

# SBA-15-functionalized sulfonic acid confined acidic ionic liquid: a powerful and water-tolerant catalyst for solvent-free esterifications

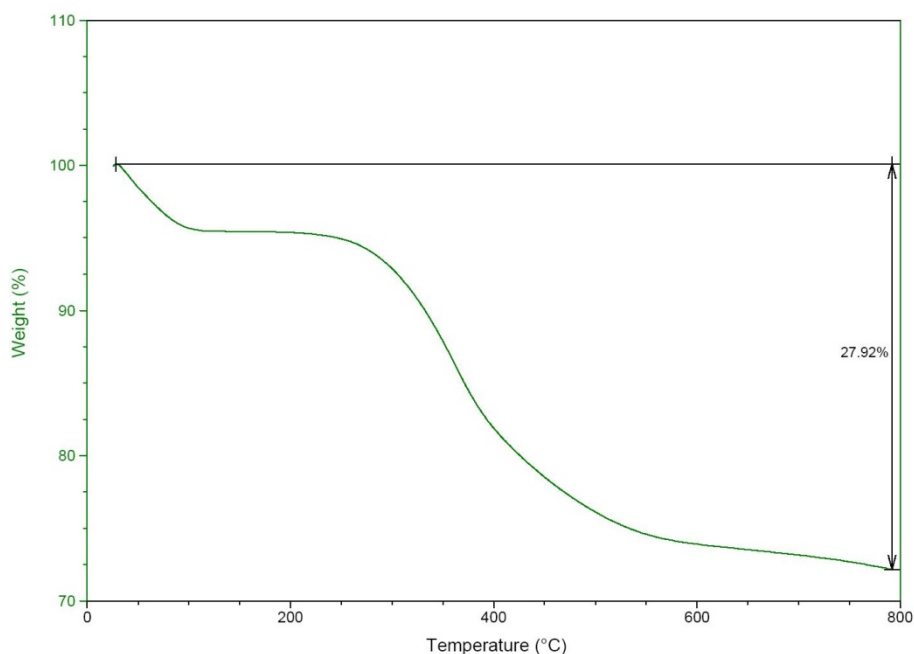
Babak Karimi<sup>\*a</sup>, Majid Vafaezadeh<sup>a</sup>

<sup>a</sup> Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P.O. Box 45195-1159, Gava Zang, Zanjan, Iran

Table of Content	Page
1. Experimental Procedure	S2
1.1. Preparation of SBA-15-Pr-SH	S2
1.2. Preparation of SBA-15-Pr-SO <sub>3</sub> H	S3
1.3. pH analysis of the SBA-15-Pr-SO <sub>3</sub> H	S3
1.4. Preparation of [MOIm][HSO <sub>4</sub>	S8
1.5. Preparation of catalyst <b>2</b> (IL@SBA-15-Pr-SO <sub>3</sub> H)	S8
1.6. pH analysis of the catalyst <b>2</b>	S8
1.7. Typical experimental procedure for solvent-free esterification at room temperature with catalyst <b>2</b>	S11
1.8. Analysis of recovered catalyst <b>2</b> after 4 <sup>th</sup> run of reaction	S12
Spectral data for Table <b>2</b> , <b>3</b> and [MOIm]HSO <sub>4</sub>	S15
Copy of <sup>1</sup> H and <sup>13</sup> C-NMR spectras	S17

## 1. Experimental Procedure

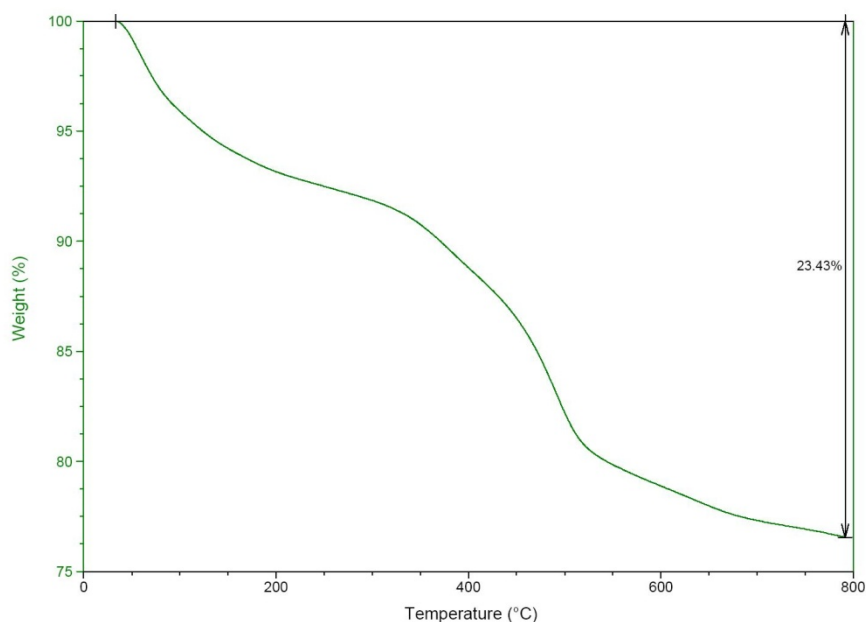
**1.1. Preparation of SBA-15-Pr-SH:** The synthesis of SBA-15-Pr-SH has been achieved using known procedure.<sup>1</sup> This procedure involved a synthetic strategy based on co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of Pluronic P123 as structure directing agent. In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw =5800) was dissolved in 125 g of 1.9 M HCl solution with stirring at room temperature. The solution was heated to 40°C before adding 6.83 g TEOS. After 3 h pre-hydrolysis of TEOS, 1.6g thiol precursor (MPTMS) was added. The resultant solution was stirred for 20 h at 40°C, after which the mixture was aged at 100°C for 24 h under static conditions. The solid was recovered by filtration and air dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhlet apparatus for 24 h. TGA diagram for SBA-15-Pr-SH is shown in Figure 1.



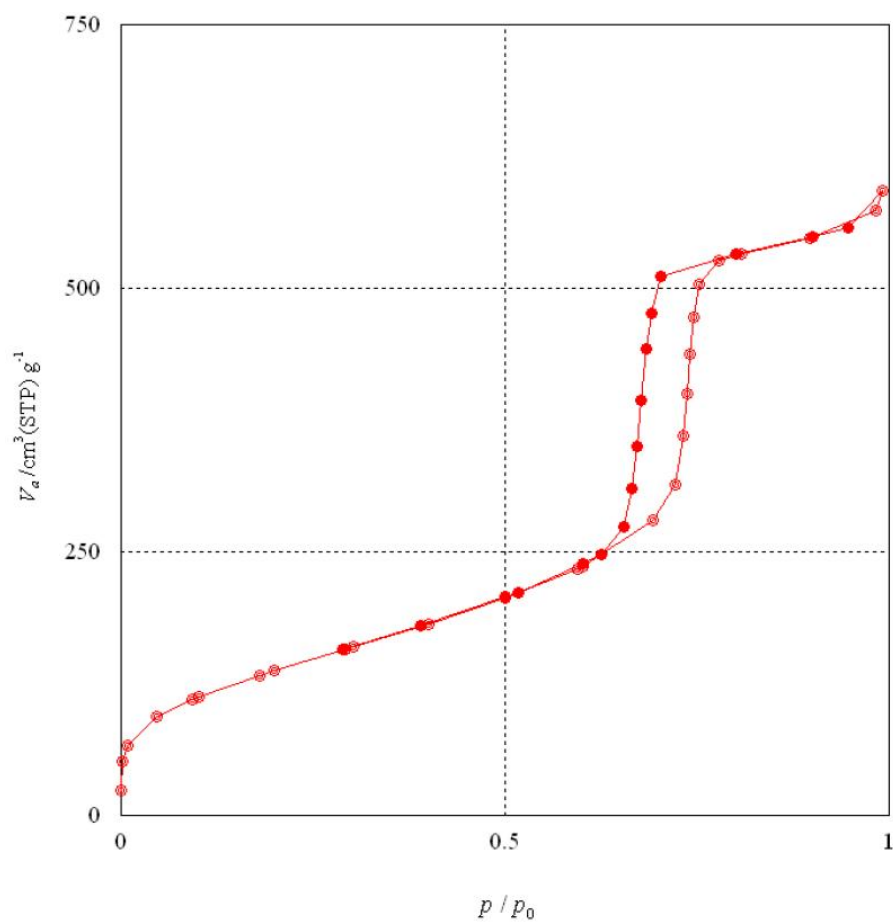
**Figure 1S.** TGA diagram for SBA-15-Pr-SH

**1.2. Preparation of SBA-15-Pr-SO<sub>3</sub>H:** Typically, 0.3 g of SBA-15-Pr-SH was suspended in 10 g of aqueous 30 wt% H<sub>2</sub>O<sub>2</sub>. This suspension was stirred at room temperature in an Argon atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H<sub>2</sub>SO<sub>4</sub> solution for 2 h and then was washed several times with deionized water and ethanol and dried at 60°C under vacuum overnight.

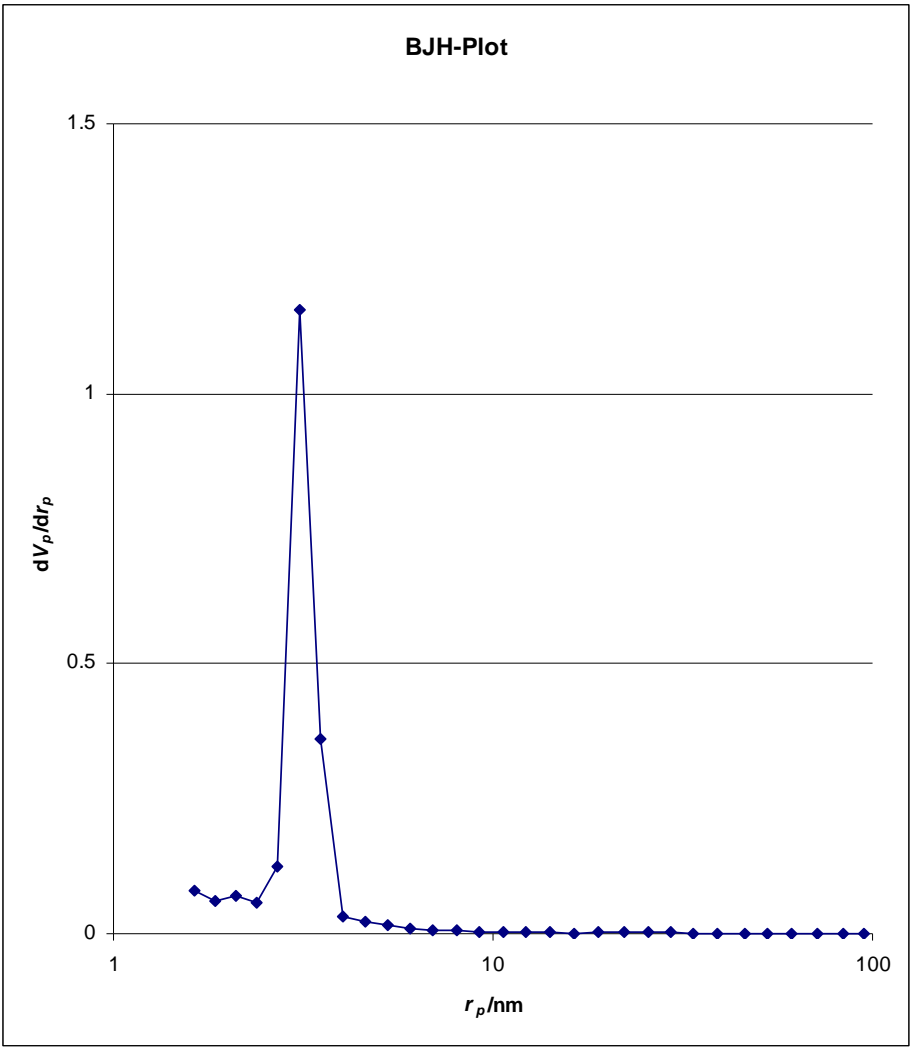
**1.3. pH analysis of the SBA-15-Pr-SO<sub>3</sub>H:** To an aqueous solution of NaCl (1M, 25 mL) with a primary pH 5.93, the catalyst (0.5 g) was added and the resulting mixture was stirred for 2h after which the pH of solution decreased to 1.51. This is equal to a loading of 1.55 mmol H<sup>+</sup>/g.



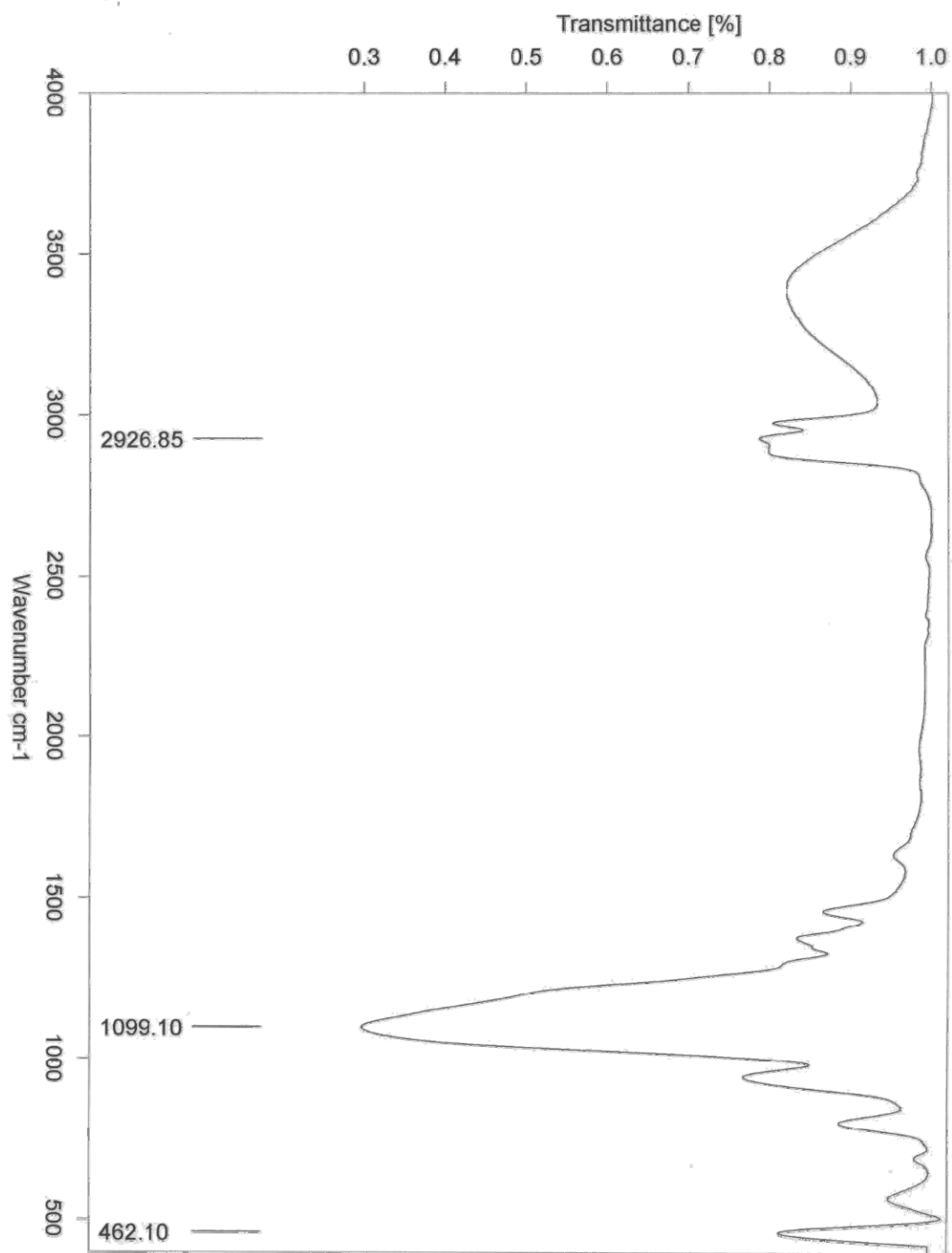
**Figure 2S.** TGA diagram for SBA-15-Pr-SO<sub>3</sub>H



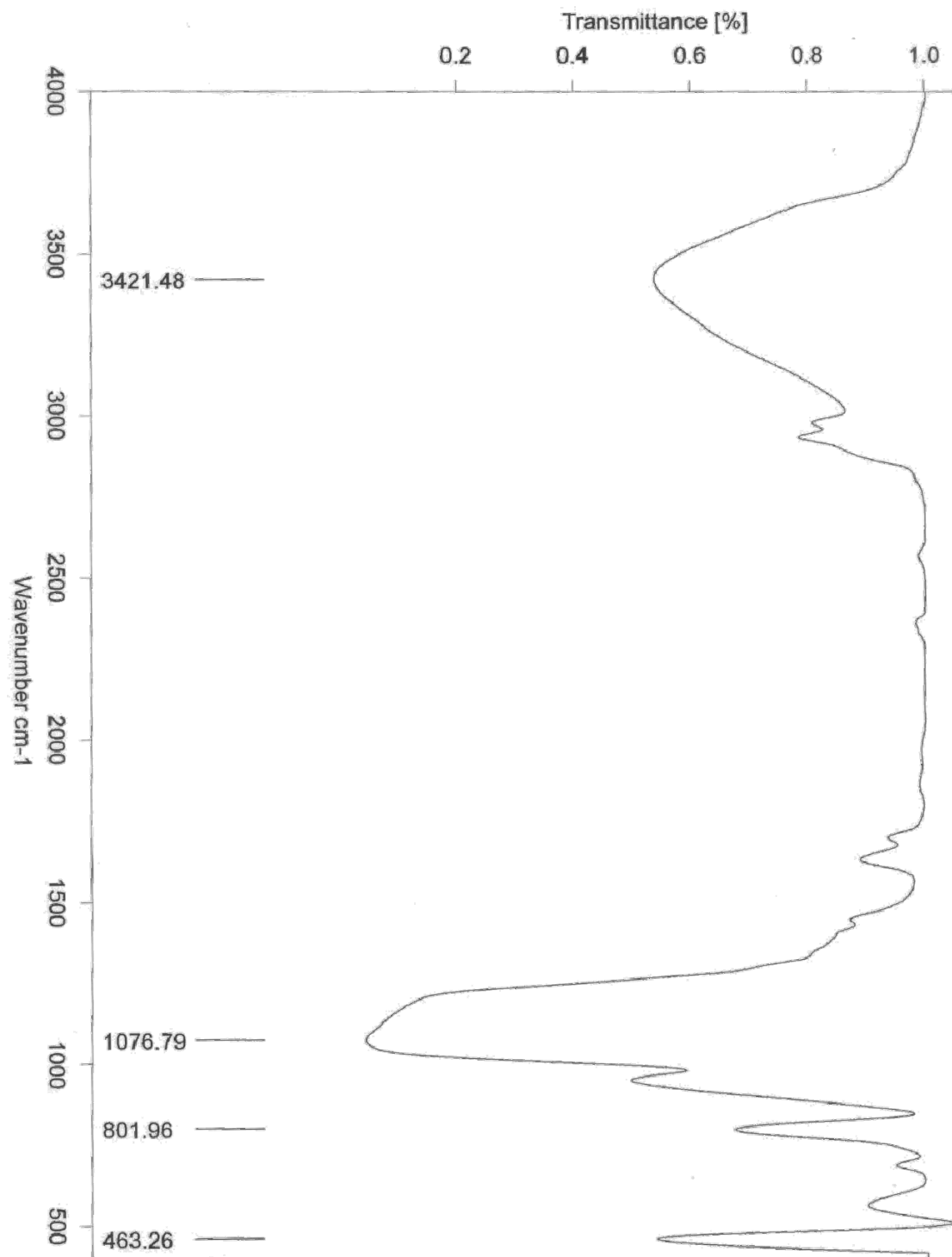
**Figure 3S.** Nitrogen adsorption-desorption isotherm for SBA-15-Pr-SO<sub>3</sub>H



**Figure 4S.** BJH average pore diameter diagram for SBA-15-Pr-SO<sub>3</sub>H



**Figure 5S.** DRIFT analysis of SBA-15-Pr-SO<sub>3</sub>H with P123



**Figure 6S.** DRIFT analysis of SBA-15-Pr-SO<sub>3</sub>H after removing the template (P123)

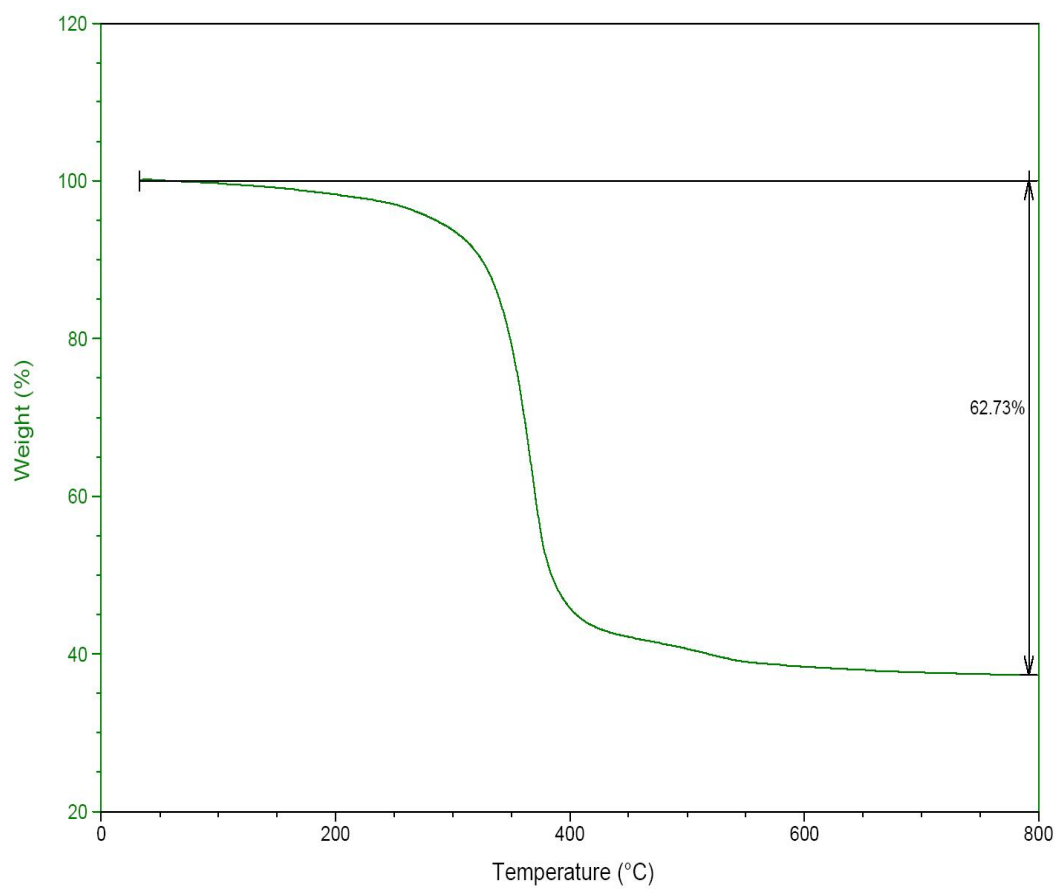
**1.4. Preparation [MOIm][HSO<sub>4</sub>]:** The synthesis of 1-methyl-3-octylimidazolium hydrogen sulfate [MOIm][HSO<sub>4</sub>] has been achieved according to patented literature.<sup>2</sup> In a flask equipped with a dropping funnel, a condenser and a magnetic stirrer 1-methyl-3-octylimidazolium bromide (7.81 g ~ 0.027 mol) was dissolved in dry methylene chloride (100 mL). The solution was cooled to 0°C with an ice bath. An aqueous solution of concentrated sulfuric acid (97%) was carefully added to this solution. To obtain a hydrogen sulfate ionic liquid, the sulfuric acid and the organic salt were used in the same molecular ratios. After the addition of the solution was completed, the mixture was heated under reflux for two days. From time to time any HBr by-product formed in the process which was distilling out of the condenser was monitored. When the formed HBr had been completely removed, the solution was cooled to room temperature and the methylene chloride was removed carefully under vacuum. To remove any water (generated from aqueous sulfuric acid used) benzene (10 mL) was added to the viscous residue and the biphasic mixture was heated to 50°C to give a nearly homogeneous solution for several hours and the benzene/water azeotrope was then removed. The resulting ionic liquid was then stored under an inert atmosphere.

**1.5. Preparation of catalyst 2 (IL@SBA-15-Pr-SO<sub>3</sub>H):**

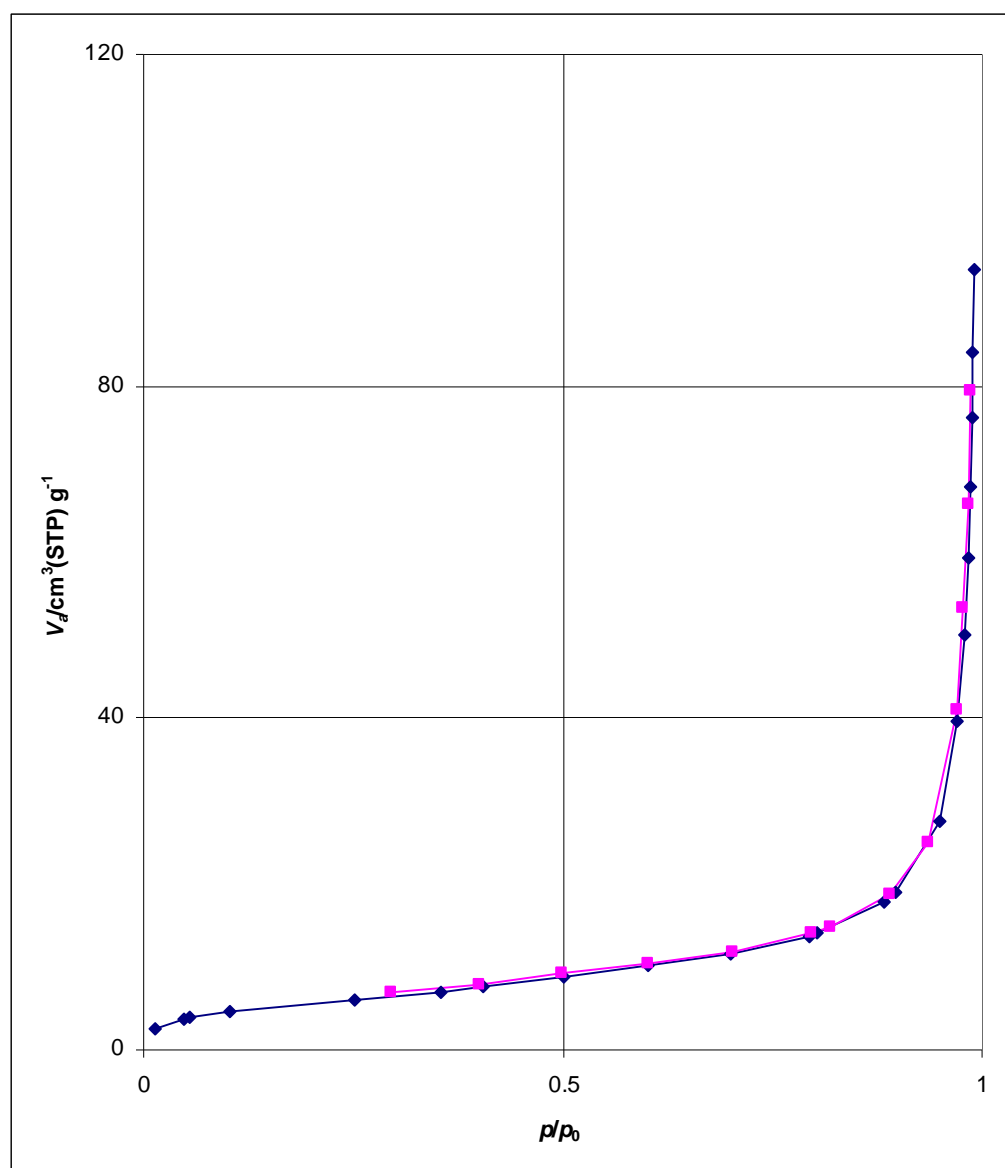
The IL@SBA-15-Pr-SO<sub>3</sub>H was prepared by one-step impregnation of SBA-15-Pr-SO<sub>3</sub>H **1** with the acetone solution of 0.8 mL of [MOIm][HSO<sub>4</sub>]. This solution then dropwise added to a mixture containing of 100 mL acetone and 1 g of SBA-15-Pr-SO<sub>3</sub>H in an Argon atmosphere. After 3 h stirring at room temperature volatile solvent was removed under reduced pressure and the IL@SBA-15-Pr-SO<sub>3</sub>H (catalyst **2**) dried for hours at 60°C in a vacuum oven.

**1.6. pH analysis of the catalyst 2**

According to the procedure described in **1.3**, the observed pH was 1.305. This is equal to a loading of 2.48 mmol H<sup>+</sup>/g



**Figure 7S.** TGA diagram of Catalyst **2**

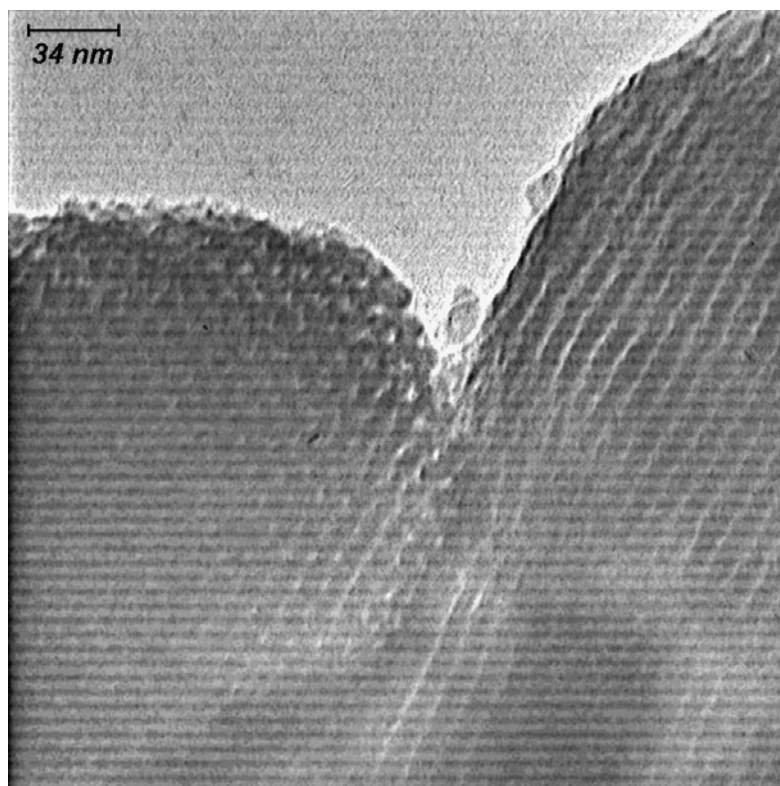


**Figure 8S.** Nitrogen adsorption-desorption isotherm for Catalyst **2**

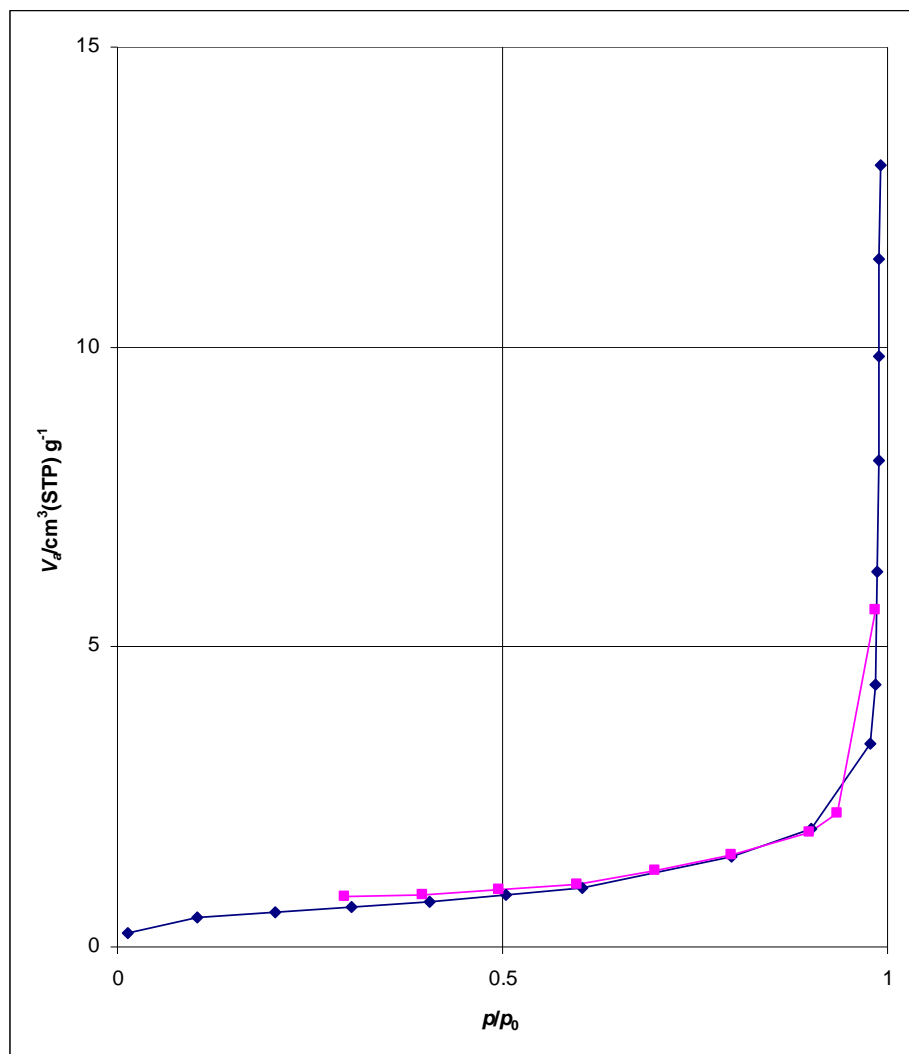
**1.7. Typical experimental procedure for solvent-free esterification at room temperature with catalyst 2:** Acetic acid (1.7 eq.) was added to a mixture of 3-phenyl-1-propanol (1 eq.) and 10 mol% ( $\sim 0.04$  g) of catalyst **2**. The reaction mixture was stirred at room temperature (25-

30°C) for 40 h. The reaction progress was monitored by TLC. After the completion of the reaction, the slurry was filtrated and the catalyst was washed with heptane (50 ml). The residual acid was quenched with saturated aqueous NaHCO<sub>3</sub> (2 × 4 mL). The mixture was dried over Na<sub>2</sub>SO<sub>4</sub>, and then the heptane was removed under reduced pressure afforded the pure 3-Phenylpropyl acetate in excellent yields.

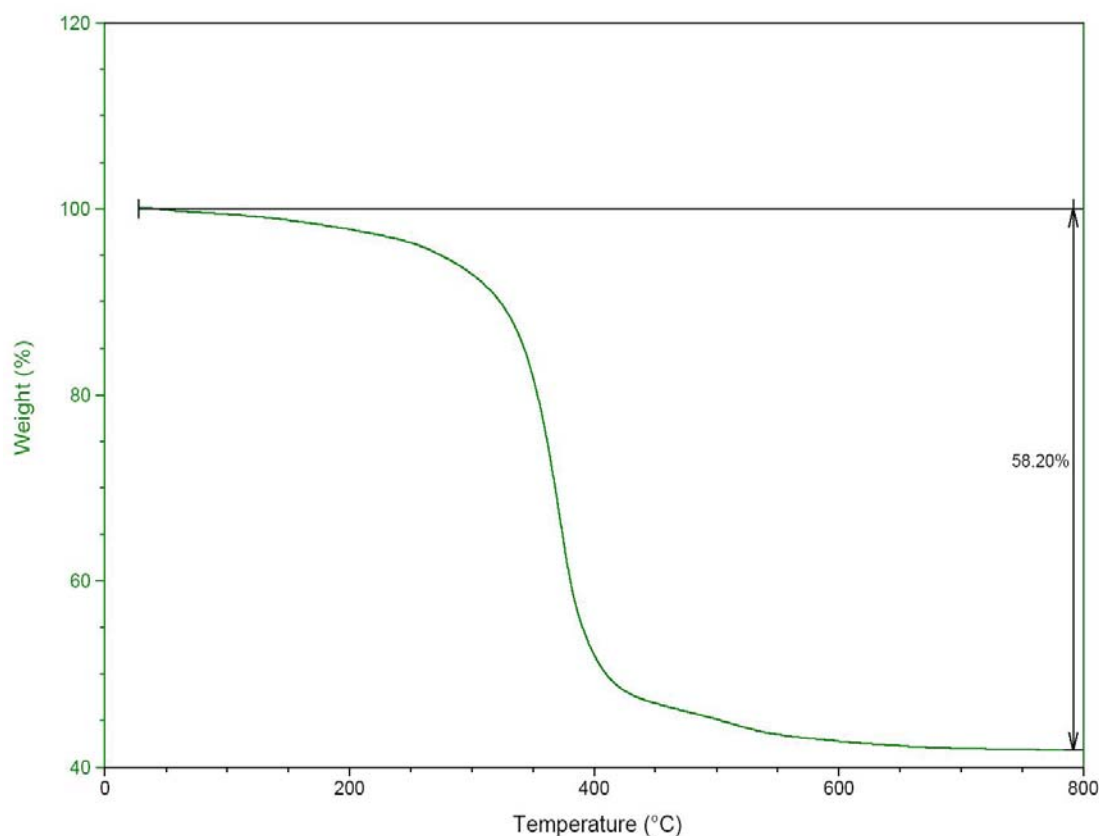
#### **1.8. Analysis of recovered catalyst 2 after 4<sup>th</sup> run of reaction**



**Figure 9S:** TEM image of Catalyst **2** across and along the mesochannels after the 4<sup>th</sup> reaction cycle



**Figure 10S.** Nitrogen adsorption-desorption isotherm for Catalyst **2** after the 4<sup>th</sup> reaction cycle



**Figure 11S.** TGA diagram for Catalyst **2** after the 4<sup>th</sup> reaction

**Table 1S** Characterization of SBA-15-functionalized sulfonic acid confined acidic ionic liquid **2**.

Entry	PMO	$S_{\text{BET}}^a$	$V_p^b$	Pore size <sup>c</sup>
1	SBA-15-PrSO <sub>3</sub> H	503	0.91	7.2
2	IL@SBA-15-PrSO <sub>3</sub> H <b>2</b>	20	0.14	-
3	SBA-15-Ph-PrSO <sub>3</sub> H	349	0.62	5.4
4	<b>2</b> (Recycled)	50	0.20	- <sup>d</sup>

<sup>a</sup> BET surface area (m<sup>2</sup>.g<sup>-1</sup>). <sup>b</sup> Total pore volume (cm<sup>3</sup>.g<sup>-1</sup>). <sup>c</sup> BJH pore size diameter (nm). <sup>d</sup> The analysis has been performed after the 4<sup>th</sup> reaction run for the recovered catalyst.

## References

- [1] a) D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* 2000, **12**, 2448; b) B. Karimi, D. Zareyee, *Org. Lett.*, 2008, **10**, 3989.  
[2] W. Keim, W. Korth, P. Wasserscheid, WO Patent 200016902 (A1) (**2000**)).

## Spectral data for Table 1, 2 and [MOIm]HSO<sub>4</sub>

**Table 2 (Entry 1):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 7.26 (brs, 5H), 4.102 (t, *J* = 6.5 Hz, 2H), 2.707 (t, *J* = 8 Hz, 2H), 2.068 (s, 3H), 1.976 (q, *J* = 6.75 Hz, 2H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 171.17, 141.20, 128.44, 128.39, 126.01, 63.83, 32.17, 30.18, 20.98.

**Table 2 (Entry 2):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): δ<sub>H</sub> = 4.021 (t, *J* = 6.75 Hz, 2H), 2.012 (s, 3H), 1.575 (brs, 2H), 1.249 (brs, 10H), 0.840 (brs, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 171.09, 64.55, 31.72, 29.16, 29.13, 28.54, 25.85, 22.57, 20.88, 13.99.

**Table 2 (Entry 3):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): δ<sub>H</sub> = 4.029 (t, *J* = 6.5 Hz, 2H), 2.021 (s, 3H), 1.582 (brs, 2H), 1.245 (brs, 12H), 0.845 (brs, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 171.16, 64.59, 31.80, 29.43, 29.21, 29.19, 28.54, 25.85, 22.60, 20.89.

**Table 2 (Entry 4):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 4.024 (t, *J* = 6.75 Hz, 2H), 2.014 (s, 3H), 1.578 (brs, 2H), 1.242 (brs, 14H), 0.841 (brs, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 171.11, 31.83, 31.54, 29.48, 29.25, 29.21, 28.55, 25.86, 22.62, 20.88, 14.02.

**Table 2 (Entry 5):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 4.017 (t, *J* = 6.25 Hz, 2H), 2.006 (s, 3H), 1.585 (brs, 2H), 1.233 (brs, 18H), 0.837 (brs, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 171.04, 64.54, 31.86, 29.59, 29.52, 29.47, 29.30, 29.21, 28.55, 25.86, 22.62, 20.85, 14.01.

**Table 2 (Entry 6):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 4.884 (q, *J* = 6.25 Hz, 1H), 2.012 (s, 3H), 1.506 (brs, 2H), 1.263 (brs, 11H), 0.853 (brs, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 170.78, 35.90, 31.71, 29.09, 25.34, 22.55, 21.36, 19.93, 14.03.

**Table 2 (Entry 7):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 4.730 (brs, 1H), 2.030 (s, 3H), 1.790 (brs, 4H), 1.354 (brs, 6H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 170.65, 72.69, 31.64, 25.35, 23.81, 21.47.

**Table 2 (Entry 8):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 7.320 (brs, 5H), 5.122 (s, 2H), 2.118 (s, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 170.91, 135.91, 128.57, 128.26, 66.32, 21.02.

**Table 2 (Entry 9):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 8.214 (d, *J* = 8.75 Hz, 2H), 7.515 (d, *J* = 8.5 Hz, 2H), 5.197 (s, 2H), 2.148 (s, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 170.52, 147.64, 143.22, 128.36, 123.77, 64.74, 20.83.

**Table 3 (Entry 2):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 8.057 (d, *J* = 8.5 Hz, 2H), 7.499 (brs, 3H), 4.388 (q, *J* = 7 Hz, 2H), 1.404 (t, *J* = 7 Hz, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 166.64, 132.81, 130.45, 129.52, 128.31, 60.95, 14.33.

**Table 3 (Entry 3):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 8.253 (brs, 4H), 4.438 (q, *J* = 7 Hz, 2H), 1.432 (t, *J* = 7 Hz, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 164.69, 157.48, 135.83, 130.65, 123.49, 61.95, 14.22.

**Table 3 (Entry 4):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 7.625 (brs, 2H), 7.332 (t, *J* = 8 Hz, 1H), 7.086 (brs, 1H), 4.371 (q, *J* = 7 Hz, 2H), 3.842 (s, 3H), 1.388 (t, *J* = 7 Hz, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 166.46, 159.49, 131.77, 129.31, 121.90, 119.27, 113.95, 61.02, 55.38, 14.30.

**Table 3 (Entry 5):** <sup>1</sup>H-NMR (250 MHz; CDCl<sub>3</sub>; TMS): 7.304 (brs, 5H), 4.140 (q, *J* = 7.25 Hz, 2H), 2.968 (t, *J* = 7.5 Hz, 2H), 2.633 (t, *J* = 8 Hz, 2H), 1.247 (t, *J* = 7 Hz, 3H); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>; TMS): δ<sub>C</sub> = 172.95, 140.58, 128.48, 128.31, 126.23, 60.43, 35.96, 30.97, 14.22.

**Table 3 (Entry 6):**  $^1\text{H}$ -NMR (250 MHz;  $\text{CDCl}_3$ ; TMS): 4.123 (q,  $J = 7.25$  Hz, 2H), 2.286 (t,  $J = 7.5$  Hz, 2H), 1.598 (brs, 2H), 1.240 (brs, 15H), 0.862 (brs, 3H);  $^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ; TMS):  $\delta_{\text{C}} = 173.96, 60.14, 34.38, 31.85, 29.40, 29.25, 29.13, 24.97, 22.65, 14.23, 14.10$ .

**Table 3 (Entry 7):**  $^1\text{H}$ -NMR (250 MHz;  $\text{CDCl}_3$ ; TMS): 4.118 (q,  $J = 7$  Hz, 2H), 2.296 (t,  $J = 7.5$  Hz, 2H), 1.596 (brs, 2H), 1.253 (brs, 19H), 0.868 (brs, 3H);  $^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ; TMS):  $\delta_{\text{C}} = 173.95, 60.14, 34.37, 31.89, 29.59, 29.45, 29.32, 29.26, 29.13, 24.97, 22.67, 14.23, 14.10$ .

**Table 3 (Entry 8):**  $^1\text{H}$ -NMR (250 MHz;  $\text{CDCl}_3$ ; TMS): 4.122 (q,  $J = 7$  Hz, 2H), 2.285 (t,  $J = 7.75$  Hz, 2H), 1.612 (brs, 2H), 1.251 (brs, 27H), 0.877 (brs, 3H);  $^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ; TMS):  $\delta_{\text{C}} = 173.95, 60.14, 34.38, 31.92, 29.68, 29.59, 29.46, 29.36, 29.27, 29.14, 24.98, 22.69, 14.24, 14.12$ .

**Table 3 (Entry 8):**  $^1\text{H}$ -NMR (250 MHz;  $\text{CDCl}_3$ ; TMS): 4.124 (q,  $J = 7$  Hz, 2H), 2.287 (t,  $J = 7.75$  Hz, 2H), 1.600 (brs, 2H), 1.252 (brs, 31H), 0.866 (brs, 3H);  $^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ; TMS):  $\delta_{\text{C}} = 173.95, 60.14, 34.39, 31.92, 29.69, 29.46, 29.37, 29.27, 29.14, 24.98, 22.69, 14.25, 14.13$ .

**[MOIm]HSO<sub>4</sub>:**  $^1\text{H}$ -NMR (250 MHz;  $\text{CDCl}_3$ ; TMS): 11.776 (s, 1H), 9.126 (s, 1H), 7.480 (s, 1H), 7.329 (s, 1H), 4.148 (t,  $J = 7.25$  Hz, 2H), 3.900 (s, 3H), 1.762 (brs, 2H), 1.170 (brs, 10H), 0.758 (brs, 3H); 136.61, 123.92, 121.96, 49.76, 36.33, 31.66, 30.12, 29.03, 28.97, 26.19, 22.53, 14.02.

## **Copy of $^1\text{H}$ and $^{13}\text{C}$ -NMR spectras**

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

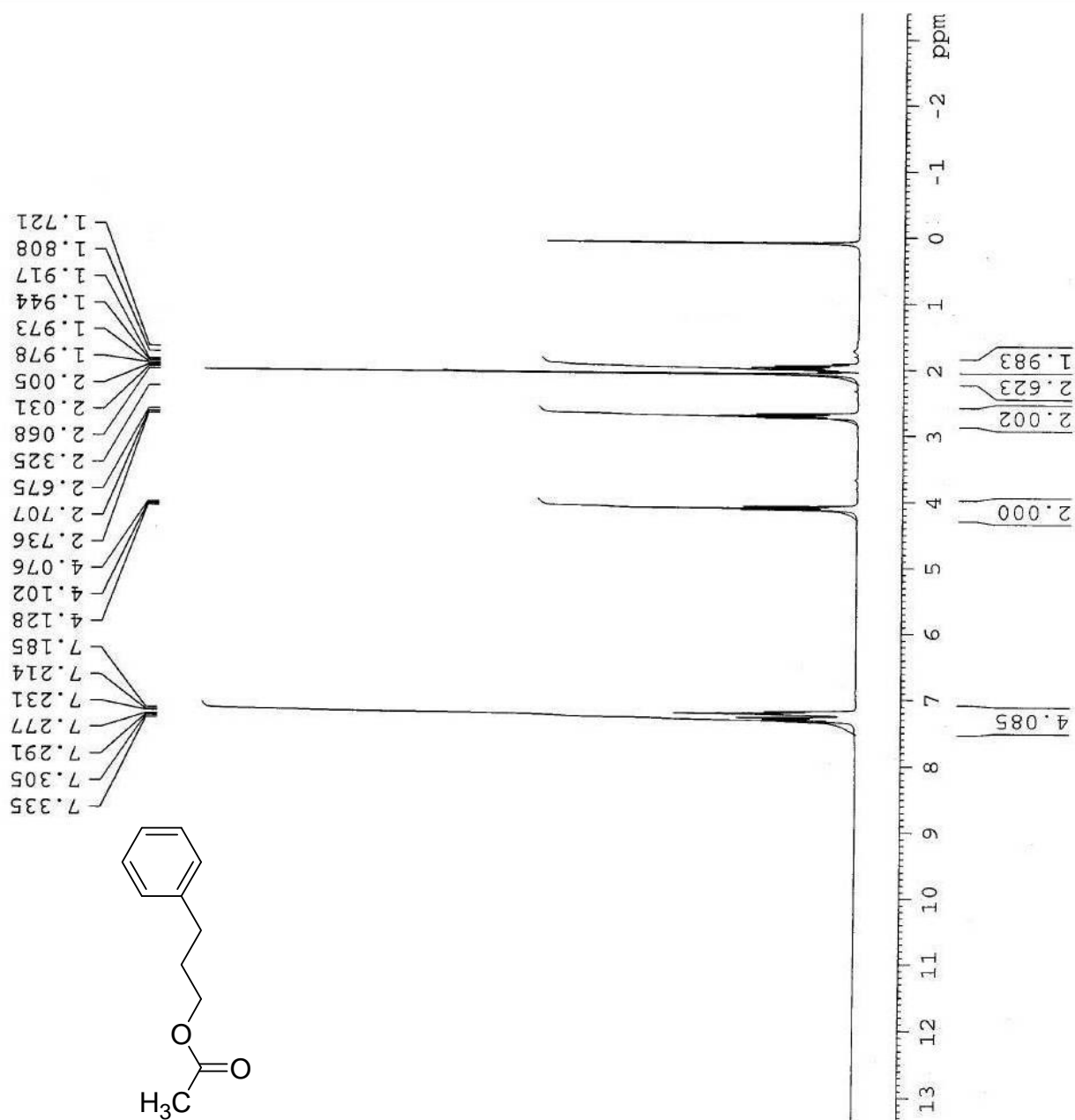


Table 2 (Entry 1)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

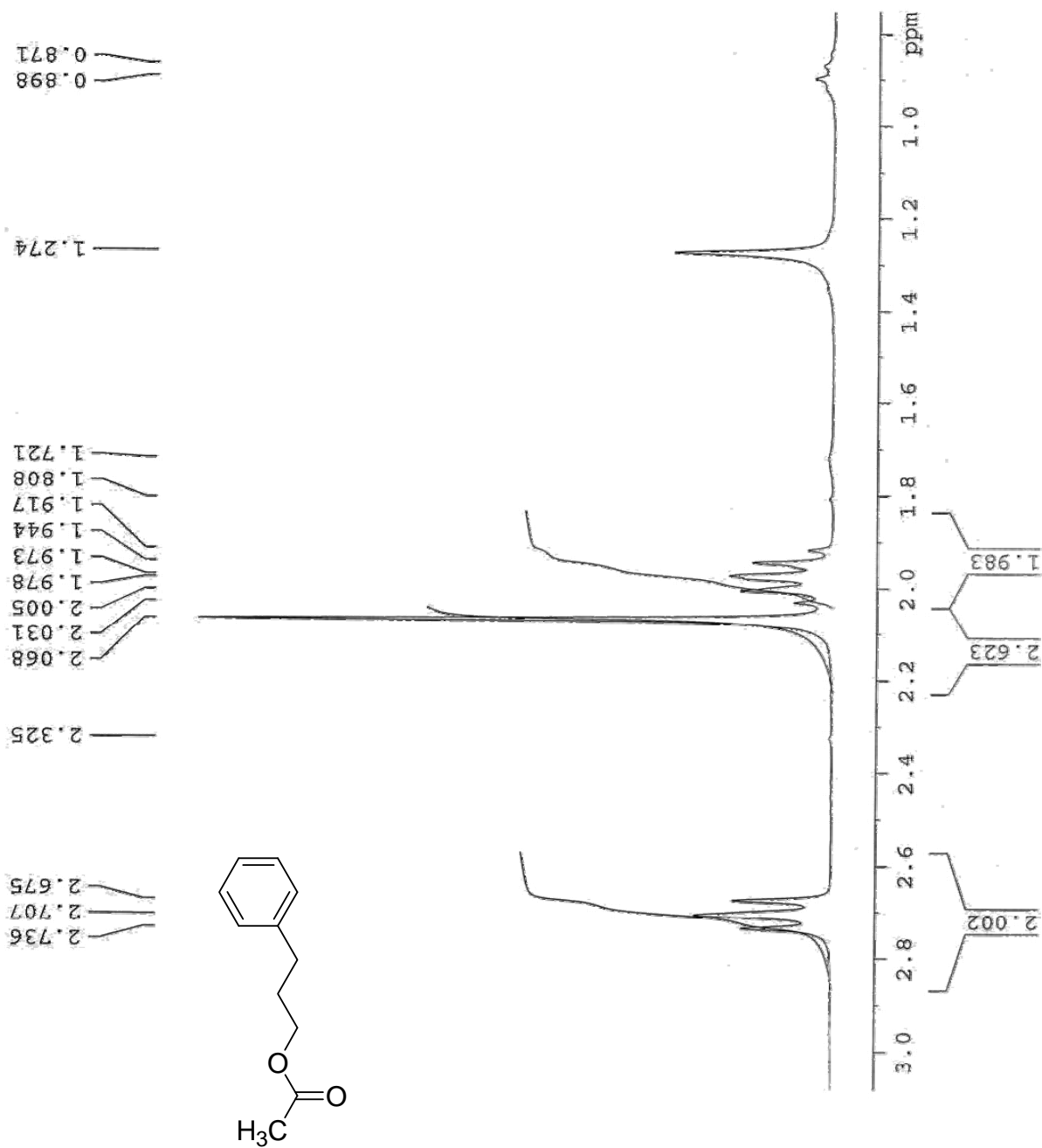
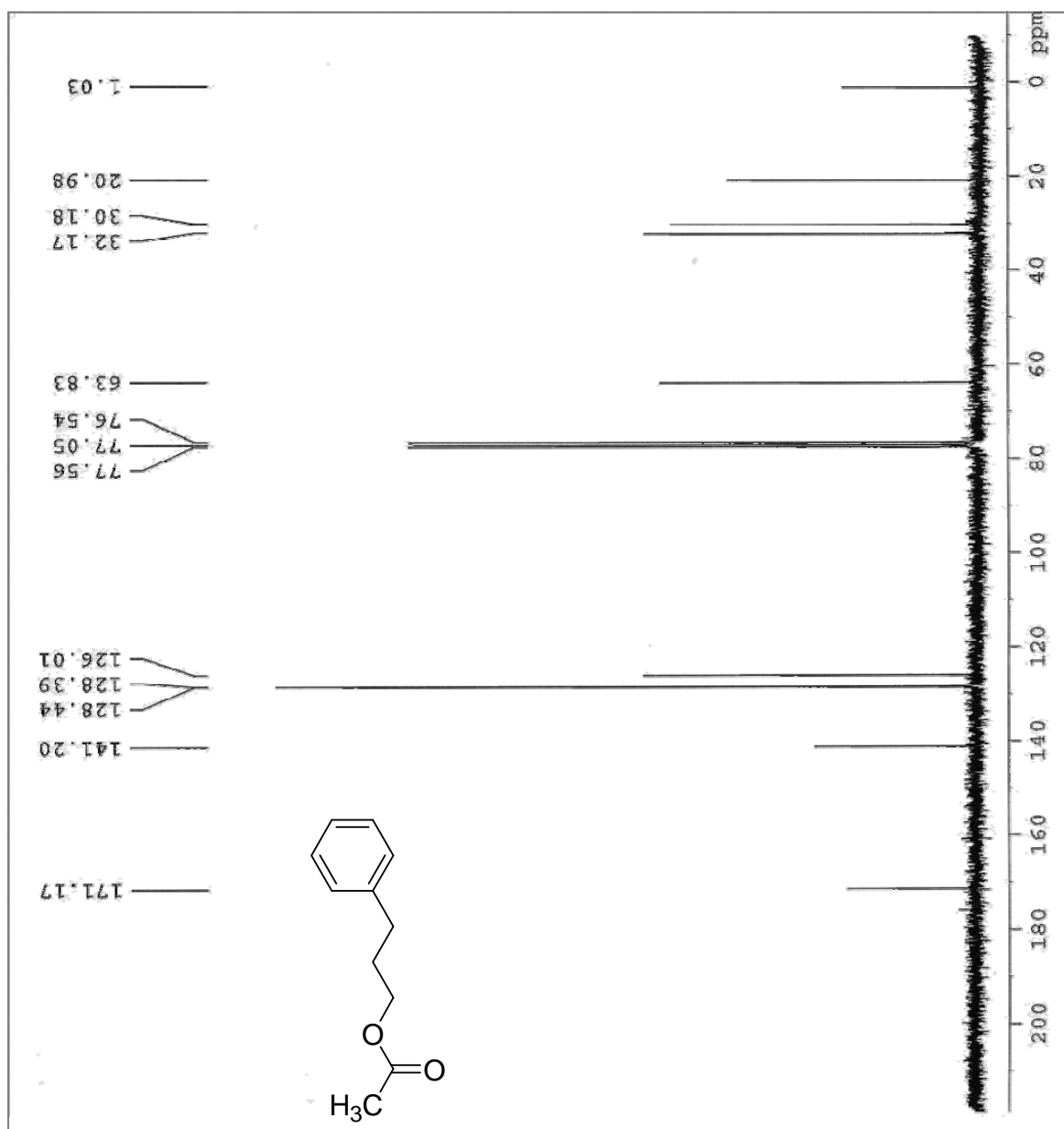


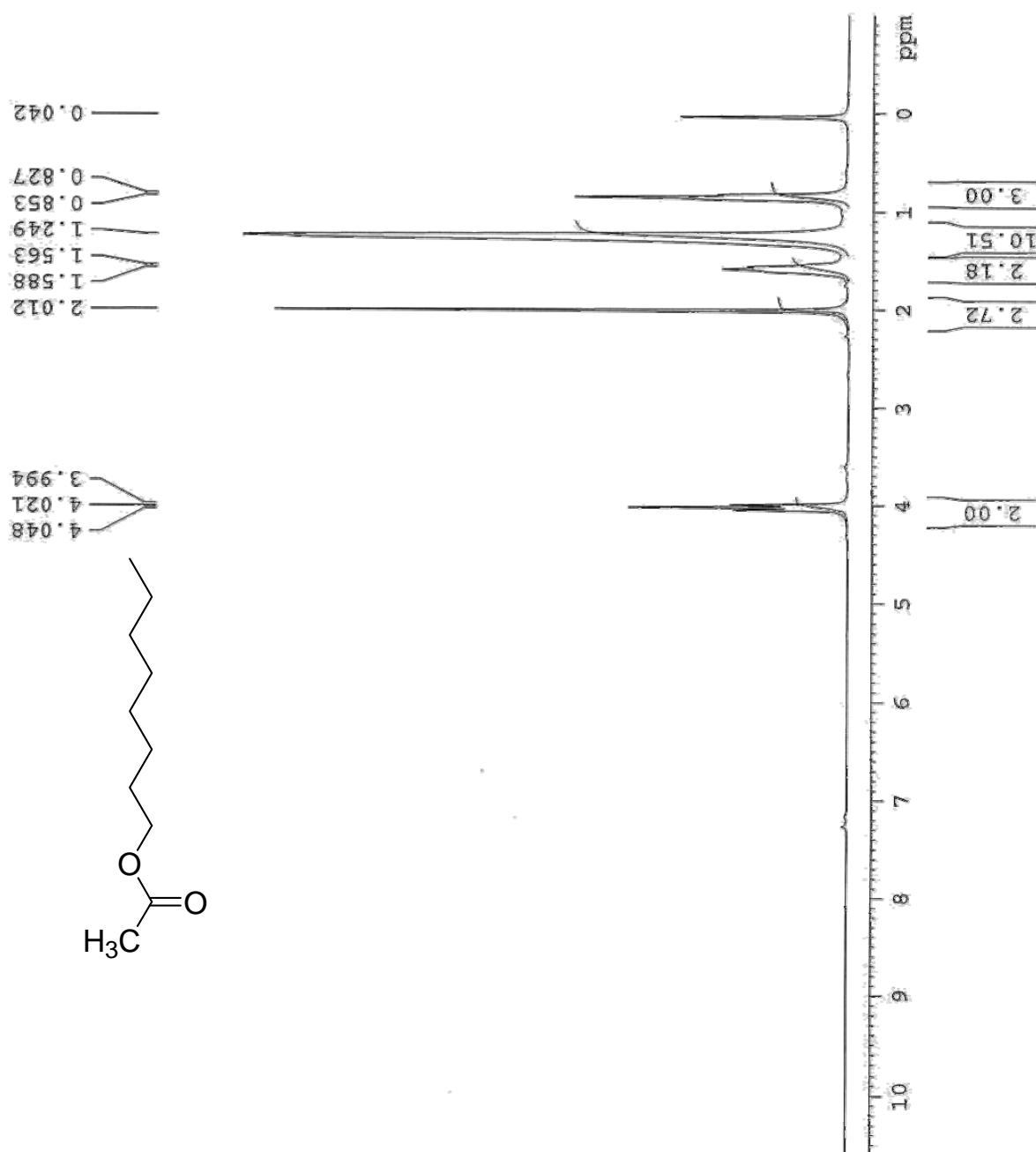
Table 2 (Entry 1)

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



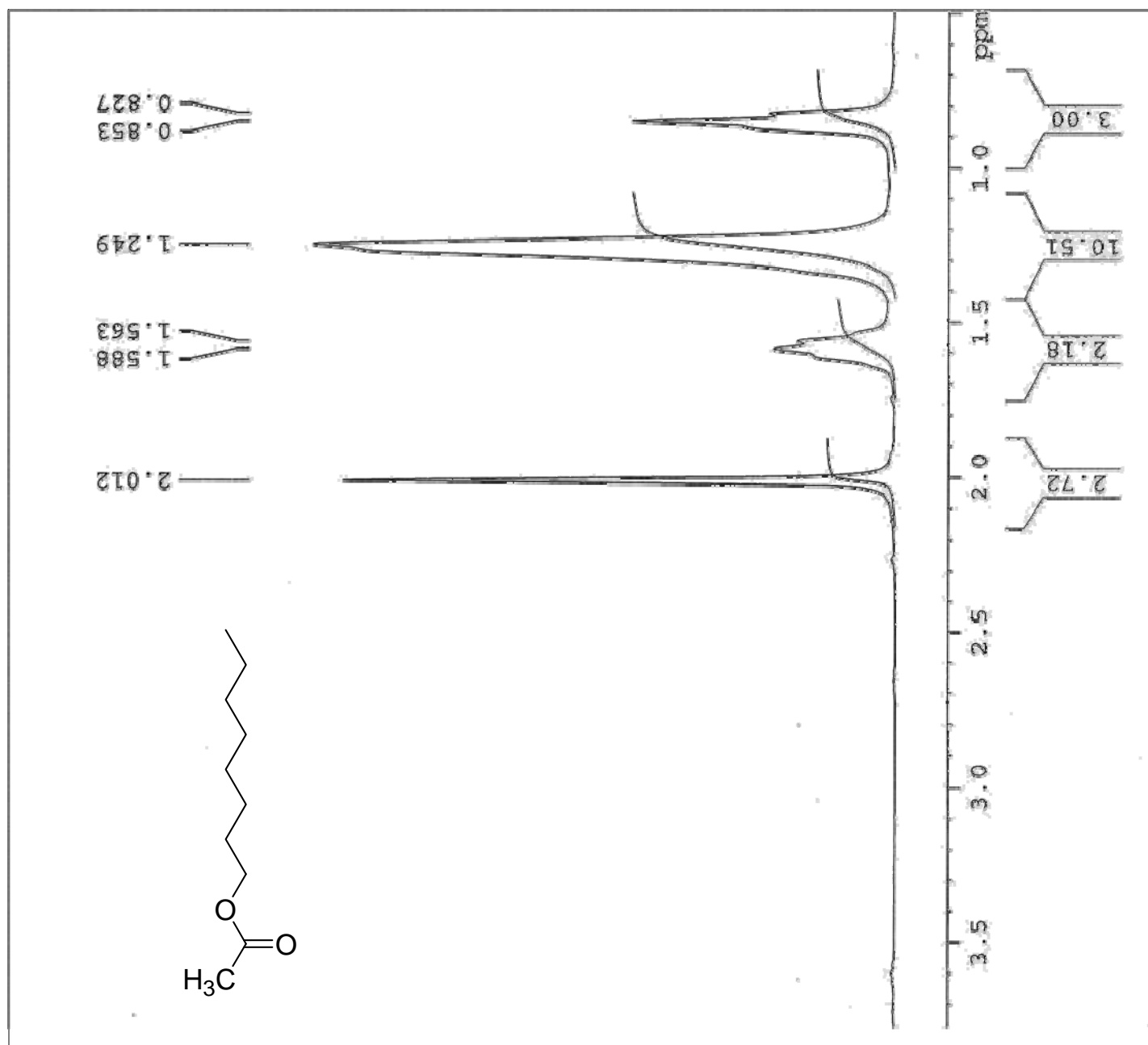
**Table 2 (Entry 1)**

**Solvent: CDCl<sub>3</sub>— Frequency: 250 MHz**



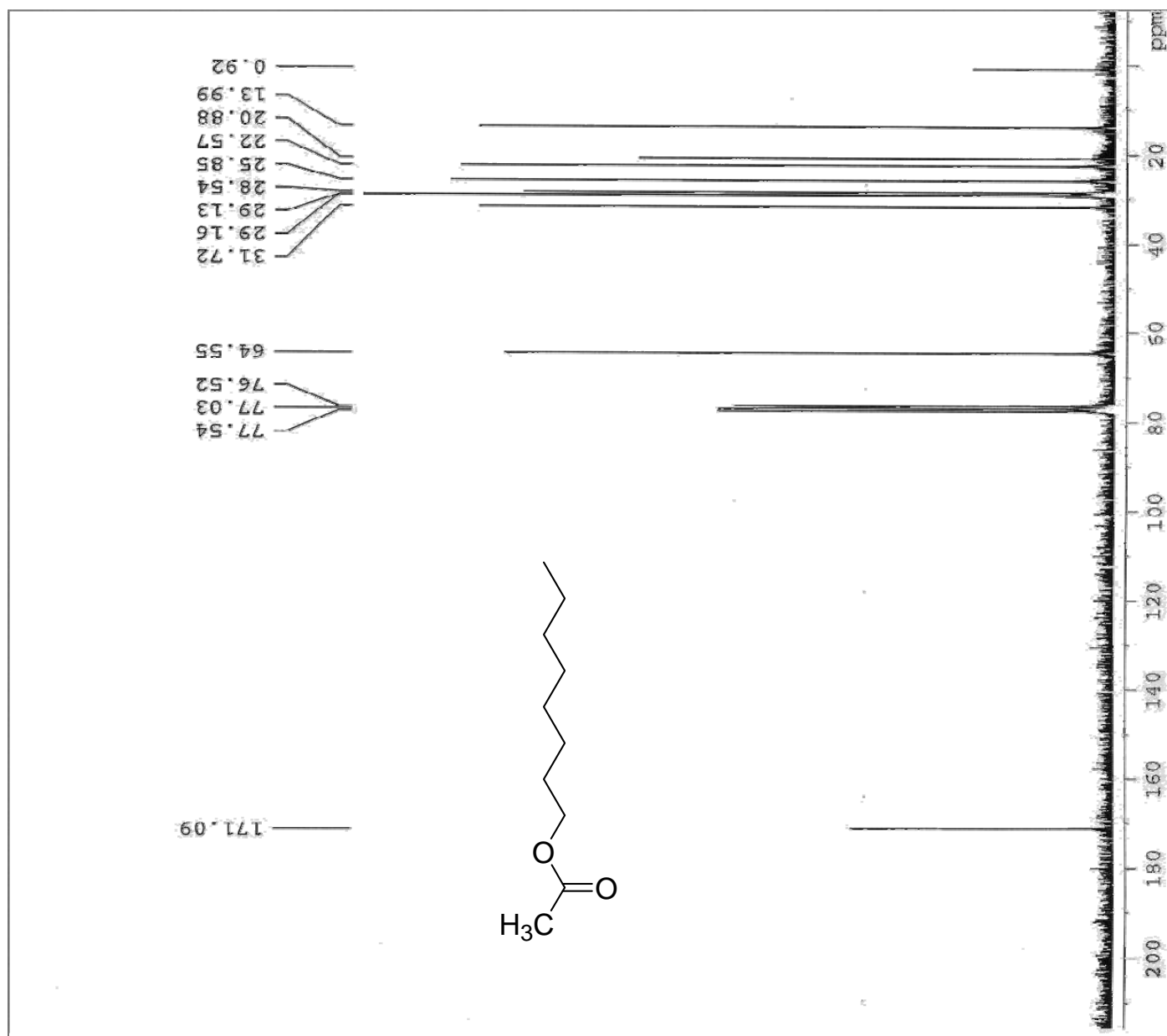
**Table 2 (Entry 2)**

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 2 (Entry 2)**

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 2 (Entry 2)**

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

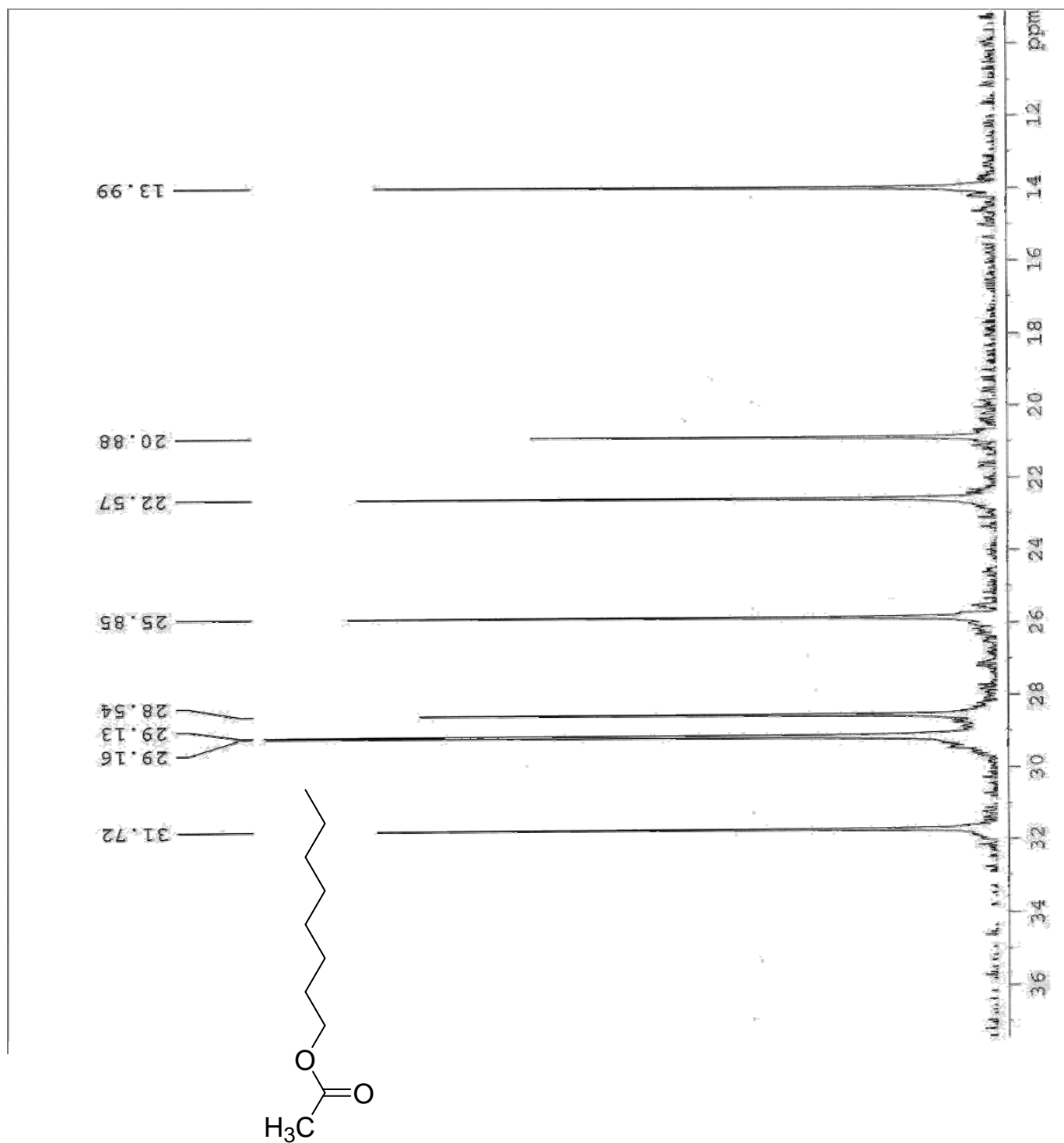


Table 2 (Entry 2)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

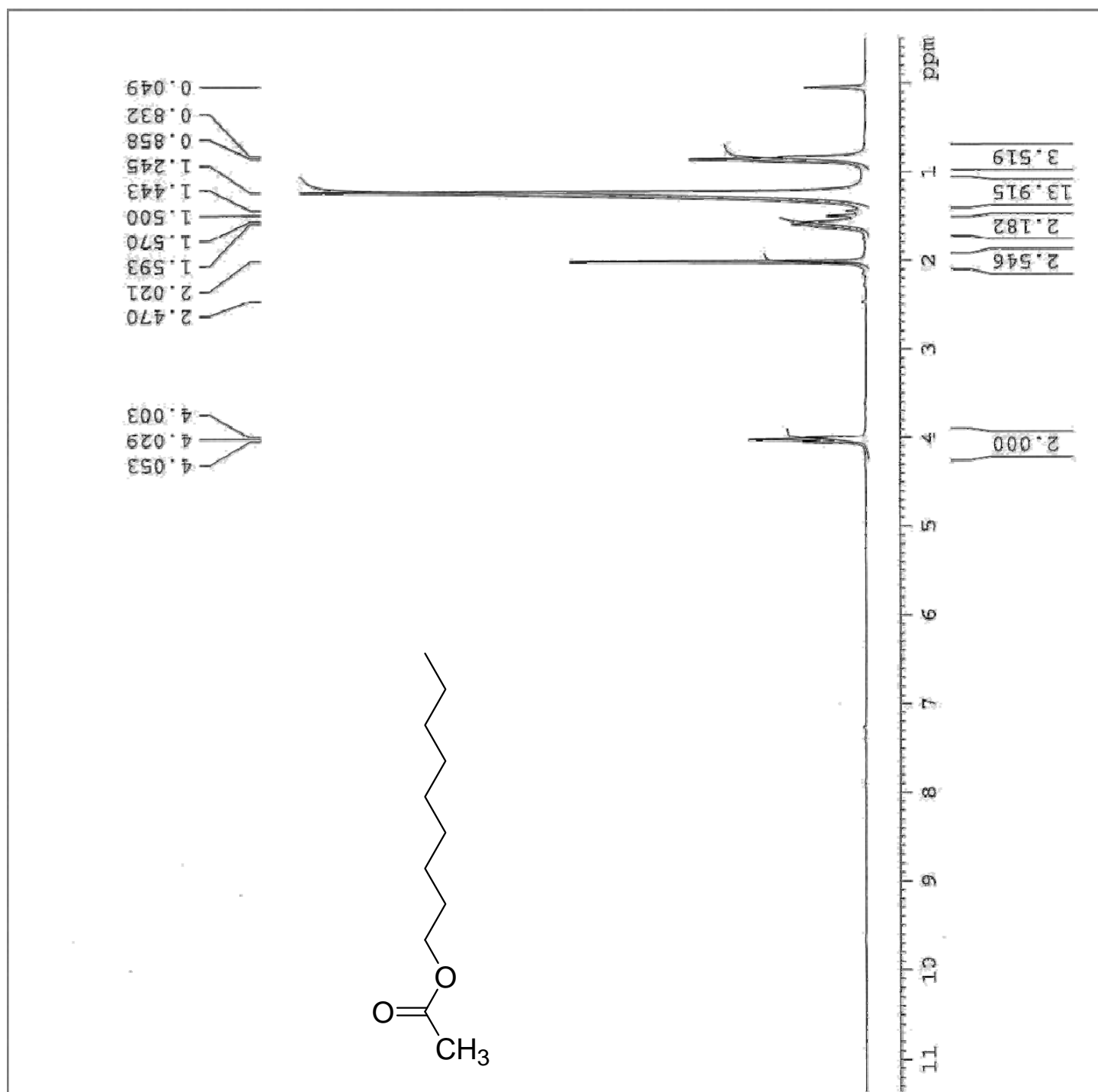


Table 2 (Entry 3)

Solvent: CDCl<sub>3</sub>— Frequency: 250 MHz

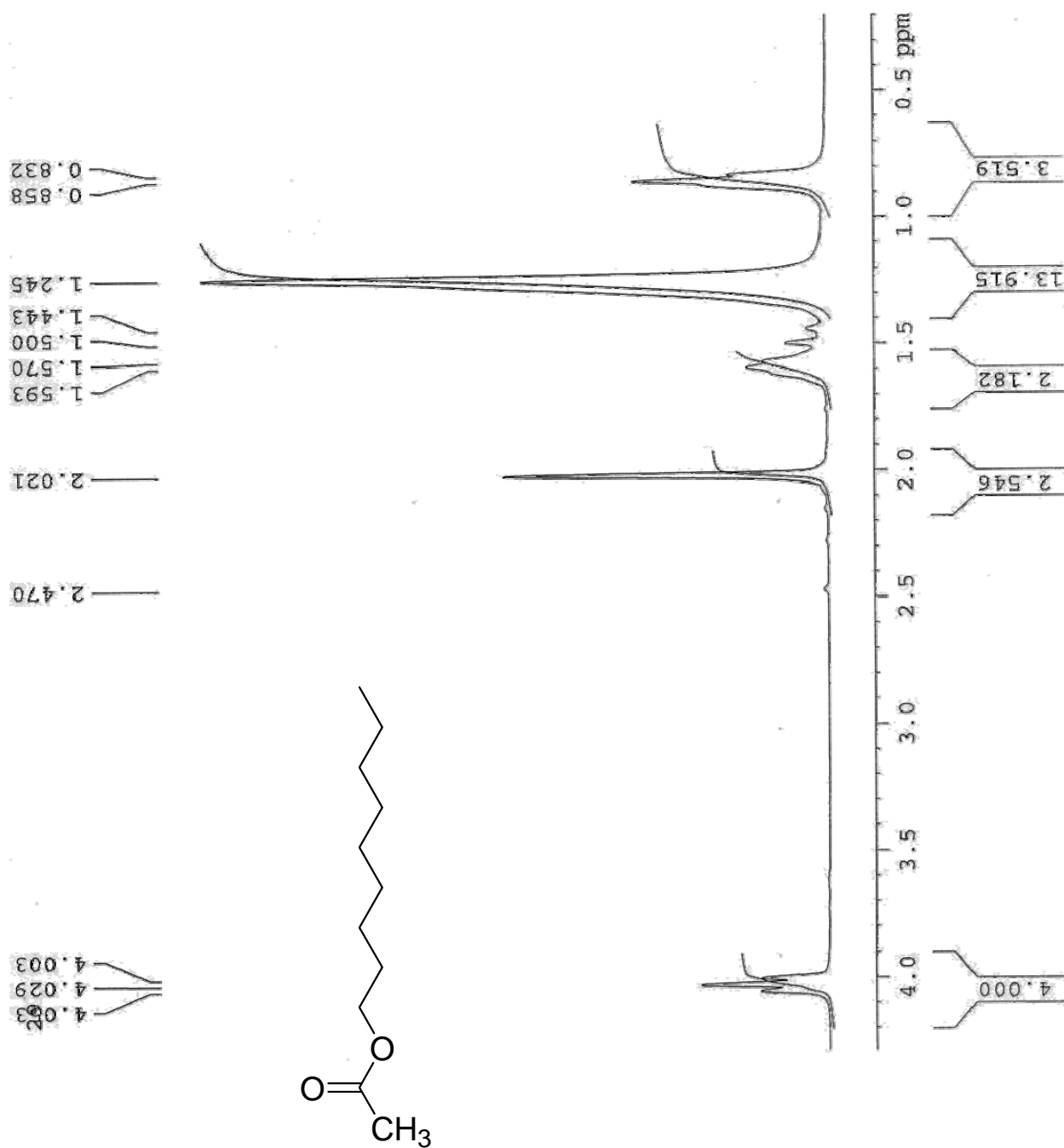


Table 2 (Entry 3)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

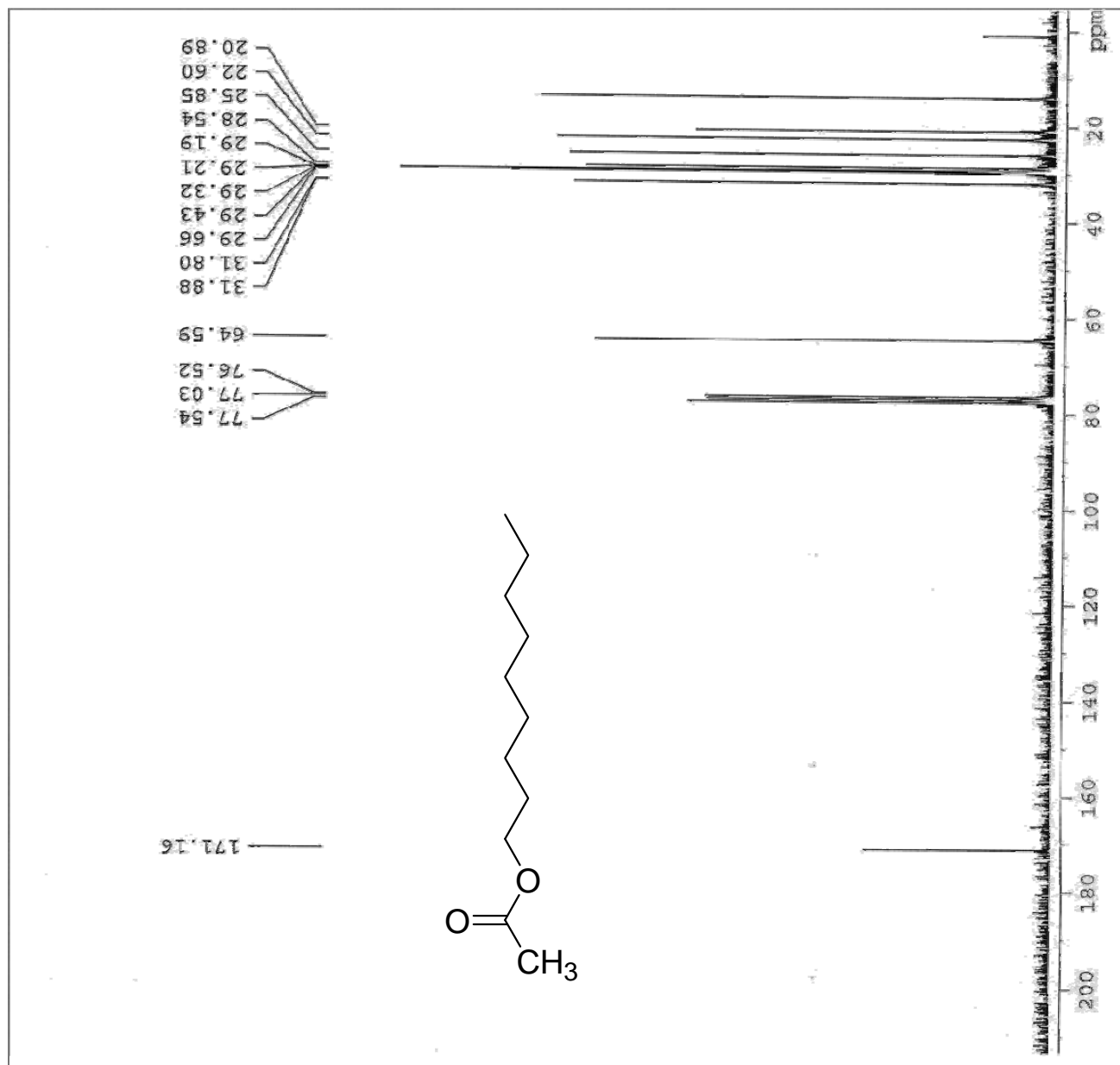


Table 2 (Entry 3)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

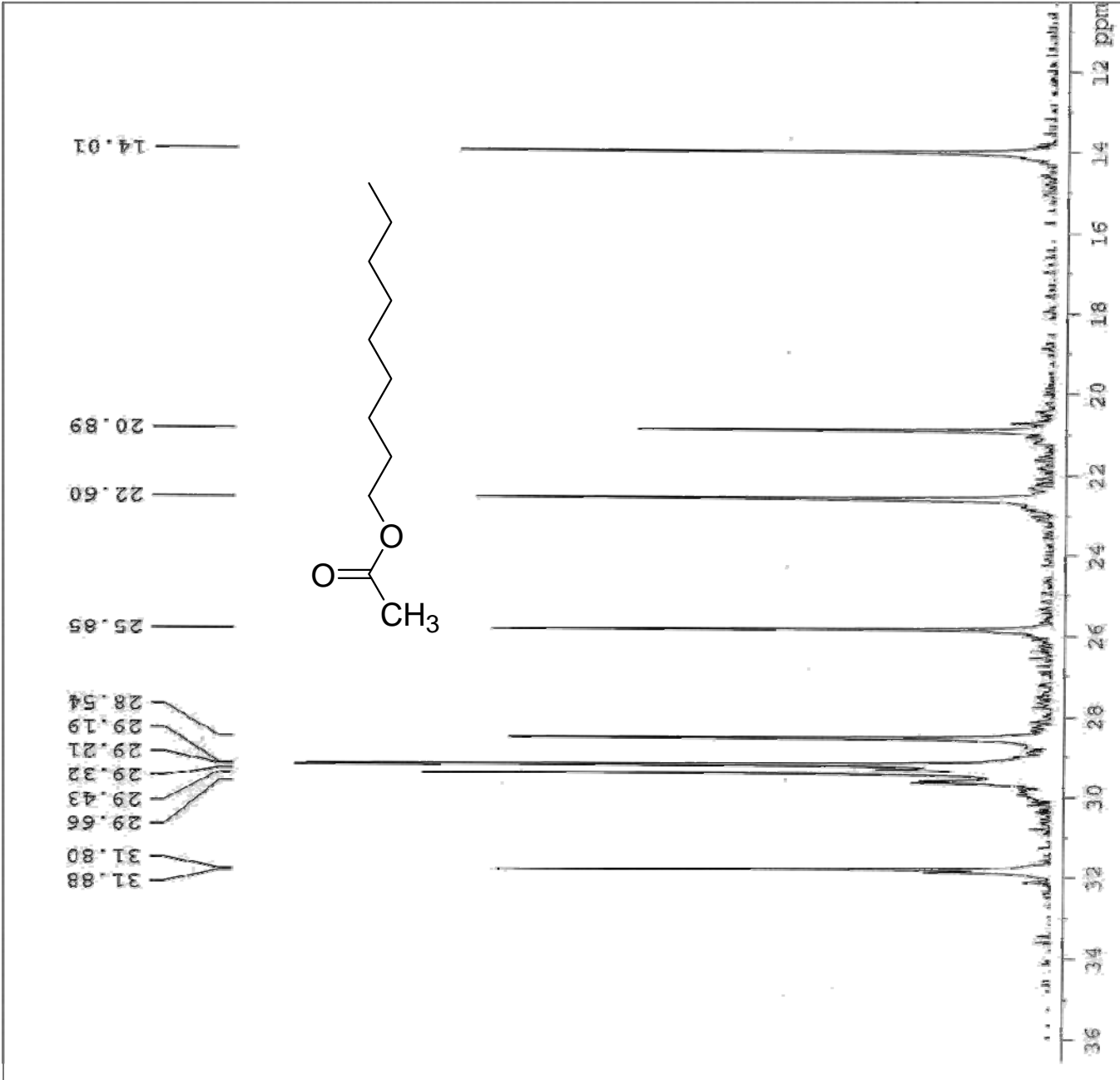


Table 2 (Entry 3)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

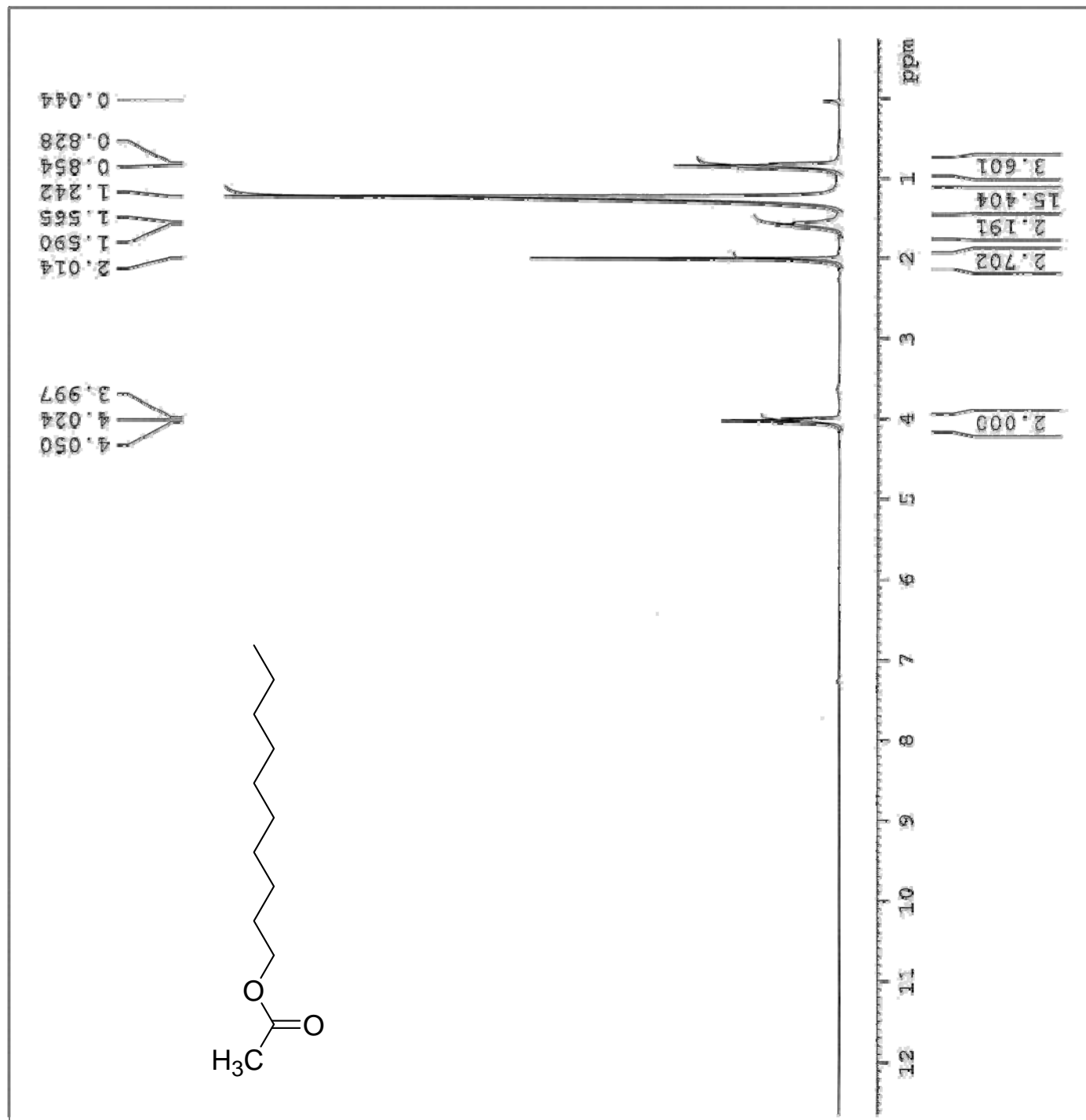
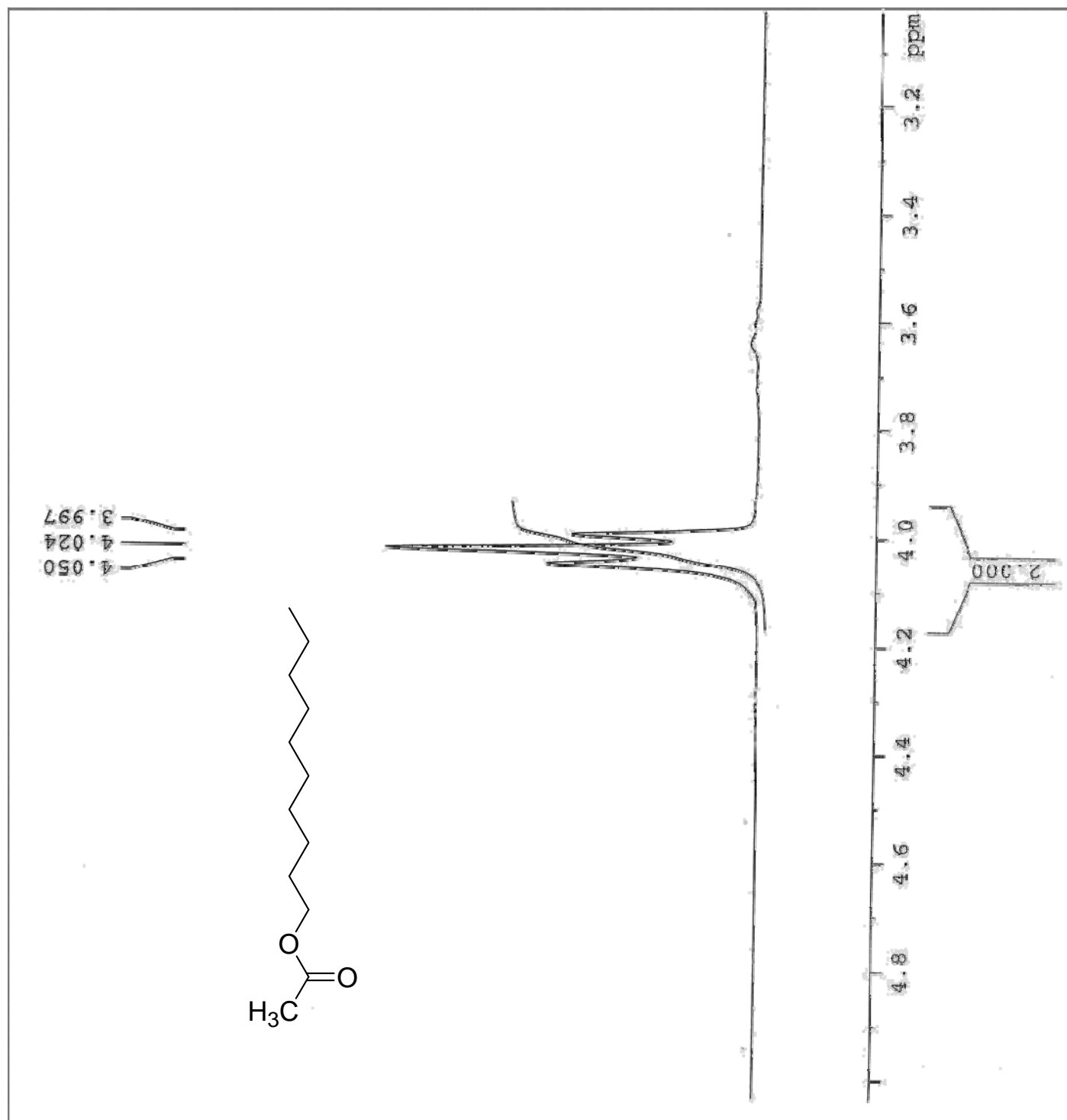


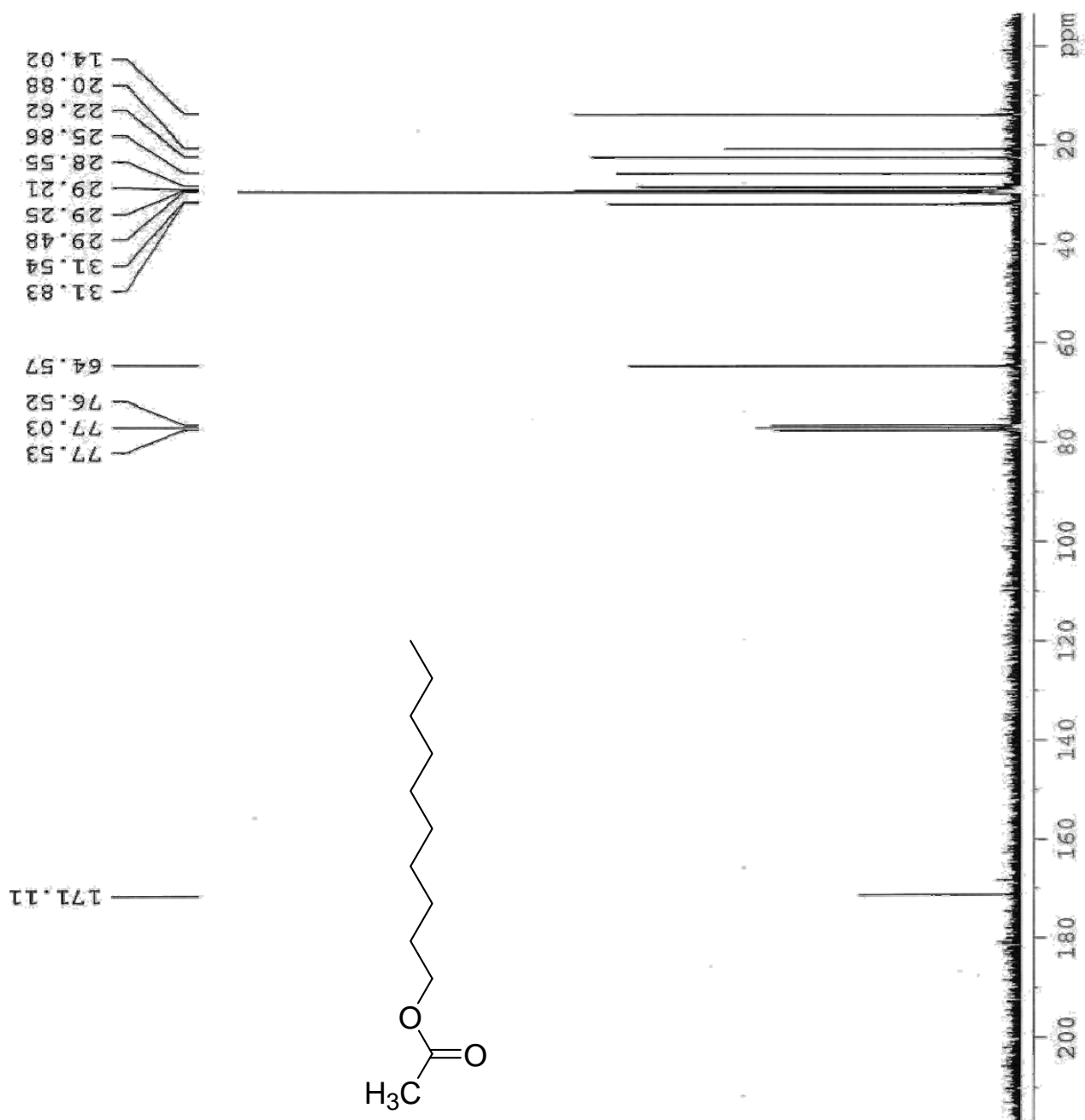
Table 2 (Entry 4)

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**

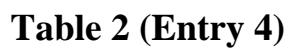


**Table 2 (Entry 4)**

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 2 (Entry 4)**



Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

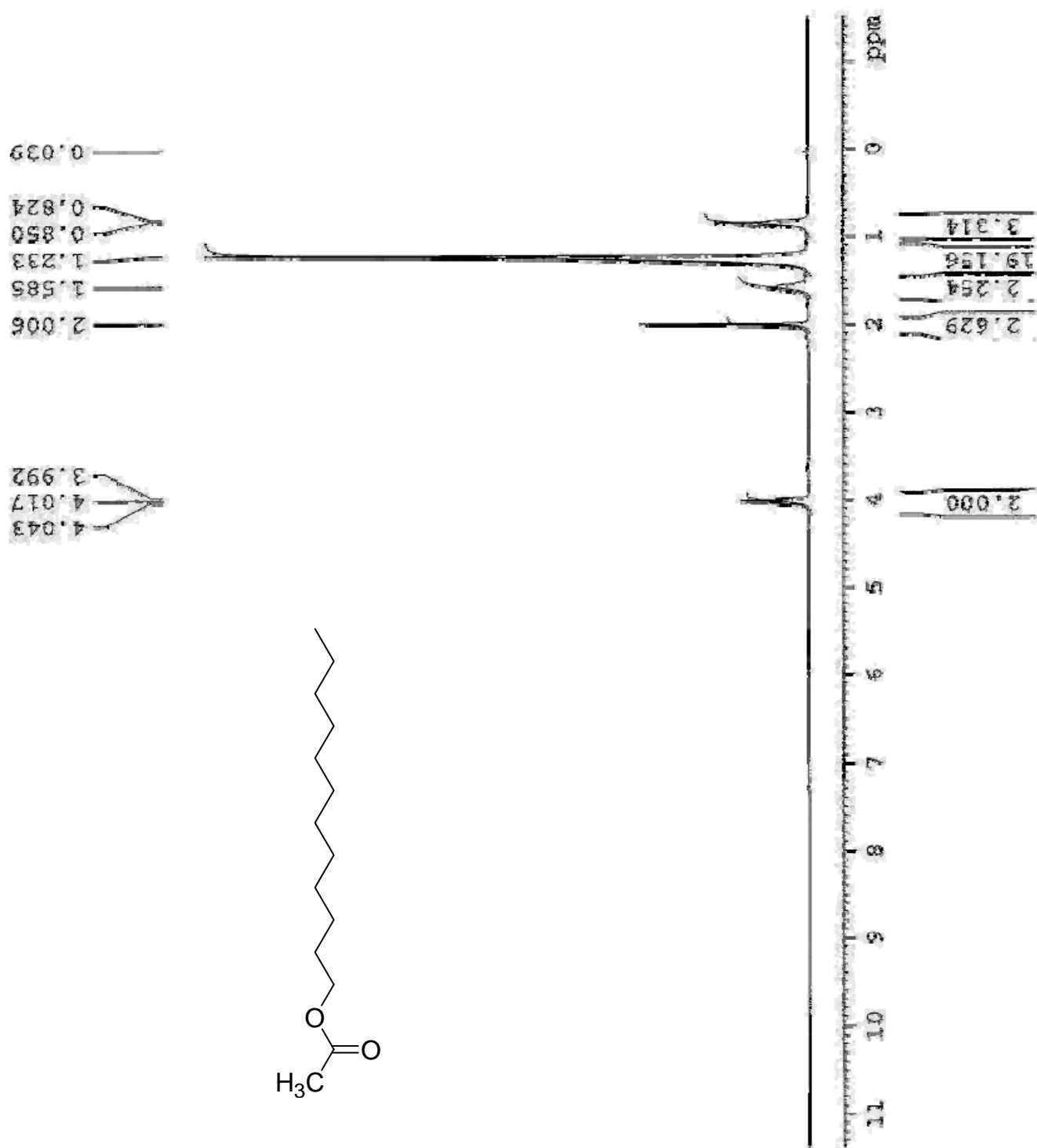


Table 2 (Entry 5)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

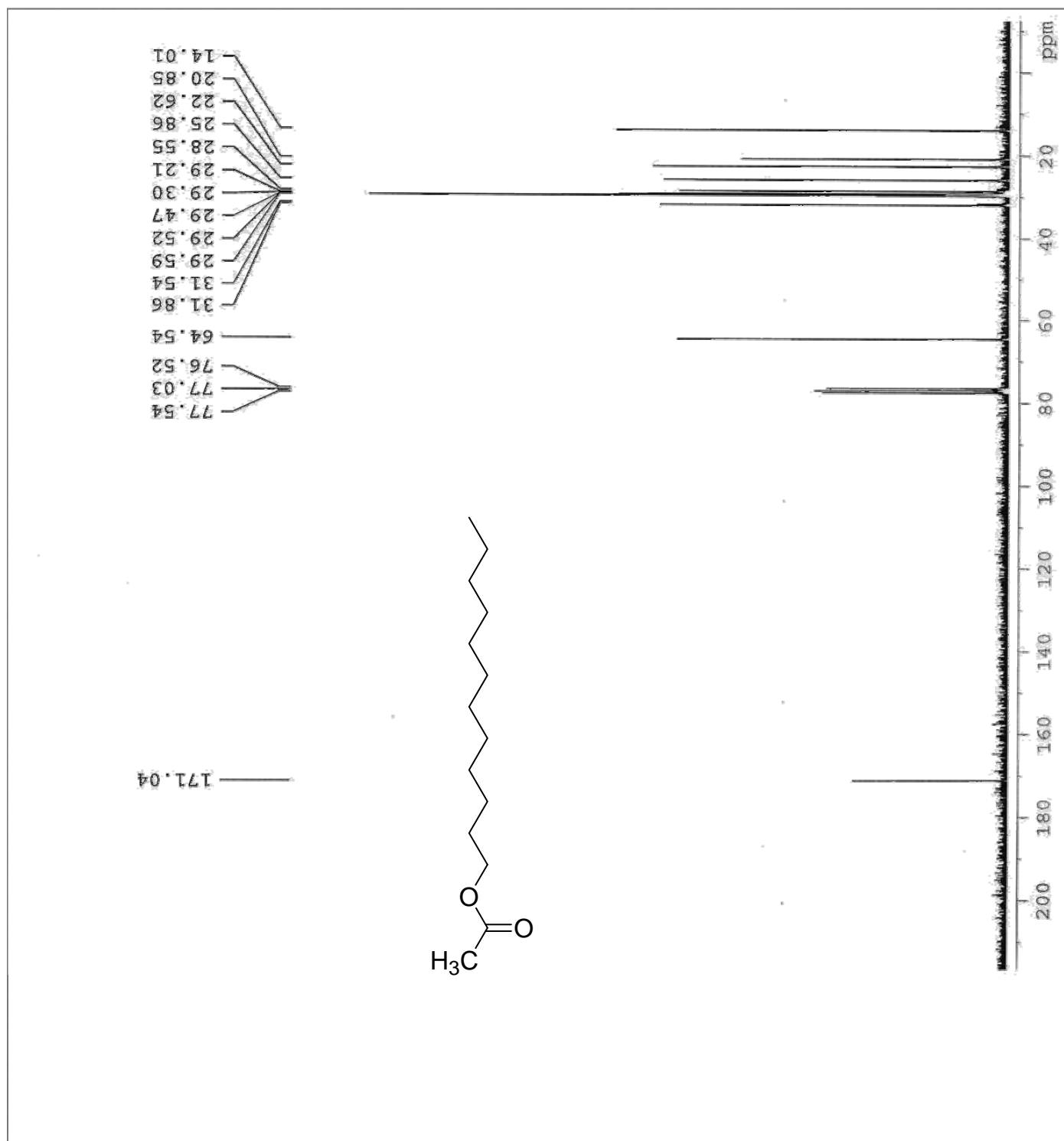


Table 2 (Entry 5)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

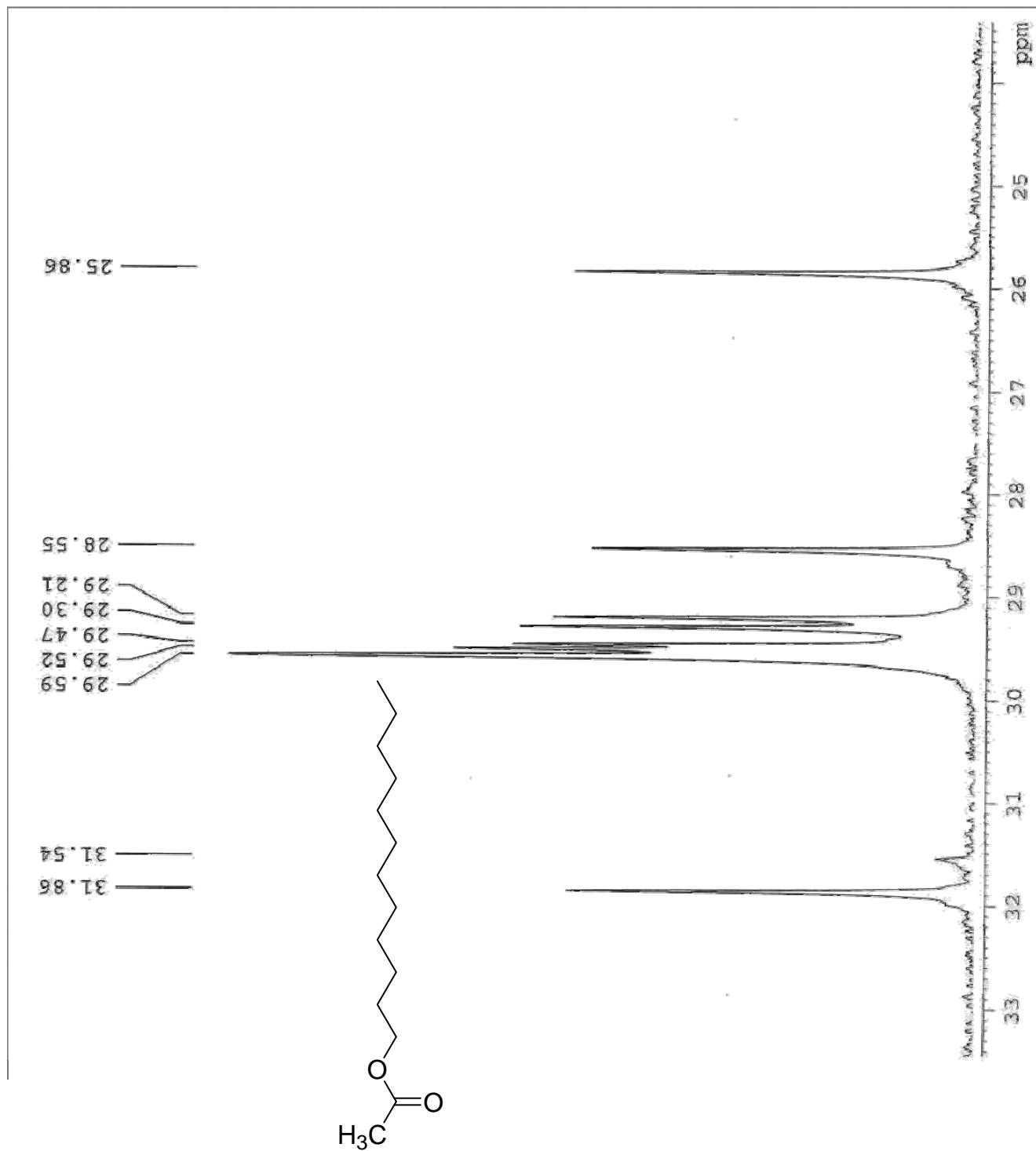


Table 2 (Entry 5)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

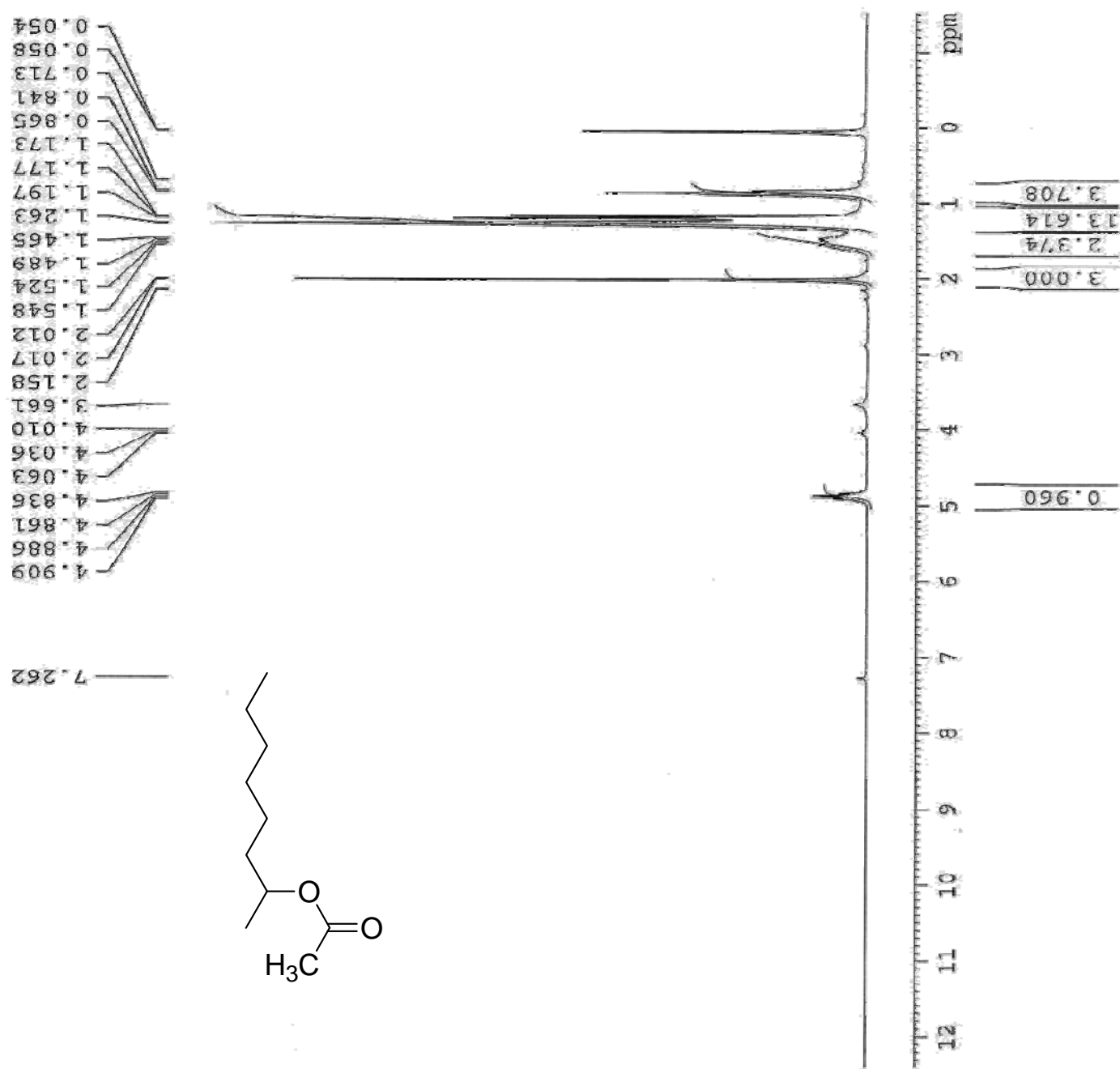


Table 2 (Entry 6)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

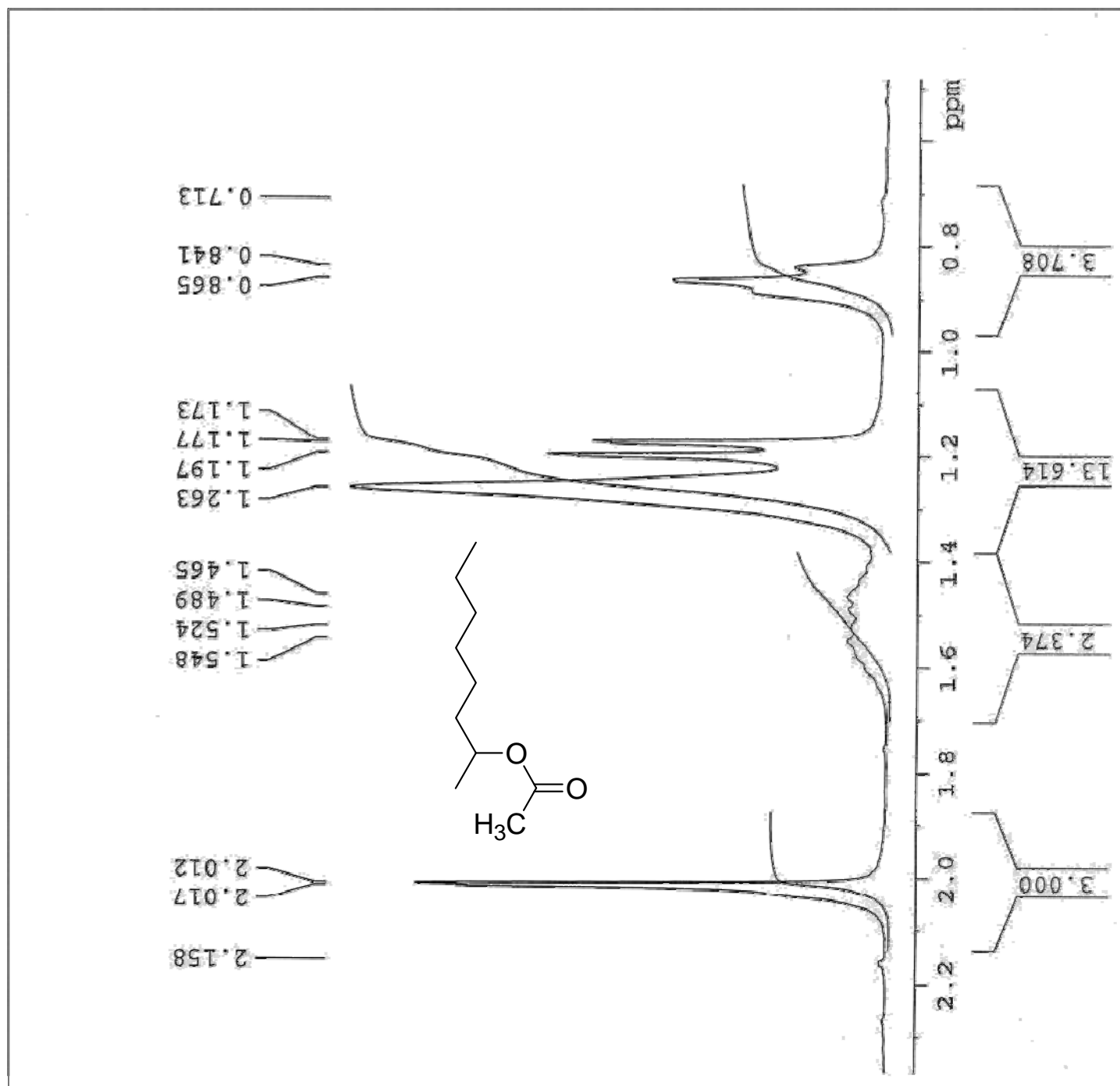


Table 2 (Entry 6)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

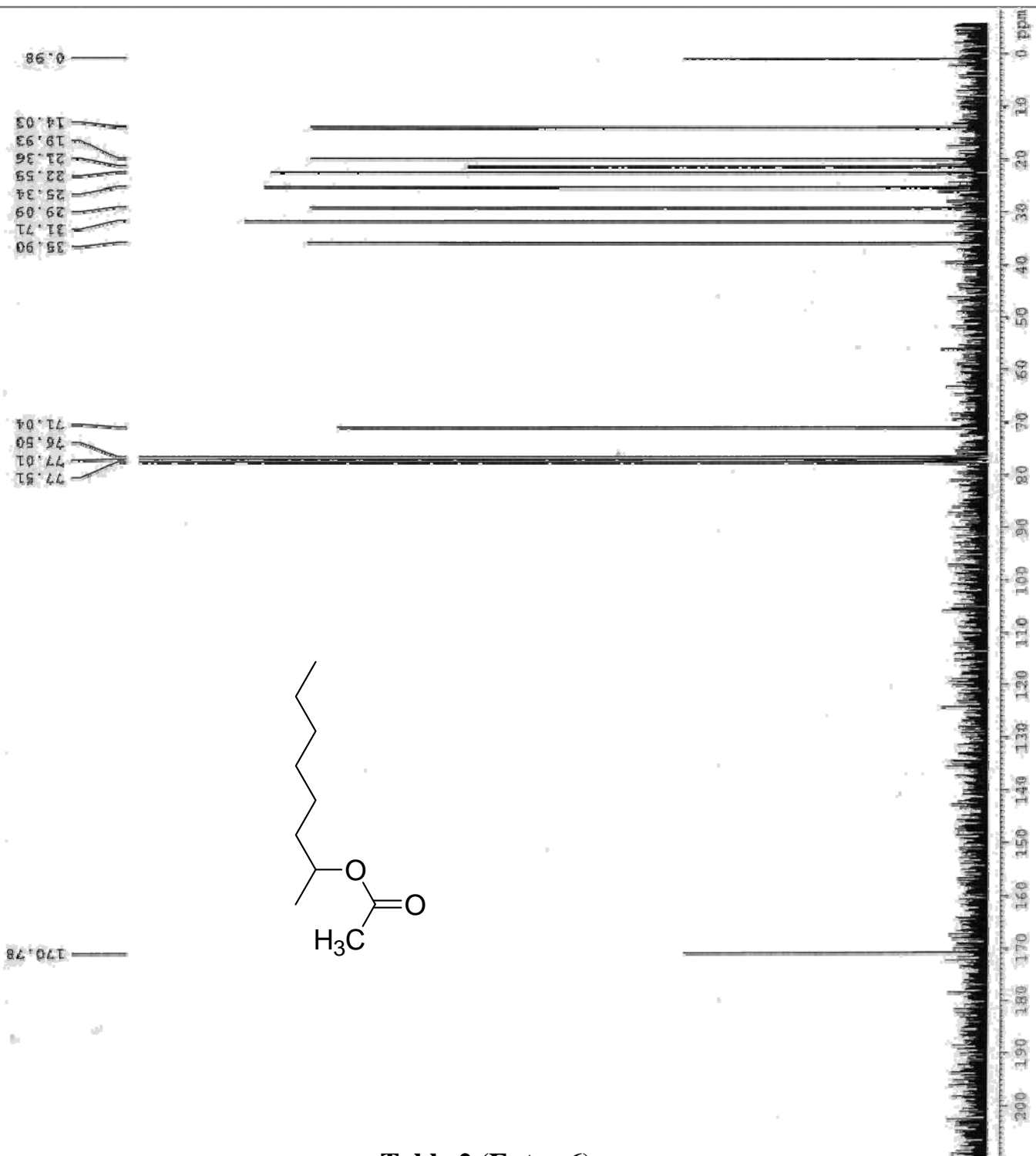


Table 2 (Entry 6)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

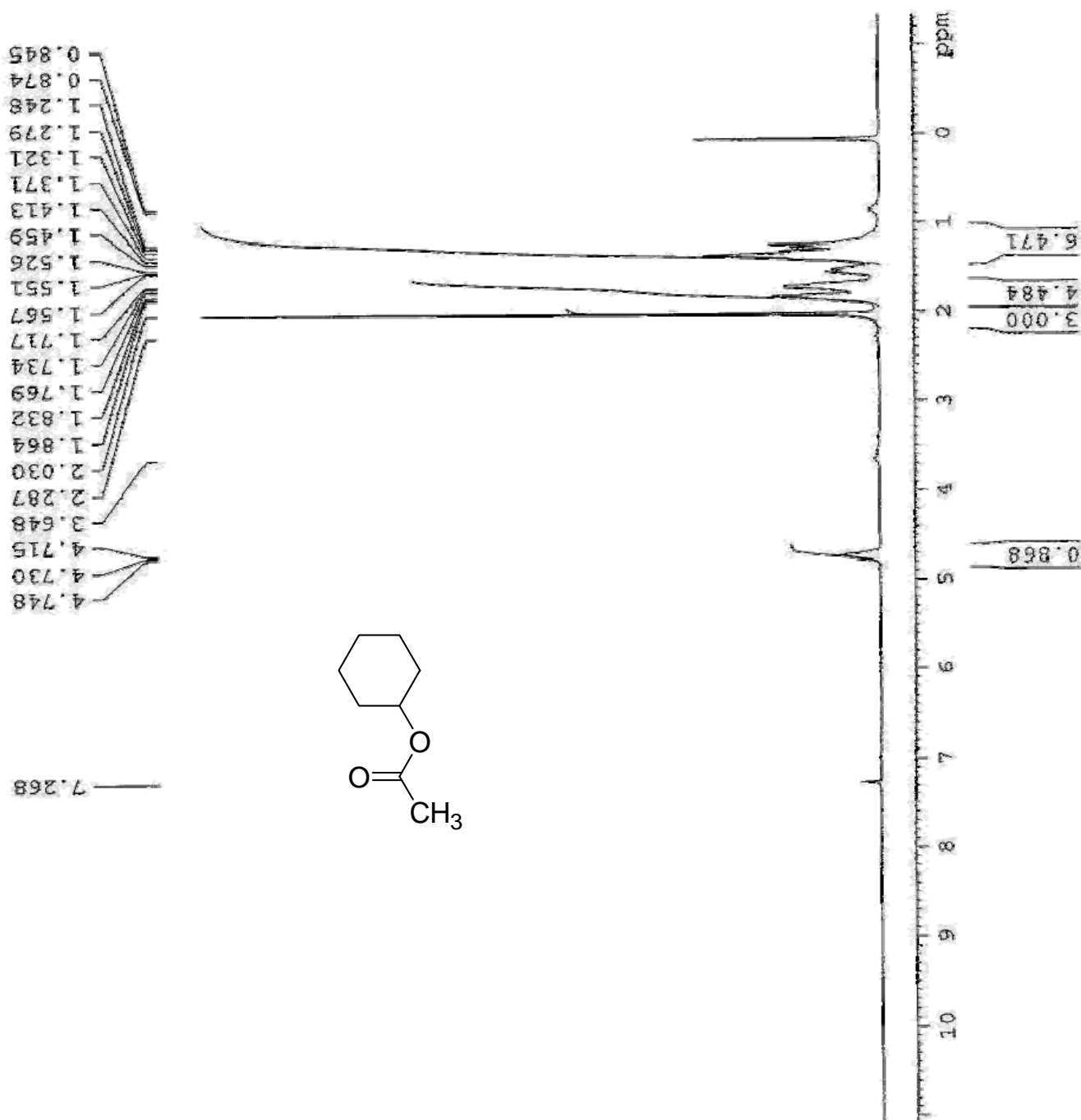


Table 2 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

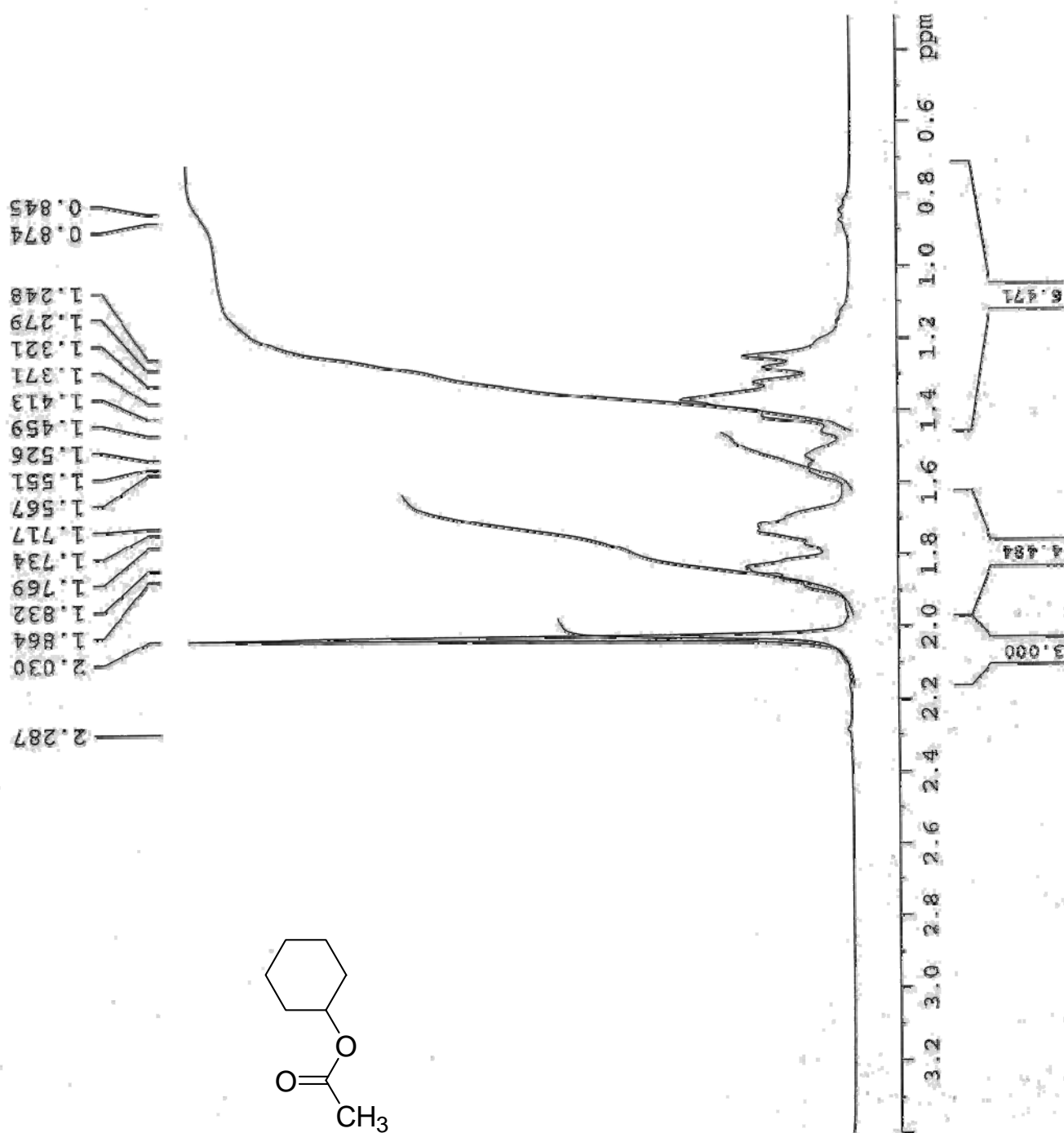


Table 2 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

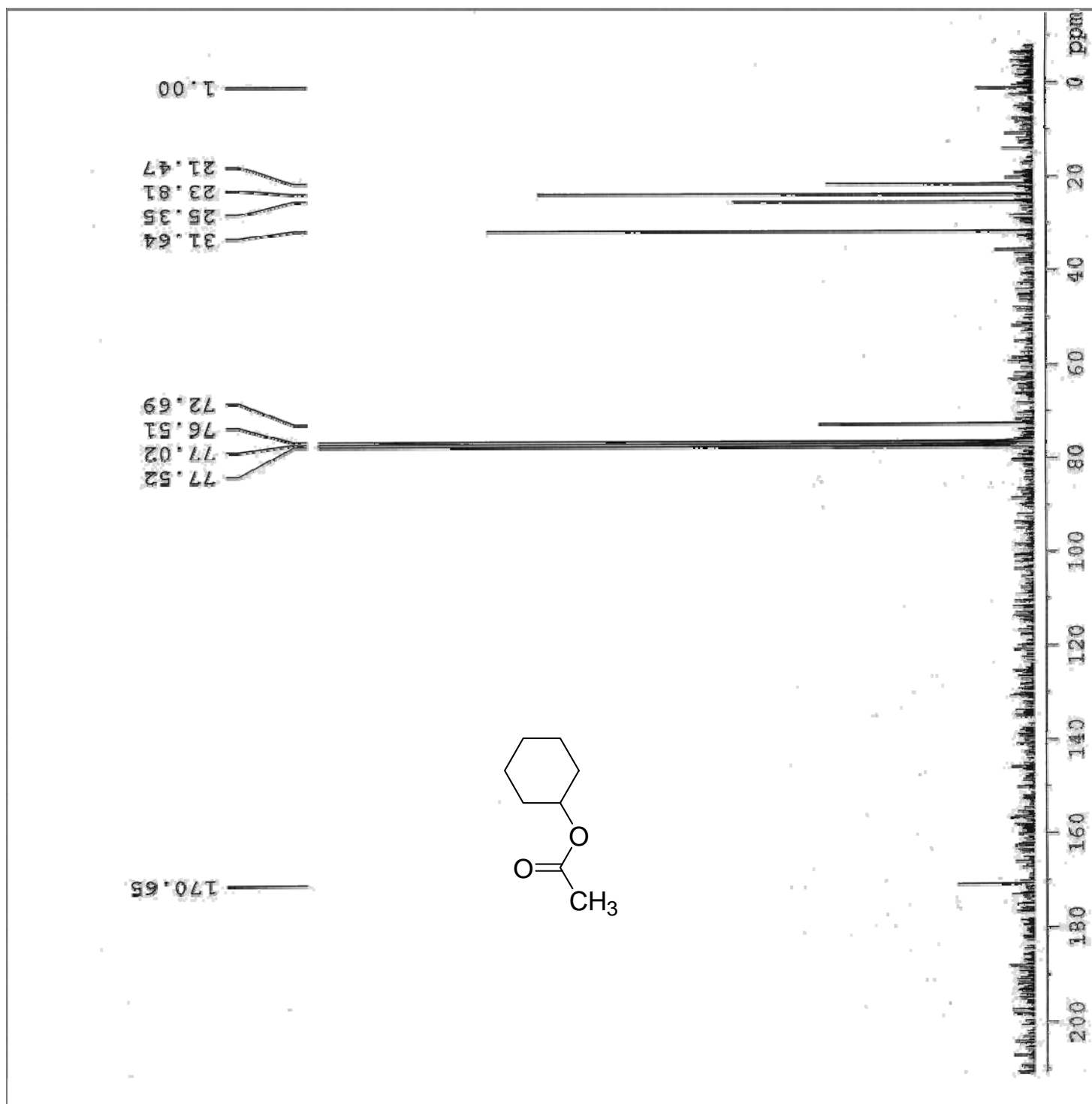


Table 2 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

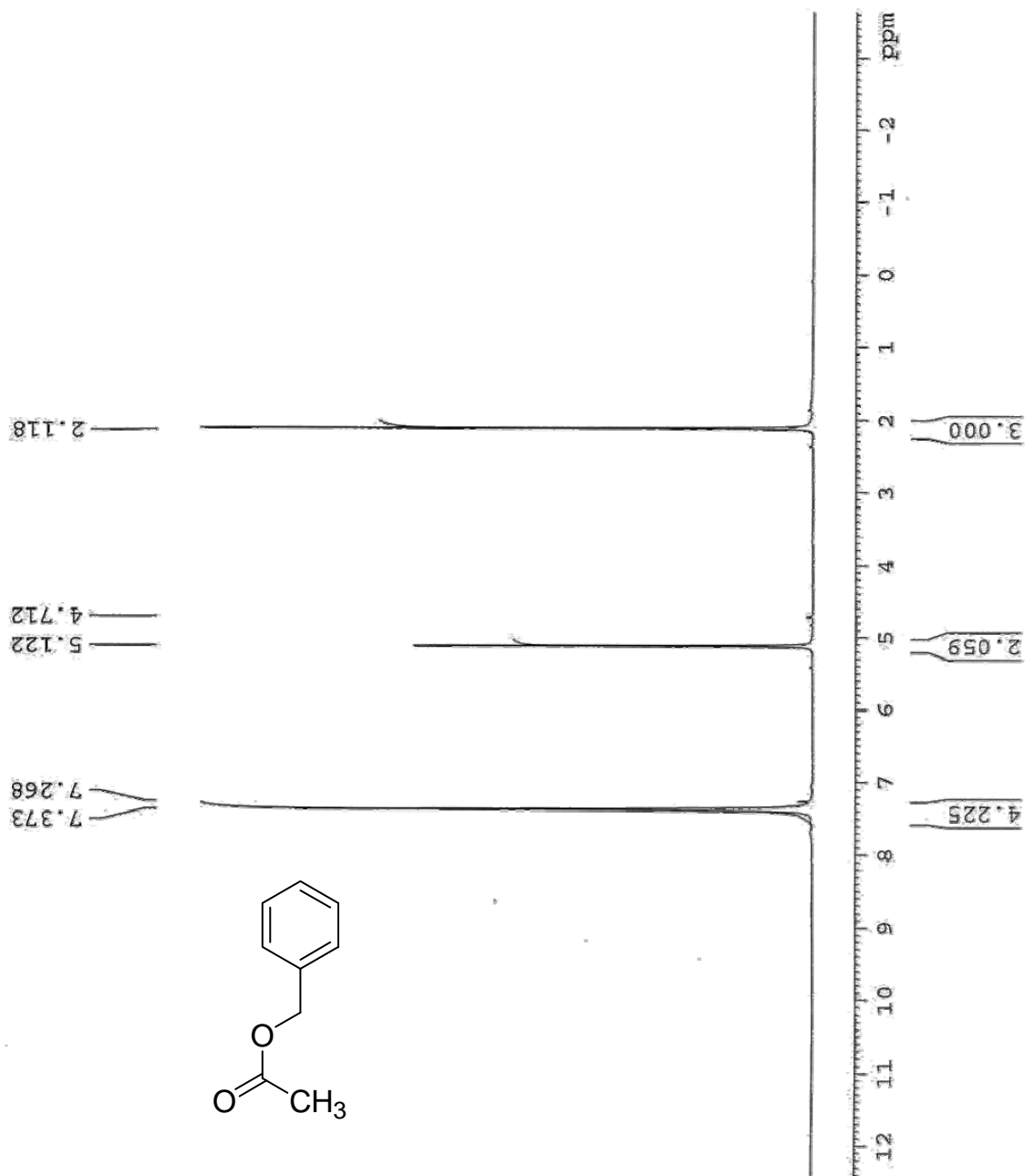


Table 2 (Entry 8)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

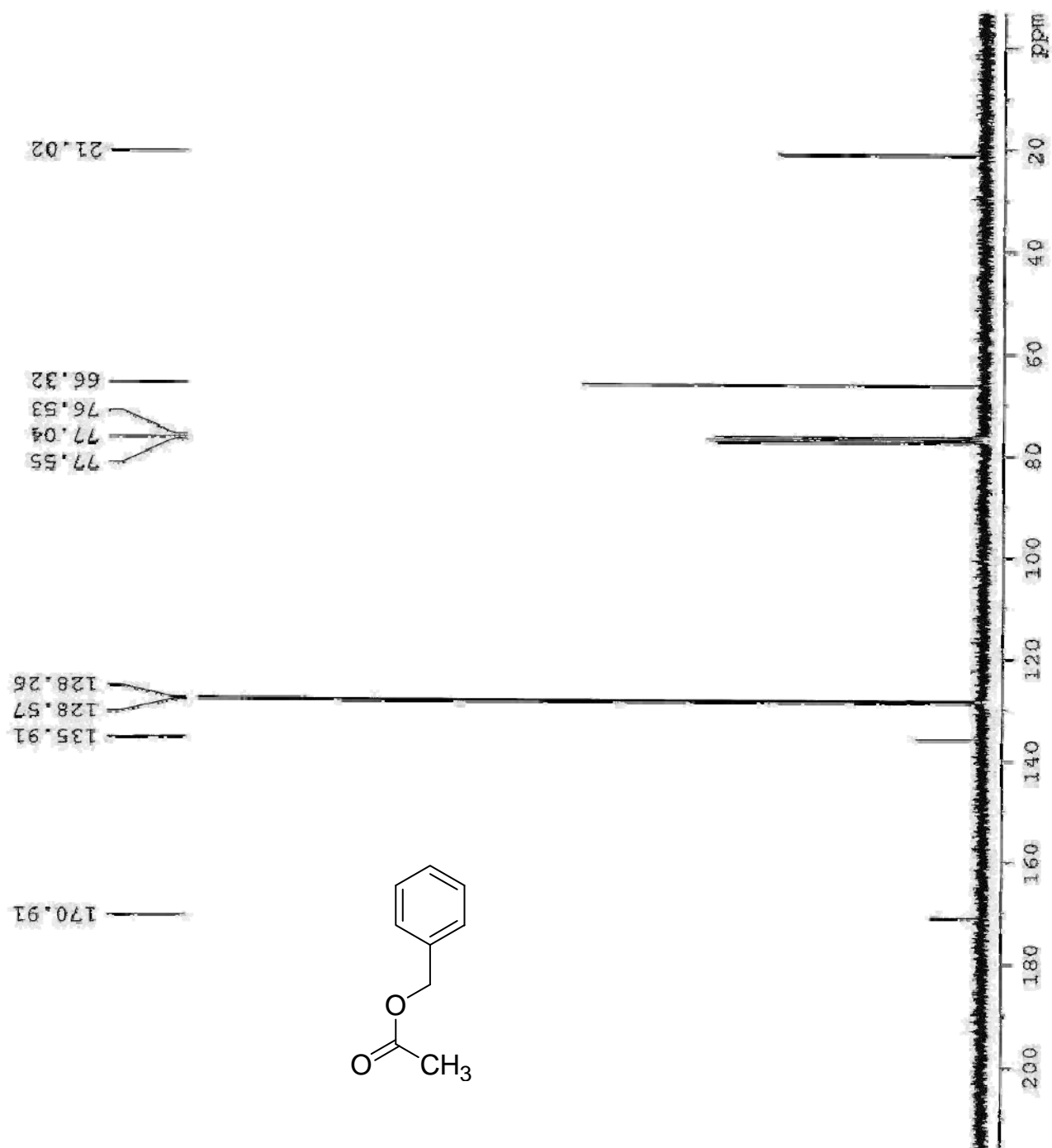
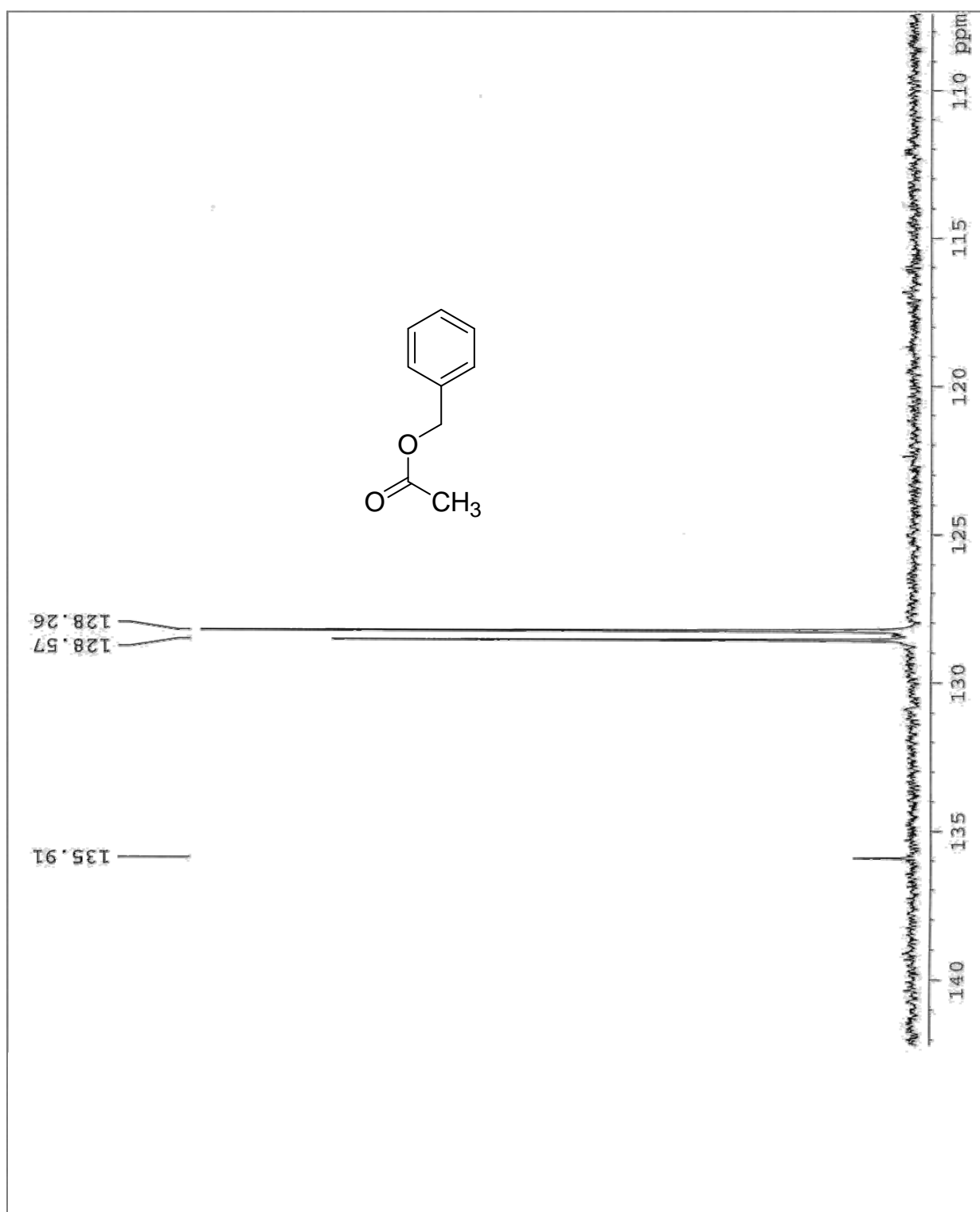


Table 2 (Entry 8)

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 2 (Entry 8)**

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

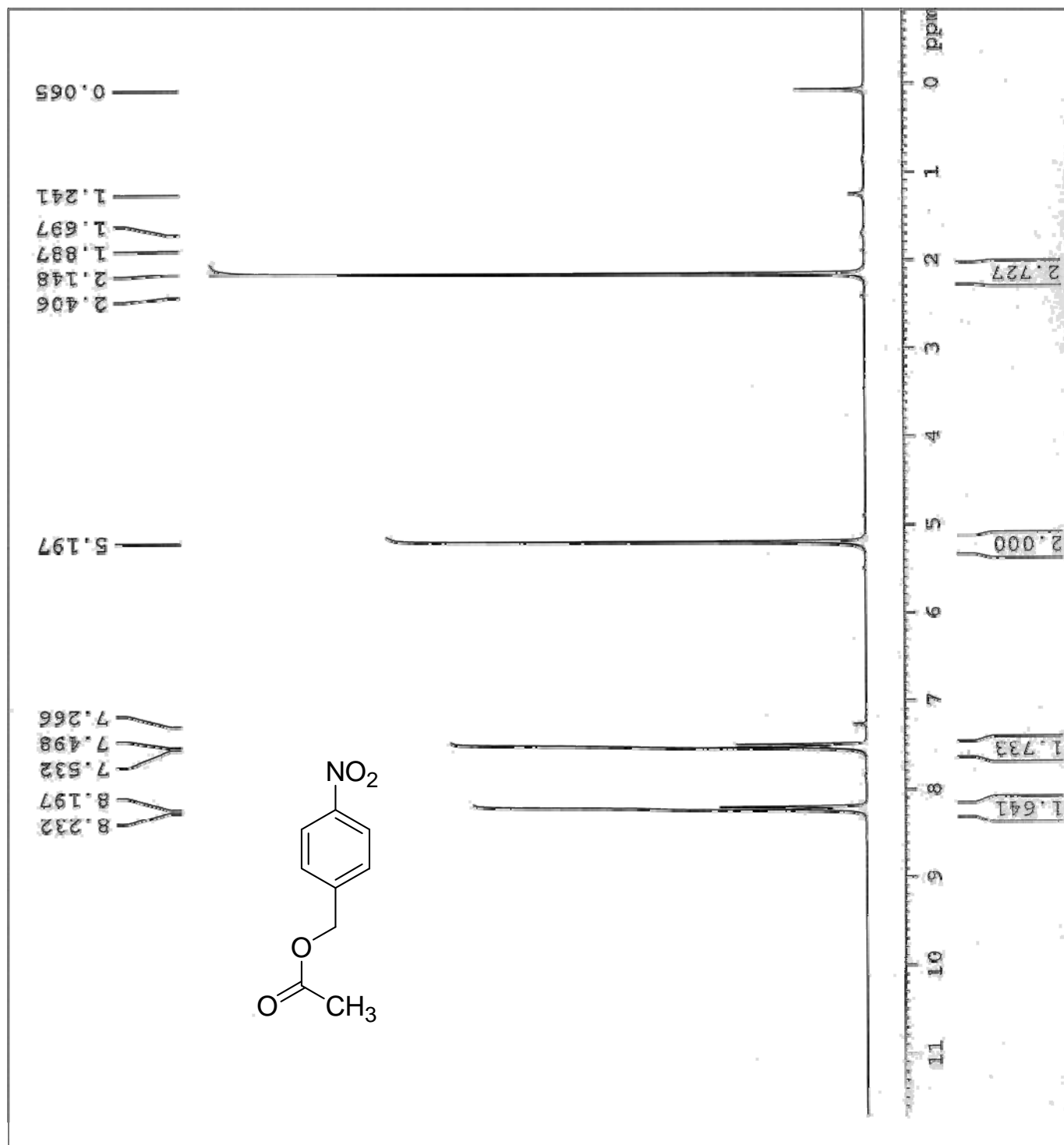


Table 2 (Entry 9)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

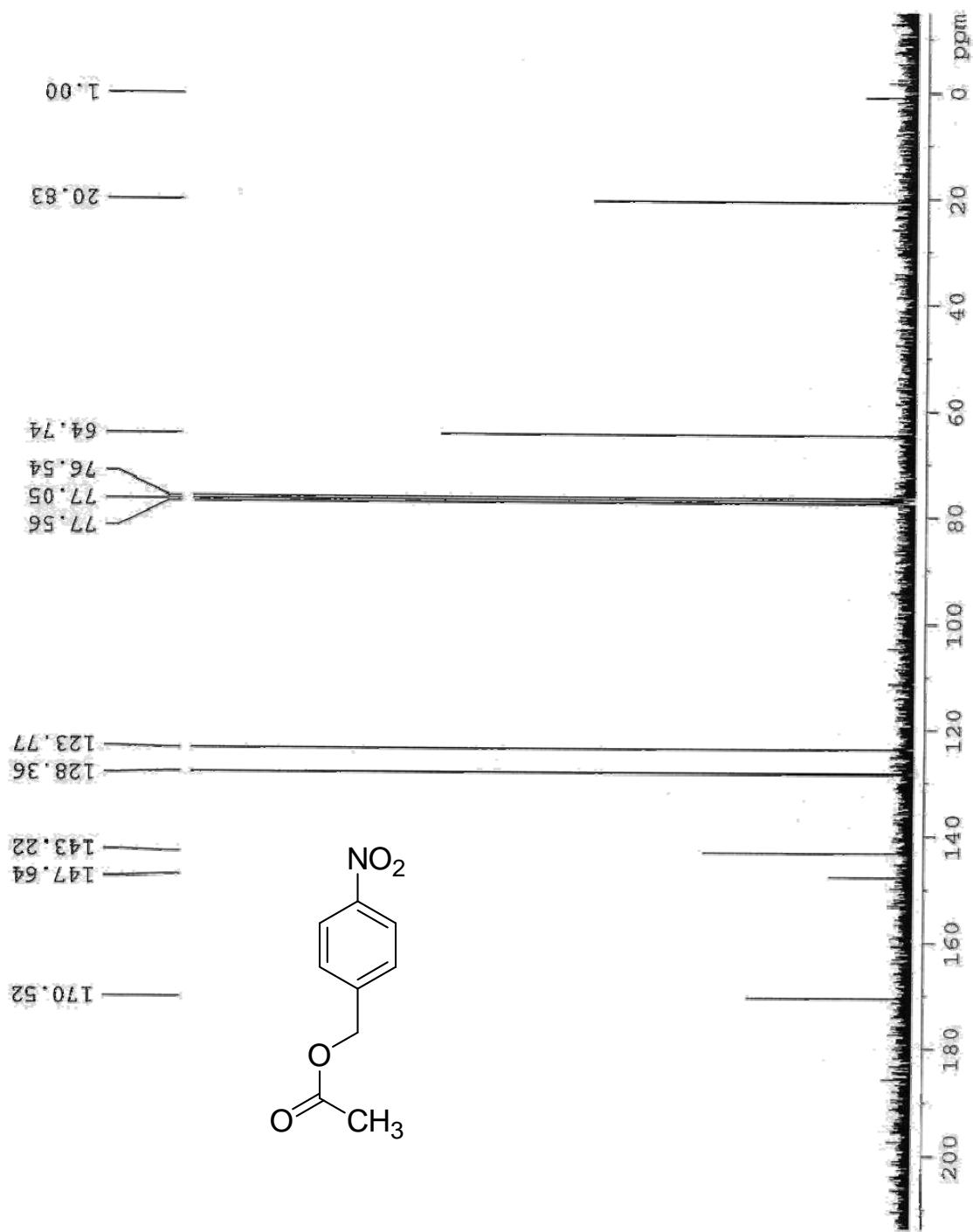


Table 2 (Entry 9)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

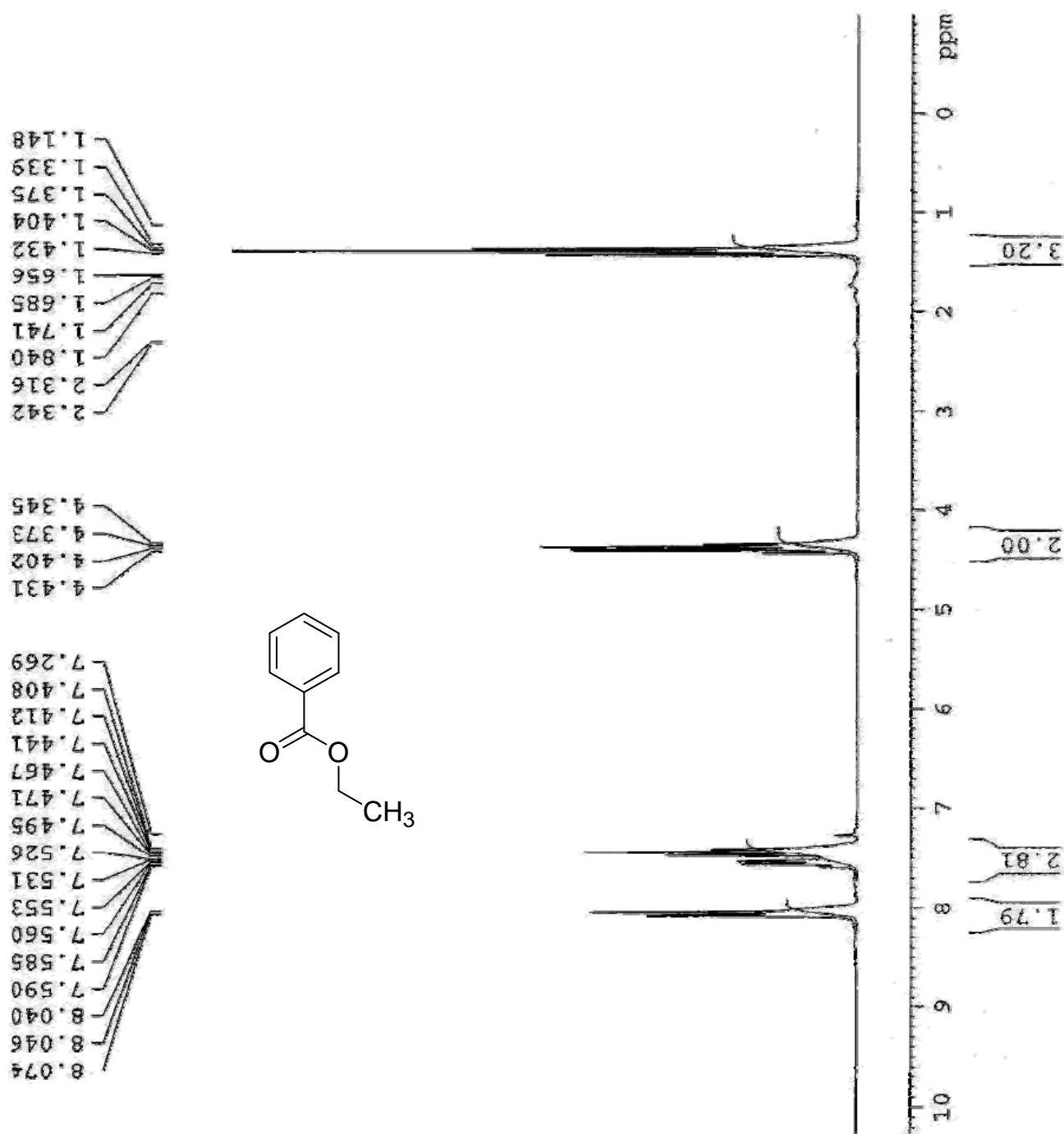
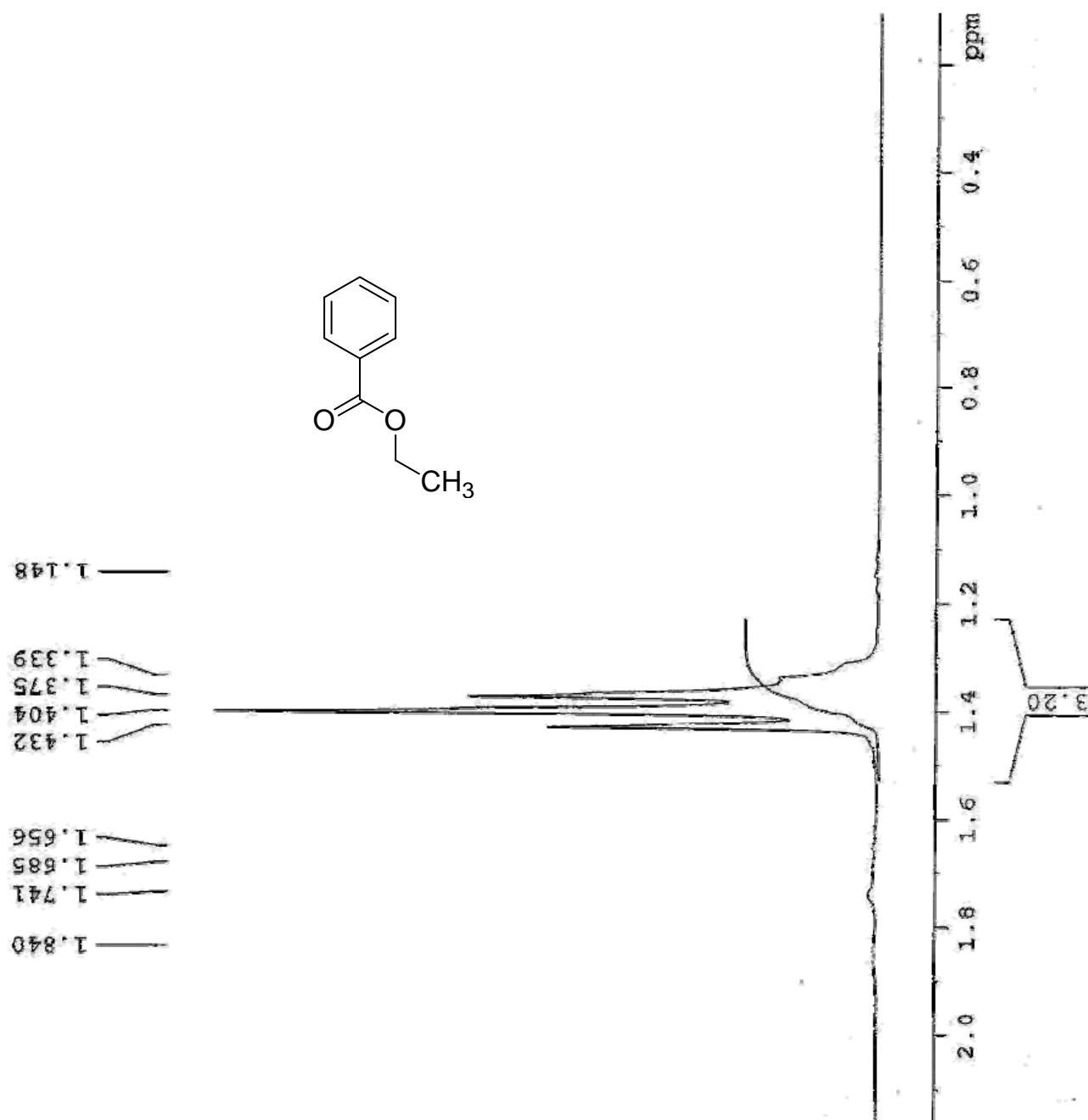


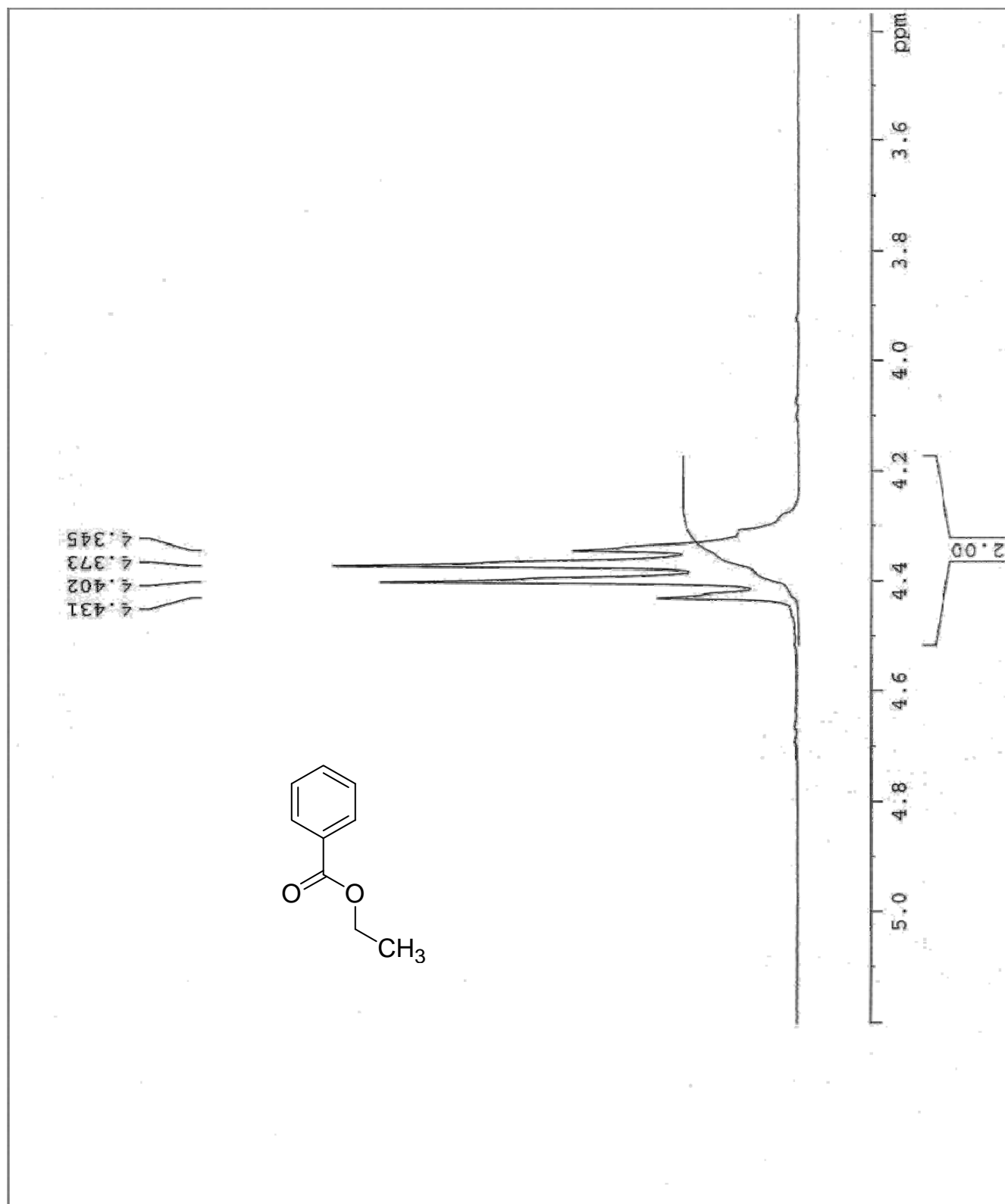
Table 3 (Entry 2)

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 3 (Entry 2)**

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 1 (Entry 2)**

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

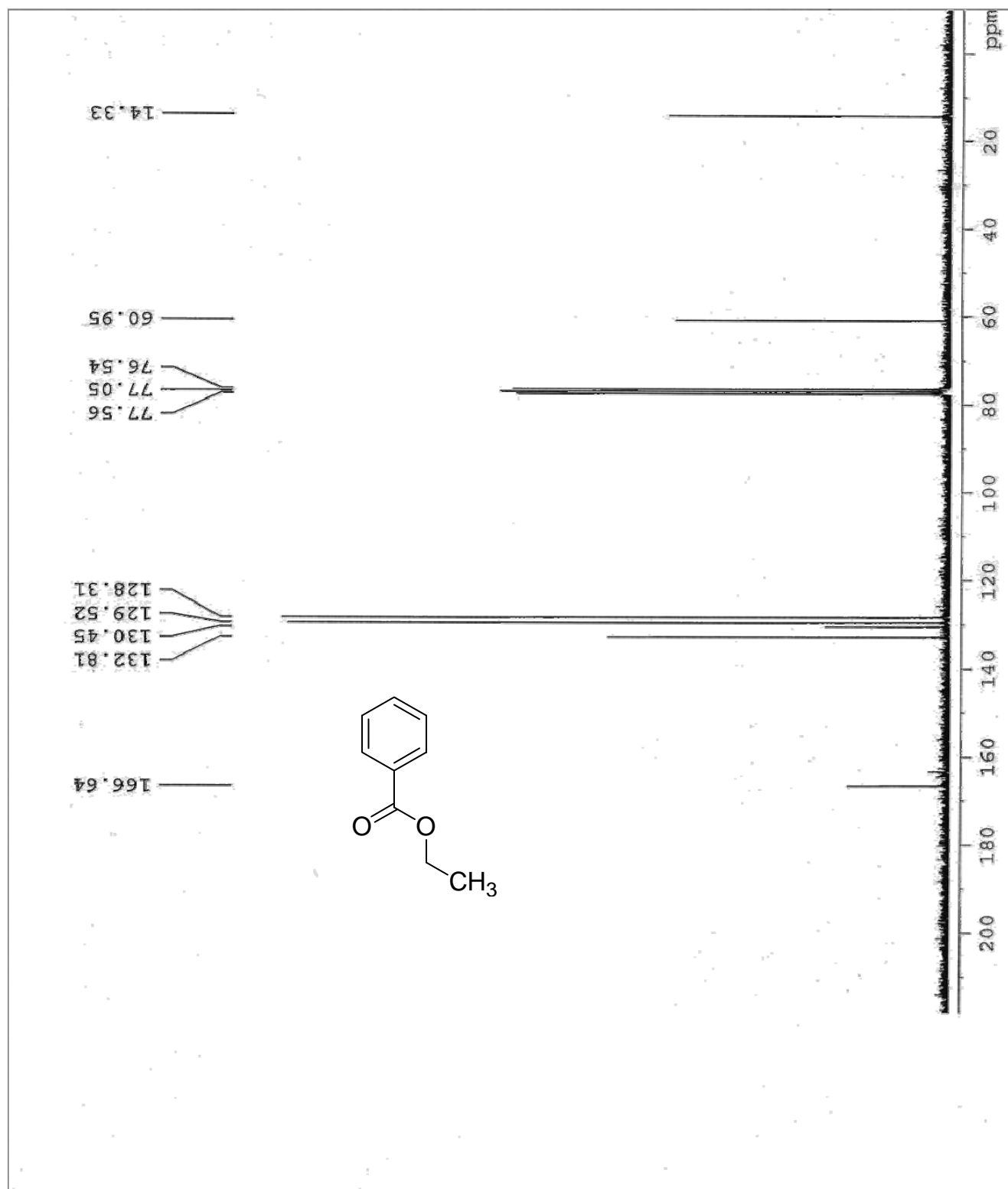


Table 3 (Entry 2)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

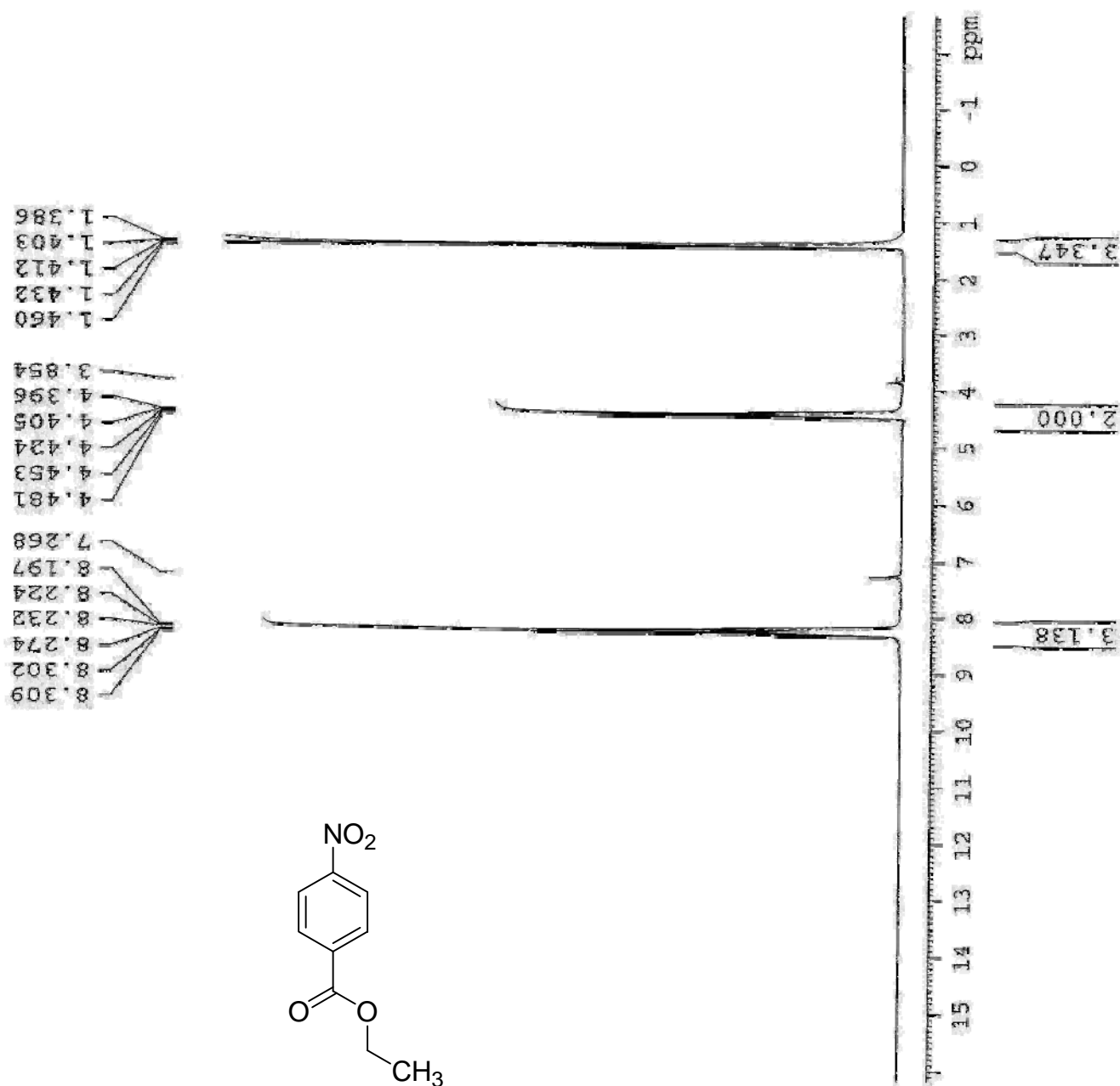
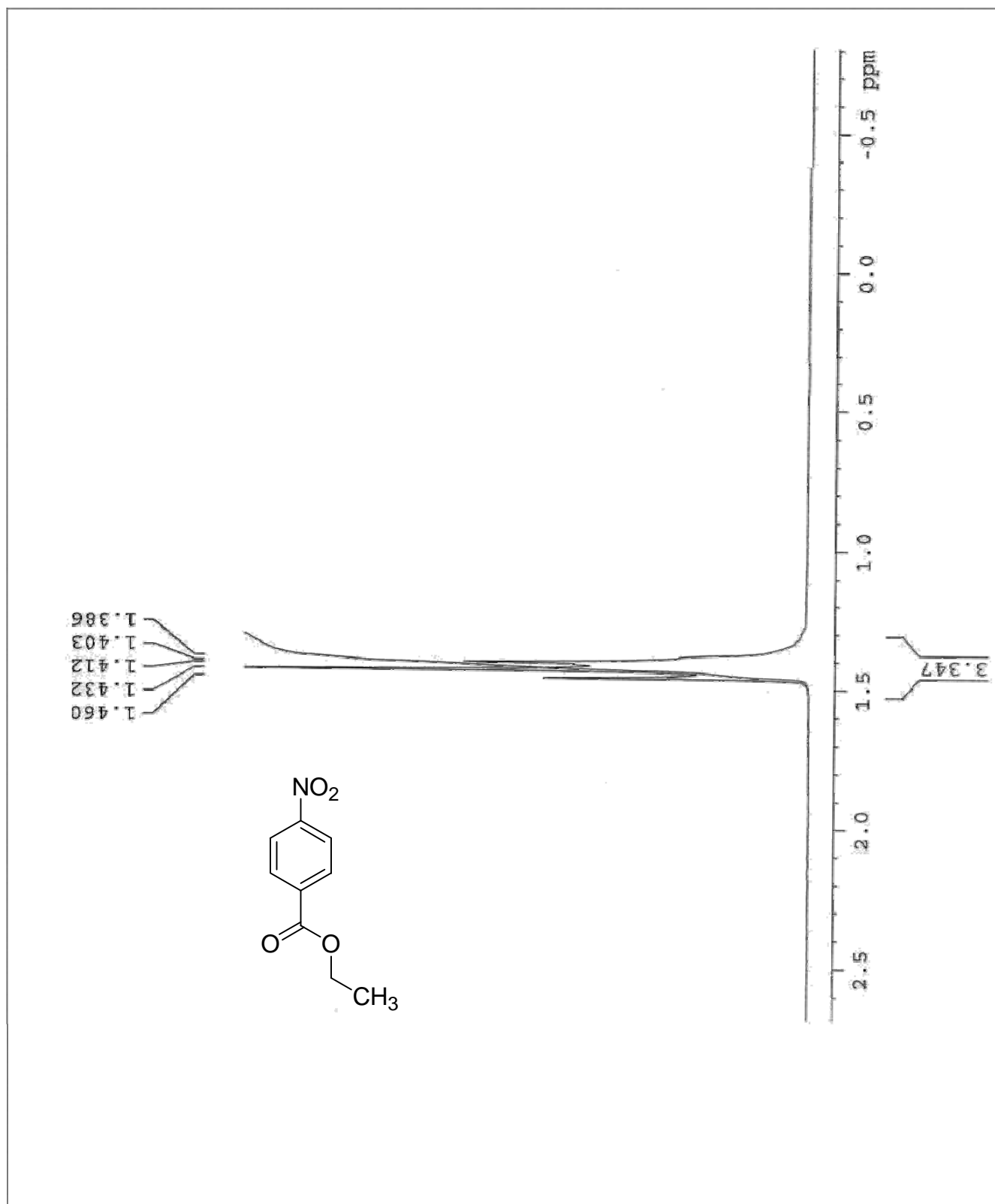


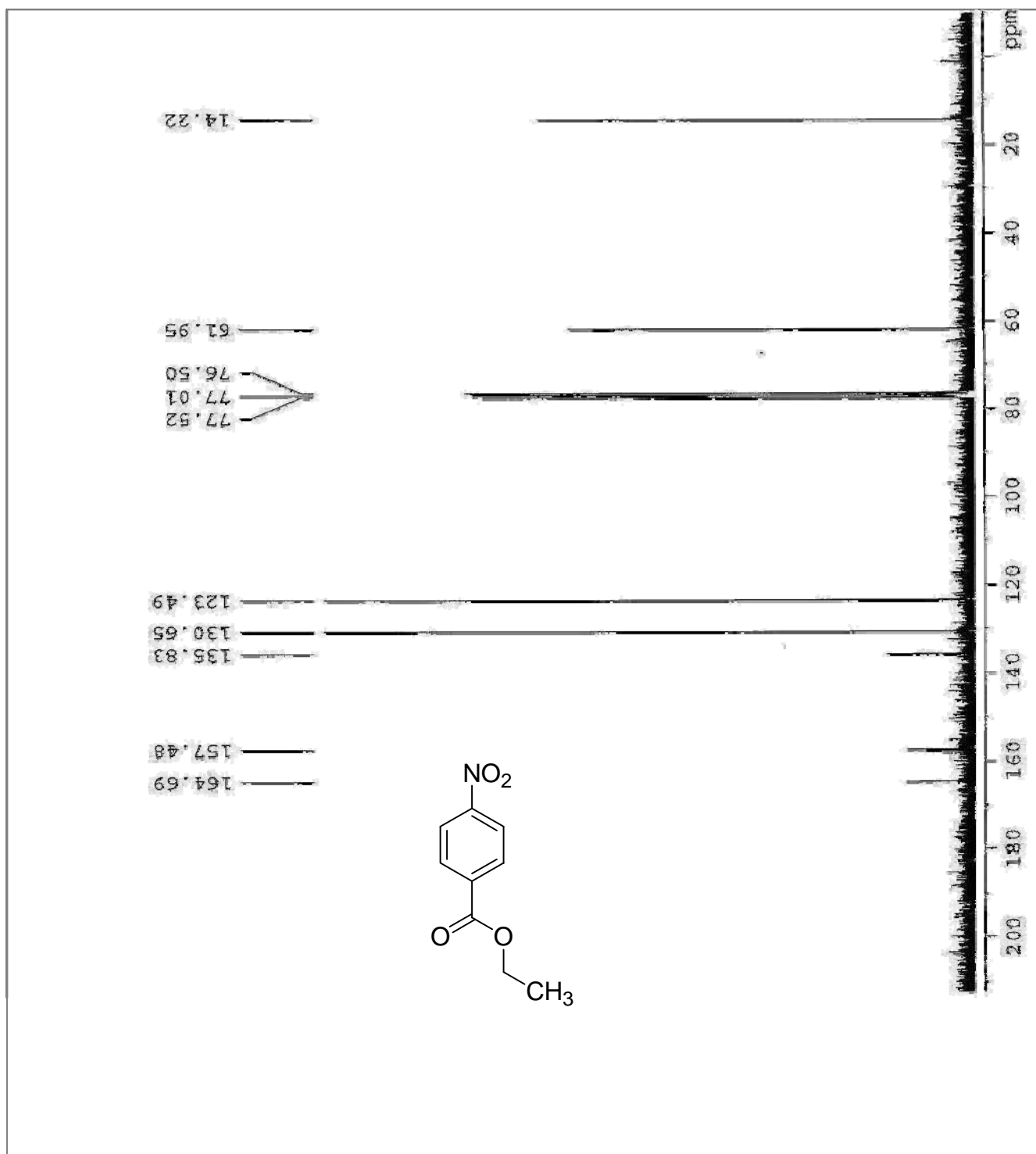
Table 3 (Entry 3)

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 3 (Entry 3)**

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 3 (Entry 3)**

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

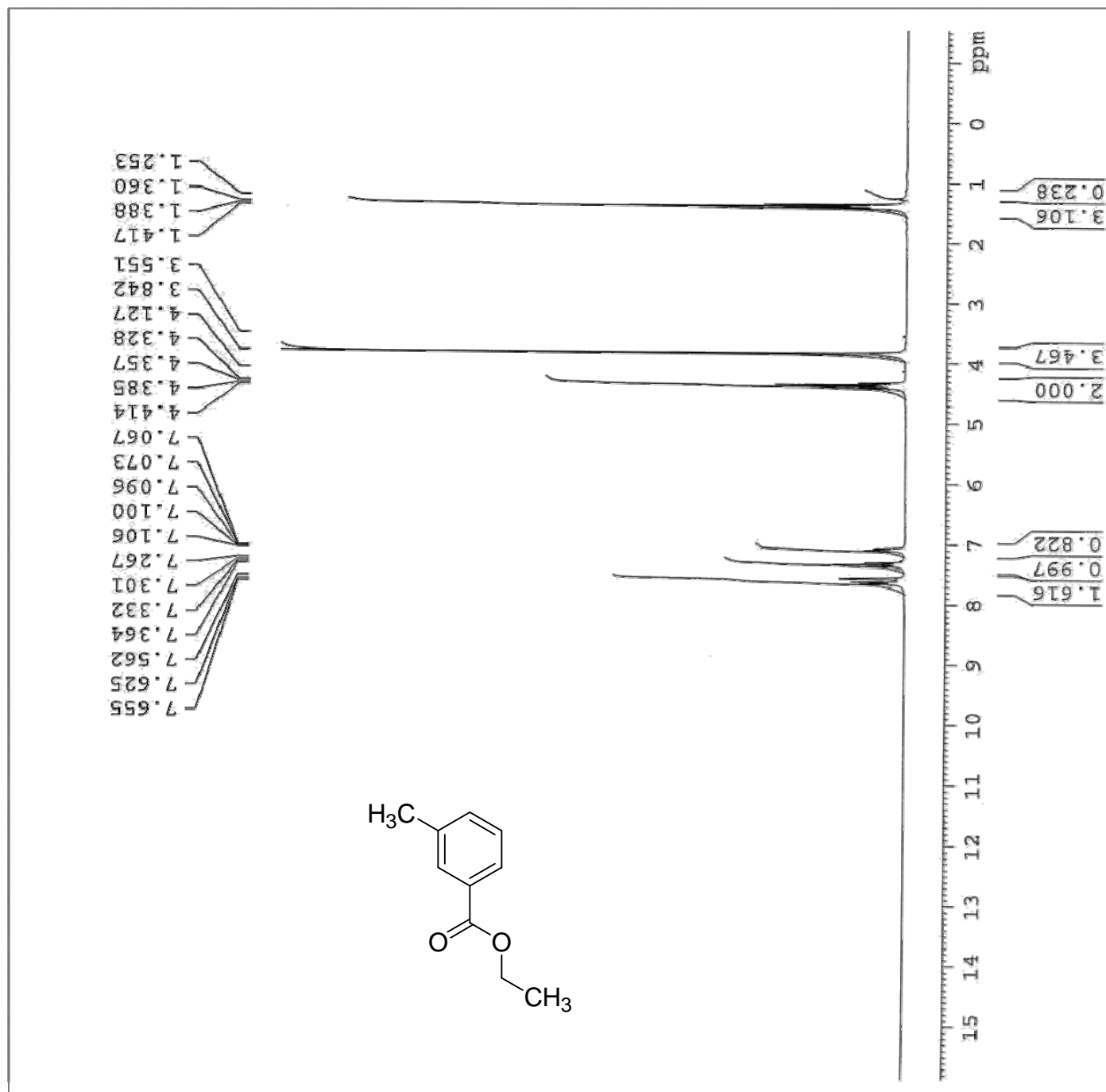
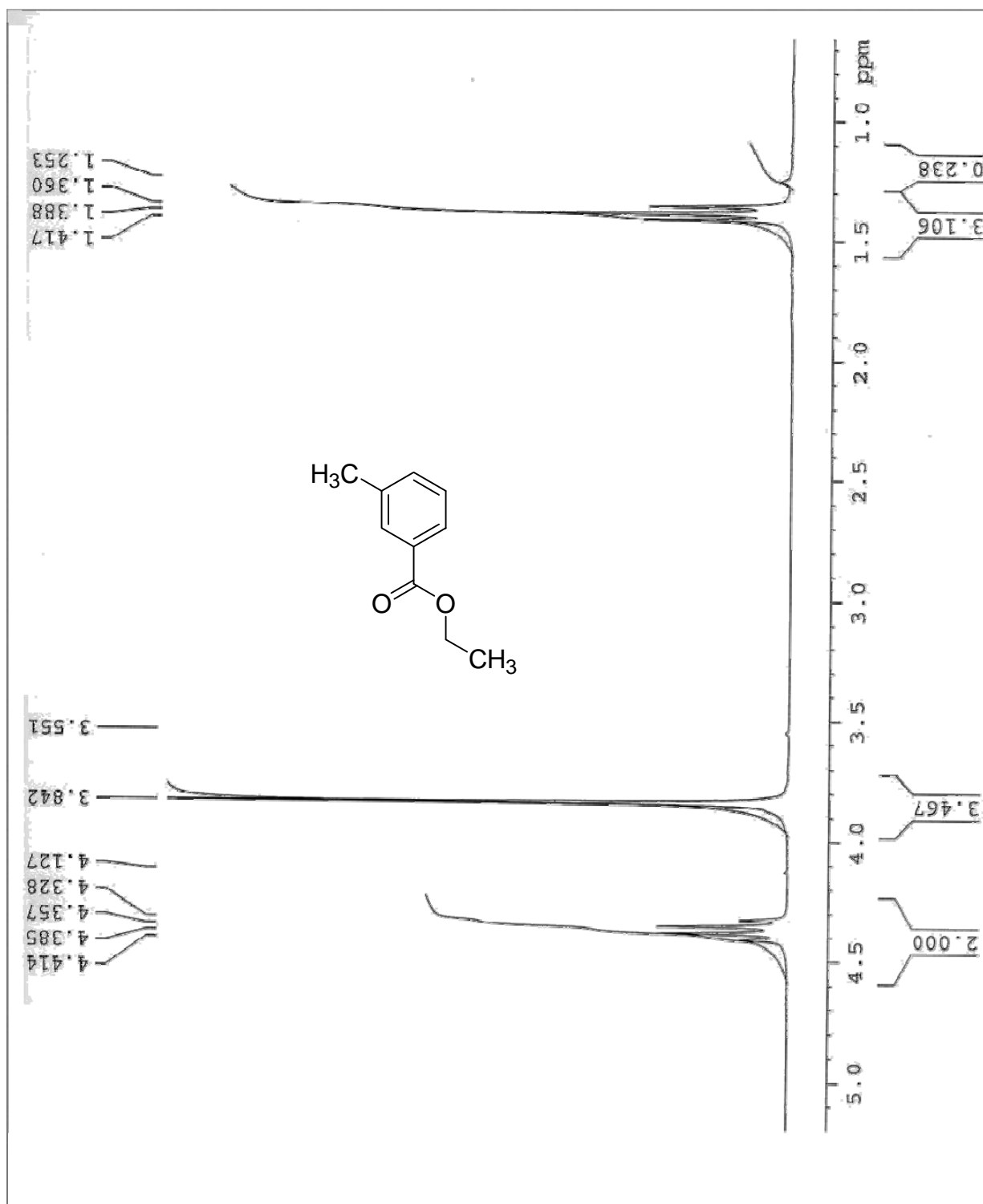


Table 3 (Entry 4)

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 3 (Entry 4)**

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

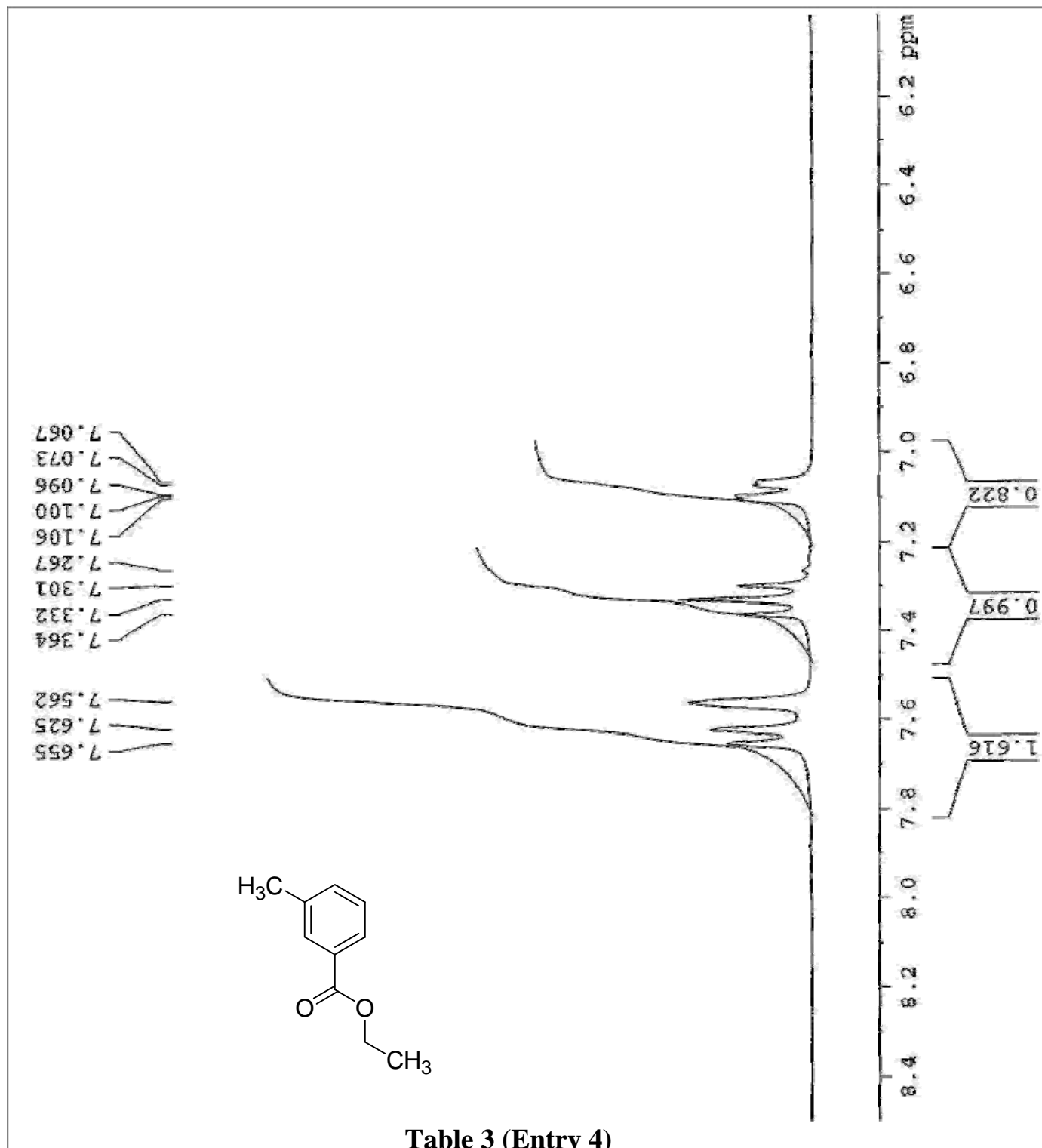


Table 3 (Entry 4)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

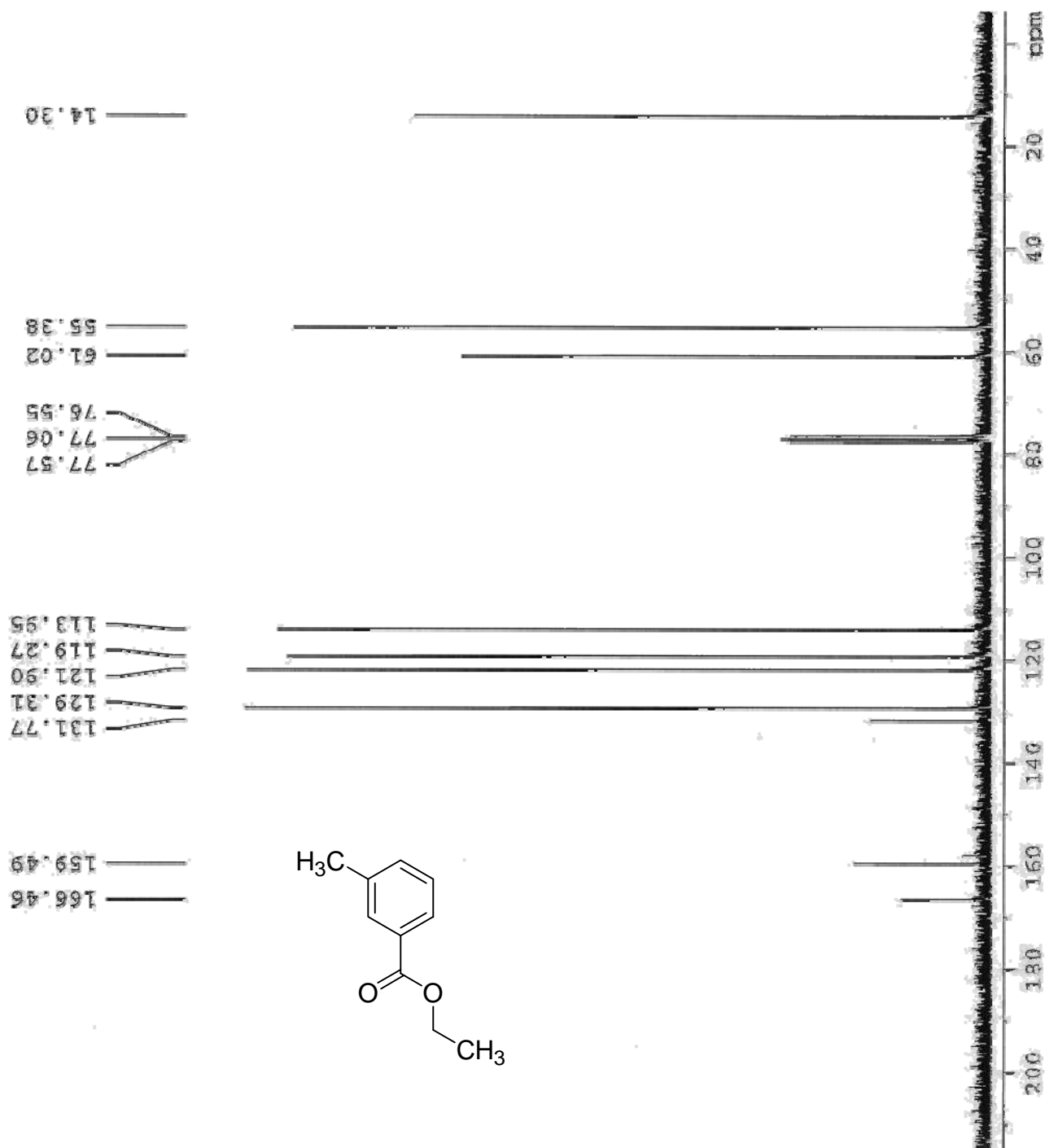


Table 3 (Entry 4)

Solvent: CDCl<sub>3</sub>— Frequency: 250 MHz

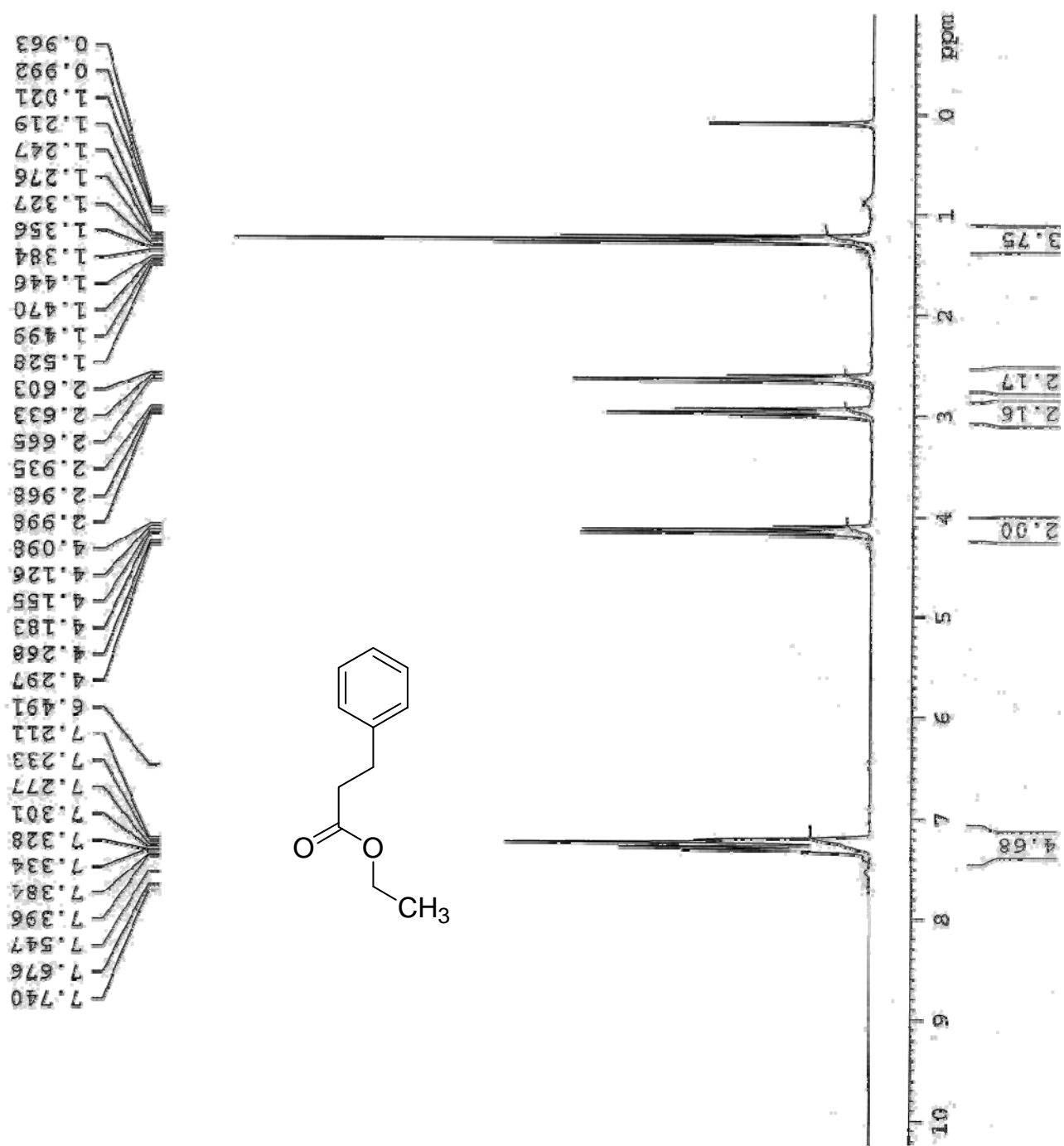
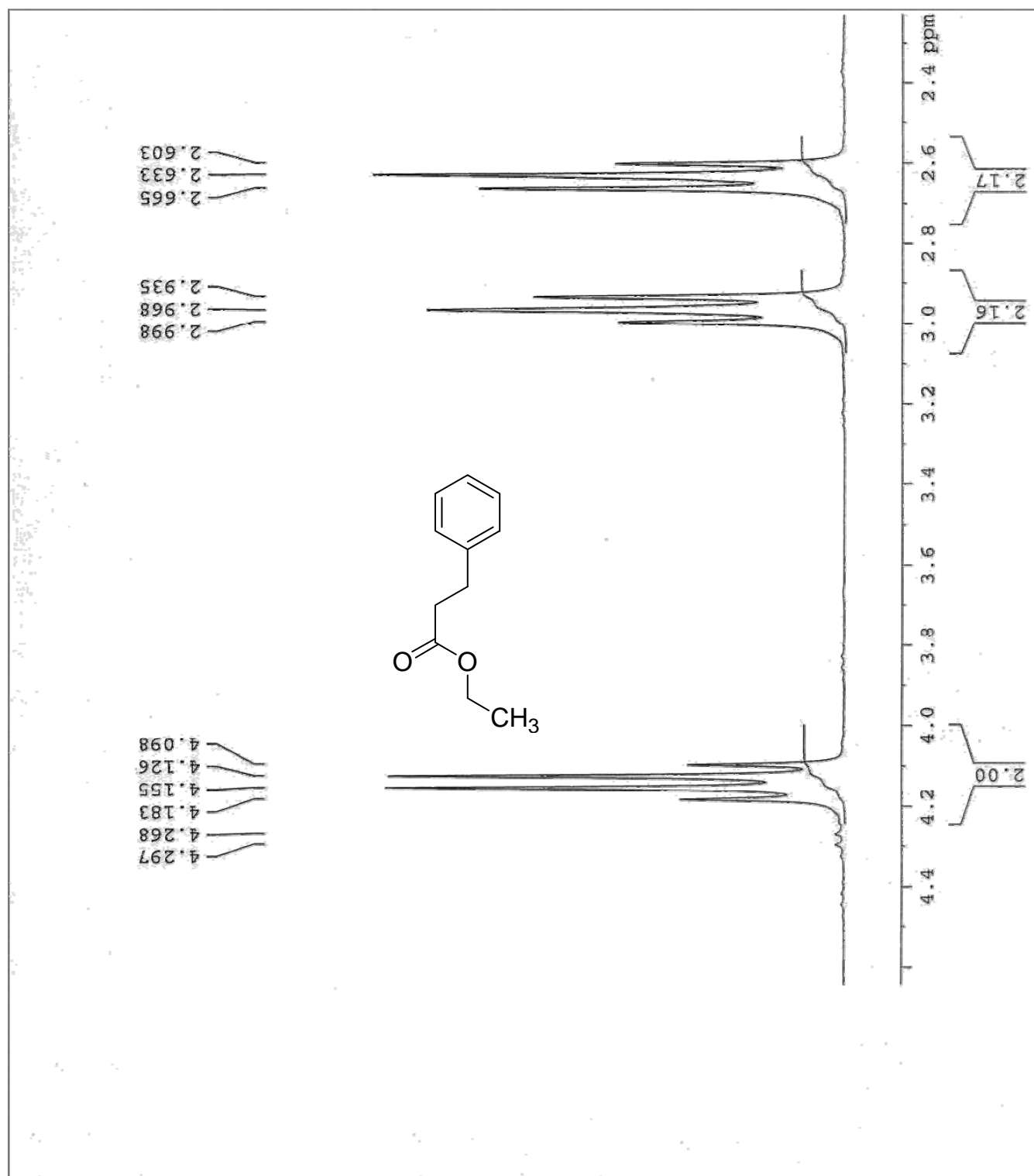


Table 3 (Entry 5)

**Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz**



**Table 3 (Entry 5)**

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

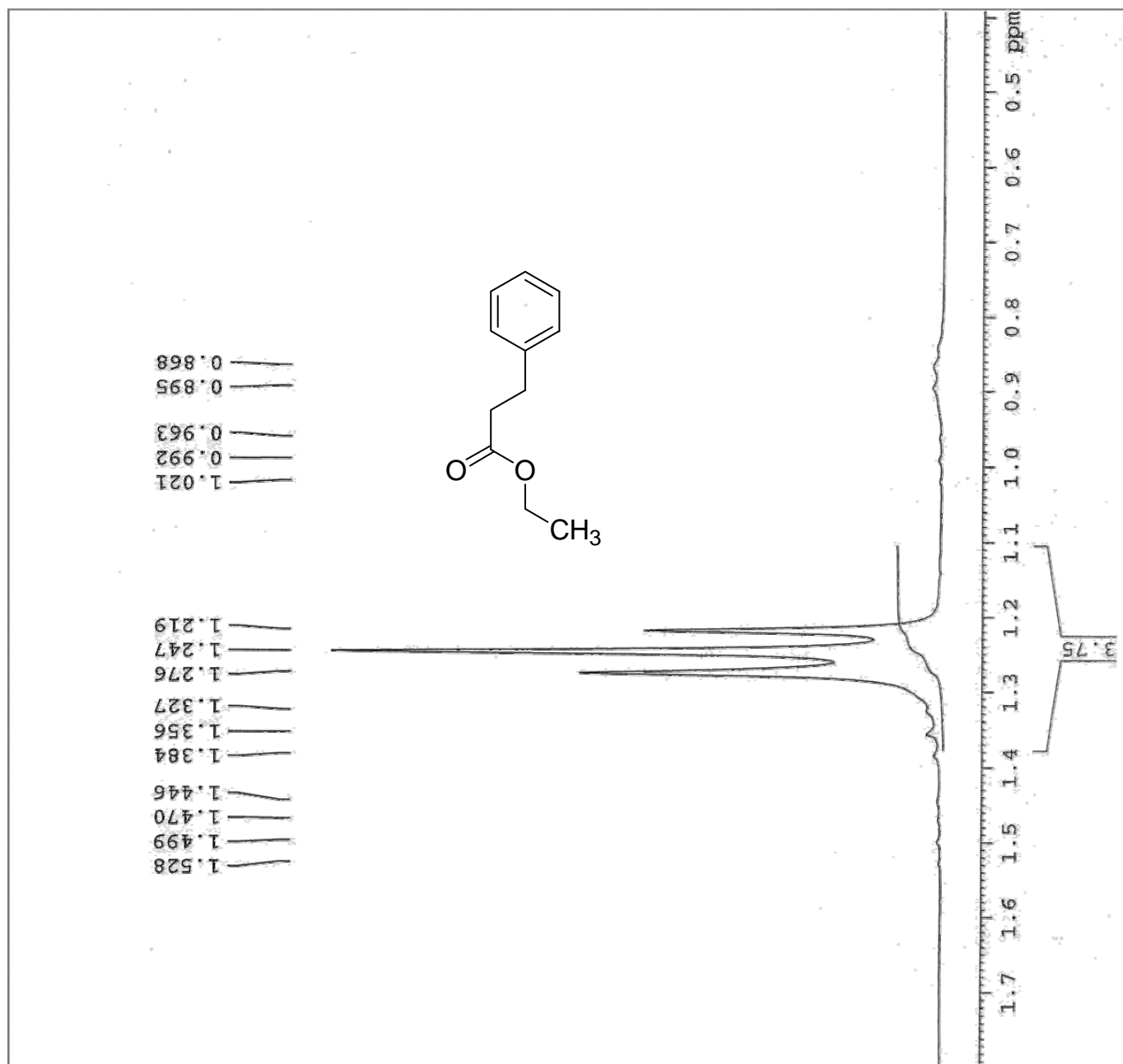


Table 3 (Entry 5)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

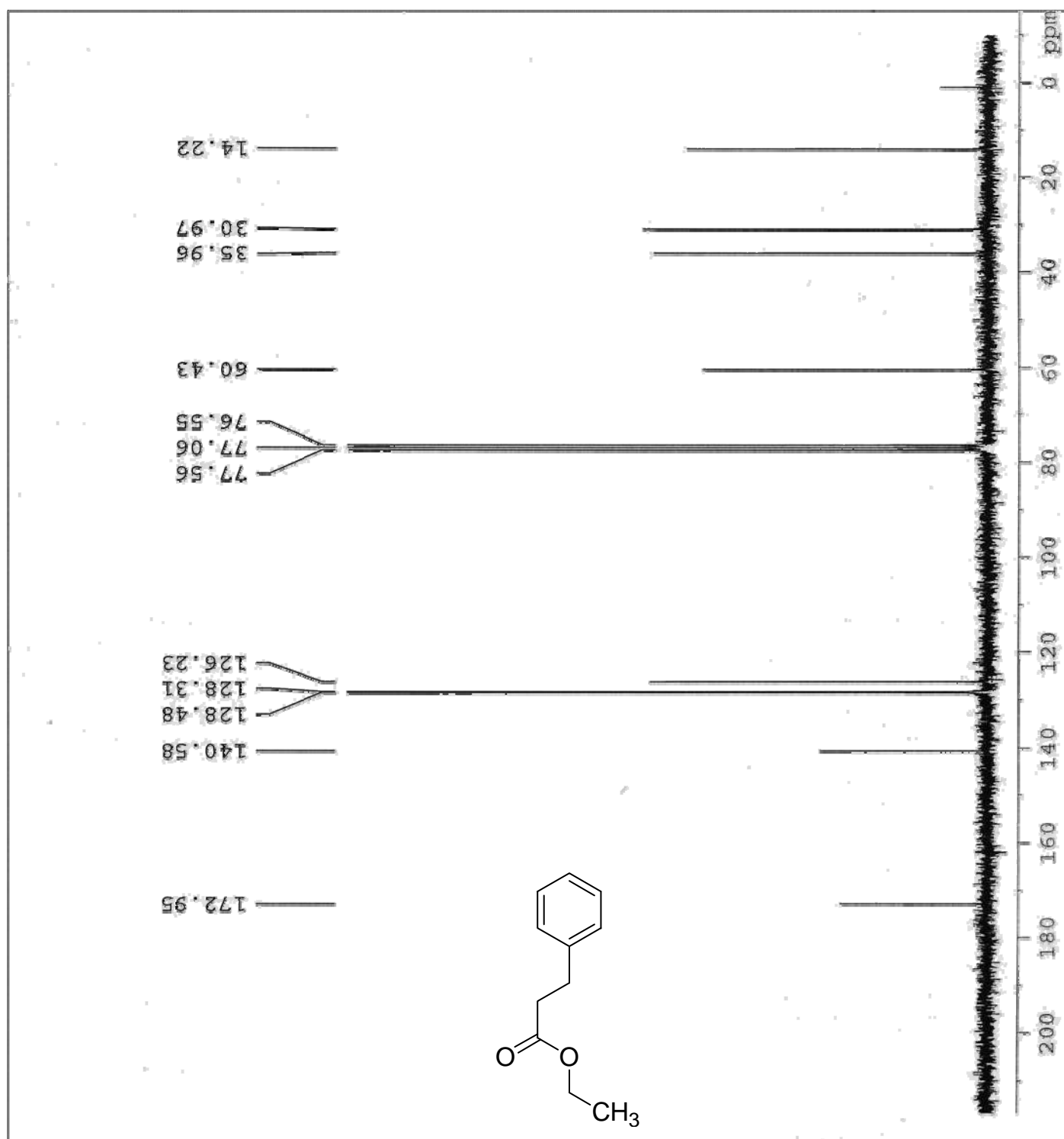


Table 3 (Entry 5)

Solvent:  $\text{CDCl}_3$ – Frequency: 250 MHz

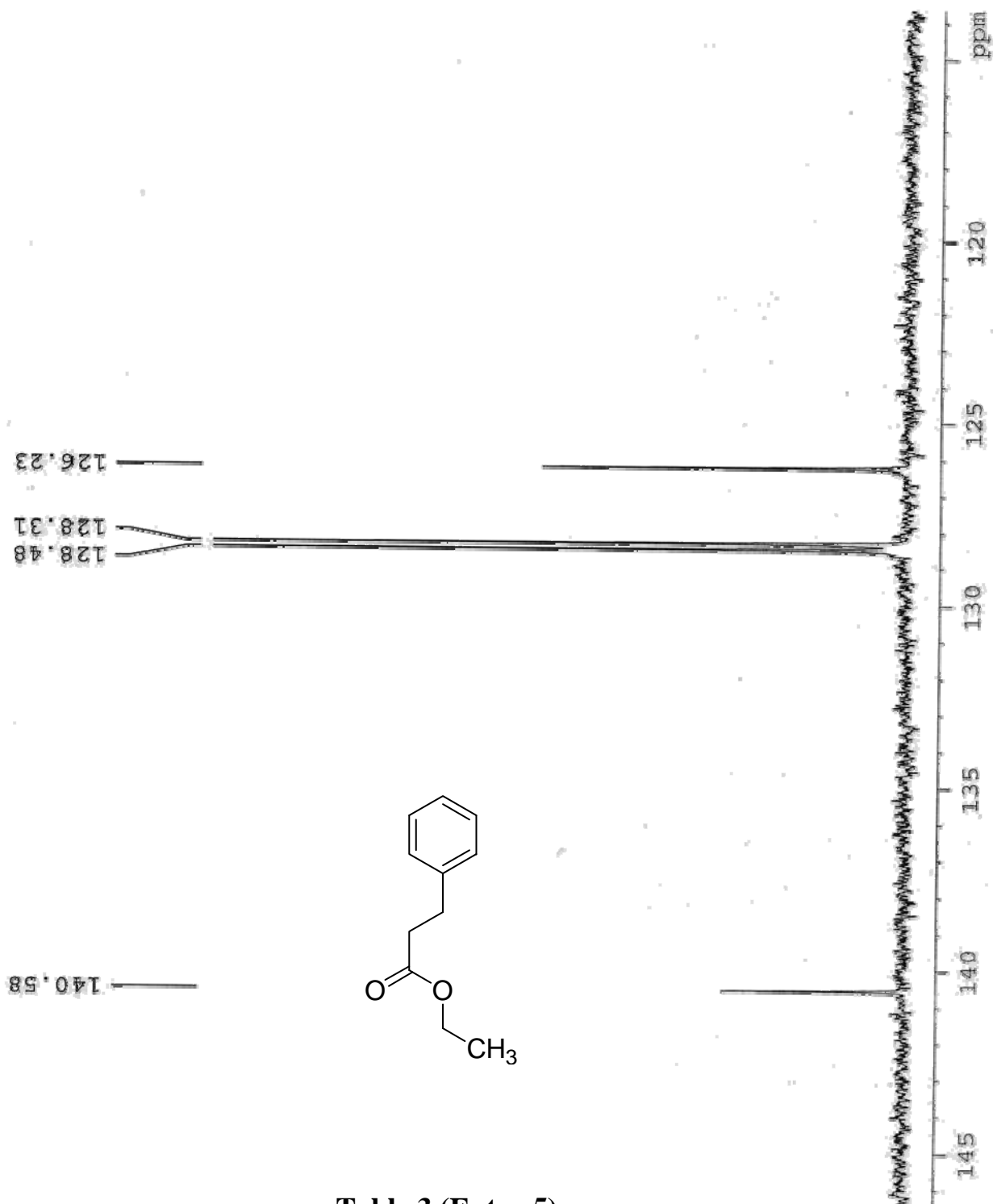


Table 3 (Entry 5)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

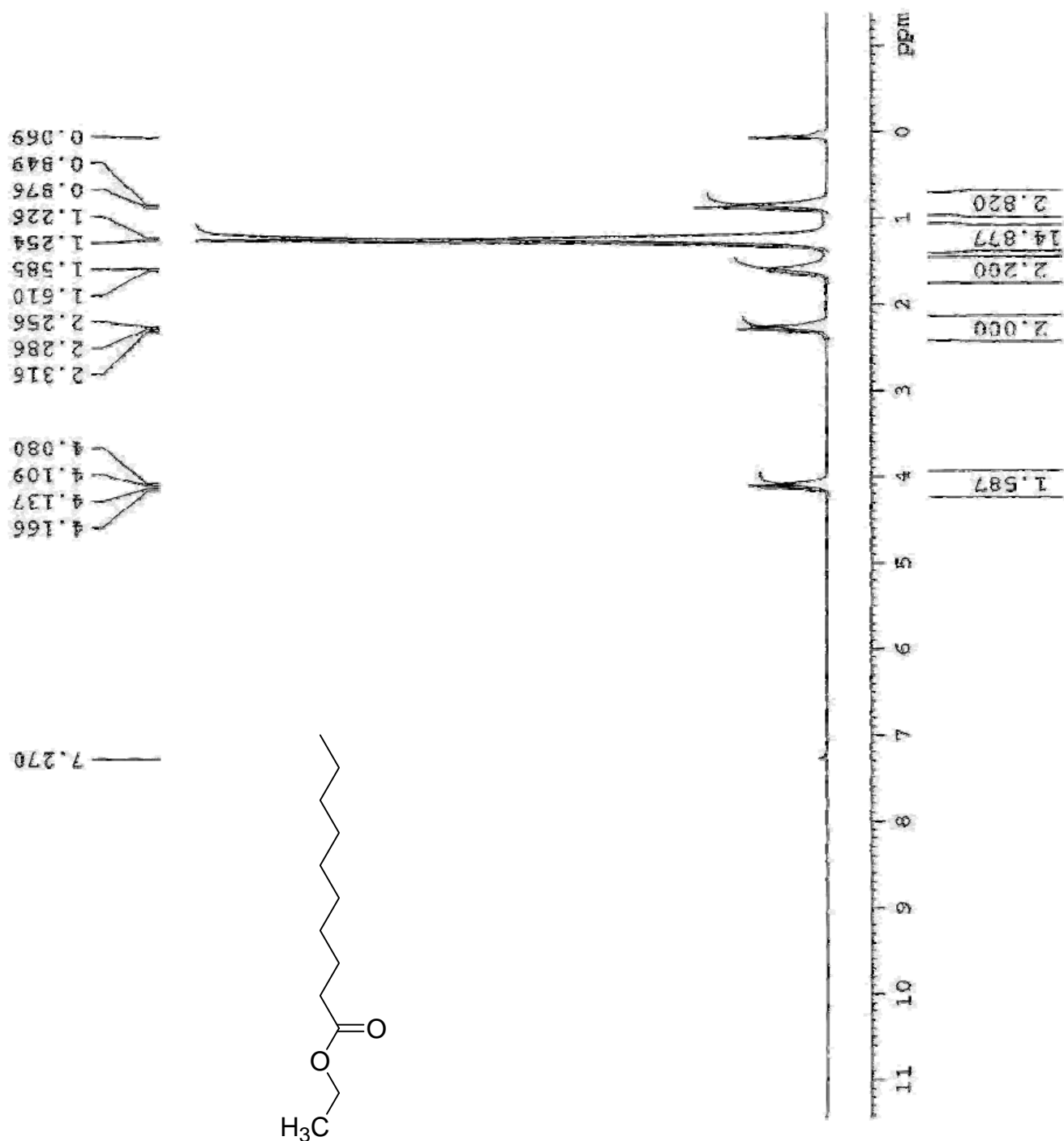


Table 3 (Entry 6)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

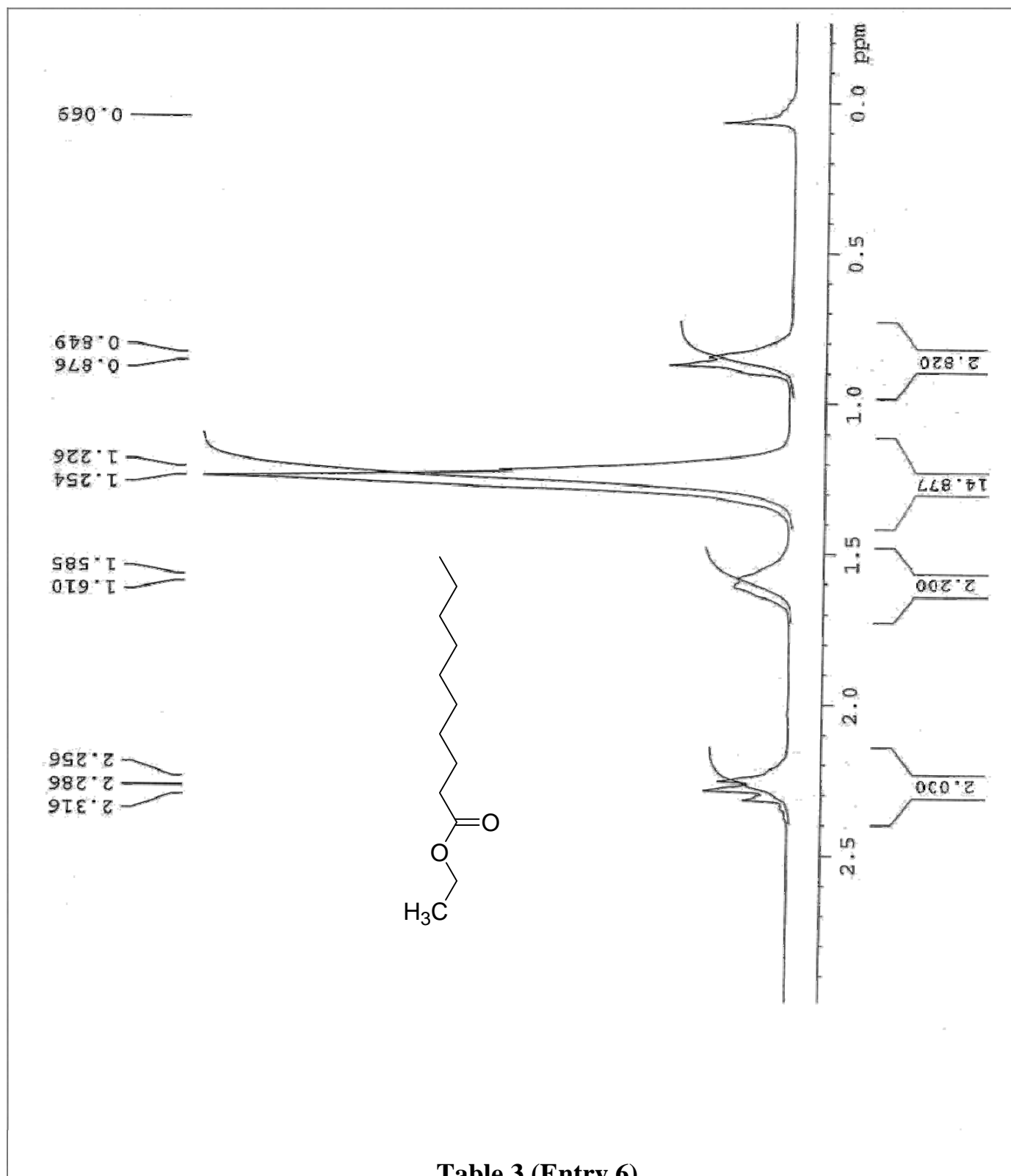


Table 3 (Entry 6)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

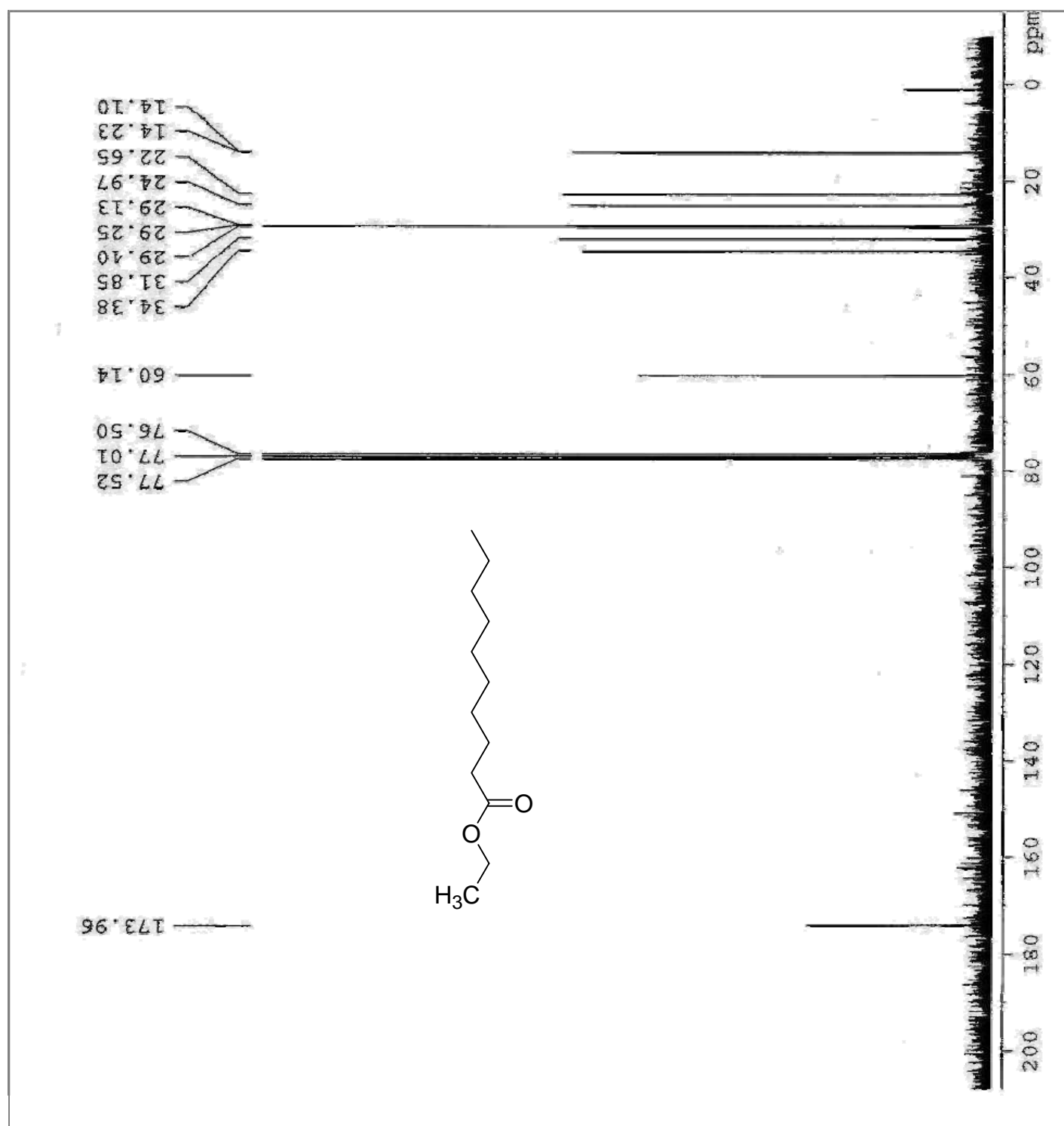


Table 3 (Entry 6)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

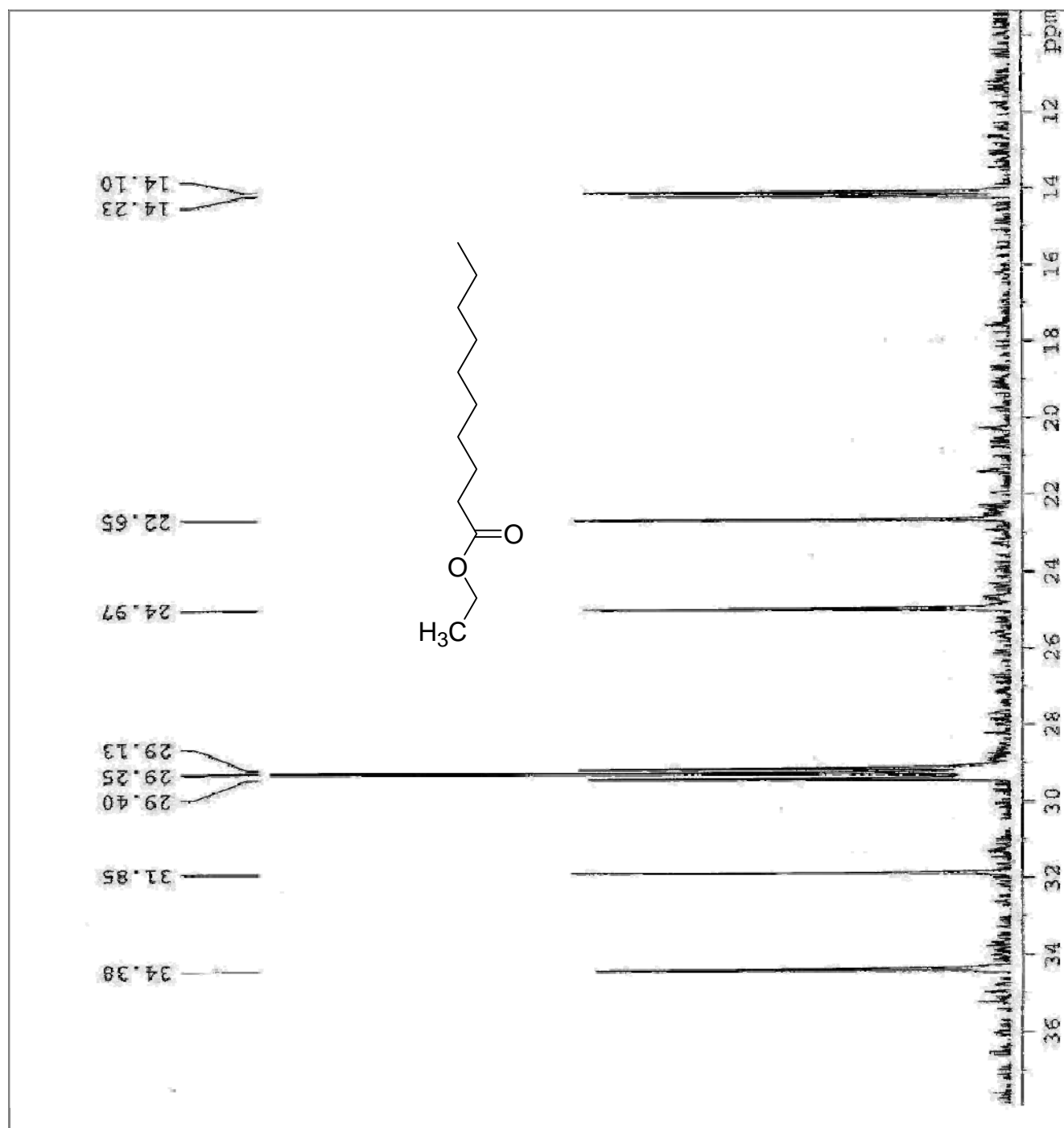


Table 3 (Entry 6)

Solvent: CDCl<sub>3</sub>— Frequency: 250 MHz

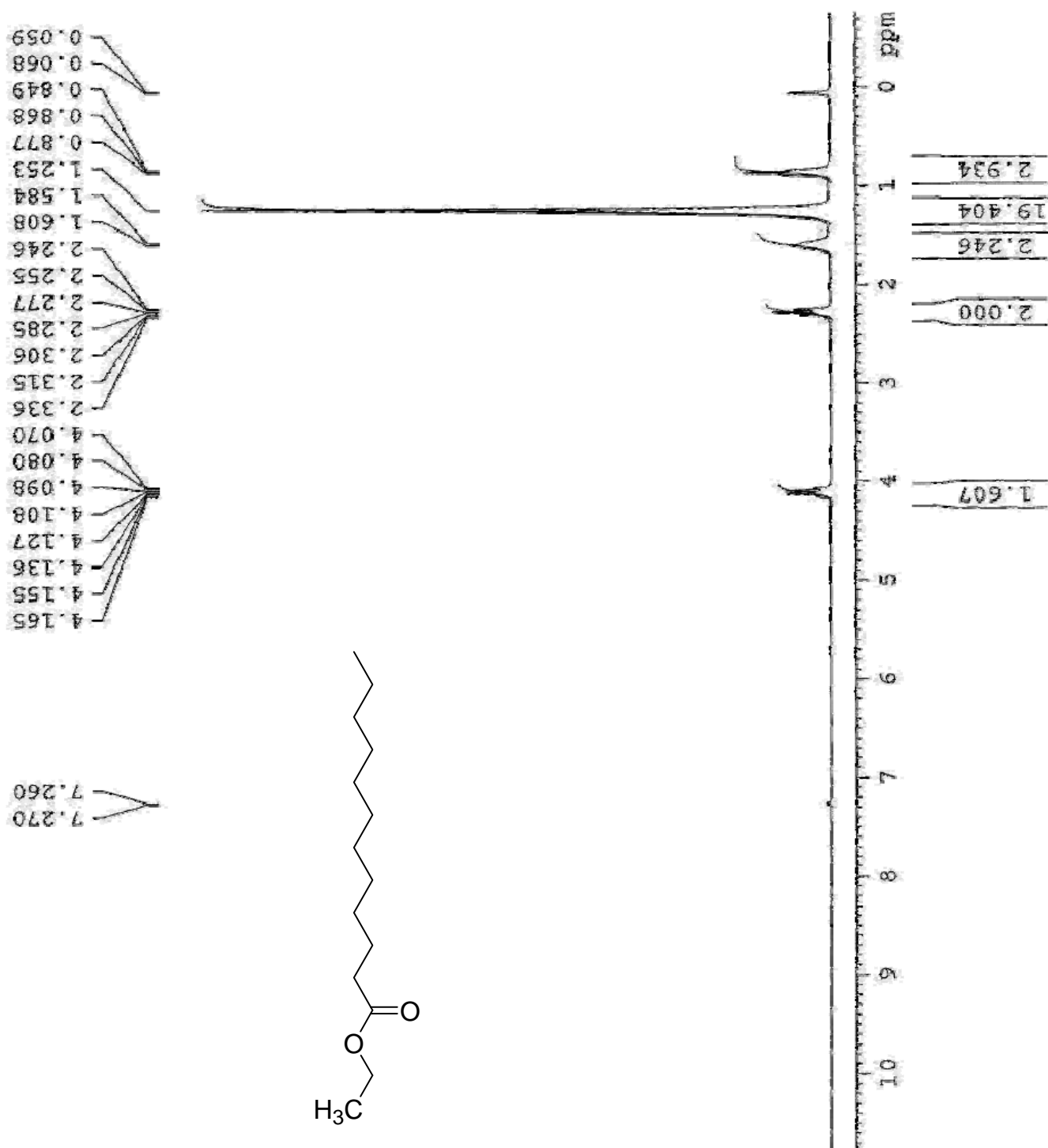


Table 3 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

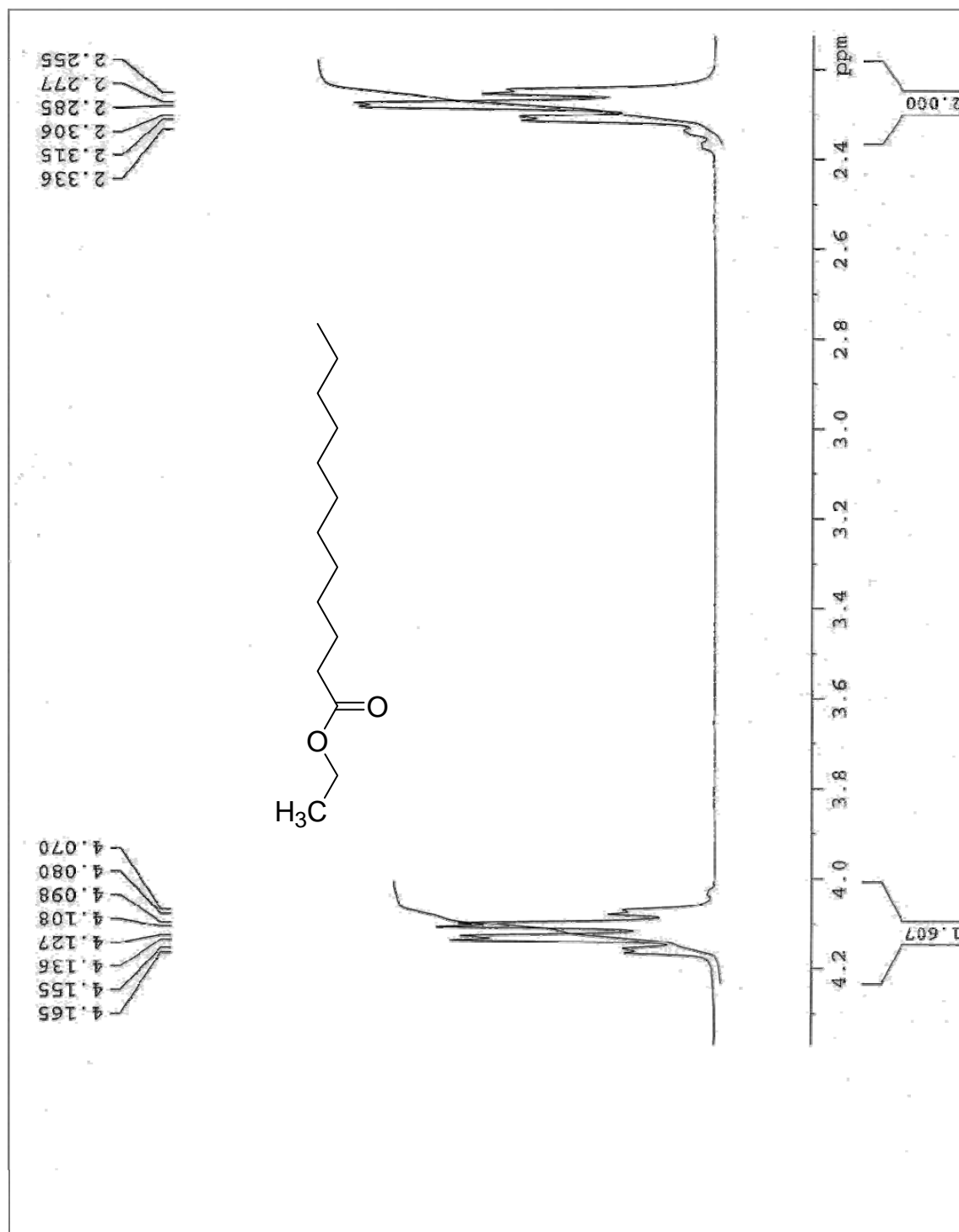


Table 3 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

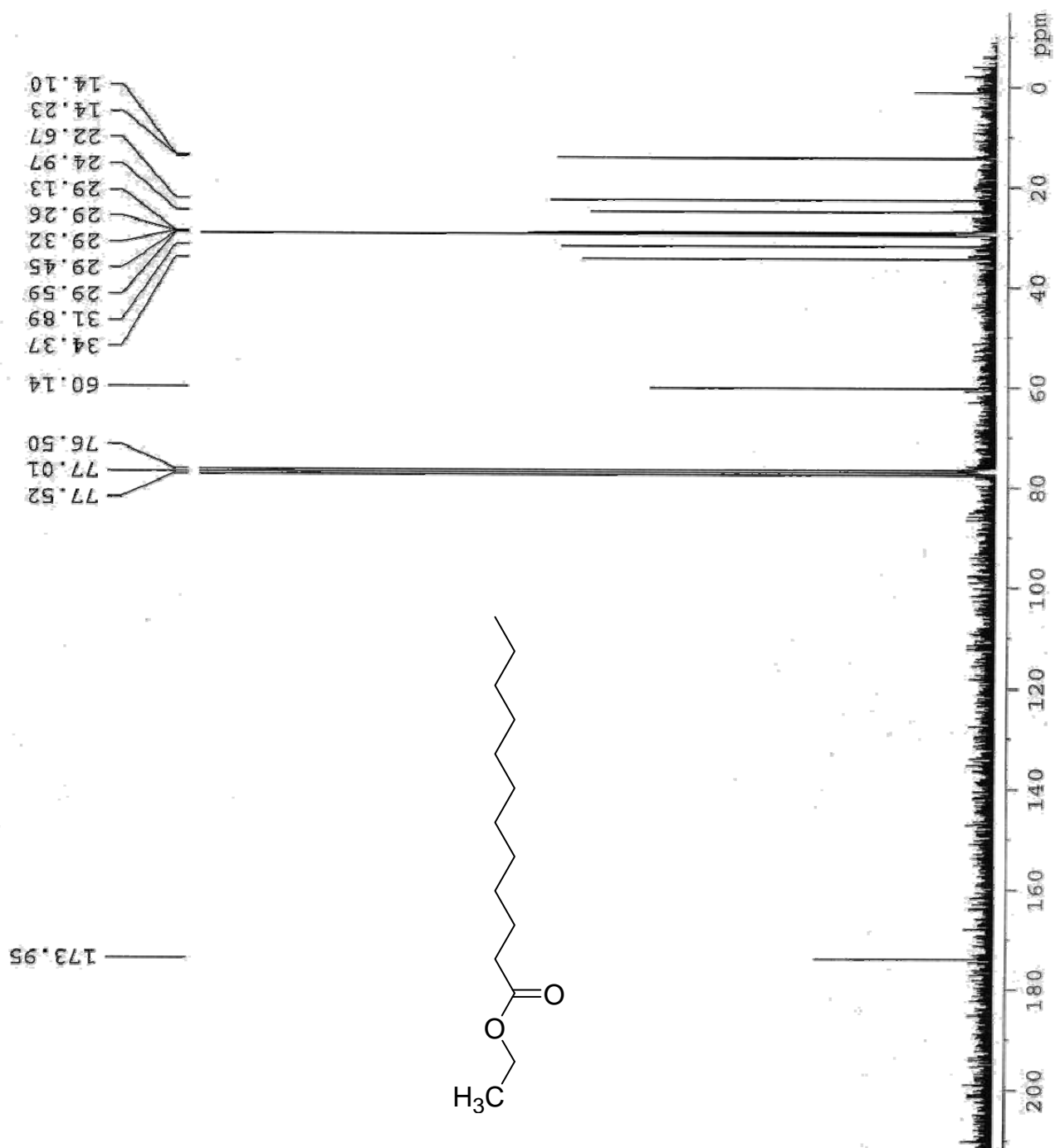


Table 3 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

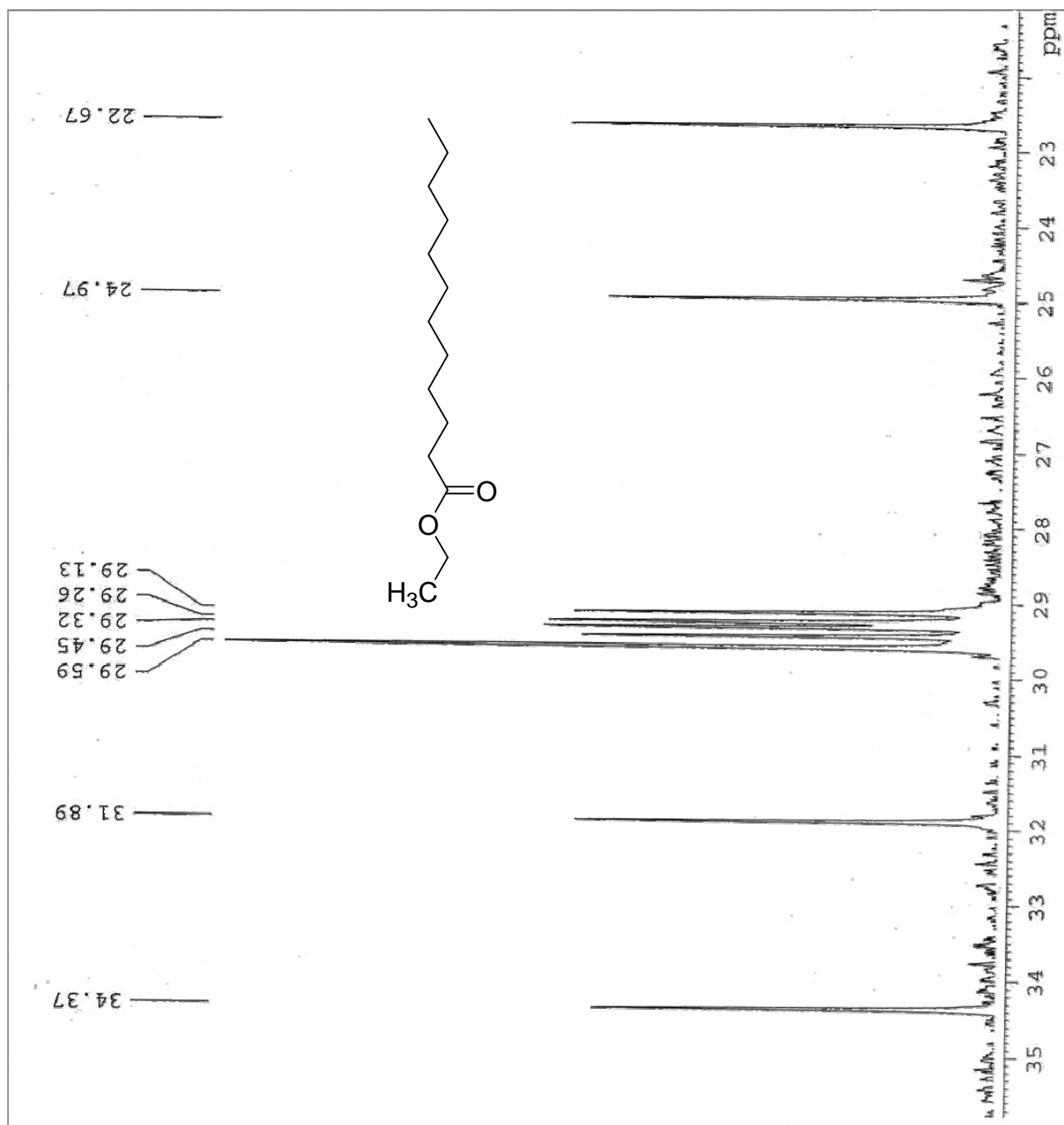


Table 3 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

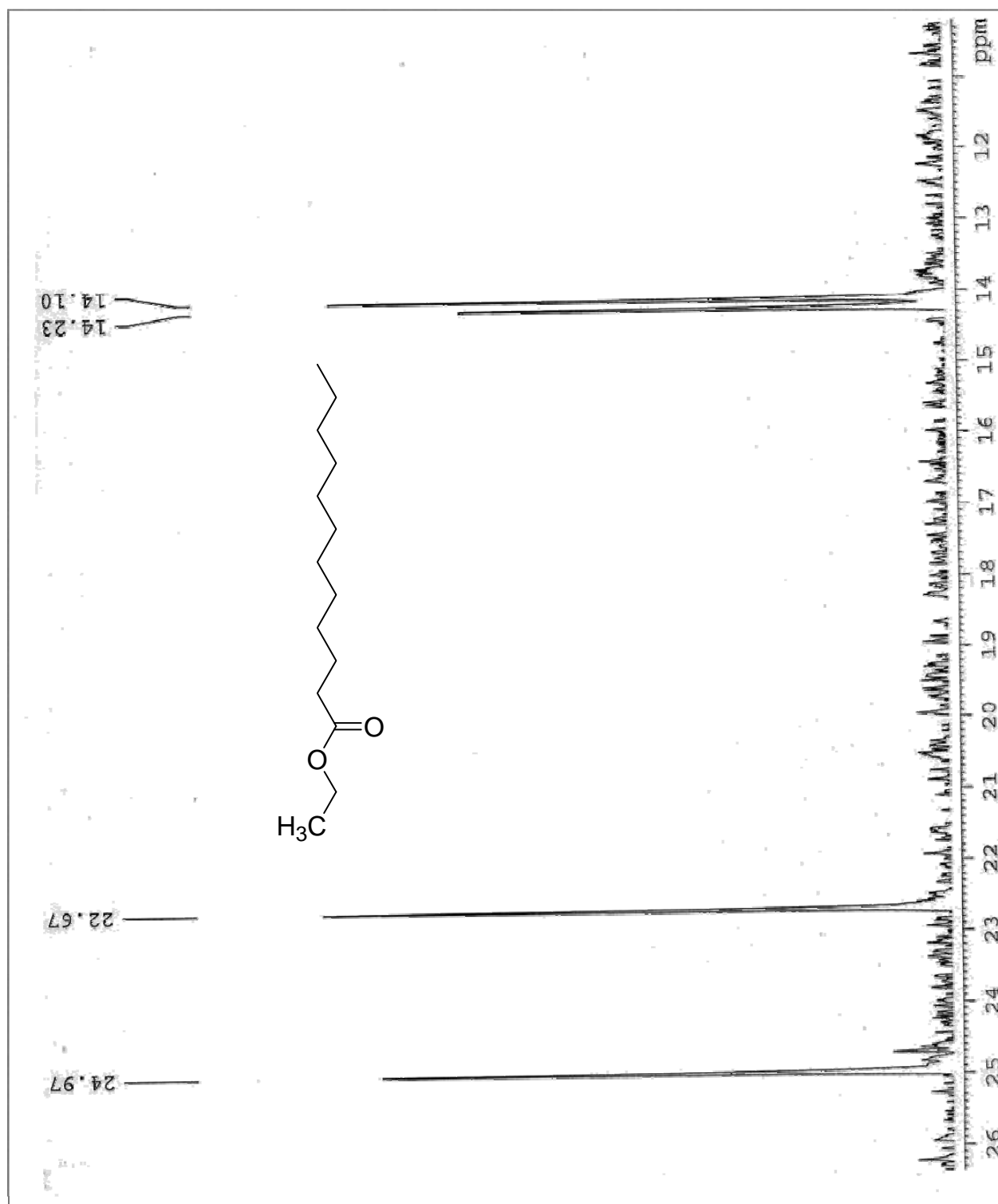


Table 3 (Entry 7)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

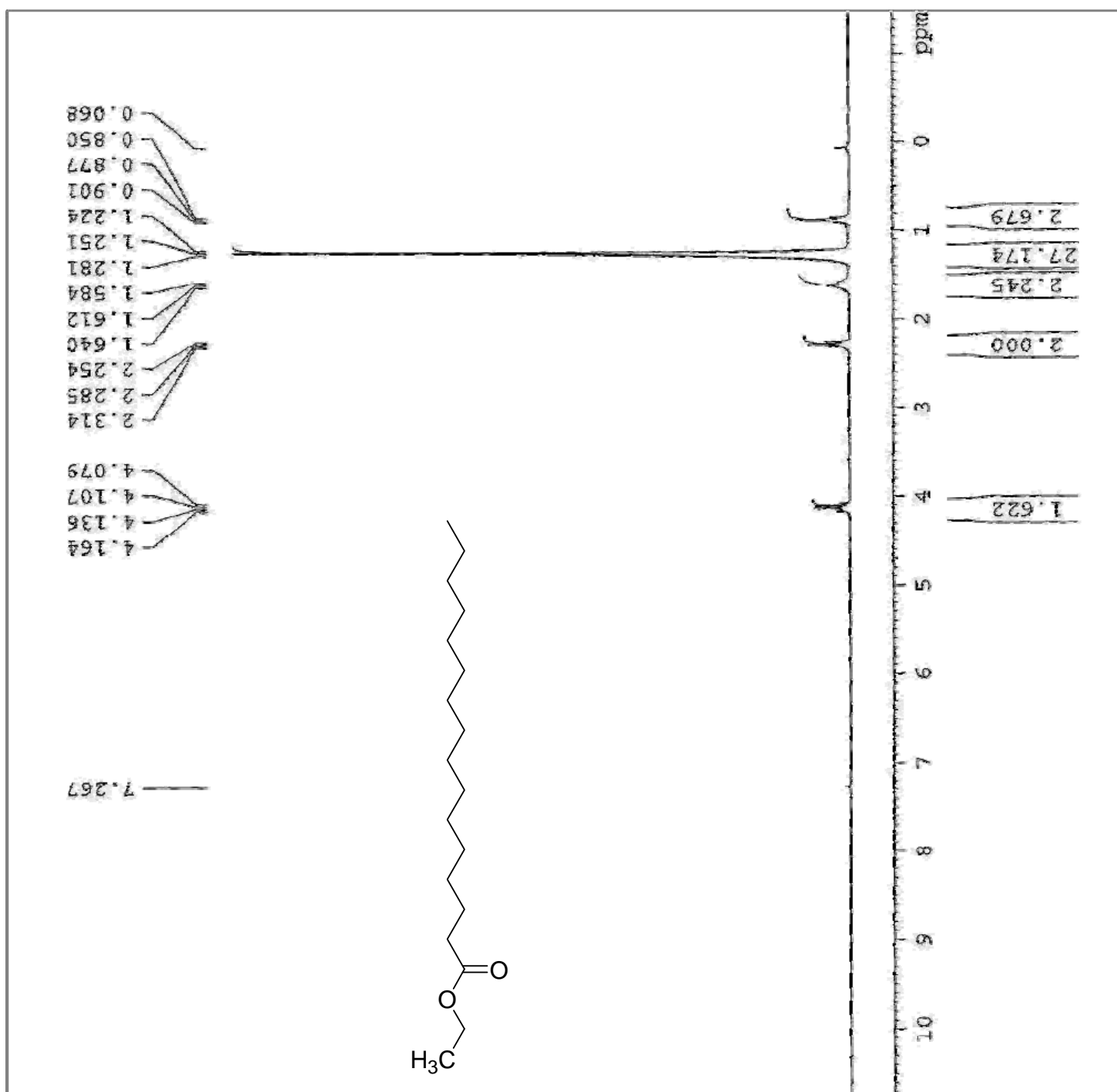


Table 3 (Entry 8)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

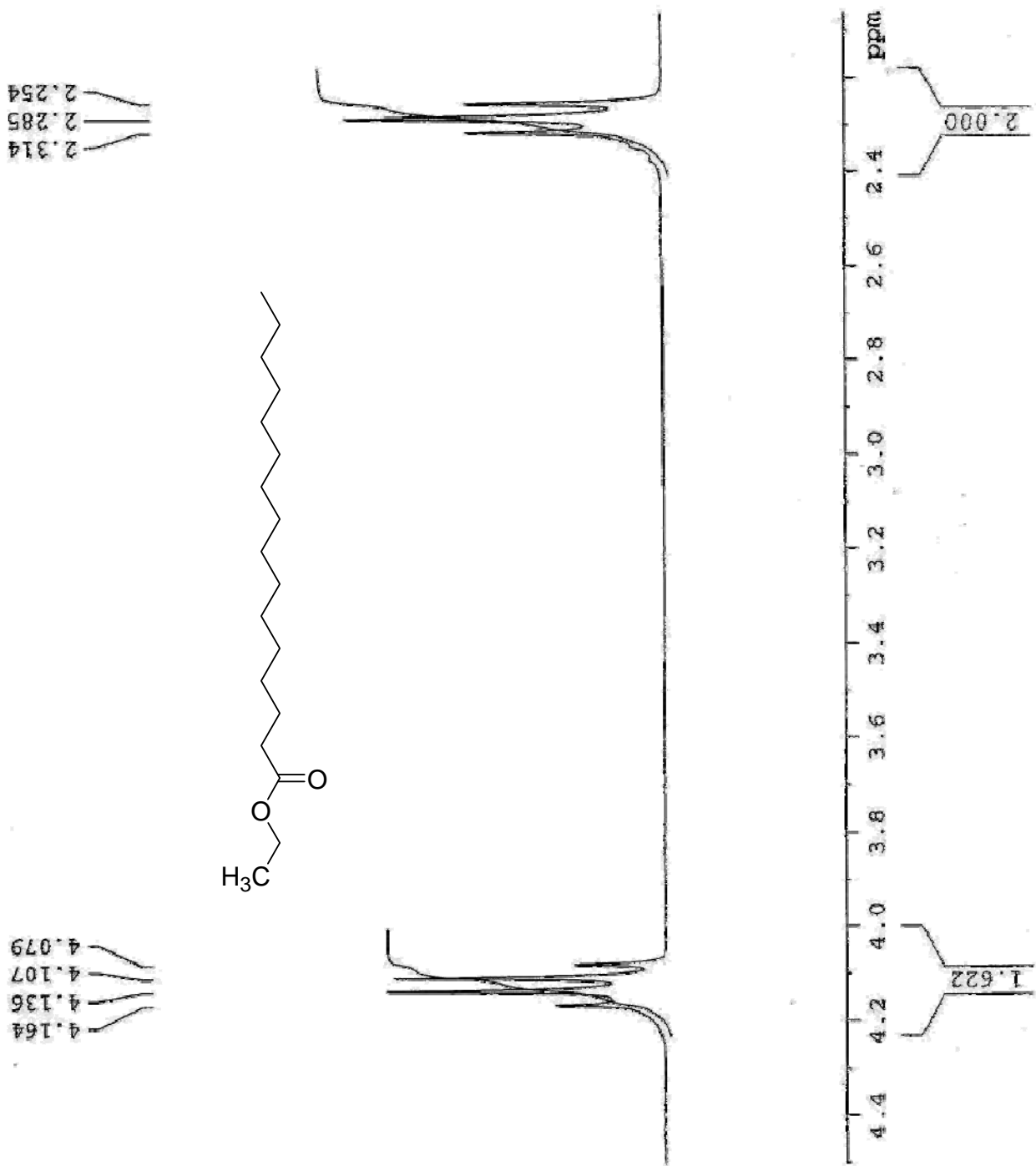


Table 3 (Entry 8)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

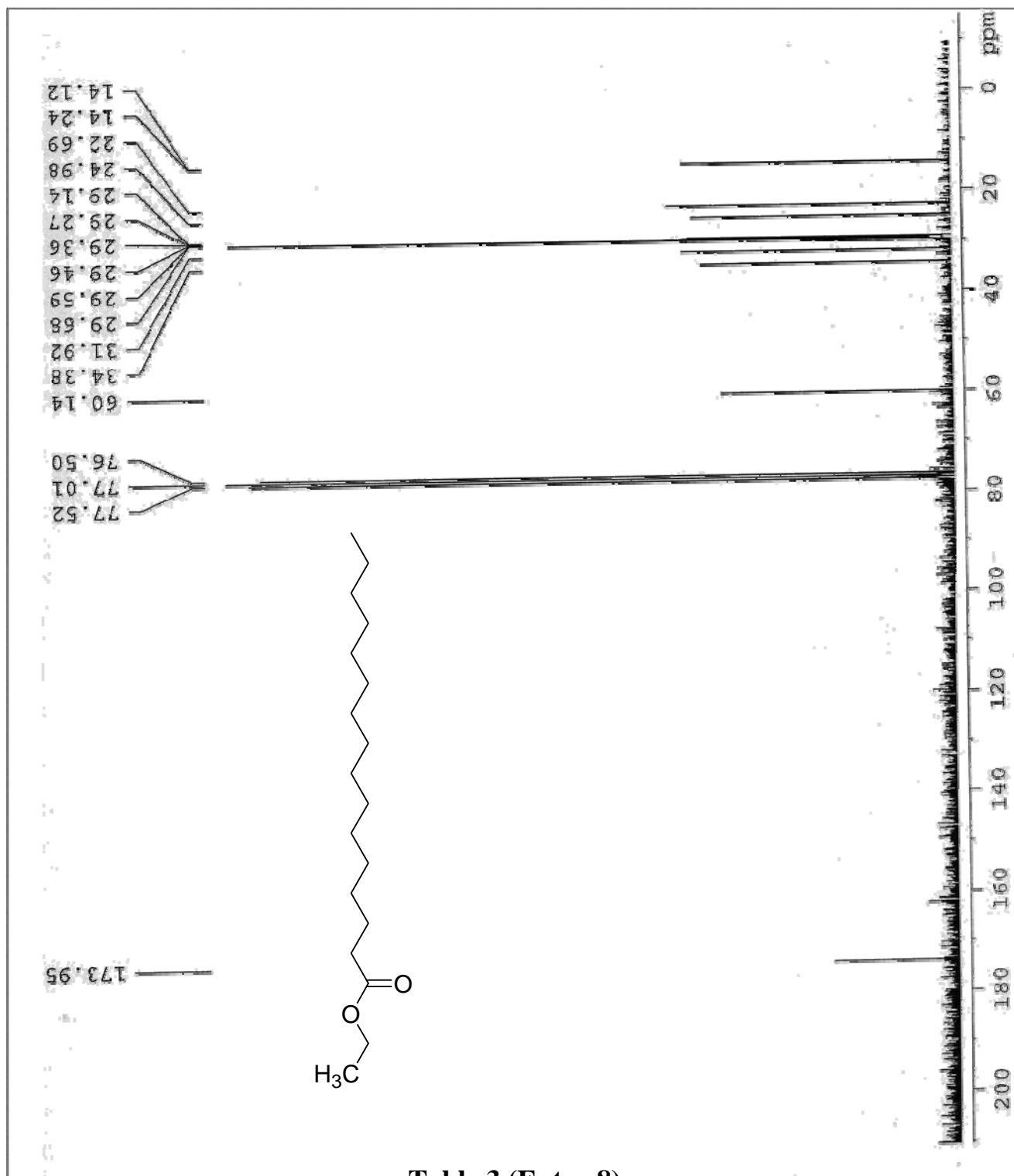


Table 3 (Entry 8)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

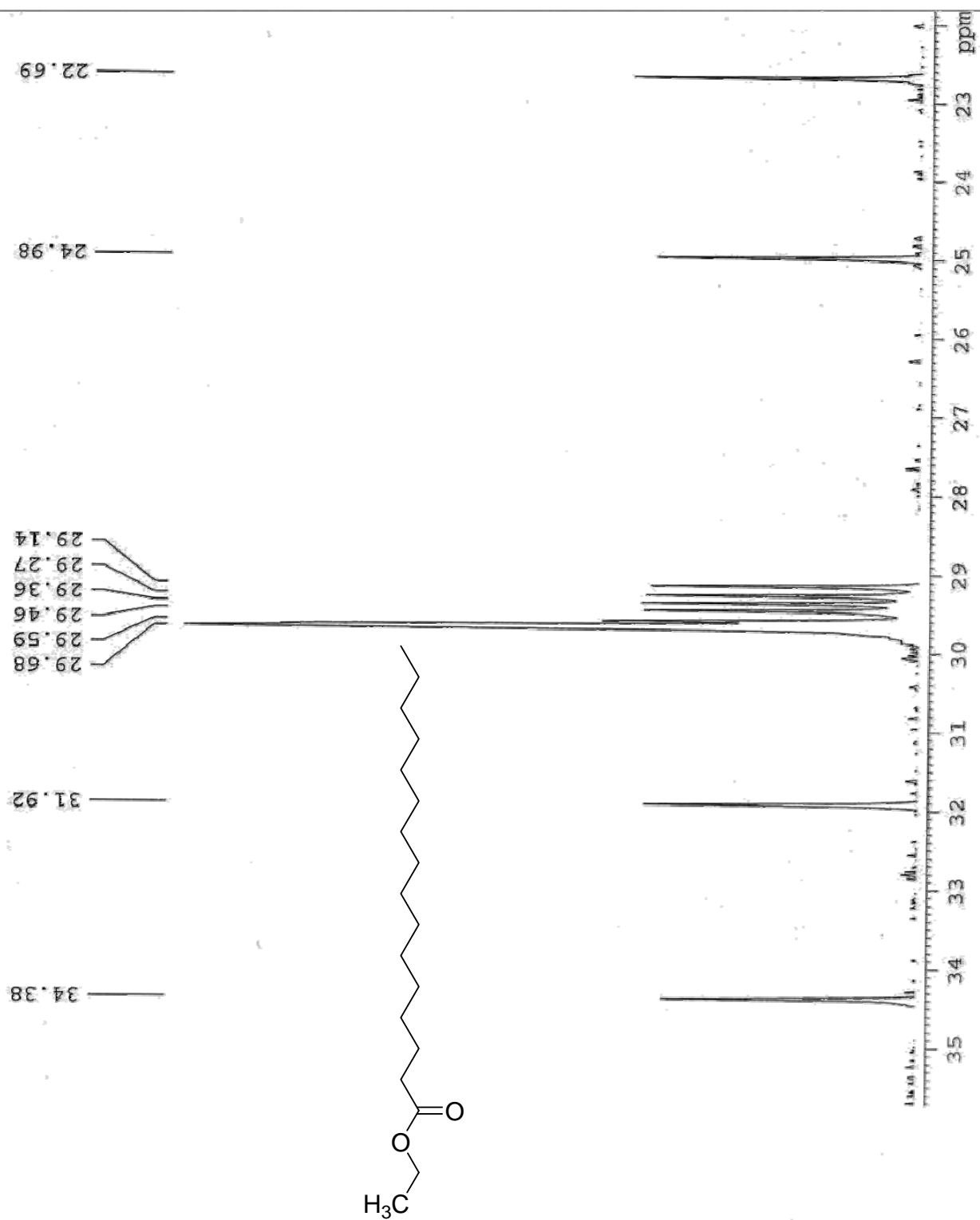


Table 3 (Entry 8)

Solvent: CDCl<sub>3</sub>— Frequency: 250 MHz

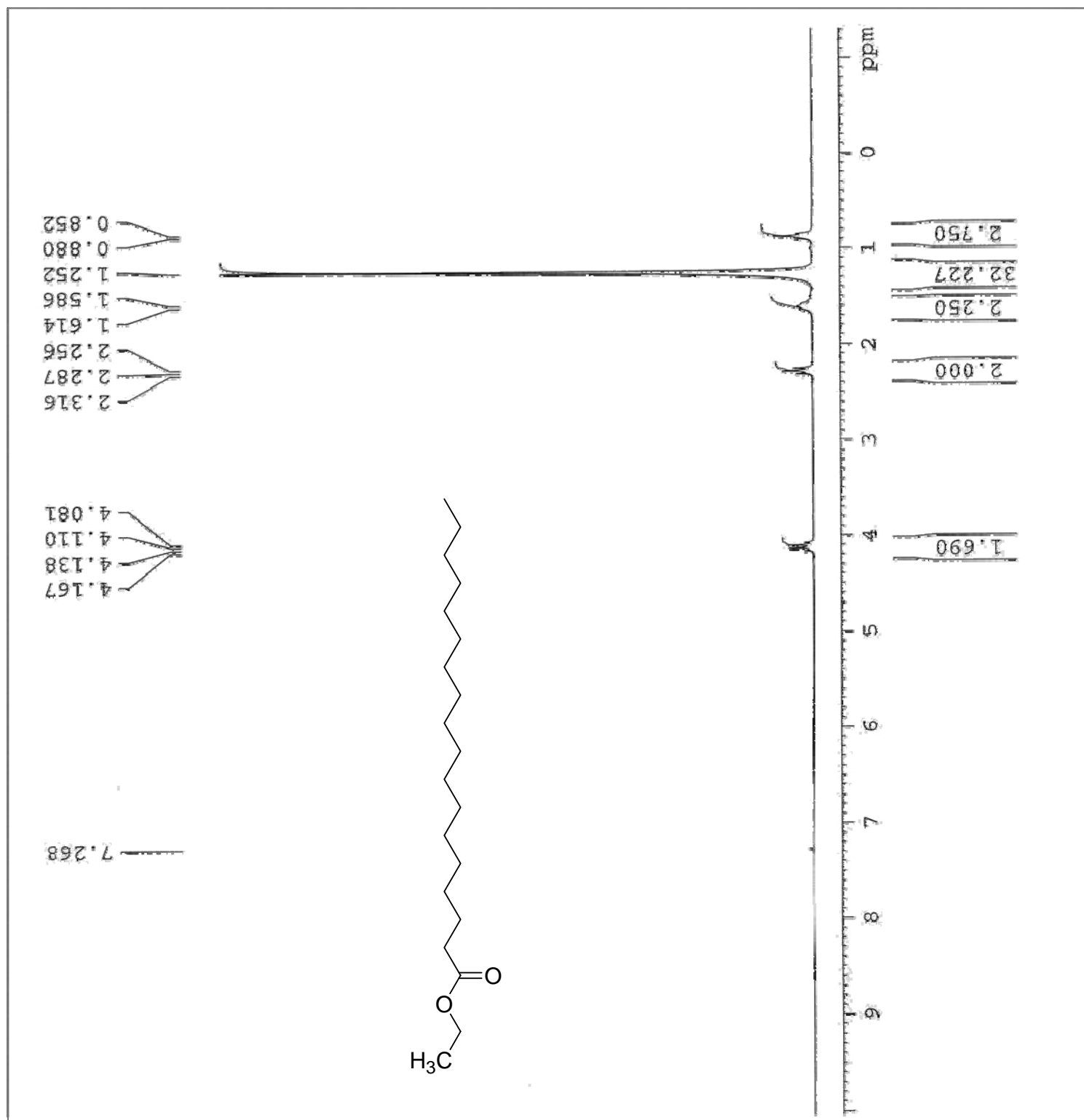


Table 3 (Entry 9)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

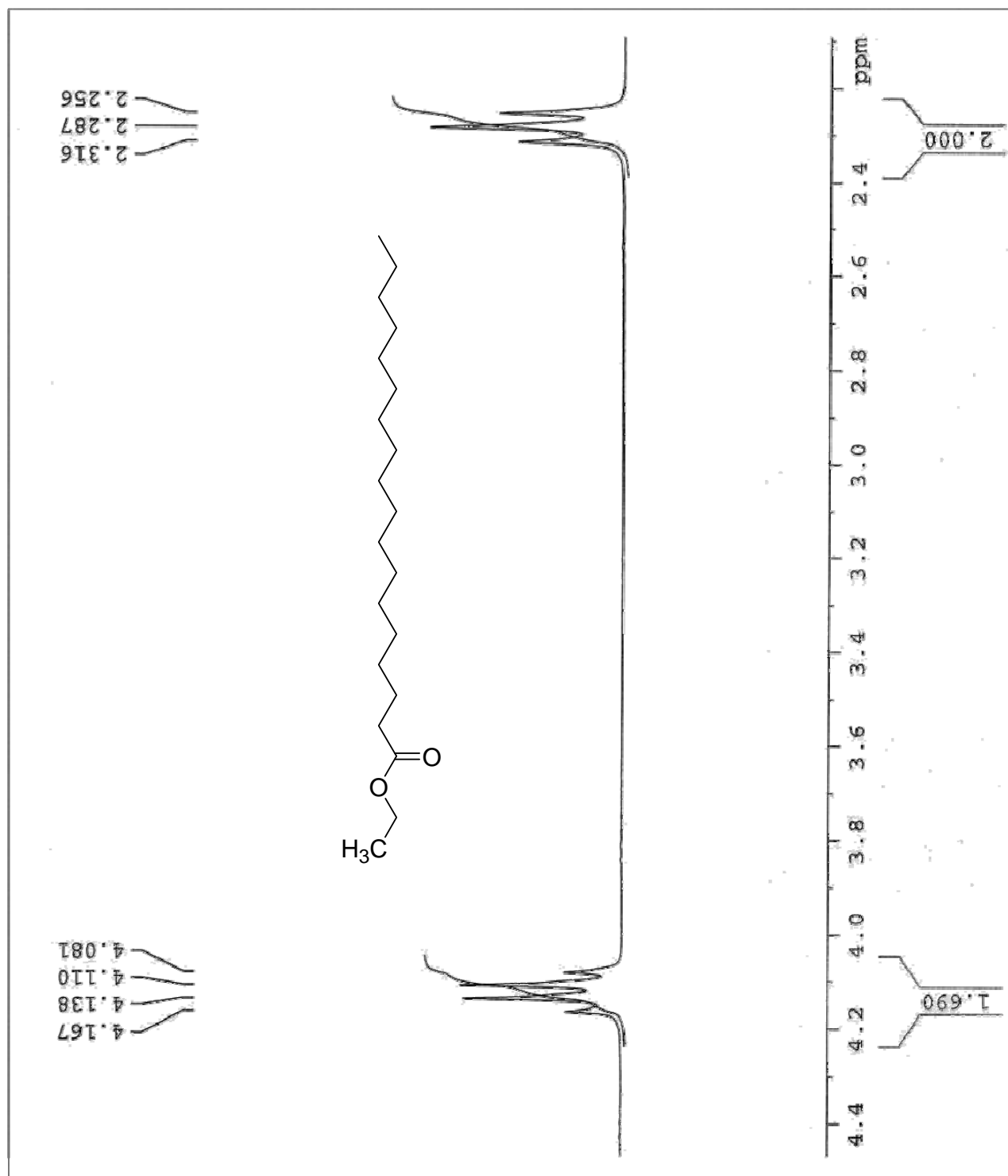


Table 3 (Entry 9)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

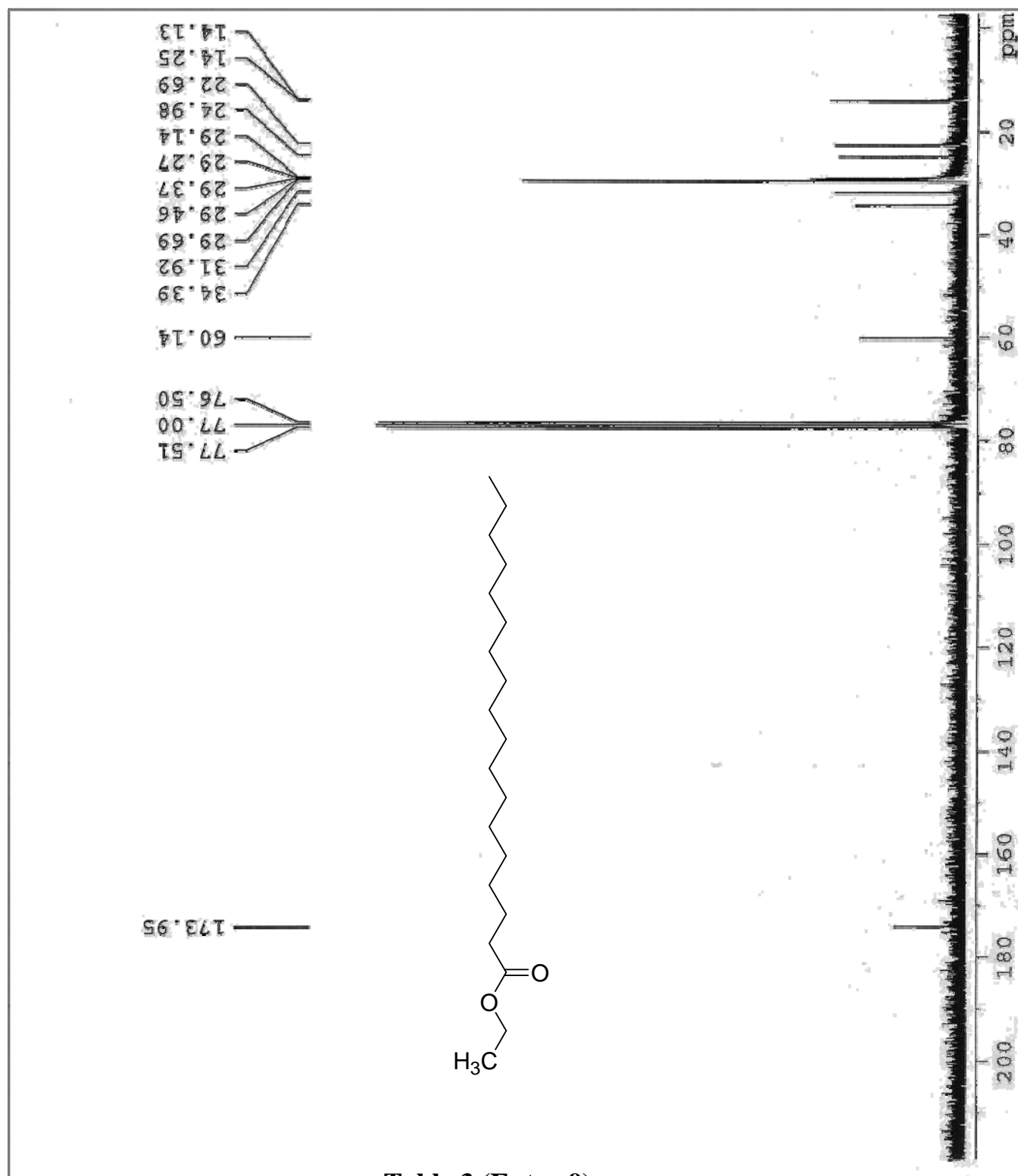


Table 3 (Entry 9)

Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

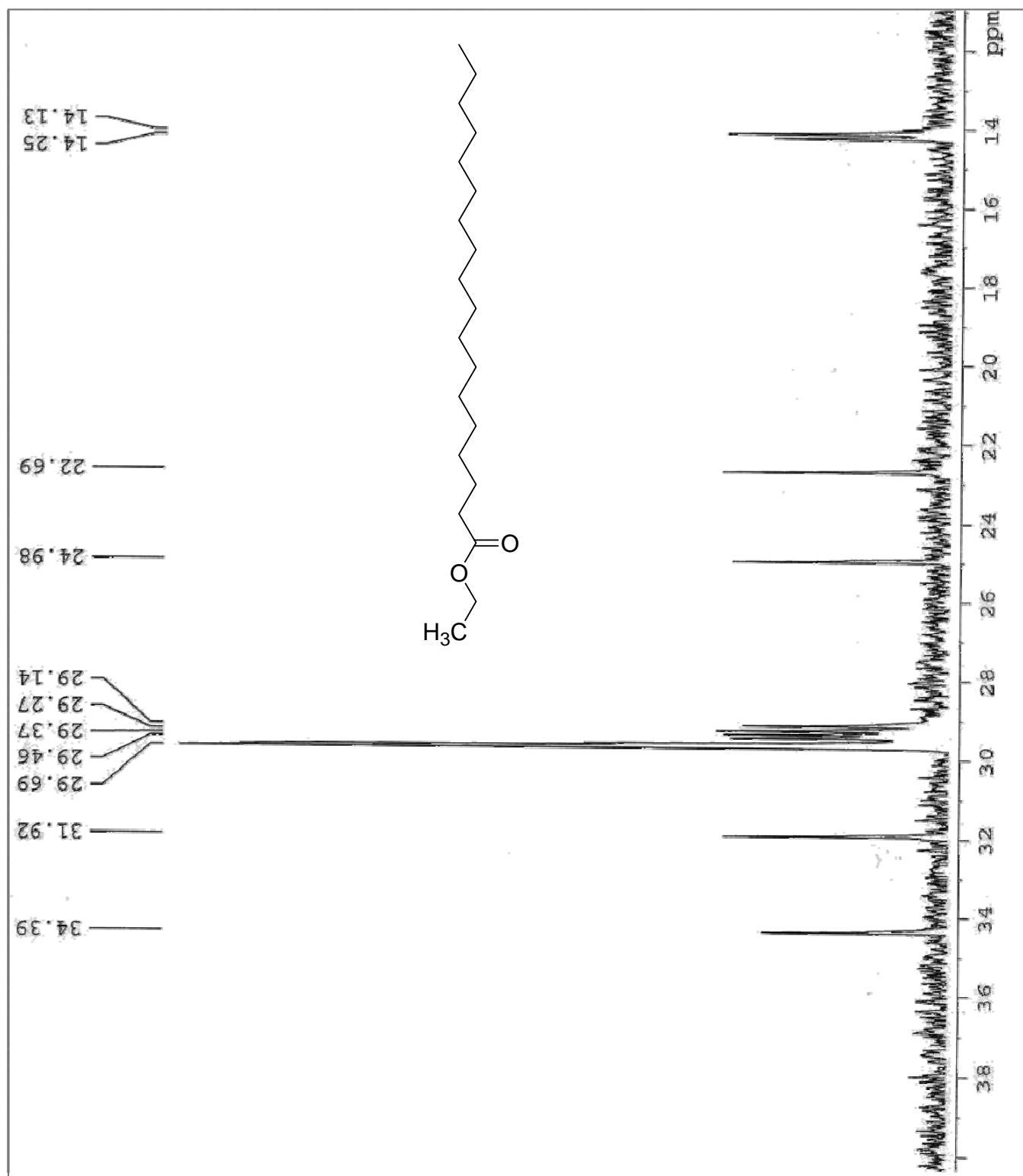
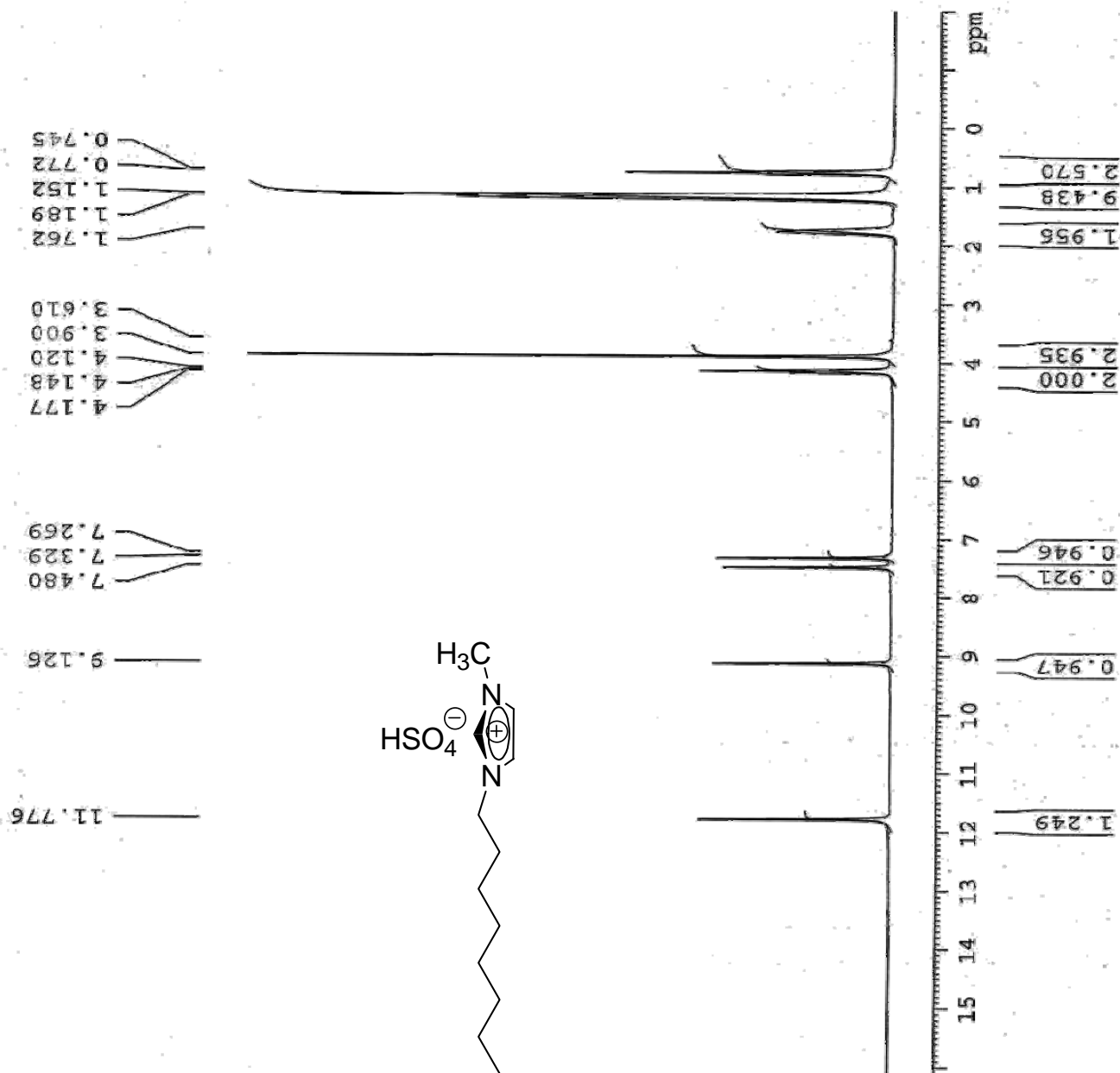
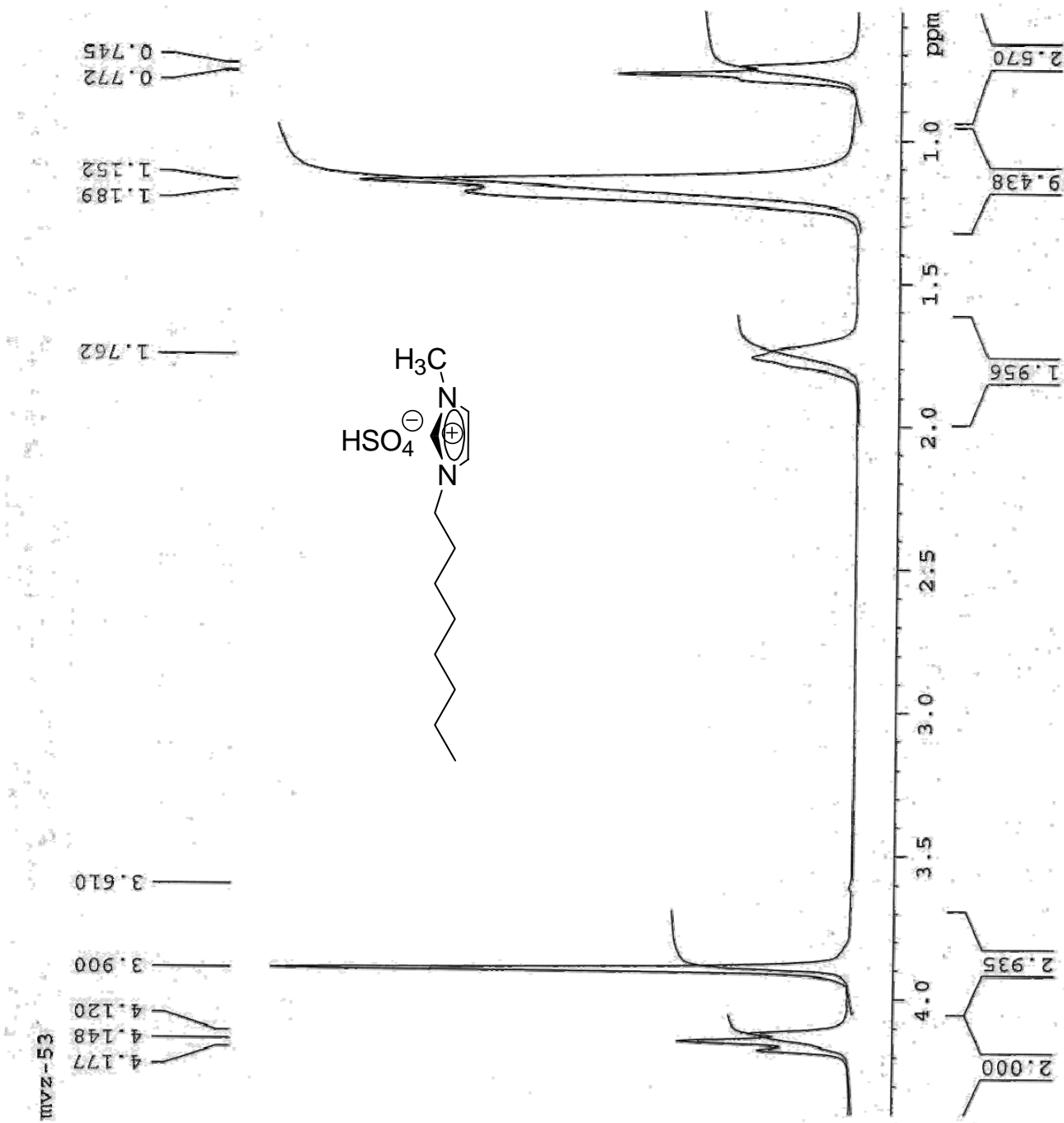


Table 3 (Entry 9)

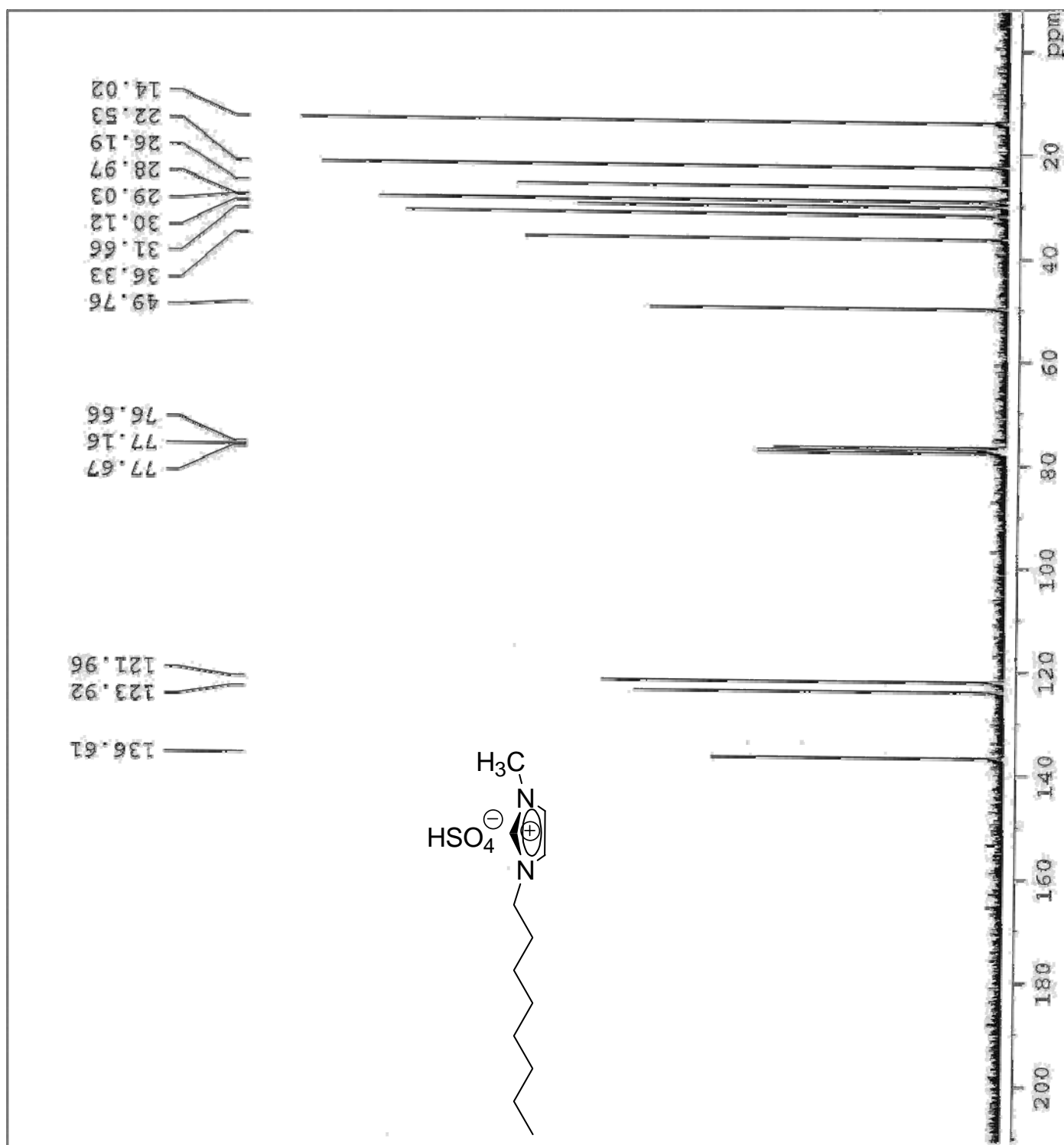
Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz



Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz



Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz



Solvent: CDCl<sub>3</sub>– Frequency: 250 MHz

