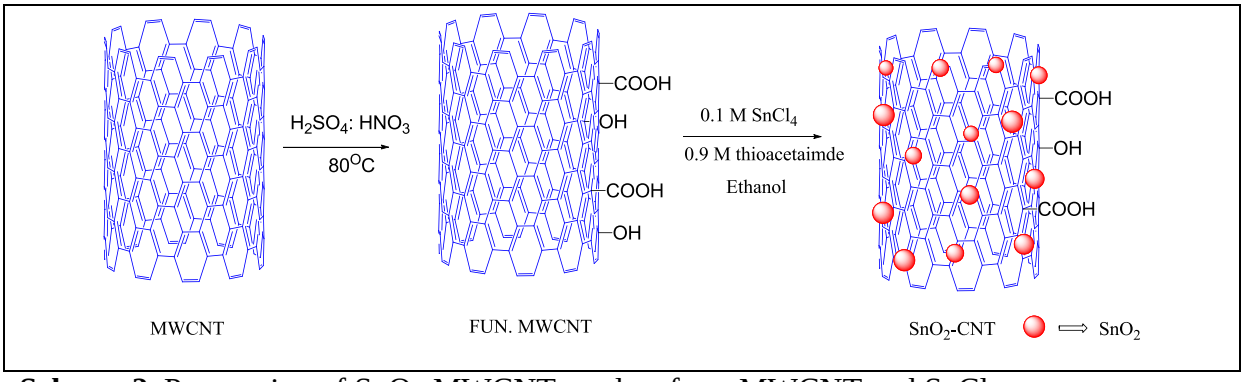
Catalyst Preparation

Preparation of Functionalized MWCNTs

0.5 g Pristine Multiwalled carbon nanotubes (MWCNTs) were functionalized by refluxing in 70 ml of a mixed acid solution H_2SO_4:HNO_3 (3:1, v/v) at 80 °C for 6 h to obtain the carboxylic acid functionalized carbon nanotubes (MWCNT-COOH). MWCNT-COOH was subsequently washed with distilled water until neutral, and finally dried in vacuum for 24 h at 50 °C.

Preparation of SnO_2-MWCNT catalyst.

In a chemical bath, 0.1 M of $SnCl_4$ was dissolved in 100 mL of 50 % distilled ethanol, following which 0.9 M thioacetamide and 5 mL of concentrated HCl (37 wt. %) were added in resulting solution. The acid treated 80 µl MWCNT was added to the above solution. The resultant solution was heated at 70 ^oC temperature for 3 h. The obtained precipitate was separated from the mother liquor by centrifugation method and washed with distilled H_2O several times. The final product was obtained after drying the precipitate at 110 °C for 12 h, followed by calcination in air at 400 °C for 2 h. A schematic representation for the preparation of SnO_2-MWCNT catalyst has been shown in **Scheme 2** for better understanding.

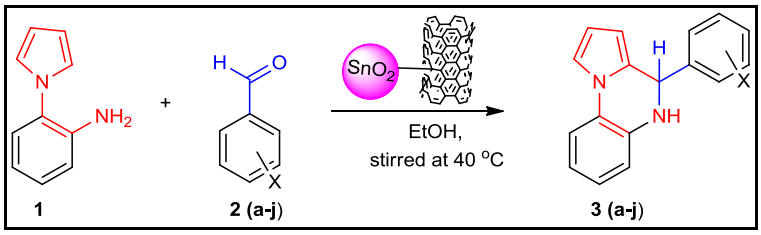


Scheme 2. Preparation of SnO_2-MWCNT catalyst from MWCNT and $SnCl_4$.

General procedure for synthesis of dihydropyrrolo[1,2-a]quinoxaline derivatives.

Mixture of 1-(2-aminophenyl)pyrrole (1 mmol), corresponding aldehydes (1 mmol) and SnO_2-MWCNT (5 wt %) in 10 mL ethanol was placed in a 100 mL round bottom flask. The resulting mixture was stirred at 40 ^oC for appropriate time. The progress of reaction was monitored through TLC (hexane:ethyl acetate; 8:2). After the complete consumption of reactants, the reaction mixture was cooled at room temperature. The cooled reaction mixture

was poured in water and extracted with ethyl acetate (10 mL x 3) in a separating funnel. The organic layer was collected and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product obtained was recrystallized using ethanol and further purified by column chromatography (petroleum ether – ethyl acetate system). The catalyst was quantitatively recovered by washing with water (3 times) and dried in oven and then it was re-claimed for next cycle. The respective structures of synthesized final compounds were confirmed via spectral study.

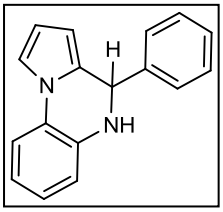


Scheme 2. Synthesis of dihydropyrrolo[1,2-a]quinoxaline from 1-(2-aminophenyl)pyrrole and aldehyde.

CHARACTERIZATION OF THE SYNTHESIZED COMPOUNDS

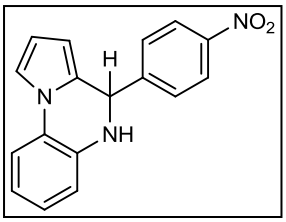
All prepared products were recrystallized and purified through column chromatography using suitable solvent system. Structure of final products were confirmed through IR, ^{1}HNMR, ^{13}CNMR and mass spectral data. The IR spectra (in cm^{-}1) were recorded on a perkin-Elmer spectrophotometer in KBr pellets. ^{1}HNMR spectra were recorded on Varian Gemini (400 MHz) spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. ^{13}CNMR spectra were recorded on 50 MHz in $CDCl_3$ solvent. All chemical shift values were reported in δ scale downfield from TMS. Homogeneity of the compound was checked by TLC on silica gel plates.

4-phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline ***3a*****:** Pale yellow solid**, IR** (KBr, in cm^{-1}): 3476,



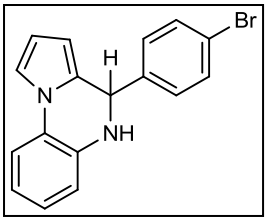
3345, 2980, 1658, 1624, 1569, 1461, 1429, 1343, 1283, 1072, 965, 795, 712, 695. **^{1}HNMR** ($CDCl_3$, in δ ppm): 7.4-7.3 (m, 4H), 7.2-7.1 (m, 4H), 6.9 (dd, 2H), 6.3 (t, 1H), 6.2 (d, 1H), 5.3 (s, 1H, NH), 4.3 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 138.9, 136.2, 133.7, 130.9, 129.0, 128.8, 128.3, 127.6, 127.0, 124.1, 123.3, 122.5, 121.4, 108.4, 106.4, 60.8. **MS** (m/z): 247 (M+1).

*4-(4-nitrophenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline **3b**:* Yellow solid, **IR** (KBr, in cm^{-1}):



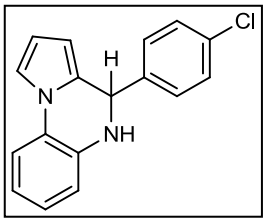
3480, 3361, 3064, 2887, 1630, 1593, 1479, 1395, 1210, 1111, 753, 712, 695. **^{1}HNMR** ($CDCl_3$, in δ ppm): 8.1 (d, 2H), 7.4 (d, 1H), 7.2 (m, 2H), 7.1-7.0 (m, 3H), 6.8 (d, 1H), 6.3 (t, 1H), 6.2 (d, 1H), 5.5 (s, 1H, NH), 4.2 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 149.2, 147.5, 133.8, 133.4, 131.0, 128.7, 127.1, 127.0, 124.0, 123.3, 122.5, 121.4, 108.4, 106.4, 60.51. **MS** (m/z): 291 (M^+).

*4-(4-bromophenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline **3c**:* Pale yellow solid, **IR** (KBr, in



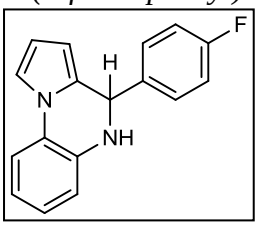
cm^{-1}): 3420, 3054, 2974, 1642, 1575, 1435, 1291, 1144, 765, 712, 647. **^{1}HNMR** ($CDCl_3$, in δ ppm): 7.8 (d, 2H), 7.4-7.3 (m, 4H), 7.1 (t, 1H), 6.7 (d, 1H), 6.6 (d, 1H), 6.2-6.1 (m, 2H), 5.4 (s, 1H, NH), 4.1 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 141.0, 136.4, 133.0, 130.8, 126.4, 125.8, 123.9, 121.6, 119.8, 115.4, 114.3, 110.0, 106.7, 56.1. **MS** (m/z): 326 (M+1).

*4-(4-chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline **3d**:* White solid, **IR** (KBr, in cm^{-1}):

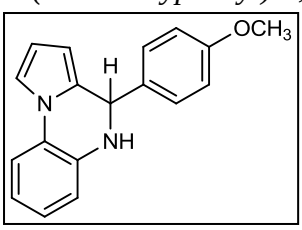


3476, 3064, 2979, 1657, 1592, 1449, 1325, 1209, 1020, 874, 716, 695. **^{1}HNMR** ($CDCl_3$, in δ ppm): 7.4 (d, 2H), 7.3-7.2 (m, 3H), 7.2-7.1 (m, 3H), 6.9 (dd, 1H), 6.2 (t, 1H), 6.1 (d, 1H), 5.4 (s, 1H, NH), 4.2 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 139.9, 134.2, 133.9, 133.8, 132.6, 131.9, 130.5, 129.2, 127.3, 127.0, 124.1, 121.5, 108.5, 106.6, 60.5. **MS** (m/z): 282 (M+2).

*4-(4-fluorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline **3e**:* colorless solid, **IR** (KBr, in cm^{-1}): 3482, 2920, 1672, 1620, 1522, 1465, 1282, 1148, 780, 672. **^{1}HNMR** ($CDCl_3$, in δ ppm): 7.5 (d, 1H), 7.4-7.3 (m, 4H), 7.2-7.1 (m, 1H), 7.0-6.9 (m, 2H), 6.6 (d, 1H), 6.2 (m, 1H), 5.9 (d, 1H), 5.4 (s, 1H, NH), 4.4 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 162.2, 140.0, 137.4, 136.9, 136.0, 131.7, 129.5, 127.9, 125.4, 123.6, 120.0, 116.5, 115.3, 112.8, 109.0, 58.9. **MS** (m/z): 265 (M+1).

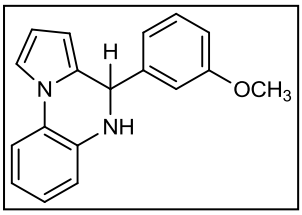


*4-(4-methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline **3f***: Yellowish-white solid, **IR**

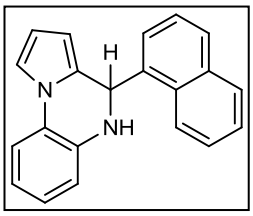


(KBr, in cm^{-1}): 3384, 3186, 2917, 2848, 1624, 1590, 1498, 1315, 1246, 1155, 1056, 926, 742, 698, 560. **^{1}HNMR** ($CDCl_3$, in δ ppm): 7.4 (d, 2H), 7.2-7.1 (m, 4H), 7.1 (m, 1H), 7.0 (d, 1H), 6.9 (d, 1H), 6.3 (t, 1H), 6.2 (d, 1H), 5.2 (s, 1H, NH), 4.3 (s, 1H), 3.8 (s, 3H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 159.1, 138.9, 133.8, 131.0, 129.9, 128.0, 127.1, 124.2, 123.3, 122.5, 121.5, 114.5, 108.4, 106.5, 60.0, 55.2. **MS** (m/z): 276 (M^+).

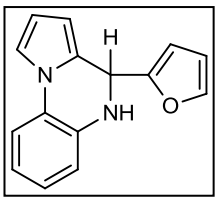
4-(3-methoxyphenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline ***3g***: White solid, **IR** (KBr, in cm^{-1}): 3406, 3055, 2962, 1652, 1526, 1490, 1450, 1356, 1268, 1100, 752, 719, 646, 540. **^{1}HNMR** ($CDCl_3$, in δ ppm): 7.5 (d, 1H), 7.3 (m, 1H), 7.1-6.9 (m, 3H), 6.8 (m, 1H), 6.7-6.6 (m, 2H), 6.5 (d, 1H), 6.3 (d, 1H), 5.9-5.8 (m, 1H), 5.4 (s, 1H, NH), 4.2 (s, 1H), 3.8 (s, 3H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 160.0, 145.1, 137.3, 131.5, 130.9, 126.4, 125.7, 122.0, 120.6, 118.7, 115.5, 114.0, 113.9, 113.1, 111.5, 108.2, 59.8, 55.0. **MS** (m/z): 276 (M+1).



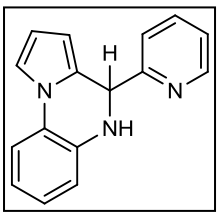
4-(Naphthalen-1-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline ***3h****:* White solid, **IR** (KBr, in cm^{-1}): 3450, 3355, 3107, 2874, 1652, 1600, 1589, 1520, 1478, 1345, 1267, 1162, 810, 781, 714, 675, 570. **^{1}HNMR** ($CDCl_3$, in δ ppm): 8.2 (d, 1H), 7.8-7.7 (m, 2H), 7.6 (d, 1H), 7.5-7.3 (m, 4H), 7.2 (d, 1H), 6.9-6.8 (m, 2H), 6.2 (d, 1H), 6.0-5.9 (m, 2H), 5.3 (s, 1H, NH), 4.2 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 138.0, 137.8, 134.7, 132.2, 130.0, 129.1, 128.9, 127.0, 126.5, 125.8, 125.0, 124.7, 123.9, 120.5, 117.4, 114.6, 113.9, 109.8, 106.4, 63.1. **MS** (m/z): 297 (M+1).



4-(Furan-2-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline ***3i*****:** Yellowish oil, **IR** (KBr, in cm^{-1}): 3402, 3147, 2953, 1645, 1580, 1482, 1408, 1336, 1291, 1202, 1063, 745, 712, 632, 540. **^{1}HNMR** ($CDCl_3$, in δ ppm): 7.5 (d, 1H), 7.3 (d, 1H), 7.1 (m, 1H), 7.0-6.9 (m, 2H), 6.7 (d, 1H), 6.5 (t, 1H), 6.3-6.2 (m, 2H), 5.9 (d, 1H), 5.4 (s, 1H, NH), 4.4 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 154.0, 143.1, 135.2, 126.4, 125.3, 124.9, 120.4, 116.3, 114.7, 114.3, 110.6, 109.9, 108.0, 106.4, 60.2. **MS** (m/z): 236 (M^+).

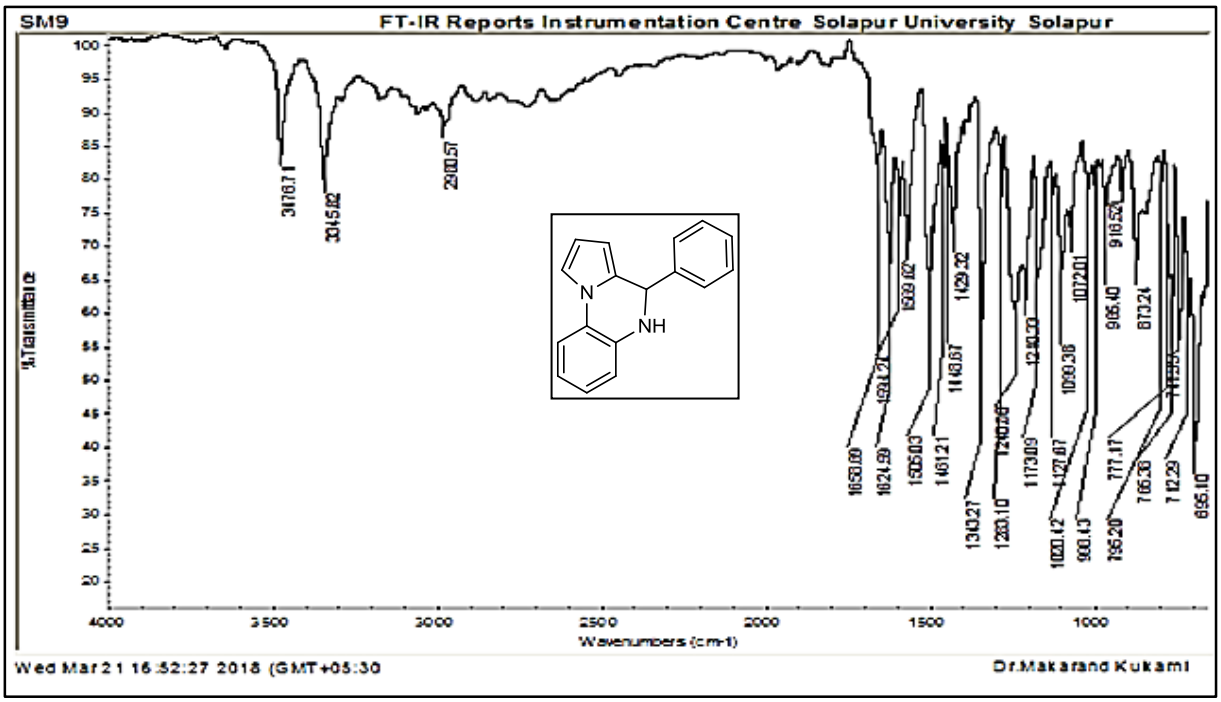


4-(pyridin-2-yl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline ***3j***: Yellow solid, **IR** (KBr, in cm^{-1}): 3468, 3068, 2980, 1652, 1601, 1516, 1482, 1420, 1346, 1278, 760, 702, 680, 635. **^{1}HNMR** ($CDCl_3$, in δ ppm): 8.5 (d, 1H), 7.7-7.6 (m, 1H), 7.4 (m, 2H), 7.3-7.2 (m, 2H), 7.0-6.9 (m, 2H), 6.7 (d, 1H), 6.3 (m, 1H), 6.0 (d, 1H), 5.4 (s, 1H, NH), 4.8 (s, 1H). **^{13}CNMR** ($CDCl_3$, in δ ppm): 160.5, 150.2, 137.3, 135.8, 127.0, 126.0, 124.8, 122.5, 121.7, 120.0, 116.5, 114.6, 113.9, 109.0, 106.5, 57.4. **MS** (m/z): 248 (M+1).

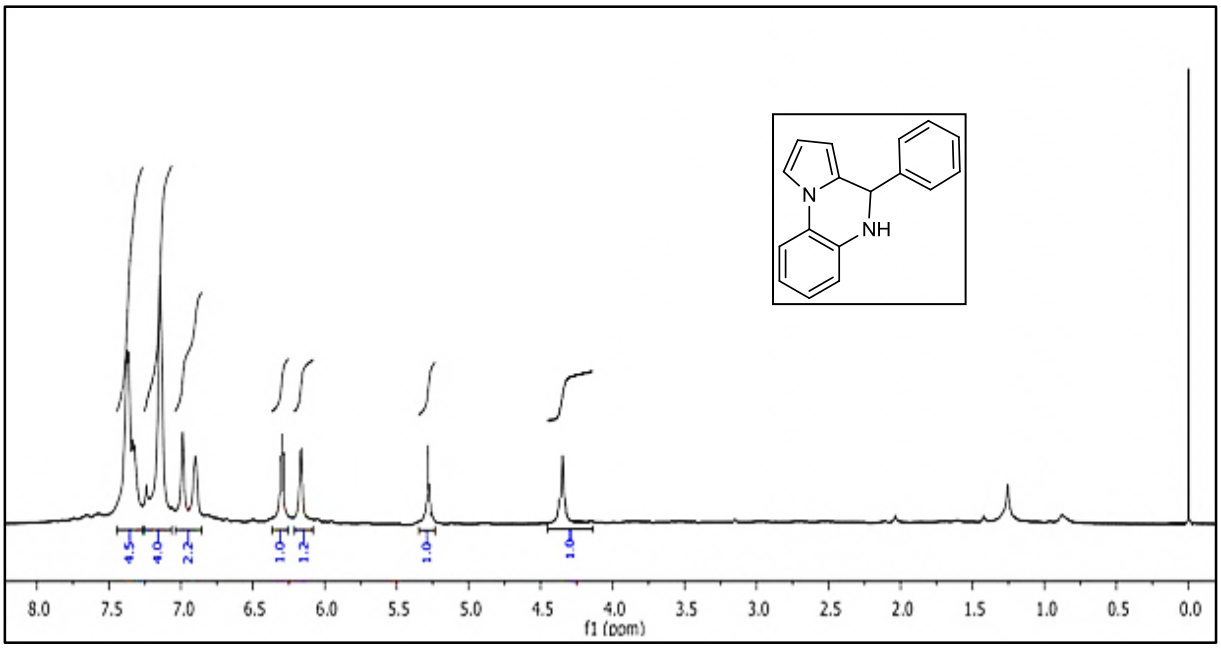


SPECTRA

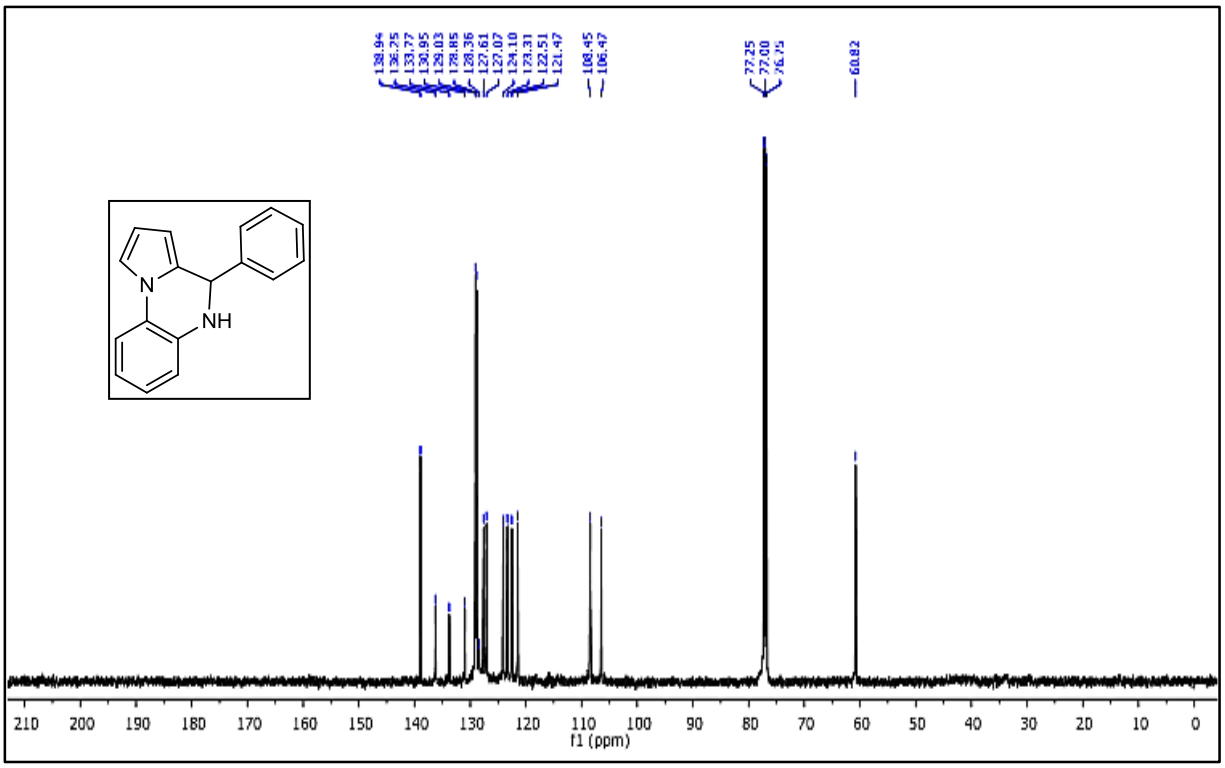
3a] 4-phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline



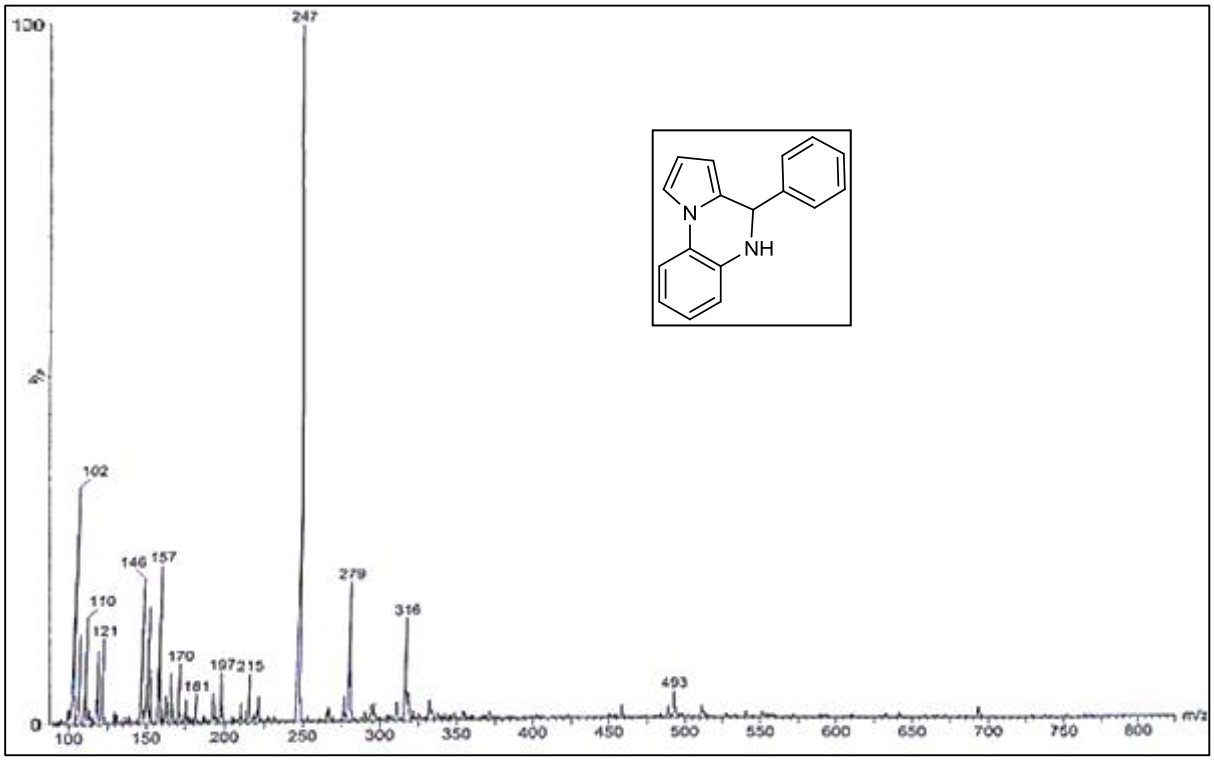
IR spectra of 4-phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline 3a.



^{1}HNMR spectra of 4-phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline 3a.

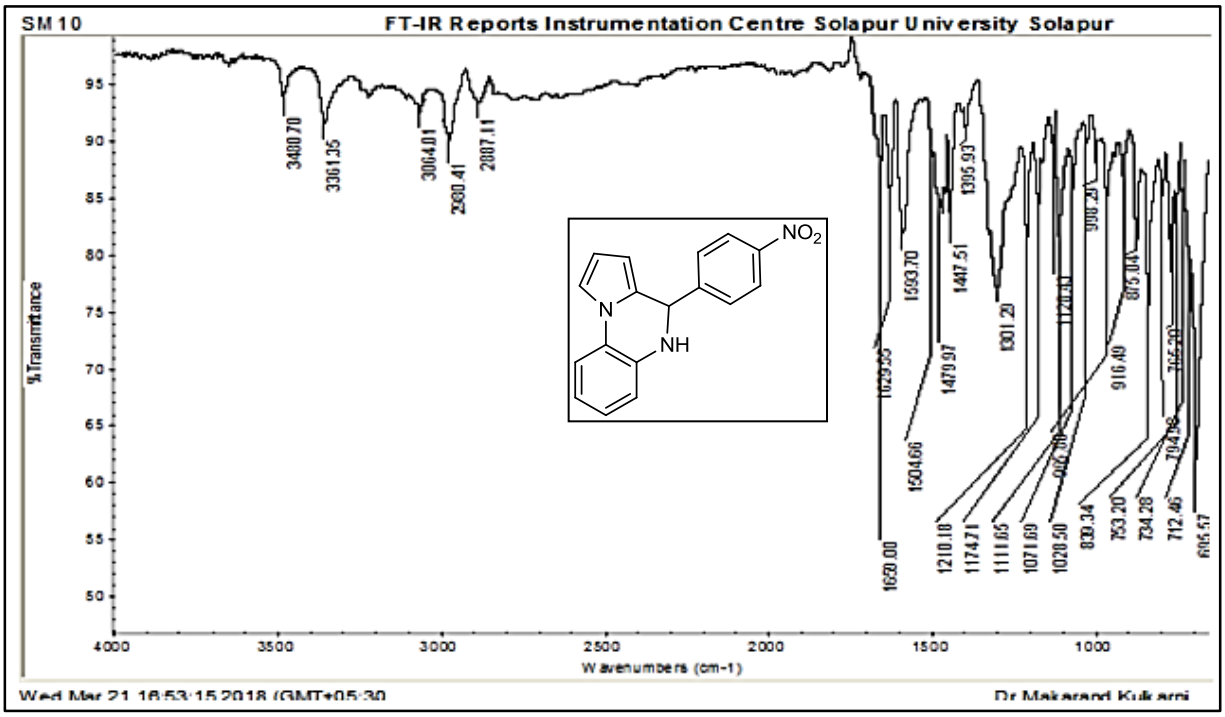


^{13}CNMR spectra of 4-phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline 3a.

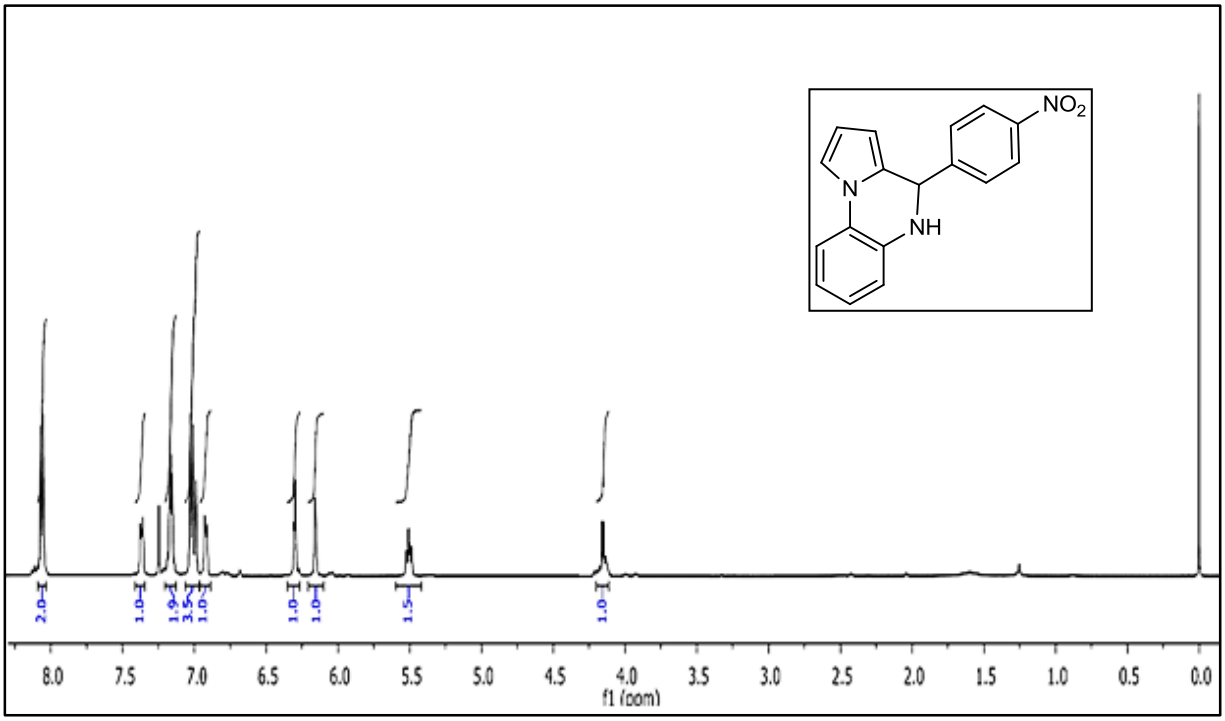


Mass spectra of 4-phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline 3a.

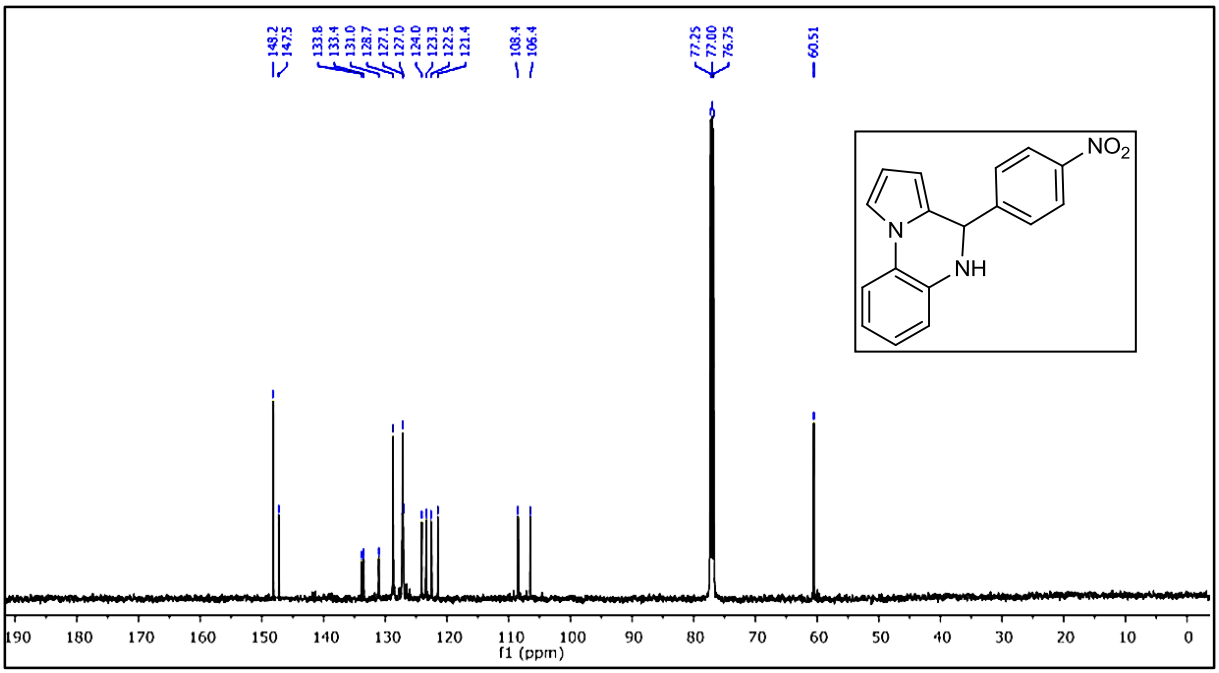
3b] 4-(4-nitrophenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline.



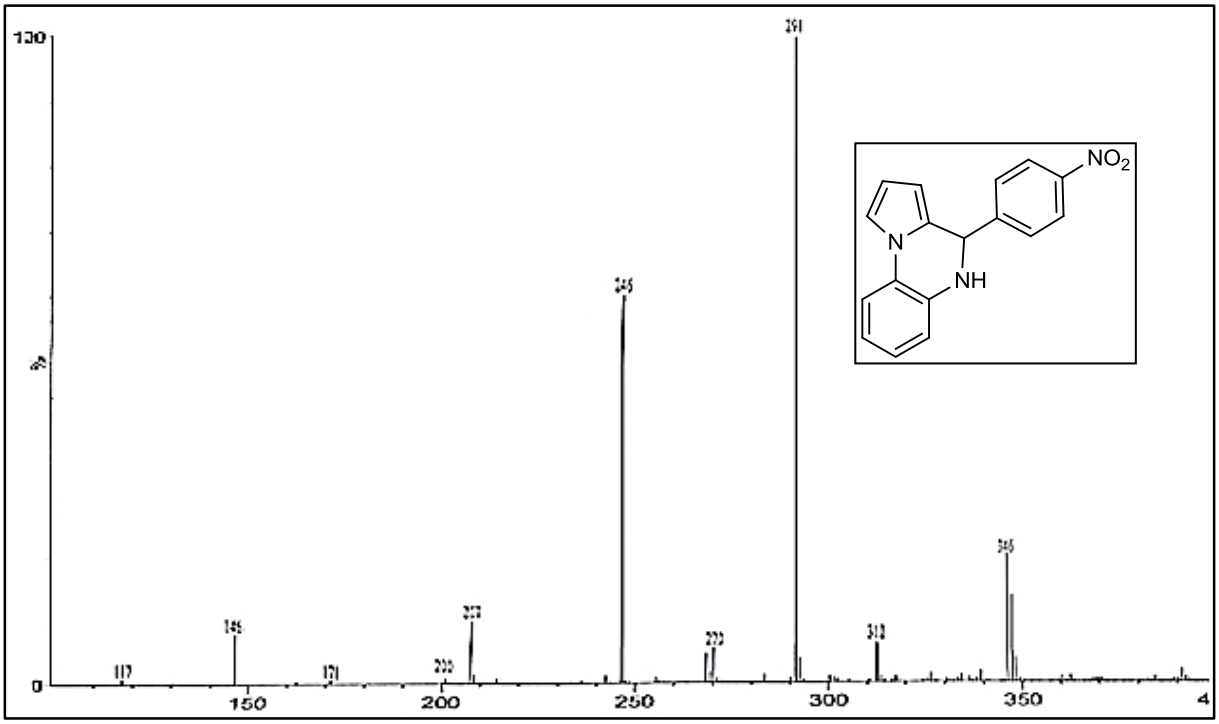
IR spectra of 4-(4-nitrophenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline 3b.



[1]HNMR spectra of 4-(4-nitrophenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline 3b.

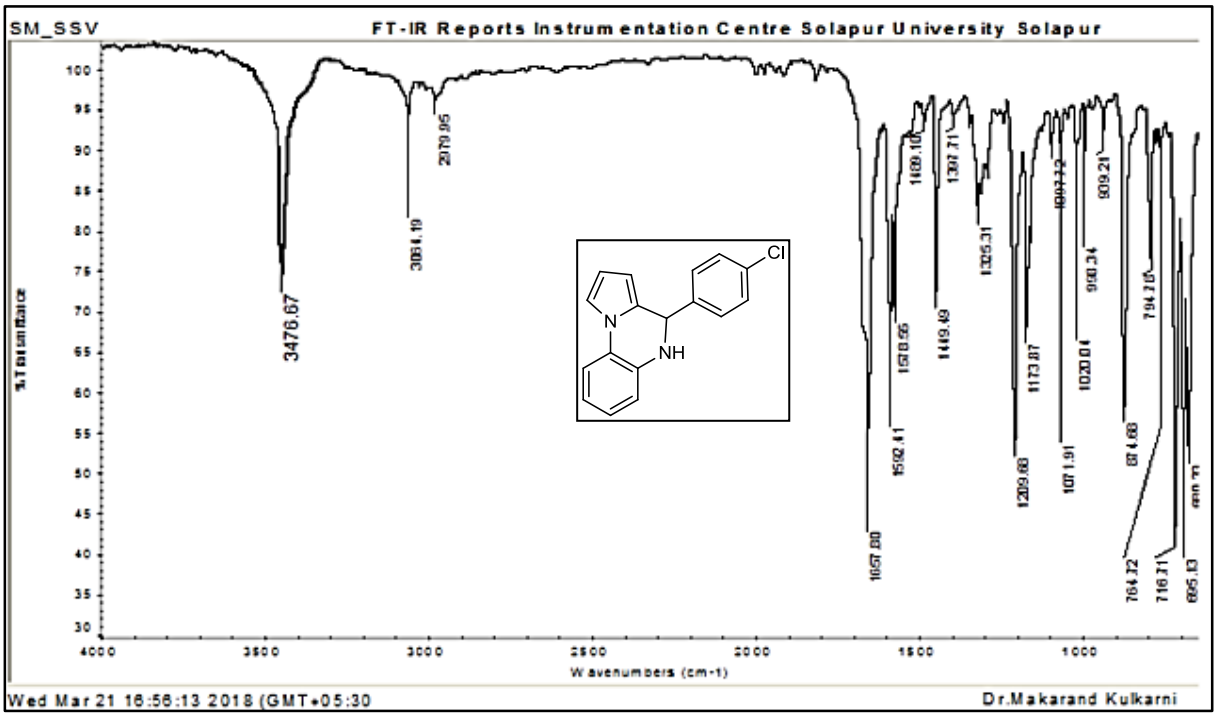


[13]CNMR spectra of 4-(4-nitrophenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline 3b.

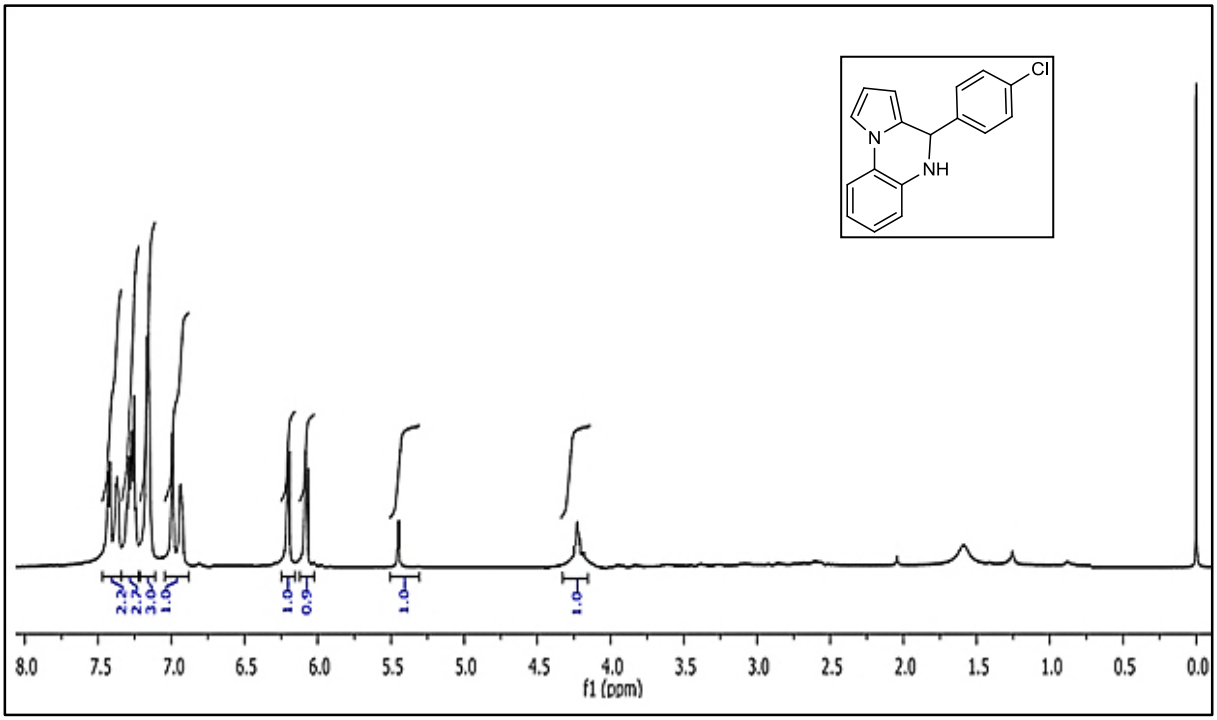


Mass spectra of 4-(4-nitrophenyl)-4, 5-dihydropyrrolo[1,2-a]quinoxaline 3b.

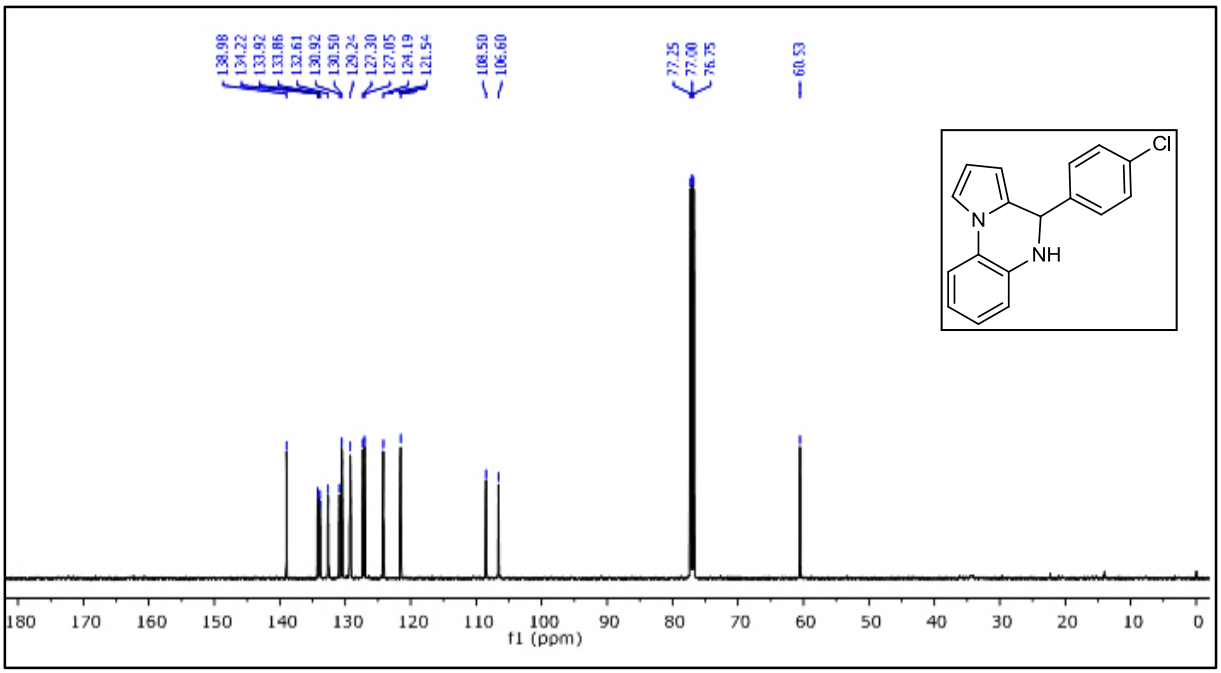
3d] 4-(4-chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline



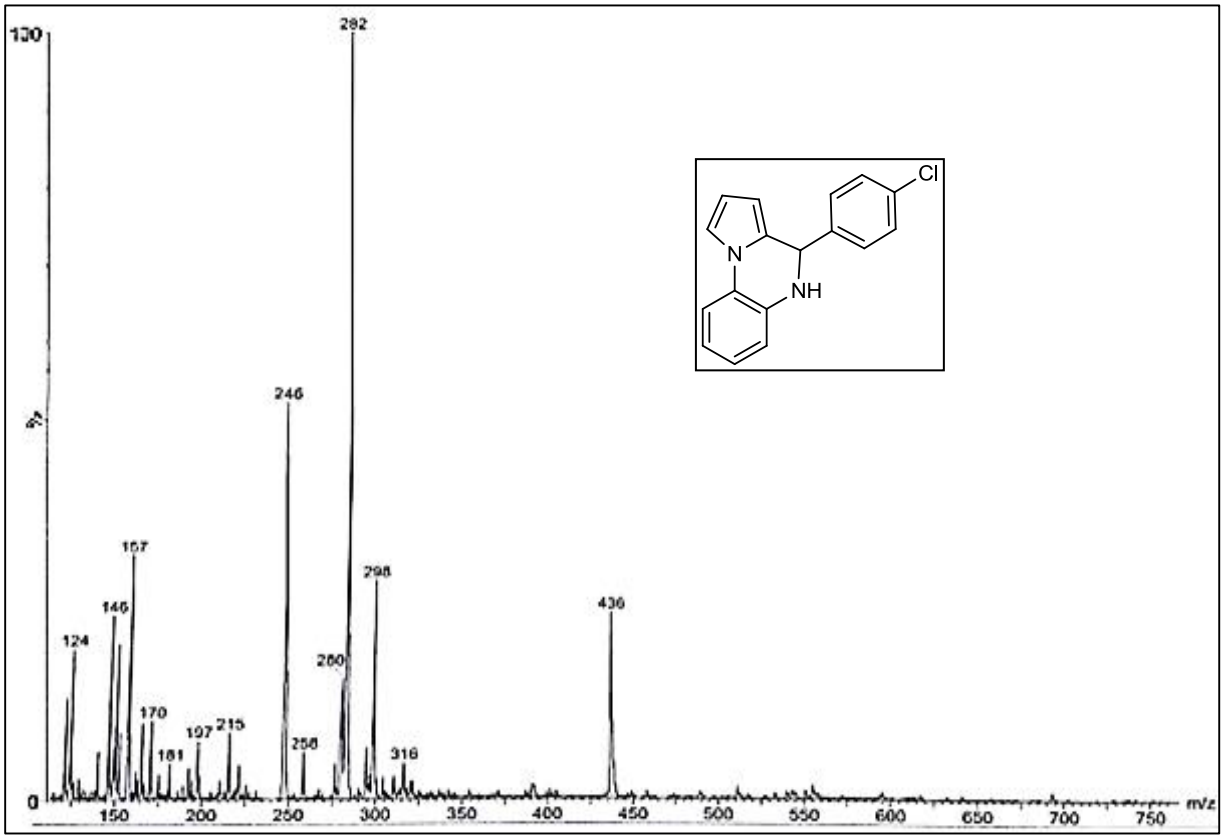
IR spectra of 4-(4-chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3d.



[1]HNMR spectra of 4-(4-chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3d.

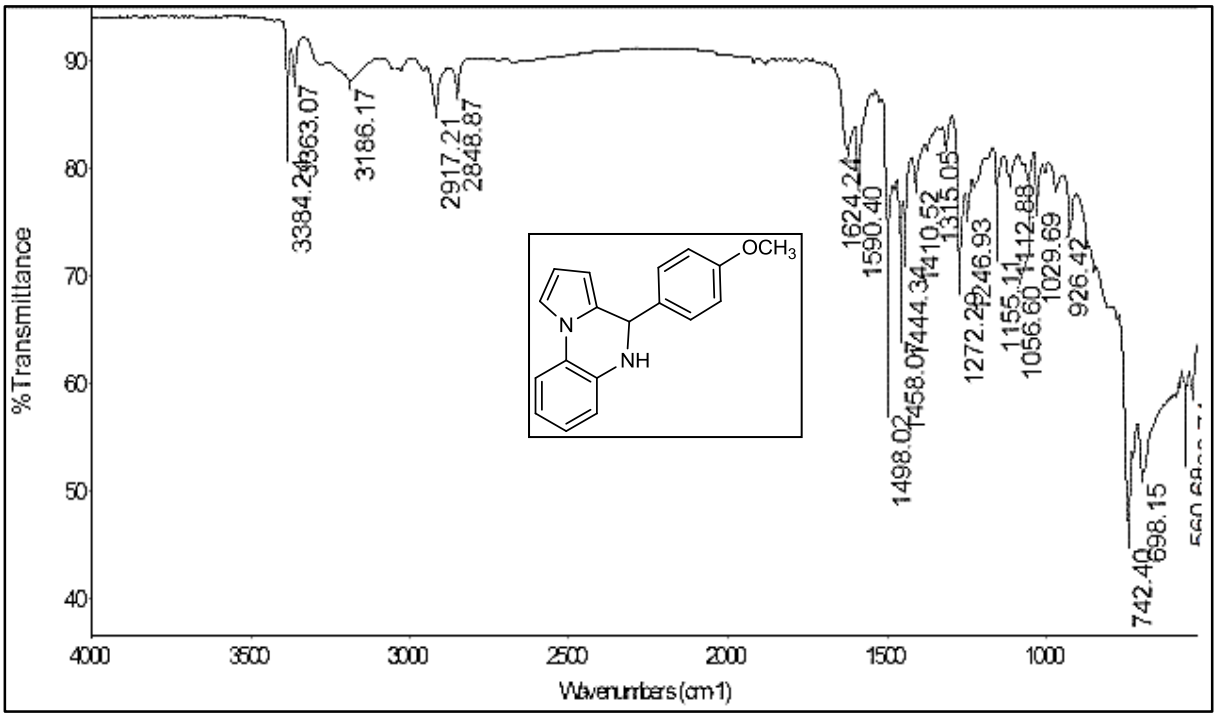


[13]CNMR spectra of 4-(4-chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3d.

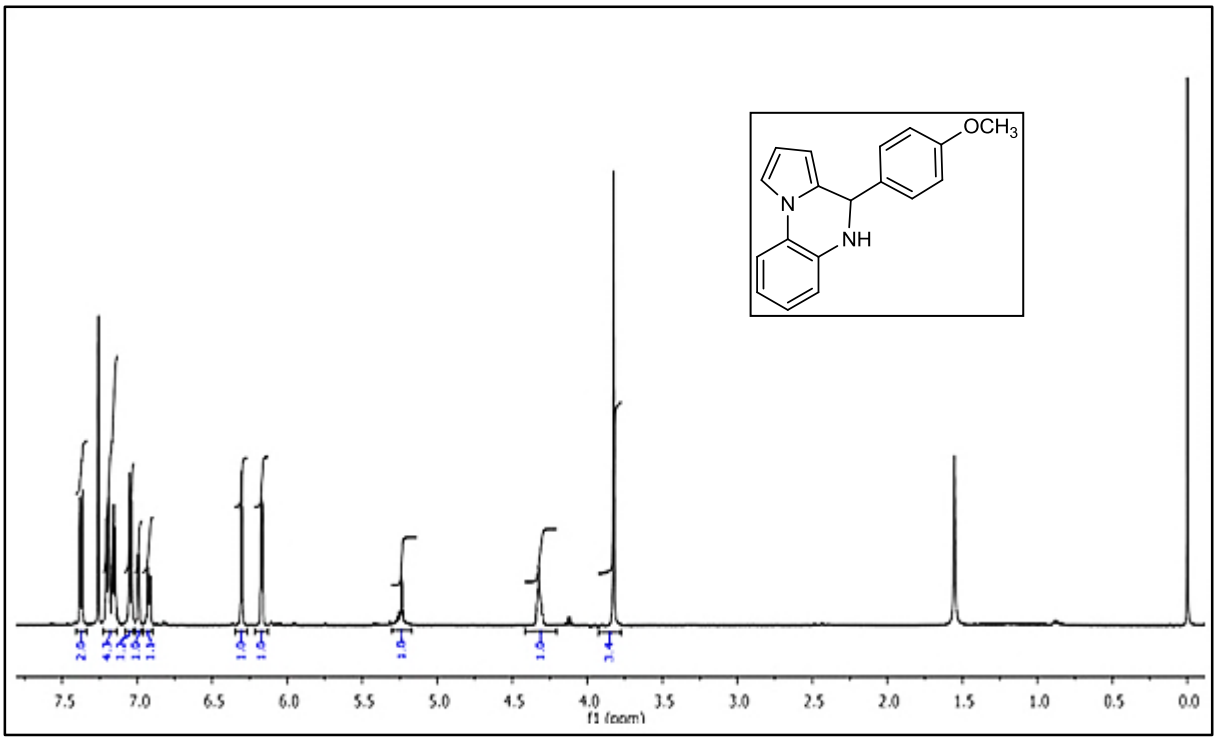


Mass spectra of 4-(4-chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3d.

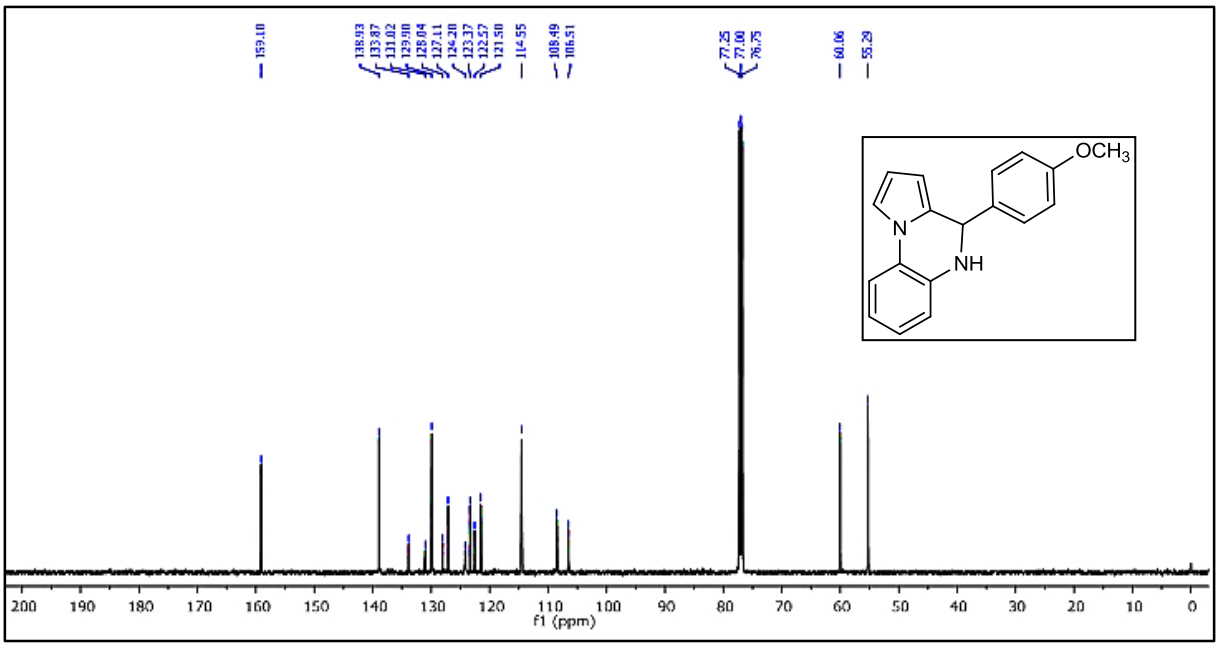
3f] 4-(4-methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline



*IR spectra of 4-(4-methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline **3f**.*



*[1]HNMR spectra of 4-(4-methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline **3f**.*



^{13}CNMR spectra of 4-(4-methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline ***3f*****.**