Supporting Information

Efficient Catalytic Hydrogenation of Alkyl Levulinates to γ-Valerolactone

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1. General Information

^{1}H-NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer and were referenced on the solvent peak. Most chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Methyl levulinate (**1a**, 98%), ethyl levulinate (**1b**, 98%), KOMe (28% in MeOH), NaOMe (25 wt. % in methanol), NaOEt (99%), **Ru-1**, **Ru-2**, **Ru-4** and **Ir-1** are commercially available and used without further purification. H_2 gas (H_2O ≤ 3 ppm; O_2 ≤ 2 ppm) was purchased from a commercial supplier as well. D_2 gas was purchased from a commercial supplier as 99.8 atom % D (H_2O ≤ 20.0 ppm; O_2 ≤ 5.0 ppm). The complexes **Ru**-**3**, **Ru-5** and **Fe**-**1**, were synthesized as described in the literature.

2. Experimental Section

General Information. All reactions involving air- or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. The complexes **Ru**-**3**, **Ru**-**5** and **Fe**-**1**, were synthesized as described in the literature.[1-3] The ^{1}H-NMR spectra were recorded on a Bruker Avance III 400 MHz or Bruker AVANCE 600 MHz spectrometer and were referenced on the solvent peak.

Chemicals handling and loading into the autoclave prior to applying H_2 was done in a glovebox. Subsequent to taking the loaded autoclave out of the glovebox, the autoclave was quickly sealed and purged three times with H_2 before applying the desired H_2 pressure.

All the starting materials and hydrogenation products are literature known compounds, and the experimental data fit those reported. All of the experimental details and analytical data can be found in the Supporting Information.

General Procedure for hydrogenation of alkyl levulinates to γ-valerolactone.

The optimization reactions were carried out on a 5 mmol scale, and the substrate scope was investigated on a 10 mmol scale under otherwise totally identical conditions to allow for a detailed comparison of the reactivity. We also carried out a 40 and 70 mmol scale hydrogenation of alkyl levulinates **1a** and **1b**, respectively. The product (**3**) may be isolated via fractional vacuum distillation to afford pure **3**. All the experiments were performed twice to corroborate the results.

For a typical hydrogenation screening experiment, **1b** (5 mmol) was charged in a glass vial, which was subsequently equipped with a magnetic stirring bar. Afterwards, the PNP catalyst (0.5 mol %) and the corresponding amount of base (0.5-7mol %) were added. The vial was sealed with a teflon-lined cap, removed from the glovebox, and placed in a seven-well reactor with a needle perforating the cap. The autoclave was sealed and flushed with hydrogen (three times), and then a hydrogen pressure of 10-30 bar was applied. The autoclave was placed in a preheated plate and stirred for 3-20 h (600 rpm). After this time, the reactor was cooled to room temperature before the hydrogen was released. The crude reaction mixture was then analyzed using ^{1}H-NMR spectroscopy in $CDCl_3$.

When the hydrogenation of alkyl levulinates (**1a** or **1b**) was carried out on a large scale (10-70 mmol), the raw material, base (0.5 mol%), complex (**Ru**-**1**, **Ru**-**4** or **Ir**-**1**) and alcohol (0.25-5.60 mL) were charged into stainless-steel autoclave. The autoclave was tightened and flushed with hydrogen three times and finally charged with hydrogen (25 bar). The reaction mixture was stirred (600 rpm) at 25 °C or 60 °C for the desired time. After reaction, the autoclave was cooled to room temperature and the pressure was released carefully. The reaction mixture was analyzed by using NMR as described above.

Recycling experiments

The catalyst recycling was evaluated by a series of hydrogenation experiments under standard reaction conditions (25 bar H_2, 60 °C, 20 h, using 70 mmol) of **1b** per loading and an initial 0.5 mol% of **Ru**-**1**. Thus, feeding the reactor with additional amounts of **1b** every 20 hours four times (350 mmol of **1b** in total) showed full conversion every time without detectable deactivation of the catalyst.

The hydrogenation of **1b** with distillation of the product prior to each substrate reloading was also attempted using an initial 0.5 mol% of **Ru**-**1** as catalyst. The first three cycles all led to full conversion, and 78-79% yields were measured for the two first cycles. The conversion after the fourth run was merely 75% affording an isolated yield of 67% (See Figure 31).

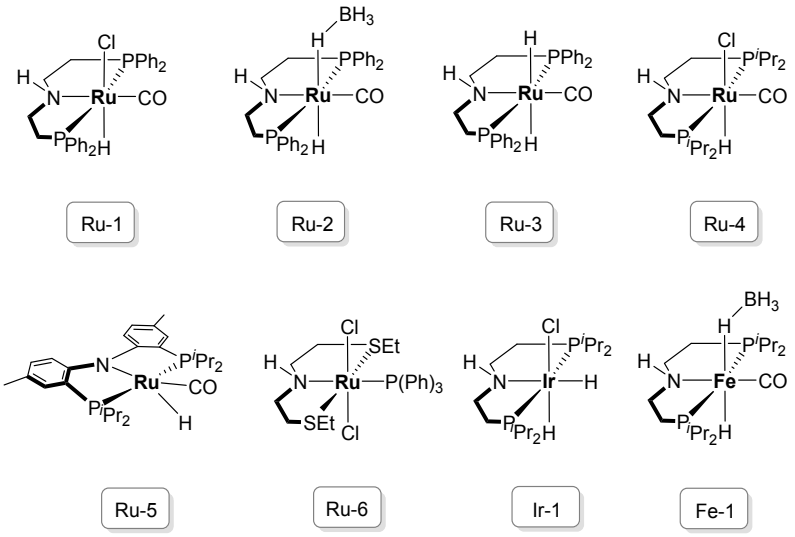
Deuterium labelling experiments

Conventional experiment procedure was carried out using **1b** as substrate on 5 mmol scale, base (5 mol %, 2.0 M solution of NaOEt in EtOH) and complex **Ru**-**1** (0.5 mol%). All the chemicals were charged into stainless-steel autoclave. The autoclave was tightened and flushed with deuterium gas three times and finally charged with deuterium (30 bar). The reaction mixture was stirred (600 rpm) at 60 °C for 24 h. After reaction, the autoclave was cooled to room temperature and the pressure was released carefully. The reaction mixture (0.4 ml) was analyzed by ^{1}H, ^{2}H and ^{13}C-NMR using a J. Young NMR tube with a toluene-d_8 capillary insert as external standard.

In another experiment, 0.05 mL of ethanol-d_6 was added to 10 mmol of **1b**, base (0.5 mol %, 2.0 M solution of NaOEt in EtOH) and complex **Ru**-**1** (0.5 mol%) in a stainless-steel autoclave. The autoclave was tightened and flushed with hydrogen gas three times and finally charged with hydrogen (30 bar). The reaction mixture was stirred at 60 °C for 24 h. After this time, the autoclave was cooled to room temperature and the pressure released. The reaction mixture (0.4 ml) was analyzed by ^{1}H, and ^{13}C- NMR using the ethanol-d_6 signals as reference.

3. NMR measurements.

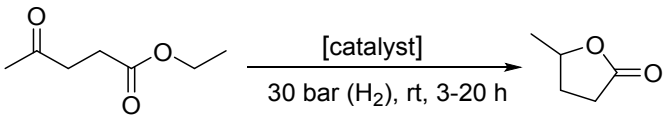
Conversions in all reactions were measured by ^{1}H-NMR spectroscopy at 400 MHz in $CDCl_3$ at 25 °C. 128 scans were taken for each sample, with a delay between scans of 30 seconds to ensure complete magnetic relaxation of the hydrogens. The conversion was calculated using the signals from the methyl (2.15 ppm) hydrogens of the unreacted monomer, and the methyl (1.35 ppm) hydrogens of **3**. Errors in the conversion measurements were estimated by comparing the results of at least three integrations of each spectrum. In addition, different NMR sampling methods as well as dilution experiments all pointed towards similar conversions. Furthermore, calibrated GC-FID measurements corroborated the NMR observed conversion within 5% of error. Finally, the conversions of both incomplete and complete reactions were verified by isolated yields.



Scheme 1. PNP metal complexes evaluated in this study.

4. Scope of the reactions. General experimental details.

Table 1. Exploratory hydrogenation experiments of **1b** to **3** with Ru and Ir catalysts.[a]



Entry	Catalyst (mol%)	Base (mol %)	P_{H2} [bar]	T [°C]	*t* [h]	Conversion [%][b]
1	**Ru-1** (0.5)	_	30	25	3	0
2	**Ru-1** (0.5)	NaOMe (10)	30	25	3	30
3	**Ru-1** (0.5)	KO^{t}Bu (10)	30	25	3	<5

Table 2. Catalyst screening and identification of suitable conditions for the formation of **3**.[a]

Entry	Catalyst (mol%)	Base (mol %)	P_{H2} [bar]	T [°C]	*t* [h]	Conversion [%][b]
1	**Ru-1** (0.2)	KOMe (7)	10	60	3	49
2	**Ru-1** (0.5)	KOMe (7)	10	60	3	>99
4	**Ru-1** (0.5)	K_3CO_2 (10)	30	25	3	0
5	**Ru-1** (0.5)	Na_2HPO_4 (10)	30	25	3	0
6	**Ru-1** (0.5)	K_3PO_4 (10)	30	25	3	<5
7	**Ru-1** (0.5)	KOMe (7)	30	25	3	15
8	**Ru-2** (0.5)	NaOMe (10)	30	25	3	<5
9	**Ru-4** (0.5)	NaOMe (10)	30	25	3	31
10	**Ru-4** (0.5)	KOMe (7)	30	25	3	30
11	**Ru-2** (0.5)	KOMe (10)	30	25	3	<10
12	**Ru-1** (0.5)	NaOMe (10)	30	25	20	>99
13	**Ru-2** (0.5)	NaOMe (10)	30	25	20	61
14	**Ru-4** (0.5)	NaOMe (10)	30	25	20	75
15	**Ru-1** (0.5)	KOMe (7)	30	25	20	>99
16	**Ru-2** (0.5)	KOMe (7)	30	25	20	77
17	**Ru-4** (0.5)	KOMe (7)	30	25	20	64
18	**Ru-1** (0.5)	NaOEt (4)	30	25	20	>99
19	**Ru-4** (0.5)	NaOEt (10)	30	25	20	57
20	**Ru-4** (0.5)	NaOEt (4)	30	25	20	34
21	**Ru-5** (0.5)	NaOEt (4)	30	25	20	<10
22	**Ir-1** (0.5)	NaOEt (4)	30	25	20	>99

[a] Standard reaction conditions: 5 mmol of **1b**. Base solutions: NaOMe: 25%/MeOH (4.5 M); KOMe: 28%/MeOH (3.0 M); NaOEt: 2.0 M/EtOH. [b] Determined by ^{1}H-NMR analysis. Conversion calculated as the conversion of **1b** to a mixture of **2b** and **3**. Whenever discernible, the **2b**/**3** ratio was minimum 20:80 in favor of **3**.

Table 3. Hydrogenation of **1b** to **3** with **Ru**-**1** and **Ir**-**1** on large scale.[a]

Entry	**1b** (mmol)	Catalyst (mol%)	P_{H2} [bar]	T [°C]	*t* [h]	Conversion [%][b]	TON_{max}
1	10	**Ru**-**1** (0.5)	10	60	72	>99	200
2	10	**Ru**-**1** (0.1)	10	60	72	>99	1000
3	10	**Ru**-**1** (0.05)	10	60	72	>99	2000
4	10	**Ru**-**1** (0.5)	10	60	72	58	200
5	10	**Ru**-**1** (0.5)	10	60	72	88	200
6	10	**Ru**-**1** (0.5)	10	60	72	64	200
7	10	**Ru**-**1** (0.5)	10	60	72	12	200
8		**Ru**-**1** (0.5)	KOMe (0.5)	10	60	3	<10
9		**Ru**-**2** (0.5)	KOMe (4)	10	60	3	15
10		**Ru**-**2** (0.5)	KOMe (4)	10	60	3	26
11		**Ru**-**2** (0.5)	KOMe (4)	10	60	3	40
12		**Ru**-**2** (0.5)	KOMe (0.5)	10	60	3	<5
13		**Ru**-**3** (0.5)	No base	10	60	20	0
14		**Ru**-**3** (0.5)	KOMe (7)	10	60	3	29
15		**Ru**-**3** (0.5)	NaOEt (4)	10	60	20	33
16		**Ru**-**4** (0.5)	KOMe (0.5)	10	60	3	0
17		**Ru**-**4** (0.5)	KOMe (3)	10	60	3	>99
18		**Ru**-**6** (0.5)	KOMe (7)	10	60	3	<10
19		**Ir**-**1** (0.5)	KOMe (5)	10	60	3	>99
20		**Ir**-**1** (0.5)	KOMe (7)	10	60	3	98
21		**Fe**-**1** (0.5)	KOMe (7)	10	0	3	<10

[a] Standard reaction conditions: 5 mmol of **1b**. Base solutions: NaOMe: 25%/MeOH (4.5 M); KOMe: 28%/MeOH (3.0 M); NaOEt: 2.0 M/EtOH. [b] Determined by ^{1}H-NMR analysis. Conversion calculated as the conversion of **1b** to a mixture of **2b** and **3**. Whenever discernible, the **2b**/**3** ratio was minimum 20:80 in favor of **3**.

4	10	**Ru**-**1** (0.01)	10	60	72	41	4100
5	10	**Ir**-**1** (0.01)	10	60	72	69	6900
6	10	**Ru**-**1** (0.5)	20	60	100	>99	200
7	10	**Ru**-**1** (0.1)	20	60	100	>99	1000
8	10	**Ru**-**1** (0.05)	20	60	72	>99	2000
9	10	**Ru**-**1** (0.05)	20	60	100	>99	2000
10	10	**Ru**-**1** (0.05)	20	60	24	>99	2000
11	10	**Ru**-**1** (0.025)	20	60	48	>99	4000
12	10	**Ru**-**1** (0.025)	20	60	24	40	1600
13	10	**Ru**-**1** (0.01)	20	60	100	74	7400
14	19	**Ru**-**1** (0.01)	20	60	24	32	3200
15	10	**Ru**-**4** (0.05)	20	60	72	36	720
16	10	**Ru**-**4** (0.01)	20	60	72	<10	-
17	10	**Ir**-**1** (0.05)	20	60	100	>99	2000
18	10	**Ir**-**1** (0.05)	20	60	48	>99	2000
19	10	**Ir**-**1** (0.05)	20	60	3	42	840
20	10	**Ir**-**1** (0.05)	20	60	24	>99	2000
21	10	**Ir**-**1** (0.025)	20	60	48	96	3840
22	10	**Ir**-**1** (0.01)	20	60	3	<10	-
23	10	**Ir**-**1** (0.01)	20	60	24	93	9300
24	70	**Ru**-**1** (0.5)	25	25	100	>99	200
25	70	**Ru**-**1** (0.05)	25	25	72	15	300
26	70	**Ir**-**1** (0.05)	25	25	48	57	1140
27	70	**Ir**-**1** (0.05)	25	25	72	>99	2400
28	70	**Ir**-**1** (0.01)	25	25	72	27	2700

[a] Standard reaction conditions: 5 mol% of NaOEt (2.0 M/EtOH).

[b] Determined by ^{1}H-NMR analysis. Whenever discernible, the **2b**/**3** ratio was minimum 20:80 in favor of **3**.

5. ^{1}H-NMR spectra of the reactions

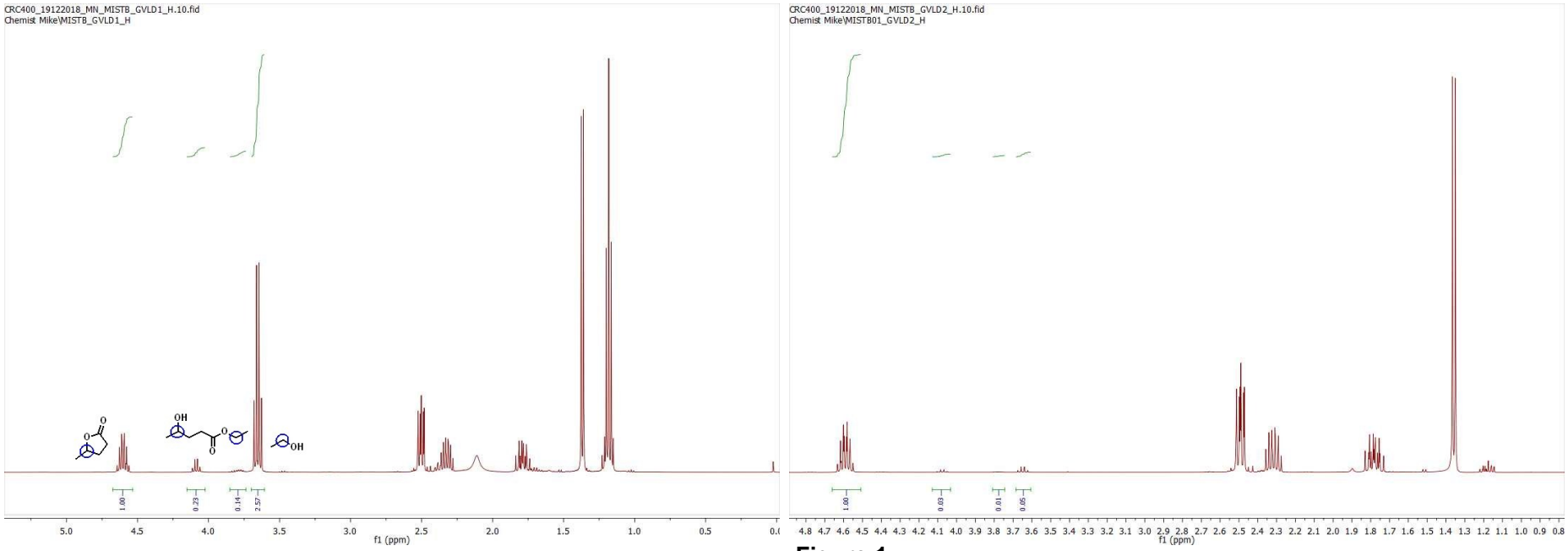


Figure 1.

Left: ^{1}H-NMR of the crude reaction of 70 mmol (10 mL) **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 1.75 mL EtOH and 3 h. Content: ethanol, γ-valerolactone (88%) and ethyl 4-hydroxypentanoate (12%).

Right: After vacuum fractional distillation. Content: γ-Valerolactone (>95%).

The yield of γ-valerolactone was 73%, corresponding to isolating 83% of the formed end product.

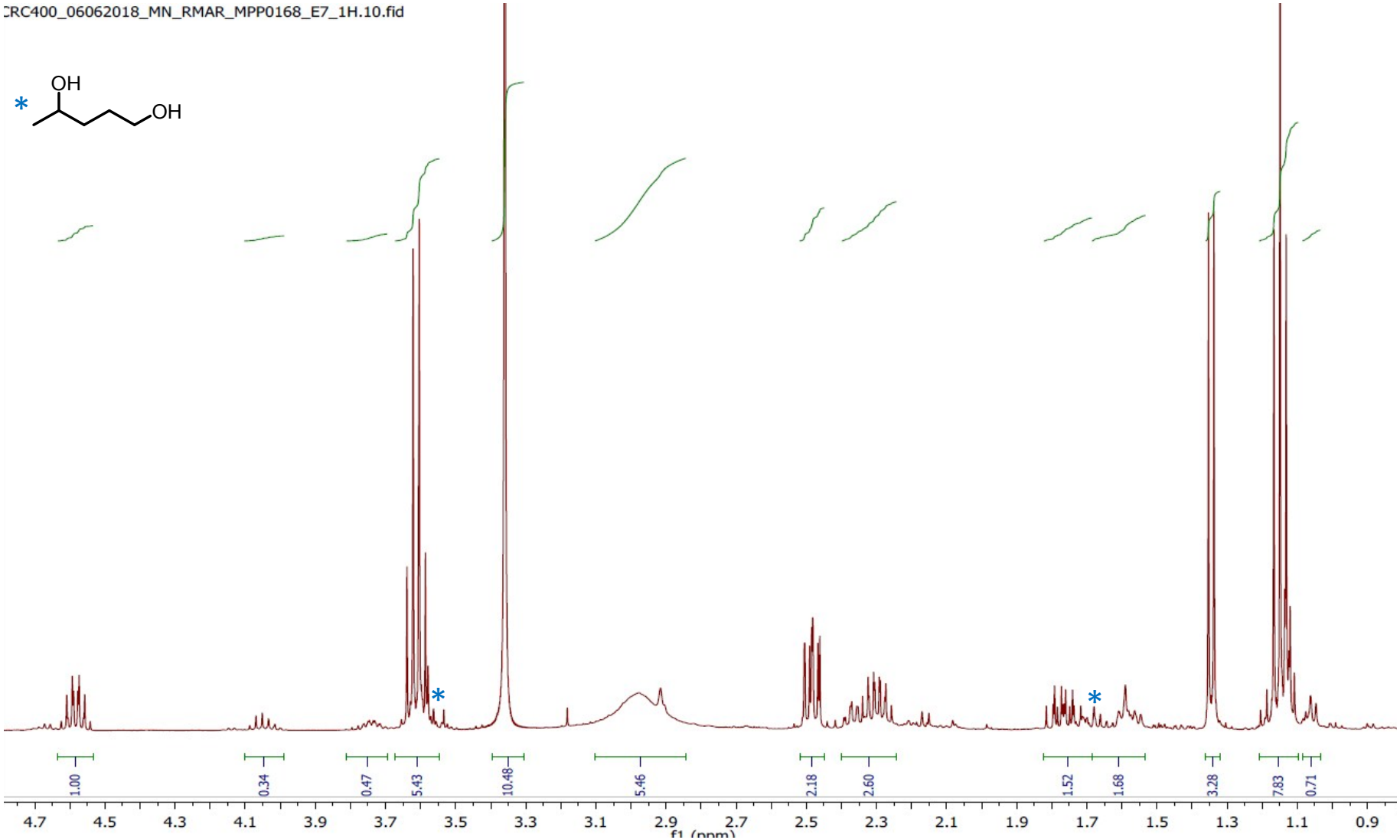


Figure 2. ^{1}H-NMR of the crude reaction of 5 mmol **1b** with **Ru**-**1** catalyst (0.5 mmol%), KOMe (15 mol%), 10 bar H_2, 60 ^{o}C, 0.220 mL MeOH and 3 h.

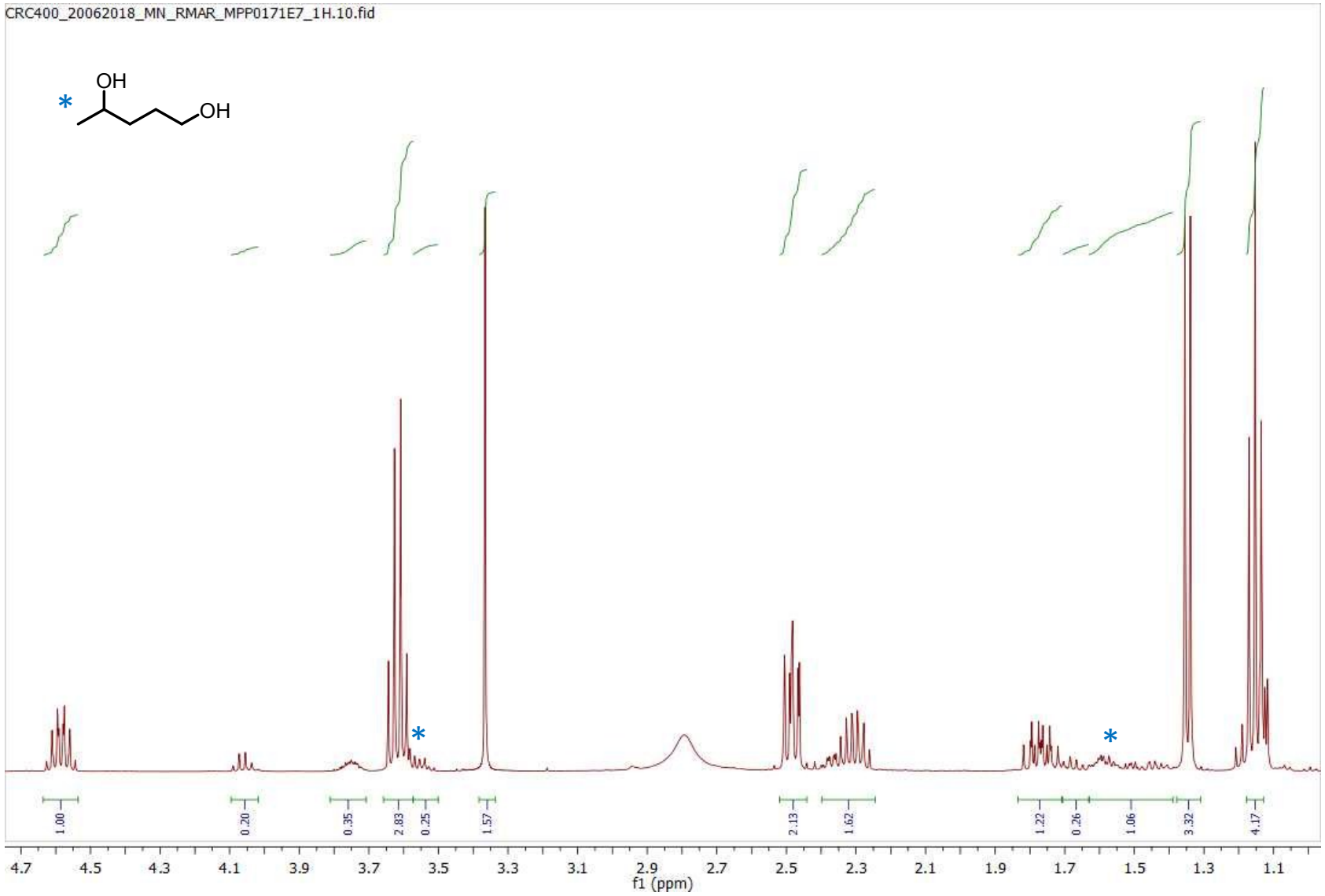


Figure 3. ^{1}H-NMR of the crude reaction of 5 mmol **1b** with **Ru**-**1** catalyst (2.8 mmol%), KOMe (7 mol%), 10 bar H_2, 60 ^{o}C, 0.097 mL MeOH and 3 h.

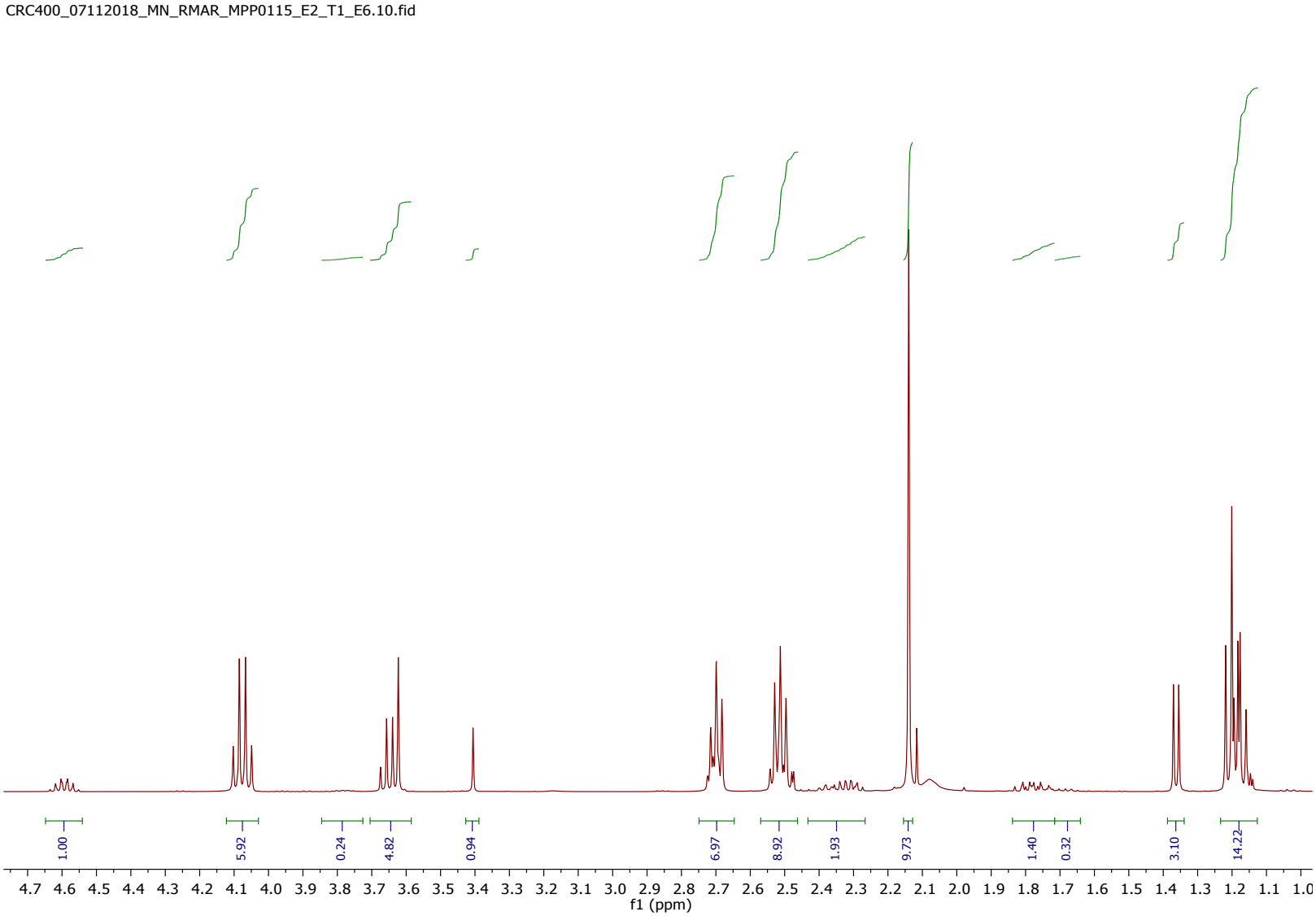


Figure 4. ^{1}H-NMR of the crude reaction of 5 mmol **1b** with **Ru-2** catalyst (0.5 mmol%), KOMe (4 mol%), 10 bar H_2, 60 ^{o}C, 0.049 mL MeOH and 3 h.

^{1}H-NMR of the scale up with 10 mmol

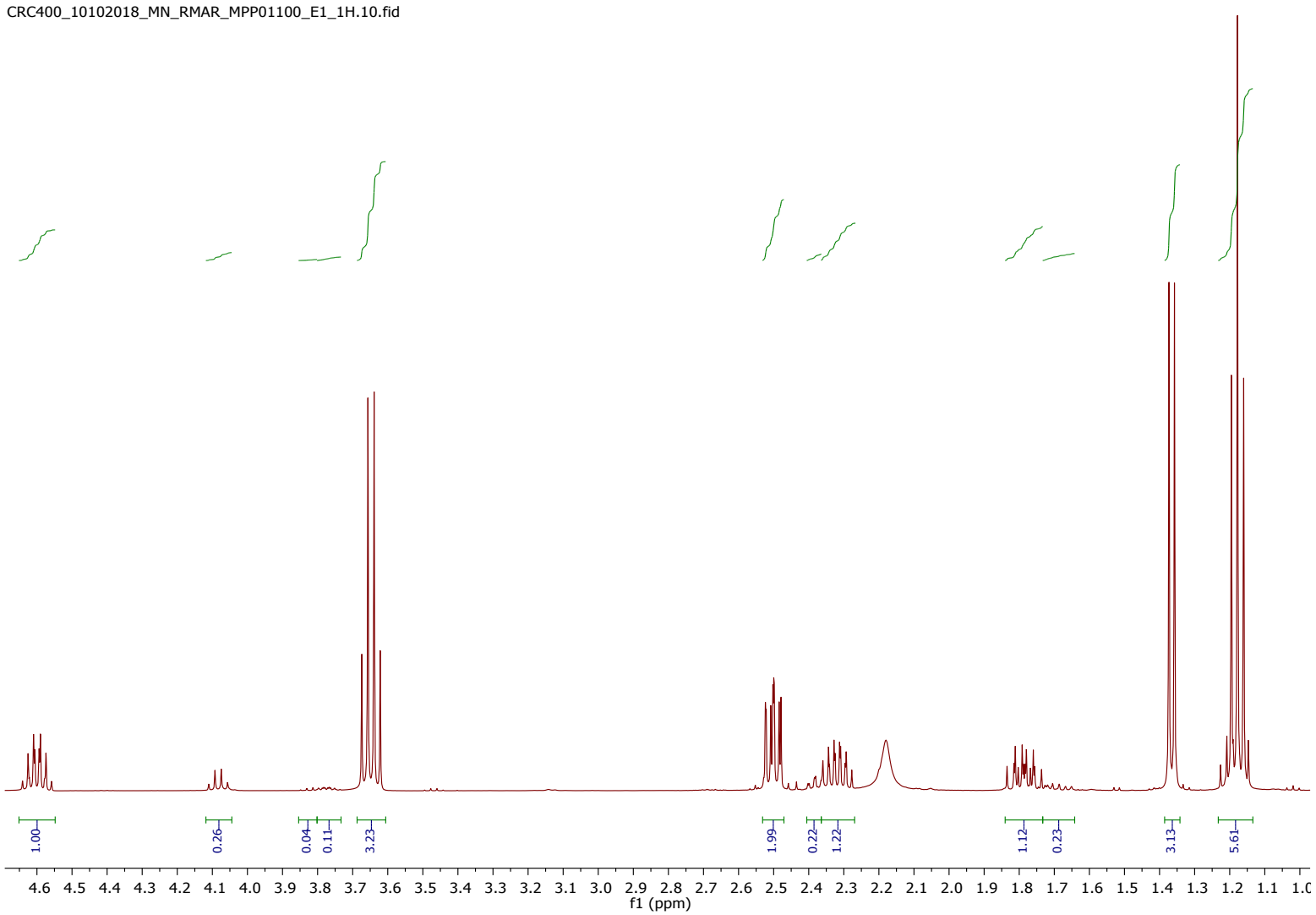


Figure 5. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru-1** (0.05 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 24 h.

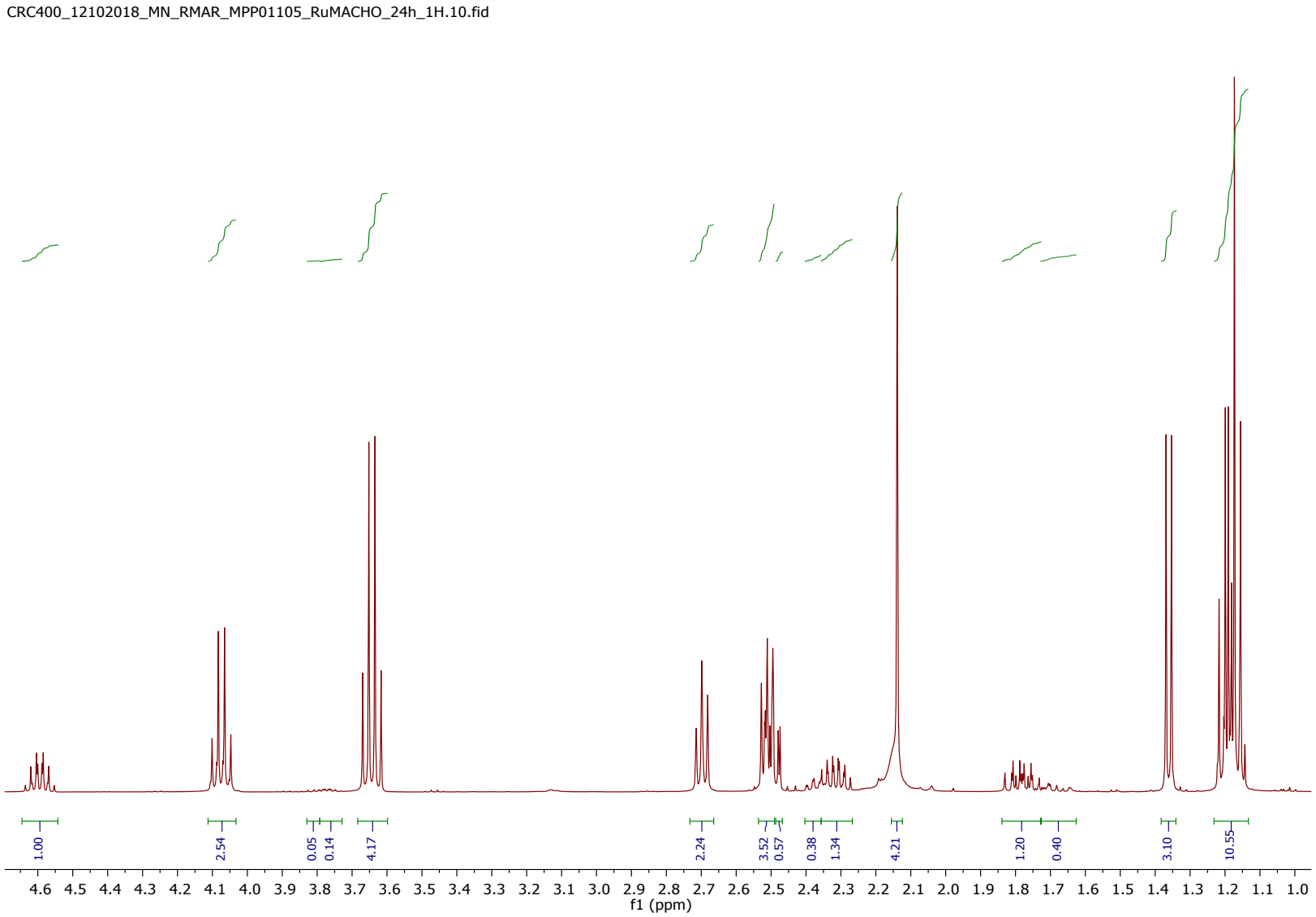


Figure 6. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru-1** (0.025 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 24 h.

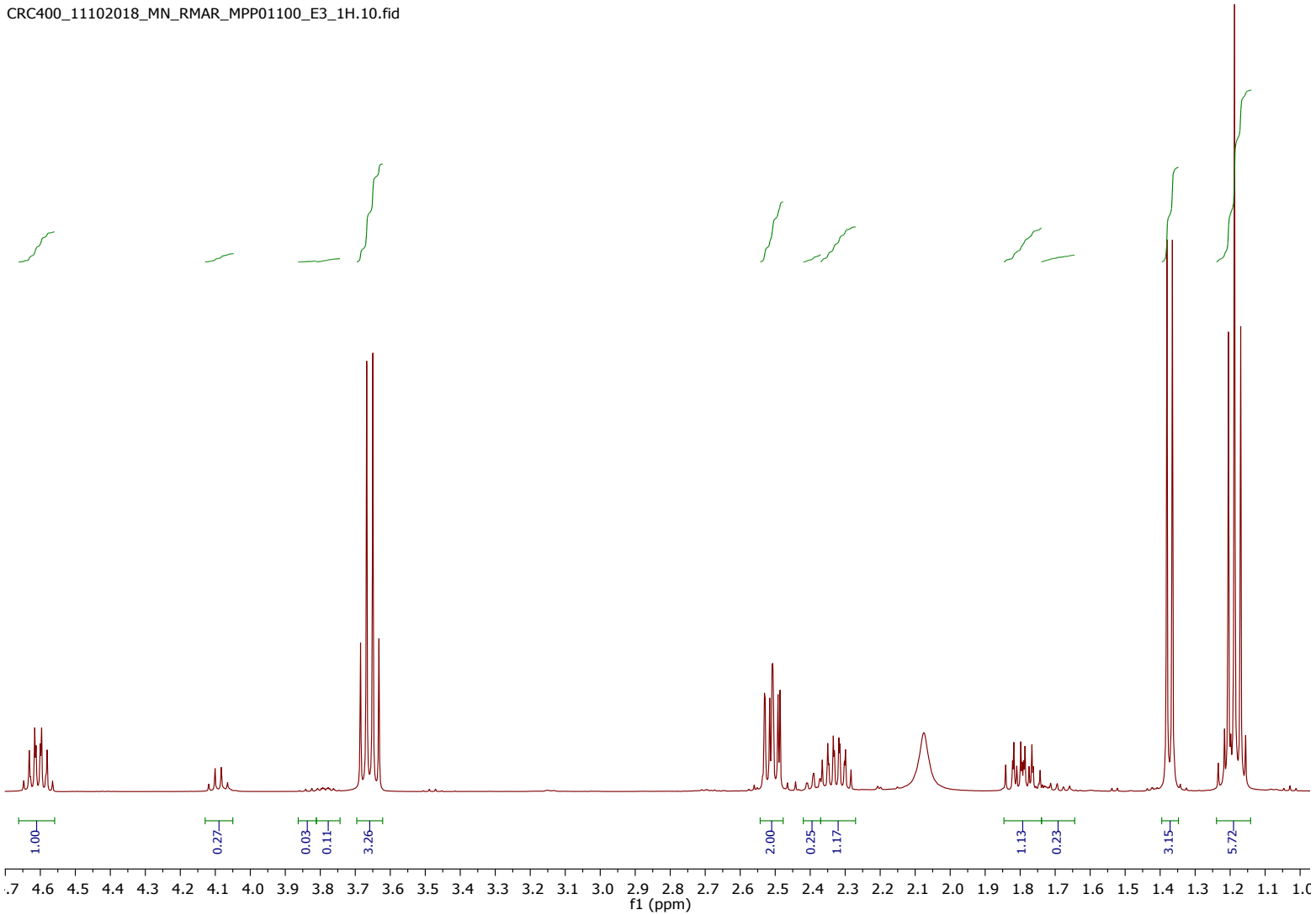


Figure 7. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru**-**1** (0.025 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 48 h.

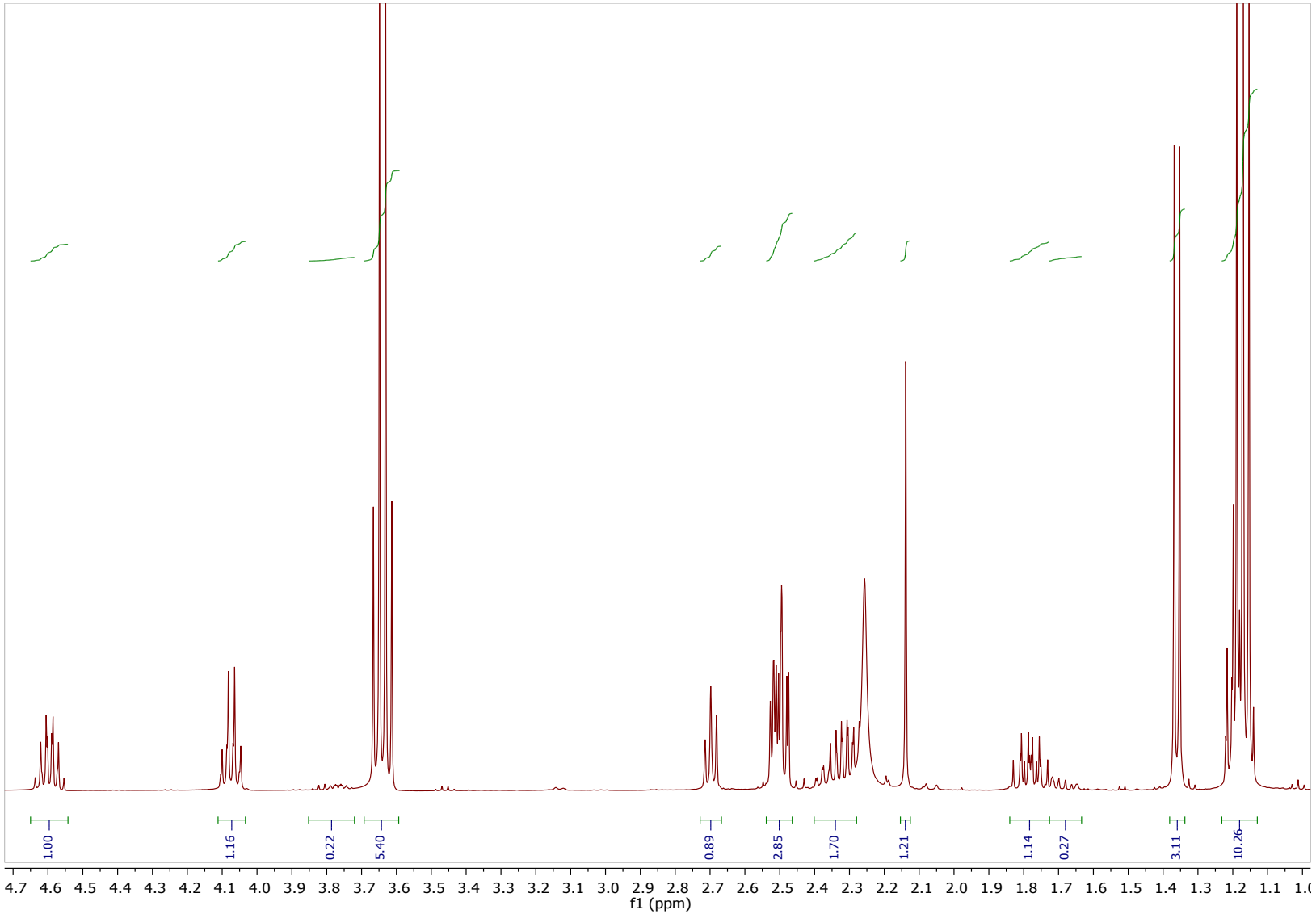


Figure 8. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru-1** (0.025 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.45 mL EtOH and 24 h.

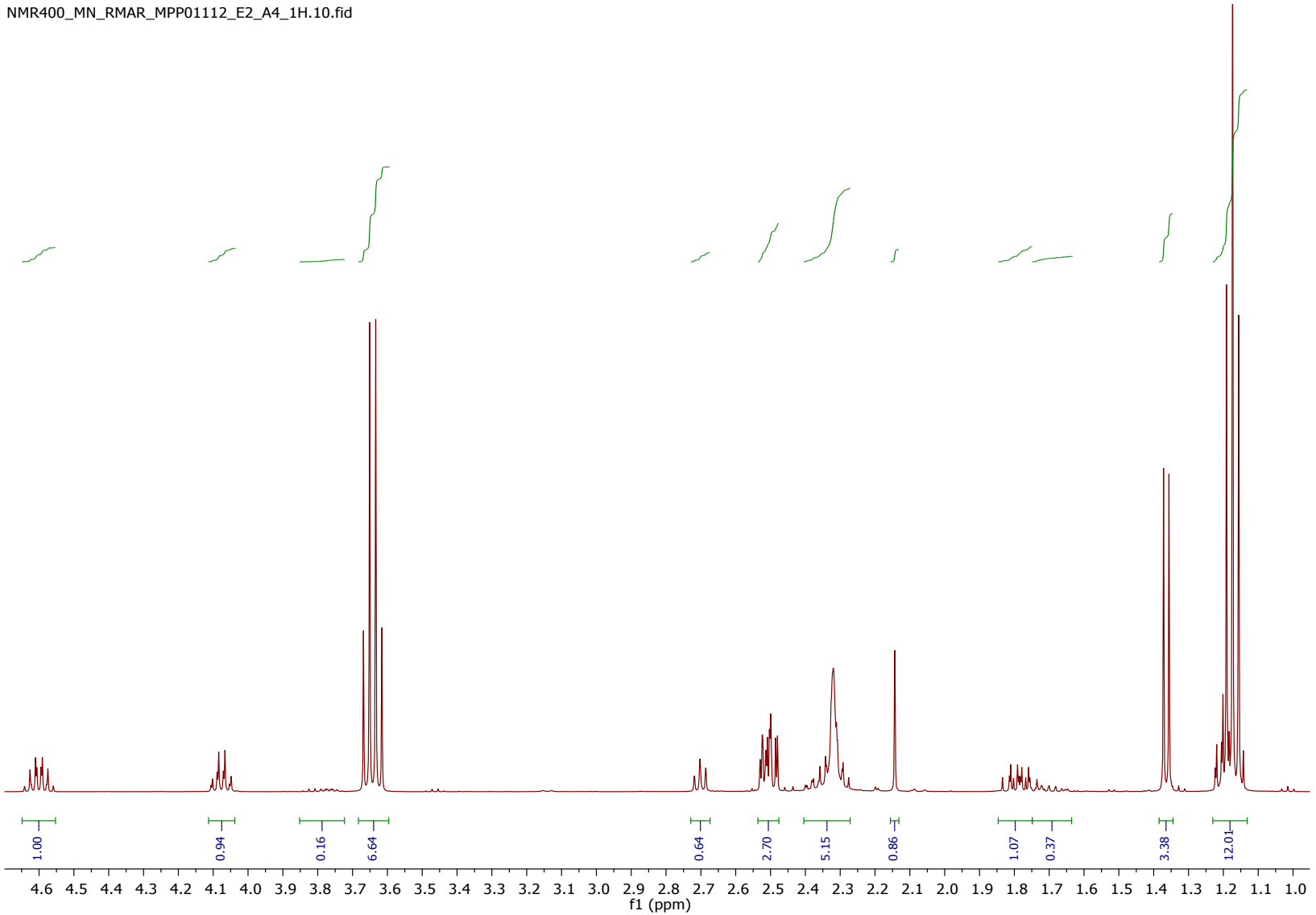


Figure 9. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru**-**1** (0.025 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.8 mL EtOH and 24 h.

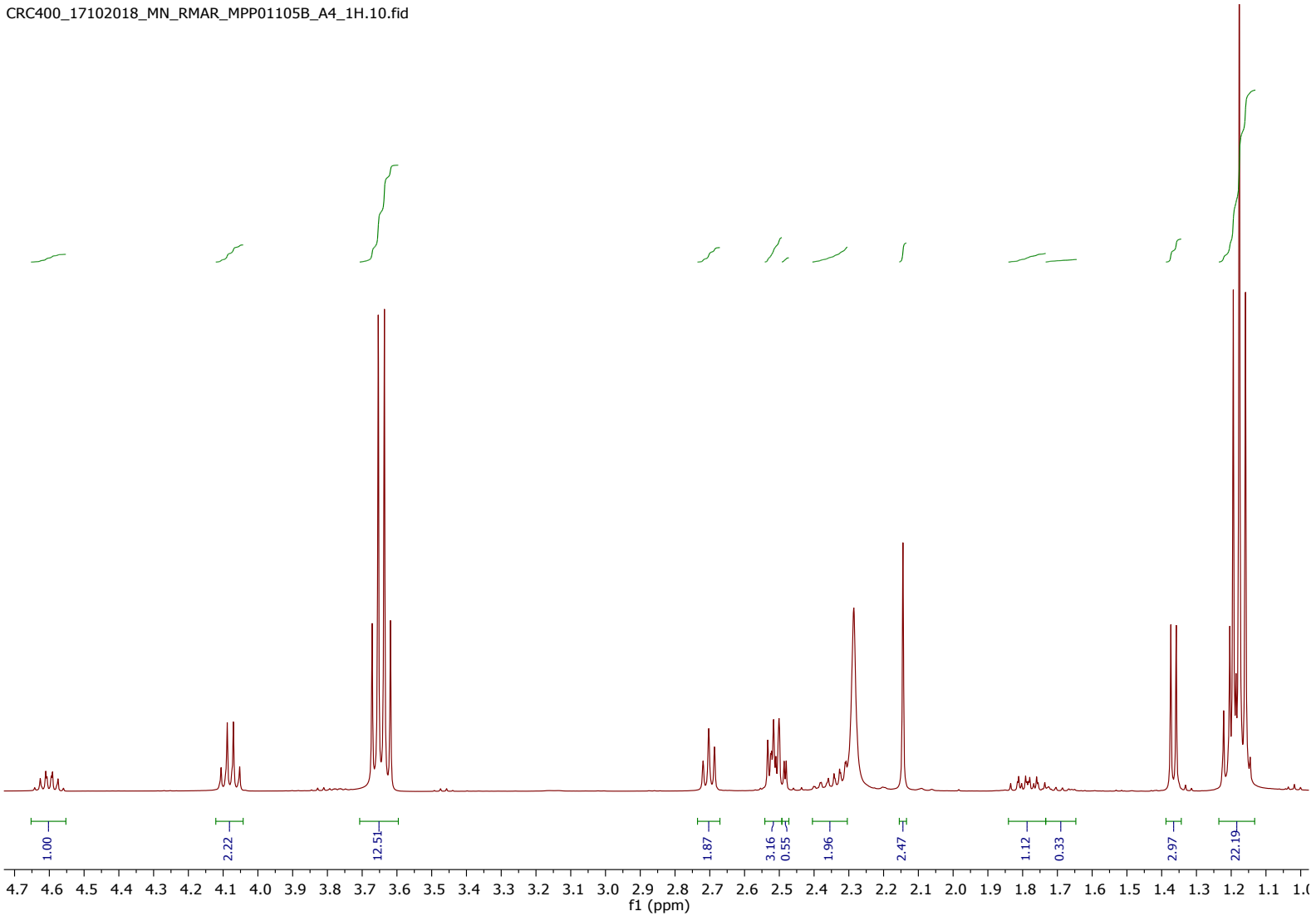


Figure 10. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru**-**1** (0.025 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 1.0 mL EtOH and 24 h.

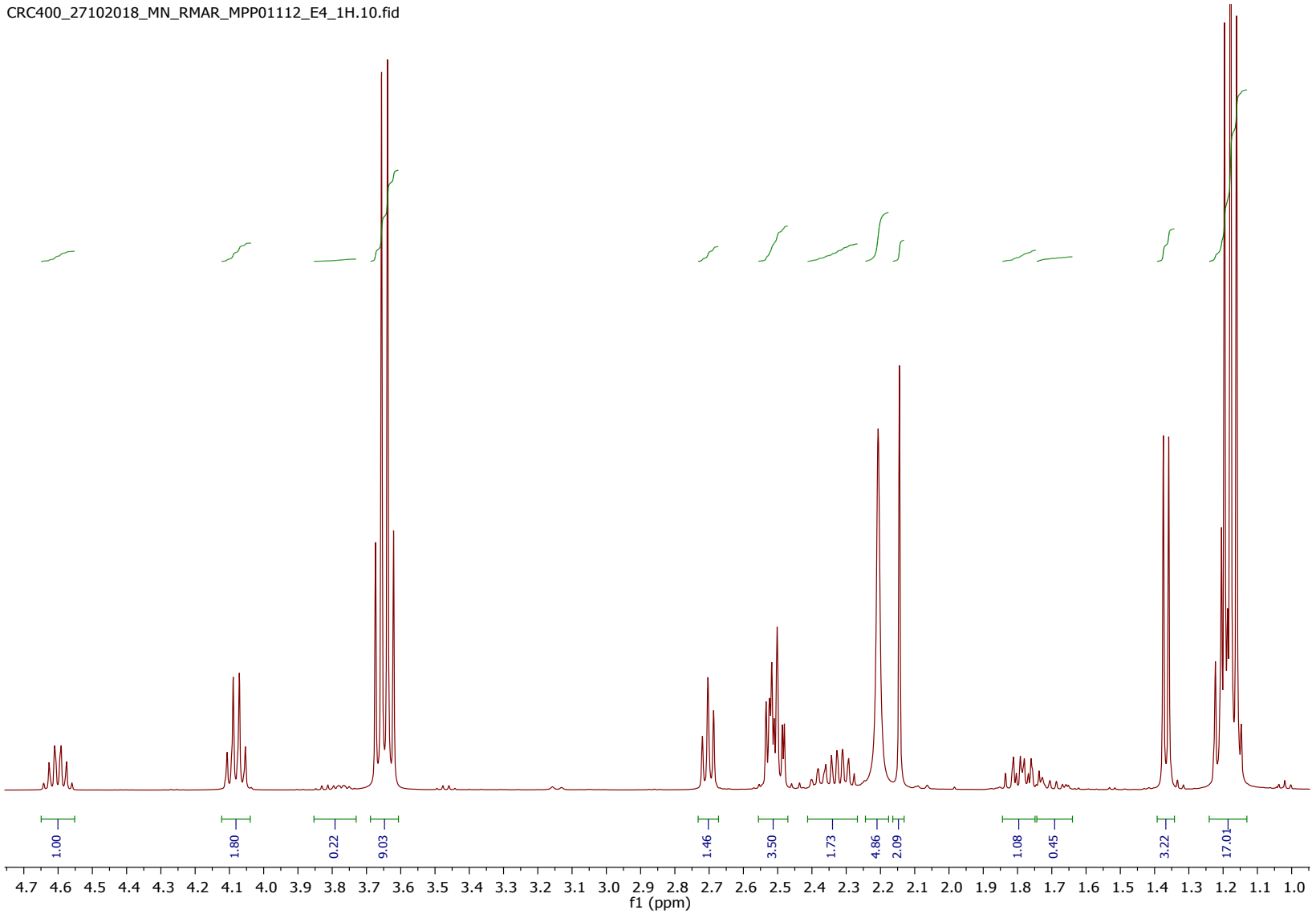


Figure 11. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru**-**1** (0.025 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 2.0 mL EtOH and 24 h.

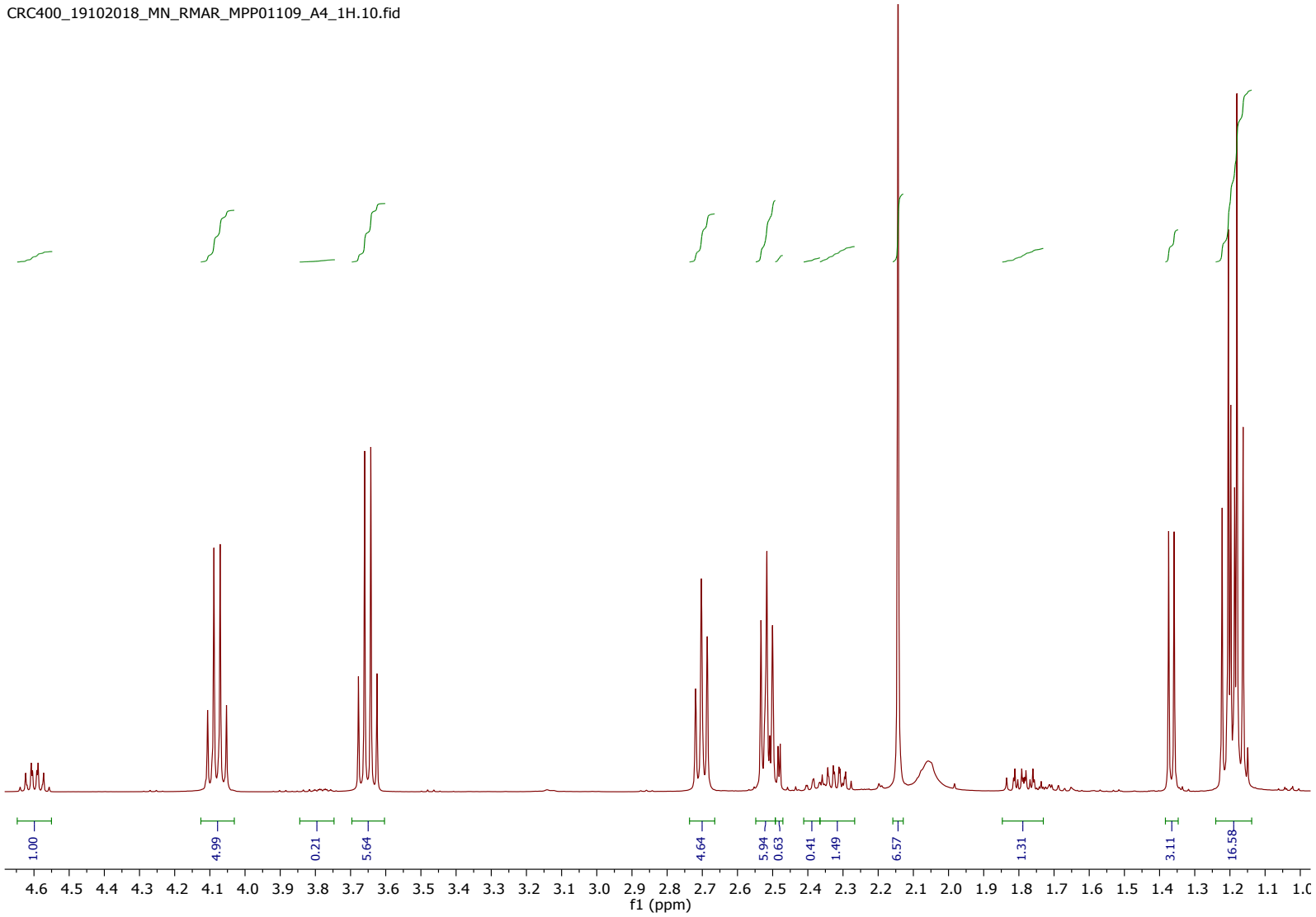


Figure 12. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru**-**1** (0.01 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 24 h.

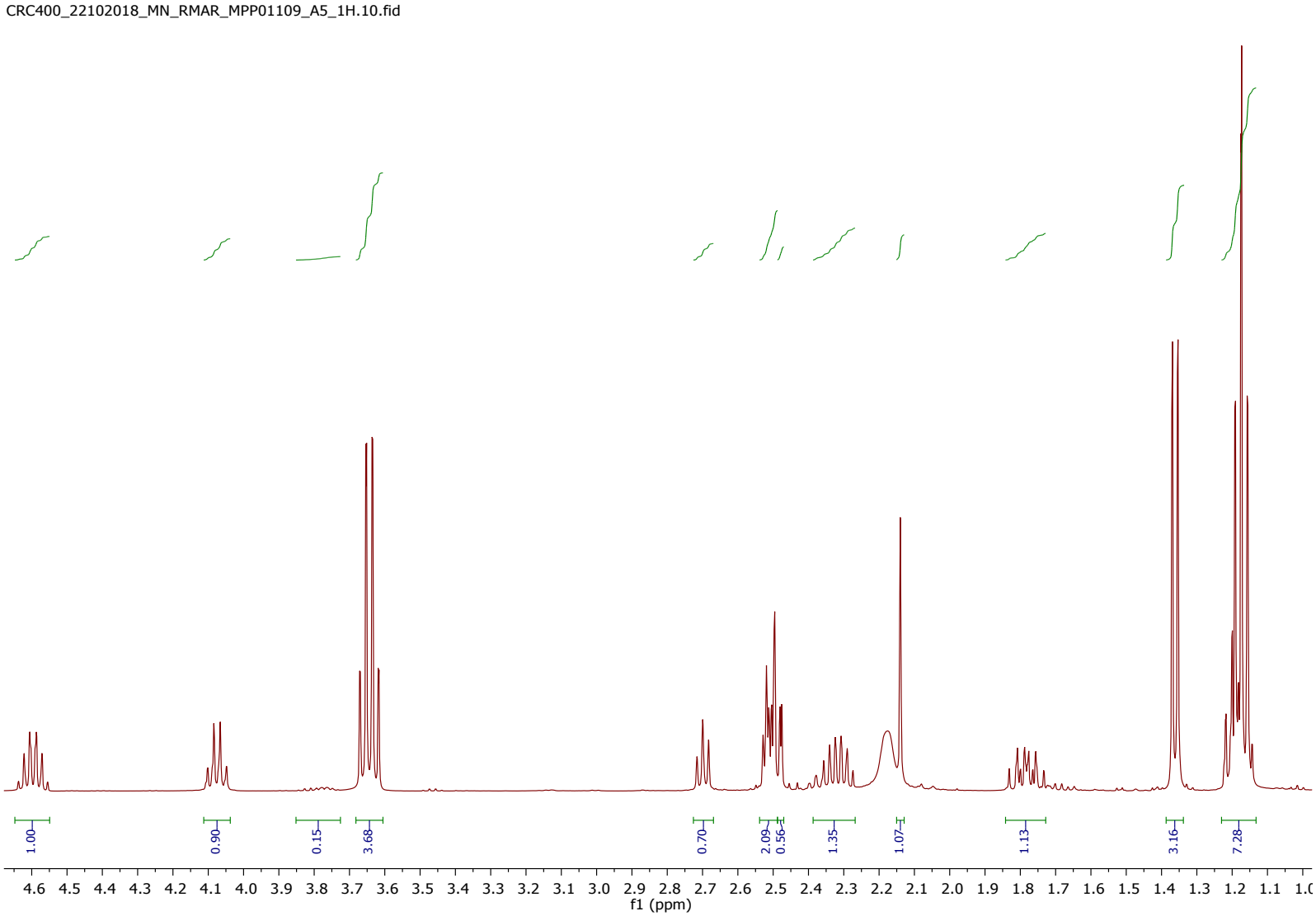


Figure 13. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru-1** (0.01 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 100 h.

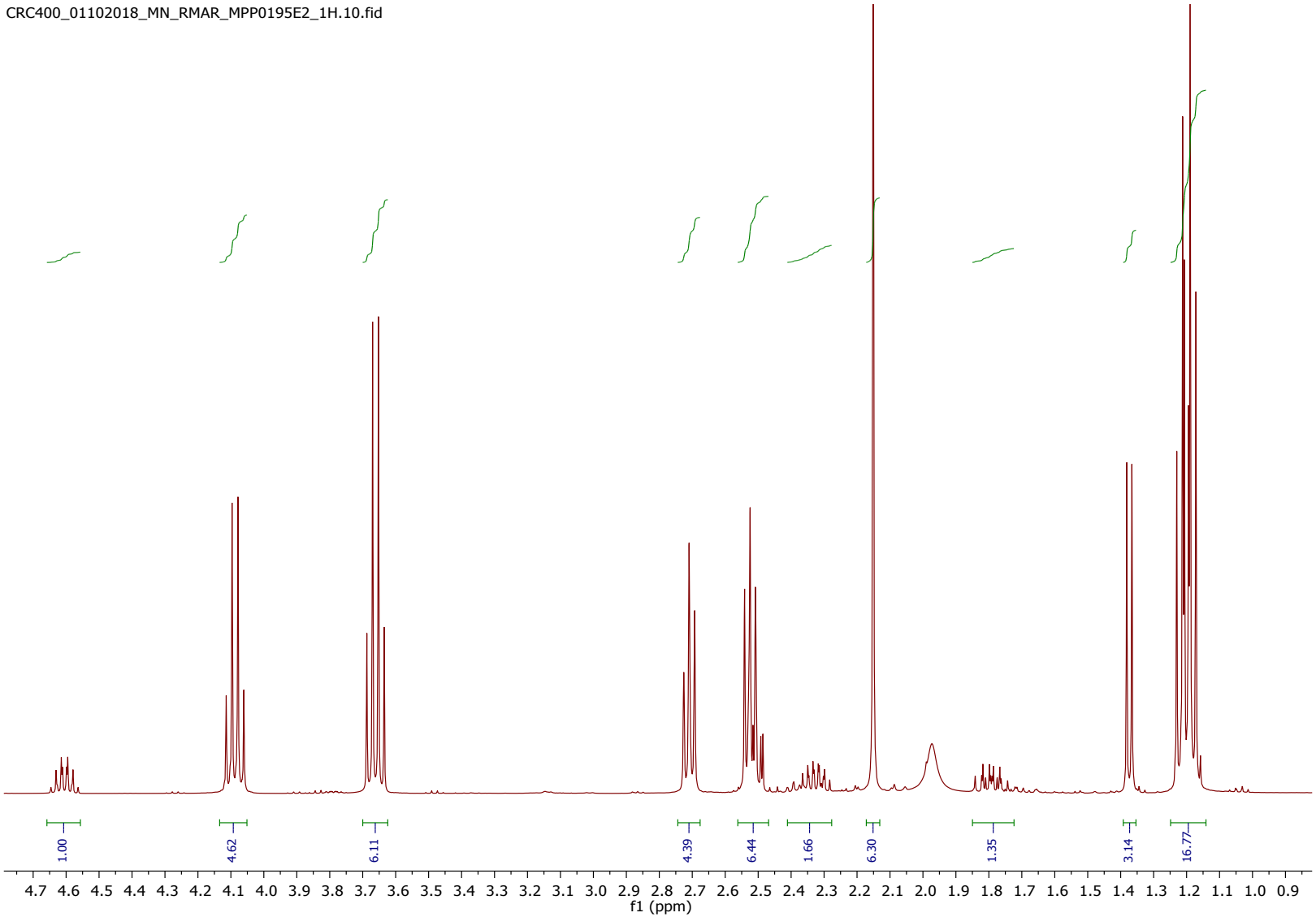


Figure 14. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru-4** (0.05 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 72 h.

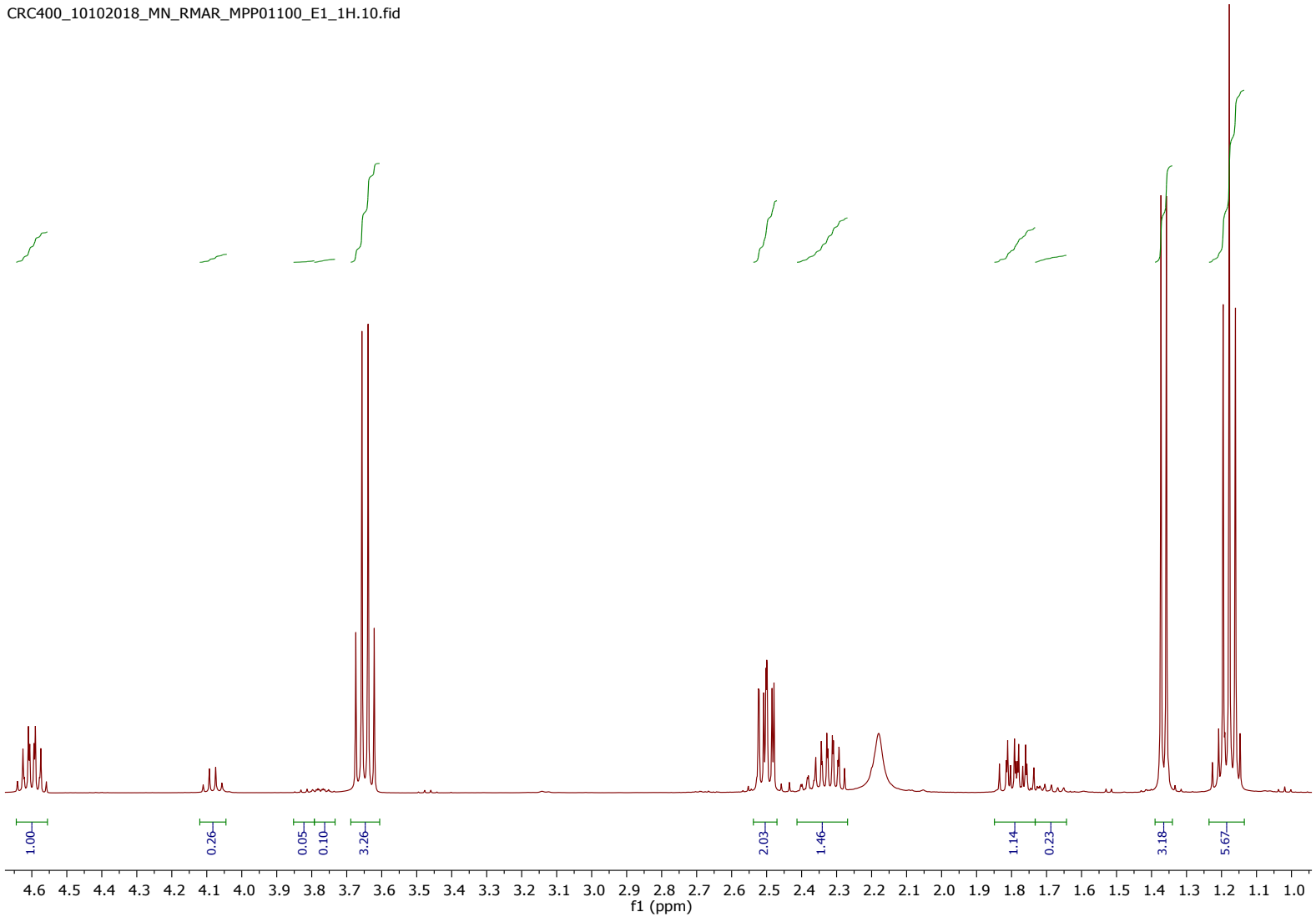


Figure 15. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ir-1** (0.05 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.8 mL EtOH and 24 h.

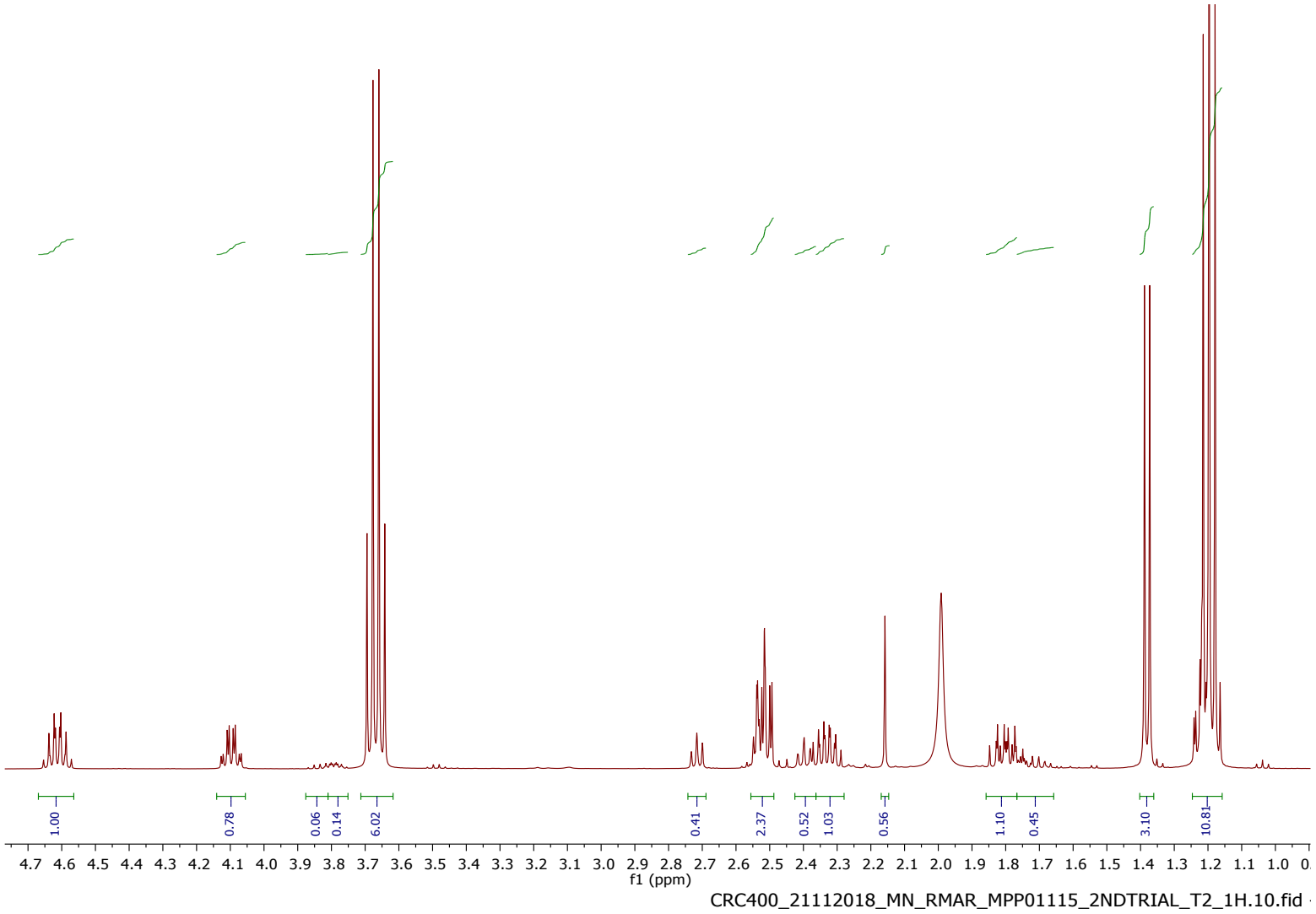


Figure 16. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ir-1** (0.05 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.8 mL EtOH and 3 h.

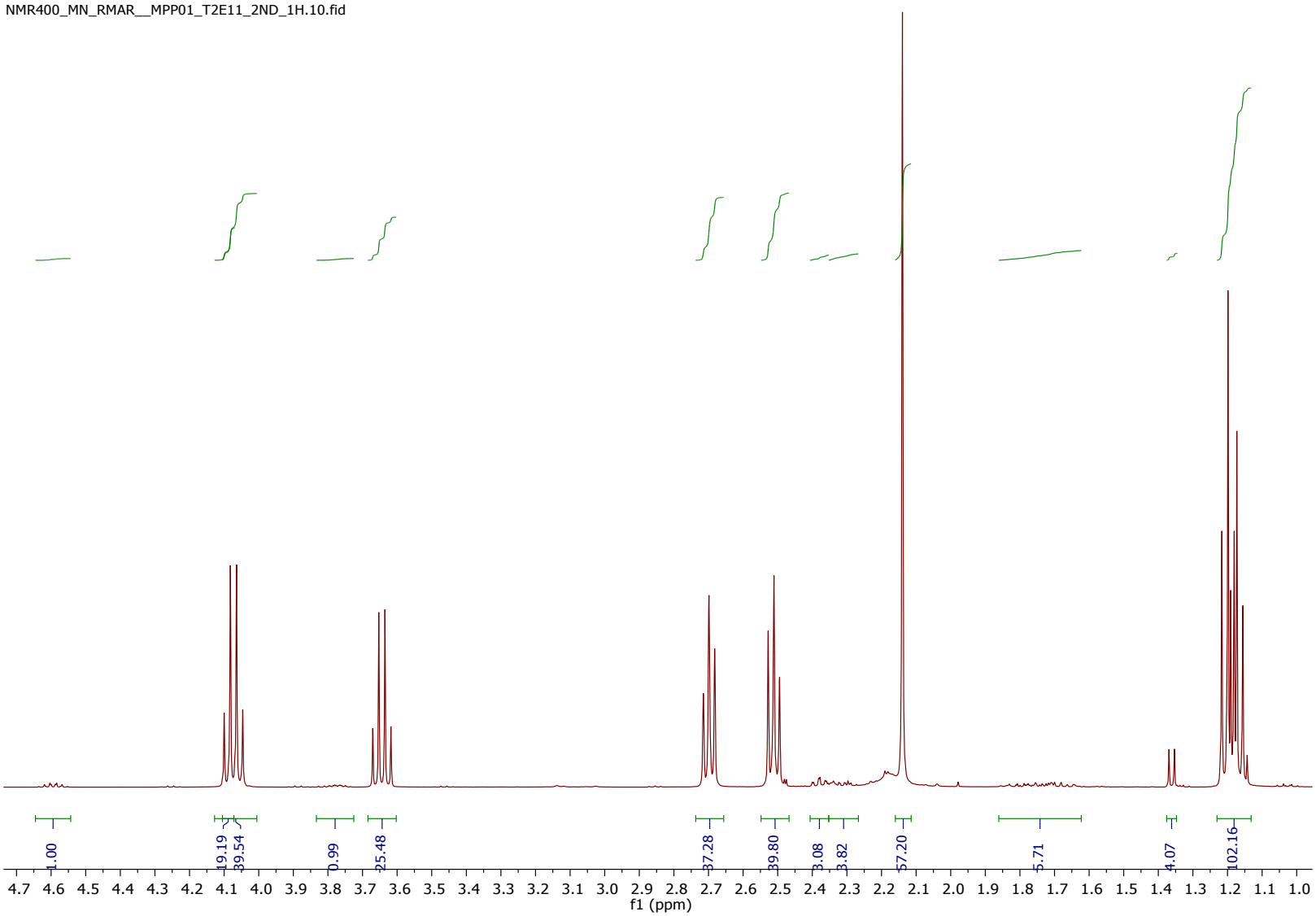


Figure 17. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ir-1** (0.01 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 3 h.

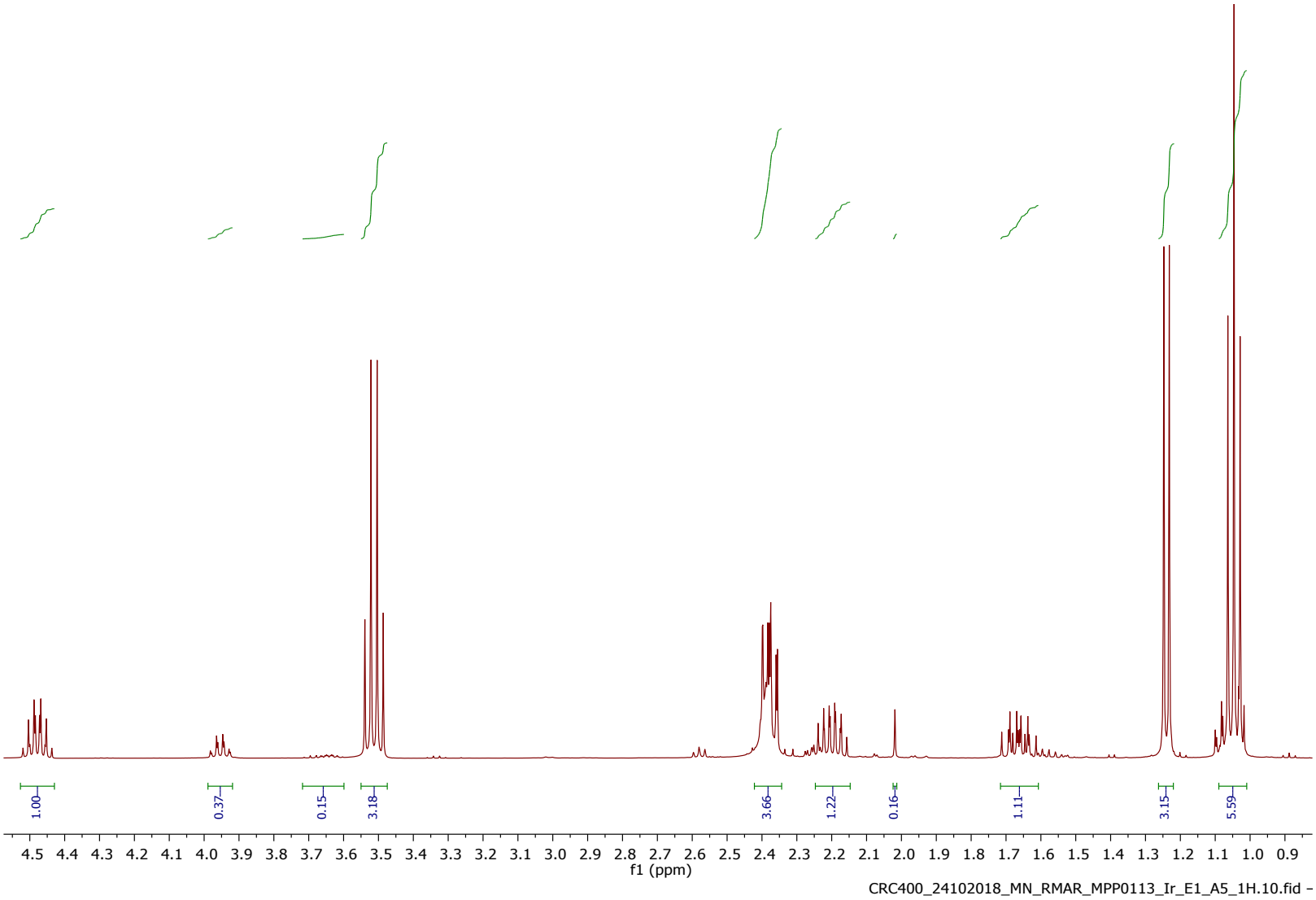


Figure 18. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ir-1** (0.01 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.25 mL EtOH and 24 h.

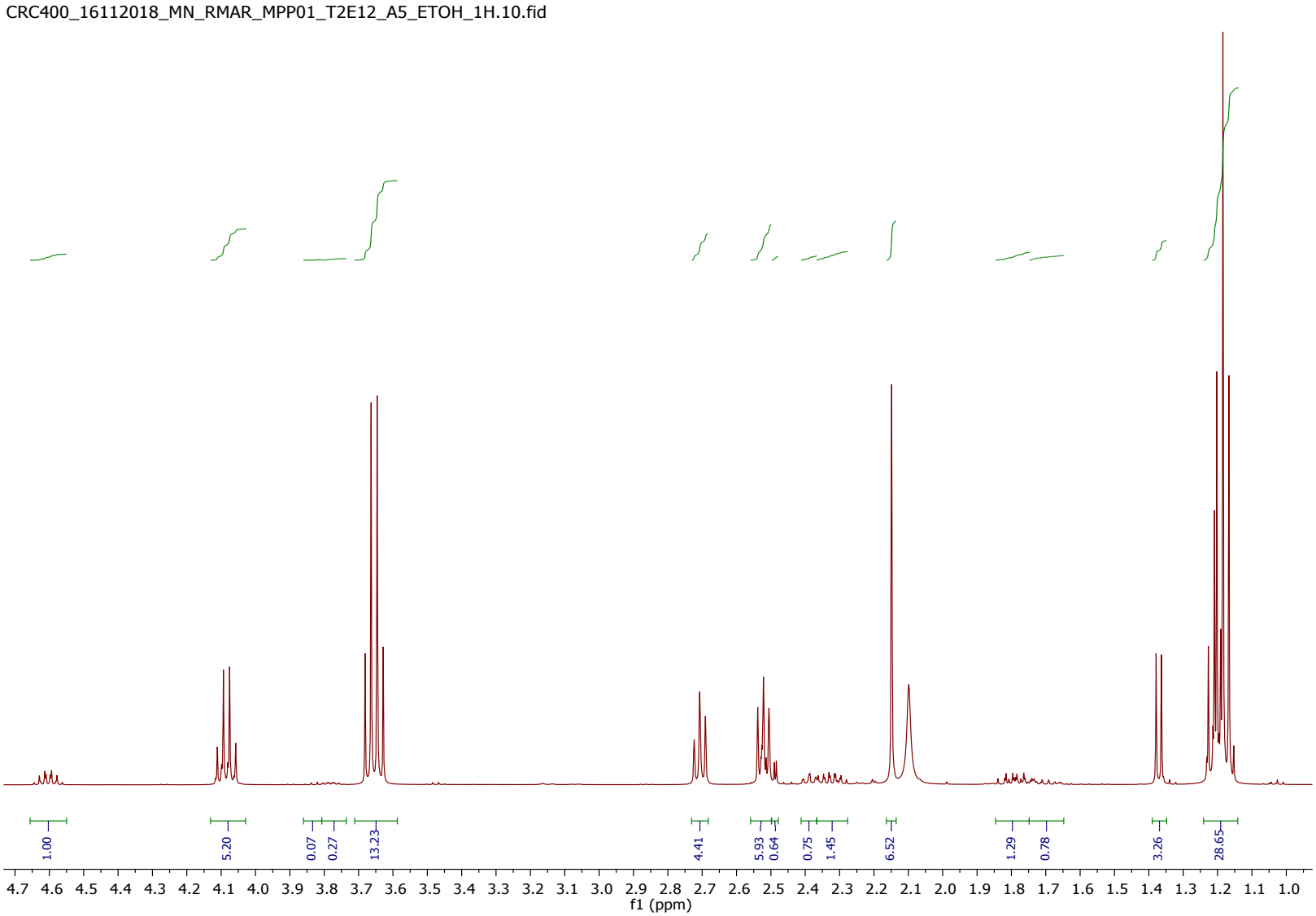


Figure 19. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ir-1** (0.01 mol%), NaOEt (5 mol%), 20 bar H_2, 60 °C, 0.8 mL EtOH and 3 h.

^{1}H-NMR of the scale up with 70 mmol

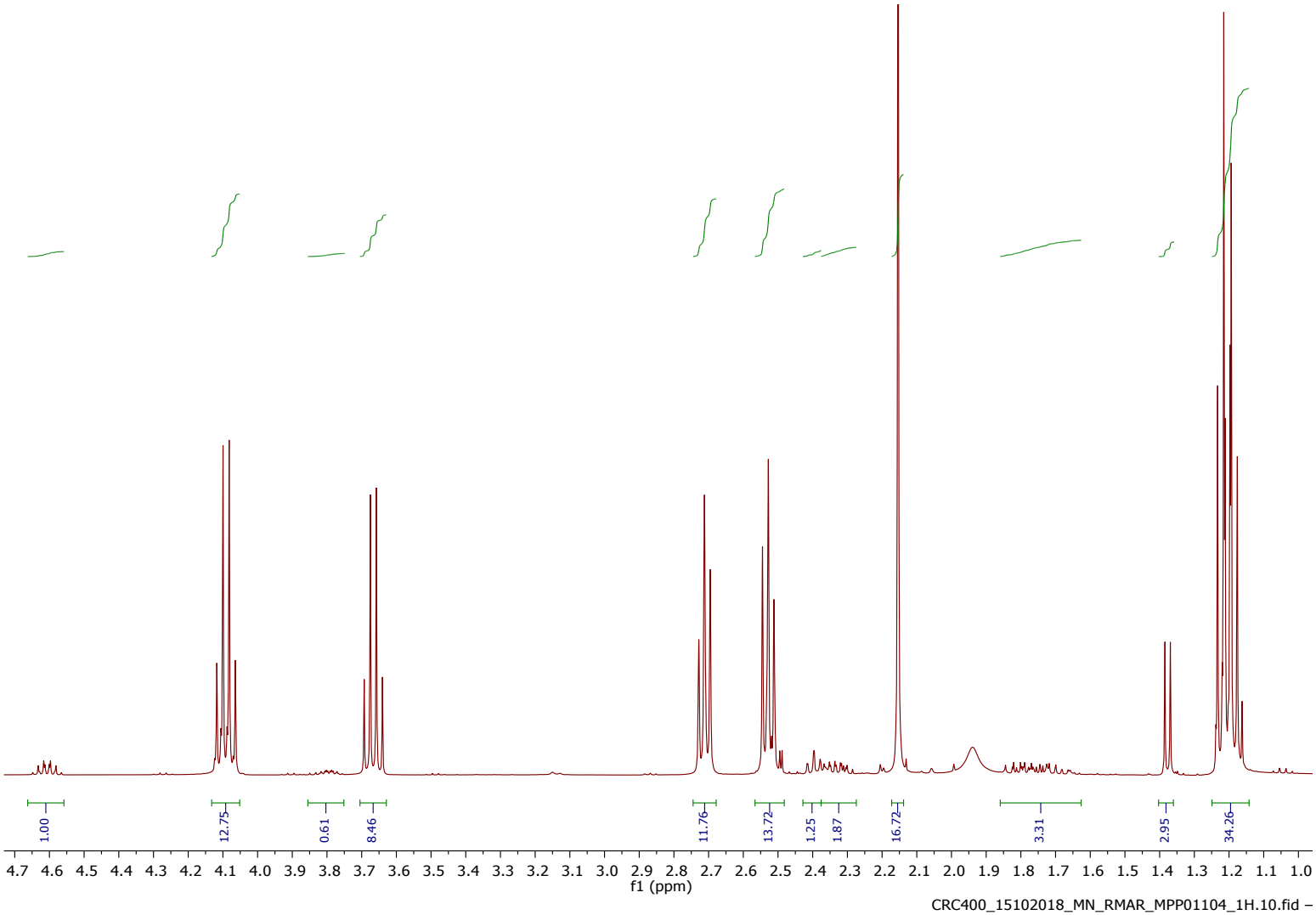


Figure 20. ^{1}H-NMR of the crude reaction of 70 mmol **1b** with **Ru-1** (0.05 mol%), NaOEt (5 mol%), 25 bar H_2, 25 °C, 1.75 mL EtOH and 72 h.

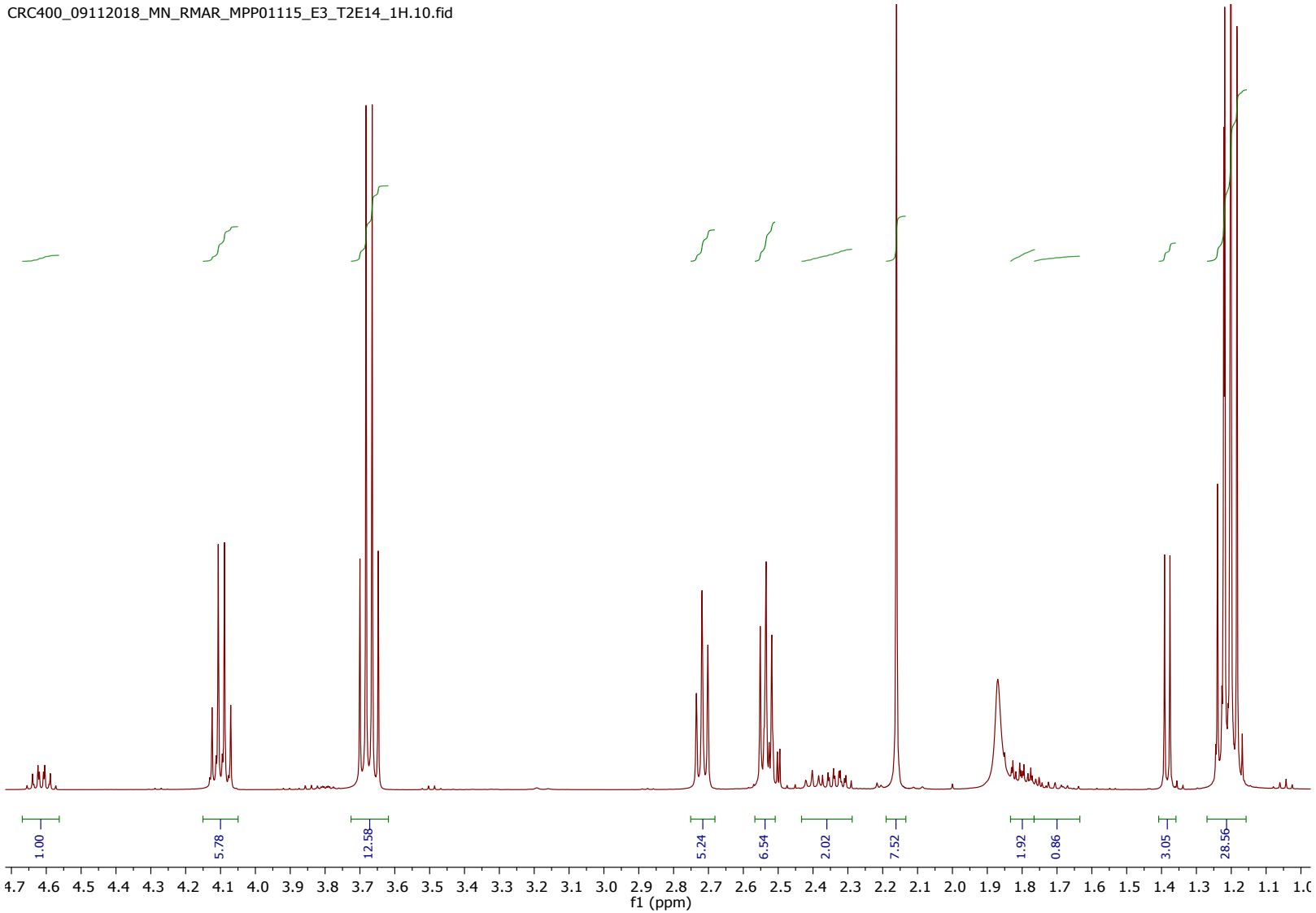


Figure 21. ^{1}H-NMR of the crude reaction of 70 mmol **1b** with **Ru-1** (0.05 mol%), NaOEt (5 mol%), 25 bar H_2, 25 °C, 5.6 mL EtOH and 72 h.

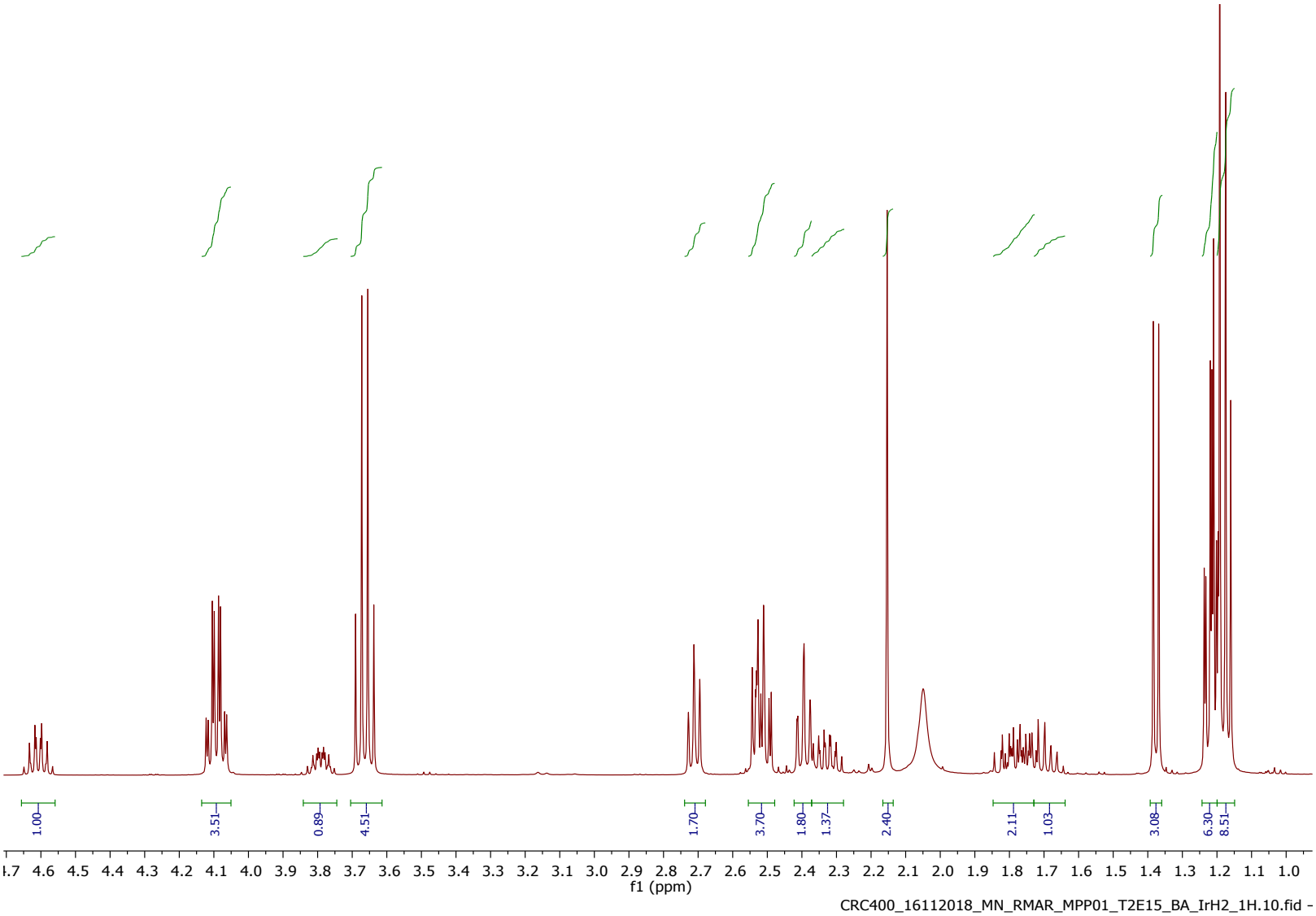


Figure 22. ^{1}H-NMR of the crude reaction of 70 mmol **1b** with **Ir-1** (0.05 mol%), NaOEt (5 mol%), 25 bar H_2, 25 °C, 1.75 mL EtOH and 48 h.

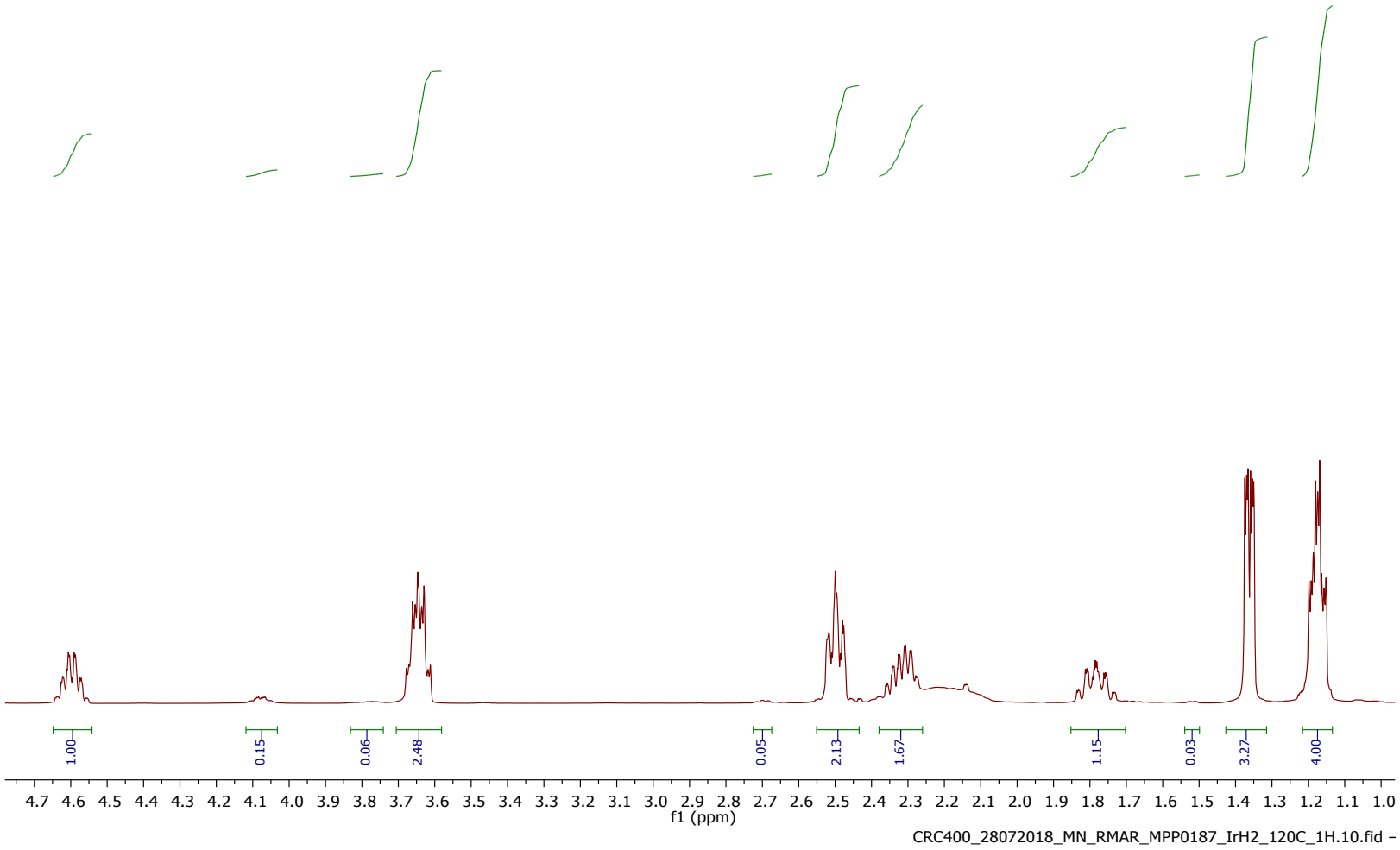


Figure 23. ^{1}H-NMR of the crude reaction of 70 mmol **1b** with **Ir-1** (0.05 mol%), NaOEt (5 mol%) , 25 bar H_2, 25 °C, 1.75 mL EtOH and 72 h.

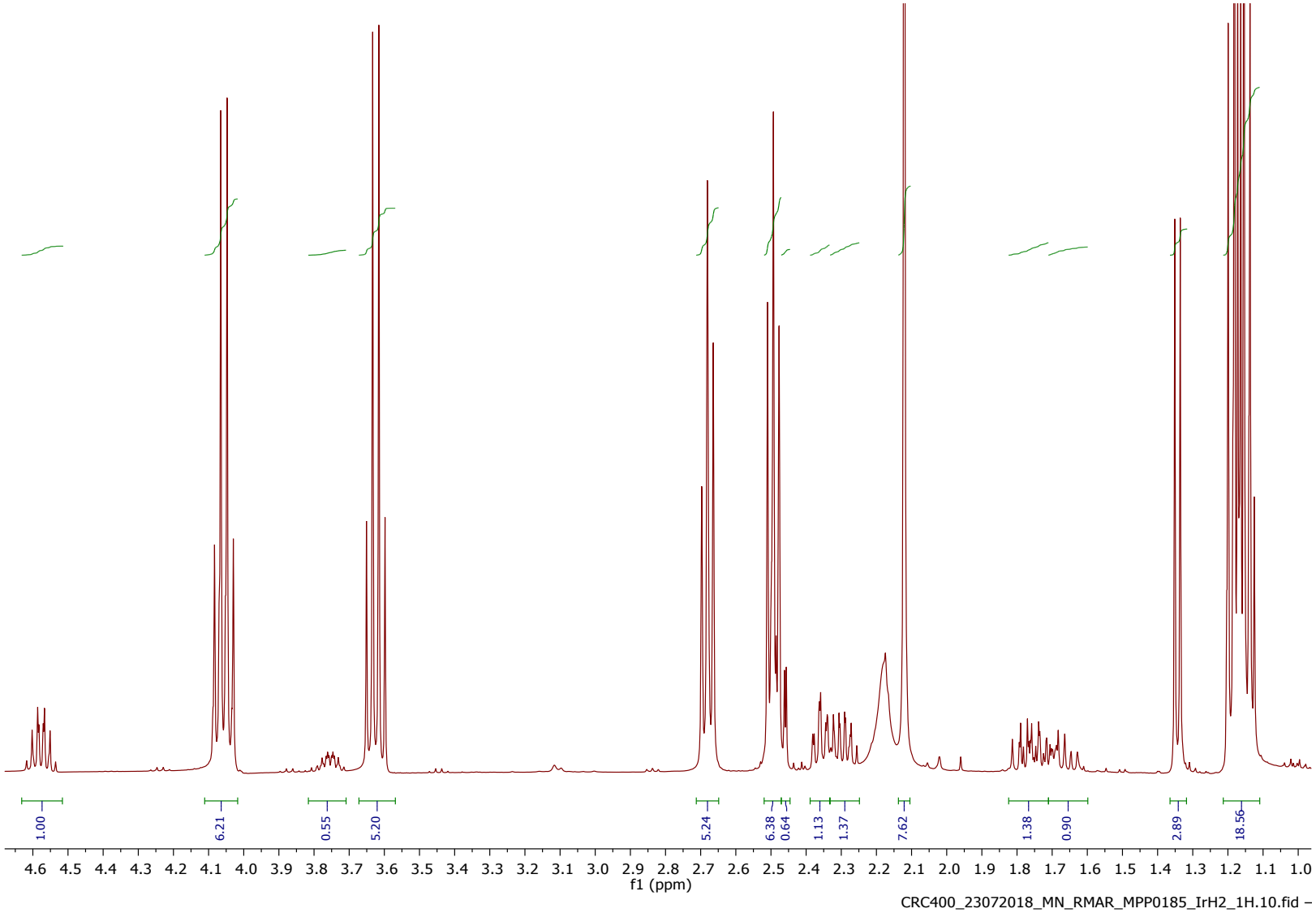


Figure 24. ^{1}H-NMR of the crude reaction of 70 mmol **1b** with **Ir-1** (0.01 mol%), NaOEt (5 mol%), 25 bar H_2, 25 °C, 1.75 mL EtOH and 72 h.

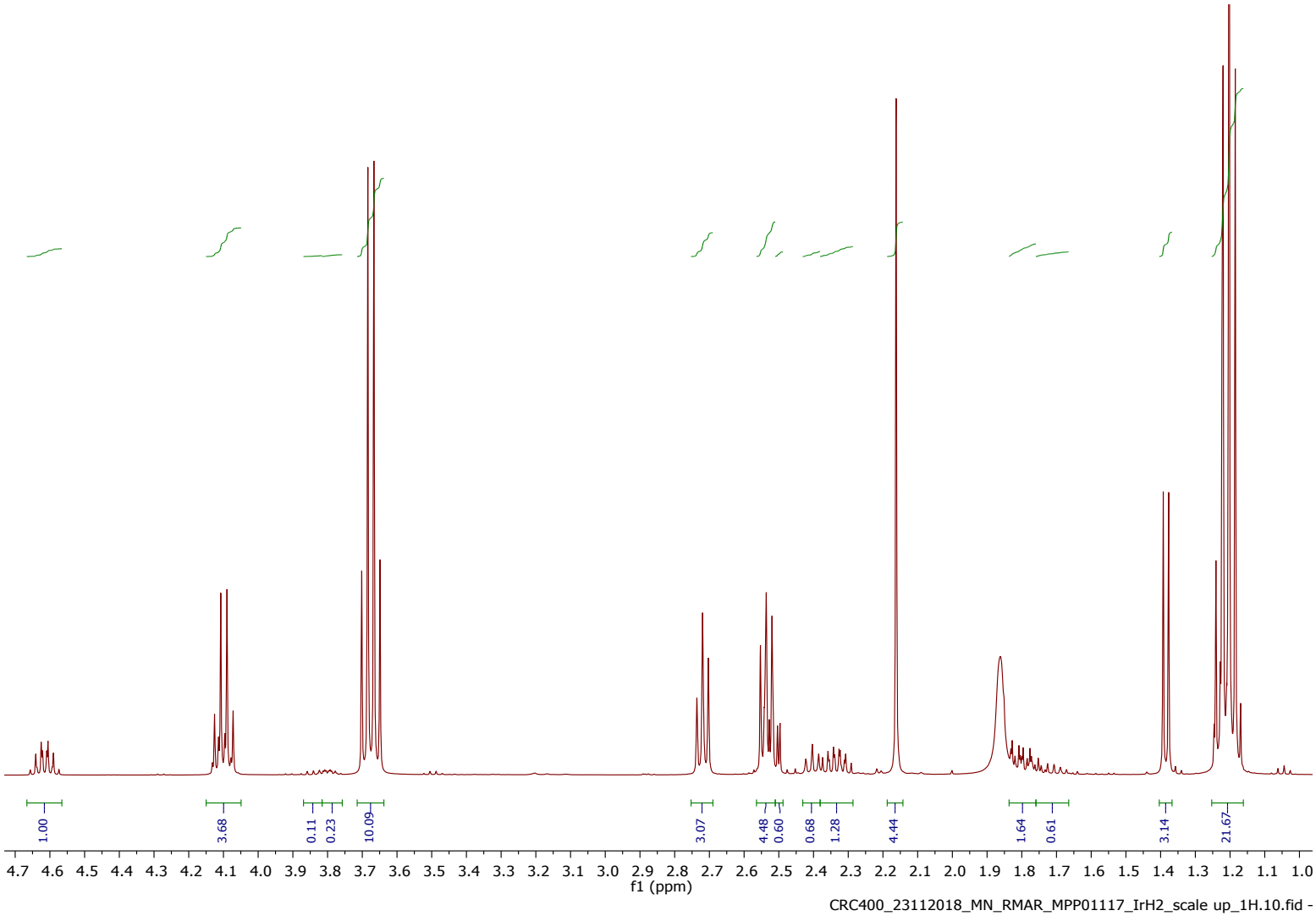


Figure 25. ^{1}H-NMR of the crude reaction of 70 mmol **1b** with **Ir-1** (0.01 mol%), NaOEt (5 mol%), 25 bar H_2, 25 °C, 5.60 mL EtOH and 72 h.

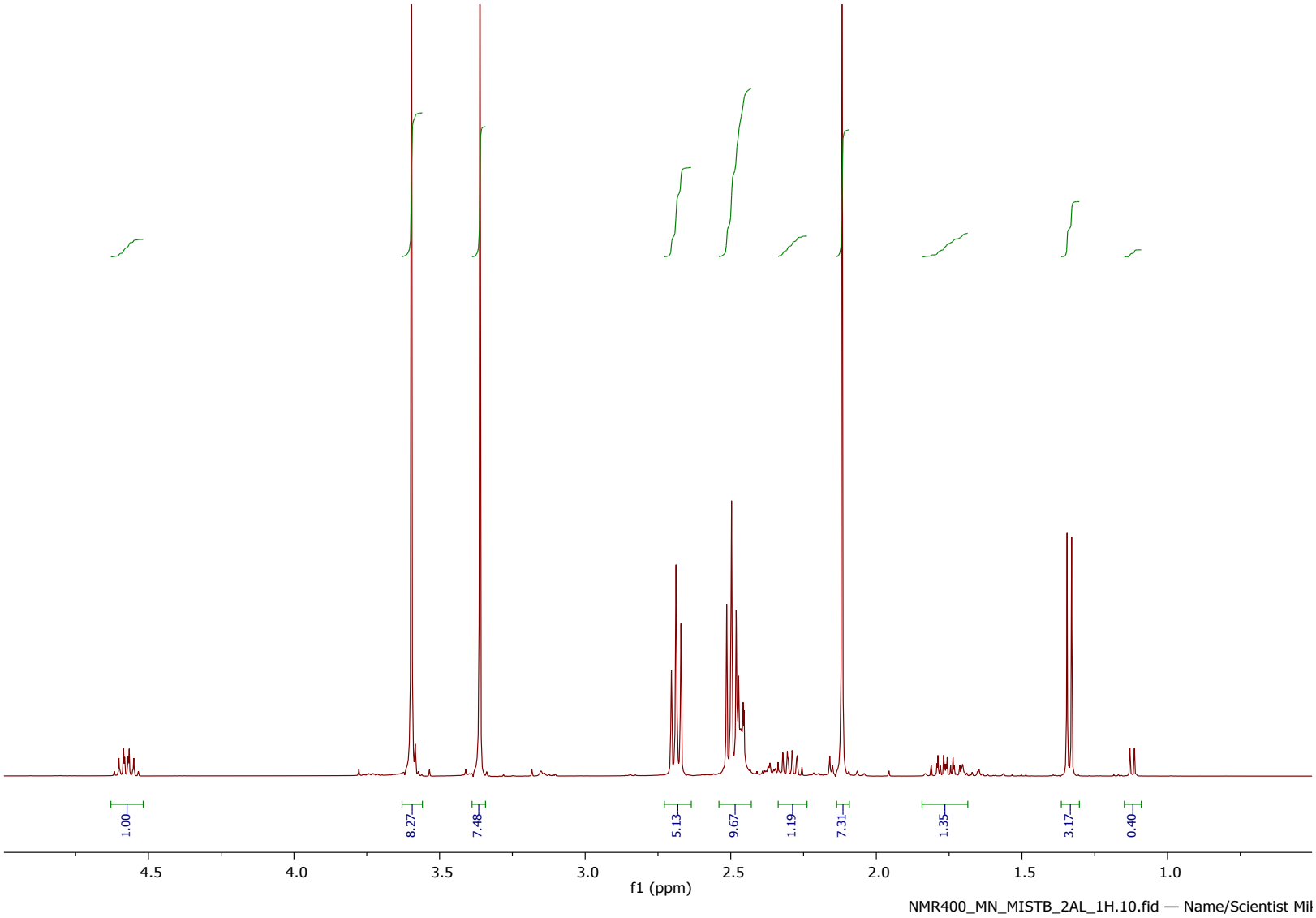


Figure 26. ^{1}H-NMR of the crude reaction of 40 mmol **1a** with **Ru-1** (0.05 mol%), NaOMe (5 mol%), 25 bar H_2, 25 °C, 0.45 mL MeOH and 72 h.

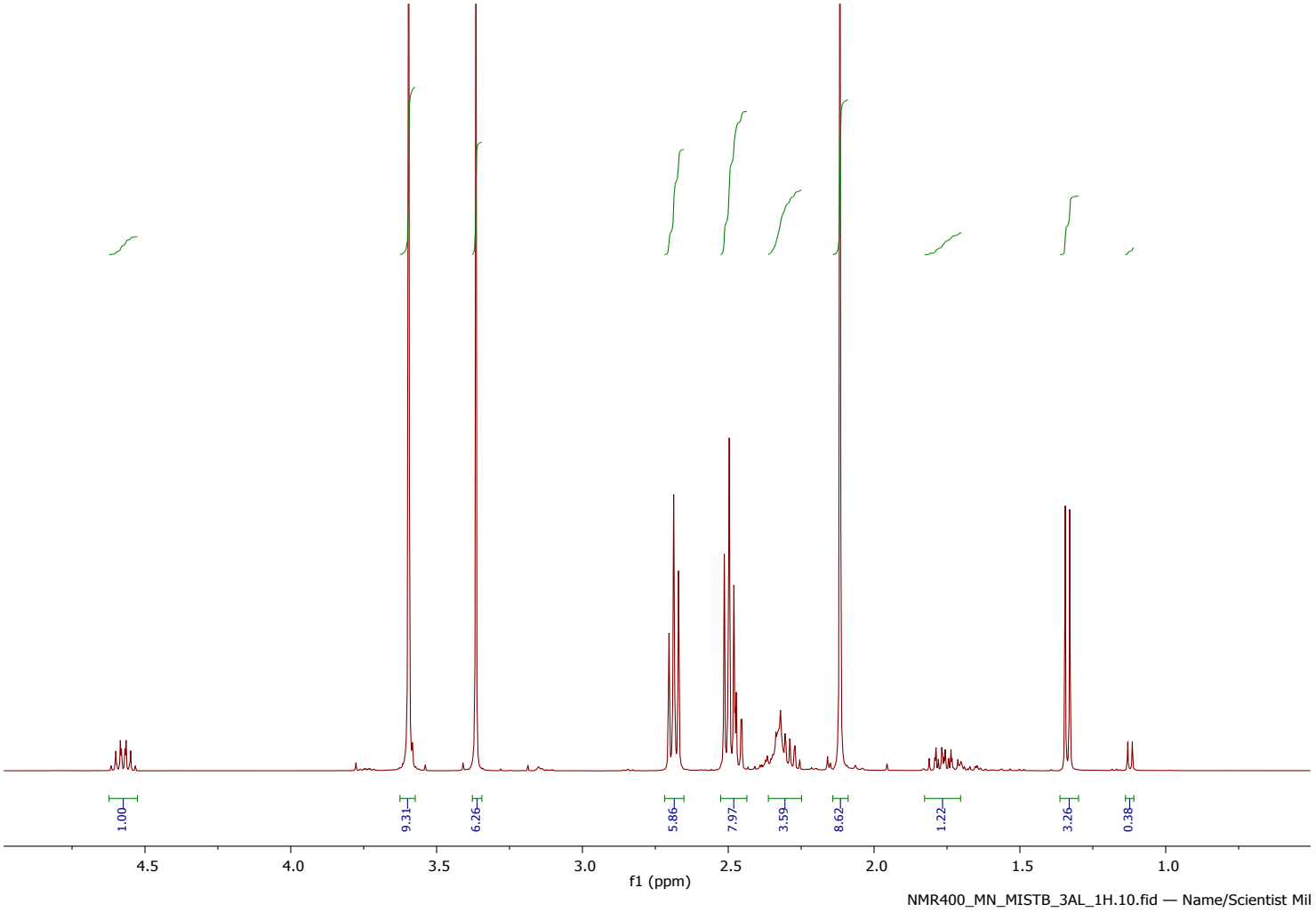


Figure 27. ^{1}H-NMR of the crude reaction of 40 mmol **1a** with **Ir-1** (0.01 mol%), NaOMe (5 mol%), 25 bar H_2, 25 °C, 0.45 mL MeOH and 72 h.

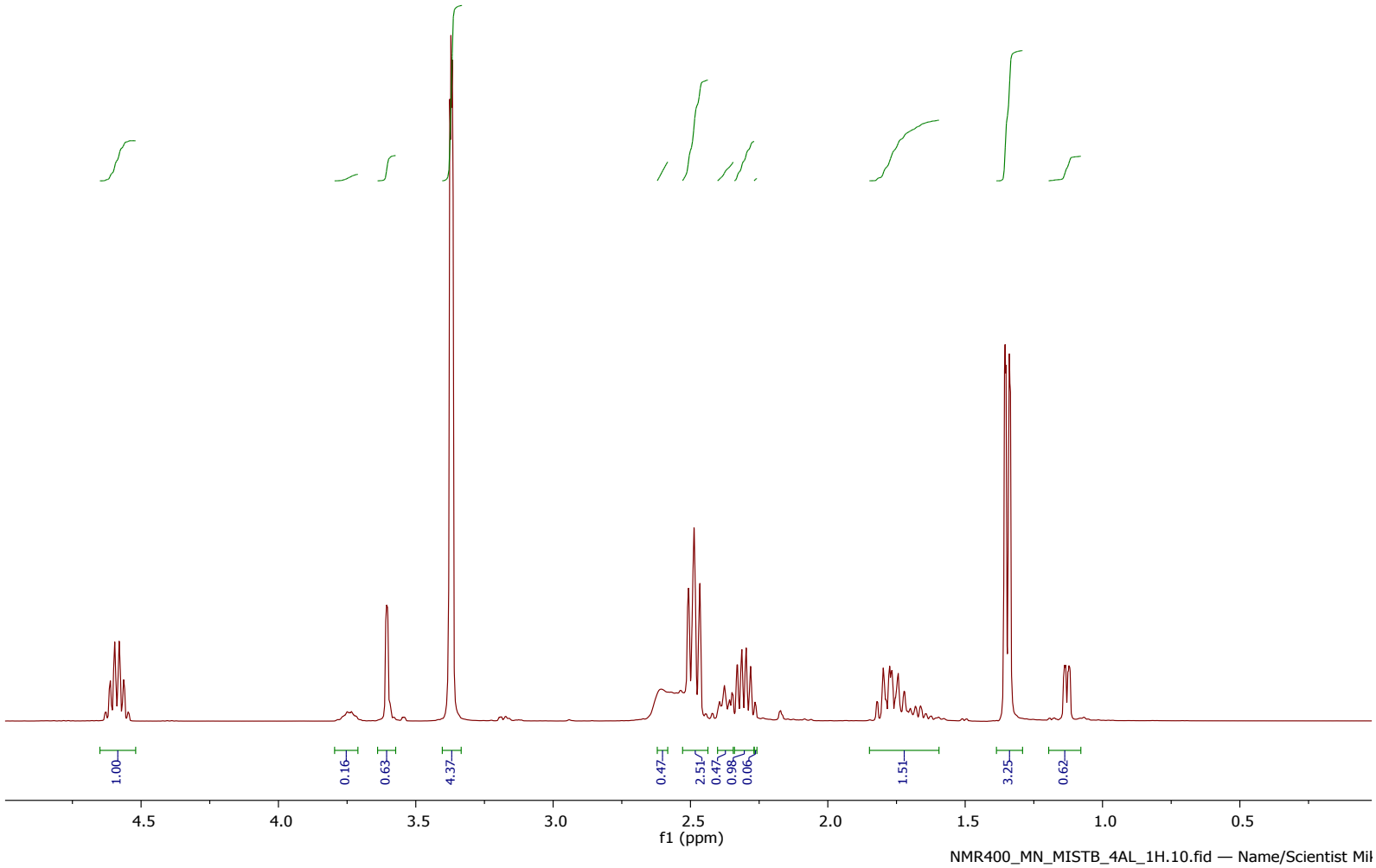


Figure 28. ^{1}H-NMR of the crude reaction 40 mmol of **1a** with **Ir-1** (0.05 mol%), NaOMe (5 mol%), 25 bar H_2, 25 °C, 0.45 mL MeOH and 72 h.

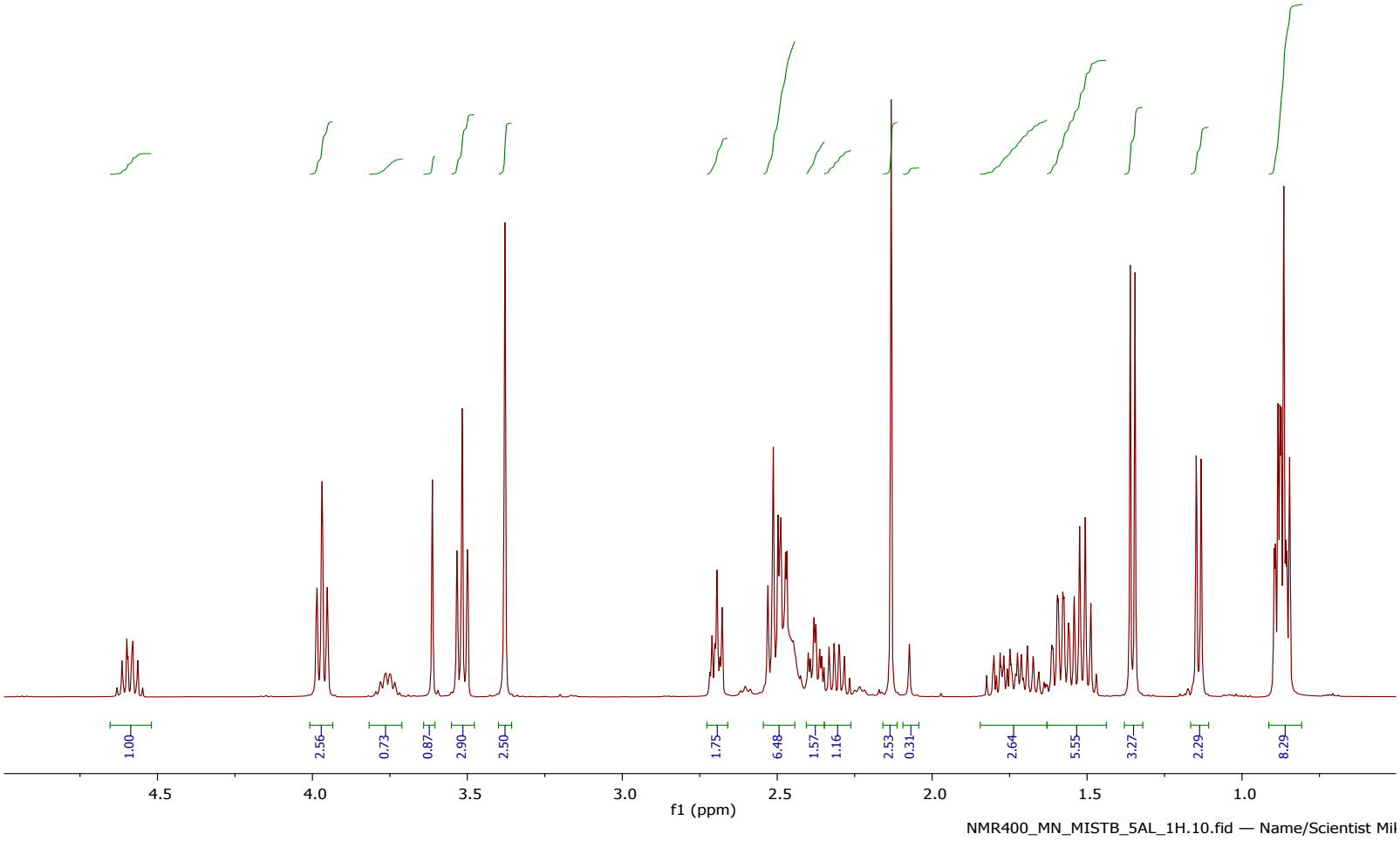


Figure 29. ^{1}H-NMR of the crude reaction 16 mmol of **1c** with **Ru-1** (0.1 mol%), NaOMe (5 mol%), 25 bar H_2, 25 °C, 0.17 mL MeOH and 72 h.

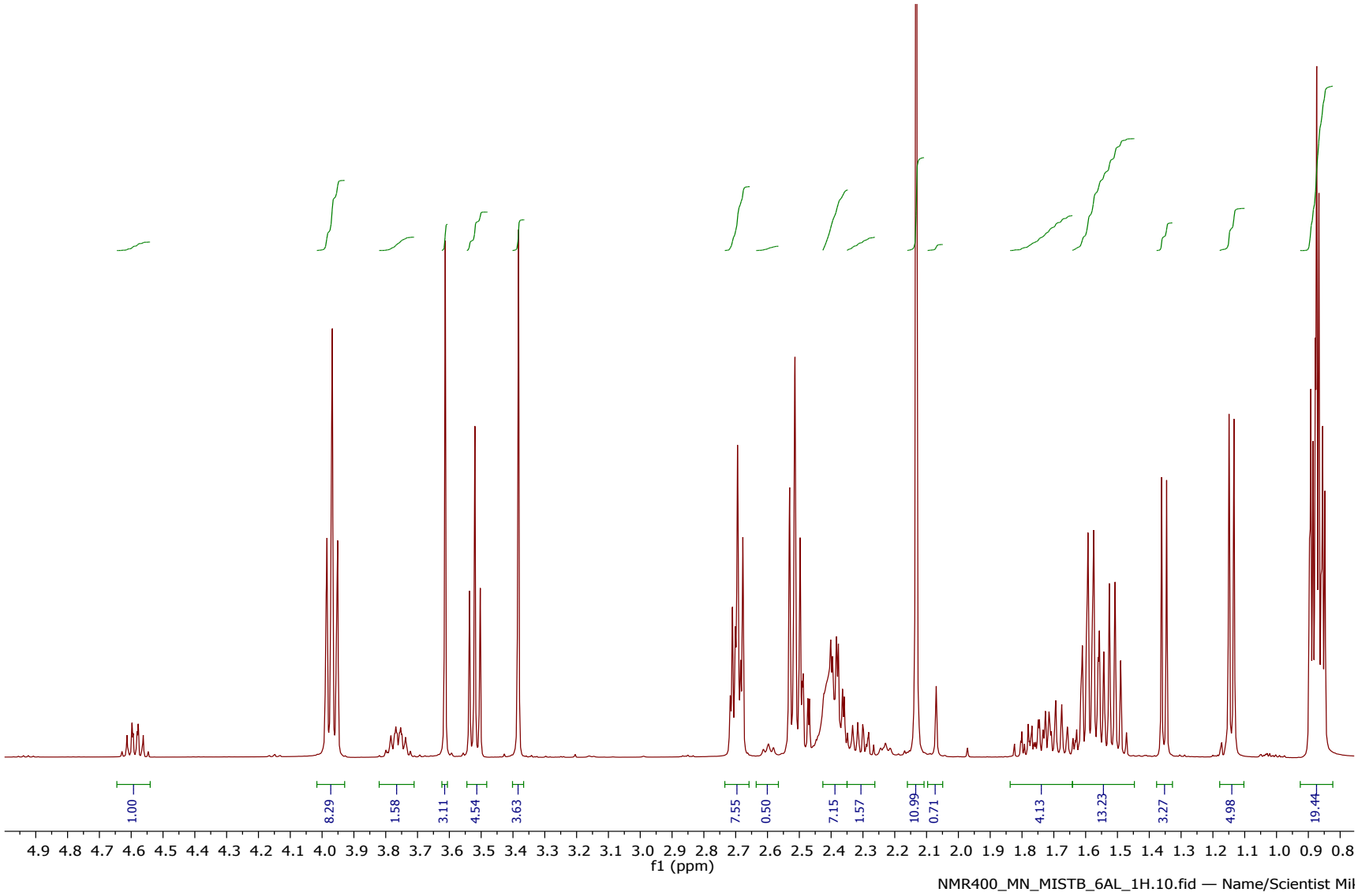
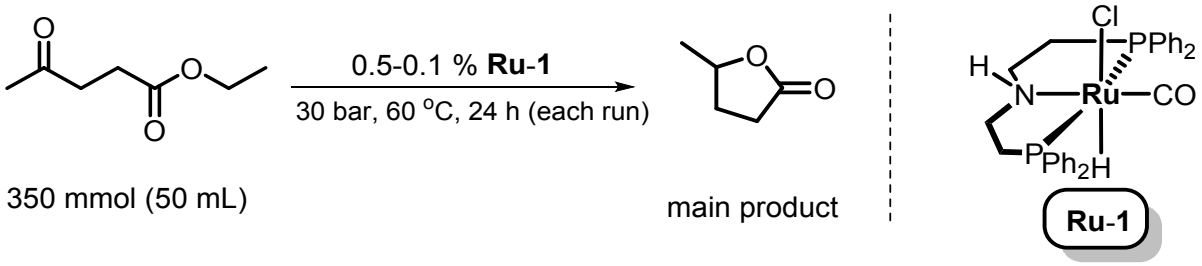
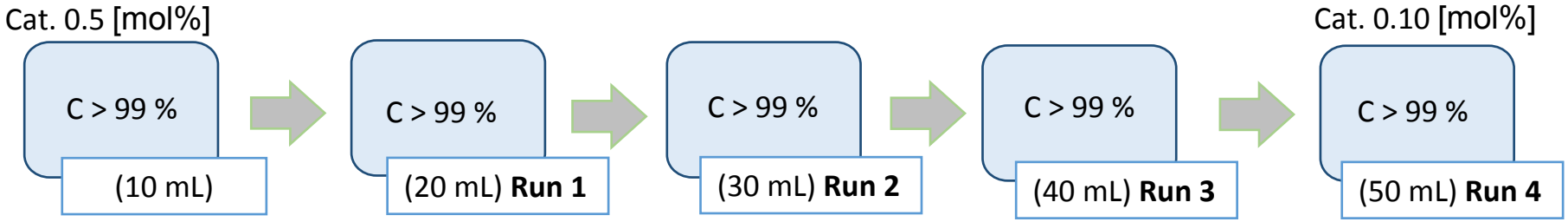


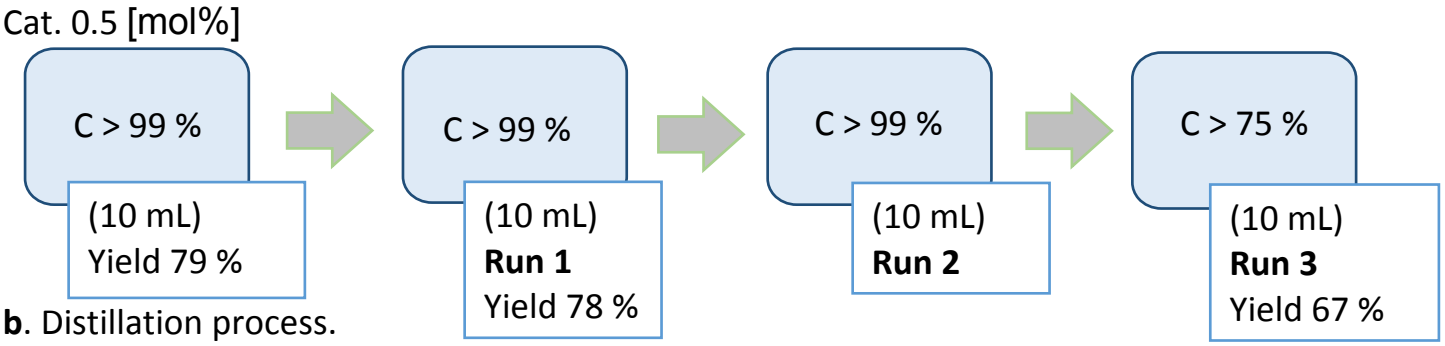
Figure 30. ^{1}H-NMR of the crude reaction 16 mmol of **1c** with **Ru-1** (0.05 mol%), NaOMe (5 mol%), 25 bar H_2, 25 °C, 0.17 mL MeOH and 72 h.

6. NMR spectra of the recycling experiments





a. Continuous feed of a reactor. C = conversion.



b. Distillation process.
C = conversion.

Figure 31. Recycling experiments with **Ru**-**1** on large scale.

Distillation methodology

Model reaction, conversion > 99%. Yield of γ-valerolactone = 79%.

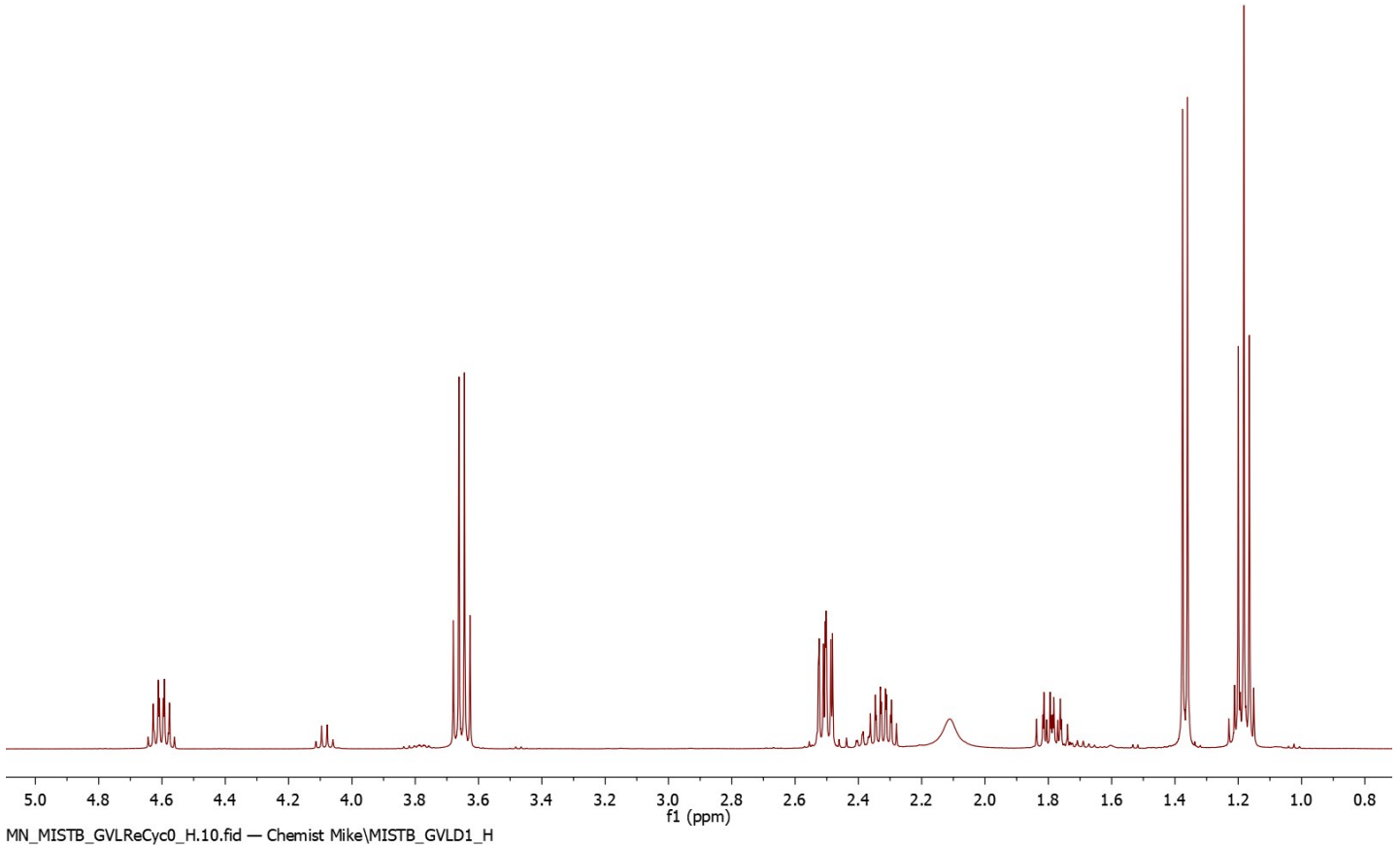


Figure 32. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Run 1 after distillation of the product, conversion > 99%. Yield of γ-valerolactone = 78%.

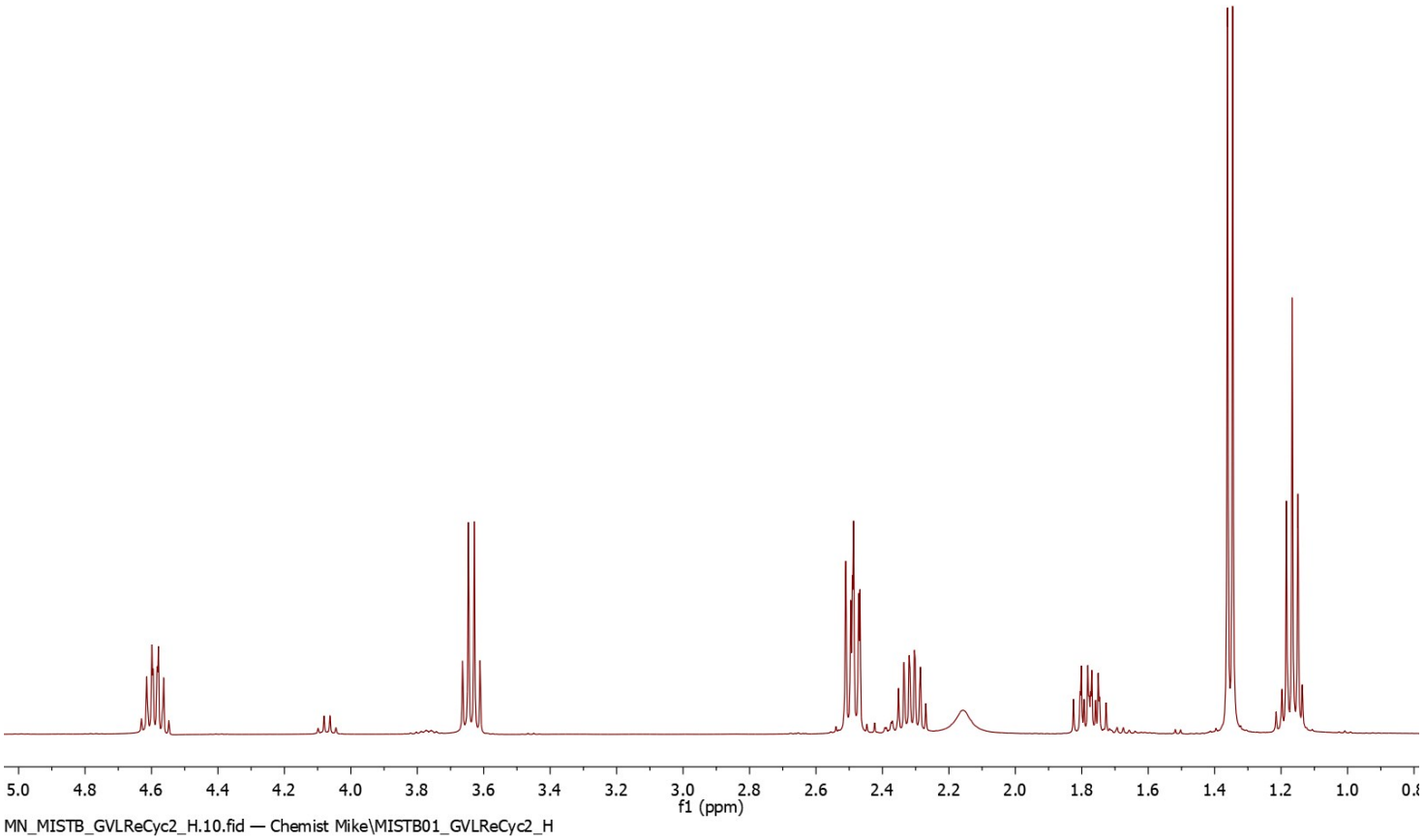


Figure 33. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Run 2 after distillation of the product, conversion > 99%. Yield of γ-valerolactone was not measured.

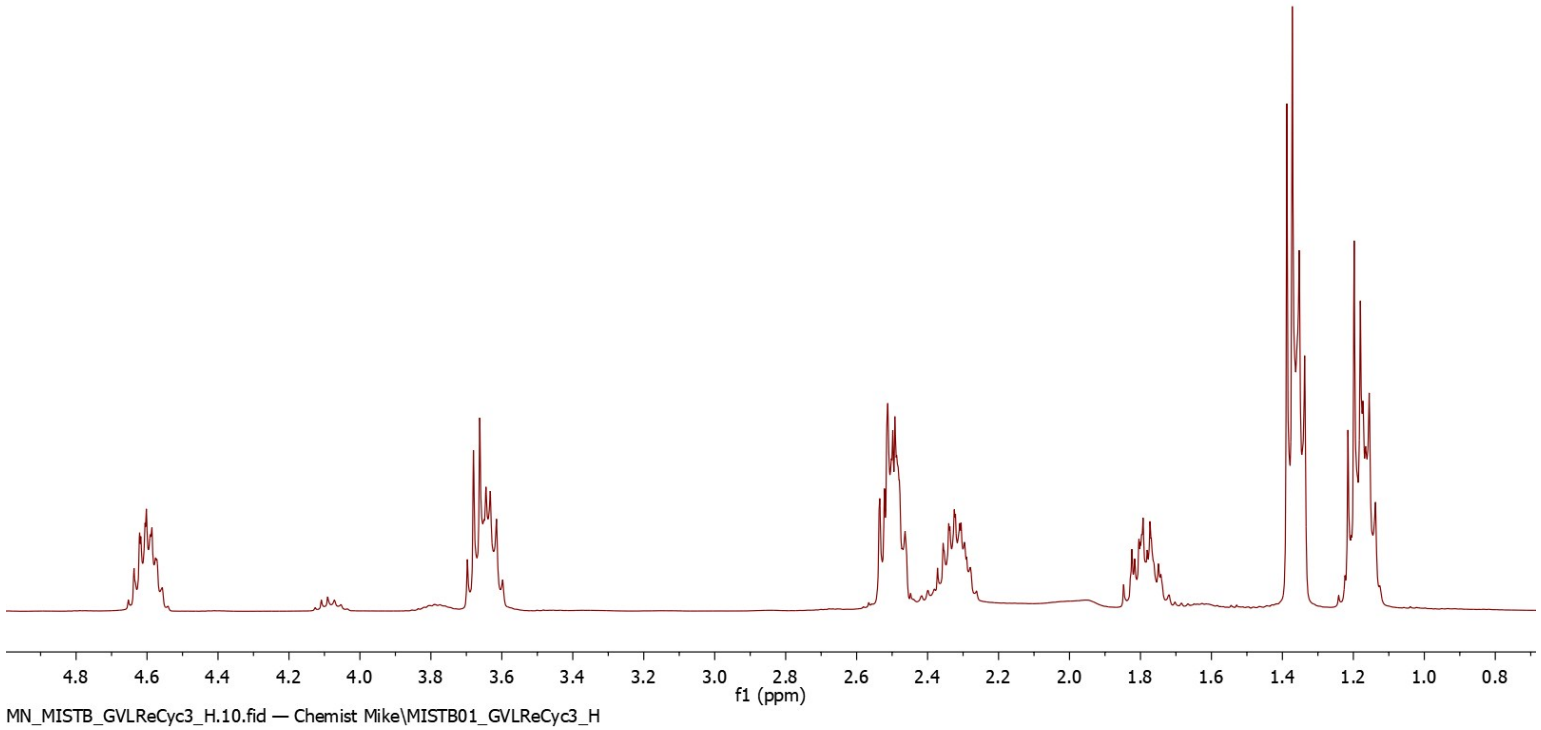


Figure 34. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Run 3 after distillation of the product, conversion 75%. Yield of γ-valerolactone = 67%.

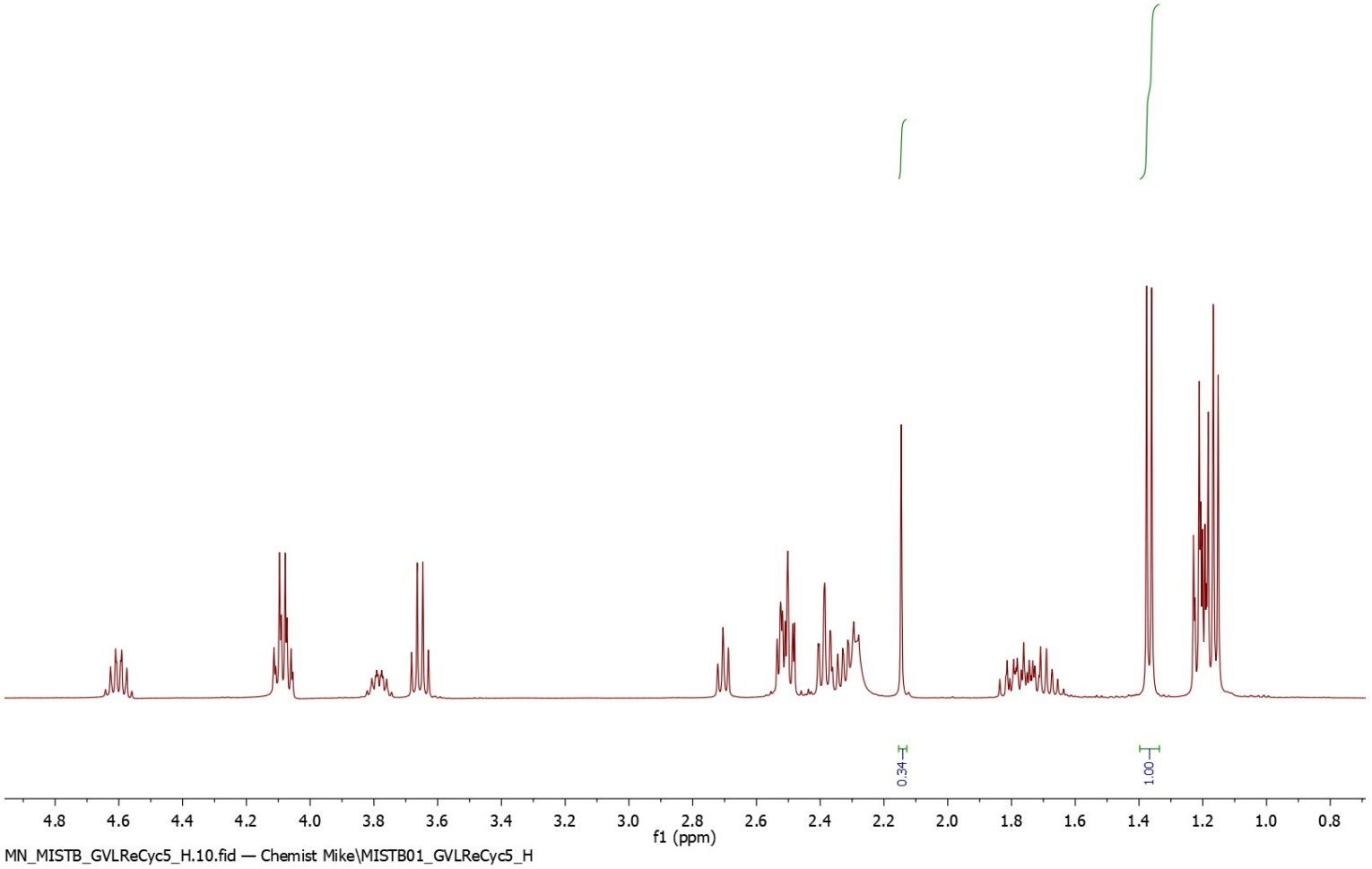


Figure 35. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Continuous feed of the reactor methodology

Model reaction, conversion > 99%

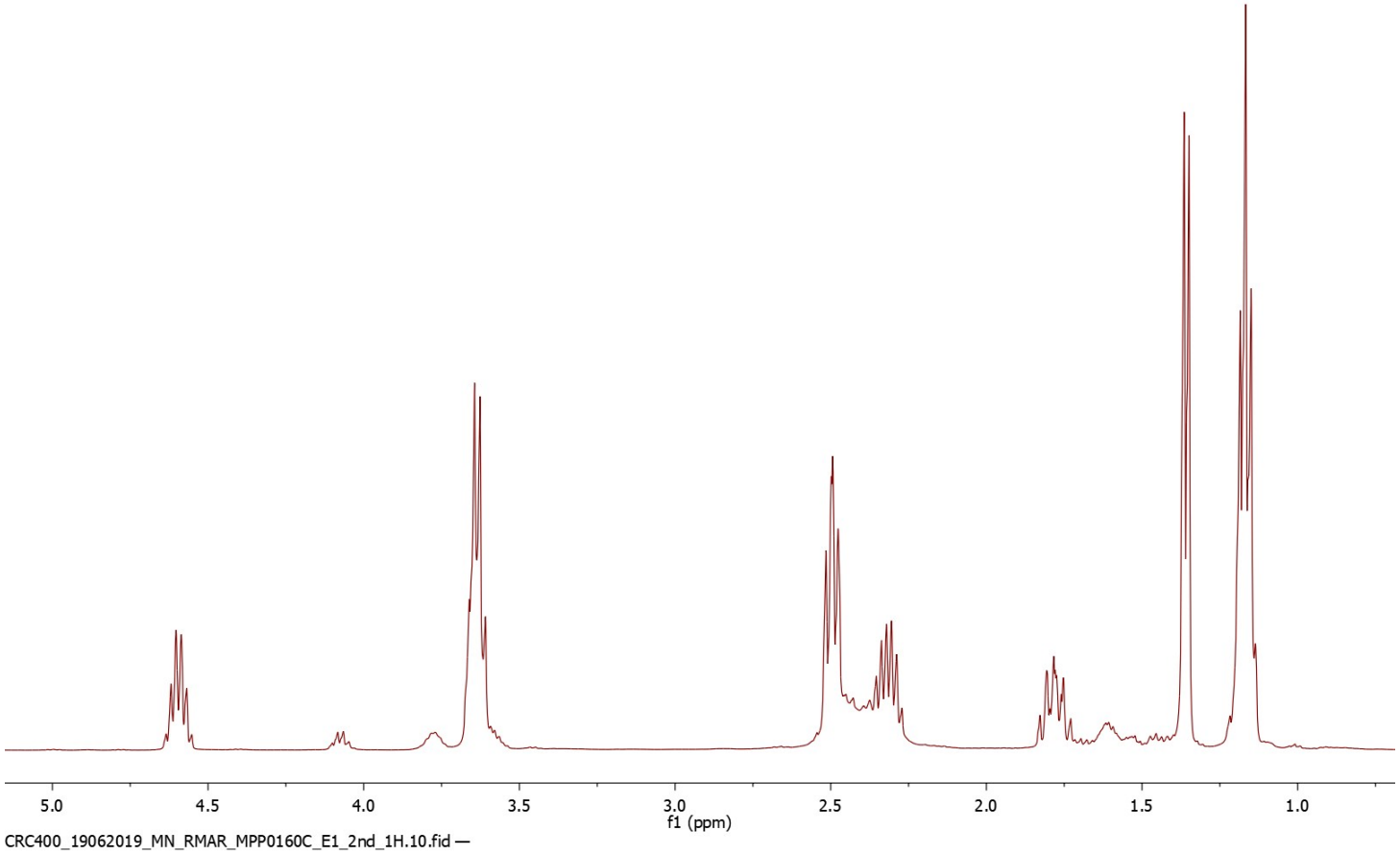


Figure 36. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Run 1 experiment, conversion > 99%

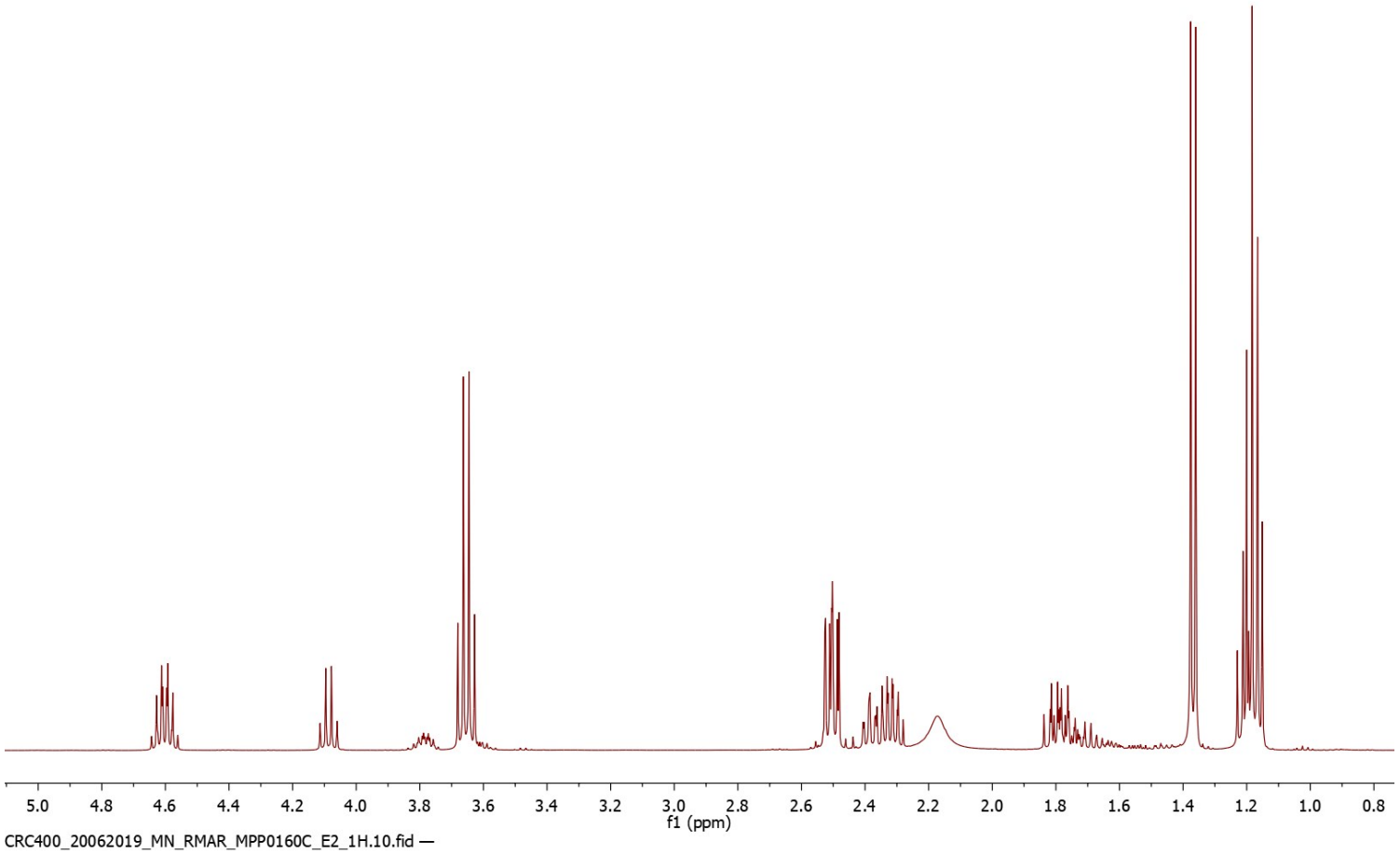


Figure 37. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Run 2 experiment, conversion > 99%

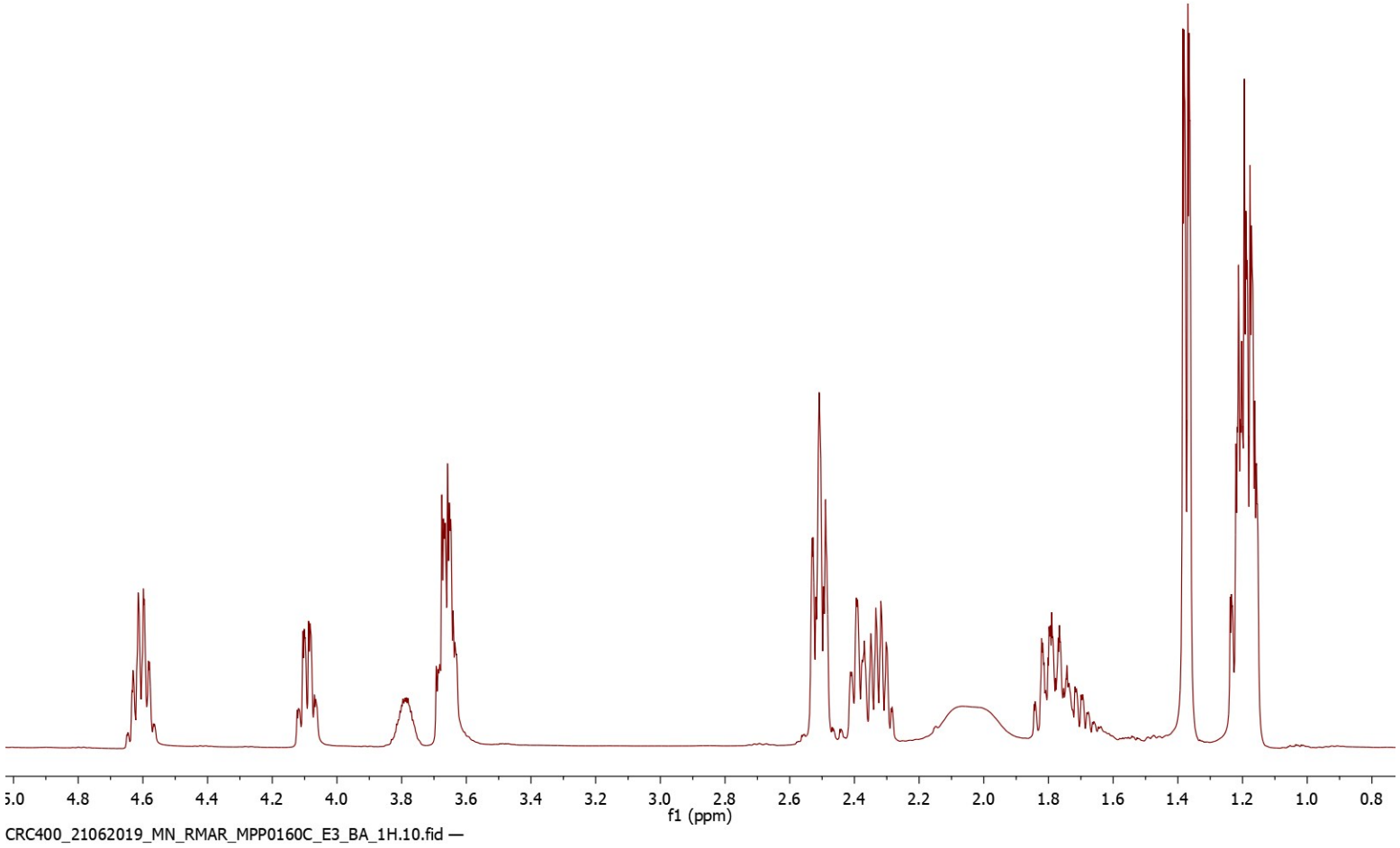


Figure 38. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Run 3 experiment, conversion > 99%

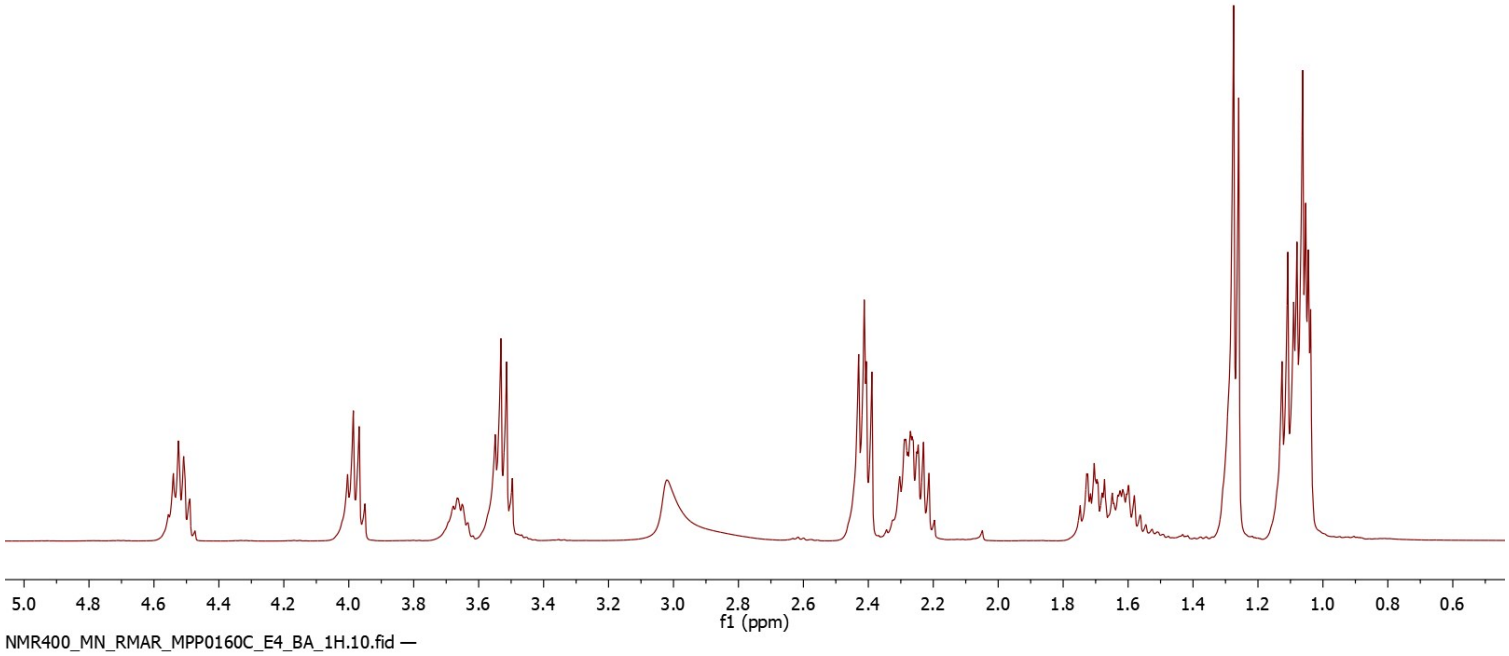


Figure 39. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h.

Run 4 experiment, conversion > 99%

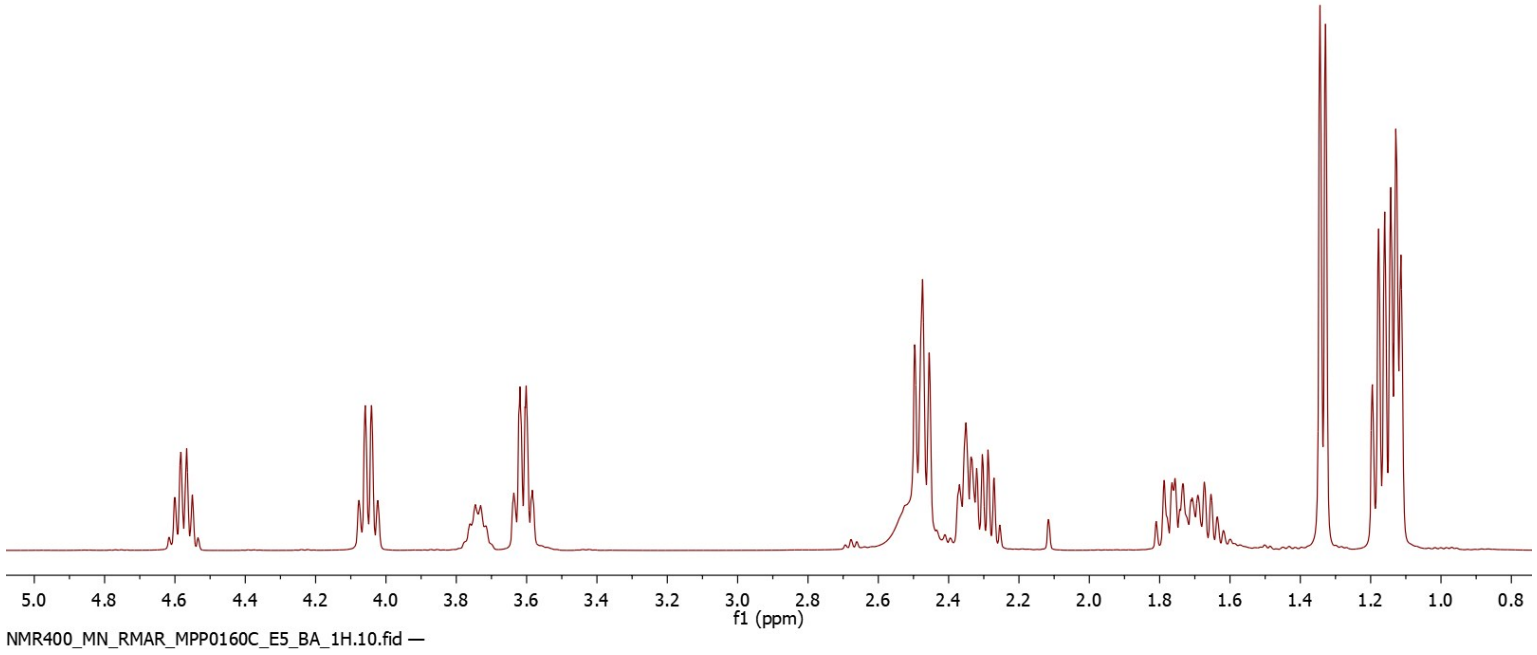


Figure 40. ^{1}H-NMR of the crude reaction 70 mmol of **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 24 h

7. NMR spectra of Ru species

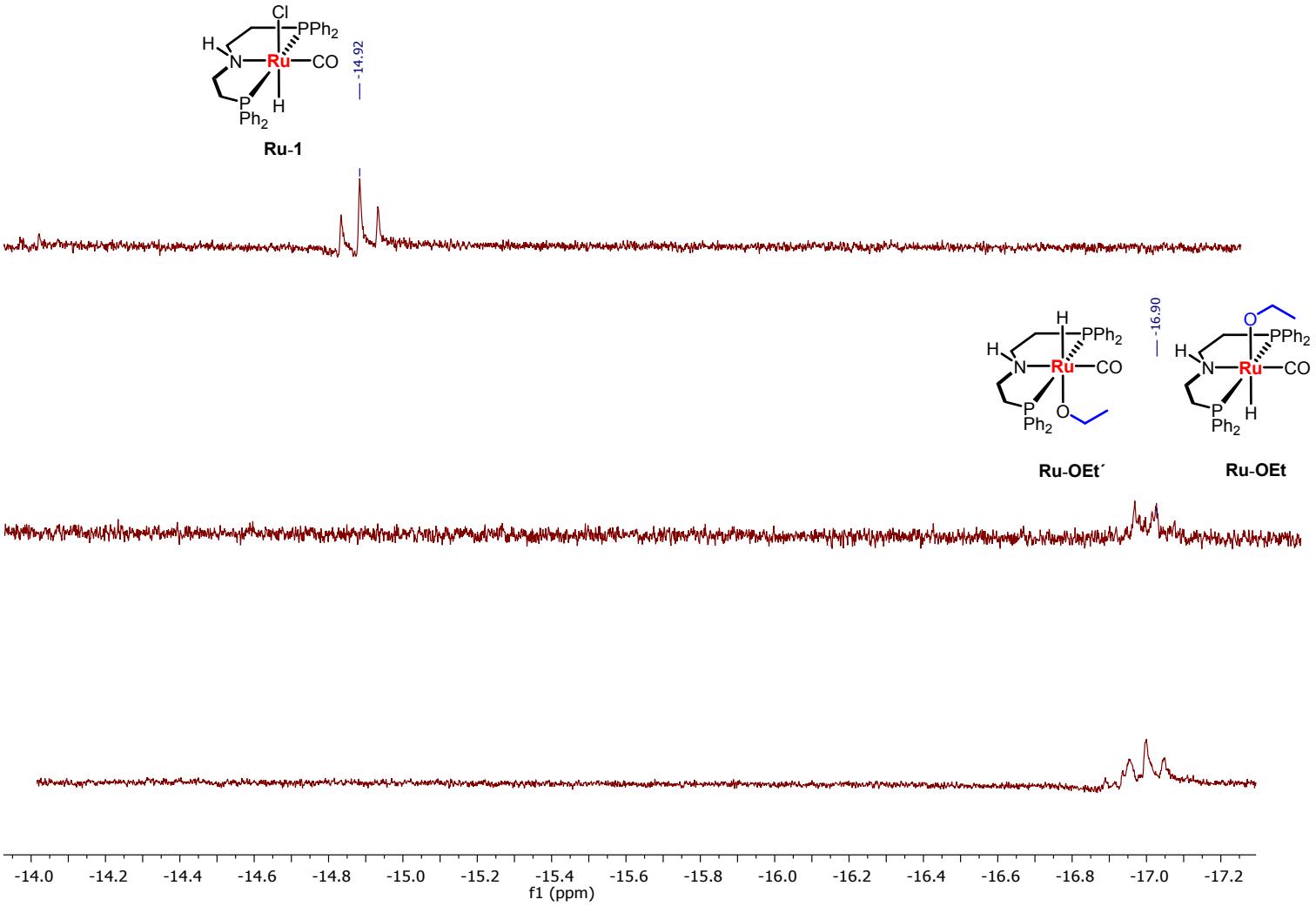


Figure 41. ^{1}H-NMR of the ruthenium hydride species present before and after the reaction with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 25 bar H_2, 60 °C and 2 h (toluene-d_8 at 25 °C). Species **Ru-OEt** and **Ru-OEt'** are tentative assignments.

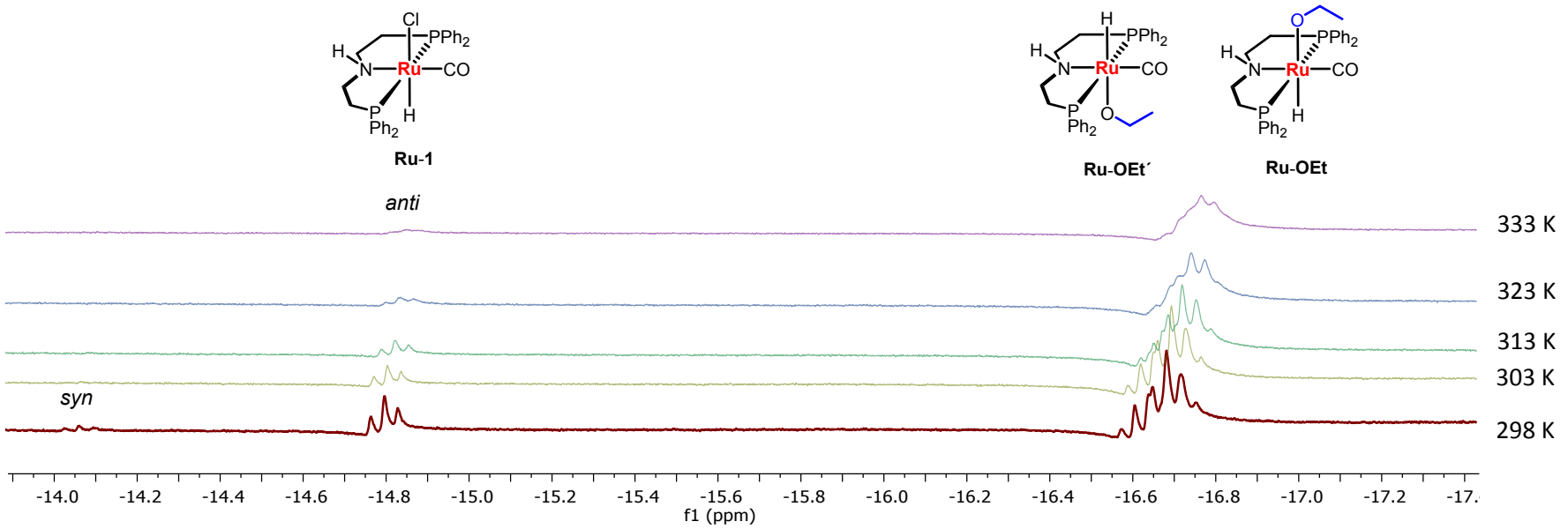


Figure 42. Stacked VT ^{1}H-NMR spectra zoomed on hydride region. Reaction mixture of **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%) in absence of H_2. (toluene-d_8). Species **Ru-OEt** and **Ru-OEt'** are tentative assignments.

8. NMR spectra of deuterium labeling of **3**

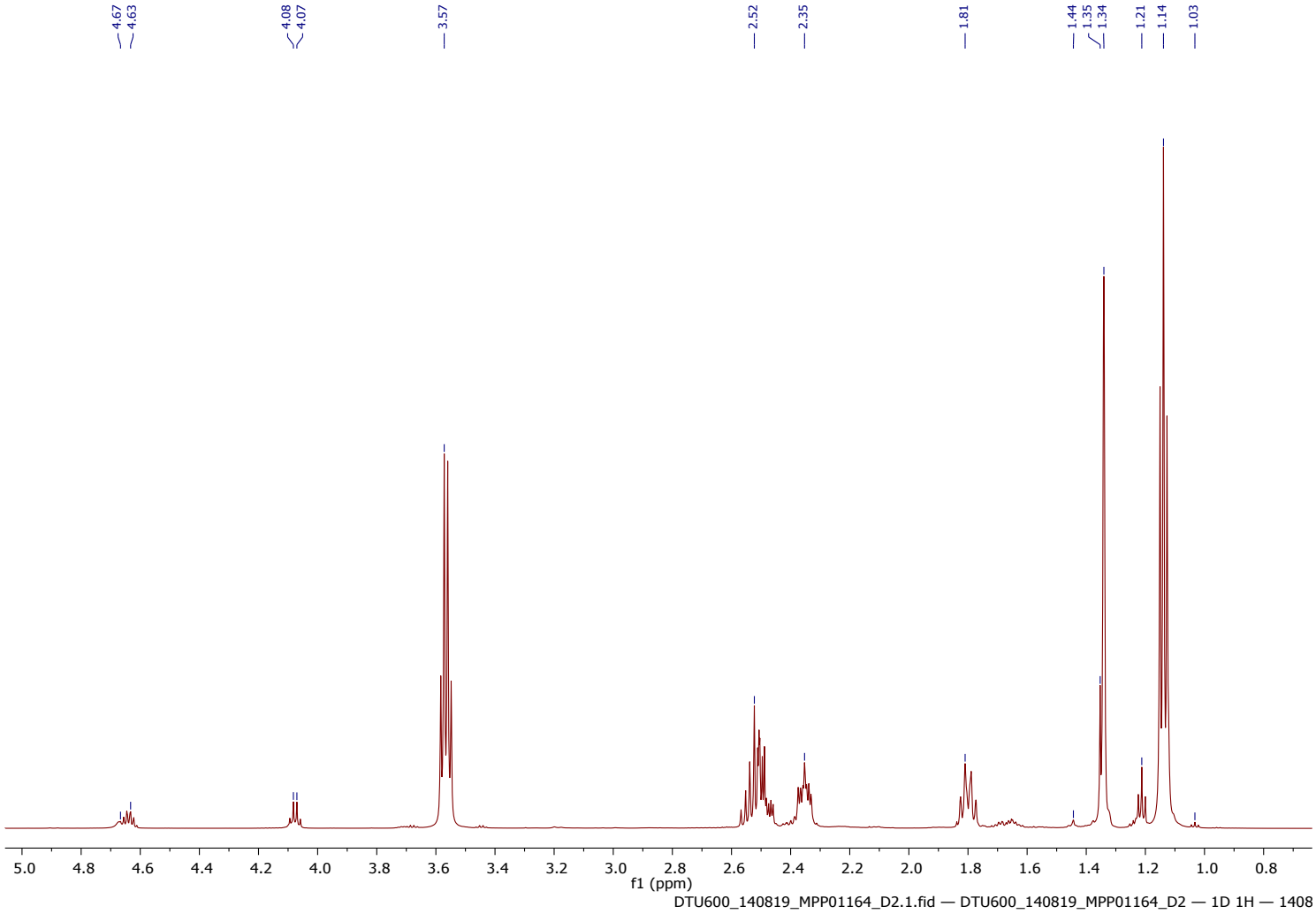


Figure 43. ^{1}H-NMR of the crude reaction of 5 mmol **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 30 bar D_2, 60 °C, 0.121 mL EtOH and 24 h (capillary insert with toluene-d_8 at 25 °C).

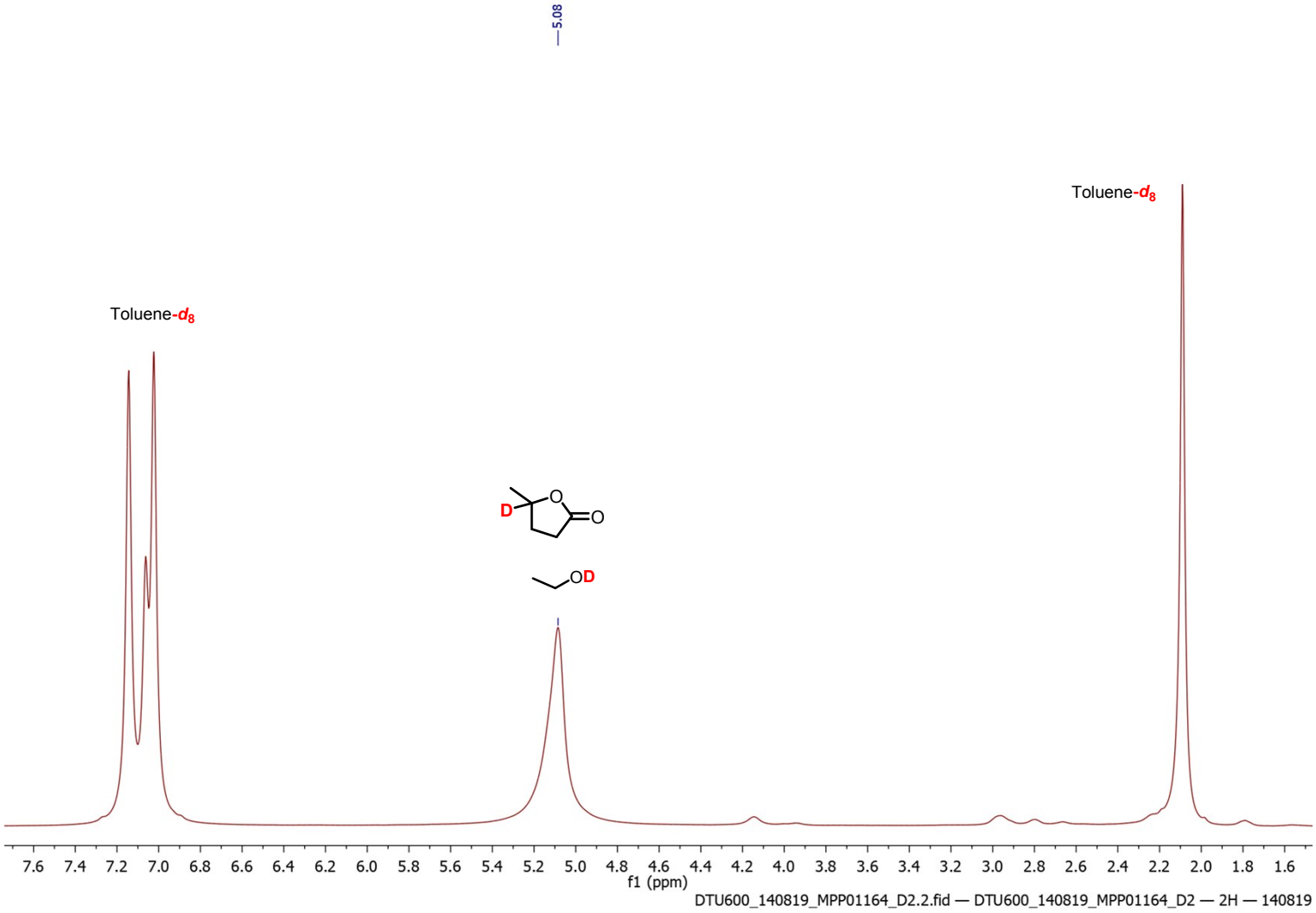


Figure 44. ^{2}H-NMR of the crude reaction of 5 mmol **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 30 bar D_2, 60 ℃, 0.121 mL EtOH and 24 h (capillary insert with toluene-d_8 at 25 °C). The peak at 5.08 ppm is tentatetively assigned as an overlap of **3-d_1** and EtOD.

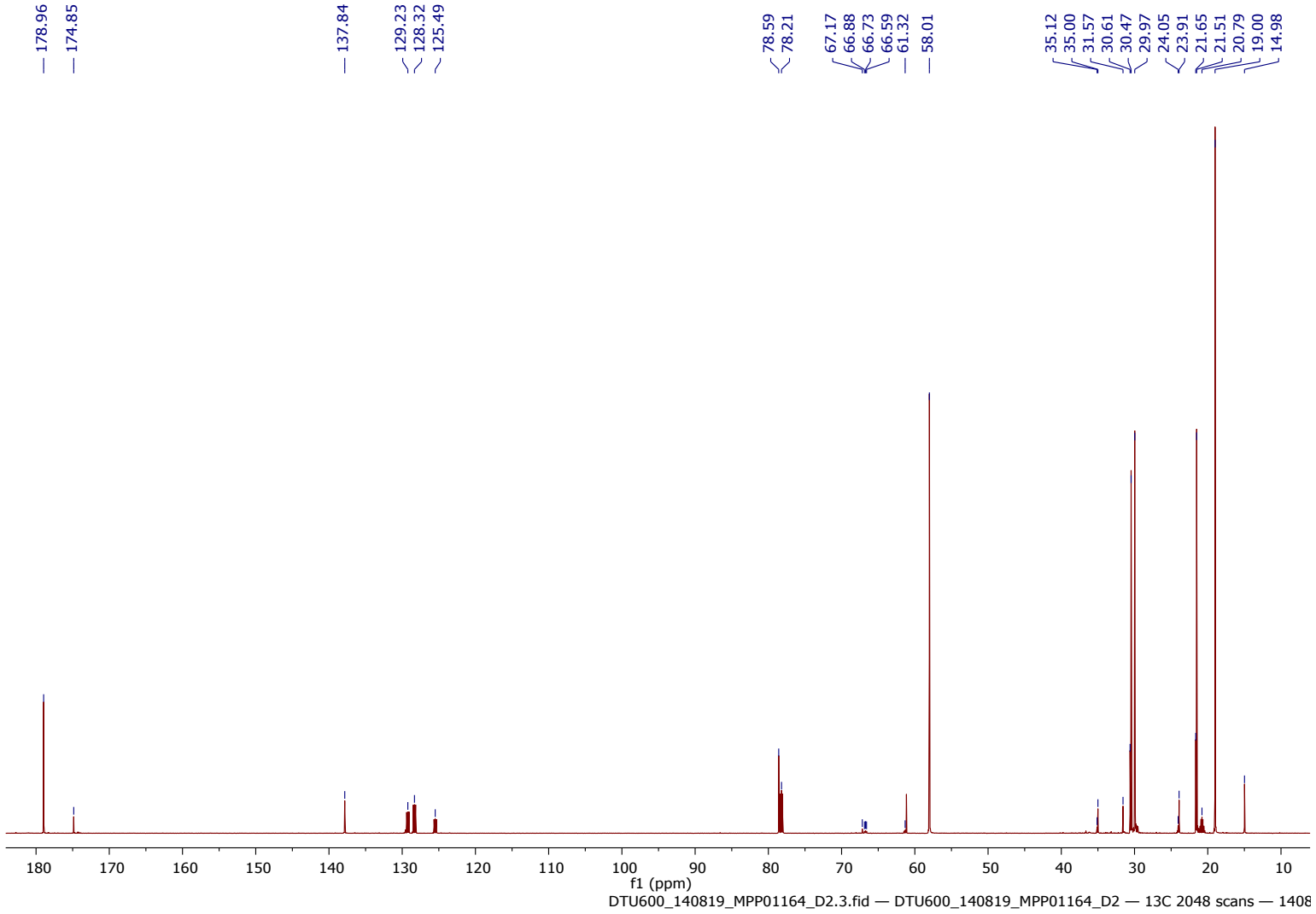


Figure 45. ^{13}C-NMR of the crude reaction of 5 mmol **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 30 bar D_2, 60 ℃, 0.121 mL EtOH and 24 h (capillary insert with toluene-d_8 at 25 °C).

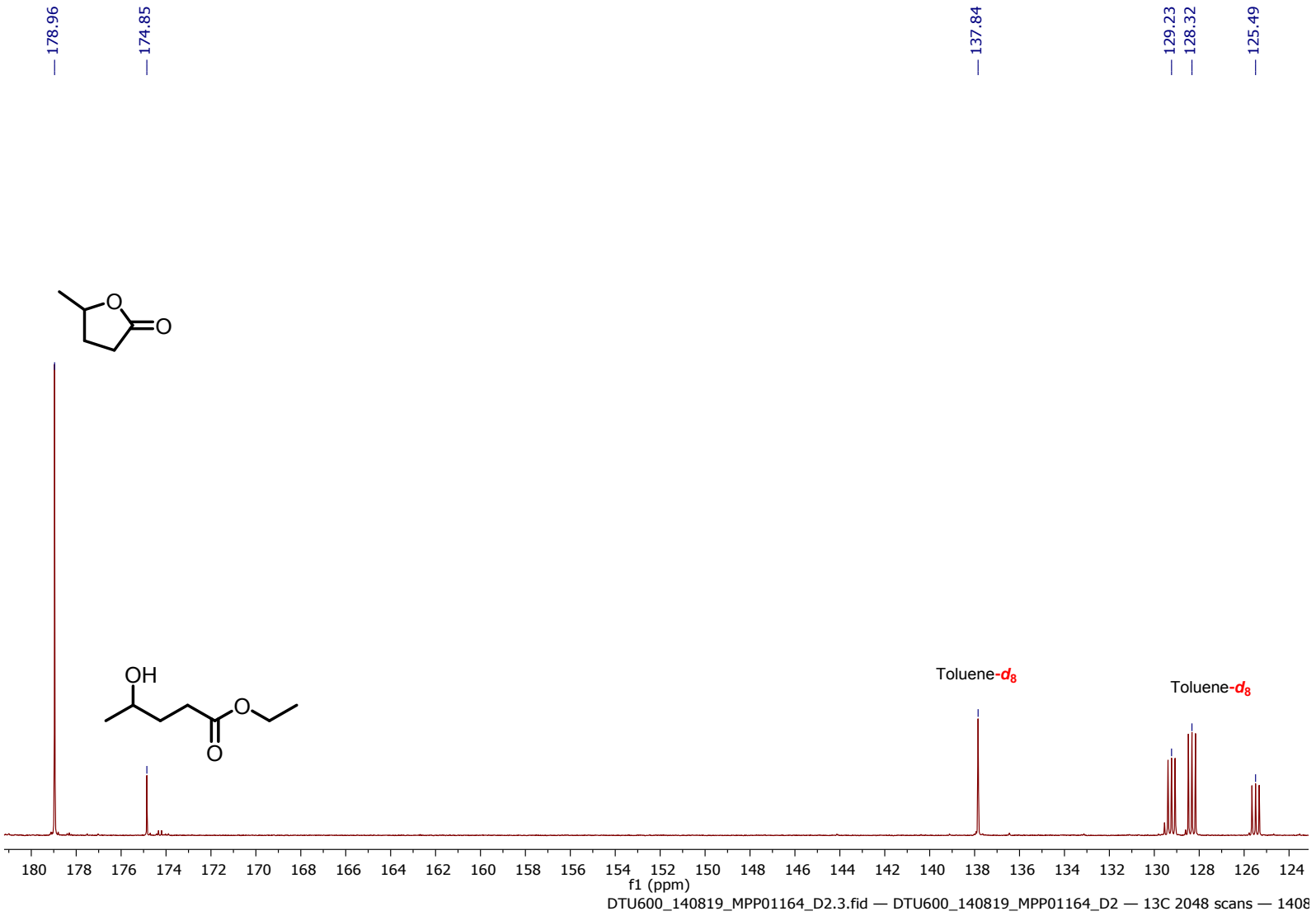


Figure 46. ^{13}C-NMR (zoomed from 180-120 ppm) of the crude reaction of 5 mmol **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 30 bar D_2, 60 °C, 0.121 mL EtOH and 24 h (capillary insert with toluene-d_8 at 25 °C).

Figure 47. ^{13}C-NMR (zoomed from 80-54 ppm) of the crude reaction of 5 mmol **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 30 bar D_2, 60 °C, 0.121 mL EtOH and 24 h (capillary insert with toluene-d_8 at 25 °C). The spectrum is showing no detecable carbon based deuterium incorporated ethanol.

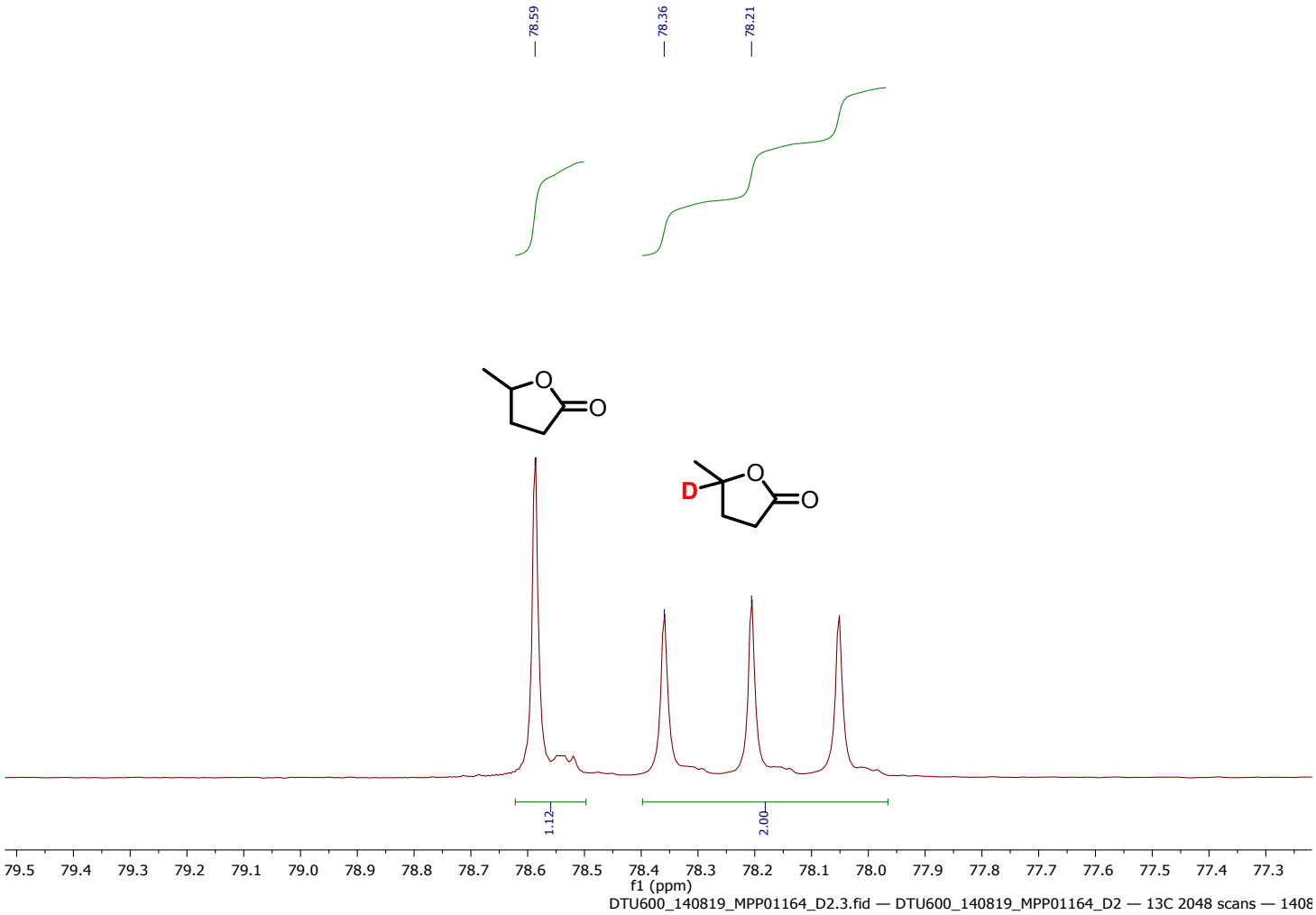


Figure 48. ^{13}C-NMR (zoomed from 80-77 ppm) of the crude reaction of 5 mmol **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 30 bar D_2, 60 °C, 0.121 mL EtOH and 24 h (capillary insert with toluene-d_8 at 25 °C).

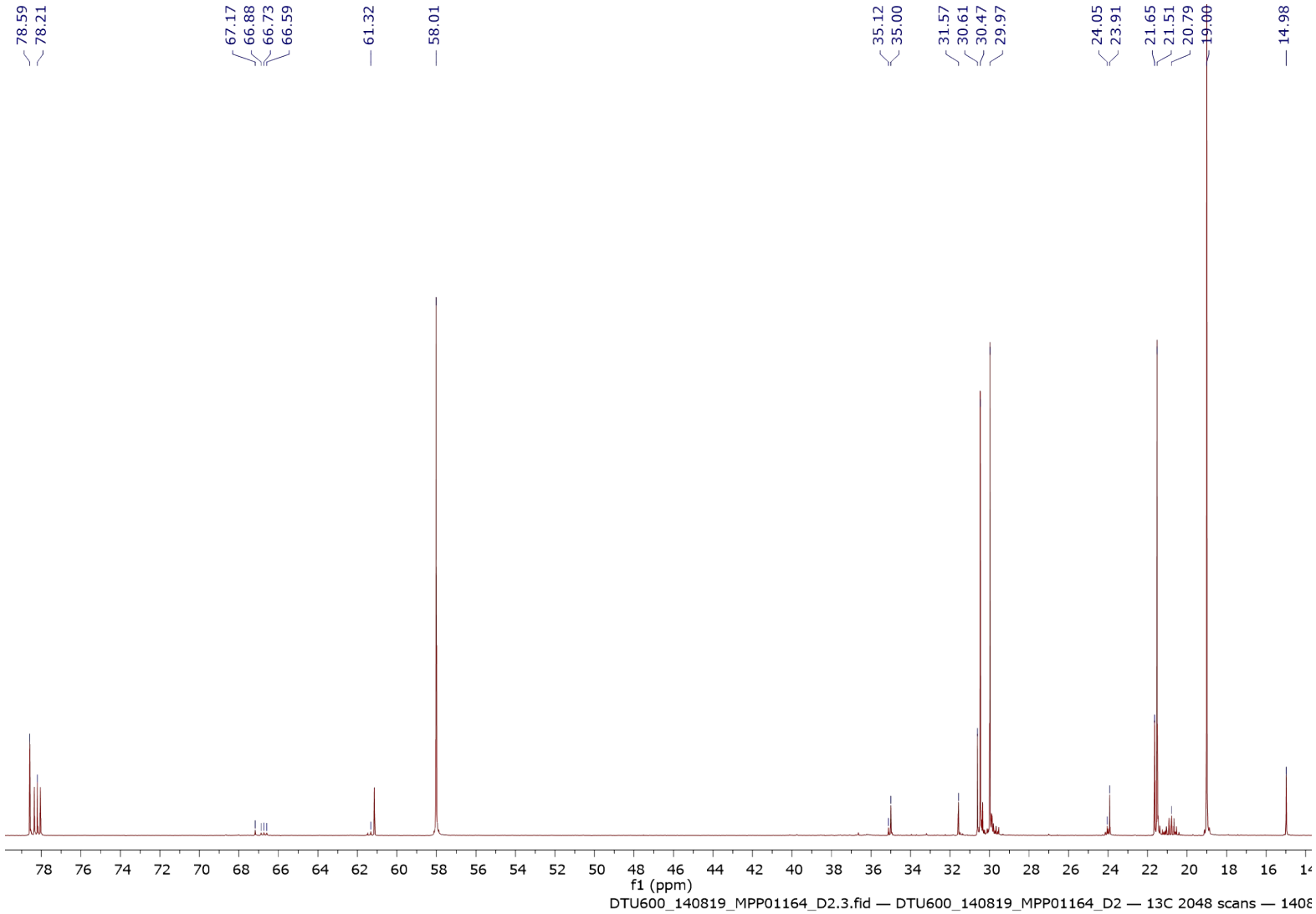


Figure 49. ^{13}C-NMR (zoomed from 78-16 ppm) of the crude reaction of 5 mmol **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 30 bar D_2, 60 °C, 0.121 mL EtOH and 24 h (capillary insert with toluene-d_8 at 25 °C).

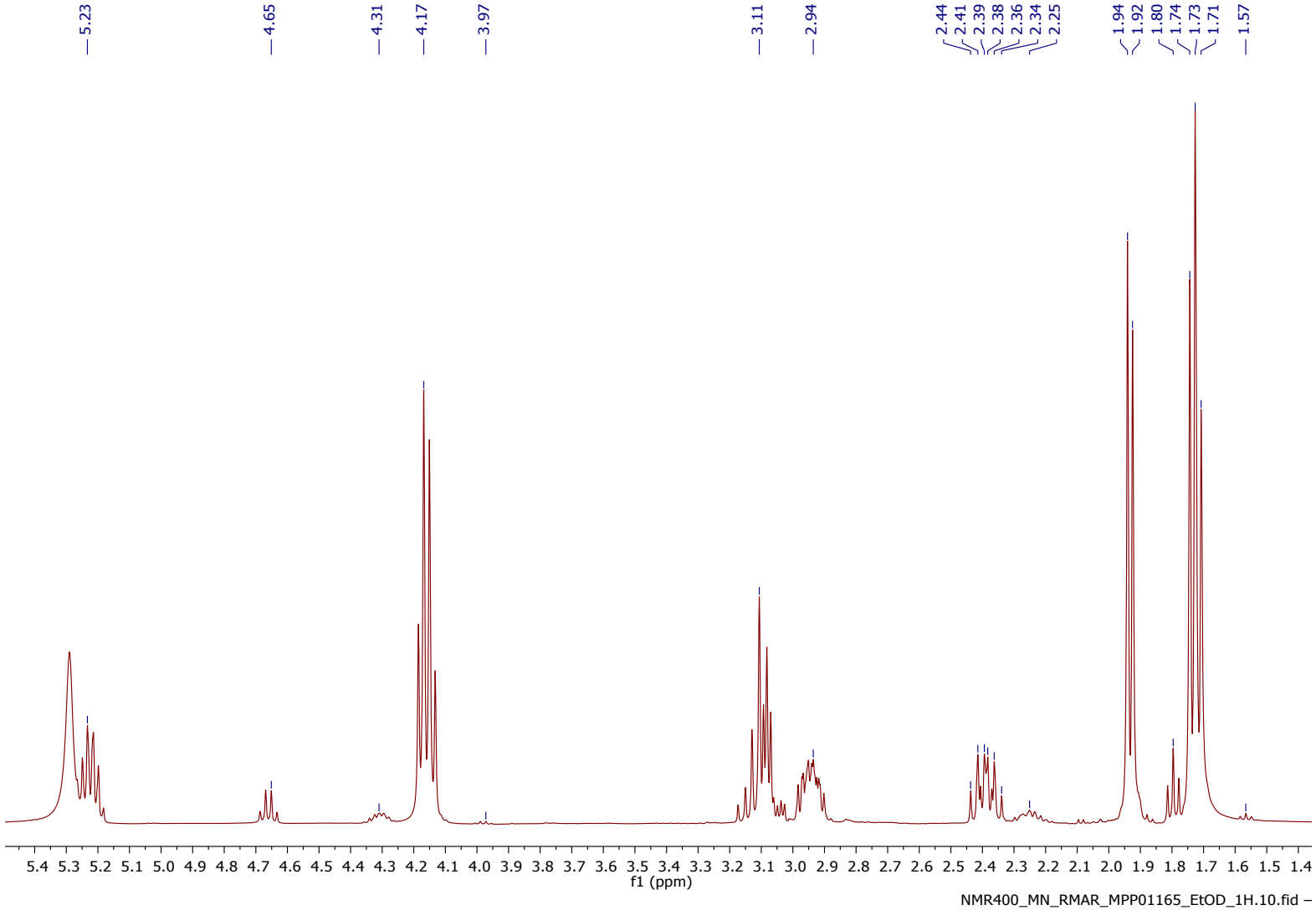


Figure 50. ^{1}H-NMR of the crude reaction of 10 mmol **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 30 bar H_2, 60 °C, 0.25 mL EtOH, 0.05 mL of ethanol-d_6 and 24 h (ethanol-d_6 signals were used as reference at 25 ºC).

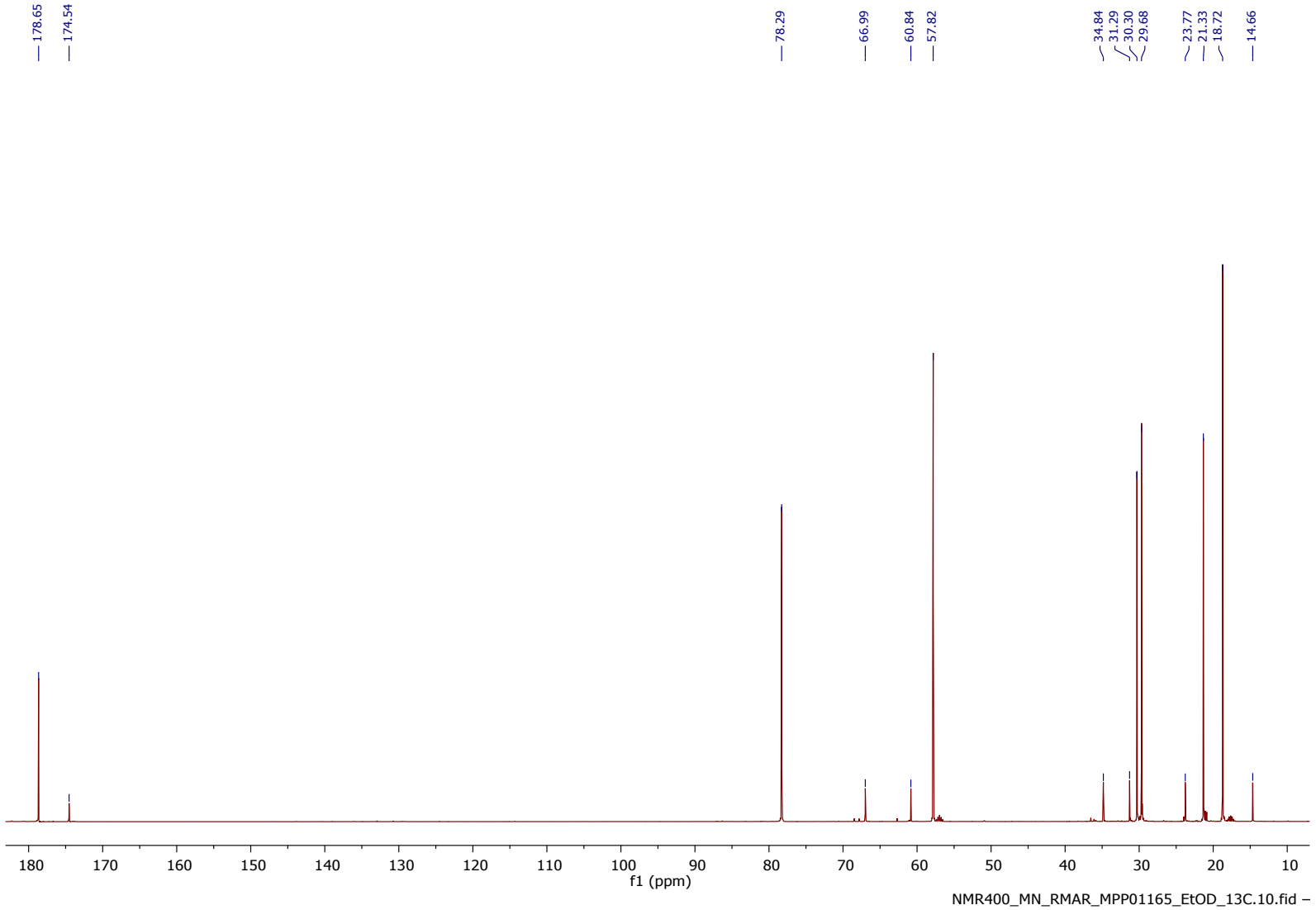


Figure 51. ^{13}C-NMR of the crude reaction of 10 mmol **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 30 bar H_2, 60 °C, 0.25 mL EtOH, 0.05 mL of ethanol-d_6 and 24 h (ethanol-d_6 signals were used as reference at 25 °C).

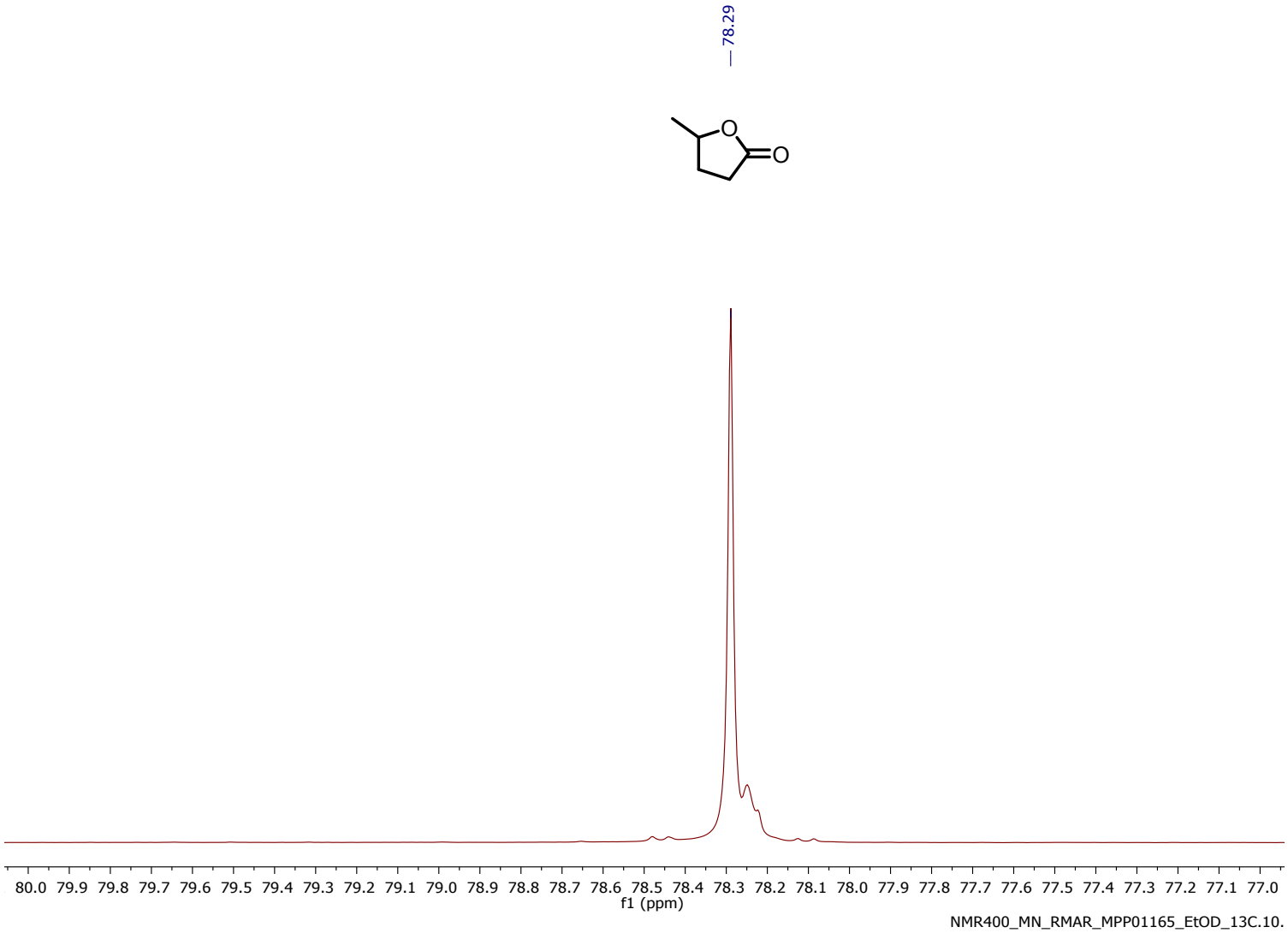


Figure 52. ^{13}C-NMR (zoomed from 80-77 ppm) of the crude reaction of 10 mmol **1b** with **Ru**-**1** (0.5 mol%), NaOEt (5 mol%), 30 bar H_2, 60 °C, 0.25 mL EtOH, 0.05 mL of ethanol-d_6 and 24 h (ethanol-d_6 signals were used as reference at 25 °C). The spectrum is showing no detecable **3**-d_1.

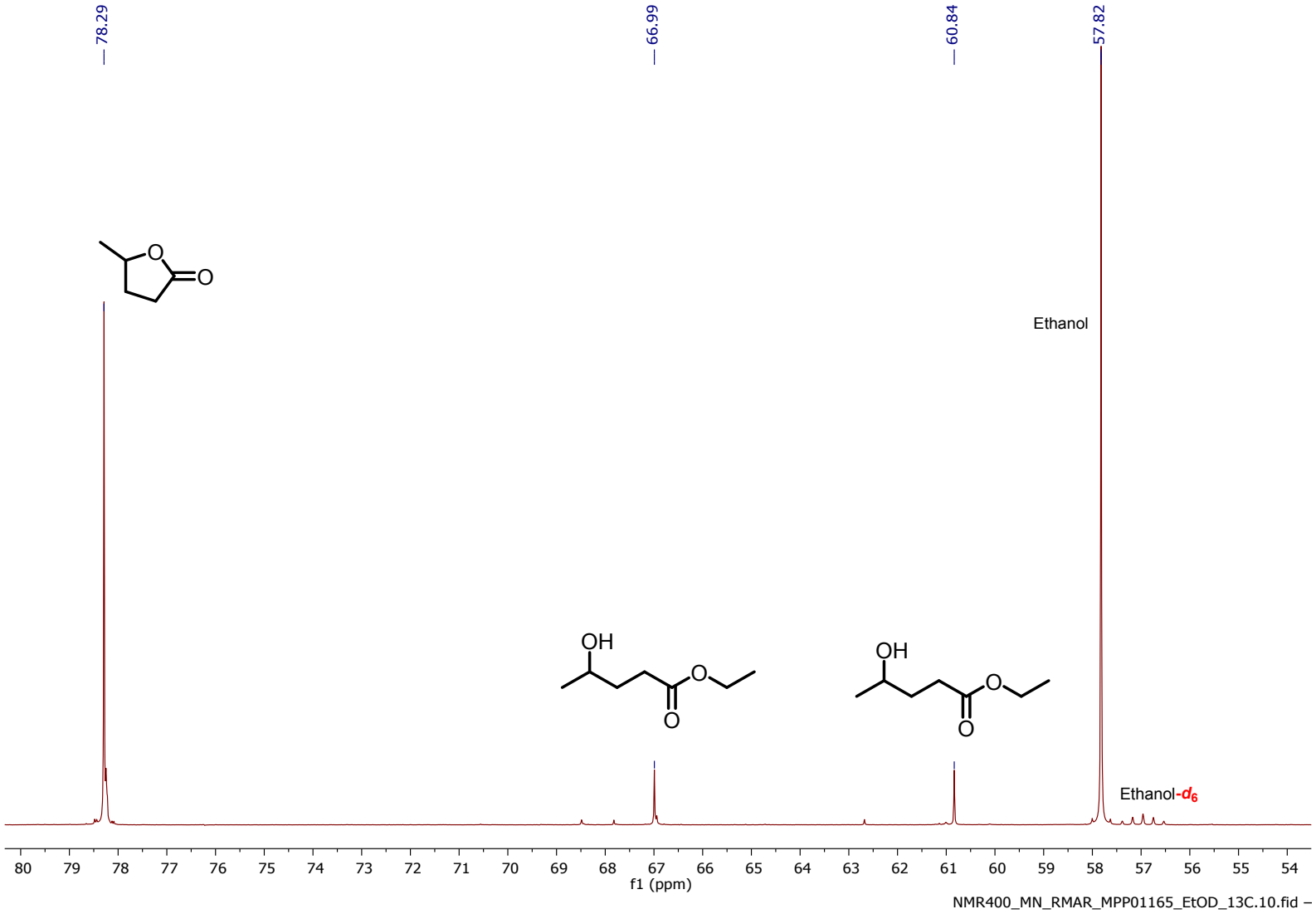


Figure 53. ^{13}C-NMR (zoomed from 80-54 ppm) of the crude reaction of 10 mmol **1b** with **Ru-1** (0.5 mol%), NaOEt (5 mol%), 30 bar H_2, 60 °C, 0.25 mL EtOH, 0.05 mL of ethanol-d_6 and 24 h (ethanol-d_6 signals were used as reference at 25 ºC).

9. References

[1] E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H.-J. Drexler, W. Baumann, H. Junge, M. Beller, *Angew*. *Chem*. *Int*. *Ed*., 2013, **52**, 14162-14166.
[2] L. Zhang, G. Raffa, D. H. Nguyen, Y. Swesi, L. Corbel-Demailly, F. Capeta, X. Trivelli, S. Desset, S.
Paul, J.-F. Paul, P. Fongarland, F. Dumeignil, R. M.Gauvin. *J. Catal.*, 2016, **340**, 331-343.
[3] R. Çelenligil-Çetin, L. A. Watson, C. Guo, B. M. Foxman, O. V. Ozerov, *Organometallics*, 2005, **24**, 186–189.