

Tuning the electrical and optical properties of dinuclear ruthenium complexes for near infrared optical sensing

Shidi Xun,^a Gaetan LeClair,^a Jidong Zhang,^b Xin Chen,^a Jian Ping Gao^a and Zhi Yuan Wang^{a,b*}

^a Department of Chemistry, Carleton University, Ottawa, Canada K1S 5B6.

^b Changchun Institute of Applied Chemistry, Changchun 130022, P. R. China.

E-mail: wangw@ccs.carleton.ca

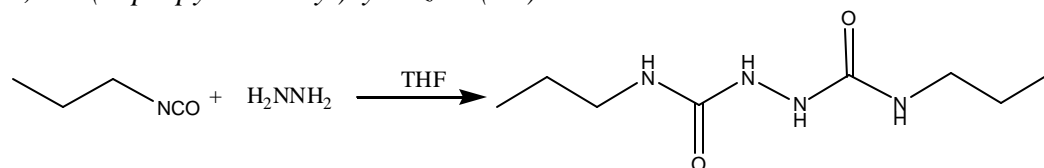
Experimental

Materials

n-Propylisocyanate, ethyl carbazate, ethyl chloroformate, benzoic hydrazide, benzoyl chloride, 2,2'-Dipyridyl and sodium carbonate were purchased from Aldrich Chemicals Inc., Canada, and used as received. Hydrazine Hydrate (85% wt/v) was purchased from ACP Inc, Montreal, Canada. RuCl₃ trihydrate was purchased from Pressure Chemicals Co. and used as received. Ru(bpy)₂Cl₂ dihydrate was prepared according to a published procedure.¹ All solvents were of ACS reagent grade or higher and used as received.

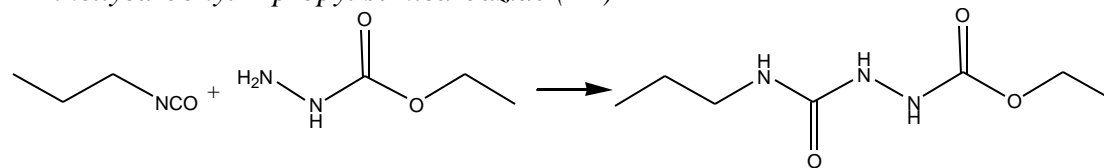
Synthesis of ligands

1,2-Di(N-propylcarbamyl)hydrazide (L1)



n-Propylisocyanate (3.6 g, 42.3 mmol), hydrazine hydrate (1.0 g, 19.9 mmol) in THF (50 ml) were placed in a 100 mL round bottomed flask (RBF) and stirred for 4 hours at room temperature (RT). The white solids were filtered, washed with fresh THF and dried over night under vacuum. The yield was 3.5 g (88%). ¹H NMR (300 MHz, d₆-DMSO): δ 0.83 (t, 6H), 1.39 (m, 4H), 2.95 (q, 4H), 6.27 (s, 2H), 7.48 (s, 2H); ¹³C NMR (75 MHz, d₆-DMSO): δ 11.7, 23.5, 41.3, 158.6; mp 262-264 °C.

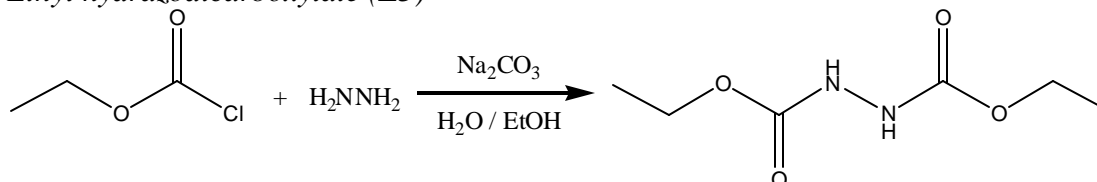
1-Ethoxycarbonyl-4-propyl semicarbazide (L2)



A mixture of ethyl carbazate (0.85 g, 10 mmol) and n-propylisocyanate (1.04 g, 10 mmol) in a mortar was ground with a pestle for 30 minutes according to a previously reported method.² The mixture was washed with dry toluene or n-hexane and the solids were filtered off and dried to give 1-ethoxycarbonyl-4-propyl semicarbazide.

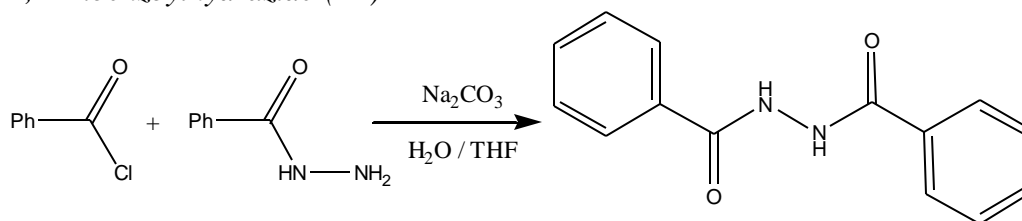
The yield was 1.51 g (80%). ^1H NMR (300 MHz, d_6 -DMSO): δ 0.81 (t, 3H), 1.17 (t, 3H), 1.37 (m, 2H), 2.95 (q, 2H), 4.01 (q, 2H), 6.32 (s, 1H), 7.63 (s, 1H), 8.73 (s, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 11.7, 15.0, 23.5, 41.4, 60.8, 157.4, 158.7; mp 103-104 °C.

Ethyl hydrazodicarboxylate (L3)



Ethyl chloroformate (10.5 g, 100 mmol) was added dropwise with stirring to a solution of hydrazine hydrate (1.8 g, 47 mmol) in 30 mL of 95% ethanol. The reaction flask was cooled in an ice bath to maintain the temperature between 15 °C and 20 °C. After exactly one-half of the ethyl chloroformate was introduced, a solution of sodium carbonate (5.3 g, 50 mmol) in 40 mL of water was added dropwise simultaneously with the remaining ethyl chloroformate. After addition of the reagents was complete, the reaction mixture was stirred for 30 minutes. The white precipitate was filtered, washed with 30 mL water then 15 mL of 95% EtOH followed by ethyl ether and dried overnight under vacuum. The yield was 3.6 g (52%). ^1H NMR (300 MHz, d_6 -DMSO): δ 1.17 (t, 6H), 4.03 (q, 4H), 8.99 (s, 2H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 15.0, 60.9, 157.0; mp 131-133 °C.

1,2-Dibenzoylhydrazide (L4)



A solution of benzoic hydrazide (2.1 g, 16.6 mmol) and sodium carbonate (1.6 g, 16.6 mmol) in THF (30 mL) and water (20 mL) was added to a stirring solution of benzoyl chloride (2.6 g, 18 mmol) in 30 mL of THF at 0 °C. The mixture was stirred for 3 hours. The white precipitate was recovered by filtration, washed three times with 25-ml portions of THF and dried overnight under vacuum. The yield was 3.0 g (75%). ^1H NMR (300 MHz, d_6 -DMSO): δ 7.51 (t, 4H), 7.58 (m, 2H), 7.92 (d, 4H), 10.54 (s, 2H); ^{13}C NMR (75 MHz, d_6 -DMSO): δ 127.8, 128.9, 131.9, 133.7, 165.7; mp 238-239 °C.

General procedure for the synthesis of DCH-Ru complexes 1-4

Combine **L4** (0.4 g, 1.7 mmol), $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (1.8 g, 3.5 mmol) and NaOH (0.3 g, 7.5 mmol) in 5:1 $\text{H}_2\text{O}/\text{EtOH}$ (60 mL). The mixture was then refluxed for approximately 24 hours under argon atmosphere. After it was cooled to room temperature, the product was precipitated by the addition of excess NH_4PF_6 . The resulting solids were collected by filtration, re-dissolved in acetone or acetonitrile, precipitated in ethyl ether, filtered and air dried. Yields of the crude complexes were in the range of 70-80 %.

Purification of crude complex was done on a 4 x 10 cm neutral alumina column using

a mixture of toluene and acetonitrile (1:1) as the mobile phase. The purple band was collected, concentrated under reduced pressure, dissolved in acetone or acetonitrile, precipitated in ethyl ether and dried under vacuum overnight.

ESI-MS analysis for complexes 1-4

1 m/z (%): 1317 (<0.1%, M+H), 1172 (6, M+H-PF₆), 514 (100, M+H-2PF₆)

2 m/z (%): 1304 (<0.1%, M+H), 1159 (2, M+H-PF₆), 507 (100, M+H-2PF₆)

3 m/z (%): 1288 (<0.1%, M+H), 1143 (29, M+H-PF₆), 499 (100, M+H-2PF₆)

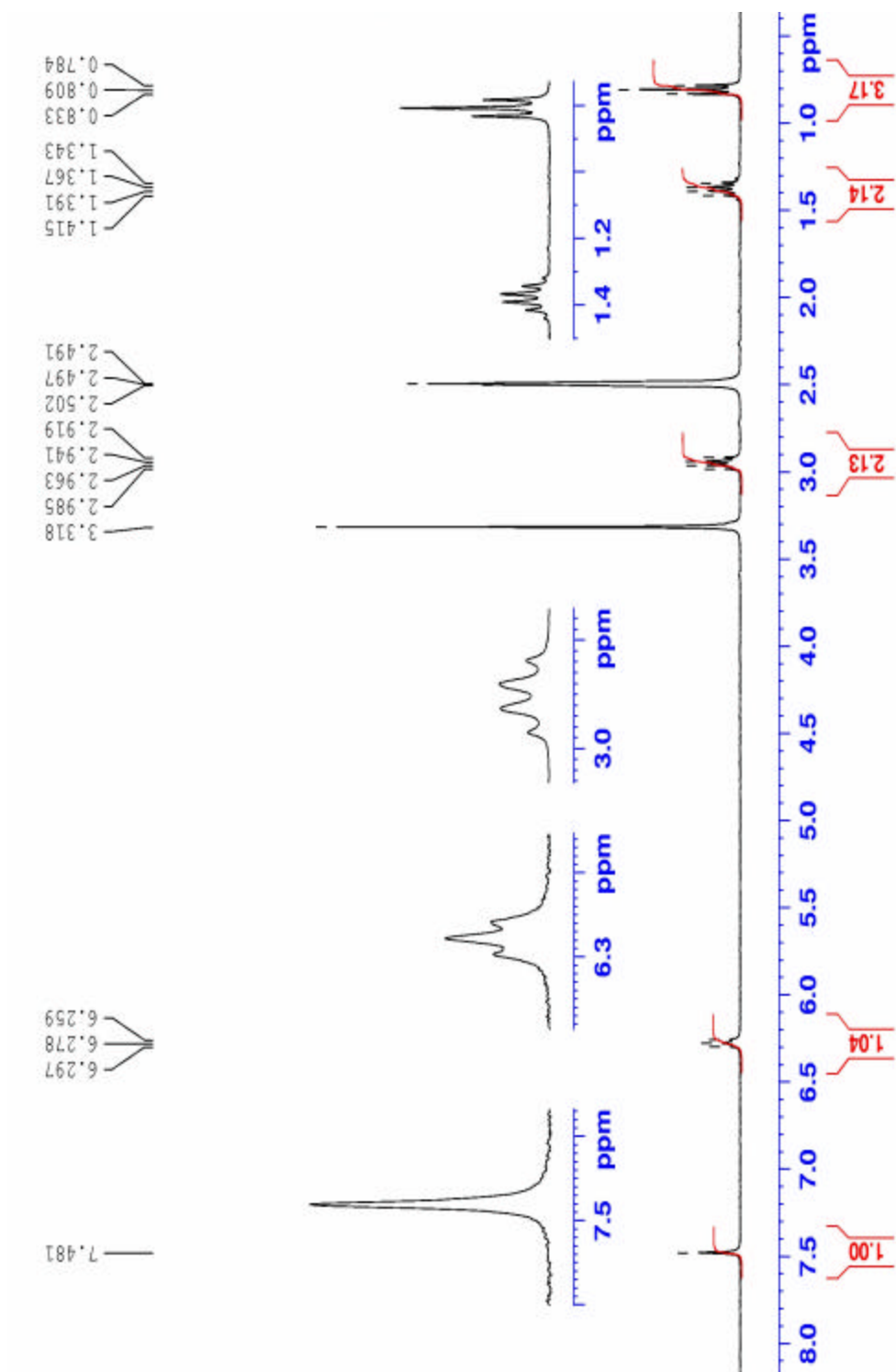
4 m/z (%): 1352 (<0.1%, M+H), 1207 (16, M+H-PF₆), 531 (100, M+H-2PF₆)

References:

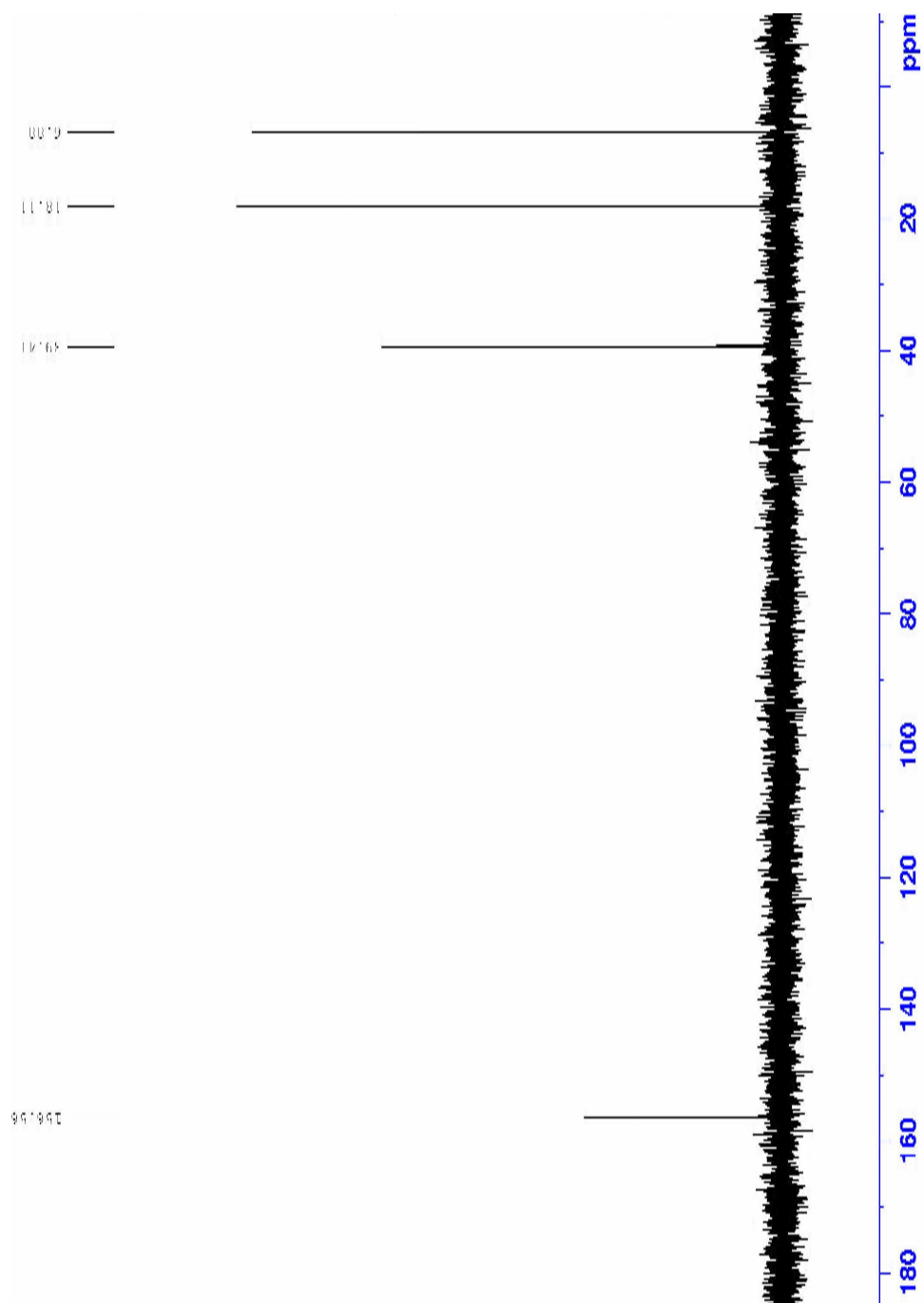
1. Sullivan, B. P.; Salmon, D.J.; Meyer, T. J. *Inorganic Chemistry*, **1978**, *17*, 3334-3341.
2. Mallakpour, S.; Hajipour, A.R., Taghizadeh, H. A. *Molecules*, **2003**, *8*, 359-362.

NMR and ESI-MS Spectra

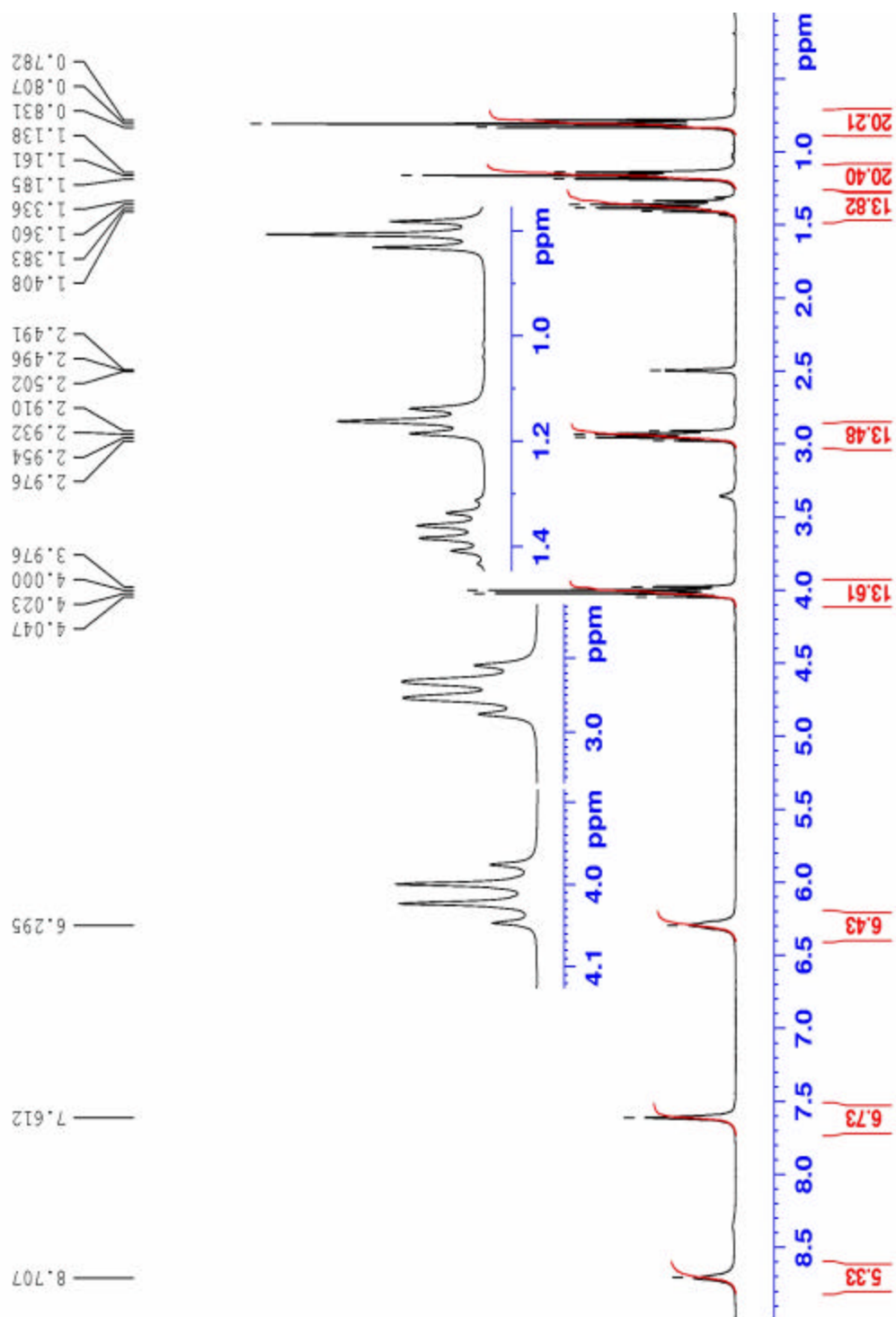
L1 (^1H NMR, 300 MHz, d_6 -DMSO)



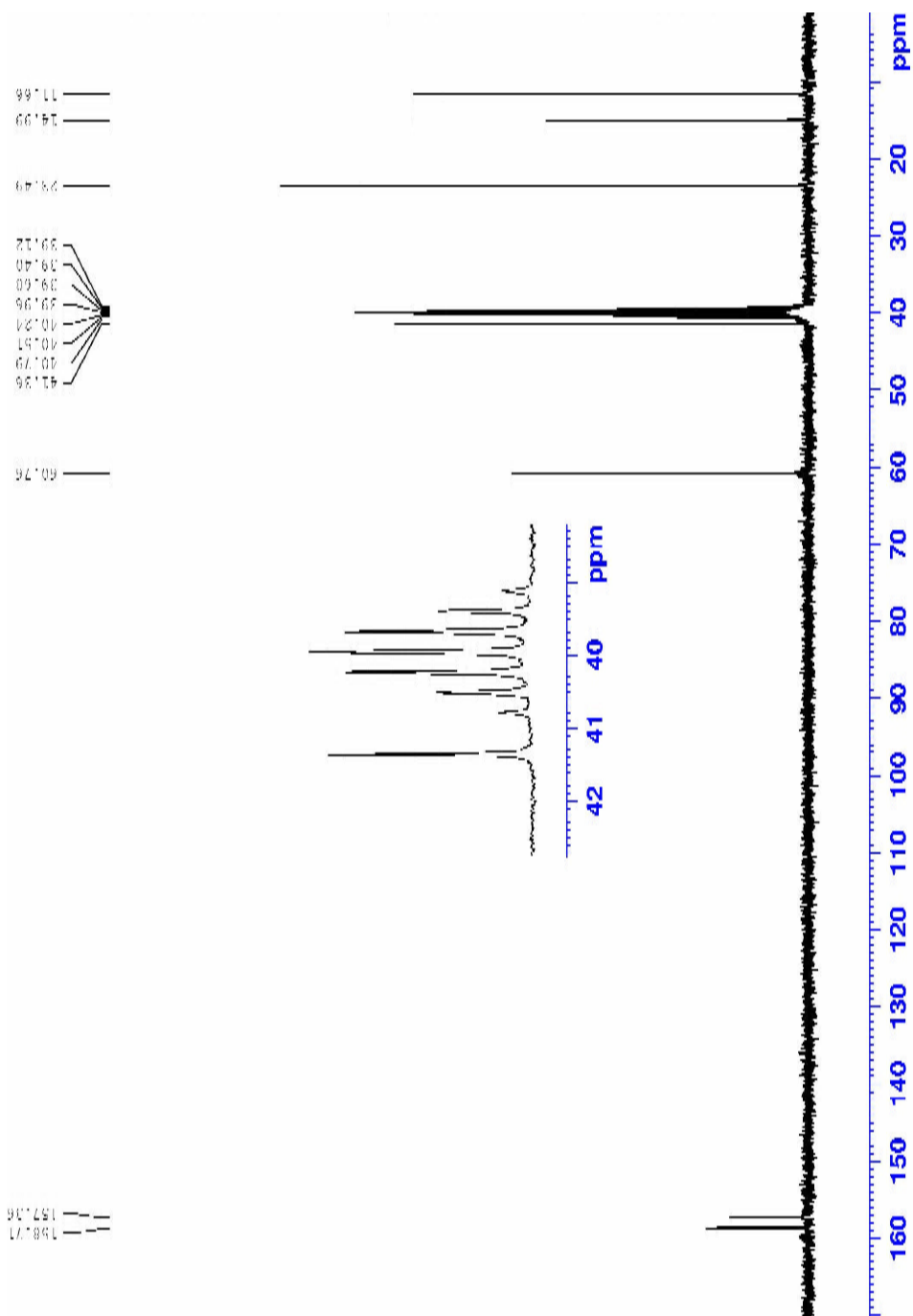
L1 (^{13}C NMR, 75 MHz, d_6 -DMSO)



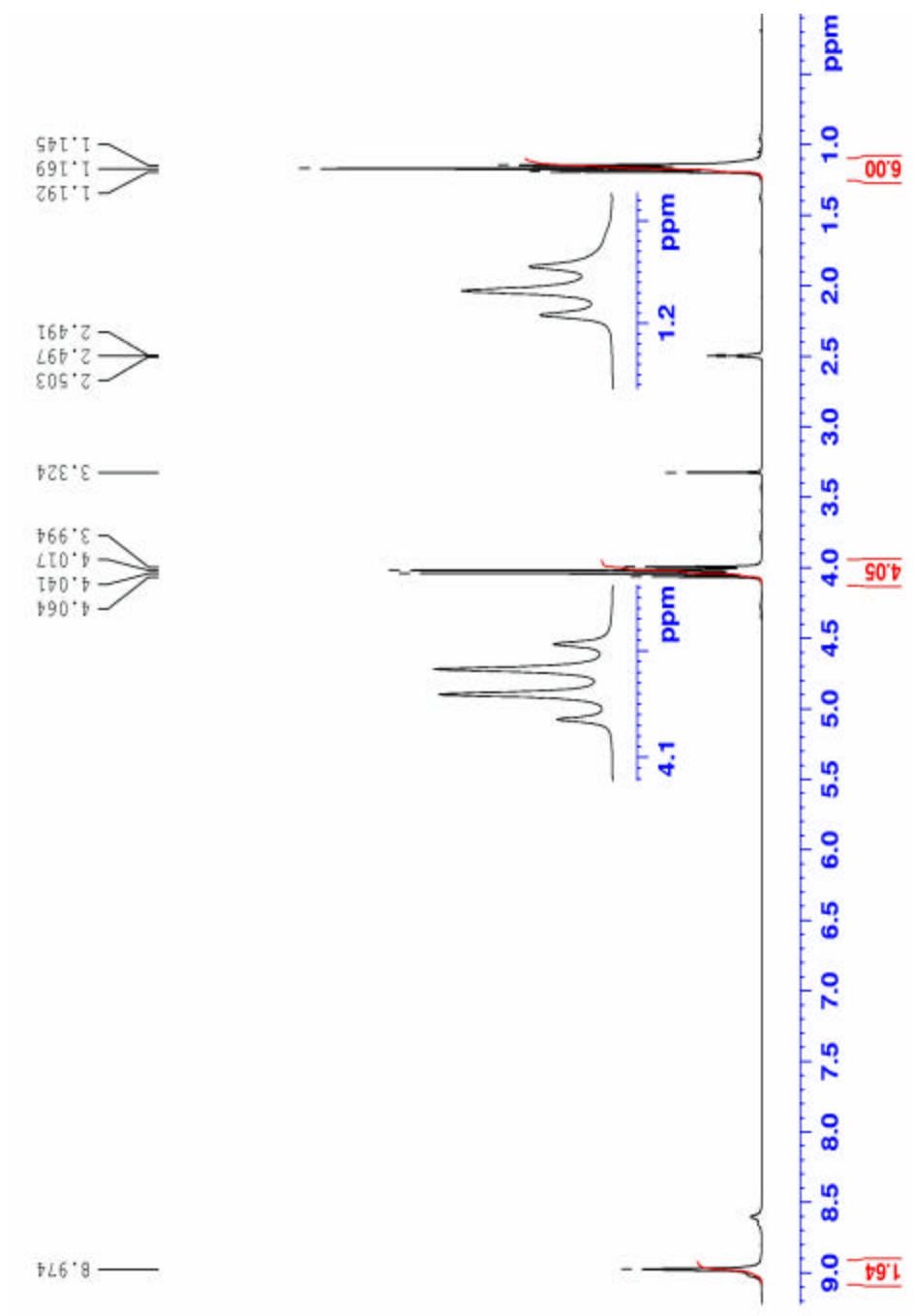
L2 (^1H NMR, 300 MHz, d_6 -DMSO)



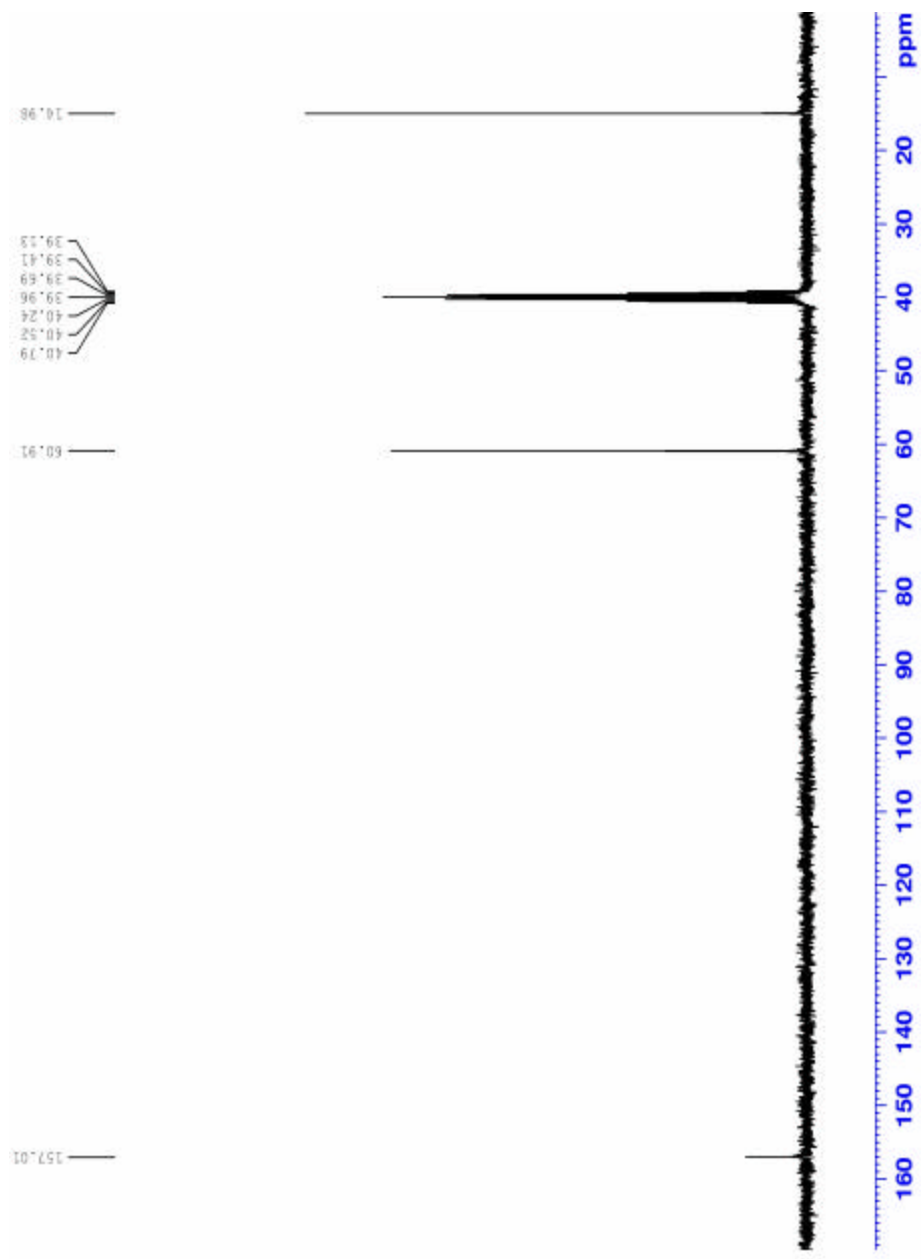
L2 (^{13}C NMR, 75 MHz, $\text{d}_6\text{-DMSO}$)



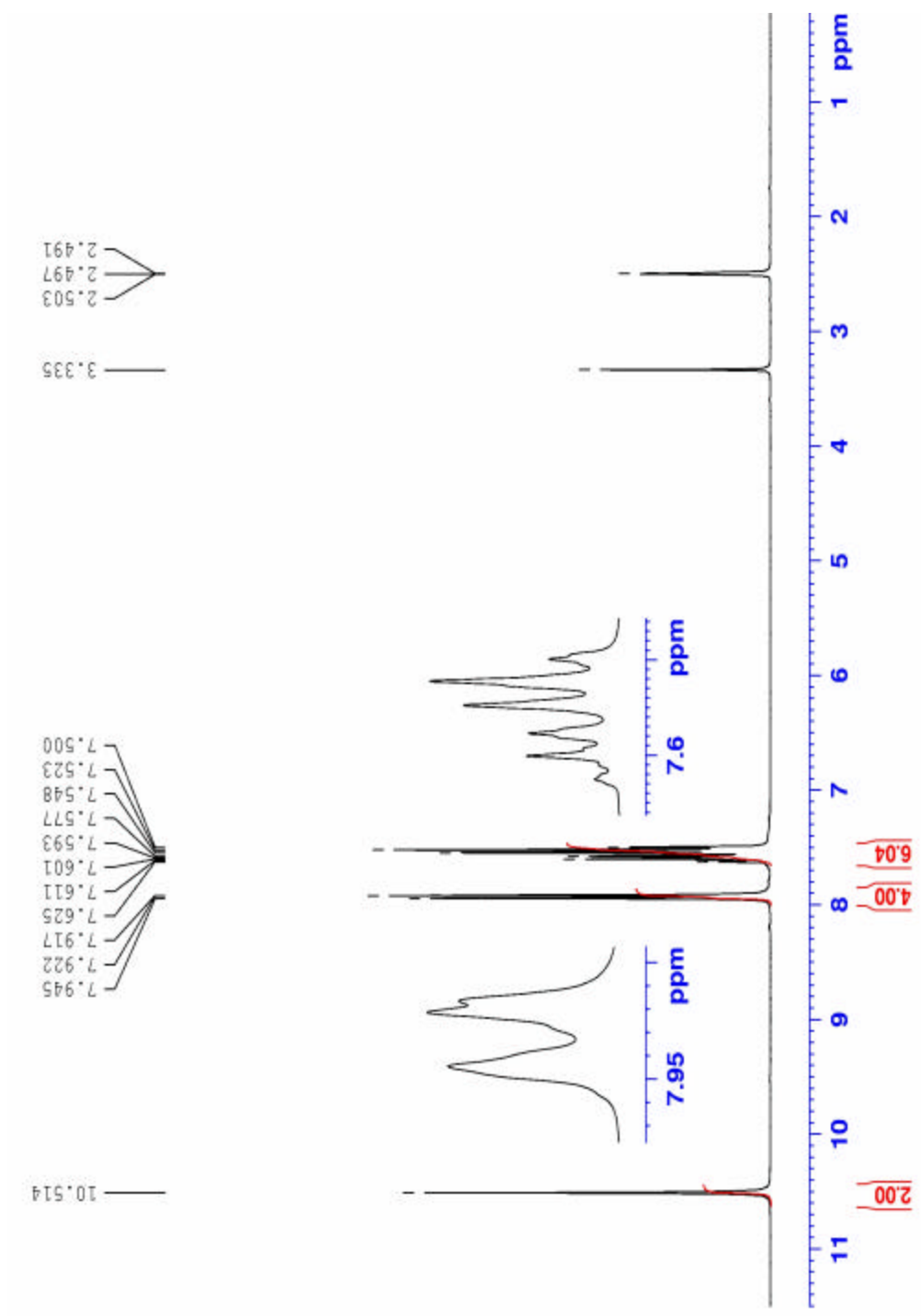
L3 (^1H NMR, 300 MHz, d_6 -DMSO)



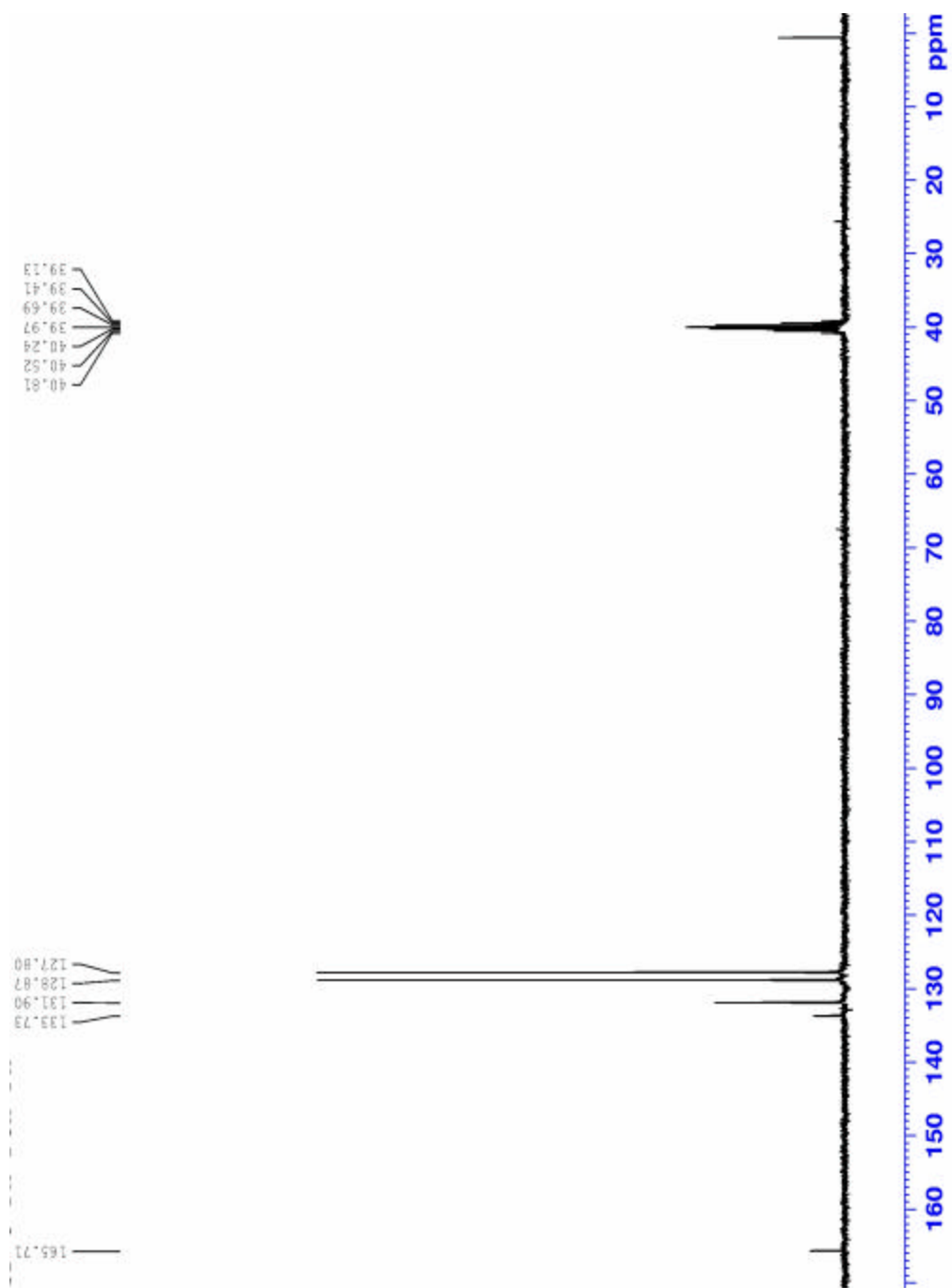
L3 (^{13}C NMR, 75 MHz, $\text{d}_6\text{-DMSO}$)



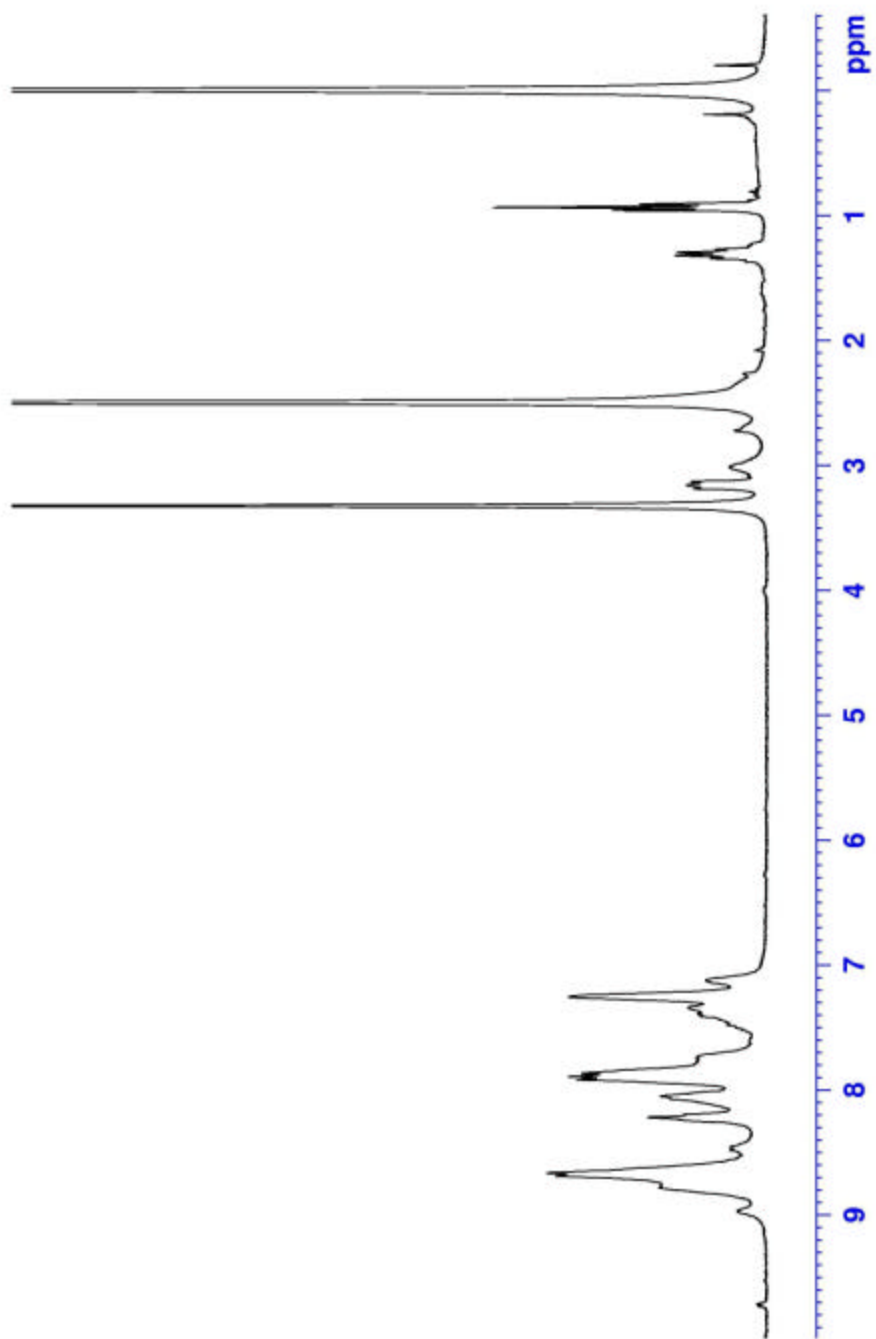
L4 (^1H NMR, 300 MHz, d_6 -DMSO)



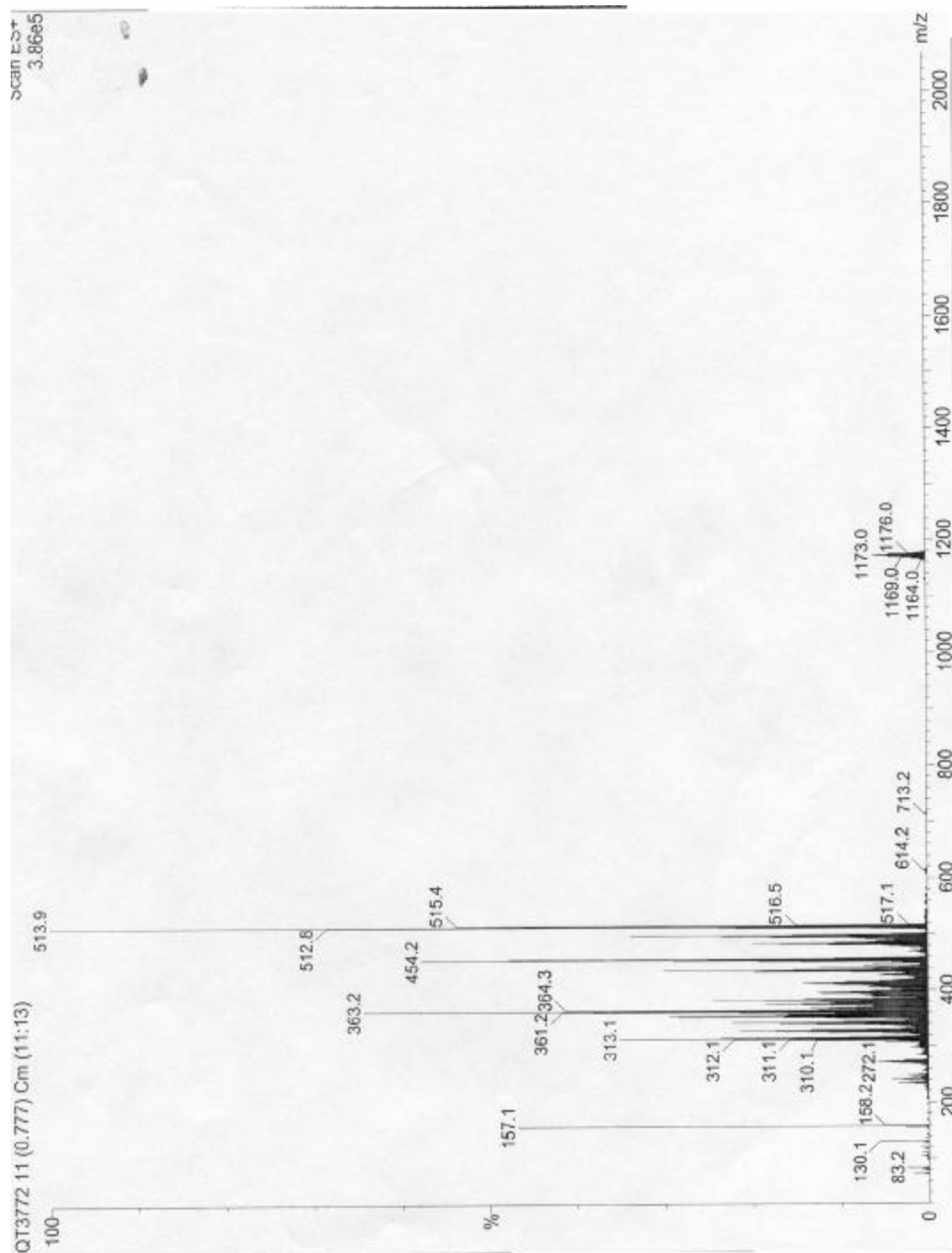
L4 (^{13}C NMR, 75 MHz, $\text{d}_6\text{-DMSO}$)



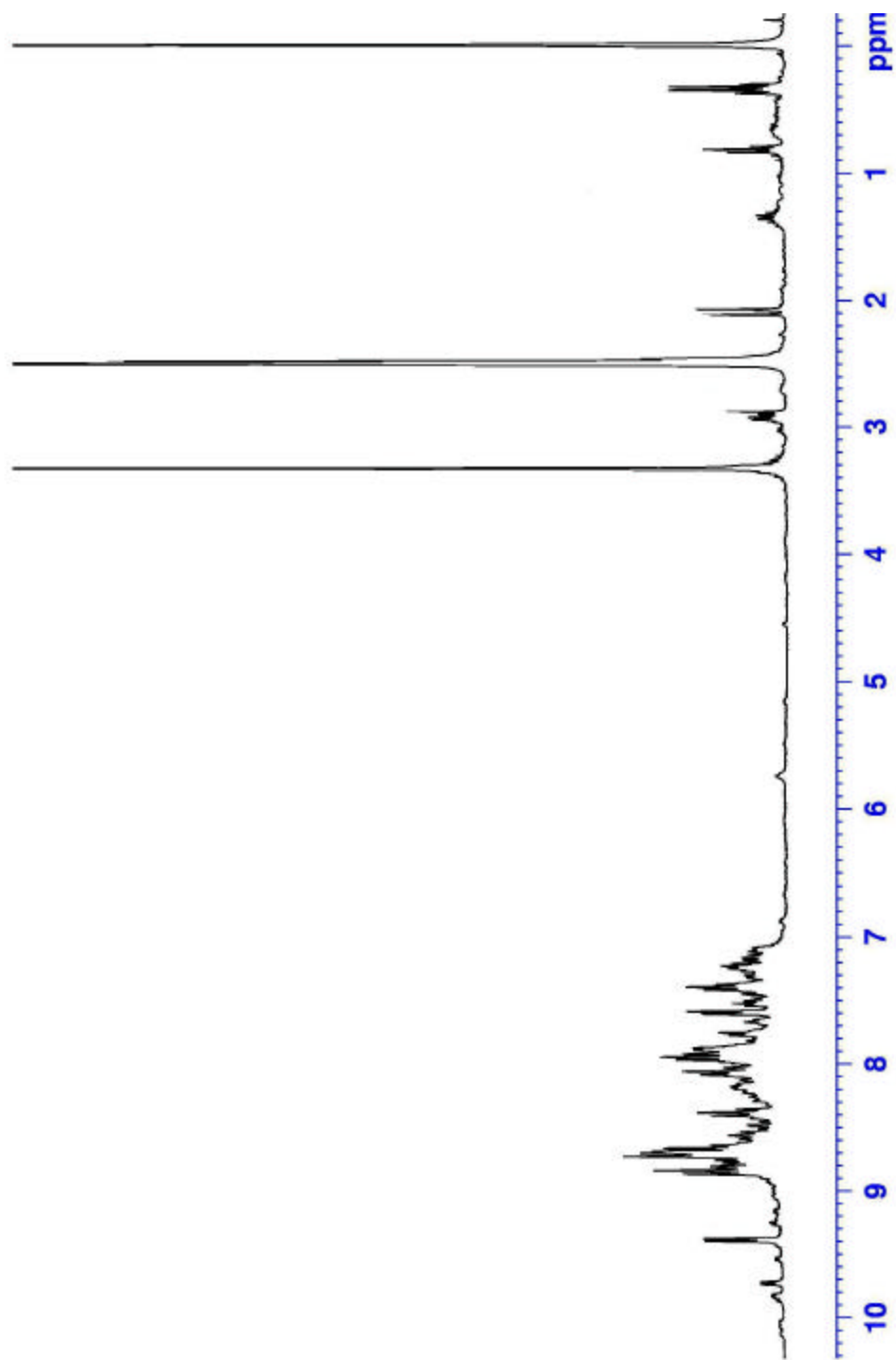
Complex 1 (^1H NMR 300 MHz d_6 -DMSO)



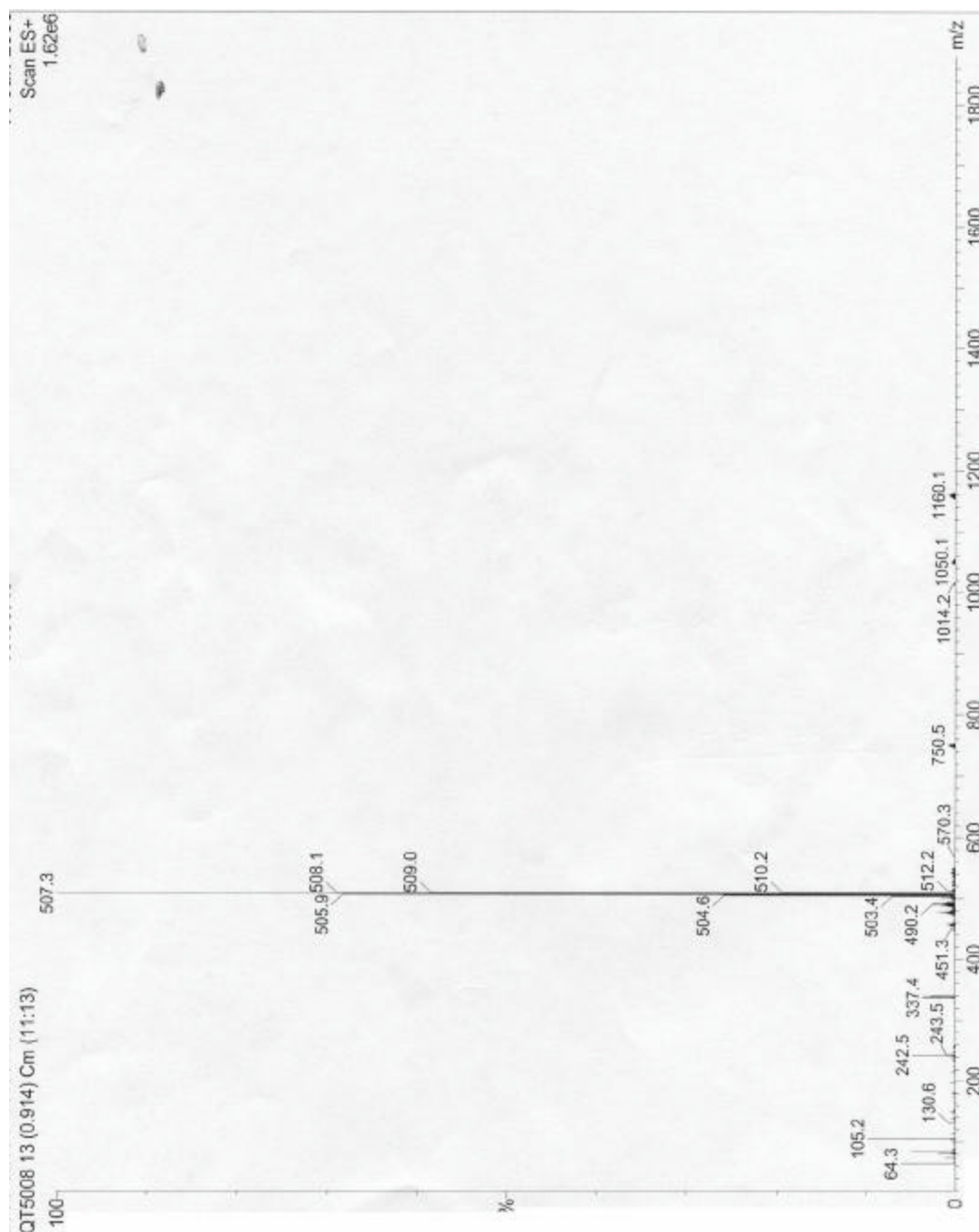
Complex 1 (ESI-MS)



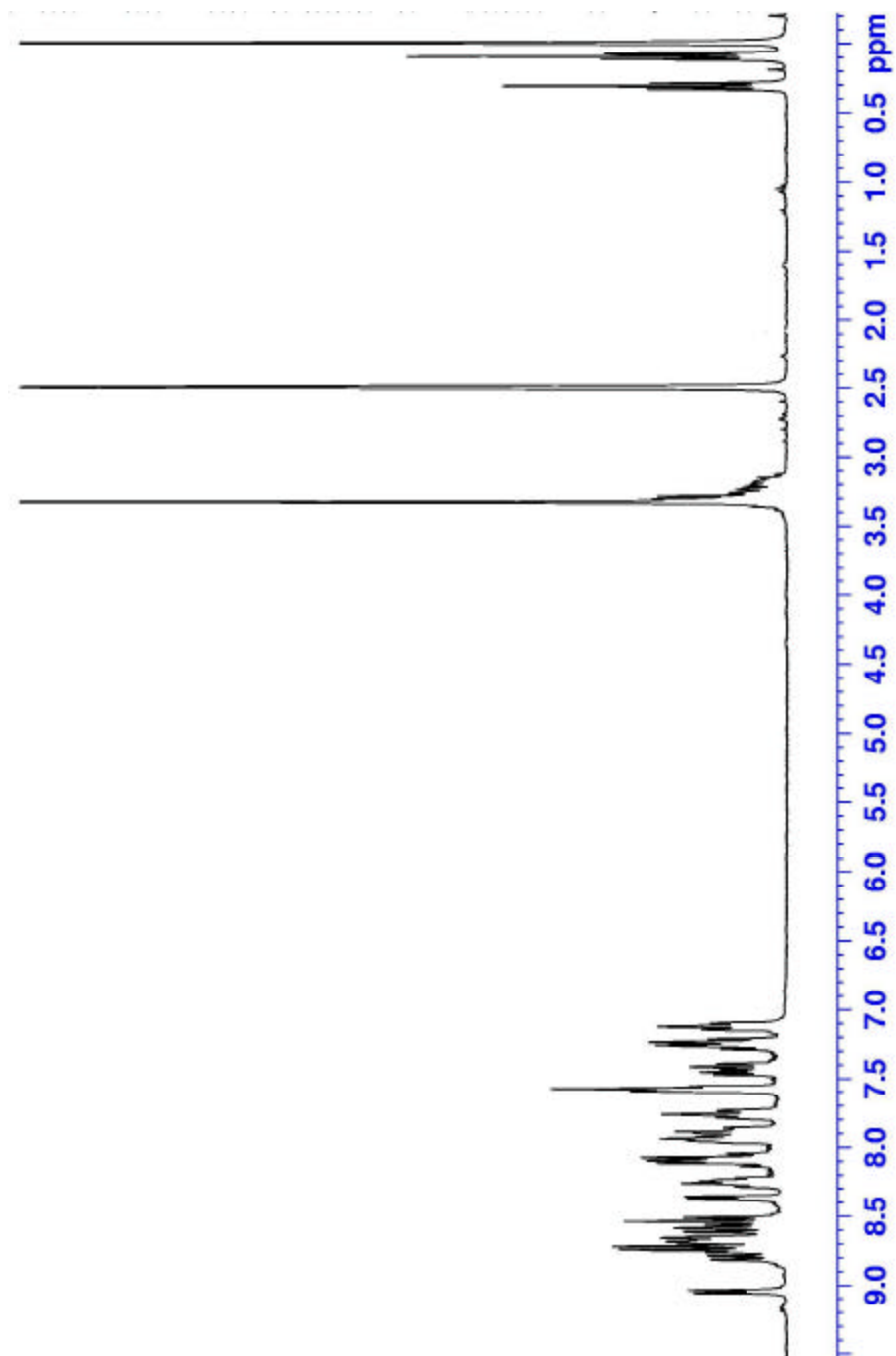
Complex 2 (^1H NMR, 300 MHz, $\text{d}_6\text{-DMSO}$)



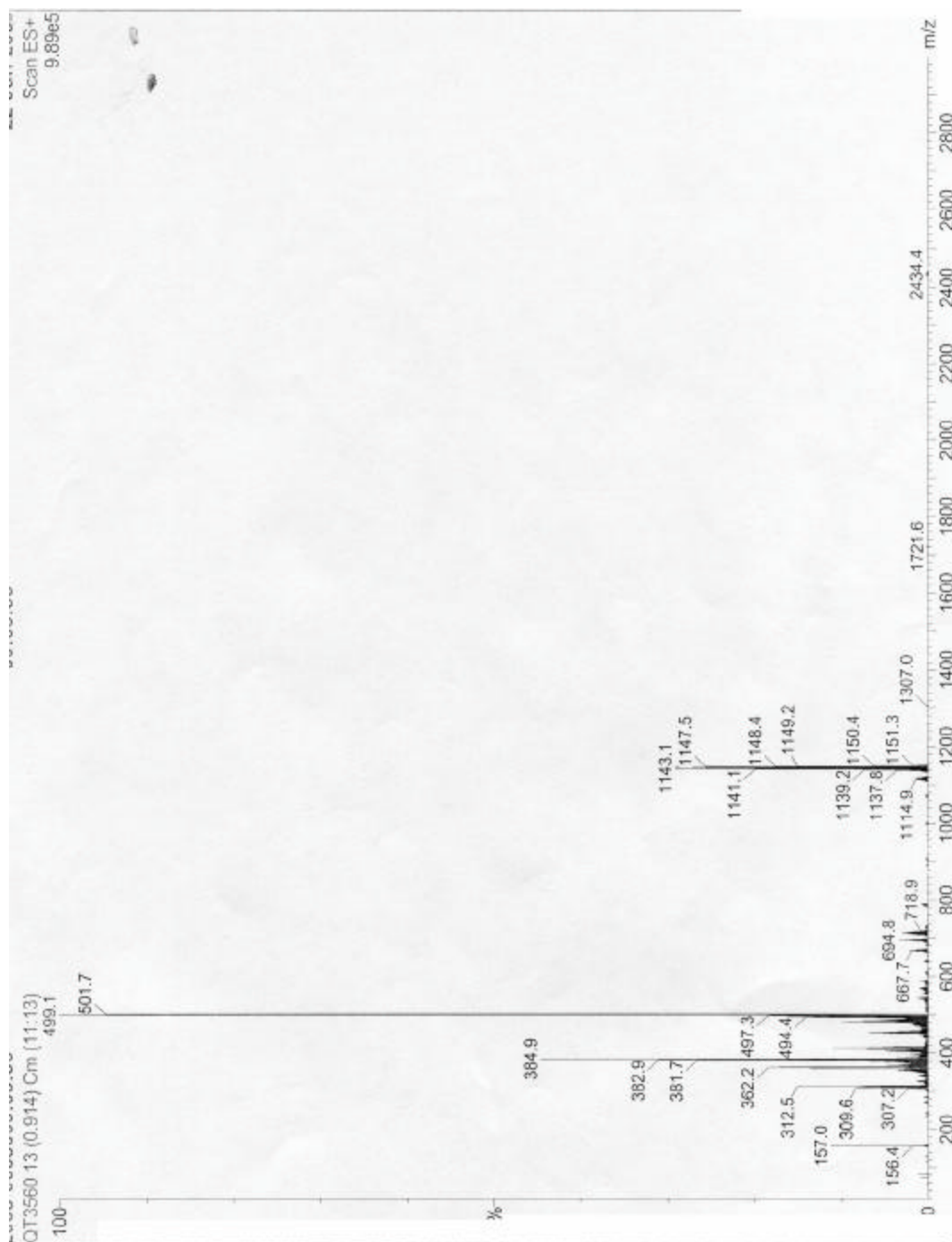
Complex 2 (ESI-MS)



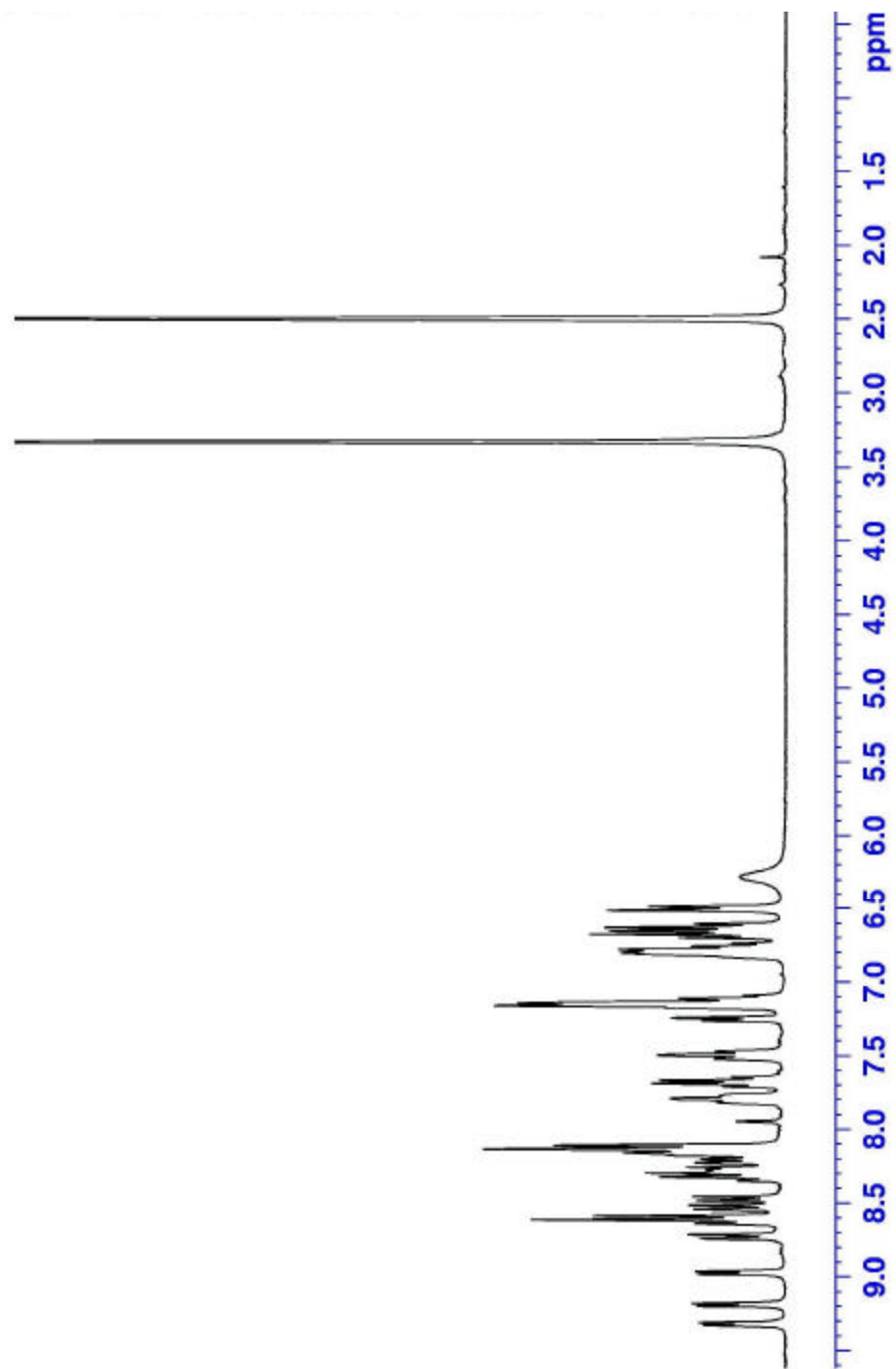
Complex 3 (^1H NMR, 300 MHz, $\text{d}_6\text{-DMSO}$)



Complex 3 (ESI-MS)



Complex 4 (^1H NMR, 300 MHz, $\text{d}_6\text{-DMSO}$)



Complex 4 (ESI-MS)

