

## Acid promoted synthesis of cyclic 1,3-dione fused symmetrical 2,8-dioxabicyclo [3.3.1]nonanes

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### Supplementary Data

#### Contents:

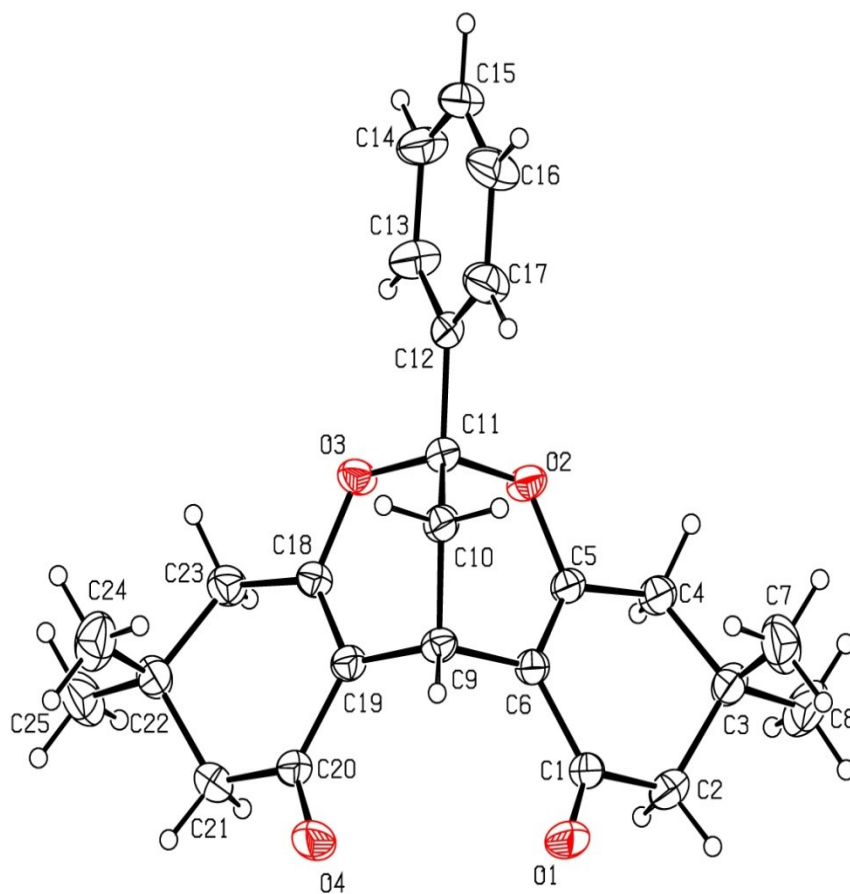
Crystallographic data for the compounds <b>4a &amp; 3b</b>	S1-S3.
<sup>1</sup> H-NMR and <sup>13</sup> C-NMR spectrums for all new compounds	S4-S35.

#### Crystallographic data for 4a and 3b compounds

**Data collection and Structure solution:** X-ray data for two compounds (4a and 3b) were collected at room temperature using the Bruker Smart Apex CCD diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ) with  $\omega$ -scan method.<sup>1</sup> Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 3351 reflections for 4a and 8574 reflections for 3b crystal data sets. Integration and scaling of intensity data were accomplished using SAINT program.<sup>1</sup> The structures were solved by Direct Methods using SHELXS97<sup>2</sup> and refinement was carried out by full-matrix least-squares technique using SHELXL97.<sup>2</sup> Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}$  for methyl atoms.

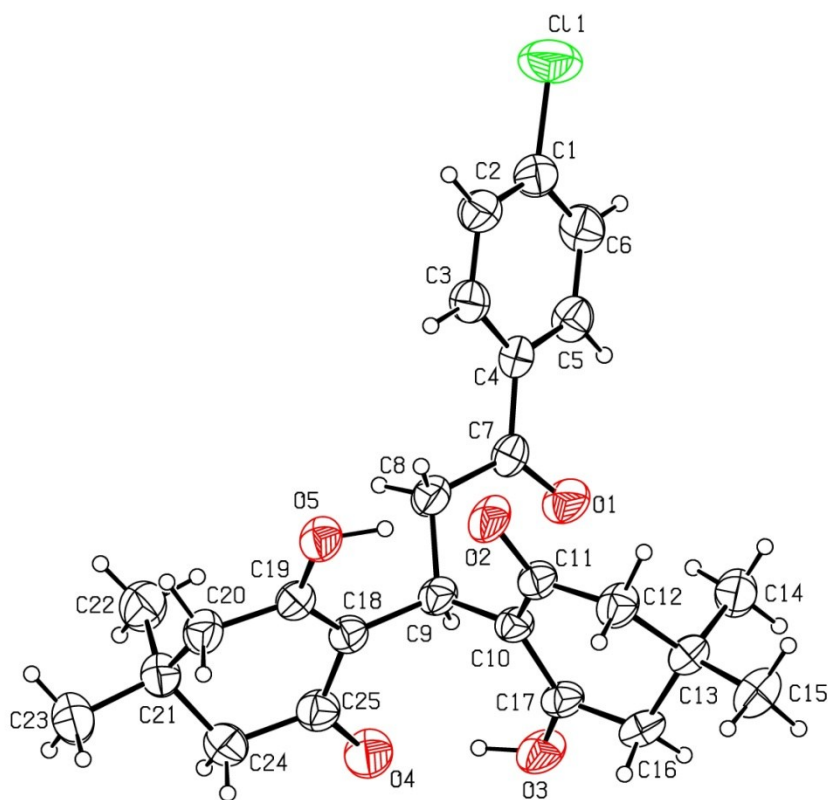
1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

**Crystal data for 4a:** C<sub>25</sub>H<sub>28</sub>O<sub>4</sub>, *M* = 392.47, colorless block, 0.43 x 0.38 x 0.29 mm<sup>3</sup>, triclinic, space group *P*1 (No. 1), *a* = 5.7508(11), *b* = 10.2102(19), *c* = 10.3282(19) Å,  $\alpha$  = 60.929(2),  $\beta$  = 80.487 (3),  $\gamma$  = 76.750(3)°, *V* = 514.89(17) Å<sup>3</sup>, *Z* = 1, *D<sub>c</sub>* = 1.266 g/cm<sup>3</sup>, *F*<sub>000</sub> = 210, CCD area detector, MoK $\alpha$  radiation,  $\lambda$  = 0.71073 Å, *T* = 293(2)K,  $2\theta_{\max}$  = 50.0°, 4878 reflections collected, 3541 unique (*R*<sub>int</sub> = 0.0182), Final *Goof* = 1.032, *RI* = 0.0392, *wR2* = 0.1066, *R* indices based on 3384 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 266 parameters, 3 restraints,  $\mu$  = 0.084 mm<sup>-1</sup>. **CCDC 1056215** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



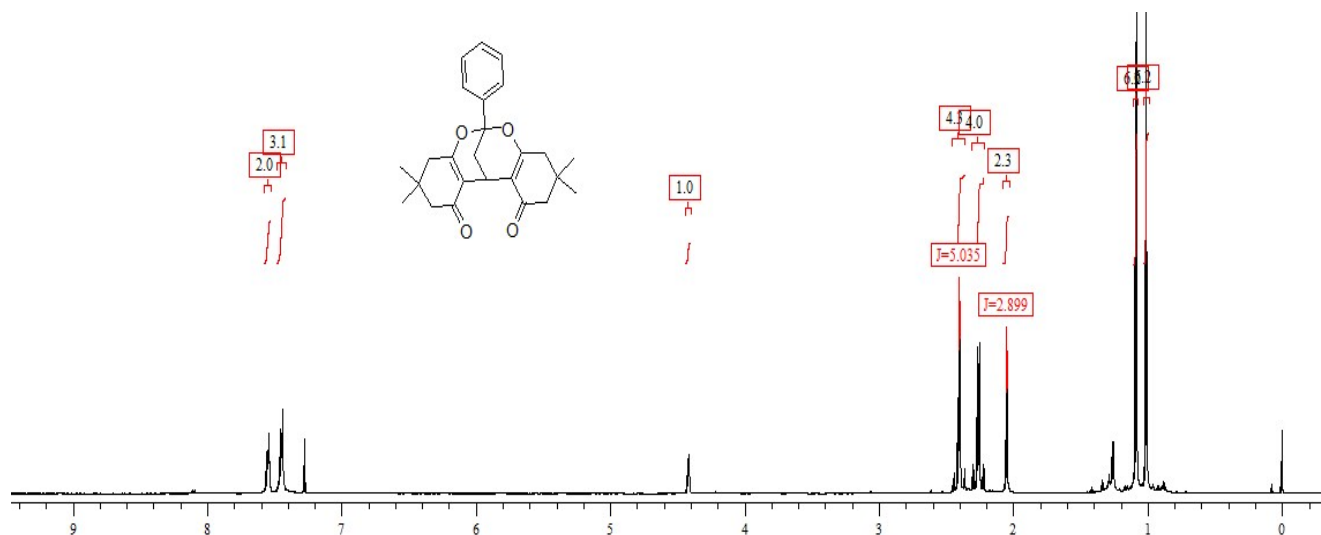
**Figure caption:** ORTEP diagram of **4a** with the atom-numbering. Displacement thermal ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

**Crystal data for 3b:** C<sub>25</sub>H<sub>29</sub>ClO<sub>5</sub>, *M* = 444.93, colorless needle, 0.40 x 0.16 x 0.07 mm<sup>3</sup>, monoclinic, space group *I*2/*a* (No. 15), *a* = 19.0793(11), *b* = 11.3954(7), *c* = 22.0551(13) Å, β = 98.7630(10)°, *V* = 4739.2(5) Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.247 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1888, CCD area detector, MoKα radiation, λ = 0.71073 Å, *T* = 293(2)K, 2θ<sub>max</sub> = 50.0°, 20502 reflections collected, 4183 unique (*R*<sub>int</sub> = 0.0190), Final *Goof* = 1.024, *R*1 = 0.0431, *wR*2 = 0.1191, *R* indices based on 3429 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 292 parameters, 1 restraint, μ = 0.193 mm<sup>-1</sup>. **CCDC 1056216** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

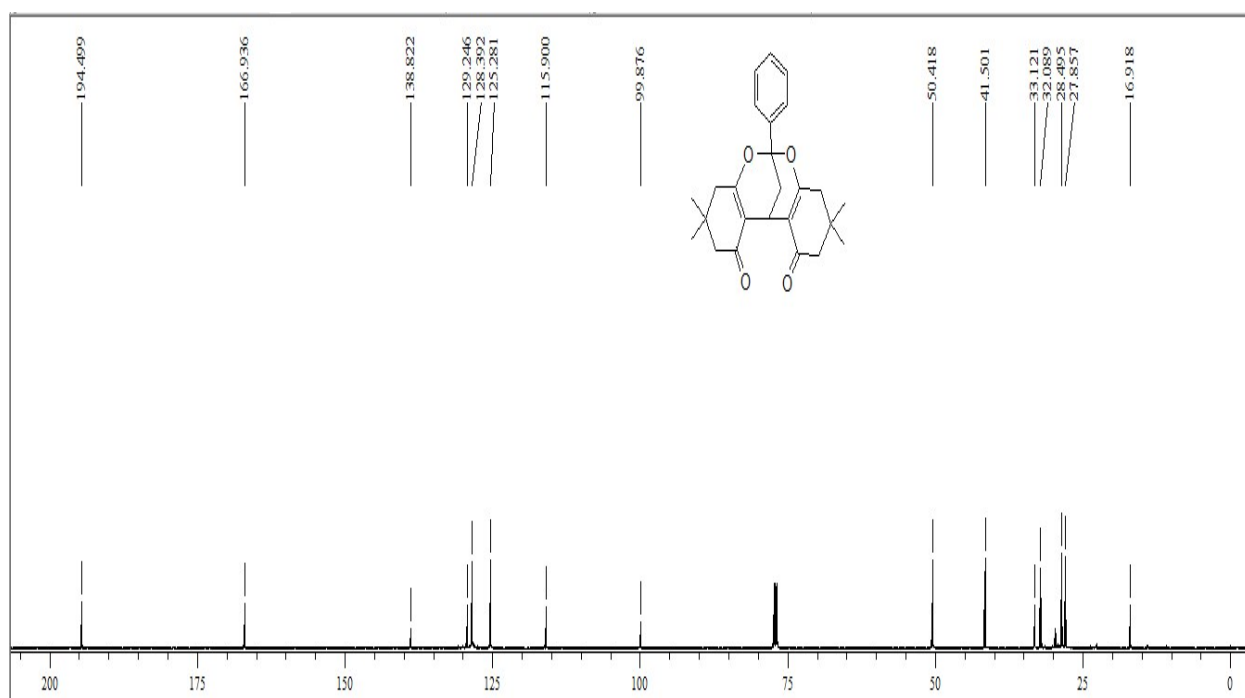


**Figure caption:** ORTEP diagram of **3b** with the atom-numbering. Displacement thermal ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

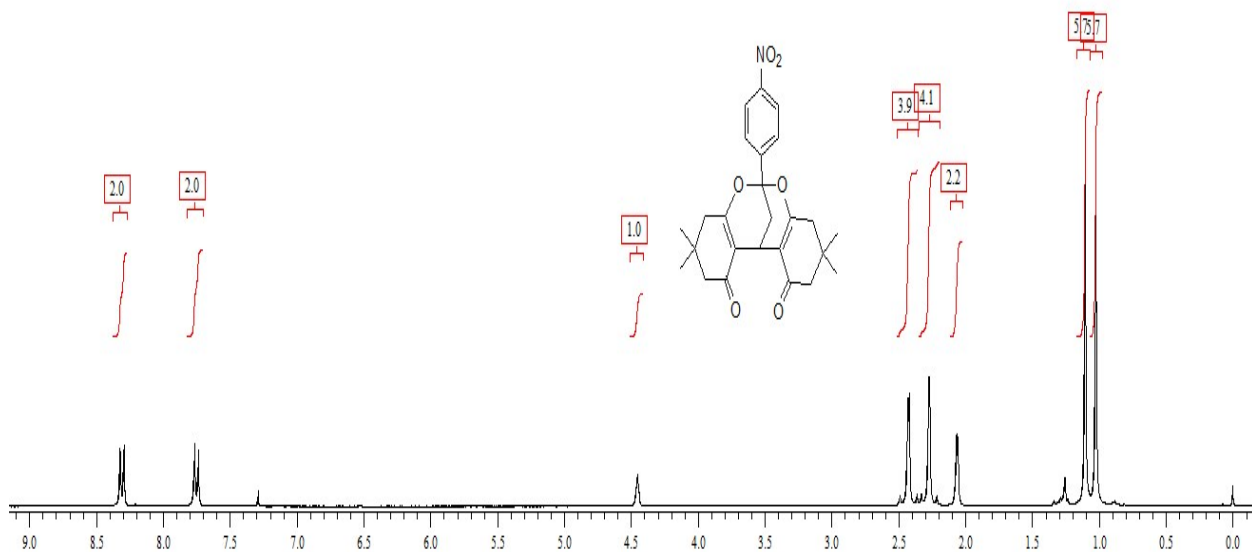
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectrums:**



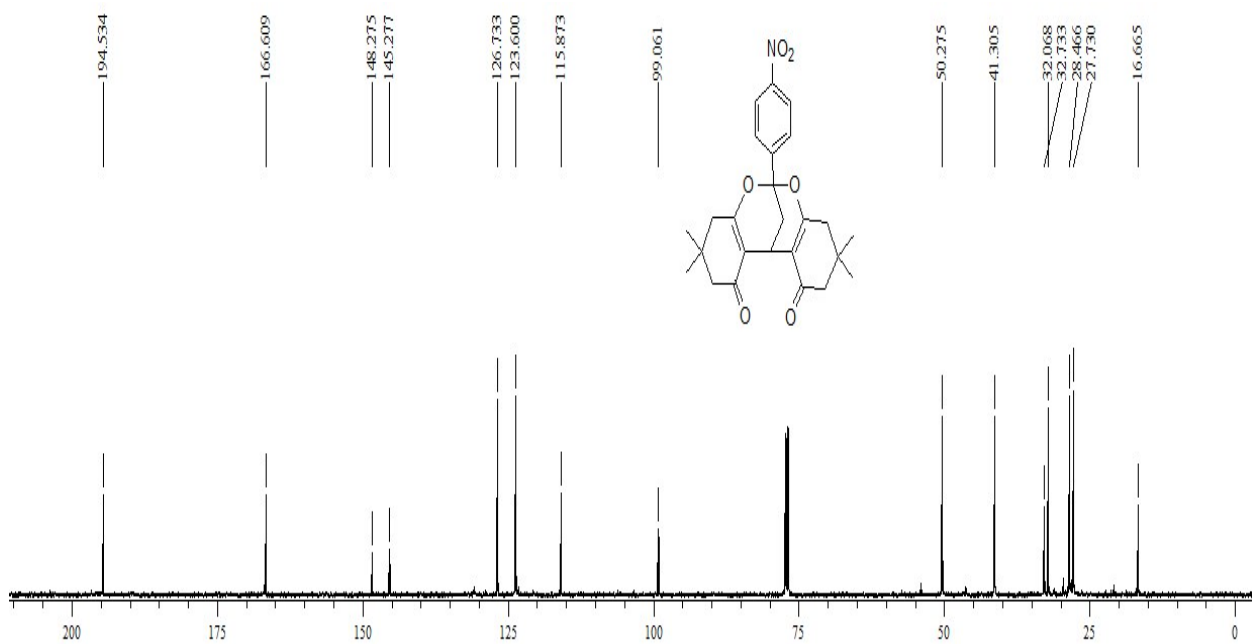
<sup>1</sup>H NMR (500 MHz) spectrum of **4a** in CDCl<sub>3</sub>.



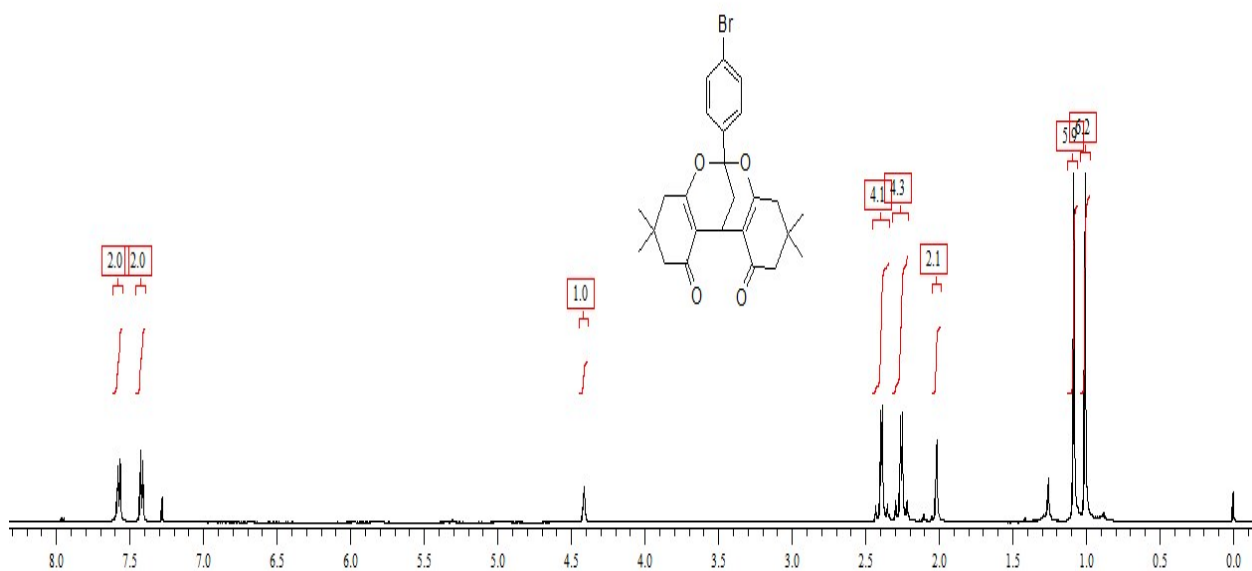
<sup>13</sup>C NMR (125 MHz) spectrum of **4a** in CDCl<sub>3</sub>.



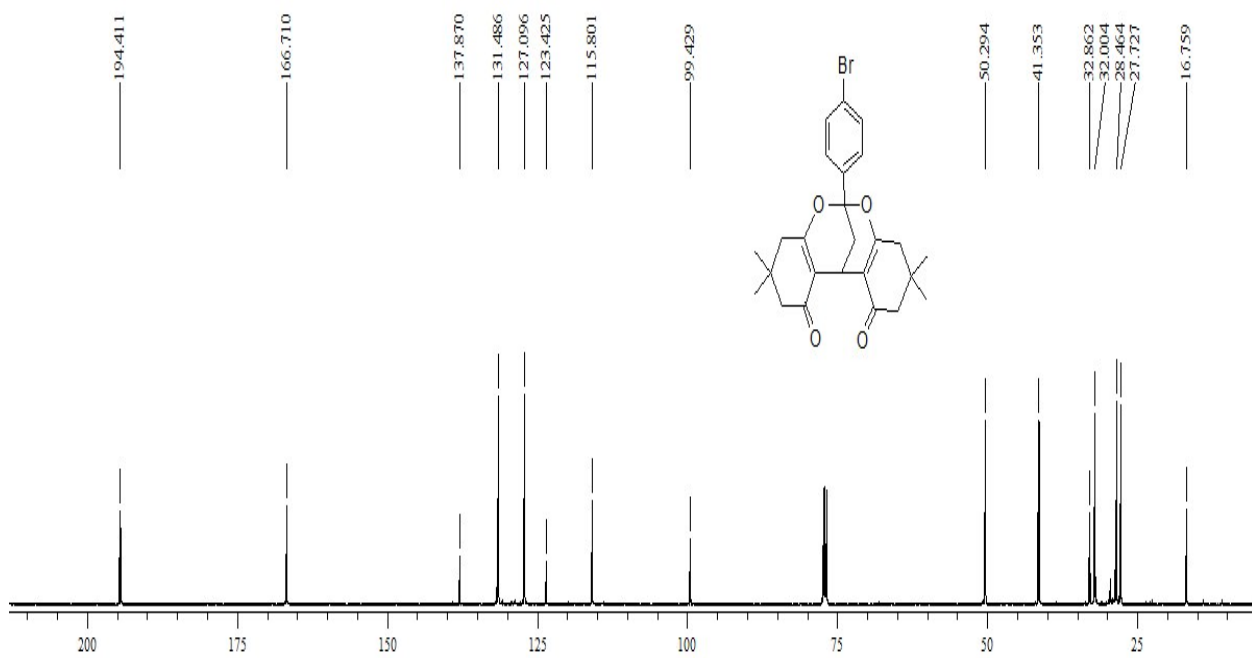
$^1\text{H}$  NMR (300 MHz) spectrum of **4b** in  $\text{CDCl}_3$ .



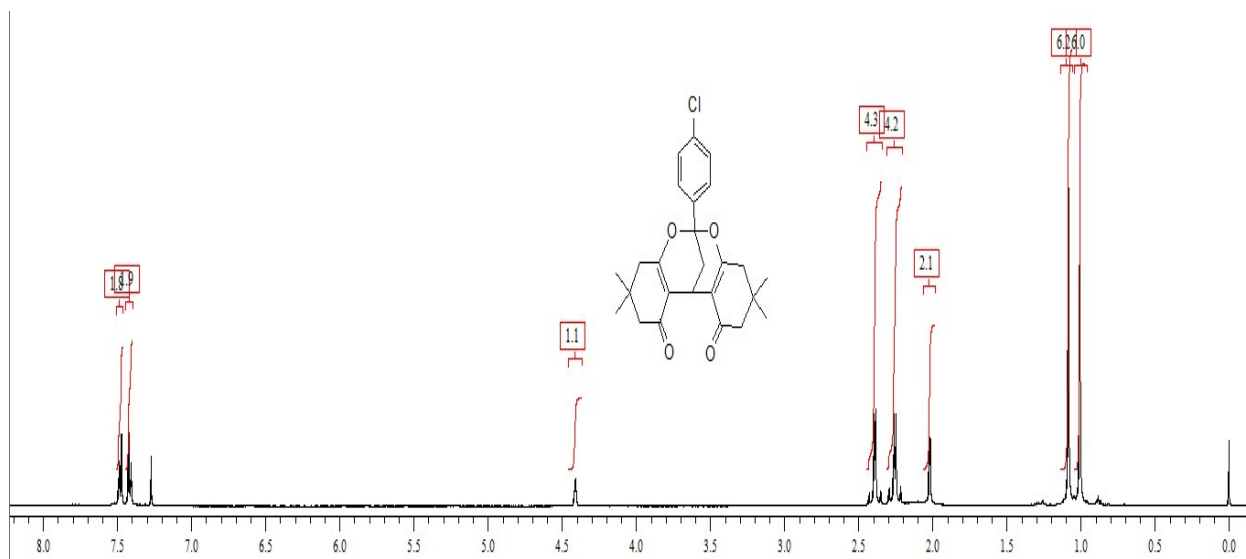
$^{13}\text{C}$  NMR (125 MHz) spectrum of **4b** in  $\text{CDCl}_3$ .



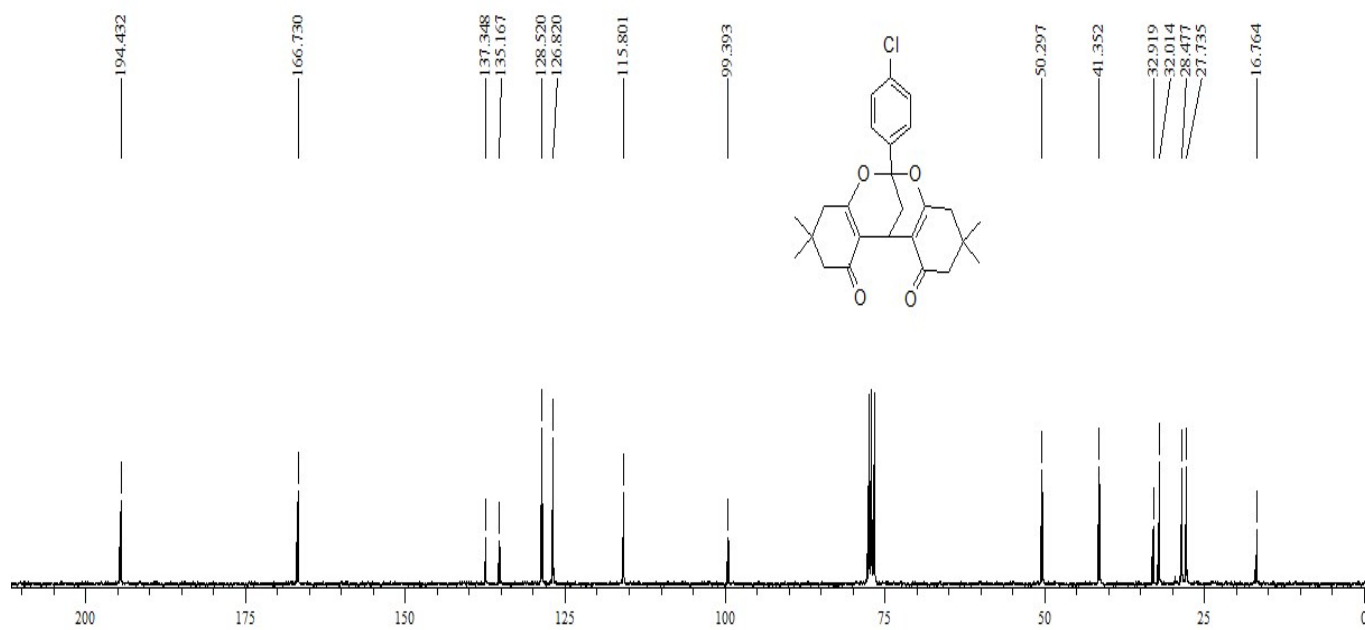
$^1\text{H NMR}$  (500 MHz) spectrum of **4c** in  $\text{CDCl}_3$ .



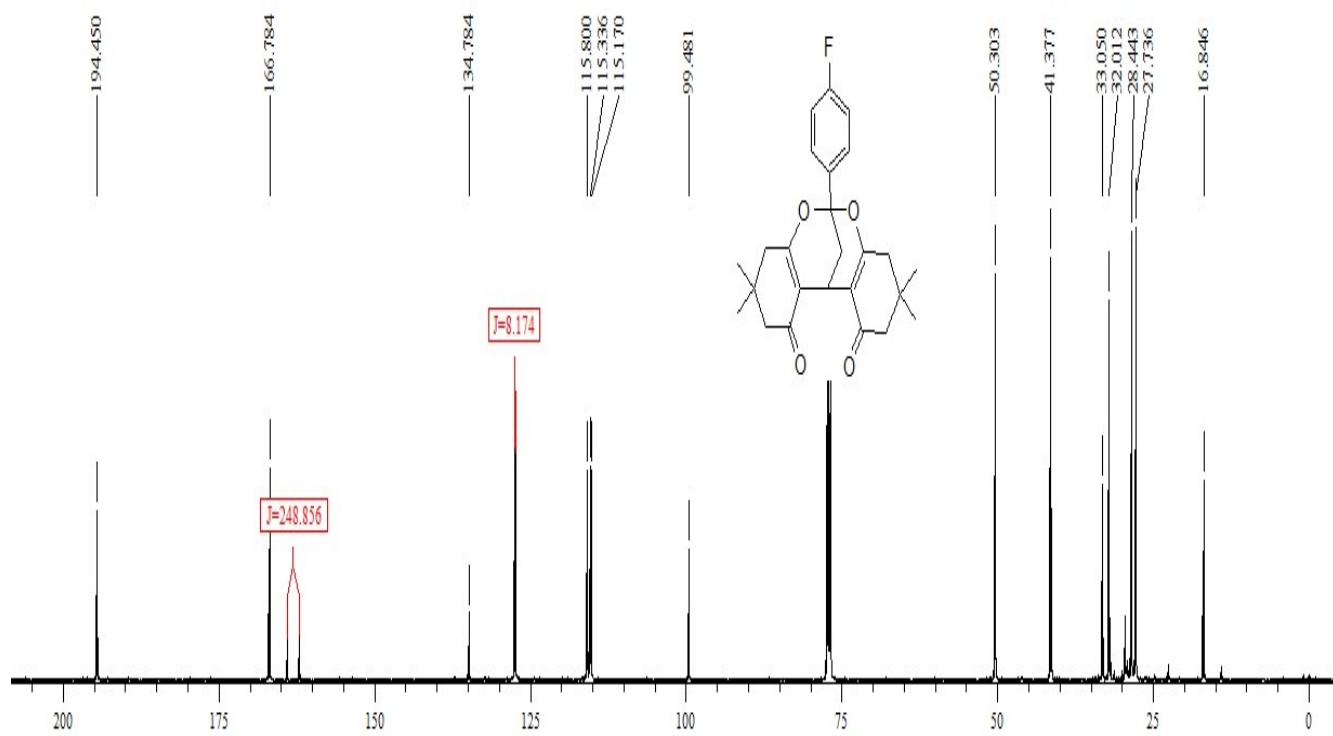
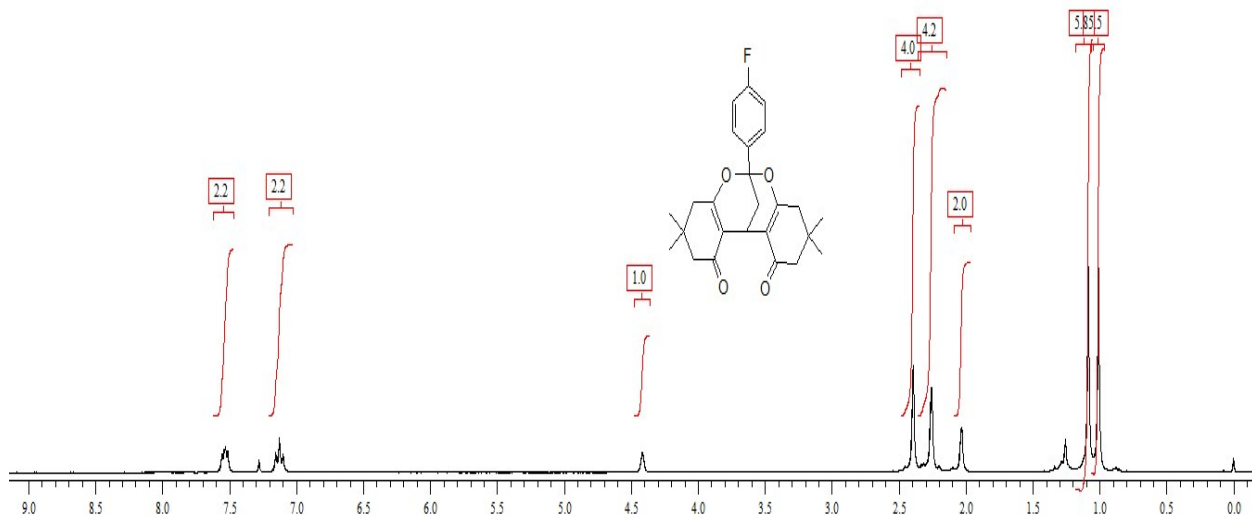
$^{13}\text{C NMR}$  (125 MHz) spectrum of **4c** in  $\text{CDCl}_3$ .



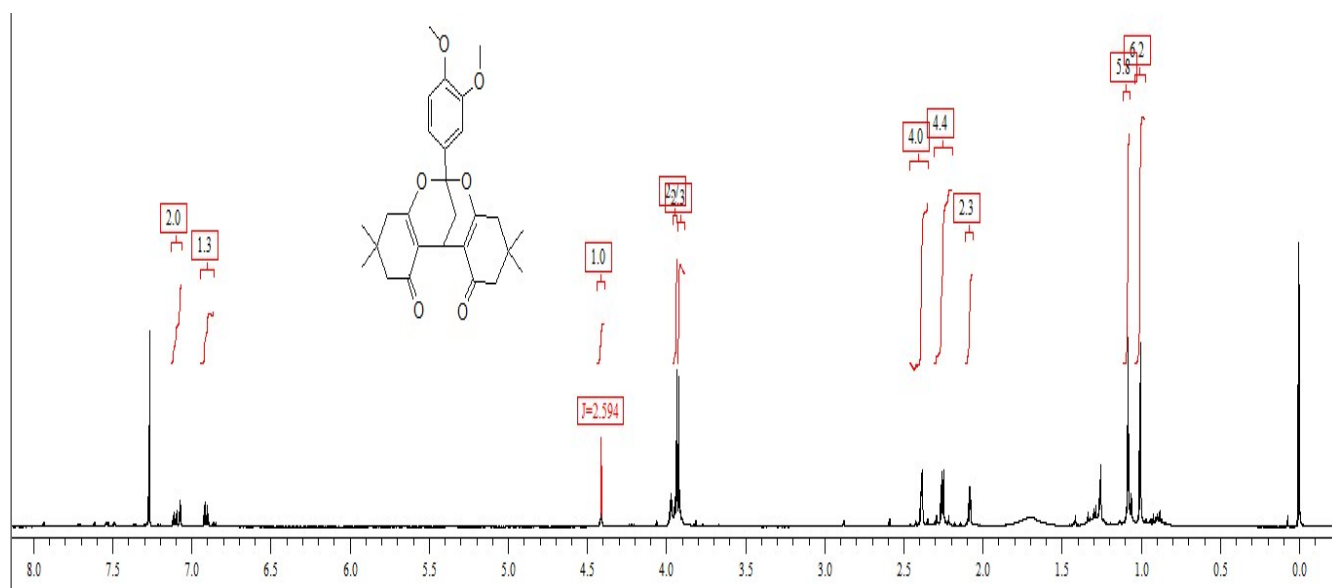
$^1\text{H}$  NMR (300 MHz) spectrum of **4d** in  $\text{CDCl}_3$ .



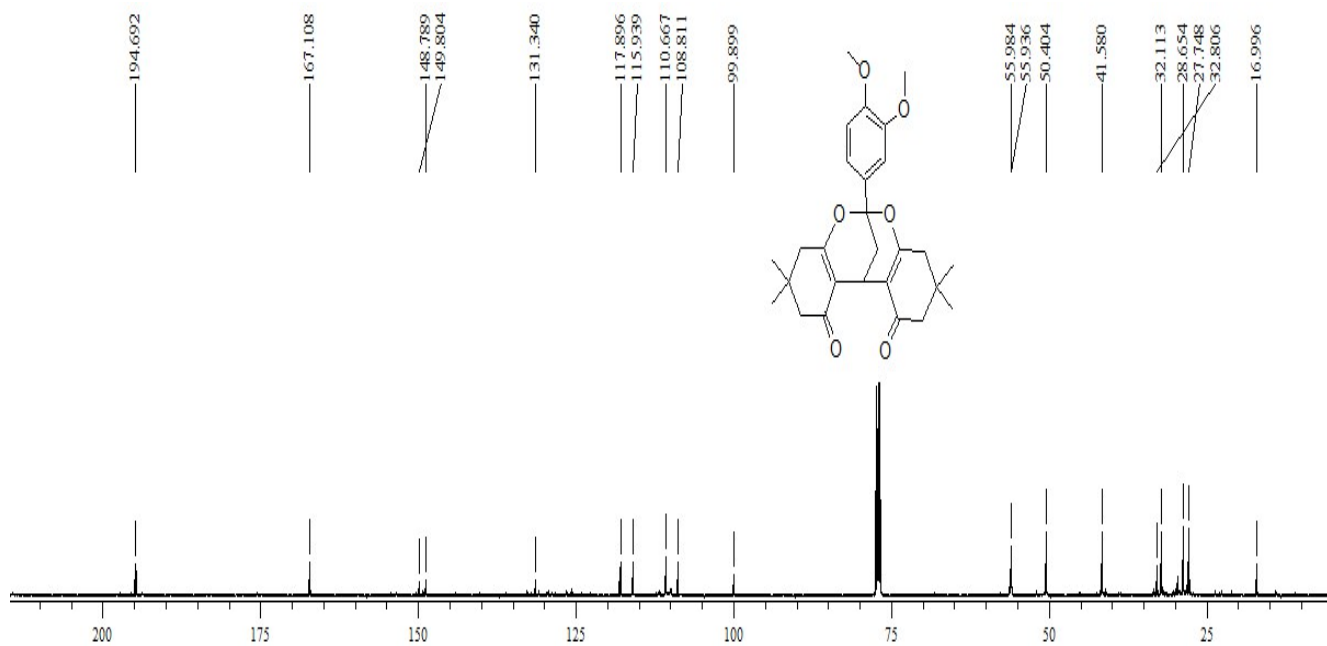
$^{13}\text{C}$  NMR (75 MHz) spectrum of **4d** in  $\text{CDCl}_3$ .



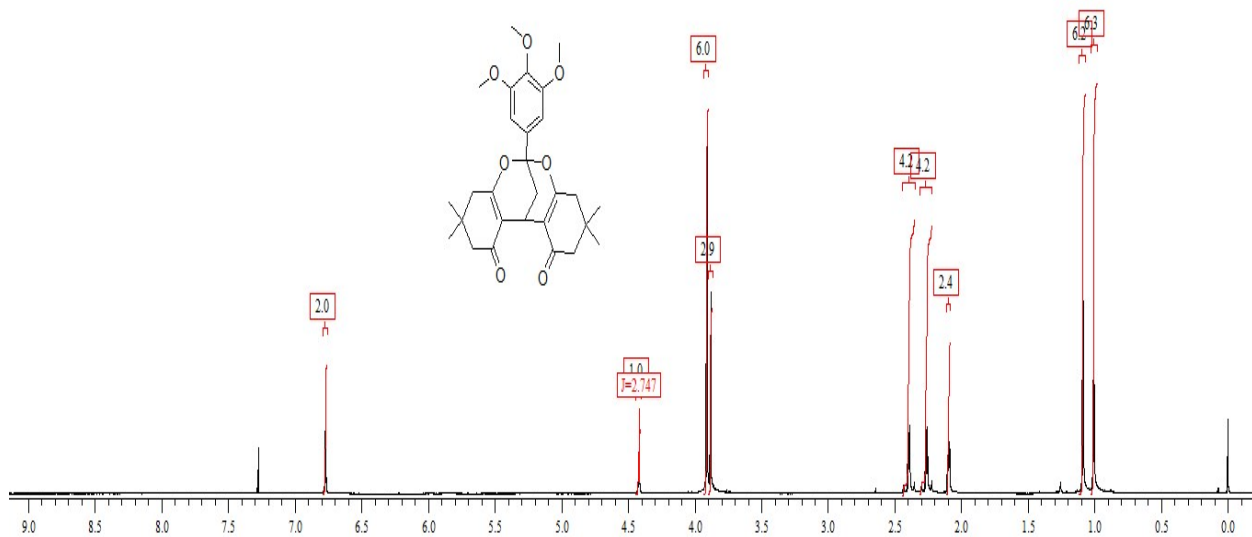




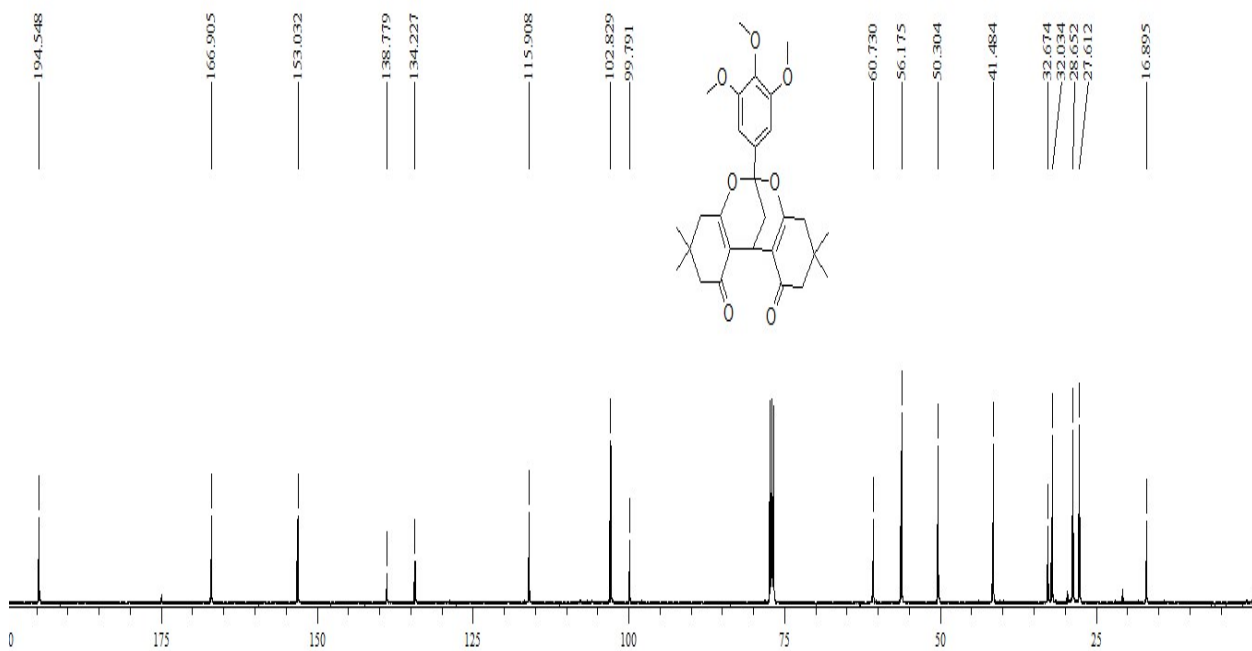
<sup>1</sup>H NMR (500 MHz) spectrum of **4f** in CDCl<sub>3</sub>.



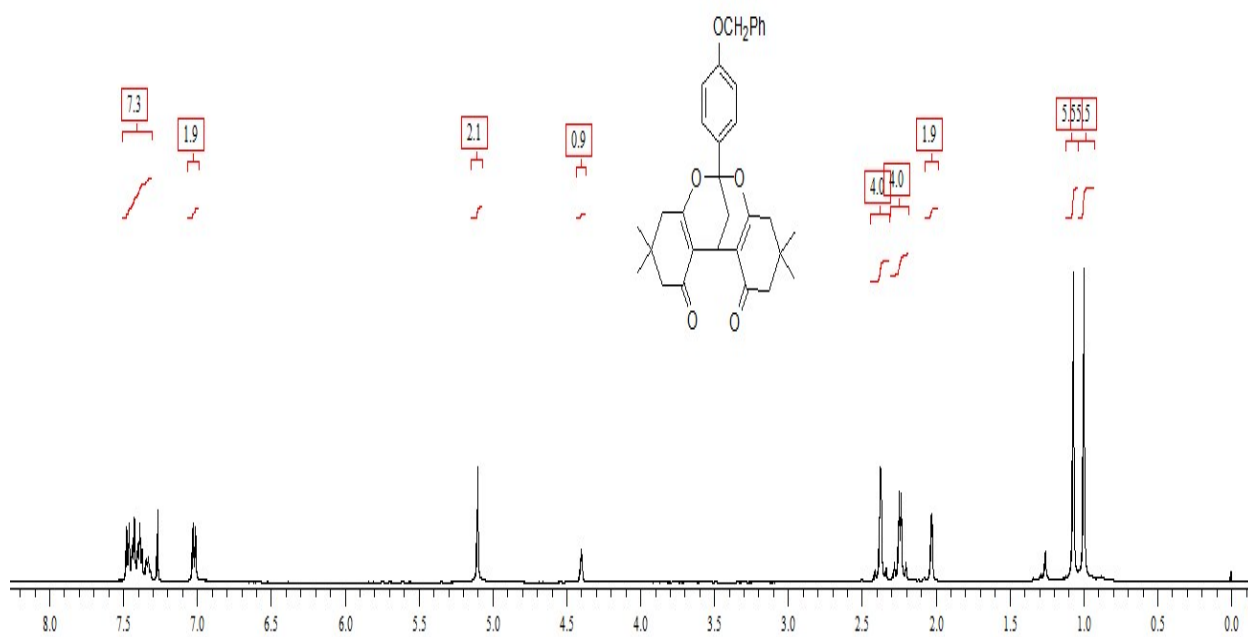
<sup>13</sup>C NMR (125 MHz) spectrum of **4f** in CDCl<sub>3</sub>.



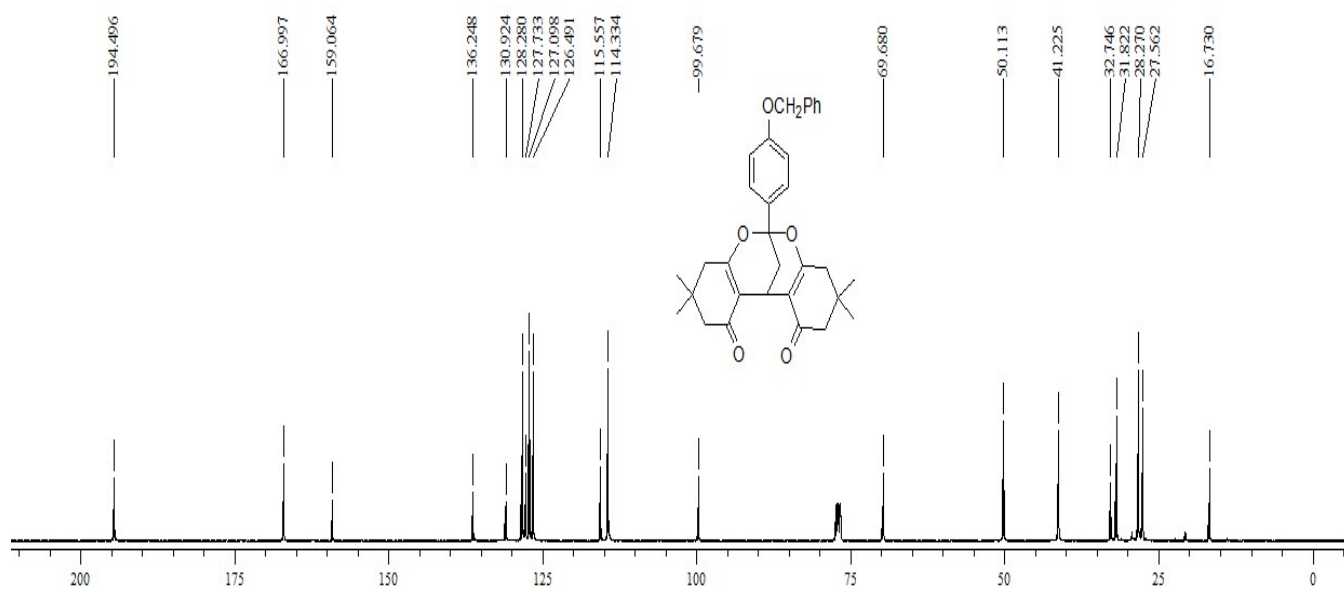
<sup>1</sup>H NMR (500 MHz) spectrum of **4g** in CDCl<sub>3</sub>.



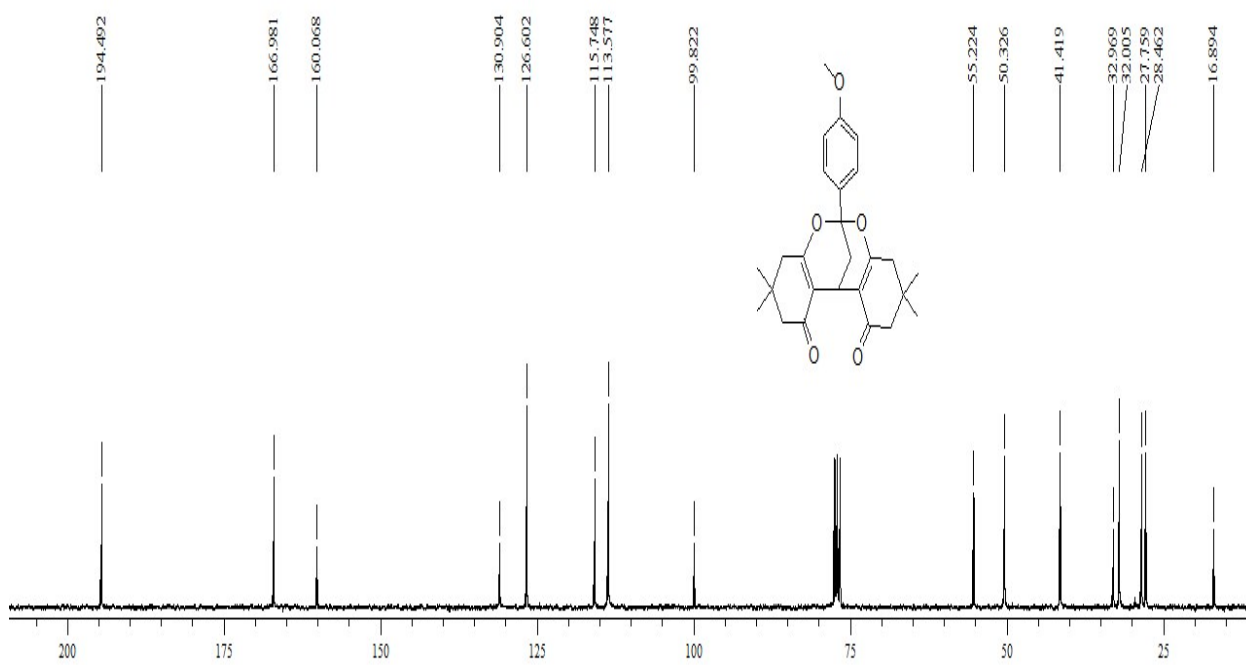
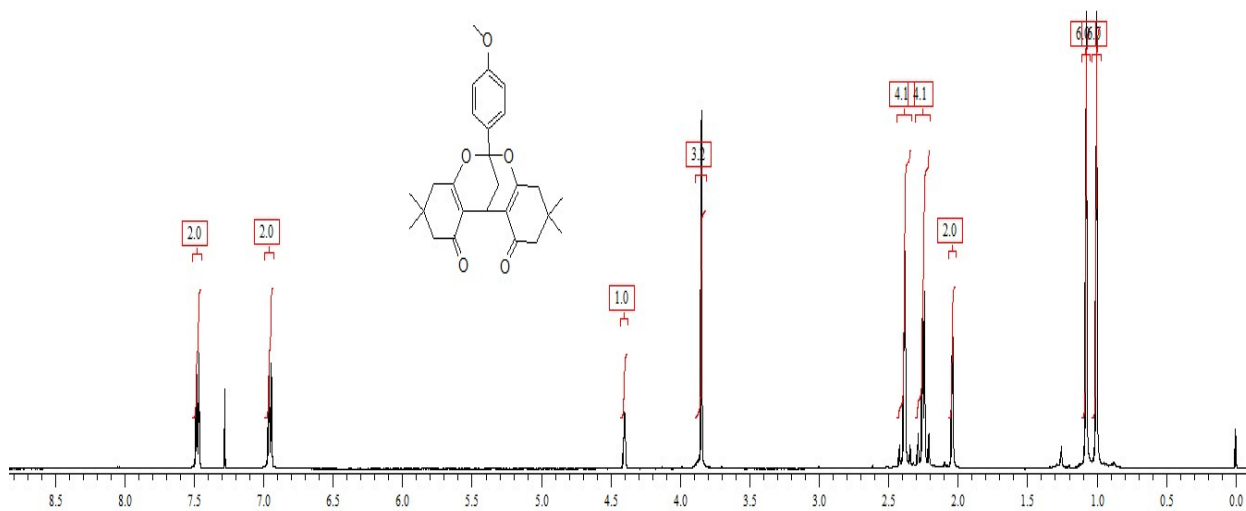
<sup>13</sup>C NMR (125 MHz) spectrum of **4g** in CDCl<sub>3</sub>.

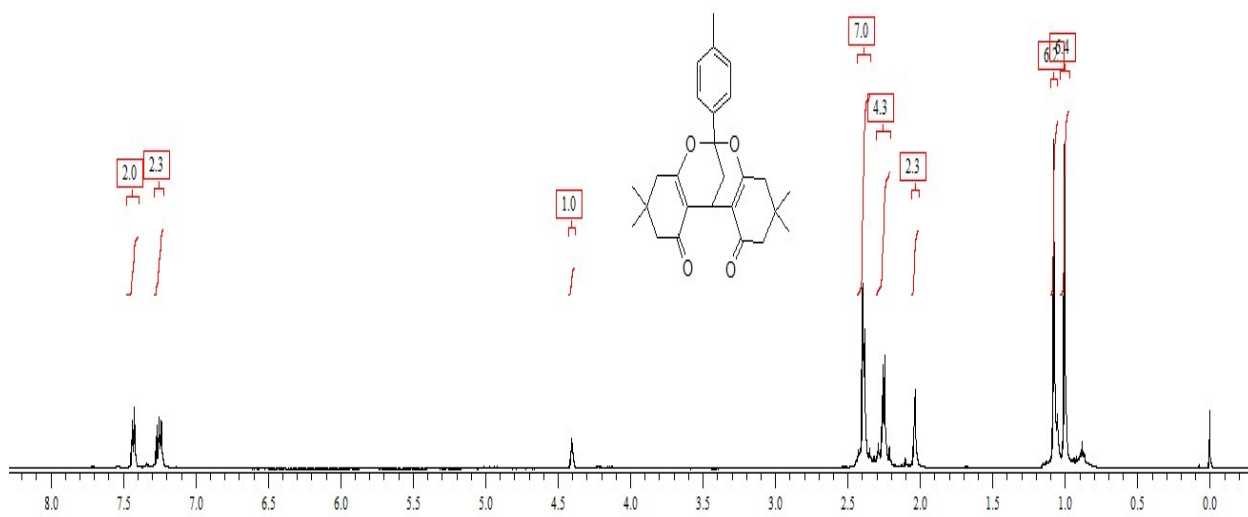


$^1\text{H NMR}$  (500 MHz) spectrum of **4h** in  $\text{CDCl}_3$ .

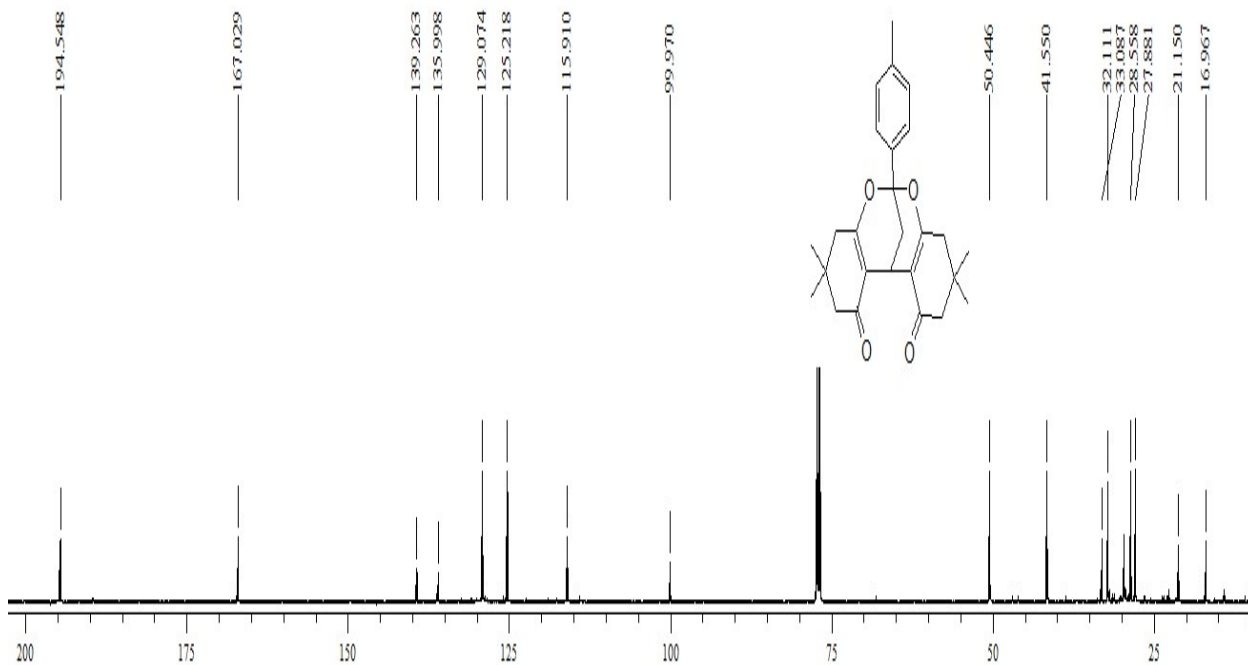


$^{13}\text{C NMR}$  (100 MHz) spectrum of **4h** in  $\text{CDCl}_3$ .

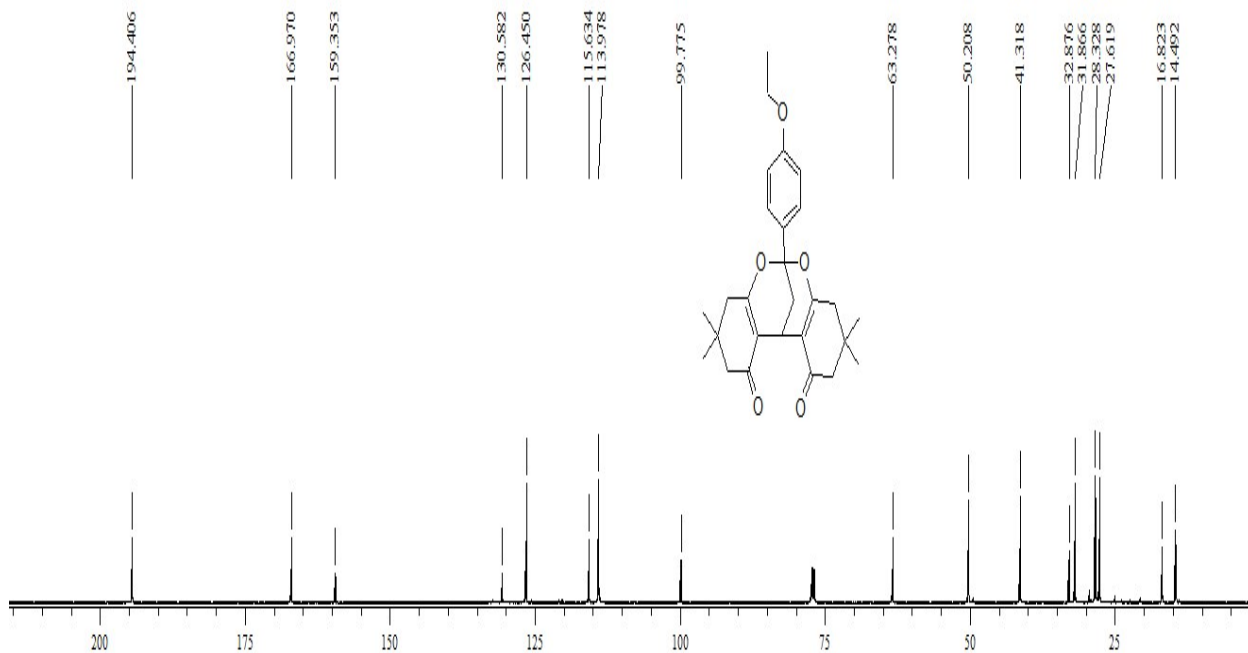
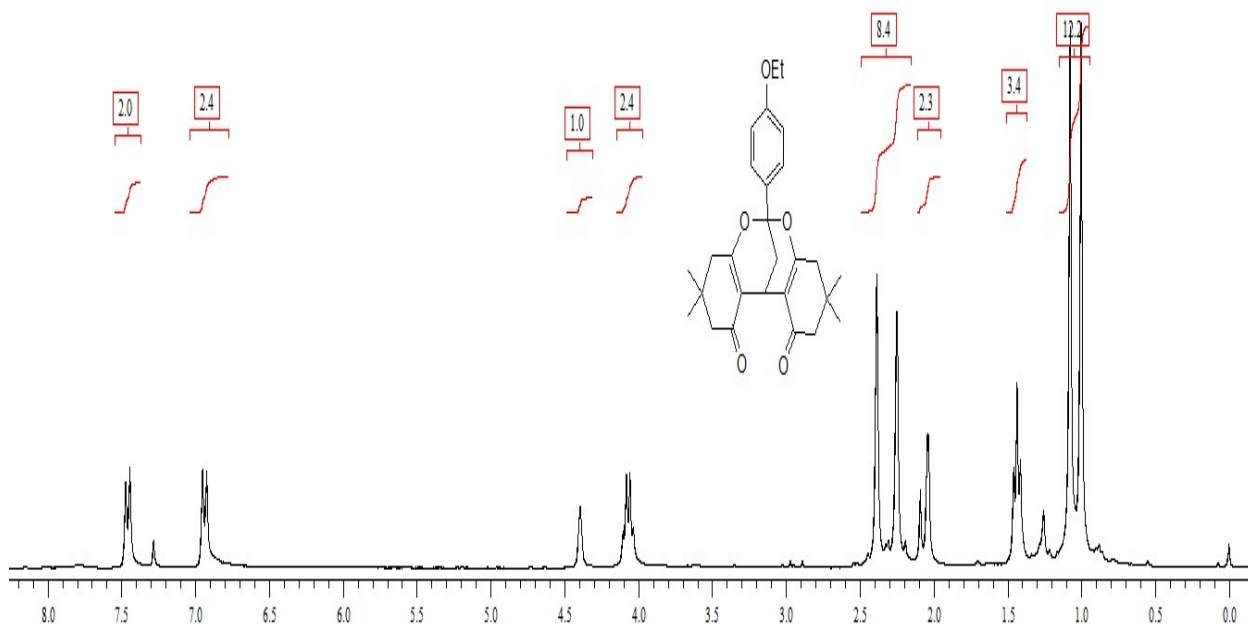


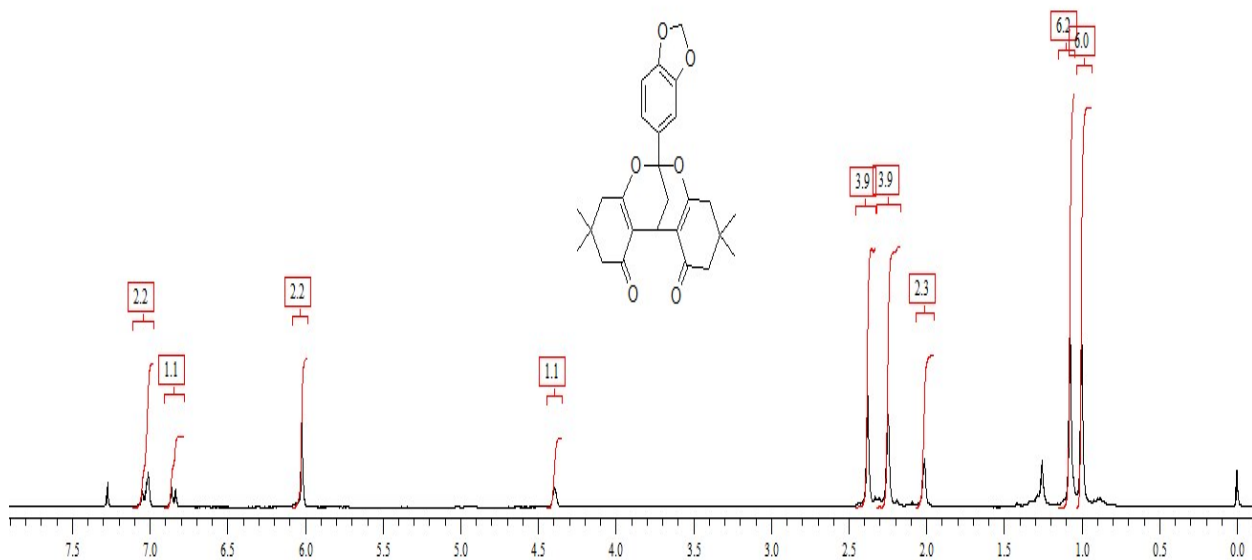


$^1\text{H}$  NMR (500 MHz) spectrum of **4j** in  $\text{CDCl}_3$ .

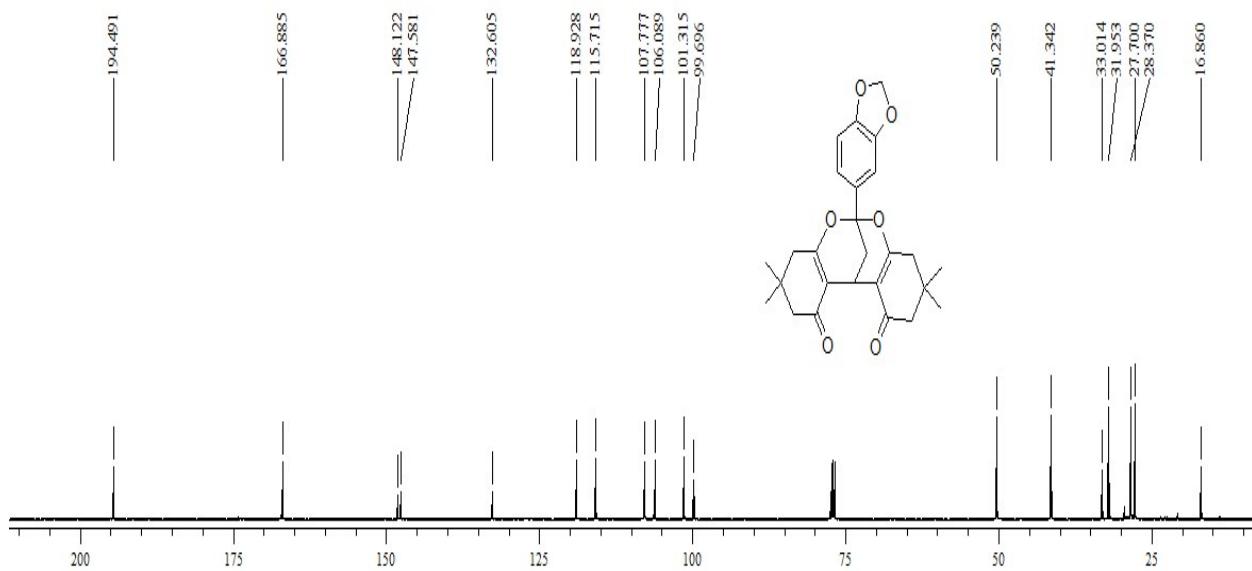


$^{13}\text{C}$  NMR (125 MHz) spectrum of **4j** in  $\text{CDCl}_3$ .

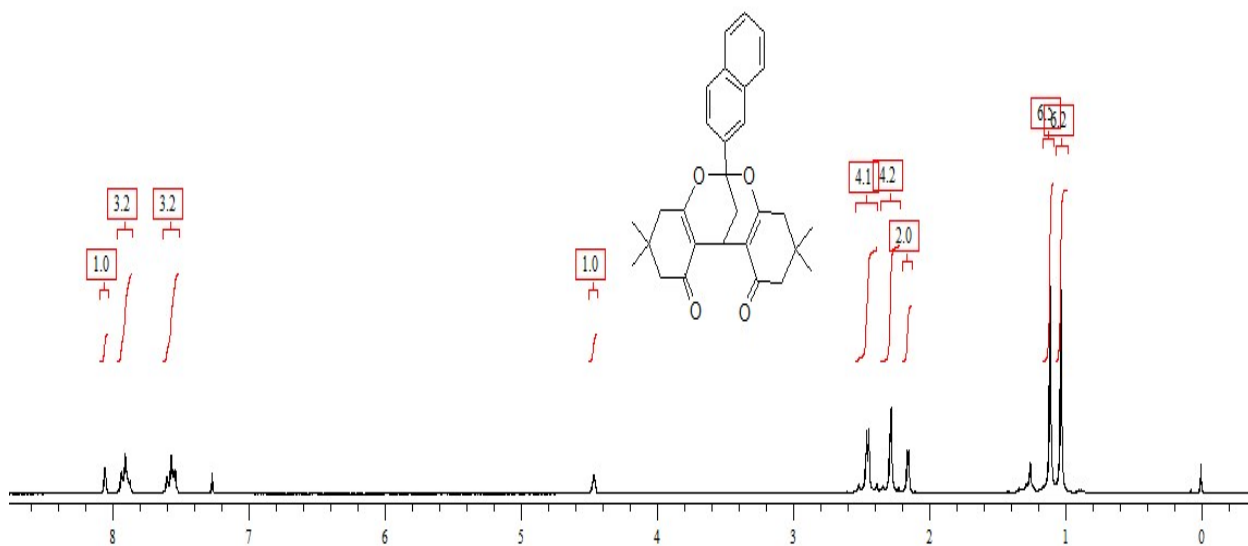




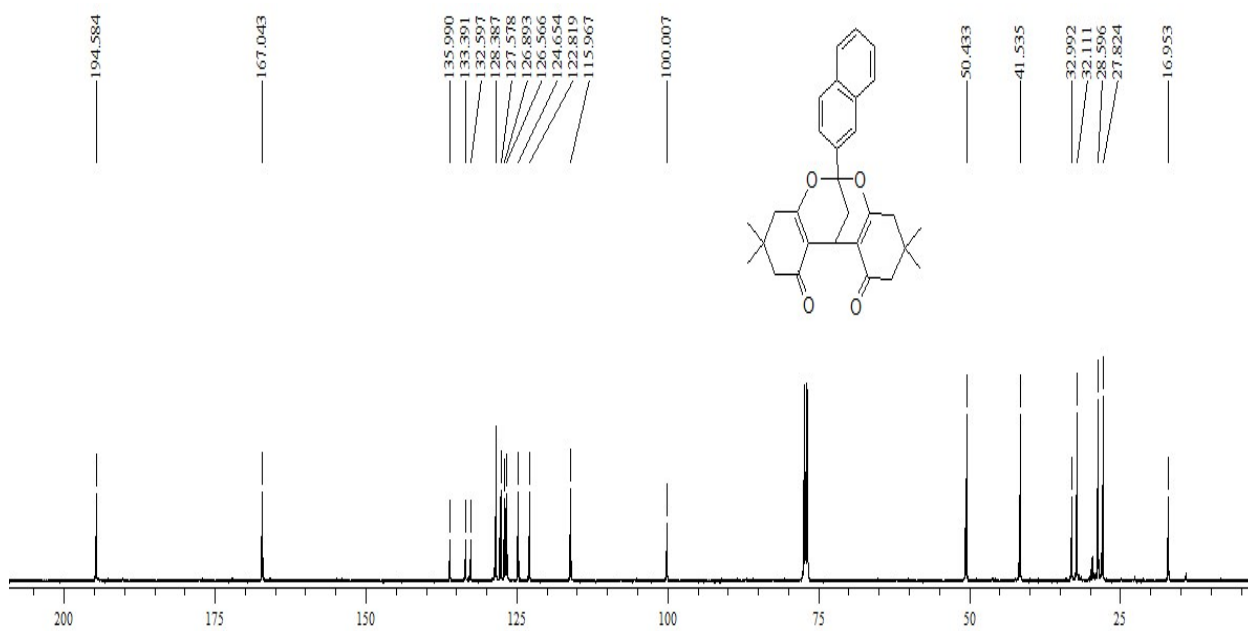
<sup>1</sup>H NMR (300 MHz) spectrum of **4I** in CDCl<sub>3</sub>.



<sup>13</sup>C NMR (125 MHz) spectrum of **4I** in CDCl<sub>3</sub>.

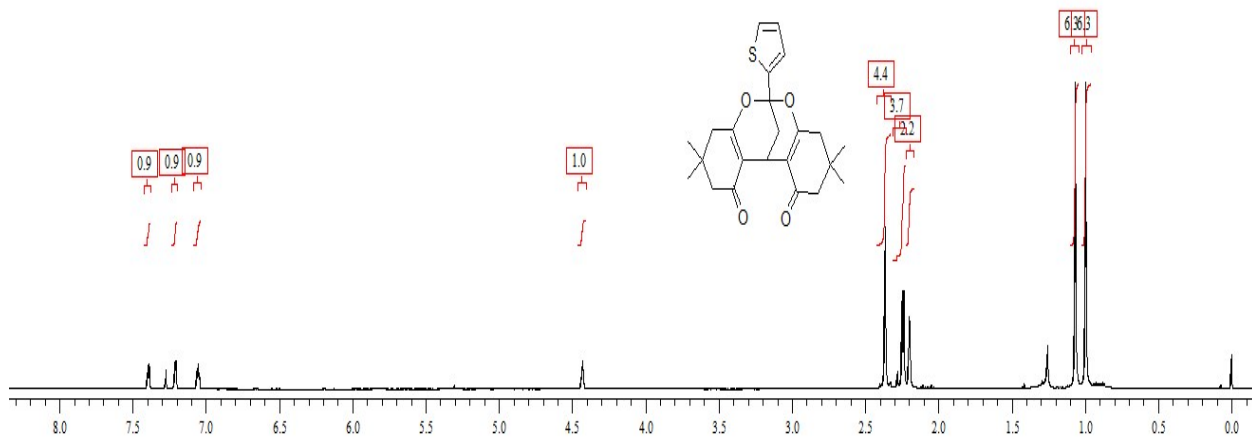


<sup>1</sup>H NMR (300 MHz) spectrum of **4m** in CDCl<sub>3</sub>.

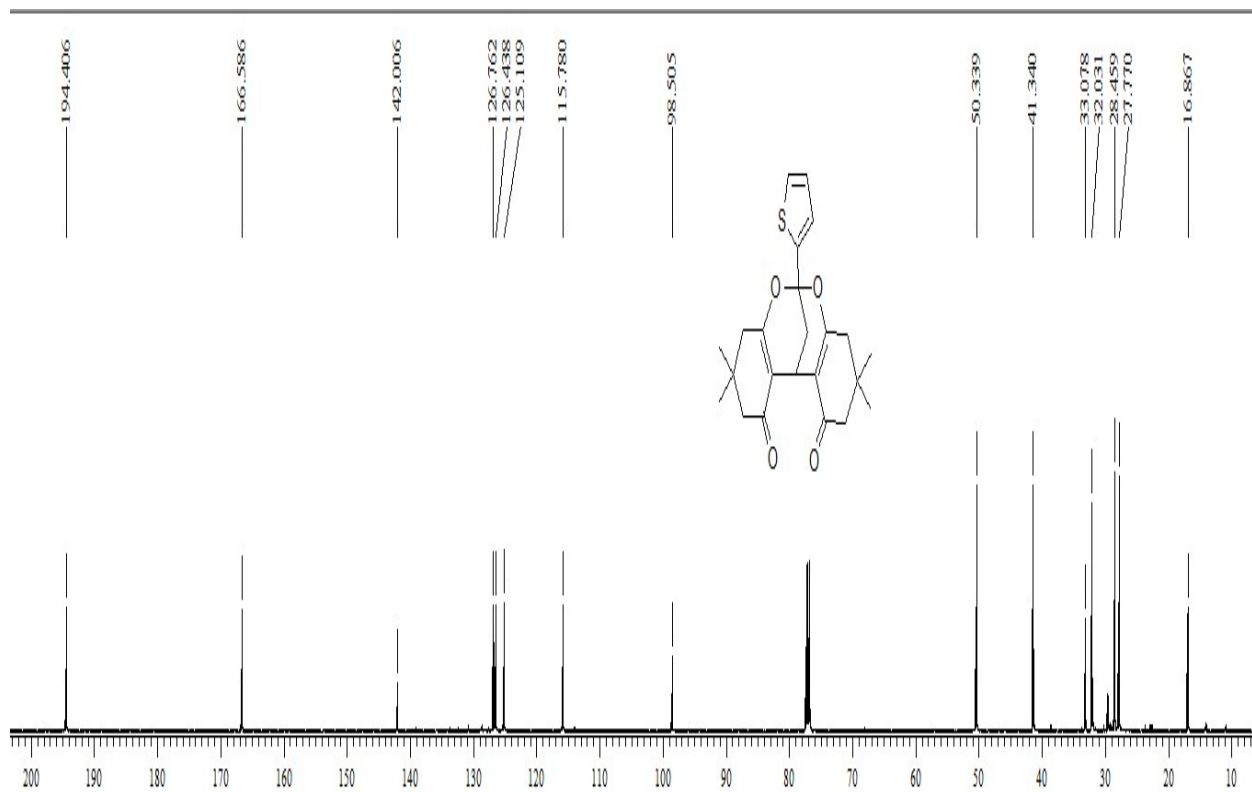


<sup>13</sup>C NMR (125 MHz) spectrum of **4m** in CDCl<sub>3</sub>.

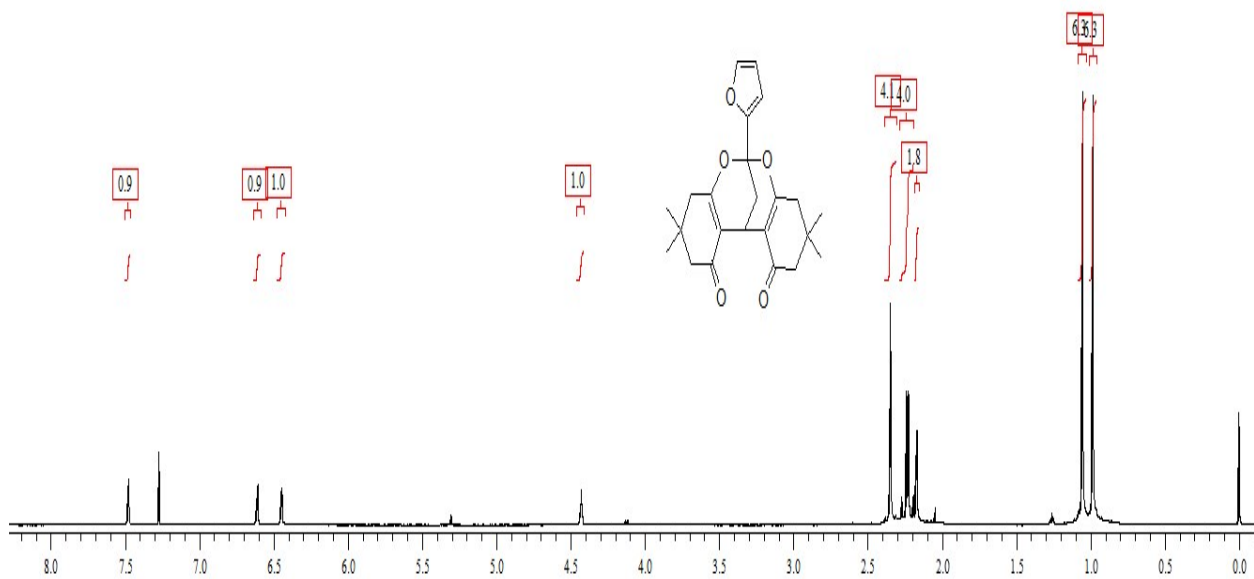




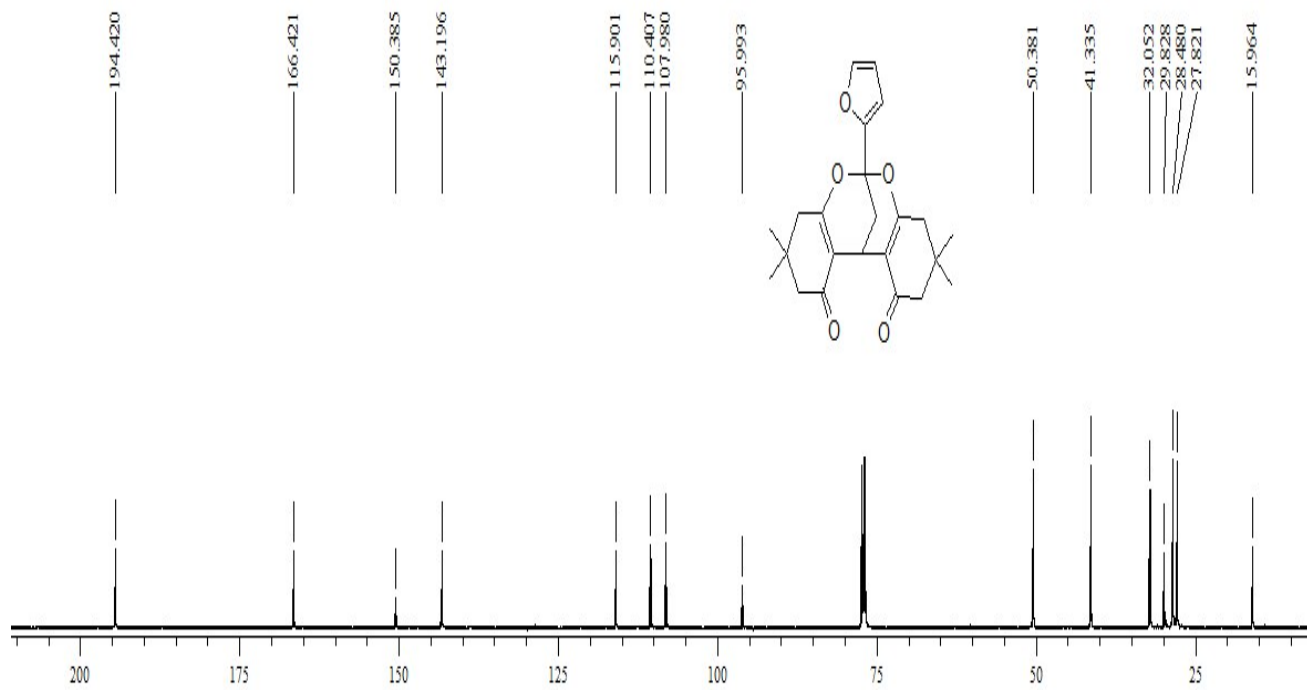
<sup>1</sup>H NMR (500 MHz) spectrum of **4n** in CDCl<sub>3</sub>.



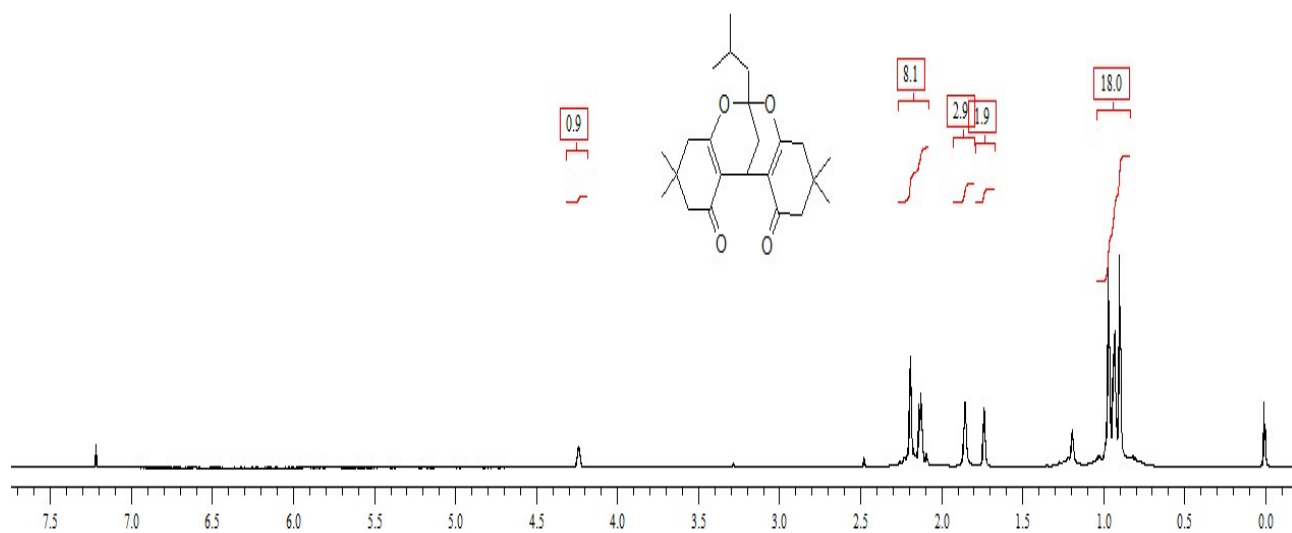
<sup>13</sup>C NMR (125 MHz) spectrum of **4n** in CDCl<sub>3</sub>.



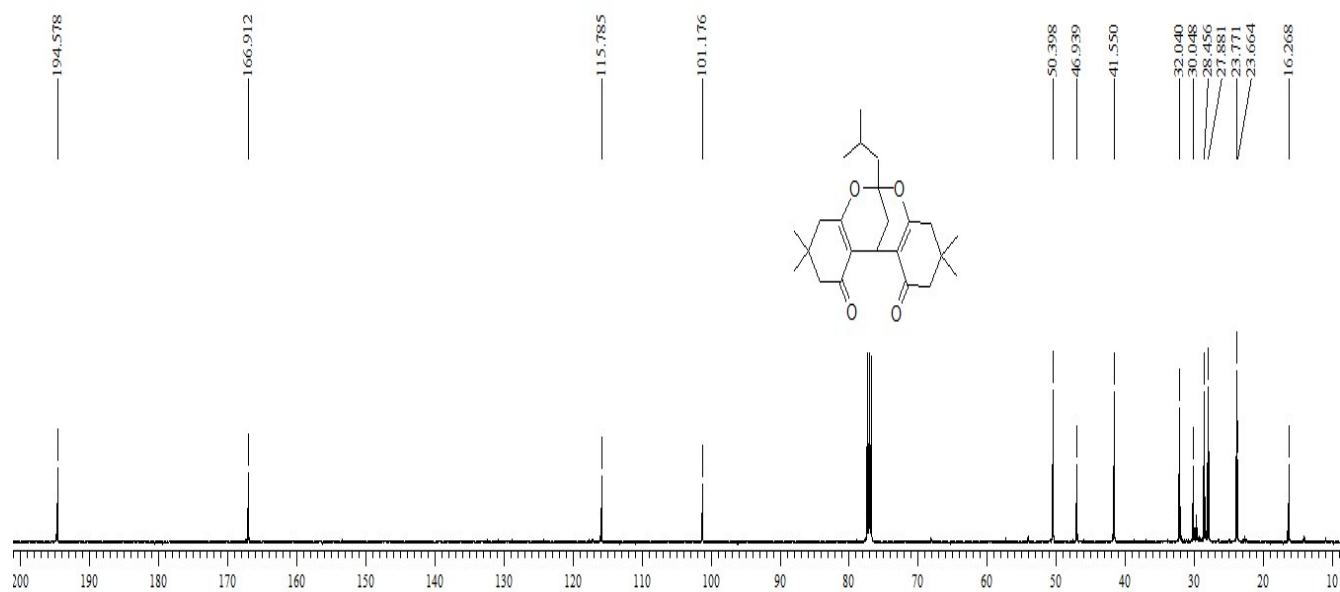
$^1\text{H}$  NMR (500 MHz) spectrum of **4o** in  $\text{CDCl}_3$ .



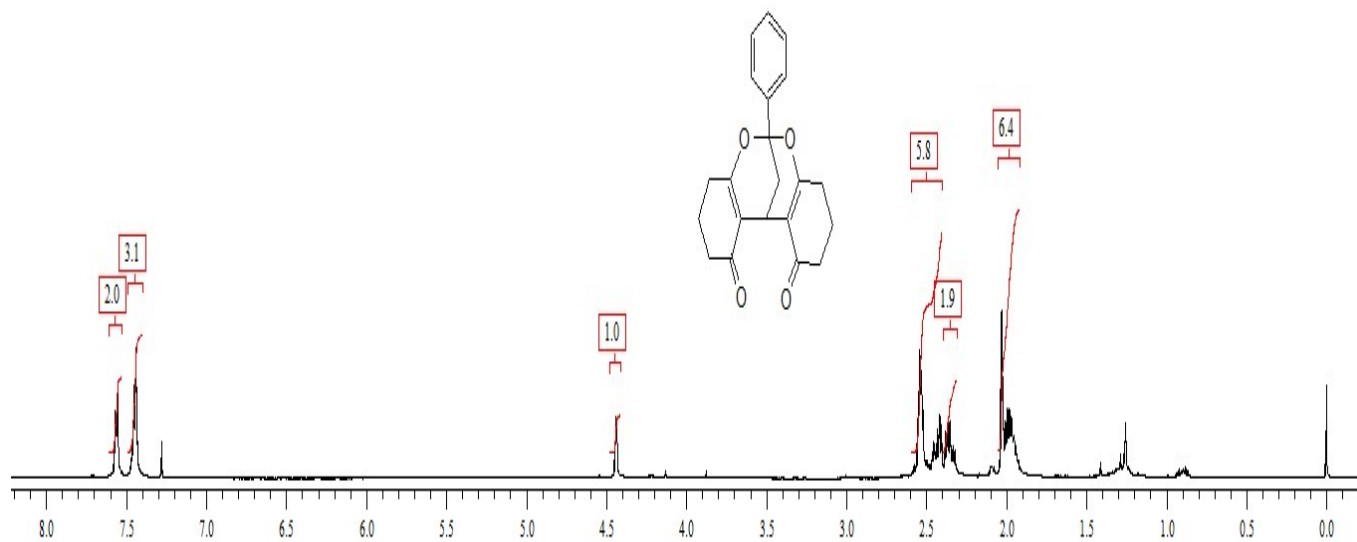
$^{13}\text{C}$  NMR (125 MHz) spectrum of **4o** in  $\text{CDCl}_3$ .



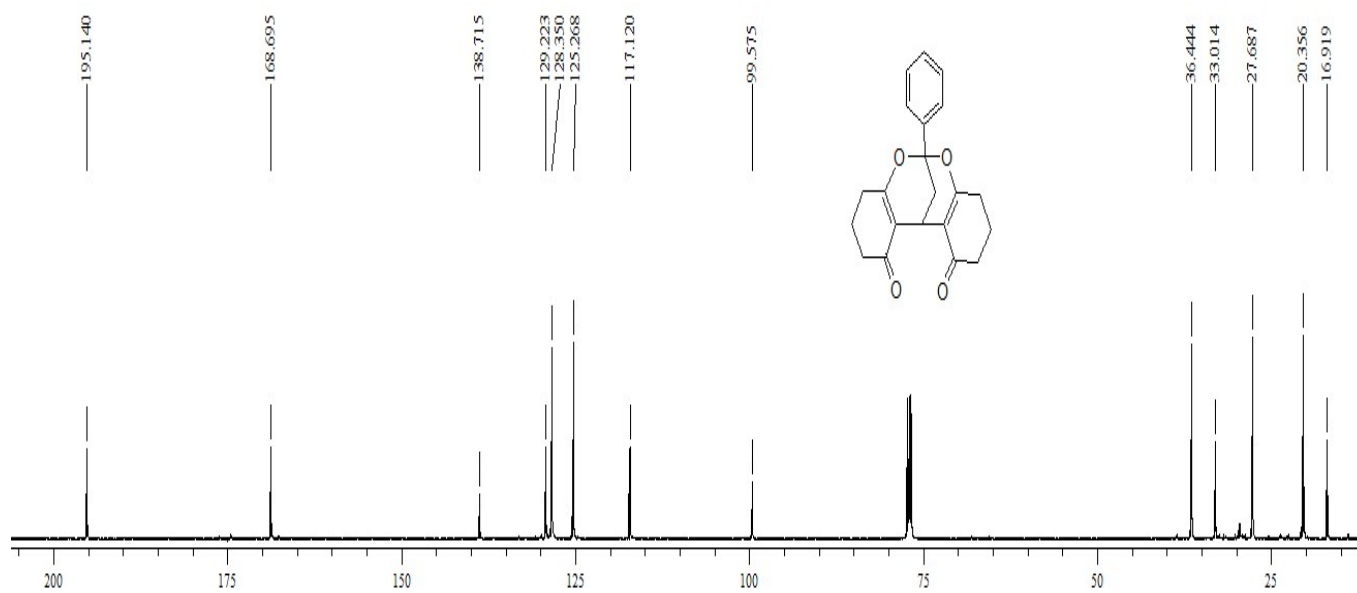
<sup>1</sup>H NMR (500 MHz) spectrum of **4p** in CDCl<sub>3</sub>.



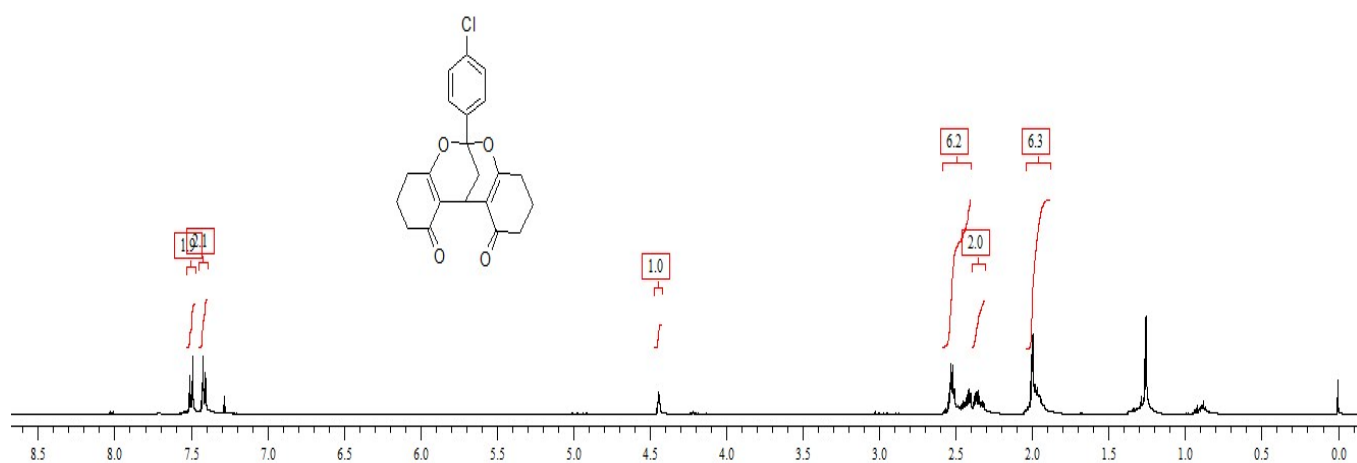
<sup>13</sup>C NMR (125 MHz) spectrum of **4p** in CDCl<sub>3</sub>.



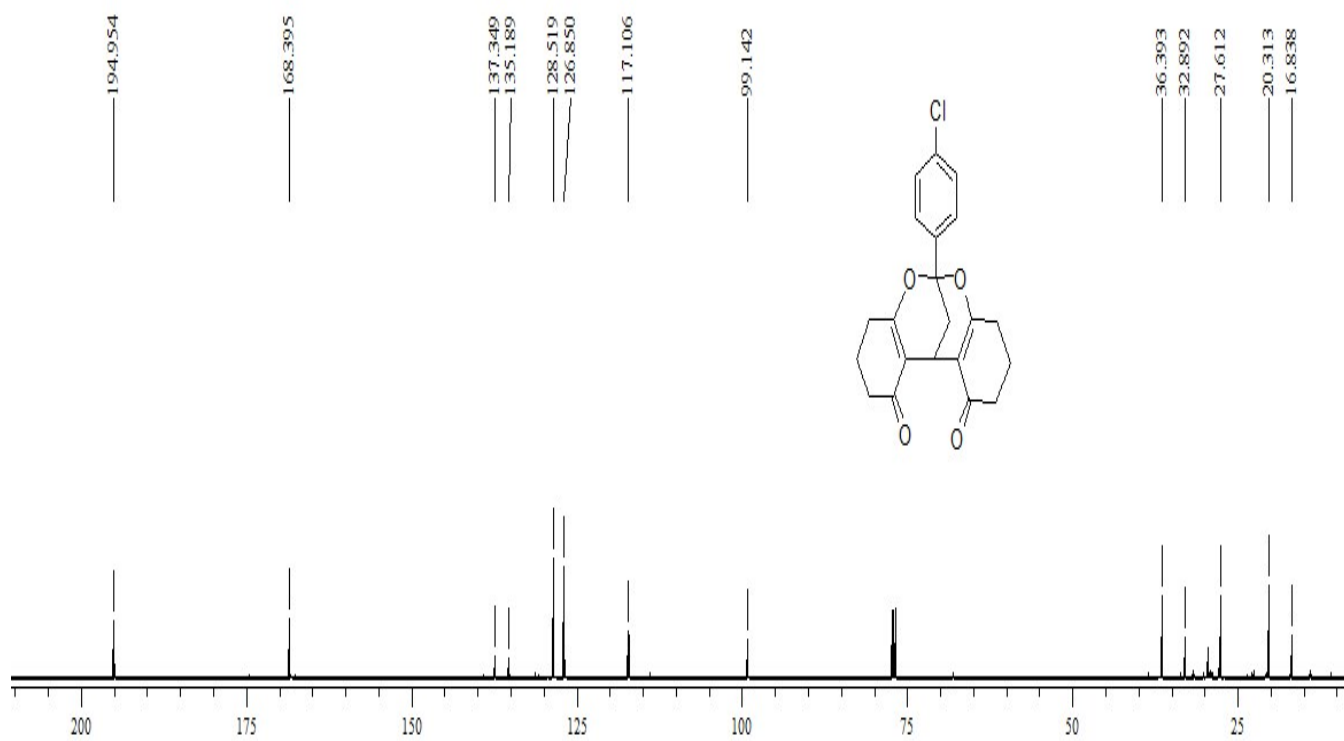
<sup>1</sup>H NMR (500 MHz) spectrum of **4q** in CDCl<sub>3</sub>.



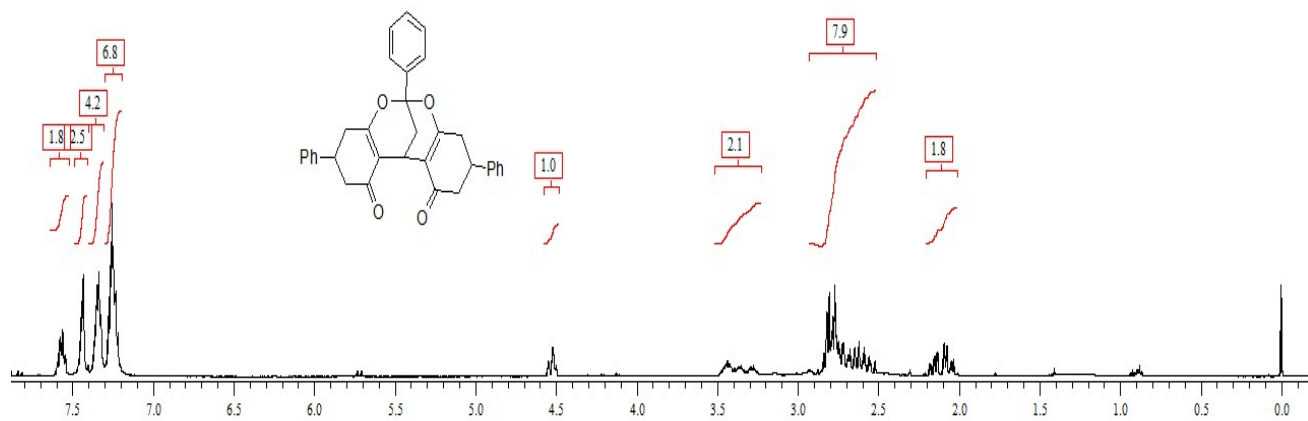
<sup>13</sup>C NMR (125 MHz) spectrum of **4q** in CDCl<sub>3</sub>.



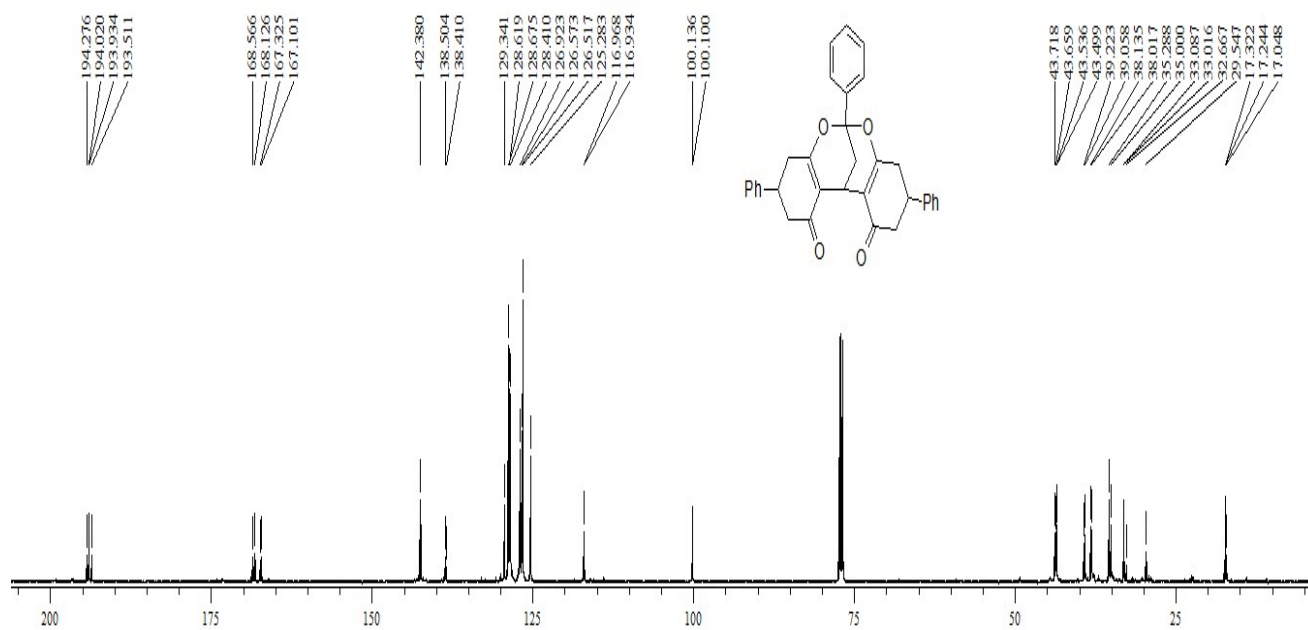
<sup>1</sup>H NMR (500 MHz) spectrum of **4r** in CDCl<sub>3</sub>.



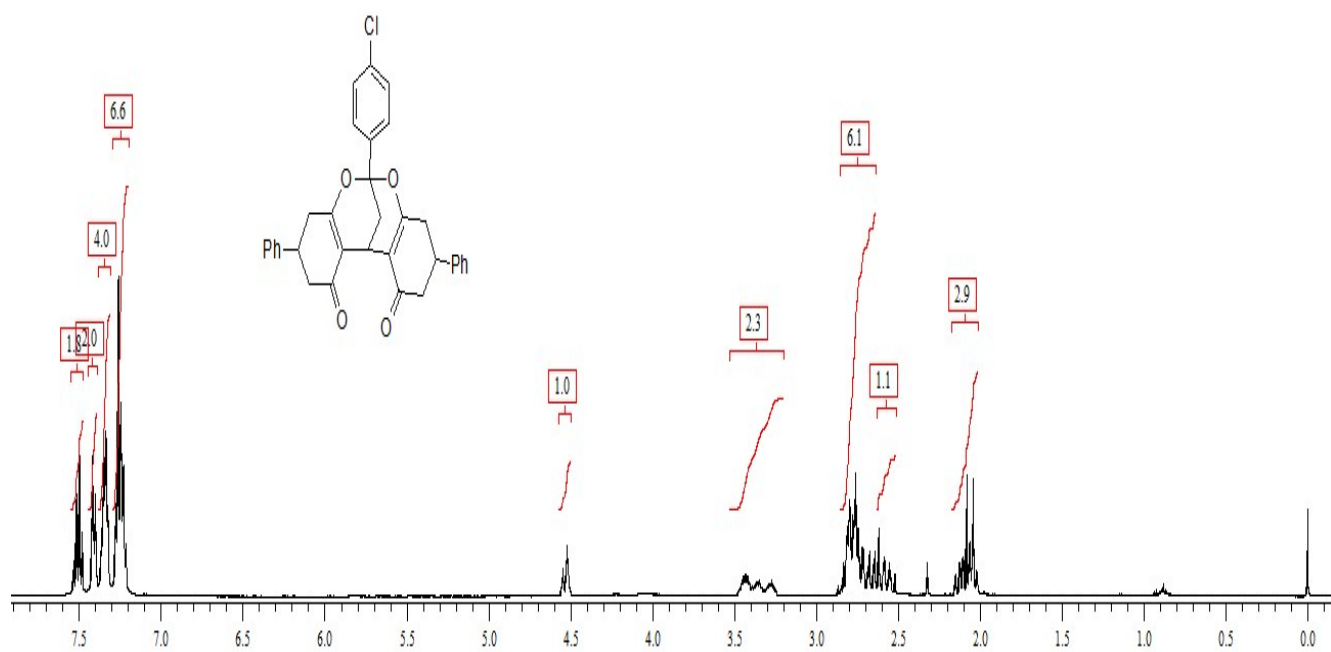
<sup>13</sup>C NMR (125 MHz) spectrum of **4r** in CDCl<sub>3</sub>.



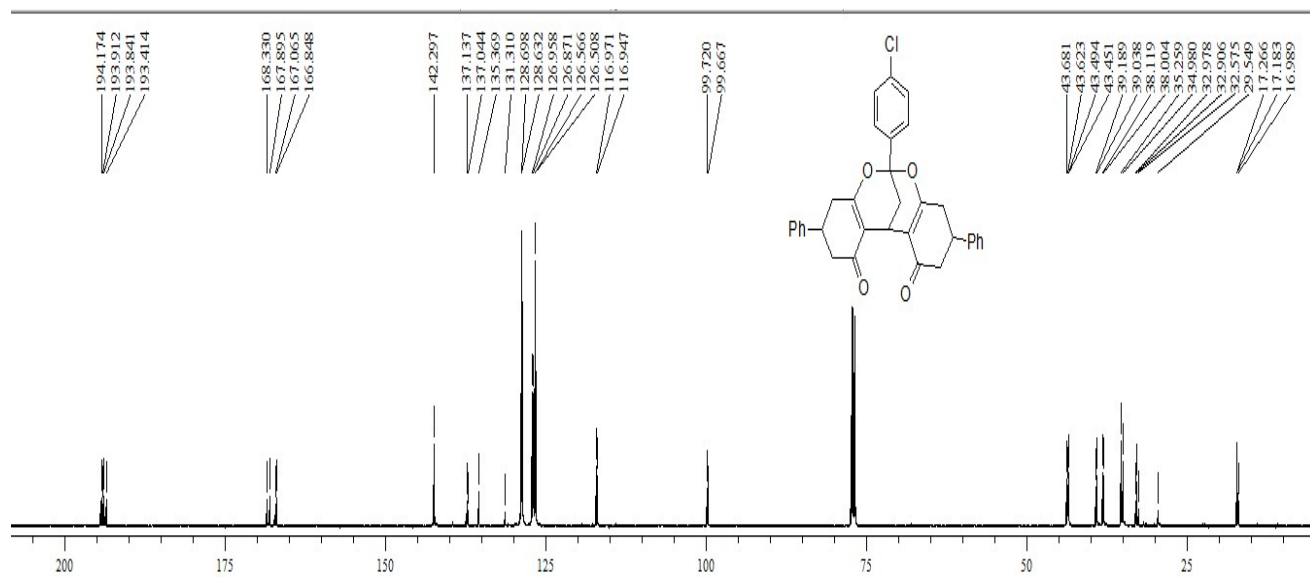
<sup>1</sup>H NMR (500 MHz) spectrum of **4s** in CDCl<sub>3</sub>.



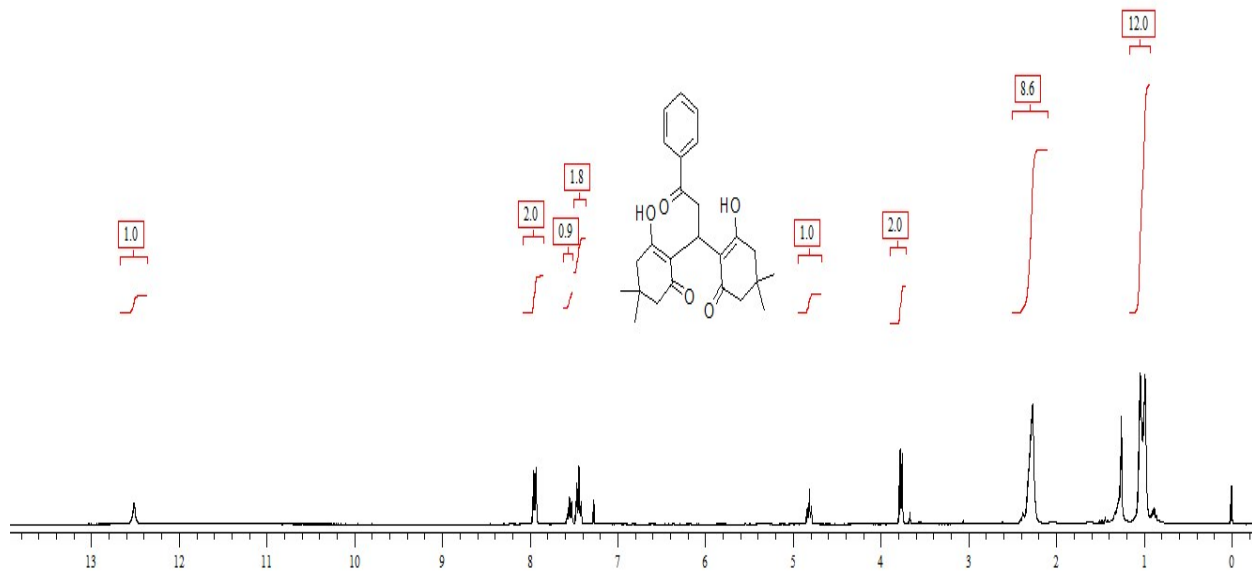
<sup>13</sup>C NMR (125 MHz) spectrum of **4s** in CDCl<sub>3</sub>.



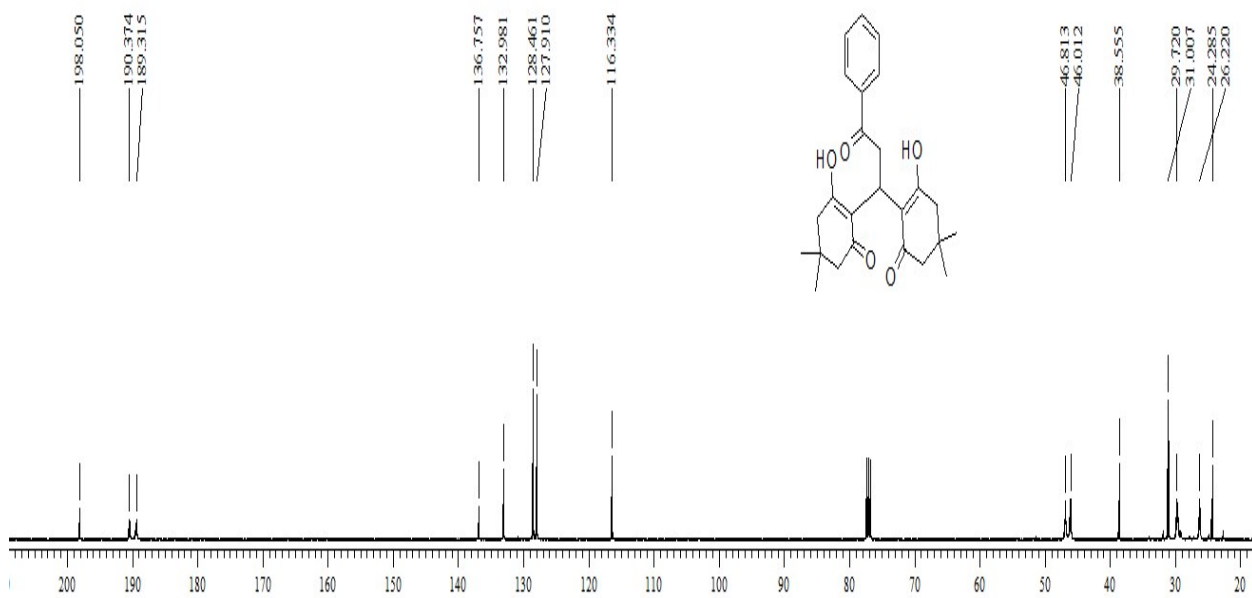
<sup>1</sup>H NMR (500 MHz) spectrum of **4t** in CDCl<sub>3</sub>.



<sup>13</sup>C NMR (125 MHz) spectrum of **4t** in CDCl<sub>3</sub>.

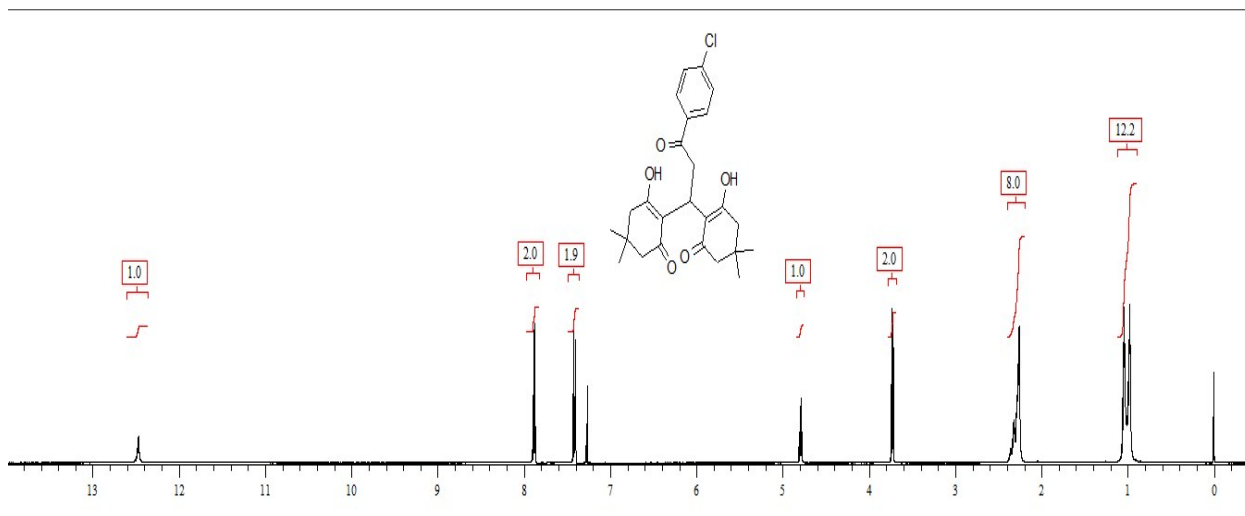


$^1\text{H NMR}$  (300 MHz) spectrum of **3a** in  $\text{CDCl}_3$ .

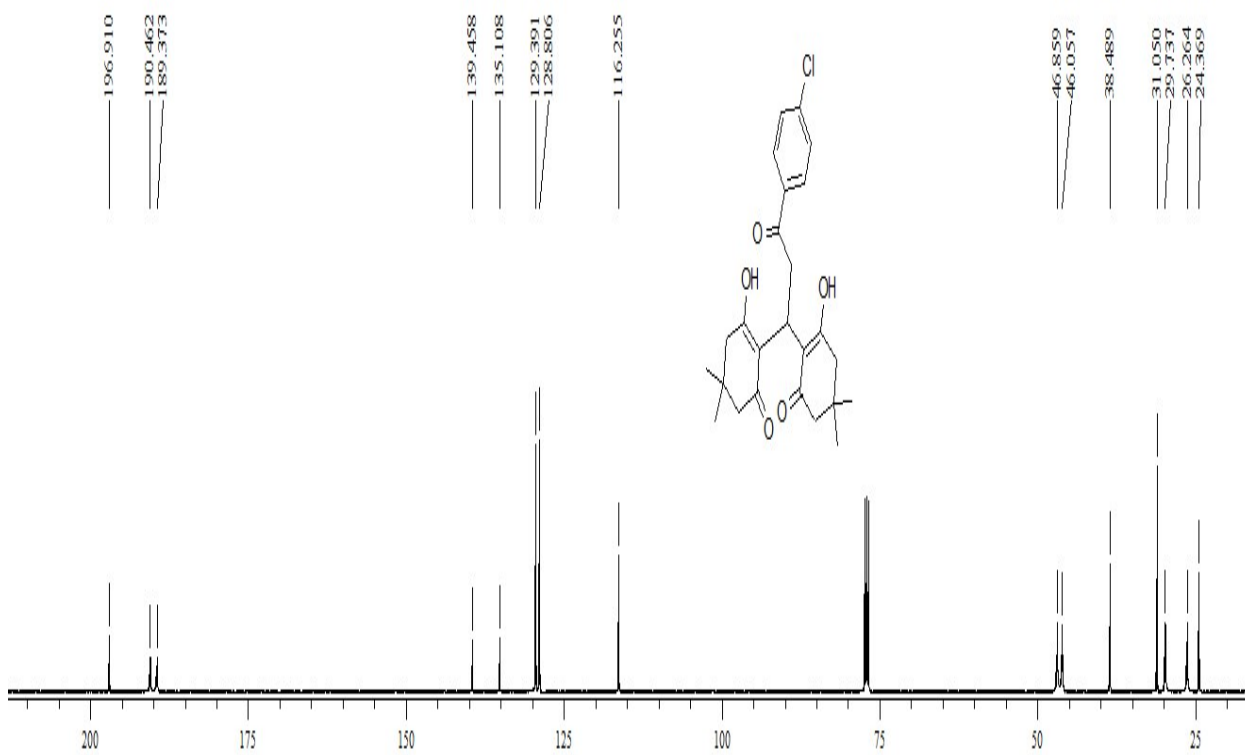


$^{13}\text{C NMR}$  (125 MHz) spectrum of **3a** in  $\text{CDCl}_3$ .

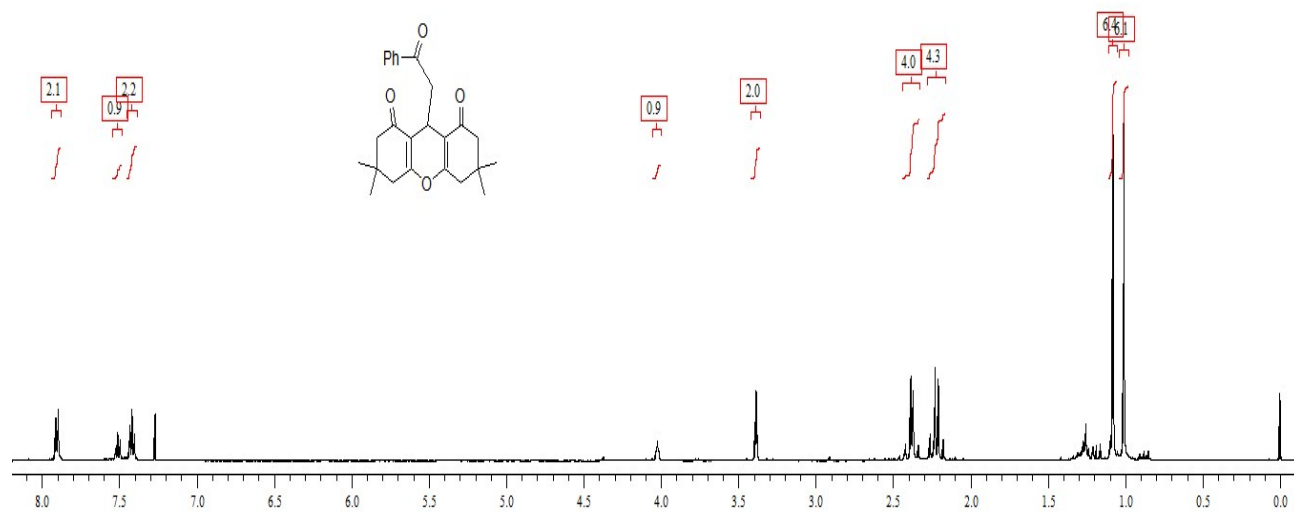




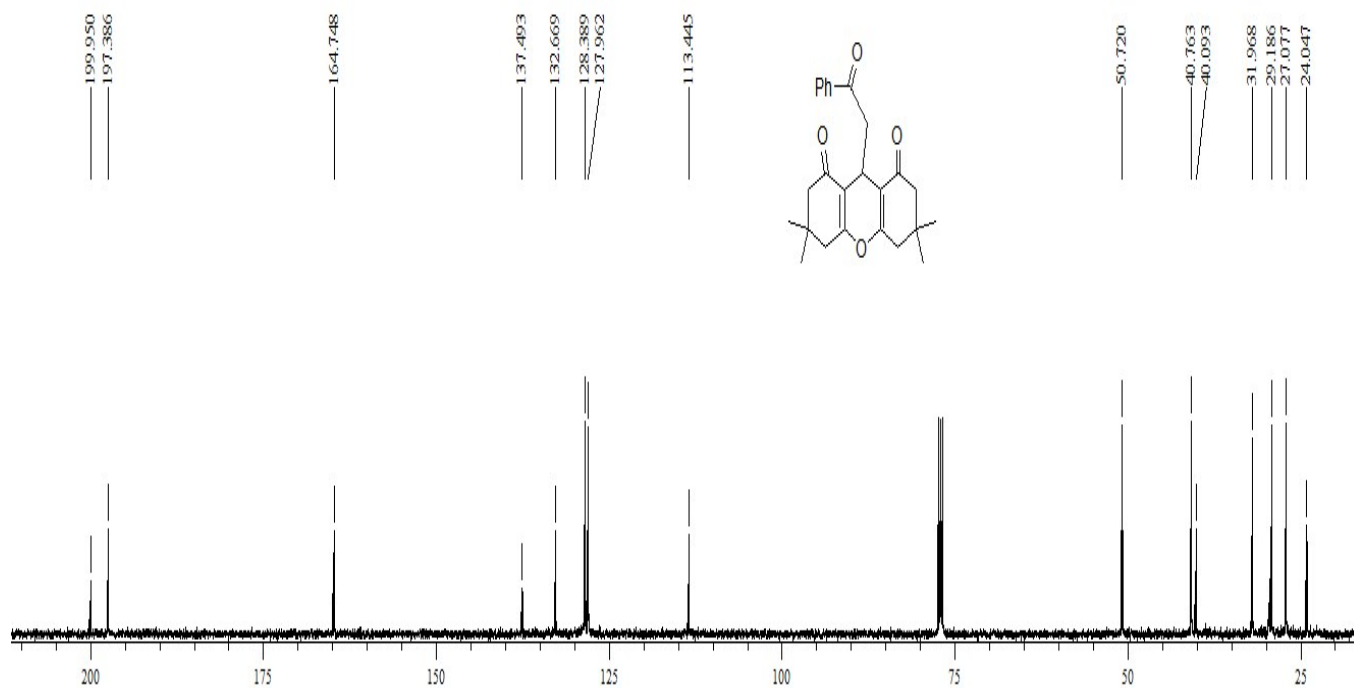
$^1\text{H}$  NMR (300 MHz) spectrum of **3b** in  $\text{CDCl}_3$ .



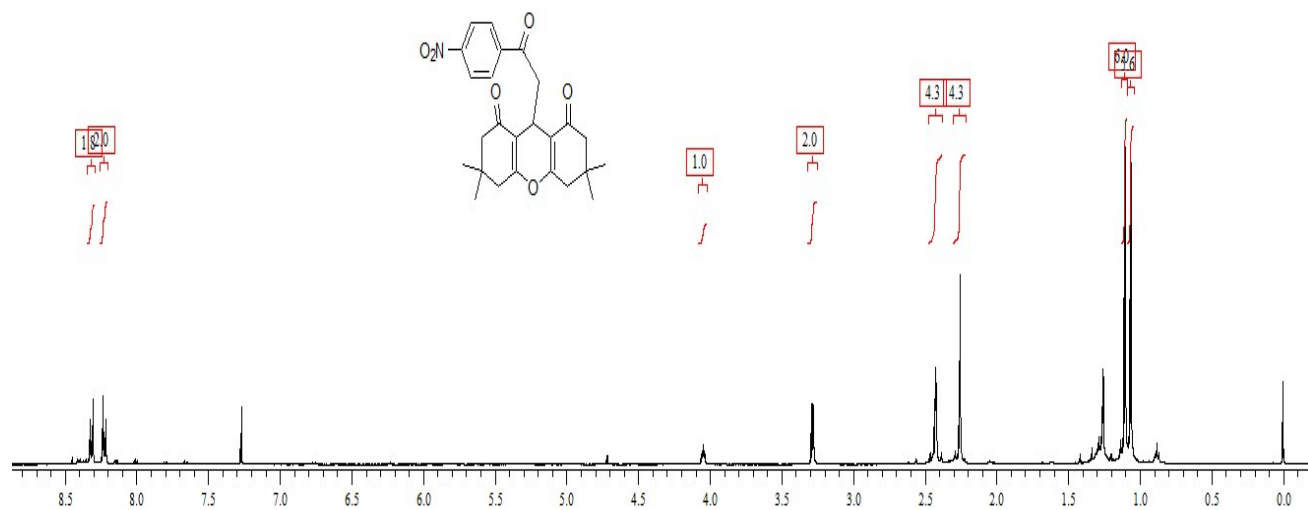
$^{13}\text{C}$  NMR (125 MHz) spectrum of **3b** in  $\text{CDCl}_3$ .



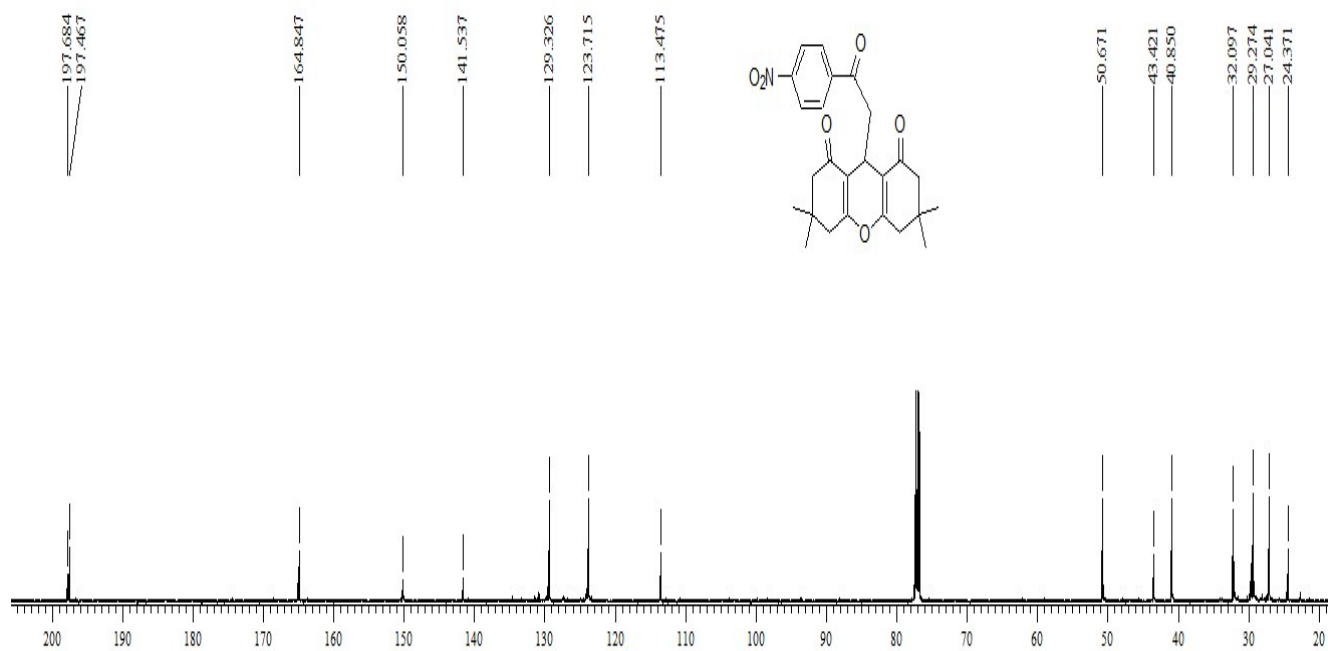
$^1\text{H}$  NMR (500 MHz) spectrum of **5a** in  $\text{CDCl}_3$ .



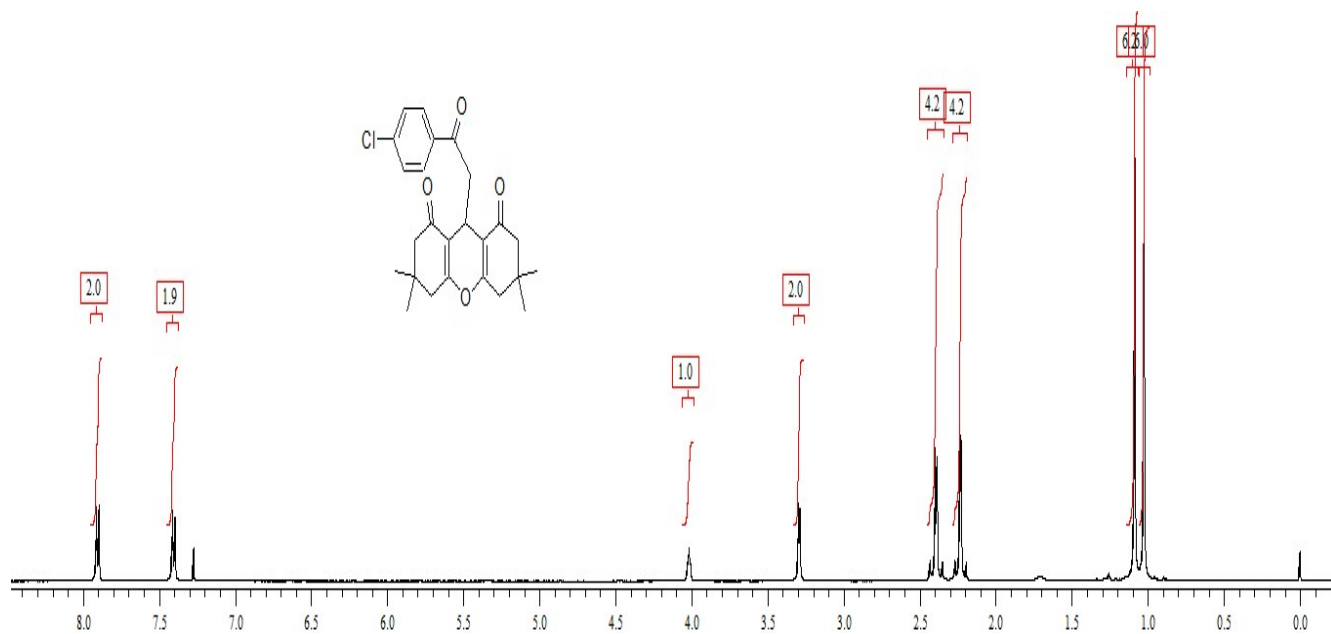
$^{13}\text{C}$  NMR (125 MHz) spectrum of **5a** in  $\text{CDCl}_3$ .



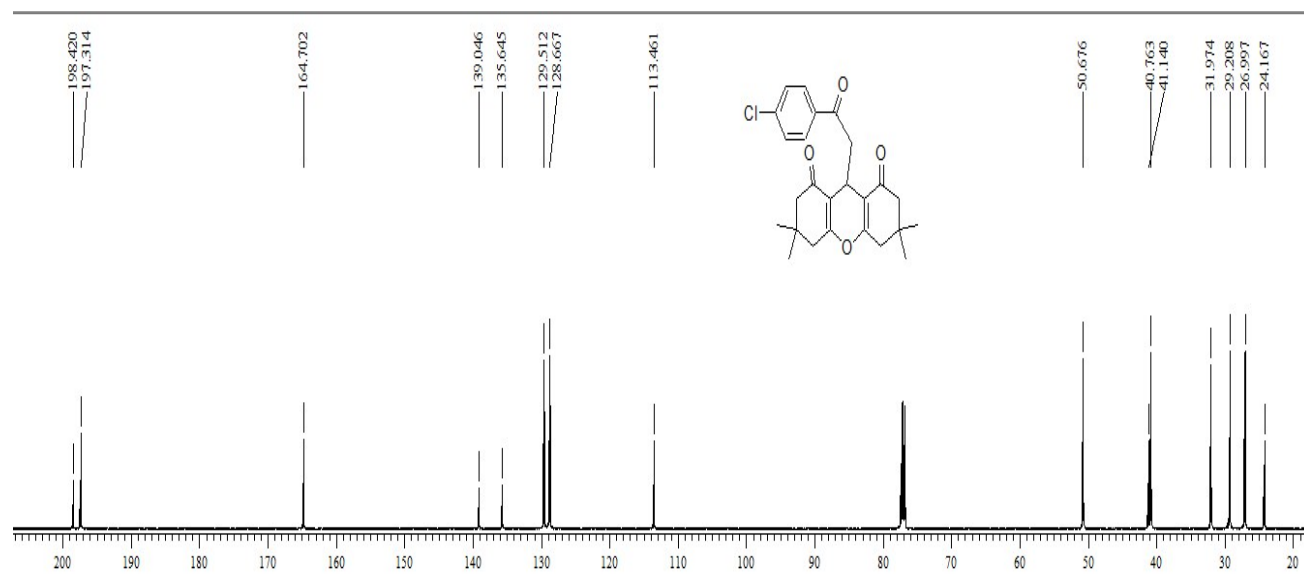
<sup>1</sup>H NMR (500 MHz) spectrum of **5b** in CDCl<sub>3</sub>.



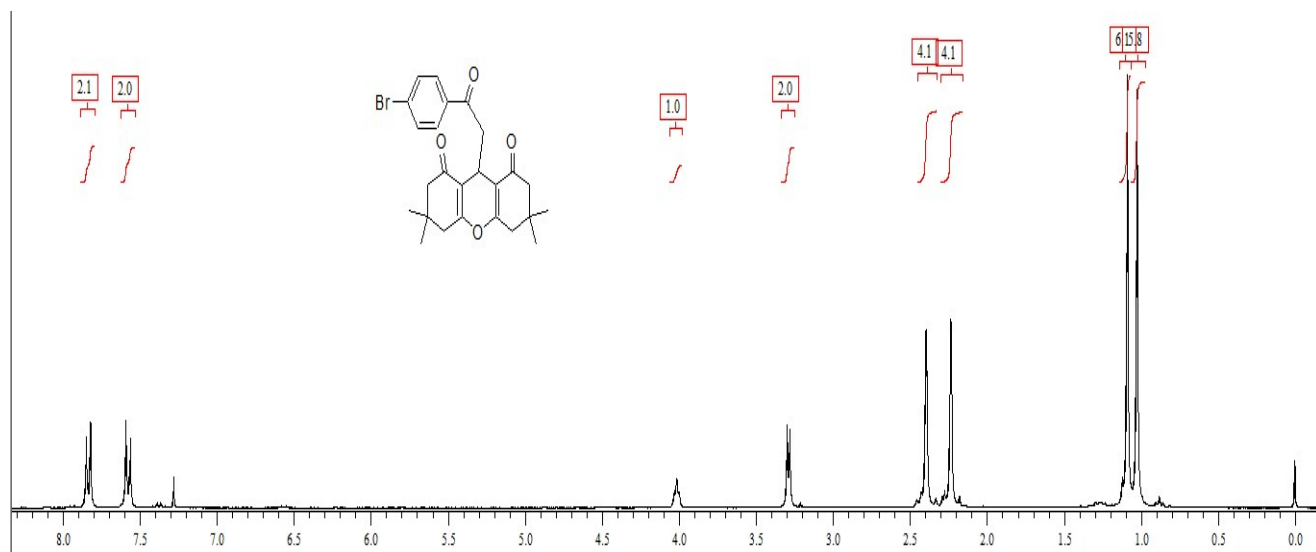
<sup>13</sup>C NMR (125 MHz) spectrum of **5b** in CDCl<sub>3</sub>.



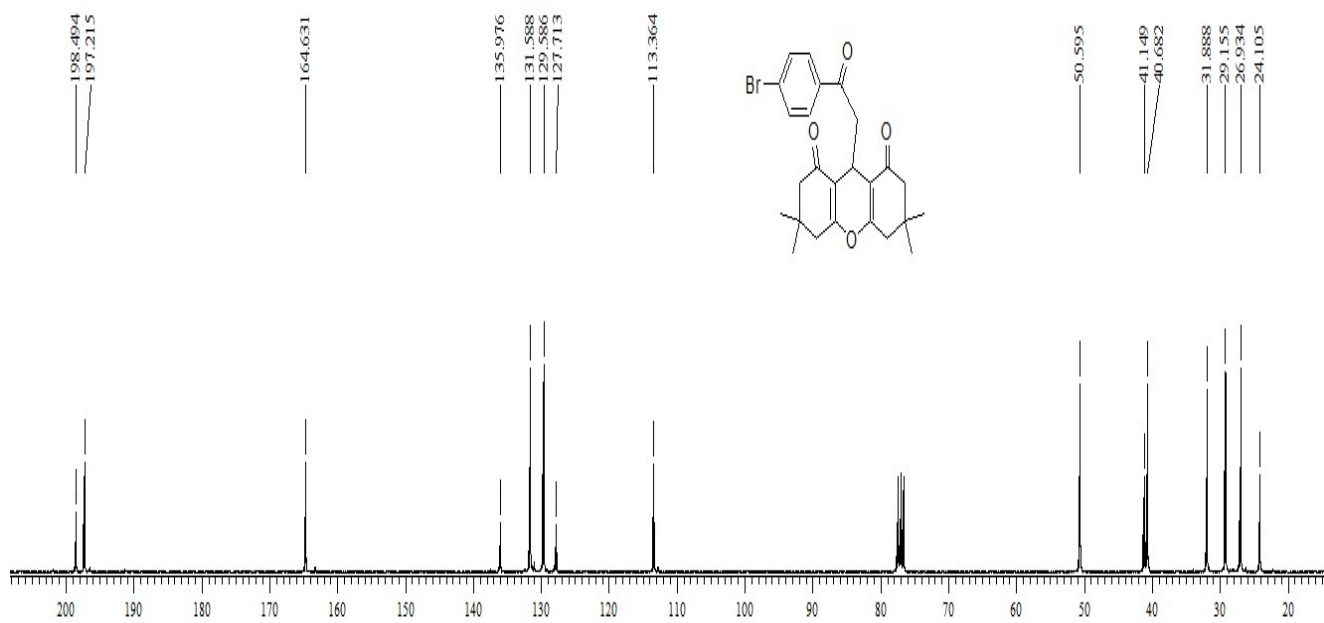
<sup>1</sup>H NMR (500 MHz) spectrum of **5c** in CDCl<sub>3</sub>.



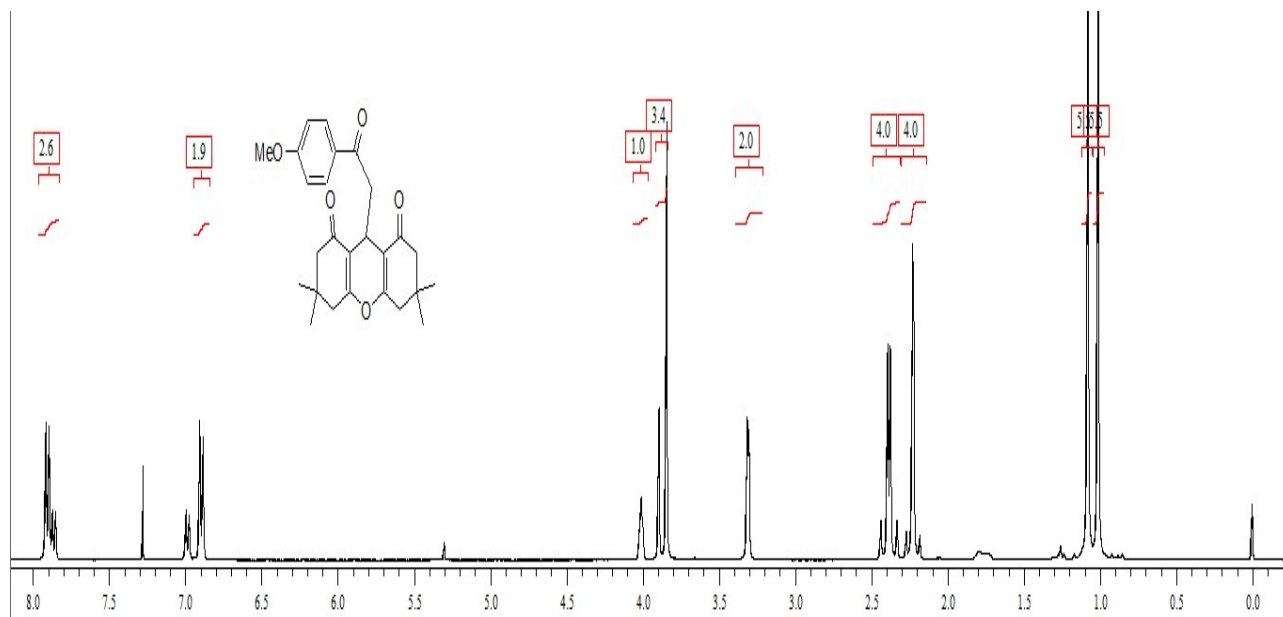
<sup>13</sup>C NMR (125 MHz) spectrum of **5c** in CDCl<sub>3</sub>.



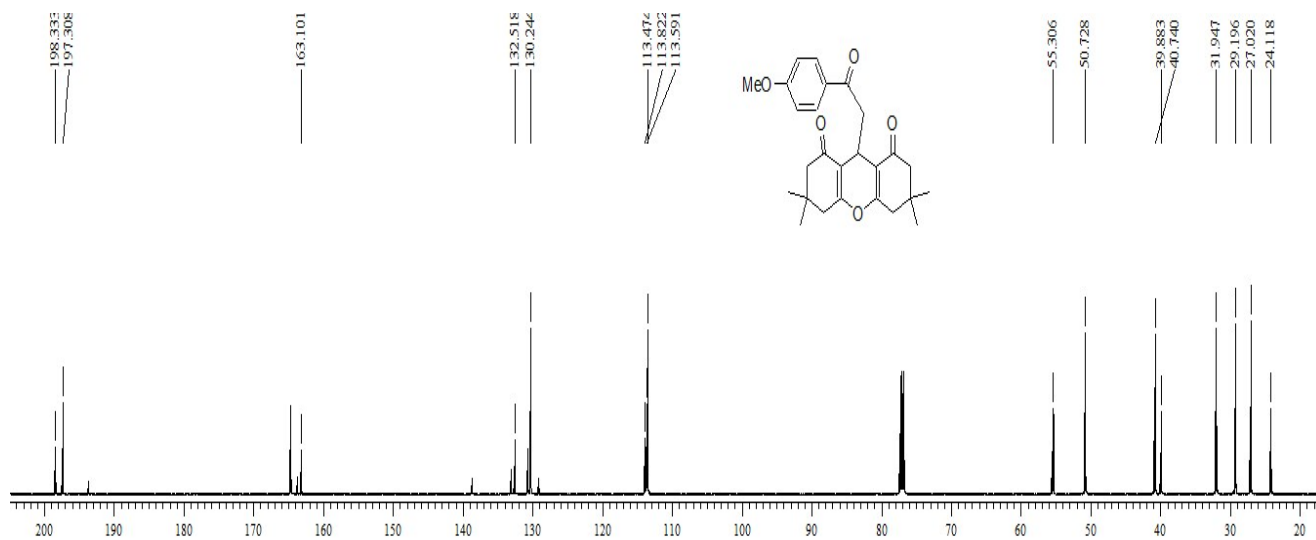
<sup>1</sup>H NMR (300 MHz) spectrum of **5d** in CDCl<sub>3</sub>.



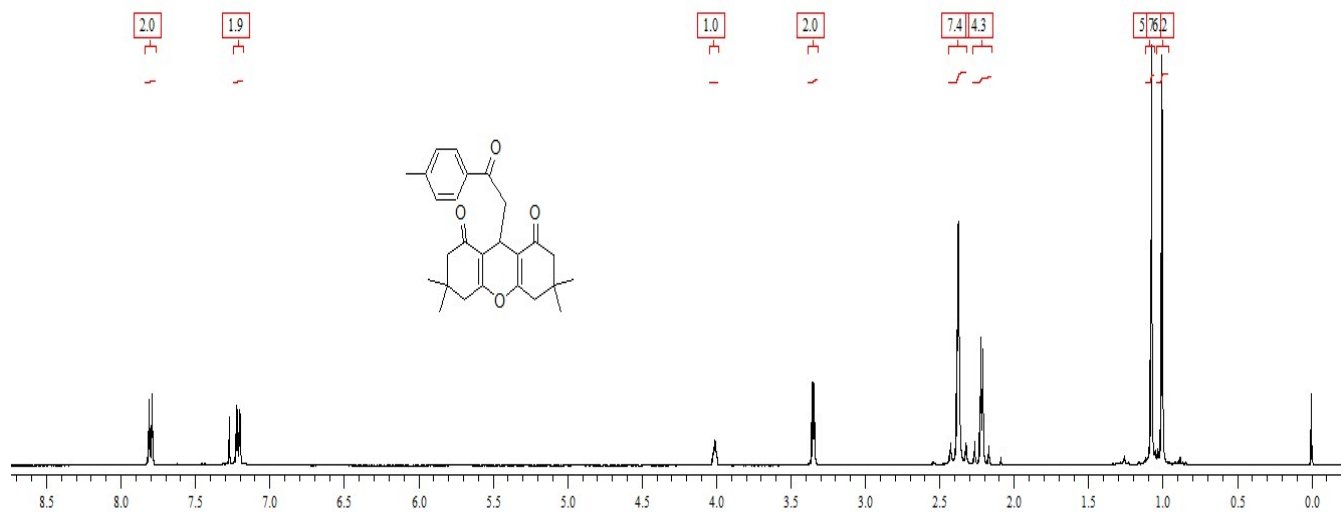
<sup>13</sup>C NMR (75 MHz) spectrum of **5d** in CDCl<sub>3</sub>.



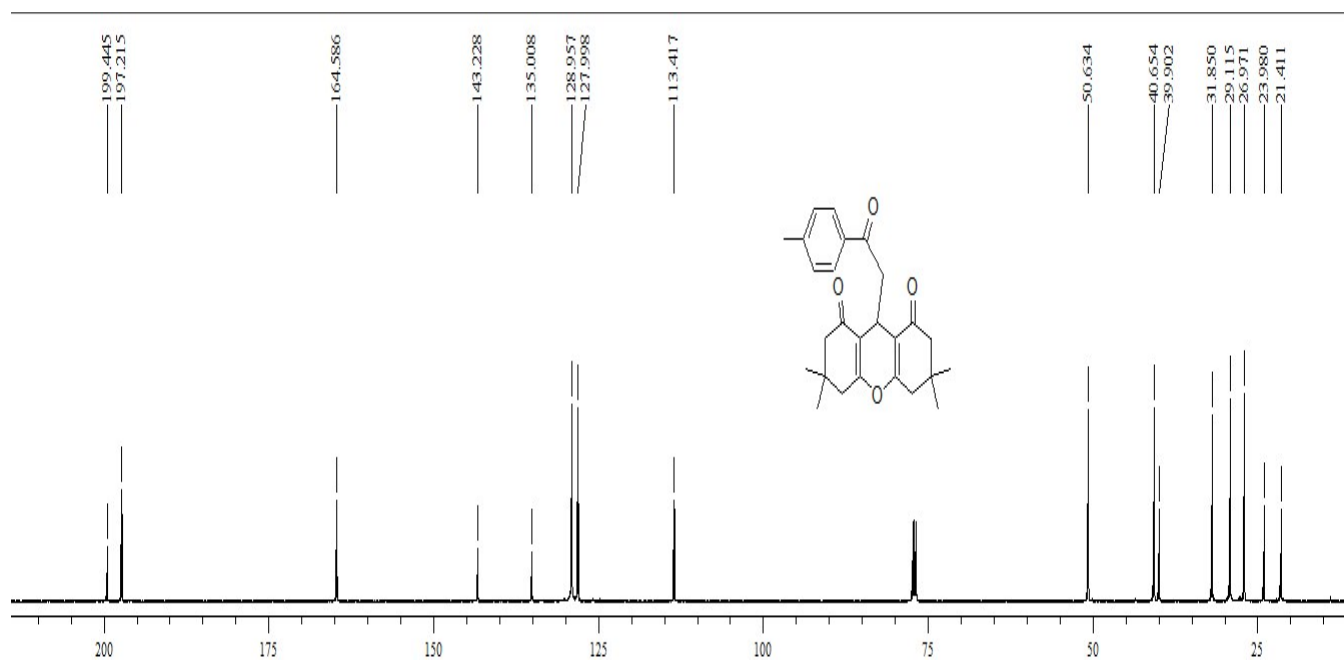
<sup>1</sup>H NMR (400 MHz) spectrum of 5e in CDCl<sub>3</sub>.



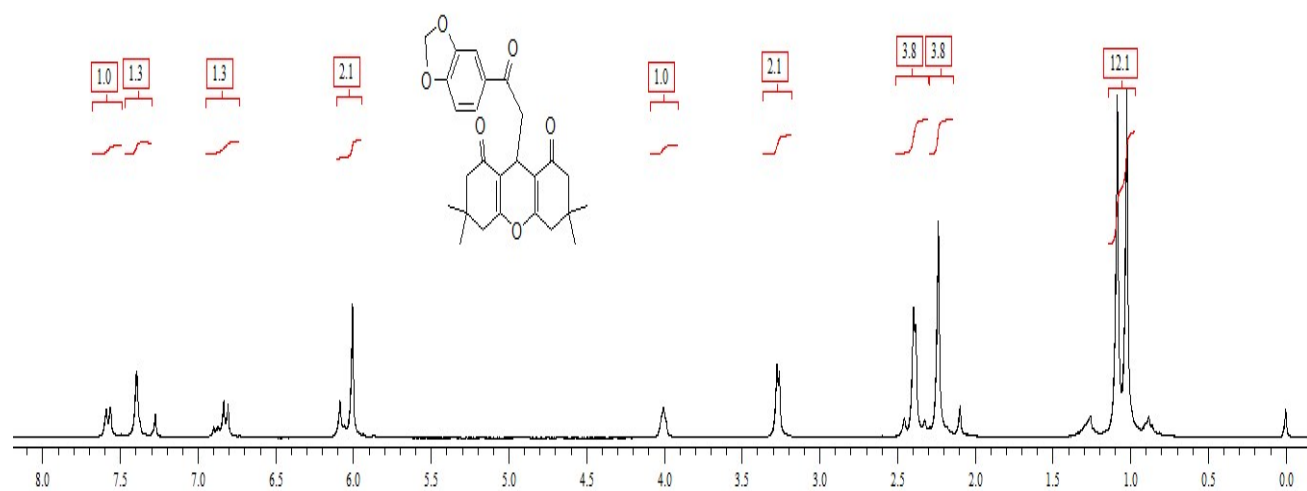
<sup>13</sup>C NMR (125 MHz) spectrum of 5e in CDCl<sub>3</sub>.



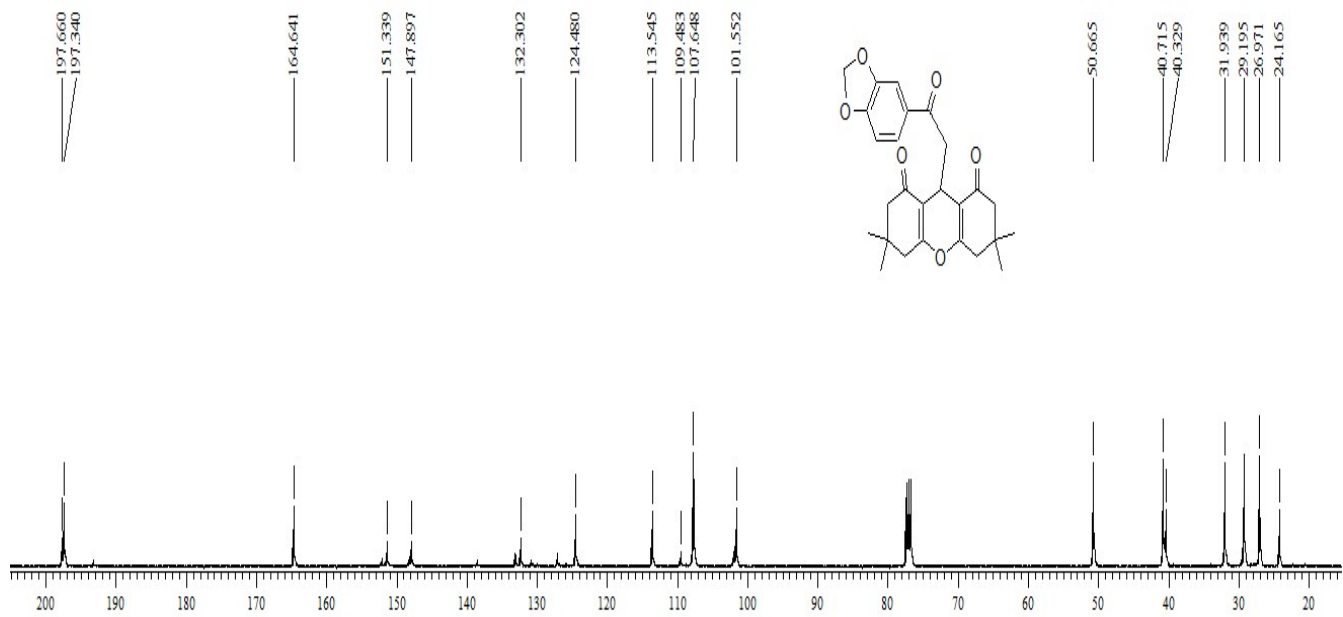
<sup>1</sup>H NMR (400 MHz) spectrum of **5f** in CDCl<sub>3</sub>.



<sup>13</sup>C NMR (125 MHz) spectrum of **5f** in CDCl<sub>3</sub>.

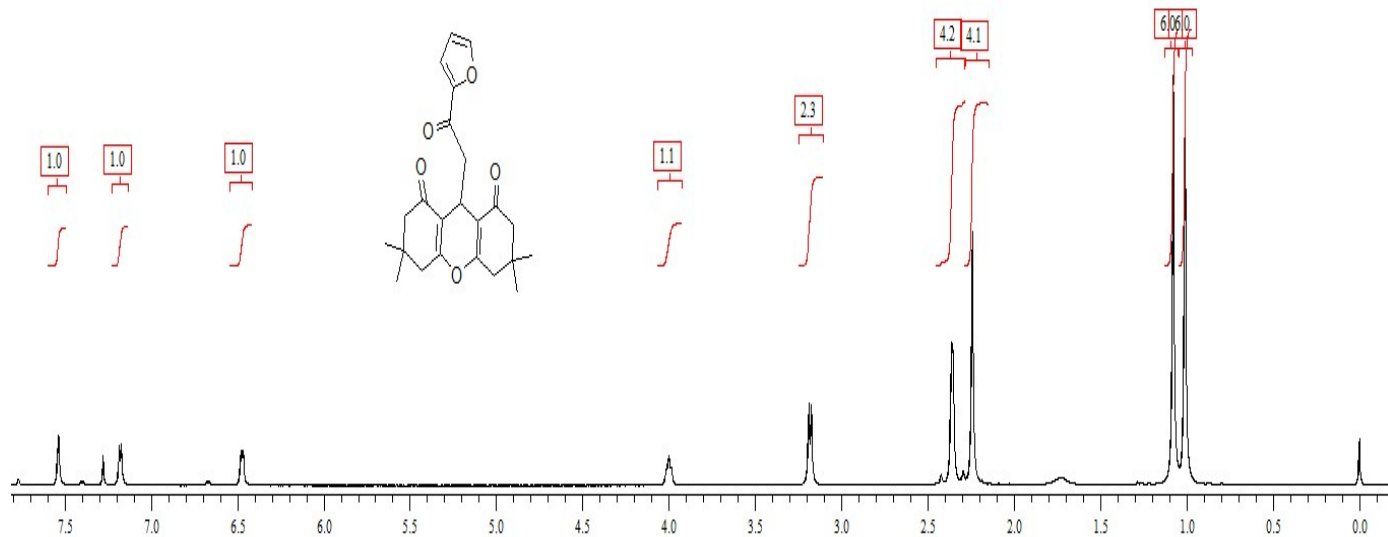


<sup>1</sup>H NMR (300 MHz) spectrum of **5g** in CDCl<sub>3</sub>.

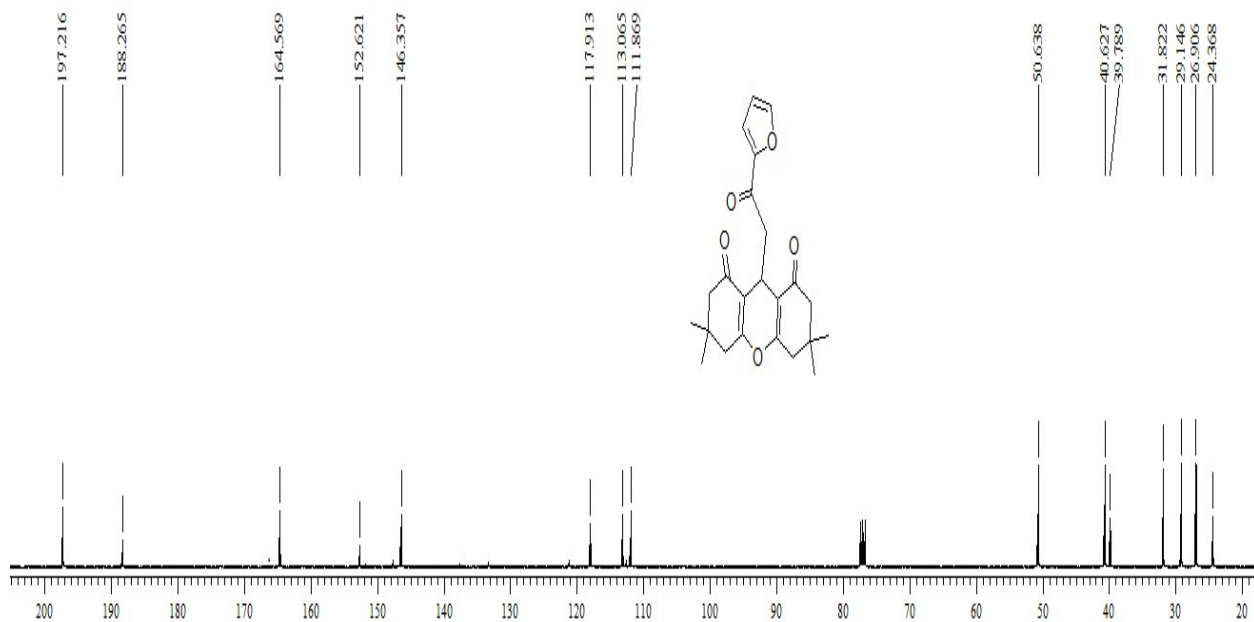


<sup>13</sup>C NMR (100 MHz) spectrum of **5g** in CDCl<sub>3</sub>.

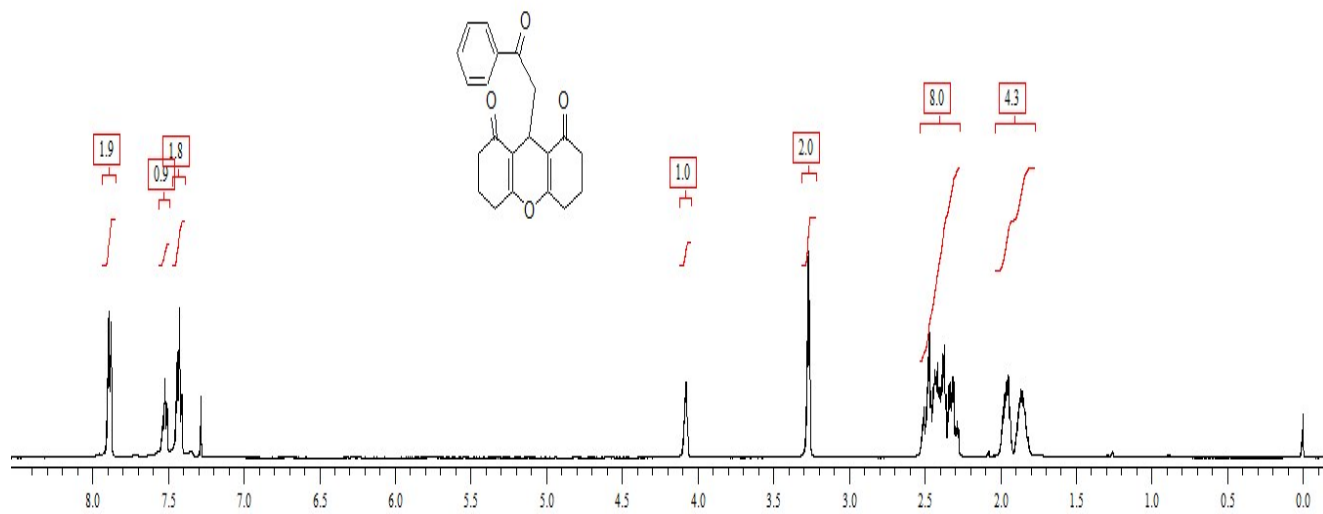




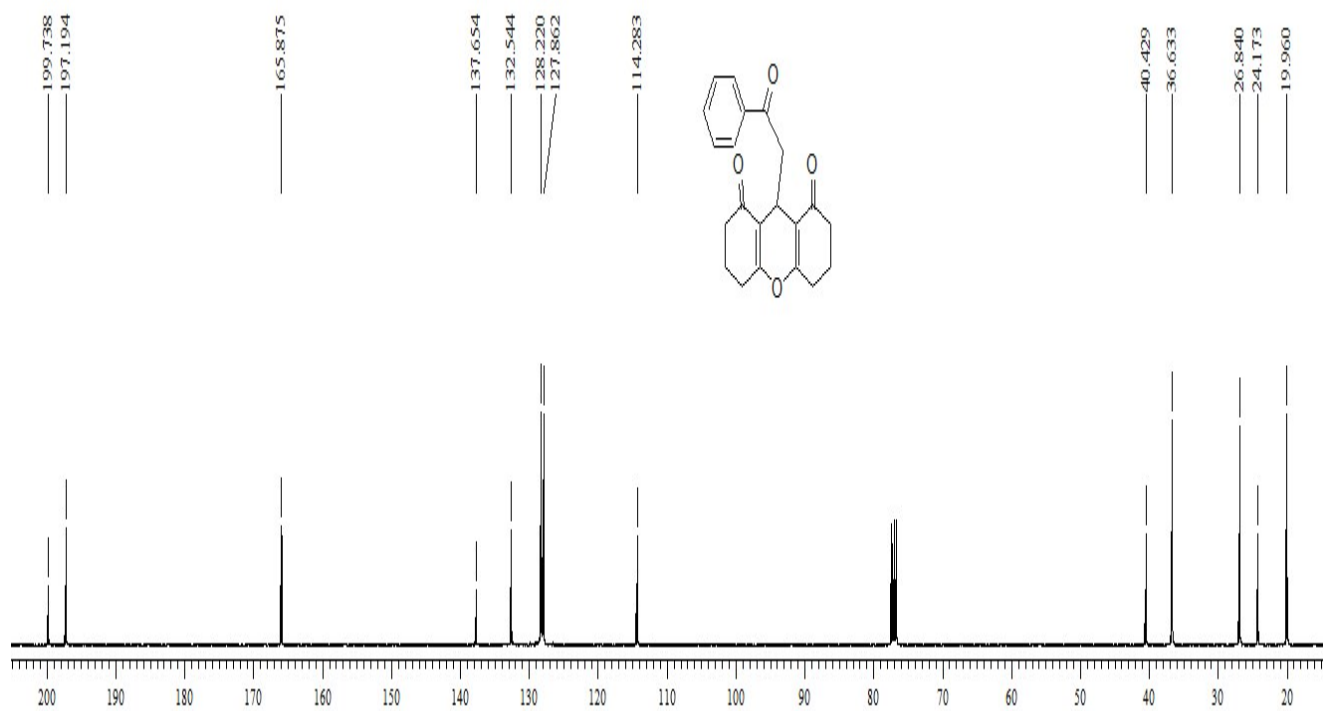
<sup>1</sup>H NMR (300 MHz) spectrum of **5h** in CDCl<sub>3</sub>.



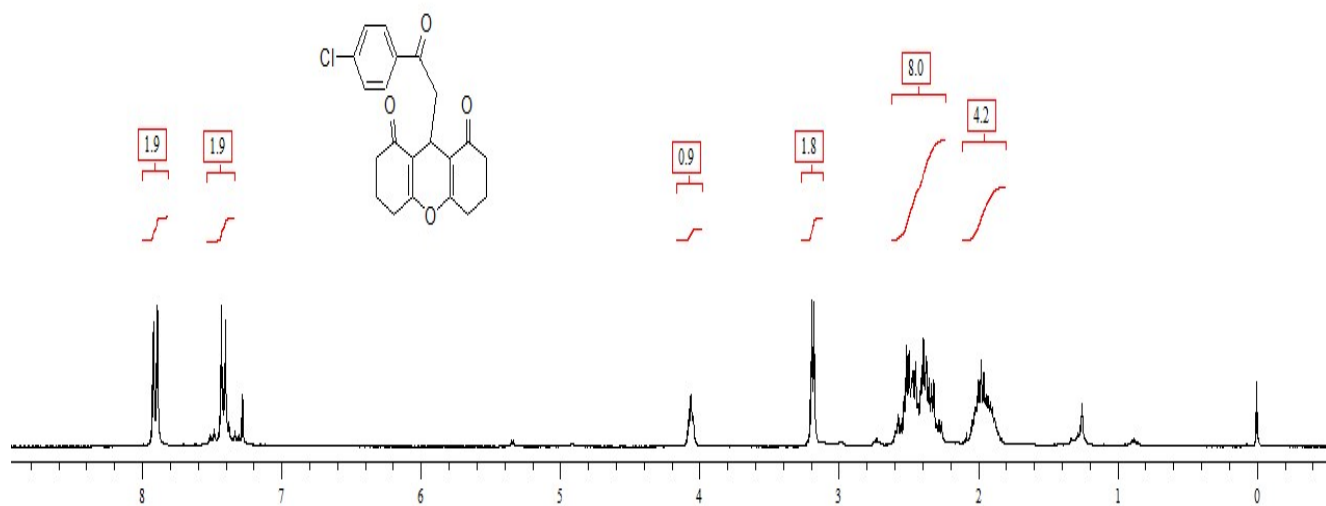
<sup>13</sup>C NMR (100 MHz) spectrum of **5h** in CDCl<sub>3</sub>.



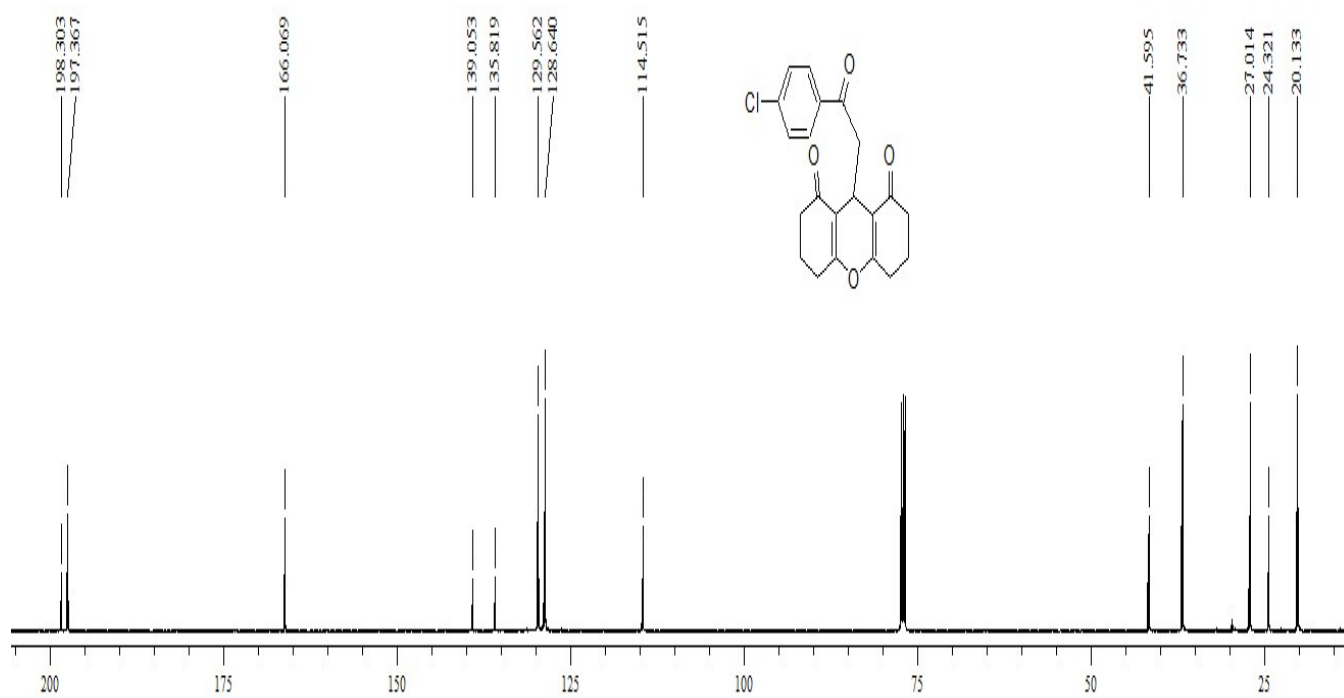
<sup>1</sup>H NMR (500 MHz) spectrum of **5i** in CDCl<sub>3</sub>.



<sup>13</sup>C NMR (100 MHz) spectrum of **5i** in CDCl<sub>3</sub>.



<sup>1</sup>H NMR (300 MHz) spectrum of **5j** in CDCl<sub>3</sub>.



<sup>13</sup>C NMR (125 MHz) spectrum of **5j** in CDCl<sub>3</sub>.