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3 **Efficient Syntheses and Antimicrobial Activities of New Thiophene Containing Pyranone and**
4 **Quinolinone Derivatives by Manganese(III) Acetate. The effect of Thiophene on Ring Closure-**
5 **Opening Reactions**
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27 **ABSTRACT**
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29 The syntheses of new series of pyranones, namely fused pyranones and quinoline-based dihydrofurans
30 accompanied by 3-alkenyl-substituted structures were described. The products were regioselectively
31 formed Mn(III)-mediated oxidation at elevated temperature in order to obtain excellent yields. The effects
32 on product distributions of the thiophene group together with the temperatures and reactions time were
33 investigated. The structures of the syntheses compounds were determined on the basis of spectroscopic
34 (IR, ¹H NMR, ¹³C NMR, COSY, HSQC, HMBC and elemental analysis) and X-ray crystallographic data.
35 In addition, the *in vitro* antimicrobial activities of the some syntheses dihydrofurans were tested against
36 G (+) and G (-) bacteria using disc diffusion method. The results indicated that the compounds containing
37 thiophene group showed a better antimicrobial effect than some commonly used antibiotics.
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49 **Keywords:** manganese(III) acetate, dihydrofuran, 3-alkenyl-substituted coumarin, thiophene,
50 antimicrobial activity
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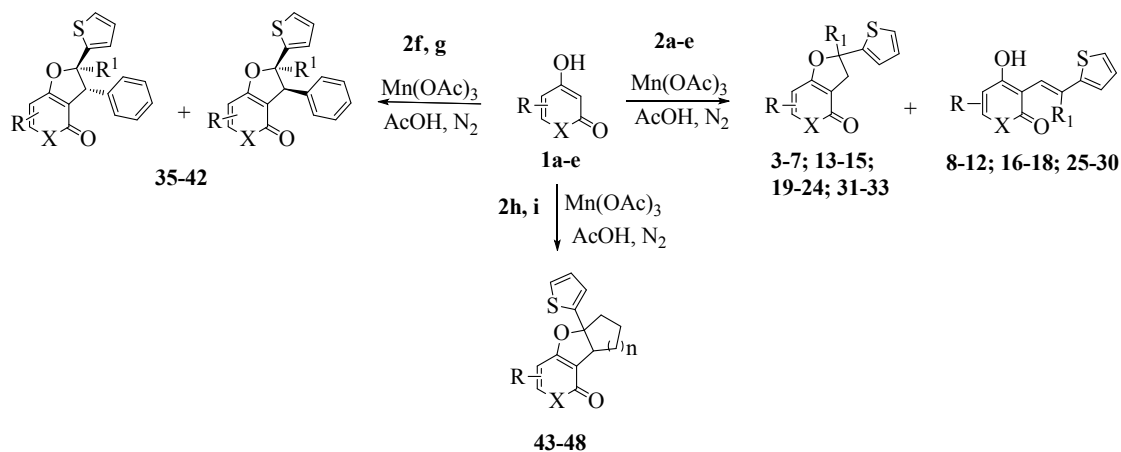
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1. Introduction

Pyranones are amongst the most abundant molecules of naturally occurring compounds and commonly used as versatile intermediates in natural product synthesis.¹ Among pyranone derivatives, coumarins and pyranocoumarines are an important class of organic compounds, and used as the building blocks of many biologically active molecules² exhibiting significant pharmacological activities such as anticoagulant,^{3a} antitumor,^{3b} anti-inflammatory,^{3c} antibacterial^{3d} and cytotoxic activities.^{3e} Moreover, 4-hydroxy-3-substituted pyranones have been used as fluorescent chemosensors,^{4a} molecular switches,^{4b} luminescence dyes^{4c} and optical sensors^{4d} owing to their conjugated features and biological activities.⁵ Quinolinone and its derivatives are in another important class of heterocycles that are widely distributed in nature.⁶ Dihydrofuroquinolinones and pyranoquinolinones, in particular, have found a great deal of interest since they have many applications in medicine and their biological activities were also demonstrated in literature.⁷ Thiophenes, another important group of heterocyclic molecules, possess versatile applications in various fields of drug development.⁸

In this respect, here we aimed at incorporating pyranone, coumarin and quinolinone as scaffold of the target molecules in the presence of thiophene moiety. Since Mn(III)-based oxidative radical cyclization using 1,3-dicarbonyl compounds has become the most preferred way of preparing a variety of heterocycles,^{9, 10} we utilized the reaction¹¹ in order to obtain heteroaromatic compounds containing dihydrofurans, and we found to synthesize highly functionalized dihydrofuran-fused pyranone, coumarin and quinolinone derivatives. We herein report a novel and efficient one-step synthetic protocol of biological active pyranones, dihydrofuran-fused and 3-alkenyl-substituted quinoline derivatives

(Scheme 1).



Scheme 1. Dihydrofuran-fused and 3-alkenyl-substituted pyranone, coumarin and quinolinone derivatives.

2. Results and discussion

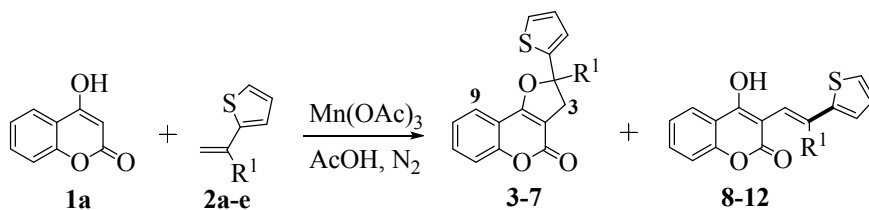
2.1. Synthesis

2.1.1 Reactions of 1,1-disubstituted alkenes with **1a-e**.

We firstly examined the reaction of 4-hydroxycoumarin (**1a**) with thienyl substituted alkenes **2a-e** under different reaction conditions (**Table 1**). During the reaction at 110 °C for 5 minutes, two products were obtained. One was dihydrofuro derivatives **3-7**, and the other was 3-alkenyl-substituted compounds **8-12** (**Table 1**).

The IR spectra of compounds **3-7** showed a characteristic strong carbonyl absorption at 1720 cm⁻¹. The chemical shifts of the carbonyl groups were found at 160-161 ppm assigned to lactone carbonyl, which demonstrated that isolated compounds were angular. In addition, **H-9** proton of the angular dihydrofurocoumarin in the ¹H NMR spectrum resonated at 7.7 ppm (dd), while in the linear 2,3-dihydro-4*H*-furo[2,3-*b*]chromen-4-one, it is **H-5** proton appeared at 8.25 ppm (dd or d).^{12a} Besides, it was determined that **H-9** and **H-3** protons correlated with **C9a** carbon, and **H-3** protons weakly interacted with **C4** ester carbonyl in the HMBC experiment.

In the reactions, 4-hydroxy-3-alkenylcoumarins **8-12** were unexpectedly obtained in the form of E/Z isomer mixture (**Table 1**). The existence of hydroxyl and alkenic protons in the ¹H NMR spectrum, supported the structure. Besides, in the ¹H NMR spectra of compounds **3-7**, **H-3** methylene protons showed a diastereotopic feature (²*J* = 15.2-15.6 Hz as a d). These protons were not observed in the spectra of compounds **8-12**. In the reaction performed using manganese(III) acetate, it was found that more alkenyl-substituted compounds such as **8-12** were produced by increasing the temperature and prolonging the duration of the reaction. Regarding the reactions performed in acetic acid for 24 h, dihydrofurocoumarins **3-7** were formed in lower yields (Entries 7, 14) or not isolated (Entries 11, 19) and alkene derivatives **8-12** were preferentially produced.

Table 1. Reaction of 4-hydroxycoumarin (**1a**) with 1,1-disubstituted alkenes **2a-e**.^a

R¹: Ph (**2a**), 4-Me-C₆H₄ (**2b**), 4-F-C₆H₄ (**2c**), Me (**2d**), 2-Thienyl (**2e**)

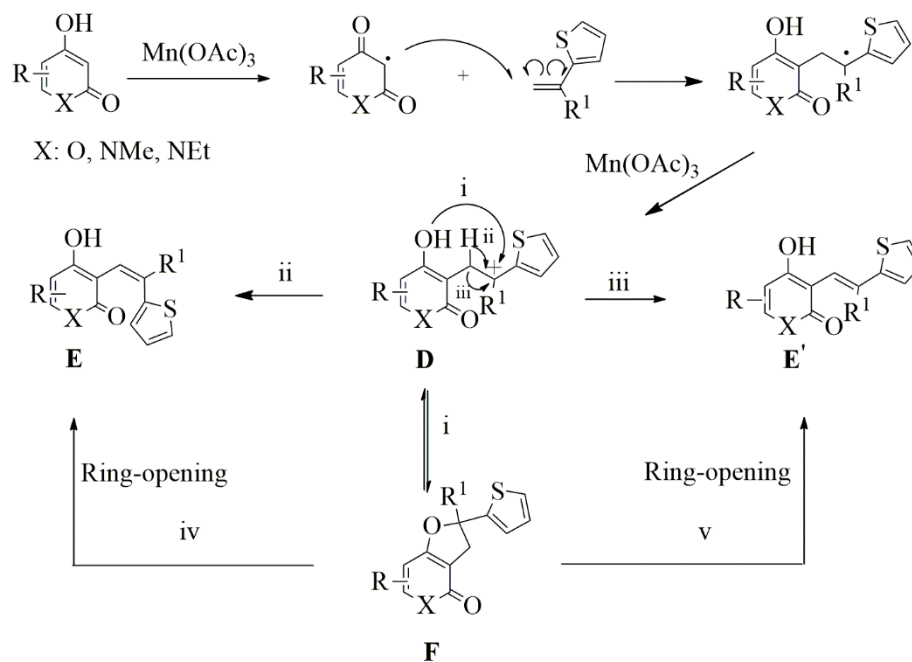
| Entry | Alkene | Temp. (°C) | Time (min.) | 3-7 (%) ^b | 8-12 (%) ^b | (<i>E/Z</i>) ^c |
|-------|-----------|------------|-------------|-----------------------------|------------------------------|-----------------------------|
| 1 | 2a | 80 | 1 | 3 (93) | ---- | ---- |
| 2 | 2a | 80 | 5 | 3 (89) | ---- | ---- |
| 3 | 2a | 80 | 10 | 3 (76) | 8 (8) | 1:1.70 |
| 4 | 2a | 80 | 60 | 3 (62) | 8 (23) | 1:1.70 |
| 5 | 2a | 70 | 5 | 3 (86) | ---- | ---- |
| 6 | 2a | 70 | 60 | 3 (63) | 8 (15) | 1:1.70 |
| 7 | 2a | 70 | 1440 | 3 (3) | 8 (67) | 1:1.70 |
| 8 | 2a | 110 | 5 | 3 (63) | 8 (27) | 1:1.70 |
| 9 | 2b | 80 | 1 | 4 (94) | ---- | ---- |
| 10 | 2b | 80 | 5 | 4 (77) | 9 (16) | 1:4.25 |
| 11 | 2b | 70 | 1440 | --- | 9 (68) | 1:4.25 |
| 12 | 2c | 80 | 1 | 5 (97) | ---- | ---- |
| 13 | 2c | 60-70 | 30 | 5 (68) | 10 (16) | 1:1.5 |
| 14 | 2c | 70 | 1440 | 5 (9) | 10 (71) | 1:1.5 |
| 15 | 2d | 80 | 1 | 6 (87) | ---- | ---- |
| 16 | 2d | 110 | 5 | 6 (85) | 11 (10) | ---- |
| 17 | 2d | 70 | 1440 | 6 (32) | 11 (14) | ---- |
| 18 | 2e | 80 | 1 | 7 (57) | 12 (28) | ---- |
| 19 | 2e | 70 | 1440 | ---- | 12 (79) | ---- |

^a All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene **2**, 4-hydroxycoumarin (**1a**) and Mn(OAc)₃ in AcOH.

^b Isolated yield based on the alkene **2**.

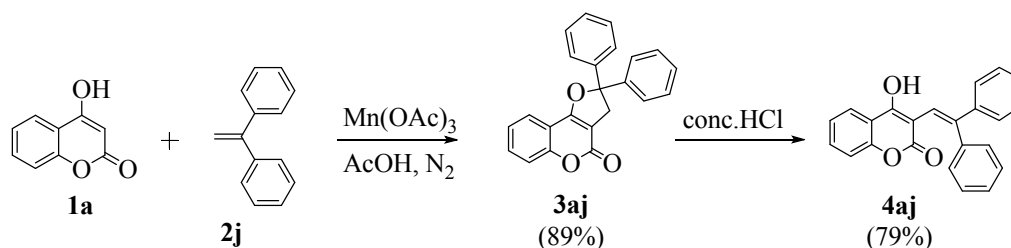
^c *E:Z* ratio determined by ¹H NMR spectrum.

This situation shows that alkenyl-substituted coumarin **8** should be formed by the ring-opening reaction of dihydrofurocoumarin **3** under acidic condition (*vi and v ways*). The proposed reaction mechanism for the formation of alkenyl substituted compounds **E** and **E'** is shown in **Scheme 2**. As it can be seen at the mechanism, the alkenyl-substituted compounds **E** and **E'** could be formed by two different ways. The first way would be the elimination of a proton from the **D** intermediate; secondly, after it would be formed dihydrofuran **F**, transforms into an alkene **E** and **E'** with the opening of the furan ring followed by deprotonation.



Scheme 2. The proposed mechanism for the formation of alkenyl-substituted compounds.

In literature, alkenyl-substituted products were not obtained in the reactions of 4-hydroxycoumarin (**1a**) with non-heteroaromatic alkenes.^{11j-k} At the reactions that we practiced, it is thought that thiophene group would be effective in the formation of alkenyl-substituted products. With the intention of comparison, the reaction was practiced using 1,1-diphenylethene (**2j**) even in the high temperature, only dihydrofurocoumarin (**3aj**) was produced^{11k} and alkenyl-substituted coumarin **4aj** was not obtained in the reaction. It was synthesized only when the obtained **3aj** was treated with the concentrated HCl (**Scheme 3**).



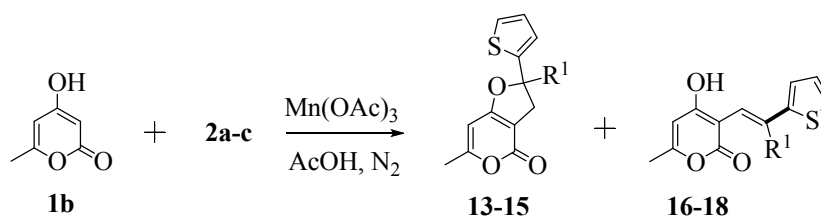
Scheme 3. Reaction of 4-hydroxycoumarin (**1a**) with **2j**.

With addition of thiophene ring to the structure, the products **8**, **11** and **12** were produced in acetic acid and effective in the yields of alkenyl-substituted compounds. This situation has the following effects; 1. Opening of the ring could occur by the electron pair over the sulfur atom at the thiophene ring and the electron pair over the oxygen at the furan ring pushing each other; 2. The enol hydrogens **8-12** and the sulfur atom at the thiophene ring could interact and constitute a more stable structure; 3. While a stronger acid was needed for the formation of **4aj**, the products **8-12**, they should be formed under the acetic

acid conditions. This might result from the redundant density of electron over the oxygen at the furan ring of **3-7**.

The reaction of 4-hydroxy-6-methyl-2*H*-pyran-2-one (**1b**) with **2a-c** gave dihydrofurofurans **13-15** and alkenyl substituted furans **16-18** (Table 2). The ester carbonyl groups were observed at 1730 cm⁻¹ in the IR spectra, and they were resonated at 160-165 ppm in ¹³C NMR spectra, so it was determined that the dihydrofurofurans **13-15** were the angular products. The alkenyl substituted furans **16-18** were obtained as an E/Z isomeric mixture. Existence of hydroxyl and alkene protons in compounds **16-18** was found by the help of ¹H NMR, COSY, HSQC and HMBC spectra. It was determined that **C-4** to which oxygen atom was bounded resonates at 166 ppm, **C-2** at 163 ppm and **C-6** resonates at 161 ppm in the analysis of ¹³C NMR spectra.

Table 2. Reaction of 4-hydroxy-6-methyl-2*H*-pyran-2-one (**1b**) with **2a-c**.^a



| Entry | 2a-c | Temp. °C | Time (min.) | 13-15 (%) ^b | 16-18 (%) ^b | (E:Z) ^c |
|-------|-------------|-------------|-------------|-------------------------------|-------------------------------|--------------------|
| 1 | 2a | 80 | 1 | 13 (93) | --- | --- |
| 2 | 2a | 70 | 1440 | 13 (28) | 16 (42) | 1:1.25 |
| 3 | 2a | 110 | 5 | 13 (78) | 16 (15) | 1:1.25 |
| 4 | 2a | 110 | 10 | 13 (48) | 16 (41) | 1:1.25 |
| 5 | 2b | 80 | 1 | 14 (94) | --- | --- |
| 6 | 2b | 80 | 5 | 14 (78) | --- | --- |
| 7 | 2b | 70 | 1440 | 14 (6) | 17 (62) | 1:2 |
| 8 | 2c | 80 | 1 | 15 (95) | --- | --- |
| 9 | 2c | 80 | 5 | 15 (86) | --- | --- |
| 10 | 2c | 70 | 1440 | 15 (17) | 18 (67) | 1:1.5 |

^a All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene **2**, **1b** and Mn(OAc)₃ in AcOH.

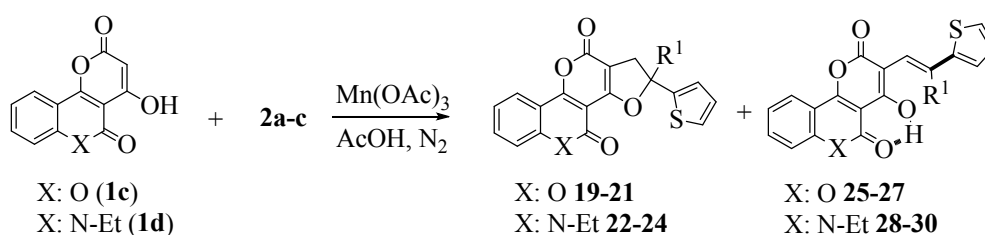
^b Isolated yield based on the alkenes **2**.

^c E/Z ratio determined by ¹H NMR spectrum.

As it is seen in Table 2, in the reactions that were practiced at 80 °C in 1 minute, the dihydrofurofurans **13-15** were produced in high yields, while alkenyl-substituted furans **16-18** were obtained in high temperatures and long periods of reaction times. Even in the reactions that lasted for 24 hours, dihydrofurofurans **13-15** were isolated.

The cyclization reactions of 4-hydroxy-2*H*,5*H*-pyrano[3,2-*c*]chromen-2,5-dione (**1c**) and 6-ethyl-4-hydroxy-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (**1d**) with **2a-c** resulted in the synthesis of both dihydrofurans **19-24** and alkenes **25-30** (Table 3). The reactions were monitored by TLC and it was determined that the alkenes **25-30** started to form after 2 minutes. Besides, in the reactions carried out at 110 °C (Entry 2 and 9), the alkenes **25** and **28** were obtained with a higher yield than the dihydrofurans **19** and **22**. The alkenyl-substituted pyranocoumarins **25-27** and pyranoquinolinones **28-30** were also isolated in *E/Z* isomeric mixtures.

Table 3. Reaction of **1c, d** with **2a-c**.



| Entry | 1c-d | 2a-c | Temp. (°C) | Time (min.) | 19-24 (%) ^b | 25-30 (%) ^b | (E:Z) ^c |
|-------|-------------|-------------|------------|-------------|-------------------------------|-------------------------------|---------------------------|
| 1 | 1c | 2a | 80 | 1 | 19 (51) | --- | --- |
| 2 | 1c | 2a | 110 | 5 | 19 (14) | 25 (42) | 1:4 |
| 3 | 1c | 2a | 70 | 1440 | --- | 25 (53) | 1:4 |
| 4 | 1c | 2b | 80 | 1 | 20 (55) | --- | --- |
| 5 | 1c | 2b | 70 | 1440 | --- | 26 (51) | 1:3.4 |
| 6 | 1c | 2c | 80 | 1 | 21 (62) | --- | --- |
| 7 | 1c | 2c | 70 | 1440 | --- | 27 (63) | 1:2 |
| 8 | 1d | 2a | 80 | 1 | 22 (36) | --- | --- |
| 9 | 1d | 2a | 110 | 5 | 22 (22) | 28 (36) | 1:2.4 |
| 10 | 1d | 2a | 70 | 1440 | --- | 28 (56) | 1:2.4 |
| 11 | 1d | 2b | 80 | 1 | 23 (38) | 29 (5) | 1:8 |
| 12 | 1d | 2b | 70 | 1440 | --- | 29 (46) | 1:8 |
| 13 | 1d | 2c | 80 | 1 | 24 (39) | 30 (13) | 1:3.3 |
| 14 | 1d | 2c | 70 | 1440 | --- | 30 (52) | 1:3.3 |

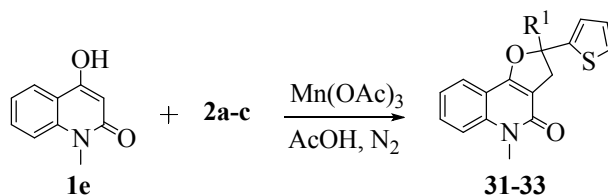
^aAll the reactions were carried out in a 1 : 2 : 3 molar ratio of alkenes **2**, pyranocoumarin **1c** or pyranoquinolinone **1d** and Mn(OAc)₃ in AcOH.

^bIsolated yield based on the alkenes **2**.

^c*E/Z* ratio determined by ¹H NMR spectrum.

The last cyclization was examined using 1,1-disubstituted alkenes **2a-c** and 4-hydroxy-1-methyl-quinoline-2-one (**1e**). As a result, only angular dihydrofuroquinolinones **31-33** were produced (**Table 4**).

Table 4. Reaction of **1e** with **2a-c**.^a

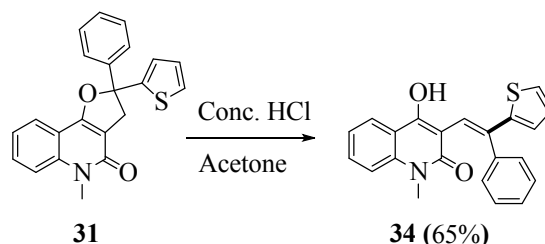


| Entry | Alkene | Temp., °C | Time, min. | 31-33 (%) ^b |
|-------|-----------|-----------|------------|-------------------------------|
| 1 | 2a | 60 | 5 | 31 (81) |
| 2 | 2a | 60 | 1440 | 31 (69) |
| 3 | 2a | 80 | 1 | 31 (75) |
| 4 | 2a | 80 | 5 | 31 (91) |
| 5 | 2a | 80 | 60 | 31 (89) |
| 6 | 2a | 80 | 360 | 31 (83) |
| 7 | 2a | 110 | 5 | 31 (73) |
| 8 | 2b | 80 | 1 | 32 (68) |
| 9 | 2b | 80 | 5 | 32 (94) |
| 10 | 2c | 80 | 1 | 33 (89) |
| 11 | 2c | 80 | 5 | 33 (96) |

^aAll the reactions were carried out in a 1 : 2 : 3 molar ratio of alkenes **2**, quinolinone **1e** and Mn(OAc)₃ in AcOH.

^bIsolated yield based on the alkenes **2**.

Both angular and linear dihydrofuroquinolinones were synthesized from the reactions with non-heteroaromatic alkenes.^{7b} Theoretical calculations have shown that the angular dihydrofuroquinolinones were thermodynamically stable, and linear dihydrofuroquinolinones were kinetically favored products. Although the present were examined at different temperatures and in different durations, no linear products were observed neither in short durations nor at low temperatures. This situation shows that the cyclization occurs regioselectively. Meanwhile, alkenyl substituted products were not observed. However, dihydrofuroquinolinone **31** could be converted into the corresponding vinyl-quinolinone **34** by treatment of concentrated HCl (**Scheme 4**).

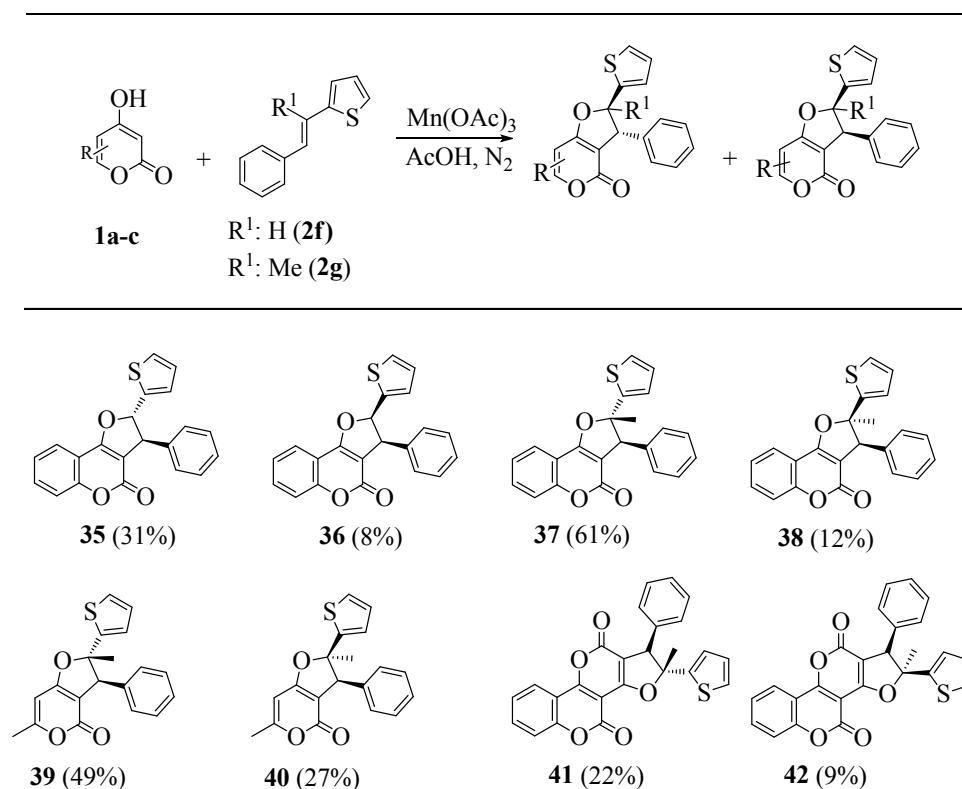


Scheme 4. Ring-opening reaction of dihydrofuroquinolinone **31**.

2.1.2 Reactions of 1,2-disubstituted **2f** and 1,1,2-trisubstituted alkenes **2g** with **1a-c** and formation of dihydrofuran as a *cis-trans* isomer.

When the reactions of 1,2-disubstituted **2f** and 1,1,2-trisubstituted alkenes **2g** with 4-hydroxycoumarin (**1a**) was carried out in the presence of manganese(III) acetate, two different dihydrofurocoumarins were isolated (**Table 5**). In order to characterize the structures, the IR, ¹H-NMR and ¹³C-NMR spectra, HSQC and HMBC spectra were taken and it was deduced that the compounds **35** and **36** were *cis* and *trans* isomer. In the ¹H-NMR spectrum, the coupling constants of **H-2** and **H-3** protons were ³J_{H-H} = 6.0 Hz in **35** and ³J_{H-H} = 9.2 Hz in **36**. By comparing with the data in the literature,^{12b,c} it was determined that **35** and **36** should be “*trans*” and “*cis*” isomers, respectively (**Table 5**).

Table 5. Reactions of **1a-c** with **2f, g**.^a



^a All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene **2**, **1a-c** and Mn(OAc)₃ in AcOH at 80 °C, 5 minutes.

^b Isolated yield based on the alkene **2**.

When HMBC experiments of the dihydrofurocoumarins **35** and **36** were performed, it was found out that **C-2** carbon interacted with thienyl **H-3** proton and **C-3** carbon interacted with ortho protons over phenyl ring. Regarding this, it was found out that in both compounds, thienyl group should be bound to **C-2** carbon and phenyl group should be bound to **C-3** carbon.

From the reaction of **2g** with **1a-c**, two different dihydrofurans *cis* and *trans* isomer **37-42** were also produced (**Table 5**). The structure of **37** was confirmed by X-ray crystallography (**Fig. 1**).¹³ According to this analysis, it was determined that phenyl and thienyl groups were in *trans* position as regards to each other.

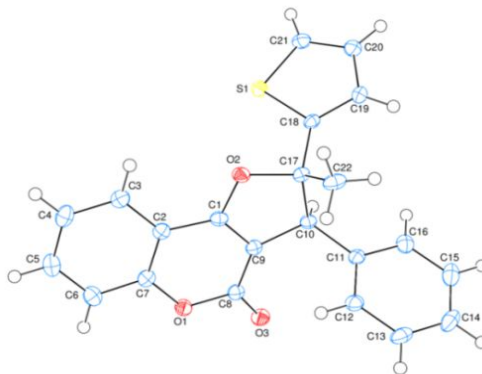
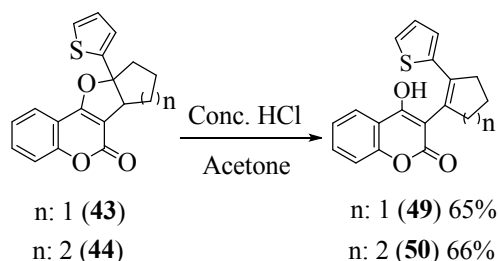


Fig. 1. The molecular entities of compound **37**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

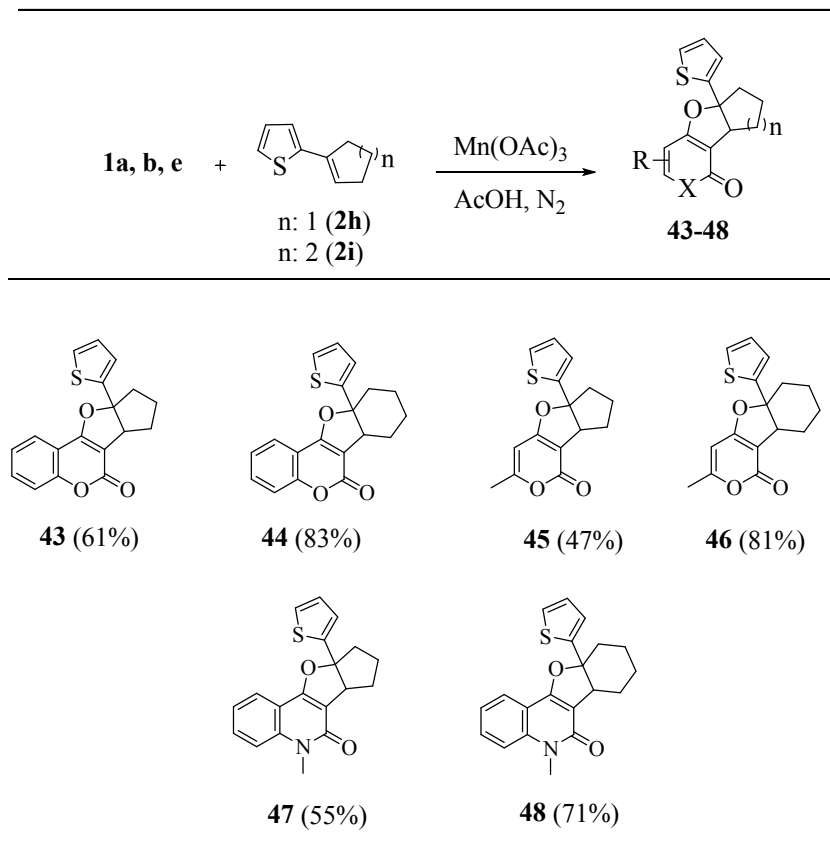
2.1.3 Reactions of cyclic alkenes **2h, i** with **1a, b** and **1e**

Finally, only dihydrofurans **43-48** were obtained from the reactions of **1a, b** and **1e** with cyclic alkenes **2h, i**. With the purpose of monitoring the formation of alkenyl substituted compounds, various experiments were carried out at high temperatures and in long durations (**Table 6**).

Unlike the reactions that were practiced with alkenes **2a-c**, alkenyl substituted compounds did not produce. However, the products **43** and **44** could be converted into **49** and **50** by treatment of concentrated HCl in 65% and 66% yields, respectively, as a single isomer (**Scheme 5**).



Scheme 5. Ring opening reaction of compounds **49** and **50**

Table 6. Reactions of **1a, b, e** with **2h, i**.^a

^a All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkenes **2h, i**, pyranones **1a, b, e** and $\text{Mn}(\text{OAc})_3$ in AcOH at 80 °C, 5 minutes.

^b Isolated yield based on the alkene **2**.

2.2 Antimicrobial activity study

When the literature studies were examined, it could be clearly seen that quinolone and coumarin derivatives had antimicrobial activities. Moreover, quinolones are among the largest antimicrobial classes.¹⁴ Quinolones are synthetic substances obtained by chemical routes different from many antibiotics obtained from living microorganisms. In this study, antimicrobial effects of some quinolone and coumarin derivatives against some gram positive and gram negative bacterial strains were determined by disk diffusion and minimum inhibitory concentration (MIC) method.^{10g}

According to the results of the disk diffusion experiment in **Table 7**, the 4-methylphenylquinolinone **32** was more effective than the phenyl- **31** and 4-fluorophenyl-quinolinone **33**. Besides, the compound **3aj** showed activity against *B. licheniformis* bacteria only. In the compounds **31** and **32**, the degree of inhibition caused by the presence of nitrogen and oxygen groups also varies. It is noticed that the utilized compounds are more effective than commonly used antibiotics such as penicillin, tetracycline, ampicillin, gentamicin compared to the data in **Table 8**.

The minimum inhibitory concentrations of the compounds were studied at concentration ranges from 125 to 2000 $\mu\text{g/mL}$ and the results are given in **Table 9**. It appears that the compound **32** was effective even at the concentration of 125 $\mu\text{g/mL}$ on B1-coded bacteria. As a consequence, it should be noted that the compound **32** could be evaluated as an active ingredient for antibiotics.

Table 7. Zone diameters (mm) of the compounds against bacteria.

| Bacteria | 3 | 4 | 5 | 3aj | 31 | 32 | 33 |
|----------------------------|----------|----------|----------|------------|-----------|-----------|-----------|
| <i>E. coli</i> ATCC 25922 | --- | 10 | --- | --- | 8 | 10 | 11 |
| <i>M. luteus</i> M3 | --- | --- | --- | --- | --- | 7 | 8 |
| <i>B.cereus</i> B9 | --- | 8 | 8 | --- | 10 | 9 | 8 |
| <i>B.licheniformis</i> M30 | 10 | --- | 10 | 8 | 9 | 15, 5 | 11 |
| <i>S. Coccus</i> | 9 | --- | 8 | --- | --- | 7 | --- |
| <i>B. subtilis</i> B1 | --- | --- | 10 | --- | --- | 9 | --- |
| <i>P. aeruginosa</i> P7 | --- | --- | --- | --- | --- | --- | --- |

E.Coli: *Escherichia coli* ATCC 25922; **M3:** *Micrococccus luteus* M3; **B9:** *Bacillus cereus* B9; **M30:** *Bacillus licheniformis* M30; **S. Coccus:** *Staphylococcus aureus* ATCC 6538; **B1:** *Bacillus subtilis* B1; **P7:** *Pseudomonas aeruginosa* P7

Table 8. Zone diameters (mm) of antibiotics against bacteria¹¹⁹.

| | Peniciline | Chloram phenicol | Tetracycline | Ampicillin | Gentamicin |
|------------------------|------------|---------------------|--------------|------------|------------|
| <i>E. coli</i> | 19 | --- | --- | --- | --- |
| <i>M. luteus</i> | 31 | --- | 9 | 28 | --- |
| <i>B.cereus</i> B9 | 16 | 31 | 16 | --- | --- |
| <i>B.licheniformis</i> | 16 | 17 | 23 | 18 | 20 |
| <i>S. Coccus</i> | --- | --- | --- | 9 | --- |
| <i>B. subtilis</i> | --- | --- | --- | 15 | --- |
| <i>P. aeruginosa</i> | --- | --- | --- | --- | 16 |

Table 9. MIC results ($\mu\text{g/mL}$).

| Bacteria | 3 | 4 | 5 | 3aj | 31 | 32 | 33 |
|------------|------|------|------|------|------|------|------|
| ATCC 25922 | --- | 1000 | --- | --- | 2000 | 1000 | 2000 |
| M3 | --- | --- | --- | --- | --- | 2000 | 2000 |
| B9 | --- | 1000 | 500 | --- | 2000 | 1000 | 2000 |
| M30 | 2000 | --- | 1000 | 1000 | 1000 | 500 | 1000 |
| ATCC 6538 | 1000 | --- | 1000 | --- | --- | 2000 | --- |
| B1 | --- | --- | 500 | --- | --- | 125 | --- |
| P7 | --- | --- | --- | --- | --- | --- | --- |

3. Conclusion

As a result, the Mn(III)-based oxidation of 4-hydroxycoumarin (**1a**), 4-hydroxy-6-methyl-2H-pyran-2-one (**1b**), 4-hydroxy-2H,5H-pyrano[3,2-c]chromen-2,5-dione (**1c**), 6-ethyl-4-hydroxy-2H-pyrano[3,2-c]quinoline-2,5-dione (**1d**) and 4-hydroxy-1-methyl-quinoline-2-one (**1e**) with thienyl-substituted alkenes **2a-i** were examined. While the radical cyclizations of 1,1-disubstituted alkenes with **1a-d** gave the dihydrofuran derivatives accompanied by 3-alkenyl-substituted structures, the reactions of **1e** gave the dihydrofuran derivatives as a sole products. The reactions of 1,2-disubstituted **2f** and 1,1,2-trisubstituted alkenes **2g** with **1a-c** was carried out, two different dihydrofuran derivatives *cis* and *trans* isomer were isolated. The structures of this compounds identified with spectroscopic method and X-ray crystallography. A similar reactions were conducted using cyclic thieny-substituted alkenes **2h-i** produced dihydrofuran derivatives. The mechanisms for the formations of the products were suggested. Apart from that, the antibacterial activities of the some synthesized compounds have been investigated and good results were obtained.

4. Experimental

4.1. Physical measurements

Melting points were determined on a Gallencamp capillary melting point instrument. IR spectra (KBr disc, CHCl_3) were obtained with a Matson 1000 FT-IR in the range of $400\text{--}4000\text{ cm}^{-1}$ with 4 cm^{-1} resolution. ^1H NMR (400 MHz), and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX-400 MHz and Varian Mercury-400 High performance Digital FT-NMR spectrophotometers. The mass spectra were measured on a Micromass UK LC/MS (APCI, 100-150 eV), and a Shimadzu GC-17A/GC-MS-QP5000 (EIMS, 70 eV) spectrophotometers. Elemental analyses were performed on a Leco 932 CHNS-O instrument. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K_α radiation ($\lambda = 0.71073\text{ \AA}$) at $T = 296(2)\text{ K}$. Absorption correction by multi-scan was applied¹⁸. Structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data¹⁹. TLC was performed on Merck aluminium-packed silica gel plates. Purification of products was performed by column chromatography on silica gel (Merck silica gel 60, 40-60 μm) or preparative TLC on silica gel of Merck ($\text{PF}_{254\text{--}366\text{ nm}}$).

4.2. Materials used for syntheses

Manganese(II) acetate tetrahydrate, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, was prepared according to the modified method described in the literature.¹⁵ All solvents, 4-hydroxycoumarin, 4-hydroxy-6-methyl-2H-pyran-2-one, 4-hydroxy-1-methylquinoline-2-one and other reagents were purchased from Merck. 4-Hydroxy-2H,5H-pyrano[3,2-c]chromen-2,5-dione (**1c**) and 6-ethyl-4-hydroxy-2H-pyrano[3,2-c]quinoline-2,5-dione (**1d**) were prepared according to the methods reported in the literature.¹⁶ The alkenes **2a-c**, **2e** and **2h-i** were prepared by dehydration from the carbinole prepared by Grignard reaction of aryl magnesium bromide and suitable carbonyl compounds.¹⁷ The other alkenes **2d**,^{11a} and **2f** and **2g**^{11d} were prepared by Wittig reaction of suitable carbonyl compounds with phosphonium ylides.

4.3. Syntheses

4.3.1. General procedure for manganese(III) acetate-based oxidative cyclization

A solution of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ in glacial AcOH was heated under N_2 at 80°C until it dissolved. Then, a solution of **1** and alkene **2** in 5 mL glacial AcOH was added to the mixture. The reaction was monitored by TLC. When the reaction was completed, water (10 mL) was added to the mixture and extracted with CHCl_3 (3×20 mL). The combined organic layers were neutralized with saturated NaHCO_3 aqueous solution, washed with water, dried over anhydrous Na_2SO_4 and evaporated. The products were purified by column chromatography on silica gel or preparative TLC on silica gel, eluting with hexane:AcOEt mixtures.

4.3.1.1. 2-Phenyl-2-thenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (**3**)

Colorless solid; mp: $154\text{--}155^\circ\text{C}$; **IR** (ν_{max} , KBr): 3104, 3093, 3069, 2974, 1716 (C=O), 1647 (C=C), 1605, 1497, 1405, 1029 (C-O-C), 729 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.82 (1H, dd, $J = 8, 1.2$ Hz, ArH), 7.59 (1H, td, $J = 8, 1.6$, ArH), 7.51 (2H, dd, $J = 8, 1.6$, ArH), 7.4-7.3 (6H, m, ArH), 7.00 (1H, dd, $J = 3.6, 1.2$ Hz, ArH), 6.97 (1H, dd, $J = 4.8, 4$ Hz, ArH), 4.05 (1H, d, $J = 15.6$ Hz, $-\text{CH}_2$), 3.81 (1H, d, $J = 15.2$ Hz, $-\text{CH}_2$); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ (ppm): 43.23 (C3), 95.19 (C2), 101.78 (C3a), 112.72, 117.29, 123.10, 124.32, 125.58 (CH^2), 126.69, 127.07, 127.09, 128.72, 128.81 (CH^2), 132.81, 143.60 (C ipso), 147.67 (C ipso), 155.36 (C5a), 160.43 (C4), 164.97 (C9b); **LC/MS** m/z (%): 346.99 (MH^+ , 100); **Anal. Calcd.** for $\text{C}_{21}\text{H}_{14}\text{O}_3\text{S}$: C 72.81, H 4.07, S 9.2. **Found:** C 72.02, H 4.27, S 8.70.

4.3.1.2. 2-(4-Methylphenyl)-2-(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (**4**)

Light pink solid; mp: $135\text{--}136^\circ\text{C}$; **IR** (ν_{max} , KBr): 3025, 1713 (C=O), 1647 (C=C), 1406, 1025 (C-O-C), 707 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.81 (1H, dd, $J = 7.6, 1.6$ Hz, ArH), 7.58 (1H, td, $J = 7.8, 1.6$ Hz, ArH), 7.39 (2H, d, $J = 8.4$ Hz, ArH), 7.39-7.37 (1H, m, ArH), 7.33-7.30 (2H, m, ArH), 7.2 (2H, d, $J = 8.8$ Hz, ArH), 7.00 (1H, dd, $J = 3.6, 1.2$ Hz, ArH), 6.96 (1H, dd, $J = 5.2, 3.6$ Hz, ArH), 4.00 (1H, d, $J = 15.6$ Hz, $-\text{CH}_2$), 3.80 (1H, d, $J = 15.2$ Hz, $-\text{CH}_2$), 2.36 (3H, CH_3); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ (ppm): 21.35 (Me), 43.18 (C3), 95.29 (C2), 101.80 (C3a), 112.76, 117.27, 123.11, 124.28, 125.57 (CH^2), 126.56, 126.98, 127.04, 129.45 (CH^2), 132.76, 138.64 (C ipso), 140.66 (C ipso), 147.88 (C ipso),

155.35 (C5a), 160.48 (C4), 165.00 (C9b); **LC/MS** m/z (%): 361.42 (MH⁺, 100); **Anal. Calcd. for** C₂₂H₁₆O₃S: C 73.31, H 4.47, S 8.90. **Found.:** C 73.04, H 4.51, S 9.06.

4.3.1.3. *2-(4-Fluorophenyl)-2-(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (5)*

Colorless solid; mp: 115-116 °C; **IR** (ν_{\max} , KBr): 3119, 3072, 2953, 1712 (C=O), 1644 (C=C), 1028 (C-O-C), 722 cm⁻¹; **¹⁹F NMR** (376 MHz, CDCl₃), δ (ppm): -113.65; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.80 (1H, dd, J = 8.0, 1.6 Hz, ArH); 7.59 (1H, td, J = 7.8, 1.2 Hz, ArH), 7.49 (2H, m, ArH), 7.40 (1H, d, J = 8.4, ArH), 7.34 (1H, dd, J = 4.8, 1.2 Hz, ArH), 7.31 (1H, d, J = 7.2 Hz, ArH), 7.08 (2H, td, J = 8.4, 2.0 Hz, ArH), 7.00 (1H, dd, J = 3.6, 1.2 Hz, ArH), 6.98 (1H, dd, J = 5.2, 3.6 Hz, ArH), 4.03 (1H, d, J = 15.2 Hz, -CH₂), 3.76 (1H, d, J = 15.2 Hz, -CH₂); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 43.29 (C3), 94.79 (C2), 101.72, 112.64, 115.7 (CH*2, d, 2J = 23.1 Hz), 117.31, 123.03, 124.34, 126.67, 127.13, 127.21, 127.60(CH*2, d, 3J = 8.4 Hz), 132.87, 139.50 (C, d, 4J = 3.1 Hz), 147.44, 155.38 (C5a), 160.27 (C4), 162.8 (C, d, 1J = 246.3 Hz), 164.81 (C9b); **LC/MS**, (ESI, m/z) : 365.37 (MH⁺, 100); **Anal. Calcd. For** C₂₁H₁₃FO₃S: C 69.22, H 3.60, S 8.80. **Found:** C 70.01, H 3.81, S 8.97.

4.3.1.4. *2-Methyl-2-(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (6)^{2e}*

Light yellow solid; mp: 79-80 °C; **IR** (ν_{\max} , KBr): 3105, 1714 (C=O), 1641 (C=C), 1604, 1280, 1026 (C-O-C), 750 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.69 (1H, dd, J = 7.6; 1.6, ArH), 7.56 (1H, td, J = 8.0; 1.6 Hz, ArH), 7.38 (1H, d, J = 9.2, ArH), 7.30 (1H, dd, J = 5.2; 1.2, ArH), 7.27 (1H, dd, J = 7.6, 0.8 Hz, ArH), 7.12 (1H, dd, J = 3.6; 1.2, ArH), 7.00 (1H, dd, J = 5.2; 3.6 Hz, ArH), 3.57 (1H, d, J = 15.6 Hz, -CH₂), 3.34 (1H, d, J = 15.2 Hz, -CH₂), 2.01 (3H, CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 29.29 (CH₃), 42.11 (C3), 92.57 (C2), 101.49 (C3a), 112.84, 117.19, 123.11, 124.17, 124.27, 125.94, 127.23, 132.65, 147.84 (C-ipso), 155.28 (C5a), 160.69 (C4), 165.09 (C9b); **LC/MS** (ESI, m/z): 285.70 (MH⁺, 100); **Anal. Calcd. For** C₁₆H₁₂O₃S: C 67.59, H 4.25, S 11.28. **Found:** C 67.41, H 3.98, S 11.33.

4.3.1.5. *2, 2-Di(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (7)*

Light purple solid; mp: 121-122 °C; **IR** (ν_{\max} , KBr): 3086, 3003, 1720 (C=O), 1649 (C=C), 1406, 1029 (C-O-C), 748 cm⁻¹; **¹H NMR** (CDCl₃), δ (ppm): 7.77 (1H, dd, J = 7.6, 1.6 Hz, ArH), 7.58 (1H, td, J = 7.6, 1.6 Hz, ArH), 7.38 (1H, dd, J = 8.4, 0.8 Hz, ArH), 7.35 (2H, dd, J = 4.8, 1.2, ArH), 7.31 (1H, td, J = 7.6, 1.2 Hz, ArH), 7.12 (2H, dd, J = 3.6, 1.2 Hz, ArH), 7.01 (2H, dd, J = 5.2, 4.0 Hz, ArH), 3.96 (2H, s, H3);

¹³C NMR (100 MHz, CDCl₃), δ (ppm): 44.39 (C3), 93.25 (C2), 101.71 (C3a), 112.66, 117.26, 123.15, 124.33, 126.37 (CH^{*}2), 126.83 (CH^{*}2), 127.18 (CH^{*}2), 132.85, 146.86 (C^{*}2), 155.36 (C5a), 160.29 (C4), 164.66 (C9b); **LC/MS** (ESI, m/z): 353.70 (MH⁺, 100); **Anal. Calcd. for** C₁₉H₁₂O₃S₂: C 64.75, H 3.43, S 18.20. **Found:** C 64.15, H 3.56 S 17.41.

4.3.1.6 4-Hydroxy-3-[2-phenyl-2-(2-thenyl)vinyl]-2H-chromen-2-one (**8**)

E:Z ratio = 1:1.70. Pale yellow solid; mp : 193-194 °C; **IR** (ν_{max}, KBr): 3078, 3005, 2978, 1658 (C=O), 1604 (C=C), 1541, 1083 (C-O-C), 700 cm⁻¹; **¹H NMR** (400 MHz, DMSO-*d*₆), δ (ppm): 7.91 (1H, dd, *J* = 8.0, 1.2 Hz, ArH) [7.80 (1H, dd, *J* = 8.8, 1.6 Hz, ArH)], 7.63 (1H, td, *J* = 7.8, 1.2 Hz, ArH) [7.56 (1H, td, *J* = 7.8, 1.6 Hz, ArH)], 7.46 (2H, dd, *J* = 4.8, 1.2 Hz, ArH) [7.53 (2H, dd, *J* = 5.2, 1.2 Hz, ArH)], 7.37 (1H, dd, *J* = 7.6 Hz, ArH) [7.41 (1H, dd, *J* = 7.6, 1.2 Hz, ArH)], 7.30-7.22 (5H+5H, m, ArH), 7.06 (1H, dd, *J* = 5.2, 3.6 Hz, ArH) [6.96 (1H, dd, *J* = 5.2, 3.6 Hz, ArH)], 6.91 (1H, dd, *J* = 3.6, 1.2 Hz, ArH) [6.83 (1H, dd, *J* = 3.6, 1.2 Hz, ArH)], 6.68 (1H, s, alkene) [6.40 (1H, s, alkene)]; **¹³C NMR** (100 MHz, DMSO-*d*₆), δ (ppm): 103.21 (103.50), 116.59 (116.73), 116.77 (116.85), 117.03, 119.54, 124.13 (124.27), 124.56 (124.65), 126.70 (126.85), 127.27 (127.66), 128.35 (128.50), 128.61 (128.80), 129.01 (129.13), 129.40, 132.72 (132.91), 140.12 (140.21), 140.91, 141.91 (143.01), 146.70, 152.81 (153.01), 161.14 (161.20), 161.25 (161.76); **LC/MS** m/z (%): 347.14 (MH⁺, 100); **Anal. Calcd. for** C₂₁H₁₄O₃S: C 72.81, H 4.07, S 9.2. **Found:** C 72.70, H 3.98, S 9.02.

4.3.1.7 4-Hydroxy-3-[2-(4-methylphenyl)-2-(2-thenyl)vinyl]-2H-chromen-2-one (**9**)

E:Z ratio = 1:4.25. Pale orange solid; mp: 145-146 °C; **IR** (ν_{max}, KBr): 3079, 2990, 1667 (C=O), 1609 (C=C), 1550, 1494, 1245, 1083 (C-O-C), 775, 700 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.62 (1H, dd, *J* = 8.0, 1.6 Hz, ArH), 7.50 (1H, td, *J* = 7.8, 1.6 Hz, ArH), 7.38-7.15 (7H+7H, m, ArH), 7.04 (1H, td) [6.97 (1H, dd, *J* = 5.2, 3.6 Hz)], 6.89 (1H, dd, *J* = 3.6, 1.2 Hz) [6.09 (1H, dd)], 6.62 (1H, s, alkene) [6.81 (1H, s, alkene)], 6.25 (1H, s, OH)[6.25 (1H, s, OH)], 2.37 (3H, s) [2.35 (3H, s)]; **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 21.40 (21.38), 103.19 (103.48), 115.08 (115.12), 116.42 (116.53), 116.72, 118.75, 123.74 (123.84), 123.90 (124.03), 126.18, 127.18, 127.46 (127.67), 128.39 (128.58), 129.08 (128.90), 130.18 (130.06), 132.08 (132.27), 134.70, 139.00 (138.82), 139.77 (139.71), 145.68, 152.62 (152.77), 157.20 (158.03), 162.95 (162.84); **LC/MS** m/z (%): 361.43 (MH⁺, 100); **Anal. Calcd. for** C₂₂H₁₆O₃S: C 73.31, H 4.47, S 8.90. **Found:** C 73.12, H 4.21, S 9.03.

4.3.1.8 4-Hydroxy-3-[2-(4-fluorophenyl)-2-(2-thenyl)vinyl]-2H-chromen-2-one (10)

E:Z ratio = 2:3. Pale orange solid; mp: 187-188 °C; **IR** (ν_{\max} , KBr): 3104, 3074, 2990, 1667 (C=O), 1602 (C=C), 1494, 1213, 1153, 1083 (C-O-C), 747, 701 cm^{-1} ; **^{19}F NMR** (376 MHz, CDCl_3), δ (ppm): -85.00, -115.51; **^1H NMR** (400 MHz, CD_3COCD_3), δ (ppm): 7.85 (1H, dd, $J = 7.6, 1.6$ Hz, ArH) [7.77 (1H, dd, $J = 7.6, 1.6$ Hz, ArH)], 7.64 (1H, td, $J = 8.4, 1.2$ Hz, ArH) [7.58 (1H, td, $J = 8.4, 1.2$ Hz, ArH)], 7.47 (1H, d, $J = 5.2$, ArH) [7.37 (1H, i, $J = 5.2$, ArH)], 7.50 (2H, td, $J = 7.0, 2.4$ Hz, ArH) [7.40 (2H, td, $J = 7.0, 2.0$ Hz, ArH)], 7.34 (1H, d, $J = 8.0$ Hz, ArH) [7.30 (1H, d, $J = 8.0$ Hz, ArH)], 7.26 (1H, d, $J = 7.6$ Hz, ArH), 7.17 (2H, td, $J = 8.4, 2.0$ Hz, ArH) [7.07 (2H, td, $J = 8.8, 2.0$ Hz, ArH)], 7.04 (1H, dd, $J = 4.8, 4.0$ Hz, ArH) [6.98 (1H, t, $J = 4$ Hz, ArH)], 6.94 (1H, d, $J = 4$ Hz, ArH) [6.89 (1H, d, $J = 3.2$ Hz)], 6.66 (1H, s) [6.41 (1H, s, alkene)]; **^{13}C NMR** (100 MHz, CD_3COCD_3), δ (ppm): 103.10, 115.12 (CH*2, d, $^2J = 21.3$ Hz) [114.97 (CH*2, d, $^2J = 21.4$ Hz)], 115.98, 116.32 (116.28), 116.42, 118.57, 123.59 (123.79), 124.01 (124.07), 126.19, 126.71 (126.86), 127.71 (127.33), 129.42, 131.44 (CH*2, d, $^3J = 8.4$ Hz) [130.68 (CH*2, d, $^3J = 8.4$ Hz)], 132.25 (132.42), 141.14 (135.67), 146.19, 153.09, 160.92 (159.66), 162.65 (C, d, $^1J = 246.3$ Hz); **LC/MS**, (ESI, m/z) : 365.14 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{21}\text{H}_{13}\text{FO}_3\text{S}$: C 69.22, H 3.60, S 8.80. **Found:** C 69.03, H 3.42, S 8.67.

4.3.1.9 (*E*)-4-Hydroxy-3-[2-(2-thenyl)-1-propenyl]-2H-chromen-2-one (11)

Yellow solid; mp: 121-122 °C; **IR** (ν_{\max} , KBr): 3079, 2990, 1667 (C=O), 1609 (C=C), 1550, 1494, 1245, 1083 (C-O-C), 775, 700 cm^{-1} ; **^1H NMR** (400 MHz, $\text{DMSO}-d_6$), δ (ppm): 7.93 (1H, dd, $J = 7.6, 1.6$ Hz, ArH), 7.60 (1H, td, $J = 7.6, 1.6$ Hz, ArH), 7.45 (1H, dd, $J = 5.2, 1.2$ Hz, ArH), 7.36 (1H, d, $J = 8.4$ Hz, ArH), 7.34 (1H, td, $J = 7.6, 1.2$ Hz, ArH), 7.23 (1H, dd, $J = 4.0, 1.2$ Hz, ArH), 7.05 (1H, dd, $J = 4.8, 3.6$ Hz, ArH), 6.44 (1H, d, $J = 1.2$ Hz, alkene), 1.94 (3H, d, $J = 1.2$ Hz, CH_3); **^{13}C NMR** (100 MHz, $\text{DMSO}-d_6$), δ (ppm): 18.81, 102.81, 116.10, 116.84, 116.88, 124.28, 124.68, 124.82, 125.82, 128.43, 132.83, 135.08, 146.81, 152.92, 160.93, 161.89; **LC/MS** (ESI, m/z): 285.60 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{16}\text{H}_{12}\text{O}_3\text{S}$: C 67.59, H 4.25, S 11.28. **Found:** C 67.41, H 4.19, S 11.07.

4.3.1.10 3-[2,2-Di(2-thenylvinyl)]-4-hydroxy-2H-chromen-2-one (12)

Purple solid; mp: 194-195 °C; **IR** (ν_{\max} , KBr): 1668 (C=O), 1602 (C=C), 1492, 1217 (C-O-C), 715 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3), δ (ppm): 7.70 (1H, dd, $J = 7.6, 0.4$ Hz, ArH), 7.53 (1H, td, $J = 7.8, 1.2$ Hz, ArH), 7.39 (1H, d, $J = 4.8$ Hz, ArH), 7.32-7.22 (4H, m, ArH), 7.09 (1H, dd, $J = 4.4, 1.2$ Hz, ArH), 7.07

(1H, dd, $J = 4.4, 1.2$ Hz, ArH), 7.00 (1H, td, $J = 4.4, 0.8$ Hz, ArH), 6.83 (1H, s, alkene), 6.50 (1H, s, OH) [disappeared after shaking with D₂O]; ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 103.20, 115.30, 116.75, 118.56, 124.07, 124.29, 126.73, 127.56, 127.73, 127.91, 128.97, 130.20, 132.17, 132.59, 138.58, 145.30, 152.96, 158.53, 162.99; **LC/MS** (ESI, m/z): 353.70; **Anal. Calcd. for** C₁₉H₁₂O₃S₂: C 64.75, H 3.43, S 18.20. **Found:** C 64.51, H 3.56, S 18.01.

4.3.1.11 2,2-Diphenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (**3aj**)^{11f}

Colorless solid; mp: 175-176 °C; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.71 (1H, d, $J = 7.6$ Hz, ArH), 7.64 (1H, t, $J = 7.6$ Hz, ArH), 7.51-7.35 (12H, m, ArH), 3.96 (2H, s, -CH₂); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 41.8 (C3), 98.1 (C2), 102.4, 113, 2, 117.8, 123.5, 124.8, 126.6 (CH^{*}2), 129.0 (CH^{*}4), 129.4 (CH^{*}4), 133.2, 144.5 (C^{*}2), 156.1 (C5a), 166.1 (C9b), 161.3 (C4).

4.3.1.12 3-(2,2-Diphenylvinyl)-4-hydroxy-2H-chromen-2-one (**4aj**)

Colorless solid; mp: 204-205 °C; **IR** (ν_{\max} , KBr): 3007, 2970, 1662 (C=O), 1600 (C=C), 1541, 1490, 1240, 1076, 754 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.61 (1H, dd, $J = 8.0, 1.6$ Hz, ArH), 7.51 (1H, td, $J = 8.0, 1.6$ Hz, ArH), 7.36-7.30 (11H, m, ArH), 7.20 (1H, d, $J = 7.6, 0.8$ Hz, ArH), 6.74 (1H, s, alkene), 6.44 (1H, s, OH); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 103.57, 115.03, 116.46, 118.69, 123.74, 123.97, 128.24 (CH^{*}2), 128.37 (CH^{*}2), 128.52, 129.31, 129.45 (CH^{*}4), 132.14, 138.61, 141.71, 146.60, 152.68, 157.08, 163.03; **LC/MS** (ESI, m/z): 341.70 (MH⁺, 100); **Anal. Calcd. for** C₂₃H₁₆O₃: C 81.16; H 4.74. **Found:** C 80.98, H 4.59.

4.3.1.13 6-Methyl-2-phenyl-2-(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]pyran-4-one (**13**)

Yellow oil; **IR** (ν_{\max} , KBr): 3090, 2924, 1732 (C=O), 1643 (C=C), 1585, 1272 (C-O-C), 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.40-7.42 (2H, m, ArH), 7.38-7.32 (3H, m, ArH), 7.28 (1H, dd, $J = 4.0, 2.4$ Hz, ArH), 6.93 (2H, dd, $J = 4.0, 1.2$ Hz, ArH), 6.06 (1H, s, alkene), 3.87 (1H, d, $J = 15.2$ Hz, -CH₂), 3.63 (1H, d, $J = 15.2$ Hz, -CH₂), 2.25 (3H, d, $J = 0.8$ Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 20, 40 (CH₃), 41.85 (C3), 94.35 (C2), 95.68, 98.75, 125.26 (CH^{*}2), 126.16, 126.61, 126.73, 128.30, 128.47 (CH^{*}2), 143.43, 147.58, 161.57 (C4), 165.73 (C6), 169.35 (C7a); **LC/MS** (ESI, m/z): 311.11 (MH⁺, 100); **Anal. Calcd. for** C₁₈H₁₄O₃S: C 69.66; H 4.55; S 10.33. **Found:** C 69.53, H 4.44, S 10.21.

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3 4.3.1.14 6-Methyl-2-(4-methylphenyl)-2-(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]pyran-4-one (**14**)
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6 Yellow oil; **IR** (ν_{\max} , KBr): 3090, 3030, 2960, 1732 (C=O), 1716, 1643 (C=C), 1585, 1272, 1172, 975, 700
7 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.31 (2H, d, $J = 8.0$ Hz, ArH), 7.27 (1H, td, $J = 3.6$ Hz, ArH),
8 7.17 (2H, d, $J = 8$ Hz, ArH), 6.92 (2H, d, $J = 3.2$ Hz, ArH), 6.04 (1H, s, alkene), 3.85 (1H, d, $J = 15.2$ Hz,
9 $-\text{CH}_2$), 3.63 (1H, d, $J = 15.2$ Hz, $-\text{CH}_2$), 2.34 (3H, CH_3), 2.24 (3H, CH_3); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ
10 (ppm): 20.70 (CH_3), 21.34 (CH_3), 42.08 (C3), 94.69 (C2), 96.00 (C7), 99.04 (C3a), 125.52 (CH^*2),
11 126.36, 126.82, 126.99, 129.39 (CH^*2), 138.43, 140.74, 148.01, 161.91 (C4), 165.95 (C6), 169.65
12 (C7a); **LC/MS** (ESI, m/z): 325.31 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}$: C 70.35, H 4.97, S 9.88.
13 **Found:** C 70.20, H 4.82, S 9.73.
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22 4.3.1.15 6-Methyl-2-(4-fluorophenyl)-2-(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]pyran-4-one (**15**)
23
24

25 Yellow oil; **IR** (ν_{\max} , KBr): 3111, 3095, 2985, 1665 (C=O), 1631 (C=C), 1573, 1407, 1005 (C-O-C), 709
26 cm^{-1} ; **$^{19}\text{F NMR}$** (376 MHz, CDCl_3), δ (ppm): -116.41; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.40 (2H, m,
27 ArH), 7.31 (1H, dd, $J = 5.2$; 1.2 Hz, ArH), 7.05 (2H, td, $J = 8.6$; 2 Hz, ArH), 6.96-6.92 (2H, m, ArH), 6.07
28 (1H, s, alkene), 3.86 (1H, d, $J = 15.2$ Hz, $-\text{CH}_2$), 3.59 (1H, d, $J = 14.8$ Hz, $-\text{CH}_2$), 2.27 (3H, CH_3); **^{13}C**
29 **NMR** (100 MHz, CDCl_3), δ (ppm): 20.68 (CH_3), 42.15 (C3), 94.15 (C2), 95.88 (C7), 98.91 (C3a), 115.62
30 (CH^*2 , d, $^2J = 23.1$ Hz), 126.48, 127.06 (CH^*2), 127.51 (CH^*2 , d, $^3J = 8.4$ Hz), 139.50 (C, d, $^4J = 3.1$
31 Hz), 147.53 (C ipso), 162.65 (C, d, $^1J = 246.1$ Hz), 161.75 (C4), 166.16 (C6), 169.49 (C7a); **LC/MS**
32 (ESI, m/z): 329.28 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{18}\text{H}_{13}\text{FO}_3\text{S}$: C 65.84, H 3.99, S 9.77. **Found:** C 65.63,
33 H 3.69, S 9.59.
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43 4.3.1.16 4-Hydroxy-6-methyl-3-[2-phenyl-2-(2-thenyl)vinyl]-2H-pyran-2-one (**16**)
44
45

46 *E:Z* ratio = 1:1.25. Brown solid; mp: 190-191 °C; **IR** (ν_{\max} , KBr): 3109 (O-H), 3079, 3030, 2960, 1668
47 (C=O), 1643 (C=C), 1575, 1407, 1254, 709 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, $\text{DMSO-}d_6$), δ (ppm): 11.33 (1H, s,
48 OH), 7.45 (1H, dd, $J = 5.2$, 1.2 Hz, ArH), 7.30-7.26 (3H, m, ArH), 7.16 (2H, dd, $J = 8.0$, 1.6 Hz, ArH),
49 7.01 (1H, dd, $J = 5.2$, 3.6 Hz, ArH), 6.82 (1H, dd, $J = 3.2$, 1.2 Hz, ArH), 6.50 (1H, s, alkene), 5.86 (1H,
50 d, $J = 0.8$ Hz, alkene), 2.11 (3H, CH_3); **$^{13}\text{C NMR}$** (100 MHz, $\text{DMSO-}d_6$), δ (ppm): 19.96, 99.69, 100.47,
51 117.90, 126.01, 126.19, 128.09, 128.28, 128.49 (CH^*2), 129.36 (CH^*2), 138.36, 141.04, 147.42, 161.89,
52 163.39, 166.02; **LC/MS** (ESI, m/z): 311.32 (MH, 100), 333.12 ($\text{M}^+ + \text{Na}$); **Anal. Calcd. for** $\text{C}_{18}\text{H}_{14}\text{O}_3\text{S}$: C
53 69.66; H 4.55; S 10.33. **Found:** C 69.49, H 4.28, S 10.57.
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3 4.3.1.17 4-Hydroxy-6-methyl-3-[2-(4-methylphenyl)-2-(2-thenyl)vinyl]2H-pyran-2-one (17)
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5

6 *E:Z* ratio = 1:2. Brown solid; mp: 163-164 °C; **IR** (ν_{\max} , KBr): 3116, 2996, 2917, 1666 (C=O), 1634 (C=C),
7
8 1574, 1407, 1254, 1050 (C-O-C), 975, 707 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.28 (2H, d, J =
9
10 7.6 Hz, ArH) [7.25 (2H, d, J = 8.0 Hz, ArH)], 7.24 (1H, dd, J = 3.6, 0.8 Hz, ArH), 7.2 (1H, d, J = 8.0 Hz,
11
12 ArH) [7.13 (1H, d, J = 8.8 Hz, ArH)], 7.06-7.04 (1H, m, ArH), 6.96 (1H, dd, J = 5.2, 4.0 Hz, ArH) [7.39
13
14 (1H, dd, J = 3.6, 2.0 Hz, ArH)], 6.86 (1H, dd, J = 3.2, 1.2 Hz, ArH), 6.69 (1H, s, alkene) [6.51(1H, s,
15
16 alkene)], 5.70 (1H, s, OH) [6.35(1H, s, OH)], 5.64 (1H, s, alkene) [5.76 (1H, s, alkene)], 2.38 (3H, CH_3)
17
18 [2.37], 2.19 (3H, CH_3) [2.24]; **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ (ppm): 19.84 (19.91), 21.42 (21.22), 100.09
19
20 (100.13), 100.81 (101.10), 116.62 (118.71), 125.84, 126.79, 127.40 (127.54), 128.29 (128.18), 129.09
21
22 (128.83), 130.03 (129.73), 135.00, 138.57 (138.05), 138.75 (139.14), 139.53 (140.09), 145.87, 161.53
23
24 (161.92), 162.08 (162.95), 164.79 (164.70); **LC/MS** (ESI, m/z): 325.41 (MH^+ , 100); **Anal. Calcd. for**
25
26 $\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}$: C 70.35, H 4.97, S 9.88. **Found**: C 70.21, H 4.78, S 9.63.
27

28 4.3.1.18 4-Hydroxy-6-methyl-3-[2-(4-fluorophenyl)-2-(2-thenyl)vinyl]2H-pyran-2-one (18)
29

30 *E:Z* ratio = 1:1.5. Brown solid; mp: 188-189 °C; **IR** (ν_{\max} , KBr): 3111, 3095, 3052, 2915, 1665 (C=O),
31
32 1631 (C=C), 1573, 1407, 1219, 1005, 843, 709 cm^{-1} ; **$^{19}\text{F NMR}$** (376 MHz, CDCl_3), δ (ppm): -116.41; **$^1\text{H-}$**
33
34 **NMR** (400 MHz, CDCl_3), δ (ppm): 7.42-7.28 (5H, m, ArH), [7.09-7.02 (5H, m)], 6.97 (1H, td, J = 4.6, 1.2
35
36 Hz, ArH), 6.83 (1H, d, J = 3.6 Hz), 6.66 (1H, s) [6.49 (1H, s, alken)], 5.83 (1H, s, OH) [6.01 (1H, s, OH)],
37
38 5.67 (1H, s, alkene) [5.76 (1H, s, alkene)], 2.20 (3H, CH_3) [2.25 (3H, CH_3)]; **$^1\text{H NMR}$** (400 MHz,
39
40 CD_3COCD_3); δ (ppm): 9.7 (1H, s, OH), 7.39 (1H, dd, J = 4.8, 1.2 Hz, ArH), 7.29 (2H, m), 7.06 (2H, m),
41
42 7.00 (1H, dd, J = 5.2, 3.6 Hz, ArH), 6.83 (1H, dd, J = 3.6, 1.2 Hz), 6.59 (1H, s, alkene), 5.86 (1H, d, J =
43
44 0.8 Hz, alkene), 2.12 (3H, CH_3); **$^{13}\text{C NMR}$** (100 MHz, CD_3COCD_3), δ (ppm): 19.02 (CH_3), 99.80 (100.11),
45
46 114.81 (CH^*2 , d, 2J = 21.4 Hz), 117.24, 125.48, 125.94, 127.61, 131.34 (CH^*2 , d, 3J = 8.4 Hz), 136.83
47
48 (C, d, 4J = 3.1 Hz), 138.64, 146.92, 161.88, 162.42 (C, d, 1J = 243.1 Hz), 162.82, 164.64; **LC/MS** (ESI,
49
50 m/z): 329.36 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{18}\text{H}_{13}\text{FO}_3\text{S}$: C 65.84, H 3.99, S 9.77. **Found**: C 65.61, H
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52 3.80, S 9.67.
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3 4.3.1.19 2-Phenyl-2-(2-thenyl)-1,2-dihydro-4H,11H-furo[2,3:4,5]pyrano[3,2-c]chromen-4,11-
4
5 dione (19)

6
7 Yellow solid; mp: 201-201 °C; IR (ν_{\max} , KBr): 1726 (C=O), 1631 (C=C), 1558, 1273, 761, 700 cm^{-1} ; **¹H**
8
9 **NMR** (400 MHz, CDCl_3), δ (ppm): 8.13 (1H, $J = 7.6$ Hz, ArH), 7.7 (1H, t, $J = 8.0$ Hz, ArH), 7.59 (2H, d, J
10
11 = 7.6 Hz, ArH), 7.42-7.33 (6H, m, ArH), 6.98-6.90 (2H, m, ArH), 4.00 (1H, d, $J = 15.6$ Hz, $-\text{CH}_2$), 3.79
12
13 (1H, d, $J = 15.6$ Hz, $-\text{CH}_2$); **¹³C NMR** (100 MHz, CDCl_3), δ (ppm): 41.63 (C3), 95.94 (C2), 97.60, 101.75,
14
15 113.56, 117.78, 124.46, 125.87 (CH²), 125.96, 127.57, 127.78, 128.62, 129.16, 129.27 (CH²), 135.72,
16
17 143.87, 147.23, 153.75, 155.77 (C11), 157.58 (C4), 164.46 (C5a), 165.73 (C11b); **LC/MS** (ESI, m/z):
18
19 415.18 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{24}\text{H}_{14}\text{O}_5\text{S}$: C 69.55, H 3.40, S 7.74. **Found:** C 68.98, H 3.71, S
20
21 6.98.
22
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24 4.3.1.20 2-(4-Methylphenyl)-2-(2-thenyl)-1,2-dihydro-4H,11H-furo[2,3:4,5]pyrano[3,2-
25
26 c]chromen-4,11-dione (20)

27
28 Yellow solid; mp: 186-187 °C; IR (ν_{\max} , KBr): 3089, 2952, 1725 (C=O), 1632 (C=C), 1559, 1274, 1104
29
30 (C-O-C), 761, 710 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3), δ (ppm): 8.11 (1H, dd, $J = 8.8, 2.0$ Hz, ArH), 7.68
31
32 (1H, td, $J = 8.8; 2.0$ Hz, ArH), 7.45 (2H, d, $J = 8.4$ Hz, ArH), 7.42-7.38 (2H, m, ArH), 7.32 (1H, dd, $J =$
33
34 5.2; 1.2 Hz, ArH), 7.2 (2H, d, $J = 8.4$ Hz, ArH), 6.97 (1H, dd, $J = 3.6, 1.2$ Hz, ArH), 6.94 (1H, dd, $J = 5.2;$
35
36 3.6 Hz, ArH), 3.95 (1H, d, $J = 15.6$ Hz, $-\text{CH}_2$), 3.76 (1H, d, $J = 15.6$ Hz, $-\text{CH}_2$), 2.36 (3H, CH_3); **¹³C NMR**
37
38 (100 MHz CDCl_3), δ (ppm): 21.13 (Me), 41.76 (C3), 96.26 (C2), 97.08, 101.62, 112.96, 117.32, 124.27,
39
40 125.13, 125.42 (CH²), 126.86, 126.94, 127.01, 129.25 (CH²), 134.91, 138.49, 139.81, 146.91, 153.60,
41
42 155.31 (C4), 157.50 (C4), 164.13 (C5a), 165.81 (C11b); **LC/MS**, (ESI, m/z): 429.34 (MH^+ , 100); **Anal.**
43
44 **Calcd. for** ($\text{C}_{25}\text{H}_{16}\text{O}_5\text{S}$): C 70.08, H 3.76, S 7.48. **Found:** C 70.92, H 3.41, S 8.24.
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47 4.3.1.21 2-(4-Fluorophenyl)-2-(2-thenyl)-1,2-dihydro-4H,11H-furo[2,3:4,5]pyrano[3,2-c]chromen-
48
49 4,11-dione (21)

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51 Yellow solid; mp: 209-210 °C; IR (ν_{\max} , KBr): 3099, 2983, 1728 (C=O), 1635 (C=C), 1560, 1160 (C-O-
52
53 C), 755 cm^{-1} ; **¹⁹F-NMR** (376 MHz, CDCl_3), δ (ppm): -113.508; **¹H NMR** (400 MHz, CDCl_3), δ (ppm): 8.13
54
55 (1H, dd, $J = 8.4; 1.6$ Hz, ArH), 7.71 (1H, td, $J = 8.0; 1.6$, ArH), 7.55-7.57 (2H, m, ArH), 7.40-7.43 (2H,
56
57 m, ArH), 7.3 (1H, dd, $J = 4.8; 1.6$ Hz, ArH), 7.08-7.12 (2H, m, ArH), 6.95-6.98 (2H, m, ArH), 3.99 (1H, d,
58
59 $J = 15.6$ Hz, $-\text{CH}_2$), 3.75 (1H, d, $J = 15.6$ Hz, $-\text{CH}_2$); **¹³C NMR** (100 MHz, CDCl_3), δ (ppm): 41.88 (C3),
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3 95.71 (C2), 96.99, 101.48, 112.92, 115.58 (CH*2, d, $^2J = 22.1$ Hz), 117.36, 124.30, 125.19, 127.01
4 (CH*2, d, $^3J = 8.4$ Hz), 127.27, 127.47, 127.52, 135.03, 138.62, 146.46, 153.62, 155.30 (C11), 157.37
5 (C4), 161.33 (C, d, $^1J = 246.2$ Hz), 163.87 (C5a), 165.67 (C11b); **LC/MS** (ESI, m/z): 433.80 (MH⁺, 100);
6
7
8 **Anal. Calcd. for** (C₂₄H₁₃FO₅S): C 66.66, H 3.03, S 7.42. **Found:** C 66.49, H 3.21, S 7.64.

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11 4.3.1.22 *5-Ethyl-7-hydroxy-9-phenyl-9-(2-thenyl)-5,8,9,10a-tetrahydro-6H-furo[3',2':5,*
12 *6]pyrano[3,2-c]quinolin-6-one (22)*

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16 Yellow solid; mp: 175-176 °C; **IR** (ν_{\max} , KBr): 3014, 1728 (C=O), 1654 (C=O), 1600 (C=C), 1556, 752,
17 740, 700 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 8.29 (1H, dd, $J = 8.4$; 1.2 Hz, ArH), 7.69 (1H, td, J
18 = 8.4; 1.2 Hz, ArH), 7.63 (2H, dd, $J = 7.6$; 1.6 Hz, ArH), 7.41-7.32 (5H, m, ArH), 7.29 (1H, dd, $J = 5.2$,
19 = 8.4; 1.2 Hz, ArH), 7.00 (1H, dd, $J = 3.6$; 1.2 Hz, ArH), 6.93 (1H, dd, $J = 5.2$; 3.6 Hz, ArH), 4.39 (2H, q, $J =$
20 7.2 Hz, -CH₂), 3.99 (1H, d, $J = 15.6$ Hz, -CH₂), 3.77 (1H, d, $J = 15.6$ Hz, -CH₂), 1.40 (3H, t, $J = 7.2$ Hz,
21 CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 12.96, 37.71, 41.83, 95.69, 101.63, 101.74, 113.77, 114.66,
22 122.88, 125.22, 125.74 (CH*2), 126.96, 127.00, 127.04, 128.54, 128.77 (CH*2), 133.93, 139.50, 143.60,
23 147.55, 157.09, 158.76, 161.12, 167.13; **LC/MS** (ESI, m/z): 442.70 (MH⁺, 100); **Anal. Calcd. for**
24 C₂₆H₁₉NO₄S: C 70.73, H 4.34, N 3.17 S 7.26. **Found:** C 70.30, H 4.11, N 3.52, S 7.06.

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32 4.3.1.23 *5-Ethyl-2-(4-methylphenyl)-2-(2-thenyl)-1,5-dihydro-4H-furo[2',3':4,5]pyrano[3, 2-*
33 *c]quinolin-4,11(2H)-dione (23)*

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36
37
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39 Yellow solid; mp: 190-191 °C; **IR** (ν_{\max} , KBr): 3089, 2952, 1721 (C=O), 1652 (C=O), 1610 (C=C), 1104
40 (C-O-C), 761 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 8.28 (1H, dd, $J = 8.4$, 1.6 Hz, ArH), 7.68 (1H,
41 td, $J = 7.8$, 1.6 Hz, ArH), 7.49 (2H, dd, $J = 8.8$, 2.0 Hz, ArH), 7.40 (2H, d, $J = 8.4$ Hz, ArH), 7.28 (1H,
42 dd, $J = 5.2$, 1.2 Hz, ArH), 7.20 (2H, d, $J = 7.6$), 6.99 (1H, dd, $J = 3.6$; 1.2 Hz, ArH), 6.93 (1H, dd, $J = 5.2$;
43 3.6 Hz, ArH), 4.39 (2H, q, $J = 7.2$ Hz, CH₂), 3.97 (1H, d, $J = 15.2$ Hz, -CH₂), 3.76 (1H, d, $J = 15.2$ Hz, -
44 CH₂), 2.36 (3H, s, CH₃), 1.39 (3H, t, $J = 7.2$ Hz, CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 12.73,
45 21.12, 37.48, 41.55, 95.56, 101.55, 102.42, 113.53, 114.43, 122.64, 124.94, 125.46 (CH*2), 126.63,
46 126.70, 126.78, 128.62, 129.18 (CH*2), 133.69, 138.17, 140.42, 147.54, 156.87, 158.59, 160.84,
47 166.92; **LC/MS** (ESI, m/z): 456.80 (MH⁺, 100); **Anal. Calcd. for** C₂₇H₂₁NO₄S: C 71.19, H 4.65, N 3.07,
48 S 7.04. **Found:** C 71.43, H 4.81, N 3.32, S 7.51.

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3 4.3.1.24 5-Ethyl-2-(4-fluorophenyl)-2-(2-thenyl)-1,5-dihydro-4H-furo[2',3':4 5]pyrano[3,2-
4 c]quinolin-4,11(2H)-dione (24)
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6

7 Yellow solid; mp: 191-192 °C; **IR** (ν_{\max} , KBr): 3078, 2972, 1722 (C=O), 1681 (C=O), 1651 (C=C), 1555,
8 1230, 941, 835 cm^{-1} ; **^{19}F NMR** (376 MHz, CDCl_3), δ (ppm): -113.99; **^1H NMR** (400 MHz, CDCl_3), δ (ppm):
9 1230, 941, 835 cm^{-1} ; **^{19}F NMR** (376 MHz, CDCl_3), δ (ppm): -113.99; **^1H NMR** (400 MHz, CDCl_3), δ (ppm):
10 8.30 (1H, dd, $J = 8.0, 1.6$ Hz, ArH), 7.7 (1H, td, $J = 8.0, 1.6$ Hz, ArH), 7.58 (2H, td, $J = 8.8, 2.0$ Hz, ArH),
11 7.42 (1H, d, $J = 8.8$ Hz, ArH), 7.35 (1H, d, $J = 8.0$ Hz, ArH), 7.31 (1H, dd, $J = 4.8; 1.2$ Hz, ArH), 7.09
12 (2H, td, $J = 8.8, 2.0$ Hz, ArH), 7.00 (1H, dd, $J = 5.2, 1.2$ Hz, ArH), 6.94 (1H, dd, $J = 4.8, 4.0$ Hz, ArH),
13 4.40 (2H, q, $J = 7.2$ Hz, CH_2), 3.99 (1H, d, $J = 15.2$ Hz, $-\text{CH}_2$), 3.73 (1H, d, $J = 15.2$ Hz, $-\text{CH}_2$), 1.40 (3H,
14 t, $J = 7.2$ Hz, CH_3); **^{13}C NMR** (100 MHz, CDCl_3), δ (ppm): 12.95, 37.73, 41.92, 95.24, 101.65 (C^* 2),
15 113.75, 114.70, 115.70 (CH^* 2, d, $^2J = 21.4$ Hz), 122.94, 125.24, 127.02, 127.11 (CH^* 2, d, $^3J = 8.4$ Hz),
16 127.70, 127.79, 134.03, 139.44 (CH , d, $^4J = 3.0$ Hz), 139.51, 147.27, 157.10, 158.71, 161.19, 162.74
17 (C, d, $^1J = 246.2$ Hz), 167.01; **LC/MS** (ESI, m/z): 460.70 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{26}\text{H}_{18}\text{FNO}_4\text{S}$: C
18 67.96, H 3.95, N 3.05, S 6.98. **Found:** C 67.80, H 4.17, N 3.27, S 6.86.
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30 4.3.1.25 4-Hydroxy-3-[2-phenyl-2-(2-thenyl)vinyl]2H,5H-pyrano[3,2-c]chromen-2, 5-dione (25)
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33 *E:Z* ratio = 1:4. Orange solid; mp: 229-231 °C; **IR** (ν_{\max} , KBr): 3438, 3144, 3082, 2925, 1727 (C=O), 1681
34 (C=C), 1414, 1106 (C-O-C), 771, 694 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3), δ (ppm): 10.89 (1H, s) [11.07
35 (1H, s)], 8.08 (1H, dd, $J = 8.4, 1.6$ Hz, ArH), 7.72 (1H, td, $J = 8.8, 1.6$ Hz, ArH), 7.44-7.49 (2H, m, ArH),
36 7.36-7.27 (6H, m, ArH), 6.96 (1H, dd, $J = 5.2, 3.6$ Hz, ArH), 6.87 (1H, d, $J = 3.6$ Hz, ArH), 6.70 (1H, s,
37 alkene) [6.45 (1H, s, alkene)]; **^{13}C NMR** (100 MHz, CDCl_3), δ (ppm): 96.71, 103.16, 114.04 (113.09),
38 116.57, 117.39 (117.45), 124.29 (124.38), 125.73 (125.45), 126.09 (126.15), 126.90 (126.37), 127.36
39 (126.70), 127.99 (CH^* 2) (128.32), 128.04 (128.60), 129.12 (CH^* 2) (128.70), 134.99 (135.0), 140.23,
40 141.80, 146.43, 152.28, 158.87, 160.83, 161.20, 163.00; **LC/MS** (ESI, m/z): 415.42 (MH^+ , 100); **Anal.**
41 **Calcd. for** $\text{C}_{24}\text{H}_{14}\text{O}_5\text{S}$: C 69.55, H 3.40, S 7.74. **Found:** C 69.65, H 3.51, S 7.80.
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51 4.3.1.26 4-Hydroxy-3-[2-(4-methylphenyl)-2-(2-thenyl)vinyl]2H, 5H-pyrano[3,2-c]chromen-2 5-
52 dione (26)
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55 *E:Z* ratio = 1:3.4. Orange solid; mp: 232-233 °C; **IR** (ν_{\max} , KBr): 3099. 3025, 1737 (C=O), 1683 (C=C),
56 1589, 1415, 1106 (C-O-C), 762, 702 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3), δ (ppm): 10.89 (1H, s, OH) [11.03
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(1H, s, OH)], 8.10 (1H, dd, $J = 8.4, 1.6$ Hz, ArH), 7.73 (1H, td, $J = 7.6, 1.6$ Hz, ArH), 7.44-7.49 (2H, m, ArH), 7.25 (1H, $J = 0.8$ Hz, ArH), 7.21 (2H, d, $J = 8.4$, ArH) [7.34 (2H, d, $J = 8.4$ Hz, ArH)], 7.09 (2H, d, $J = 8.4$, ArH) [7.16 (2H, d, $J = 8.4$ Hz, ArH)], 6.97 (1H, dd, $J = 5.2; 3.6$ Hz, ArH), 6.89 (1H, dd, $J = 5.2, 1.2$ Hz, ArH), 6.67 (1H, s, alkene) [6.44 (1H, s, alkene)], 2.33 (3H, CH₃) [2.39 (3H, CH₃)]; **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 21.36 (Me), 96.81, 103.40, 113.66, 117.38, 124.28, 125.64, 126.07 (126.27), 126.79, 127.31, 128.73 (CH²) (128.58), 128.98 (CH²), 134.93, 137.29, 137.75, 141.48, 143.90, 146.66, 152.26, 158.86, 160.75, 161.10, 163.03; **LC/MS** (ESI, m/z): 429.85 (MH⁺), 451.86 (M+ Na, 100); **Anal. Calcd. for** (C₂₅H₁₆O₅S): C 70.08, H 3.76, S 7.48. **Found:** C 70.22, H 3.51, S 7.81.

4.3.1.27 *4-Hydroxy-3-[2-(4-fluorophenyl)-2-(2-thenyl)vinyl]-2H, 5H-pyrano[3,2-c]chromen-2,5-dione (27)*

E:Z ratio = 1:2. Orange solid; mp: 214-215 °C; **IR** (ν_{\max} , KBr): 2965, 1758, 1724, 1702, 1673, 1099, 768 cm⁻¹; **¹⁹F NMR** (376 MHz, CDCl₃), δ (ppm): -113.90, -114.10; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 10.98 (1H, s, OH) [11.05 (1H, s, OH)], 8.10 (1H, dd, $J = 8.0; 2.0$ Hz, ArH) [8.15 (1H, dd, $J = 8.0; 2.0$ Hz, ArH)], 7.75 (1H, td, $J = 8.0, 2.0$ Hz; ArH), 7.40-7.50 (3H, m, ArH), 7.27-7.32 (2H, m, ArH), 6.96-7.05 (3H, m, ArH), 6.85 (1H, dd, $J = 3.6, 0.8$ Hz, ArH) [6.93 (1H, dd, $J = 3.6, 1.2$ Hz, ArH)], 6.70 (1H, s, alkene) [6.41 (1H, s, alkene)]; **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 76.94, 96.89, 103.15 (103.61), 113.28 (113.36), 114.53, 115.30 (CH, d, $^2J = 21.3$ Hz) [115.14 (CH, d, $^2J = 21.3$ Hz)], 116.66, 117.67 (117.70), 124.53 (124.61), 126.15, 126.38 (126.80), 127.06 (127.01), 127.67 (128.85), 131.11 (CH, d, $^3J = 7.7$ Hz) [130.60 (CH, d, $^3J = 8.4$ Hz)], 135.36 (135.38), 136.43 (C, d, $^4J = 3.8$ Hz) (136.89), 140.94 (140.15), 146.51 (142.25), 152.55 (152.64), 159.01 (159.09), 161.18 (161.31), 161.60 (162.23), 162.69 (C, d, $^1J = 245.4$) [163.19 (C, d, $^1J = 246.1$)], 163.26 (163.32); **LC/MS** (ESI, m/z): 433.62 (MH⁺, 100); **Anal. Calcd. for** (C₂₄H₁₃FO₅S): C 66.66, H 3.03, S 7.42. **Found:** C 66.48, H 3.18, S 7.29.

4.3.1.28 *6-Ethyl-4-hydroxy-3-[2-phenyl-2-(2-thenyl)vinyl]-2H, 5H-pyrano[3,2-c]quinolin-2,5-dione (28)*

E:Z ratio = 1:2.4. Orange solid; mp: 198-199 °C; **IR** (ν_{\max} , KBr): 3465 (O-H), 3065 (Ar-H), 2983 (R-H), 1742 (C=O), 1668 (C=O), 1615 (C=C), 1548, 1106 (C-O-C), 758 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 13.28 (1H, s, OH) [13.44 (1H, s, OH)], 8.26 (1H, d, $J = 7.6$, ArH), 7.71-7.78 (1H, m, ArH), 7.48 (1H, d, $J = 8.4$ Hz, ArH) [7.51 (1H, d, $J = 8.4$ Hz, ArH)], 7.38-7.45 (1H, m, ArH), 7.32-7.36 (3H, m, ArH),

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3 7.25-7.29 (2H, m, ArH), 7.23 (1H, d, $J = 5.2$ Hz, ArH), 6.92-6.96 (1H, m, ArH), 6.86 (1H, d, $J = 3.6$, ArH),
4
5 6.75 (1H, s, alkene) [6.50 (1H, s, alkene)], 4.37 (2H, q, $J = 7.2$ Hz) [4.41 (2H, q, $J = 7.2$ Hz)], 1.38 (3H,
6
7 t, $J = 7.2$ Hz, N-CH₃) [(3H, t, $J = 7.2$ Hz, N-CH₃)]; ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 12.75 (12.79),
8
9 37.65, 99.92, 102.18, 113.99 (114.06), 114.77 (114.54), 115.03 (114.83), 123.95 (124.01), 124.88
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11 (124.98), 125.28, 126.45 (126.51), 127.23, 127.73, 127.85 (CH²), 129.22 (CH²), 133.70 (133.78),
12
13 137.56 (137.68), 140.56, 140.90, 146.88, 157.50, 159.97, 162.74 (162.83), 164.07 (164.77); **LC/MS**
14
15 (ESI, m/z): 442.34 (MH⁺, 100); **Anal. Calcd. for** C₂₆H₁₉NO₄S: C 70.73, H 4.34, N 3.17 S 7.26. **Found:**
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17 C 71.49, H 4.81, N 3.61, S 7.46.

19 **4.3.1.29** *6-Ethyl-4-hydroxy-3-[2-(4-methylphenyl)-2-(2-thenyl)vinyl]-2H-pyrano[3,2-c]quinolin-*
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21 *2,5(6H)-dione (29)*

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24 *E:Z* ratio = 1:8. Orange solid; mp: 236-237 °C; **IR** (ν_{\max} , KBr): 3071, 2920 (R-H), 1735 (C=O), 1661
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26 (C=O), 1421 (C=C), 759 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 13.28 (1H, s, OH) [13.44 (1H, s,
27
28 OH)], 8.26 (1H, dd, $J = 7.6, 1.2$ Hz, ArH), 7.74 (1H, td, $J = 7.6, 1.6$ Hz, ArH), 7.48 (1H, d, $J = 8.4$ Hz,
29
30 ArH), 7.40 (1H, d, $J = 8.0, 0.8$ Hz, ArH), 7.29 (2H, d, $J = 8.0$ Hz, ArH), 7.21 (1H, d, $J = 1.2$ Hz, ArH), 7.07
31
32 (2H, d, $J = 7.6$ Hz, ArH), 6.95 (1H, dd, $J = 5.2, 3.6$ Hz, ArH), 6.89 (1H, dd, $J = 3.6, 1.2$ Hz, ArH), 6.72
33
34 (1H, s, alkene), 4.38 (2H, q, $J = 7.2$ Hz), 2.32 (3H, s) [2.38 (3H, s)], 1.46 (3H, t, $J = 7.2$ Hz, N-CH₃); ¹³C
35
36 **NMR** (100 MHz, CDCl₃), δ (ppm): 13.01, 21.62, 37.89, 100.19, 102.65, 114.26, 114.87, 115.00, 124.18,
37
38 125.12, 125.45, 126.60, 127.43, 128.86 (CH²), 129.30 (CH²), 133.90, 137.60, 137.78, 137.83, 141.03,
39
40 147.35, 157.68, 160.10, 162.99, 164.31; **LC/MS** (ESI, m/z): 456.70 (MH⁺, 100); **Anal. Calcd. for**
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42 C₂₇H₂₁NO₄S: C 71.19, H 4.65, N 3.07, S 7.04. **Found:** C 71.31, H 4.71, N 3.29, S 7.31.

44 **4.3.1.30** *6-Ethyl-3-[2-(4-fluorophenyl)-2-(2-thenyl)vinyl]-4-hydroxy-2H-pyrano[3,2-c]quinolin-*
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46 *2,5(6H)-dione (30)*

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49 *E:Z* ratio = 1:3.3. Orange solid; mp: 249-250 °C; **IR** (ν_{\max} , KBr): 3671, 2987 (R-H), 1736 (C=O), 1668
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51 (C=O), 1504, 1219, 757 cm⁻¹; **¹⁹F NMR** (376 MHz, CDCl₃), δ (ppm): -114.53, -114.66; **¹H NMR** (400
52
53 MHz, CDCl₃), δ (ppm): 13.37 (1H, s, OH) [13.48 (1H, s, OH)], 8.25 (1H, dd, $J = 8.0$ Hz, ArH) [8.31 (1H,
54
55 dd, $J = 7.6$ Hz, ArH)], 7.74 (1H, t, $J = 8.8$ Hz, ArH), 7.50-7.38 (2H, m, ArH), 7.33-7.30 (2H, m, ArH), 7.24
56
57 (1H, d, $J = 4.4$ Hz, ArH), 7.00-6.93 (3H, m, ArH), 6.84 (1H, d, $J = 4.0$ Hz, ArH), 6.73 (1H, s, alkene) [6.44
58
59 (1H, s, alkene)], 4.38 (2H, q, $J = 7.6$ Hz, CH₂), 1.38 (3H, t, $J = 8.0$ Hz, -CH₃); ¹³C **NMR** (100 MHz, CDCl₃),
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3 δ (ppm): 12.77, 37.71, 99.86, 101.94, 102.43, 113.97, 114.67, 114.79, 114.83, 115.00, 115.32, 117.47,
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5 124.03, 124.90, 124.99, 125.47, 126.22, 126.38, 126.59, 127.31, 128.39, 130.31, 130.40, 130.90,
6
7 130.98, 133.82, 136.55, 136.52, 137.62, 137.71, 138.93, 139.75, 142.57, 146.73, 157.59, 157.72,
8
9 159.96, 160.01, 161.08, 162.74, 162.84, 163.53, 164.03, 164.19, 164.83; **LC/MS** (ESI, m/z): 460.13
10
11 (MH⁺, 100); **Anal. Calcd. for** C₂₆H₁₈FNO₄S: C 67.96, H 3.95, N 3.05, S 6.98; **Found:** C 70.13, H 4.09,
12
13 N 3.25, S 7.06.

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16 **4.3.1.31** *5-Methyl-2-phenyl-2-thenyl-3, 5-dihydrofuro[3,2-c]quinolin-4H-one (31)*

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18 Colorless solid; mp: 181-182 °C; **IR** (ν_{\max} , KBr): 3107, 3001, 2918, 1656 (C=O), 1639 (C=C), 1598, 1240,
19
20 1107, 742 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃), δ (ppm): 7.95 (1H, dd, J = 8.0; 1.6 Hz, ArH), 7.59 (1H, td,
21
22 J = 7.8; 1.6 Hz, ArH), 7.52 (1H, dd, J = 8.4; 1.6 Hz, ArH), 7.38 (1H, dd, J = 8.4, 0.8 Hz, ArH), 7.25-7.36
23
24 (6H, m, ArH), 7.09 (1H, dd, J = 3.6, 1.2 Hz, ArH), 6.94 (1H, d, J = 5.2, 4.0 Hz, ArH), 4.1 (1H, d, J = 15.6
25
26 Hz, H3), 3.87 (1H, d, J = 15.6 Hz, H3), 3.70 (3H, s, N-CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 29.38
27
28 (CH₃), 44.50 (C3), 93.60 (C2), 107.70, 112.76, 114.82, 122.00, 123.47, 125.68 (CH*2), 126.12, 126.50,
29
30 126.90, 128.33, 128.65 (CH*2), 131.38, 141.01, 144.47 (C ipso), 148.83 (C ipso), 160.95 (C4), 161.22
31
32 (C9b); **LC/MS** (ESI, m/z): 360.01 (MH⁺, 100); **Anal. Calcd. for** C₂₂H₁₇NO₂S: C 73.51, H 4.77, N 3.90, S
33
34 8.92. **Found:** C 72.68, H 4.86, N 3.75, S 8.26.

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36
37 **4.3.1.32** *5-Methyl-2-(4-methylphenyl)-2-thenyl-3,5-dihydrofuro[3,2-c]quinolin-4H-one (32)*

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39 Colorless solid; mp: 144-145 °C; **IR** (ν_{\max} , KBr): 3084 (Ar-H), 2979 (R-H), 1657 (C=O), 1635 (C=C), 1597,
40
41 1450, 1240, 1106, 754, 698 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.94 (1H, dd, J = 8.0, 1.6 Hz,
42
43 ArH), 7.59 (1H, td, J = 8.0, 1.6 Hz, ArH), 7.42 (2H, d, J = 8.0 Hz, ArH), 7.38 (1H, d, J = 8.4 Hz, ArH),
44
45 7.28-7.24 (2H, m, ArH), 7.17 (2H, d, J = 8.0 Hz, ArH), 7.0 (1H, dd, J = 3.6, 1.2 Hz, ArH), 6.94 (1H, dd, J
46
47 = 5.2, 3.2 Hz, ArH), 4.07 (1H, d, J = 15.6 Hz, H3), 3.87 (1H, d, J = 15, 6 Hz, H3), 3.7 (3H, s, N-CH₃),
48
49 2.34 (3H, CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 21.09 (CH₃), 29.11 (CH₃), 44.19 (C3), 93.37 (C2),
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51 107.54, 112.53, 114.54, 121.70, 123.24, 125.41 (CH*2), 125.75, 126.15, 126.62, 129.05 (CH*2), 131.08,
52
53 137.91, 140.73, 141.26, 148.78, 160.68 (C4), 160.98 (C9b); **LC/MS** (ESI, m/z): 374.41 (M⁺, 100); **Anal.**
54
55 **Calcd. for** C₂₃H₁₉NO₂S: C 73.97, H 5.13, N 3.75, S 8.79. **Found:** C 74.13, H 5.42, N 3.16, S 7.99.

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3 4.3.1.33 *5-Methyl-2-(4-fluorophenyl)-2-thenyl-3,5-dihydrofuro[3,2-c]quinolin-4H-one (33)*
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6 Colorless solid; mp: 143-144 °C; **IR** (ν_{\max} , KBr): 3084 (Ar-H), 2979 (R-H), 1657 (C=O), 1635 (C=C), 1597,
7 1240 (C-O-C), 1106, 754 cm^{-1} ; **^{19}F NMR** (376 MHz, CDCl_3), δ (ppm): -114.42; **^1H NMR** (400 MHz,
8 CDCl_3), δ (ppm): 7.92 (1H, dd, $J = 8.0, 1.6$ Hz, ArH), 7.61 (1H, td, $J = 7.8; 1.6$ Hz, ArH), 7.52-7.49 (2H,
9 m, ArH), 7.39 (1H, d, $J = 8.8$ Hz, ArH), 7.30-7.25 (2H, m, ArH), 7.07-7.03 (2H, m, ArH), 7.00 (1H, dd, J
10 = 3.6, 1.2 Hz, ArH), 6.95 (1H, dd, $J = 5.2, 3.6$ Hz, ArH), 4.09 (1H, d, $J = 15.6$ Hz, H3), 3.82 (1H, d, $J =$
11 15.6 Hz, H3), 3.71 (3H, s, N- CH_3); **^{13}C NMR** (100 MHz, CDCl_3), δ (ppm): 29.38 (CH_3), 44.55 (C3), 93.14
12 (C2), 107.65, 112.63, 114.85, 115.55 (CH, d, $^2J = 21.4$ Hz), 122.04, 123.40, 126.18, 126.88, 126.97,
13 127.60 (CH, d, $^3J = 8.3$ Hz), 129.81 (CH, d, $^3J = 8.4$ Hz), 131.46, 132.86, 140.31 (C, d, $^4J = 3.0$ Hz),
14 141.01, 148.53, 160.77 (C4), 161.13 (C9b), 162.64 (C, d, $^1J = 246.1$); **LC/MS** (ESI, m/z): 378.42 (MH^+ ,
15 100); **Anal. Calcd. for** $\text{C}_{22}\text{H}_{16}\text{FNO}_2\text{S}$: C 70.01, H 4.27, N 3.71, S 8.50. **Found:** C 70.11, H 4.29, N 3.80,
16 S 8.55.
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28 4.3.1.34 *4-Hydroxy-1-methyl-3-[2-phenyl-2-(2-thenyl)vinyl]quinolin-2(1H)-one (34)*
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31 *E:Z* ratio = 1:2.17. Yellow solid; mp: 204-205 °C; **IR** (ν_{\max} , KBr): 3109, 3075, 1617 (C=O), 1575 (C=C),
32 1161 (C-O-C), 754 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3), δ (ppm): 7.74 (1H, dd, $J = 7.6; 1.6$ Hz, ArH) [7.89
33 (1H, td, $J = 8.0, 1.6$ Hz, ArH)], 7.52 (1H, td, $J = 7.8; 1.6$ Hz, ArH) [7.57(1H, td, $J = 7.2; 1.6$ Hz, ArH)],
34 7.43-7.40 (6H, m, ArH) [7.36-7.29 (6H, m, ArH)], 7.26 (1H, dd, $J = 3.2; 1.6$ Hz, ArH), 7.14 (1H, t, $J = 8.0$
35 Hz, ArH) [7.20 (1H, t, $J = 8.0$ Hz, ArH)], 7.05 (1H, s, alkene) [6.80 (1H, s, alkene)], 6.97 (1H, td, $J = 5.2,$
36 1.2 Hz, ArH), 6.89 (1H, dd, $J = 3.6, 1.2$ Hz, ArH), 5.85 (1H, s, OH) [6.12 (1H, s, OH)], 3.72 (3H, s, N-
37 CH_3) [3.74 (3H, s, N- CH_3)]; **^{13}C NMR** (100 MHz, CDCl_3), δ (ppm): 29.74 (CH_3), 108.58, 113.96 (114.08),
38 115.53, 119.72 (122.11), 121.84 (121.95), 124.38 (124.56), 125.96, 127.01, 127.57 (127.65), 128.29
39 (128.36), 128.80 (128.63), 129.38 (129.44), 129.52 (130.06), 131.18 (131.39), 138.45 (138.02), 138.88,
40 139.33 (139.51), 140.32 (142.59), 146.29, 154.11 (154.94), 163.39; **LC/MS** (ESI, m/z): 360.70 (MH^+ ,
41 100); **Anal. Calcd. for** ($\text{C}_{22}\text{H}_{17}\text{NO}_2\text{S}$): C 73.51, H 4.77, N 3.90, S 8.92; **Found:** C 73.61, H 4.83, N 3.97,
42 S 9.01.
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3 4.3.1.35 *3-Phenyl-2-thenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (35)*

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6 Colorless solid; mp: 153-154°C; **IR** (ν_{\max} , KBr): 3025 (Ar-H), 1718 (C=O), 1641 (C=C), 1496, 1406, 1035
7
8 (C-O-C), 700 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.77 (1H, dd, $J = 8.0, 1.6$ Hz, ArH), 7.61 (1H,
9
10 td, $J = 8.2, 1.6$ Hz, ArH), 7.43-7.27 (8H, m, ArH), 7.18 (1H, d, $J = 2.8$ Hz, ArH), 7.05 (1H, dd, $J = 4.8,$
11
12 3.6 Hz, ArH), 6.05 (1H, d, $J = 6.4$ Hz, H2), 4.83 (1H, d, $J = 6.0$ Hz, H3); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ
13
14 (ppm): 54.94 (C3), 91.93 (C3), 104.96, 112.69, 117.32, 123.37, 124.29, 126.85, 127.21, 127.42, 127.57,
15
16 128.11, 128.59, 129.00, 129.36, 133.05, 139.91, 141.67, 155.72 (C5a), 159.82 (C4), 166.12 (C9b);
17
18 **LC/MS** (ESI, m/z): 346.97 (MH^+ , 100); **Anal. Calcd. for** ($\text{C}_{21}\text{H}_{14}\text{O}_3\text{S}$): C 72.81, H 4.07, O 13.86, S 9.26.
19
20 **Found:** C 72.41, H 4.27, S 8.20.

21
22
23 4.3.1.36 *3-Phenyl-2-thenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (36)*

24
25 Light yellow solid; mp: 131-132°C; **IR** (ν_{\max} , KBr): 3028 (Ar-H), 1710 (C=O), 1635 (C=C), 1409, 1026
26
27 (C-O-C), 788 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.8 (1H, dd, $J = 8.0, 1.6$ Hz, ArH), 7.63 (1H, td,
28
29 $J = 7.8, 1.6$ Hz, ArH), 7.45 (1H, dd, $J = 8.4, 0.8$ Hz, ArH), 7.35 (1H, td, $J = 7.6, 1.2$ Hz, ArH), 7.16-7.13
30
31 (4H, m, ArH), 6.96-6.94 (2H, m, ArH), 6.85-6.83 (1H, m, ArH), 6.82 (1H, dd, $J = 5.2, 4.0$ Hz, ArH), 6.52
32
33 (1H, d, $J = 9.2, \text{H}_2$), 4.86 (1H, d, $J = 9.2$ Hz, H3); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ (ppm): 51.00 (C3),
34
35 89.00 (C2), 106.00, 112.50, 117.00, 123.42, 124.37, 126.35, 127.17, 127.57, 127.98, 128.59 (CH^2),
36
37 128.98 (CH^2), 133.13, 135.79, 137.27, 155.55 (C5a), 159.88 (C4), 167.01 (C9b); **LC/MS**, (ESI, m/z):
38
39 347.70 (MH^+ , 100); **Anal. Calcd. for** ($\text{C}_{21}\text{H}_{14}\text{O}_3\text{S}$): C 72.81, H 4.07, O 13.86, S 9.26. **Found:** C 73.12,
40
41 H 4.31, S 8.46.

42
43
44 4.3.1.37 *(2S, 3S)-2-Methyl-3-phenyl-2-(2-thenyl)-4H-furo[3,2-c]chromen-4-one (37)*

45
46 Colorless solid; mp: 137-138 °C; **IR** (ν_{\max} , KBr): 3028 (Ar-H), 2989 (R-H), 1722 (C=O), 1647 (C=C), 1406,
47
48 1029, 727 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.80 (1H, dd, $J = 8.0, 1.6$ Hz, ArH), 7.60 (1H, td, J
49
50 = 7.8, 1.6 Hz, ArH), 7.42 (1H, d, $J = 8.4$ Hz, ArH), 7.35-7.30 (4H, m, ArH), 7.27 (1H, dd, $J = 5.2, 1.2$ Hz,
51
52 ArH), 7.17 (2H, dd, $J = 8.4, 1.6$ Hz, ArH), 7.13 (1H, dd, $J = 3.6, 1.2$ Hz, ArH), 7.00 (1H, dd, $J = 5.2, 4.0$
53
54 Hz, ArH), 4.93 (1H, s, H3), 1.48 (3H, s, CH_3); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ (ppm): 26.07 (CH_3), 58.15
55
56 (C3), 95.84 (C2), 104.51, 112.71, 117.33, 123.36, 123.69, 124.34, 125.48, 127.29, 128.28, 128.87
57
58 (CH^2), 129.01 (CH^2), 133.06, 136.40, 149.70, 155.61 (C5a), 159.99 (C4), 166.02 (C9b); **LC/MS**, (ESI,
59
60

m/z) : 361.41 (MH⁺, 100); **Anal. Calcd. for** (C₂₂H₁₆O₃S): C 73.31, H 4.47, S 8.90. **Found:** C 73.02, H 4.51, S 9.06.

4.3.1.38 *2-Methyl-3-phenyl-2-(2-thenyl)-4H-furo[3,2-c]chromen-4-one (38)*

Light yellow solid; mp: 161-162 °C; **IR** (ν_{\max} , KBr): 3099 (Ar-H), 2918 (R-H), 1718 (C=O), 1633 (C=C), 1573, 1408, 825, 759 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.86 (1H, dd, J = 7.6, 1.6 Hz, ArH), 7.64 (1H, td, J = 7.8, 1.6 Hz, ArH), 7.44 (1H, d, J = 8.0 Hz), 7.38 (1H, t, J = 7.6 Hz), 7.08-7.06 (3H, m, ArH), 7.02 (1H, dd, J = 5.2, 0.8 Hz), 6.89 (2H, m, ArH), 6.70 (1H, dd, J = 5.2, 3.6 Hz), 6.56 (1H, dd, J = 3.6, 0.8 Hz), 4.63 (1H, s), 2.11 (3H, s); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 30.43 (CH₃), 58.64 (C3), 97.31 (C2), 104.94, 112.72, 117.36, 123.36, 124.31, 125.03, 125.12, 126.74, 127.61, 128.22 (CH²), 128.61 (CH²), 133.04, 136.73, 143.60, 155.59 (C5a), 160.08 (C4), 165.76 (C9b); **LC/MS**, (ESI, m/z): 361.61 (MH⁺, 100); **Anal. Calcd. for** (C₂₂H₁₆O₃S): C 73.31, H 4.47, S 8.90. **Found:** C 72.90, H 4.60, S 8.32.

4.3.1.39 *2, 6-Dimethyl-3-phenyl-2-(2-thenyl)-2,3-dihydro-4H-furo[3,2-c]piran-4-one (39)*

Light yellow oil; **IR** (ν_{\max} , KBr): 3089 (Ar-H), 2989 (R-H), 1716 (C=O), 1637 (C=C), 1571, 1446, 1259, 977, 723 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.35-7.25 (4H, m, ArH), 7.13 (2H, d, J = 6.8, ArH), 7.06 (1H, d, J = 3.2, Hz, ArH), 6.99 (1H, dd, J = 5.2; 3.6, ArH), 6.06 (1H, s, alkene), 4.77 (1H, s, H3), 2.29 (3H, CH₃), 1.35 (3H, s, CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 20.82 (CH₃), 25.80 (CH₃), 57.13 (C3), 95.11 (C2), 95.93, 101.62, 123.67, 125.40, 127.23, 128.12, 128.83 (CH²), 128.89(CH²), 136.51, 149.67, 161.51 (C4), 166.61 (C6), 170.57 (C7a); **LC/MS**, (ESI, m/z): 325.37 (MH⁺, 100); **Anal. Calcd. for** (C₁₉H₁₆O₃S): C 70.35, H 4.97, S 9.88. **Found:** C 70.17, H 4.80, S 9.71.

4.3.1.40 *2, 6-Dimethyl-3-phenyl-2-(2-thenyl)-2, 3-dihydro-4H-furo[3, 2-c]piran-4-one (40)*

Light yellow oil; **IR** (ν_{\max} , KBr): 3089 (Ar-H), 2989 (R-H), 1716 (C=O), 1637 (C=C), 1571, 1446, 1259, 977, 696 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.07-7.05 (3H, m, ArH), 6.99 (1H, dd, J = 4.8, 1.2 Hz, ArH), 6.86-6.83 (2H, m, ArH), 6.68 (1H, dd, J = 5.2; 3.6, ArH), 6.49 (1H, dd, J = 3.2, 1.2 Hz, ArH), 6.13 (1H, s, alkene), 4.46 (1H, s, H3), 2.33 (3H, CH₃), 2.00 (3H, s, CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 20.85 (CH₃), 30.23 (CH₃), 57.62 (C3), 95.92 (C2), 96.64, 102.21, 124.86, 124.94, 126.69, 127.47, 128.13 (CH²), 128.57 (CH²), 136.93, 143.71, 161.63 (C4), 166.54 (C6), 170.38 (C7a); **LC/MS**, (ESI,

m/z) : 325.37 (MH⁺, 100); **Anal. Calcd. for** (C₁₉H₁₆O₃S): C 70.35, H 4.97, S 9.88. **Found:** C 70.11, H 4.78, S 9.73.

4.3.1.41 *2-Methyl-1-phenyl-2-(2-thenyl)-1,2-dihydro-4H,11H-furo[2,3:4,5]pyrano[3,2-c]chromen-4,11-dione (41)*

White solid; mp: 231-232 °C; **IR** (ν_{\max} , KBr): 3096, 3010, 1724 (C=O), 1624 (C=C), 1558, 1224, 761, 725 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 8.15 (1H, d, *J* = 8.4 Hz, ArH), 7.72 (2H, t, *J* = 8.4 Hz, ArH), 7.43 (1H, d, *J* = 8.4 Hz, ArH), 7.40-7.37 (3H, m, ArH), 7.31 (1H, dd, *J* = 5.2 Hz, ArH), 7.20-7.17 (3H, m, ArH), 7.01 (1H, t, *J* = 4.4 Hz, ArH), 4.87 (1H, s, H₃), 1.53 (3H, s, CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 26.07 (CH₃), 56.99 (C₃), 97.11 (C₂), 97.24, 104.82, 113.23, 117.59, 124.15, 124.68, 125.44, 125.66, 127.25, 128.52, 128.78 (CH²), 129.13 (CH²), 135.35, 135.81, 148.95, 153.91, 155.77 (C₁₁), 157.25 (C₄), 164.91 (C_{5a}), 166.95 (C_{11b}); **LC/MS**, (ESI, m/z): 429.40 (MH⁺, 100); **Anal. Calcd. for** (C₂₅H₁₆O₅S): C 70.08, H 3.76, S 7.48. **Found.:** C 70.40, H 4.01, S 6.98.

4.3.1.42 *2-Methyl-1-phenyl-2-(2-thenyl)-1,2-dihydro-4H,11H-furo[2,3:4,5]pyrano[3,2-c]chromen-4,11-dione (42)*

Colorless solid; mp: 207-208 °C; **IR** (ν_{\max} , KBr): 3096, 3010, 1726 (C=O), 1625 (C=C), 1554, 1224, 759, 692 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 8.16 (1H, dd, *J* = 8.4, 1.6 Hz, ArH), 7.72 (1H, td, *J* = 8.0, 1.6 Hz, ArH), 7.45-7.40 (2H, m, ArH), 7.11-7.10 (3H, m, ArH), 7.01 (1H, dd, *J* = 4.4, 3.0, ArH), 6.91-6.89 (2H, m, ArH), 6.68 (1H, dd, *J* = 4.8, 3.6 Hz, ArH), 6.56 (1H, dd, *J* = 3.2, 1.2 Hz, ArH), 4.60 (1H, s, H₃), 2.14 (3H, s, CH₃); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 30.49 (CH₃), 55.56 (C₃), 97.07 (C₂), 98.58, 104.80, 113.25, 117.61, 124.70, 125.26, 125.36, 125.42, 126.71, 127.87, 128.34 (CH²), 128.56 (CH²), 135.33, 135.99, 142.71, 153.97, 155.69 (C₁₁), 157.28 (C₄), 164.90 (C_{5a}), 166.85 (C_{11b}); **LC/MS**, (ESI, m/z) : 429.80 (MH⁺, 100); **Anal. Calcd. for** (C₂₅H₁₆O₅S): C 70.08, H 3.76, S 7.48. **Found:** C 70.31, H 3.51, S 6.99.

4.3.1.43 *9a-(2-Thenyl)-7,8,9,9a-tetrahydro-6H,6H-cyclopenta[4,5]furo[3,2-c]chromen-6-one (43)*

Light yellow solid; mp: 125-126 °C; **IR** (ν_{\max} , KBr): 3107, 2966, 1708 (C=O), 1643 (C=C), 1604, 1404, 1325, 893, 750 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.70 (1H, dd, *J* = 7.6, 1.2 Hz), 7.57 (1H, td,

1
2
3 $J = 7.8, 1.6$ Hz, ArH), 7.38 (1H, d, $J = 8.8$ Hz), 7.30 (2H, m), 7.10 (1H, dd, $J = 3.6, 1.2$ Hz), 7.00 (1H, dd,
4
5 $J = 5.2, 4.0$ Hz), 4.01 (1H, d, $J = 7.6$ Hz), 2.67 (1H, dd, $J = 14.0, 6.0$ Hz), 2.28 (1H, td, $J = 13.6, 6.4$ Hz),
6
7 2.19-2.08 (2H, m), 1.97-1.94 (1H, m), 1.76-1.70 (1H, m); $^{13}\text{C NMR}$ (100 MHz, CDCl_3), δ (ppm): 25.07,
8
9 32.70, 42.55, 53.05, 103.19, 105.02, 112.64, 117.20, 123.32, 124.08, 124.16, 125.89, 127.31, 132.63,
10
11 146.14, 155.27, 160.76 (C6), 165.66 (C10a); **LC/MS**, (ESI, m/z): 311.34 (MH^+ , 100); **Anal. Calcd. for**
12
13 $\text{C}_{18}\text{H}_{14}\text{O}_3\text{S}$: C 69.66, H 4.55, S 10.33. **Found**: C 69.02, H 4.67, S 9.06.

14
15
16 4.3.1.44 *10a-(2-Thenyl)-6b,7 8 9 10,10a-hexahydro-6H-benzofuro[3, 2-c]chromen-6-one (44)*

17
18 Light yellow oil; **IR** (ν_{max} , KBr): 2937, 2860, 1720 (C=O), 1639 (C=C), 1604, 1404, 1028 (C-O-C), 754
19
20 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm): 7.70 (1H, dd, $J = 7.6, 1.6$ Hz), 7.54 (1H, td, $J = 8.0, 1.6$ Hz,
21
22 ArH), 7.36 (1H, d, $J = 7.6$ Hz, ArH), 7.29-7.25 (2H, m, ArH), 7.16 (1H, dd, $J = 3.6, 1.2$ Hz), 7.00 (1H, dd,
23
24 $J = 5.2, 3.6$ Hz), 3.85 (1H, t, $J = 6.4$ Hz), 2.30-2.27 (2H, m), 2.25-2.28 (1H, m), 1.99-1.93 (1H, m), 1.68-
25
26 1.63 (1H, m), 1.60-1.49 (3H, m); $^{13}\text{C NMR}$ (100 MHz, CDCl_3), δ (ppm): 19.09, 19.26, 23.73, 34.23, 46.65,
27
28 94.22, 105.66, 113.06, 117.13, 123.05, 124.14, 124.50, 125.72, 127.19, 132.60, 147.64, 155.28, 160.61
29
30 (C6), 165.59 (C11a); **LC/MS** (ESI, m/z): 325.37 (MH^+ , 100); **Anal. Calcd. for** $\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}$: C 70.35, H
31
32 4.97, S 9.88. **Found**: C 70.09, H 4.71, S 9.73.

33
34
35 4.3.1.45 *3-Methyl-5a-(2-thenyl)-5a, 7, 8, 8a-tetrahydro-1H,6H-cyclopenta[4,5]furo[3 2-c]pyran-*
36
37 *1-one (45)*

38
39 Light yellow oil; **IR** (ν_{max} , KBr): 3089, 2968, 1710 (C=O), 1637 (C=C), 1577, 1446, 1278, 977, 920, 700
40
41 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm): 7.25 (1H, dd, $J = 5.2, 1.2$ Hz), 7.00 (1H, dd, $J = 4.0, 1.2$ Hz),
42
43 6.95 (1H, dd, $J = 5.2, 3.6$ Hz), 5.90 (1H, s), 3.83 (1H, d, $J = 8.0$ Hz), 2.50 (1H, dd, $J = 14.4, 6.0$ Hz), 2.22
44
45 (3H, s), 2.15 (1H, td, $J = 12.8, 6.4$ Hz), 2.06-1.95 (2H, m), 1.89-1.85 (1H, m), 1.67-1.60 (1H, m); ^{13}C
46
47 **NMR** (100 MHz, CDCl_3), δ (ppm): 20.63, 24.92, 32.59, 42.37, 51.93, 95.71, 102.42, 102.48, 123.89,
48
49 125.70, 127.23, 146.23, 162.15, 165.61, 170.28; **LC/MS** (ESI, m/z) : 275.60 (MH^+ , 100); **Anal. Calcd.**
50
51 **for** $\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}$: C 65.67, H 5.14, S 11.69. **Found**: C 65.41, H 4.97, S 11.57.

4.3.1.46 *3-Methyl-5a-(2-thenyl)-5a,6,7,8,9,9a-hexahydro-1H-pyrano[4,3-b]benzofuran-1-one*
(46)

Light yellow oil; **IR** (ν_{\max} , KBr): 3091, 2937, 1708 (C=O), 1633 (C=C), 1575, 1446, 979, 748, 700 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.28 (1H, dd, $J = 4.8, 1.2$ Hz, ArH), 7.11 (1H, dd, $J = 3.6, 1.2$ Hz, ArH), 6.99 (1H, dd, $J = 4.8, 3.6$ Hz, ArH), 5.95 (1H, s), 3.70 (1H, t, $J = 5.2$ Hz), 2.25 (3H, s), 2.21-2.11 (3H, m), 1.90-1.84 (1H, m), 1.58-1.65 (1H, m), 1.46-1.56 (3H, m); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ (ppm): 19.01, 19.24, 20.68, 23.53, 34.11, 45.56, 93.46, 96.28, 102.77, 124.37, 125.58, 127.10, 147.61, 162.07, 165.78, 170.19; **LC/MS**, (ESI, m/z): 289.61 ($\text{M}^+ + \text{H}$, 100); **Anal. Calcd. for** $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$: C 66.64, H 5.59, S 11.12. **Found**: C 66.46, H 5.37, S 11.01.

4.3.1.47 *5-Methyl-9a-(2-thenyl)-5,6b,7,8,9,9a-hexahydro-6H-cyclopenta[4,5]furo[3,2-c]quinolin-6-one* (47)

Light yellow oil; **IR** (ν_{\max} , KBr): 2972, 2939, 1658 (C=O), 1637 (C=C), 1597, 1068 (C-O-C), 702 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.80 (1H, dd, $J = 7.6, 1.6$ Hz, ArH), 7.56 (1H, td, $J = 8.0, 1.6$ Hz, ArH), 7.36 (1H, d, $J = 8.4$ Hz, ArH), 7.25-7.20 (2H, m), 7.07 (1H, dd, $J = 4.0, 1.2$ Hz), 6.96 (1H, dd, $J = 5.2, 3.6$ Hz, ArH), 4.06 (1H, dd, $J = 8.0, 2.0$ Hz), 3.69 (3H, s), 2.63 (1H, dd, $J = 13.6, 6.0$ Hz), 2.25 (1H, td, $J = 13.6, 6.0$ Hz), 2.17-2.09 (2H, m), 1.92-1.89 (1H, m), 1.73-1.69 (1H, m); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ (ppm): 25.20, 29.21, 32.88, 42.86, 54.33, 101.34, 110.88, 112.57, 114.70, 121.79, 123.42, 123.68, 125.25, 127.13, 131.18, 140.92, 147.55, 161.40 (C6), 161.68 (C10a); **LC/MS**, (ESI, m/z): 324.70 ($\text{M}^+ + \text{H}$, 100); **Anal. Calcd. for** $\text{C}_{19}\text{H}_{17}\text{NO}_2\text{S}$: C 70.56, H 5.30, N 4.33, S 9.91. **Found**: C 70.29, H 5.12, N 4.03, S 9.86.

4.3.1.48 *5-Methyl-10a-(2-thenyl)-6b,7,8,9,10,10a-hexahydrobenzofuro[3,2-c]quinolin-6(5H)-one* (48)

Light yellow oil; **IR** (ν_{\max} , KBr): 3093, 3062, 2939, 1649 (C=O), 1631 (C=C), 1593, 1305, 1157, 1101 (C-O-C), 742, 711 cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3), δ (ppm): 7.84 (1H, dd, $J = 8.0, 1.2$ Hz, ArH), 7.56 (1H, td, $J = 7.8, 1.6$ Hz, ArH), 7.35 (1H, d, $J = 8.4$ Hz, ArH), 7.24-7.20 (2H, m), 7.12 (1H, dd, $J = 4.0, 1.2$ Hz, ArH), 6.95 (1H, dd, $J = 5.2, 3.6$ Hz, ArH), 3.87 (1H, t, $J = 5.6$ Hz), 3.68 (3H, s), 2.32 (1H, dt, $J = 14.4, 6.4$ Hz, ArH), 2.26-2.04 (3H, m), 1.67-1.59 (2H, m), 1.56-1.50 (2H, m); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3), δ

(ppm): 19.34, 19.48, 24.53, 29.12, 34.56, 47.75, 92.44, 111.98, 113.11, 114.68, 121.77, 123.43, 123.74, 124.90, 126.94, 131.14, 140.92, 149.62, 161.47, 161.48; **LC/MS**, (ESI, m/z) : 338.72 (MH⁺, 100); **Anal. Calcd.** for C₂₀H₁₉NO₂S: C 71.19, H 5.68, N 4.15, S 9.50. **Found:** C 71.01, H 5.43, N 3.98, S 9.36.

4.3.1.49 4-Hydroxy-3-[2-(2-thenyl)cyclopent-1-en-1-yl]-2H-chromen-2-one (49)

Colorless solid; mp: 198-200 °C; **IR** (ν_{\max} , KBr): 3101, 3077, 2948, 1665 (C=O), 1601 (C=C), 1557, 1495, 1107, 754; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.90 (1H, dd, J = 8.0, 1.6 Hz), 7.67 (1H, td, J = 7.8, 1.6 Hz, ArH), 7.39-7.35 (2H, m, ArH), 7.26 (1H, dd, J = 5.2, 1.2 Hz), 7.02 (1H, dd, J = 3.6, 1.2 Hz), 6.95 (1H, dd, J = 5.2, 3.6 Hz, ArH), 3.00-2.88 (4H, m), 2.65-2.61 (2H, m); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 22.31, 37.19, 37.34, 103.20, 114.68, 116.70, 123.75, 124.02, 126.53, 126.59, 126.76, 126.95, 132.48, 137.51, 137.59, 153.25, 159.31, 160.96; **LC/MS** (ESI, m/z): 311.60 (MH⁺, 100); **Anal. Calcd.** for C₁₈H₁₄O₃S: C 69.66, H 4.55, S 10.33. **Found:** C 69.02, H 4.67, S 9.06.

4.3.1.50 4-Hydroxy-3-[2-(2-thenyl)cyclohexen-1-yl]-2H-chromen-2-one (50)

Colorless solid; mp: 162-163 °C; **IR** (ν_{\max} , KBr): 3210, 2940, 2920, 1678 (C=O), 1603, 1633, 1177 (C-O-C), 757, 699 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃), δ (ppm): 7.75 (1H, dd, J = 8.0, 1.6 Hz), 7.54 (1H, td, J = 8.4, 1.6 Hz, ArH), 7.35 (1H, d, J = 8.4 Hz), 7.26 (1H, td, J = 8.0, 0.8 Hz, ArH), 7.09 (1H, dd, J = 5.2, 1.6 Hz), 7.03 (1H, dd, J = 3.6, 1.6 Hz), 6.86 (1H, dd, J = 4.8, 4.0 Hz), 6.43 (1H, s, OH), 2.78-2.20 (2H, m), 2.58-2.52 (1H, m), 2.05-1.97 (2H, m), 1.86-1.76 (3H, m); **¹³C NMR** (100 MHz, CDCl₃), δ (ppm): 22.22, 22.91, 29.63, 31.12, 107.62, 114.77, 116.62, 123.70, 123.87, 124.84, 125.61, 125.75, 126.57, 132.23, 134.33, 142.03, 153.15, 158.39, 161.52; **LC/MS** (ESI, m/z): 325.80 (MH⁺, 100); **Anal. Calcd.** for C₁₉H₁₆O₃S: C 70.35, H 4.97, S 9.88. **Found:** C 70.03, H 4.71, S 9.69.

4.4. Evaluation of *in vitro* antimicrobial activity

Escherichia coli ATCC 25922, *Micrococcus luteus* M3, *Bacillus cereus* B9, *Bacillus licheniformis* M30, *Staphylococcus aureus* ATCC 6538, *Bacillus subtilis* B1, *Pseudomonas aeruginosa* P7 were the test microorganisms used in the study. Muller-Hinton agar was sterilized at 121 °C, 1.5 atm for 15 min, and poured into each sterile petri dish (20 mL). These petri dishes were seeded with 500 μ L of bacteria, that had been previously awakened in a Nutrient-Broth medium at 37 °C for 48 hours, and spread. Bacteria were allowed to grown on solid medium and the prepared sterile discs were placed on the medium. 5

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3 mg/mL of the compounds to be investigated for antimicrobial activity were filtered with a pore size of
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5 0.45 mm and dissolved in DMSO. 50 mL of compounds were dropped onto discs and petri dishes were
6
7 incubated at 37 °C for 24 hours. Finally, the measurements obtained.
8

9 10 **Conflicts of interest**

11
12 There are no conflicts of interest to declare.
13
14

15 16 **Acknowledgments**

17
18 This work was supported by a research grant from the Scientific and Technical Research Council of
19
20 Turkey (TBAG-2380, 103T124) and Ankara University BAP (10B4240006).
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23 24 **Appendix A. Supplementary data**

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26 NMR spectra of synthesized compounds; ORTEP view, crystallographic data and explanations for
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28 compounds **37** (PDF).
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31 32 **References**

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14 13. **CCDC**-1579314 contain the supplementary crystallographic data for the structure of compound **37**.
15 These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from
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Scheme Captions

Scheme 1. Dihydrofuran-fused and 3-alkenyl-substituted pyranone, coumarin and quinolinone derivatives.

Scheme 2. The proposed mechanism for the formation of alkenyl-substituted compounds.

Scheme 3. Reaction of 4-hydroxycoumarin (**1a**) with **2j**.

Scheme 4. Ring-opening reaction of dihydrofuroquinolinone **31**.

Scheme 5. Ring opening reaction of compounds **49** and **50**

Table Captions

Table 1. Reaction of 4-hydroxycoumarin (**1a**) with 1,1-disubstituted alkenes **2a-e**.^a

Table 2. Reaction of 4-hydroxy-6-methyl-2*H*-pyran-2-one (**1b**) with **2a-c**.^a

Table 3. Reaction of **1c, d** with **2a-c**.

Table 4. Reaction of **1e** with **2a-c**.^a

Table 5. Reactions of **1a-c** with **2f, g**.^a

Table 6. Reactions of **1a, b, e** with **2h, i**.^a

Table 7. Zone diameters (mm) of the compounds against bacteria.

Table 8. Zone diameters (mm) of antibiotics against bacteria¹¹⁹.

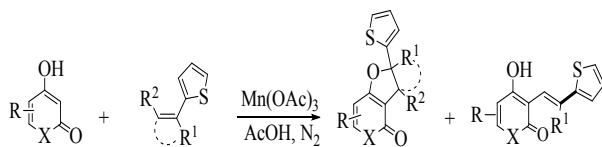
Table 9. MIC results ($\mu\text{g/mL}$).

Figure Caption

Fig. 1. The molecular entities of compound **37**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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The syntheses, spectroscopic properties, and antimicrobial activities of new pyranones and quinoline-based dihydrofurans accompanied by 3-alkenyl-substituted structures were investigated.



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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 ... Cg1ⁱ (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.

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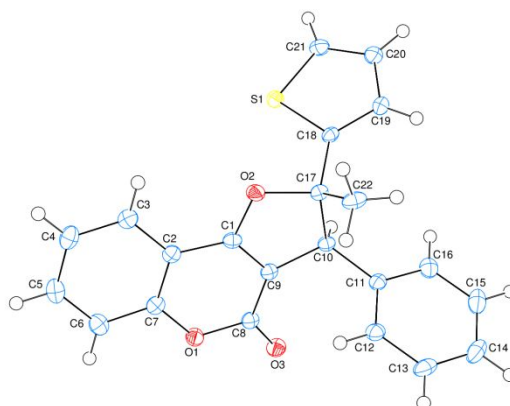


Figure 1. The molecular entities of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

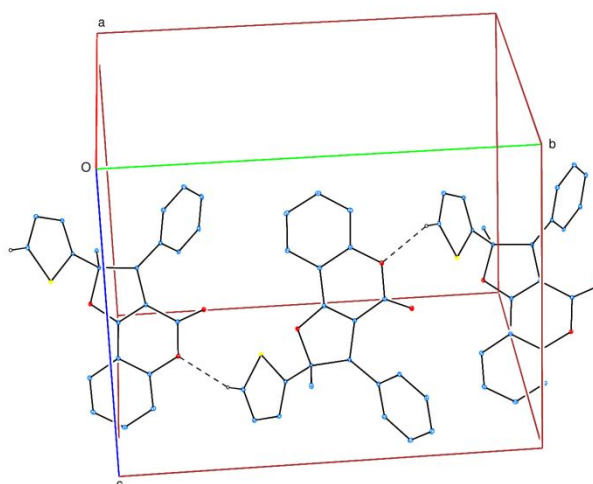


Figure 2. A partial packing diagram of the title compound. Intermolecular C-H ...O hydrogen bonds are shown as dashed lines. Nonbonding H atoms have been omitted for clarity.

Table 1. Crystallographic data.

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| Empirical Formula | C ₂₂ H ₁₆ O ₃ S |
| Fw | 360.41 |
| Crystal System | monoclinic |
| Space Group | <i>P</i> 2 ₁ / <i>c</i> |
| <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 |

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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) |

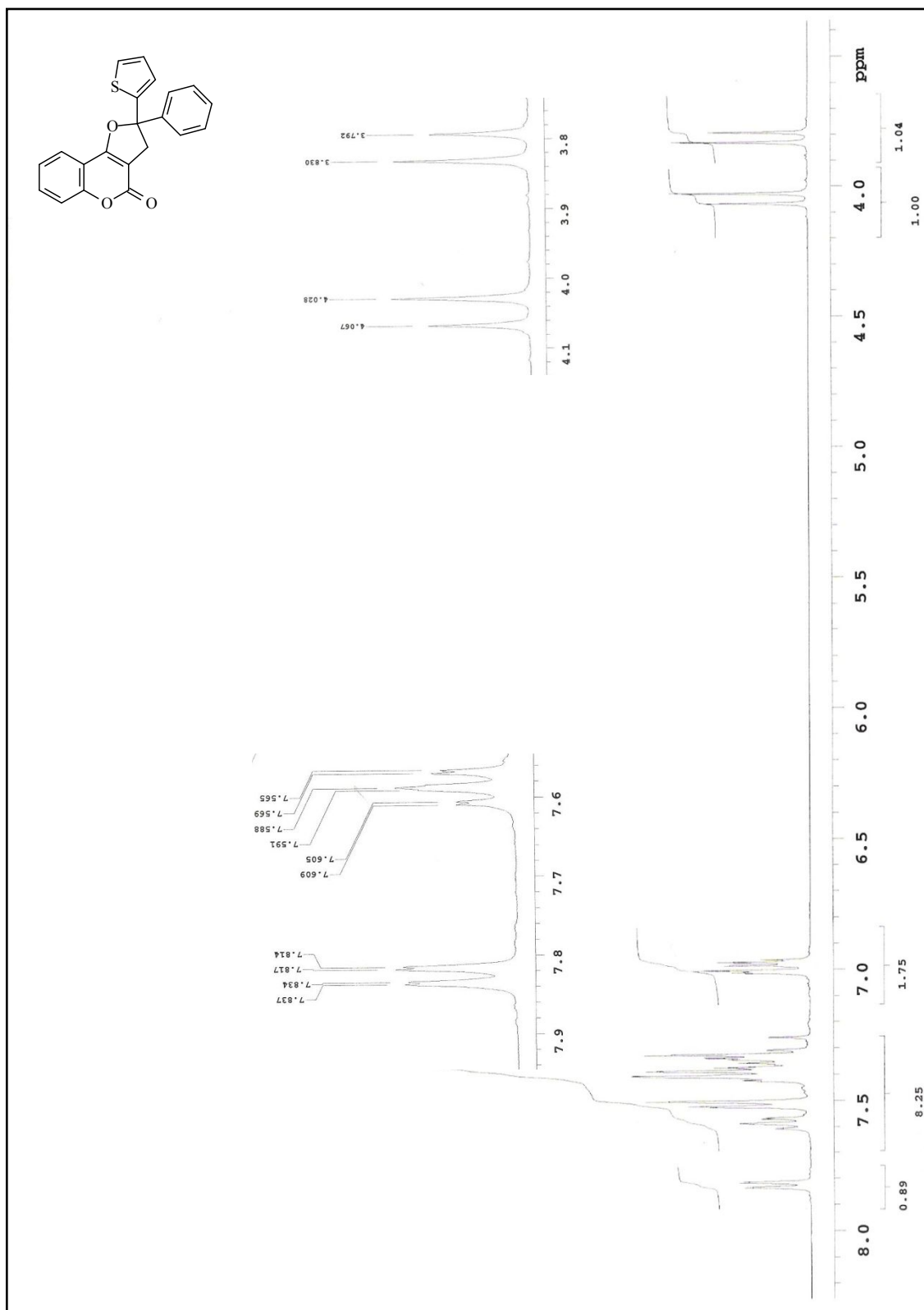
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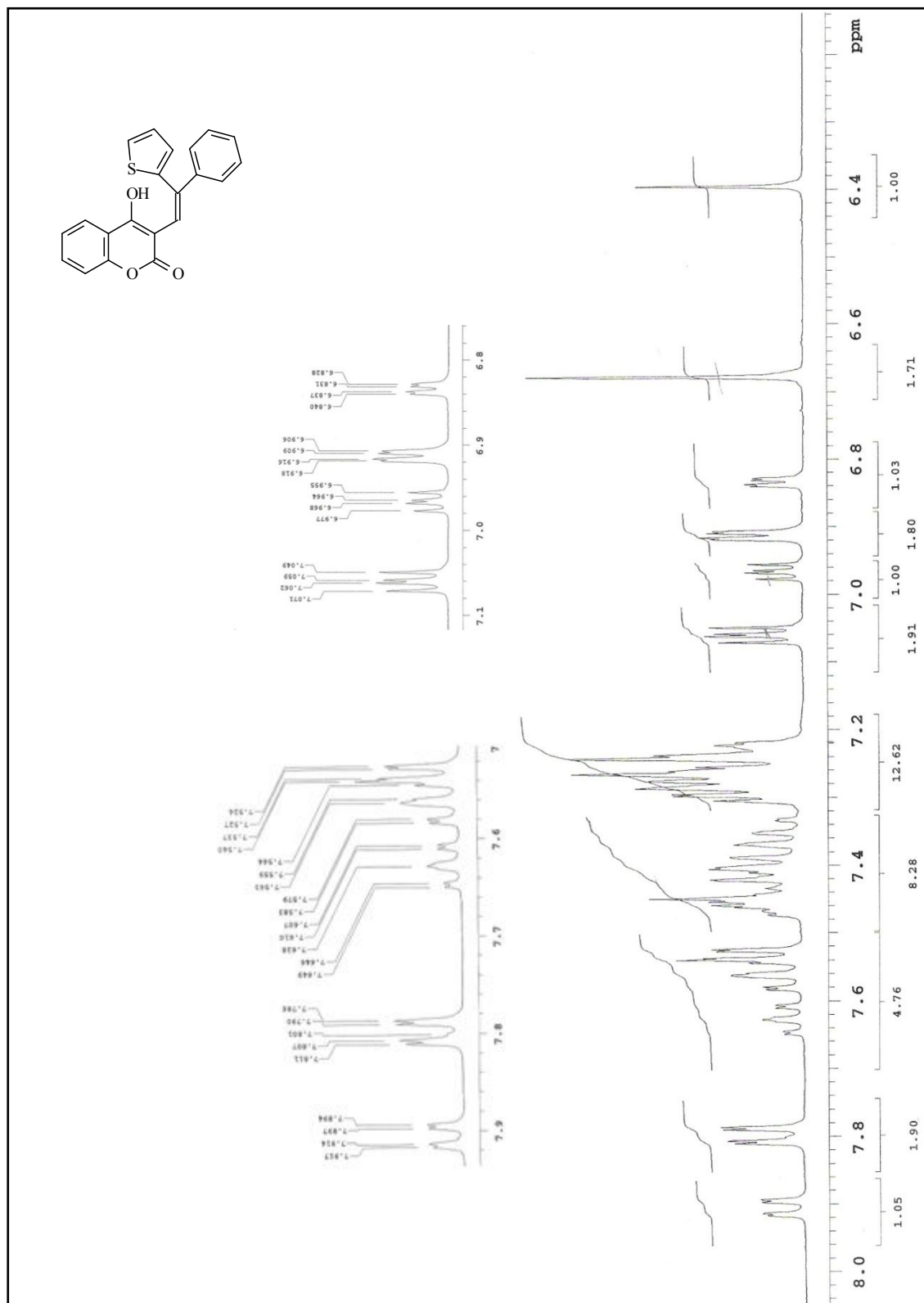
Table 3 Hydrogen-bond geometry (Å,°)

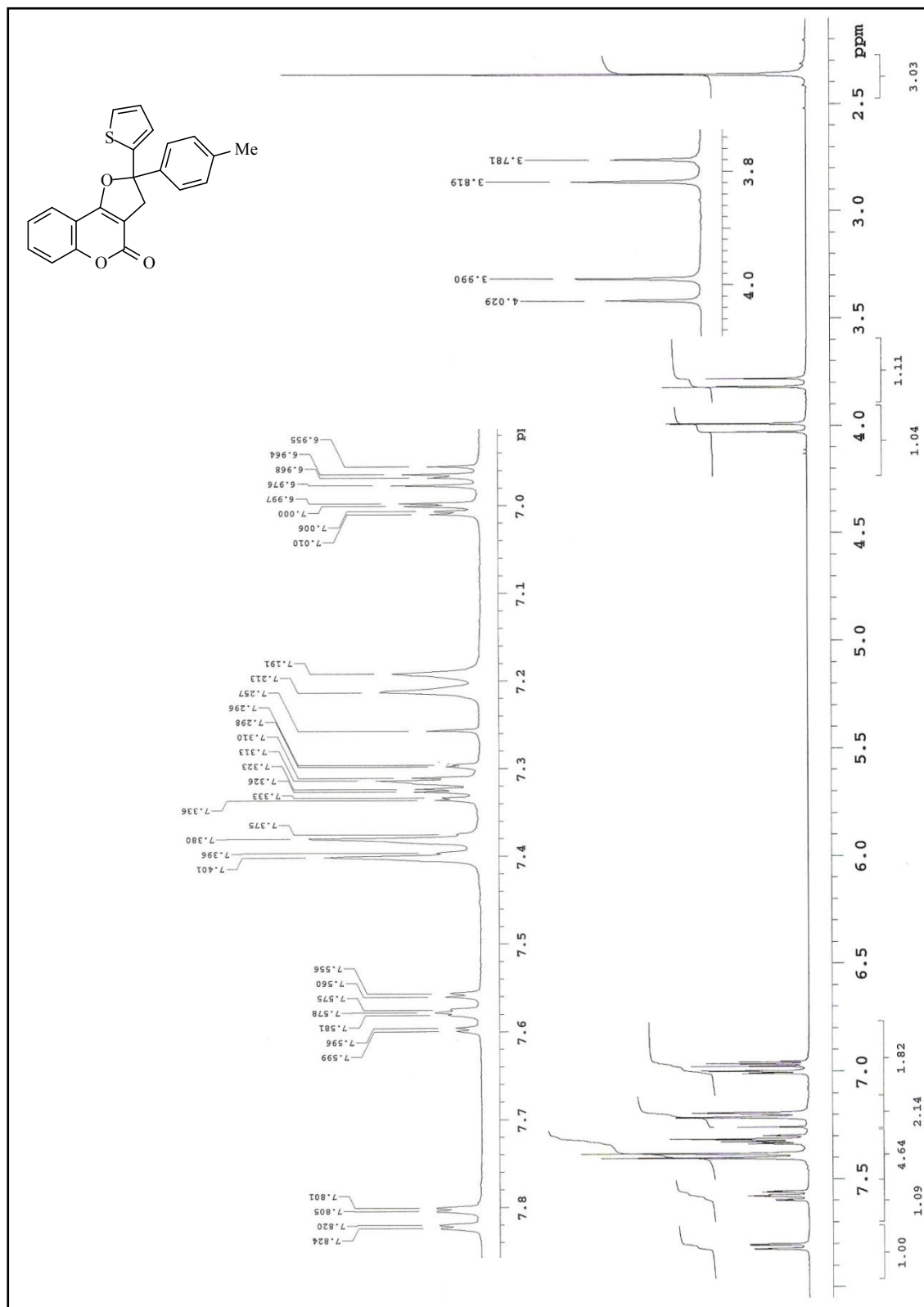
| D-H ...A | D-H | H ...A | D ...A | D-H ...A |
|-----------------------------|------|--------|-------------|----------|
| C21—H21...O1 ⁱ | 0.93 | 2.43 | 3.2052 (16) | 141 |
| C13—H13...Cg1 ⁱⁱ | 0.93 | 3.08 | 4.0018 (15) | 173 |

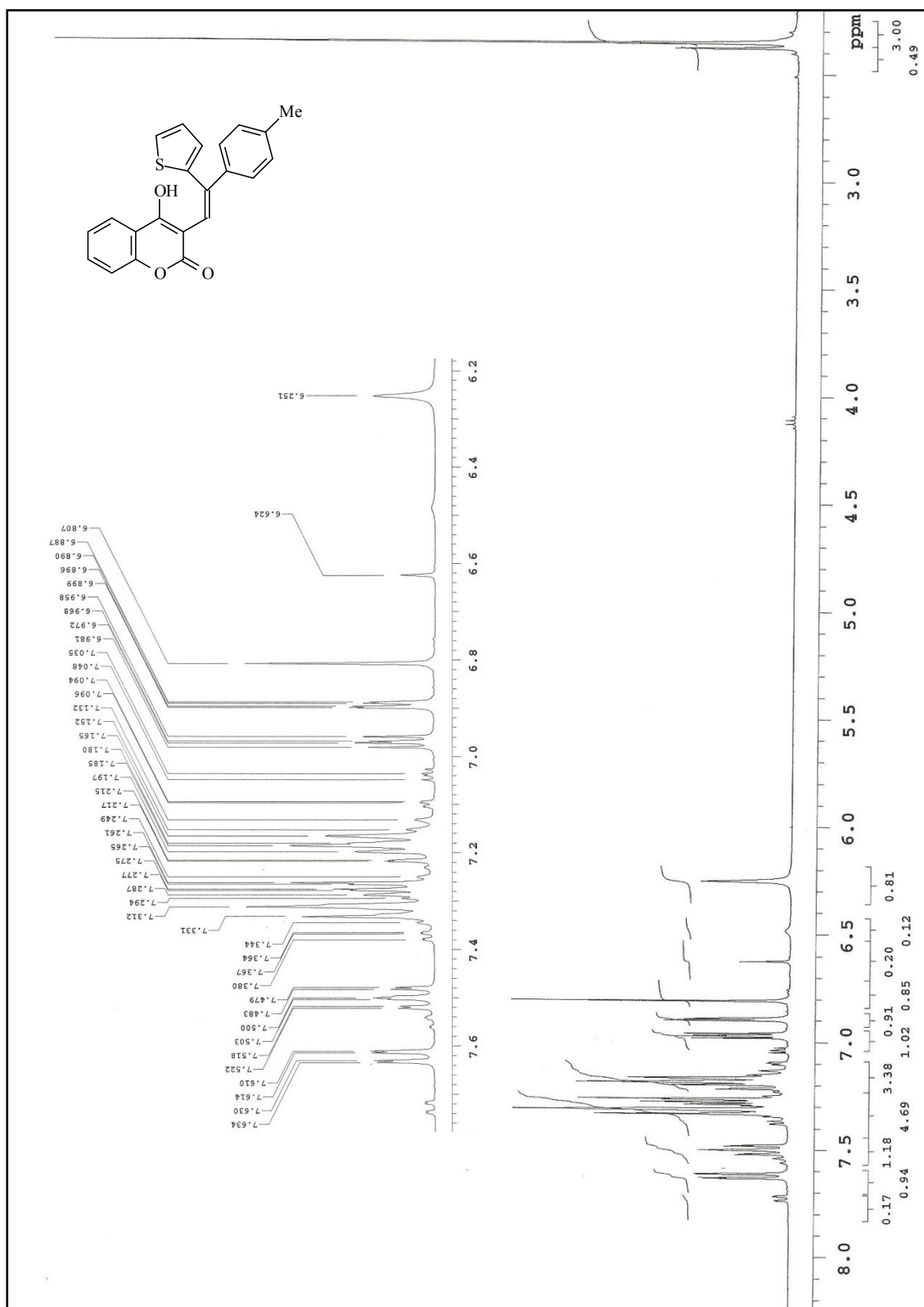
Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $-x+2, y+1/2, -z+3/2$. Cg1 is the centroid of ring (C2-C7).

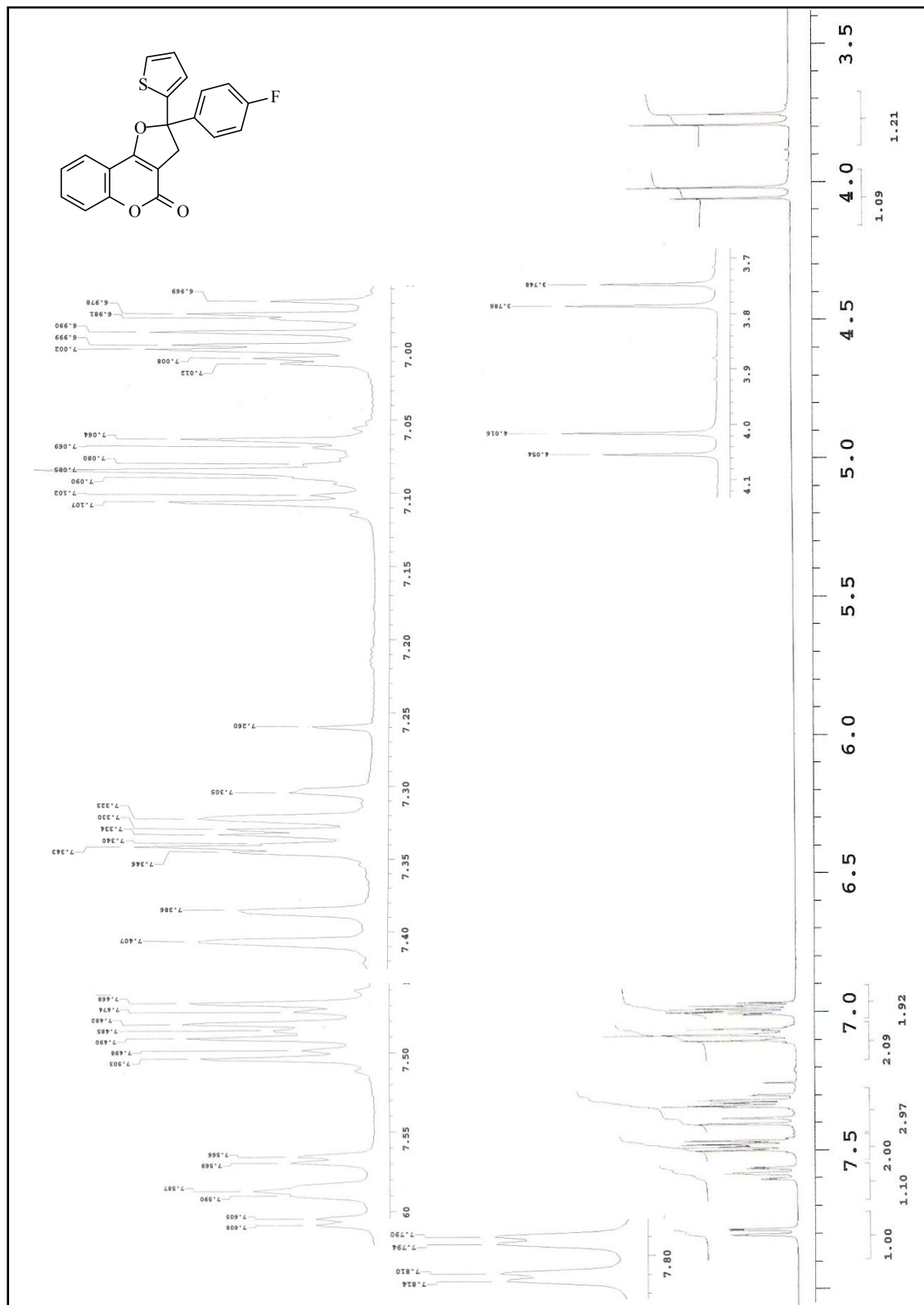
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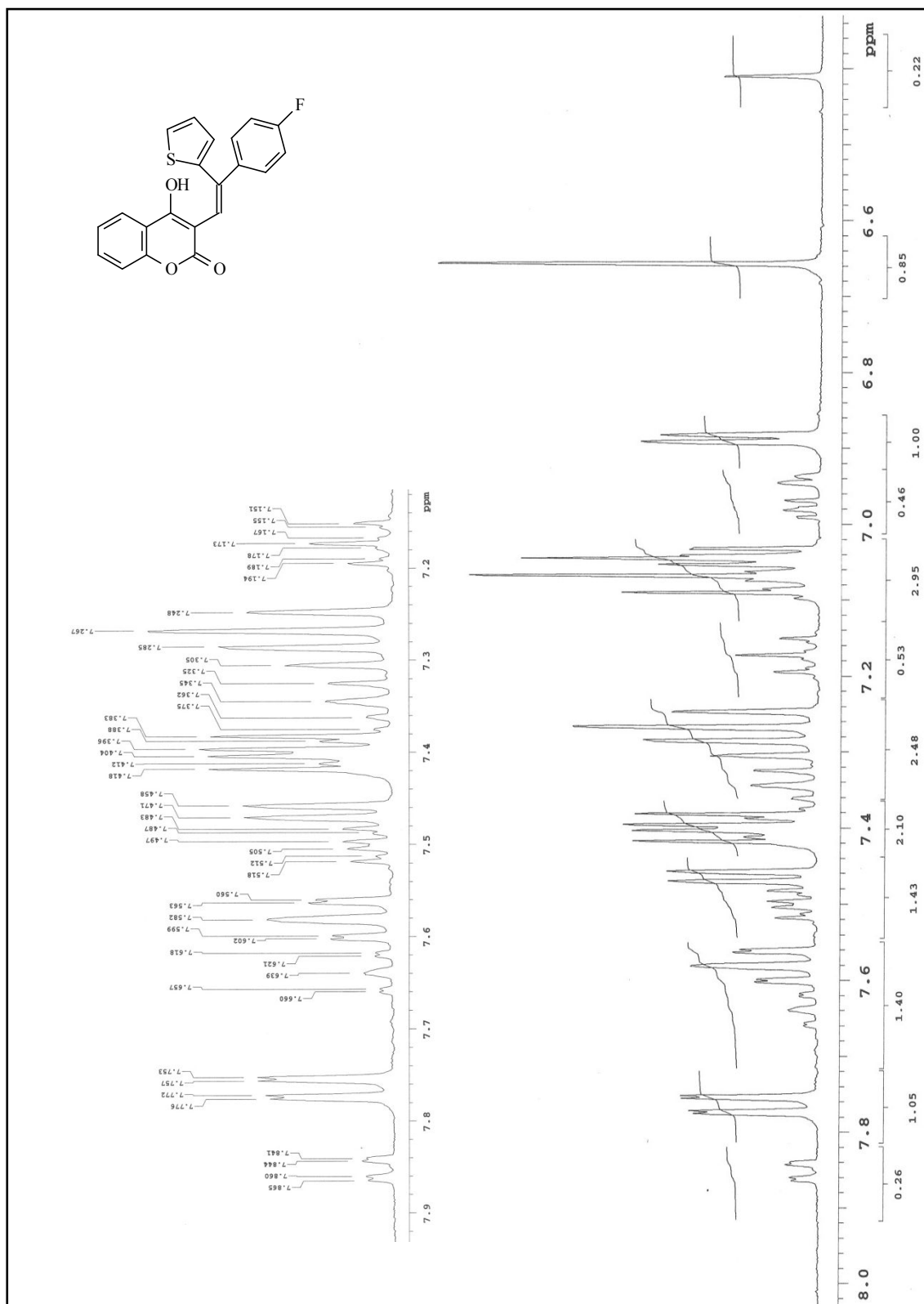
¹H-NMR of COMPOUNDS2.1 ¹H-NMR spectra of **3**

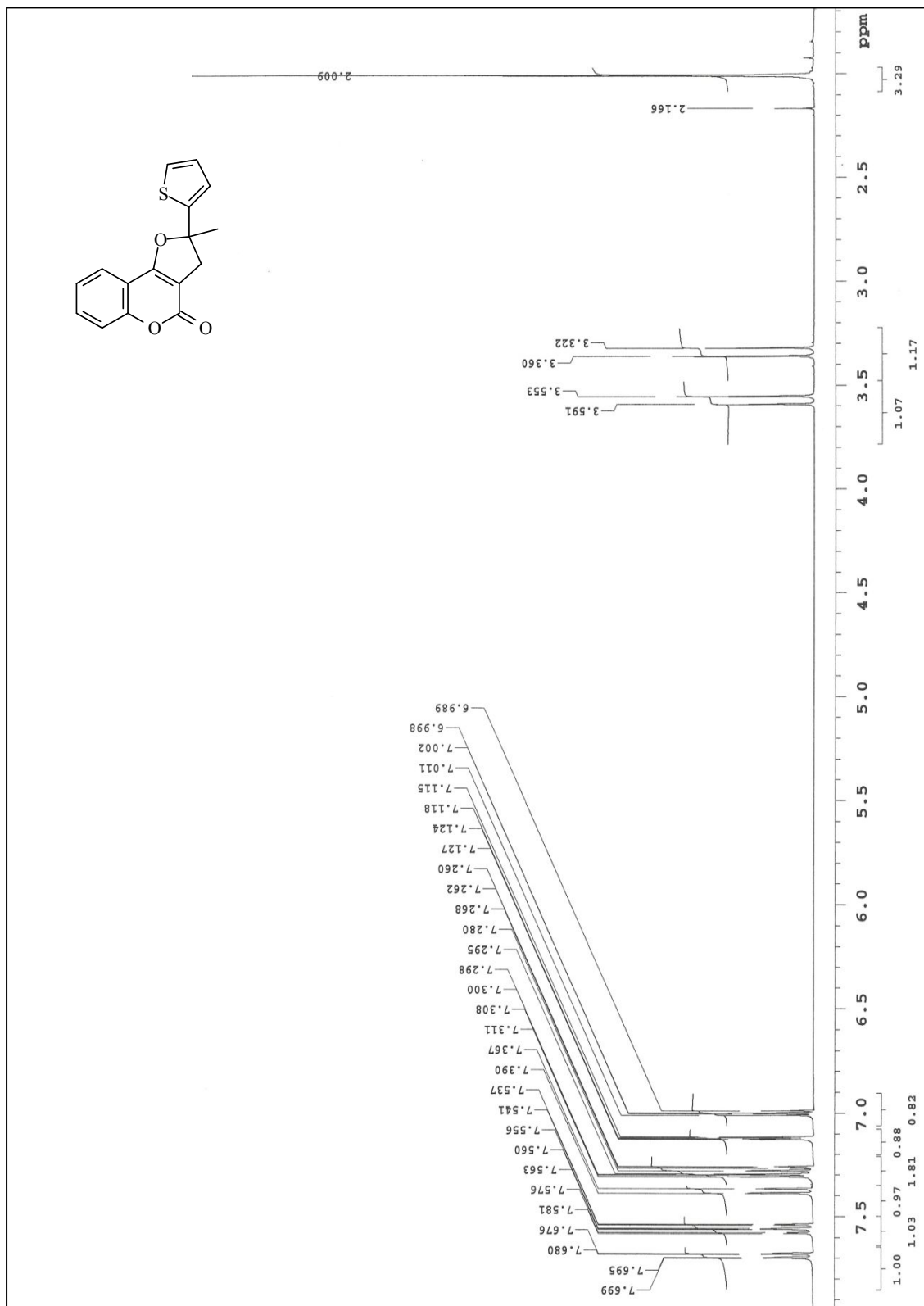
2.2 ¹H-NMR spectra of **8**

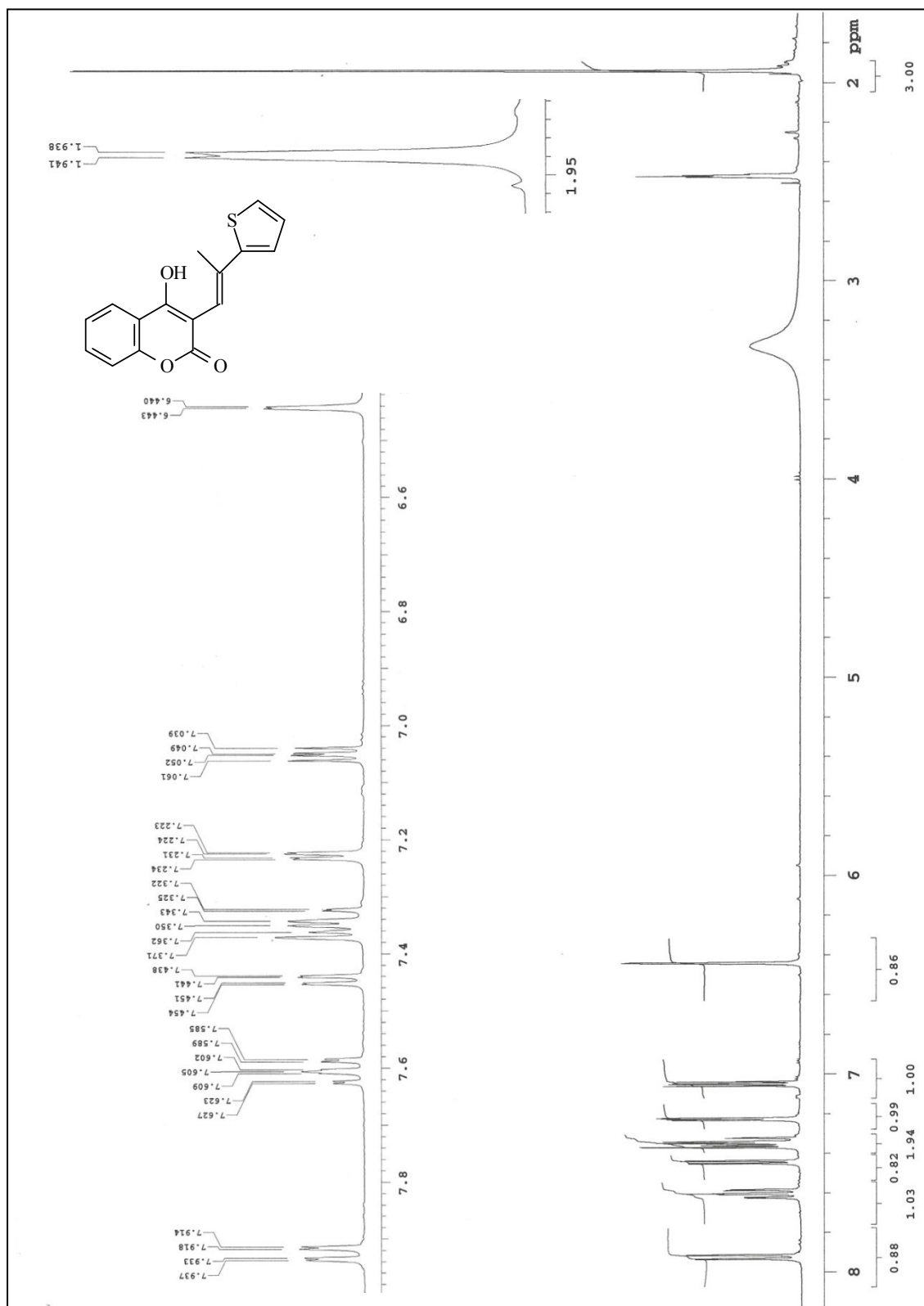
2.3 ¹H-NMR spectra of 4

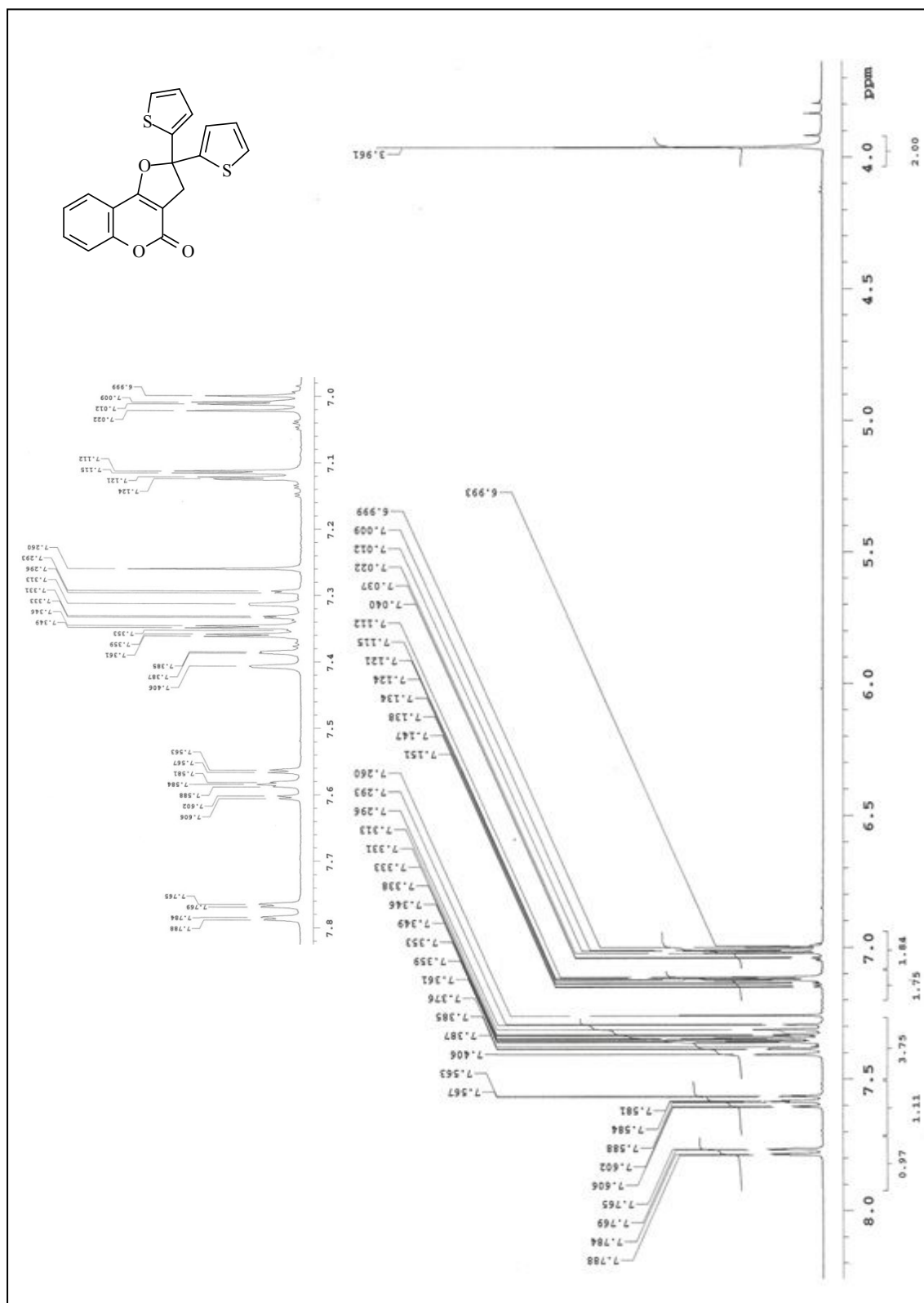
2.4 $^1\text{H-NMR}$ spectra of **9**

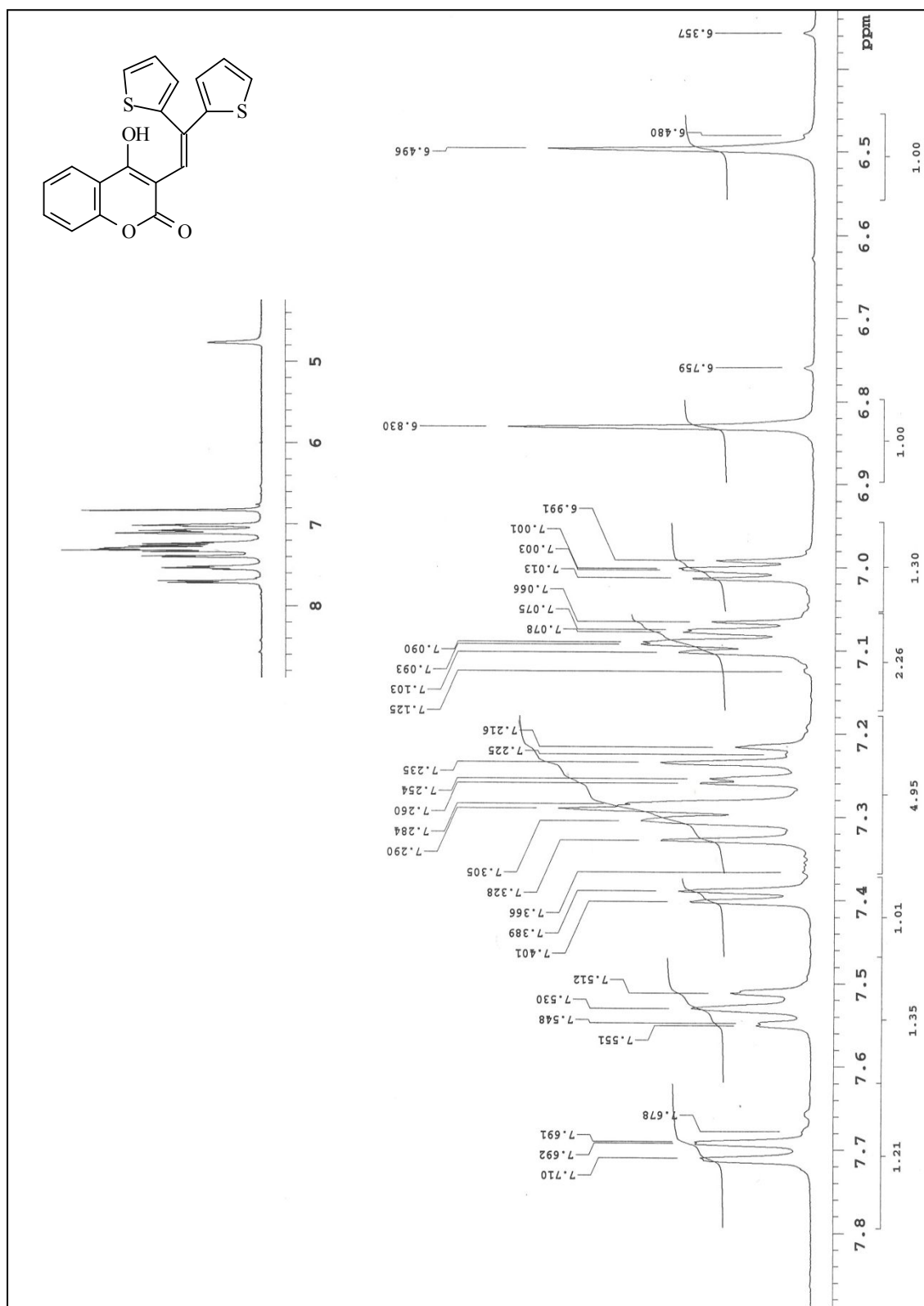
2.5 $^1\text{H-NMR}$ spectra of **5**

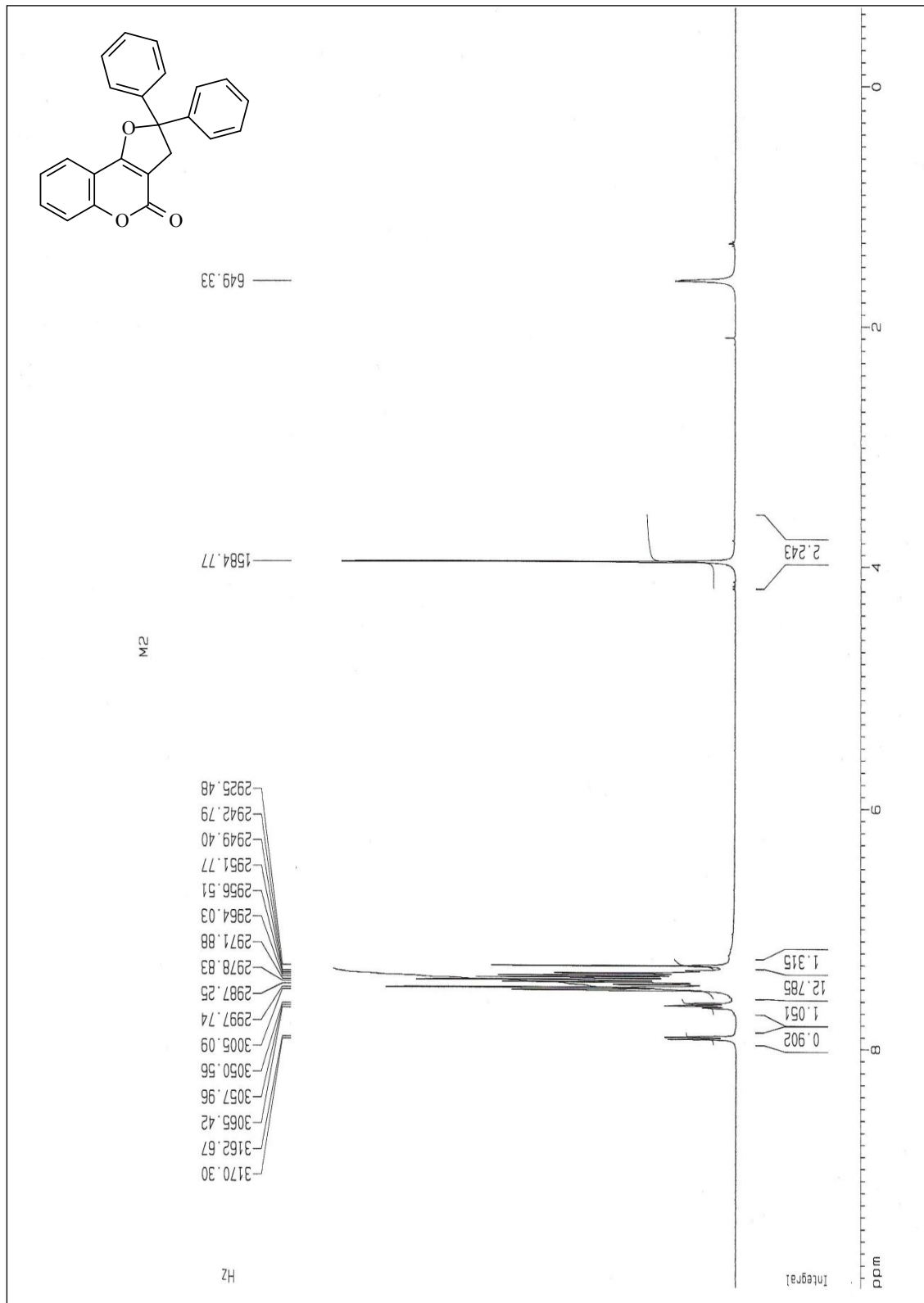
2.6 $^1\text{H-NMR}$ spectra of **10**

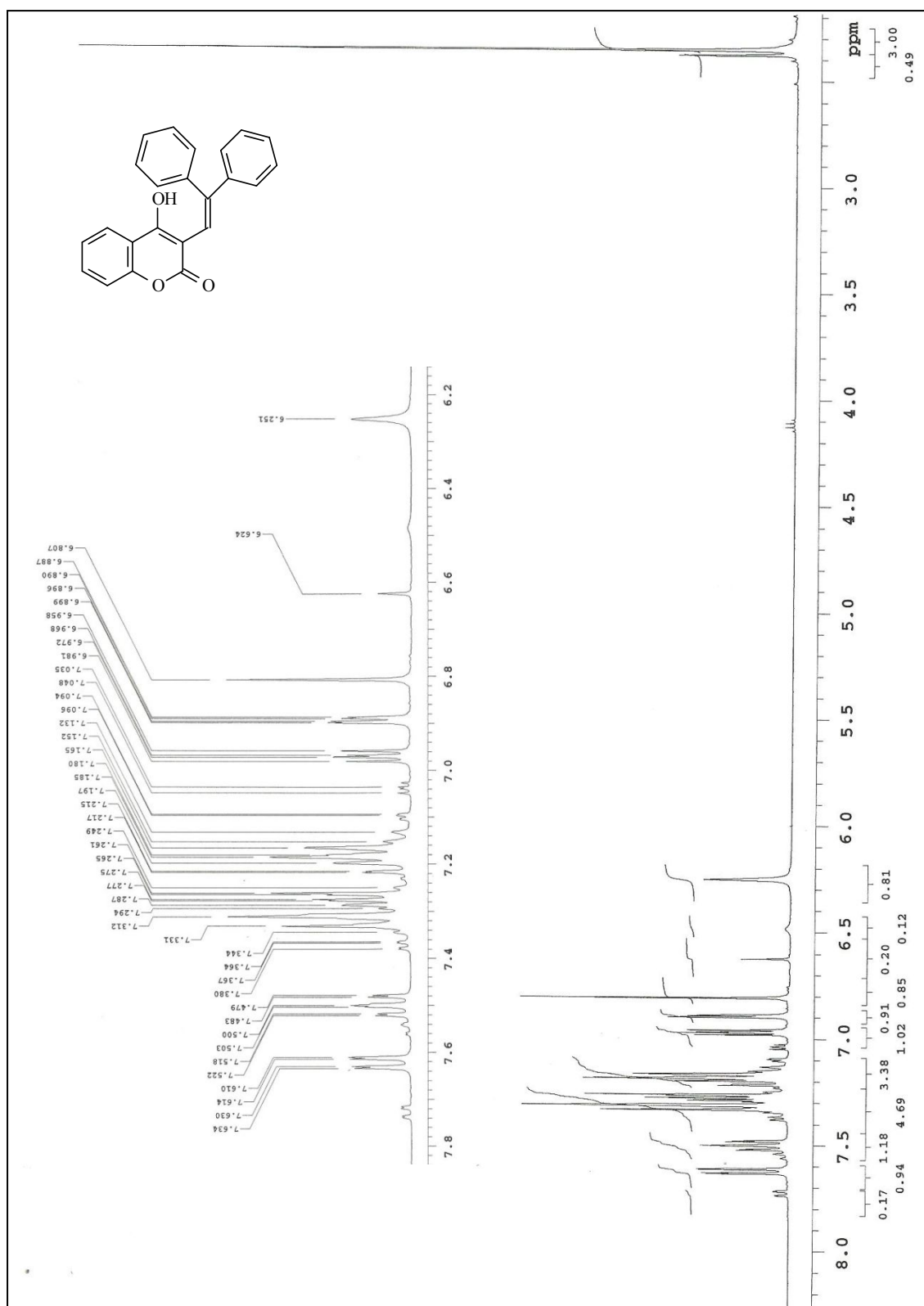
2.7 $^1\text{H-NMR}$ spectra of **6**

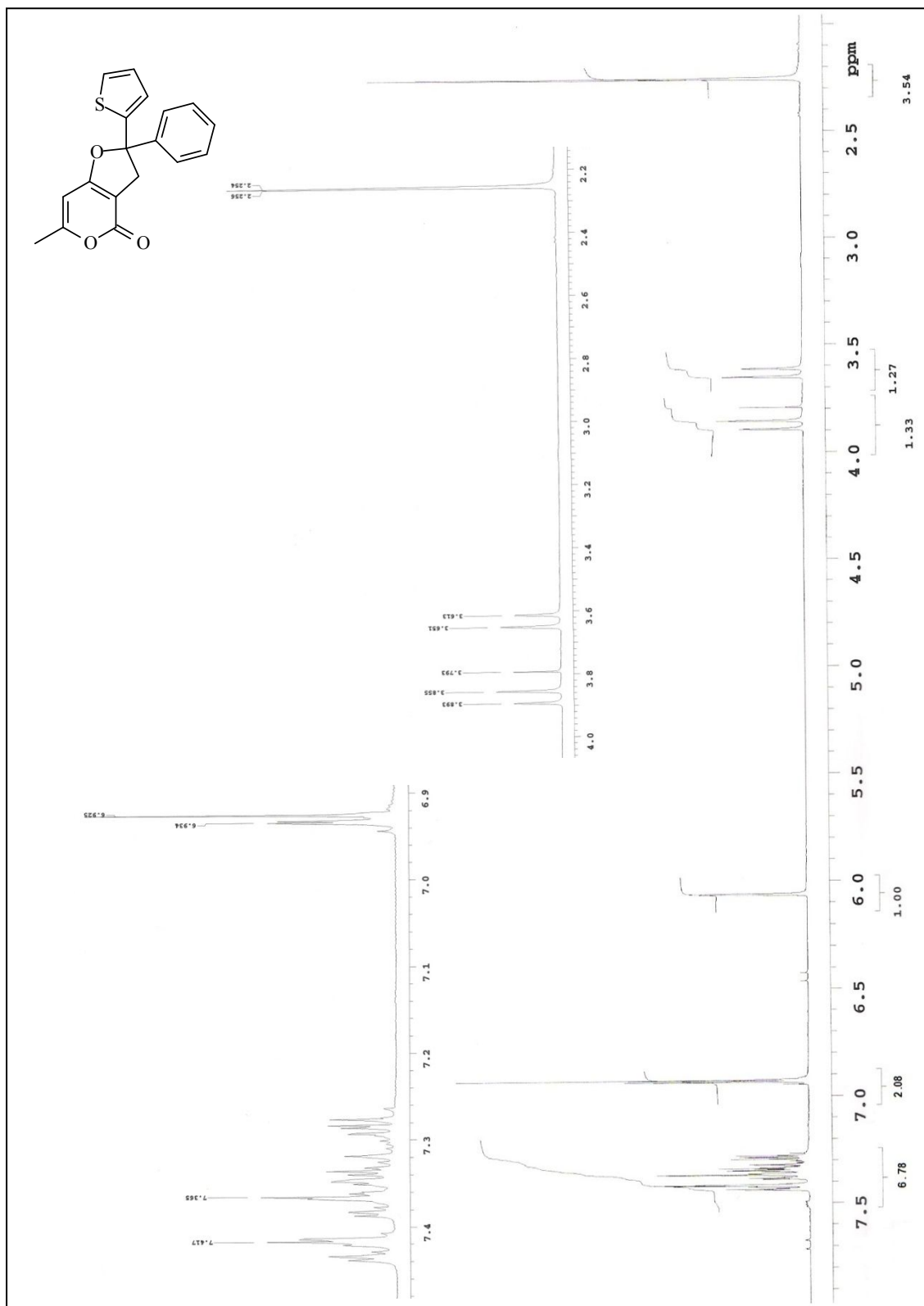
2.8 $^1\text{H-NMR}$ spectra of **11**

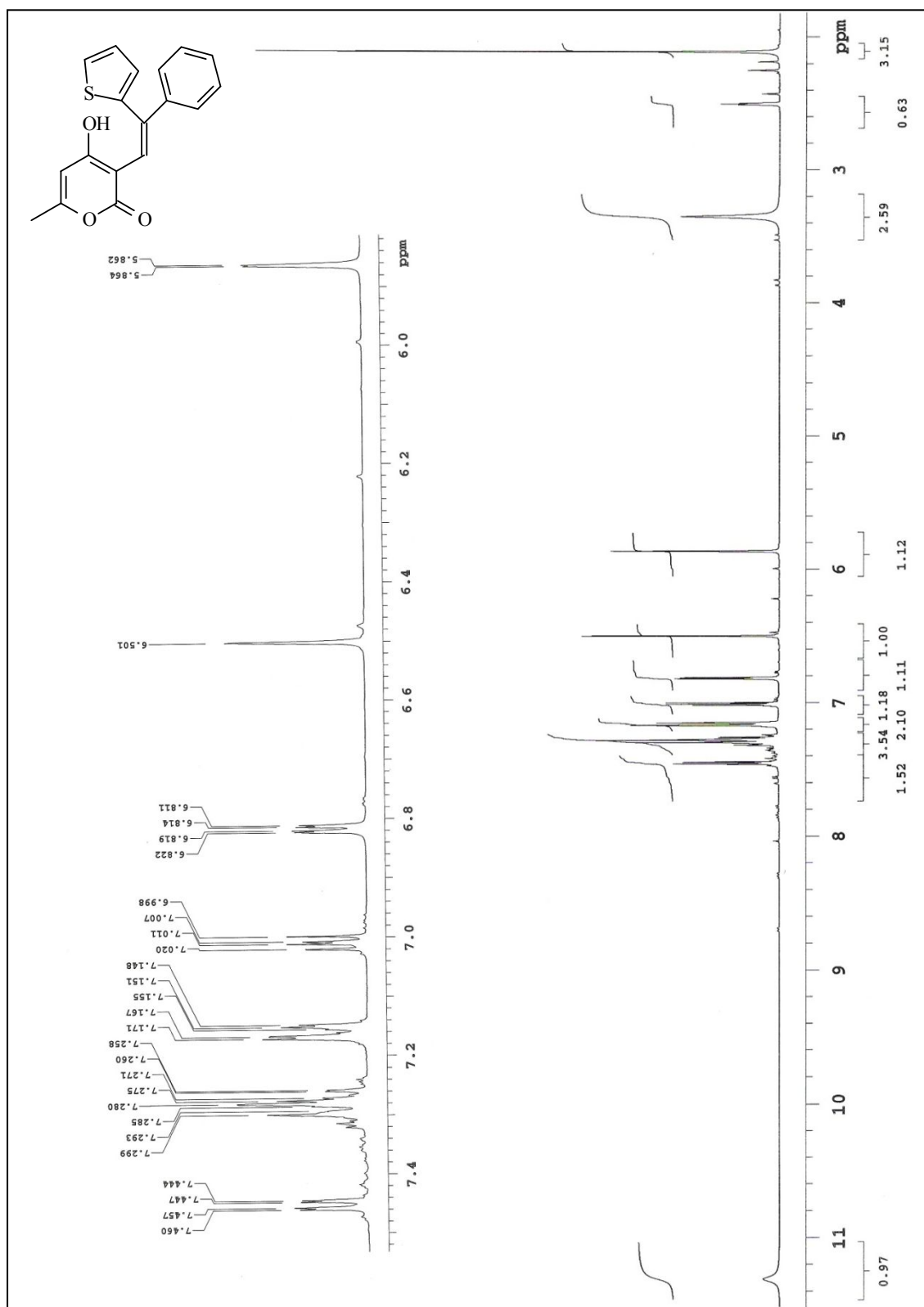
2.9 $^1\text{H-NMR}$ spectra of **7**

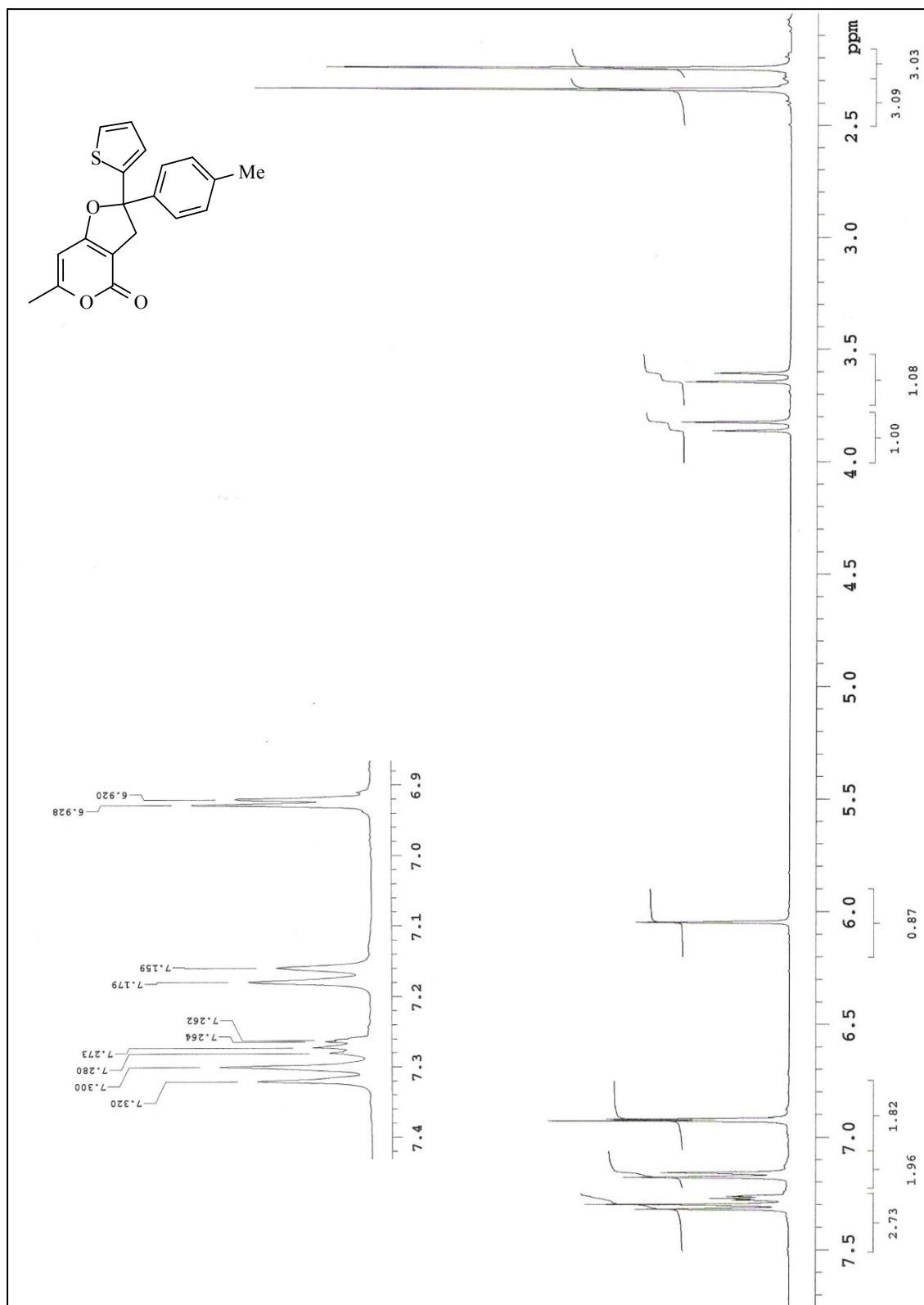
2.10 $^1\text{H-NMR}$ spectra of **12**

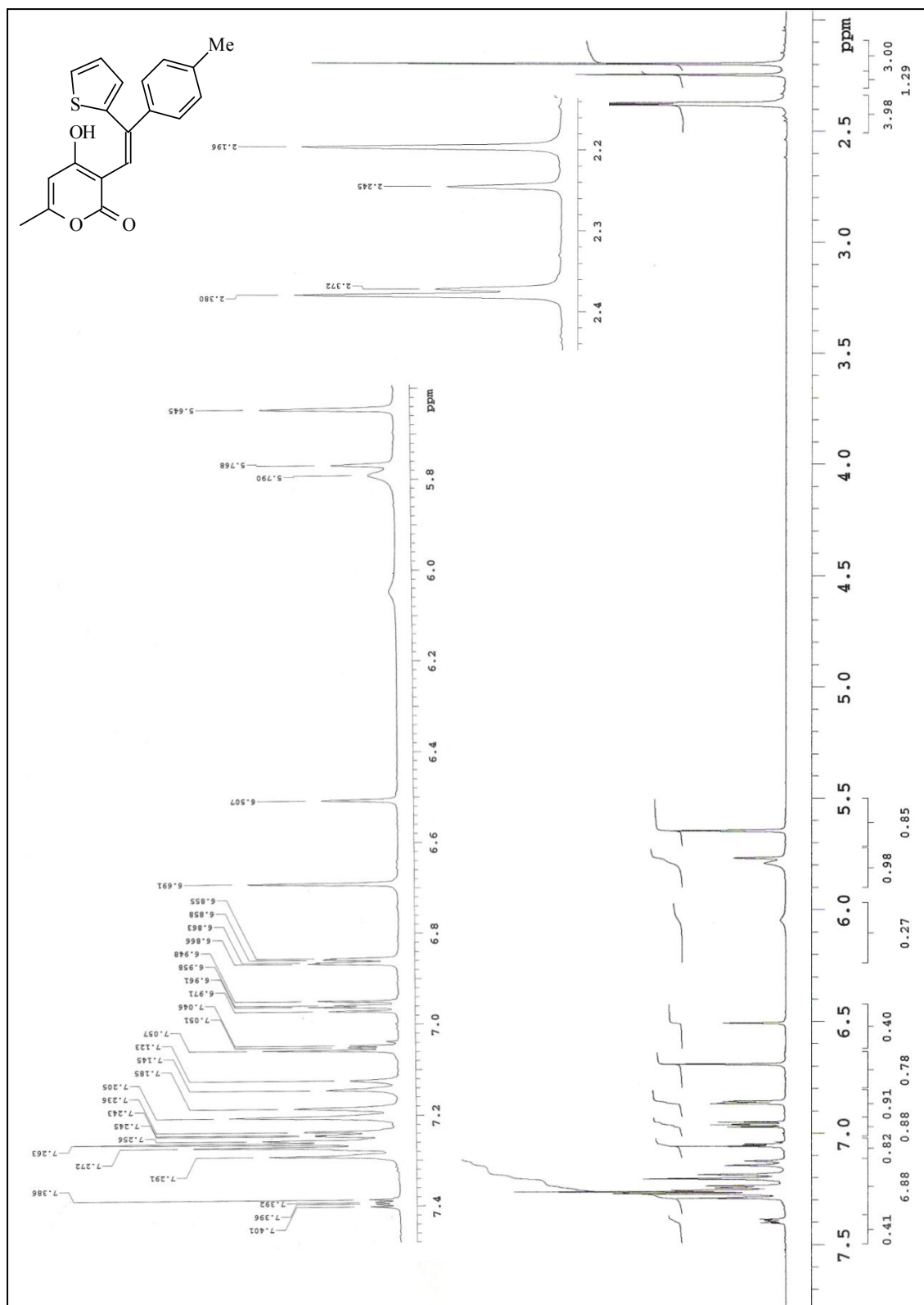
2.11 $^1\text{H-NMR}$ spectra of **3aj**

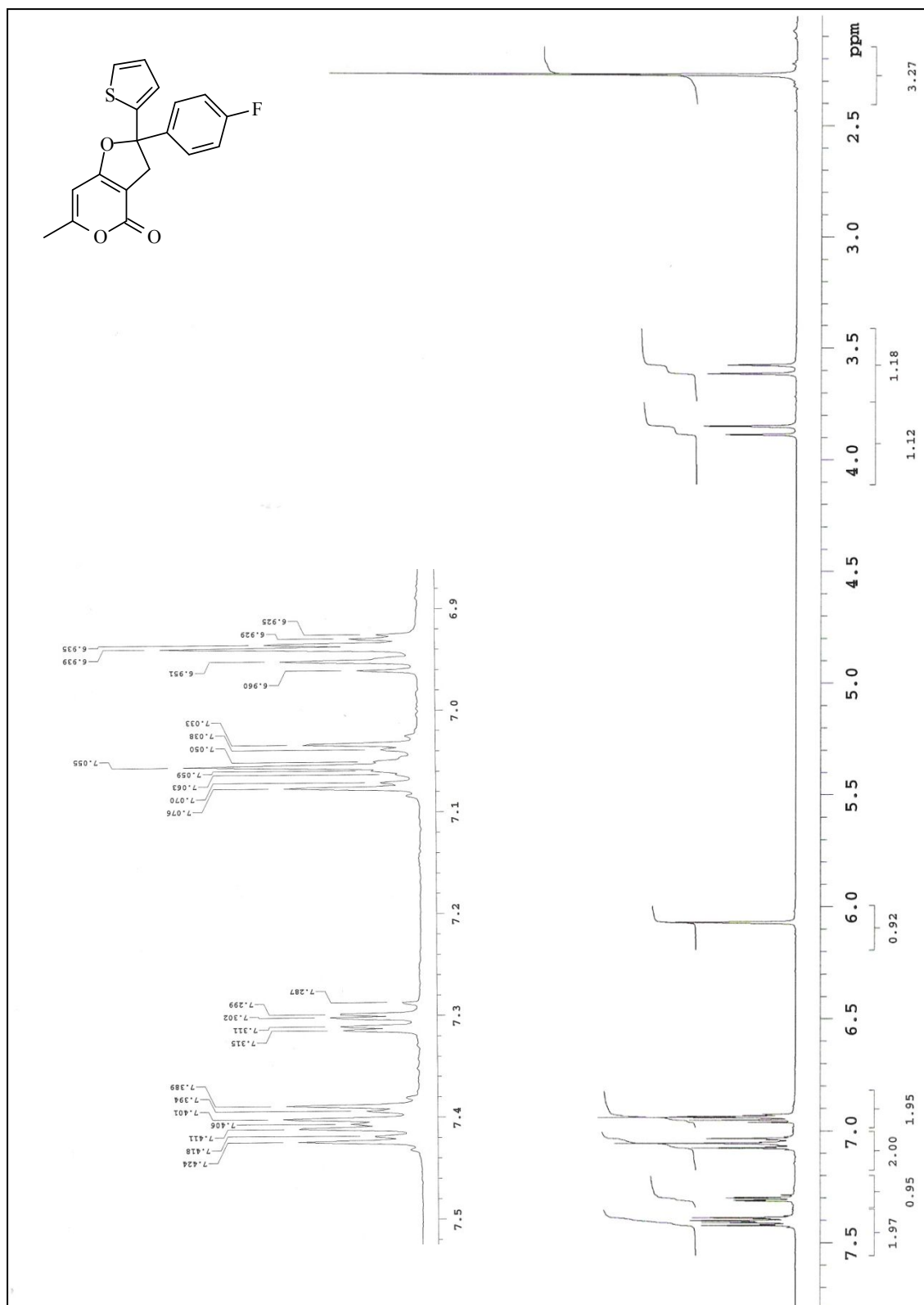
2.12 $^1\text{H-NMR}$ spectra of **4aj**

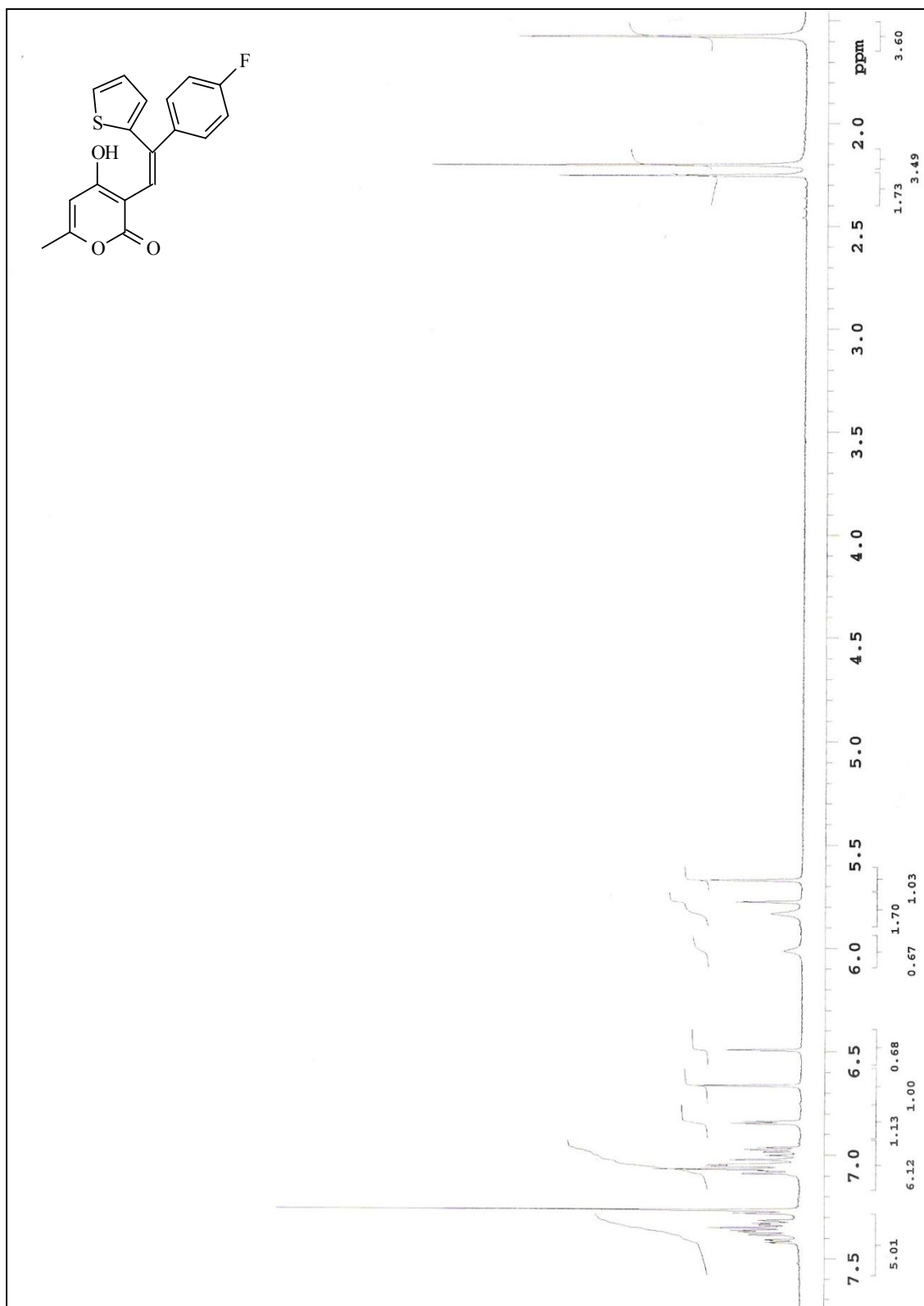
2.13 $^1\text{H-NMR}$ spectra of **13**

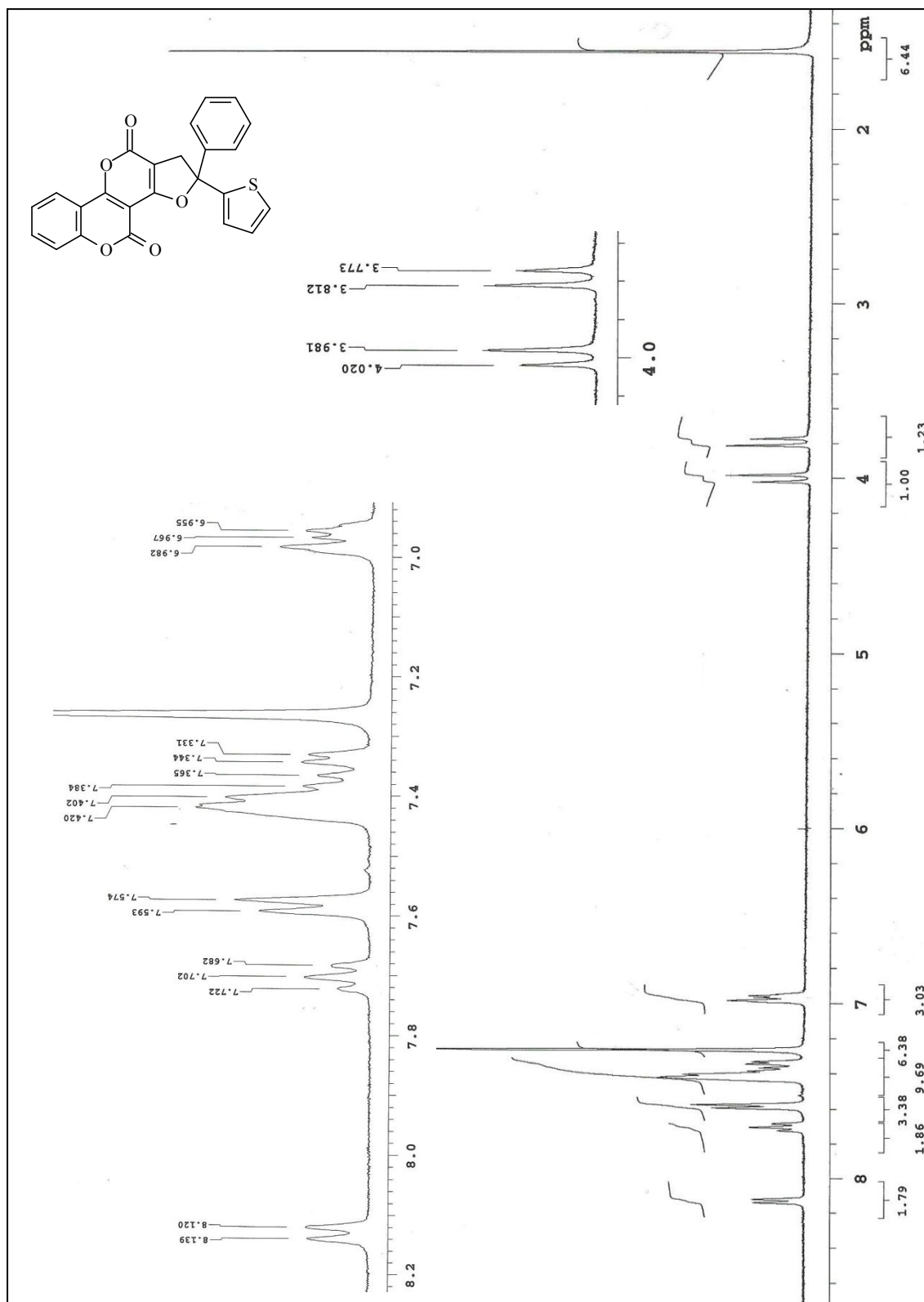
2.14 ¹H-NMR spectra of 16

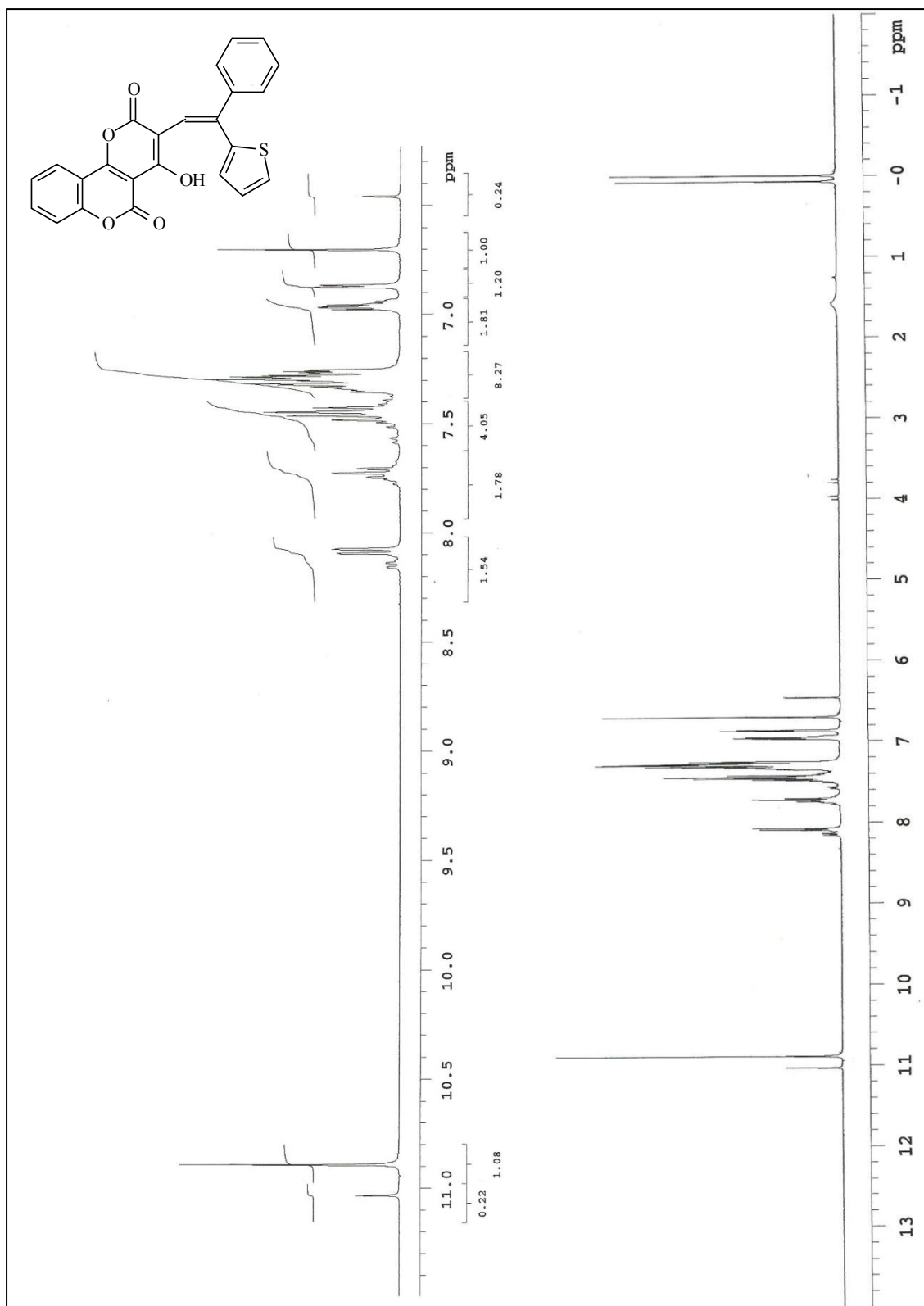
2.15 $^1\text{H-NMR}$ spectra of **14**

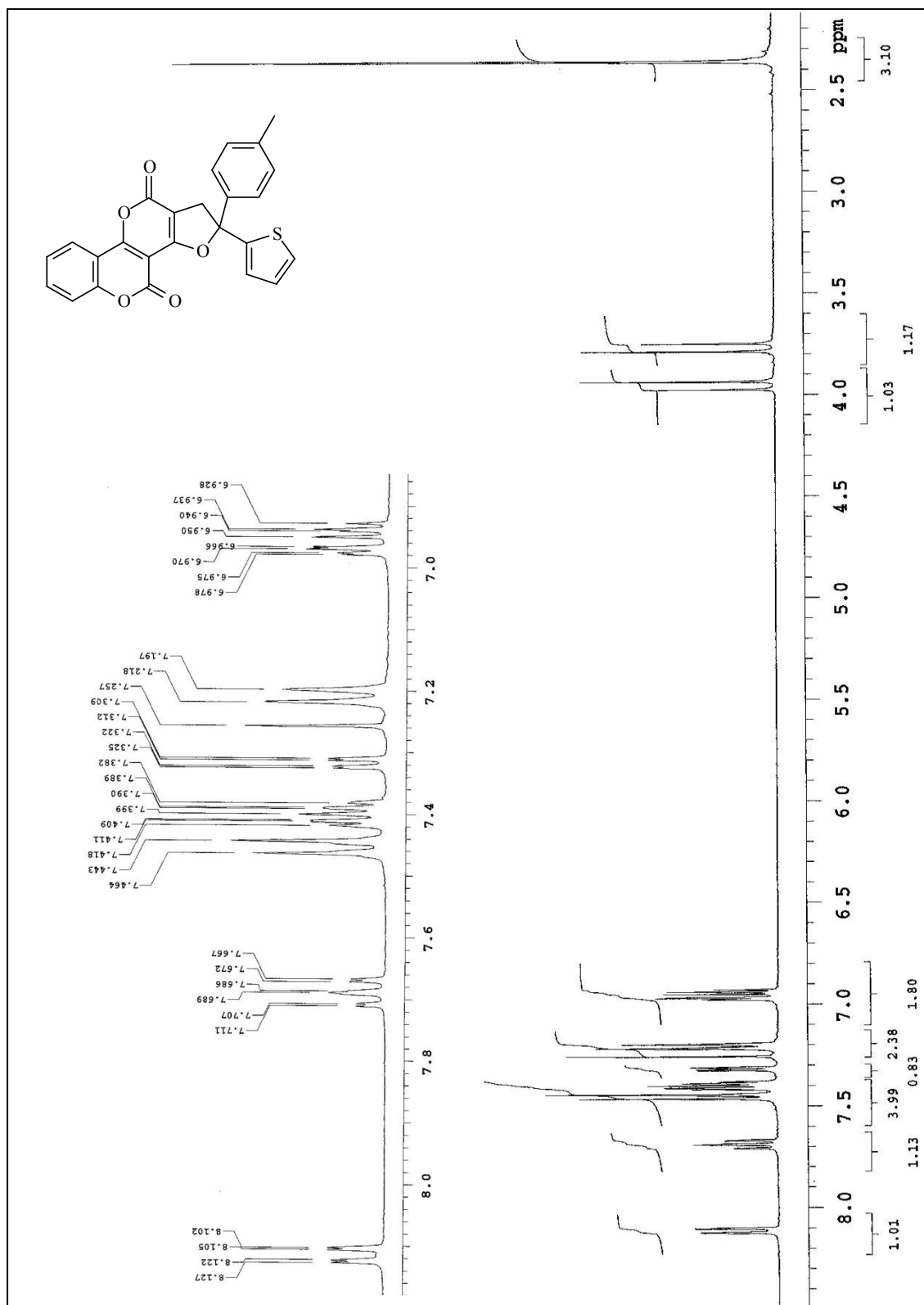
2.16 $^1\text{H-NMR}$ spectra of **17**

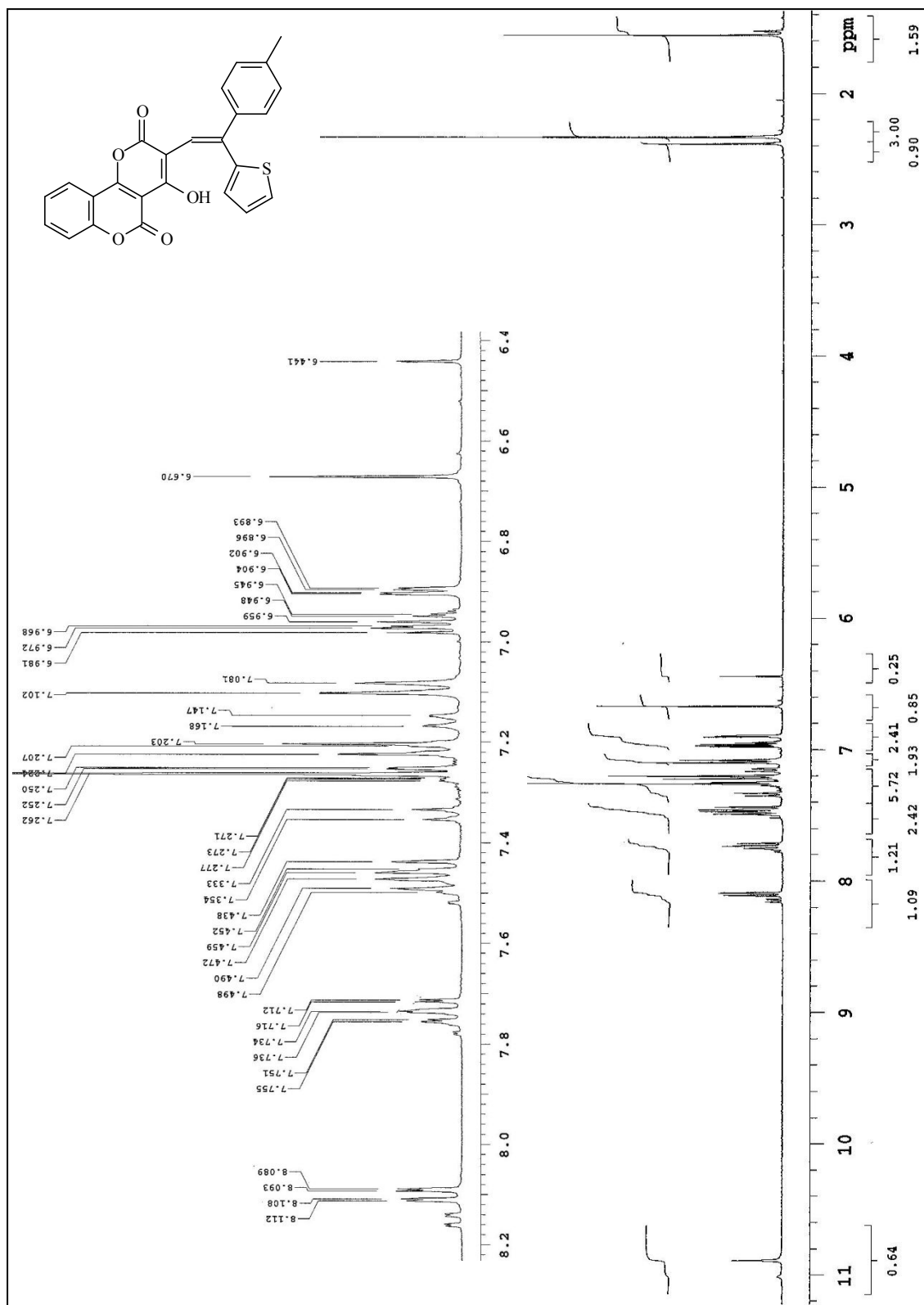
2.17 $^1\text{H-NMR}$ spectra of **15**

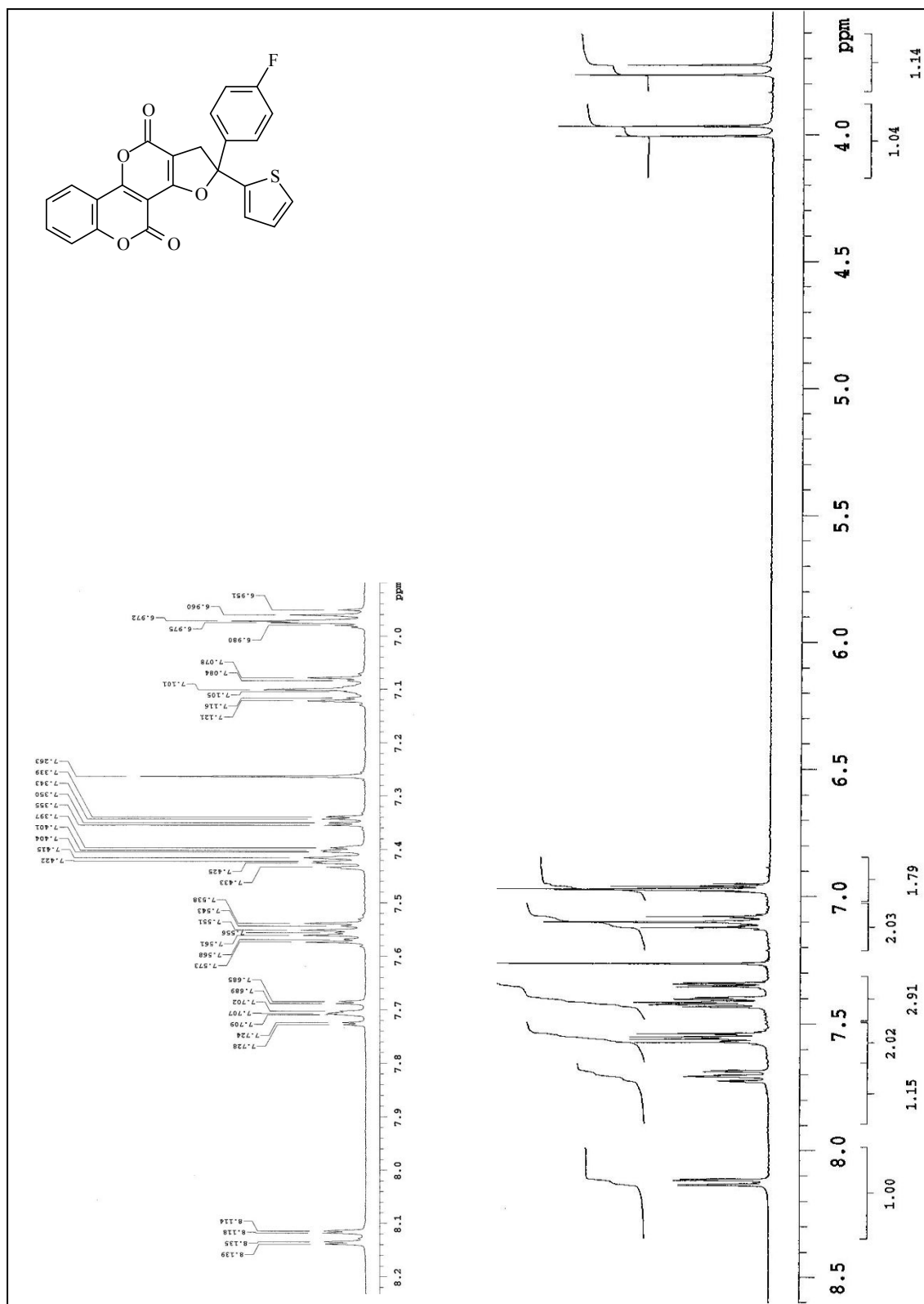
2.18 $^1\text{H-NMR}$ spectra of **18**

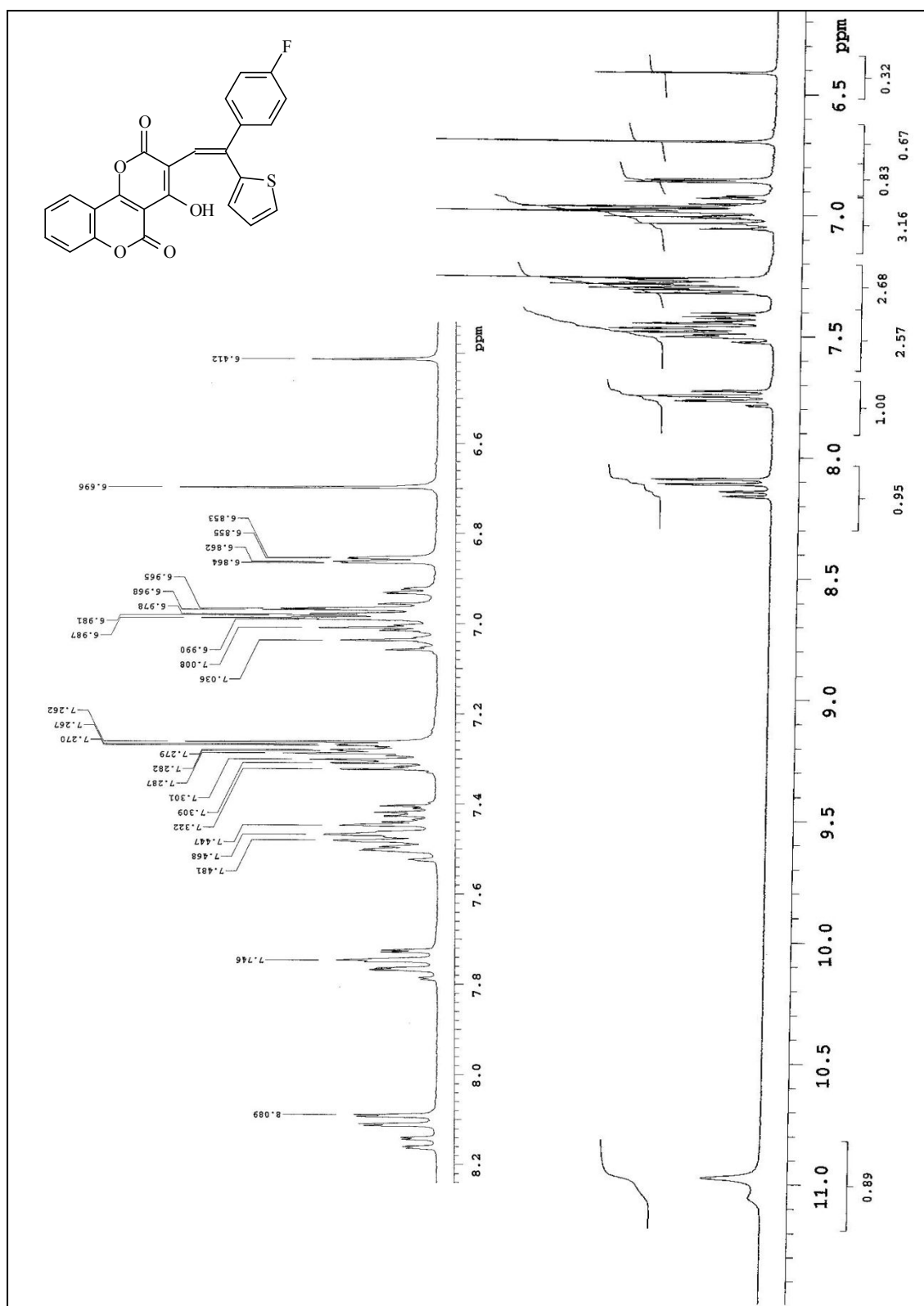
2.19 $^1\text{H-NMR}$ spectra of **19**

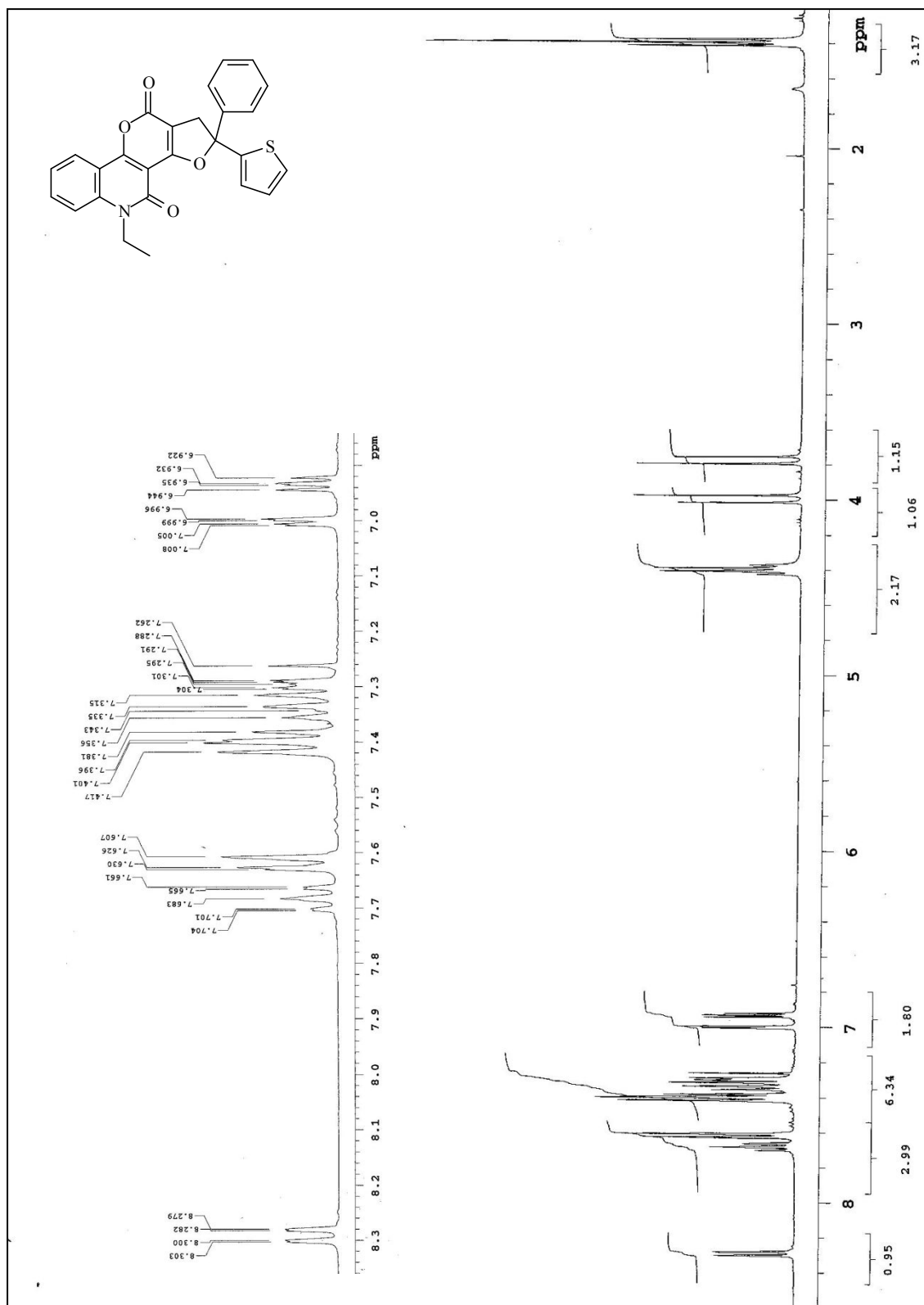
2.20 $^1\text{H-NMR}$ spectra of **25**

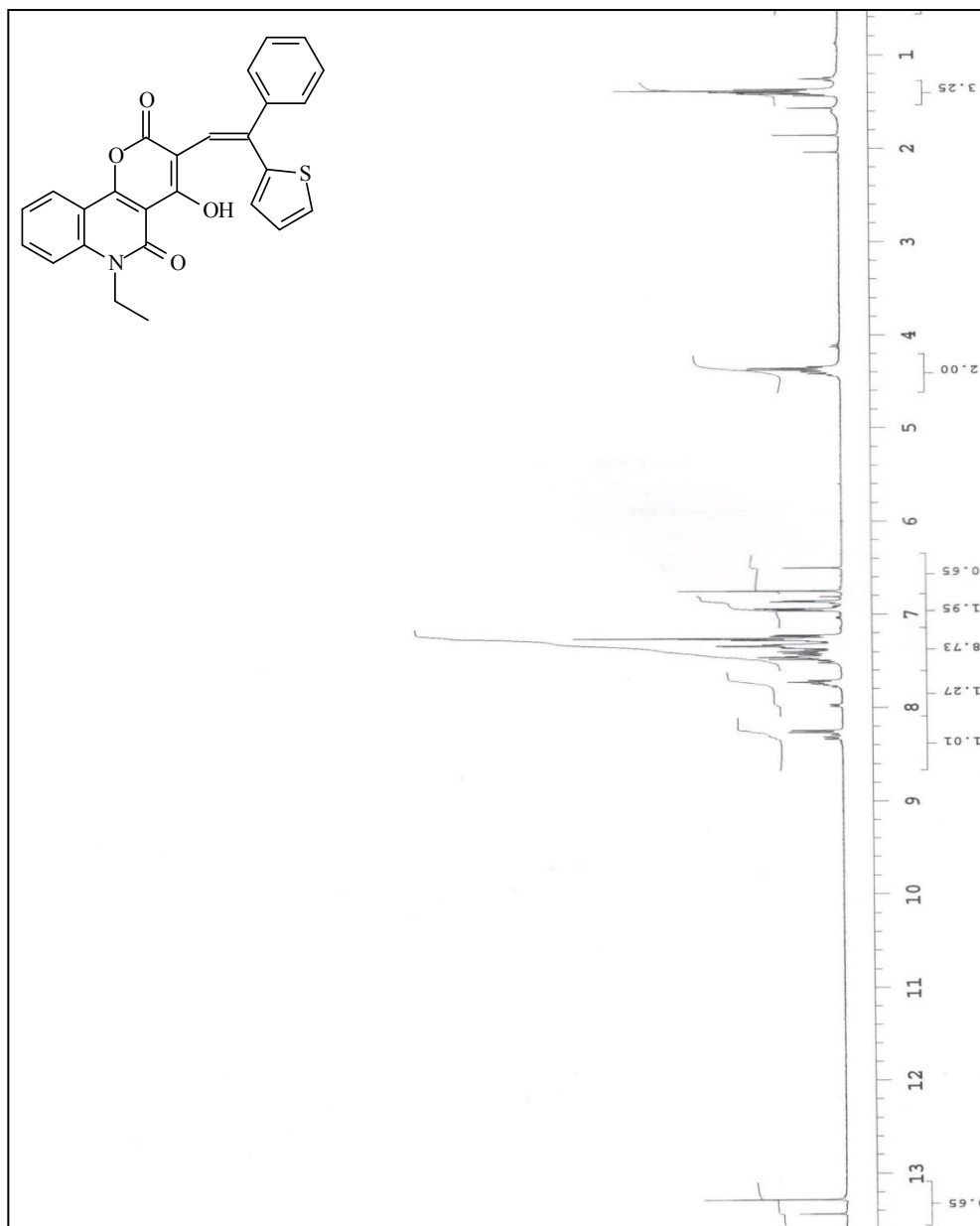
2.21 $^1\text{H-NMR}$ spectra of **20**

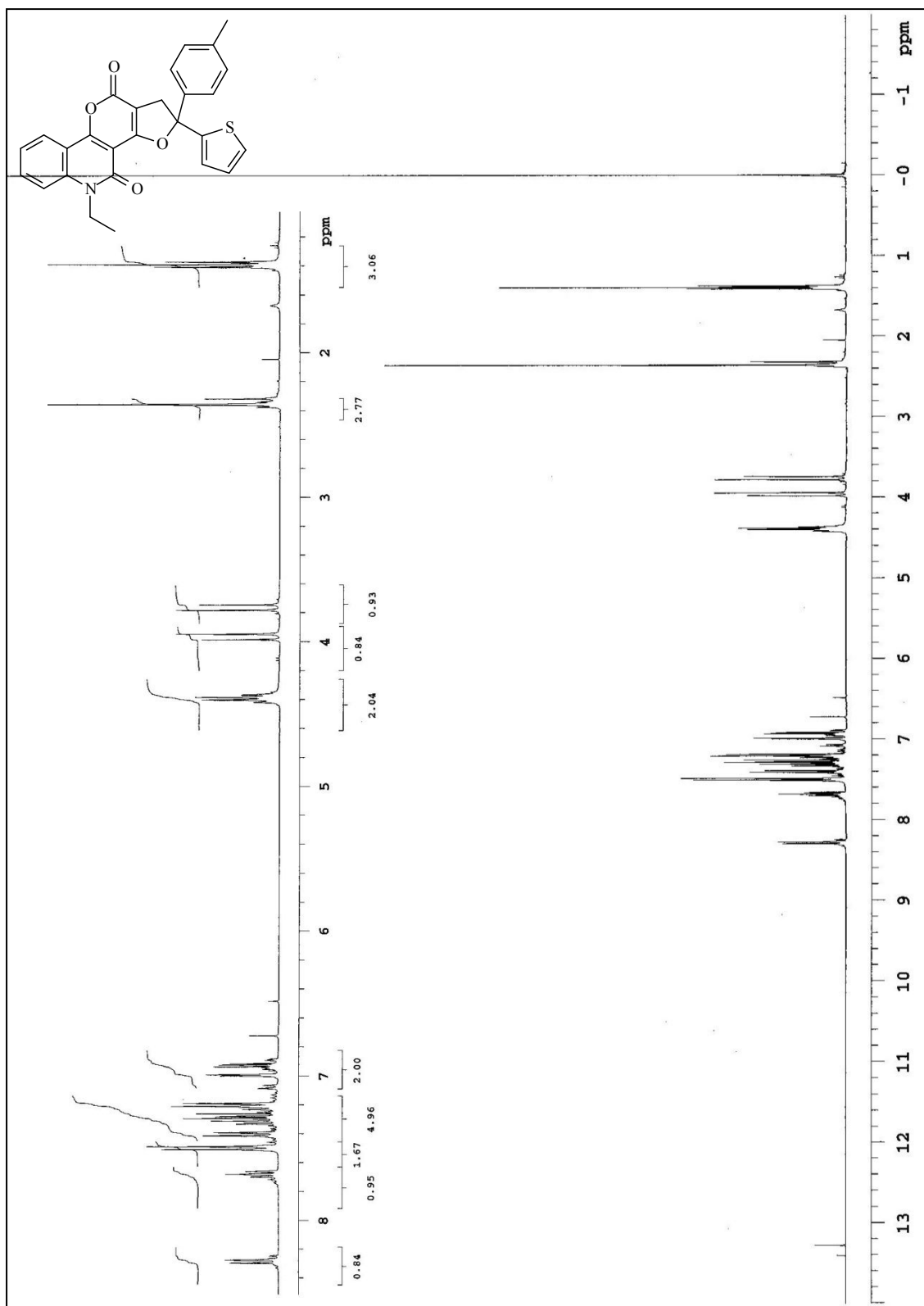
2.22 $^1\text{H-NMR}$ spectra of **26**

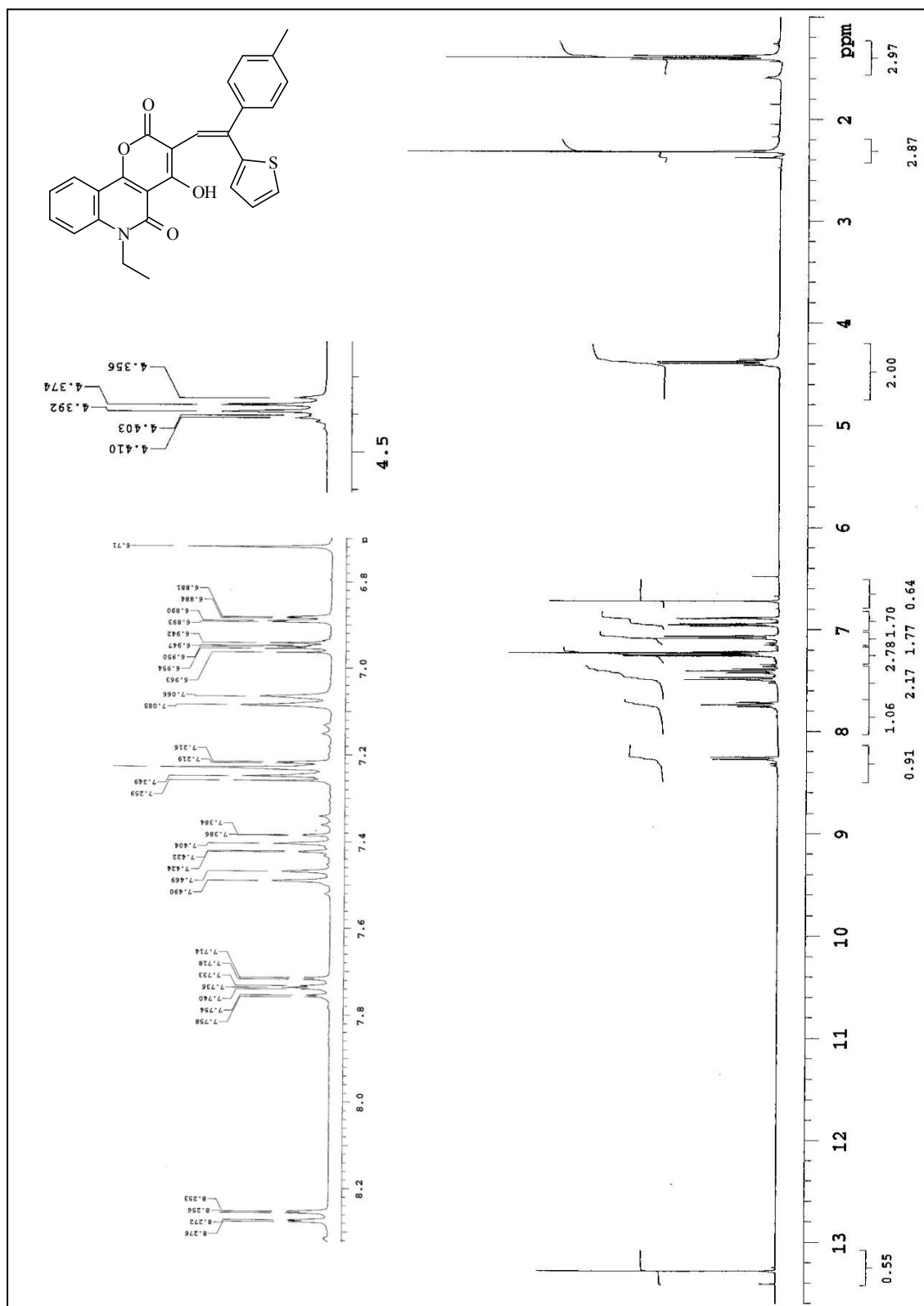
2.23 $^1\text{H-NMR}$ spectra of **21**

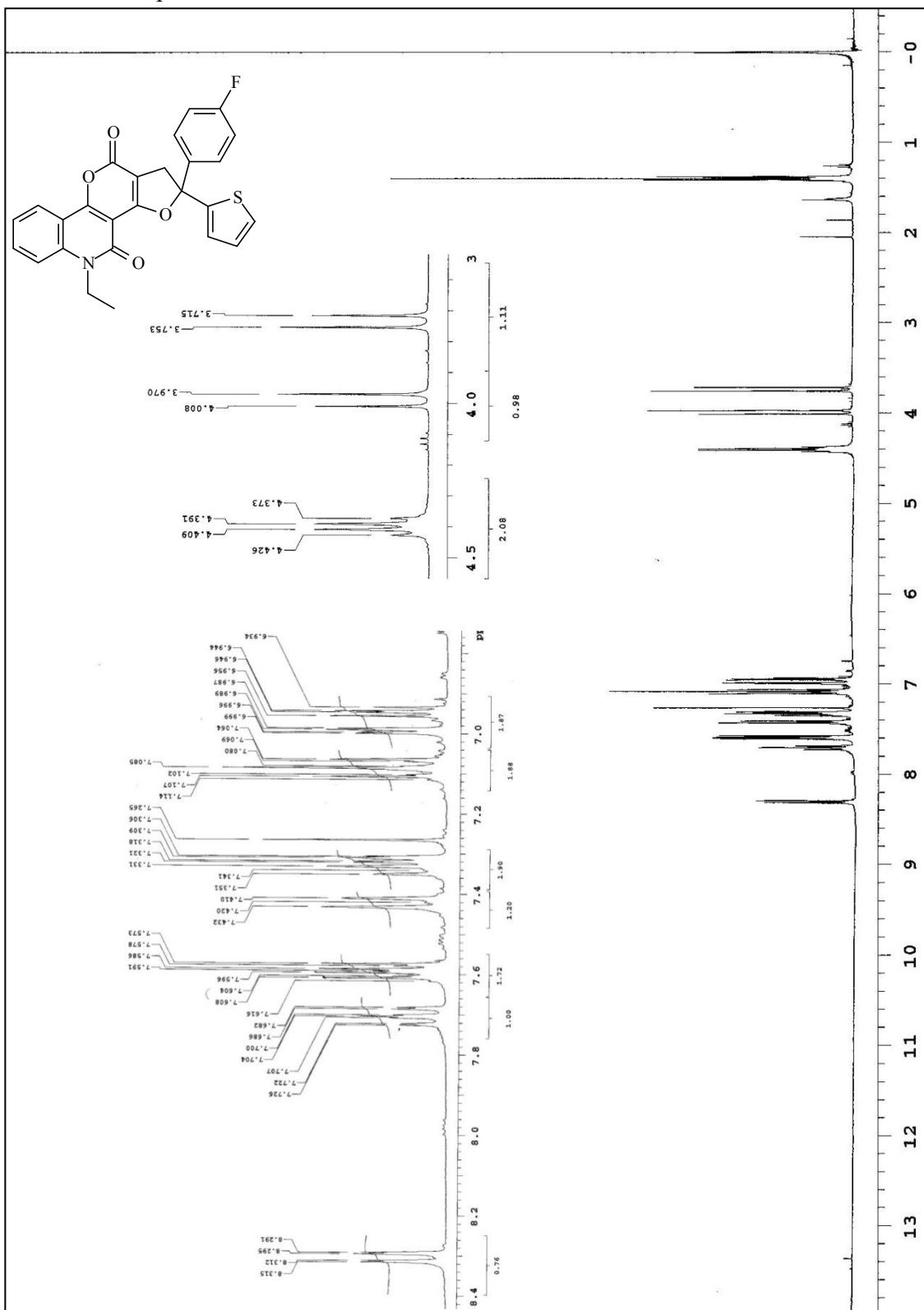
2.24 $^1\text{H-NMR}$ spectra of **27**

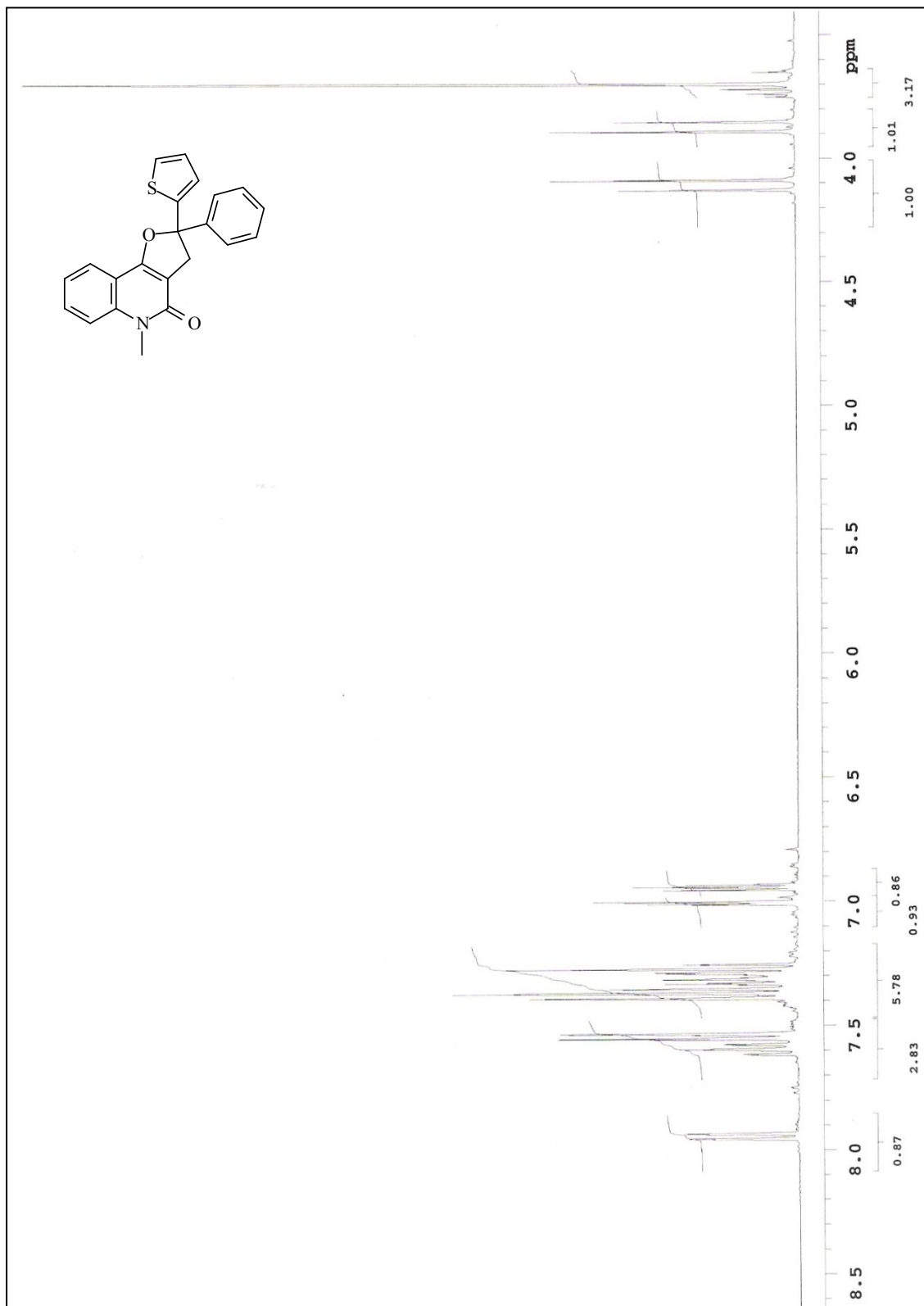
2.25 $^1\text{H-NMR}$ spectra of **22**1
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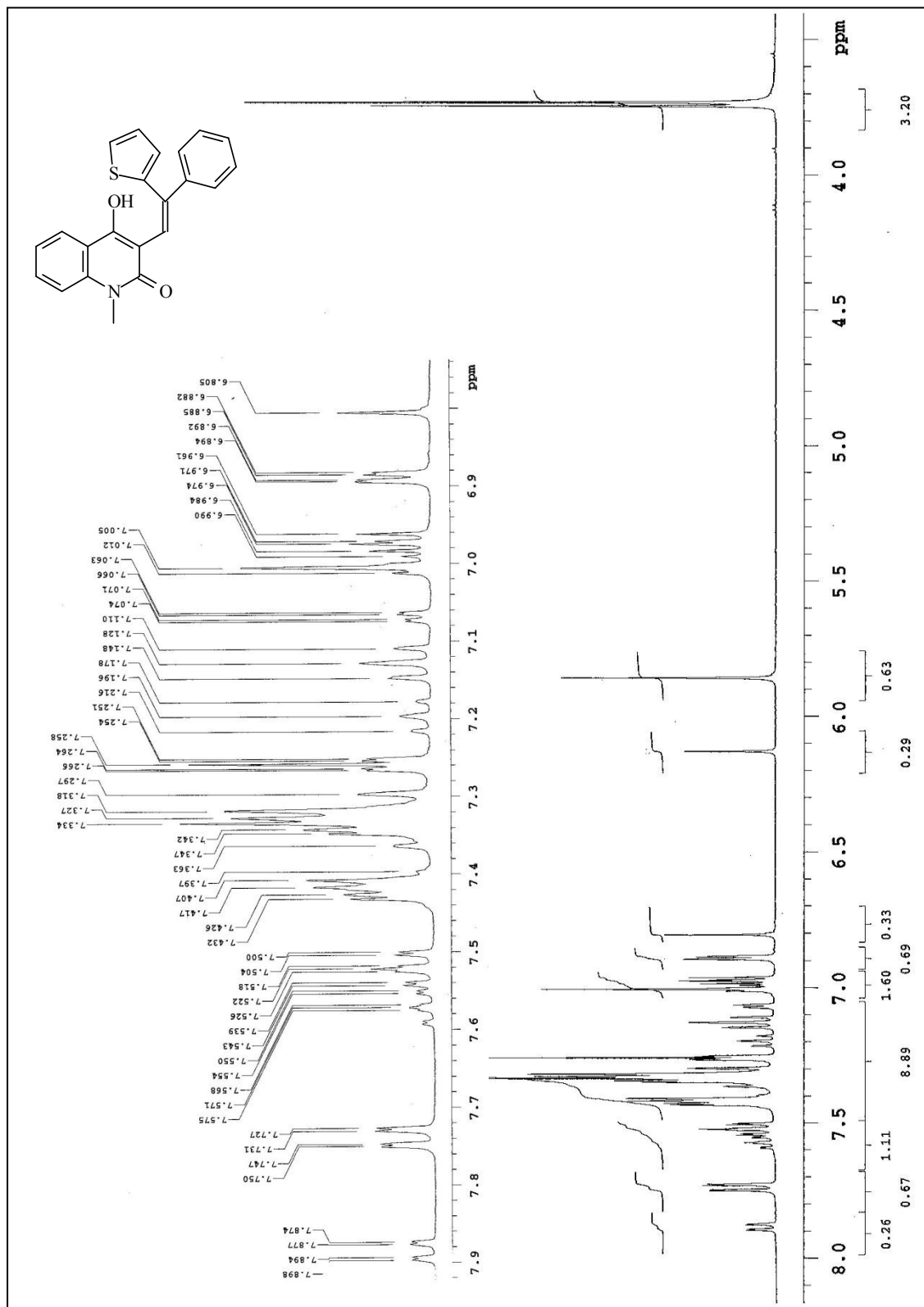
2.26 $^1\text{H-NMR}$ spectra of **28**

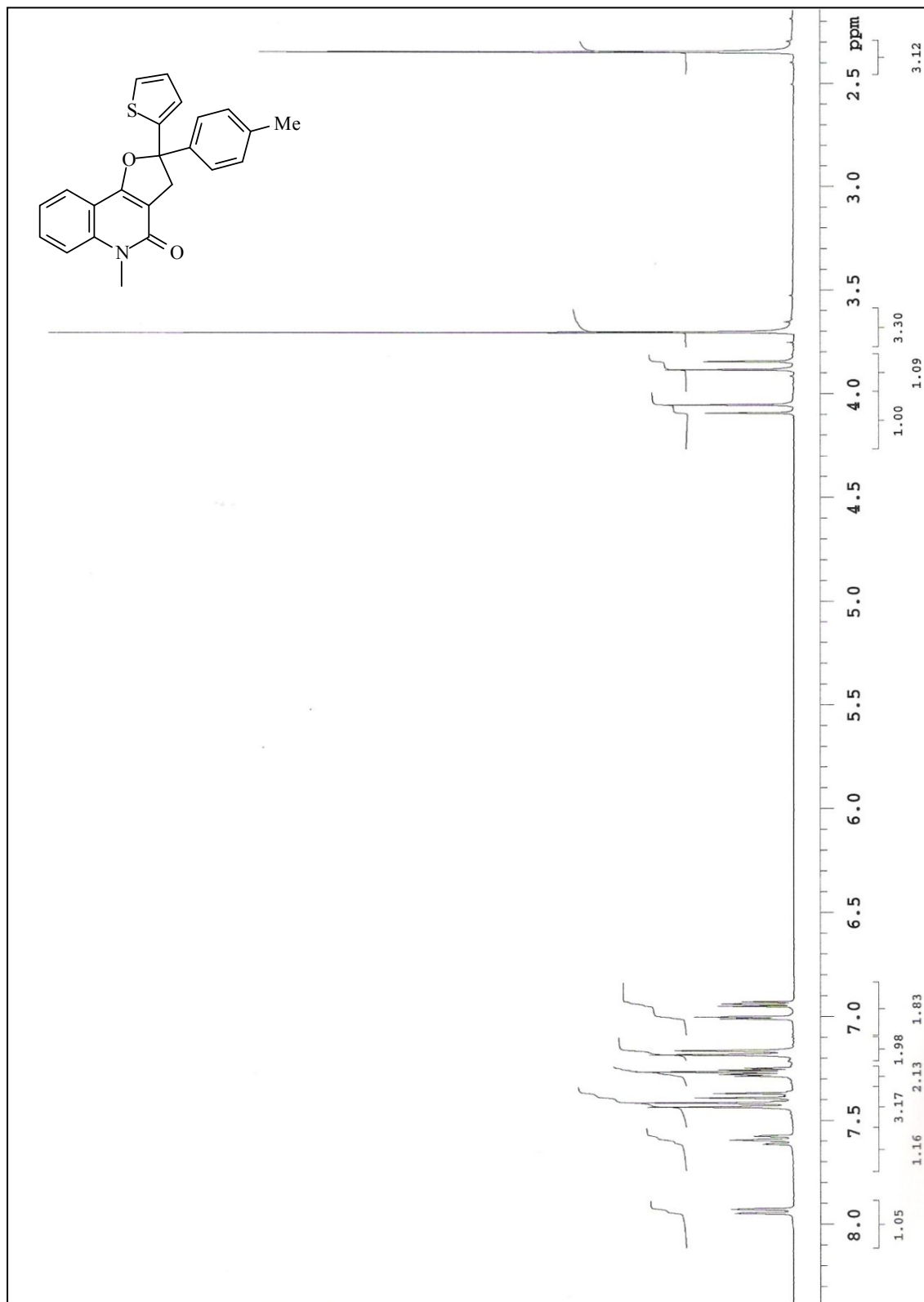
2.27 $^1\text{H-NMR}$ spectra of **23**

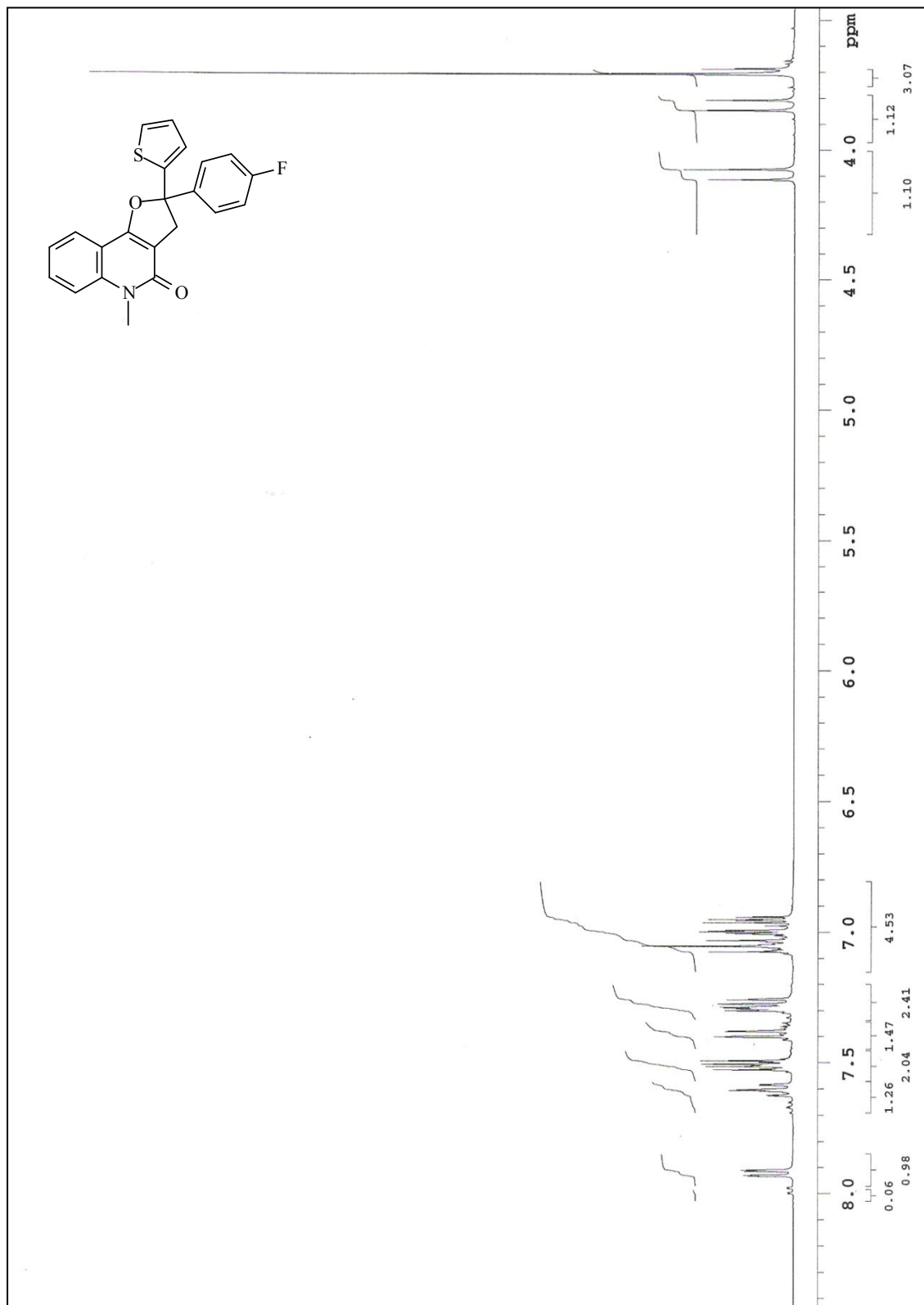
2.28 $^1\text{H-NMR}$ spectra of **29**

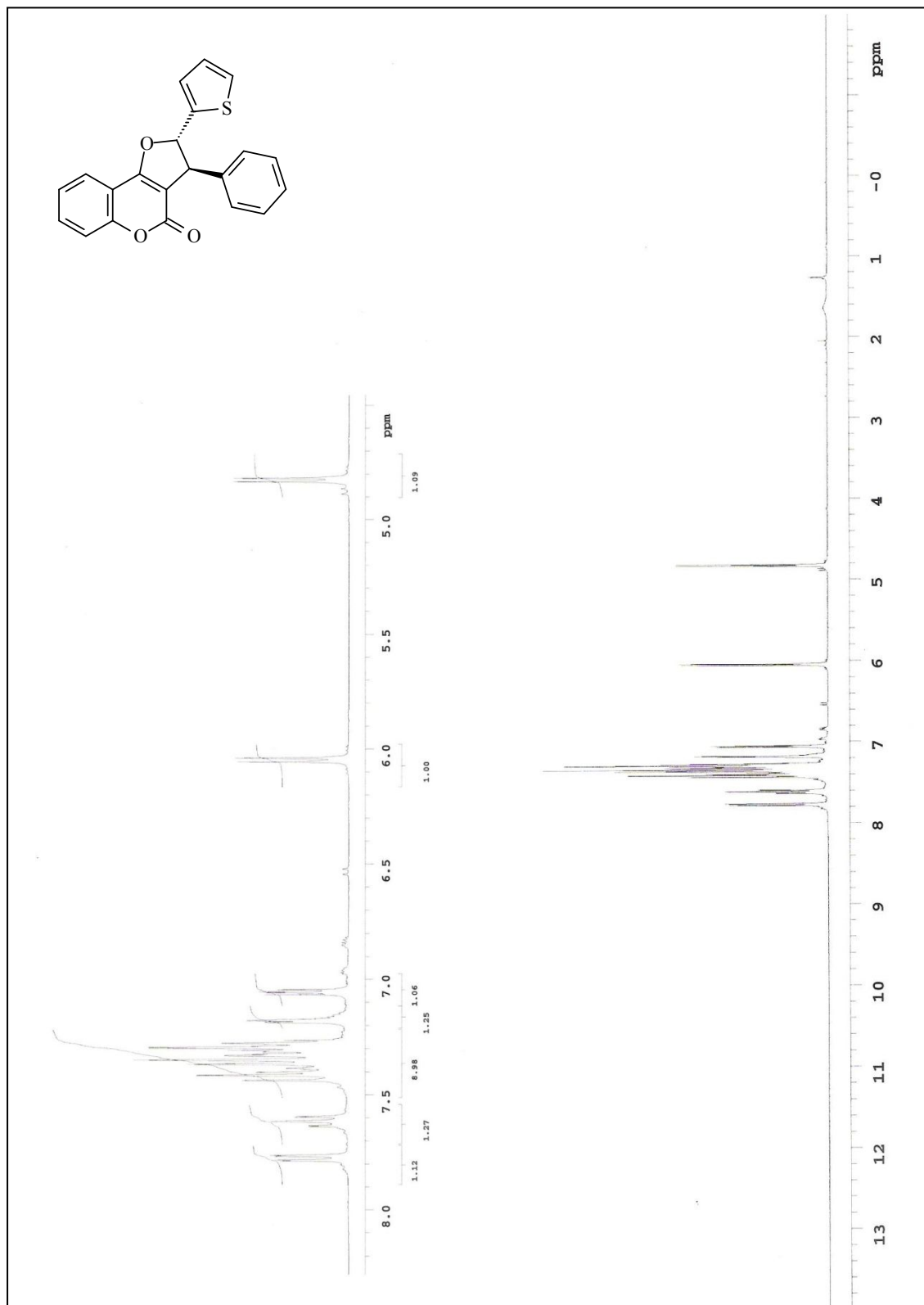
2.29 ¹H-NMR spectra of 24

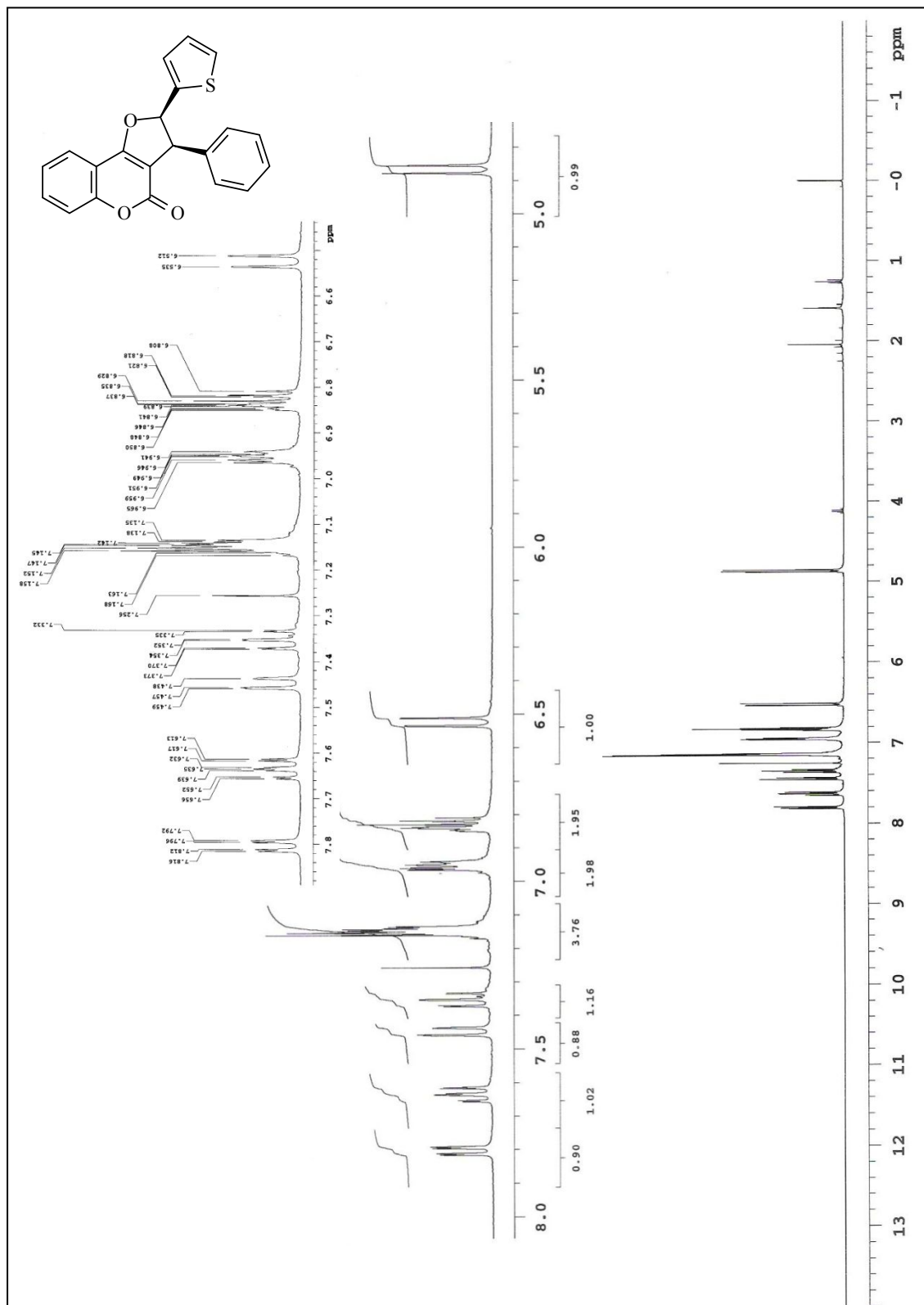
2.31 $^1\text{H-NMR}$ spectra of **31**

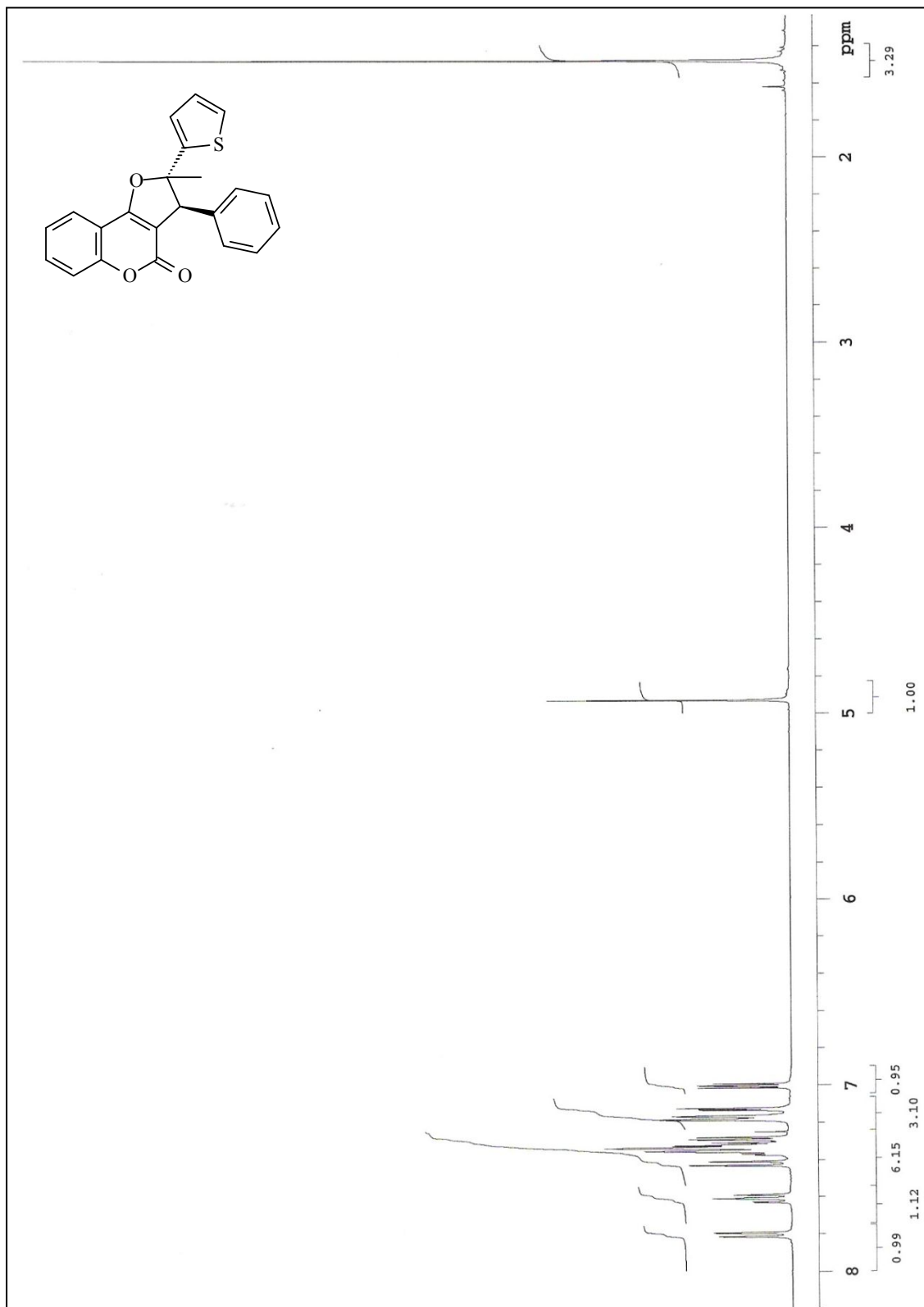
2.32 ¹H-NMR spectra of **34**

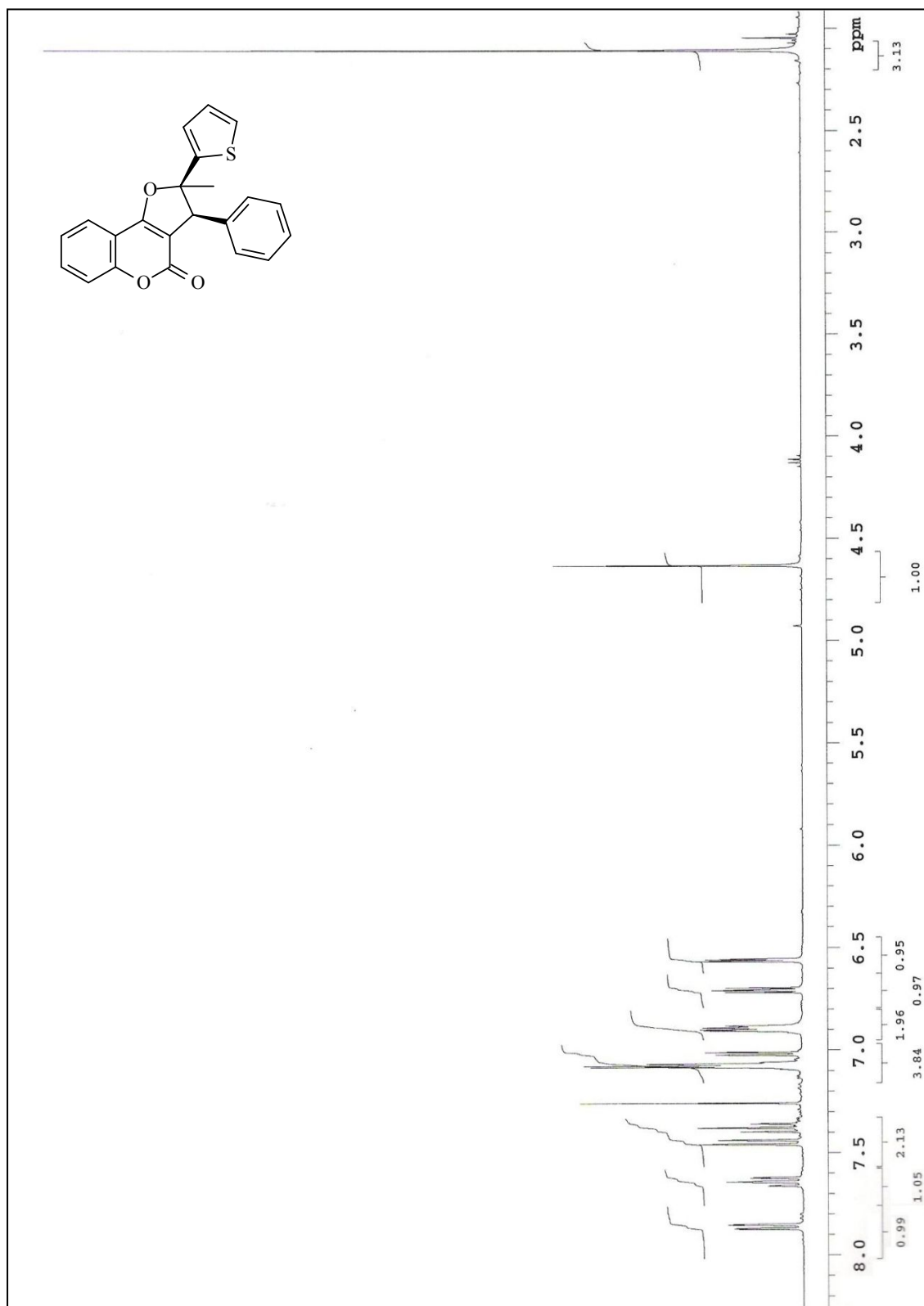
2.33 $^1\text{H-NMR}$ spectra of **32**

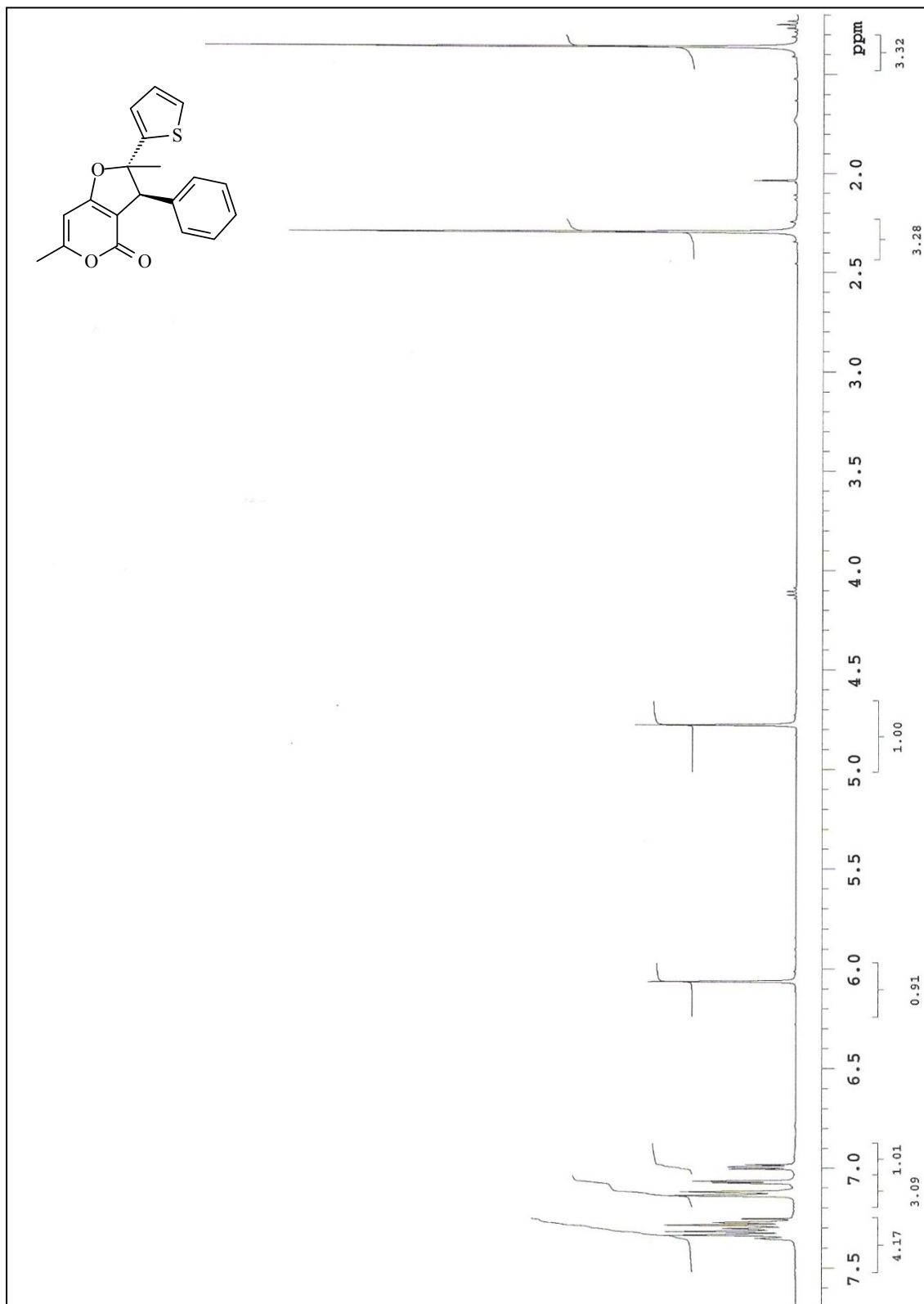
2.34 $^1\text{H-NMR}$ spectra of **33**

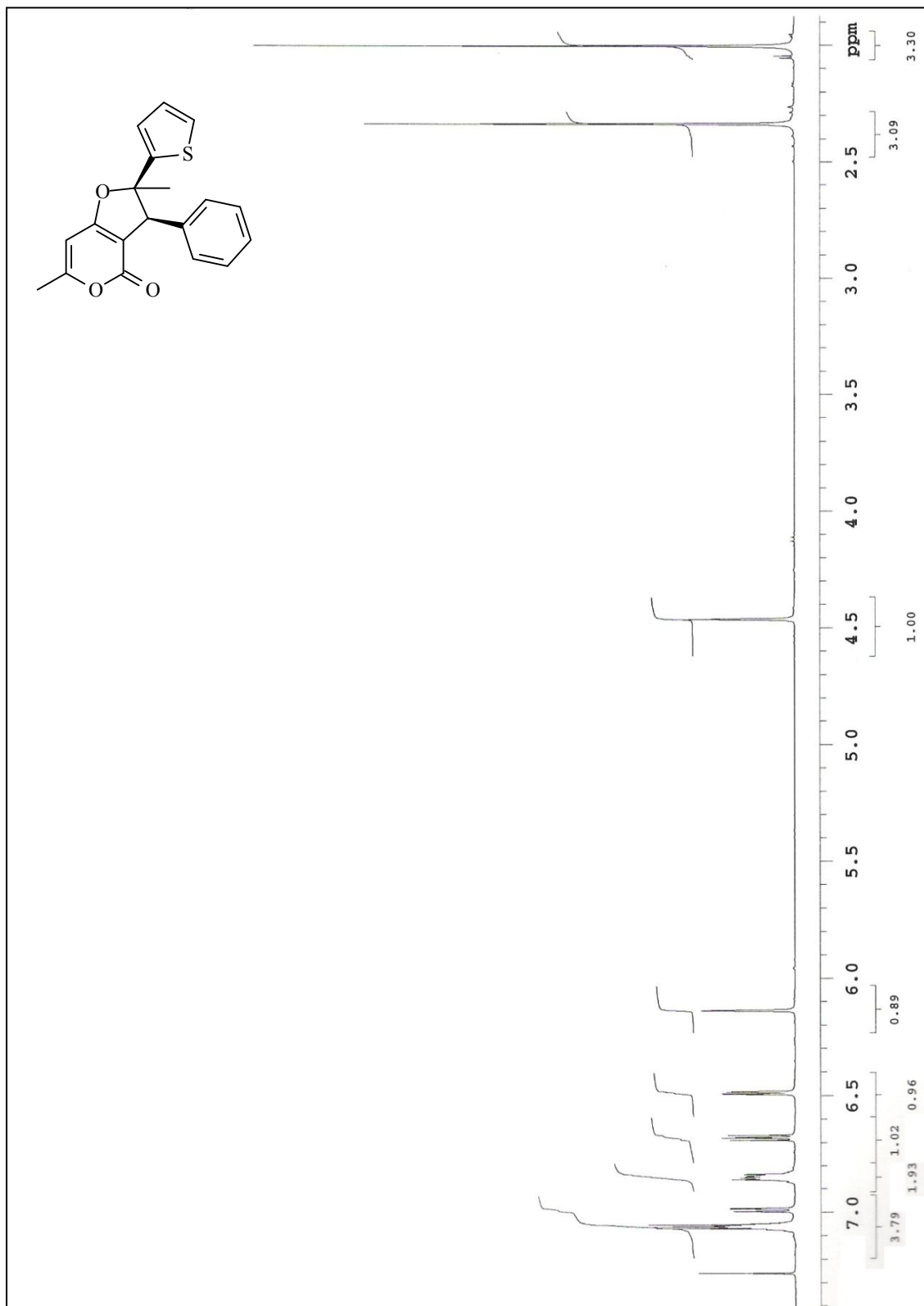
2.35 $^1\text{H-NMR}$ spectra of **35**

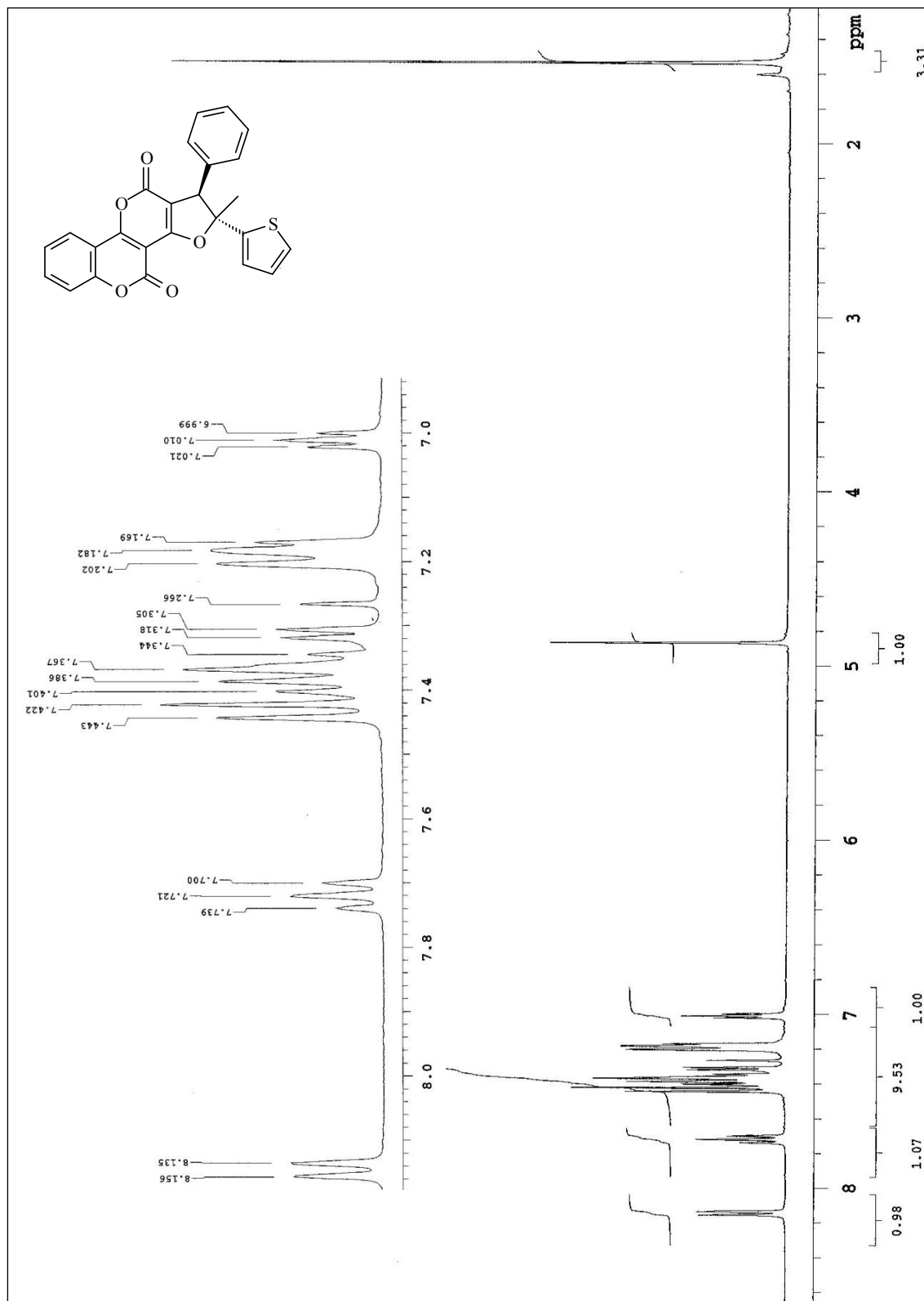
2.36 $^1\text{H-NMR}$ spectra of **36**

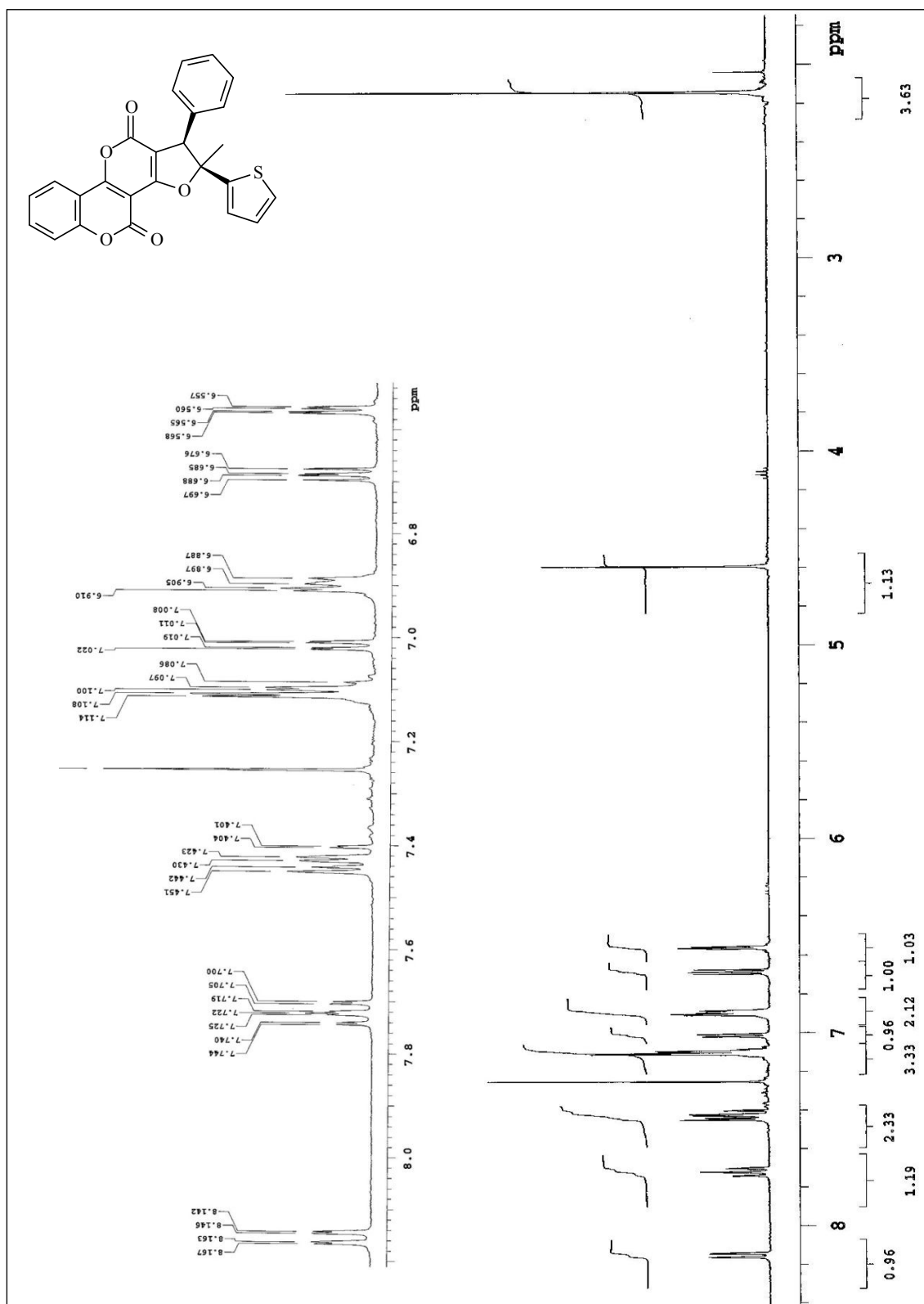
2.37 $^1\text{H-NMR}$ spectra of **37**

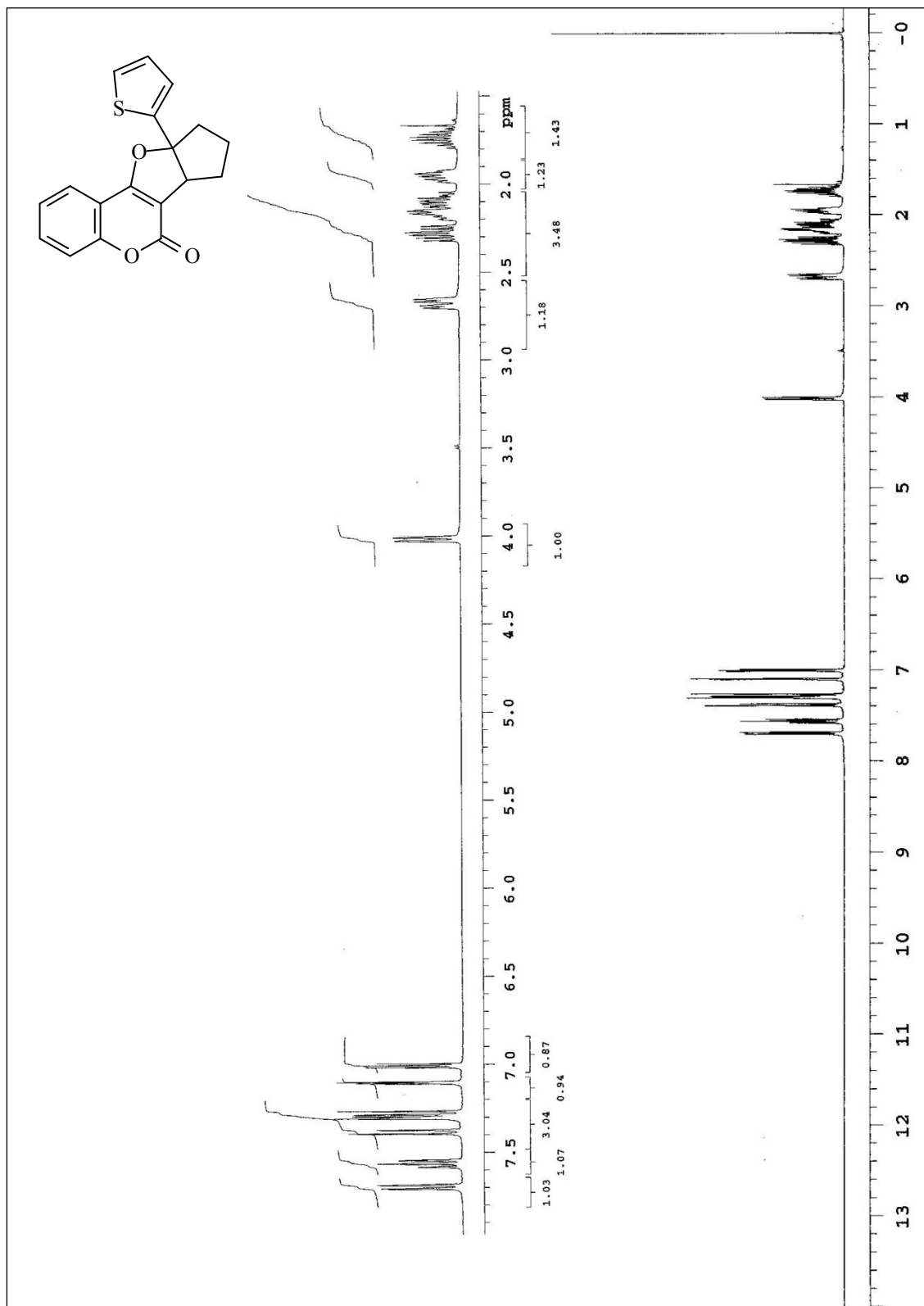
2.38 $^1\text{H-NMR}$ spectra of **38**

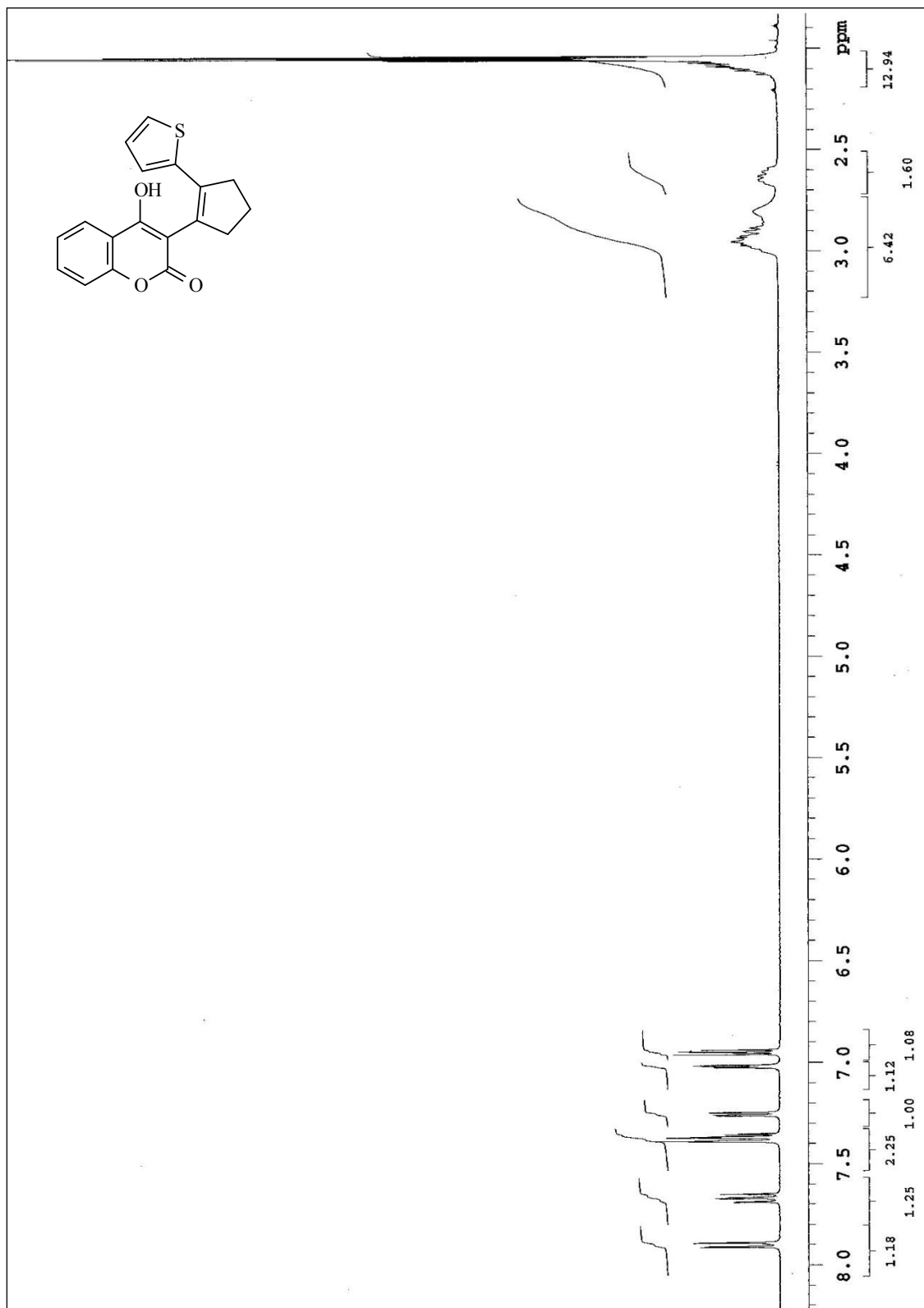
2.39 $^1\text{H-NMR}$ spectra of **39**

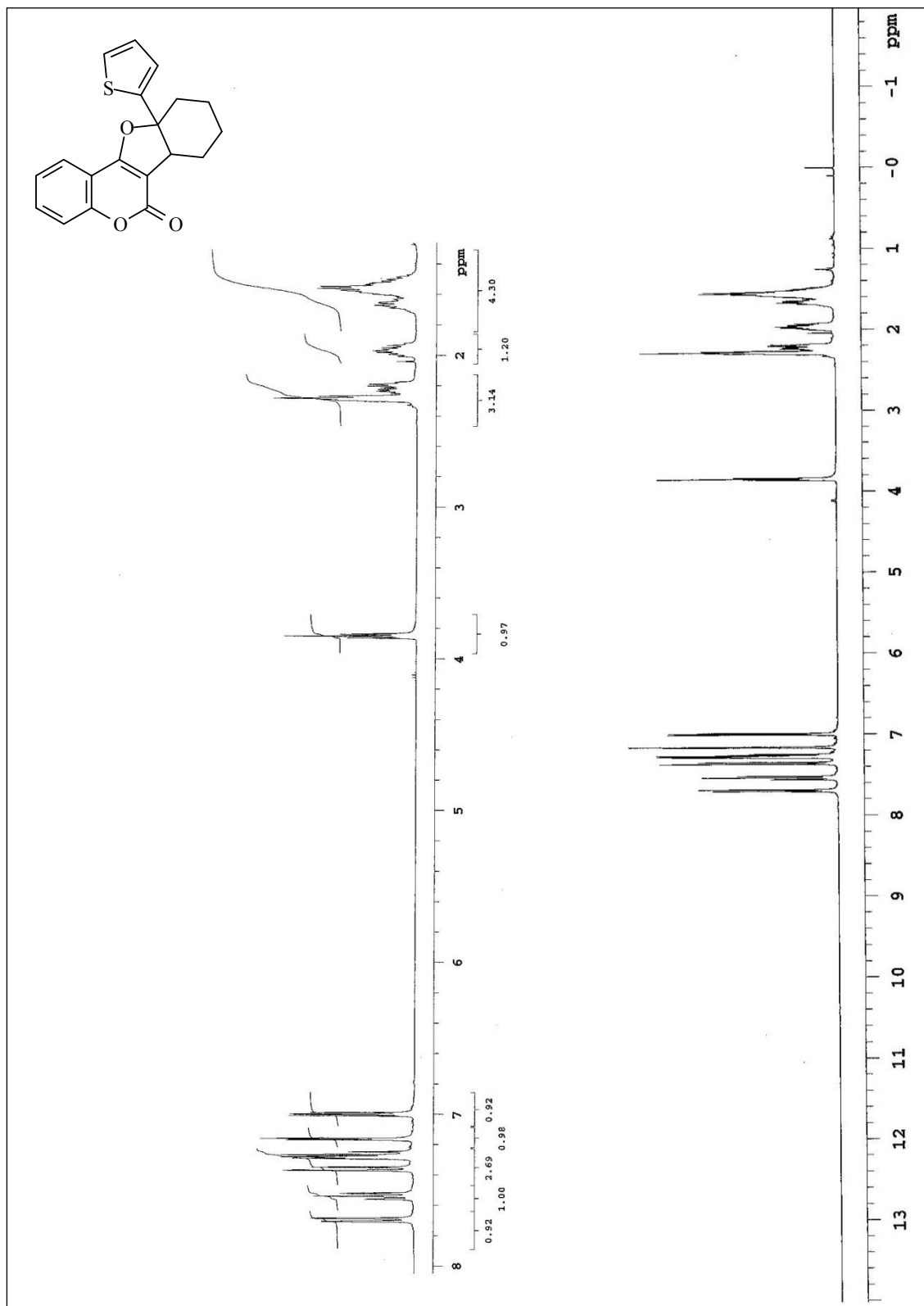
2.40 $^1\text{H-NMR}$ spectra of **40**

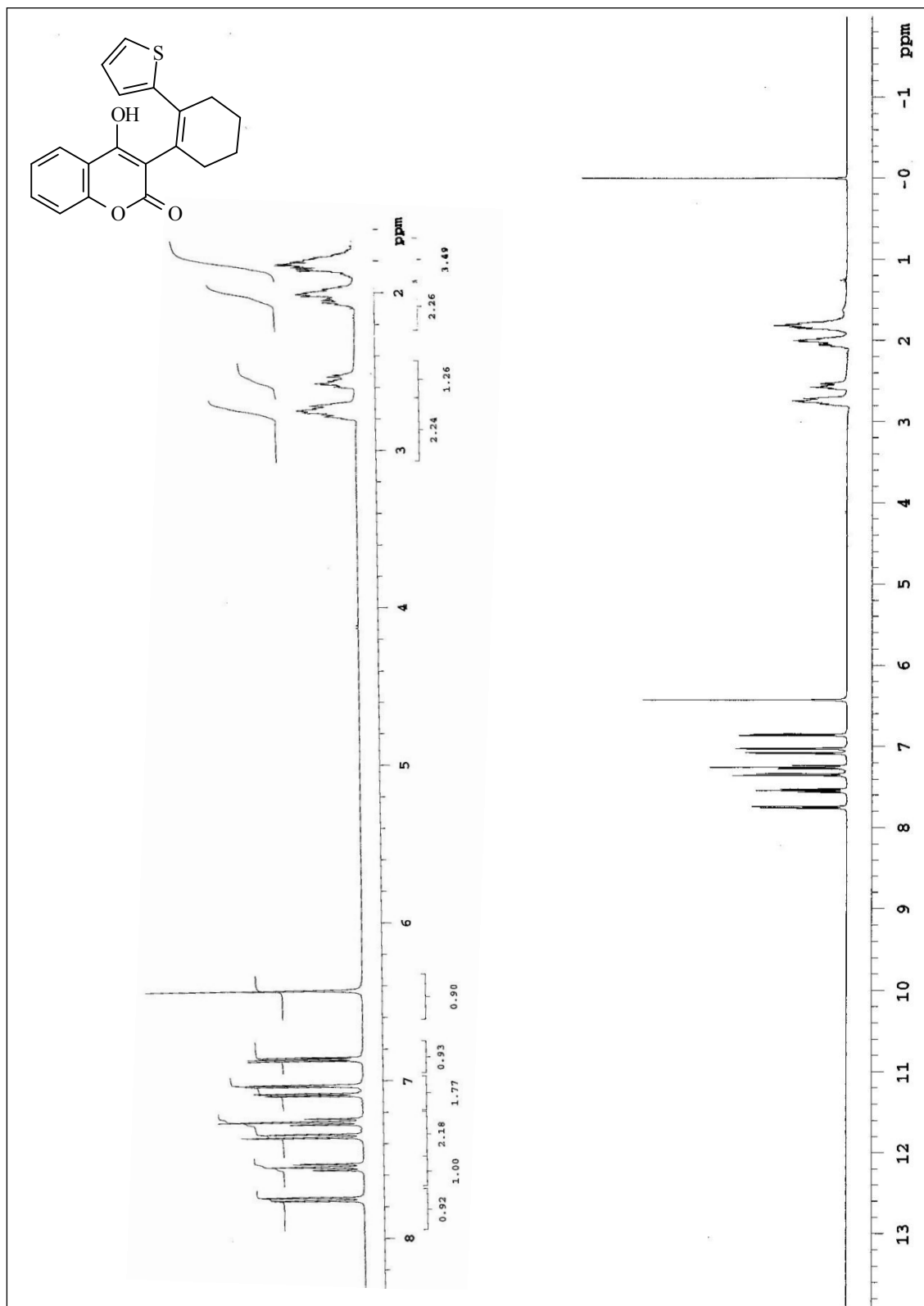
2.41 $^1\text{H-NMR}$ spectra of **41**

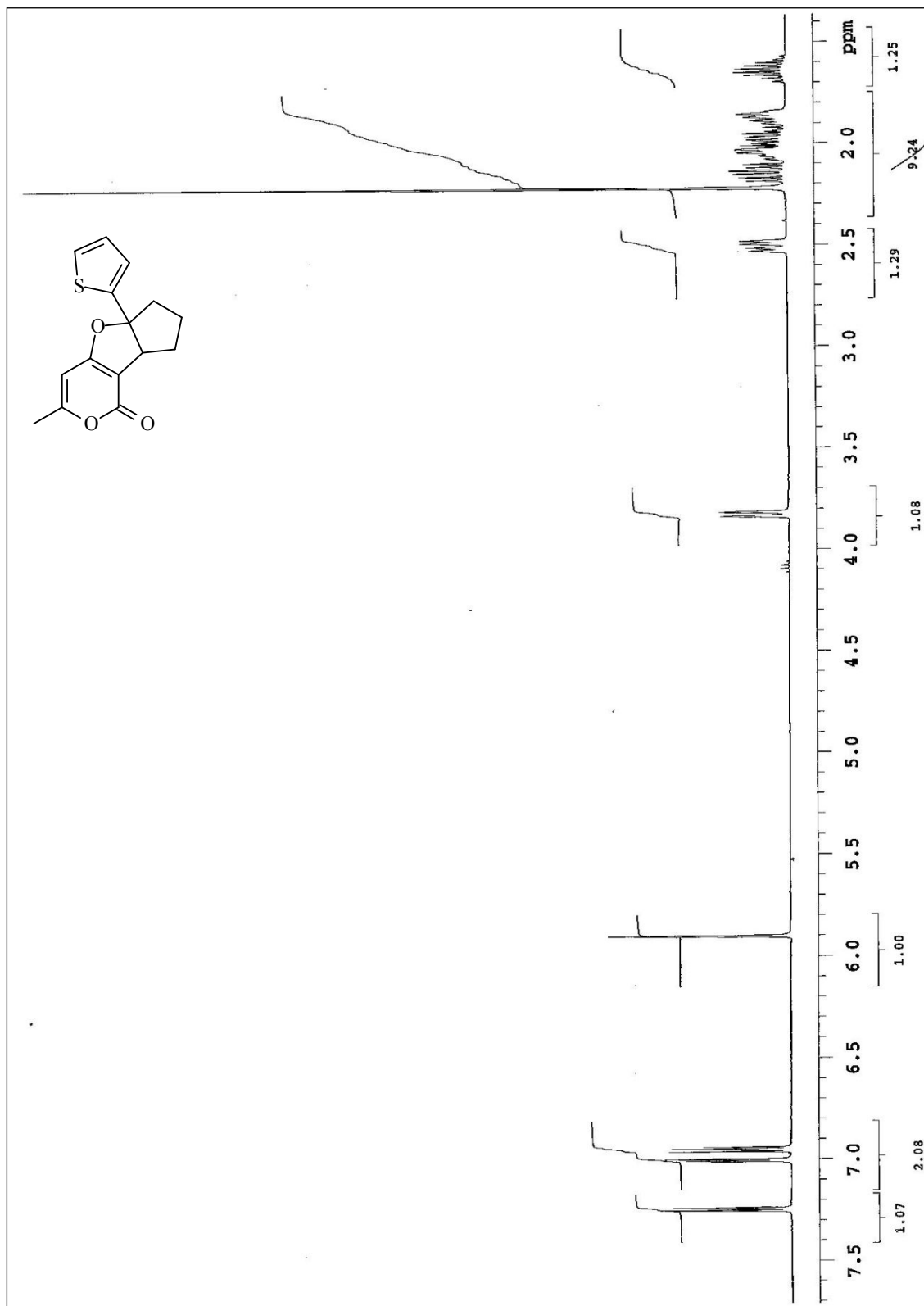
2.42 ¹H-NMR spectra of 42

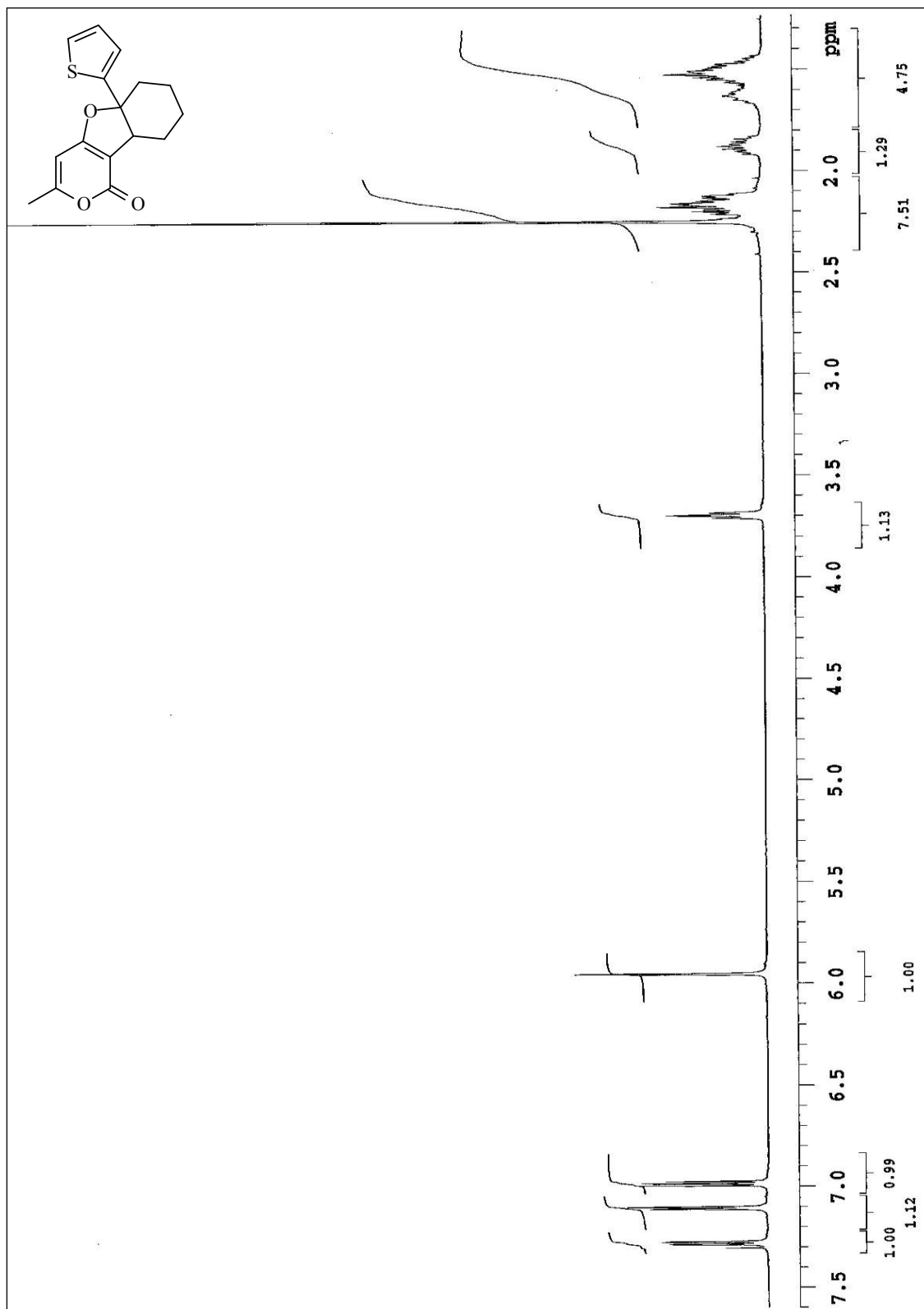
2.43 $^1\text{H-NMR}$ spectra of **43**

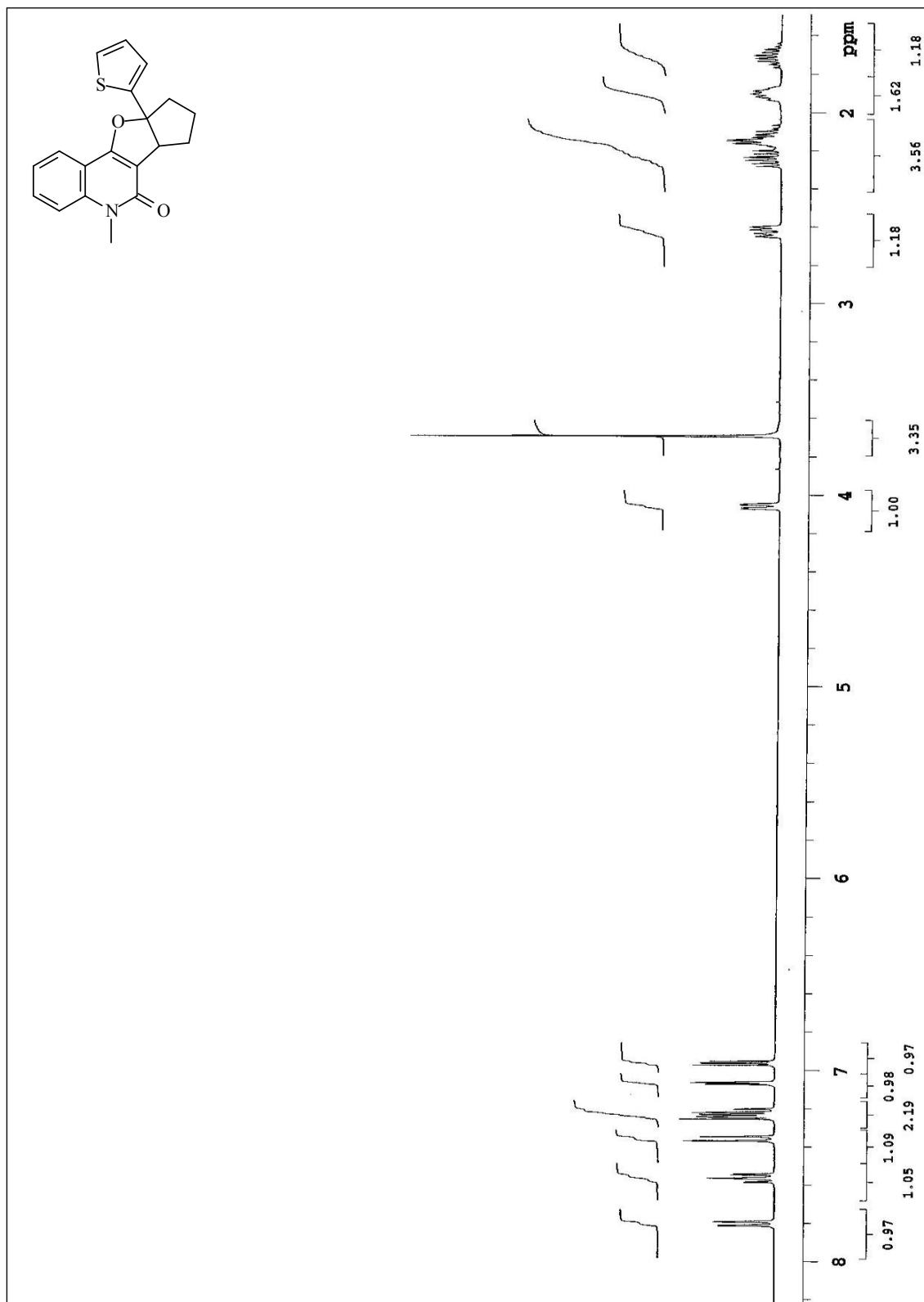
2.44 $^1\text{H-NMR}$ spectra of **49**

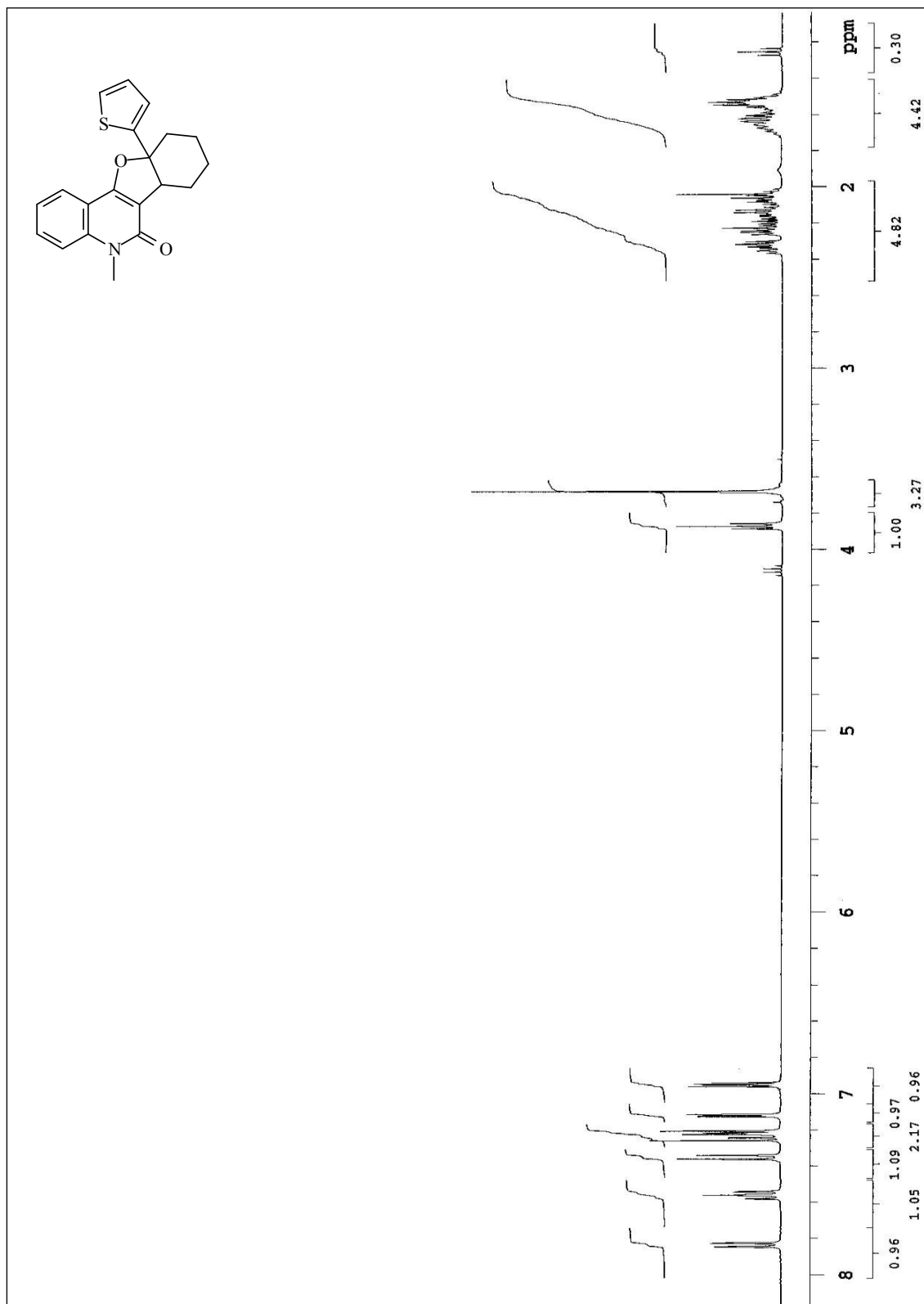
2.45 $^1\text{H-NMR}$ spectra of **44**

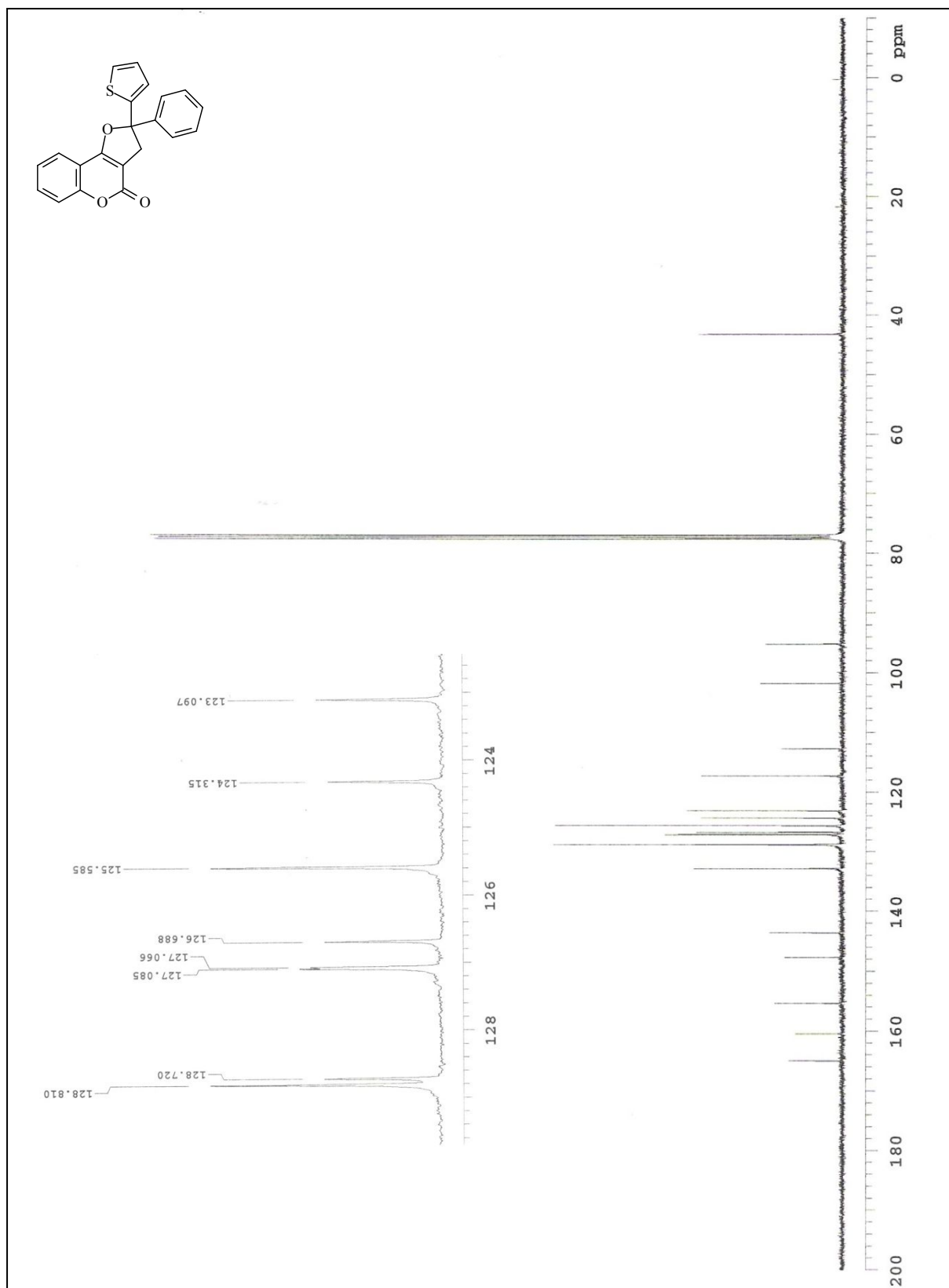
2.46 $^1\text{H-NMR}$ spectra of **50**

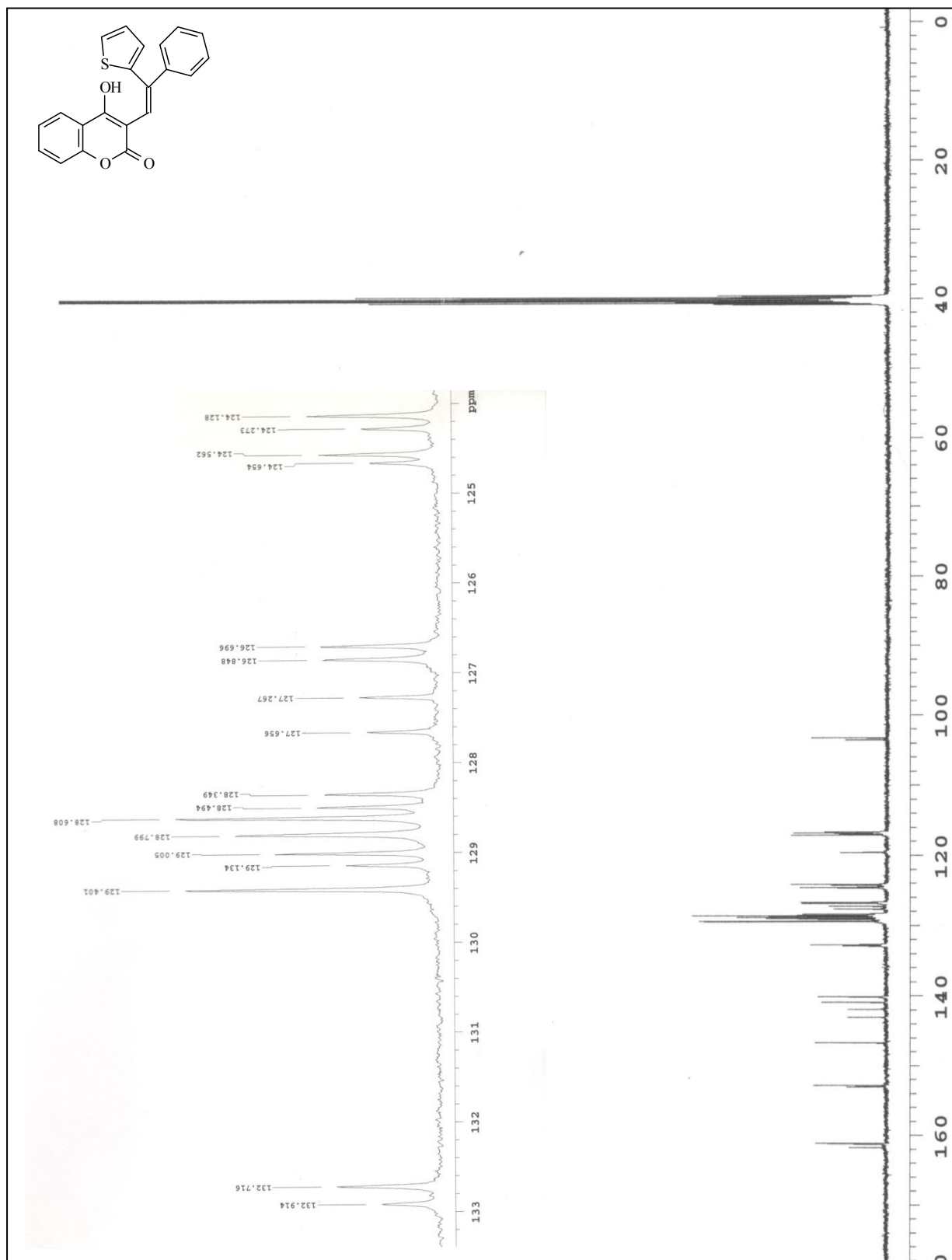
2.47 $^1\text{H-NMR}$ spectra of **45**

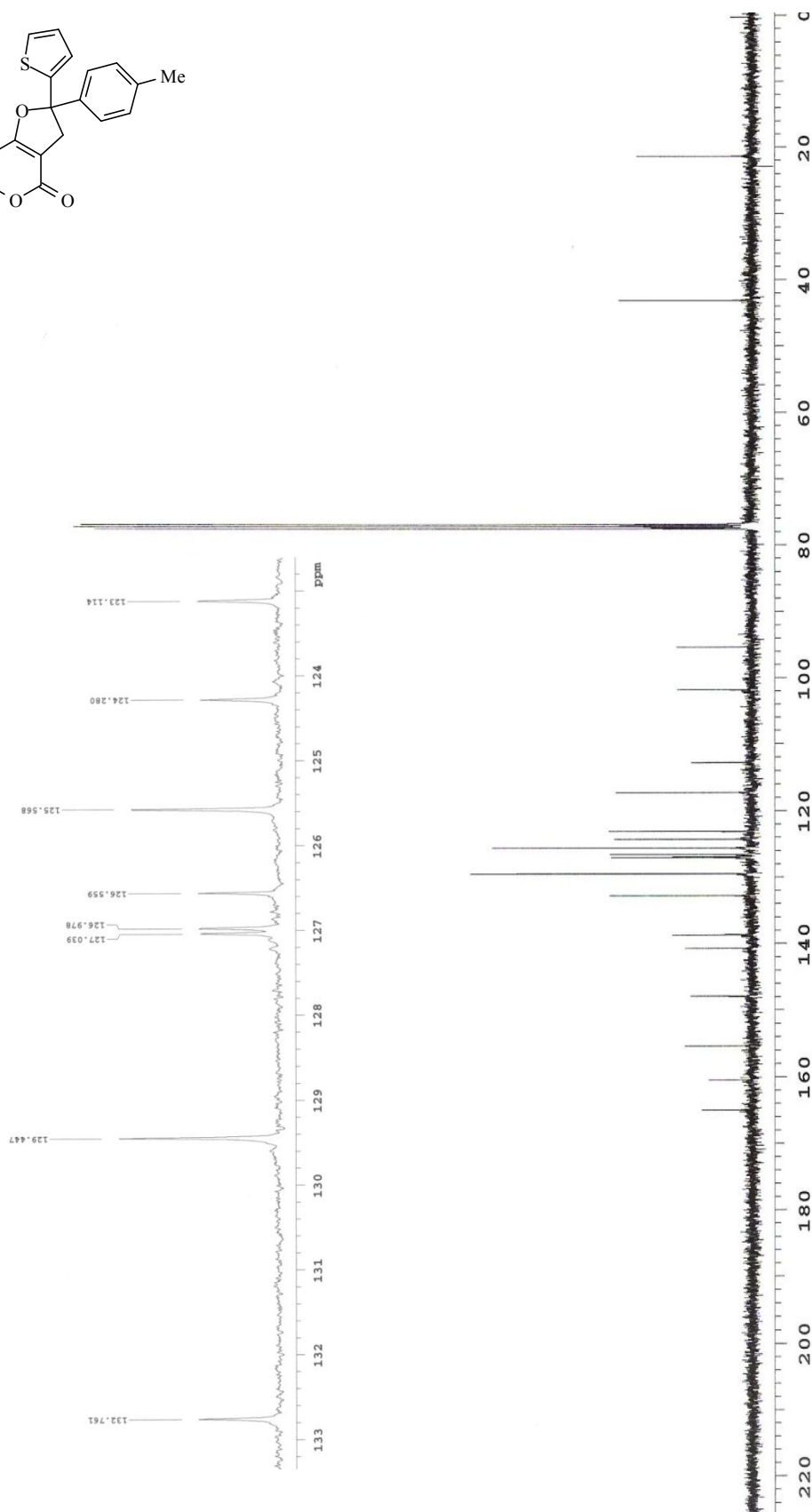
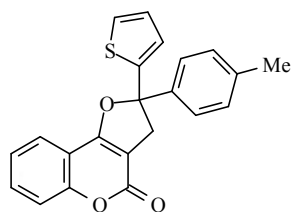
2.48 $^1\text{H-NMR}$ spectra of **46**

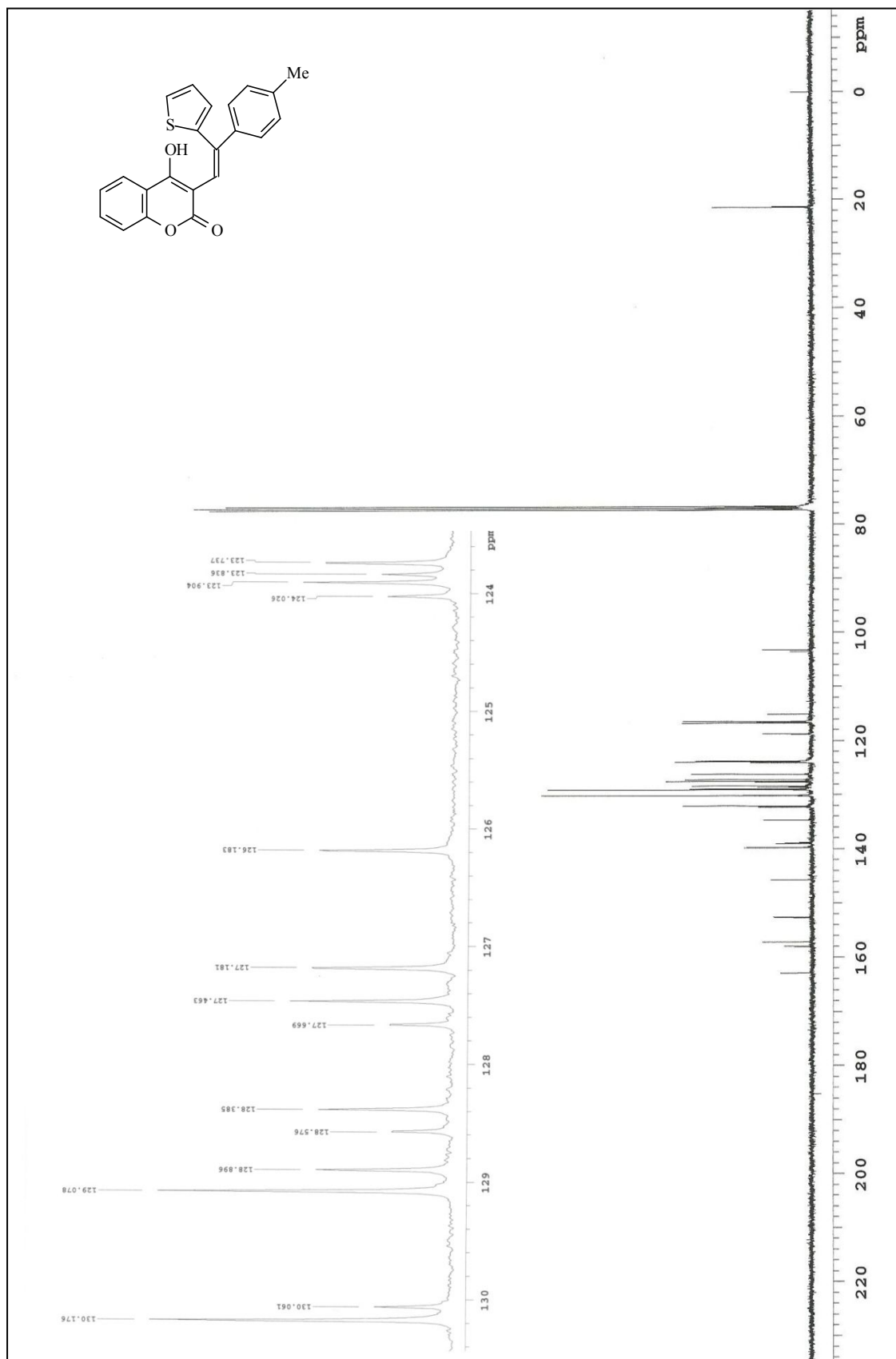
2.49 ¹H-NMR spectra of **47**

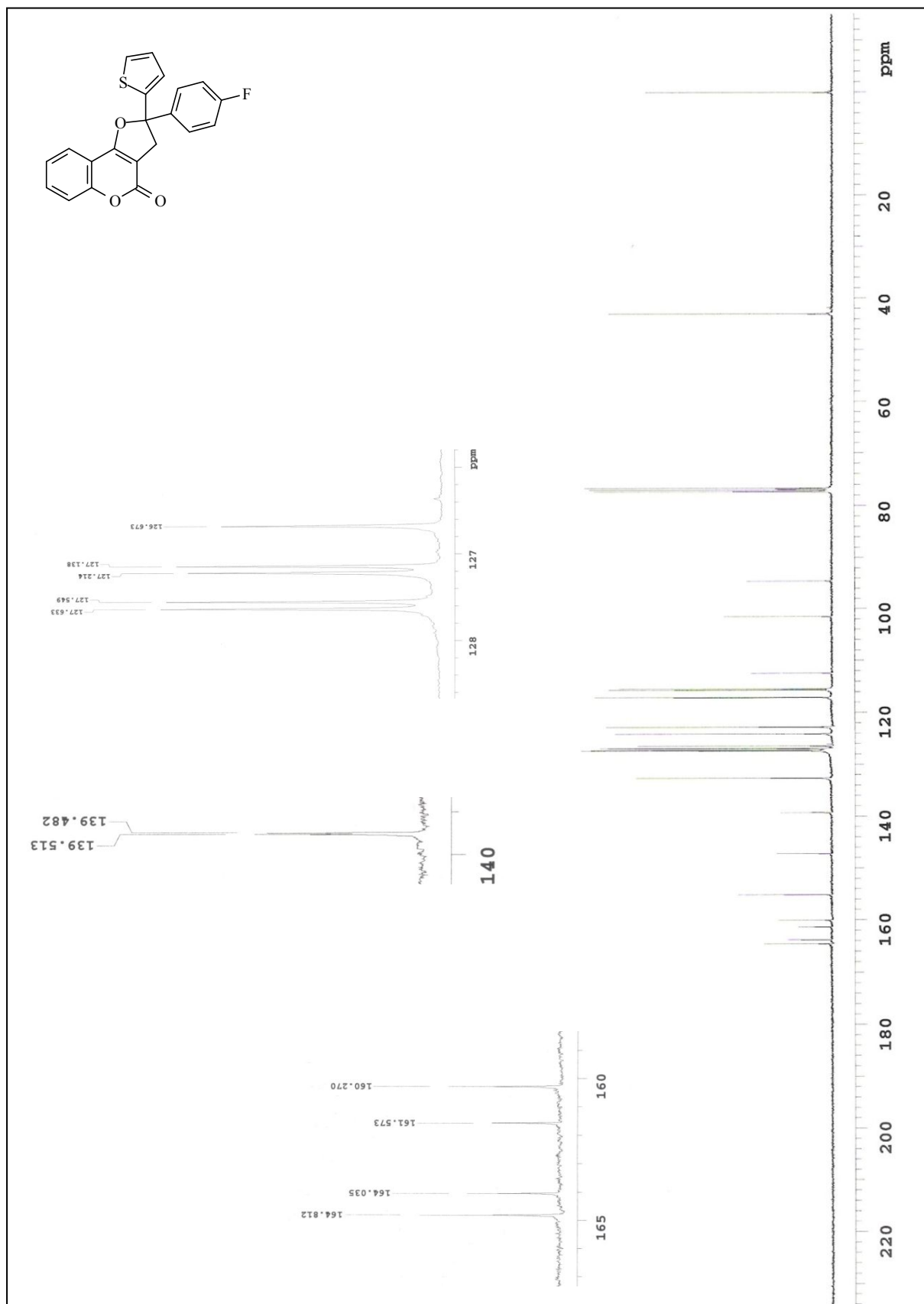
2.50 $^1\text{H-NMR}$ spectra of **48**

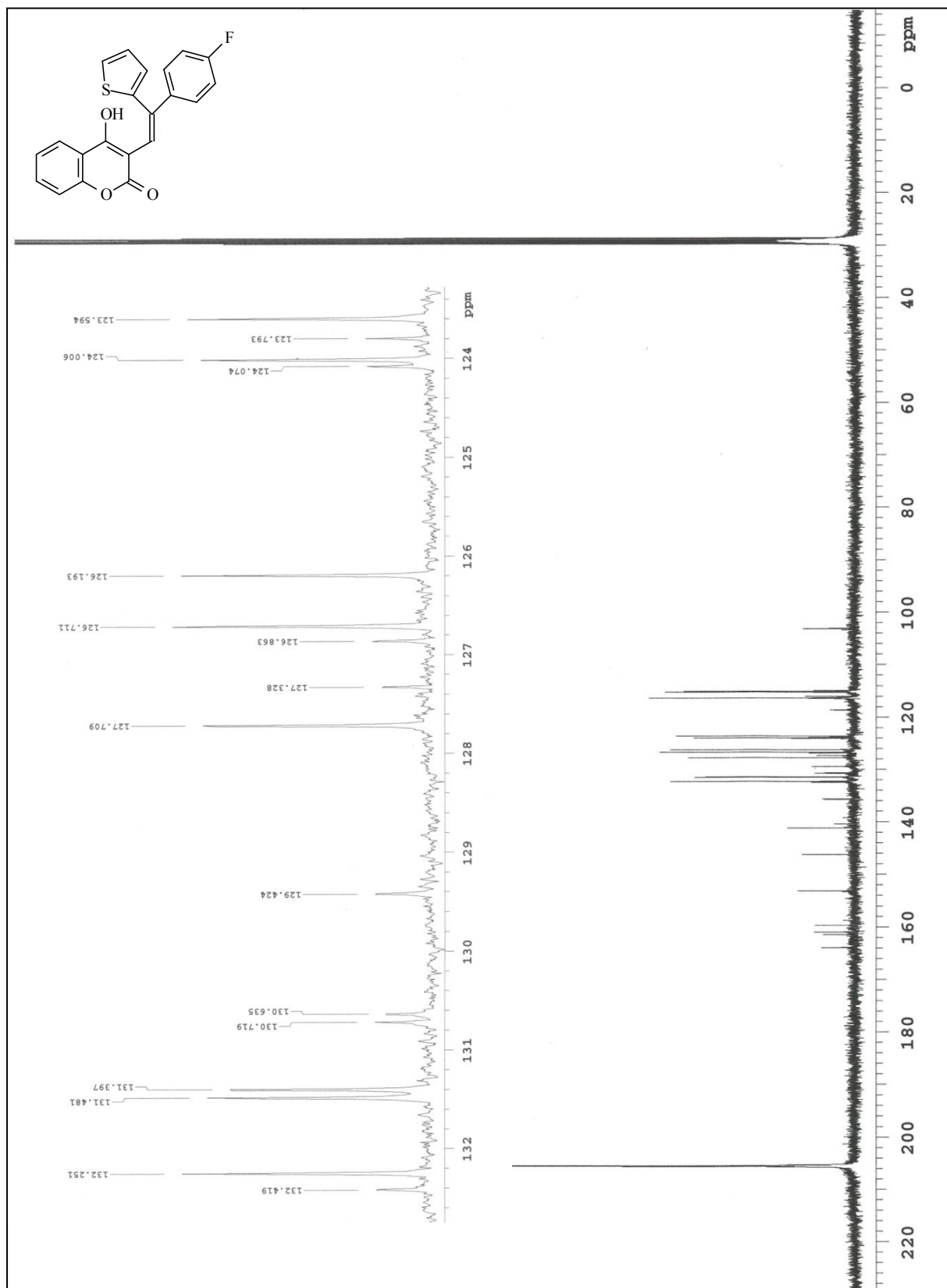
^{13}C -NMR of COMPOUNDS3.1 ^{13}C -NMR spectra of **3**

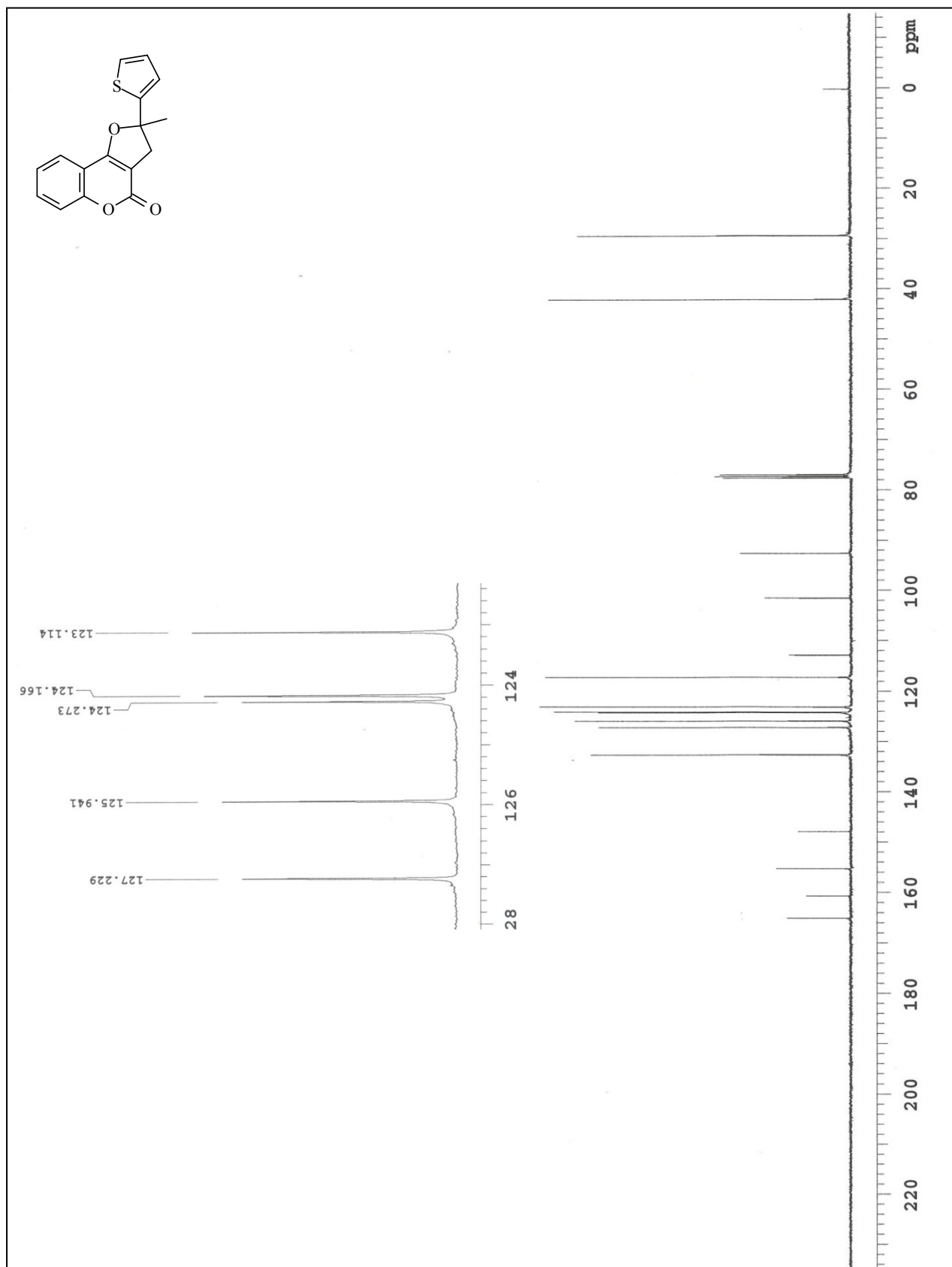
3.2 ^{13}C -NMR spectra of **8**

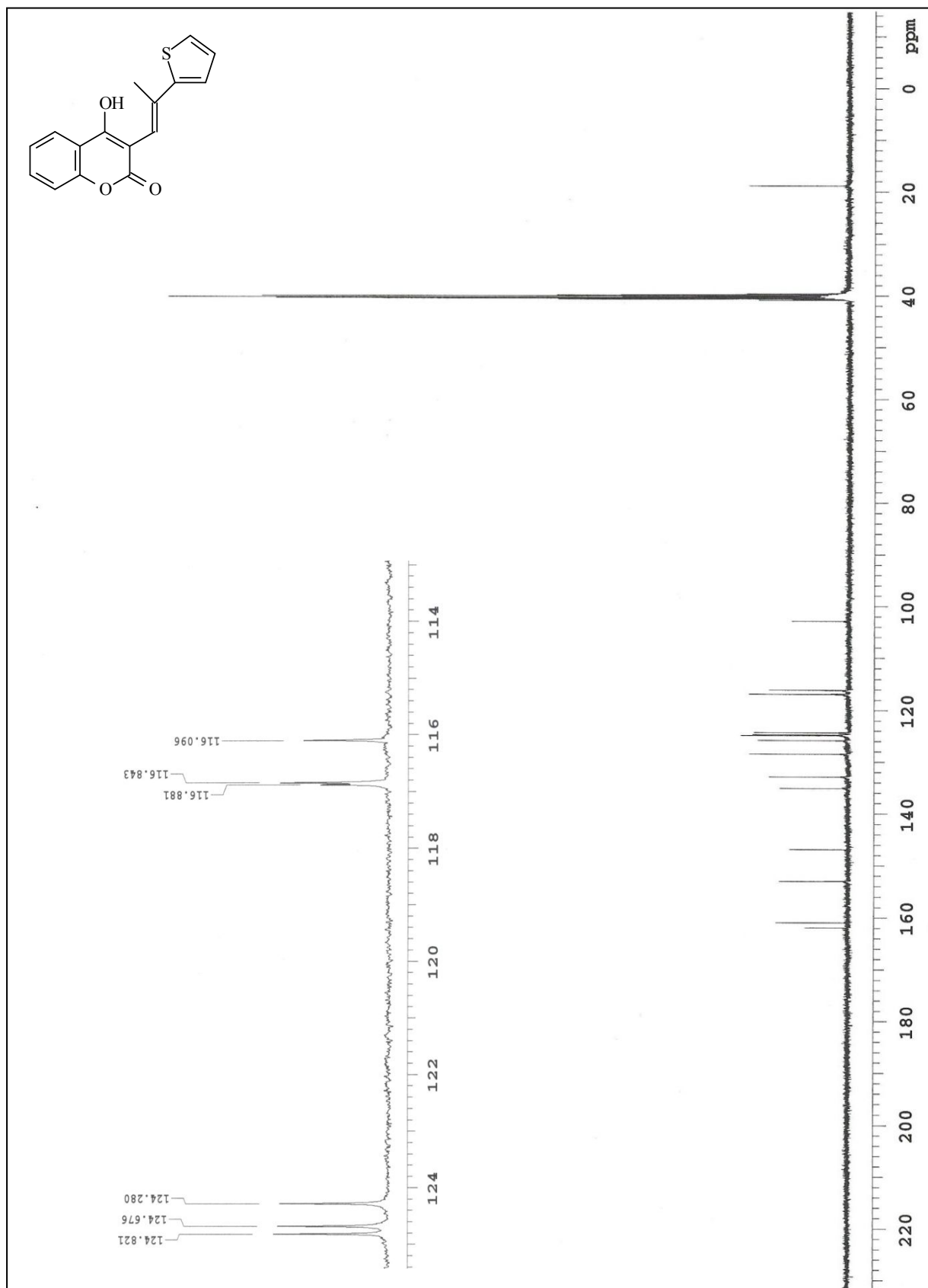
3.3 ^{13}C -NMR spectra of 4

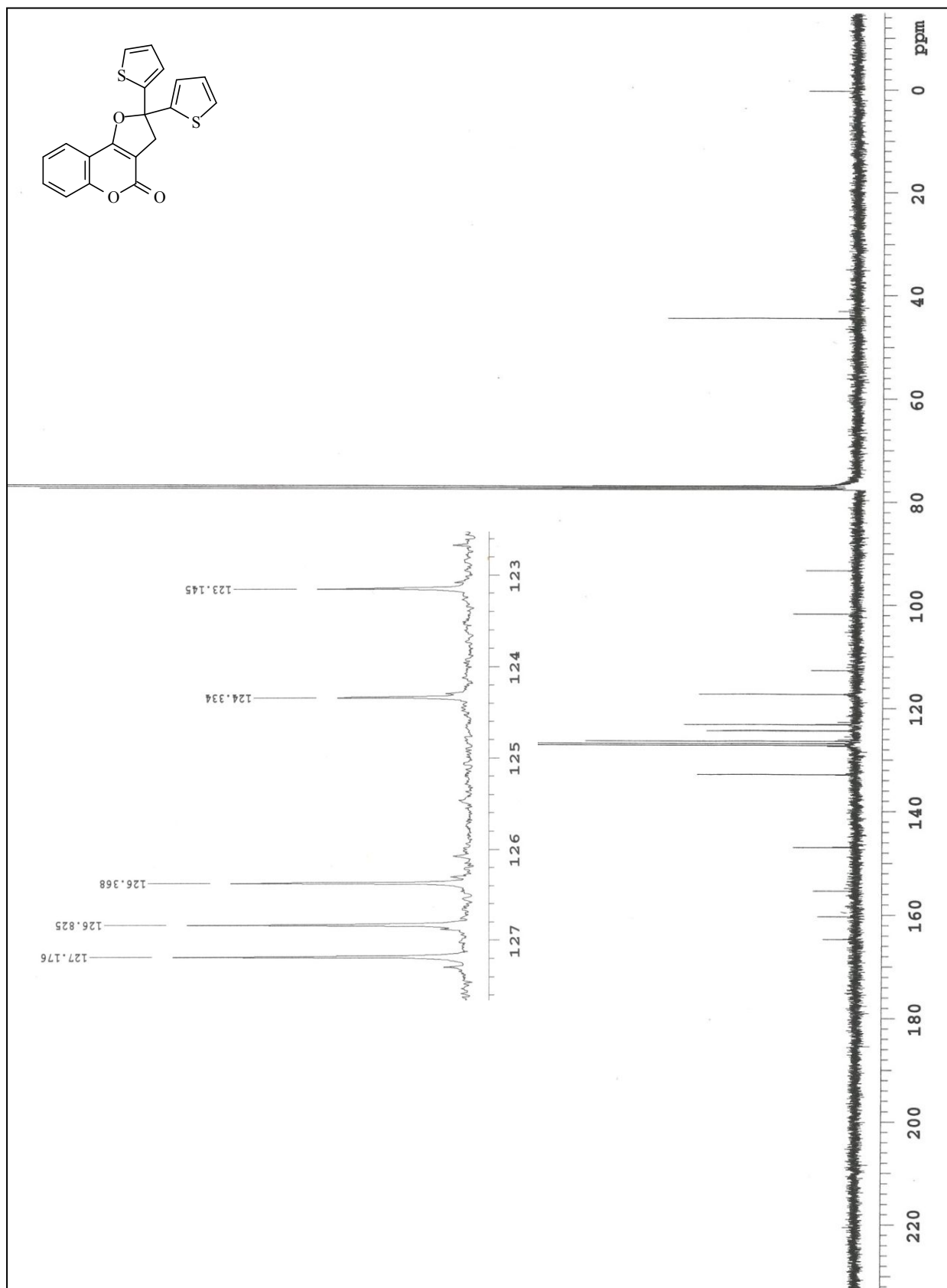
3.4 ^{13}C -NMR spectra of **9**

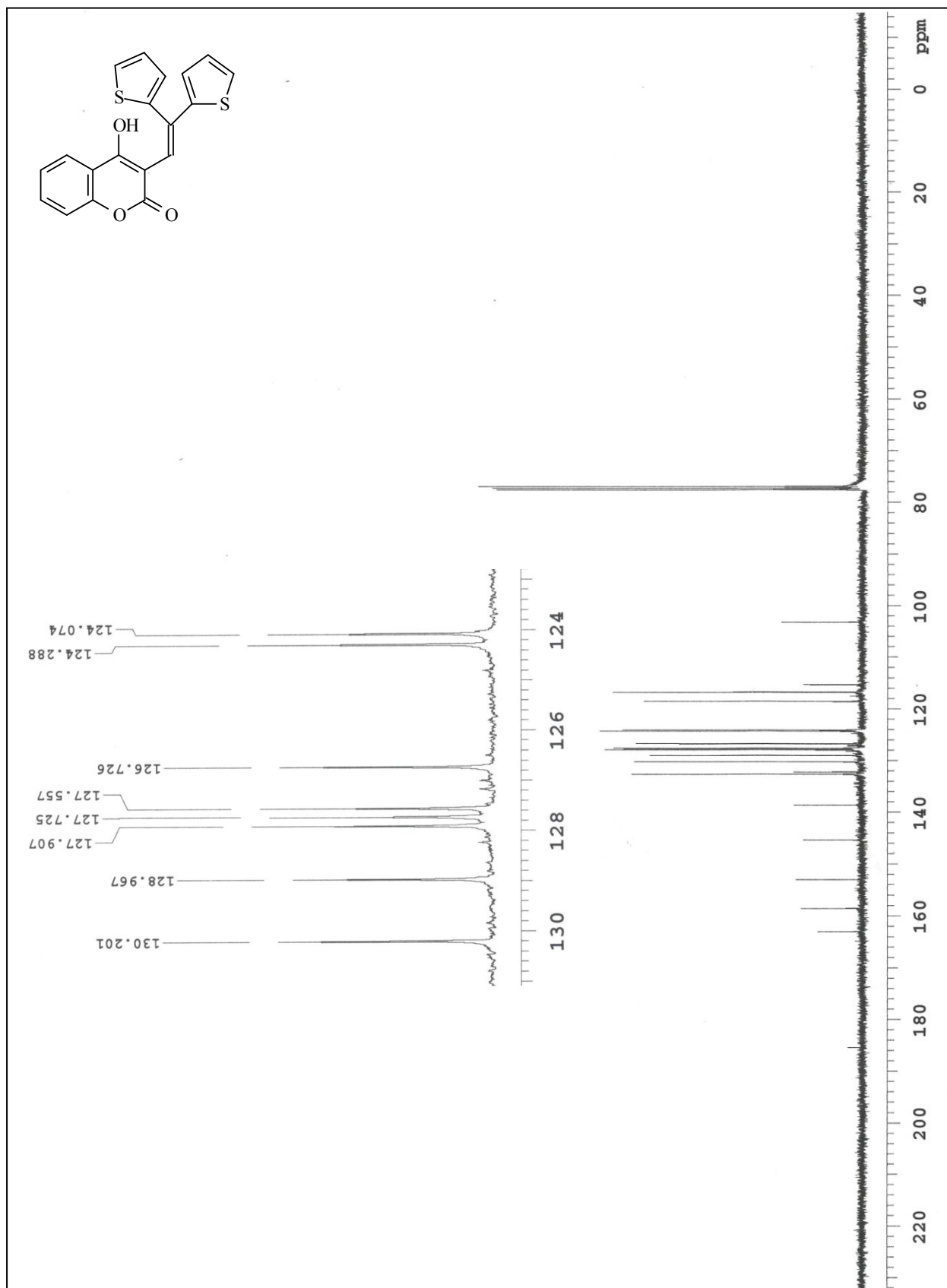
3.5 ^{13}C -NMR spectra of **5**

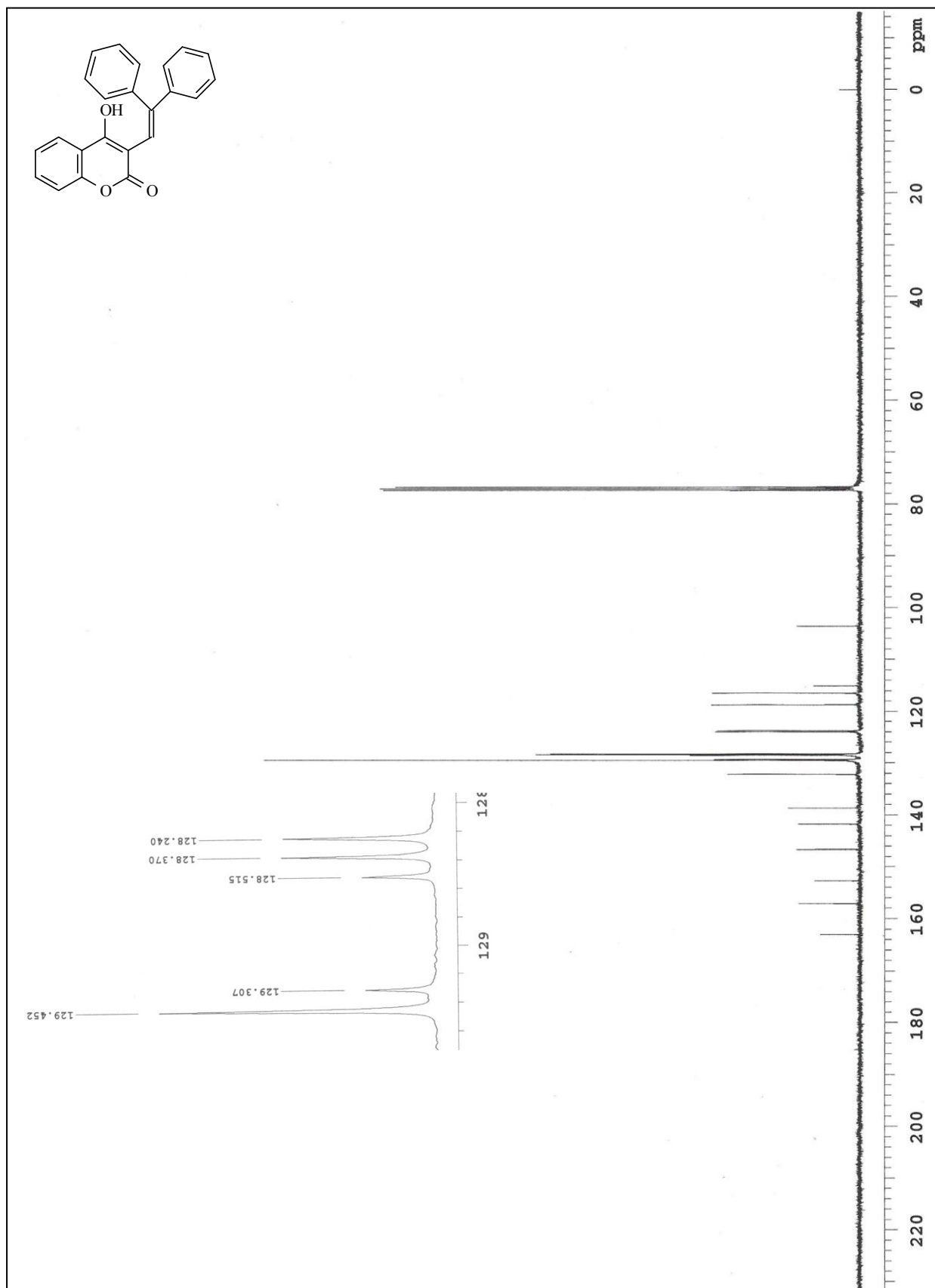
3.6 ^{13}C -NMR spectra of **10**

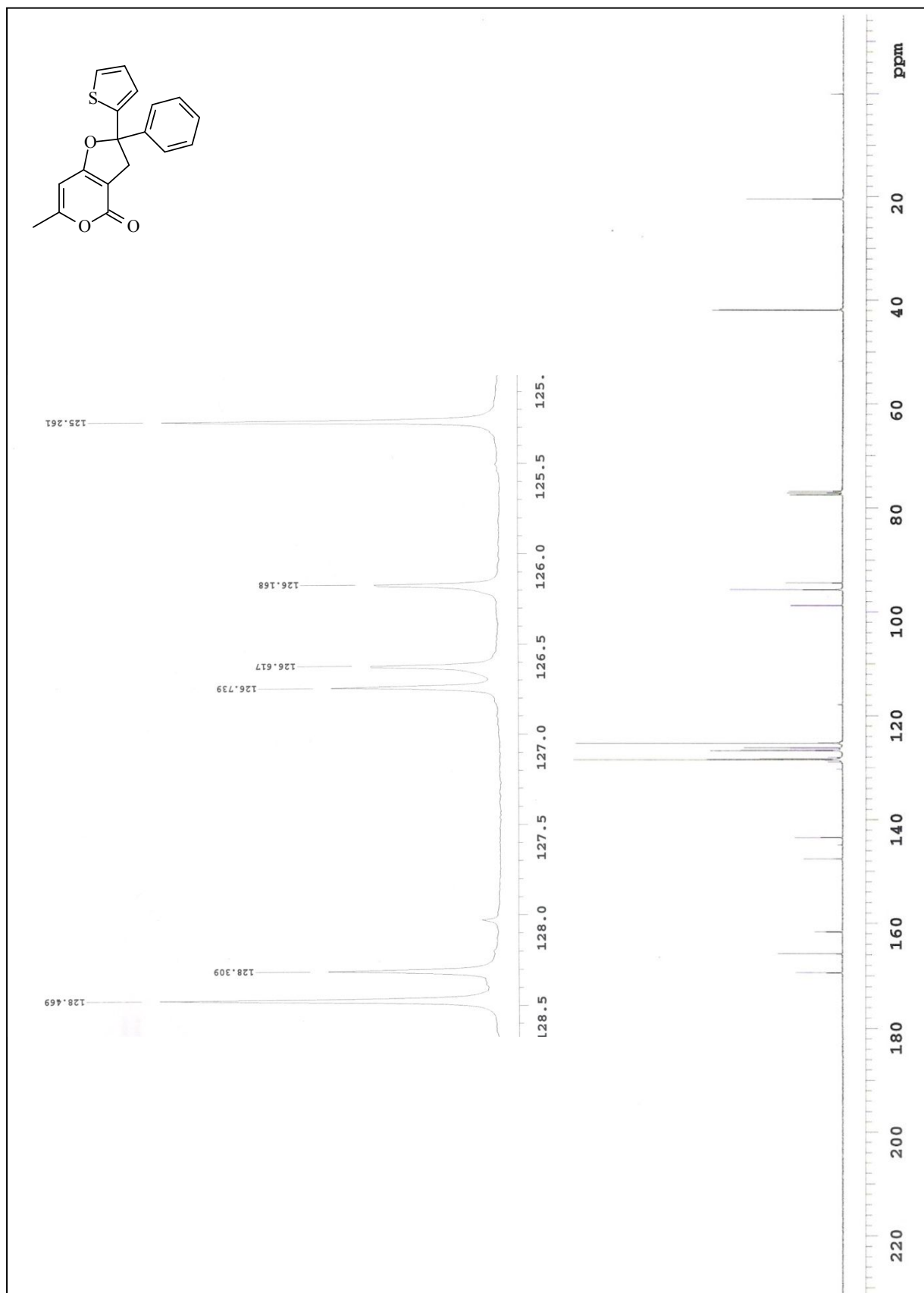
3.7 ^{13}C -NMR spectra of **6**

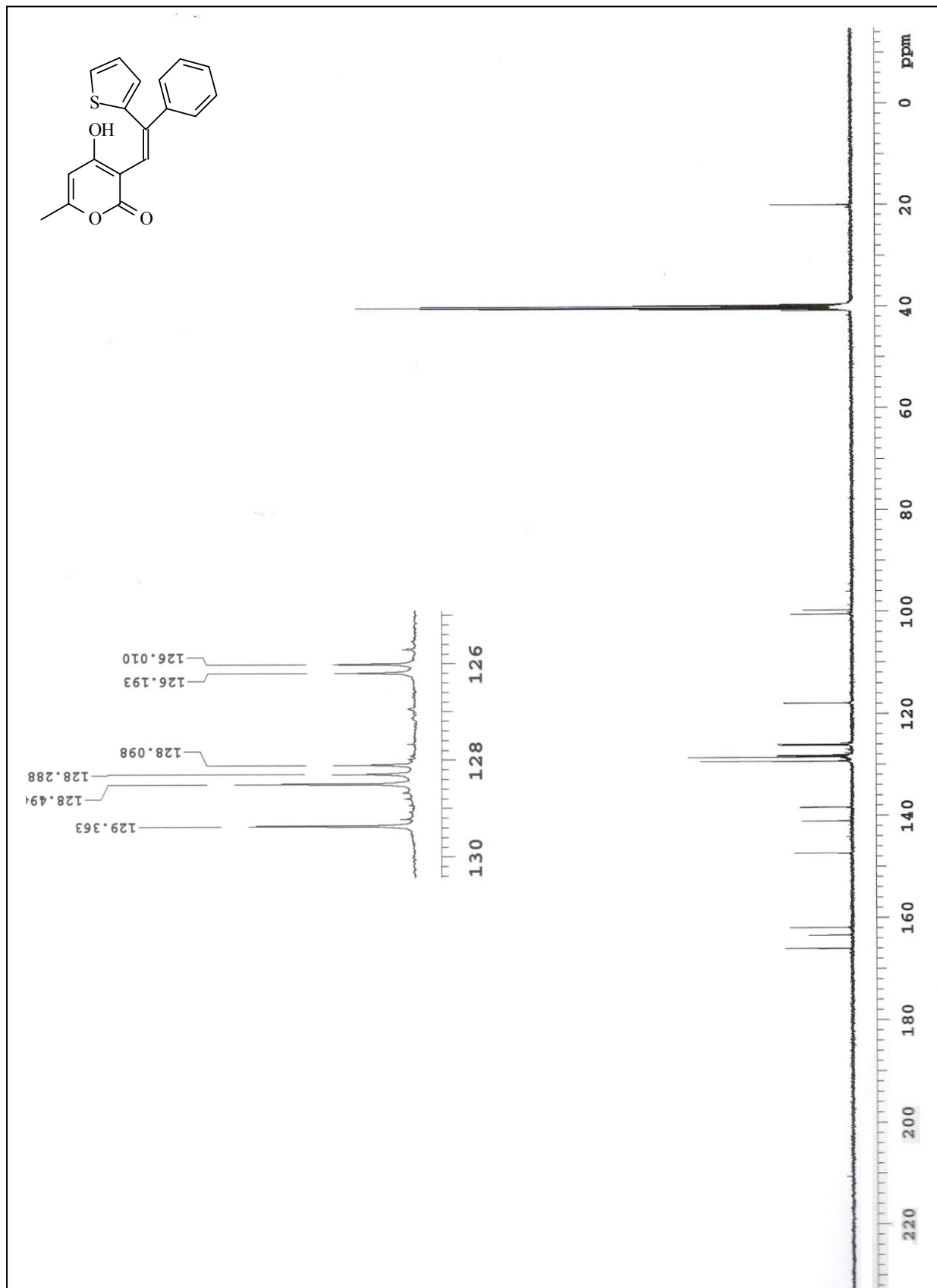
3.8 ^{13}C -NMR spectra of **11**

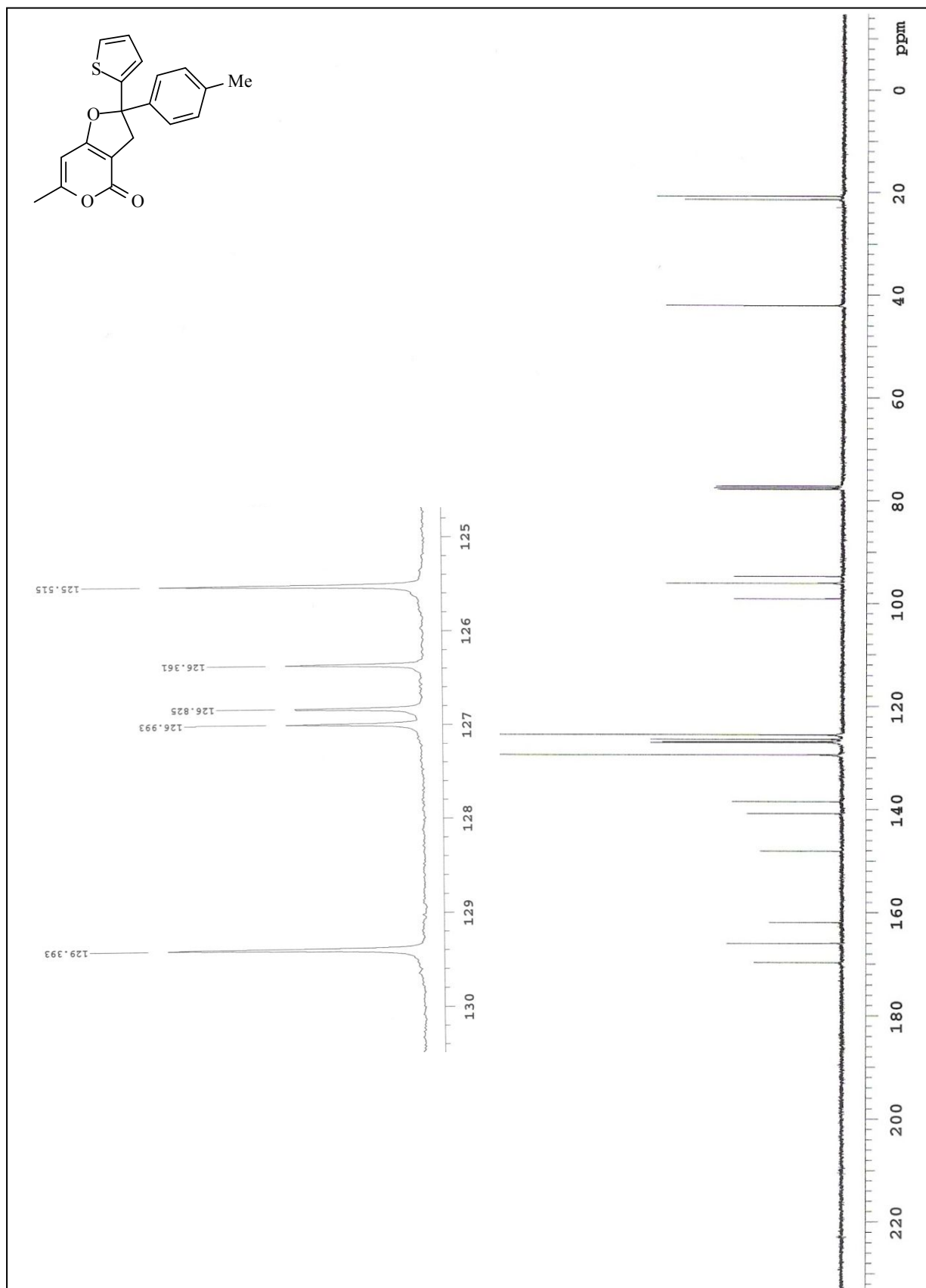
3.9 ^{13}C -NMR spectra of 7

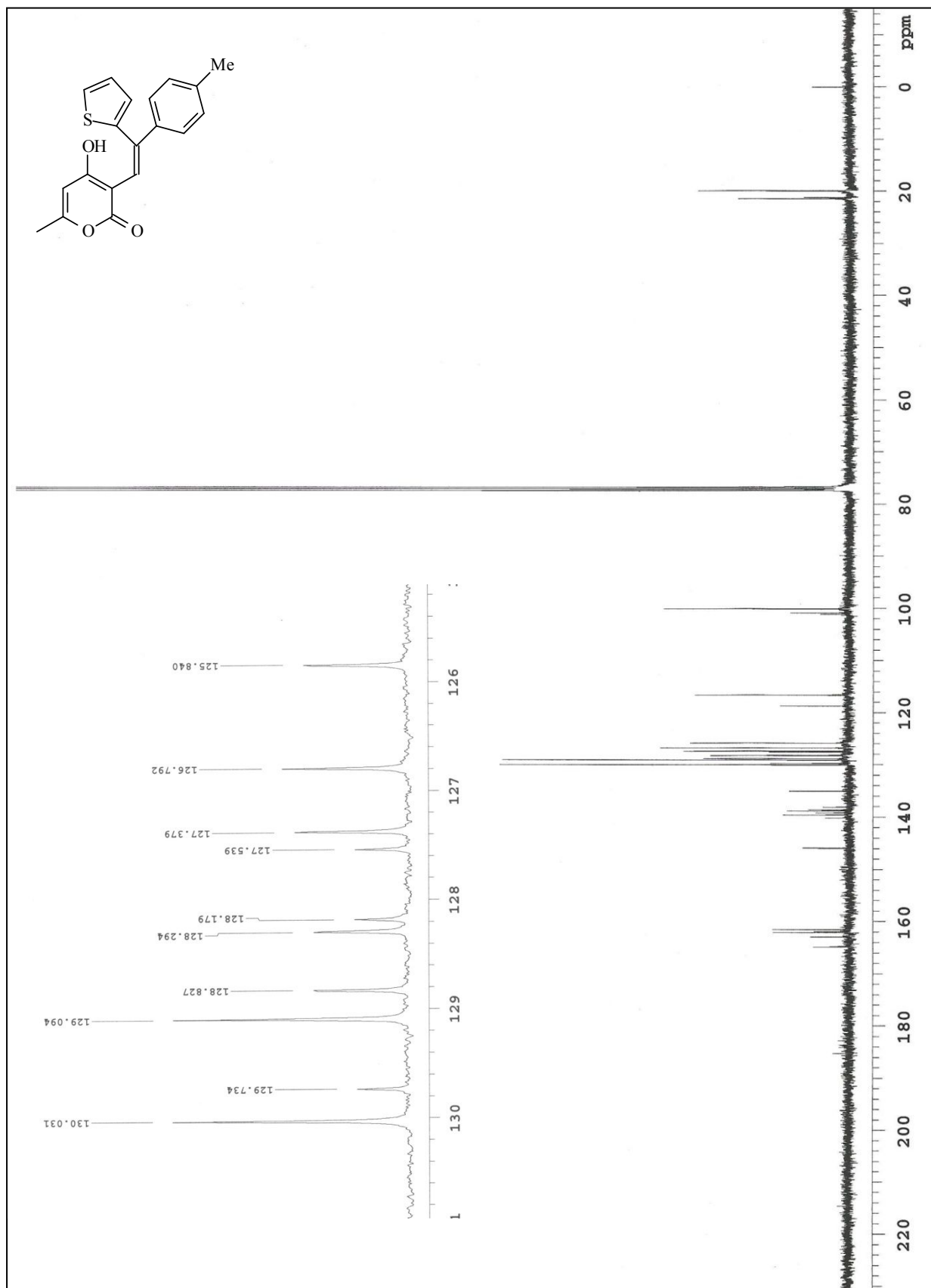
3.10 ^{13}C -NMR spectra of **12**

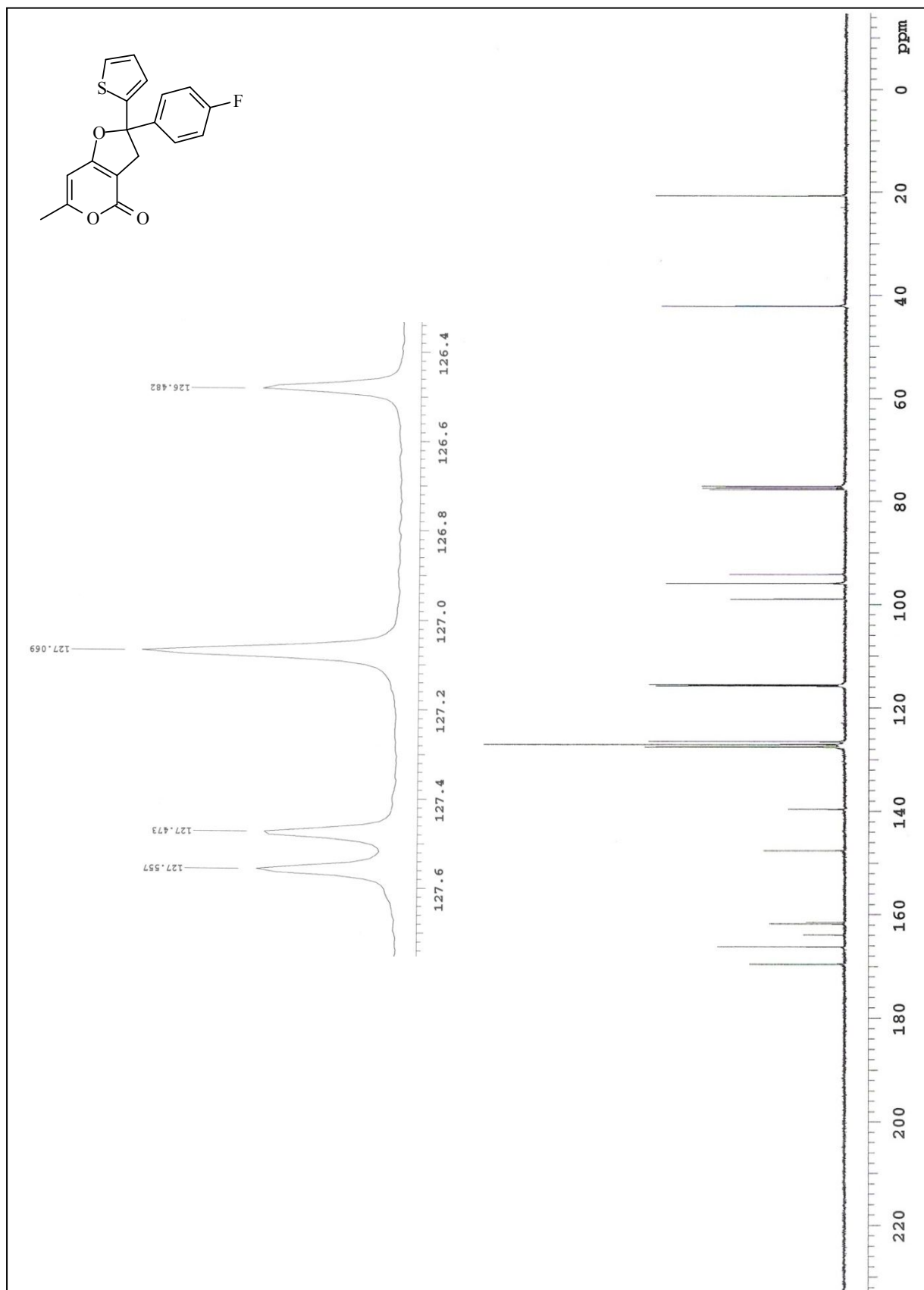
3.11 ^{13}C -NMR spectra of **4aj**

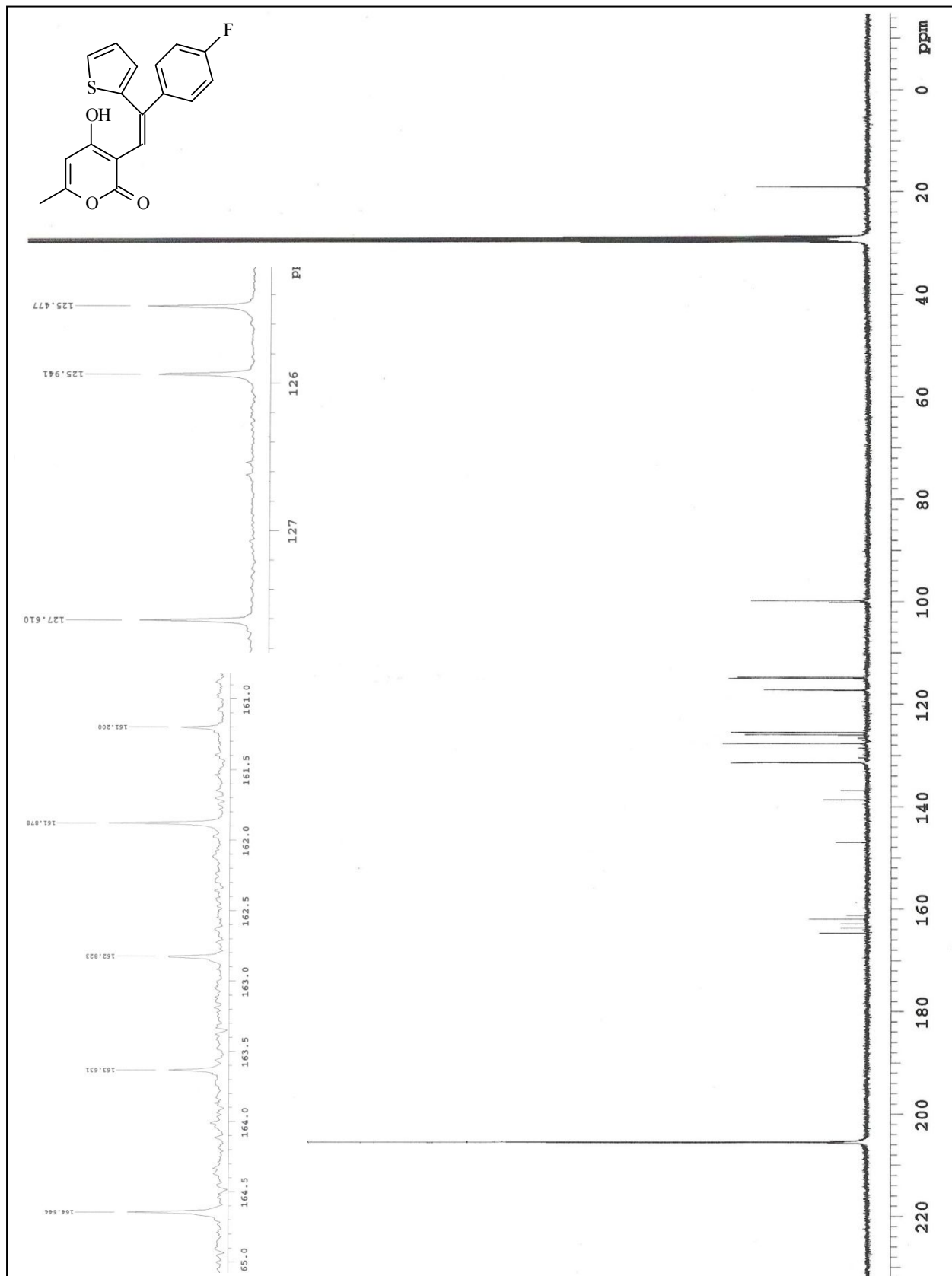
3.12 ^{13}C -NMR spectra of **13**

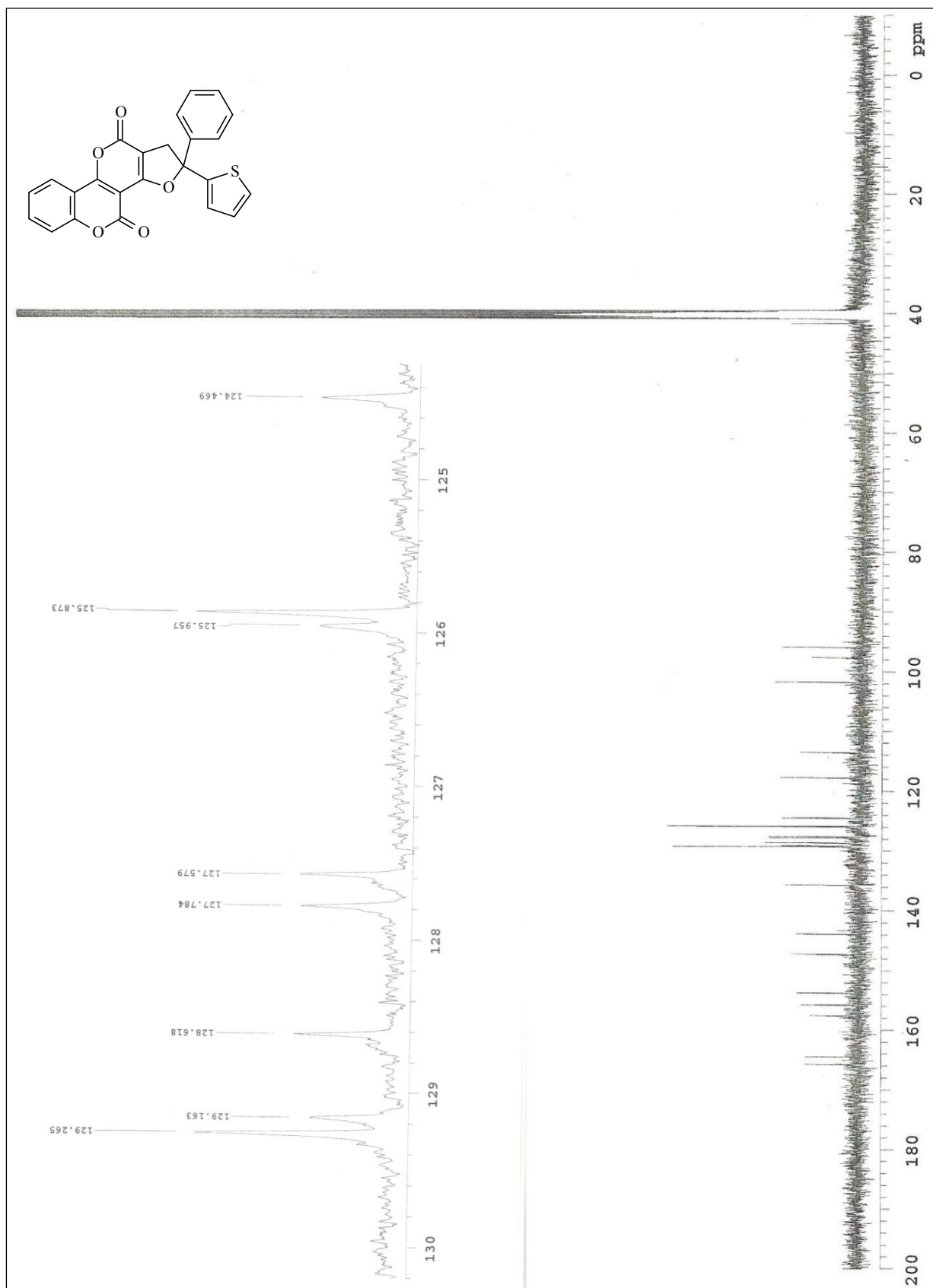
3.13 ^{13}C -NMR spectra of **16**

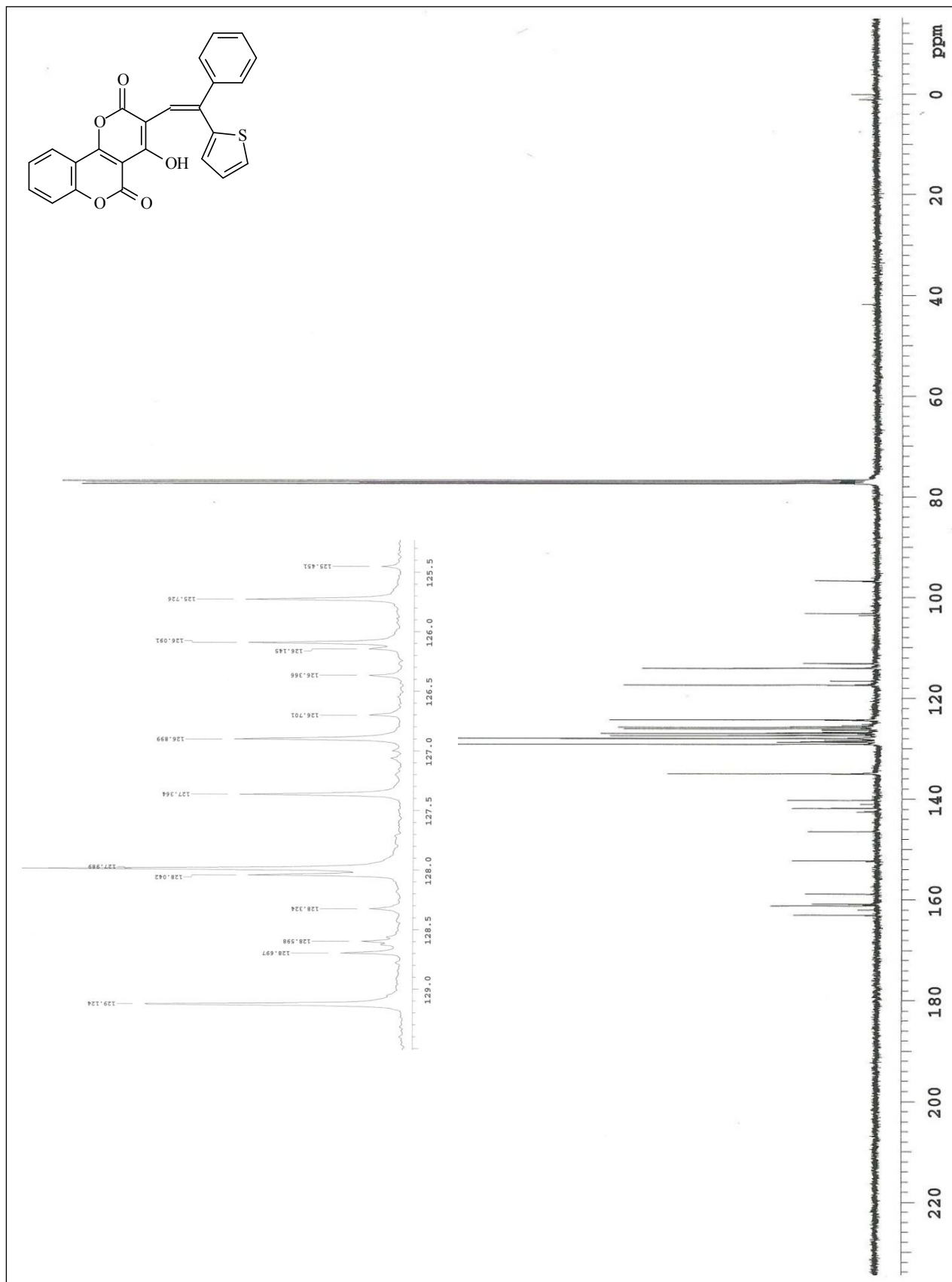
3.14 ^{13}C -NMR spectra of **14**

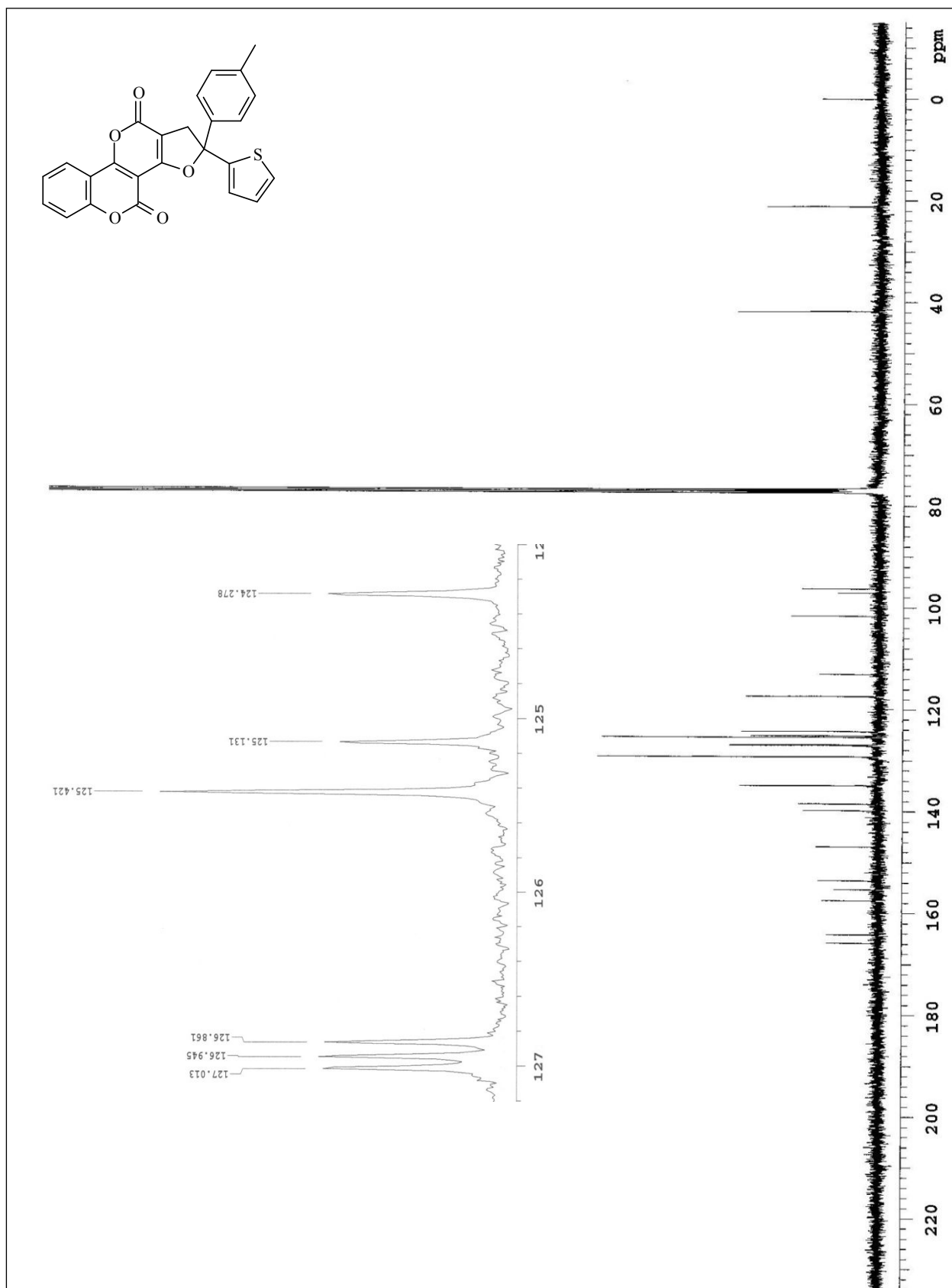
3.15 ^{13}C -NMR spectra of **17**

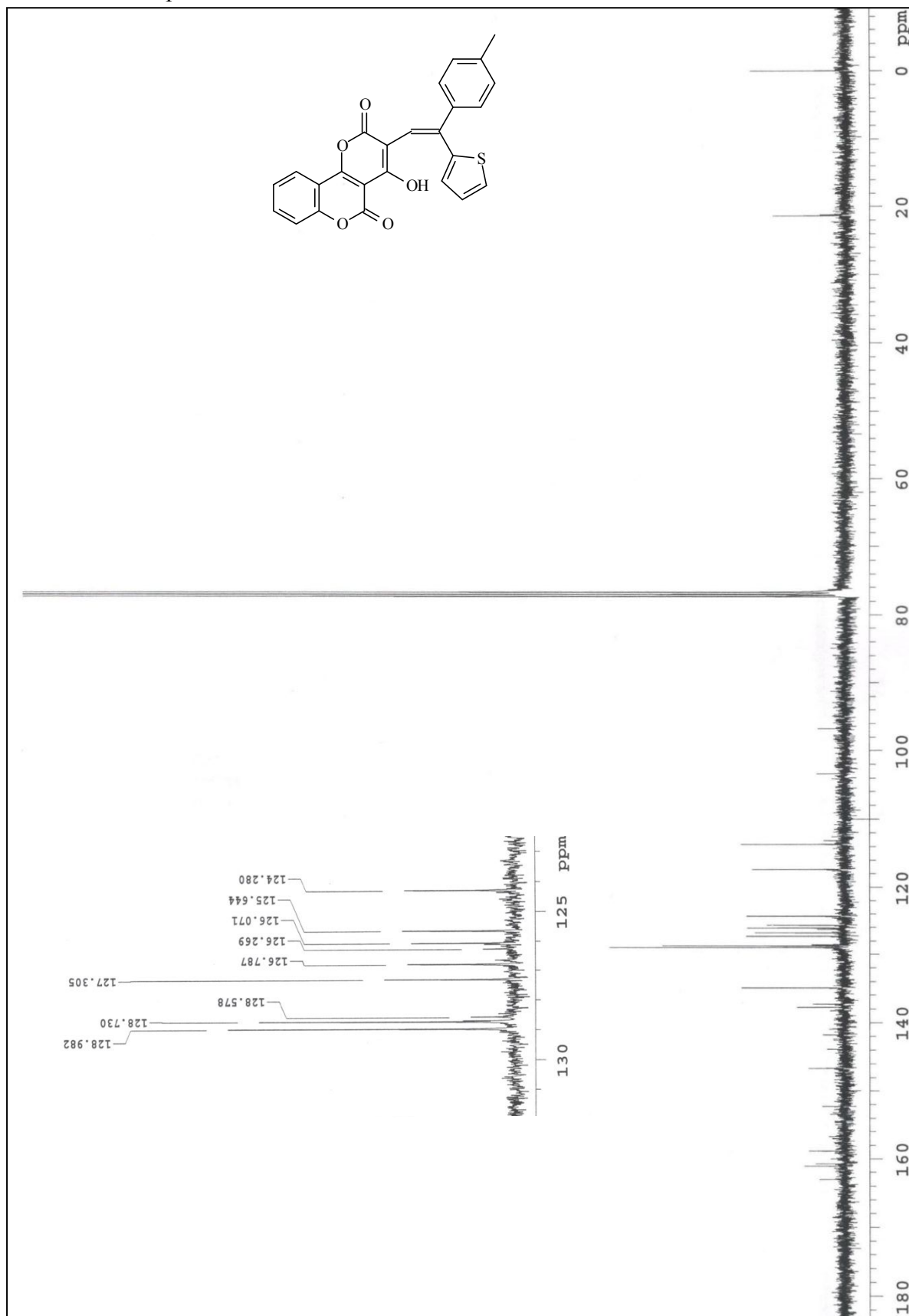
3.16 ^{13}C -NMR spectra of **15**

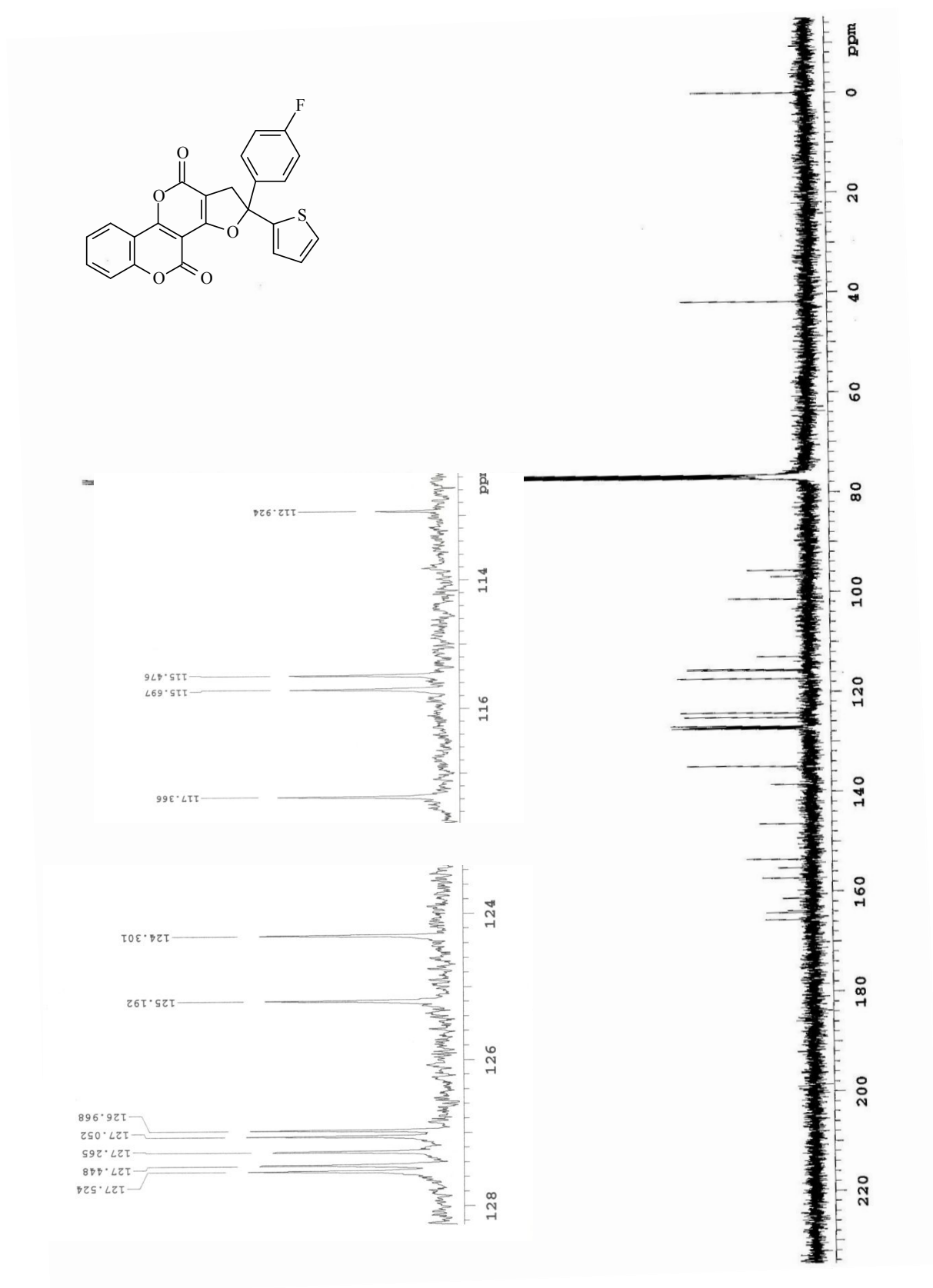
3.17 ^{13}C -NMR spectra of **18**

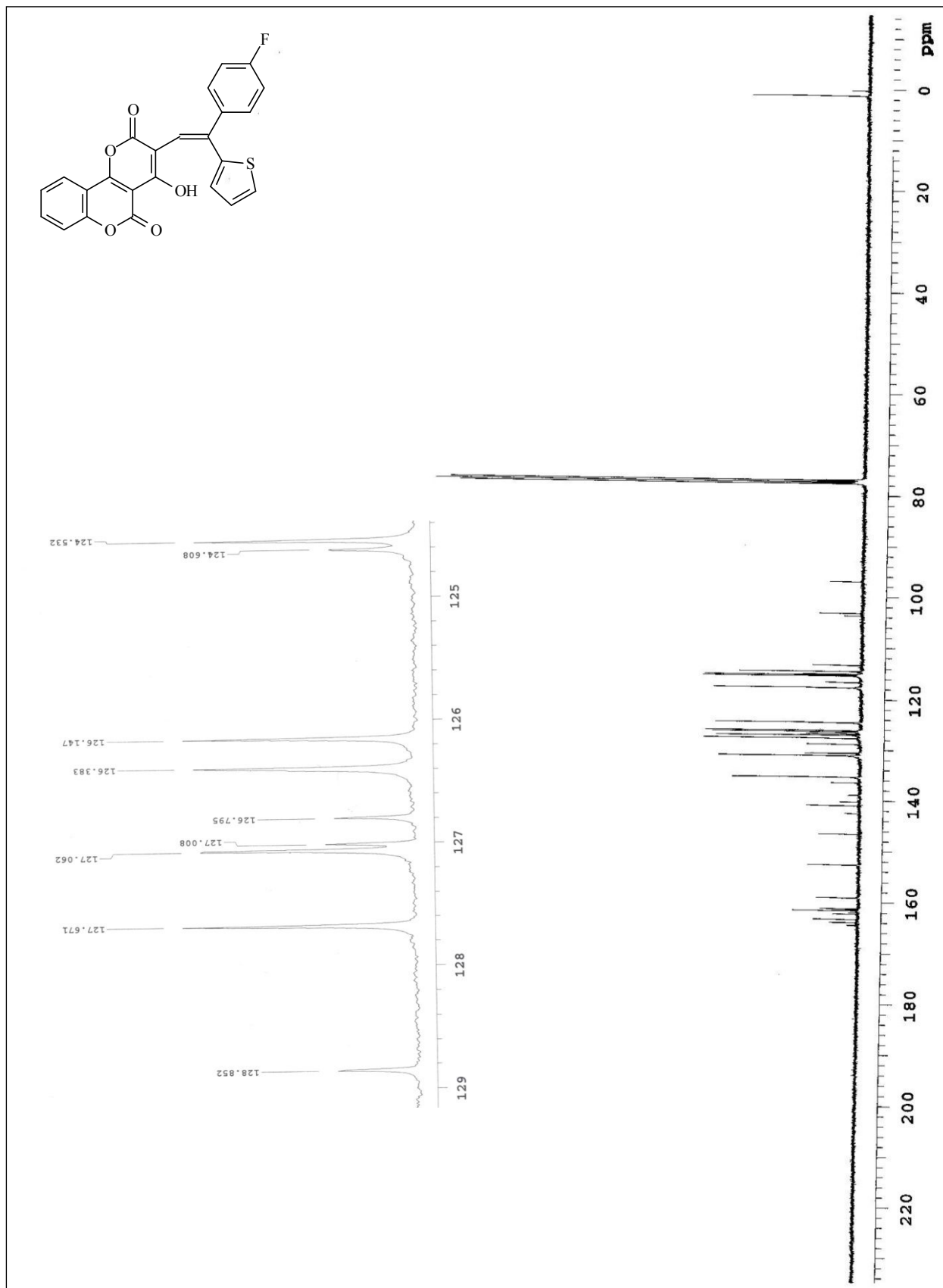
3.18 ^{13}C -NMR spectra of **19**

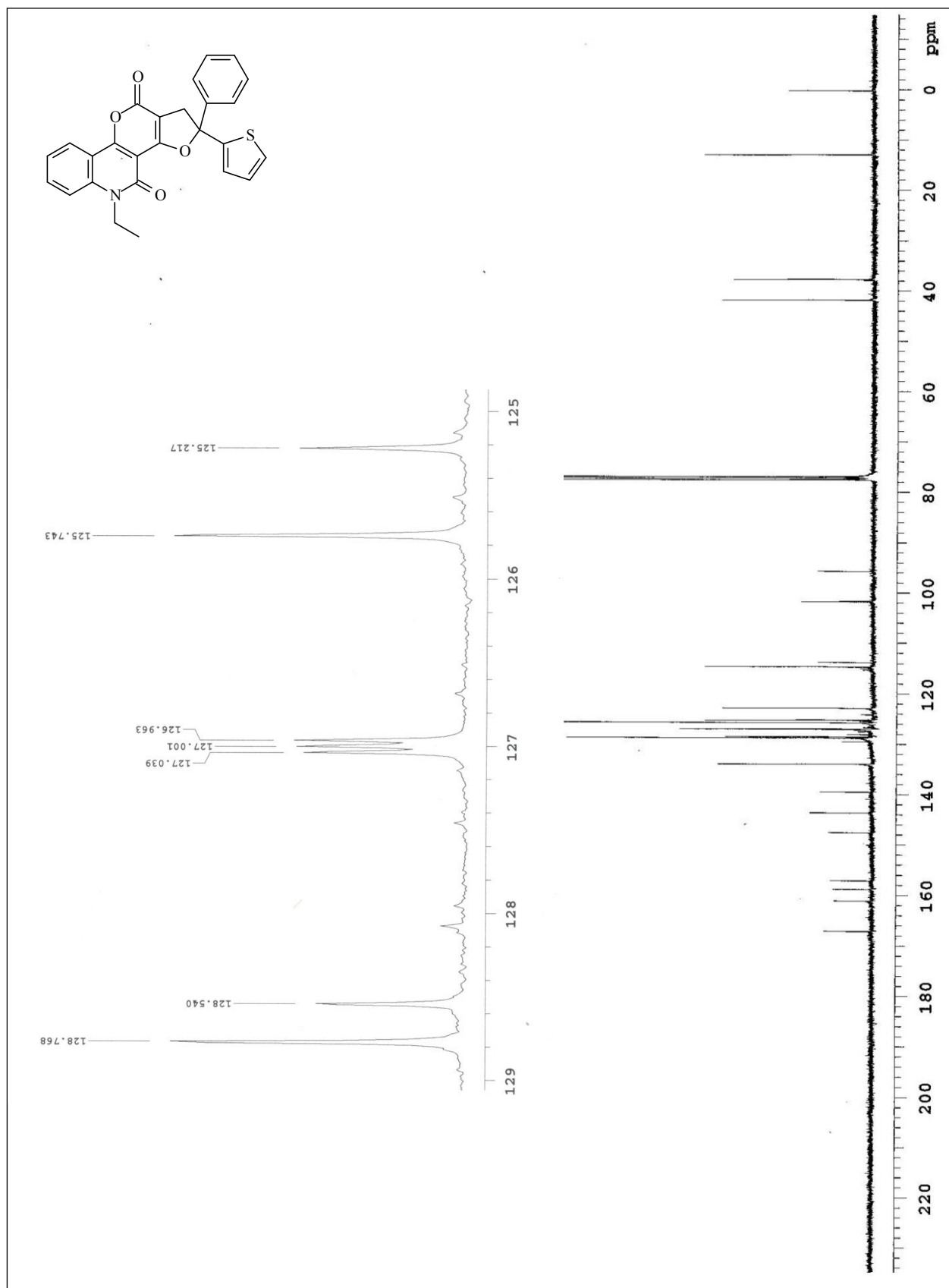
3.19 ^{13}C -NMR spectra of **25**

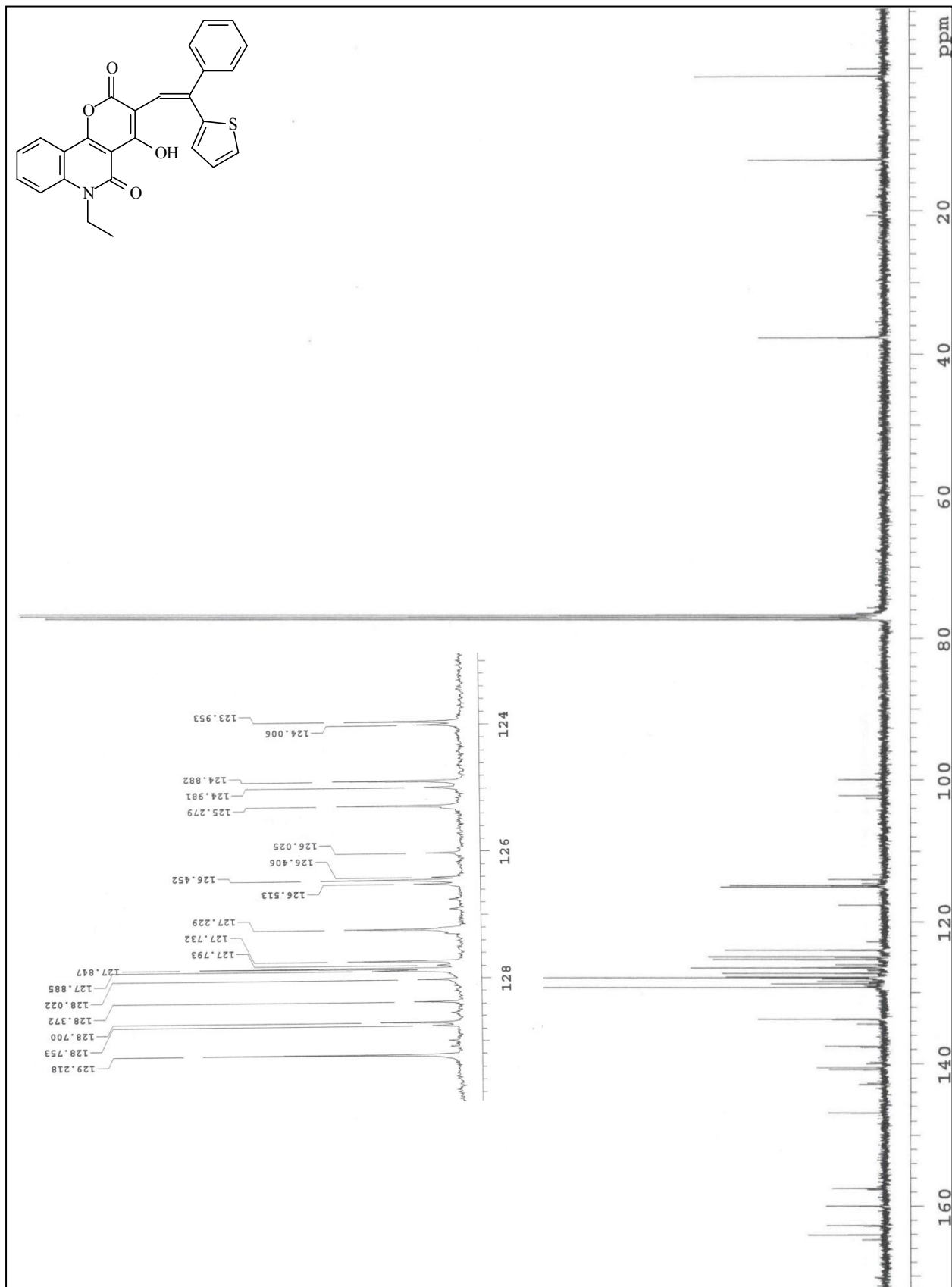
3.20 ^{13}C -NMR spectra of **20**

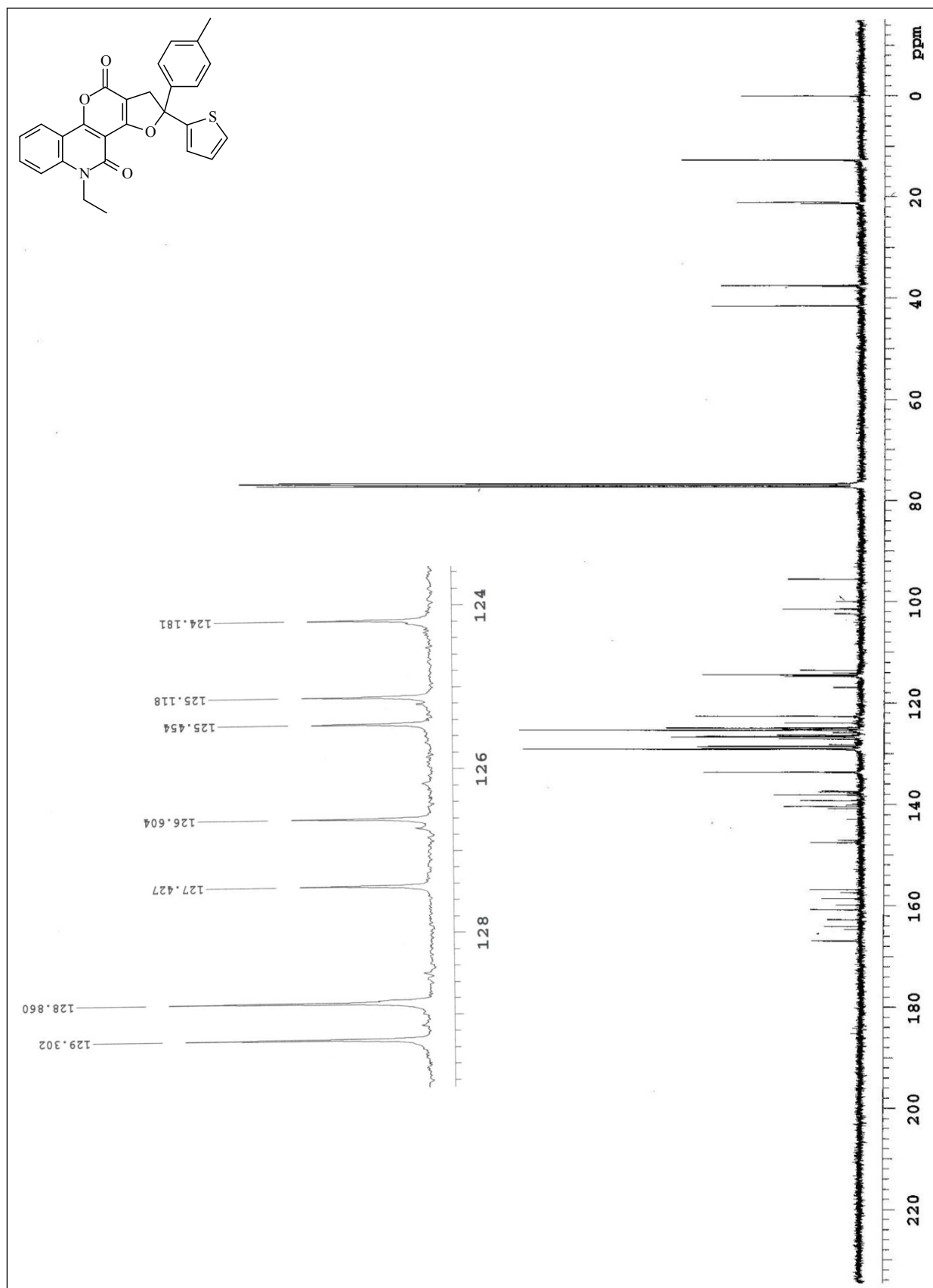
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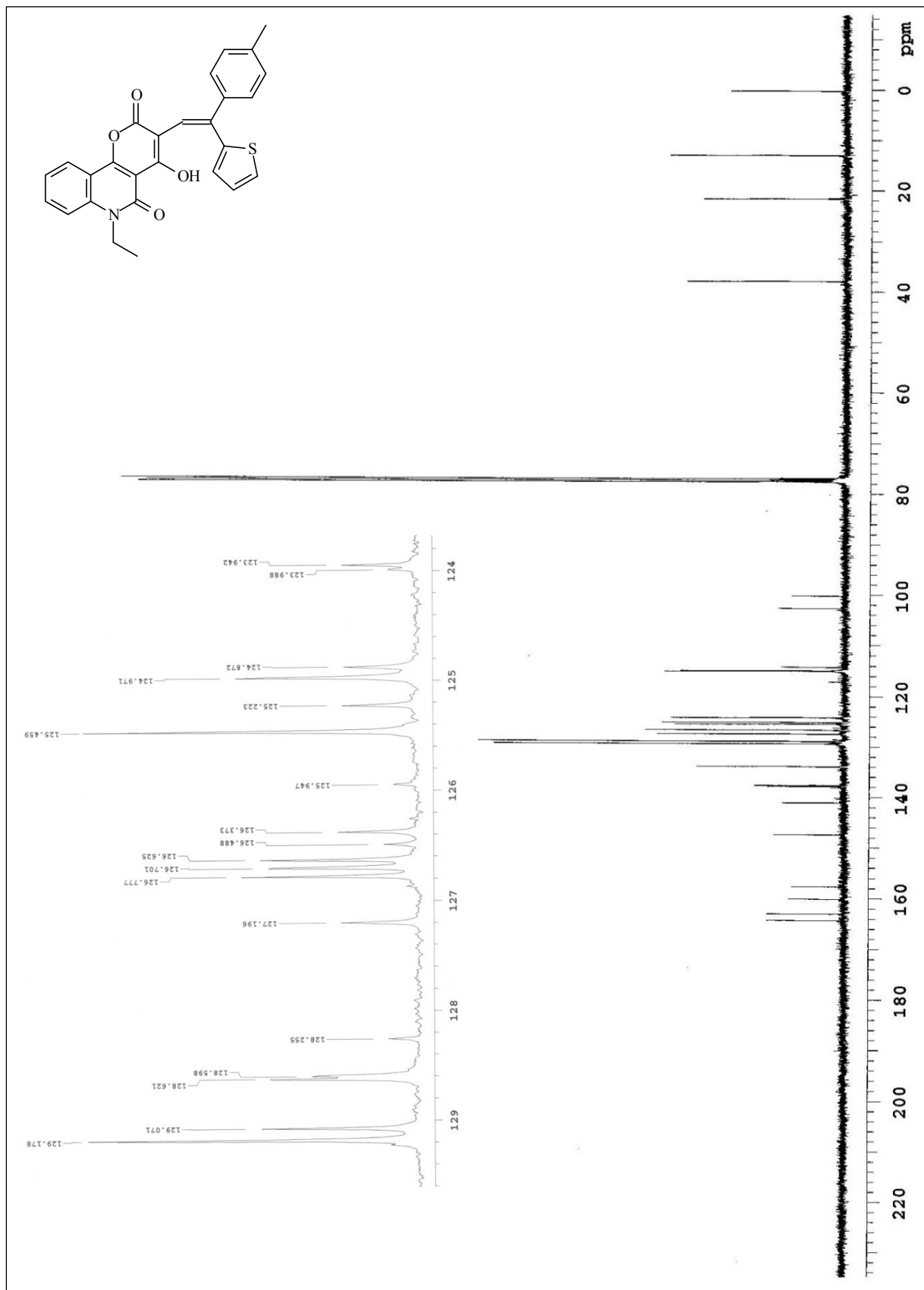
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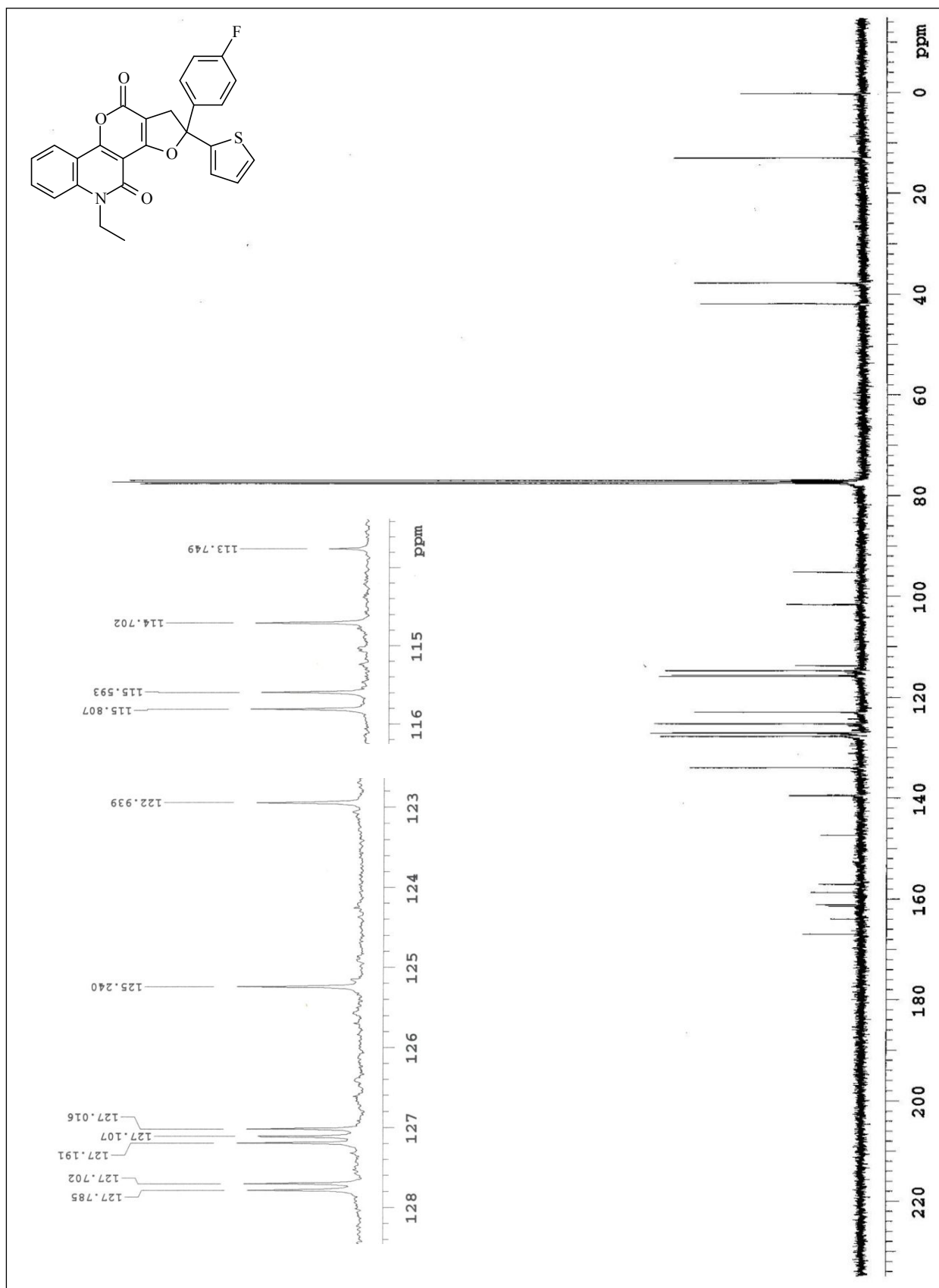
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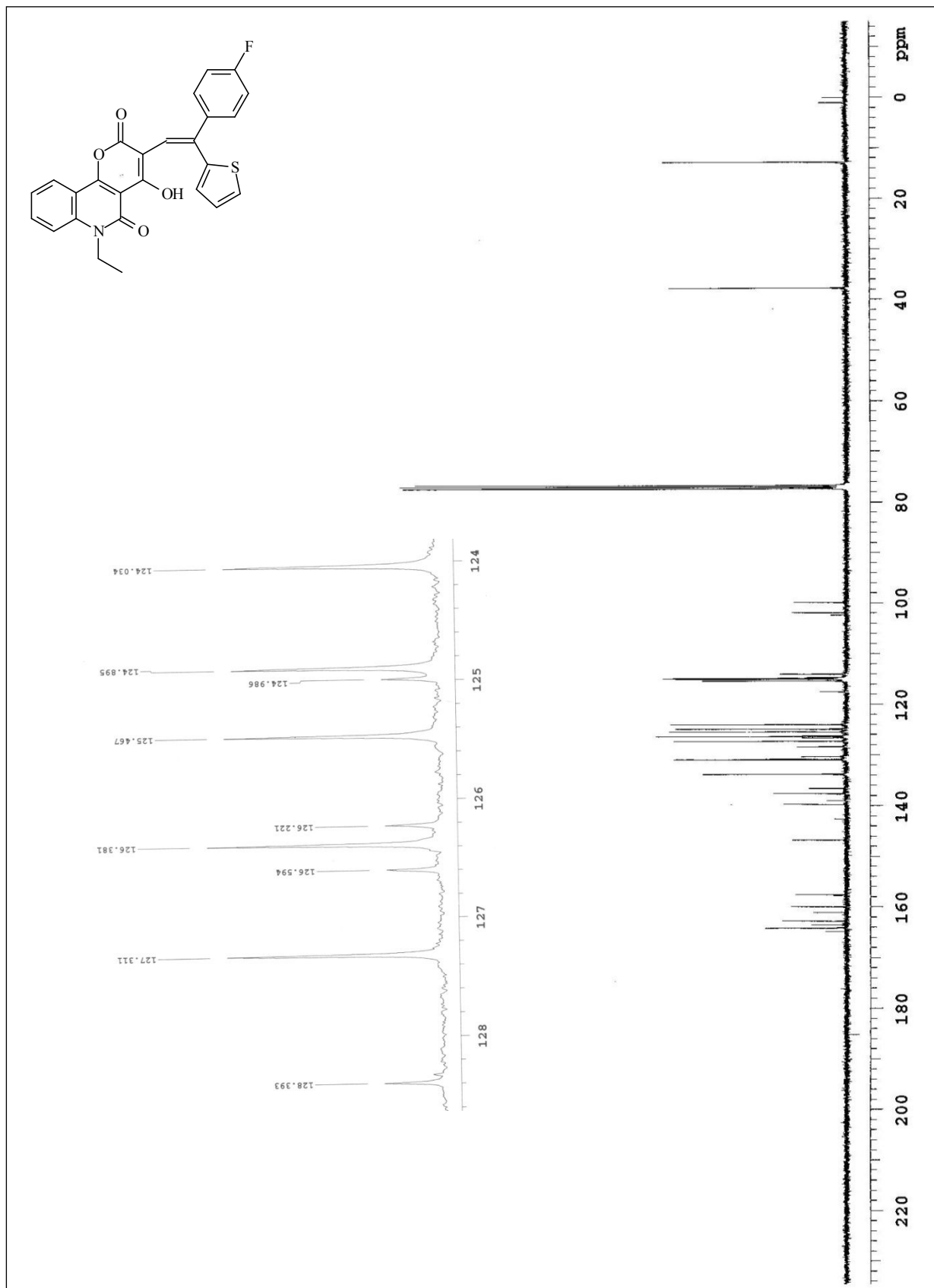
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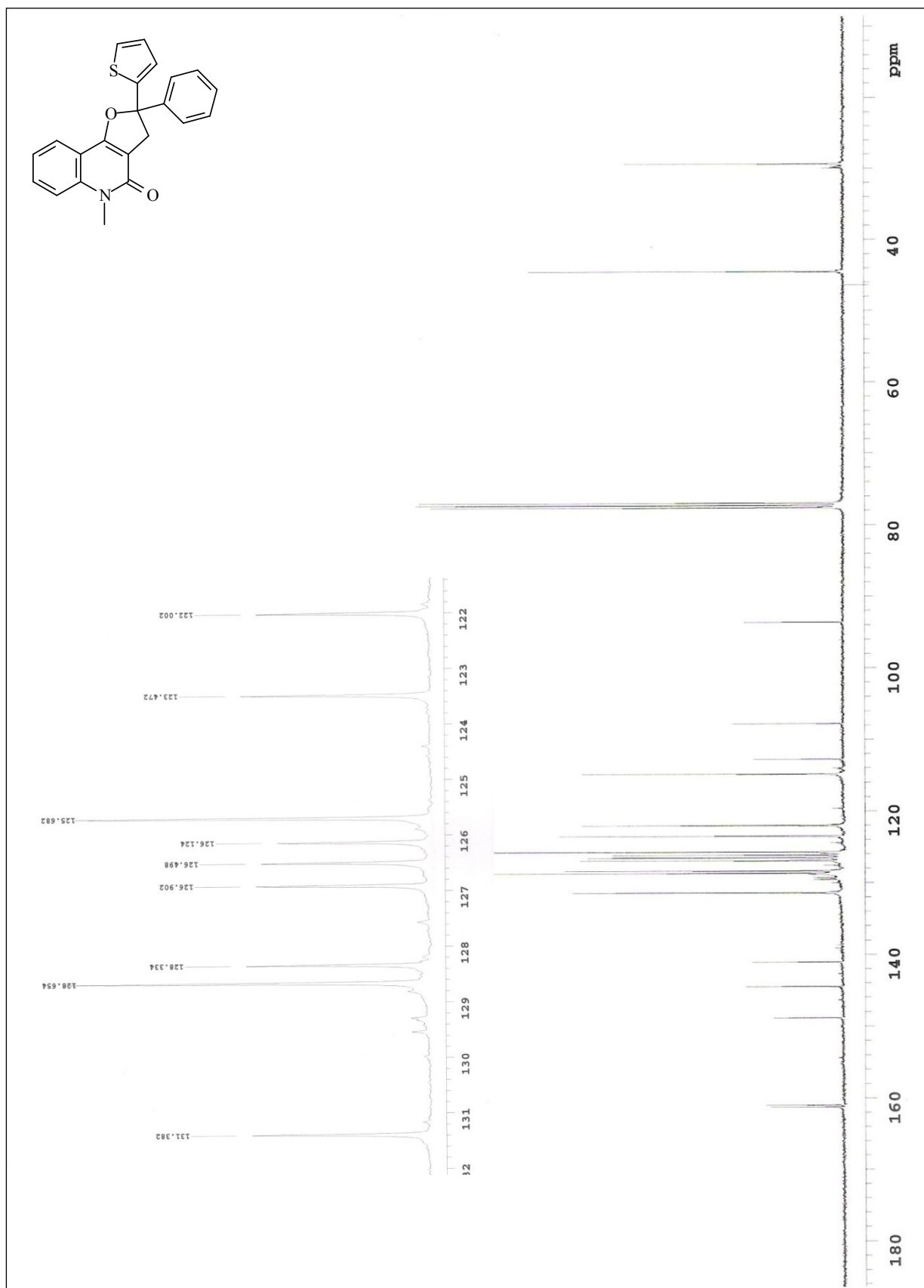
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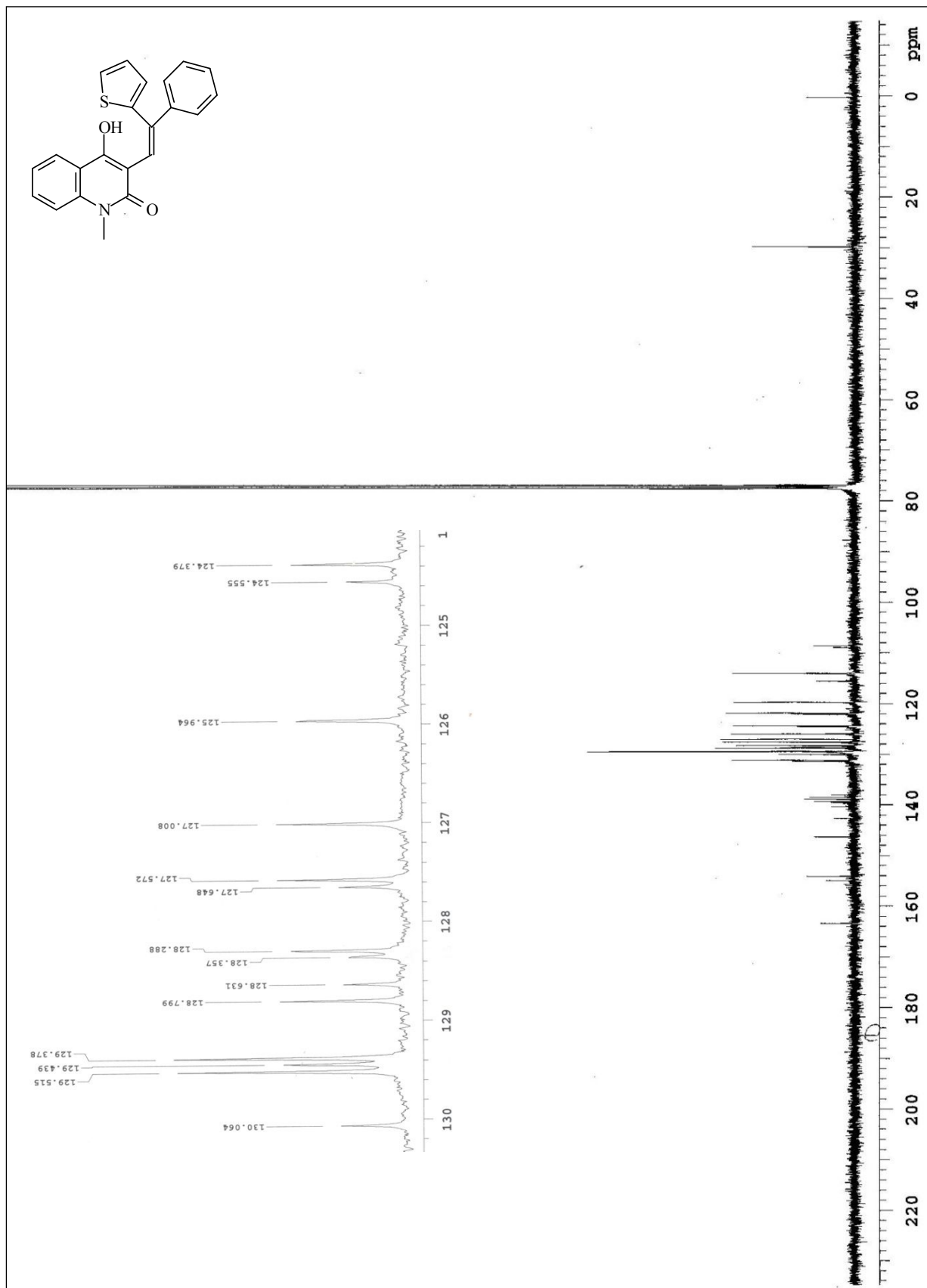
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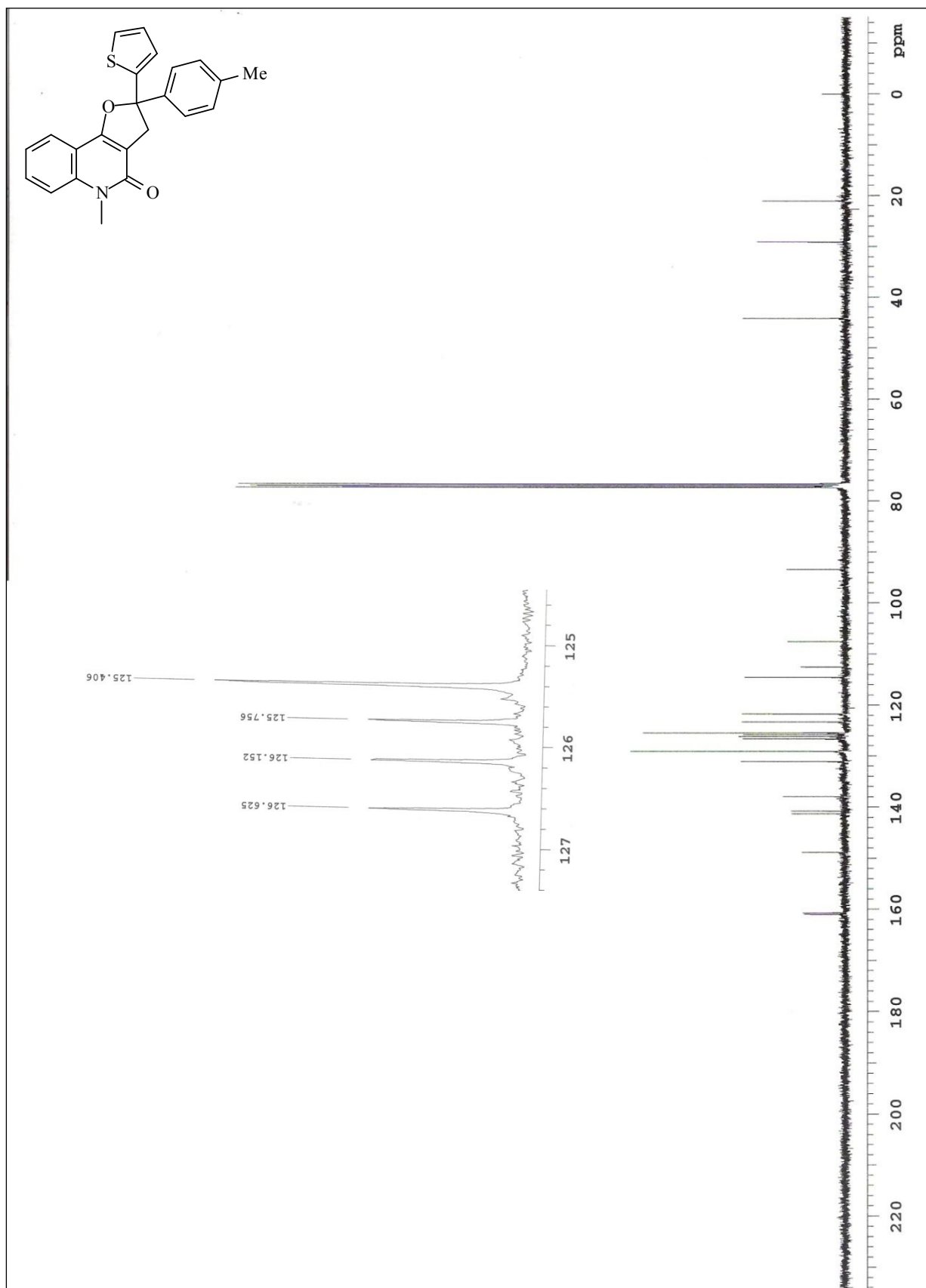
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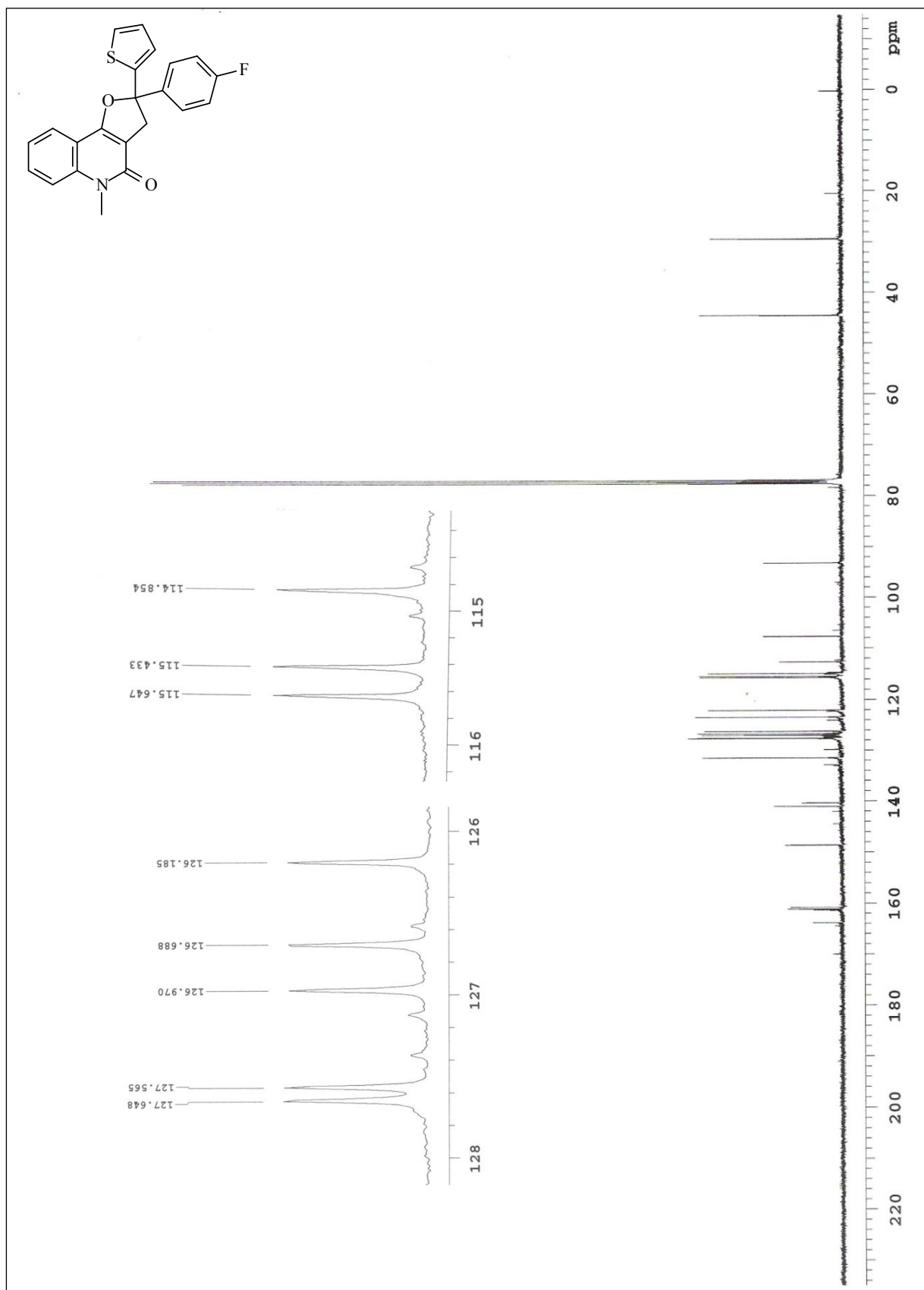
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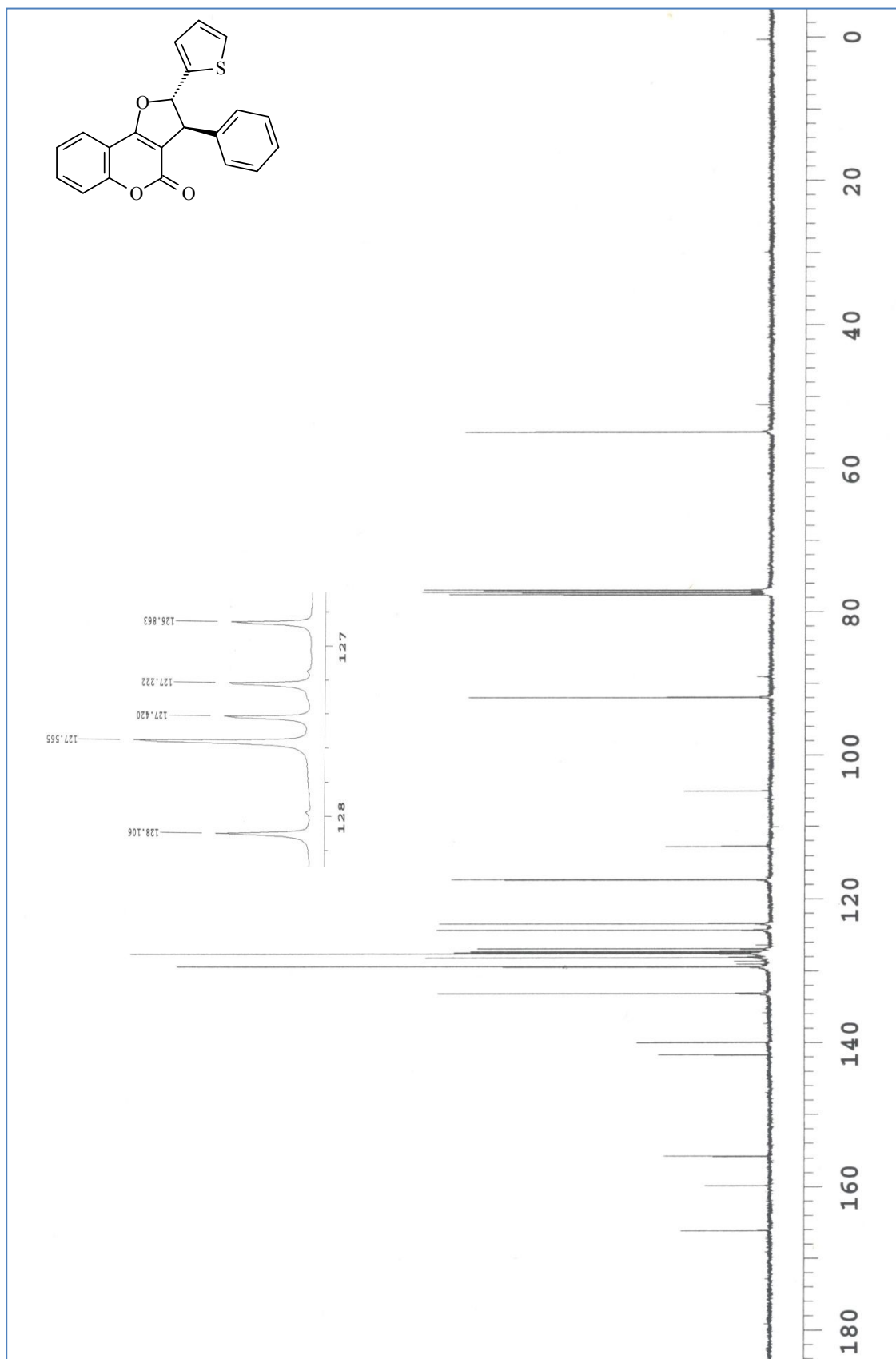
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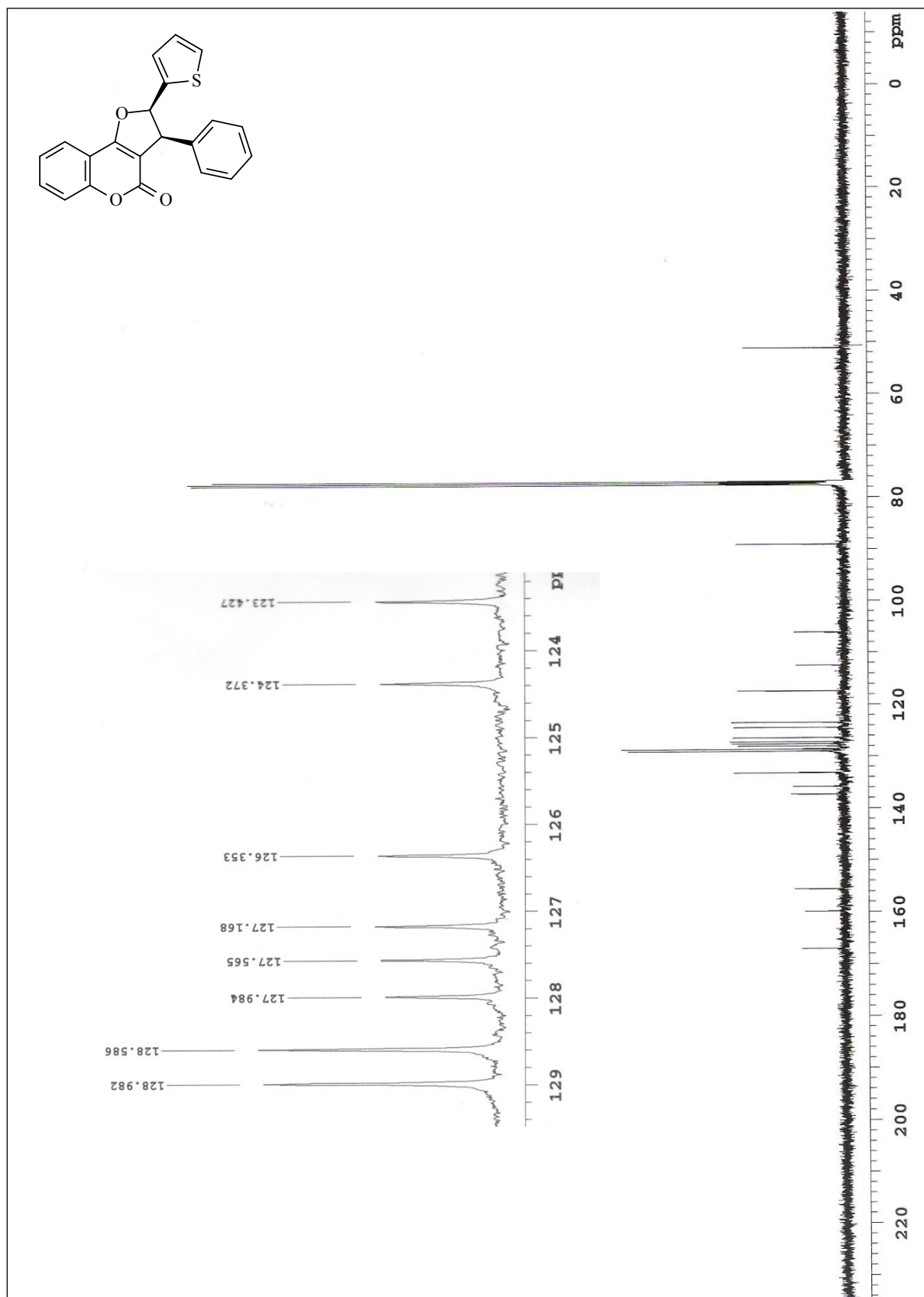
3.30 ^{13}C -NMR spectra of **31**

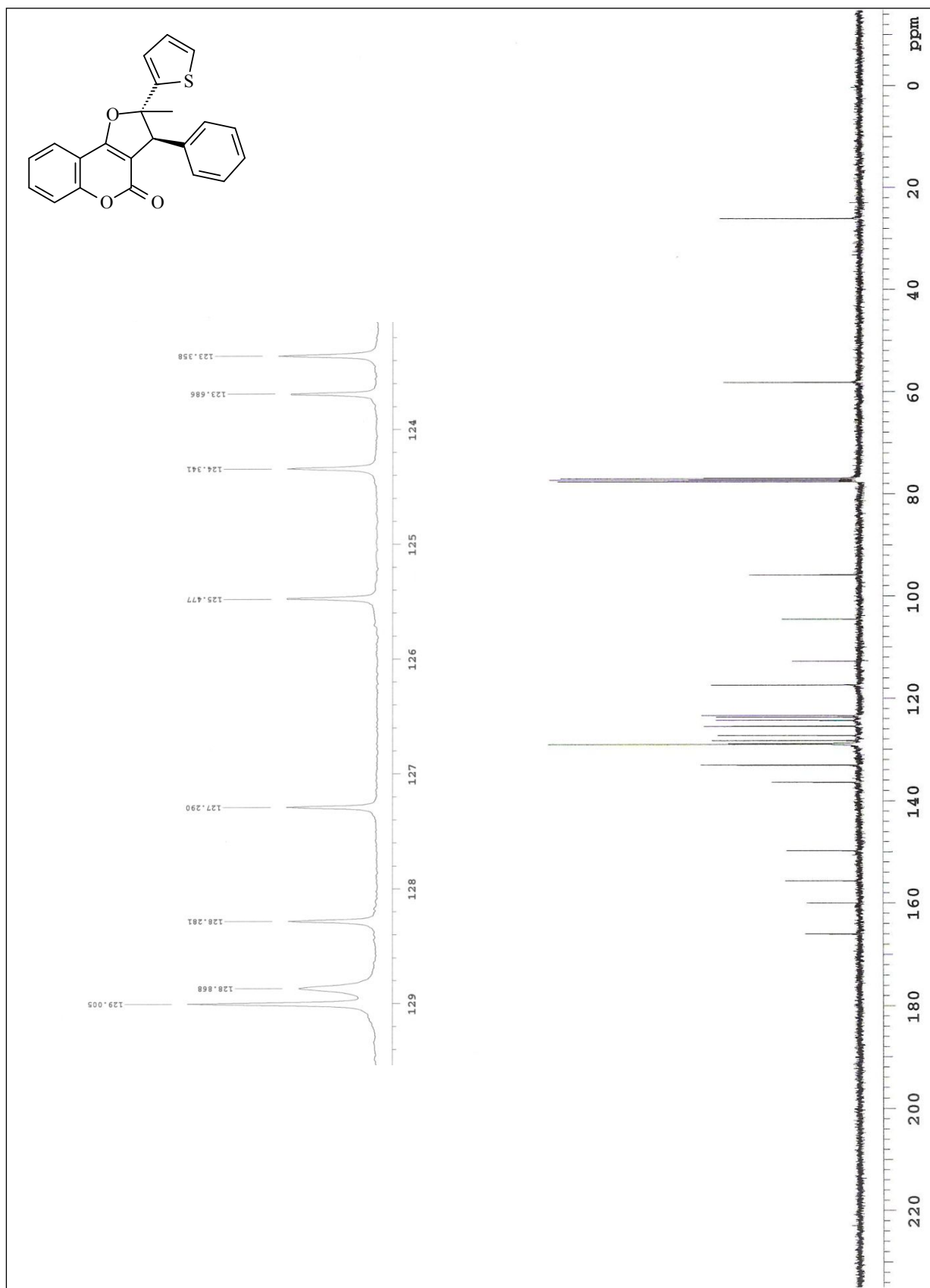
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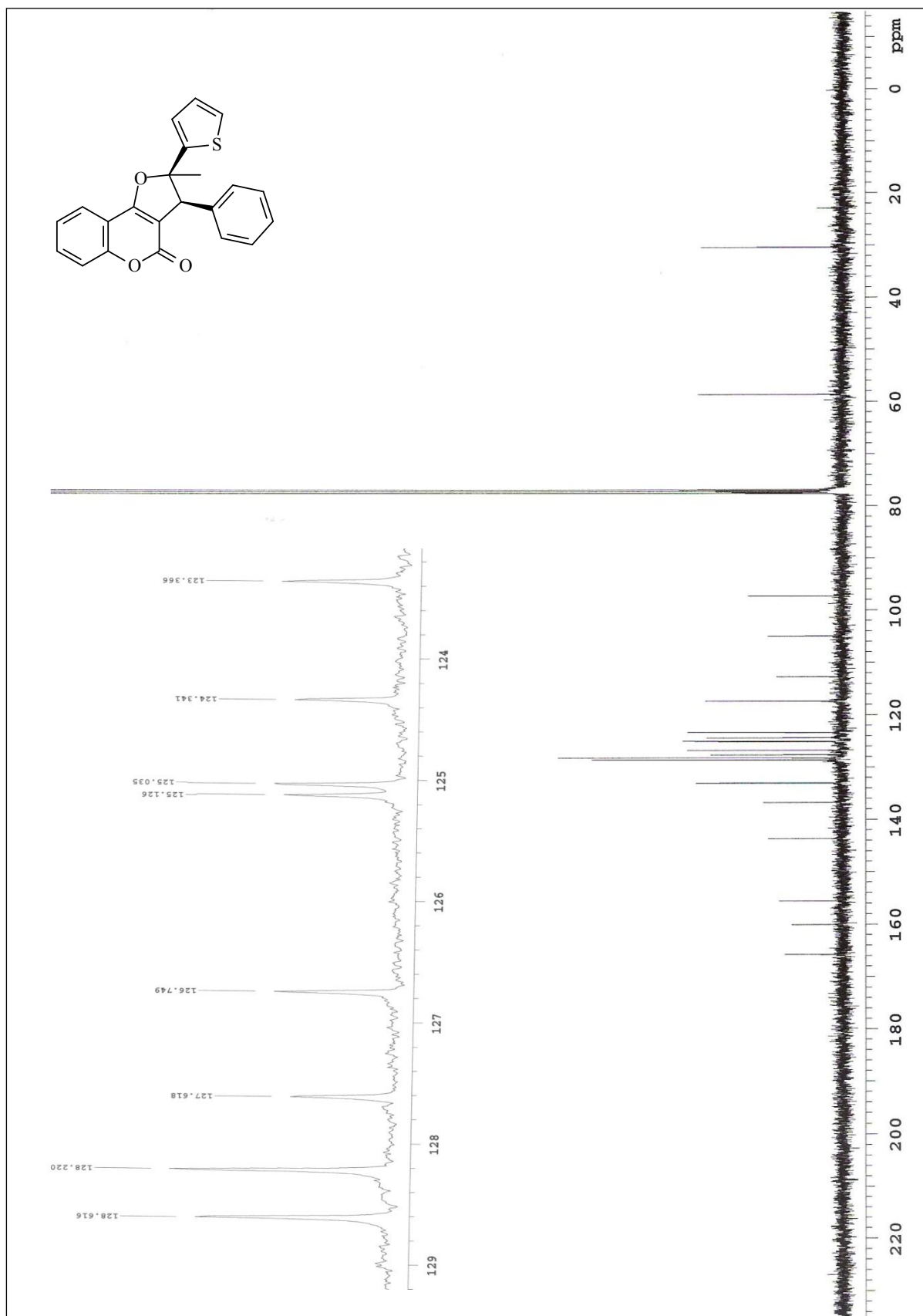
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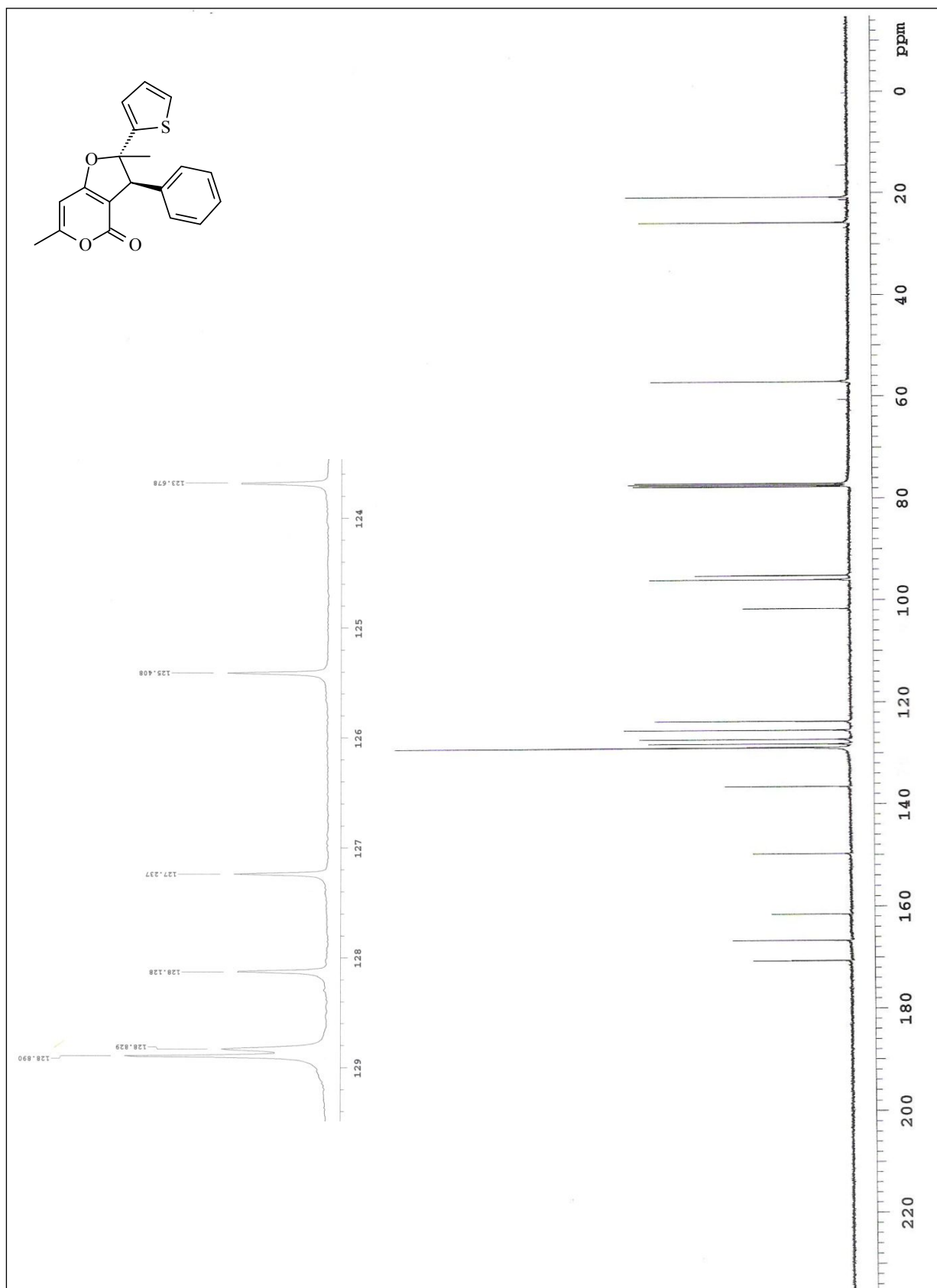
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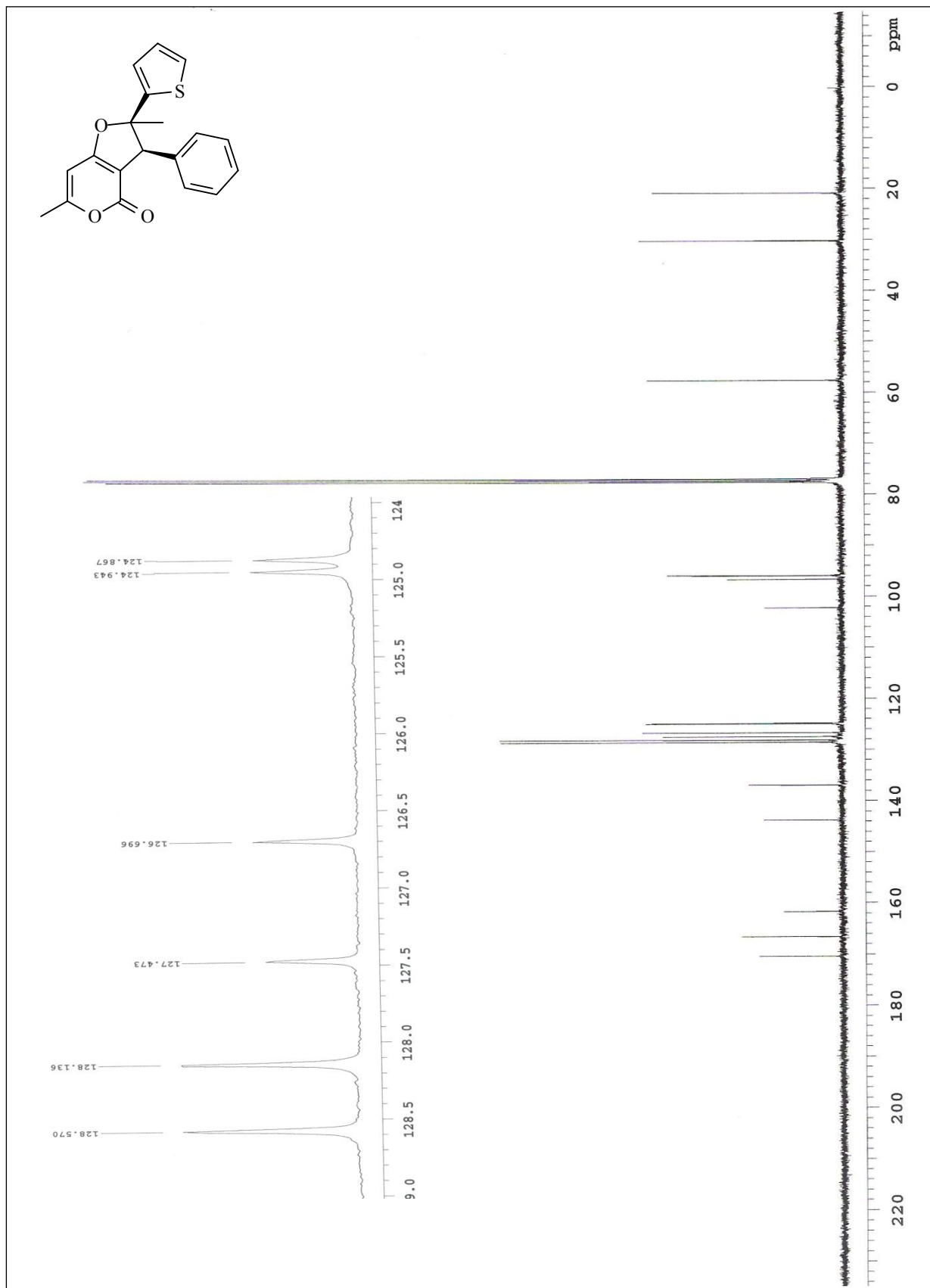
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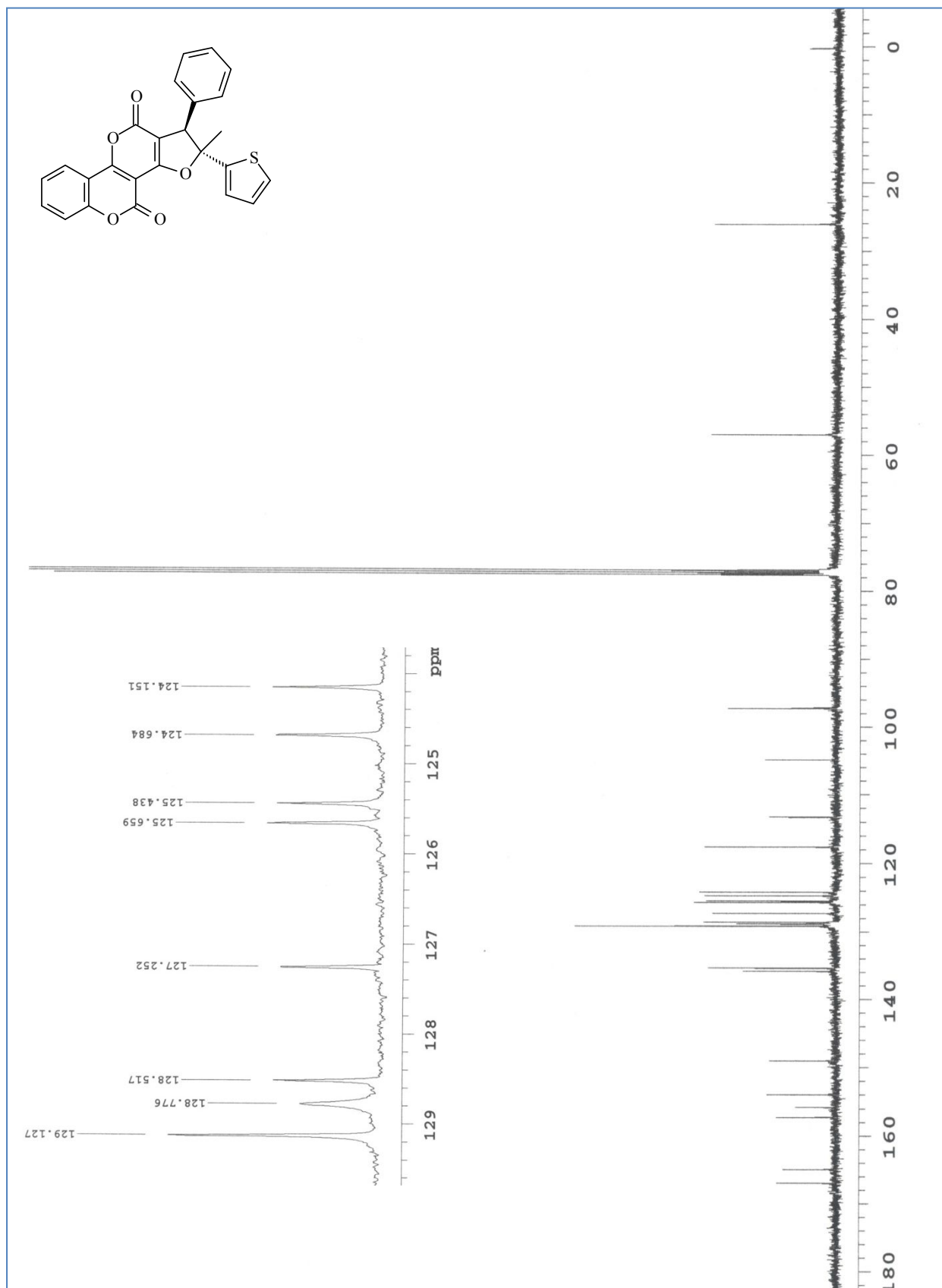
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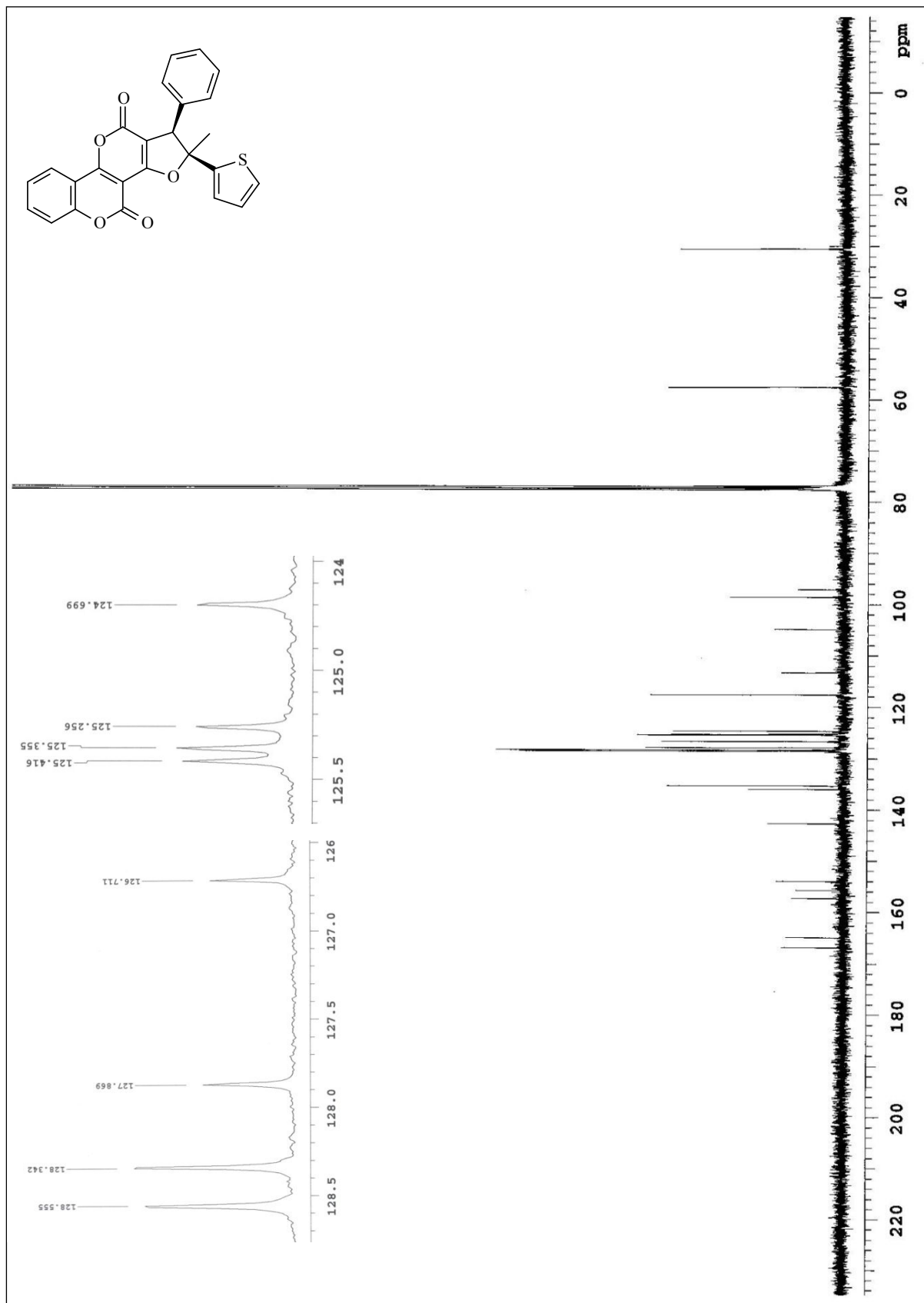
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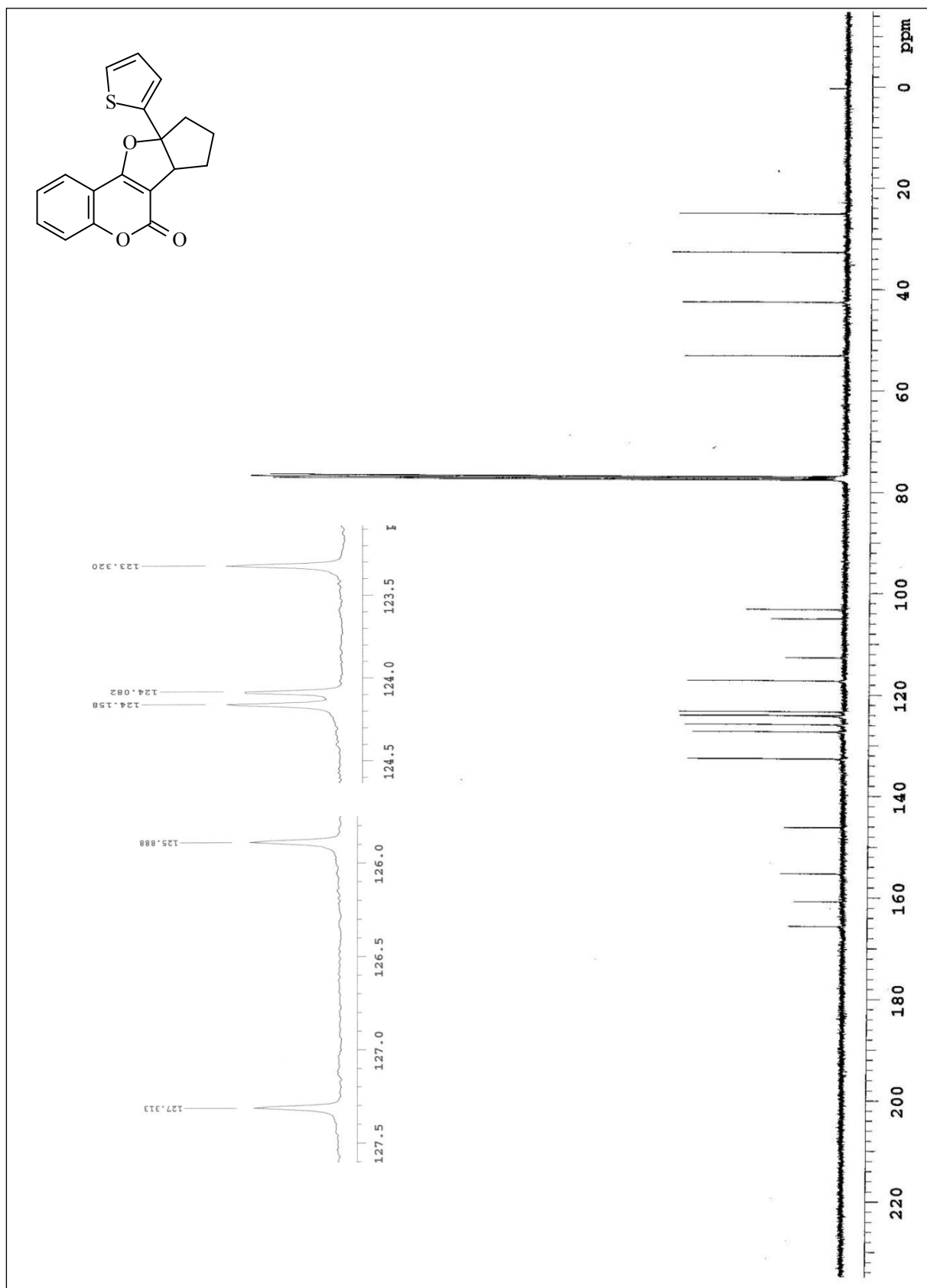
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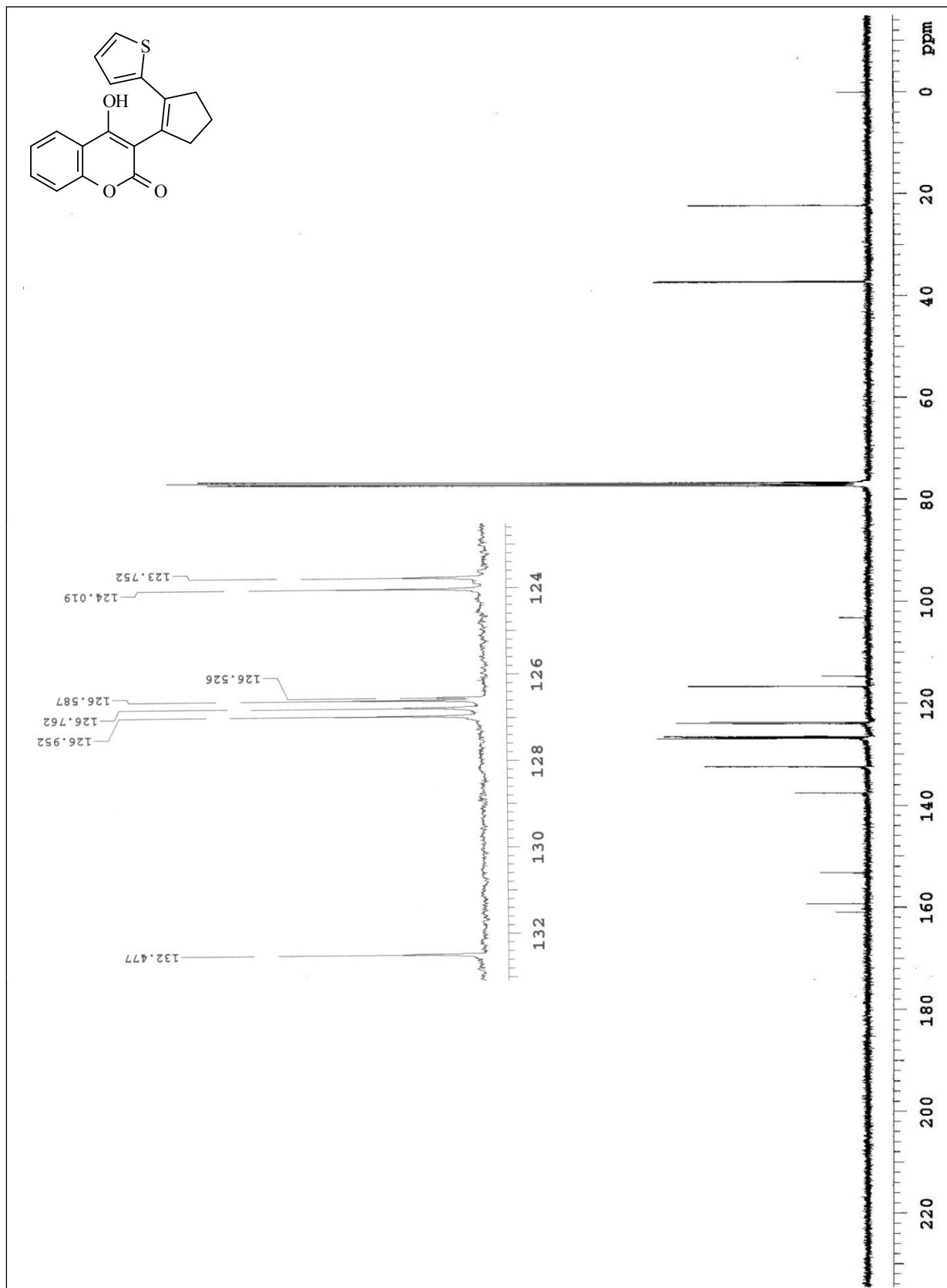
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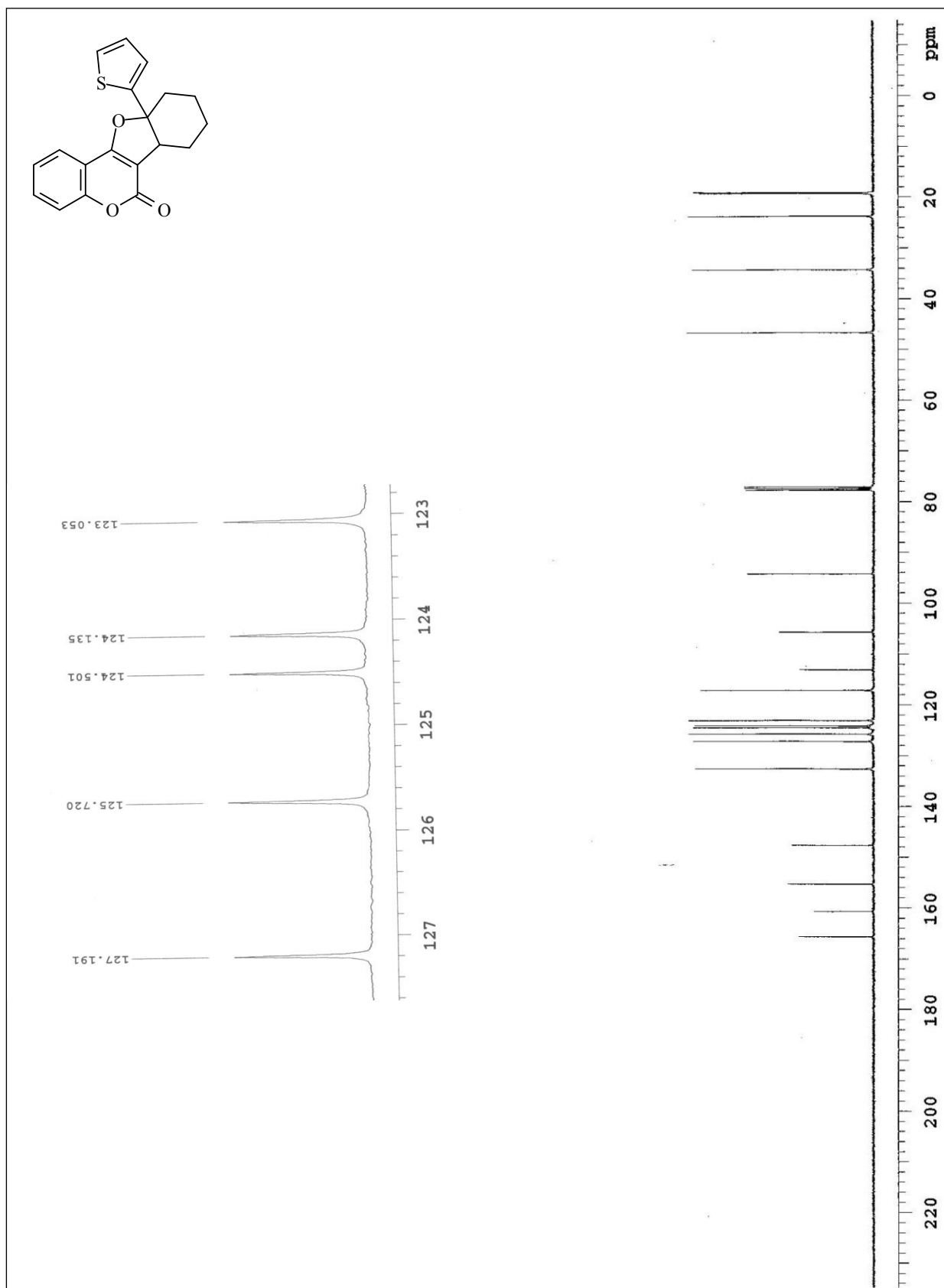
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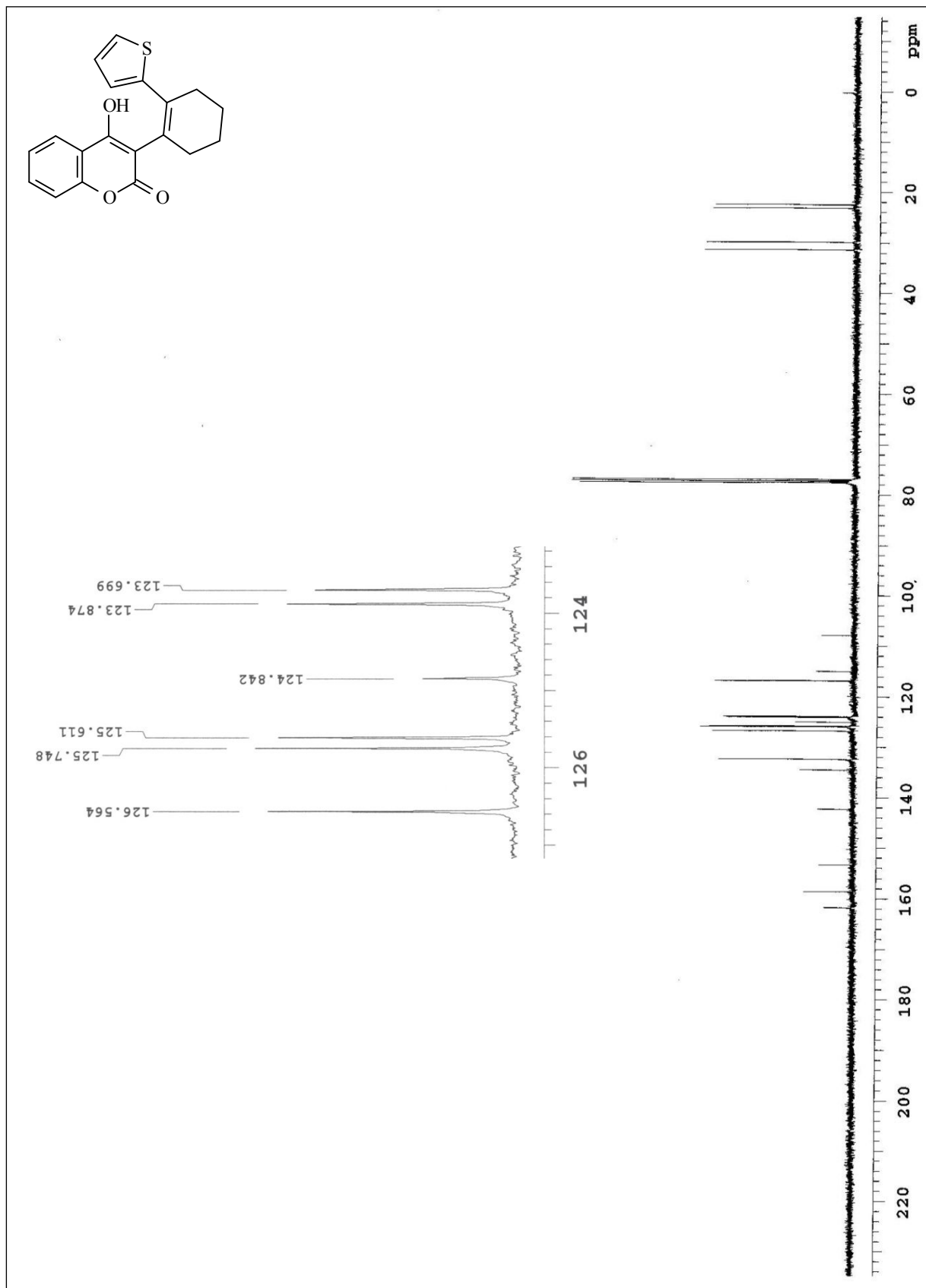
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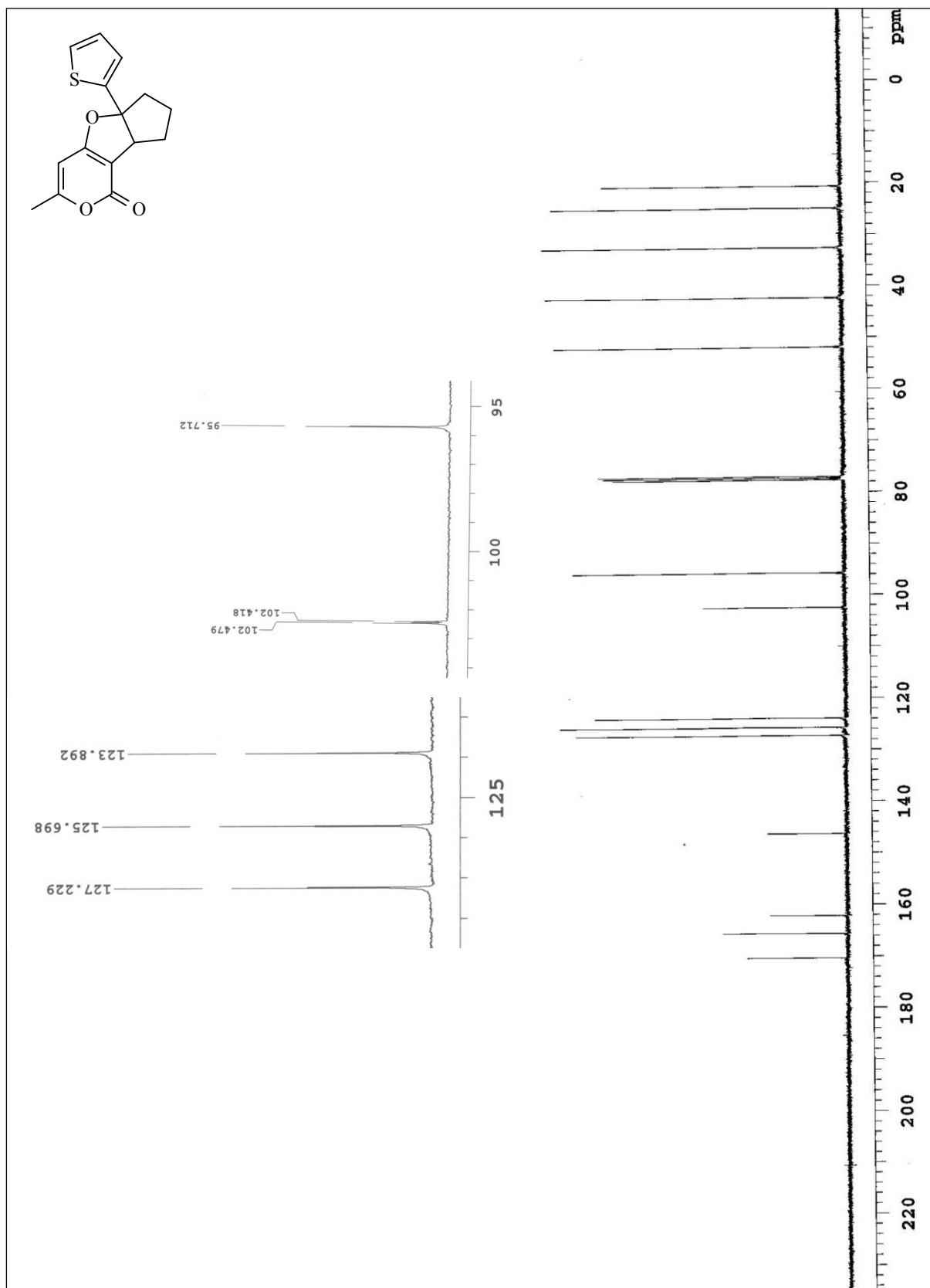
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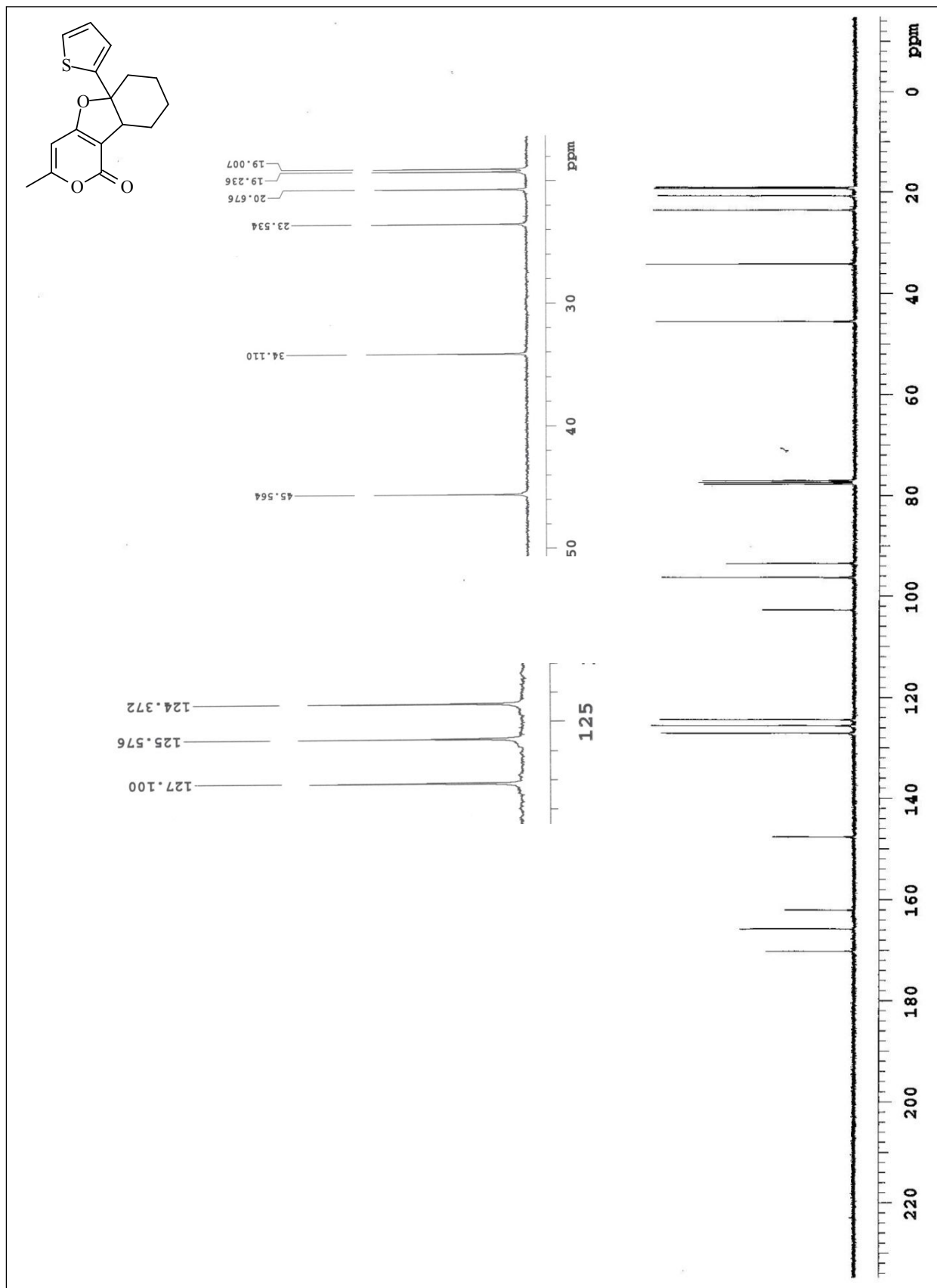
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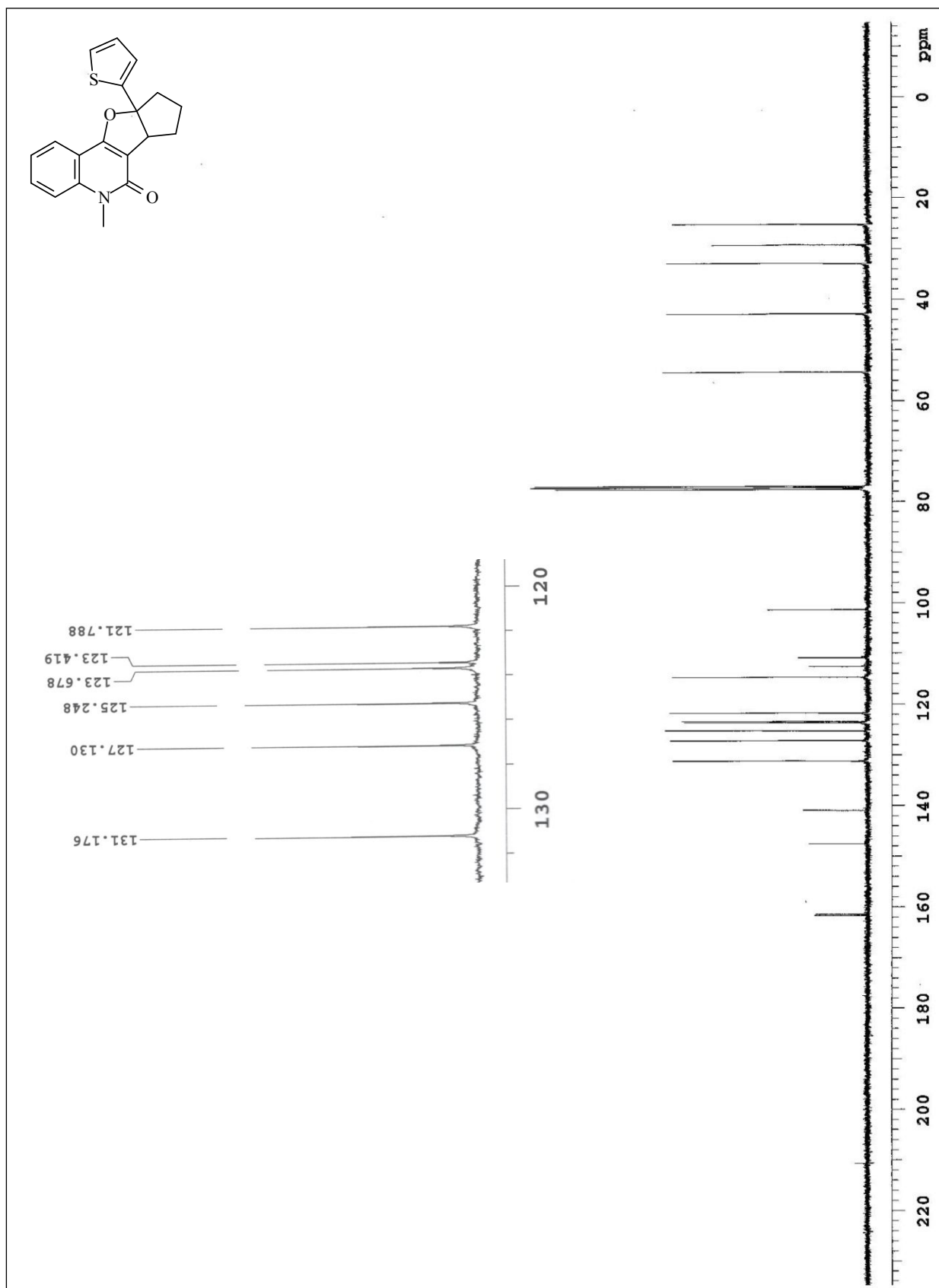
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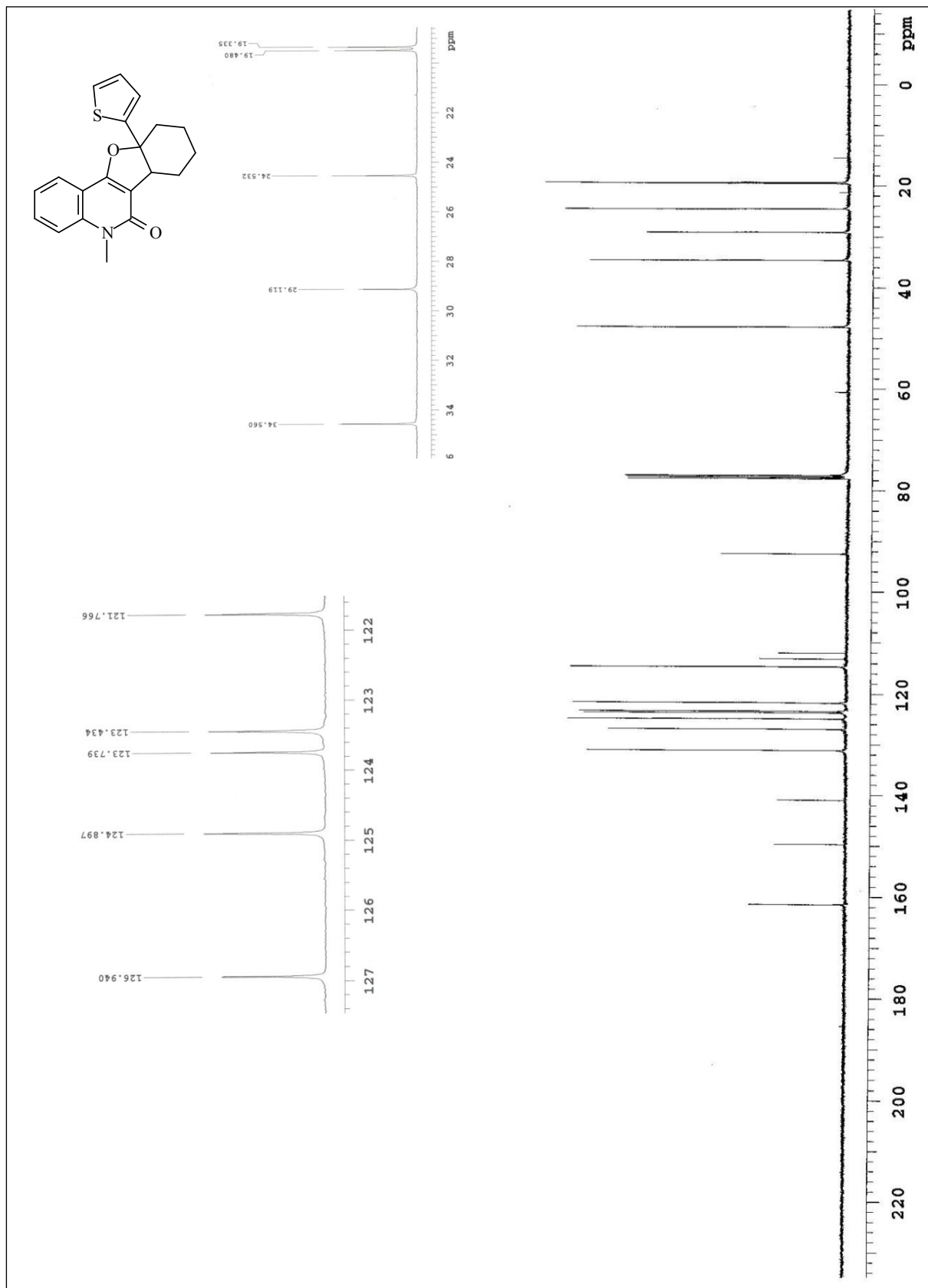
3.44 ^{13}C -NMR spectra of **44**

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

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

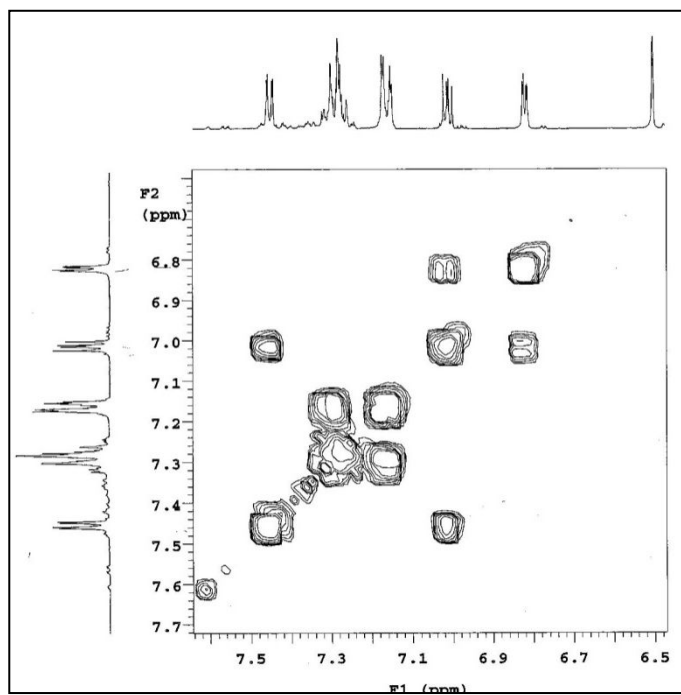
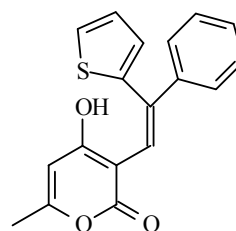
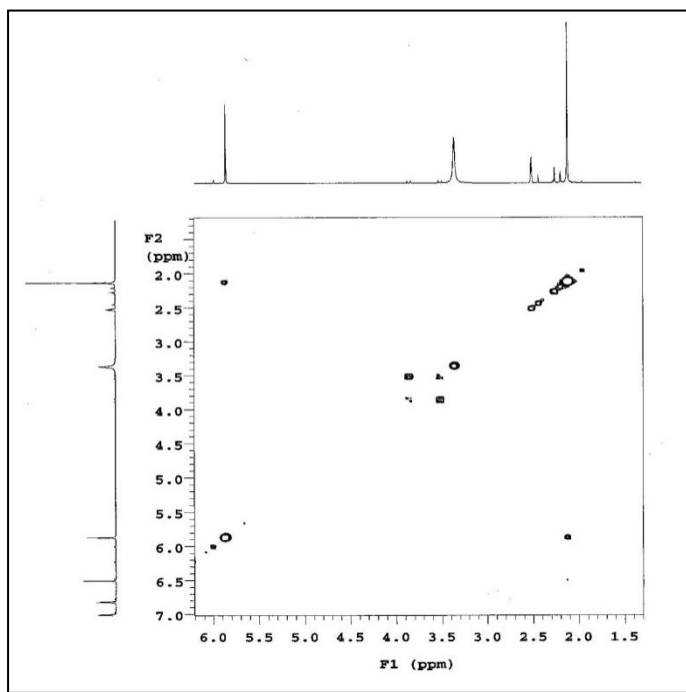
3.47 ^{13}C -NMR spectra of **46**

3.48 ^{13}C -NMR spectra of 47

3.49 ^{13}C -NMR spectra of **48**

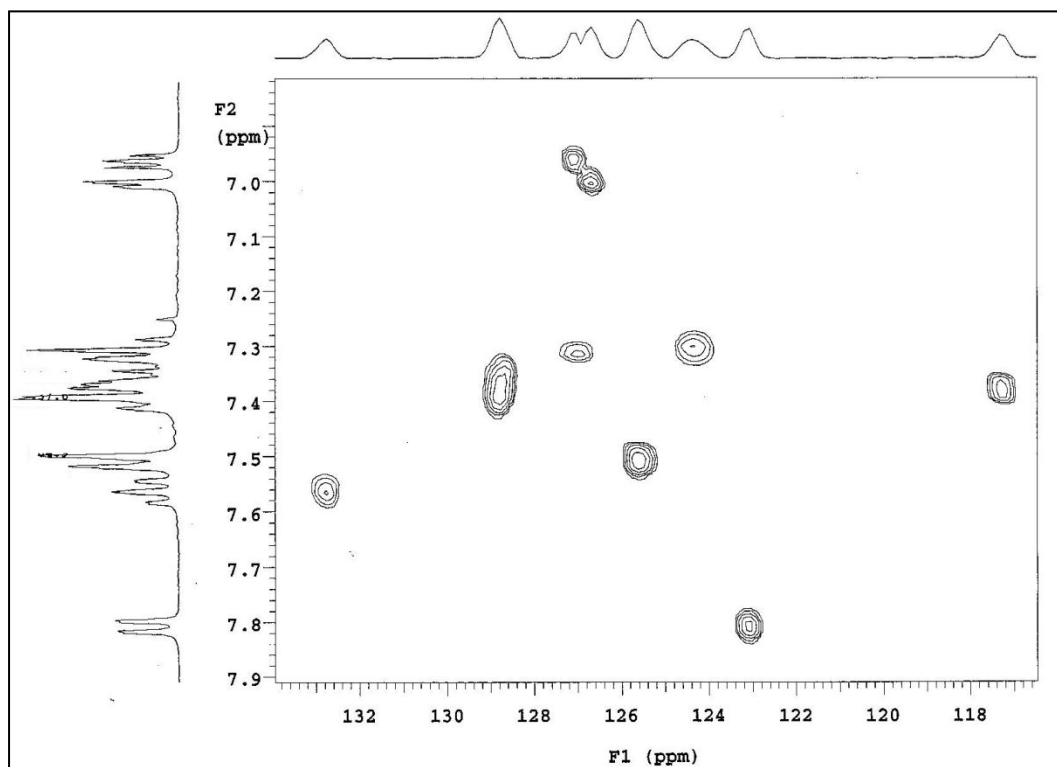
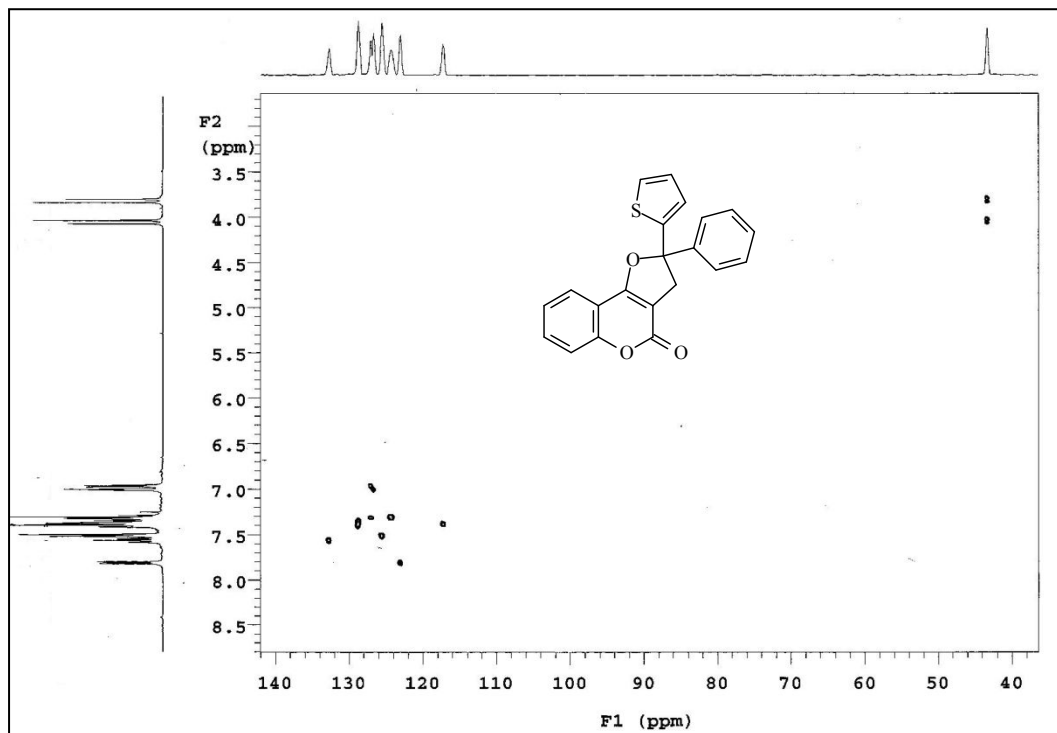
4. COSY Spectra of Compound

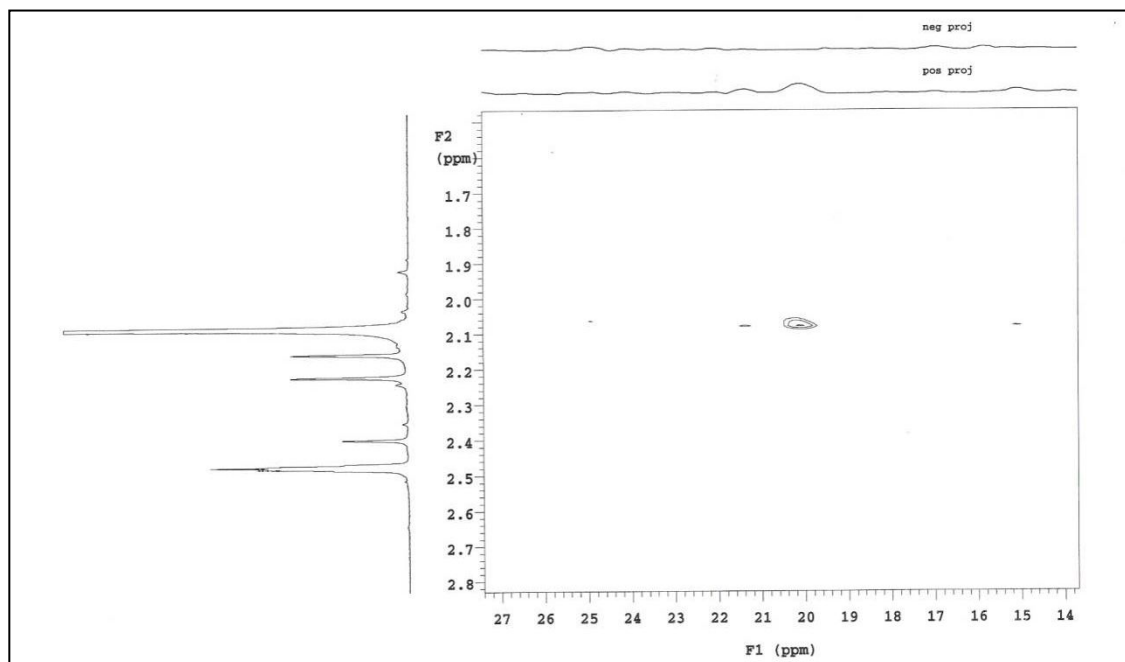
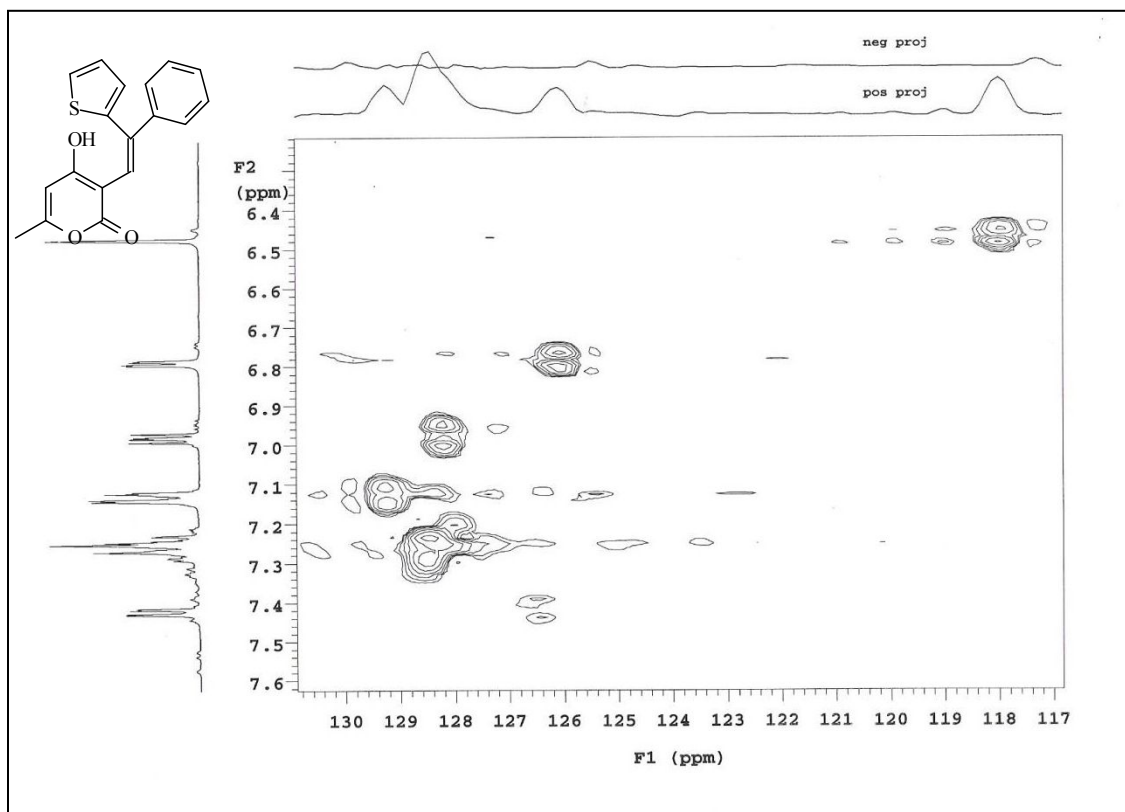
4.1 COSY spectra of 16

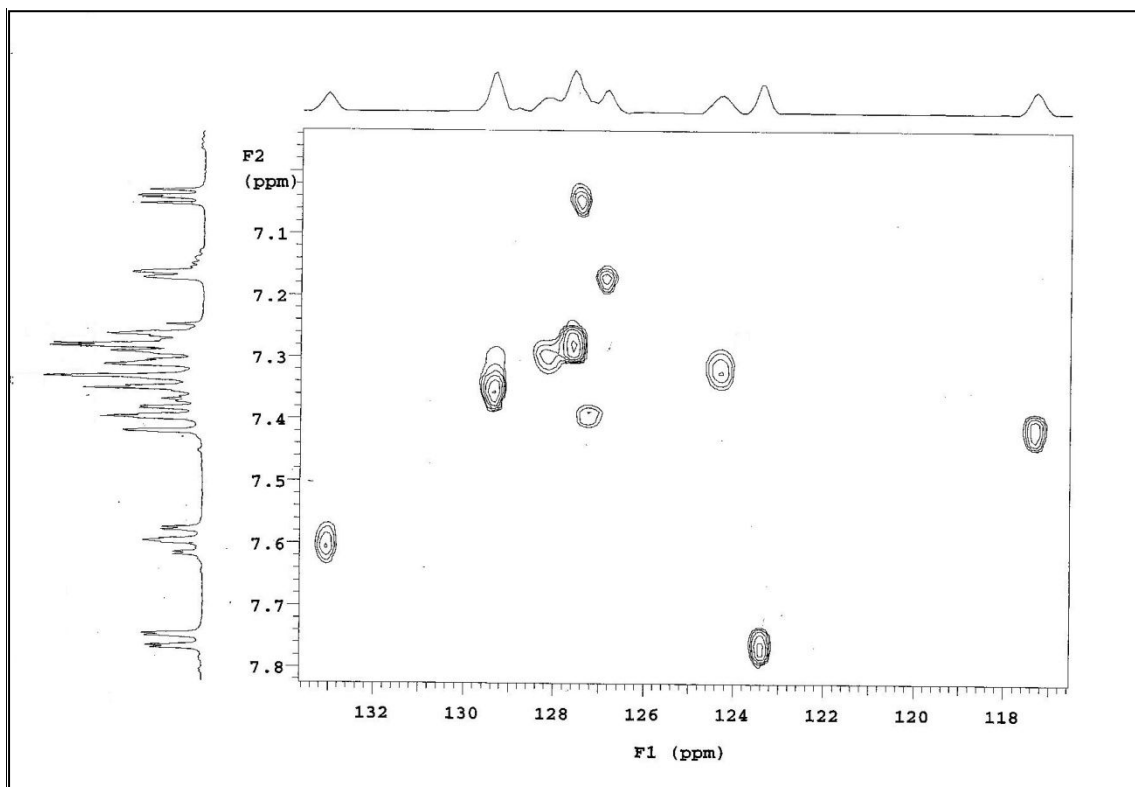
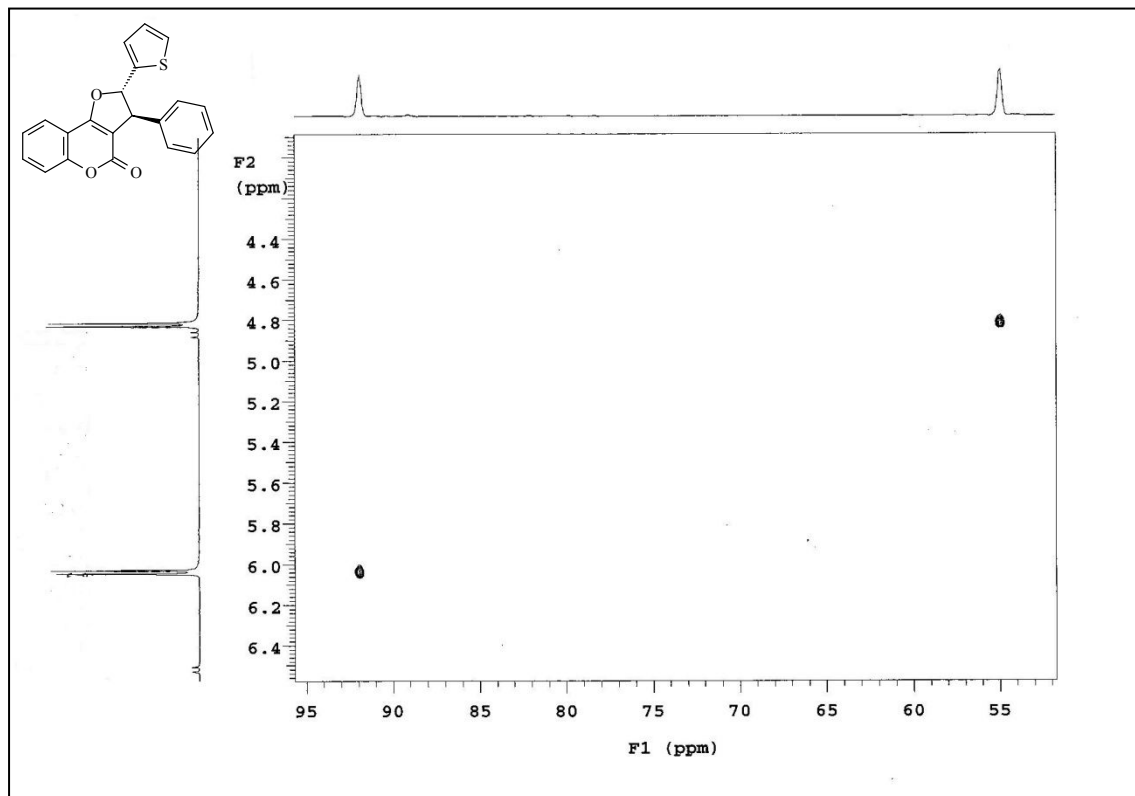


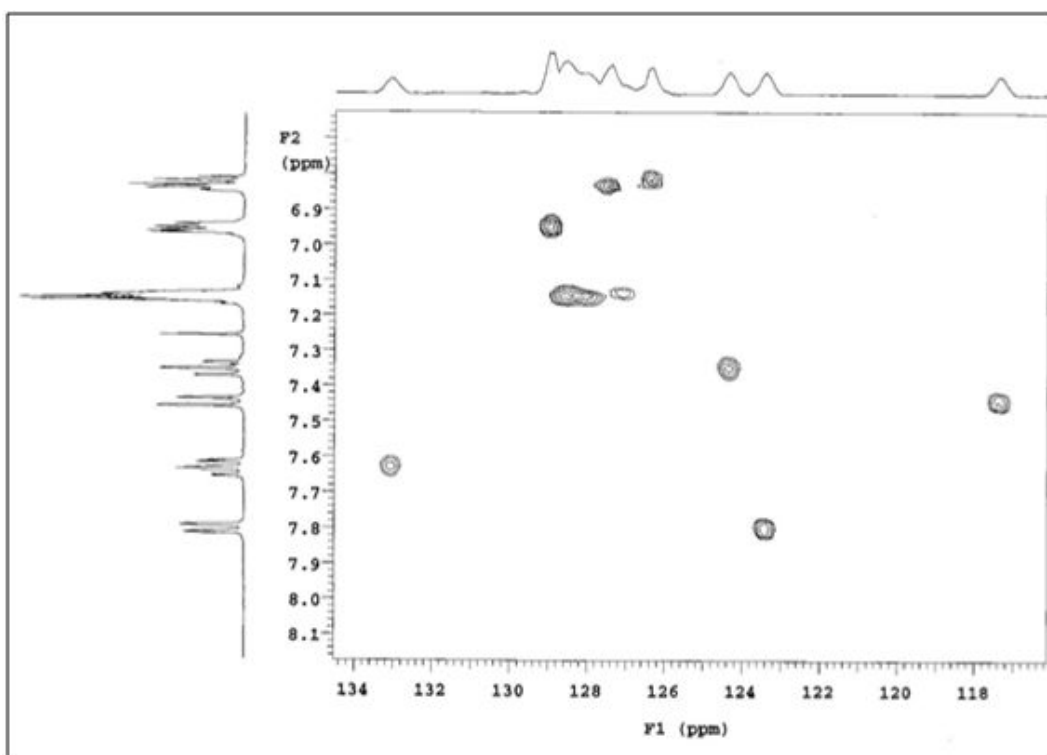
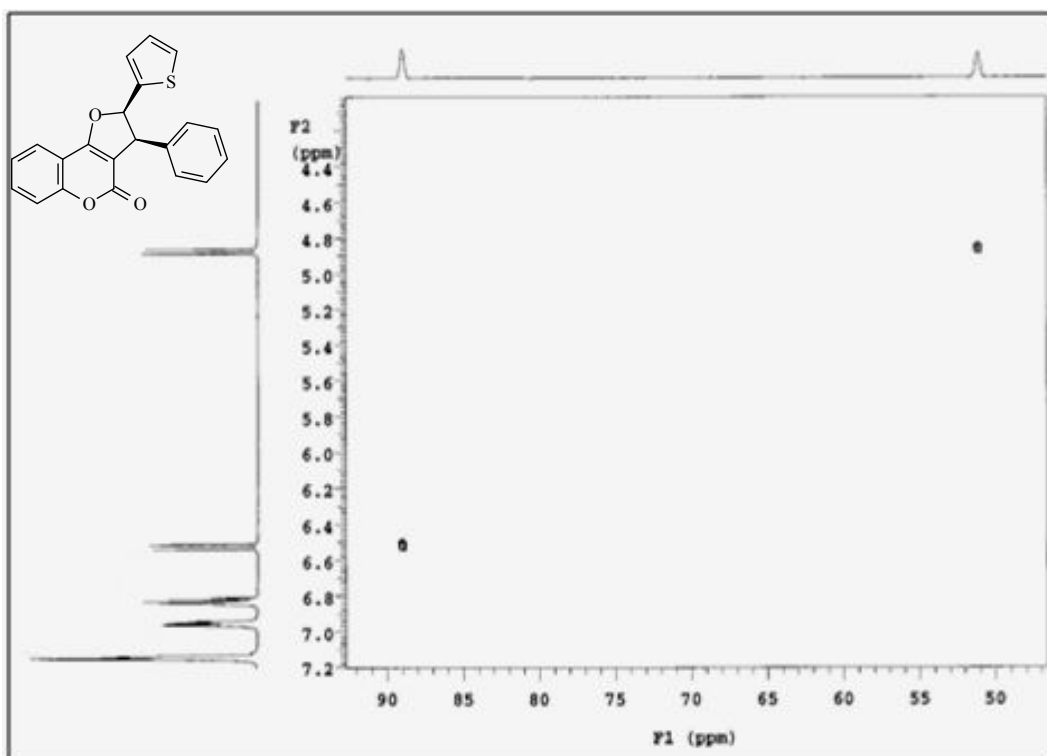
5. HSQC Spectra of Compounds

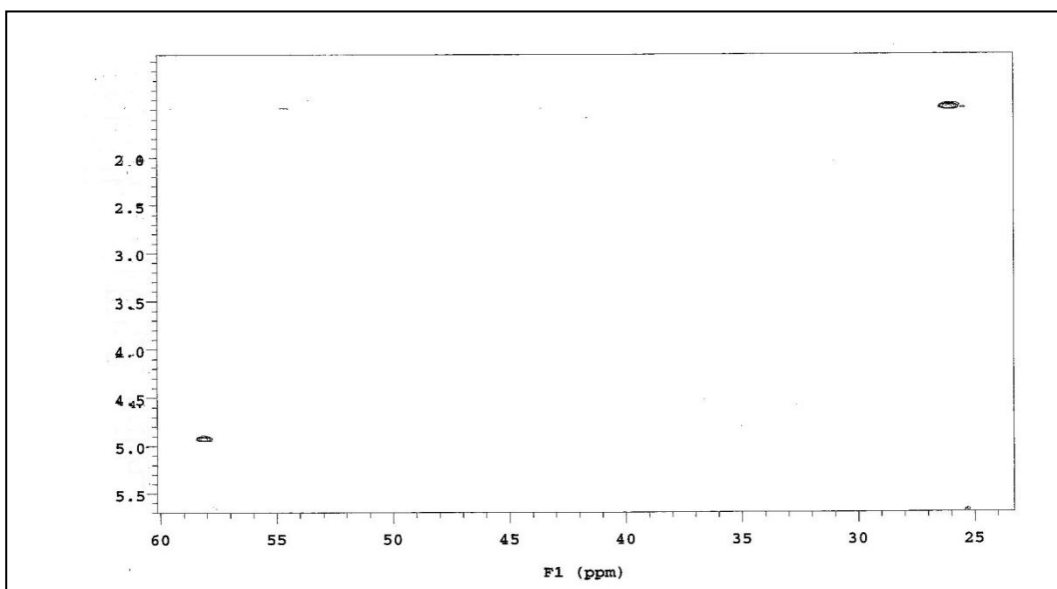
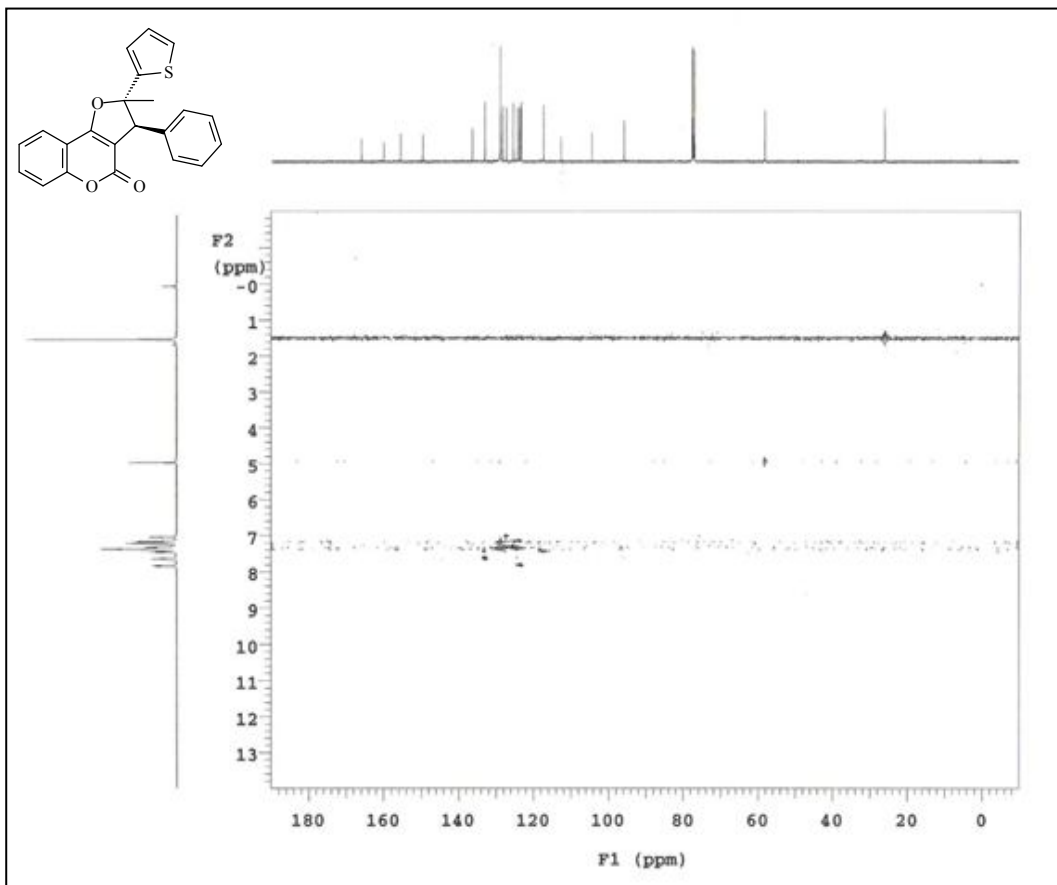
5.1 HSQC spectra of 3

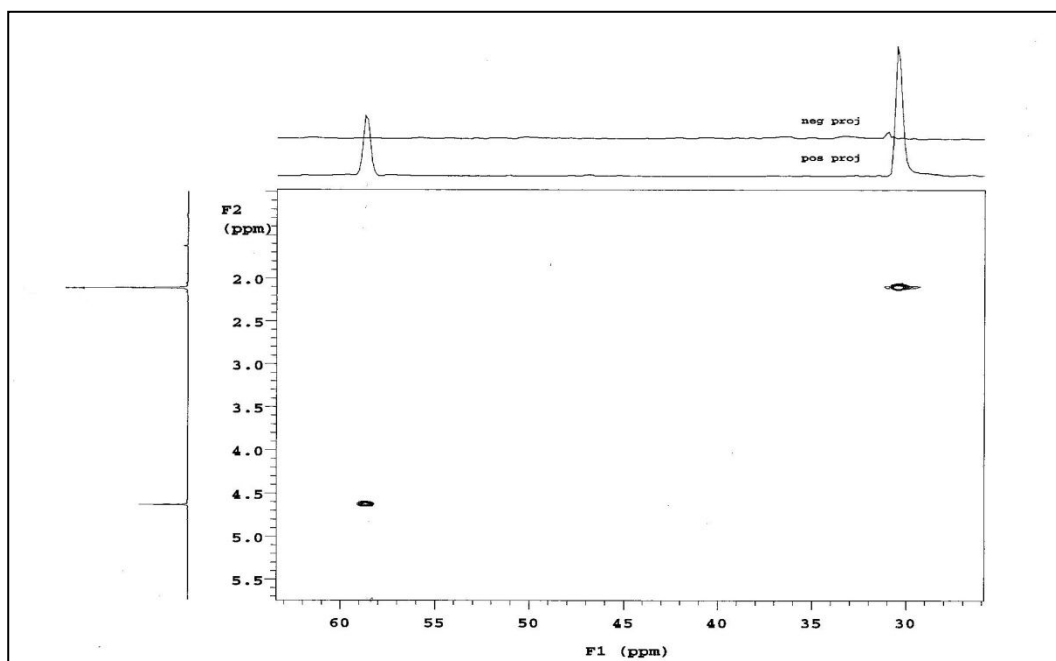
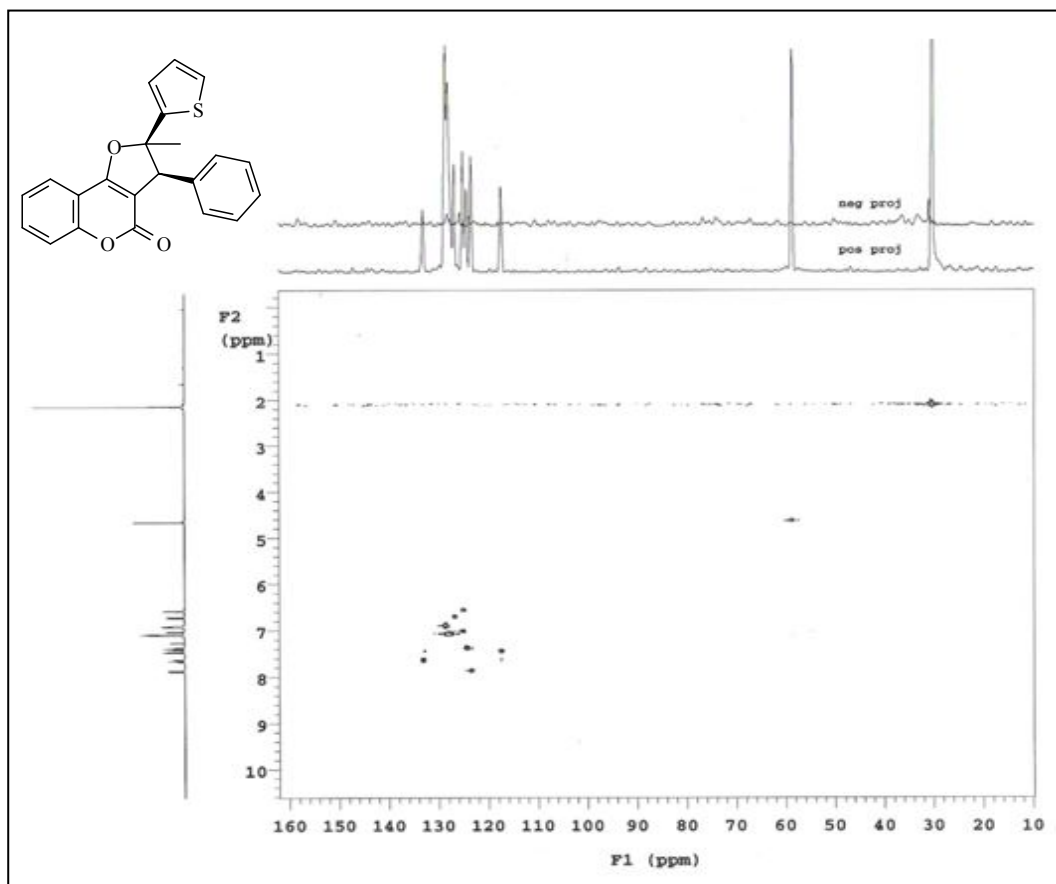


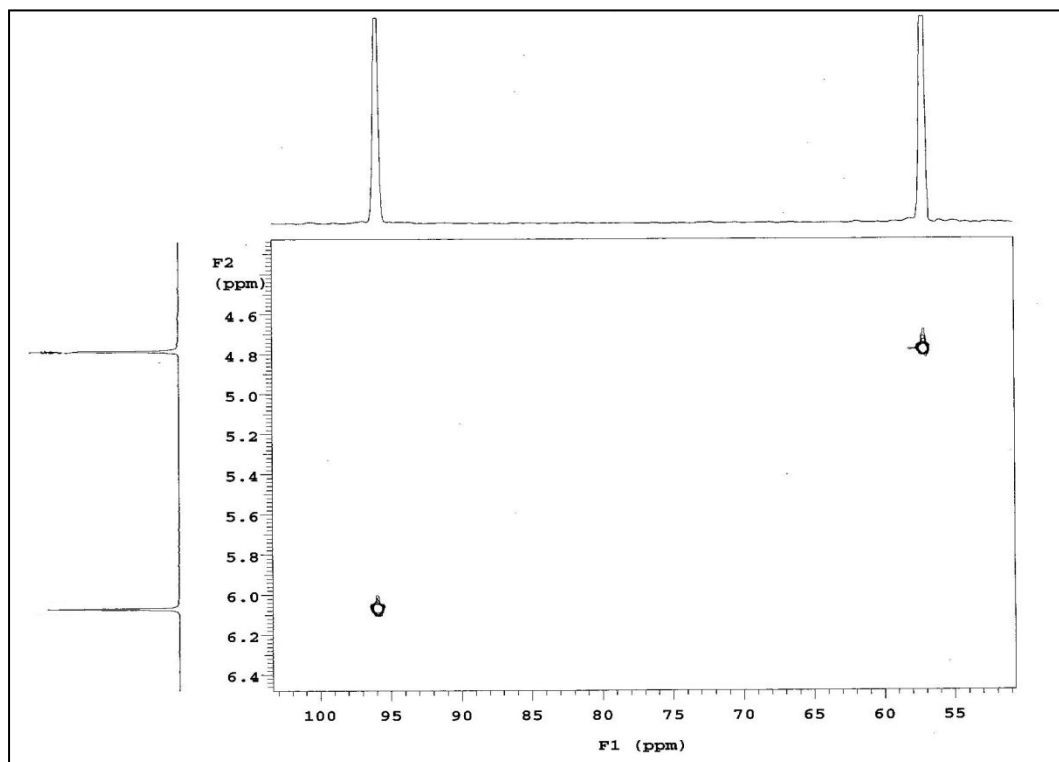
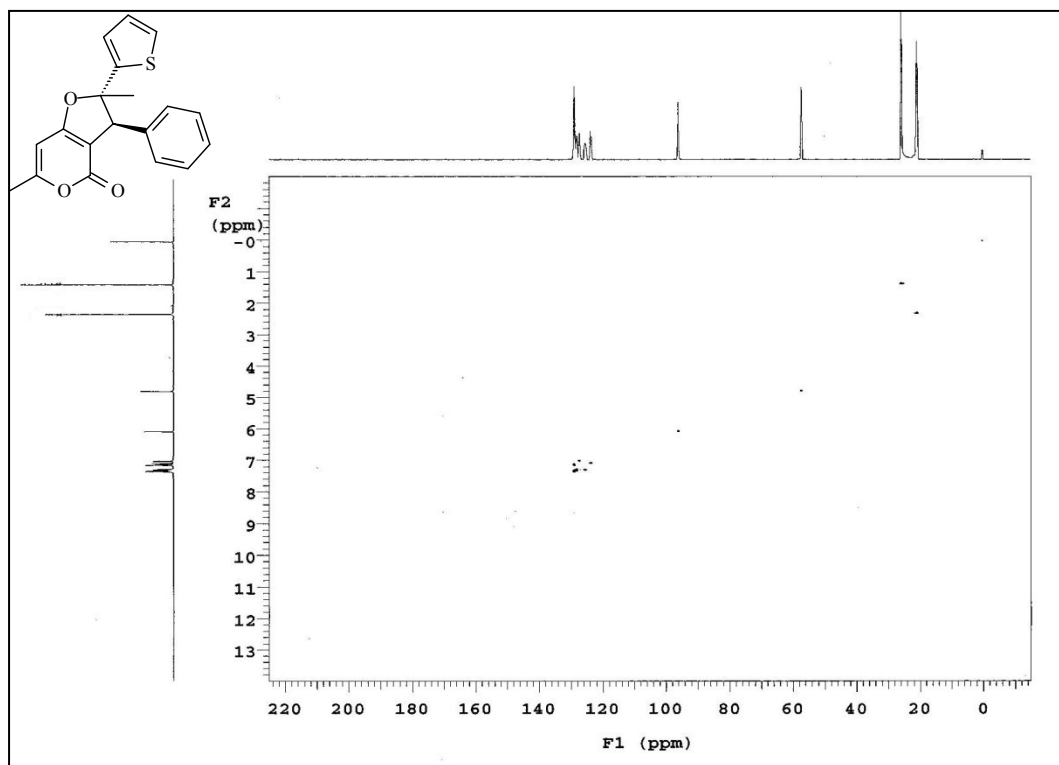
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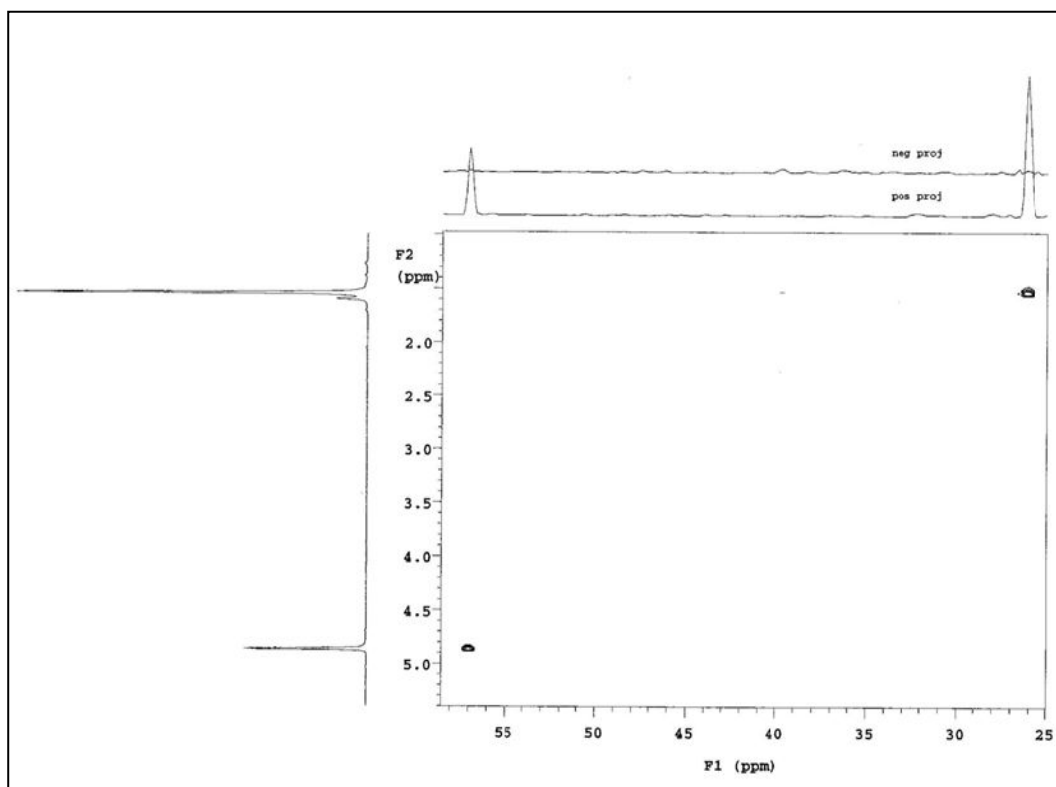
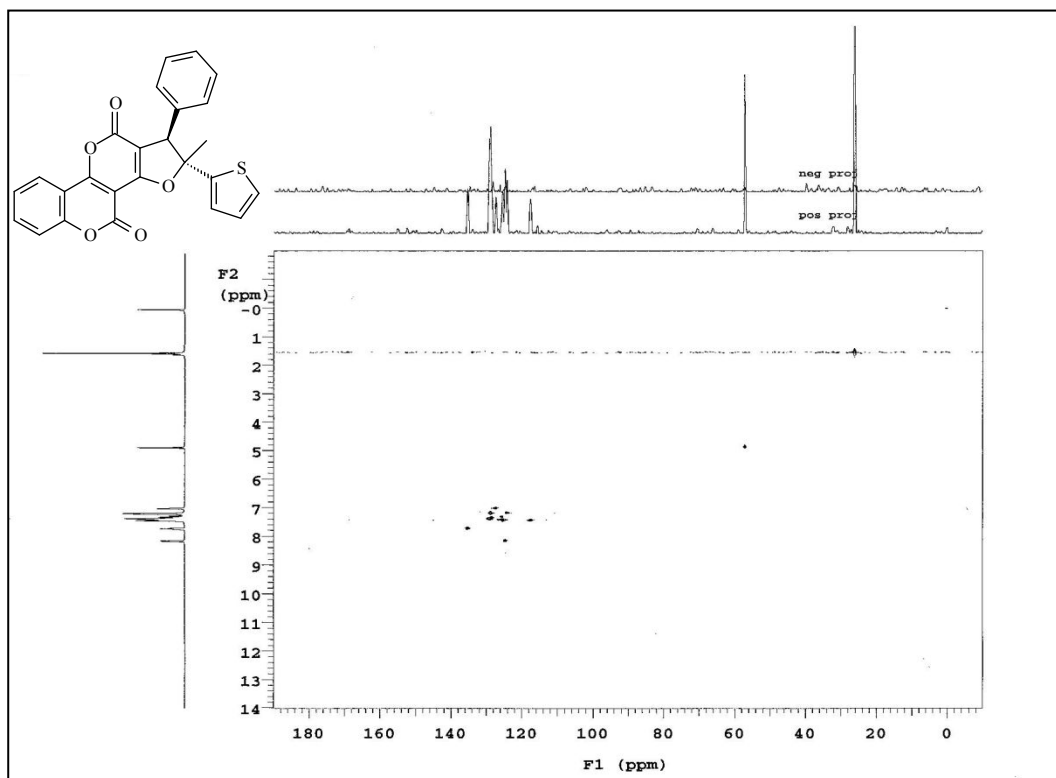
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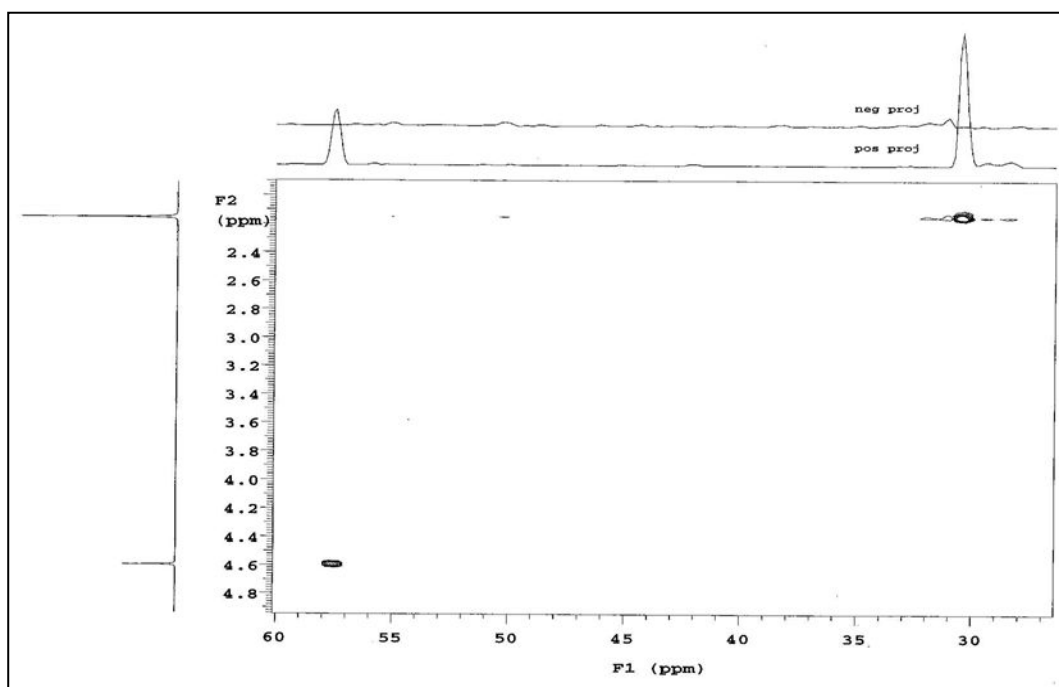
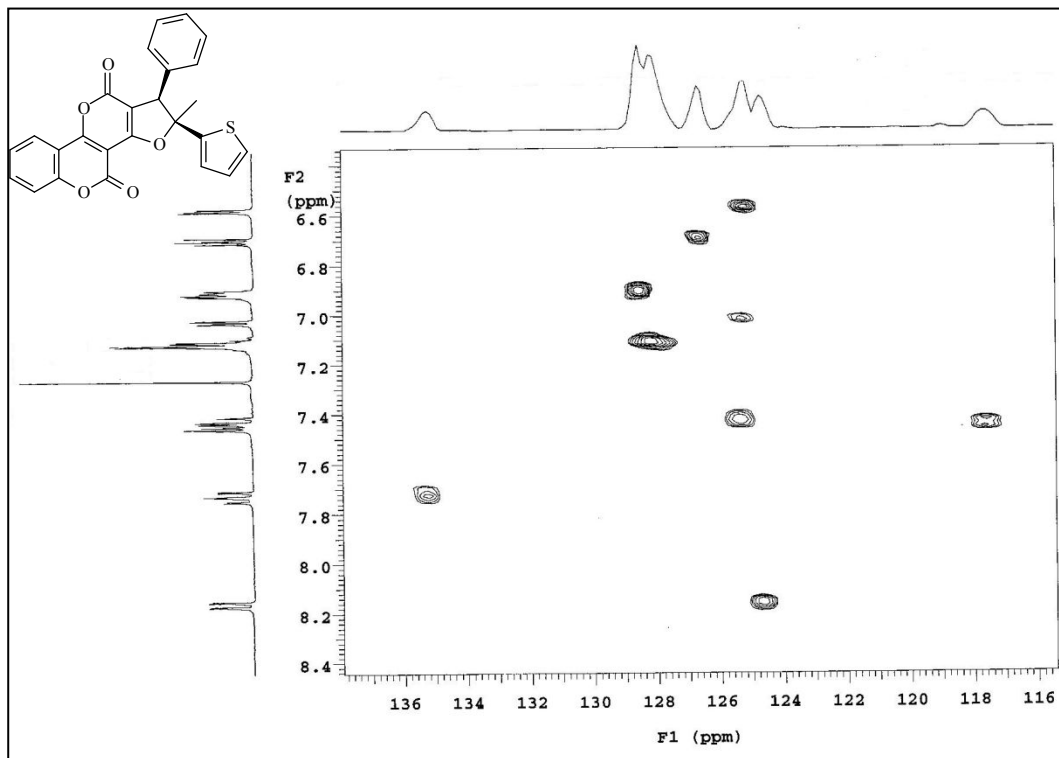
5.4 HSQC spectra of **36**

5.5 HSQC spectra of **37**

5.6 HSQC spectra of **38**

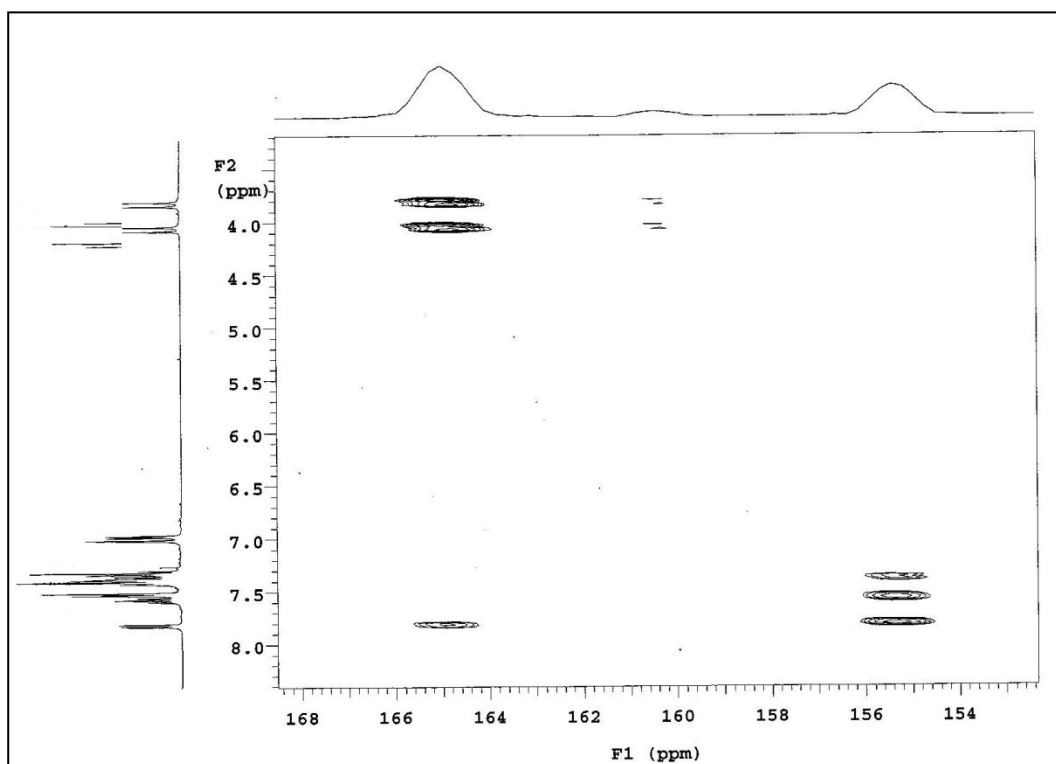
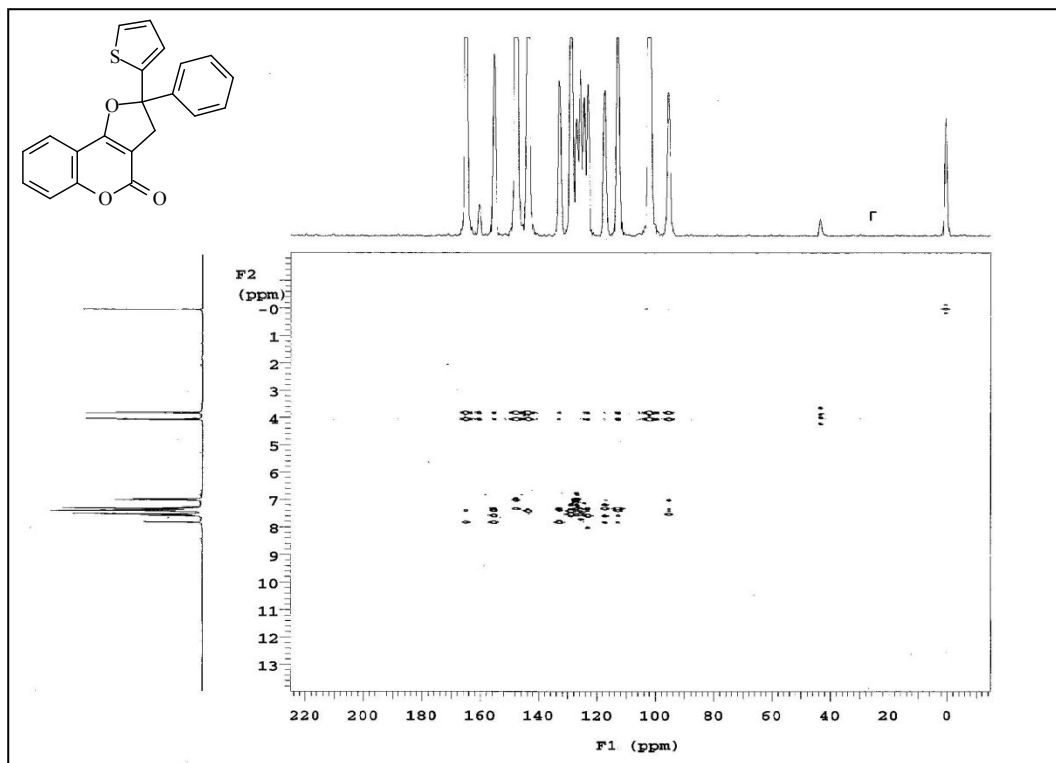
5.7 HSQC spectra of **39**

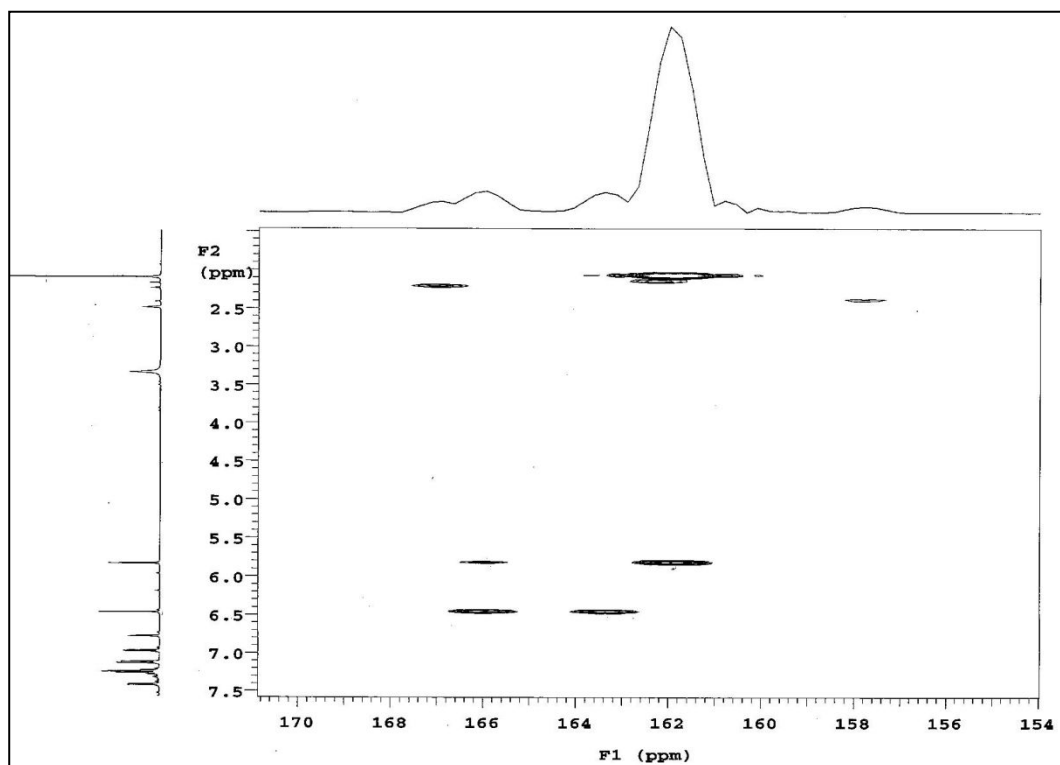
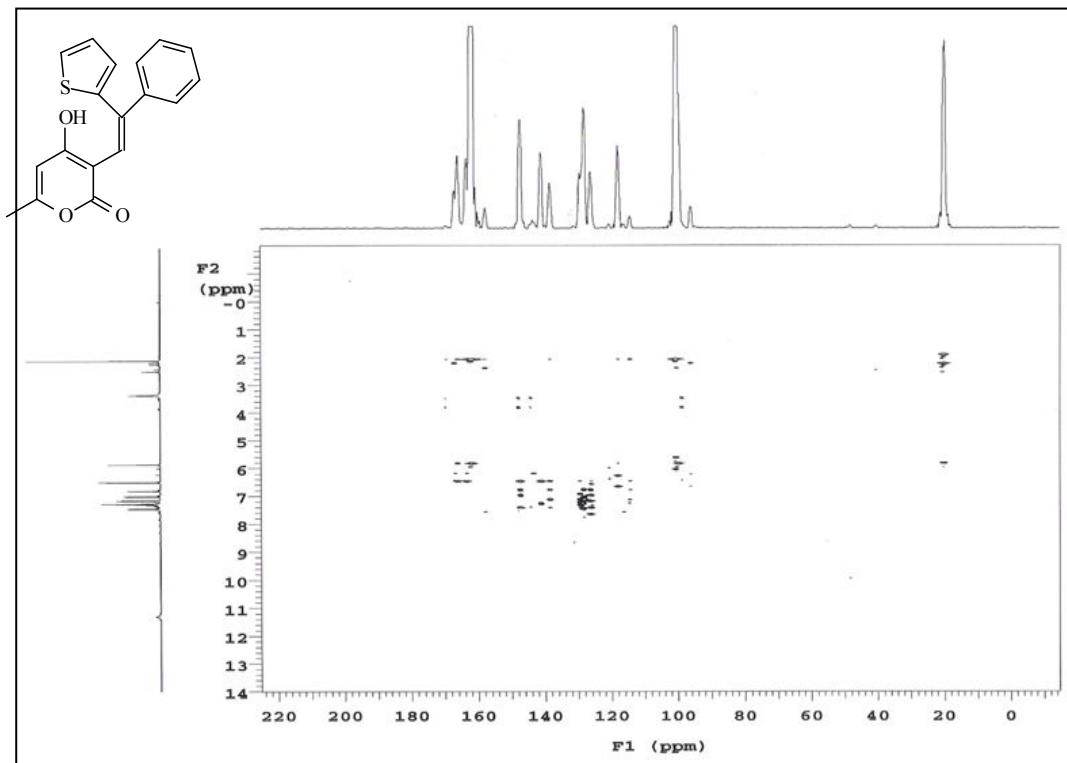
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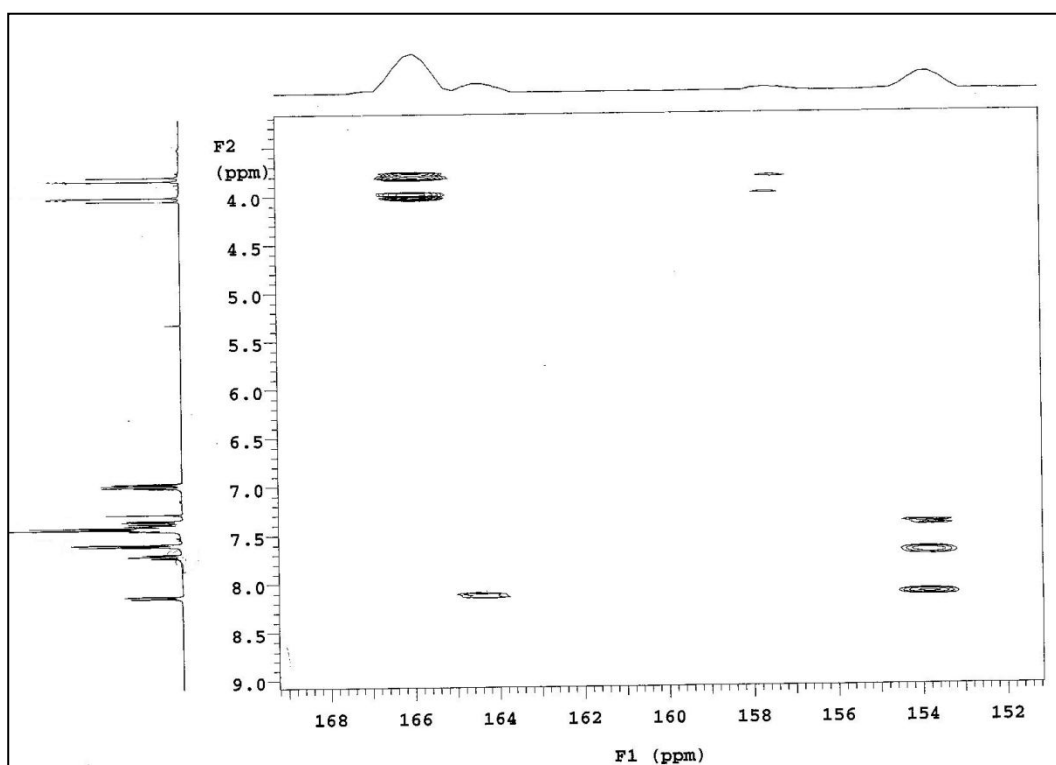
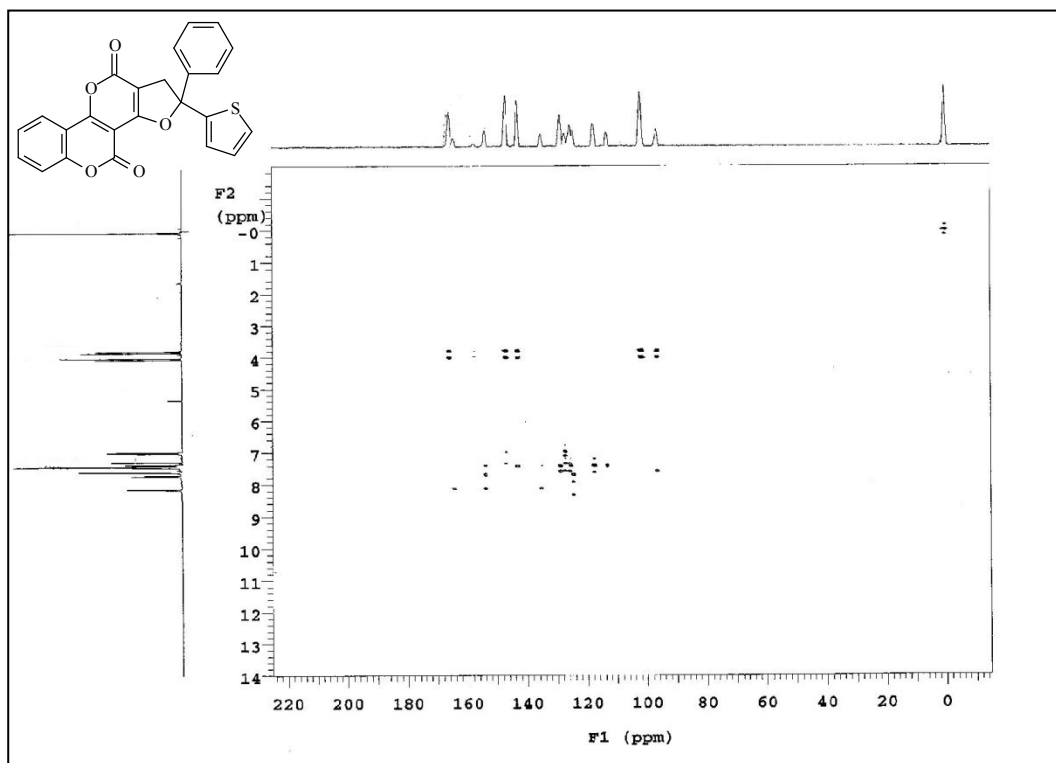
5.9 HSQC spectra of **42**

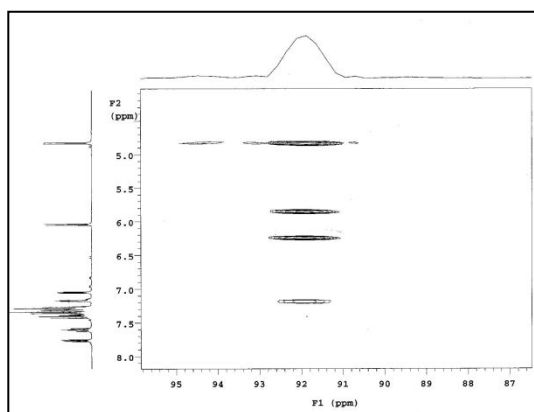
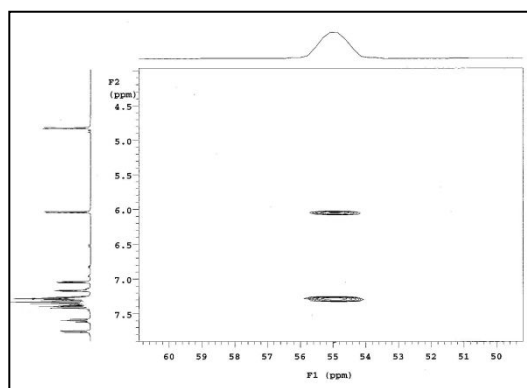
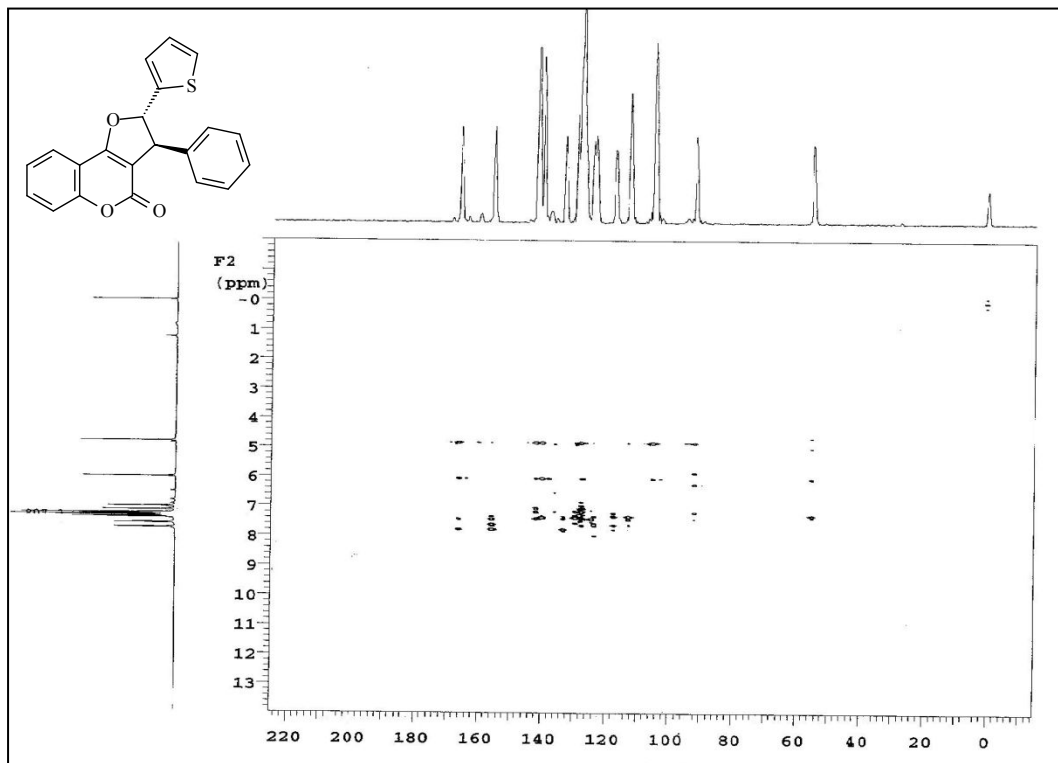
6. HMBC Spectra of COMPOUNDS

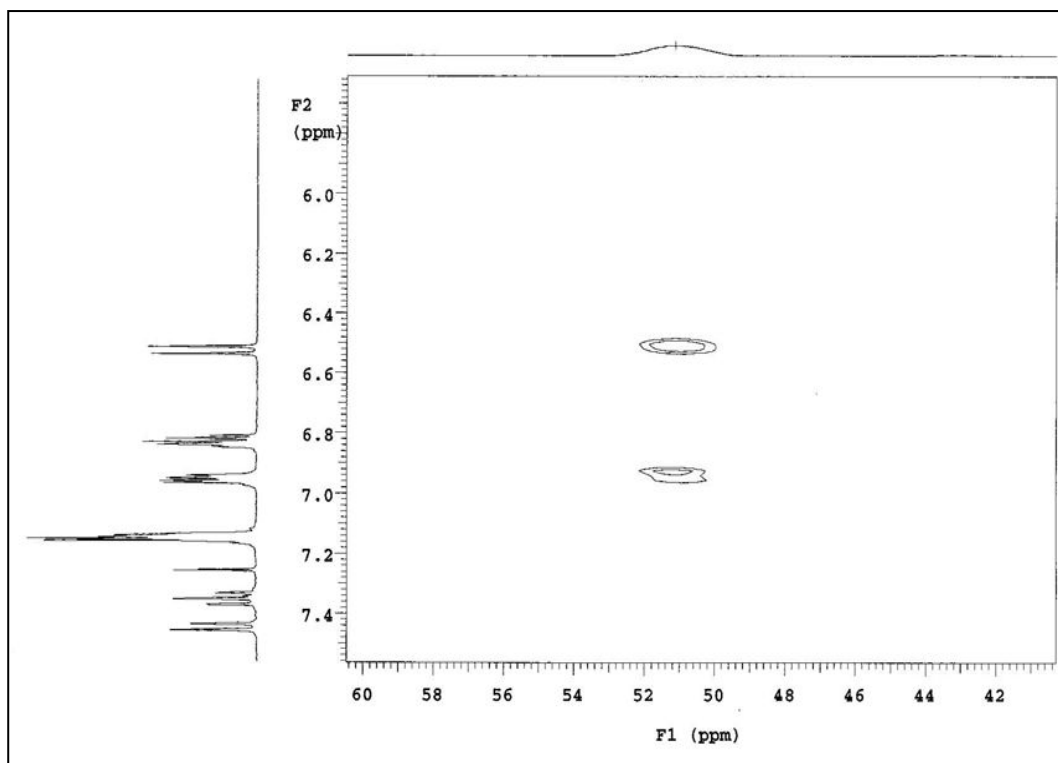
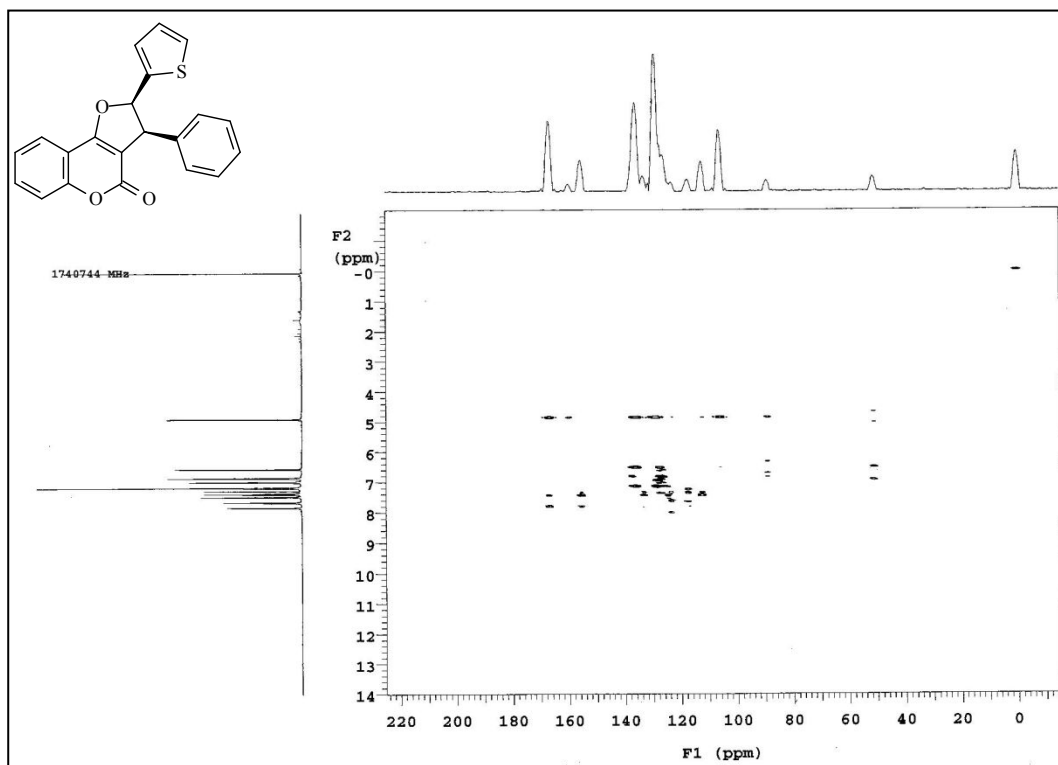
6.1 HMBA spectra of 3

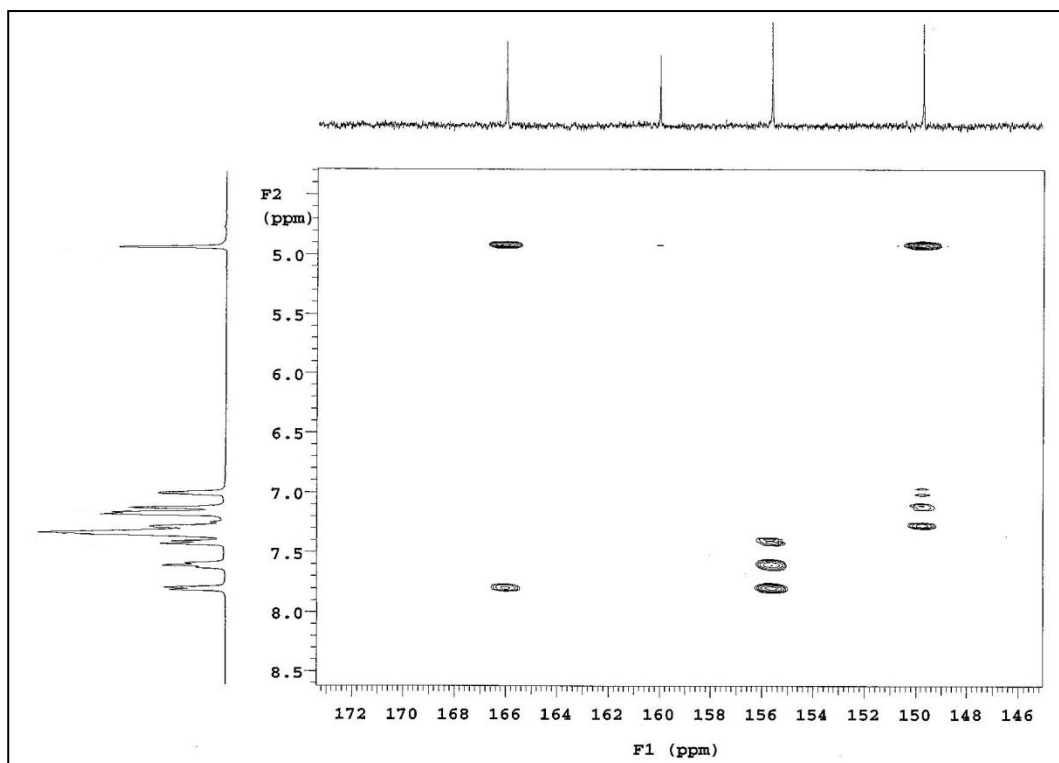
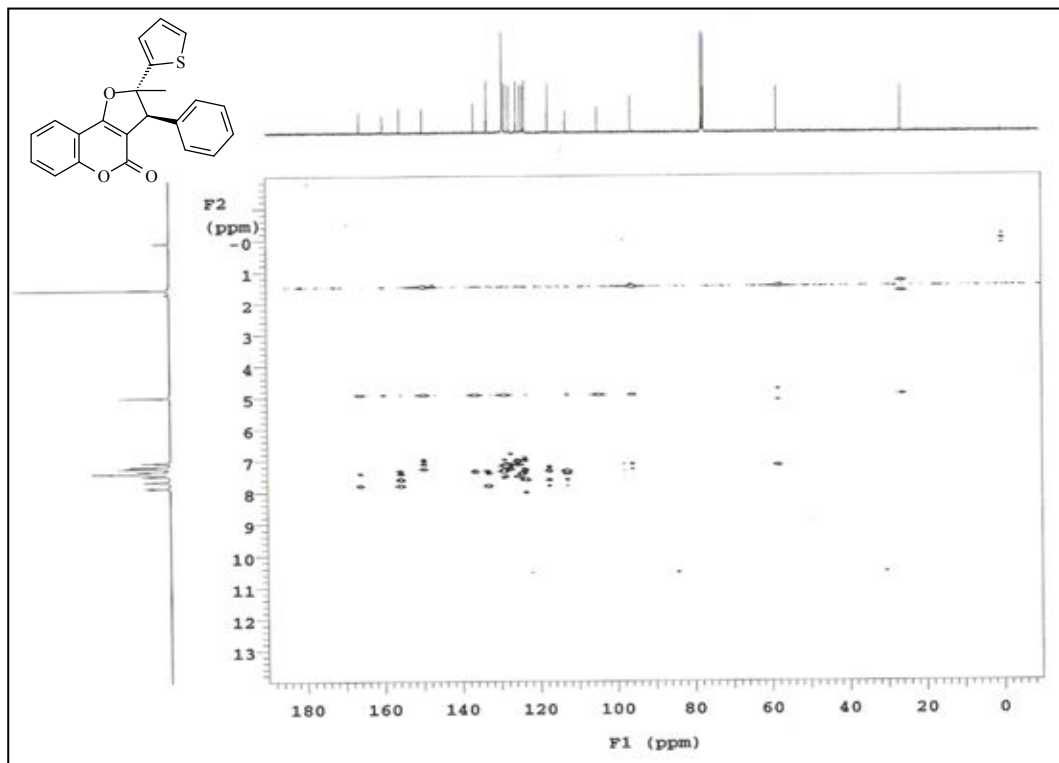


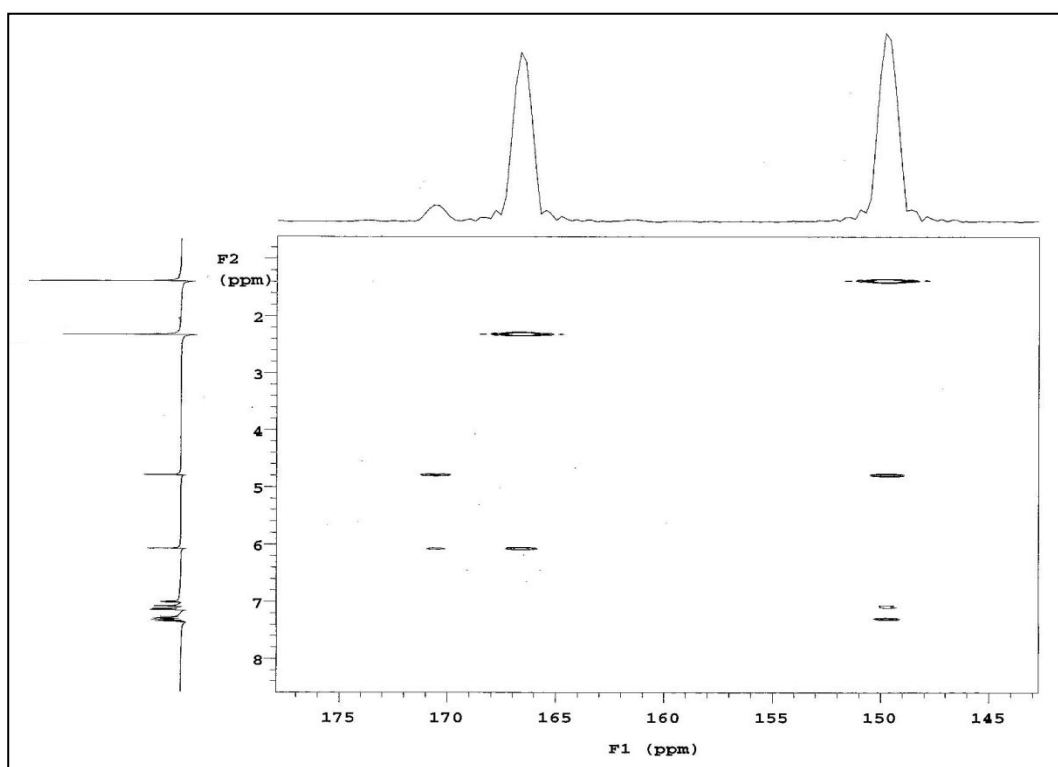
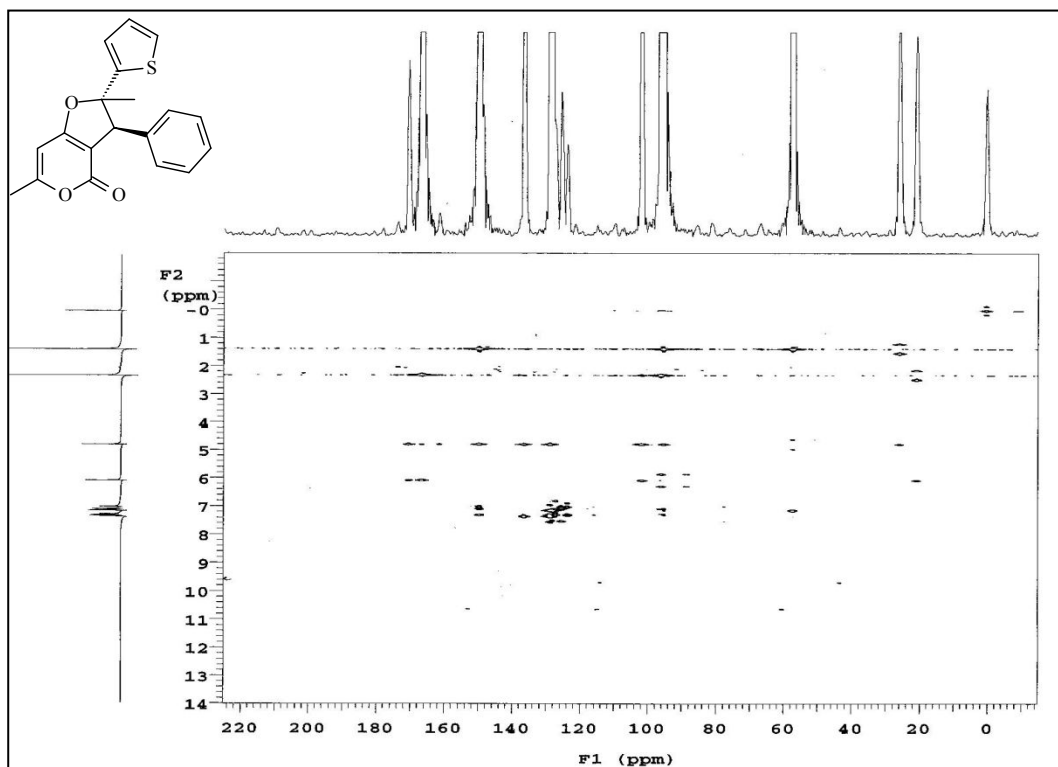
6.2 HMBC spectra of **16**

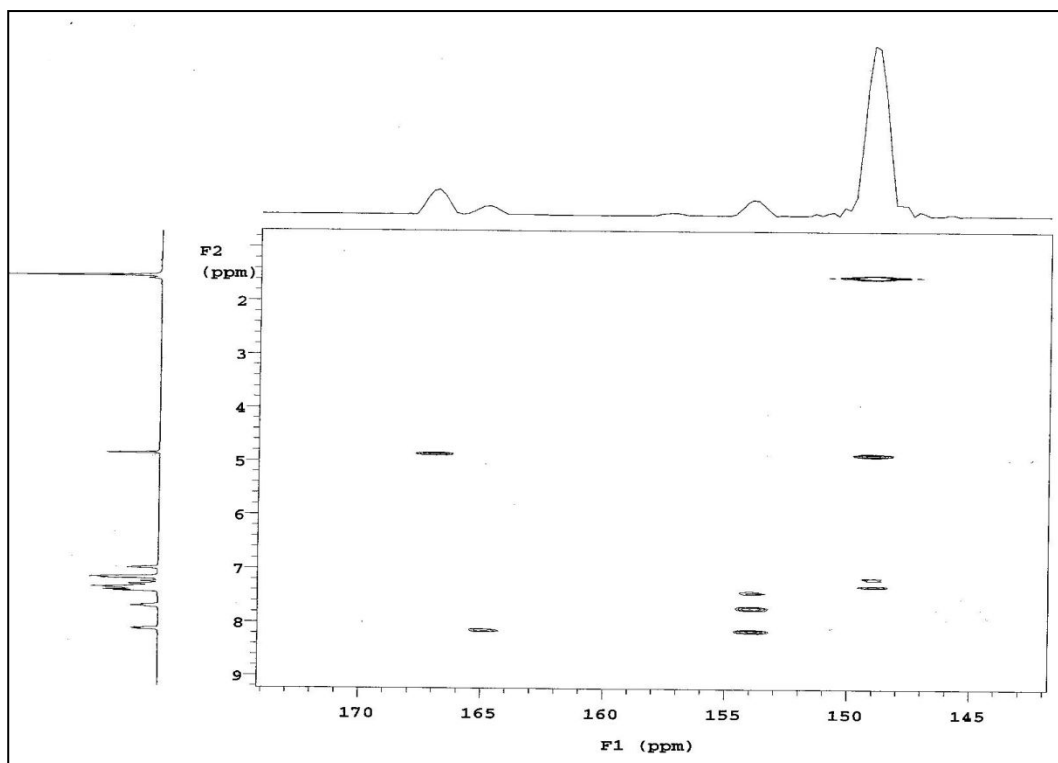
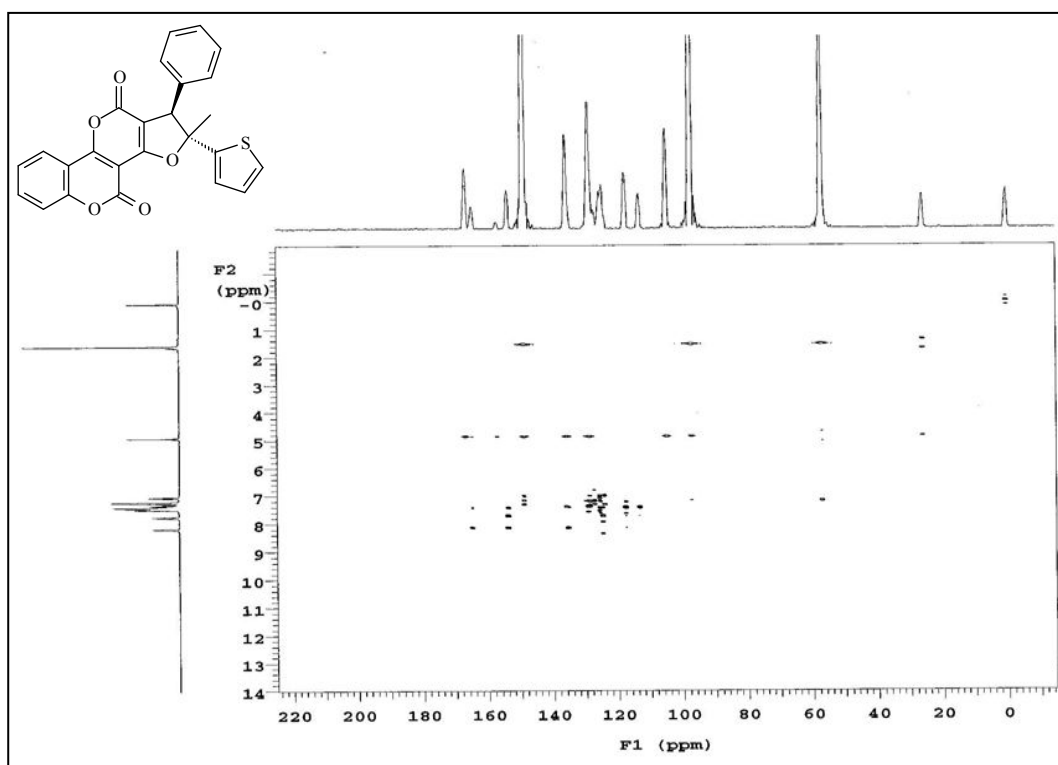
6.3 HMBC spectra of **19**

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**

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16 0.03149 0.00908 0.01900 0.00771
17 AFIX 43
18 H15 2 0.086131 -0.199515 0.570428 11.00000 -1.20000
19 AFIX 0
20 C5 1 0.351309 -0.005892 -0.215800 11.00000 0.01938 0.03341 =
21 0.01912 0.00334 0.00684 0.00219
22 AFIX 43
23 H5 2 0.370391 -0.007222 -0.289384 11.00000 -1.20000
24 AFIX 0
25 C20 1 0.364240 0.170890 0.553913 11.00000 0.02733 0.01971 =
26 0.01822 -0.00195 0.00745 -0.00389
27 AFIX 43
28 H20 2 0.367094 0.191214 0.630094 11.00000 -1.20000
29 HKLF 4
30
31
```

```
32 REM md501_0m in P 21/c
```

```
33 REM R1 = 0.0322 for 3772 Fo > 4sig(Fo) and 0.0381 for all 4292 data
```

```
34 REM 239 parameters refined using 0 restraints
```

```
35
36 END
```

```
37
38 WGHT 0.0369 0.8327
```

```
39 REM Highest difference peak 0.354, deepest hole -0.265, 1-sigma level 0.045
```

```
40 Q1 1 0.2374 0.0651 0.3278 11.00000 0.05 0.35
```

```
41 Q2 1 0.2898 -0.1171 0.1570 11.00000 0.05 0.35
```

```
42 Q3 1 0.2807 -0.0014 0.0575 11.00000 0.05 0.35
```

```
43 Q4 1 0.3327 0.1150 0.3624 11.00000 0.05 0.35
```

```
44 Q5 1 0.2625 -0.0755 0.2339 11.00000 0.05 0.33
```

```
45 Q6 1 0.3250 -0.0818 -0.1042 11.00000 0.05 0.33
```

```
46 Q7 1 0.2002 -0.0943 0.3168 11.00000 0.05 0.33
```

```
47 Q8 1 0.3108 0.1409 0.5222 11.00000 0.05 0.33
```

```
48 Q9 1 0.2454 -0.0515 0.1366 11.00000 0.05 0.32
```

```
49 Q10 1 0.2902 -0.0397 0.1633 11.00000 0.05 0.32
```

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50
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1
2
3 Q11 1 0.2172 -0.0147 0.2910 11.00000 0.05 0.31
4 Q12 1 0.2991 -0.0386 -0.0220 11.00000 0.05 0.30
5 Q13 1 0.2777 0.0356 -0.0346 11.00000 0.05 0.30
6 Q14 1 0.1162 0.0368 0.2690 11.00000 0.05 0.29
7 Q15 1 0.1642 -0.1329 0.3920 11.00000 0.05 0.29
8 Q16 1 0.0909 -0.1455 0.2966 11.00000 0.05 0.29
9 Q17 1 0.4052 0.1912 0.5155 11.00000 0.05 0.28
10 Q18 1 0.1191 -0.1665 0.4635 11.00000 0.05 0.27
11 Q19 1 0.4470 0.1725 0.4376 11.00000 0.05 0.27
12 Q20 1 0.0072 -0.1932 0.2649 11.00000 0.05 0.26
13

14 ;

15
16
17 _audit_creation_method SHELXL-97
18 _chemical_name_systematic
19 ;
20 ?
21 ;
22 ;
23 _chemical_name_common ?
24 _chemical_melting_point ?
25 _chemical_formula_moiety 'C22 H16 O3 S'
26 _chemical_formula_sum
27 'C22 H16 O3 S'
28 _chemical_formula_weight 360.41
29

30 loop_

31
32 _atom_type_symbol
33 _atom_type_description
34 _atom_type_scatter_dispersion_real
35 _atom_type_scatter_dispersion_imag
36 _atom_type_scatter_source
37 'C' 'C' 0.0033 0.0016
38 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
39 'H' 'H' 0.0000 0.0000
40 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
41 'O' 'O' 0.0106 0.0060
42 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
43 'S' 'S' 0.1246 0.1234
44 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
45
46

47
48 _symmetry_cell_setting monoclinic
49 _symmetry_space_group_name_H-M 'P 21/c'
50 _symmetry_space_group_name_Hall '-P 2ybc'
51

52
53 loop_

54
55 _symmetry_equiv_pos_as_xyz
56
57
58
59
60

1
2
3 'x, y, z'
4 '-x, y+1/2, -z+1/2'
5 '-x, -y, -z'
6 'x, -y-1/2, z-1/2'
7
8
9 _cell_length_a 9.9226(2)
10 _cell_length_b 15.7155(3)
11 _cell_length_c 11.5782(2)
12 _cell_angle_alpha 90.00
13 _cell_angle_beta 108.572(3)
14 _cell_angle_gamma 90.00
15 _cell_volume 1711.47(6)
16 _cell_formula_units_Z 4
17 _cell_measurement_temperature 296(2)
18 _cell_measurement_reflns_used 8525
19 _cell_measurement_theta_min 2.26
20 _cell_measurement_theta_max 28.39
21
22
23
24 _exptl_crystal_description block
25 _exptl_crystal_colour colourless
26 _exptl_crystal_size_max 0.32
27 _exptl_crystal_size_mid 0.25
28 _exptl_crystal_size_min 0.16
29 _exptl_crystal_density_meas ?
30 _exptl_crystal_density_diffn 1.399
31 _exptl_crystal_density_method 'not measured'
32 _exptl_crystal_F_000 752
33 _exptl_absorpt_coefficient_mu 0.209
34 _exptl_absorpt_correction_type multi-scan
35 _exptl_absorpt_correction_T_min 0.9263
36 _exptl_absorpt_correction_T_max 0.9774
37 _exptl_absorpt_process_details 'SADABS; Bruker, 2012'
38
39
40
41 _exptl_special_details
42 ;
43 ?
44 ;
45 ;
46
47 _diffn_ambient_temperature 296(2)
48 _diffn_radiation_wavelength 0.71073
49 _diffn_radiation_type MoK\a
50 _diffn_radiation_source 'fine-focus sealed tube'
51 _diffn_radiation_monochromator graphite
52 _diffn_measurement_device_type 'Bruker APEX-II CCD'
53 _diffn_measurement_method '\f and \w scans'
54 _diffn_detector_area_resol_mean ?
55
56
57
58
59
60

```

1
2
3   _diffn_standards_number      ?
4   _diffn_standards_interval_count ?
5   _diffn_standards_interval_time ?
6   _diffn_standards_decay_%     ?
7
8   _diffn_reflns_number         16080
9   _diffn_reflns_av_R_equivalents 0.0193
10  _diffn_reflns_av_sigmal/netI  0.0188
11  _diffn_reflns_limit_h_min     -13
12  _diffn_reflns_limit_h_max     13
13  _diffn_reflns_limit_k_min     -16
14  _diffn_reflns_limit_k_max     21
15  _diffn_reflns_limit_l_min     -15
16  _diffn_reflns_limit_l_max     13
17  _diffn_reflns_theta_min       2.17
18  _diffn_reflns_theta_max       28.42
19
20  _reflns_number_total          4292
21  _reflns_number_gt            3772
22  _reflns_threshold_expression  I>2\s(I)
23
24
25  _computing_data_collection    'APEX2 (Bruker, 2007)'
26  _computing_cell_refinement    'SAINT (Bruker, 2007)'
27  _computing_data_reduction     'SAINT'
28  _computing_structure_solution  'SHELXS97 (Sheldrick, 2008)'
29  _computing_structure_refinement 'SHELXL97 (Sheldrick, 2008)'
30  _computing_molecular_graphics 'Ortep-3 for Windows (Farrugia, 1997)'
31  _computing_publication_material
32  'WinGX publication routines (Farrugia, 1999) and PLATON (Spek, 2003)'
33
34
35  _refine_special_details
36  ;
37  ;
38  Refinement of F2 against ALL reflections. The weighted R-factor wR and
39  goodness of fit S are based on F2, conventional R-factors R are based
40  on F, with F set to zero for negative F2. The threshold expression of
41  F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
42  not relevant to the choice of reflections for refinement. R-factors based
43  on F2 are statistically about twice as large as those based on F, and R-
44  factors based on ALL data will be even larger.
45  ;
46  ;
47
48  _refine_ls_structure_factor_coef Fsqd
49  _refine_ls_matrix_type        full
50  _refine_ls_weighting_scheme    calc
51  _refine_ls_weighting_details
52  'calc w=1/[s2(Fo2)+(0.0369P)2+0.8327P] where P=(Fo2+2Fc2)/3'
53
54  _atom_sites_solution_primary   direct
55  _atom_sites_solution_secondary difmap
56
57
58
59
60

```

```
1
2
3  _atom_sites_solution_hydrogens geom
4  _refine_ls_hydrogen_treatment mixed
5  _refine_ls_extinction_method none
6  _refine_ls_extinction_coef ?
7  _refine_ls_number_reflns 4292
8  _refine_ls_number_parameters 239
9  _refine_ls_number_restraints 0
10 _refine_ls_R_factor_all 0.0381
11 _refine_ls_R_factor_gt 0.0322
12 _refine_ls_wR_factor_ref 0.0841
13 _refine_ls_wR_factor_gt 0.0802
14 _refine_ls_goodness_of_fit_ref 1.030
15 _refine_ls_restrained_S_all 1.030
16 _refine_ls_shift/su_max 0.000
17 _refine_ls_shift/su_mean 0.000
18
19
20
21 loop_
22  _atom_site_label
23  _atom_site_type_symbol
24  _atom_site_fract_x
25  _atom_site_fract_y
26  _atom_site_fract_z
27  _atom_site_U_iso_or_equiv
28  _atom_site_adp_type
29  _atom_site_occupancy
30  _atom_site_symmetry_multiplicity
31  _atom_site_calc_flag
32  _atom_site_refinement_flags
33  _atom_site_disorder_assembly
34  _atom_site_disorder_group
35
36 S1 S 0.42215(3) 0.145520(19) 0.35739(3) 0.02068(8) Uani 1 1 d . . .
37 O1 O 0.34055(9) -0.15145(5) 0.02362(8) 0.01977(18) Uani 1 1 d . . .
38 O2 O 0.21733(9) 0.06109(5) 0.16356(7) 0.01845(17) Uani 1 1 d . . .
39 O3 O 0.35645(9) -0.22249(5) 0.19309(8) 0.02135(18) Uani 1 1 d . . .
40 C1 C 0.26179(11) -0.00652(7) 0.11491(10) 0.0160(2) Uani 1 1 d . . .
41 C2 C 0.29110(11) -0.00043(7) 0.00187(10) 0.0169(2) Uani 1 1 d . . .
42 C3 C 0.28714(12) 0.07453(8) -0.06446(11) 0.0199(2) Uani 1 1 d . . .
43 H3 H 0.2639 0.1260 -0.0360 0.024 Uiso 1 1 calc R . .
44 C4 C 0.31800(13) 0.07144(8) -0.17241(11) 0.0234(3) Uani 1 1 d . . .
45 H4 H 0.3166 0.1211 -0.2164 0.028 Uiso 1 1 calc R . .
46 C5 C 0.35131(13) -0.00589(9) -0.21580(11) 0.0238(3) Uani 1 1 d . . .
47 H5 H 0.3704 -0.0072 -0.2894 0.029 Uiso 1 1 calc R . .
48 C6 C 0.35652(12) -0.08076(8) -0.15141(11) 0.0223(2) Uani 1 1 d . . .
49 H6 H 0.3781 -0.1322 -0.1811 0.027 Uiso 1 1 calc R . .
50 C7 C 0.32859(12) -0.07698(7) -0.04120(11) 0.0179(2) Uani 1 1 d . . .
51 C8 C 0.32791(11) -0.15539(7) 0.14024(11) 0.0172(2) Uani 1 1 d . . .
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2
3 C9 C 0.27935(11) -0.07868(7) 0.18122(10) 0.0159(2) Uani 1 1 d . . .
4 C10 C 0.25207(11) -0.06187(7) 0.29958(10) 0.0151(2) Uani 1 1 d . . .
5 H10 H 0.3423(15) -0.0617(9) 0.3662(12) 0.016(3) Uiso 1 1 d . . .
6 C11 C 0.15417(12) -0.12395(7) 0.33329(11) 0.0166(2) Uani 1 1 d . . .
7 C12 C 0.04835(12) -0.16765(7) 0.24489(11) 0.0198(2) Uani 1 1 d . . .
8 H12 H 0.0381 -0.1597 0.1629 0.024 Uiso 1 1 calc R . .
9 C13 C -0.04215(13) -0.22303(8) 0.27803(13) 0.0247(3) Uani 1 1 d . . .
10 H13 H -0.1123 -0.2521 0.2183 0.030 Uiso 1 1 calc R . .
11 C14 C -0.02799(14) -0.23503(8) 0.40002(14) 0.0285(3) Uani 1 1 d . . .
12 H14 H -0.0887 -0.2720 0.4222 0.034 Uiso 1 1 calc R . .
13 C15 C 0.07672(14) -0.19176(9) 0.48859(13) 0.0277(3) Uani 1 1 d . . .
14 H15 H 0.0861 -0.1995 0.5704 0.033 Uiso 1 1 calc R . .
15 C16 C 0.16785(13) -0.13674(8) 0.45556(12) 0.0215(2) Uani 1 1 d . . .
16 H16 H 0.2385 -0.1082 0.5156 0.026 Uiso 1 1 calc R . .
17 C17 C 0.19315(12) 0.03307(7) 0.27823(10) 0.0157(2) Uani 1 1 d . . .
18 C18 C 0.27743(11) 0.09305(7) 0.37520(10) 0.0148(2) Uani 1 1 d . . .
19 C19 C 0.25905(13) 0.11304(8) 0.48353(11) 0.0199(2) Uani 1 1 d . . .
20 H19 H 0.1859 0.0914 0.5090 0.024 Uiso 1 1 calc R . .
21 C20 C 0.36424(13) 0.17089(8) 0.55391(11) 0.0217(2) Uani 1 1 d . . .
22 H20 H 0.3671 0.1912 0.6301 0.026 Uiso 1 1 calc R . .
23 C21 C 0.45968(13) 0.19292(8) 0.49718(11) 0.0208(2) Uani 1 1 d . . .
24 H21 H 0.5361 0.2293 0.5303 0.025 Uiso 1 1 calc R . .
25 C22 C 0.03465(12) 0.04066(7) 0.25668(12) 0.0211(2) Uani 1 1 d . . .
26 H22A H -0.0154 0.0014 0.1942 0.032 Uiso 1 1 calc R . .
27 H22B H 0.0042 0.0976 0.2315 0.032 Uiso 1 1 calc R . .
28 H22C H 0.0148 0.0278 0.3307 0.032 Uiso 1 1 calc R . .
29
30
31
32
33
34 loop_
35 _atom_site_aniso_label
36 _atom_site_aniso_U_11
37 _atom_site_aniso_U_22
38 _atom_site_aniso_U_33
39 _atom_site_aniso_U_23
40 _atom_site_aniso_U_13
41 _atom_site_aniso_U_12
42
43 S1 0.01945(14) 0.02135(15) 0.02482(16) -0.00592(11) 0.01208(11) -0.00720(11)
44 O1 0.0227(4) 0.0165(4) 0.0225(4) 0.0002(3) 0.0106(3) 0.0031(3)
45 O2 0.0254(4) 0.0132(4) 0.0163(4) 0.0005(3) 0.0061(3) 0.0019(3)
46 O3 0.0232(4) 0.0158(4) 0.0259(4) 0.0022(3) 0.0090(3) 0.0042(3)
47 C1 0.0133(5) 0.0153(5) 0.0179(5) -0.0016(4) 0.0026(4) -0.0005(4)
48 C2 0.0135(5) 0.0187(5) 0.0165(5) 0.0000(4) 0.0021(4) -0.0014(4)
49 C3 0.0189(5) 0.0191(6) 0.0201(6) 0.0015(4) 0.0038(4) -0.0002(4)
50 C4 0.0204(5) 0.0267(6) 0.0225(6) 0.0072(5) 0.0058(5) 0.0001(5)
51 C5 0.0194(5) 0.0334(7) 0.0191(6) 0.0033(5) 0.0068(5) 0.0022(5)
52 C6 0.0185(5) 0.0267(6) 0.0222(6) -0.0014(5) 0.0072(5) 0.0028(5)
53 C7 0.0139(5) 0.0190(5) 0.0201(5) 0.0013(4) 0.0043(4) 0.0001(4)
54
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1
2
3 C8 0.0141(5) 0.0169(5) 0.0209(5) -0.0008(4) 0.0060(4) -0.0001(4)
4 C9 0.0138(5) 0.0150(5) 0.0189(5) -0.0003(4) 0.0052(4) 0.0000(4)
5 C10 0.0146(5) 0.0127(5) 0.0174(5) 0.0000(4) 0.0041(4) 0.0006(4)
6 C11 0.0169(5) 0.0122(5) 0.0220(6) 0.0008(4) 0.0082(4) 0.0025(4)
7 C12 0.0215(5) 0.0147(5) 0.0244(6) -0.0013(4) 0.0089(5) 0.0005(4)
8 C13 0.0213(6) 0.0138(5) 0.0405(7) -0.0023(5) 0.0118(5) -0.0015(4)
9 C14 0.0274(6) 0.0178(6) 0.0481(8) 0.0078(6) 0.0230(6) 0.0027(5)
10 C15 0.0316(7) 0.0263(7) 0.0315(7) 0.0091(5) 0.0190(6) 0.0077(5)
11 C16 0.0228(6) 0.0205(6) 0.0224(6) 0.0022(5) 0.0090(5) 0.0041(4)
12 C17 0.0159(5) 0.0134(5) 0.0174(5) 0.0003(4) 0.0048(4) -0.0003(4)
13 C18 0.0124(5) 0.0126(5) 0.0199(5) 0.0006(4) 0.0058(4) -0.0003(4)
14 C19 0.0216(5) 0.0199(6) 0.0209(6) -0.0009(5) 0.0105(5) -0.0042(4)
15 C20 0.0273(6) 0.0197(6) 0.0182(6) -0.0019(4) 0.0074(5) -0.0039(5)
16 C21 0.0212(5) 0.0175(6) 0.0223(6) -0.0034(4) 0.0049(5) -0.0046(4)
17 C22 0.0144(5) 0.0149(5) 0.0310(6) -0.0010(5) 0.0028(5) 0.0000(4)

21 _geom_special_details

22 ;

23
24 All esds (except the esd in the dihedral angle between two l.s. planes)
25 are estimated using the full covariance matrix. The cell esds are taken
26 into account individually in the estimation of esds in distances, angles
27 and torsion angles; correlations between esds in cell parameters are only
28 used when they are defined by crystal symmetry. An approximate (isotropic)
29 treatment of cell esds is used for estimating esds involving l.s. planes.
30

31 ;

32
33 loop_

34 _geom_bond_atom_site_label_1

35 _geom_bond_atom_site_label_2

36 _geom_bond_distance

37 _geom_bond_site_symmetry_2

38 _geom_bond_publ_flag

39 S1 C18 1.7243(11) . ?

40 S1 C21 1.7114(12) . ?

41 O1 C7 1.3749(14) . ?

42 O1 C8 1.3967(14) . ?

43 O2 C1 1.3414(14) . ?

44 O2 C17 1.4890(14) . ?

45 O3 C8 1.2068(14) . ?

46 C2 C1 1.4316(16) . ?

47 C2 C3 1.4000(16) . ?

48 C3 H3 0.9300 . ?

49 C4 C3 1.3793(17) . ?

50 C4 C5 1.3944(19) . ?

51 C4 H4 0.9300 . ?

52 C5 H5 0.9300 . ?

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2
3 C6 C5 1.3850(18) . ?
4 C6 H6 0.9300 . ?
5 C7 C6 1.3907(17) . ?
6 C7 C2 1.3973(16) . ?
7 C9 C1 1.3492(16) . ?
8 C9 C8 1.4339(15) . ?
9 C9 C10 1.5025(16) . ?
10 C10 C11 1.5130(15) . ?
11 C10 C17 1.5927(15) . ?
12 C10 H10 0.978(14) . ?
13 C11 C12 1.3918(16) . ?
14 C12 H12 0.9300 . ?
15 C13 C12 1.3894(17) . ?
16 C13 C14 1.387(2) . ?
17 C13 H13 0.9300 . ?
18 C14 C15 1.384(2) . ?
19 C14 H14 0.9300 . ?
20 C15 H15 0.9300 . ?
21 C16 C15 1.3900(18) . ?
22 C16 C11 1.3931(17) . ?
23 C16 H16 0.9300 . ?
24 C17 C22 1.5166(15) . ?
25 C18 C17 1.5001(15) . ?
26 C18 C19 1.3605(16) . ?
27 C19 C20 1.4276(16) . ?
28 C19 H19 0.9300 . ?
29 C20 H20 0.9300 . ?
30 C21 C20 1.3581(17) . ?
31 C21 H21 0.9300 . ?
32 C22 H22A 0.9600 . ?
33 C22 H22B 0.9600 . ?
34 C22 H22C 0.9600 . ?
35
36 loop_
37 _geom_angle_atom_site_label_1
38 _geom_angle_atom_site_label_2
39 _geom_angle_atom_site_label_3
40 _geom_angle
41 _geom_angle_site_symmetry_1
42 _geom_angle_site_symmetry_3
43 _geom_angle_publ_flag
44 C21 S1 C18 91.93(6) . . ?
45 C7 O1 C8 123.15(9) . . ?
46 C1 O2 C17 107.94(8) . . ?
47 O2 C1 C2 121.38(10) . . ?
48 O2 C1 C9 115.28(10) . . ?
49
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2
3 C9 C1 C2 123.32(10) .. ?
4 C3 C2 C1 125.41(11) .. ?
5 C7 C2 C1 115.05(10) .. ?
6 C7 C2 C3 119.53(11) .. ?
7 C2 C3 H3 120.3 .. ?
8 C4 C3 C2 119.46(11) .. ?
9 C4 C3 H3 120.3 .. ?
10 C3 C4 C5 120.25(12) .. ?
11 C3 C4 H4 119.9 .. ?
12 C5 C4 H4 119.9 .. ?
13 C4 C5 H5 119.4 .. ?
14 C6 C5 C4 121.26(12) .. ?
15 C6 C5 H5 119.4 .. ?
16 C5 C6 C7 118.26(12) .. ?
17 C5 C6 H6 120.9 .. ?
18 C7 C6 H6 120.9 .. ?
19 O1 C7 C2 121.64(10) .. ?
20 O1 C7 C6 117.18(11) .. ?
21 C6 C7 C2 121.18(11) .. ?
22 O1 C8 C9 115.19(10) .. ?
23 O3 C8 O1 116.75(10) .. ?
24 O3 C8 C9 128.05(11) .. ?
25 C1 C9 C8 120.96(11) .. ?
26 C1 C9 C10 110.06(10) .. ?
27 C8 C9 C10 128.81(10) .. ?
28 C9 C10 C11 116.03(9) .. ?
29 C9 C10 C17 100.78(9) .. ?
30 C9 C10 H10 109.5(8) .. ?
31 C11 C10 C17 114.21(9) .. ?
32 C11 C10 H10 107.5(8) .. ?
33 C17 C10 H10 108.6(8) .. ?
34 C12 C11 C10 121.64(11) .. ?
35 C12 C11 C16 118.85(11) .. ?
36 C16 C11 C10 119.50(10) .. ?
37 C11 C12 H12 119.7 .. ?
38 C13 C12 C11 120.57(12) .. ?
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40 C12 C13 H13 119.9 .. ?
41 C14 C13 C12 120.11(12) .. ?
42 C14 C13 H13 119.9 .. ?
43 C13 C14 H14 120.1 .. ?
44 C15 C14 C13 119.76(12) .. ?
45 C15 C14 H14 120.1 .. ?
46 C14 C15 C16 120.17(12) .. ?
47 C14 C15 H15 119.9 .. ?
48 C16 C15 H15 119.9 .. ?
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3 C11 C16 H16 119.7 . . ?
4 C15 C16 C11 120.53(12) . . ?
5 C15 C16 H16 119.7 . . ?
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7 O2 C17 C22 106.45(9) . . ?
8 O2 C17 C10 105.07(8) . . ?
9 C18 C17 C22 112.05(9) . . ?
10 C18 C17 C10 112.51(9) . . ?
11 C22 C17 C10 114.17(9) . . ?
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13 C19 C18 S1 111.17(8) . . ?
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16 C18 C19 H19 123.7 . . ?
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26 C17 C22 H22C 109.5 . . ?
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29 H22B C22 H22C 109.5 . . ?
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31 loop_
32 _geom_torsion_atom_site_label_1
33 _geom_torsion_atom_site_label_2
34 _geom_torsion_atom_site_label_3
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36 _geom_torsion
37 _geom_torsion_site_symmetry_1
38 _geom_torsion_site_symmetry_2
39 _geom_torsion_site_symmetry_3
40 _geom_torsion_site_symmetry_4
41 _geom_torsion_publ_flag
42 C21 S1 C18 C17 -177.70(9) ?
43 C21 S1 C18 C19 1.01(9) ?
44 C18 S1 C21 C20 -1.13(10) ?
45 C8 O1 C7 C2 -5.34(16) ?
46 C8 O1 C7 C6 174.17(10) ?
47 C7 O1 C8 O3 -171.81(10) ?
48 C7 O1 C8 C9 9.40(15) ?
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3 C17 O2 C1 C2 178.54(9) ?
4 C17 O2 C1 C9 -2.88(12) ?
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6 C1 O2 C17 C18 126.83(9) ?
7 C1 O2 C17 C22 -113.82(10) ?
8 C3 C2 C1 O2 4.68(17) ?
9 C3 C2 C1 C9 -173.79(11) ?
10 C7 C2 C1 O2 -176.46(10) ?
11 C7 C2 C1 C9 5.08(16) ?
12 C1 C2 C3 C4 179.90(11) ?
13 C7 C2 C3 C4 1.08(17) ?
14 C5 C4 C3 C2 0.72(18) ?
15 C3 C4 C5 C6 -1.04(19) ?
16 C7 C6 C5 C4 -0.47(18) ?
17 O1 C7 C2 C1 -2.09(15) ?
18 O1 C7 C2 C3 176.85(10) ?
19 C6 C7 C2 C1 178.43(10) ?
20 C6 C7 C2 C3 -2.64(17) ?
21 O1 C7 C6 C5 -177.20(10) ?
22 C2 C7 C6 C5 2.31(17) ?
23 C8 C9 C1 O2 -179.33(10) ?
24 C8 C9 C1 C2 -0.78(17) ?
25 C10 C9 C1 O2 -3.62(13) ?
26 C10 C9 C1 C2 174.94(10) ?
27 C1 C9 C8 O1 -6.30(15) ?
28 C1 C9 C8 O3 175.07(11) ?
29 C10 C9 C8 O1 178.87(10) ?
30 C10 C9 C8 O3 0.2(2) ?
31 C1 C9 C10 C11 131.66(10) ?
32 C1 C9 C10 C17 7.78(11) ?
33 C8 C9 C10 C11 -53.06(15) ?
34 C8 C9 C10 C17 -176.94(11) ?
35 C9 C10 C11 C12 -28.12(15) ?
36 C9 C10 C11 C16 153.18(10) ?
37 C17 C10 C11 C12 88.48(13) ?
38 C17 C10 C11 C16 -90.23(13) ?
39 C9 C10 C17 O2 -9.00(10) ?
40 C9 C10 C17 C18 -123.60(10) ?
41 C9 C10 C17 C22 107.26(11) ?
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43 C11 C10 C17 C18 111.28(11) ?
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45 C10 C11 C12 C13 -178.66(10) ?
46 C16 C11 C12 C13 0.05(17) ?
47 C14 C13 C12 C11 0.21(18) ?
48 C12 C13 C14 C15 -0.09(19) ?
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 3 C13 C14 C15 C16 -0.29(19) ?
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 6 C11 C16 C15 C14 0.57(19) ?
 7 S1 C18 C17 O2 -24.36(11) ?
 8 S1 C18 C17 C10 89.81(10) ?
 9 S1 C18 C17 C22 -139.95(9) ?
 10 C19 C18 C17 O2 157.18(11) ?
 11 C19 C18 C17 C10 -88.64(14) ?
 12 C19 C18 C17 C22 41.60(16) ?
 13 S1 C18 C19 C20 -0.65(13) ?
 14 C17 C18 C19 C20 177.91(11) ?
 15 C18 C19 C20 C21 -0.20(16) ?
 16 S1 C21 C20 C19 0.96(14) ?
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 22 _geom_hbond_atom_site_label_D
 23 _geom_hbond_atom_site_label_H
 24 _geom_hbond_atom_site_label_A
 25 _geom_hbond_distance_DH
 26 _geom_hbond_distance_HA
 27 _geom_hbond_distance_DA
 28 _geom_hbond_angle_DHA
 29 _geom_hbond_site_symmetry_A
 30 _geom_hbond_publ_flag
 31
 32 #
 33 #D H A D - H H...A D...A D - H...A symm(A)
 34 #
 35 C21 H21 O1 0.93 2.4300 3.2052(16) 141 2_655 yes
 36 C13 H13 Cg1 0.93 3.0773 4.0018(15) 173 2_756 yes
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 39 _diffn_measured_fraction_theta_max 0.997
 40 _diffn_reflns_theta_full 28.42
 41 _diffn_measured_fraction_theta_full 0.997
 42 _refine_diff_density_max 0.354
 43 _refine_diff_density_min -0.265
 44 _refine_diff_density_rms 0.045
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