

## Supporting information

### High-yield, fast, and green synthesis of acridine derivatives using Co/C catalyst from rice husks under microwave-assisted method

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## Section S1: Chemical and equipment

### 2.1. Chemical

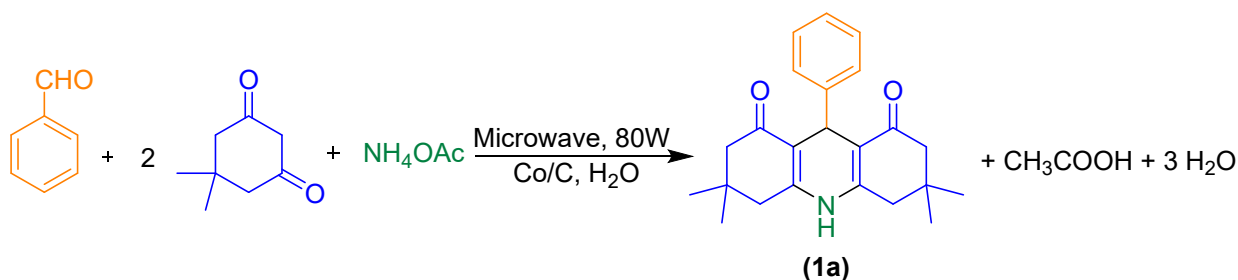
Dimedone (99.5%) was purchased from India. Vanillin (99%) was purchased from Sigma-Aldrich. 1,3-Cyclohexanedione (97%) was purchased from Fisher. 2-Chlorobenzaldehyde (99%), 4-chlorobenzaldehyde (98.5%), 4-hydroxybenzaldehyde (99%), 2-fluorobenzaldehyde (97%), 4-bromobenzaldehyde (99%) were purchased from Acros. Benzaldehyde (99%), 4-methylbenzaldehyde (97%), 4-methoxybenzaldehyde (98%), ammonium acetate (98%) were purchased from Merch. 4-Fluorobenzaldehyde (98.49%), aniline (99.5%), ethyl acetate (for analysis) were purchased from China. Ethanol (for analysis) was purchased from Viet Nam. Silica gel-coated aluminium plates (F-254) were used for thin-layer chromatography (TLC). Column chromatography was carried out with silica gel (230–400 mesh, Merck).

### 2.2. Techniques for analysis

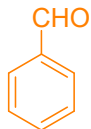
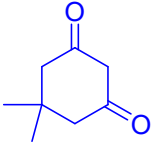
With either TMS or solvent peaks serving as the internal standard,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  were recorded using a Bruker Avance 500 MHz instrument. Fourier-transform infrared (FT-IR) spectra were acquired using a Bruker E400 FT-IR spectrometer. Thermogravimetric analysis (TGA) was carried out using a Q-500 thermal gravimetric analyzer with airflow over a temperature gradient of  $5\text{ }^\circ\text{C min}^{-1}$ . Powder X-ray diffraction (PXRD) data for refinement were collected on a Bruker D8 Advance utilizing Ni-filtered Cu K ( $\lambda = 1.54059$ ) radiation. The morphology of the material was viewed with an XZS-107T digital microscope in conjunction with an NHV-CAM camera using the software eScope and a Hitachi S-4800 scanning electron microscope (SEM). The Quantachrome NOVA 3200e system operates at 77 K, and was used to quantify the  $\text{N}_2$  isotherm. Energy-dispersive X-ray spectroscopy (EDX) was performed utilizing an EMAX energy EX-400 EDX equipment. High-resolution mass data were recorded on a Bruker micrOTOF-QII MS in positive electrospray ionization (80 eV).

## Section S2: Assessment of green metrics

The green chemistry matrix has been computed for the synthesis of 1a using the specified parameters:<sup>1-4</sup>



**Scheme S1.** Model reaction for green matrix calculation

Compound name			NH <sub>4</sub> OAc	(1a)	CH <sub>3</sub> COOH	H <sub>2</sub> O
M.W. (g/mol)	106.0419	140.0837	77.0477	349.2042	60.0211	18.0106
In present work M.W. (mg)	106.0419	280.1674	77.0477	349.2042	60.0211	54.0318

The total mass of reactants = 463.2570

Obtained product = 0.3038 g = 303.8 mg

Solvent: H<sub>2</sub>O (2.0 mL) = 1.99 mg

### 2.1. Environmental factor(E-factor)

$$\text{E-Factor} = \frac{\text{Mass of waste}}{\text{Mass of product}}$$

In which, the mass of waste is included acetic acid and H<sub>2</sub>O

$$\text{E-Factor} = \frac{60.0211 + 54.0318}{303.8} = 0.38$$

(Ideal value of E-factor is considered zero)

### 2.2. Atom-economy (AE)

The optimal value of the AE factor is 100%, indicating that all initial material is fully transformed into the final output.

$$\text{AE} = \frac{\text{MW of product}}{\sum \text{MW of stoichiometric reactants}} \times 100$$

$$\text{AE} = \frac{349.2042}{106.0419 + 280.1674 + 77.0477} \times 100 = 75.38\%$$

### 2.3. Process mass intensity (PMI)

$$\text{PMI} = \frac{\sum (\text{Mass of stoichiometric reactants} + \text{solvent})}{\text{Mass of product}}$$

$$\text{PMI} = \frac{463.2570 + 1.99}{303.8} = 1.53$$

Ideal value of PMI = E-Factor + 1 = 0.38 + 1 = 1.38

The variation in value between both findings is rather small.

#### 2.4. Reaction mass efficiency (RME)

$$\text{RME} = \frac{\text{Mass of product}}{\sum (\text{mass of stoichiometric reactants})} \times 100$$

$$\text{RME} = \frac{303.8}{463.2570} \times 100 = 65.58\%$$

#### 2.5. Eco-score (E-score)

Ideal reactions Eco-score value is 100.

Eco-scale from 0 to 100 using the following scores: > 75, excellent; > 50, acceptable; and < 50, inadequate.

E-score has been calculated for the reaction based on the following 6 parameters below.

Entry	Parameter	Values	Penalty points
1	Yield	(100-87)/2	6.5
2	Price of the reaction component	Inexpensive	0.0
3	Safety (Reactant)	T(Toxic) = 4+5+5 = 14	14.0
4	Technical setup	Common setup	0.0
5	Temperature /time	MW (80W)/ 15 min	0.0
6	Workup and purification	Crystallization	1.0
Total penalty points			21.5

Based on the hazard warning symbols

Eco-Score = 100 – The sum of individual penalties = 100 – 21.5 = 78.5 (>75, excellent synthesis)

As per the above results, it was concluded that the reaction has a low Environment-factor (E-factor = 0.38), high atom economy (AE = 75.38%), high process mass intensity (PMI

= 1.38), and medium reaction mass efficiency (RME = 65.58%), with high eco-score (78.5%). These values clearly indicated the eco-friendliness of the present synthesis.

### Section S3. NMR spectrum

#### *3,3,6,6-Tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (1a)*<sup>5,6</sup>

Benzaldehyde (106 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The white powder was obtained with 87%.  $R_f = 0.51$  (*n*-hexane:EA = 1:4); Mp. = 273-274 °C;<sup>6</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.86$  (s, 6H), 1.01 (s, 6H), 1.99 (d,  $J = 15.5$  Hz, 2H), 2.17 (d,  $J = 16.0$  Hz, 2H), 2.33 (d,  $J = 17.0$  Hz, 2H), 2.45 (d,  $J = 17.0$  Hz, 2H), 4.81 (s, 1H), 7.01-7.05 (m, 1H), 7.13-7.16 (m, 4H), 9.72 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 26.9, 29.6, 32.6, 33.3, 50.7, 111.9, 125.9, 128.0, 128.1, 147.6, 149.8, 194.8$  ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3274.8, 3070.7, 2941.6, 1625.0, 1474.8, 1371.6, 1212.0, 1148.6, 989.1, 815.4, 681.6, 571.3.

#### *9-(2-Fluorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (2a)*<sup>7</sup>

2-Fluorobenzaldehyde (124 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The white powder was obtained with 84%.  $R_f = 0.51$  (*n*-hexane:EA = 1:4); Mp. = 300-302 °C;<sup>7</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.84$  (s, 6H), 1.00 (s, 6H), 1.93 (d,  $J = 16.5$  Hz, 2H), 2.15 (d,  $J = 16.0$  Hz, 2H), 2.28 (d,  $J = 17.0$  Hz, 2H), 2.45 (d,  $J = 17.0$  Hz, 2H), 4.95 (s, 1H), 6.91-6.94 (m, 1H), 6.97-7.00 (m, 1H), 7.04-7.08 (m, 1H), 7.18-7.21 (m, 1H), 9.31 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 26.6, 29.2, 29.6, 32.5, 50.7, 110.9, 115.3$  (d,  $J = 22.5$  Hz), 123.8 (d,  $J = 2.5$  Hz), 127.8 (d,  $J = 8.8$  Hz), 131.5 (d,  $J = 5.0$  Hz), 134.2 (d,  $J = 13.8$  Hz), 150.0, 160.2 (d,  $J = 246.3$  Hz), 194.6 ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3277.2, 3202.1, 3068.3, 2948.6, 1629.7, 1479.5, 1369.2, 1223.7, 1136.9, 1010.2, 878.8, 749.7, 569.0.

#### *9-(4-Chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (3a)*<sup>5,7</sup>

4-Chlorobenzaldehyde (141 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The yellow powder was obtained with 85%.  $R_f = 0.49$  (*n*-hexane:EA = 1:4); Mp. = 305-306 °C;<sup>7</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.86$  (s, 6H), 1.00 (s, 6H), 1.99 (d,  $J = 16.0$  Hz, 2H), 2.18 (d,  $J = 16.0$  Hz, 2H), 2.33 (d,  $J = 17.0$  Hz, 2H), 2.45 (d,  $J = 17.0$  Hz, 2H), 4.78 (s, 1H), 7.15 (d,  $J = 8.5$  Hz, 2H), 7.22 (d,  $J = 8.5$  Hz, 2H), 9.33 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 27.0, 29.5, 32.6, 33.1, 50.6, 111.5, 128.0, 129.9, 130.4, 146.6, 150.0, 194.8$  ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3174.1, 3055.4, 2950.5, 1631.7, 1492.5, 1364.7, 1218.7, 1143.4, 1008.8, 753.3.

#### *9-(4-Bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione*

**(4a)**<sup>8,9</sup>

4-Bromobenzaldehyde (185 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The yellow powder was obtained with 85%.  $R_f = 0.49$  (*n*-hexane:EA = 1:4); Mp. = 302-303 °C;<sup>9</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.86$  (s, 6H), 1.01 (s, 6H), 1.99 (d,  $J = 16.0$  Hz, 2H), 2.17 (d,  $J = 16.0$  Hz, 2H), 2.33 (d,  $J = 17.0$  Hz, 2H), 2.45 (d,  $J = 17.0$  Hz, 2H), 4.77 (s, 1H), 7.10 (d,  $J = 8.5$  Hz, 2H), 7.35 (d,  $J = 8.5$  Hz, 2H), 9.32 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 27.0, 29.5, 32.6, 33.3, 50.6, 111.5, 118.9, 130.4, 130.9, 147.0, 150.0, 194.8$  ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3269.9, 3174.1, 3055.4, 2950.5, 2882.0, 1647.7, 1606.6, 1492.5, 1367.0, 1218.7, 1145.7, 1011.1, 887.9, 835.4, 753.3, 611.8, 563.9, 520.5.

*9-(4-Hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione*  
**(5a)**<sup>8,9</sup>

4-Hydroxybenzaldehyde (122 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The light-yellow powder was obtained with 76%.  $R_f = 0.32$  (*n*-hexane:EA = 1:4); Mp. = 295-297 °C;<sup>9</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.87$  (s, 6H), 1.00 (s, 6H), 1.98 (d,  $J = 16.0$  Hz, 2H), 2.16 (d,  $J = 16.0$  Hz, 2H), 2.30 (d,  $J = 17.0$  Hz, 2H), 2.42 (d,  $J = 17.0$  Hz, 2H), 4.70 (s, 1H), 6.52 (d,  $J = 8.5$  Hz, 2H), 6.92 (d,  $J = 8.5$  Hz, 2H), 8.98 (s, 1H), 9.19 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 26.9, 29.6, 32.1, 32.6, 50.8, 112.3, 114.8, 128.9, 138.4, 149.4, 155.5, 194.8$  ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3276.7, 3196.9, 2955.0, 2813.6, 2681.2, 2603.7, 2503.3, 1613.4, 1469.7, 1371.6, 1223.3, 1138.9, 1004.2, 938.1, 885.6, 837.7, 725.9, 680.3, 657.4, 614.1, 561.6, 534.4.

*9-(4-Hydroxy-3-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione*  
**(6a)**

4-Hydroxy-3-methoxybenzaldehyde (152 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The white powder was obtained with 75%.  $R_f = 0.26$  (*n*-hexane:EA = 1:4); Mp. = 320-322 °C; <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.88$  (s, 6H), 1.01 (s, 6H), 2.00 (d,  $J = 16.0$  Hz, 2H), 2.17 (d,  $J = 16.0$  Hz, 2H), 2.31 (d,  $J = 17.5$  Hz, 2H), 2.43 (d,  $J = 17.0$  Hz, 2H), 3.65 (s, 3H), 4.72 (s, 1H), 6.50-6.55 (m, 2H), 6.70 (d,  $J = 1.5$  Hz, 1H), 8.56 (s, 1H), 9.21 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 26.9, 29.6, 32.4, 32.5, 50.8, 56.0, 112.2, 112.7, 115.2, 120.3, 139.0, 144.8, 147.2, 149.4, 194.9$  ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3265.3, 3167.2, 3046.3, 2948.2, 1613.4, 1497.1, 1362.5, 1216.4, 1148.0, 1022.5, 732.7, 689.4, 563.9.

*9-(4-Fluorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione*

**(7a)**<sup>8,9</sup>

4-Fluorobenzaldehyde (124 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The light green powder was obtained with 80%,  $R_f = 0.14$  (*n*-hexane:EA = 5:5); Mp. = 253-255 °C;<sup>9</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.86$  (s, 6H), 1.01 (s, 6H), 1.99 (d,  $J = 16.0$  Hz, 2H), 2.17 (d,  $J = 16.0$  Hz, 2H), 2.31-2.34 (m, 2H), 2.44 (d;  $J = 17.0$  Hz, 2H), 4.80 (s, 1H), 6.97 (t,  $J = 9.0$  Hz, 2H), 7.15 (m, 2H), 9.30 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 26.96, 29.51, 32.60, 32.75, 50.68, 111.80, 114.56, 114.73, 129.7$  (d,  $J = 7.5$  Hz), 143.8 (d,  $J = 2.5$  Hz), 149.8, 159.8, 161.7, 194.9 ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3530.0, 3347.5, 3269.9, 3162.7, 3046.3, 2955.0, 1613.4, 1487.9, 1367.0, 1218.7, 1148.0, 849.1, 684.8, 561.6.

*9-(4-Methylphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione*

**(8a)**<sup>8</sup>

4-Methylbenzaldehyde (120 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The light green powder was obtained with 29%<sup>c</sup>  $R_f = 0.15$  (*n*-hexane:EA = 5:5); Mp. = 322-323 °C;<sup>8</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.86$  (s, 6H), 1.00 (s, 6H), 1.95-1.98 (m, 2H), 2.14 (s, 2H), 2.18 (s, 3H), 2.28-2.34 (m, 2H), 2.43 (d,  $J = 17.0$  Hz, 2H), 4.75 (s, 1H), 6.94 (d,  $J = 8.0$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 2H), 8.09 (s, 1H), 9.23 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 21.0, 26.9, 29.6, 32.6, 32.9, 50.7, 112.1, 128.0, 128.6, 134.7, 144.8, 149.6, 194.8$  ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3269.9, 3185.5, 3062.3, 2943.6, 1720.7, 1608.9, 1487.9, 1376.1, 1230.1, 1132.0, 1020.2.

*9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione*  
**(9a)**<sup>8,10</sup>

4-Methoxybenzaldehyde (136 mg), dimedone (280 mg), ammonium acetate (77 mg), Co/C (10 mg). The white powder was obtained with 40%,  $R_f = 0.13$  (*n*-hexane:EA = 5:5); Mp. = 282-283 °C;<sup>10</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.87$  (s, 6H), 1.00 (s, 6H),  $\delta = 1.98$  (d,  $J = 16.0$  Hz, 2H), 2.16 (d,  $J = 16.0$  Hz, 2H), 2.31 (d,  $J = 17.0$  Hz, 2H), 2.43 (d,  $J = 16.5$  Hz, 2H), 3.65 (s, 3H), 4.74 (s, 1H), 6.71 (d,  $J = 8.5$  Hz, 2H), 7.05 (d,  $J = 8.5$  Hz, 2H), 9.22 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 27.0, 29.6, 32.3, 32.6, 50.7, 55.3, 112.2, 113.3, 140.0, 149.5, 157.6, 194.9$  ppm.

*9-Phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione* **(10b)**<sup>9</sup>

Benzaldehyde (106 mg), 1,3-cyclohexanedione (224 mg), ammonium acetate (77 mg), Co/C (10 mg). The brown powder was obtained with 86%.  $R_f = 0.13$  (*n*-hexane:EA = 1:4); Mp. = 298-299 °C;<sup>9</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 1.74$ -1.83 (m, 4H), 1.88-1.94 (m, 4H), 2.20



(t,  $J = 5.0$  Hz, 4H), 4.91 (s, 1H), 7.02-7.05 (m, 1H), 7.13-7.15 (m, 4H), 9.42 (s, 1H) ppm.  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 21.3, 26.8, 32.6, 37.2, 112.9, 125.9, 127.9, 128.2, 147.8, 151.8, 195.3$  ppm. FT-IR (KBr, 4000-500  $\text{cm}^{-1}$ ): 3164.9, 3041.7, 2934.5, 1636.3, 1481.1, 1360.2, 1273.5, 1232.4, 1175.4, 1129.7, 696.2.

*9-(2-chlorophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (11b)*

2-Chlorobenzaldehyde (141 mg), 1,3-cyclohexanedione (224 mg), ammonium acetate (77 mg), Co/C (10 mg). The brown powder was obtained with 79%.  $R_f = 0.13$  (*n*-hexane:EA = 1:4); Mp. = 305-307 °C;  $^1\text{H}$ -NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 1.68$ -1.77 (m, 4H), 1.86-1.91 (m, 4H), 2.08-2.17 (m, 4H), 5.11 (s, 1H), 7.02-7.05 (m, 1H), 7.12-7.18 (m, 2H), 7.26-7.28 (m, 1H), 9.47 (s, 1H) ppm.  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 21.2, 26.8, 33.3, 37.3, 112.5, 126.9, 127.4, 129.4, 132.5, 132.9, 145.0, 151.9, 194.8$  ppm. FT-IR (KBr, 4000-500  $\text{cm}^{-1}$ ): 3279.0, 3190.0, 3060.0, 2943.6, 2879.7, 1711.5, 1643.1, 1606.6, 1483.4, 1360.2, 1282.6, 1230.1, 1177.6, 1132.0, 1036.2, 960.9, 906.1, 853.7, 769.2, 703.1, 616.4, 527.4.

*9-(2-Fluorophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (12b)*

2-Fluorobenzaldehyde (124 mg), 1,3-cyclohexanedione (224 mg), ammonium acetate (77 mg), Co/C (10 mg). The brown powder was obtained with 78%.  $R_f = 0.13$  (*n*-hexane:EA = 1:4); Mp. = 310-311 °C;  $^1\text{H}$ -NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 1.69$ -1.77 (m, 4H), 1.86-1.91 (m, 4H), 2.11-2.18 (m, 4H), 5.00 (s, 1H), 6.91 (t,  $J = 8.5$  Hz, 1H), 6.98 (t,  $J = 7.0$  Hz, 1H), 7.05-7.08 (m, 1H), 7.18 (t,  $J = 8.0$  Hz, 1H) 9.47 (s, 1H) ppm.  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 21.3, 26.8, 28.8, 37.2, 112.2, 115.2$  (d,  $J = 22.5$  Hz), 124.1 (d,  $J = 2.5$  Hz), 127.8 (d,  $J = 7.5$  Hz), 131.4 (d,  $J = 5.0$  Hz), 134.9 (d,  $J = 13.8$  Hz), 151.9, 160.1 (d,  $J = 245.0$  Hz), 194.9 ppm. FT-IR (KBr, 4000-500  $\text{cm}^{-1}$ ): 3415.9, 3267.6, 3171.8, 3048.6, 2948.2, 1640.8, 1597.5, 1481.1, 1360.2, 1275.8, 1230.1, 1175.4, 1129.7, 954.0, 753.3.

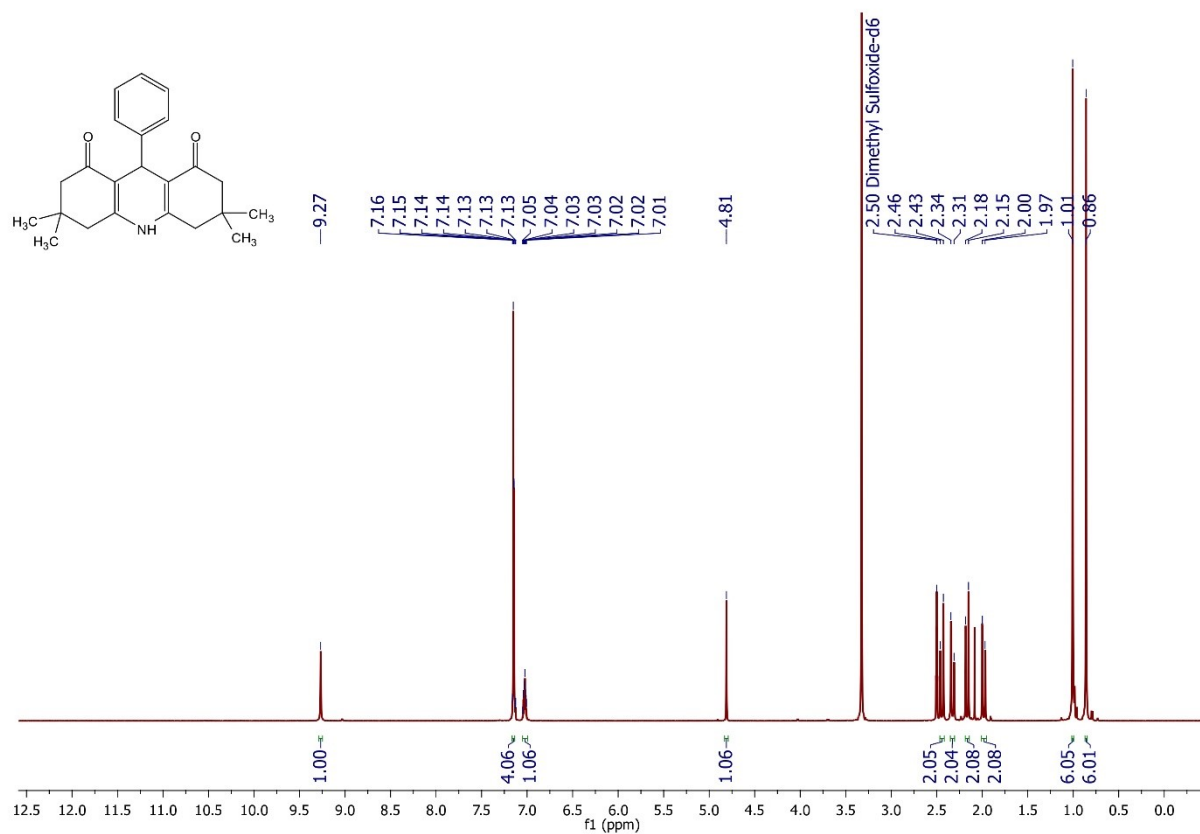
*9-(4-Chlorophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (13b)*

4-Chlorobenzaldehyde (141 mg), 1,3-cyclohexanedione (224 mg), ammonium acetate (77 mg), Co/C (10 mg). The brown powder was obtained with 77%.  $R_f = 0.11$  (*n*-hexane:EA = 1:4); Mp. = 307-309 °C;  $^1\text{H}$ -NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 1.73$ -1.82 (m, 4H), 1.88-1.93 (m, 4H), 2.16-2.22 (m, 4H), 4.88 (s, 1H), 7.15 (d,  $J = 8.5$  Hz, 2H), 7.21 (d,  $J = 8.5$  Hz, 2H), 9.49 (s, 1H) ppm.  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 21.2, 26.8, 32.4, 37.2, 112.5, 128.1, 129.8, 130.5, 146.7, 152.0, 195.3$  ppm. FT-IR (KBr, 4000-500  $\text{cm}^{-1}$ ): 3267.6, 3199.2, 3057.7, 2932.2, 2877.4, 1638.5, 1602.0, 1472.0, 1360.2, 1227.8, 1173.1, 1129.7, 1013.4, 954.0, 906.1, 826.3, 741.9.

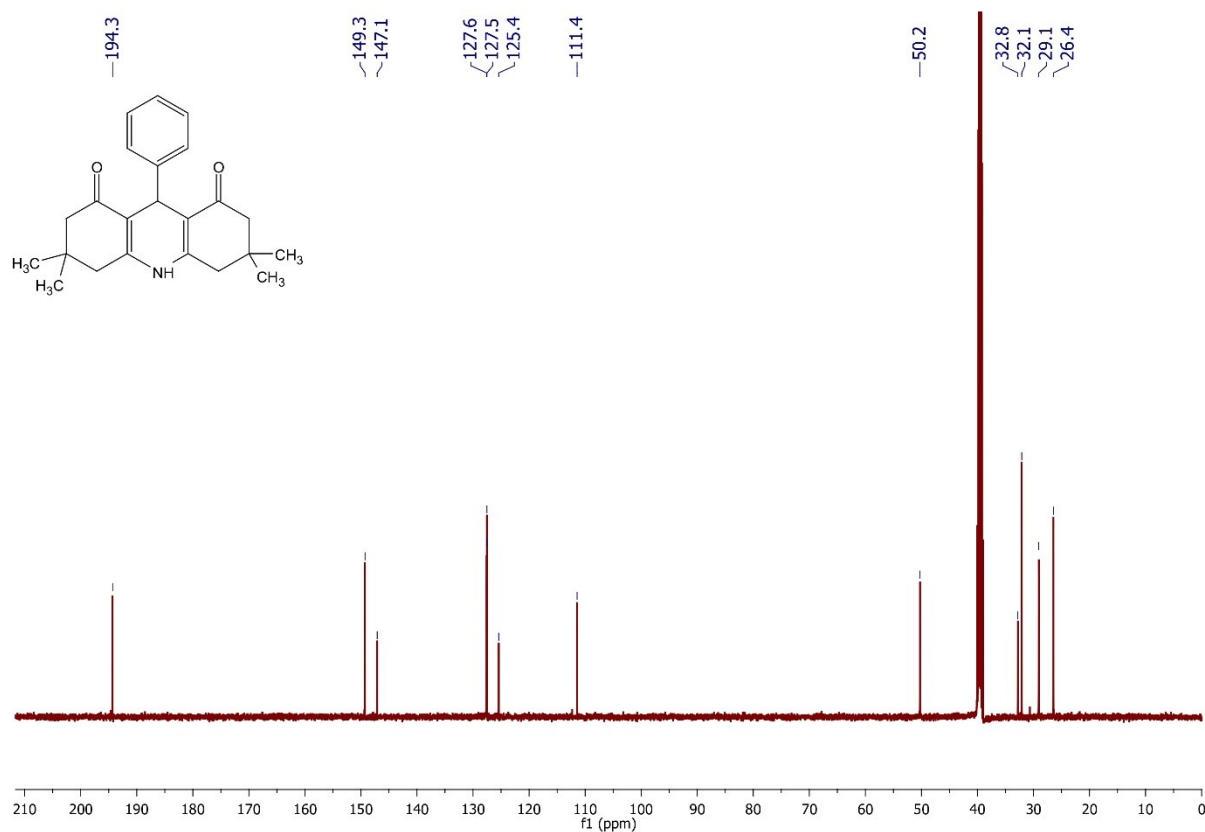
*9-(4-Bromophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (14b)*<sup>9</sup>

4-Bromobenzaldehyde (185 mg), 1,3-cyclohexanedione (224 mg), ammonium acetate (77 mg), Co/C (10 mg). The brown powder was obtained with 80%.  $R_f = 0.19$  (*n*-hexane:EA = 1:4); Mp. = 300-302 °C;<sup>9</sup> <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 1.75$ -1.81 (m, 4H), 1.88-1.93 (m, 4H), 2.18-2.22 (m, 4H), 4.86 (s, 1H), 7.10 (d,  $J = 8.5$  Hz, 2H), 7.34 (d,  $J = 8.5$  Hz, 2H), 9.48 (s, 1H) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 20.8, 26.3, 32.1, 36.7, 112.0, 118.5, 129.8, 130.6, 146.7, 151.5, 194.8$  ppm. FT-IR (KBr, 4000-500 cm<sup>-1</sup>): 3269.9, 3201.4, 3060.0, 2932.2, 2877.4, 1711.5, 1640.8, 1597.5, 1474.3, 1362.5, 1227.8, 1175.4, 1129.7, 1063.6, 1004.2, 951.8, 908.4, 826.3, 744.1, 527.4.

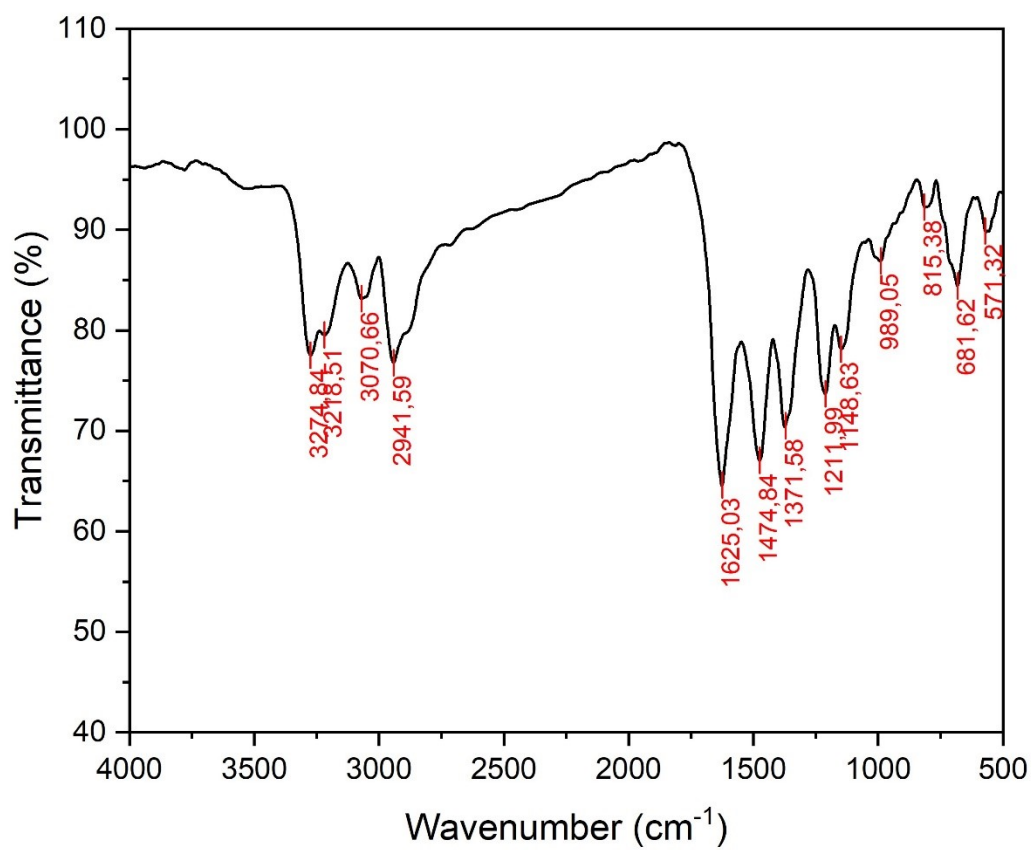
## Section S3. Spectral data



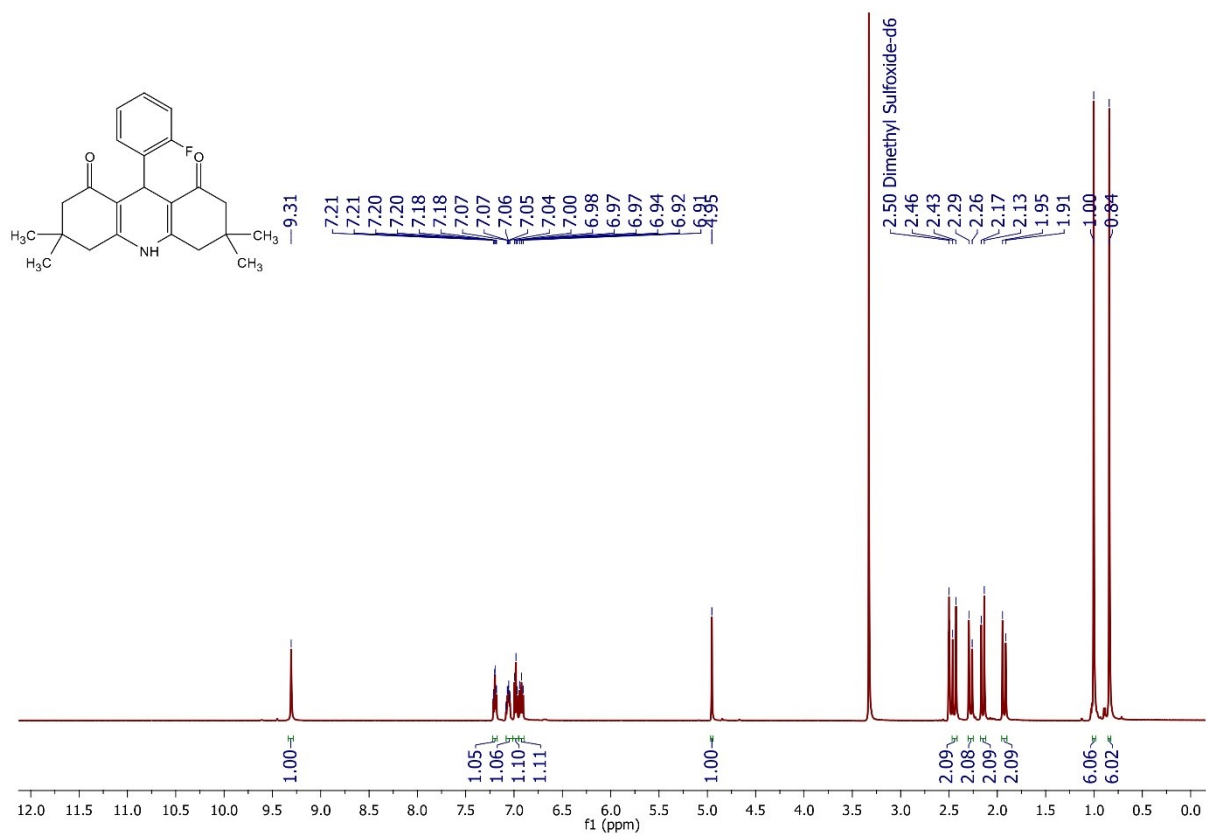
**Figure S2-1.1.**  $^1\text{H}$ -NMR spectrum of **1a**



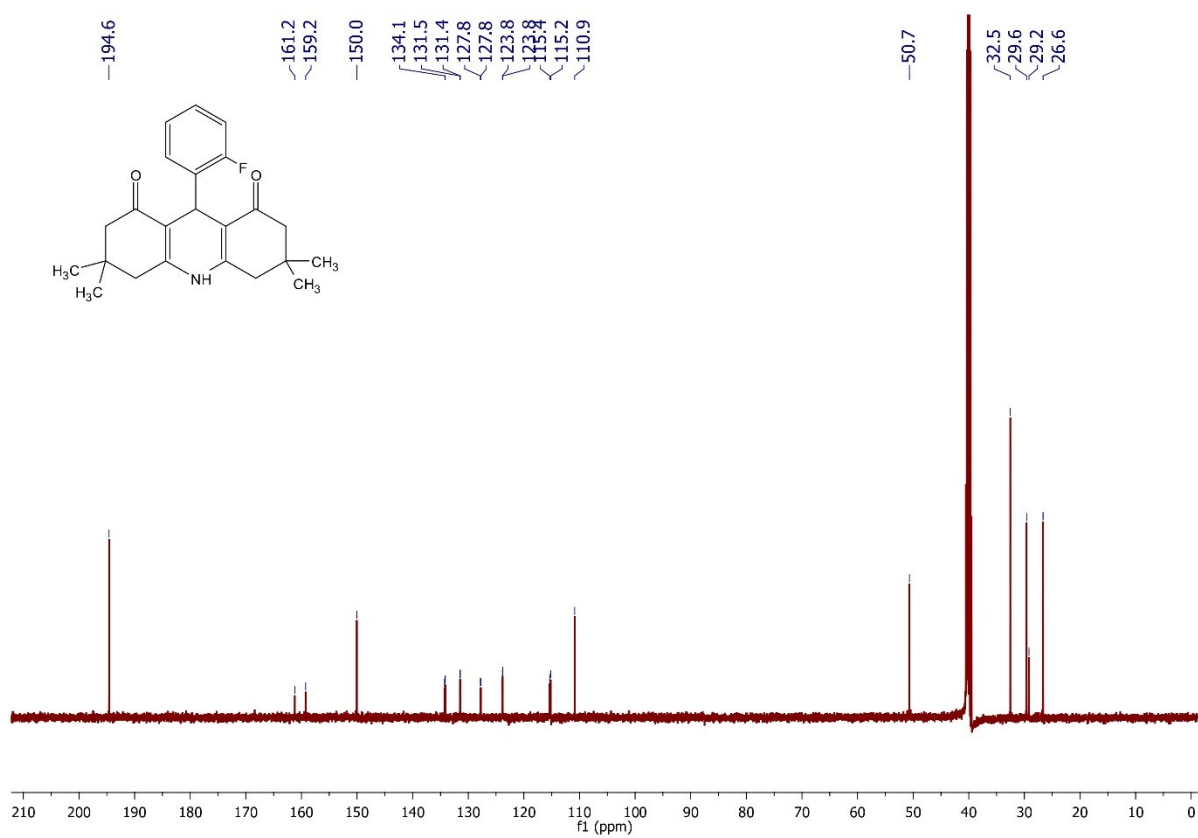
**Figure S2-1.2.**  $^{13}\text{C}$ -NMR spectrum of **1a**



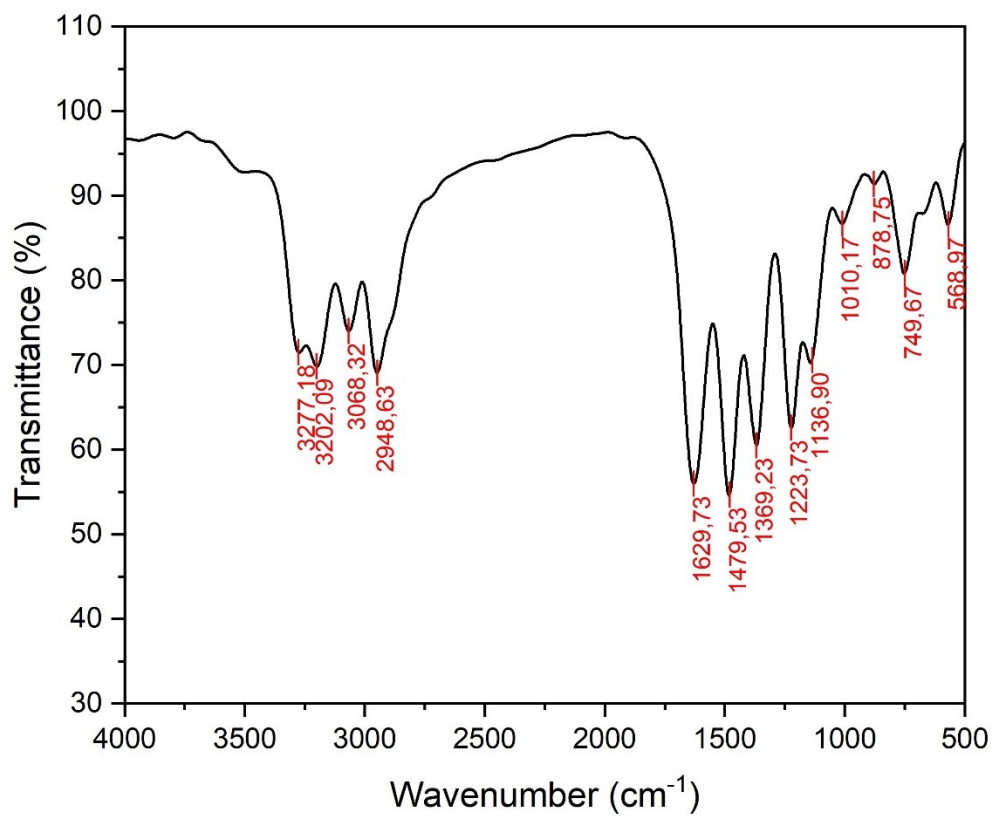
**Figure S2-1.3.** FT-IR spectra of **1a**



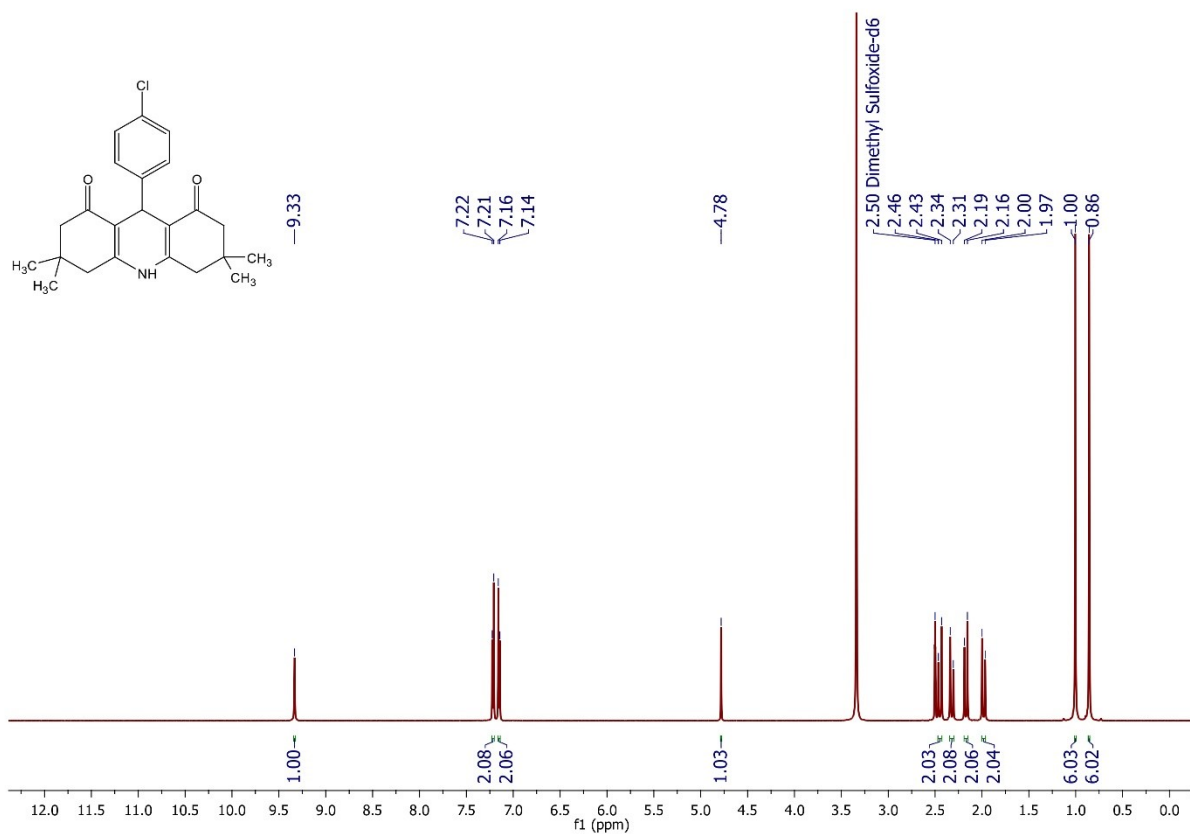
**Figure S2-2.1.  $^1\text{H}$ -NMR spectrum of **2a****



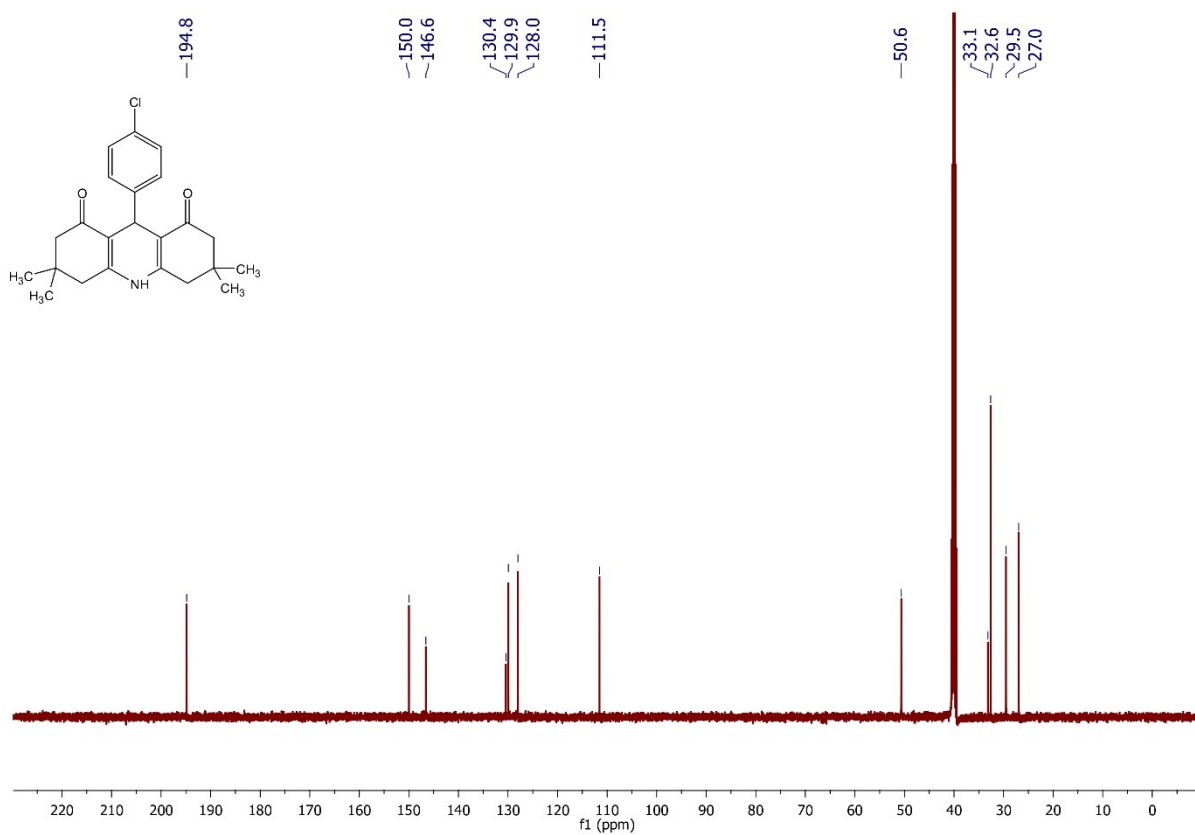
**Figure S2-2.2.  $^{13}\text{C}$ -NMR spectrum of **2a****



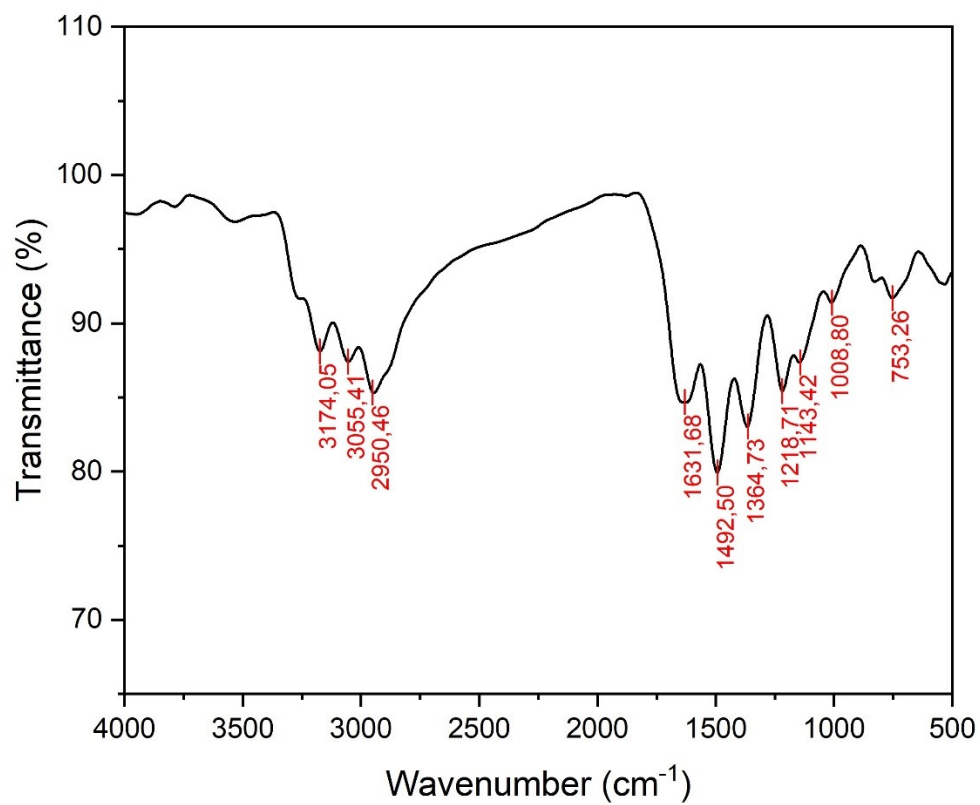
**Figure S2-2.3.** FT-IR spectra of **2a**



**Figure S2-3.1.  $^1\text{H}$ -NMR spectrum of **3a****



**Figure S2-3.2.  $^{13}\text{C}$ -NMR spectrum of **3a****



**Figure S2-3.3.** FT-IR spectra of **3a**



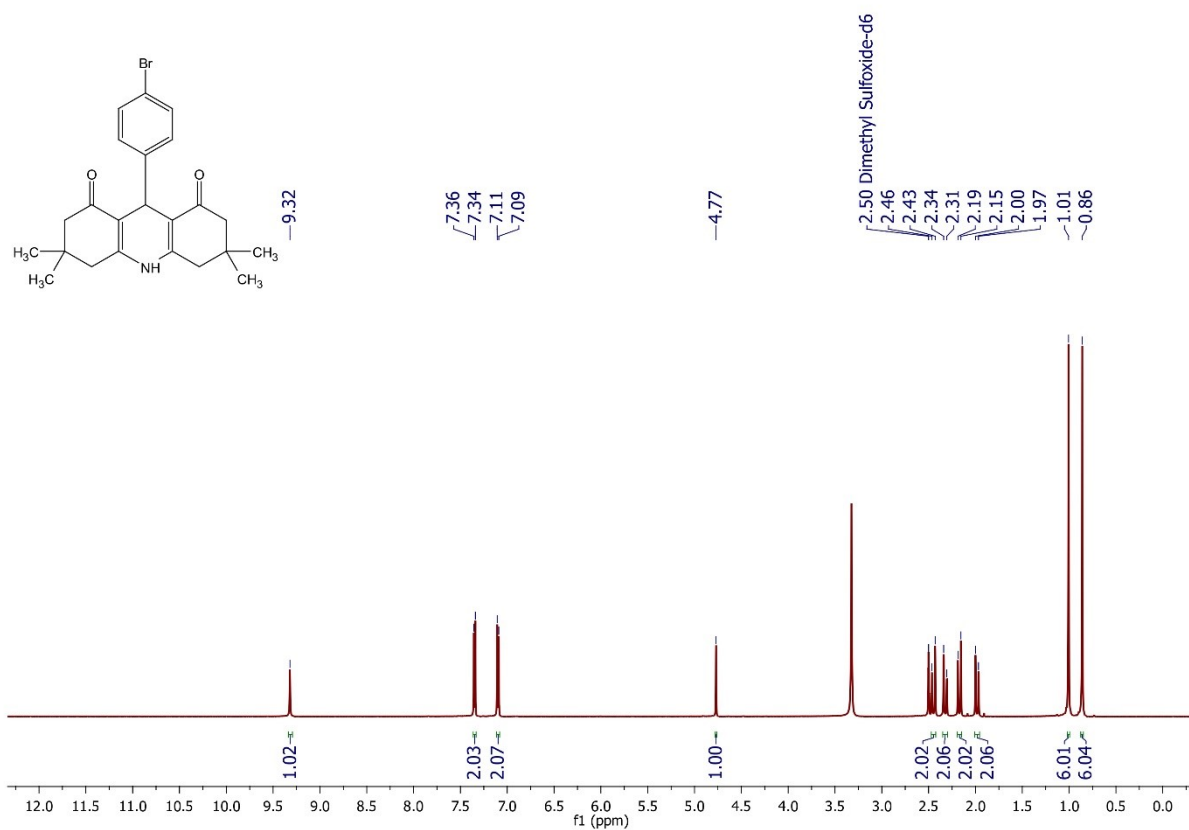


Figure S2-4.1.  $^1\text{H-NMR}$  spectrum of 4a

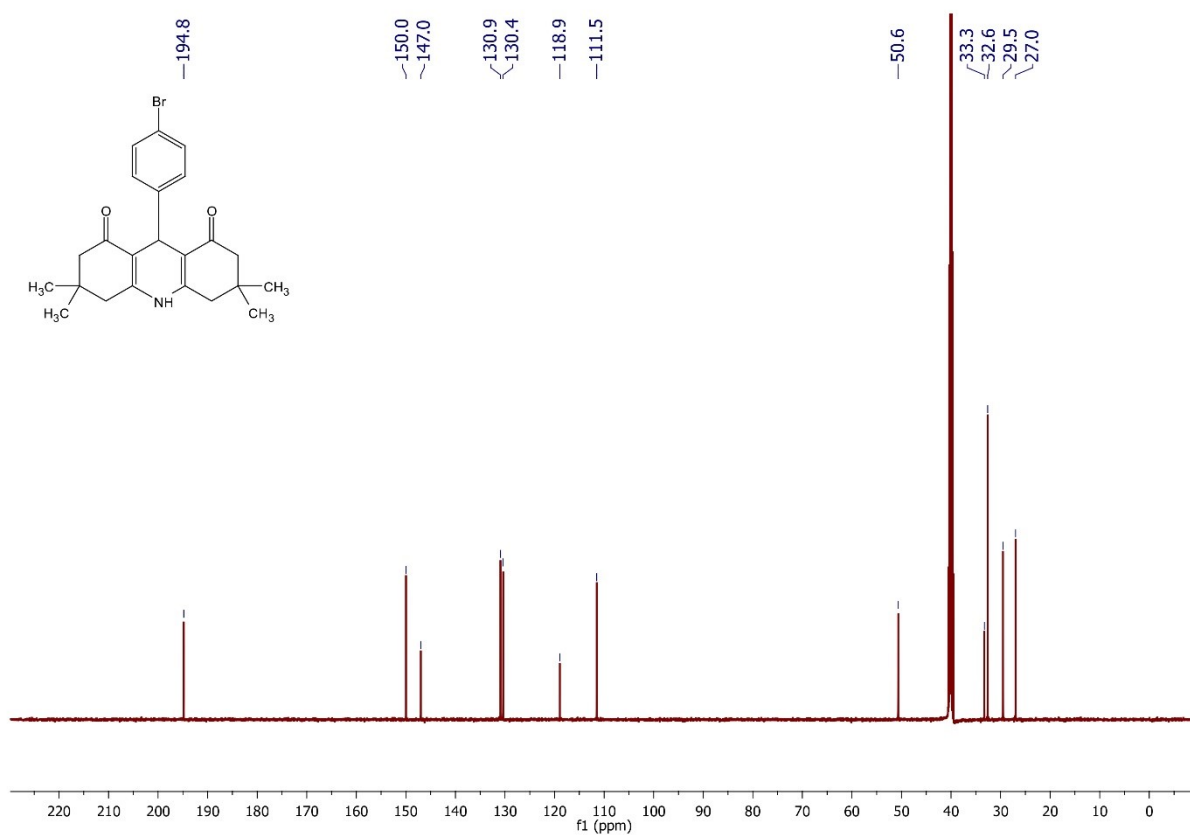
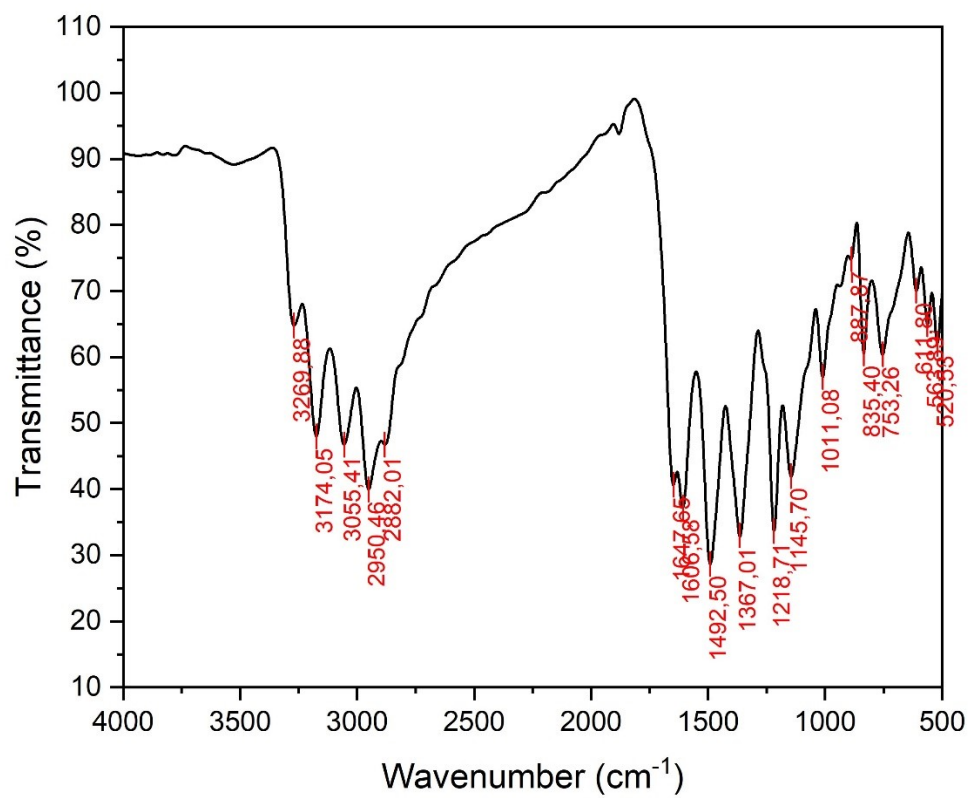
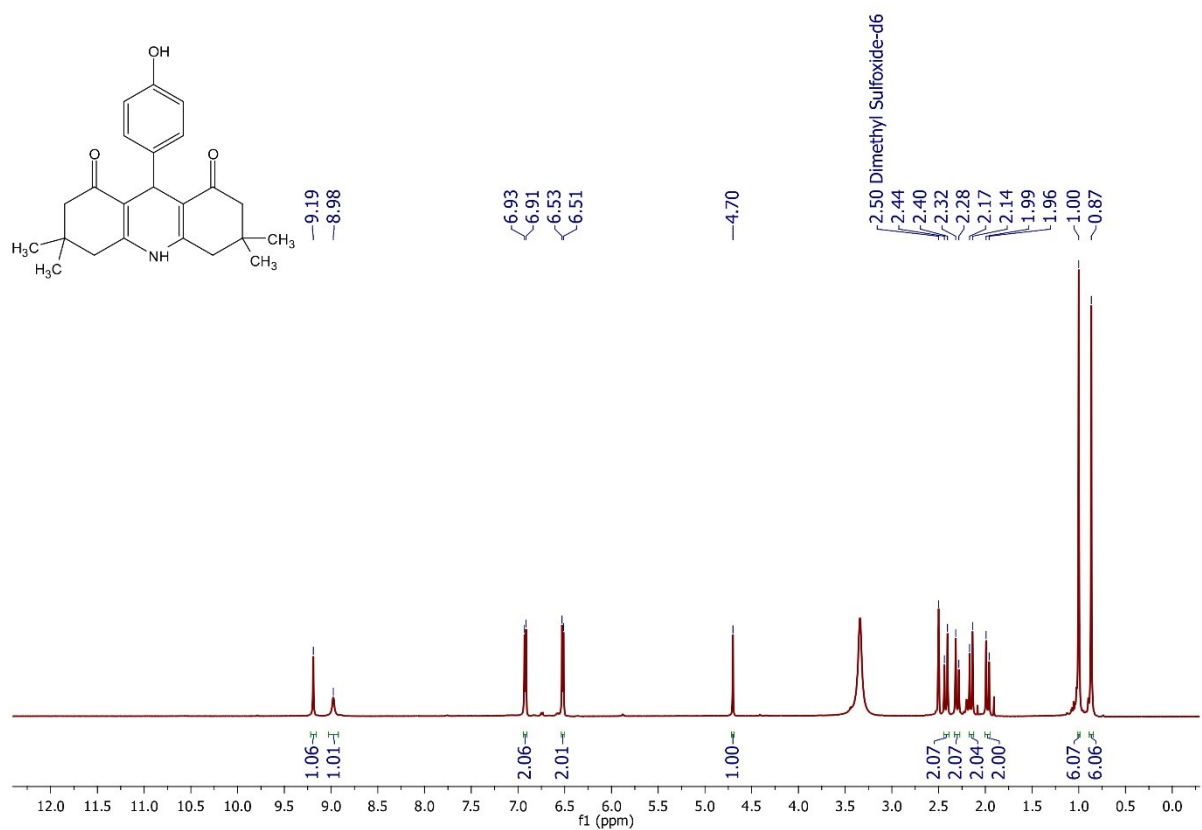


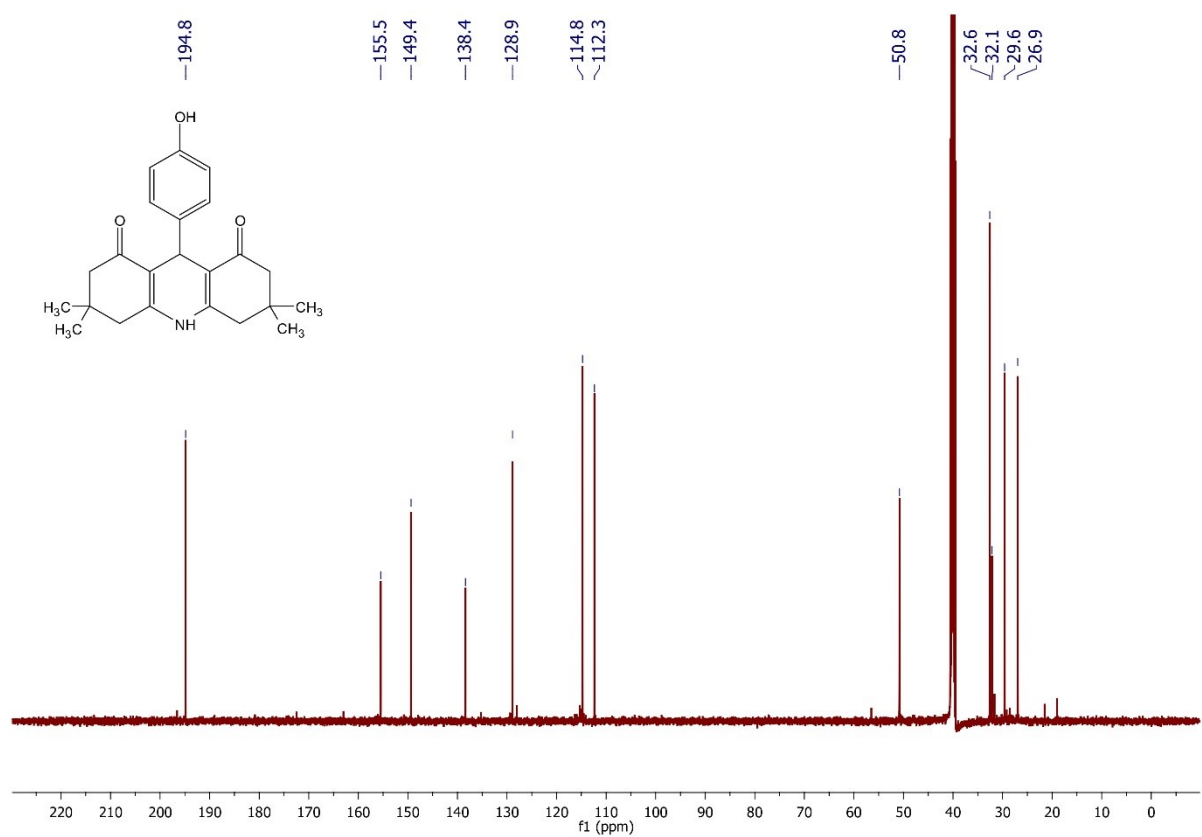
Figure S2-4.2.  $^{13}\text{C-NMR}$  spectrum of 4a



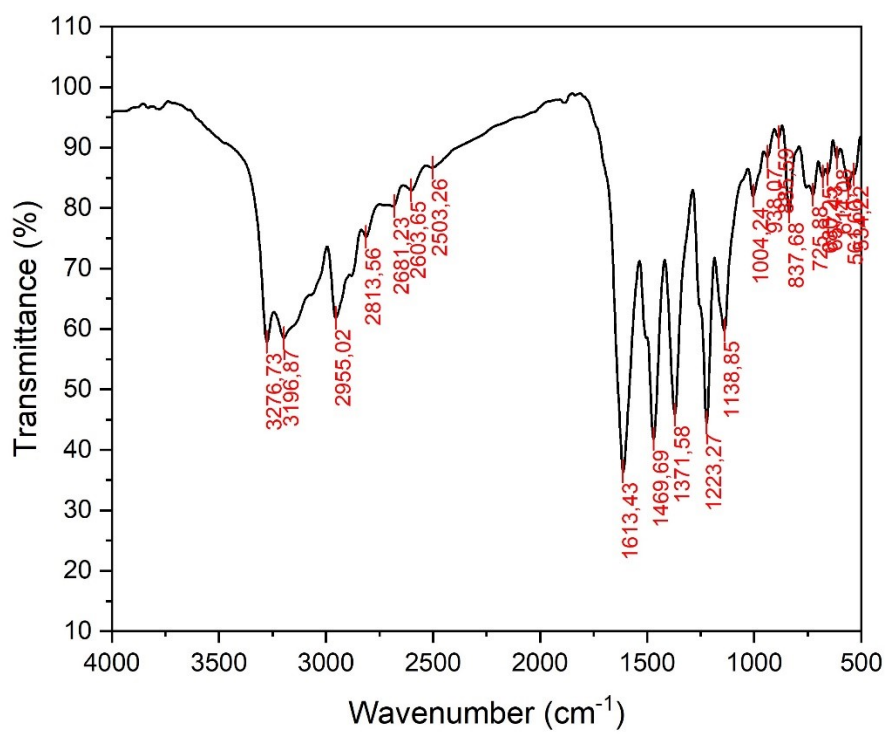
**Figure S2-4.3.** FT-IR spectra of 4a



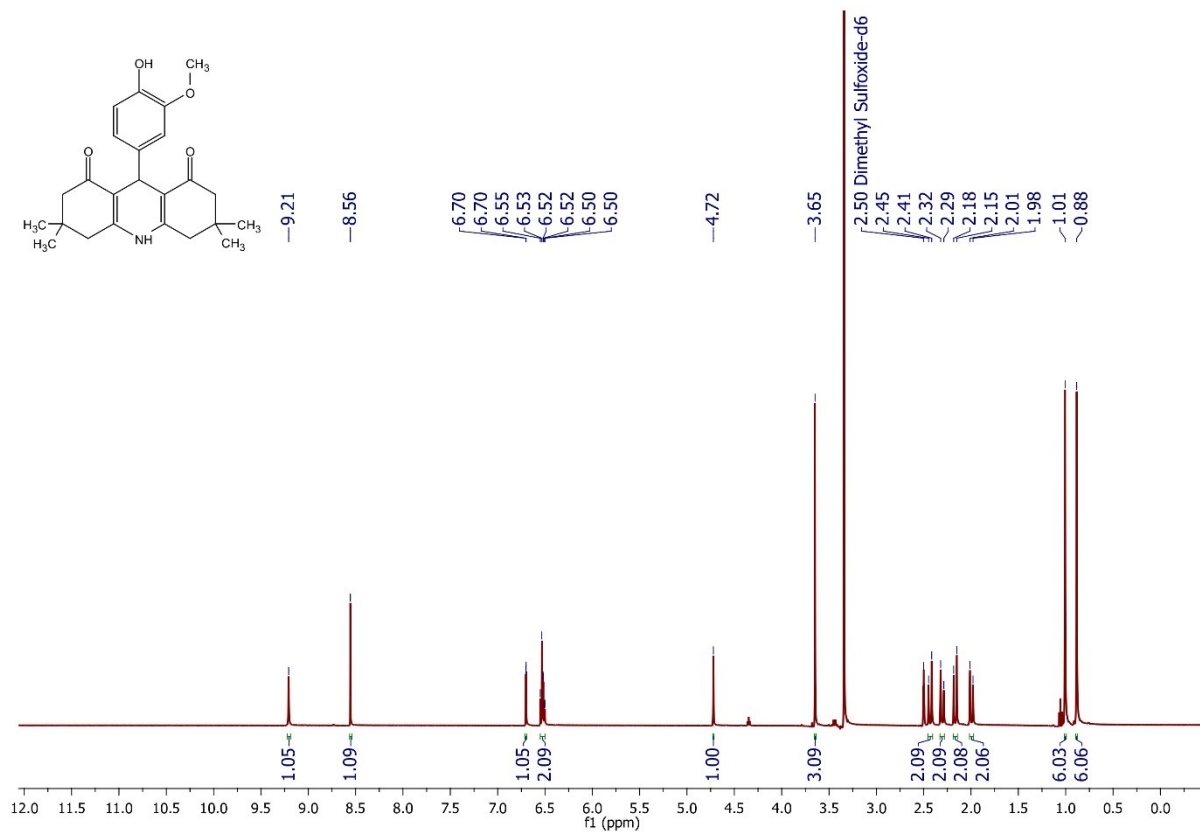
**Figure S2-5.1.**  $^1\text{H}$ -NMR spectrum of **5a**



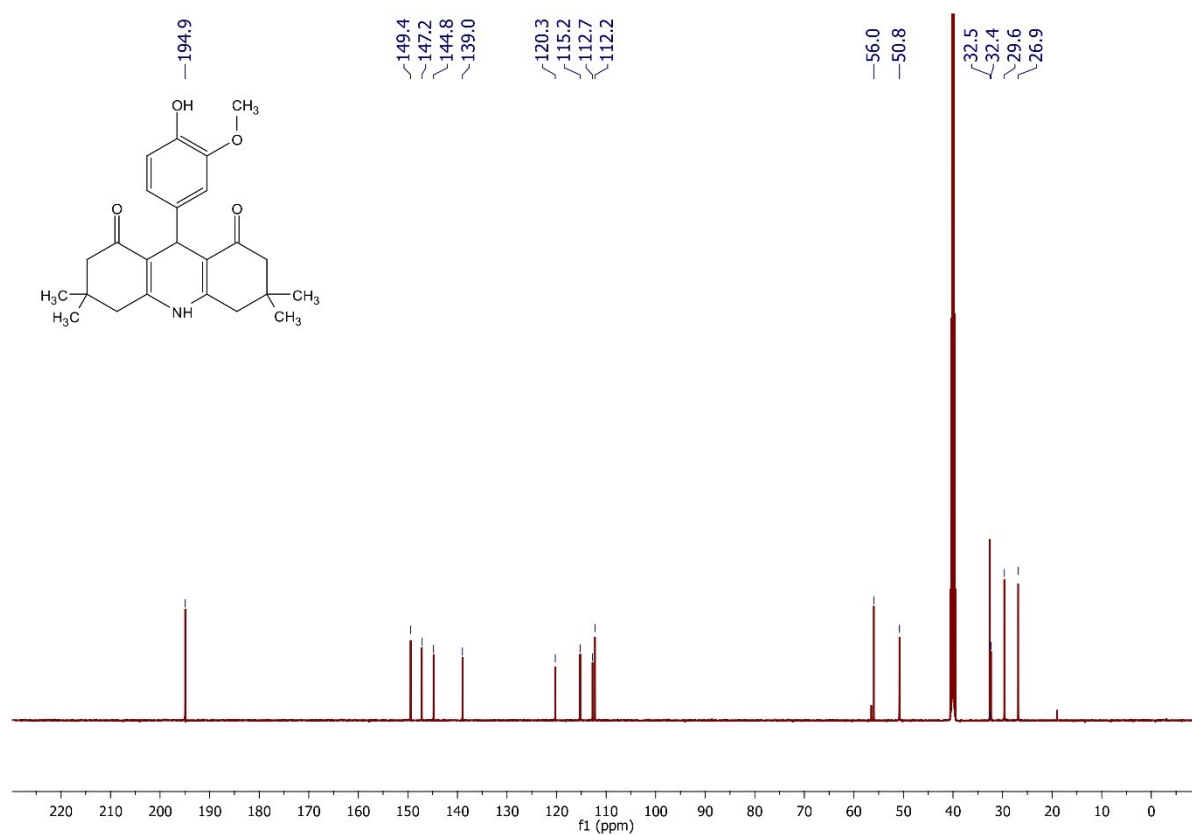
**Figure S2-5.2.**  $^{13}\text{C}$ -NMR spectrum of **5a**



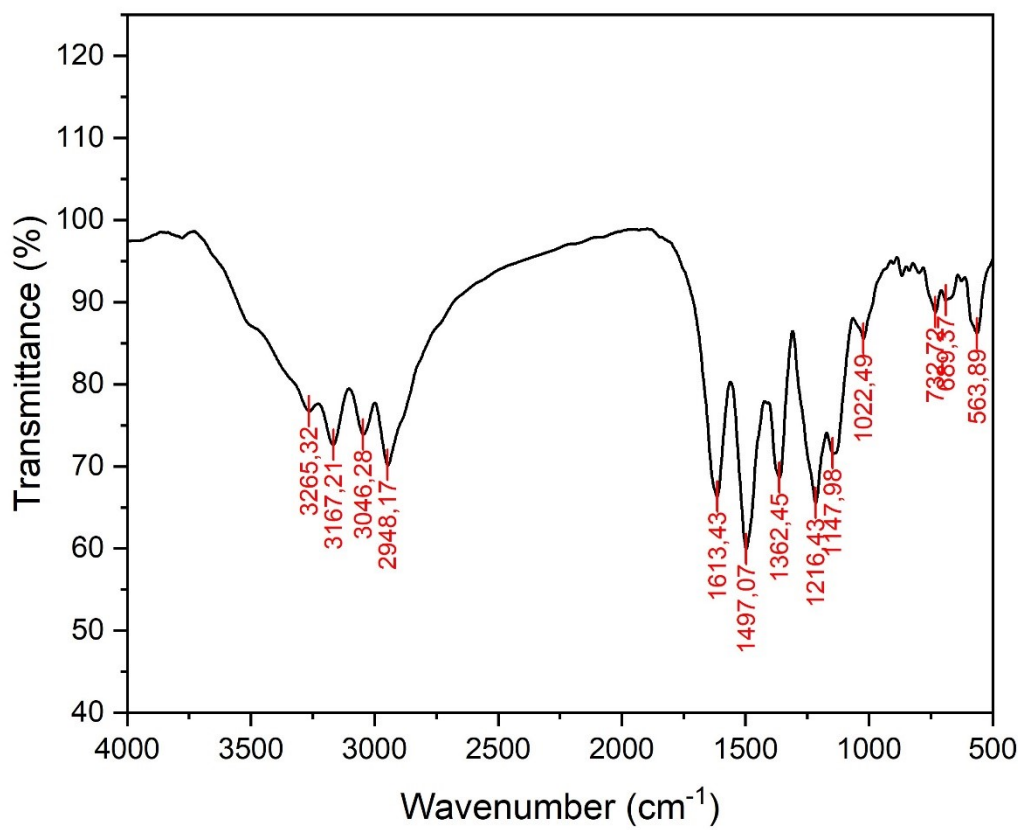
**Figure S2-5.3.** FT-IR spectra of **5a**



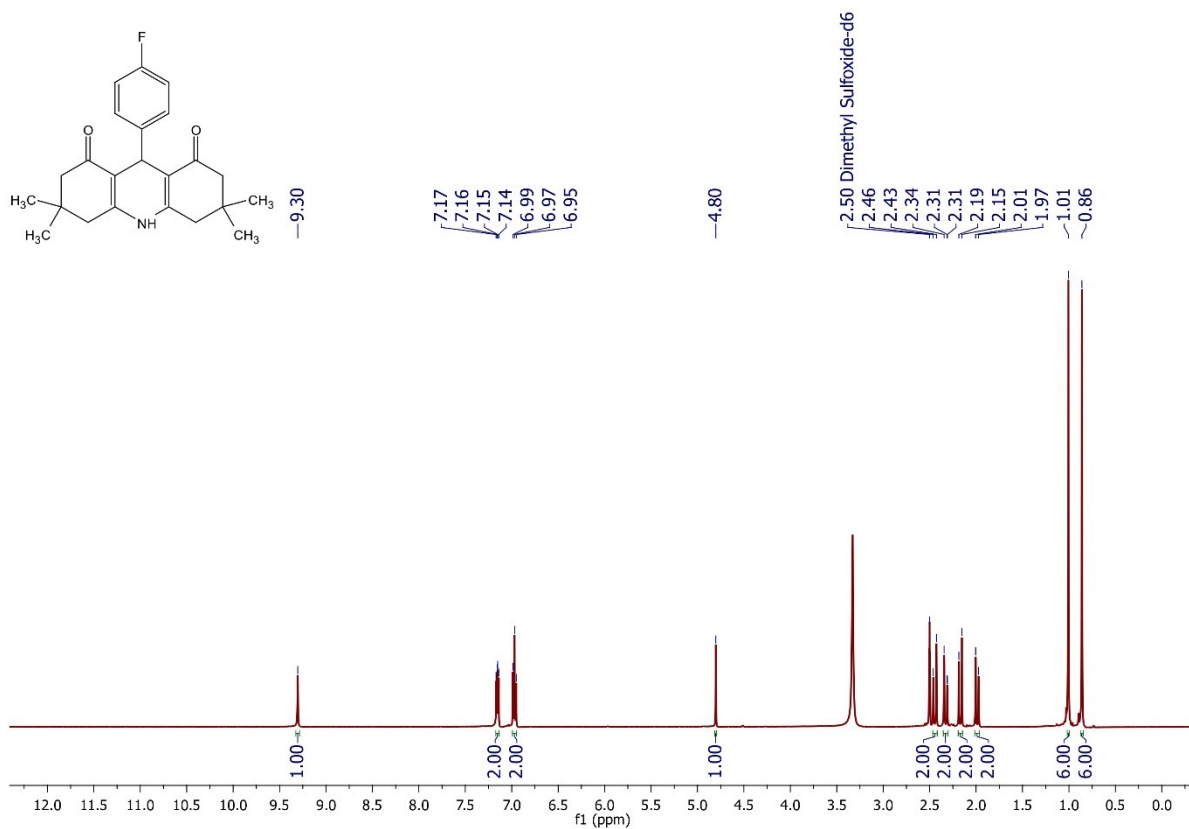
**Figure S2-6.1.** <sup>1</sup>H-NMR spectrum of **6a**



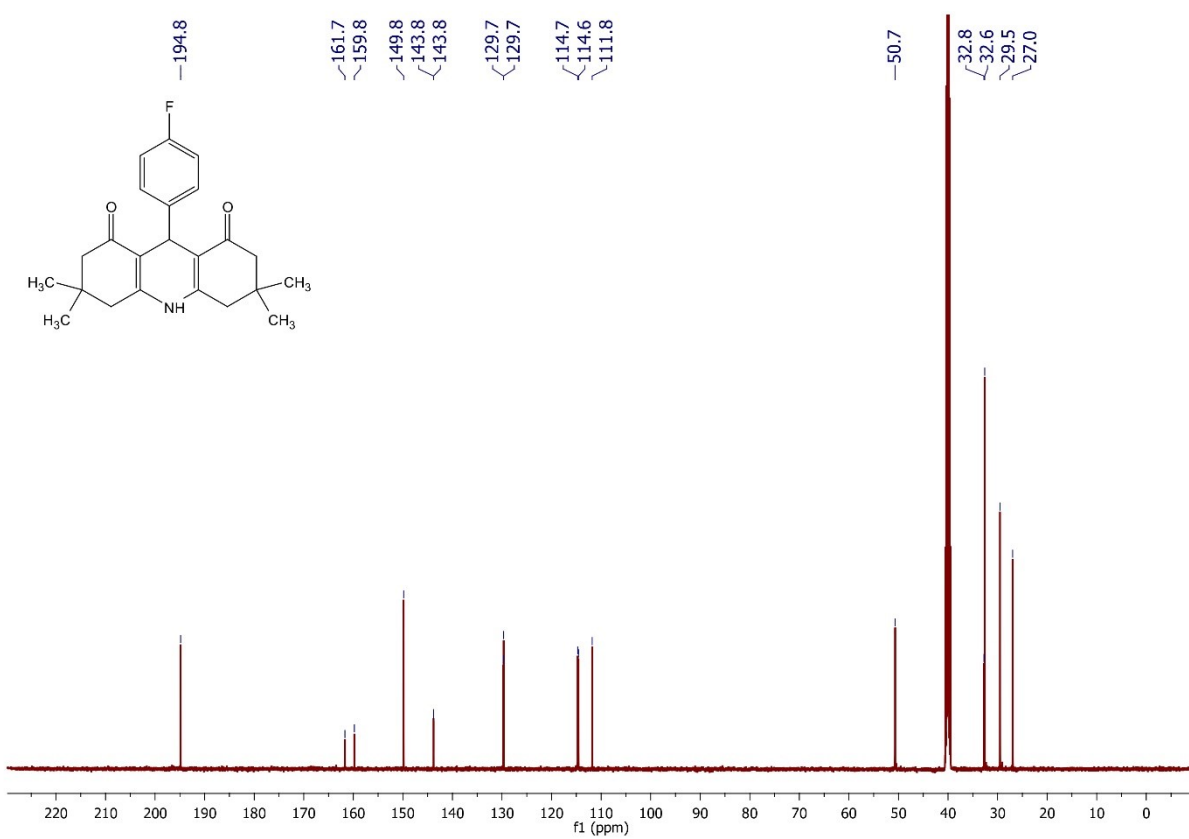
**Figure S2-6.2.** <sup>13</sup>C-NMR spectrum of **6a**



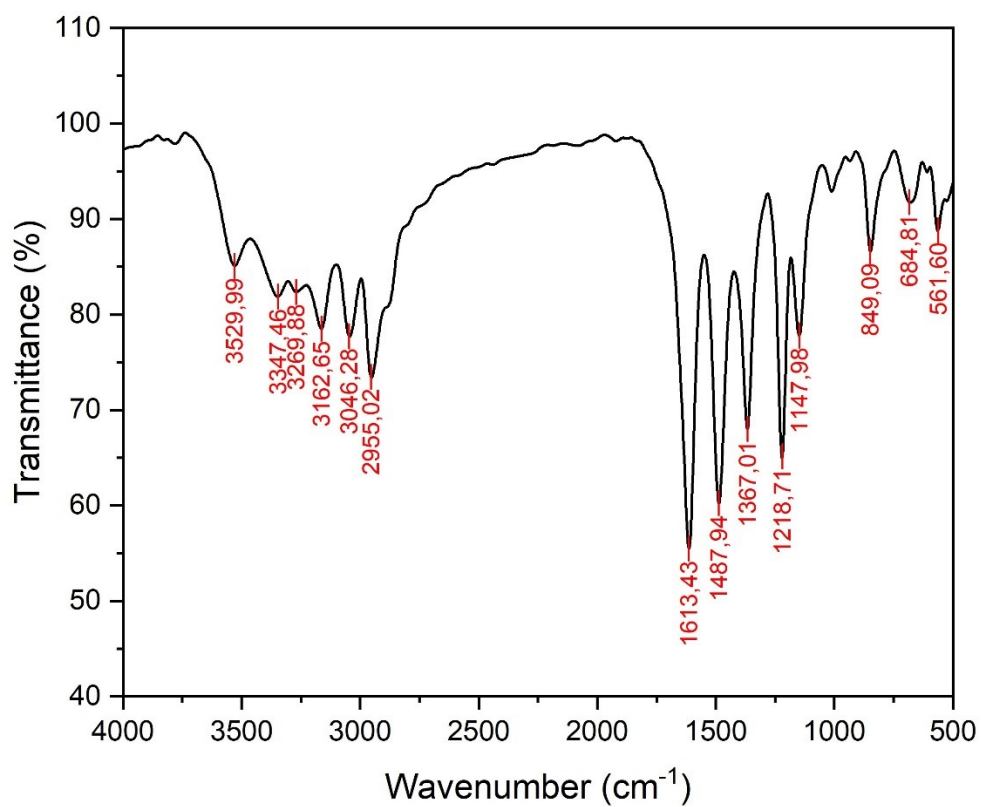
**Figure S2-6.3.** FT-IR spectra of **6a**



**Figure S2-7.1. <sup>1</sup>H-NMR spectrum of 7a**

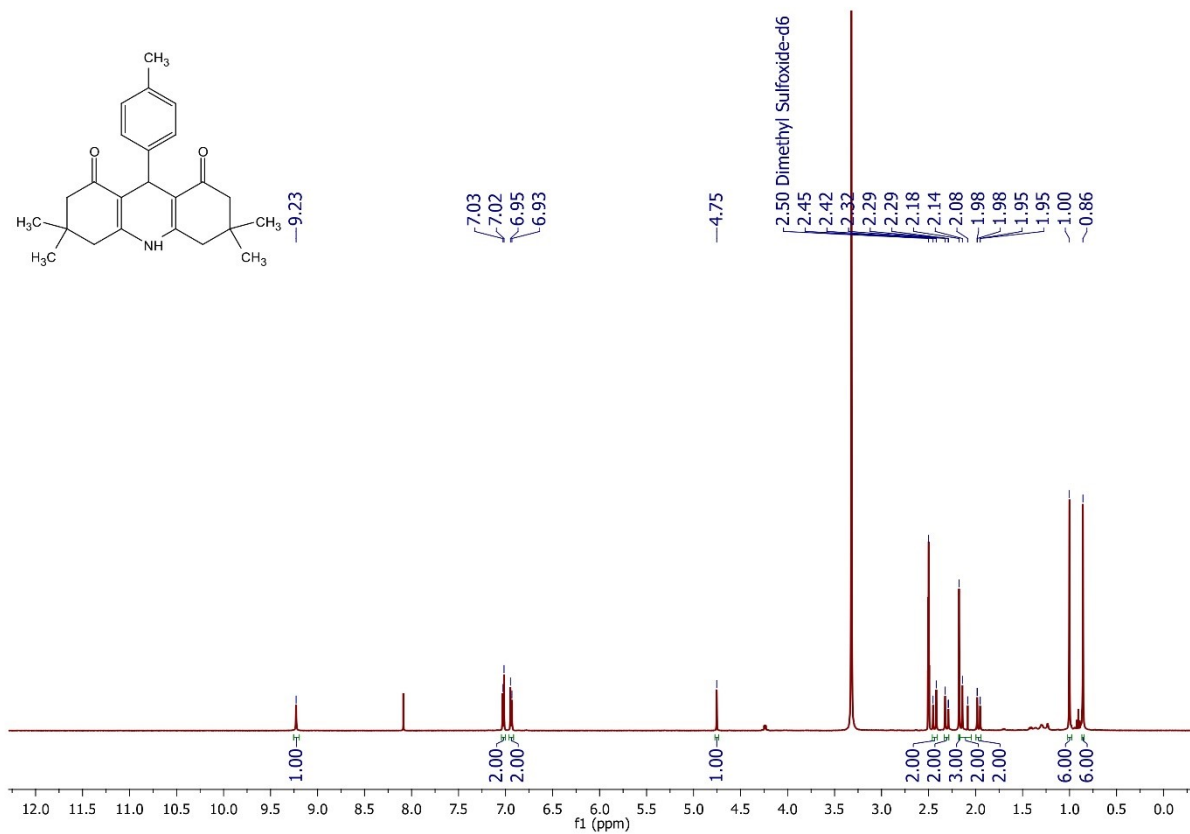


**Figure S2-7.2. <sup>13</sup>C-NMR spectrum of 7a**

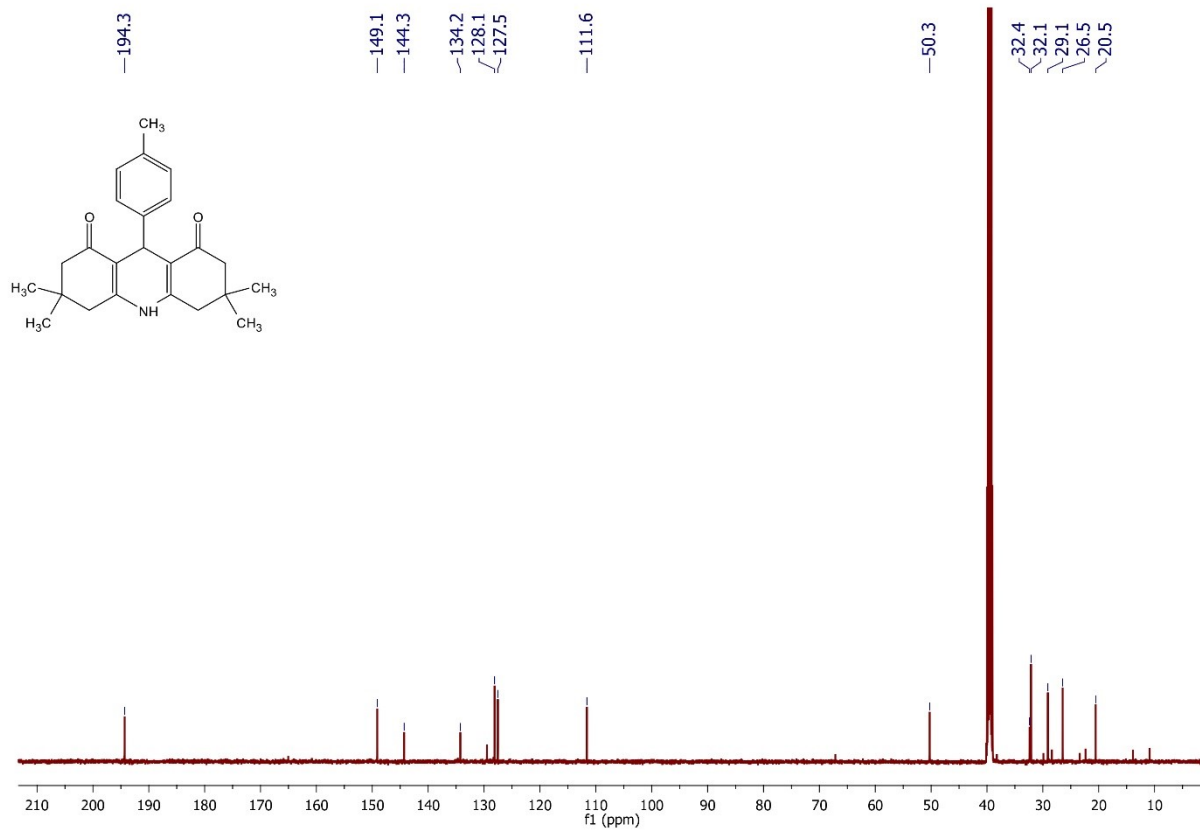


**Figure S2-7.3.** FT-IR spectra of **7a**

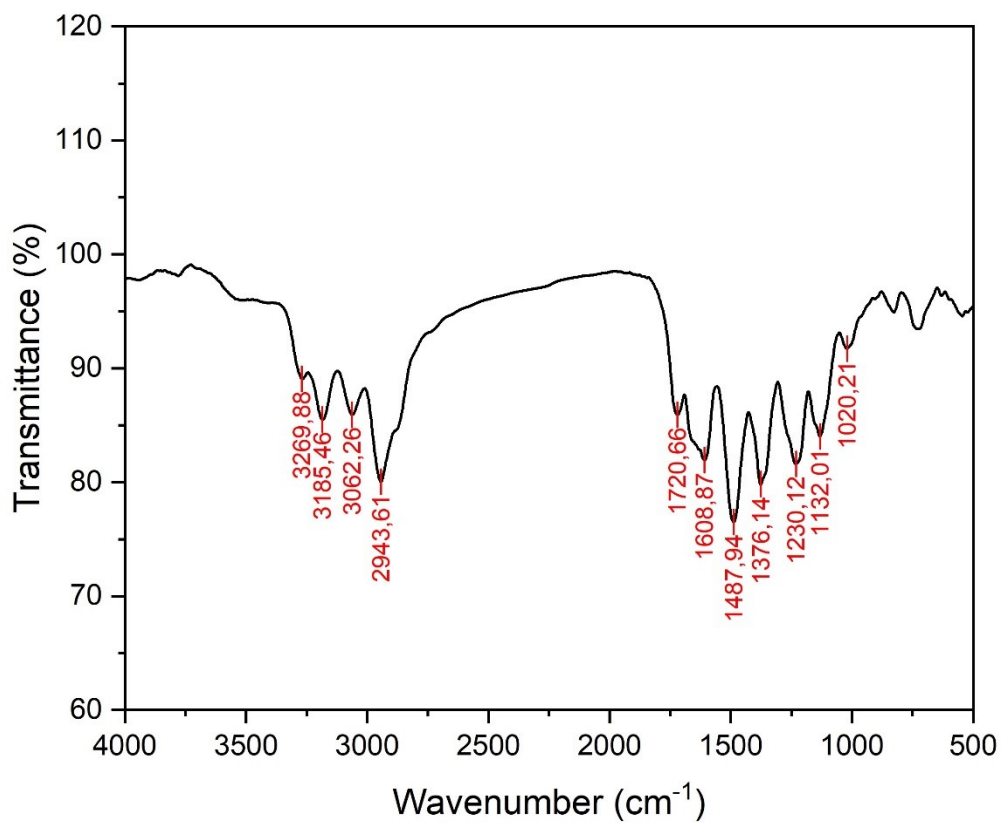




**Figure S2-8.1.**  $^1\text{H-NMR}$  spectrum of **8a**



**Figure S2-8.2.**  $^{13}\text{C-NMR}$  spectrum of **8a**



**Figure S2-8.3.** FT-IR spectra of **8a**

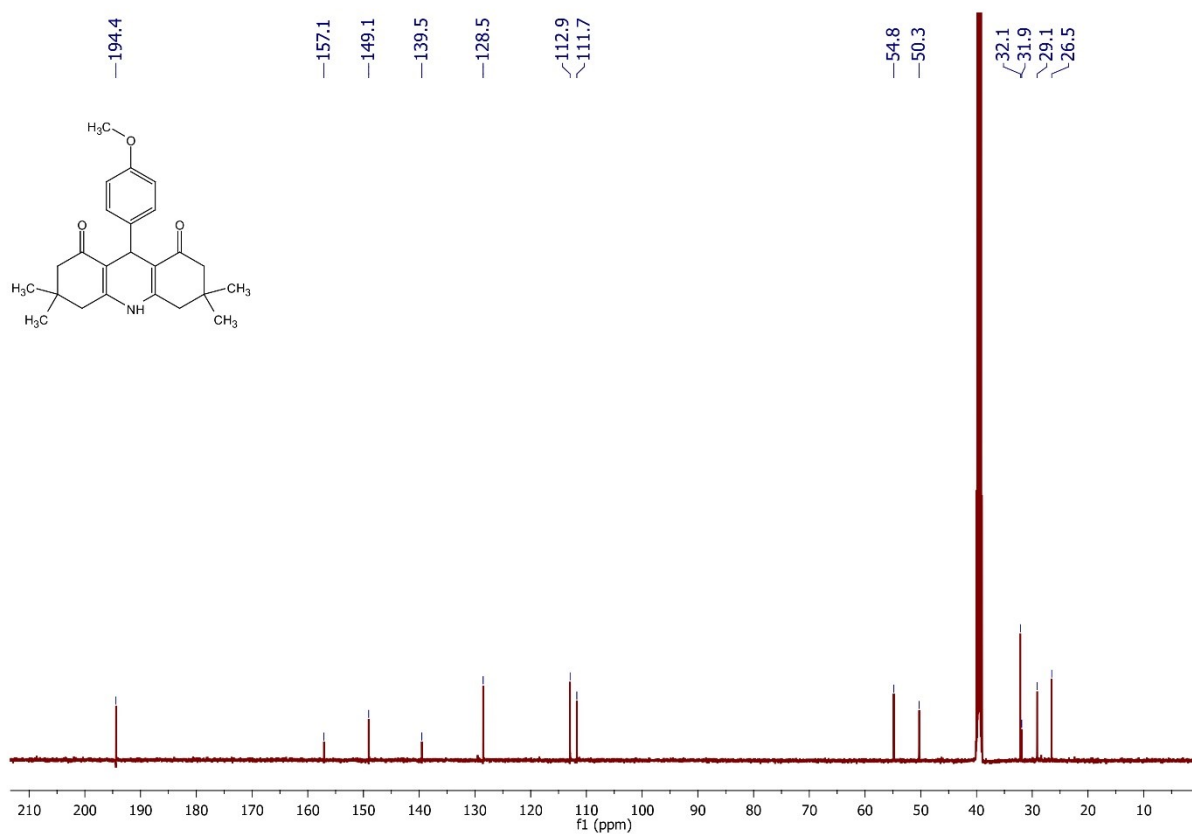


Figure S2-9.1.  $^1\text{H}$ -NMR spectrum of **9a**

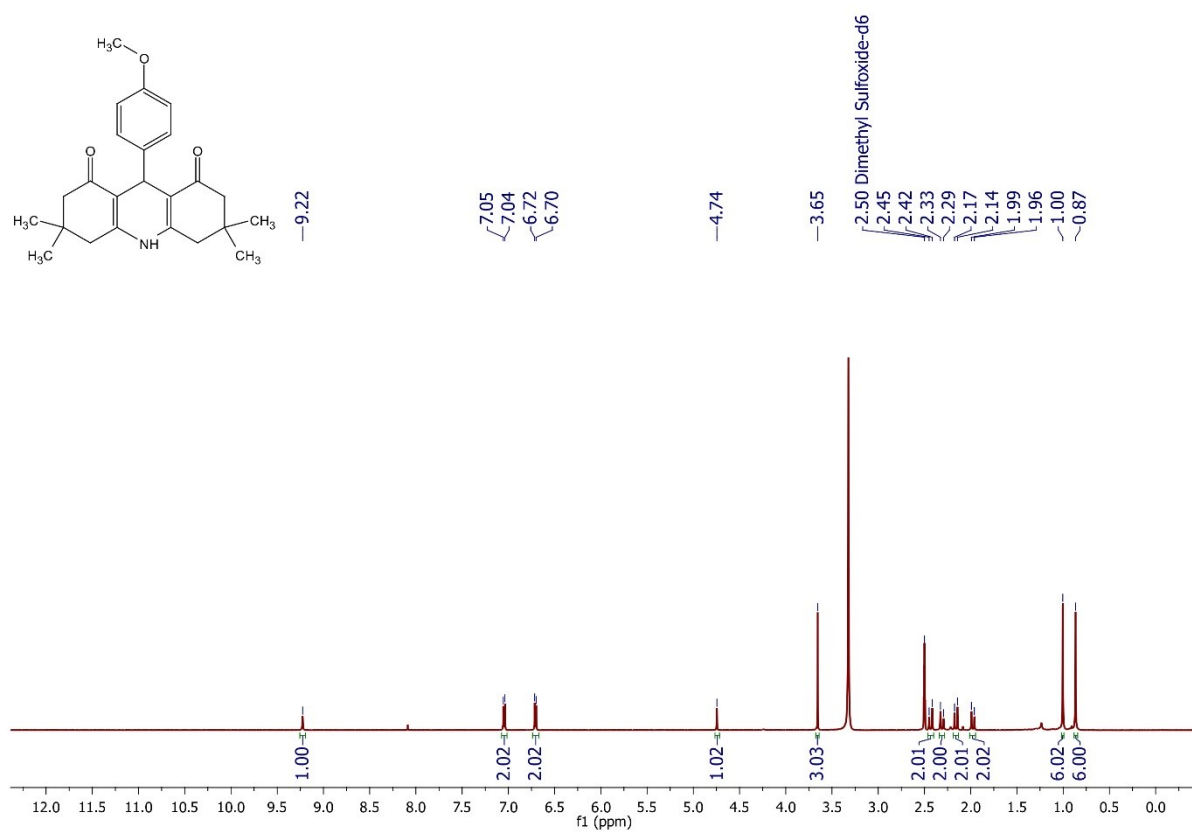


Figure S2-9.2.  $^{13}\text{C}$ -NMR spectrum of **9a**

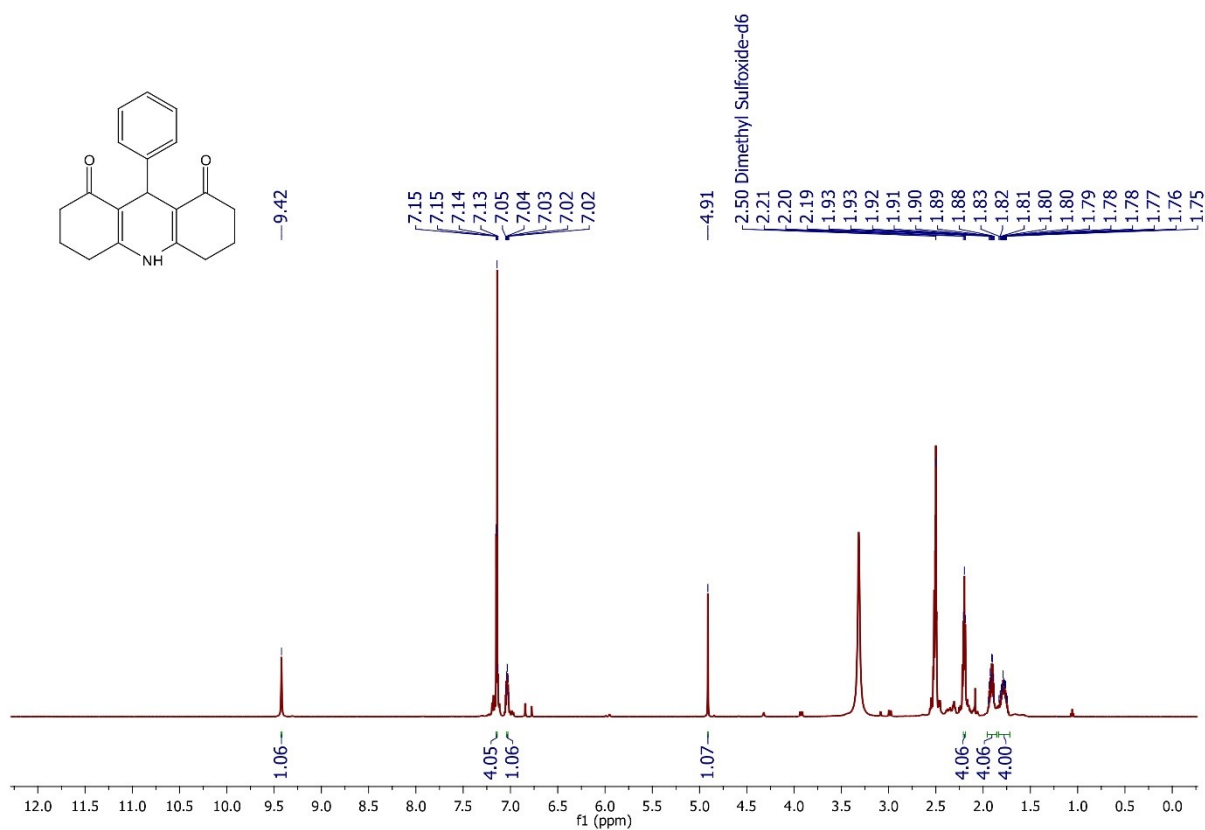


Figure S2-10.1.  $^1\text{H-NMR}$  spectrum of 10b

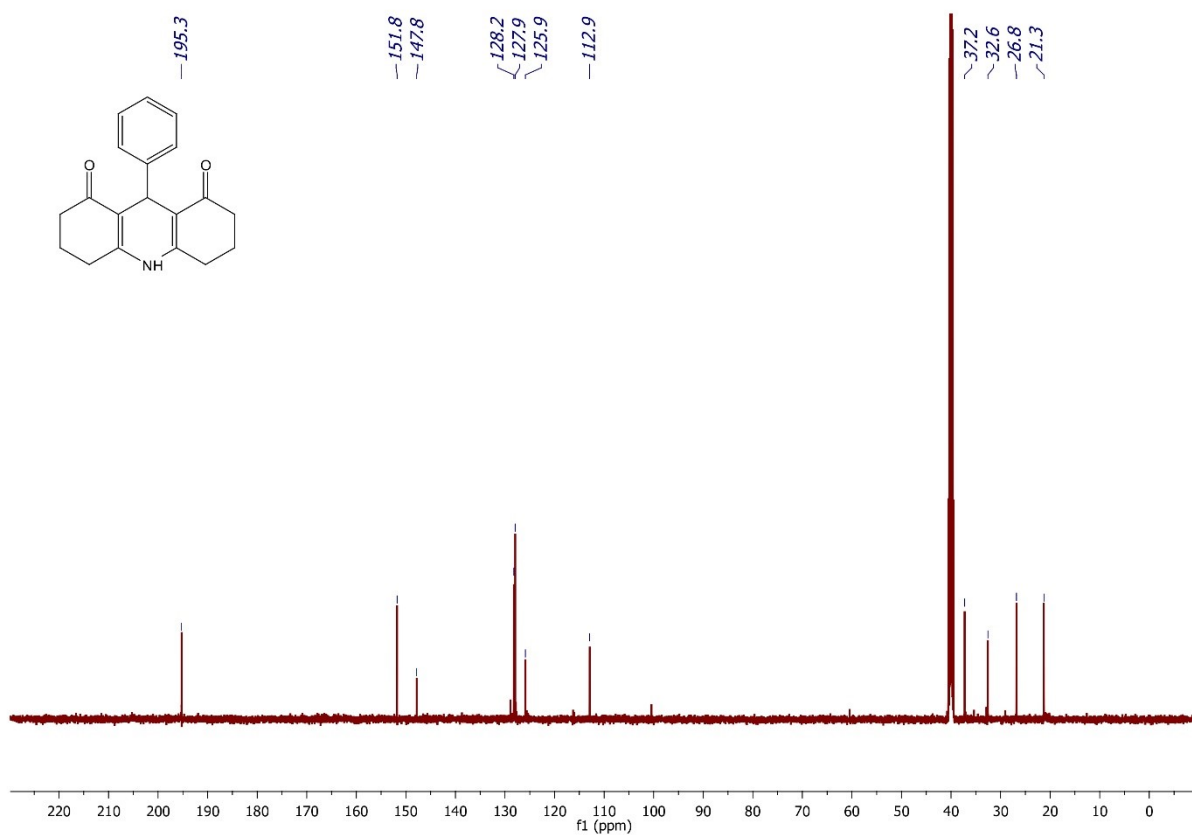
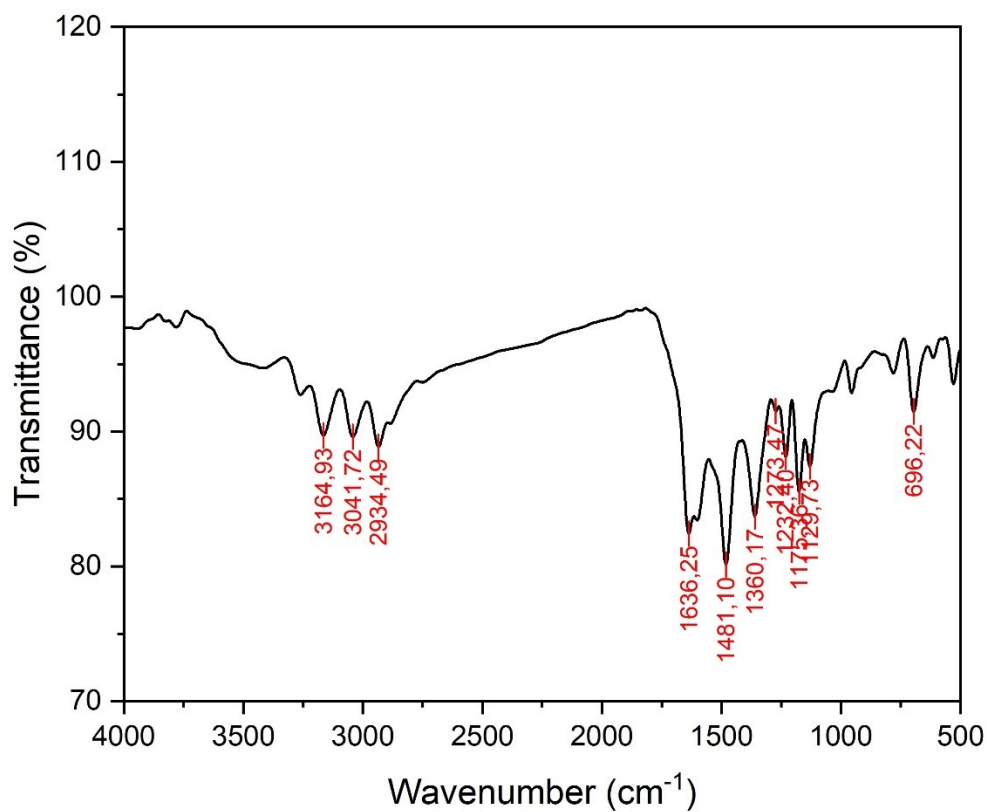
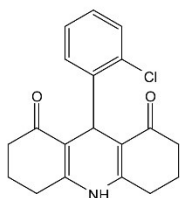
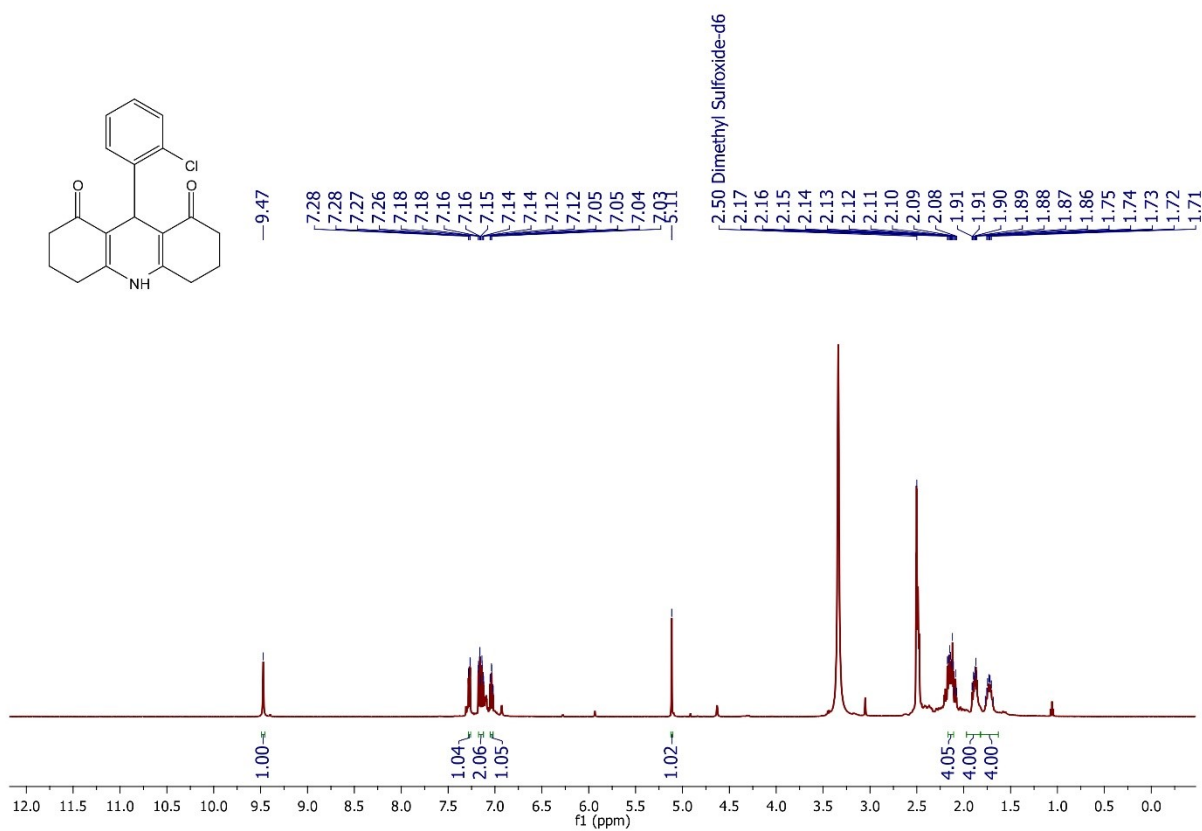


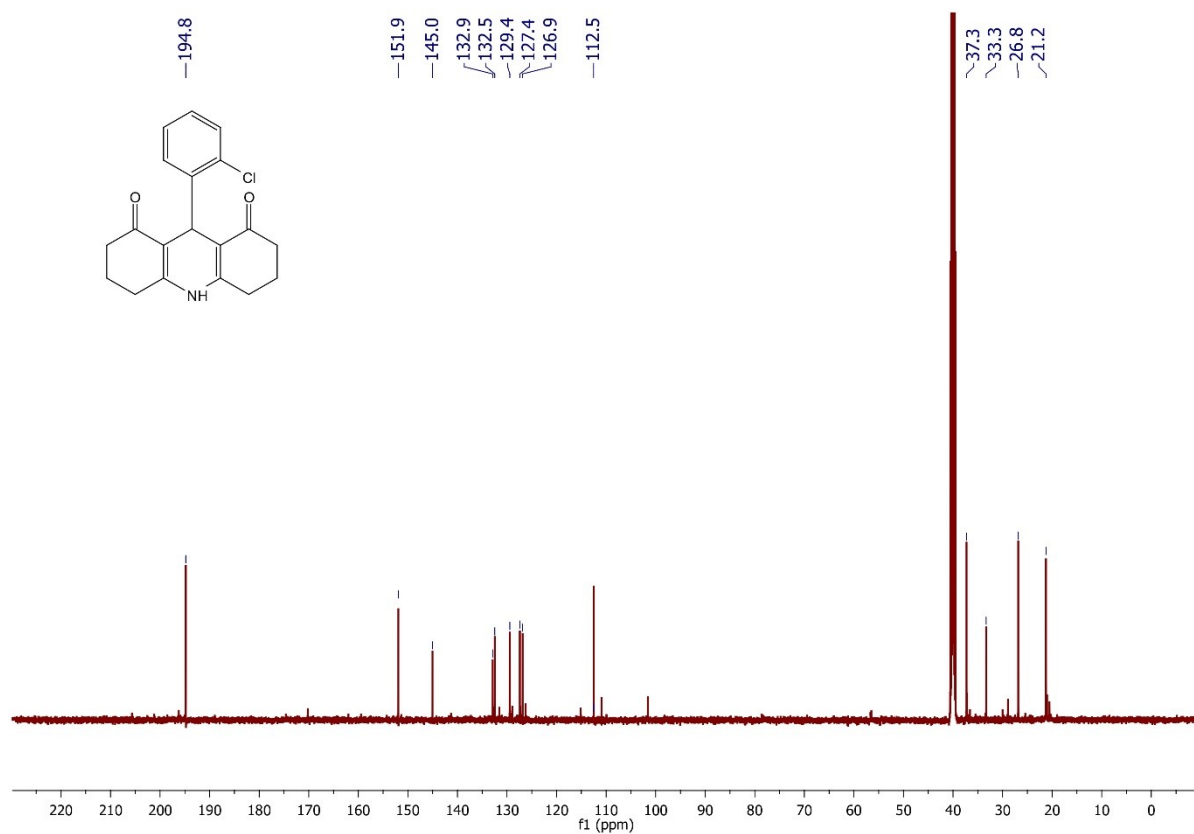
Figure S2-10.2.  $^{13}\text{C-NMR}$  spectrum of 10b



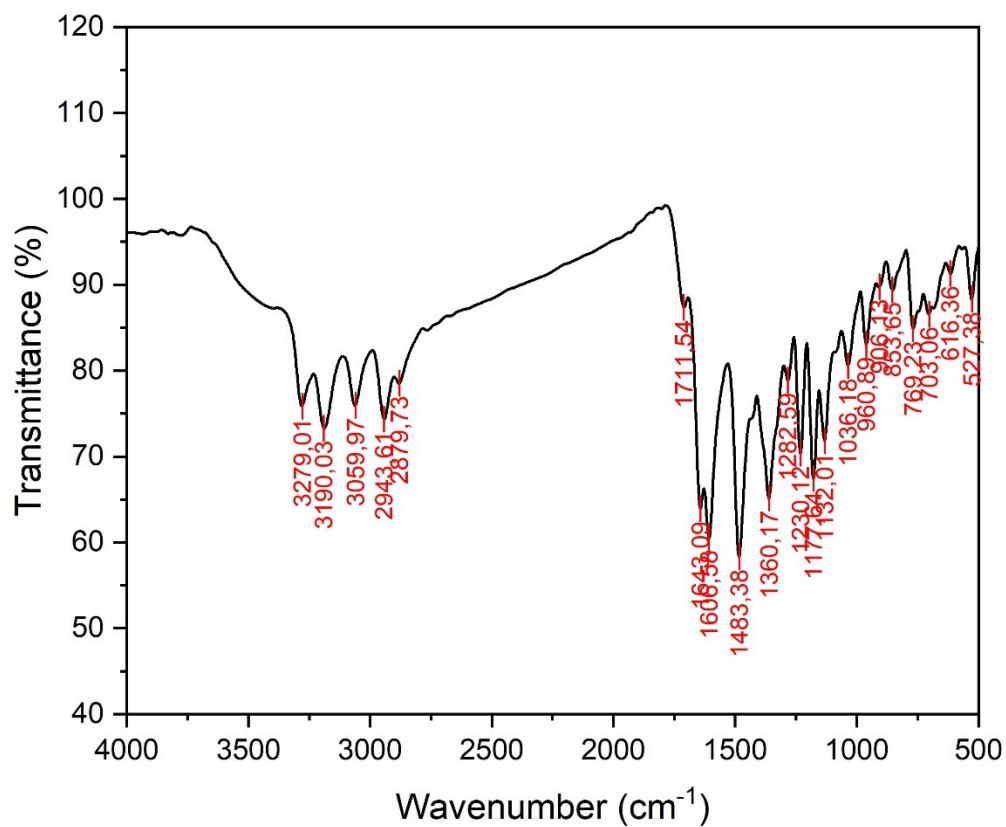
**Figure S2-10.3.** FT-IR spectra of **10b**



**Figure S2-11.1.**  $^1\text{H}$ -NMR spectrum of **11b**



**Figure S2-11.2.**  $^{13}\text{C}$ -NMR spectrum of **11b**



**Figure S2-11.3.** FT-IR spectra of **11b**

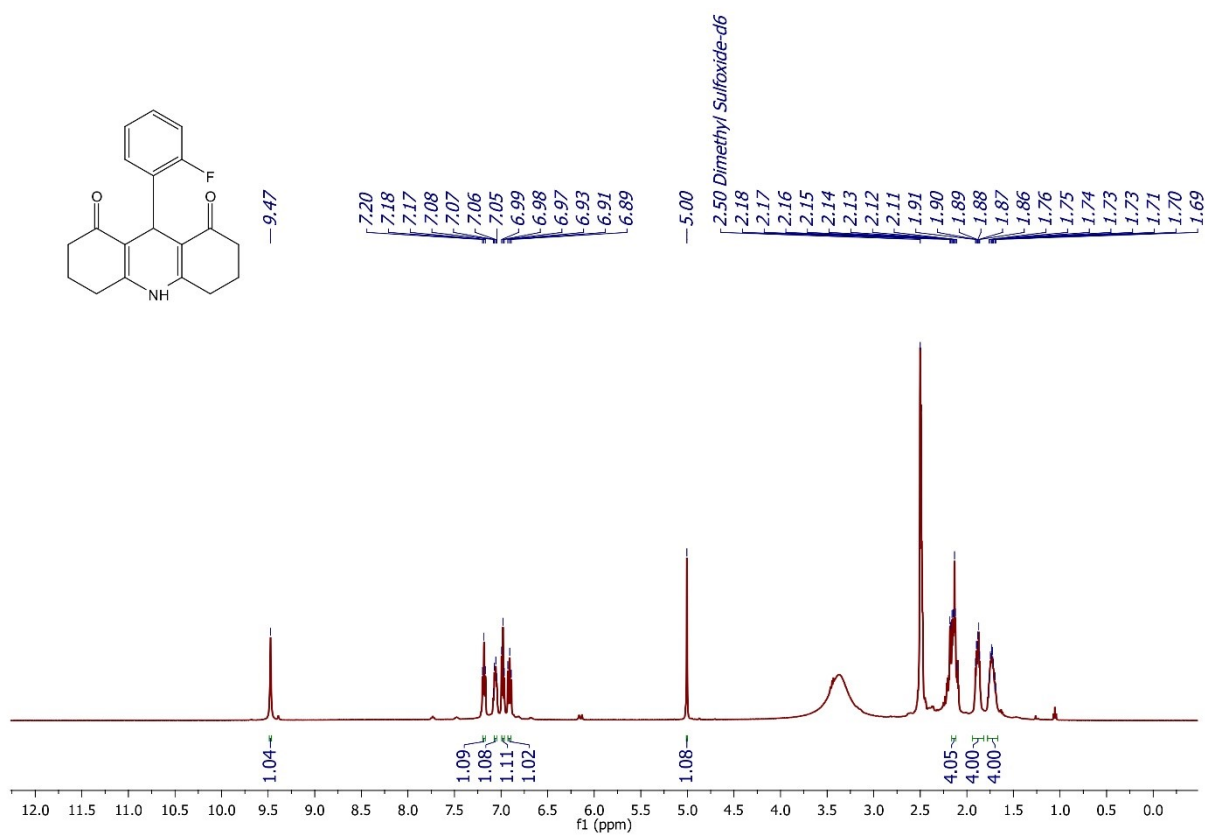


Figure S2-12.1.  $^1\text{H-NMR}$  spectrum of 12b

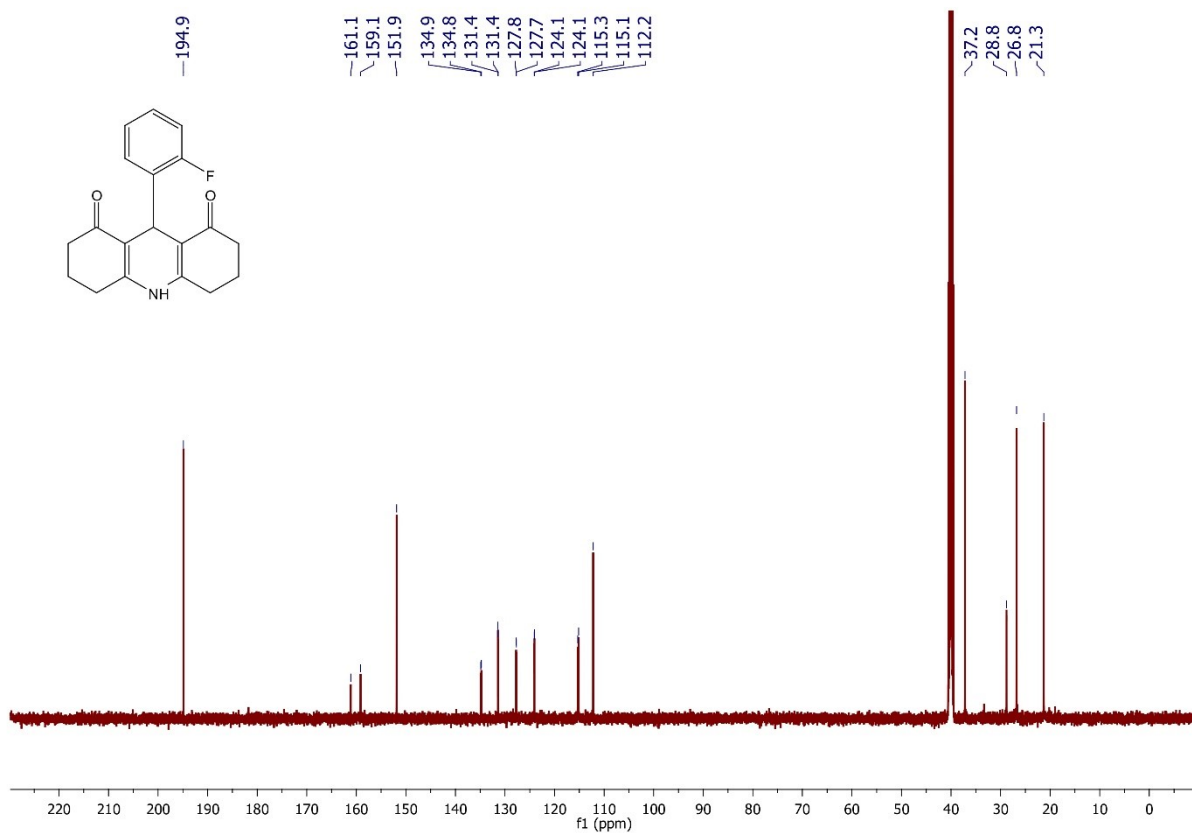
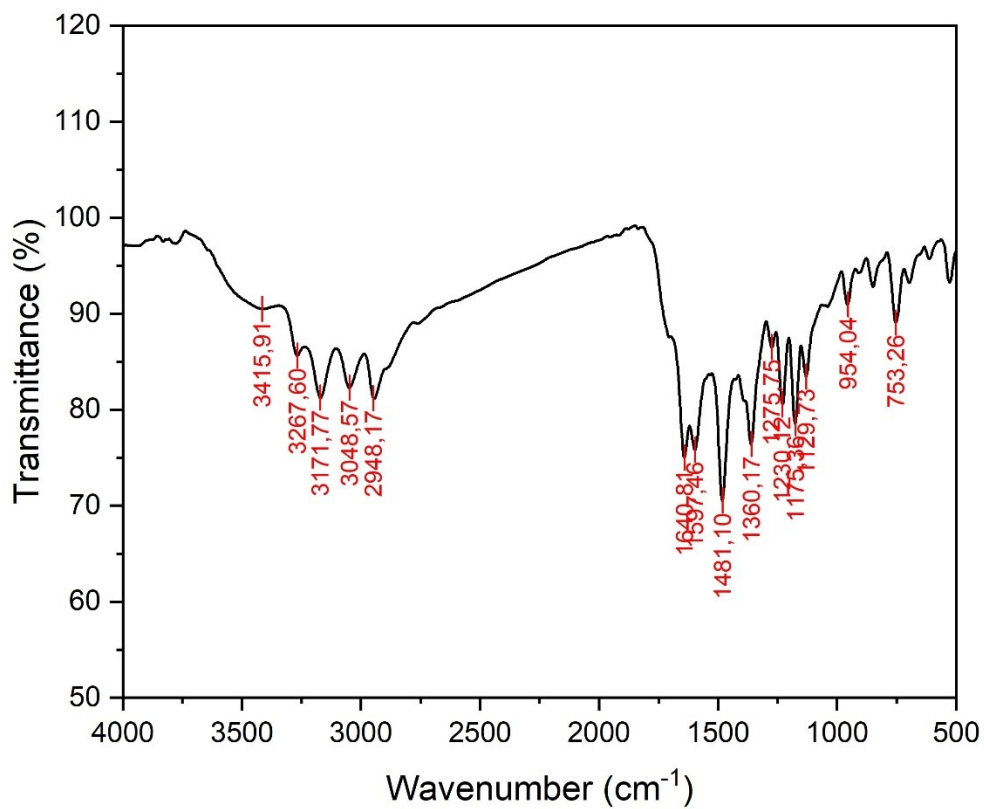


Figure S2-12.2.  $^{13}\text{C-NMR}$  spectrum of 12b





**Figure S2-12.3.** FT-IR spectra of **12b**

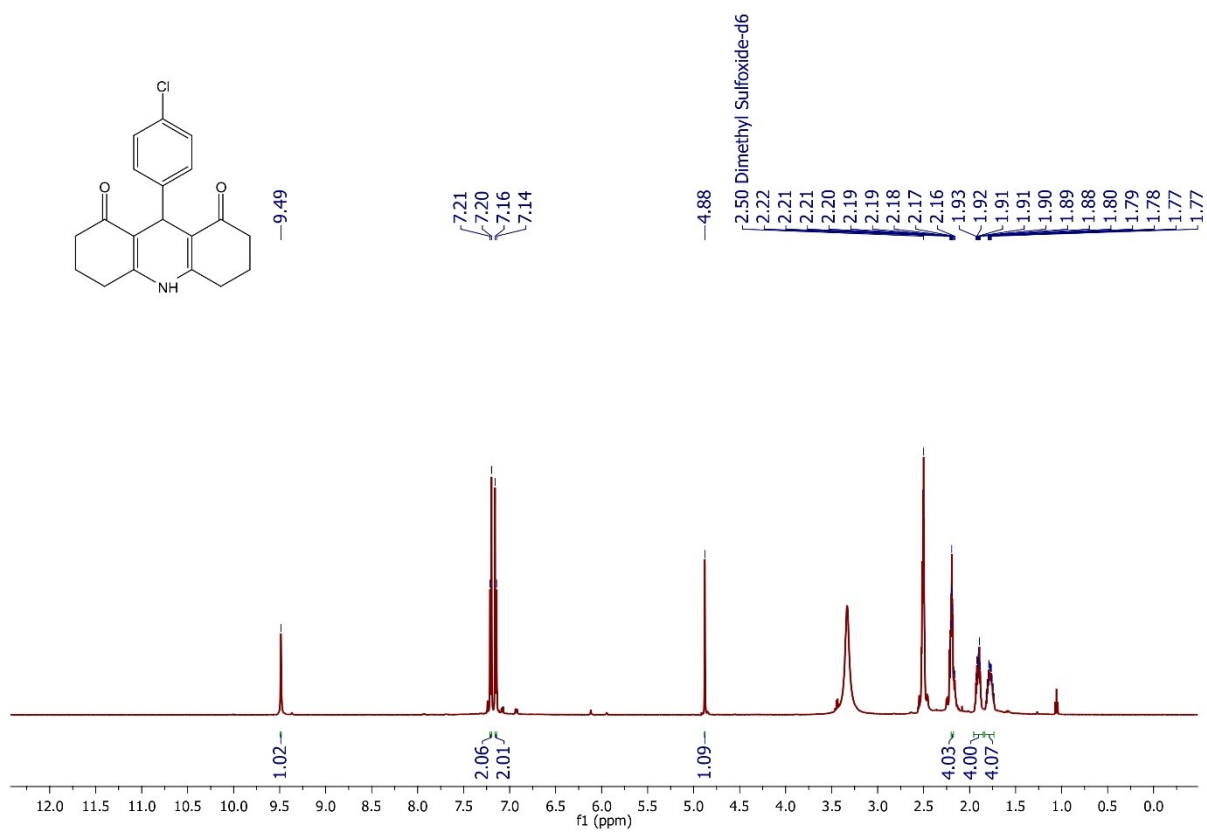


Figure S2-13.1. <sup>1</sup>H-NMR spectrum of 13b

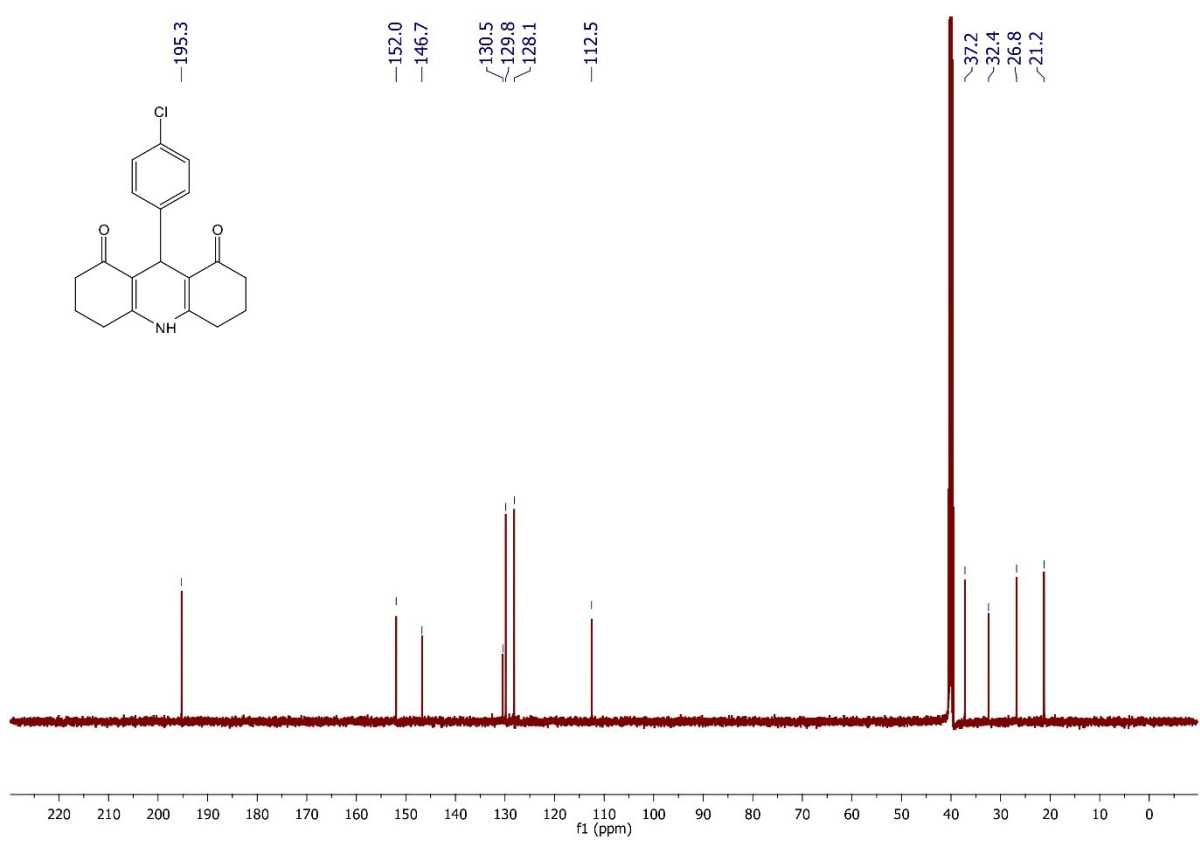
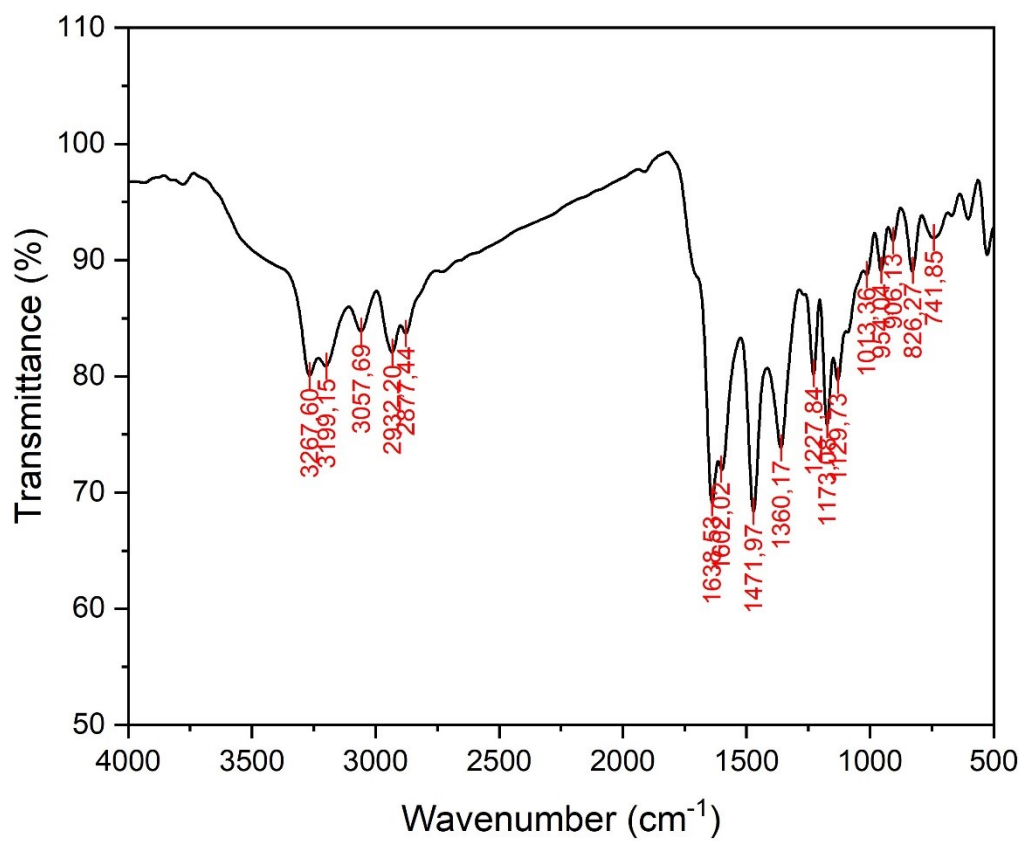


Figure S2-13.2. <sup>13</sup>C-NMR spectrum of 13b



**Figure S2-13.3.** FT-IR spectra of **13b**

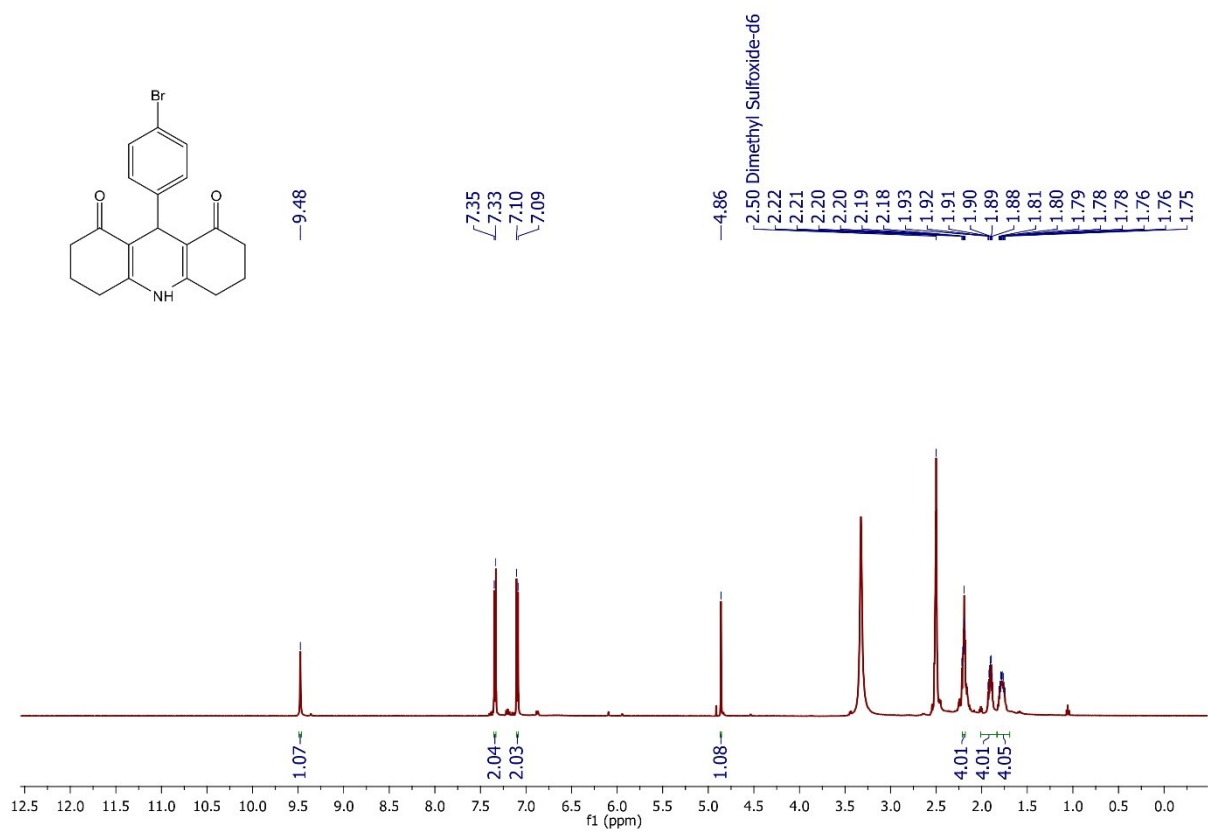


Figure S2-14.1. <sup>1</sup>H-NMR spectrum of 14b

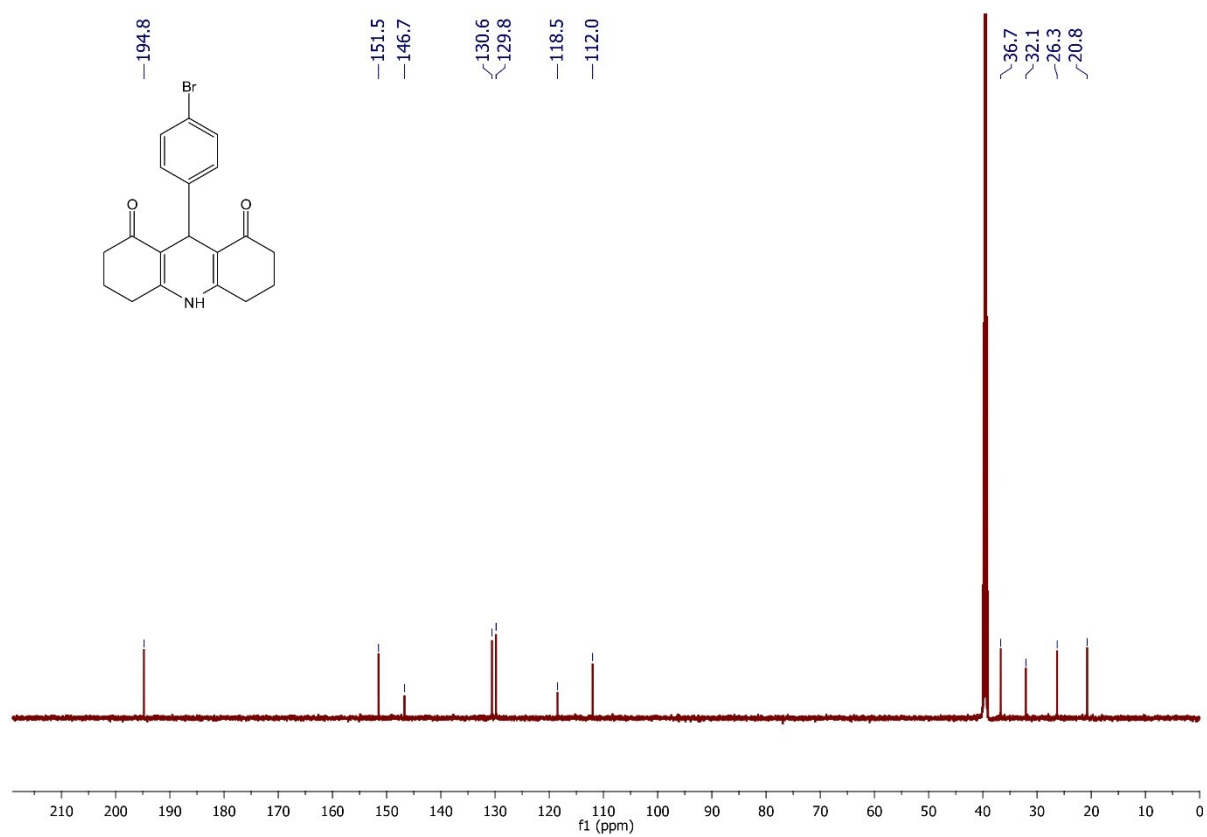
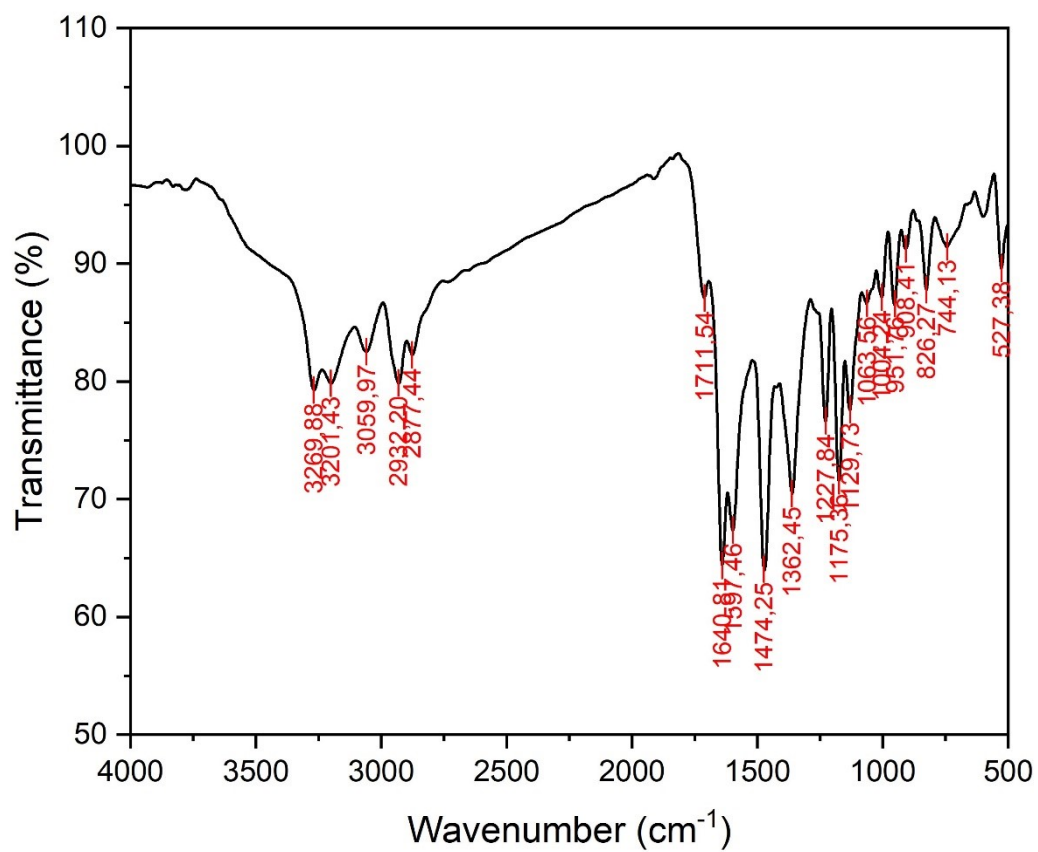


Figure S2-14.2. <sup>13</sup>C-NMR spectrum of 14b



**Figure S2-14.3.** FT-IR spectra of **14b**

## Section S4. References

1. R. A. Sheldon, *ACS Sustainable Chem. Eng.*, 2018, **6**, 32-48.
2. D. J. C. Constable, A. D. Curzons and V. L. Cunningham, *Green Chem.*, 2002, **4**, 521-527.
3. K. Van Aken, L. Streckowski and L. Patiny, *Beilstein J. Org. Chem.*, 2006, **2**, 3.
4. N. Sahiba, A. Sethiya, J. Soni and S. Agarwal, *ChemistrySelect*, 2020, **5**, 13076-13080.
5. P. N. Chavan, D. N. Pansare and R. N. Shelke, *J. Chin. Chem. Soc.*, 2019, **66**, 822-828.
6. B. Zeynizadeh and M. Gilanizadeh, *Curr. Chem. Lett.*, 2020, 71-78.
7. R. Eyvazzadeh-Keihan, N. Bahrami, R. Taheri-Ledari and A. Maleki, *Diam. Relat. Mater.*, 2020, **102**.
8. S. S. Mansoor, K. Aswin, K. Logaiya and S. P. N. Sudhan, *J. Taibah Univ. Sci.*, 2018, **8**, 265-275.
9. M. Kiani and M. Mohammadipour, *RSC. Adv.*, 2017, **7**, 997-1007.
10. E. Eidi, M. Z. Kassaei and Z. Nasresfahani, *Appl. Organomet. Chem.*, 2015, **29**, 793-797.