Electronic Supplementary Material (ESI) for RSC Advances

SBA-15 functionalized sulfonic acid confined hydrophobic and acidic ionic liquid: a highly efficient catalyst for solvent-free thioacetalization of carbonyl compounds at room temperature

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Experimental

Characterizations

The pore characteristics of the prepared materials were verified by the nitrogen sorption isotherm. Pore size distributions, pore volumes, surface areas, and BET isotherms were determined from N_2 adsorption-desorption experiments by using Barrett-Joyner-Halenda (BJH) method, and Brunauer-Emmett-Teller (BET) analysis. The NMR spectra was recorded by Bruker NMR spectrometer (^{1}H frequency: 250 MHz, ^{13}C frequency: 62.9 MHz). The melting points were recorded by the Buchi 510 apparatus.

Materials

3-Mercaptopropyltrimethoxysilane (MPTMS) was obtained from (Merck). Pluronic P123 ($EO_{20}PO_{70}EO_{20}$)(EO= ethylene Oxide, PO= Propylene Oxide), M_{av}= 5800) was purchased from Aldrich. Other chemicals and solvents were purchased from Fluka and Merck and used without further purification.

Preparation of the SBA-15-Pr-SH

The synthesis of SBA-15-Pr-SH has been achieved using the known procedure described by Stucky and his co-workers.[1] This procedure involved a synthetic strategy based on co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of Pluronic P123 as the 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 6.83g TEOS. After 3 h pre-hydrolysis of TEOS, 1.6 g 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 Soxhelet apparatus for 24 h.

Preparation of the SBA-15-Pr-SO_3H

Typically, 0.3 g of SBA-15-Pr-SH was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar 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_2SO_4 solution for 2h and then was washed several times with deionized water and ethanol and dried at 60 °C vacuum overnight.

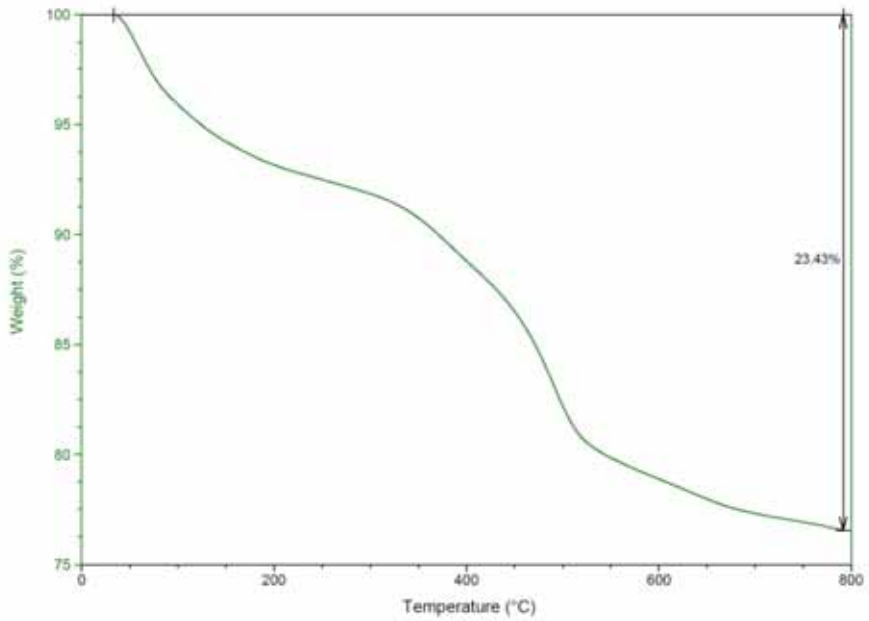


Fig. 1S TGA diagram of SBA-15-Pr-SO_3H[4]

pH analysis of the SBA-15-Pr-SO_3H

To an aqueous solution of NaCl (1 M, 25 mL) with a primary pH 5.93, the catalyst (0.5 g) was added, and the resulting mixture was stirred for 2 h after which the pH of solution decreased to 1.51. This is equal to a loading of 1.55 mmol H^+/g.[2]

Preparation of 1-methyl-3-octylimidazolium hydrogen sulfate [$MOIm^+$][HSO_4^-]

The synthesis of 1-methyl-3-octylimidazolium hydrogen sulfate [$MOIm^+$][HSO_4^-] has been achieved according to patented literature[3] with a little modification. In a flask equipped with a dropping funnel, a condenser and a magnetic stirrer 1-methyl-3-octylimidazolium bromide (7.81 g ~ 0.028 mol) salt was dissolved in dry dichloromethane (100 mL). Then, the same molecular

ratios of aqueous solution of concentrated sulfuric acid (97%) were carefully added to this solution. Then the mixture was heated under reflux for two days. From time to time, any HBr by-product formed in the process was monitored by pH indicator papers. After the reaction completion, the solution was cooled to room temperature, and the dichloromethane was removed under vacuum. To remove any water (generated from aqueous sulfuric acid used) the ionic liquid was dried in a vacuum oven at 60°C over night.

Preparation of the catalyst 1

The catalyst **1** was prepared by one-step impregnation of SBA-15-Pr-SO_3H with the acetone solution of certain volume of [MOIm][HSO_4] according to BET analysis of the synthesized SBA-15-Pr-SO_3H. 0.8 ml of [MOIm][HSO_4] was dissolved in absolute acetone (5mL). This solution then dropwise added to a mixture containing of 100 mL acetone and 1 g of SBA-15-Pr-SO_3H in an Ar atmosphere. After 3 h stirring at room temperature volatile solvent was removed under reduced pressure and the catalyst **1** was dried for hours at 60 °C in a vacuum oven.

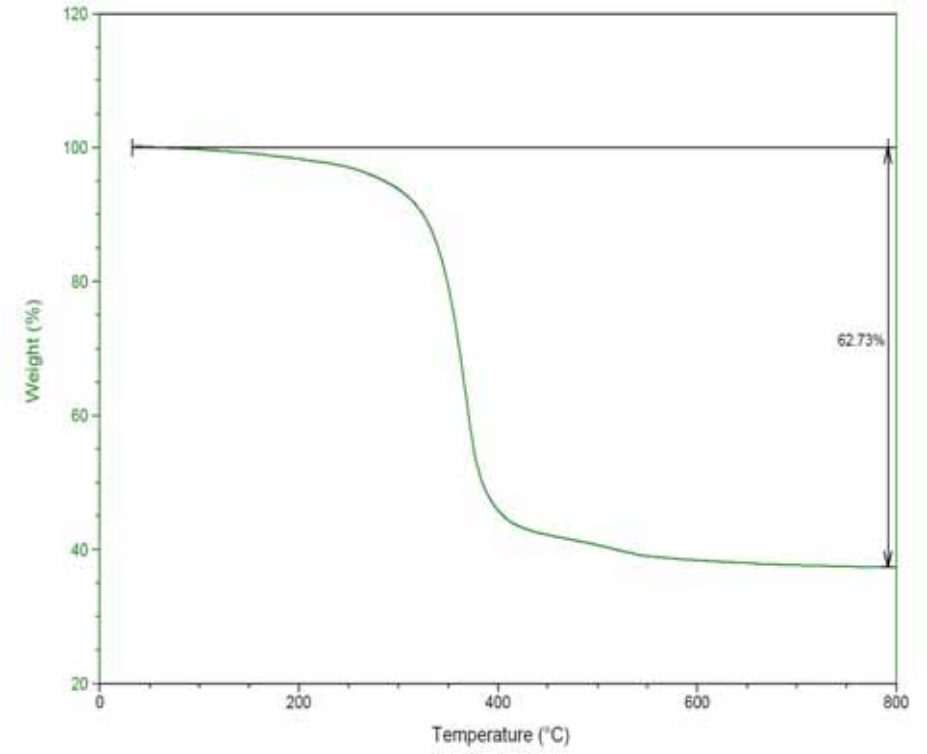


Fig. 2S TGA diagram of IL@SBA-15-Pr-SO_3H (Catalyst 1)[4]

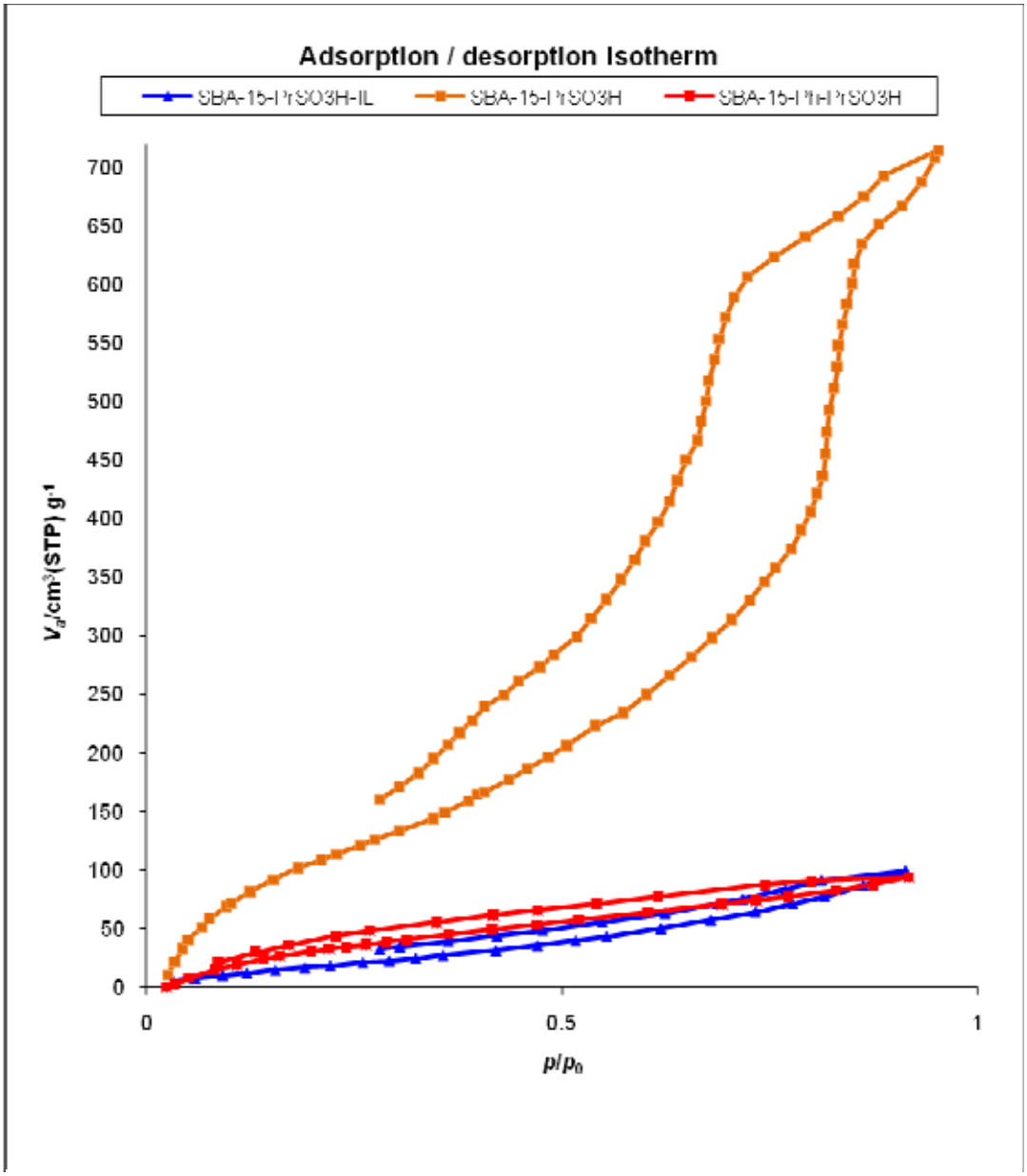


Fig. 3S Water adsorption-desorption of SBA-15-Pr-SO_3H (organge plot), IL@SBA-15-Pr-SO_3H (Catalyst 1) (blue plot) and SBA-15-Ph-Pr-SO_3H (red plot) in the gas phase at 25 °C.

pH analysis of the catalyst 1

According to the procedure described in 2.4, the observed pH was 1.305. This is equal to a loading of 2.48 mmol H^+/g of the catalyst **1**.

General procedure for solvent-free thioacetalization of carbonyl compounds at room temperature

The carbonyl compound (1 mmol), 1,3-Propanedithiol (0.25-0.45 mL), and the catalyst **1** (~ 3 mol%, 0.012 g) were combined together at room temperature for times indicated in Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst **1** was filtered off and washed with heptane (100 mL). Then 50 mL Et_2O was added to the filtrate and the organic layer were washed with aqueous NaOH (3×15 mL, 10%) and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave the almost pure corresponding thioacetal and thioketal derivatives. Further purification of the products could be achieved by re-crystallization of the derivatives in hexane to afford the corresponding pure products.

References

1 D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka,and G. D. Stucky, *Chem. Mater.* 2000, **12**, 2448.

2 Karimi, D. Zareyee, *Org. Lett*., 2008, **10**, 3989.

3 W. Keim, W. Korth, P. Wasserscheid, *WO Patent* 200016902 (A1) (2000).

4. B. Karimi, and M. Vafaeezadeh, *Chem. Commun.* 2012, **48**, 3327.

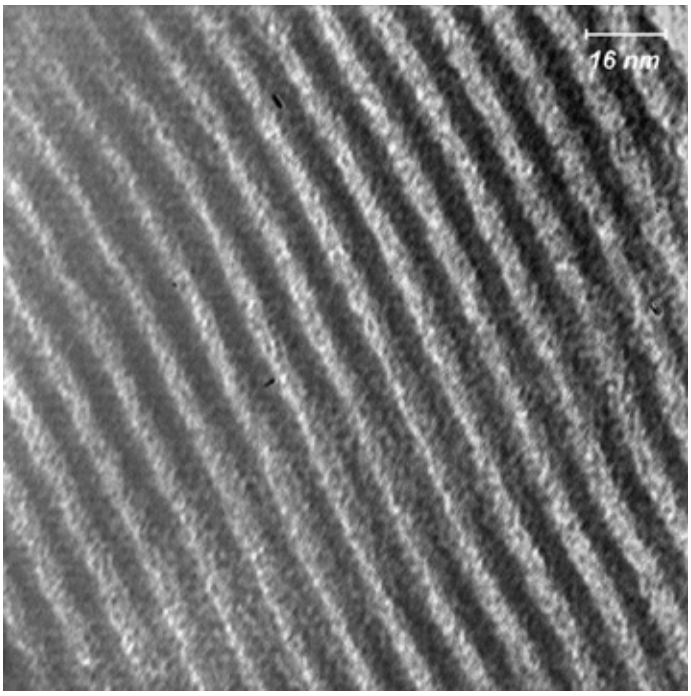


Fig 4S TEM image of the as-synthesized catalyst **1**

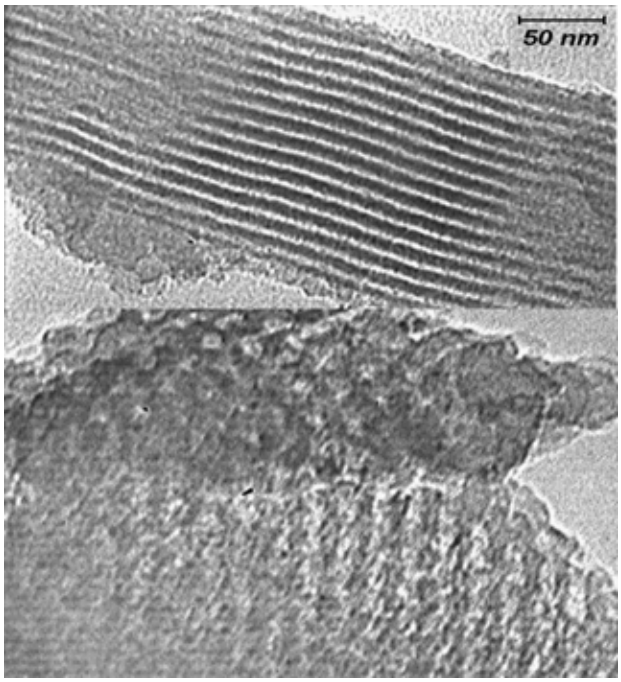


Fig 5S TEM image of the recovered catalyst **1** after the 8th reaction run from the thioacetalization of benzaldehyde with 1,3-propanethiol

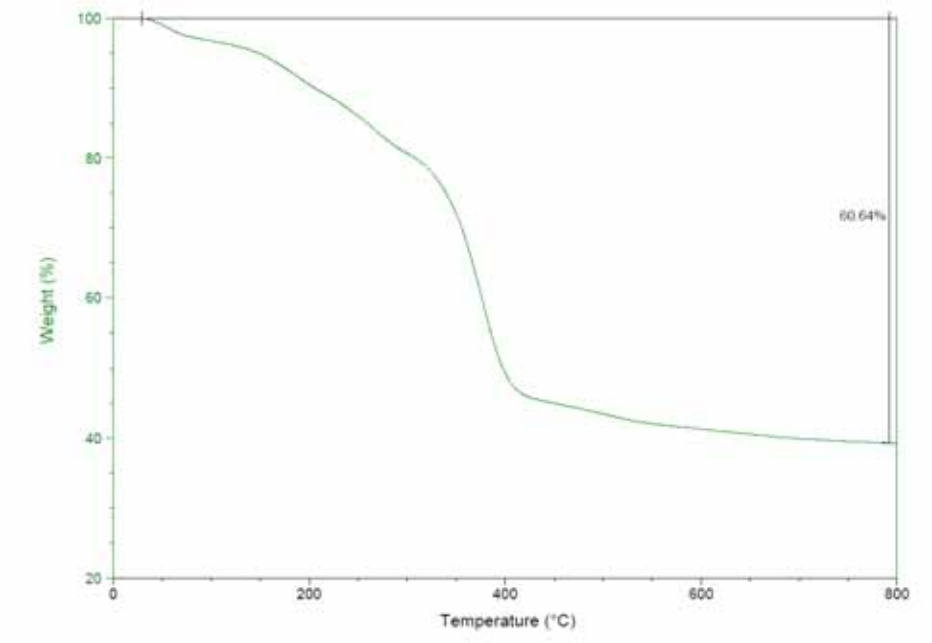


Fig. 6S TGA diagram for catalyst **1** after the 8th reaction run

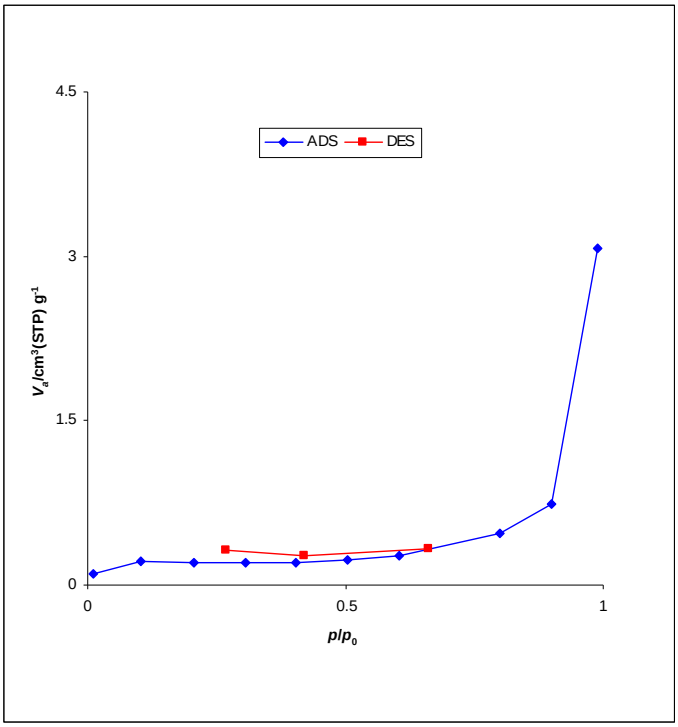


Fig. 7S Nitrogen adsorption-desorption isotherm catalyst **1** after the 8th reaction run

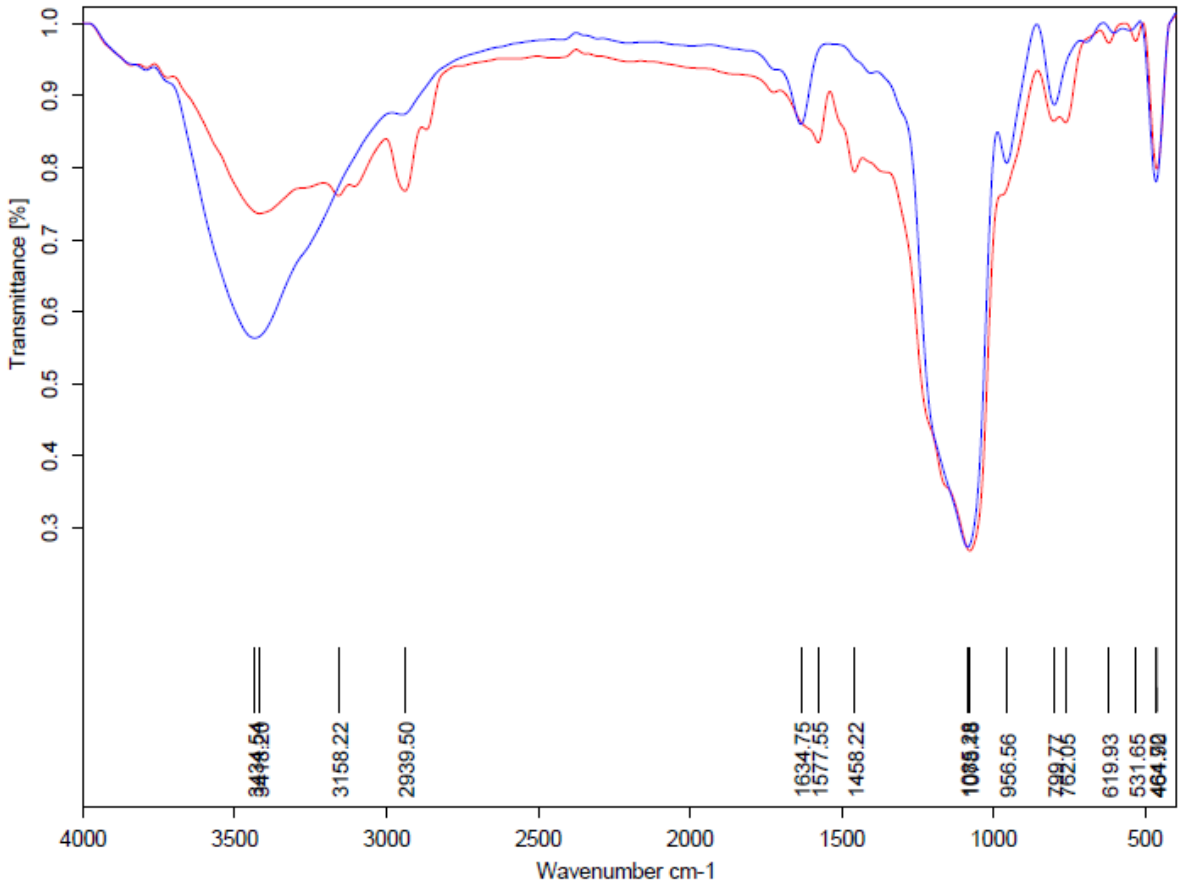


Fig. 8S FT-IR spectra of fresh catalyst **1** (red spectrum) and EtOH-washed catalyst (blue spectrum)

Spectral data for Table 1:

Table 1 (Entry 1): White solid, mp 72-74 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.4-7.5 (m, 2H), 7.3-7.4 (m, 3H), 5.18, (s, 1H), 2.9-3.1 (m, 4H), 2.1-2.2 (m, 1H), 2.0 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 139.2, 128.7, 128.5, 127.8, 51.5, 32.1, 25.1.

Table 1 (Entry 2): White solid, mp 58-60.4 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.39 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 5.16 (s, 1H), 3.0-3.1 (m, 2H), 2.8-2.9 (m, 3H), 2.1-2.2 (m, 1H), 1.9-2.0 (m, 1H), 1.1-1.4 (m, 6H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 149.1, 136.4, 127.6, 126.8, 51.2, 33.8, 32.1, 25.1, 23.9.

Table 1 (Entry 3): White solid, mp 134.5-137.1 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.50 (d, *J* = 7.8 Hz, 1H), 7.0-7.1 (m, 2H), 5.3 (s, 1H), 3.0-3.1 (m, 2H), 2.9-3.0 (m, 2H), 2.43 (s, 3H), 2.31 (s, 3H), 2.1-2.3 (m, 1H), 1.8-2.1 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 137.9, 134.8, 134.2, 131.2, 127.8, 127.3, 48.0, 32.4, 25.3, 21.1, 19.0.

Table 1 (Entry 4): White solid, mp 66.8-69 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.2-7.3 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 5.16 (s, 1H), 2.8-3.1 (m, 4H), 2.2 (s, 3H), 2.1-2.2 (m, 1H), 1.8-2.0 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 139.1, 138.4, 129.2, 128.6, 128.4, 124.8, 51.5, 32.1, 25.19, 21.4.

Table 1 (Entry 5): White solid, mp 90.6-93.1 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.7 (d, *J* = 7.2 Hz, 1H), 7.2-7.4 (m, 3H), 5.65 (s, 1H), 3.1 (t, *J* = 12.2 Hz, 2H), 2.89-2.94 (m, 2H), 2.1-2.2 (m, 1H), 1.9-2.0 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 136.5, 132.4, 129.6, 129.6, 129.4, 127.4, 47.6, 32.2, 25.1.

Table 1 (Entry 6): White solid, mp 80-82 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.50 (d, *J* =1.5 Hz, 1H), 7.4 (m, 2H), 7.2-7.3 (m, 1H), 5.11 (s, 1H), 2.9-3.1 (m, 4H), 2.1-2.2 (m, 1 H), 1.9-2.0 (m, 1 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 141.3, 131.5, 130.9, 130.3, 126.5, 122.6, 50.6, 31.94, 24.9.

Table 1 (Entry 7): White solid, mp 105.1-106.8 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.4-7.5 (m, 2H), 7.02 (t, *J* = 8.8 Hz, 2H), 5.15 (s, 1H), 2.9-3.1 (m, 4H), 2.1-2.2 (m, 1H), 1.9-2.0 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 164.4, 160.5, 129.6, 129.5, 115.8, 115.4, 50.4, 32.0, 25.0.

Table 1 (Entry 8): Viscose oil at room temperature

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.36 (s, 1H), 6.3-6.4 (m, 2 H), 5.21 (s, 1H), 2.9-3.0 (m, 4H), 2.1-2.2 (m, 1H), 2.0-2.1 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 151.7, 142.29, 110.6, 107.8, 42.0, 30.2, 25.2.

Table 1 (Entry 9): White solid, mp 80-82.7 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.26 (d, J = 5 Hz, 1H), 7.16 (d, J = 2.5 Hz, 1H), 6.94-6.98 (m, 3H), 5.41 (s, 1H), 2.9-3.1 (m, 4H), 2.1-2.2 (m, 1H), 1.9-2.1 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 126.7, 126.2, 125.6, 44.7, 31.0, 25.0.

Table 1 (Entry 10): White solid, mp 115.5-116.5 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.40 (d, J = 8.8 Hz, 2H), 6.87, (d, J = 8.8 Hz, 2H), 5.14 (s, 1H), 3.78 (s, 1H), 2.8-3.1 (m, 4 H), 2.1-2.2 (m, 1 H), 1.9-2.0 (m, 1 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 159.6, 131.3, 128.9, 114.1, 55.2, 50.7, 32.1, 25.1.

Table 1 (Entry 11): White solid, mp 93-94 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.38 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 5.12 (s, 1H), 2.8-3.1 (m, 4H), 2.44 (s, 3H), 2.1-2.2 (m, 1H), 1.9-2.1 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 138.9, 135.8, 128.2, 126.5, 50.8, 32.0, 25.0, 15.6.

Table 1 (Entry 12): White solid, mp 59.3-61.4 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.2-7.3 (m, 5H), 6.76 (d, J = 15.8 Hz, 1H), (dd, J_1 = 7.8 Hz , J_2 = 15.8 Hz), 4.82 (d, J = 7.8 Hz, 1H), 2.8-3.0 (m, 4H), 2.1-2.2 (m, 1H), 1.8-2.0 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 136.0, 133.4, 128.5, 128.0, 126.6, 126.0, 47.6, 30.2, 25.1.

Table 1 (Entry 13): White solid, mp 134.3-136.5 °C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 8.36 (d, J = 8.2 Hz, 1H), 7.8-7.9 (m, 3H), 7.5-7.6 (m, 3H), 5.95 (s, 1H), 3.1-3.3 (m, 2H), 2.9-3.0 (m, 2H), 2.18-2.24 (m, 1H), 1.9-2.1 (m, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 135.0, 133.9, 130.2, 129.0, 128.9, 126.3, 126.2, 125.9, 125.6, 123.3, 48.4, 32.7, 25.5.

Table 1 (Entry 14): Viscose oil at room temperature

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 4.04 (t, J = 6.8 Hz, 1H), 2.8-2.9 (m, 4H), 2.1-2.2 (m, 1H), 1.7-1.9 (m, 3H), 1.4-1.6 (m, 2H), 1.2-1.4 (m, 5H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 47.6, 35.1, 30.5, 28.7, 26.0, 22.3, 13.8.

Table 1 (Entry 15): White solid, mp 35.3-37 $^{\circ}$C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 2.7-2.8 (m, 4H), 1.9-2.0 (m, 6H), 1.8-1.9 (m, 1H), 1.5-1.6 (m, 4H), 1.3-1.5 (m, 2H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 50.3, 37.8, 26.1, 25.8, 25.8, 21.9.

Table 1 (Entry 16): Viscose oil at room temperature

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 2.8-2.9 (m, 4H), 1.9-2.2 (m, 6H), 1.7-1.9 (m, 4H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 55.2, 42.0, 29.3, 25.6, 24.3.

Table 1 (Entry 17): Viscose oil at room temperature

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.2-7.4 (m, 5H), 2.7-3.0 (m, 6H), 2.2-2.3 (m, 2H), 1.9-2.1 (m, 2H), 1.70 (s, 3H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 141.8, 128.5, 125.9, 49.0, 43.4, 31.3, 27.8, 26.5, 25.2.

Table 1 (Entry 18): White solid, mp 51.3-52.3 $^{\circ}$C (*n*-Hexane)

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 7.87 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.32 (dd, J_1 = 1.8 Hz, J_2 = 6.9 Hz, 2H), 2.6-2.8 (m, 4H), 1.8-2.0 (m, 2H), 1.8 (s, 3H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 142.5, 132.9, 129.4, 128.6, 53.4, 32.8, 28.0, 24.5.

Table 1 (Entry 19): Viscose oil at room temperature

^{1}H-NMR (250 MHz; $CDCl_3$): δ_H = 2.86 (m, 4H), 1.95 (m, 2H), 0.9 (m, 2H), 0.7 (m, 4H), 0.5 (m, 4H)**;** ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ_C = 53.5, 26.7, 25.1, 20.3, 2.6.

Electronic Supplementary Material (ESI) for RSC Advances

Copy of ^{1}H-NMR and ^{13}C-NMR spectra of selected thioacetal and thioketal derivatives

Table 1 (Entries 1-19) and [MOIM]HSO_4

Solvent: $CDCl_3$ – Frequency: 250 MHz

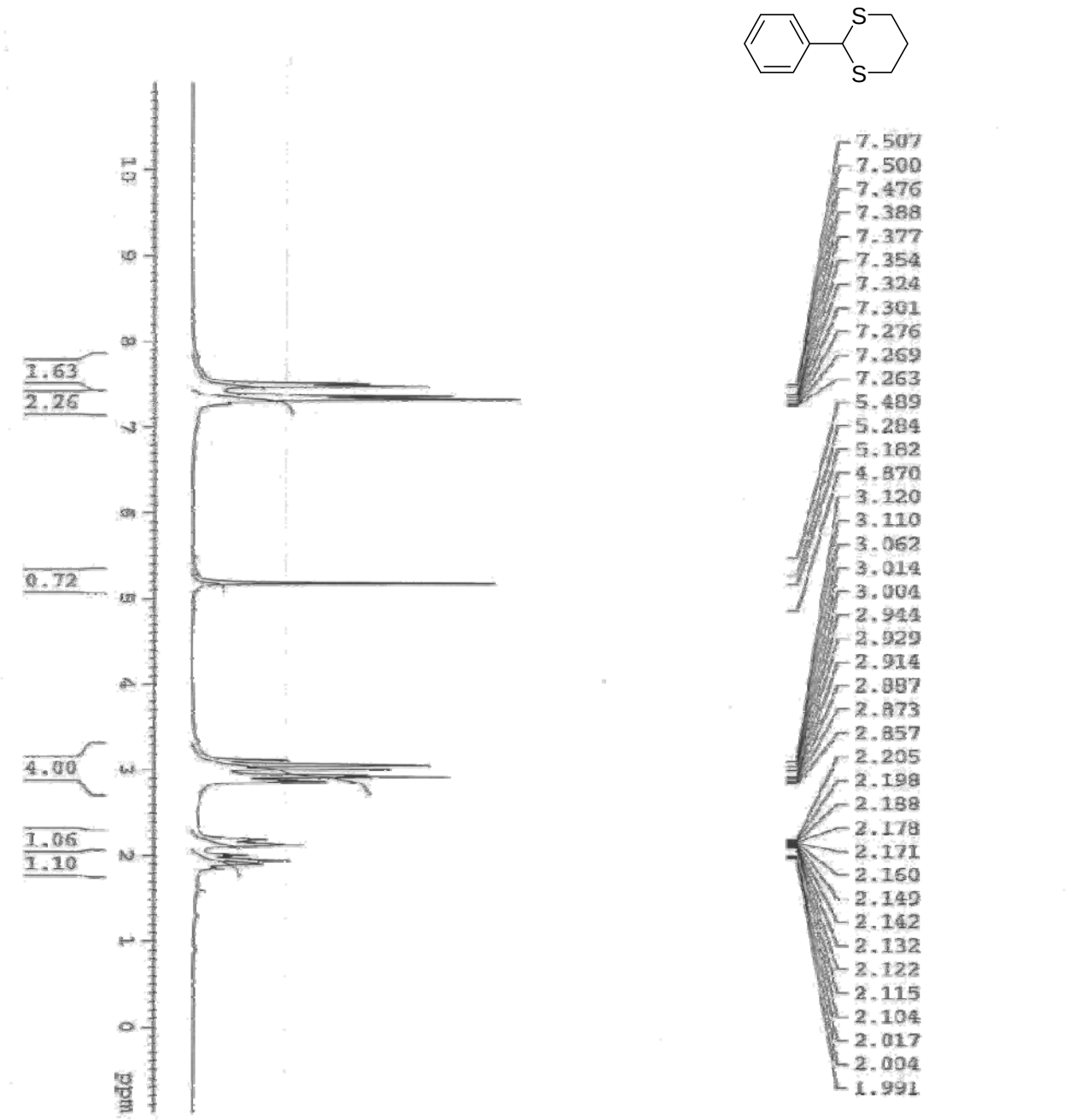


Table 1 (Entry 1)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

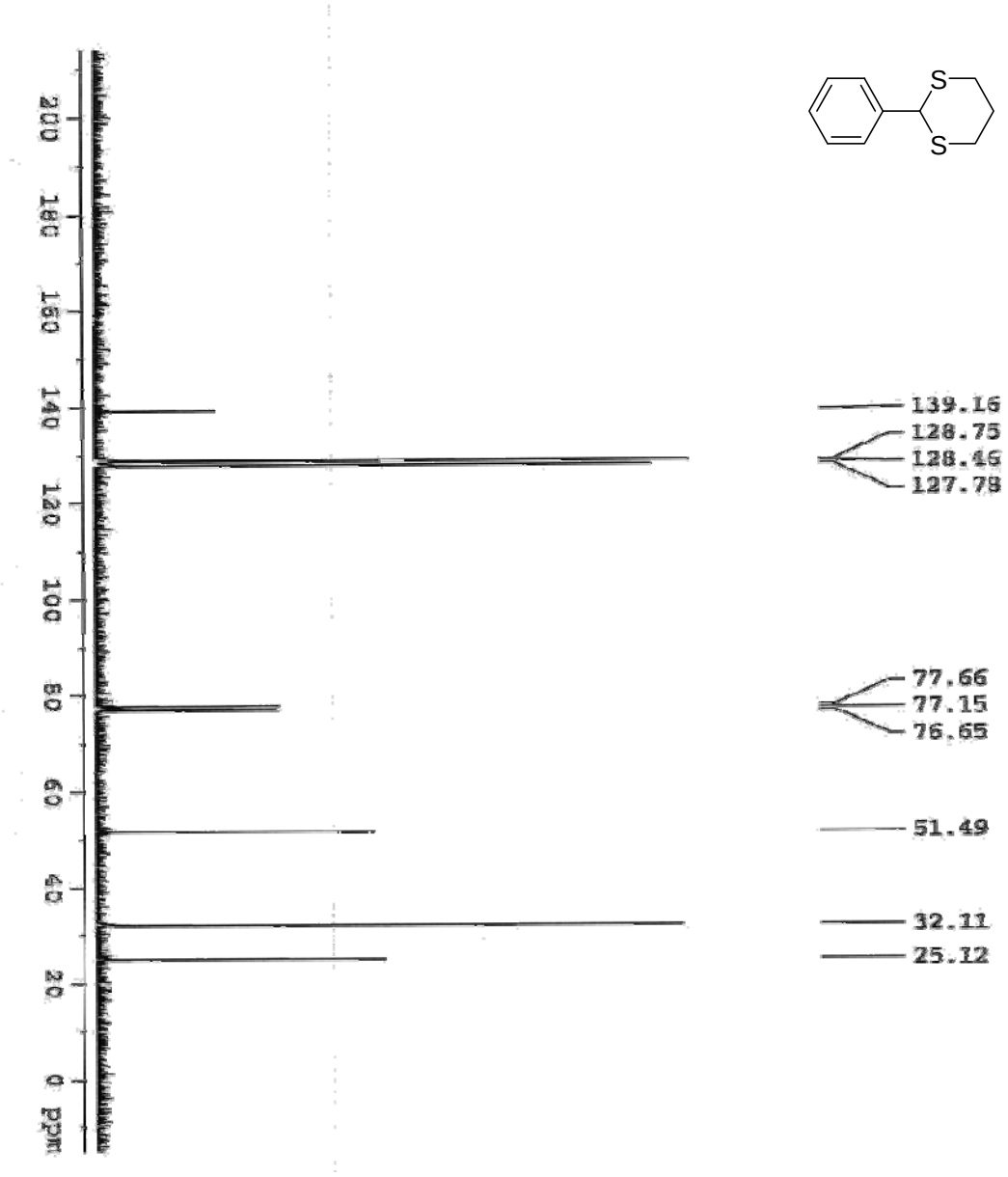


Table 1 (Entry 1)

Solvent: $CDCl_3$ – Frequency: 250 MHz

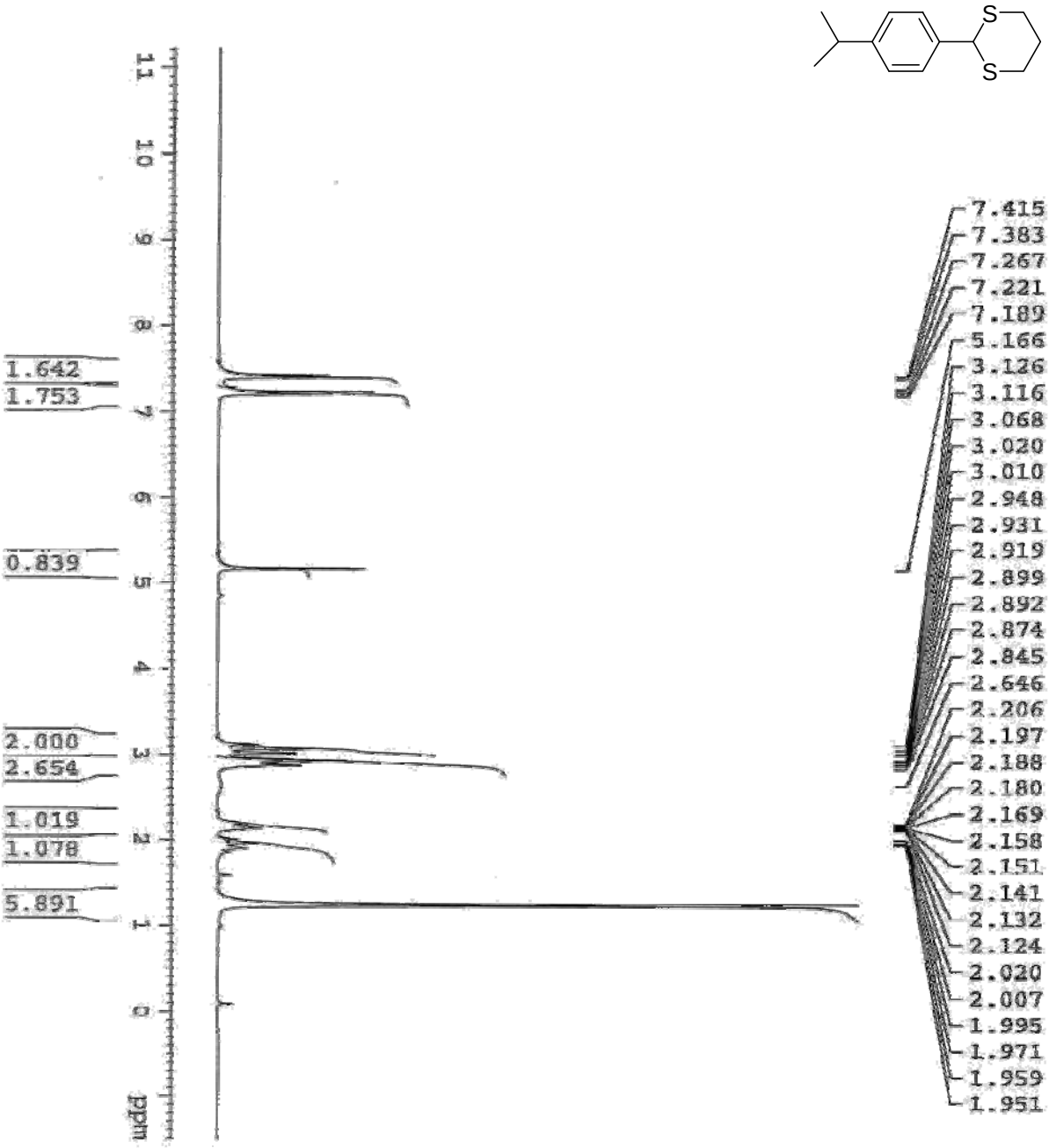
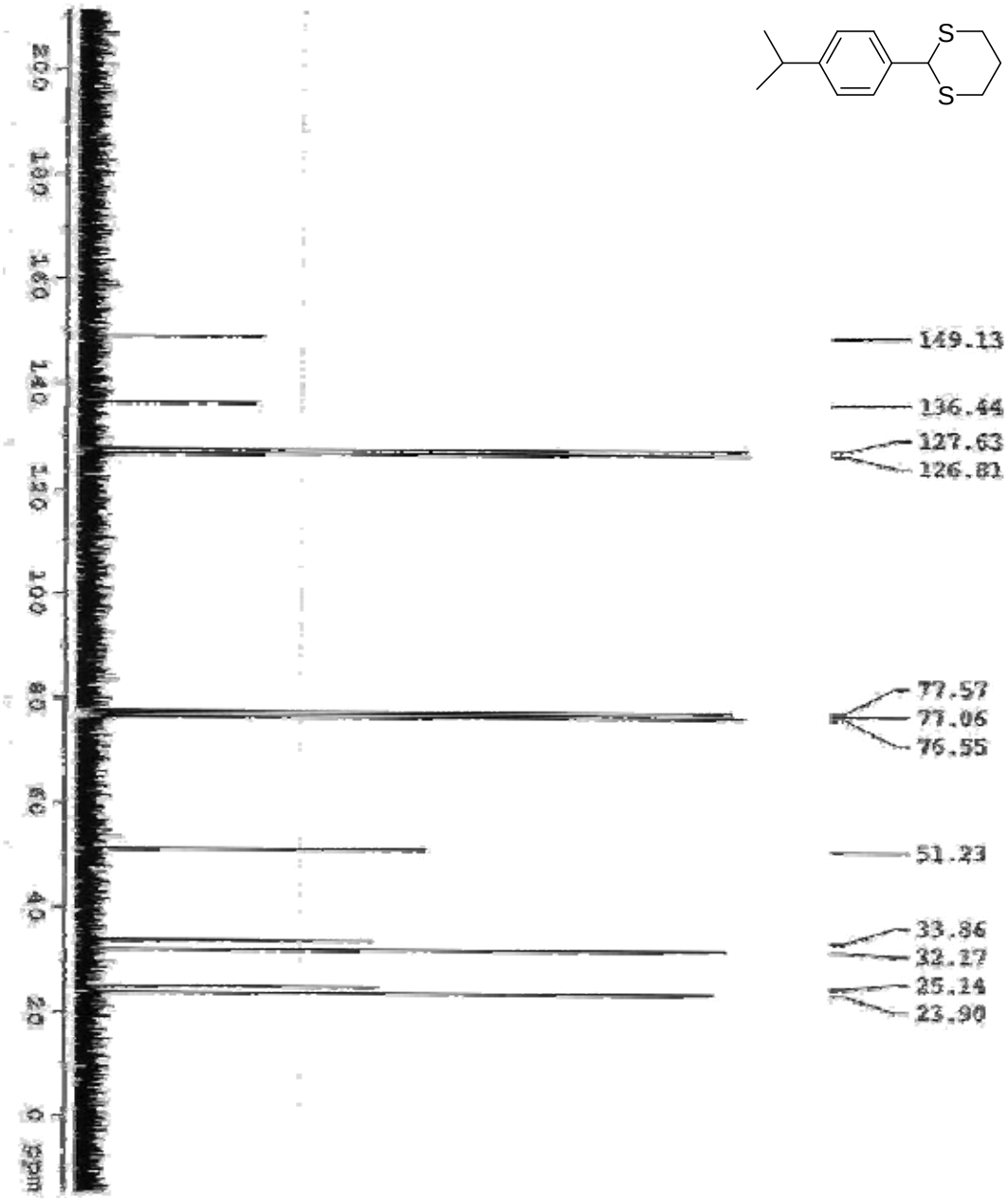


Table 1 (Entry 2)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz



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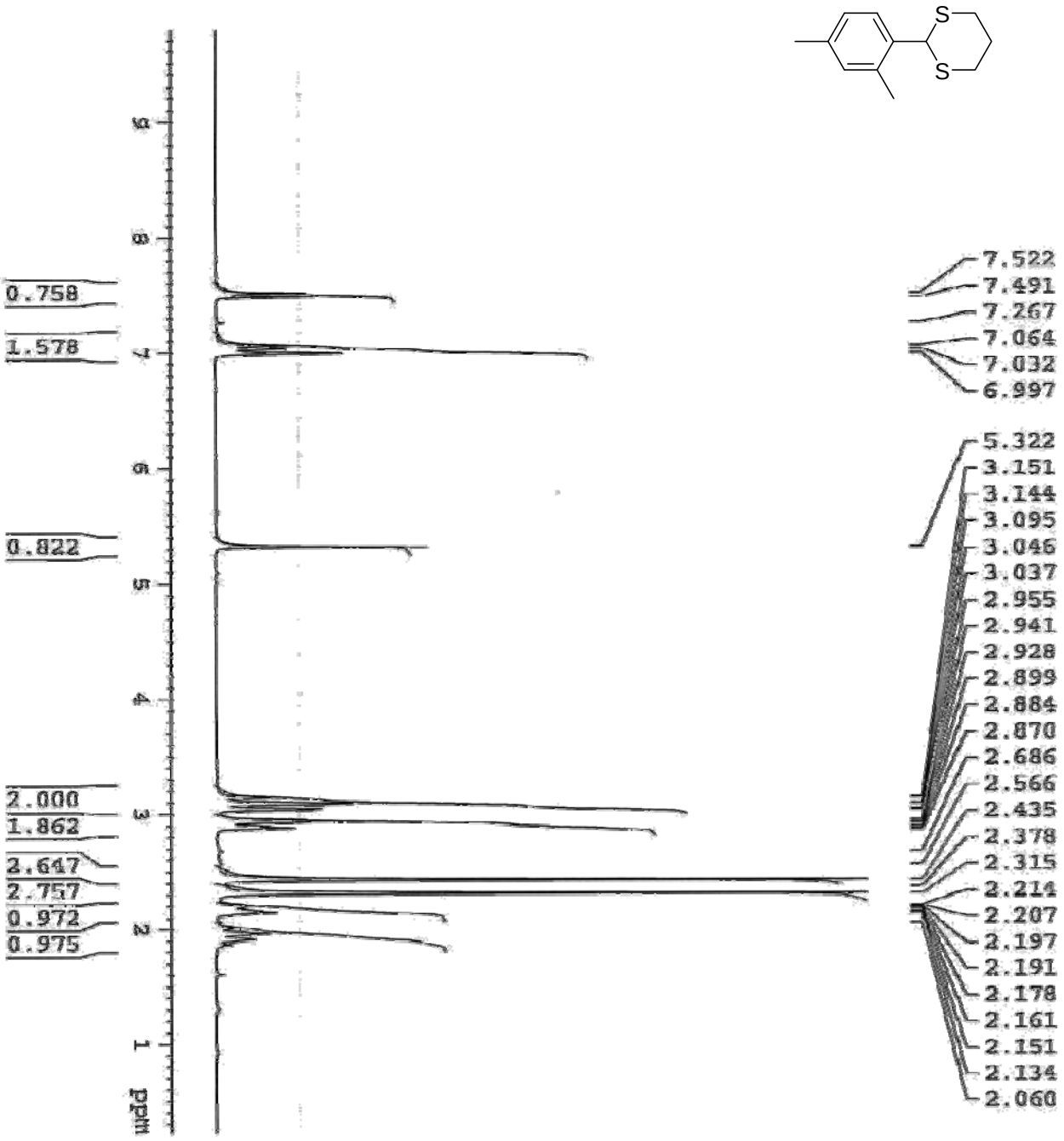

Table 1 (Entry 3)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

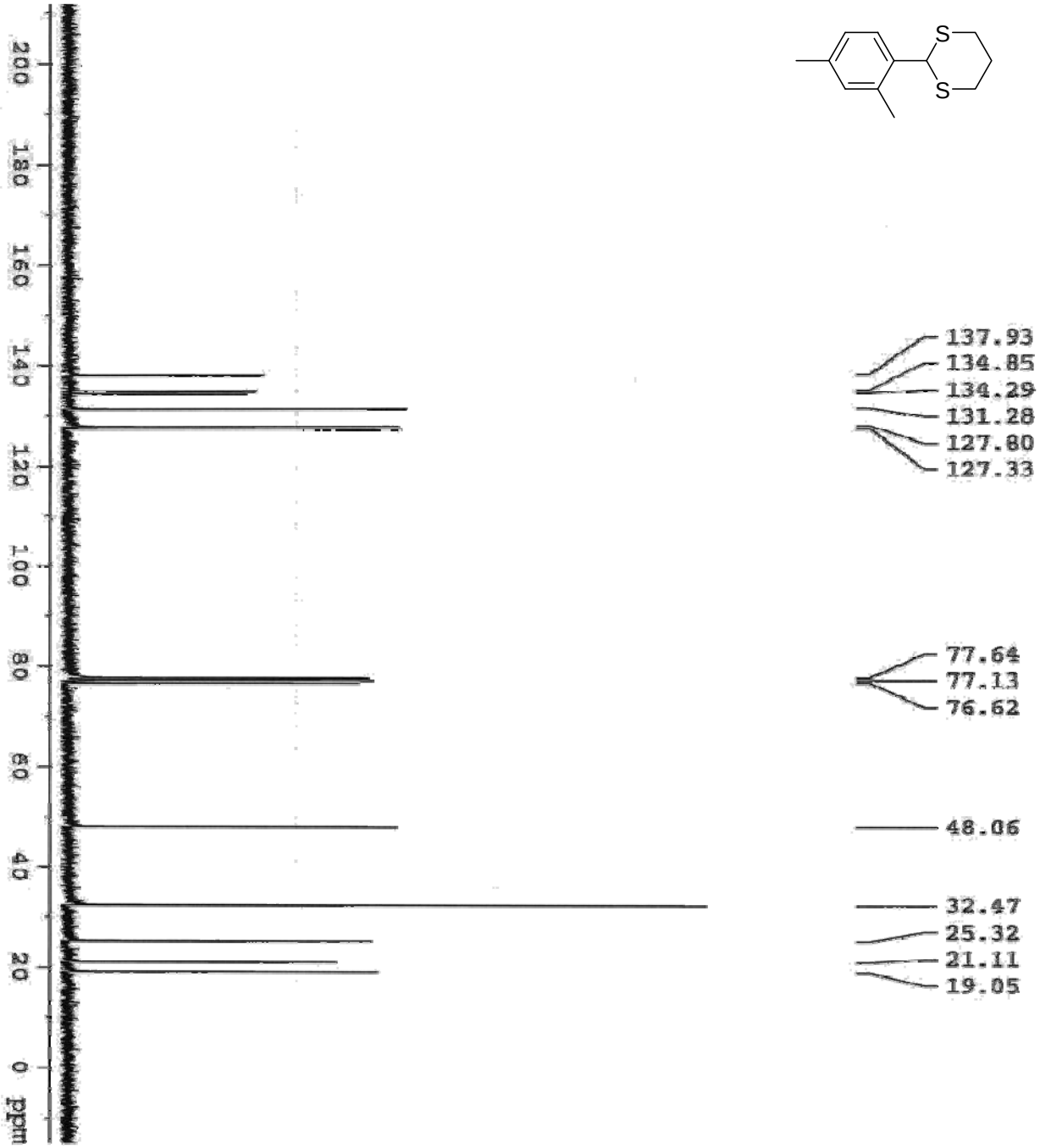

Table 1 (Entry 3)

Solvent: $CDCl_3$ – Frequency: 250 MHz

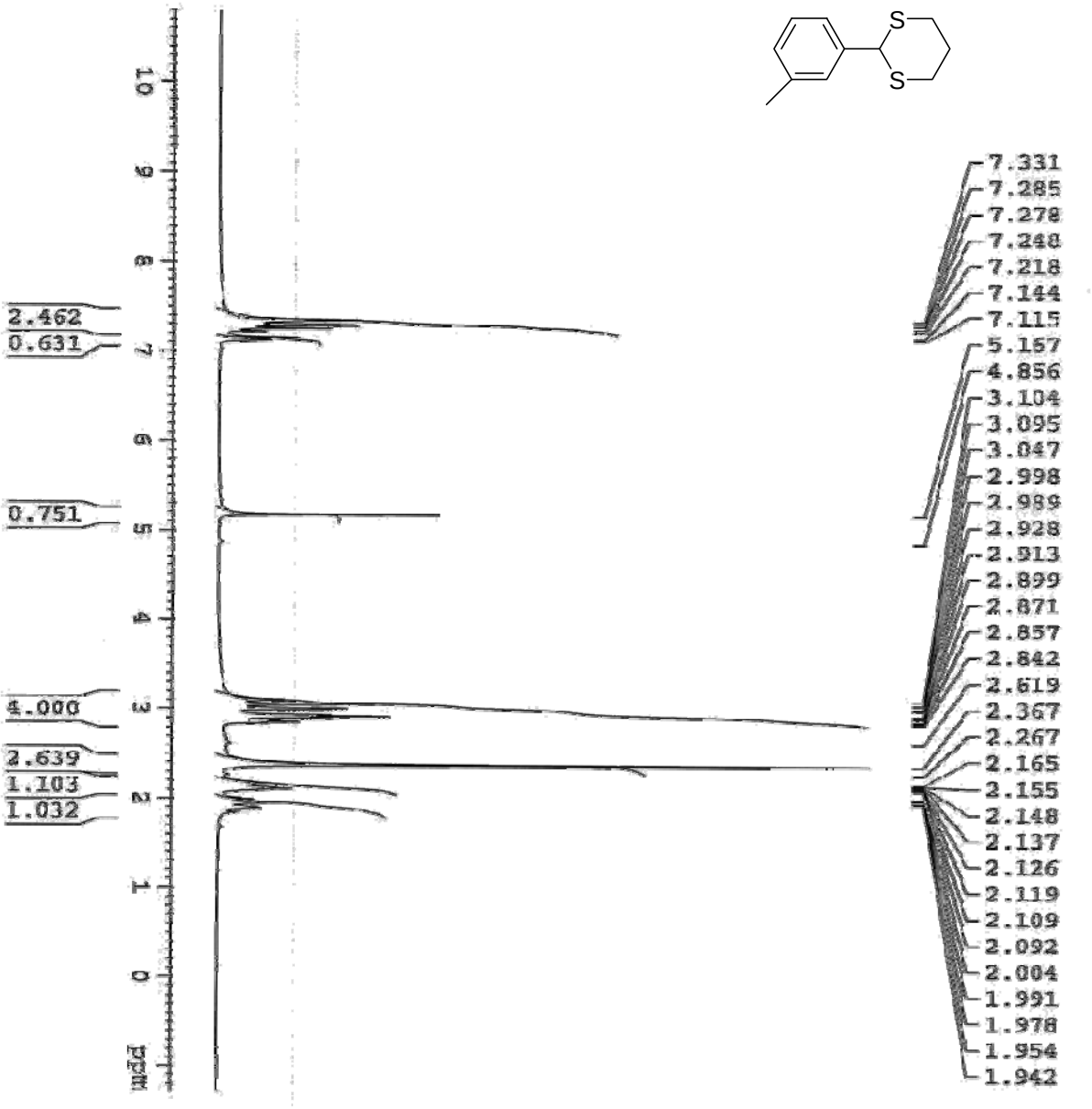

Table 1 (Entry 4)

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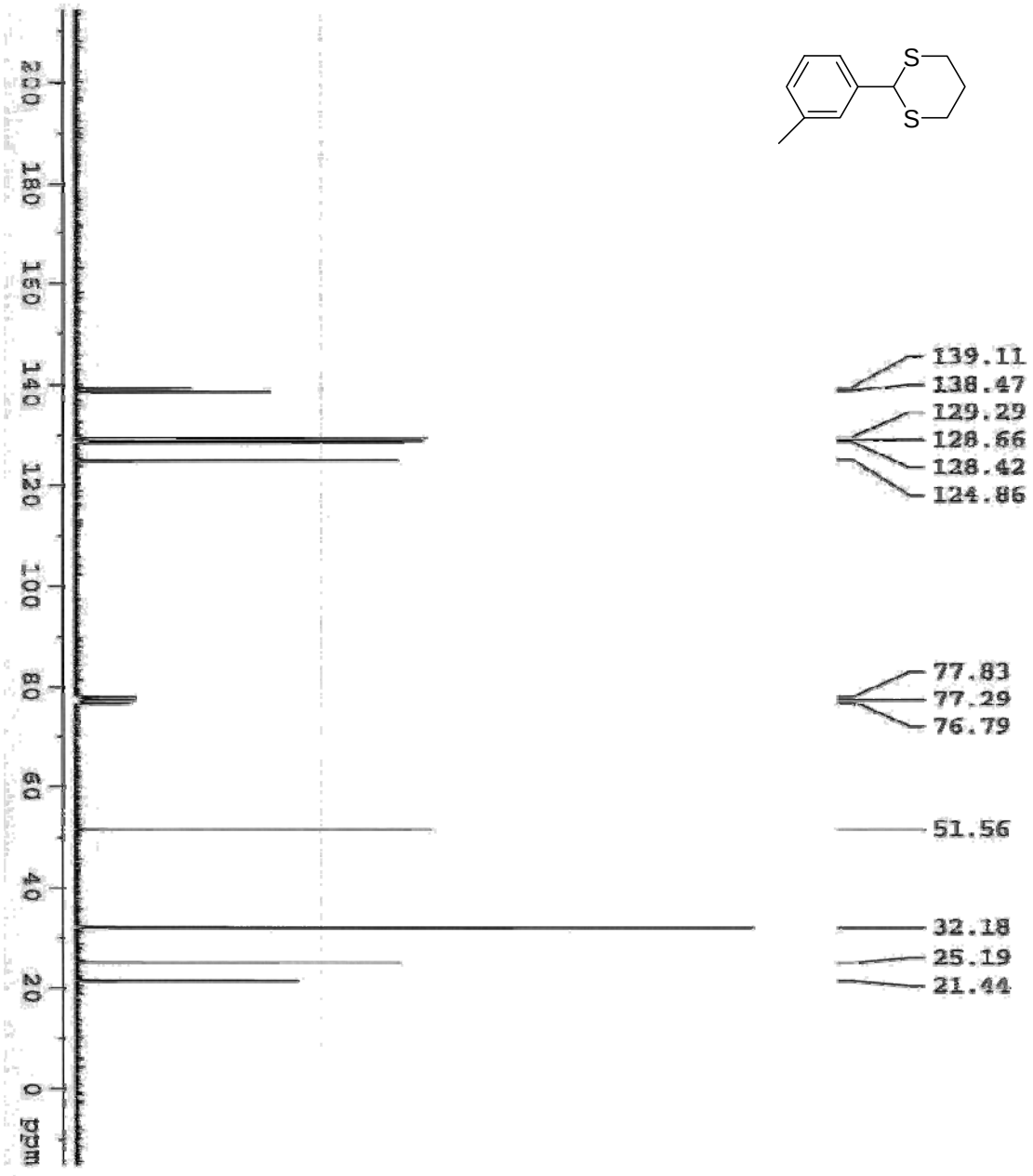


Table 1 (Entry 4)

Solvent: $CDCl_3$ – Frequency: 250 MHz

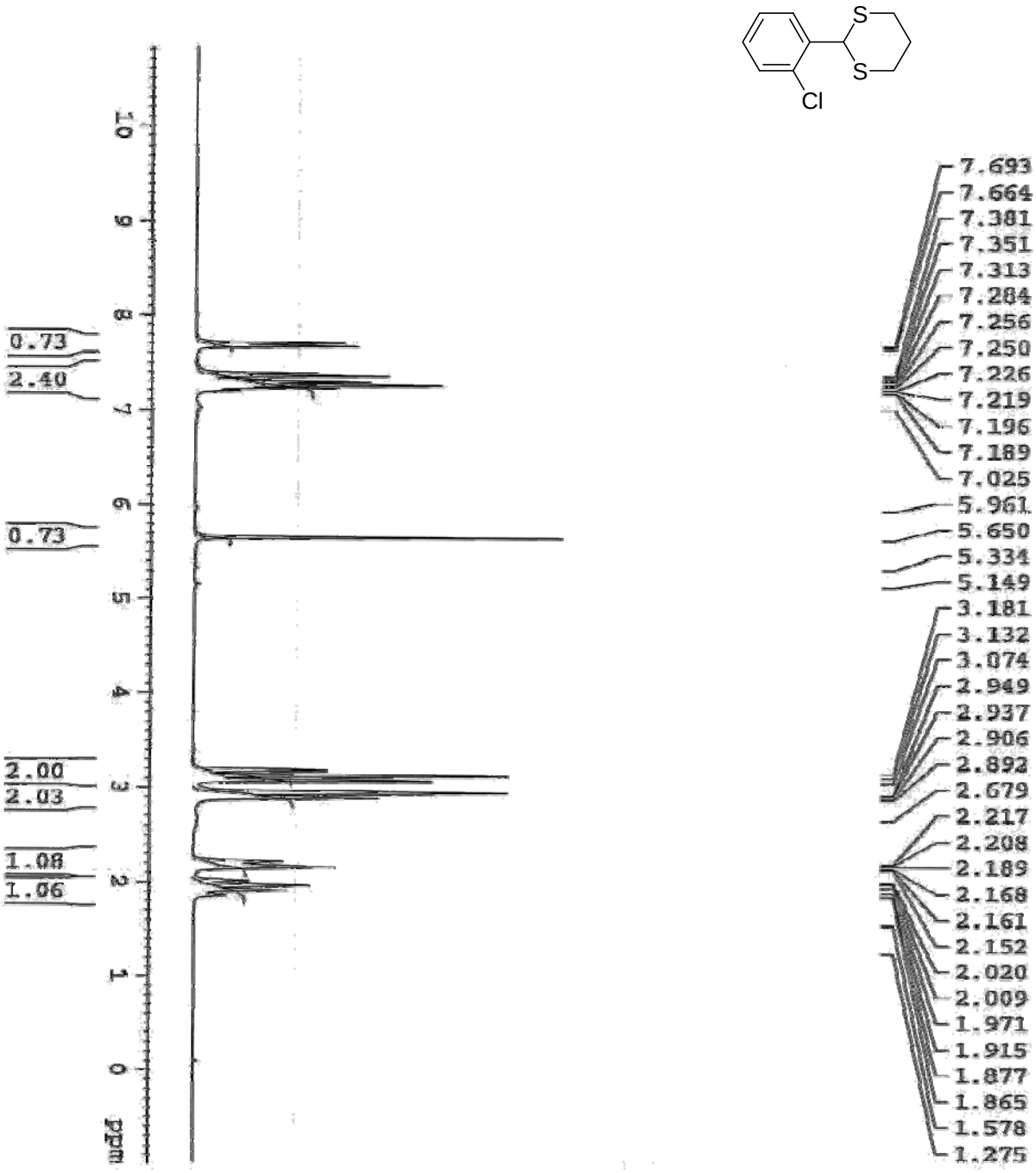


Table 1 (Entry 5)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

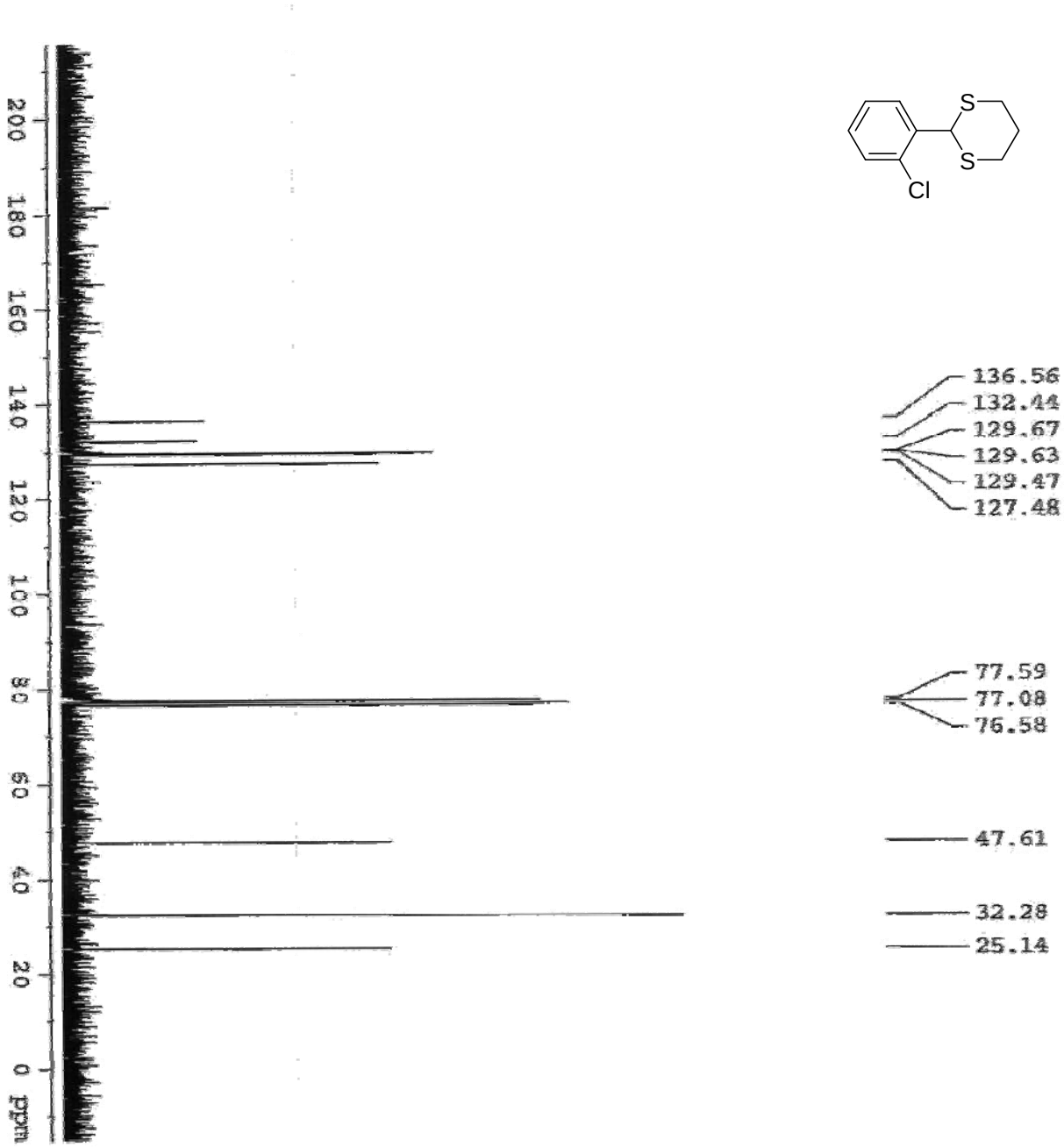


Table 1 (Entry 5)

Solvent: $CDCl_3$ – Frequency: 250 MHz

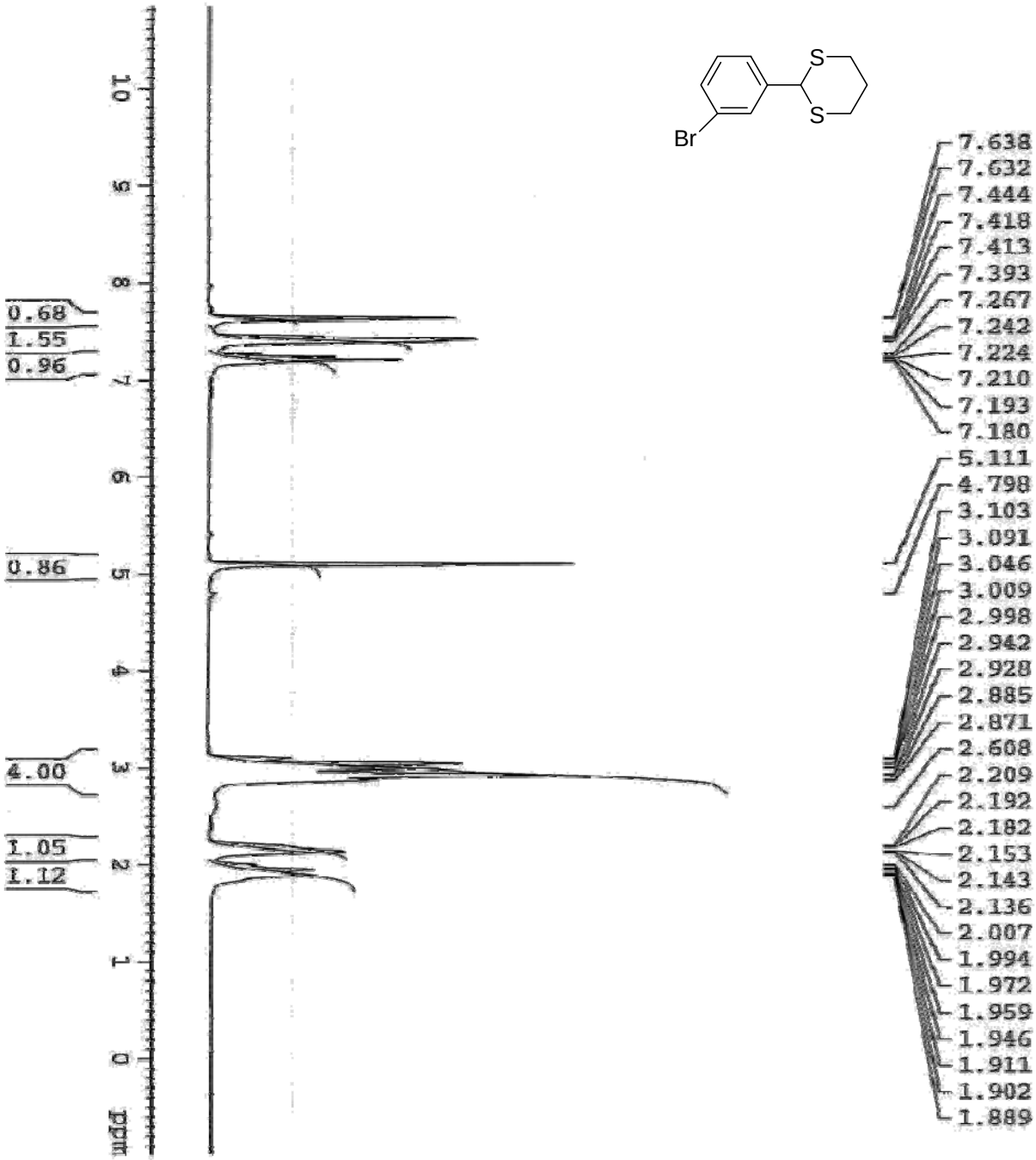


Table 1 (Entry 6)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

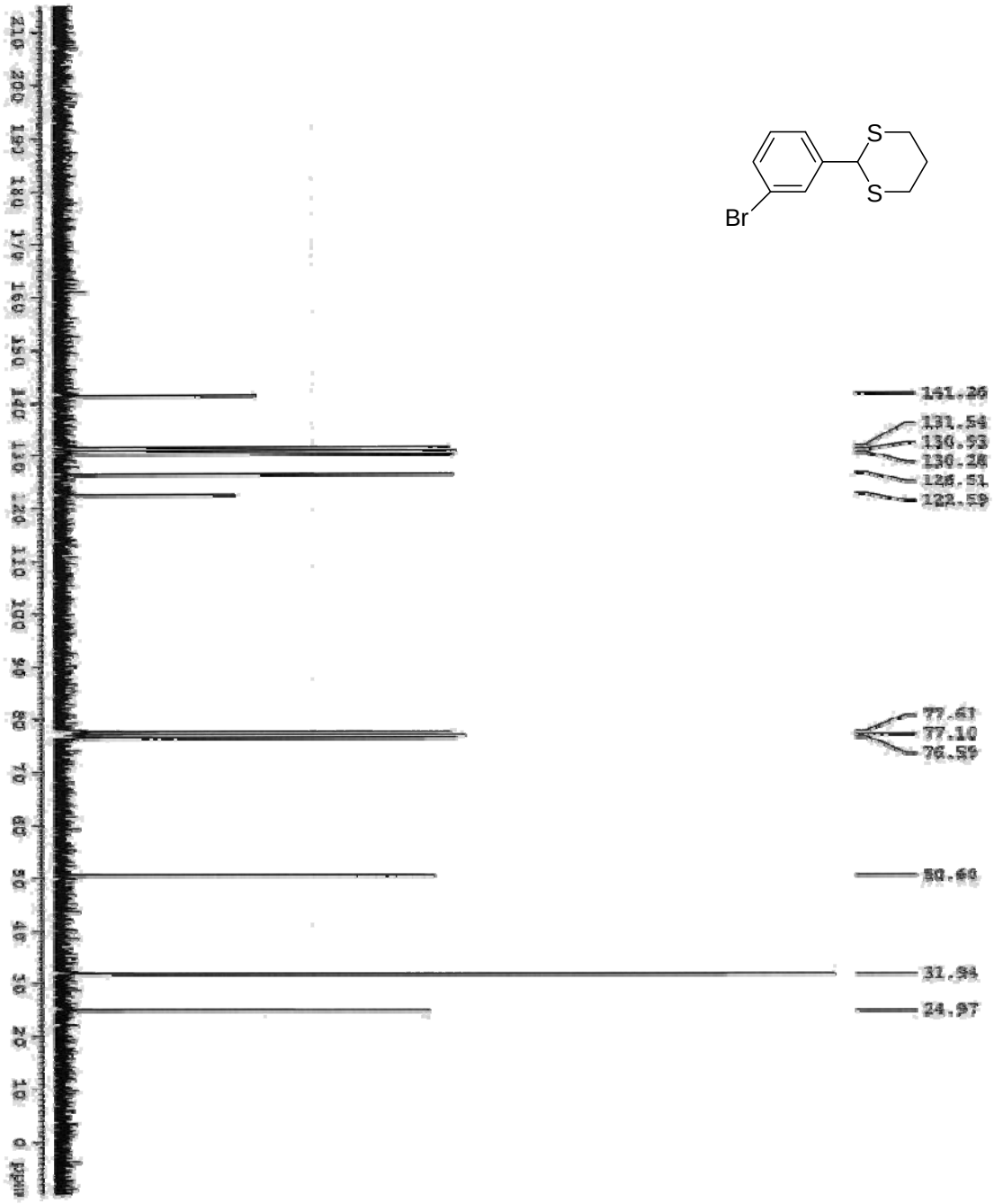


Table 1 (Entry 6)

Solvent: $CDCl_3$ – Frequency: 250 MHz

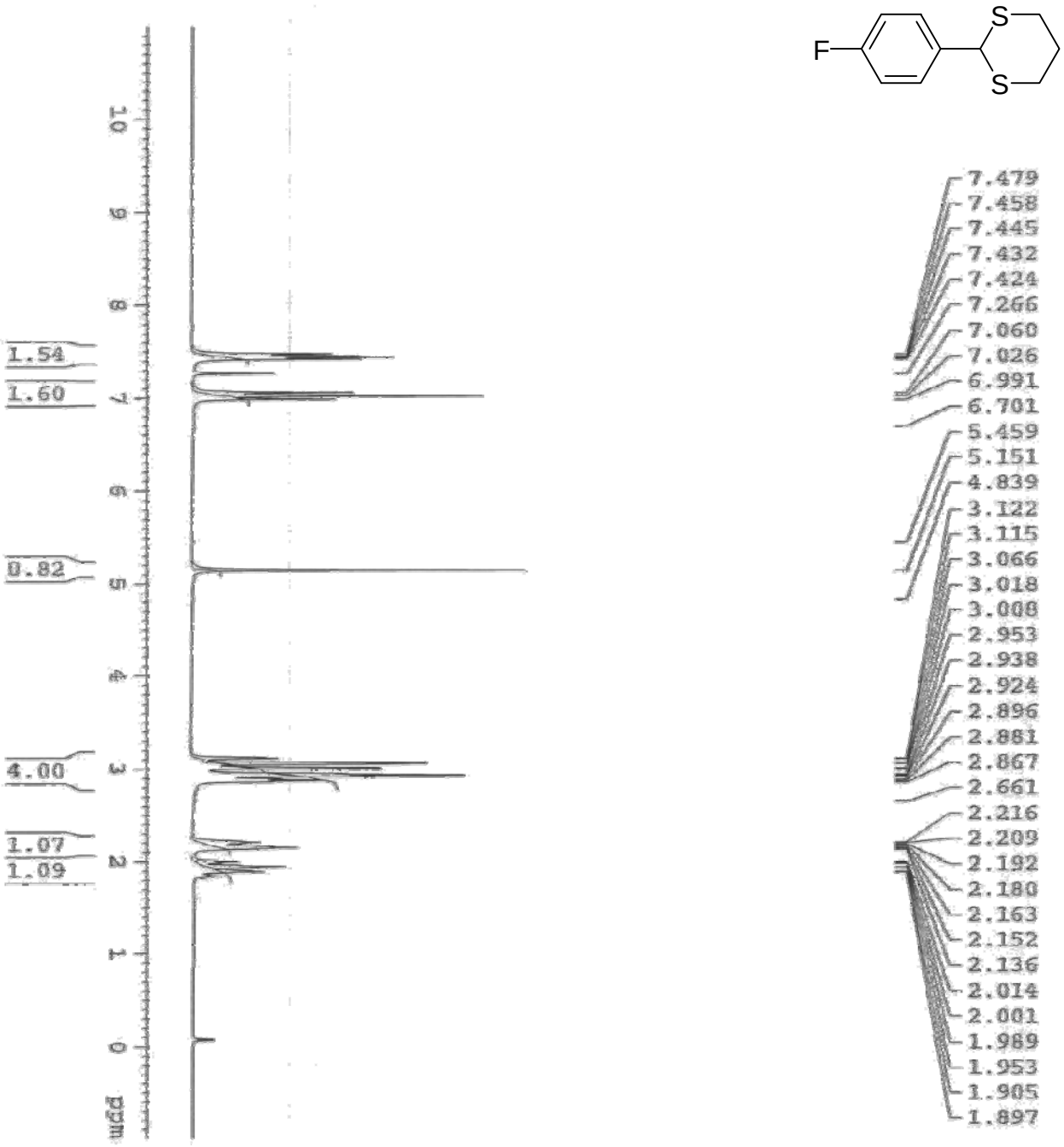


Table 1 (Entry 7)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

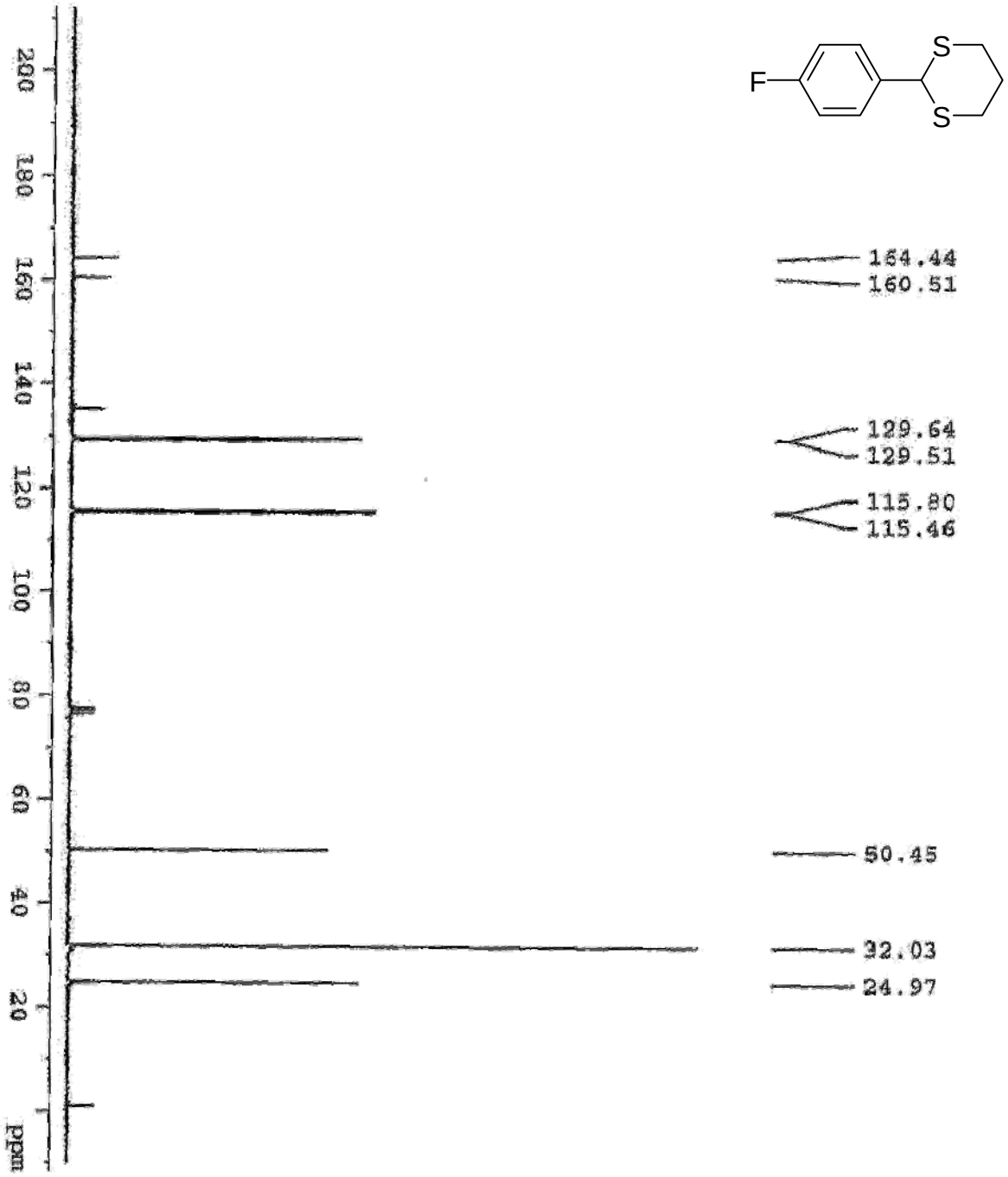


Table 1 (Entry 7)

Solvent: $CDCl_3$ – Frequency: 250 MHz

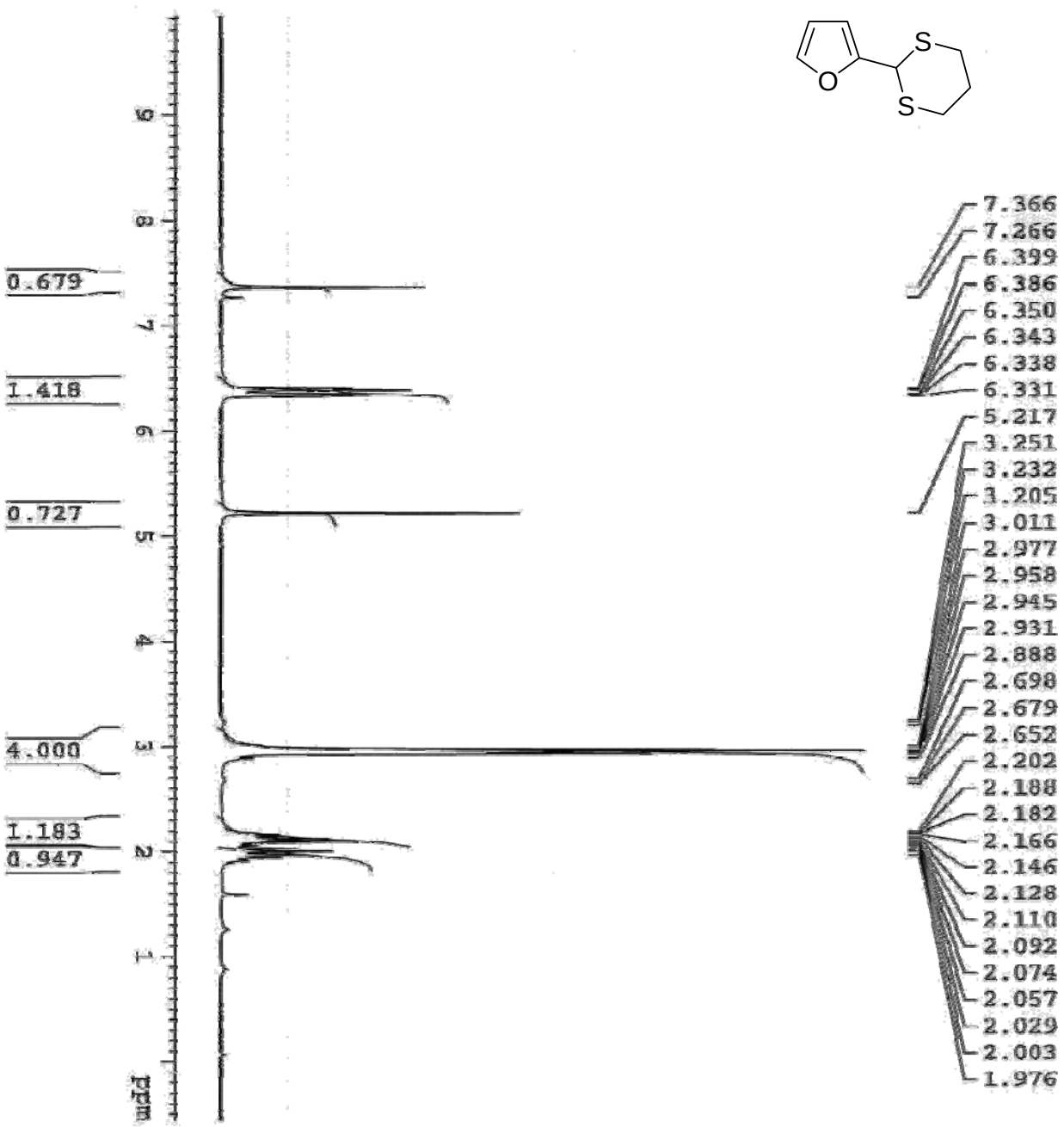


Table 1 (Entry 8)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

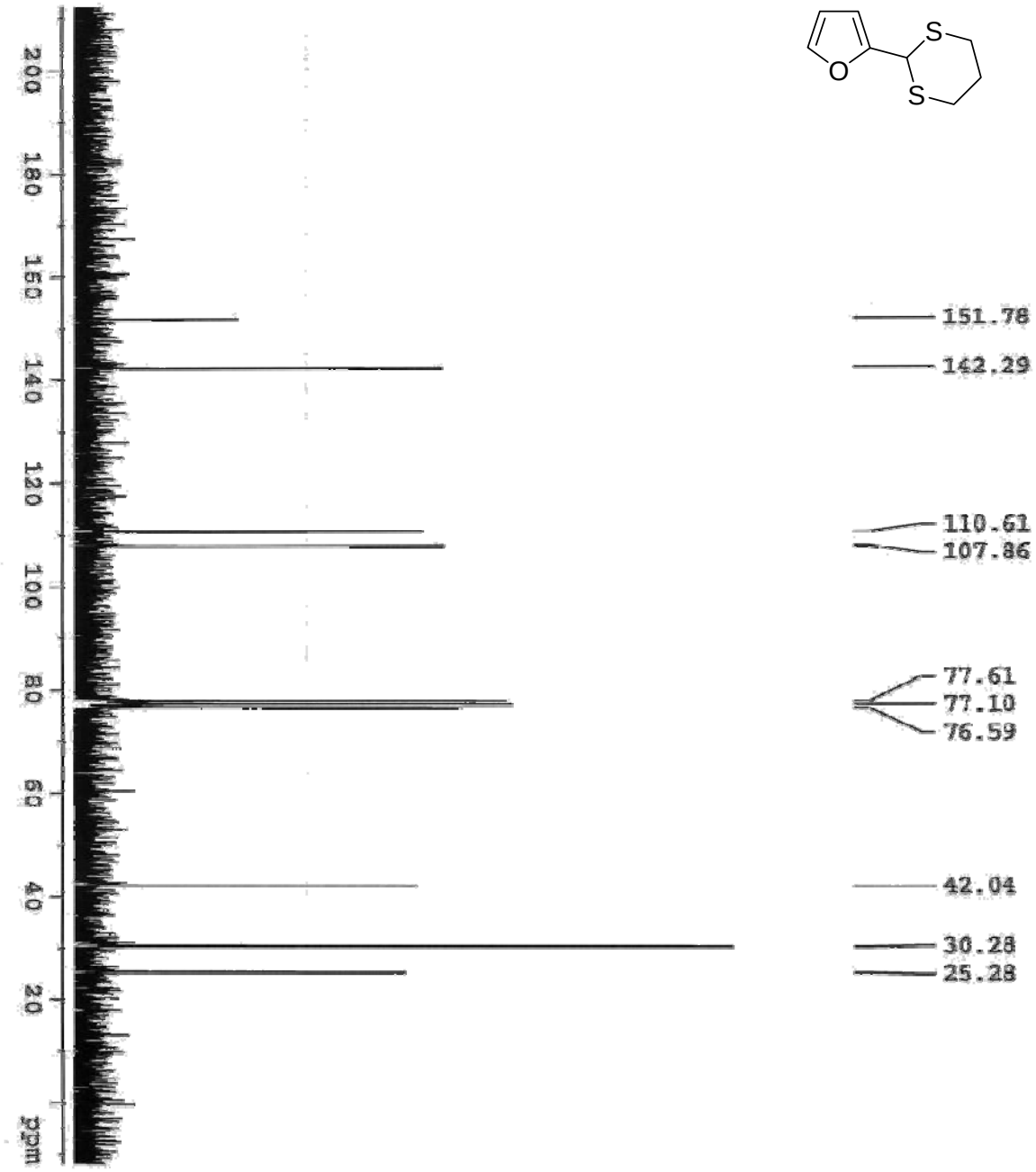


Table 1 (Entry 8)

Solvent: $CDCl_3$ – Frequency: 250 MHz

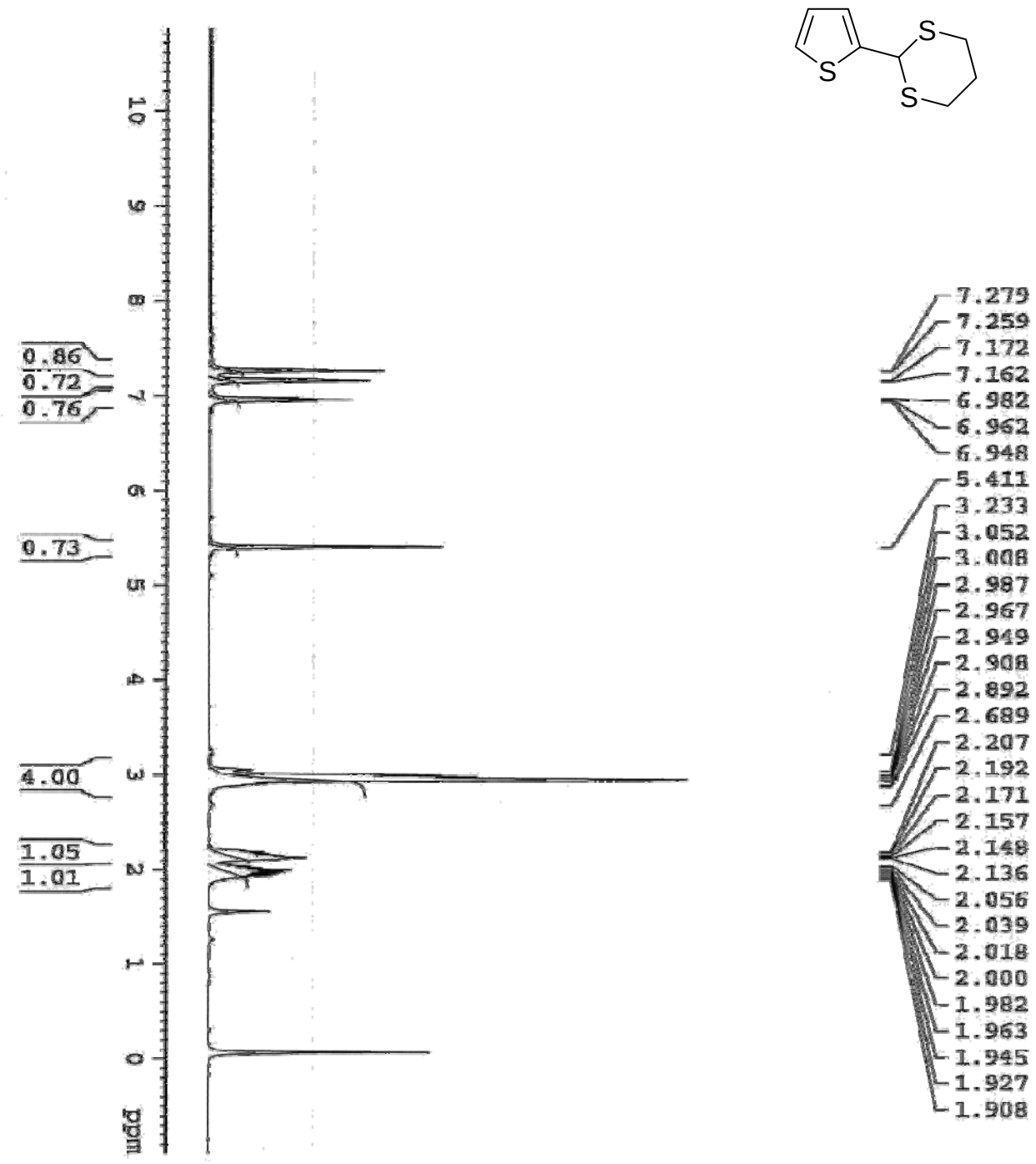


Table 1 (Entry 9)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

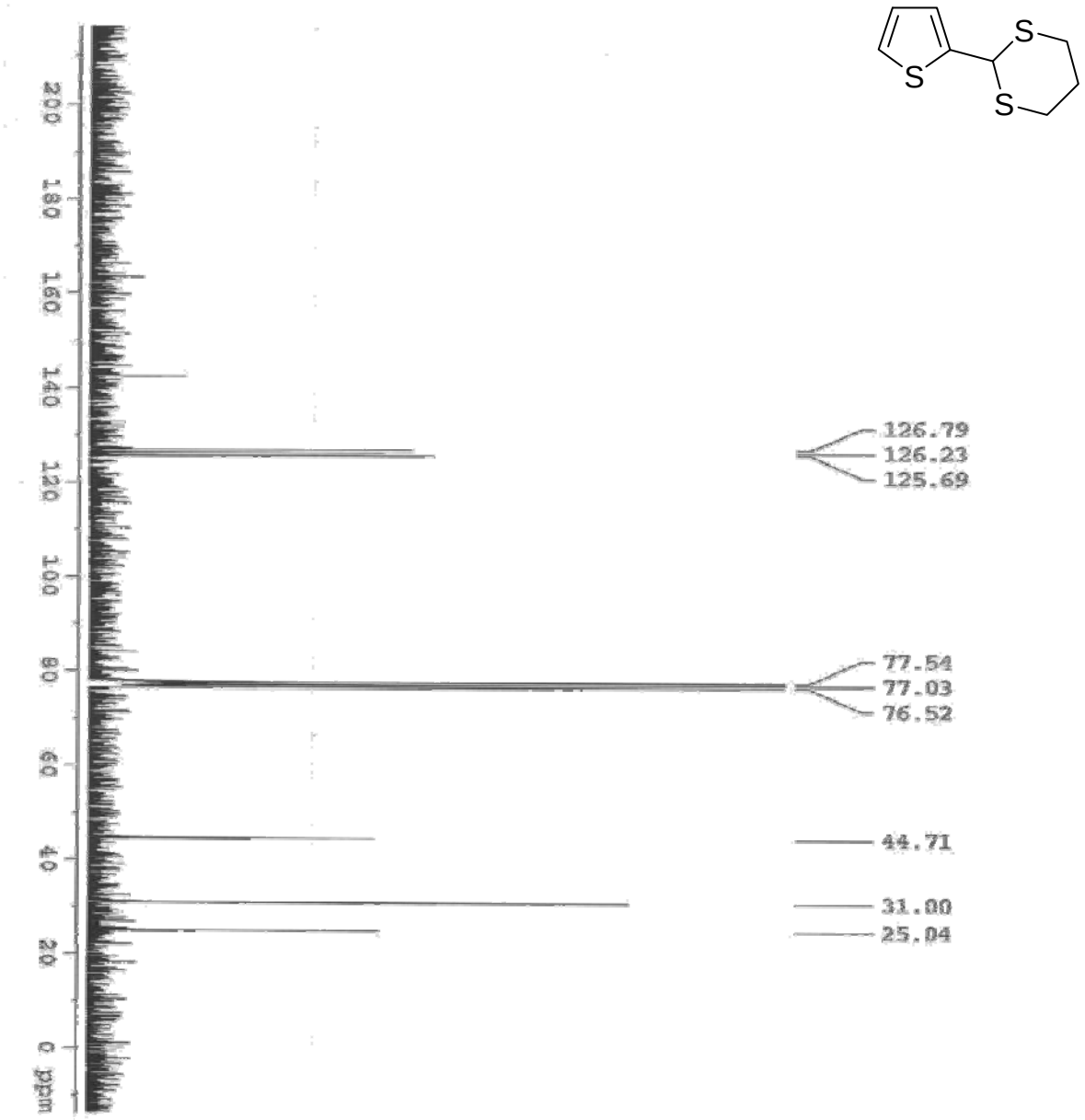


Table 1 (Entry 9)

Solvent: $CDCl_3$ – Frequency: 250 MHz

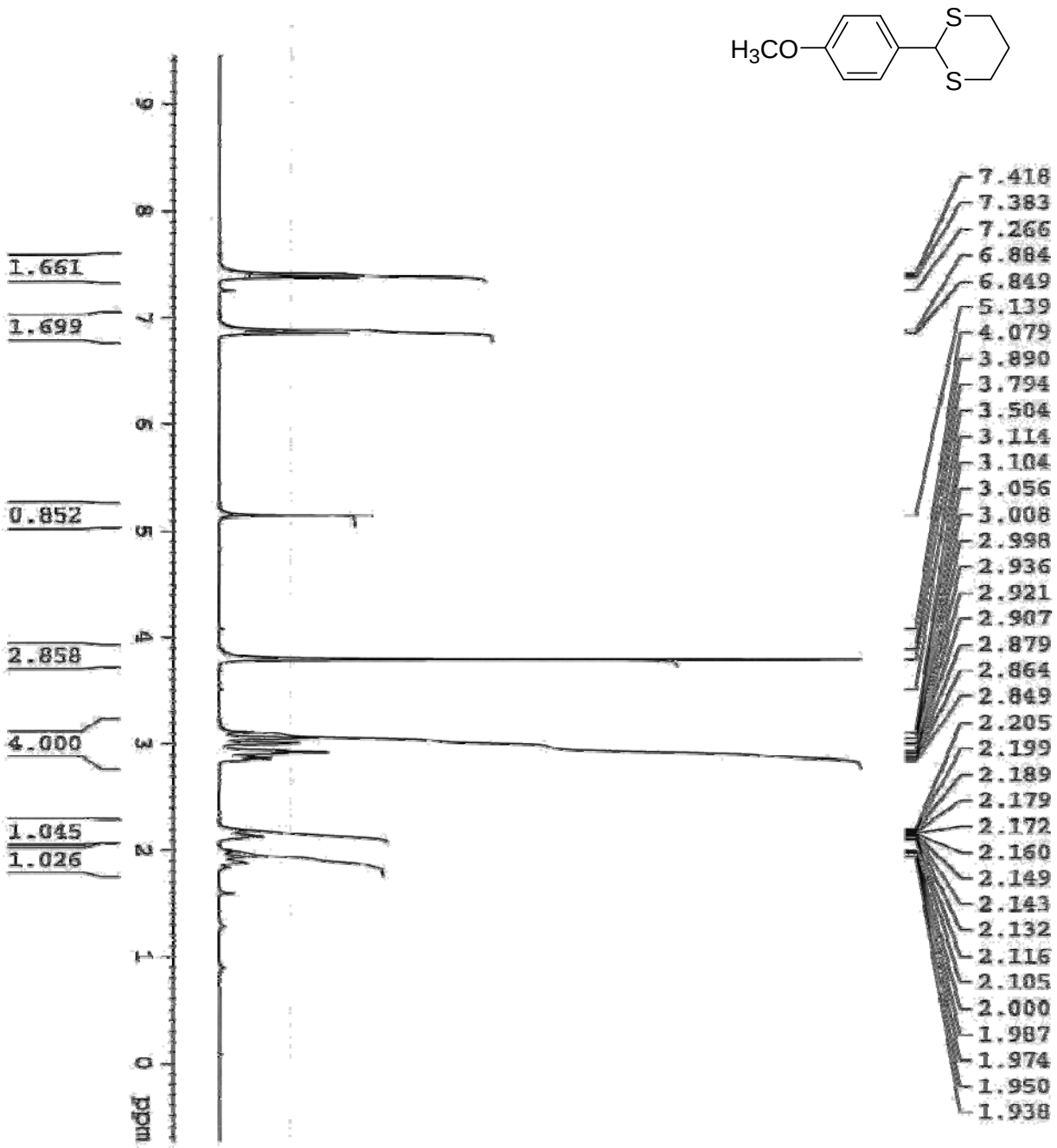


Table 1 (Entry 10)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

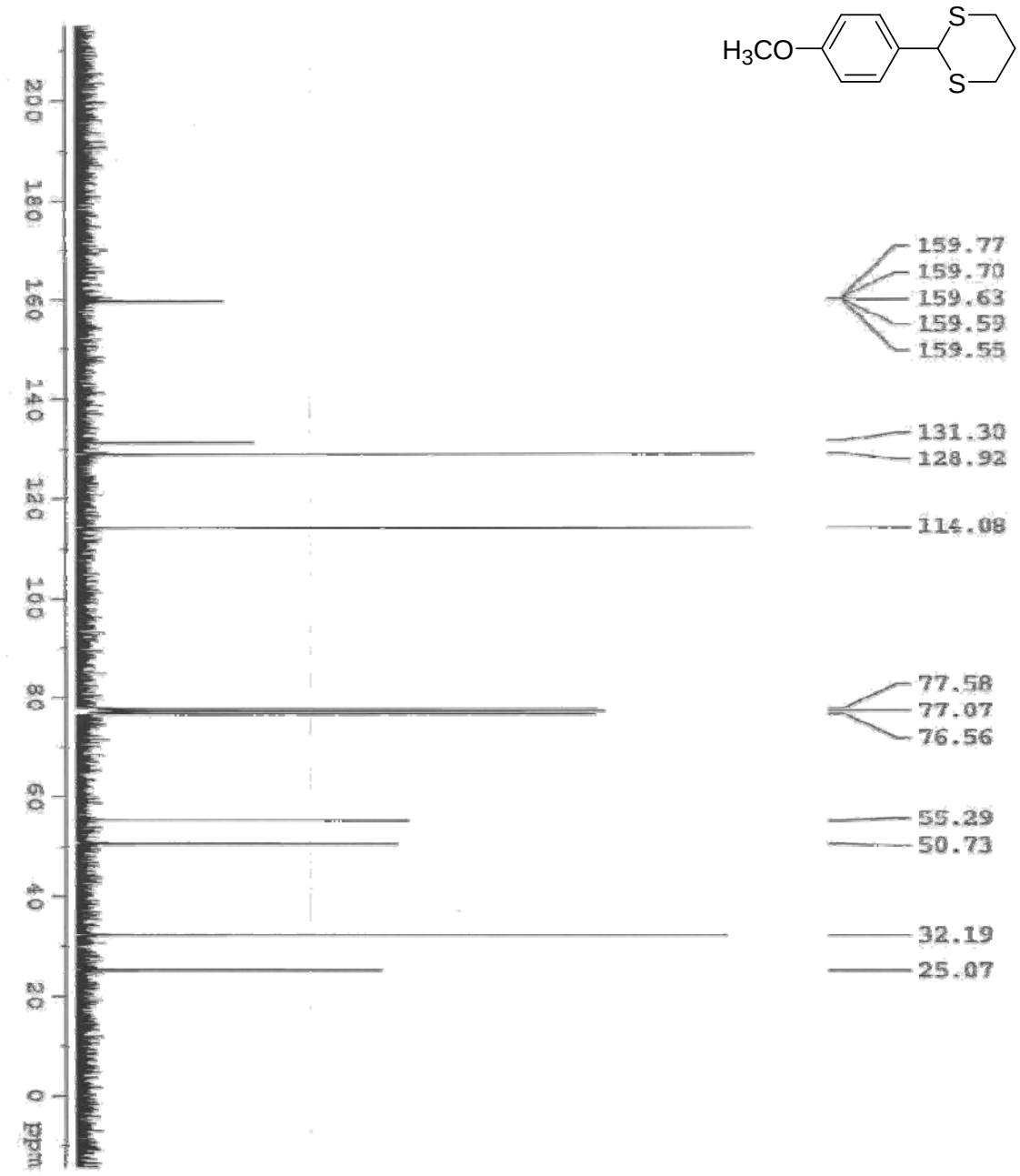


Table 1 (Entry 10)

Solvent: $CDCl_3$ – Frequency: 250 MHz

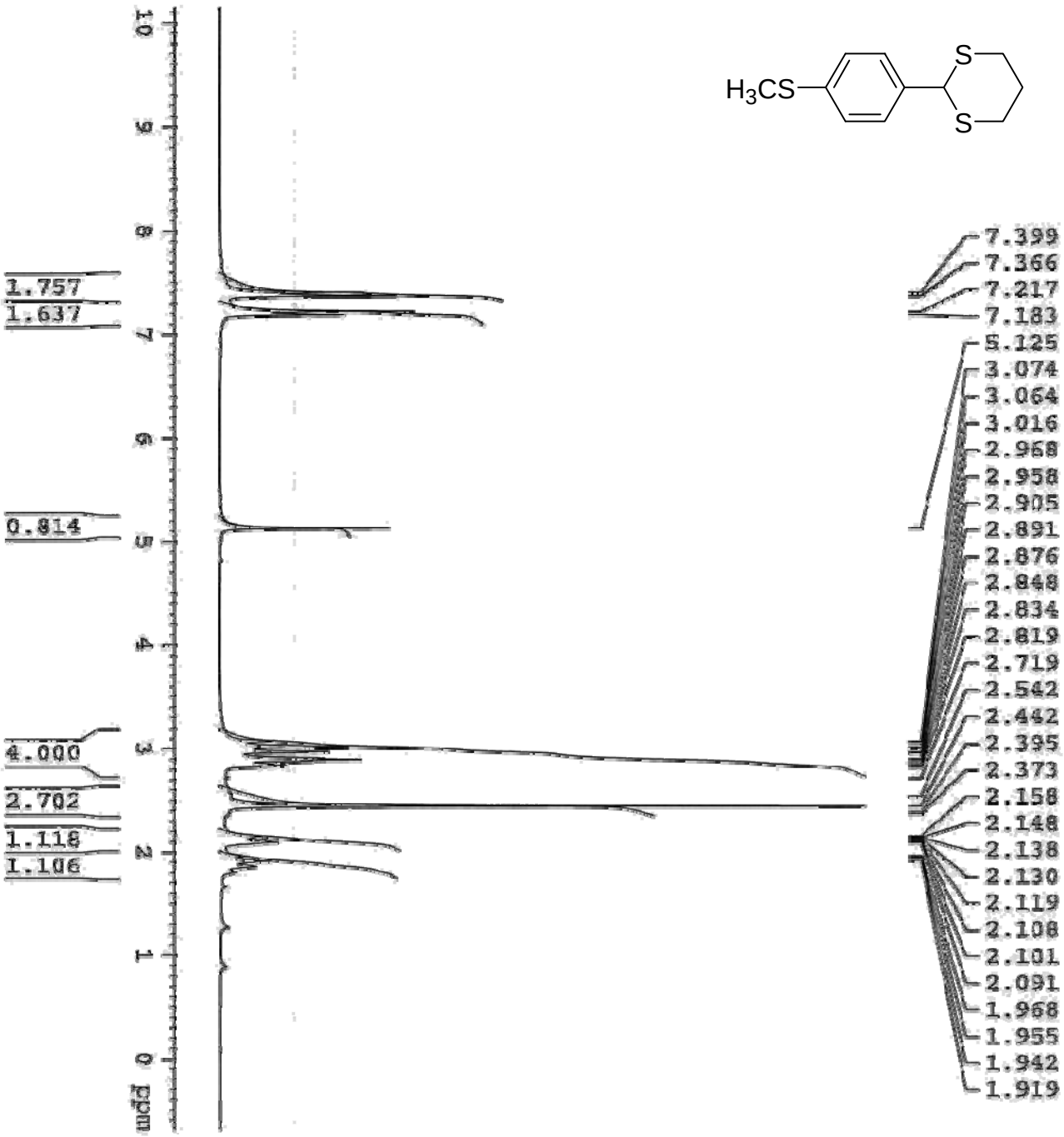


Table 1 (Entry 11)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

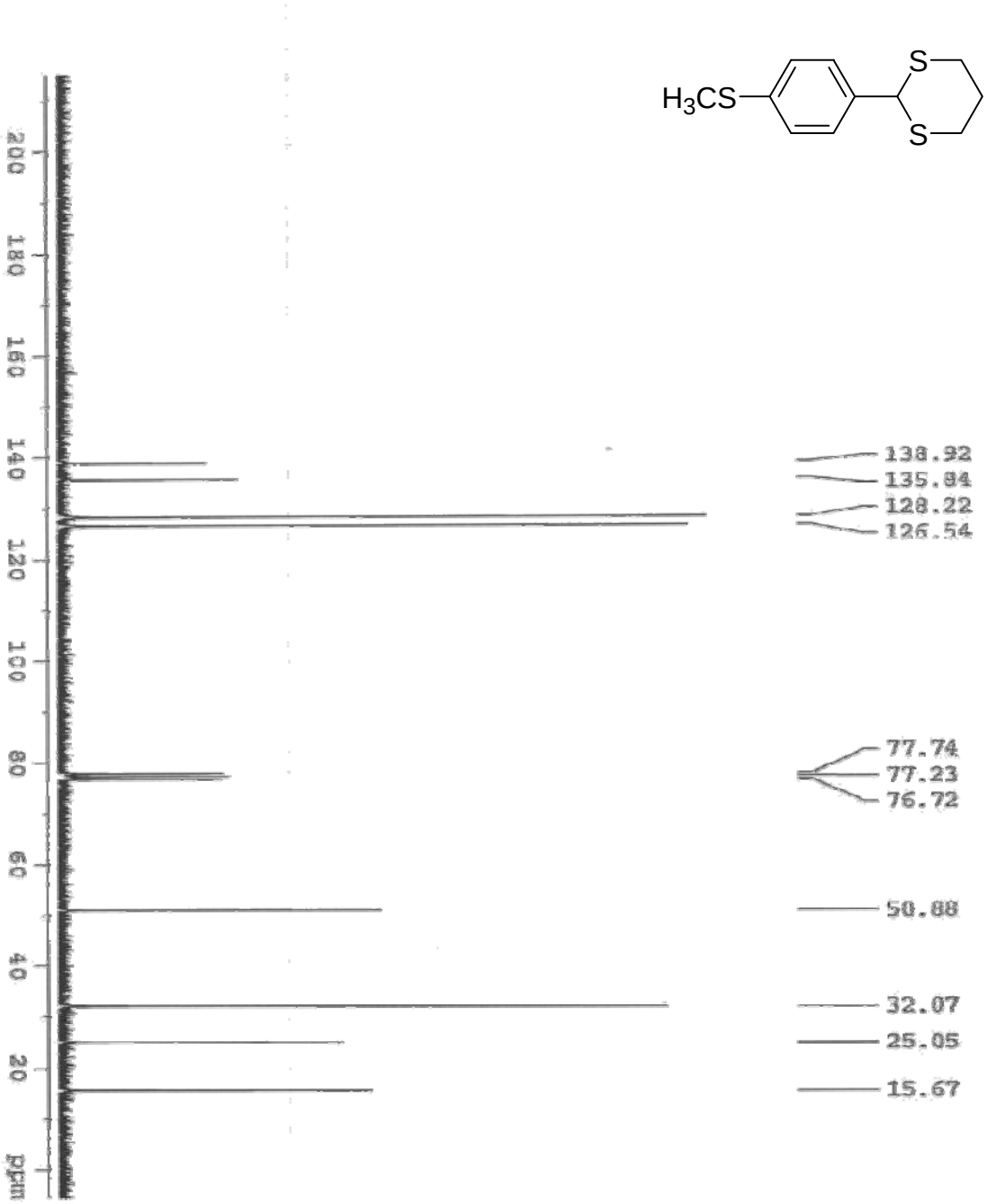


Table 1 (Entry 11)

Solvent: $CDCl_3$ – Frequency: 250 MHz

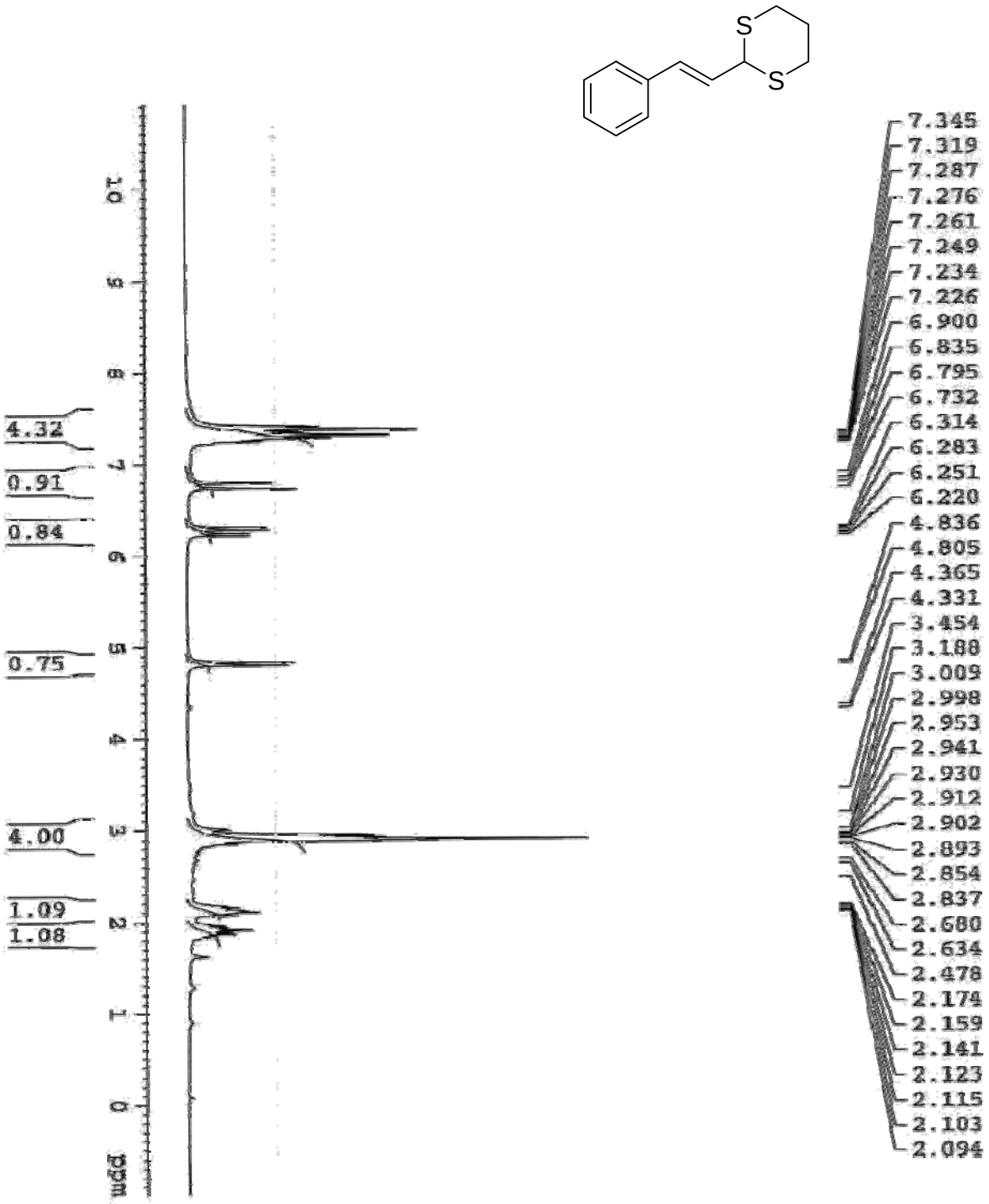


Table 1 (Entry 12)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

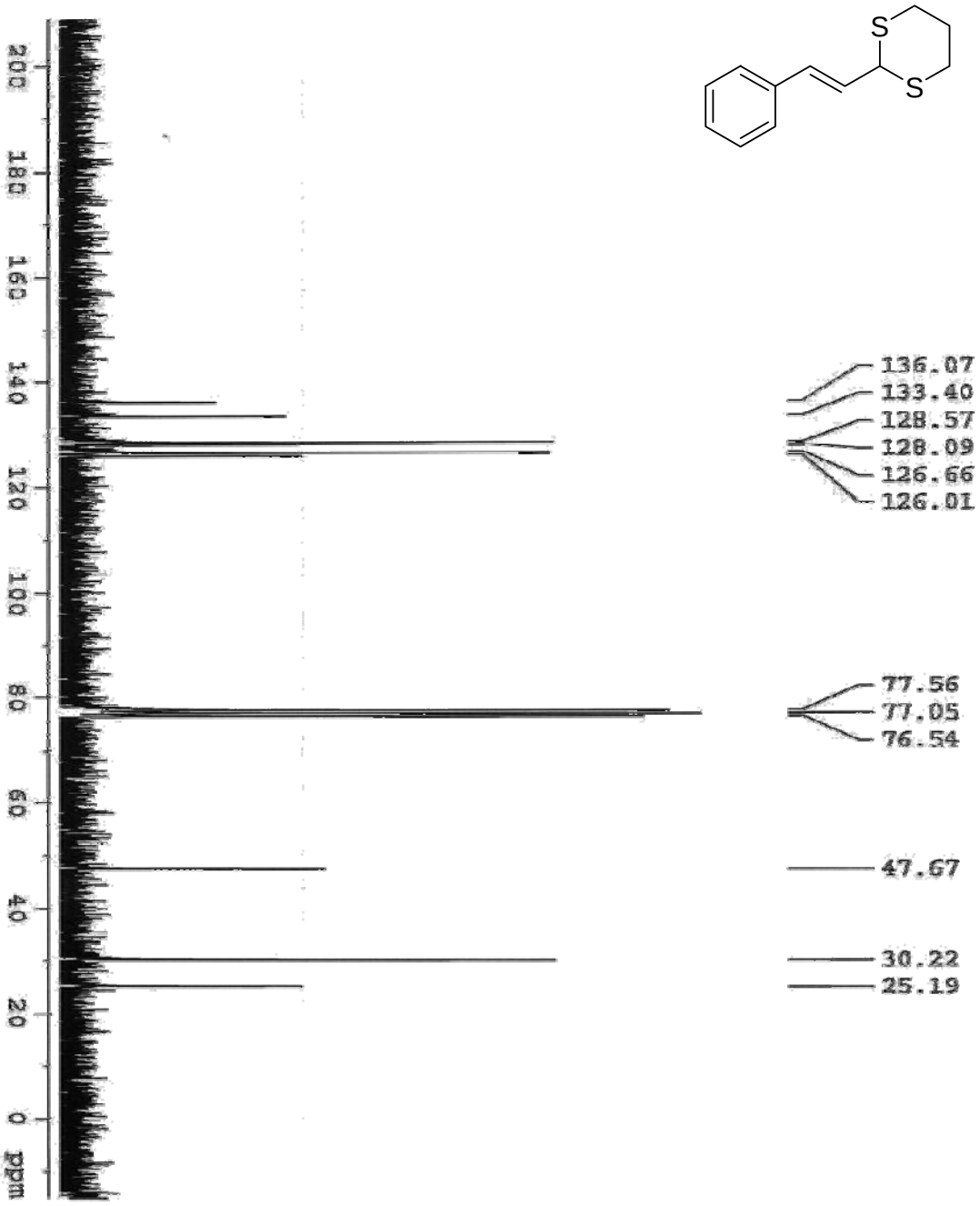


Table 1 (Entry 12)

Solvent: $CDCl_3$ – Frequency: 250 MHz

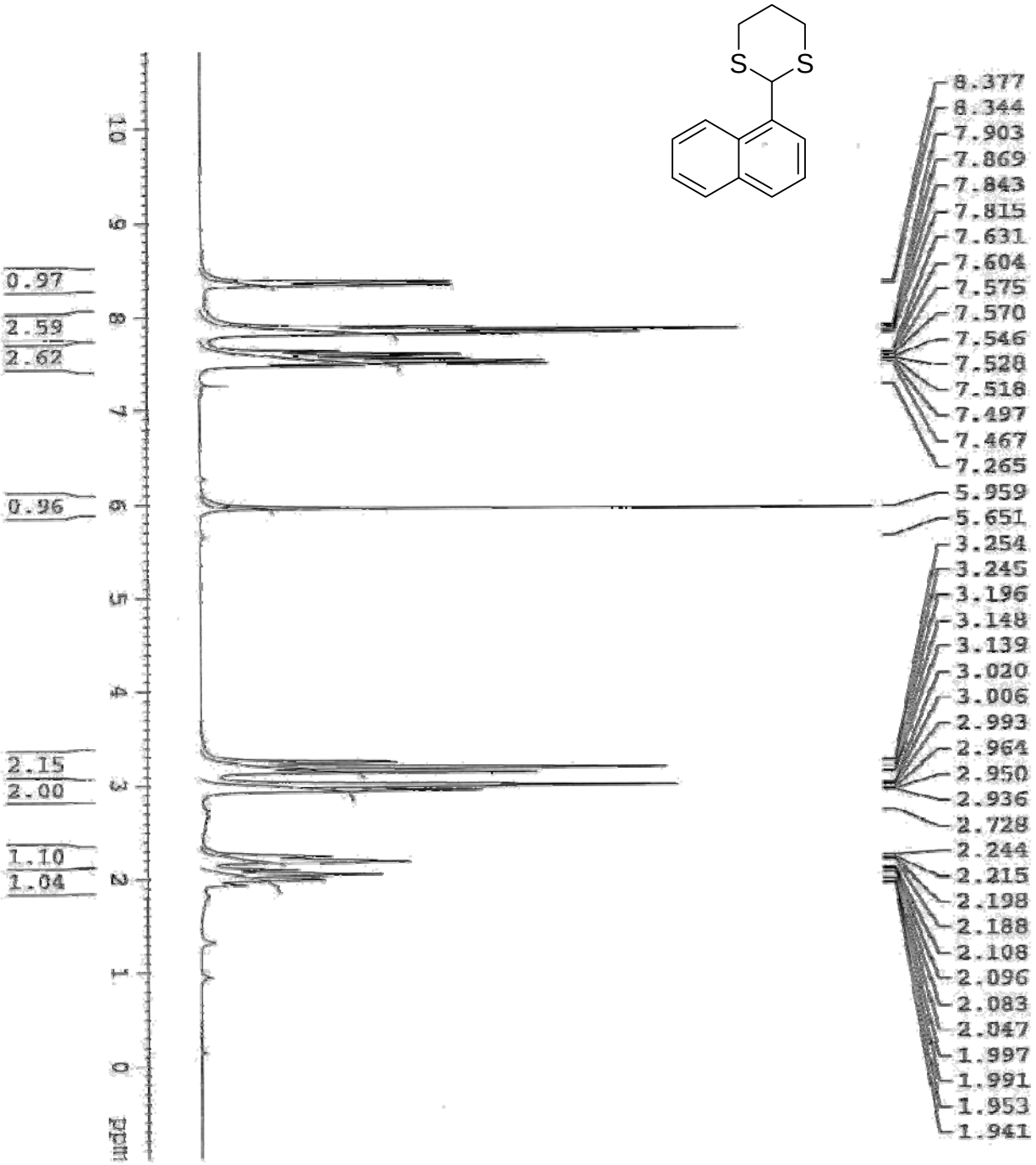


Table 1 (Entry 13)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

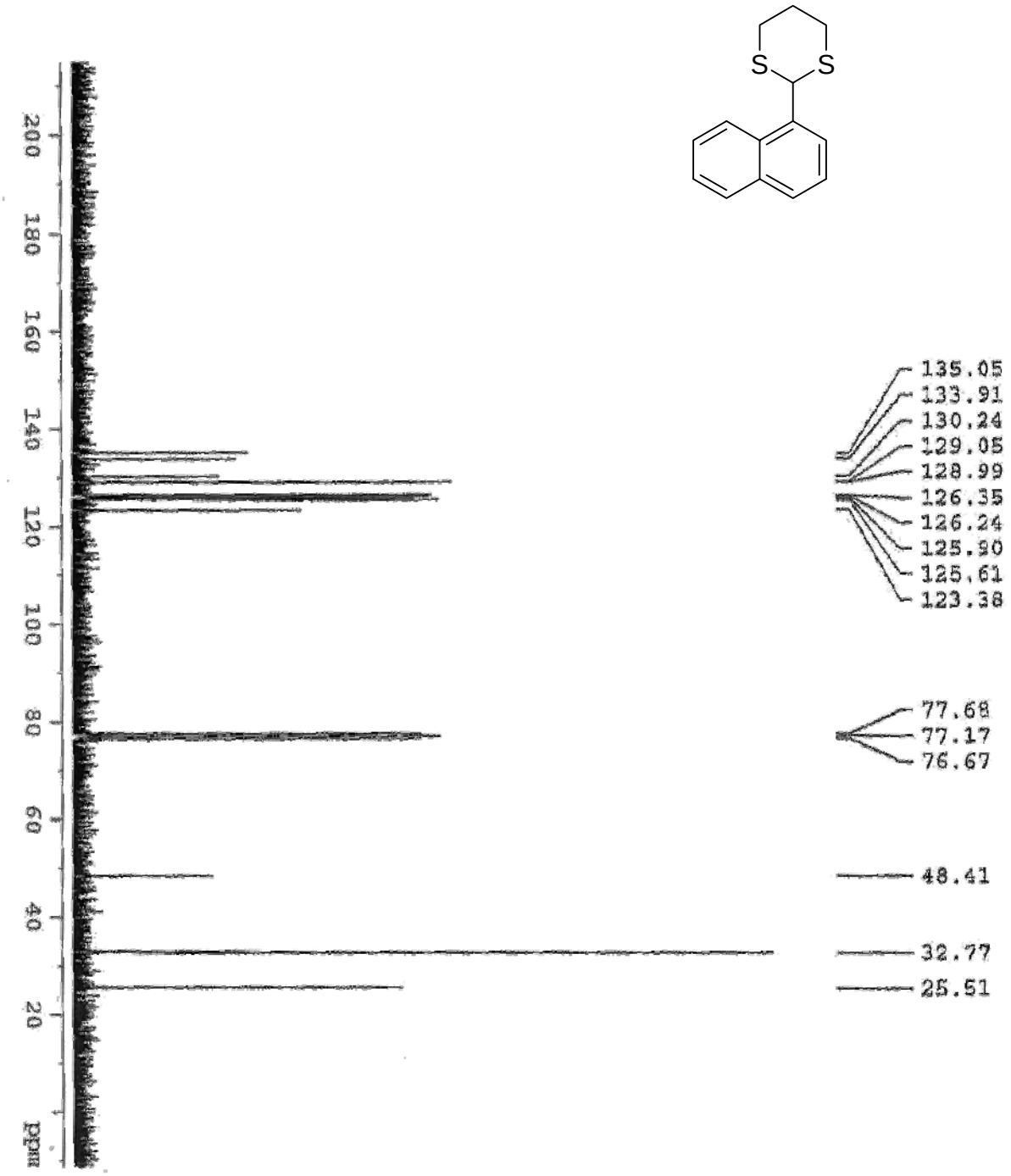


Table 1 (Entry 13)

Solvent: $CDCl_3$ – Frequency: 250 MHz

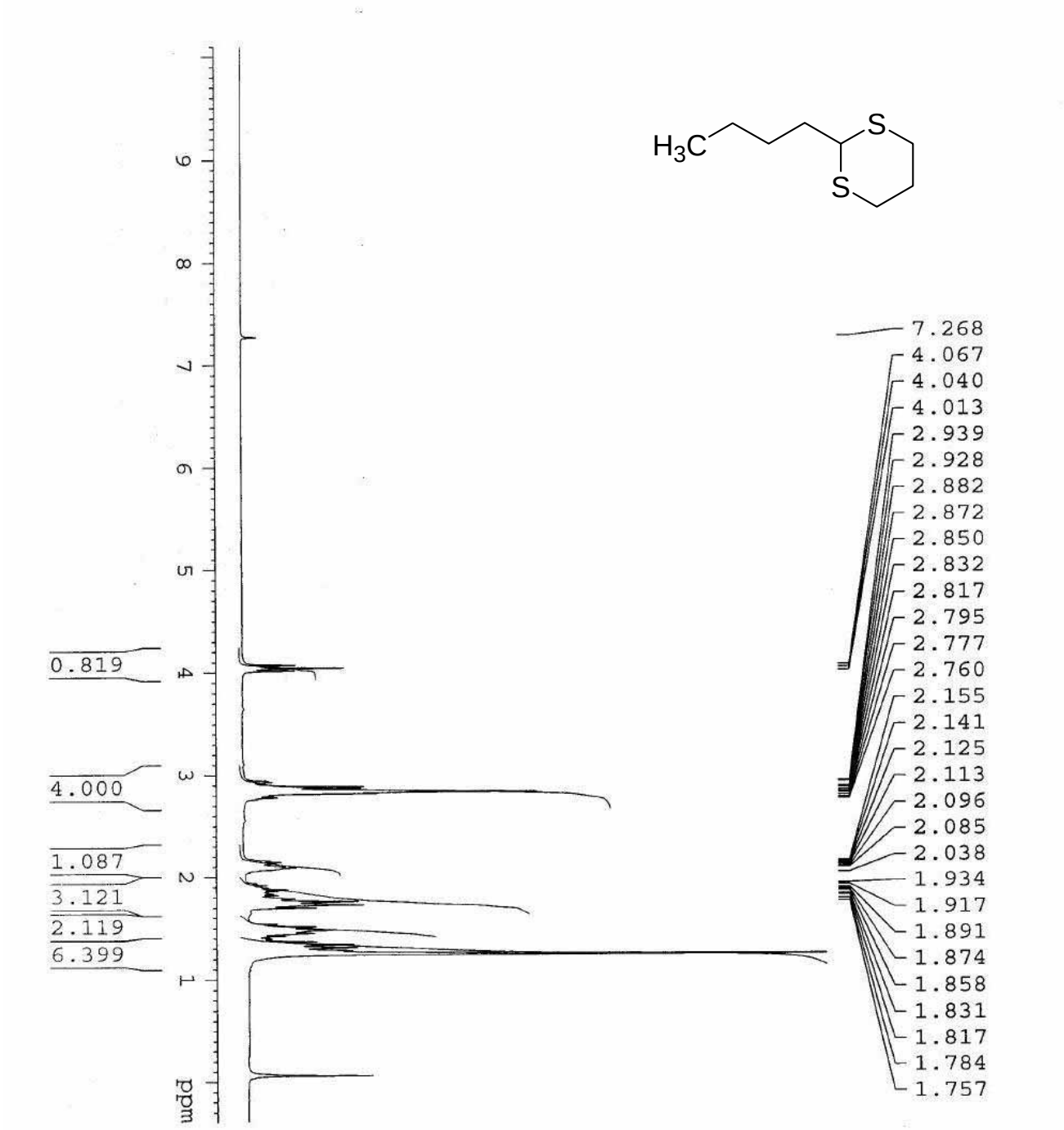


Table 1 (Entry 14)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

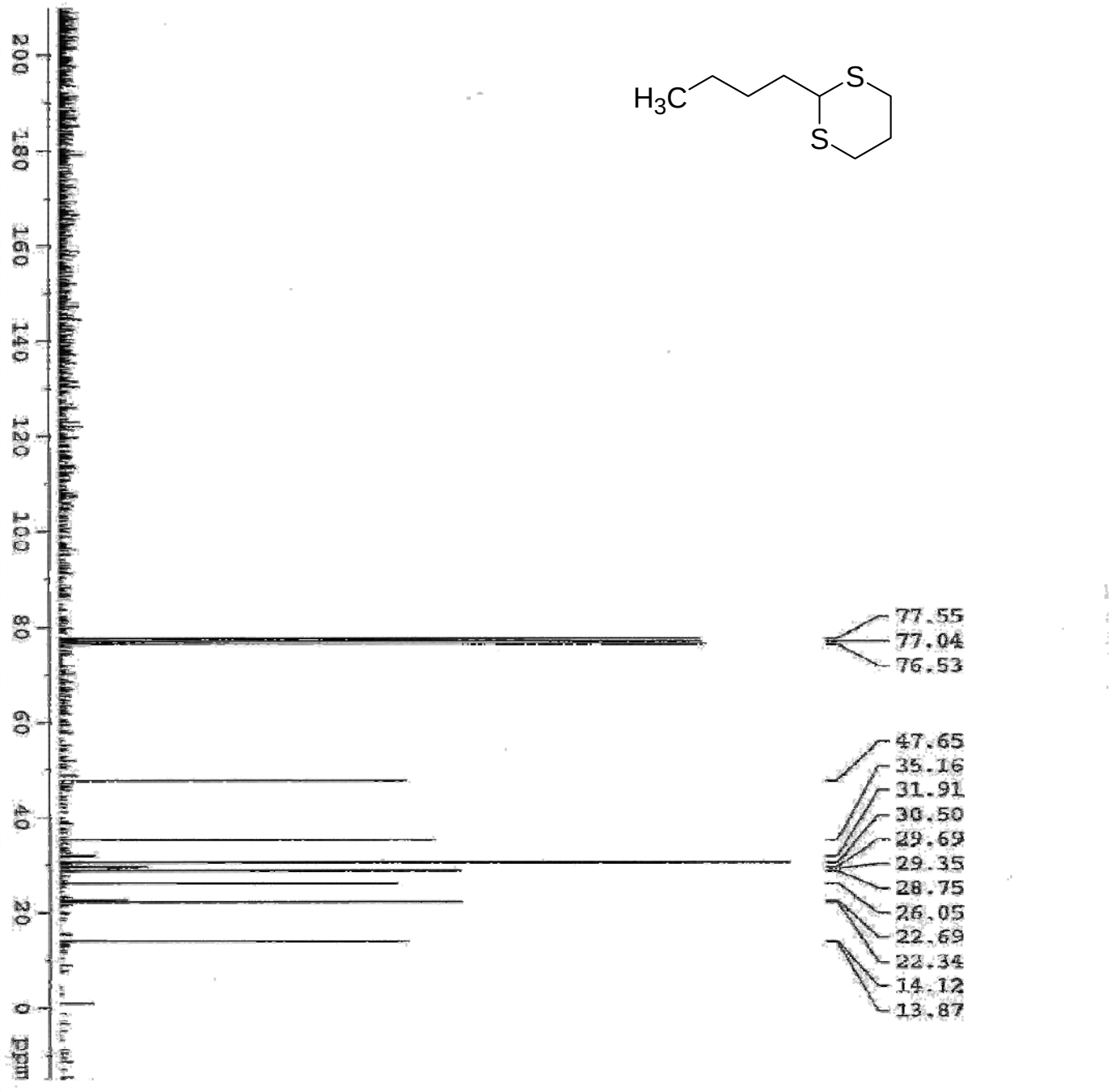


Table 1 (Entry 14)

Solvent: $CDCl_3$ – Frequency: 250 MHz

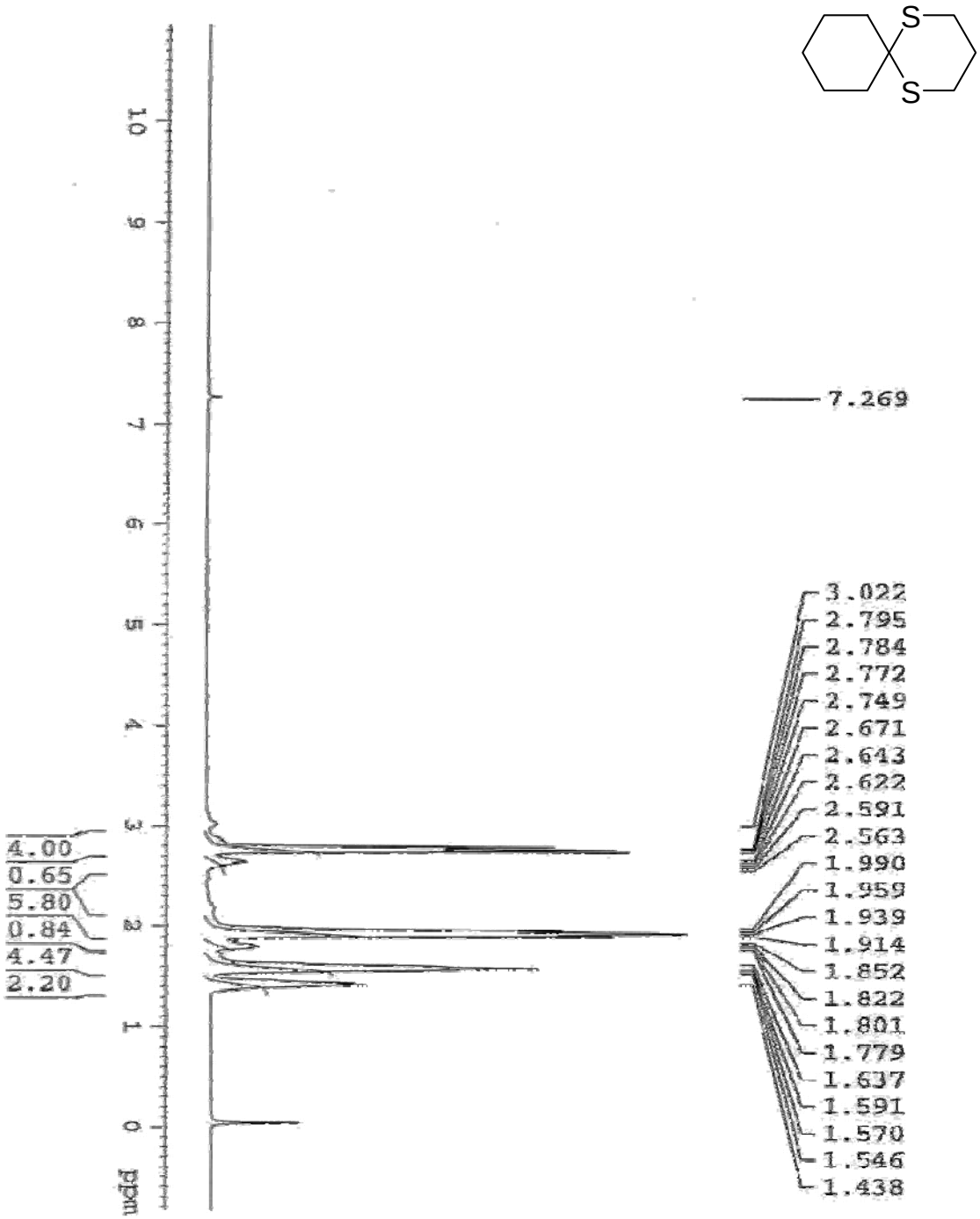


Table 1 (Entry 15)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

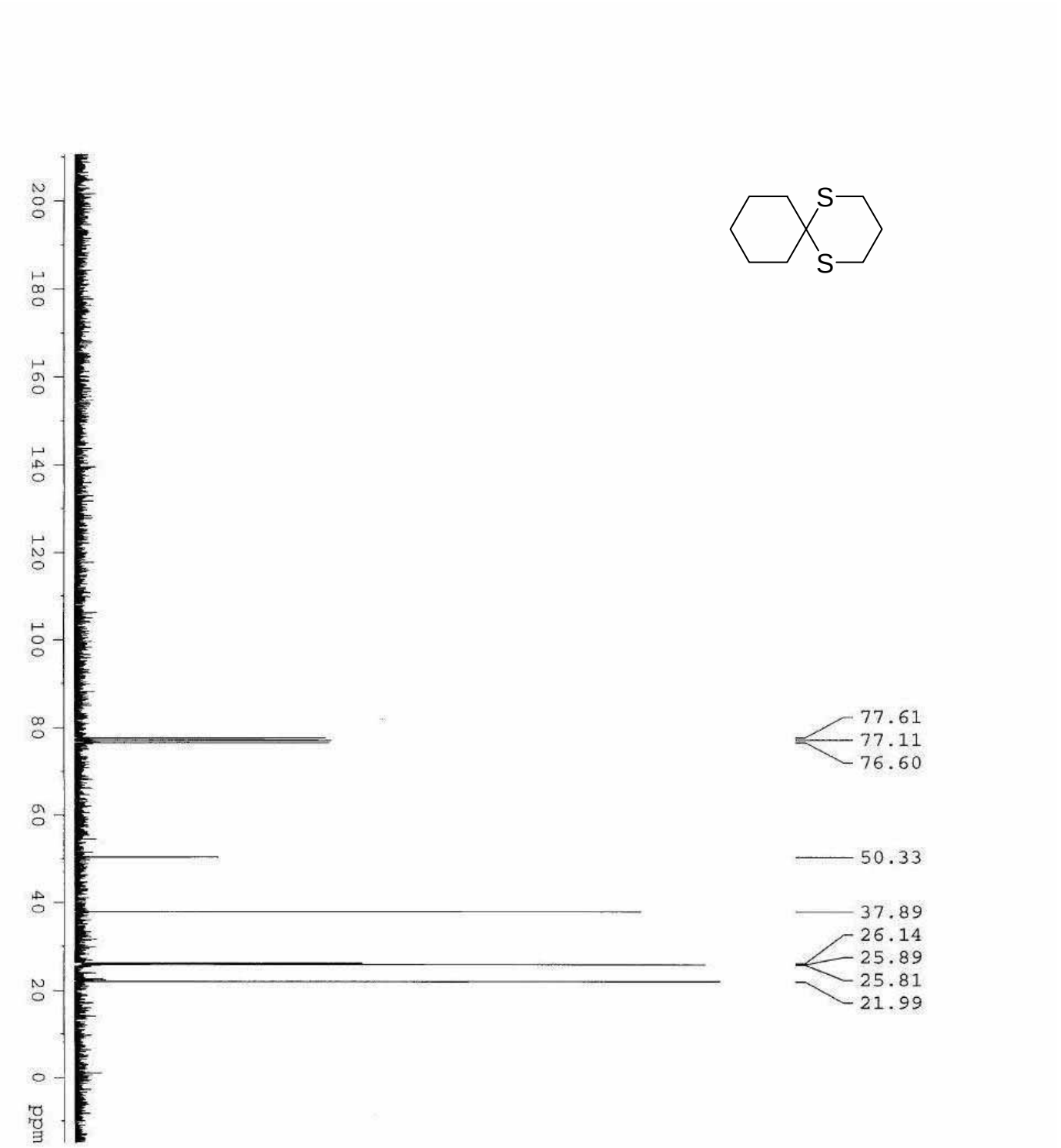


Table 1 (Entry 15)

Solvent: $CDCl_3$ – Frequency: 250 MHz

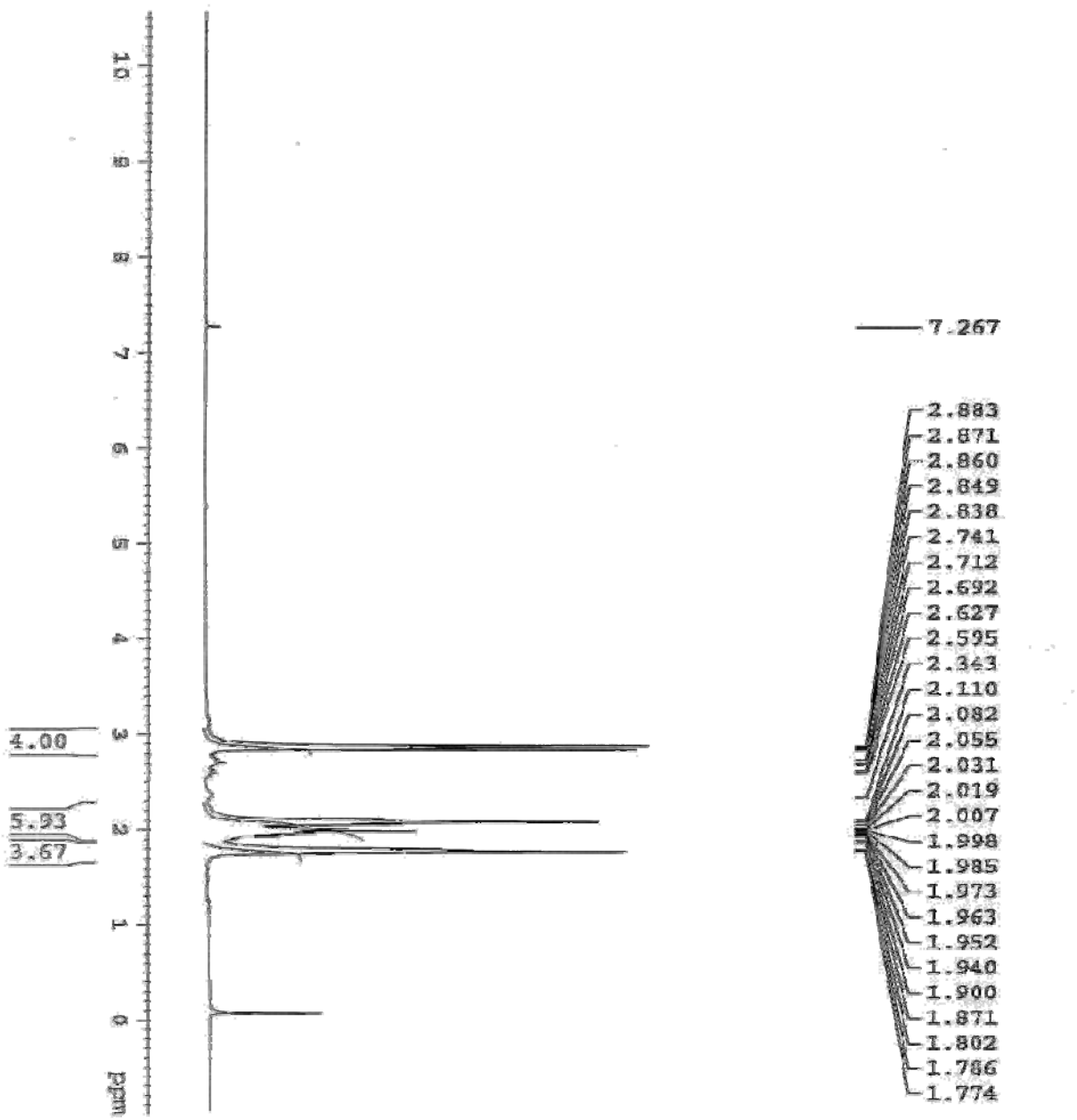


Table 1 (Entry 16)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

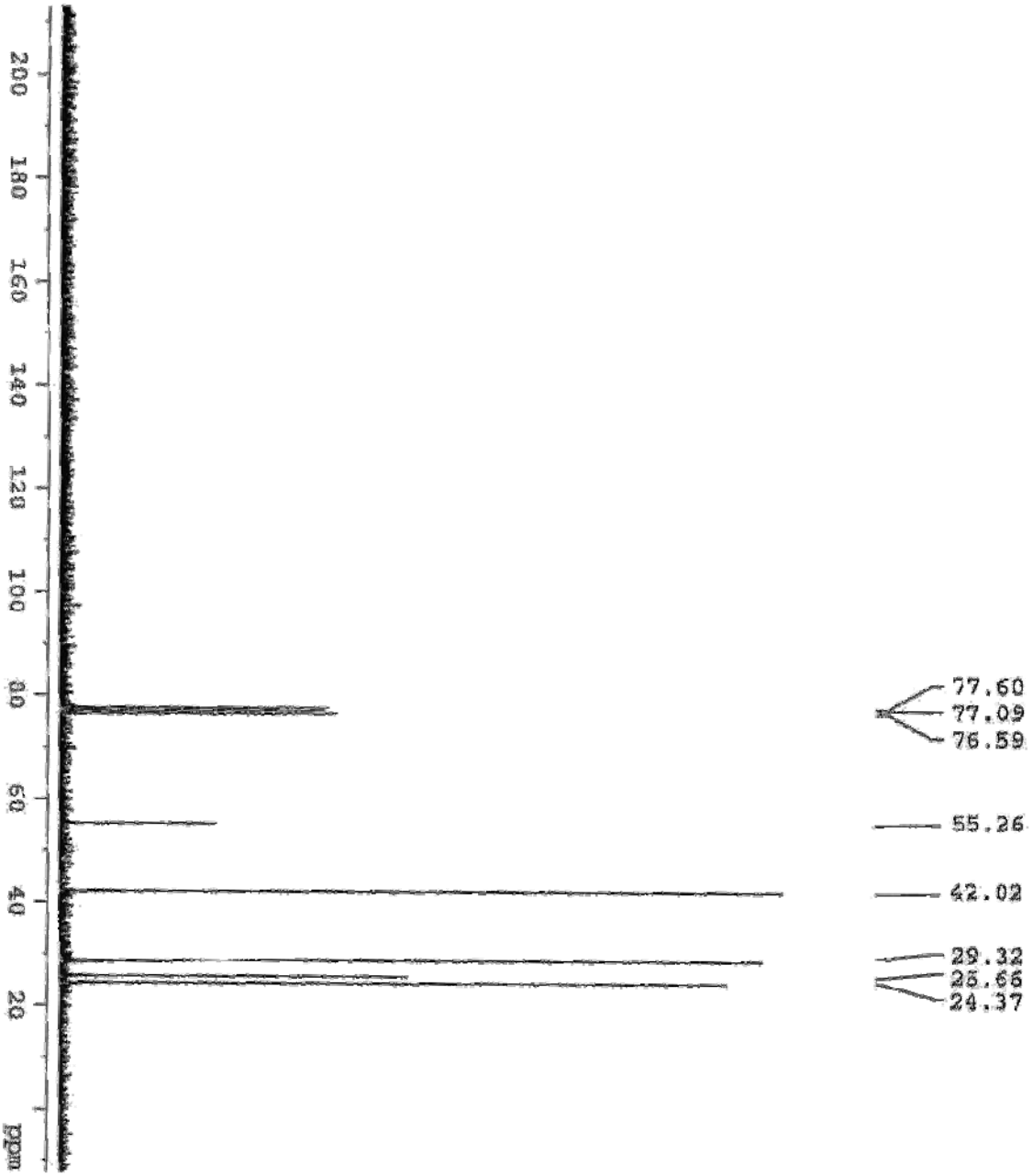


Table 1 (Entry 16)

Solvent: $CDCl_3$ – Frequency: 250 MHz

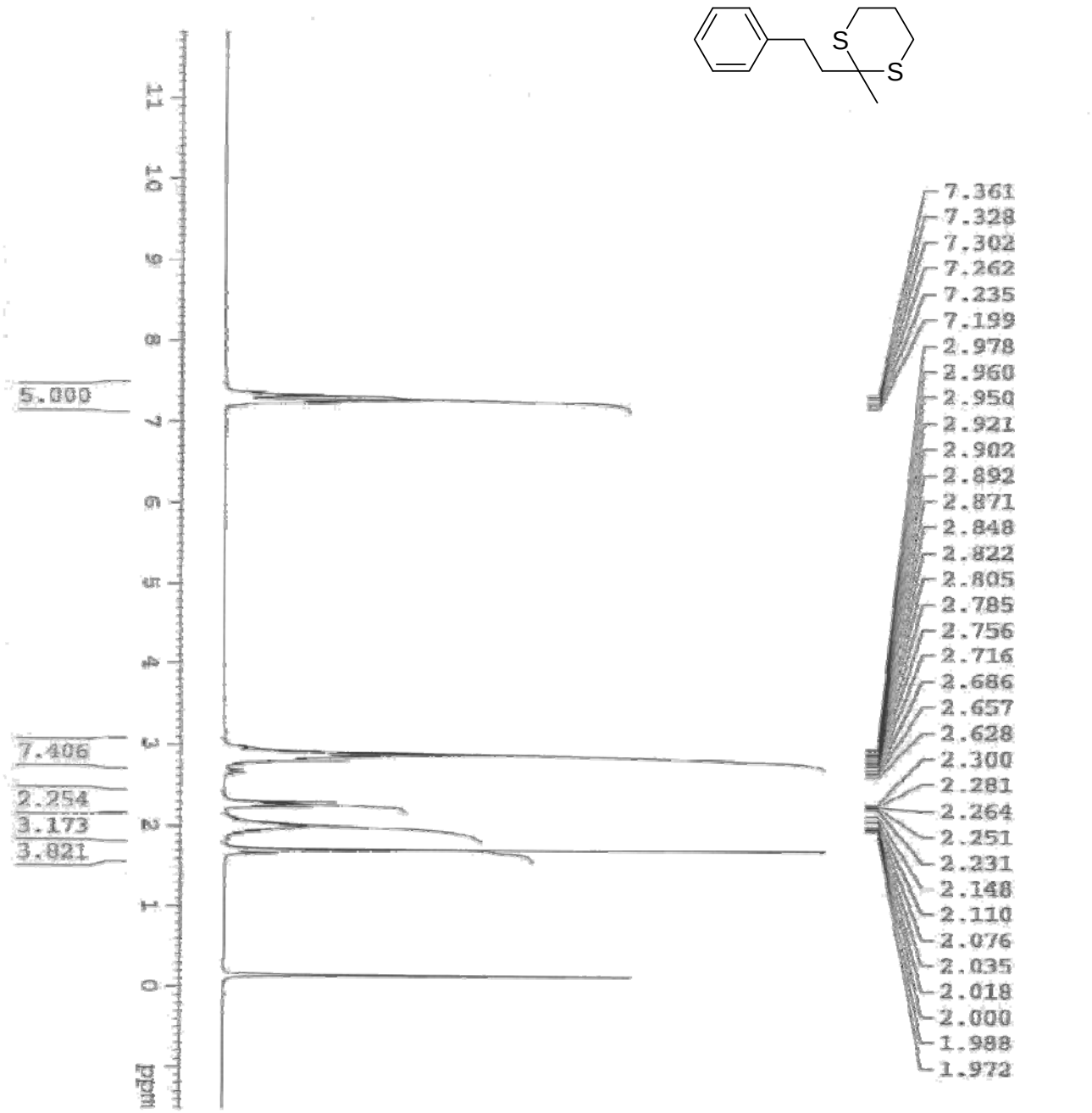


Table 1 (Entry 17)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

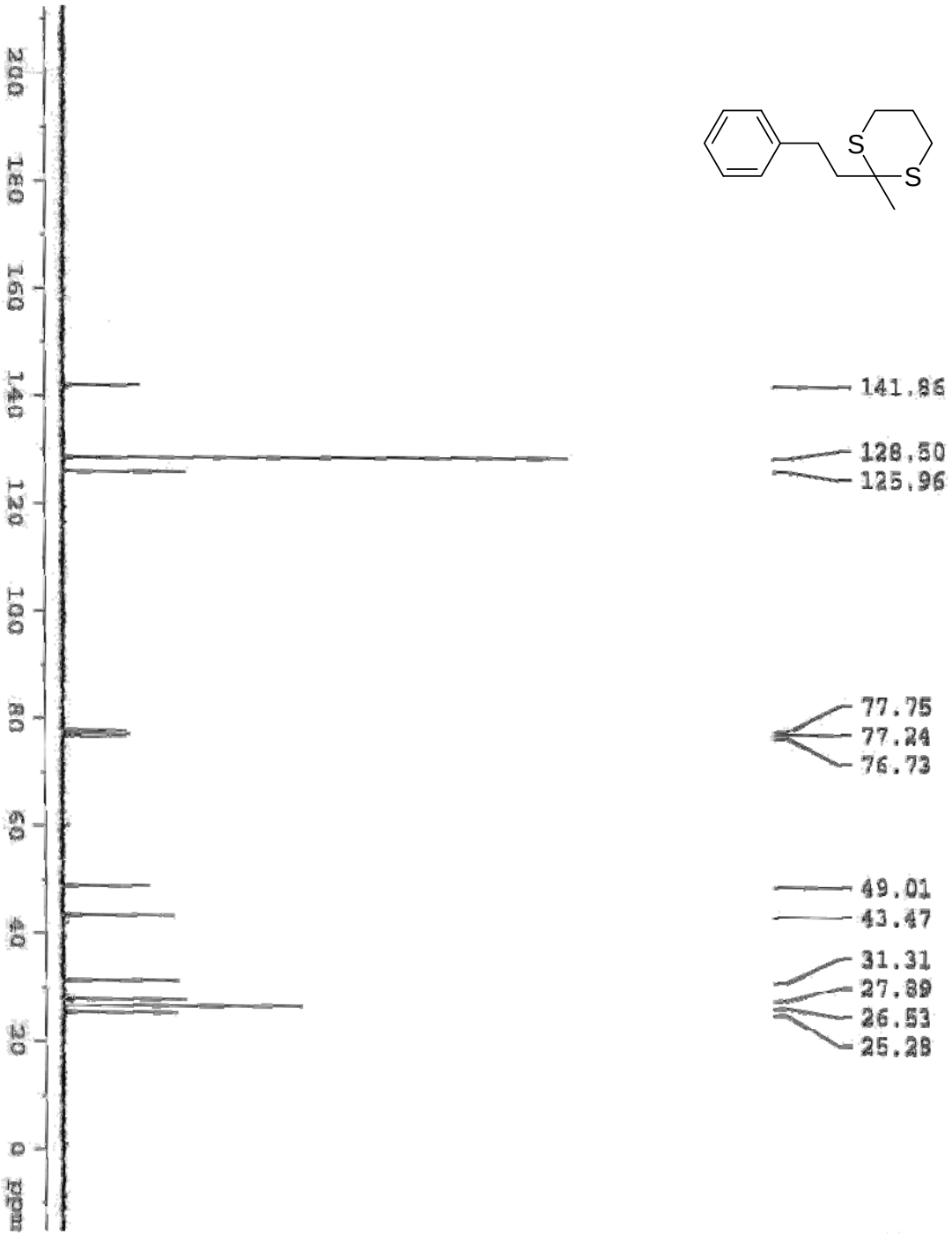


Table 1 (Entry 17)

Solvent: $CDCl_3$ – Frequency: 250 MHz

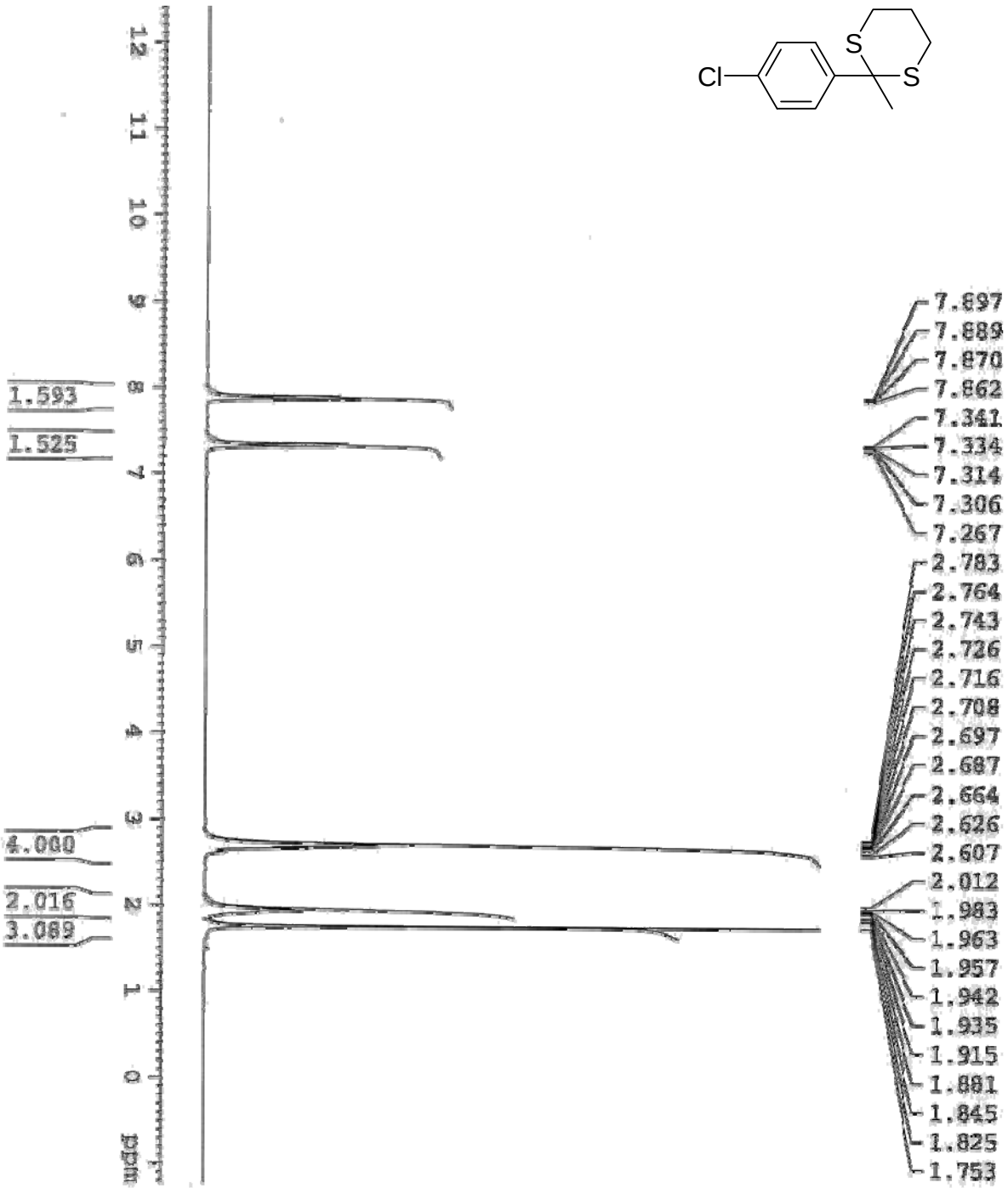


Table 1 (Entry 18)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

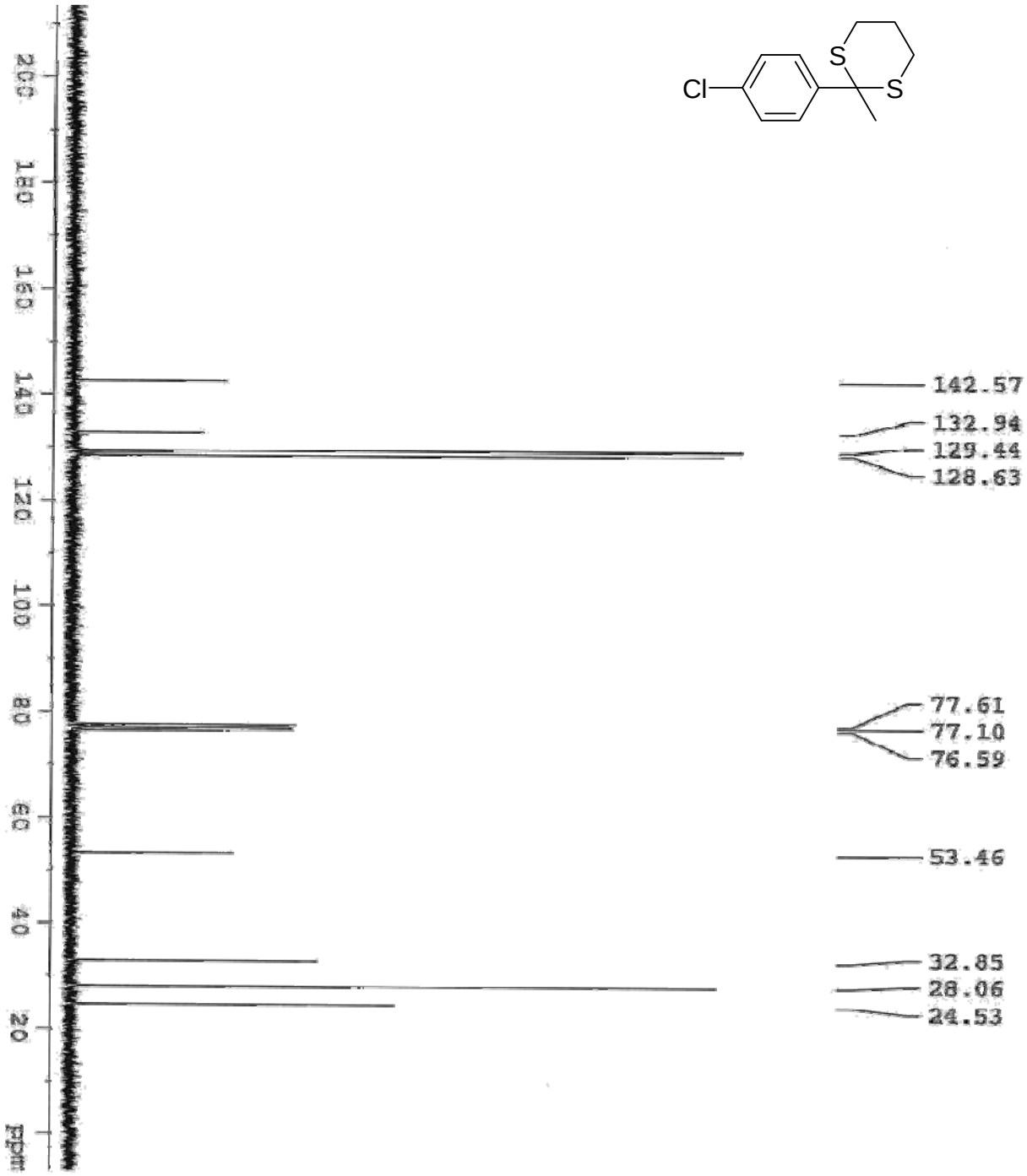


Table 1 (Entry 18)

Solvent: $CDCl_3$ – Frequency: 250 MHz

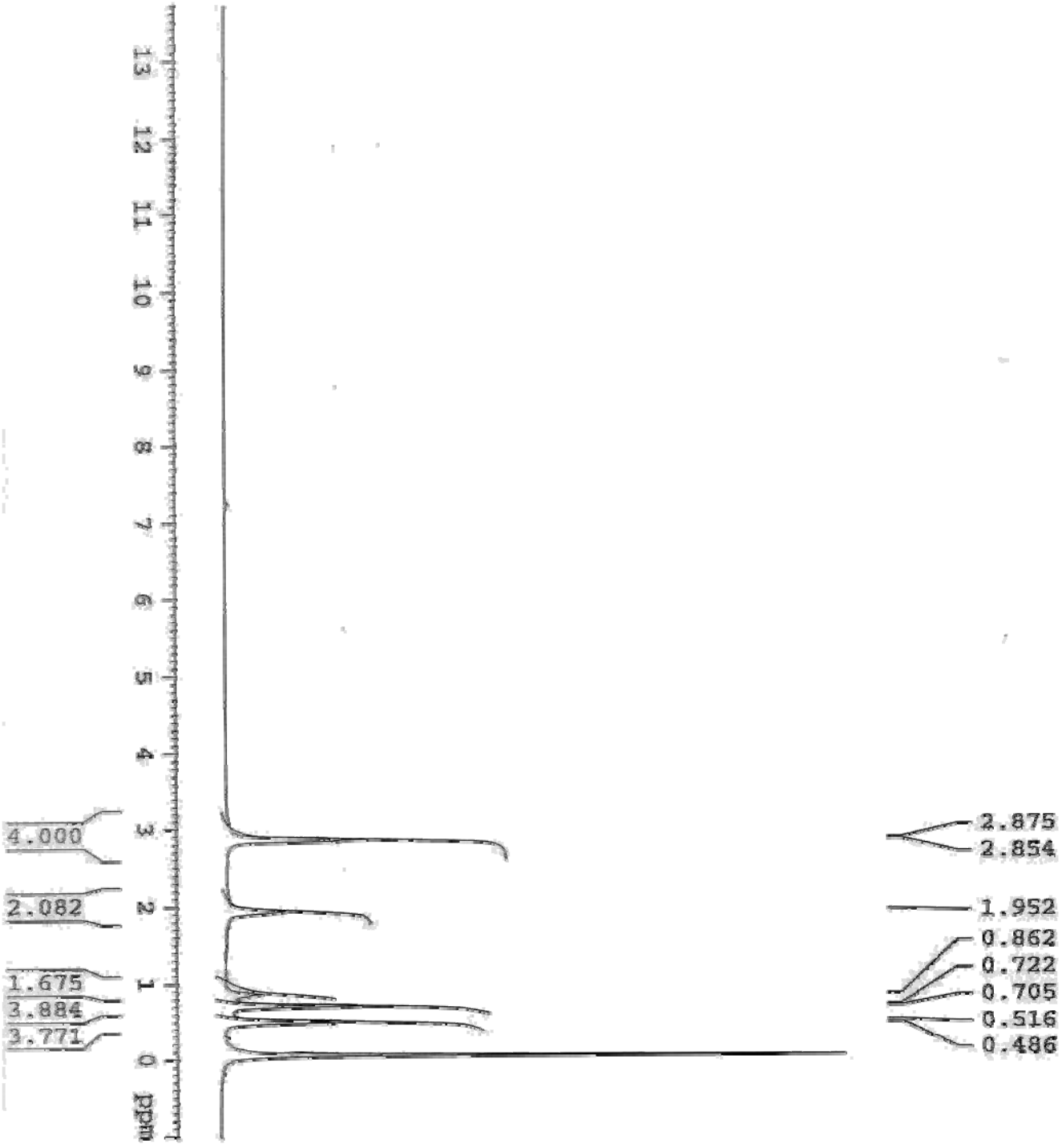


Table 1 (Entry 19)

Solvent: $CDCl_3$ – Frequency: 62.9 MHz

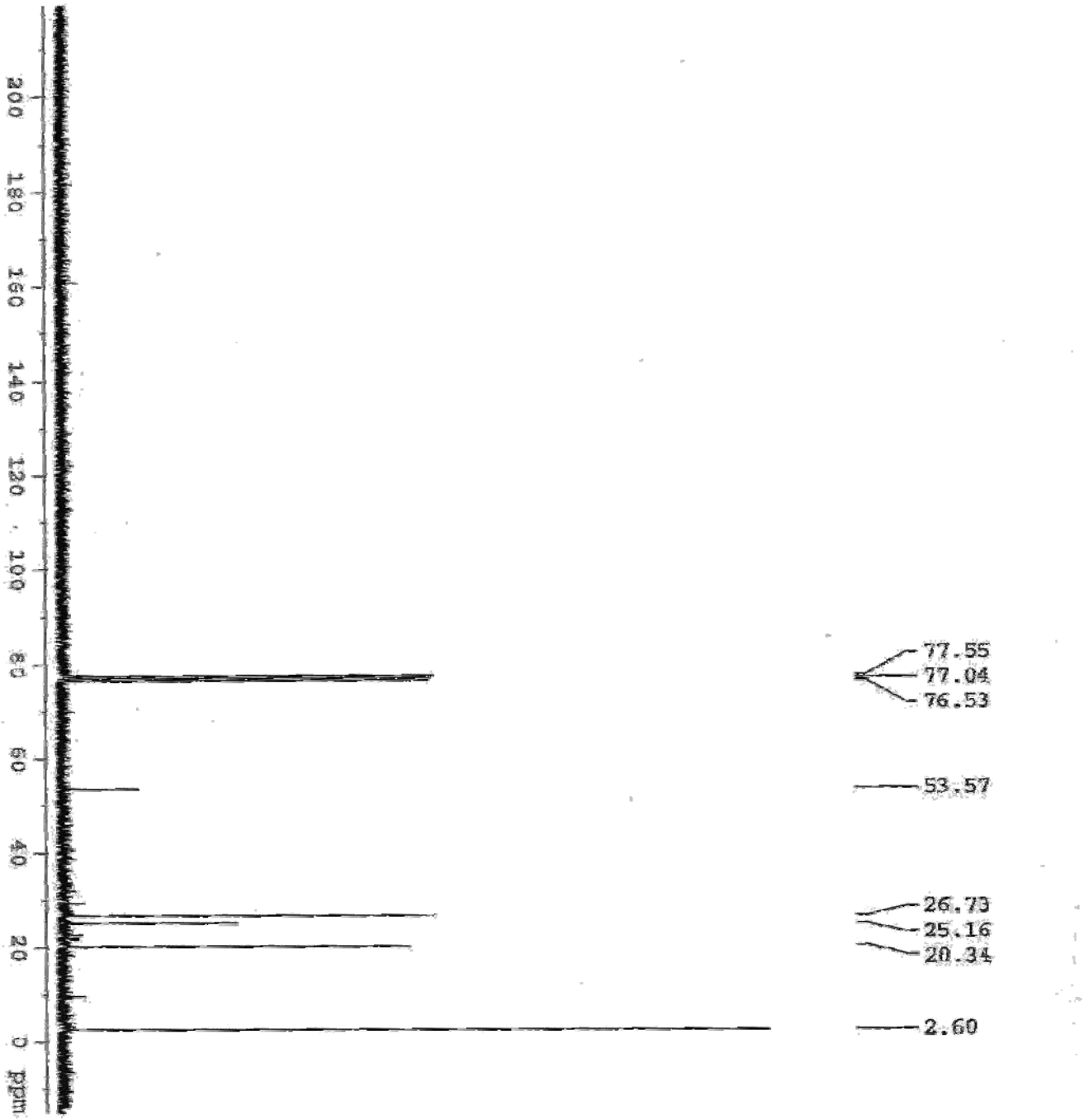
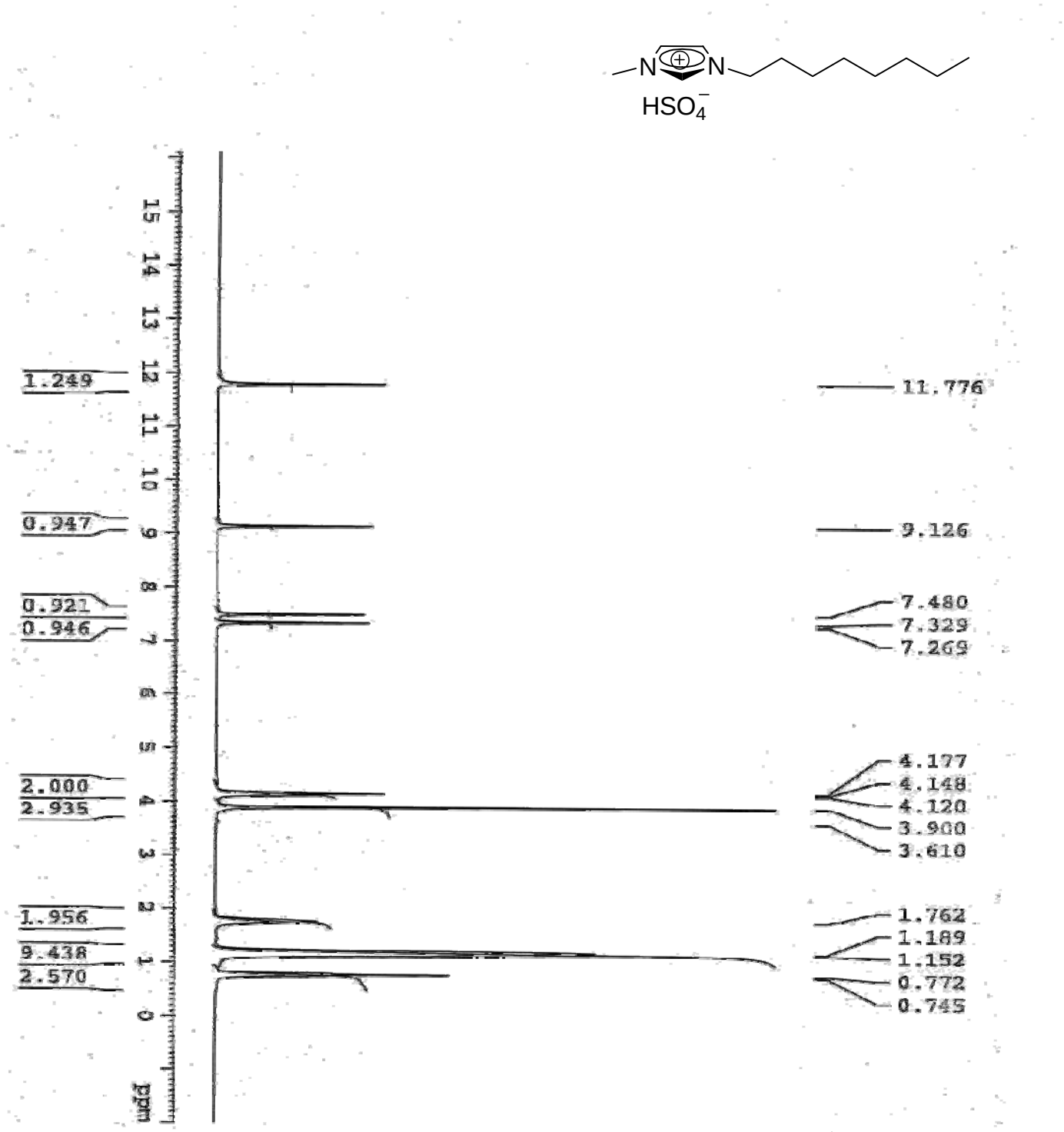


Table 1 (Entry 19)

Solvent: $CDCl_3$ – Frequency: 250 MHz



Solvent: $CDCl_3$ – Frequency: 62.9 MHz