

**Efficient Syntheses and Antimicrobial Activities of New Thiophene
Containing Pyranone and Quinolinone Derivatives by Manganese(III)
Acetate. The effect of Thiophene on Ring Closure-Opening Reactions**

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Supplementary Materials

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X-ray Crystallography data

The colourless block shaped crystals of the title compound **37** was crystallized from Hexane/Ethylacetate at room temperature. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K α radiation ($\lambda=0.71073$ Å) at T=296(2) K. Absorption correction by multi-scan [1] was applied. Structure was solved by direct methods and refined by full-matrix least squares against F² using all data [2]. All non-H atoms were refined anisotropically. Methine H atom was located in a difference Fourier map and refined freely. The remaining C-bound H-atoms were positioned geometrically with C---H = 0.93 and 0.96 Å for aromatic and methyl H-atoms, respectively, and constrained to ride on their parent atoms, with U_{iso} (H) = k x U_{eq}(C), where k = 1.5 for methyl H-atoms and k = 1.2 for aromatic H-atoms.

Crystal structure

In the molecule of the compound **37** (Fig. 1), the bond lengths and angles (Table 2) are generally within normal ranges. The benzene, A (C2-C7) and D (C11-C16), and the thiophene, E (S1/C18-C21), rings are planar, and they are oriented at dihedral angles of A/B = 62.67(4)°, A/E = 60.75(4)° and B/E = 24.44(4)°. But, ring B (C1/C2/C7/O1/C8/C9) is in flattened-boat conformation with puckering parameters of $\varphi = -61.4(3)^\circ$, $\theta = 74.5(3)^\circ$ and $Q_T = 0.244(4)$ Å [3]. The furan, C (C1/C9/C10/C17/O2), ring is in envelope conformation with atom C10 at the flap position, and it is -1.1519(11) Å away from the best least-squares plane of the other four atoms. Atoms C10 and C17 are the chiral centres with chirality S. In the crystal structure, intermolecular C-H ... O hydrogen bonds (Table 3) link the molecules into infinite chains along the b-axis (Fig. 2), additional π ... π contacts between the parallel benzene rings, A, Cg1 ... Cg1¹ (where Cg1 is the centroid of ring A) may further stabilize the structure, with centroid-to-centroid distance of 3.6131(7) Å. A weak C-H ... π interaction (Table 3) is also observed.

References

[1] Bruker (2012). *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.

[2] Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112--122.

[3] Cremer, D & Pople, J.A. (1975). *J. Amer. Chem. Soc.* **97**, 1354-1358.

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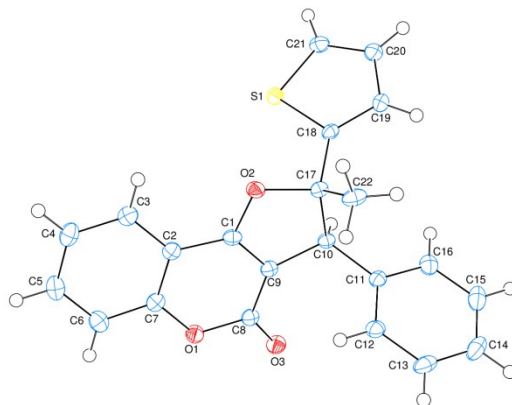


Figure 1. The molecular entities of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

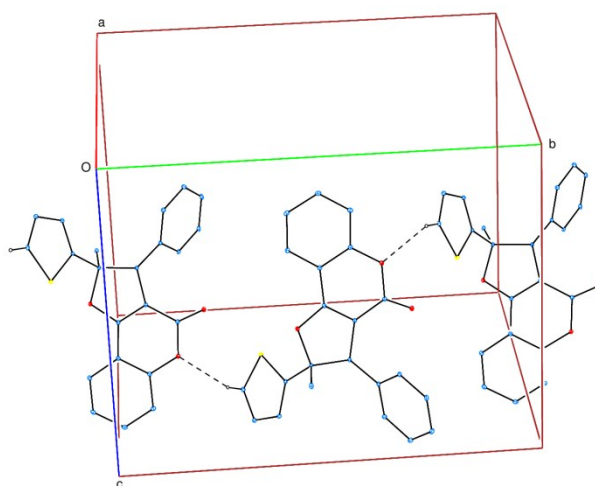


Figure 2. A partial packing diagram of the title compound. Intermolecular C-H ...O hydrogen bonds are shown as dashed lines. Nonbonding H atoms have been omitted for clarity.

Empirical Formula	C ₂₂ H ₁₆ O ₃ S
Fw	360.41
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ /c
<i>a</i> (Å)	9.9226 (2)
<i>b</i> (Å)	15.7155 (3)
<i>c</i> (Å)	11.5782 (2)
α (°)	90
β (°)	108.572 (3)
γ (°)	90
<i>V</i> (Å ³)	1711.47 (6)
<i>Z</i>	4
μ (MoK α) (mm ⁻¹)	0.21
ρ (calcd) (g cm ⁻³)	1.399
Number of Reflections Total	16080
Number of Reflections Unique	4292
Number of Reflections Observed [<i>I</i> > 2 σ (<i>I</i>)]	3772
<i>R</i> _{int}	0.019
2 θ _{max} (°)	56.8
<i>T</i> _{min} / <i>T</i> _{max}	0.926 / 0.977
Number of Parameters	239
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.032
<i>wR</i>	0.084
<i>S</i>	1.03
$\Delta\rho$ _{max} (e Å ⁻³)	0.35
$\Delta\rho$ _{min} (e Å ⁻³)	-0.27

Table 2. The Selected Bond Lengths (Å) and Angles (deg).

O1– C7	1.3749 (14)
O1– C8	1.3967 (14)
O2– C1	1.3414 (14)
O2– C17	1.4890 (14)
O3– C8	1.2068 (14)
S1– C18	1.7243 (11)
S1– C21	1.7114 (12)
C7– O1– C8	123.15 (9)
C1– O2– C17	107.94 (8)
O1– C8– O3	116.75 (10)
O3– C8– C9	128.05 (11)
O2–C17–C10	105.07 (8)
C18–S1– C21	91.93 (6)
S1–C18–C17	119.87 (8)
O2–C17–C18	105.77 (8)

Table 3 Hydrogen-bond geometry (Å,°)

D-H ...A	D-H	H ...A	D ...A	D-H ...A
C21—H21...O1 ⁱ	0.93	2.43	3.2052 (16)	141
C13—H13...Cg1 ⁱⁱ	0.93	3.08	4.0018 (15)	173

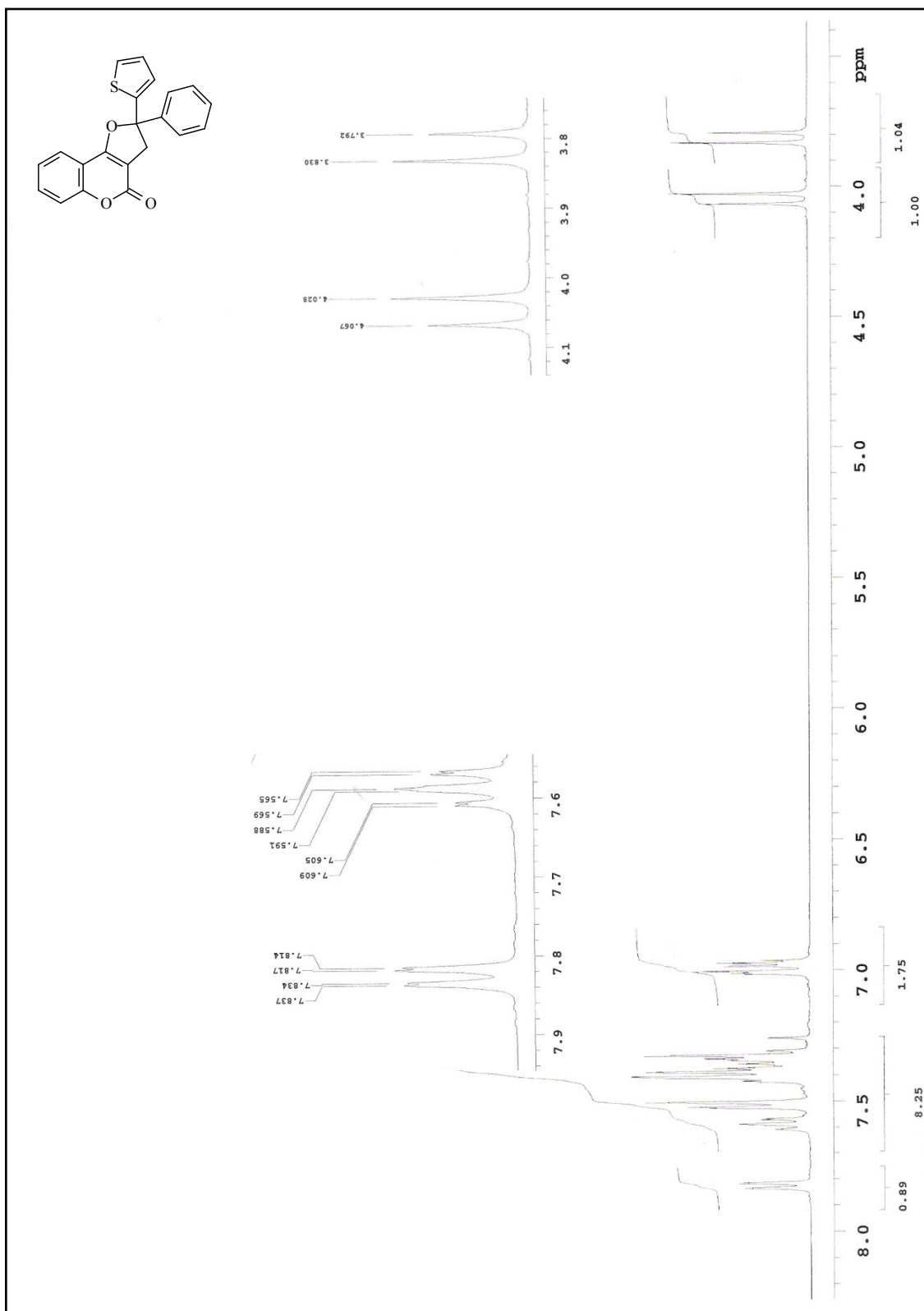
Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $-x+2, y+1/2, -z+3/2$. Cg1 is the centroid of ring

(C2-C7).

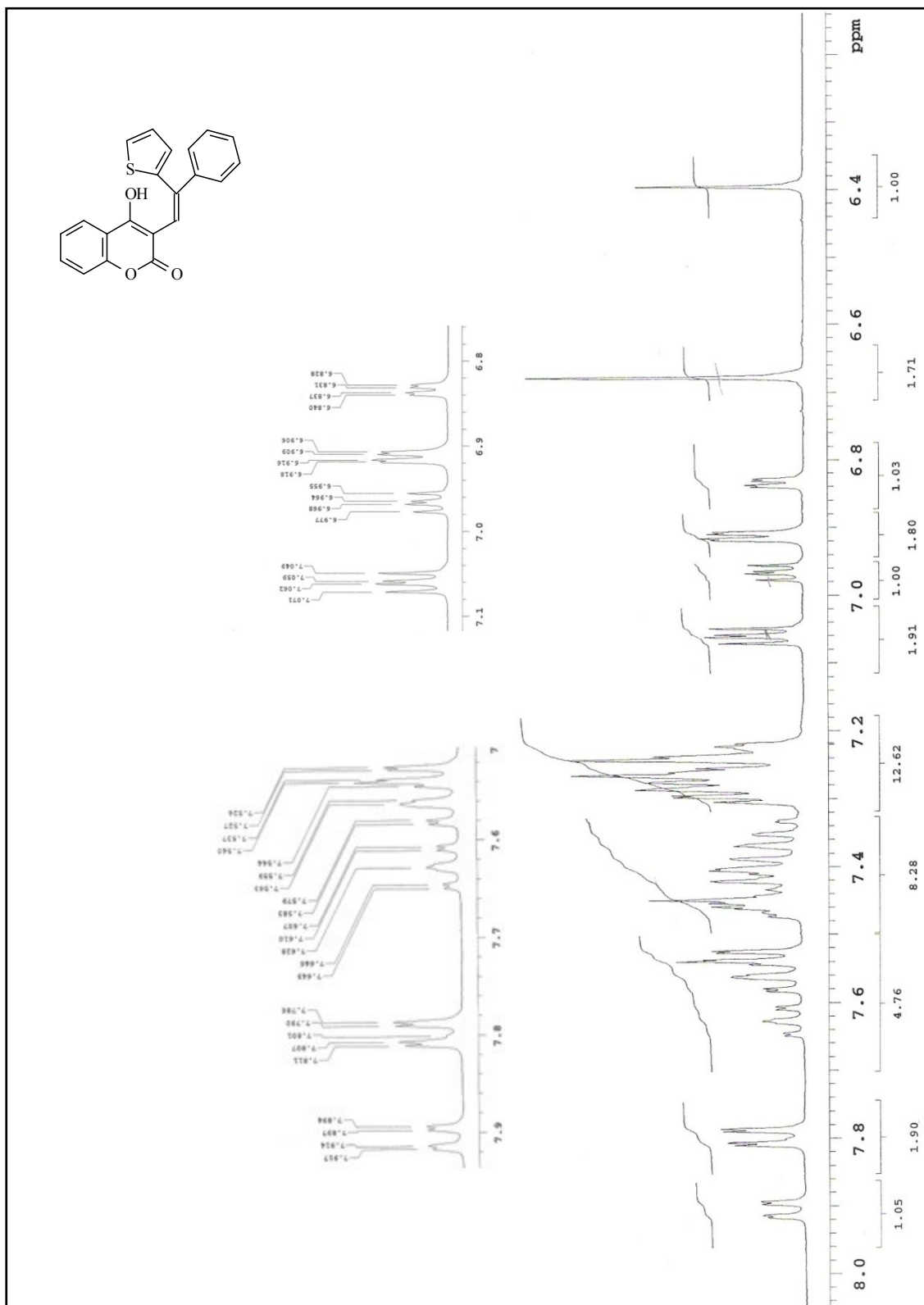
A

¹H-NMR of COMPOUNDS

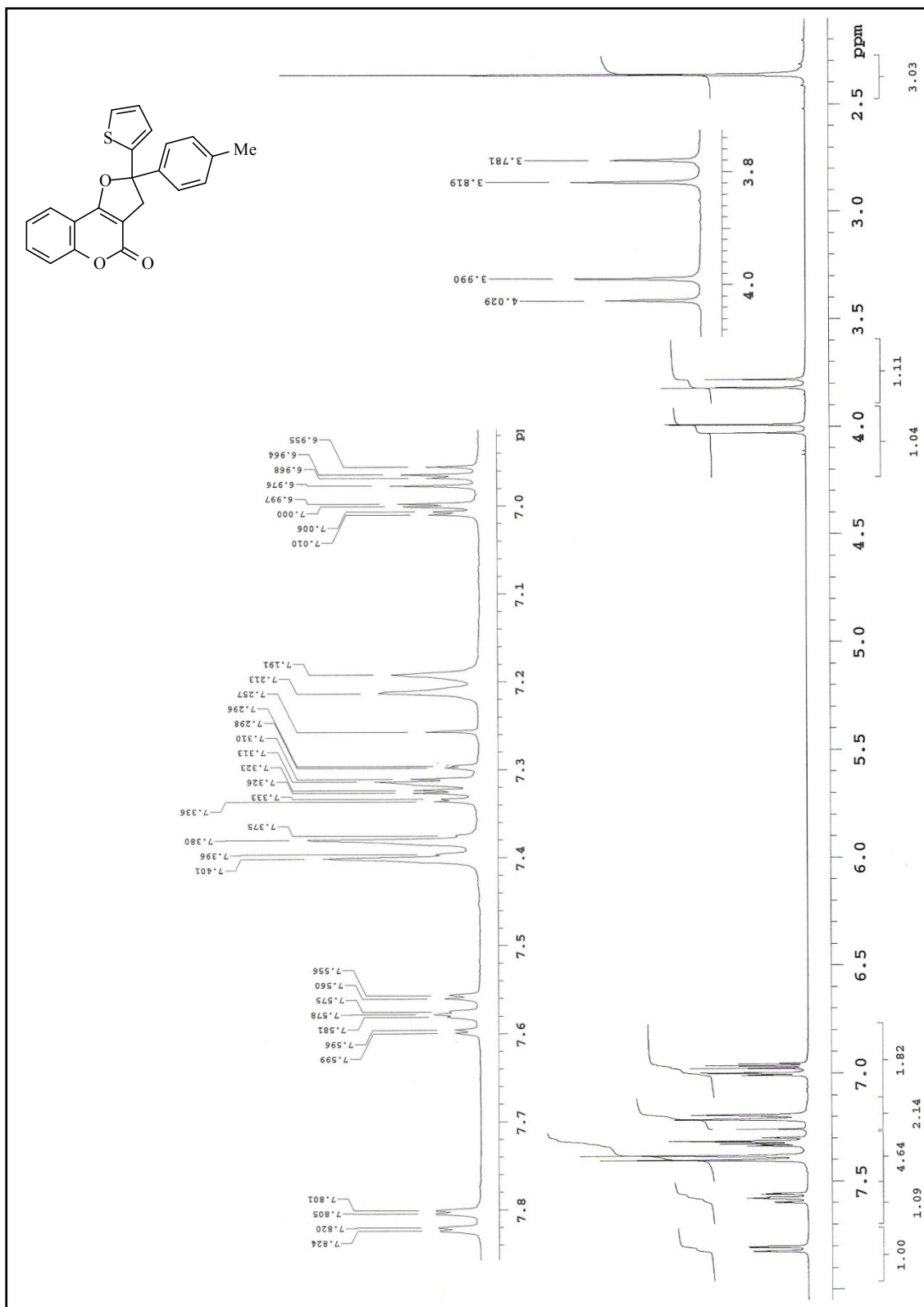
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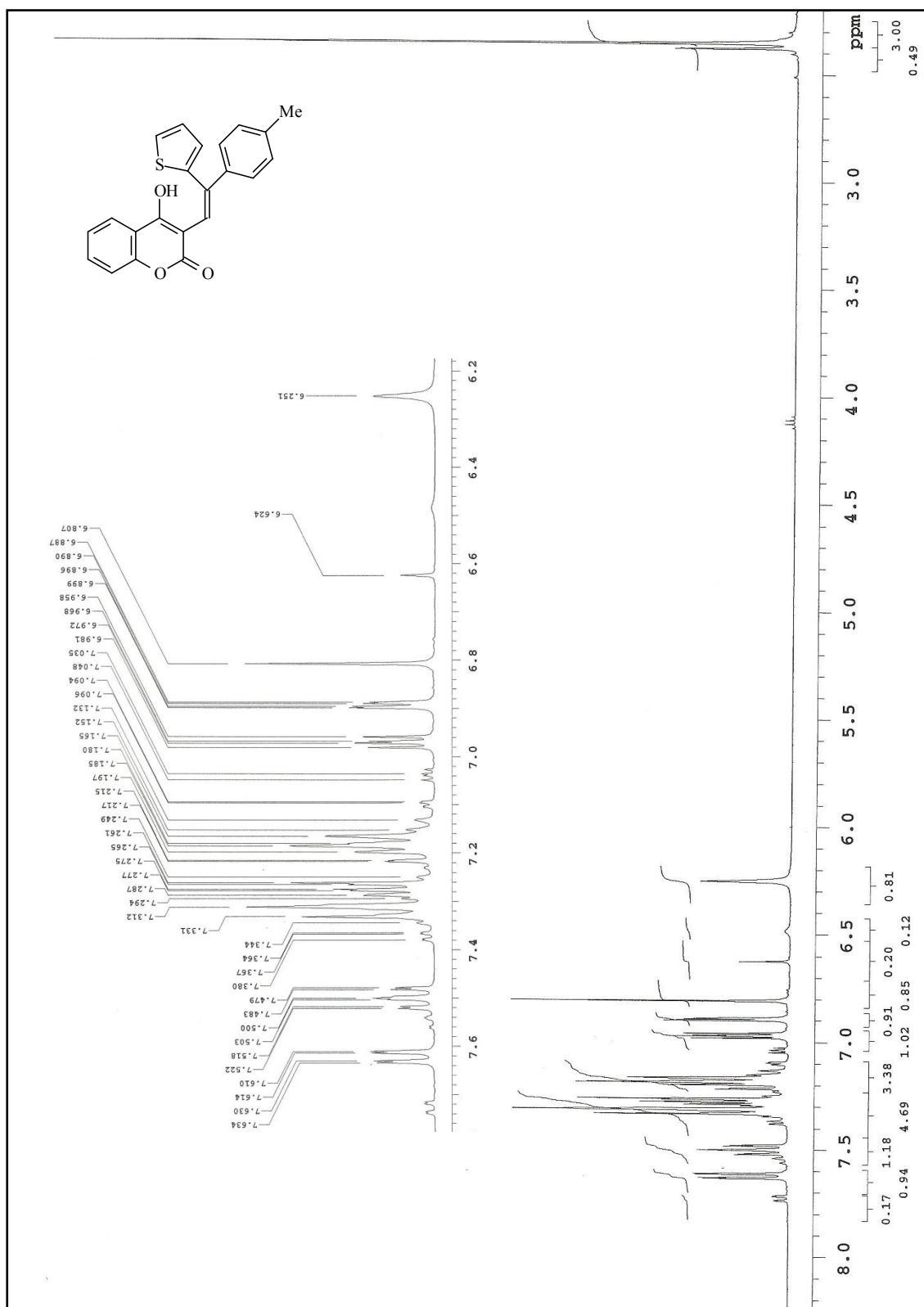
2.2 $^1\text{H-NMR}$ spectra of **8**



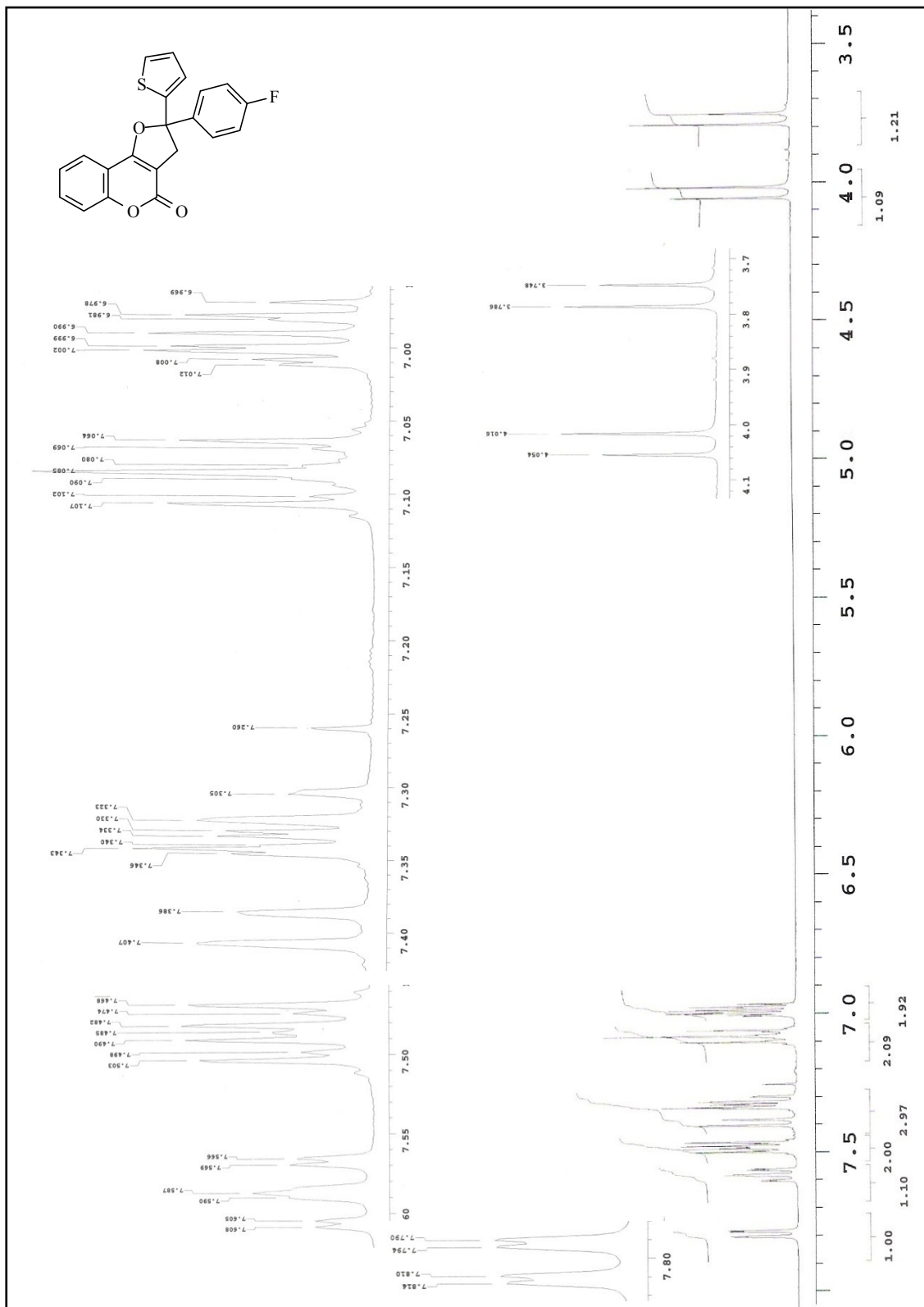
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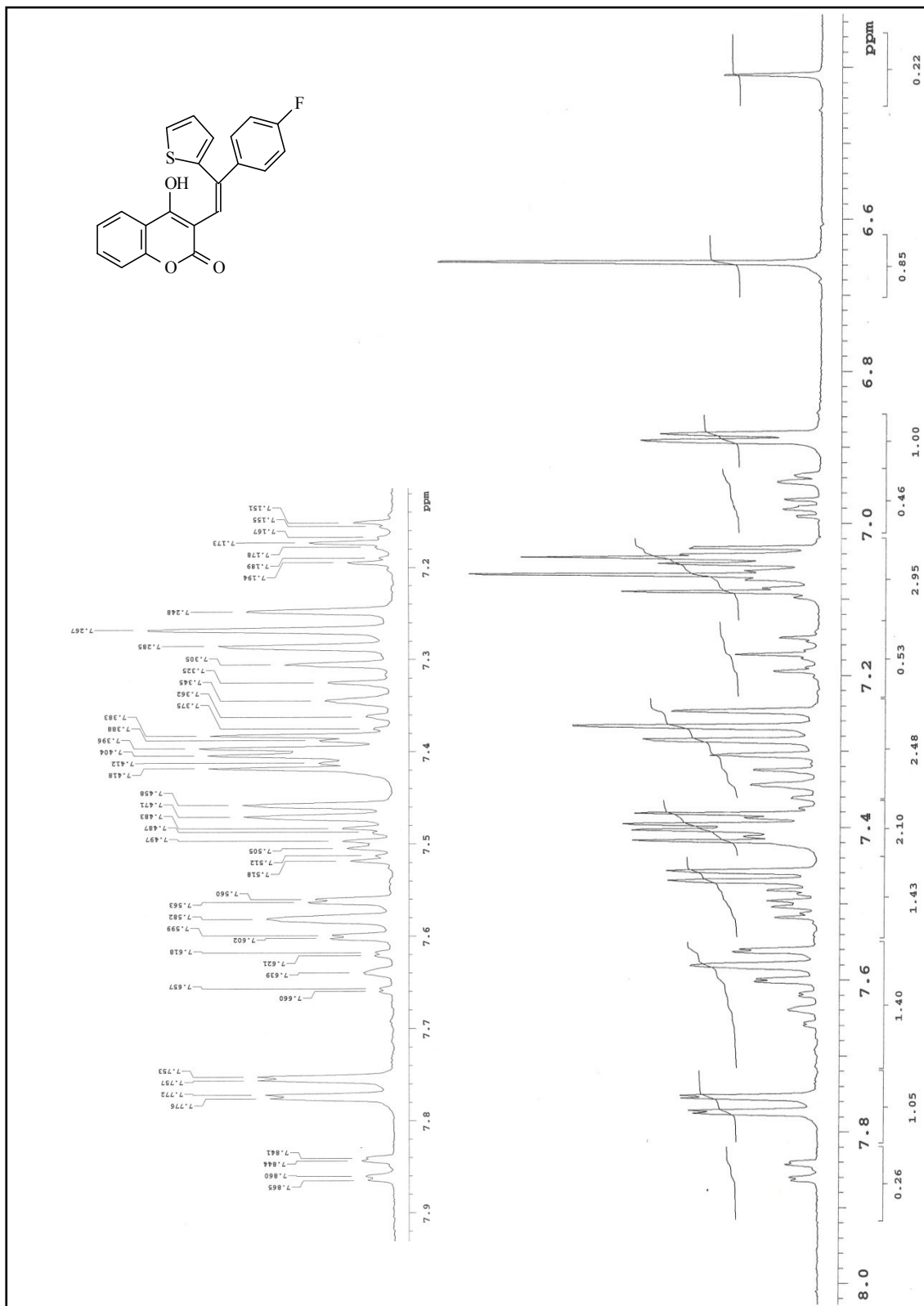
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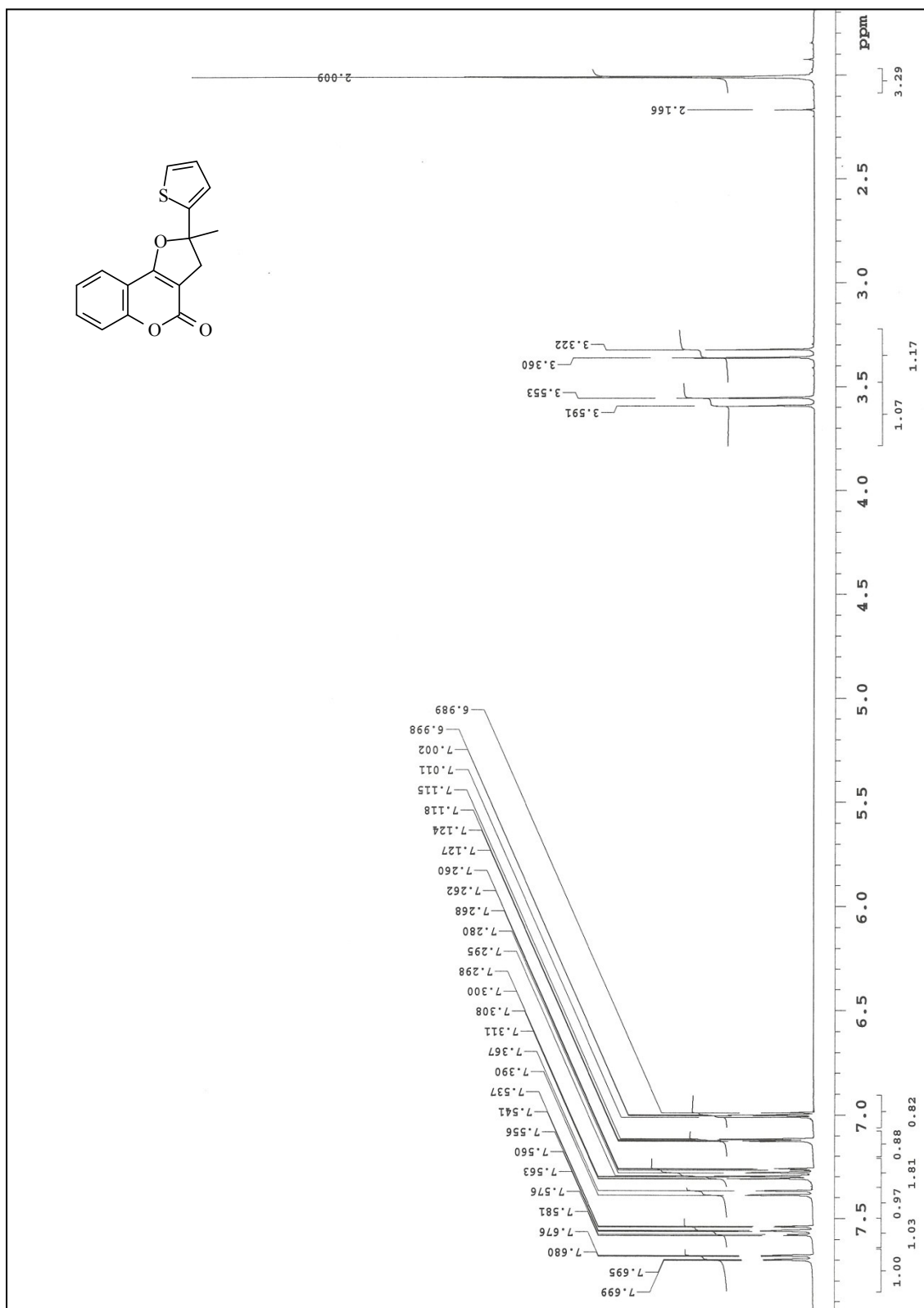
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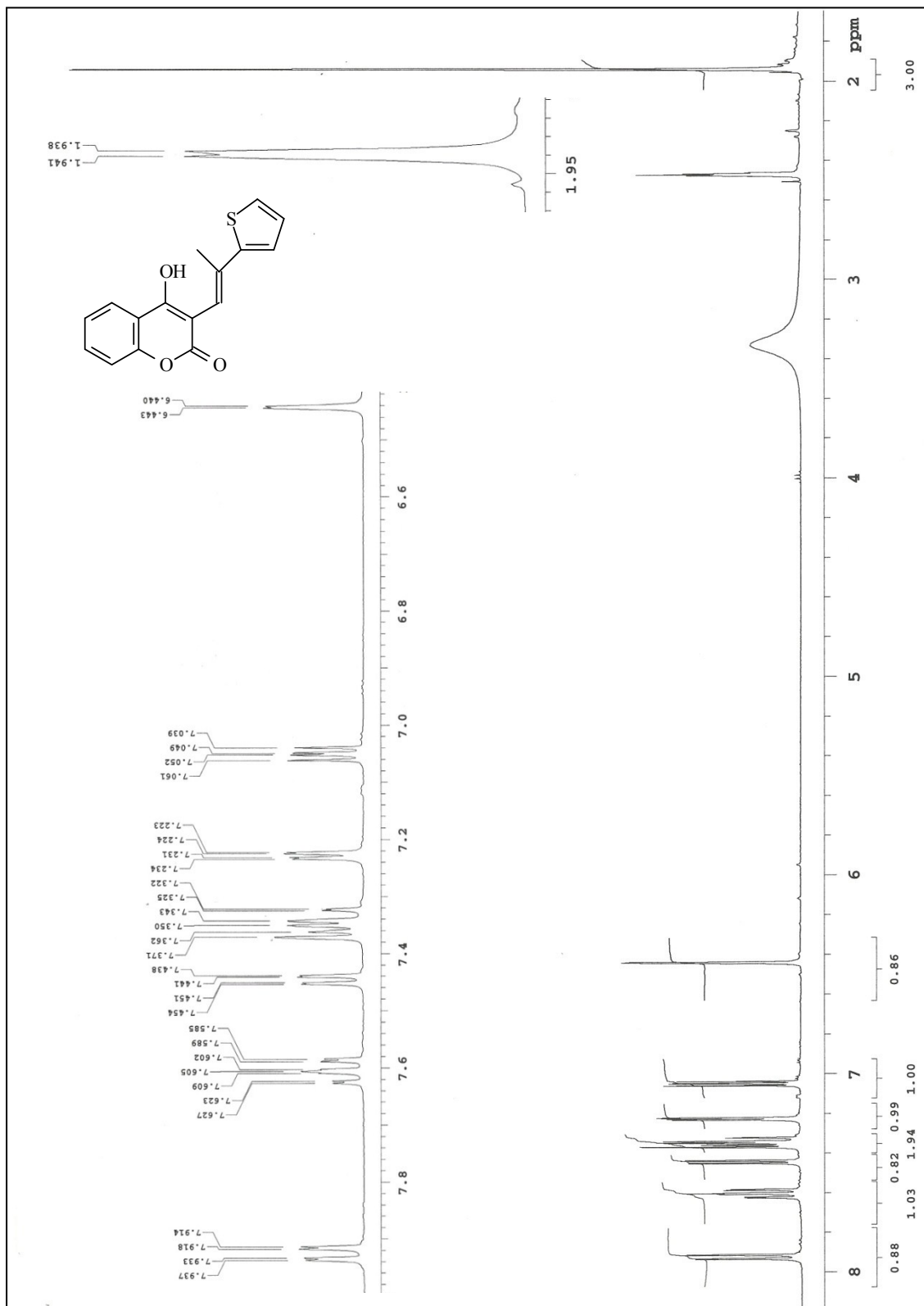
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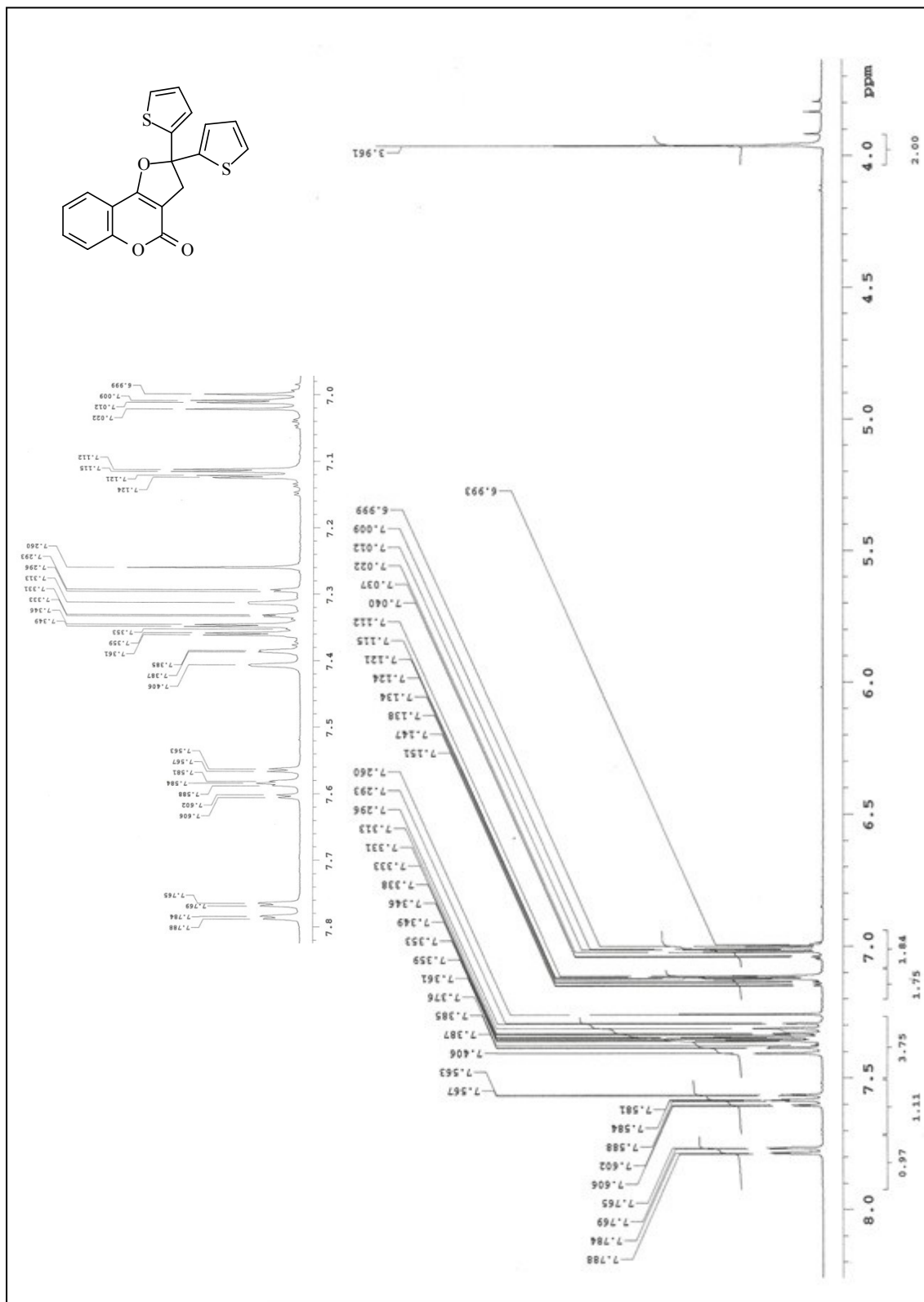
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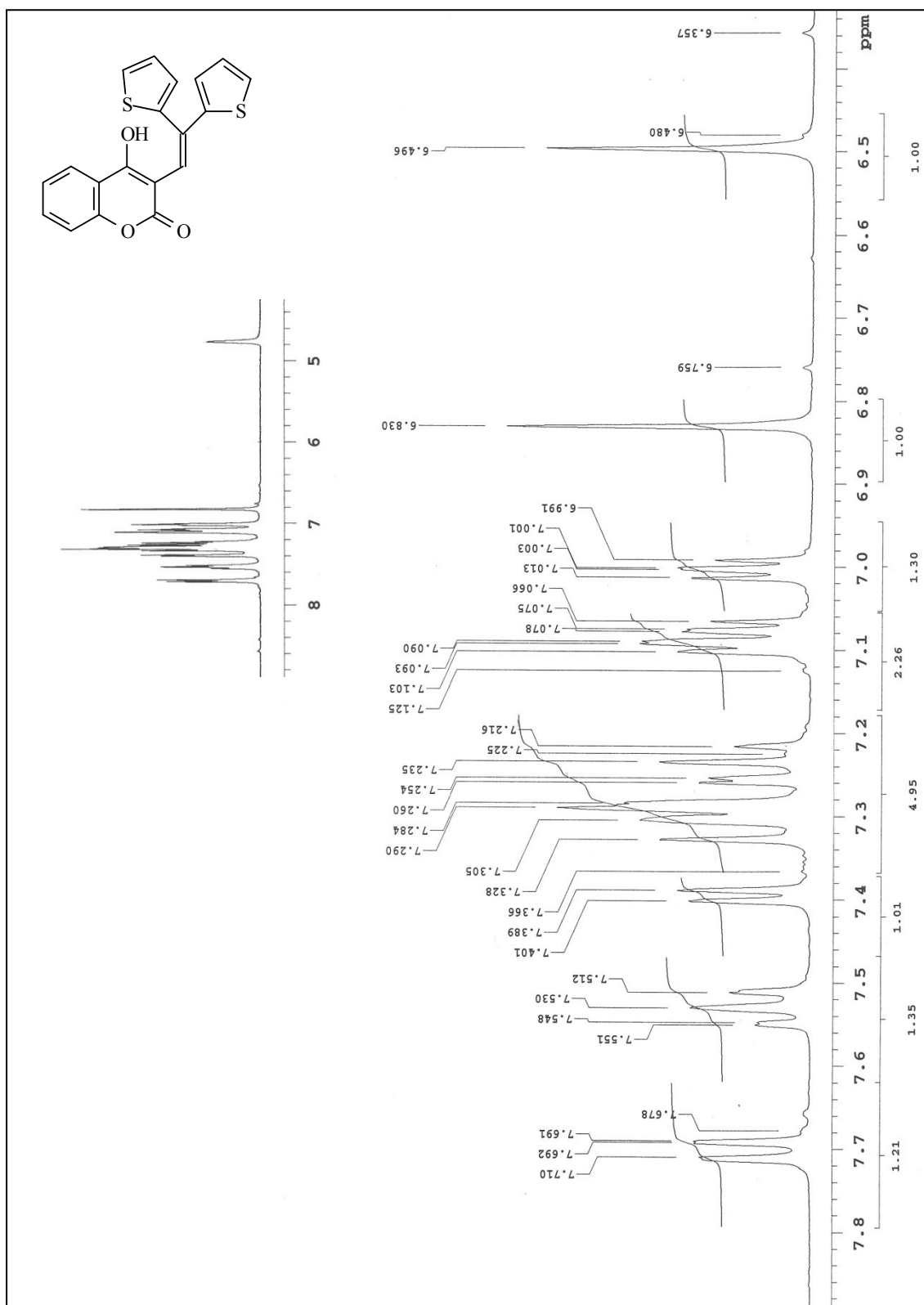
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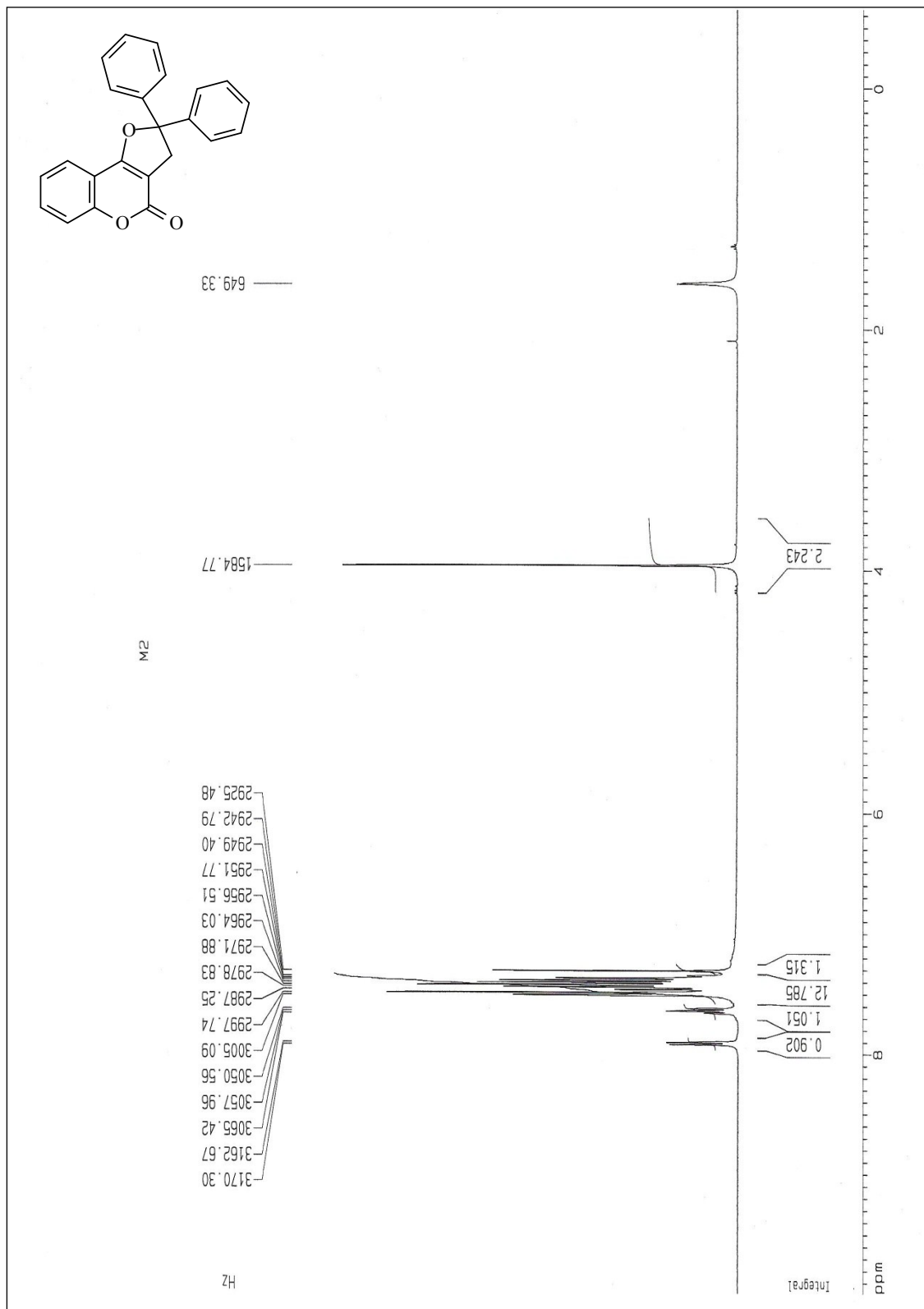
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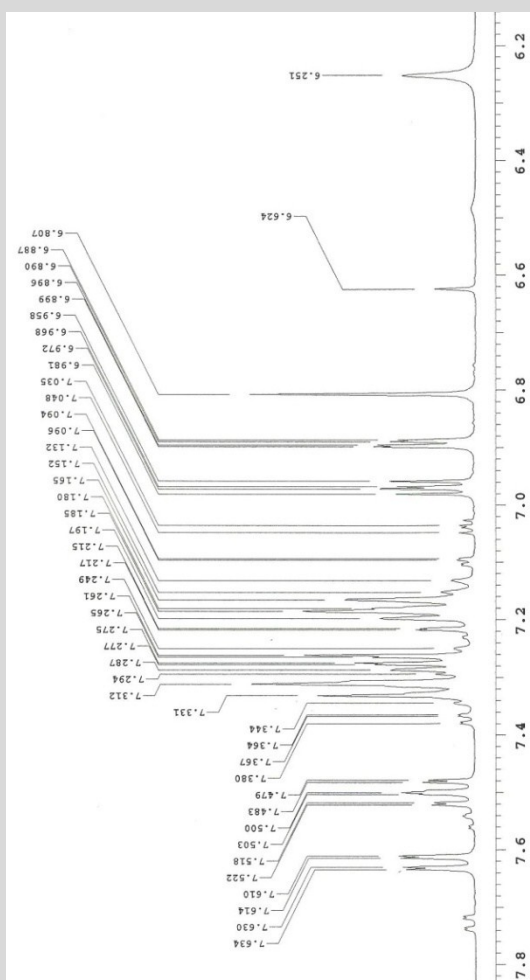
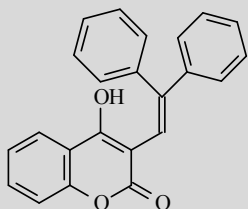
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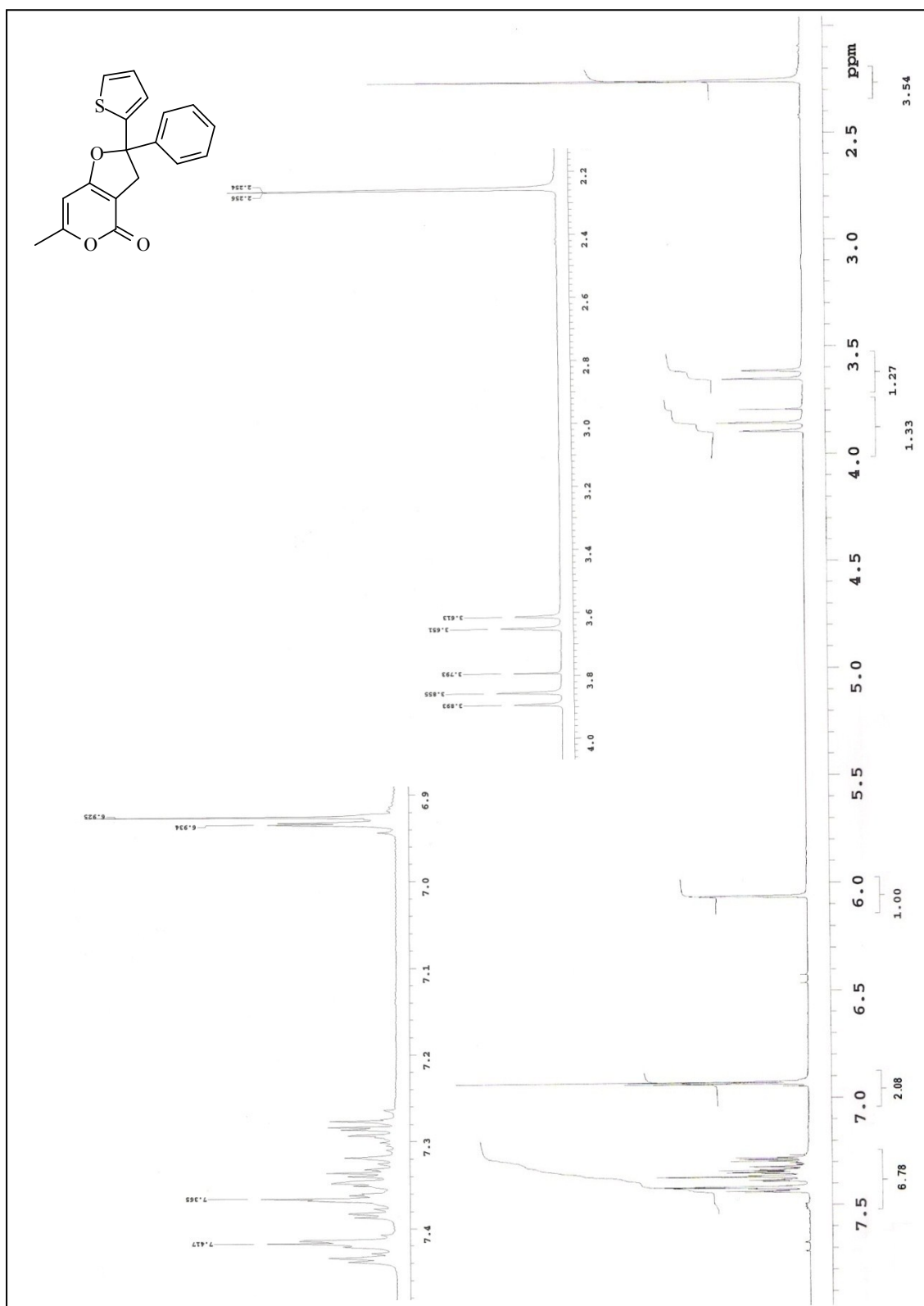
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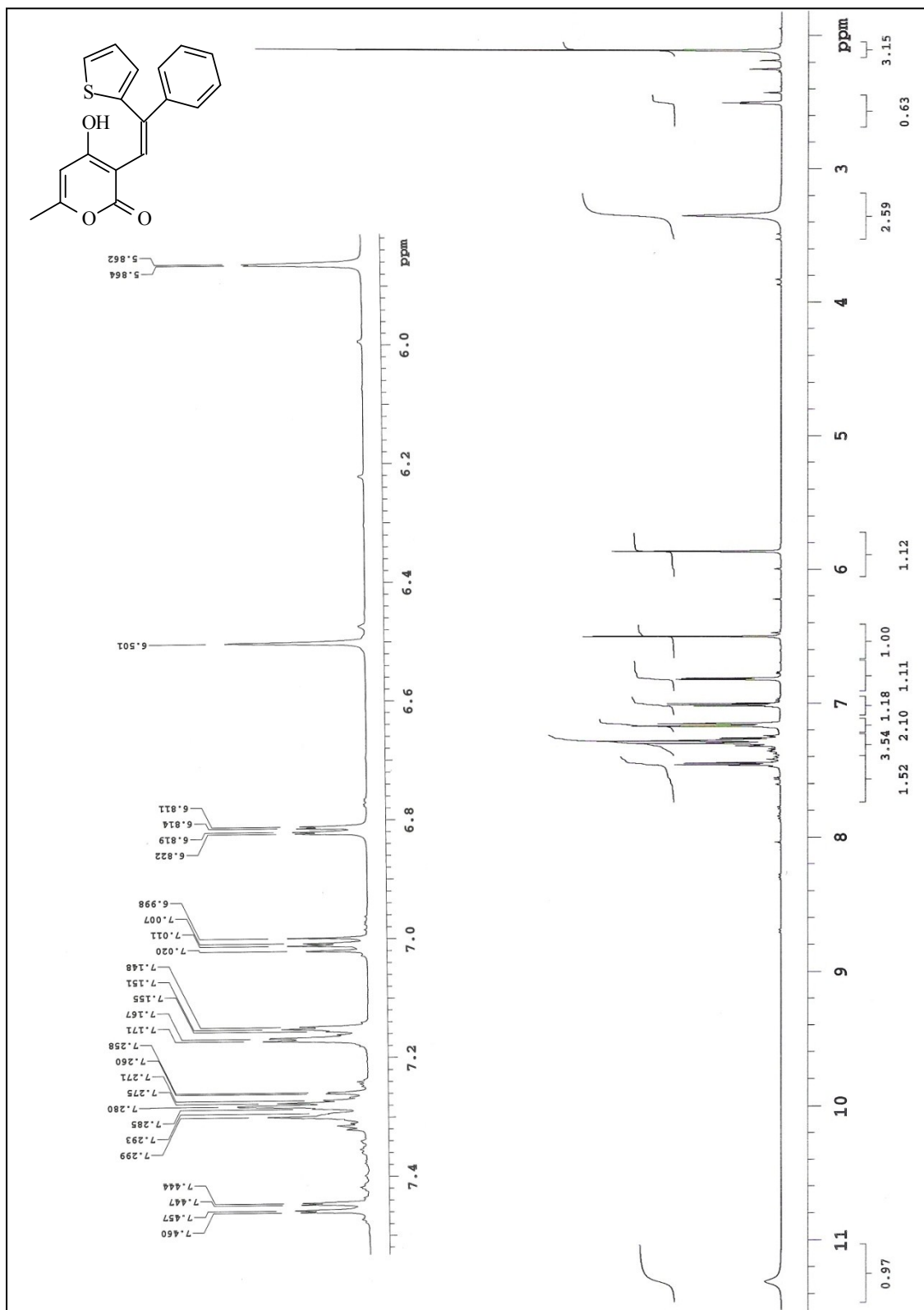
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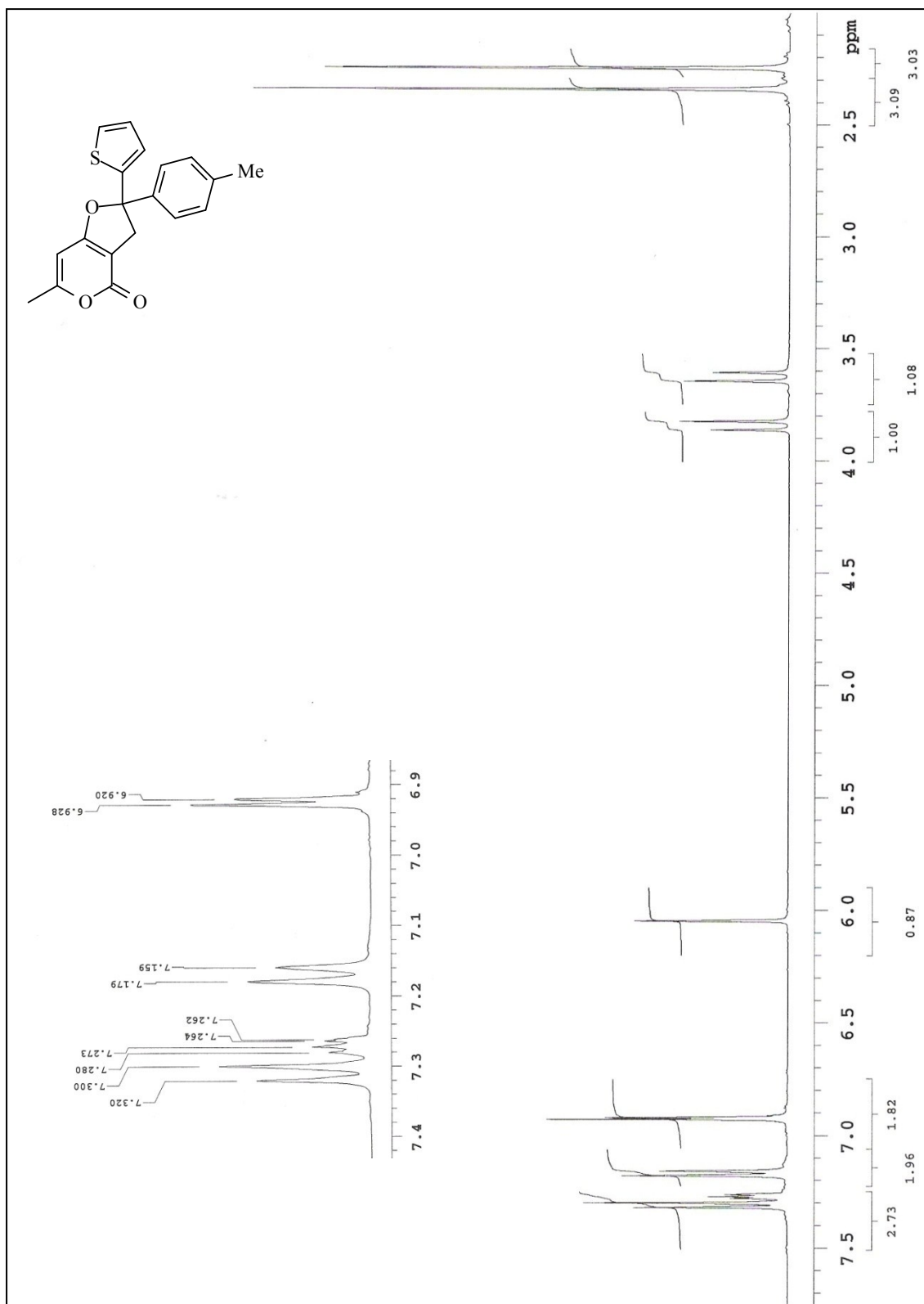
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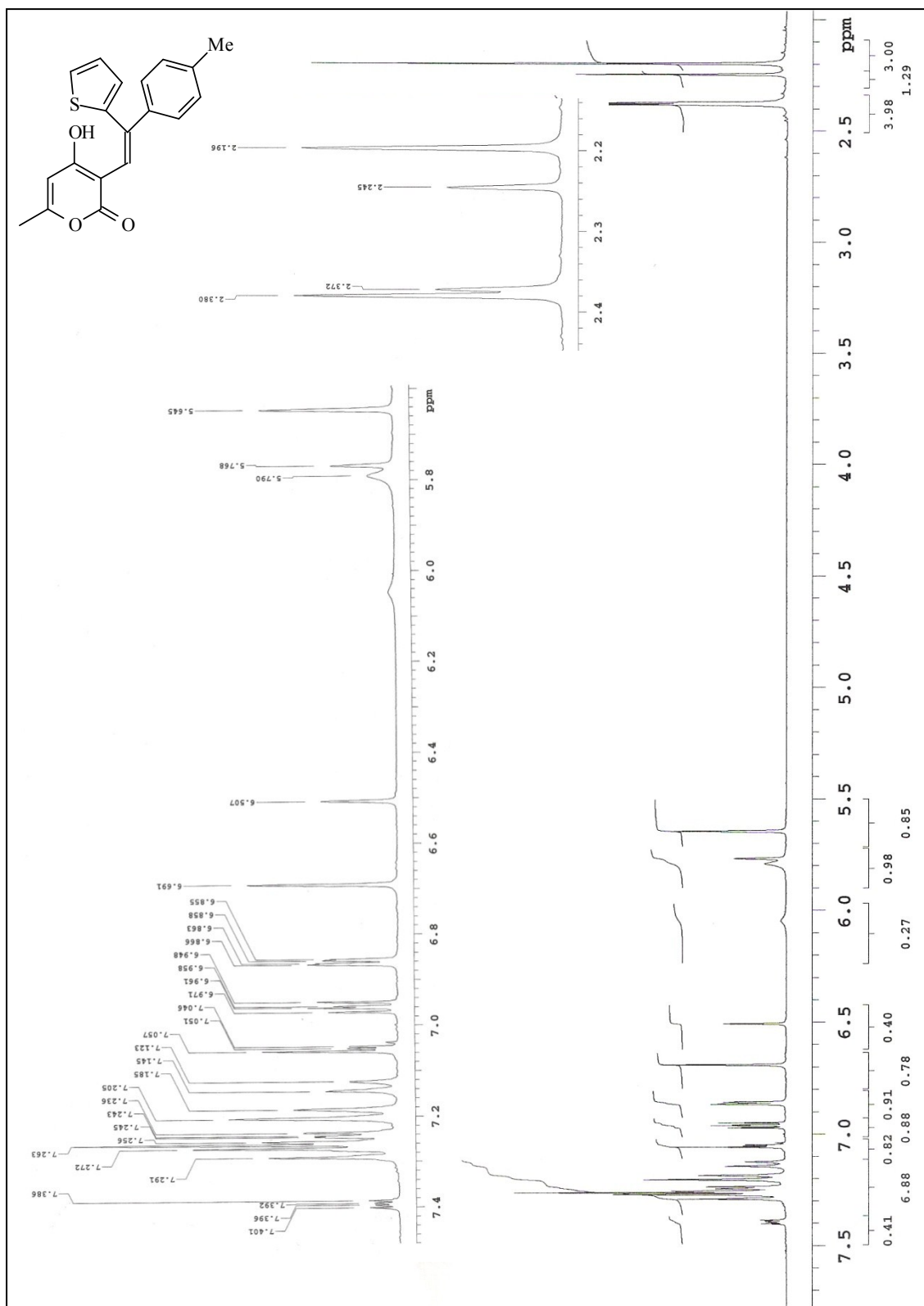
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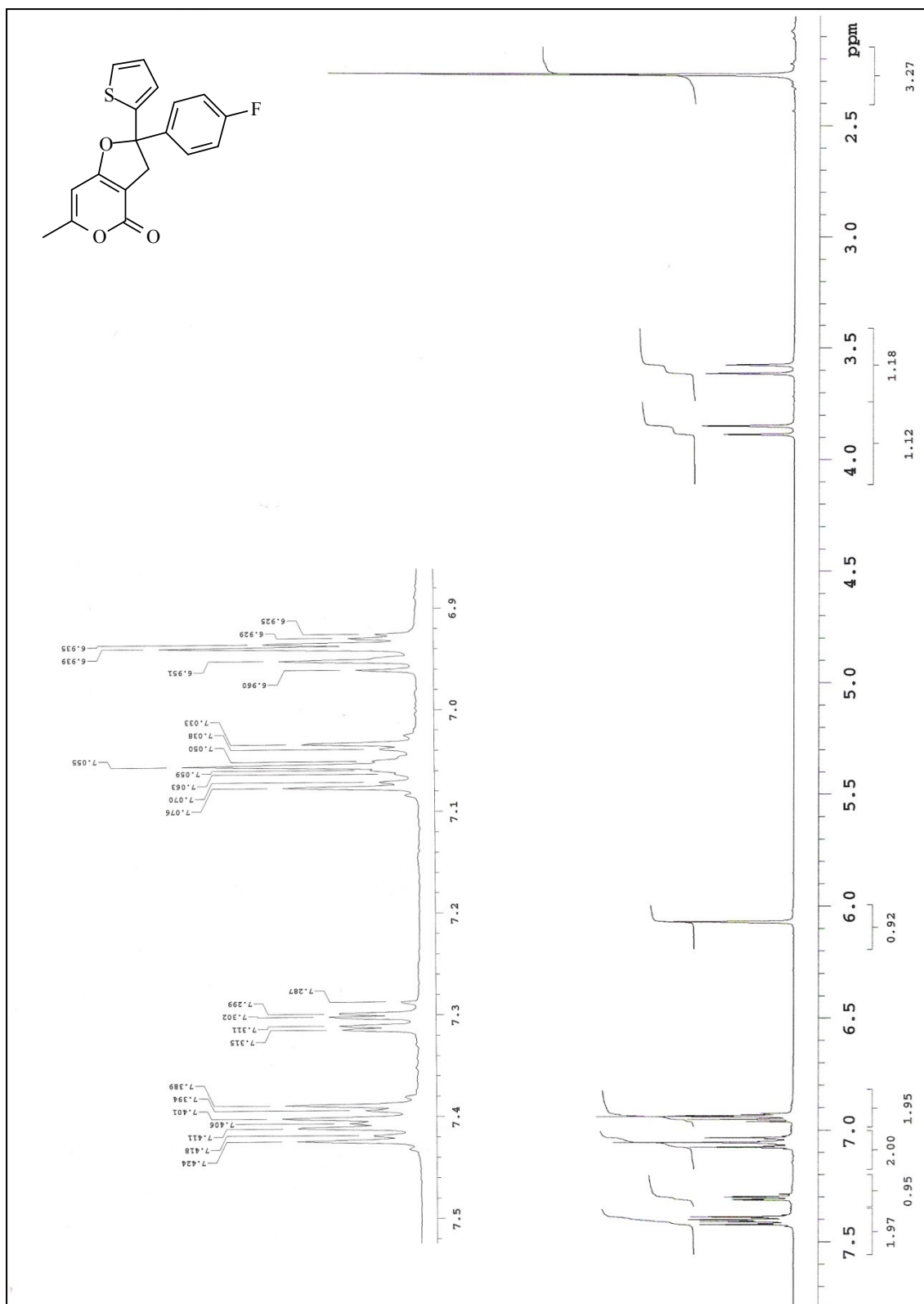
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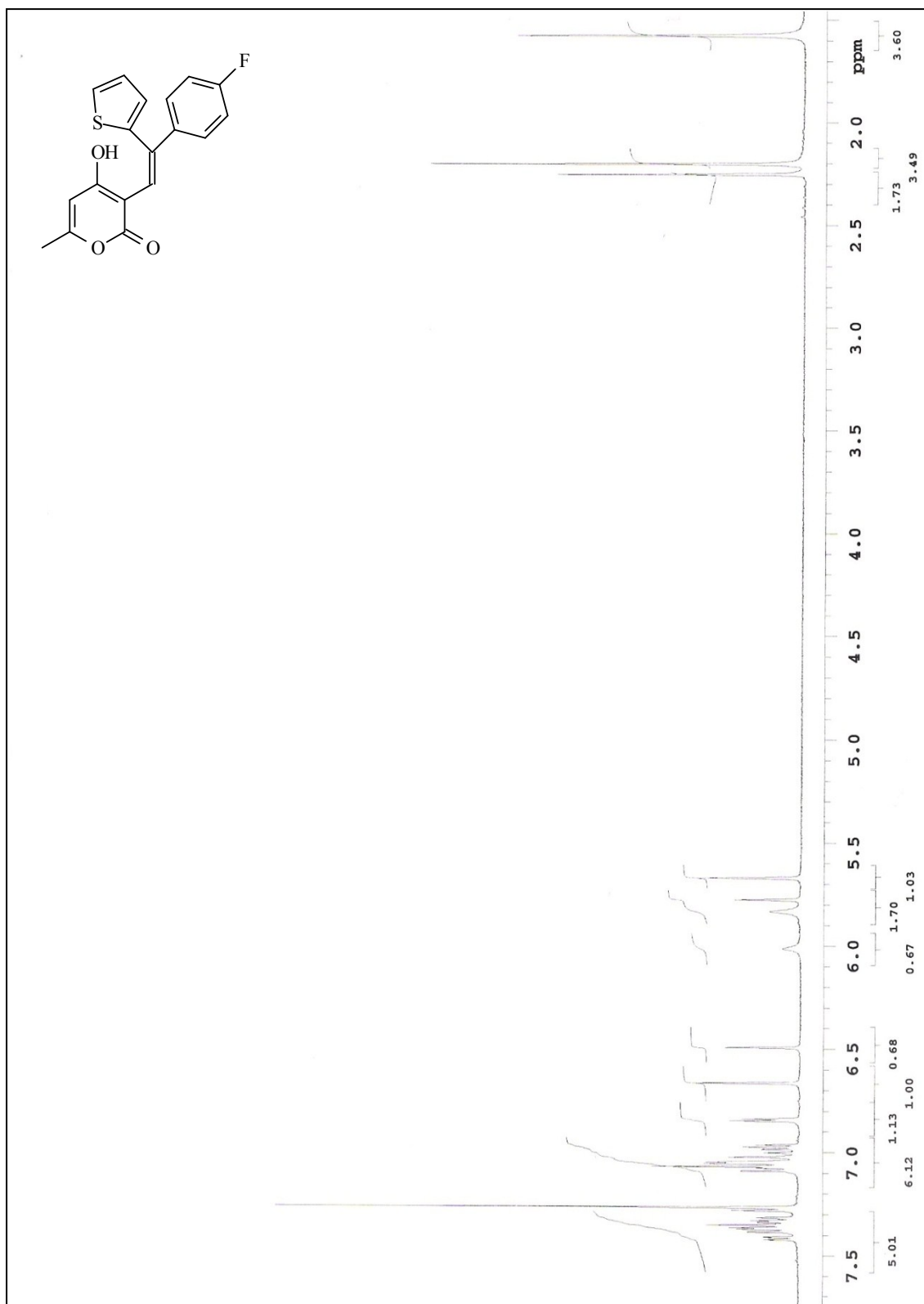
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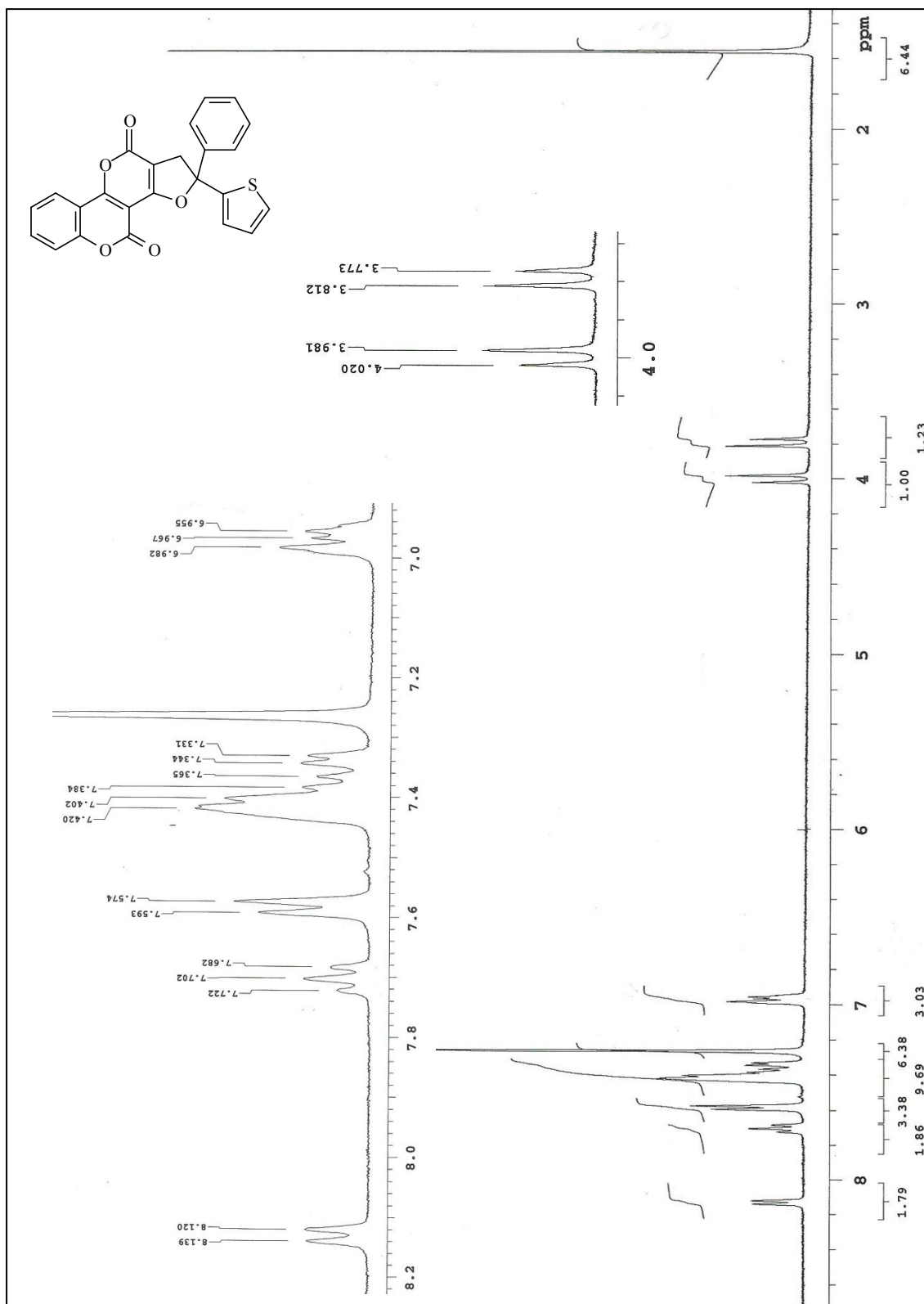
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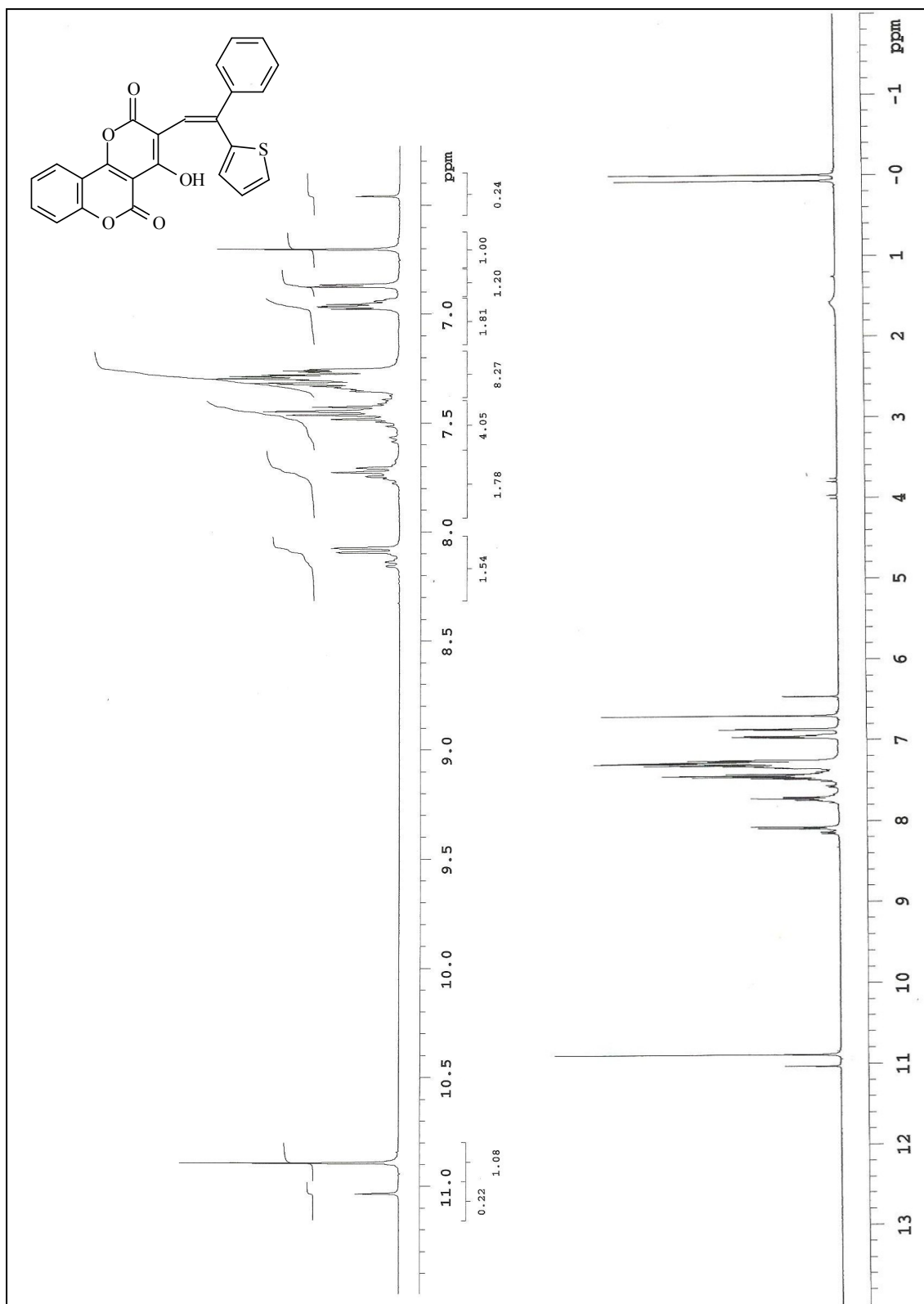
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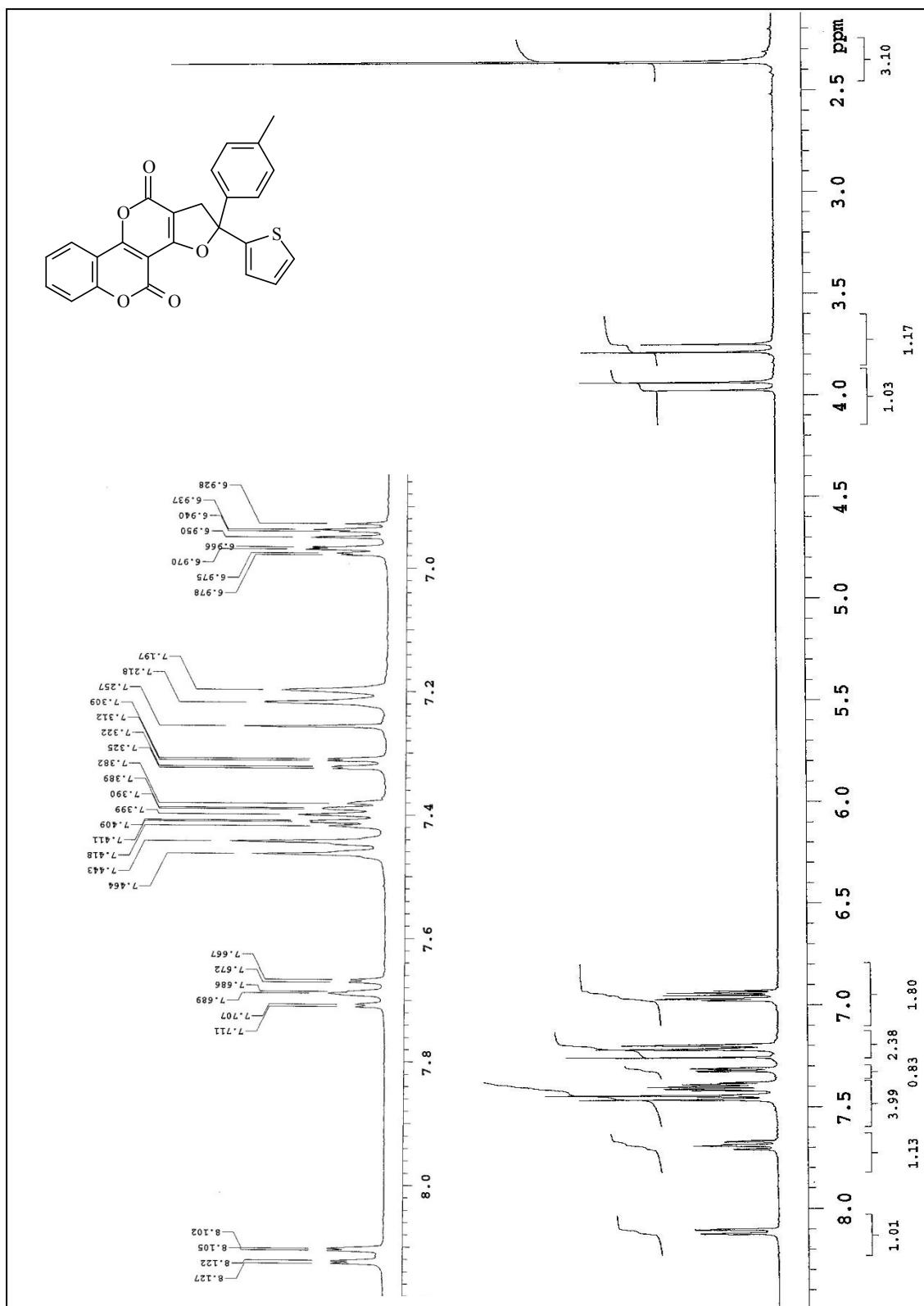
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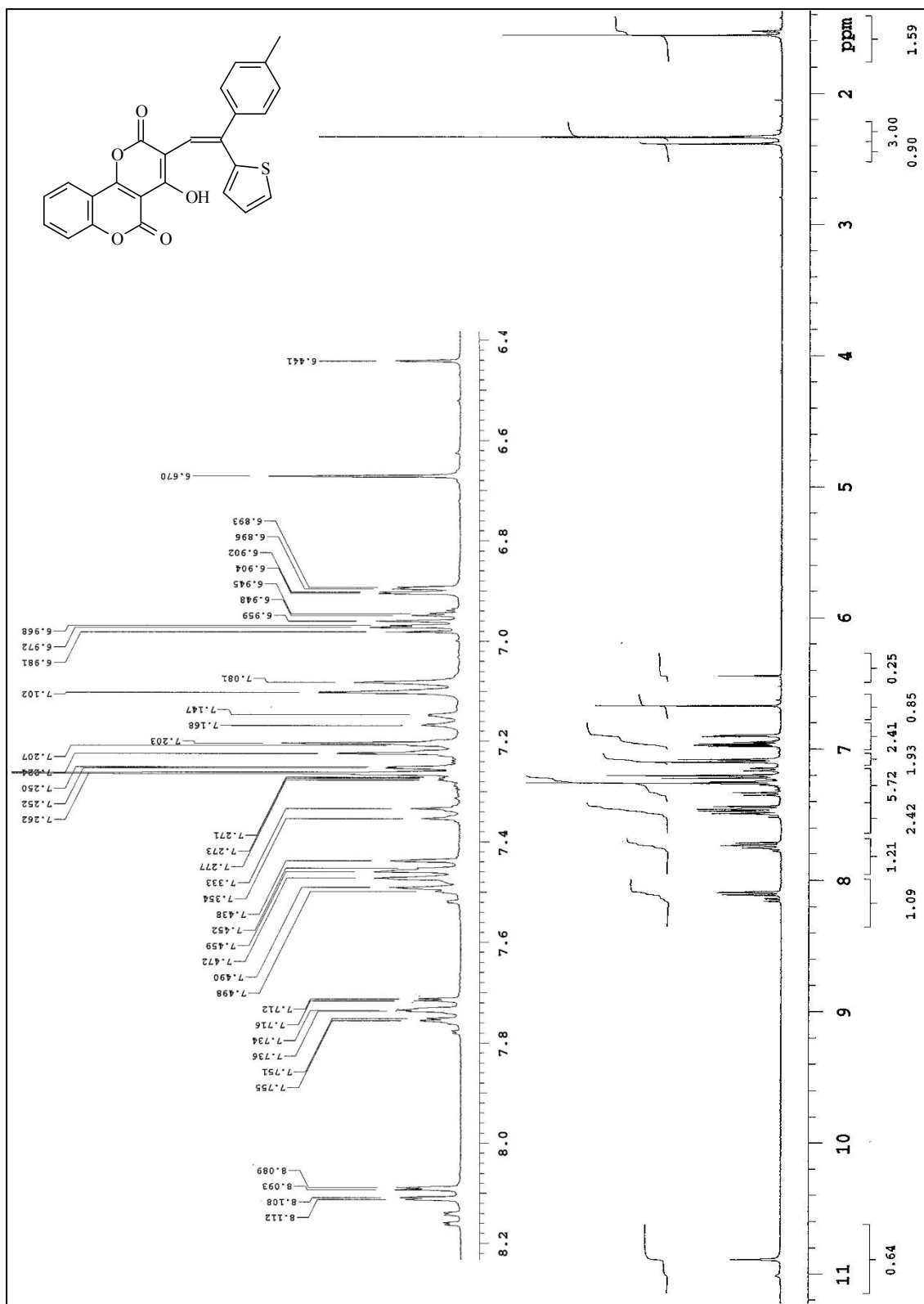
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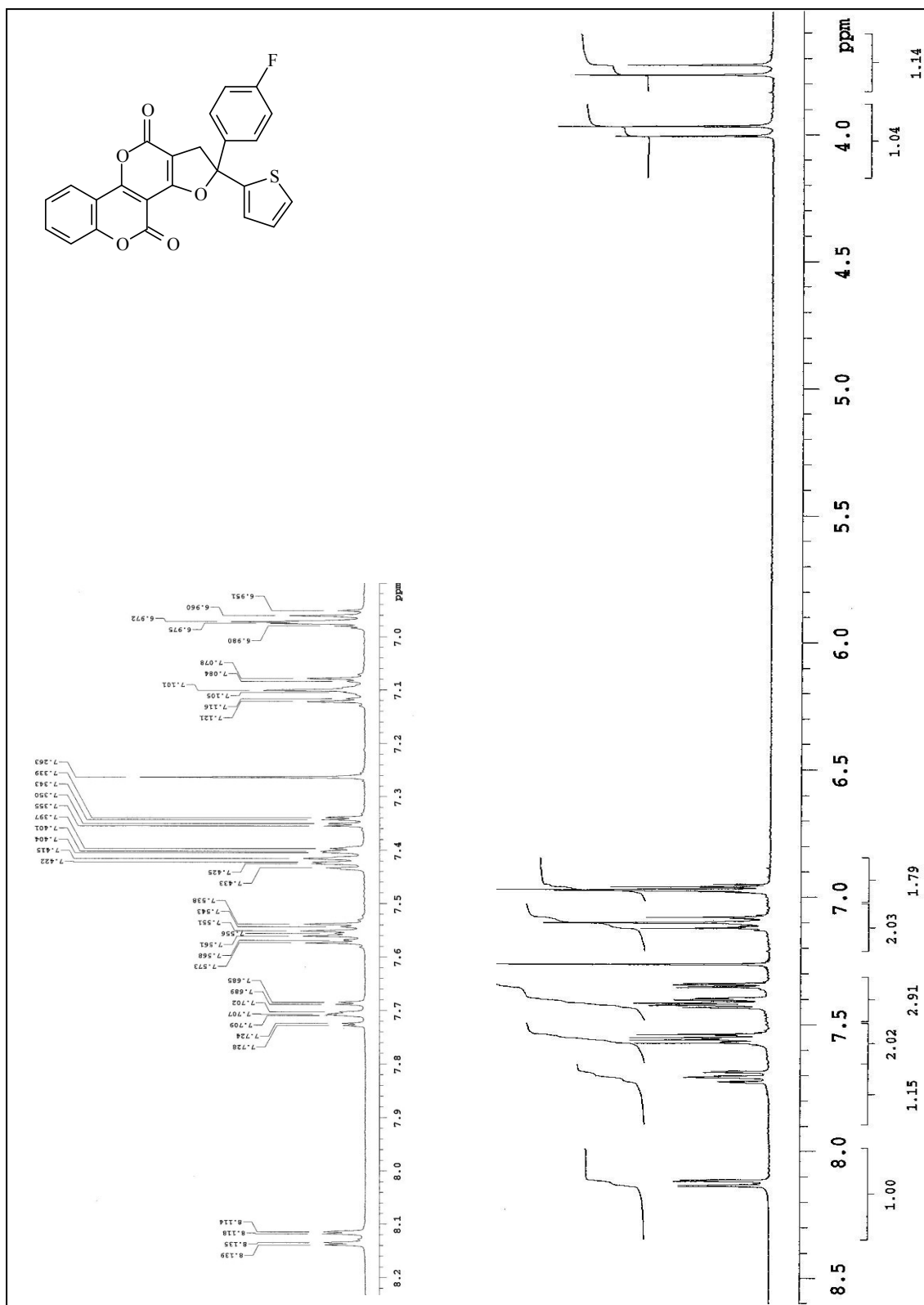
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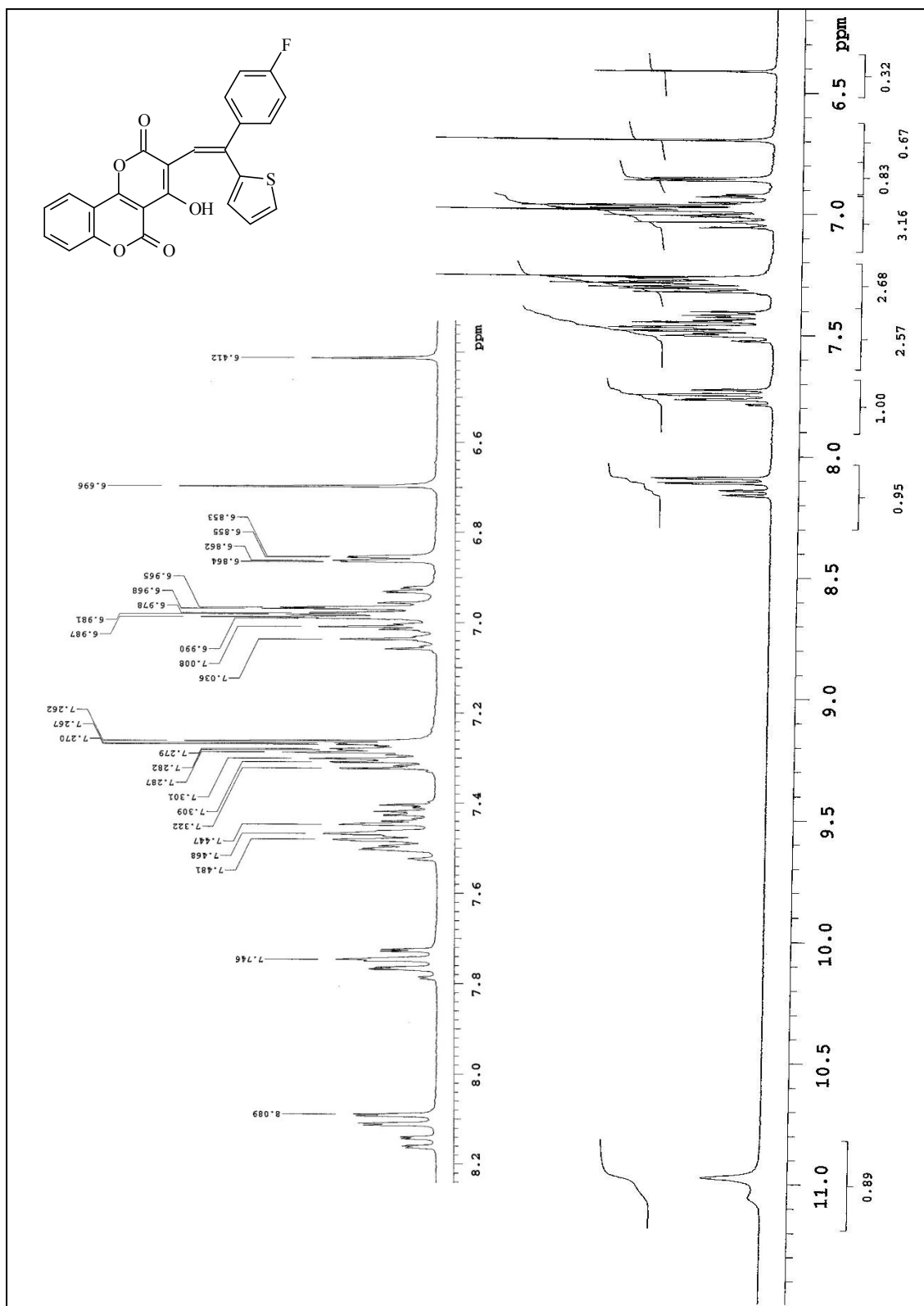
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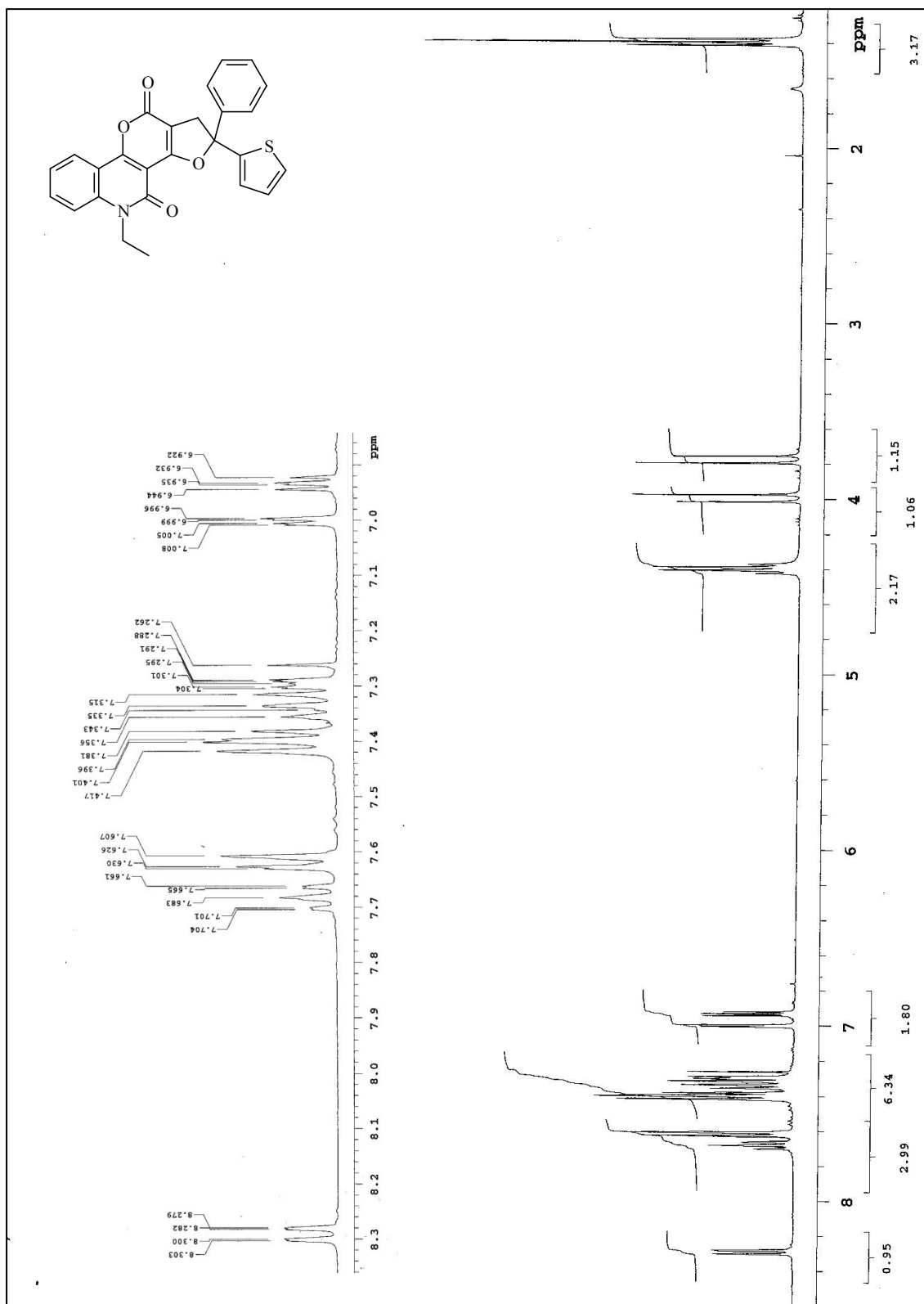
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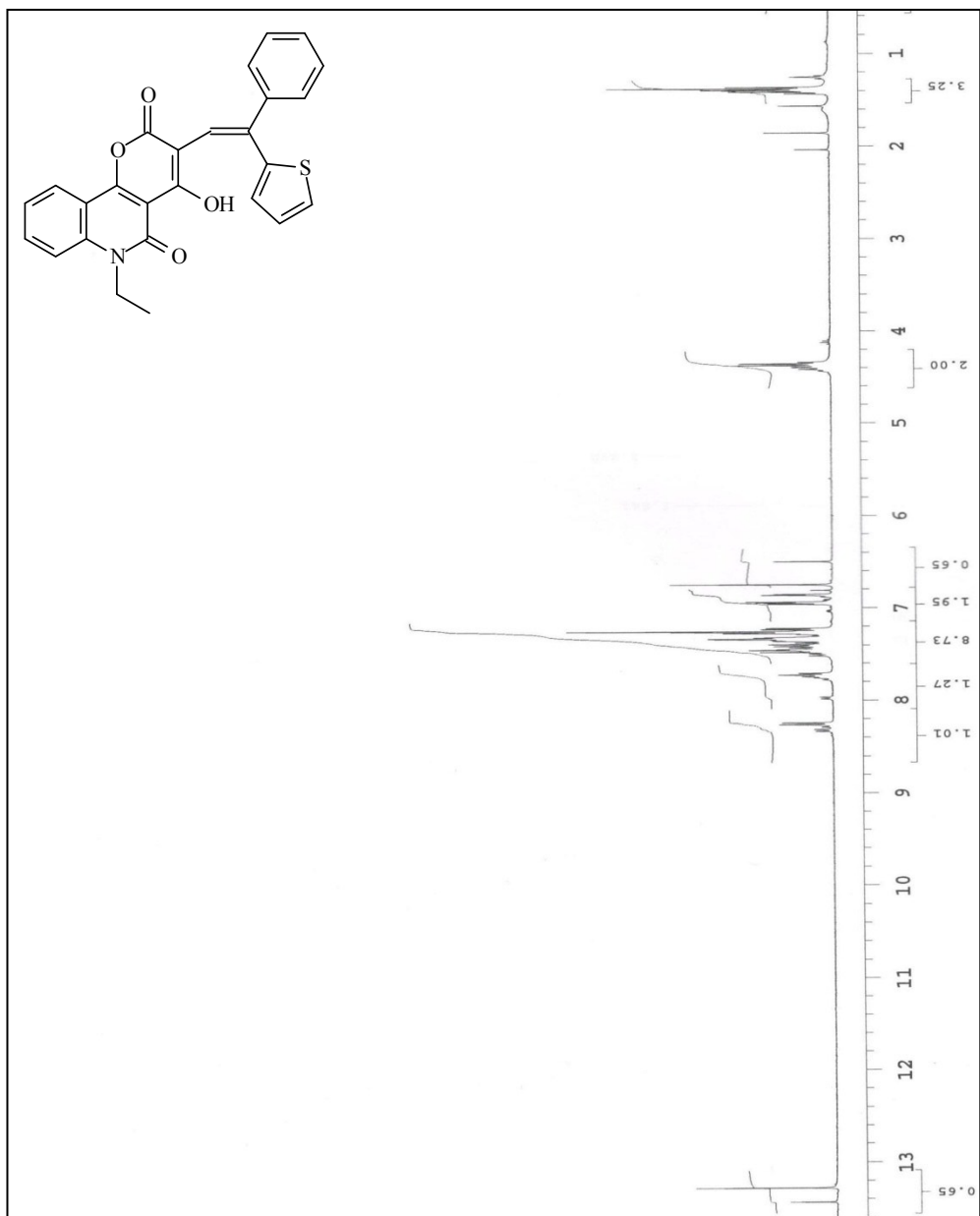
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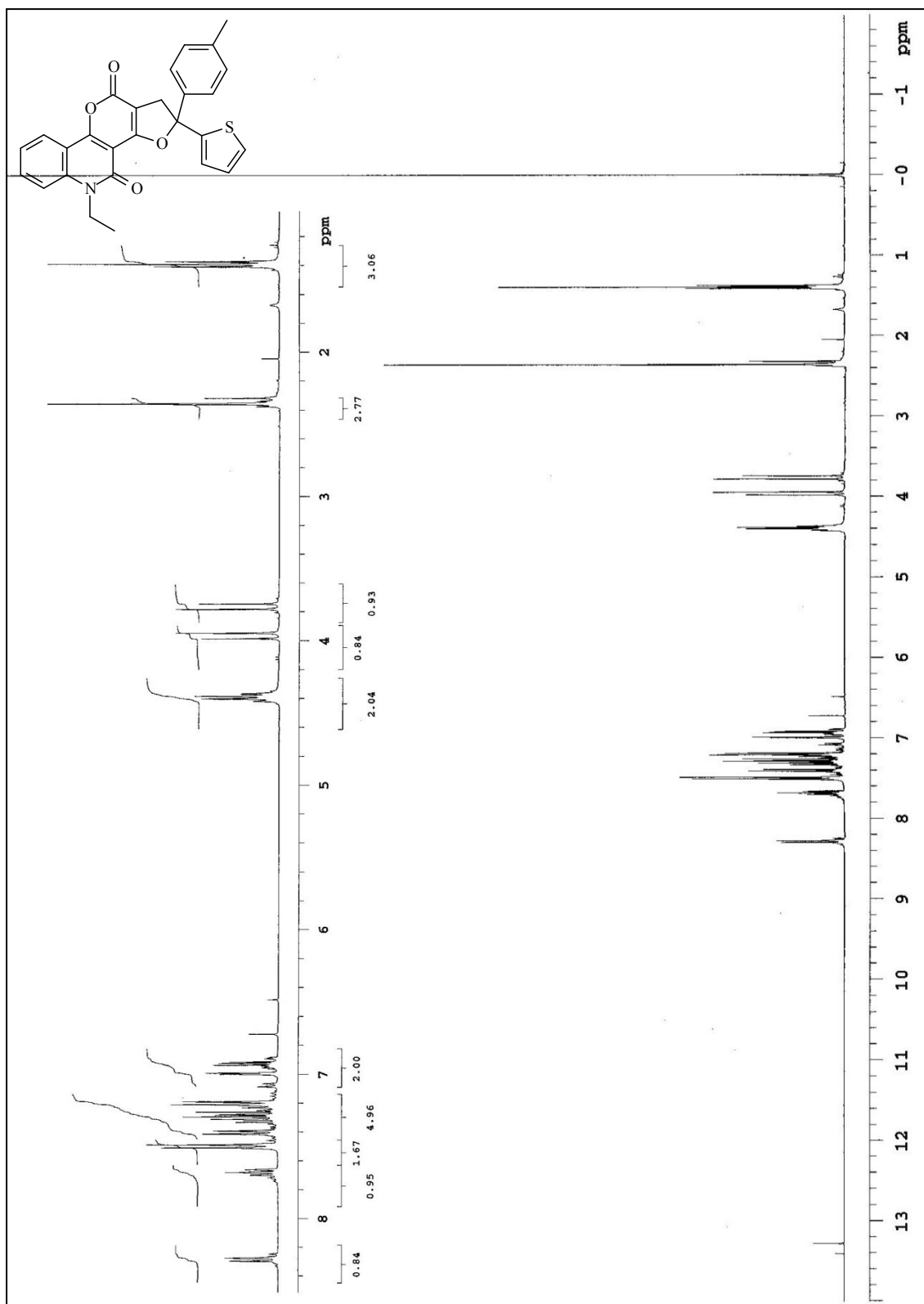
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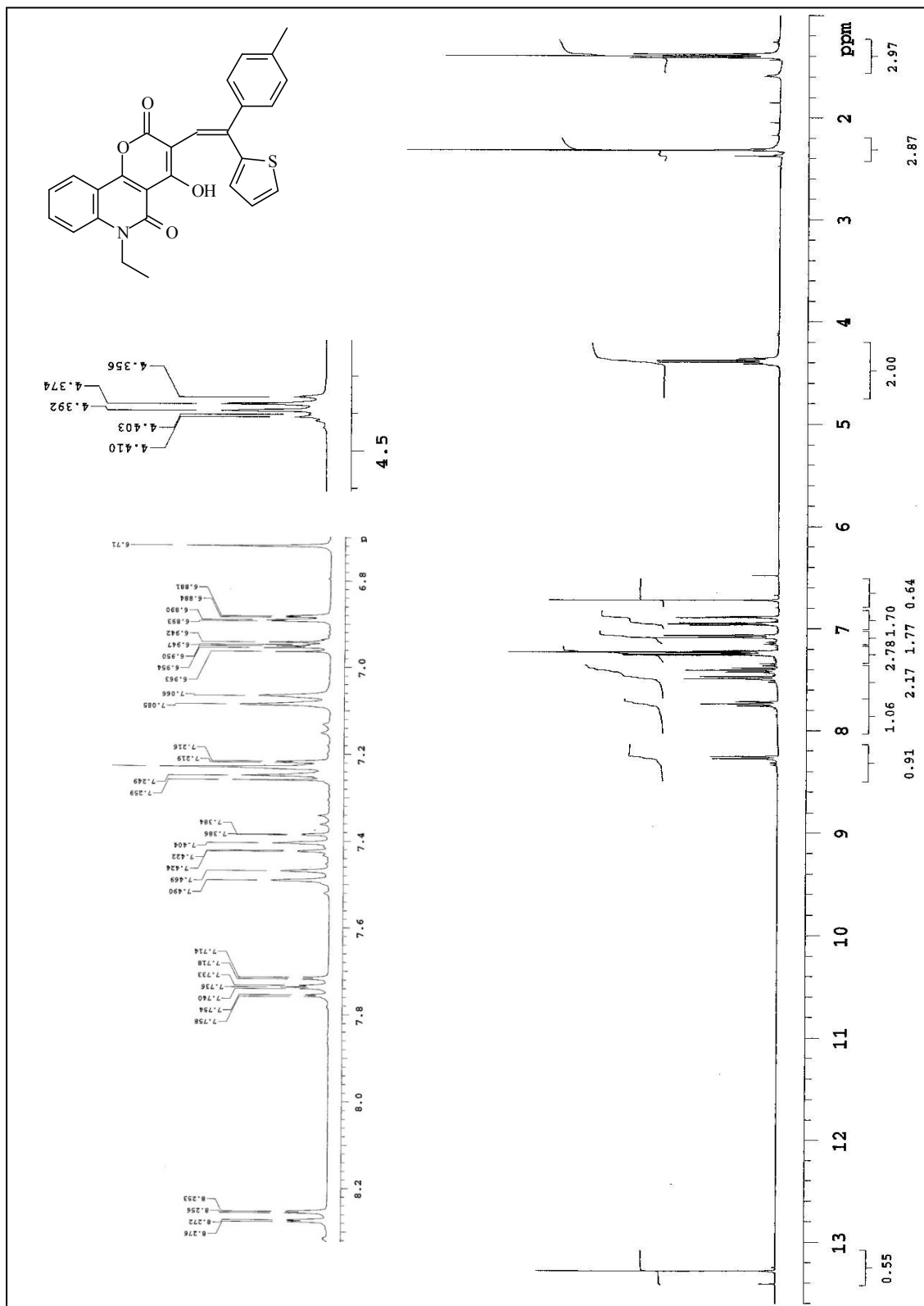
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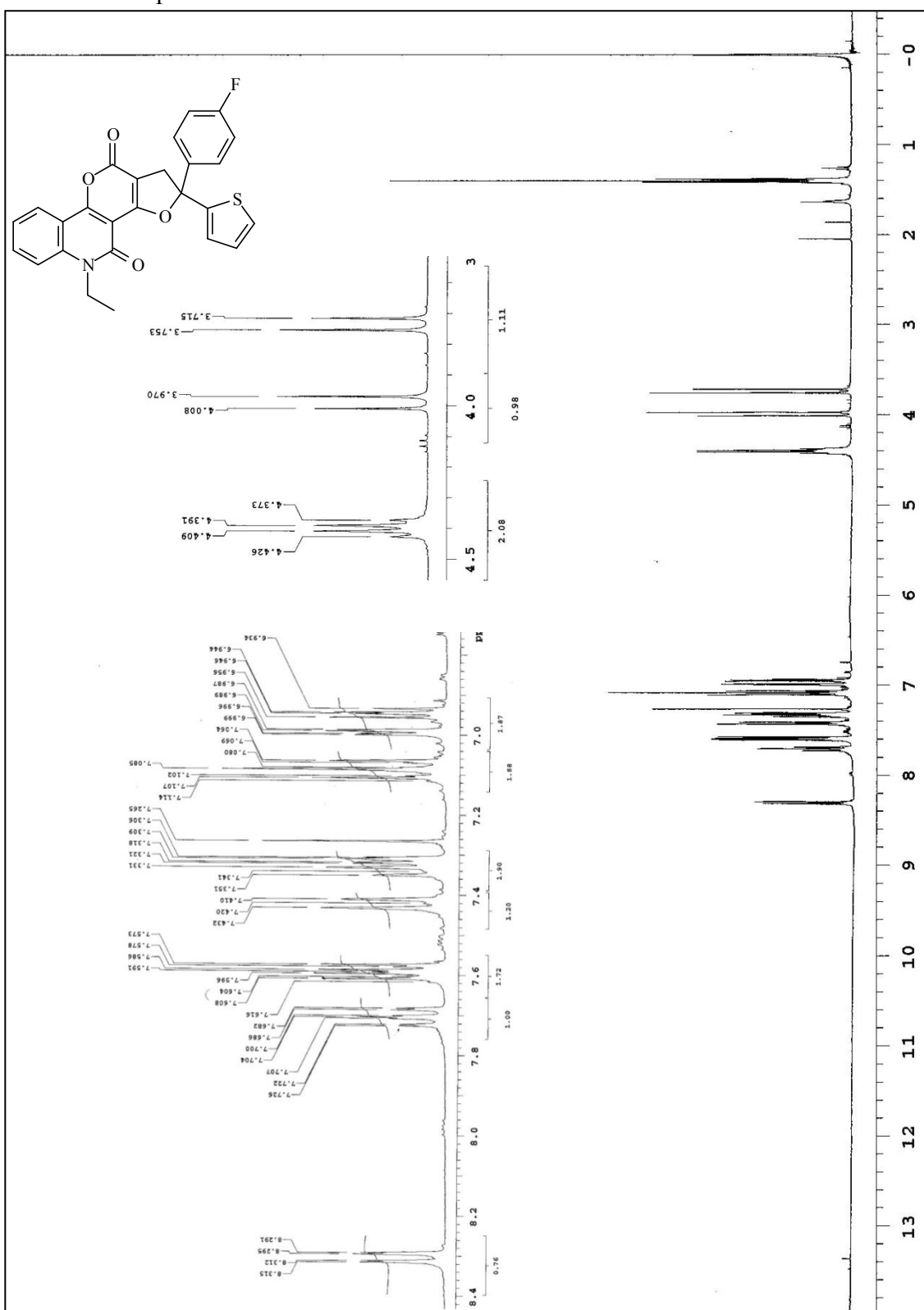
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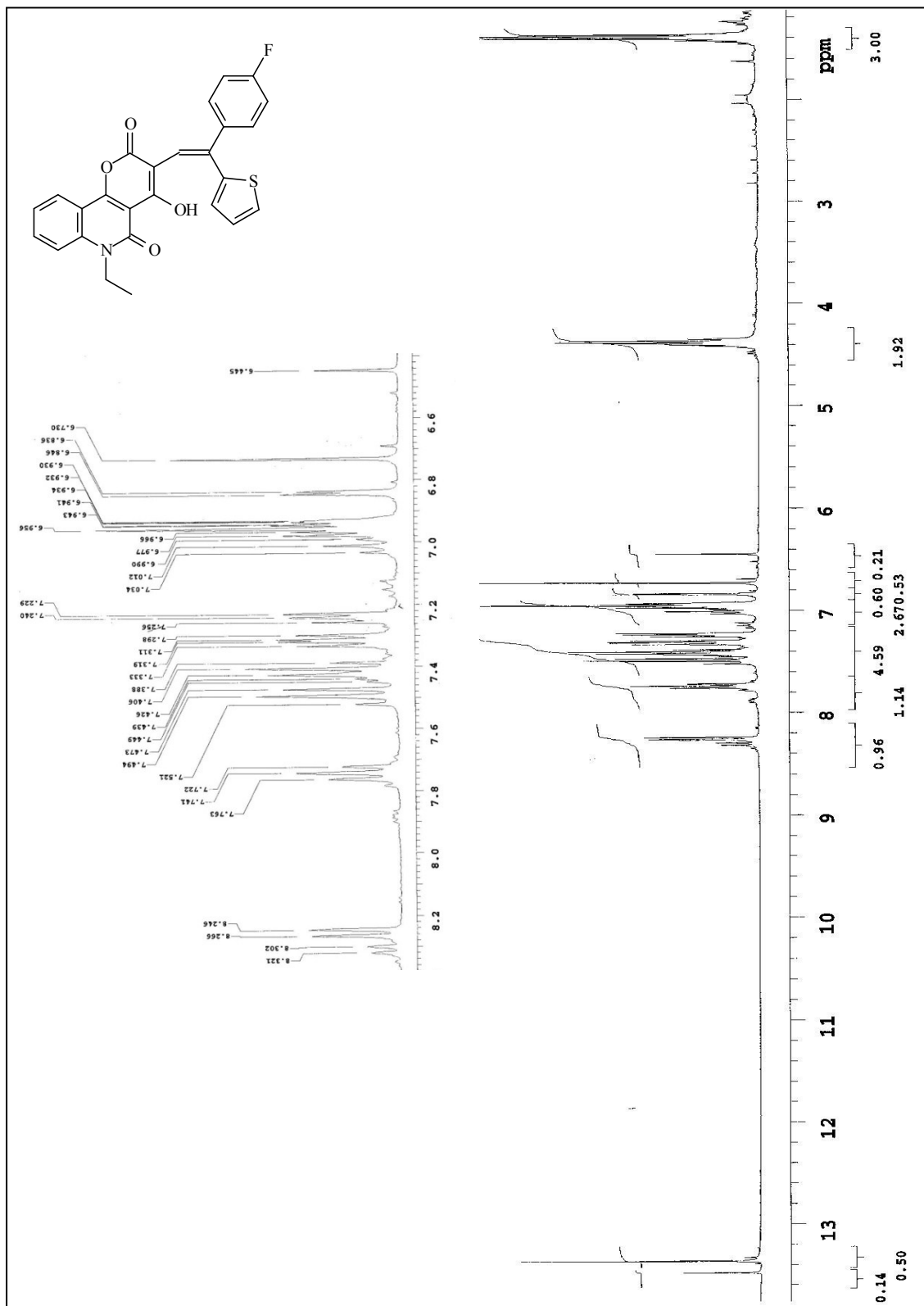
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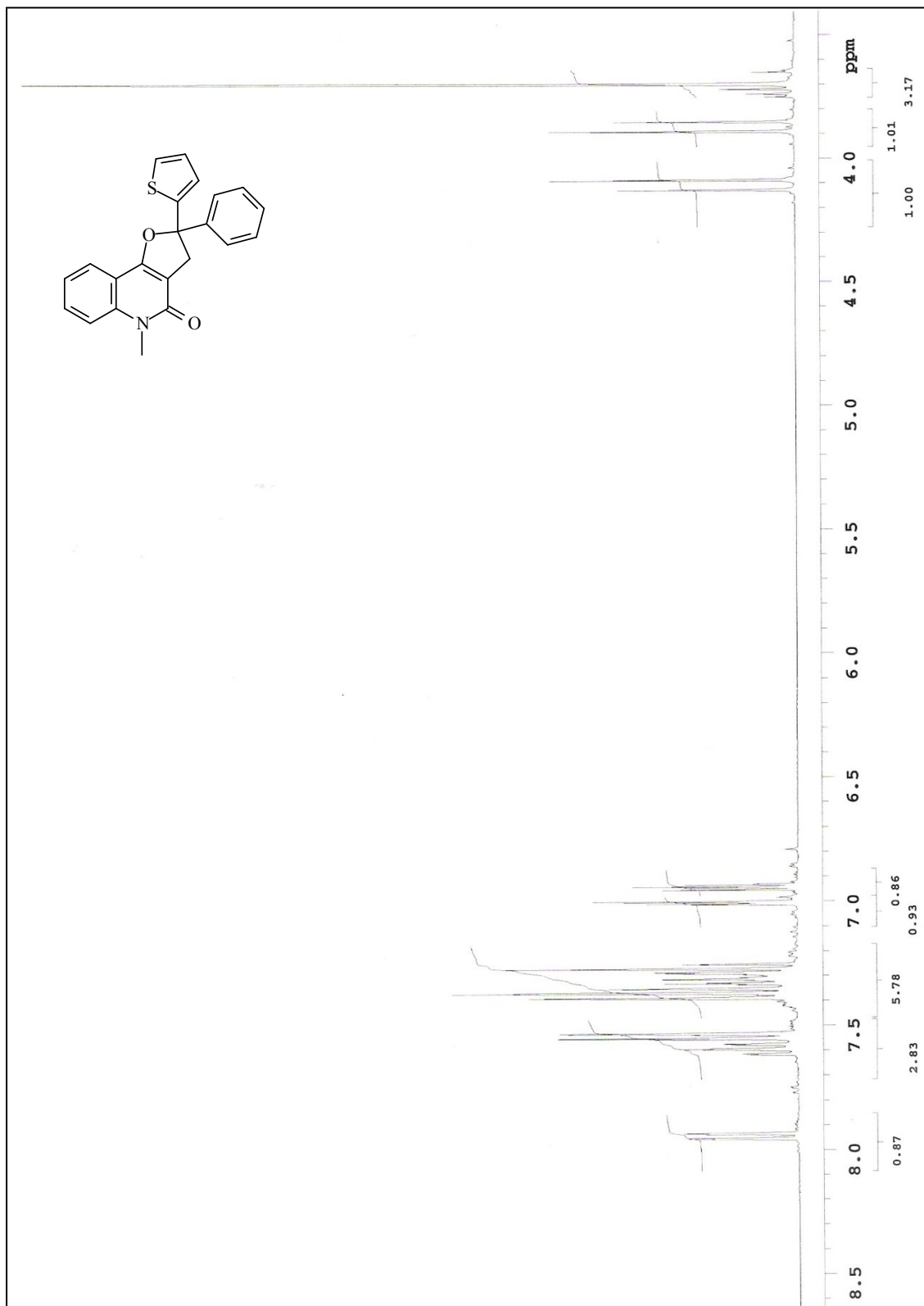
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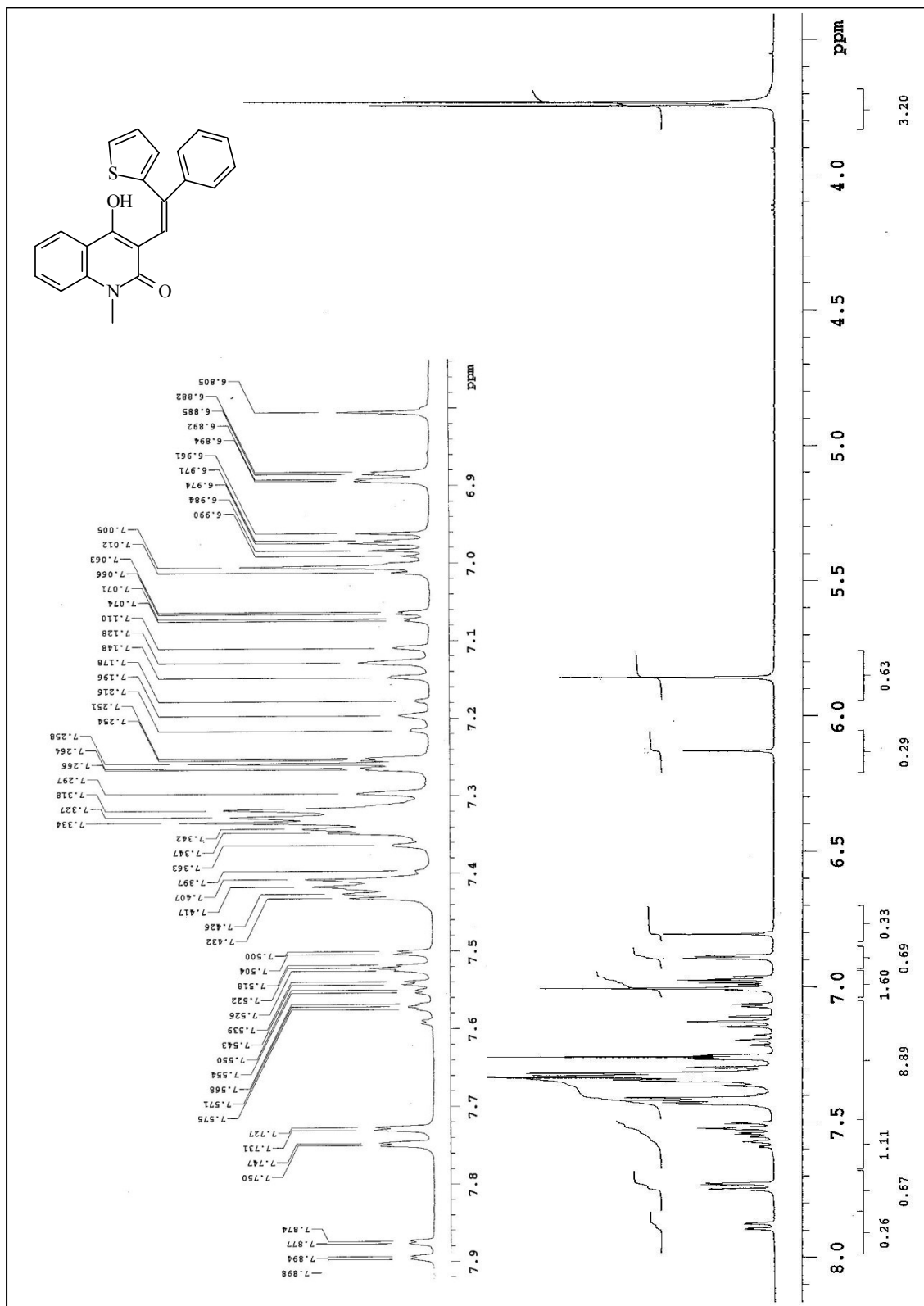
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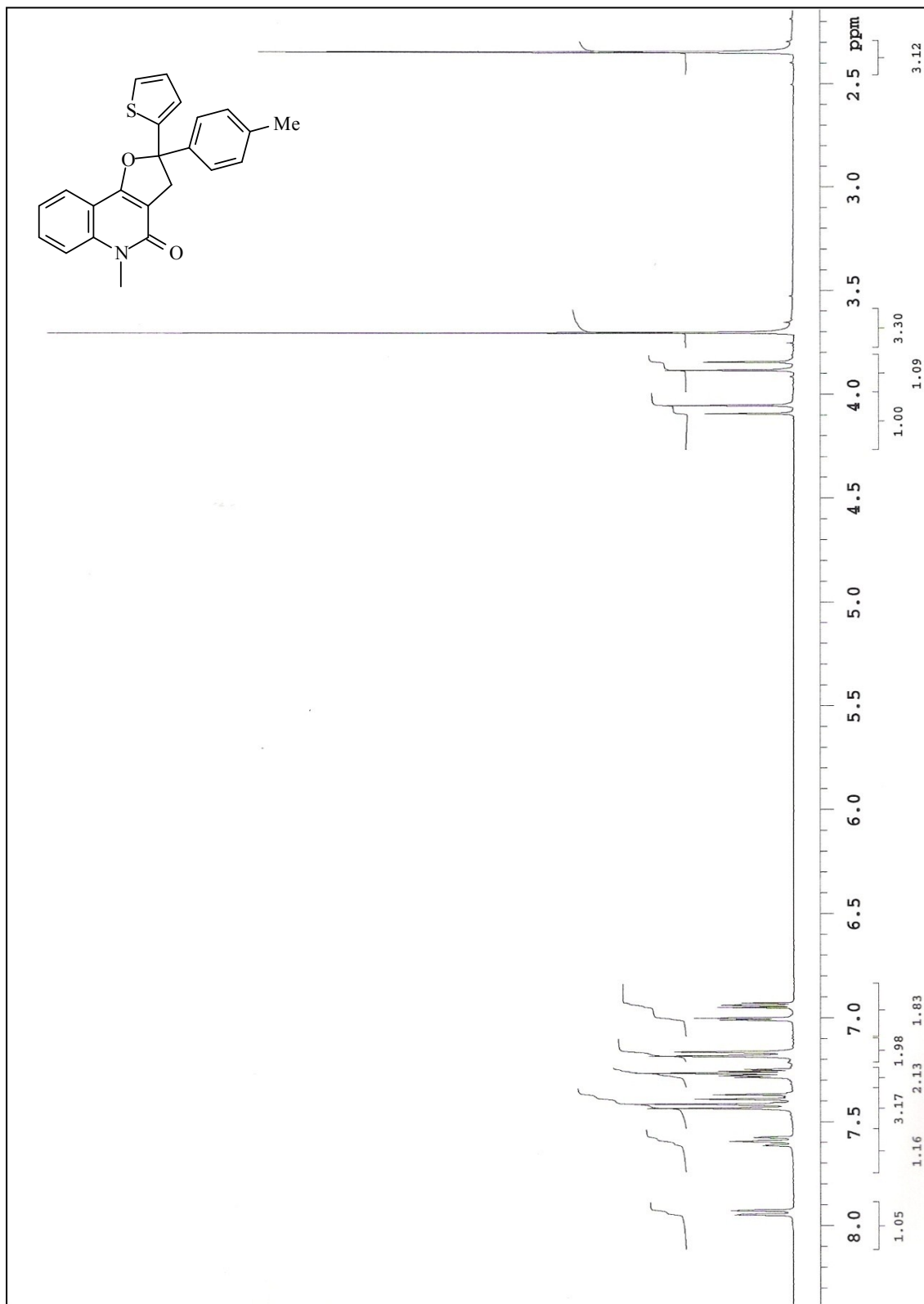
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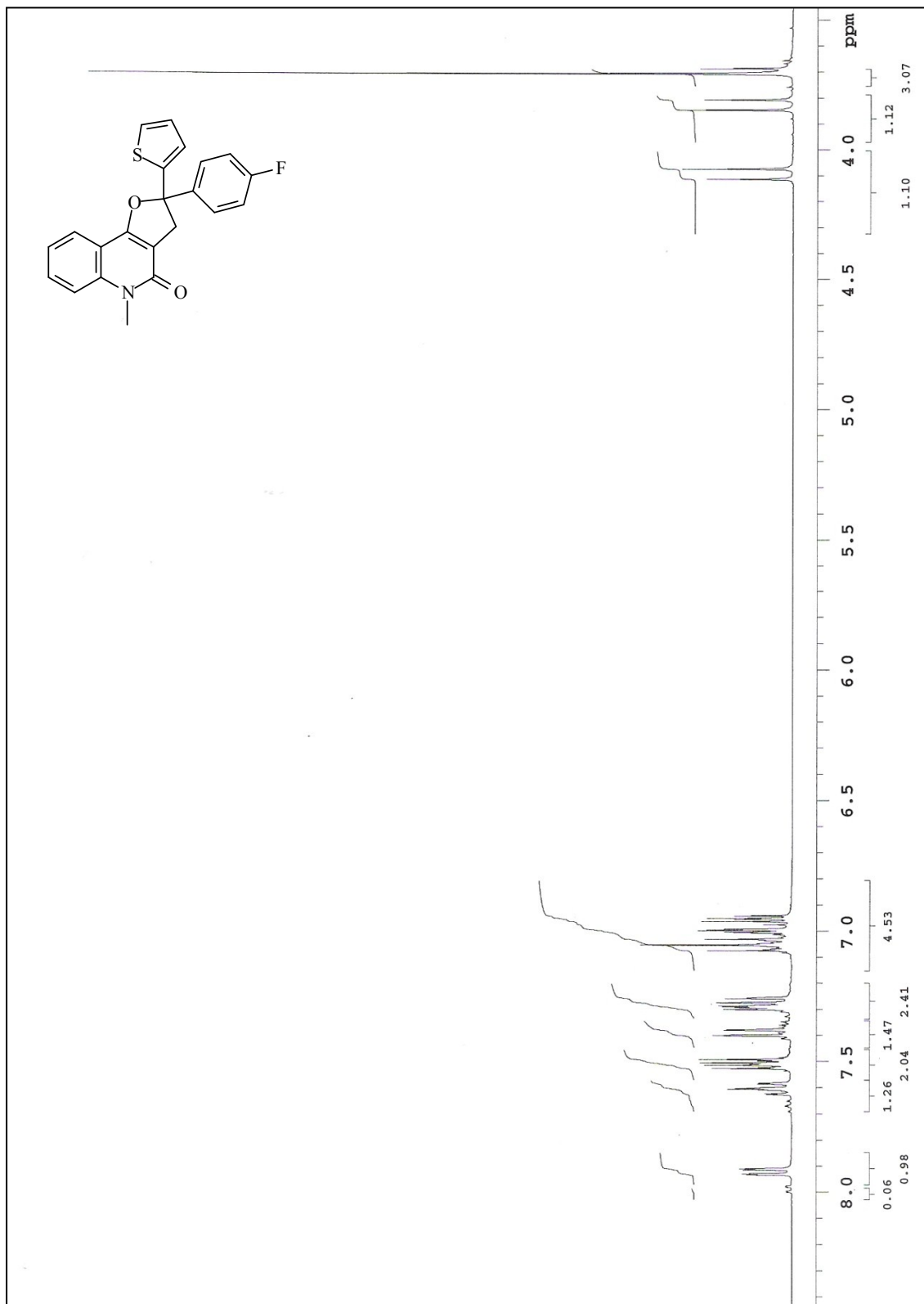
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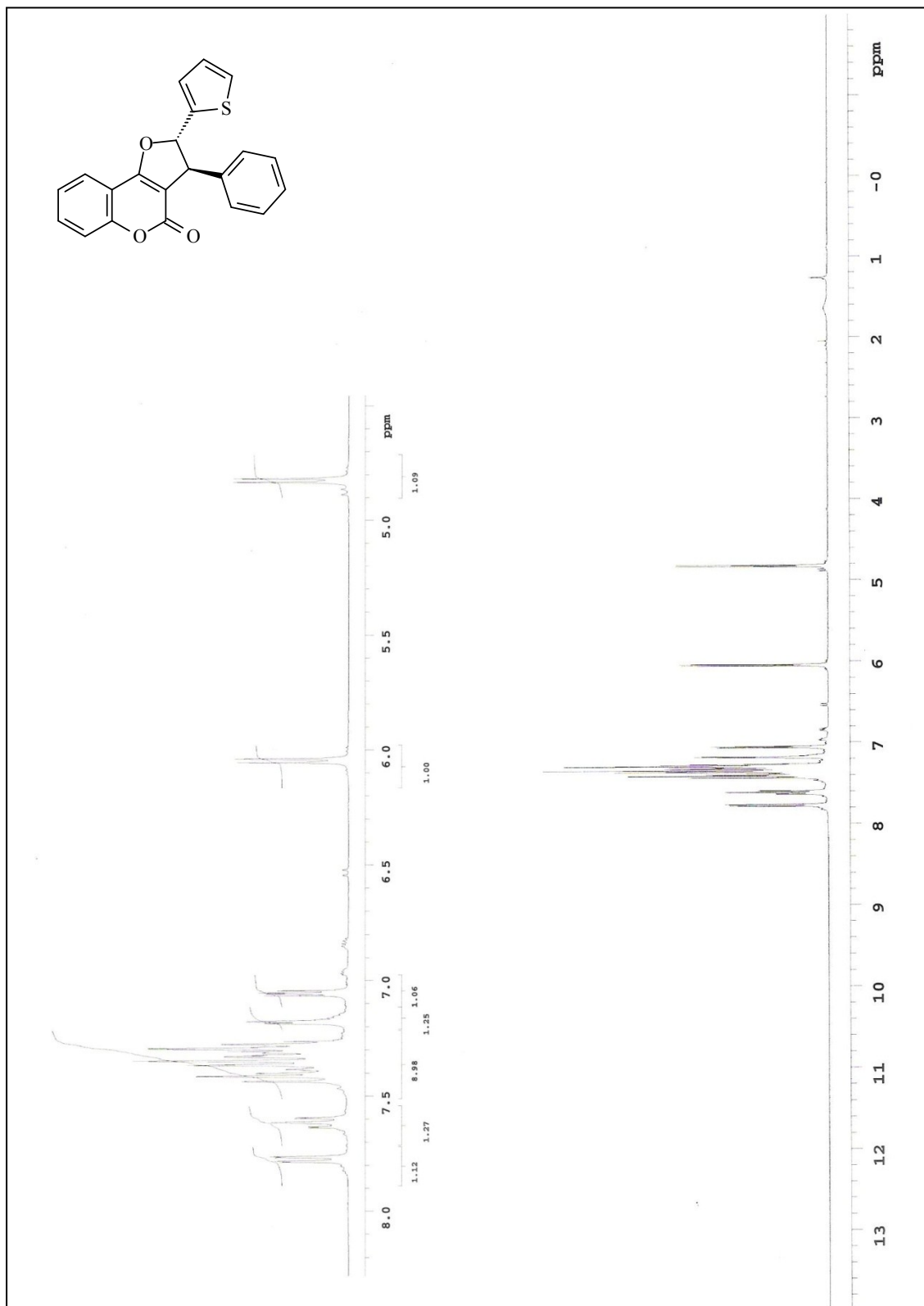
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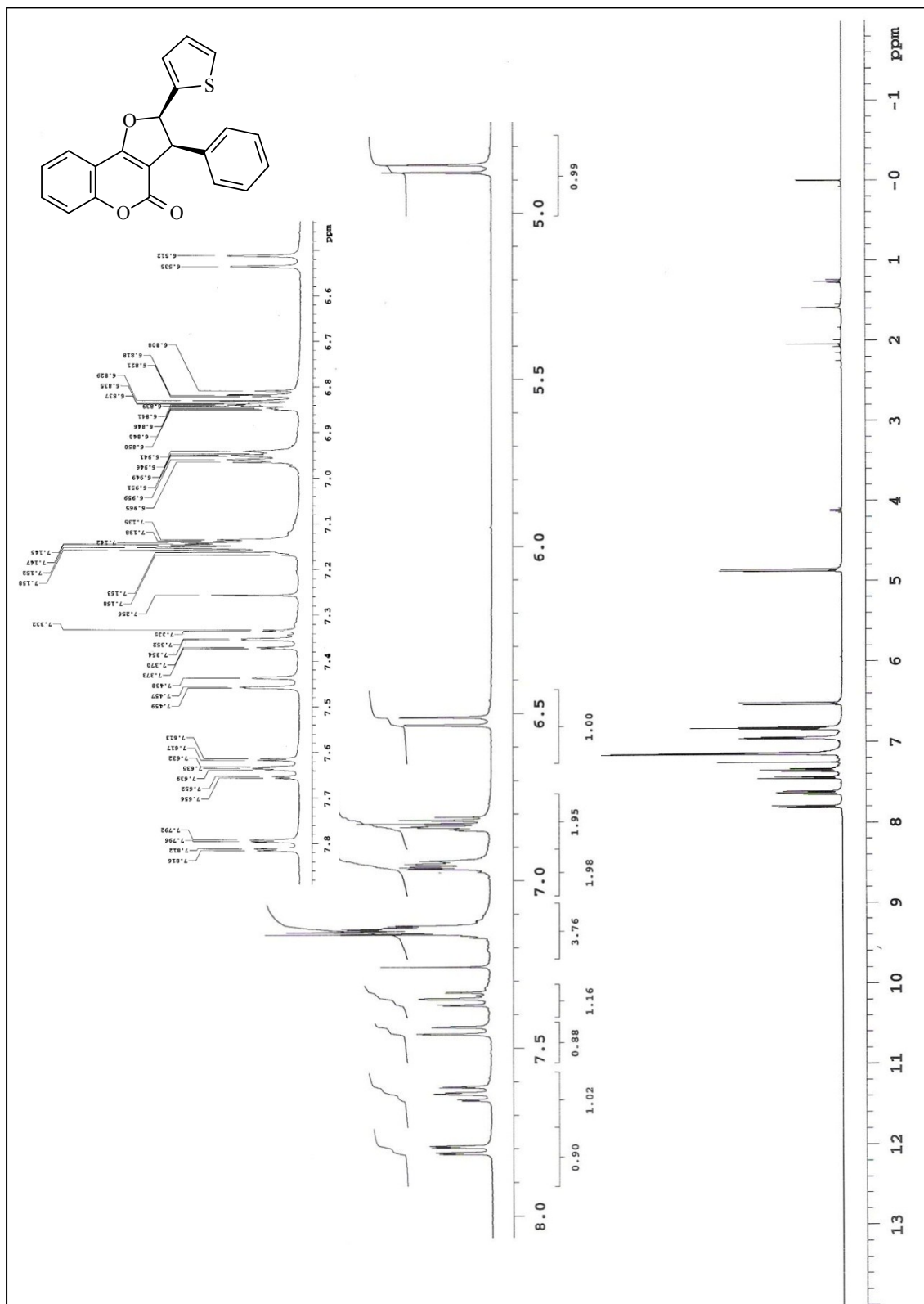
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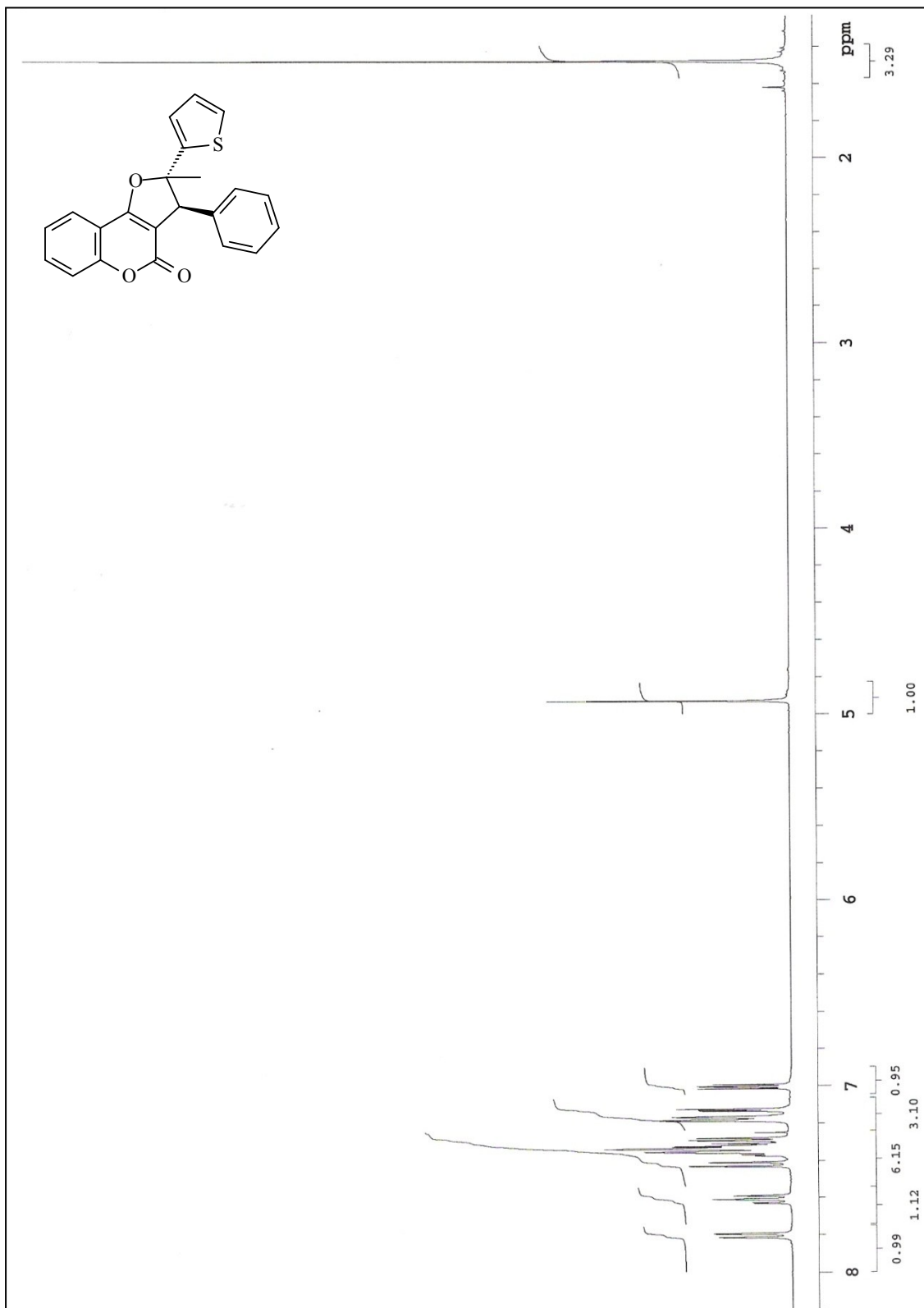
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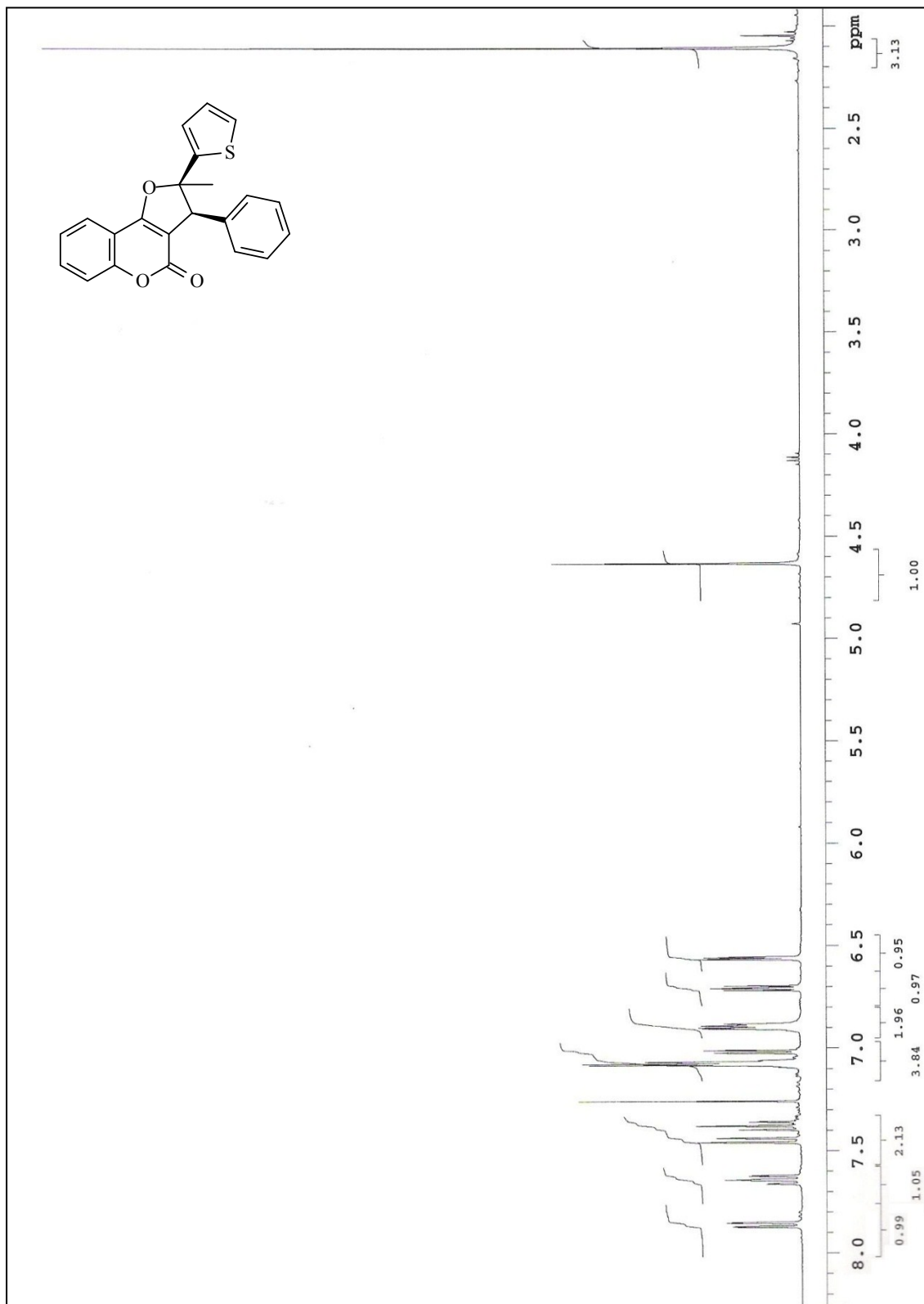
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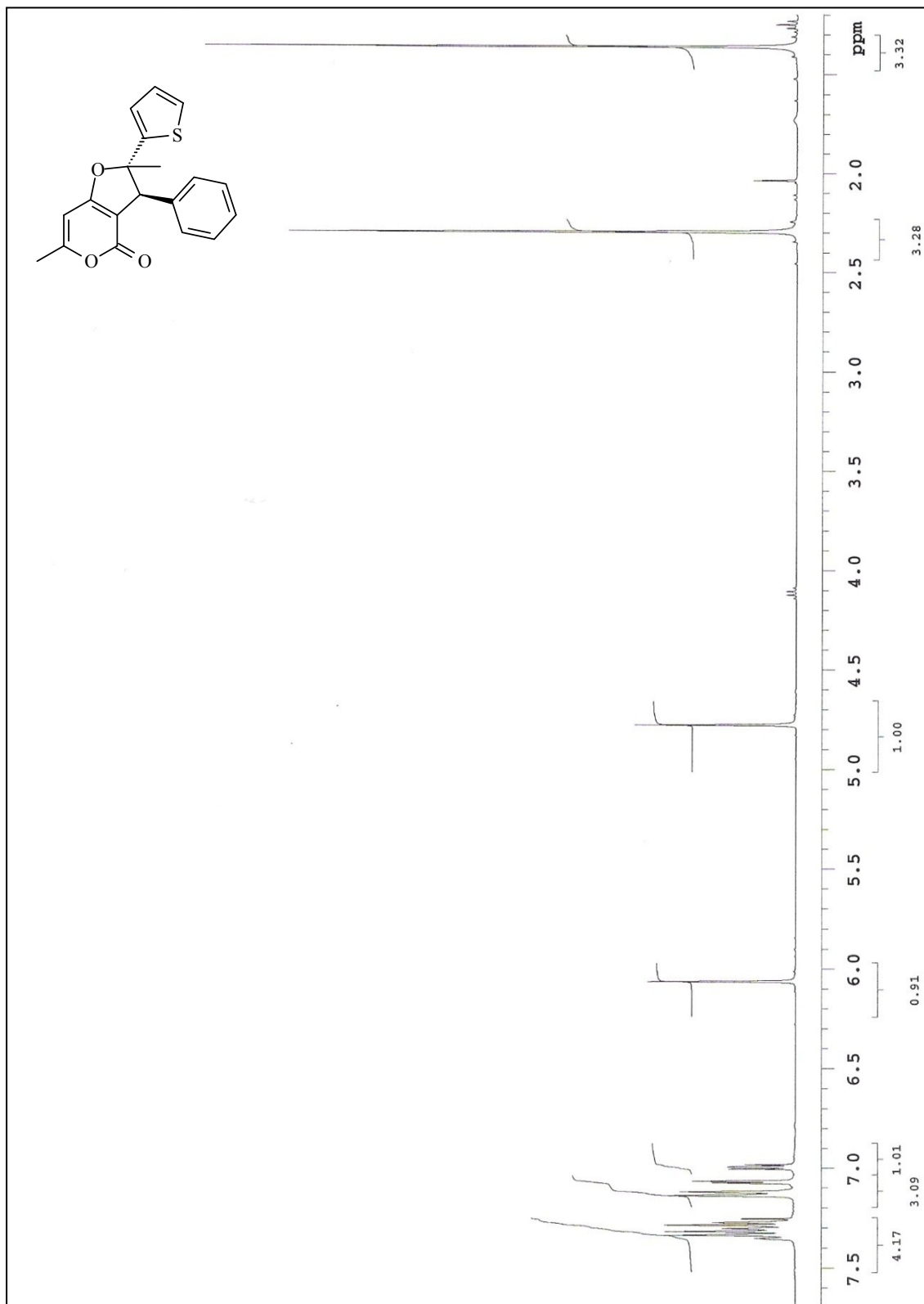
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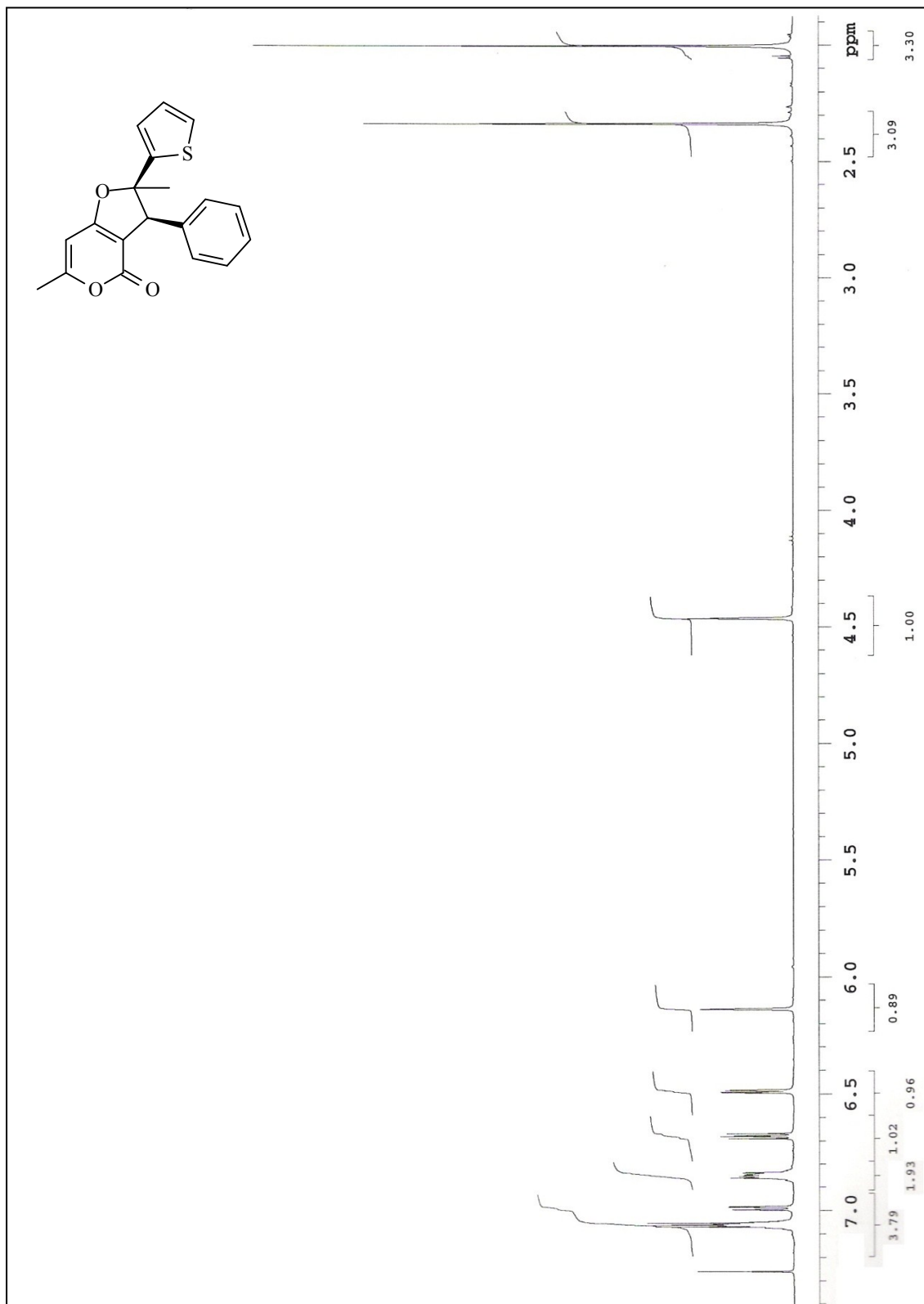
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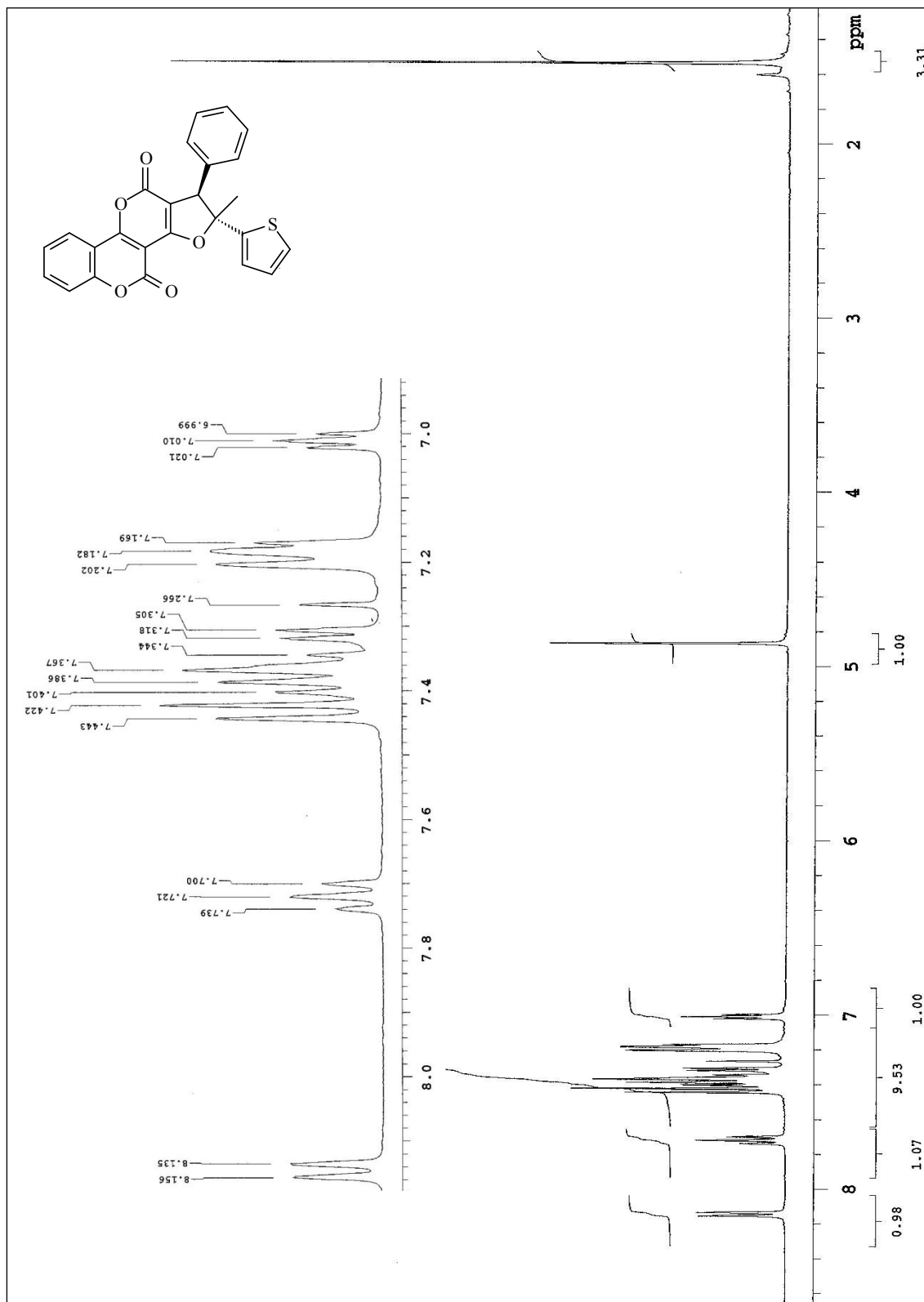
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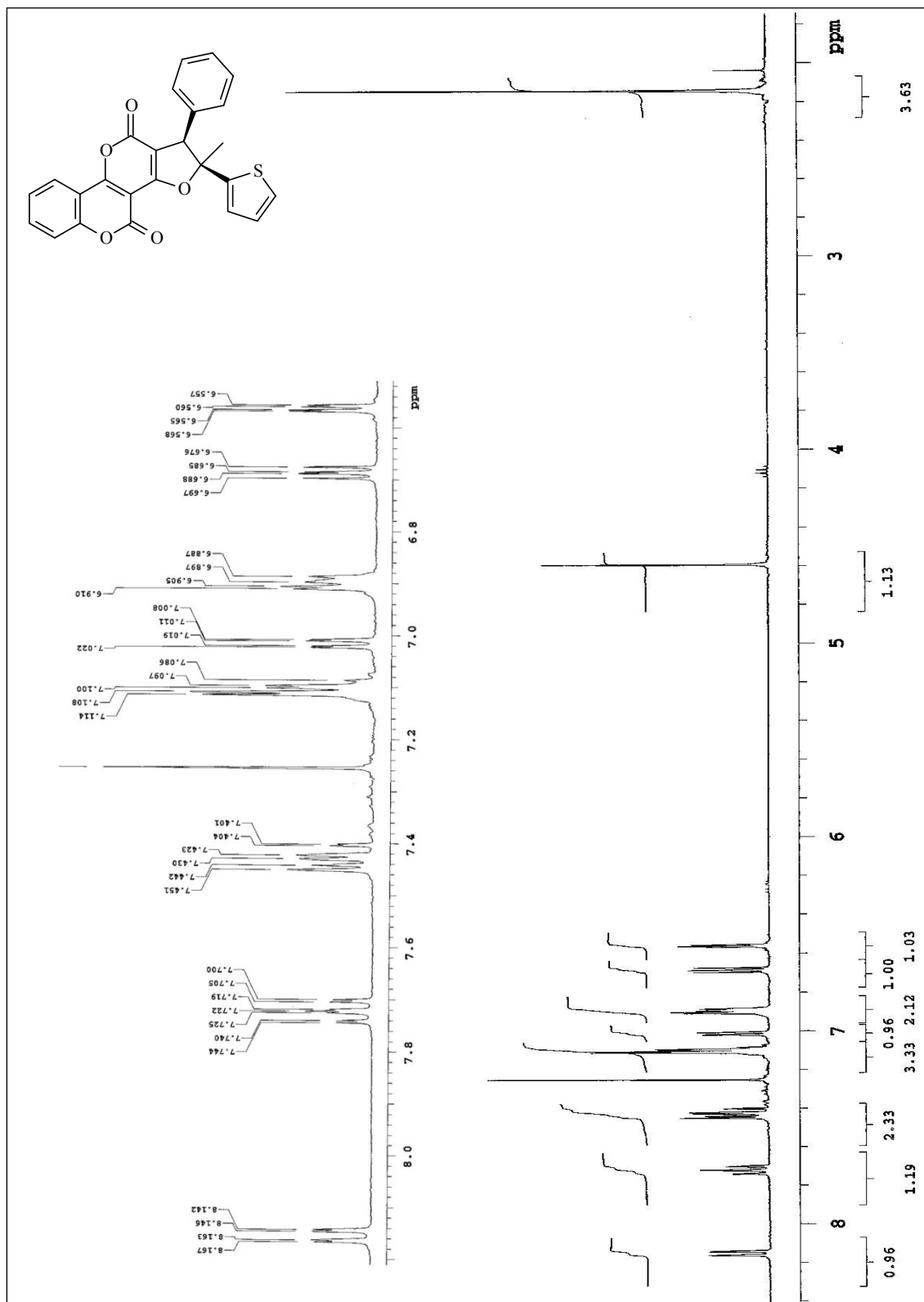
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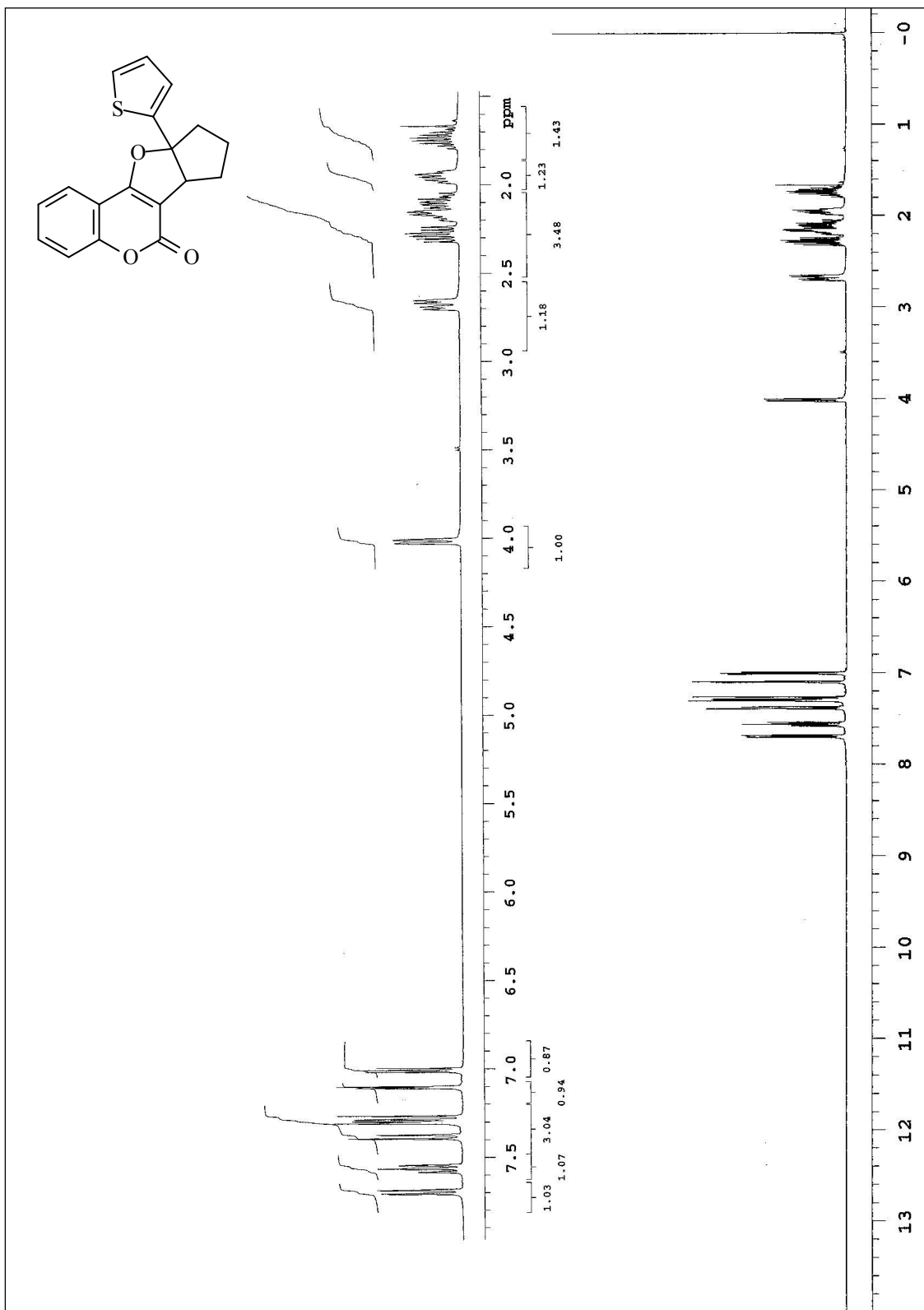
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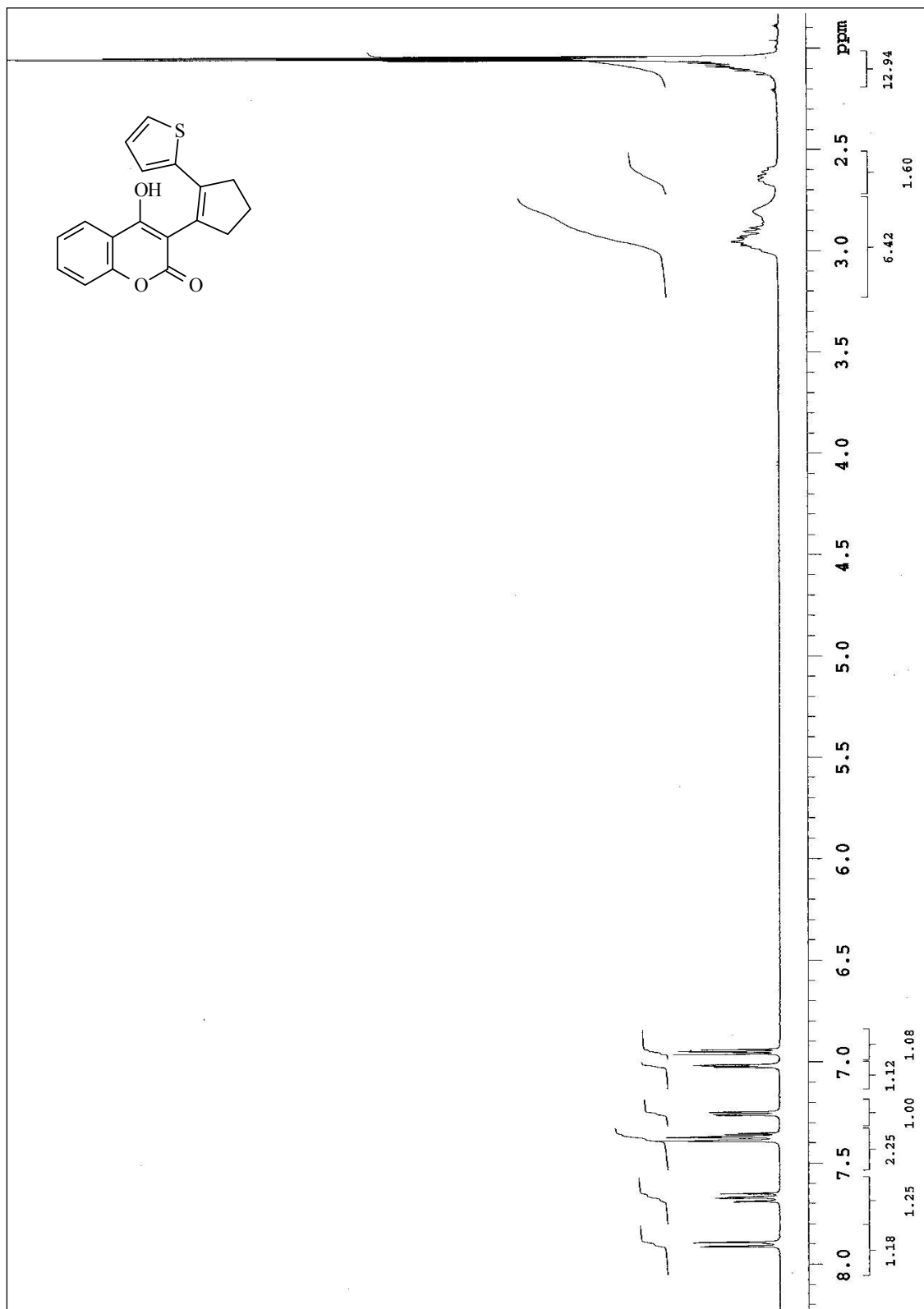
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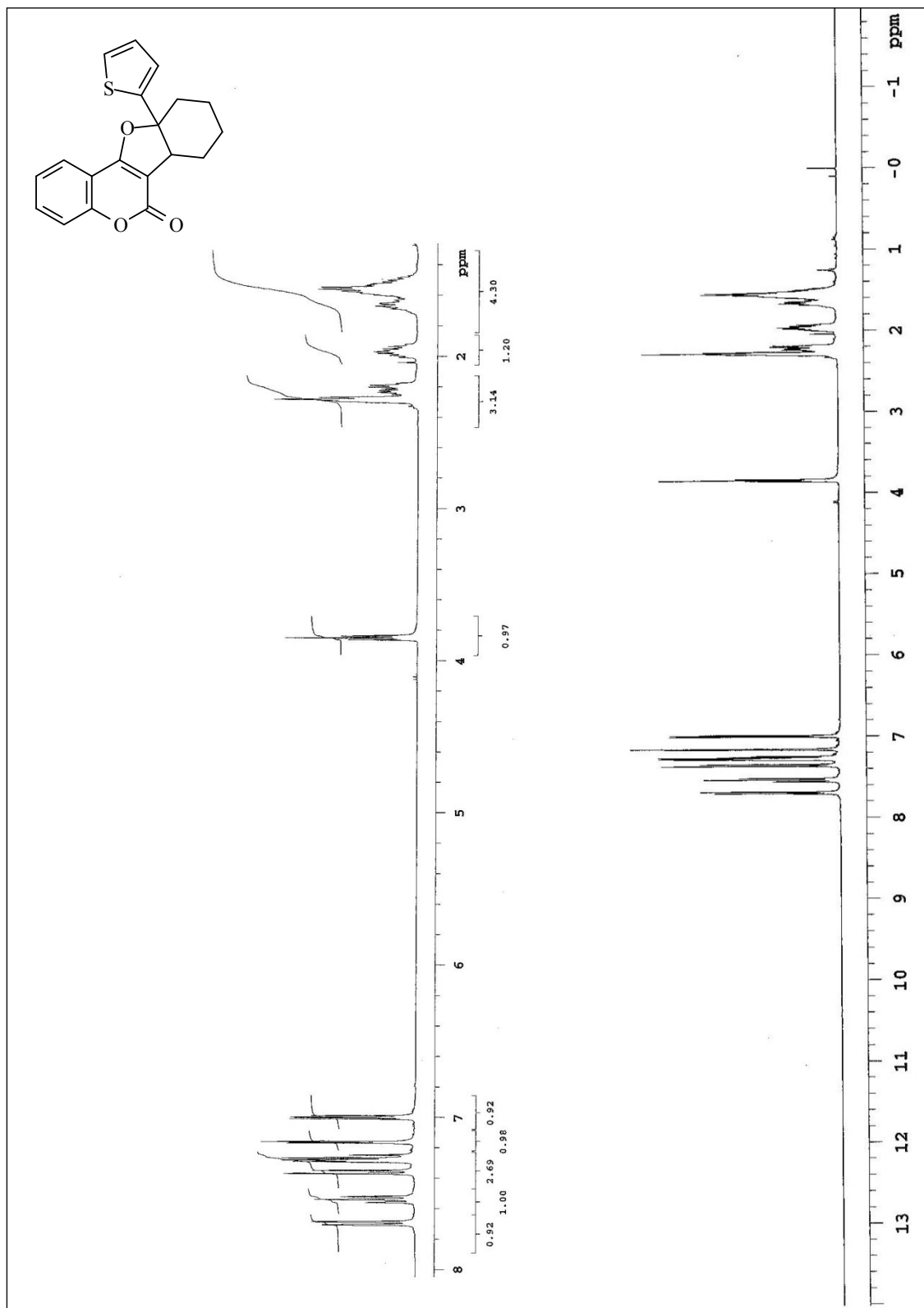
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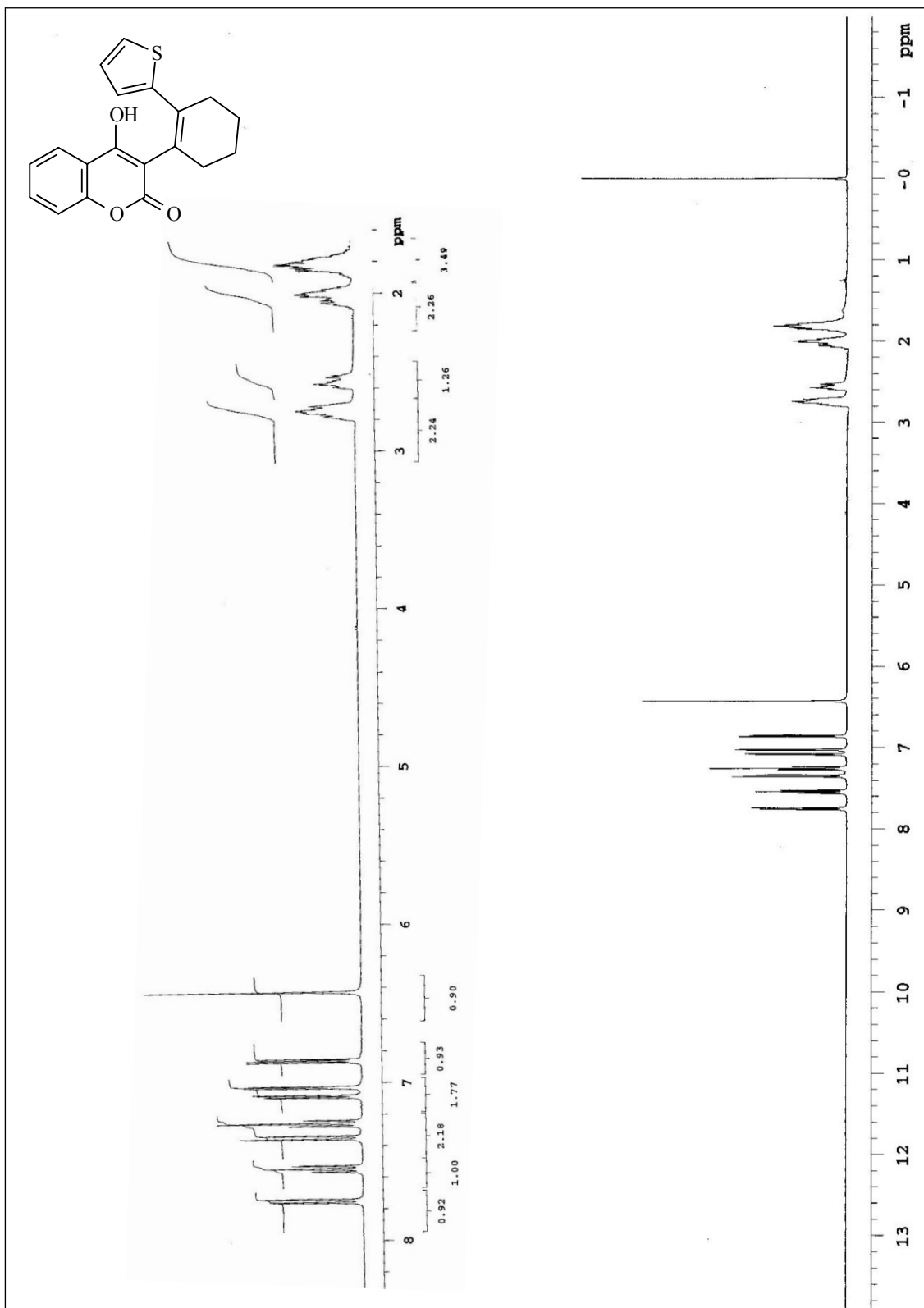
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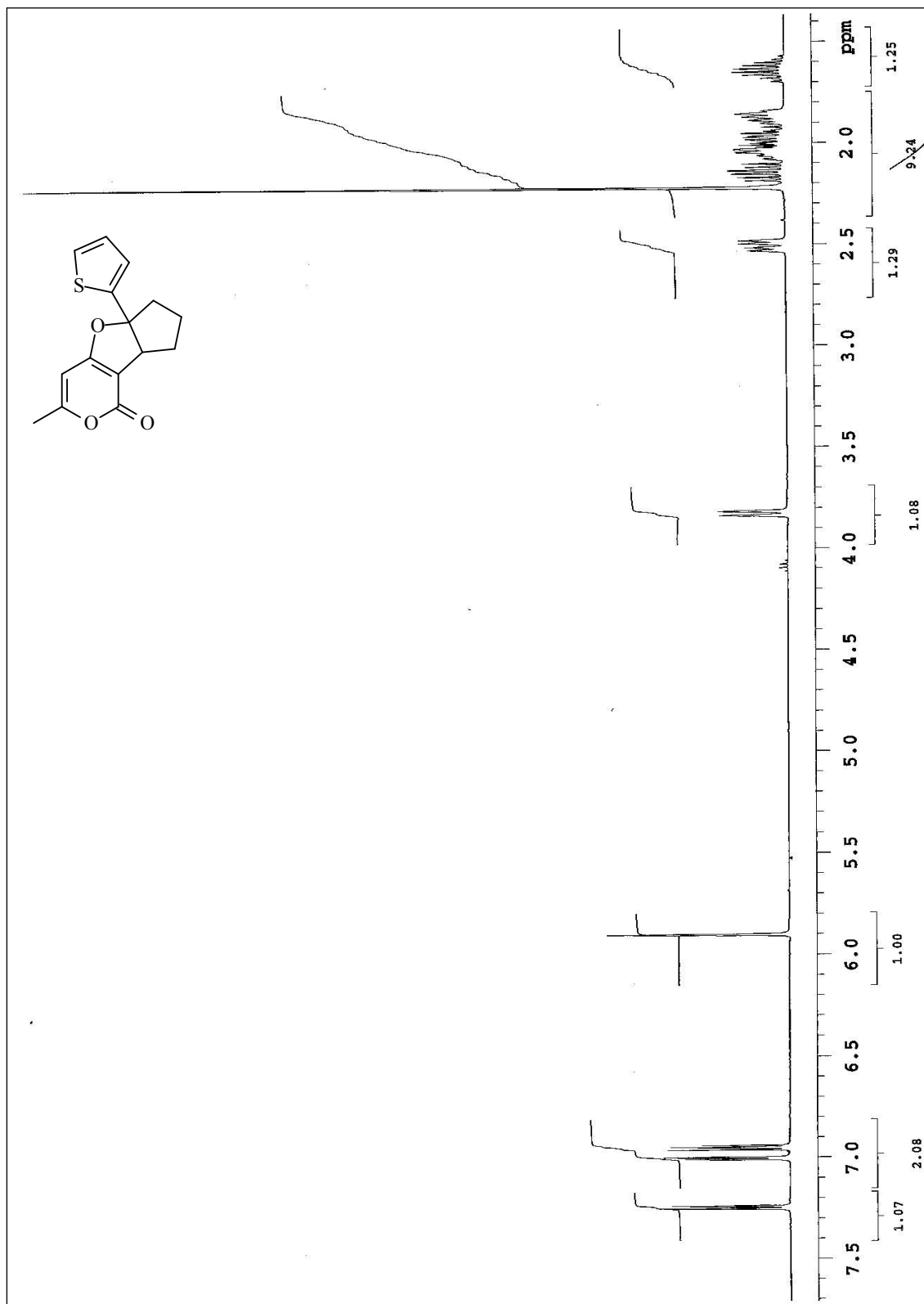
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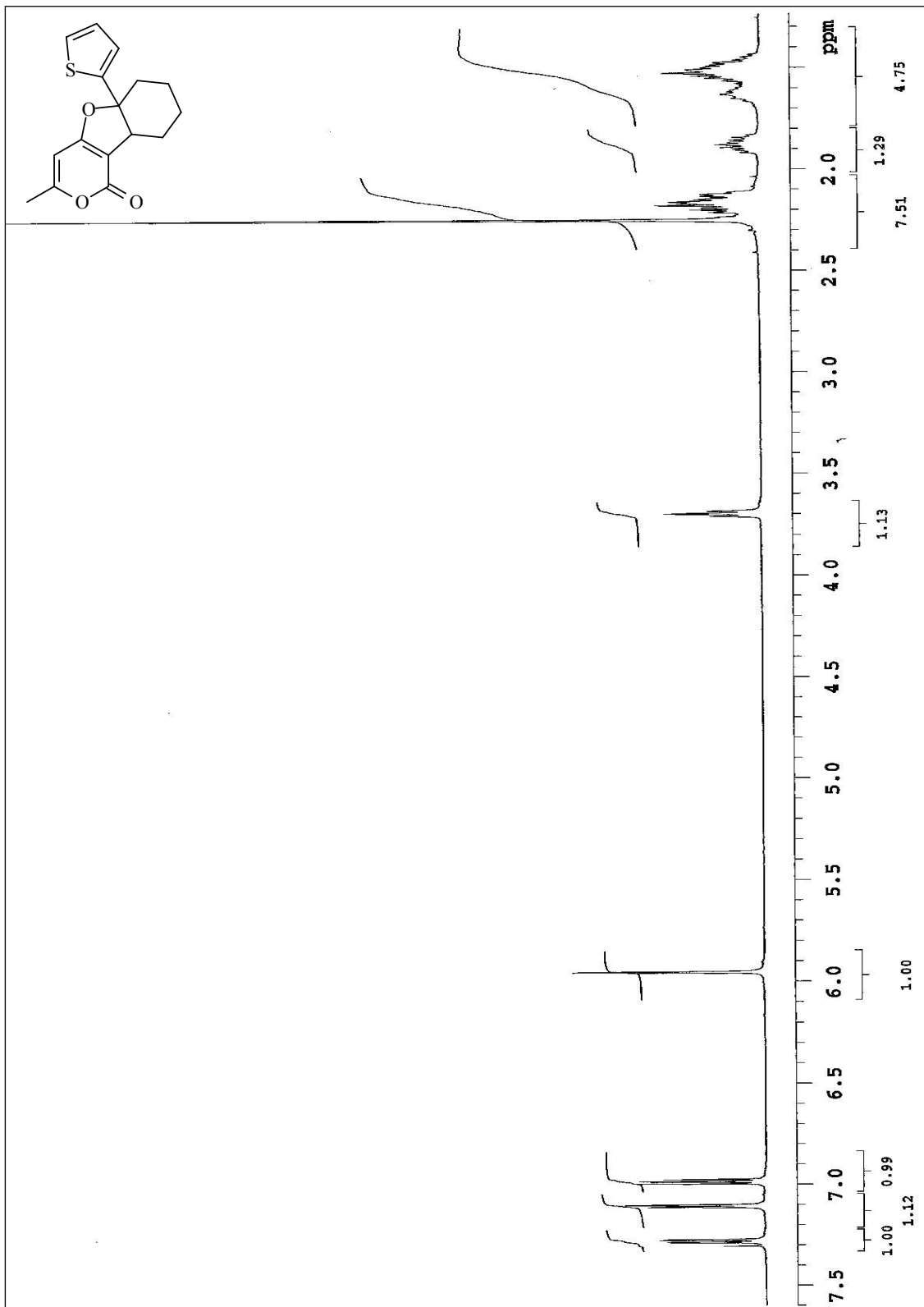
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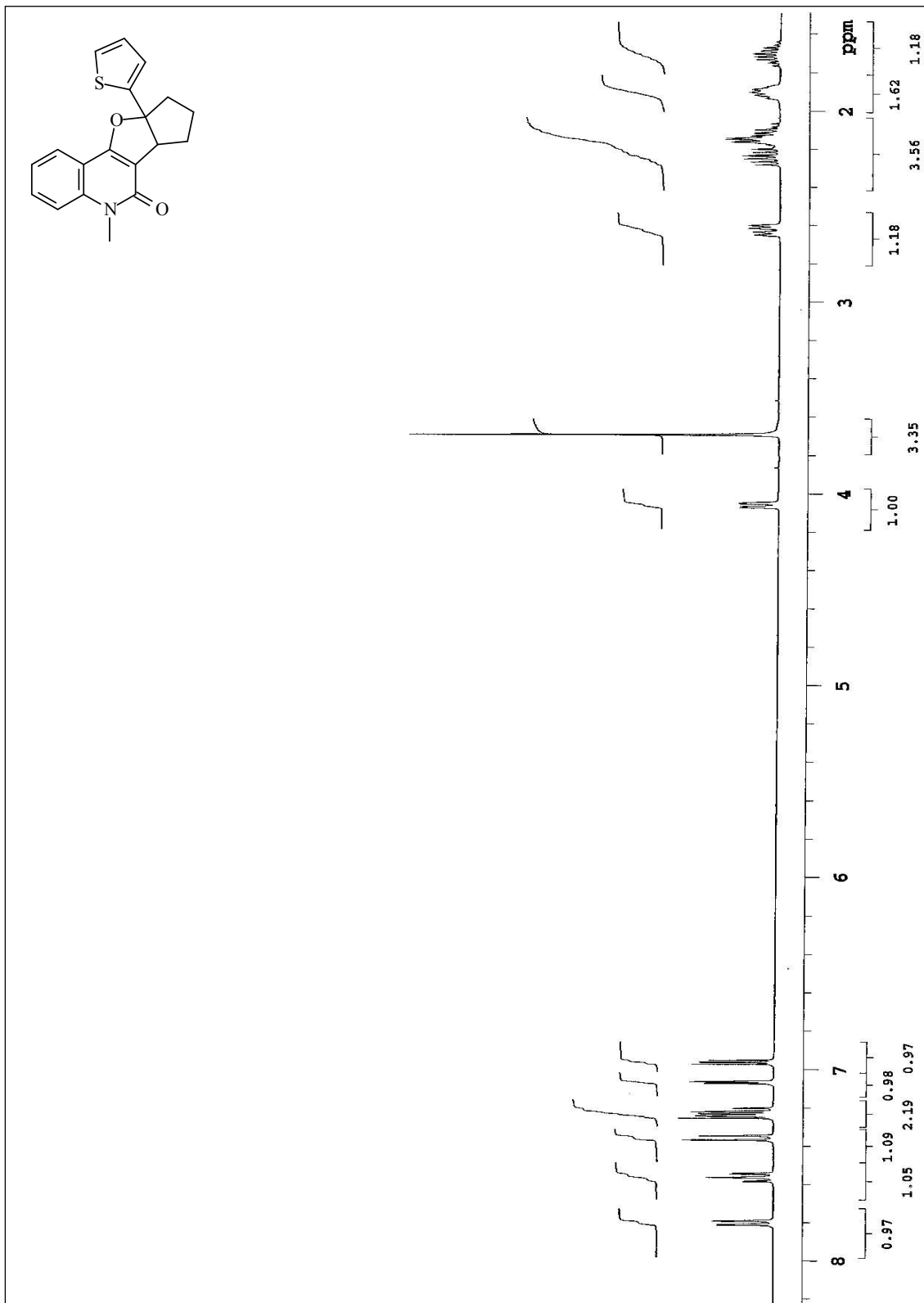
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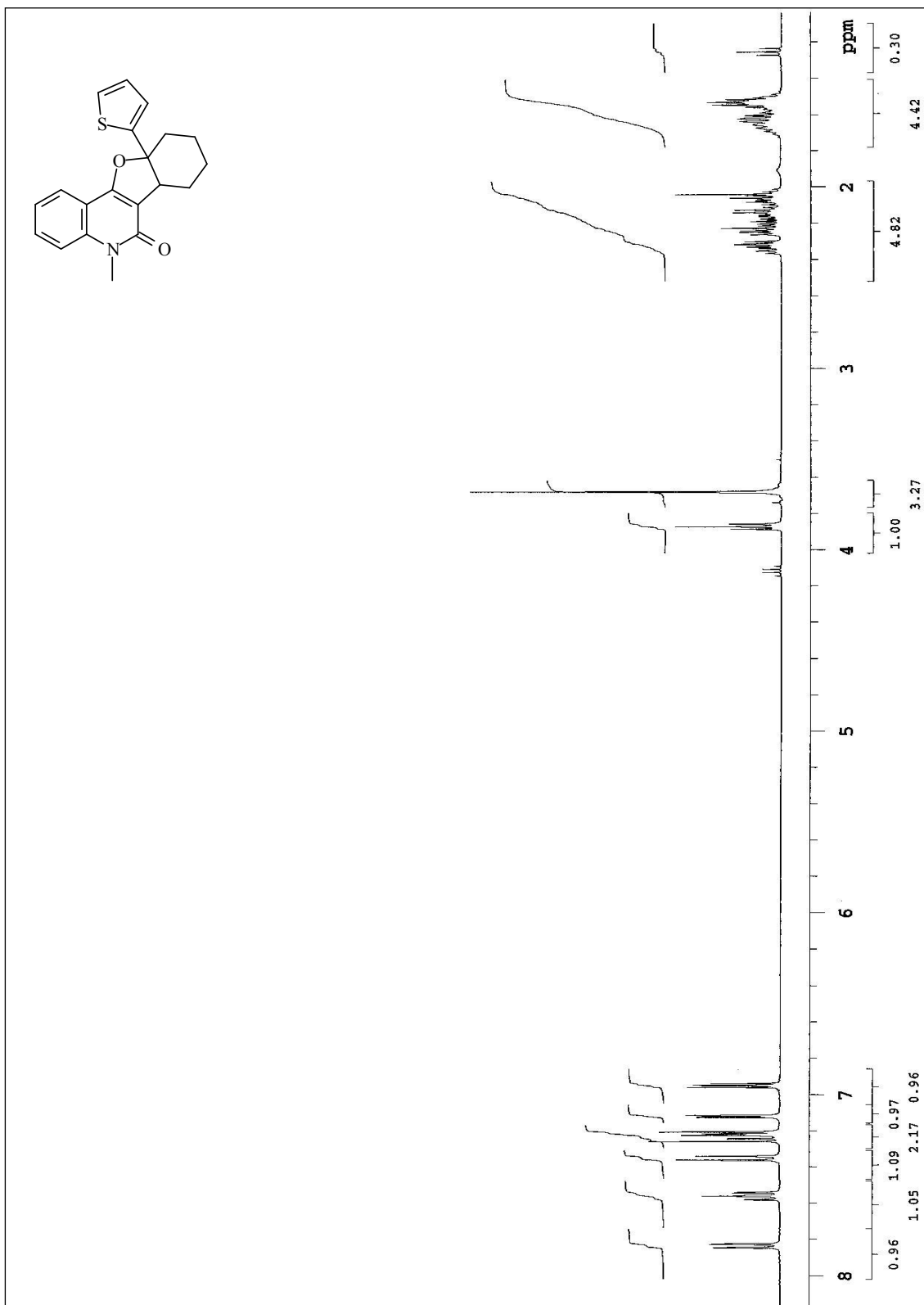
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2.49 ¹H-NMR spectra of 47

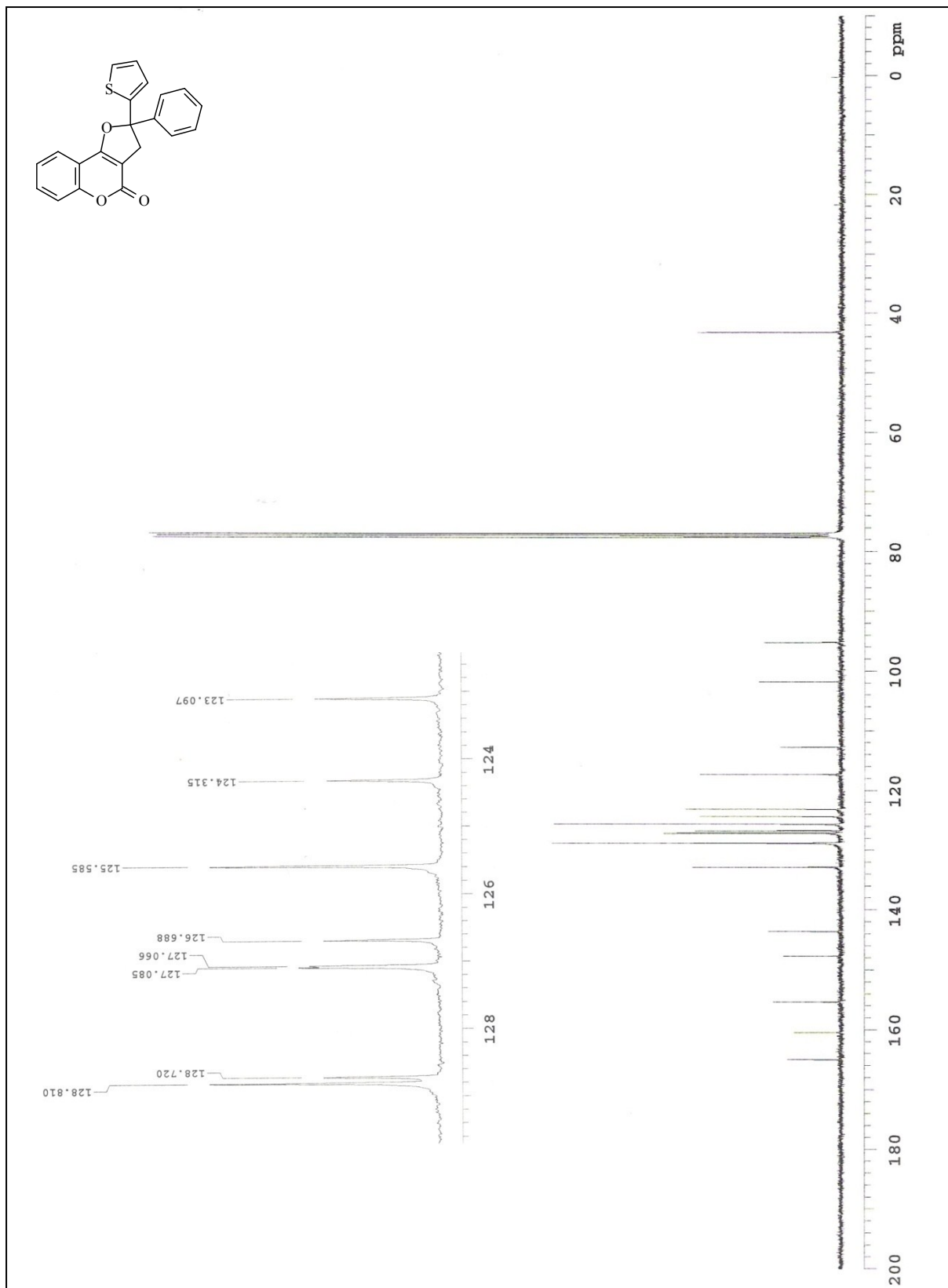


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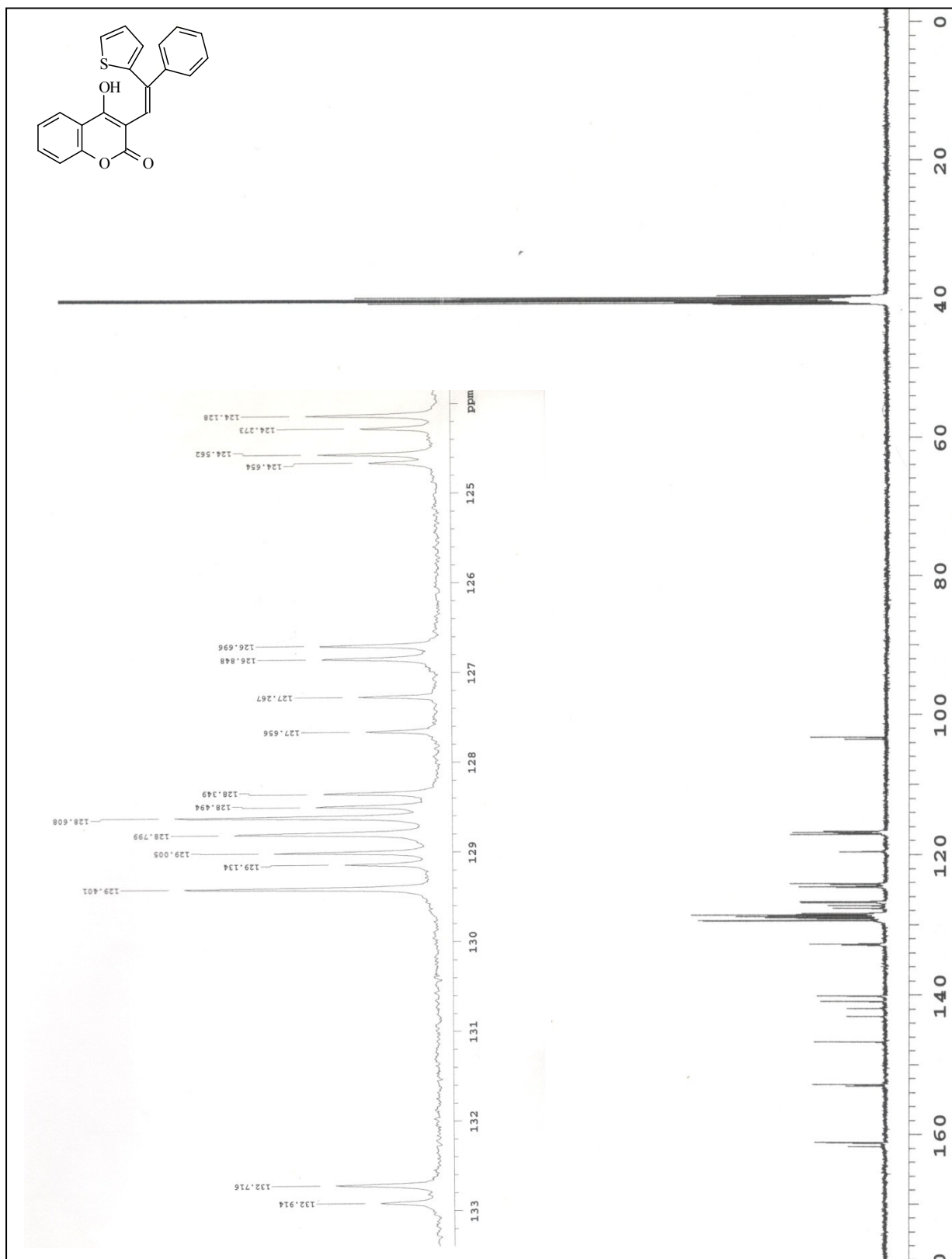


¹³C-NMR of COMPOUNDS

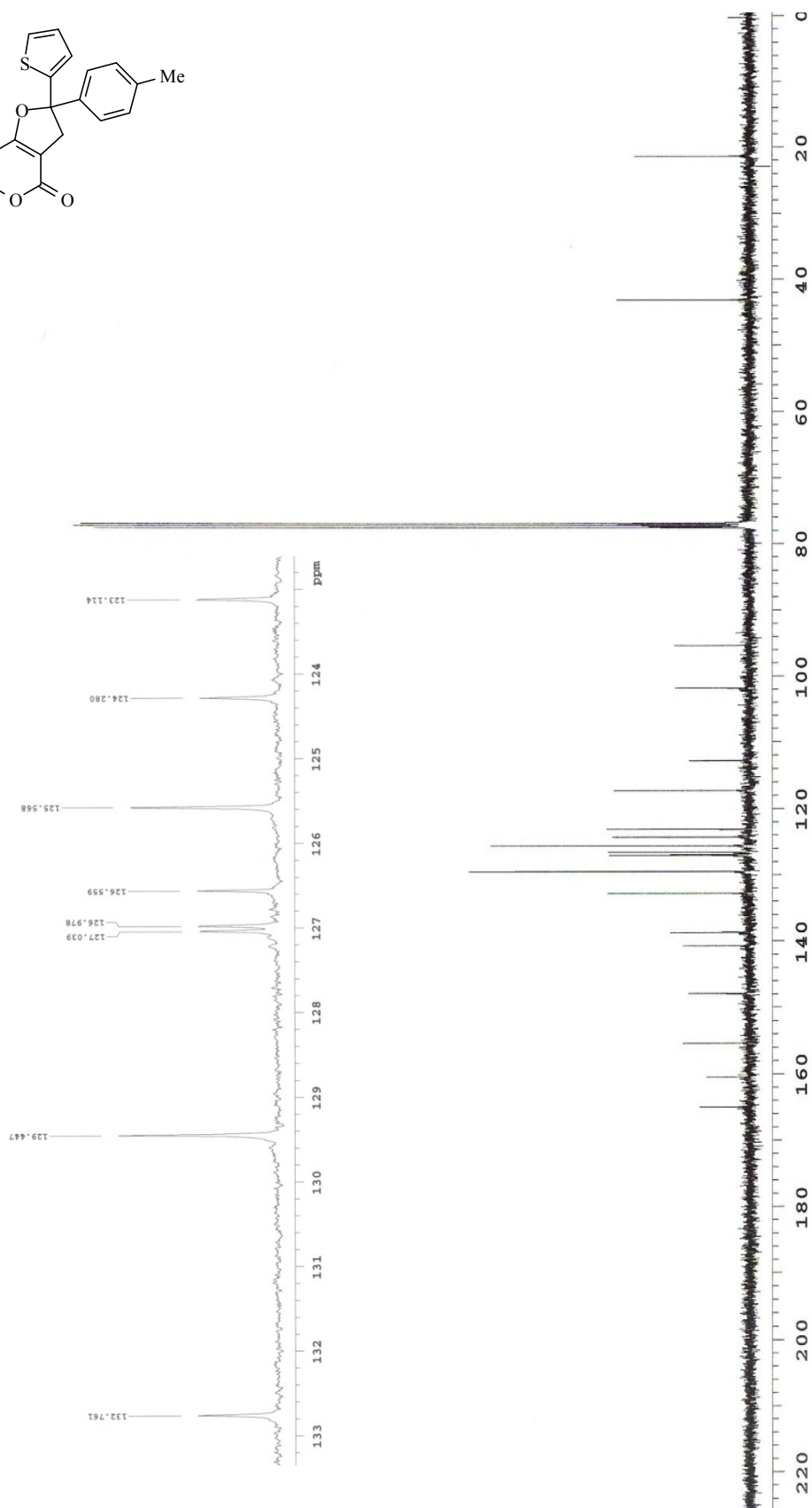
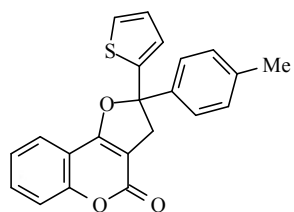
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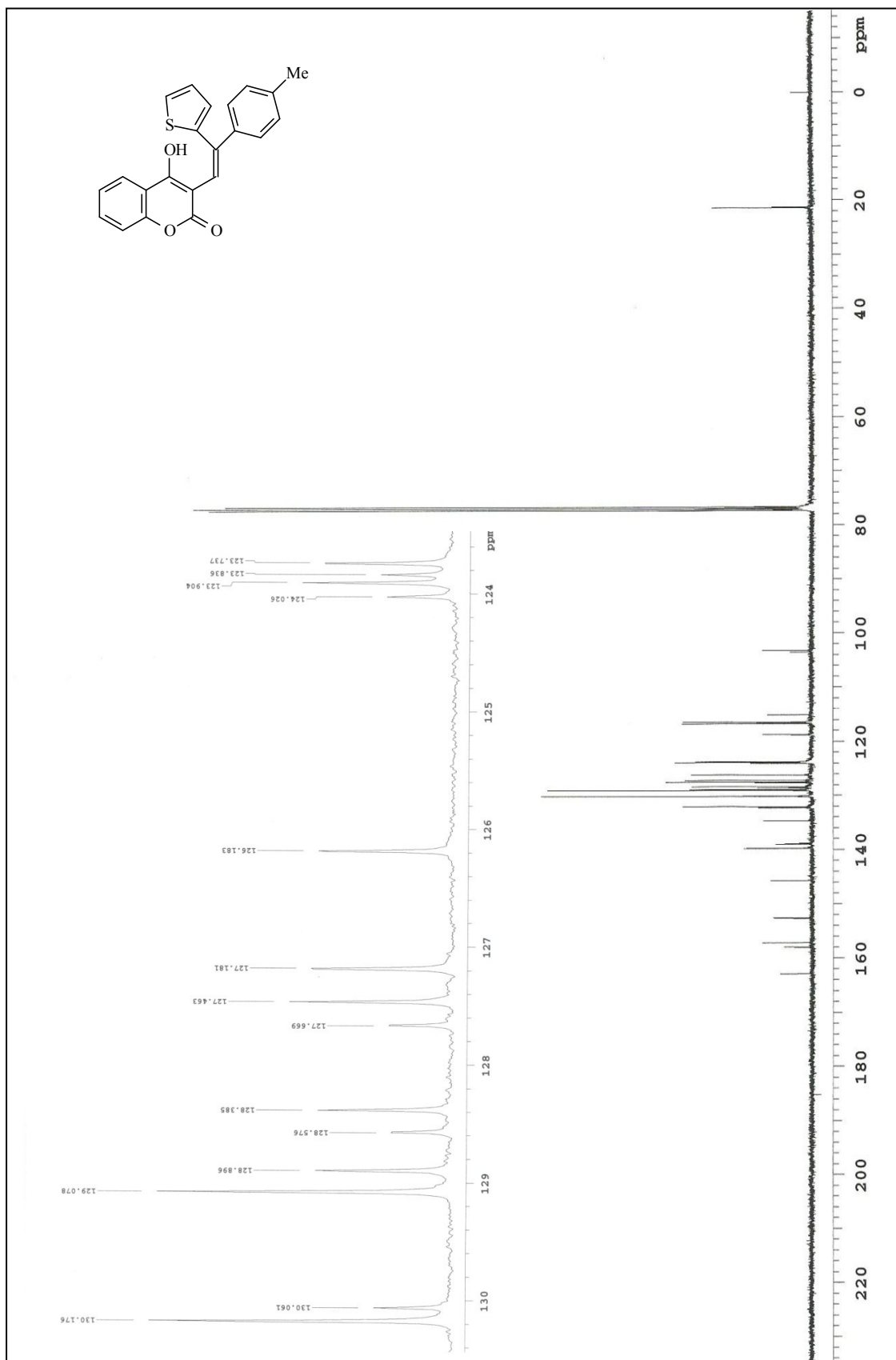
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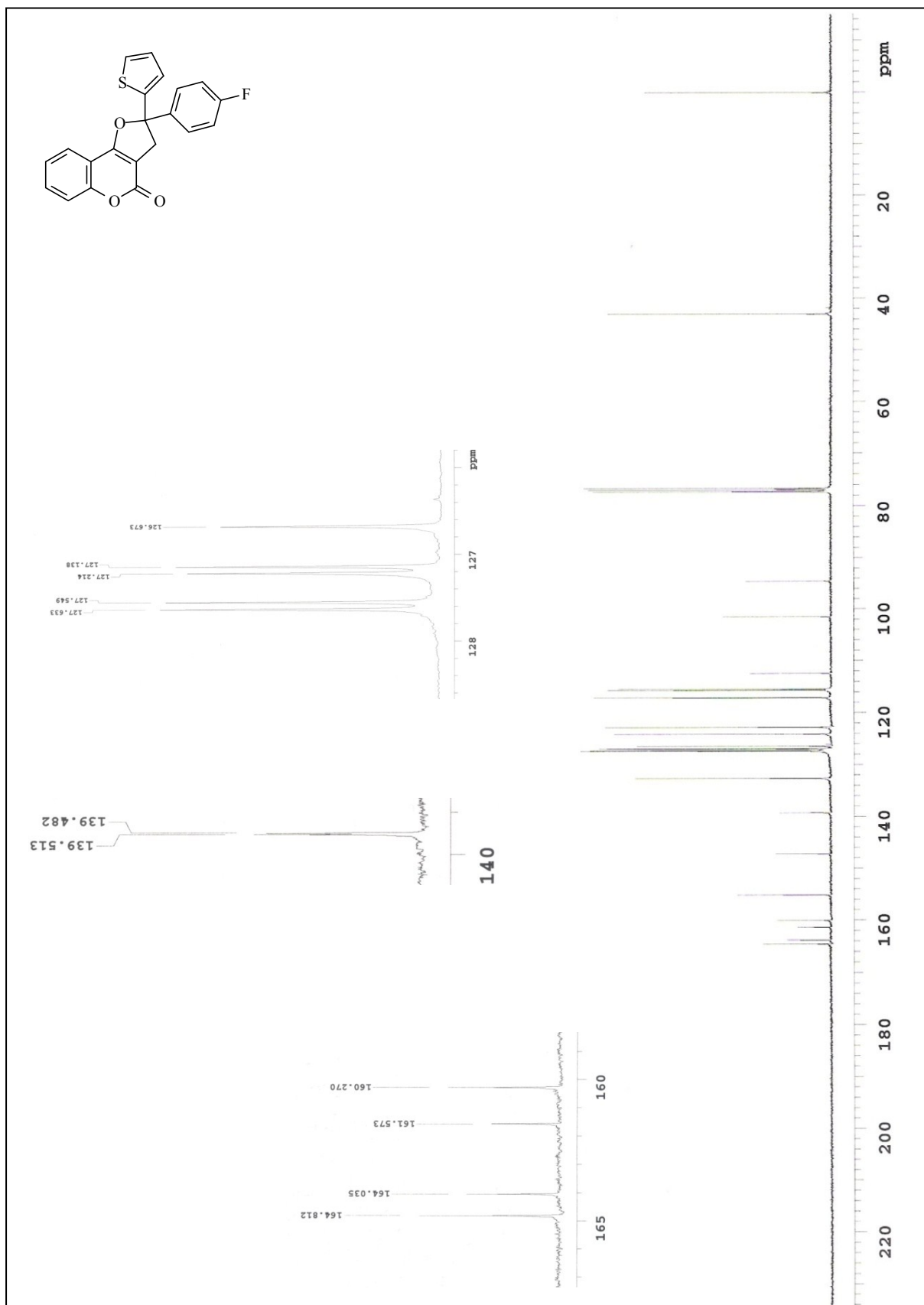
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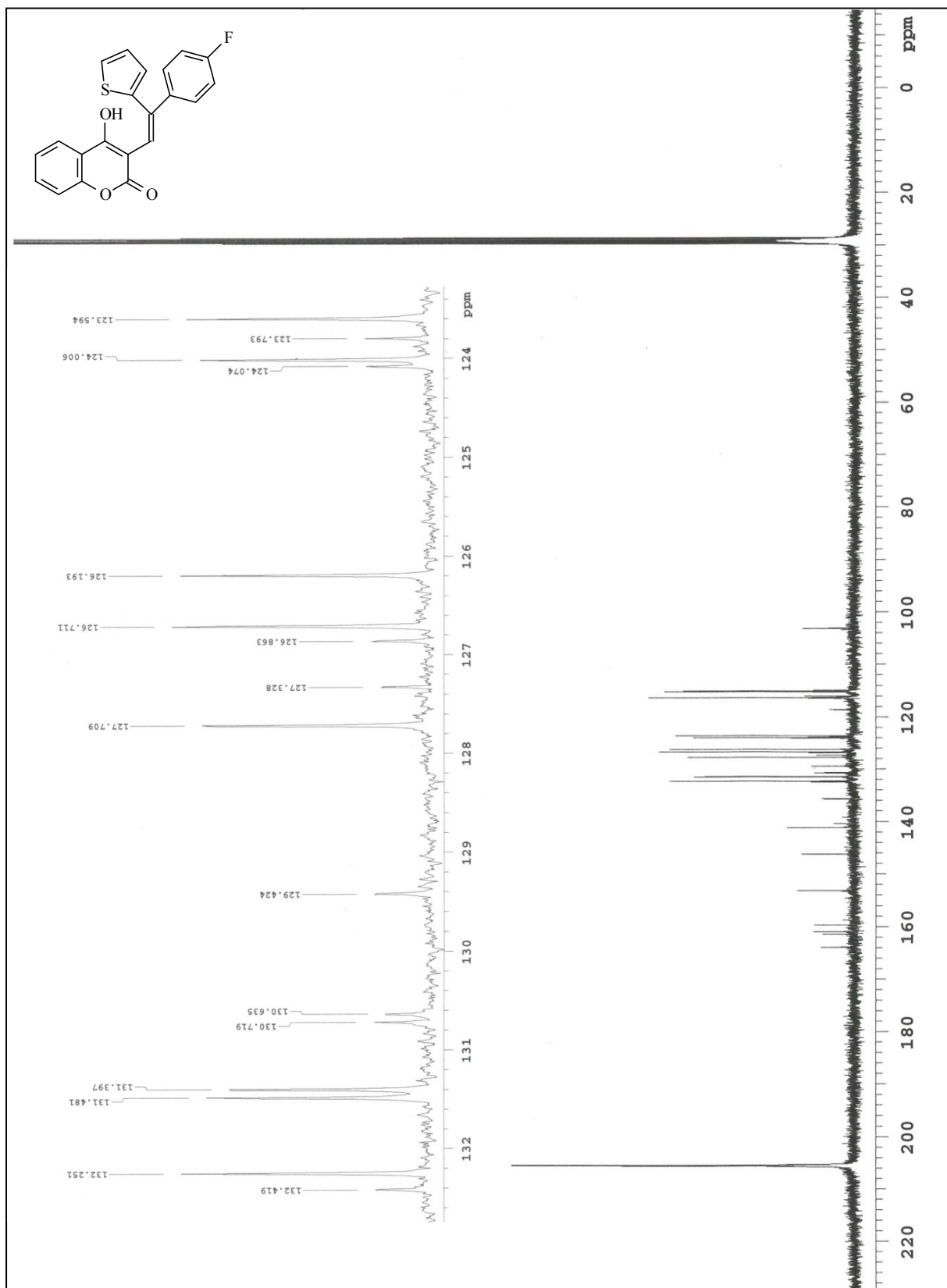
3.4 ^{13}C -NMR spectra of **9**



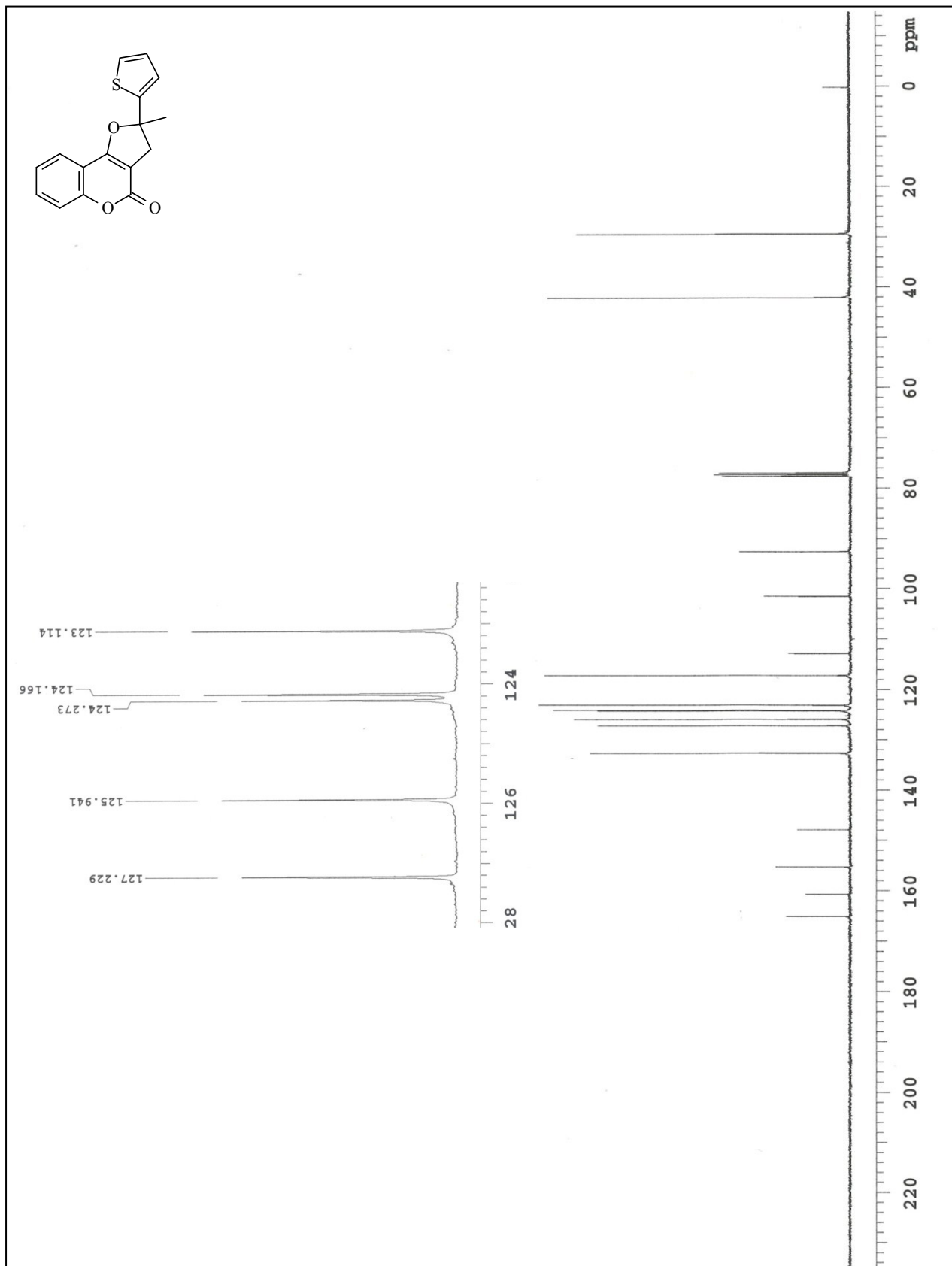
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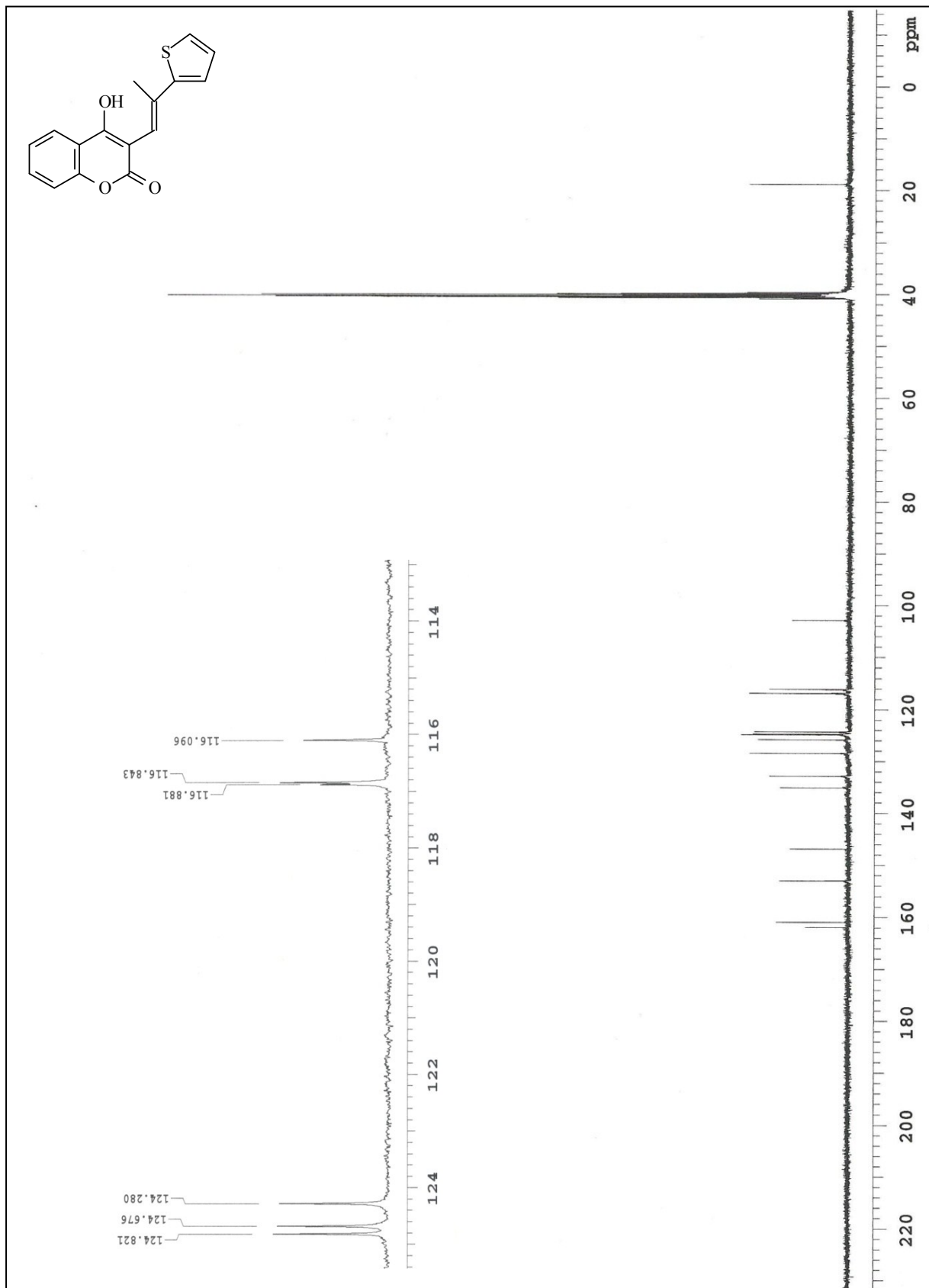
3.6 ^{13}C -NMR spectra of **10**



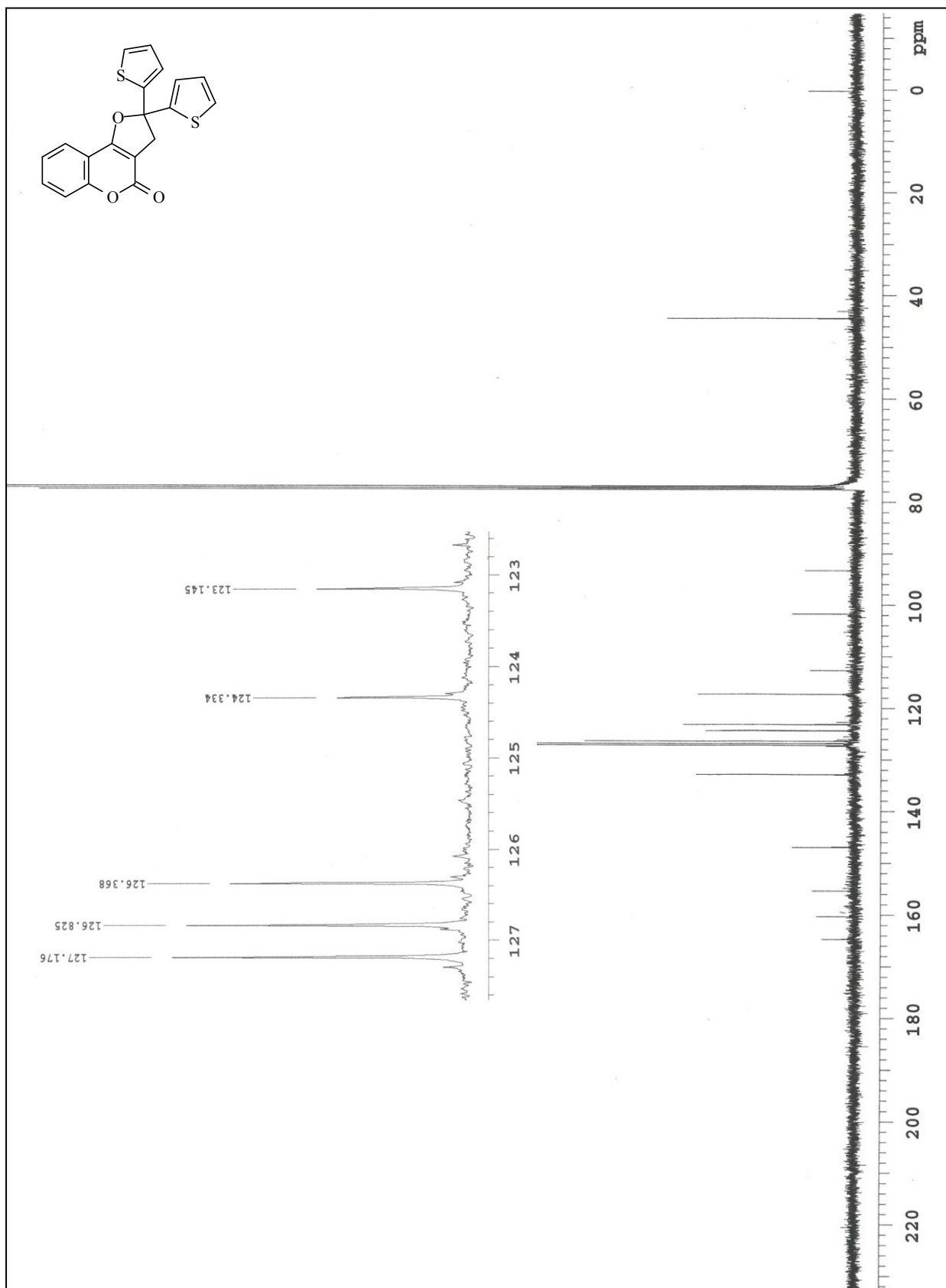
3.7 ^{13}C -NMR spectra of **6**



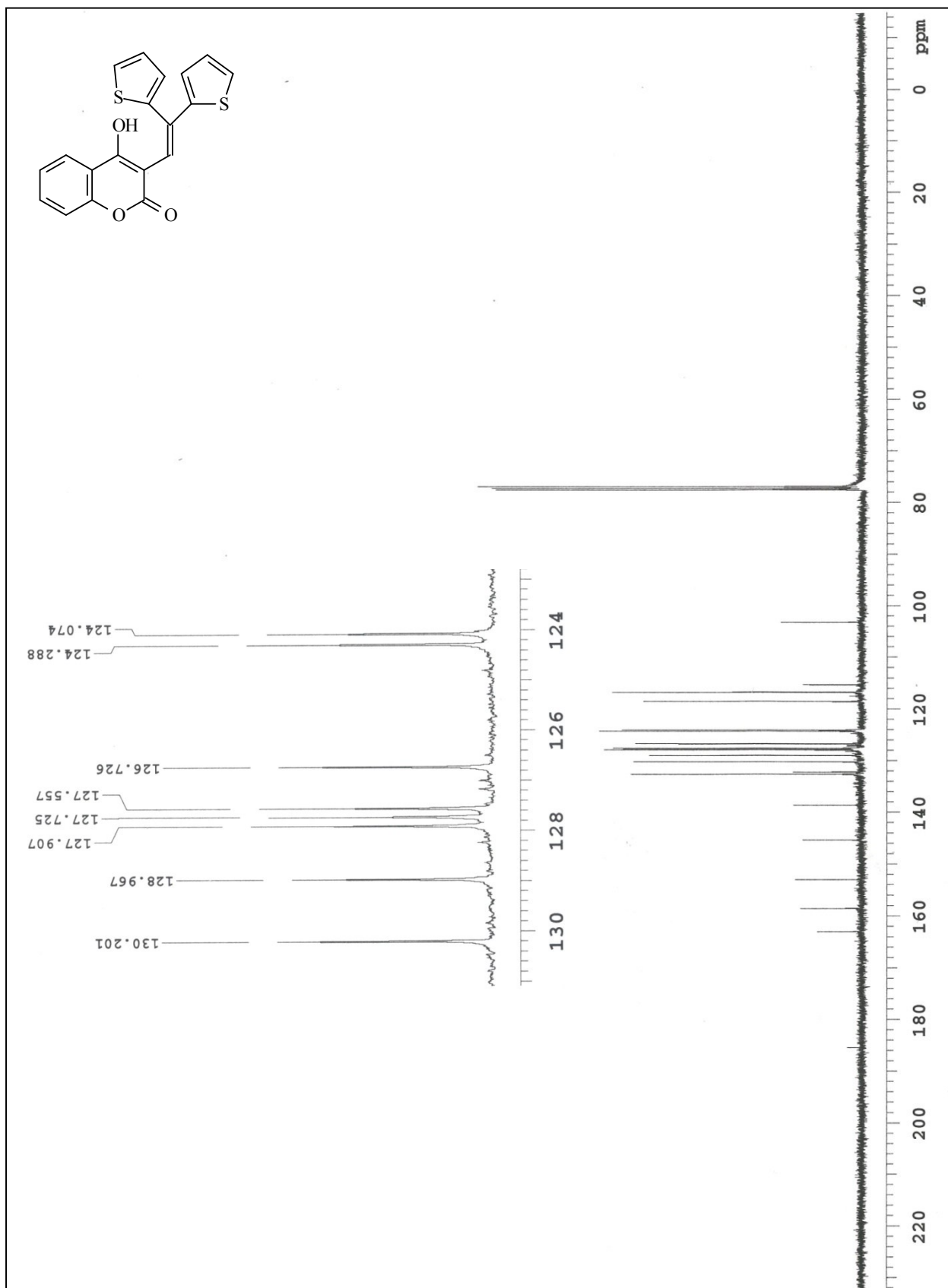
3.8 ^{13}C -NMR spectra of **11**



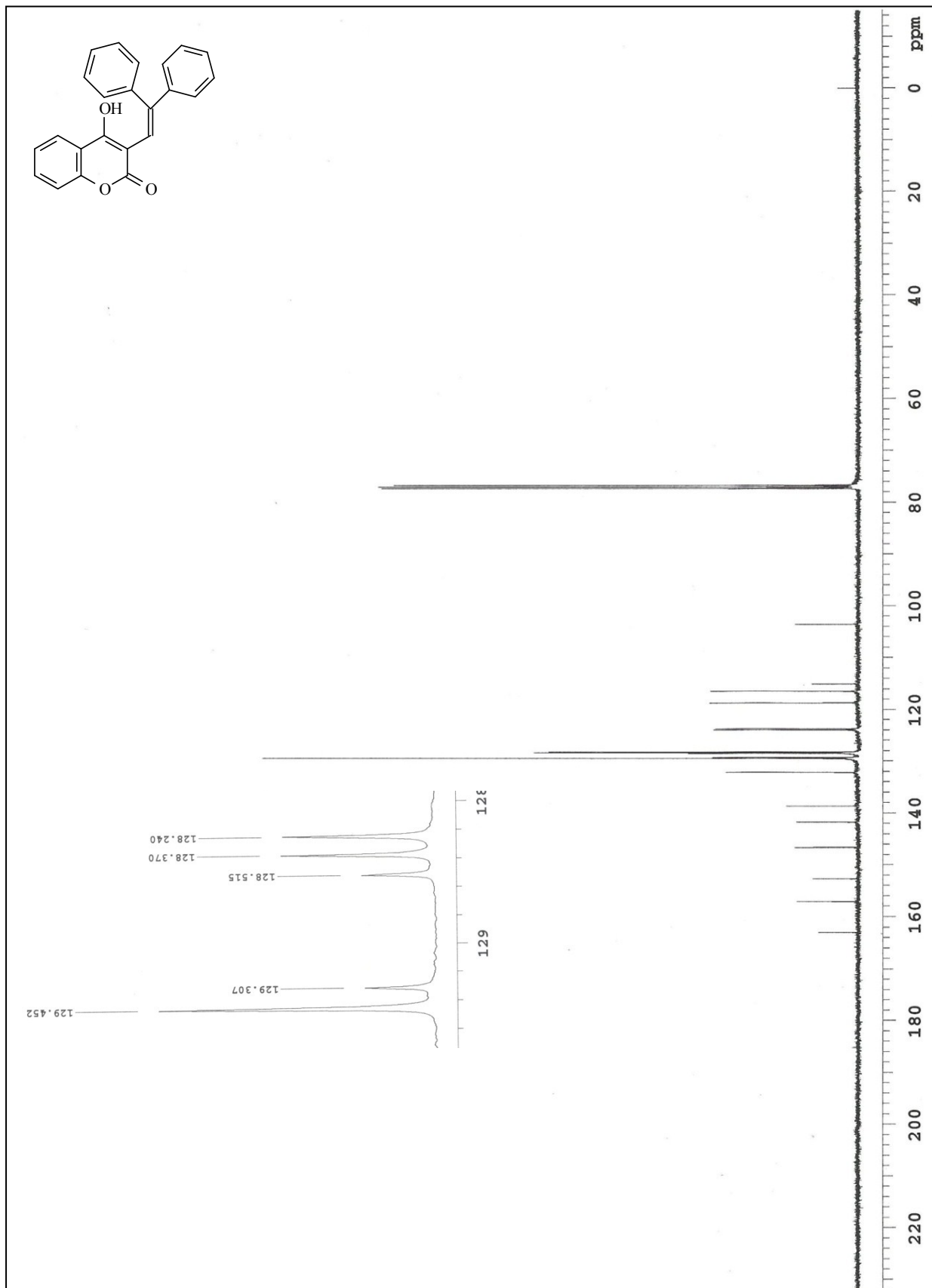
3.9 ^{13}C -NMR spectra of 7



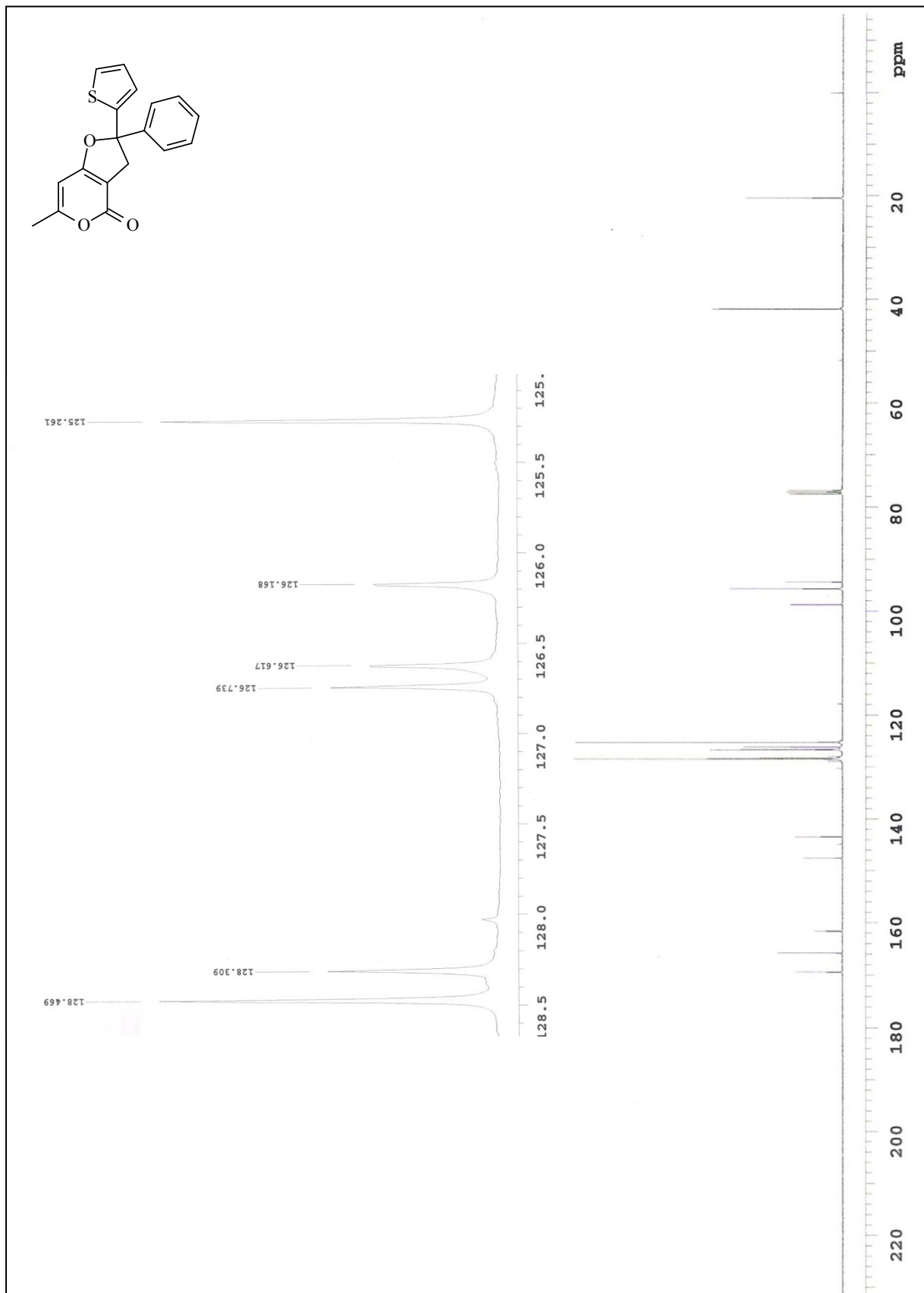
3.10 ^{13}C -NMR spectra of **12**



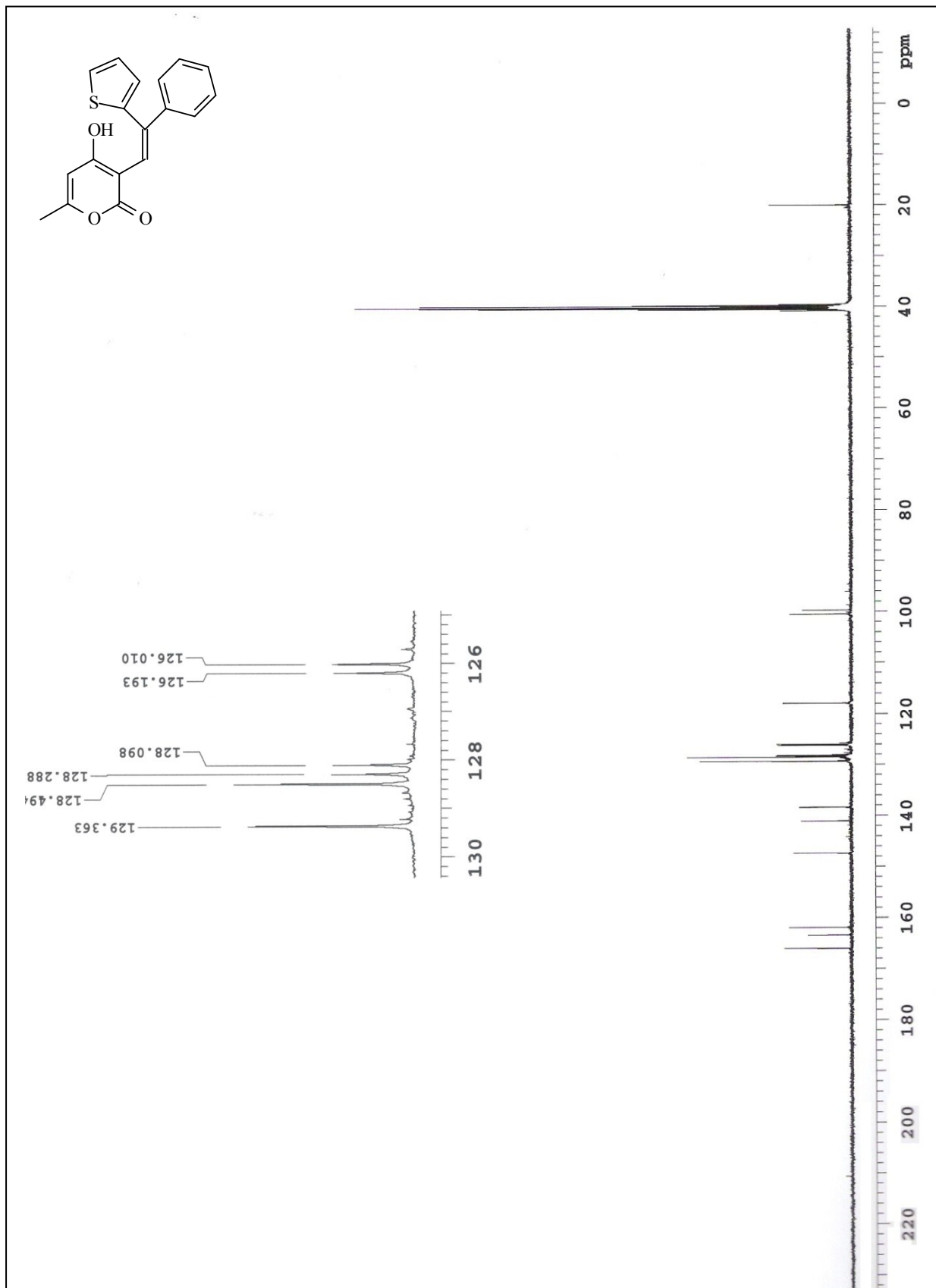
3.11 ^{13}C -NMR spectra of **4aj**



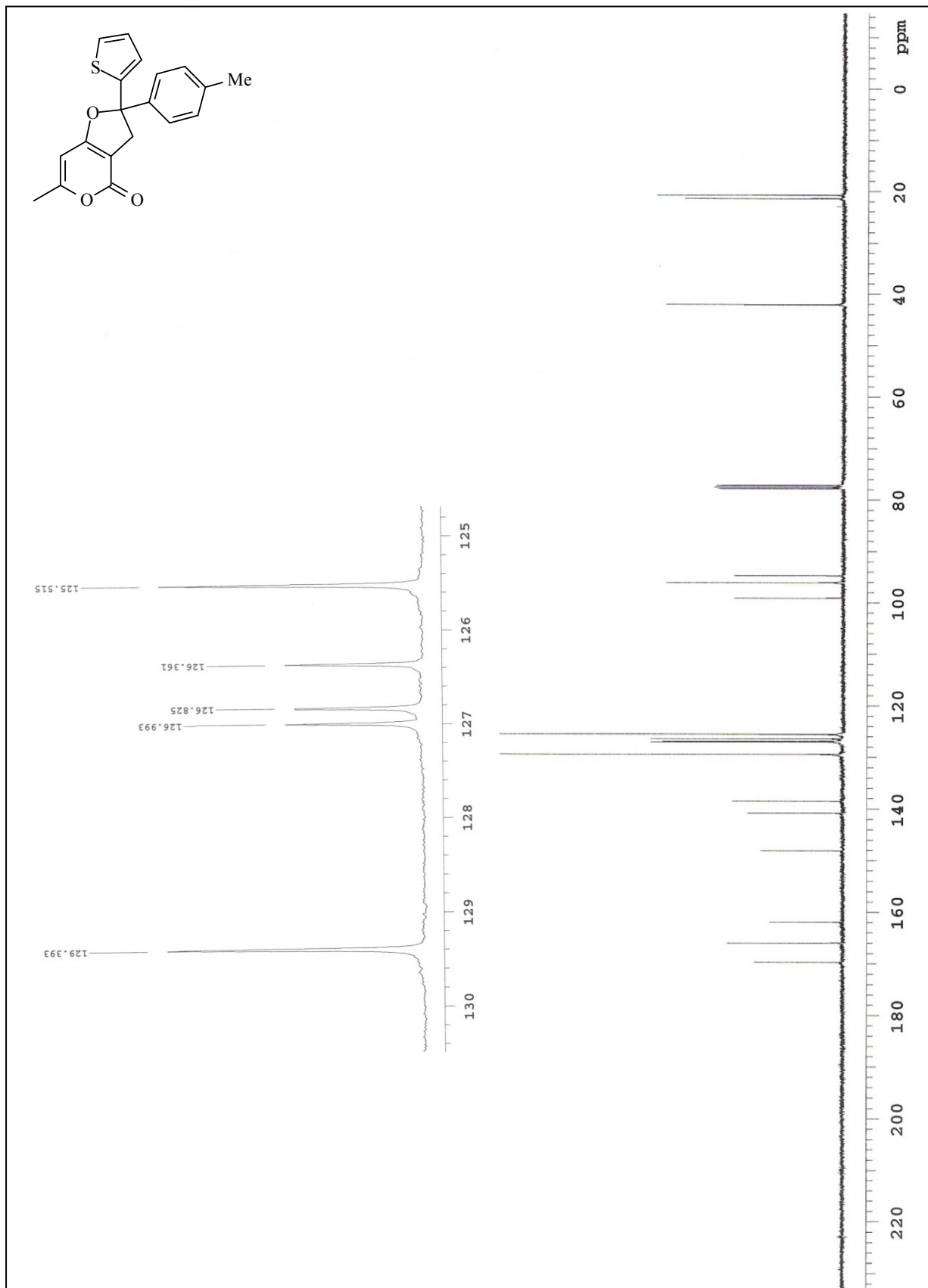
3.12 ^{13}C -NMR spectra of **13**



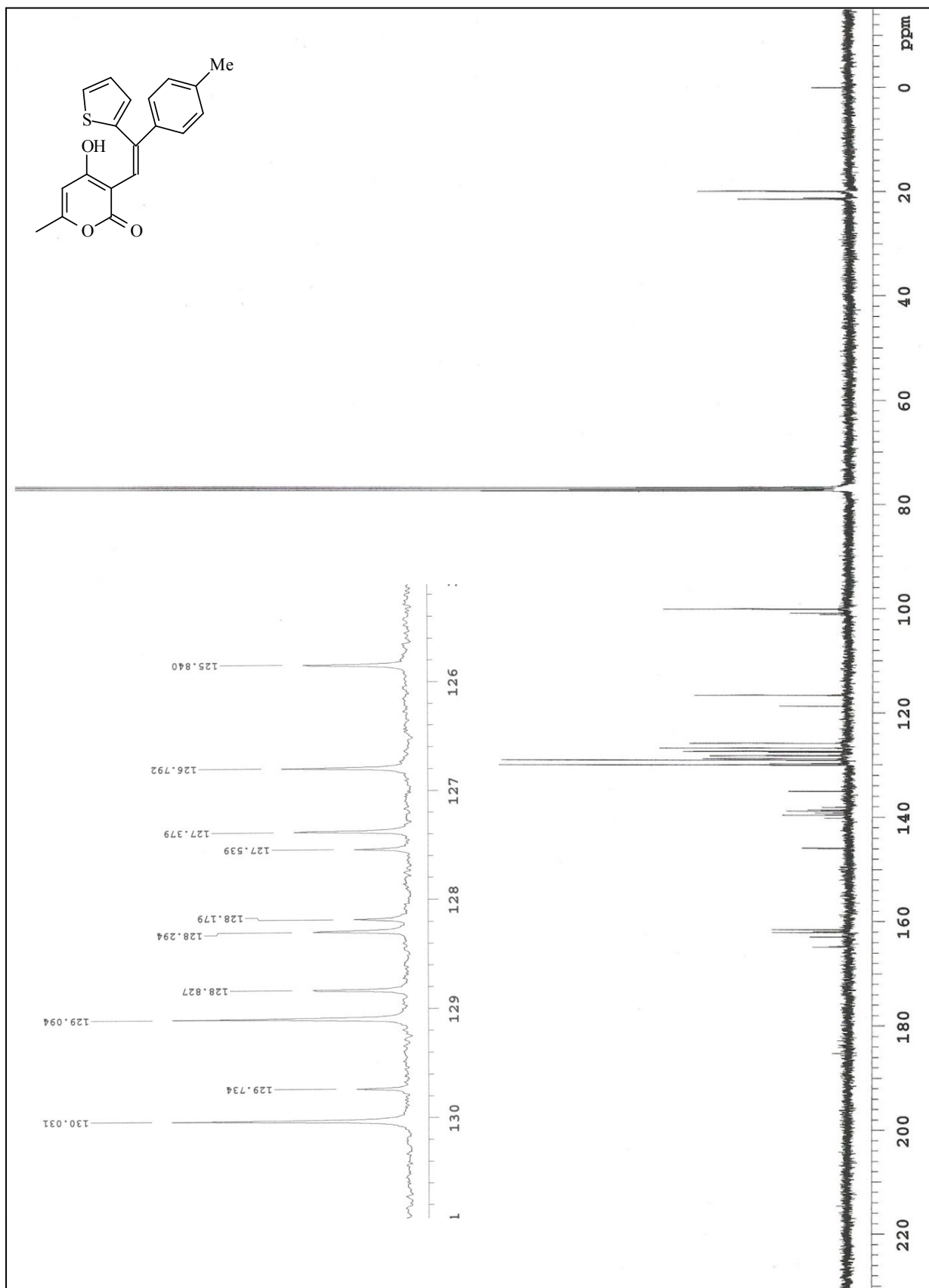
3.13 ^{13}C -NMR spectra of **16**



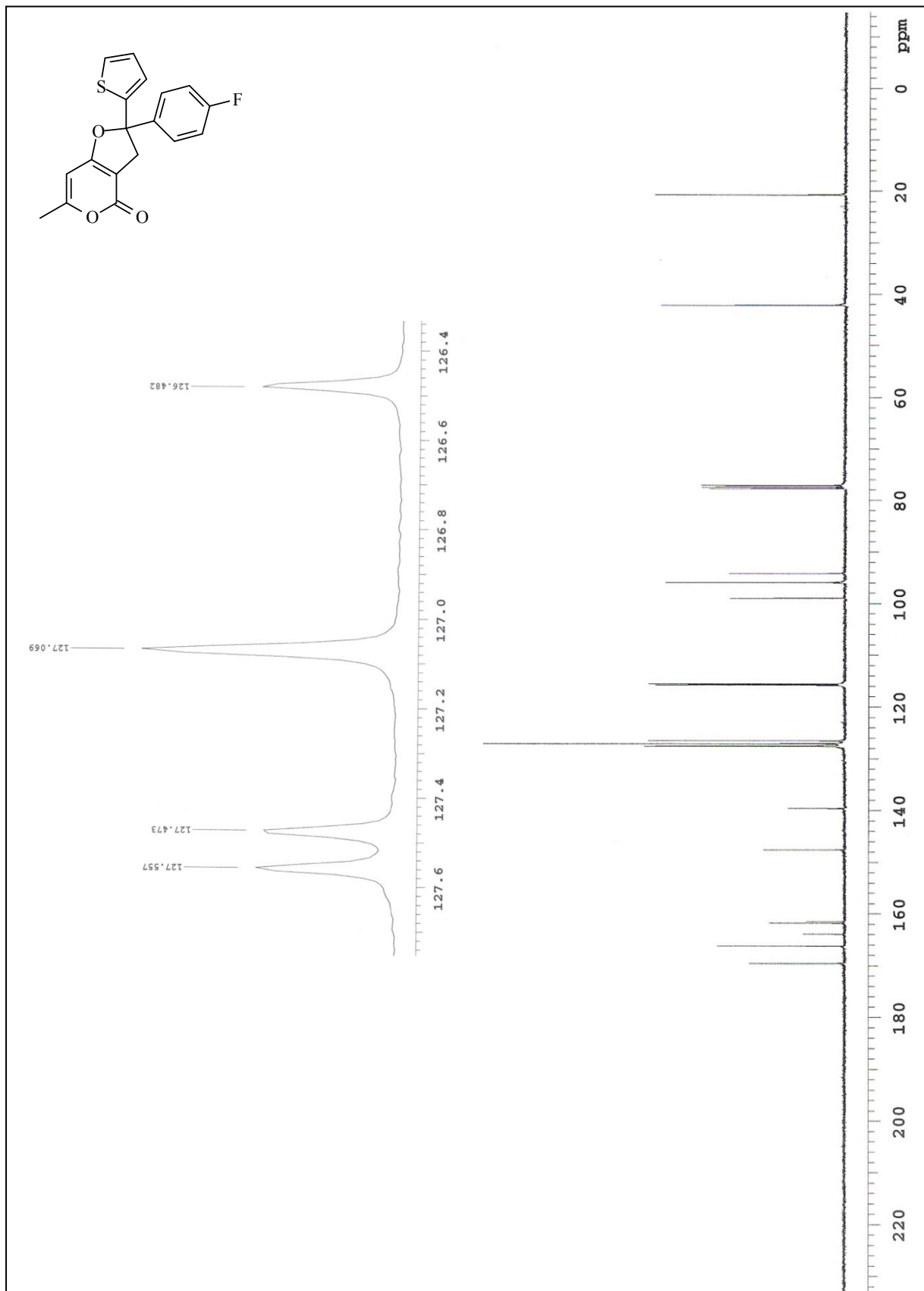
3.14 ^{13}C -NMR spectra of **14**



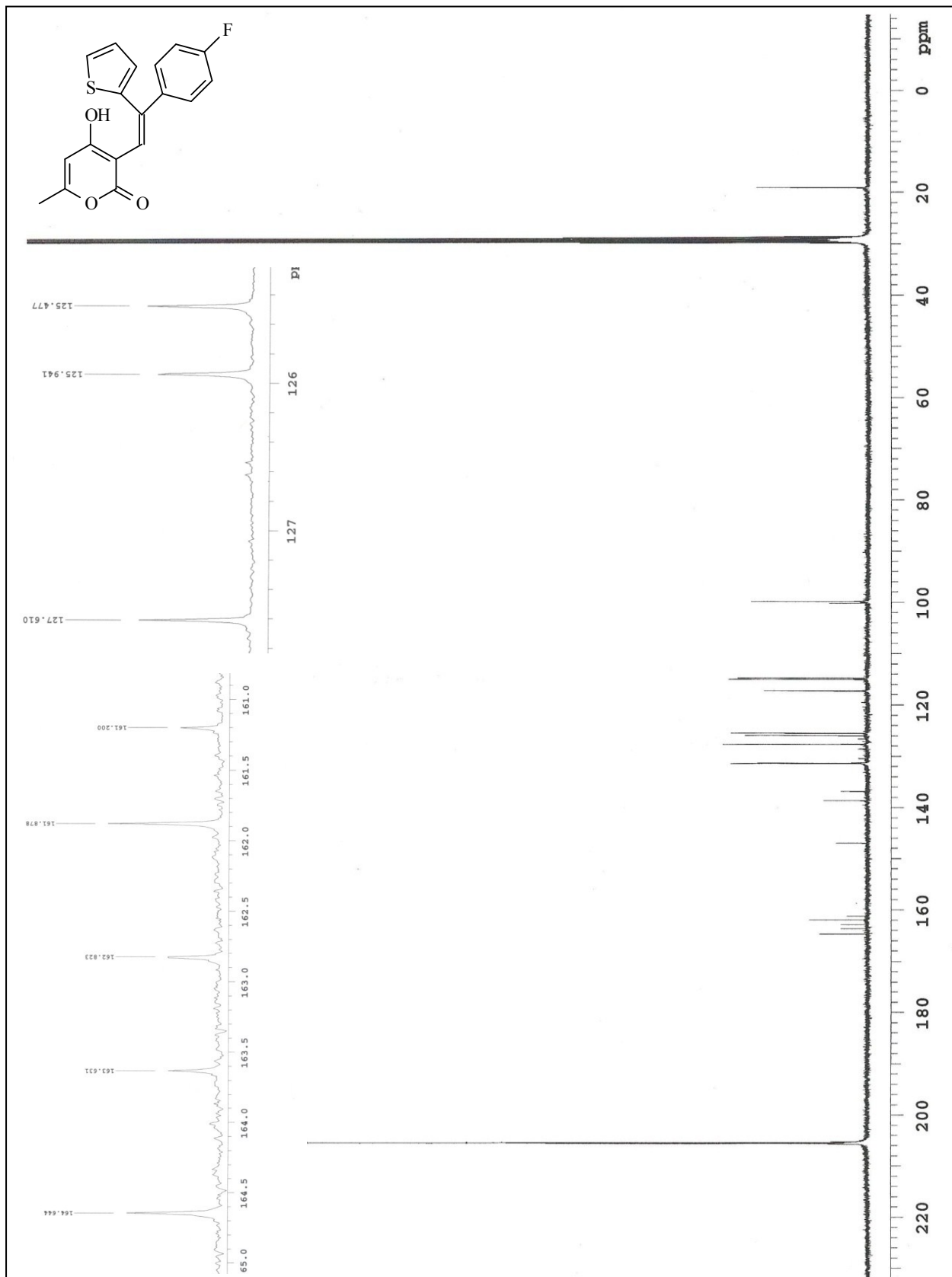
3.15 ^{13}C -NMR spectra of **17**



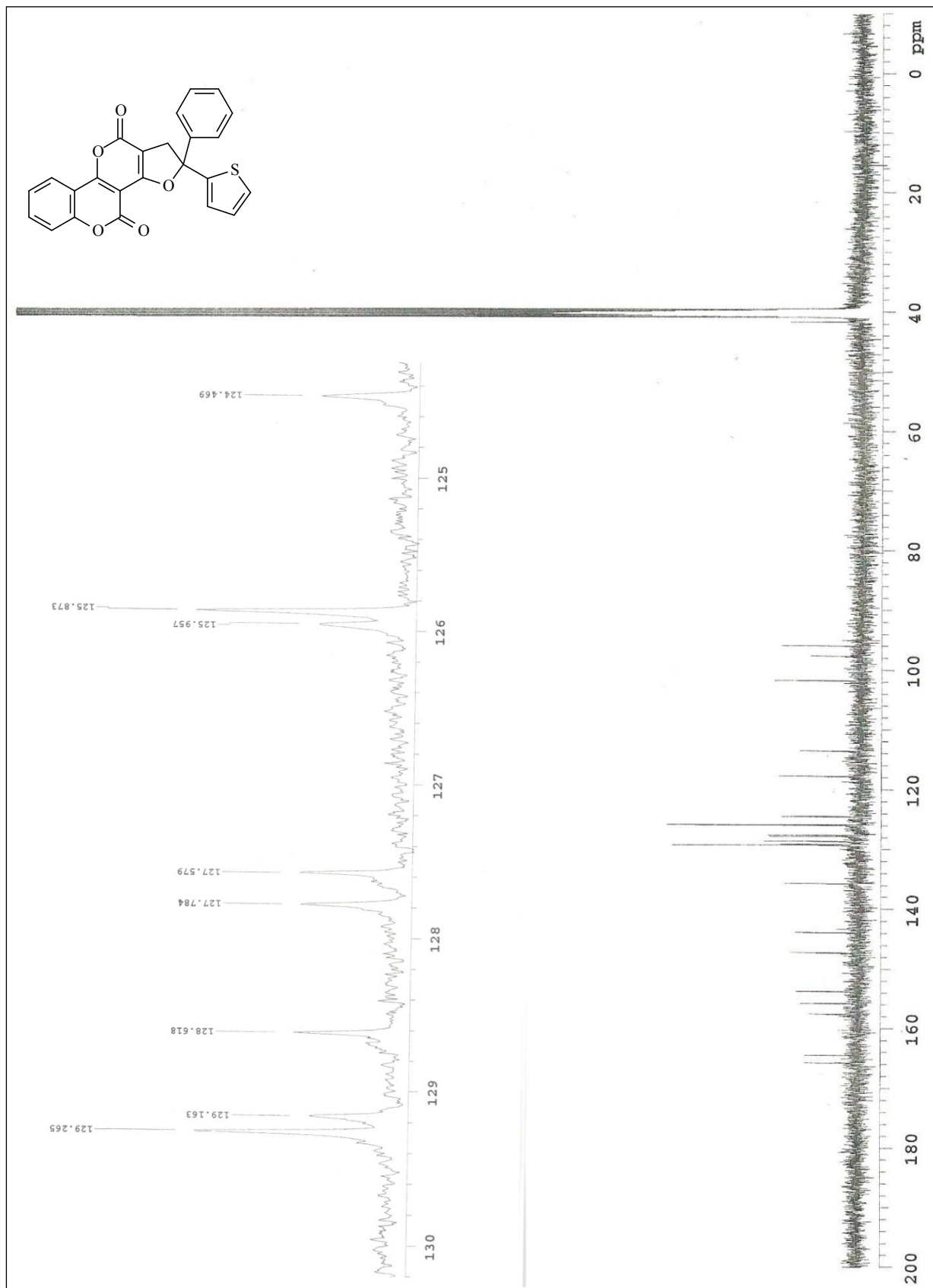
3.16 ^{13}C -NMR spectra of **15**



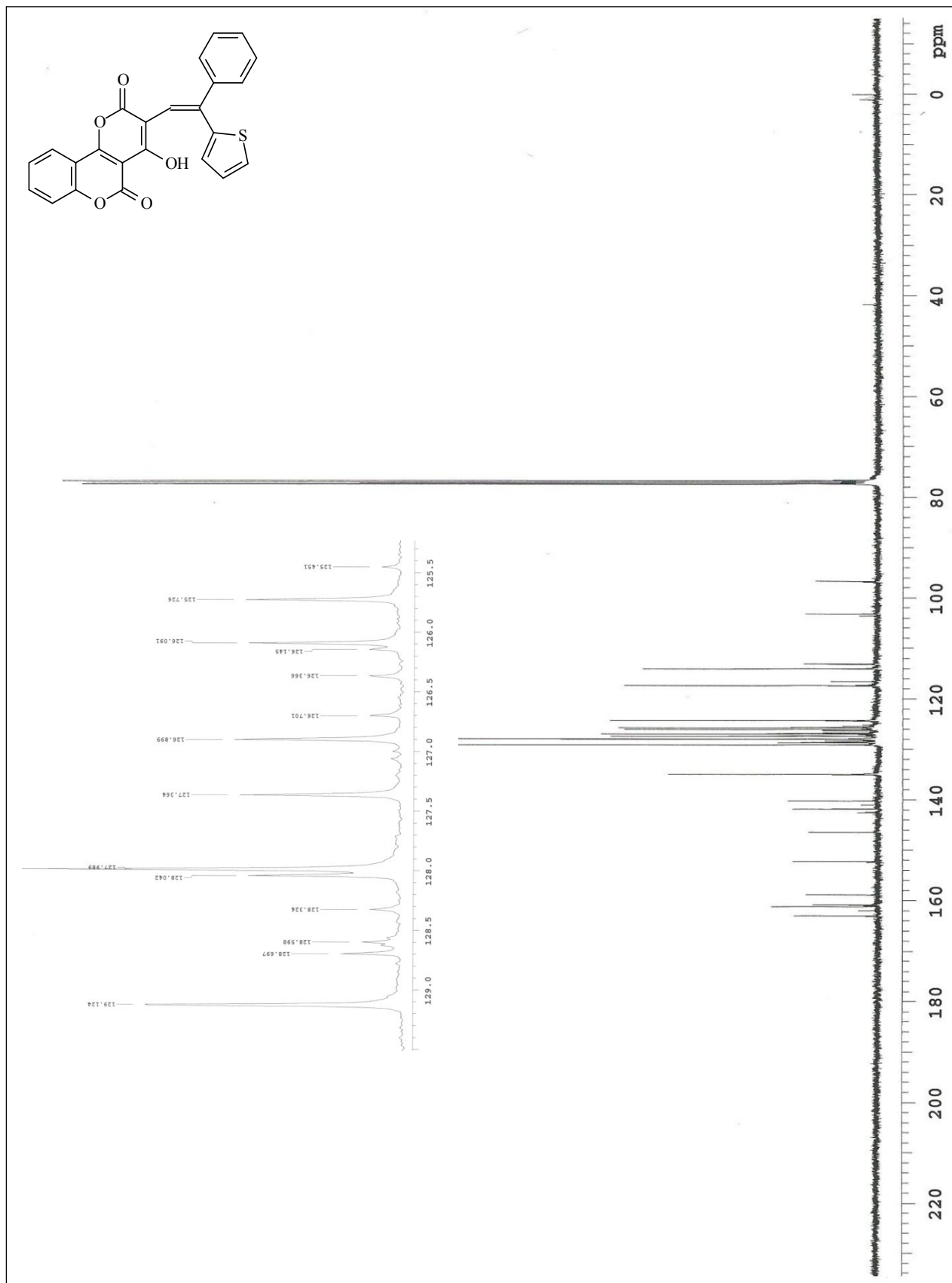
3.17 ^{13}C -NMR spectra of **18**



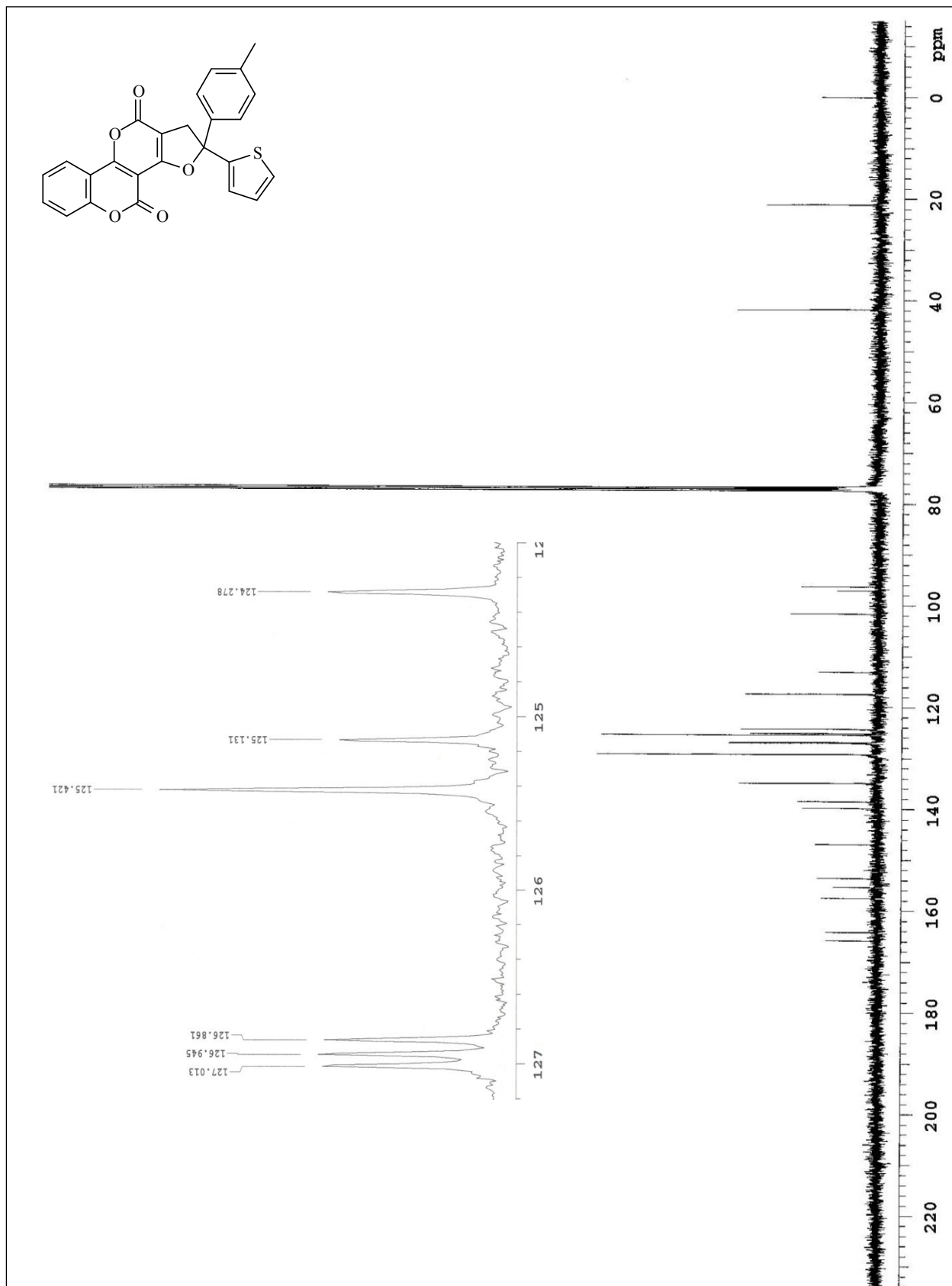
3.18 ^{13}C -NMR spectra of **19**



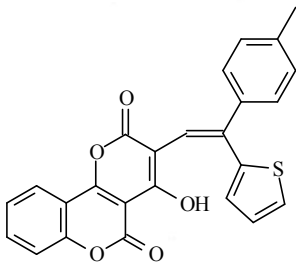
3.19 ^{13}C -NMR spectra of **25**



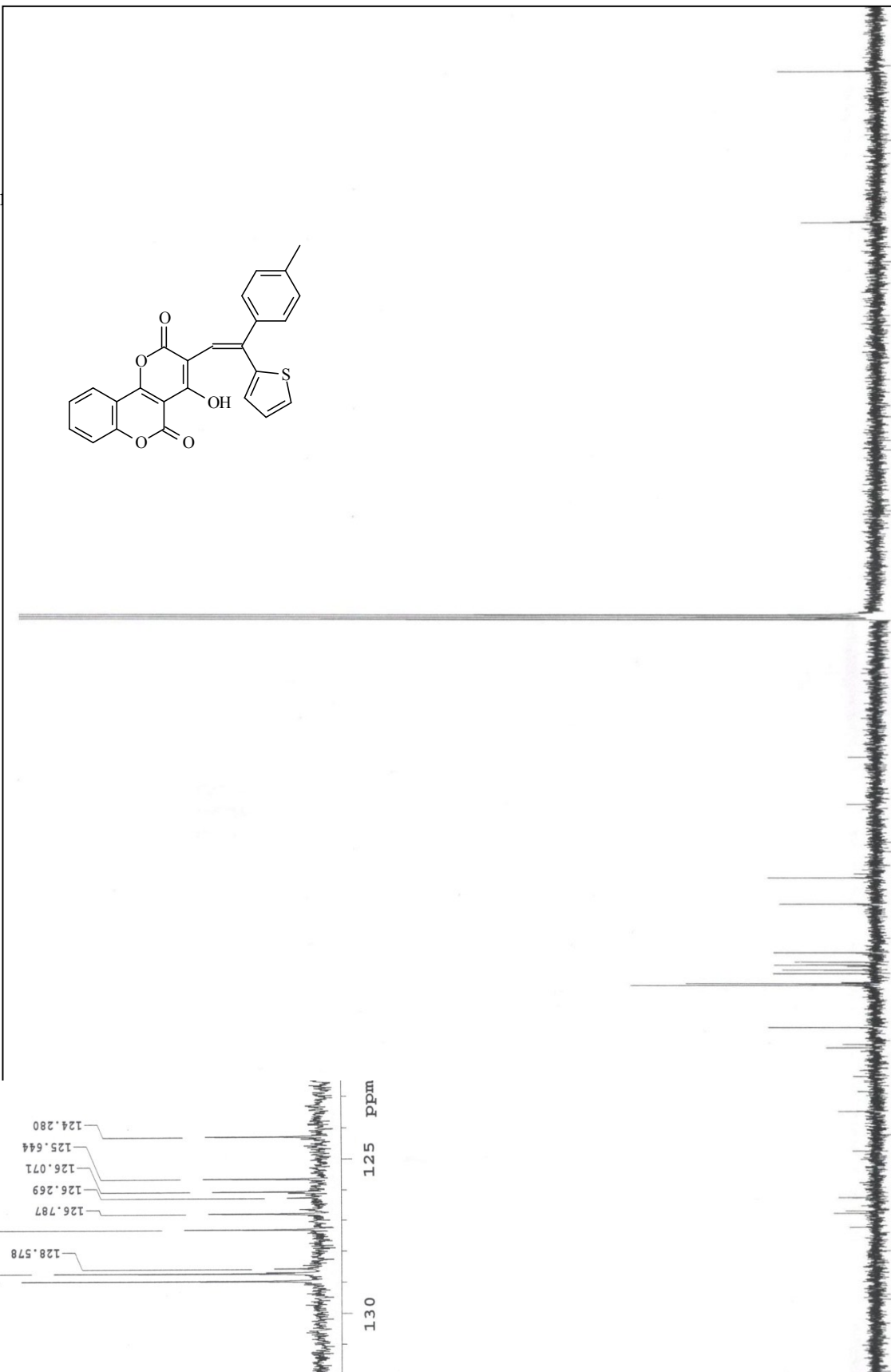
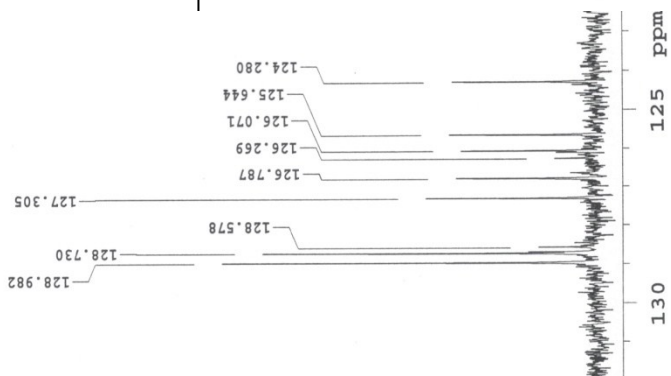
3.20 ^{13}C -NMR spectra of **20**

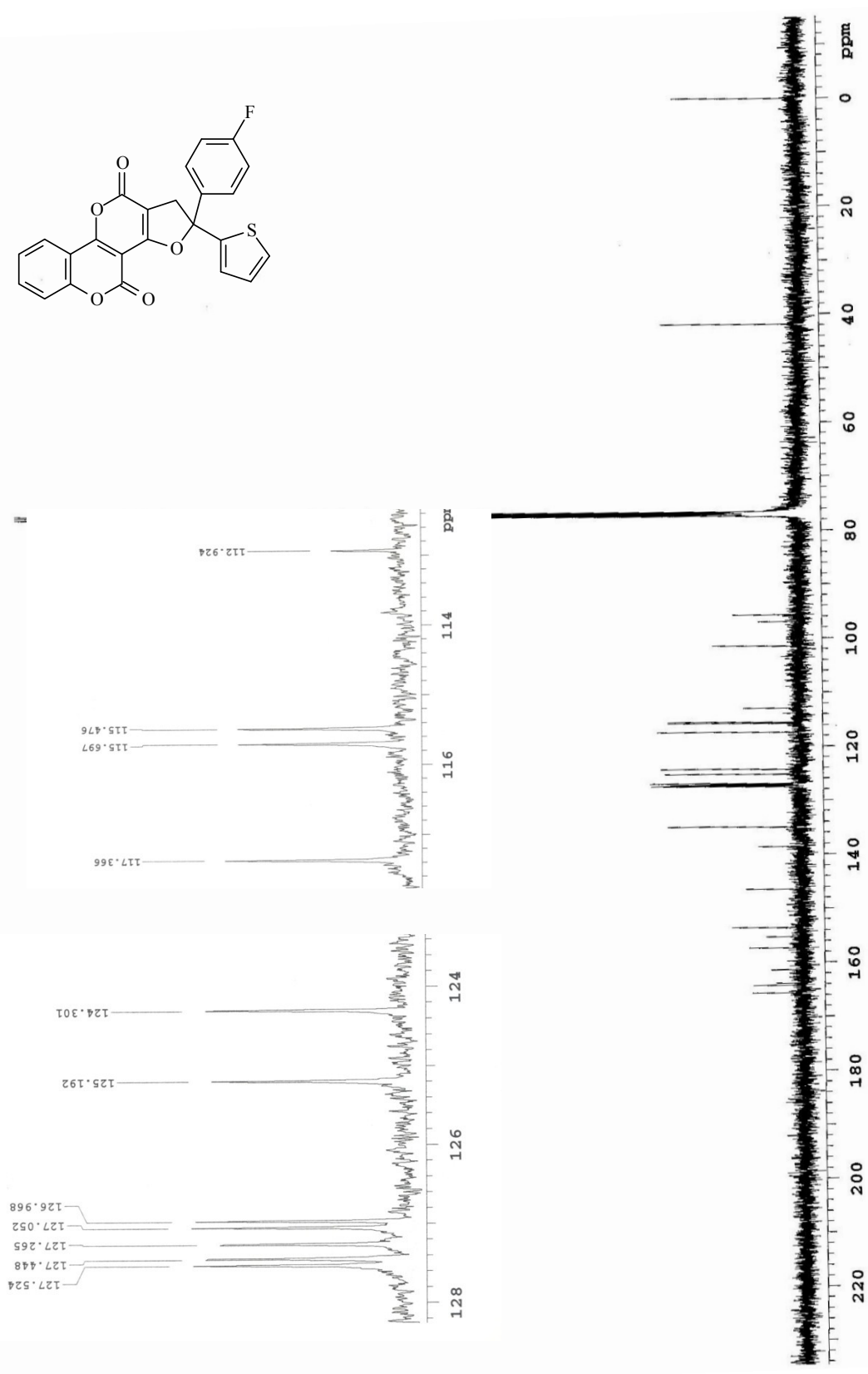
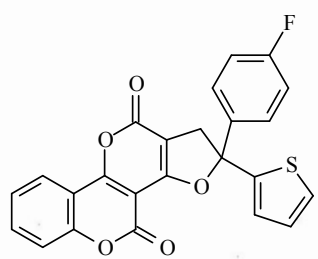


3.21 ^{13}C -NMR spect

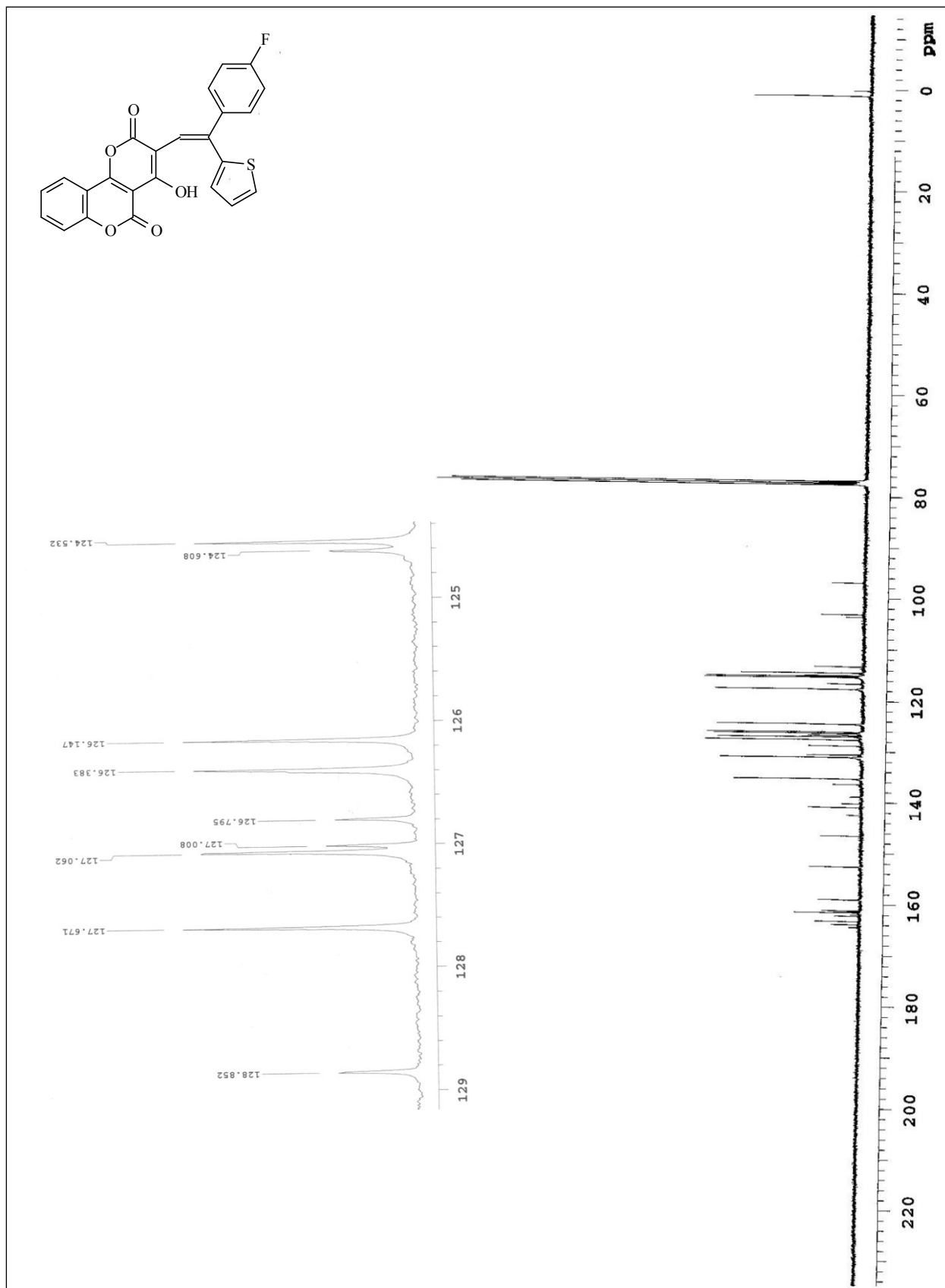


3.

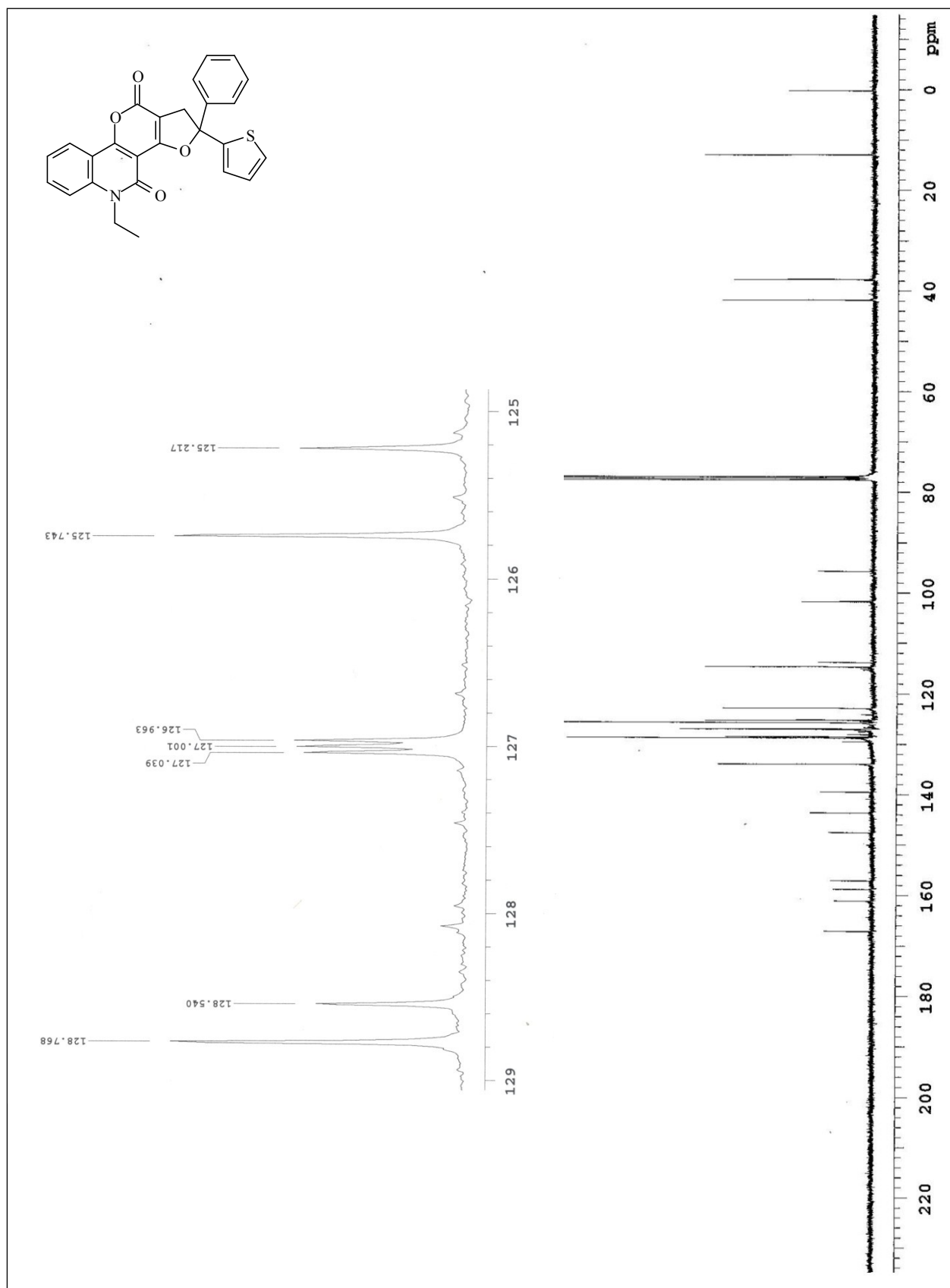




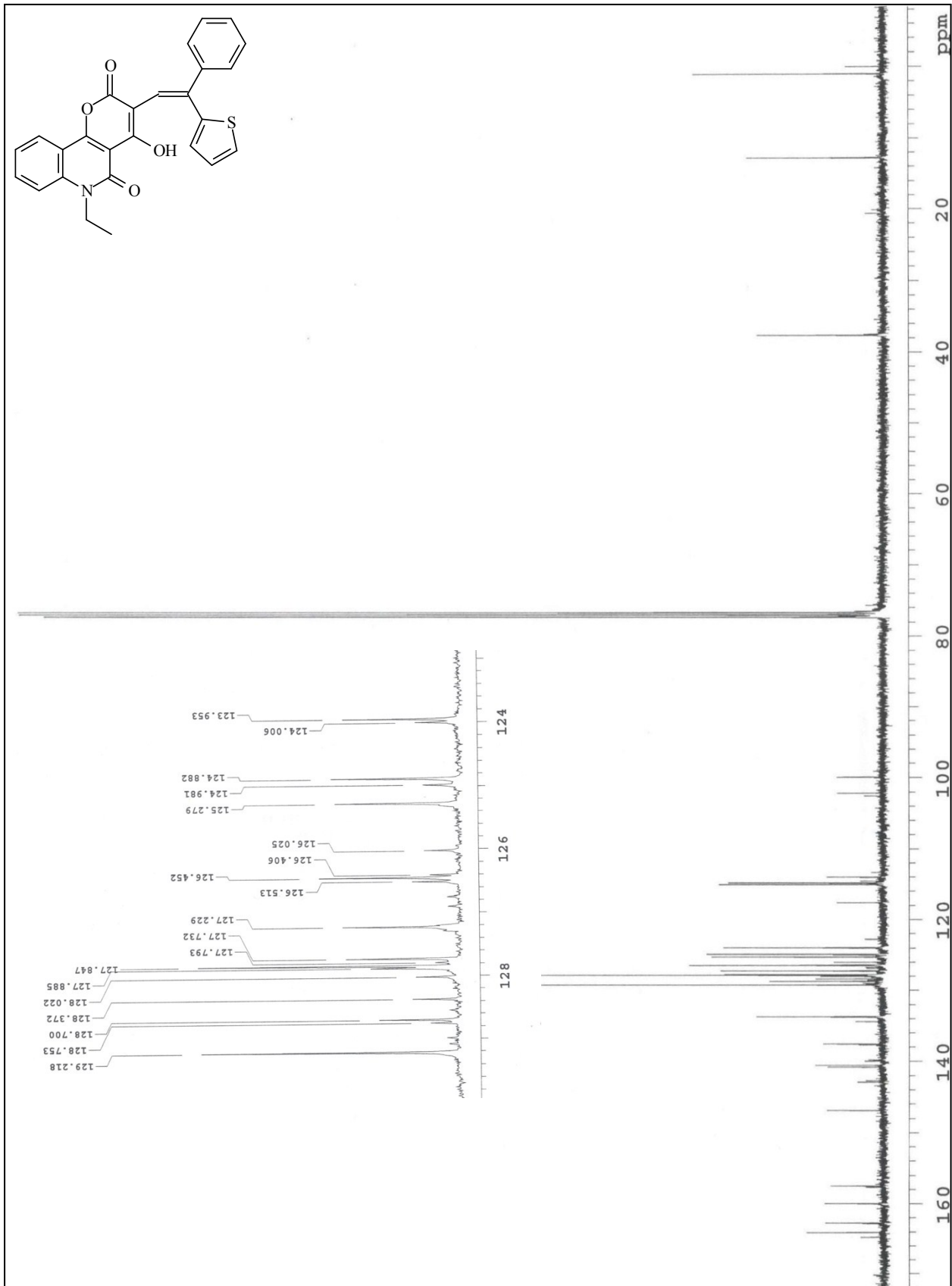
3.23 $^{13}\text{C-NMR}$ spectra of 27



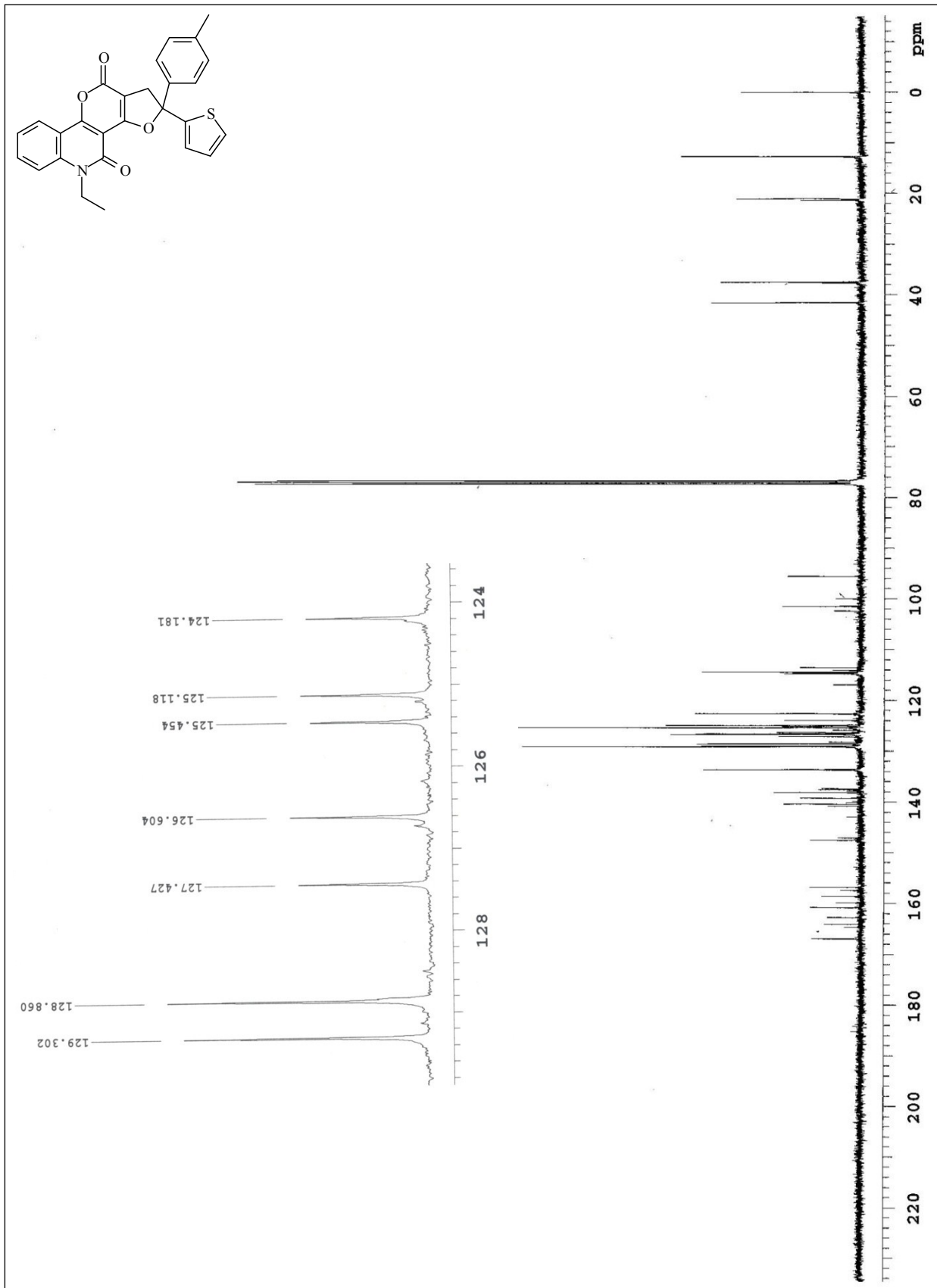
3.24 ^{13}C -NMR spectra of **22**



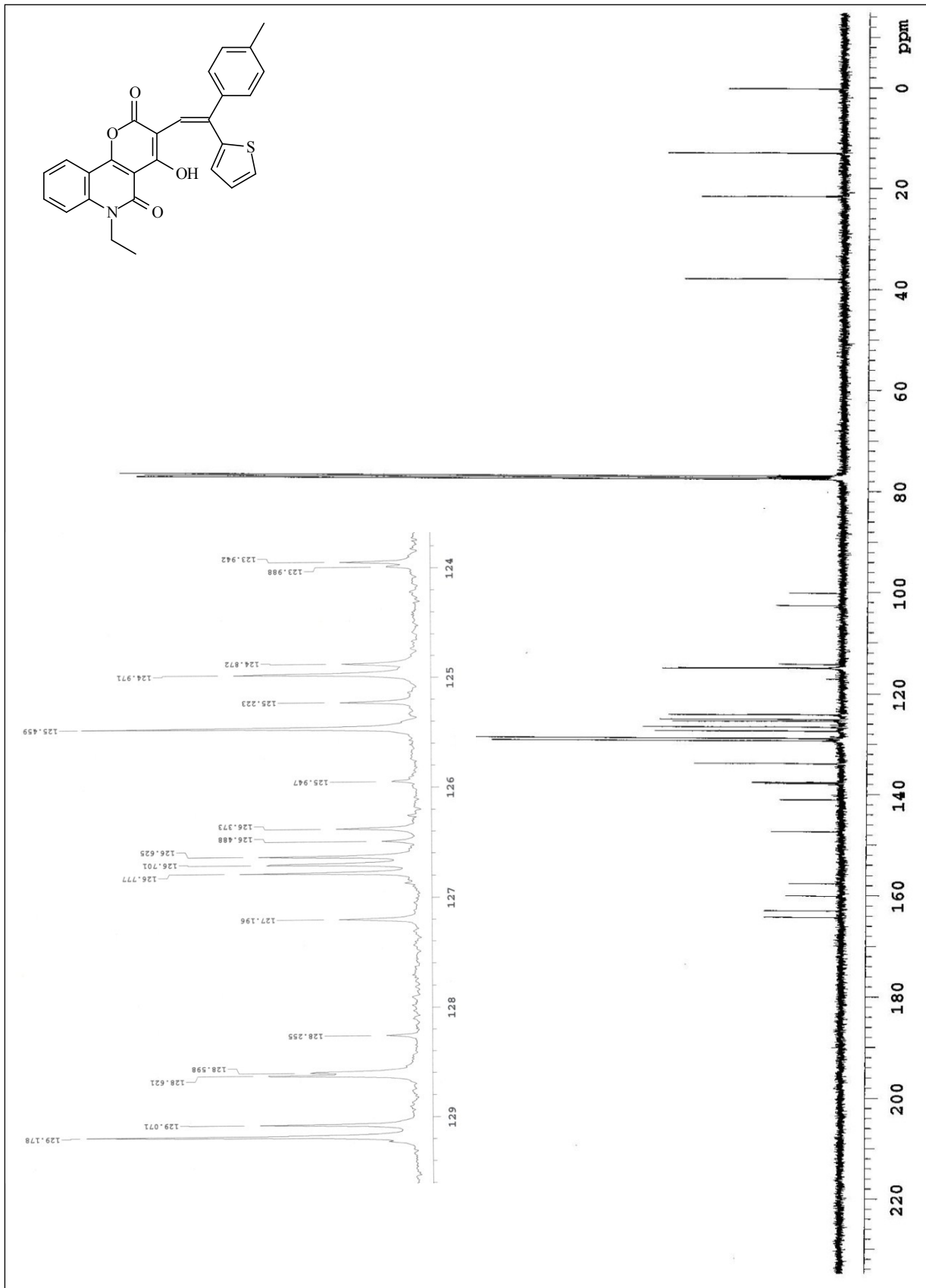
3.25 ^{13}C -NMR spectra of **28**



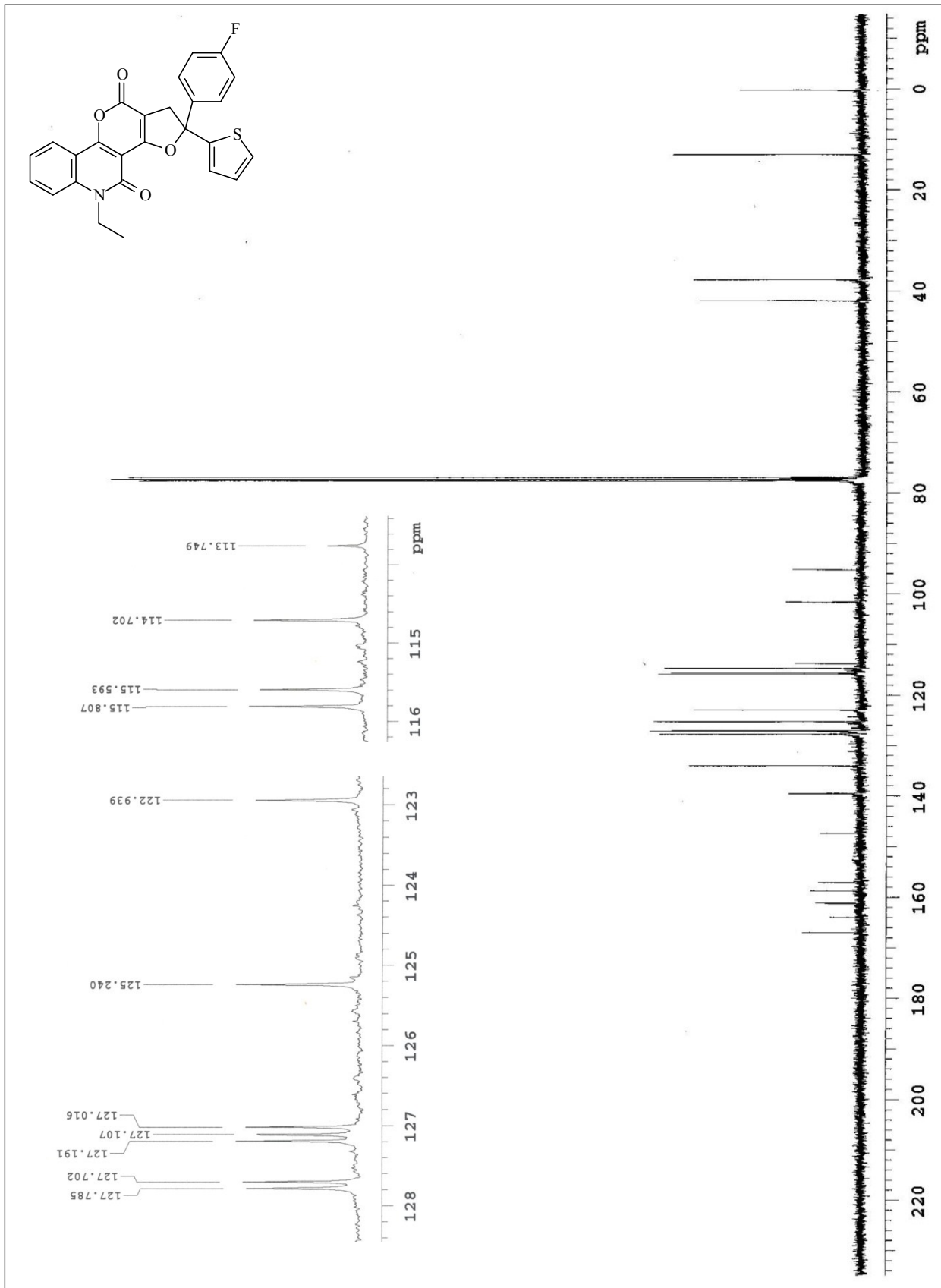
3.26 ¹³C-NMR spectra of 23



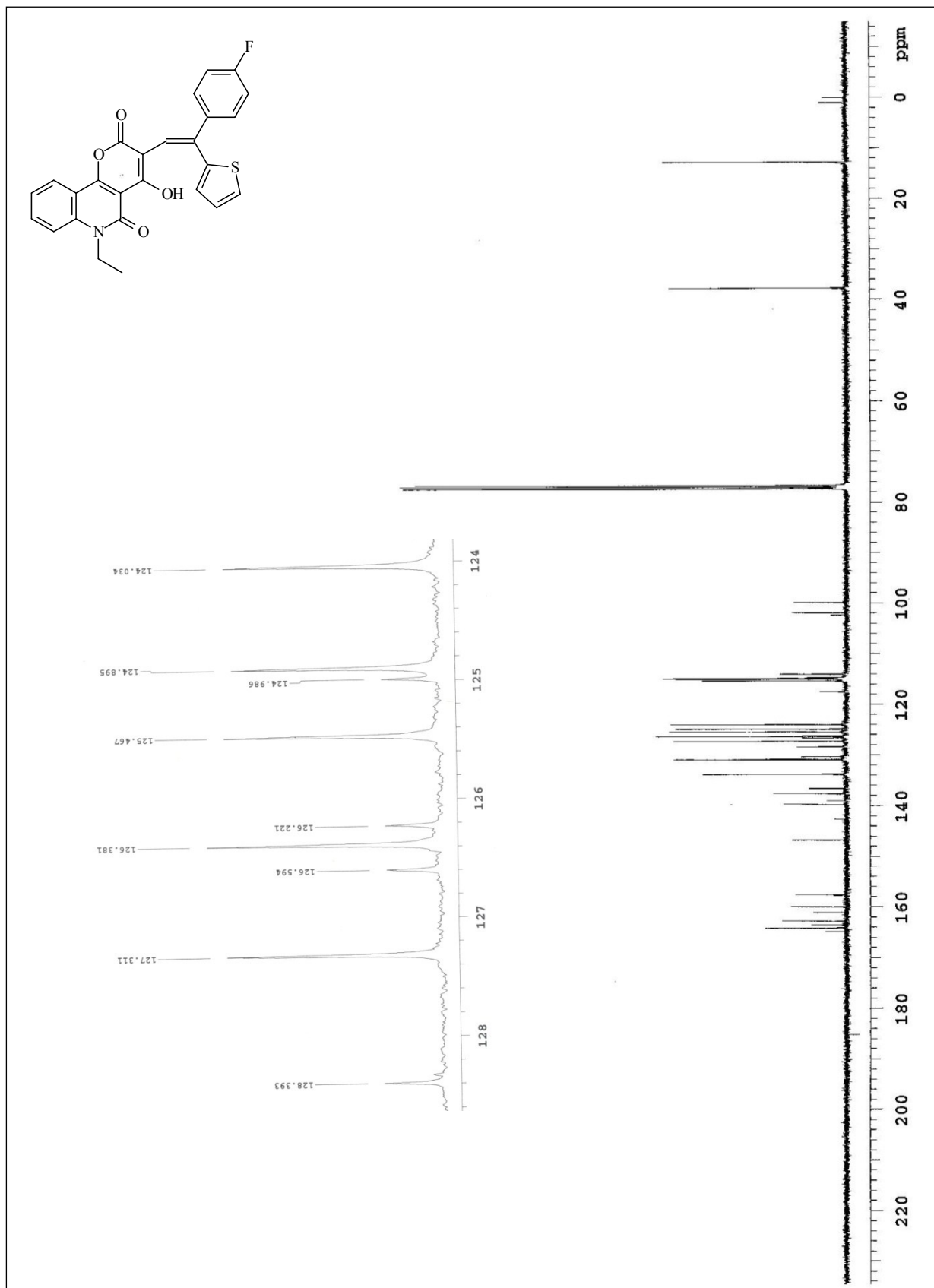
3.27 ^{13}C -NMR spectra of **29**



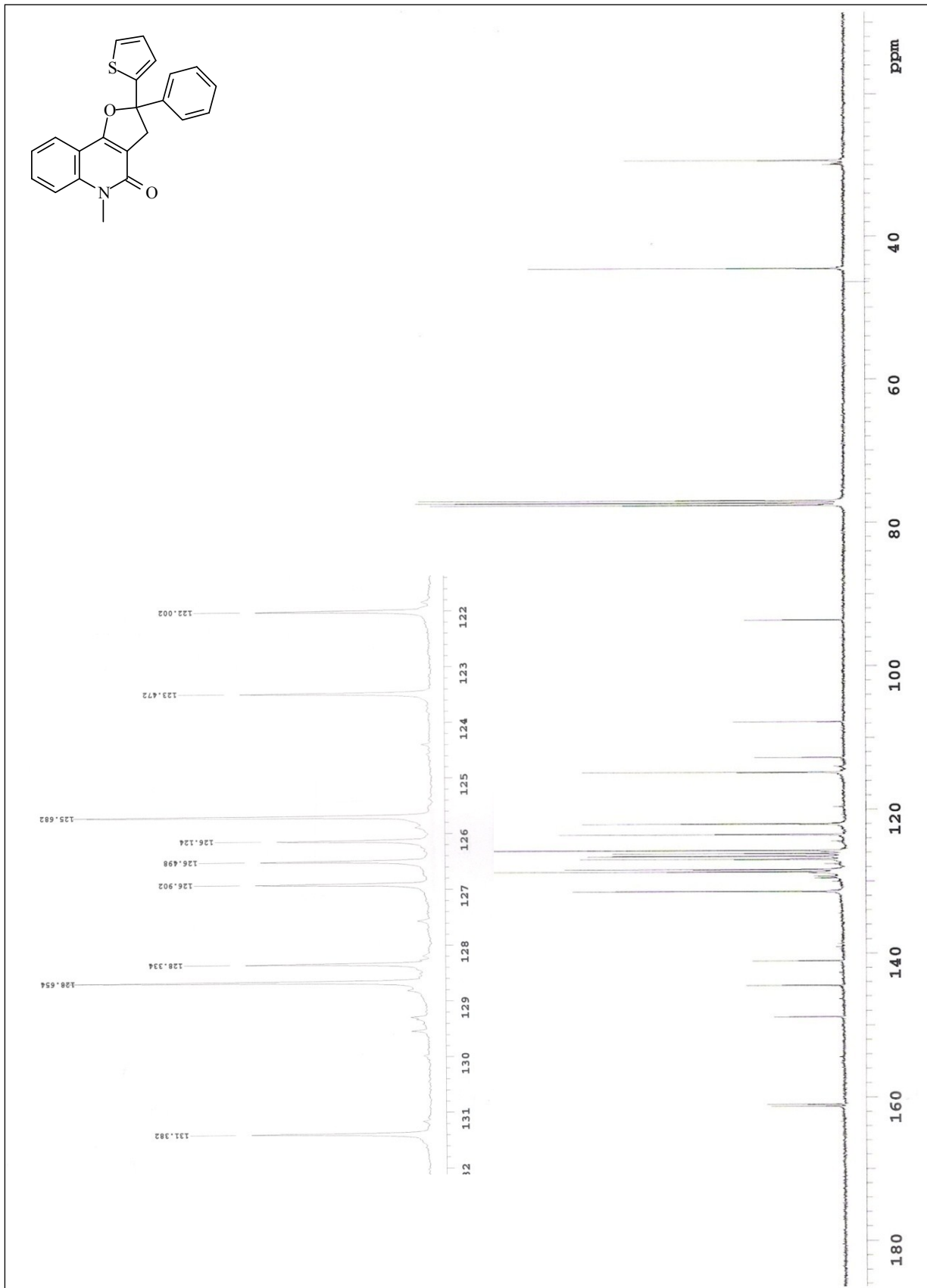
3.28 ^{13}C -NMR spectra of 24



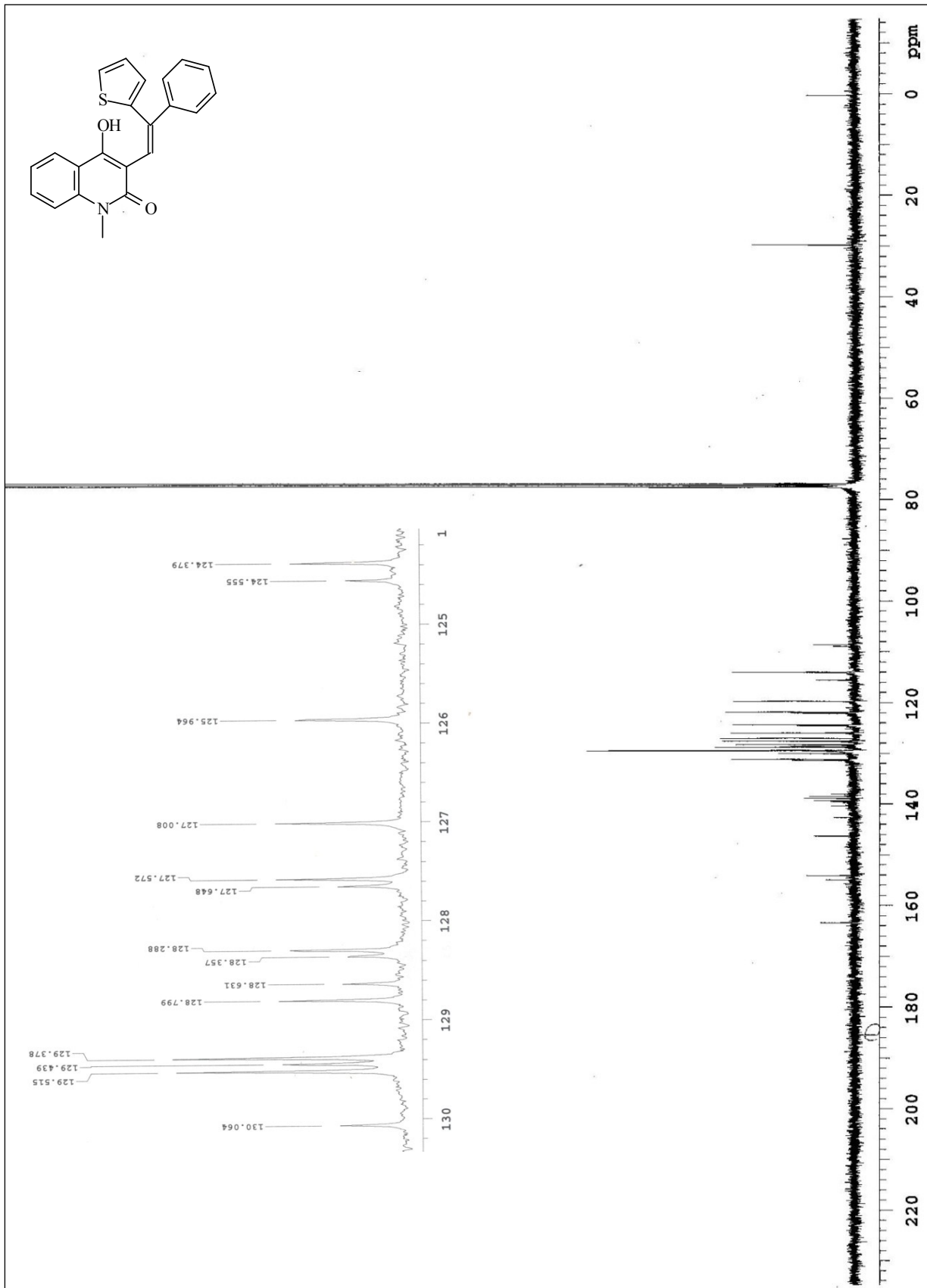
3.29 $^{13}\text{C-NMR}$ spectra of **30**



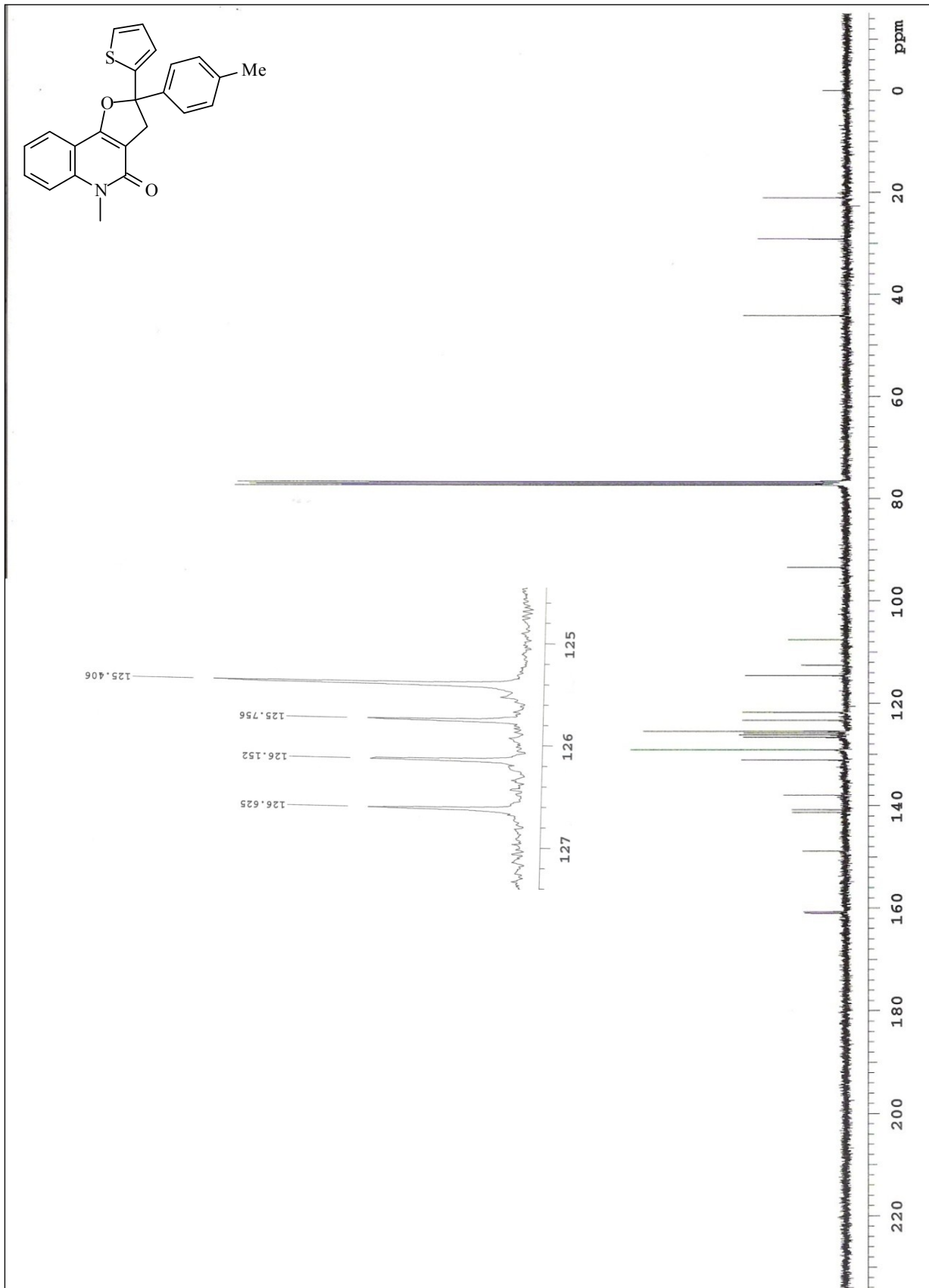
3.30 ^{13}C -NMR spectra of **31**



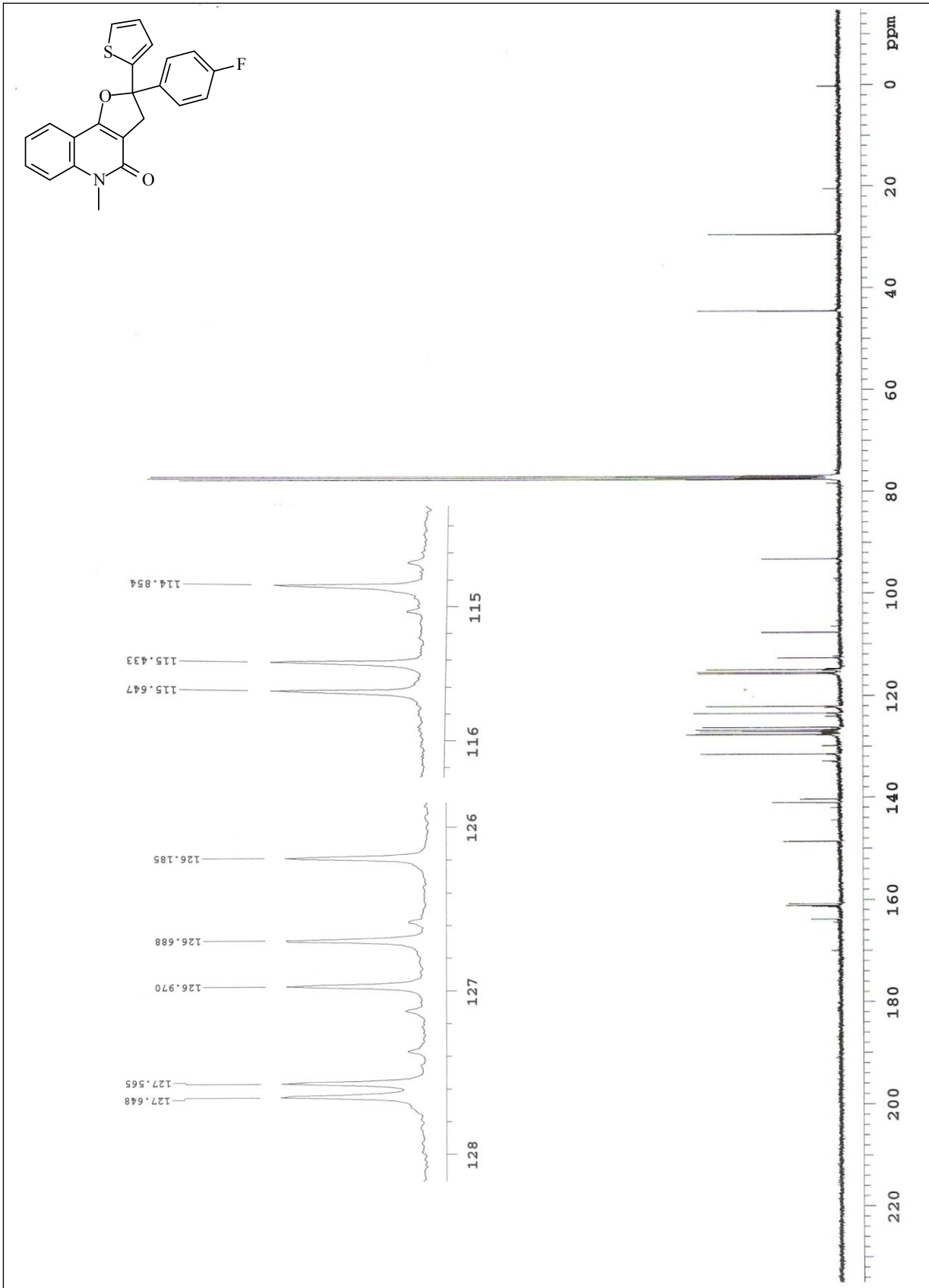
3.31 ^{13}C -NMR spectra of **34**



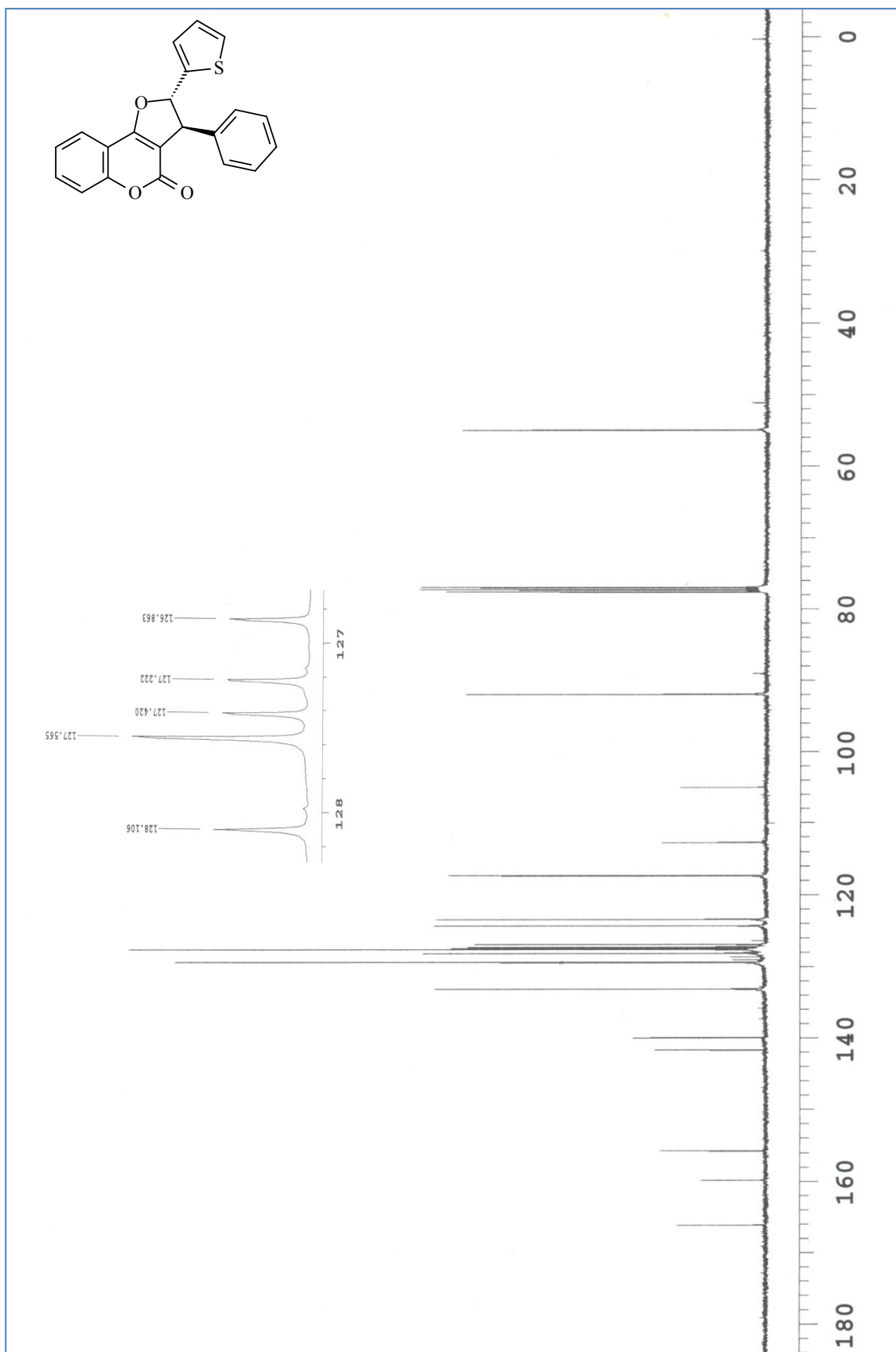
3.32 ^{13}C -NMR spectra of **32**



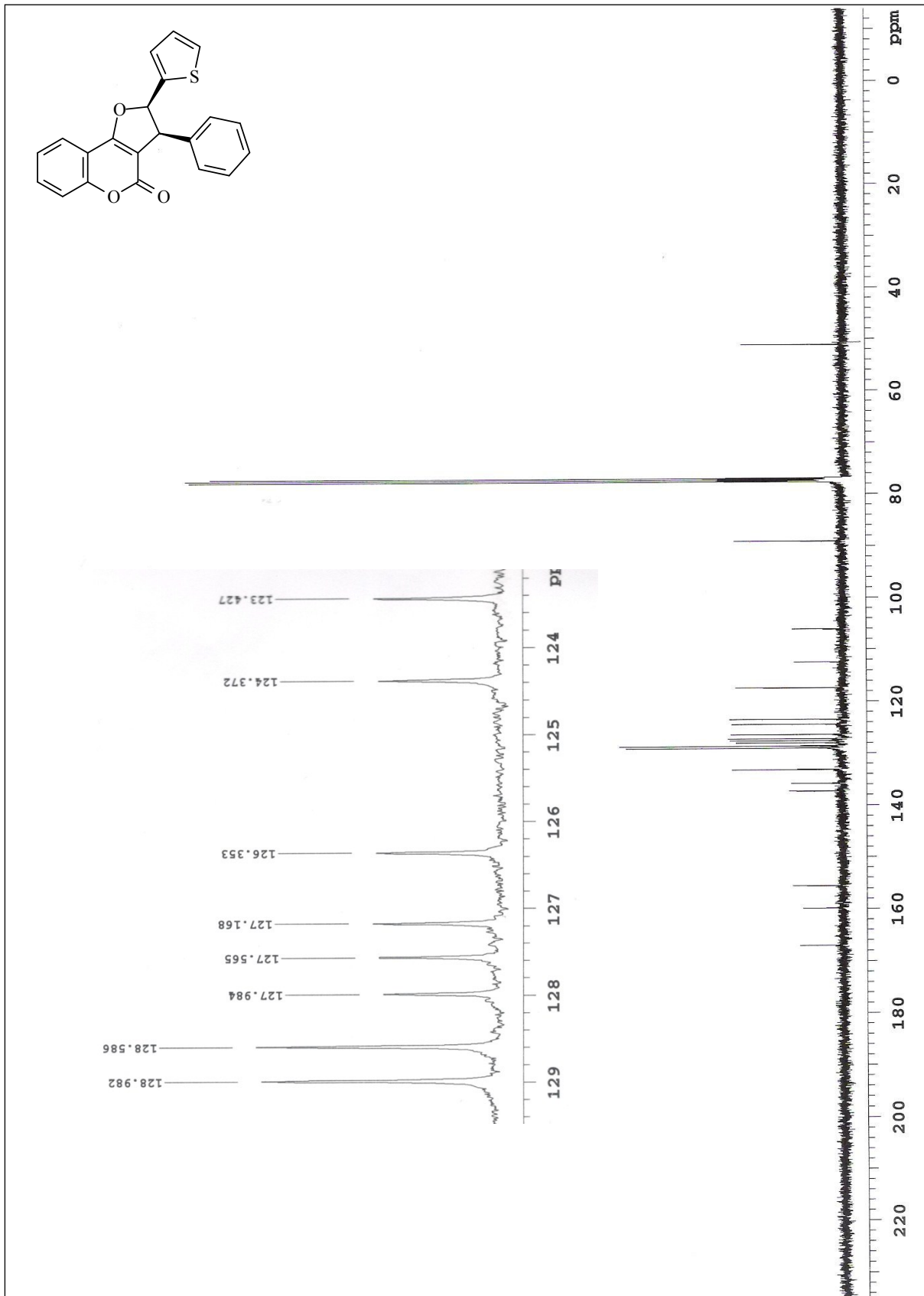
3.33 ^{13}C -NMR spectra of **33**



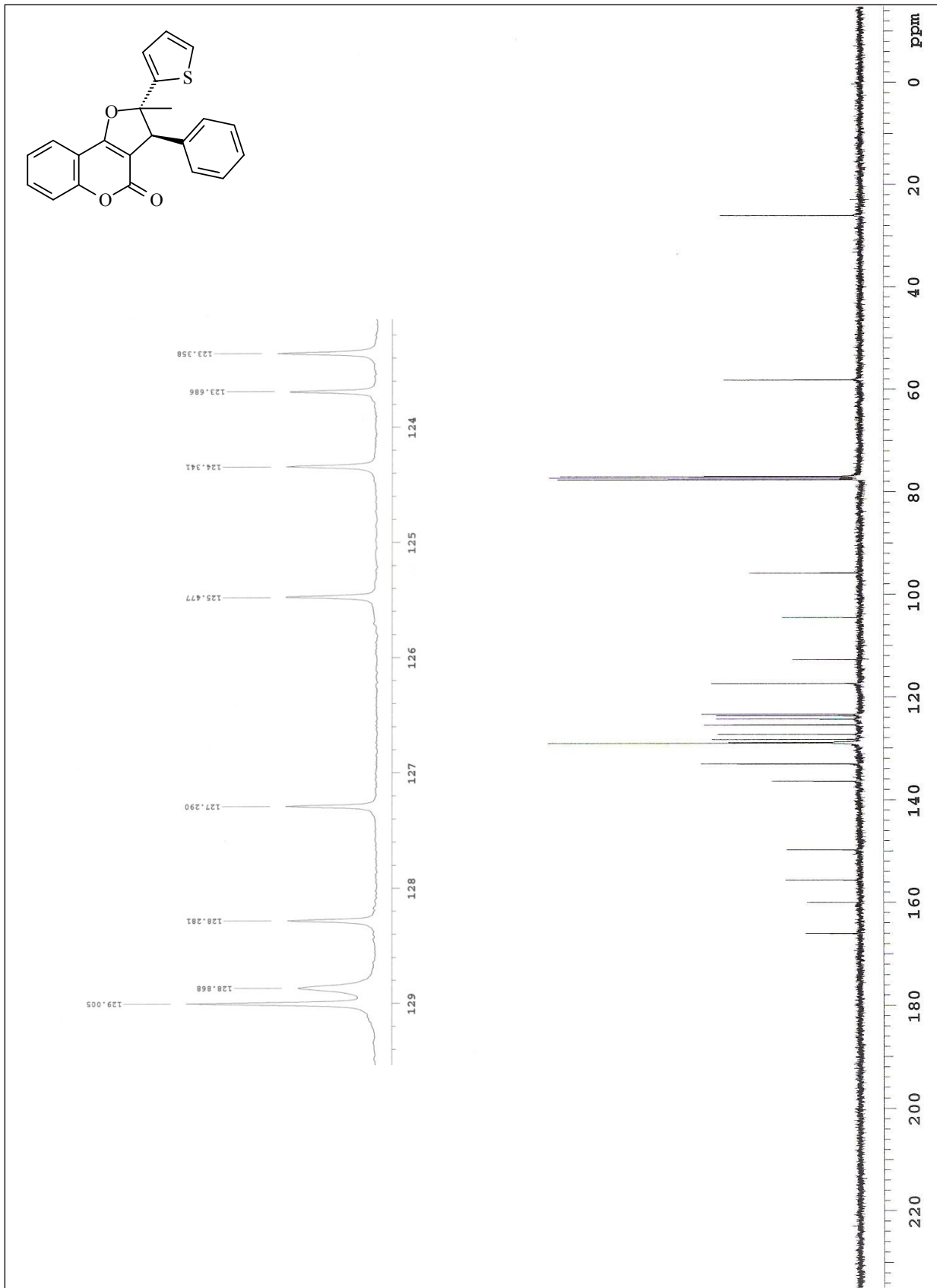
3.34 ^{13}C -NMR spectra of **35**



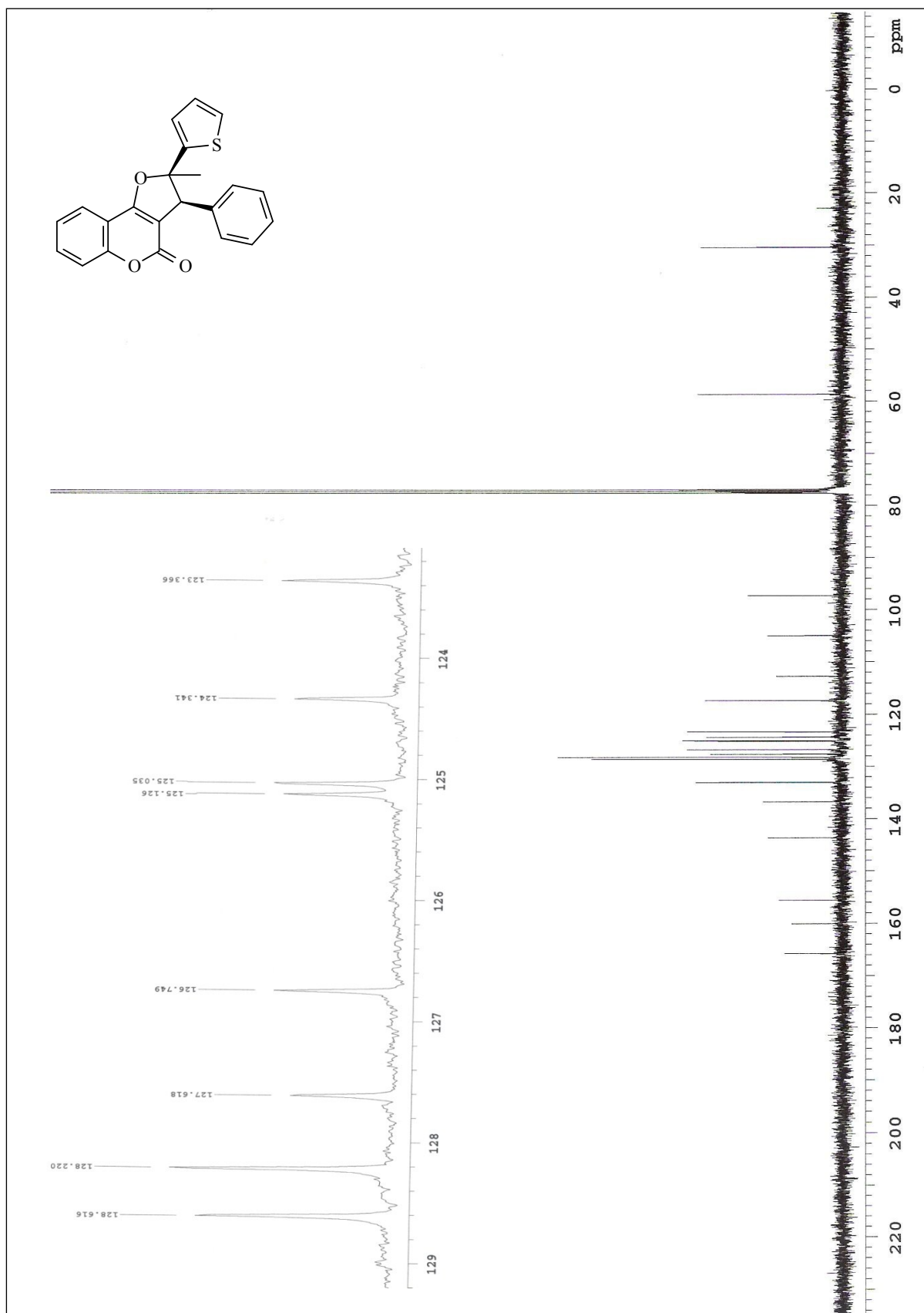
3.35 ^{13}C -NMR spectra of **36**



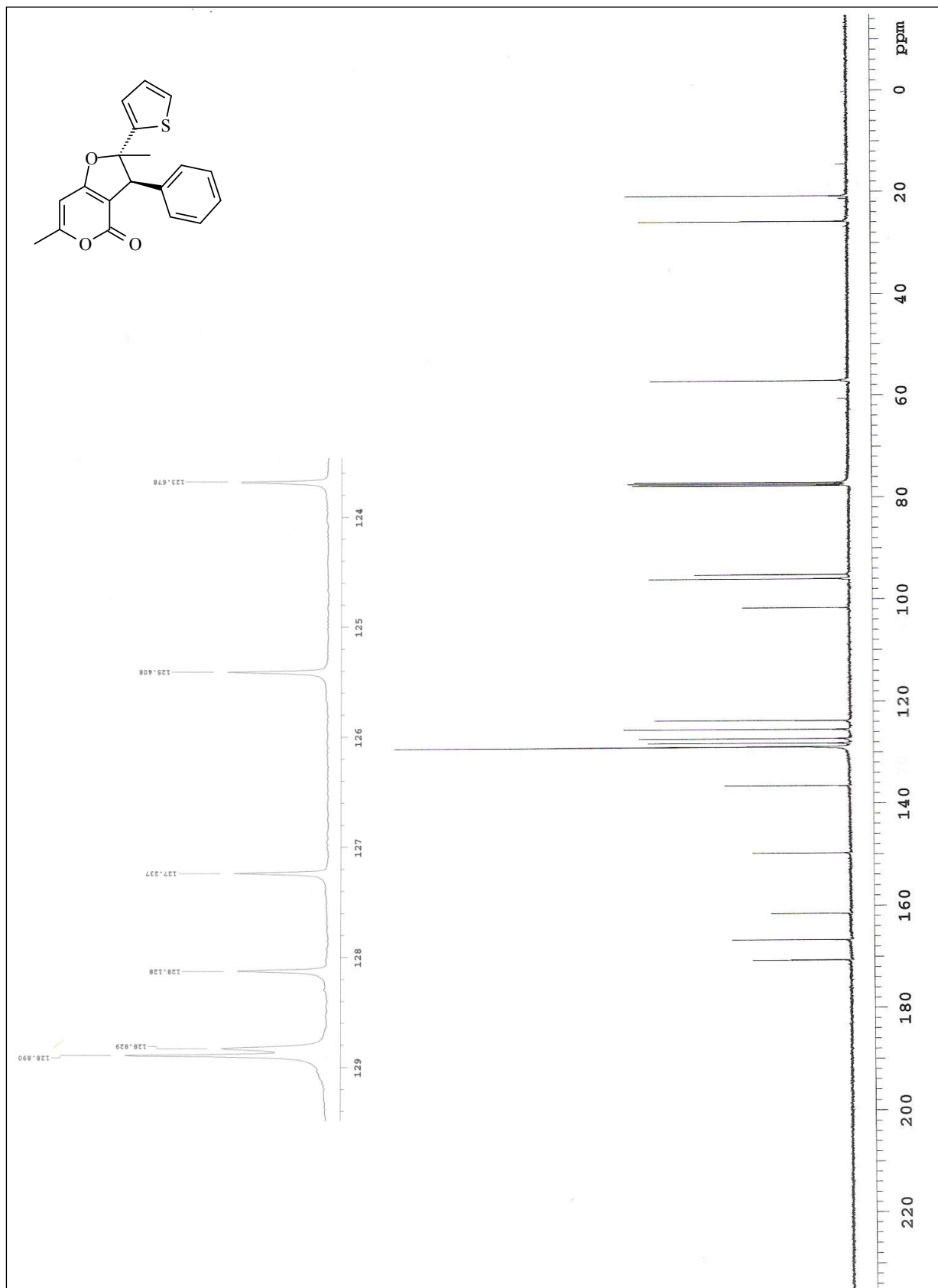
3.36 ^{13}C -NMR spectra of 37



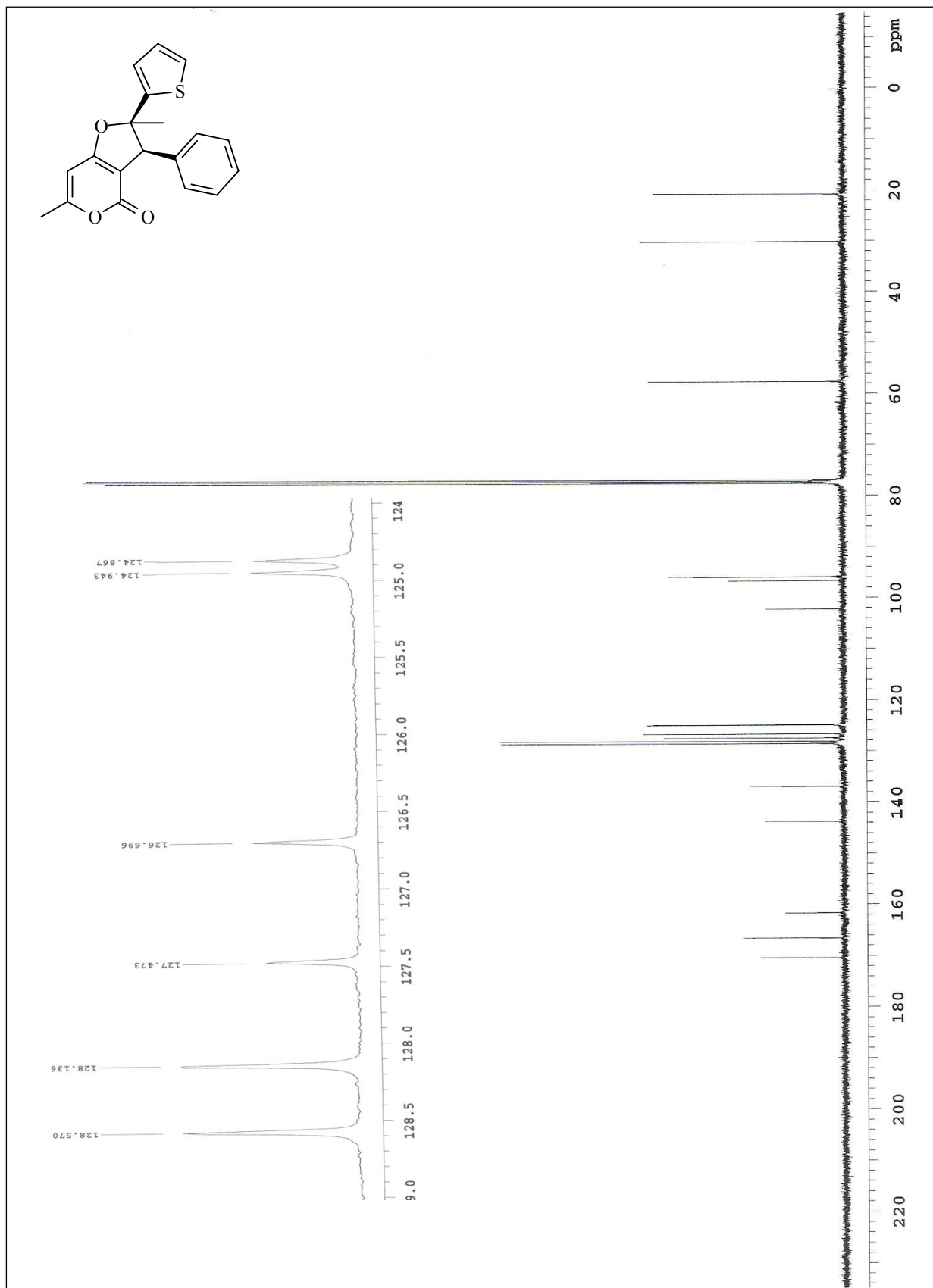
3.37 ^{13}C -NMR spectra of **38**



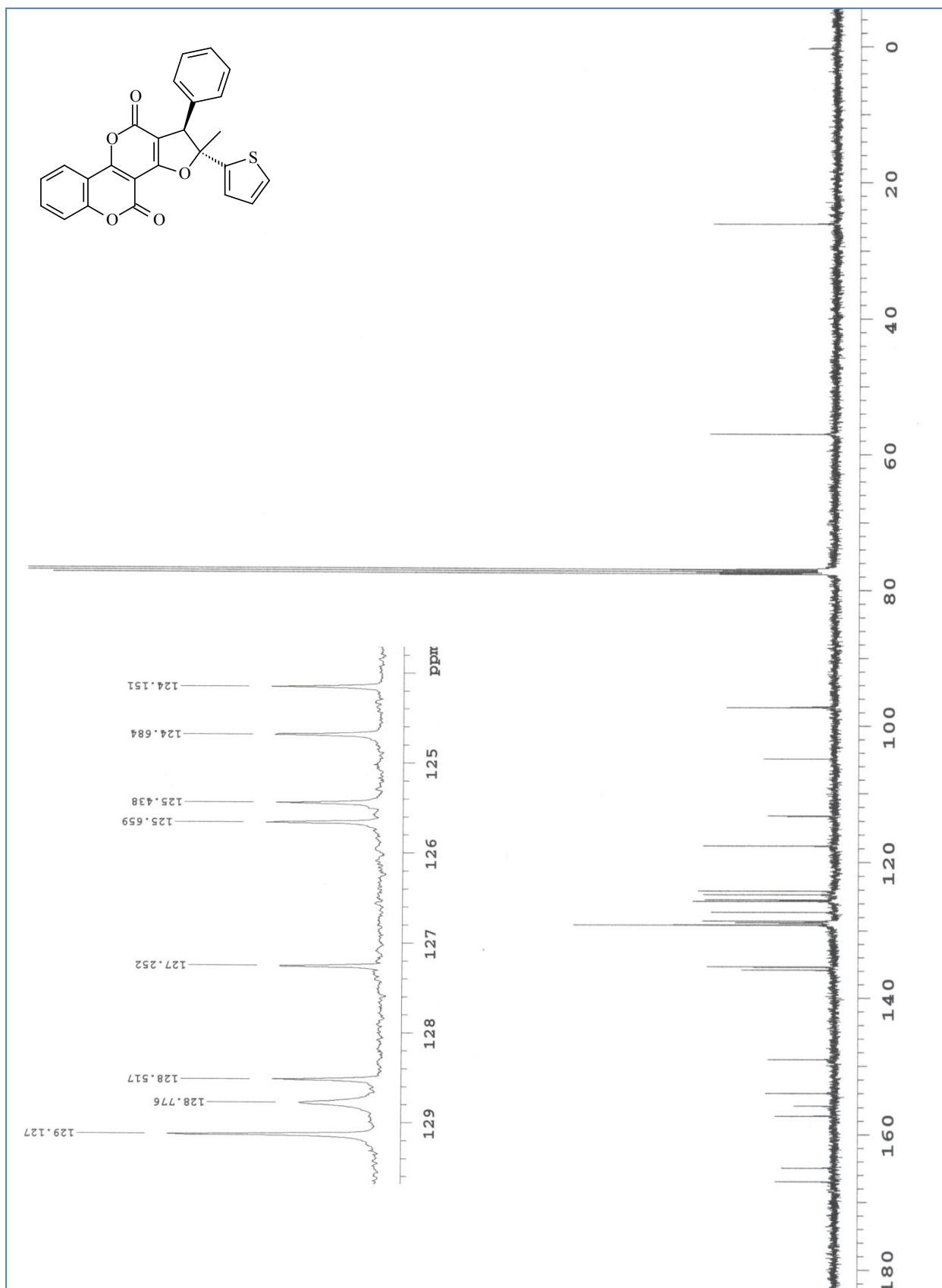
3.38 ^{13}C -NMR spectra of **39**



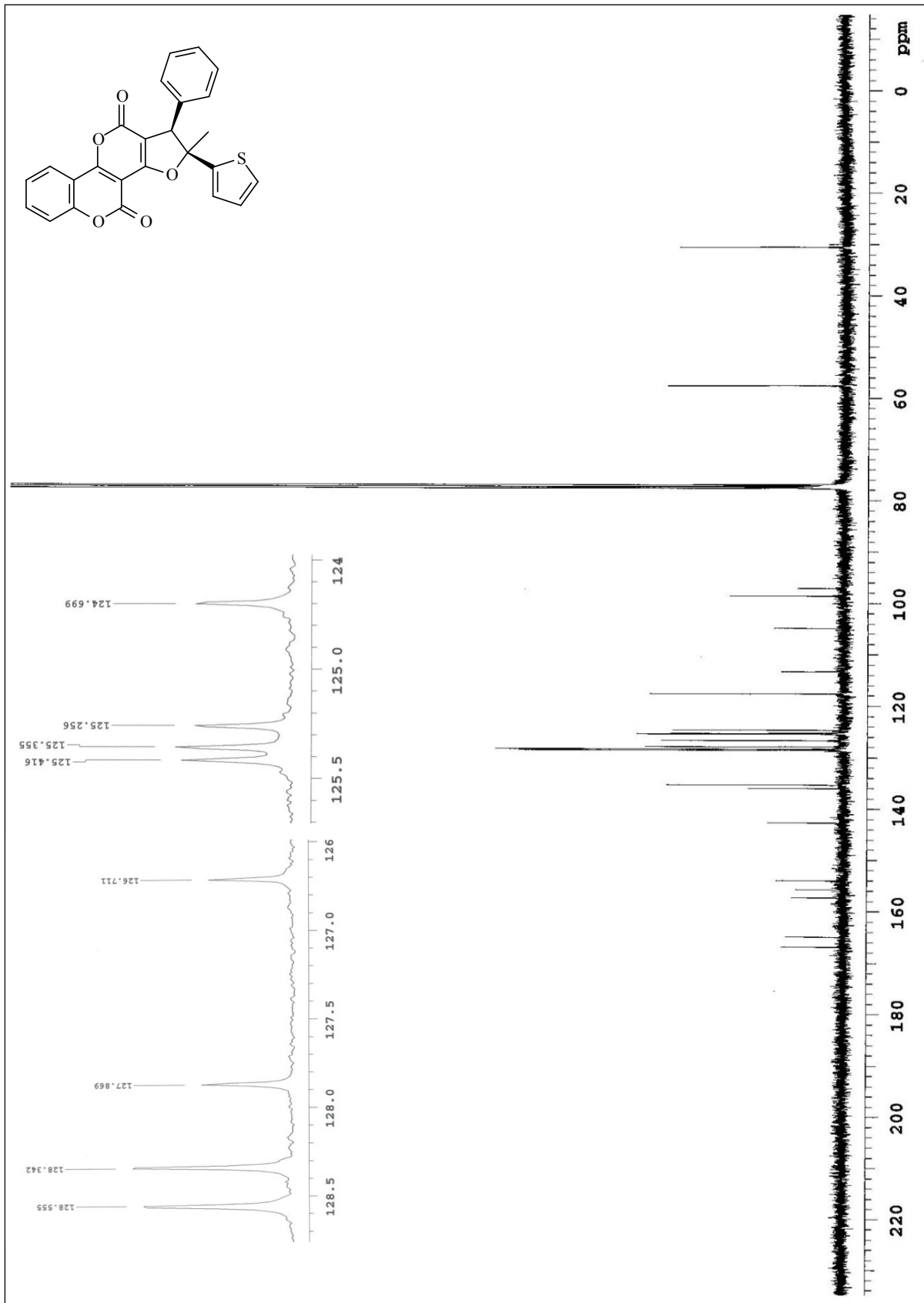
3.39 ^{13}C -NMR spectra of **40**



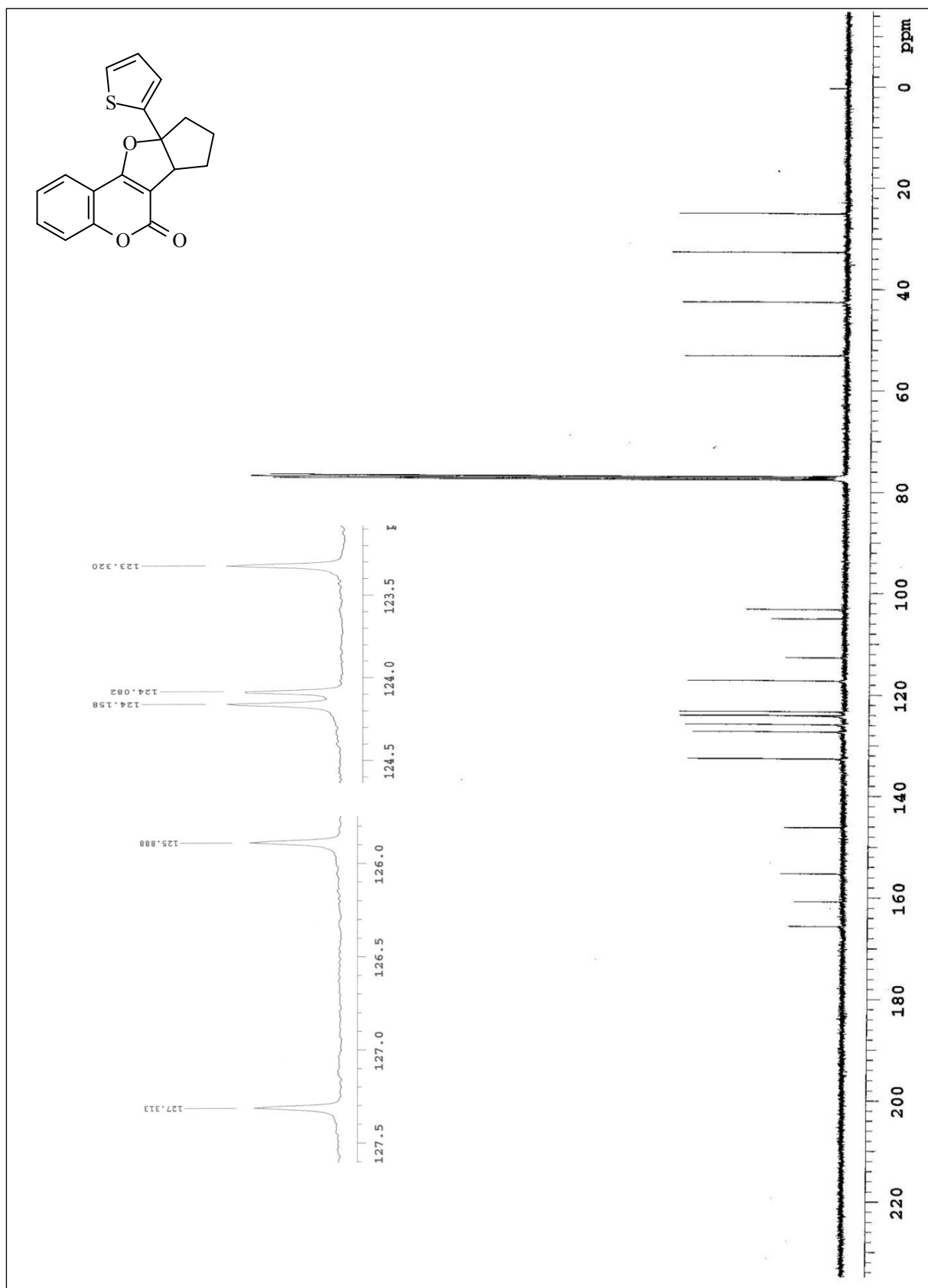
3.40 ^{13}C -NMR spectra of **41**



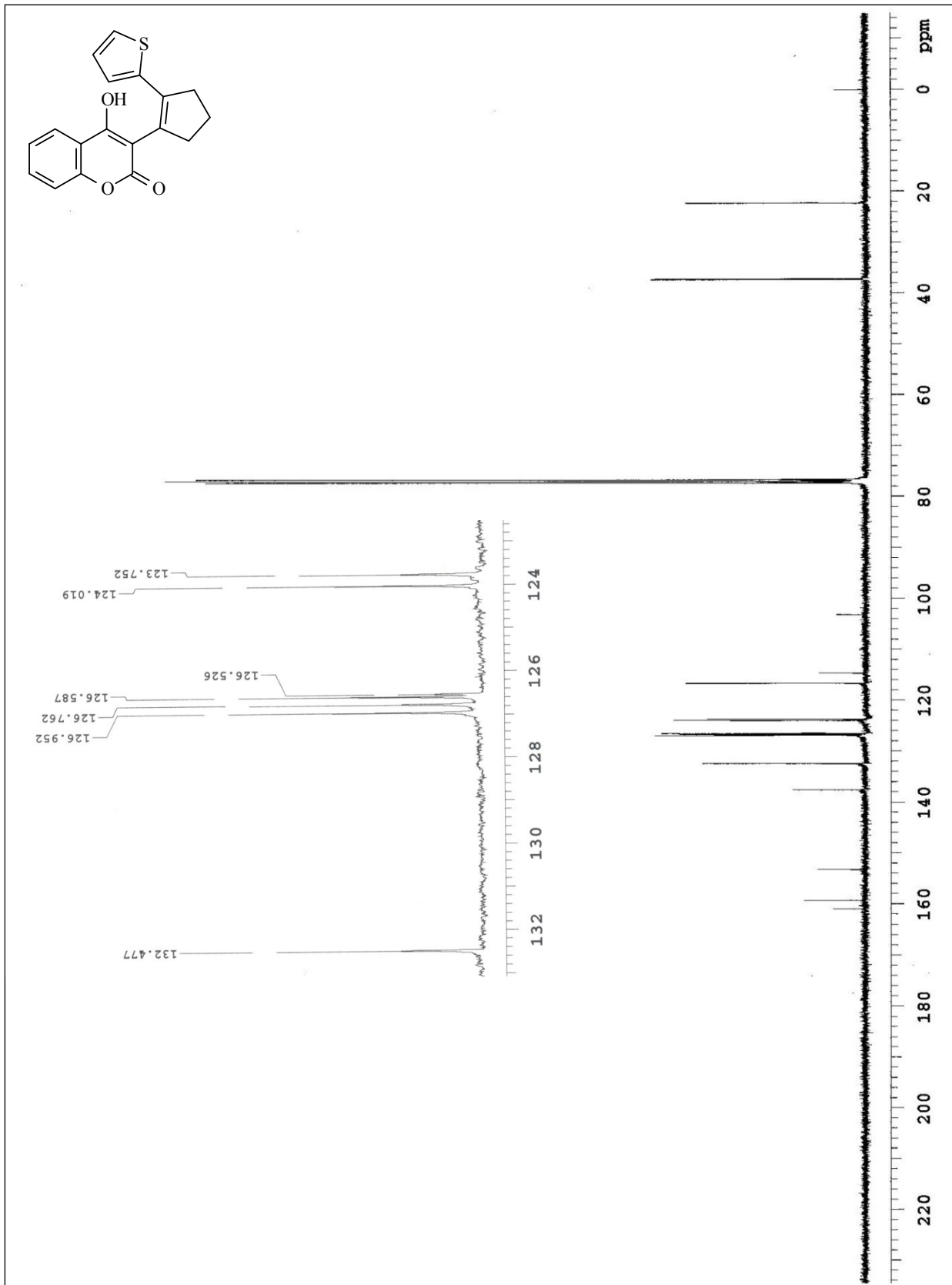
3.41 $^{13}\text{C-NMR}$ spectra of **42**



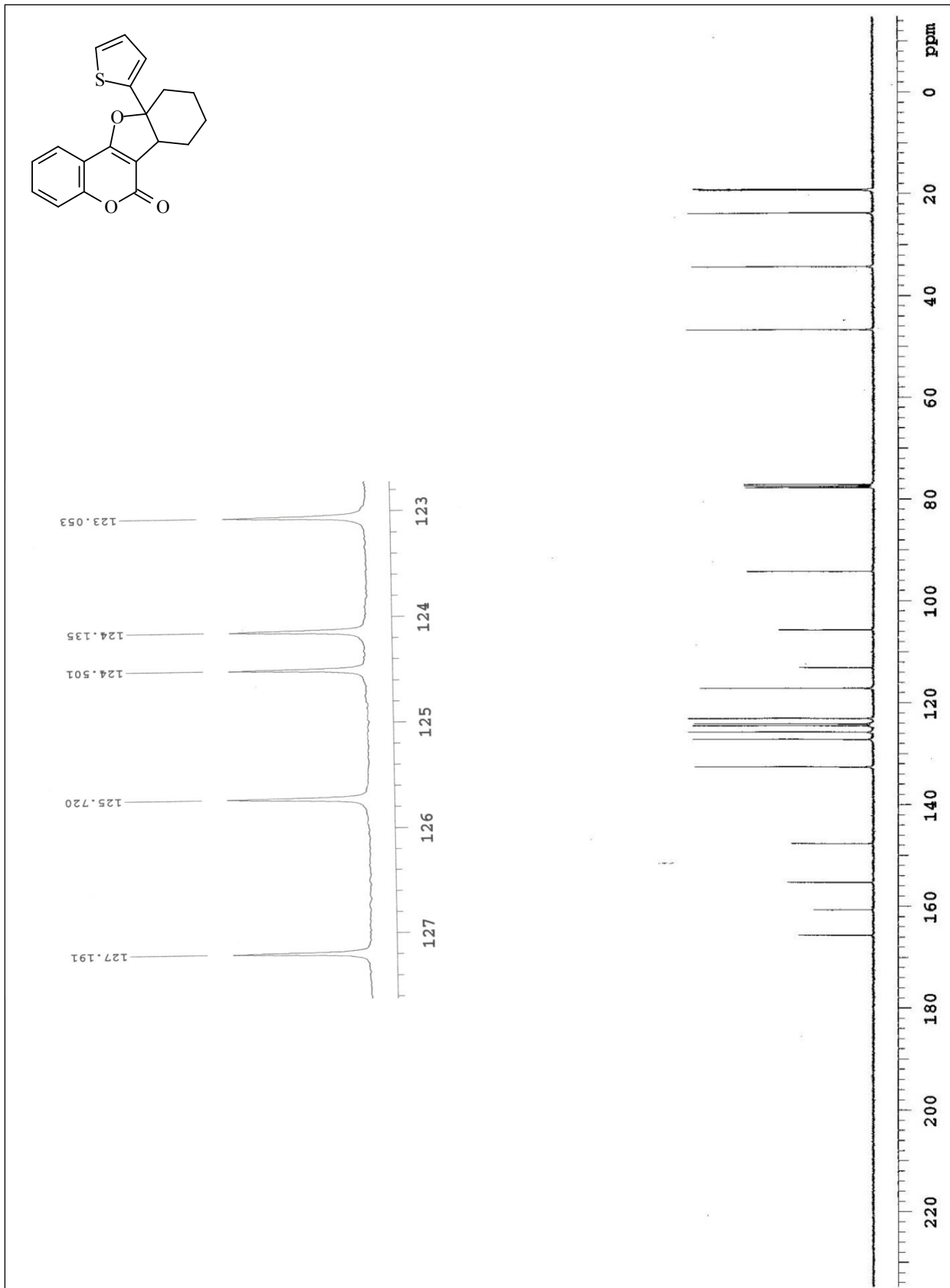
3.42 ^{13}C -NMR spectra of **43**



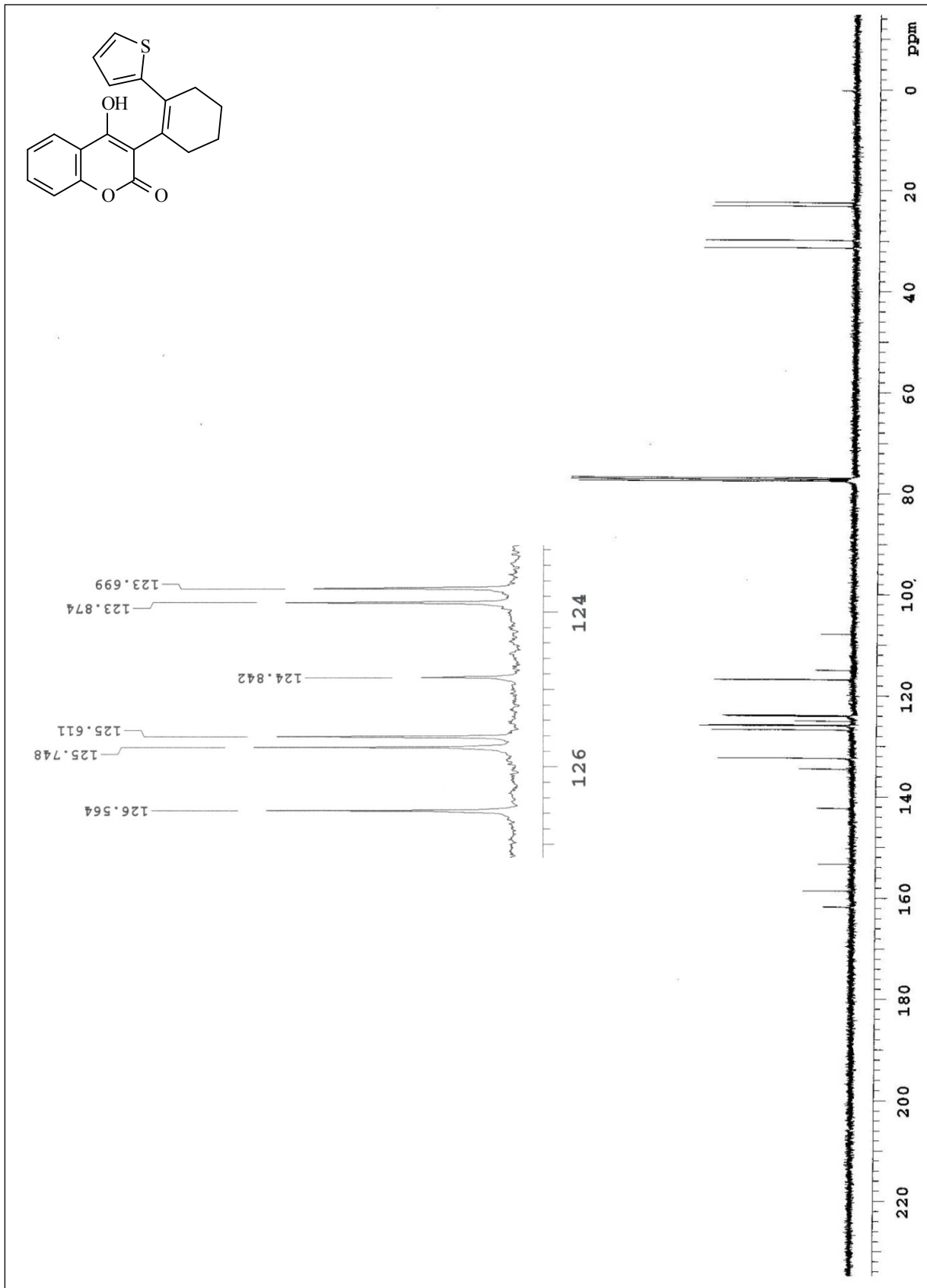
3.43 ^{13}C -NMR spectra of **49**



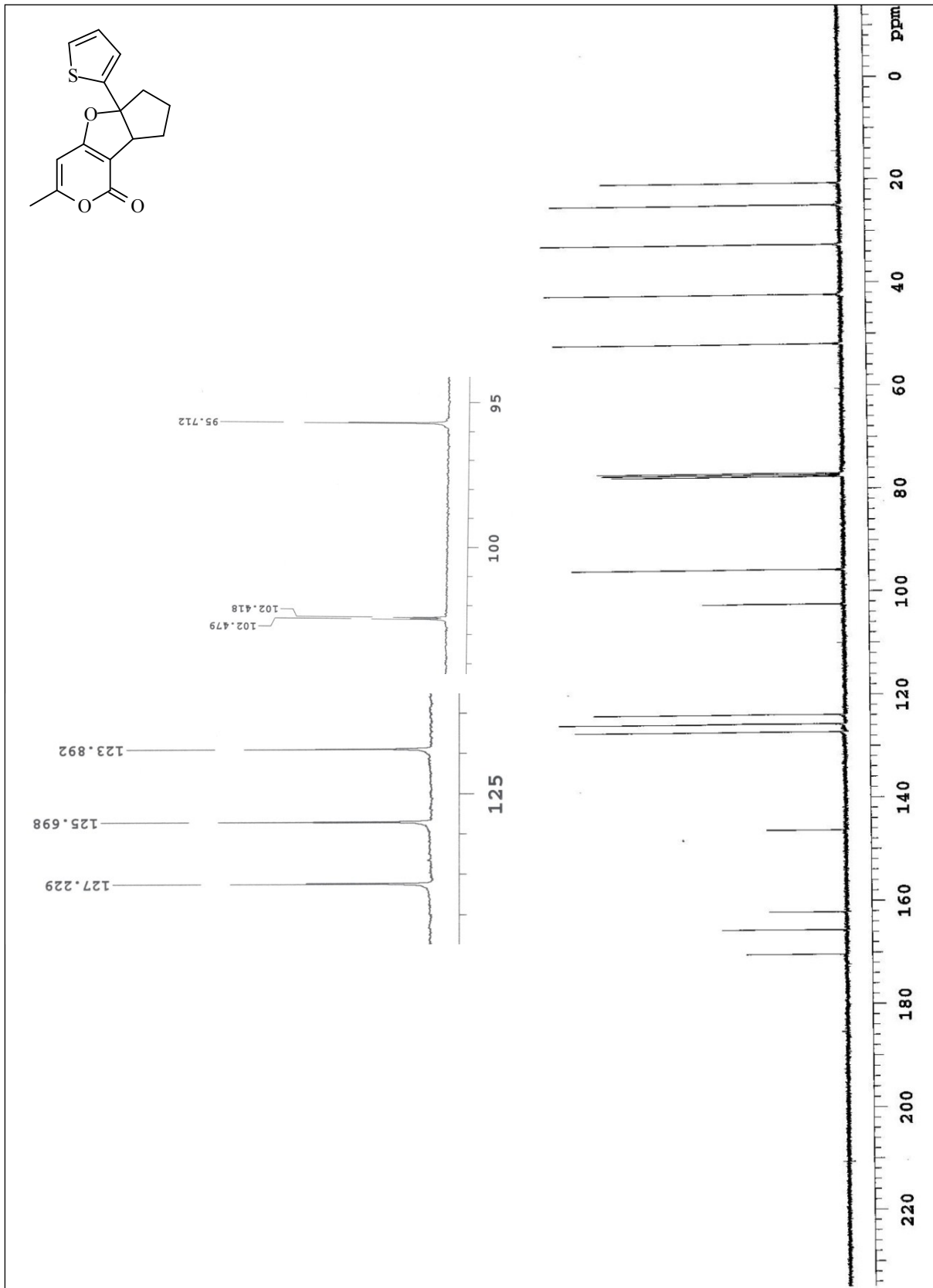
3.44 ^{13}C -NMR spectra of 44



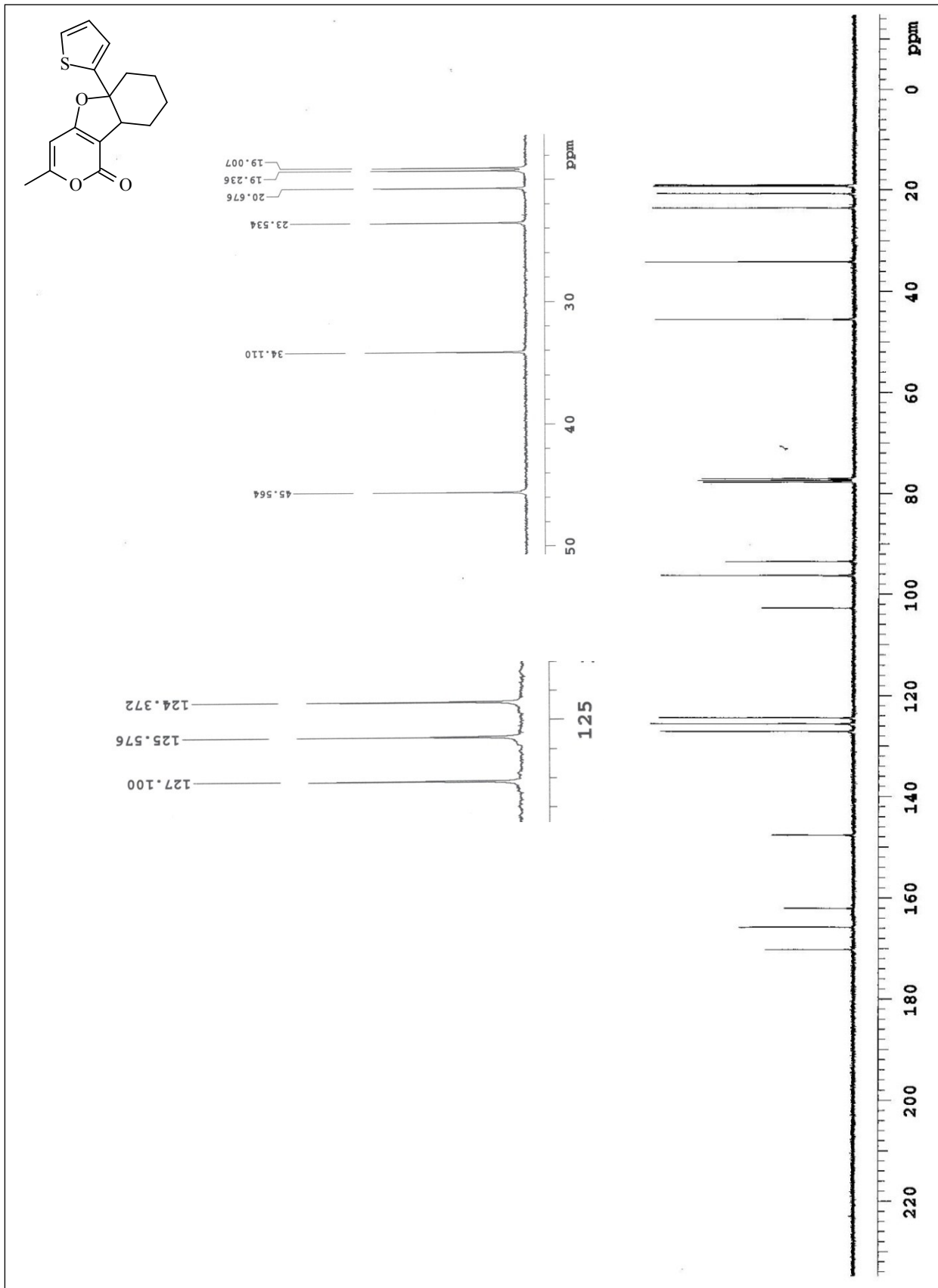
3.45 ^{13}C -NMR spectra of **50**



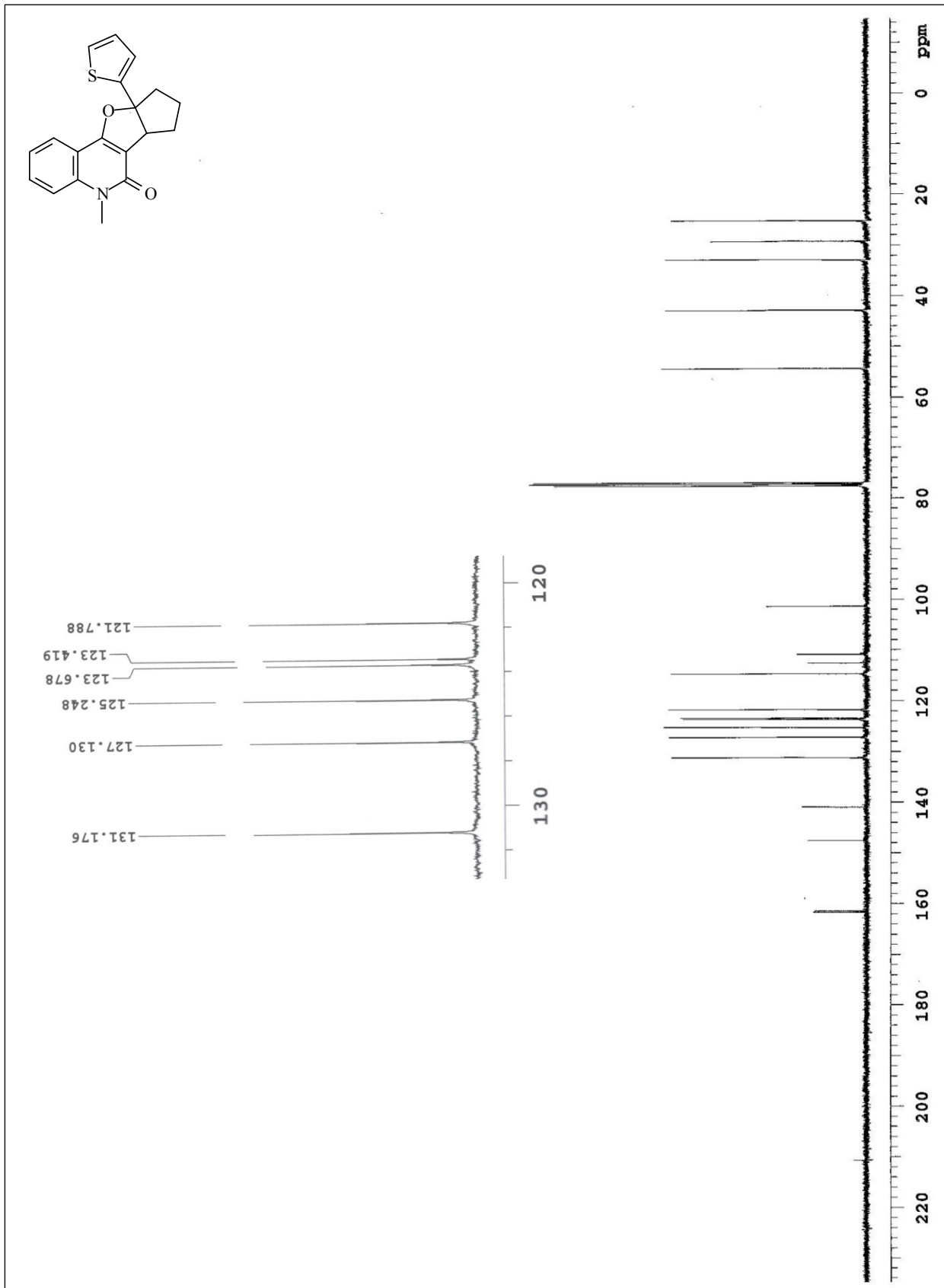
3.46 ^{13}C -NMR spectra of **45**



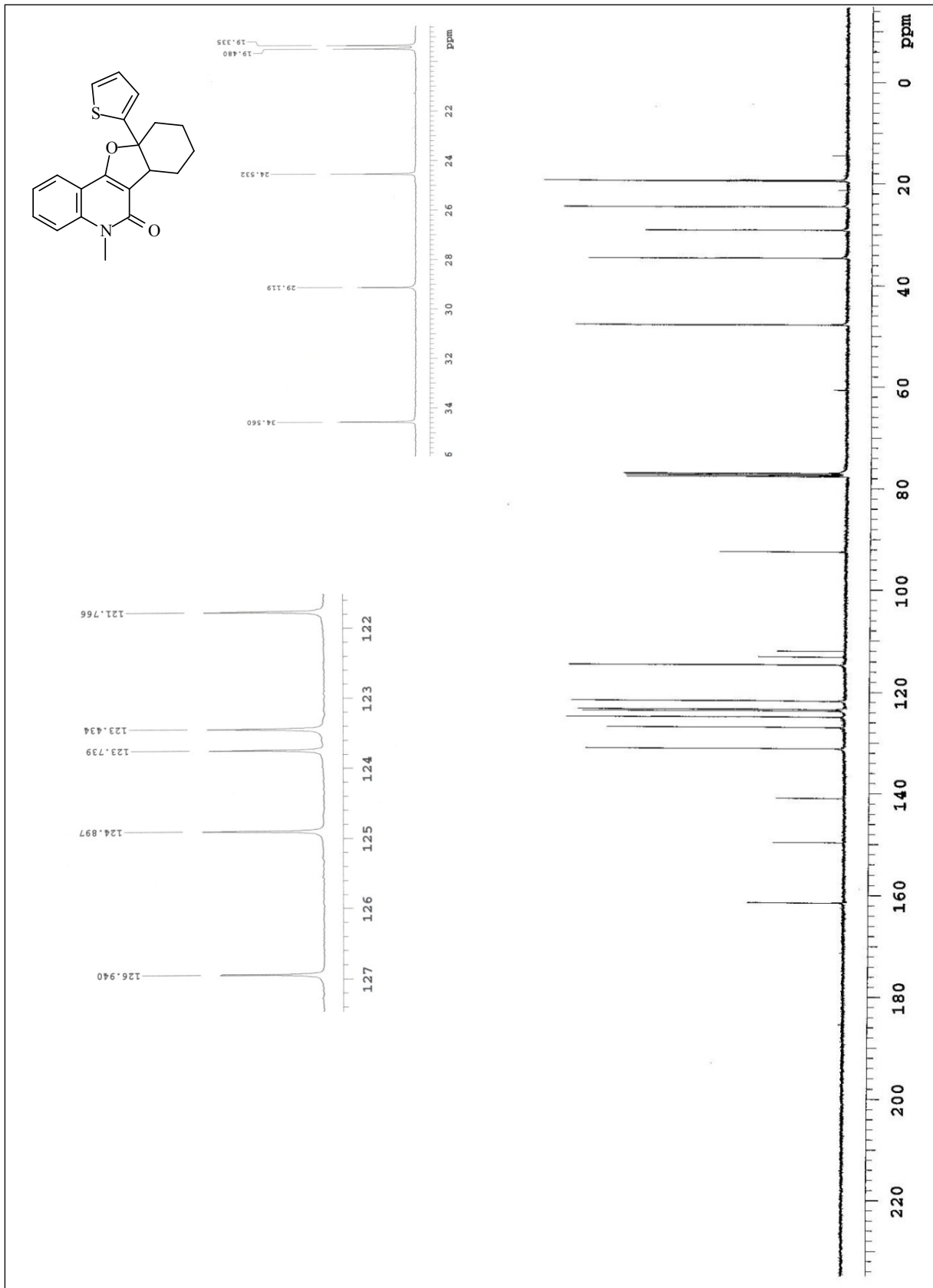
3.47 $^{13}\text{C-NMR}$ spectra of 46



3.48 $^{13}\text{C-NMR}$ spectra of 47

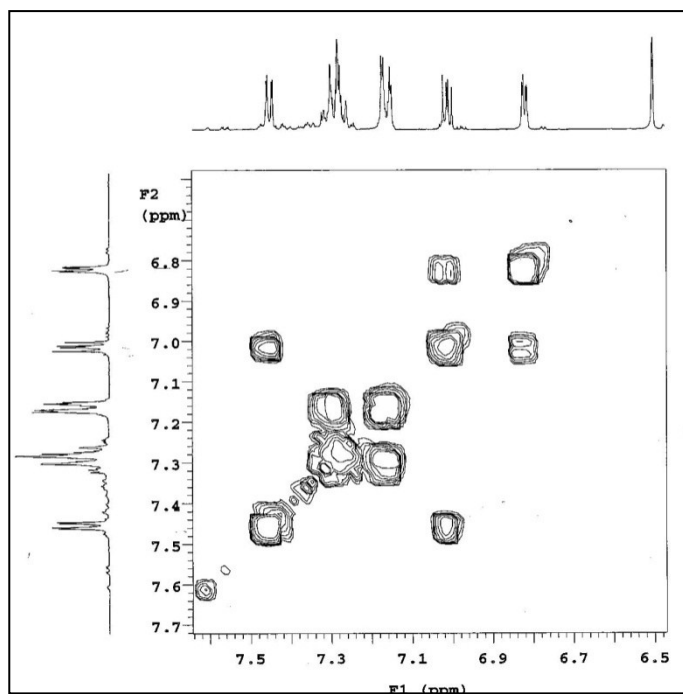
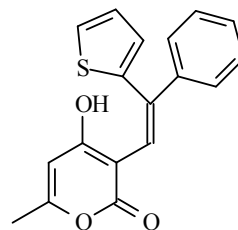
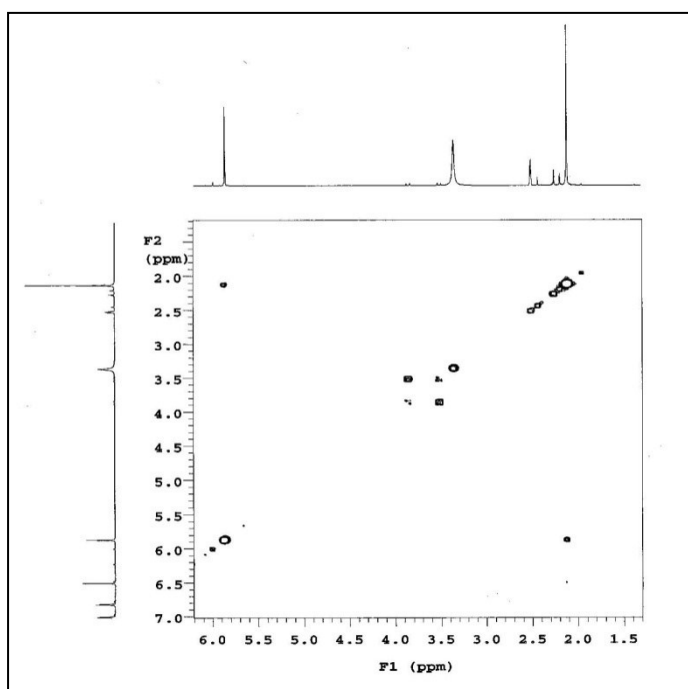


3.49 ^{13}C -NMR spectra of 48



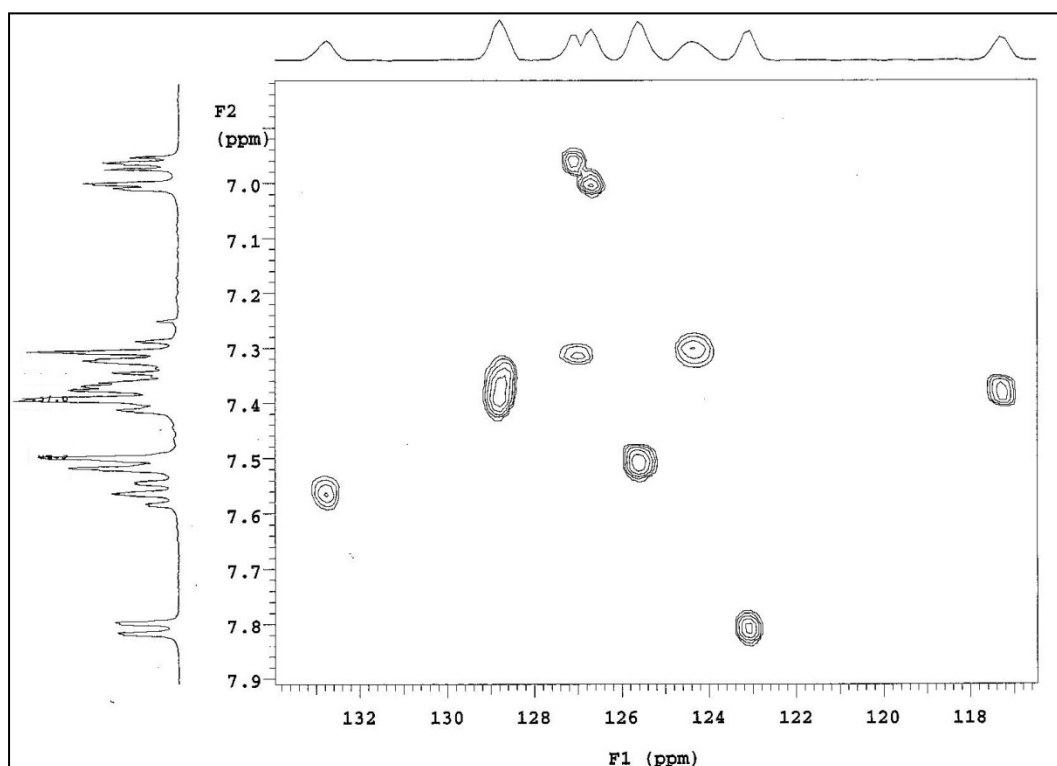
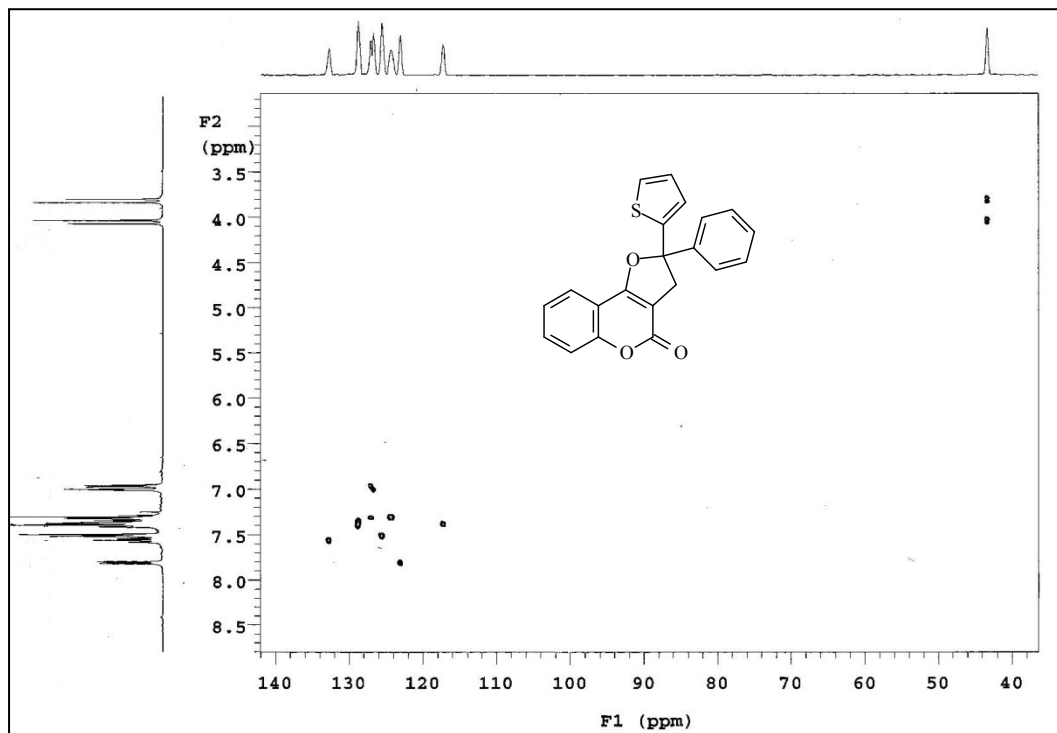
4. COSY Spectra of Compound

4.1 COSY spectra of 16

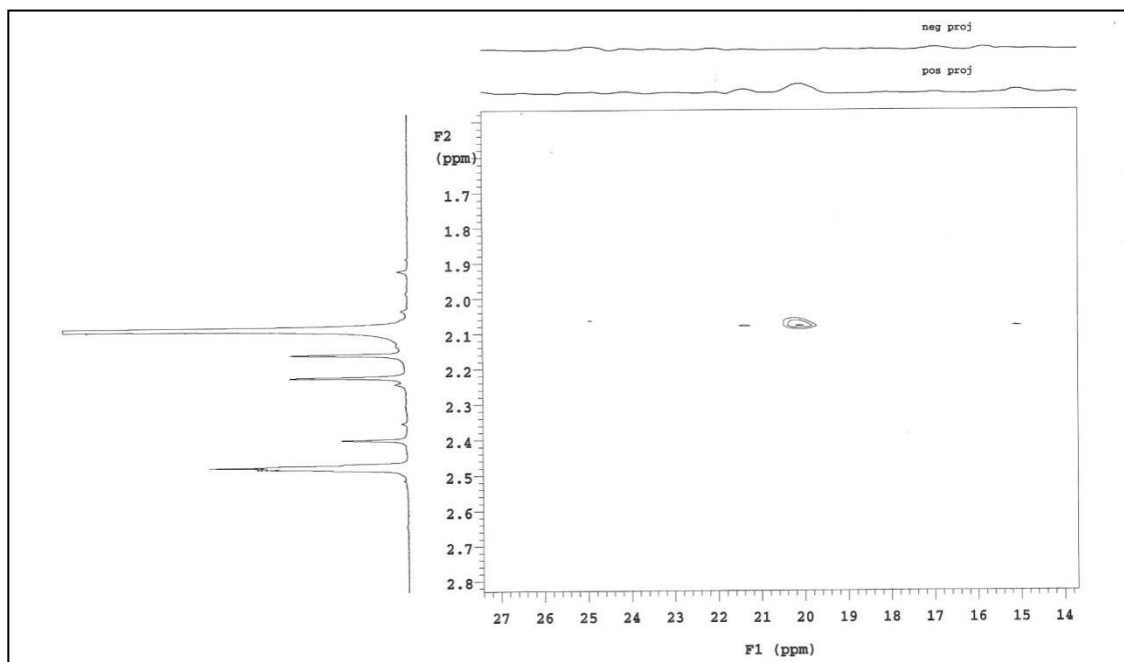
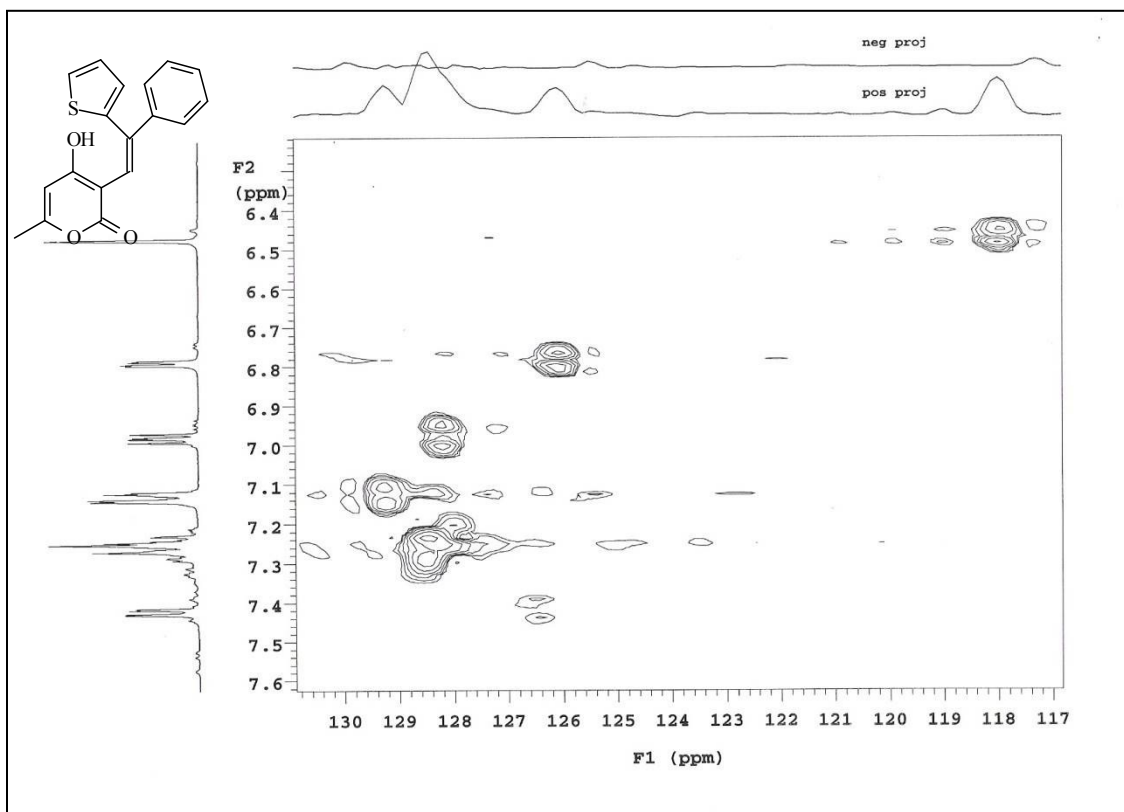


5. HSQC Spectra of Compounds

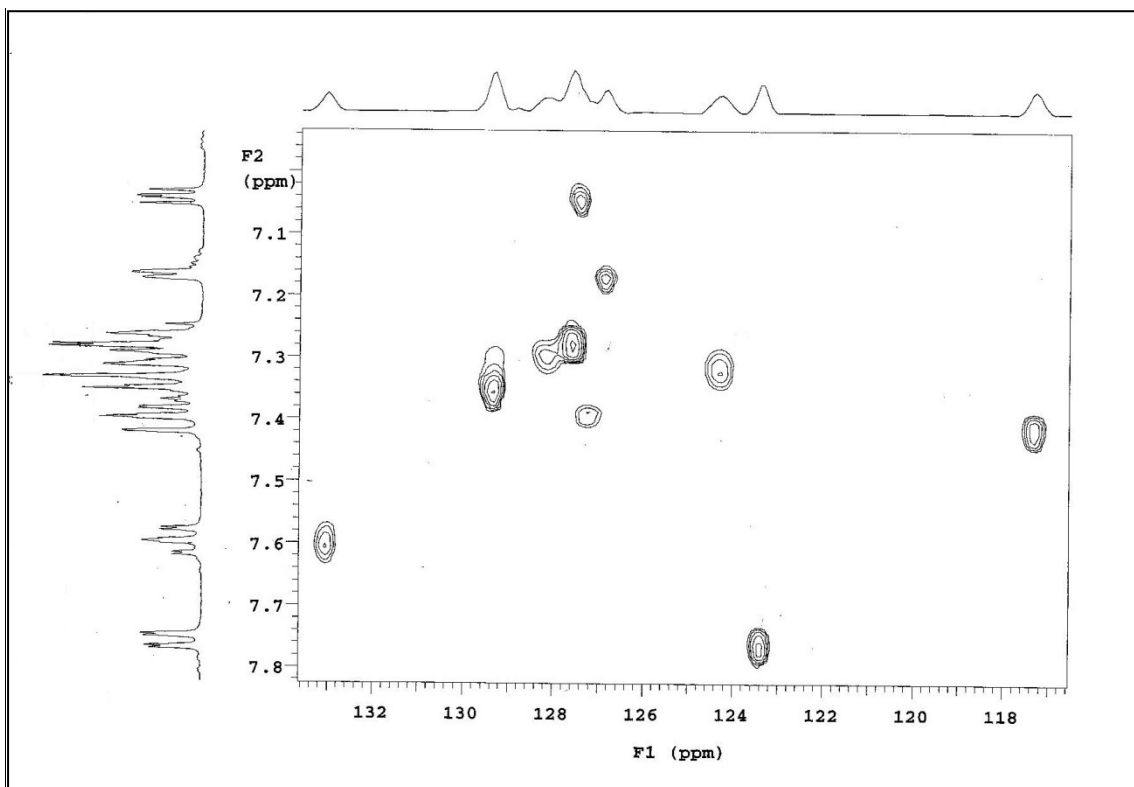
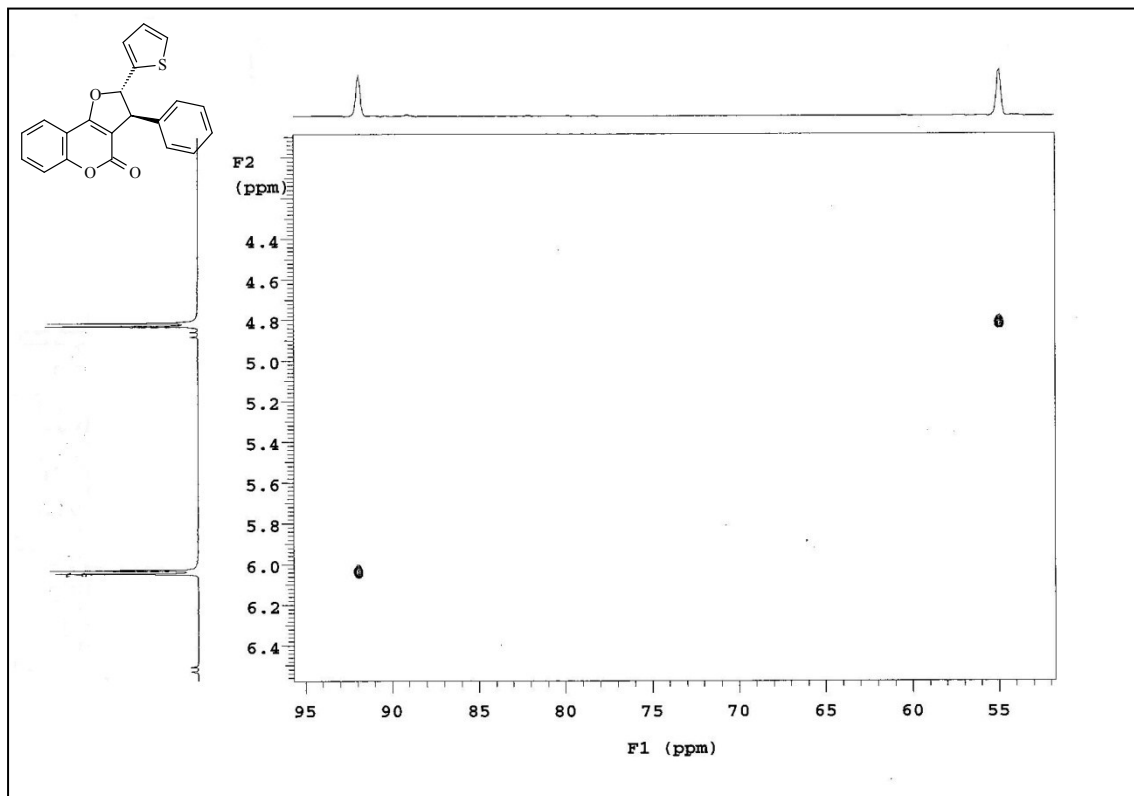
5.1 HSQC spectra of 3



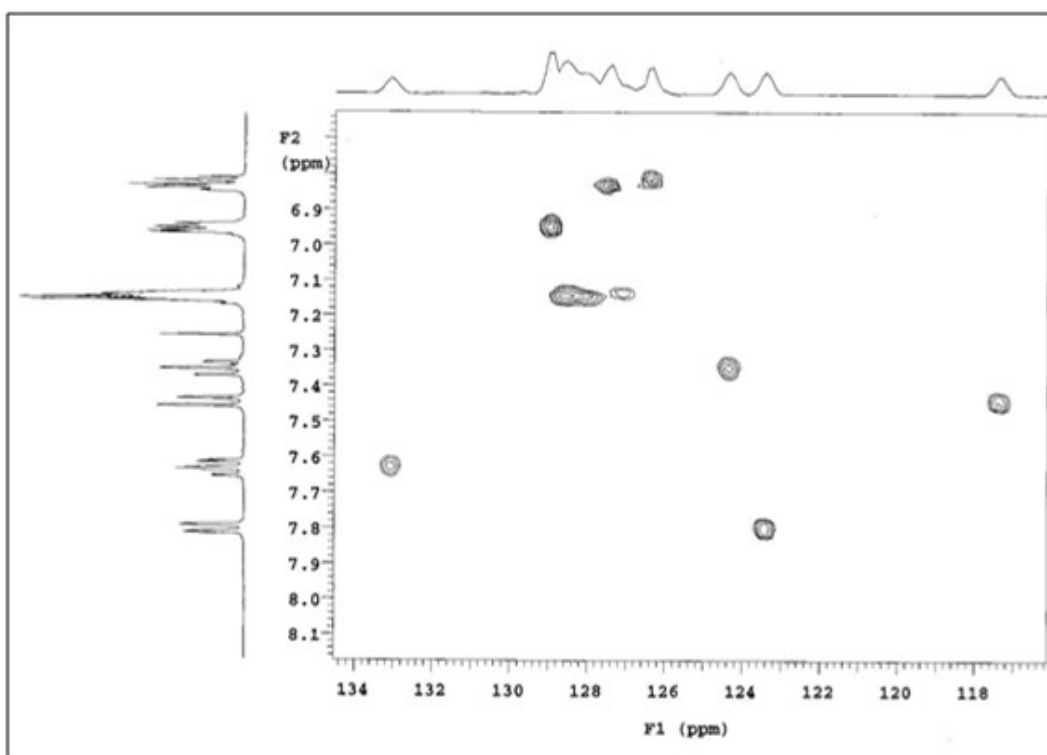
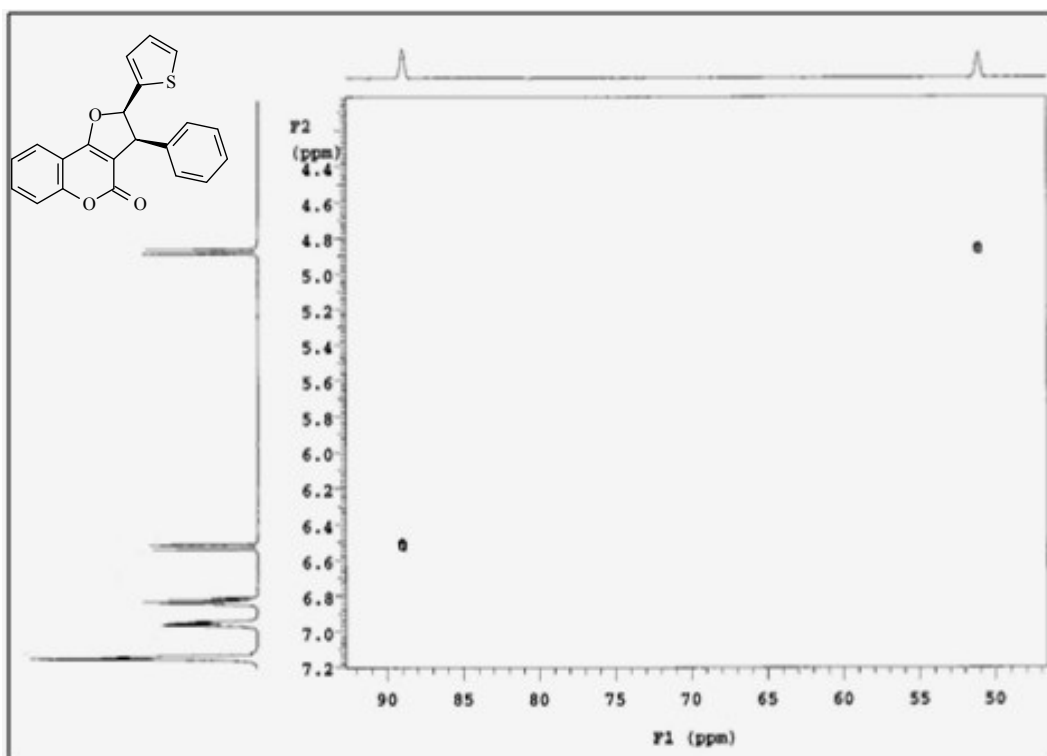
5.2 HSQC spectra of 16



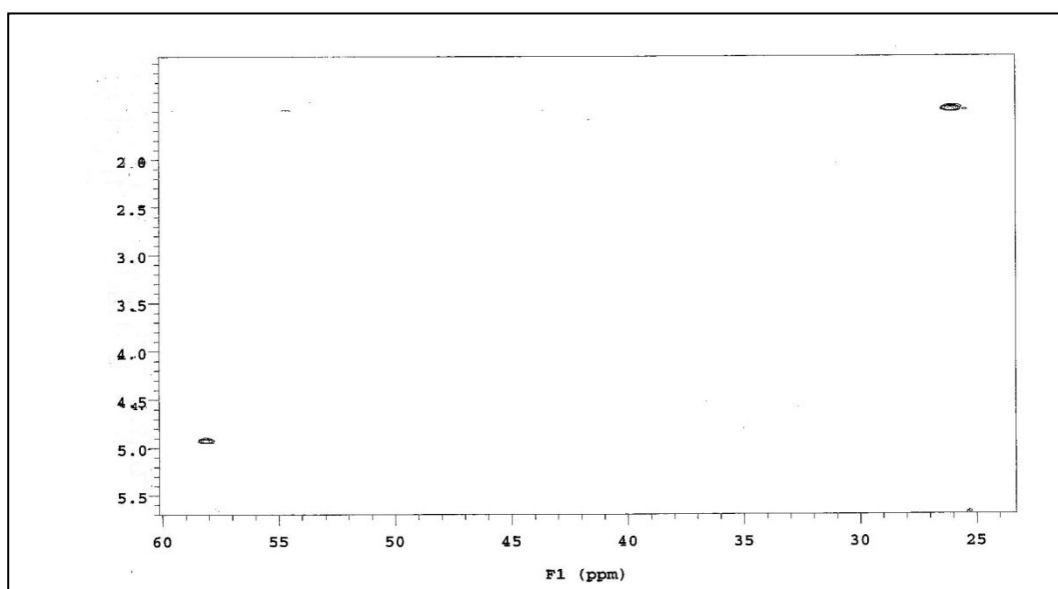
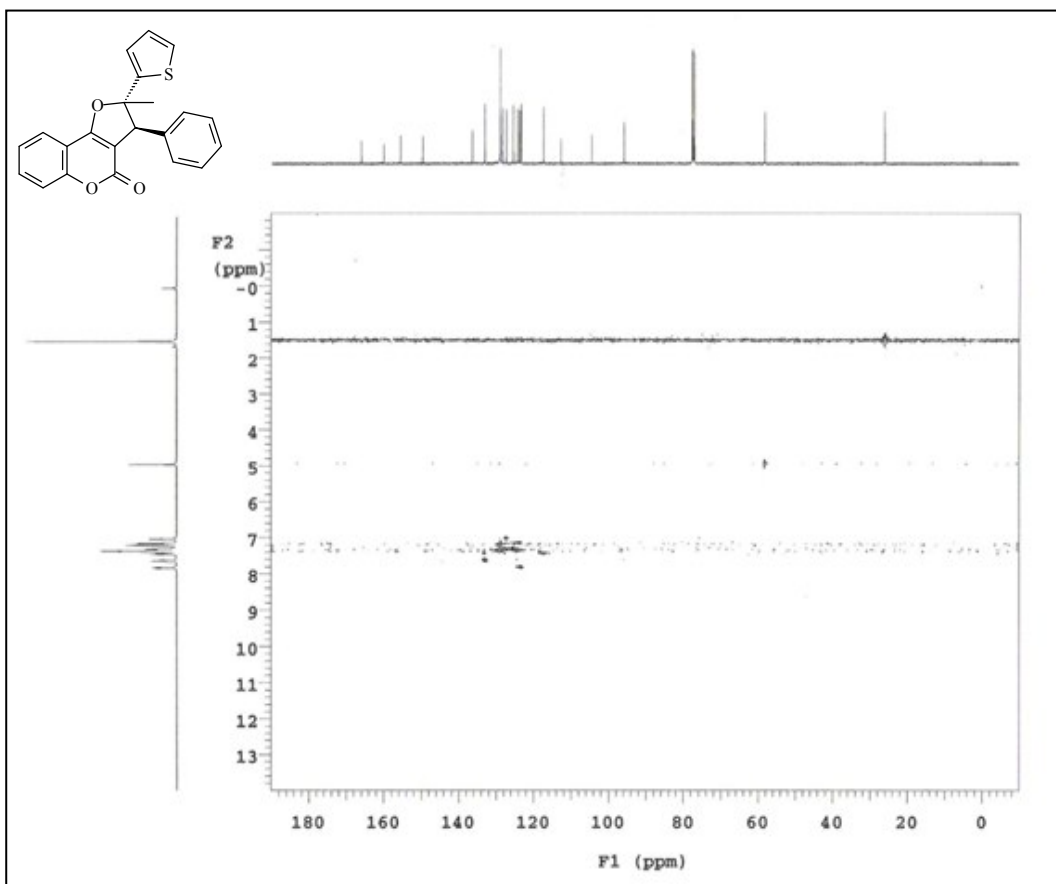
5.3 HSQC spectra of **35**



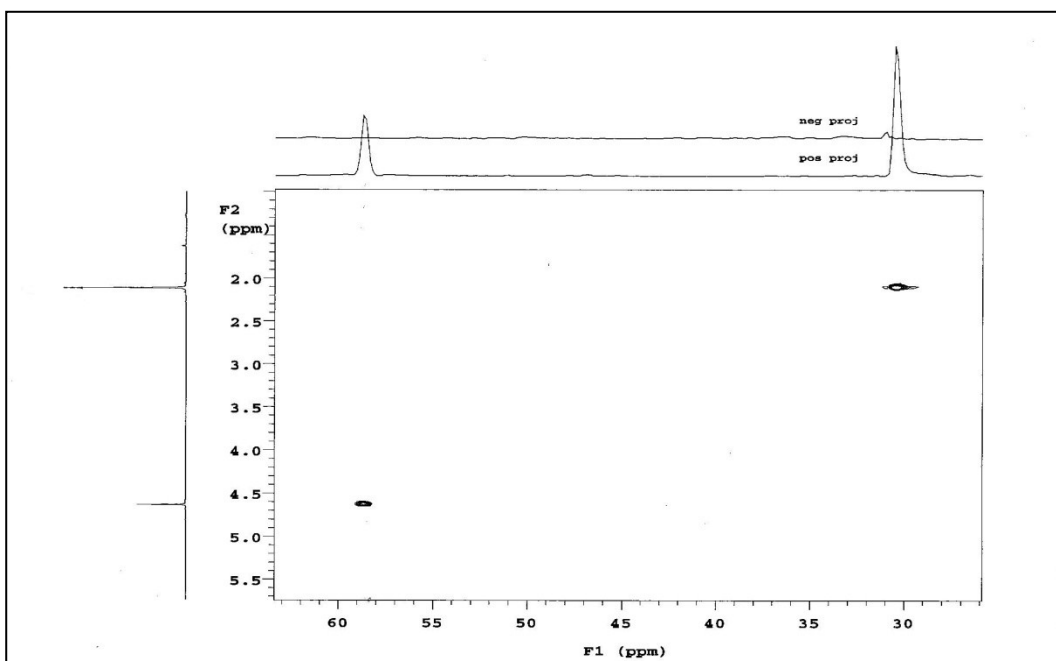
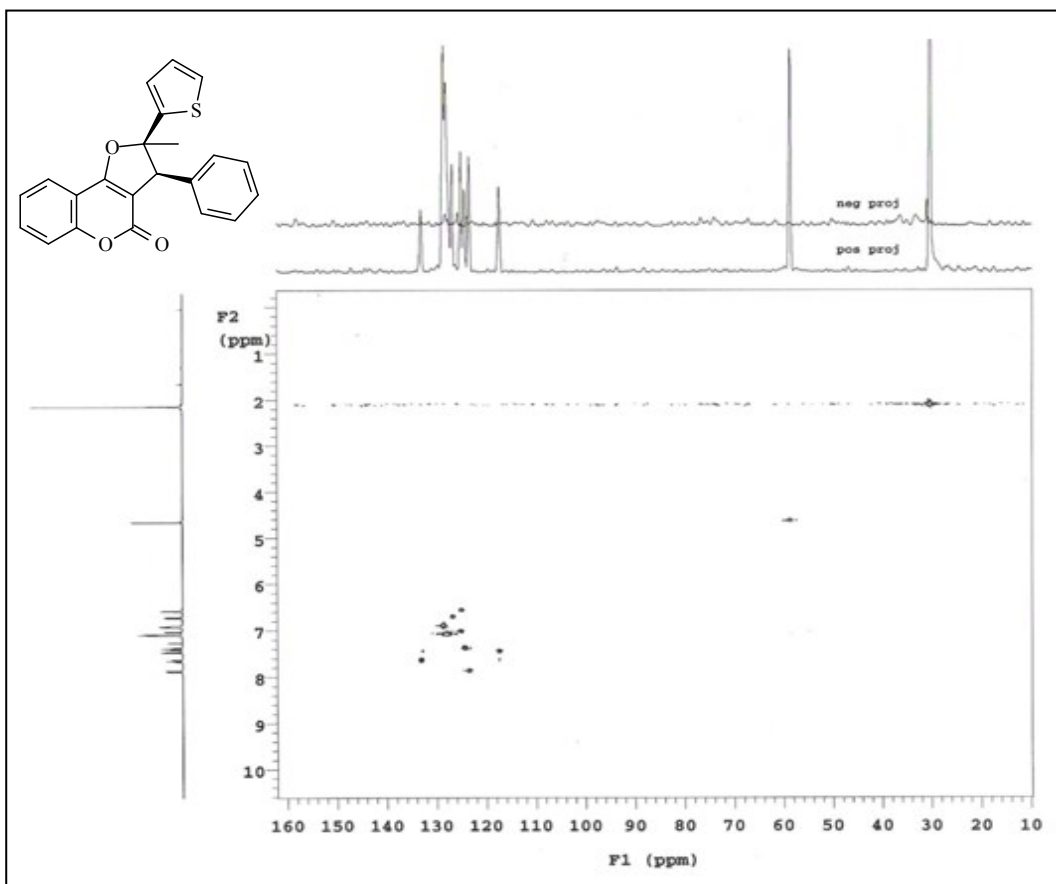
5.4 HSQC spectra of 36



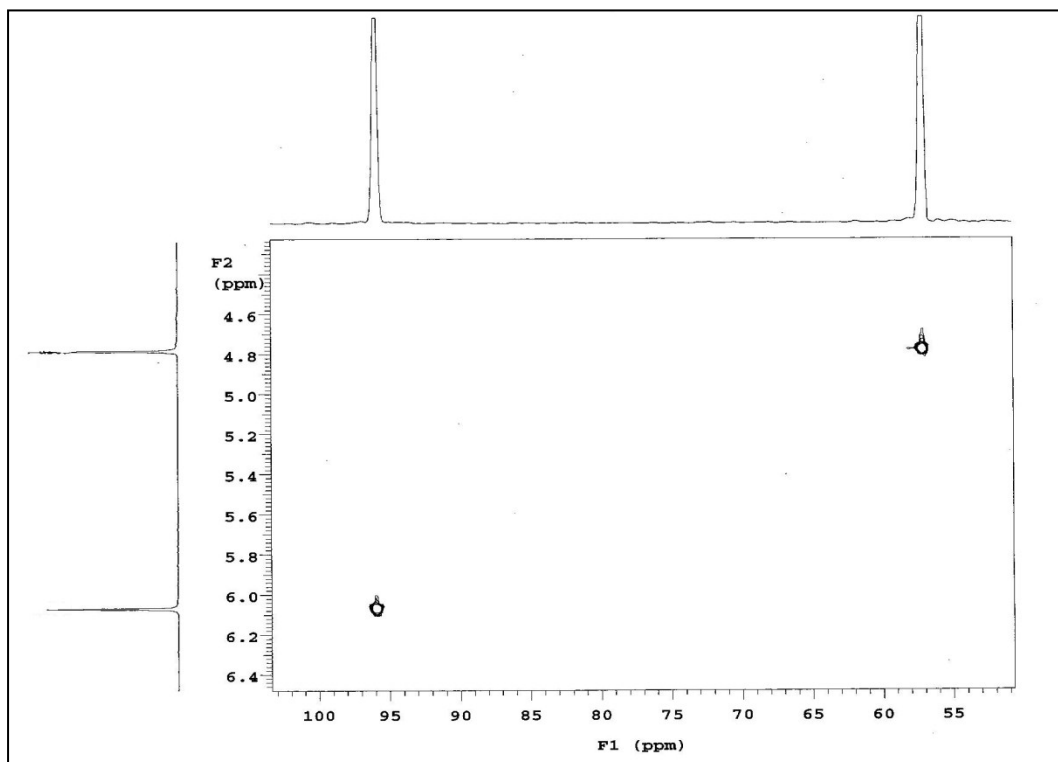
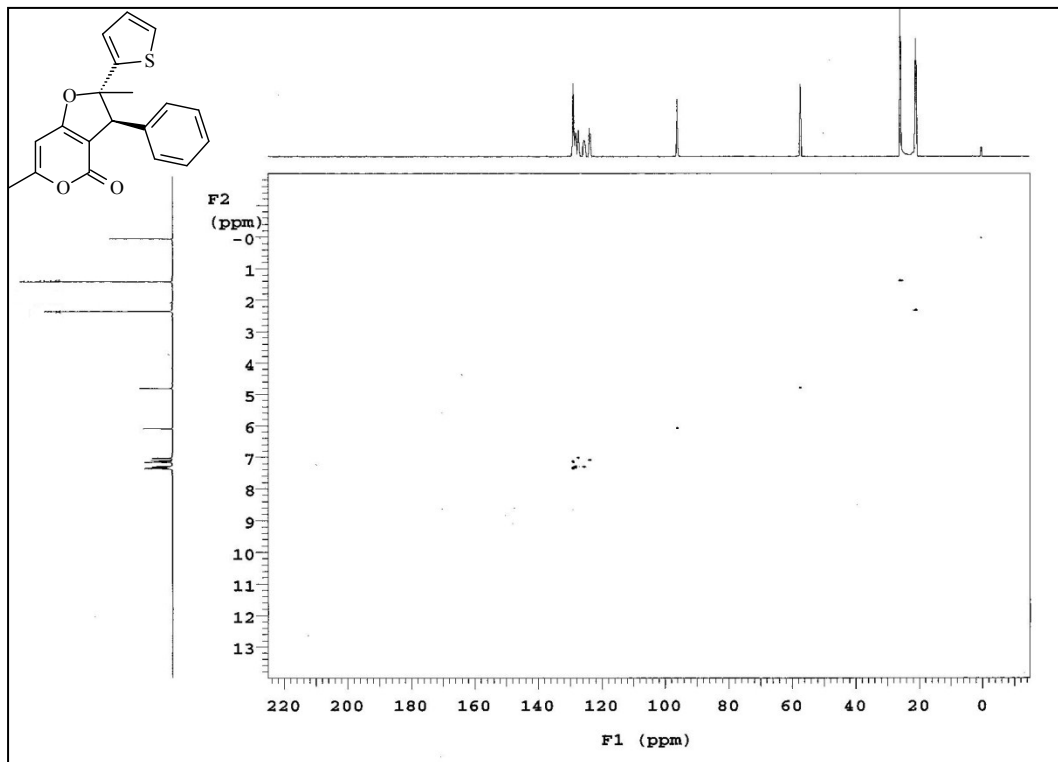
5.5 HSQC spectra of **37**



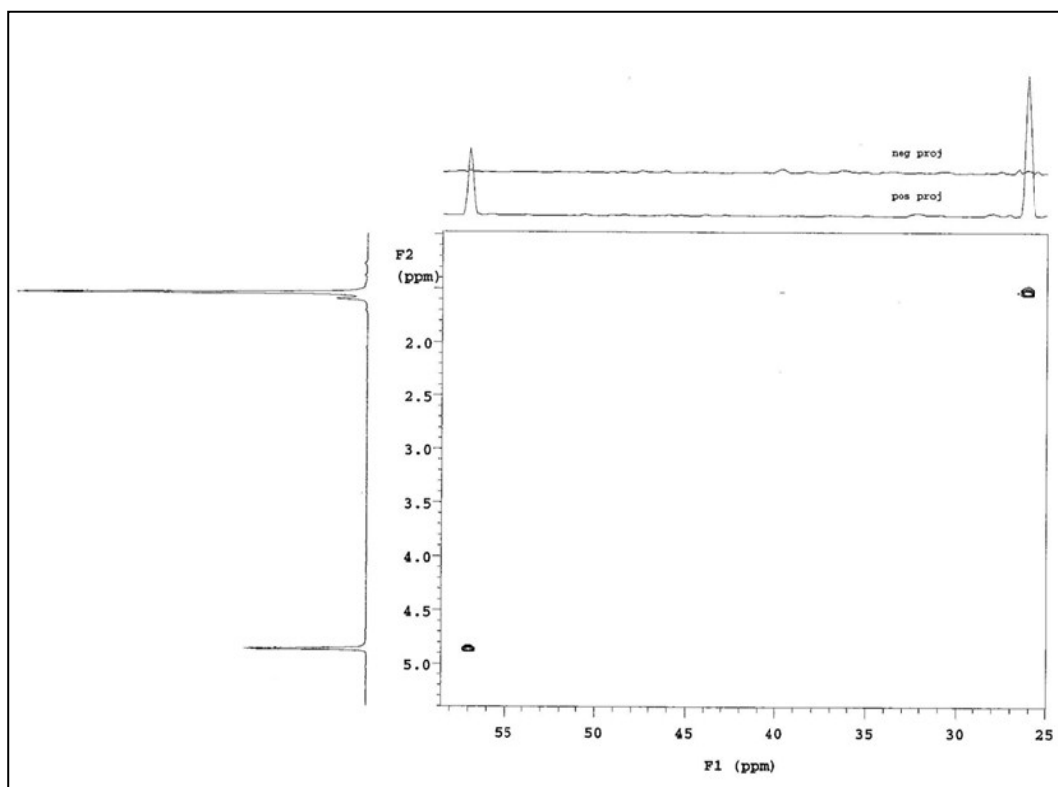
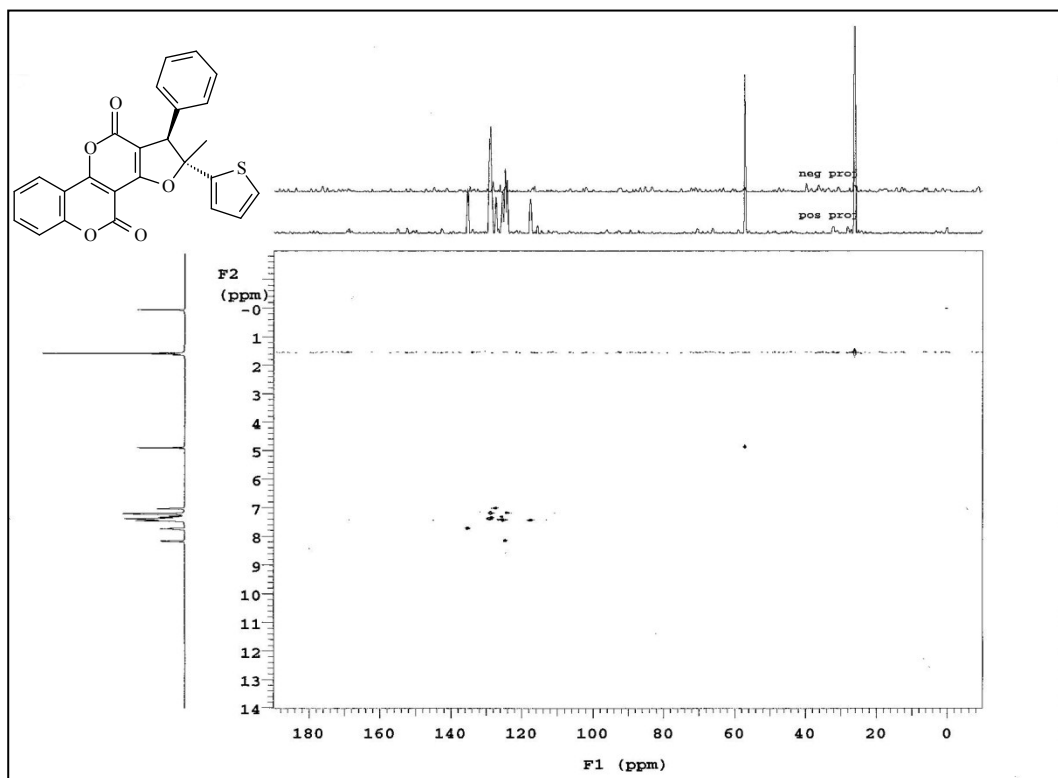
5.6 HSQC spectra of **38**



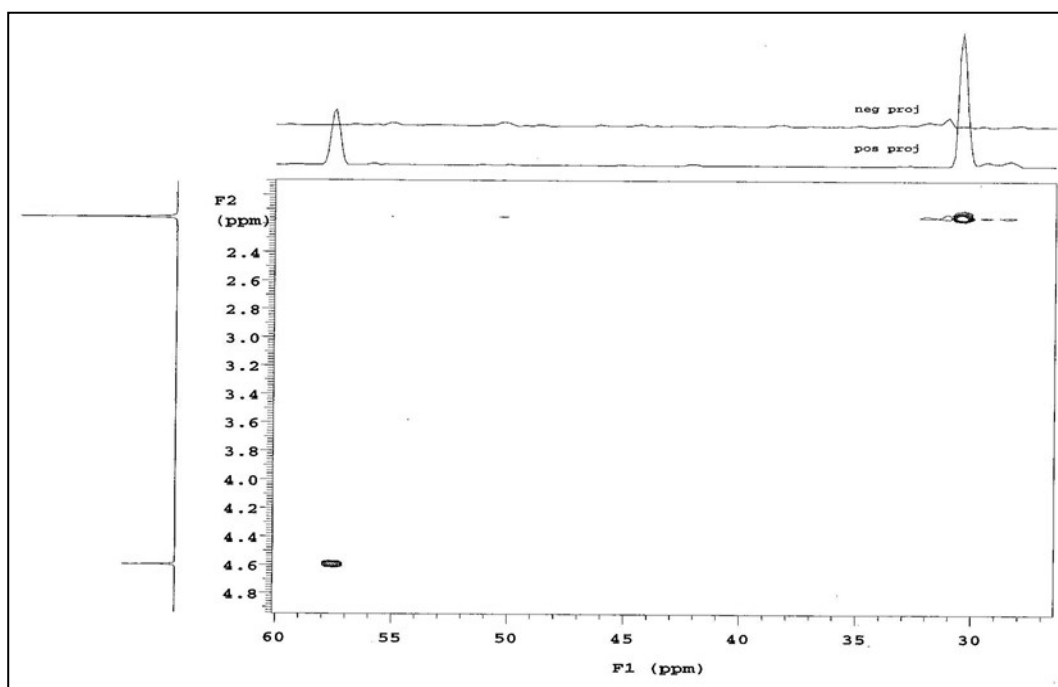
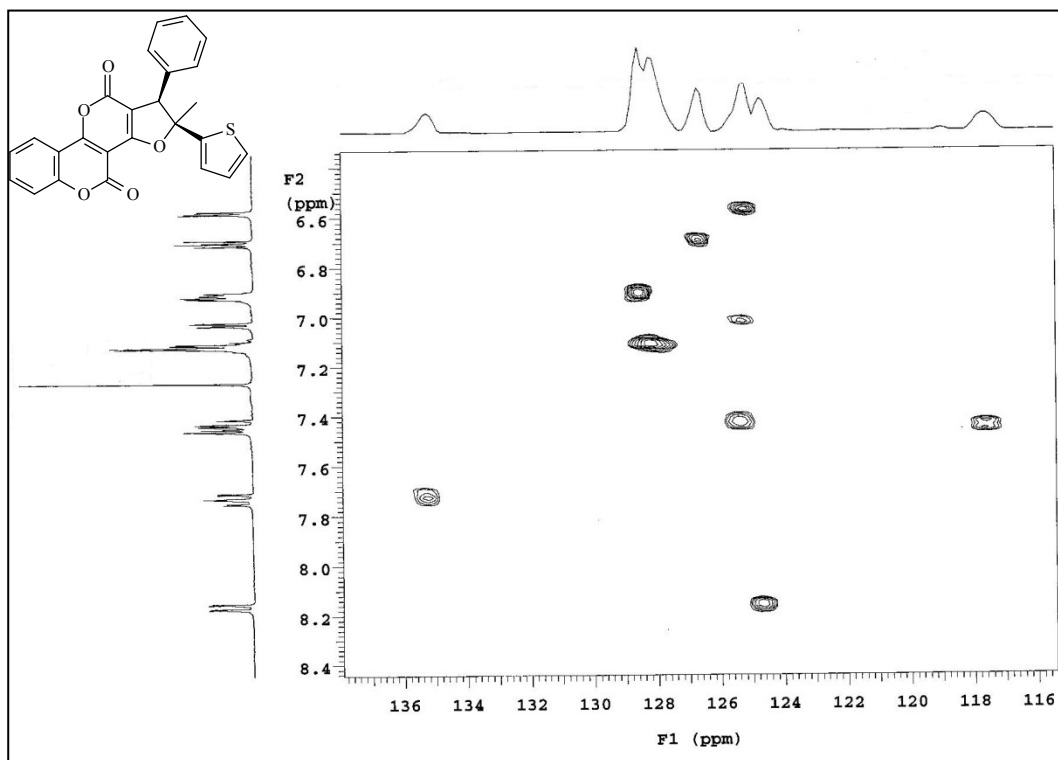
5.7 HSQC spectra of **39**



5.8 HSQC spectra of 41

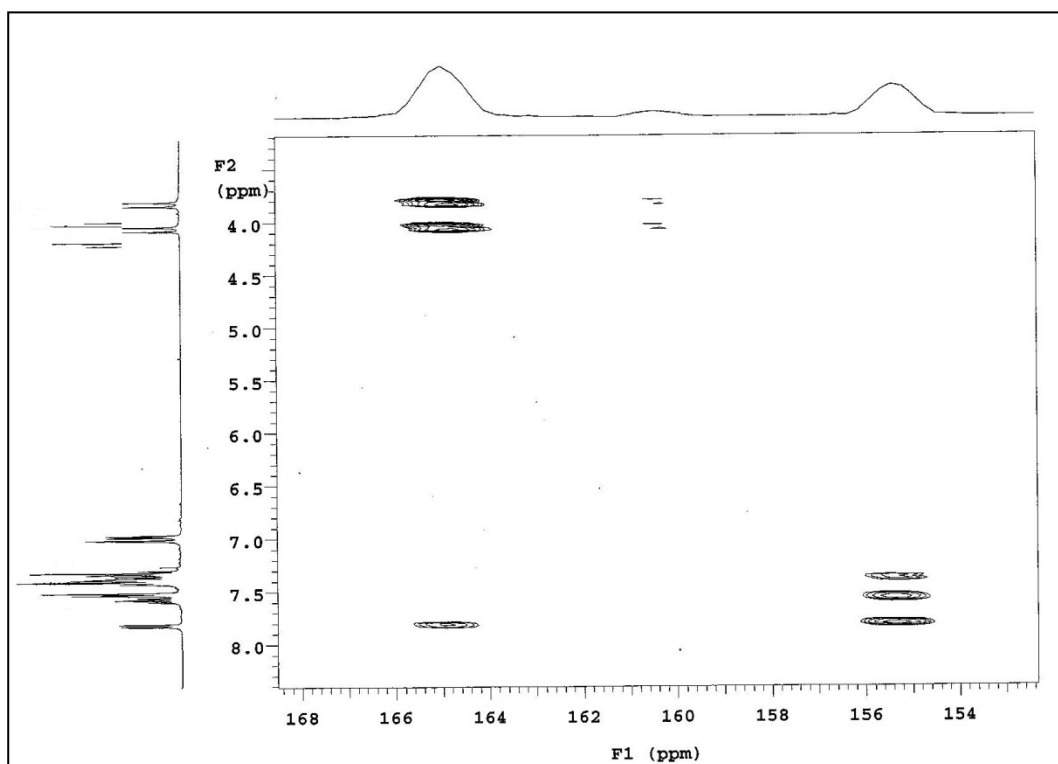
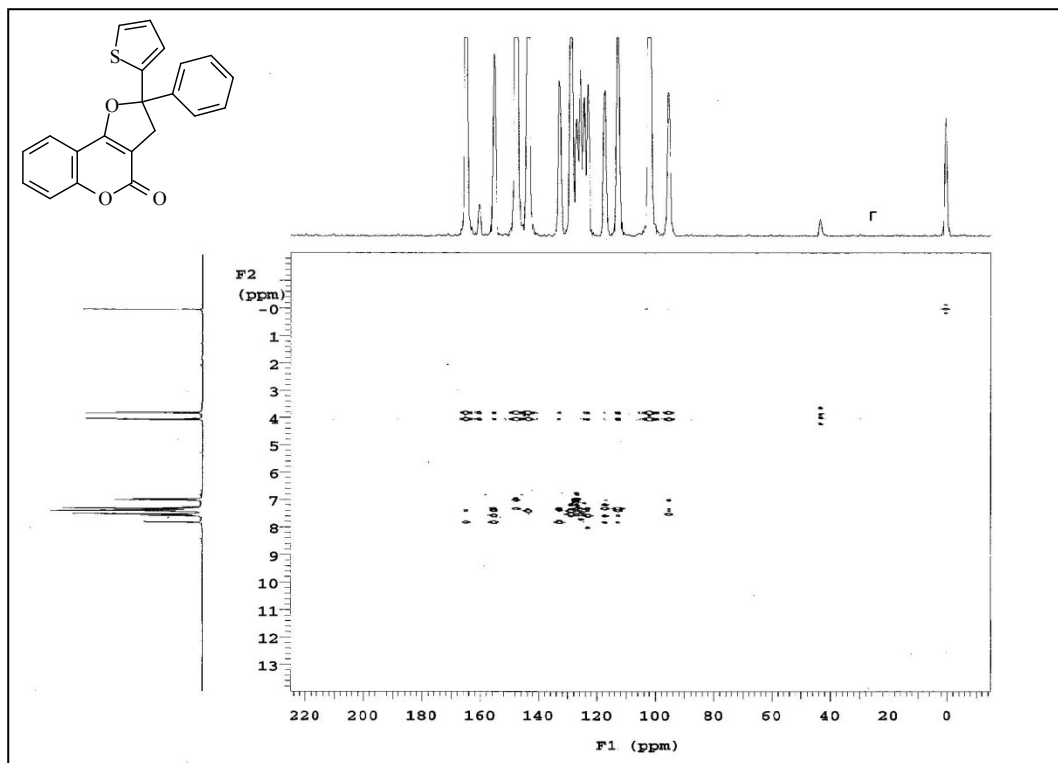


5.9 HSQC spectra of 42

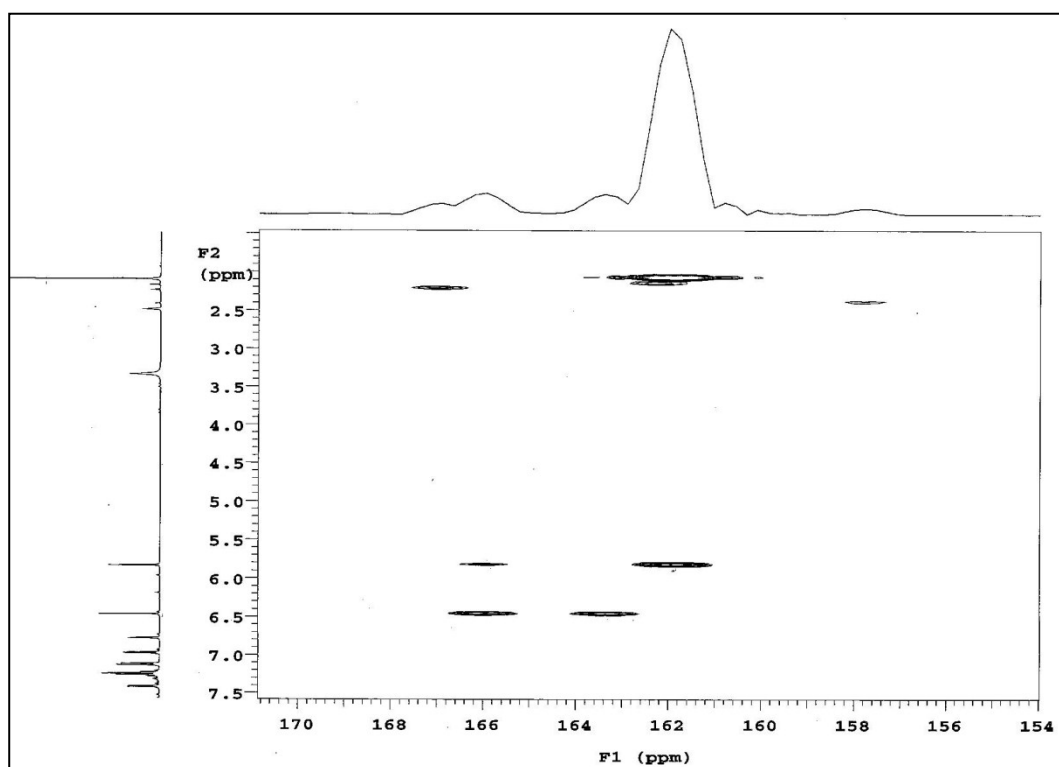
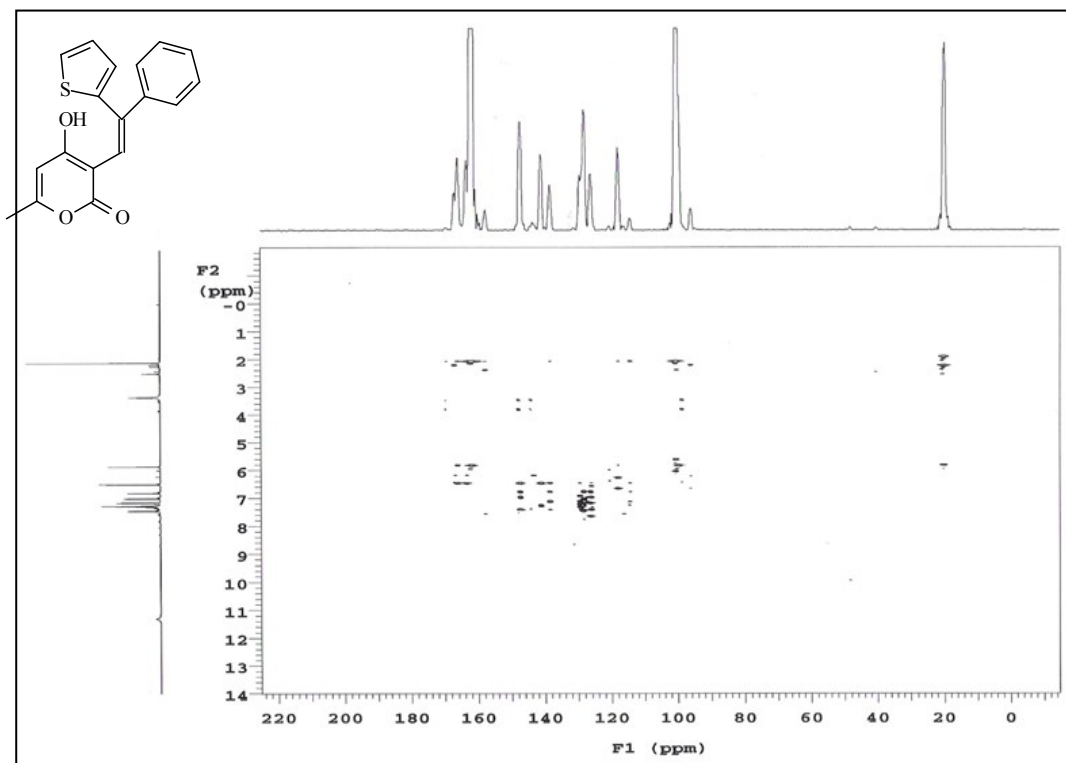


6. HMBC Spectra of COMPOUNDS

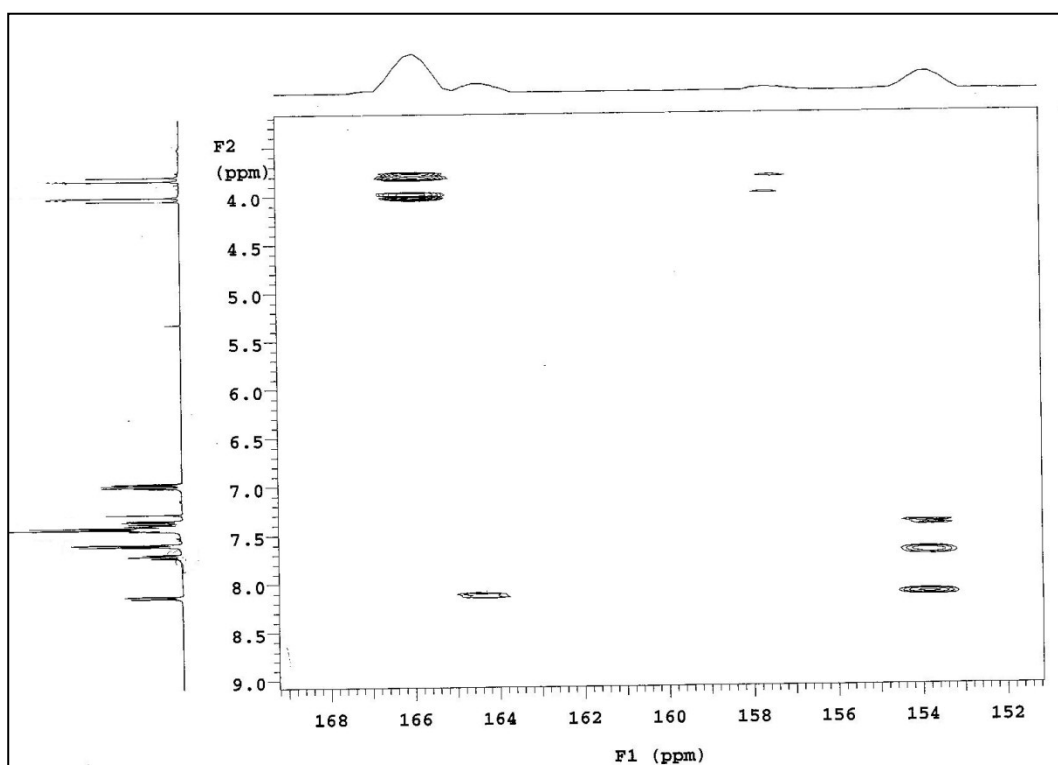
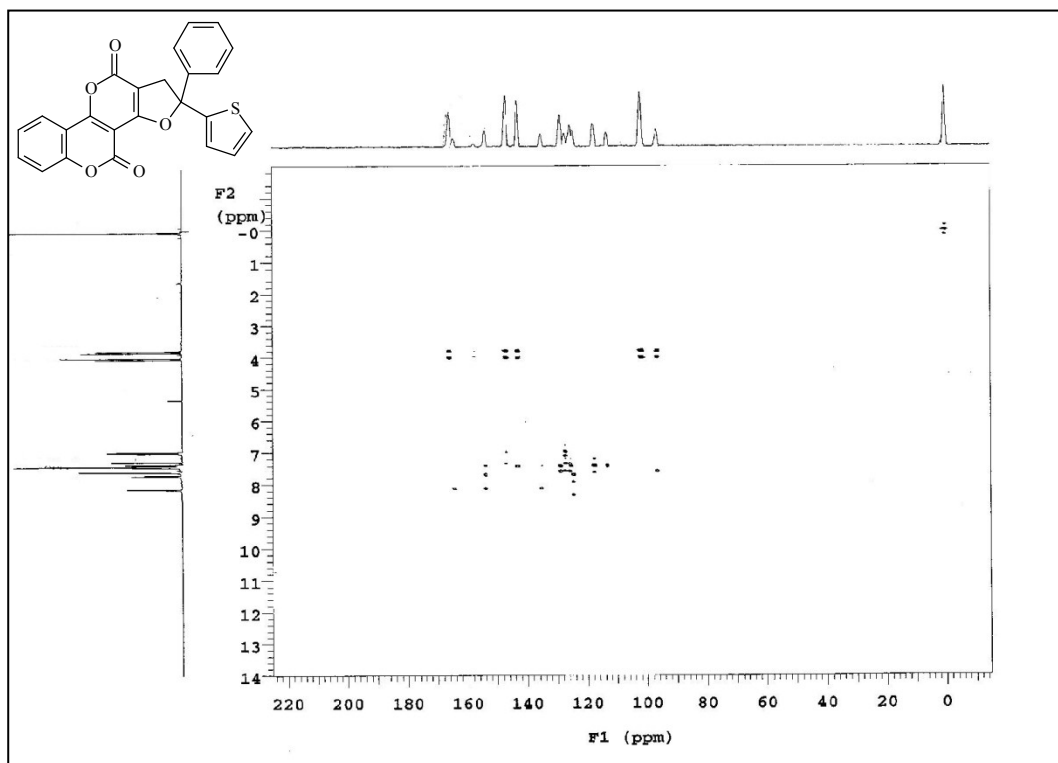
6.1 HMBA spectra of 3



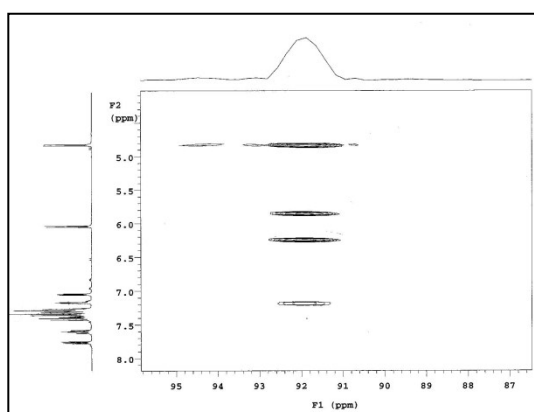
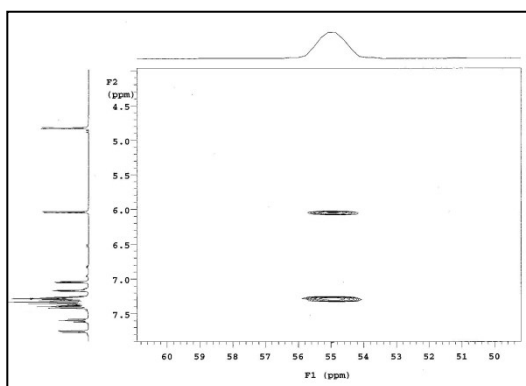
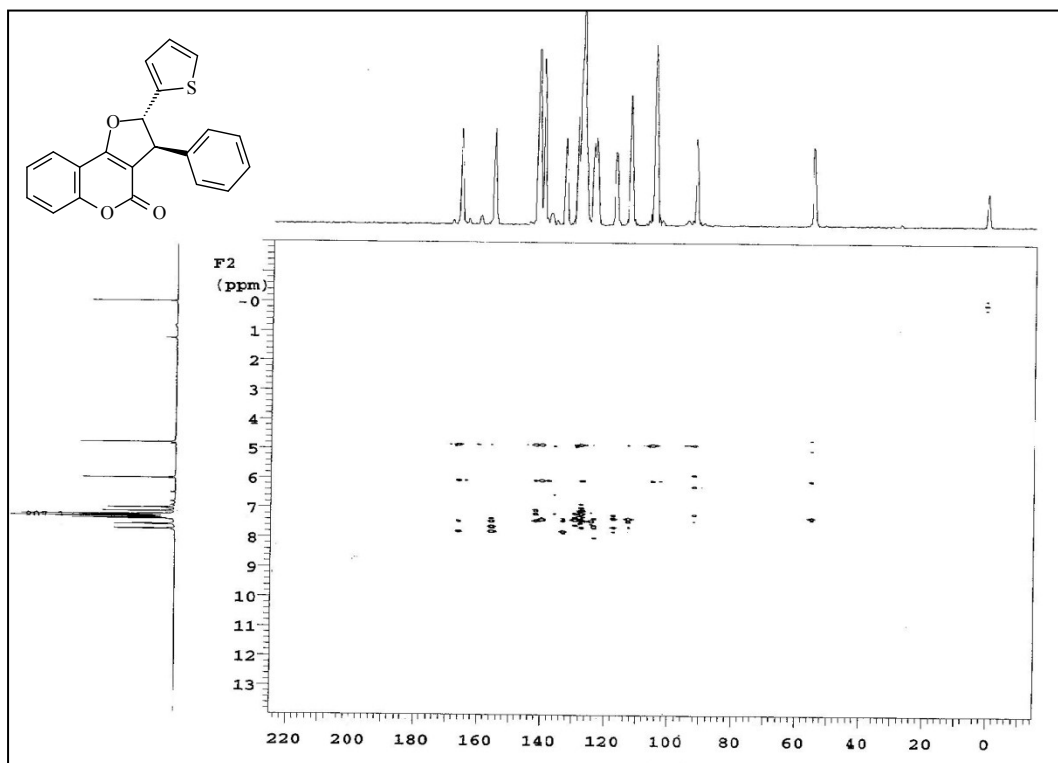
6.2 HMBC spectra of 16



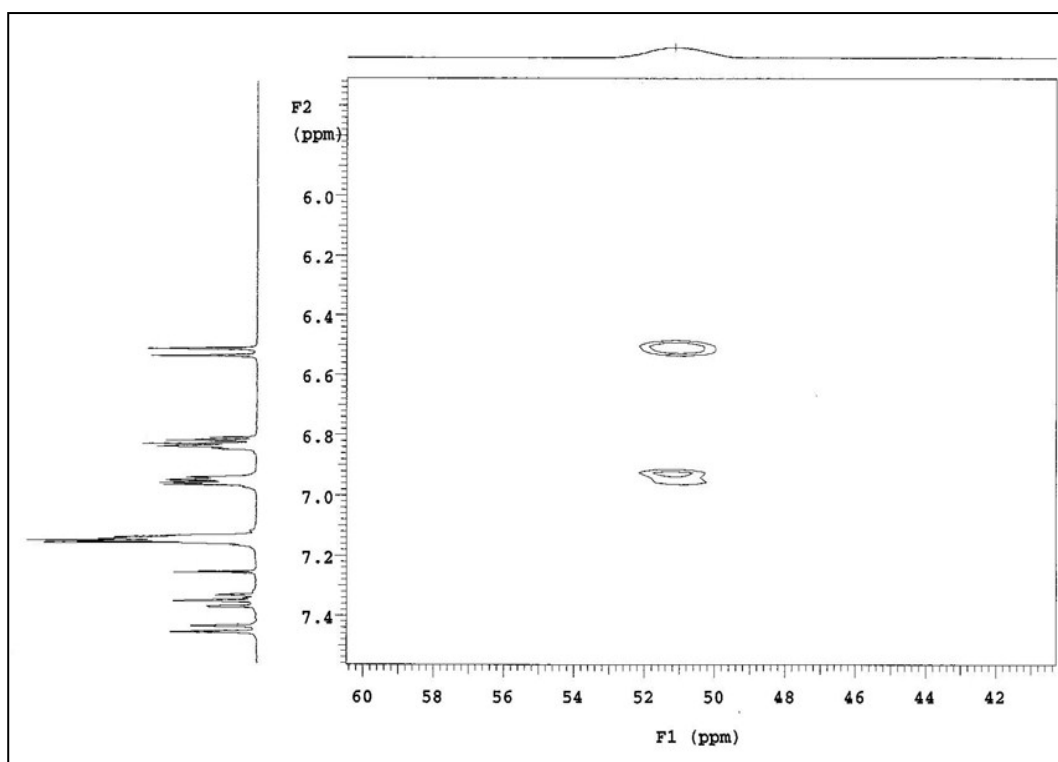
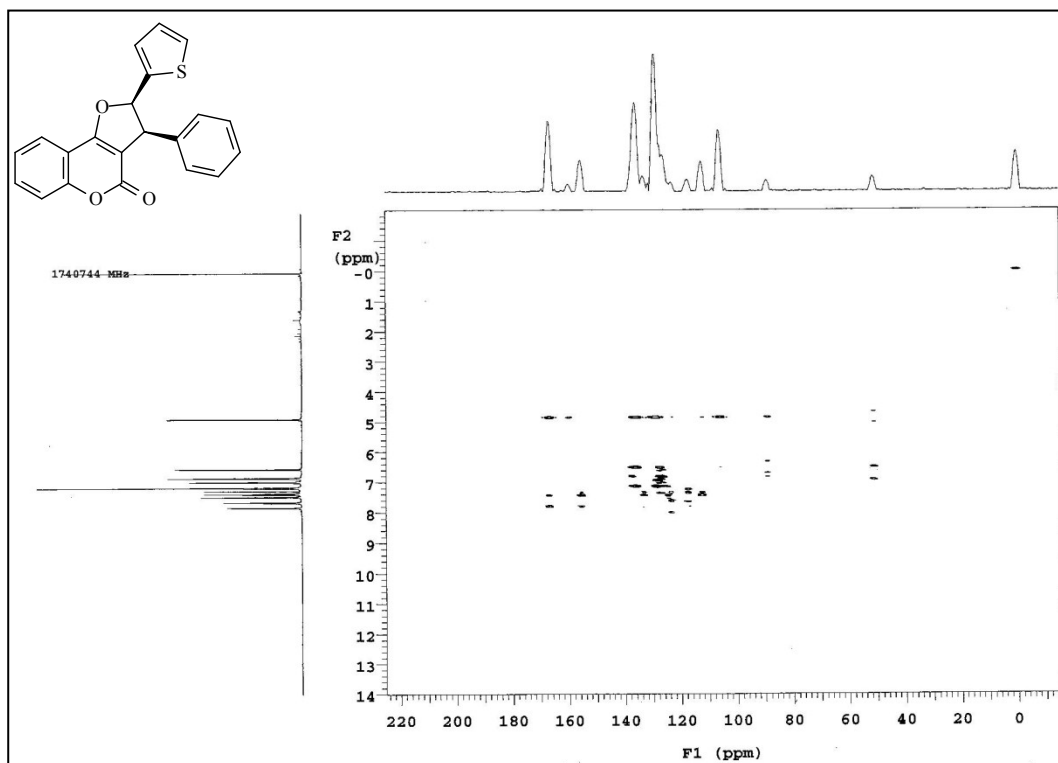
6.3 HMBC spectra of **19**



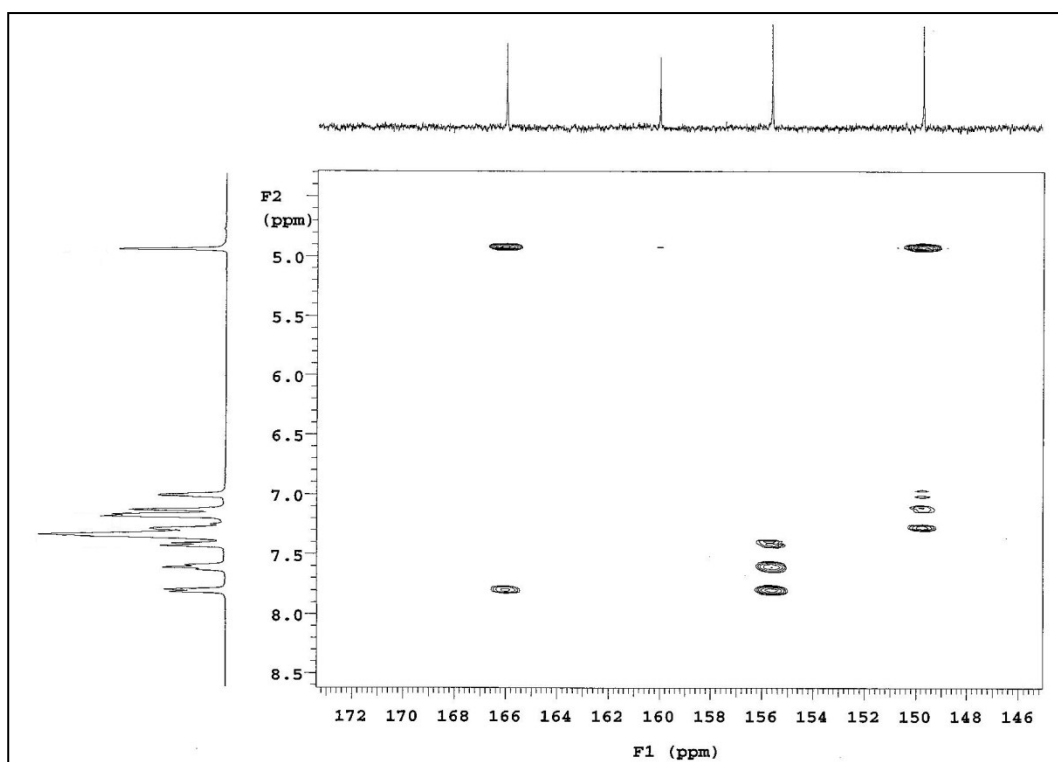
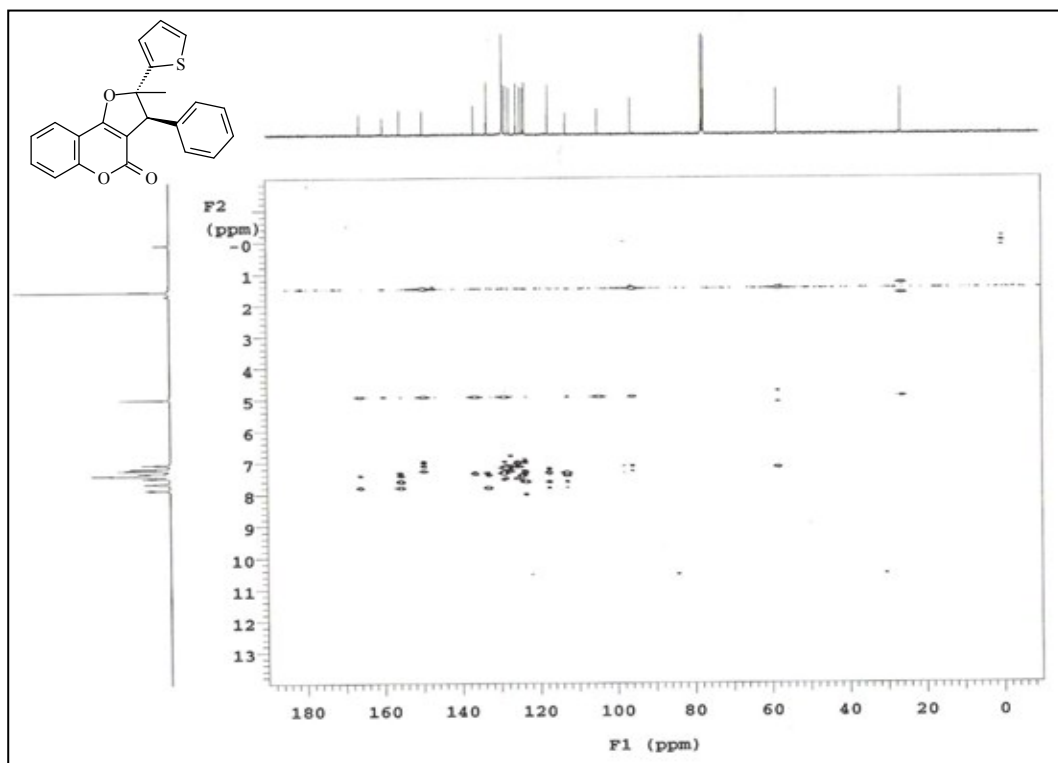
6.4 HMBC spectra of **35**



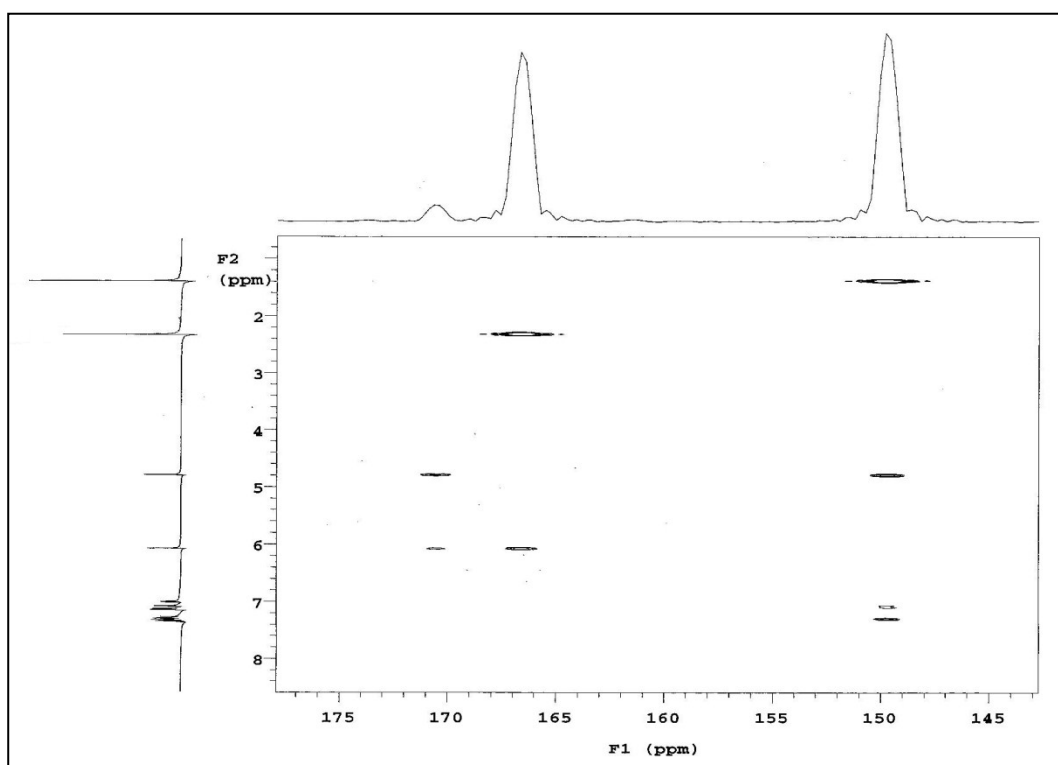
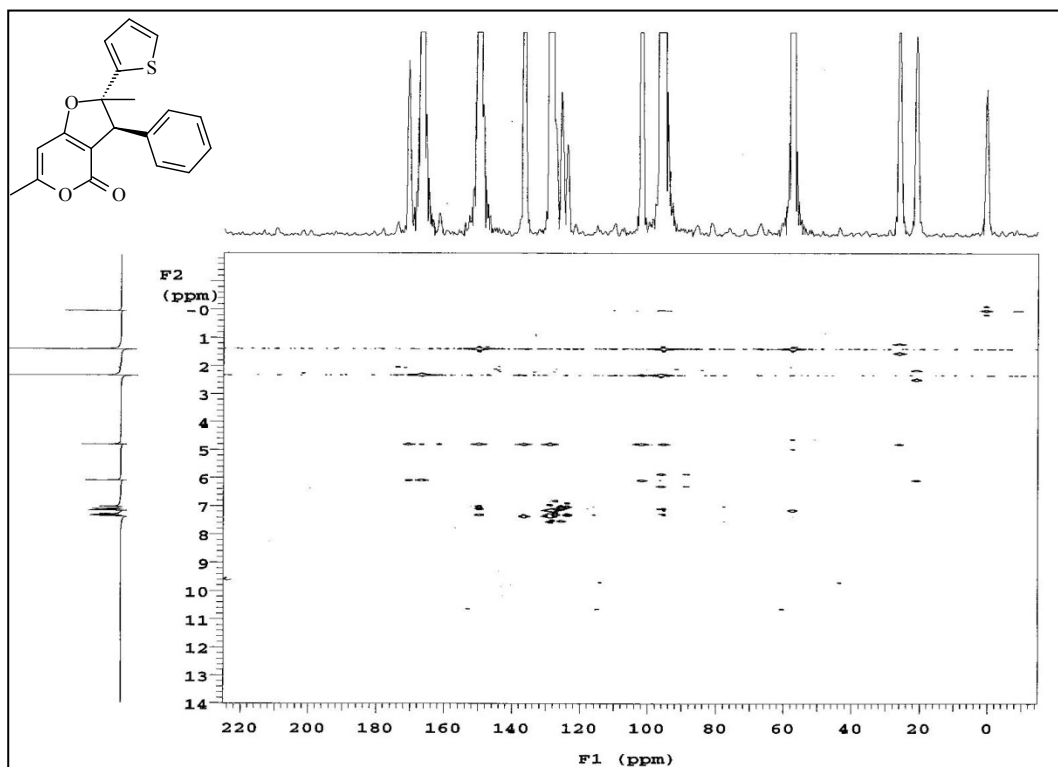
6.5 HMBC spectra of 36



6.6 HMBC spectra of 37



6.7 HMBC spectra of **39**



6.8 HMBC spectra of **39**

