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A practical carbocatalysis by Graphene Oxide nanosheets in aqueous medium towards the synthesis of diversified dibenzo[1,4]diazepine scaffold

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Materials and Methods

^{1}H-NMR and ^{13}C-NMR spectral analysis were carried out on Bruker-Advance Digital 300 MHz and 75 MHz instruments where tetramethylsilane (TMS) was used as internal standard. Infrared spectra were recorded in KBr pallets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer.Melting points were determined on a Köfler Block apparatus and are uncorrected. Synthetic grade chemicals from Sigma-Aldrich, Spectrochem and E-Merck were used for carrying out the organic reactions. Elemental analyses were done using an autoanalyzer. Mass spectra (ESI-MS) of compound **4c** and **4t** were recorded on Waters Xevo G-2 SQ TOF electrospray ionization mass spectrophotometer. The morphology of synthesized GO was characterized using a transmission electron microscope (TEM-JEOL-JEM-2100 with a 200 kV accelerating voltage) and field emission scanning electron microscopy (FESEM-ZEISS Auriga instrument). Samples for TEM analysis were prepared by drying a droplet of material suspension on a carbon coated copper grid. FESEM samples were prepared by drying a droplet of the suspension on a silicon substrate coated with gold in the sputters coater. X-ray diffraction (XRD) patterns were recorded on an X-PERT-PRO Panalytical diffractometer using Cu Kα (λ=1.5406) as the X-ray source at a scanning rate of 1°/min and generator voltage of 40 kV and current of 30 mA. The Fourier transform infrared (FTIR) spectroscopic experiments of GO were performed with a Bruker-Optics Alpha-T spectrophotometer over the range 400 to 4000 cm^{-1}.

Experimental:

Preparation of GO nanosheets:

Natural graphite powder was used for the synthesis of the GO nanosheets. Graphite powder (1000 mg) and $NaNO_3$ (1000 mg) were added to 35 ml of concentrated H_2SO4 (98%) under vigorous stirring in a 250 ml conical flask placed in an ice bath. The whole mass was converted to a black slurry (which takes 2 min), then KMnO4 (5000 mg) was added slowly to the slurry while maintaining the reaction temperature between 15 ^oC and 20 ^oC. After 3 h, the entire system was taken out of the ice bath and the mixture diluted with 100 ml of water and then further stirred for 3 h at ambient temperature. 200 ml of hot water was added to the above reaction mixture followed by 30% H_2O_2, until the excess permanganate and manganese dioxide had been reduced to colourless soluble manganese sulfate. The resultant yellow precipitate was washed with distilled water several times and then was subjected to centrifugation to obtain the pure graphene oxide powder. After repeated centrifugation, salts and ions resulting from the oxidation process can be removed from the GO suspension. The GO nanosheet sample was collected and dried at 60 ^oC for 24 h. The GO nanosheets were characterized using XRD, FTIR, and FESEM and TEM images.

Synthesis of dibenzo[1,4]diazepine

o-Phenylenediamine (1 mmol), 1,3-dicarbonyl compound (1 mmol) and aldehyde/ketone derivatives (1 mmol) were stirred in water (5 ml) in presence of GO nanosheets (15 mg) at 70^oC. After completion of reaction (indicated by TLC), the reaction mixture was extracted with ethyl acetate (2 x 3 ml).Solvent (ethyl acetate) removal followed by column chromatography (eluent: ethyl acetate/petroleum ether 1:5) led to the pure products. GO nanosheet, which is completely

insoluble in ethyl acetate remains at aqueous layer.GO nanosheets can be recycled from the aqueous layer through evaporation of water. GO thus obtained can be used further after proper drying. All compounds were well characterized by ^{1}H, ^{13}C NMR and FT-IR analysis.

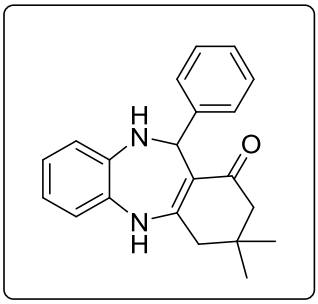
Hot filtration test for leaching of GO nanosheets:

Leaching of GO nanosheets was studied by performing hot filtration test of compound **4p** under optimized condition. During this test, the GO nanosheets were removed from the reaction mixture by filtration after 30 min of the reaction and the filtrate was monitored for continued activity. It was found that after removal of the catalyst, the reaction proceeded negligibly (approx. 1%). Yield of the compound after 30 min of reaction (with GO catalyst): 40.8% (0.147 mg)

Yield of the compound after 60 min of reaction (GO was removed after 30 min): 41.9% (0.151 mg).

This observation indicates that almost no catalytically active GO remained in filtrate and hence indicates no significant leaching of the catalyst.

3,3-dimethyl-11-phenyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4a)



Yield: 90% (0.286 g)

Characteristic: Pale green solid

Mp: 248-250 °C

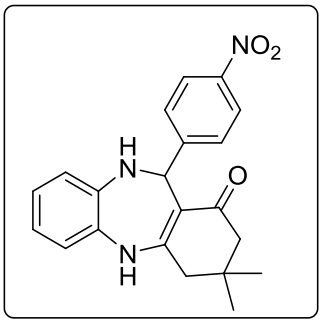
IR (KBr): 3293, 3239, 3056, 2951, 1680, 1275 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.86 (6H, s), 1.71 (2H, s), 2.22 (2H, s), 5.06 (1H, d, *J*=4.5 Hz), 6.97-7.08 (3H, m), 7.28-7.39 (2H, m), 7.55 (2H, d, *J*= 8.7 Hz), 7.76 (1H, d, *J*= 7.5), 8.03 (1H, d, *J*= 8.1), 8.13 (1H, d, *J*= 8.7), 9.76 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 26.0, 26.9, 28.9, 29.7, 31.9, 49.5, 111.9, 112.8, 116.7, 116.9, 119.6, 122.8, 123.4, 125.2, 129.0, 129.6, 131.3, 145.7, 151.6, 152.1, 154.5, 195.1;

Anal.calcd for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80 %. Found: C, 79.28; H, 6.87; N, 8.72 %.

3,3-dimethyl-11-(4-nitrophenyl)-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one(4b)



Yield: 97% (0.352 g)

Characteristic: Yellow solid

Mp: 277-279 °C

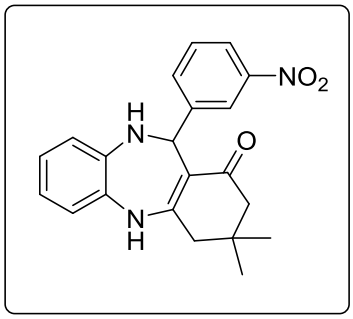
IR (KBr): 3290, 3231, 3042, 2950, 1682, 1276 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ1.03 (3H, s), 1.09 (3H, s), 2.50 (2H, s), 2.62 (2H, s), 5.79 (1H, d, *J*= 5.7), 6.37 (1H, d, *J*= 5.7), 6.51-6.54 (1H, m), 6.59-6.66 (2H, m), 6.96-6.99 (1H, m), 7.32 (2H, d, *J*= 8.7), 8.01 (2H, d, *J*= 8.7), 8.95 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 28.1, 28.7, 32.2, 44.5. 49.8, 56.4, 109.4, 120.5, 120.7, 120.9, 123.5, 128.8, 131.5, 138.3, 146.2, 153.3, 155.5, 192.7;

Anal.calcd for $C_{21}H_{21}N_3O_3$: C, 69.41; H, 5.82; N, 11.56 %. Found: C 63.89, H 3.56, N 17.21 %.

3,3-dimethyl-11-(3-nitrophenyl)-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4c)



Yield: 95% (0.345 g)

Characteristic: Pale yellow solid

Mp: 160-162 °C

IR (KBr): 3356, 3281, 3181, 2955, 1690, 1512, 1422, 1278 cm^{-1};

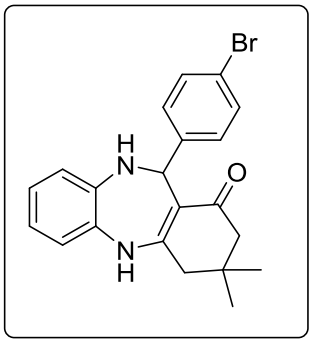
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.95 (3H, s), 1.03 (3H, s), 2.36 (2H, s), 2.48 (2H, s), 5.64 (1H, d, *J*= 5.7 Hz), 6.22 (1H, d, *J*= 5.7 Hz), 6.39 (1H, d, *J*= 6.6 Hz), 6.47-6.49 (2H, m), 6.83-6.85 (1H, m), 7.17-7.19 (2H, m), 7.85-7.88 (2H, m), 8.79 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 27.4, 28.2, 31.6, 44.4, 49.4, 56.4, 108.9, 120.2, 120.6, 122.1, 122.5, 122.9, 127.9, 130.8, 137.2, 145.5, 152.2, 155.0, 192.7;

HRMS calcdfor$C_{21}H_{21}N_3O_3$ ($[M+H]^+$): 364.1656;found : 364.1750.

Anal.calcd for $C_{21}H_{21}N_3O_3$: C, 69.41; H, 5.82; N, 11.56 %. Found: C 63.89, H 3.56, N 17.21 %.

11-(4-bromophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4d)



Yield: 88% (0.348 g)

Characteristic: Green solid

Mp: 290-292 °C

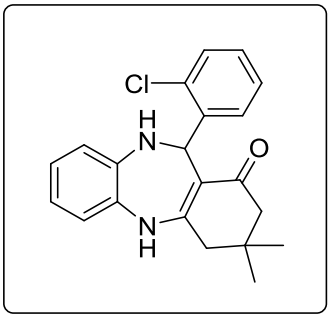
IR (KBr): 3352, 3272, 3185, 2951, 1692, 1270 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.94 (3H, s), 1.00 (3H, s), 2.42 (2H, s), 2.53 (2H, s), 5.69 (1H, d, *J*= 5.4 Hz), 6.28 (1H, d, *J*= 5.7 Hz), 6.43-6.46 (1H, m), 6.53-6.55 (2H, s), 6.89-6.90 (1H, m), 7.24 (2H, d, *J*= 8.1 Hz), 7.93 (2H, d, *J*= 7.8 Hz), 8.86 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 28.0, 28.6, 32.2, 44.5, 49.8, 56.3, 109.3, 120.5, 120.7, 120.9, 123.5, 128.8, 131.4, 138.8, 142.1, 146.1, 153.3, 155.5, 192.6;

Anal.calcd for $C_{21}H_{21}BrN_2O$: C, 63.48; H, 5.33; N, 7.05 %. Found: C, 63.62; H, 6.03; N, 7.25 %.

11-(2-chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4e)



Yield: 91% (0.320 g)

Characteristic: White solid

Mp: 235-238 °C

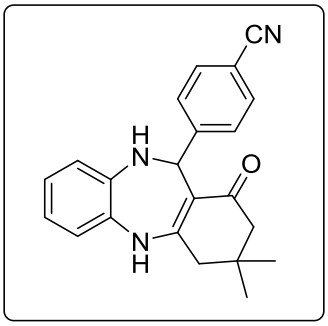
IR (KBr): 3354, 3279, 3181, 2956, 1691, 1278 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.94 (3H, s), 0.99 (3H, s), 2.42 (2H, s), 2.53 (2H, s), 5.69 (1H, d, *J*= 5.7 Hz), 6.28 (1H, d, *J*= 6.0 Hz), 6.42-6.46 (1H, m), 6.52-6.56 (2H, m), 6.87-6.90 (1H, m), 7.23 (2H, d, *J*= 8.7 Hz), 7.92 (2H, d, *J*= 8.7 Hz), 8.86 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 28.1, 28.7, 32.2, 44.5, 49.5, 49.8, 109.4, 120.5, 120.7, 120.9, 123.5, 128.8, 131.4, 138.3, 146.2, 153.3, 155.5, 192.7;

Anal.calcd for $C_{21}H_{21}ClN_2O$: C, 71.48; H, 6.00; N, 7.94 %. Found: C, 72.02; H, 6.18; N, 7.99 %.

4-(3,3-dimethyl-1-oxo-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-11 yl)benzonitrile (4f)



Yield: 85% (0.292 g)

Characteristic: Yellow solid

Mp: 225-227 °C

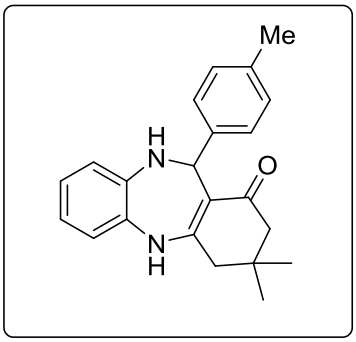
IR (KBr): 3385, 3291, 3078, 2953, 2221, 1687, 1585cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (3H, s), 0.98 (3H, s), 2.39 (2H, s), 2.51 (2H, s), 5.67 (1H, d, *J*= 5.7 Hz), 6.27 (1H, d, *J*= 5.7 Hz), 6.41-6.43 (1H, m), 6.49-6.55 (2H, m), 6.86-6.88 (1H, m), 7.21 (2H, d, *J*= 8.4 Hz), 7.90 (2H, d, *J*= 7.8 Hz), 8.84 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 28.6, 32.2, 44.4, 49.8, 56.2, 109.3, 120.6, 120.7, 120.9, 123.5, 123.8, 131.5, 138.3, 142.1, 146.1, 153.2, 155.6, 192.3;

Anal.calcd for $C_{22}H_{21}N_3O$: C, 76.94; H, 6.16; N, 12.24 %. Found: C 77.04; H, 6.19; N, 12.29 %.

3,3-dimethyl-11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4g)



Yield: 86% (0.286 g)

Characteristic: Green solid

Mp: 220-222 °C

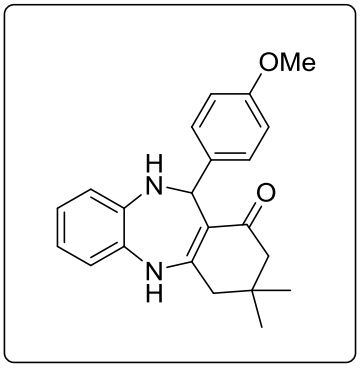
IR (KBr): 3311, 3040, 2962, 2359, 1995, 1680, 1584cm^{-1};

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.04 (3H, s), 1.22 (3H, s), 2.39 (2H, s), 2.49 (2H, s), 2.78 (3H, s), 4.41 (1H, d, *J*= 5.7 Hz), 6.29 (1H, d, *J*= 5.7 Hz), 7.09 (1H, d, *J*= 8.7 Hz), 7.14-7.54 (5H, m), 8.10 (2H, d, *J*= 8.7 Hz), 9.13 (1H, s);

^{13}C NMR (75 MHz, DMSO-d$_6$): δ 20.4, 27.9, 28.3, 31.6, 44.4, 49.4, 56.3, 108.9, 120.2, 120.6, 122.2, 122.5, 122.9, 127.9, 130.9, 137.2, 145.6, 152.3, 155.0, 160.7, 193.6;

Anal.calcd for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43 %. Found: C, 80.21; H, 7.30; N, 8.53 %.

11-(4-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4h)



Yield: 88% (0.306 g)

Characteristic: Cream colored solid

Mp: 215-217 °C

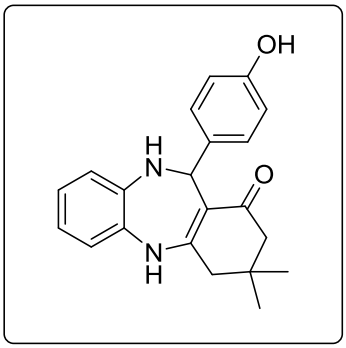
IR (KBr): 3312, 2965, 2362, 1584, 1538 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.04 (3H, s), 1.21 (3H, s), 2.49 (2H, s), 2.51 (2H, s), 3.83 (3H, s), 4.40 (1H, d, *J*= 5.7 Hz), 6.59 (1H, d, *J*= 5.7 Hz), 7.08-7.54 (6H, m), 8.10 (2H, d, *J*= 8.7 Hz), 9.14 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 27.5, 28.2, 31.7, 49.3, 56.3, 58.4, 108.5, 120.2, 120.6, 122.2, 122.6, 122.9, 127.9, 130.9, 137.2, 145.6, 152.3, 155.1, 192.3;

Anal.calcd for $C_{22}H_{24}N_2O_2$: C, C, 75.83; H, 6.94; N, 8.04% Found: C, 75.76; H, 6.90; N, 8.02%

11-(4-hydroxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4i)



Yield: 83% (0.277 g)

Characteristic: Green solid

Mp: 270-272 °C

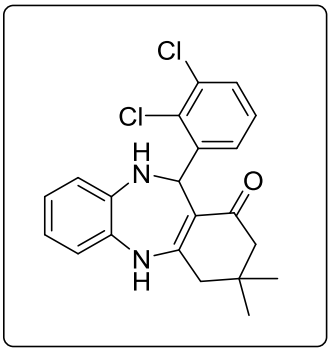
IR (KBr): 3620, 3309, 3243, 3101, 1599, 1384, 1528, 1424, 1275 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.58 (3H, s), 0.65 (3H, s), 1.93 (2H, s), 2.13 (2H, s), 5.28 (1H, m), 5.44 (1H, s), 6.03-6.49 (4H, m), 6.81 (2H, d, *J*= 7.8 Hz), 7.43 (2H, d, *J*= 7.5 Hz), 8.23 (2H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 28.2, 28.6, 31.2, 32.2, 49.8, 56.5, 109.3, 120.7, 120.9, 121.2, 123.5, 128.9, 131.1, 138.1, 146.3, 153.2, 155.7, 192.6;

Anal.calcd for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38 % Found: C, 75.49; H, 6.68; N, 8.37%.

11-(2,3-dichlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4j)



Yield: 90% (0.347 g)

Characteristic: Green solid

Mp: 256-258 °C

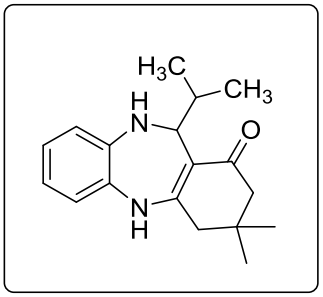
IR (KBr): 3325, 3256, 2961, 2343, 1576 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.02 (3H, s), 1.08 (3H, s), 2.49 (2H, s), 2.62 (2H, s), 5.77 (1H, d, *J*= 6.9), 6.55 (1H, d, *J*= 7.5), 6.62-6.64 (2H, m), 6.98-7.00 (1H, m), 7.32 (2H, d, *J*= 8.1), 8.00 (2H, d, *J*= 8.7), 8.44 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 28.1, 28.7, 31.1, 32.3, 44.5, 49.8, 56.4, 109.4, 120.7, 120.8, 121.1, 123.5, 128.8, 131.5, 138.1, 146.2, 153.2, 155.6, 192.7;

Anal.calcd for $C_{21}H_{20}Cl_2N_2O$: C, 65.12; H, 5.21; N, 7.23 %. Found: C, 65.23; H, 5.26; N, 7.29 %.

11-isopropyl-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4k)



Yield: 82% (0.233 g)

Characteristic: White solid

Mp:202-205 °C

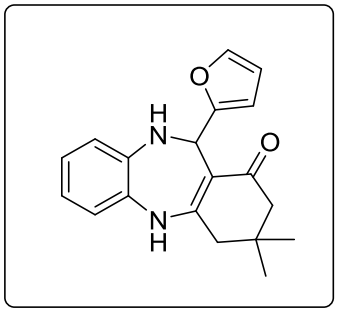
IR (KBr): 3311, 3237, 2959, 1599, 1425, 1278 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.63 (3H, d, *J*= 6.6 Hz), 0.74 (3H, d, *J*= 6.6 Hz), 0.92 (3H, s), 0.96 (3H, s), 1.99-2.07 (1H, m), 2.37 (2H, s), 2.39 (2H, s), 4.04 (1H, d, *J*= 3.9 Hz), 5.69 (1H, d, *J*= 5.7 Hz) 6.55-6.58 (1H, m), 6.64-6.66 (1H, m), 6.88 (2H, d, *J*= 8.1 Hz), 8.46 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 20.3, 20.8, 27.4, 29.5, 31.8, 33.4, 44.5, 49.9, 56.9, 113.5, 119.2, 120.0, 120.2, 122.8, 131.0, 138.6, 154.1, 192.5;

Anal.calcd for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85 %. Found: C, 76.13; H, 8.71; N, 10.05 %.

11-(furan-2-yl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one(4l)



Yield: 80% (0.246 g)

Characteristic: Pale yellow solid

Mp: 216-218 °C

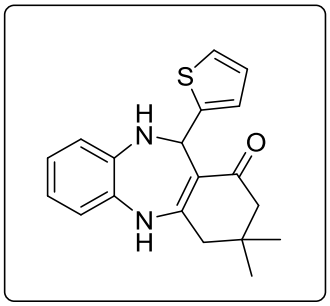
IR (KBr): 3303, 3245, 2949, 1581, 1537 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.59 (3H, s), 0.65 (3H, s), 1.93 (2H, s), 2.13 (2H, s), 4.45 (1H, d, *J*= 5.7 Hz), 6.59 (1H, d, *J*= 5.7 Hz), 7.21-7.84 (7H, m), 9.25 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 27.4, 32.6, 44.4, 49.8, 56.2, 109.4, 120.6, 120.7, 120.9, 123.4, 128.7, 131.3, 138.3, 142.1, 146.2, 193.6;

Anal.calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08 %. Found: C, 74.21; H, 6.66; N, 9.24 %.

3,3-dimethyl-11-(thiophen-2-yl)-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4m)



Yield: 82% (0.266 g)

Characteristic: Pale yellow solid

Mp: 225-227 °C

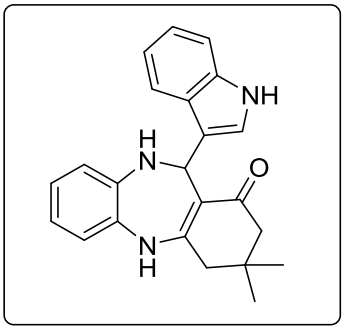
IR (KBr): 3312, 3242, 2946, 1584, 1535cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.79 (3H, s), 0.86 (3H, s), 1.92 (2H, s), 2.10 (2H, s), 4.95 (1H, d, *J*= 5.7 Hz), 6.59 (1H, d, *J*= 5.7 Hz), 7.13-7.47 (5H, m), 7.64 (1H, d, *J*= 6.9 Hz), 7.75 (1H, d, *J*= 7.1 Hz), 9.16 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 27.6, 32.2, 44.5, 49.7, 56.3, 109.3, 120.6, 120.7, 120.8, 123.4, 128.7, 131.4, 138.2, 142.1, 146.2, 193.4;

Anal.calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63 %. Found: C 71.02; H, 6.31; N, 8.72 %.

11-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4n)



Yield: 83% (0.296 g)

Characteristic: Yellow solid

Mp: 287-289 °C

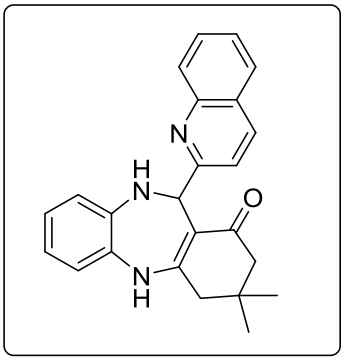
IR (KBr): 3315, 3240, 3115, 1592, 1270 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.97 (3H, s), 1.02 (3H, s), 2.49 (2H, s), 2.62 (2H, s), 5.79 (1H, s), 6.55 (1H, s), 6.62-6.64 (2H, m), 6.97-6.99 (2H, m), 7.32 (2H, d, *J*= 8.4), 7.99 (2H, d, *J*= 7.5), 8.44 (1H, s), 9.97 (2H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 31.1, 32.3, 44.5, 49.8, 56.4, 109.3, 120.7, 120.8, 121.1, 123.5, 124.8, 128.8, 131.5, 138.1, 146.2, 153.2, 155.2, 192.7;

Anal.calcd for $C_{23}H_{23}N_3O$: C, 77.28; H, 6.49; N, 11.76 %. Found: C, 77.34; H, 6.55; N, 11.77%

3,3-dimethyl-11-(quinolin-2-yl)-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4o)



Yield: 87% (0.321 g)

Characteristic: Yellow solid

Mp: 290-292°C

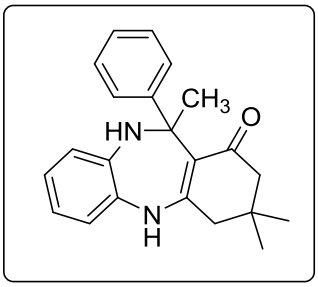
IR (KBr): 3318, 3247, 1473, 1582, 1271 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.12 (3H, s), 1.17 (3H, s), 2.58 (2H, s), 2.70 (2H, s), 5.87 (1H, s), 6.63 (1H, s), 6.71-6.73 (2H, m), 7.05-7.08 (3H, m), 7.40 (3H, d, *J*= 8.7), 8.08 (2H, d, *J*=8.4), 8.52 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 28.1, 28.7, 31.1, 40.5, 49.8, 56.4, 109.3, 113.3, 120.7, 120.8, 121.1, 123.5, 128.8, 131.5, 138.1, 142.3, 146.2, 148.7, 153.2, 155.7, 158.7, 192.7;

Anal.calcd for $C_{24}H_{23}N_3O$: C, 78.02; H, 6.27; N, 11.37%. Found: C, 78.13; H, 6.33; N, 11.42%.

3,3,11-trimethyl-11-phenyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one(4p)



Yield: 80% (0.266 g)

Characteristic: Yellow solid

Mp: 252-254 °C

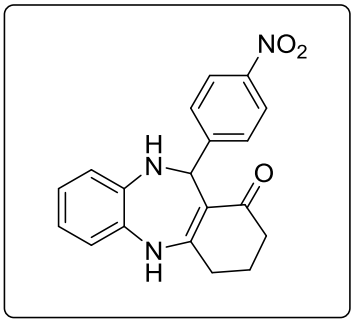
IR (KBr): 3292, 3231, 3051, 2952, 1594, 1269 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.98 (3H, s), 1.03 (3H, s), 1.78 (3H, s), 2.49 (2H, s), 2.65 (2H, s), 5.63 (1H, s), 7.28 (2H, t, *J*= 7.7), 7.49 (2H, d, *J*= 8.4), 7.62 (1H, t, *J*= 6.9), 8.04-8.13 (4H, m), 8.49 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 31.2, 32.2, 44.6, 49.8, 56.5, 109.4, 120.6, 120.8, 121.1, 123.4, 124.8, 128.9, 131.6, 138.0, 146.3, 153.1, 155.3, 192.2;

Anal.calcd for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43 %. Found: C, 80.02; H, 7.32; N, 8.55%.

11-(4-nitrophenyl)-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4q)



Yield: 84% (0.281 g)

Characteristic: Yellow solid

Mp: 255-257 °C

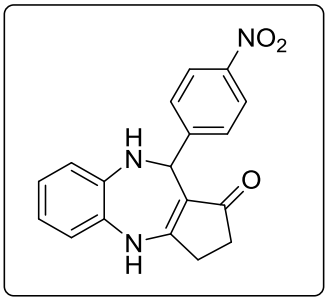
IR (KBr): 3290, 3234, 1682, 1592cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.35-1.41 (2H, m), 2.36 (2H, t, *J*= 4.5), 2.80 (2H, t, *J*= 4.5), 5.23 (1H, s), 6.25 (1H, s), 6.59 (1H, d, *J*= 6.9), 6.68-6.76 (2H, m), 7.01 (1H, d, *J*= 7.5), 7.34 (2H, d, *J*= 8.7), 8.04 (2H, d, *J*= 8.7), 10.51 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): 21.5, 27.1, 33.4, 56.6, 113.5, 120.5, 121.2, 122.7, 123.6, 128.7, 131.8, 137.8, 146.5, 152.5, 167.7, 172.4, 199.8;

Anal.calcd for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53 %. Found: C, 68.11; H, 5.19; N, 12.72 %.

10-(4-nitrophenyl)-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one(4r)



Yield: 96% (0.308 g)

Characteristic: Bright yellow solid

Mp: 223-224 °C

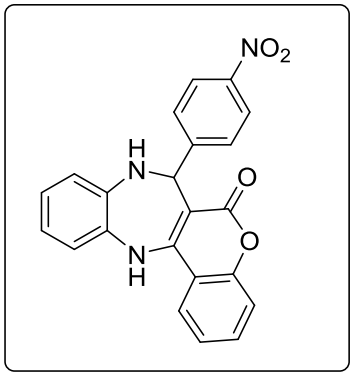
IR (KBr): 3292, 3231, 1613,1432, 1245 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.36 (2H, t, *J*= 4.5), 2.80 (2H, t, *J*= 4.5), 5.23 (1H, s), 6.24 (1H, s), 6.59 (1H, d, *J*= 6.9), 6.70-6.75 (2H, m), 7.00 (1H, d, *J*= 7.5), 7.33 (2H, d. *J*= 8.7), 8.03 (2H, d, *J*= 8.7), 9.89 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 27.1, 33.4, 56.6, 113.5, 120.5, 121.2, 122.7, 123.6, 128.7, 131.8, 137.8, 146.5, 152.5, 167.7, 172.4, 199.8.

Anal.calcd for $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08 %. Found: C, 67.55; H, 4.91; N, 13.77 %.

7-(4-nitrophenyl)-8,13-dihydrobenzo[*b*]chromeno[4,3-*e*][1,4]diazepin-6(7*H*)-one (4s)



Yield: 95% (0.366 g)

Characteristic: Light yellow solid

Mp:280-282°C

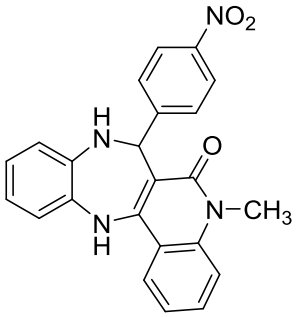
IR (KBr): 3385, 3292, 1755, 1666 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.29 (1H, s), 7.28 (2H, t, *J*= 7.5), 7.48-7.64 (6H, m), 8.04-8.13 (4H, m), 8.43 (1H, s), 10.84 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 55.7, 106.2, 114.1, 114.6, 114.9, 117.2, 119.9, 120.5, 122.1, 123.4, 124.6, 128.4, 128.9, 129.3, 131.3, 134.1, 147.5, 151.8, 157.2, 159.3;

Anal.calcd for $C_{22}H_{15}N_3O_4$: C, 68.57; H, 3.92; N, 10.90 %. Found: C, 68.76; H, 4.02; N, 11.03 %.

5-methyl-7-(4-nitrophenyl)-5,7,8,13-tetrahydro-6*H*-benzo[2,3][1,4]diazepino[6,5-*c*]quinolin-6-one (4t)



Yield: 96% (0.382 g)

Characteristic: Yellow solid

Mp:>300 °C

IR (KBr): 3385, 3201, 2945, 1675 cm^{-1};

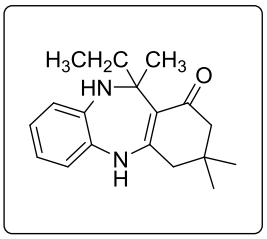
^{1}H NMR (300 MHz, DMSO-d_6): δ 4.10 (3H, s), 6.29 (1H, s), 7.28 (2H, t, *J*= 7.5 Hz), 7.49 (5H, d, *J*= 8.4 Hz), 7.62 (1H, t, *J*= 7.1 Hz), 8.04-8.13 (4H, m), 8.42 (1H, s), 10.73 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 30.1, 53.9, 109.7, 114.9, 116.5, 121.8, 123.7, 127.9, 129.7, 129.9, 131.3, 139.1, 146.2, 149.8, 157.5, 163.0, 167.1;

HRMS calcd for $C_{23}H_{18}N_4O_3$ ($[M+H]^+$): 399.1452; found : 399.1455.

Anal.calcd for $C_{23}H_{18}N_4O_3$: C, 69.34; H, 4.55; N, 14.06 %. Found: C, 69.42; H, 4.62; N, 14.18 %.

11-ethyl-3,3,11-trimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4u)



Yield: 86% (0.244 g)

Characteristic: White solid

Mp: 200-202 °C

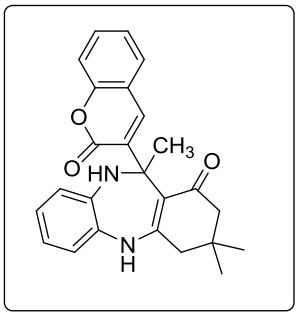
IR (KBr): 3381, 3205, 2941, 1678 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (6H, s), 0.97 (3H, t, *J*= 6.5), 1.42 (3H, s), 1.69-1.77 (2H, m), 2.14 (2H, s), 2.37 (2H, s), 6.37 (1H, s), 6.54 (1H, d, *J*= 8.1`), 6.73 (1H, t, *J*=7.5), 7.23-7.33 (2H, m), 7.57 (1H, s);

^{13}C NMR (75 MHz, $CDCl_3$): δ8.1, 27.5, 34.8, 38.7, 44.2, 51.1, 114.4, 118.5, 128.3, 133.9, 160.6, 196.9;

Anal.calcd for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85 %. Found:C, 77.00; H, 9.01; N, 10.08 %.

3,3,11-trimethyl-11-(2-oxo-2*H*-chromen-3-yl)-2,3,4,5,10,11-hexahydro-1*H* dibenzo[*b*,*e*][1,4]diazepin-1-one (4v)



Yield: 81% (0.324 g)

Characteristic: Yellow solid

Mp:>300 °C

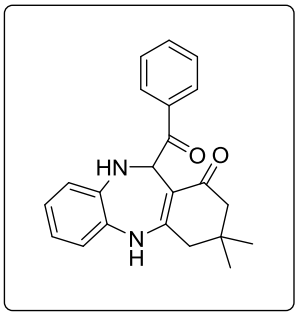
IR (KBr): 3345, 3215, 2942, 1745, 1668, 1596 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.19 (6H, s), 1.59 (3H, s), 2.90 (2H, s), 2.98 (2H, s), 6.79 (1H, t, *J*=7.2), 6.80-7.09 (3H, m), 7.21-7.35 (3H,m), 7.50 (1H, t, *J*=7.9), 7.99 (1H, s), 9.91 (1H, s), 11.55 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ31.1, 32.3, 44.9, 49.8, 56.6, 109.6, 120.7, 120.8, 121.4, 123.4, 124.3, 128.3, 131.8, 138.0, 146.1, 153.0, 155.3, 192.2;

Anal.calcd for $C_{25}H_{24}N_2O_3$: C, 74.98; H, 6.04; N, 7.00%. Found: C, 75.15; H, 6.27; N, 7.18 %.

11-benzoyl-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[b,e][1,4]diazepin-1-one (4w)



Yield: 80% (0.277 g)

Characteristic: Yellow solid

Mp:287-287 °C

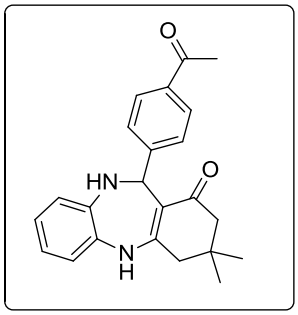
IR (KBr): 3340, 3212, 2954, 1742, 1668, 1689, 1596 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.94 (3H, s), 1.03 (3H, s), 2.36 (2H, s), 2.48 (2H, s), 6.54 (1H, d, *J*=6.9), 7.16 (1H, d, *J*=7.2), 7.40-7.47 (6H, m), 7.73-7.78 (2H, m), 8.29 (1H, d, J=8.1), 9.23 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 26.5, 26.9, 28.9, 29.7, 31.9, 40.6, 111.9, 112.1, 116.8, 116.9, 119.6, 122.8, 123.4, 125.2, 129.0, 129.7, 131.3, 151.6, 152.1, 180.9, 195.2;

Anal.calcd for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09%. Found: C, 76.32; H, 6.48; N, 8.16 %.

11-(4-acetylphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (4x)



Yield: 90% (0.325 g)

Characteristic: White solid

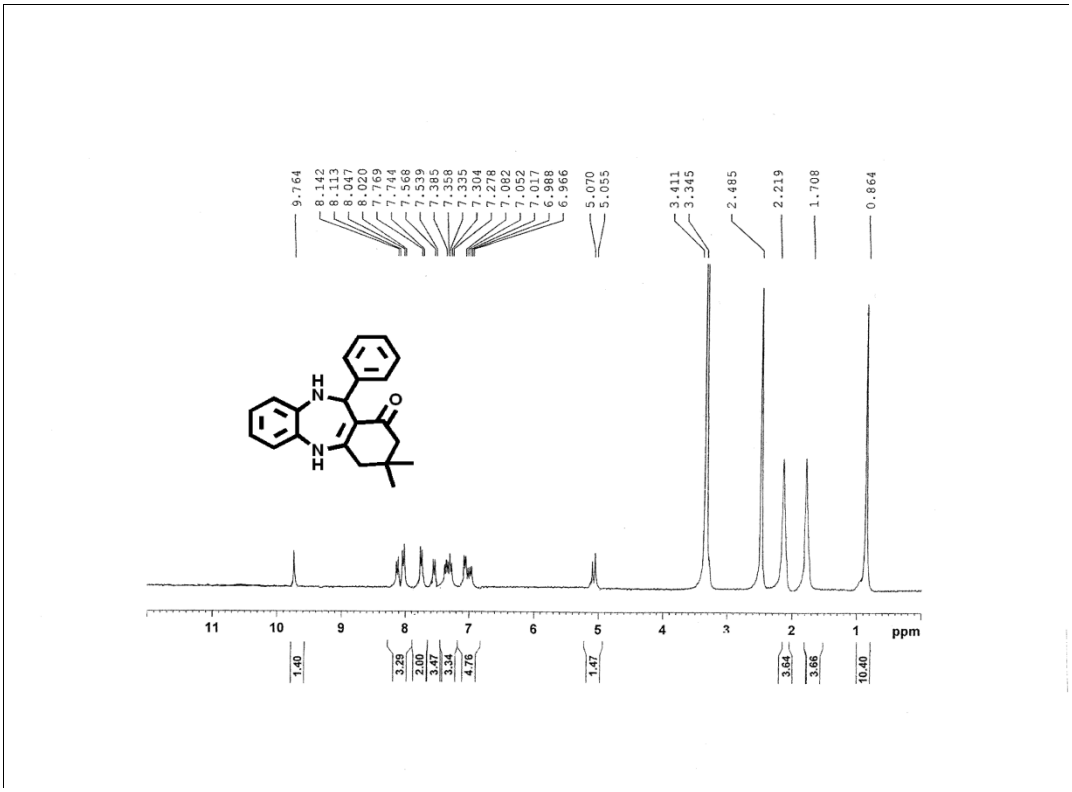
Mp: 270-272 °C

IR (KBr): 3369, 3134, 2918, 1715, 1691, 1512 cm^{-1};

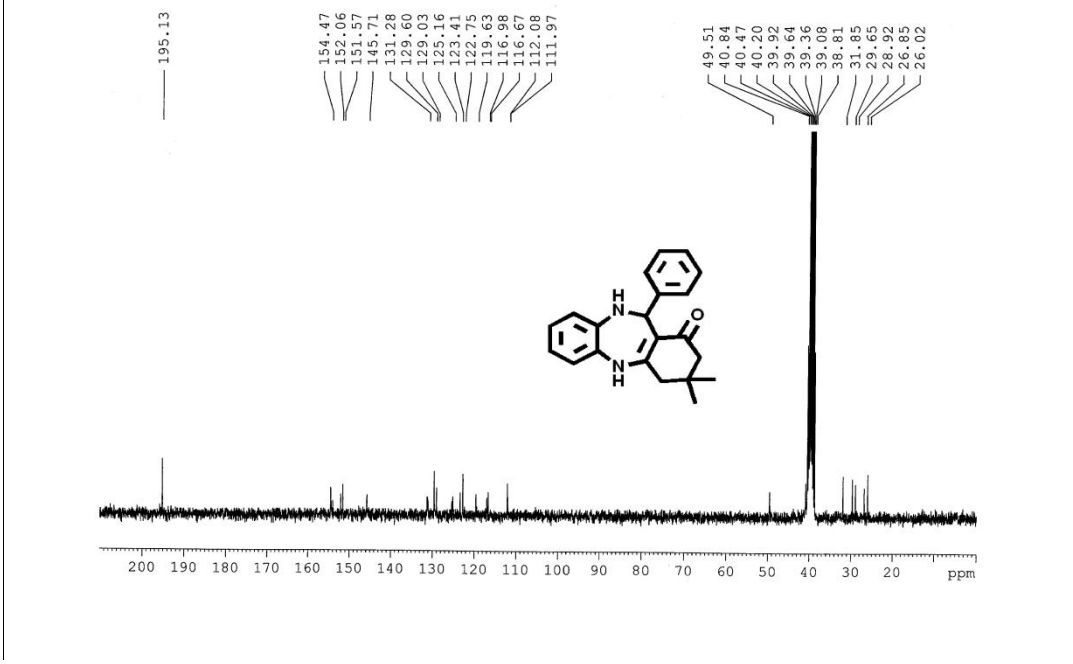
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.04 (3H, s), 1.21 (3H, s), 2.38 (2H, s), 2.49 (2H, s), 2.79 (3H, s), 4.41 (1H, d, *J*=6.3), 6.29 (1H, d, *J*=6.0), 7.09-7.54 (6H, m), 8.10 (2H, d, J=9.0), 9.12 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 27.4, 28.3, 31.7, 44.5, 49.3, 56.4, 58.4, 108.5, 120.2, 120.6, 122.2, 122.9, 127.9, 130.9, 137.2, 152.3, 155.1, 188.3, 192.3;

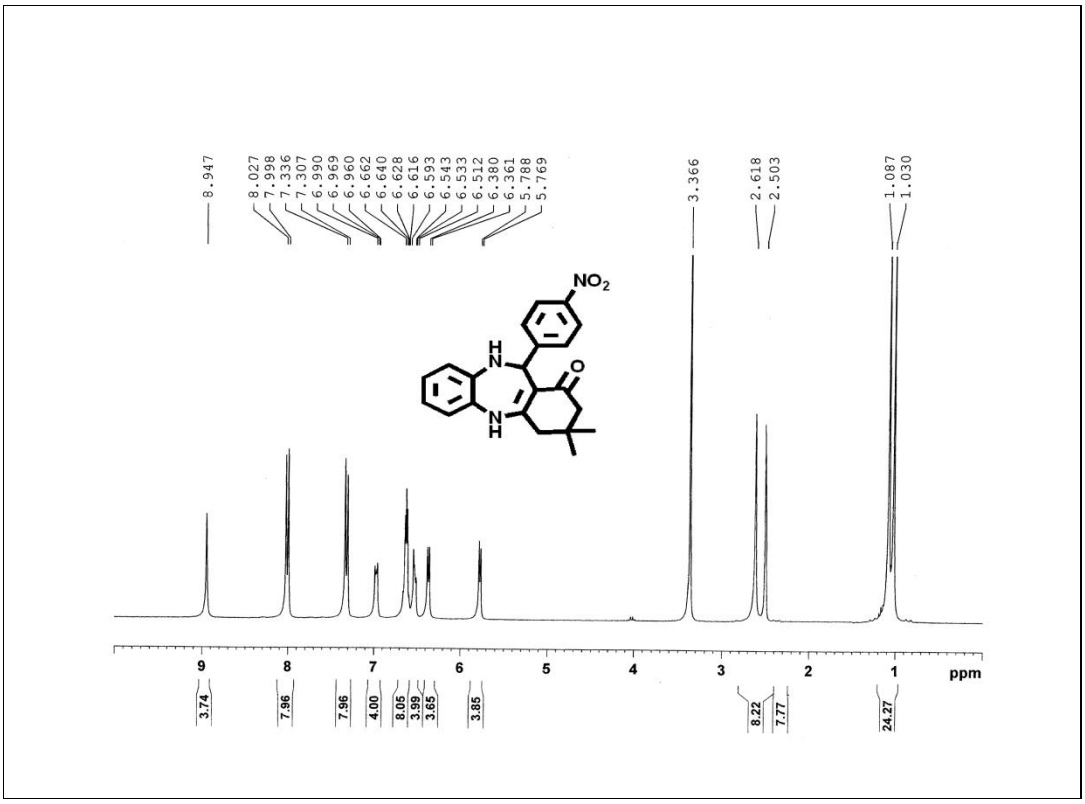
Anal.calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77 %. Found: C, 76.89; H, 6.69; N, 7.99 %.



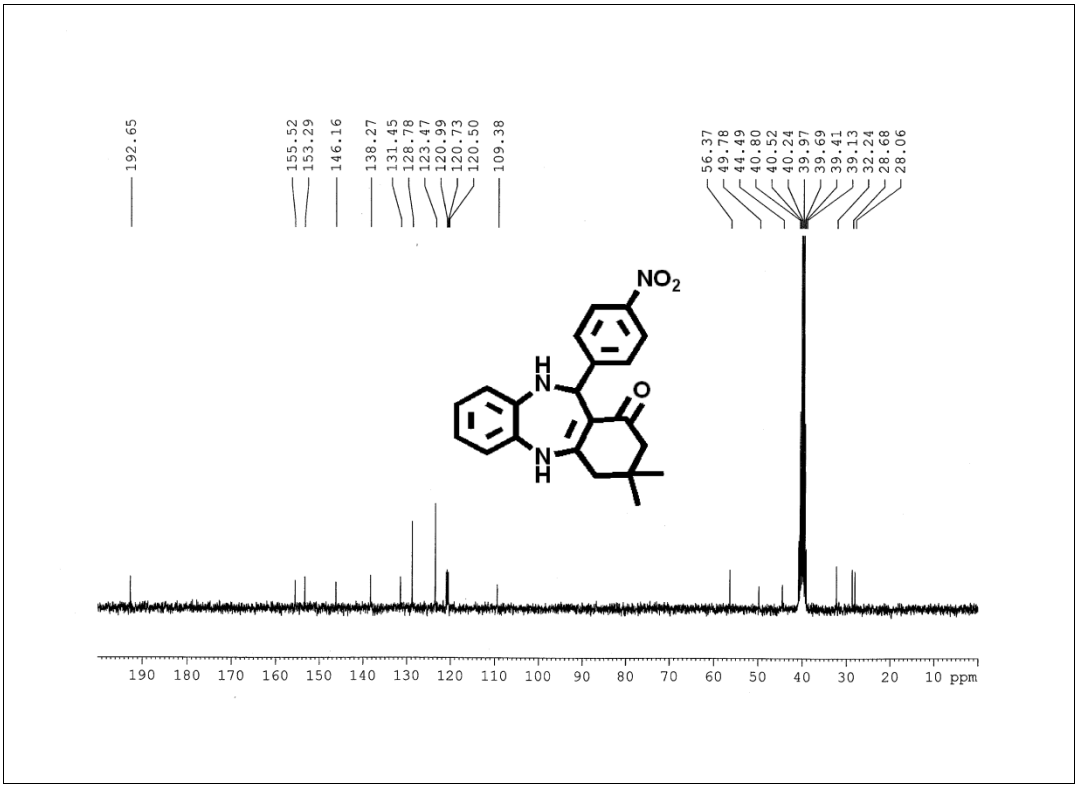
^{1}H NMR spectra of compound **4a**



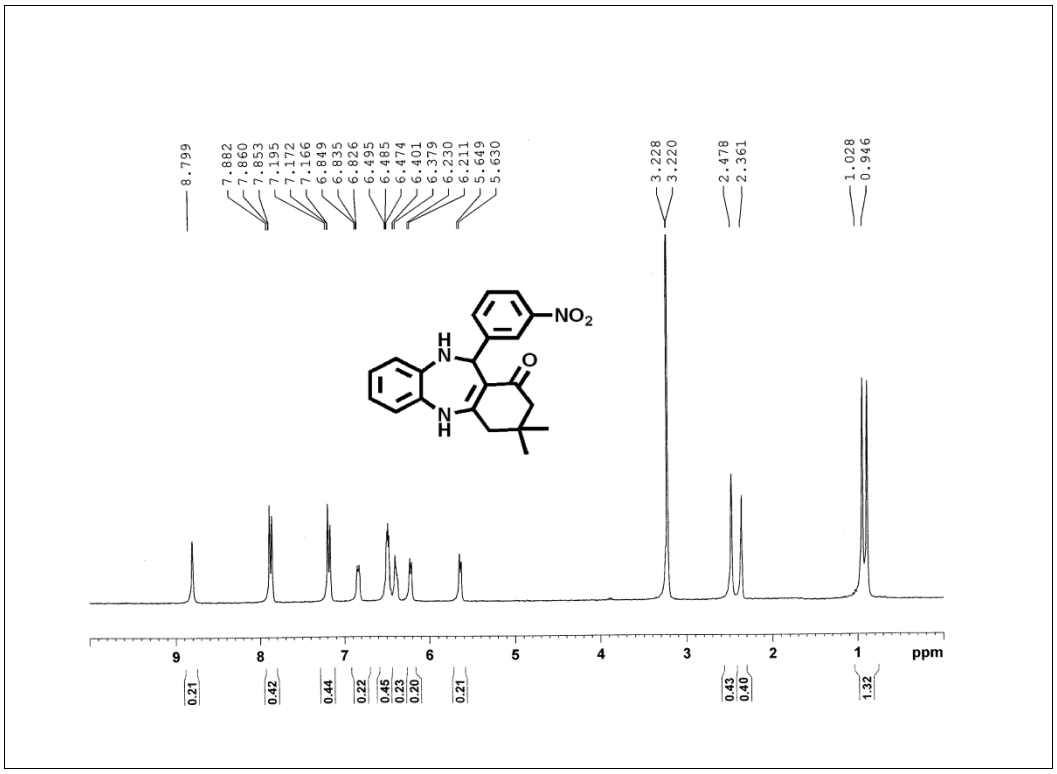
^{13}C NMR spectra of compound **4a**



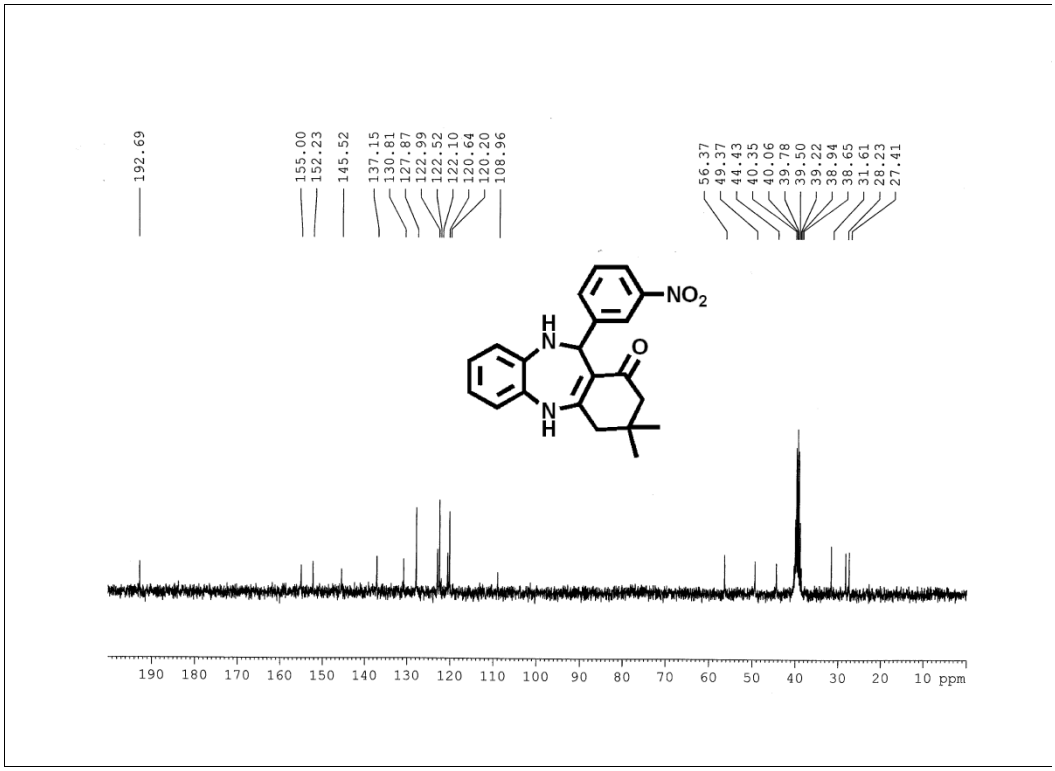
^{1}H NMR spectra of compound **4b**



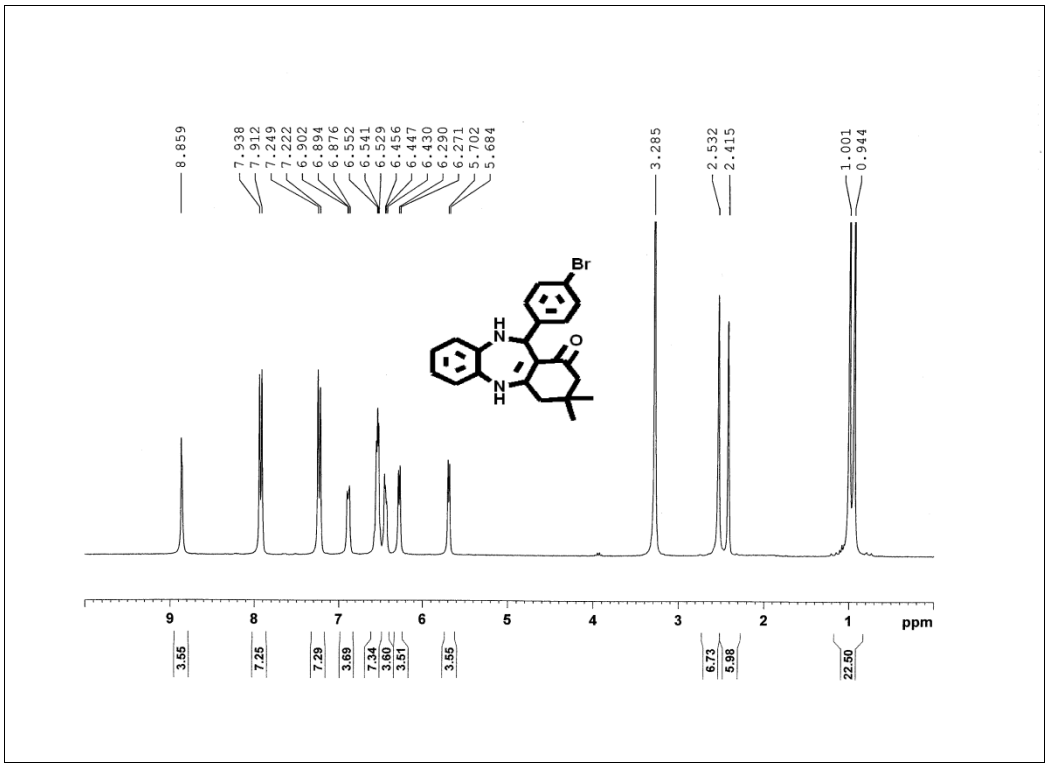
^{13}C NMR spectra of compound **4b**



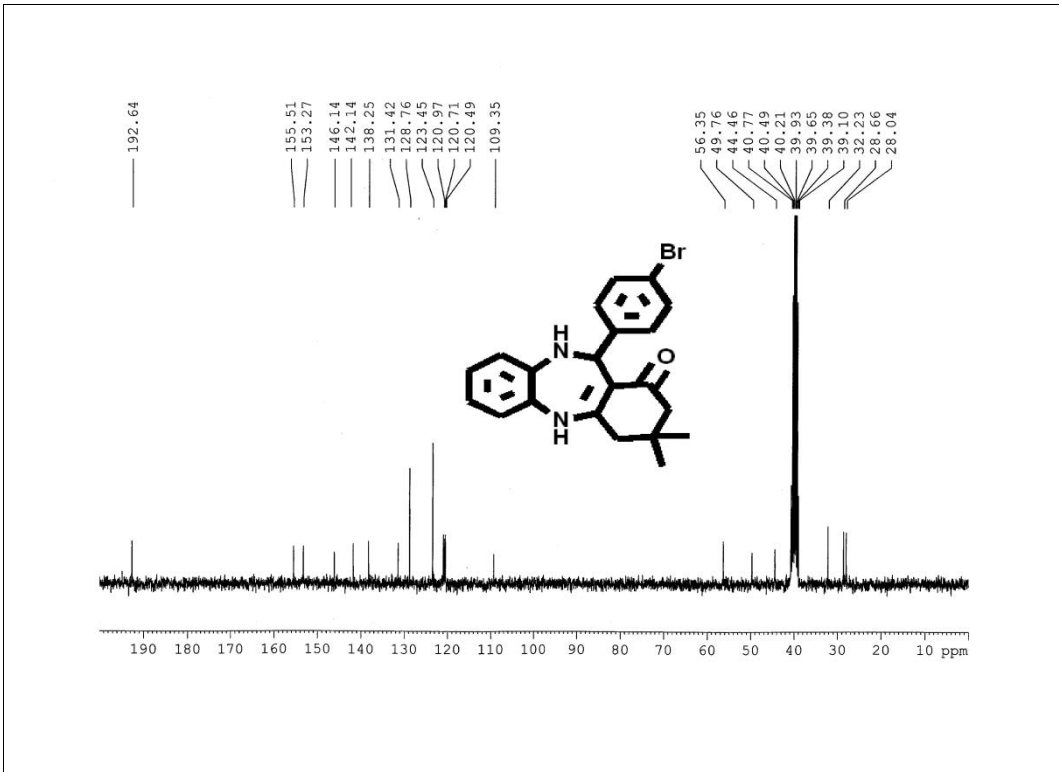
^{1}H NMR spectra of compound **4c**



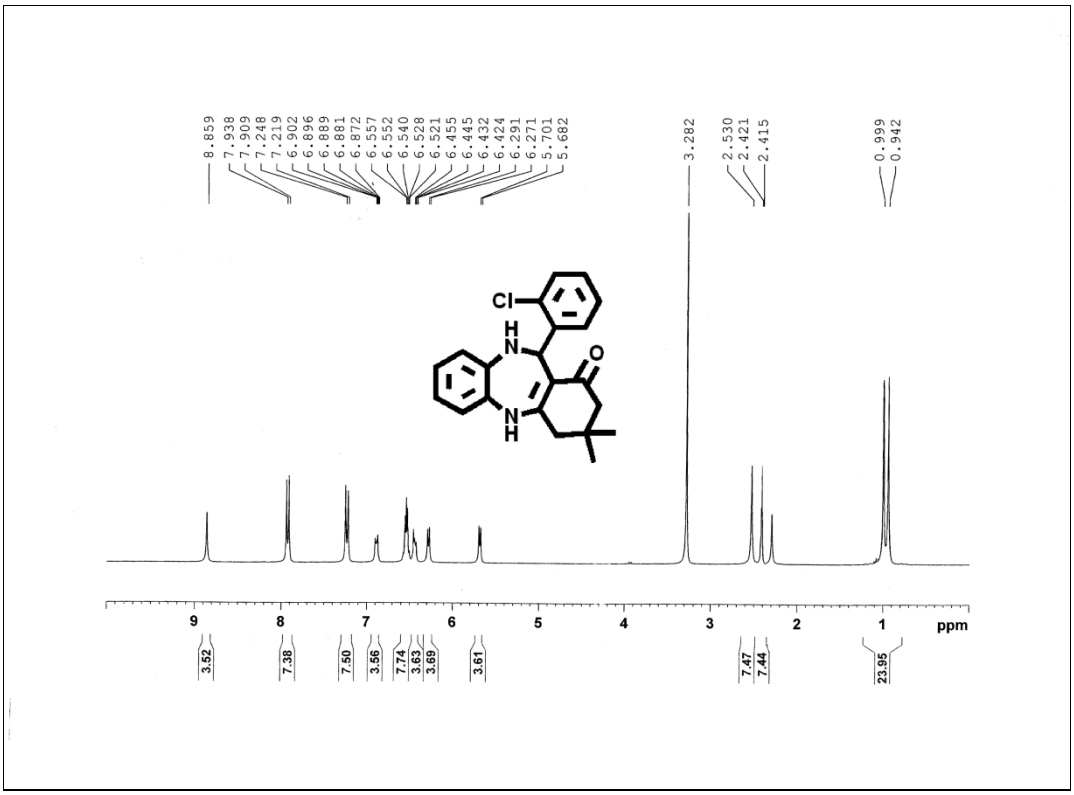
^{13}C NMR spectra of compound **4c**



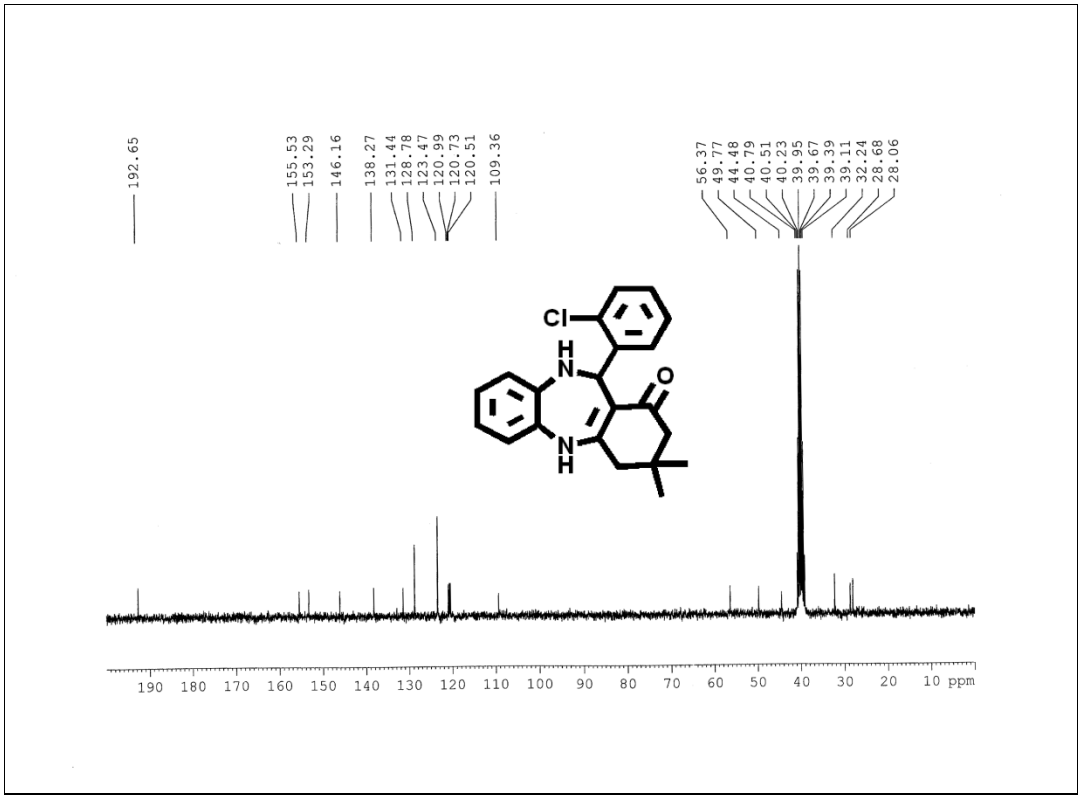
^{1}H NMR spectra of compound **4d**



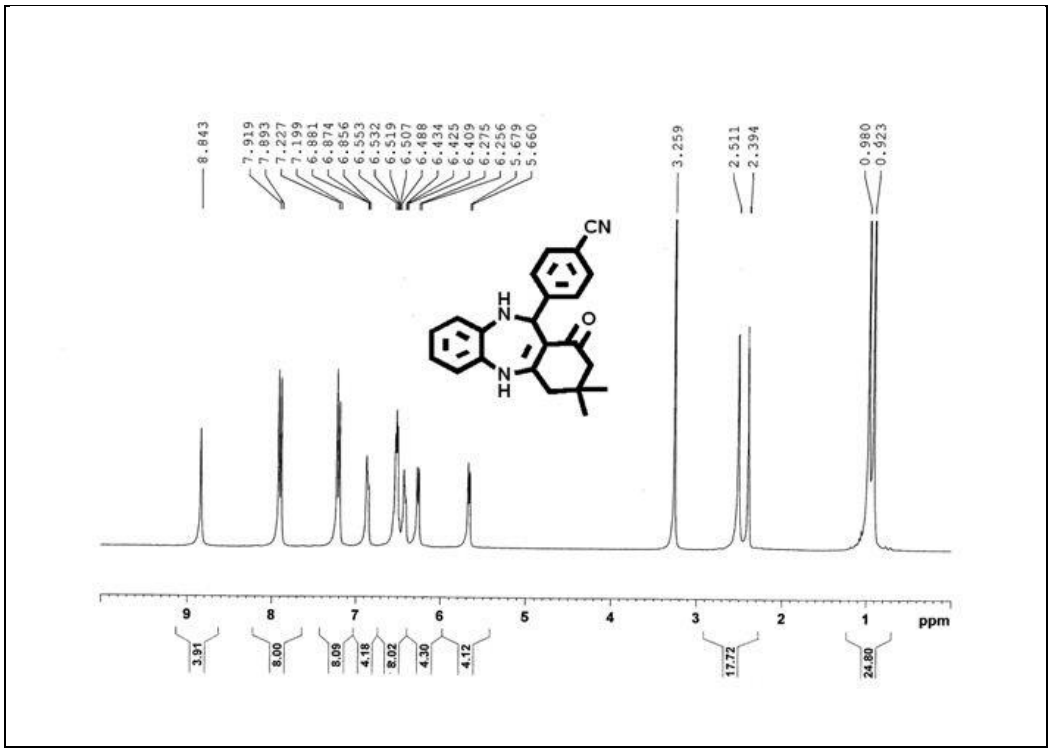
^{13}C NMR spectra of compound **4d**



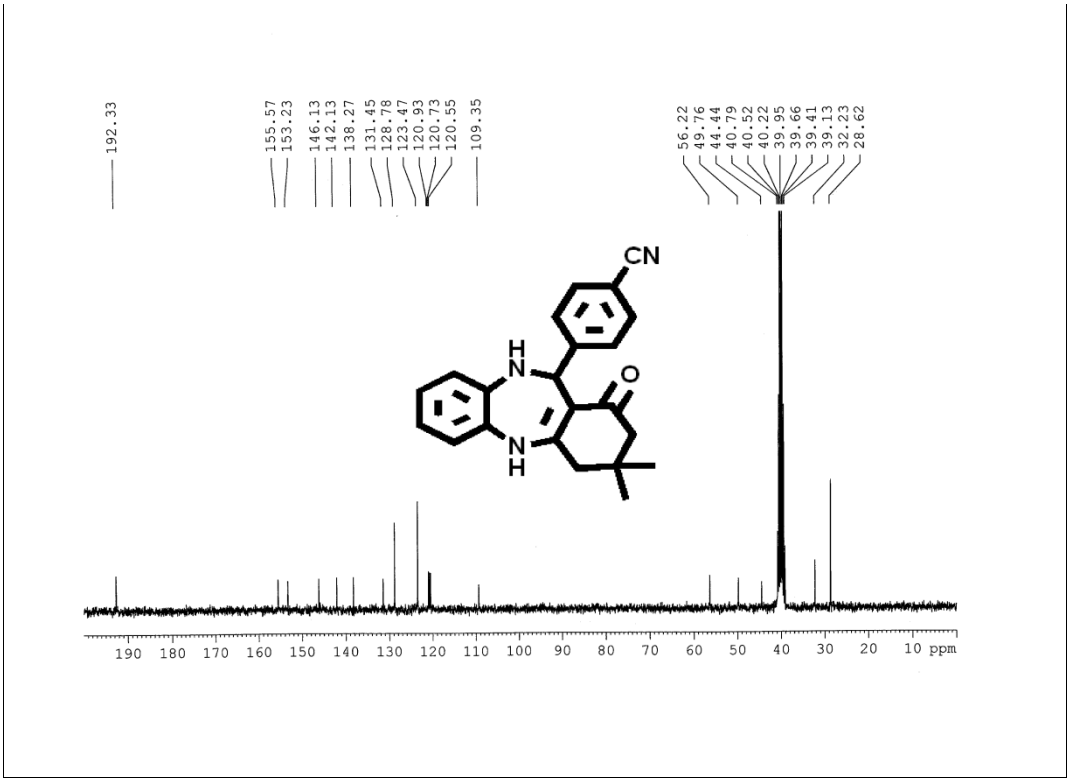
^{1}H NMR spectra of compound **4e**



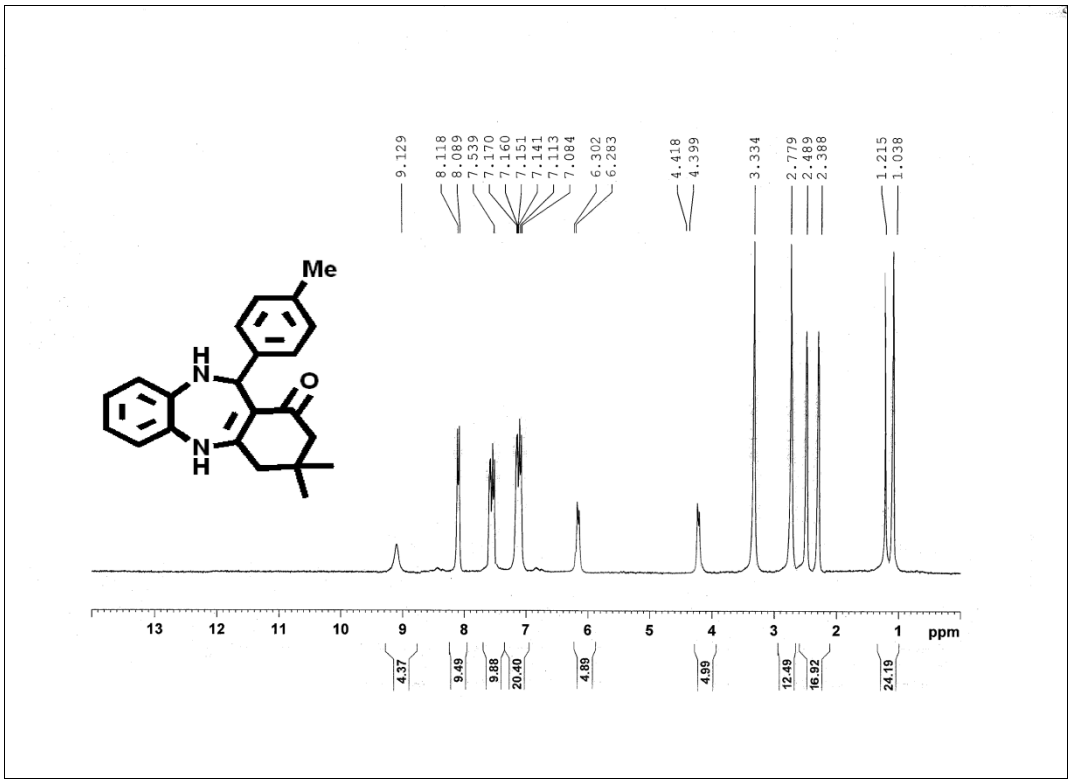
^{13}C NMR spectra of compound **4e**



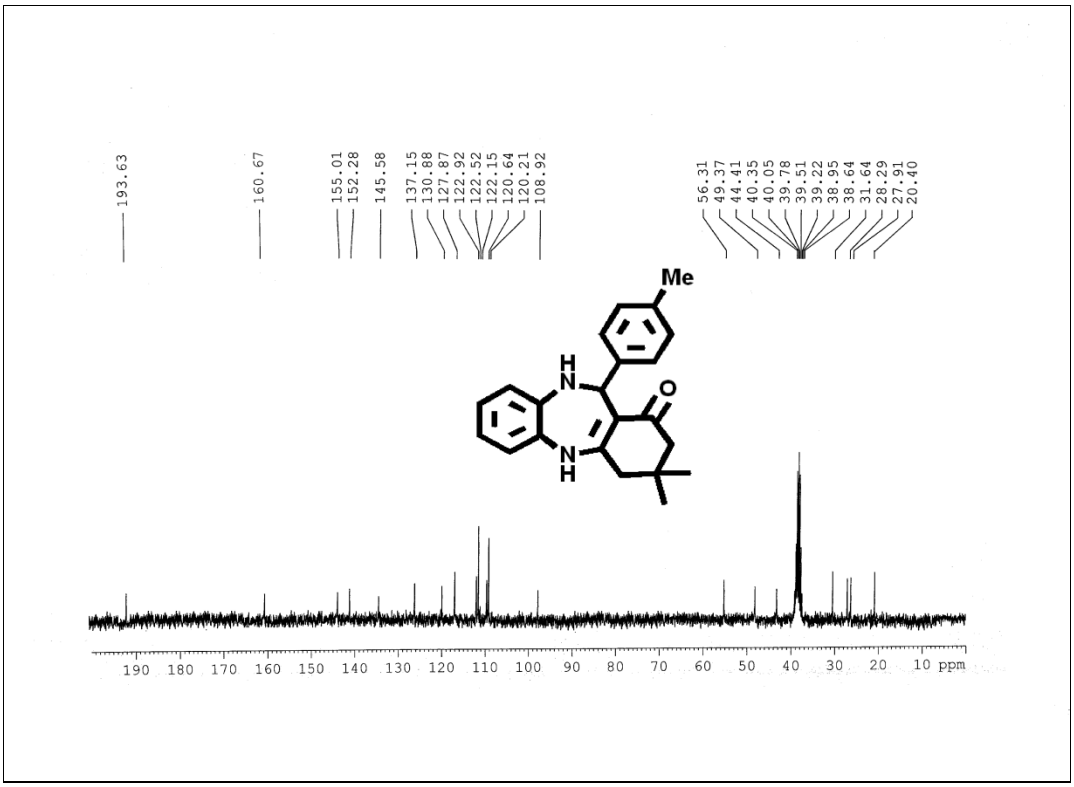
^{1}H NMR spectra of compound **4f**



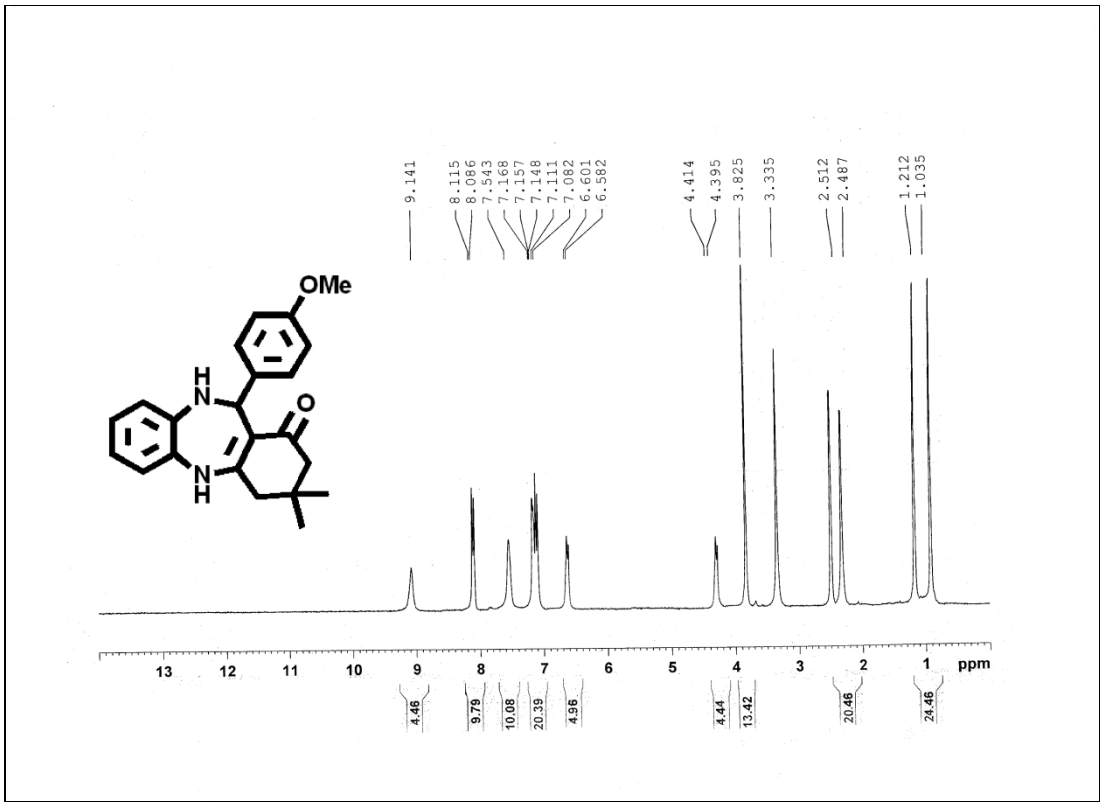
^{13}C NMR spectra of compound **4f**



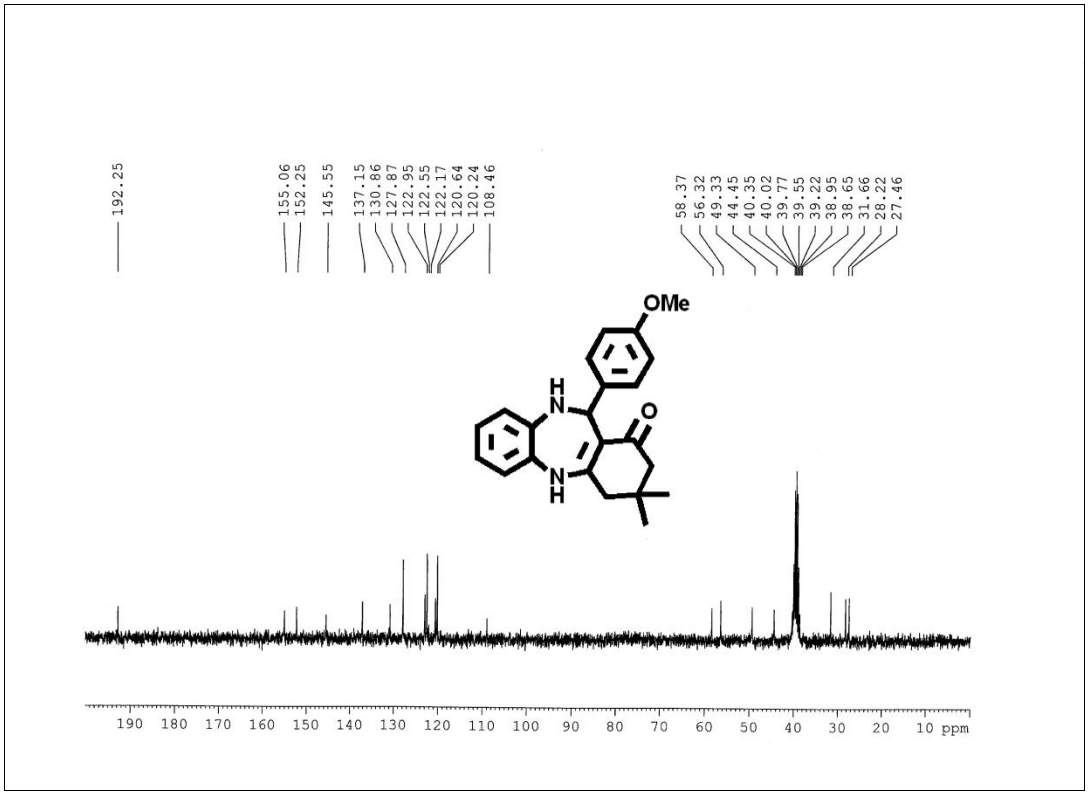
^{1}H NMR spectra of compound **4g**



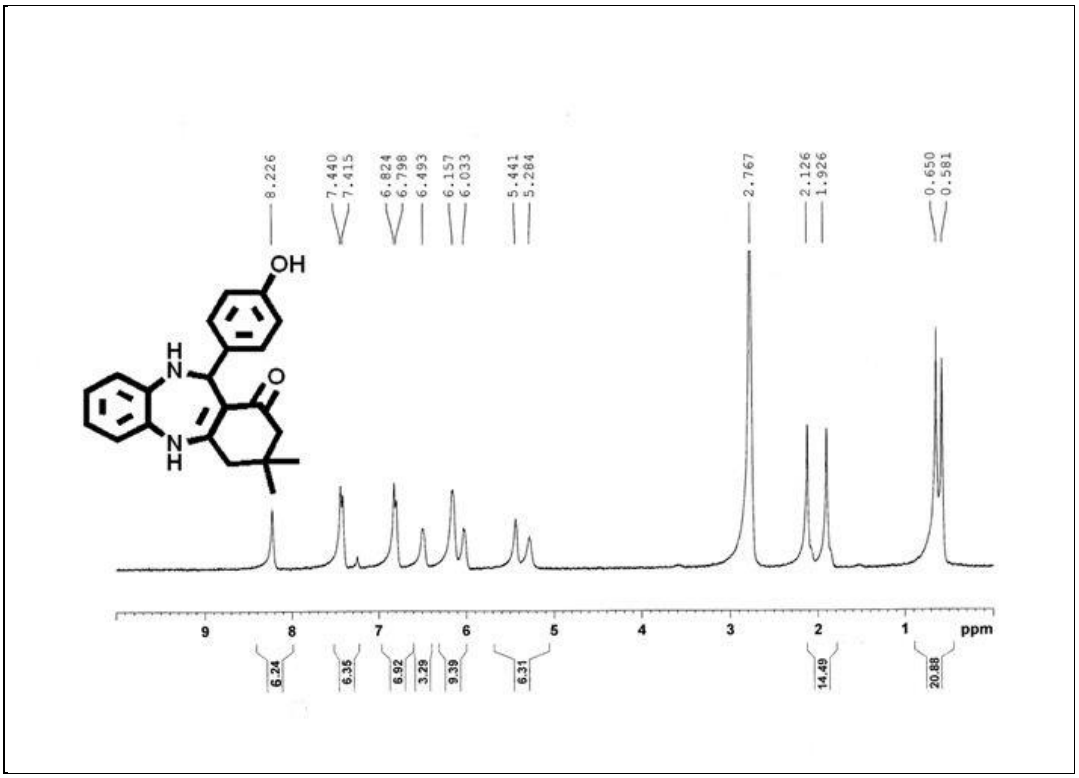
^{1}H NMR spectra of compound **4g**



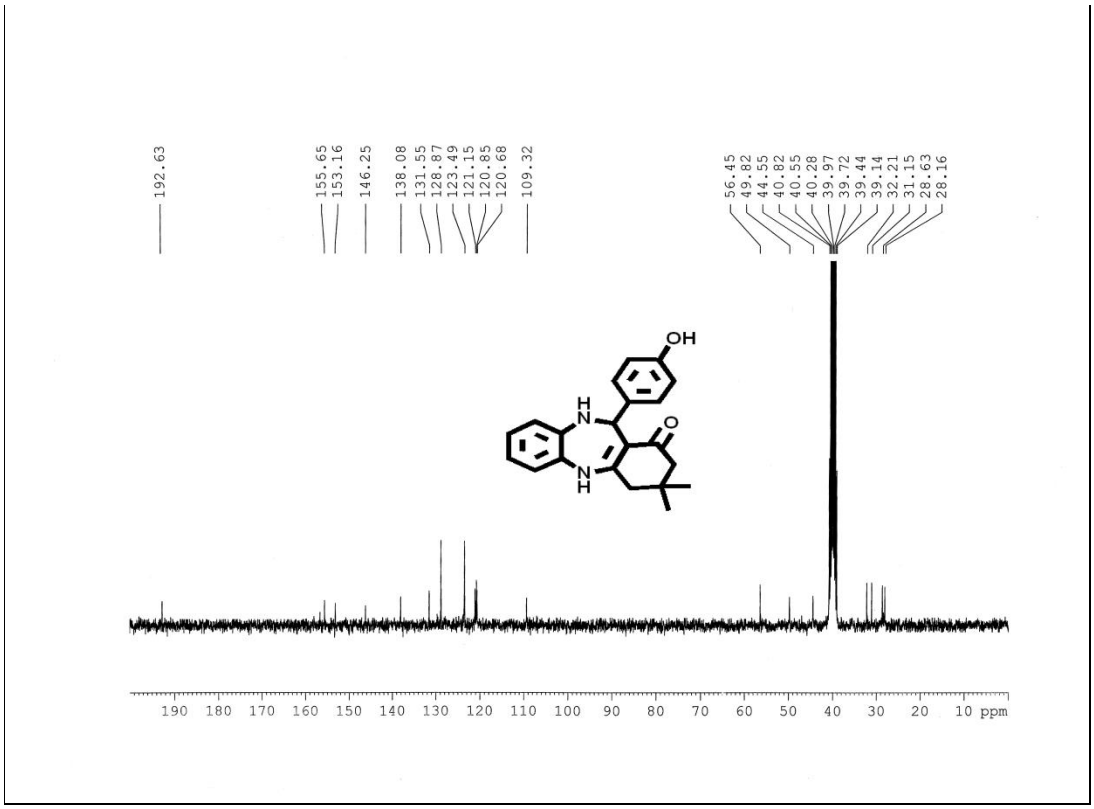
^{1}H NMR spectra of compound **4h**



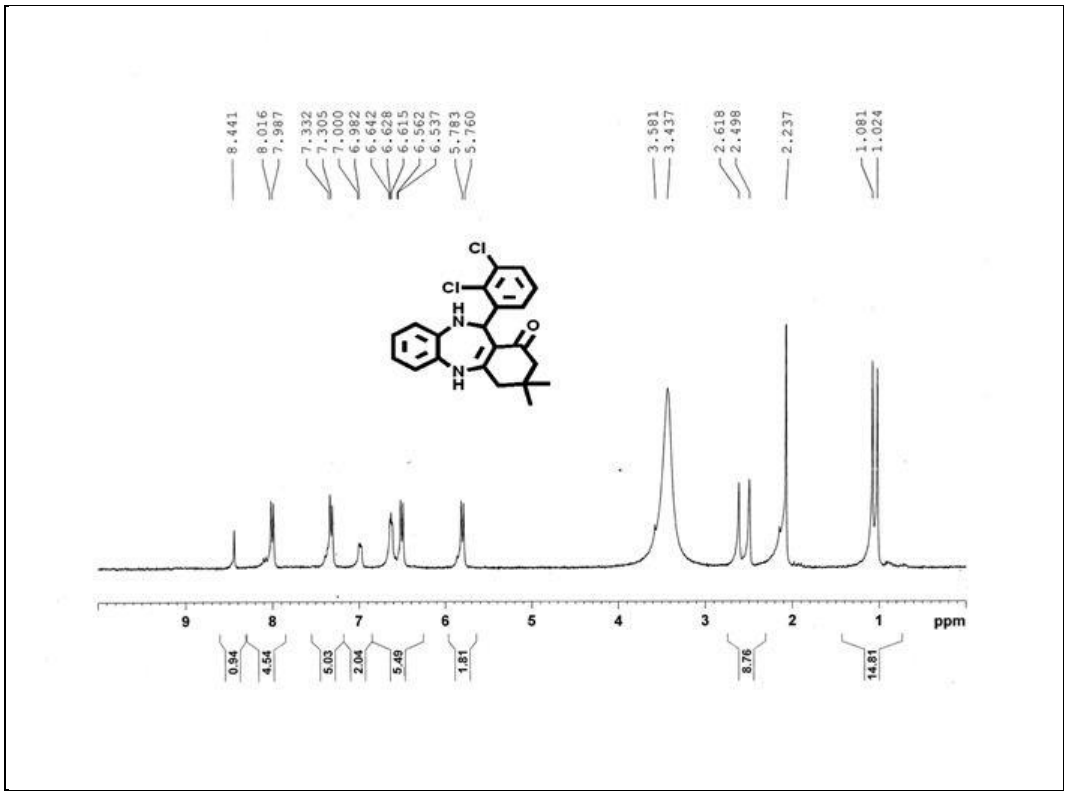
^{13}C NMR spectra of compound **4h**



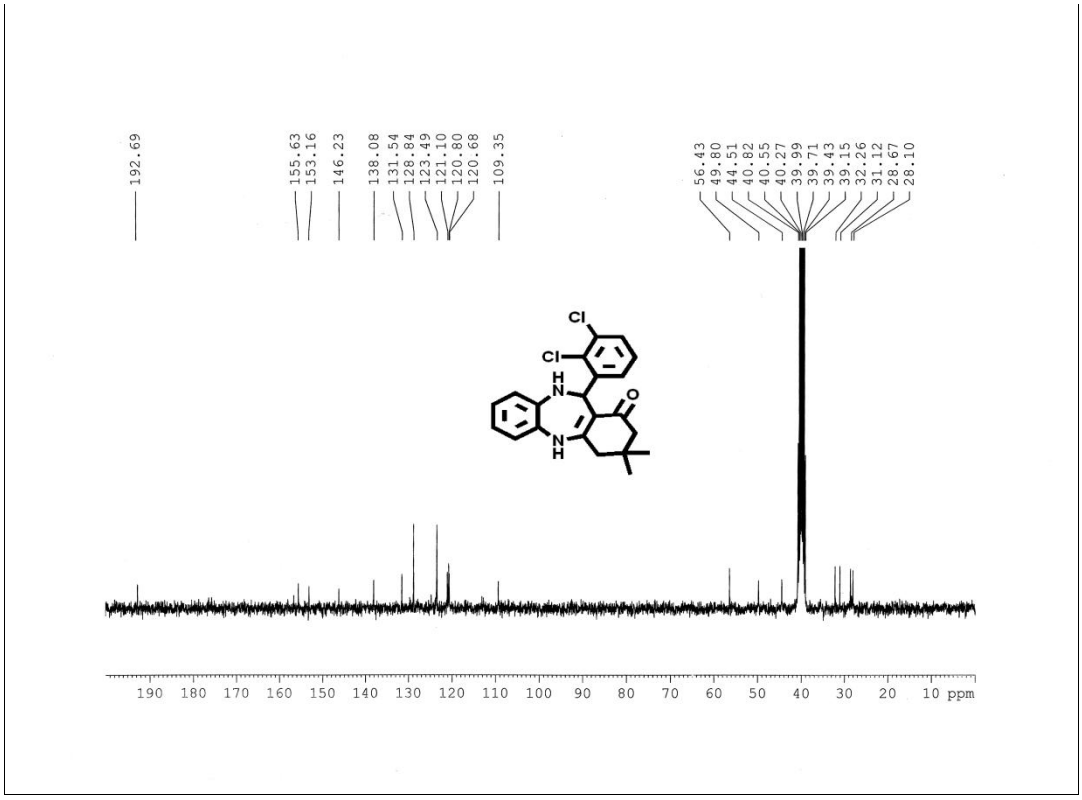
^{1}H NMR spectra of compound **4i**



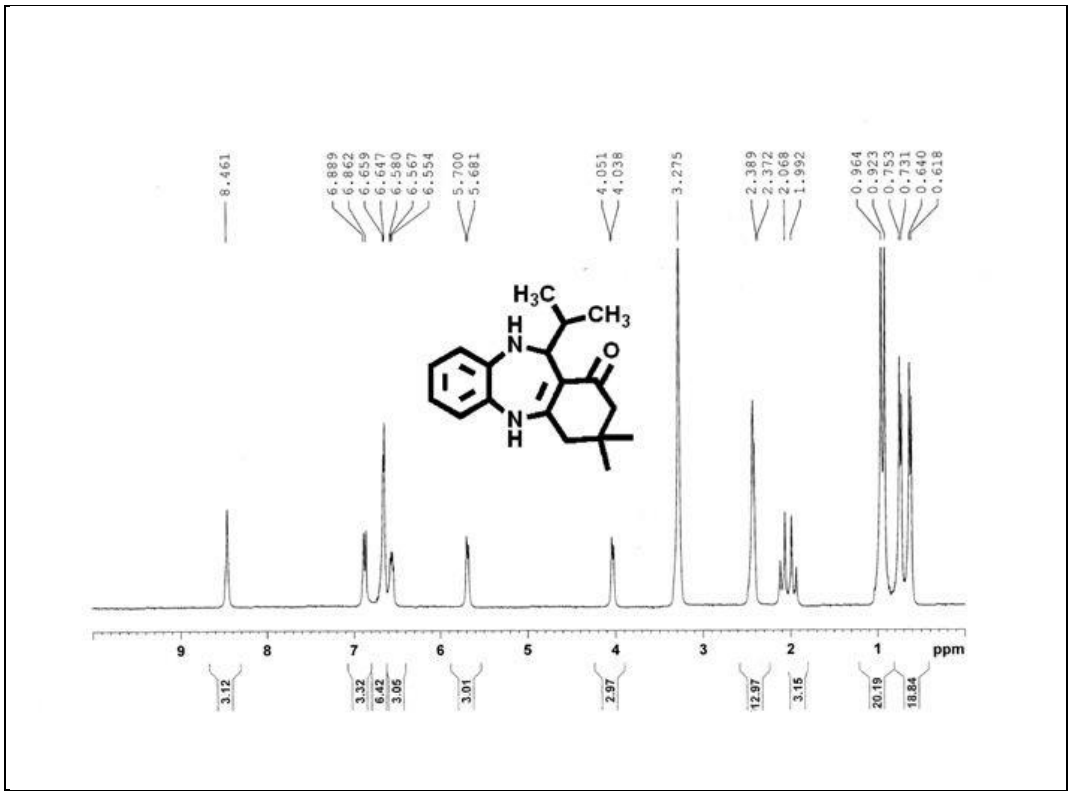
^{1}H NMR spectra of compound **4i**



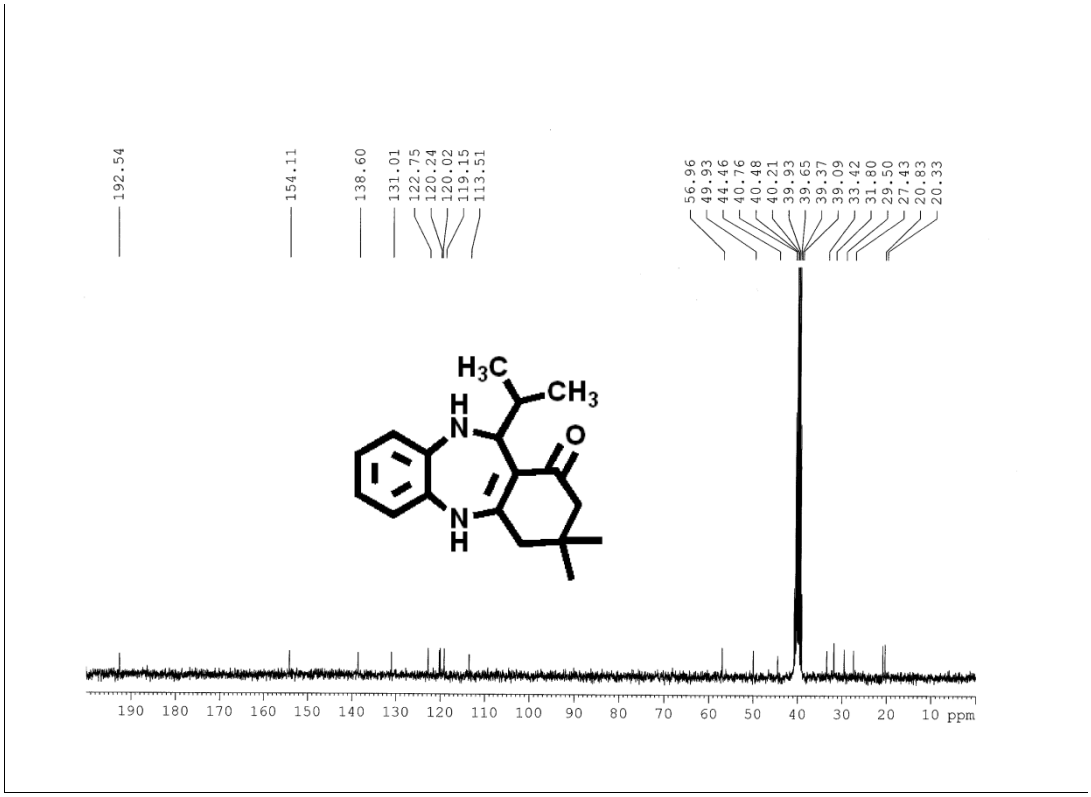
^{1}H NMR spectra of compound **4j**



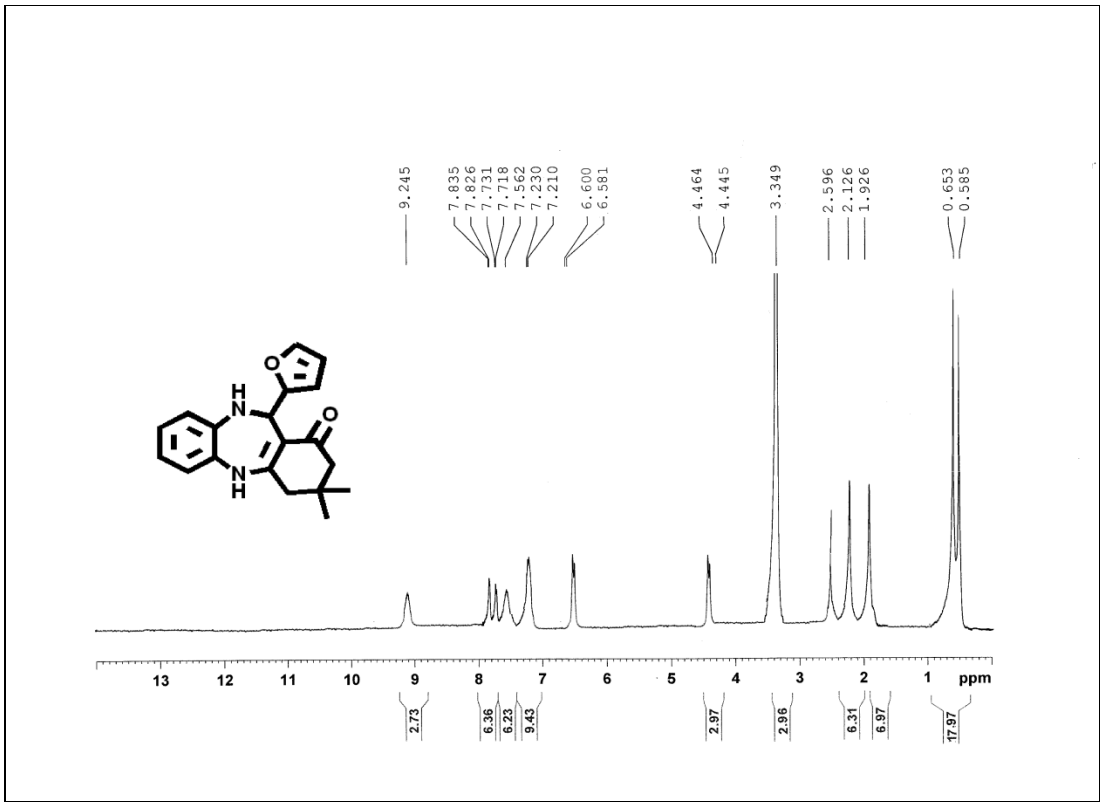
^{13}C NMR spectra of compound **4j**



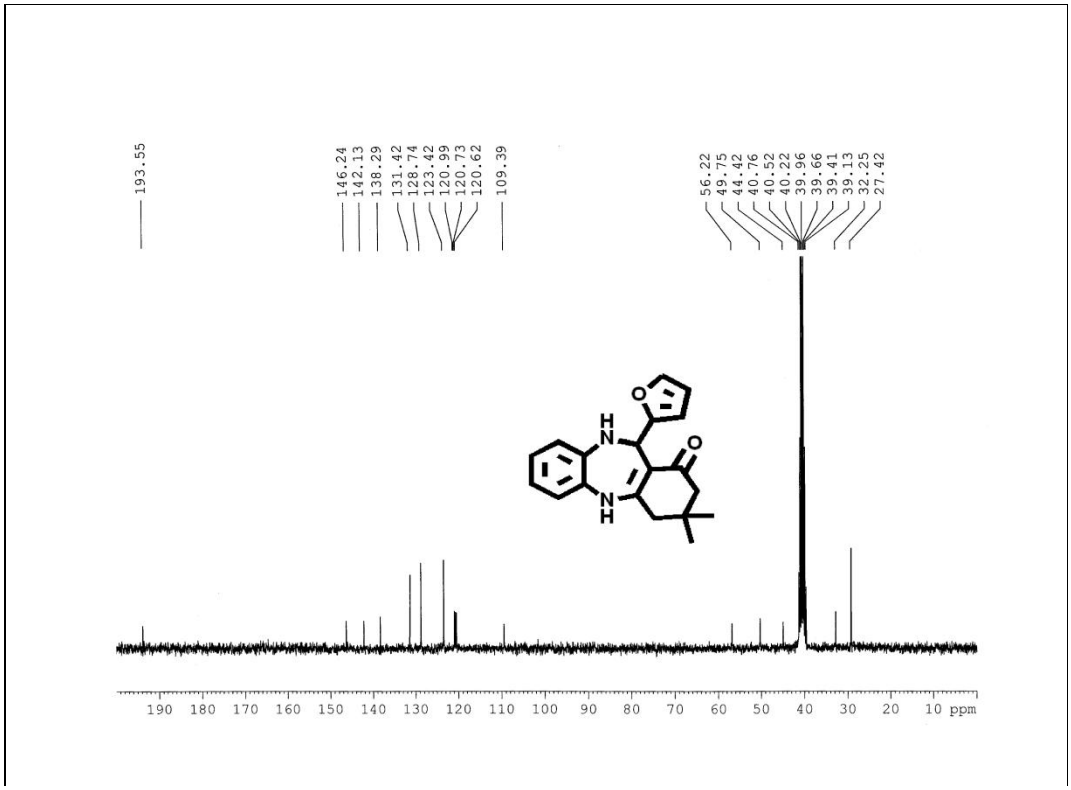
^{1}H NMR spectra of compound **4k**



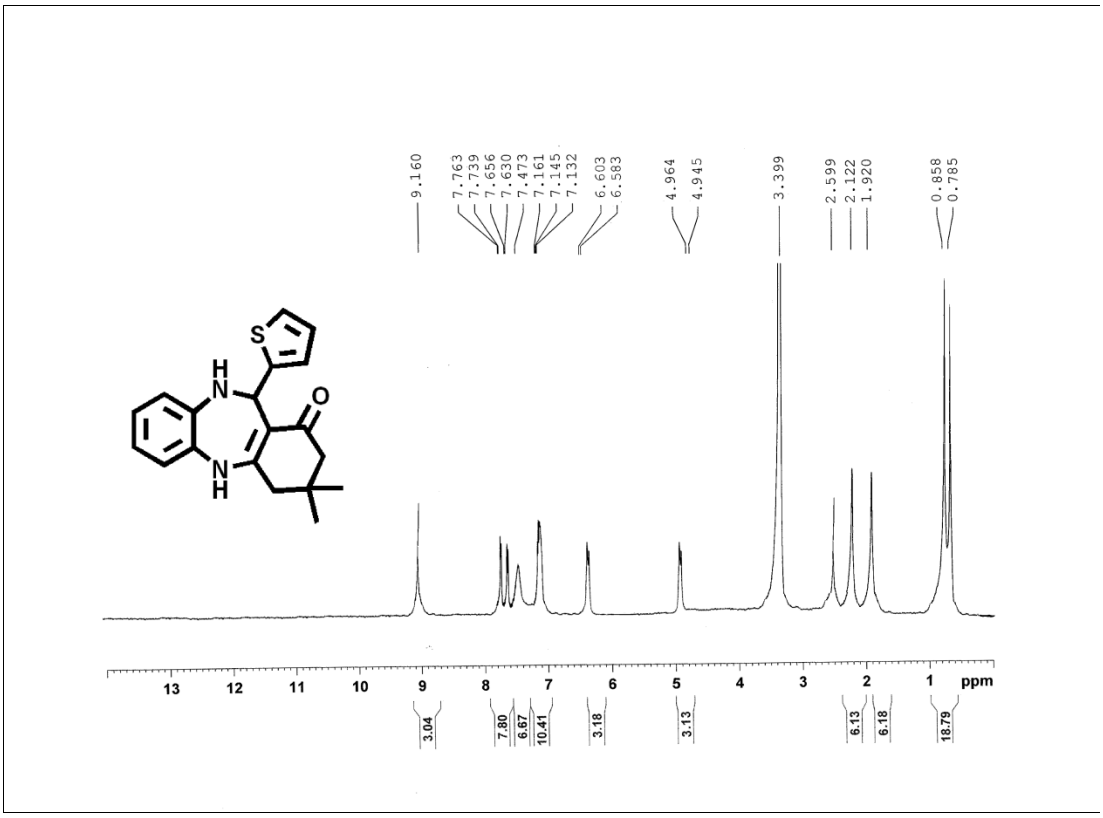
^{13}C NMR spectra of compound **4k**



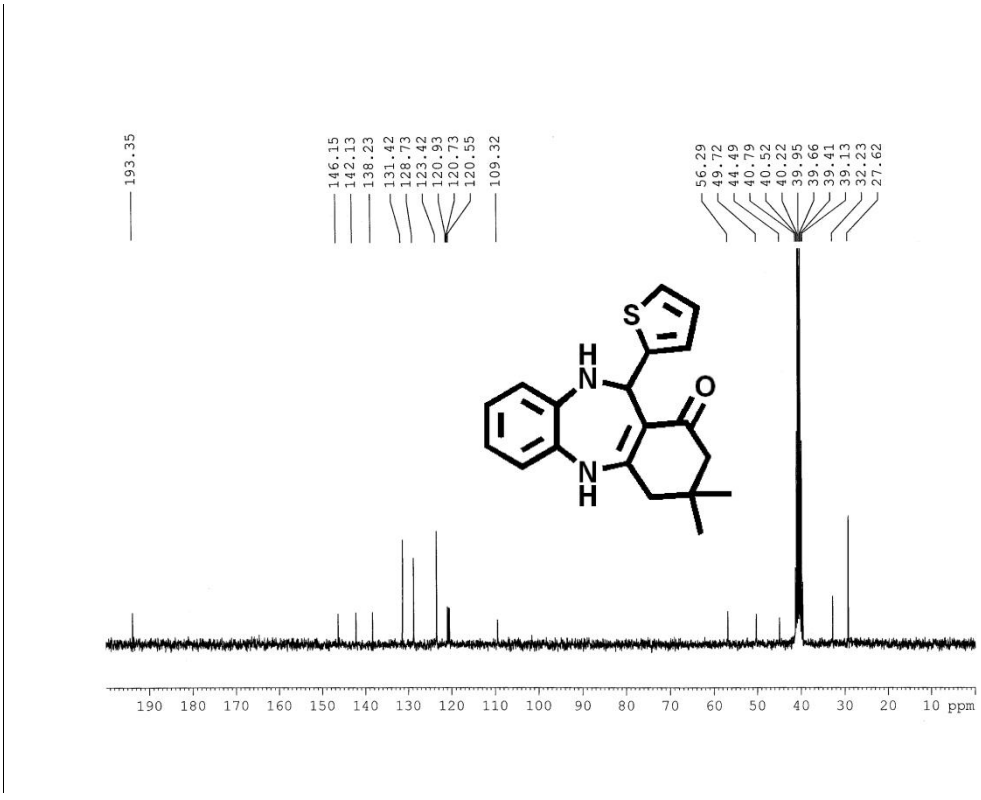
^{1}H NMR spectra of compound **4l**



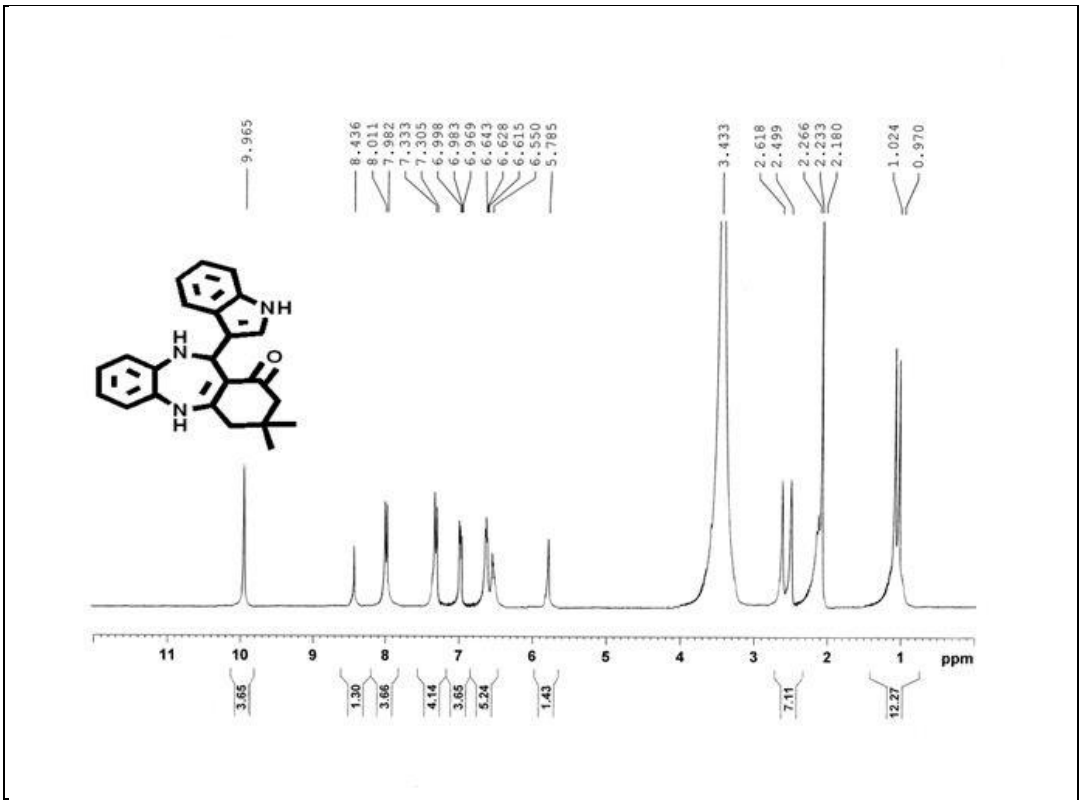
^{13}C NMR spectra of compound **4l**



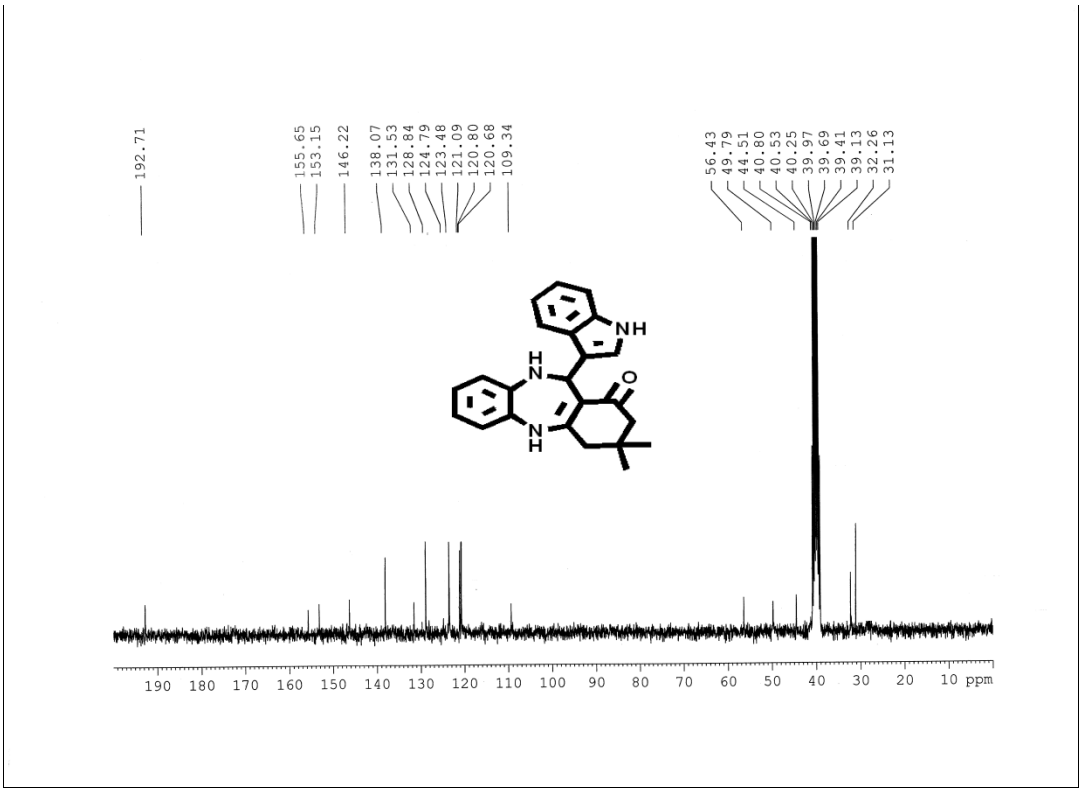
^{1}H NMR spectra of compound **4m**



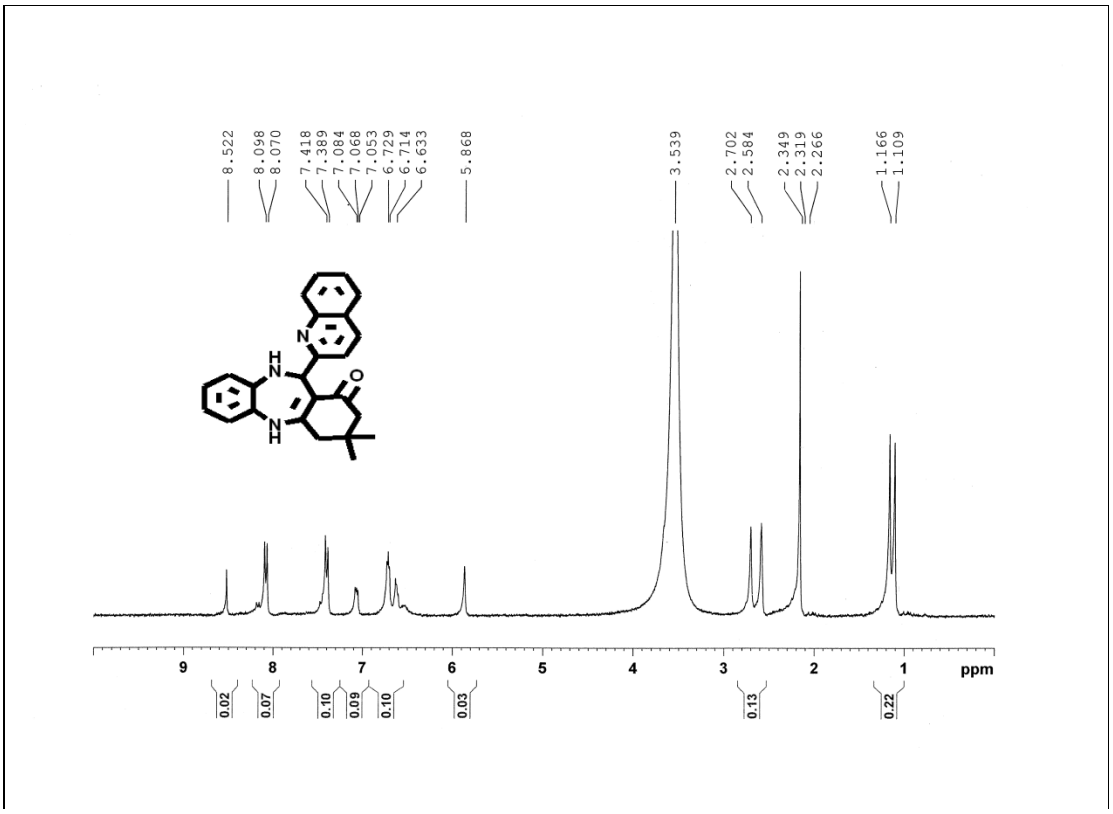
^{13}C NMR spectra of compound **4m**



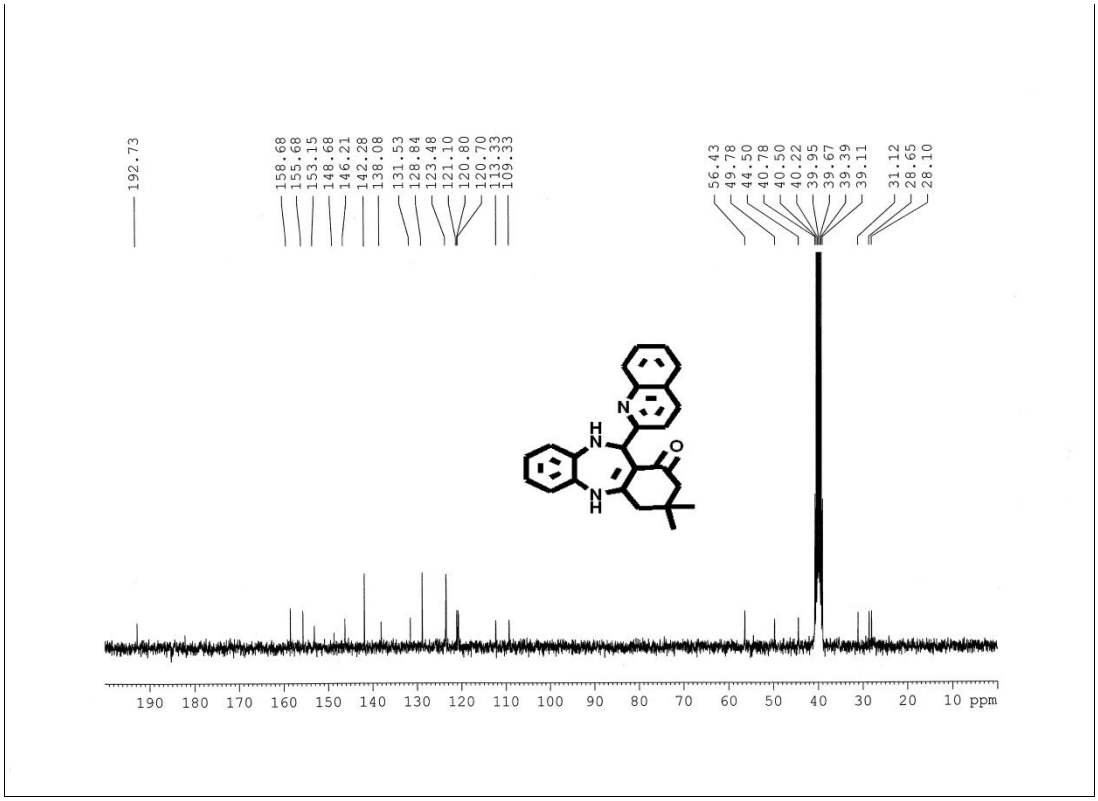
^{1}H NMR spectra of compound **4n**



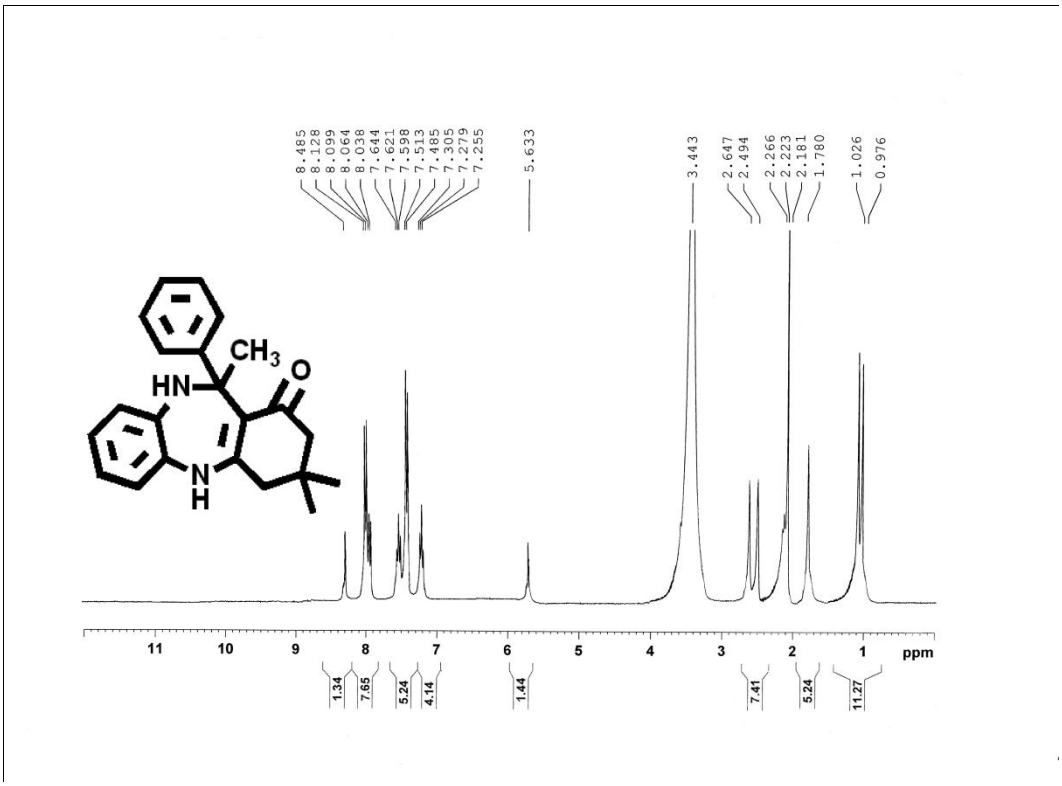
^{13}C NMR spectra of compound **4n**



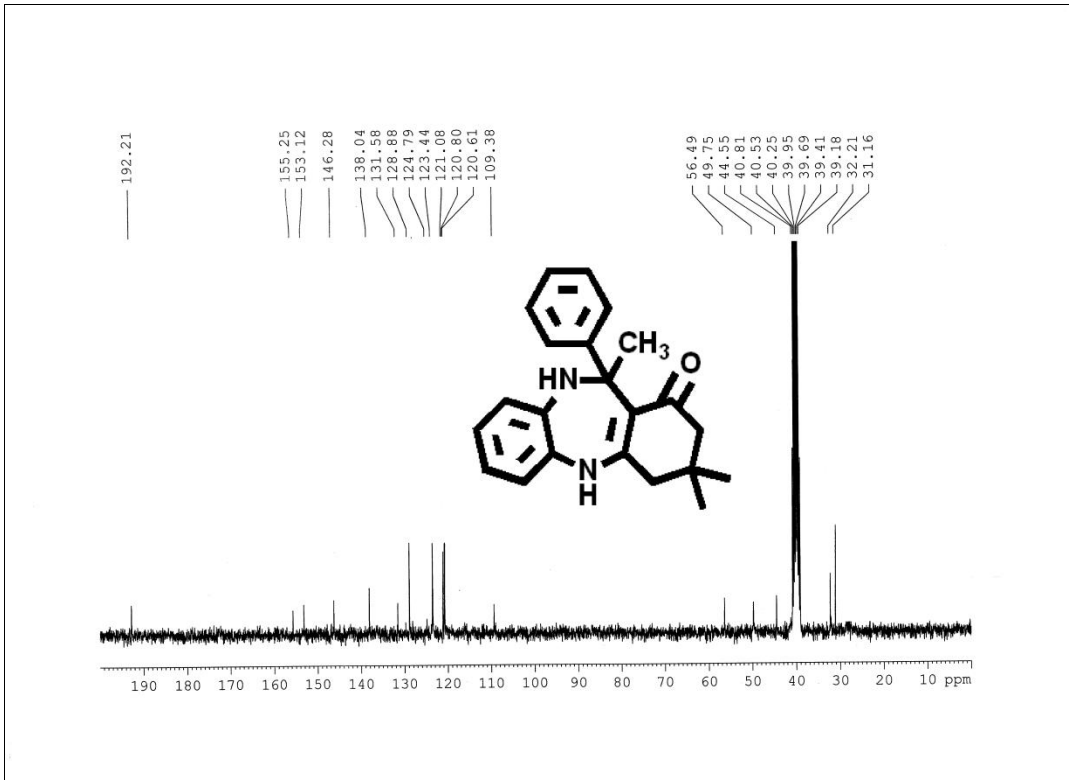
^{1}H NMR spectra of compound **4o**



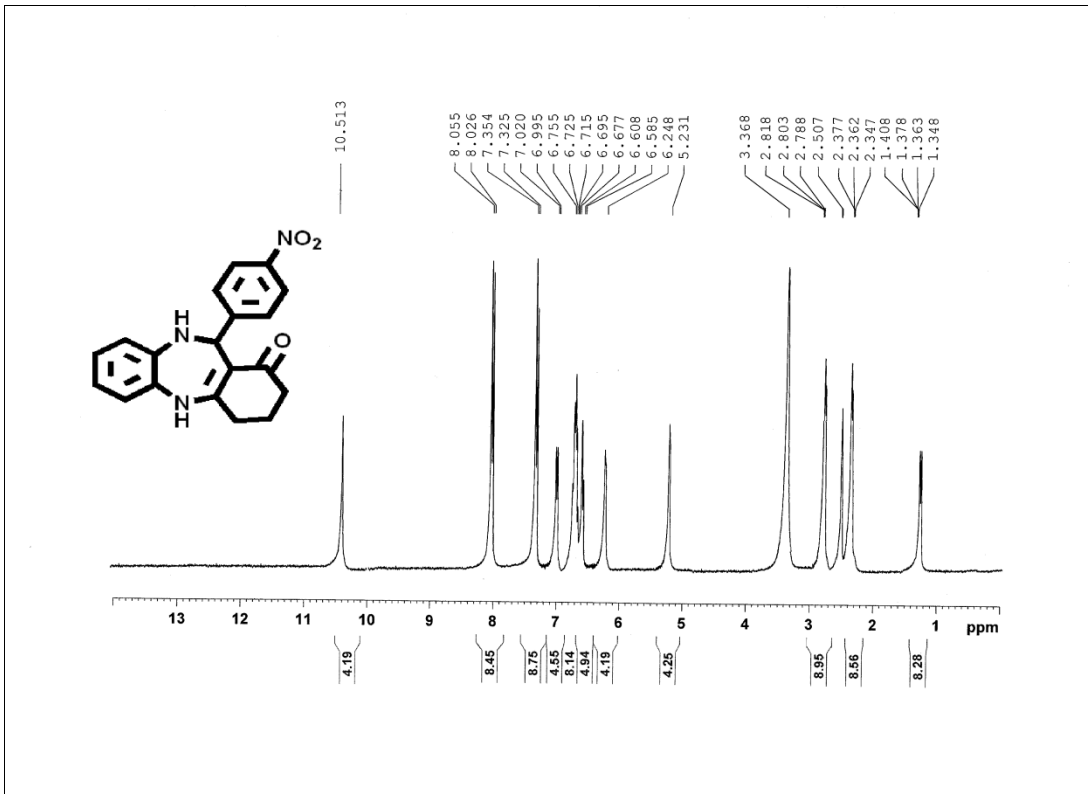
^{13}C NMR spectra of compound **4o**



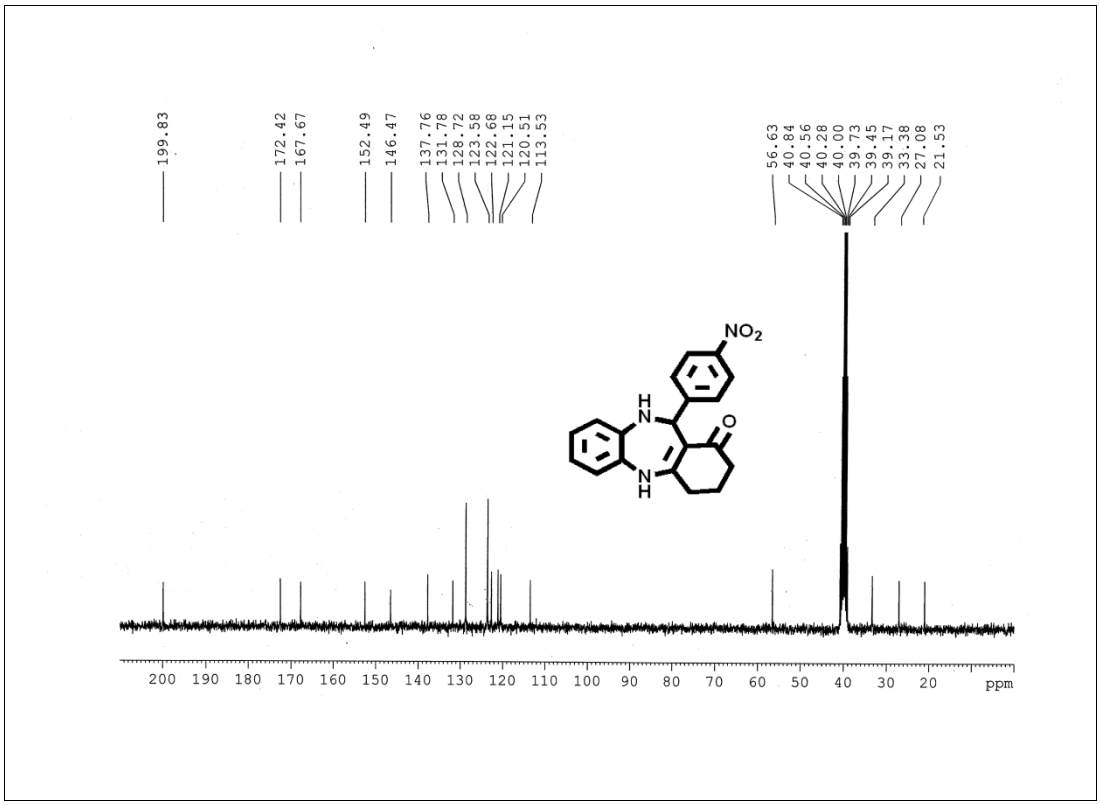
^{1}H NMR spectra of compound **4p**



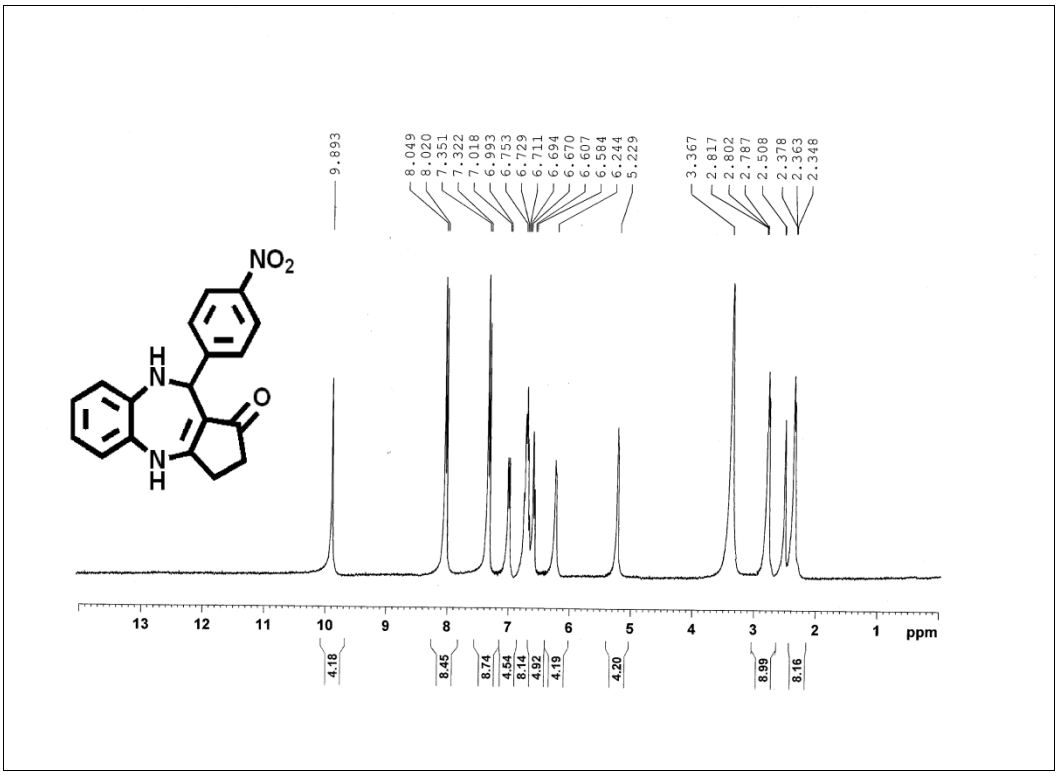
^{13}C NMR spectra of compound **4p**



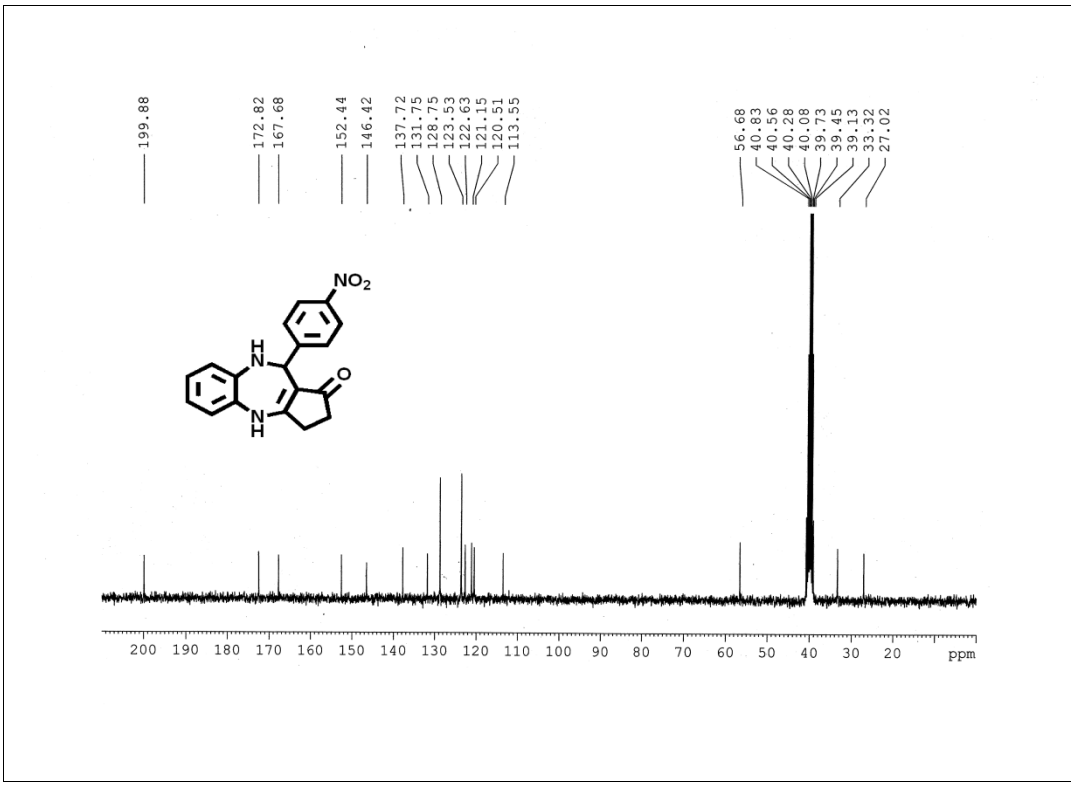
^{1}H NMR spectra of compound **4q**



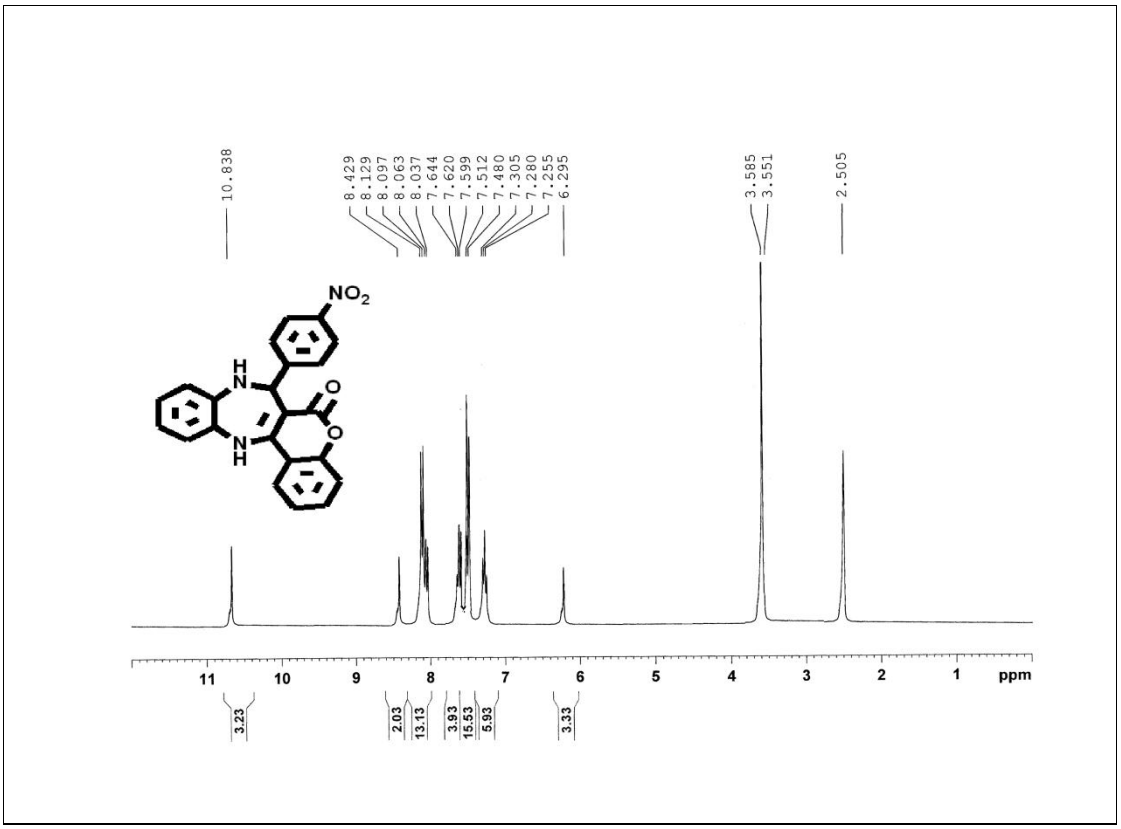
^{13}C NMR spectra of compound **4q**



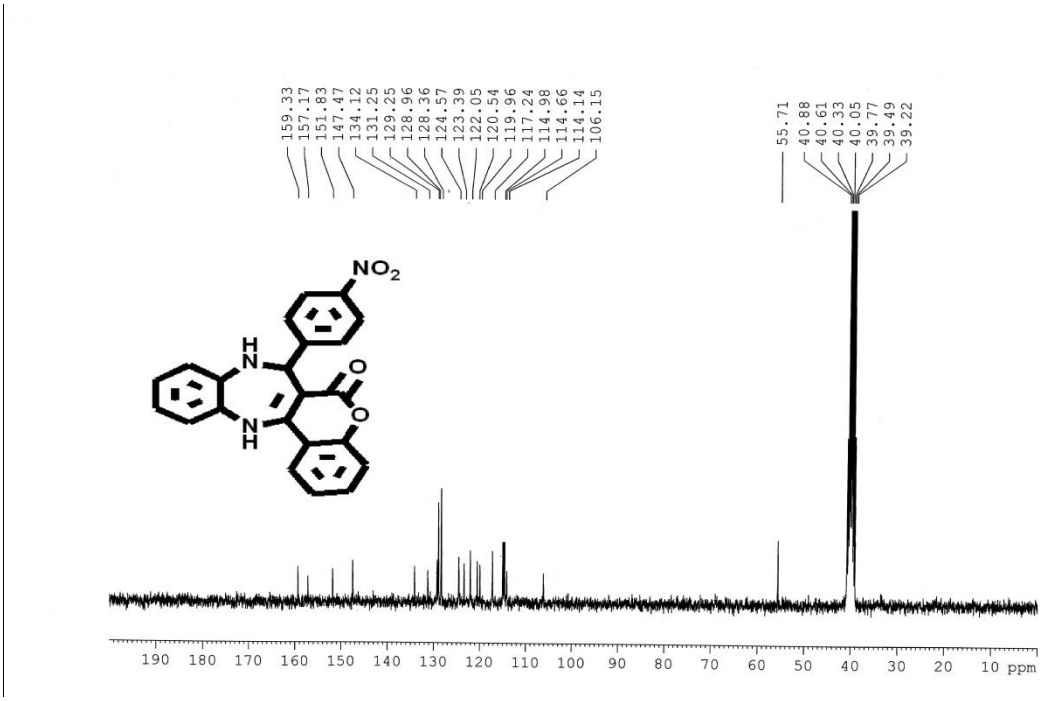
^{1}H NMR spectra of compound **4r**



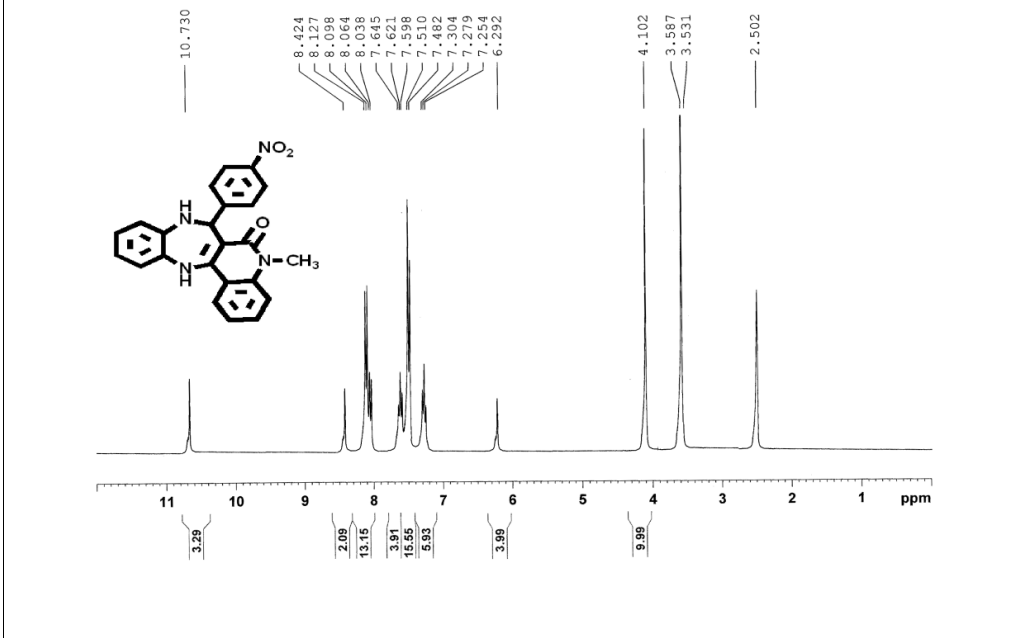
^{13}C NMR spectra of compound **4r**



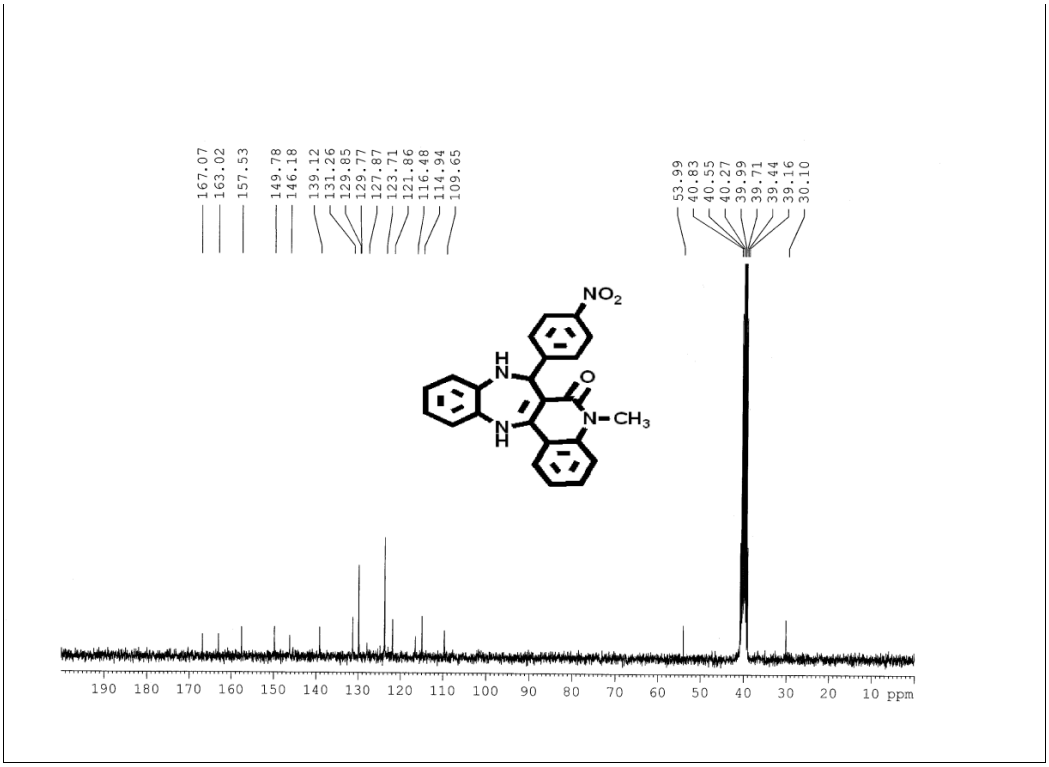
^{1}H NMR spectra of compound **4s**



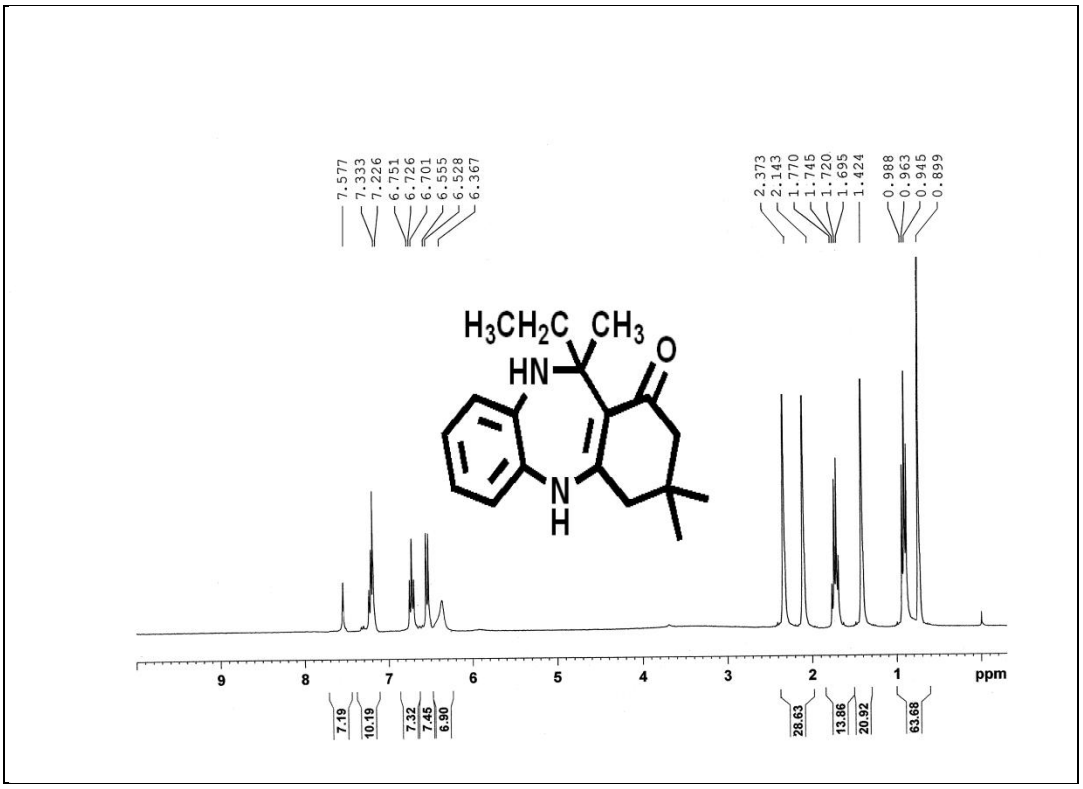
^{13}C NMR spectra of compound **4s**



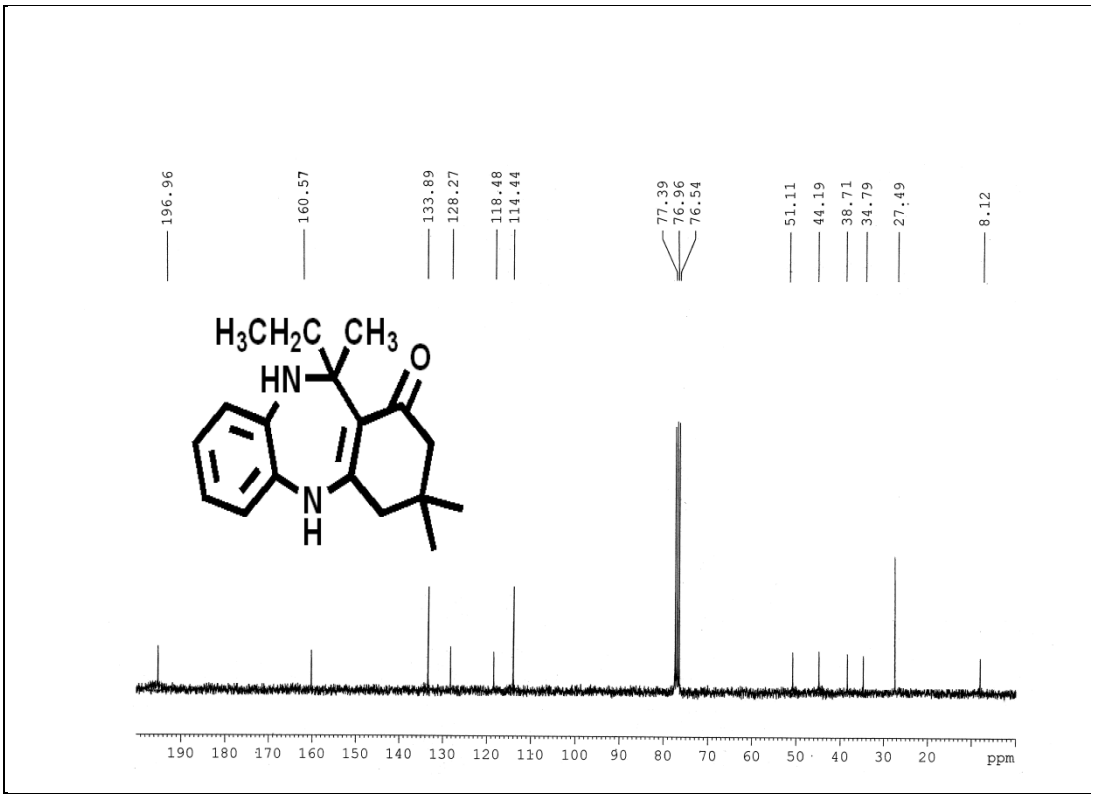
^{1}H NMR spectra of compound **4t**



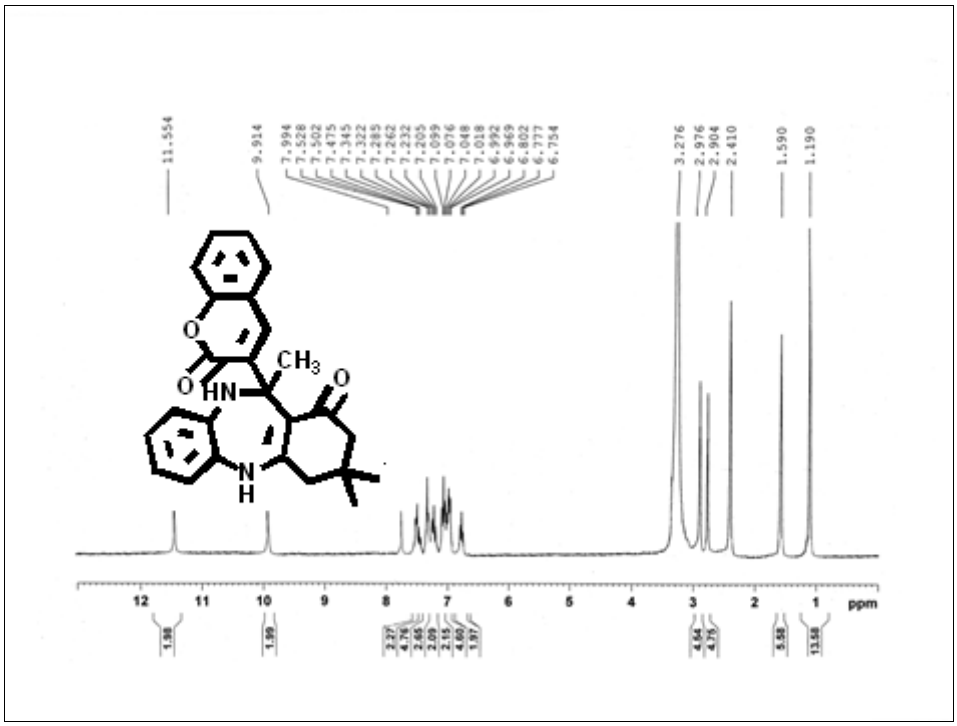
^{13}C NMR spectra of compound **4t**



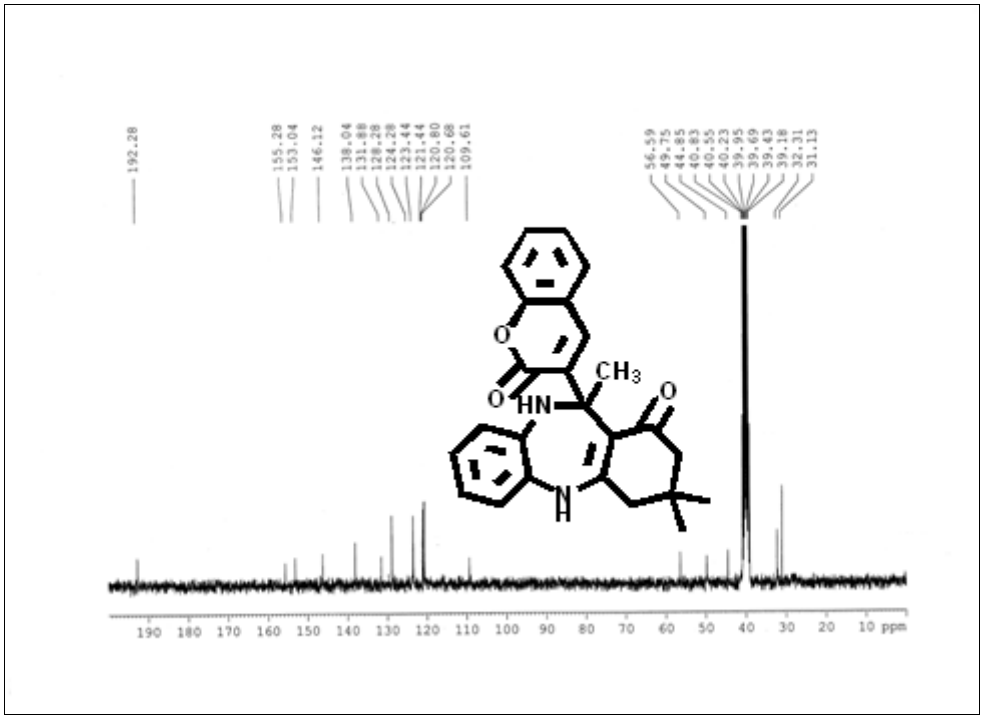
^{1}H NMR spectra of compound **4u**



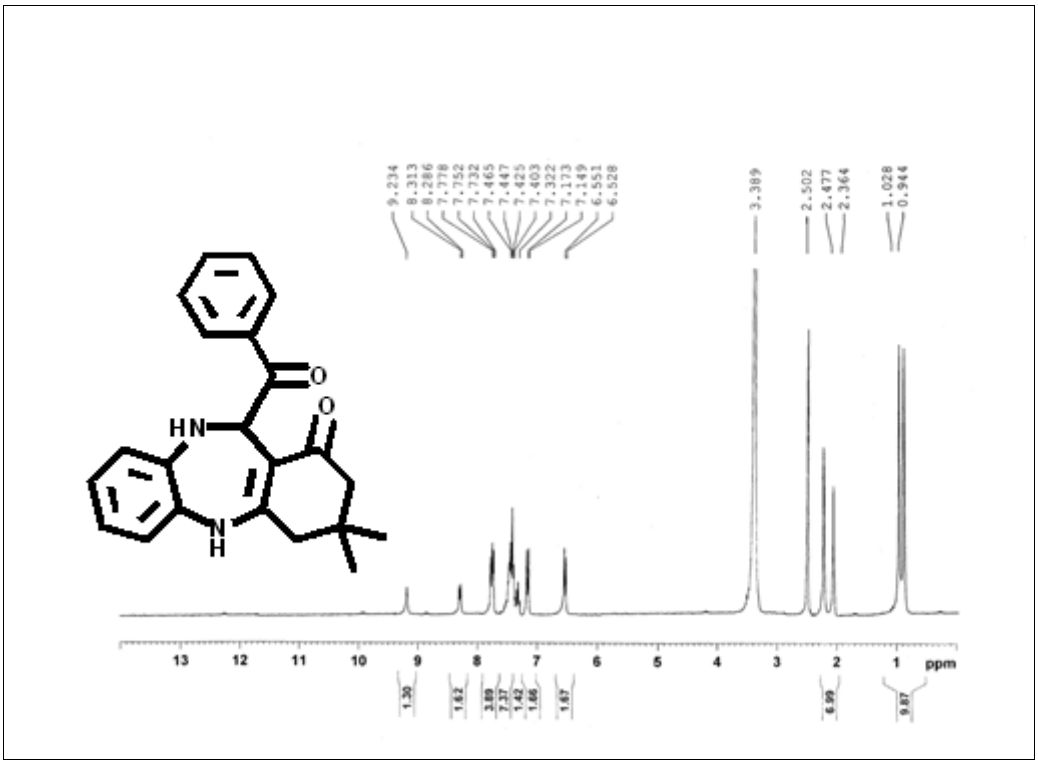
^{13}C NMR spectra of compound **4u**



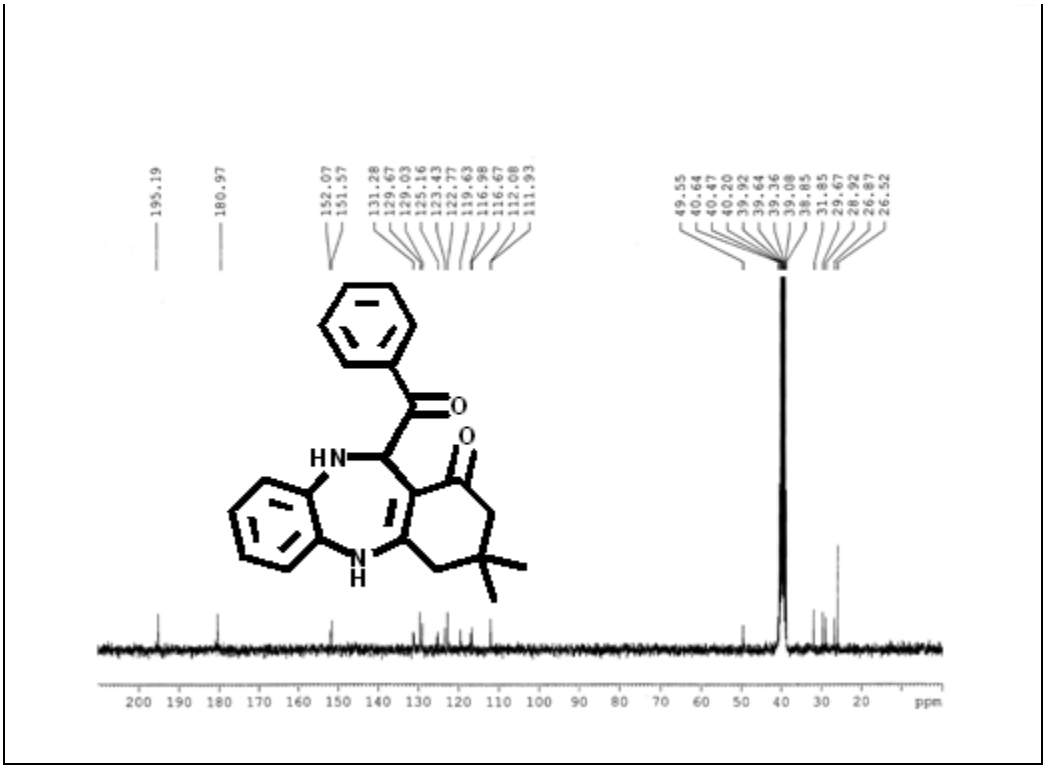
^{1}H NMR spectra of compound **4v**



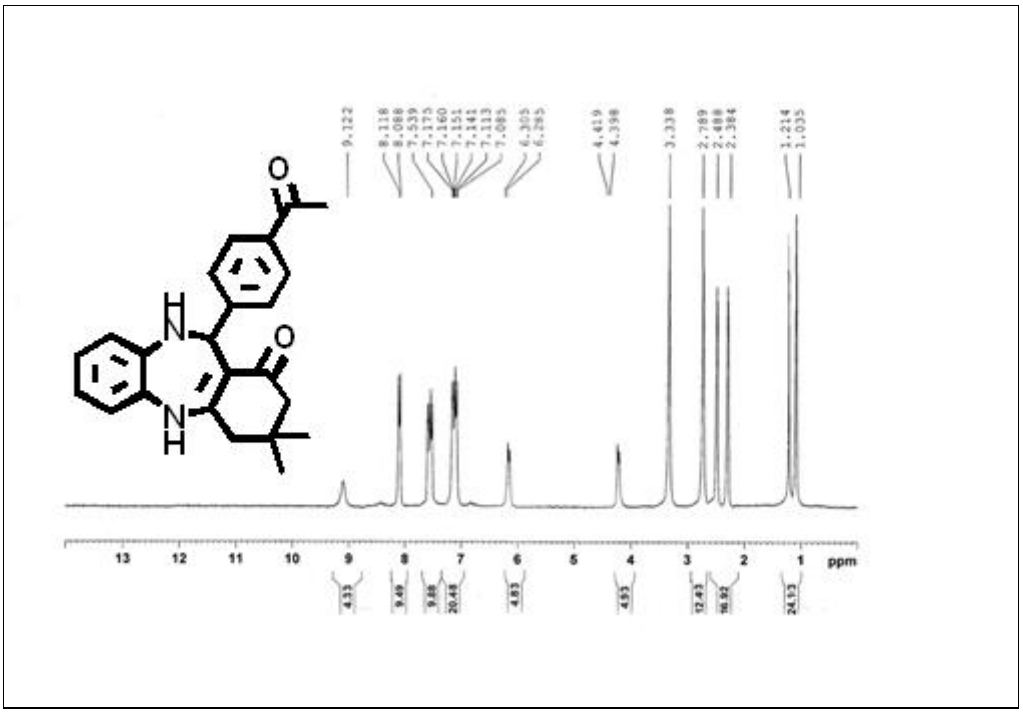
^{13}C NMR spectra of compound **4v**



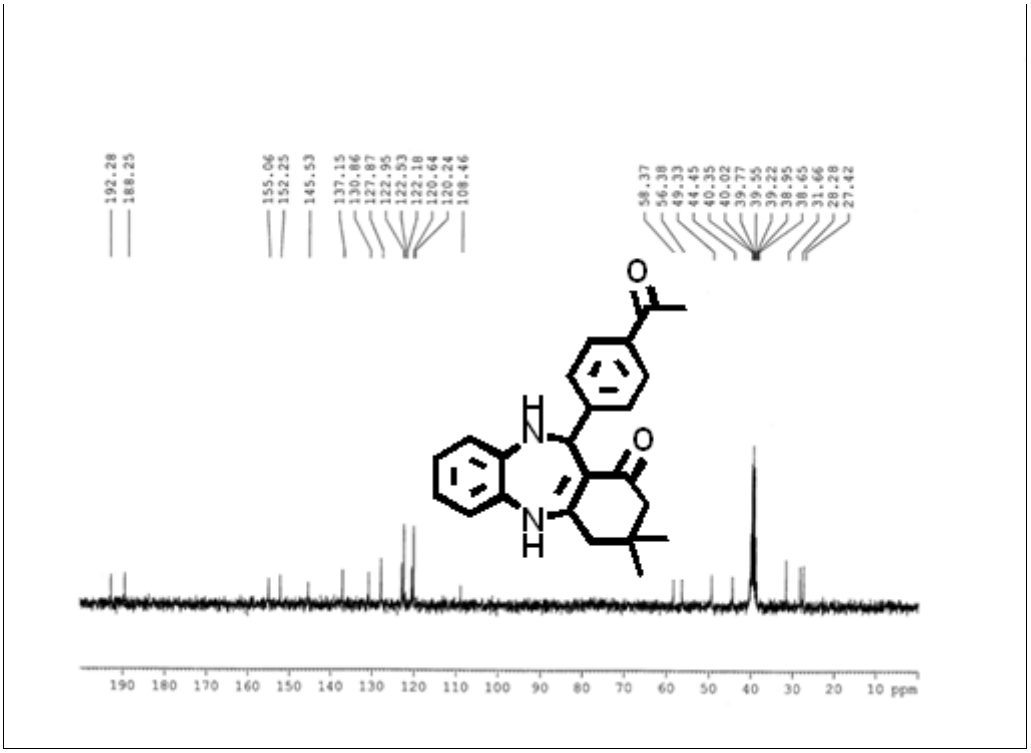
^{1}H NMR of compound **4w**



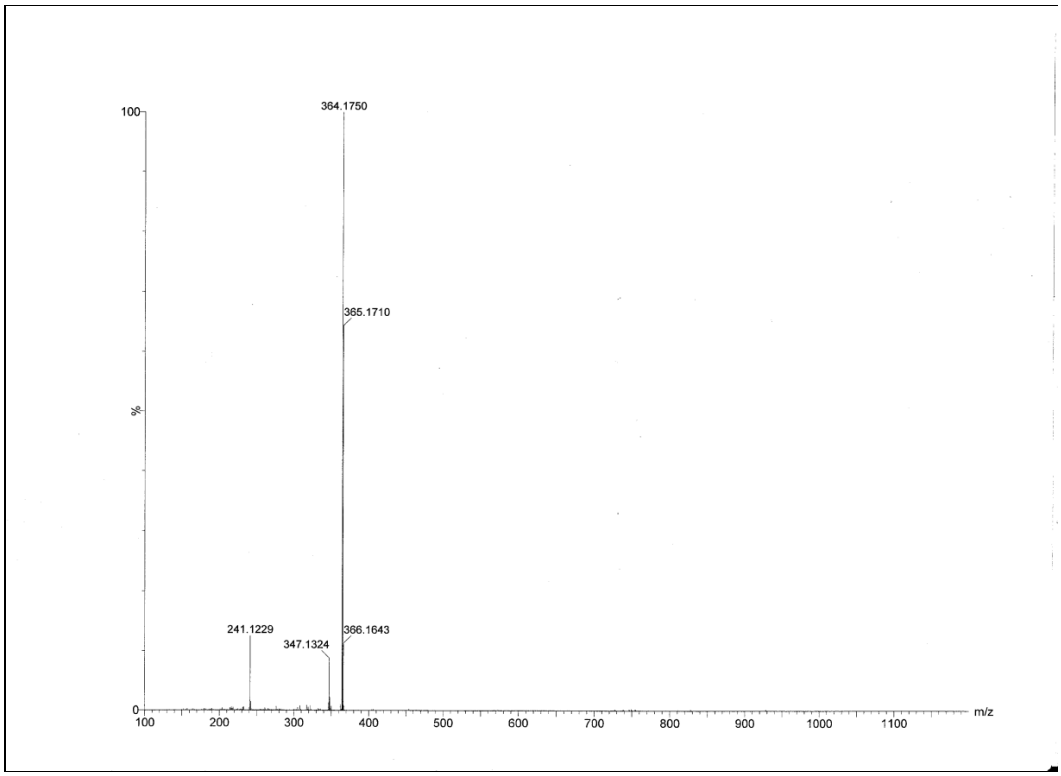
^{13}C NMR of compound **4w**



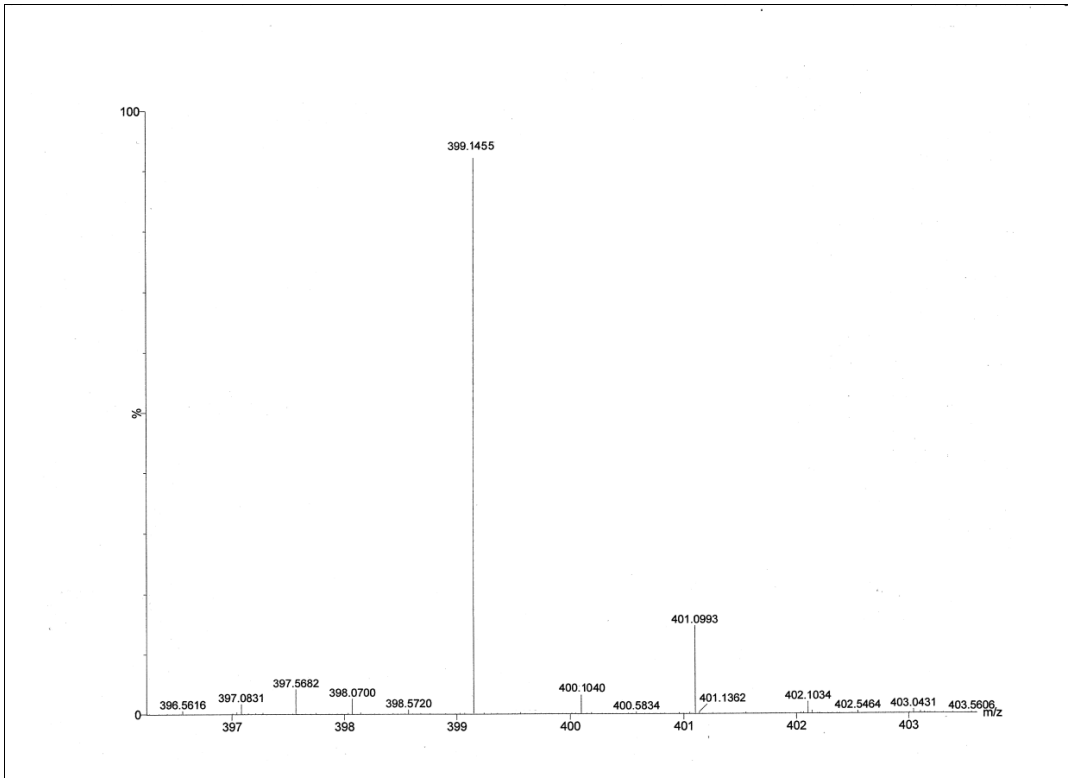
^{1}H NMR of compound **4x**



^{13}C NMR of compound **4x**



ESI-MS of compound **4c**



ESI-MS of compound **4t**