Electronic Supporting Information

One-pot synthesis of lactones from ketoacids involving microwave heating and sodium borohydride: application in biomass conversion

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Section A. Experimental information

A1. Materials

Levulinic acid (LA), γ–valerolactone (GVL), and deuterium oxide (D_2O), tetrahydrofuran (THF), methanol (MeOH), sodium borohydride ($NaBH_4$), dioxane, toluene, deuterated chloroform ($CDCl_3$) were obtained from Sigma-Aldrich. The Type 1 (milli-Q) and Type 2 ($DD-H_2O$) water purified by Merck-Millipore was used directly.

A2. Instrumentation

<u>*Gas chromatography-mass spectrometry (GC-MS)*</u> was recorded using Agilent 8860 gas chromatograph, incorporated with an Agilent 5977C mass spectrometer platform (GC-MS, Agilent Technologies India Pvt Ltd), with chromatographic Agilent HP-5MS ((5%-phenyl)-methylpolysiloxane) capillary GC columns (30 m × 0.25 mm × 0.25 µm).

The oven temperature was heated from 50 °C (1 min holds time) to 300 °C (3 min holds time) at ramp rate of 10 °C/min using Helium (He) as a carrier gas (570 Kpa). The LA conversion, GVL yield and selectivity were calculated *via* formulae provided in SI, Eqns. S1–S3.

<u>*Nuclear magnetic resonance (NMR)*</u> The ^1H (400 MHz), ^{13}C (100 MHz), correlation spectroscopy (COSY), and Diffusion ordered spectroscopy (DOSY) NMR solution spectra were carried out on a Bruker Avance-II spectrometer using D_2O and $CDCl_3$ solvent systems at 298 K.
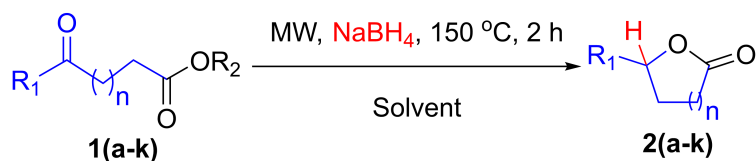
A3. Mathematical expressions

$$\text{Product yield (\%)} = \frac{\text{Mole of product formed}}{\text{Mole of reactant}} \times 100 \quad \cdots\cdots\cdots(S1)$$

$$\text{Reactant conversion (\%)} = \frac{\text{Intial reactant moles} - \text{Residual reactant moles}}{\text{Intial moles of reactant}} \times 100 \quad \cdots\cdots\cdots(S2)$$

$$\text{Product selectivity (\%)} = \frac{\text{product yield}}{\text{reactant conversion}} \quad \cdots\cdots\cdots(S3)$$

## Section B: Synthesis and characterization data

B1. General procedure for ketoacids to lactone synthesis

The reaction was conducted in a microwave (MW) reactor (Monowave 200, Anton Paar) using a 10 mL MW reaction vessel. The vessel was charged with 1 mL of solvent, keto acid (0.176 mmol, 1 equiv.), and NaBH$_4$ (0.079 mmol, 0.45 equiv.). The equipment irradiates at 150 °C for 2 h, with continuous magnetic stirring at 600 rpm, that generates ~ 9 W power and ~18 bar pressure. After the completion of the irradiation, the reaction mixture was subjected to liquid-liquid extraction using H$_2$O and ethyl acetate (EtOAc), followed by the products were isolated by the column and preparative thin-layer chromatography (PTLC) with EtOAc/hexane 1:9 as elution system. The isolated product was then analyzed by NMR and GC-MS techniques.
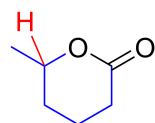
## B2. Spectral details of lactone products

2a. γ–valerolactone (GVL)
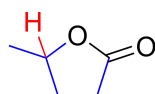
^{1}H-NMR (400 MHz, D$_2$O, 298 K, ppm): δ = 4.84 (q, J = 6.39 Hz, 1H), 2.71 – 2.64 (m, 2H), 2.39 – 2.49 (m, 1H), 1.99 – 1.87 (m, 1H), 1.42 (d, J = 6.32, 3H); ^{13}C-NMR (100 MHz, D$_2$O, 298 K, ppm): δ = 182.37, 80.10, 29.10, 28.88, 19.93; GC-MS: m/z = 100.05 Daltons.

2b. 6-methyltetrahydro-2H-pyran-2-one

^{1}H-NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ = 4.94 – 4.94 (m, 1H), 2.32 – 2.24 (m, 2H), 1.69 – 1.49 (m, 4H), 1.20 (d, J = 6.2 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ = 173.05, 70.57, 35.33, 34.32, 20.94, 20.02; GC-MS: m/z = 114.07 Daltons.

### 2d. dihydrofuran-2,5-dione (succinic anhydride)
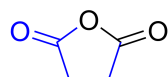
^{1}H-NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ = 3.0 (s, 4H); ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ = 170.68, 28.51; GC-MS: m/z = 100.02 Daltons.

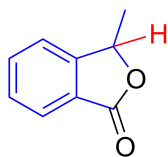### 2g. 5-phenyldihydrofuran-2(3H)-one
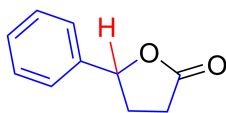
^{1}H-NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ = 7.4 –7.33 (m, 5H), 5.52 (t, J = 7.12 Hz, 1H), 2.71 – 2.63 (m, 3H), 2.24 – 2.14 (m, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ = 177.03, 139.52, 128.92, 128.60, 125.41, 81.37, 31.12, 29.09; GC-MS: m/z = 162.07 Daltons.

2h. 3-phenylisobenzofuran-1(3H)-one
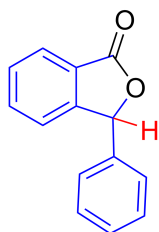
^{1}H-NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ = 7.88 – 7.86 (m, 1H), 7.57 – 7.53 (m, 1H), 7.47 – 7.43 (m, 1H), 7.30 – 7.16 (m, 7H), 6.30 (s, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ = 170.66, 149.84, 136.57, 134.46, 129.51, 129.46, 129.13, 127.13, 125.83, 125.77, 123.01, 82.88; GC-MS: m/z = 210.07 Daltons.

2i. 3-methylisobenzofuran-1(3H)-one

^{1}H-NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ = δ 7.90 – 7.88 (m, 1H), 7.69 – 7.65 (m, 1H), 7.54 – 7.42 (m, 2H), 5.56 (q, J = 6.7 Hz, 1H), 1.63 (d, J = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ 170.61, 151.32, 134.17, 129.19, 125.92, 125.84, 121.66, 77.87, 20.51; GC-MS: m/z = 148.05 Daltons.

2k. 5-(4-methoxyphenyl)dihydrofuran-2(3H)-one
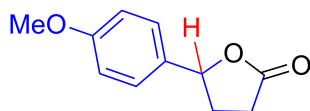
^{1}H-NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ = 7.29 – 7.25 (m, 2H), 6.91 (d, J = 8.68 Hz, 2H), 5.48 – 5.45 (m, 1H), 3.82 (s, 3H), 2.68 – 2.59 (m, 3H), 2.25 – 2.18 (m, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ = 177.07, 159.92, 131.31, 127.09, 114.27, 81.48, 55.49, 31.05, 29.36; GC-MS: m/z = 192.08 Daltons.

B3. ^{1}H-, ^{13}C-NMR and mass spectral profiles of lactone-product
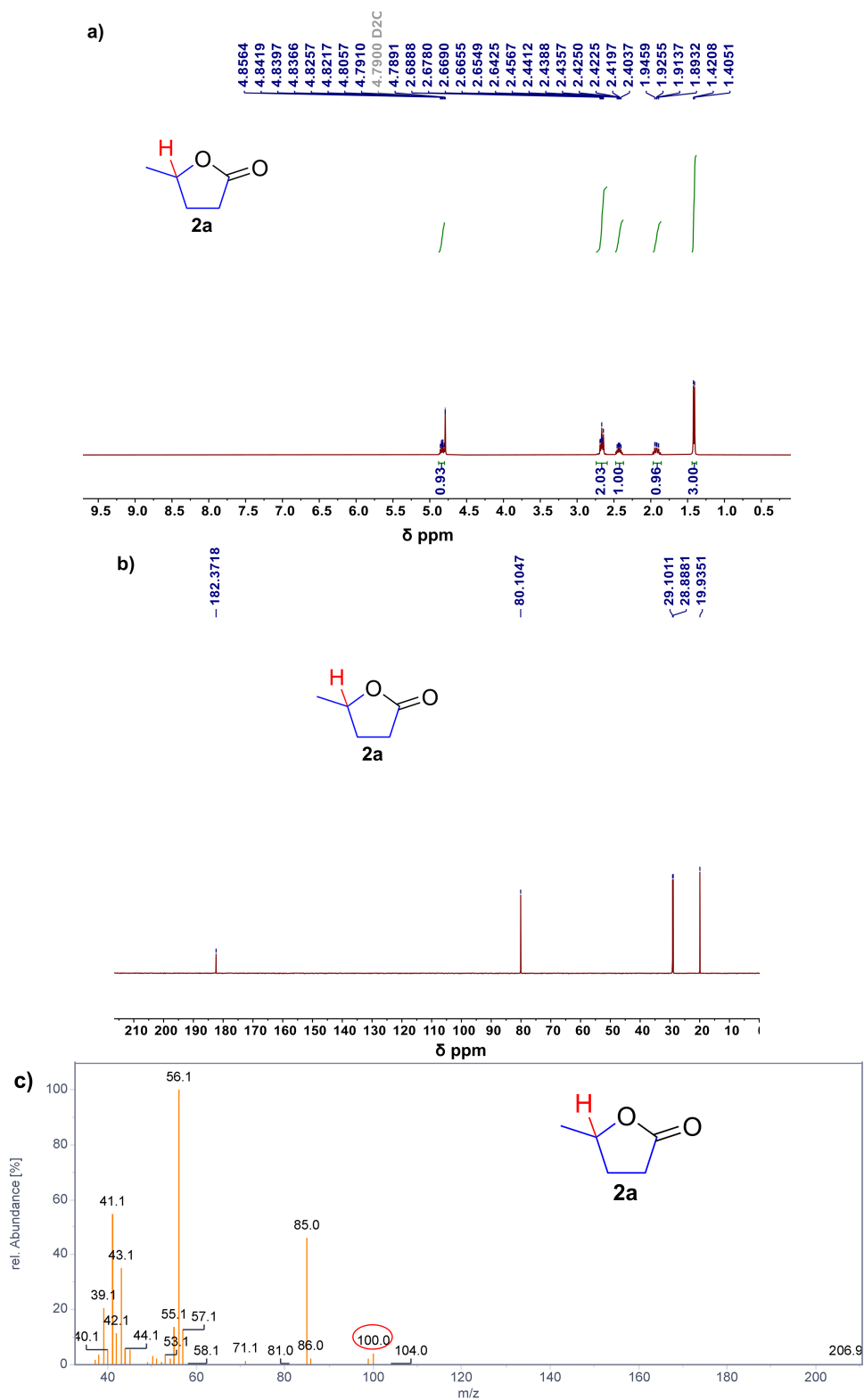
Fig. S1. a) ^{1}H-NMR (400 MHz, D$_2$O, 298 K), b) ^{13}C-NMR (100 MHz, D$_2$O, 298 K), and c) GC-MS spectra of **2a**.
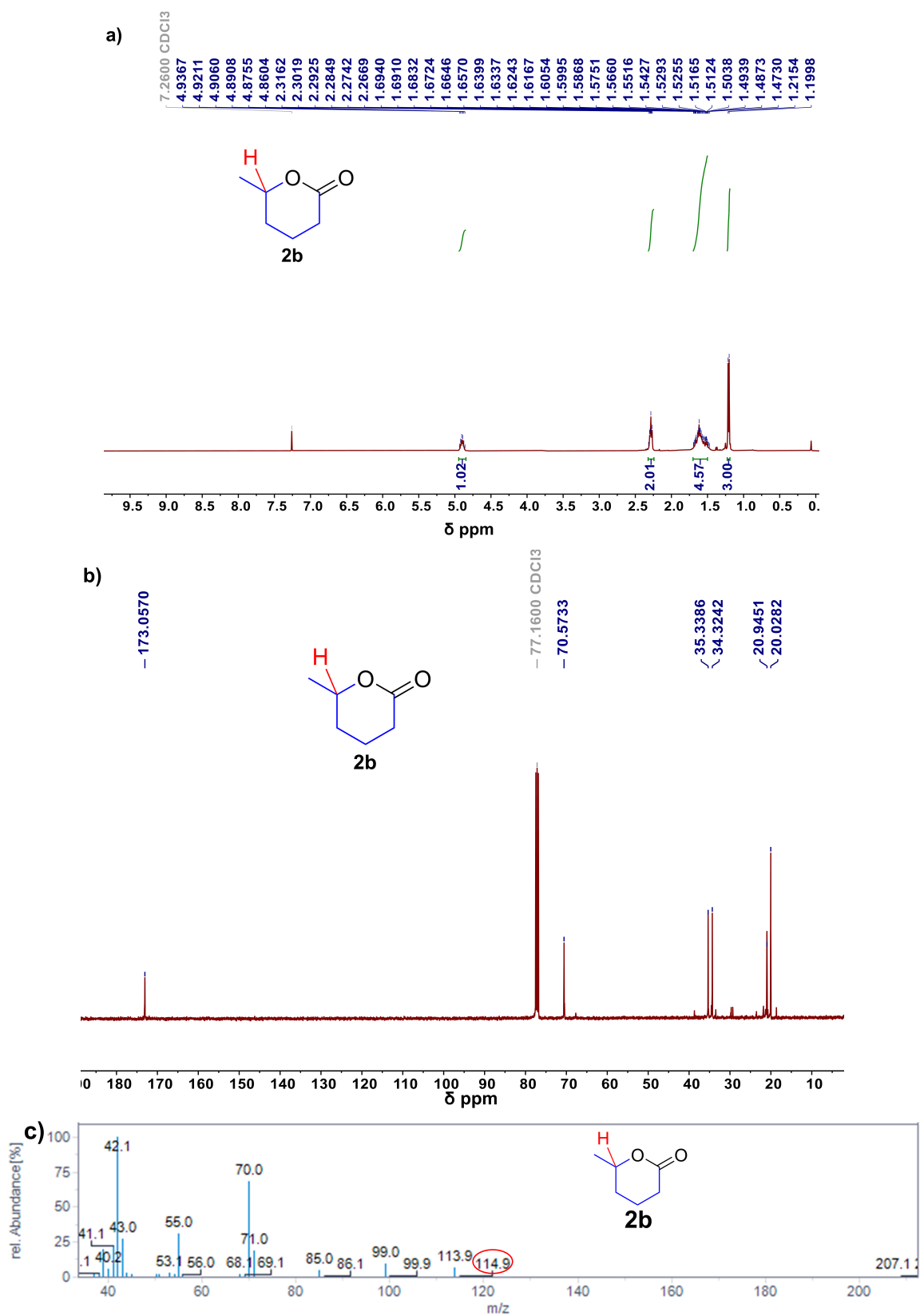
Fig. S2. a) ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K), b) ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K), and c) GC-MS spectra of **2b**.
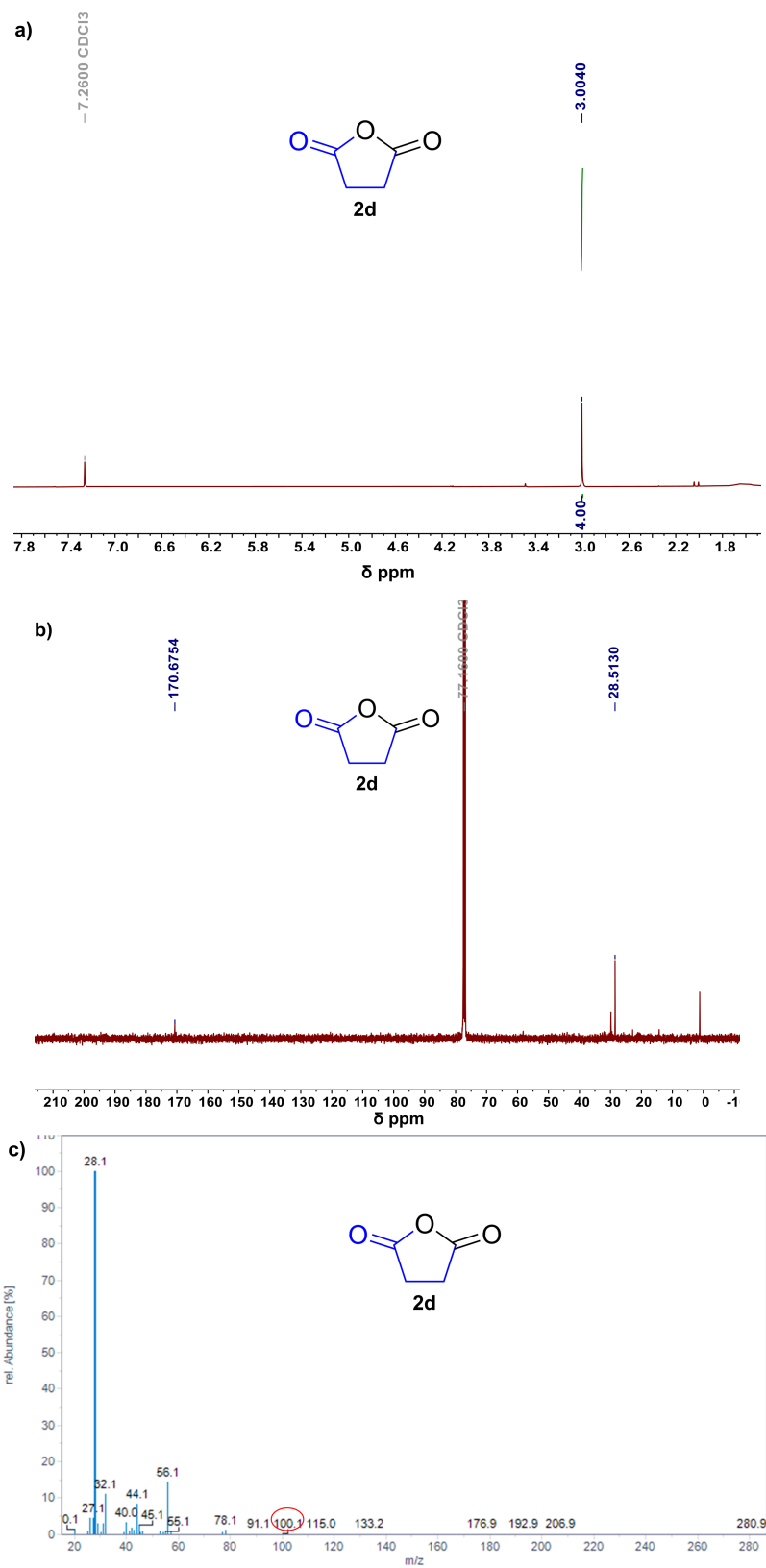
Fig. S3. a) ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K), b) ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K), and c) GC-MS spectra of **2d**.

Fig. S4 a) ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K), b) ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K), and c) GC-MS spectra of **2g**.

a)

7.8750
7.8560
7.5669
7.5643
7.5484
7.5455
7.5296
7.5268
7.4723
7.4536
7.4349
7.2956
7.2864
7.2831
7.2757
7.2696
7.2600 CDCl:
7.2427
7.2235
7.2000
7.1873
7.1779
7.1686
7.1630
7.1560
6.3047

2h

1.06
1.09
1.12
7.05
1.00

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

δ ppm

b)

170.66

149.84
136.57
134.46
129.51
129.46
129.13
127.13
125.83
125.77
123.01

82.88
77.16 CDCl

2h

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

δ ppm

c)

105.1

210.1

2h

77.1
104.1
165.1
51.1
76.1
133.0
152.1
181.1
209.1
28.1
38.1
62.1 78.1 89.1
106.1
126.1
150.1
182.1
212.1 223.0
253.1
280.9
327.0 340.9 355.1
0.2

rel. Abundance [%]

100
75
50
25
0

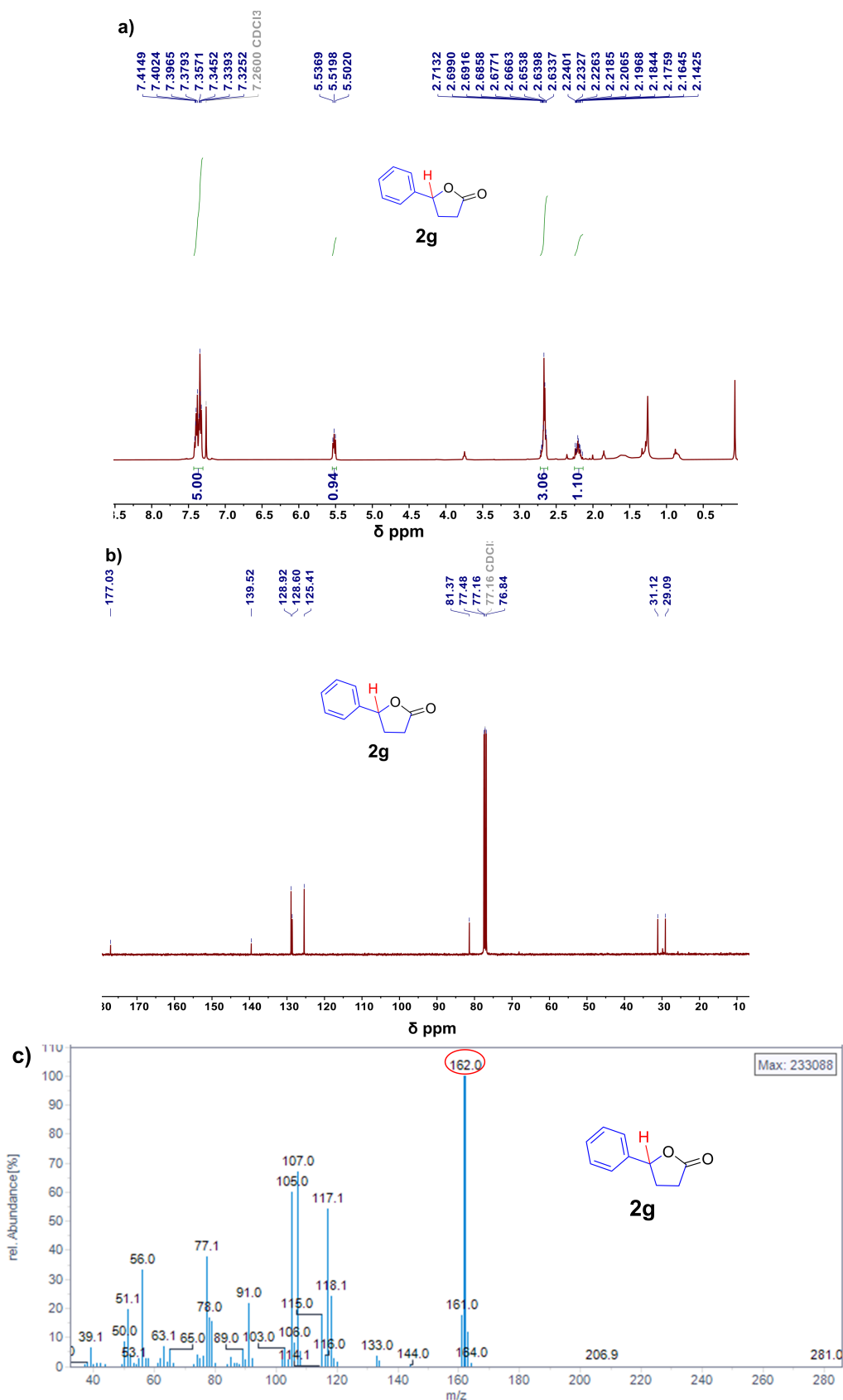25 50 75 100 125 150 175 200 225 250 275 300 325 350

m/z

Fig. S5. a) ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K), b) ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K), and c) GC-MS spectra of **2h**.

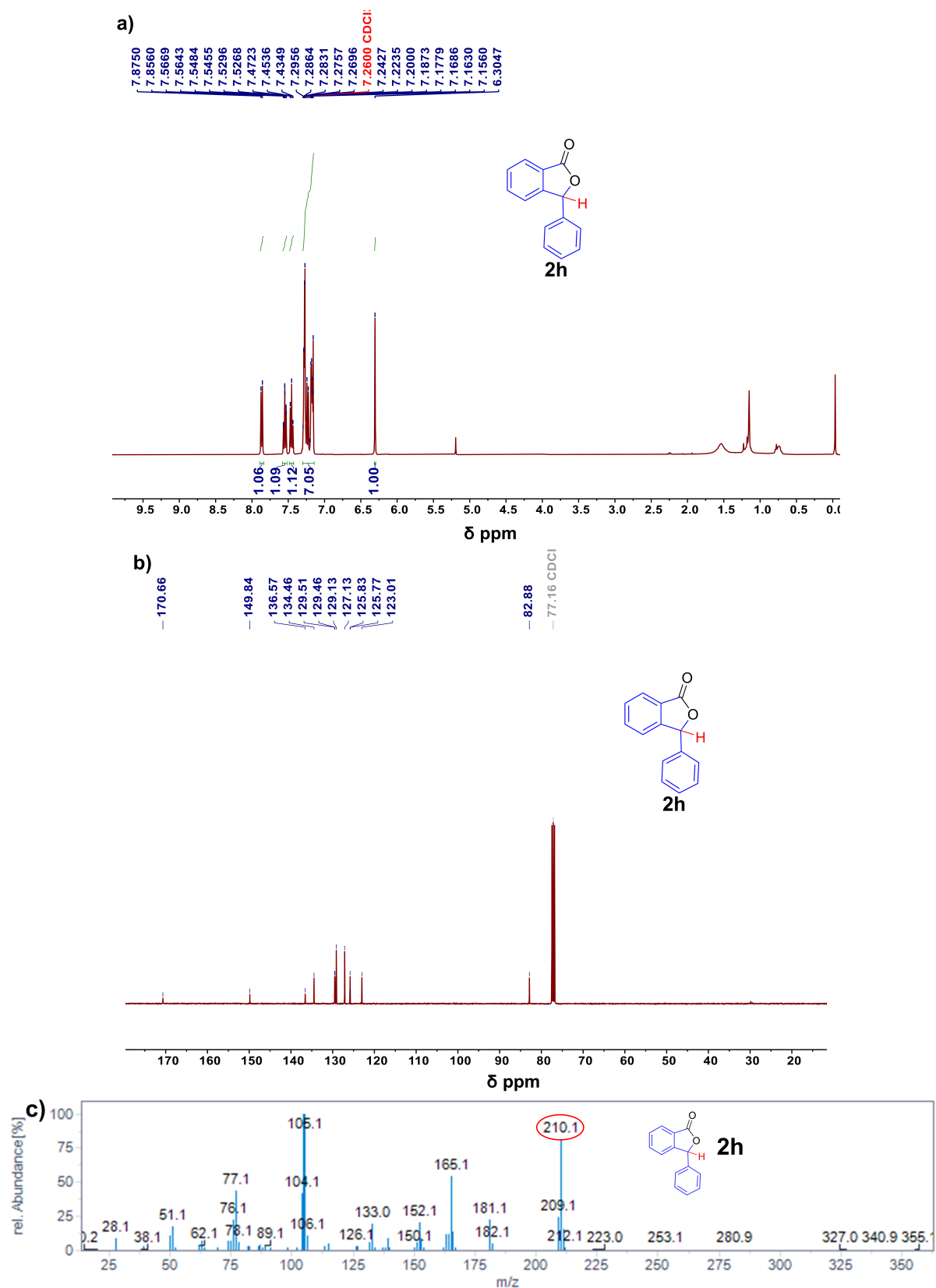**Fig. S6.** a) ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K), b) ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K), and c) GC-MS spectra of **2i**.

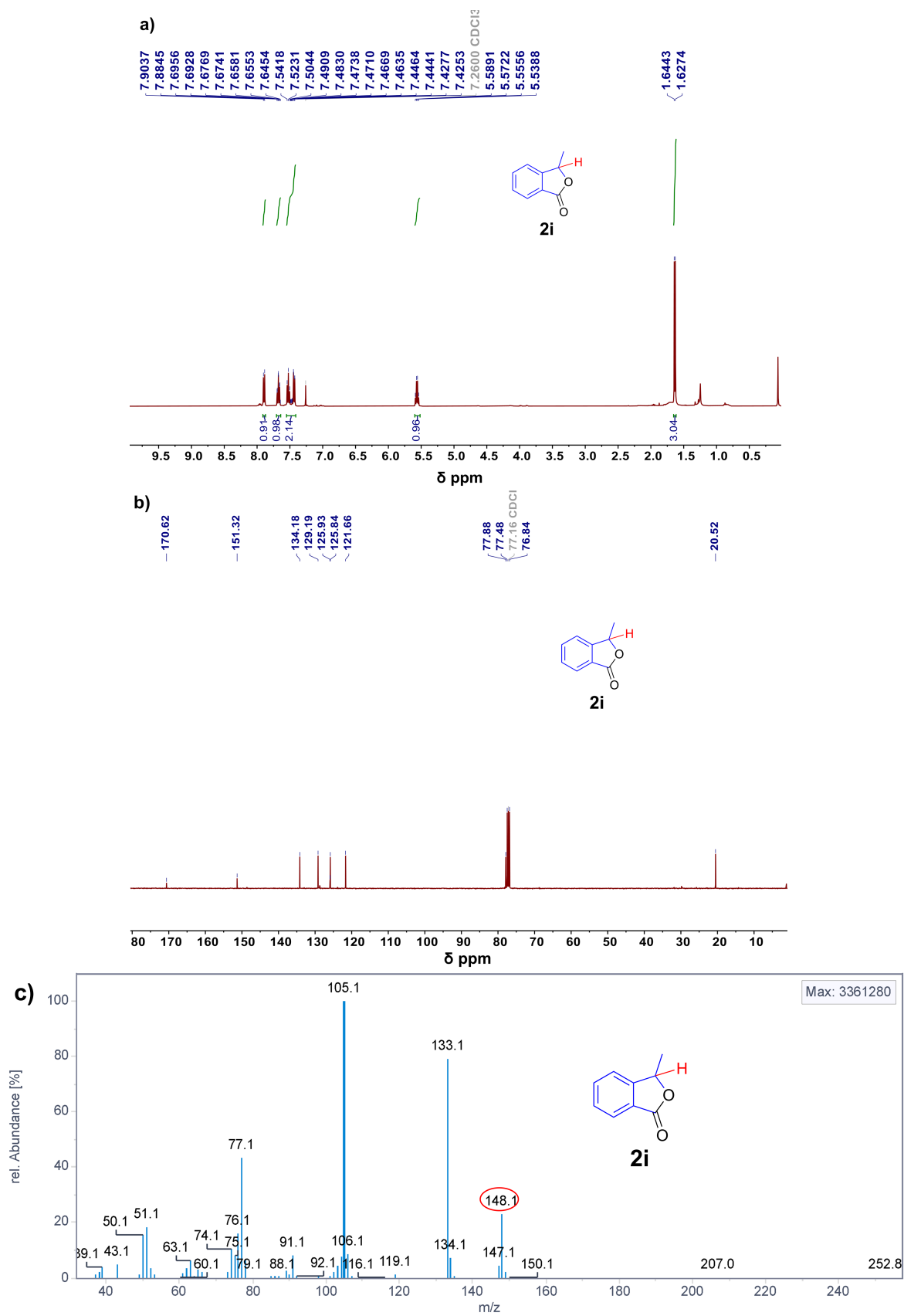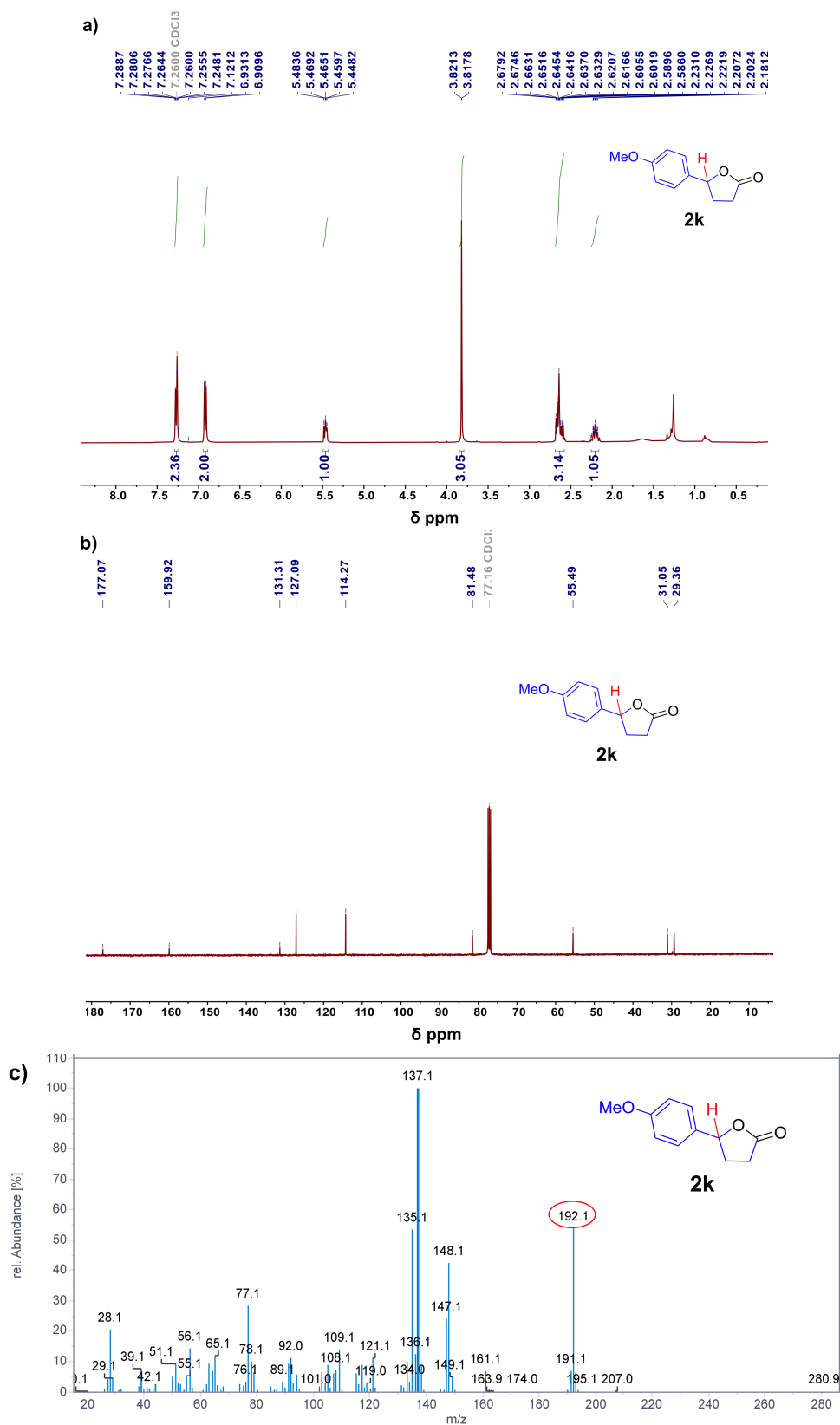**Fig. S7.** a) ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K), b) ^{13}C-NMR (100 MHz, CDCl$_3$, 298 K), and c) GC-MS spectra of **2k**.

B4. NMR and HRMS studies of LA to GVL hydrogenation

Reaction Conditions: LA (0.176 mmol, 1 equiv.), NaBH$_4$ (0.079, 0.45 equiv.), D$_2$O (1 mL), 150 °C, 60 min.

d)

{4.79,1.63e-05}

γ-Valerolactone

4-hydroxypentanoic acid

δ ppm
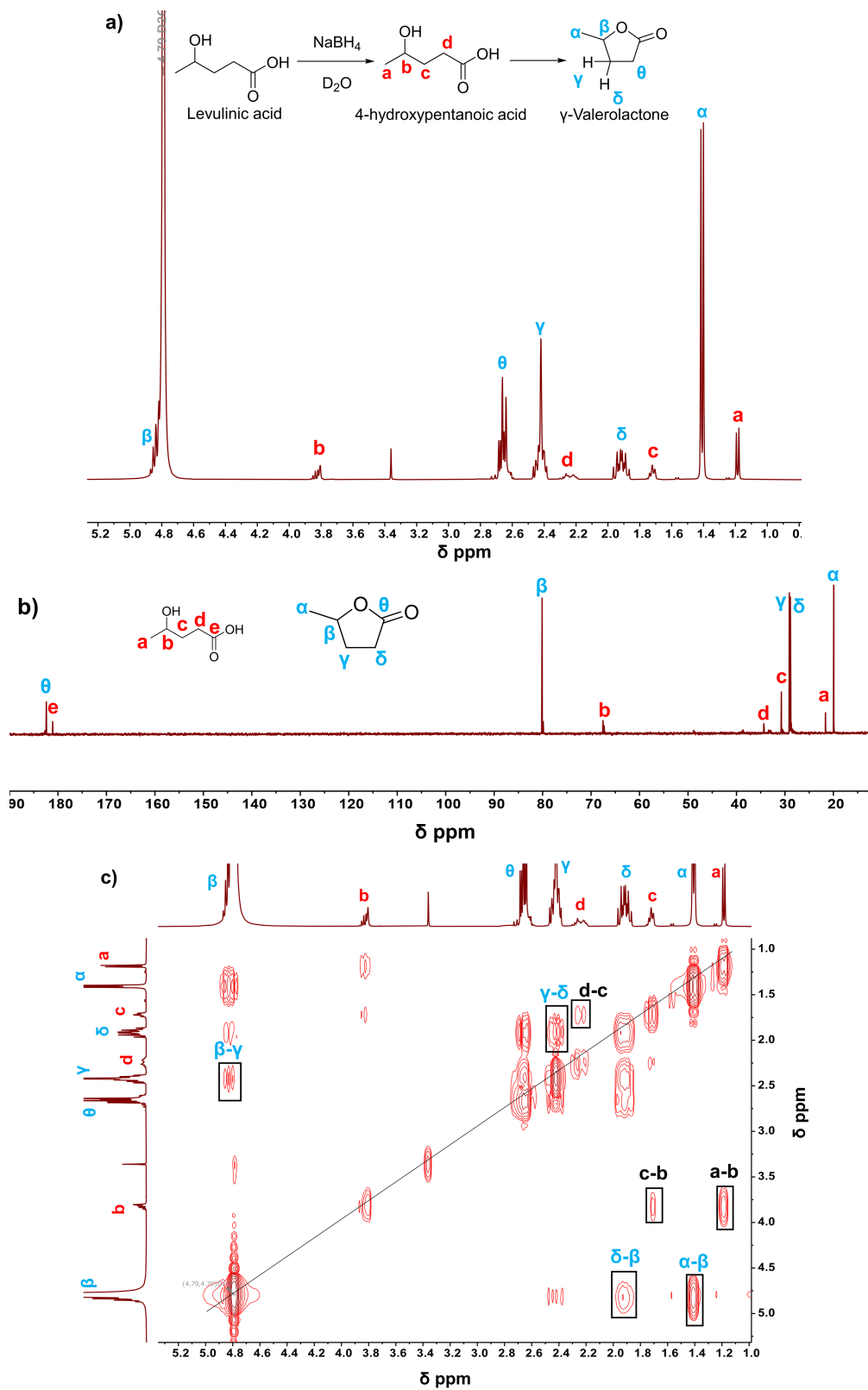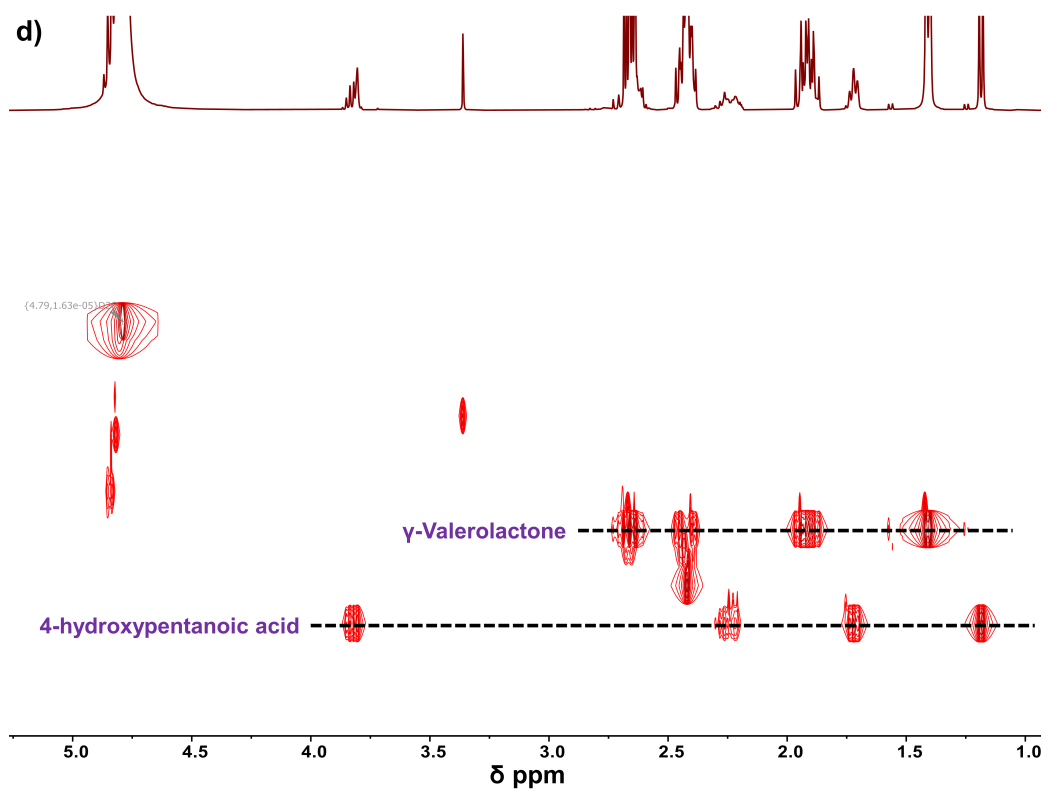
Fig. S8. a) ^{1}H-NMR (400 MHz, D_2O, 298 K), b) ^{13}C-NMR (100 MHz, D_2O, 298 K), c) COSY, and d) DOSY spectra of LA reaction mixture.
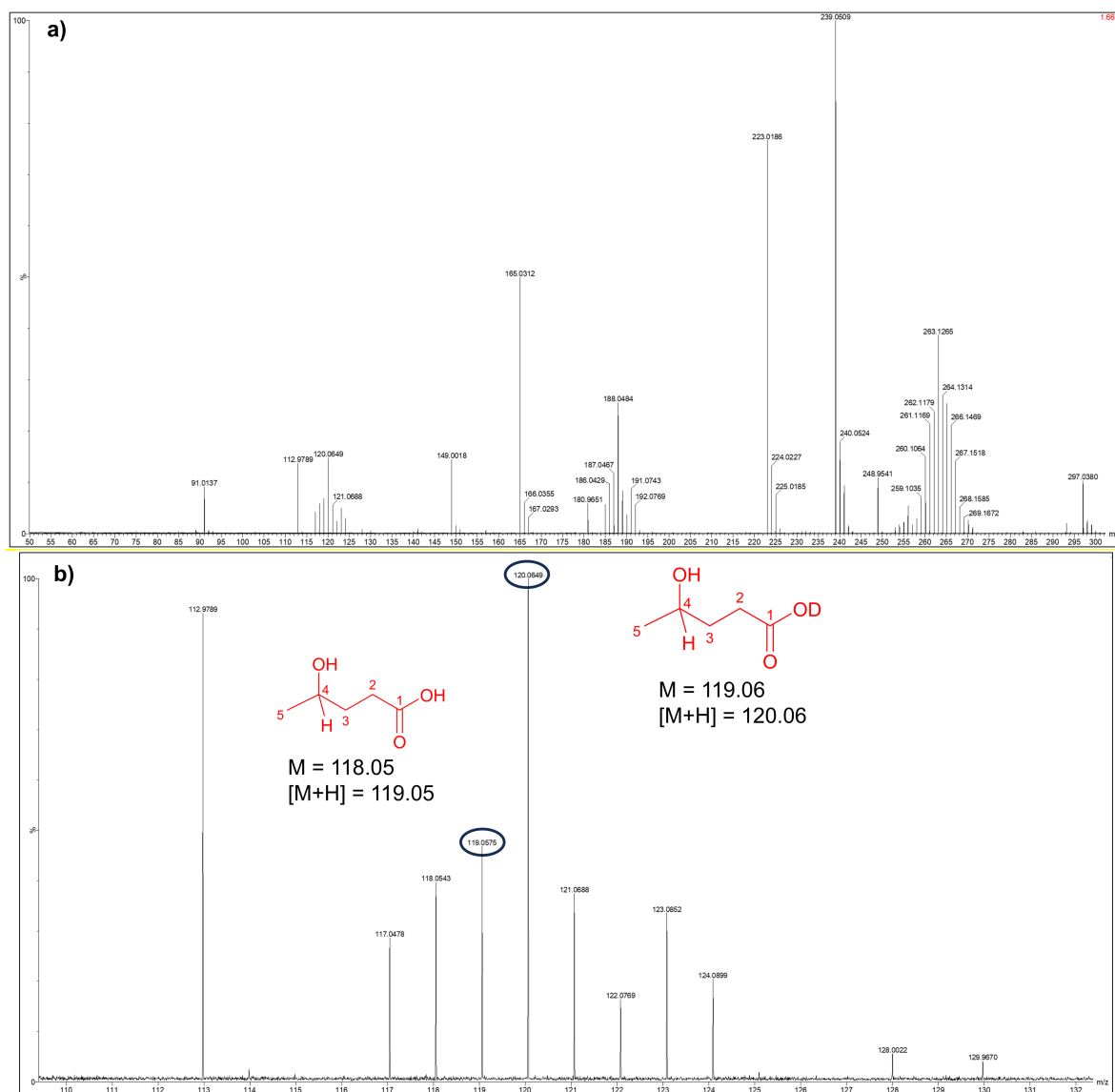
Fig. S9. a) HR-MS spectrum (*m/z* range: 50-300) of LA reaction mixture, b) zoomed between 105-132 *m/z*.

B5. Time study for LA and methyl levulinate conversion to GVL
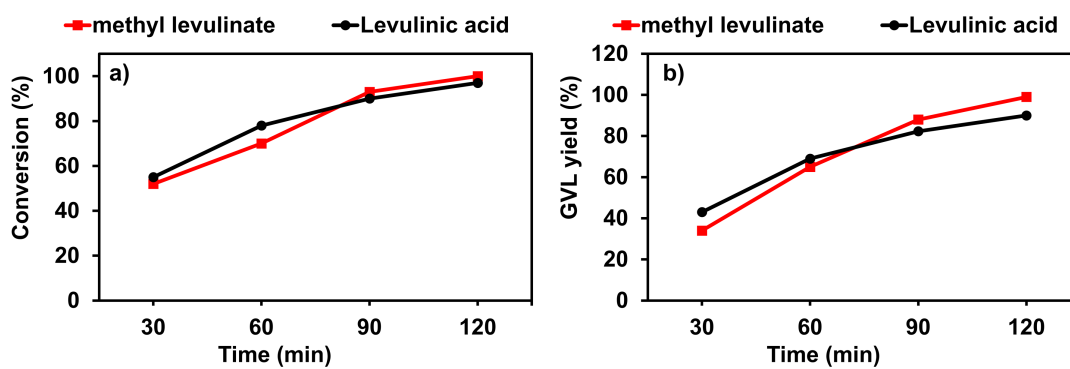
Fig. S10. Effect of time on the, a) conversion (%) of LA and methyl levulinate, and b) GVL yield

(%) synthesis from LA and methyl levulinate. Reaction conditions: LA/methyl levulinate (0.176 mmol, 1 equiv.), NaBH$_4$ (0.079, 0.45 equiv.), H$_2$O (1 mL), MW heating: 150 °C.

The conversion rates (%) of LA and methyl levulinate, along with GVL synthesis (%), were compared over time at 150 °C to demonstrate that the LA-to-GVL method reported in this study is significantly more efficient than the methyl levulinate-to-GVL method under the optimized conditions (Fig. S10). The results demonstrate that GVL forms at a similar conversion rate for both substrates, indicating that the catalytic system is effective for both LA and methyl levulinate. However, since methyl levulinate is commercially synthesized from LA—a platform chemical derived from glucose dehydration—our system simplifies the process by enabling a high conversion rate (98%) and yield (90%) of GVL directly from LA, thereby eliminating the additional esterification step.

Section C. Green metrics parameters

I. a. Environmental factor (*E*-factor) = [Total mass of waste/ mass of product]••••••••••••••••(S4)

b. Total mass of waste = mass of reactant – mass of product

II. Atom economy (AE, %) = [Molecular weight of product/ molecular weight of reactant]•••(S5)

III. Reaction mass efficiency (%) = [Mass of product/ total mass of reactant]••••••••••••••••••(S6)

IV. Carbon economy (%) = [Total carbon in product/total carbon in reactant]••••••••••••••••••(S7)

V. Process mass intensity = [(Total mass in process)/total mass of product]•••••••••••••••••••••(S8)

Table S1. Green metrics parameters for LA to GVL conversion using NaBH$_4$.

S.No.	Green metrics parameters	Ideal value (100% yield)	Calculated value (90% yield)
1	*E*-factor	0.16	0.3
2	Atom economy (%)	86.2	86.2
3	Reaction mass efficiency (%)	86.2	77.5
4	Carbon economy (%)	100	100
5	Process mass intensity	1	1.48

Reaction conditions: Levulinic acid (0.176 mmol, 1 equiv.), NaBH$_4$ (0.079, 0.45 equiv.), H$_2$O (1 mL), 120 min, 150 °C.

Section D. Literature comparison table

Table S2. Literature survey of homogenous catalysts for LA to GVL conversion.

S. No.	Catalyst	Temp (ºC)	H$_2$ (bar)	Time (h)	Solvent	GVL Yield (%)	Ref.
1	NaBH$_4$	150	–	2	H$_2$O	90	This work
2	Shvo's catalyst	100	–	8	H$_2$O	99	S1
3	[Ru(acac)$_3$]PBu$_3$	135	100	8	H$_2$O	99	S2
4	Casey catalyst	100	–	19	H$_2$O	95	S3
5	[Ru(acac)$_3$]/tetraphos	140	80	22	H$_2$O	73	S4
6	Ni(OAc)$_2$].3H$_2$O/triphos	150	1	20	H$_2$O	98	S5
7	[(PPh$_3$)$_2$Cu(k^2-O,O-LVA)]/dippe	140	20	24	hexane	99	S6
8	Ru/C+ChCl	150	5	2.5	H$_2$O	99	S7
9	I$_2$/Et$_3$SiH	rt	–	2	CH$_2$Cl$_2$	88	S8
10	NHC-Ir	100	1	4	H$_2$O	92	S9

Section E. References

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