Supporting Information

Quantitative formation of gamma-valerolactone from furfural aldehyde with a recyclable acidic system and Ru-MACHO catalyst under a H_2 atmosphere

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1. Experimental Section

General Information. Most chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. FA, HMF, acidic resins (Amberlyst-15, Amberlyst-36, Amberlite IR 120, **Ru-1**, **Ru-2,** and **Ru-3** are commercially available and used without further purification. **Ru-(4-5)**[1], **Ru-(6-12)**[2] and **Ru-(13-14)**[3] were synthesised according to the literature. H_2 gas ($H_2O \leq 3$ ppm; $O_2 \leq 2$ ppm) was purchased from a commercial supplier as well. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox.

Nuclear Magnetic Resonance spectroscopy (NMR)

NMR spectra were obtained using a Bruker Ascend 400, or 800 MHz spectrometer equipped with BBFO and TCI CryoProbe probes. Chemical shifts are expressed in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C spectra using residual solvent signal peaks or TMS as internal reference. Residual solvent chemical shifts are explained according to literature.[4] Coupling constants, if available, are given in Hz as absolute values. Multiplicities are given as singlets (s), doublets (d), triplets (t), heptets (hept), doublets of a doublet of a doublet (ddd) and multiplets (m). Literature-known compounds were analysed only using ^1H-NMR spectroscopy to confirm purity. NMR spectra were analysed using MestReNova software.

Reactor specifications

Figure S1. Custom high-pressure reactor used in this study. 7-well reactor (Alloy 600, reactor capacity: 483 mL). The pressure gauge is non-electronic and subject to error.

General Procedure for hydrogenation of HMF to DHMF

For a typical hydrogenation screening experiment, the high-pressure reactor was loaded with the Ru-PNP complex (0.25 - 2 mol%), FAL (0.79 mmol), acidic resins (2 - 20 mol%) and 2 mL of solvent (EtOH, H_2O and variable ratio of the mixture EtOH: H_2O). Subsequently, the reactor was equipped with a magnetic stirring bar and sealed. The system was flushed with nitrogen/hydrogen (three times). Next, a H_2 pressure of 5-30 bar was applied. The reaction mixture was stirred for 24 hours (250 rpm) at the desired temperature. After this time, the reactor was cooled down to room temperature and the gas was released. The crude reaction mixture was then analysed using ^{1}H-NMR spectroscopy in D_2O or $CDCl_3$ to check both the conversion and the NMR yield of the desired product. For NMR analysis, an internal standard, dimethyl sulfone (DMS) (10.0 mg, 0.106 mmol), was added to the reaction mixture. The solution was stirred for 5 min to ensure thorough mixing. A sample was then taken from the mixture for NMR analysis. All the experiments were replicated to corroborate the results.

Physical properties of Amberlyst-36 and determination of catalyst loading

Amberlyst-36^{TM} pellets (wet) were manufactured by Dow Chemicals. The commercial resin is made from cross-linked styrene divinylbenzene copolymers with active sites of sulfonic groups (–RSO3H). The resin pellets (0.6–0.85 mm in diameter) have a density of 1.2 g/mL at 25 °C, pore volume of 0.2 mL/g, surface area of 33 m2/g, proton (H+) content of 5.4 mol/g and maximum working temperature of 150 °C.

According to the manufacturer's specifications, Amberlyst-36 has an acid capacity of 5.4 mmol H^+ g^{-1}. In the present work, 8 mg (0.008 g) of Amberlyst-36 was used, corresponding to 0.04 mmol of acidic sites, calculated as follows:

Catalyst loading (mol%) =
[(mass of Amberlyst-36 in g) × (acid capacity in mmol H^+ per g)] ÷ (mmol of substrate) × 100

0.008 g × 5.4 mmol H^+ g^{-1} = 0.04 mmol H^+.

For a reaction performed with 0.79 mmol of substrate, this amount of acidic sites corresponds to a catalyst loading of 5 mol% based on acidic proton equivalents. This method for expressing catalyst loading is standard practice in heterogeneous acid catalysis and allows meaningful comparison with homogeneous Brønsted acid catalysts.

Recyclability test

Amberlyst 36 was regenerated and reused over multiple catalytic cycles following a literature reported ion exchange procedure.[5] After each reaction, the spent resin was separated from the mixture and washed sequentially with acetone and a chloroform/methanol solution (4:1 v/v) to

remove adsorbed organic species. The cleaned resin was then subjected to an ion exchange treatment in concentrated sulfuric acid, where it was left to equilibrate and subsequently stirred under ambient conditions. Following acid treatment, the resin was isolated, thoroughly washed with deionized water, and dried at room temperature. The regenerated Amberlyst 36 was then directly reused in subsequent catalytic cycles under identical reaction conditions.

NMR measurements

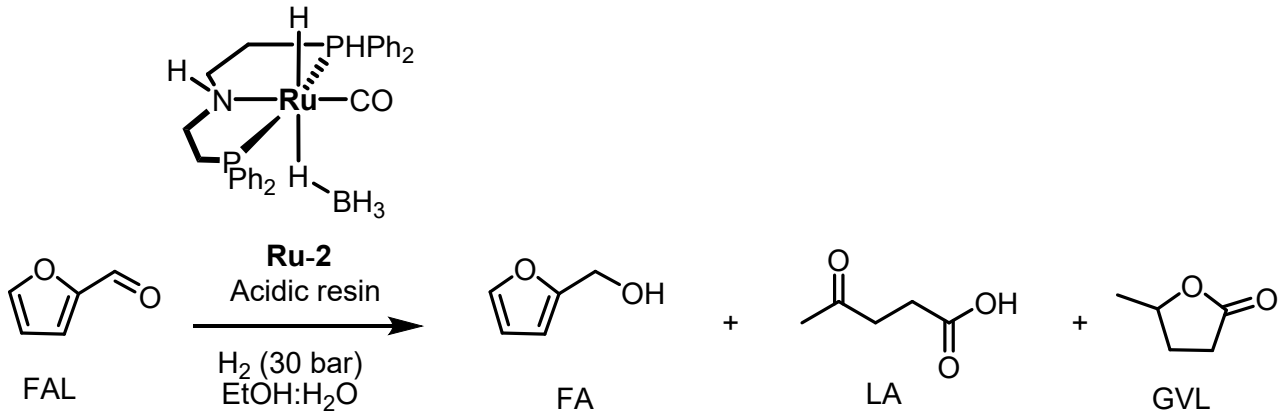
Conversions in all reactions were measured by ^{1}H-NMR spectroscopy at 400 MHz in D_2O or $CDCl_3$ at 25 °C. Then, 128 scans were applied for each sample, with a delay between scans of 30 seconds to ensure complete relaxation of the hydrogens. The conversion was calculated using the signals from the CH (6.67 ppm) hydrogen of the unreacted substrate FA and the CH_3 (1.4 ppm, d) hydrogens of GVL. Errors in the conversion measurements were estimated by comparing the results of at least three integrations of each spectrum.

2. Contextualization of our approach

Catalyst type	Representative system	Conditions	Yield / Selectivity	Notes
Homogeneous	Ru-PNP pincer complexes (e.g., Ru-MACHO)	100–150 °C, H_2 (20–50 bar), alcohol solvents	Up to 99% GVL	High activity; limited recyclability without immobilization
Heterogeneous	ZrO_2, Nb_2O_5, or supported metal oxides	150–200 °C, H_2 or transfer hydrogenation	60–95% GVL	Robust solids; often require higher temperatures
Hybrid / bifunctional	Zr/Nb mixed oxides; metal–acid combinations	120–180 °C, H_2	Up to quantitative GVL	Continuous operation possible
This work	Ru-MACHO-BH + Amberlyst-36	120 °C, 30 bar H_2, EtOH	99% GVL, 100% selectivity	Mild conditions; resin regenerable with H_2SO_4(aq)

3. Results for the hydrogenation of FAL to GVL

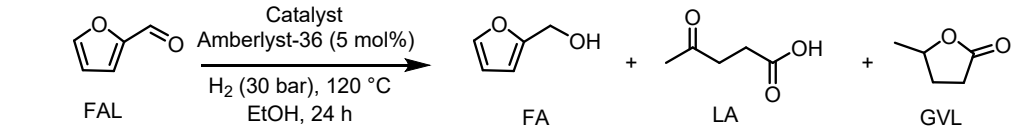
Table S1. Variables screening and identification of suitable conditions for the formation of GVL from FAL in catalytic acidic conditions. [a]

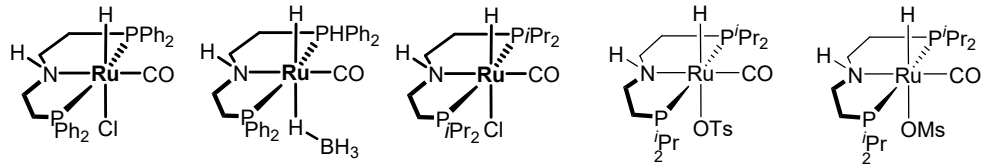


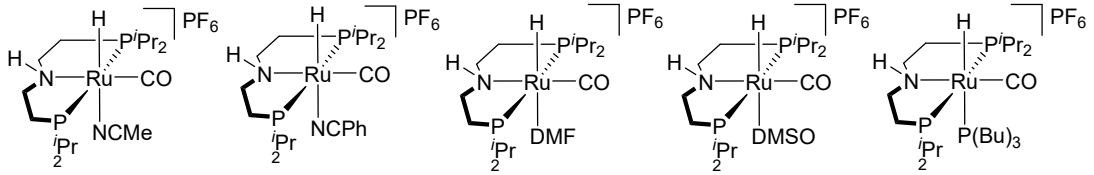
Entry	Mol% Ru-2	Acidic Resins (mol%)	EtOH:H_2O	Temp. (°C)	Time (h)	Conv. (%)[b]	FA:LA:GVL[b]	GVL-route selectivity (%)
1	2	Amberlyst-36 (5)	3:7	120	24	100	0:0:45	45
2	2	Amberlyst-36 (2.5)	3:7	120	24	100	0:0:36	36
3	1	Amberlyst-36 (5)	3:7	120	24	100	0:22:28	50
4[c]	2	Amberlyst-36 (5)	3:7	120	24	100	5:16:28	49
5	2	Amberlyst-36 (5)	0:10	120	24	100	0:0:13	13
6	2	Amberlyst-36 (5)	5:5	120	24	100	0:0:60	60
7	2	Amberlyst-36 (5)	7:3	120	24	100	0:0:75	75
8	2	Amberlyst-36 (5)	9:1	120	24	100	0:0:55	55
9	2	Amberlyst-36 (5)	9.5:0.5	120	24	100	0:0:92	92
10	2	Amberlyst-36 (5)	10:0	120	24	100	0:0:100	100
11[d]	2	Amberlyst-36 (5)	10:0	120	24	100	0:0:24	24
12	2	Amberlyst-15 (5)	3:7	120	24	100	0:0:50	50
13 [e]	2	Amberlyst-15 (5)	3:7	120	24	100	0:0:28	28
14 [c]	2	Amberlyst-15 (5)	3:7	120	24	100	0:0:41	41
15	2	Amberlyst-15 (5)	10:0	120	24	100	0:0:39	39
16	2	Amberlite IR120 (5)	3:7	120	24	100	73:0:0	73
17	2	Amberlite IR120 (2)	3:7	120	24	100	54:0:0	54
18	2	Amberlyst-36 (5)	3:7	80	72	100	0:0:71	71
19	2	Amberlyst-36 (5)	10:0	80	24	100	44:0:55	99

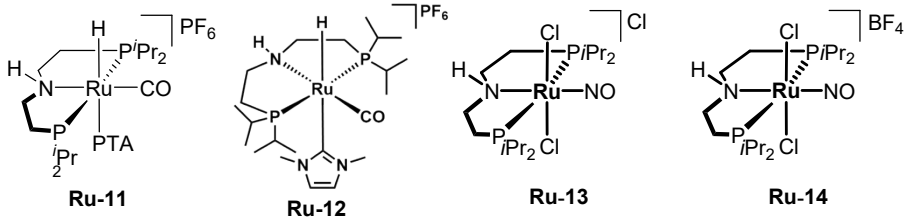
[a] Standard reaction conditions: 0.79 mmol of FAL (76 mg), **Ru-2** in a mixture of EtOH:H_2O (2.0 mL), H_2 (30 bar), 24 h at 120 °C. [b] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard. [c] 4 mL EtOH:H_2O 3:7. [d] 1 mL EtOH. High concentration promotes higher levels of humins formation. [e] 1 mL EtOH:H_2O 3:7.

Table S2. Catalyst screening and identification of suitable conditions for the formation of GVL from FAL in catalytic acidic conditions. [a]





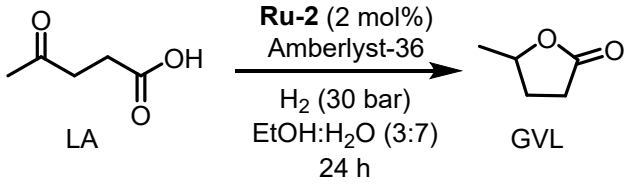




Entry	Catalyst (mol%)	Conv. (%)[b]	FA:LA:GVL[b]	GVL-route selectivity (%)
1	**Ru-1** (2)	100	0:13:85	98
2	**Ru-2** (2)	100	0:0:100	100
3	**Ru-2** (1)	100	0:0:100	100
4	**Ru-2** (0.5)	100	0:0:100	100
5[c]	**Ru-2** (0.5)	100	21:41:37	99
6[d]	**Ru-2** (0.5)	100	0:23:88	100
4[e]	**Ru-2** (0.5)	100	0:0:100	100
4[f]	**Ru-2** (0.5)	100	0:0:100	100
4[g]	**Ru-2** (0.5)	100	0:10:70	80
7	**Ru-2** (0.25)	100	0:25:75	100
8	**Ru-2** (0.1)	86	0:75:9	84
9	**Ru-3** (2)	100	0:81:18	99
10	**Ru-4** (2)	100	0:0:61	61
11	**Ru-5** (2)	100	0:28:44	72
12	**Ru-6** (2)	100	0:10:89	99
13	**Ru-7** (2)	100	17:13:55	85
14	**Ru-8** (2)	100	0:60:40	100
15	**Ru-9** (2)	100	0:50:55	100
16	**Ru-10** (2)	100	0:0:100	100
17	**Ru-10** (0.5)	100	0:63:40	100
18	**Ru-11** (2)	100	20:47:20	87
19	**Ru-12** (2)	100	0:50:13	63
20	**Ru-13** (2)	100	0:55:0	55
21	**Ru-14** (2)	100	0:64:0	64

[a] Standard reaction conditions: 0.79 mmol of FAL (76 mg), **Ru-2** in a mixture of EtOH:H_2O (2.0 mL), H_2 (30 bar), 24 h at 120 °C. [b] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard. [c] 100 °C. [d] 18 h. [e] 20 bar H_2. [f] 10 bar H_2. [g] 5 bar H_2.

Table S3. Evaluation of Amberlyst-36 loading on LA conversion. [a]



Entry	Substrate	Catalyst (mol%)	Acidic Resins (mol%)	Conv. (%)[b]	Product (% Yield) [b]
1	**LA**	**Ru-2** (2)	Amberlyst-36 (10)	97	GVL (97)
2	**LA**	**Ru-2** (2)	Amberlyst-36 (20)	61	GVL (61)
3[c]	**LA**	**Ru-2** (2)	Amberlyst-36 (20)	11	GVL (11)
4	**LA**	**Ru-2** (2)	Amberlyst-36 (5)	60	GVL (54)

[a] Standard reaction conditions: 0.79 mmol of LA (91 mg), 2 mol% of **Ru-2** in a mixture of EtOH:H_2O 3:7 (2.0 mL), H_2 (30 bar), 24 h at 120 °C. [b] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard. [c] EtOH (2 mL).

Table S4. Amberlyst-36 recycling cycles without reactivation of the acid resin. [a]

Entry	Cycle	Conversion (%)	FA:LA:GVL[b]	GVL-route selectivity (%)
1	**I**	>99	0:0:100	100
2	**II**	>99	0:0:100	100
3	**III**	>99	0:0:100	100
4	**IV**	>99	22:4:74	100
5	**V**	>99	17:6:81	100
6	**VI**	>99	29:6:67	100
7	**VII**	>99	59:5:34	98

8	**VIII**	>99	57:10:30	l97

[a] Standard reaction conditions: 0.79 mmol of FAL (76 mg), 2 mol% **Ru-2**, 5 mol% Amberlyst-36, in EtOH (2.0 mL), H_2 (30 bar), 24 h at 120 °C. The same resin Amberlyst-36: was reused for several catalytic cycles after washing with EtOH. [b] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard.

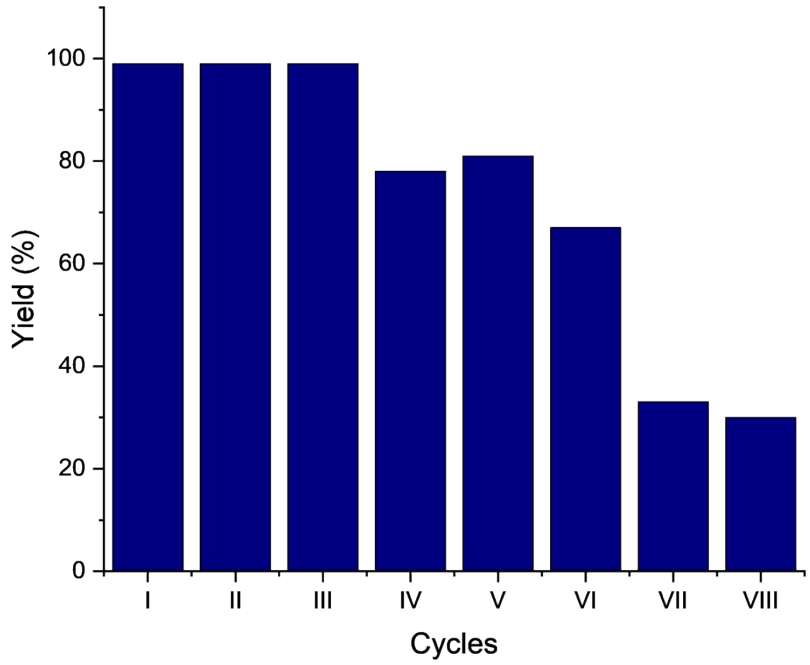


Image S1. Amberlyst-36 recycling cycles without reactivation of the acidic resin.

Table S5. Amberlyst-36 recycling cycles with reactivation of the acid resin after each cycle.[a]

Entry	Cycle	Conversion (%)	FA:LA:GVL[b]	GVL-route selectivity (%)
1	**I**	>99	0:0:100	100
2	**II**	>99	0:0:100	100
3	**III**	>99	0:0:100	100
4	**IV**	>99	0:0:100	100
5	**V**	>99	0:0:100	100
6	**VI**	>99	0:0:100	100

7	**VII**	>99	0:0:100	100
8	**VIII**	>99	0:0:100	100
9	**IX**	>99	0:0:100	100
10	**X**	>99	0:0:100	100

[a] Standard reaction conditions: 0.79 mmol of FAL (76 mg), 2 mol% **Ru-2**, 5 mol% Amberlyst-36, in EtOH (2.0 mL), H_2 (30 bar), 24 h at 120 °C. The same resin Amberlyst-36: was reused for several catalytic cycles after reactivating it as described in literature. [b] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard.

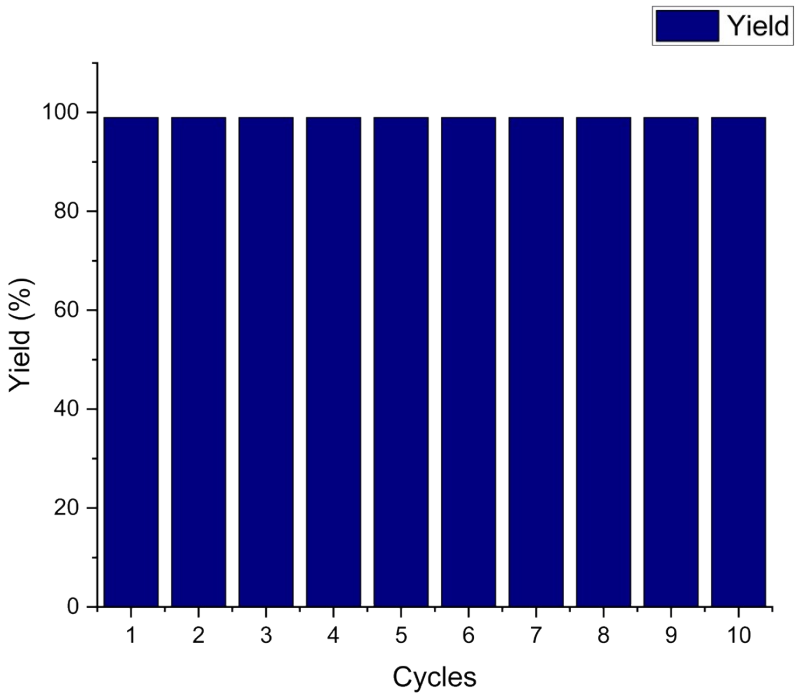


Image S2. Amberlyst-36 recycling cycles with reactivation of the acidic resin

Table S6. Scale up of the reaction conditions for the formation of GVL from FAL in catalytic acidic conditions.

Entry	Catalyst (mol%)	Solvent (mL)	Conv. (%)[a]	FA:LA:GVL[a]	GVL-route selectivity (%)
1[b]	**Ru-2** (0.5)	EtOH (20)	100	0:0:65	65
2[c]	**Ru-2** (0.5)	EtOH (50)	100	0:0:72	72
3[c]	**Ru-2** (1)	EtOH (50)	100	0:0:100	100

[a] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard.[b] Standard reaction conditions 7.9 mmol of FAL (765 mg), 0.5 mol% **Ru-2**, 5 mol% Amberlyst-36 in 20 mL of EtOH, H_2 (30 bar), 24 h at 120 °C. [c] Standard reaction

conditions 20 mmol of FAL (1912 mg), 0.5-1 mol% **Ru-2**, 5 mol% Amberlyst-36 in 50 mL of EtOH, H_2 (30 bar), 24 h at 120 °C.

Representative NMR spectra for the hydrogenation of FA to GVL

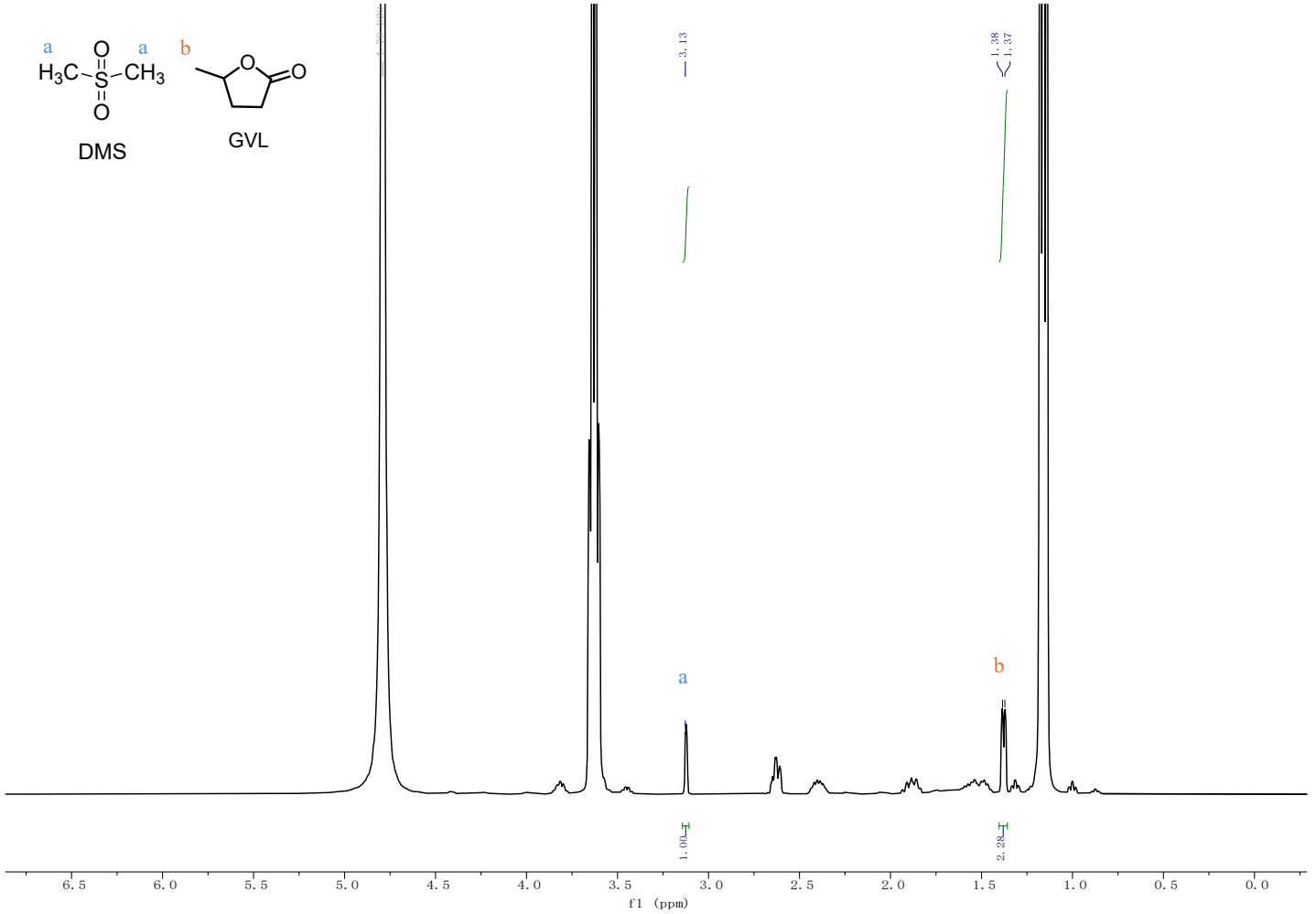


Image S3. ^{1}H-NMR (D_2O, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (2 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), H_2O:EtOH 1:1 (2 mL) at 120 °C after 24 h (conversion= >99%, $yield_{GVL}$= 60% Table S1, entry 6).

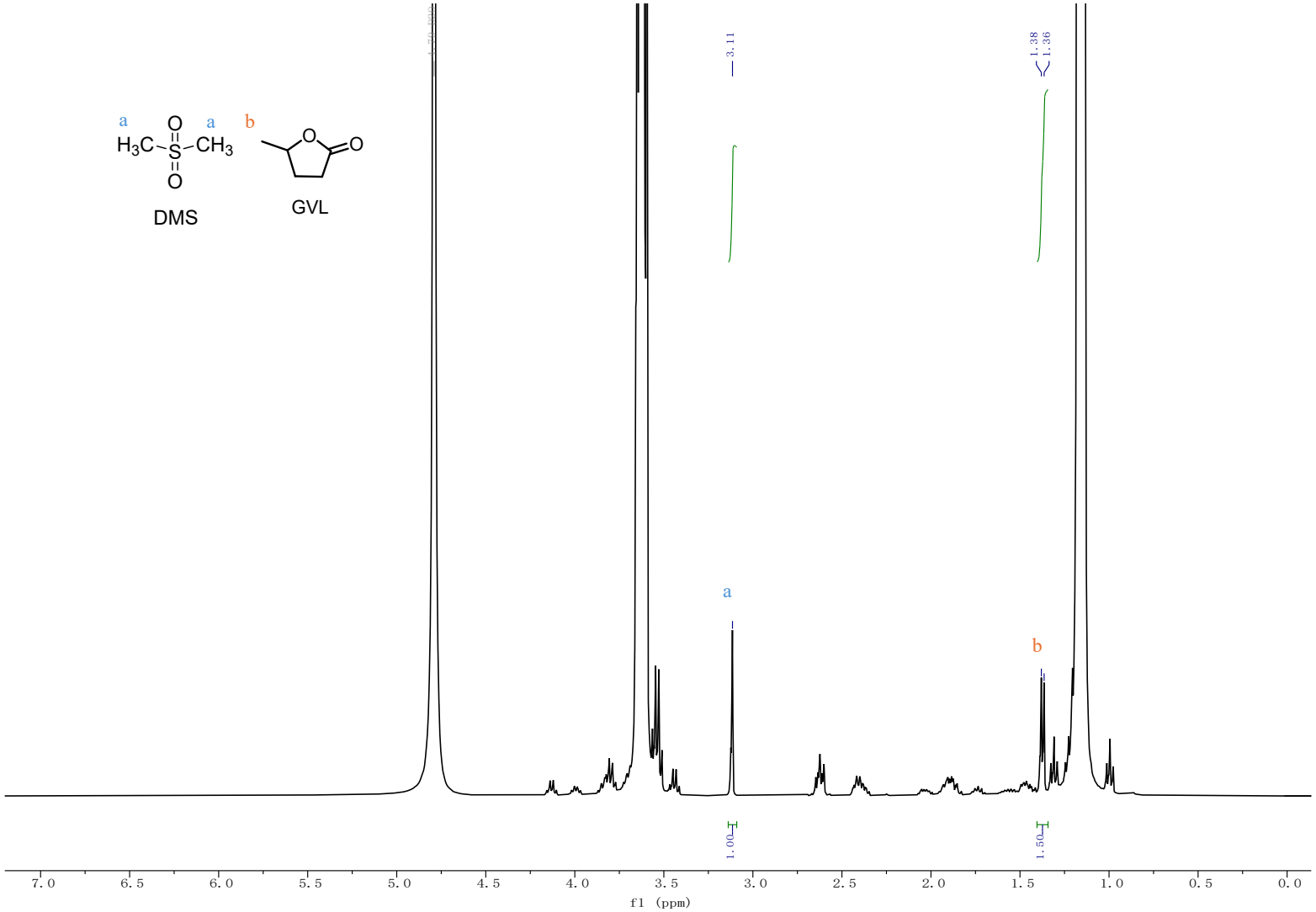


Image S4. ^{1}H-NMR (D_2O, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (2 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), H_2O:EtOH 7:3 (2 mL) at 120 °C after 24 h (conversion= >99%, $yield_{GVL}$= 41% Table S1, entry 14).

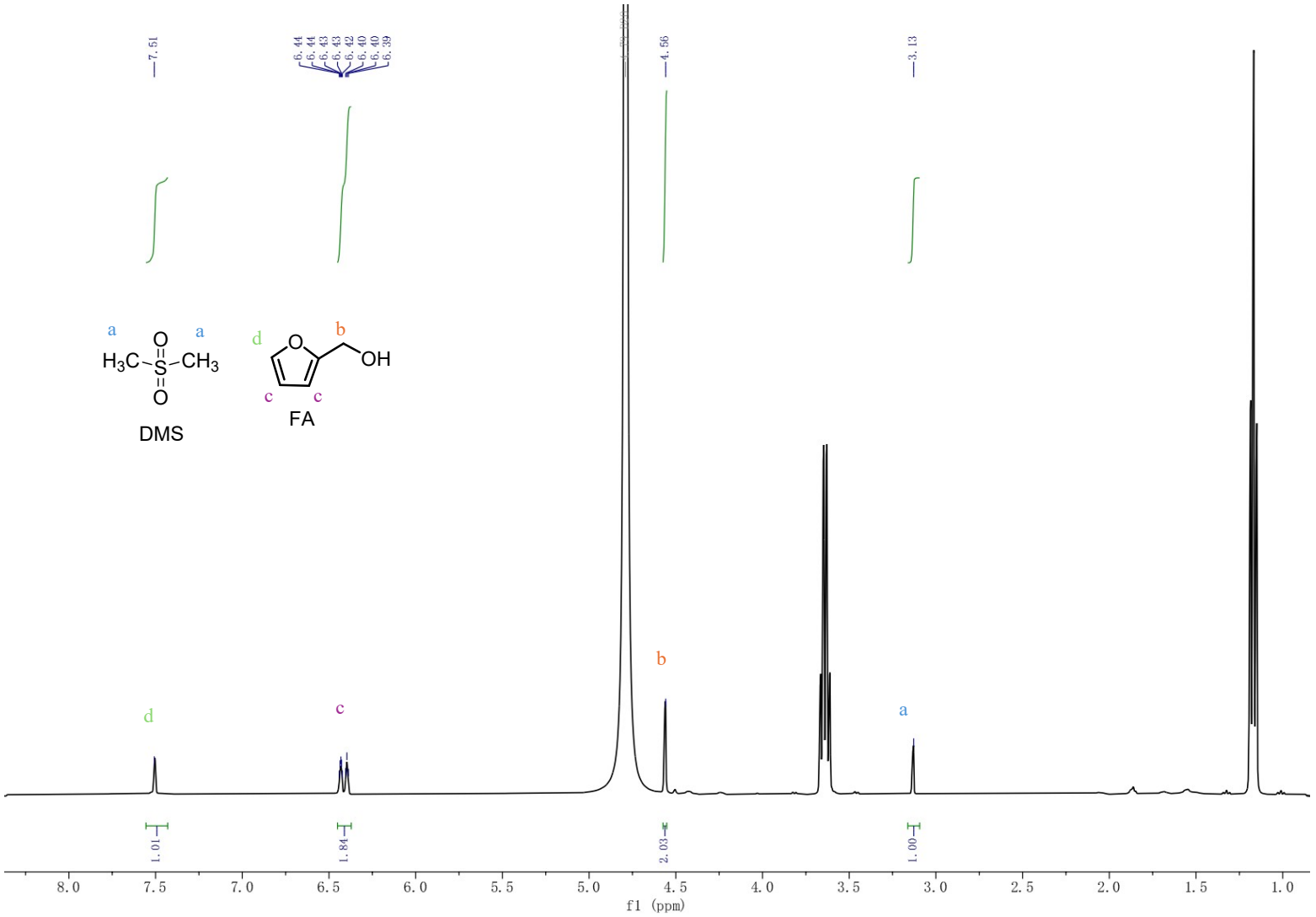


Image S5. ^{1}H-NMR (D_2O, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (2 mol%), Amberlite IR120 (5 mol%), H_2 (30 bar), H_2O:EtOH 7:3 (2 mL) at 120 °C after 24 h (conversion= >99%, $yield_{FA}$= 73% Table S1, entry 16).

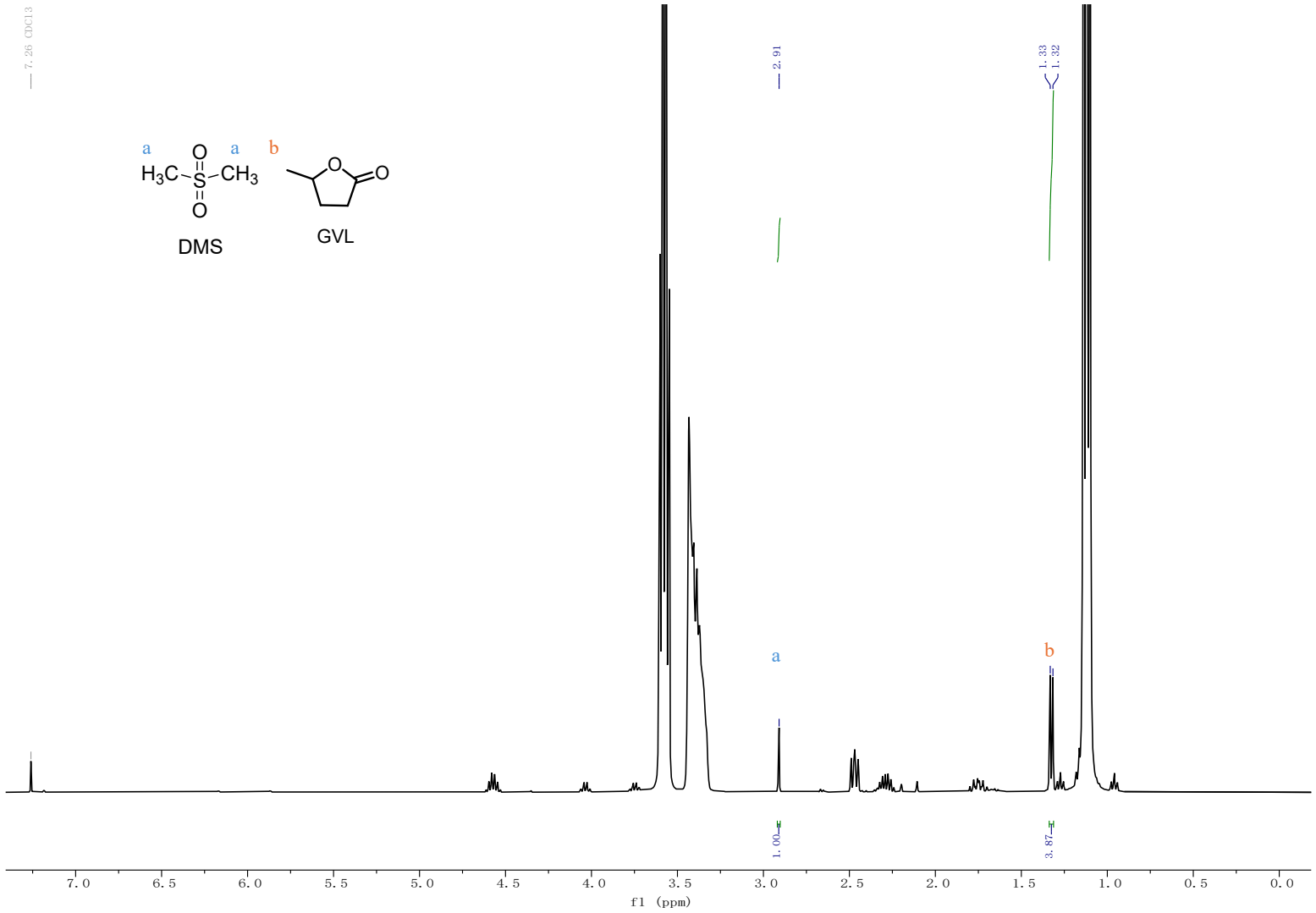


Image S6. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h (conversion= >99%, yield GVL= >99% Table S2, entry 4).

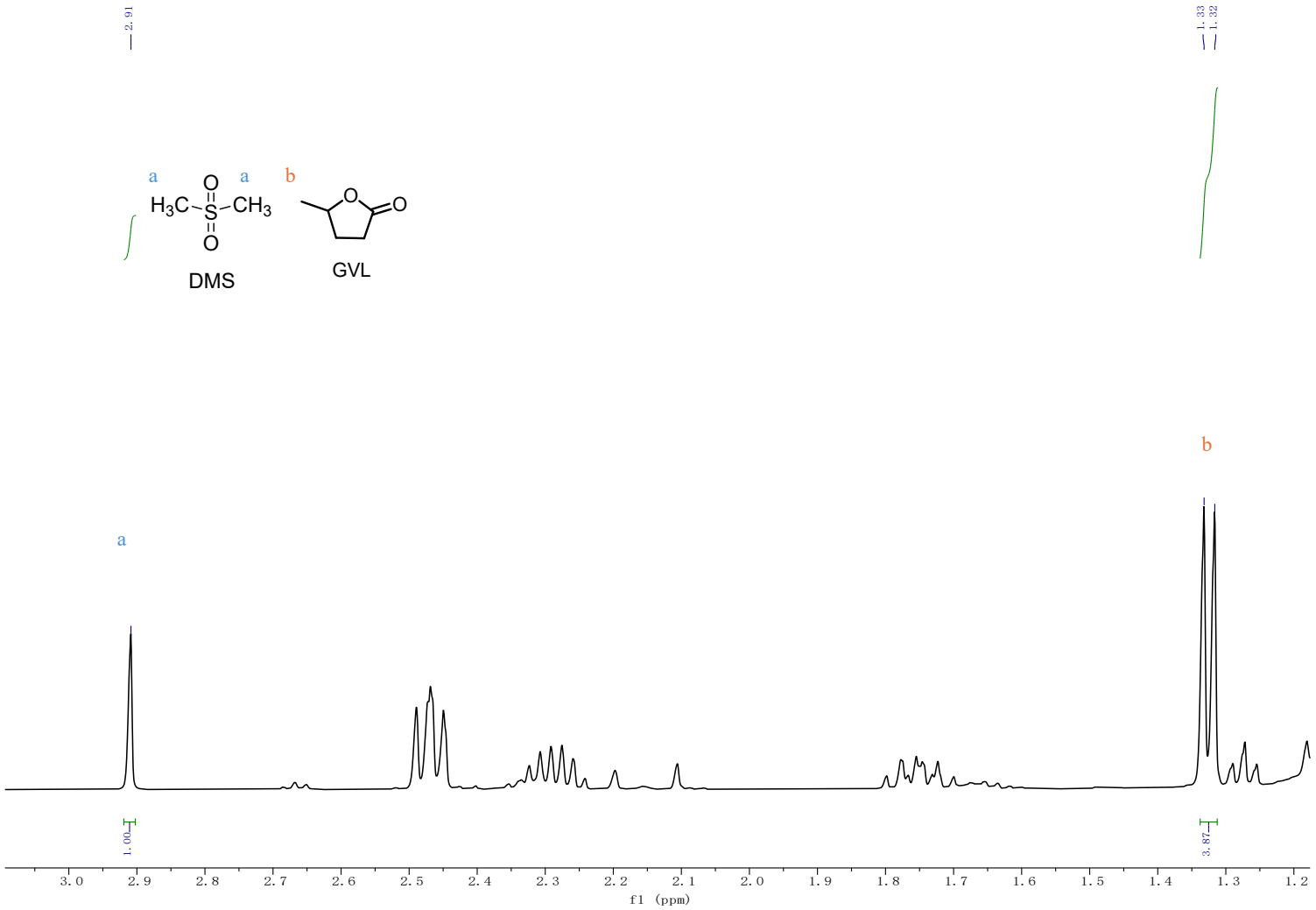


Image S7. Zoom in of the ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h (conversion= >99%, yield GVL= >99% Table S2, entry 4).

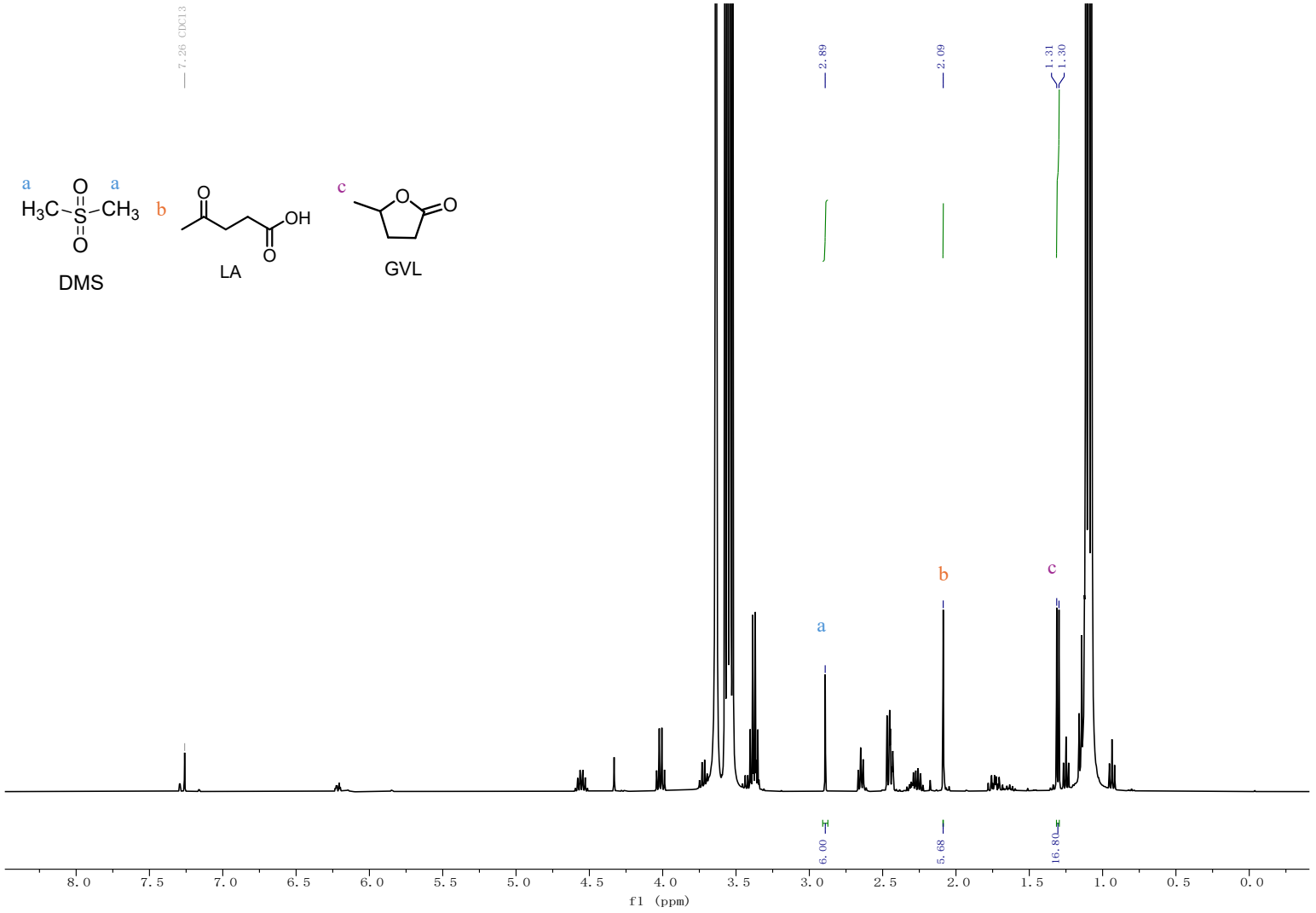


Image S8. [1]H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.25 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h (conversion= >99%, $yield_{LA}$= 25%, $yield_{GVL}$= 75% Table S2, entry 7).

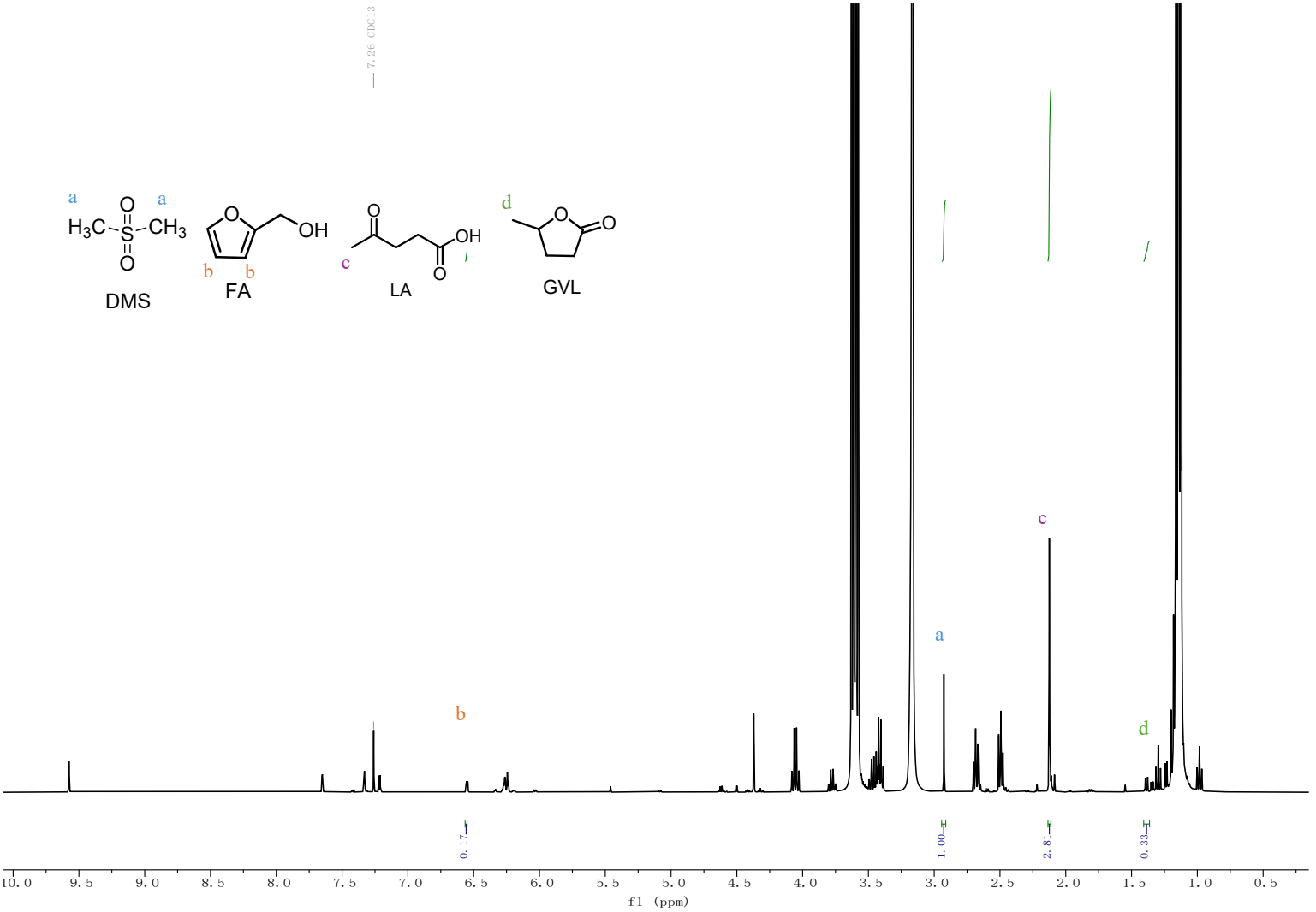


Image S9. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.1 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h (conversion= 86%, $yield_{LA}$= 75%, $yield_{GVL}$= 9% Table S2, entry 7).

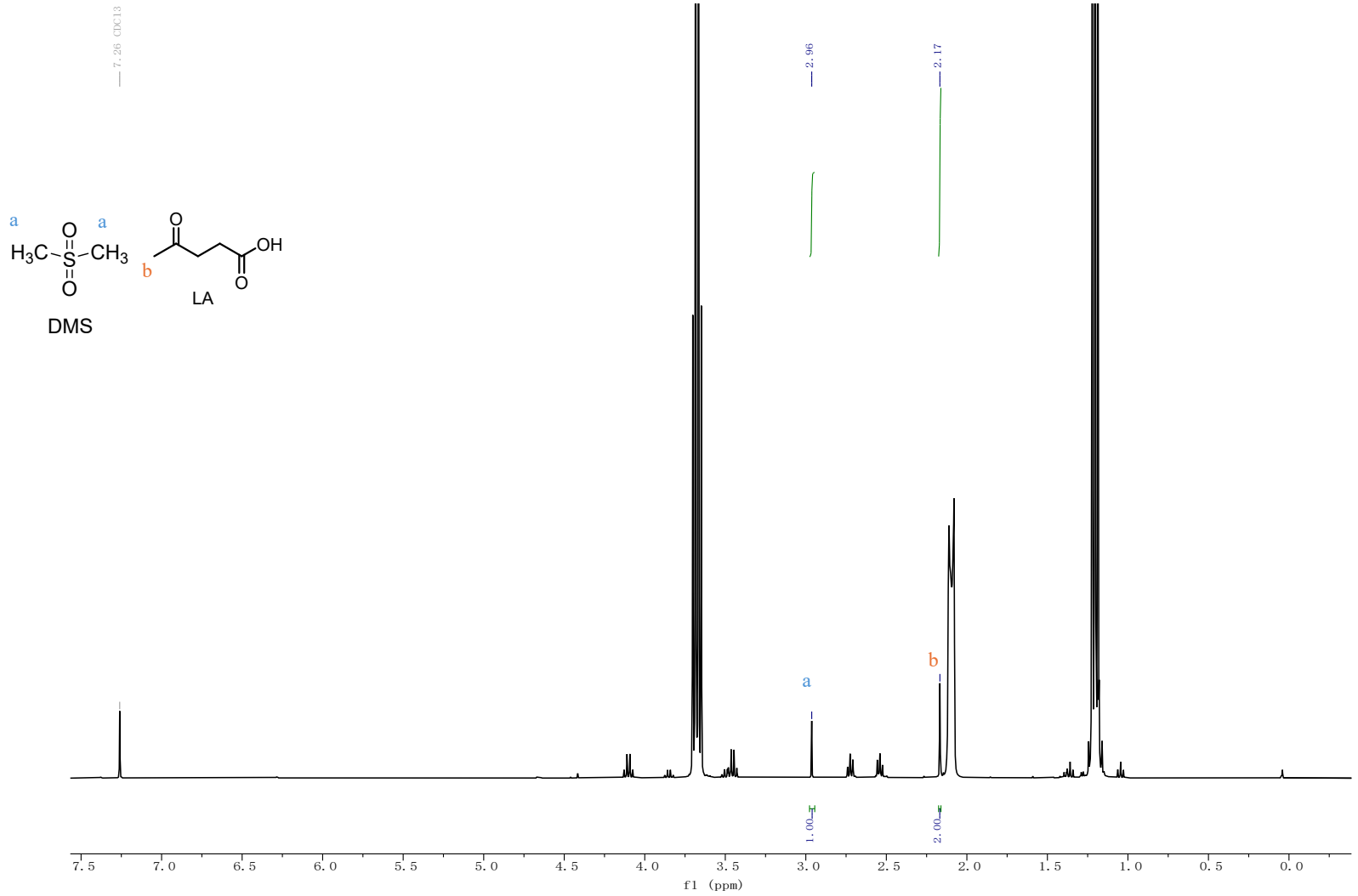


Image S10.[1]H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-13** (2 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h (conversion= >99%, $yield_{LA}$= 54%, $yield_{GVL}$= 0% Table S2, entry 20).

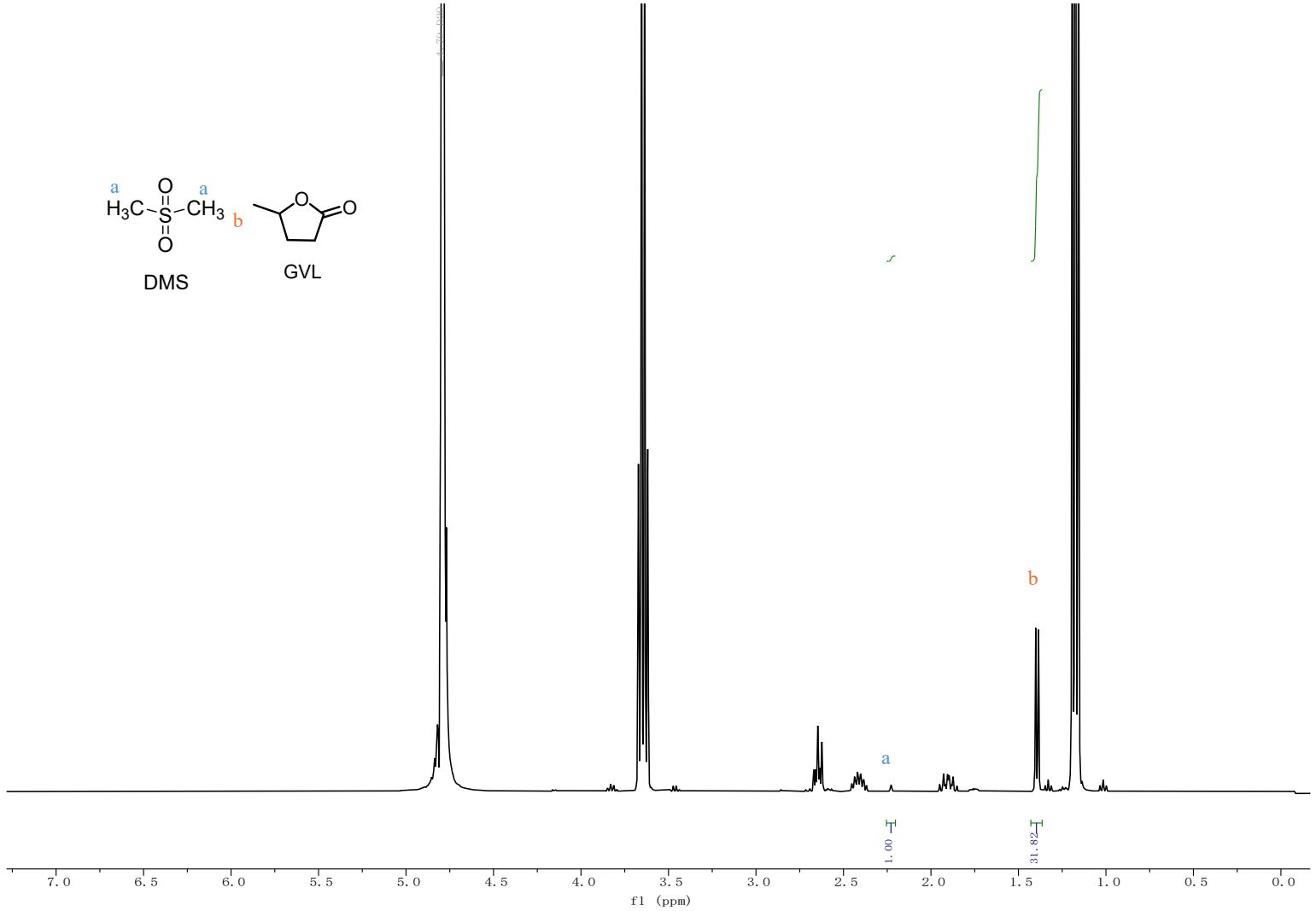


Image S11. ^{1}H-NMR (D_2O, 400 MHz, 25 °C) of the crude reaction of LA with **Ru-2** (2 mol%), Amberlyst-36 (10 mol%), H_2 (30 bar), H_2O:EtOH 7:3 (2 mL) at 120 °C after 24 h (conversion= 97%, $yield_{GVL}$= 97%, Table S3, entry 1).

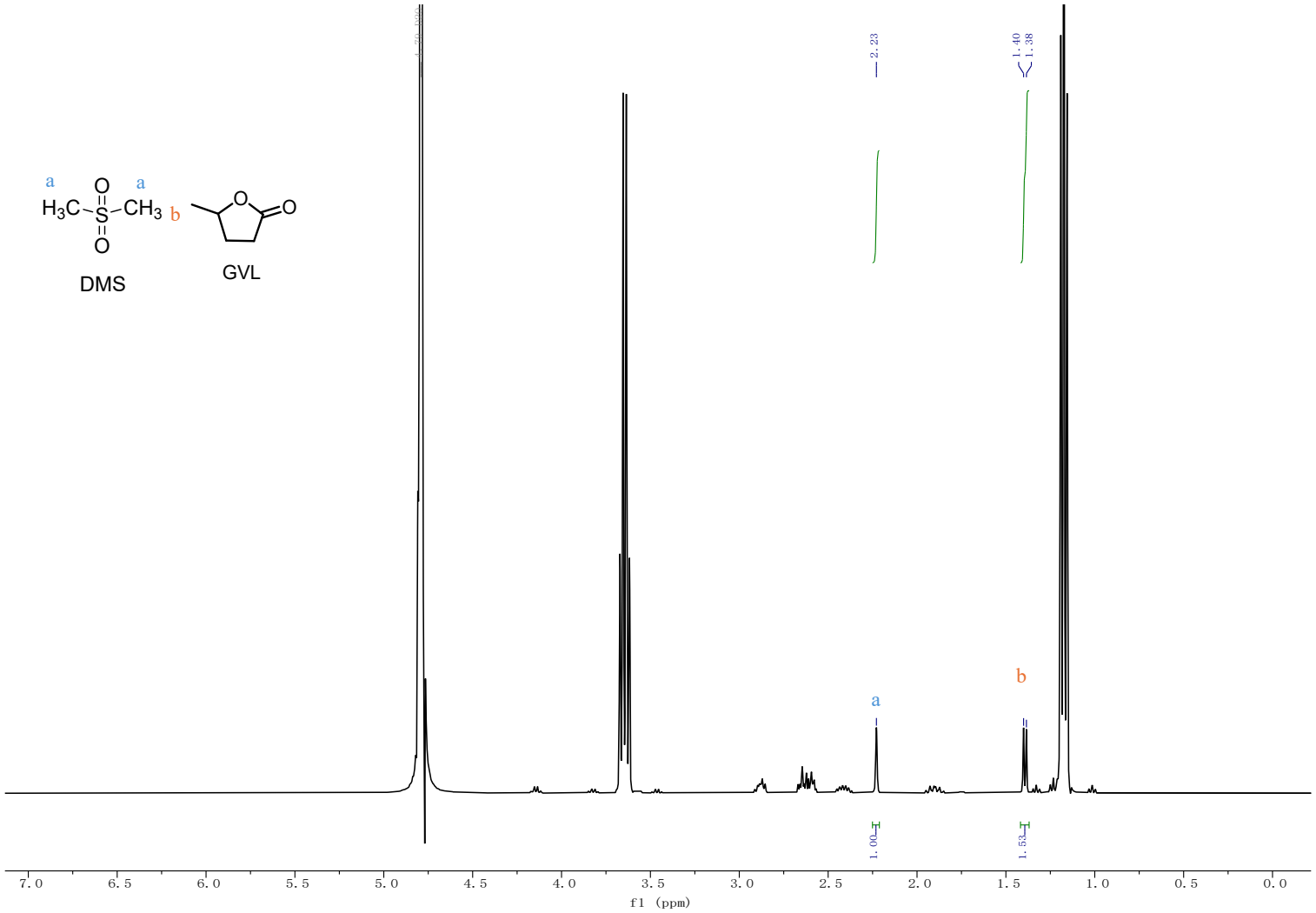
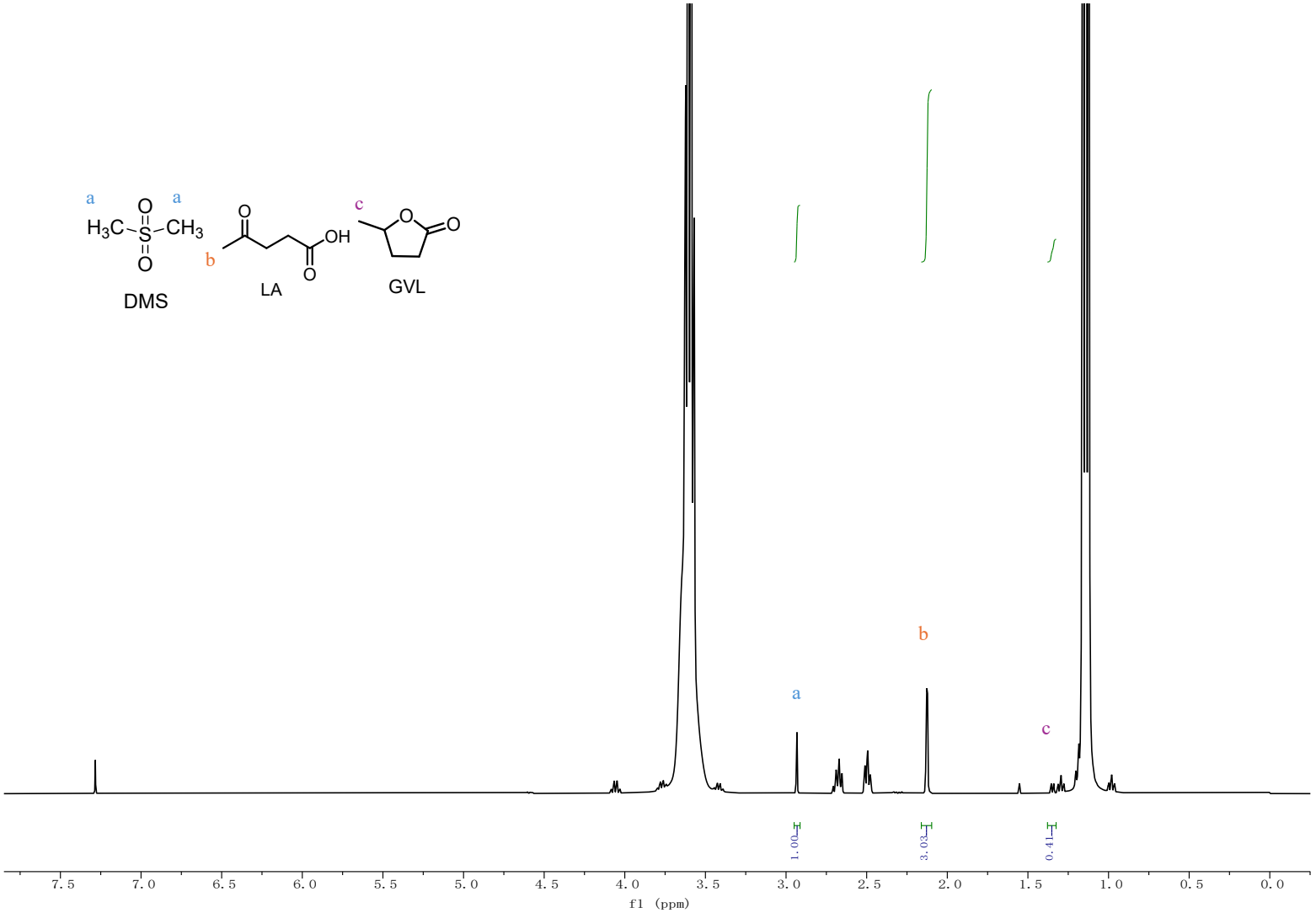


Image S12. ^{1}H-NMR (D_2O, 400 MHz, 25 °C) of the crude reaction of LA with **Ru-2** (2 mol%), Amberlyst-36 (20 mol%), H_2 (30 bar), H_2O:EtOH 7:3 (2 mL) at 120 °C after 24 h (conversion= 61%, $yield_{GVL}$= 61%, Table S3, entry 2).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H3C
S
CH3
O
O
DMS
b
OH
LA
c
GVL
a
b
c
1.00
3.03
0.41
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
f1 (ppm)

Image S13. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of LA with **Ru-2** (2 mol%), Amberlyst-36 (20 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h (conversion= 11%, $yield_{GVL}$= 11%, Table S3, entry 3).

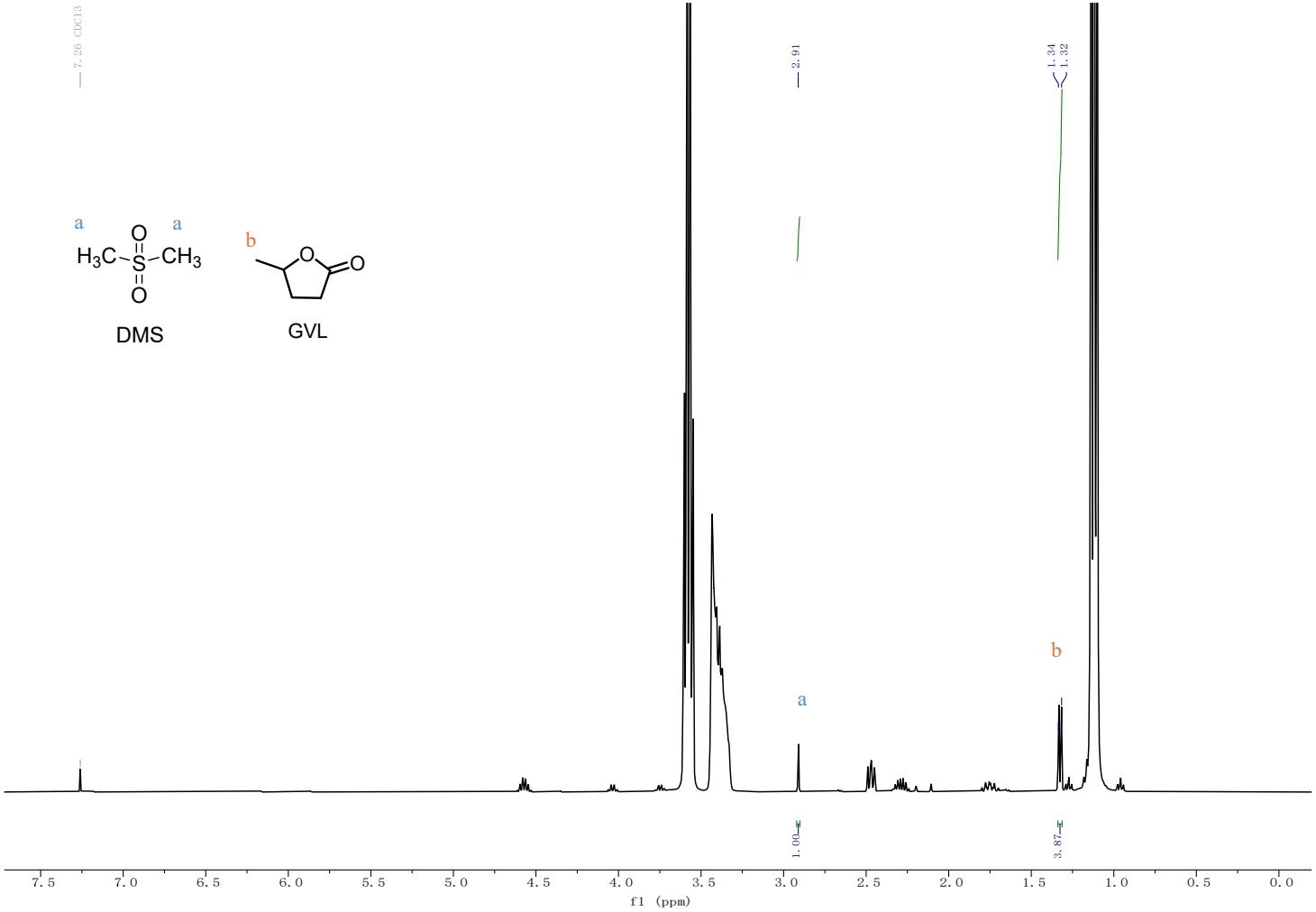

Image S14. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h reusing the Amberlyst-36 resin after washing it with EtOH (III cycle) (conversion= 100%, $yield_{GVL}$= 100%, Table S4, entry 3).

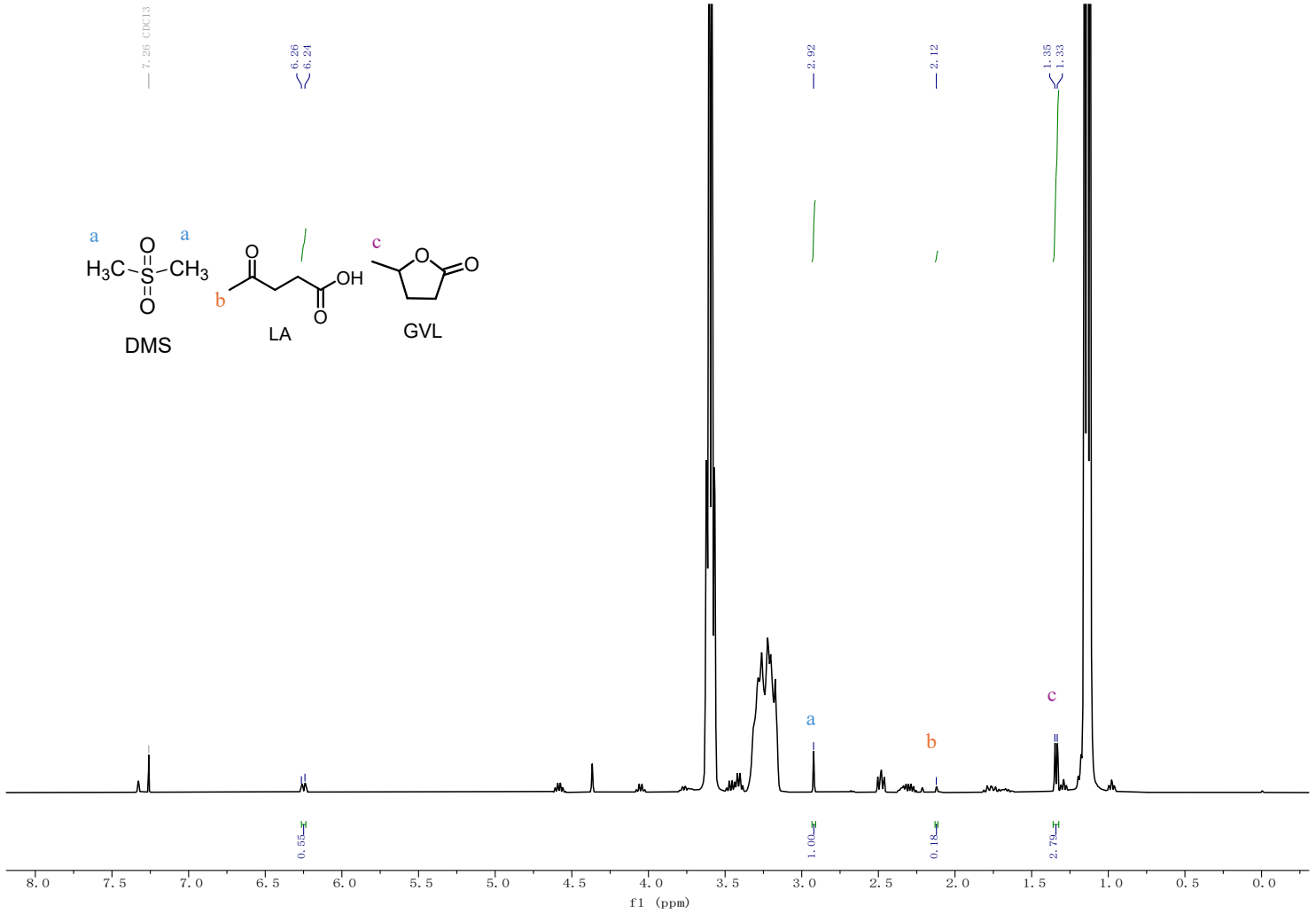

Image S15. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h reusing the Amberlyst-36 resin after washing it with EtOH (IV cycle) (conversion= 100%, $yield_{FA}$= 22%, $yield_{LA}$= 4%, $yield_{GVL}$= 74%, Table S4, entry 4).

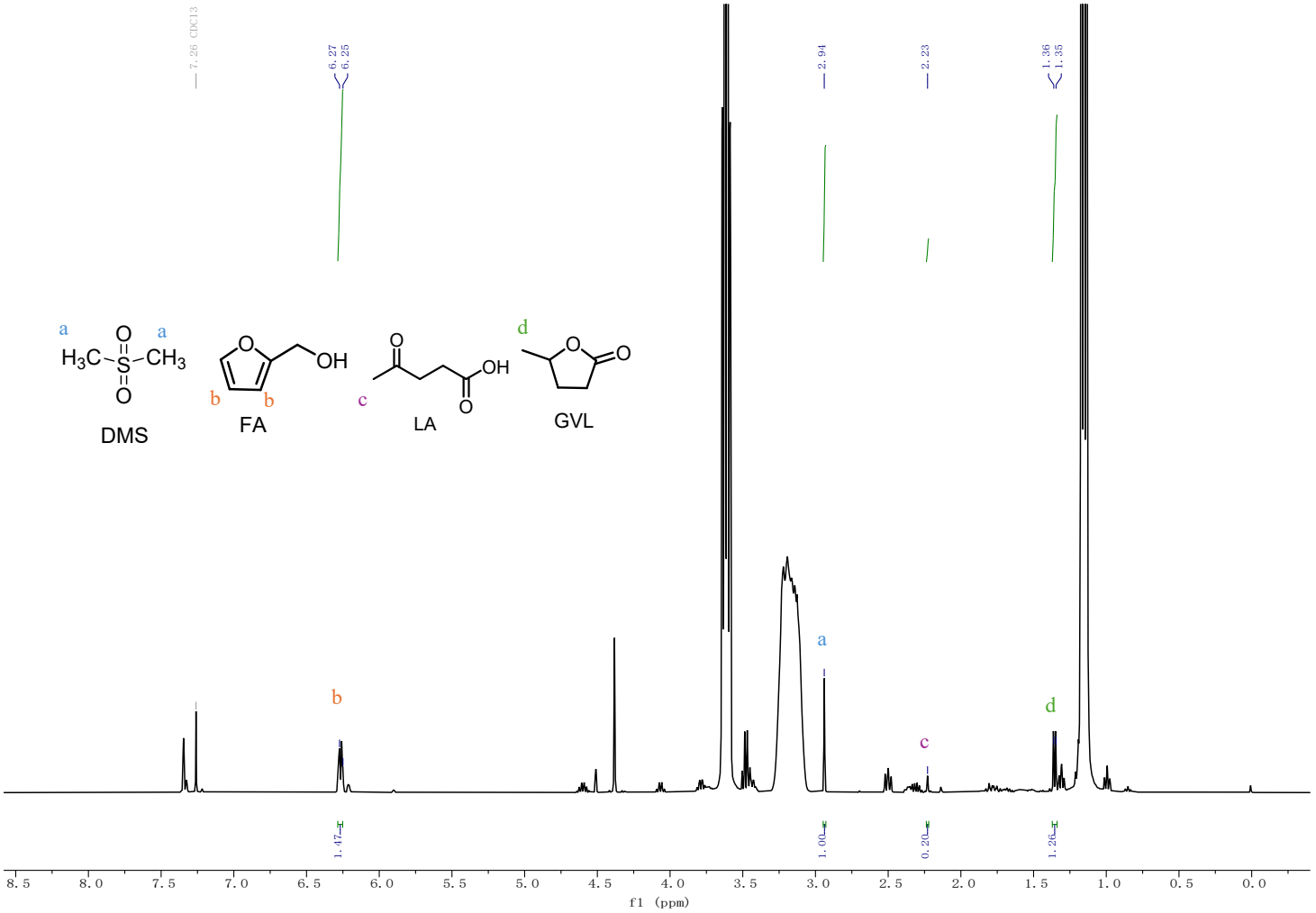

Image S16. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h reusing the Amberlyst-36 resin after washing it with EtOH (IV cycle) (conversion= 100%, $yield_{FA}$= 22%, $yield_{LA}$= 4%, $yield_{GVL}$= 74%, Table S4, entry 4).

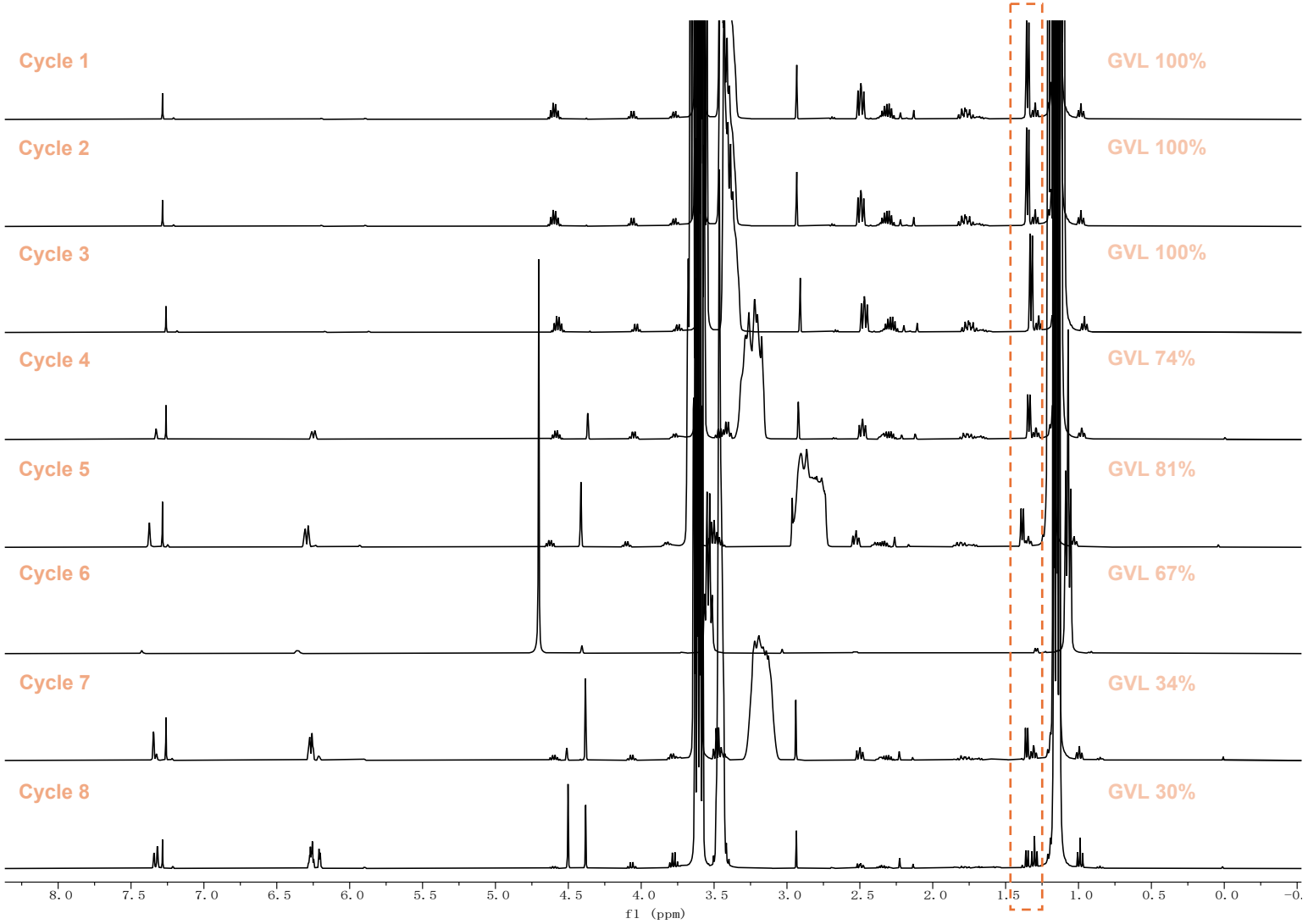

Image S17. ^{1}H NMR spectra of the cycle experiments of FAL hydrogenation with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h using the same acidic resin Amberlyst-36 after washing it with EtOH after each cycle.

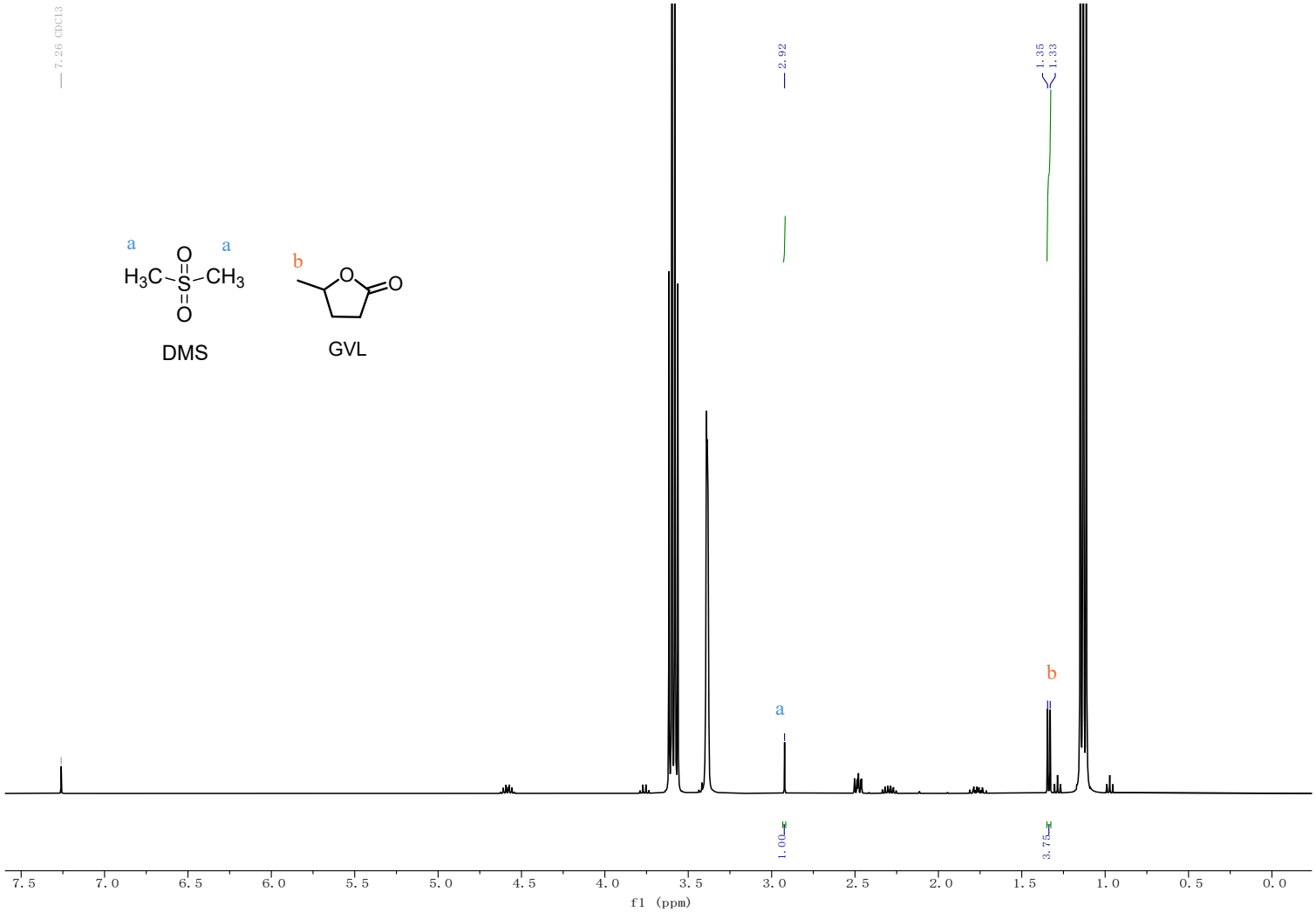

Image S18. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h reactivate and reuse the Amberlyst-36 resin (X cycle) (conversion= 100%, $yield_{GVL}$= 100%, Table S5, entry 10).

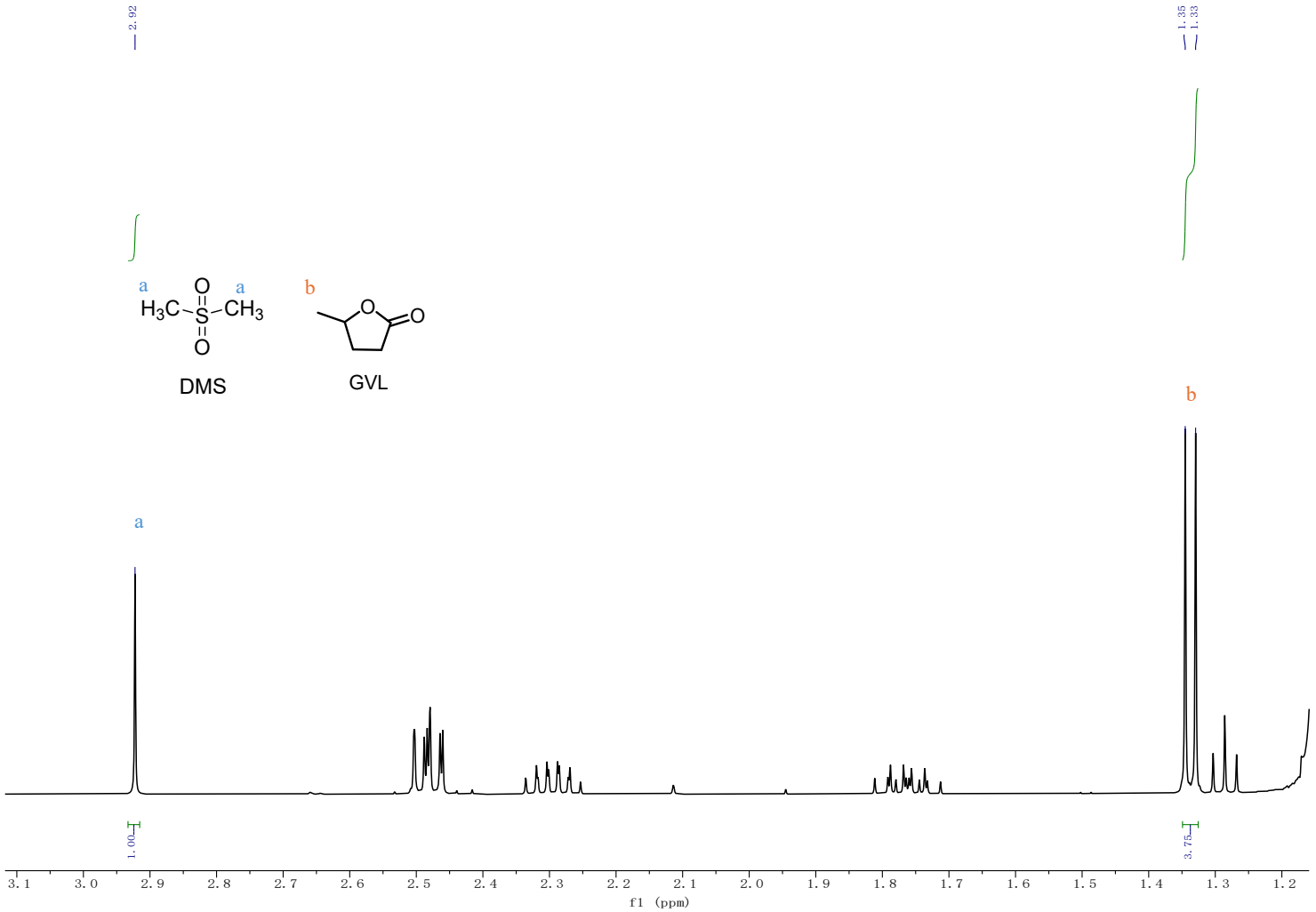

Image S19. Zoom in of the ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h reactivate and reuse the Amberlyst-36 resin (X cycle) (conversion= 100%, $yield_{GVL}$= 100%, Table S5, entry 10).

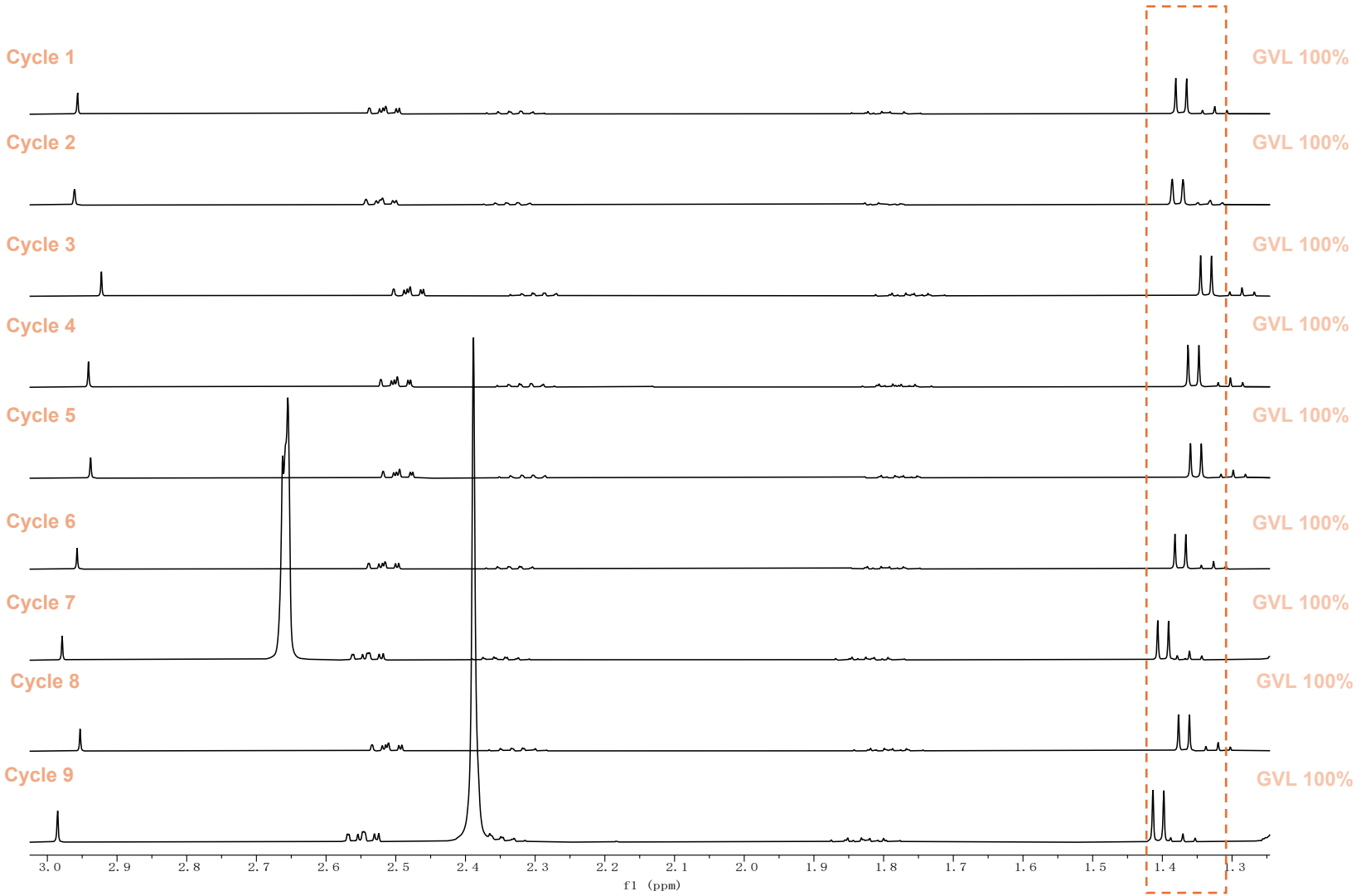

Image S20. ^{1}H NMR spectra of the cycle experiments of FAL hydrogenation with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h using the same acidic resin Amberlyst-36 after reactivating it after each cycle.

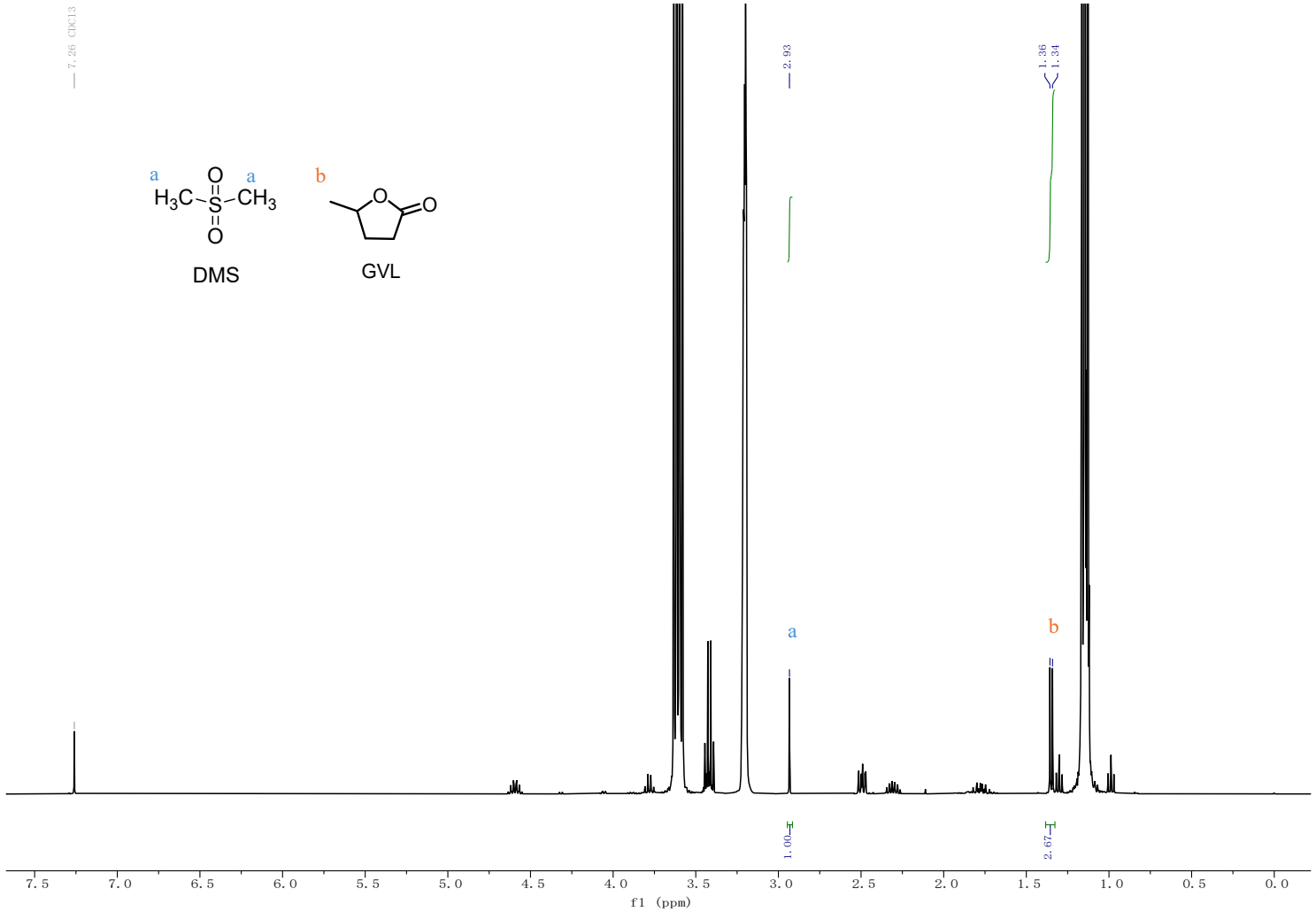

Image S21. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) of the crude reaction of 20 mmol of FAL with **Ru-2** (0.5 mol%), Amberlyst-36 (5 mol%), H_2 (30 bar), EtOH (2 mL) at 120 °C after 24 h (conversion= 100%, $yield_{GVL}$= 72%, Table S6, entry 2).

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