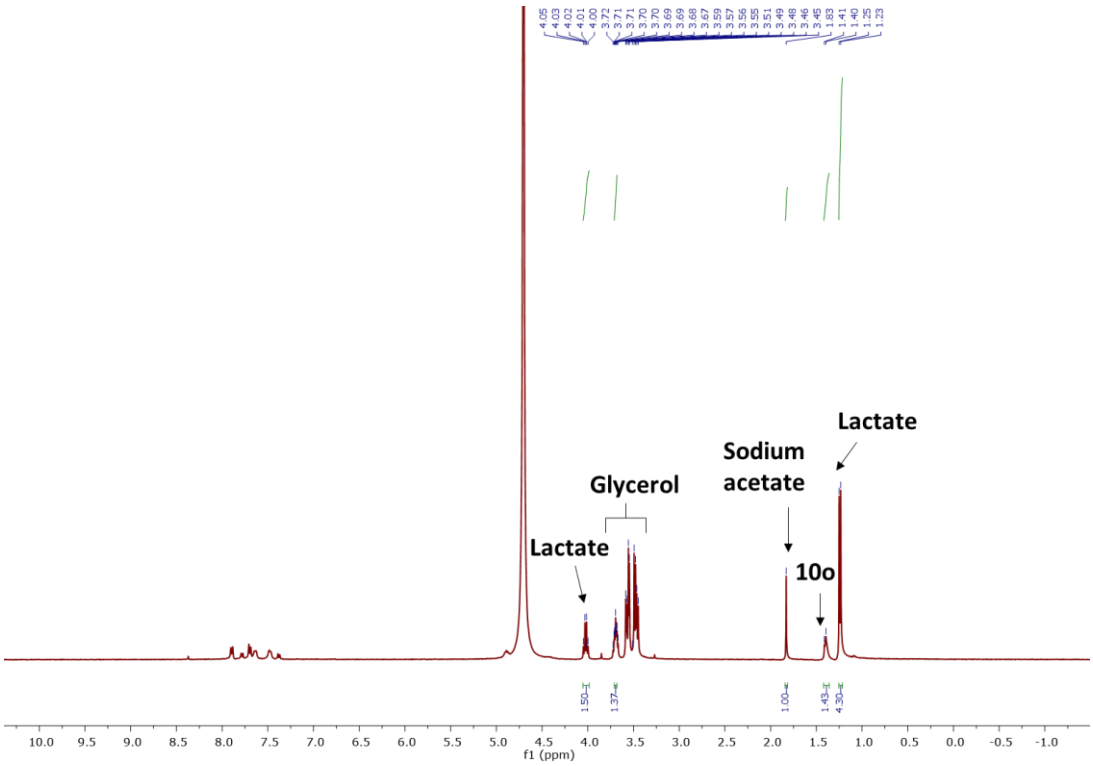

Figure S70.[1]H NMR spectrum of glycerol (**7**) dehydrogenation to lactate (**9**) using 4-trifluoro methyl acetophenone (**8o**) as acceptor, catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.) at 140 ºC in D_2O. (Entry 15, Table 2)

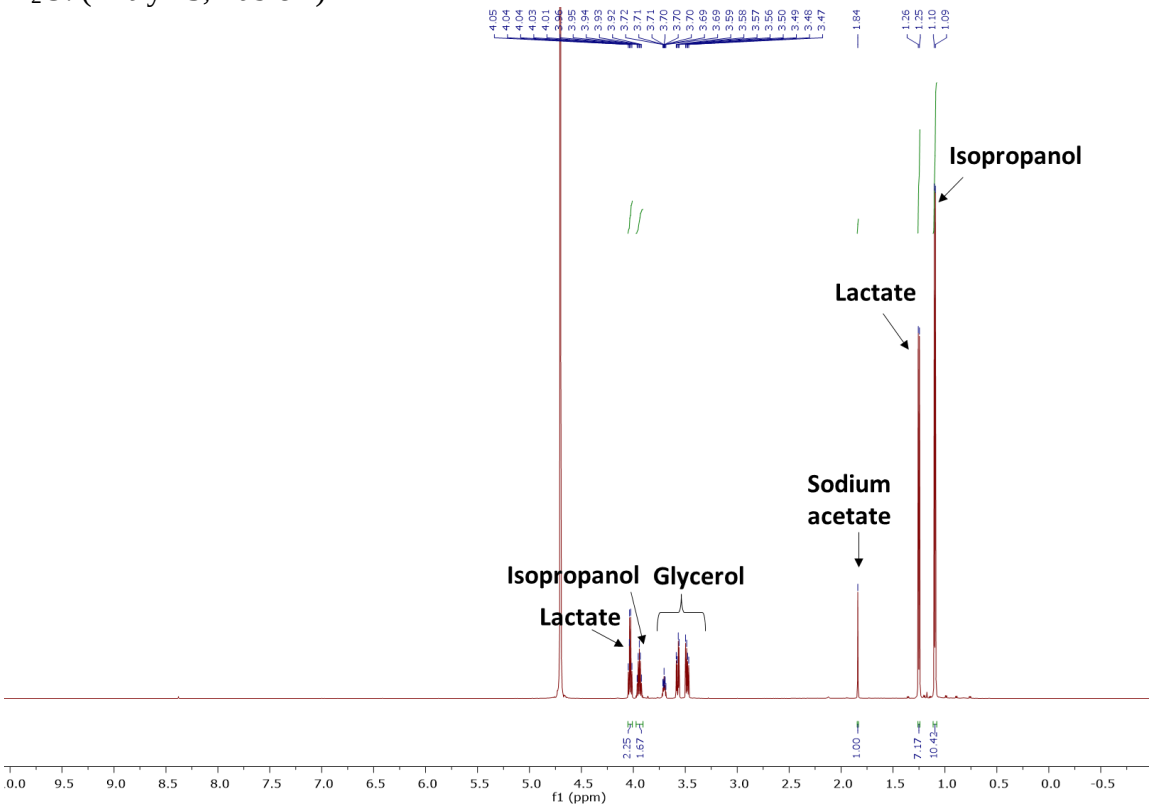

Figure S71. [1]H NMR spectra of glycerol (**7**) dehydrogenation to lactate (**9**), catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.), in the presence of 0.5 mol% of PPh_3 at 140 ºC in D_2O. (Scheme 2, equation 2).

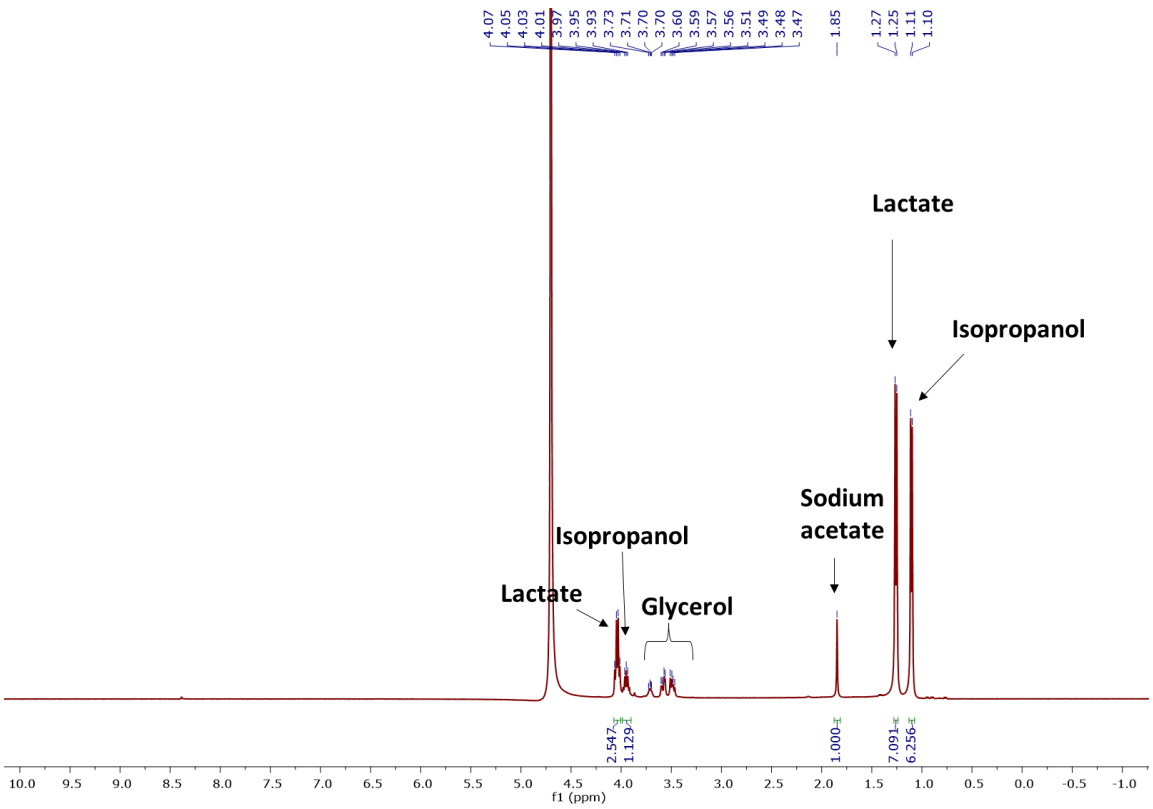

Figure S72. ^{1}H NMR spectra of glycerol (**7**) dehydrogenation to lactate (**9**), catalyzed by **6d** (2.5 mol%), NaOH (1 equiv.), in the presence of 0.5 mol% of PPh_3 at 140 ºC in D_2O. (Scheme 2, equation 3).

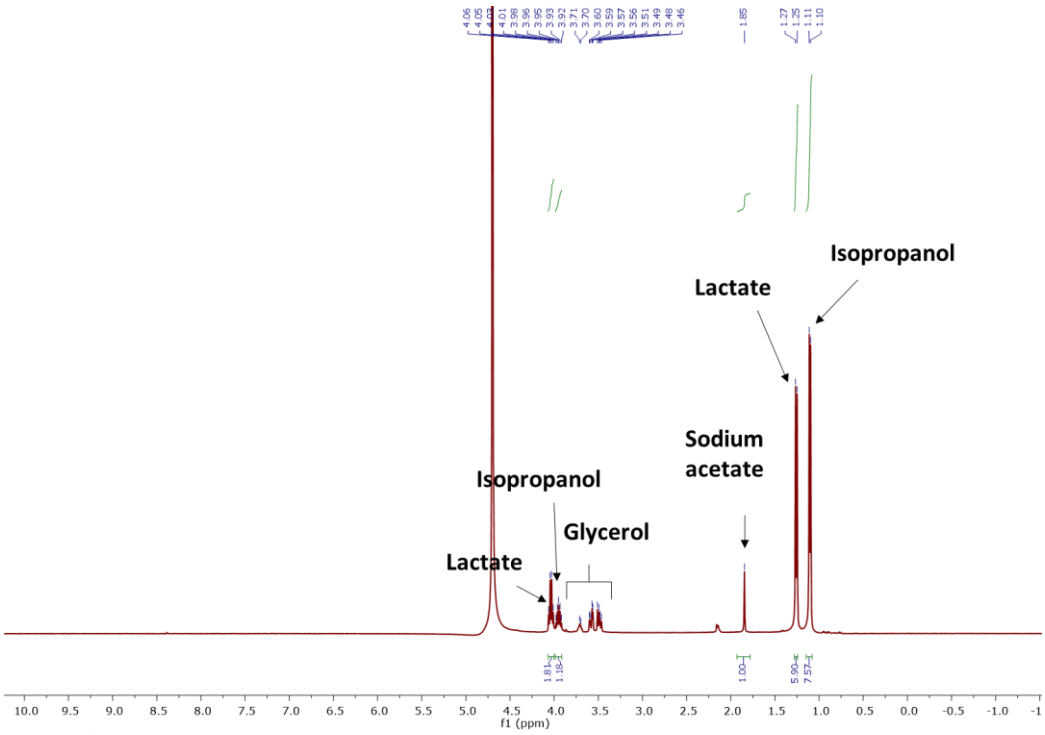

Figure S73. ^{1}H NMR spectra of glycerol (**7**) dehydrogenation to lactate (**9**), catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.), in the presence of 0.5 mol% of CS_2 at 140 ºC in D_2O. (Scheme 2, equation 4).

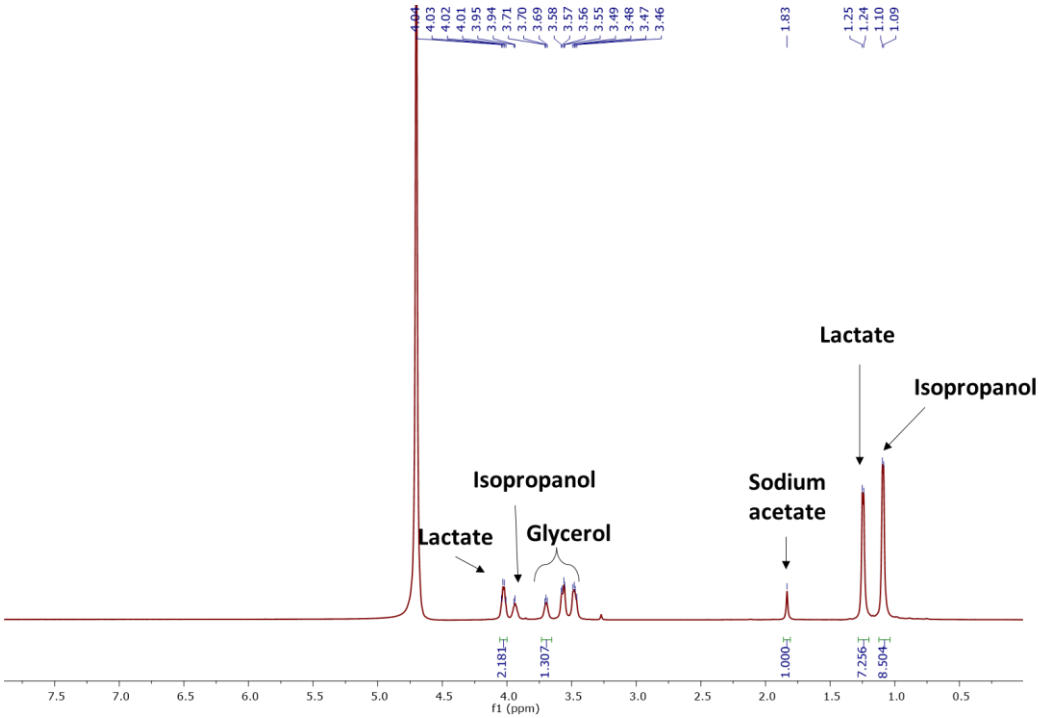

Figure S74. ^{1}H NMR spectra of glycerol (**7**) dehydrogenation to lactate (**9**), catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.), in the presence of 2.5 mol% of CS_2 at 140 ºC in D_2O. (Scheme 2, equation 5).

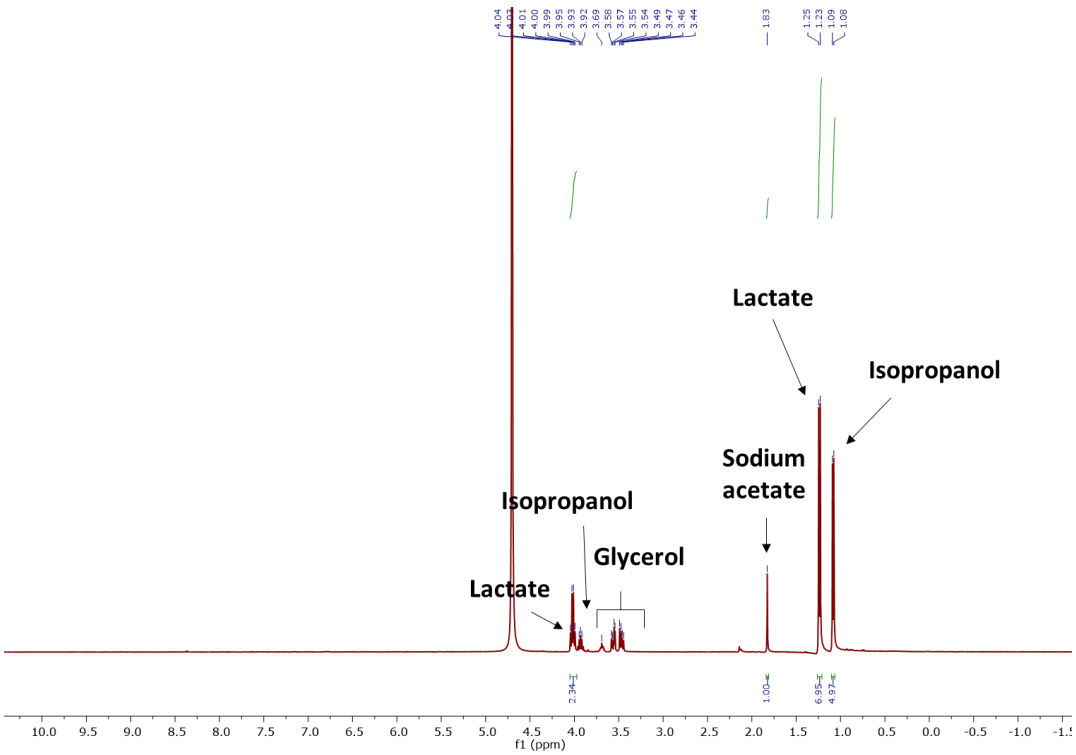

Figure S75. ^{1}H NMR spectra of glycerol (**7**) dehydrogenation to lactate (**9**), catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.), in the presence of excess Hg at 140 ºC in D_2O. (Scheme 2, equation 6).

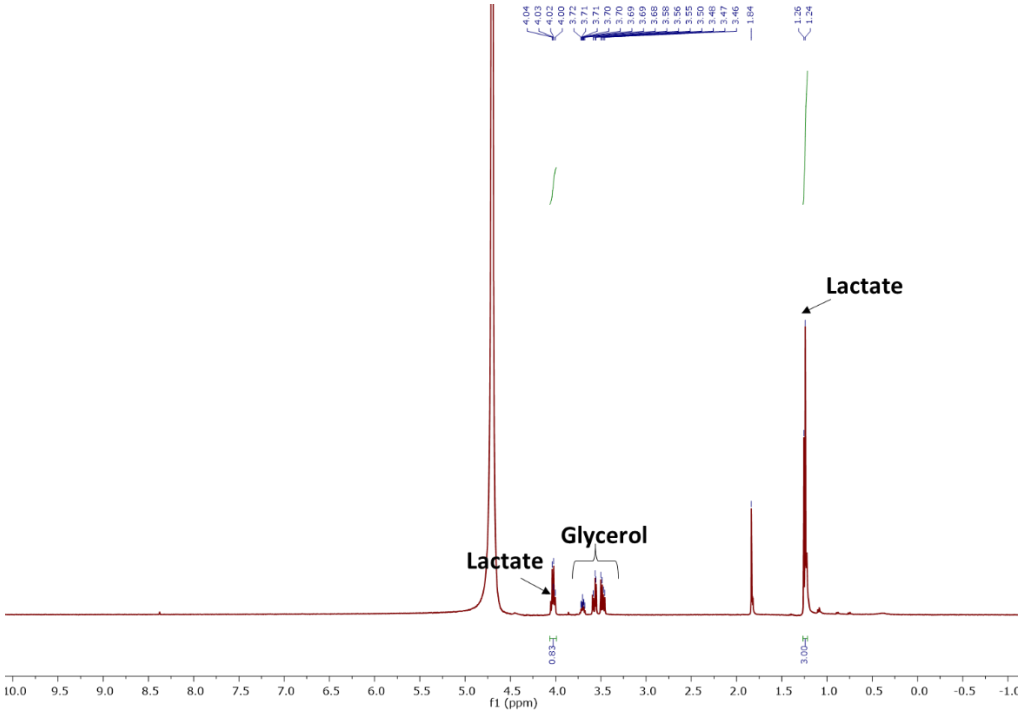

Figure S76. [1]H NMR spectra of deuterium labelling experiment of glycerol (**7**) transfer dehydrogenation to lactate (**9**) catalyzed by 0.5 mol% **6d**, 1 equivalent NaOH using acetone as hydrogen acceptor, at 140 °C. (Scheme 2, equation 7).

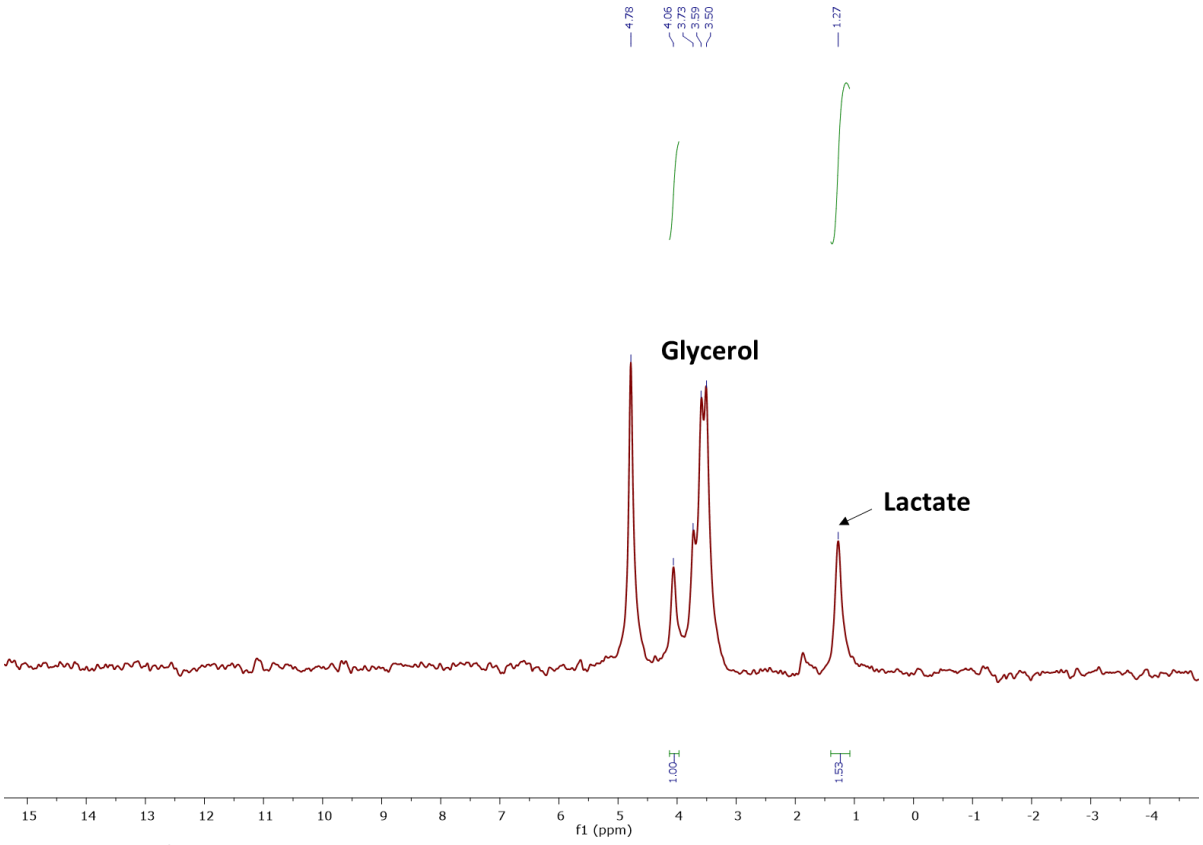

Figure S77. [2]H NMR spectra of deuterium labelling experiment of glycerol (**7**) transfer dehydrogenation to lactate (**9**) catalyzed by 0.5 mol% **6d**, 1 equivalent NaOH using acetone as hydrogen acceptor, at 140 °C. (Scheme 2, equation 7).

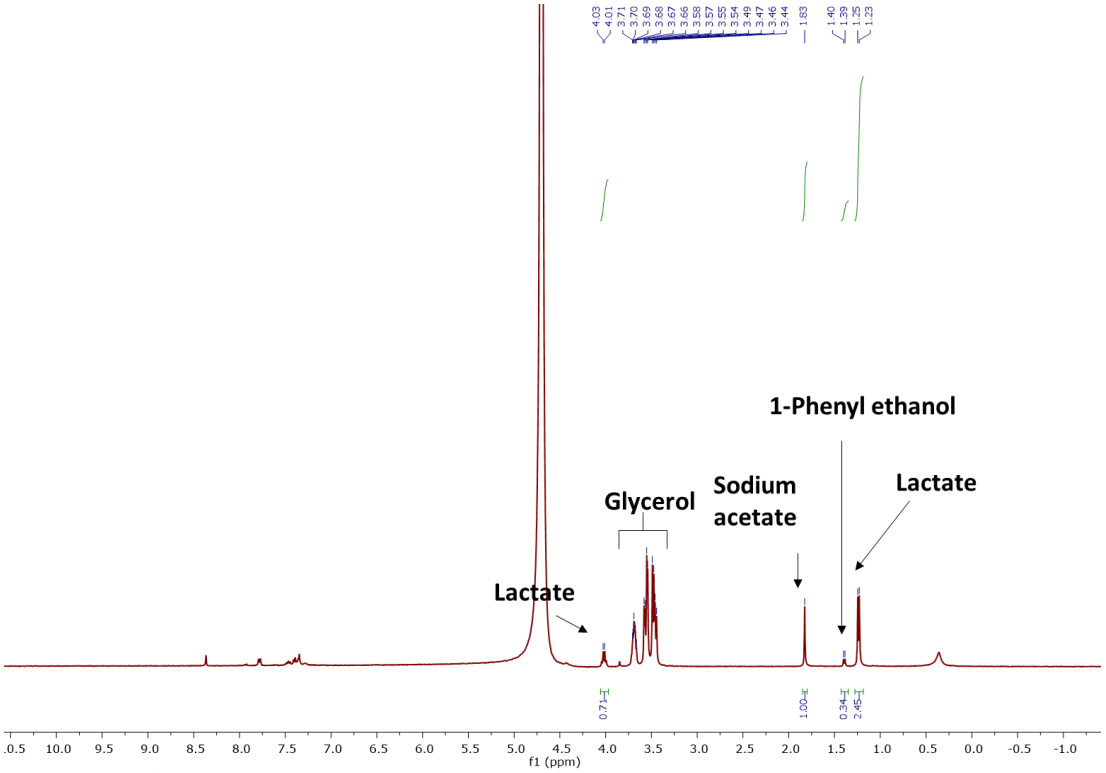

Figure S78. ^{1}H NMR spectra of glycerol (**7**) dehydrogenation to lactate (**9**), using acetophenone (**8a**) as acceptor catalyzed by **6d** (0.5 mol%), NaOH (1 equiv.), under open vessel condition at 140 ºC in D_2O. (Scheme 2, equation 8).

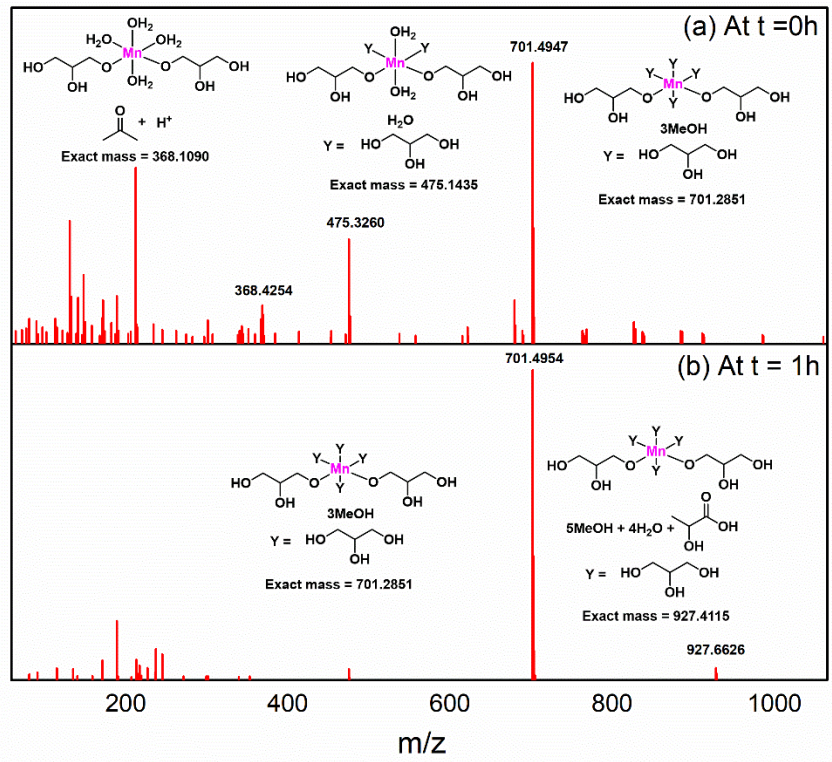

Figure S79. HRMS analysis of reaction mixture obtained from the $MnCl_2.4H_2O$ catalyzed transfer dehydrogenation of glycerol under the optimized conditions at (a) t = 0h and (b) t = 1h.