Supporting Information

Efficient and Selective Catalytic Hydrogenation of Furanic Aldehydes using well defined Ru and Ir Pincer Complexes

Rosa Padilla,[a] Sakhitha Koranchalil,[a] and Martin Nielsen*[a]

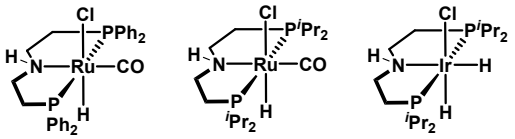
[a] *Department of Chemistry, Technical University of Denmark. Kemitorvet 207, DK-2800, Lyngby Denmark*.

Table of contents

1. Experimental Section

General Information. Most chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Hydroxymethylfurfural (**HMF**, 99%), 5-methylfurfural (**MF,** 99%), furfural (**FAL**, 99%), NaOEt (99%), **Ru-1**, **Ru-2** 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. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. The ^{1}H, ^{2}H, ^{31}P, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 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.



Ru-1 **Ru-2** **Ir-1**

Figure S1. Pincer complexes used in this study.

General Procedure for hydrogenation of furanic aldehydes to furanic alcohols. The optimization reactions were carried out on a 0.79-0.90 mmol scale. We also carried out a 4.36 mmol and 7.93 mmol scale hydrogenation of **HMF** to **DHMF**. All the experiments were performed twice to corroborate the results.

For a typical hydrogenation screening experiment, in a glass vial under argon atmosphere, furanic aldehyde (0.79-0.90 mmol) was charged and dissolved in 1 mL of solvent (EtOH of H_2O), subsequently, the container was equipped with a magnetic stirring bar. Afterwards, the PNP catalyst (0.01-0.05 mol%) and the corresponding amount of base (0.5-2 mol%) were added. The vial was sealed with a teflon-lined cap, removed from the glovebox, and placed in a seven-well reactor. Afterwards, a needle was placed through the rubber stopper of the vials and the autoclave was sealed and flushed with argon/hydrogen (three times). Next, hydrogen pressure of 10-30 bar was applied. The autoclave was stirred for 1-120 minutes (600 rpm) at the desired temperature. 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 $CDCl_3$ or D_2O.

When the hydrogenation of **HMF** was carried out on a large scale (4.36-7.93 mmol), the raw material, base (0.2 mol%), complex **Ru-2** (0.01 mol%) and solvent (ethanol, 5.60-10.0 mL) were charged into stainless-steel autoclave. The autoclave was tightened and flushed with argon/hydrogen three times and finally charged with hydrogen (10-30 bar). The reaction mixture was stirred (600 rpm) at 25 °C for the desired time. After reaction, the autoclave pressure was released carefully. The reaction mixture was analyzed by using NMR as described above. In order to isolate the products (**DHMF** or **MFA**), we performed a filtration of the crude reaction (7.93 mmol scale) using silica gel pad and EtOH to wash the it; after that, the solvent was evaporated under vacuum to form a white powder or brown oil in a practically quantitative yield (99.6 and 97.3%, respectively)**.**

In the case of the isolation of **FA**, the reaction was performed with 7.93 mmol of **FAL** in EtOH using 0.1% **Ru-2** under 30 bar H_2 at 25 ^{o}C for 10 h. After this time, the reaction mixture was filtered over silica gel to remove humins and catalyst affording 84.4 % yield.

Consecutive addition experiments. The first hydrogenation was carried out using 0.79 mmol of **HMF**, base (0.2 mol%), complex **Ru-2** (0.05 mol%) and solvent (ethanol, 1.0 mL) which were charged into stainless-steel autoclave. The autoclave was tightened and flushed with argon/hydrogen three times and finally charged with hydrogen (30 bar). The reaction mixture was stirred (600 rpm) at 25 °C for 10 min. After reaction, the autoclave was depressurized. For the next addition, 0.79 mmol of **HMF** was added. Then the autoclave was sealed and flushed three times with argon/hydrogen and charged with 30 bar H_2. The reaction mixture was stirred again (600 rpm) at 25 °C for 30 min. The next two cycles/additions were performed using the same procedure. Before each addition, an aliquot of the crude reaction (10μl) was analyzed by ^{1}H NMR to determine the conversion.

Deuterium labeling experiments. Conventional experiment procedure was carried out using **HMF** as substrate on 0.79 mmol scale, 2 mol% of base (NaOEt or LiOH) and complex **Ru-2** (0.1 mol%) in EtOH or H_2O. All the chemicals were charged into stainless steel autoclave. The autoclave was tightened and flushed with argon/deuterium three times and finally charged with deuterium (30 bar). The reaction mixture was stirred (600 rpm) at 25 °C for 30 min. After reaction, 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. The D-incorporation label was calculated by partial integration of ^{13}C NMR signals of -CH_2OH/-CHDOH at 57-56 ppm.

*Ethanol as solvent (see **Figure S33**):*

$$\text{Mol\%(DHMF-}d_1\text{)} = \frac{\frac{0.91}{0.91 + \frac{1.00 - 0.91}{2}} * 100\%}{} = 95.3\% > 95\%$$

*Water as solvent (see **Figure S37**):*

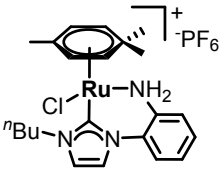
Minor **HMF** peak at 56.7 ppm is disregarded.

$$\text{Mol\%}(\textbf{DHMF-}d_1) = \frac{\frac{0.35 * 1.5}{1.00 - \frac{0.35}{2} - (0.35 * 1.5)}}{0.35 * 1.5 + \frac{}{2}} * 100\% = 77.7\% \approx 80\%$$

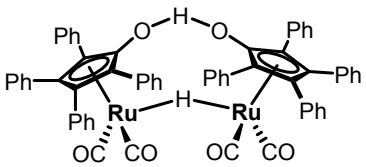
2. **NMR measurements.** Conversions in all reactions were measured by ^{1}H-NMR spectroscopy at 400 MHz in $CDCl_3$ or D_2O at 25 °C. 128 scans were taken for each sample, with a delay between scans of 30s to ensure complete relaxation of the hydrogens. The conversion was calculated using the signals from one of the CH (6.73 ppm) hydrogens of the unreacted substrate, and the CH (6.20 ppm) hydrogens of **DHMF**. 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. Finally, the conversions of both complete in and complete reactions were verified by isolated yields.

3. Examples of literature reports for the hydrogenation of **HMF** and **FAL** by homogeneous catalysis.

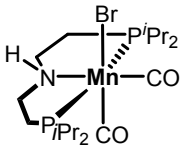
Previous catalytic systems (**HMF**)



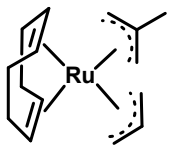
Elsevier
TOF = 1.7 min^{-1}
1 mol %
70 °C, 50 bar H_2
KOtBu/THF
2 h, yield = 99 %



Mazzoni
TOF = 8.3 min^{-1}
0.1 mol%
H_2 (10 bar), 90 °C
No additive
Toluene/H_2O
2 hours
NMR yield = 99%

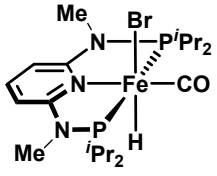


Beller
TOF = 0.063 min^{-1}
1 mol%
H_2 (30 bar), 100 °C
NaO^{t}Bu
Toluene
24 hours
Yield = 64%

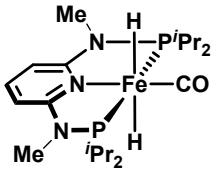


Hashmi
4.5 mol%
120 °C, 10 bar H_2
KO^{t}Bu/Toluene
Bispyridine(2%)
16 h, yield = 98 %

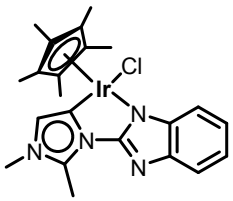
Previous catalytic systems (**FAL**)



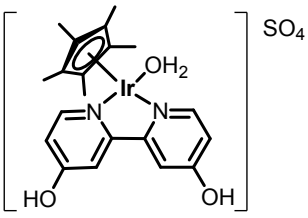
Hoffmann
TOF = 3.3 min^{-1}
0.5 mol %
25 °C, 50 bar H_2
IL/DBU
1 h, yield = 98%



Kichner
TOF = 3.3 min^{-1}
0.5 mol %
25 °C, 10 bar H_2
IL/*n*-heptane/DBU
1 h, yield = 87 %



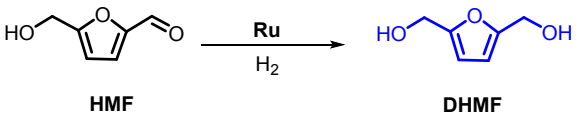
Choudhury
TOF = 1.7 min^{-1}
0.5 mol%
30 °C, 1 bar H_2
EtOH/H_2O
2 h, yield = 94 %



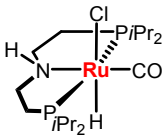
J. Deng and Y. Fu
TOF = 13800 h^{-1}
0.0017 mol%
120 °C, 10 bar H_2
H_2O, HCOOH/HCOONa
1 hr, yield 23 %

4. Screening of the reactions for the hydrogenation of **HMF** to **DHMF**

Table S1. Hydrogenation of **HMF** to **DHMF** under 10 bar H_2 at 25 °C in ethanol.



HMF **DHMF**



Ru-2

Entry	Catalyst	Cat. load [mol%]	$p(H_2)$ [bar]	T [°C]	T [min]	Conv. [%][c]
1	**Ru-1**[a]	0.1	10	25	90	76
2	**Ir-1**[a]	0.1	10	25	90	93
3	**Ru-2**[b]	0.05	10	25	10	94
4	**Ru-2**[b]	0.05	10	25	15	96
5	**Ru-2**[b]	0.05	10	25	20	≥99

Standard reaction conditions:

a) 0.79 mmol of **HMF** and 5 mol% base (NaOEt: 2.0 M/EtOH).

b) 0.79 mmol of **HMF** and 2 mol% base (NaOEt: 2.0 M/EtOH)

c) Determined by integration of ^{1}H-NMR analysis.

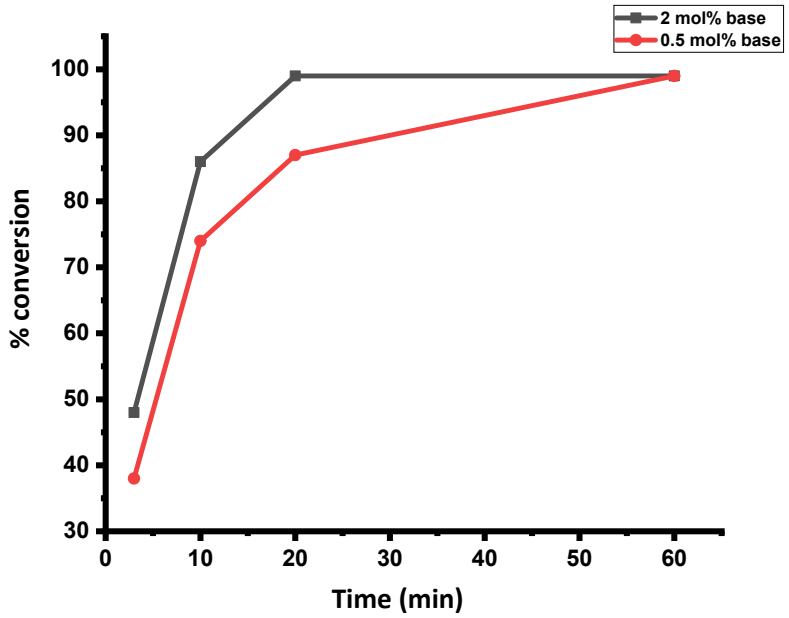


Figure S2. Effect of base on the catalyzed hydrogenation of **HMF** to **DHMF**. Reaction conditions: 0.79 mmol of HMF, 0.05 mol% of **Ru**-**2** and 2 or 0.5 mol% base (NaOEt: 2.0 M/EtOH). Conversion determined by integration of ^{1}H-NMR analysis.

Table S2. Hydrogenation of **HMF** to **DHMF** with **Ru**-**2** complexes on small scale (different concentrations in EtOH).

Entry	**HMF** [mmol]	Cat. load [mol%][a]	Ethanol addition [mL]	$p(H_2)$ [bar]	T [^oC]	*t* [min]	Conv. [%][b]
1	0.79	**Ru**-**2** (0.05)	0.258	10	25	10	91
2	0.79	**Ru**-**2** (0.05)	0.508	10	25	10	≥99
3	0.79	**Ru**-**2** (0.05)	0.608	10	25	10	≥99
4	0.79	**Ru**-**2** (0.05)	1.008	10	25	10	≥99
5	0.79	**Ru**-**2** (0.05)	1.208	10	25	10	≥99
6	0.79	**Ru**-**2** (0.05)	1.508	10	25	10	≥99
7	0.79	**Ru**-**2** (0.05)	2.008	10	25	10	≥99
8	0.79	**Ru**-**2** (0.05)	3.008	10	25	10	≥99
9	0.79	**Ru**-**2** (0.05)	5.008	10	25	10	≥99

a) Standard reaction conditions: 2 mol% base (NaOEt: 2.0 M/EtOH).

b) Determined by ^{1}H-NMR analysis.

TON Max 12,500

Table S3. Hydrogenation of **HMF** to **DHMF** with **Ru-2** complexes on small scale (different concentrations in EtOH).

Entry	**HMF** [mmol]	Cat. load [mol%][a]	Ethanol addition [mL]	$p(H_2)$ [bar]	T [°C]	*t* [min]	Conv. [%][b]
1	0.79	**Ru-2** (0.05)	0.508	10	25	3	40
2	0.79	**Ru-2** (0.05)	1.208	10	25	3	55
3	0.79	**Ru-2** (0.05)	2.008	10	25	3	49
4	0.79	**Ru-2** (0.05)	5.008	10	25	3	49

a) Standard reaction conditions: 2 mol% base (NaOEt: 2.0 M/EtOH).

b) Determined by 1H-NMR analysis.

TON Max 12,500

Table S4. Hydrogenation of **HMF** to **DHMF** with **Ru-2** complex on small scale at 30 bar (low catalyst loading).

Entry	**HMF** [mmol]	Cat. load [mol%][a]	Ethanol addition [mL]	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	0.79	**Ru-2** (0.05)	1.008	30	25	1	>95	>1900	>1900
2	0.79	**Ru-2** (0.05)	1.008	30	25	4	≥99	2000	500

a) Standard reaction conditions: 2 mol% base (NaOEt: 2.0 M/EtOH).

b) Determined by ^{1}H-NMR analysis.

Table S5. Hydrogenation of **HMF** to **DHMF** with **Ru-2** complexes using big scale (low catalyst loading).

Entry	**HMF** [mmol]	Cat. load [mol%][a]	Ethanol addition [mL]	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	4.36	**Ru-2** (0.01)	5.544	30	25	10	51	5100	510
2	4.36	**Ru-2** (0.01)	5.544	30	25	30	65	6500	217
3	4.36	**Ru-2** (0.01)	5.544	30	25	75	77	7700	103
4	4.36	**Ru-2** (0.01)	5.544	30	25	120	≥99	10000	83

a) Standard reaction conditions: 2 mol% base (NaOEt: 2.0 M/EtOH).

b) Determined by ^{1}H-NMR analysis.

Table S6. Hydrogenation of **HMF** to **DHMF** with **Ru-2** complex in presence of different additives in water.

Entry	**HMF** [mmol]	Cat. load [mol%][a]	Additive	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	0.79	**Ru-2** (0.1)	KOH	10	25	180	≥99	1000	6
2	0.79	**Ru-2** (0.1)	KOH	10	25	60	63	630	11
3	0.79	**Ru-2** (0.1)	NaOH	10	25	60	≥99	1000	17
4	0.79	**Ru-2** (0.1)	$CsOH·H_2O$	10	25	60	≥99	1000	17
5	0.79	**Ru-2** (0.1)	LiOH	10	25	60	≥99	1000	17
6	0.79	**Ru-2** (0.05)	LiOH	10	25	300	≥99	2000	7
7	0.79	**Ru-2** (0.05)	$CsOH·H_2O$	10	25	300	62	1240	248
8	0.79	**Ru-2** (0.05)	NaOH	10	25	300	76	1520	304

a) Standard reaction conditions: 2 mol% (solid base).

b) Determined by ^{1}H-NMR analysis.

Amount of water (1 mL)

Table S7. Conversion and kinetic data for the hydrogenation of **HMF** under 30 bar H_2 at 25 °C in water.

Entry	**Ru-2** [mol%][a]	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	0.1	30	25	10	75	750	75
2	0.1	30	25	30	≥99	1000	33
3	0.05	30	25	10	26	520	52
4	0.05	30	25	30	42	840	28
5	0.05	30	25	120	≥99	2000	17
6	0.05	10	25	300	≥99	2000	6
7	NC	30	25	30	-	-	-

a) Standard reaction conditions: 0.79 mmol of **HMF**, 0.1 or 0.05 mol% of **Ru-2** and 2 mol% LiOH.

b) Determined by integration of ^{1}H-NMR analysis.

* NC = No catalyst

Table S8. Conversion and kinetic data for the hydrogenation of **HMF** under 30 bar H_2 at 25 °C in ethanol/water.

Entry	**Ru-2** [mol%][a]	Ethanol/water ratio	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	0.1	95:5	30	25	15	≥95	>950	>63
2	0.1	80:20	30	25	15	≥95	>950	>63
3	0.05	95:5	30	25	15	≥95	>1900	>127
4	0.05	80:20	30	25	15	≥95	>1900	>127

a) Standard reaction conditions: 0.79 mmol of **HMF**, 0.1 or 0.05 mol% of **Ru-2** and 2 mol% LiOH.

b) Determined by integration of ^{1}H-NMR analysis.

5. Screening of reactions for the hydrogenation of **MF** to **MFA**

Table S9. Conversion and kinetic data for the hydrogenation of **MF** to **MFA** under 30 bar H_2 at 60 °C in ethanol.

Entry	Catalyst [mol%][a]	Ethanol	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	**Ru**-**2** (0.1)	1.008	30	60	10	<10	-	-
2	**Ir**-**1**(0.1)	1.008	30	60	10	≥99	1000	100
3	**Ir**-**1**(0.05)	1.008	30	60	30	52	1040	35
4	**Ir**-**1**(0.05)	1.008	30	60	60	71	1420	24
5	**Ir**-**1**(0.05)	1.008	30	60	150	≥99	2000	13
6	**Ir-1**(0.01)[c]	1.508	30	120	30	71	7100	237
7	**Ir-1**(0.005)[c]	1.508	30	120	300	14	2800	9

a) Standard reaction conditions: 0.90 mmol of **MF** and 2.0 mol% base (NaOEt: 2.0 M/EtOH)

b) Determined by integration of ^{1}H-NMR analysis.

c) Scale up to 7.9 mmol of **MF**

Table S10. Conversion and kinetic data for the hydrogenation of **MF** to **MFA** under 30 bar H_2 at 60 °C in ethanol/water.

Entry	Catalyst [mol%][a]	Ethanol/water ratio	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	**Ru**-**2** (0.05)	95:5	30	60	180	<10	-	-
2	**Ru**-**2** (0.05)	80:20	30	60	180	<10	-	-
3	**Ir**-**1**(0.05)	95:5	30	60	180	≥99	2000	11
4	**Ir**-**1**(0.05)	80:20	30	60	180	94	1880	10

a) Standard reaction conditions: 0.79 mmol of **MF**, 0.1 or 0.05 mol% of **Ru-2** and 2 mol% base (NaOEt: 2.0 M/EtOH). b) Determined by integration of ^{1}H-NMR analysis.

Table S11. Conversion and kinetic data for the hydrogenation of neat **MF** under 30 bar H_2 at 120 °C.

Entry	Catalyst	Catalyst [mol%][a]	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	**Ru-1**	0.005	30	120	300	≥95	19000	63
2	**Ru-2**	0.005	30	120	300	21	4200	14
3	**Ru-2**	0.005	30	120	1200	52	10400	9
4	**Ir-1**	0.005	30	120	300	91	18200	60
5	**Ir-1**[c]	0.005	30	120	300	-	-	-
6	**-**	-	30	120	300	-	-	-

a) Standard reaction conditions: 15.89 mmol of **MF** and 2.0 mol% base (NaOEt: 2.0 M/EtOH)

b) Determined by integration of ^{1}H-NMR analysis.

c) Experiment in the absence of base.

Table S12. Scale up for the hydrogenation of neat **MF** under 30 bar H_2 at 120 °C.

Entry	Catalyst	Catalyst [mol%][a]	$p_{(H_2)}$ [bar]	T [°C]	*t* [h]	Conv. [%][b]	TON	TOF [min^{-1}]
1	**Ru-1**	0.0005	30	120	5	17	34000	113
2	**Ru-1**	0.0005	30	120	24	61	122000	85
3	**Ru-1**	0.0005	30	120	48	74	148000	51
4	**Ir-1**	0.0005	30	120	5	6	12000	40
5	**Ir-1**	0.0005	30	120	24	36	72000	50
6	**Ir-1**	0.0005	30	120	48	56	112000	39

a) Standard reaction conditions: 59.6 mmol and 1 mol of **MF**, and 2 mol% base (NaOEt: 2.0 M/EtOH)

b) Determined by integration of ^{1}H-NMR analysis.

6. Screening of reactions for the hydrogenation of **FAL** to **FA**

Table S13. Conversion and kinetic data for the hydrogenation of **FAL** under 30 bar H_2 at 25 °C in ethanol.

Entry	**Ru-2** [mol%][a]	Ethanol	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	**Ru-2** (0.1)	1.008	30	25	10	62	620	62
2	**Ru-2** (0.1)	1.008	30	25	30	≥99	1200	40
3	**Ru-2** (0.05)	1.008	30	25	10	40	800	80
4	**Ru-2** (0.05)	1.008	30	25	30	≥99	2000	67
5	**Ru-1** (0.1)	1.008	30	25	10	24	240	24
6	**Ir-1** (0.1)	1.008	30	25	10	<10	-	-

a) Standard reaction conditions: 0.90 mmol of **FAL** and 2.0% base (NaOEt: 2.0 M/EtOH)

b) Determined by integration of ^{1}H-NMR analysis.

Table S14. Conversion and kinetic data for the hydrogenation of **FAL** under 30 bar H_2 at 25 °C in water.

Entry	Catalyst [mol%][a]	$p_{(H_2)}$ [bar]	T [°C]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	**Ru-2** (0.1)	30	25	10	≥99	1000	100
2	**Ru-2** (0.05)	30	25	10	93	1860	186
Formation of an insoluble brown solid observed (humins) in the reactions with water as solvent.							

Table S15. Conversion and kinetic data for the hydrogenation of **FAL** under 30 bar H_2 at 25 °C in ethanol/water.

Entry	catalyst [mol%][a]	Ethanol/H_2O ratio	$p_{(H_2)}$ [bar]	T [^oC]	*t* [min]	Conv. [%][b]	TON	TOF [min^{-1}]
1	**Ru-2** (0.1)	95:5	30	25	10	83	830	83
2	**Ru-2** (0.1)	95:5	30	25	30	≥99	1000	33
3	**Ru-2** (0.1)	80:20	30	25	10	85	850	85
4	**Ru-2** (0.1)	80:20	30	25	30	≥99	1000	33
5	**Ru-2** (0.05)	95:5	30	25	10	44	880	88
6	**Ru-2** (0.05)	95:5	30	25	30	58	1160	39
7	**Ru-2** (0.05)	80:20	30	25	10	86	1720	172
8	**Ru-2** (0.05)	80:20	30	25	30	≥99	2000	67
9	**Ru-1** (0.1)	95:5	30	25	10	13	130	13
10	**Ru-1** (0.1)	95:5	30	25	30	46	460	15
11	**Ru-1** (0.1)	80:20	30	25	10	40	400	40
12	**Ru-1** (0.1)	80:20	30	25	30	≥99	1000	33
13	**Ir-1** (0.1)	95:5	30	25	10	11	110	11
14	**Ir-1** (0.1)	95:5	30	25	30	15	150	5
15	**Ir-1** (0.1)	80:20	30	25	10	-	-	-
16	**Ir-1** (0.1)	80:20	30	25	30	10	100	3

a) Standard reaction conditions: 0.90 mmol of **FAL**, 0.1 or 0.05 mol% of **Ru-2** and 2% base (NaOEt: 2.0 M/EtOH). b) Determined by integration of ^{1}H-NMR analysis.

7. ^{1}H-NMR spectra of the reactions

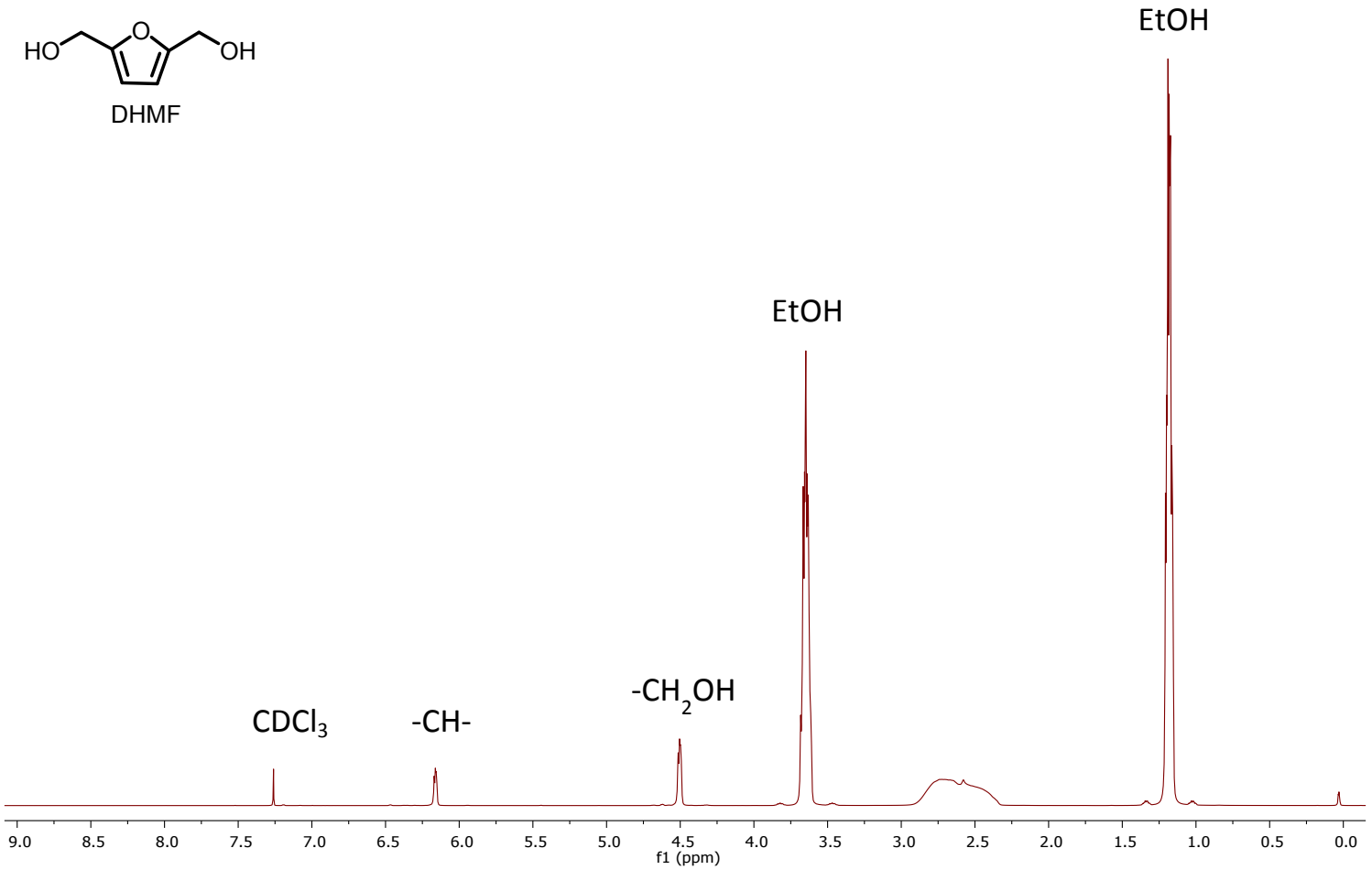


Figure S3. ^{1}H-NMR in $CDCl_3$ of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.05 mol%), 10 bar of H_2 and 25 ^{o}C and 1 min in ethanol (conversion >95%).

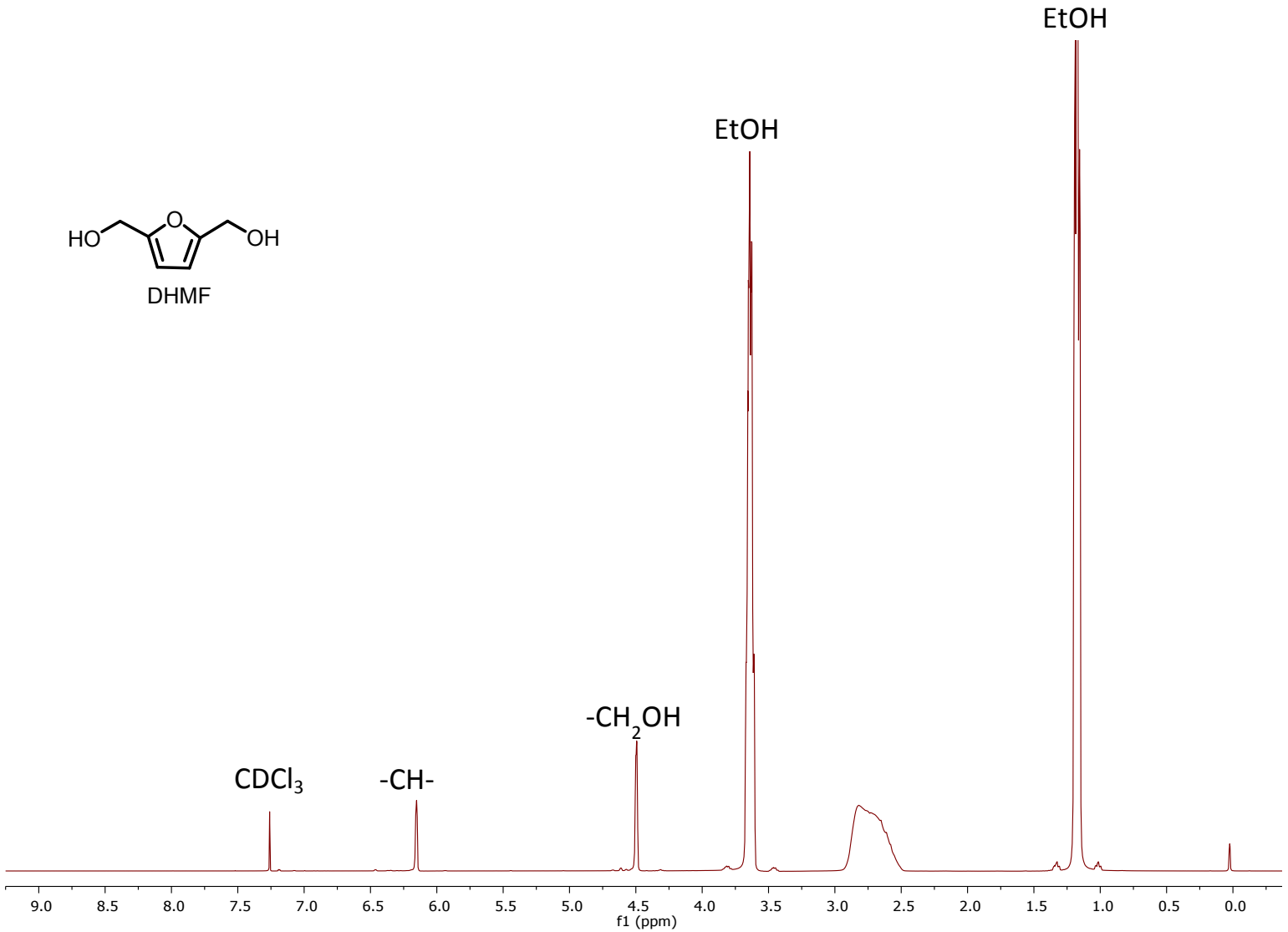


Figure S4. ^{1}H-NMR in $CDCl_3$.of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.05 mol%), 30 bar of H_2 and 25 ^{o}C and 4 min in ethanol (conversion ≥99%).

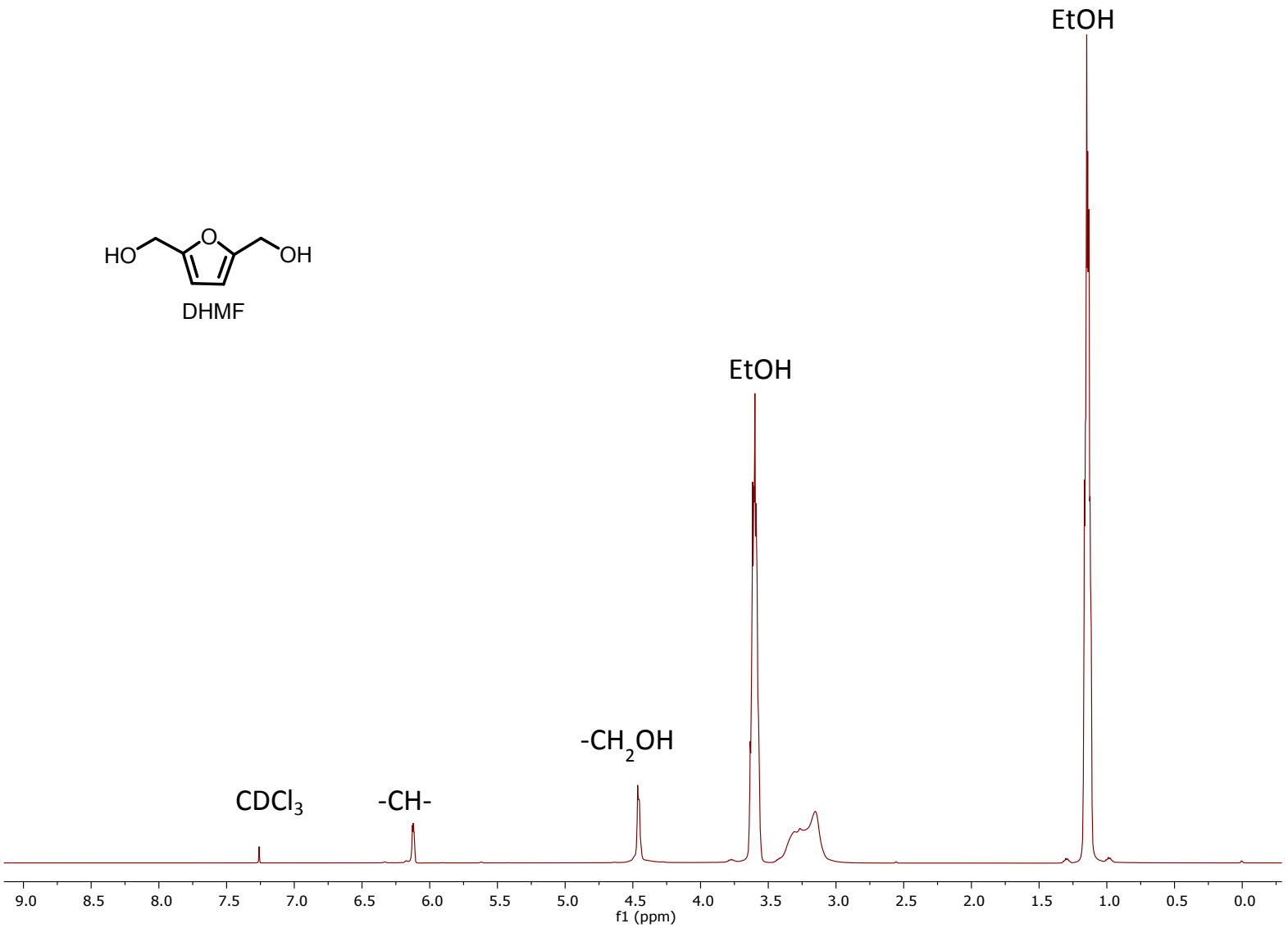


Figure S5. ^{1}H-NMR in $CDCl_3$.of the crude reaction of 4.36 mmol **HMF** with **Ru-2** (0.01 mol%), 30 bar of H_2 and 25 ^{o}C and 120 min in ethanol (conversion ≥99%).

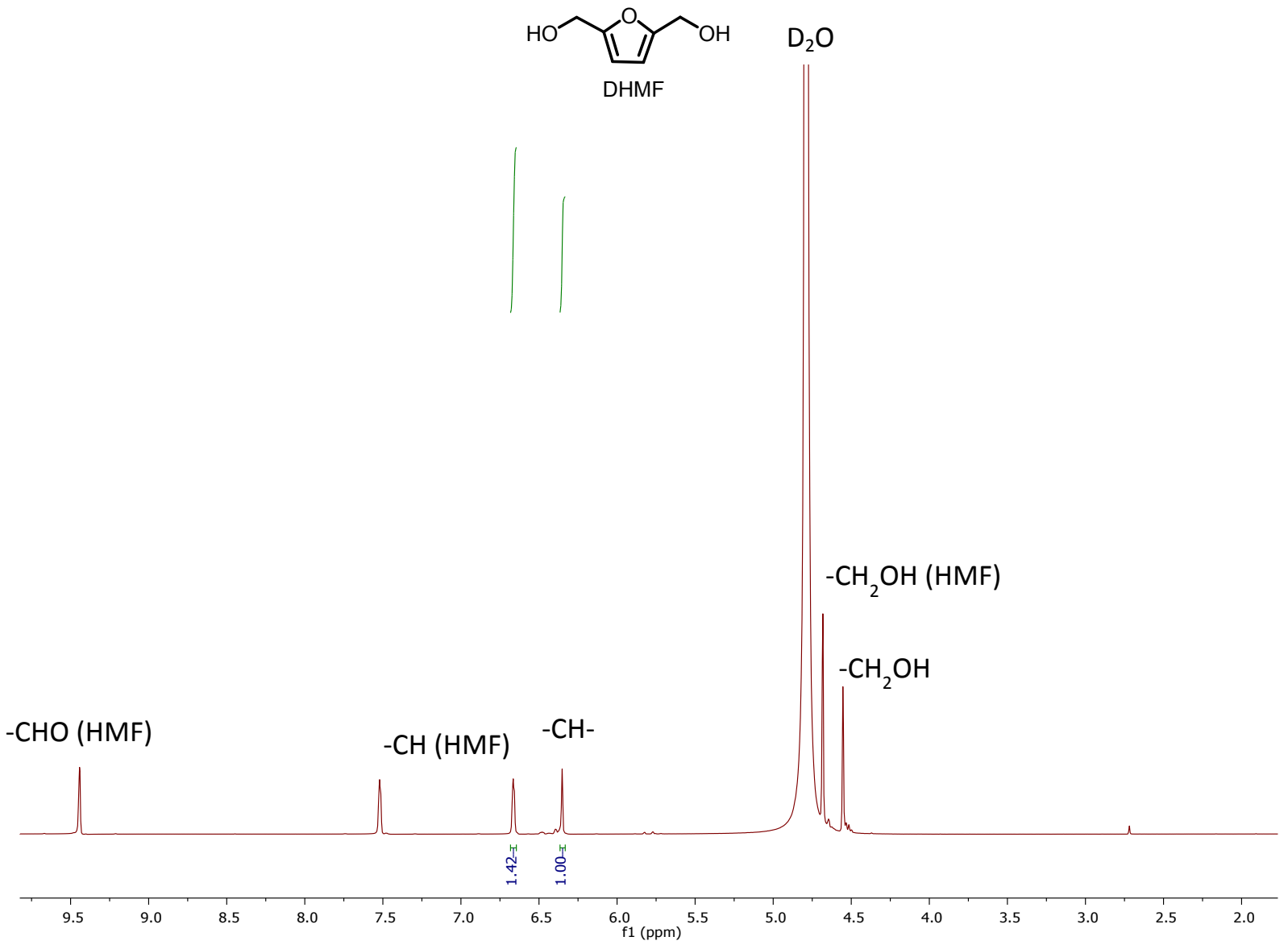


Figure S6. ^{1}H-NMR in D_2O.of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.05 mol%), 30 bar of H_2 and 25 ^{o}C and 10 min in water (conversion 26%).

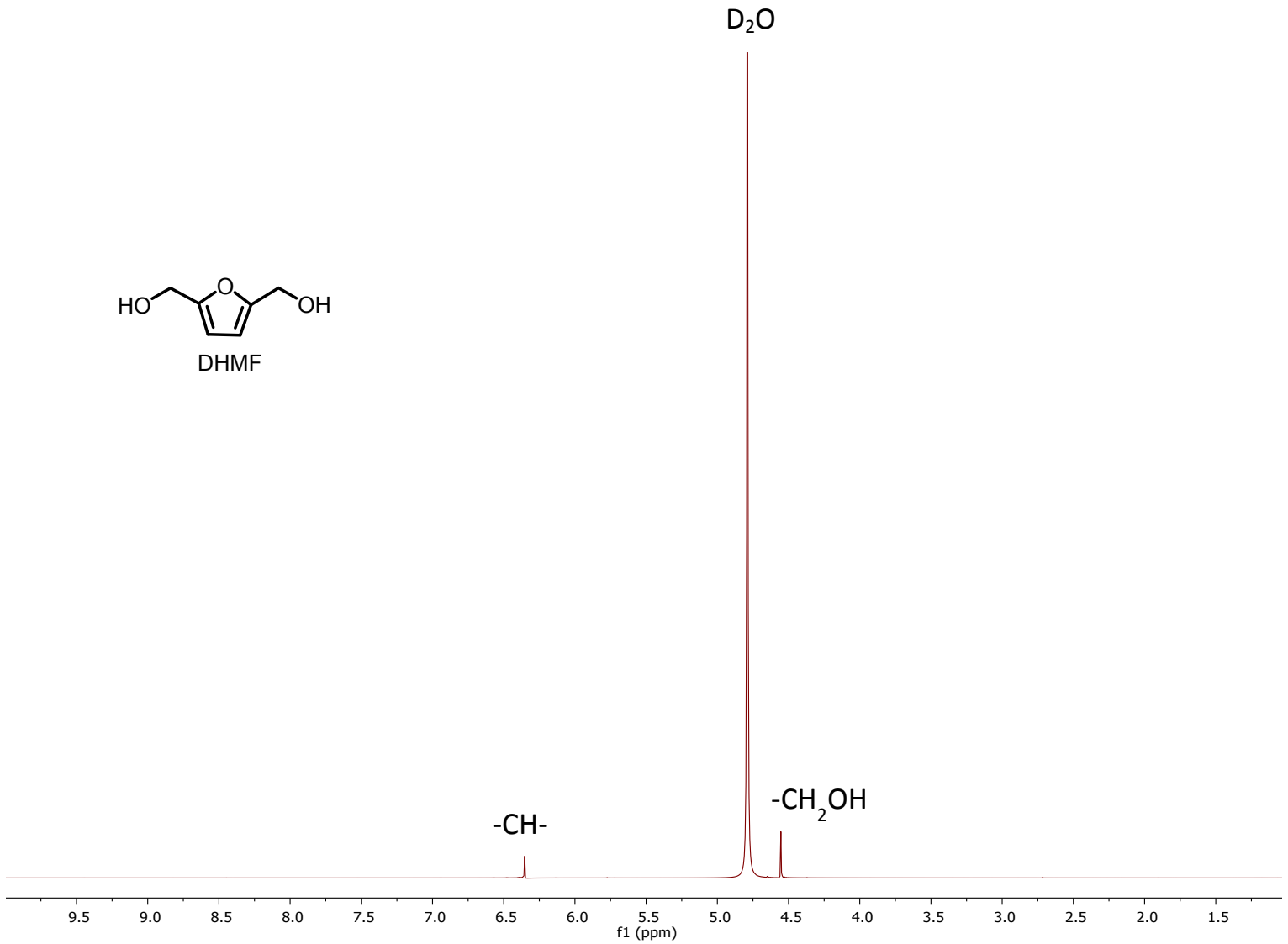


Figure S7. ^{1}H-NMR in $CDCl_3$ of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.05 mol%), 30 bar of H_2 and 25 ^{o}C and 120 min in water (conversion ≥99%).

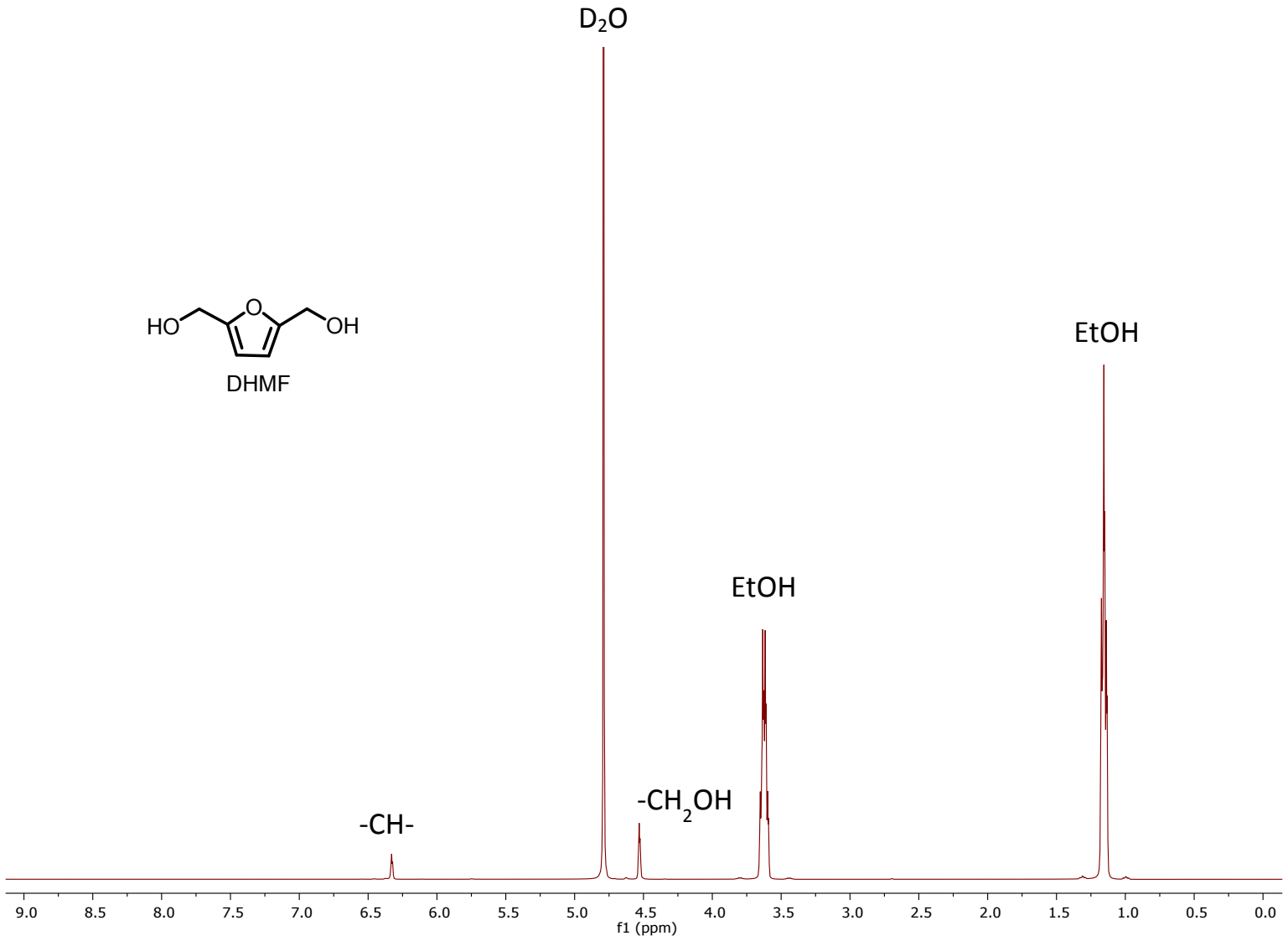


Figure S8. ^{1}H-NMR in D_2O of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.05 mol%), 30 bar of H_2 and 25 ^{o}C and 15 min in ethanol/water (95:5) (conversion ≥95%).

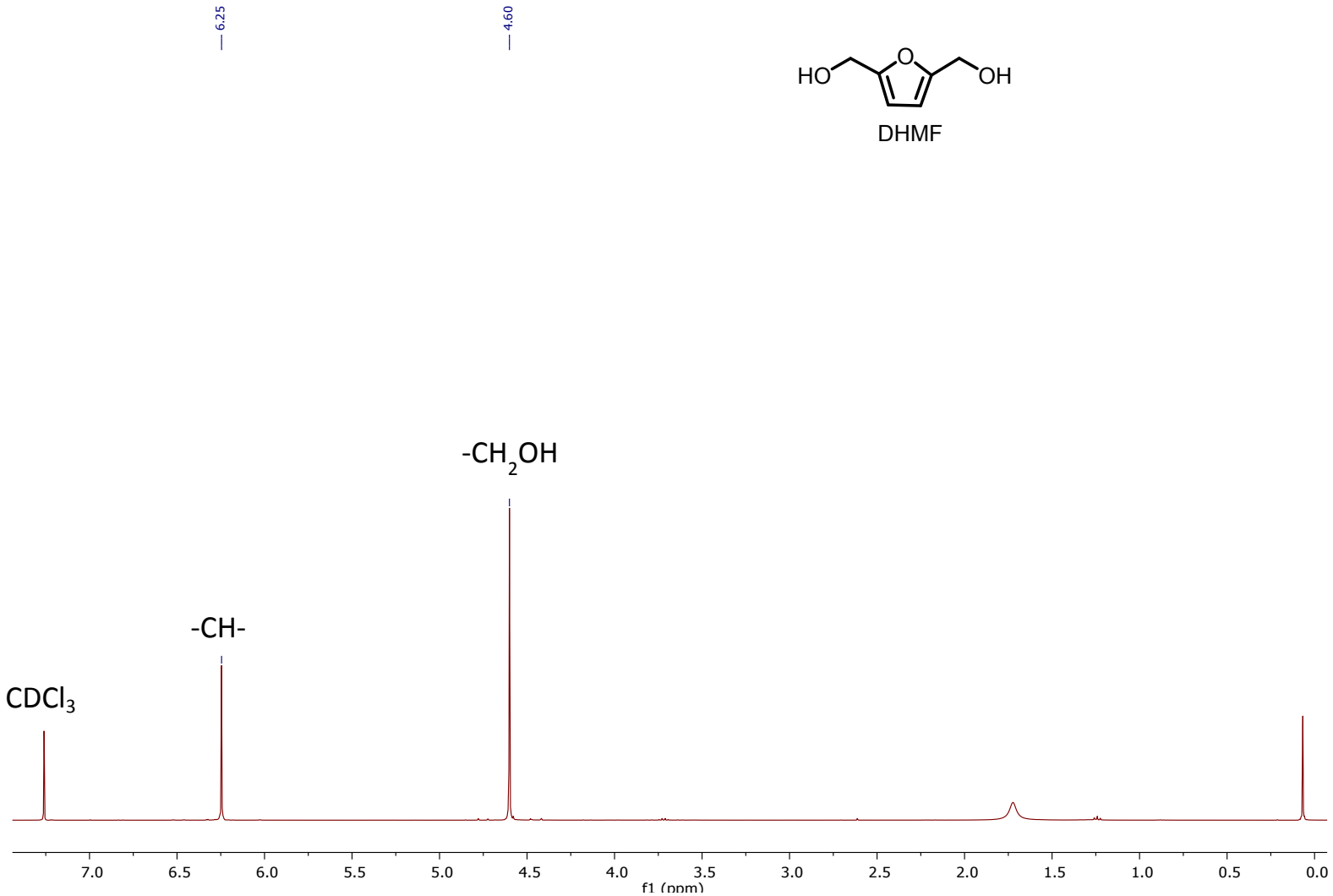


Figure S9. ^{1}H-NMR in $CDCl_3$ of **DHMF** product from reaction of 1 g scale HMF with **Ru-2** (0.1 mol%) after filtration in a silica pad.

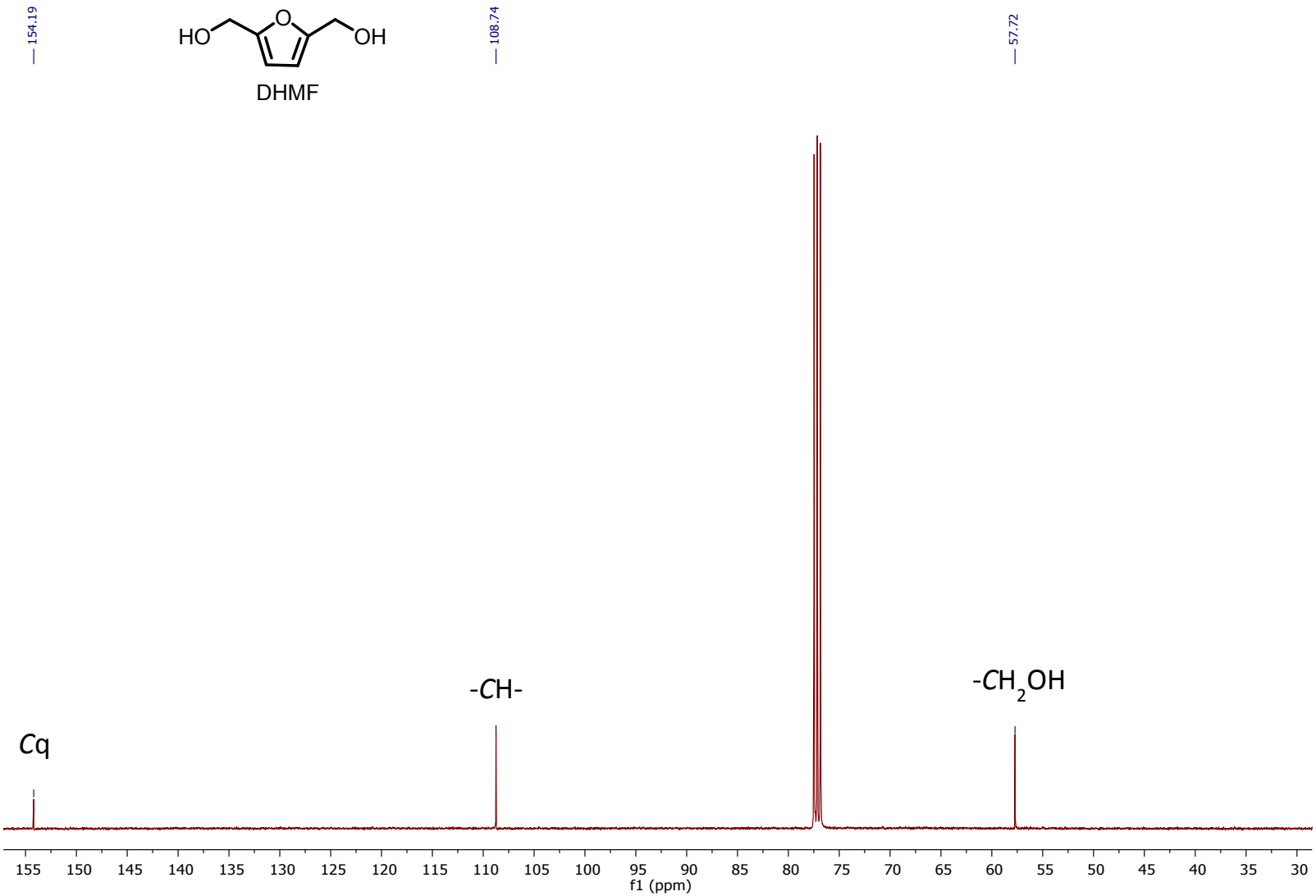


Figure S10. ^{1}H-NMR in $CDCl_3$ of **DHMF** product from reaction of 1 g scale HMF with **Ru-2** (0.1 mol%) after filtration in a silica pad.

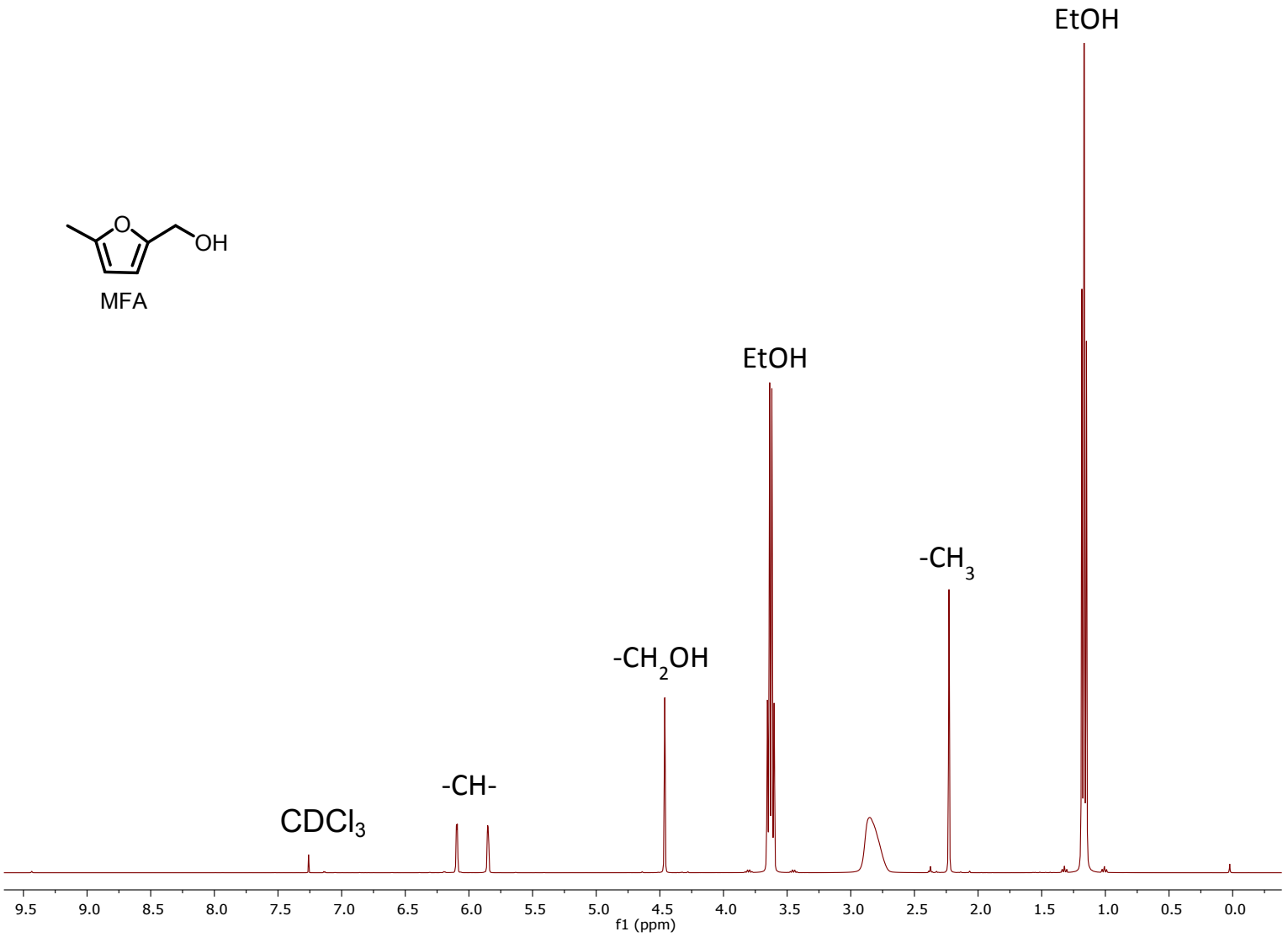


Figure S11. ^{1}H-NMR in $CDCl_3$ of the crude reaction of 0.79 mmol **MF** with **Ir-1** (0.1 mol%), 30 bar of H_2 and 60 ^{o}C and 10 min in ethanol (conversion ≥99%).

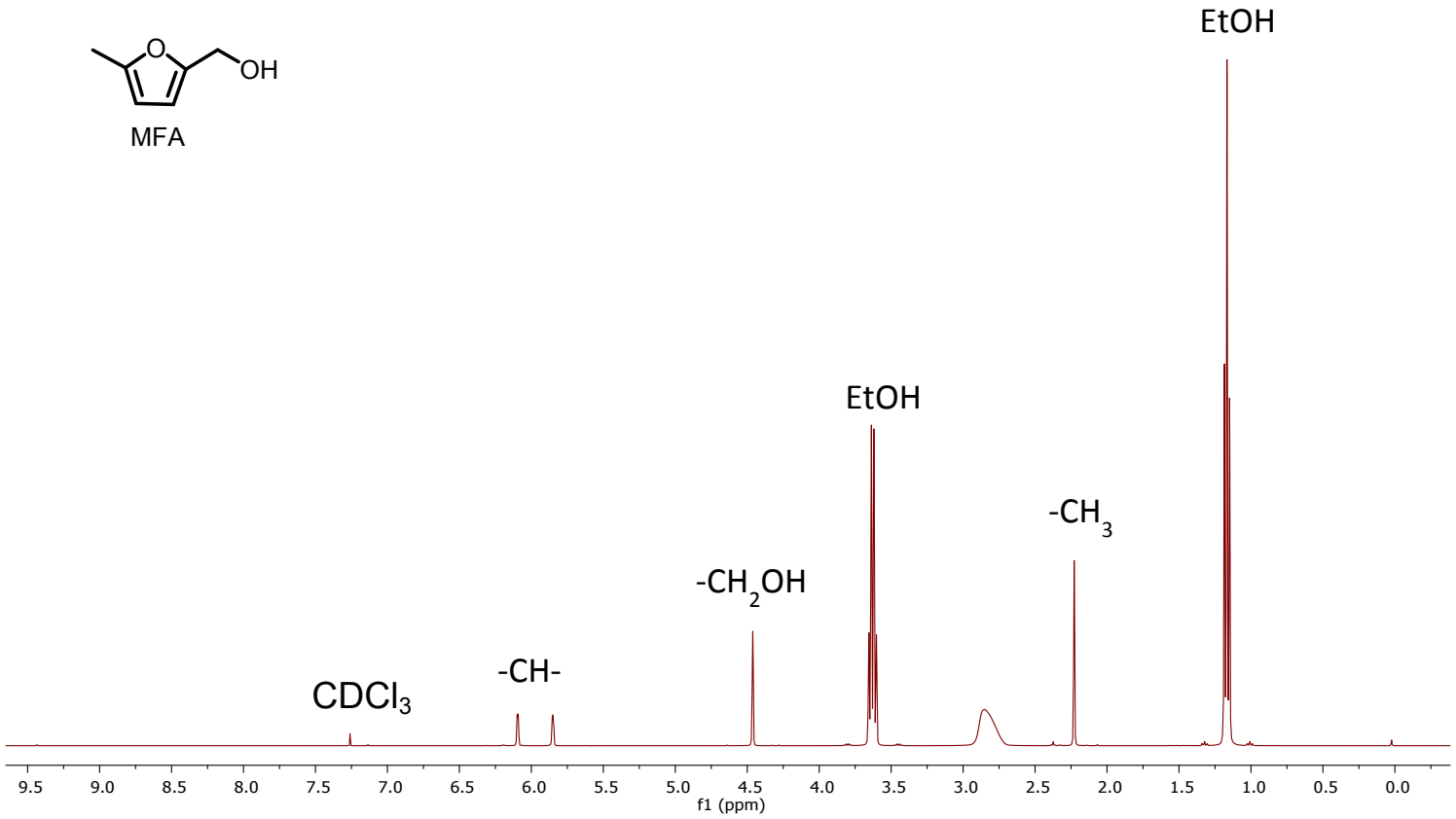


Figure S12. ^{1}H-NMR in $CDCl_3$ of the crude reaction of 0.79 mmol **MF** with **Ir-1** (0.05 mol%), 30 bar of H_2 and 60 ^{o}C and 150 min in ethanol (conversion ≥99%).

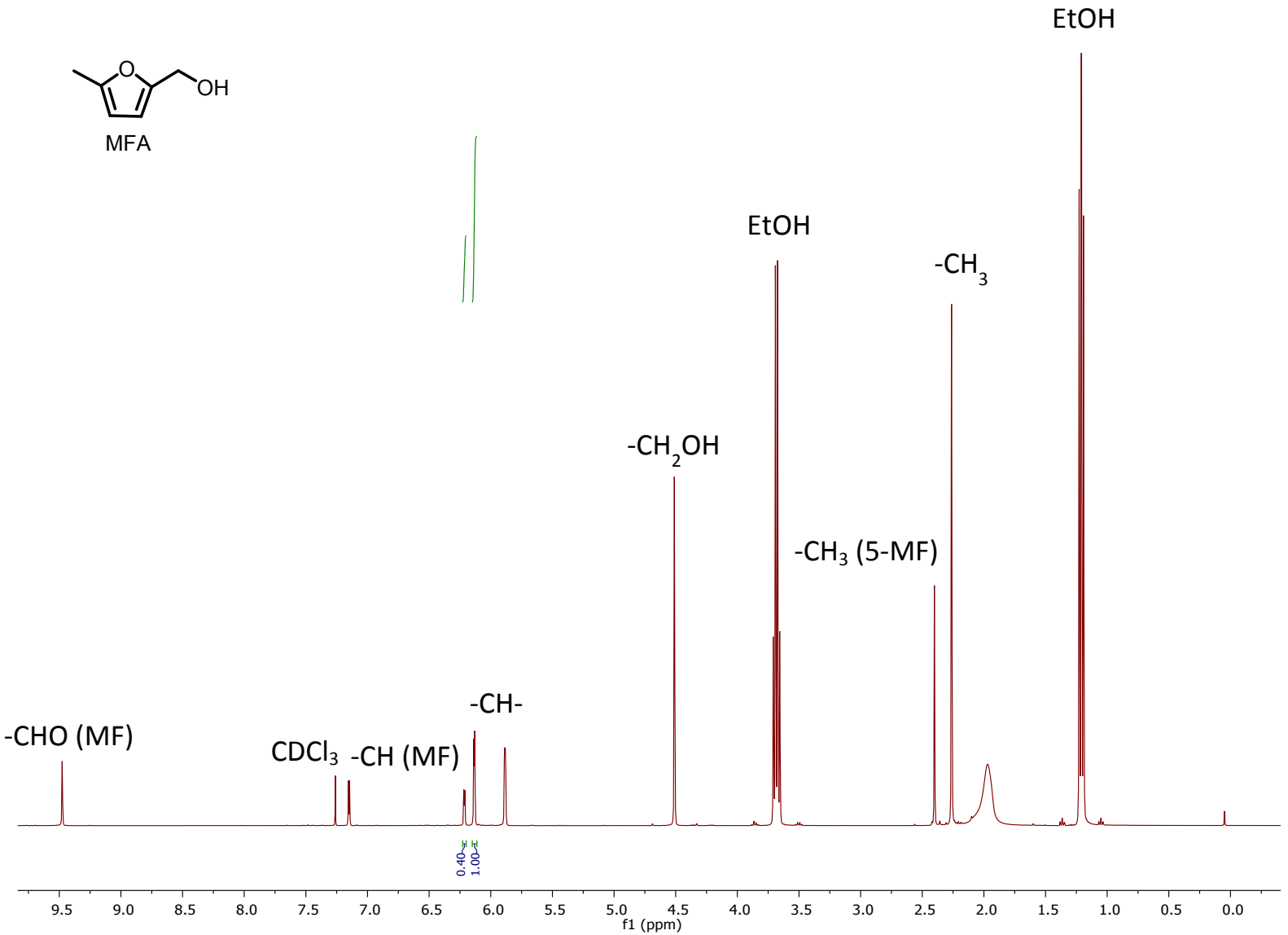


Figure S13. ^{1}H-NMR in $CDCl_3$ of the crude reaction of 7.90 mmol **MF** with **Ir-1** (0.01 mol%), 30 bar of H_2 and 120 ^{o}C and 30 min in ethanol (conversion ≥71%).

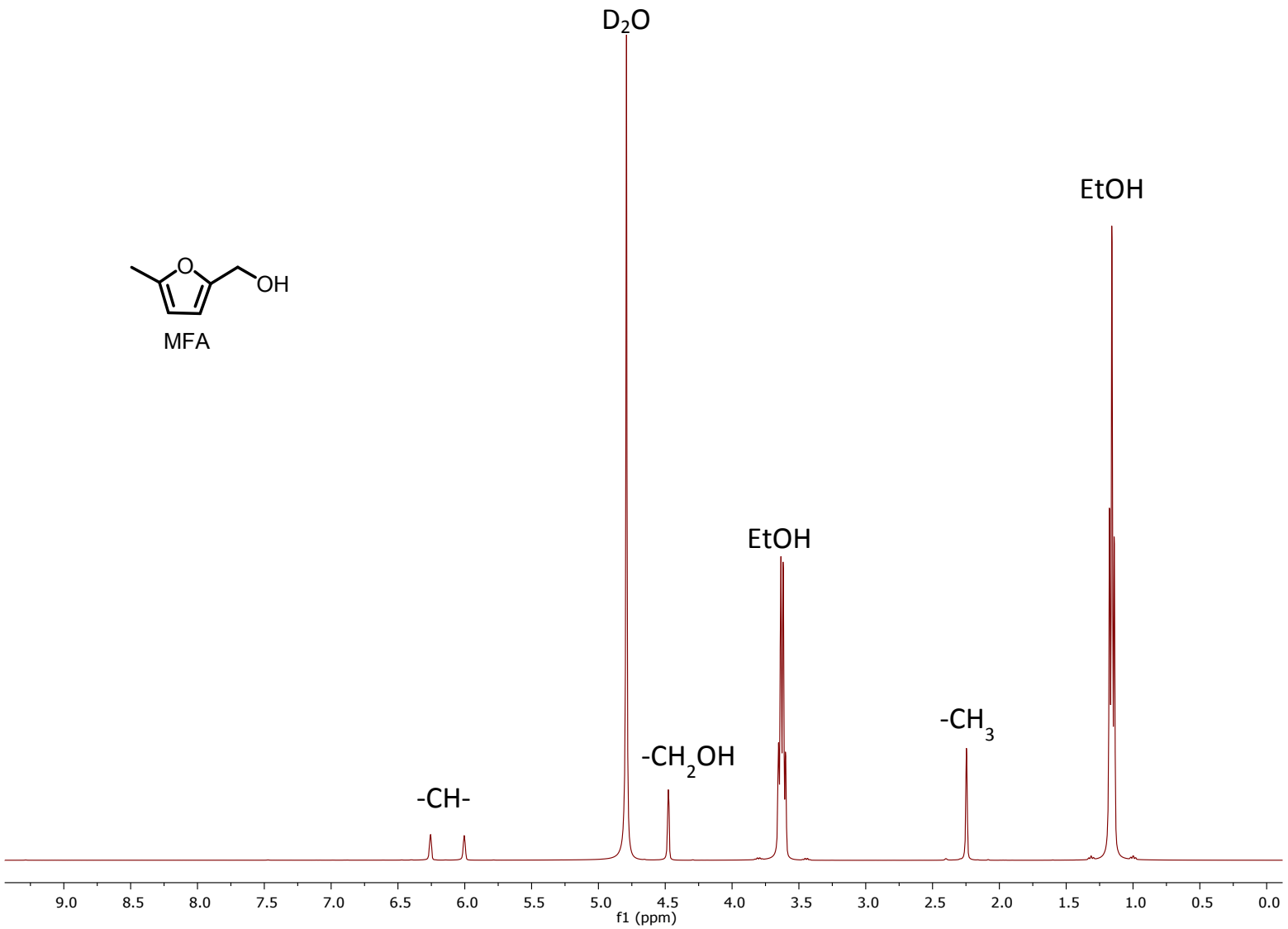


Figure S14. ^{1}H-NMR in D_2O of the crude reaction of 0.79 mmol **MF** with **Ir-1** (0.05 mol%), 30 bar of H_2 and 60 ^{o}C and 180 min in ethanol/water 95:5 (conversion ≥99%).

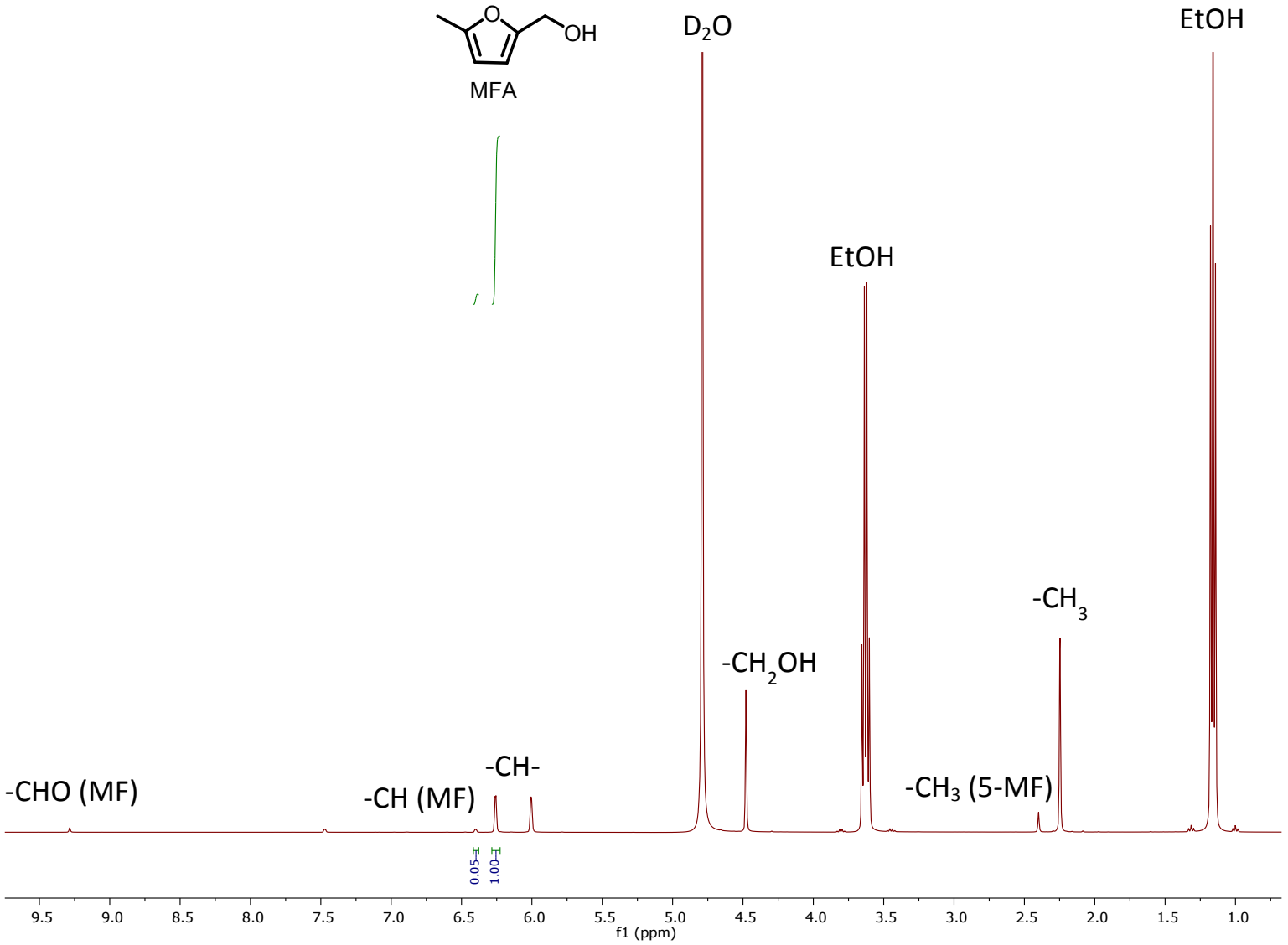


Figure S15. ^{1}H-NMR in D_2O of the crude reaction of 0.79 mmol **MF** with **Ir-1** (0.05 mol%), 30 bar of H_2 and 60 ^{o}C and 180 min in ethanol/water 80:20 (conversion >94%).

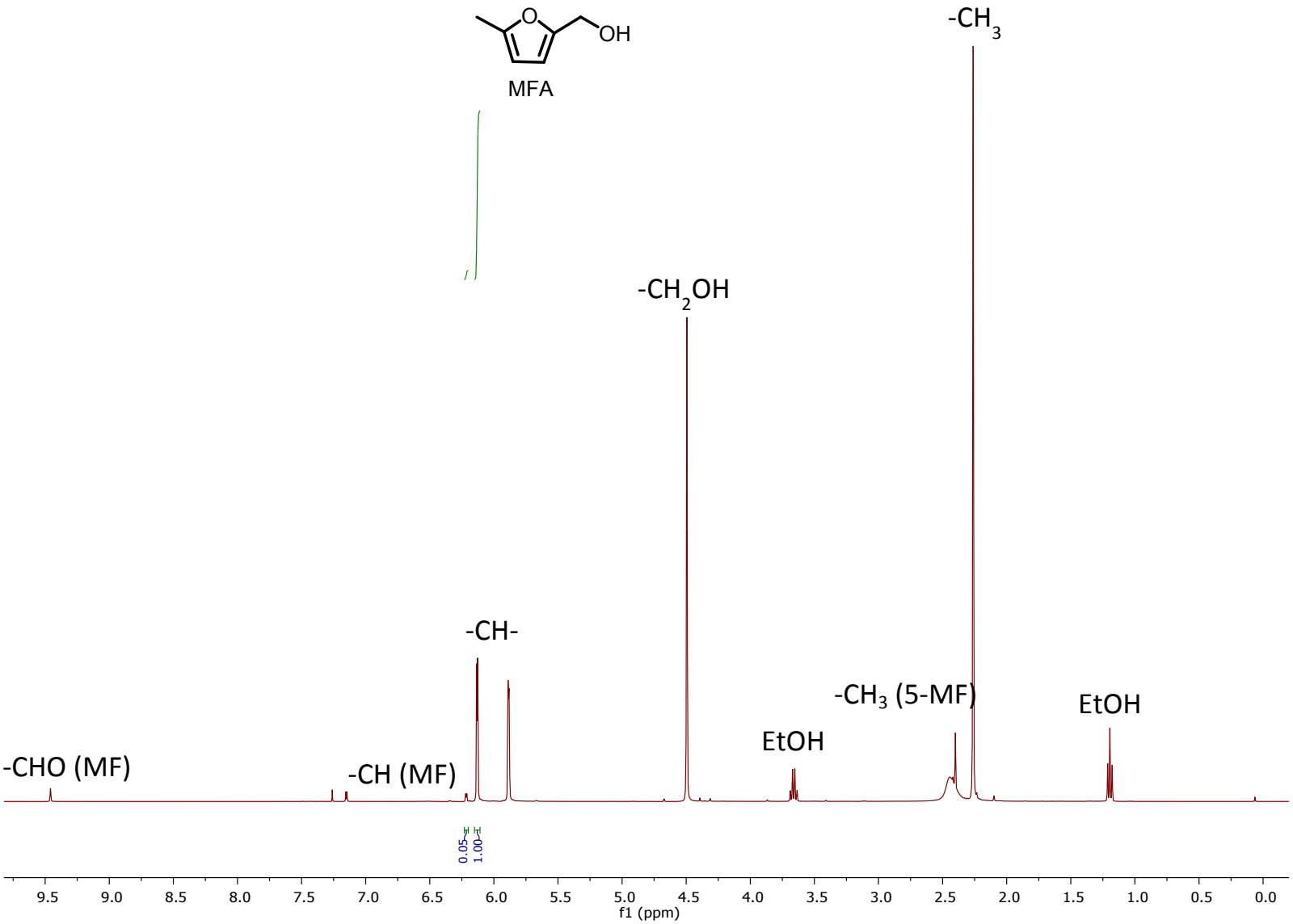


Figure S16. ^{1}H-NMR of the crude reaction of 15.89 mmol neat **MF** with **Ru-1** (0.005 mol%), 30 bar of H_2 and 120 ^{o}C and 5h (conversion 95%) in $CDCl_3$.

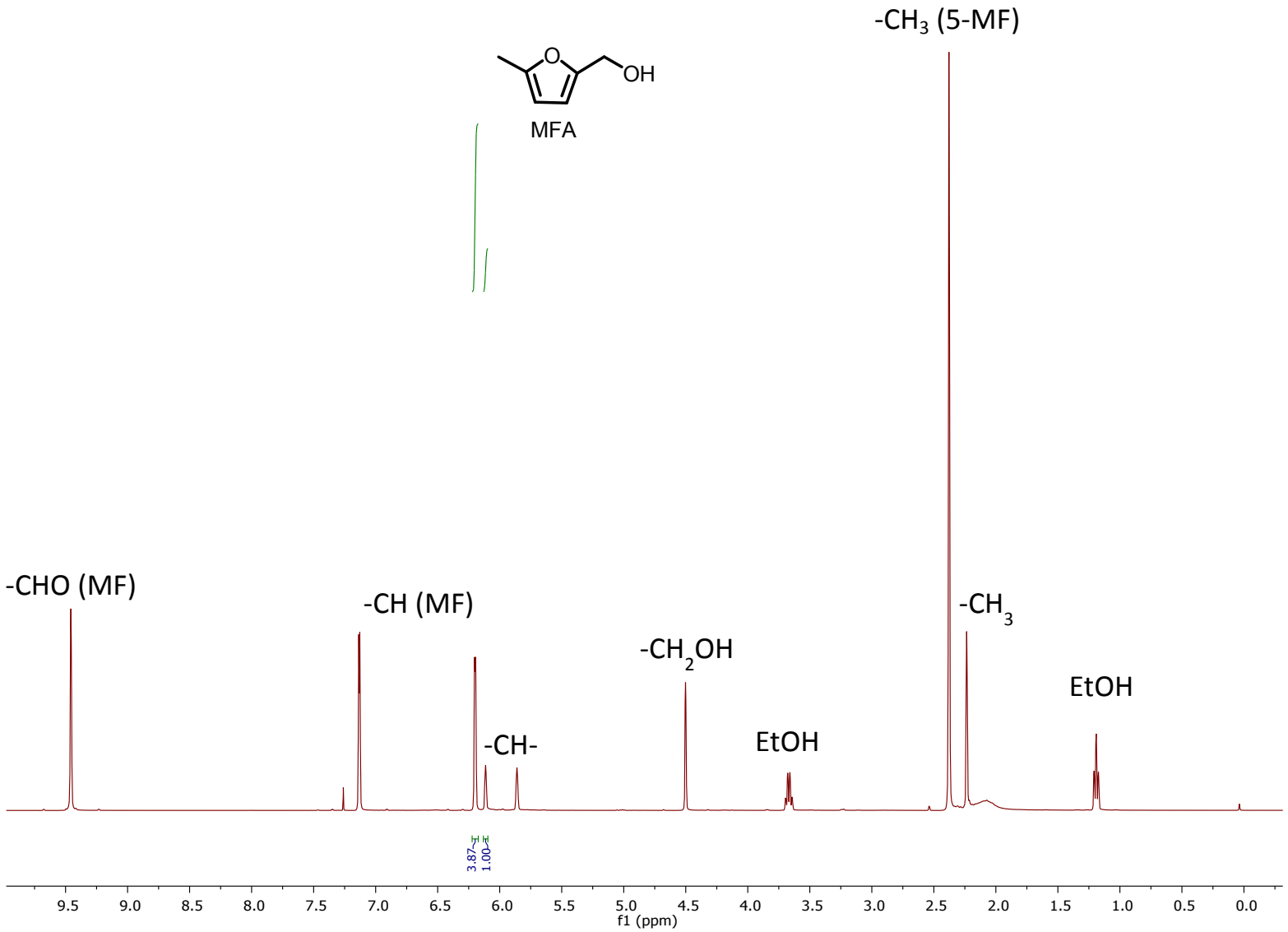


Figure S17. ^{1}H-NMR of the crude reaction of 15.89 mmol neat **MF** with **Ru-2** (0.005 mol%), 30 bar of H_2 and 120 ^{o}C and 5h (conversion 21%) in $CDCl_3$.

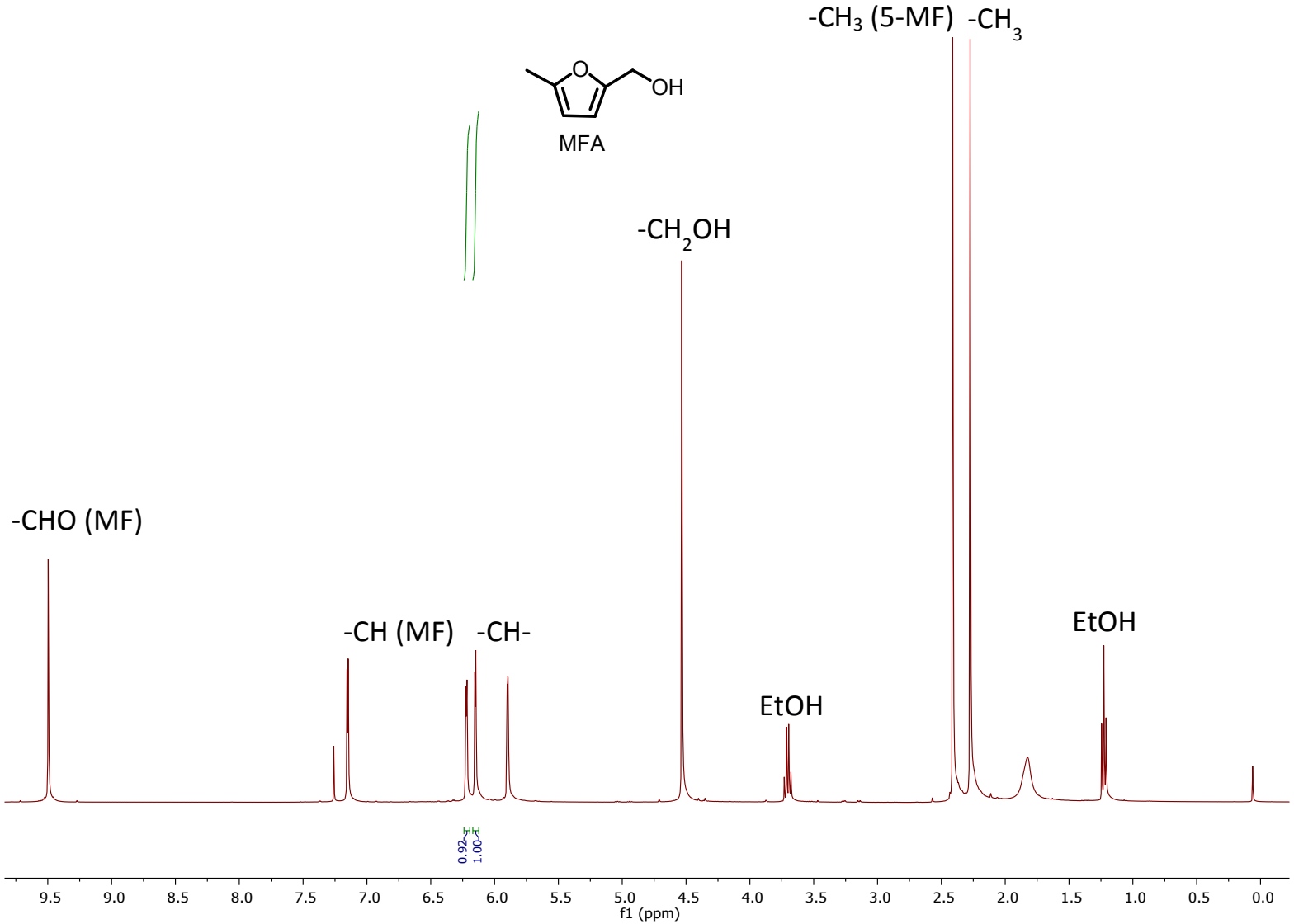


Figure S18. ^{1}H-NMR of the crude reaction of 15.89 mmol neat **MF** with **Ir-1** (0.005 mol%), 30 bar of H_2 and 120 ^{o}C and 20h (conversion 52%) in $CDCl_3$.

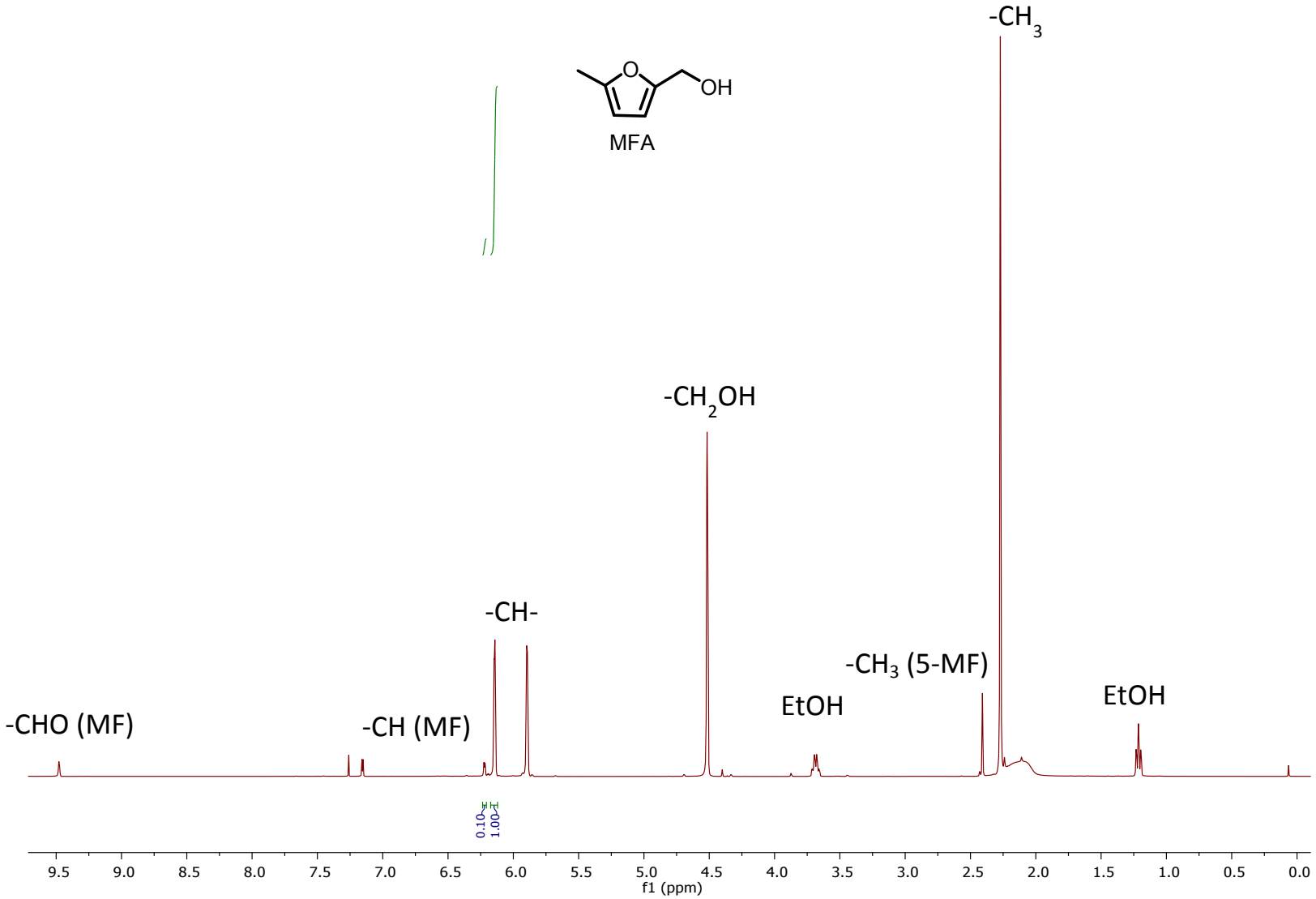


Figure S19. ^{1}H-NMR of the crude reaction of 59.6 mmol neat **MF** with **Ir-1** (0.005 mol%), 30 bar of H_2 and 120 ^{o}C and 5h (conversion 91%) in $CDCl_3$.

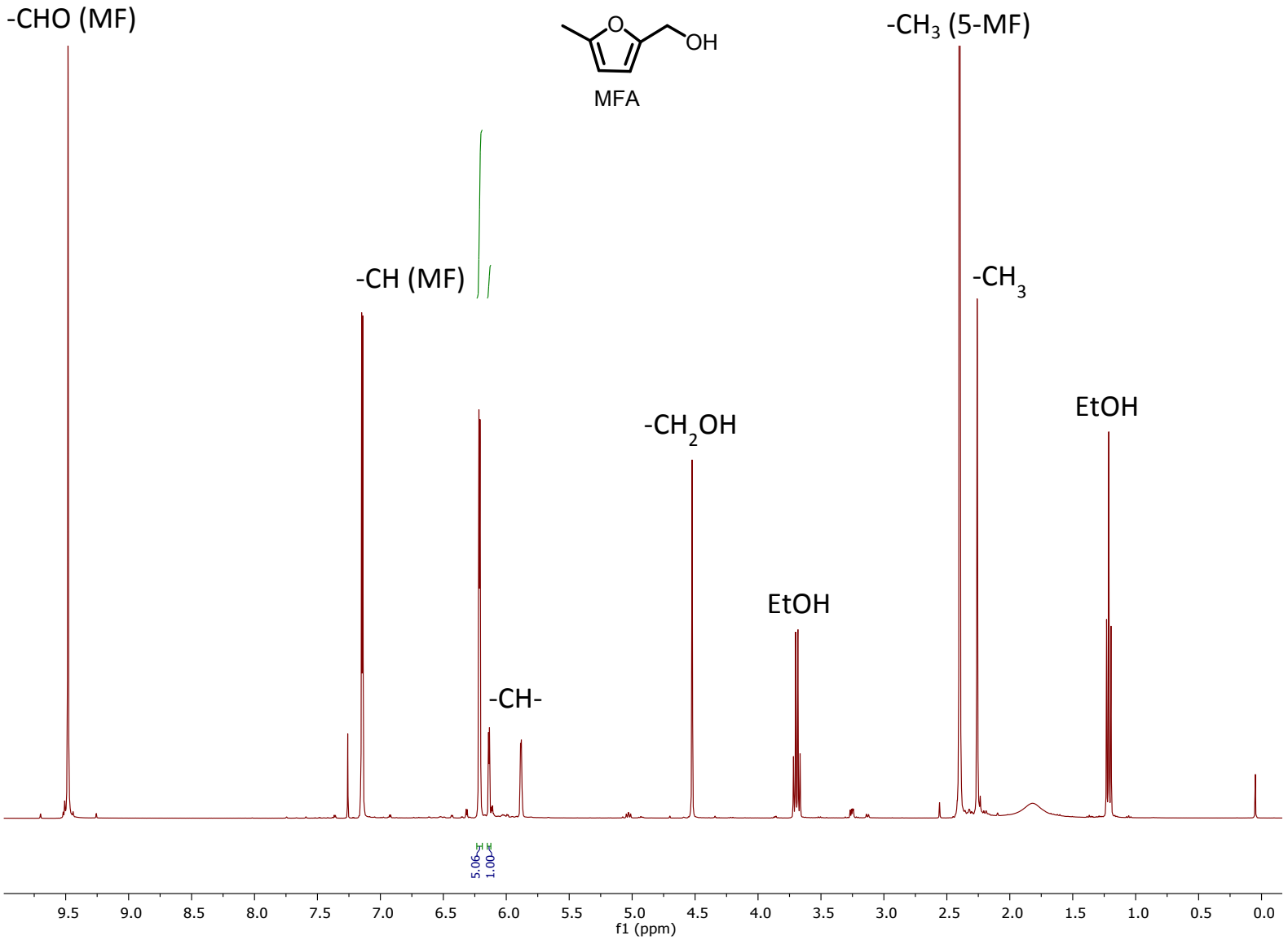


Figure S20. ^{1}H-NMR of the crude reaction of 59.6 mmol neat **MF** with **Ru-1** (0.0005 mol%), 30 bar of H_2 and 120 ^{o}C and 5h (conversion 17%) in $CDCl_3$.

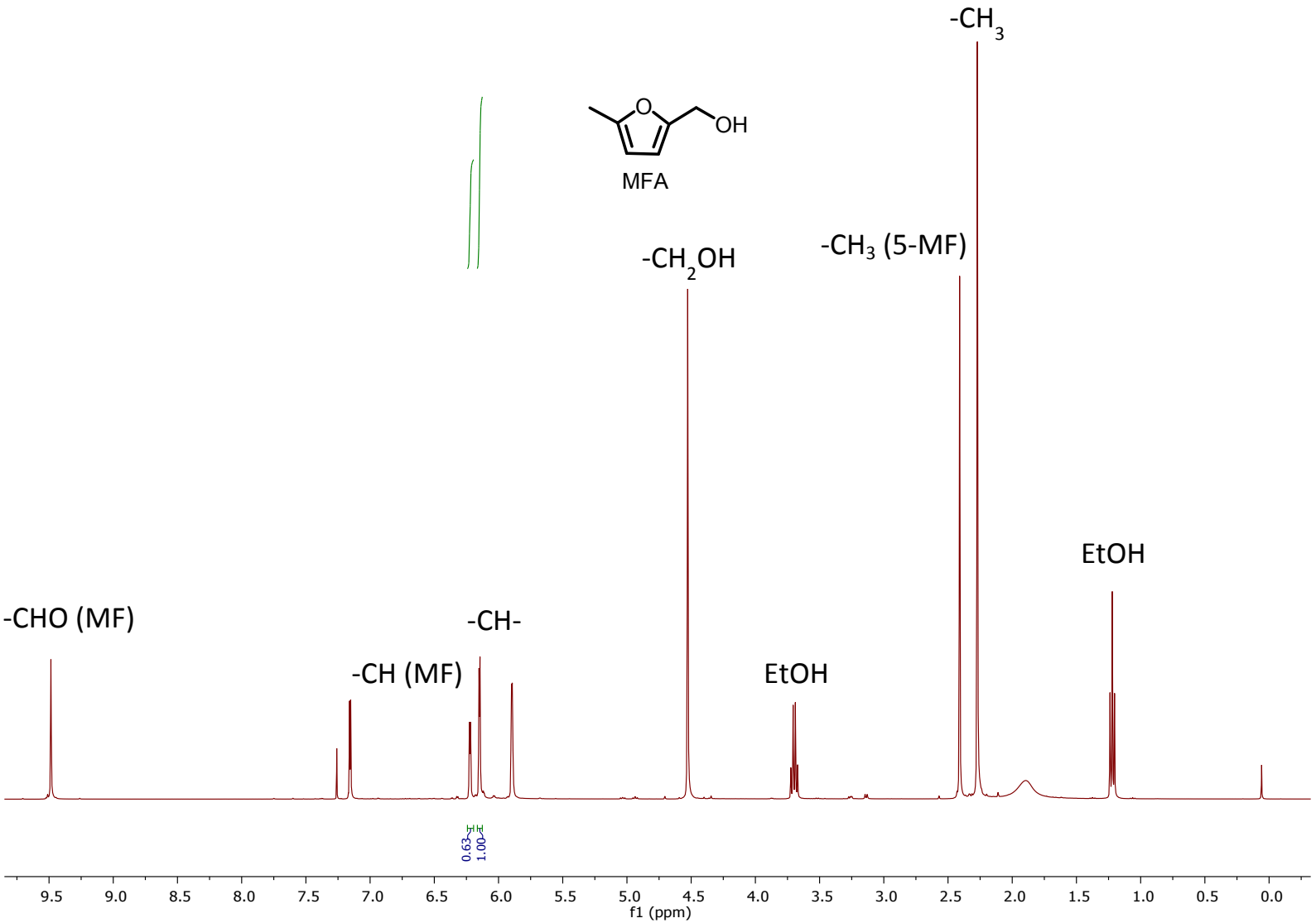


Figure S21. ^{1}H-NMR of the crude reaction of 59.6 mmol neat **MF** with **Ru**-**1** (0.0005 mol%), 30 bar of H_2 and 120 ^{o}C and 5h (conversion 61%) in $CDCl_3$.

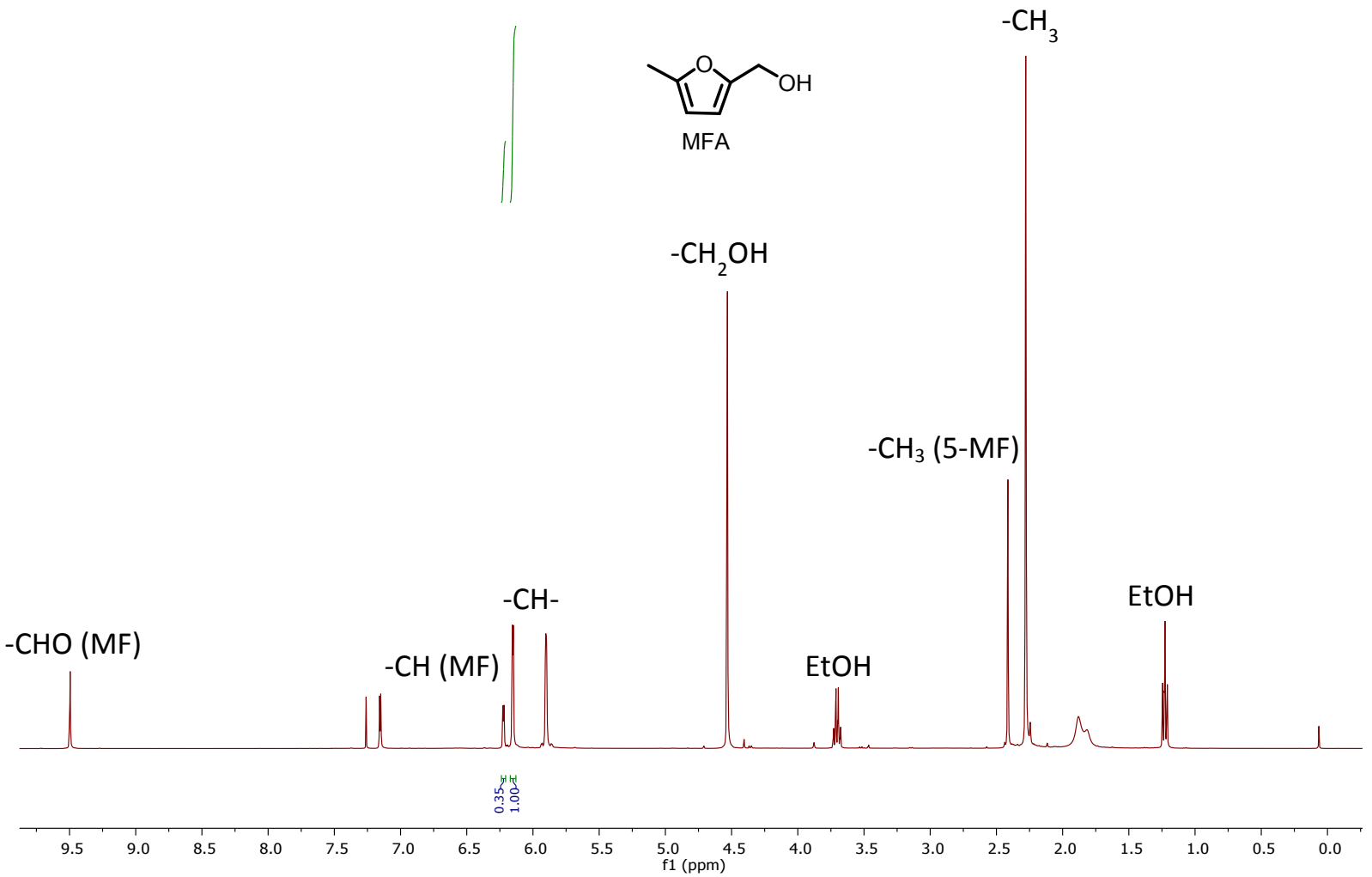


Figure S22. ^{1}H-NMR of the crude reaction of 59.6 mmol neat **MF** with **Ru-1** (0.0005 mol%), 30 bar of H_2 and 120 ^{o}C and 5h (conversion 74%) in $CDCl_3$.

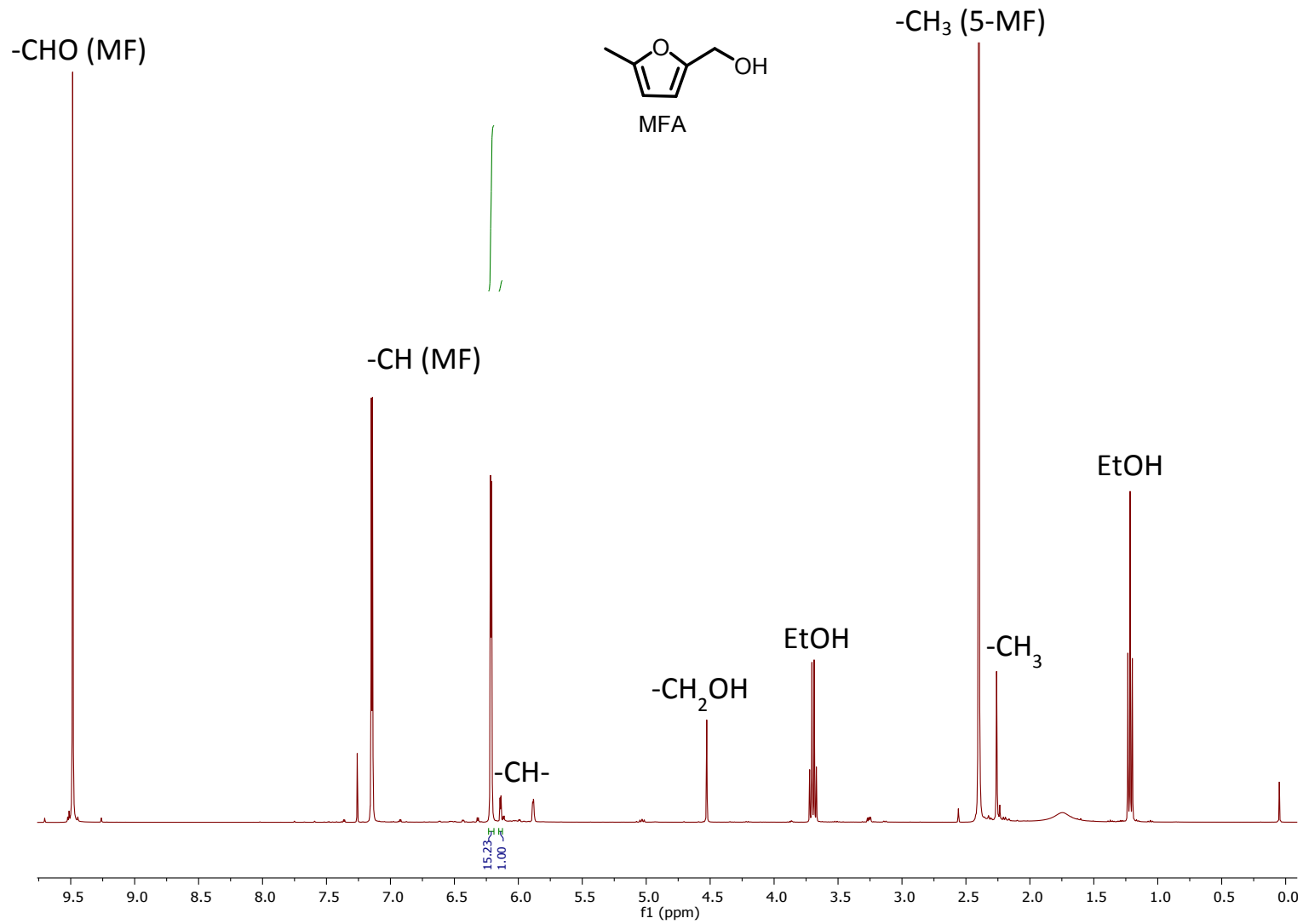


Figure S23. ^{1}H-NMR of the crude reaction of 59.6 mmol neat **MF** with **Ir-1** (0.0005 mol%), 30 bar of H_2 and 120 ^{o}C and 5h (conversion ≈6%) in $CDCl_3$.

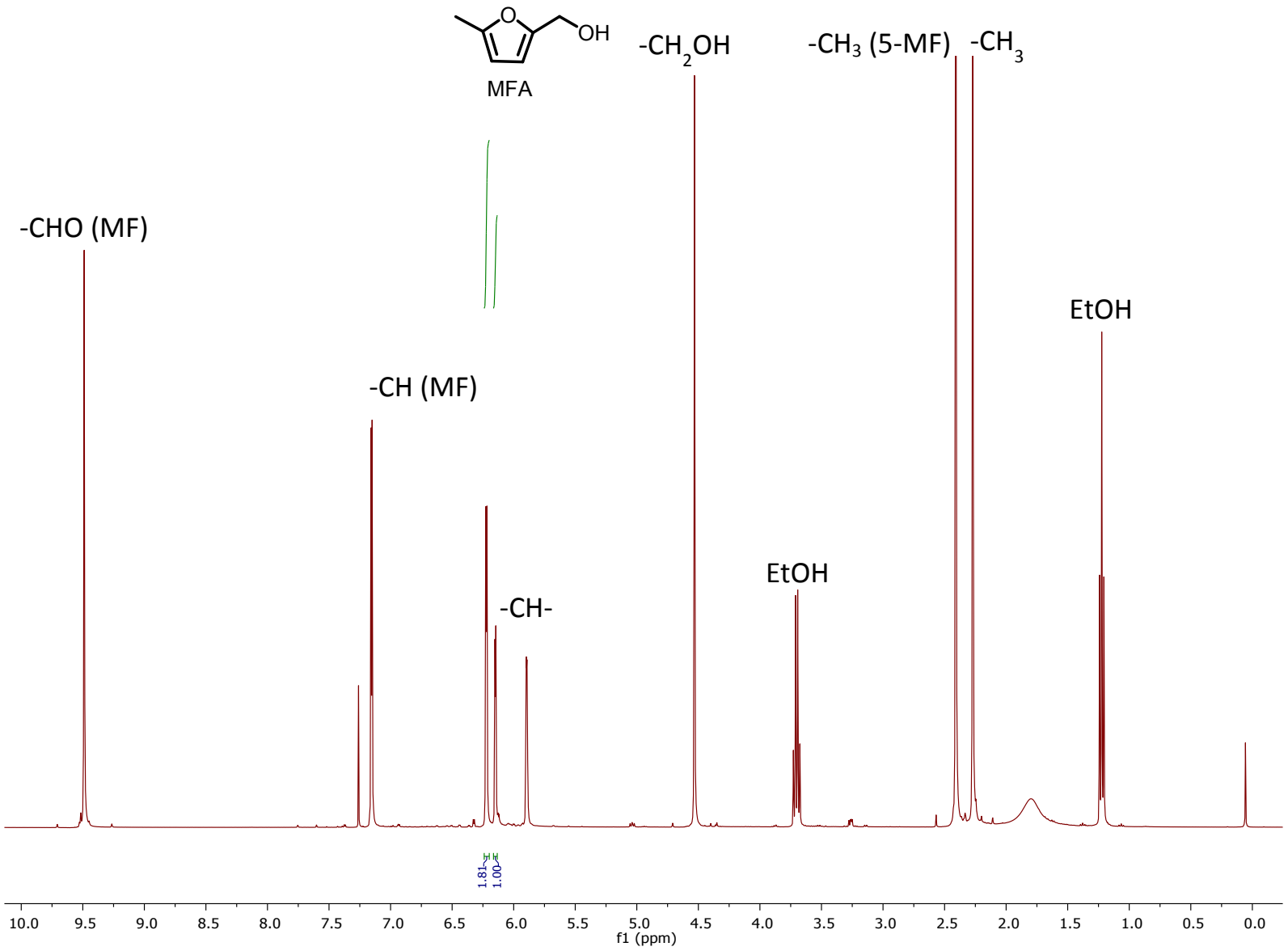


Figure S24. ^{1}H-NMR of the crude reaction of 59.6 mmol neat **MF** with **Ir-1** (0.0005 mol%), 30 bar of H_2 and 120 ^{o}C and 24h (conversion 36%) in $CDCl_3$.

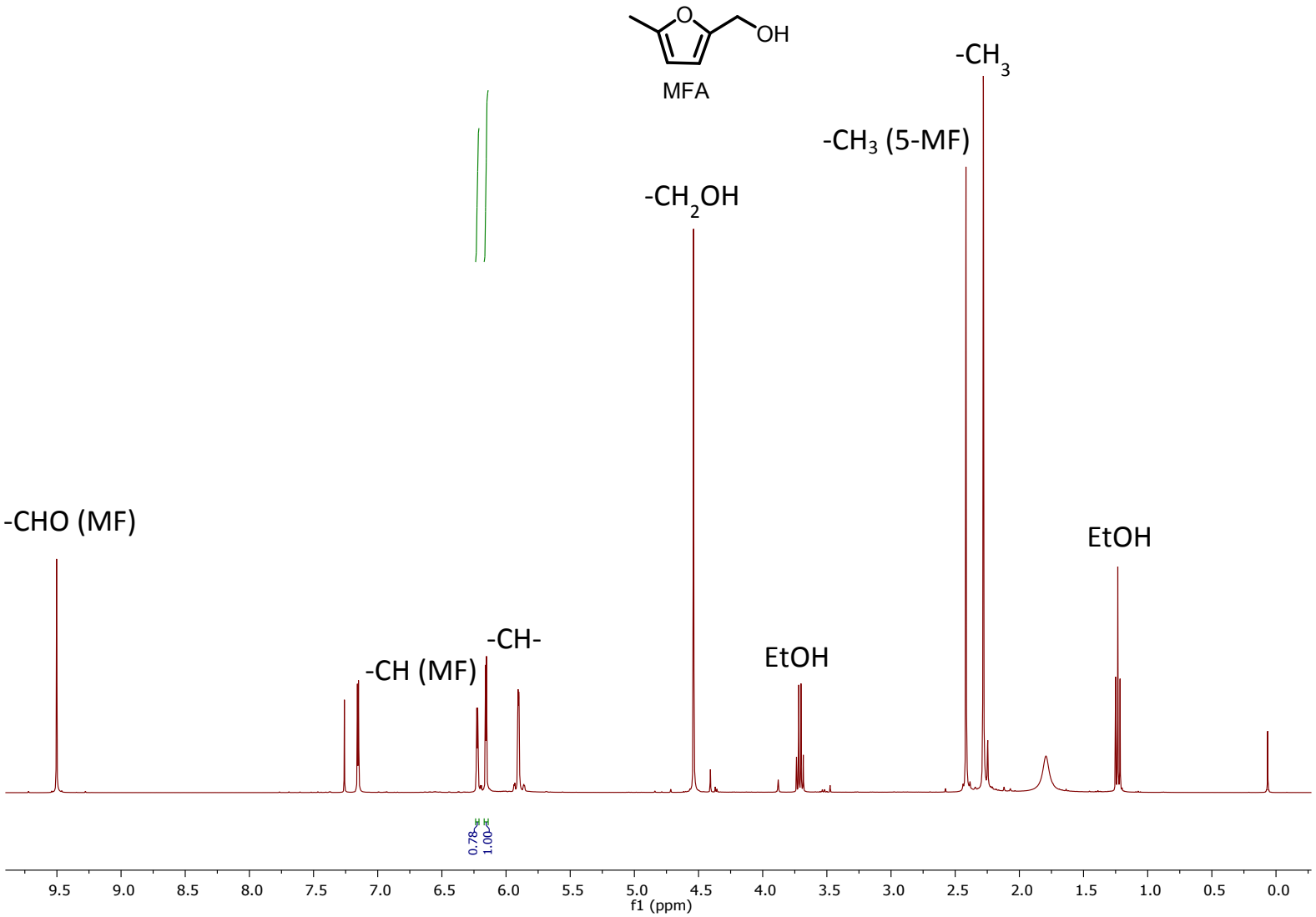


Figure S25. ^{1}H-NMR of the crude reaction of 59.6 mmol neat **MF** with **Ir-1** (0.0005 mol%), 30 bar of H_2 and 120 ^{o}C and 24h (conversion 56%) in $CDCl_3$.

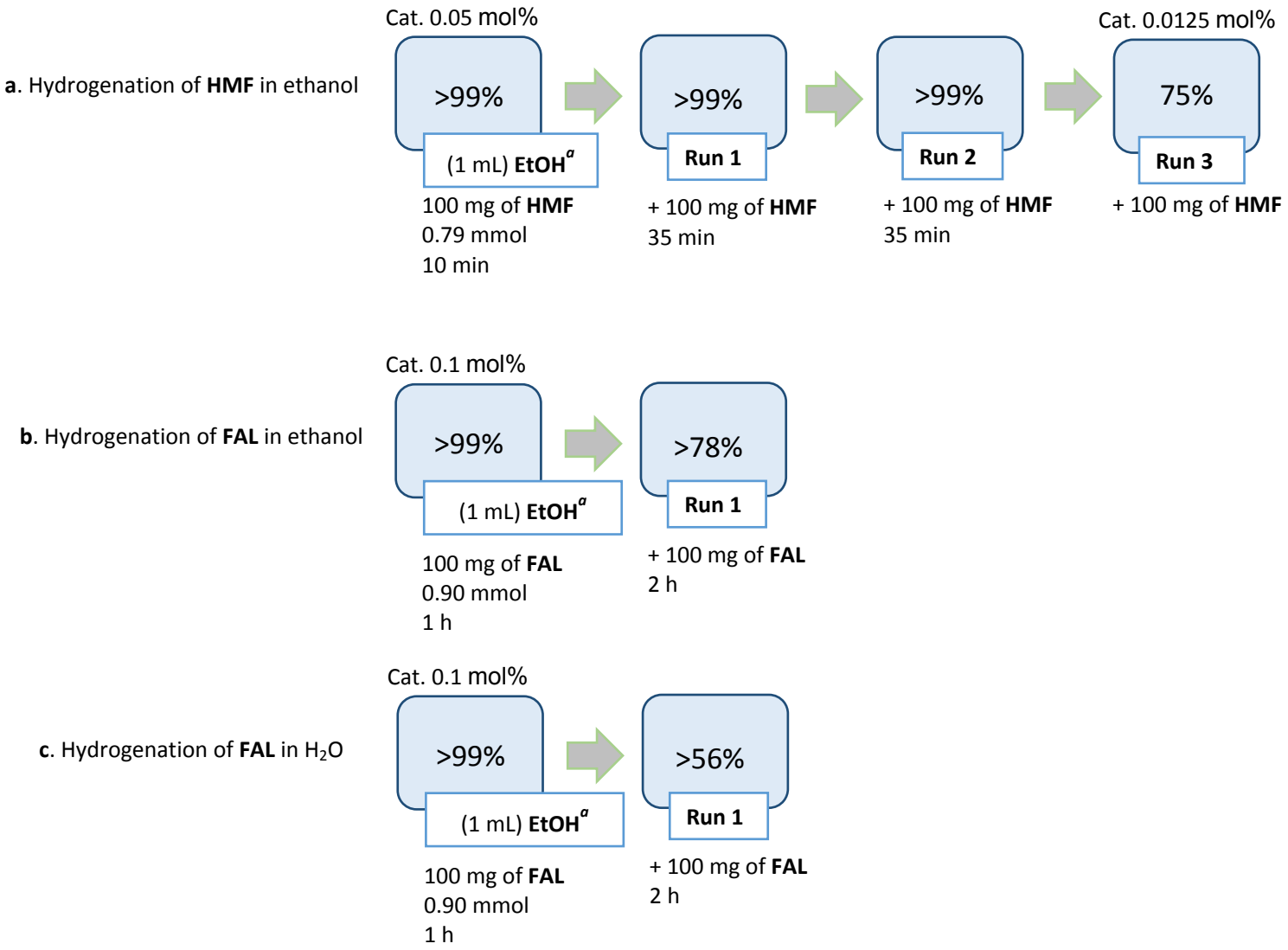


Figure S26. Consecutive addition experiments of **HMF** and **FAL** employing **Ru-2** catalyst on large scale with ethanol and water.

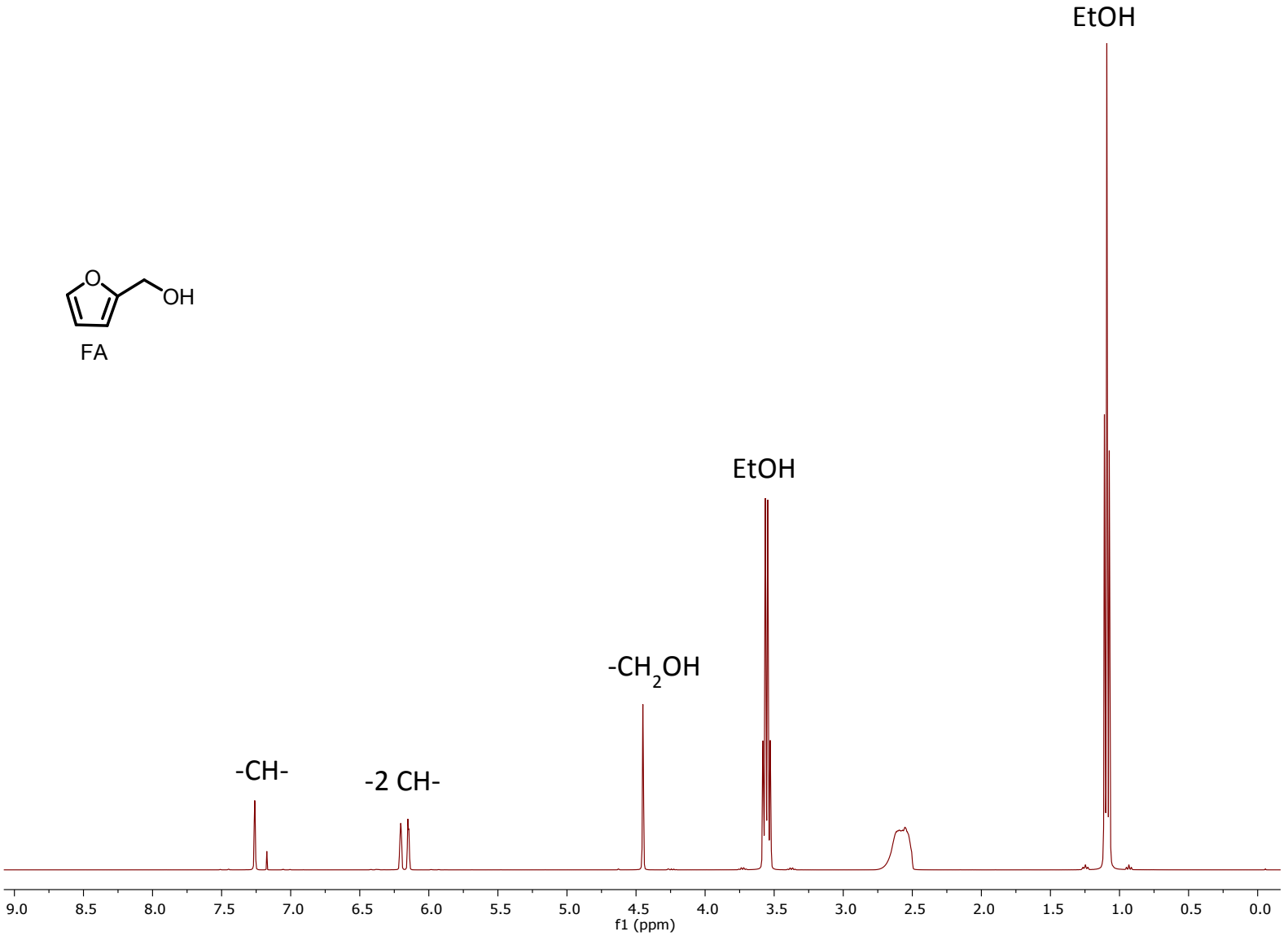


Figure S27. ^{1}H-NMR of the crude reaction of 0.90 mmol **FAL** with **Ru-2** (0.05 mol%), 30 bar of H_2 and 25 ^{o}C and 30 min in ethanol (conversion ≥99%) in $CDCl_3$.

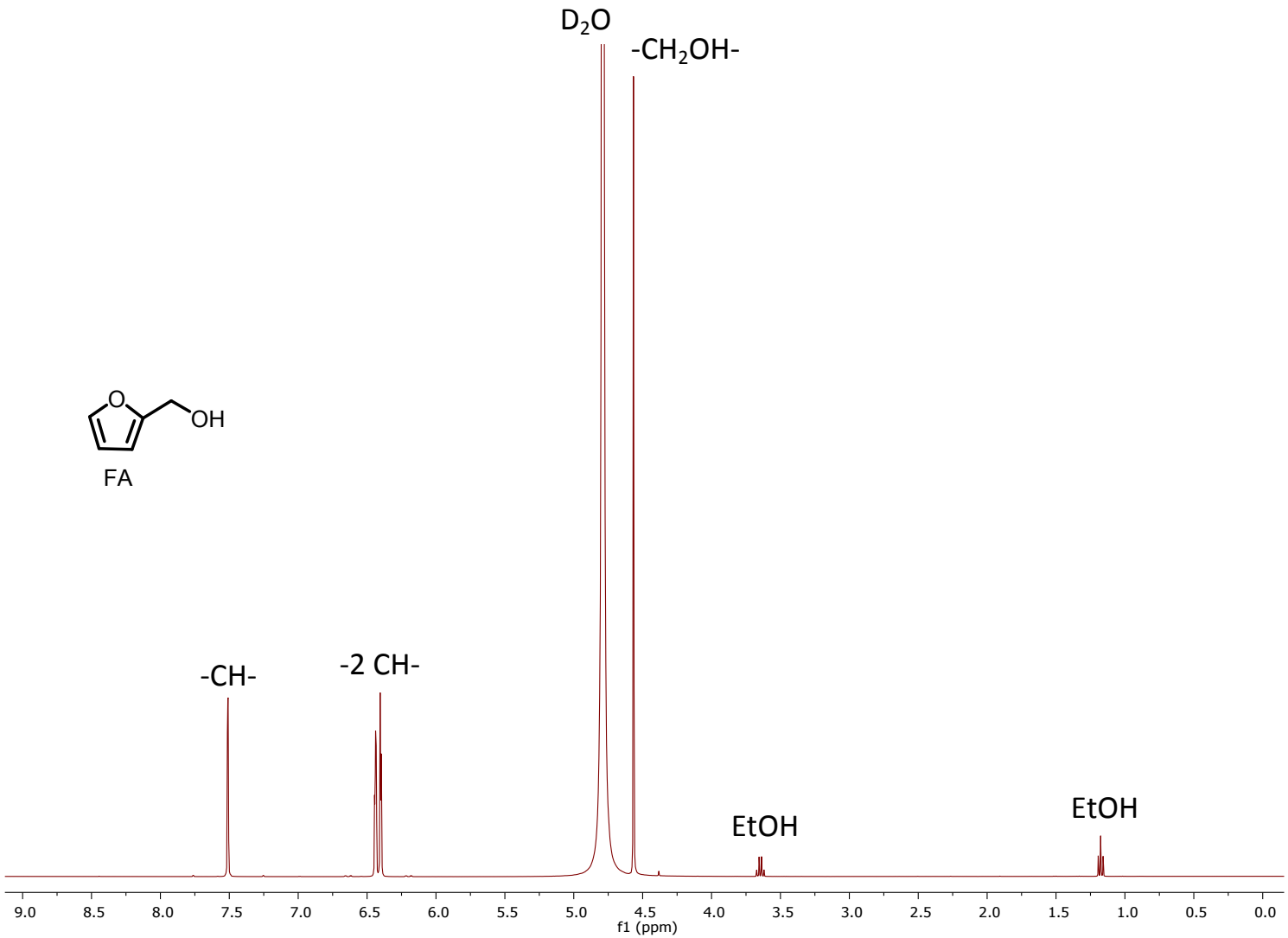


Figure S28. ^{1}H-NMR of the crude reaction of 0.90 mmol **FAL** with **Ru-2** (0.1 mol%), 30 bar of H_2 and 25 ^{o}C and 30 min in water (conversion ≥99%) in D_2O.

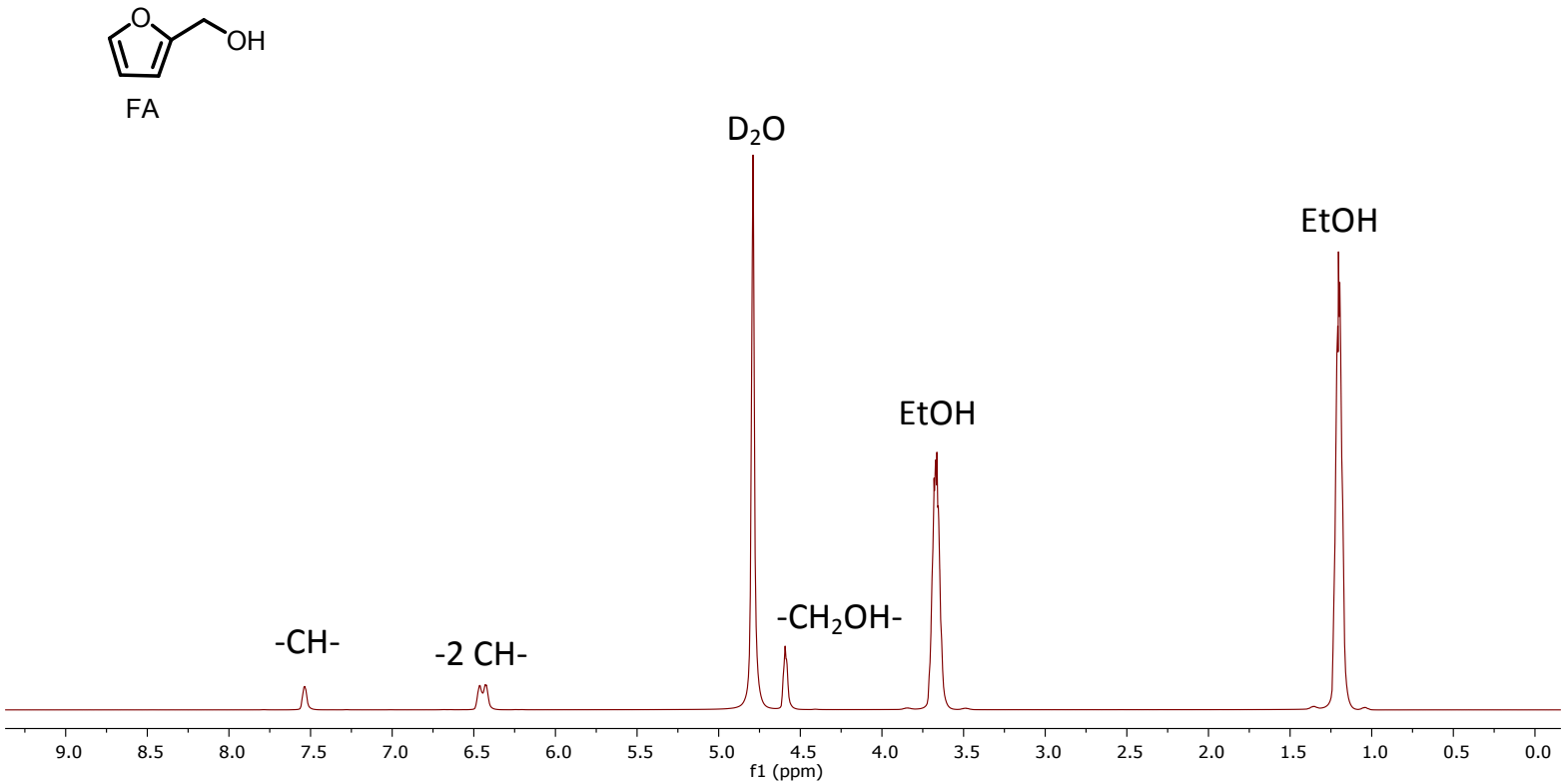


Figure S29. ^{1}H-NMR of the crude reaction of 0.90 mmol **FAL** with **Ru-2** (0.1 mol%), 30 bar of H_2 and 25 ^{o}C and 30 min in ethanol/water 95:5 (conversion ≥99%) in D_2O.

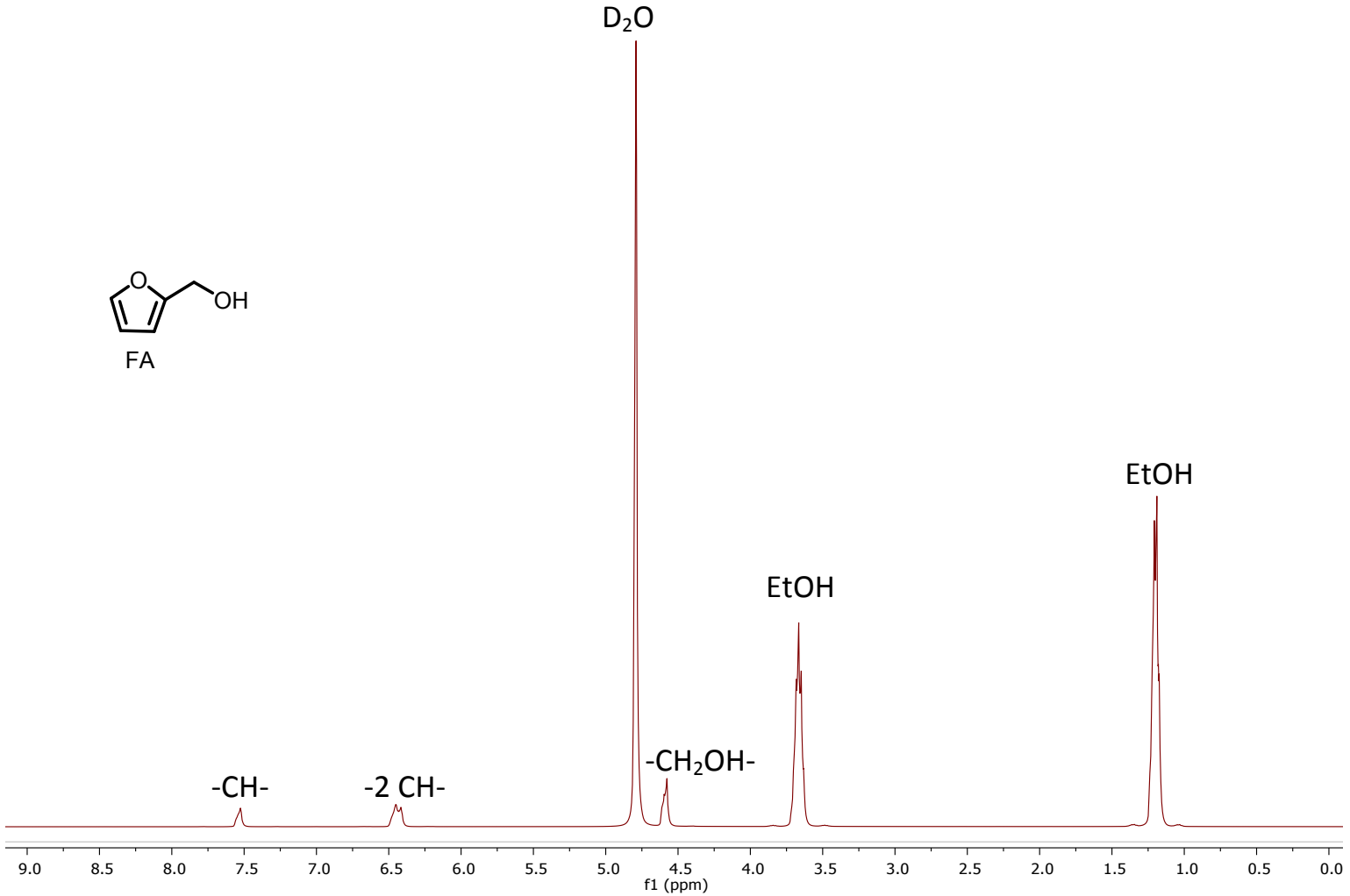


Figure S30. ^{1}H-NMR of the crude reaction of 0.90 mmol **FAL** with **Ru-2** (0.05 mol%), 30 bar of H_2 and 25 ^{o}C and 30 min in ethanol/water 80:20 (conversion ≥99%) in D_2O

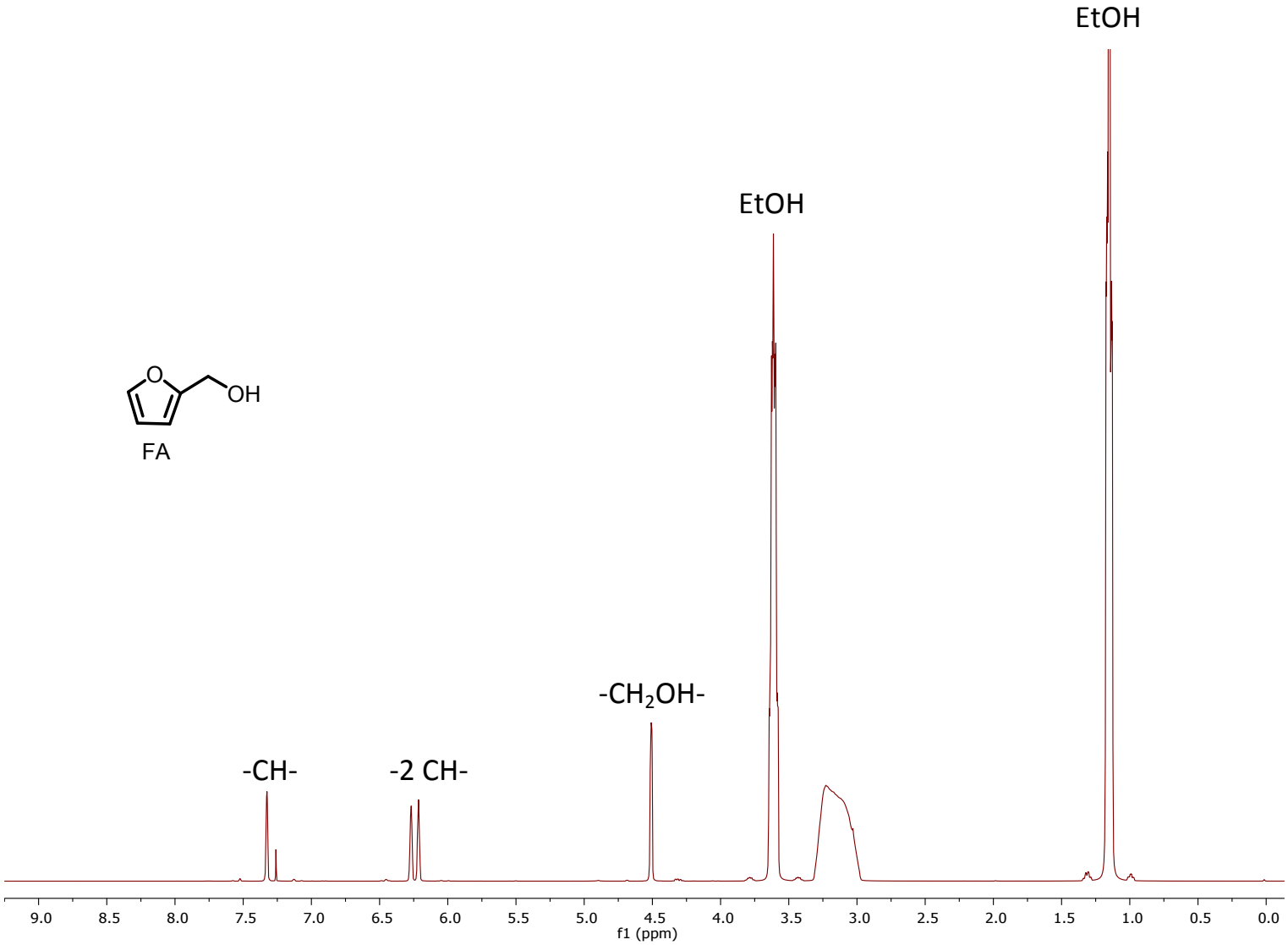


Figure S31. ^{1}H-NMR of the crude reaction of 0.90 mmol **FAL** with **Ru-1** (0.1 mol%), 30 bar of H_2 and 25 ^{o}C and 30 min in ethanol/water 80:20 (conversion ≥99%) in $CDCl_3$.

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

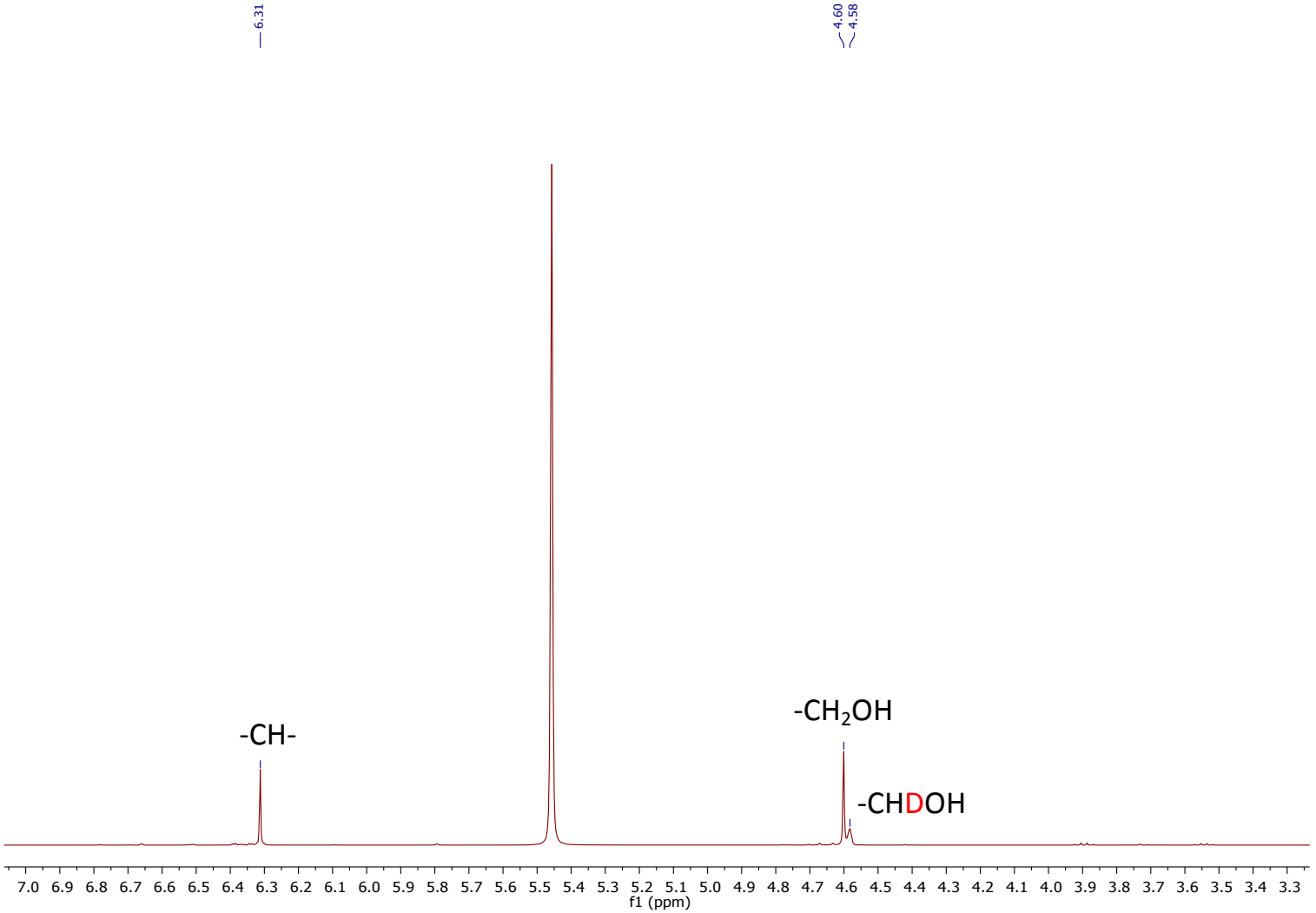


Figure S32. ^{1}H-NMR of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of NaOEt and 25 ^{o}C and 30 min in ethanol (capillary insert with toluene-d_8 at 25 °C).

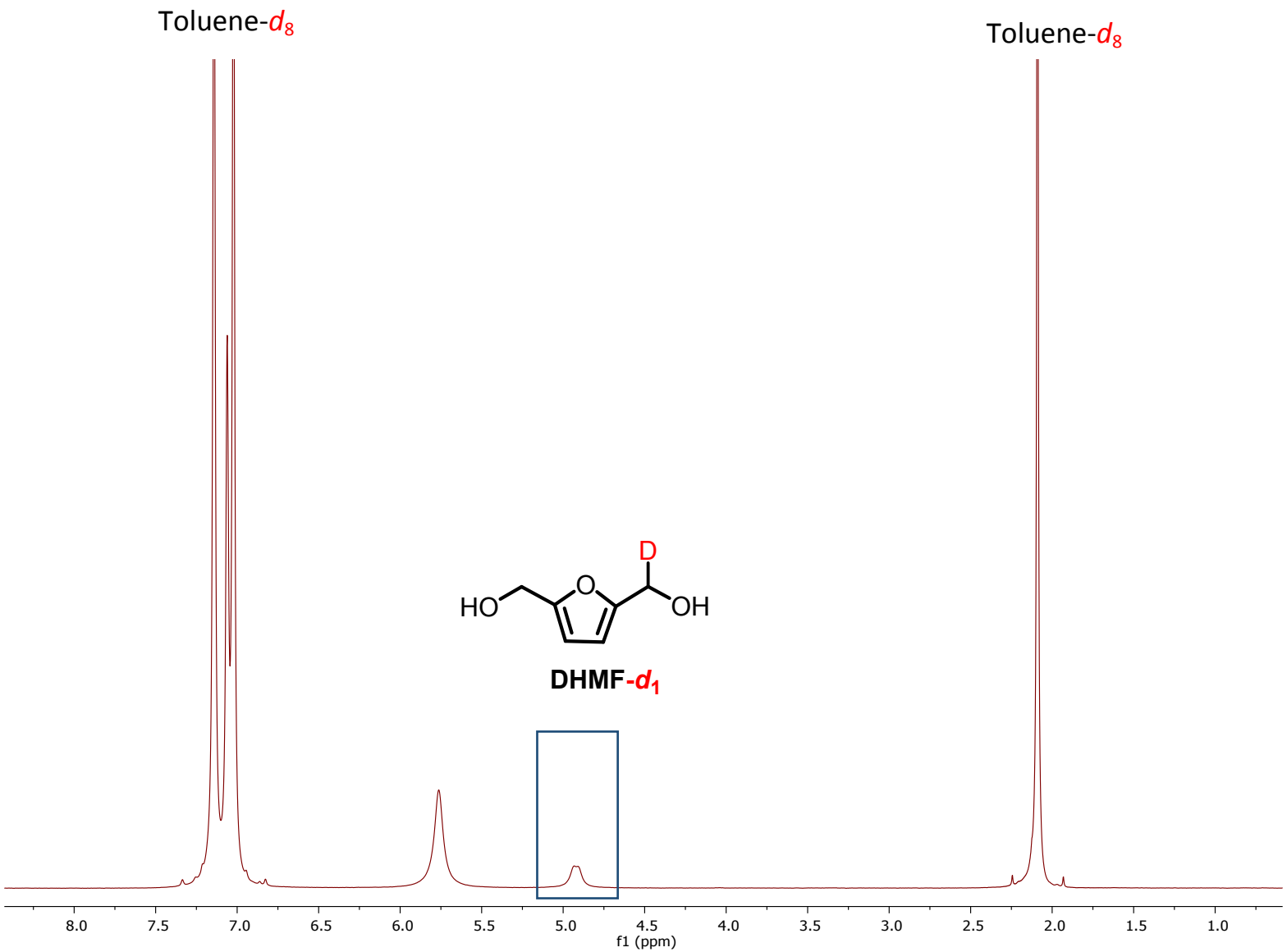


Figure S33. ^{2}H-NMR of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of NaOEt and 25 ^{o}C and 30 min in ethanol (capillary insert with toluene-d_8 at 25 °C).

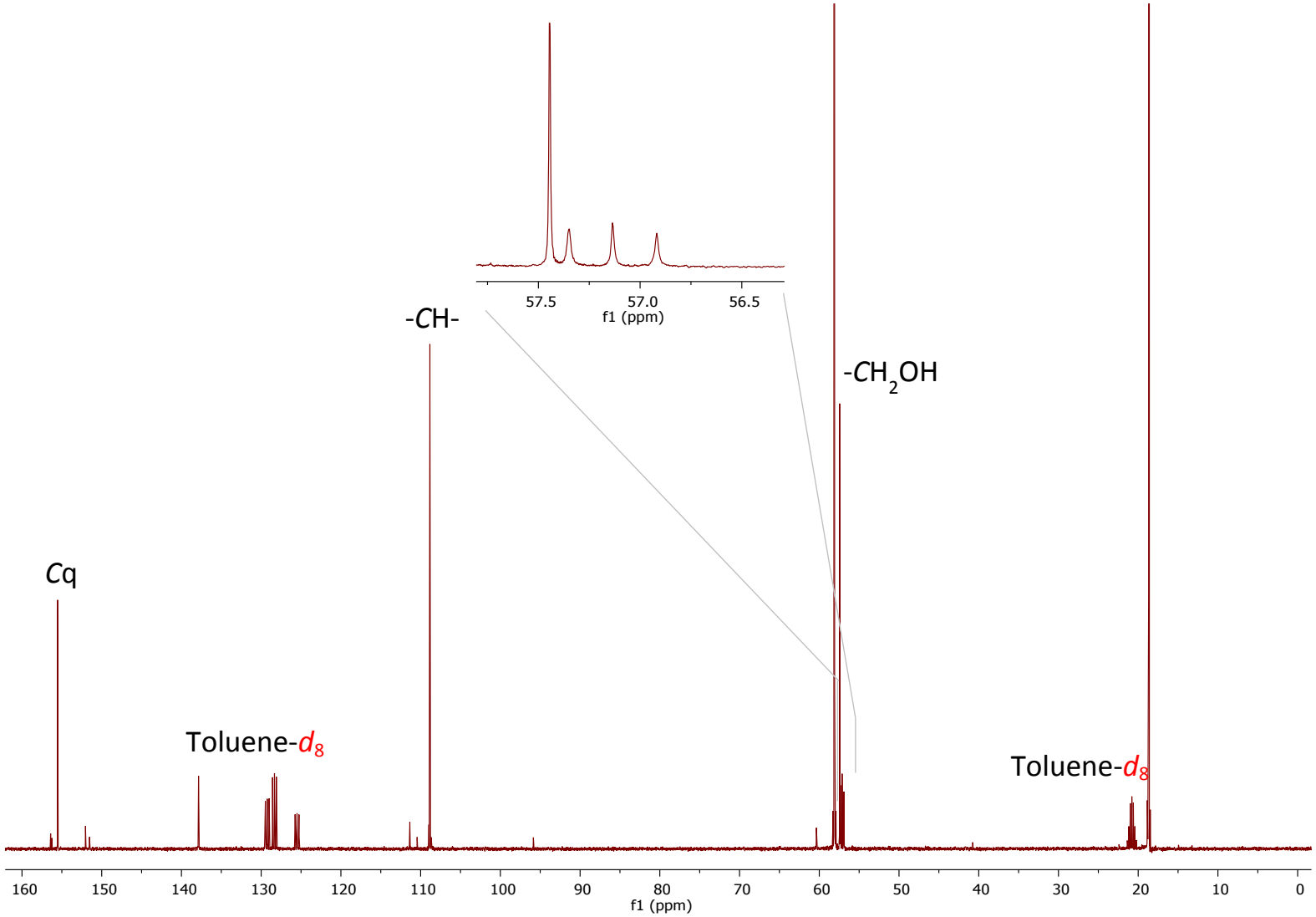


Figure S34. ^{13}C-NMR of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of NaOEt and 25 °C and 30 min in ethanol (capillary insert with toluene-d_8 at 25 °C).

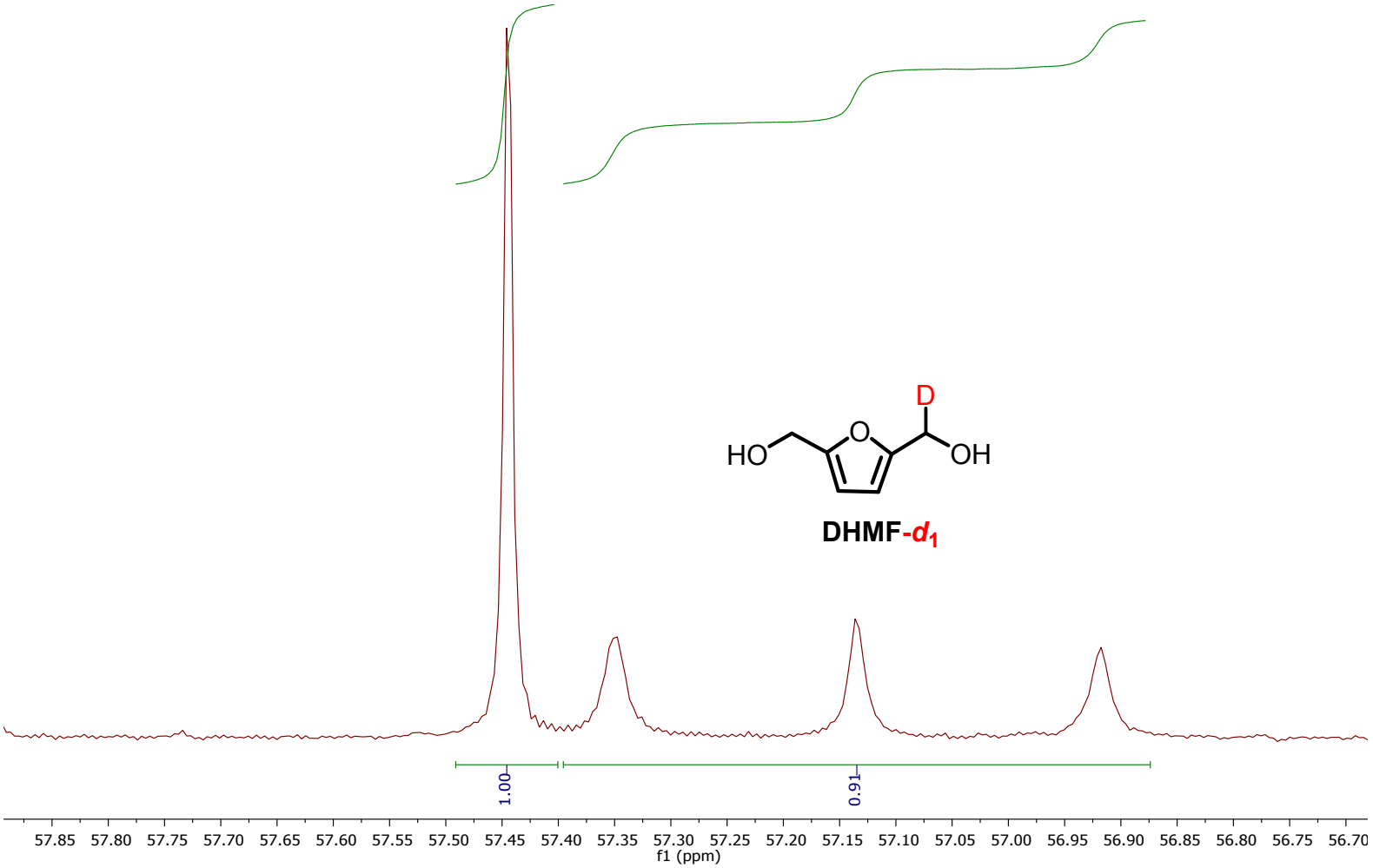


Figure S35. ^{13}C-NMR (zoomed from 58-56 ppm) of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of NaOEt and 25 °C and 30 min in ethanol (capillary insert with toluene-d_8 at 25 °C).

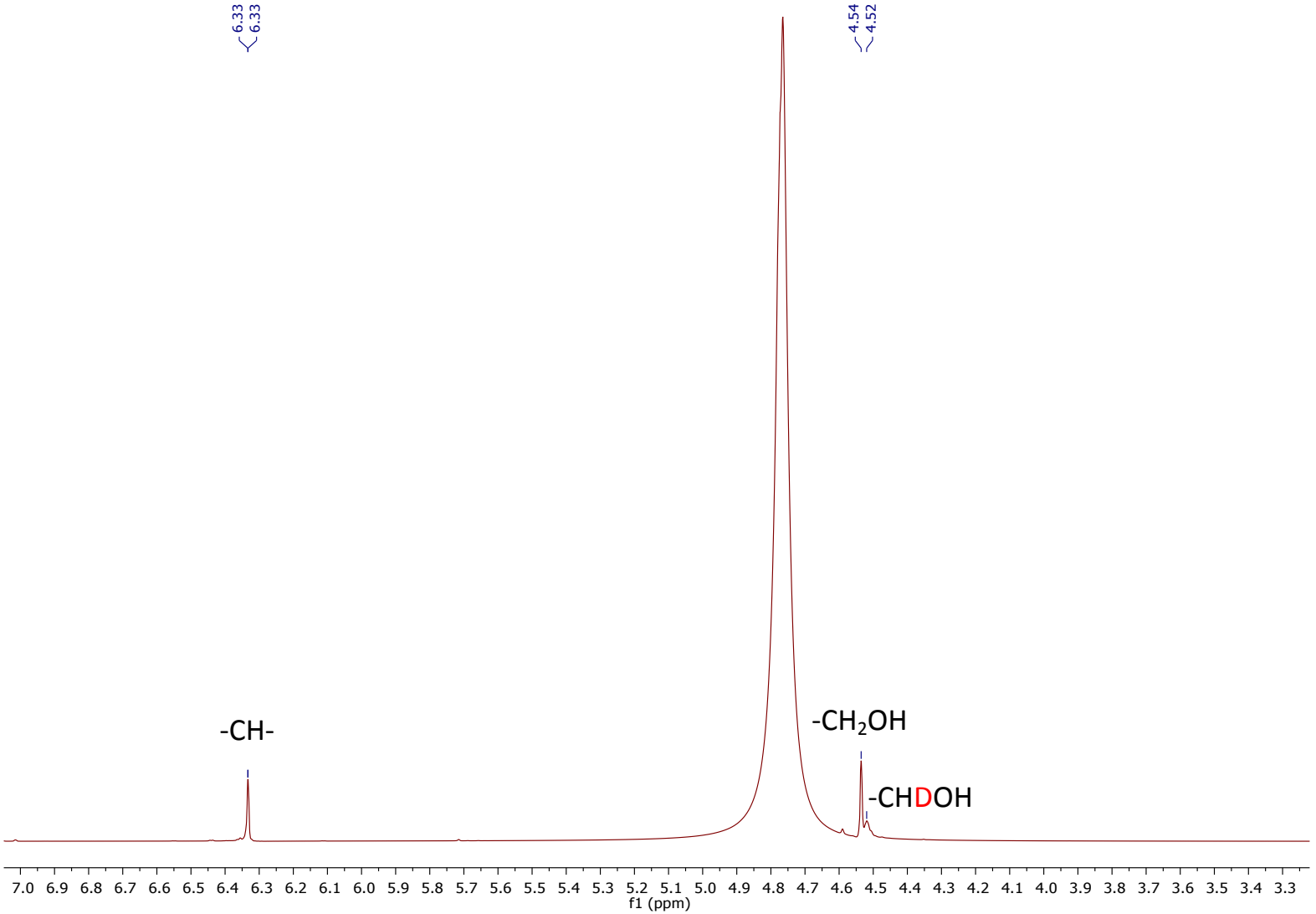


Figure S36. ^{1}H-NMR of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of LiOH and 25 ^{o}C and 30 min in water (capillary insert with toluene-d_8 at 25 °C).

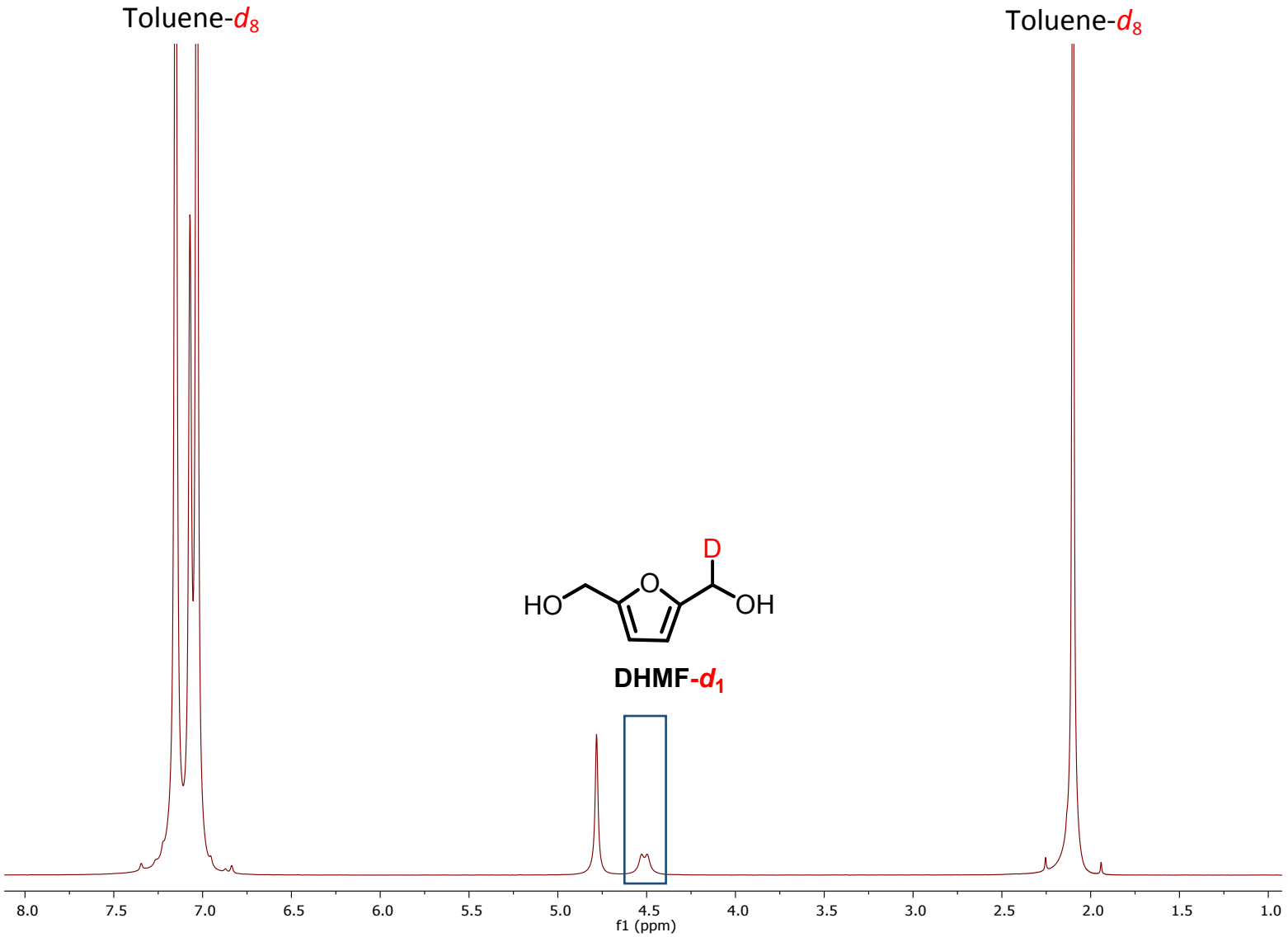


Figure S37. ^{2}H-NMR of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of LiOH and 25 °C and 30 min in water (capillary insert with toluene-d_8 at 25 °C).

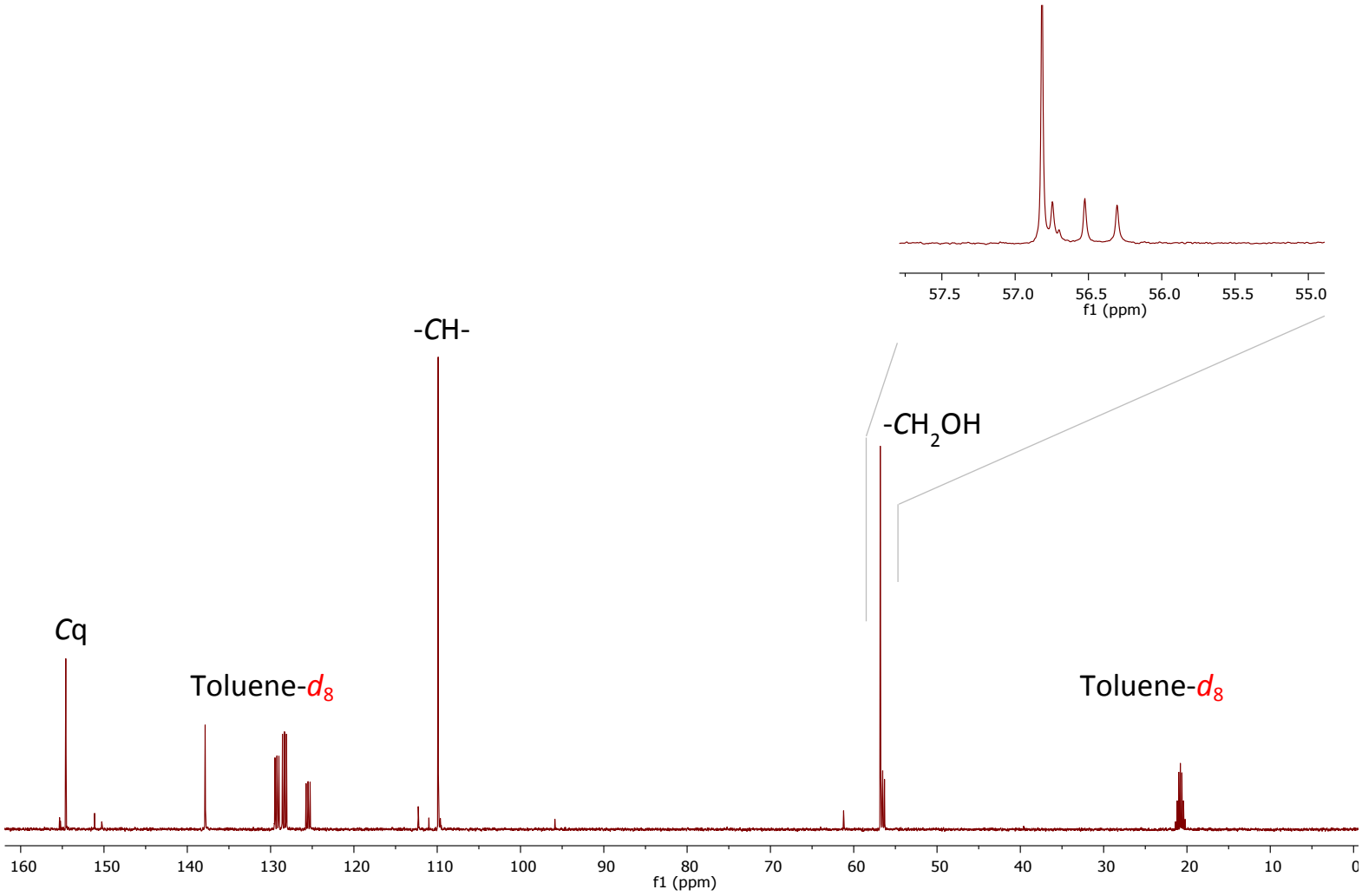


Figure S38. ^{13}C-NMR of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of LiOH and 25 °C and 30 min in water (capillary insert with toluene-d_8 at 25 °C).

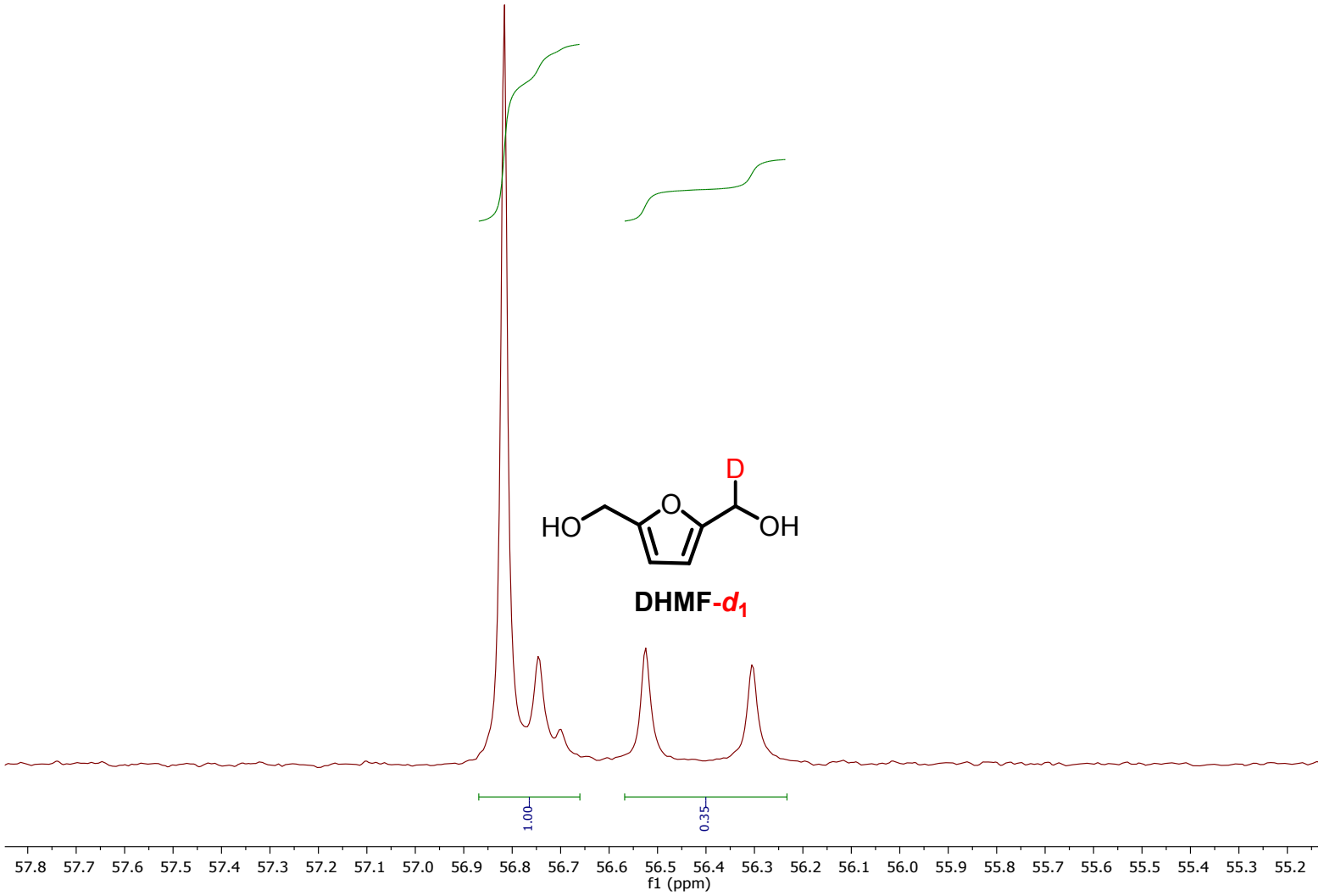


Figure S39. ^{13}C-NMR (zoomed from 57-55 ppm) of the crude reaction of 0.79 mmol **HMF** with **Ru-2** (0.1 mol%), 30 bar of D_2 and 2 mol% of LiOH and 25 ^{o}C and 30 min in water (capillary insert with toluene-d_8 at 25 °C).

9. NMR spectra of Ru species

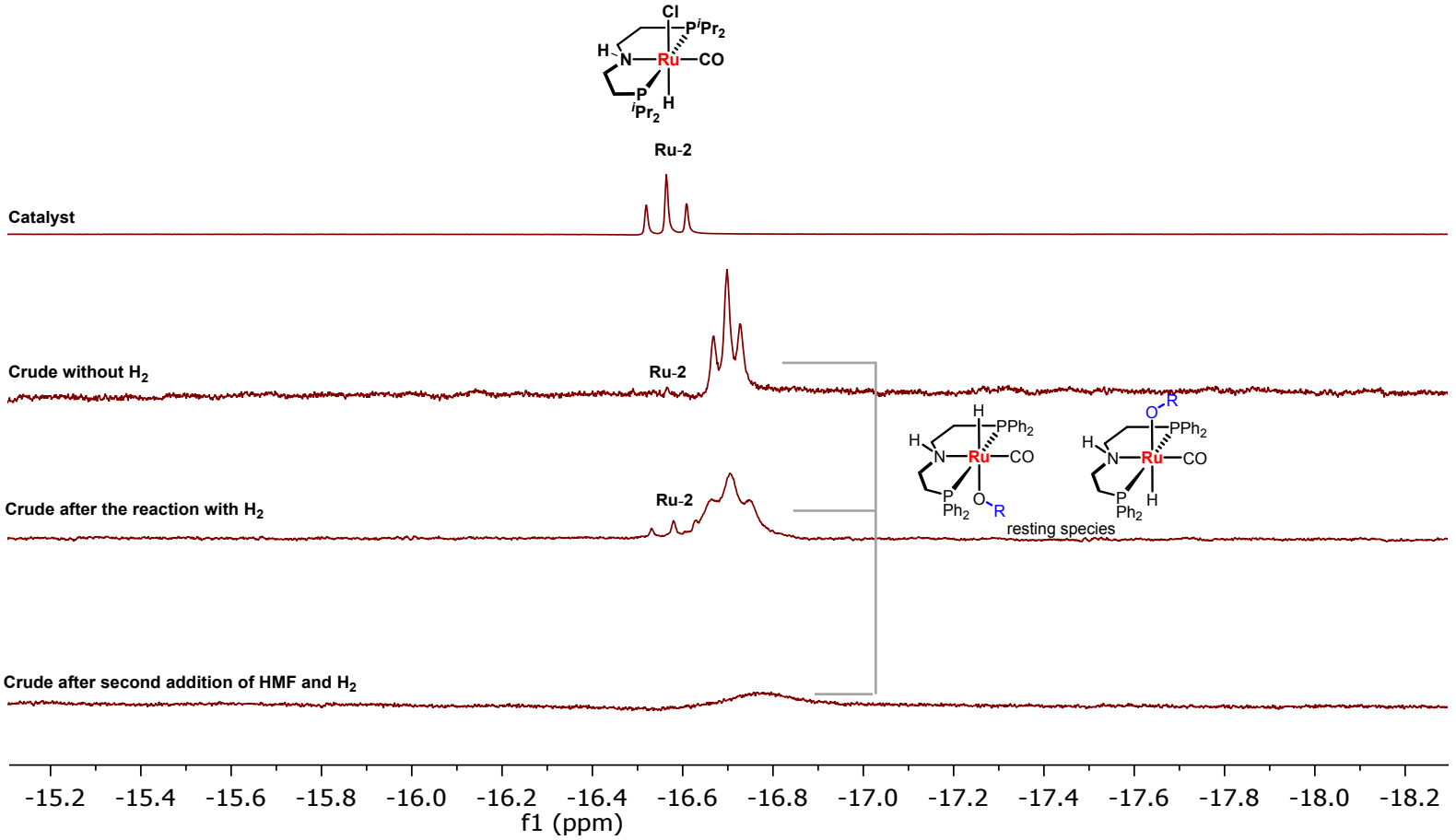


Figure S40. ^{1}H-NMR of the ruthenium hydride species in the crude before and after the reaction with **Ru-2** (1 mol%), NaOEt (2 mol%), 30 bar H_2, 25 °C and 10 minutes (toluene-d_8 at 25 °C). **Ru-OR** corresponds to the coordinated furanic alkoxide.

10. References

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