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Electronic Supplementary Information

# Efficient synthesis of new 6-arylphenanthridines based on microwave-assisted Suzuki-Miyaura cross-coupling and Pictet-Spengler dehydrogenative cyclization in a zinc chloride/[Bmim]$BF_4$ mixture

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## Contents

# 1 General information

The reagents and solvents used in the synthesis of the intermediate and final compounds were of purity grade for synthesis, of the brands Merck, Sigma-Aldrich, J. T. Baker and Alfa Aesar.

The composition and monitoring of the reactions, as well as the preliminary analysis of the purity of the synthesized compounds were carried out by thin layer chromatography (TLC) on Silufol UV254 plates of 0.25 mm thickness, revealed in a UV light chamber of 254 nm or in an ethanolic solution of phosphomolybdic-sulfuric acids. The purification of the isolated compounds as solid products was carried out mainly by recrystallization techniques in absolute ethanol. Likewise, for the compounds that required it, the purification was carried out by column chromatography (CC), using silica gel 60 Mesh as stationary phase (solid support) and relevant mixtures of petroleum ether/ethyl acetate as eluents.

The melting points of the products were determined in a Fisher–Jöns melting point apparatus, the values were not corrected, reporting the average of three measurements; the elucidation of molecular structures was performed by instrumental methods.

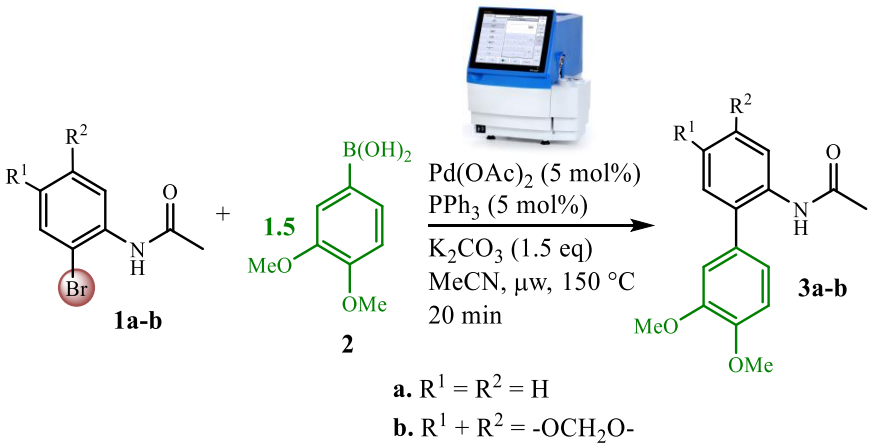
The acquisition of nuclear magnetic resonance spectra $^{1}H$, $^{13}C$-APT and 2D variants was performed on a Bruker Avance–400 spectrometer (400 MHz for $^{1}H$ and 100 MHz for $^{13}C$) using deuterated chloroform ($CDCl_3$, 99.8% Merck®) as a solvent. Chemical shift values (δ) are expressed in ppm. In some $^{1}H$ NMR spectra, tetramethylsilane, TMS, was used as the internal standard, and in others, the scale was adjusted from the residual chloroform signal (7.26 ppm). Similarly, the $^{13}C$-APT spectra are scaled from the signal characteristic of the solvent ($CDCl_3$) and the phase of the signals is assigned as (+) positive phase, (-) negative phase. Coupling constants ($^{n}J$) are described at *n* bonds and are given in Hz; the multiplicity of signals is expressed by the following abbreviations: (s) singlet, (br s) broad singlet, (d) doublet, (dd) doublet of doublets, (ddd) doublet of doublet of doublets, (*td ap*) apparent triplet of doublets, (*t ap*) apparent triplet and (m) multiplet.

Mass spectra were taken on an Agilent/HP 6890 PLUS Gas Chromatograph coupled to an Agilent 5973 Network Mass Selective Detector MSD G2570A, equipped with a 60 m capillary column coated with HP-5 [5%-phenyl-poly(dimethyl-siloxane)]. The ionization method is positive ESI, acquisition software: HP MS ChemStation Data system was used for MS identification at 70 eV.

The implementation of the established reaction conditions and their extrapolation to heating by microwave activation were carried out in high-precision glass vials with crimper sealing and 0.5-2 mL, 2-5 mL, and 10-20 mL capacity. , in a Biotage Initiator+ variable power fourth generation microwave reactor with *in situ* pressure and temperature gauge. Radiation absorption levels vary according to the nature of the solvent used.

# 2 Experimental procedures

**Synthesis of the *N*-([1,1'-biphenyl]-2-yl)acetamides 3a-b by means of the Suzuki-Miyaura cross-coupling reaction; general procedure**

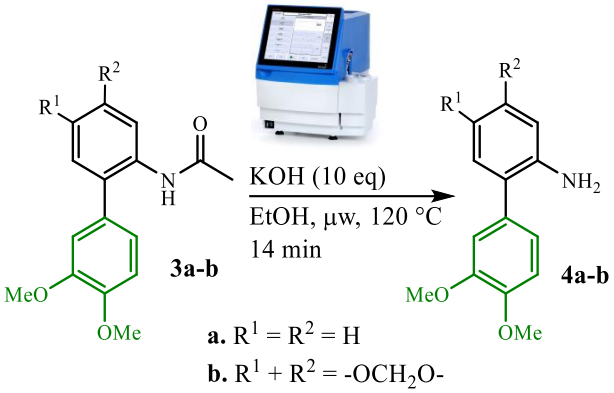



**a.** $R^1 = R^2 = H$

**b.** $R^1 + R^2 = -OCH_2O-$

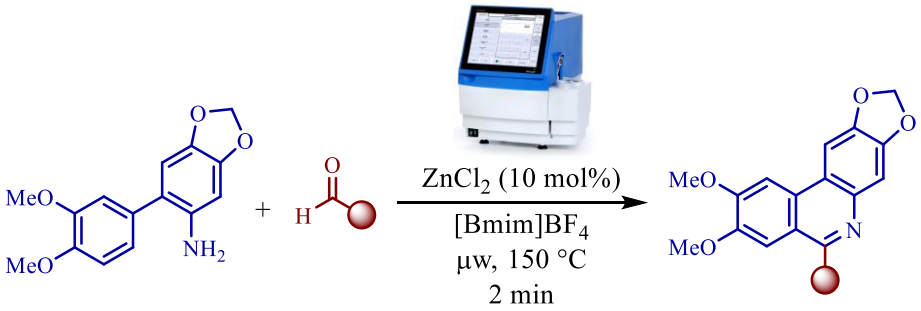
In a microwave vial of 2–5 mL capacity, equipped with a magnetic stirrer, the following were added: acetanilides **1a-b** (1.0 mmol), 3,4-dimethoxyphenylboronic acid **2** (1.5 mmol), $Pd(OAc)_2$ (5% mol) (0.05 mmol), $PPh_3$ (5 mol%) (0.05 mmol), $K_2CO_3$ (1.5 eq.) (1.5 mmol) and 2 mL of MeCN (0.5 M) as solvent. The vial was sealed with a crimper cap and the reactions were carried out in a Biotag Initiator+ microwave reactor with the following programming: reaction time = 20 min, activation temperature = 150 °C, radiation absorption level = high. After that time, the reaction mixtures were allowed to cool to room temperature and the formation of the corresponding *N*-([1,1'-biphenyl]-2-yl)acetamide **3a-b** was verified (control by TLC), they were diluted with ethyl acetate and filtered through a pre-column with a layer of celite. The filtrates were washed with distilled water (50 mL) and treated with sodium bicarbonate ($NaHCO_3$) until they reached a pH = 8. The reaction crudes were placed in an Erlenmeyer flask over anhydrous sodium sulfate. Finally, the solvent was removed by distillation under reduced pressure, and the organic residues that remained were purified by column chromatography on silica gel, using an isocratic mixture of ethyl acetate–petroleum ether at 50 % (1:1 *v*/*v*) as eluent.

**_N_-deprotection of _N_-([1,1'-biphenyl]-2-yl)acetamides 3a-b by basic ethanolic hydrolysis. Synthesis of the [1,1'-biphenyl]-2-amines 4a-b; general procedure**




In a 10-20 mL capacity vial, _N_-([1,1'-biphenyl]-2-yl)acetamide **3a-b** (1.0 mmol) was suspended in a solution containing potassium hydroxide (10 mmol) in 10 mL of a mixture of EtOH/$H_2O$ (9:1). The vial was sealed with a crimper cap and the reaction was carried out in a Biotag Initiator+ microwave reactor with the following programming: reaction time = 14 min, activation temperature = 120 °C, radiation absorption level = high. After that time, the reaction mixture was allowed to cool to room temperature and the formation of the corresponding [1,1'-biphenyl]-2-amine **4a-b** was verified (control by TLC). The reaction mixture was poured into distilled water (20 mL) and it was treated with a 1 M HCl solution until pH = 7. It was extracted with ethyl acetate (3x20 mL), the organic phase was separated, dried over anhydrous sodium sulfate in an Erlenmeyer flask and filtered, to finally remove the solvent by distillation under reduced pressure. The product was then used without further purification.

**Synthesis of 6-aryl/styryl/phenethyl-phenanthridines by intramolecular Pictet-Spengler cyclization**




In microwave vials of 2–5 mL capacity, equipped with a magnetic stirrer, the following were added: [1,1'-biphenyl]-2-amine **4a-b** (1.0 mmol), aldehyde **5** (1.5 mmol), $ZnCl_2$ (10 mol%), and 0.5 mL of ionic liquid [Bmim]$BF_4$ as solvent. The vials were sealed with a crimper cap

and the reactions were carried out in a Biotage Initiator+ microwave reactor with the following programming: reaction time = 2 min, activation temperature = 150 °C, radiation absorption level = very high. After this time, the reaction mixtures were allowed to cool to room temperature and the formation of the corresponding phenanthridines was verified (TLC control), they were poured onto 200 mL of distilled water and extracted with AcOEt (3x20 mL). The organic phase was dried over anhydrous $Na_2SO_4$, to finally be concentrated by distillation under reduced pressure. The reaction crudes obtained were purified by column chromatography on silica gel, using an isocratic mixture of ethyl acetate-petroleum ether at 30 % (3:7 *v*/*v*).

**Figure 1**. Photographic evidence of color change of reaction mixture after microwave irradiation.

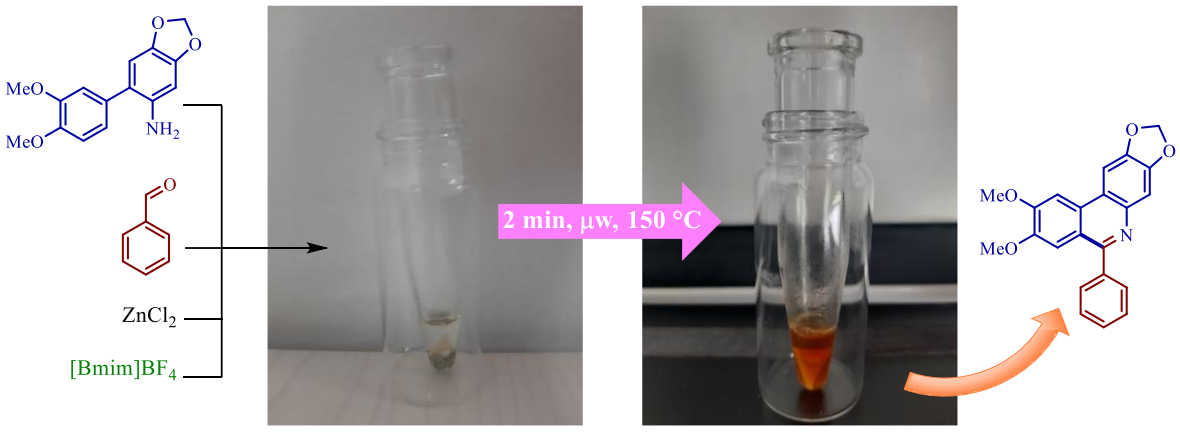
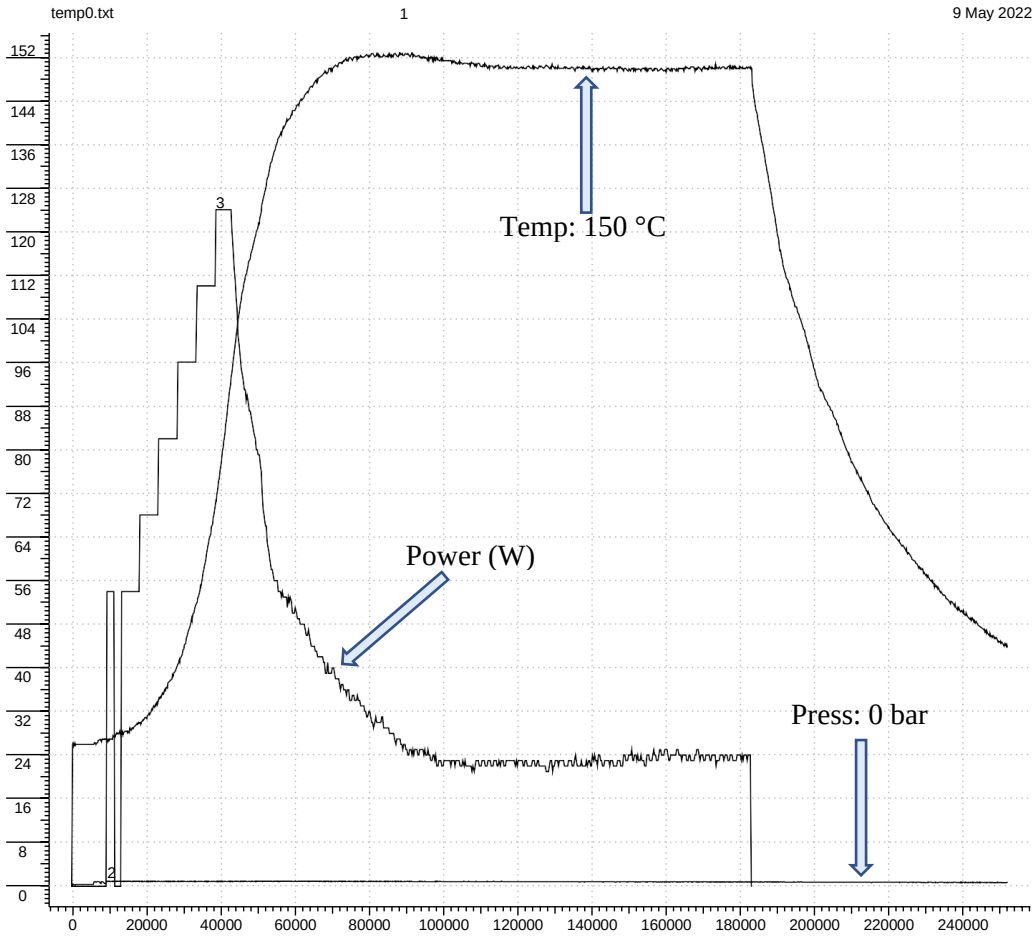


**Figure 2**. Microwave conditions on Biotage Initiator+ reactor for Pictet-Spengler cyclization.

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| 3 | E:\INITIATOR\RESULTS\POWER0.TXT | | | |
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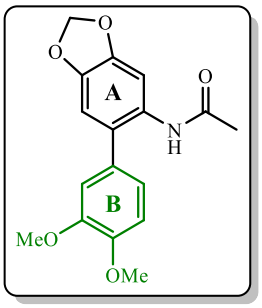
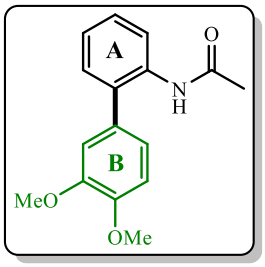
# 3 Characterization data of products

***N*-(6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-yl)acetamide 3a.**



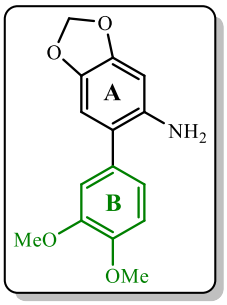

From 0.258 g (1.0 mmol) of *N*-(6-bromobenzo[*d*][1,3]dioxol-5-yl)acetamide, 0.280 g (1.5 mmol) of 3,4-dimethoxiphenylboronic acid, 11 mg (0.05 mmol) of palladium acetate, 13 mg (0.05 mmol) of triphenylphosphine and 0.310 g (2.25 mmol) of potassium carbonate in acetonitrile (2 mL), it was obtained 0.290 g.(0.919 mmol, 92%) of *N*-(6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-yl)acetamide, $C_{17}H_{17}NO_5$ (315,33 g/mol), as a white solid; m.p. = 155–157 °C; $R_f$ = 0.22 (50% ethyl acetate–petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]**= 3323 (m), 3306 (m), 3088 (vw), 2907 (w), 2790 (vw), 1658 (s), 1543 (s), 1474 (vs), 1234 (vs), 1178 (vs), 1036 (vs), 812 (vs), 592 (s), 509 (s), 442 (s). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.72 (s, 1H, 3-H, ring A), 7.05 (s, 1H, N-H), 6.94 (d, $^3J$ = 8.2 Hz, 1H, 5-H, ring B), 6.85 (dd, $^3J$ = 8.1, $^4J$ = 1.6 Hz, 1H, 6-H, ring B), 6.81 (d, $^4J$ = 1.6 Hz, 1H, 2-H, ring B), 6.71 (s, 1H, 6-H, ring A), 5.97 (s, 2H, -$OCH_2$O-), 3.92 (s, 3H, 3-OMe, ring B), 3.87 (s, 3H, 4-OMe, ring B), 1.99 (s, 3H, -C(O)-$CH_3$). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm) =** 168.29 (C=O, +), 149.37 (+), 148.80 (+), 147.11 (+), 144.41 (+), 130.78 (+), 128.98(+), 126.06 (+), 121.66 (-), 112.65 (-), 111.62 (-), 109.64 (-), 104.07 (-), 101.51 (1C, -$OCH_2$O-, +), 56.10 (-), 56.08 (-), 24.52 (-). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 64.75; H, 5.43; N, 4.44; found (%): C, 64.89; H, 5.38; N, 4.51.

***N*-(3',4'-dimethoxy-[1,1'-biphenyl]-2-yl)acetamide 3b.**



From 0.214 g (1.0 mmol) of *N*-(2-bromophenyl)acetamide, 0.280 g (1.5 mmol) of 3,4-dimethoxyphenyl boronic acid, 11 mg (0.05 mmol) palladium acetate, 13 mg (0.05 mmol) of triphenylphosphine and 0.310 g (2.25 mmol) of potassium carbonate in acetonitrile (2 mL), it was obtained 0.265 g.(0.979 mmol, 98%) of the *N*-(3',4'-dimethoxy-[1,1'-biphenyl]-2-yl)acetamide **3b**, $C_{16}H_{17}NO_3$ (271,32 g/mol) as a white stable solid; m.p. = 138–140 °C; $R_f$ = 0.30 (50% ethyl acetate–petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3214 (w), 3177 (w), 3029 (w), 3002 (w), 2974 (w), 2939 (w), 2836 (w), 1638 (s), 1541 (s), 1415 (s), 1302 (s), 1223 (s), 1182 (s), 1040 (s), 876 (m), 795 (s), 755 (vs), 699 (vs), 607 (s). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.20 (d, $^3J$ = 8.1 Hz, 1H, 6-H, ring A), 7.32 – 7.28 (m, 2H, N-H, 5-H, ring A) 7.21 (d, $^3J$ = 7.1 Hz, 1H, 3-H, ring A), 7.12 (t *ap*, *J* = 7.4 Hz, 1H, 4-H, ring A), 6.94 (d, $^3J$ = 8.2 Hz, 1H, 5-H, ring B), 6.88 (dd, $^3J$ = 8.2, $^4J$ = 1.9 Hz, 1H, 5-H, ring B), 6.84 (d, $^4J$ = 1.8 Hz, 1H, 2-H, ring B), 3.89 (s, 3H, -OMe), 3.84 (s, 3H, -OMe), 1.99 (s, 3H, -C(O)-$CH_3$). **$^{13}$C–APT NMR (100 MHz, $CDCl_3$) δ(ppm) =** 168.21 (1C, C=O, +), 149.26 (1C, 1-C, ring B, +), 148.75 (1C, 3-C, ring B, +), 134.87 (1C, 2-C, ring A, +), 132.10 (1C, 4-C, ring B, +), 130.60 (1C, 1-C, ring A, +), 130.02 (1C, 3-C, ring A, -), 128.13 (1C, 5-C, ring A, -), 124.26 (1C, 4-C, ring A, -), 121.63 (1C, 6-C, ring B, -), 121.38 (1C, 6-C, ring A, -), 112.40 (1C, 2-C, ring B, -), 111.53 (1C, 5-C, ring B, -), 55.94 (1C, 4-OMe, ring B, -), 55.92 (1C, 3-OMe, ring B, -), 24.53 (1C, -$CH_3$, -). Anal. Calcd. (%) for [$C_{16}H_{17}NO_3$]: C, 70.83; H, 6.32; N, 5.16; found (%): C, 69.98; H, 6.38; N, 5.11.

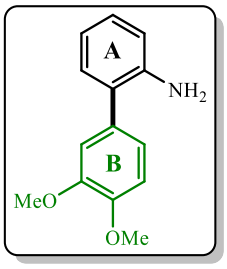
**6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine 4a.**




From 0.315 g (1.0 mmol) of *N*-(6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-yl)acetamide **3a**, 0.561 g (10 mmol) of potassium hydroxide in 10 mL of a solution of ethanol–water (9:1 *v*/*v*), it was obtained 0.271 g.(0.99 mmol, 99%) of the corresponding 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine, $C_{15}H_{15}NO_4$ (273,29 g/mol), as a grey solid; m.p. = 105–109 °C; $R_f$ = 0.50 (50% ethyl acetate–petroleum ether). ). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3412 (w), 3345 (w), 3067 (vw), 2991 (w), 2931 (w), 2834 (w), 1584 (w), 1482 (vs), 1168 (vs), 1138 (s), 1029 (vs), 930 (s), 813 (s), 595 (m), 537 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 6.93 – 6.92 (m, 3H, 2-H, 5-H, 6-H, ring B), 6.64 (s, 1H, 6-H, ring A), 6.35 (s, 1H, 3-H, ring A), 5.88 (s, 2H, -$OCH_2O$-), 3.91 (s, 3H, 3-OMe, ring B), 3.88 (s, 3H, 4-OMe, ring B), 3.32 (br s, 2H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm) =** 149.19 (+),

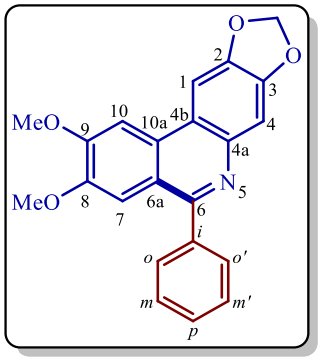
148.17 (+), 147.52 (+), 140.59 (+), 138.41 (+), 132.18 (+), 121.56 (-), 119.77 (+), 112.67 (-), 111.61 (-), 110.12 (-), 100.82 (1C, -$OCH_2O$-, +), 97.84 (-), 56.06 (-), 56.03 (-).Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 65.92; H, 5.53; N, 5.13; found (%): C, 65.90; H, 5.49; N, 5.10.

**_N_-3',4'-dimethoxy-[1,1'-biphenyl]-2-amine 4b.**



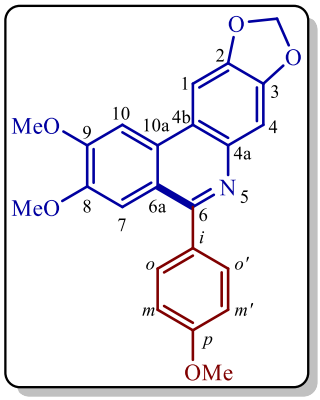

From 0.271 g (1.0 mmol) of *N*-(3',4'-dimethoxy-[1,1'-biphenyl]-2-yl)acetamide **3b**, 0.561 g (10 mmol) of potassium hydroxide in 10 mL of ethanol–water (9:1 *v*/*v*), it was obtained 0.227 g.(0.9 mmol, 99%) de la *N*-3',4'-dimethoxy-[1,1'-biphenyl]-2-amine **4b**, $C_{14}H_{15}NO_2$ (229,28 g/mol), as a grey solid, m.p. = 133–135 °C; $R_f$ = 0.60 (50% ethyl acetate–petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]**= 3375 (m), 2991 (w), 2955 (w), 2929 (w), 2831 (w), 1686 (s), 1580 (m), 1515 (vs), 1145 (s), 1028 (s), 765 (s), 647 (s), 594 (s), 541 (s). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.14 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.00 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.80 (ddd (td *ap*), *J* = 7.5, 1.2 Hz, 1H), 6.76 – 6.72 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.74 (br s, 2H). **$^{13}$C–APT NMR (100 MHz, $CDCl_3$) δ(ppm) =** 149.11 (1C, +), 148.22 (1C, +), 143.65 (1C, +), 132.16 (1C, +), 130.40 (1C, -), 128.33 (1C, -), 127.52 (1C, +), 121.27 (1C, -), 118.62 (1C, -), 115.59 (1C, -), 112.41 (1C, -), 111.53 (1C, -), 55.98 (1C, -), 55.95 (1C, -). Anal. Calcd. (%) for [$C_{14}H_{15}NO_2$]: C, 73.34; H, 6.59; N, 6.11; found (%): C, 73.45; H, 6.39; N, 6.14.

**2,3-dimethoxy-5-phenyl-[1,3]dioxolo[4,5-*b*]phenanthridine 6a.**



From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 28 μL (0.27 mmol) of benzaldehyde **5a**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.042 g (0.12 mmol, 65%) of 2,3-dimethoxy-5-phenyl-[1,3]dioxolo[4,5-*b*]phenanthridine **6a**, $C_{22}H_{17}NO_4$ (359.38 g/mol), as a white solid, which was recrystallized in absolute ethanol; m.p. = 240–242 °C, $R_f$ = 0.42 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2993 (w), 2965 (w), 2938 (w), 2907 (w), 2825 (vw), 1620 (m), 1492 (vs), 1463 (vs), 1325 (m), 1238 (vs), 1195 (vs), 1156 (vs), 1032 (vs), 945 (s), 802 (s), 706 (s), 614 (m), 560 (m), 473 (w). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.73 – 7.70 (m, 2H), 7.69 (s, 1H, 4-H), 7.64 (s, 1H, 10-H), 7.56 – 7.48 (m, 4H, 1-H, ), 7.37 (s, 1H, 7-H), 6.10 (s, 2H, -$OCH_2O$-), 4.10 (s, 3H, 9-OMe), 3.83 (s, 3H, 8-OMe). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 157.46 (+), 152.31 (+), 148.90(+), 148.83 (+), 147.88 (+), 140.86 (+), 140.34 (+), 129.66 (-), 129.39 (+), 128.57 (-), 128.54 (-), 119.66 (+), 119.37 (+), 107.91 (-), 107.83 (-), 101.74 (1C, -$OCH_2O$-, +), 101.69 (-), 98.66 (-), 56.13 (-), 55.94 (-). **GC/MS (70 eV), $t_R$** = 81.449 min.; *m/z* (%) = 360.10 ([M+1], 23), 359.10 ($M^{+\bullet}$, 100), 358.10 (39), 344.10 (36), 329.10 (31). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 73.53; H, 4.77; N, 3.90; found (%): C, 73.58; H, 4.80; N, 3.86.

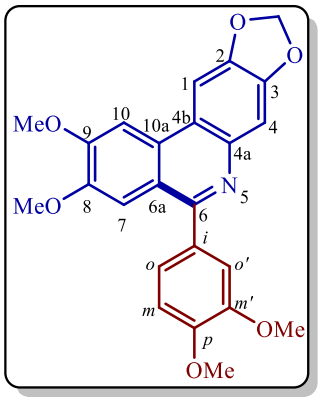
**2,3-dimethoxi-5-(4-methoxyphenyl)-[1,3]dioxolo[4,5-*b*]phenanthridine 6b.**




From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 33 μL (0.27 mmol) of 4-methoxybenzaldehyde **5b**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.041 g (0.104 mmol, 58%) of 2,3-dimethoxy-5-(4-methoxyphenyl)-[1,3]dioxolo[4,5-*b*]phenanthridine **6b**, $C_{23}H_{19}NO_5$ (389.41 g/mol), as a white solid; m.p. = 245–247 °C, $R_f$ = 0.56 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2997 (w), 2906 (w), 2838 (w), 2788 (vw), 1607 (m), 1497 (s), 1456 (vs), 1247 (vs), 1200 (s), 1159 (s), 1029 (s), 825 (s), 797 (s), 588 (s), 552 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.72 (s, 1H, 4-H), 7.68 (s, 1H, 10-H), 7.68 (d, $^3J$ = 8.8 Hz, 2H, *o*-H, *o'*-H), 7.52 (s, 1H, 1-H), 7.43 (s, 1H, 7-H), 7.07 (d, $^3J$ = 8.8 Hz, 2H, *m*-H, *m'*-H), 6.11 (s, 2H, -$OCH_2O$-), 4.12 (s, 3H, 9-OMe), 3.90 (s, 3H, *p*-OMe), 3.87 (s, 3H, 8-OMe).**$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 160.00 (+), 157.24 (+), 152.33 (+), 148.92 (+), 148.86 (+), 147.81 (+),

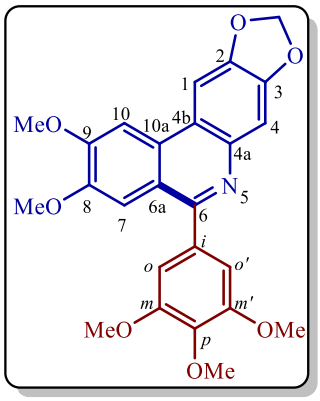
140.96 (+), 132.85 (+), 131.03 (-), 129.50 (+), 119.85 (+), 119.29 (+), 114.06 (-), 108.09 (-), 107.80 (-), 101.77 (-), 101.74 (1C, -$OCH_2O$-, +), 98.73 (-), 56.19 (-), 56.02 (-), 55.54 (-). **GC/MS (70 eV), $t_R$** = 97.092 min.; *m*/*z* (%) = 390.20 ([M+1], 23), 389.20 ($M^{+}$•, 100), 388.10 (34), 374.10 (45), 358.10 (21). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 70.94; H, 4.92; N, 3.60; found (%): C, 70.84; H, 4.98; N, 3.72.

**5-(3,4-dimethoxyphenyl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine 6c.**



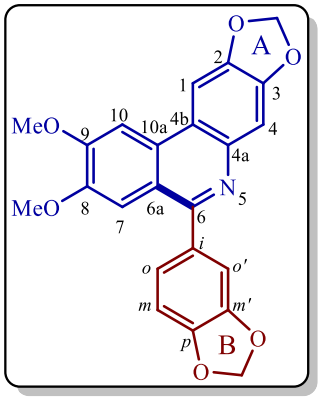

From 0.08 g (0.29 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.074 g (0.44 mmol) of 3,4-dimethoxybenzaldehyde **5c**, 6.5 mg (0.029 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.092 g (0.219 mmol, 76%) of 5-(3,4-dimethoxyphenyl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine **6c**, $C_{24}H_{21}NO_6$ (419.43 g/mol), as a white solid; m.p. = 115–117 °C, $R_f$ = 0.58 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ ($cm^{-1}$)]** = 2998 (w), 2917 (w), 2834 (w), 1602 (m), 1463 (vs), 1417 (vs), 1254 (vs), 1229 (vs), 1027 (vs), 933 (m), 847 (m), 803 (m), 600 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.71 (s, 1H, 4-H), 7.67 (s, 1H, 10-H), 7.60 (s, 1H, 1-H), 7.46 (s, 1H, 7-H), 7.32 (d, $^4J$ = 1.8 Hz, 1H, *o'*-H), 7.29 (dd, $^3J$ = 8.1, $^4J$ = 1.8 Hz, 1H, *o*-H), 7.04 (d, $^3J$ = 8.2 Hz, 1H, *m*-H), 6.12 (s, 2H, -$OCH_2O$-), 4.12 (s, 3H, 9-OMe), 3.98 (s, 3H, *m*'-OMe), 3.95 (s, 3H, *p*-OMe), 3.87 (s, 3H, 8-OMe). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 156.88 (+), 152.63 (+), 149.62 (+), 149.07 (+), 149.01 (+), 147.97 (+), 129.71 (+), 122.50 (-), 119.63 (+), 119.36 (+), 113.09 (-), 111.12 (-), 108.10 (-), 107.15 (-), 101.82 (1C, -$OCH_2O$-, +), 101.74 (-), 98.70 (-), 56.19 (-), 56.12 (-), 56.00 (-). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 68.73; H, 5.05; N, 3.34; found (%): C, 68.89; H, 5.13; N, 3.31.

**2,3-dimethoxy-5-(3,4,5-trimethoxyphenyl)-[1,3]dioxolo[4,5-*b*]phenanthridine 6d.**



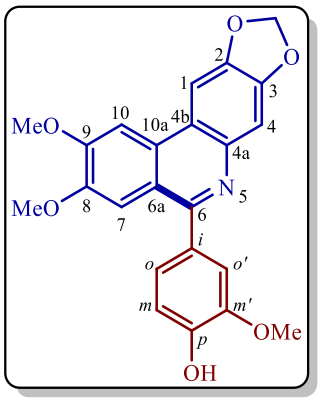

From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.053 g (0.27 mmol) of 3,4,5-trimethoxybenzadehyde **5d**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.042 g (0.094 mmol, 52%) of 2,3-dimethoxy-5-(3,4,5-trimethoxyphenyl)-[1,3]dioxolo[4,5-*b*]phenanthridine **6d**, $C_{25}H_{23}NO_7$ (449.46 g/mol), as a white solid; m.p. = 234–236 °C, $R_f$ = 0.66 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3061 (vw), 2997 (w), 2956 (m), 2932 (m), 2838 (m), 1621 (m), 1577 (m), 1494 (m), 1460 (s), 1411 (s), 1119 (vs), 1018 (s), 838 (s), 729 (m), 638 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.73 (s, 1H, 10-H), 7.69 (s, 1H, -H), 7.53 (s, 1H, -H), 7.45 (s, 1H, 7-H), 6.94 (s, 2H, *o*-H, *o'*-H), 6.13 (s, 2H, -$OCH_2O$-), 4.12 (s, 3H, 8-OMe), 3.92 (s, 3H, *p*-OMe), 3.91 (s, 6H, *m*-OMe, *m*'-OMe), 3.87 (s, 3H, 9-OMe). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 157.26 (+), 153.41 (+), 152.47 (+), 149.00 (+), 148.96 (+), 148.01 (+), 140.75 (+), 138.43 (+), 135.87 ( +), 129.53 (+), 119.61 (+), 119.45 (+), 107.92 (-), 107.81 (-), 106.95 (-), 101.81 (1C, -$OCH_2O$-, +), 101.77 (-), 98.75 (-), 61.05 (-), 56.36 (-), 56.22 (-), 56.10 (-). **GC/MS (70 eV), $t_R$** = 121.925 min.; *m*/*z*(%) = 449.20 ($M^{+\bullet}$, 100), 448.20 (22), 434.10 (44), 418.10 (31). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 66.81; H, 5.16; N, 3.12; found (%): C, 66.99; H, 5.22; N, 3.20.

**5-(benzo[*d*][1,3]dioxol-5-yl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine 6e.**



From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.041 g (0.27 mmol) of piperonal **5e**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.038 g (0.094 mmol, 52%) of 5-(benzo[*d*][1,3]dioxol-5-yl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine **6e**, $C_{23}H_{17}NO_6$ (403.39 g/mol), as a white solid; m.p. = 228–230 °C, $R_f$ = 0.38 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2984 (m), 2901 (m), 2780 (vw), 1618 (m), 1492 (s), 1234 (vs), 1152 (s), 1032 (s), 832 (s), 571 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.71 (s, 1H), 7.67 (s, 1H), 7.51 (s, 1H), 7.43 (s, 1H), 7.22 (d, $^4J$ = 1.6 Hz, 1H), 7.19 (dd, $^3J$ = 7.9, $^4J$ = 1.7 Hz, 1H), 6.97 (d, $^3J$ = 7.9 Hz, 1H), 6.11 (s, 2H), 6.05 (s, 2H), 4.11 (s, 3H), 3.88 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 156.94 (+), 152.42 (+), 148.98 (+), 148.91 (+), 148.02 (+), 147.97 (+), 147.92 (+), 140.82 (+), 134.33 (+), 129.54 (+), 123.62 (-), 119.73 (+), 119.37 (+), 110.36 (-), 108.40 (-), 107.96 (-), 107.78 (-), 101.78 (-), 101.77 (+), 101.37 (1C, -$OCH_2O$-, +), 98.72 (-), 56.19 (-), 56.08 (-). **GC/MS (70 eV), $t_R$** = 107.192 min.; *m*/*z* (%) = 404.10 (M+1, 24), 403.10 ($M^{+\bullet}$, 100), 402.10 (46), 388.10 (49), 372.10 (18). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 68.48; H, 4.25; N, 3.47; found (%): C, 68.34; H, 4.22; N, 3.56.

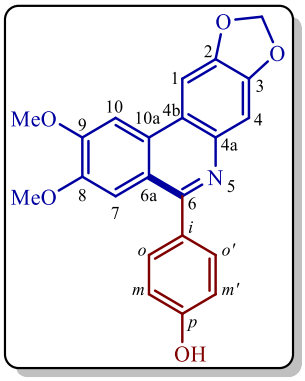
**4-(2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridin-5-yl)-2-methoxyphenol 6f.**




From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.041 g (0.27 mmol) of vanillin **5f**, 2.5 mg (0.014 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.071 g (0.176 mmol, 98%) of 4-(2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridin-5-yl)-2-methoxyphenol **6f**, $C_{23}H_{19}NO_6$ (405.41 g/mol), as a white solid; m.p. = 257 °C, $R_f$ = 0.52 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2986 (m), 2934 (m), 2902 (m), 2829 (m), 1593 (m), 1520 (s), 1461 (s), 1411 (s), 1236 (vs), 1030 (s), 833 (s), 601 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 9.31 (s, 1H), 8.25 (s, 1H), 8.01 (s, 1H), 7.45 (s, 1H), 7.38 (s, 1H), 7.28 (d, $^4J$ = 1.3 Hz, 1H), 7.15 (dd, $^3J$ = 8.0, $^4J$ = 1.5 Hz, 1H), 6.96 (d, $^3J$ = 8.1 Hz, 1H), 6.21 (s, 2H), 4.05 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 156.30 (+), 152.16 (+), 148.56 (+), 148.38 (+), 147.35 (+), 147.30 (+), 146.97 (+), 140.11 (+), 130.90 (+), 129.11 (+), 122.55 (-), 118.77 (+), 118.69 (+), 115.21 (-), 113.75 (-), 107.33 (-), 106.50 (-), 102.93 (-), 101.70

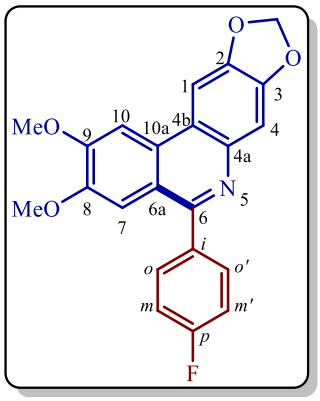
(1C, -$OCH_2O$-, +), 99.85 (-), 56.13 (-), 55.77 (-), 55.24 (-). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 68.14; H, 4.72; N, 3.46; found (%): C, 68.29; H, 4.79; N, 3.51.

**4-(2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridin-5-yl)phenol 6g.**



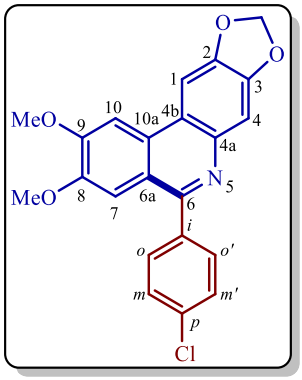

From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.033 g (0.27 mmol) of 4-hydroxybenzadehyde **5g**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.062 g (0.166 mmol, 92%) of 4-(2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridin-5-yl)phenol **6g**, $C_{22}H_{17}NO_5$ (375.38 g/mol), as a white solid; m.p. = >300 °C, $R_f$ = 0.24 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2998 (w), 2896 (w), 1609 (m), 1469 (s), 1235 (vs), 1033 (s), 846 (s), 735 (m), 587 (m). **$^1$H NMR (400 MHz, DMSO-$d_6$) δ(ppm)** = 9.96 (s, 1H, -OH), 8.28 (s, 1H), 8.04 (s, 1H), 7.55 (d, $^3J$ = 8.5 Hz, 2H), 7.41 (s, 1H), 7.39 (s, 1H), 6.98 (d, $^3J$ = 8.5 Hz, 2H), 6.21 (s, 2H), 4.05 (s, 3H), 3.76 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 158.39 (+), 156.82 (+), 149.10 (+), 148.91 (+), 147.86 (+), 131.39 (-), 129.65 (+), 119.25 (+), 119.16 (+), 115.57 (-), 107.82 (-), 103.51 (-), 102.21 (+), 100.41 (-), 56.67 (-), 55.74 (-). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 70.39; H, 4.56; N, 3.73; found (%): C, 70.42; H, 4.60; N, 3.63.

**5-(4-fluorophenyl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine 6h.**



From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.034 g (0.27 mmol) of 4-fluorobenzadehyde **5h**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.034 g (0.09 mmol, 50%) of 5-(4-fluorophenyl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine **6h**, $C_{22}H_{16}FNO_4$ (377.37 g/mol), as a white solid; m.p. = 221–222 °C, $R_f$ = 0.55 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2993 (m), 2912 (m), 2828 (w), 1621 (m), 1492 (s), 1463 (s), 1238 (vs), 1031 (s), 834 (s), 580 (s), 550 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.70 (t, *J* = 7.1 Hz, 2H), 7.69 (s, 1H), 7.65 (s, 1H), 7.49 (s, 1H), 7.30 (s, 1H), 7.23 (t, *J* = 8.7 Hz, 2H), 6.11 (s, 2H), 4.11 (s, 3H), 3.85 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 164.31 (+), 161.85 (+), 156.37 (+), 152.43 (+), 149.03 (+), 148.95 (+), 148.01 (+), 140.80 (+), 136.44 (+), 136.40 (+), 131.54 (-), 131.45 (-), 129.48 (+), 119.62 (+), 119.44 (+), 115.69 (-), 115.48 (-), 107.75 (-), 107.61 (-), 101.81 (1C, -$OCH_2O$-, +), 101.79 (-), 98.70 (-), 56.18 (-), 55.98 (-). **GC/MS (70 eV), $t_R$** = 80.037 min.; *m*/*z* (%) = 378.20 (M+1, 22), 377.10 ($M^{+\bullet}$, 100), 376.10 (28), 362.10 (37), 347.10 (31). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 70.02; H, 4.27; N, 3.71; found (%): C, 70.19; H, 4.41; N, 3.51.

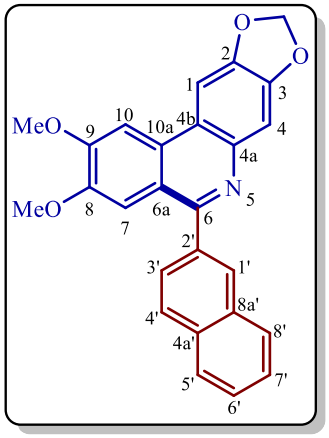
**5-(4-chlorophenyl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine 6i.**




From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.038 g (0.27 mmol) of 4-chlorobenzadehyde **5i**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.041 g (0.104 mmol, 58%) of 5-(4-chlorophenyl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine **6i**, $C_{22}H_{16}ClNO_4$ (393.82 g/mol), as a white solid; m.p. = 210–212 °C, $R_f$ = 0.45 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2918 (m), 1618 (m), 1462 (vs), 1322 (w), 1236 (vs), 1157 (vs), 1035 (s), 823 (s), 566 (s), 471 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 7.71 (s, 1H), 7.67 (s, 1H), 7.66 (d, $^3J$ = 8.6 Hz, 2H), 7.52 (d, $^3J$ = 8.6 Hz, 2H), 7.49 (s, 1H), 7.30 (s, 1H), 6.12 (s, 2H), 4.12 (s, 3H), 3.86 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 156.17 (+), 152.49 (+), 149.11 (+), 149.00 (+), 148.11 (+), 140.84 (+), 138.83 (+), 134.67 (+), 131.10 (-), 129.52 (+), 128.84 (-), 119.52 (+), 119.49 (+), 107.79 (-), 107.47 (-), 101.84 (1C, -$OCH_2O$-, +), 101.83 (-), 98.72 (-), 56.21 (-), 56.04 (-). **GC/MS (70 eV), $t_R$** = 91.804 min.; *m*/*z* 395.10

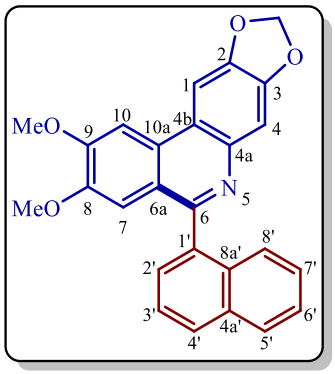
(35), 394.10 ([M+1], 30), 393.10 ($M^{+}$•, 100), 392.10 (25). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 67.10; H, 4.10; N, 3.56; found (%): C, 67.23; H, 4.23; N, 3.58.

**2,3-dimethoxy-5-(naphtalen-2-yl)-[1,3]dioxolo[4,5-*b*]phenanthridine 6j.**



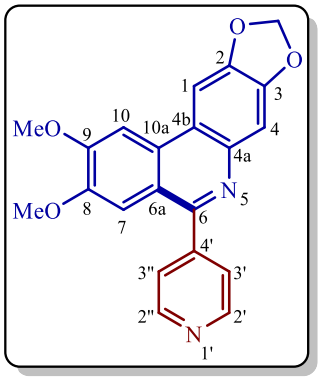

From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.042 g (0.27 mmol) of 2-naphtaldehyde **5j**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.029 g (0.072 mmol, 40%) of 2,3-dimethoxy-5-(naphtalen-2-yl)-[1,3]dioxolo[4,5-*b*]phenanthridine **6j**, $C_{26}H_{19}NO_4$ (409.44 g/mol), as a pale yellow solid, m.p. = 145–146 °C, $R_f$ = 0.28 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3002 (w), 2908 (m), 2835 (m), 1617 (m), 1459 (s), 1233 (s), 1156 (s), 1032 (s), 756 (m), 579 (m), 491 (m). **$^{1}$H RMN (400 MHz, $CDCl_3$) δ(ppm)** = 8.22 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.85 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.76 (s, 1H), 7.71 (s, 1H), 7.57 (s, 1H), 7.56 – 7.54 (m, 2H), 7.43 (s, 1H), 6.13 (s, 2H), 4.13 (s, 3H), 3.79 (s, 3H). **$^{13}$C–APT RMN (100 MHz, $CDCl_3$) δ(ppm)** = 157.41 (+), 152.45 (+), 149.06 (+), 148.97 (+), 148.02 (+), 140.99 (+), 137.81 (+), 133.53 (+), 133.40 (+), 129.54 (+), 129.12 (-), 128.57 (-), 128.17 (-), 127.89 (-), 127.49 (-), 126.60 (-), 126.49 (-), 119.89 (+), 119.51 (+), 107.99 (-), 107.88 (-), 101.81 (+), 101.80 (-), 98.77 (-), 56.21 (-), 56.02 (-). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 76.27; H, 4.68; N, 3.42; found (%): C, 76.09; H, 4.56; N, 3.58.

**2,3-dimethoxy-5-(naphtalen-1-yl)-[1,3]dioxolo[4,5-*b*]phenanthridine 6k.**




From 0.05 g (0.18 mmol) of 6-(3,4-dimetoxifenil)benzo[*d*][1,3]dioxol-5-amina **4a** and 0.042 g (0.27 mmol) of 1-naphtaldehyde **5k**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.046 g (0.113 mmol, 63%) of 2,3-dimethoxy-5-(naphtalen-1-yl)-[1,3]dioxolo[4,5-*b*]phenanthridine **6k**, $C_{26}H_{19}NO_4$ (409.44 g/mol), as a white solid, m.p. = 110–111 °C, $R_f$ = 0.45 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3051 (w), 3002 (w), 2915 (m), 2850 (m), 1614 (m), 1464 (m), 1247 (s), 1202 (s), 1034 (s), 718 (s), 641 (s), 506 (m). **$^1$H RMN (400 MHz, $CDCl_3$) δ(ppm)** = 7.99 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.83 (s, 1H), 7.75 (s, 1H), 7.68 – 7.61 (m, 2H), 7.58 (s, 1H), 7.50 – 7.45 (m, 2H), 7.34 – 7.29 (m, 1H), 6.89 (s, 1H), 6.14 (s, 2H), 4.13 (s, 3H), 3.56 (s, 3H). **$^{13}$C–APT RMN (100 MHz, $CDCl_3$) δ(ppm)** = 157.04 (+), 152.66 (+), 149.08 (+), 148.99 (+), 148.14 (+), 140.97 (+), 137.60 (+), 133.93 (+), 132.31 (+), 129.16 (+), 128.94 (-), 128.37 (-), 127.54 (-), 126.36 (-), 126.27 (-), 126.08 (-), 125.51 (-), 121.17 (+), 119.72 (+), 108.10 (-), 107.98 (-), 101.83 (+), 101.62 (-), 98.84 (-), 56.23 (-), 55.86 (-). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 76.27; H, 4.68; N, 3.42; found (%): C, 76.39; H, 4.56; N, 3.56.

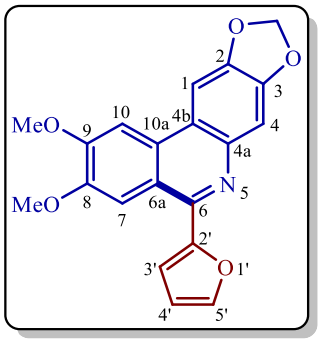
**2,3-dimethoxy-5-(pyridin-4-yl)-[1,3]dioxolo[4,5-*b*]phenanthridine 6m.**




From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.029 g (0.27 mmol) of 4-pyridincarbaldehyde **5m**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL

of ionic liquid [Bmim]$BF_4$, it was obtained 0.04 g (0.109 mmol, 61%) of 2,3-dimethoxy-5-(pyridin-4-yl)-[1,3]dioxolo[4,5-*b*]phenanthridine **6m**, $C_{21}H_{16}N_2O_4$ (360.37 g/mol), as a white solid; m.p. = 242 °C, $R_f$ = 0.32 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ ($cm^{-1}$)]** = 3044 (w), 2955 (m), 2920 (m), 2836 (m), 1618 (m), 1596 (m), 1458 (s), 1411 (s), 1258 (s), 1038 (s), 830 (s), 723 (s), 613 (m), 569 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.80 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.71 (s, 1H), 7.67 (s, 1H), 7.65 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.48 (s, 1H), 7.24 (s, 1H), 6.12 (s, 2H), 4.11 (s, 3H), 3.85 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 154.47 (+), 152.71 (+), 150.13 (-), 149.35 (+), 149.16 (+), 148.48 (+), 148.12 (+), 140.74 (+), 129.57 (+), 124.47 (-), 119.83 (+), 118.95 (+), 107.77 (-), 106.77 (-), 101.95 (1C, -$OCH_2O$-, +), 101.90 (-), 98.72 (-), 56.23 (-), 56.06 (-). **GC/MS (70 eV), $t_R$** = 85.023 min.; *m*/*z* (%) = 361.10 (M+1, 23), 360.10 ($M^{+\bullet}$, 100), 359.10 (21), 345.10 (32), 330.10 (27). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 69.99; H, 4.48; N, 7.77; found (%): C, 70.03; H, 4.59; N, 7.86.

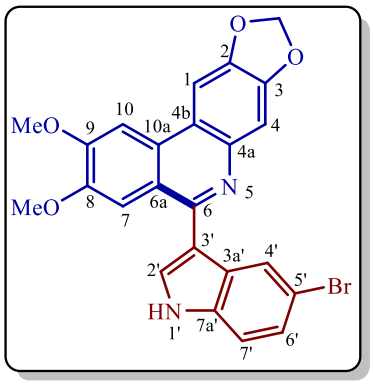
**5-(furan-2-yl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine 6n.**




From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** and 0.026 g (0.27 mmol) of 2-furancarbaldehyde **5n**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.04 g (0.113 mmol, 63%) of 5-(furan-2-yl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine **6n**, $C_{20}H_{15}NO_5$ (349.34 g/mol), as a white solid; m.p. = 180–182 °C, $R_f$ = 0.43 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ ($cm^{-1}$)]** = 3132 (m), 3002 (w), 1961 (m), 2897 (m), 2839 (m), 1781 (w), 1619 (m), 1459 (vs), 1244 (vs), 1154 (vs), 1015 (s), 849 (s), 760 (s), 600 (m), 551 (m). **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.07 (s, 1H), 7.71 (dd, $^3J$ = 1.8, $^3J$ = 0.7 Hz, 1H, 5'-H), 7.63 (s, 1H), 7.59 (s, 1H), 7.49 (s, 1H), 7.16 (dd, $^3J$ = 3.4, $^3J$ =0.7 Hz, 1H, 3'-H), 6.64 (dd, $^3J$ = 3.4, $^3J$ = 1.8 Hz, 1H, 4'-H), 6.11 (s, 2H), 4.09 (s, 3H), 4.02 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 154.04 (+), 152.29 (+), 149.34 (+), 148.98 (+), 148.14 (+), 146.01 (+), 143.52 (-), 140.77 (+), 129.74 (+), 119.54 (+), 118.75 (+), 112.21 (-), 111.79 (-), 107.61 (-), 107.04 (-), 101.82 (1C, -$OCH_2O$-, +), 101.66 (-), 98.68 (-), 56.07 (-), 56.03 (-). **GC/MS (70 eV), $t_R$** = 77.296 min.; *m*/*z* (%) = 350.10 (M+1, 23), 349.10 ($M^{+\bullet}$, 100), 306.10 (10), 177.00 (9), 174.60

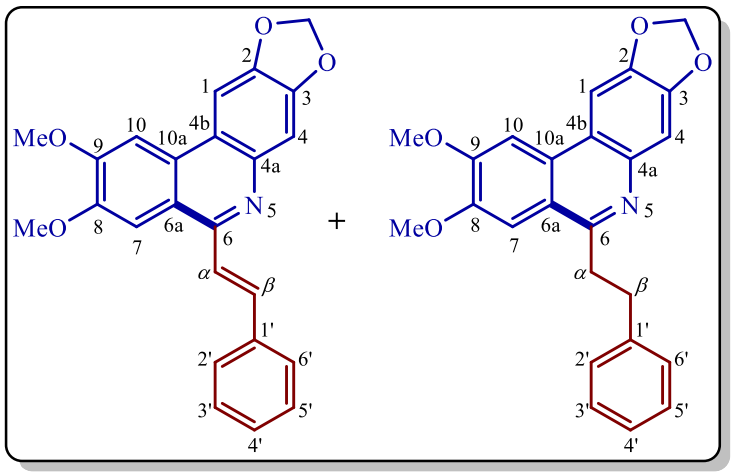
(9). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 68.76; H, 4.33; N, 4.01; found (%): C, 68.79; H, 4.27; N, 3.97.

**5-(5-bromo-1*H*-indol-3-yl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine 6o.**



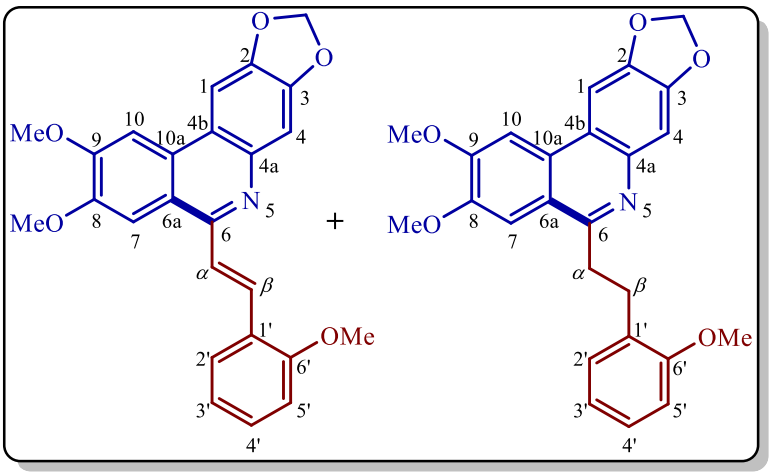

From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** y 0.060 g (0.27 mmol) of 4-bromo-1*H*-indol-3-carbaldehyde **5o**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.072 g (0.151 mmol, 84%) of 5-(4-bromo-1*H*-indol-3-yl)-2,3-dimethoxy-[1,3]dioxolo[4,5-*b*]phenanthridine **6o**, $C_{24}H_{17}BrN_2O_4$ (477.31 g/mol), as a pale yellow solid, m.p. = 198 °C, $R_f$ = 0.52 (30% ethyl acetate–petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3222 (m), 2917 (m), 1651 (m), 1616 (m), 1462 (s), 1254 (s), 1200 (s), 1156 (s), 1032 (s), 942 (m). **$^1$H RMN (400 MHz, DMSO–$d_6$) δ(ppm)** = 11.81 (d, $^3J$ = 1.8 Hz, 1H), 8.30 (s, 1H), 8.11 (d, $J$ = 2.6 Hz, 1H), 8.07 (s, 1H), 8.06 (d, $J$ = 2.1 Hz, 1H), 7.75 (s, 1H), 7.50 (d, $^3J$ = 8.6 Hz, 1H), 7.40 (s, 1H), 7.32 (dd, $^3J$ = 8.6, $^4J$ = 2.0 Hz, 1H), 6.22 (s, 2H), 4.07 (s, 3H), 3.82 (s, 3H). **$^{13}$C–APT RMN (100 MHz, DMSO–$d_6$) δ(ppm)** = 152.28 (+), 151.11 (+), 148.82 (+), 148.48 (+), 147.24 (+), 140.26 (+), 135.08 (+), 129.15 (+), 128.64 (-), 128.61 (+), 124.29 (-), 123.11 (-), 119.04 (+), 118.33 (+), 113.96 (+), 113.86 (-), 112.31 (+), 107.41 (-), 106.17 (-), 103.06 (-), 101.71 (1C, -$OCH_2O$-, +), 99.99 (-), 56.18 (-), 55.22 (-). Anal. Calcd. (%) for [$C_{17}H_{17}NO_5$]: C, 60.39; H, 3.59; N, 5.87; found (%): C, 60.22; H, 3.64; N, 5.93.

**(*E*)-2,3-dimethoxy-5-styryl-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-phenethyl-[1,3]dioxolo[4,5-*b*]phenanthridine mixture 6p.**



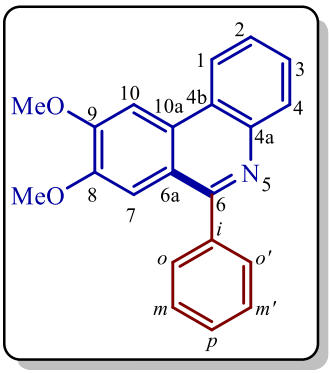
From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** y 34 μL (0.27 mmol) of cinnamaldehyde **5p**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.035 g of the (*E*)-2,3-dimethoxy-5-styryl-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-phenethyl-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6p** (3:2 ratio), $C_{24}H_{19}NO_4$ (385.42 g/mol) and $C_{24}H_{21}NO_4$ (387.44 g/mol), as a white solid, m.p. = 215–217 °C, $R_f$ = 0.46 and 0.41 (30% ethyl acetate–petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3063 (w), 3022 (w), 2963 (m), 2916 (m), 2841 (m), 1618 (m), 1456 (s), 1257 (s), 1205 (s), 1157 (s), 1033 (s), 945 (m), 836 (s), 469 (m). **$^1$H RMN (400 MHz, $CDCl_3$) δ(ppm)** = 7.98, 7.94, 7.85, 7.81, 7.71, 7.69, 7.66, 7.64, 7.61, 7.59, 7.58, 7.49, 7.48, 7.44, 7.43, 7.41, 7.33, 7.32, 7.31, 7.31, 7.26, 6.11, 6.10, 4.09, 4.09, 4.07, 3.97, 3.56, 3.54, 3.53, 3.52, 3.27, 3.26, 3.25, 3.24, 3.23. **$^{13}$C–APT RMN (100 MHz, $CDCl_3$) δ(ppm)** = 157.16, 152.24, 151.23, 149.16, 149.08, 148.94, 148.73, 147.76, 147.53, 142.33, 141.07, 137.27, 135.92, 129.20, 128.85, 128.65, 128.57, 127.53, 126.19, 123.86, 119.83, 119.72, 119.63, 119.21, 107.49, 105.45, 104.95, 101.99, 101.90, 101.75, 101.71, 98.83, 98.76, 56.17, 56.12, 56.06, 37.87, 35.18. **GC/MS (70 eV), $t_R$** = 88.578 min.; *m*/*z* (%) = 387.20 ($M^{+}$•, 100), 386.20 (44), 372.10 (77), 310.10 (23), 91.00 (45); **$t_R$** = 109.626 min.; *m*/*z* = 386.10 (M+1, 25), 385.10 ($M^{+}$•, 82), 371.10 (25), 370.10 (100), 327.10 (24).

**(*E*)-2,3-dimethoxy-5-(2-methoxystyryl)-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-(2-methoxyphenethyl)-[1,3]dioxolo[4,5-*b*]phenanthridine mixture 6q.**



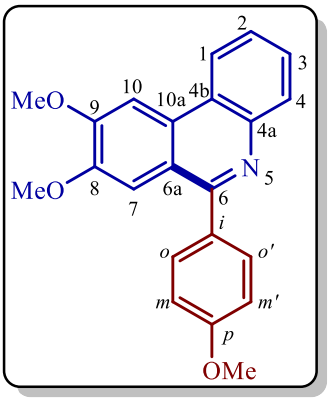

From 0.05 g (0.18 mmol) of 6-(3,4-dimethoxyphenyl)benzo[*d*][1,3]dioxol-5-amine **4a** y 0.046 g (0.27 mmol) of (*E*)-3-(2-methoxyphenyl)acrylaldehyde **5q**, 2.5 mg (0.018 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.034 g of (*E*)-2,3-dimethoxy-5-(2-methoxystyryl)-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-(2-methoxyphenethyl)-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6q** (3:2 ratio), $C_{22}H_{21}NO_5$ (415.45 g/mol) and $C_{22}H_{23}NO_5$ (417.45 g/mol), as a pale yellow solid, m.p. = 198 °C, $R_f$ = 0.52 (30% ethyl acetate–petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3065 (w), 2966 (w), 2910 (m), 2834 (w), 1618 (m), 1464 (s), 1257 (m), 1119 (s), 1036 (s), 840 (m), 943 (m), 728 (m), 529 (m). **$^1$H RMN (400 MHz, DMSO–$d_6$) δ(ppm)** = 8.22, 8.18, 7.93, 7.89, 7.74, 7.74, 7.72, 7.72, 7.66, 7.63, 7.61, 7.59, 7.53, 7.51, 7.47, 7.34, 7.33, 7.30, 7.30, 7.29, 7.28, 7.28, 7.23, 7.23, 7.21, 7.21, 7.19, 7.19, 7.04, 7.03, 7.02, 7.00, 6.96, 6.96, 6.94, 6.94, 6.92, 6.92, 6.90, 6.90, 6.89, 6.87, 6.10, 6.09, 4.09, 4.06, 4.02, 3.93, 3.81, 3.53, 3.51, 3.49, 3.23, 3.21, 3.19. **$^{13}$C–APT RMN (100 MHz, DMSO–$d_6$) δ(ppm)** = 158.18, 157.89, 157.74, 156.84, 152.10, 152.05, 149.02, 148.97, 148.82, 148.62, 147.60, 147.37, 141.17, 140.77, 131.41, 130.49, 130.46, 130.28, 129.60, 129.16, 129.14, 128.86, 128.16, 127.88, 127.52, 126.44, 125.08, 120.80, 120.79, 120.18, 119.91, 119.88, 119.50, 119.19, 111.10, 110.49, 107.61, 107.32, 106.11, 105.29, 101.87, 101.85, 101.68, 98.80, 98.73, 56.07, 56.05, 56.00, 55.62, 55.56, 55.45, 55.34, 36.88, 30.68.

**8,9-dimethoxy-6-phenylphenanthridine 6r.**




From 0.05 g (0.22 mmol) of *N*-3',4'-dimethoxy-[1,1'-biphenyl]-2-amine **4b** and 34 µL (0.33 mmol) of benzaldehyde **5a**, 3 mg (0.022 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.042 g (0.12 mmol, 60%) of 8,9-dimethoxy-6-phenylphenanthridine **6r**, $C_{21}H_{17}NO_2$ (315.37 g/mol), as a white solid m.p. = 153-155 °C, $R_f$ = 0.44 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3052, 2997, 2917, 2825, 1614, 1520, 1258, 1033, 752, 701. **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.47 (dd, $^3J$ = 8.2 Hz, $^4J$ = 1.2 Hz, 1H), 8.22 (dd, $^3J$ = 8.1, $^4J$ = 1.1 Hz, 1H), 7.97 (s, 1H), 7.75 (dd, $J$ = 8.0, 1.4 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.66 – 7.61 (m, 1H), 7.59 – 7.51 (m, 3H), 7.43 (s, 1H), 4.15 (s, 3H), 3.86 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 159.77 (+), 152.59 (+), 149.46 (+), 143.61 (+), 140.21 (+), 130.42 (-), 129.64 (-), 129.43 (+), 128.79 (-), 128.62 (-), 128.11 (-), 126.59 (-), 123.62 (+), 121.61 (-), 120.59 (+), 108.51 (-), 102.24 (-), 56.26 (-), 56.02 (-).Anal. Calcd. (%) for [$C_{21}H_{17}NO_2$]: C, 79.98; H, 5.43; N, 4.44; found (%): C, 80.01; H, 5.47; N, 4.32.

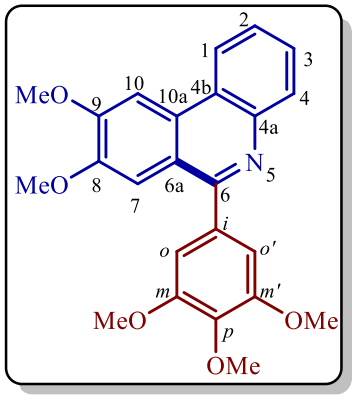
**8,9-dimethoxy-6-(4-methoxyphenyl)phenanthridine 6s.**




From 0.05 g (0.22 mmol) of *N*-3',4'-dimethoxy-[1,1'-biphenyl]-2-amine **4b** and 40 µL (0.33 mmol) of 4-methoxybenzaldehyde **5b**, 3 mg (0.022 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.051 g (0.145 mmol, 66%) of 8,9-dimethoxy-6-(4-

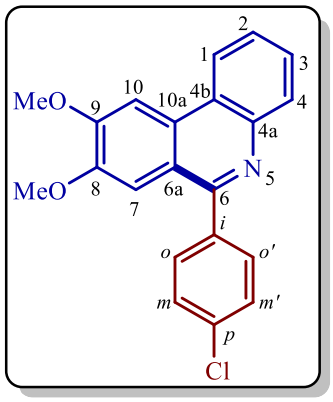
methoxyphenyl)phenanthridine **6s**, $C_{22}H_{19}NO_3$ (345.40 g/mol), as a white solid; m.p. = 157–158 °C, $R_f$ = 0.56 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3005, 2933, 2835, 1604, 1249, 1225, 1022, 741. **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.45 (dd, $^3J$ = 8.0, $^4J$ = 0.9 Hz, 1H), 8.19 (dd, $^3J$ = 8.1, $^4J$ = 1.4 Hz, 1H), 7.95 (s, 1H), 7.71 (d, $^3J$ = 8.8 Hz, 2H), 7.69 – 7.66 (m, 1H), 7.62 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.4 Hz, 1H), 7.49 (s, 1H), 7.09 (d, $^3J$ = 8.8 Hz, 2H), 4.15 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 160.14 (+), 159.42 (+), 152.46 (+), 149.38 (+), 143.73 (+), 132.79 (+), 131.03 (-), 130.38 (-), 129.41 (+), 128.04 (-), 126.38 (-), 123.49 (+), 121.57 (-), 120.68 (+), 114.07 (-), 108.56 (-), 102.24 (-), 77.16 (-), 56.24 (-), 56.05 (-), 55.54 (-). Anal. Calcd. (%) for [$C_{22}H_{19}NO_3$]: C, 76.50; H, 5.54; N, 4.06; found (%): C, 75.97; H, 5.42; N, 4.31.

**8,9-dimethoxy-6-(3,4,5-trimethoxyphenyl)phenanthridine 6t.**



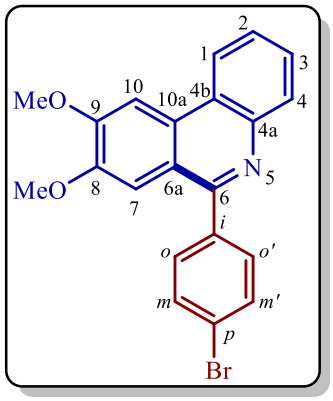

From 0.05 g (0.22 mmol) of *N*-3',4'-dimethoxy-[1,1'-biphenyl]-2-amine **4b** and 0.065 g (0.33 mmol) of 3,4,5-trimethoxybenzadehyde **5d**, 3 mg (0.022 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.053 g (0.128 mmol, 59%) of 8,9-dimethoxy-6-(3,4,5-trimethoxyphenyl)phenanthridine **6t**, $C_{24}H_{23}NO_5$ (405.45 g/mol), as a white solid; m.p. = 176-178 °C, $R_f$ = 0.66 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2996, 2930, 2836, 1584, 1410, 1122, 1018, 754, 638, 577. **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.48 (dd, $^3J$ = 8.1, $^4J$ = 1.4 Hz, 1H), 8.21 (d, $^3J$ = 7.8 Hz, 1H), 7.99 (s, 1H), 7.71 (ddd, $^3J$ = 8.2, $^3J$ = 7.0, $^4J$ = 1.5 Hz, 1H), 7.65 (ddd, $^3J$ = 8.3, $^3J$ = 7.0, $^4J$ = 1.5 Hz, 1H), 7.52 (s, 1H), 6.97 (s, 2H), 4.17 (s, 3H), 3.94 (s, 3H), 3.92 (s, 6H), 3.90 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 159.51 (+), 153.48 (+), 152.70 (+), 149.52 (+), 135.81 (+), 130.44 (-), 129.53 (+), 128.21 (-), 126.69 (-), 123.63 (+), 121.65 (-), 120.49 (+), 108.46 (-), 106.95 (-), 102.30 (-), 77.16 (-), 61.10 (-), 56.40 (-), 56.32 (-), 56.18 (-). Anal. Calcd. (%) for [$C_{24}H_{23}NO_5$]: C, 71.10; H, 5.72; N, 3.45; found (%): C, 71.29; H, 5.80; N, 3.51.

**6-(4-chlorophenyl)-8,9-dimethoxyphenanthridine 6u.**




From 0.05 g (0.22 mmol) of *N*-3',4'-dimethoxy-[1,1'-biphenyl]-2-amine **4b** and 0.047 g (0.33 mmol) of 4-chlorobenzadehyde **5i**, 3 mg (0.022 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid [Bmim]$BF_4$, it was obtained 0.046 g (0.128 mmol, 59%) of 6-(4-chlorophenyl)-8,9-dimethoxyphenanthridine **6u**, $C_{22}H_{16}ClNO_2$ (349.81 g/mol), as a white solid; m.p. = 209–211 °C, $R_f$ = 0.40 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 2992, 2944, 2914, 2833, 1613, 1519, 1256, 1204, 799, 751, 598, 445. **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.48 (dd, $^3J$ = 8.0, $^4J$ = 1.6 Hz, 1H), 8.19 (dd, $^3J$ = 7.8, $^4J$ = 1.5 Hz, 1H), 7.98 (s, 1H), 7.70 (d, $^3J$ = 8.6 Hz, 3H), 7.68 – 7.63 (m, 1H), 7.54 (d, $^3J$ = 8.6 Hz, 2H), 7.37 (s, 1H), 4.16 (s, 3H), 3.88 (s, 3H). **$^{13}$C-APT NMR (100 MHz, $CDCl_3$) δ(ppm)** = 158.49 (+), 152.73 (+), 149.63 (+), 143.60 (+), 138.77 (+), 134.94 (+), 131.07 (-), 130.47 (-), 129.53 (+), 128.91 (-), 128.74 (-), 128.26 (-), 126.82 (-), 123.66 (+), 121.67 (-), 120.37 (+), 108.04 (-), 102.36 (-), 77.16 (-), 56.32 (-), 56.11 (-). Anal. Calcd. (%) for [$C_{22}H_{16}ClNO_2$]: C, 72.10; H, 4.61; N, 4.00; found (%): C, 71.97; H, 4.63; N, 4.09.

**6-(4-bromophenyl)-8,9-dimethoxyphenanthridine 6v.**




From 0.05 g (0.22 mmol) of *N*-3',4'-dimethoxy-[1,1'-biphenyl]-2-amine **4b** and 0.061 g (0.33 mmol) of 4-bromobenzadehyde **5v**, 3 mg (0.022 mmol) of $ZnCl_2$ in 0.5 mL of ionic liquid

[Bmim]$BF_4$, it was obtained 0.053 g (0.129 mmol, 60%) of 6-(4-bromophenyl)-8,9-dimethoxyphenanthridine **6v**, $C_{21}H_{16}BrNO_2$ (394.27 g/mol), as a white solid; m.p. = 202–203 °C, $R_f$ = 0.41 (30% ethyl acetate-petroleum ether). **IR [ATR, $\bar{\nu}$ (cm$^{-1}$)]** = 3057, 2923, 2833, 1612, 1501, 1392, 1257, 1204, 1007, 926, 732, 633, 593, 500. **$^1$H NMR (400 MHz, $CDCl_3$) δ(ppm)** = 8.49 (dd, $^3J$ = 8.1, $^4J$ = 1.5 Hz, 1H), 8.21 (dd, $^3J$ = 7.8, $^4J$ = 1.4 Hz, 1H), 7.99 (s, 1H), 7.75 – 7.64 (m, 6H), 7.39 (s, 1H), 4.18 (s, 3H), 3.91 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ(ppm)** = 158.45, 152.68, 149.58, 143.57, 139.21, 131.83, 131.34, 130.45, 129.48, 128.23, 126.80, 123.62, 123.17, 121.65, 120.24, 107.94, 102.30, 77.16, 56.29, 56.10. Anal. Calcd. (%) for [$C_{21}H_{16}BrNO_2$]: C, 63.97; H, 4.09; N, 3.55; found (%): C, 64.02; H, 4.13; N, 3.69.

# 4 Copies of NMR and GC/MS spectra of products

**Figure 3**. $^{1}H$ NMR spectra of compound **3** ($CDCl_3$, 400 MHz).

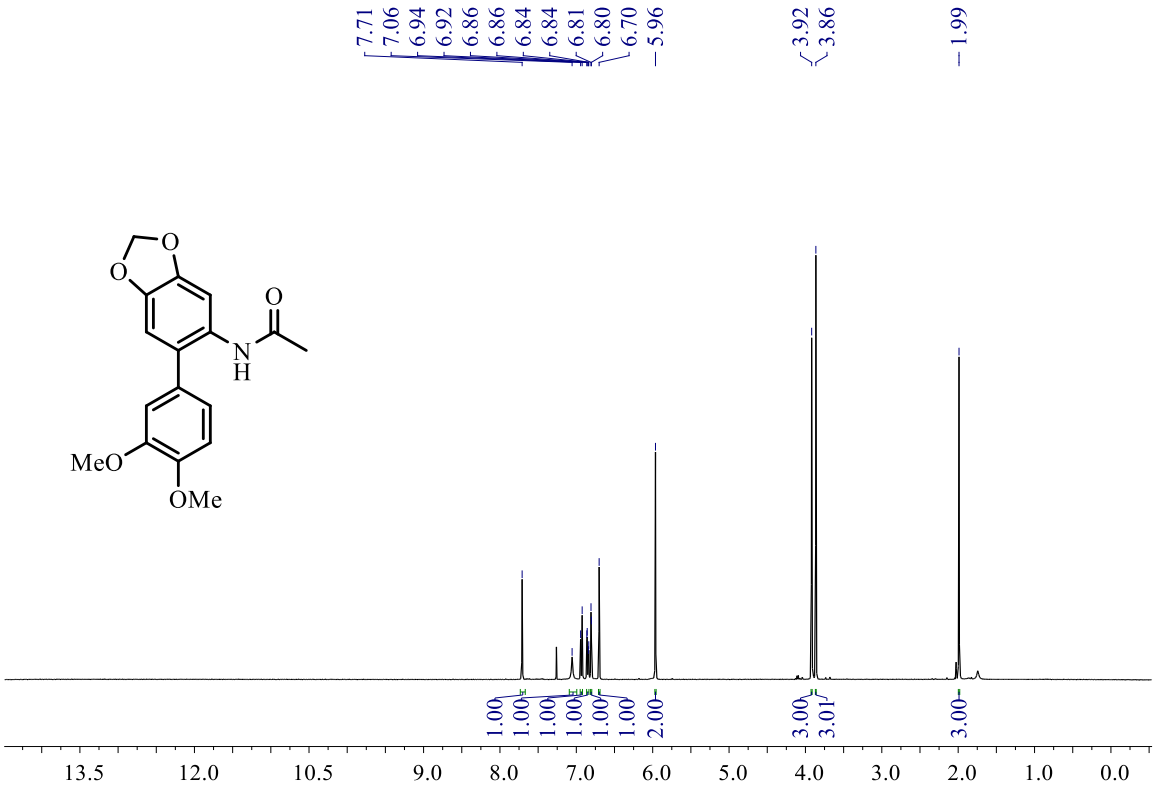


**Figure 4**. Expansion of $^{1}H$ NMR spectra of compound **3** ($CDCl_3$, 400 MHz).

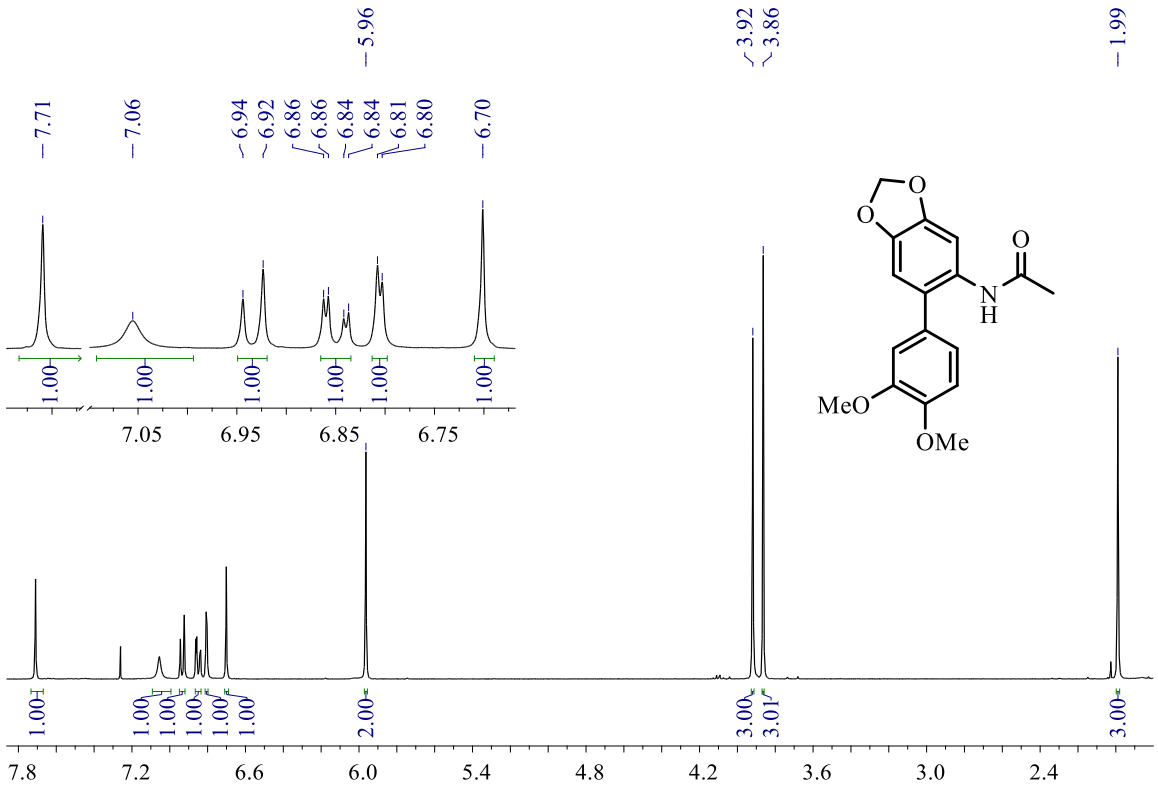


**Figure 5**. $^{13}C$ NMR spectra of compound **3** ($CDCl_3$, 100 MHz).

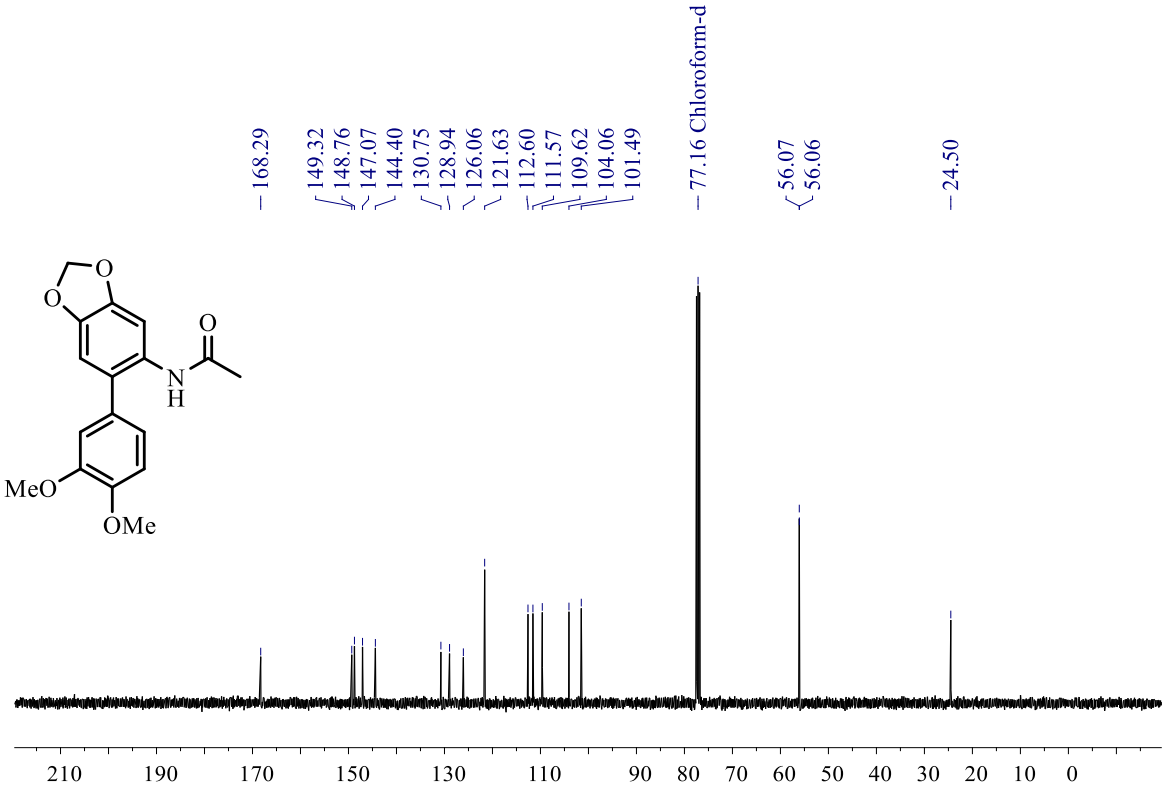


**Figure 6**. $^{13}$C-APT NMR spectra of compound **3** ($CDCl_3$, 100 MHz).

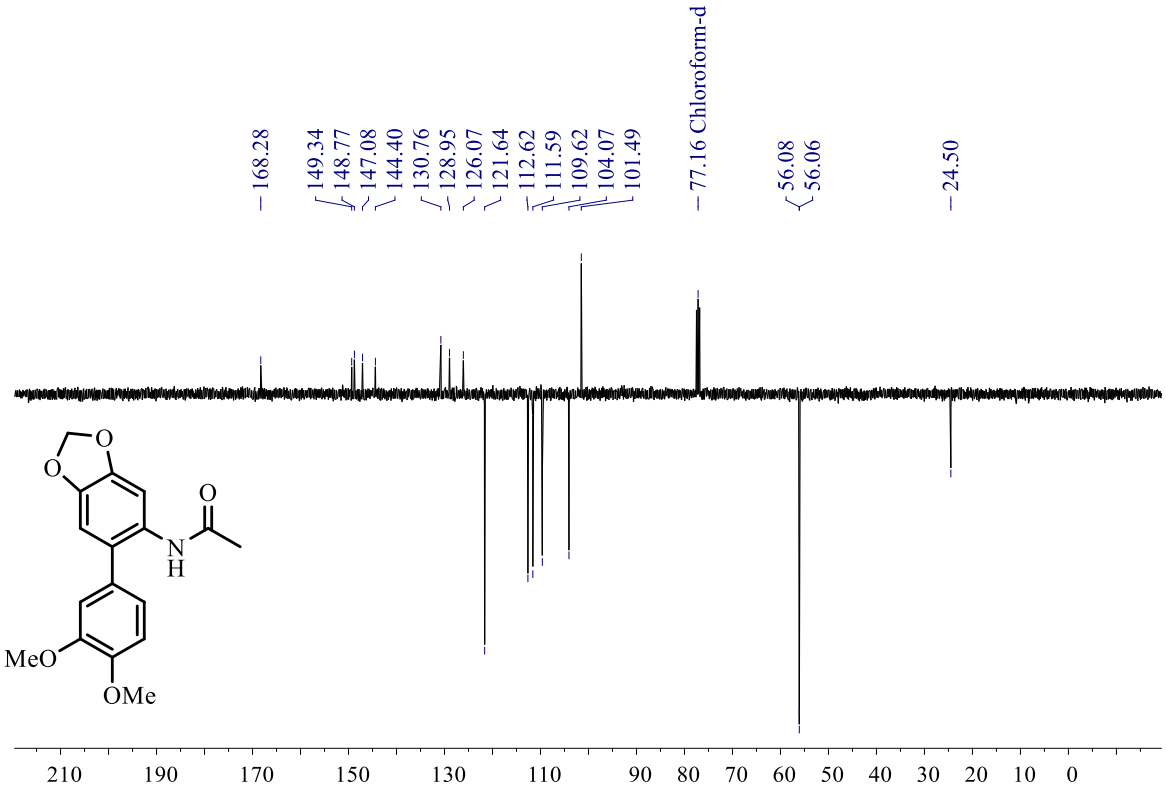


**Figure 7**. Expansion of $^{13}$C-APT NMR spectra of compound **3** ($CDCl_3$, 100 MHz).

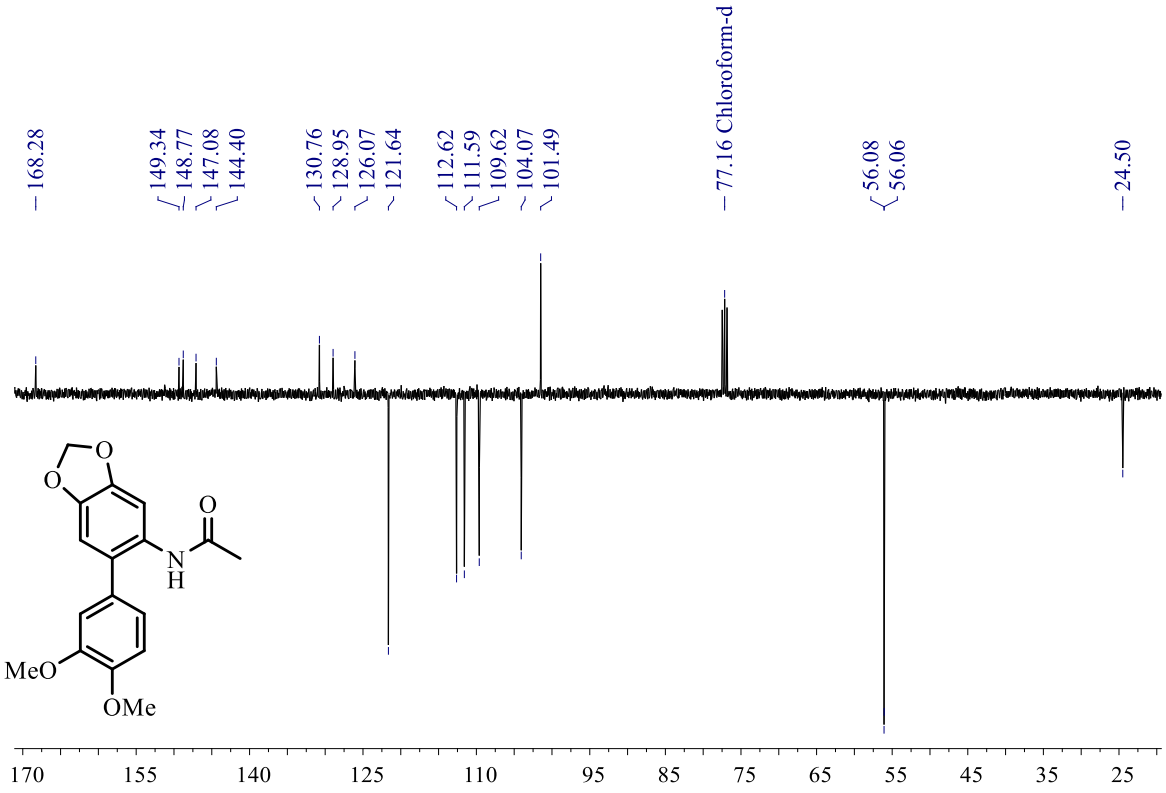


**Figure 8**. $^{1}H$ NMR spectra of compound **4** ($CDCl_3$, 400 MHz).

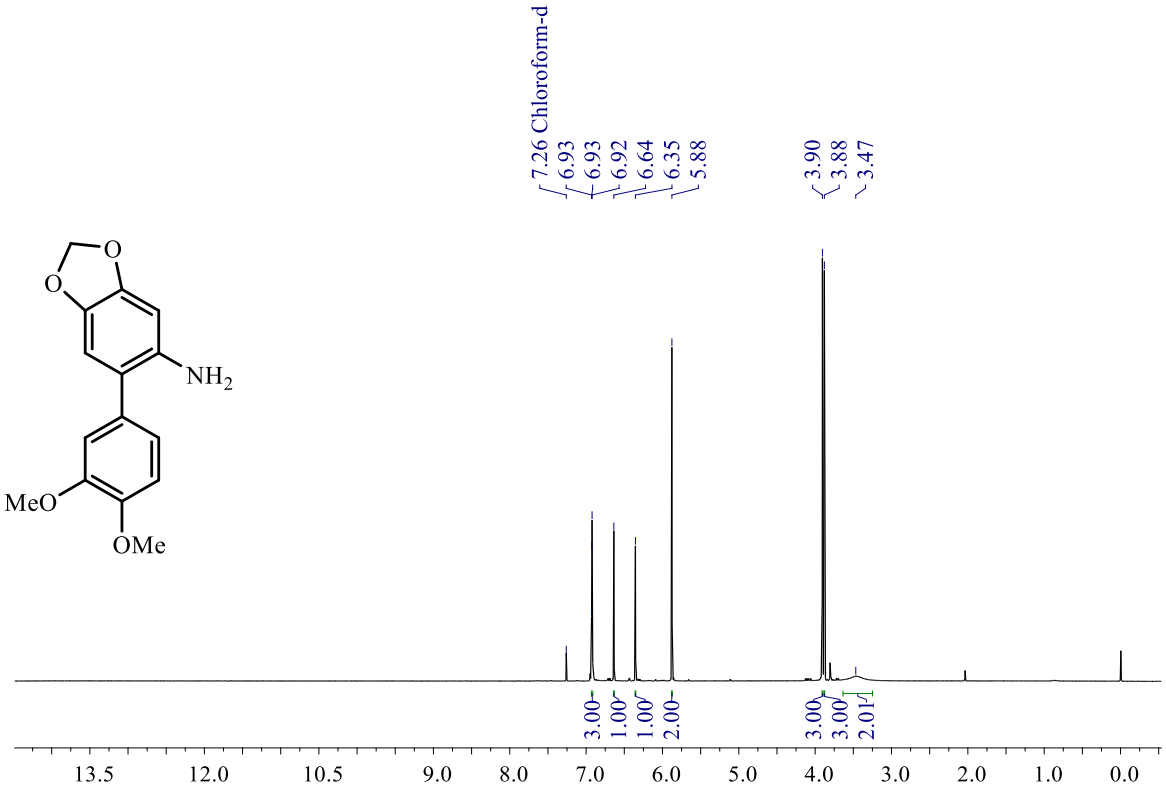


**Figure 9**. Expansion of $^{1}H$ NMR spectra of compound **4** ($CDCl_3$, 400 MHz).

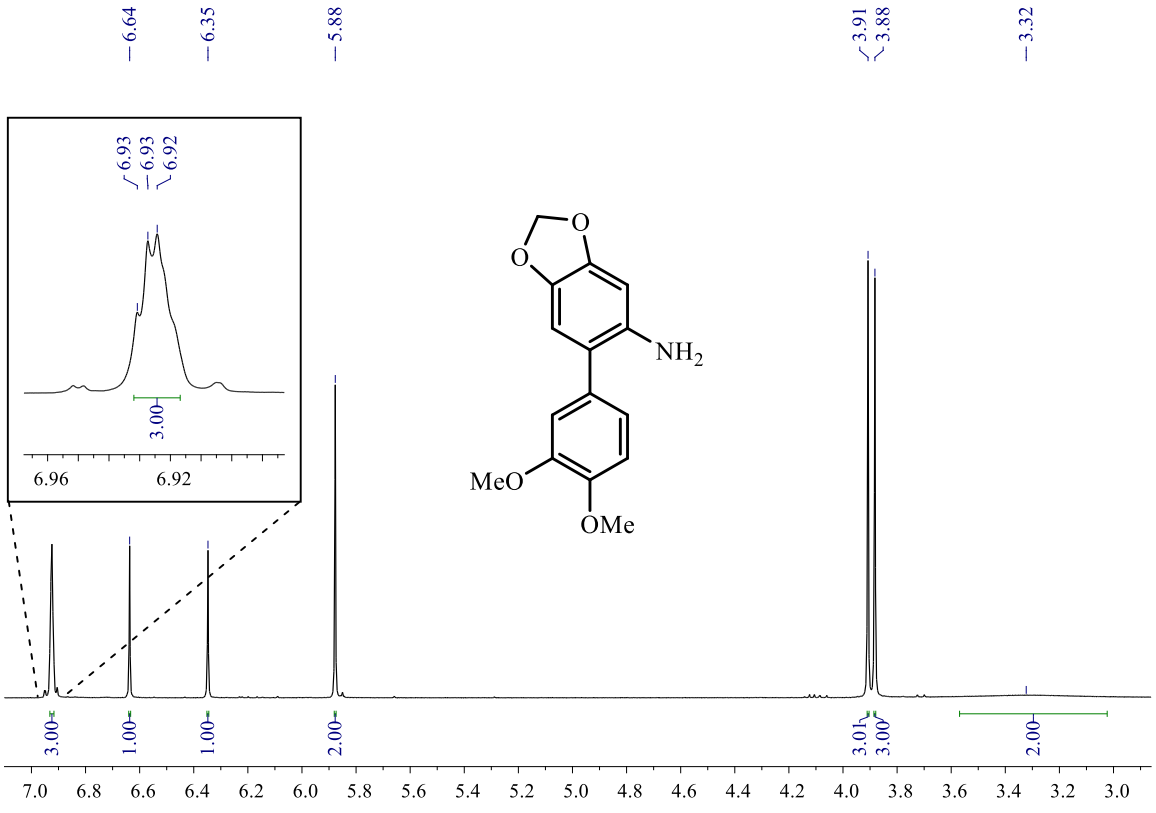


**Figure 10**. $^{13}C$ NMR spectra of compound **4** ($CDCl_3$, 100 MHz).

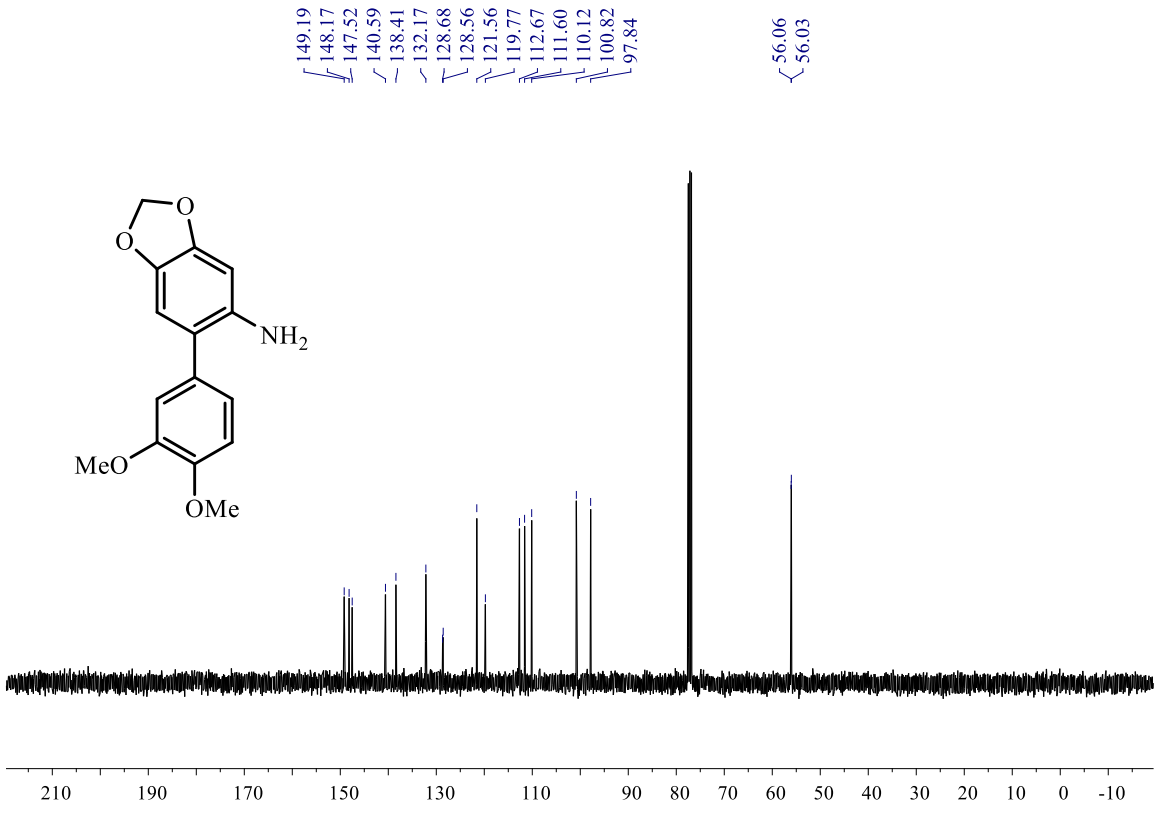


**Figure 11**. $^{13}$C-APT NMR spectra of compound **4** ($CDCl_3$, 100 MHz).

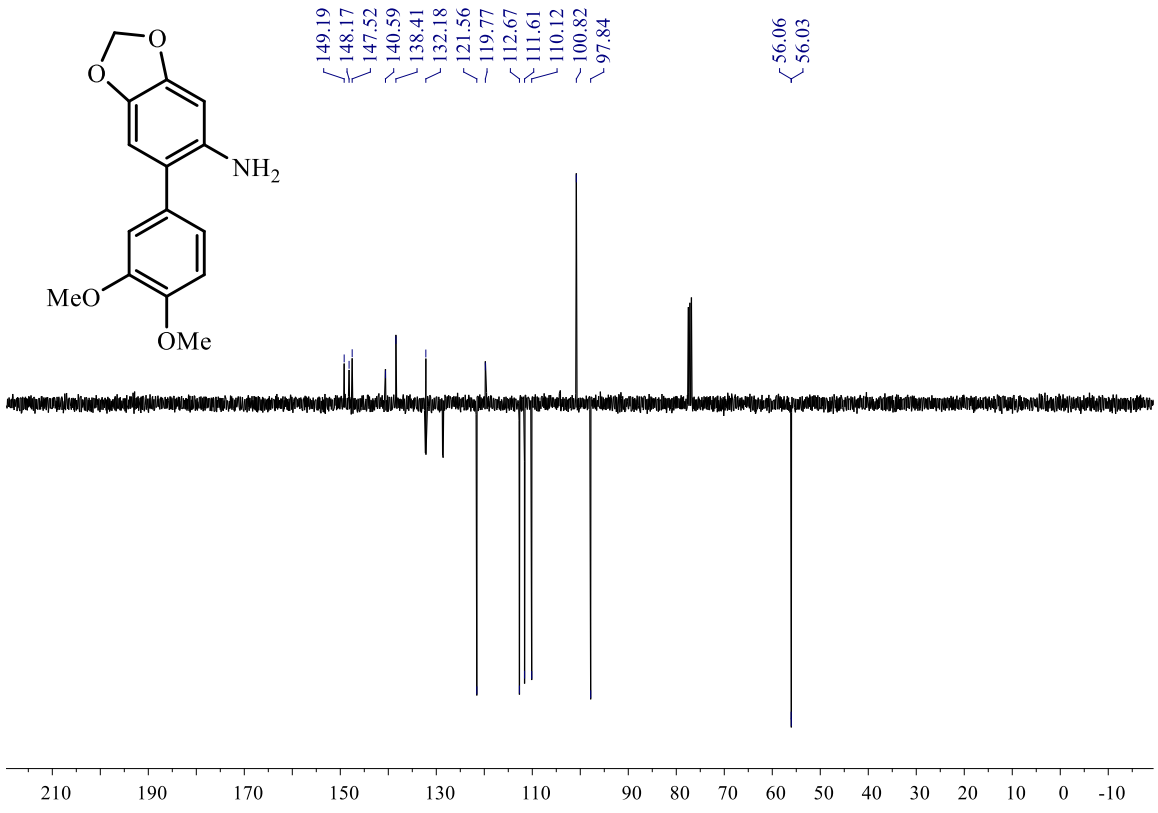


**Figure 12**. Expansion of $^{13}$C-APT NMR spectra of compound **4** ($CDCl_3$, 100 MHz).

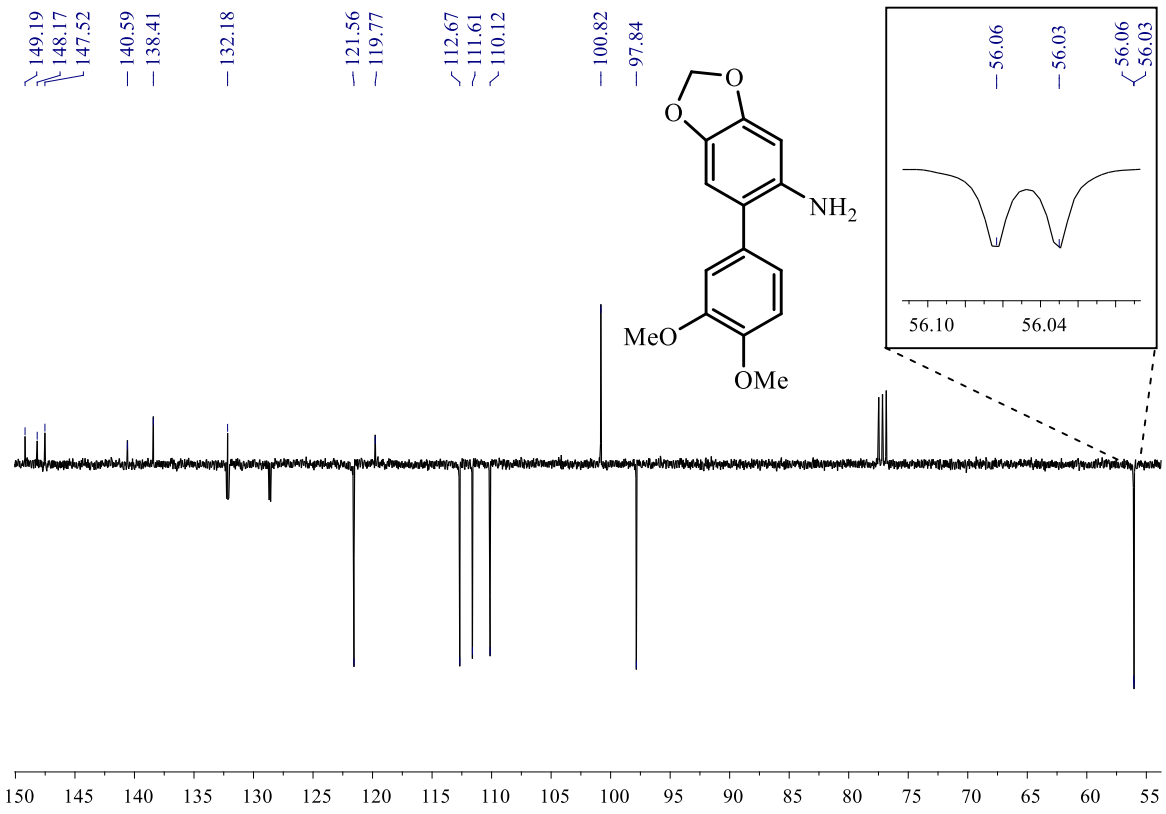


**Figure 13**. $^{1}H$ NMR spectra of compound **6a** ($CDCl_3$, 400 MHz).

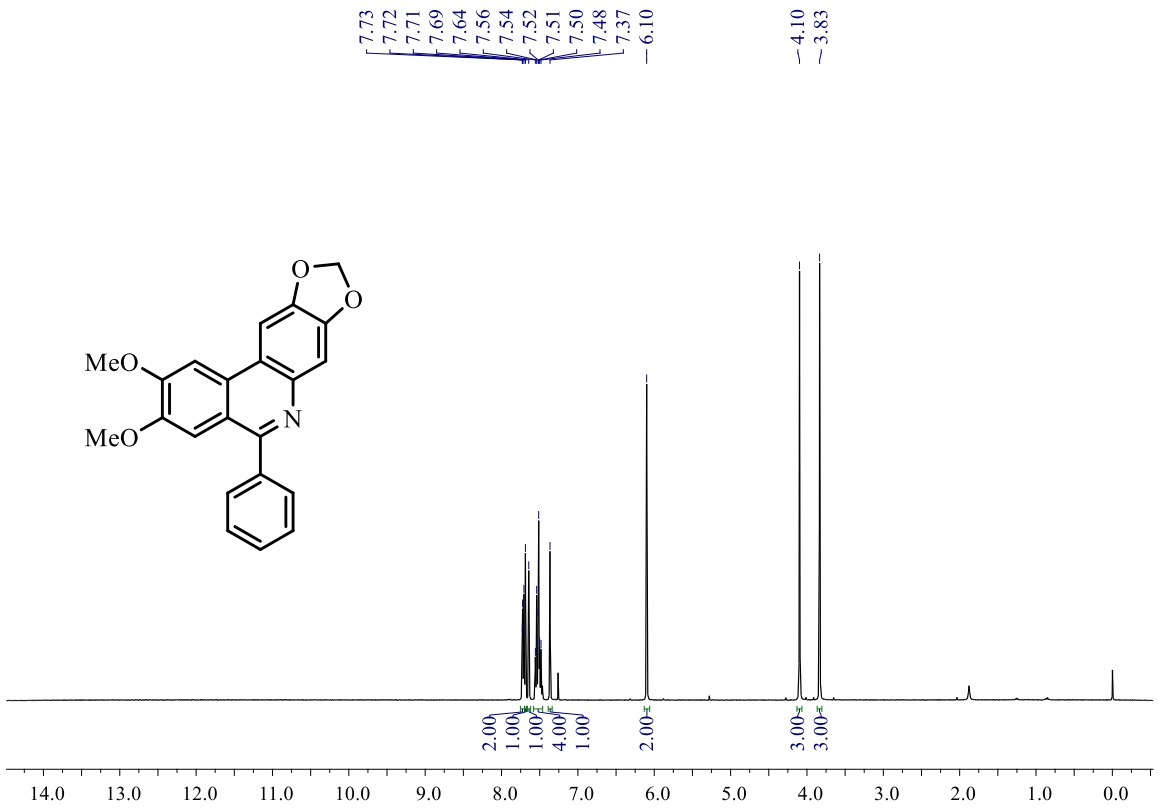


**Figura 14**. Expansion of $^{1}H$ NMR spectra of compound **6a** ($CDCl_3$, 400 MHz).

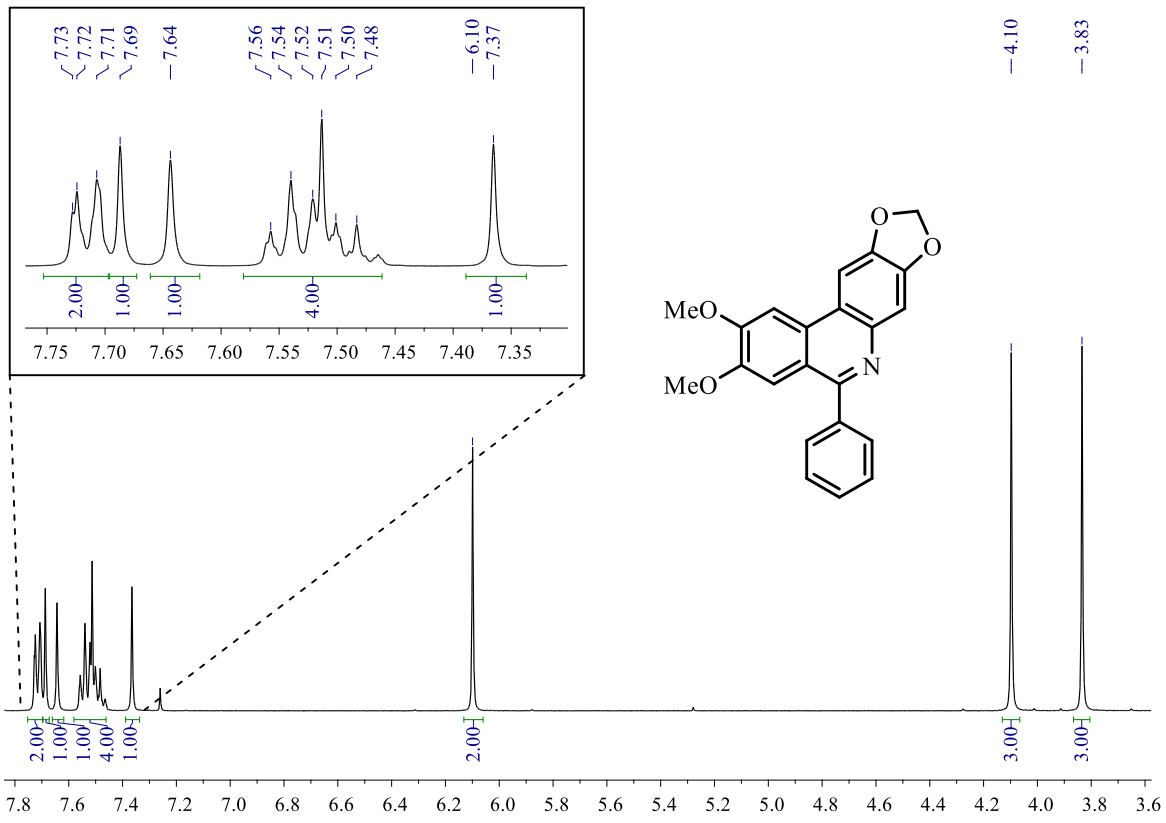


**Figure 15**. $^{13}C$ NMR spectra of compound **6a** ($CDCl_3$, 100 MHz).

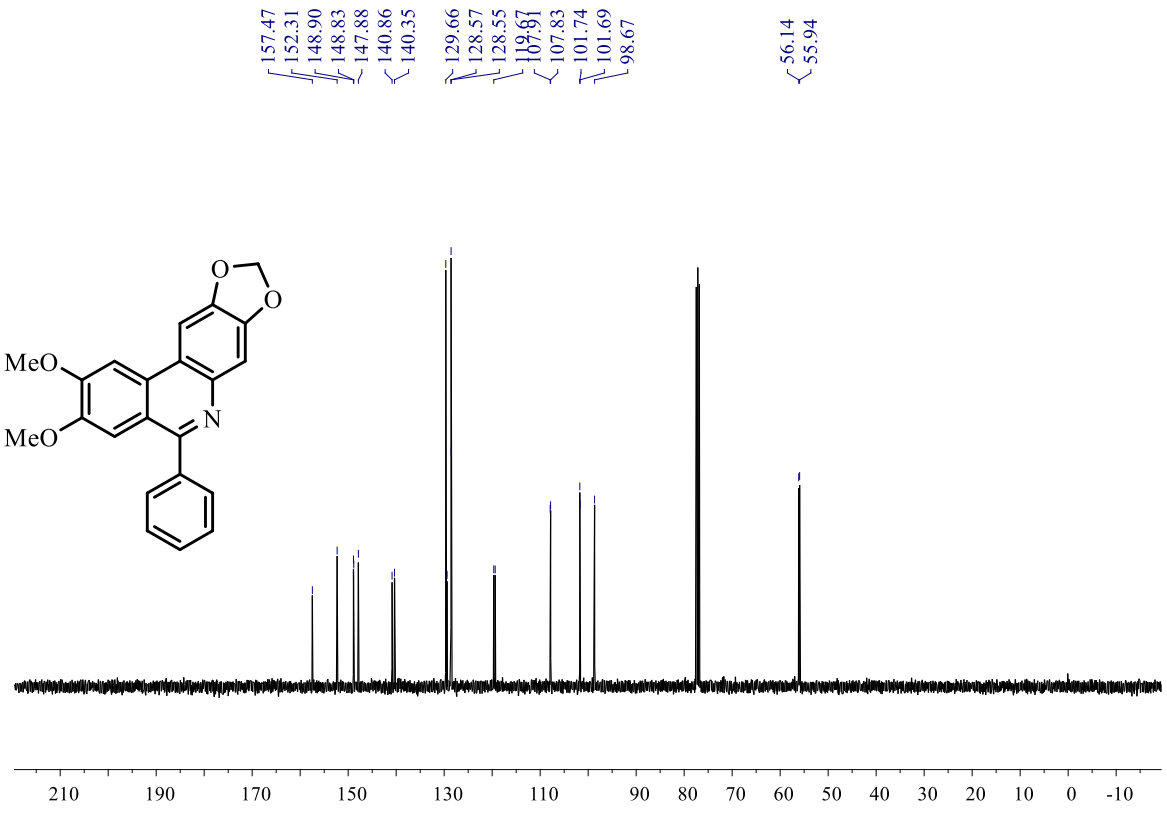


**Figure 16**. $^{13}$C-APT NMR spectra of compound **6a** ($CDCl_3$, 100 MHz).

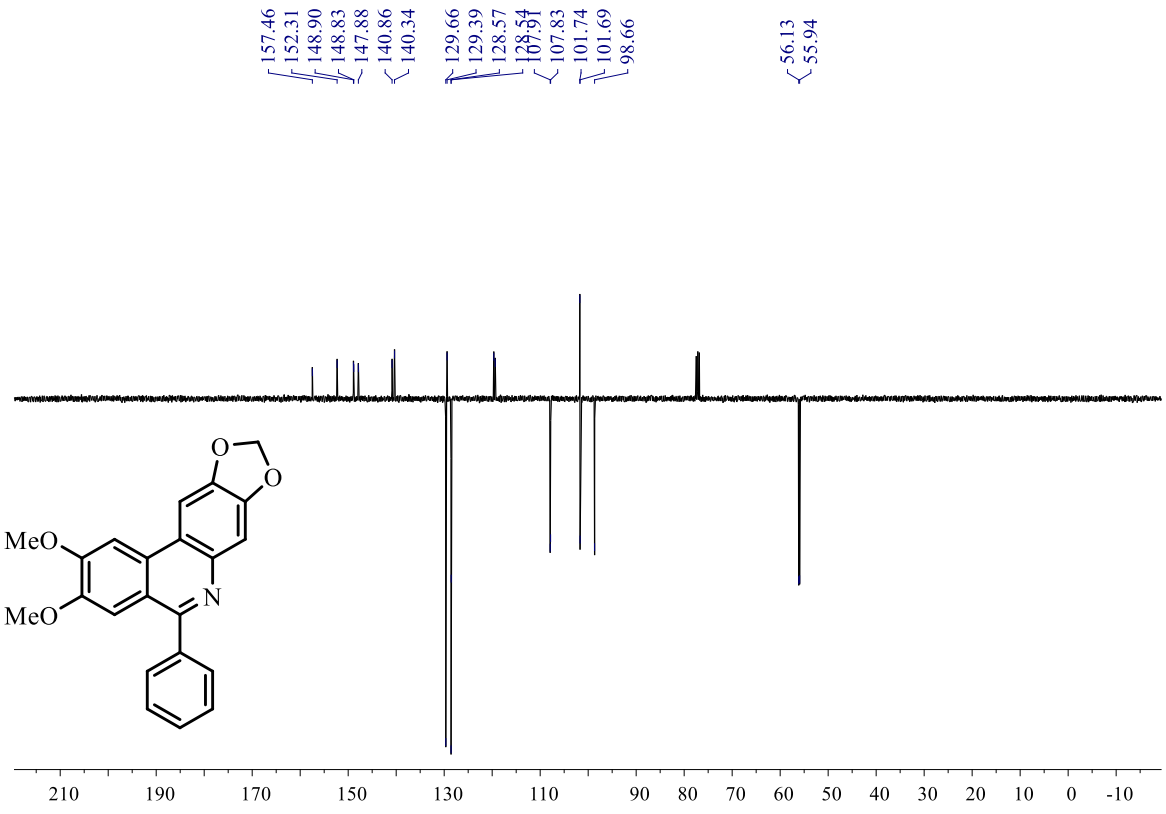


**Figure 17**. Expansion of $^{13}$C-APT NMR spectra of compound **6a** ($CDCl_3$, 100 MHz).

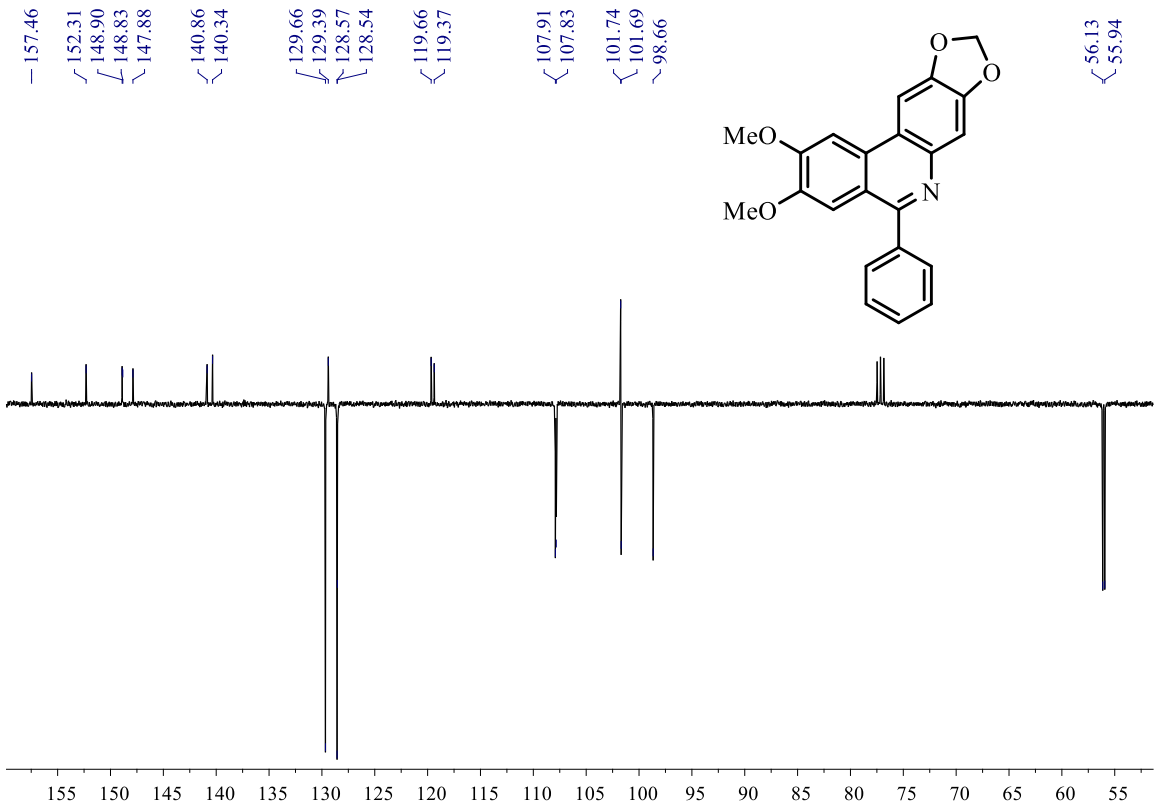


**Figure 18**. GC-MS of compound **6a** (70 eV).

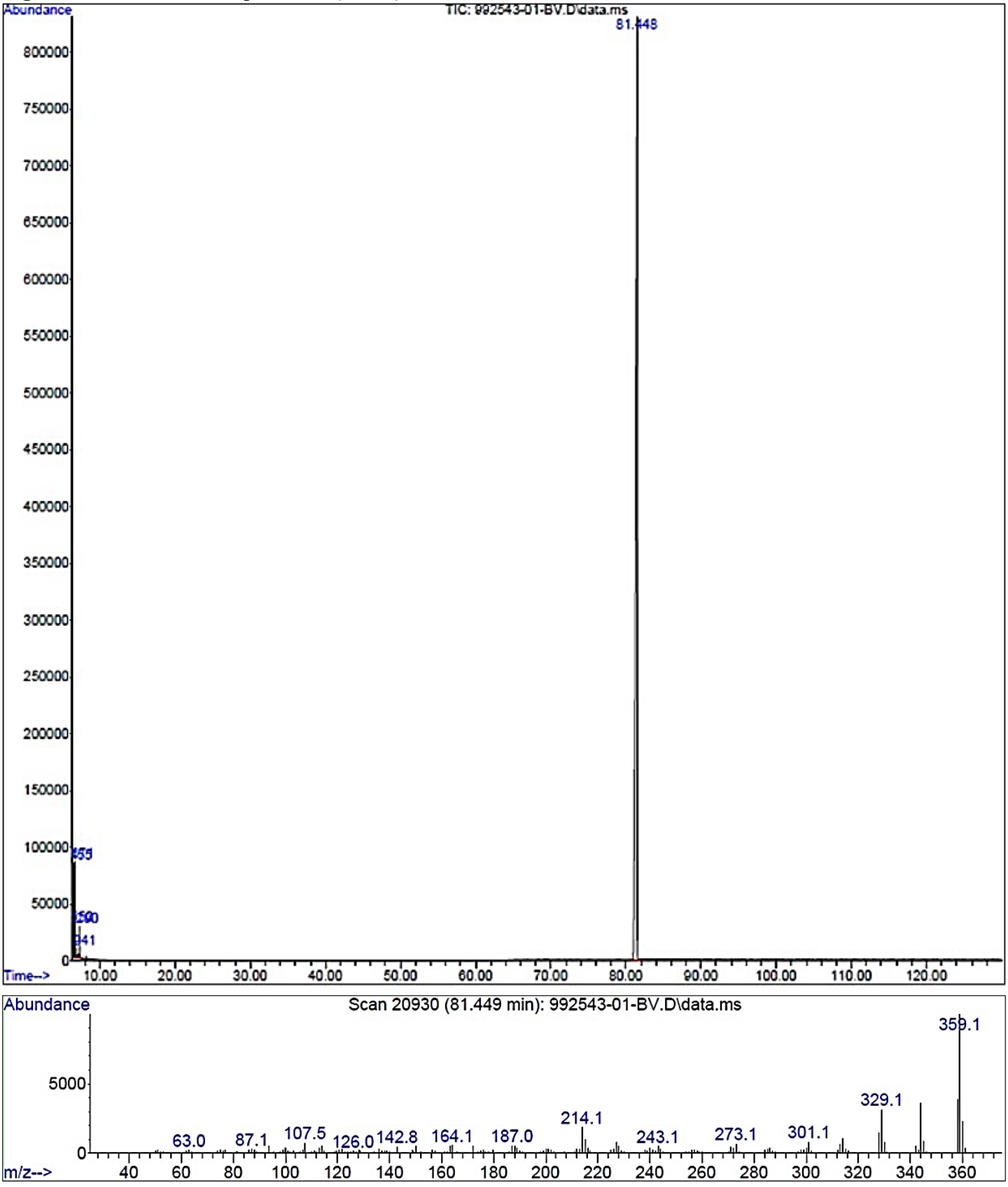


**Figure 19**. $^{1}H$ NMR spectra of compound **6b** ($CDCl_3$, 400 MHz).

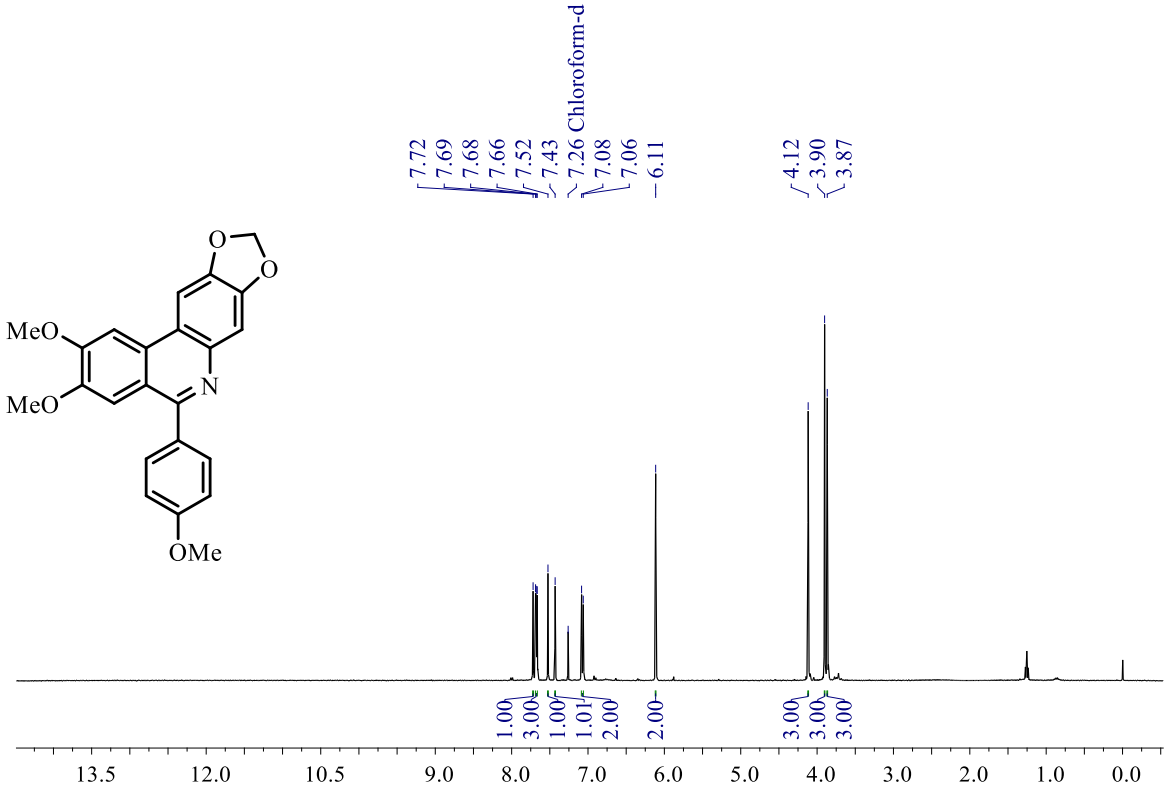


**Figure 20**. Expansion of $^{1}H$ NMR spectra of compound **6b** ($CDCl_3$, 400 MHz).

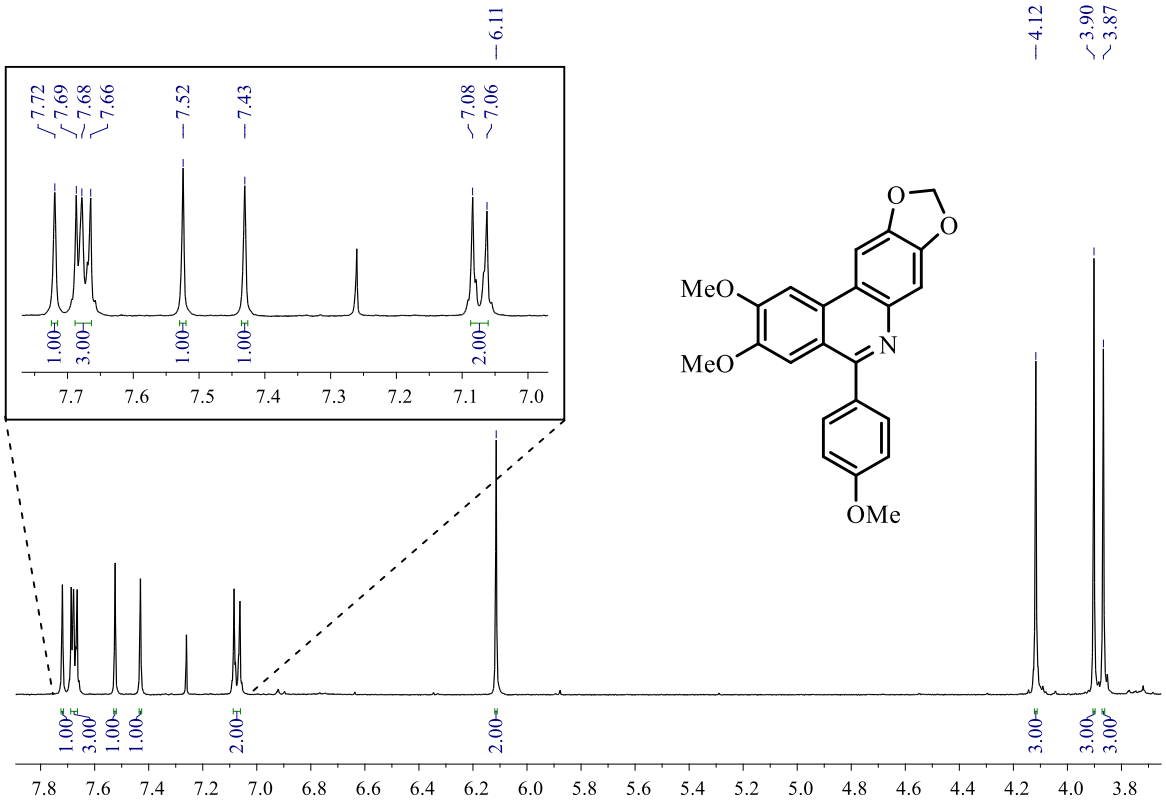


**Figure 21**. $^{13}C$ NMR spectra of compound **6b** ($CDCl_3$, 100 MHz).

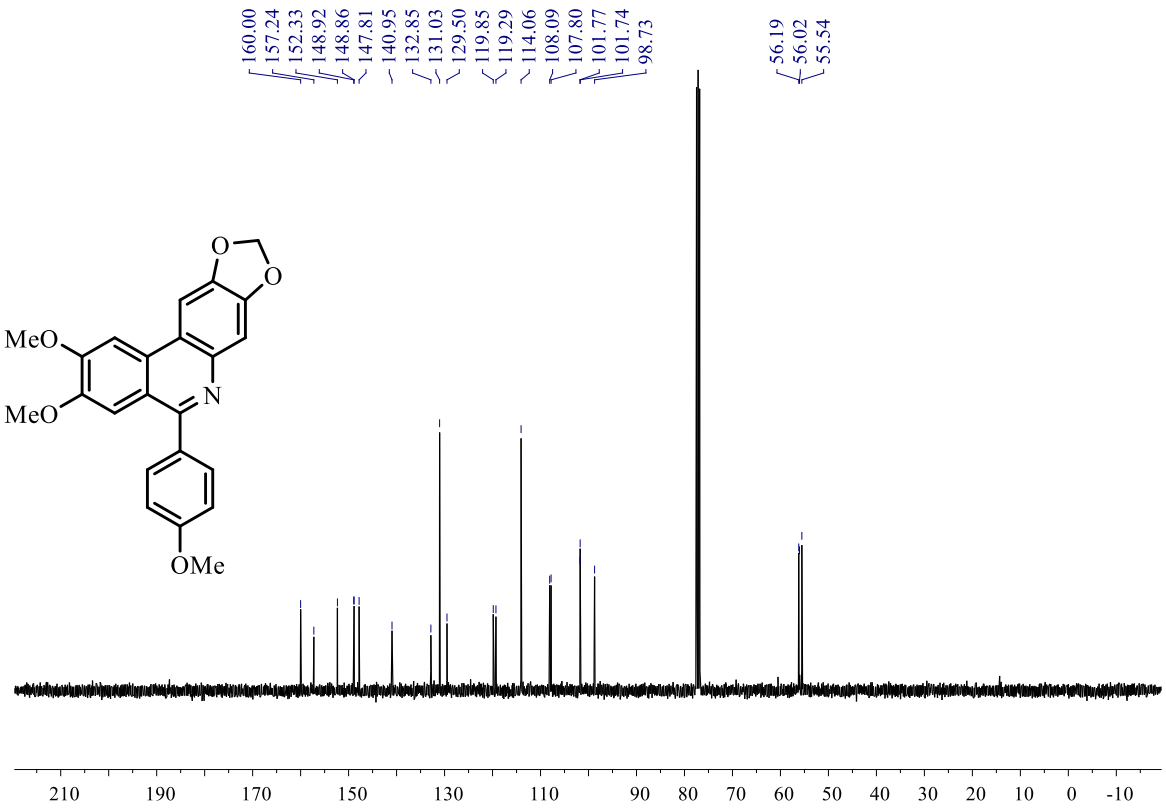


**Figure 22**. $^{13}$C-APT NMR spectra of compound **6b** ($CDCl_3$, 100 MHz).

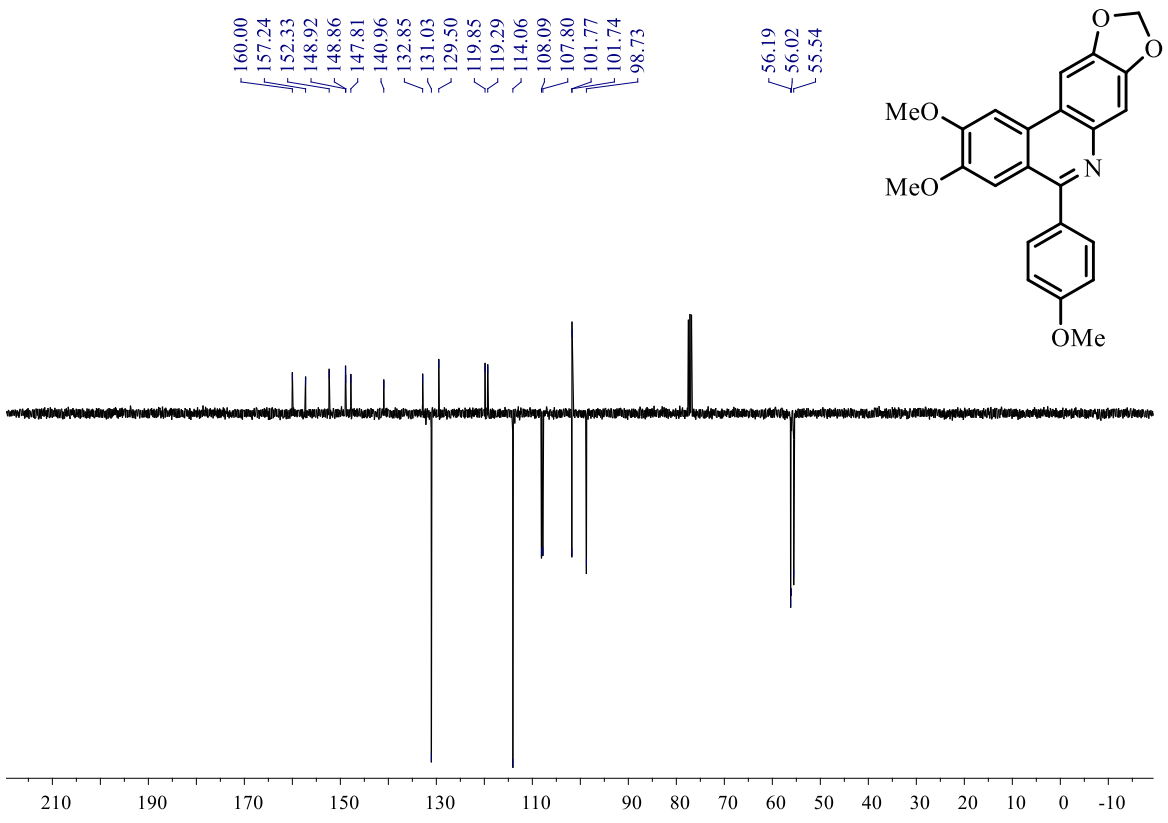


**Figure 23**. Expansion of $^{13}$C-APT NMR spectra of compound **6b** ($CDCl_3$, 100 MHz).

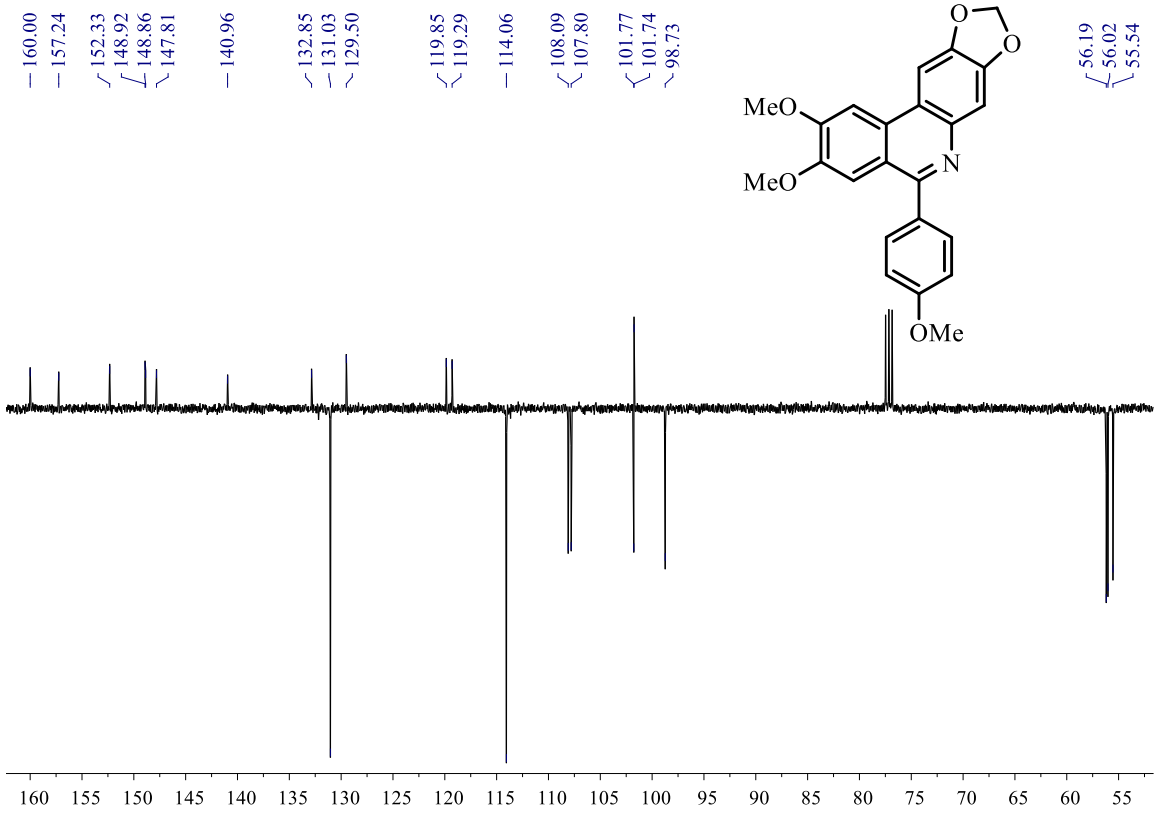


**Figure 24**. GC-MS of compound **6b** (70 eV).

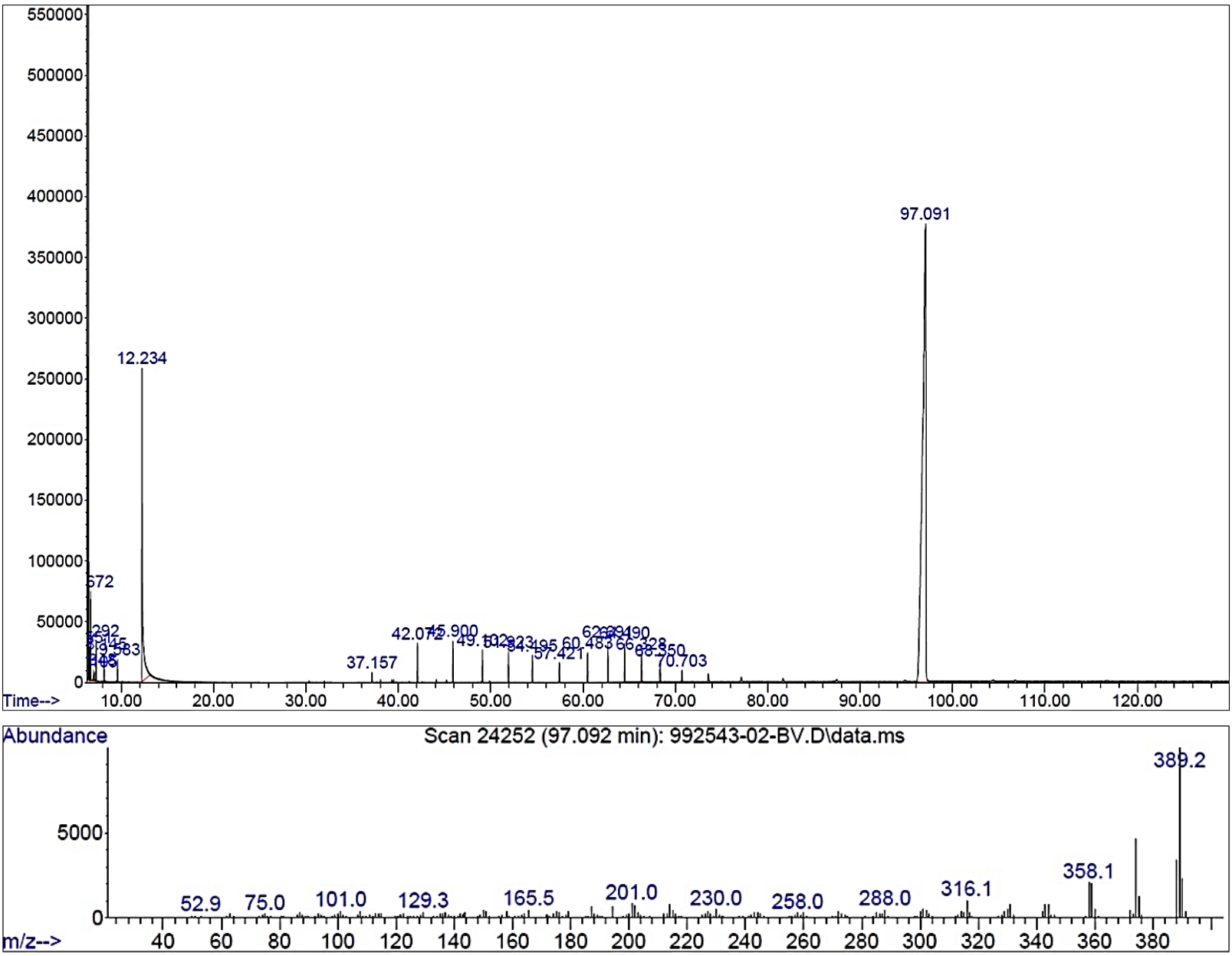


**Figure 25**. $^{1}H$ NMR spectra of compound **6c** ($CDCl_3$, 400 MHz).

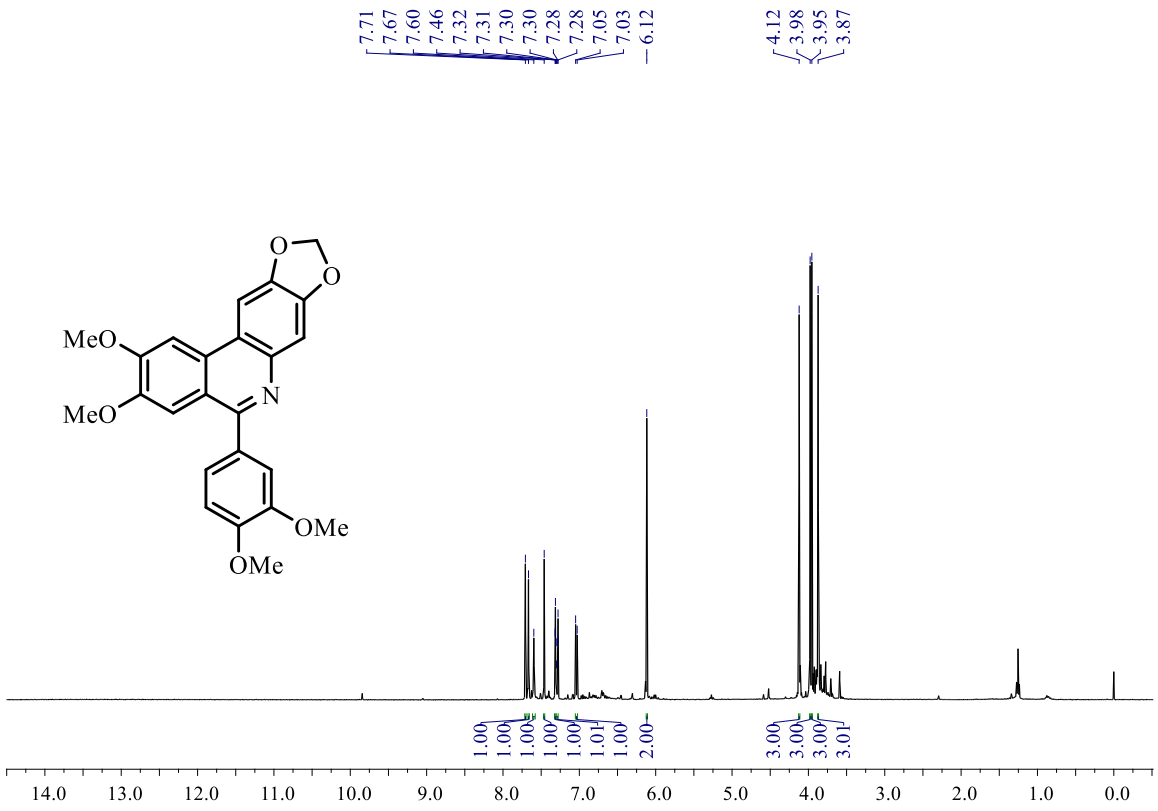


**Figure 26**. Expansion of $^{1}H$ NMR spectra of compound **6c** ($CDCl_3$, 400 MHz).

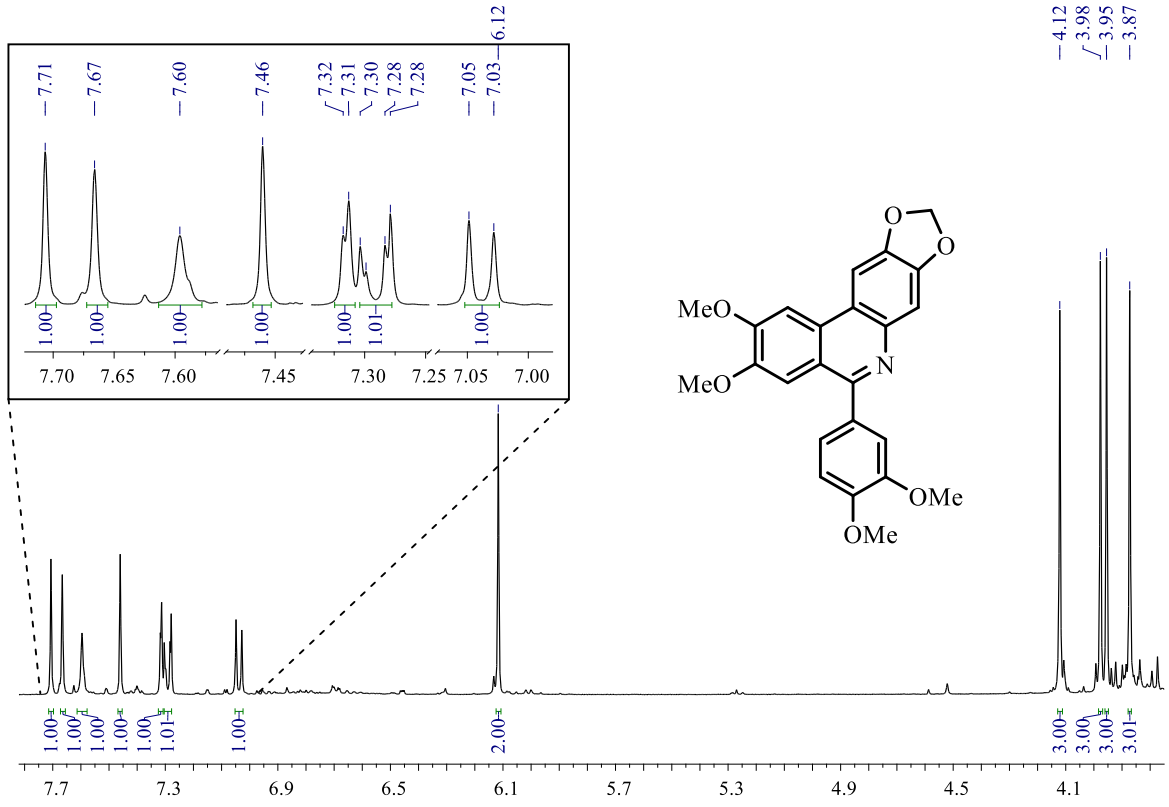


**Figure 27**. $^{13}C$ NMR spectra of compound **6c** ($CDCl_3$, 100 MHz).

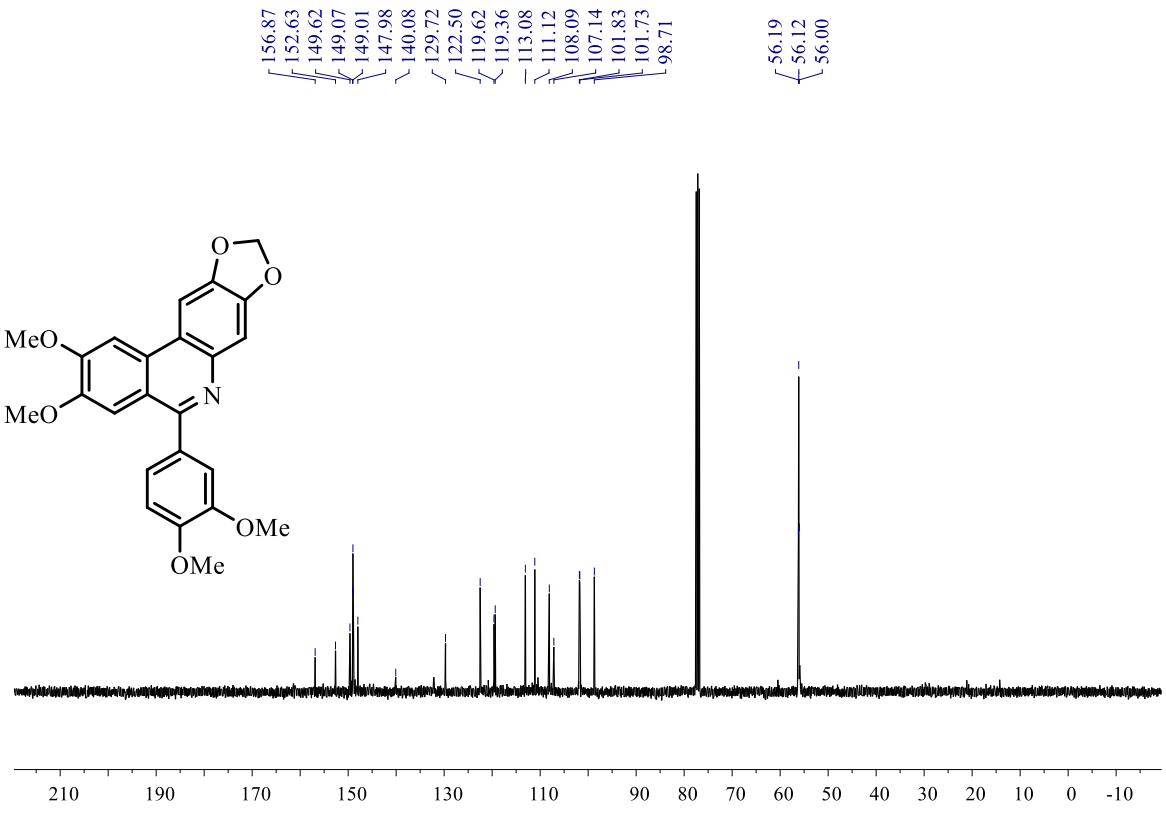


**Figure 28**. $^{13}$C-APT NMR spectra of compound **6c** ($CDCl_3$, 100 MHz).

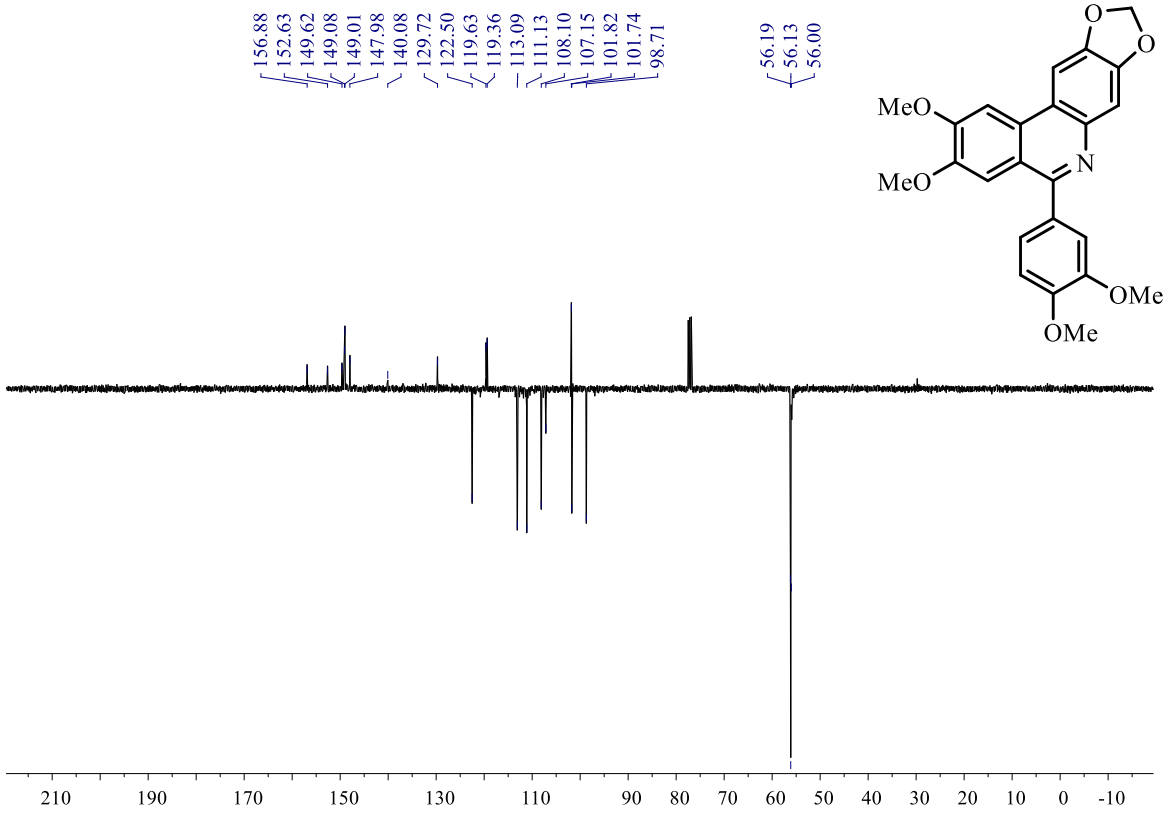


**Figure 29**. Expansion of $^{13}$C-APT NMR spectra of compound **6c** ($CDCl_3$, 100 MHz).

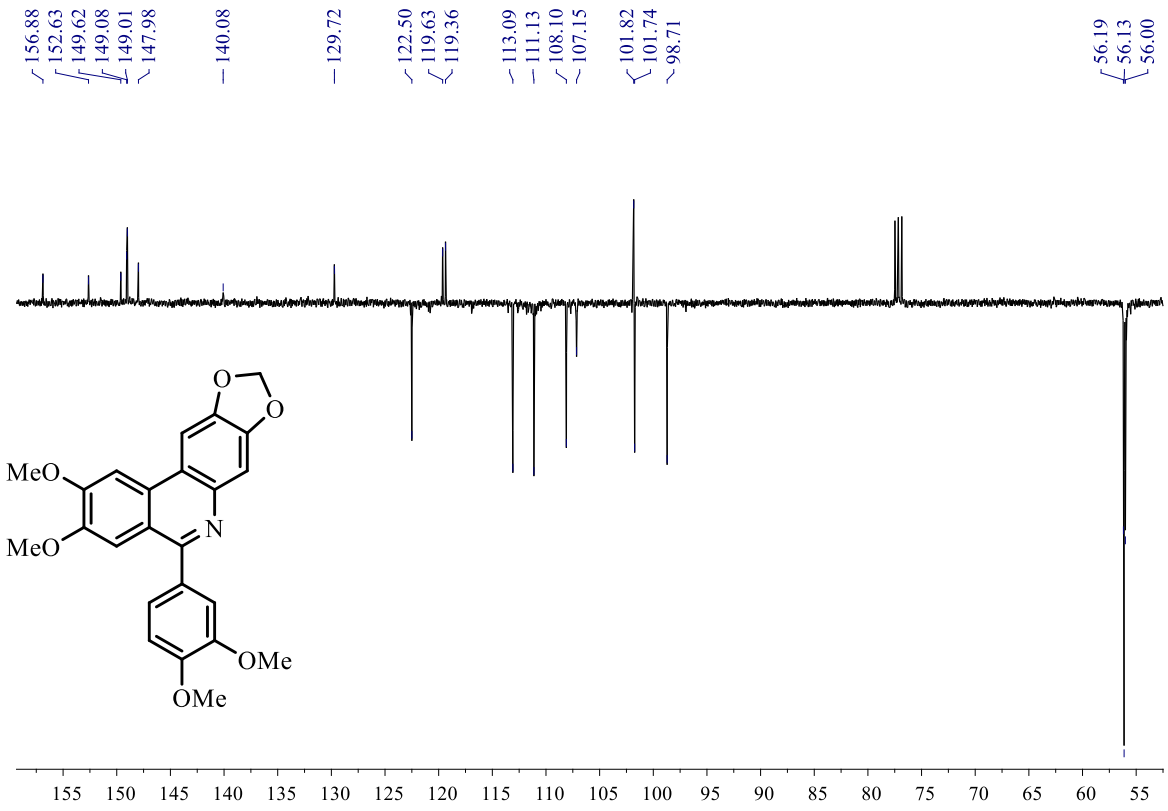


**Figure 30**. $^{1}H$ NMR spectra of compound **6d** ($CDCl_3$, 400 MHz).

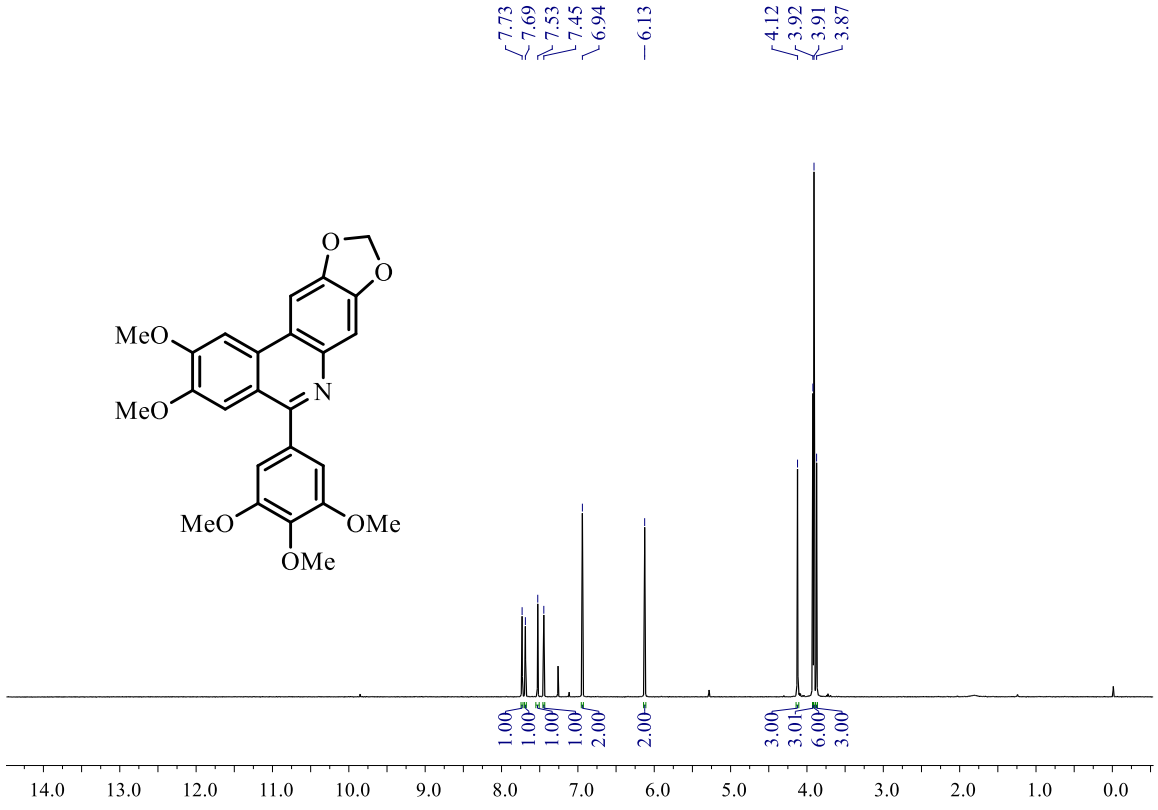


**Figure 31**. Expansion of $^{1}H$ NMR spectra of compound **6d** ($CDCl_3$, 400 MHz).

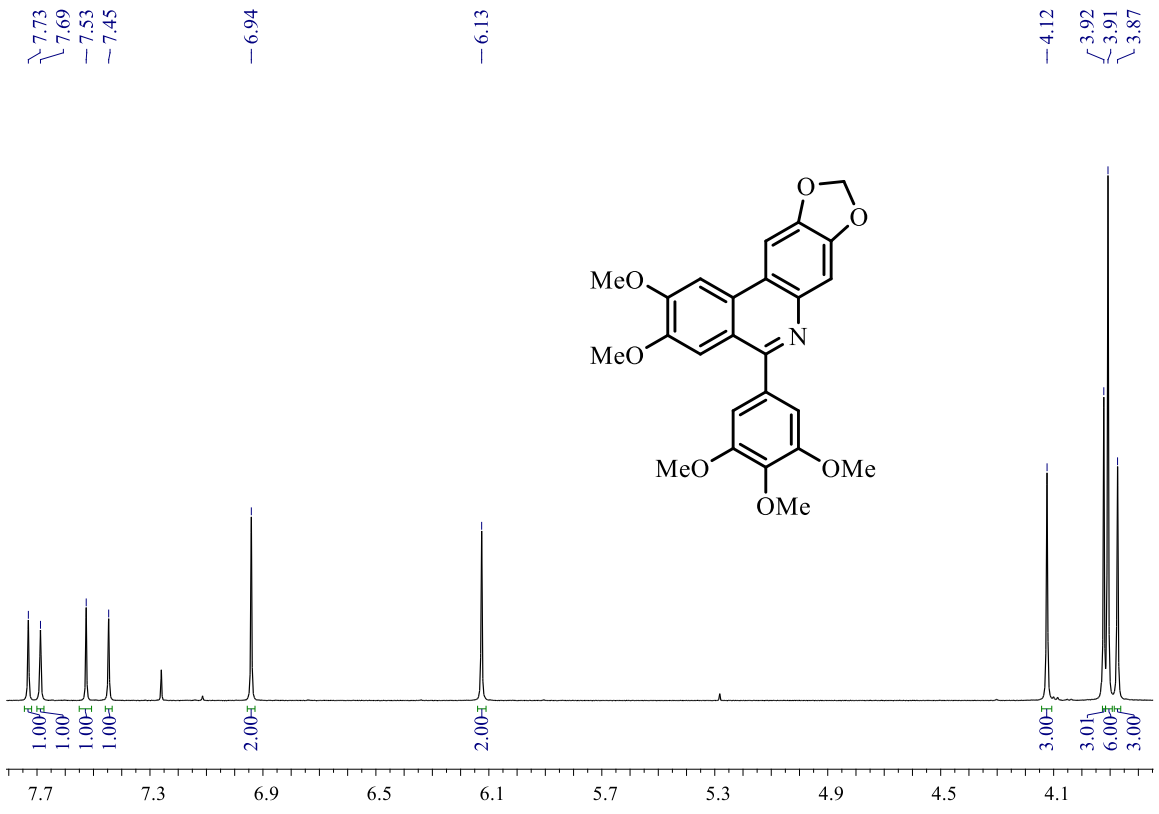


**Figure 32**. $^{13}C$ NMR spectra of compound **6d** ($CDCl_3$, 100 MHz).

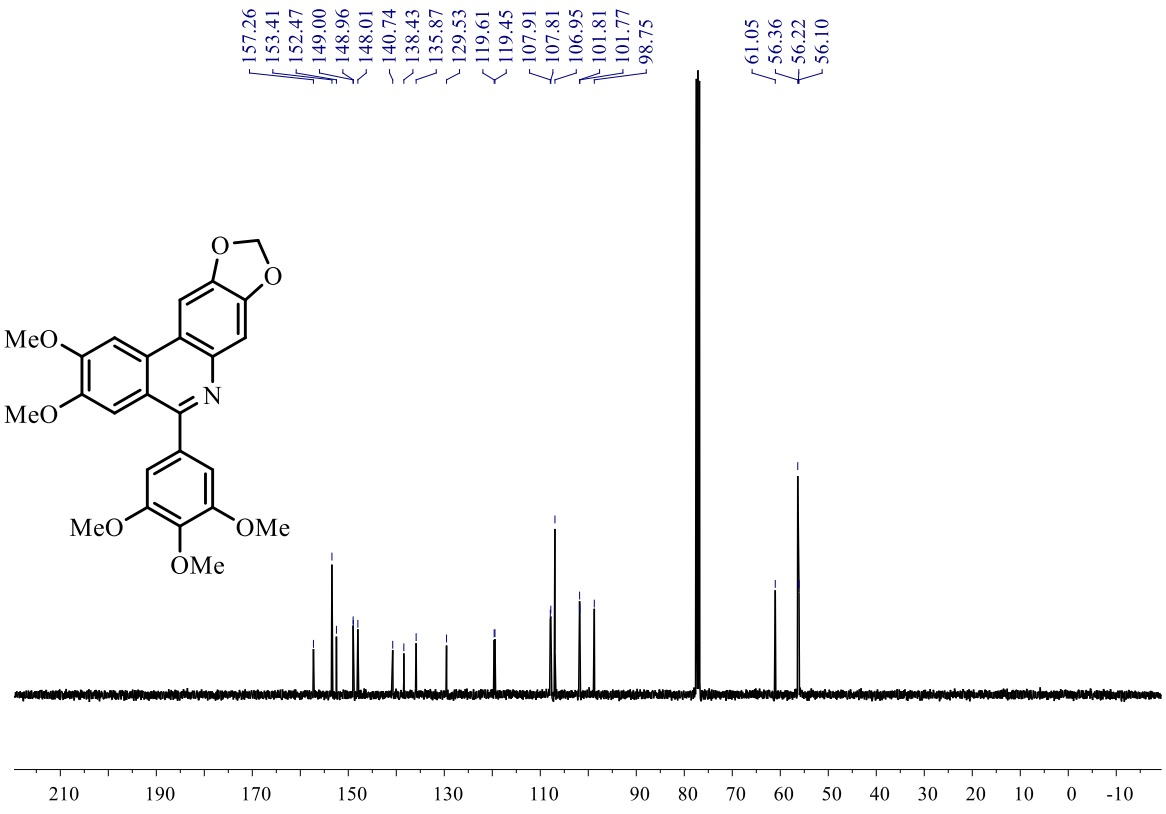


**Figure 33**. $^{13}$C-APT NMR spectra of compound **6d** ($CDCl_3$, 100 MHz).

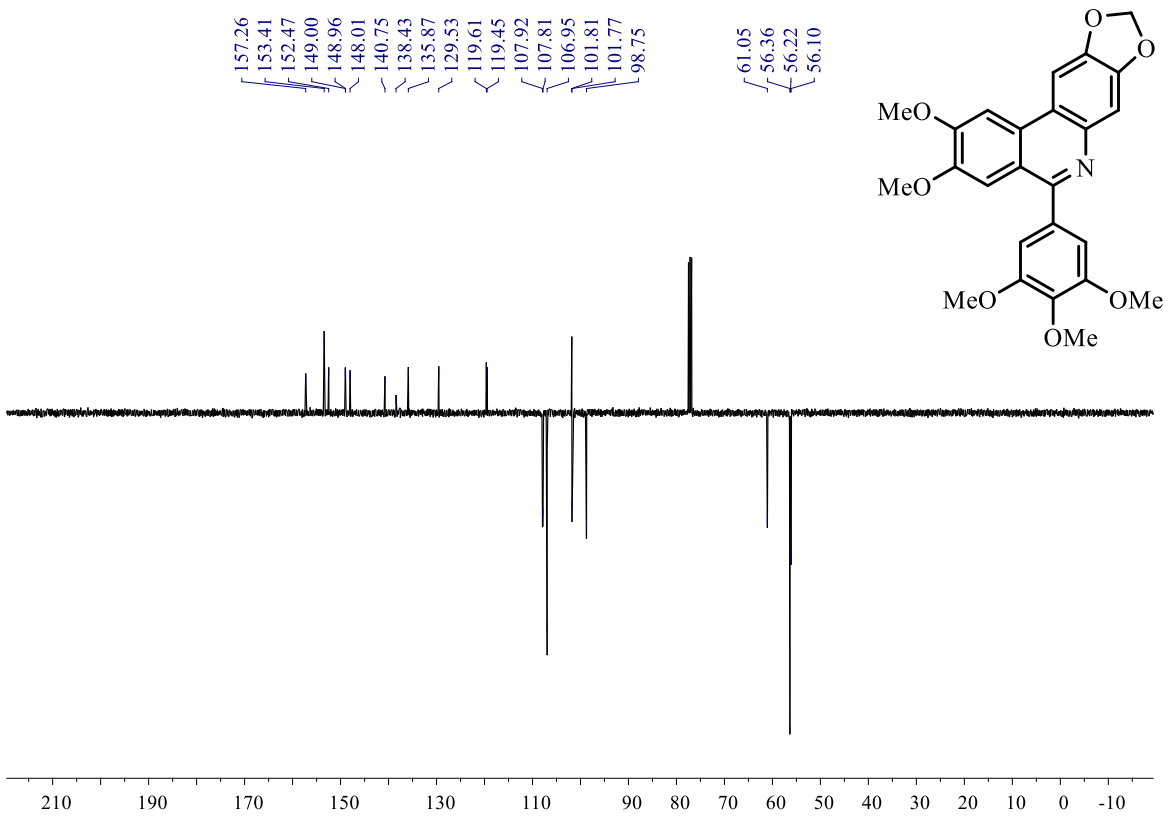


**Figure 34**. Expansion of $^{13}$C-APT NMR spectra of compound **6d** ($CDCl_3$, 100 MHz).

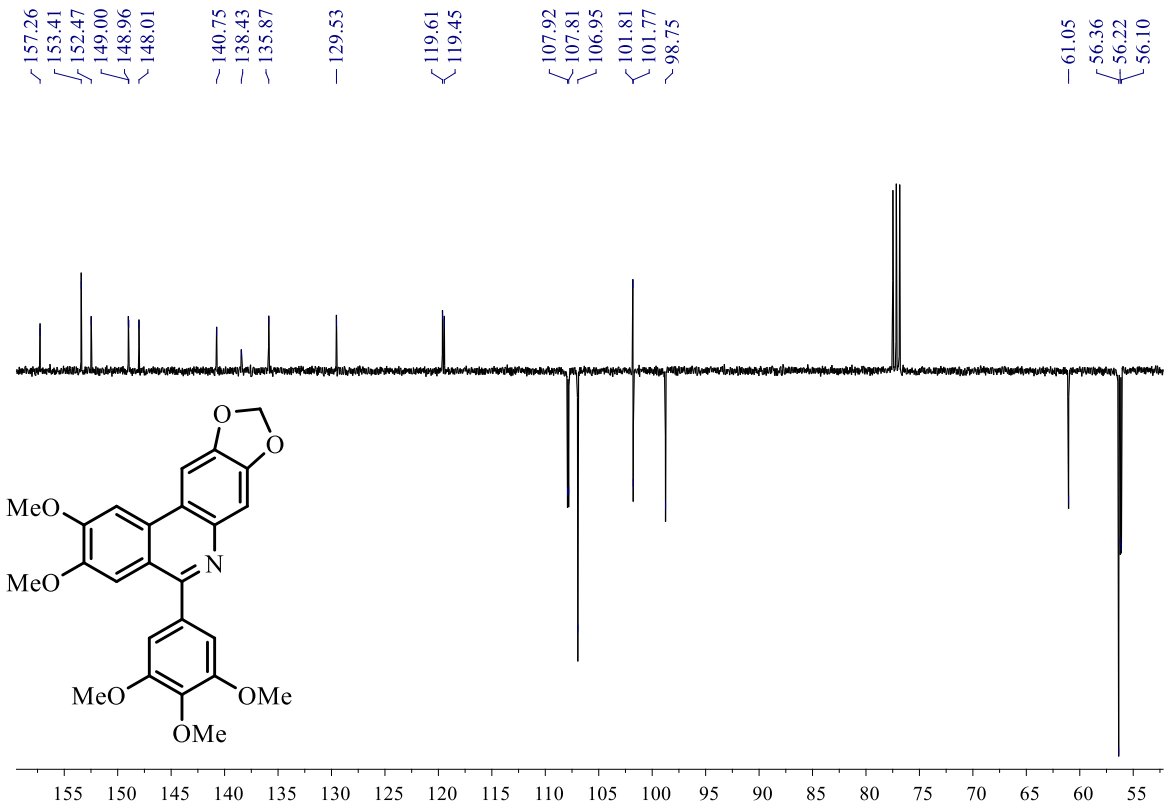


**Figure 35**. $^{1}H$-$^{13}C$-APT HSQC NMR spectra of compound **6d** ($CDCl_3$).

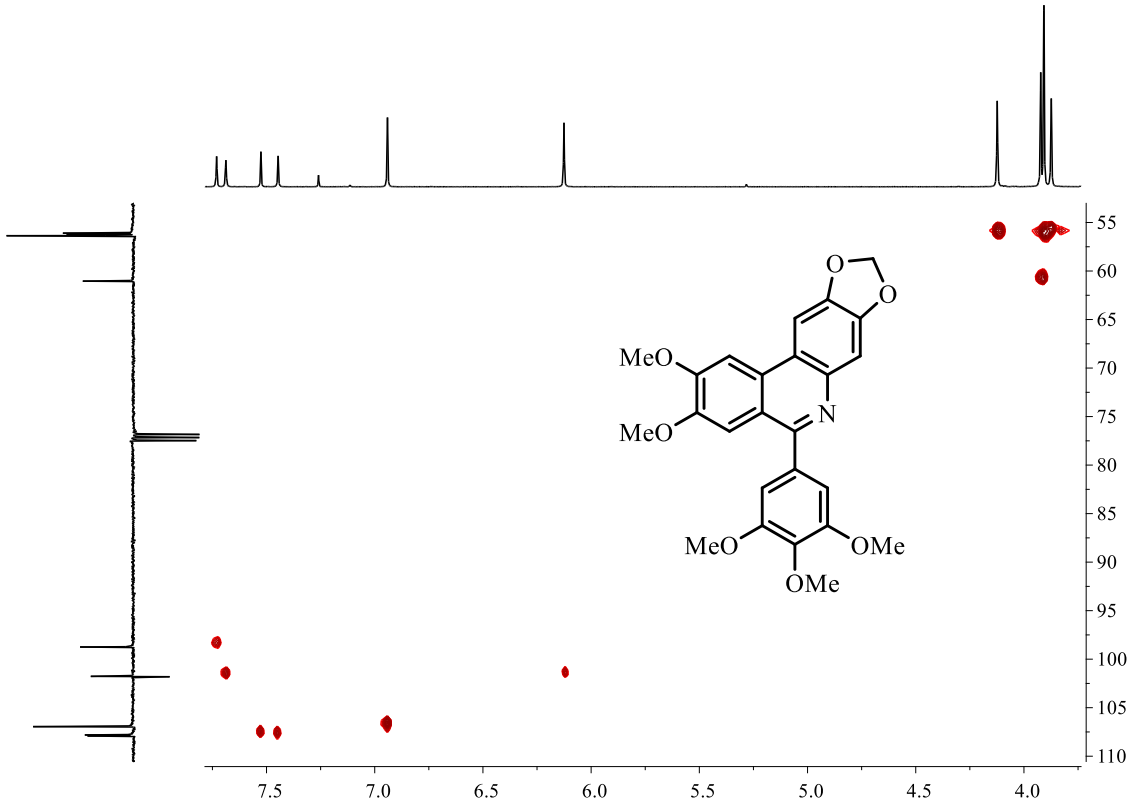


**Figure 36**. $^{1}H$-$^{13}C$-APT HMBC NMR spectra of compound **6d** ($CDCl_3$).

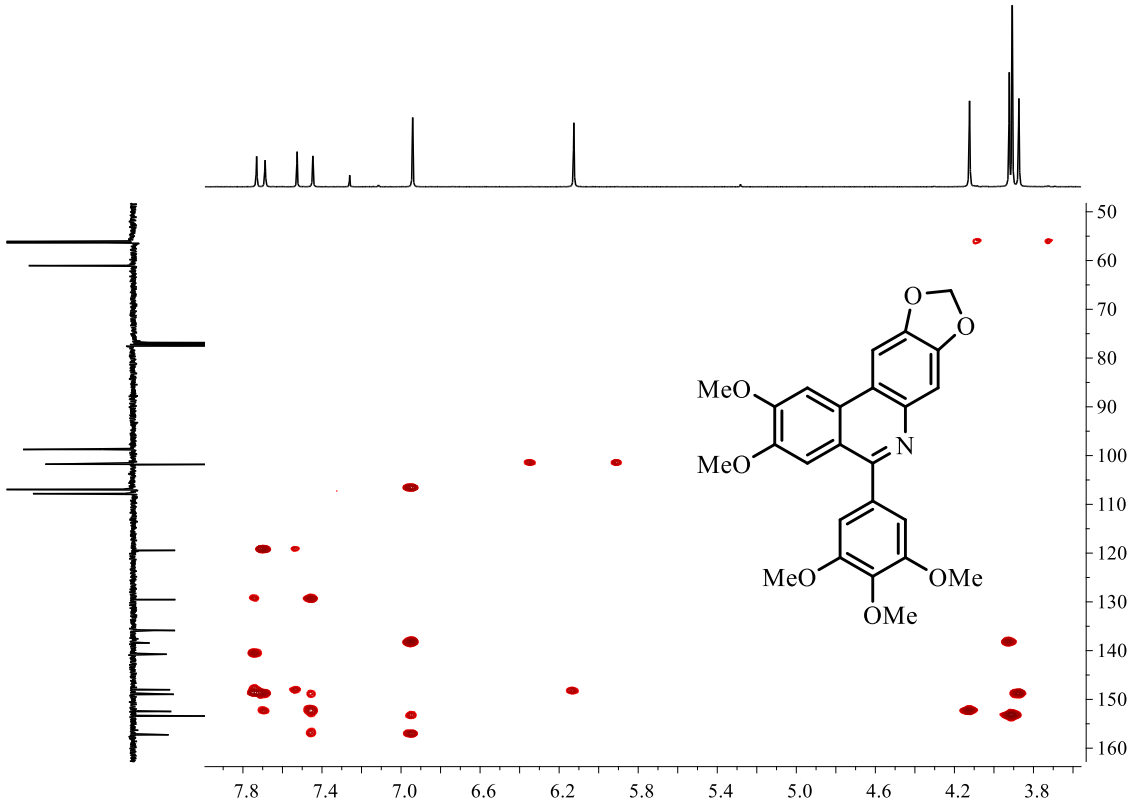
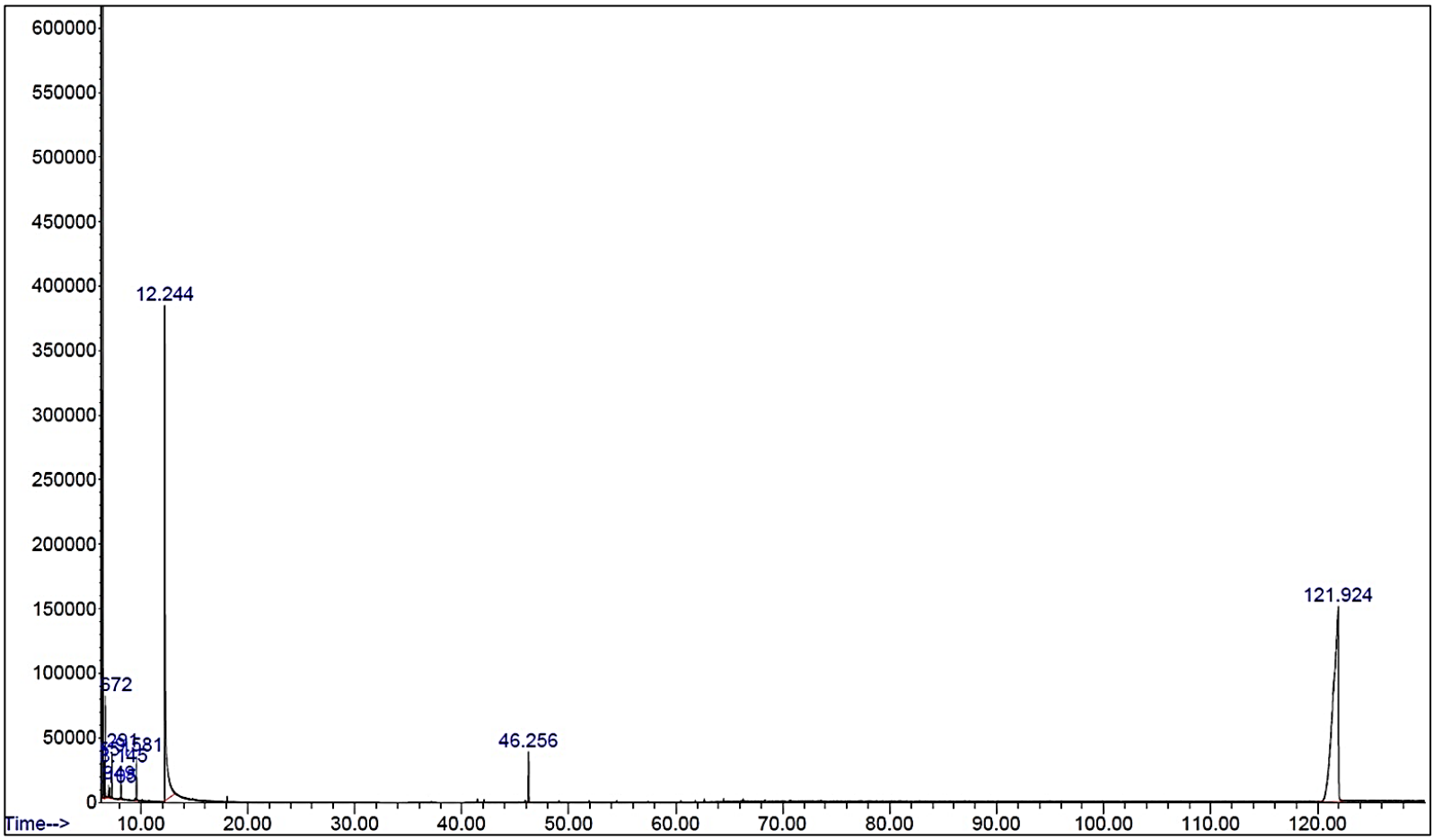


**Figure 37**. GC-MS of compound **6d** (70 eV).



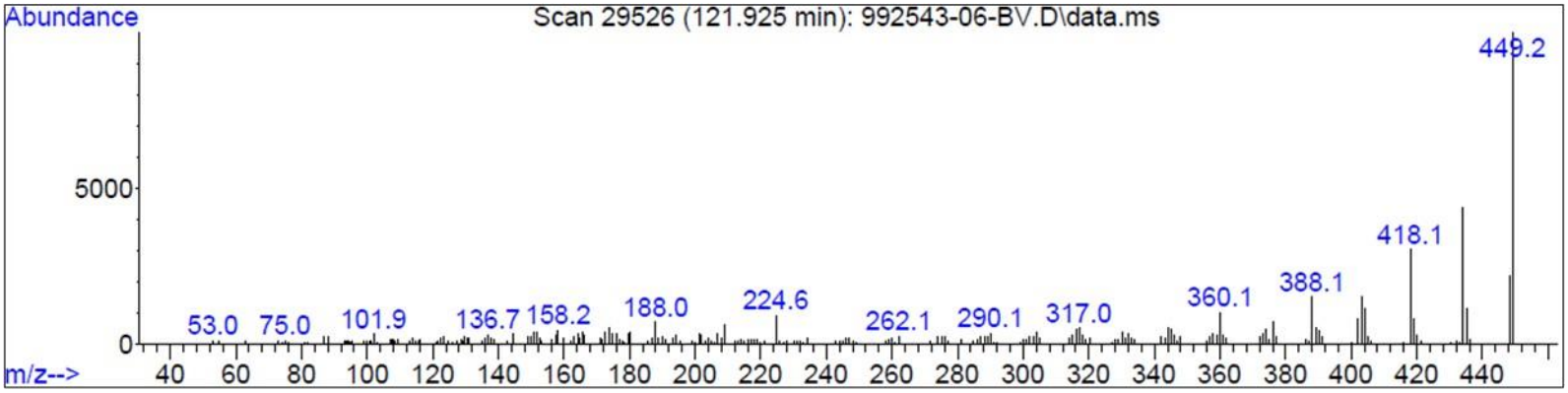



**Figure 38**. $^{1}H$ NMR spectra of compound **6e** ($CDCl_3$, 400 MHz).

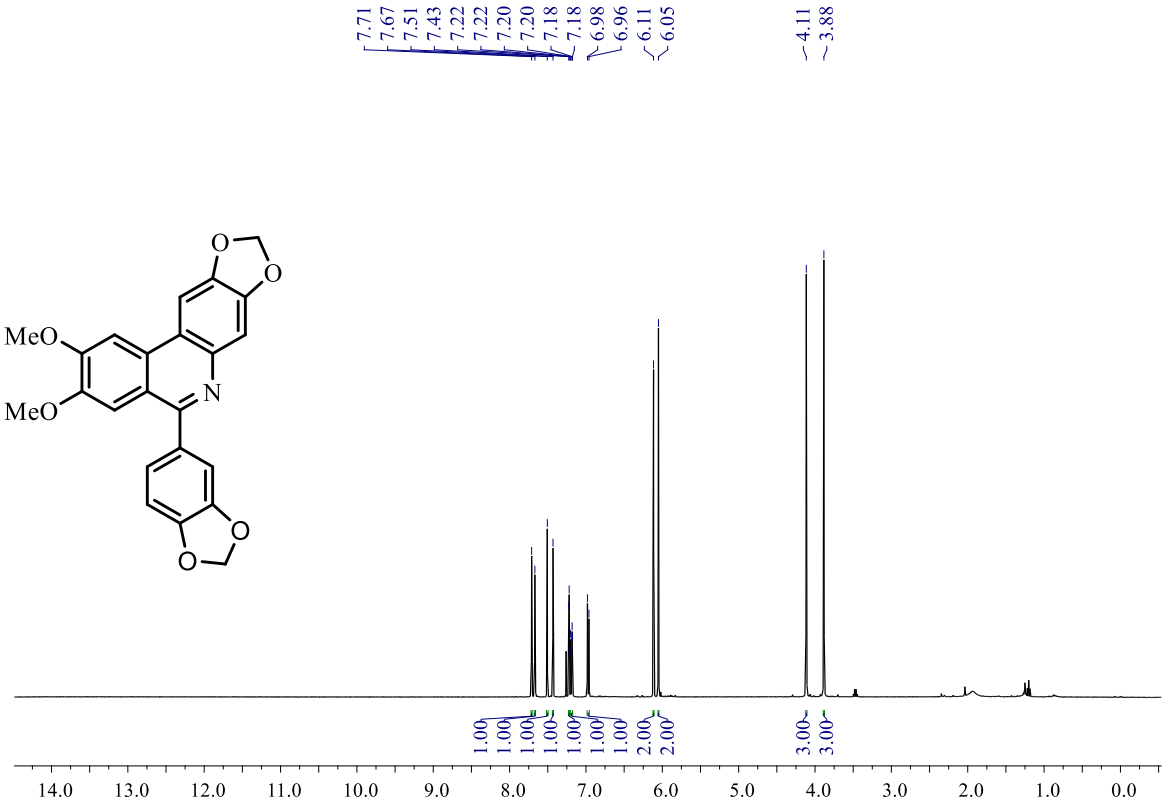


**Figure 39**. Expansion of $^{1}H$ NMR spectra of compound **6e** ($CDCl_3$, 400 MHz).

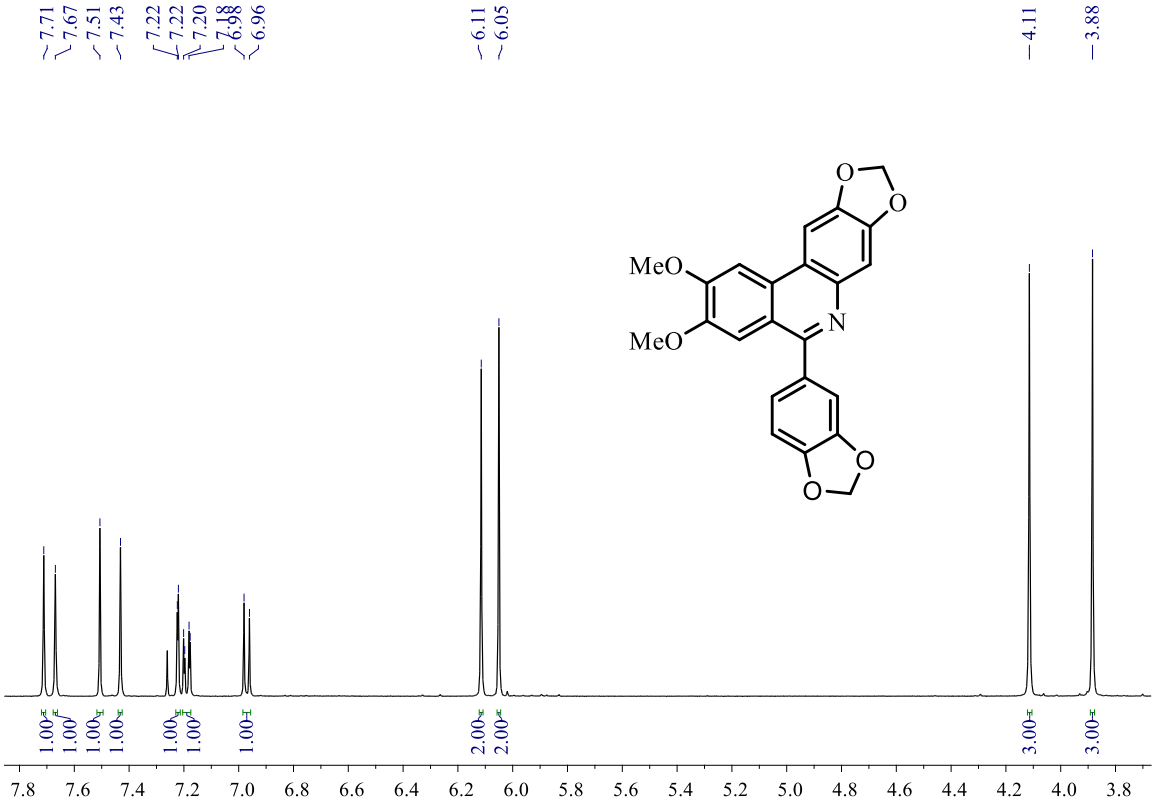


**Figure 40**. $^{13}C$ NMR spectra of compound **6e** ($CDCl_3$, 100 MHz).

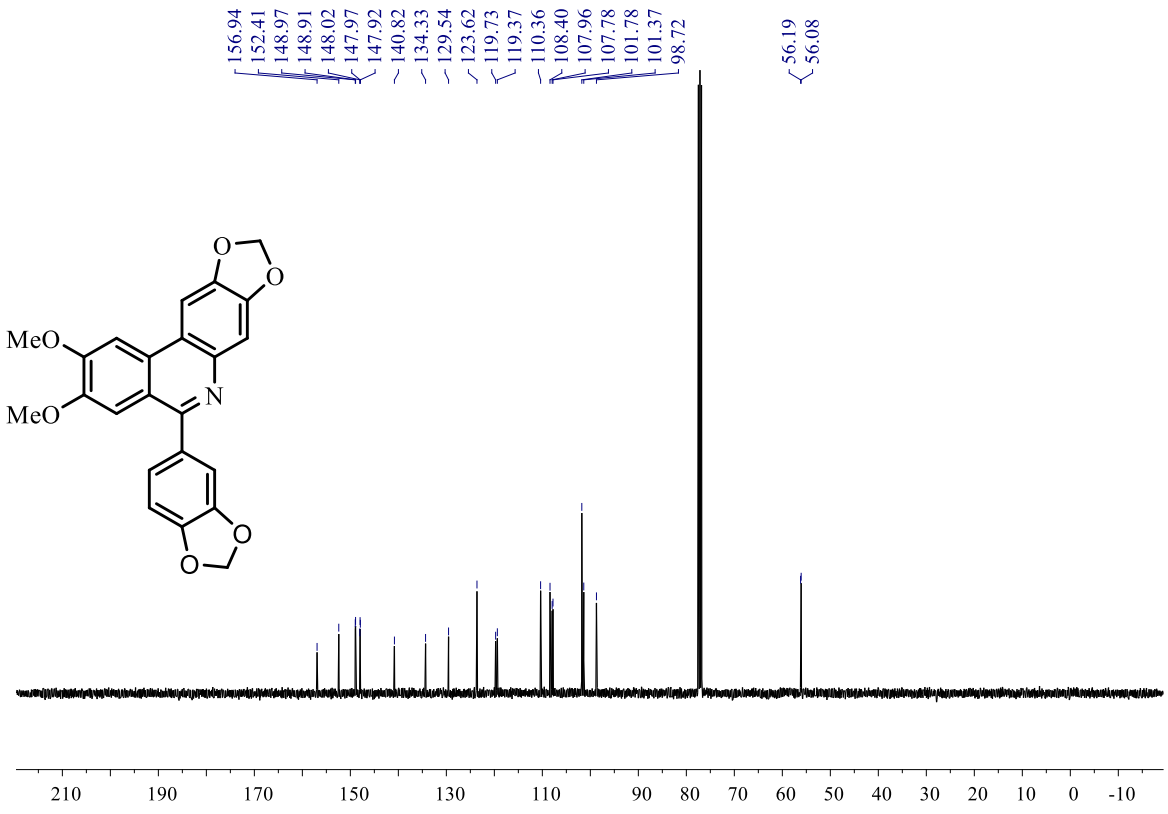


**Figure 41**. $^{13}$C-APT NMR spectra of compound **6e** ($CDCl_3$, 100 MHz).

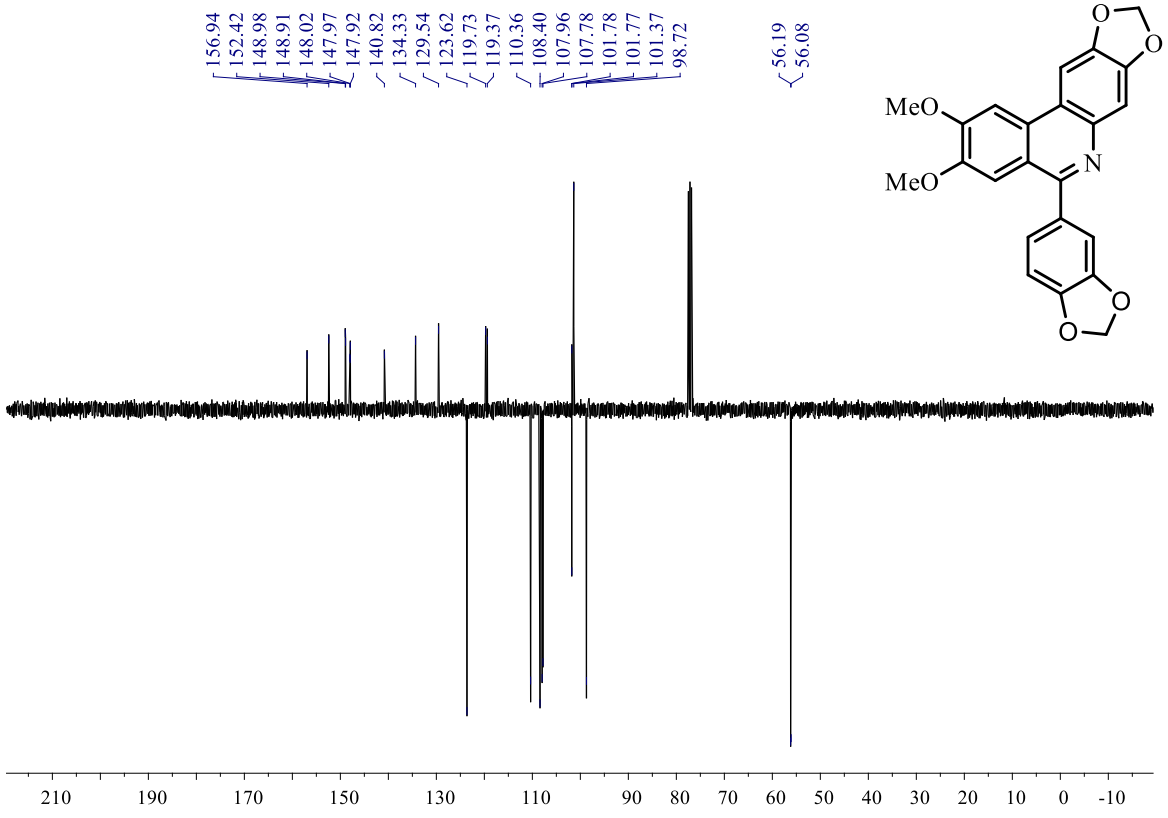


**Figure 42**. Expansion of $^{13}$C-APT NMR spectra of compound **6e** ($CDCl_3$, 100 MHz).

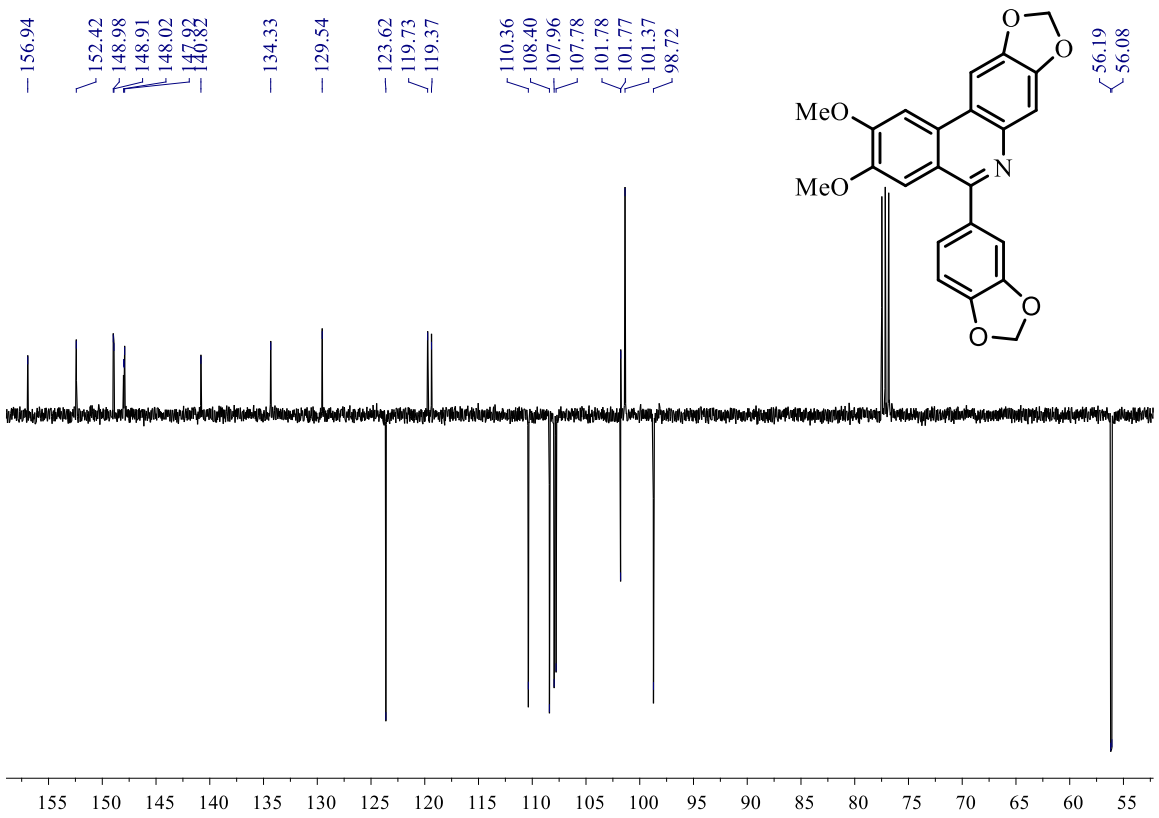


**Figure 43**. GC-MS of compound **6e** (70 eV).

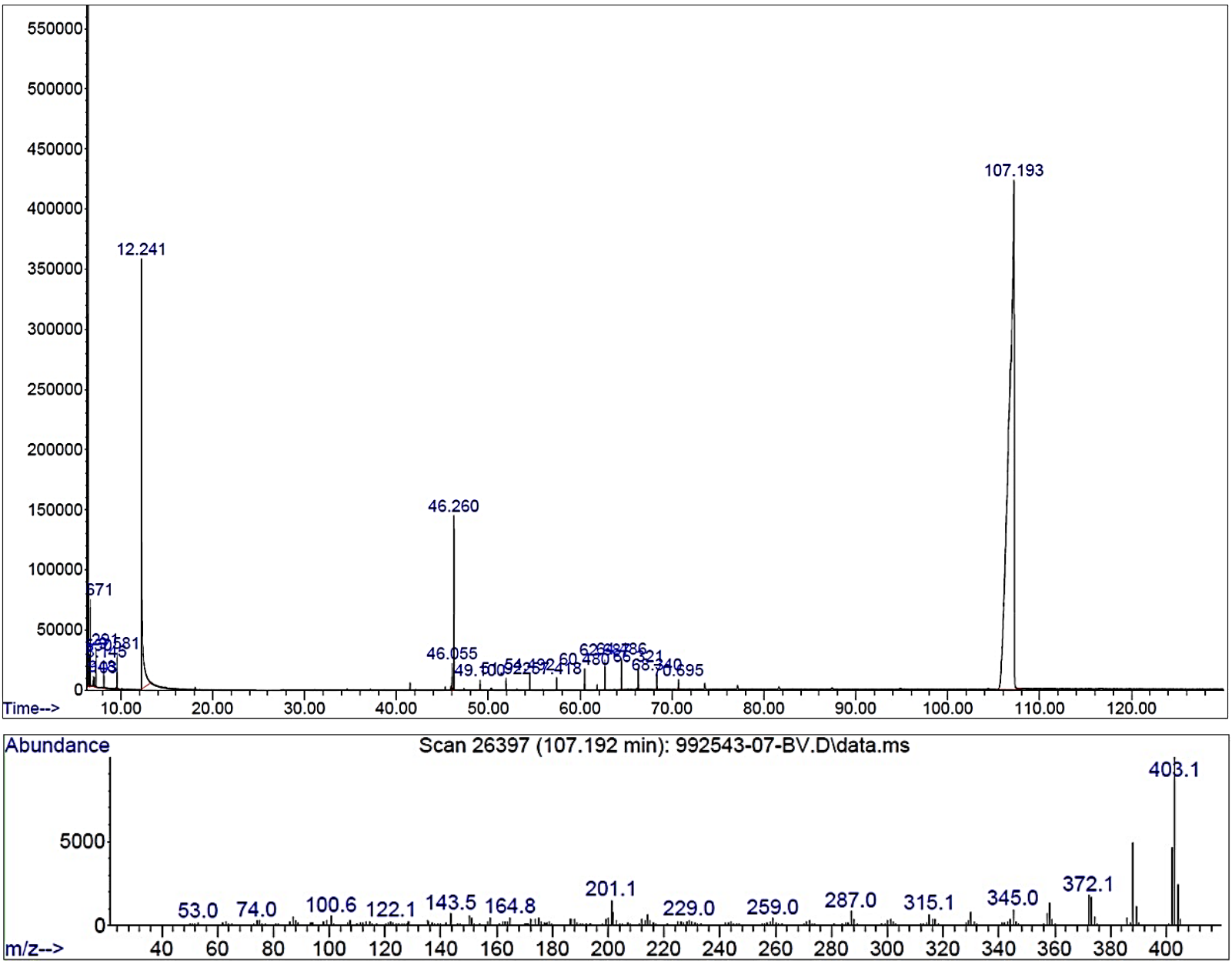


**Figure 44**. $^{1}$H NMR spectra of compound **6f** (DMSO-$d_6$, 400 MHz).

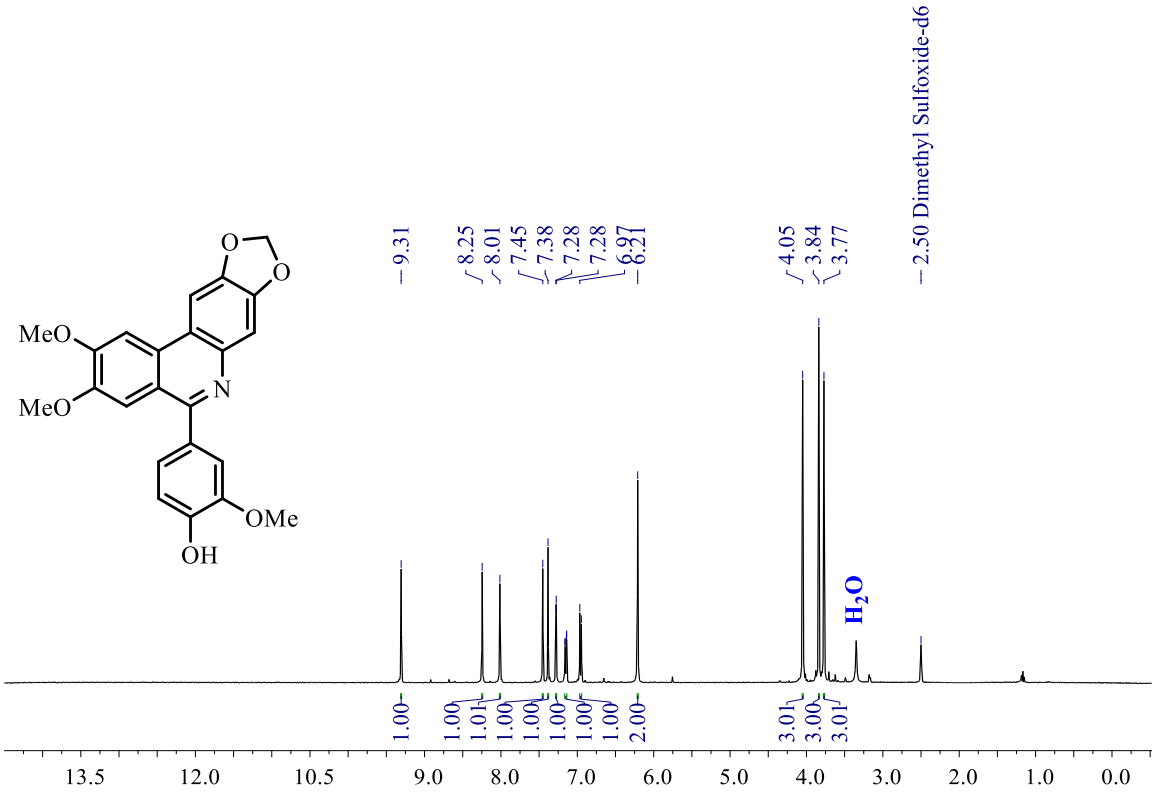


**Figure 45**. Expansion of $^{1}$H NMR spectra of compound **6f** (DMSO-$d_6$, 400 MHz).

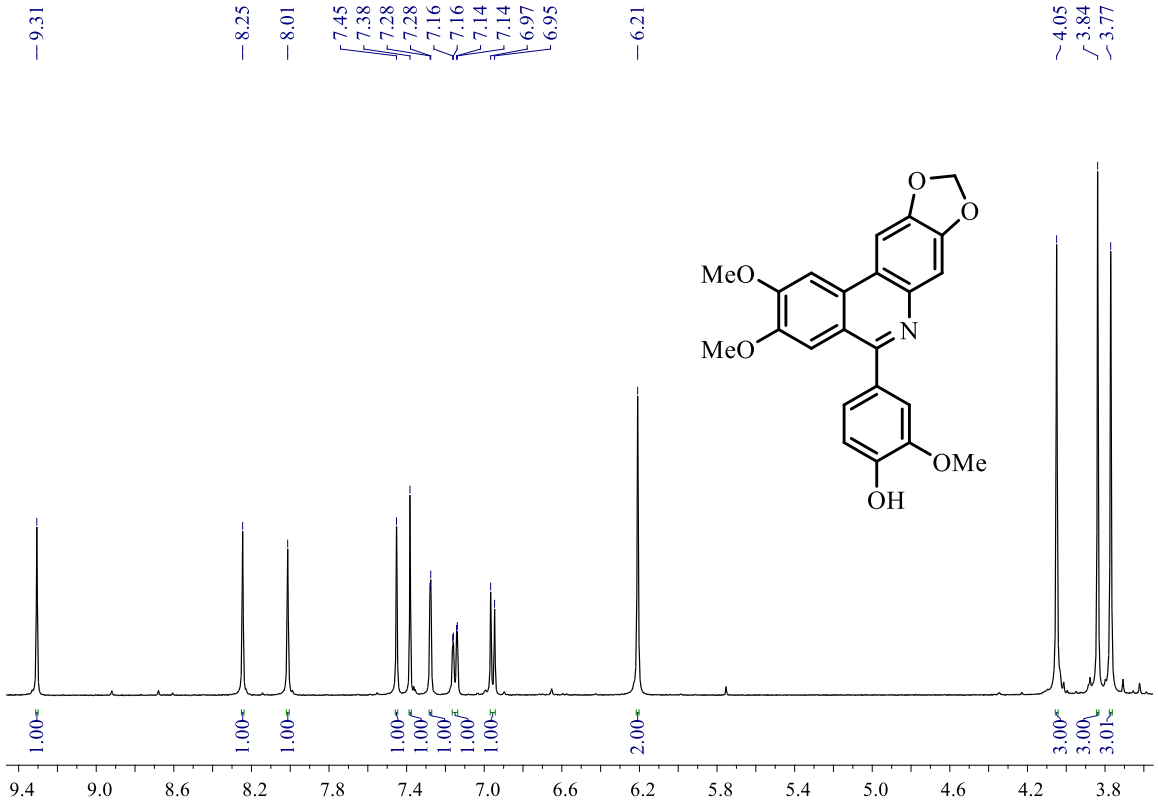


**Figure 46**. $^{13}$C NMR spectra of compound **6f** (DMSO-$d_6$, 100 MHz).

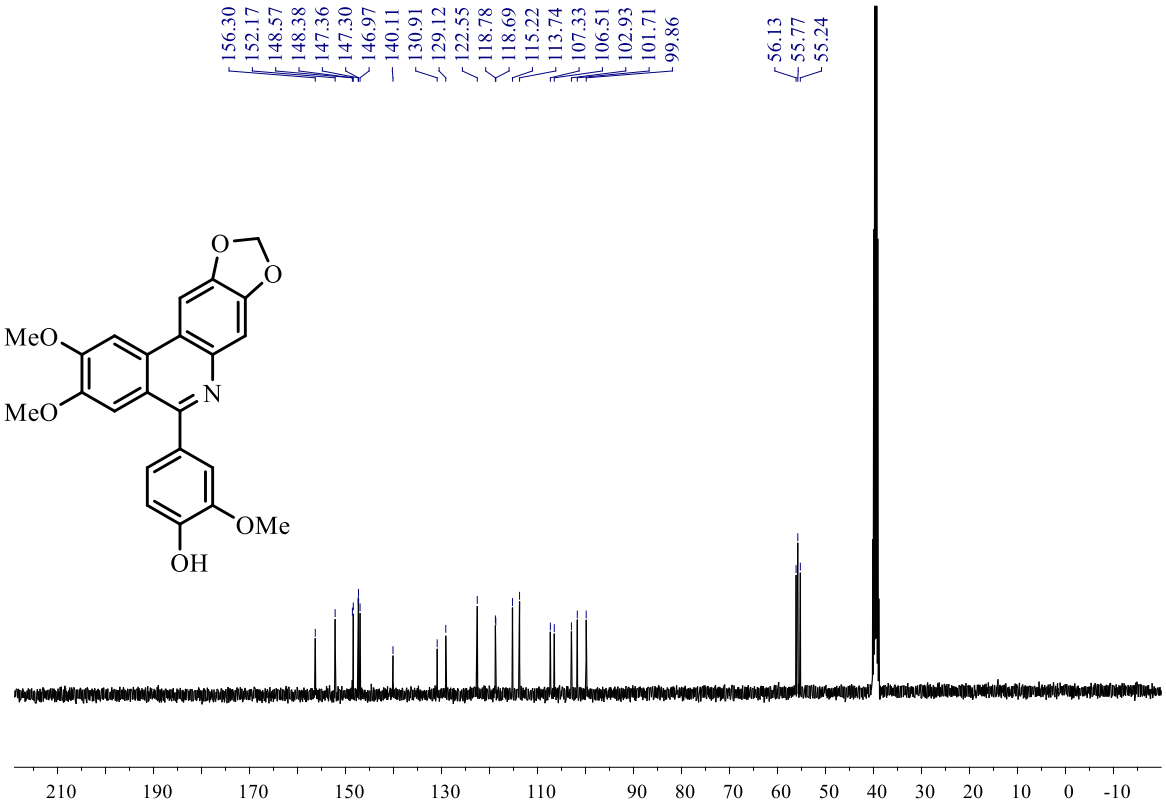


**Figure 47**. $^{13}$C-APT NMR spectra of compound **6f** (DMSO-$d_6$, 100 MHz).

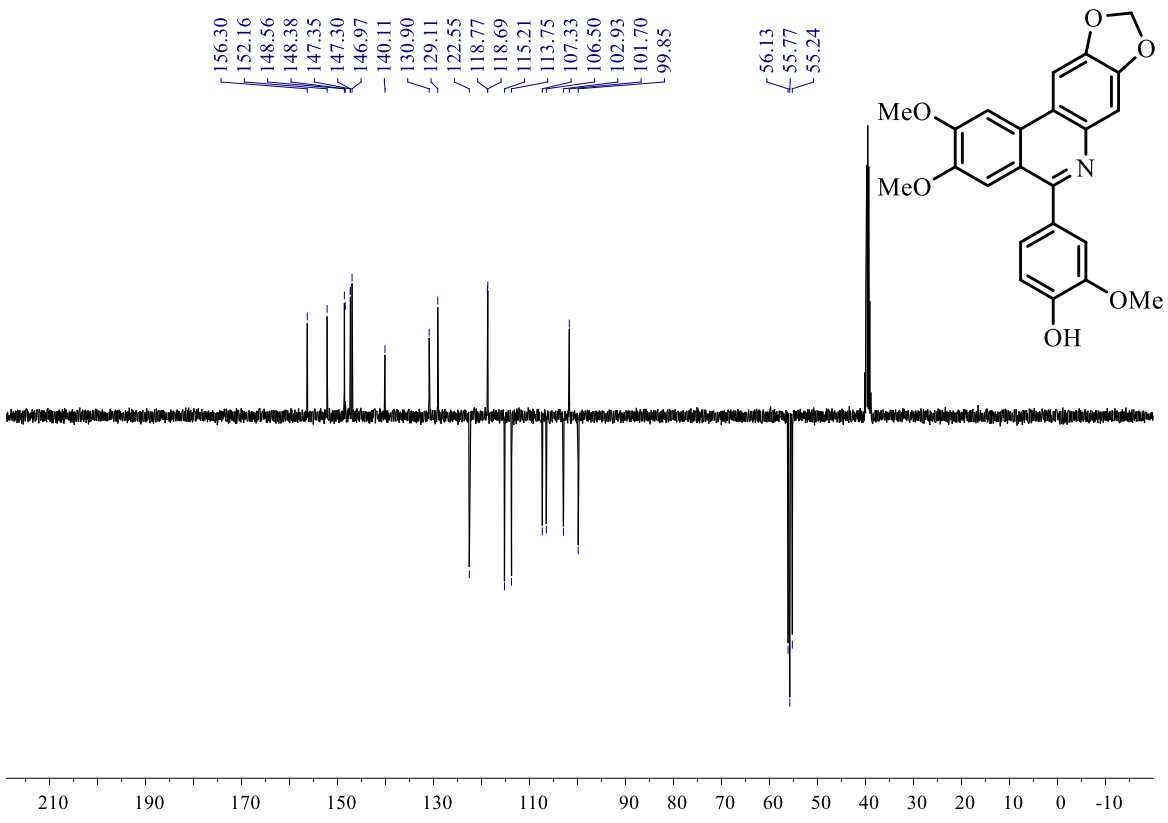


**Figure 48**. Expansion of $^{13}$C-APT NMR spectra of compound **6f** (DMSO-$d_6$, 100 MHz).

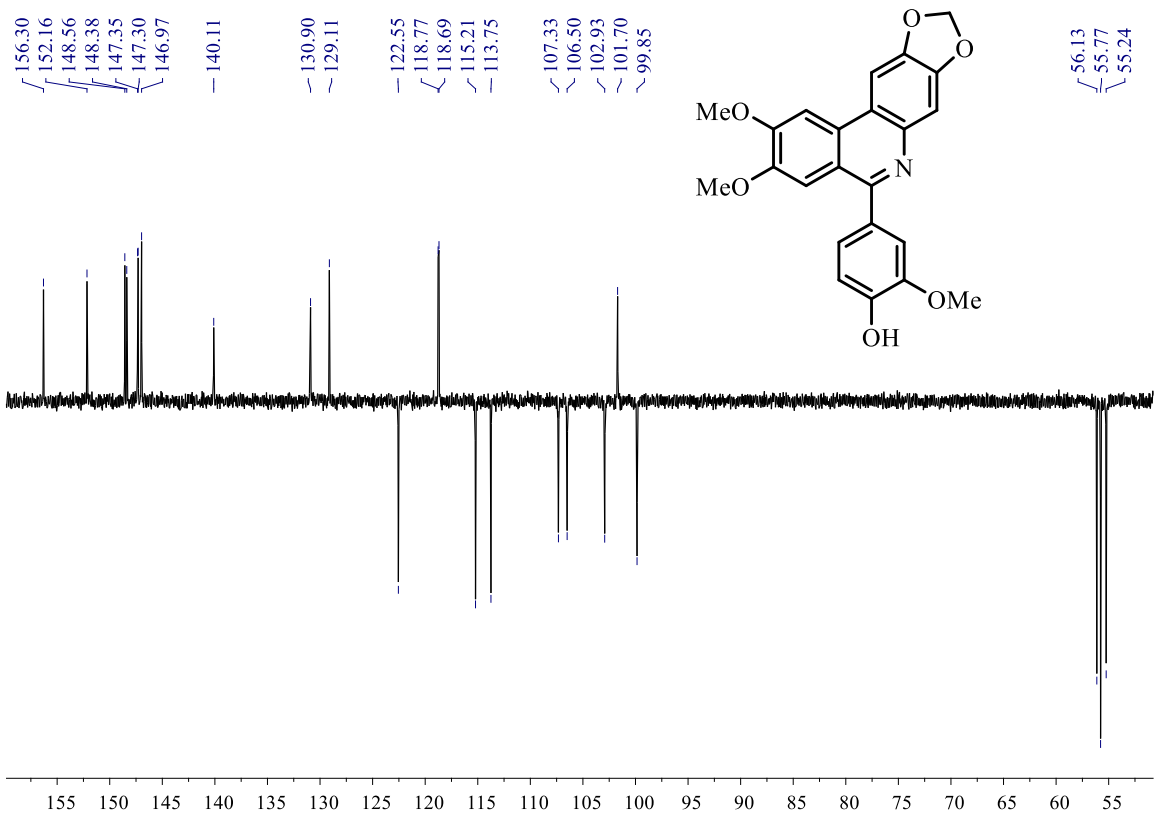


**Figure 49**. $^{1}$H NMR spectra of compound **6g** (DMSO-$d_6$, 400 MHz).

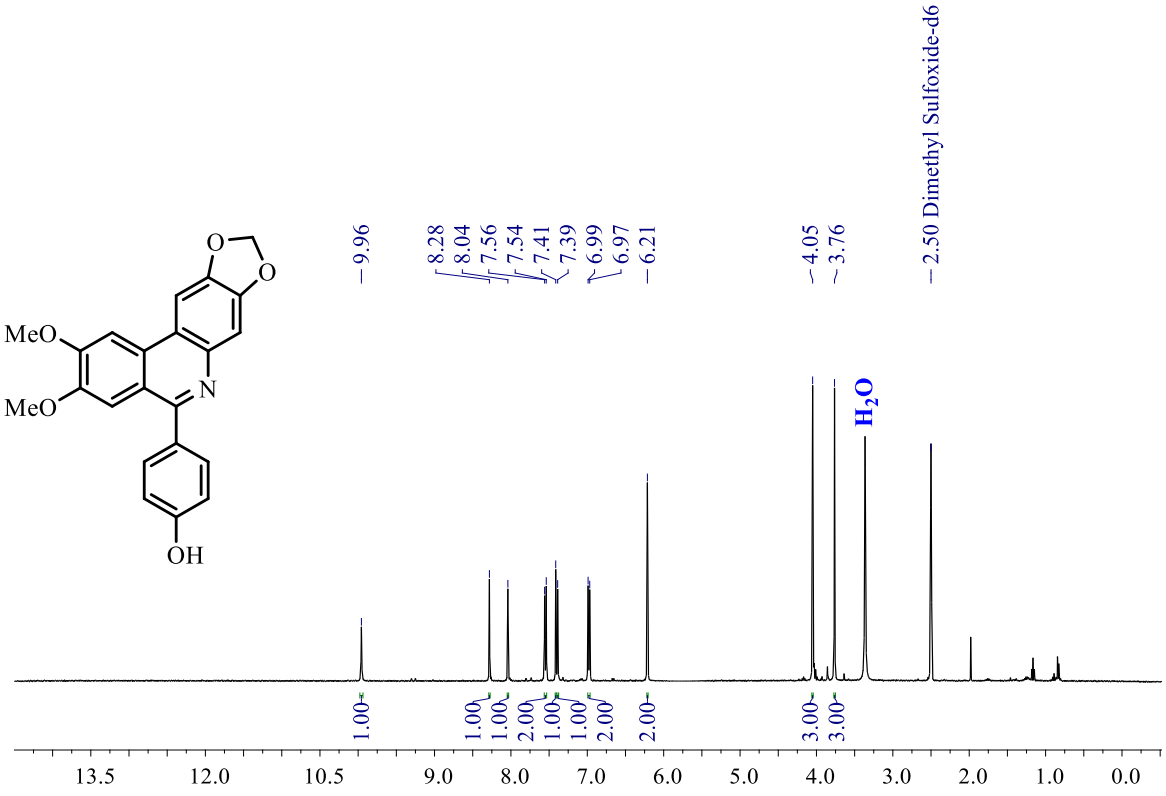


**Figure 50**. Expansion of $^{1}$H NMR spectra of compound **6g** (DMSO-$d_6$, 400 MHz).

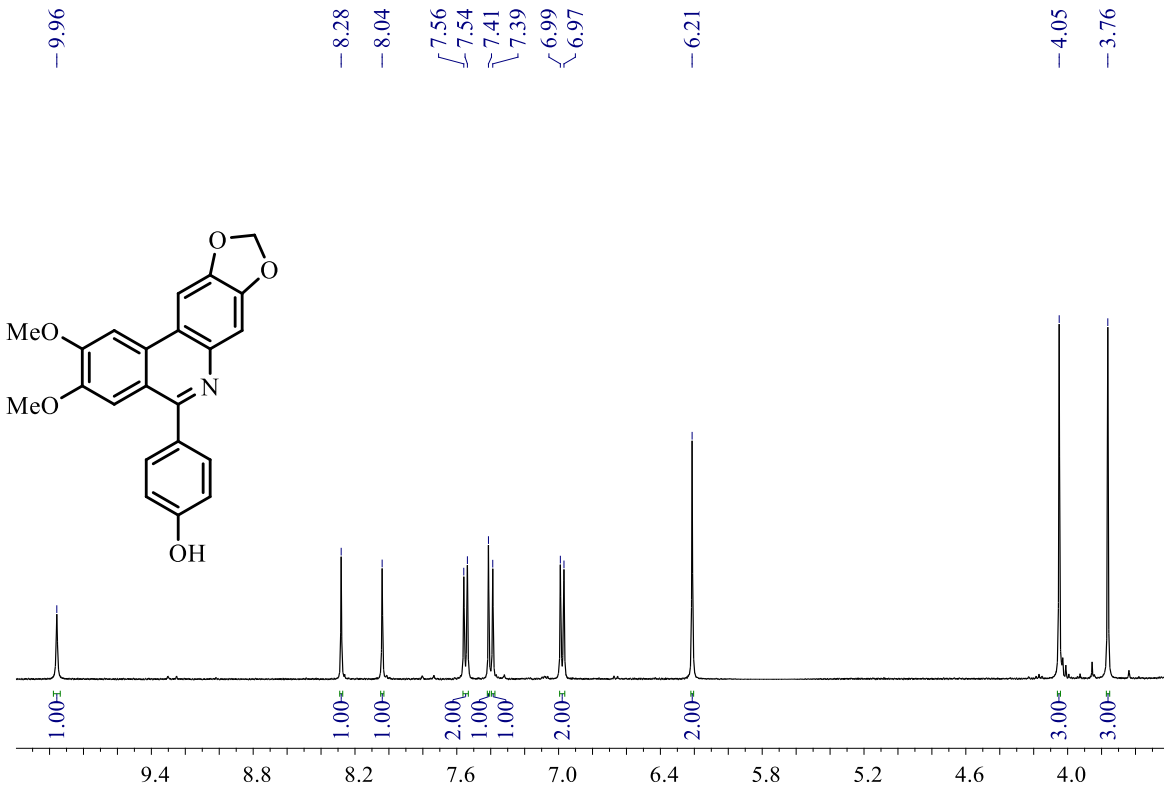


**Figure 51**. $^{13}$C NMR spectra of compound **6g** (DMSO-$d_6$, 100 MHz).

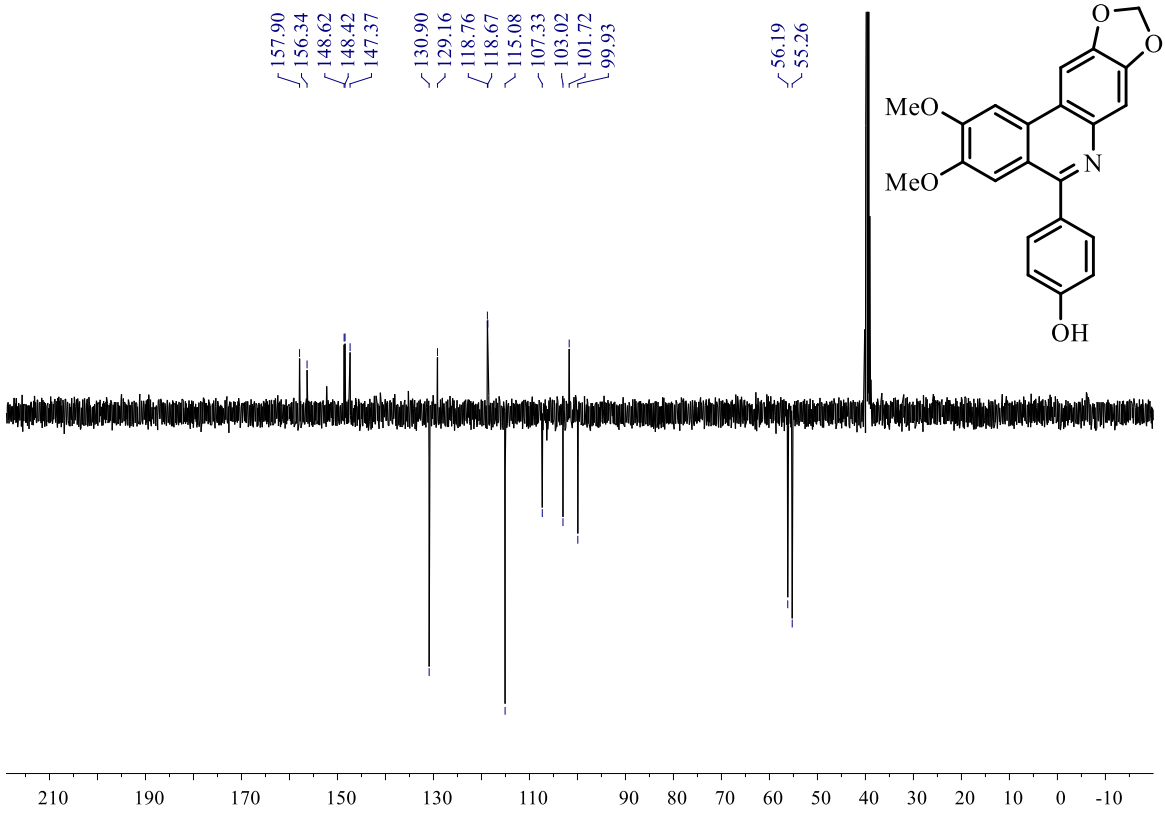


**Figura 52**. $^{13}$C-APT NMR spectra of compound **6g** (DMSO-$d_6$, 100 MHz).

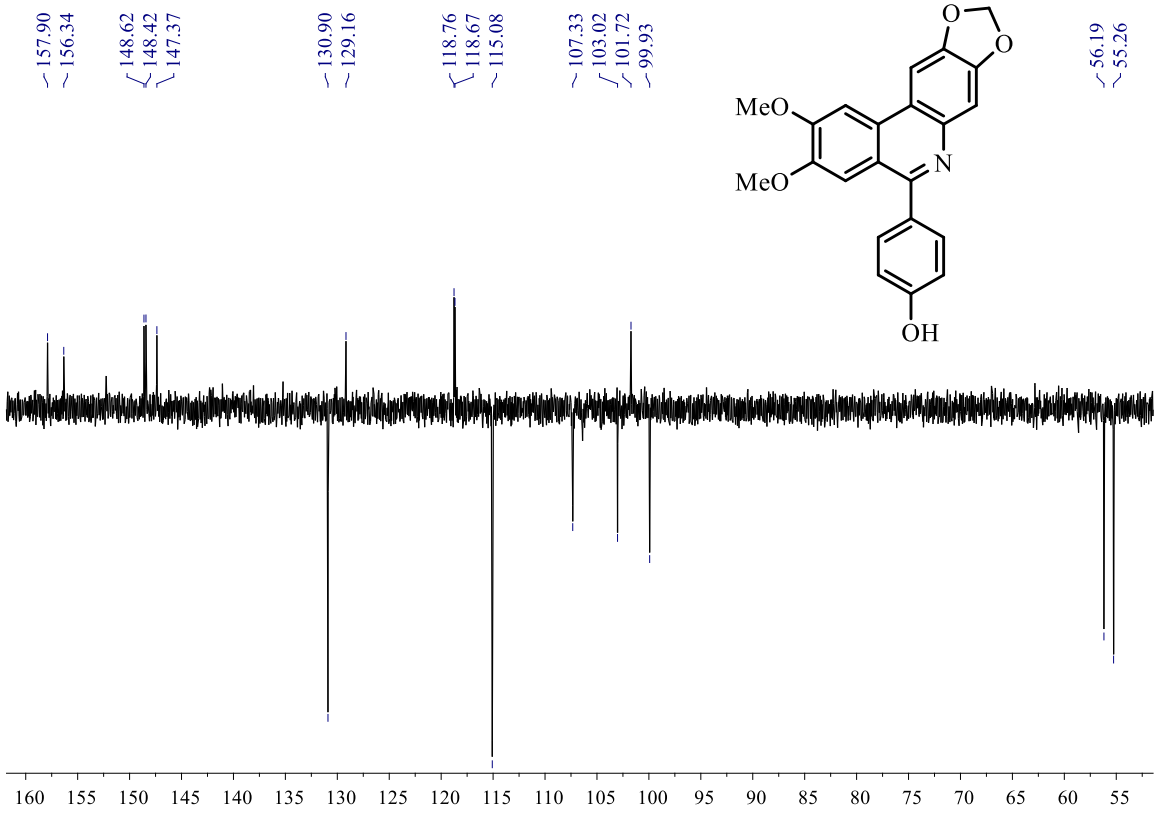


**Figure 53**. $^{1}H$ NMR spectra of compound **6h** ($CDCl_3$, 400 MHz).

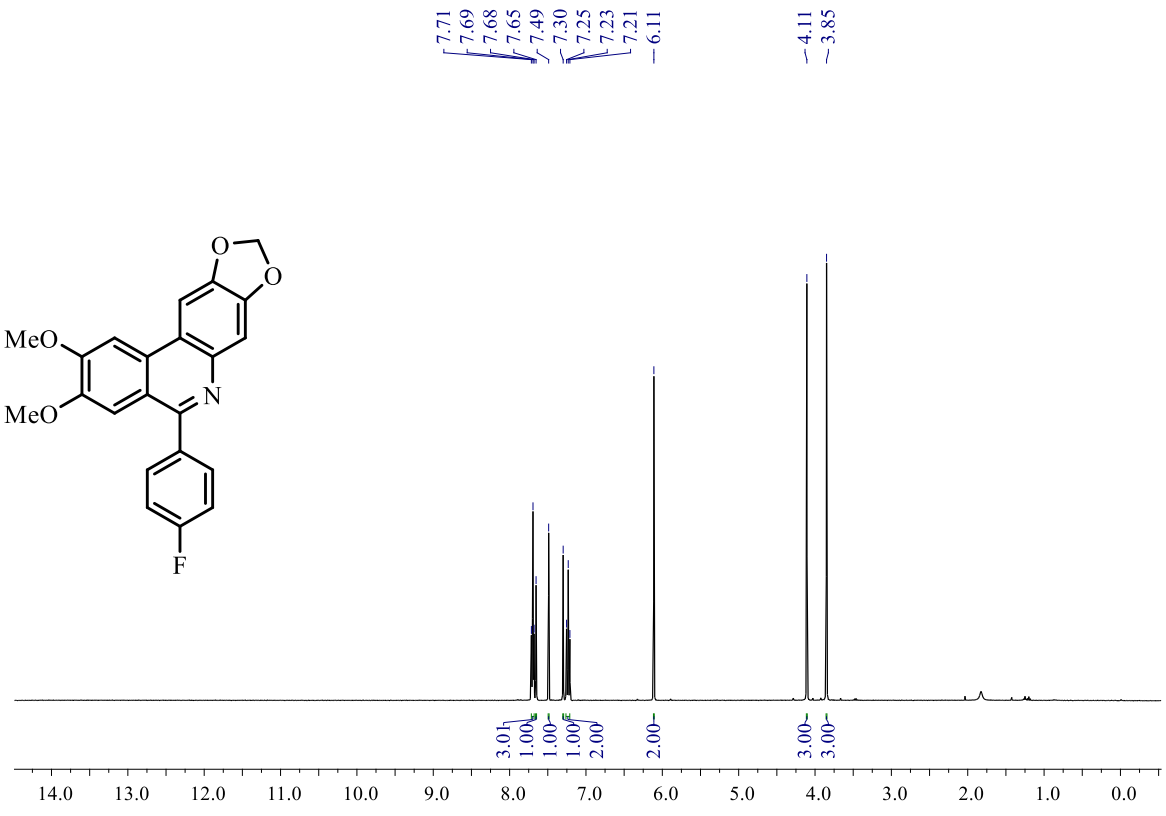


**Figure 54**. Expansion of $^{1}H$ NMR spectra of compound **6h** ($CDCl_3$, 400 MHz).

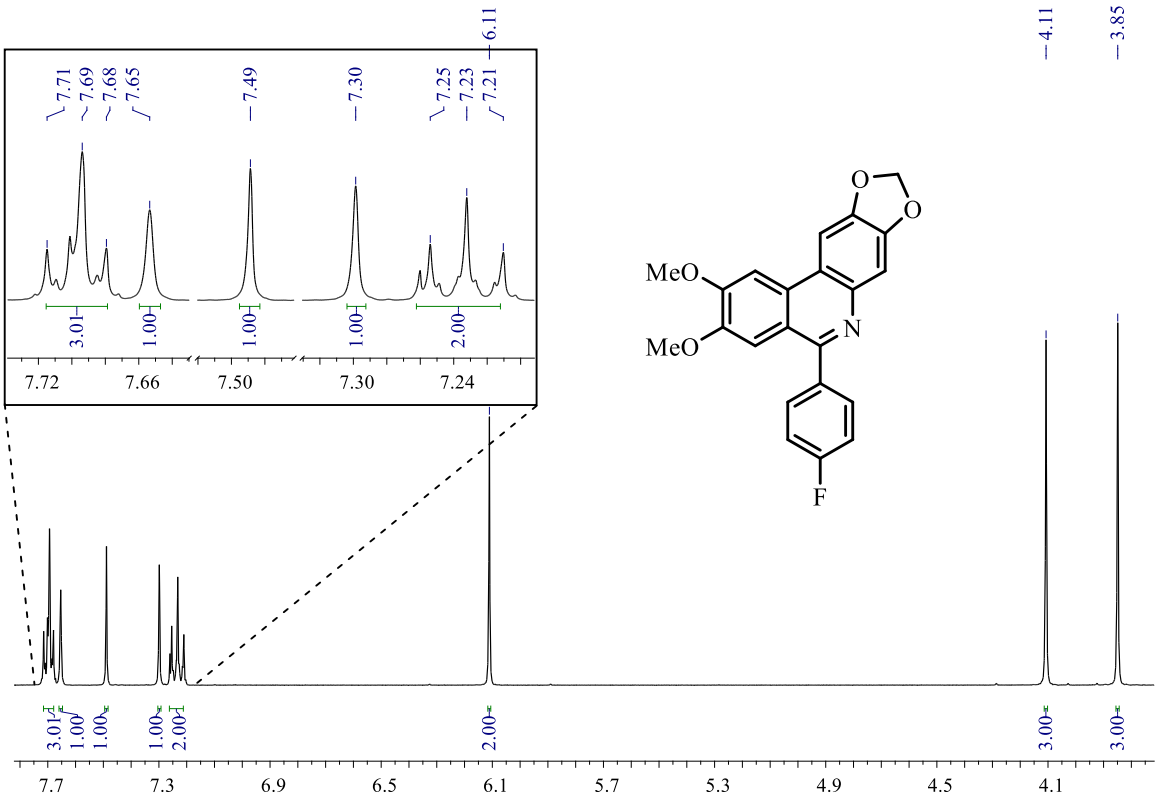


**Figure 55**. $^{13}C$ NMR spectra of compound **6h** ($CDCl_3$, 100 MHz).

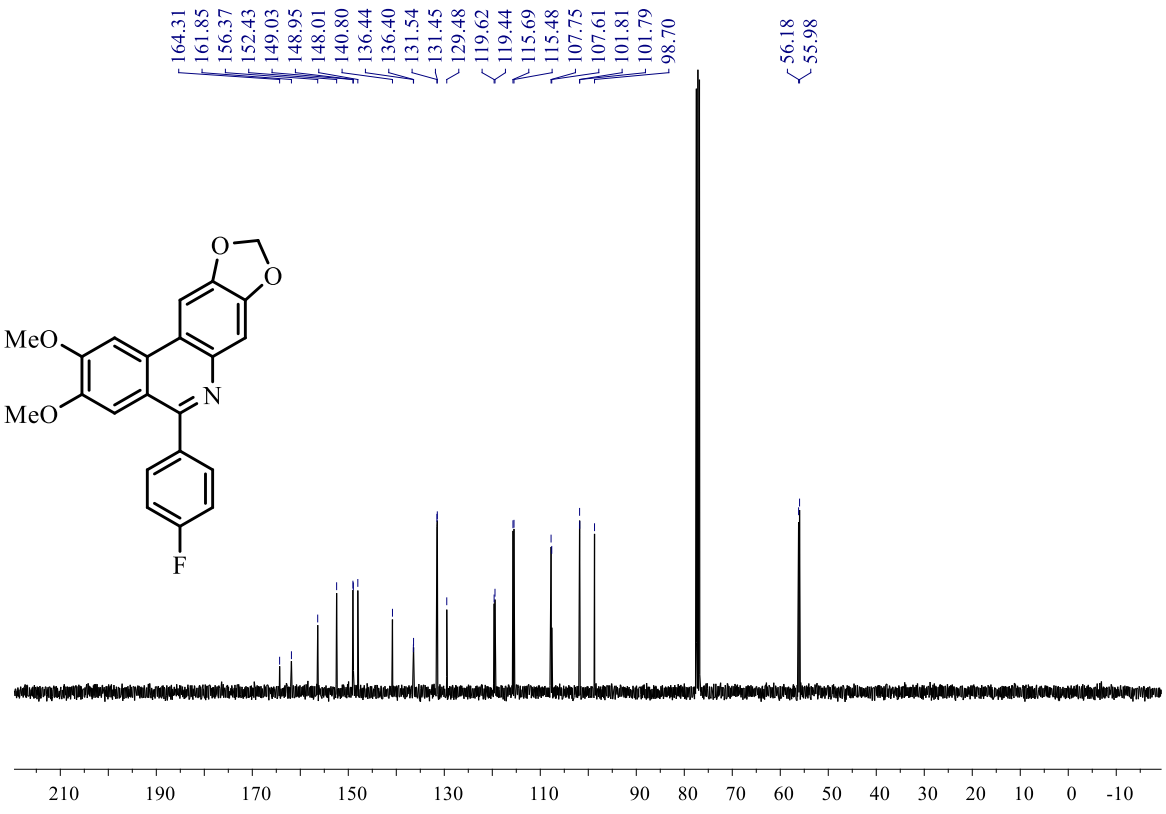


**Figure 56**. $^{13}$C-APT NMR spectra of compound **6h** ($CDCl_3$, 100 MHz).

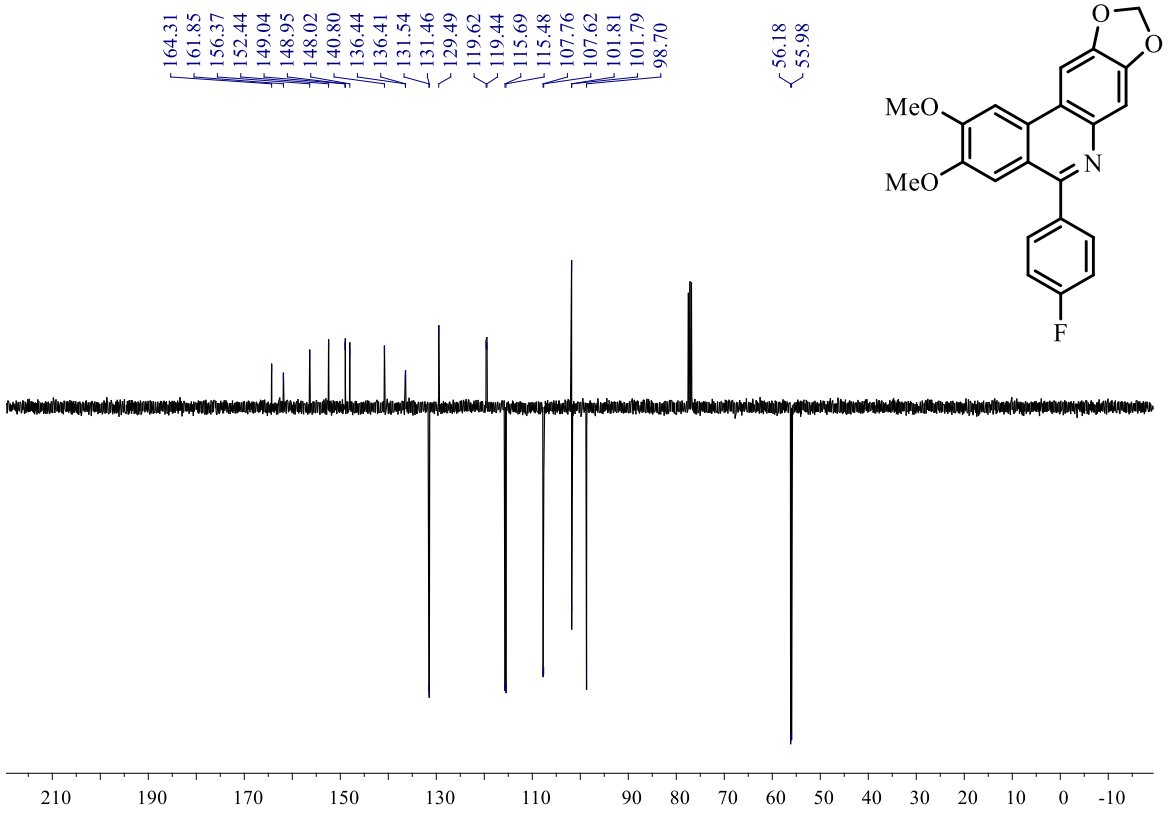


**Figure 57**. Expansion of $^{13}$C-APT NMR spectra of compound **6h** ($CDCl_3$, 100 MHz).

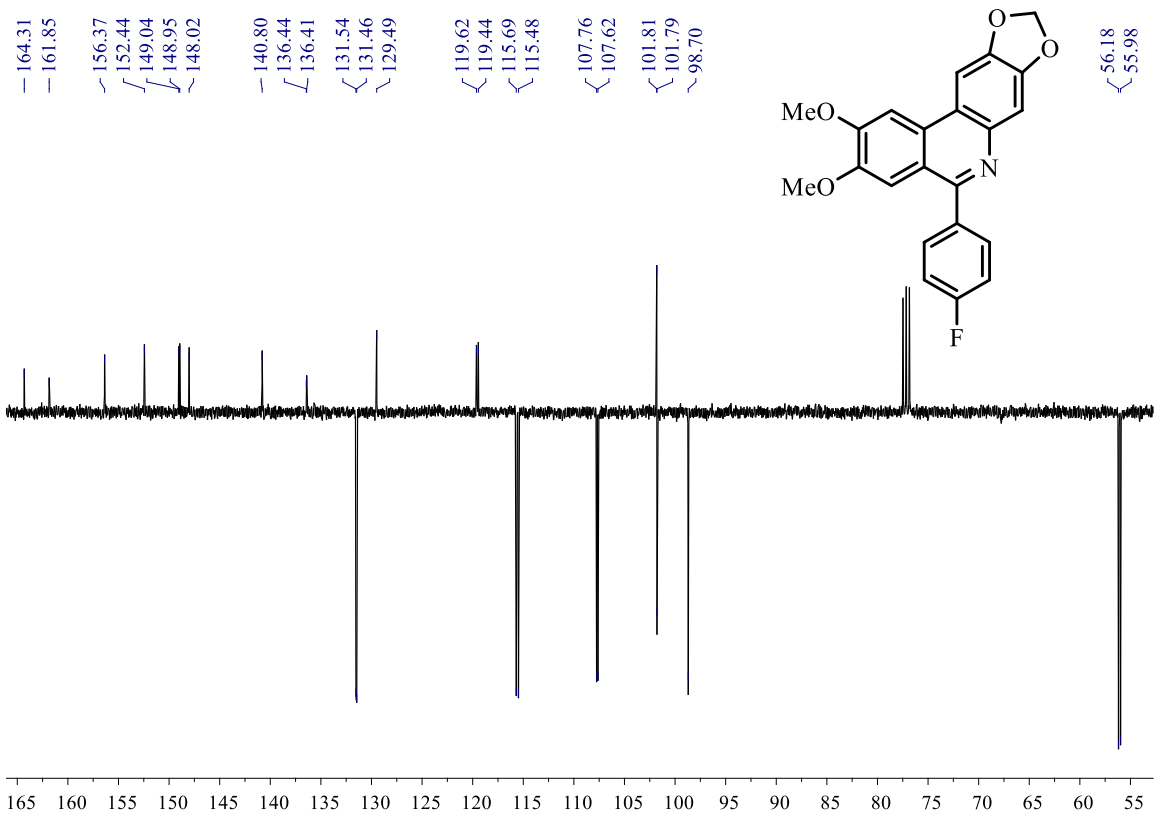


**Figure 58**. GC-MS of compound **6h** (70 eV).

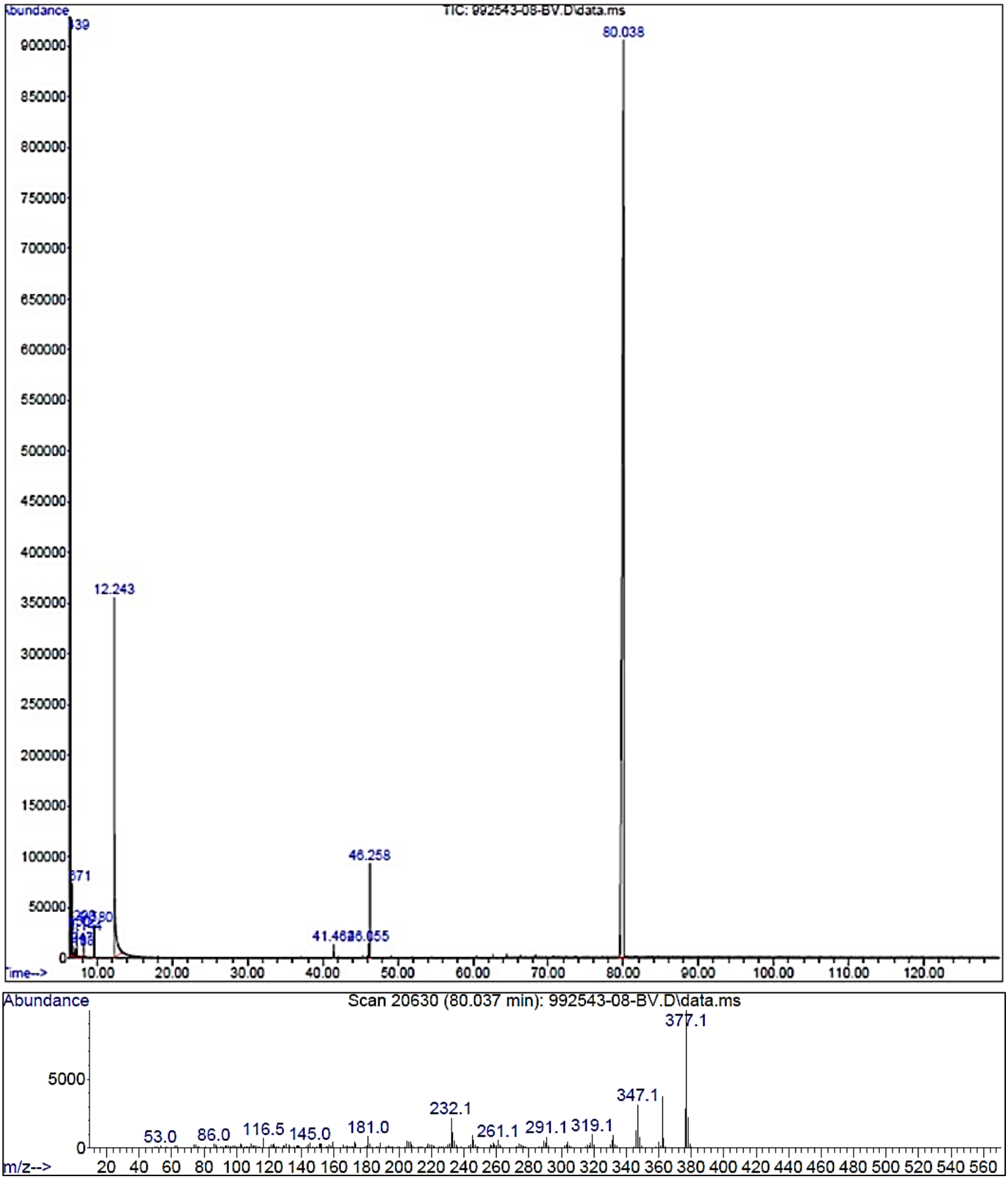


**Figure 59**. $^{1}H$ NMR spectra of compound **6i** ($CDCl_3$, 400 MHz).

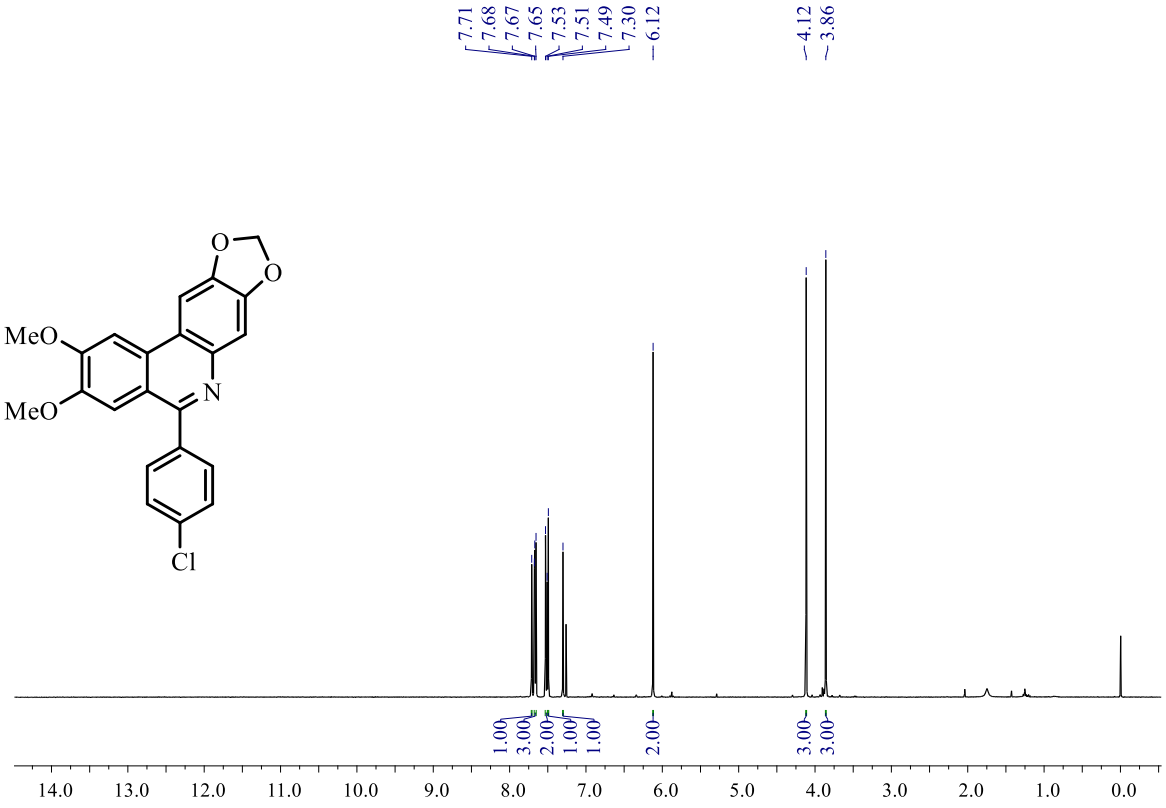


**Figure 60**. Expansion of $^{1}H$ NMR spectra of compound **6i** ($CDCl_3$, 400 MHz).

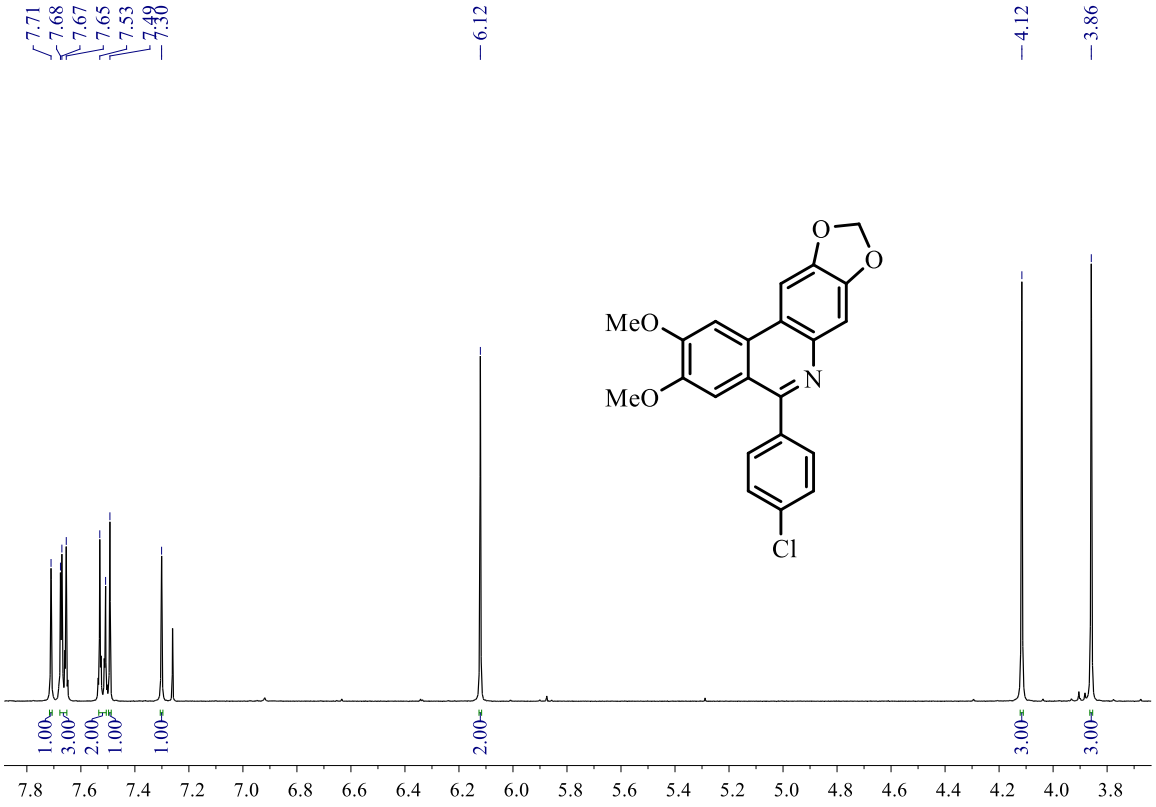


**Figure 61**. $^{13}C$ NMR spectra of compound **6i** ($CDCl_3$, 100 MHz).

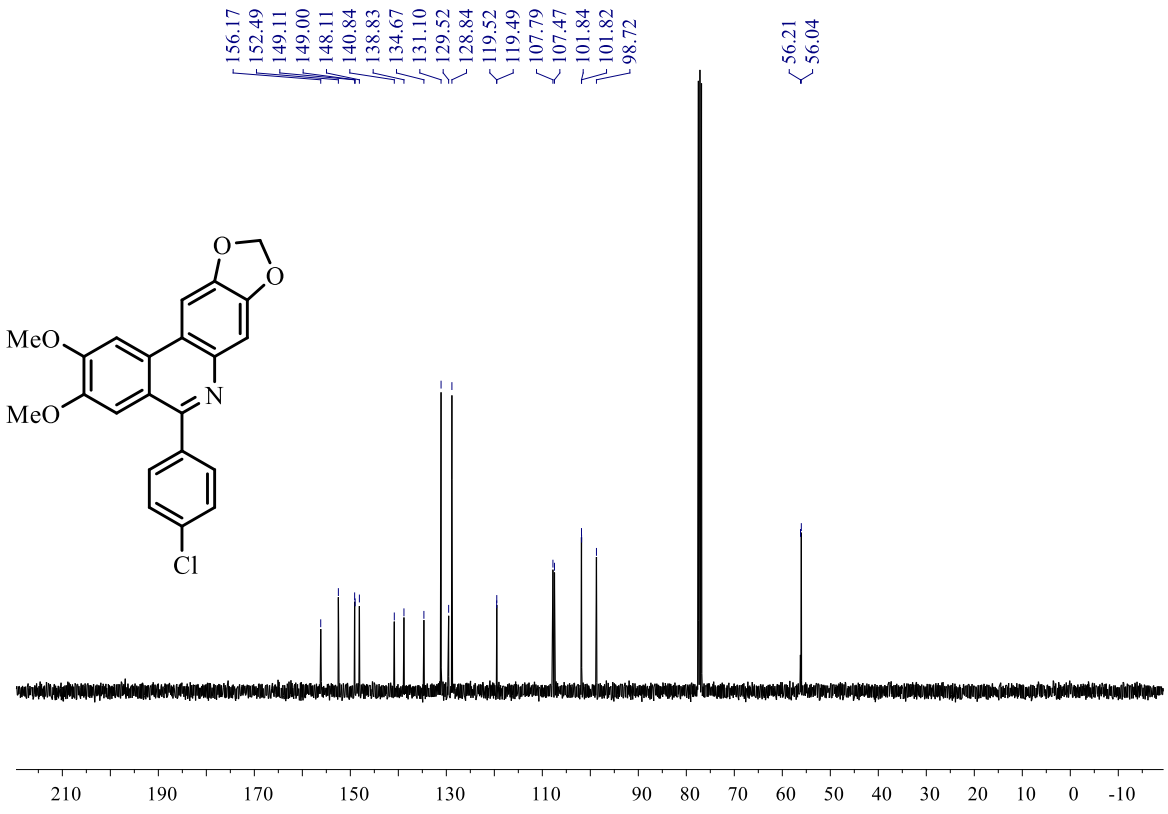


**Figure 62**. $^{13}$C-APT NMR spectra of compound **6i** ($CDCl_3$, 100 MHz).

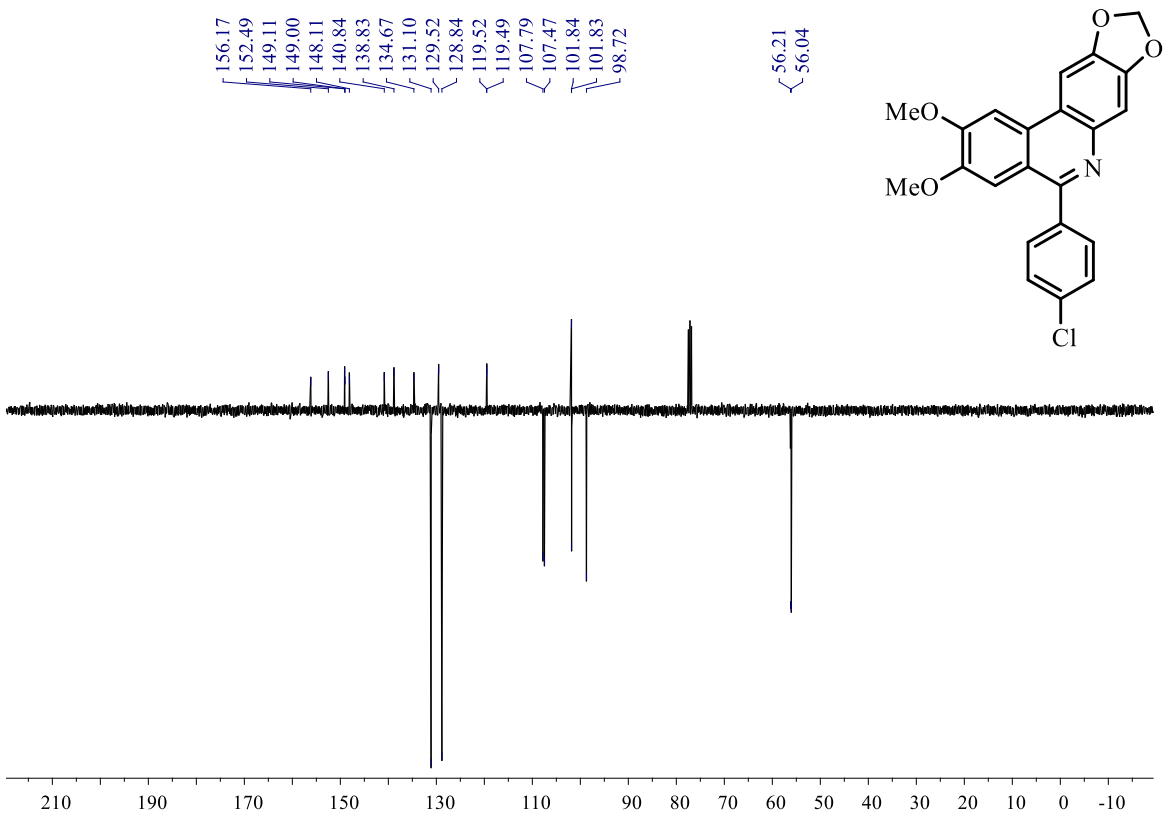


**Figure 63**. Expansion of $^{13}$C-APT NMR spectra of compound **6i** ($CDCl_3$, 100 MHz).

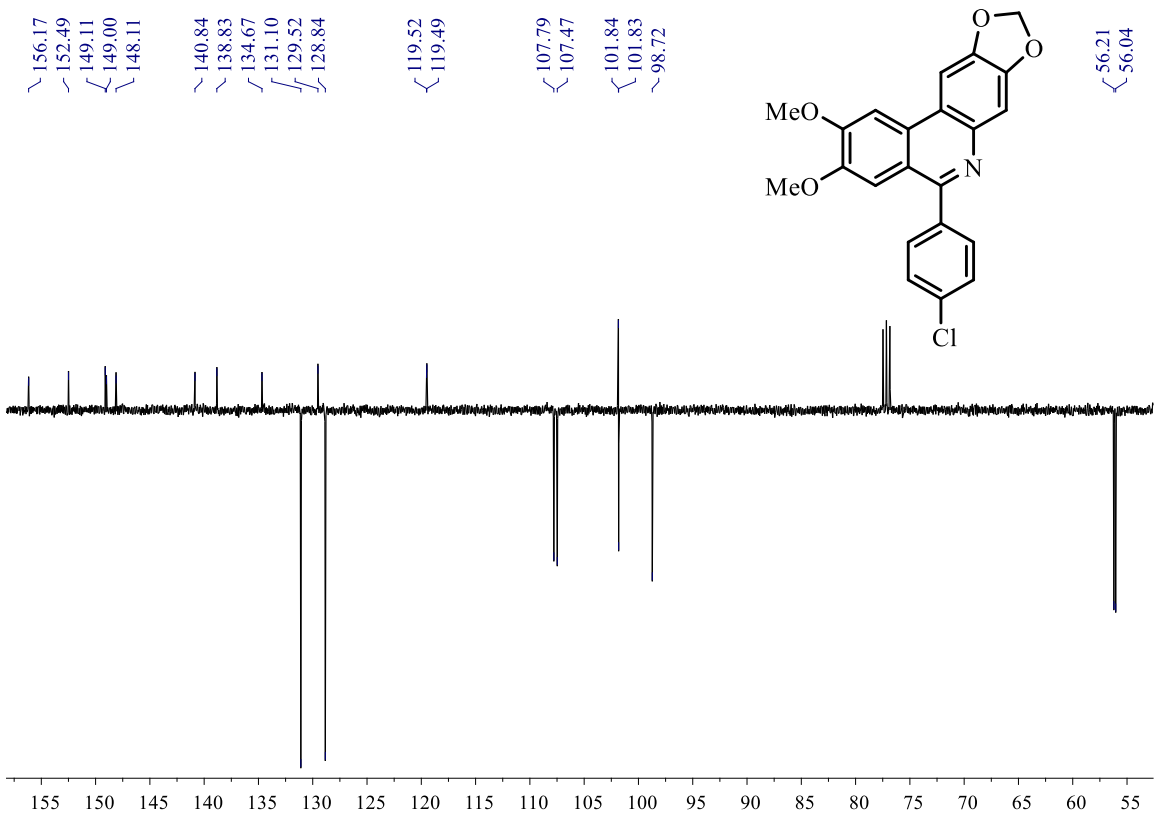


**Figure 64**. GC-MS of compound **6i** (70 eV).

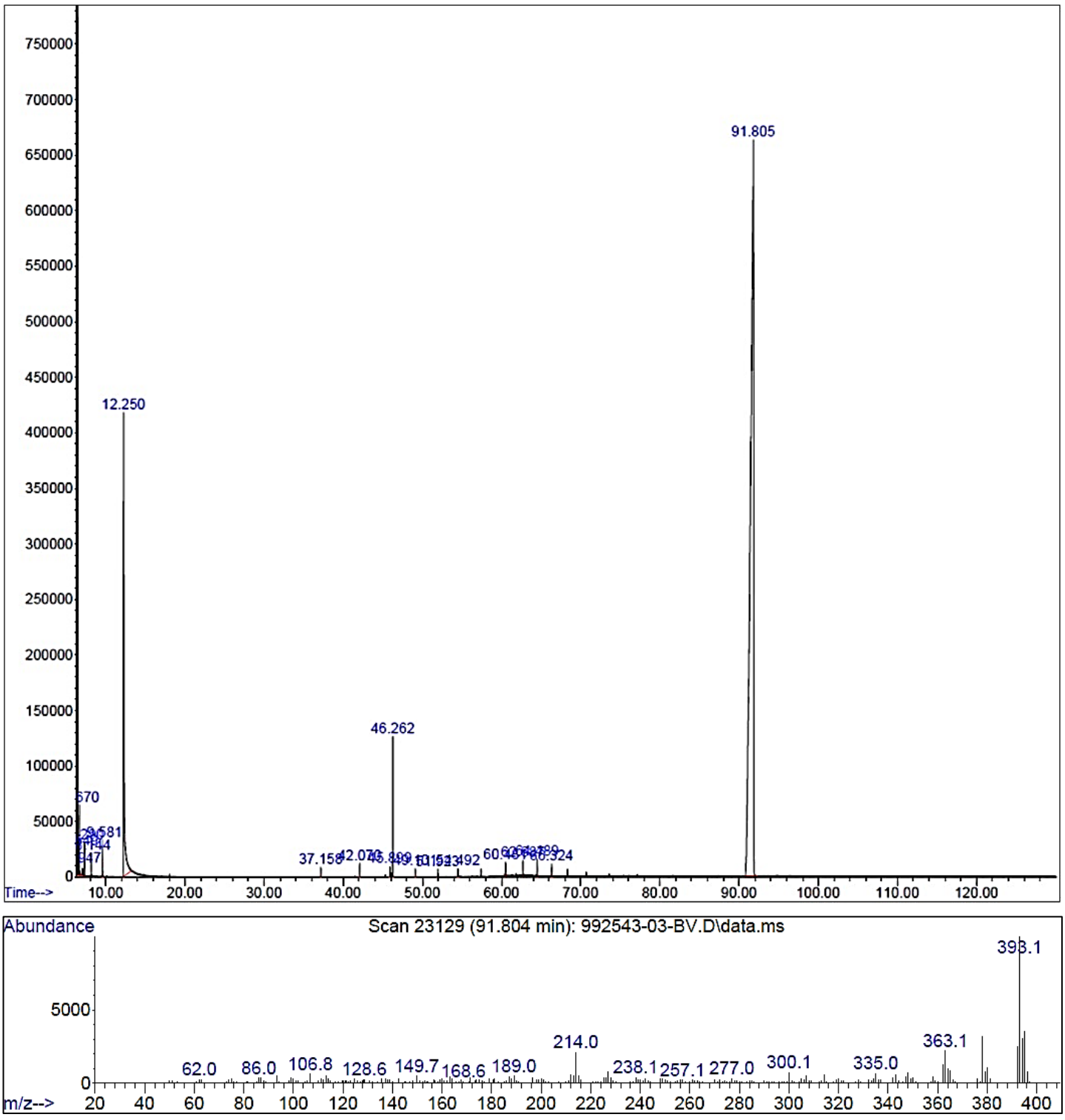


**Figure 65**. $^{1}H$ NMR spectra of compound **6j** ($CDCl_3$, 400 MHz).

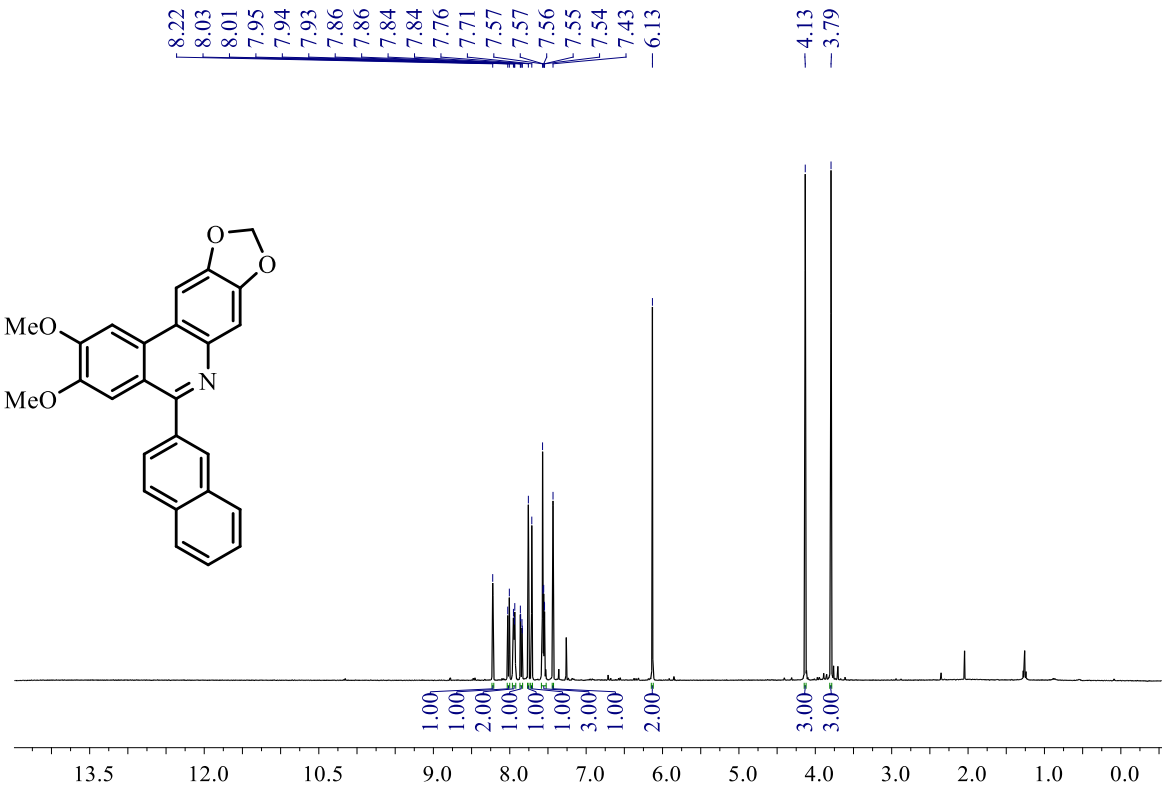


**Figure 66**. Expansion of $^{1}H$ NMR spectra of compound **6j** ($CDCl_3$, 400 MHz).

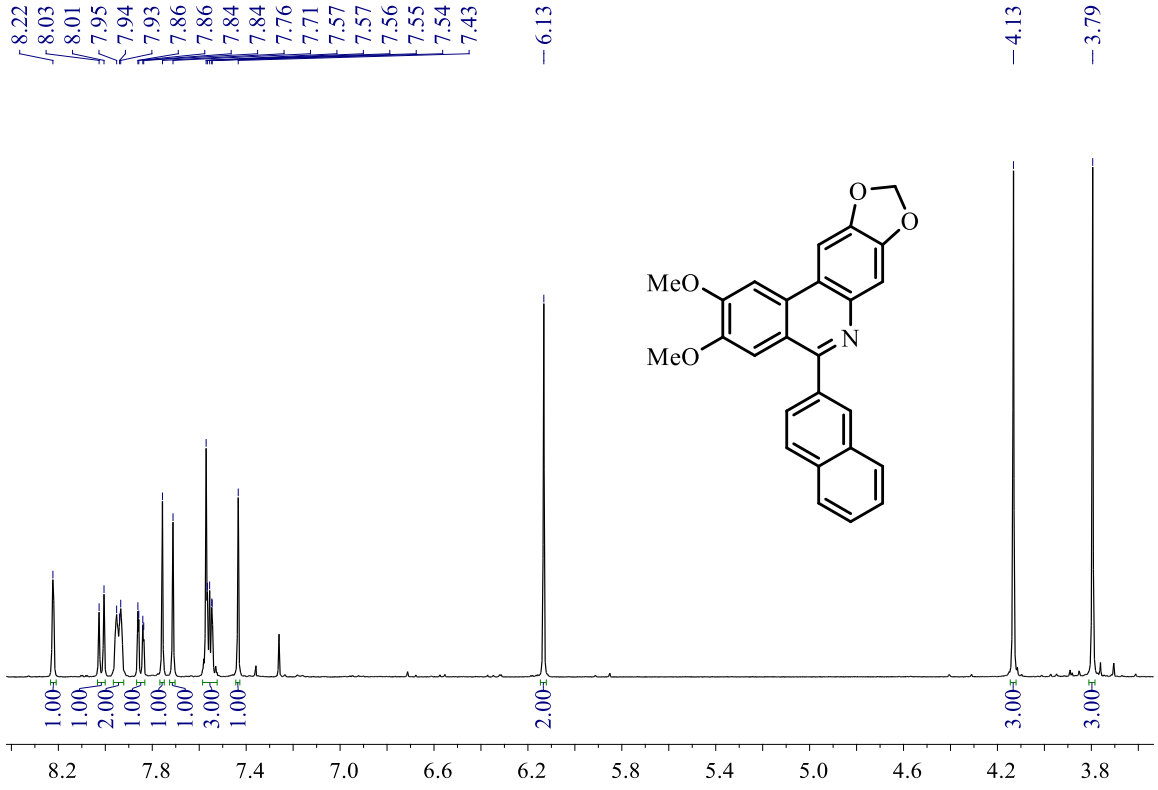


**Figure 67**. $^{13}C$ NMR spectra of compound **6j** ($CDCl_3$, 100 MHz).

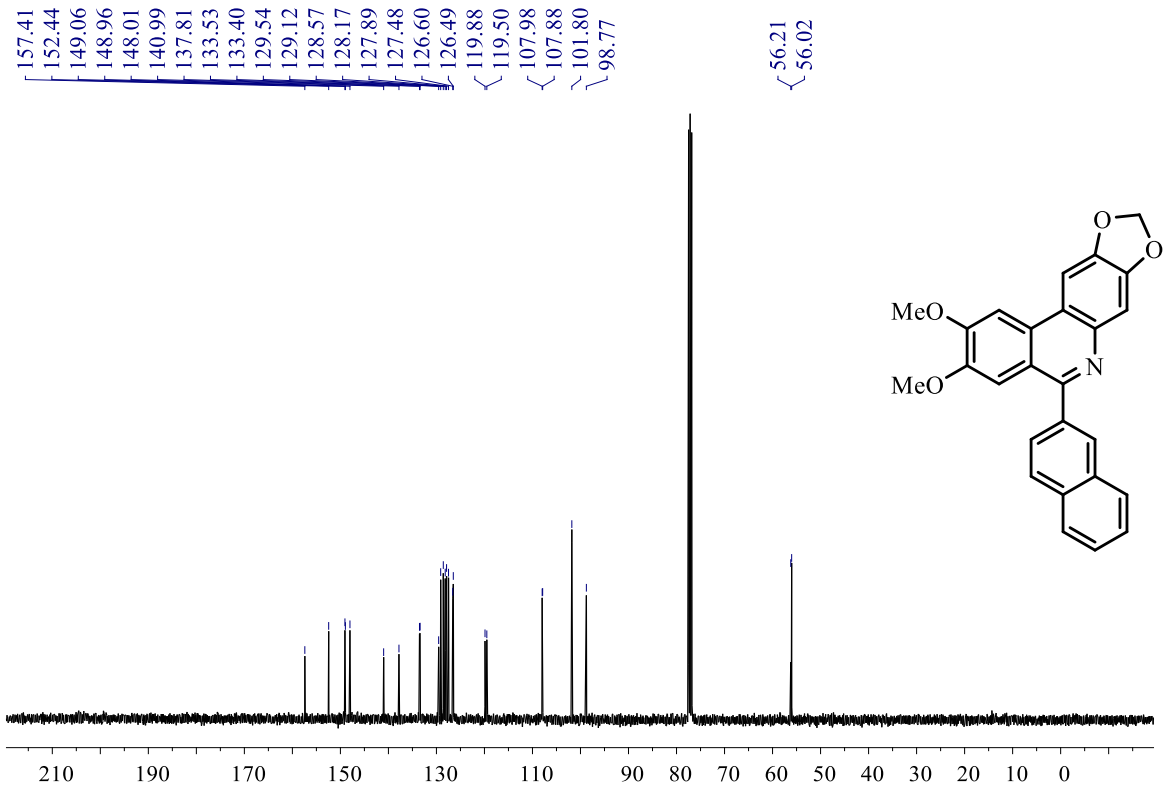


**Figure 68**. $^{13}C$–APT NMR spectra of compound **6j** ($CDCl_3$, 100 MHz).

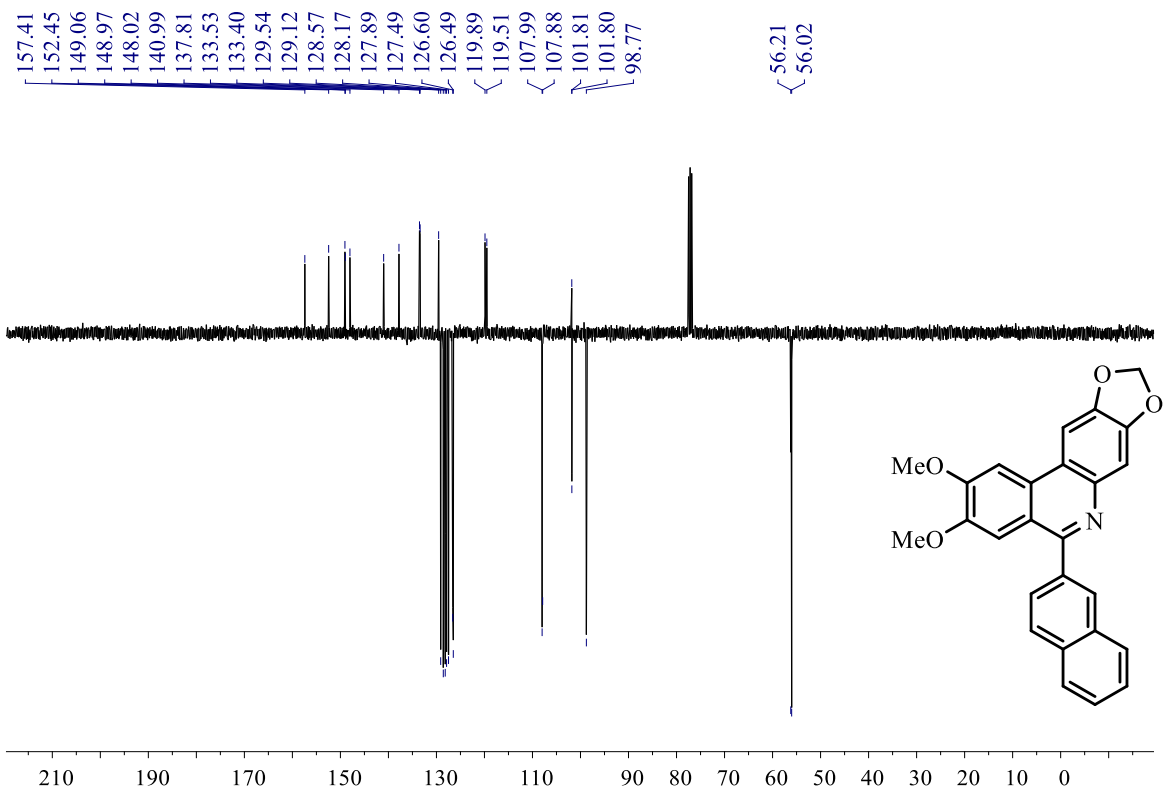


**Figure 69**. Expansion of $^{13}C$–APT NMR spectra of compound **6j** ($CDCl_3$, 100 MHz).

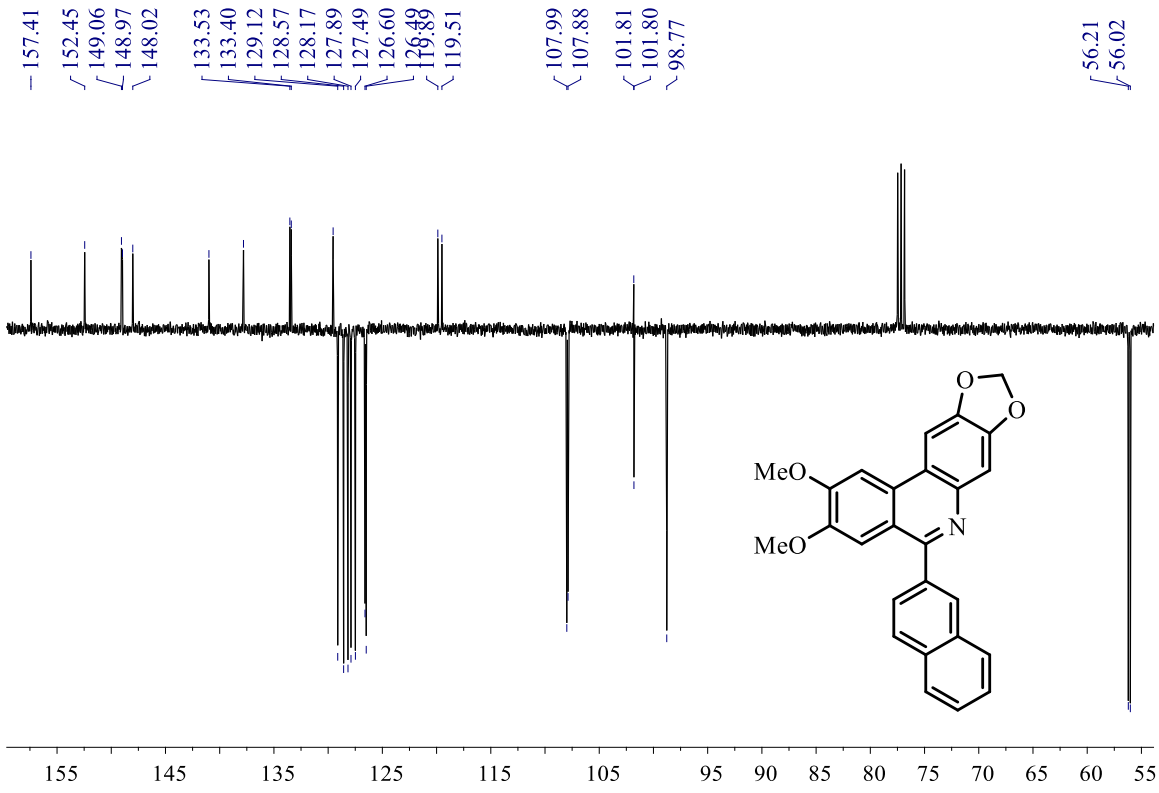


**Figure 70.** $^{1}H$ NMR spectra of compound **6k** ($CDCl_3$, 400 MHz).

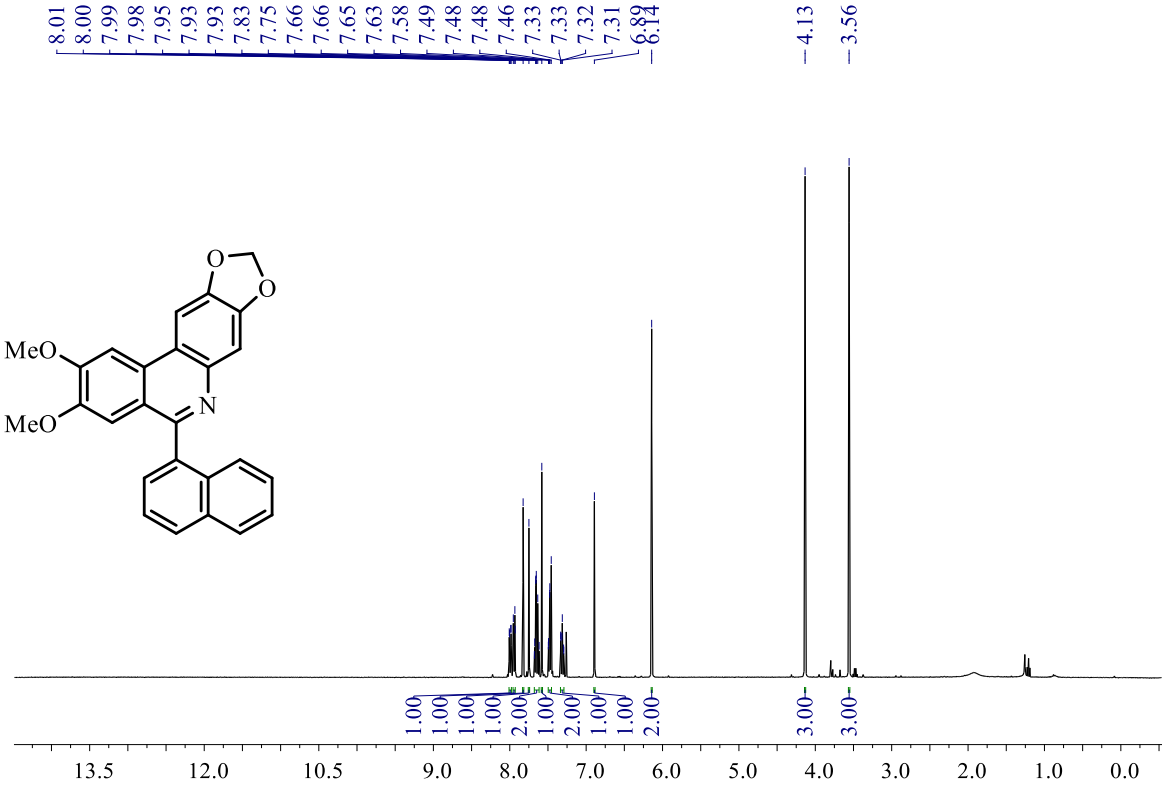


**Figure 71**. Expansion of $^{1}H$ NMR spectra of compound **6k** ($CDCl_3$, 400 MHz).

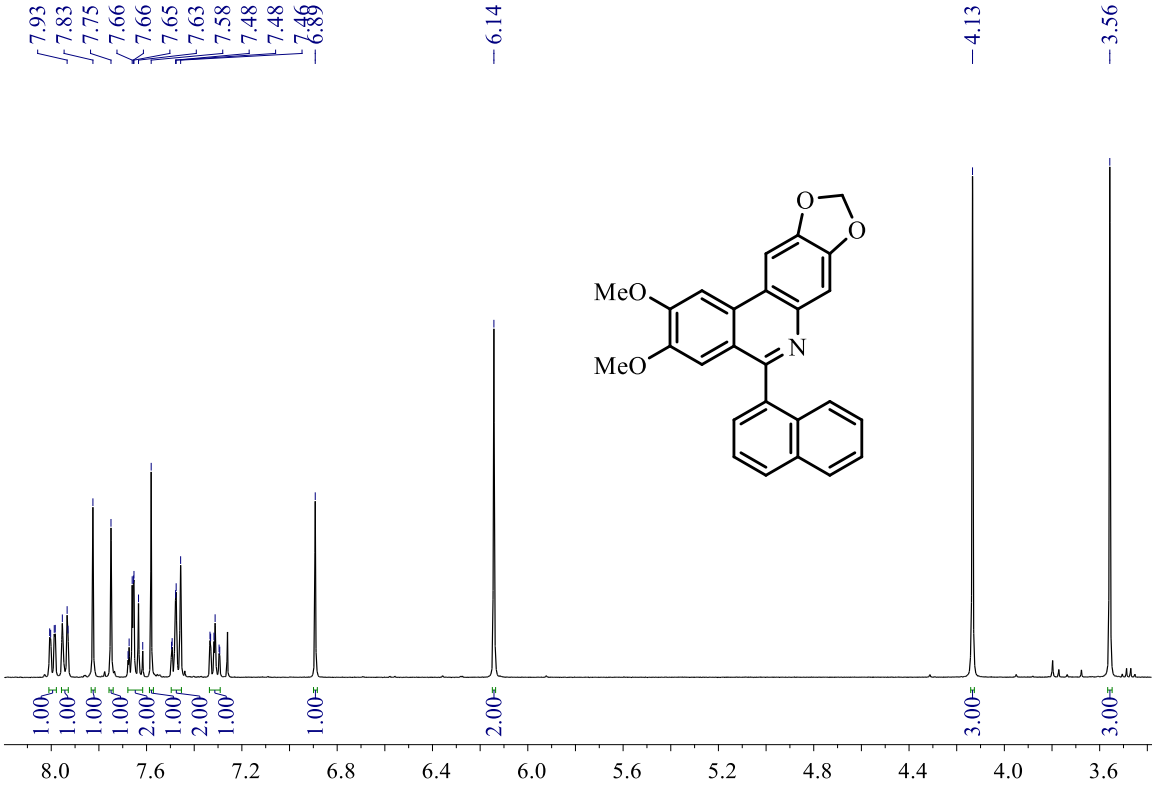


**Figure 72.** $^{13}C$ NMR spectra of compound **6k** ($CDCl_3$, 100 MHz).

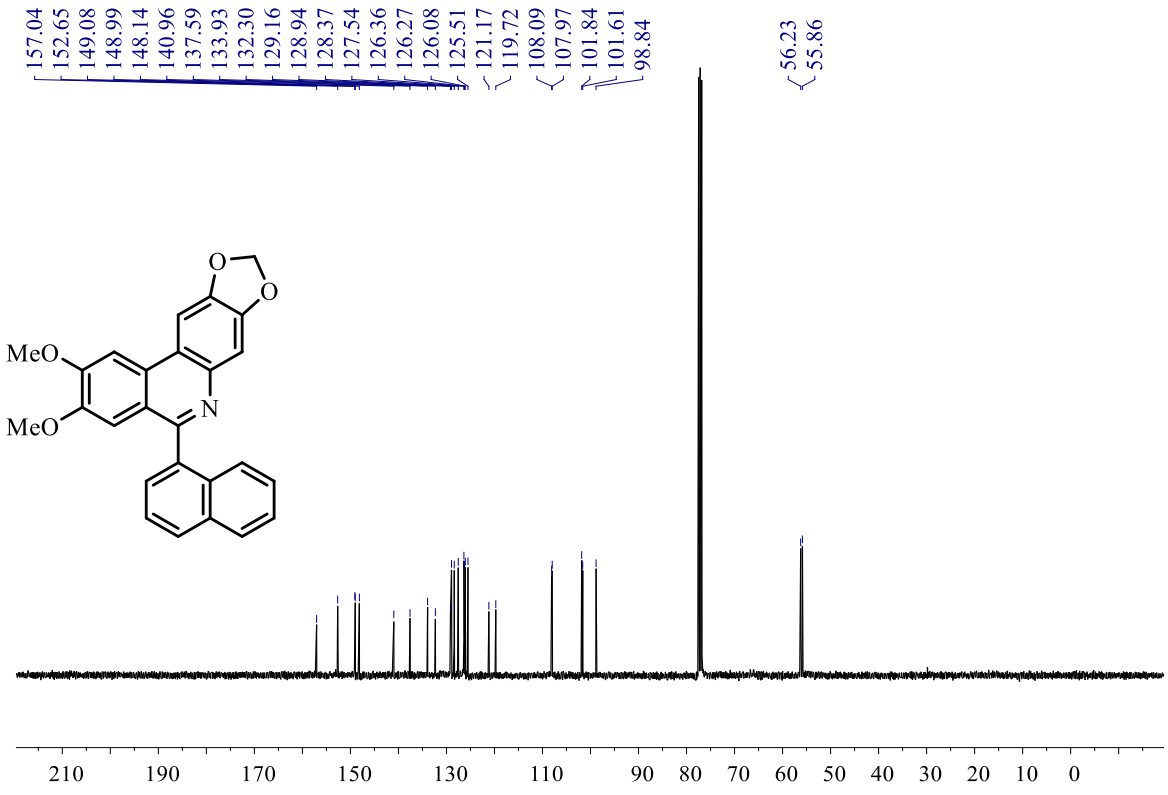


**Figure 73**. $^{13}C$–APT NMR spectra of compound **6k** ($CDCl_3$, 100 MHz).

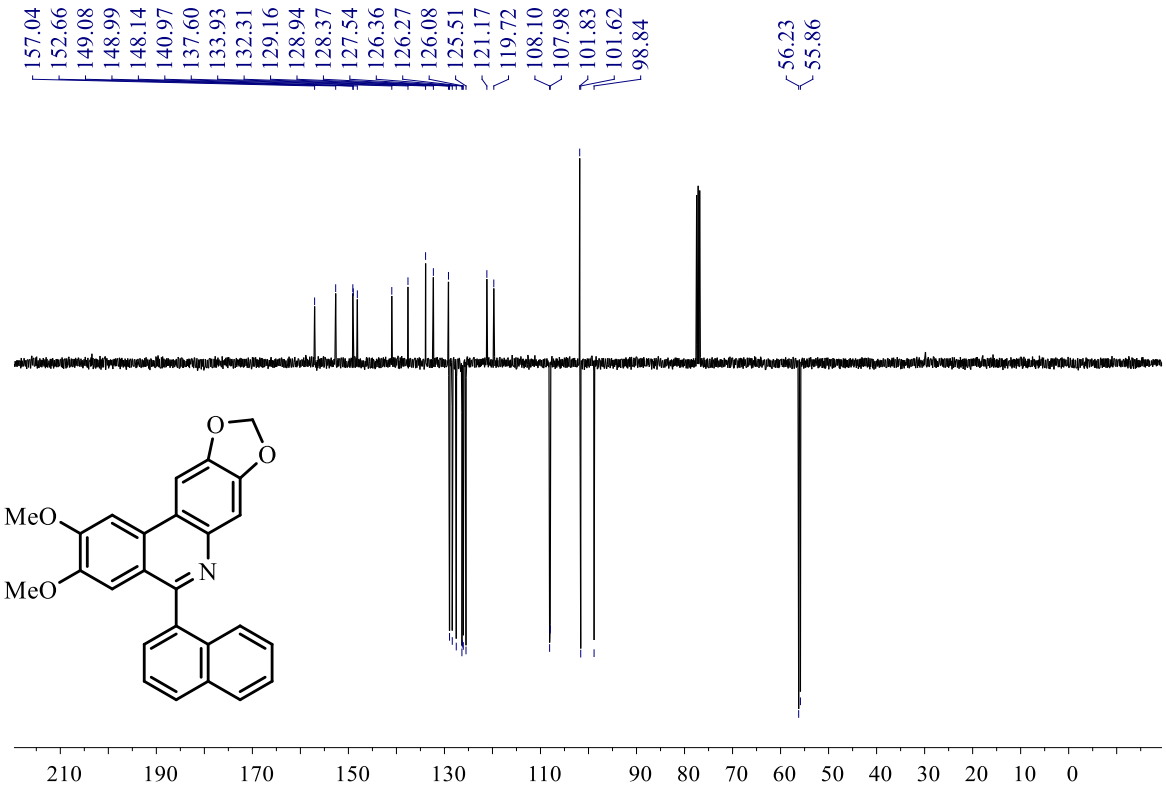


**Figure 74**. Expansion of $^{13}C$–APT NMR spectra of compound **6k** ($CDCl_3$, 100 MHz).

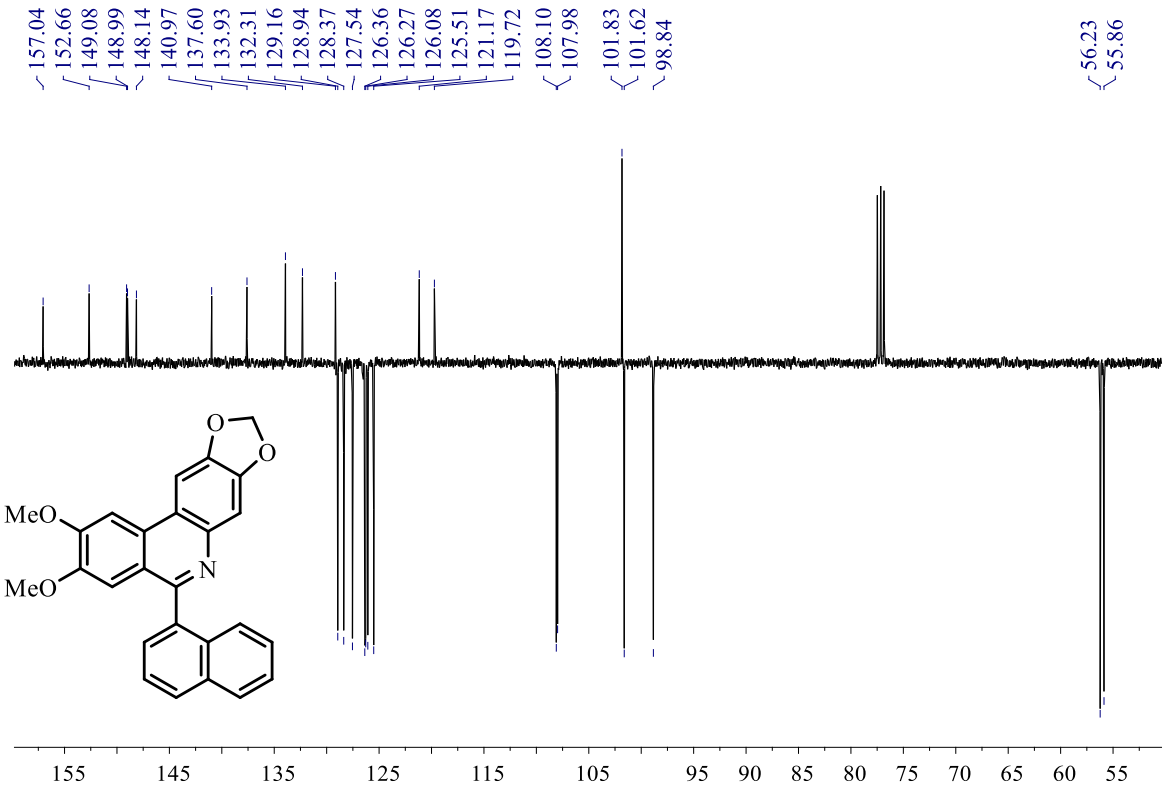


**Figure 75**. $^{1}H$ NMR spectra of compound **6m** ($CDCl_3$, 400 MHz).

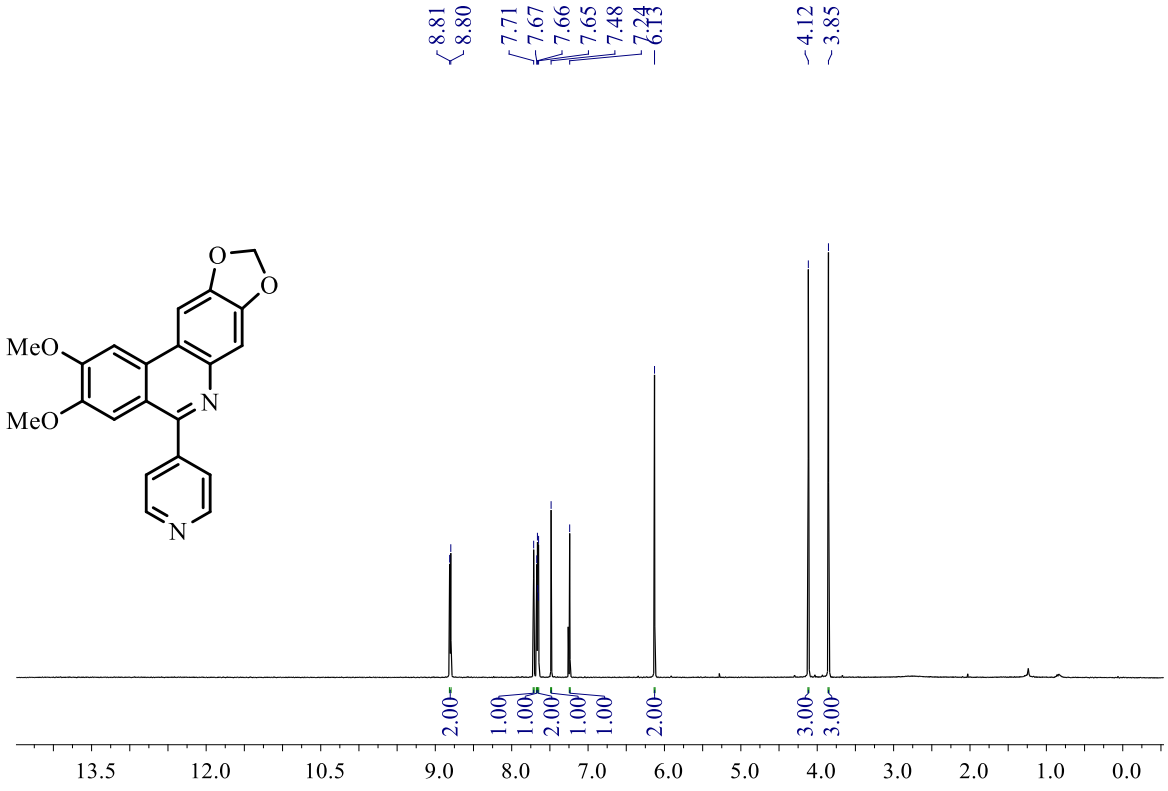


**Figure 76**. Expansion of $^{1}H$ NMR spectra of compound **6m** ($CDCl_3$, 400 MHz).

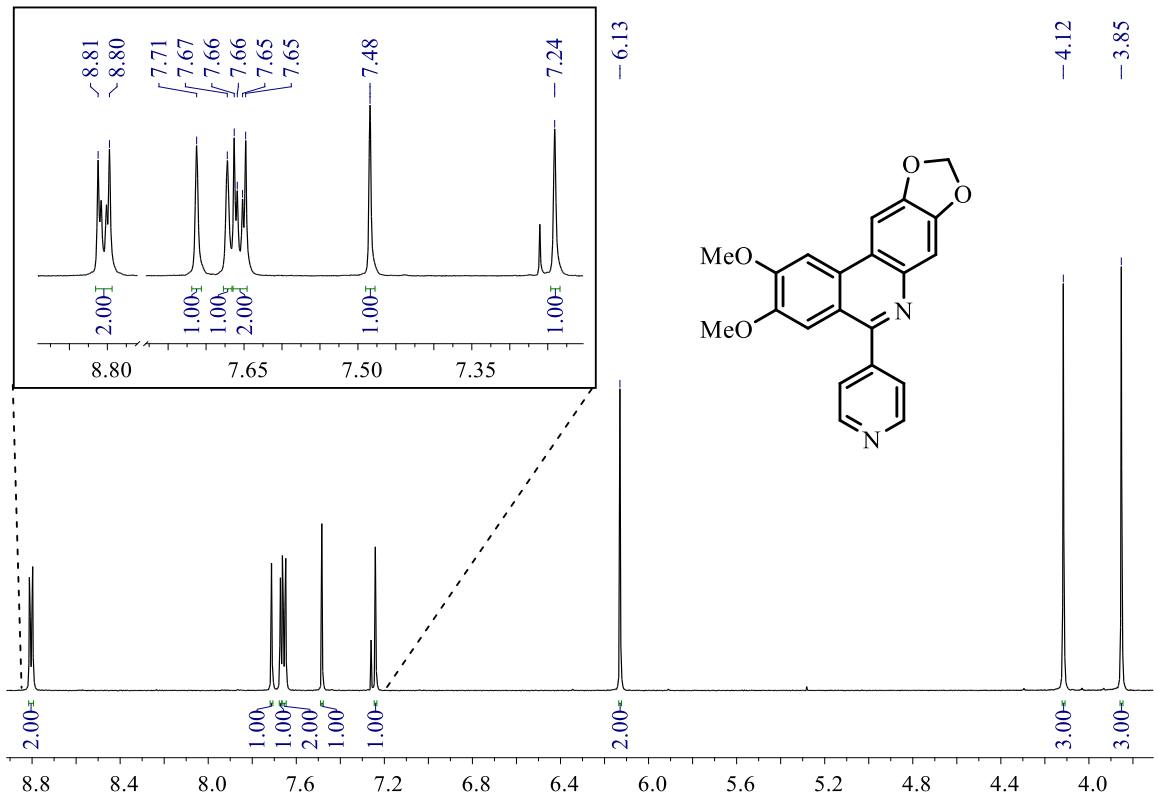


**Figure 77**. $^{13}C$ NMR spectra of compound **6m** ($CDCl_3$, 100 MHz).

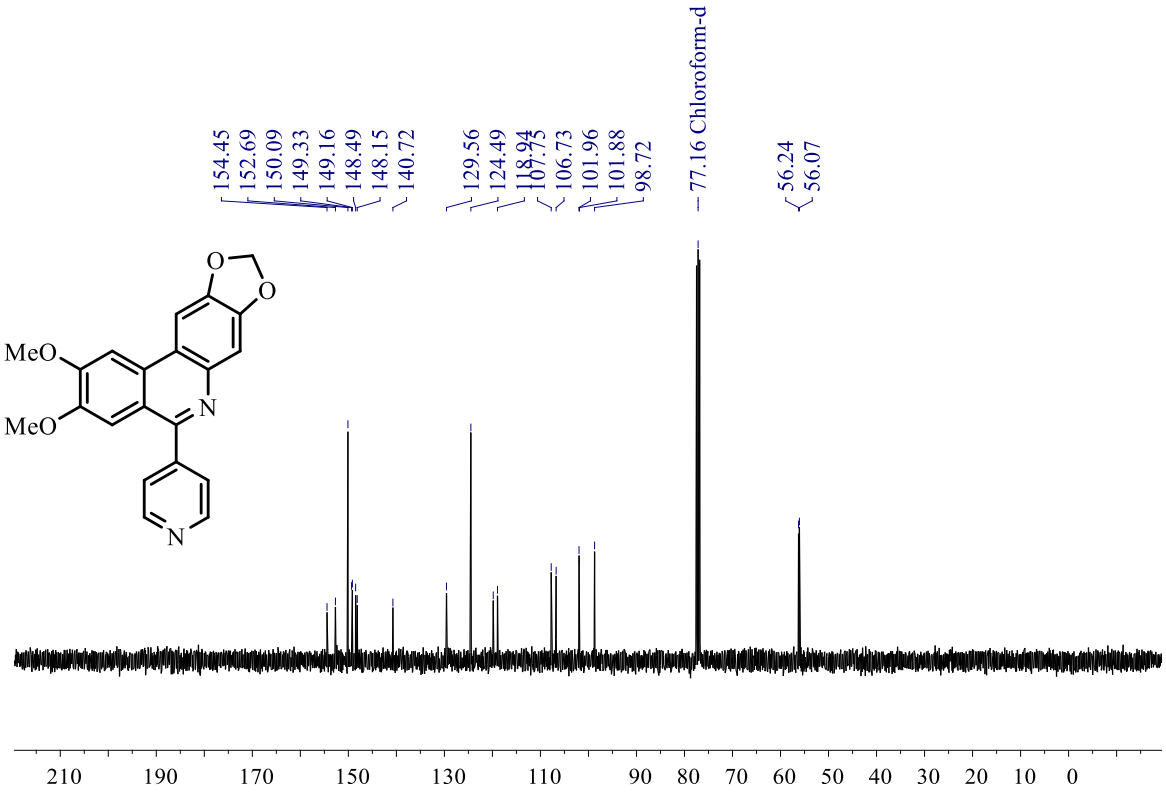


**Figure 78**. $^{13}$C-APT NMR spectra of compound **6m** ($CDCl_3$, 100 MHz).

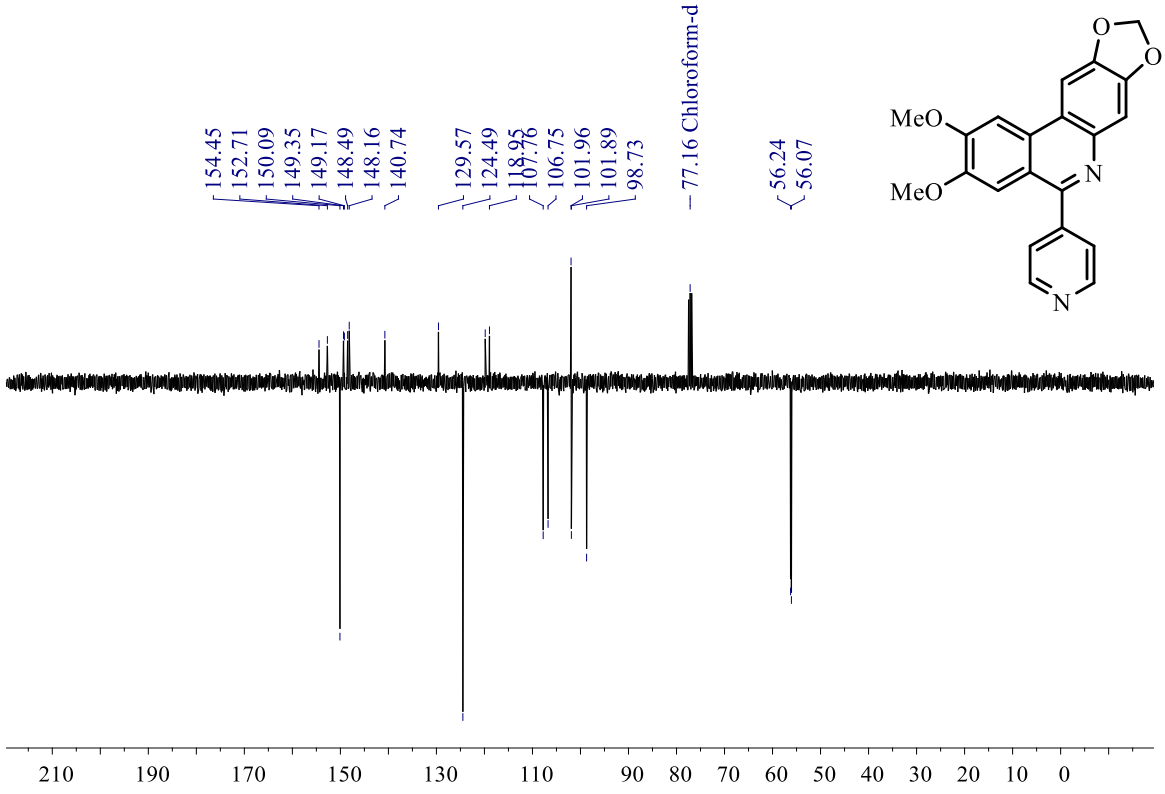


**Figure 79**. Expansion of $^{13}$C-APT NMR spectra of compound **6m** ($CDCl_3$, 100 MHz).

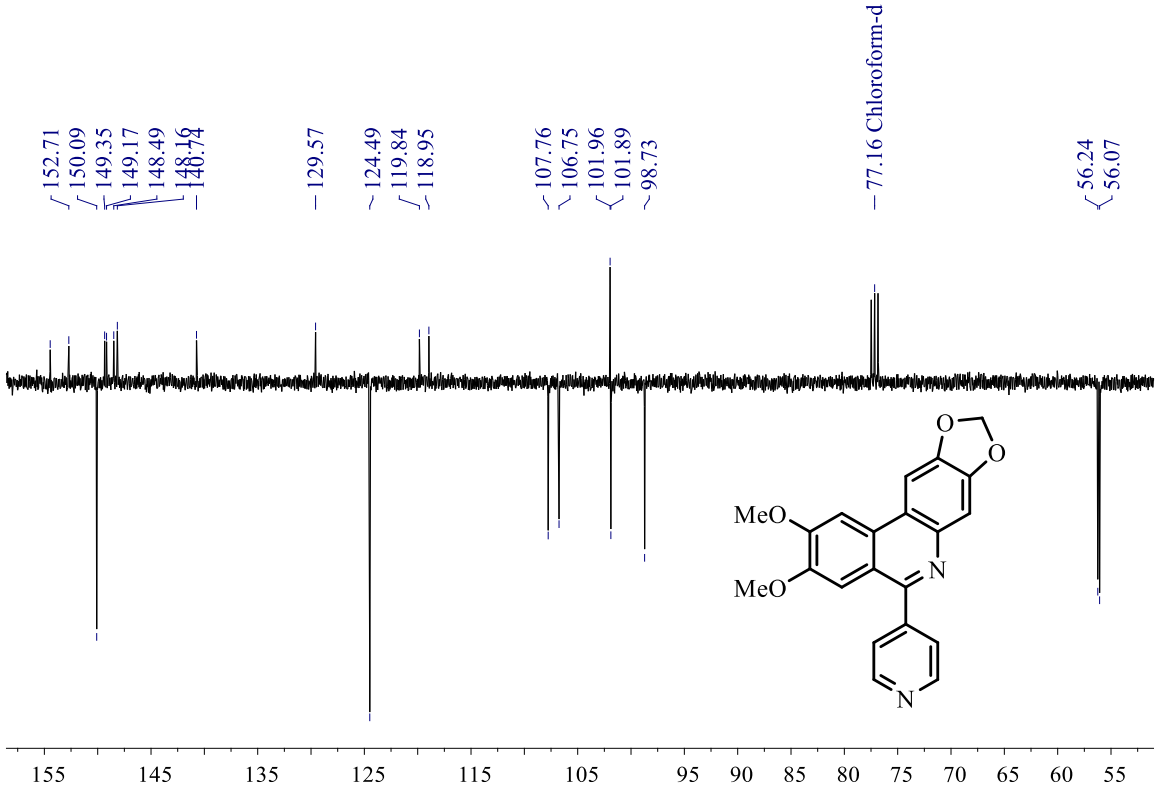


**Figure 80**. GC-MS of compound **6m** (70 eV).

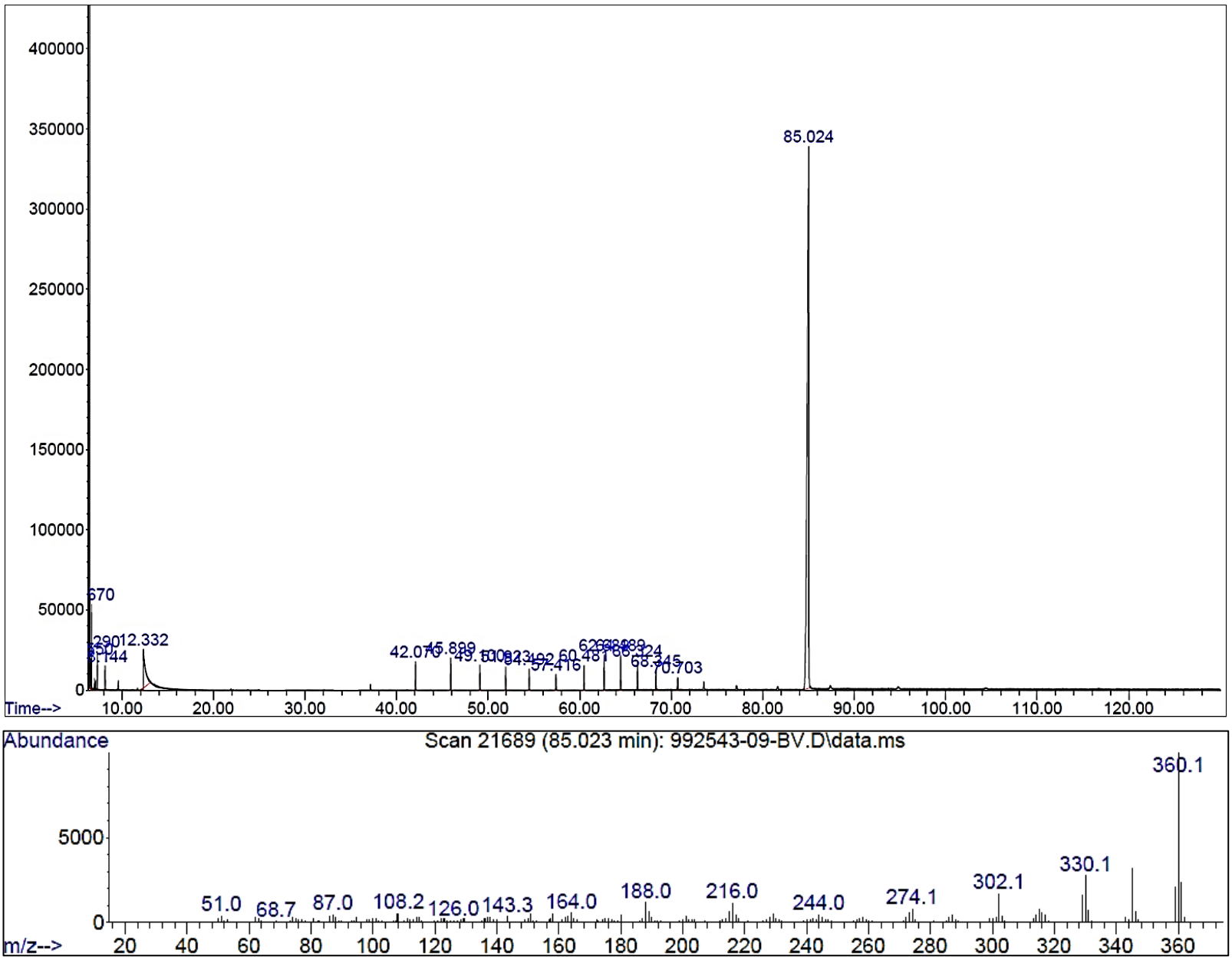


**Figure 81**. $^{1}H$ NMR spectra of compound **6n** ($CDCl_3$, 400 MHz).

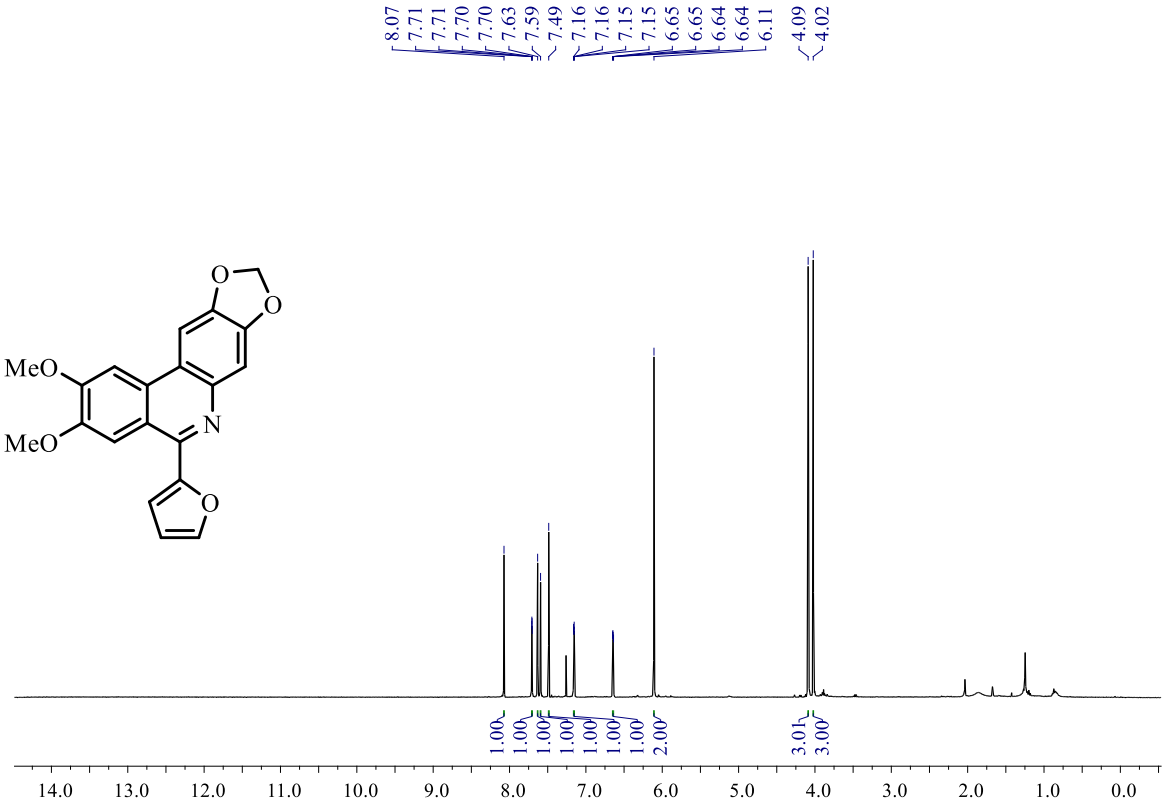


**Figure 82**. Expansion of $^{1}H$ NMR spectra of compound **6n** ($CDCl_3$, 400 MHz).

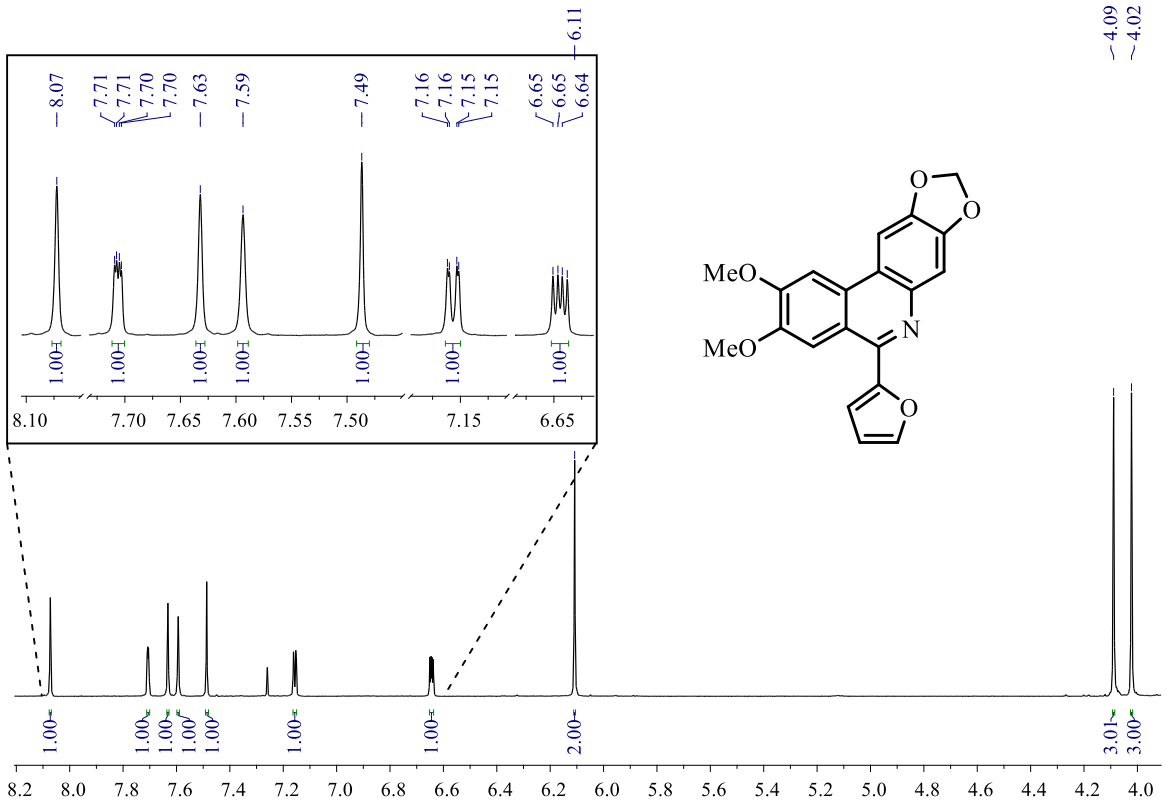


**Figure 83**. $^{13}C$ NMR spectra of compound **6n** ($CDCl_3$, 100 MHz).

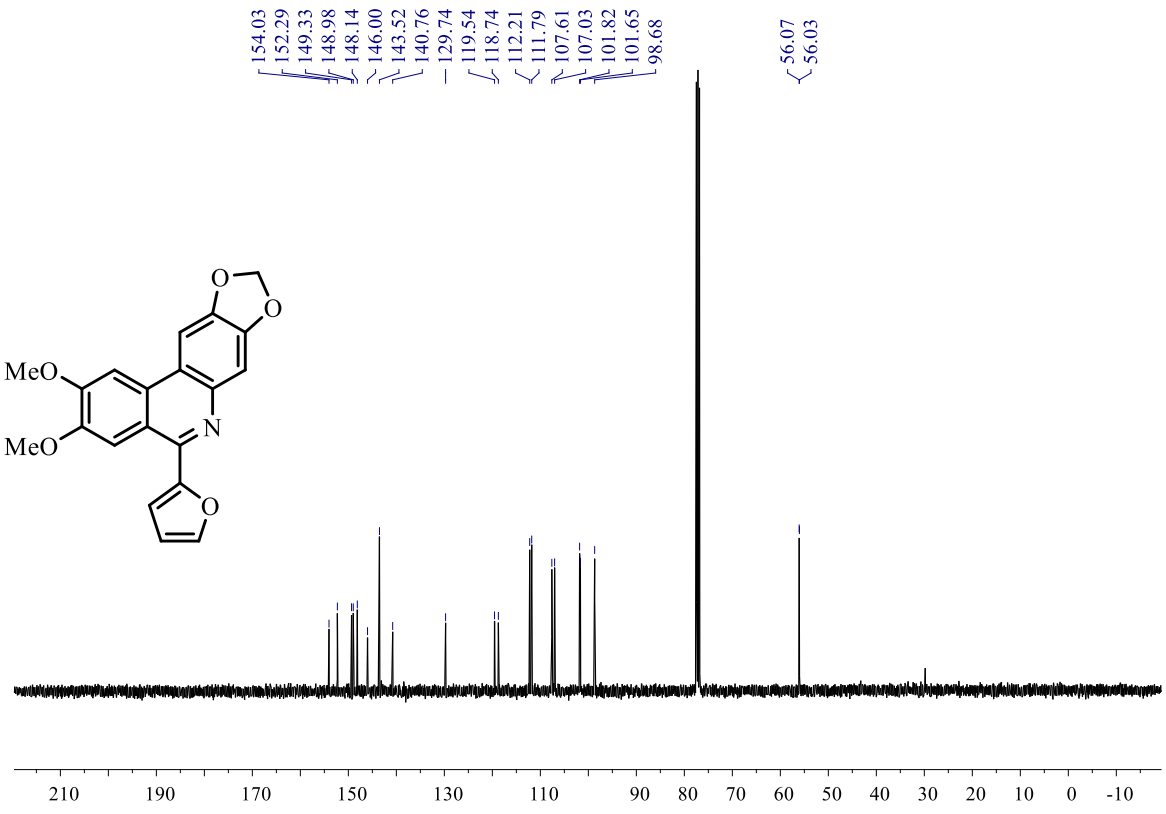


**Figure 84.** $^{13}$C-APT NMR spectra of compound **6n** ($CDCl_3$, 100 MHz).

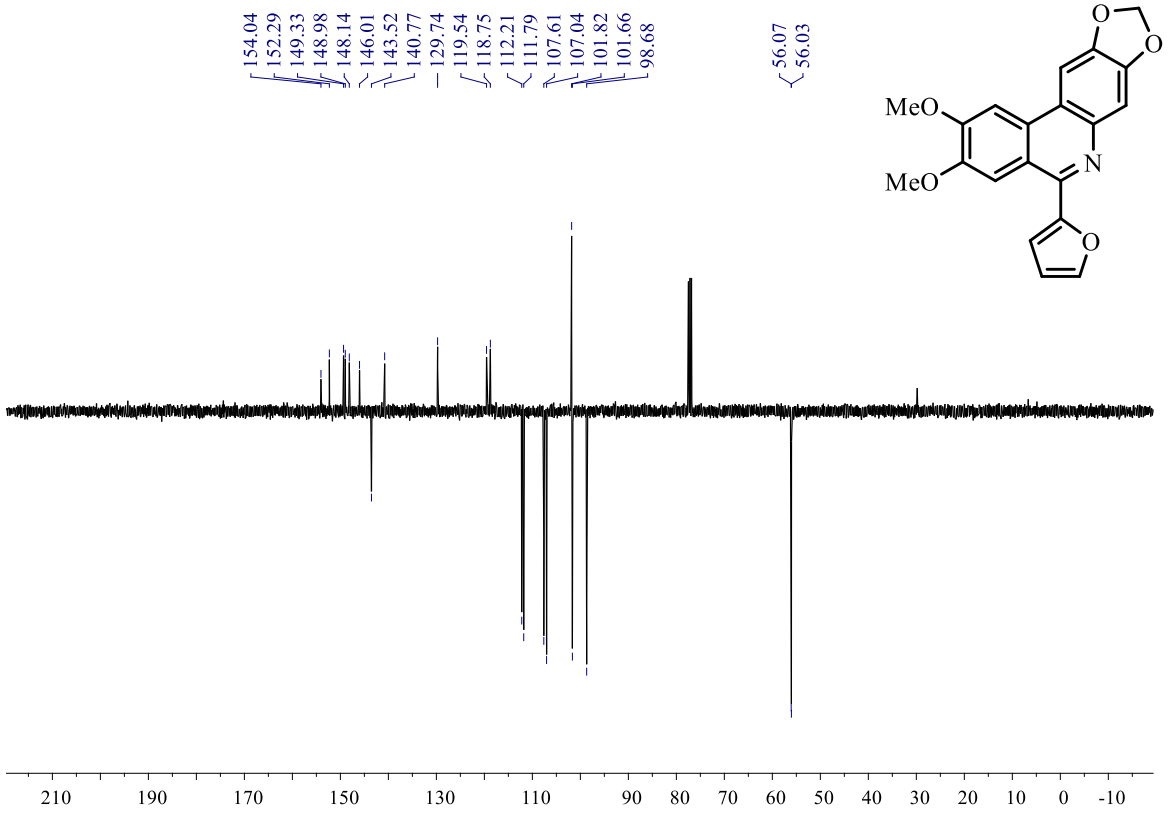


**Figure 85**. Expansion of $^{13}$C-APT NMR spectra of compound **6n** ($CDCl_3$, 100 MHz).

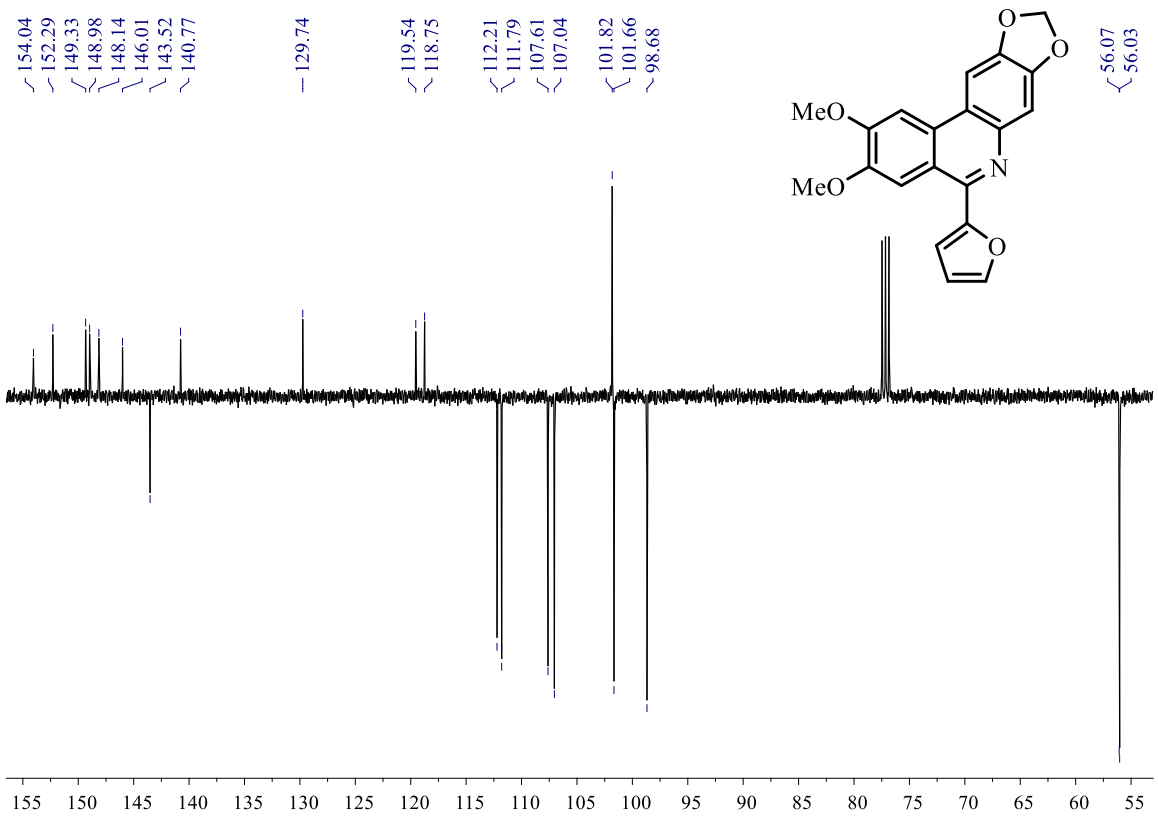


**Figure 86**. GC-MS of compound **6n** (70 eV).

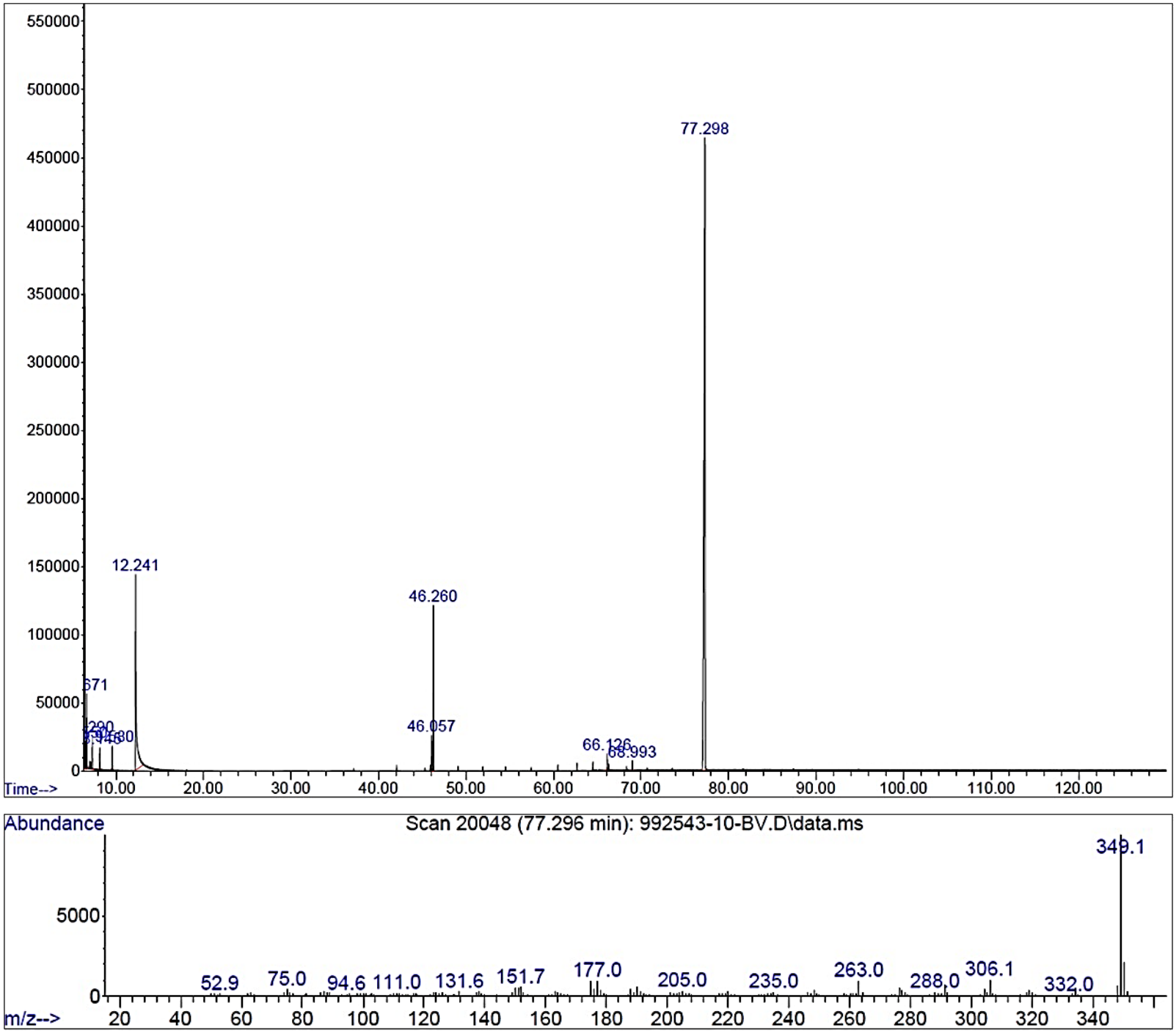


**Figure 87**. $^{1}$H NMR spectra of compound **6o** (DMSO-$d_6$, 400 MHz).

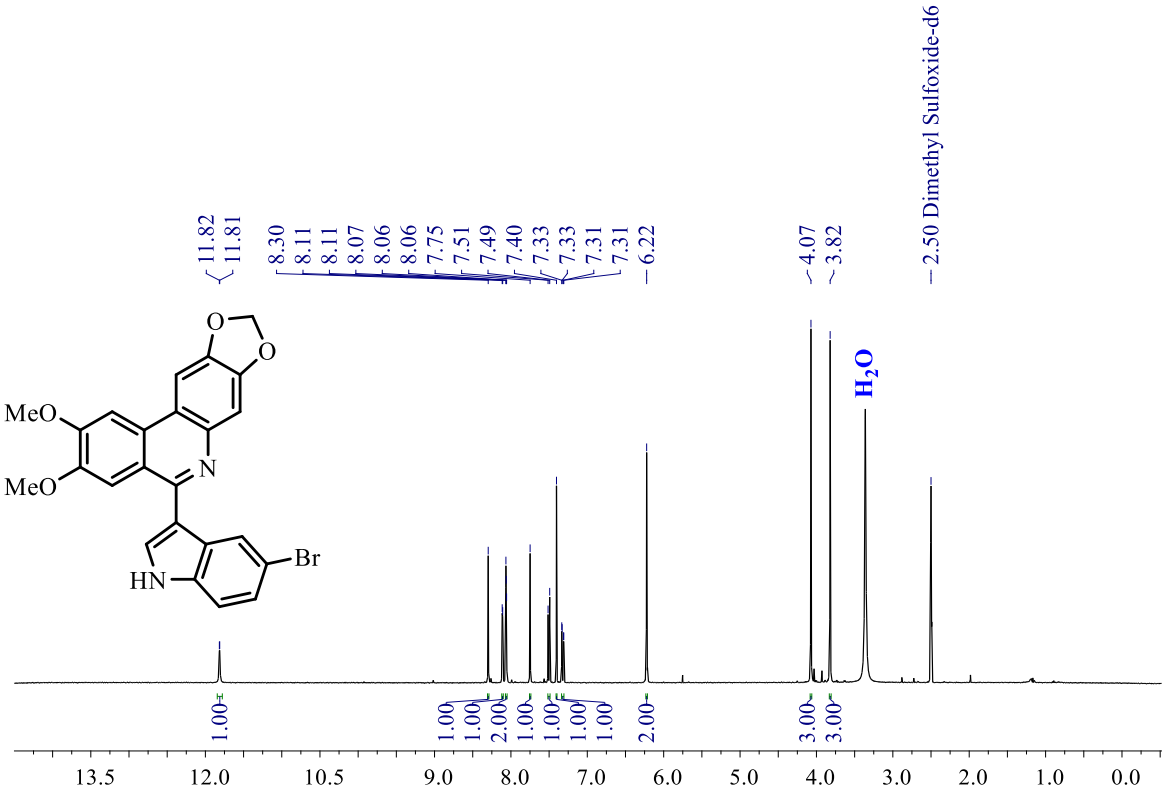


**Figure 88**. Expansion of $^{1}$H NMR spectra of compound **6o** (DMSO-$d_6$, 400 MHz).

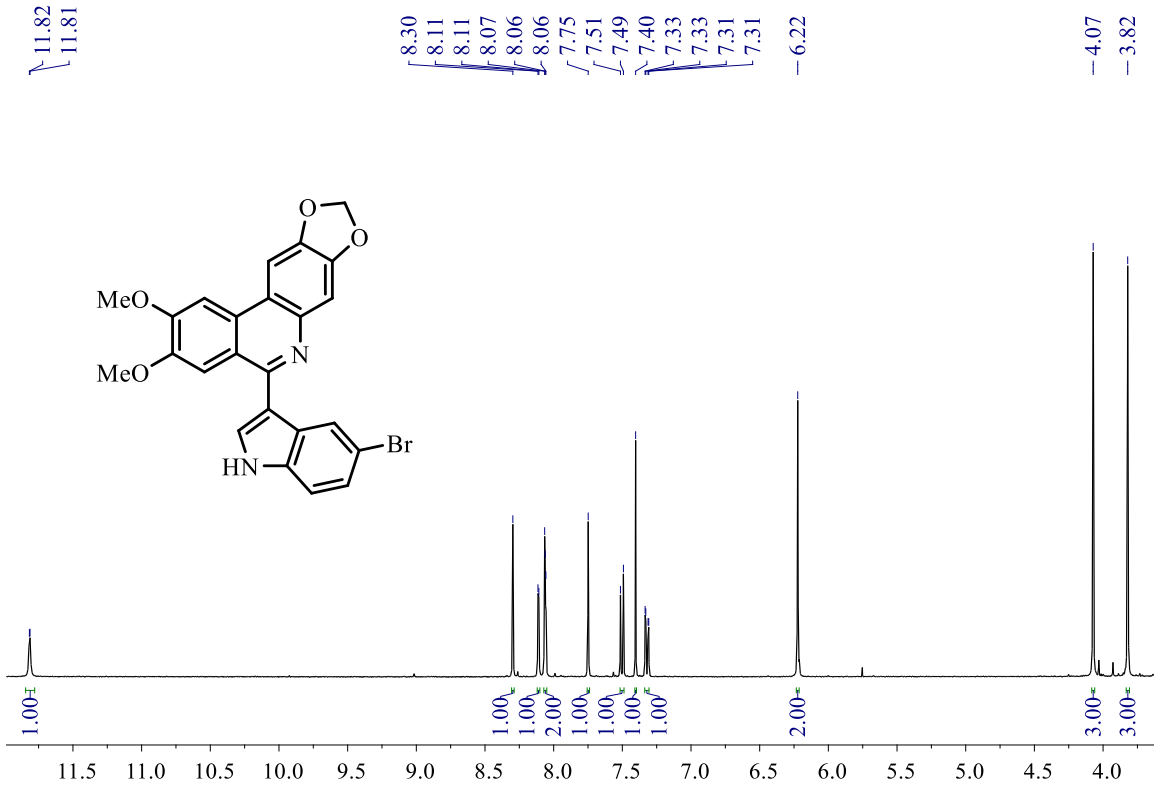


**Figure 89**. $^{13}$C NMR spectra of compound **6o** (DMSO-$d_6$, 100 MHz).

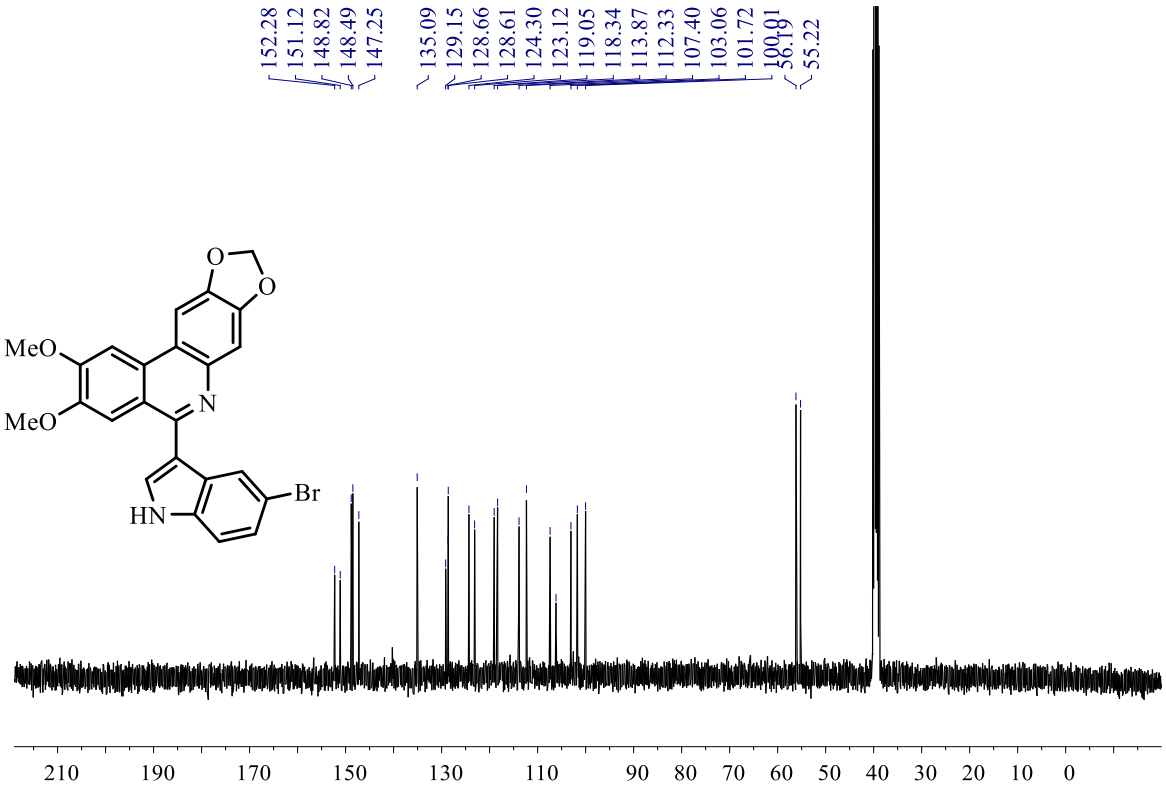


**Figure 90**. $^{13}$C-APT NMR spectra of compound **6o** (DMSO-$d_6$, 100 MHz).

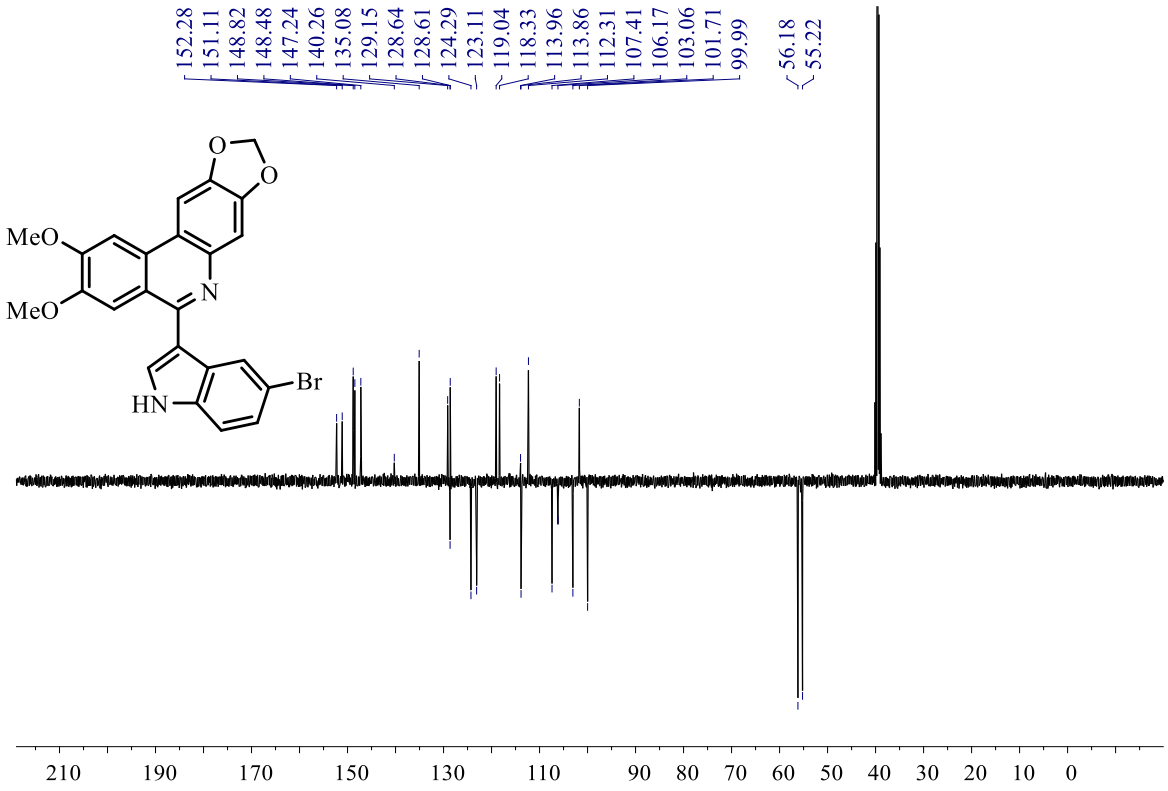


**Figure 91**. Expansion of $^{13}$C-APT NMR spectra of compound **6o** (DMSO-$d_6$, 100 MHz).

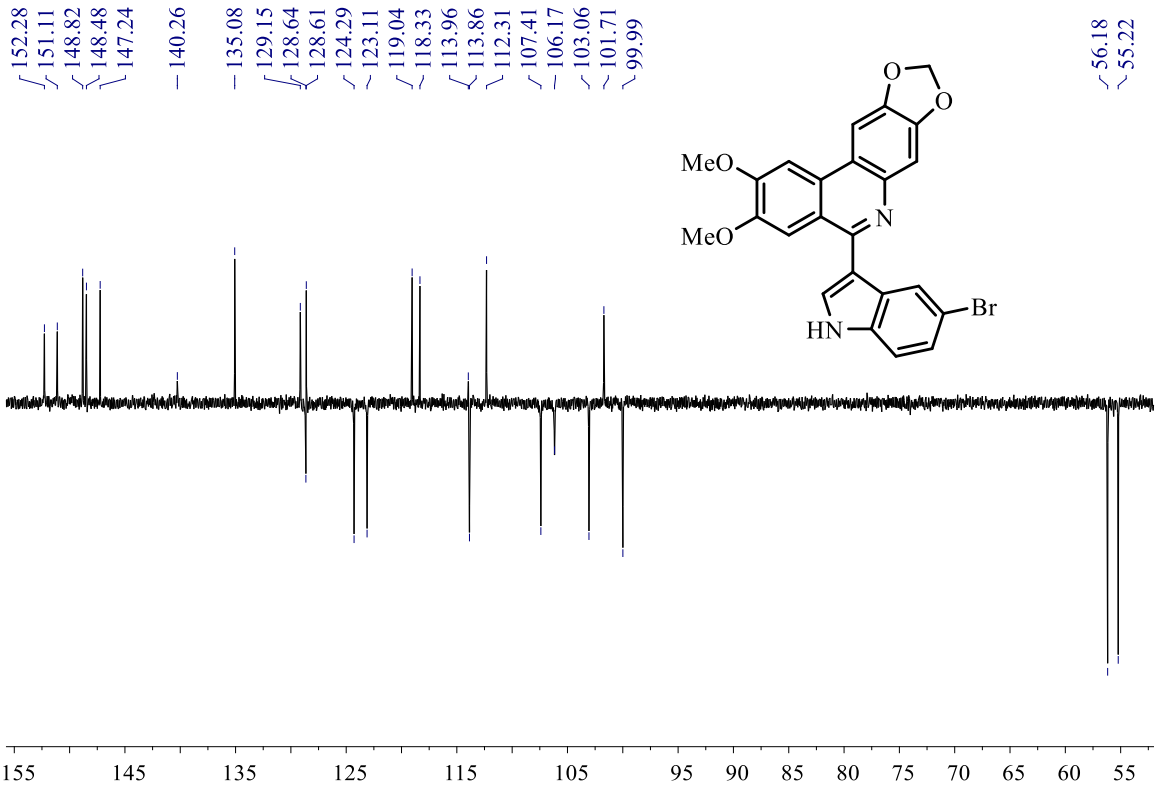


**Figure 92**. $^{1}H$ NMR spectrum of (*E*)-2,3-dimethoxy-5-styryl-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-phenethyl-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6p** ($CDCl_3$, 400 MHz).

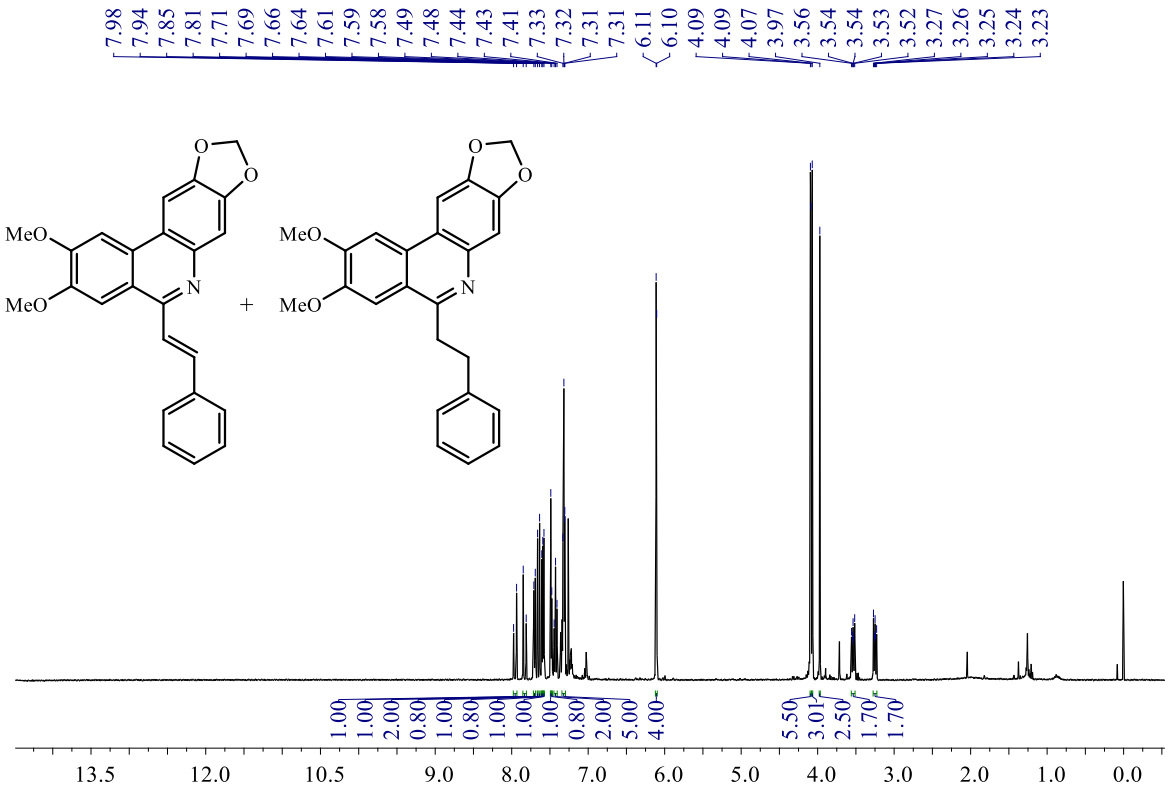


**Figure 93**. $^{13}C$ NMR spectrum of (*E*)-2,3-dimethoxy-5-styryl-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-phenethyl-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6p** ($CDCl_3$, 100 MHz).

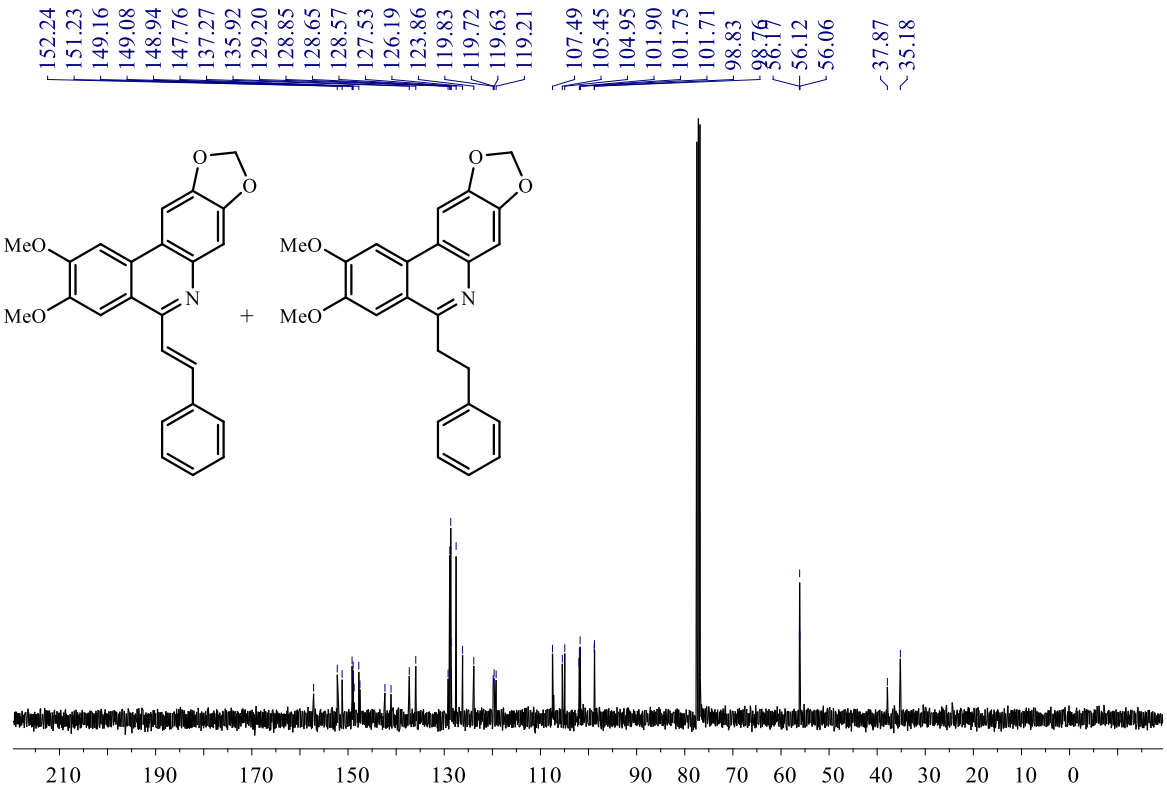


**Figure 94**. $^{13}C$–APT NMR spectrum of (*E*)-2,3-dimethoxy-5-styryl-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-phenethyl-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6p** ($CDCl_3$, 100 MHz).

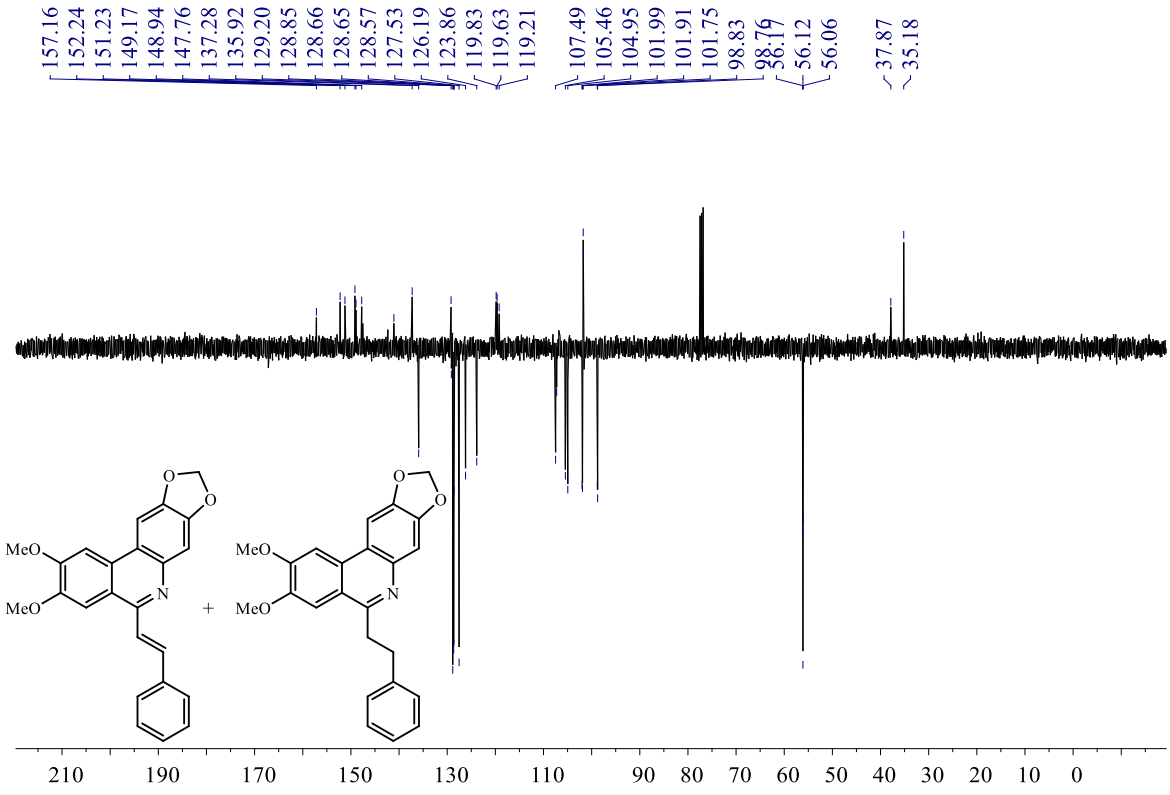


**Figure 95**. GC of mixture of compounds **6p**.

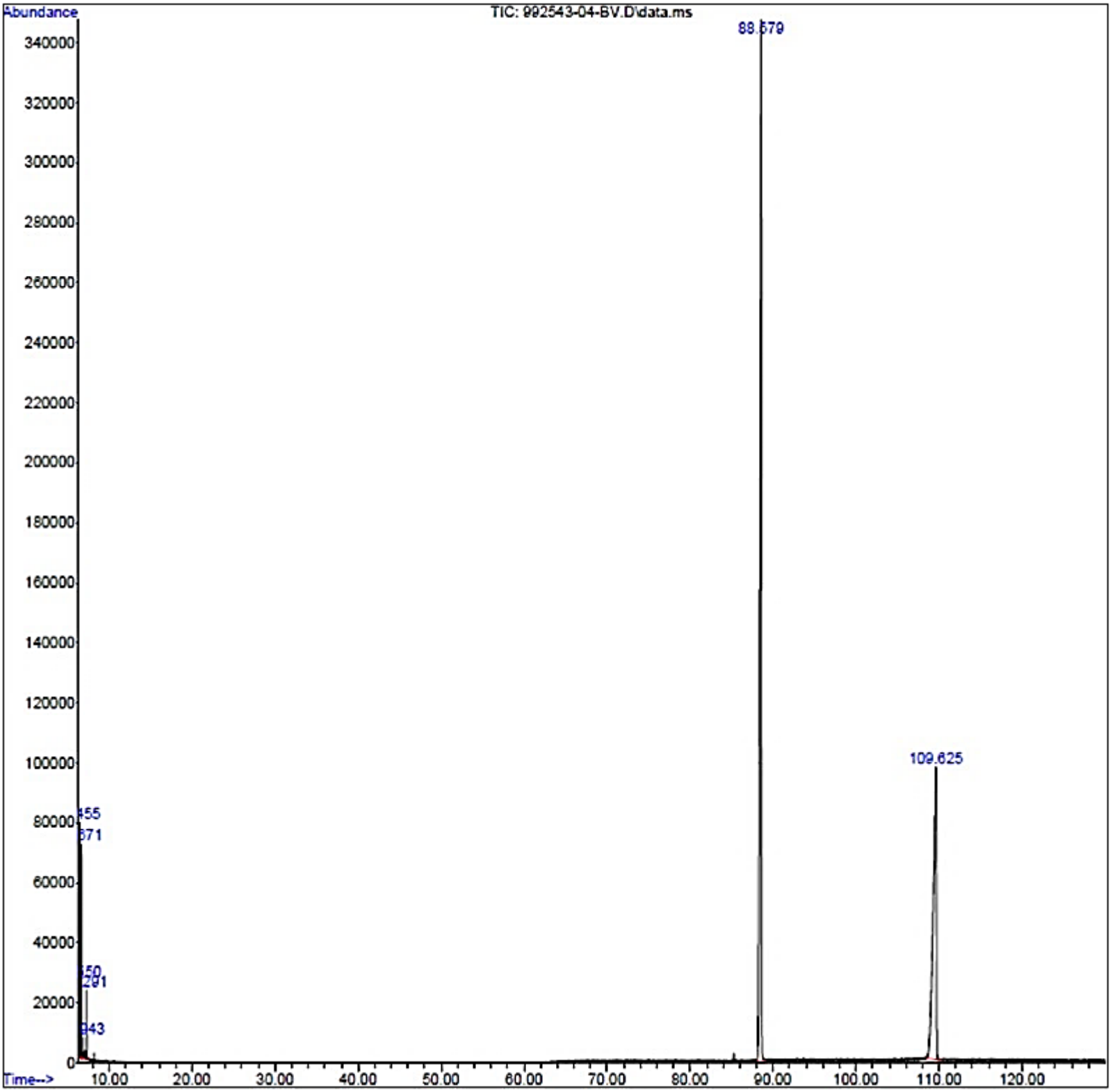


**Figure 96**.MS spectra of mixture of compounds **6p** (70 eV).

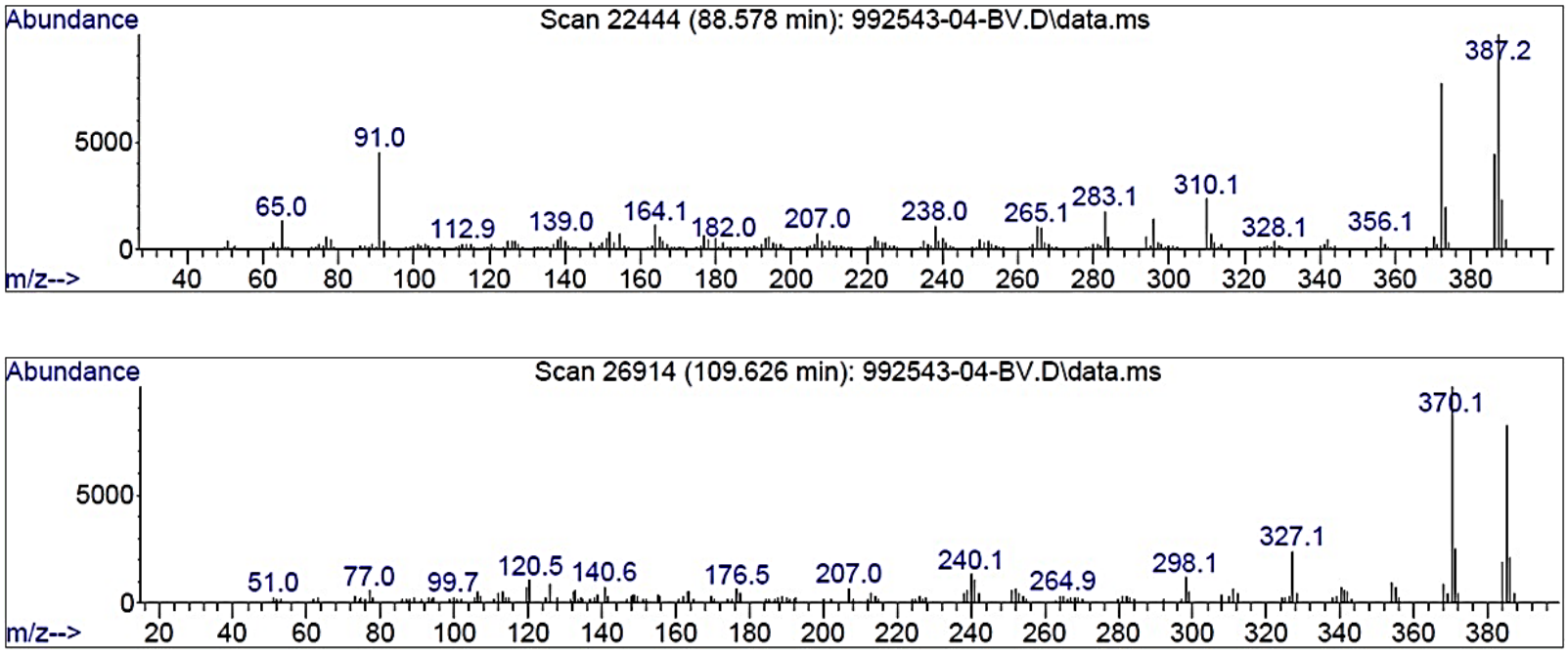


**Figure 97**. $^{1}$H NMR spectrum of (*E*)-2,3-dimethoxy-5-(2-methoxystyryl)-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-(2-methoxyphenethyl)-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6q** ($CDCl_3$, 400 MHz).

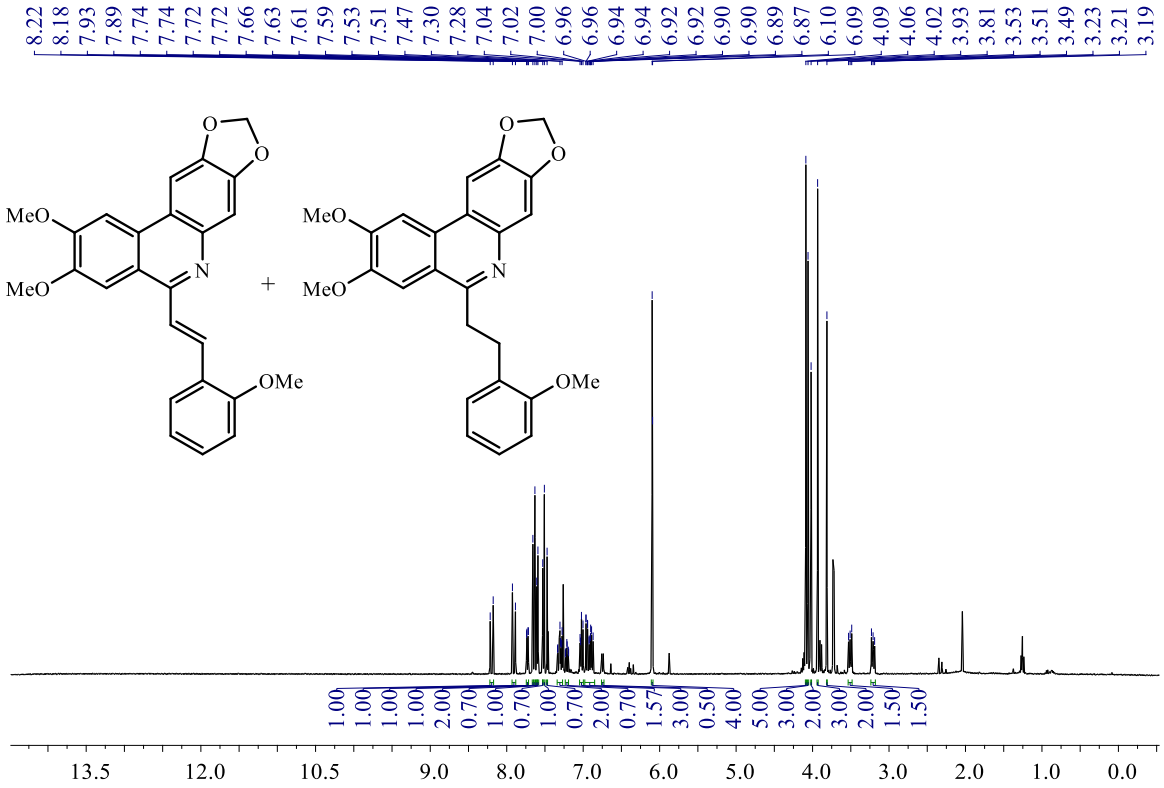


**Figure 98**. $^{13}C$ NMR spectrum of (*E*)-2,3-dimethoxy-5-(2-methoxystyryl)-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-(2-methoxyphenethyl)-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6q** ($CDCl_3$, 100 MHz).

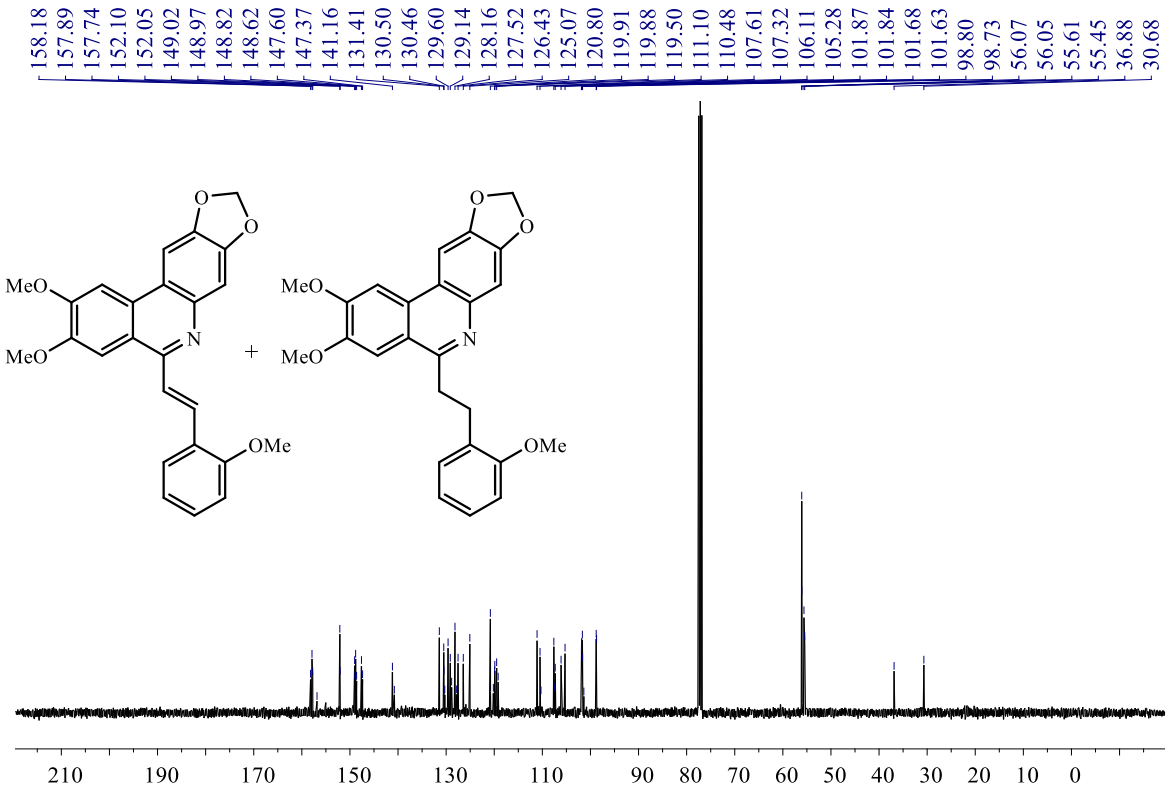


**Figure 99**. $^{13}$C–APT NMR spectrum of (*E*)-2,3-dimethoxy-5-(2-methoxystyryl)-[1,3]dioxolo[4,5-*b*]phenanthridine and 2,3-dimethoxy-5-(2-methoxyphenethyl)-[1,3]dioxolo[4,5-*b*]phenanthridine mixture **6q** ($CDCl_3$, 100 MHz).

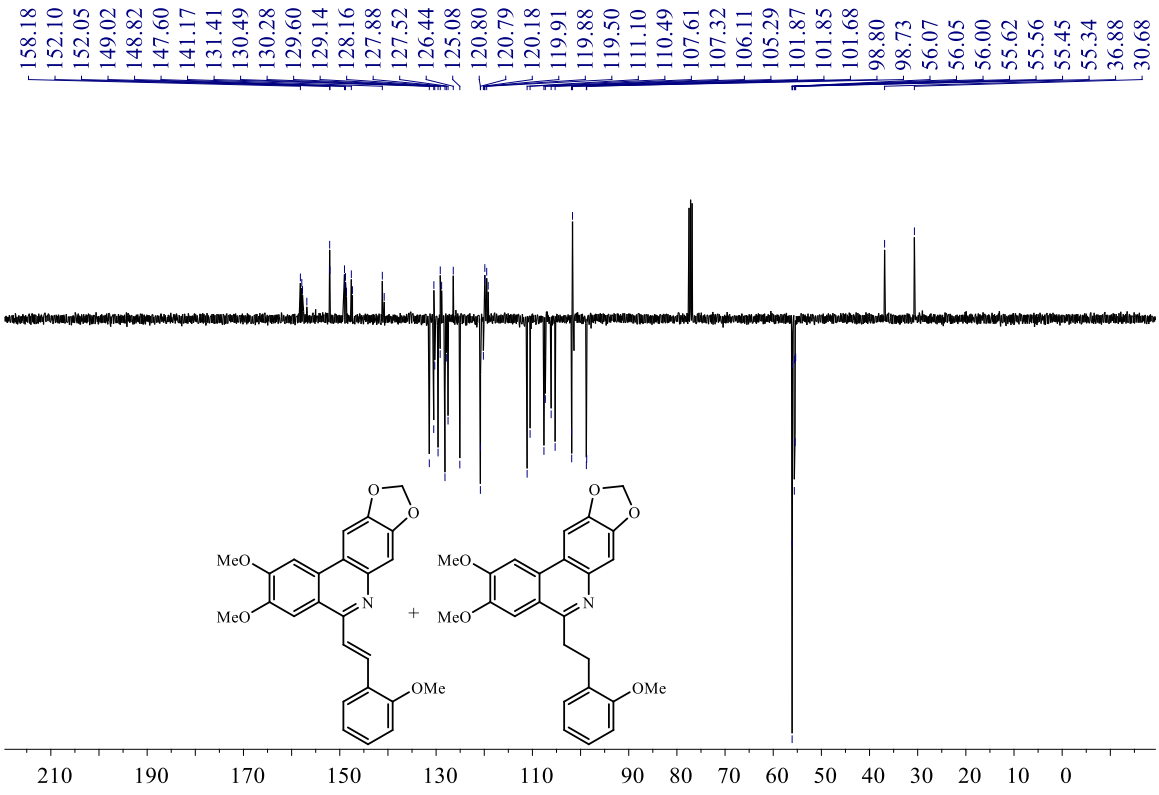


**Figure 100**. $^{1}H$ NMR spectra of compound **6r** ($CDCl_3$, 400 MHz).

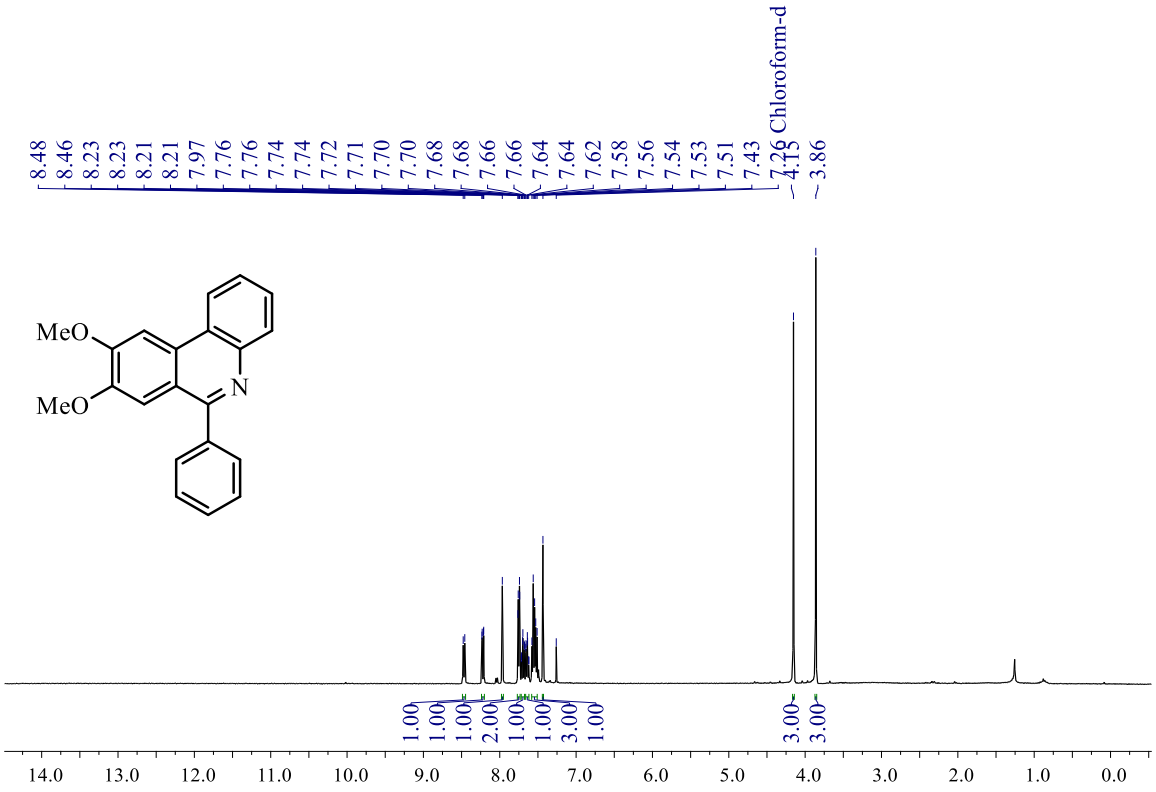


**Figure 101**. Expansion of the $^{1}H$ NMR spectra of compound **6r** ($CDCl_3$, 400 MHz).

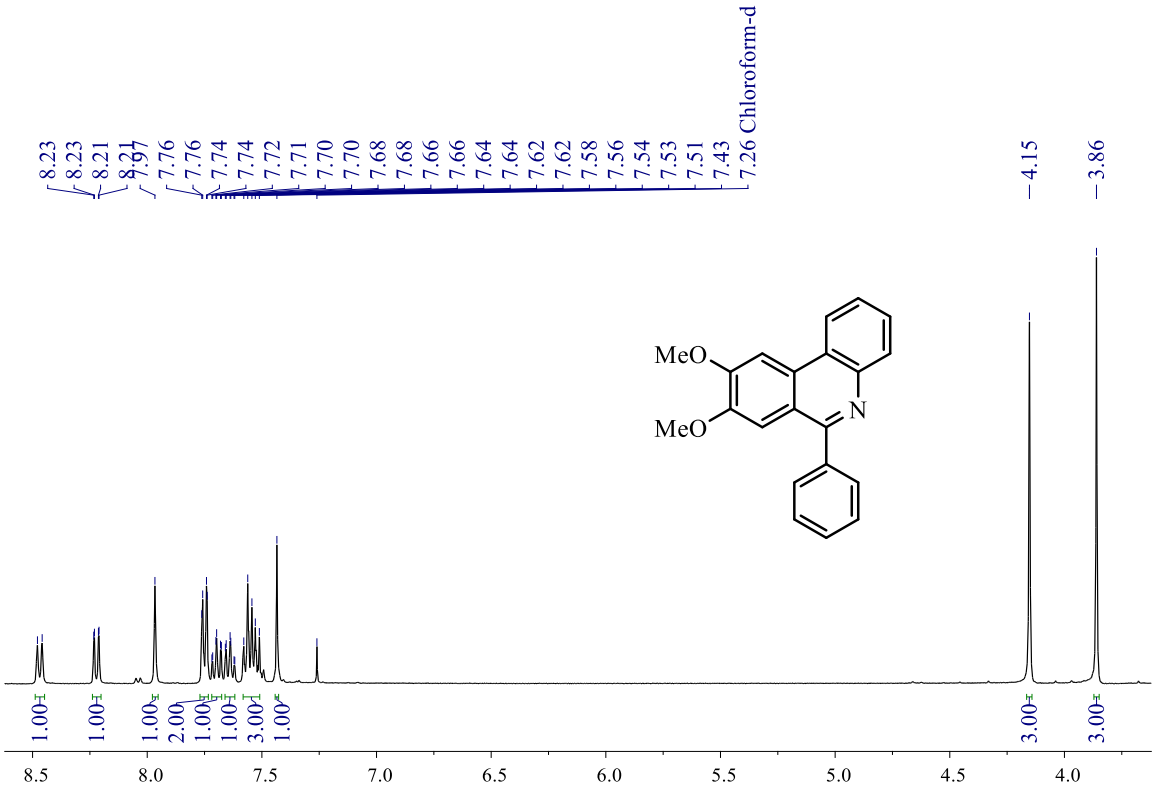


**Figure 102**. $^{13}C$ NMR spectra of compound **6r** ($CDCl_3$, 100 MHz).

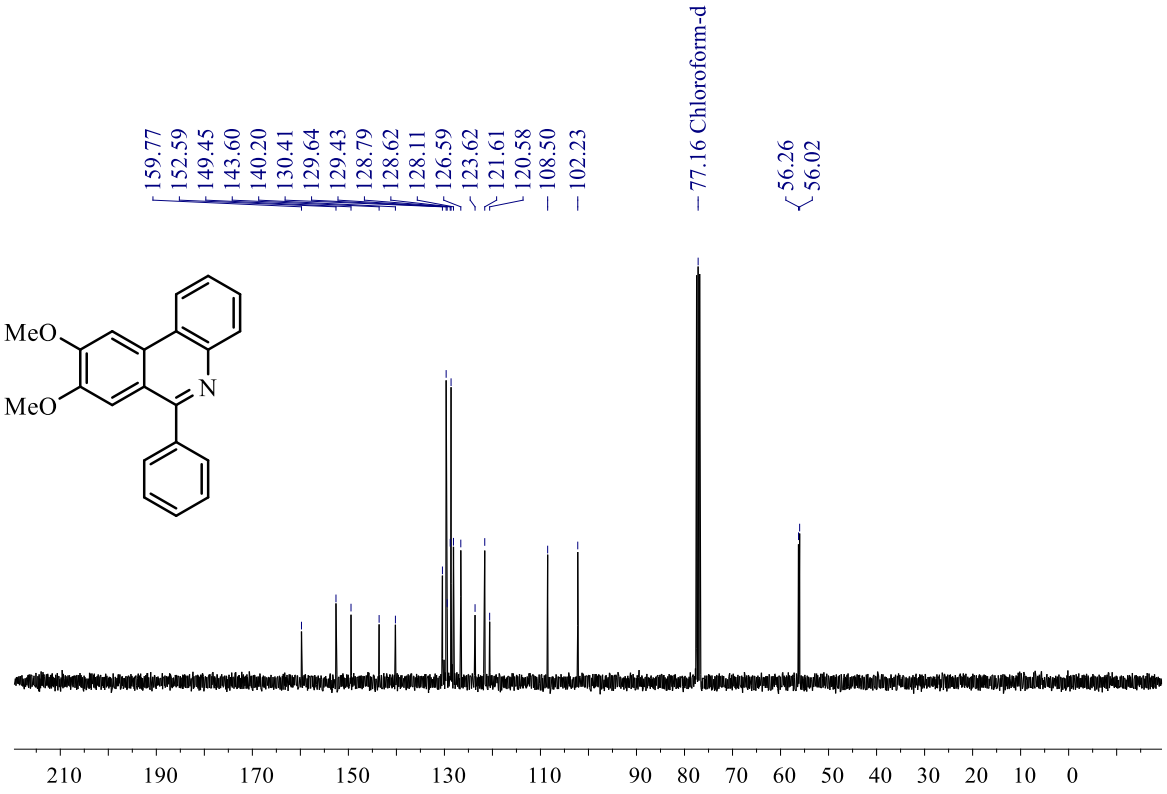


**Figure 103**. $^{13}$C-APT NMR spectra of compound **6r** ($CDCl_3$, 100 MHz).

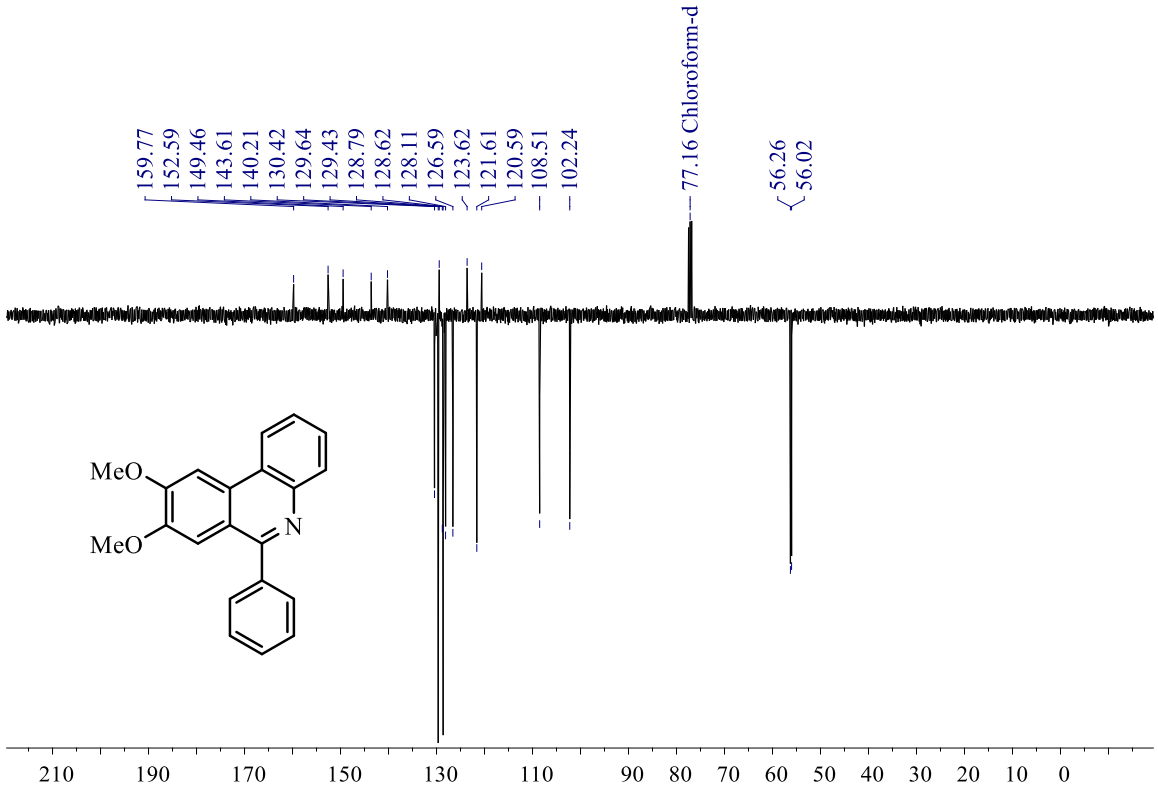


**Figure 104**. $^{1}H$ NMR spectra of compound **6s** ($CDCl_3$, 400 MHz).

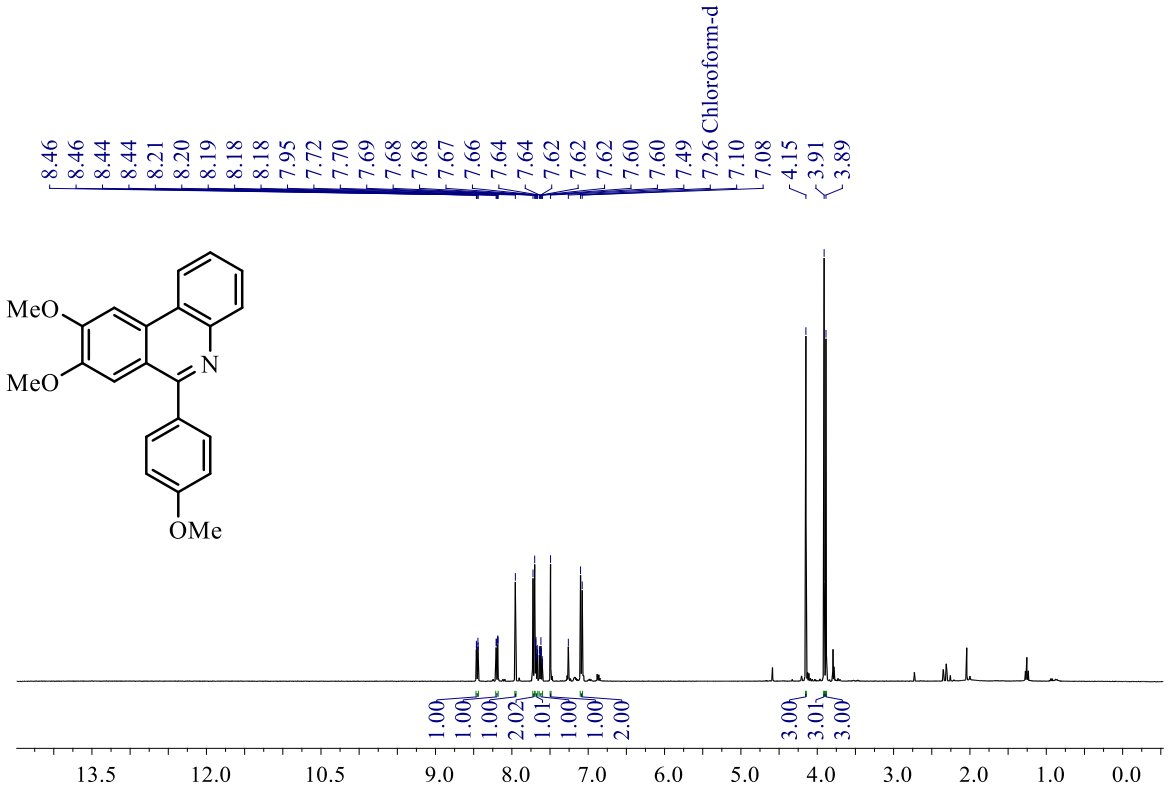


**Figure 105**. Expansion of the $^{1}H$ NMR spectra of compound **6s** ($CDCl_3$, 400 MHz).

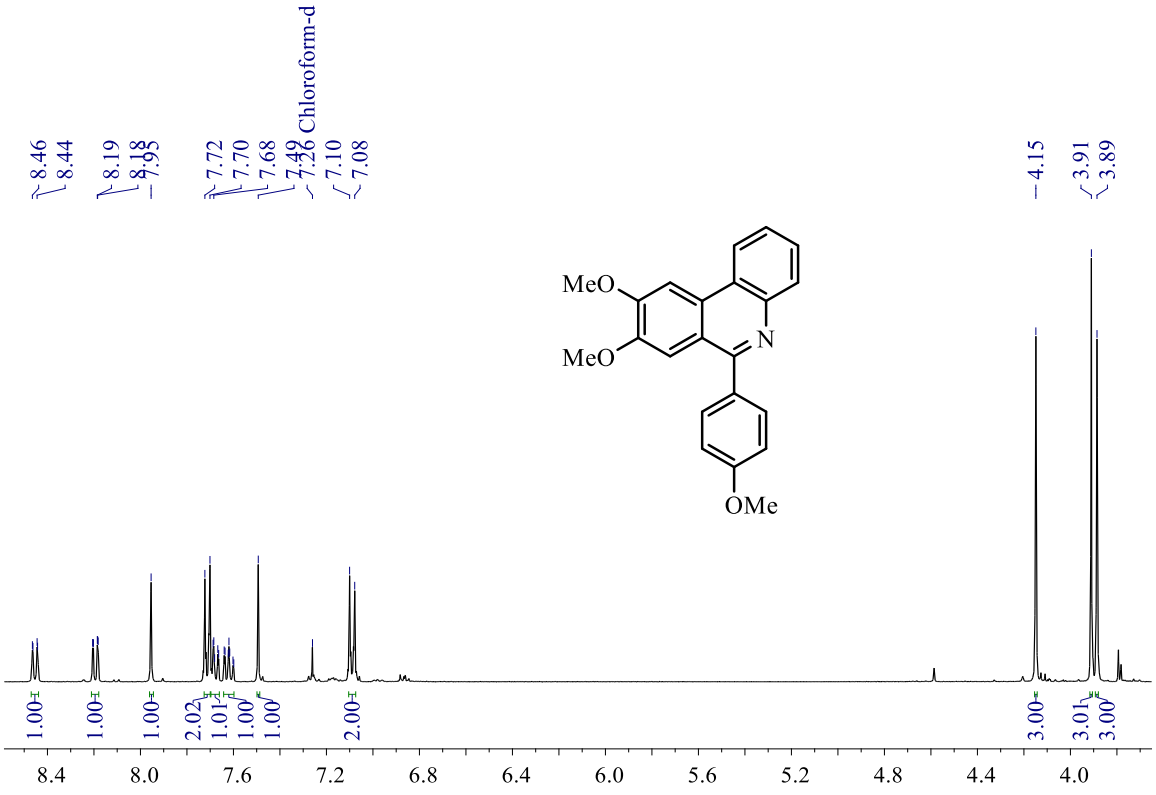


**Figure 106**. $^{13}C$ NMR spectra of compound **6s** ($CDCl_3$, 100 MHz).

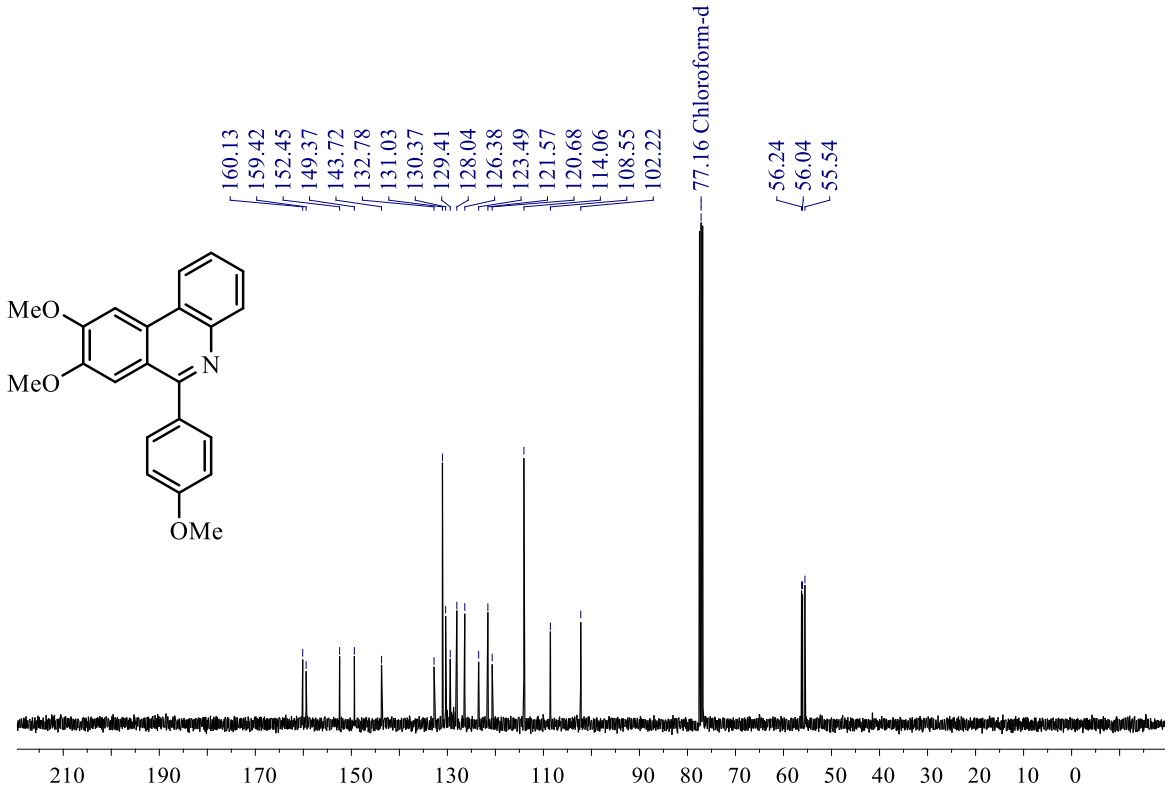


**Figure 107**. $^{13}$C-APT NMR spectra of compound **6s** ($CDCl_3$, 100 MHz).

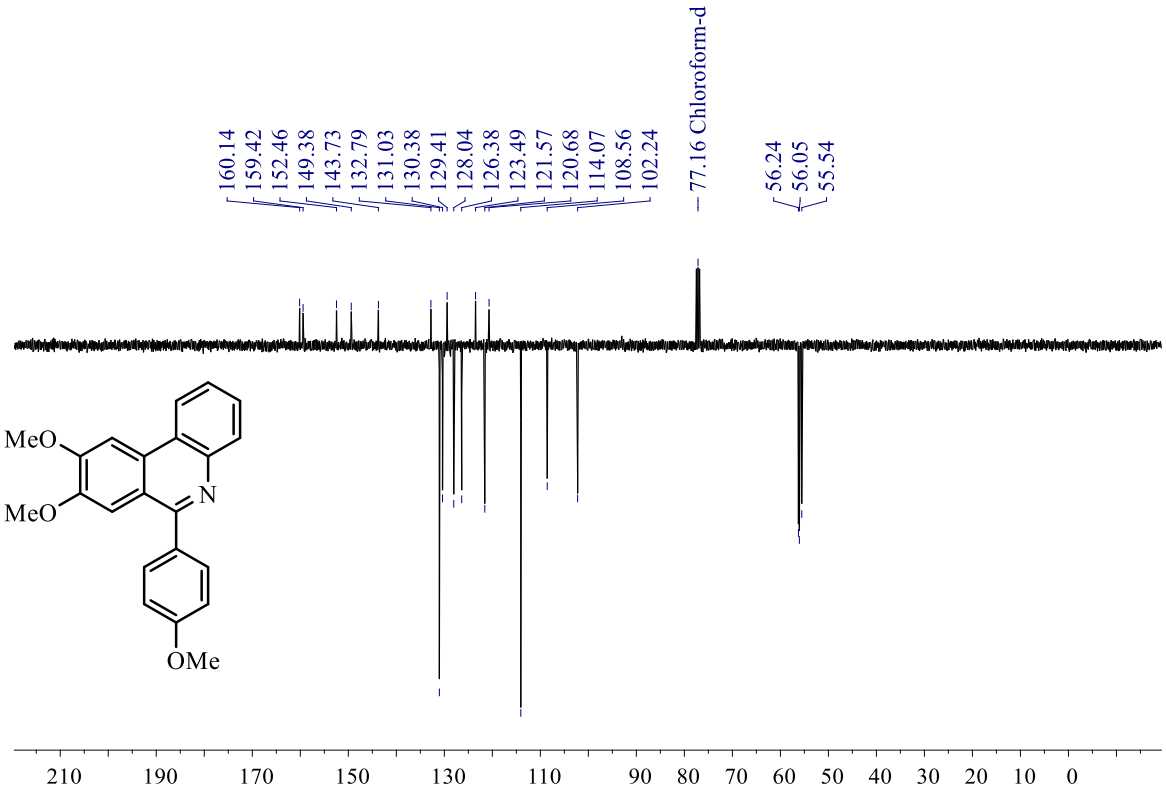


**Figure 108**. $^{1}H$ NMR spectra of compound **6t** ($CDCl_3$, 400 MHz).

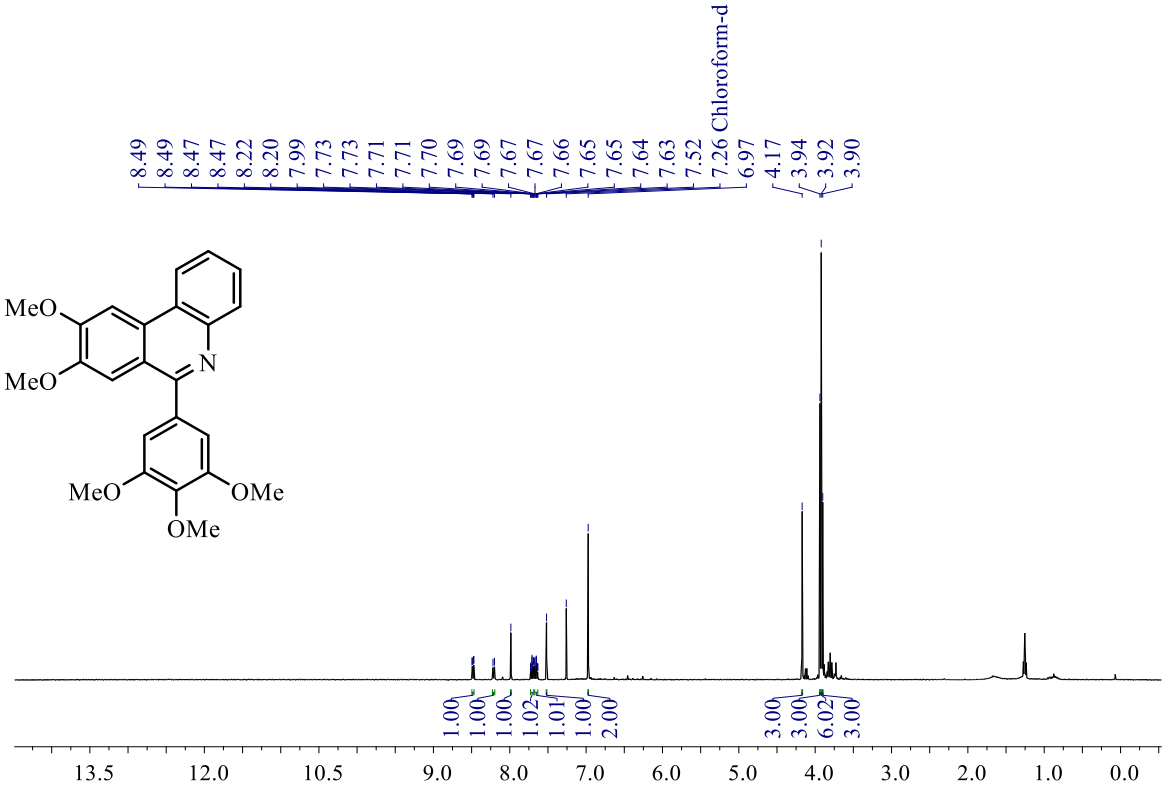


**Figure 109**. Expansion of the $^{1}H$ NMR spectra of compound **6t** ($CDCl_3$, 400 MHz).

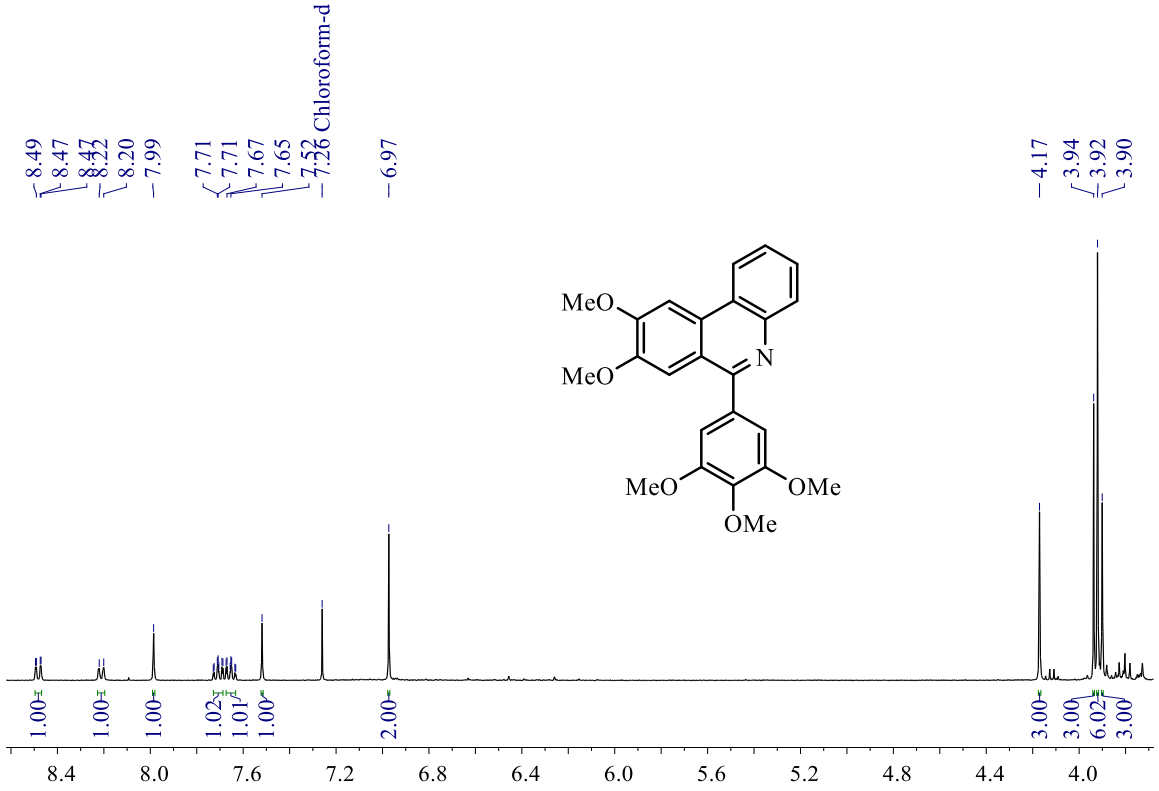


**Figure 110**. $^{13}C$ NMR spectra of compound **6t** ($CDCl_3$, 100 MHz).

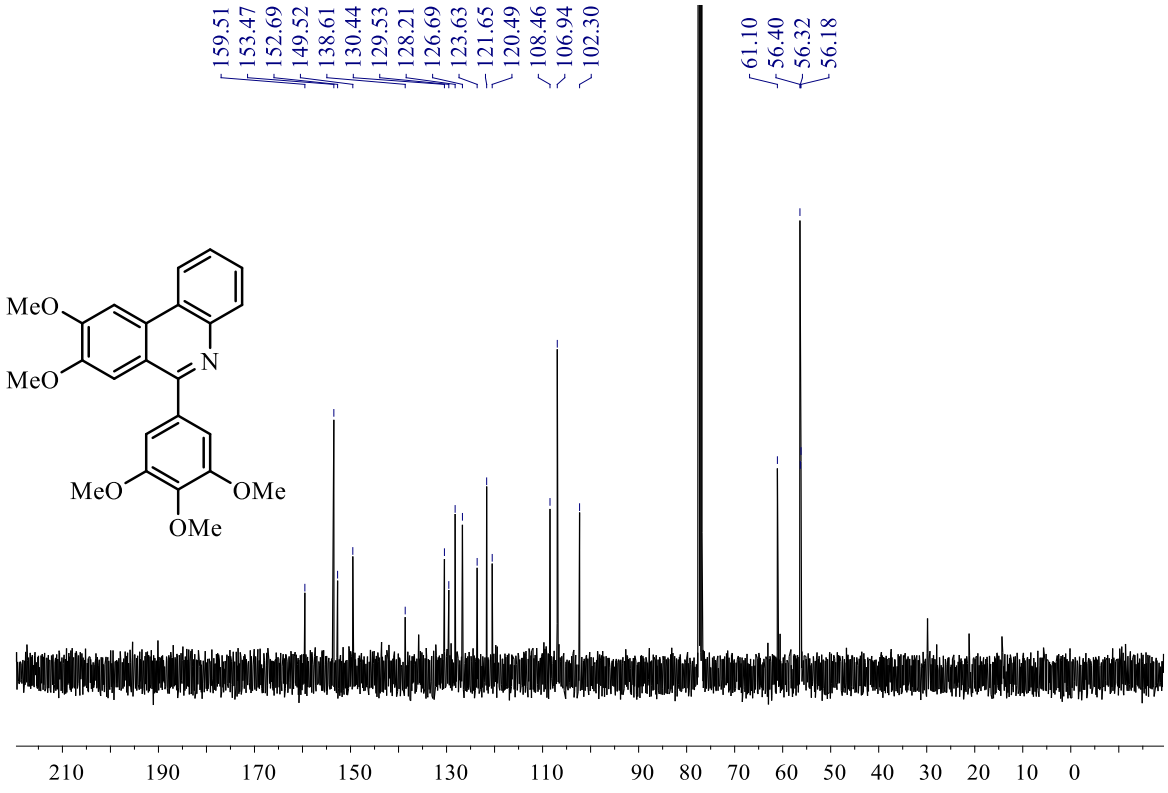


**Figure 111**. $^{13}$C-APT NMR spectra of compound **6t** ($CDCl_3$, 100 MHz).

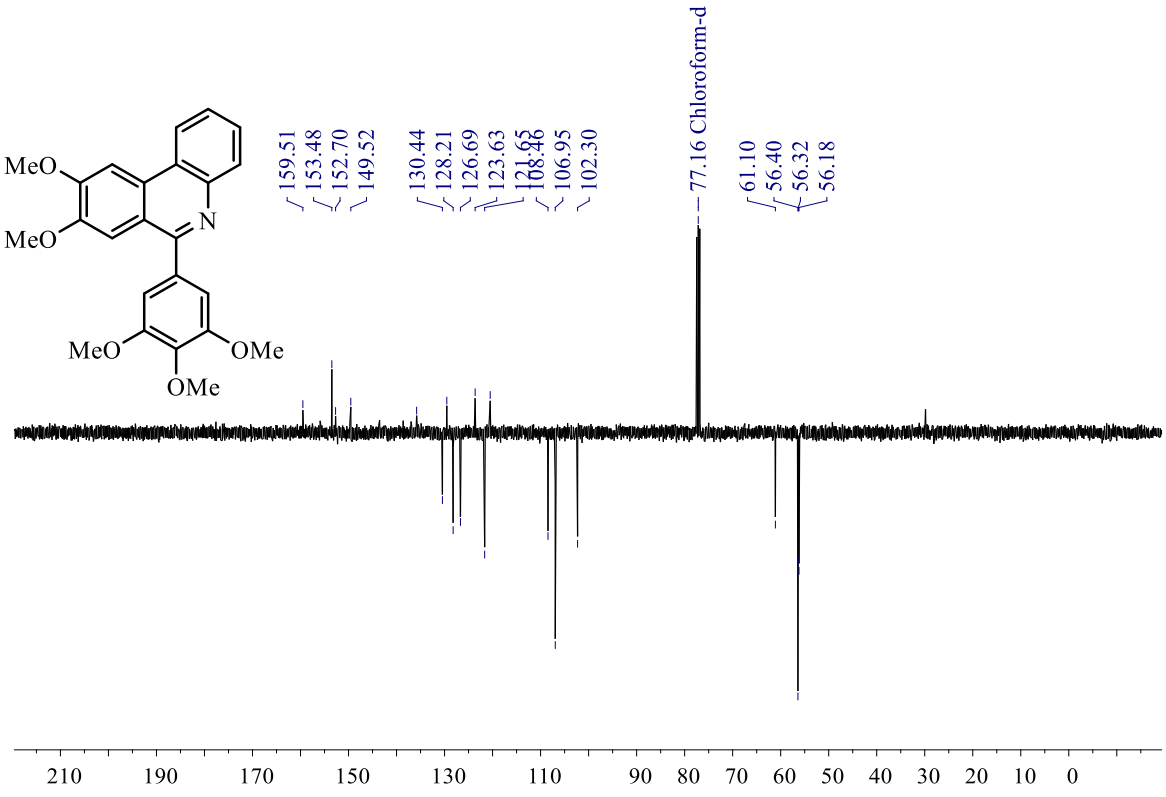


**Figure 112**. $^{1}H$ NMR spectra of compound **6u** ($CDCl_3$, 400 MHz).

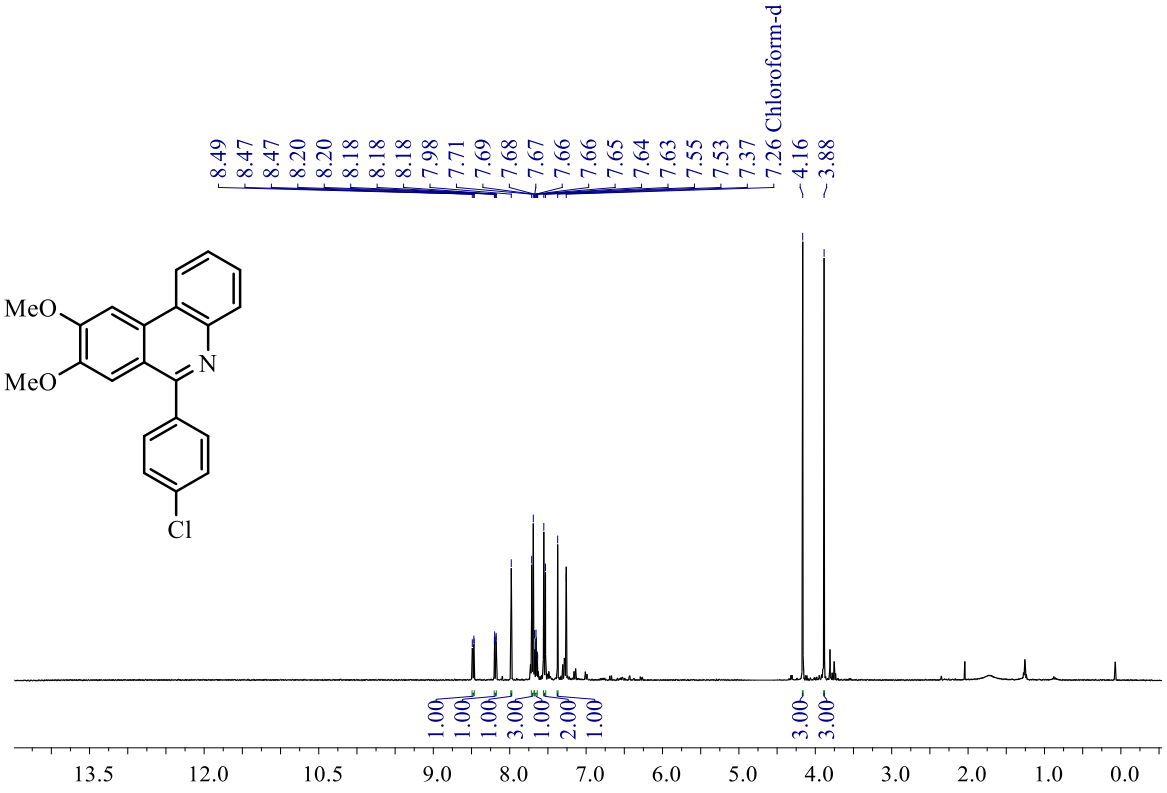


**Figure 113**. Expansion of the $^{1}H$ NMR spectra of compound **6u** ($CDCl_3$, 400 MHz).

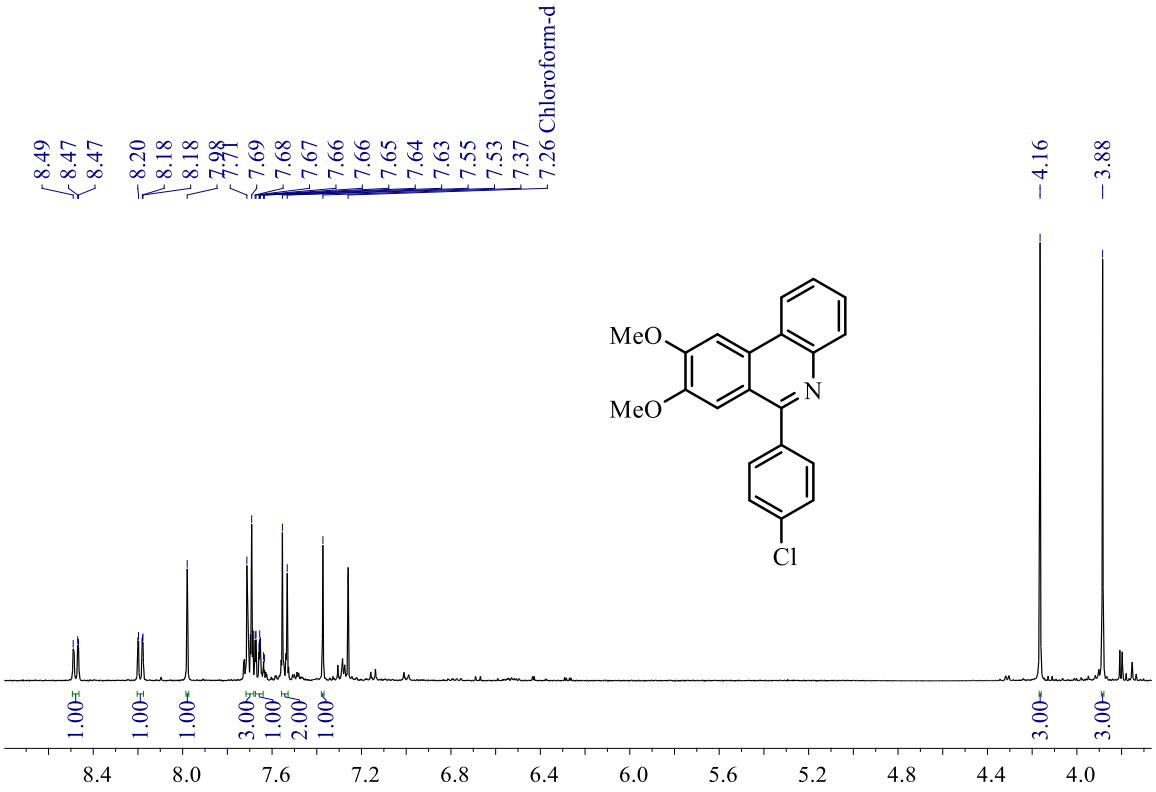


**Figure 114**. $^{13}C$ NMR spectra of compound **6u** ($CDCl_3$, 100 MHz).

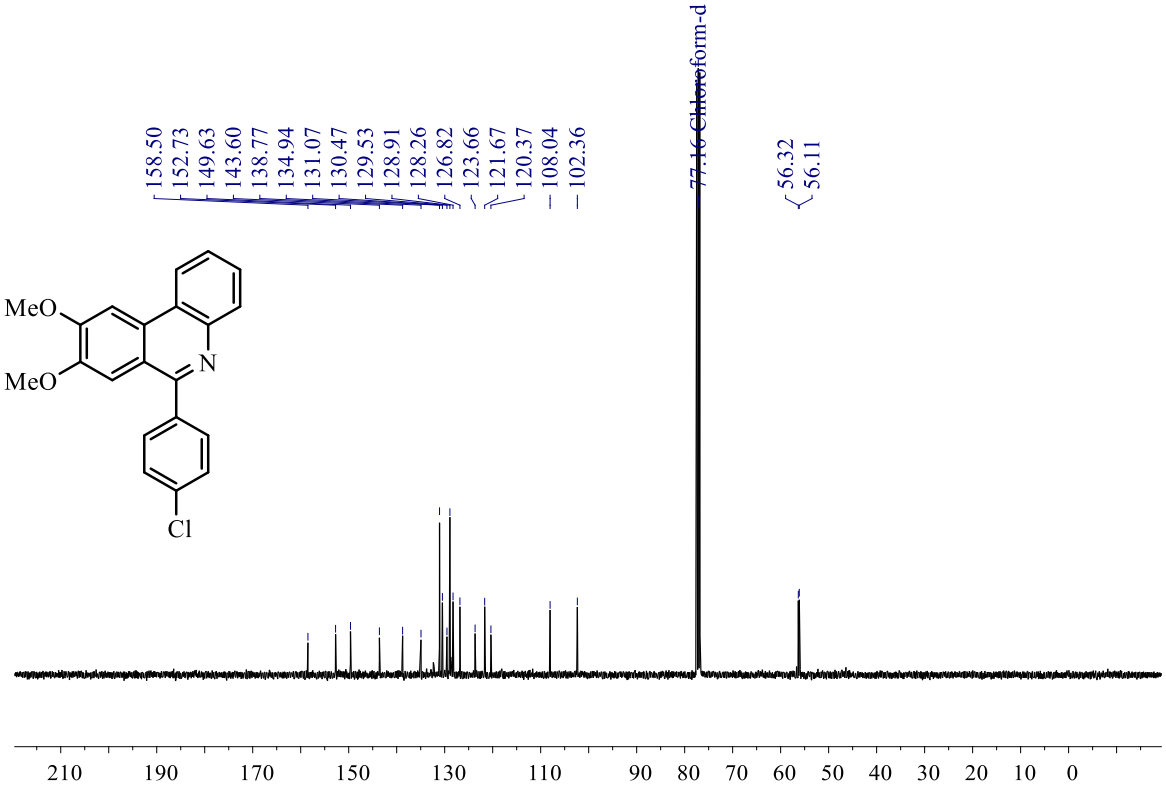


**Figure 115**. $^{13}$C-APT NMR spectra of compound **6u** ($CDCl_3$, 100 MHz).

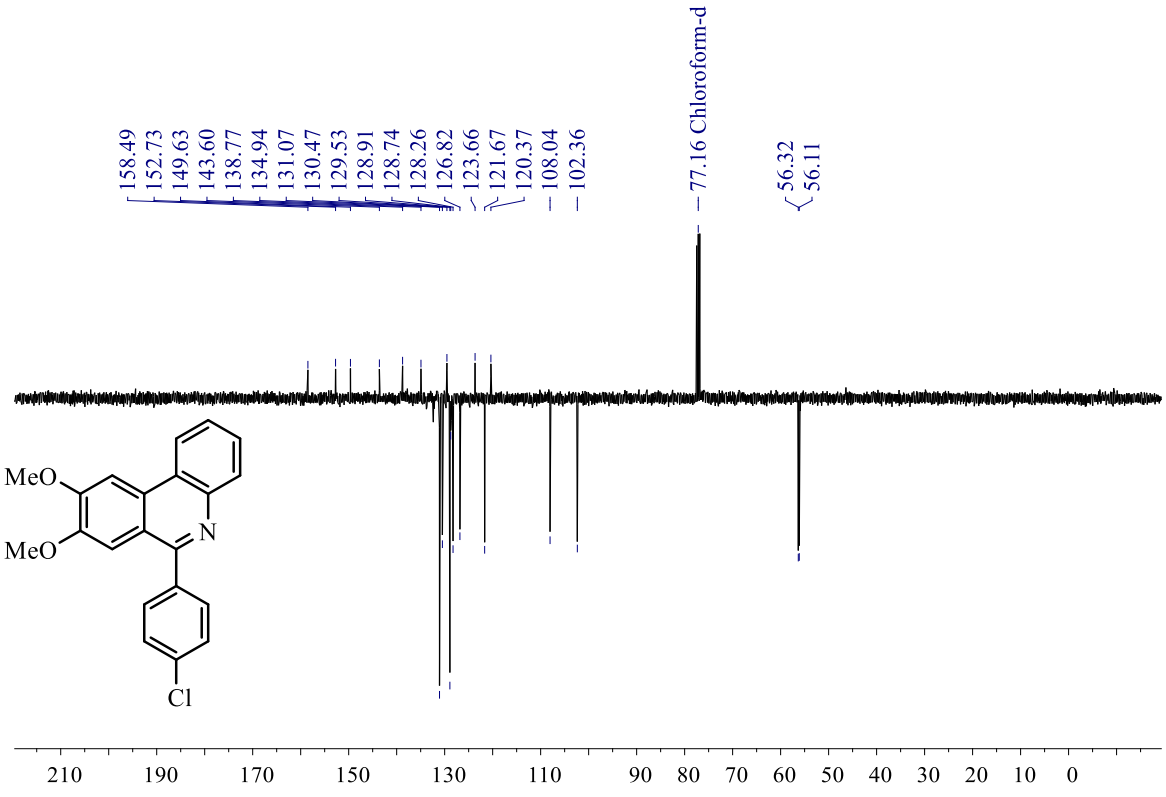


**Figure 116**. $^{1}H$ NMR spectra of compound **6v** ($CDCl_3$, 400 MHz).

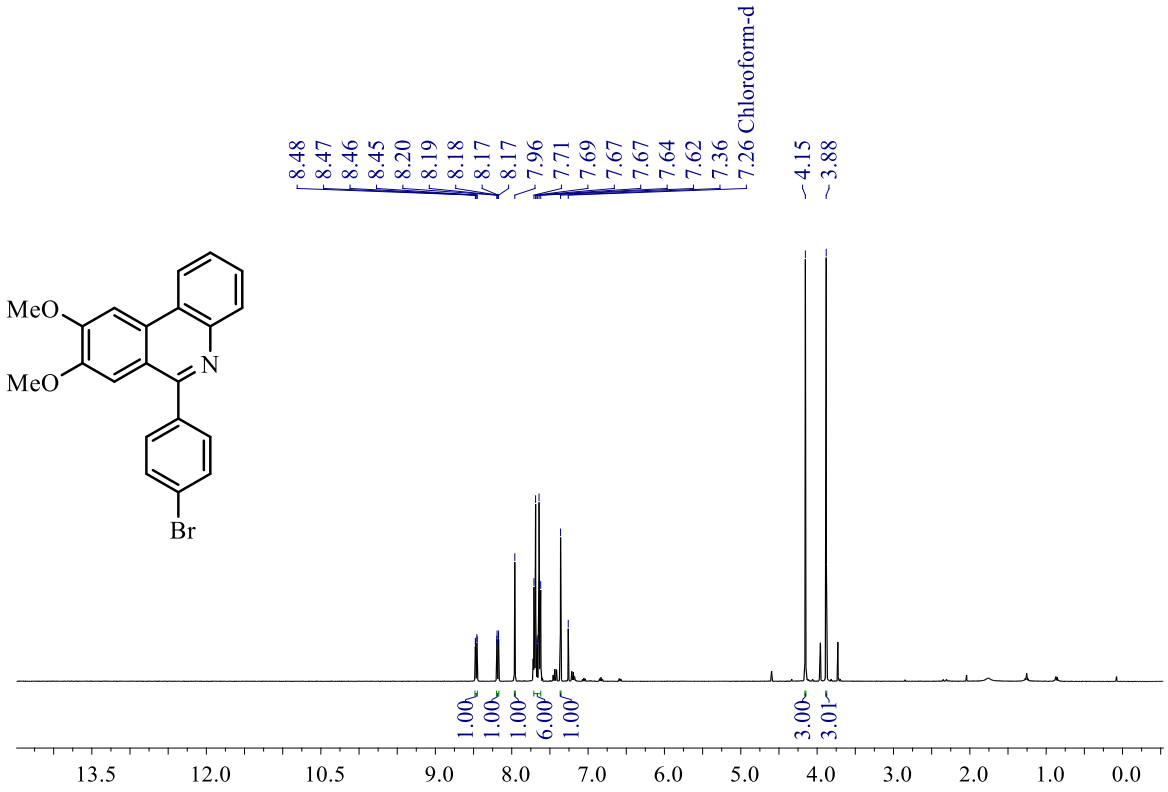


**Figure 117**. Expansion of the $^{1}H$ NMR spectra of compound **6v** ($CDCl_3$, 400 MHz).

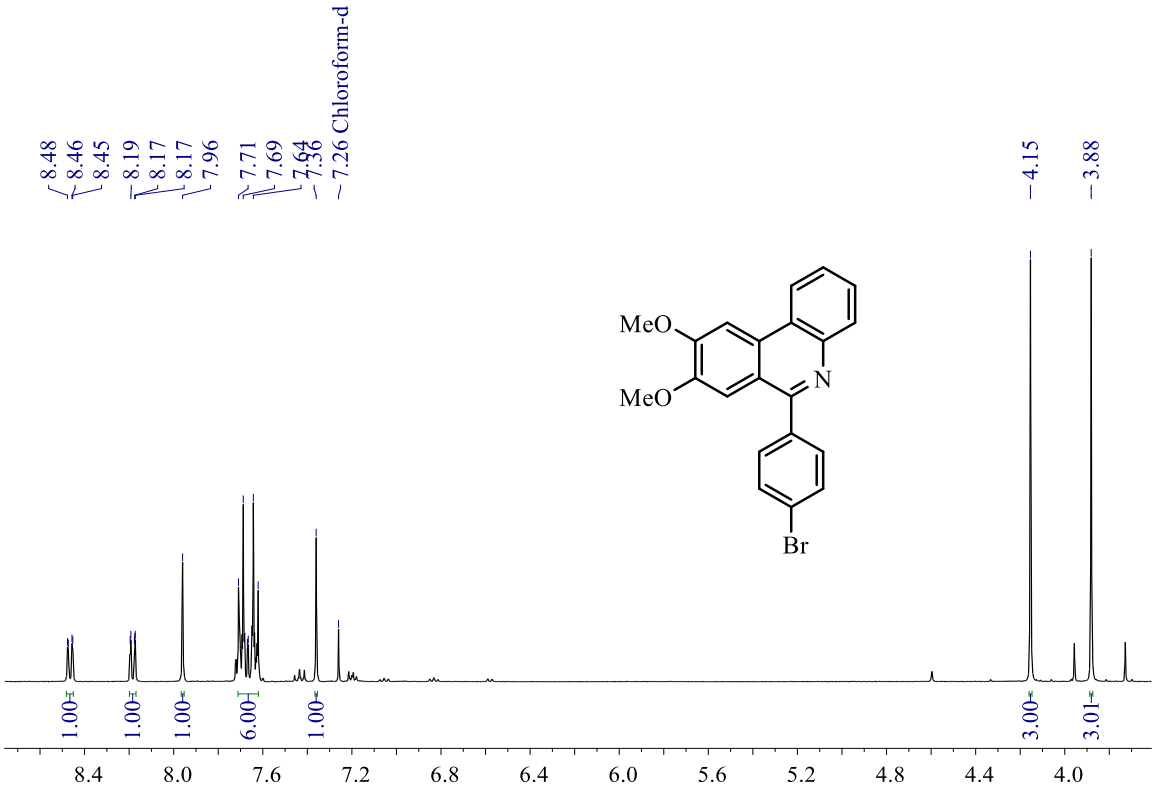


**Figure 118**. $^{13}C$ NMR spectra of compound **6v** ($CDCl_3$, 100 MHz).