Supporting Information 1

# Covalently anchored carboxylic acid on uniform spherical silica nanoparticles with narrow slit like mesopores for the synthesis of pyrroloacridinones: CuI-catalyzed further C(sp3)-H oxyfunctionalization for C=O formation

**Suman Ray[a], Asim Bhaumik[b], Malay Pramanik[b] and Chhanda Mukhopadhyay[a]***

*a: Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata-700009, India*
*b: Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India.*

*cmukhop@yahoo.co.in* *

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### A. Materials and instrumentation

The $^{1}H$- and $^{13}C$-NMR analyses were carried out on Bruker-Advanced Digital 300 MHz instrument in $d_6$-DMSO with TMS as an internal reference. IR spectra were recorded in KBr pellets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. CHN analysis was performed using a Perkin-Elmer 2400 Series II CHN analyzer. X-ray single crystal analysis was performed in a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator. Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb 1C at 77 K. Prior to gas adsorption, all the samples were degassed for 2 h at 403 K. Transmission electron microscopic images were recorded on a JEOL 2010 TEM operated at 200 kV in Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India. Carbon 13 CP MAS NMR and 29Si MAS NMR was referenced with respect to external TMS and 10-12 kHz speed in BRUKER DSX-300 solid state NMR spectrometer in NMR Research Centre, IISc, Bangalore-560012.

### B. Preparation of uniform spherical mesoporous silica nanoparticles (SMSNP)

In a typical procedure, first, 390 g (390 mL) water and 317 g (400 mL) MeOH was taken in a 1litre open beaker fitted with a magnetic stirrer. Then 3.52 g CTAB was added at room temperature (30-35°C) and stirred for 30 min. After a clear solution was obtained, tetraethylorthosilicate (TEOS) was added dropwise from a dropping funnel under stirring condition. Then 10 mL 0.4 N NaOH solution was added drop wise taking 1h period of time. The stirring was continued for the next 8h at room temperature and then aged overnight (12-14h) at room temperature. Then it was filtered and washed thoroughly with deionized water and dried at 35-40°C for 5 days. The dry powder was calcined at 550°C for 6-8h under static air to obtain the uniform spherical mesoporous silica nanoparticles.

### C. Preparation of SMSNP supported mercaptopropane (1)

The surface modification of the SMSNP by post synthesis grafting method was achieved by reacting the silanols of the SMSNP with MPS (3-mercaptopropyltrimethoxysilane) (Aldrich) under nitrogen atmosphere. 20 mmol of MPS was slowly added to a dry toluene solution containing 10 g of SMSNP and refluxed for 18 h under $N_2$. The material was filtered after cooling to ambient temperature, washed with dry toluene and dichloromethane. Soxhlet extraction was carried out for 24 h in dichloromethane (DCM) to remove occluded organosilane. The sample was dried in vacuum for 10 h and characterized by solid state 13C CP MAS NMR spectra and CHN analysis.

### D. Preparation of spherical mesoporous silica nanoparticles supported carboxylic acid (SMSNP-CA) catalyst (3)

In a typical procedure 5g of mercaptopropane anchored SMSNP (**1**) was reacted with 10 mmol of bromo-acetic acid (**2**) in dry toluene at room temperature (30-35°C) for 18h in presence of 1mmol triethylamine. The liberated HCl was removed through a $CaCl_2$ drying tube under reduced pressure to a water trap. The solid was washed successively with water (10 times), ethanol (3 times) and dried at 110°C for 3h. No precipitate was obtained on treatment of silver nitrate solution with the aqueous extract of the solid after washing it ten times with distilled water. The aforesaid observation conclusively proved the absence of $Br^-$ on the solid catalyst after thorough washing with distilled water. The as prepared SMSNP supported -COOH catalyst (**3**) was abbreviated as **SMSNP-CA** (**3**).

### E. General synthesis of the pyrrolo[2,3,4-kl]acridinone derivatives

All the reactions were carried out in round bottomed flask equipped with a magnetic stirrer and a reflux condenser. In a typical reaction a mixture of cyclic-1,3-diketones (**4**) (1 mmol) and different amines (**6**) (1 mmol) in EtOH (2 ml) were refluxed on a water bath for 1h using 20 mg **SMSNP-CA** (**3**). Then isatin (**5**) (1 mmol) was added and again refluxed till completion. The completion of the reaction was indicated by the disappearance of the starting materials in thin layer chromatography. The products precipitated out once their formation started. After completion of the reaction, the crude product was filtered. The residue contained both the crude product and the catalyst. Then the product was taken in dichloromethane (DCM) and filtered again to separate the product as filtrate from the catalyst (as residue). The DCM was evaporated in rotary evaporator and the crude product was further purified by silica gel column chromatography using EtOAc/petroleum ether (8%/92% v/v) as eluent.

### F. General procedure for the CuI catalyzed oxidation of 4,5-dihydropyrrolo[2,3,4-*kl*]acridinones

This reaction was carried out in a three necked round-bottomed flask equipped with a magnetic stirrer, an oxygen inlet having a steady flow of oxygen (10 mL/min). In a typical reaction 4,5-dihydropyrrolo[2,3,4-*kl*]acridinone (**7**) was refluxed in EtOH with 10 mol% CuI in steady flow of oxygen until completion. The completion of the reaction was indicated by the disappearance of the starting material in thin layer chromatography. After completion of the reaction the excess ethanol was evaporated. The compound was taken in dichloromethane and filtered to separate the product as filtrate from catalyst (CuI) as residue. The filtrate was evaporated in a rotary evaporator and the crude

product was further purified by silica gel column chromatography using EtOAc/petroleum ether (60-80 ºC)(10%/90% v/v) as eluant.

G. FTIR spectrum of **SMSNP-CA** (**3**).

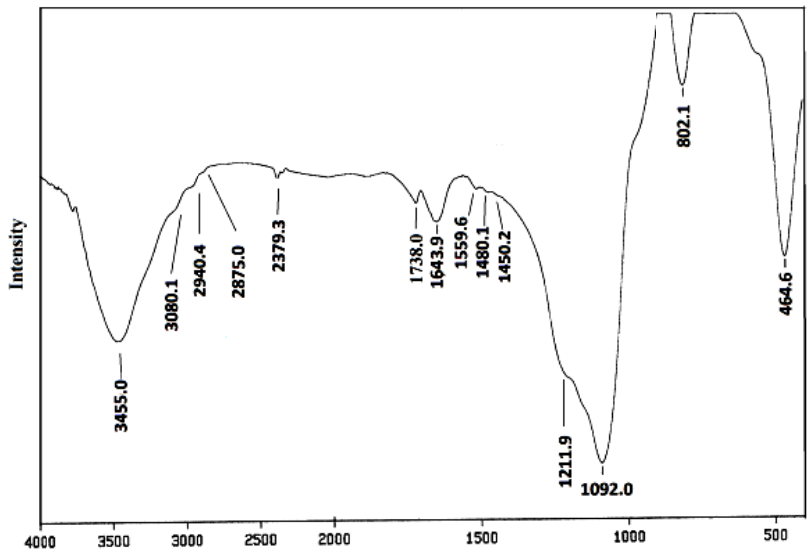



***Figure 1***. FTIR spectrum of **SMSNP-CA** (**3**).

## H. ORTEP diagram of 7n

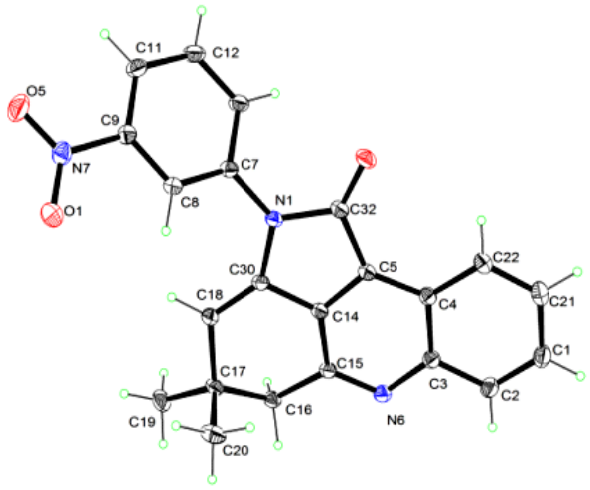
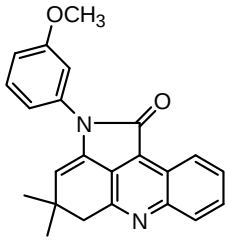



***Figure 2***. X-ray single crystal structure of **7n** (**CCDC 972996**).

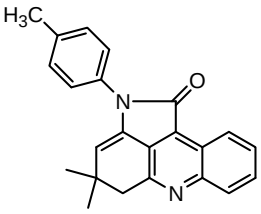
## I. Spectroscopic characterization of 7a-7n

### 4,5-dihydro-2-(3-methoxyphenyl)-4,4-dimethylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7a):



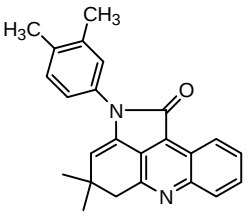

Light yellow colored solid; m.p. 200-202 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86%. Found: C, 77.52; H, 5.67; N, 7.87%; IR (KBr) $cm^{-1}$: 3387, 2956, 1704, 1544, 1188, 839, 723, 523; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.25 (6H, s, 2x$CH_3$), 3.14 (2H, s, $CH_2$), 3.80 (3H, s, $OCH_3$), 5.58 (1H, s, CH), 6.88 (1H, dd, J = 8.3 Hz, J = 2.1 Hz, arom.), 7.00-7.01 (2H, m, arom.), 7.37 (1H, t, J = 8.1 Hz, arom.), 7.59 (1H, t, J = 7.2 Hz, arom.), 7.68 (1H, dt, J = 8.1 Hz, J = 1.5 Hz, arom.), 8.10 (1H, d, J = 8.1 Hz, arom.), 8.65 (1H, d, J = 7.3 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 30.8, 37.1, 44.2, 55.5, 112.3, 113.2, 118.5, 118.6, 122.6, 124.2, 125.0, 126.4, 127.8, 129.4, 129.5, 130.0, 133.4, 135.9, 149.7, 154.6, 160.3, 166.6.

### 4,5-dihydro-4,4-dimethyl-2-p-tolylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7b):



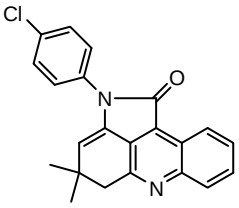

Light yellow colored solid; m.p. 220-222 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23%. Found: C, 81.18; H, 5.93; N, 8.24%; IR (KBr) $cm^{-1}$: 3074, 2959, 1719, 1467, 1354, 1140, 837, 732, 477; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.29 (6H, s, 2x$CH_3$), 2.41 (3H, s, $CH_3$), 3.18 (2H, s, $CH_2$), 5.56 (1H, s, CH), 7.30-7.37 (4H, m, arom.), 7.62 (1H, t, J = 7.7 Hz, arom.), 7.72 (1H, dt, J = 7.7 Hz, J = 1.5 Hz, arom.), 8.14 (1H, d, J = 8.4 Hz, arom.), 8.70 (1H, dd, J = 8.0 Hz, J = 1.5 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.2, 30.9, 37.1, 44.2, 118.1, 122.7, 124.3, 125.1, 126.2, 126.3, 126.4, 126.4, 127.7, 129.4, 129.9, 130.0, 132.1, 133.6, 137.5, 149.7, 154.6, 166.8.

### 4,5-dihydro-4,4-dimethyl-2-(3,4-dimethylphenyl)pyrrolo[2,3,4-kl]acridin-1(2H)-one (7c):



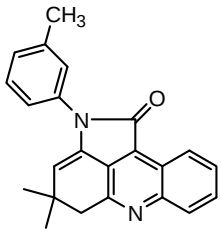
Light yellow colored solid; m.p. 194-196 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{24}H_{22}N_2O$: C, 81.33; H, 6.26; N, 7.90%. Found: C, 81.35; H, 6.27; N, 7.91%; IR (KBr) $cm^{-1}$: 3420, 2974, 1703, 1502, 1445, 1028, 781; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.33 (6H, s, 2x$CH_3$), 2.35 (3H, s, $CH_3$), 2.36 (3H, s, $CH_3$), 3.22 (2H, s, $CH_2$), 5.60 (1H, s, CH), 7.20-7.22 (1H, m, arom.), 7.28-7.32 (2H, m, arom.), 7.67 (1H, t, J = 7.2 Hz, arom.), 7.76 (1H, t, J = 7.8 Hz, arom.), 8.18 (1H, d, J = 8.4 Hz, arom.), 8.74 (1H, dd, J = 8.4 Hz, J = 1.2 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 19.4, 19.9, 30.8, 37.0, 43.8, 118.3, 122.6, 123.7, 124.2, 125.3, 126.3, 127.5, 127.8, 128.9, 129.6, 130.3, 132.1, 133.5, 136.3, 137.8, 149.0, 154.4, 166.6.

**2-(4-chlorophenyl)-4,5-dihydro-4,4-dimethylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7d):**



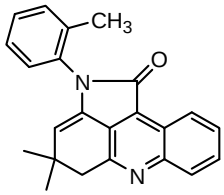
Light yellow colored solid; m.p. 189-191 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{22}H_{17}ClN_2O$: C, 73.23; H, 4.75; N, 7.76%. Found: C, 73.24; H, 4.76; N, 7.77%; IR (KBr) $cm^{-1}$: 3087, 2971, 1724, 1481, 1365, 1160, 837, 745, 499; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.29 (6H, s, 2x$CH_3$), 3.18 (2H, s, $CH_2$), 5.56 (1H, s, CH), 7.42 (4H, q, J = 7.8 Hz, arom.), 7.59 (1H, t, J = 7.2 Hz, arom.), 7.69 (1H, dt, J = 7.8 Hz, J = 1.2 Hz, arom.), 8.10 (1H, d, J = 8.4 Hz, arom.), 8.62 (1H, dd, J = 8.1 Hz, J = 0.6 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 30.8, 37.1, 44.1, 118.4, 122.5, 124.2, 124.8, 126.4, 127.5, 127.6, 127.9, 129.5, 129.6, 129,7, 133.1, 133.3, 149.7, 154.5, 166.6.

**4,5-dihydro-4,4-dimethyl-2-m-tolylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7e):**



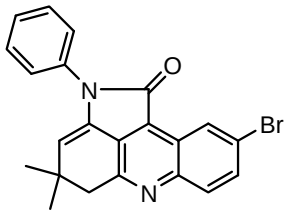
Light yellow colored solid; m.p. 218-220 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23%. Found: C, 81.17; H, 5.93; N, 8.24%; IR (KBr) $cm^{-1}$: 3077, 2961, 1717, 1479, 1345, 1158, 833, 742, 497; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.35 (6H, s, 2x$CH_3$), 2.47 (3H, s, $CH_3$), 3.25 (2H, s, $CH_2$), 5.64 (1H, s, CH), 7.23-7.30 (2H, m, arom.), 7.35 (1H, s, arom.), 7.44 (1H, t, J = 7.8 Hz, arom.), 7.69 (1H, t, J = 7.8 Hz, arom.), 7.78 (1H, t, J = 7.8 Hz, arom.), 8.22 (1H, d, J = 8.4 Hz, arom.), 8.75 (1H, d, J = 8.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.4, 30.8, 37.1, 44.0, 118.4, 122.6, 123.4, 124.2, 125.2, 126.4, 127.1, 127.8, 128.4, 129.1, 129.2, 129.6, 133.4, 134.6, 139.4, 149.4, 154.5, 166.7.

**4,5-dihydro-4,4-dimethyl-2-o-tolylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7f):**



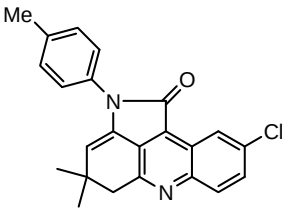

Light yellow colored solid; m.p. 200-202 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23%. Found: C, 81.17; H, 5.93; N, 8.25%; IR (KBr) $cm^{-1}$: 3064, 2964, 1709, 1465, 1344, 1138, 832, 772, 447; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.19 (3H, s, $CH_3$), 1.20 (3H, s, $CH_3$), 2.11 (3H, s, $CH_3$), 3.11 (2H, s, $CH_2$), 5.17 (1H, s, CH), 7.21-7.28 (4H, m, arom.), 7.53-7.64 (2H, m, arom.), 8.08 (1H, d, J = 8.4 Hz, arom.), 8.61 (1H, d, J = 7.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 18.0, 30.8, 31.0, 37.1, 44.3, 117.8, 122.7, 124.3, 125.2, 126.7, 126.9, 127.7, 128.8, 129.0, 129.4, 129.5, 131.3, 133.3, 133.7, 136.8, 149.7, 154.6, 166.7.

**9-Bromo-4,4-dimethyl-2-phenyl-4,5-dihydro-2H-pyrrolo[2,3,4-kl]acridin-1-one (7g):**



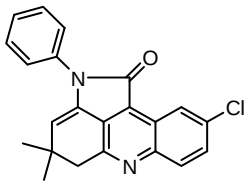

Light yellow colored solid; m.p. 165-167 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{22}H_{17}BrN_2O$: C, 65.20; H, 4.23; N, 6.91%. Found: C, 65.21; H, 4.24; N, 6.92%; IR (KBr) $cm^{-1}$: 3068, 1701, 1599, 1498, 1354, 1144, 848, 738, 590; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.33 (6H, s, 2x$CH_3$), 3.18 (2H, s, $CH_2$), 5.67 (1H, s, CH), 7.40-7.54 (5H, m, arom.), 7.79 (1H, dd, J = 9.0 Hz, J = 2.4 Hz, arom.), 7.99 (1H, d, J = 9.3 Hz, arom.), 8.84 (1H, d, J = 1.8 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 30.8, 37.1, 44.0, 119.1, 122.0, 123.5, 123.9, 126.2, 126.4, 126.8, 127.5, 129.3, 130.9, 132.8, 133.0, 134.5, 148.1, 155.0, 166.0.

**9-Chloro-4,4-dimethyl-2-p-tolyl-4,5-dihydro-2H-pyrrolo[2,3,4-kl]acridin-1-one (7h):**



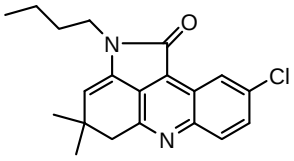

Light yellow colored solid; m.p. 190-192 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{19}ClN_2O$: C, 73.69; H, 5.11; N, 7.47%. Found: C, 73.71; H, 5.12; N, 7.48%; IR (KBr) $cm^{-1}$: 3074, 2961, 1719, 1469, 1332, 1139, 833, 767, 449; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.10 (6H, s, 2x$CH_3$), 2.21 (3H, s, $CH_3$), 2.98 (2H, s, $CH_2$), 5.41 (1H, s, CH), 7.13 (4H, t, J = 8.4 Hz, arom.), 7.44 (1H, dd, J = 9.0 Hz, J = 2.1 Hz, arom.), 7.88 (1H, d, J = 9.0 Hz, arom.), 8.48 (1H, d, J = 2.4 Hz, arom.).

**9-chloro-4,5-dihydro-4,4-dimethyl-2-phenylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7i):**




Light yellow colored solid; m.p. 185-187 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{22}H_{17}ClN_2O$: C, 73.23; H, 4.75; N, 7.76%. Found: C, 73.24; H, 4.76; N, 7.77%; IR (KBr) $cm^{-1}$: 3048, 1697, 1596, 1498, 1340, 1140, 845, 734, 499; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.25 (6H, s, 2x$CH_3$), 3.15 (2H, s, $CH_2$), 5.59 (1H, s, CH), 7.31-7.52 (5H, m, arom.), 7.59 (1H, dd, J = 9.0 Hz, J = 2.4 Hz, arom.), 8.00 (1H, d, J = 9.0 Hz, arom.), 8.60 (1H, d, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 30.4, 36.7, 43.6, 118.7, 122.7, 122.8, 123.7, 125.9, 126.5, 127.1, 128.9, 129.9, 130.4, 132.7, 133.4, 134.2, 147.5, 154.4, 165.7.

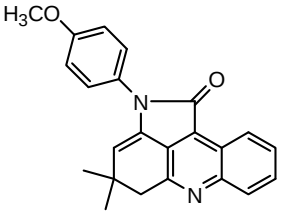
**2-butyl-9-chloro-4,5-dihydro-4,4-dimethylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7j):**




Light yellow colored solid; m.p. 148-150 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{20}H_{21}ClN_2O$: C, 70.48; H, 6.21; N, 8.22%. Found: C, 70.49; H, 6.22; N, 8.23%; IR (KBr) $cm^{-1}$: 3084, 2954, 1713, 1460, 1326, 1128, 834, 772, 597, 449; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 0.90 (3H, t, J = 7.2 Hz, $CH_3$), 1.27-1.38

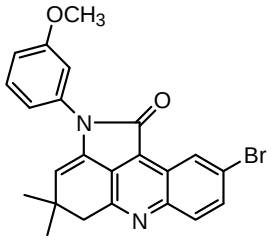
(8H, m, 2x$CH_3$, $CH_2$), 1.59-1.69 (2H, m, $CH_2$), 3.07 (2H, s, $CH_2$), 3.73 (2H, t, J = 7.2 Hz, $CH_2$), 5.48 (1H, s, CH), 7.57 (1H, dd, J = 9.0 Hz, J = 2.4 Hz, arom.), 7.96 (1H, d, J = 9.0 Hz, arom.), 8.57 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 13.7, 20.2, 31.0, 31.1, 37.1, 40.0, 44.1, 117.3, 123.2, 125.0, 127.0, 130.1, 130.7, 133.1, 133.6, 148.0, 154.6, 167.0.

**4,5-dihydro-2-(4-methoxyphenyl)-4,4-dimethylpyrrolo[2,3,4-kl]acridin-1(2H)-one (7k):**




Light yellow colored solid; m.p. 185-187 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86%. Found: C, 77.52; H, 5.67; N, 7.87%; IR (KBr) $cm^{-1}$: 3377, 2954, 1712, 1514, 1258, 829, 777, 521; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.29 (6H, s, 2x$CH_3$), 3.19 (2H, s, $CH_2$), 3.84 (3H, s, $CH_3$), 5.53 (1H, s, CH), 7.03 (2H, d, J = 8.7 Hz, arom.), 7.38 (2H, d, J = 8.7 Hz, arom.), 7.62 (1H, t, J = 7.8 Hz, arom.), 7.72 (1H, t, J = 7.8 Hz, arom.), 8.15 (1H, d, J = 8.4 Hz, arom.), 8.69 (1H, d, J = 8.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 30.9, 37.0, 44.2, 55.5, 114.6, 118.0, 122.6, 124.2, 125.1, 126.4, 127.4, 127.7, 127.8, 129.3, 129.5, 133.8, 149.6, 154.5, 158.8, 166.9.

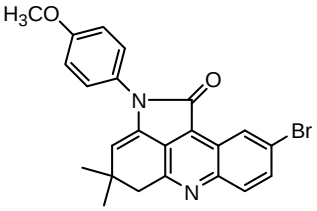
**9-Bromo-2-(3-methoxy-phenyl)-4,4-dimethyl-4,5-dihydro-2H-pyrrolo[2,3,4-kl]acridin-1-one (7l):**




Light yellow colored solid; m.p. 170-172 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{19}BrN_2O_2$: C, 63.46; H, 4.40; N, 6.44%. Found: C, 63.47; H, 4.41; N, 6.46%; IR (KBr) $cm^{-1}$: 3379, 2955, 1722, 1510, 1260, 830, 779, 523; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.26 (6H, s, 2x$CH_3$), 3.12 (2H, s, $CH_2$), 3.80 (3H, s, $OCH_3$), 5.63 (1H, s, CH), 6.89 (1H, dd, J = 6.3 Hz, J = 2.4 Hz, arom.), 6.98-7.00 (2H, m, arom.), 7.39 (1H, dt, J = 8.4 Hz, J = 3.9 Hz, arom.), 7.74 (1H, dd, J = 9.0 Hz, J = 2.4 Hz, arom.), 7.96 (1H, dd, J = 9.0 Hz, J = 3.6 Hz, arom.),

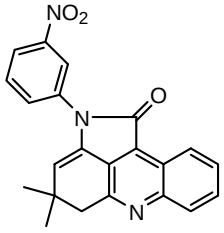
7.80 (1H, d, J = 2.4 Hz, arom.) ; $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 30.8, 37.1, 44.1, 55.5, 112.3, 113.3, 118.5, 119.4, 122.1, 123.6, 124.0, 126.5, 126.9, 130.0, 130.9, 133.0, 133.1, 135.7, 148.2, 155.0, 160.3, 166.1.

**9-Bromo-2-(3-methoxy-phenyl)-4,4-dimethyl-4,5-dihydro-2H-pyrrolo[2,3,4-kl]acridin-1-one (7m):**



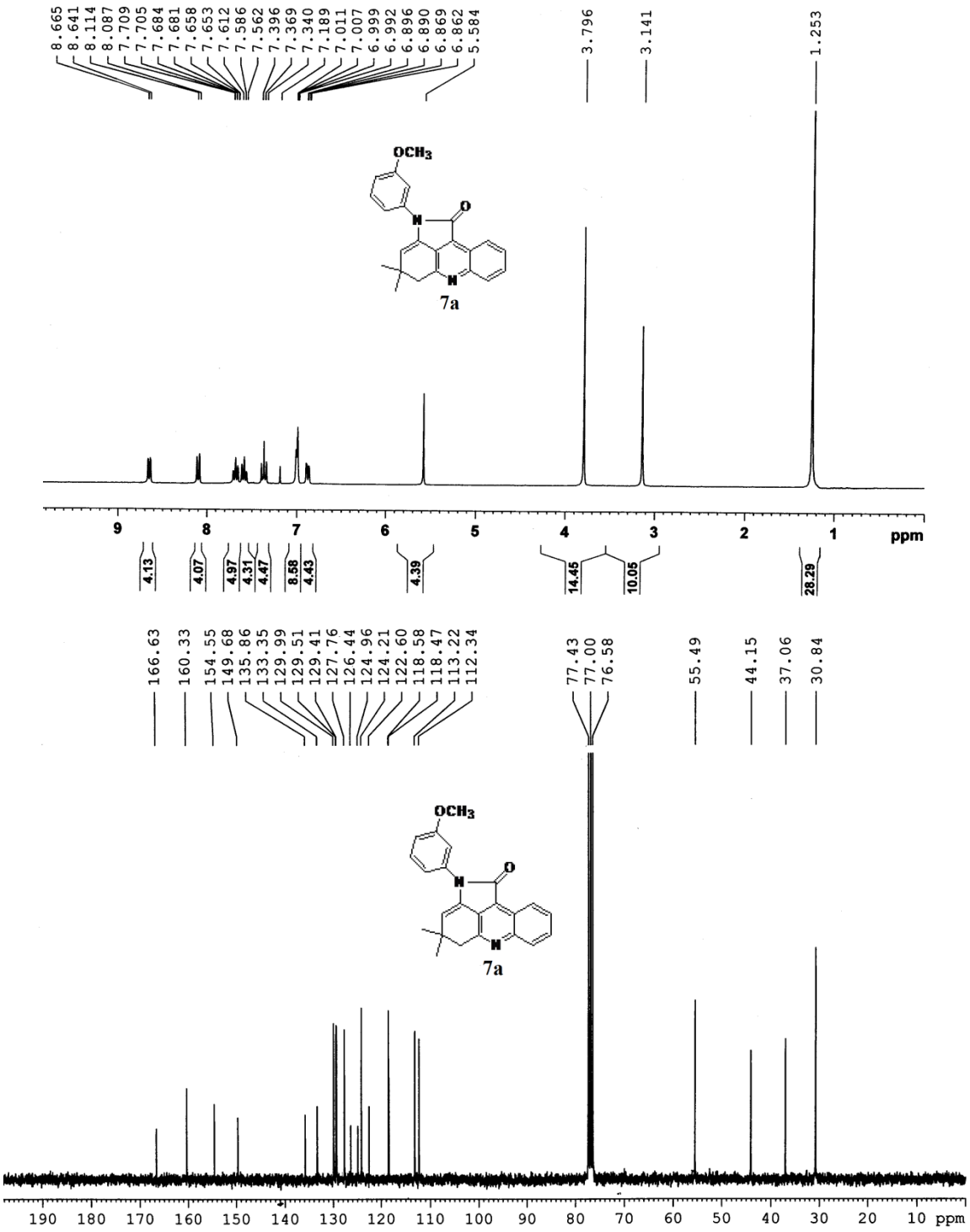

Light yellow colored solid; m.p. 196-198 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{23}H_{19}BrN_2O_2$: C, 63.46; H, 4.40; N, 6.44%. Found: C, 63.48; H, 4.41; N, 6.45%; IR (KBr) $cm^{-1}$: 3366, 2964, 1732, 1504, 1148, 819, 779, 529; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.25 (6H, s, 2x$CH_3$), 3.12 (2H, s, $CH_2$), 3.81 (3H, s, $OCH_3$), 5.52 (1H, s, CH), 6.99 (2H, d, J = 8.7 Hz, arom.), 7.32 (2H, d, J = 9.0 Hz, arom.), 7.75 (1H, dd, J = 9.0 Hz, J = 2.1 Hz, arom.), 7.96 (1H, d, J = 9.0 Hz, arom.), 8.80 (1H, d, J = 1.8 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 24.6, 30.8, 37.8, 49.3, 108.4, 112.6, 115.8, 117.4, 120.3, 120.6, 120.9, 121.5, 124.6, 126.7, 127.3, 141.9, 148.7, 152.7, 158.5, 166.2.

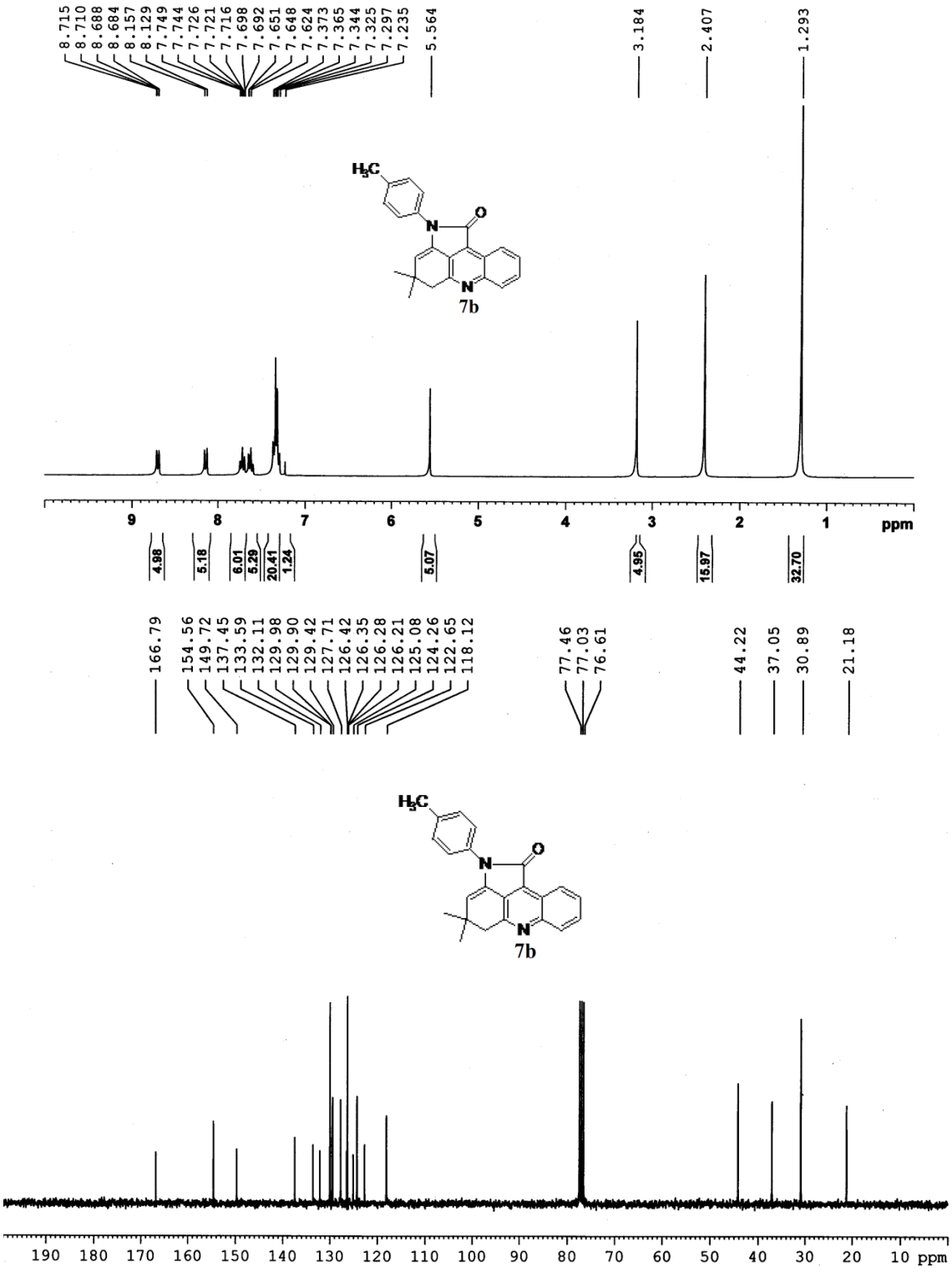
**4,4-Dimethyl-2-(3-nitro-phenyl)-4,5-dihydro-2H-pyrrolo[2,3,4-kl]acridin-1-one (7n):**




Light yellow colored solid; m.p. 180-182 °C (recrystallized from EtOAc/DCM, equal volume); Anal. Calcd for $C_{22}H_{17}N_3O_3$: C, 71.15; H, 4.61; N, 11.31%. Found: C, 71.17; H, 4.62; N, 11.32%; IR (KBr) $cm^{-1}$: 3078, 1699, 1598, 1488, 1357, 1167, 849, 736, 569, 499; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.36 (6H, s, 2x$CH_3$), 3.25 (2H, s, $CH_2$), 5.70 (1H, s, CH), 7.70-7.82 (3H, m, arom.), 7.92 (1H, dd, J = 8.4 Hz, J = 1.2 Hz, arom.), 8.20 (1H, d, J = 8.4 Hz, arom.), 8.27 (1H, dd, J = 8.4 Hz, J = 0.9 Hz, arom.), 8.43 (1H, t, J = 1.8 Hz, arom.), 8.71 (1H, d, J = 8.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 30.8, 37.2, 44.1, 118.6, 121.1, 121.9, 122.4, 124.2, 126.5, 128.1, 129.7, 129.9, 130.2, 132.0, 132.6, 136.2, 141.5, 148.9, 149.9, 154.5, 166.4.

**J. $^{1}$H and $^{13}$C NMR Spectra of 7a-7n**

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8.129
7.749
7.744
7.726
7.721
7.716
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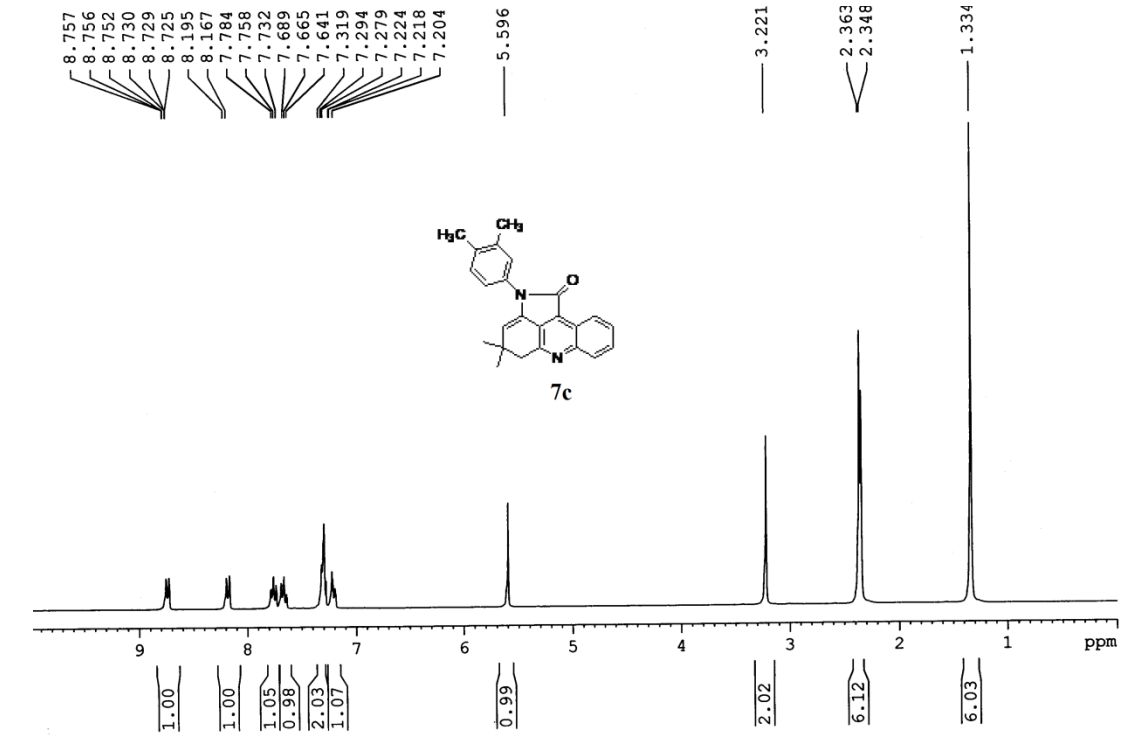
7.692
7.651
7.648
7.624
7.373
7.365
7.344
7.325
7.297
7.235
5.564
3.184
2.407
1.293
H3C
O
N
N
7b
9
8
7
6
5
4
3
2
1
ppm
4.98
5.18
6.01
5.29
20.41
1.24
5.07
4.95
15.97
32.70
166.79
154.56
149.72
137.45
133.59
132.11
129.98
129.90
129.42
127.71
126.42
126.35
126.28
126.21
125.08
124.26
122.65
118.12
77.46
77.03
76.61
44.22
37.05
30.89
21.18
H3C
O
N
N
7b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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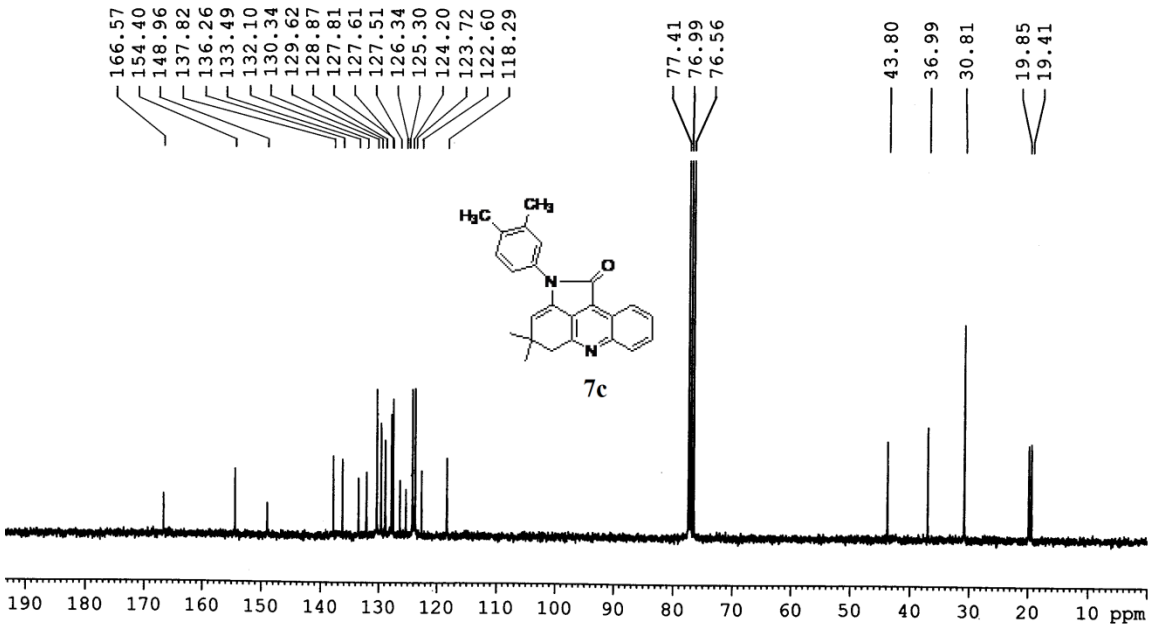
8.752
8.730
8.729
8.725
8.195
8.167
7.784
7.758
7.732
7.689
7.665
7.641
7.319
7.294
7.279
7.224
7.218
7.204
5.596
3.221
2.363
2.348
1.334
H3C
CH3
N
O
N
7c
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.05
0.98
2.03
1.07
0.99
2.02
6.12
6.03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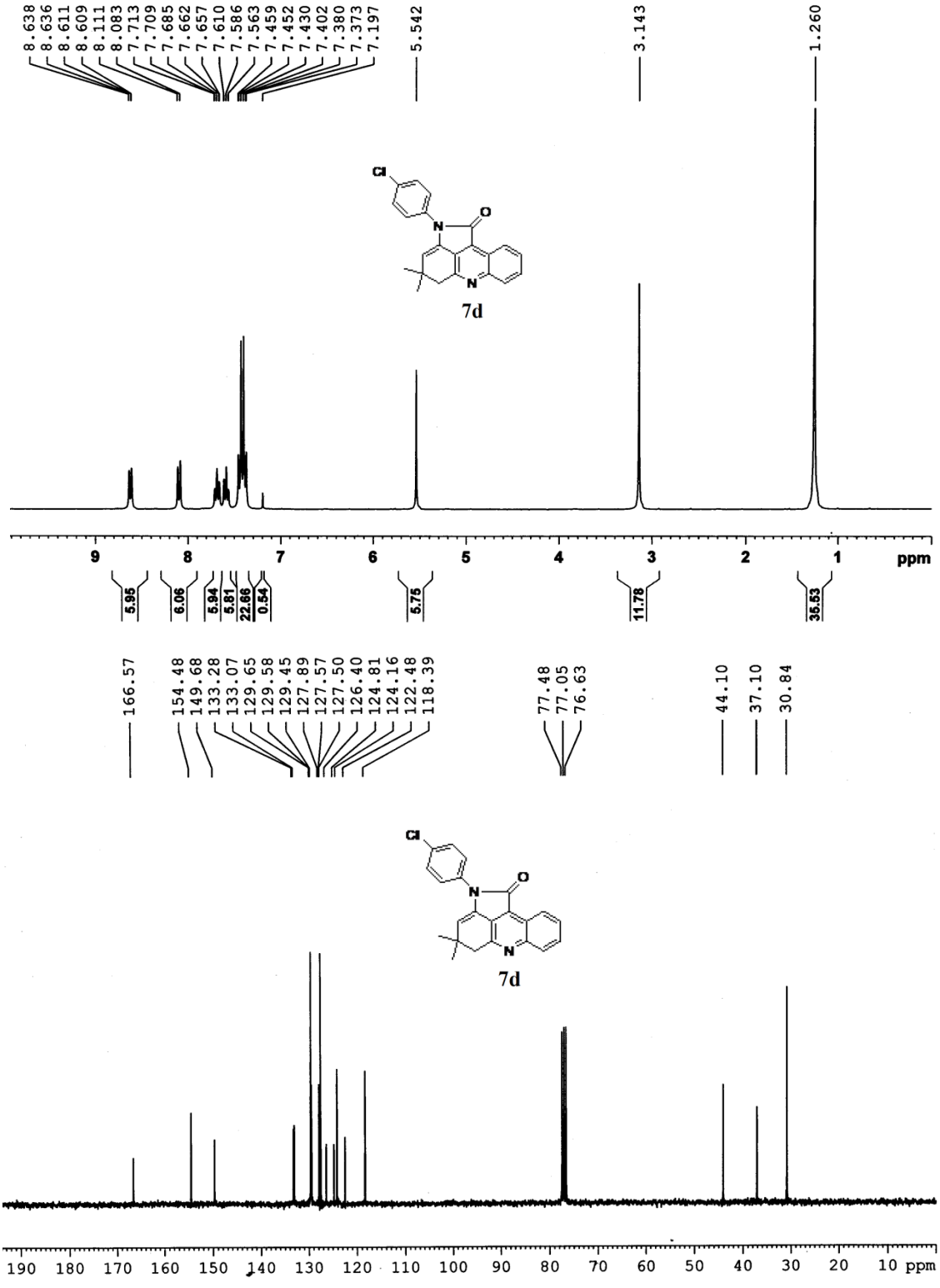
154.40
148.96
137.82
136.26
133.49
132.10
130.34
129.62
128.87
127.81
127.61
127.51
126.34
125.30
124.20
123.72
122.60
118.29
77.41
76.99
76.56
43.80
36.99
30.81
19.85
19.41
H3C
CH3
N
O
N
7c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.636
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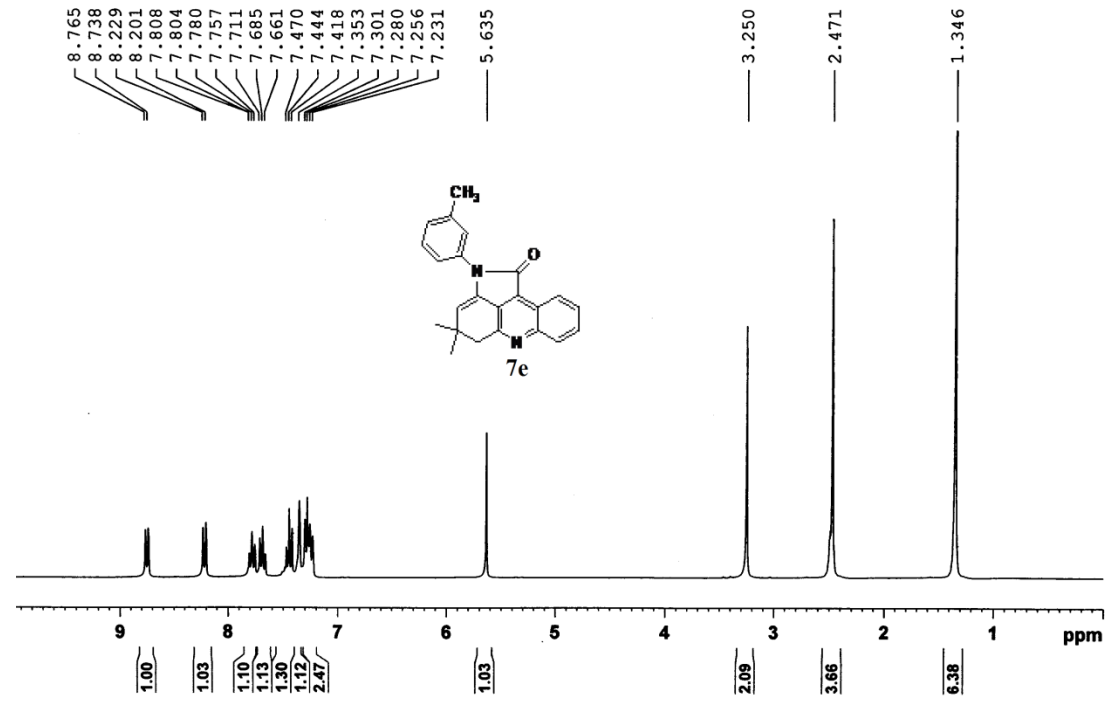
8.609
8.111
8.083
7.713
7.709
7.685
7.662
7.657
7.610
7.586
7.563
7.459
7.452
7.430
7.402
7.380
7.373
7.197
5.542
3.143
1.260
Cl
O
N
N
7d
9
8
7
6
5
4
3
2
1
ppm
5.95
6.06
5.94
5.81
22.66
0.54
5.75
11.78
35.53
166.57
154.48
149.68
133.28
133.07
129.65
129.58
129.45
127.89
127.57
127.50
126.40
124.81
124.16
122.48
118.39
77.48
77.05
76.63
44.10
37.10
30.84
Cl
O
N
N
7d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.229
8.201
7.808
7.804
7.780
7.757
7.711
7.685
7.661
7.470
7.444
7.418
7.353
7.301
7.280
7.256
7.231
5.635
3.250
2.471
1.346
7e
9
8
7
6
5
4
3
2
1
ppm
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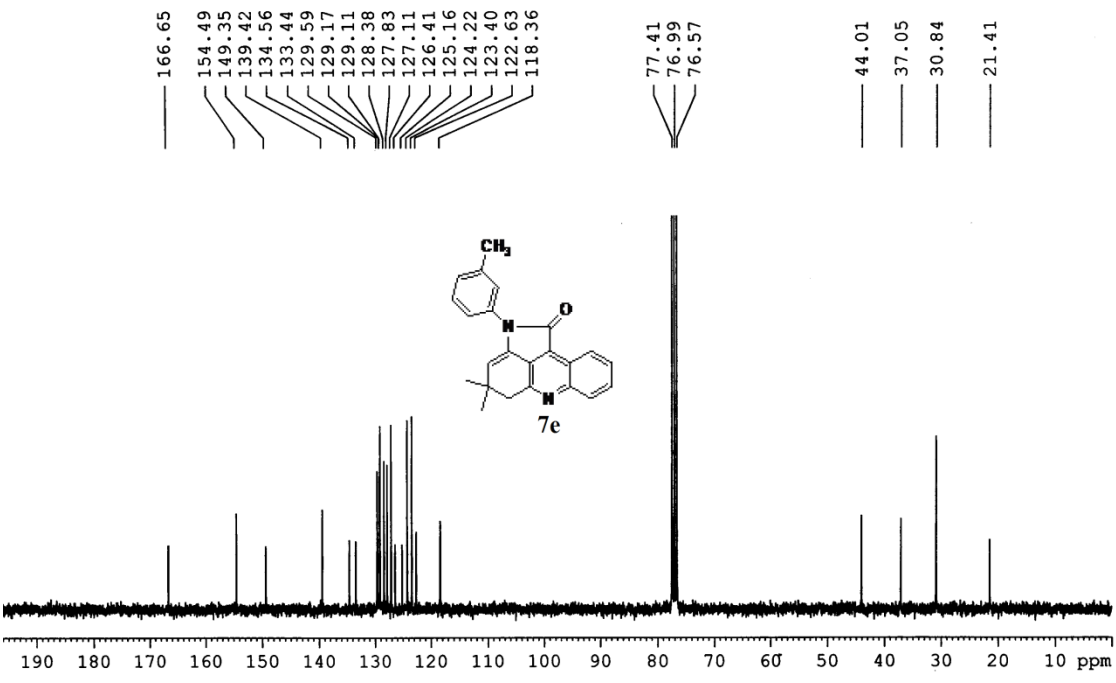
1.03
1.10
1.13
1.30
1.12
2.47
1.03
2.09
3.66
6.38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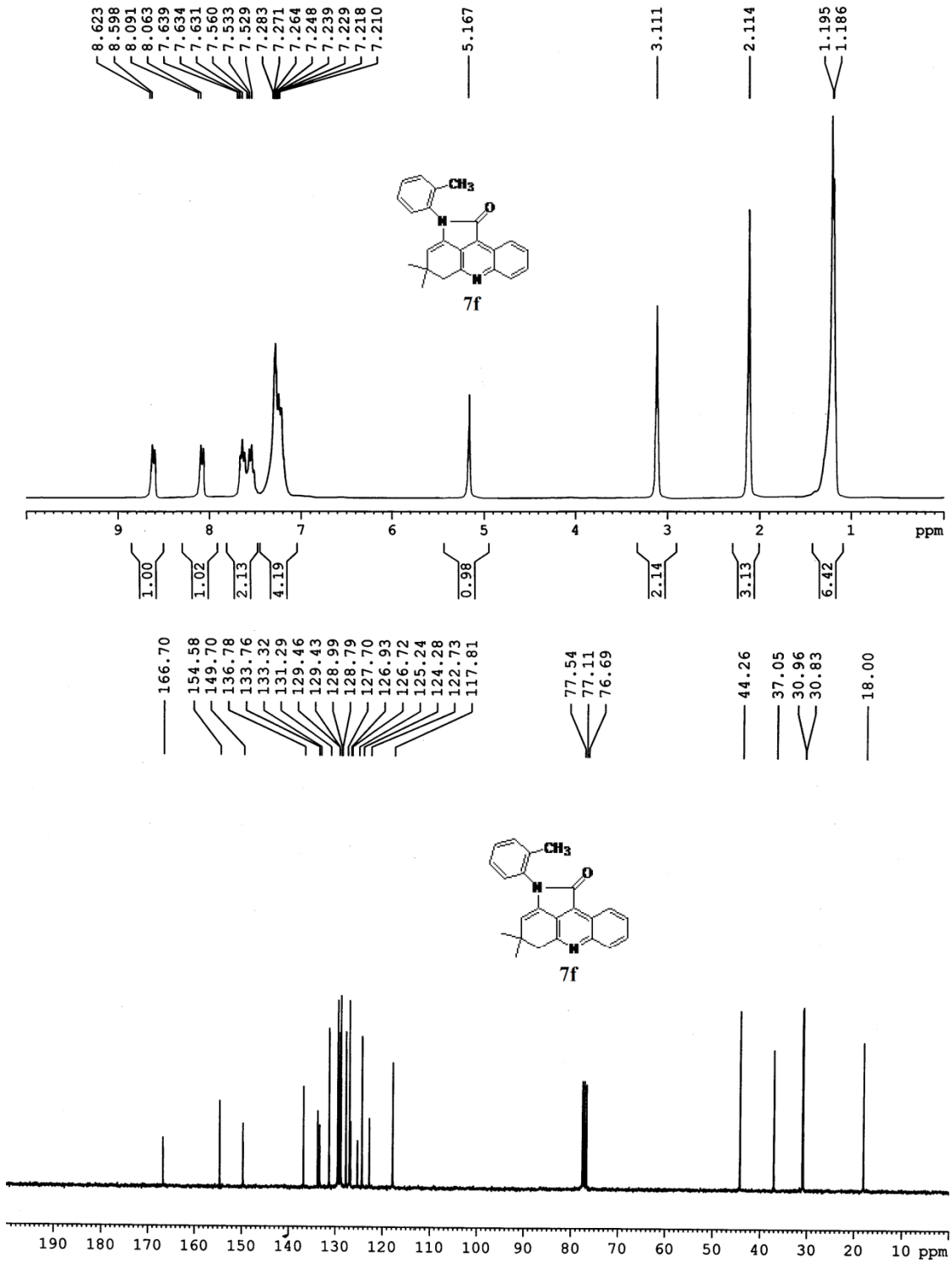
154.49
149.35
139.42
134.56
133.44
129.59
129.17
129.11
128.38
127.83
127.11
126.41
125.16
124.22
123.40
122.63
118.36
77.41
76.99
76.57
44.01
37.05
30.84
21.41
7e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.529
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7.271
7.264
7.248
7.239
7.229
7.218
7.210
5.167
3.111
2.114
1.195
1.186
CH3
N
O
N
7f
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
2.13
4.19
0.98
2.14
3.13
6.42
166.70
154.58
149.70
136.78
133.76
133.32
131.29
129.46
129.43
128.99
128.79
127.70
126.93
126.72
125.24
124.28
122.73
117.81
77.54
77.11
76.69
44.26
37.05
30.96
30.83
18.00
CH3
N
O
N
7f
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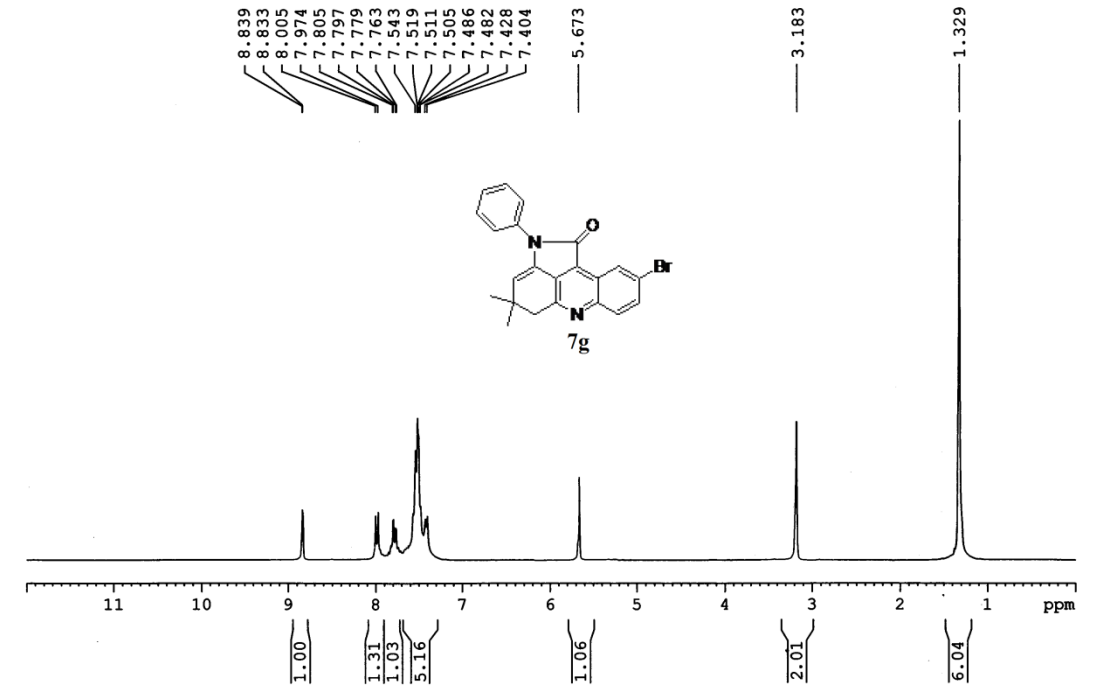
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.805
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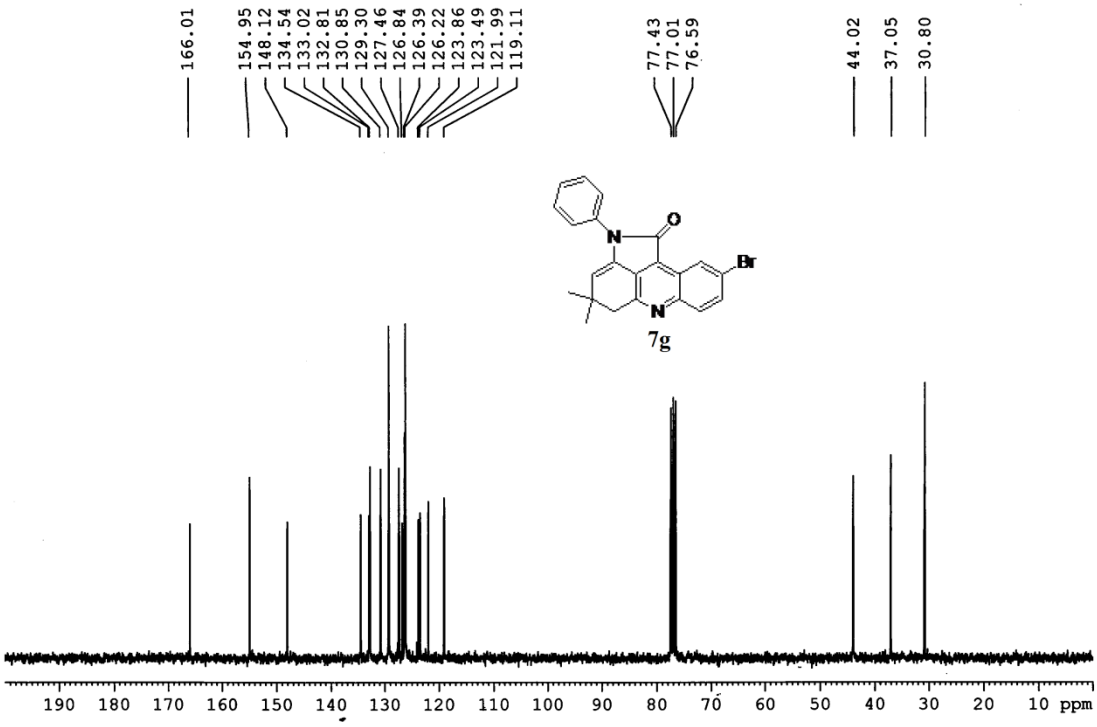
7.779
7.763
7.543
7.519
7.511
7.505
7.486
7.482
7.428
7.404
5.673
3.183
1.329
O
N
Br
N
7g
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.31
1.03
5.16
1.06
2.01
6.04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154.95
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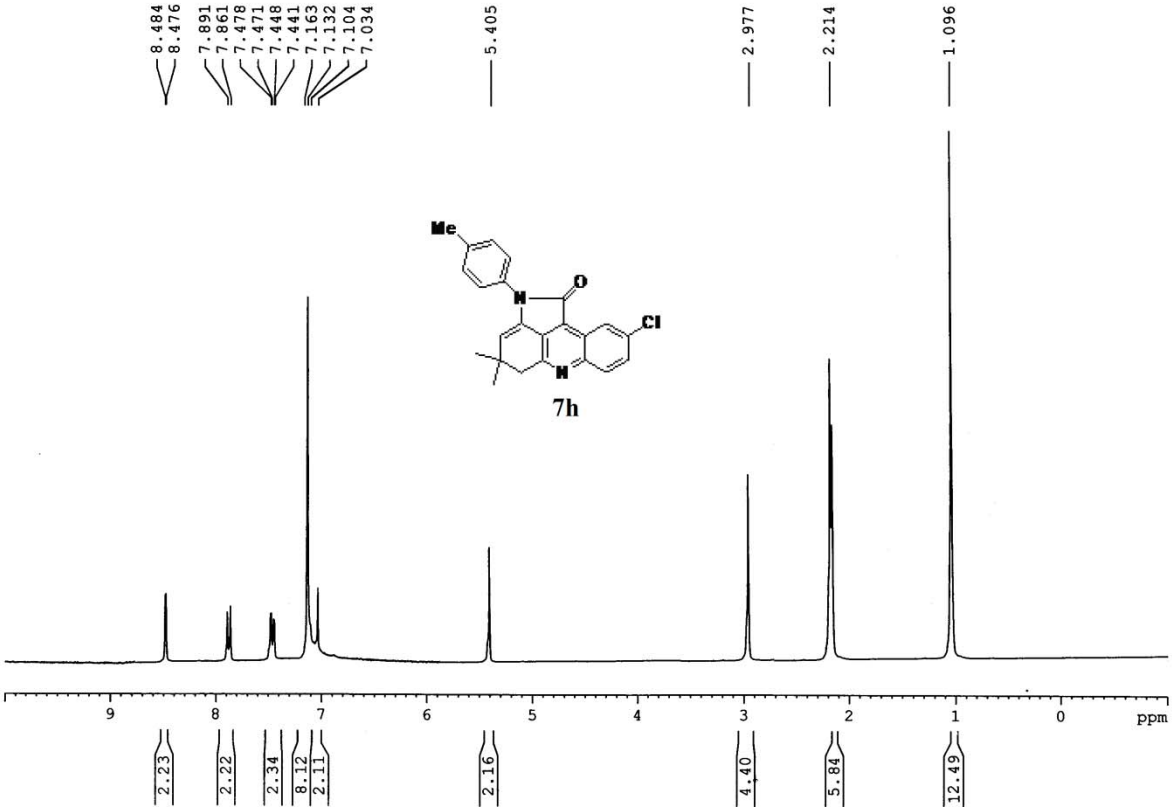
134.54
133.02
132.81
130.85
129.30
127.46
126.84
126.39
126.22
123.86
123.49
121.99
119.11
77.43
77.01
76.59
44.02
37.05
30.80
O
N
Br
N
7g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.478
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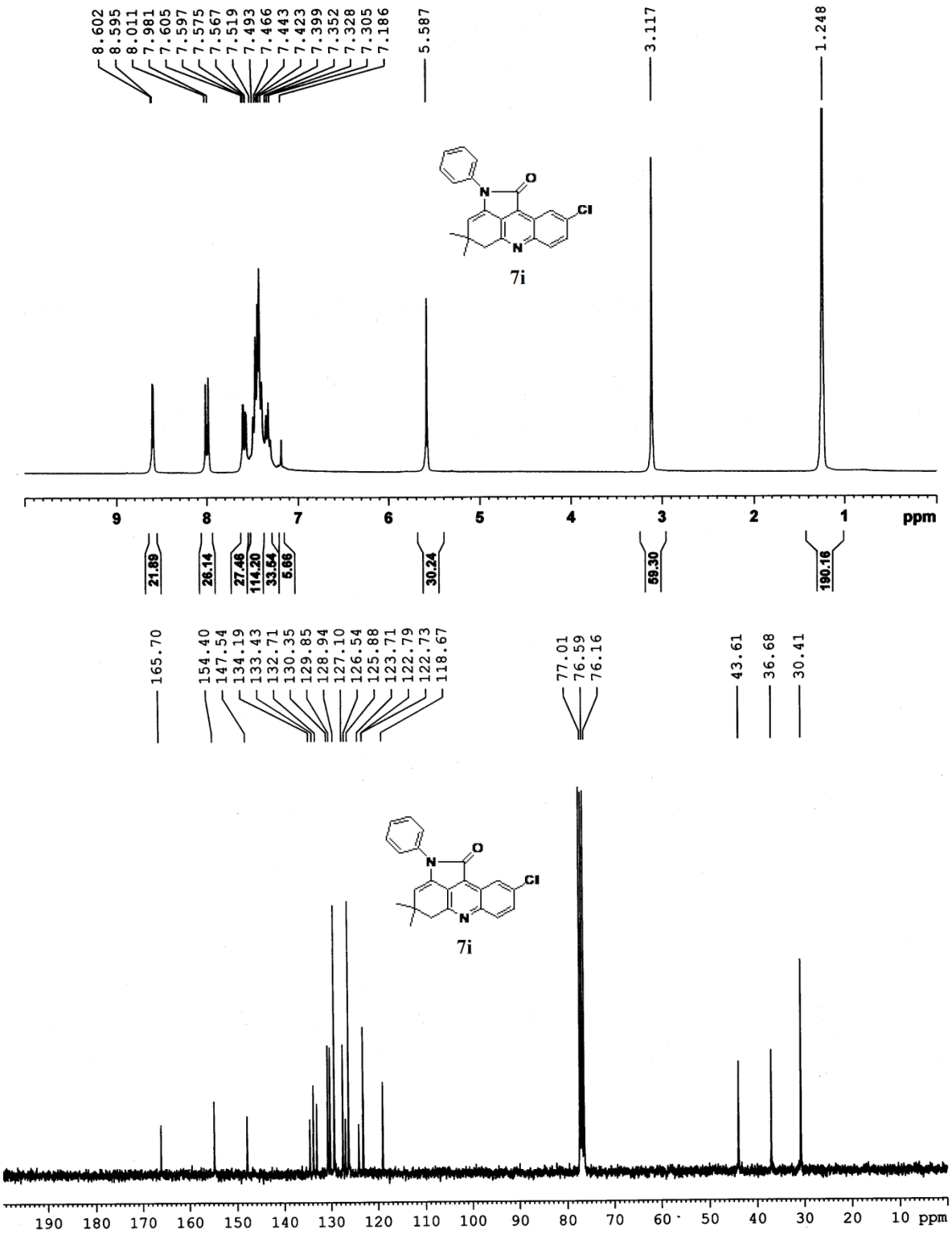
7.448
7.441
7.163
7.132
7.104
7.034
5.405
2.977
2.214
1.096
Me
H
O
Cl
H
9
8
7
6
5
4
3
2
1
0
ppm
2.23
2.22
2.34
8.12
2.11
2.16
4.40
5.84
12.49

7h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7.597
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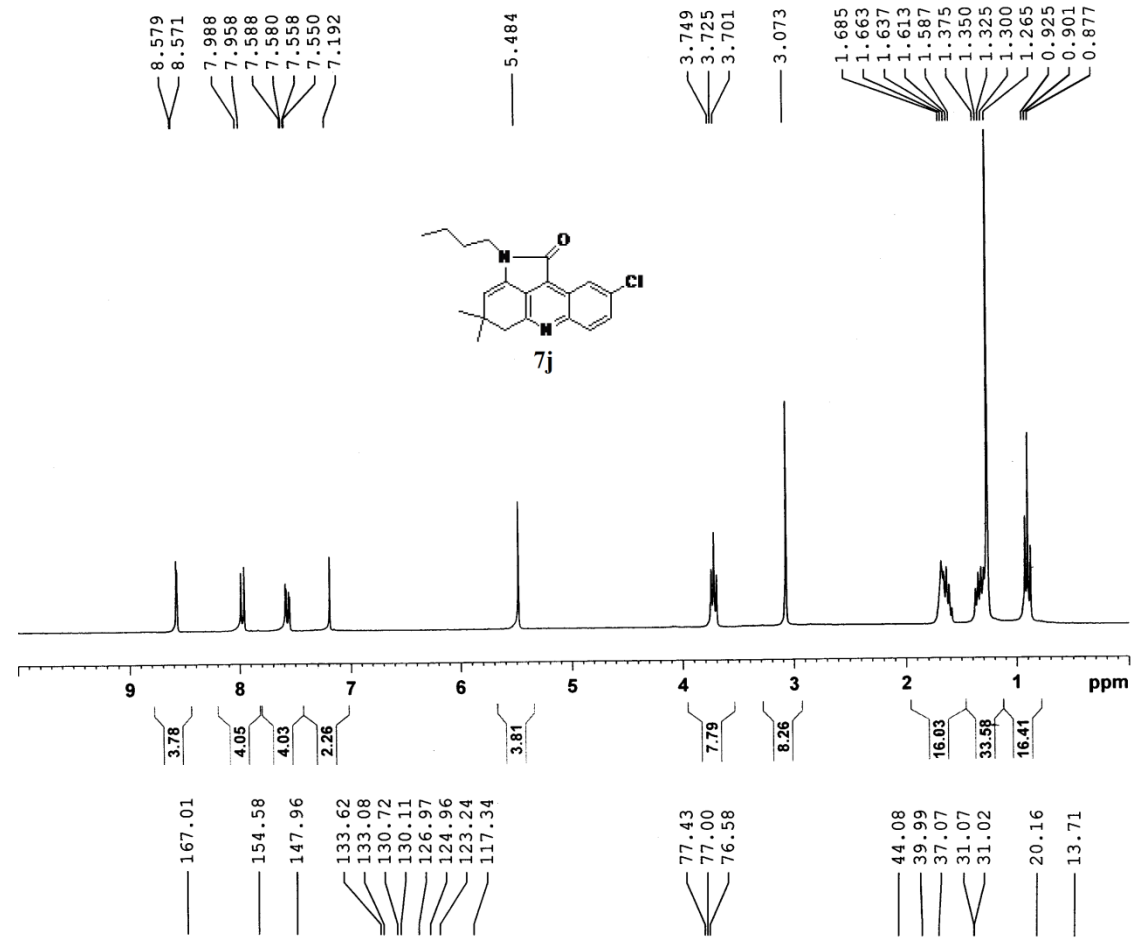
7.567
7.519
7.493
7.466
7.443
7.423
7.399
7.352
7.328
7.305
7.186
5.587
3.117
1.248
7i
9
8
7
6
5
4
3
2
1
ppm
21.89
26.14
27.46
114.20
33.54
5.66
30.24
59.30
190.16
165.70
154.40
147.54
134.19
133.43
132.71
130.35
129.85
128.94
127.10
126.54
125.88
123.71
122.79
122.73
118.67
77.01
76.59
76.16
43.61
36.68
30.41
7i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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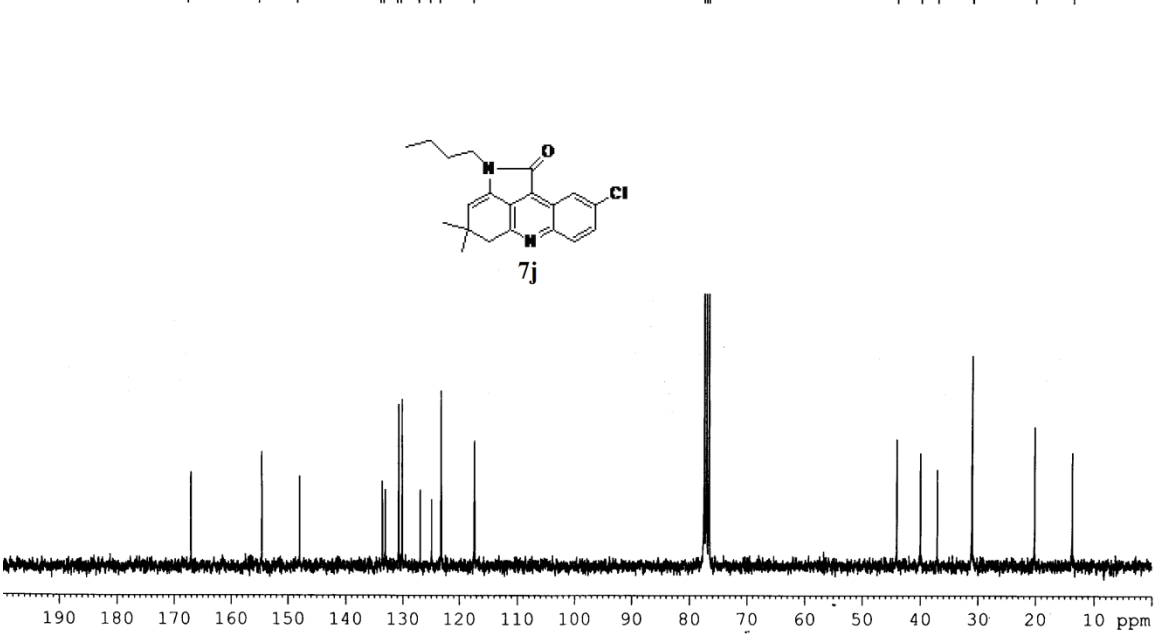
7.588
7.580
7.558
7.550
7.192
5.484
3.749
3.725
3.701
3.073
1.685
1.663
1.637
1.613
1.587
1.375
1.350
1.325
1.300
1.265
0.925
0.901
0.877
7j
ppm
3.78
4.05
4.03
2.26
3.81
7.79
8.26
16.03
33.58
16.41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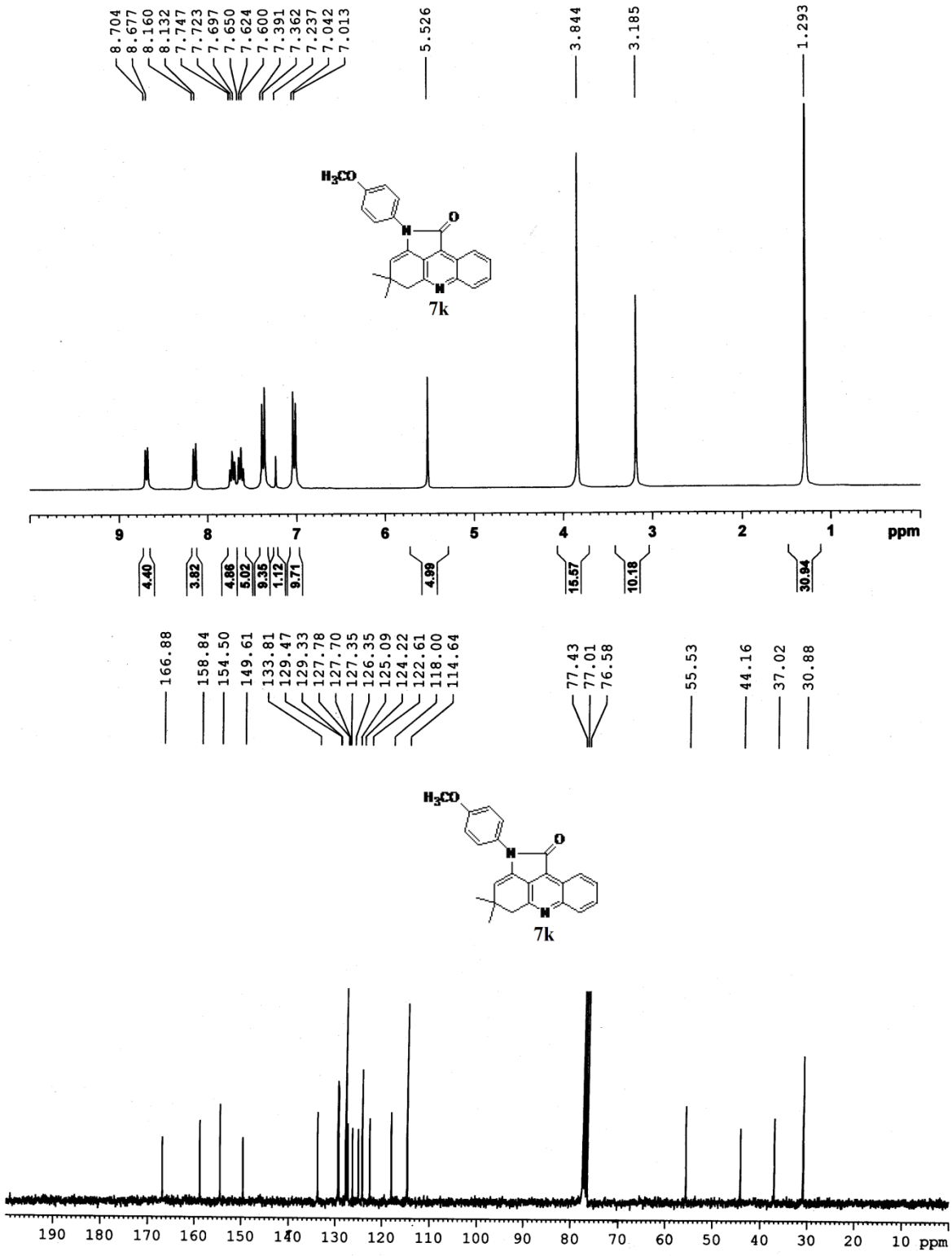
147.96
133.62
133.08
130.72
130.11
126.97
124.96
123.24
117.34
77.43
77.00
76.58
44.08
39.99
37.07
31.07
31.02
20.16
13.71
7j
ppm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7.624
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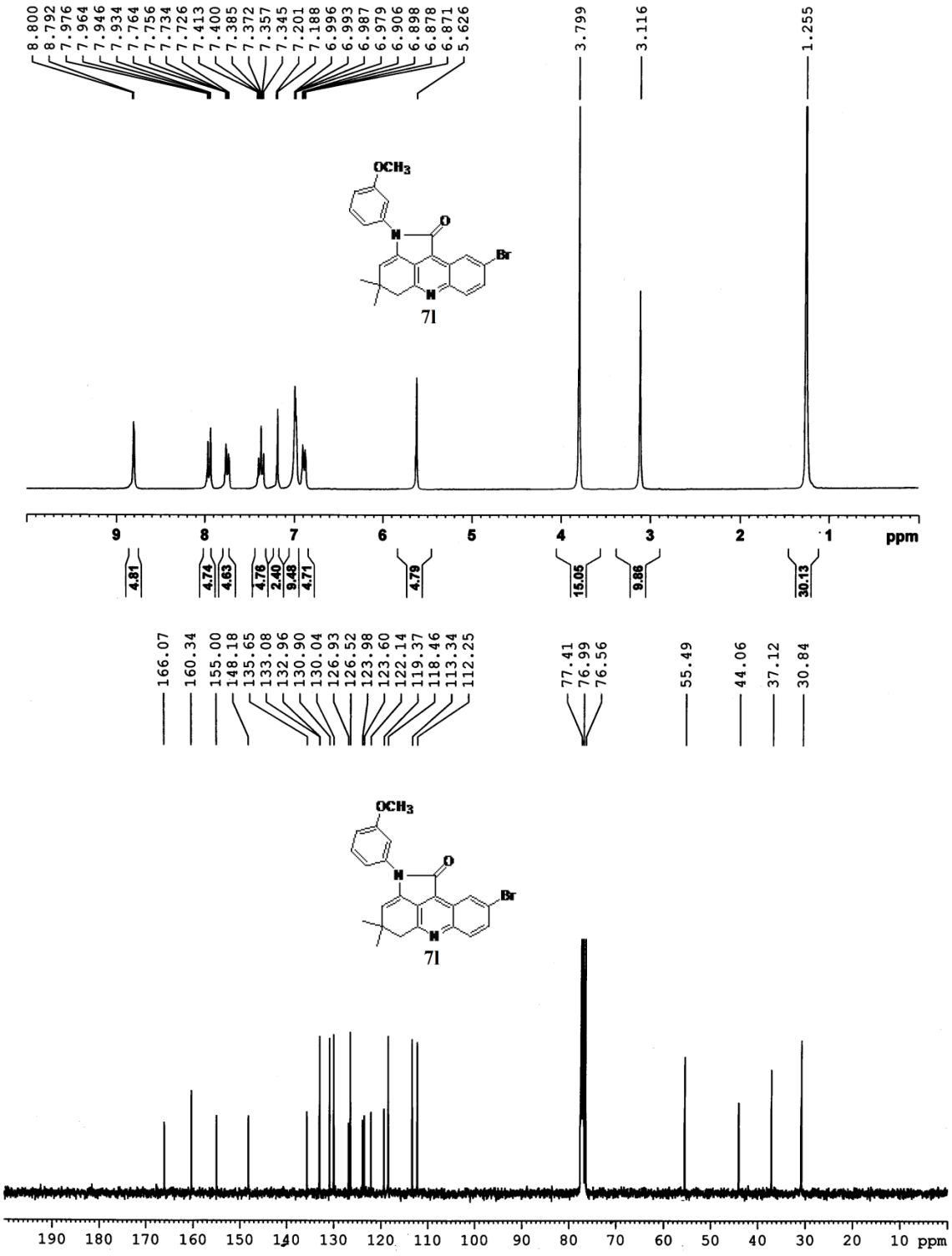
7.237
7.042
7.013
5.526
3.844
3.185
1.293
H3CO
O
N
N
7k
9
8
7
6
5
4
3
2
1
ppm
4.40
3.82
4.86
5.02
9.35
1.12
9.71
4.99
15.57
10.18
30.94
166.88
158.84
154.50
149.61
133.81
129.47
129.33
127.78
127.70
127.35
126.35
125.09
124.22
122.61
118.00
114.64
77.43
77.01
76.58
55.53
44.16
37.02
30.88
H3CO
O
N
N
7k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.934
7.764
7.756
7.734
7.726
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7.400
7.385
7.372
7.357
7.345
7.201
7.188
6.996
6.993
6.987
6.979
6.906
6.898
6.878
6.871
5.626
3.799
3.116
1.255
OCH3
N
O
Br
N
7l
9
8
7
6
5
4
3
2
1
ppm
4.81
4.74
4.63
4.78
2.40
9.48
4.71
4.79
15.05
9.86
30.13
166.07
160.34
155.00
148.18
135.65
133.08
132.96
130.90
130.04
126.93
126.52
123.98
123.60
122.14
119.37
118.46
113.34
112.25
77.41
76.99
76.56
55.49
44.06
37.12
30.84
OCH3
N
O
Br
N
7l
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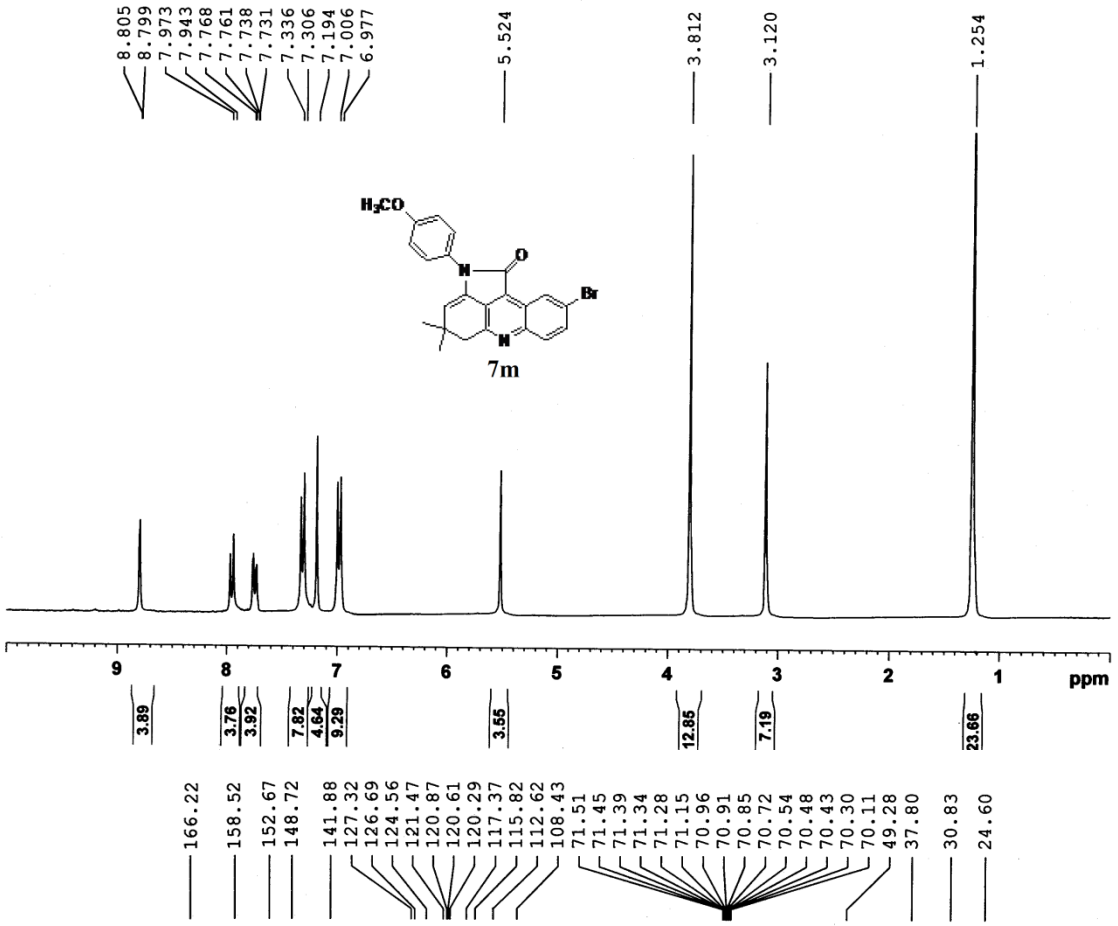
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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6.977
5.524
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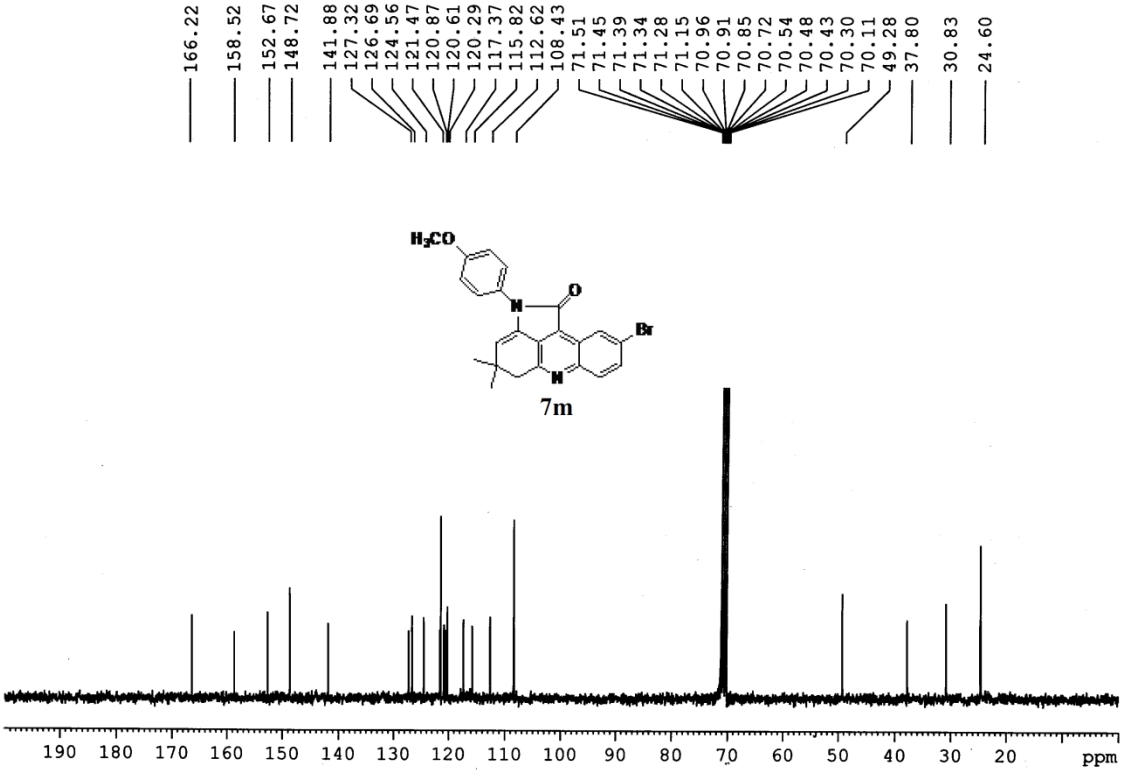
23.66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115.82
112.62
108.43
71.51
71.45
71.39
71.34
71.28
71.15
70.96
70.91
70.85
70.72
70.54
70.48
70.43
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49.28
37.80
30.83
24.60
H3CO
O
N
Br
N
7m
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180
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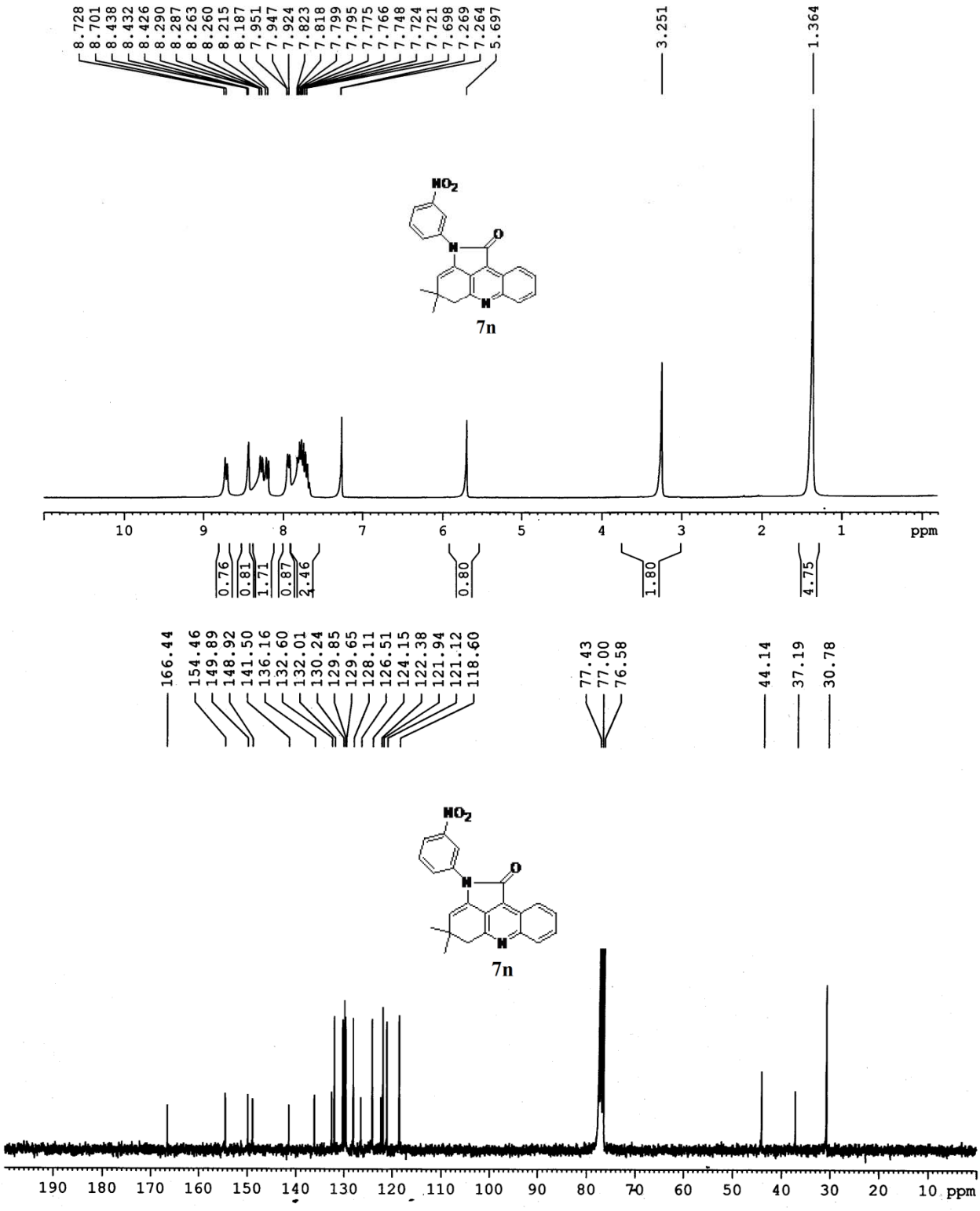
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.947
7.924
7.823
7.818
7.799
7.795
7.775
7.766
7.748
7.724
7.721
7.698
7.269
7.264
5.697
3.251
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NO2
O
N
N
7n
10
9
8
7
6
5
4
3
2
1
ppm
0.76
0.81
1.71
0.87
2.46
0.80
1.80
4.75
166.44
154.46
149.89
148.92
141.50
136.16
132.60
132.01
130.24
129.85
129.65
128.11
126.51
124.15
122.38
121.94
121.12
118.60
77.43
77.00
76.58
44.14
37.19
30.78
NO2
O
N
N
7n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Supporting Information 2

# Covalently anchored carboxylic acid on uniform spherical silica nanoparticles with narrow slit like mesopores for the synthesis of pyrroloacridinones: CuI-catalyzed further C(sp3)-H oxyfunctionalization for C=O formation

**Suman Ray[a], Asim Bhaumik[b], Malay Pramanik[b] and Chhanda Mukhopadhyay[a]***

*a: Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata-700009, India*
*b: Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India.*

*cmukhop@yahoo.co.in* *

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**A. ORTEP diagram of 8p**

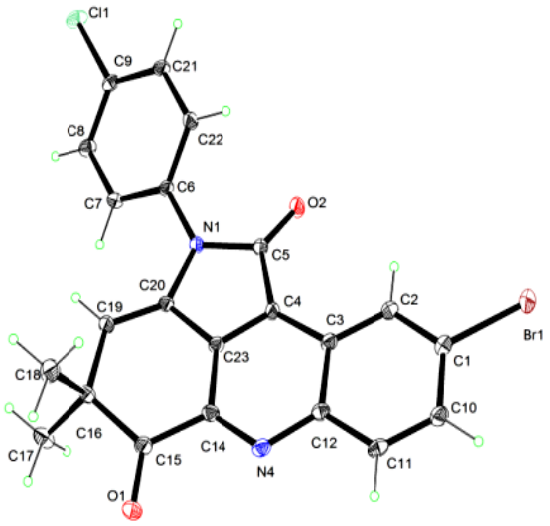
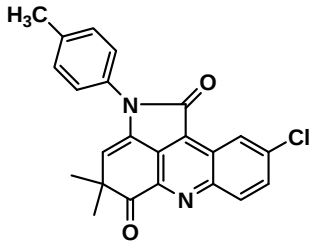



***Figure 1***. X-ray single crystal structure of **8p** (**CCDC 972994**).

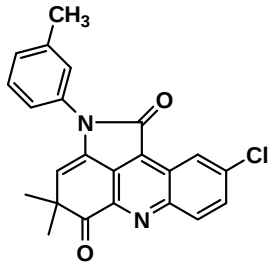
**B. Spectroscopic characterization of 8a-8s**

**9-chloro-4,4-dimethyl-2-p-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8a):**



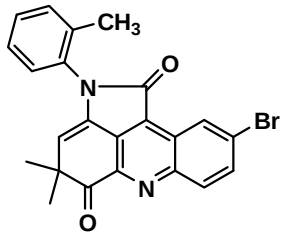

Deep yellow colored solid; m.p. 230-232 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{17}ClN_2O_2$: C, 71.04; H, 4.41; N, 7.20%. Found: C, 71.05; H, 4.42; N, 7.21%; IR (KBr) $cm^{-1}$: 3055, 2972, 2933, 1705, 1667, 1446, 1338, 1278, 1130, 777; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.51 (6H, s, 2x$CH_3$), 2.44 (3H, s, $CH_3$), 5.84 (1H, s, CH), 7.39 (4H, t, J = 8.7 Hz, arom.), 7.80 (1H, dd, J = 9.3 Hz, J = 2.1 Hz, arom.), 8.41 (1H, d, J = 9.0 Hz, arom.), 8.79 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.2, 27.6, 48.9, 118.2, 123.0, 125.3, 126.3, 127.3, 130.2, 130.9, 131.3, 131.8, 132.1, 133.6, 137.9, 138.2, 142.8, 148.5, 165.1, 199.2.

**9-chloro-4,4-dimethyl-2-m-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8b):**



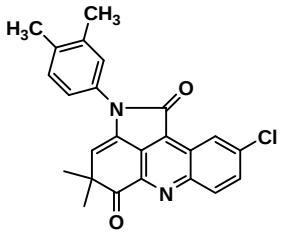

Deep yellow colored solid; m.p. 180-182 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{17}ClN_2O_2$: C, 71.04; H, 4.41; N, 7.20%. Found: C, 71.05; H, 4.42; N, 7.21%; IR (KBr) $cm^{-1}$: 3054, 2970, 2932, 1702, 1666, 1444, 1336, 1276, 1128, 771; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (6H, s, 2x$CH_3$), 2.48 (3H, s, $CH_3$), 5.87 (1H, s, CH), 7.29 (2H, d, J = 7.5 Hz, arom.), 7.34 (1H, s, arom), 7.47 (1H, t, J = 7.5 Hz, arom.), 7.82 (1H, d, J = 9.0 Hz, arom.), 8.44 (1H, d, J = 9.3 Hz, arom.), 8.82 (1H, d, J = 1.5 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.5, 27.6, 48.9, 118.4, 123.1, 123.5, 125.3, 127.2, 127.3, 129.0, 129.4, 130.8, 130.9, 131.9, 132.1, 133.6, 133.7, 138.0, 139.8, 142.8, 148.5, 165.2, 199.3.

**9-bromo-4,4-dimethyl-2-o-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8c):**



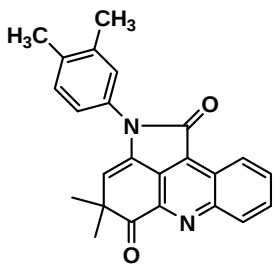
Deep yellow colored solid; m.p. 148-150 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{17}BrN_2O_2$: C, 63.75; H, 3.95; N, 6.47%. Found: C, 63.76; H, 3.96; N, 6.48%; IR (KBr) $cm^{-1}$: 3059, 2968, 2930, 1704, 1666, 1448, 1339, 1277, 1134, 777; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.49 (3H, s, $CH_3$), 1.50 (3H, s, $CH_3$), 2.25 (3H, s, $CH_3$), 5.53 (1H, s, CH), 7.31-7.45 (4H, m, arom.), 7.82 (1H, dd, J = 9.0 Hz, J = 2.4 Hz, arom.), 8.46 (1H, d, J = 9.0 Hz, arom.), 8.83 (1H, d, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 18.0, 27.5, 27.7, 49.0, 118.0, 123.2, 125.5, 127.2, 127.6, 128.6, 129.5, 131.0, 131.6, 131.9, 132.4, 132.5, 133.7, 136.7, 138.0, 142.9, 148.6, 165.1, 199.3.

**9-chloro-4,4-dimethyl-2-(3,4-dimethylphenyl)pyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8d):**



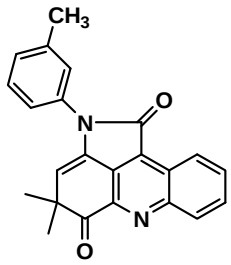
Deep yellow colored solid; m.p. 172-174 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{24}H_{19}ClN_2O_2$: C, 71.55; H, 4.75; N, 6.95%. Found: C, 71.57; H, 4.76; N, 6.96%; IR (KBr) $cm^{-1}$: 3050, 2968, 2922, 1701, 1668, 1447, 1338, 1273, 1118, 776; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.50 (6H, s, 2x$CH_3$), 2.32 (3H, s, $CH_3$), 2.34 (3H, s, $CH_3$), 5.82 (1H, s, CH), 7.19 (1H, dd, J = 8.4 Hz, J = 2.1 Hz, arom.), 7.26-7.33 (2H, m, arom.), 7.80 (1H, dd, J = 9.3 Hz, J = 2.4 Hz, arom.), 8.42 (1H, d, J = 9.3 Hz, arom.), 8.81 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 13.3, 13.7, 21.4, 42.7, 112.0, 116.9, 117.6, 119.1, 121.2, 121.4, 124.4, 124.8, 125.3, 125.6, 125.9, 127.4, 130.8, 131.7, 132.0, 136.6, 142.3, 159.0, 193.1.

**4,4-dimethyl-2-(3,4-dimethylphenyl)pyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8e):**



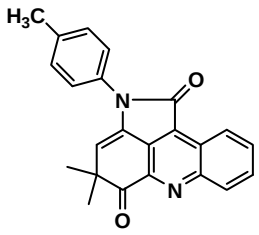
Deep yellow colored solid; m.p. 190-192 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60%. Found: C, 78.25; H, 5.48; N, 7.61%; IR (KBr) $cm^{-1}$: 3399, 2955, 2930, 1701, 1650, 1335, 1111, 770, 699; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (6H, s, 2x$CH_3$), 2.37 (3H, s, $CH_3$), 2.38 (3H, s, $CH_3$), 5.82 (1H, s, CH), 7.22-7.36 (3H, m, arom.), 7.85-7.94 (2H, m, arom.), 8.54 (1H, dd, J = 9.3 Hz, J = 1.8 Hz, arom.), 8.88 (1H, dd, J = 8.6 Hz, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 19.6, 20.0, 27.7, 48.9, 117.4, 123.9, 124.1, 125.0, 127.7, 128.2, 130.6, 130.7, 131.2, 131.5, 131.7, 132.4, 136.9, 138.2, 142.8, 150.3, 165.8, 199.7.

**4,4-dimethyl-2-m-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8f):**




Deep yellow colored solid; m.p. 185-187 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12; N, 7.90%. Found: C, 77.96; H, 5.13; N, 7.91%; IR (KBr) $cm^{-1}$: 3394, 2952, 2929, 1704, 1645, 1345, 1110, 777, 696; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.45 (6H, s, 2x$CH_3$), 2.40 (3H, s, $CH_3$), 5.75 (1H, s, CH), 7.21 (2H, t, J = 7.2 Hz, arom.), 7.28 (1H, s, arom.), 7.39 (1H, t, J = 7.8 Hz, arom.), 7.77-7.85 (2H, m, arom.), 8.45 (1H, dd, J = 9.3 Hz, J = 1.8 Hz, arom.), 8.78 (1H, dd, J = 6.9 Hz, J = 1.8 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.4, 27.6, 48.8, 117.5, 123.5, 124.0, 124.9, 127.3, 128.1, 128.9, 129.3, 130.7, 131.1, 131.2, 131.5, 132.4, 134.0, 139.7, 142.8, 150.3, 165.6, 199.6.

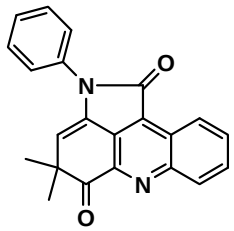
**4,4-dimethyl-2-p-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8g):**




Deep yellow colored solid; m.p. 182-184 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12; N, 7.90%. Found: C, 77.96; H, 5.13; N, 7.91%; IR (KBr) $cm^{-1}$: 3399, 2945, 2932, 1702, 1647, 1344, 1109, 777, 695; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.50 (6H, s, 2x$CH_3$), 2.44 (3H, s, $CH_3$), 5.27 (1H, s, CH), 7.77-7.85 (4H, m, arom.), 7.77-7.85 (2H, m, arom.), 8.51 (1H, dd, J = 10.5 Hz, J = 1.8 Hz, arom.), 8.83 (1H, d, J = 7.5

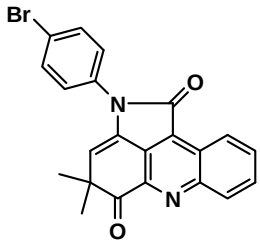
Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.2, 27.7, 48.9, 117.4, 124.1, 124.9, 126.3, 126.4, 128.2, 130.1, 130.2, 130.7, 131.1, 131.2, 132.4, 138.1, 142.8, 150.3, 162.3, 165.7, 199.7.

**4,4-dimethyl-2-phenylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8h):**



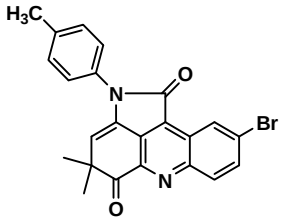
Deep yellow colored solid; m.p. 190-192 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23%. Found: C, 77.64; H, 4.75; N, 8.24%; IR (KBr) $cm^{-1}$: 3409, 2965, 2933, 1701, 1649, 1345, 1101, 777, 699; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.52 (6H, s, 2x$CH_3$), 5.84 (1H, s, CH), 7.44-7.57 (5H, m, arom.), 7.85 (2H, d, J = 7.5 Hz, arom.), 8.47 (1H, d, J = 8.1 Hz, arom.), 8.79 (1H, d, J = 7.8 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 27.5, 48.7, 117.5, 123.9, 124.7, 126.4, 127.9, 129.5, 130.6, 130.8, 131.1, 131.4, 132.2, 134.1, 142.7, 150.1, 165.4, 199.4.

**2-(4-bromophenyl)-4,4-dimethylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8i):**



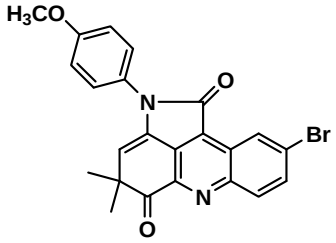
Deep yellow colored solid; m.p. 168-170 °C (recrystallized from EtOAc/DCM); nal. Calcd for $C_{22}H_{15}BrN_2O_2$: C, 63.02; H, 3.61; N, 6.68%. Found: C, 63.03; H, 3.62; N, 6.69%; IR (KBr) $cm^{-1}$: 3398, 2944, 2934, 1702, 1640, 1324, 1109, 774, 690; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (6H, s, 2x$CH_3$), 5.84 (1H, s, CH), 7.42 (2H, dd, J = 6.9 Hz, J = 1.8 Hz, arom.), 7.71 (2H, dd, J = 6.0 Hz, J = 1.8 Hz, arom.), 7.87-7.91 (2H, m, arom.), 8.52 (1H, dd, J = 8.1 Hz, J = 2.1 Hz, arom.), 8.84 (1H, dd, J = 8.6 Hz, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 27.6, 48.9, 118.4, 121.9, 125.5, 126.4, 128.0, 130.4, 132.0, 132.9, 133.1, 133.7, 134.6, 142.9, 148.7, 164.9, 198.9.

**9-bromo-4,4-dimethyl-2-p-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8j):**



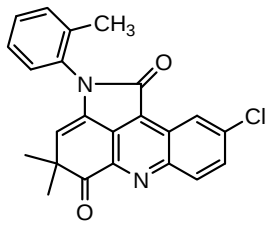

Deep yellow colored solid; m.p. 190-192 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{17}BrN_2O_2$: C, 63.75; H, 3.95; N, 6.47%. Found: C, 63.76; H, 3.96; N, 6.48%; IR (KBr) $cm^{-1}$: 3057, 2962, 2924, 1705, 1669, 1599, 1514, 1444, 1356, 1278, 1156, 776; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.52 (6H, s, 2x$CH_3$), 2.46 (3H, s, $CH_3$), 5.85 (1H, s, CH), 7.36-7.39 (4H, m, arom.), 7.96 (1H, dd, J = 9.1 Hz, J = 2.1 Hz, arom.), 8.37 (1H, d, J = 9.0 Hz, arom.), 9.02 (1H, d, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 20.4, 27.6, 48.9, 118.2, 125.6, 126.3, 126.6, 127.1, 130.1, 130.8, 131.3, 130.8, 131.3, 132.0, 133.6, 134.4, 138.2, 142.9, 148.7, 165.1, 199.2.

**9-bromo-2-(4-methoxyphenyl)-4,4-dimethylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8k):**



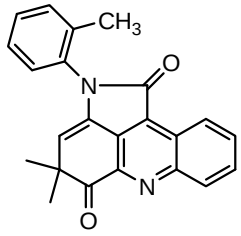

Deep yellow colored solid; m.p. 182-184 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{17}BrN_2O_3$: C, 61.48; H, 3.81; N, 6.23%. Found: C, 61.49; H, 3.82; N, 6.24%; IR (KBr) $cm^{-1}$: 3389, 2947, 2933, 1704, 1645, 1320, 1109, 767, 699; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (6H, s, 2x$CH_3$), 3.91 (3H, s, $OCH_3$), 5.82 (1H, s, CH), 7.10 (2H, d, J = 8.7 Hz, arom.), 7.43 (2H, d, J = 9.0 Hz, arom.), 7.97 (1H, dd, J = 9.3 Hz, J = 2.1 Hz, arom.), 8.36 (1H, d, J = 9.3 Hz, arom.), 9.02 (1H, d, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 27.7, 48.9, 55.6, 114.9, 118.1, 125.6, 126.5, 126.5, 126.6, 127.2, 127.9, 131.2, 132.0, 133.6, 134.5, 142.9, 148.7, 159.3, 165.3, 199.2.

**9-chloro-4,4-dimethyl-2-o-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8l):**



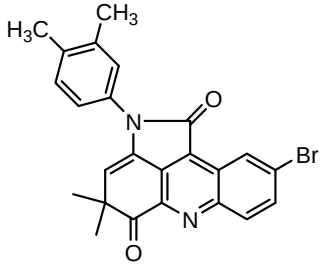
Deep yellow colored solid; m.p. 160-162 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{17}ClN_2O_2$: C, 71.04; H, 4.41; N, 7.20%. Found: C, 71.14; H, 4.40; N, 7.24%; IR (KBr) $cm^{-1}$: 3059, 2965, 2929, 1703, 1670, 1562, 1515, 1447, 1355, 1283, 1167, 770; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.49 (3H, s, $CH_3$), 1.50 (3H, s, $CH_3$), 2.25 (3H, s, $CH_3$), 5.46 (1H, s, CH), 7.20-7.38 (4H, m, arom.), 7.90 (1H, td, J = 9.0 Hz, J = 1.2 Hz, arom.), 8.31 (1H, d, J = 9.0 Hz, arom.), 8.94 (1H, d, J = 1.5 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 17.8, 27.4, 27.6, 48.8, 117.8, 122.7, 125.6, 126.4, 126.5, 127.0, 128.4, 129.3, 130.9, 131.4, 132.2, 132.4, 133.5, 134.3, 136.5, 142.6, 148.6, 164.9, 199.1.

**4,4-dimethyl-2-o-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8m):**




Deep yellow colored solid; m.p. 200-202 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12; N, 7.90%. Found: C, 77.99; H, 5.10; N, 7.95%; IR (KBr) $cm^{-1}$: 3058, 2965, 2929, 1700, 1656, 1599, 1516, 1434, 1366, 1278, 1166, 777; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (6H, s, 2x$CH_3$), 2.48 (3H, s, $CH_3$), 5.50 (1H, s, CH), 7.35-7.45 (4H, m, arom.), 7.87-7.92 (2H, m, arom.), 8.55 (1H, dd, J = 9.3 Hz, J = 2.1 Hz, arom.), 8.87 (1H, dd, J = 9.9 Hz, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.5, 27.6, 48.9, 117.6, 121.9, 124.0, 124.9, 127.3, 128.2, 128.9, 129.3, 130.1, 131.1, 131.2, 131.5, 132.4, 134.0, 139.7, 142.8, 149.3, 165.6, 199.6.

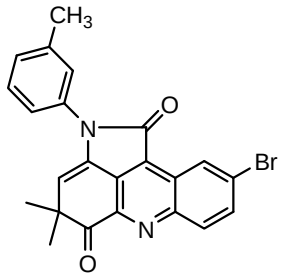
**9-bromo-4,4-dimethyl-2-(3,4-dimethylphenyl)pyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8n):**




Yellow colored solid; m.p. 190-192 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{24}H_{19}BrN_2O_2$: C, 64.44; H, 4.28; N, 6.26%. Found: C, 64.47; H, 4.29; N, 6.26%; IR (KBr) $cm^{-1}$: 3052, 2922, 1702, 1664, 1502, 1443, 1335, 1213, 845, 779, 620; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.44 (3H, s, $CH_3$), 2.28 (3H, s, $CH_3$), 2.29 (3H, s, $CH_3$), 5.76 (1H, s, CH), 7.12-7.27 (3H, m, Hz, arom.), 7.79 (1H, dd, J = 9.0 Hz, J = 2.1 Hz, arom.), 8.29 (1H, d, J = 9.3 Hz,

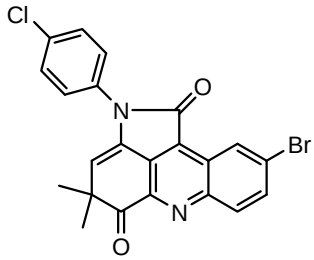
arom.), 8.95 (1H, d, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 19.6, 20.0, 27.6, 28.2, 49.0, 118.2, 123.2, 125.7, 126.5, 126.7, 127.3, 128.6, 129.6, 131.0, 131.4, 132.1, 132.1, 133.3, 134.2, 137.1, 138.3, 142.9, 148.7, 164.3, 199.4.

**9-bromo-4,4-dimethyl-2-m-tolylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8o):**



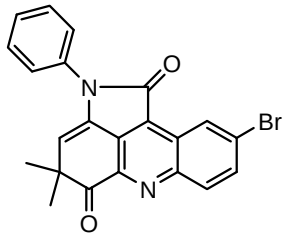

Yellow colored solid; m.p. 168-170 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{23}H_{17}BrN_2O_2$: C, 63.75; H, 3.95; N, 6.47%. Found: C, 63.70; H, 3.94; N, 6.50%; IR (KBr) $cm^{-1}$: Anal. 3051, 2929, 1706, 1666, 1505, 1447, 1333, 1215, 855, 777, 622; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.50 (6H, s, 2x$CH_3$), 2.44 (3H, s, $CH_3$), 5.87 (1H, s, CH), 7.13-7.48 (4H, m, arom.), 7.97 (1H, d, J = 9.3 Hz, arom.), 8.37 (1H, d, J = 9.3 Hz, arom.), 9.03 (1H, br s, arom.).

**9-bromo-2-(4-chlorophenyl)-4,4-dimethylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8p):**



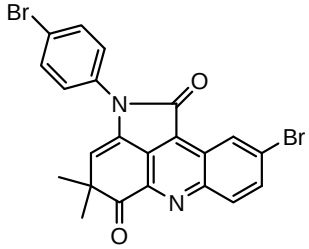

Deep yellow colored solid; m.p. 188-190 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{22}H_{14}BrClN_2O_2$: C, 58.24; H, 3.11; N, 6.17%. Found: C, 58.29; H, 3.11; N, 6.14%; IR (KBr) $cm^{-1}$: 3054, 2955, 1701, 1669, 1499, 1444, 1336, 1278, 1133, 834, 769, 492; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.51-1.49 (6H, s, 2x$CH_3$), 2.25 (3H, s, $CH_3$), 5.54 (1H, s, CH), 7.41 (4H, q, J = 7.5 Hz, arom.), 7.83 (1H, dd, J = 9.0 Hz, J = 2.4 Hz, arom.), 8.46 (1H, d, J = 9.0 Hz, arom.), 8.83 (1H, d, J = 2.1 Hz, arom.).

**9-Bromo-4,4-dimethyl-2-phenyl-2,4-dihydro-pyrrolo[2,3,4-kl]acridine-1,5-dione (8q):**



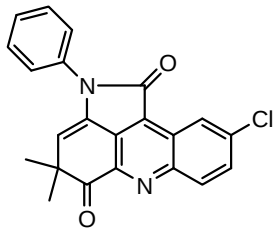

Deep yellow colored solid; m.p. 168-170 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{22}H_{15}BrN_2O_2$: C, 63.02; H, 3.61; N, 6.68%. Found: C, 63.03; H, 3.62; N, 6.69%; IR (KBr) $cm^{-1}$: 3056, 2965, 1705, 1677, 1489, 1454, 1339, 1279, 1153, 839, 777, 499; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (6H, s, 2x$CH_3$), 5.91 (1H, s, CH), 7.42-7.62 (5H, m, arom.), 7.97 (1H, dd, J = 9.3 Hz, J = 2.1 Hz, arom.), 8.38 (1H, d, J = 9.0 Hz, arom.), 9.03 (1H, d, J = 2.1 Hz, arom.).

**9-bromo-2-(4-bromophenyl)-4,4-dimethylpyrrolo[2,3,4-kl]acridine-1,5(2H,4H)-dione (8r):**




Deep yellow colored solid; m.p. 180-182 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{22}H_{14}Br_2N_2O_2$: C, 53.04; H, 2.83; N, 5.62%. Found: C, 53.00; H, 2.80; N, 5.65%; IR (KBr) $cm^{-1}$: 3053, 2965, 1706, 1668, 1490, 1445, 1336, 1277, 1158, 830, 768, 491; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (3H, s, $CH_3$), 5.89 (1H, s, CH), 7.42 (2H, dd, J = 8.7 Hz, J = 3.0 Hz, arom.), 7.72 (2H, dd, J = 6.6 Hz, J = 3.3 Hz, arom.), 7.97 (1H, dd, J = 9.3 Hz, J = 1.5 Hz, arom.), 8.36 (1H, d, J = 9.3 Hz, arom.), 9.0 (1H, s, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 27.6, 48.9, 118.4, 121.9, 125.5, 126.4, 128.0, 130.4, 132.0, 132.9, 133.1, 133.7, 134.6, 142.9, 148.7, 164.9, 198.9.

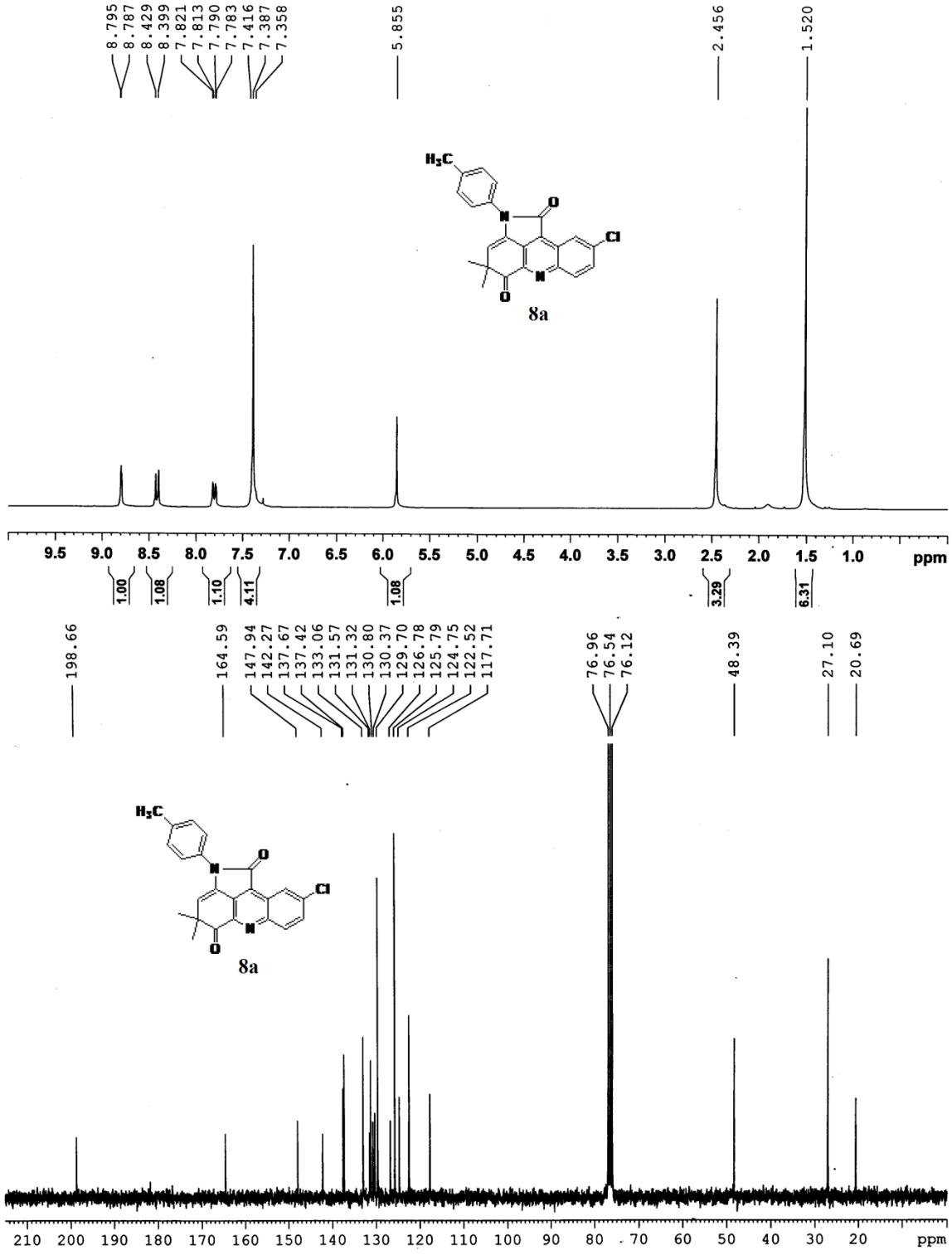
**9-Chloro-4,4-dimethyl-2-phenyl-2,4-dihydro-pyrrolo[2,3,4-kl]acridine-1,5-dione (8s):**

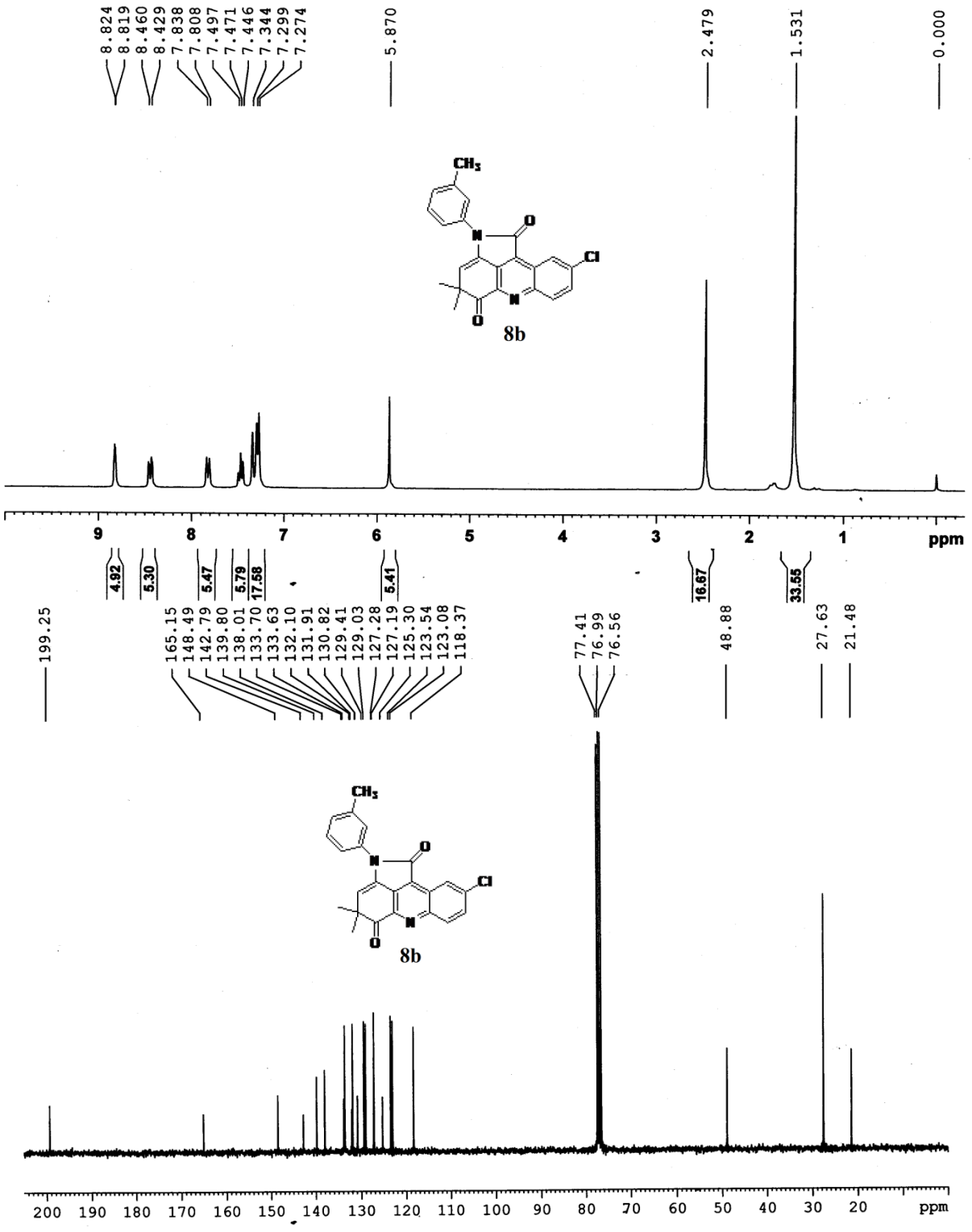



Yellow colored solid; m.p. 160-162 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{22}H_{15}ClN_2O_2$: C, 70.50; H, 4.03; N, 7.47%. Found: C, 70.52; H, 4.05; N, 7.49%; IR (KBr) $cm^{-1}$: 3385, 3044, 2958, 1704, 1663, 1499, 1443,

1333, 1282, 1125, 856, 751; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 1.53 (6H, s, 2x$CH_3$), 5.88 (1H, s, CH), 7.39-7.57 (5H, m, arom.), 7.83 (1H, dd, J = 9.2 Hz, J = 1.5 Hz, arom.), 8.46 (1H, d, J = 9.0 Hz, arom.), 8.85 (1H, s, arom.).

**C. $^{1}H$ and $^{13}C$ NMR Spectra of 8a-8s**

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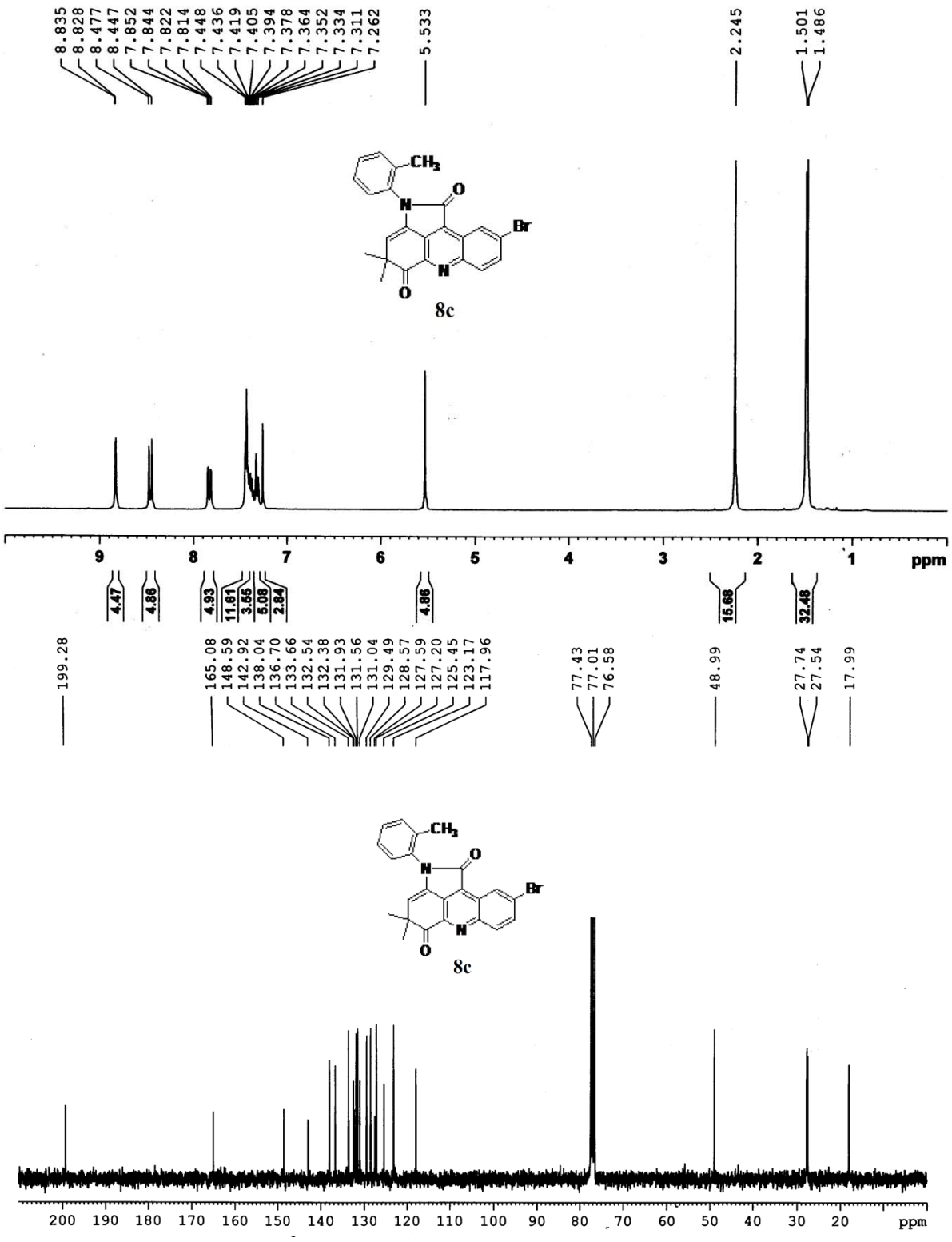
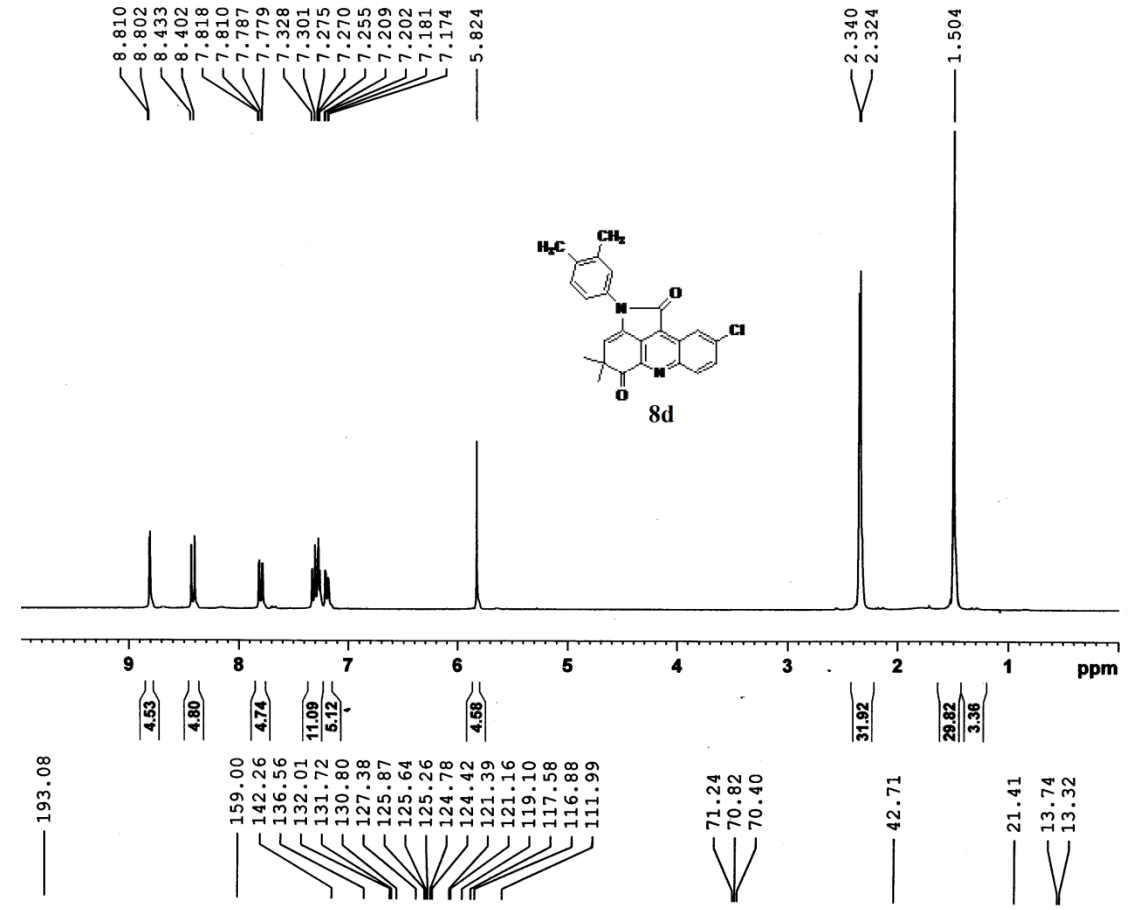
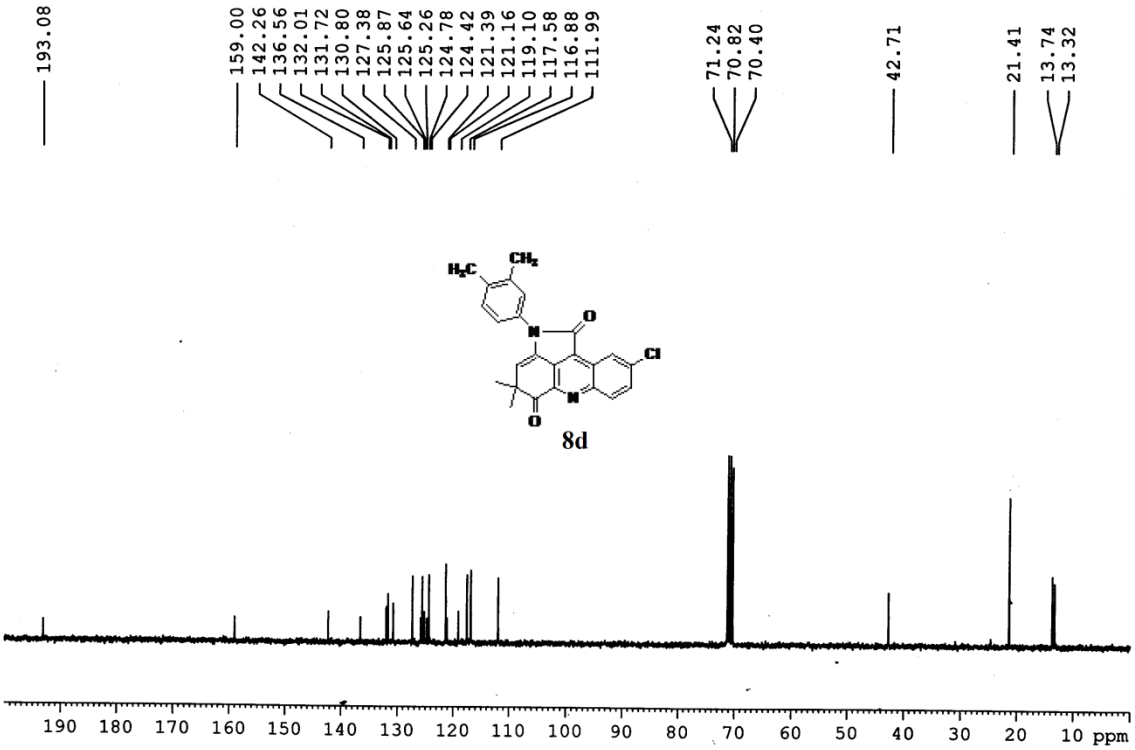
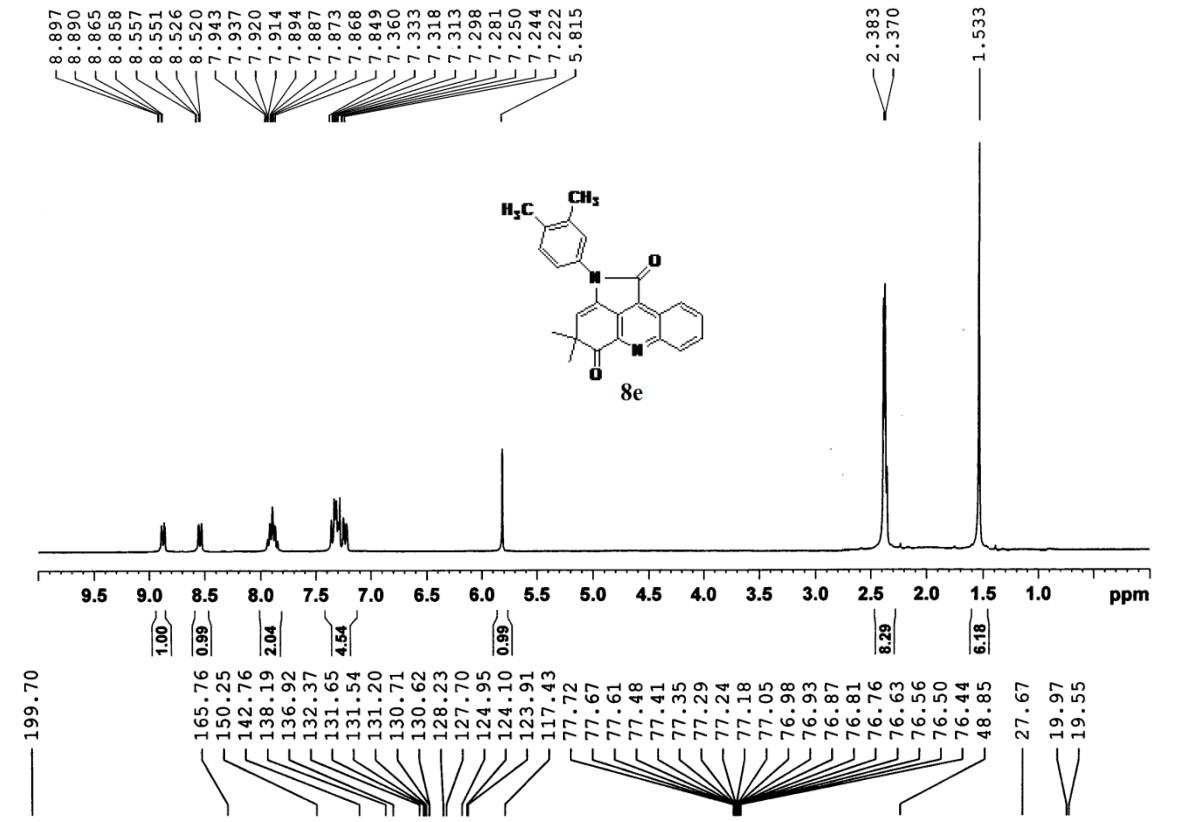
8.460
8.429
7.838
7.808
7.497
7.471
7.446
7.344
7.299
7.274
5.870
2.479
1.531
0.000
CH3
O
N
Cl
O
N
8b
9
8
7
6
5
4
3
2
1
ppm
4.92
5.30
5.47
5.79
17.58
5.41
16.67
33.55
199.25
165.15
148.49
142.79
139.80
138.01
133.70
133.63
132.10
131.91
130.82
129.41
129.03
127.28
127.19
125.30
123.54
123.08
118.37
77.41
76.99
76.56
48.88
27.63
21.48
CH3
O
N
Cl
O
N
8b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.835
8.828
8.477
8.447
7.852
7.844
7.822
7.814
7.448
7.436
7.419
7.405
7.394
7.378
7.364
7.352
7.334
7.311
7.262
5.533
2.245
1.501
1.486
CH3
N
O
Br
H
O
8c
9
8
7
6
5
4
3
2
1
ppm
4.47
4.86
4.93
11.61
3.65
5.08
2.84
4.86
15.68
32.48
199.28
165.08
148.59
142.92
138.04
136.70
133.66
132.54
132.38
131.93
131.56
131.04
129.49
128.57
127.59
127.20
125.45
123.17
117.96
77.43
77.01
76.58
48.99
27.74
27.54
17.99
CH3
N
O
Br
H
O
8c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.810
8.802
8.433
8.402
7.818
7.810
7.787
7.779
7.328
7.301
7.275
7.270
7.255
7.209
7.202
7.181
7.174
5.824
2.340
2.324
1.504
8d
9
8
7
6
5
4
3
2
1
ppm
4.53
4.80
4.74
11.09
5.12
4.68
31.92
29.82
3.36


193.08
159.00
142.26
136.56
132.01
131.72
130.80
127.38
125.87
125.64
125.26
124.78
124.42
121.39
121.16
119.10
117.58
116.88
111.99
71.24
70.82
70.40
42.71
21.41
13.74
13.32
8d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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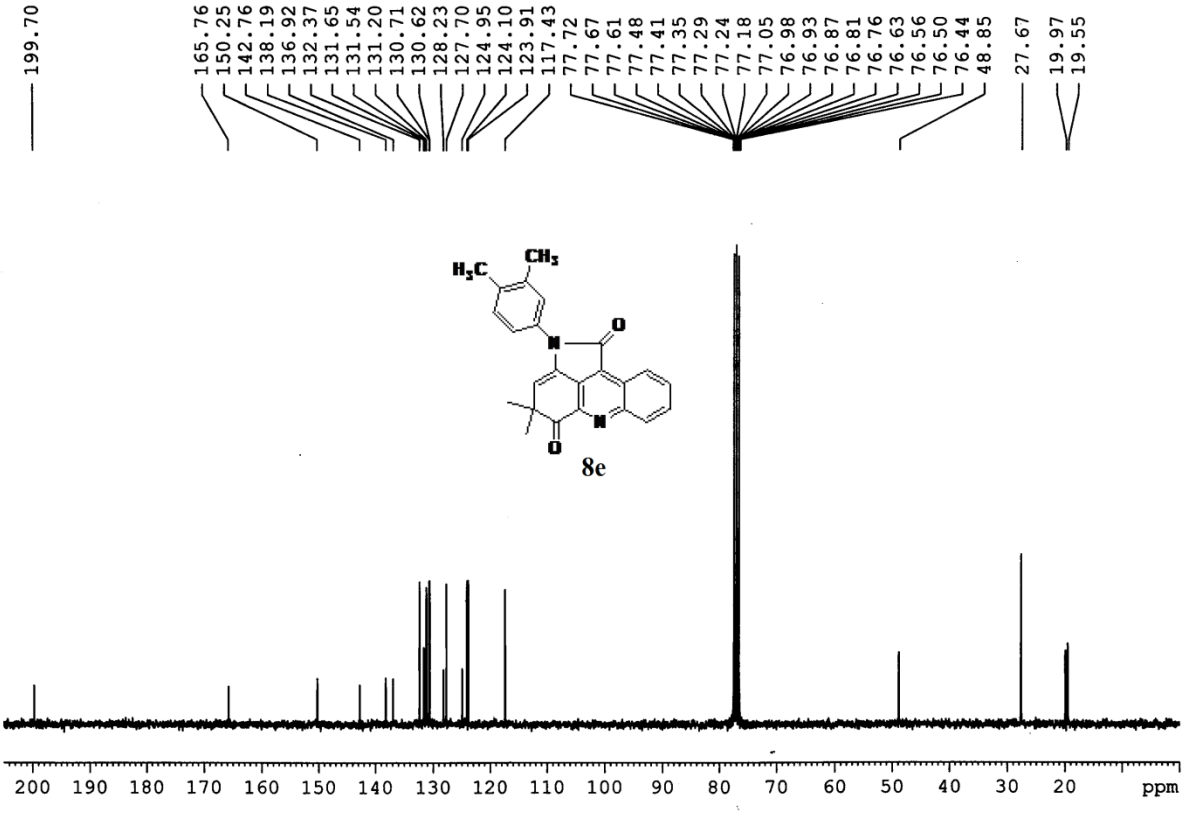
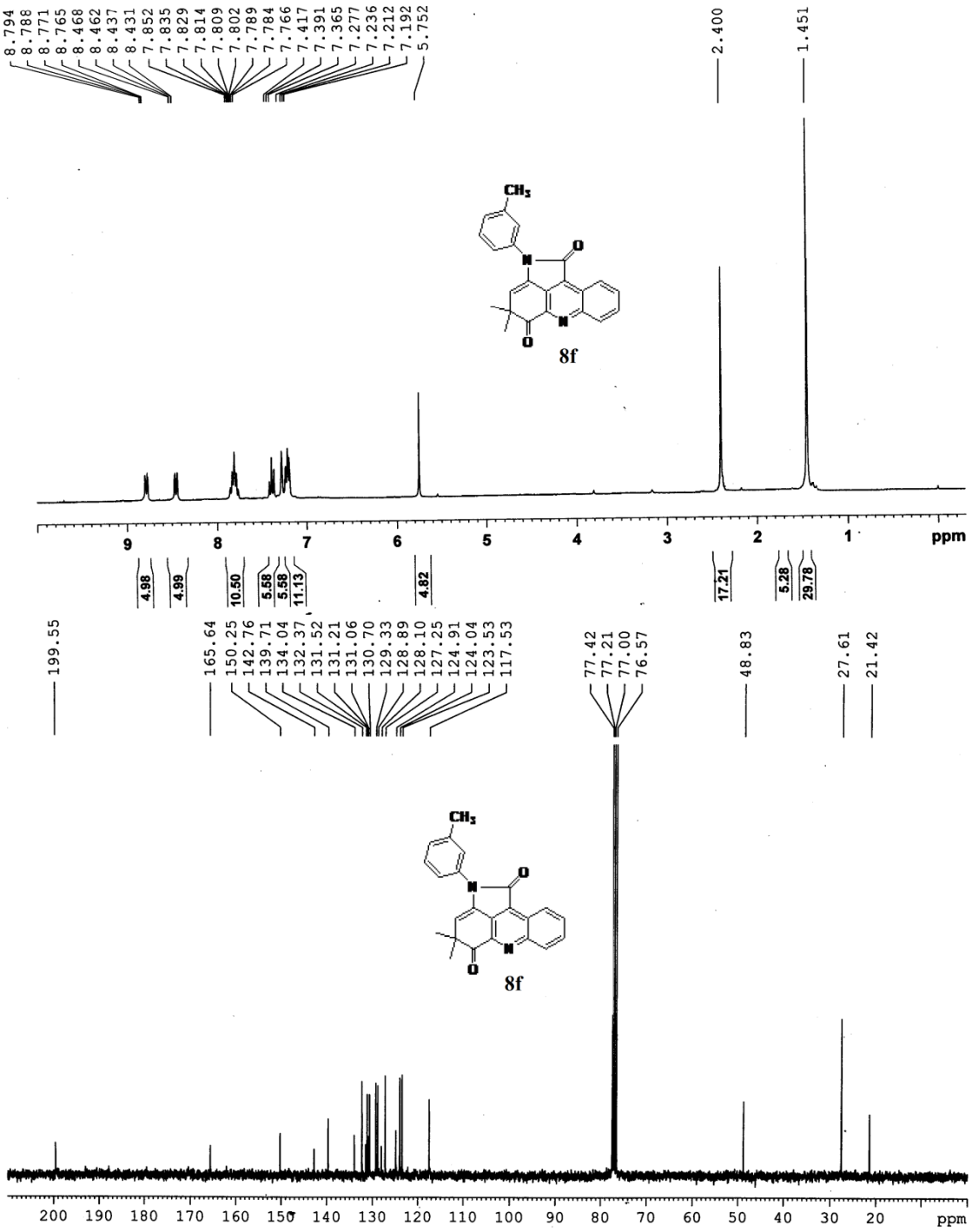
8.865
8.858
8.557
8.551
8.526
8.520
7.943
7.937
7.920
7.914
7.894
7.887
7.873
7.868
7.849
7.360
7.333
7.318
7.313
7.298
7.281
7.250
7.244
7.222
5.815
2.383
2.370
1.533
8e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
0.99
2.04
4.54
0.99
8.29
6.18


199.70
165.76
150.25
142.76
138.19
136.92
132.37
131.65
131.54
131.20
130.71
130.62
128.23
127.70
124.95
124.10
123.91
117.43
77.72
77.67
77.61
77.48
77.41
77.35
77.29
77.24
77.18
77.05
76.98
76.93
76.87
76.81
76.76
76.63
76.56
76.50
76.44
48.85
27.67
19.97
19.55
8e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.788
8.771
8.765
8.468
8.462
8.437
8.431
7.852
7.835
7.829
7.814
7.809
7.802
7.789
7.784
7.766
7.417
7.391
7.365
7.277
7.236
7.212
7.192
5.752
2.400
1.451
CH3
O
N
O
N
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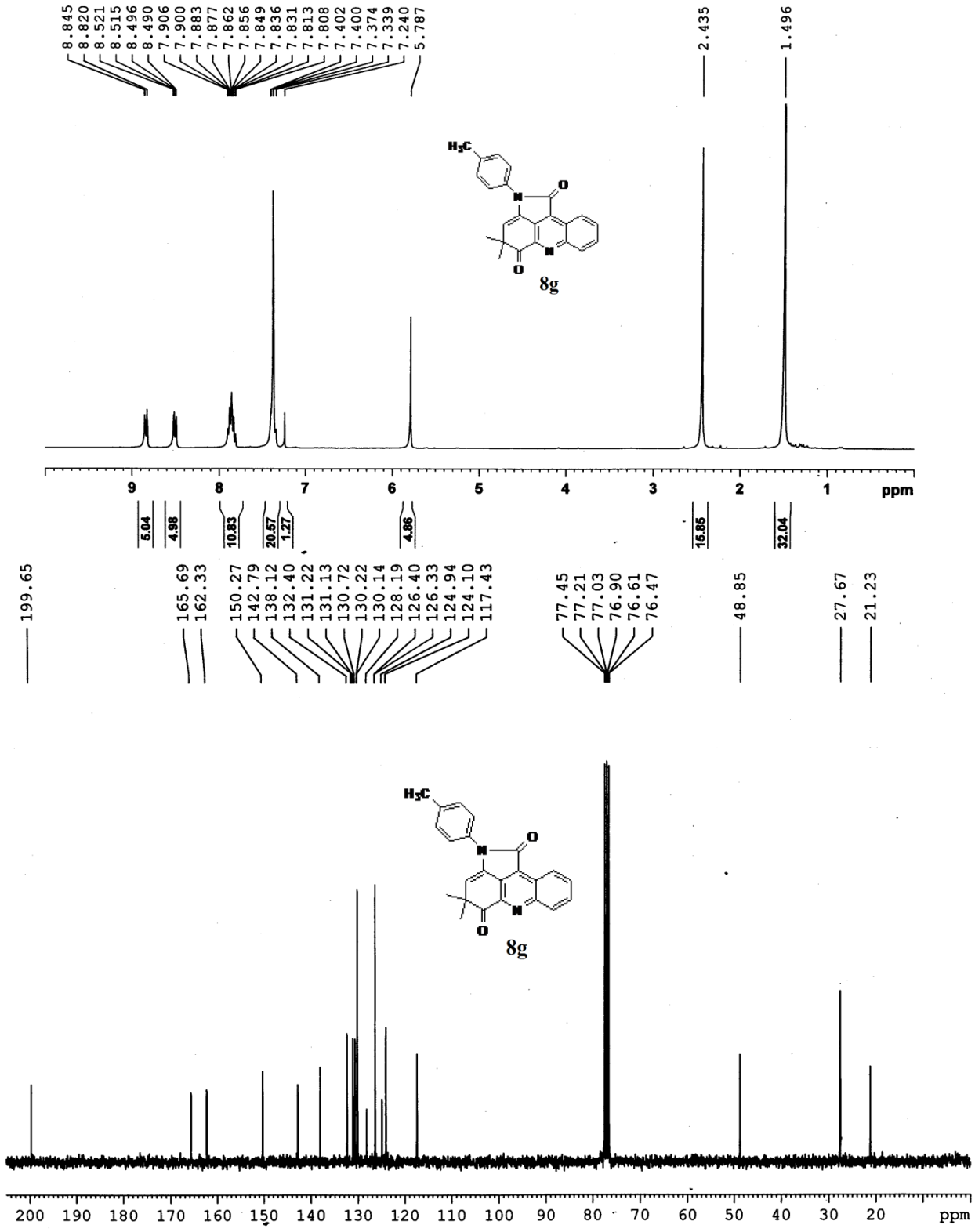
8f
9
8
7
6
5
4
3
2
1
ppm
4.98
4.99
10.50
5.58
5.58
11.13
4.82
17.21
5.28
29.78
199.55
165.64
150.25
142.76
139.71
134.04
132.37
131.52
131.21
131.06
130.70
129.33
128.89
128.10
127.25
124.91
124.04
123.53
117.53
77.42
77.21
77.00
76.57
48.83
27.61
21.42
CH3
O
N
O
N
O
8f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.515
8.496
8.490
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7.877
7.862
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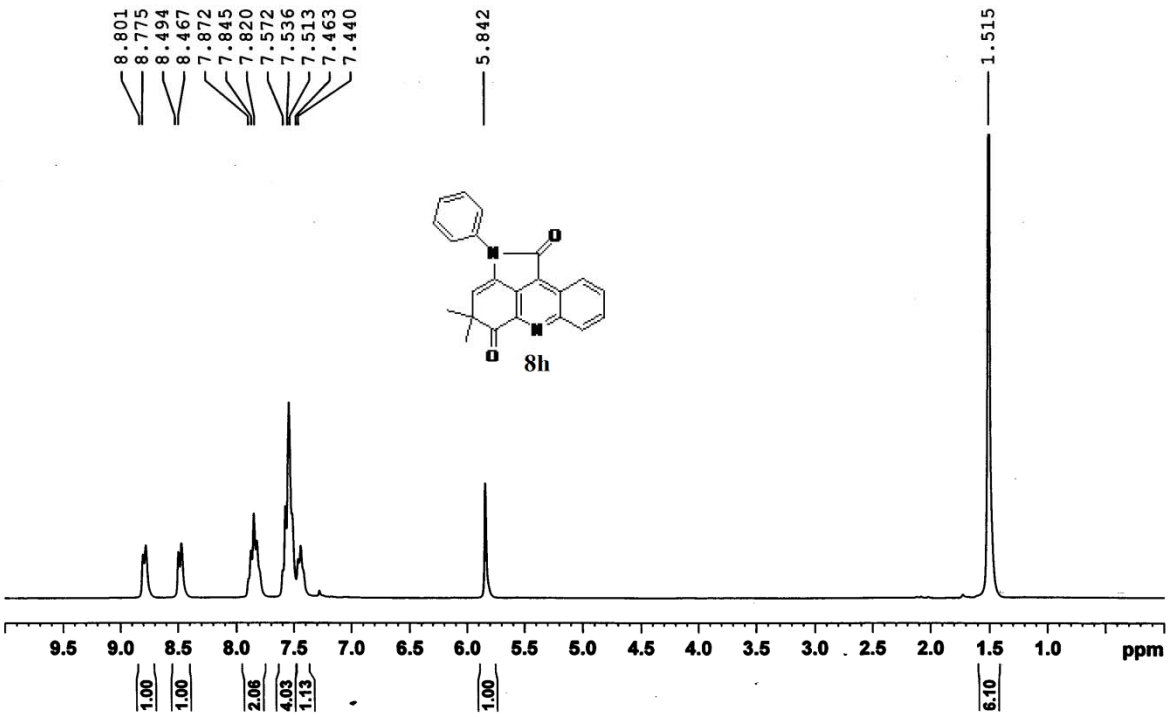
8g
ppm
5.04
4.98
10.83
20.57
1.27
4.86
15.85
32.04
199.65
165.69
162.33
150.27
142.79
138.12
132.40
131.22
131.13
130.72
130.22
130.14
128.19
126.40
126.33
124.94
124.10
117.43
77.45
77.21
77.03
76.90
76.61
76.47
48.85
27.67
21.23
8g
ppm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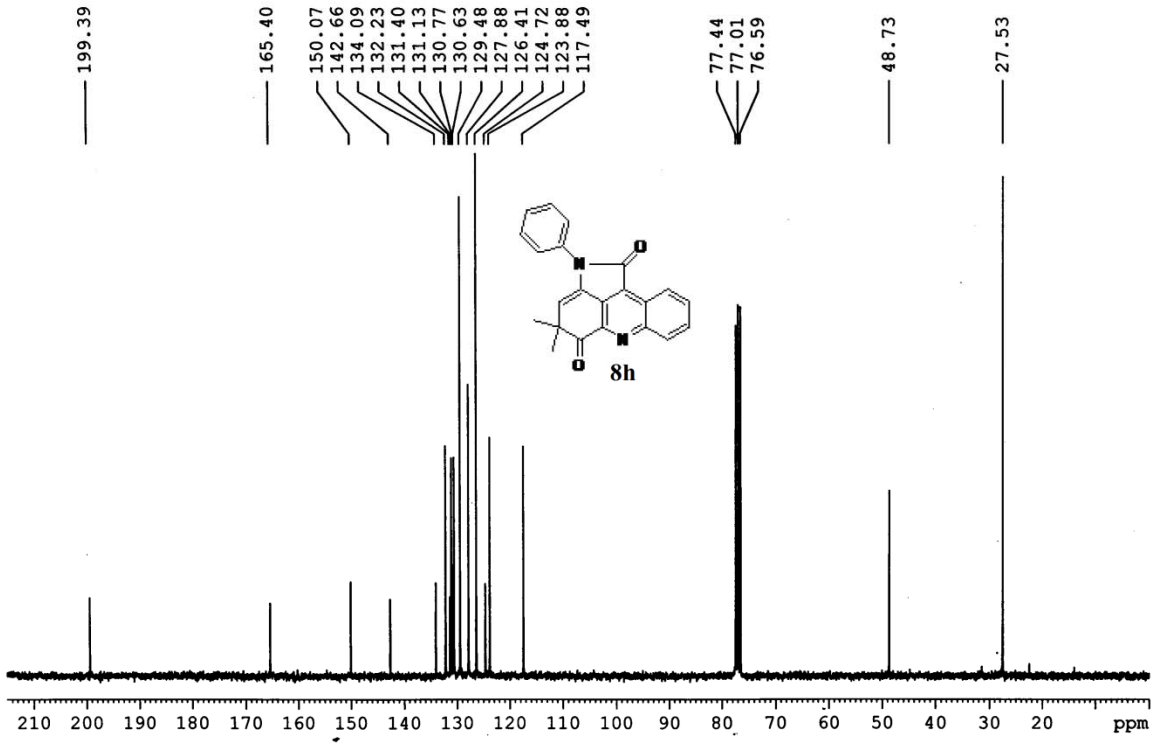
8.775
8.494
8.467
7.872
7.845
7.820
7.572
7.536
7.513
7.463
7.440
5.842
1.515
8h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.00
2.06
4.03
1.13
1.00
6.10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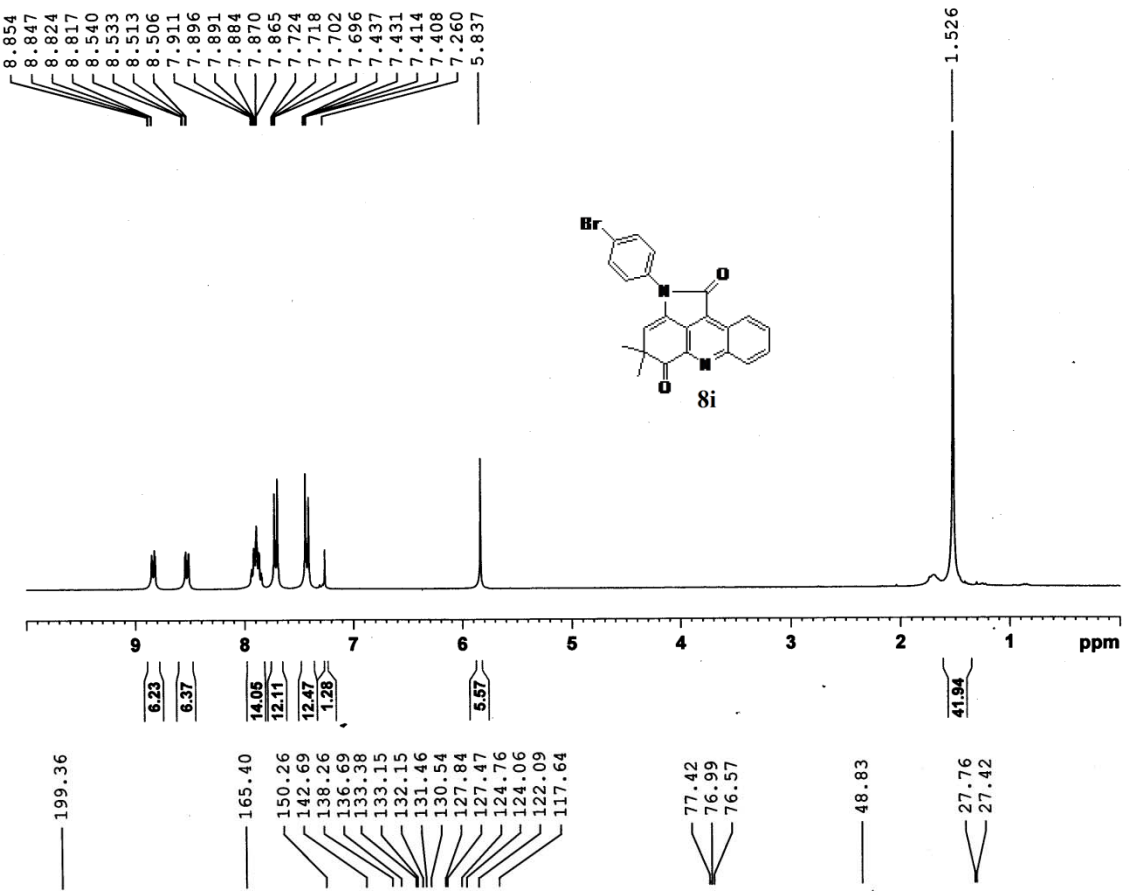
165.40
150.07
142.66
134.09
132.23
131.40
131.13
130.77
130.63
129.48
127.88
126.41
124.72
123.88
117.49
77.44
77.01
76.59
48.73
27.53
8h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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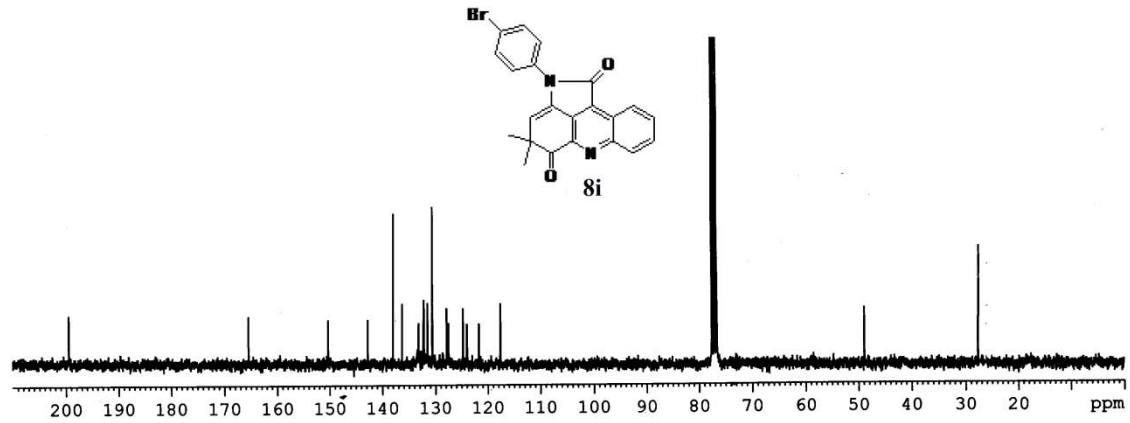
8.847
8.824
8.817
8.540
8.533
8.513
8.506
7.911
7.896
7.891
7.884
7.870
7.865
7.724
7.718
7.702
7.696
7.437
7.431
7.414
7.408
7.260
5.837
1.526
Br
O
N
O
N
O
8i
9
8
7
6
5
4
3
2
1
ppm
6.23
6.37
14.05
12.11
12.47
1.28
5.57
41.94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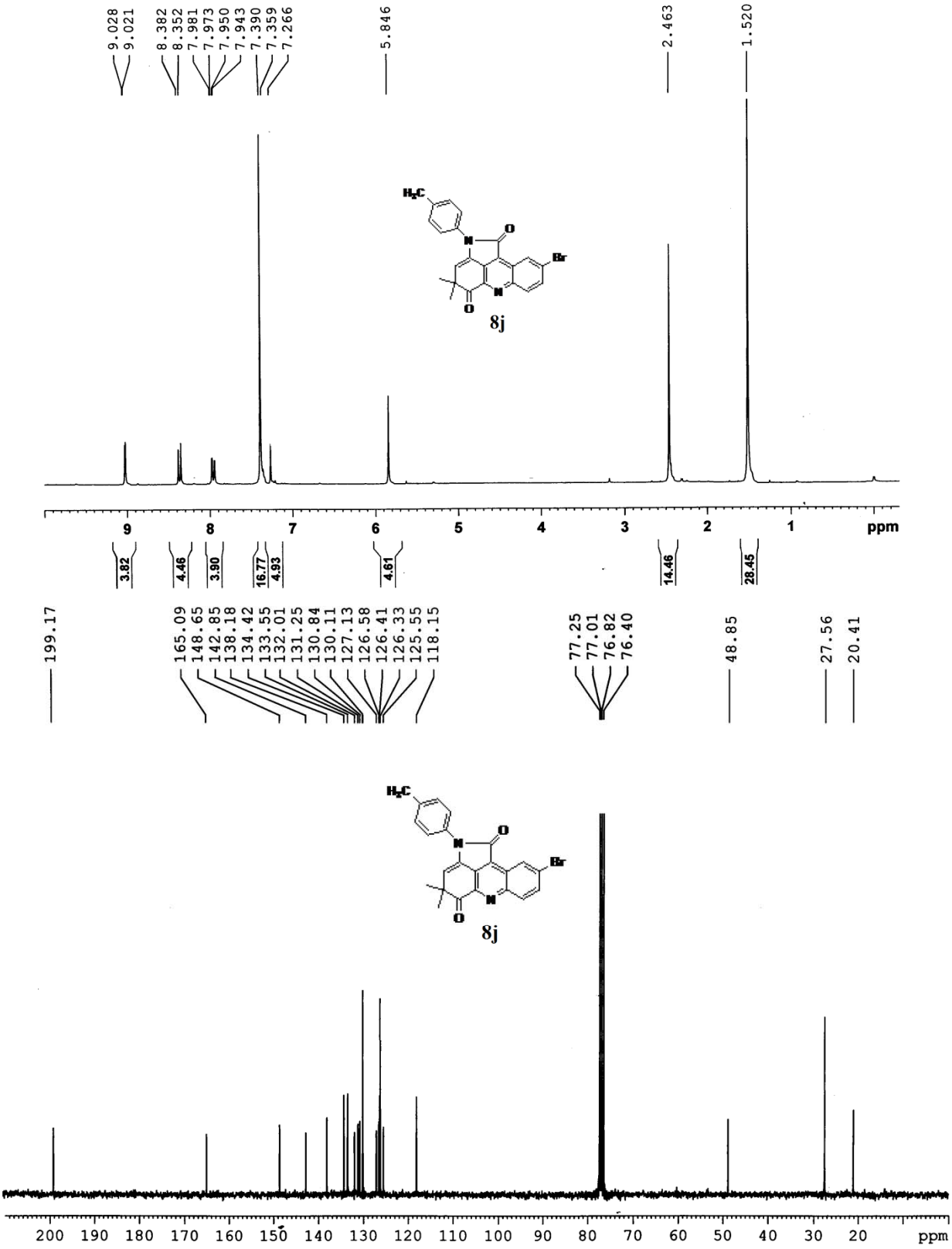
150.26
142.69
138.26
136.69
133.38
133.15
132.15
131.46
130.54
127.84
127.47
124.76
124.06
122.09
117.64
77.42
76.99
76.57
48.83
27.76
27.42
Br
O
N
O
N
O
8i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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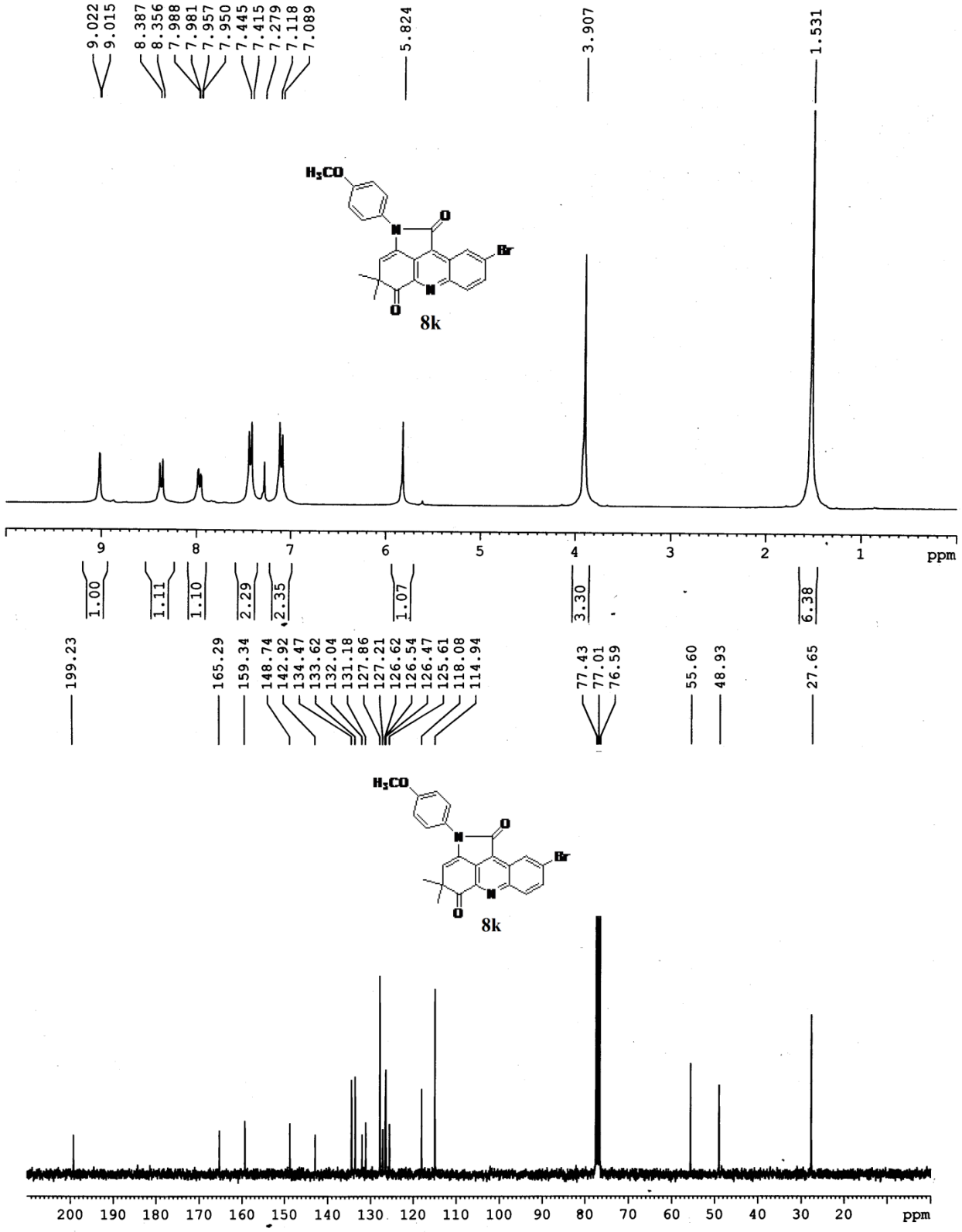
7.973
7.950
7.943
7.390
7.359
7.266
5.846
2.463
1.520
8j
9
8
7
6
5
4
3
2
1
ppm
3.82
4.46
3.90
16.77
4.93
4.61
14.46
28.45
199.17
165.09
148.65
142.85
138.18
134.42
133.55
132.01
131.25
130.84
130.11
127.13
126.58
126.41
126.33
125.55
118.15
77.25
77.01
76.82
76.40
48.85
27.56
20.41
8j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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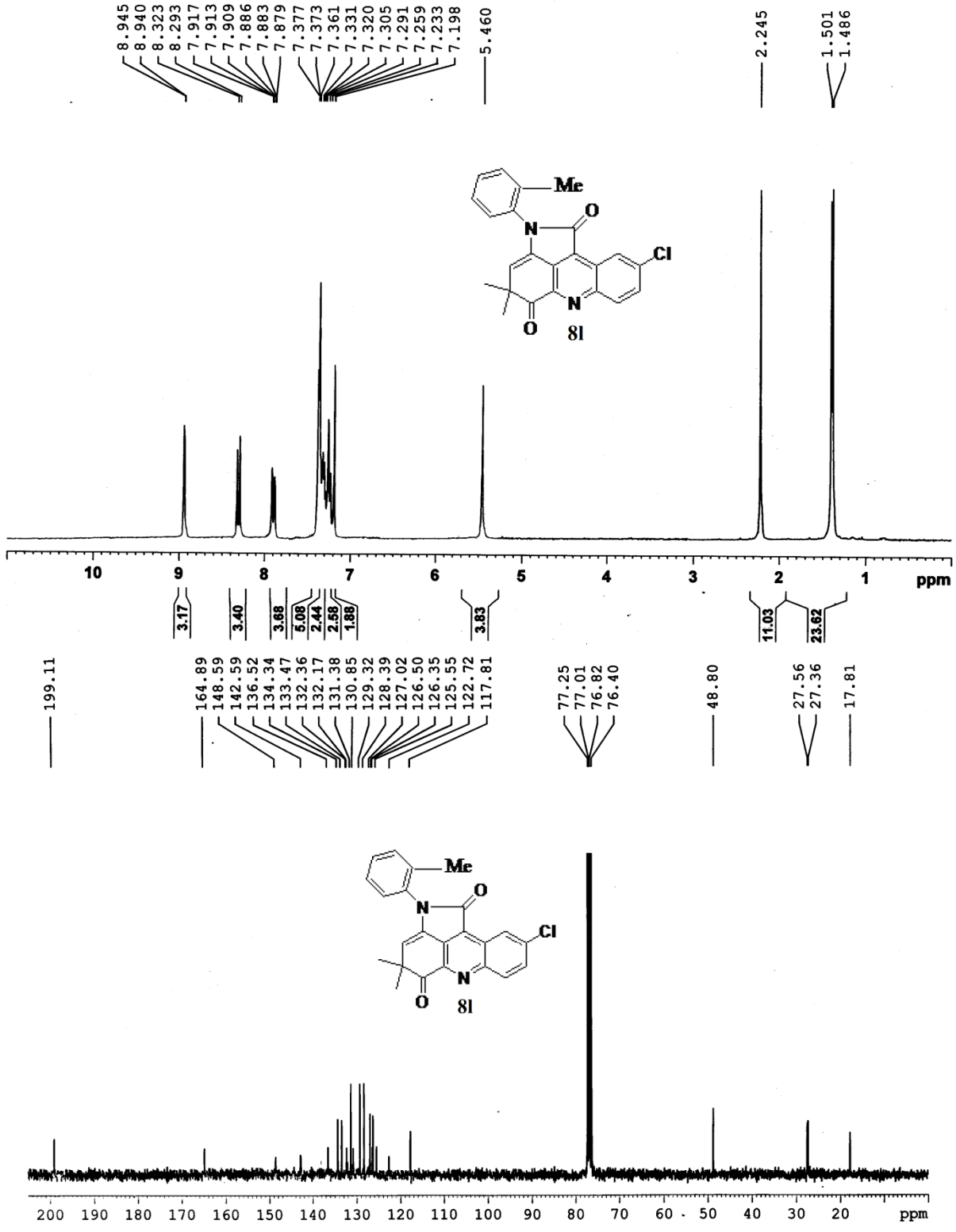
9.015
8.387
8.356
7.988
7.981
7.957
7.950
7.445
7.415
7.279
7.118
7.089
5.824
3.907
1.531
H3CO
O
N
Br
N
O
8k
9
8
7
6
5
4
3
2
1
ppm
1.00
1.11
1.10
2.29
2.35
1.07
3.30
6.38
199.23
165.29
159.34
148.74
142.92
134.47
133.62
132.04
131.18
127.86
127.21
126.62
126.54
126.47
125.61
118.08
114.94
77.43
77.01
76.59
55.60
48.93
27.65
H3CO
O
N
Br
N
O
8k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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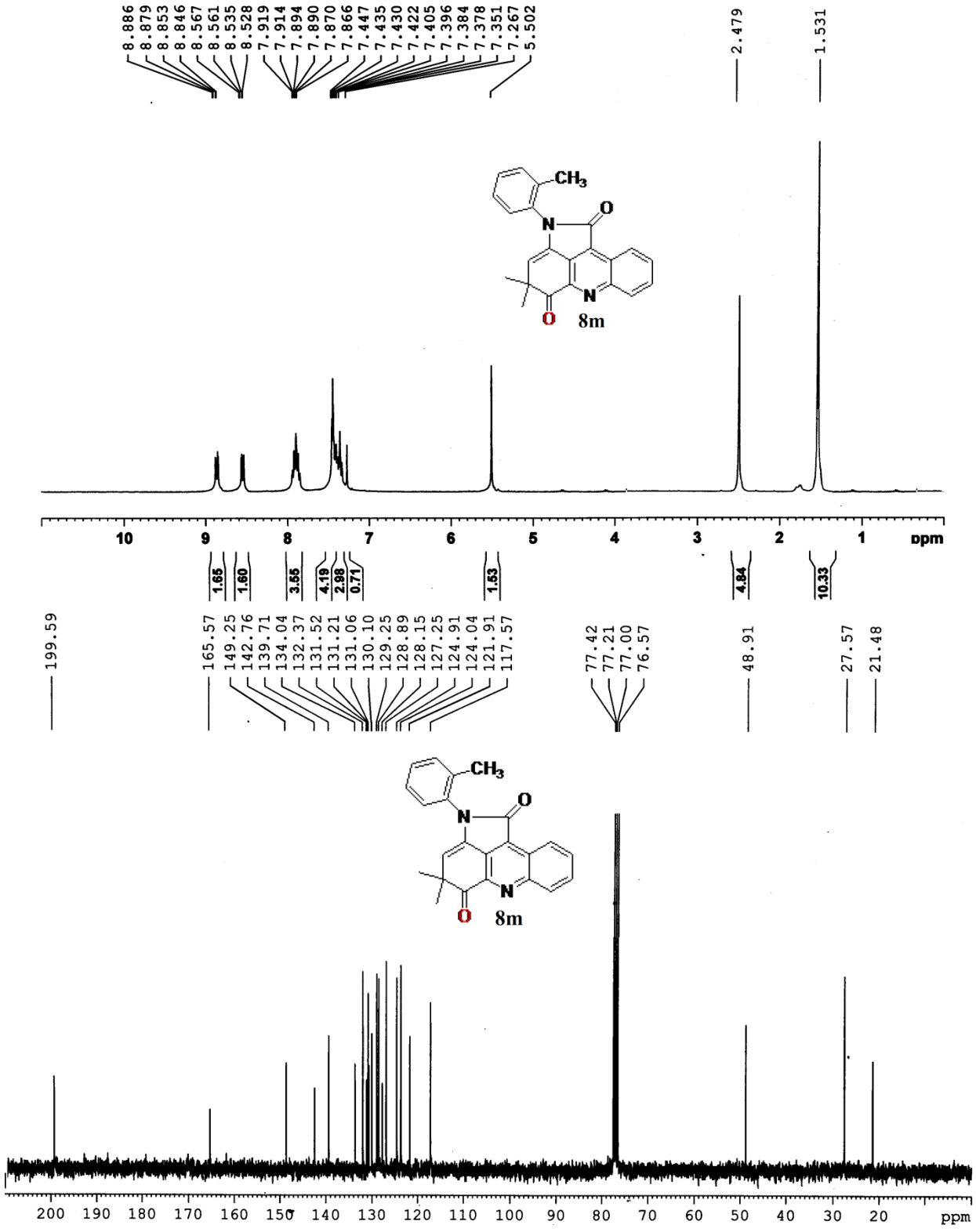
8.940
8.323
8.293
7.917
7.913
7.909
7.886
7.883
7.879
7.377
7.373
7.361
7.331
7.320
7.305
7.291
7.259
7.233
7.198
5.460
2.245
1.501
1.486
Me
O
N
Cl
N
O
8l
10
9
8
7
6
5
4
3
2
1
ppm
3.17
3.40
3.68
5.08
2.44
2.58
1.88
3.83
11.03
23.62
199.11
164.89
148.59
142.59
136.52
134.34
133.47
132.36
132.17
131.38
130.85
129.32
128.39
127.02
126.50
126.35
125.55
122.72
117.81
77.25
77.01
76.82
76.40
48.80
27.56
27.36
17.81
Me
O
N
Cl
N
O
8l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.879
8.853
8.846
8.567
8.561
8.535
8.528
7.919
7.914
7.894
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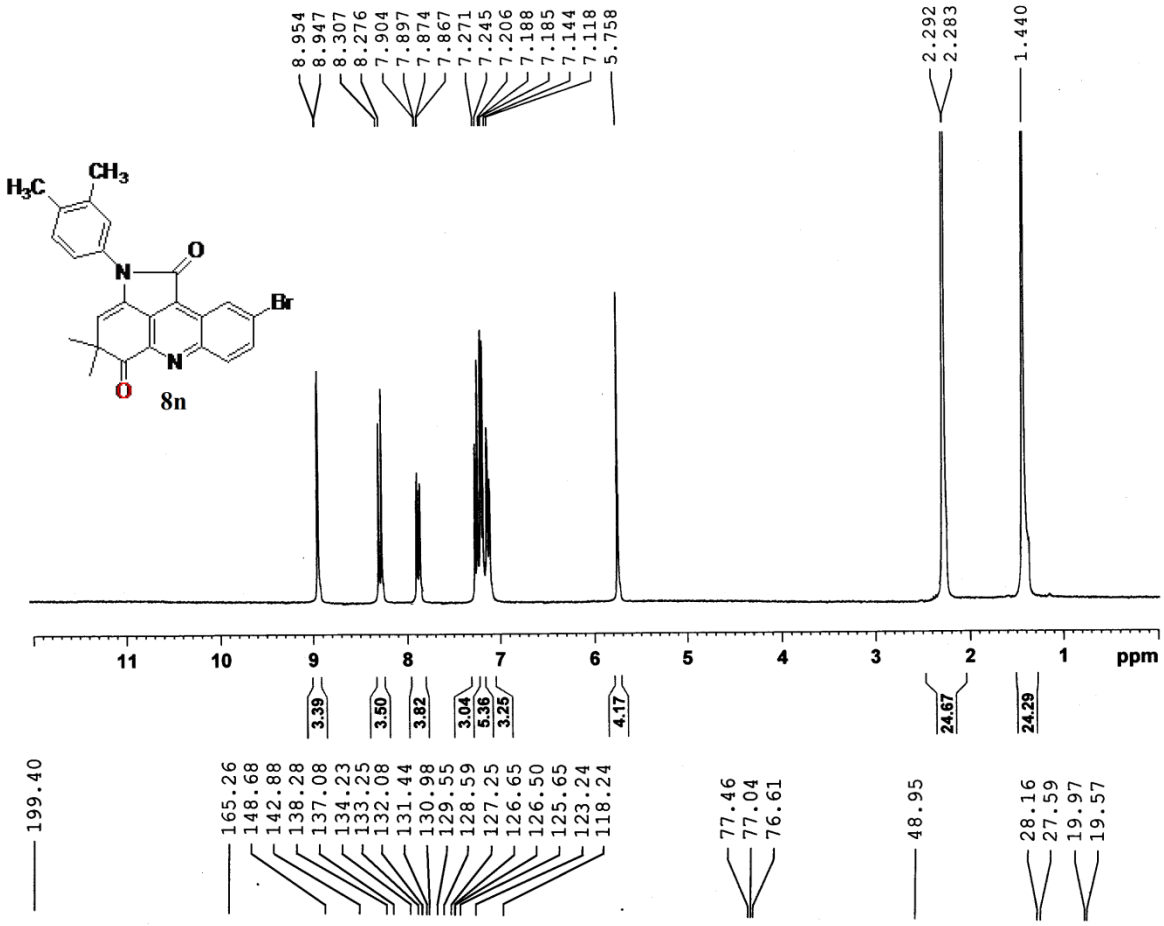
7.870
7.866
7.447
7.435
7.430
7.422
7.405
7.396
7.384
7.378
7.351
7.267
5.502
2.479
1.531
CH3
O
N
O
N
O
8m
10
9
8
7
6
5
4
3
2
1
ppm
1.65
1.60
3.55
4.19
2.98
0.71
1.53
4.84
10.33
199.59
165.57
149.25
142.76
139.71
134.04
132.37
131.52
131.21
131.06
130.10
129.25
128.89
128.15
127.25
124.91
124.04
121.91
117.57
77.42
77.21
77.00
76.57
48.91
27.57
21.48
CH3
O
N
O
N
O
8m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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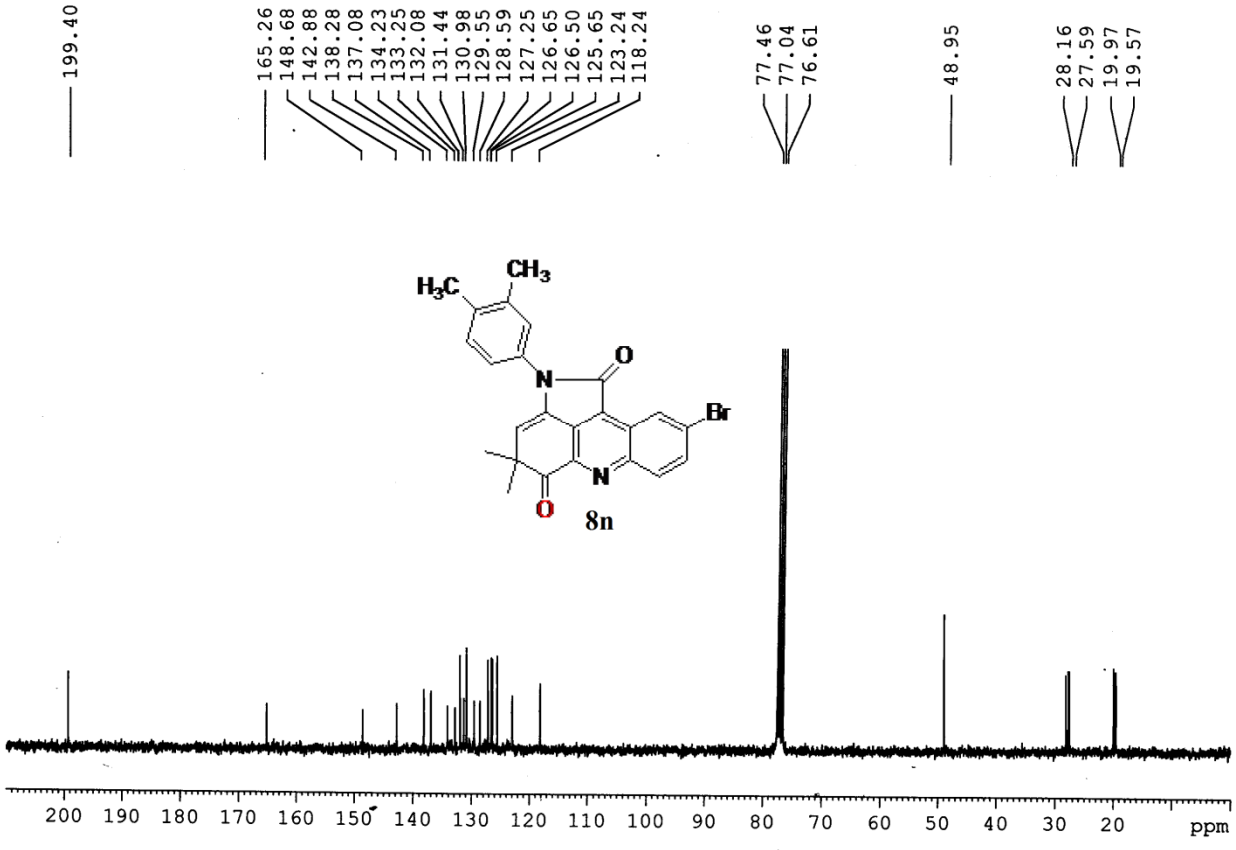
8.947
8.307
8.276
7.904
7.897
7.874
7.867
7.271
7.245
7.206
7.188
7.185
7.144
7.118
5.758
2.292
2.283
1.440
H3C
CH3
N
O
Br
N
O
8n
11
10
9
8
7
6
5
4
3
2
1
ppm
3.39
3.50
3.82
3.04
5.36
3.25
4.17
24.67
24.29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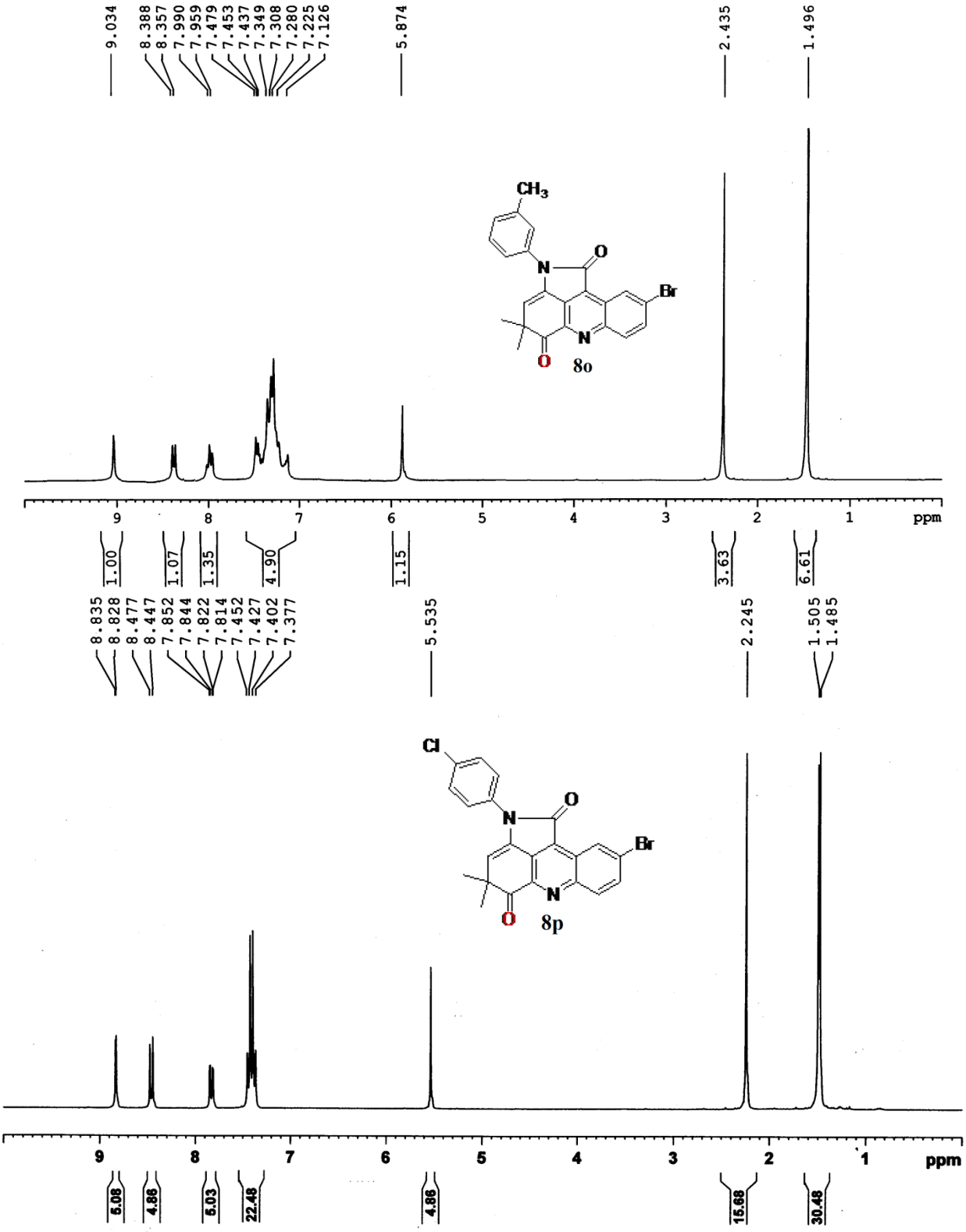
165.26
148.68
142.88
138.28
137.08
134.23
133.25
132.08
131.44
130.98
129.55
128.59
127.25
126.65
126.50
125.65
123.24
118.24
77.46
77.04
76.61
48.95
28.16
27.59
19.97
19.57
H3C
CH3
N
O
Br
N
O
8n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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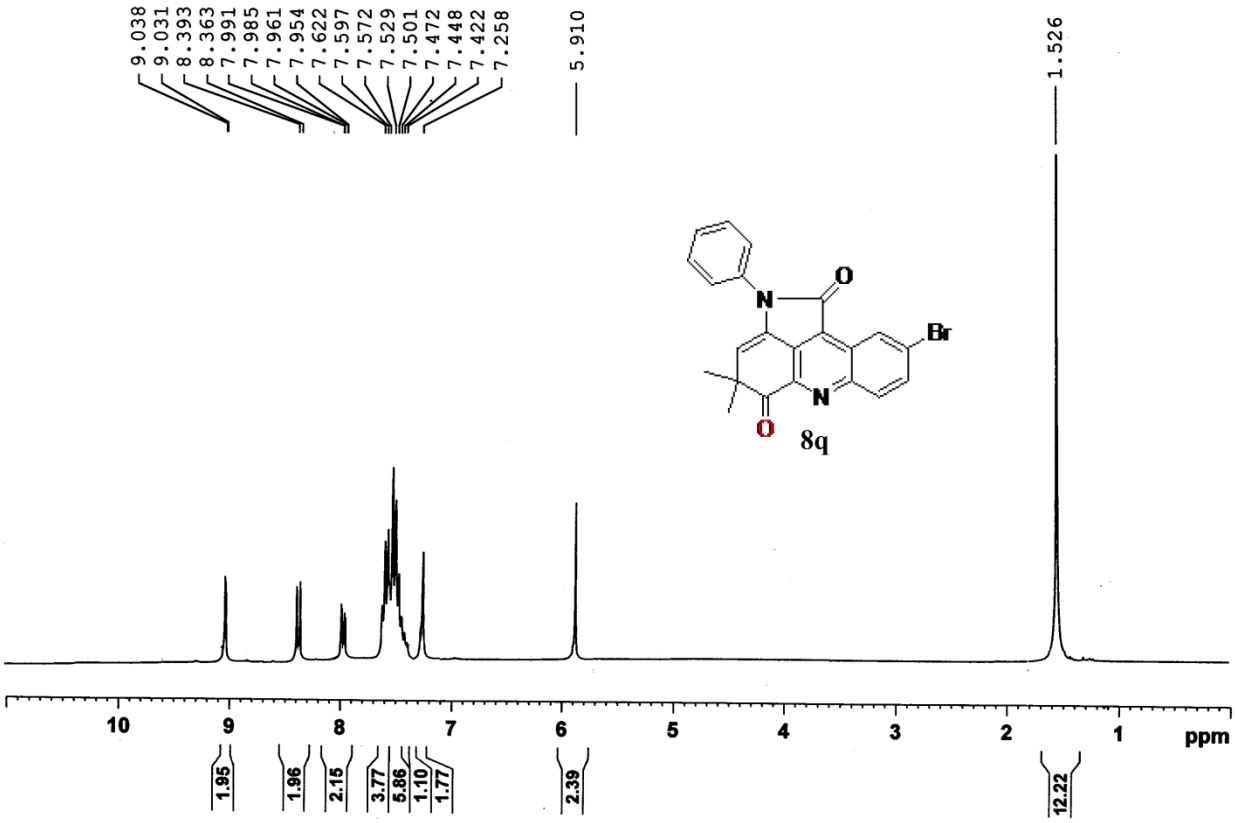
7.959
7.479
7.453
7.437
7.349
7.308
7.280
7.225
7.126
5.874
2.435
1.496
CH3
N
O
Br
N
O
8o
9
8
7
6
5
4
3
2
1
ppm
1.00
1.07
1.35
4.90
1.15
3.63
6.61
8.835
8.828
8.477
8.447
7.852
7.844
7.822
7.814
7.452
7.427
7.402
7.377
5.535
2.245
1.505
1.485
Cl
N
O
Br
N
O
8p
9
8
7
6
5
4
3
2
1
ppm
5.08
4.86
5.03
22.48
4.86
15.68
30.48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7.985
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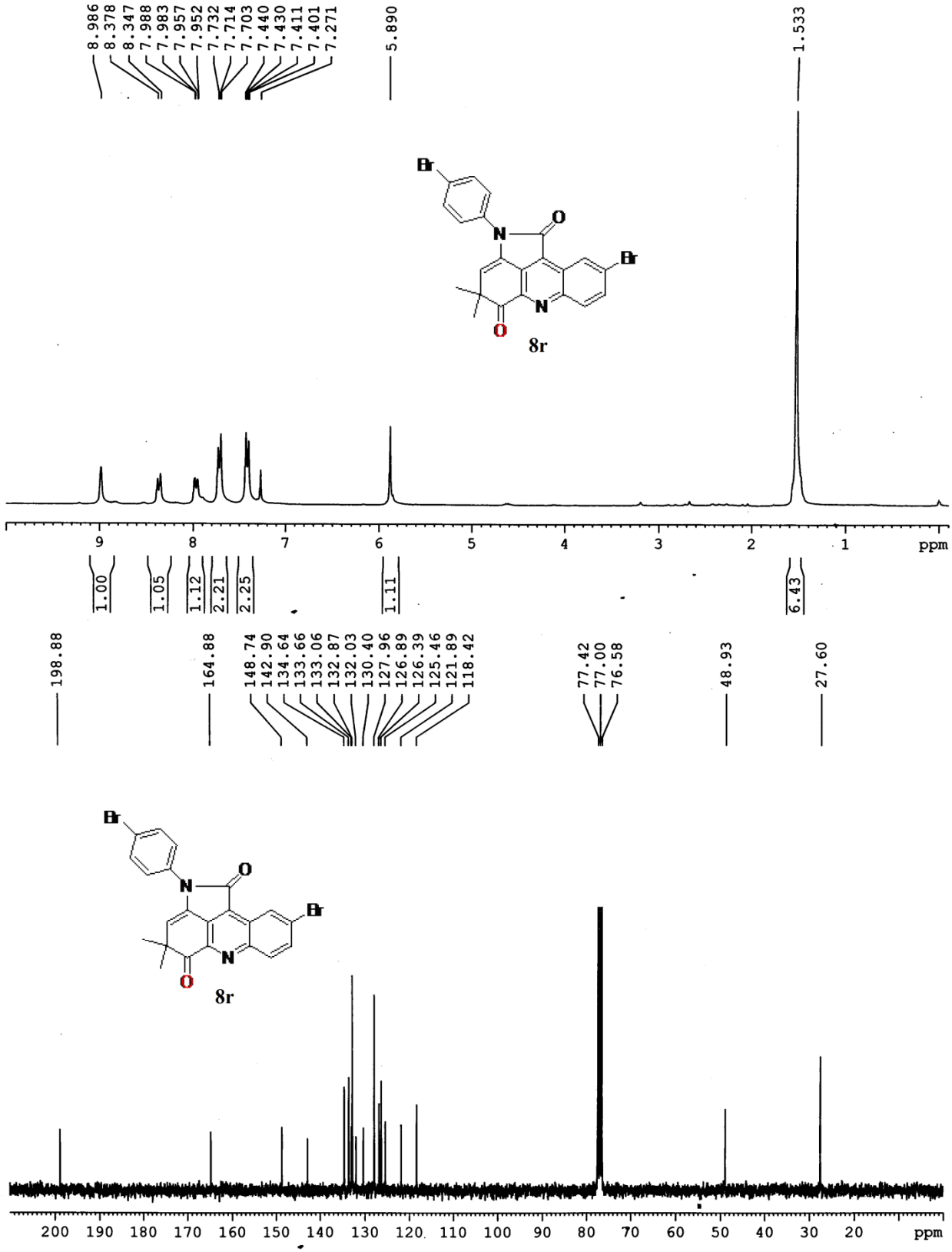
7.954
7.622
7.597
7.572
7.529
7.501
7.472
7.448
7.422
7.258
5.910
1.526
O
N
Br
N
O
8q
10
9
8
7
6
5
4
3
2
1
ppm
1.95
1.96
2.15
3.77
5.86
1.10
1.77
2.39
12.22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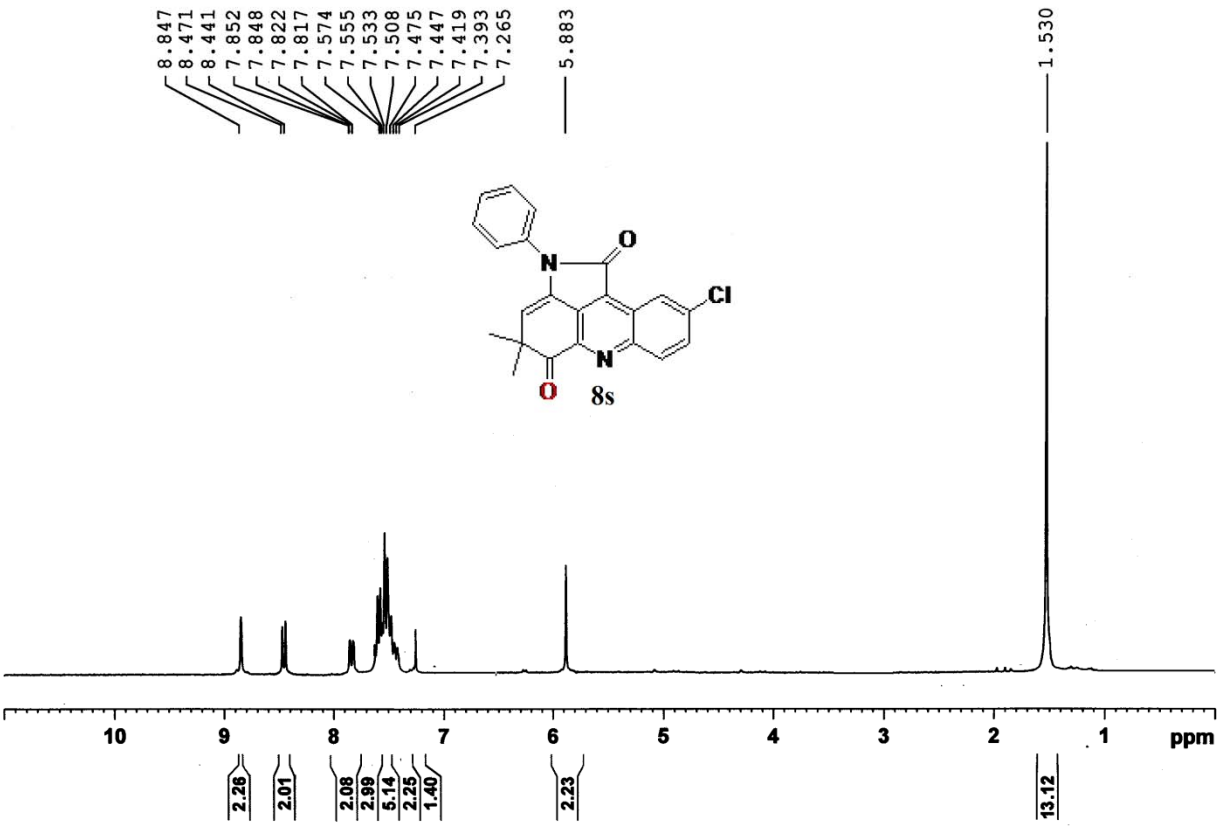
7.957
7.952
7.732
7.714
7.703
7.440
7.430
7.411
7.401
7.271
5.890
1.533
Br
N
O
Br
N
O
8r
9
8
7
6
5
4
3
2
1
ppm
1.00
1.05
1.12
2.21
2.25
1.11
6.43
198.88
164.88
148.74
142.90
134.64
133.66
133.06
132.87
132.03
130.40
127.96
126.89
126.39
125.46
121.89
118.42
77.42
77.00
76.58
48.93
27.60
Br
N
O
Br
N
O
8r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.847
8.471
8.441
7.852
7.848
7.822
7.817
7.574
7.555
7.533
7.508
7.475
7.447
7.419
7.393
7.265
5.883
1.530
O
N
Cl
N
O
8s
10
9
8
7
6
5
4
3
2
1
ppm
2.26
2.01
2.08
2.99
5.14
2.25
1.40
2.23
13.12

Supporting Information 3

# Covalently anchored carboxylic acid on uniform spherical silica nanoparticles with narrow slit like mesopores for the synthesis of pyrroloacridinones: CuI-catalyzed further C(sp3)-H oxyfunctionalization for C=O formation

**Suman Ray[a], Asim Bhaumik[b], Malay Pramanik[b] and Chhanda Mukhopadhyay[a]***

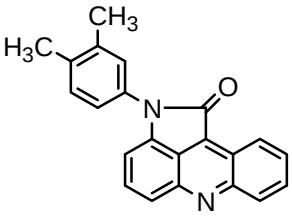
*a: Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata-700009, India*
*b: Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India.*

*cmukhop@yahoo.co.in* *

**Table of Contents**

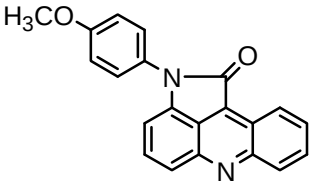
**Spectroscopic characterization of 13a-13t**

**2-(3,4-Dimethyl-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13a):**



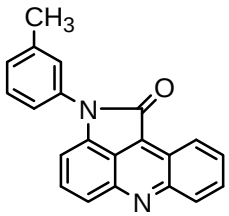
Red colored solid; m.p. 218-220 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.64%. Found: C, 81.48; H, 4.98; N, 8.65%; IR (KBr) $cm^{-1}$: 3411, 2912, 1721, 1603, 1528, 1474, 1111, 754, 730, 541, 469; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.285 (3H, s, $CH_3$), 2.29 (3H, s, $CH_3$), 6.88 (1H, d, J = 6.9 Hz, arom.), 7.26-7.32 (3H, m, arom.), 7.57-7.62 (1H, m, arom.), 7.70-7.87 (3H, m, arom.), 8.36 (1H, d, J = 9.0 Hz, arom.), 8.81 (1H, d, J = 9.0 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 19.5, 19.9, 105.9, 119.7, 122.4, 123.0, 123.3, 124.2, 127.0, 127.7, 129.1, 130.6, 130.7, 132.3, 132.8, 136.4, 138.1, 140.5, 146.4, 151.8, 167.3.

**2-(4-Methoxy-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13b):**



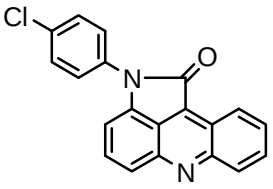
Red colored solid; m.p. 198-200 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58%. Found: C, 77.30; H, 4.33; N, 8.59%; IR (KBr) $cm^{-1}$: 3021, 1717, 1654, 1639, 1489, 1246, 1161, 1200, 1016, 783, 575; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 3.92 (3H, s, $OCH_3$), 6.94 (1H, d, J = 6.9 Hz, arom.), 7.10-7.13 (2H, m, arom.), 7.53-7.56 (2H, m, arom.), 7.70-7.72 (1H, m, arom.), 7.83-7.95 (3H, m, arom.), 8.47 (1H, d, J = 8.7 Hz, arom.), 8.94 (1H, d, J = 8.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 55.6, 105.8, 114.9, 119.7, 122.4, 123.1, 124.2, 127.4, 127.4, 127.8, 129.2, 130.6, 130.7, 133.0, 140.6, 146.3, 151.8, 159.0, 167.4.

**2-m-Tolyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13c):**



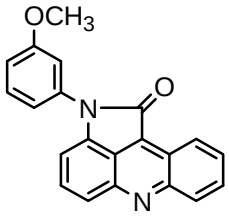
Brown colored solid; m.p. 230-232 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03%. Found: C, 81.28; H, 4.56; N, 9.05%; IR (KBr) $cm^{-1}$: 3399, 2919, 1701, 1636, 1518, 1444, 1115, 777, 739, 535; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.49 (3H, s, $CH_3$), 6.99 (1H, d, J = 6.9 Hz, arom.), 7.26 (1H, d, J = 5.1 Hz, arom.), 7.41-7.51 (3H, m, arom.), 7.68 (1H, t, J = 7.5 Hz, arom.), 7.78-7.95 (3H, m, arom.), 8.43 (1H, d, J = 8.7 Hz, arom.), 8.91 (1H, d, J = 8.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.5, 106.0, 119.7, 122.5, 122.9, 123.0, 124.1, 126.6, 127.6, 128.5, 129.2, 129.3, 130.6, 130.7, 132.8, 134.7, 139.6, 140.2, 146.4, 151.8, 167.1.

**2-(4-Chloro-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13d):**



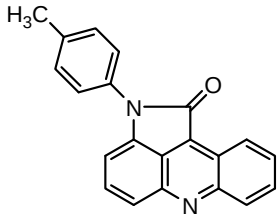

Red colored solid; m.p. 250-252 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{20}H_{11}ClN_2O$: C, 72.62; H, 3.35; N, 8.47%. Found: C, 72.63; H, 3.36; N, 8.48%; IR (KBr) $cm^{-1}$: 3019, 1726, 1654, 1646, 1500, 1216, 1263, 1110, 1016, 782, 595; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 6.92 (1H, d, J = 6.9 Hz, arom.), 7.47-7.54 (4H, m, arom.), 7.60-7.65 (1H, m, arom.), 7.75 (1H, t, J = 8.4 Hz, arom.), 7.82-7.89 (2H, m, arom.), 8.38 (1H, d, J = 9.0 Hz, arom.), 8.85 (1H, d, J = 9.0 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 106.0, 119.8, 122.7, 123.0, 124.1, 125.4, 127.1, 129.5, 129.8, 130.6, 131.0, 132.9, 133.4, 138.1, 139.6, 146.3, 151.7, 166.9.(2 c less)

**2-(3-Methoxy-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13e):**



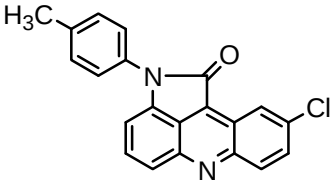

Red colored solid; m.p. 158-160 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58%. Found: C, 77.30; H, 4.32; N, 8.59%; IR (KBr) $cm^{-1}$: 3011, 1716, 1650, 1636, 1497, 1226, 1163, 1111, 1006, 780, 585; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 3.90 (3H, s, $OCH_3$), 6.99-7.03 (2H, m, arom.), 7.21-7.23 (2H, m, arom.), 7.47-7.50 (1H, m, arom.), 7.65-7.70 (1H, m, arom.), 7.793-7.92 (3H, m, arom.), 8.42 (1H, d, J = 9.0 Hz, arom.), 8.89 (1H, d, J = 8.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 55.5, 106.1, 111.7, 113.5, 118.0, 119.7, 122.6, 122.9, 124.1, 127.4, 129.2, 130.2, 130.6, 130.7, 132.7, 135.9, 140.0, 146.4, 151.8, 160.5, 167.0.

**2-p-tolylpyrrolo[2,3,4-kl]acridin-1(2H)-one (13f):**



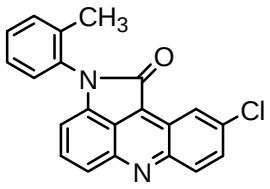
Red colored solid; m.p. 222-224 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03%. Found: C, 81.28; H, 4.56; N, 9.05%; IR (KBr) $cm^{-1}$: 3419, 2939, 1710, 1635, 1509, 1465, 1111, 777, 731, 583; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.39 (3H, s, $CH_3$), 6.89 (1H, d, J = 6.9 Hz, arom.), 7.31 (2H, d, J = 8.1 Hz, arom.), 7.43 (2H, d, J = 8.4 Hz, arom.), 7.60 (1H, t, J = 8.1 Hz, arom.), 7.40-7.87 (3H, m, arom.), 8.36 (1H, d, J = 9.0 Hz, arom.), 8.81 (1H, d, J = 9.0 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.2, 105.9, 119.8, 122.5, 123.0, 124.2, 125.8, 127.7, 129.2, 130.2, 130.3, 130.7, 132.1, 132.8, 137.7, 140.4, 146.5, 151.9, 167.2.

**9-Chloro-2-p-tolyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13g):**



Red colored solid; m.p. 188-190 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{13}ClN_2O$: C, 73.15; H, 3.80; N, 8.12%. Found: C, 73.17; H, 3.81; N, 8.13%; IR (KBr) $cm^{-1}$: 3399, 2912, 1718, 1635, 1515, 1466, 1111, 775, 726, 573; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.40 (3H, s, $CH_3$), 6.92 (1H, d, J = 6.9 Hz, arom.), 7.32 (2H, d, J = 8.4 Hz, arom.), 7.42 (2H, d, J = 8.4 Hz, arom.), 7.60-7.65 (1H, m, arom.), 7.76-7.81 (2H, m, arom.), 8.31 (1H, d, J = 9.3 Hz, arom.), 8.82 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.2, 106.5, 120.0, 122.3, 122.9, 123.1, 125.7, 127.2, 130.3, 131.9, 132.2, 133.4, 135.9, 137.9, 140.3, 146.2, 149.1, 166.7.

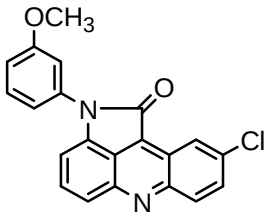
**9-Chloro-2-o-tolyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13h):**



Brown colored solid; m.p. 178-180 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{13}ClN_2O$: C, 73.15; H, 3.80; N, 8.12%. Found: C, 73.16; H, 3.81; N, 8.13%; IR (KBr) $cm^{-1}$: 3397, 2901, 1701, 1643, 1498, 1434, 1211, 779, 727, 565; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.28 (3H, s, $CH_3$), 6.66 (1H, d, J = 6.9 Hz, arom.), 7.39-7.41 (2H,

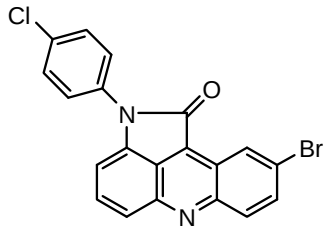
m, arom.), 7.44-7.47 (2H, m, arom.), 7.63-7.68 (1H, m, arom.), 7.82-7.86 (2H, m, arom.), 8.37 (1H, d, J = 9.3 Hz, arom.), 8.88 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 18.1, 106.1, 120.3, 122.4, 122.9, 123.2, 127.0, 127.1, 127.2, 128.4, 129.3, 131.6, 132.0, 132.2, 133.2, 135.8, 136.8, 140.6, 146.5, 150.1, 166.6.

**9-Chloro-2-(3-methoxy-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13i):**



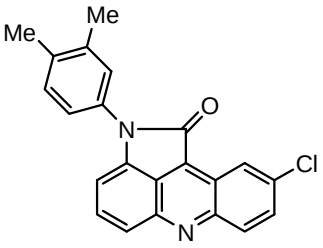

Red colored solid; m.p. 180-182 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{13}ClN_2O_2$: C, 69.91; H, 3.63; Cl, 9.83; N, 7.76%. Found: C, 69.92; H, 3.64; Cl, 9.84; N, 7.76%; IR (KBr) $cm^{-1}$: 3429, 1717, 1639, 1499, 1466, 1330, 1100, 1064, 739, 496; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 3.90 (3H, s, $OCH_3$), 7.02-7.05 (2H, m, arom.), 7.19-7.22 (2H, m, arom.), 7.50 (1H, t, J = 6.9 Hz, arom.), 6.68 (1H, t, J = 6.9 Hz, arom.), 7.80-7.84 (2H, m, arom.), 8.32 (1H, d, J = 9.6 Hz, arom.), 8.82 (1H, d, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 55.5, 106.7, 111.7, 113.6, 117.9, 119.9, 122.6, 122.7, 122.9, 126.5, 130.3, 131.9, 132.2, 133.0, 135.7, 135.9, 139.9, 146.5, 150.0, 160.6, 166.5.

**9-bromo-2-(4-chlorophenyl)pyrrolo[2,3,4-kl]acridin-1(2H)-one (13j):**



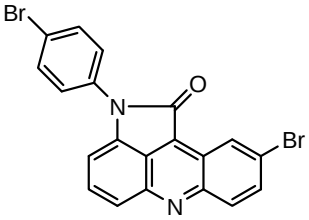

Red colored solid; m.p. 221-223 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{20}H_{10}BrClN_2O$: C, 58.64; H, 2.46; N, 6.84%. Found: C, 58.66; H, 2.47; N, 6.85%; IR (KBr) $cm^{-1}$: 3429, 1717, 1626, 1500, 1469, 1334, 1107, 1069, 737, 506; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 6.95 (1H, d, J = 6.9 Hz, arom.), 7.50 (4H, br s, arom.), 7.66 (1H, t, J = 6.9 Hz, arom.), 7.84 (1H, d, J = 9.0 Hz, arom.), 7.92 (1H, dd, J = 9.3 Hz, J = 2.1 Hz, arom.), 8.26 (1H, d, J = 9.3 Hz, arom.), 8.99 (1H, d, J = 2.1 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 106.7, 119.2, 120.1, 122.5, 123.4, 124.8, 126.2, 127.0, 129.9, 131.7, 133.1, 133.5, 134.9, 137.5, 139.6, 146.1, 149.7, 167.5.

**9-Chloro-2-(3,4-dimethyl-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13k):**



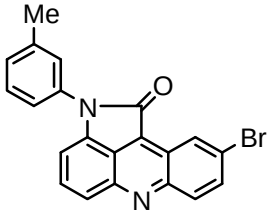

Red colored solid; m.p. 178-180 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{22}H_{15}ClN_2O$: C, 73.64; H, 4.21; N, 7.81%. Found: C, 73.66; H, 4.22; N, 7.83%; IR (KBr) $cm^{-1}$: 3409, 2928, 1711, 1633, 1508, 1464, 1111, 773, 730, 581; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.39 (3H, s, $CH_3$), 2.392 (3H, s, $CH_3$), 7.00 (1H, d, J = 6.9 Hz, arom.), 7.34-7.40 (3H, m, arom.), 7.72 (1H, t, J = 8.1 Hz, arom.), 7.88 (2H, dt, J = 7.5 Hz, J = 2.4 Hz, arom.), 8.42 (1H, d, J = 9.3 Hz, arom.), 8.93 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 19.5, 20.0, 106.6, 120.0, 120.1, 122.9, 123.1, 123.2, 127.0, 130.7, 131.8, 132.0, 132.2, 133.5, 135.9, 136.6, 138.2, 140.4, 146.0, 149.4, 159.1, 166.7.

**9-Bromo-2-(4-bromo-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13l):**




Red colored solid; m.p. 182-184 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{20}H_{10}Br_2N_2O$: C, 52.90; H, 2.22; N, 6.17%. Found: C, 52.92; H, 2.23; N, 6.18%; IR (KBr) $cm^{-1}$: 3417, 1712, 1634, 1496, 1461, 1325, 1123, 1068, 719, 490; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 7.03 (1H, d, J = 6.9 Hz, arom.), 7.52 (2H, d, J = 8.7 Hz, arom.), 7.67-7.70 (3H, m, arom.), 7.85-7.01 (2H, m, arom.), 8.34 (1H, d, J = 9.3 Hz, arom.), 9.08 (1H, d, J = 2.1 Hz, arom.)

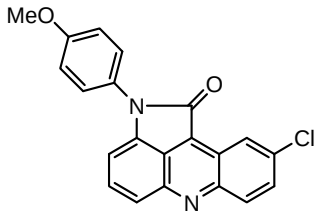
**9-Bromo-2-m-tolyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13m):**




Brown colored solid; m.p. 190-192 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{13}BrN_2O$: C, 64.80; H, 3.37; N, 7.20%. Found: C, 64.81; H, 3.38; N, 7.21%; IR (KBr) $cm^{-1}$: 3419, 2938, 1717, 1634, 1508, 1466, 1112, 777, 731, 581, 498; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.46 (3H, s, $CH_3$), 6.99 (1H, d, J = 6.6 Hz, arom.), 7.26-7.27

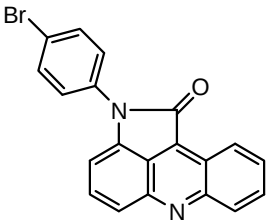
(1H, m, arom.), 7.39-7.40 (3H, m, arom.), 7.69 (1H, t, J = 8.1 Hz, arom.), 7.83 (1H, d, J = 9.0 Hz, arom.), 7.95 (1H, d, J = 9.0 Hz, arom.), 8.26 (1H, d, J = 9.3 Hz, arom.), 9.05 (1H, s, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 21.5, 106.6, 119.9, 122.6, 122.8, 123.4, 124.4, 126.3, 126.5, 126.6, 128.6, 129.4, 132.1, 133.2, 134.4, 134.5, 139.7, 140.1, 146.6, 150.1, 166.6.

**9-chloro-2-(4-methoxyphenyl)pyrrolo[2,3,4-kl]acridin-1(2H)-one (13n):**



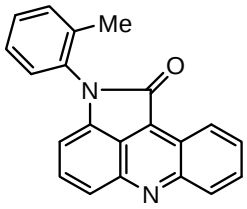

Red colored solid; m.p. 208-210 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{13}ClN_2O_2$: C, 69.91; H, 3.63; N, 7.76%. Found: C, 69.92; H, 3.64; N, 7.77%; IR (KBr) $cm^{-1}$: 3427, 1714, 1636, 1498, 1463, 1329, 1127, 1071, 736, 499; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 3.92 (3H, s, $OCH_3$), 6.97 (1H, d, J = 6.9 Hz, arom.), 7.12 (2H, dd, J = 6.9 Hz, J = 2.4 Hz, arom.), 7.53 (2H, dd, J = 6.9 Hz, J = 2.4 Hz, arom.), 7.73 (1H, d, J = 6.9 Hz, arom.), 7.86-7.91 (2H, m, arom.), 8.42 (1H, d, J = 9.3 Hz, arom.), 8.93 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 55.6, 106.3, 115.0, 116.4, 122.4, 122.9, 123.1, 126.1, 127.2, 127.4, 132.0, 133.3, 135.9, 140.6, 146.4, 150.0, 154.2, 159.2, 166.9.

**2-(4-Bromo-phenyl)-2H-pyrrolo[2,3,4-kl]acridin-1-one (13o):**



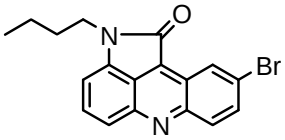

Red colored solid; m.p. 196-198 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{20}H_{11}BrN_2O$: C, 64.02; H, 2.95; N, 7.47%. Found: C, 64.3; H, 2.96; N, 7.48%; IR (KBr) $cm^{-1}$: 3434, 1721, 1656, 1499, 1466, 1331, 1129, 1073, 739, 490; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 6.90 (1H, d, J = 6.9 Hz, arom.), 7.43 (2H, d, J = 8.4 Hz, arom.), 7.62 (3H, d, J = 8.4 Hz, arom.), 7.73 (1H, t, J = 8.1 Hz, arom.), 7.84 (2H, t, J = 9.0 Hz, arom.), 8.37 (1H, d, J = 9.0 Hz, arom.), 8.81 (1H, d, J = 8.7 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 106.0, 120.9, 122.7, 124.1, 125.4, 127.4, 129.5, 130.6, 131.0, 132.8, 133.0, 133.9, 138.0, 139.9, 145.7, 149.0, 166.4.

**2-o-Tolyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13p):**



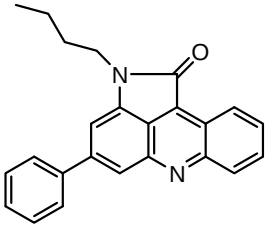

Brown colored solid; m.p. 228-230 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03%. Found: C, 81.29; H, 4.56; N, 9.04%; IR (KBr) $cm^{-1}$: 3410, 2930, 1701, 1613, 1509, 1466, 1101, 777, 729, 591; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.30 (3H, s, $CH_3$), 6.65 (1H, d, J = 6.9 Hz, arom.), 7.42-7.46 (4H, m, arom.), 7.67 (1H, d, J = 6.9 Hz, arom.), 7.81-7.97 (3H, m, arom.), 8.44 (1H, d, J = 8.7 Hz, arom.), 8.92 (1H, d, J = 8.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 18.1, 105.5, 120.0, 122.4, 123.1, 124.1, 127.1, 127.7, 128.4, 129.1, 129.1, 130.5, 130.8, 131.5, 132.8, 133.3, 136.8, 140.7, 146.5, 151.9, 167.1.

**9-Bromo-2-butyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13q):**




Red colored solid; m.p. 132-134 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{18}H_{15}BrN_2O$: C, 60.86; H, 4.26; N, 7.89%. Found: C, 60.88; H, 4.27; N, 7.90%; IR (KBr) $cm^{-1}$: 3419, 2922, 1710, 1630, 1519, 1466, 1200, 777, 720, 587, 530, 487; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 0.96 (3H, t, J = 7.2 Hz, $CH_3$), 1.42-1.44 (2H, m, $CH_2$), 1.76-1.81 (2H, m, $CH_2$), 3.94 (2H, t, J = 7.2 Hz, $CH_2$), 6.85 (1H, d, J = 6.6 Hz, arom.), 7.65-7.67 (1H, m, arom.), 7.71-7.74 (1H, m, arom.), 7.89 (1H, dd, J = 9.3 Hz, J = 2.4 Hz, arom.), 8.19 (1H, d, J = 9.6 Hz, arom.), 8.97 (1H, d, J = 2.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 13.7, 20.2, 30.9, 40.4, 105.2, 120.0, 122.0, 123.3, 124.1, 126.3, 127.3, 132.1, 133.2, 134.2, 140.3, 146.5, 150.1, 167.5.

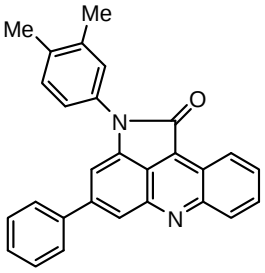
**2-Butyl-4-phenyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13r):**




Red colored solid; m.p. 135-137 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95%. Found: C, 81.80; H, 5.73; N, 7.96%; IR (KBr) $cm^{-1}$: 2954, 2387, 1705, 1633, 1502, 1479, 1377,

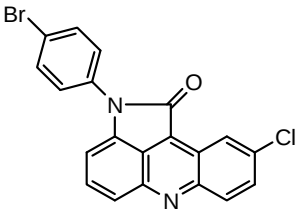
1322, 1104, 1077, 844, 766, 590; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 0.98 (3H, t, J = 7.2 Hz, $CH_3$), 1.42-1.49 (2H, m, $CH_2$), 1.77-1.84 (2H, m, $CH_2$), 3.91 (2H, t, J = 7.2 Hz, $CH_2$), 6.98 (1H, s, arom.), 7.41-7.52 (3H, m, arom.), 7.63-7.71 (3H, m, arom.), 7.76-7.84 (2H, m, arom.), 8.28 (1H, d, J = 8.4 Hz, arom.), 8.70 (1H, d, J = 8.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 13.7, 20.1, 30.9, 40.2, 105.0, 119.0, 119.4, 122.5, 123.9, 127.5, 127.7, 128.3, 128.5, 128.9, 130.2, 130.4, 140.4, 140.9, 146.1, 146.2, 152.0, 167.9.

**2-(3,4-Dimethyl-phenyl)-4-phenyl-2H-pyrrolo[2,3,4-kl]acridin-1-one (13s):**



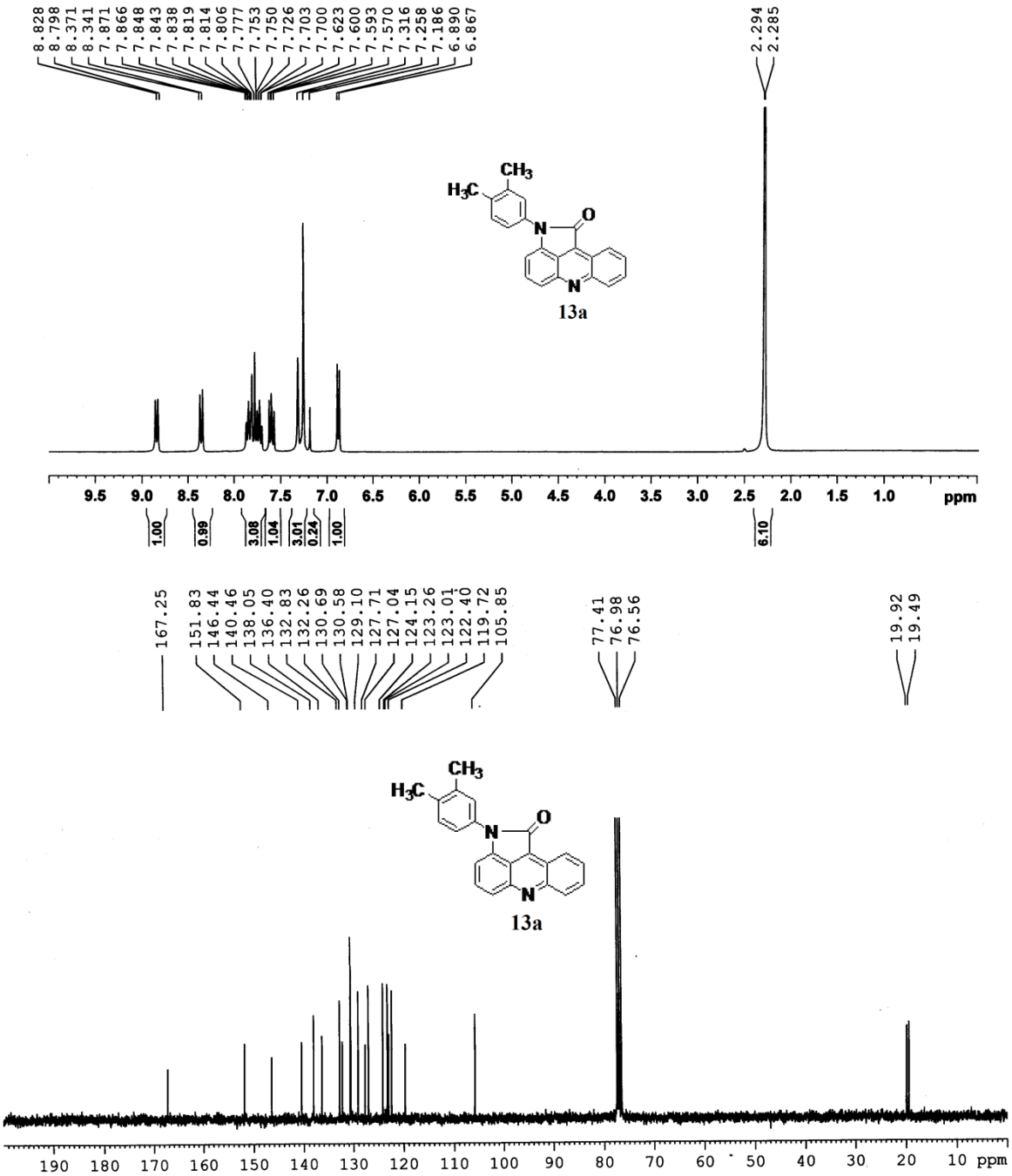

Red colored solid; m.p. 230-232 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{28}H_{20}N_2O$: C, 83.98; H, 5.03; N, 7.00%. Found: C, 83.99; H, 5.04; N, 7.01%; IR (KBr) $cm^{-1}$: 2944, 2385, 1701, 1631, 1501, 1481, 1372, 1323, 1109, 1089, 854, 768, 595; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 2.36 (6H, s, 2x$CH_3$), 7.16 (1H, s, arom.), 7.33 (2H, s, arom.), 7.40-7.49 (4H, m, arom.), 7.66-7.76 (3H, m, arom.), 7.84-7.89 (1H, m, arom.), 7.99 (1H, s, arom.), 8.37 (1H, d, J = 8.7 Hz, arom.), 8.83 (1H, d, J = 8.4 Hz, arom.); $\delta_C$ ppm (75 MHz, $CDCl_3$, TMS) 19.5, 19.9, 106.5, 119.2, 119.9, 122.8, 123.4, 124.1, 127.2, 127.3, 127.6, 128.4, 128.9, 129.0, 130.5, 130.6, 132.2, 136.5, 138.1, 140.8, 140.9, 146.4, 146.5, 152.3, 167.4.

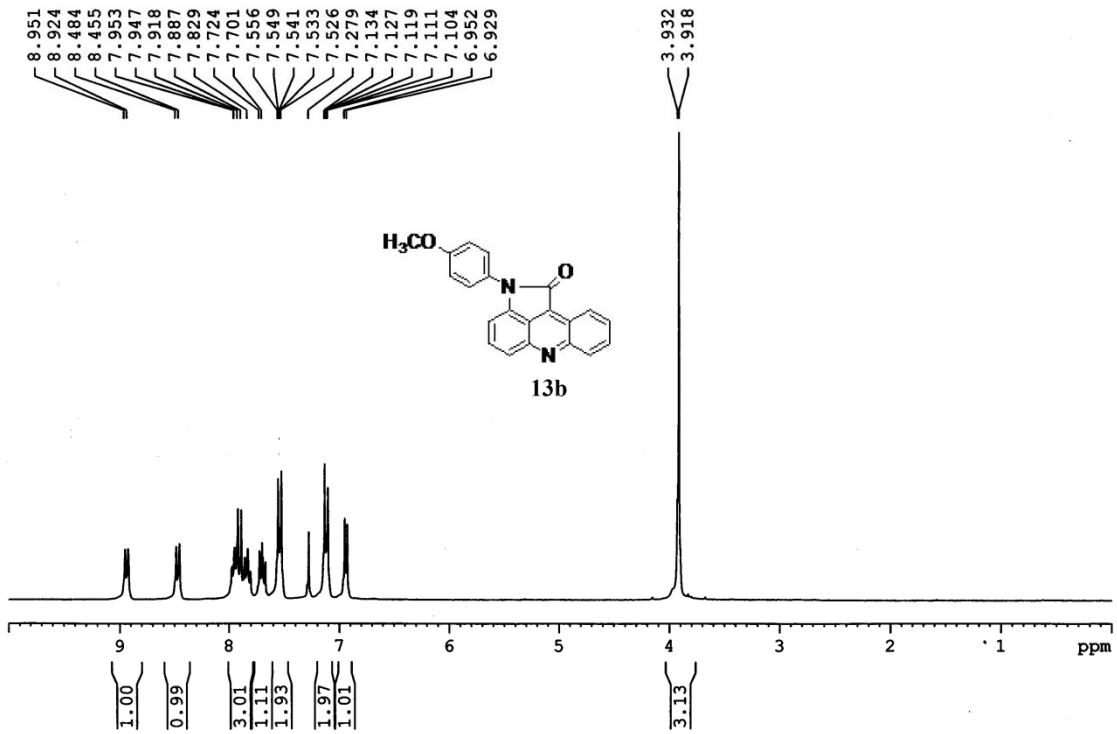
**2-(4-Bromo-phenyl)-9-chloro-2H-pyrrolo[2,3,4-kl]acridin-1-one (13t):**




Red colored solid; m.p. 218-220 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{20}H_{10}BrClN_2O$: C, 58.64; H, 2.46; N, 6.84%. Found: C, 58.65; H, 2.47; N, 6.86%; IR (KBr) $cm^{-1}$: 3419, 1717, 1637, 1499, 1460, 1332, 1120, 1064, 721, 495; $\delta_H$ ppm (300 MHz; $CDCl_3$; TMS) 7.18 (1H, d, J = 6.6 Hz, arom.), 7.67 (2H, dd, J = 8.7 Hz, J = 3.6 Hz, arom.), 7.83-7.92 (4H, m, arom.), 7.16 (1H, dd, J = 9.3 Hz, J = 2.1 Hz, arom.), 8.38 (1H, d, J = 9.3 Hz, arom.), 8.87 (1H, d, J = 2.1 Hz, arom.).

**$^{1}$H and $^{13}$C NMR Spectra of 13a-13t**

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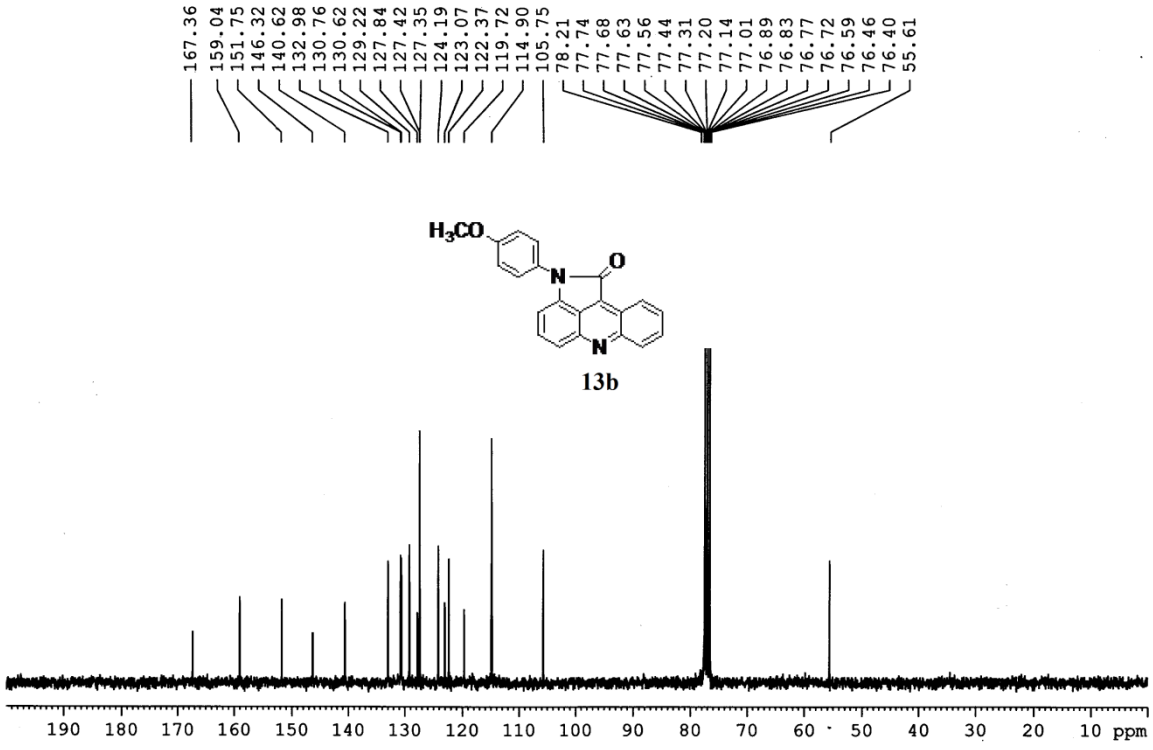
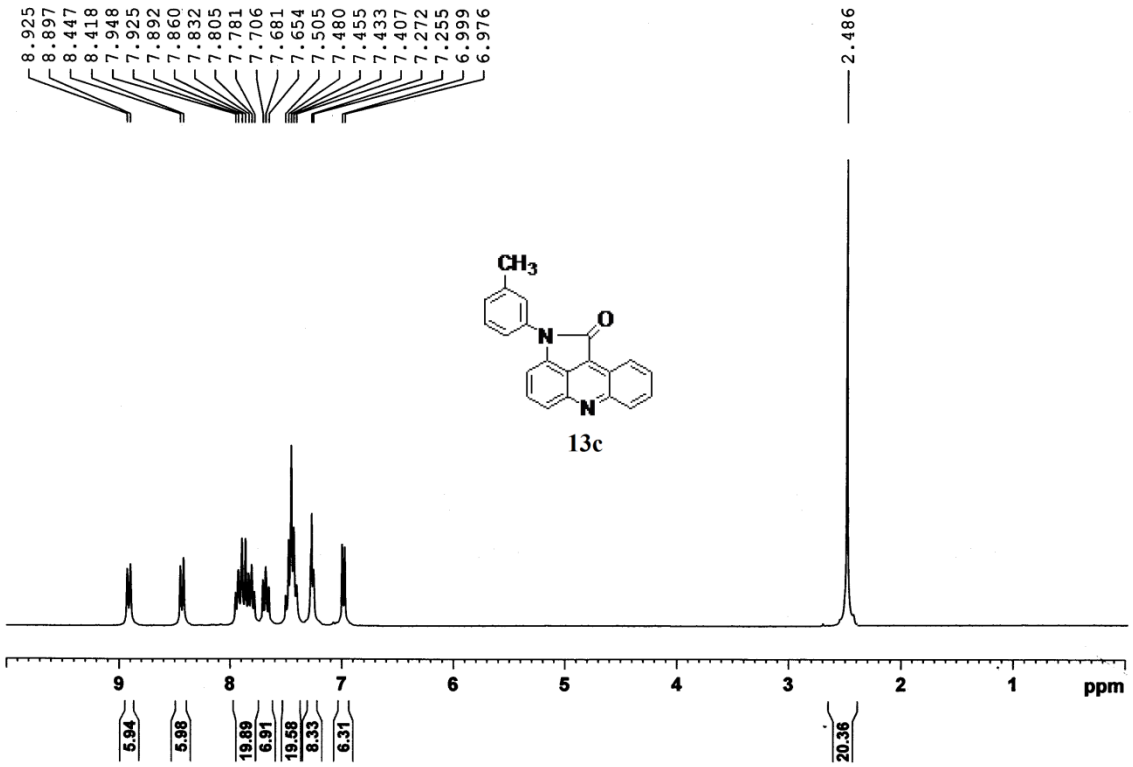
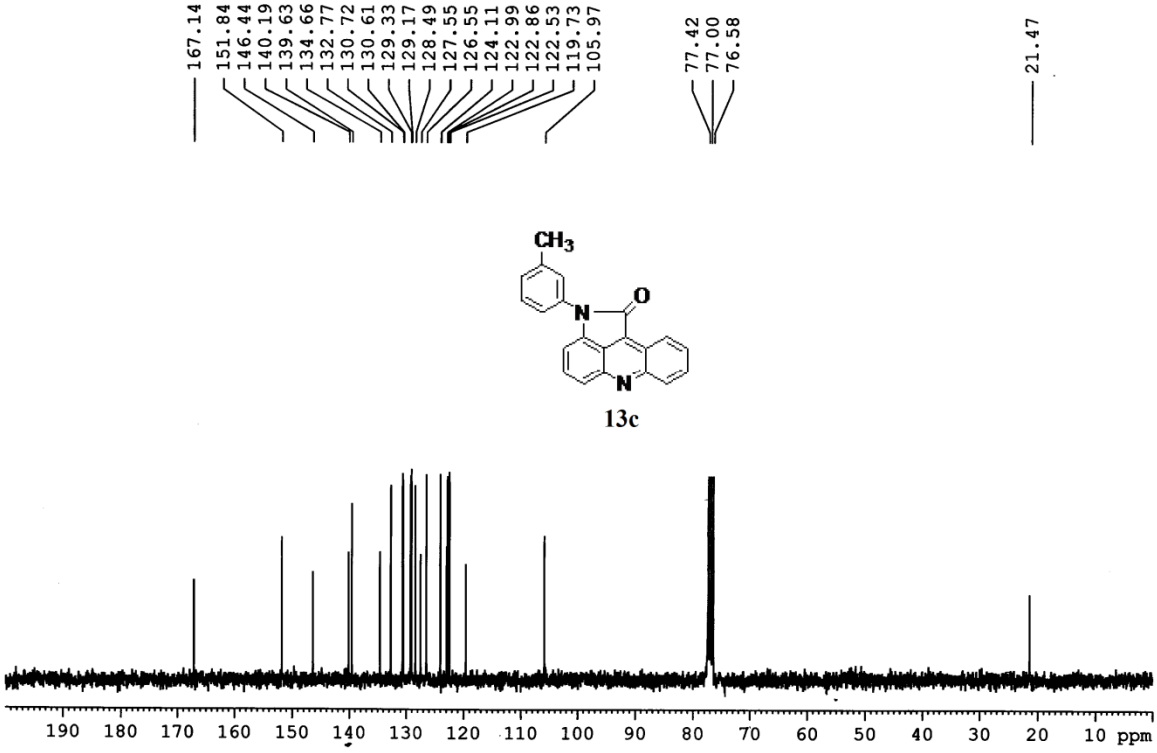
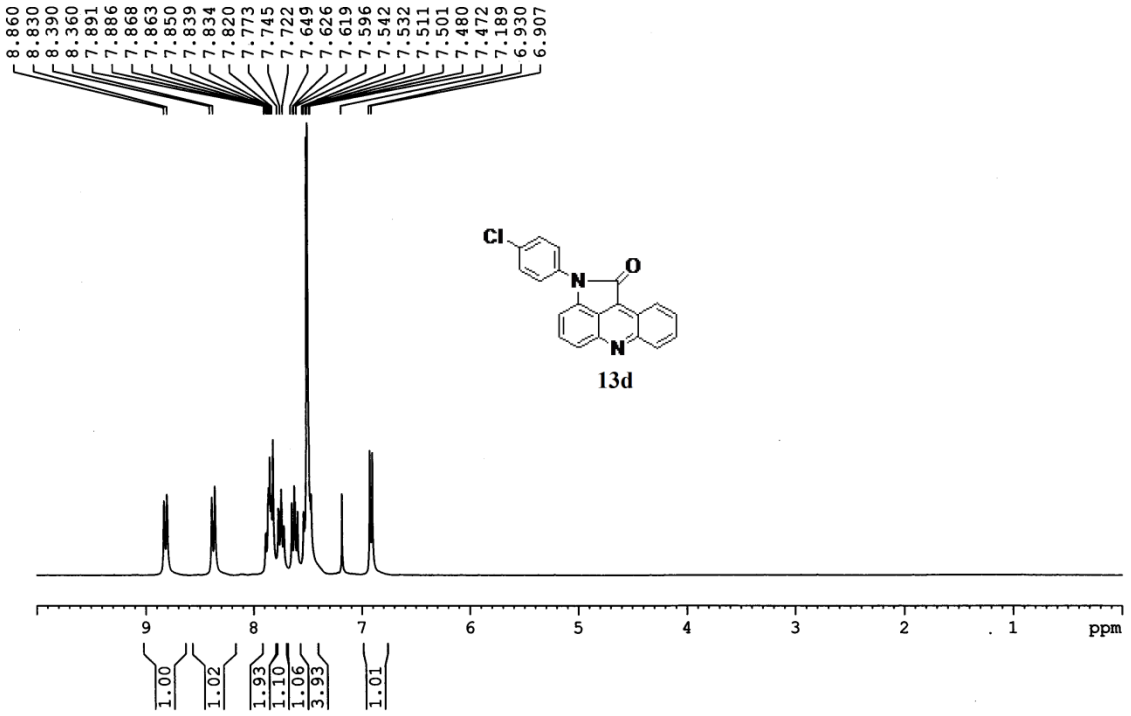
8.924
8.484
8.455
7.953
7.947
7.918
7.887
7.829
7.724
7.701
7.556
7.549
7.541
7.533
7.526
7.279
7.134
7.127
7.119
7.111
7.104
6.952
6.929
3.932
3.918
H3CO
O
N
N
13b
9
8
7
6
5
4
3
2
1
ppm
1.00
0.99
3.01
1.11
1.93
1.97
1.01
3.13


167.36
159.04
151.75
146.32
140.62
132.98
130.76
130.62
129.22
127.84
127.42
127.35
124.19
123.07
122.37
119.72
114.90
105.75
78.21
77.74
77.68
77.63
77.56
77.44
77.31
77.20
77.14
77.01
76.89
76.83
76.77
76.72
76.59
76.46
76.40
55.61
H3CO
O
N
N
13b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.925
8.897
8.447
8.418
7.948
7.925
7.892
7.860
7.832
7.805
7.781
7.706
7.681
7.654
7.505
7.480
7.455
7.433
7.407
7.272
7.255
6.999
6.976
2.486
CH3
N
O
N
13c
9
8
7
6
5
4
3
2
1
ppm
5.94
5.98
19.89
6.91
19.58
8.33
6.31
20.36


167.14
151.84
146.44
140.19
139.63
134.66
132.77
130.72
130.61
129.33
129.17
128.49
127.55
126.55
124.11
122.99
122.86
122.53
119.73
105.97
77.42
77.00
76.58
21.47
CH3
N
O
N
13c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.860
8.830
8.390
8.360
7.891
7.886
7.868
7.863
7.850
7.839
7.834
7.820
7.773
7.745
7.722
7.649
7.626
7.619
7.596
7.542
7.532
7.511
7.501
7.480
7.472
7.189
6.930
6.907
Cl
N
O
N
13d
9
8
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4
3
2
1
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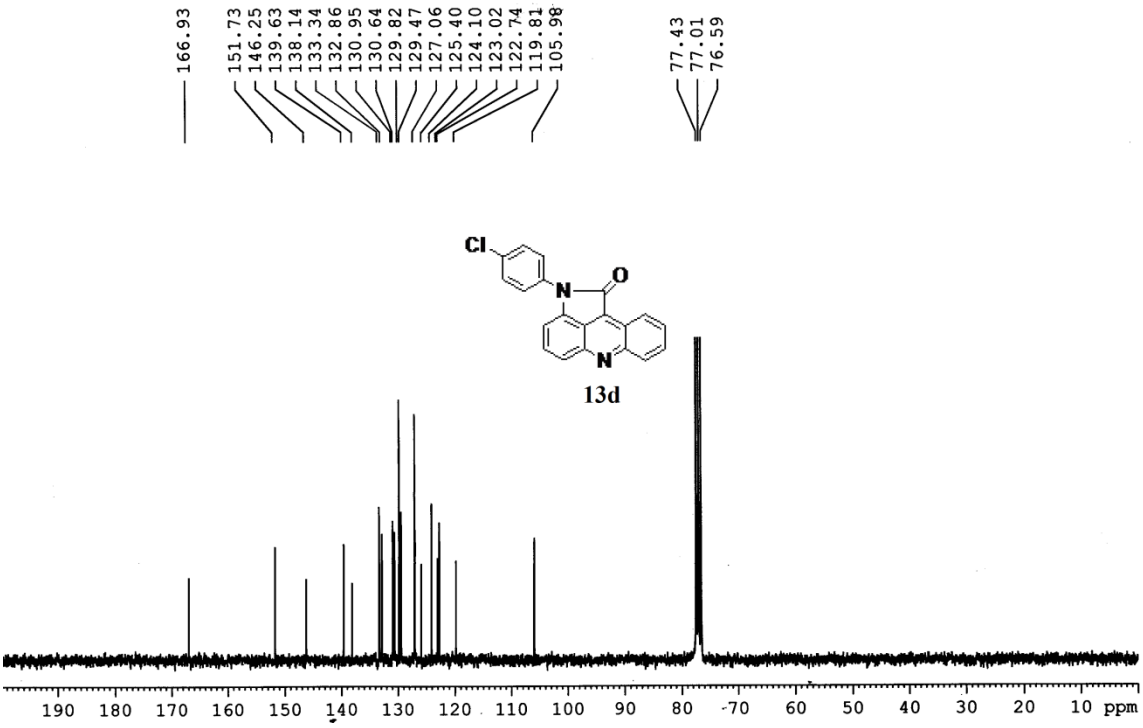
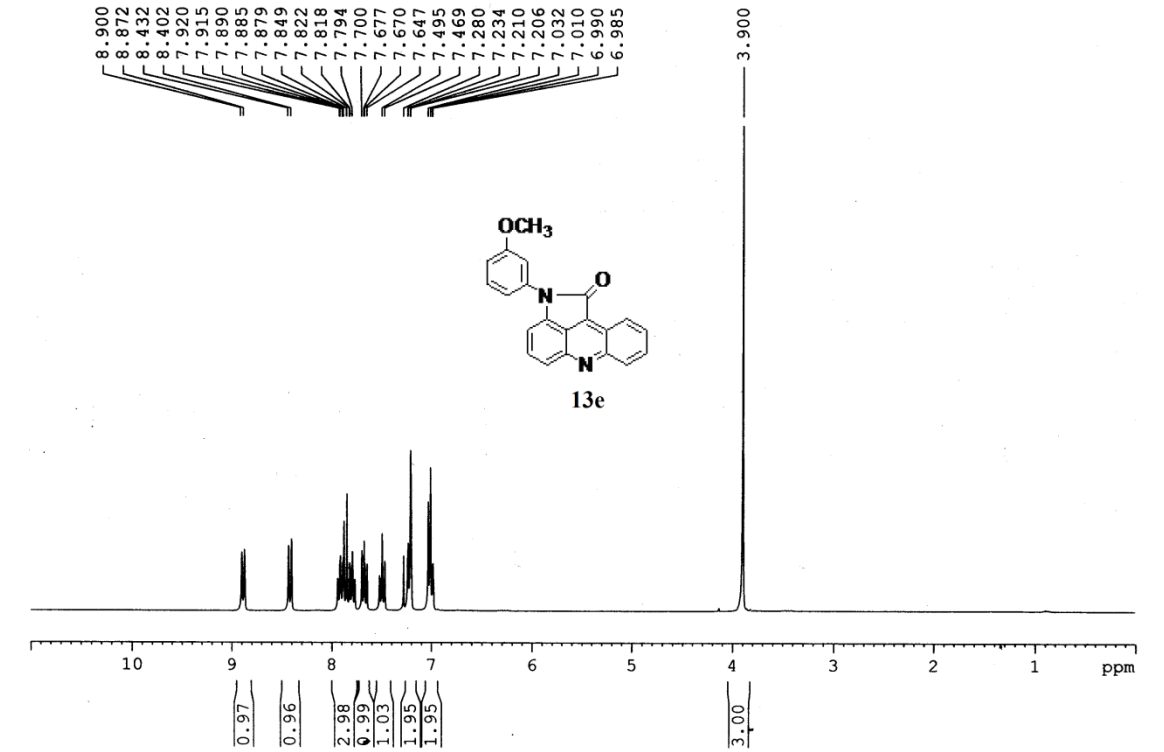
1.02
1.93
1.10
1.06
3.93
1.01


166.93
151.73
146.25
139.63
138.14
133.34
132.86
130.95
130.64
129.82
129.47
127.06
125.40
124.10
123.02
122.74
119.81
105.98
77.43
77.01
76.59
Cl
N
O
N
13d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.872
8.432
8.402
7.920
7.915
7.890
7.885
7.879
7.849
7.822
7.818
7.794
7.700
7.677
7.670
7.647
7.495
7.469
7.280
7.234
7.210
7.206
7.032
7.010
6.990
6.985
3.900
OCH3
N
O
N
13e
10
9
8
7
6
5
4
3
2
1
ppm
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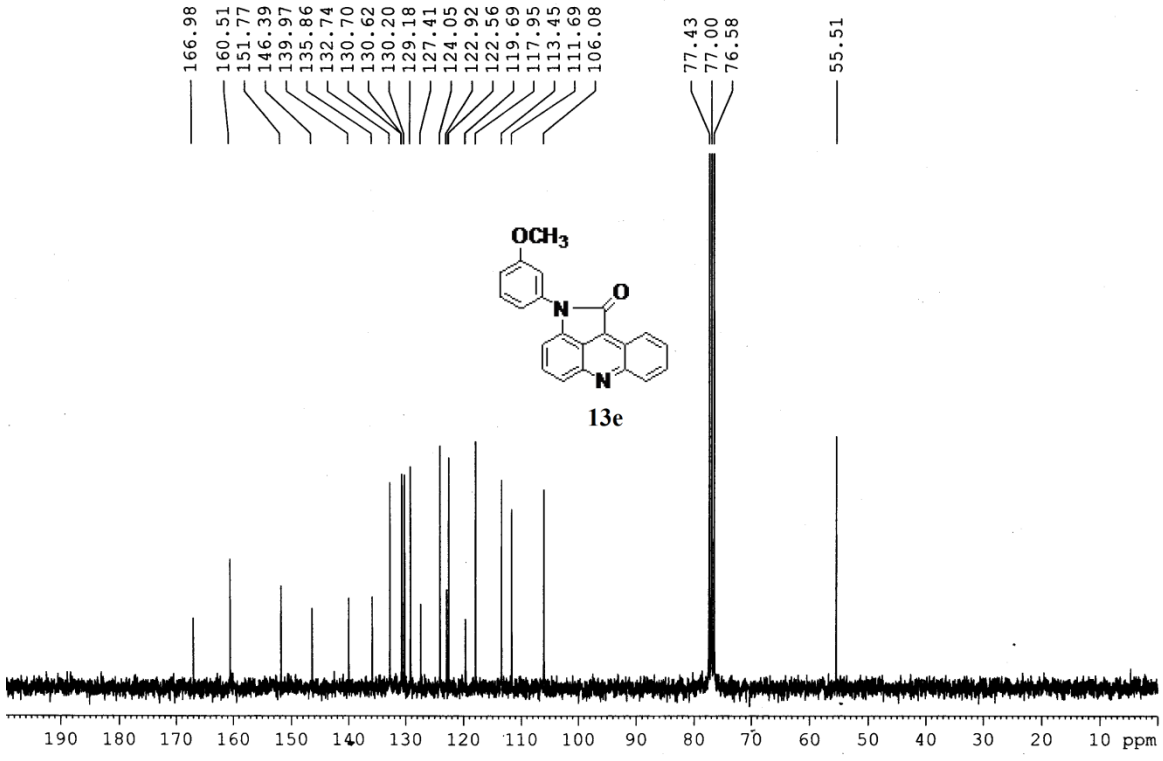
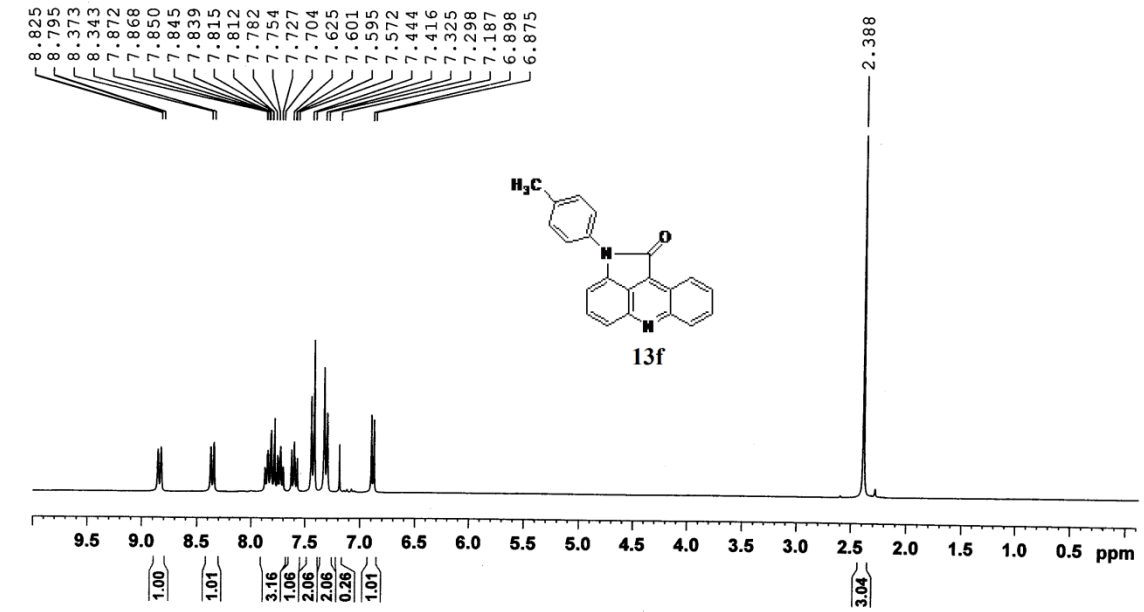
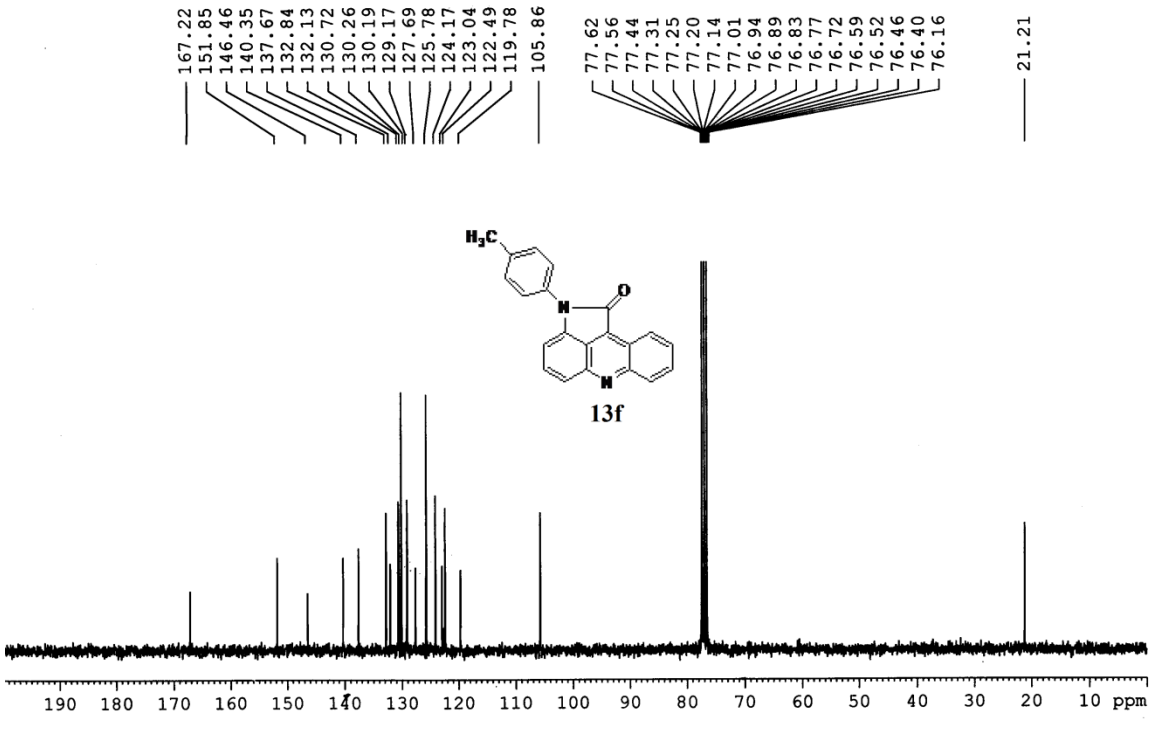
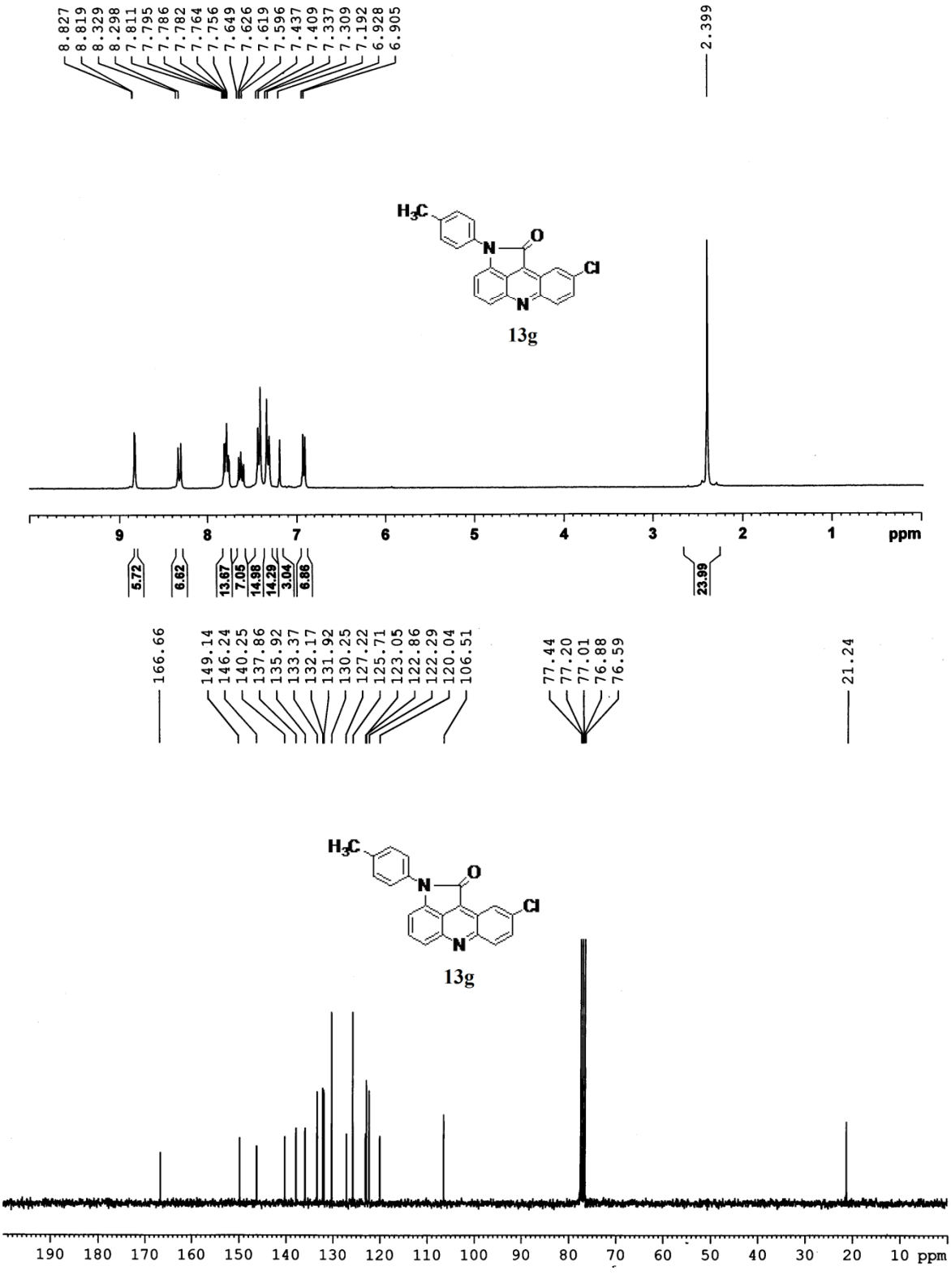
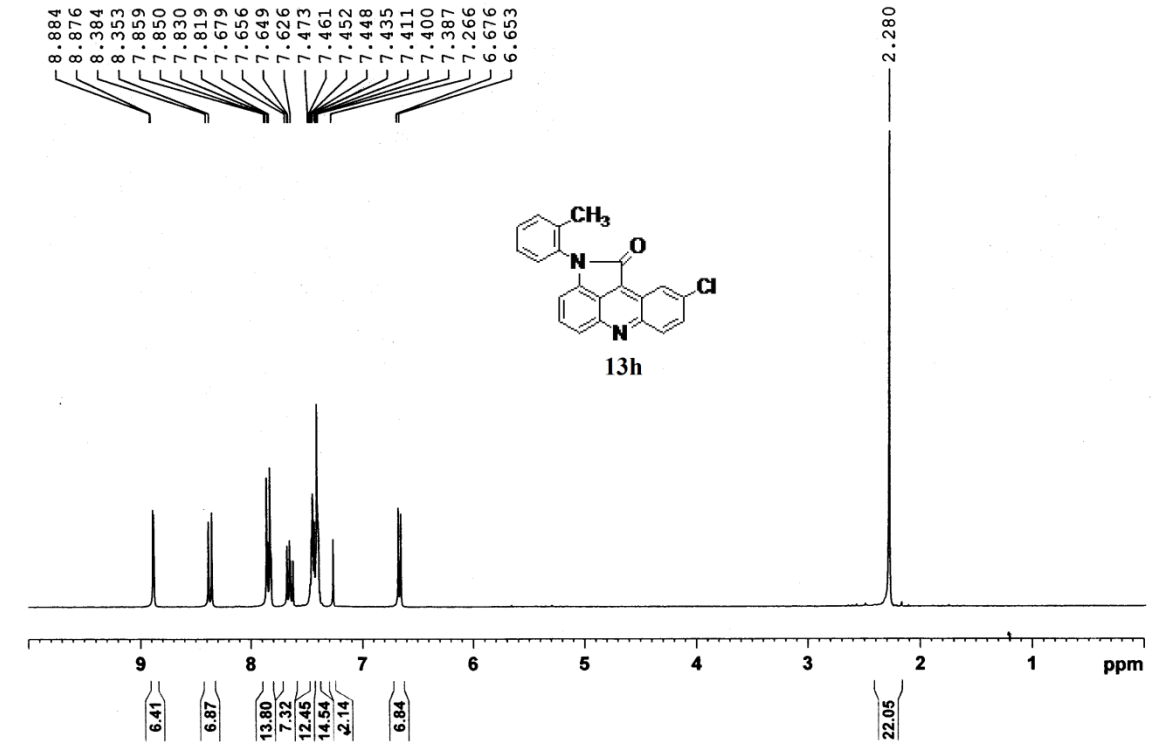
0.96
2.98
0.99
1.03
1.95
1.95
3.00


166.98
160.51
151.77
146.39
139.97
135.86
132.74
130.70
130.62
130.20
129.18
127.41
124.05
122.92
122.56
119.69
117.95
113.45
111.69
106.08
77.43
77.00
76.58
55.51
OCH3
N
O
N
13e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.825
8.795
8.373
8.343
7.872
7.868
7.850
7.845
7.839
7.815
7.812
7.782
7.754
7.727
7.704
7.625
7.601
7.595
7.572
7.444
7.416
7.325
7.298
7.187
6.898
6.875
2.388
H3C
O
N
H
13f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.01
3.16
1.06
2.06
2.06
0.26
1.01
3.04


167.22
151.85
146.46
140.35
137.67
132.84
132.13
130.72
130.26
130.19
129.17
127.69
125.78
124.17
123.04
122.49
119.78
105.86
77.62
77.56
77.44
77.31
77.25
77.20
77.14
77.01
76.94
76.89
76.83
76.77
76.72
76.59
76.52
76.46
76.40
76.16
21.21
H3C
O
N
H
13f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.827
8.819
8.329
8.298
7.811
7.795
7.786
7.782
7.764
7.756
7.649
7.626
7.619
7.596
7.437
7.409
7.337
7.309
7.192
6.928
6.905
2.399
H3C
N
O
Cl
N
13g
9
8
7
6
5
4
3
2
1
ppm
5.72
6.62
13.67
7.05
14.98
14.29
3.04
6.86
23.99
166.66
149.14
146.24
140.25
137.86
135.92
133.37
132.17
131.92
130.25
127.22
125.71
123.05
122.86
122.29
120.04
106.51
77.44
77.20
77.01
76.88
76.59
21.24
H3C
N
O
Cl
N
13g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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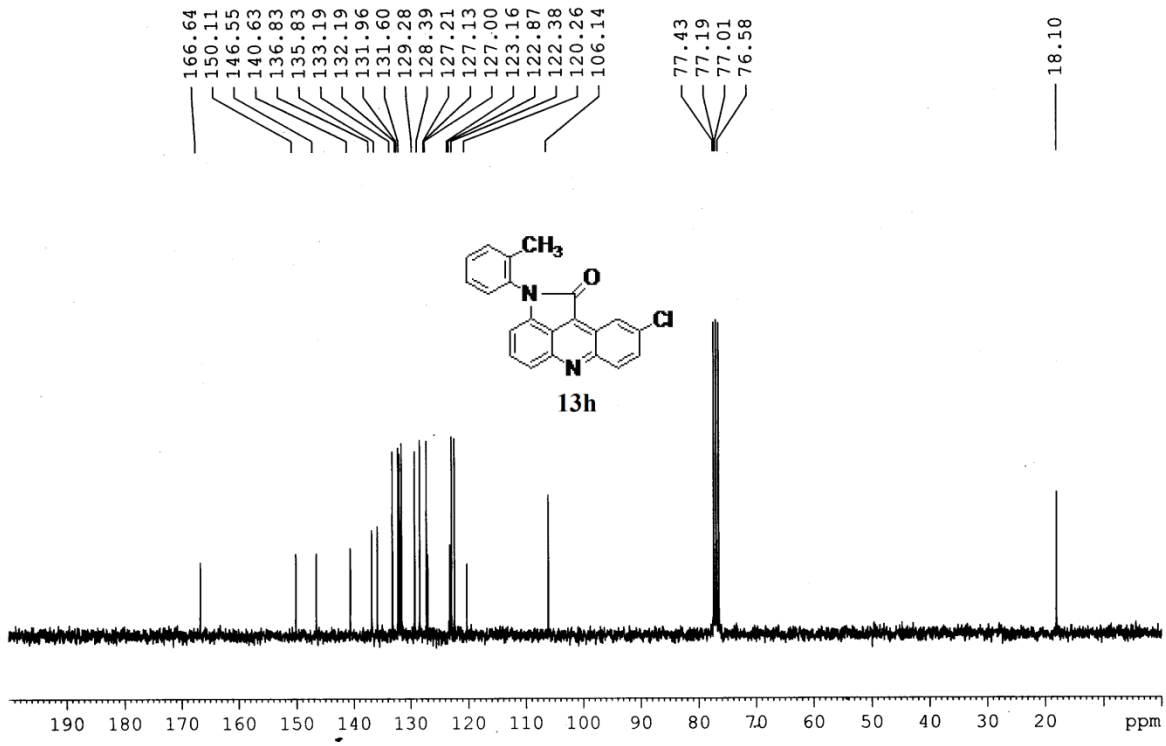
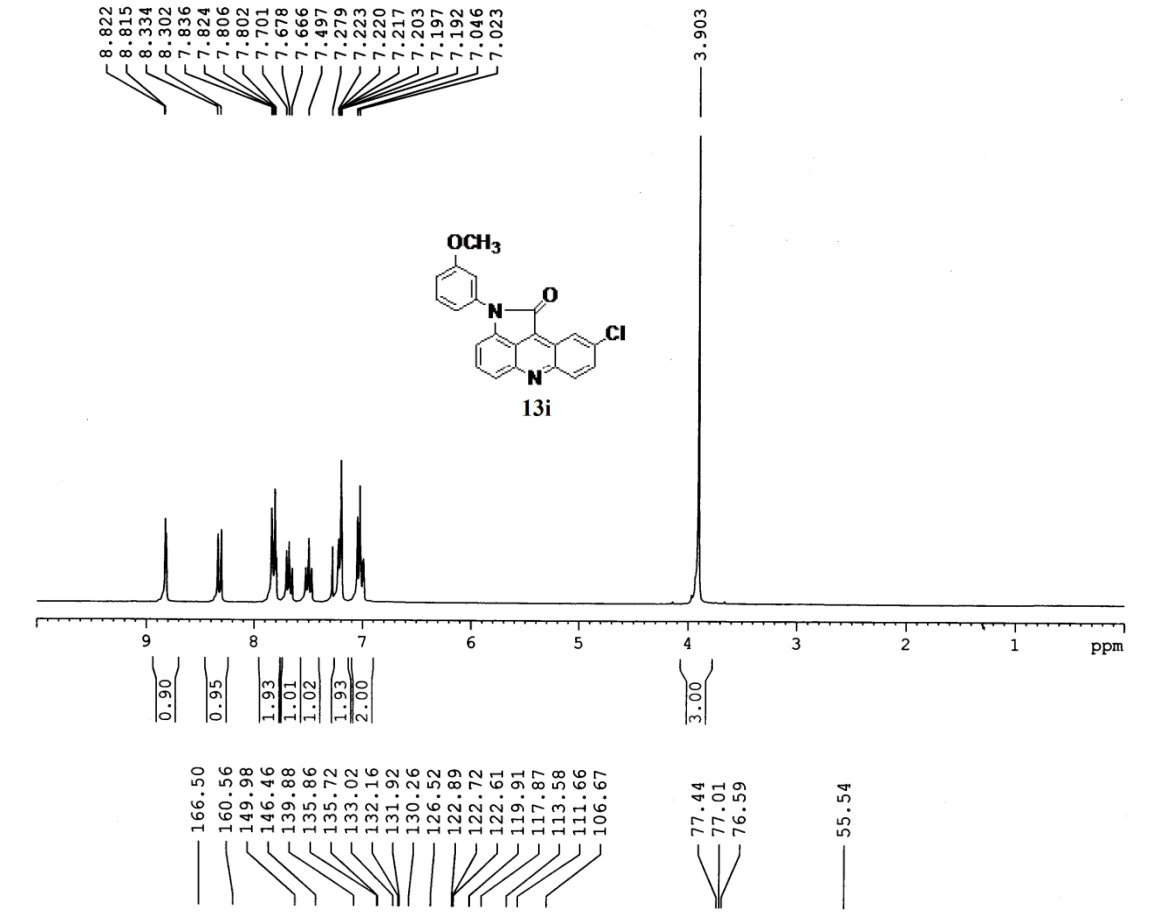
8.353
7.859
7.850
7.830
7.819
7.679
7.656
7.649
7.626
7.473
7.461
7.452
7.448
7.435
7.411
7.400
7.387
7.266
6.676
6.653
2.280
CH3
N
O
Cl
N
13h
9
8
7
6
5
4
3
2
1
ppm
6.41
6.87
13.80
7.32
12.45
14.54
2.14
6.84
22.05


166.64
150.11
146.55
140.63
136.83
135.83
133.19
132.19
131.96
131.60
129.28
128.39
127.21
127.13
127.00
123.16
122.87
122.38
120.26
106.14
77.43
77.19
77.01
76.58
18.10
CH3
N
O
Cl
N
13h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.822
8.815
8.334
8.302
7.836
7.824
7.806
7.802
7.701
7.678
7.666
7.497
7.279
7.223
7.220
7.217
7.203
7.197
7.192
7.046
7.023
3.903
OCH3
O
N
Cl
N
13i
9
8
7
6
5
4
3
2
1
ppm
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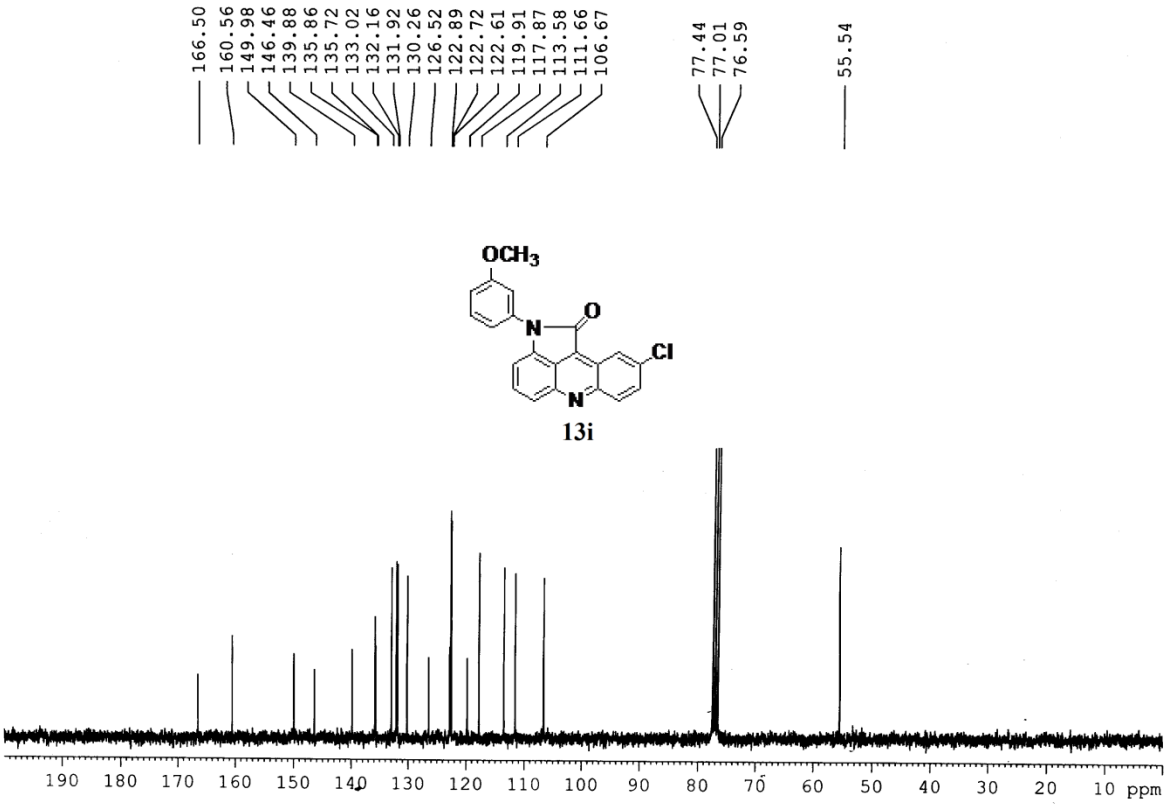
0.95
1.93
1.01
1.02
1.93
2.00
3.00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160.56
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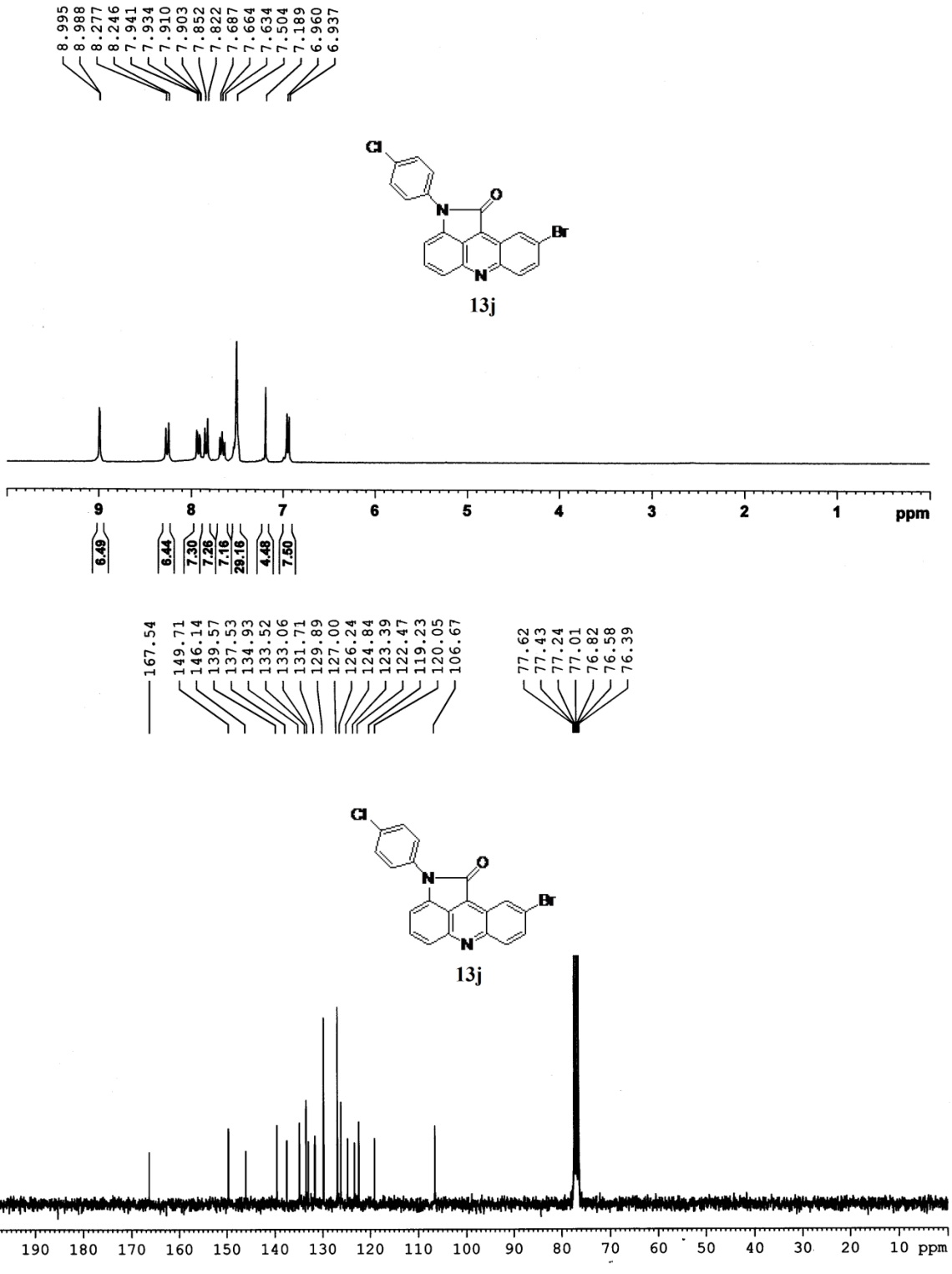
146.46
139.88
135.86
135.72
133.02
132.16
131.92
130.26
126.52
122.89
122.72
122.61
119.91
117.87
113.58
111.66
106.67
77.44
77.01
76.59
55.54
OCH3
O
N
Cl
N
13i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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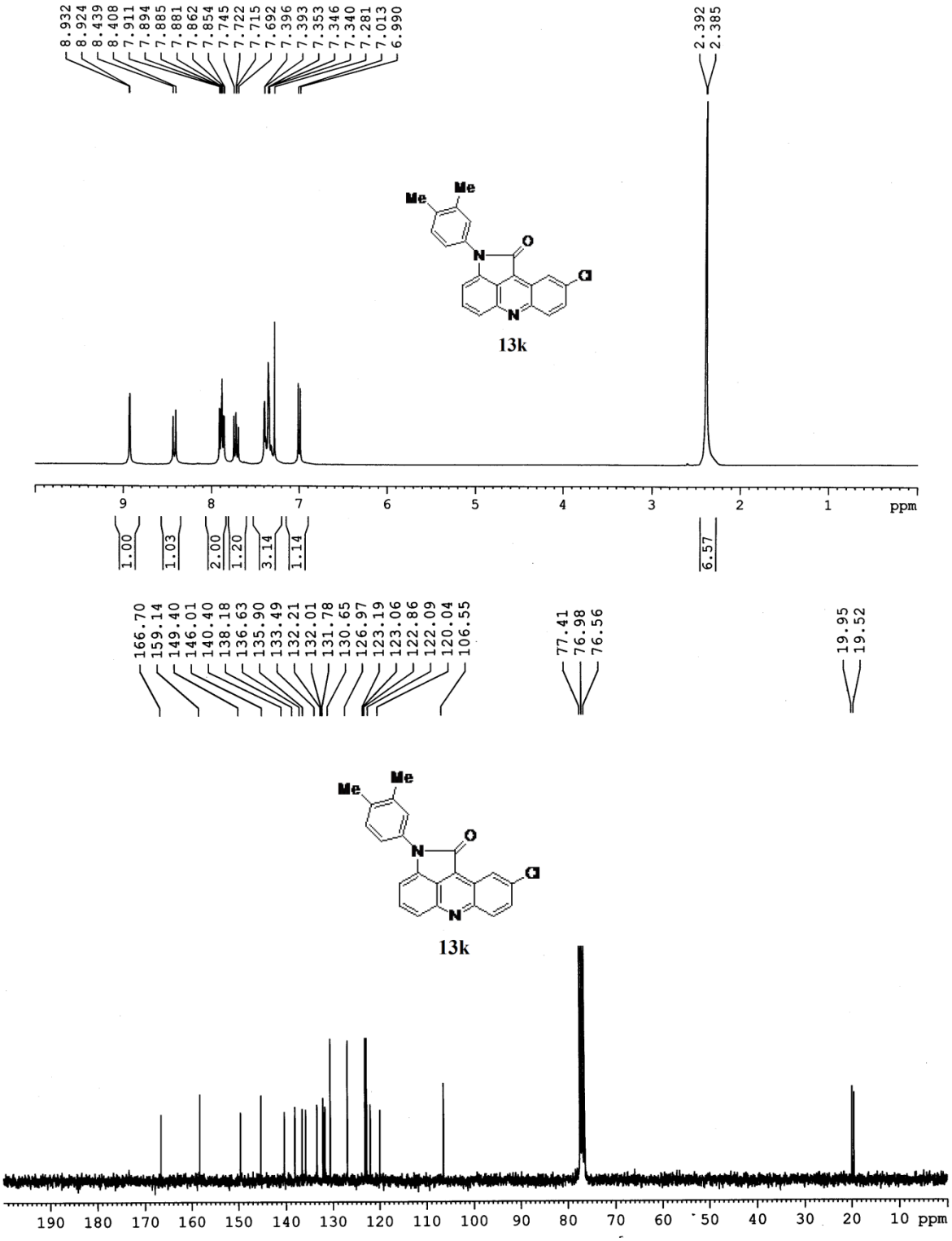
8.277
8.246
7.941
7.934
7.910
7.903
7.852
7.822
7.687
7.664
7.634
7.504
7.189
6.960
6.937
Cl
O
N
Br
N
13j
9
8
7
6
5
4
3
2
1
ppm
6.49
6.44
7.30
7.26
7.16
29.16
4.48
7.50
167.54
149.71
146.14
139.57
137.53
134.93
133.52
133.06
131.71
129.89
127.00
126.24
124.84
123.39
122.47
119.23
120.05
106.67
77.62
77.43
77.24
77.01
76.82
76.58
76.39
Cl
O
N
Br
N
13j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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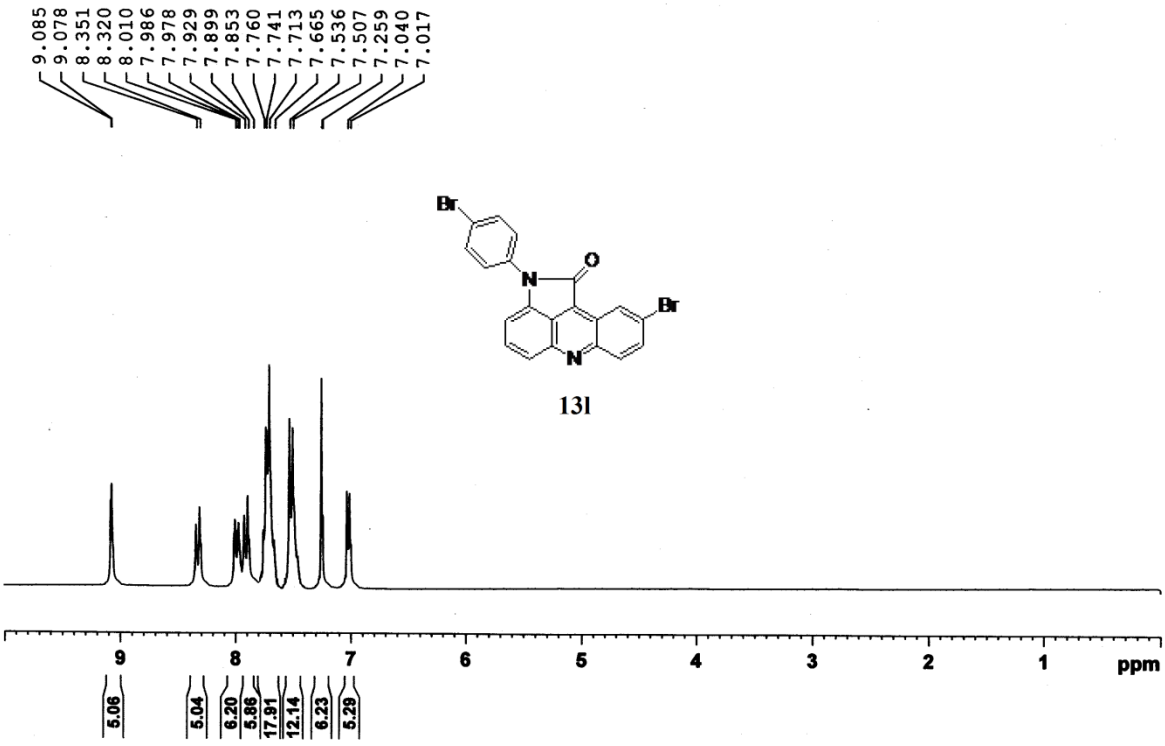
8.439
8.408
7.911
7.894
7.885
7.881
7.862
7.854
7.745
7.722
7.715
7.692
7.396
7.393
7.353
7.346
7.340
7.281
7.013
6.990
2.392
2.385
Me
Me
O
N
Cl
N
13k
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
2.00
1.20
3.14
1.14
6.57
166.70
159.14
149.40
146.01
140.40
138.18
136.63
135.90
133.49
132.21
132.01
131.78
130.65
126.97
123.19
123.06
122.86
122.09
120.04
106.55
77.41
76.98
76.56
19.95
19.52
Me
Me
O
N
Cl
N
13k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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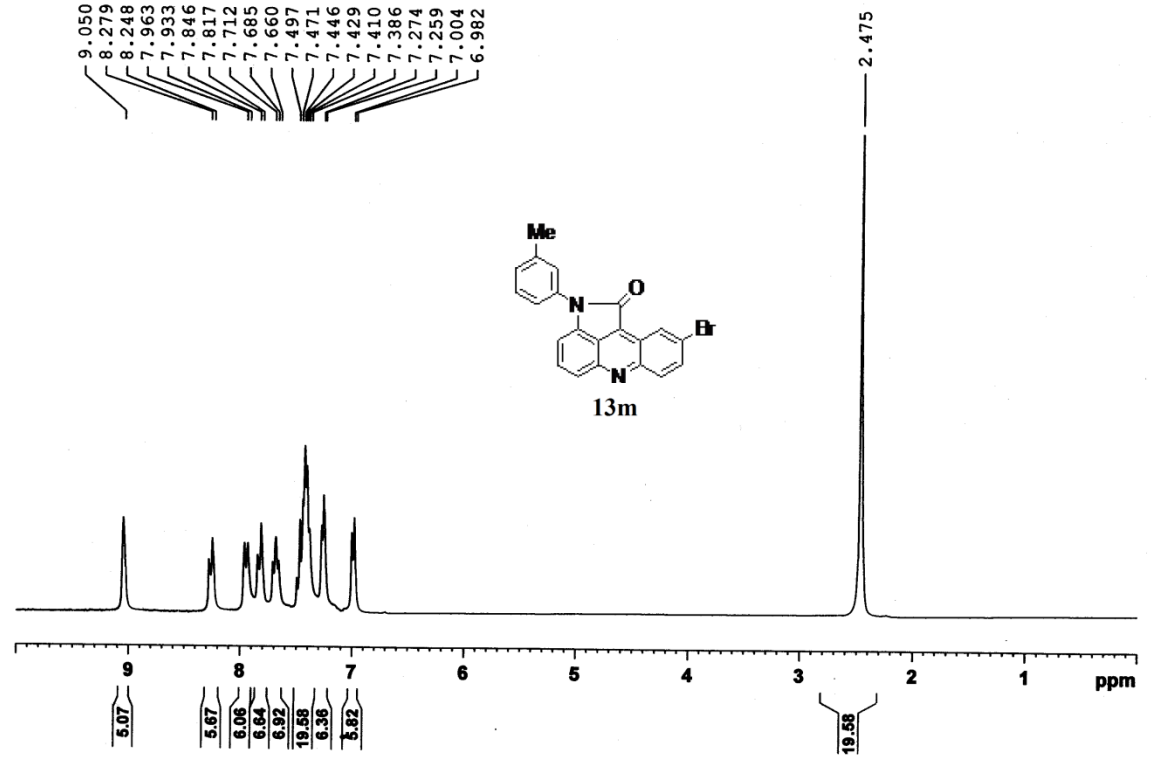
9.078
8.351
8.320
8.010
7.986
7.978
7.929
7.899
7.853
7.760
7.741
7.713
7.665
7.536
7.507
7.259
7.040
7.017
Br
N
O
Br
N
13l
9
8
7
6
5
4
3
2
1
ppm
5.06
5.04
6.20
5.86
17.91
12.14
6.23
5.29


9.050
8.279
8.248
7.963
7.933
7.846
7.817
7.712
7.685
7.660
7.497
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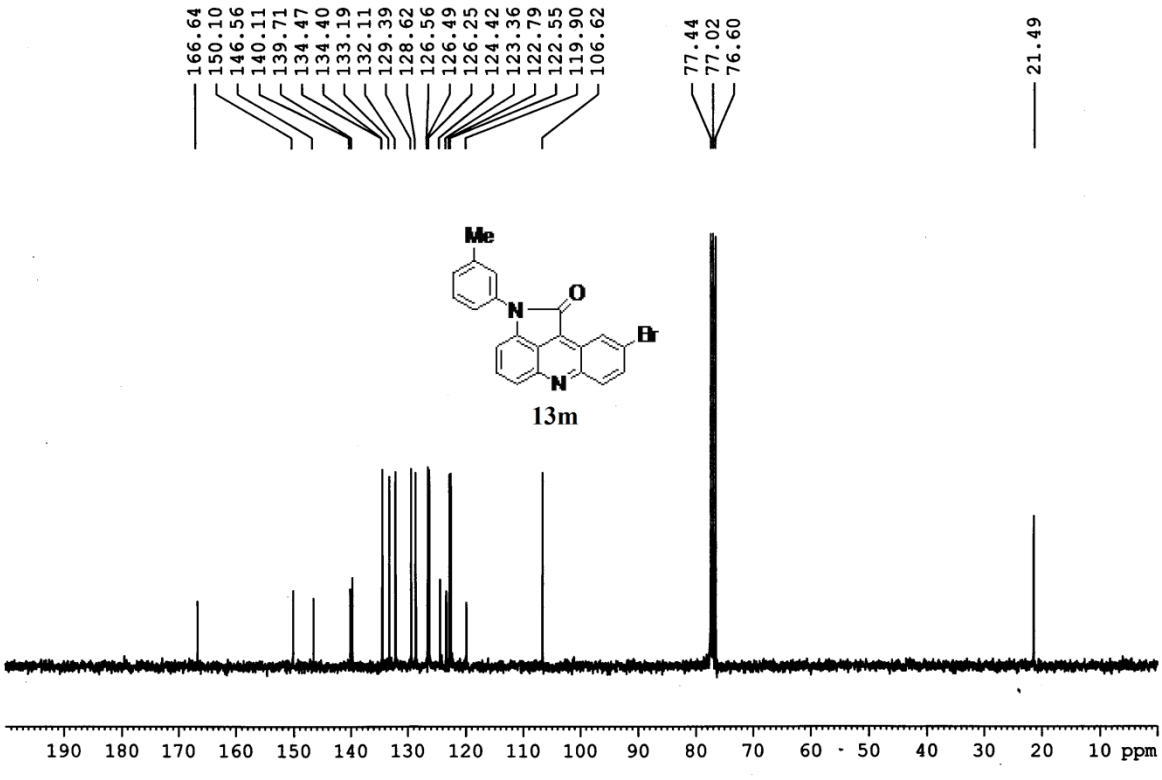
7.446
7.429
7.410
7.386
7.274
7.259
7.004
6.982
2.475
Me
N
O
Br
N
13m
9
8
7
6
5
4
3
2
1
ppm
5.07
5.67
6.06
6.64
6.92
19.58
6.36
5.82
19.58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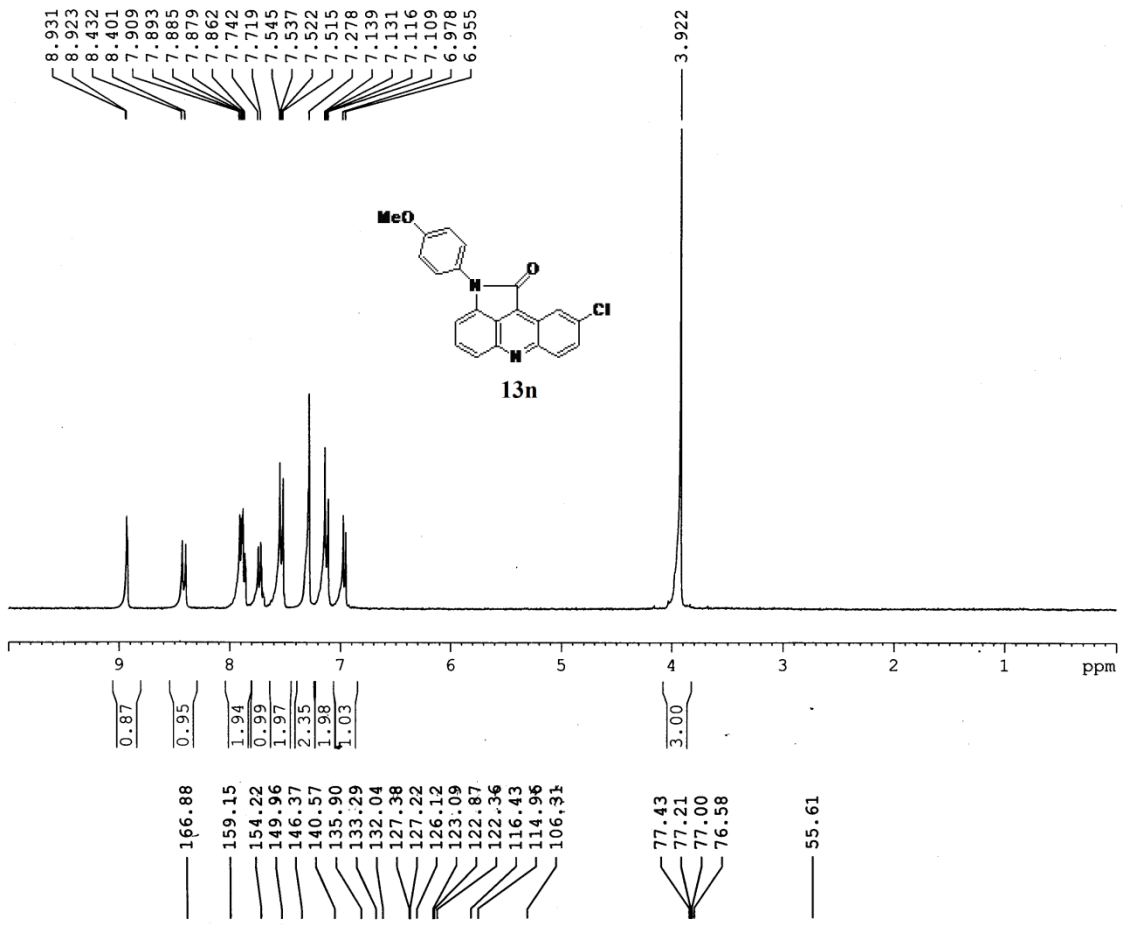
150.10
146.56
140.11
139.71
134.47
134.40
133.19
132.11
129.39
128.62
126.56
126.49
126.25
124.42
123.36
122.79
122.55
119.90
106.62
77.44
77.02
76.60
21.49
Me
N
O
Br
N
13m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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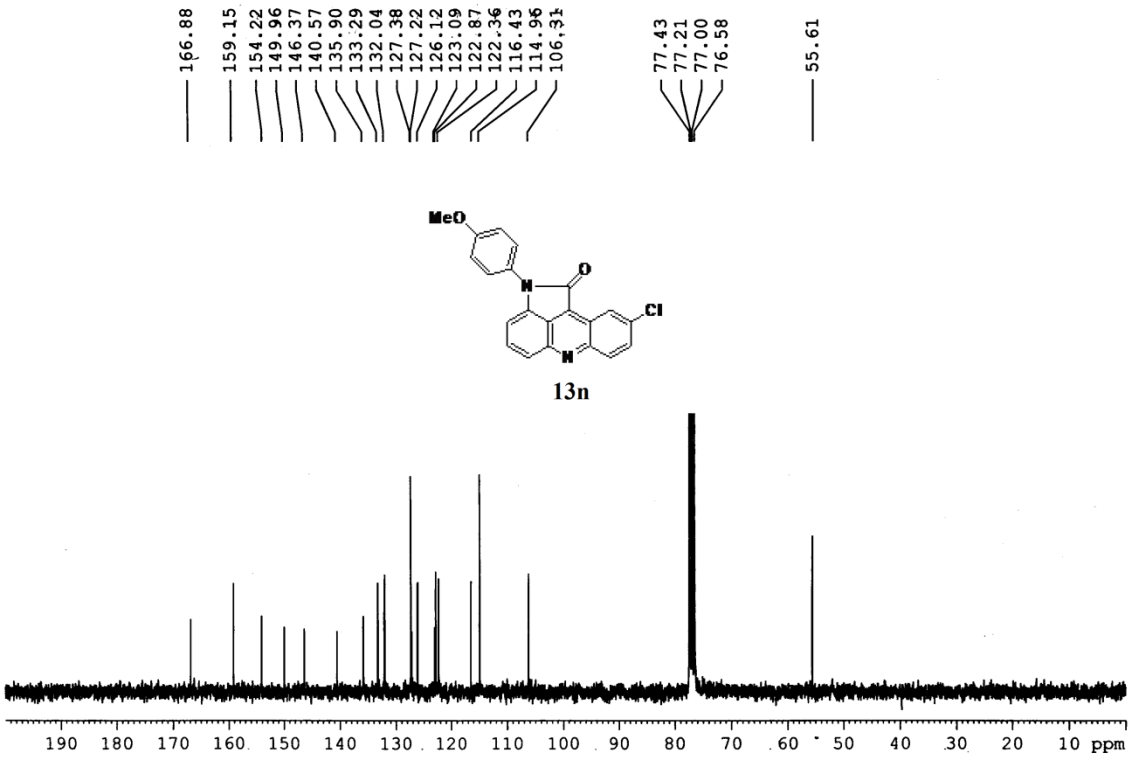
8.923
8.432
8.401
7.909
7.893
7.885
7.879
7.862
7.742
7.719
7.545
7.537
7.522
7.515
7.278
7.139
7.131
7.116
7.109
6.978
6.955
3.922
MeO
O
N
Cl
N
13n
9
8
7
6
5
4
3
2
1
ppm
0.87
0.95
1.94
0.99
1.97
2.35
1.98
1.03
3.00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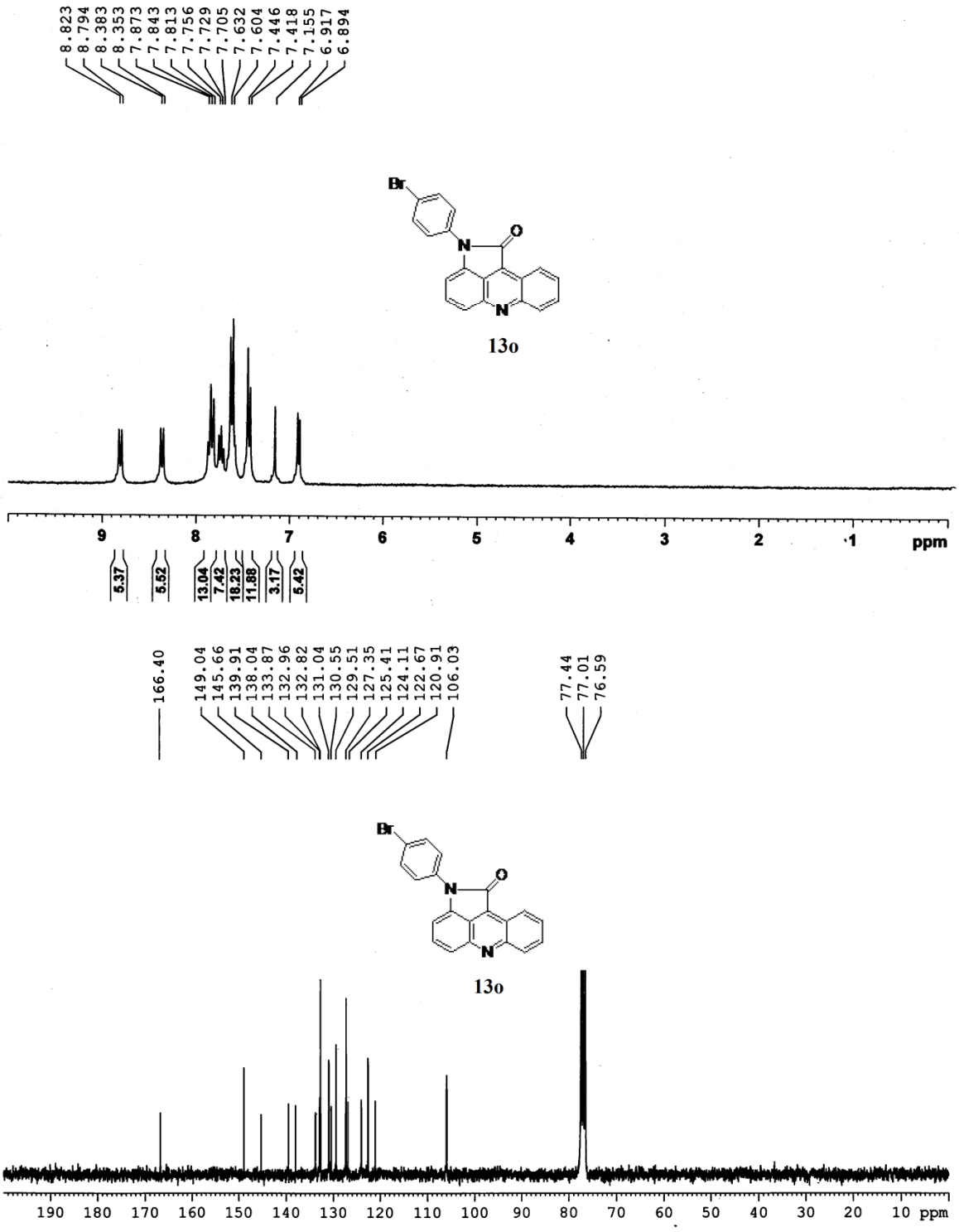
159.15
154.22
149.96
146.37
140.57
135.90
133.29
132.04
127.38
127.22
126.12
123.09
122.87
122.36
116.43
114.96
106.31
77.43
77.21
77.00
76.58
55.61


MeO
O
N
Cl
N

13n


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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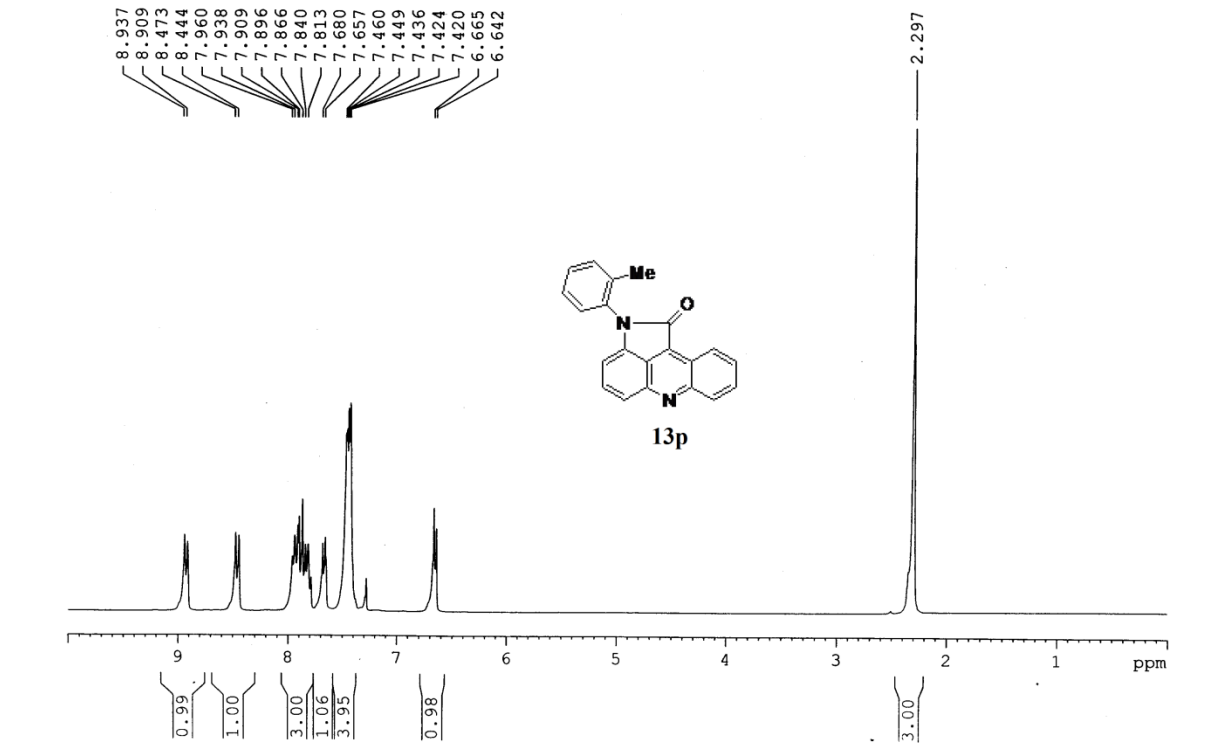
8.794
8.383
8.353
7.873
7.843
7.813
7.756
7.729
7.705
7.632
7.604
7.446
7.418
7.155
6.917
6.894
Br
N
O
N
13o
9
8
7
6
5
4
3
2
1
ppm
5.37
5.52
13.04
7.42
18.23
11.88
3.17
5.42
166.40
149.04
145.66
139.91
138.04
133.87
132.96
132.82
131.04
130.55
129.51
127.35
125.41
124.11
122.67
120.91
106.03
77.44
77.01
76.59
Br
N
O
N
13o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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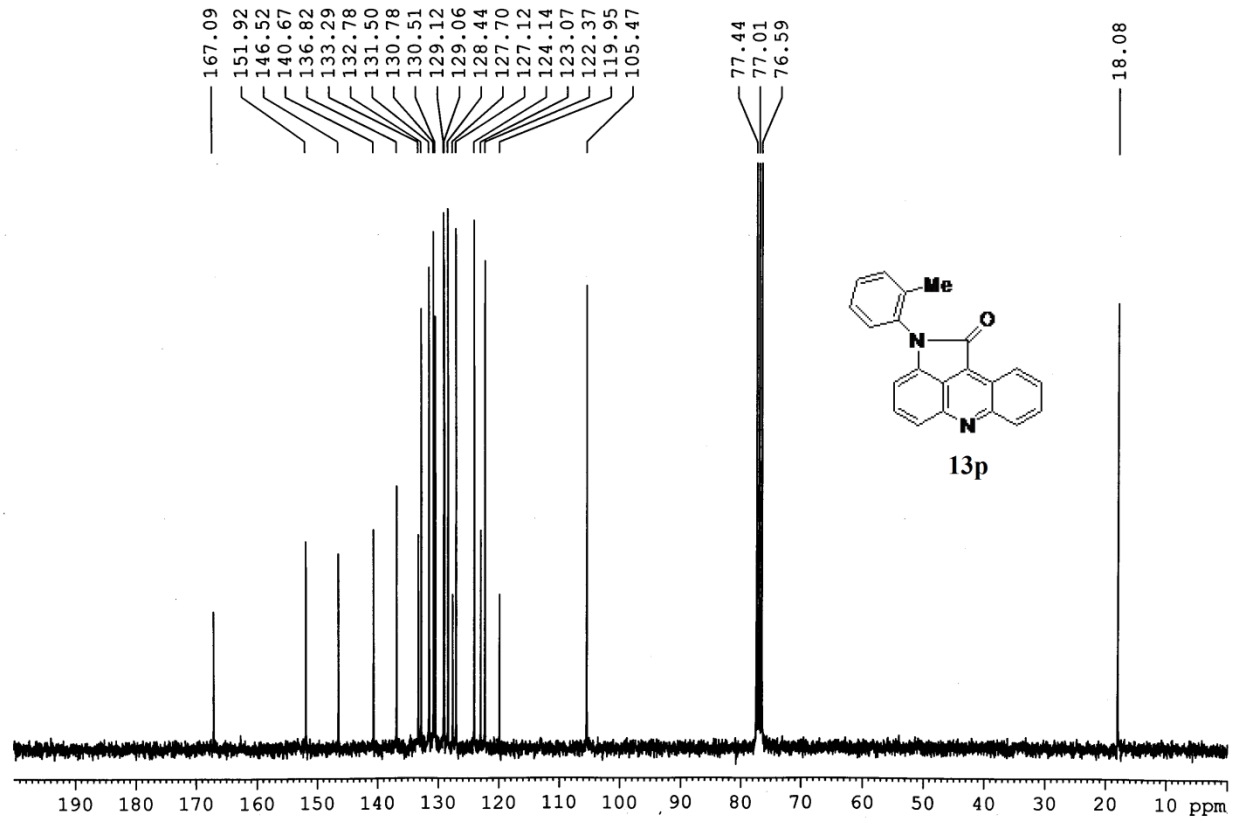
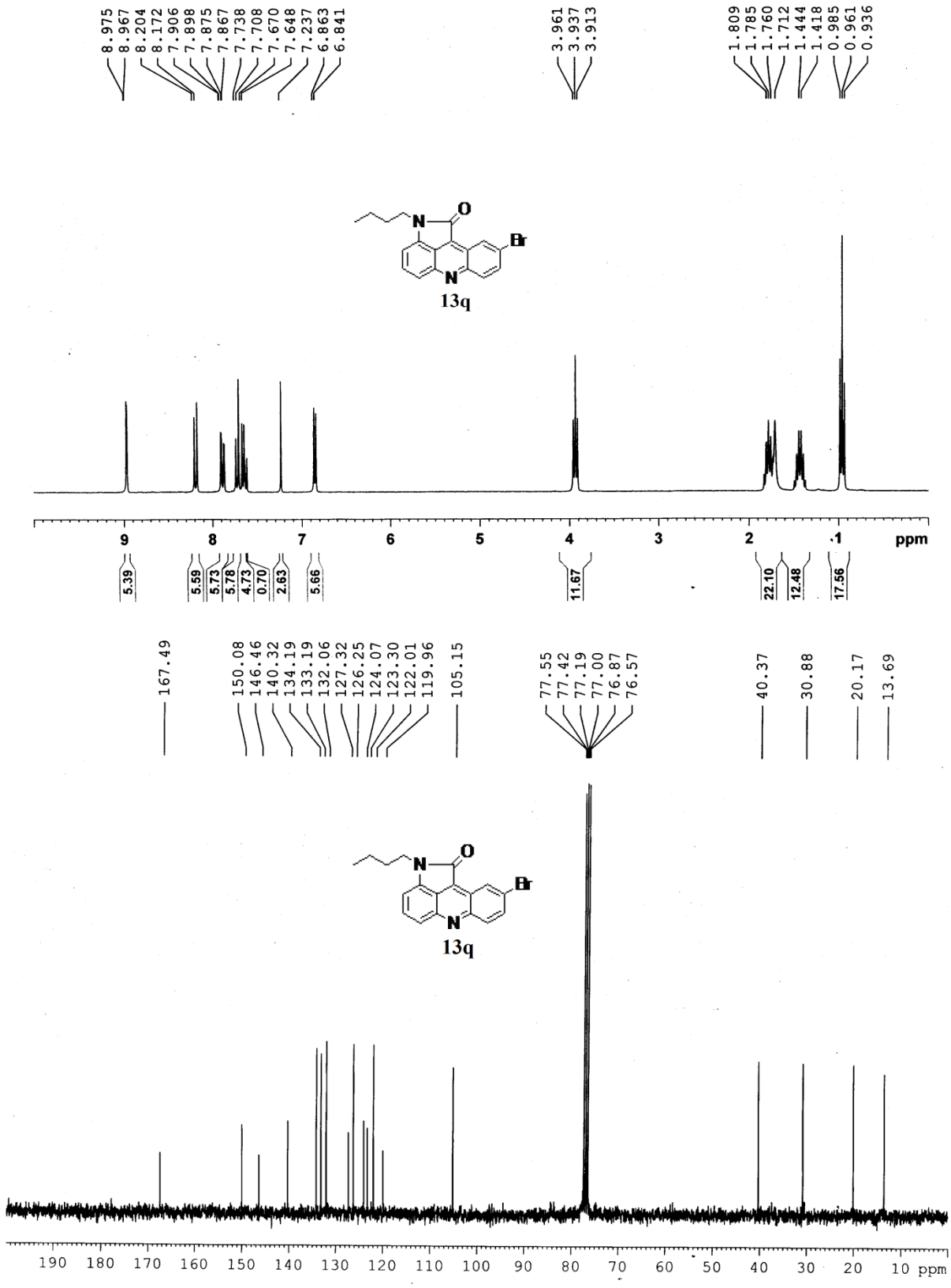
8.909
8.473
8.444
7.960
7.938
7.909
7.896
7.866
7.840
7.813
7.680
7.657
7.460
7.449
7.436
7.424
7.420
6.665
6.642
2.297
Me
N
O
N
13p
9
8
7
6
5
4
3
2
1
ppm
0.99
1.00
3.00
1.06
3.95
0.98
3.00


167.09
151.92
146.52
140.67
136.82
133.29
132.78
131.50
130.78
130.51
129.12
129.06
128.44
127.70
127.12
124.14
123.07
122.37
119.95
105.47
77.44
77.01
76.59
18.08
Me
N
O
N
13p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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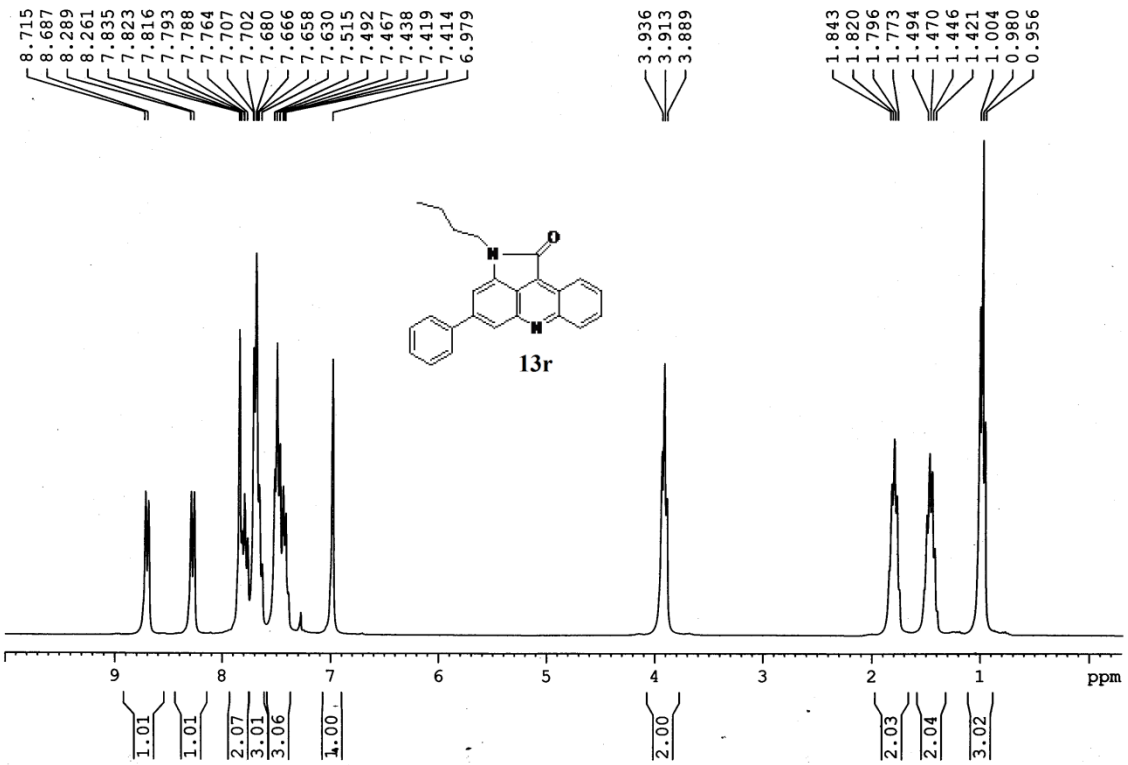
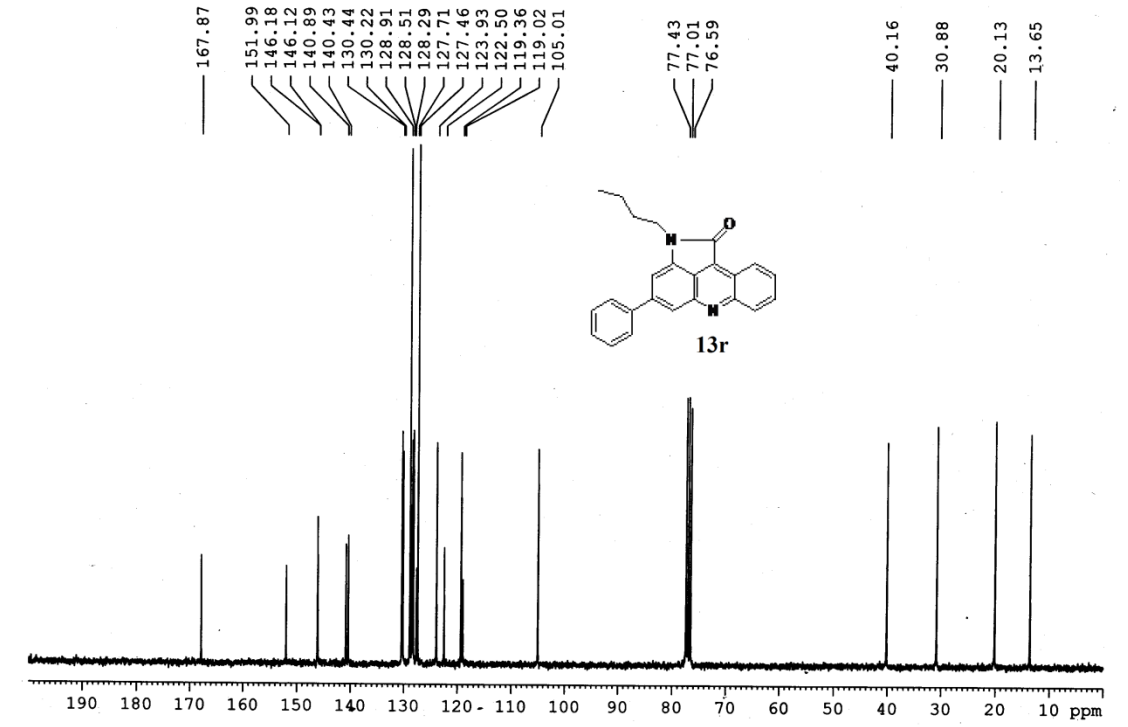
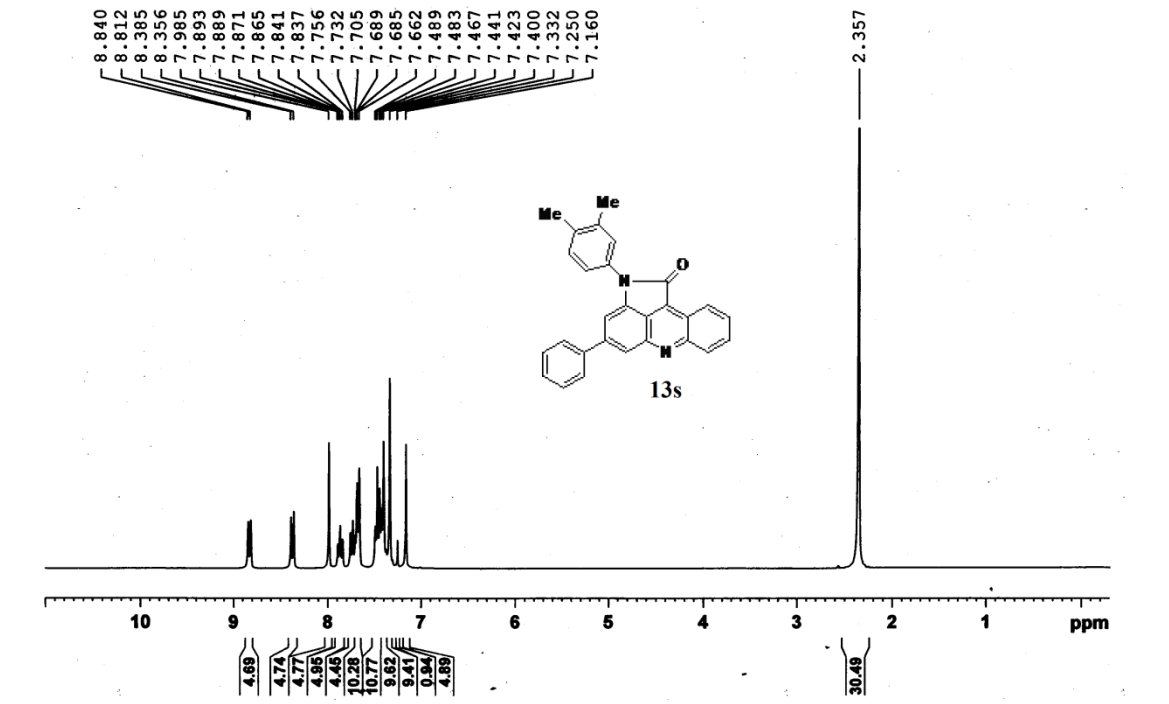
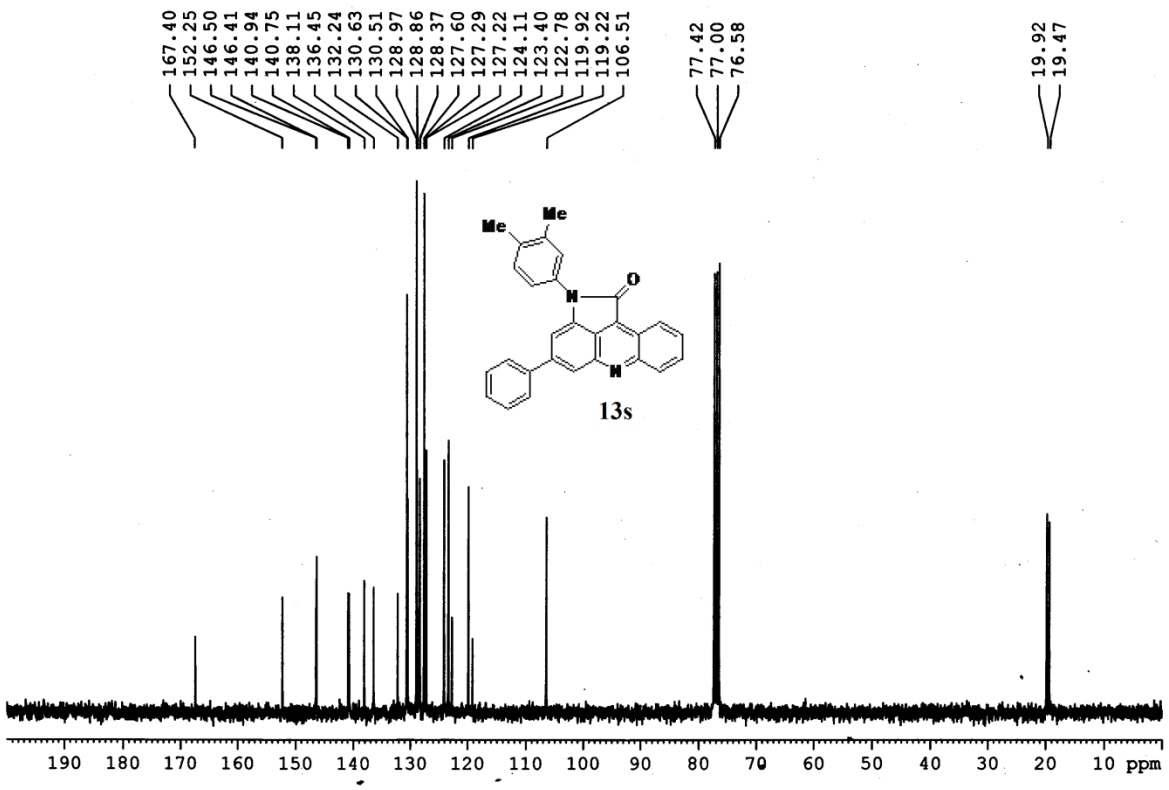
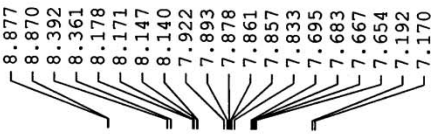
8.967
8.204
8.172
7.906
7.898
7.875
7.867
7.738
7.708
7.670
7.648
7.237
6.863
6.841
3.961
3.937
3.913
1.809
1.785
1.760
1.712
1.444
1.418
0.985
0.961
0.936
13q
ppm
5.39
5.59
5.73
5.78
4.73
0.70
2.63
5.66
11.67
22.10
12.48
17.56
167.49
150.08
146.46
140.32
134.19
133.19
132.06
127.32
126.25
124.07
123.30
122.01
119.96
105.15
77.55
77.42
77.19
77.00
76.87
76.57
40.37
30.88
20.17
13.69
13q
10 ppm

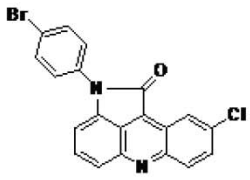

8.715
8.687
8.289
8.261
7.835
7.823
7.816
7.793
7.788
7.764
7.707
7.702
7.680
7.666
7.658
7.630
7.515
7.492
7.467
7.438
7.419
7.414
6.979
3.936
3.913
3.889
1.843
1.820
1.796
1.773
1.494
1.470
1.446
1.421
1.004
0.980
0.956
13r
9
8
7
6
5
4
3
2
1
ppm
1.01
1.01
2.07
3.01
3.06
1.00
2.00
2.03
2.04
3.02


167.87
151.99
146.18
146.12
140.89
140.43
130.44
130.22
128.91
128.51
128.29
127.71
127.46
123.93
122.50
119.36
119.02
105.01
77.43
77.01
76.59
40.16
30.88
20.13
13.65
13r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

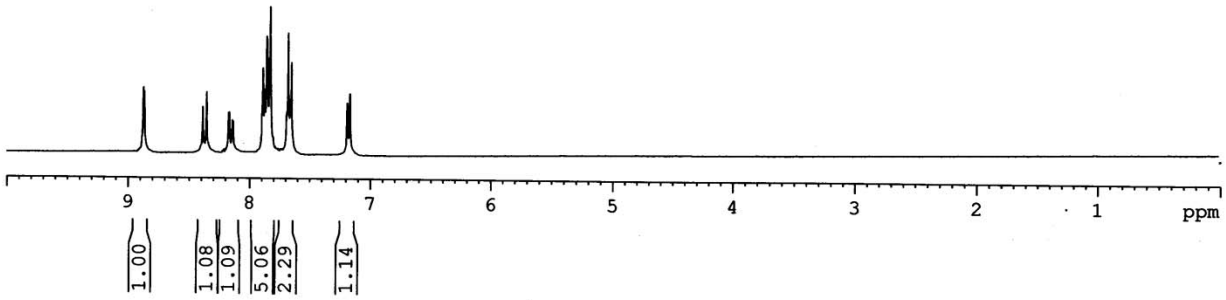

8.840
8.812
8.385
8.356
7.985
7.893
7.889
7.871
7.865
7.841
7.837
7.756
7.732
7.705
7.689
7.685
7.662
7.489
7.483
7.467
7.441
7.423
7.400
7.332
7.250
7.160
2.357
Me
Me
N
O
N
13s
10
9
8
7
6
5
4
3
2
1
ppm
4.69
4.74
4.77
4.96
4.46
10.28
10.77
9.62
9.41
0.94
4.89
30.49


167.40
152.25
146.50
146.41
140.94
140.75
138.11
136.45
132.24
130.63
130.51
128.97
128.86
128.37
127.60
127.29
127.22
124.11
123.40
122.78
119.92
119.22
106.51
77.42
77.00
76.58
19.92
19.47
Me
Me
N
O
N
13s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

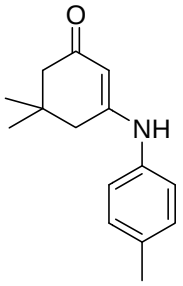

8.877
8.870
8.392
8.361
8.178
8.171
8.147
8.140
7.922
7.893
7.878
7.861
7.857
7.833
7.695
7.683
7.667
7.654
7.192
7.170


Br
O
N
Cl
H

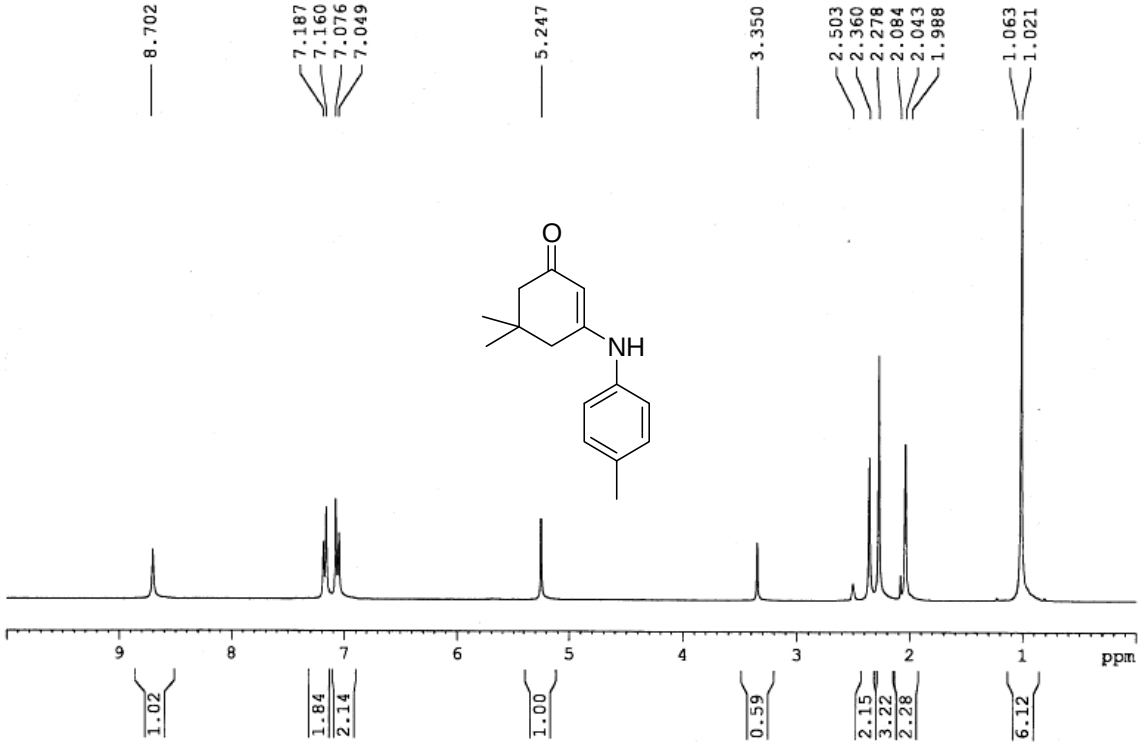
**13t**

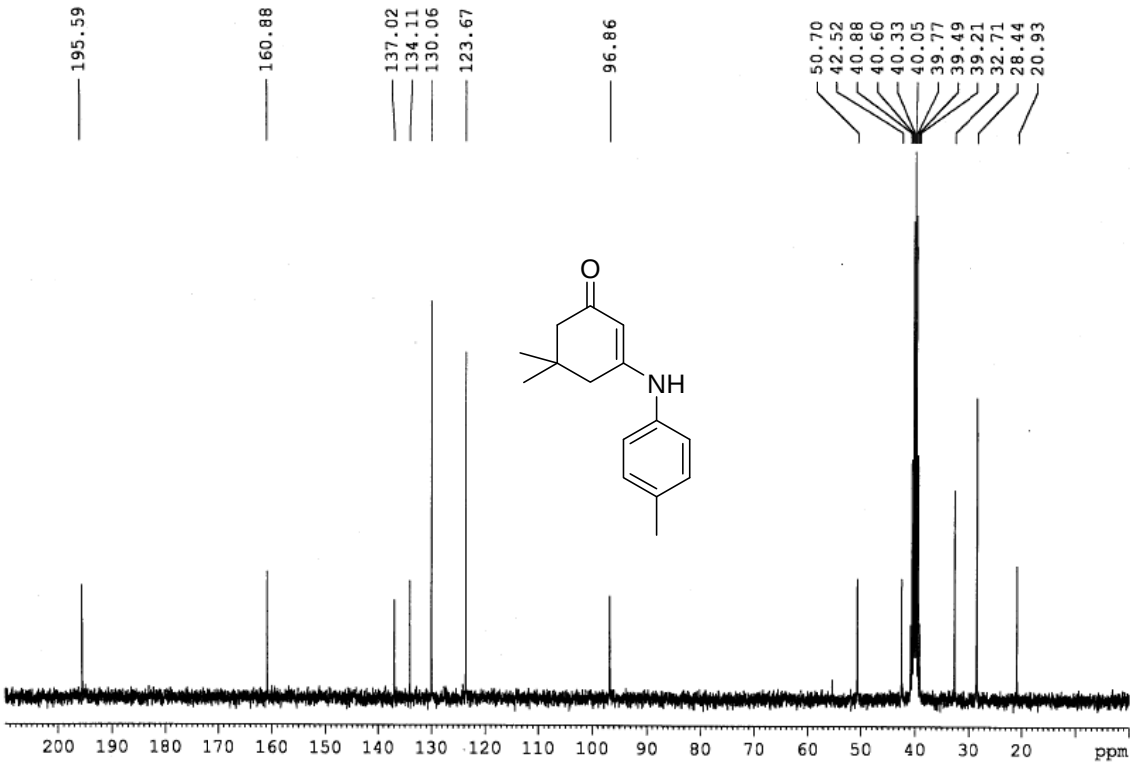

9
8
7
6
5
4
3
2
1
ppm
1.00
1.08
1.09
5.06
2.29
1.14

**3-(*p*-tolylamino)-5,5-dimethylcyclohex-2-enone (9):**




Yellow solid; m.p. 214-216 °C (recrystallized from EtOAc/DCM, equal volume); Anal. calcd. for $C_{15}H_{19}NO$; C: 78.56; H: 8.35; N: 6.11%. Found: C: 78.76; H: 8.29; N: 6.03 %; IR (KBr) $cm^{-1}$: 3416, 2915, 1687, 1610, 1453, 1098 $\delta_H$ ppm (300 MHz; DMSO-$d_6$; TMS) 1.02 (6H, s, 2× $CH_3$), 2.04 (2H, s, $CH_2$), 2.28 (3H, s, $CH_3$), 2.36 (2H, s, $CH_2$), 5.25 (1H, s, vinylic CH), 7.06 (2H, d, *J*=8.1 Hz, ArH), 7.17 (2H, d, *J*=8.1 Hz, ArH), 8.70 (1H, s, NH); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta_C$: 20.9, 28.4, 32.7, 42.5, 50.7, 96.9, 123.7, 130.1, 134.1, 137.0, 160.9, 195.6.




195.59
160.88
137.02
134.11
130.06
123.67
96.86
50.70
42.52
40.88
40.60
40.33
40.05
39.77
39.49
39.21
32.71
28.44
20.93
O
NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm