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An efficient five-component synthesis of thio ether containing dihydropyrano[2,3-*c*]pyrazoles : A green domino strategy

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Experimental Section

General Remarks:

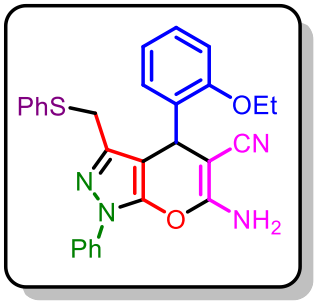
The melting points were measured in open capillary tubes and are uncorrected. The reaction was monitored by TLC on Merck GF 254 with detection by UV light for visualization using a mixture of petroleum ether (60-80 ˚C) and ethyl acetate (7:3) as the eluent. Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR) spectra were recorded on a Bruker (Advance) 300 MHz spectrometer in DMSO-d_6 using TMS as an internal standard. Chemical shifts are reported in parts per million (δ), coupling constants (*J* values) are reported in Hertz (Hz) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), (multiplet). ^{13}C NMR spectra were routinely run with broadband decoupling. Absorption spectra studies of all samples were recorded on Agilent Technologies 8453 spectrophotometer by taking the solution in a 1 cm path length quartz cell in the wavelength range of 200-1100 nm. Elemental analyses were carried out with Perkin-Elmer 2400 series II analyzer. Electrospray ionization mass spectrometry (ESI-MS) was recorded in LCQ Fleet, Thermo Fisher Instruments Limited, US and High resolution mass spectra were recorded on a Water Q-TOF micro mass spectrometer using ESI mode.

General procedure for the synthesis of pyrano[2,3-*c*]pyrazole derivatives (6)

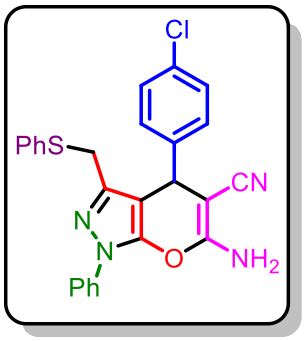
A mixture of commercially available ethyl 4-chloro-3-oxobutanoate **1** (1.0 equiv.) and the substituted benzenethiol **2** (1.1 equiv.) was heated at 120 °C for 10 minutes under solvent free conditions. TLC was used to check the reaction, followed by the addition of phenylhydrazine **3** (1.1 equiv.) at 120 °C and the same temperature was maintained for 5 minutes. After TLC monitoring, subsequent additions of the aldehyde **4** (1.1 equiv.) and malononitrile **5** (1.1 equiv.) were performed under solvent free conditions. Completion of the reaction was monitored using TLC. The reaction mixture was cooled to room temperature, followed by addition of ethanol (5 mL). The product appeared as a solid, through trituration with ethanol, was filtered and washed with another 2 mL of EtOH to remove the other impurities. Finally, the product **6** was dried under reduced pressure and was pure enough for the spectral investigations.

Characterization data for compounds (6a-z)

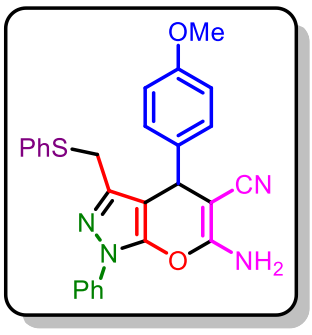
6-amino-4-(2-ethoxyphenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6a). Isolated as white solid; R_f = 0.41 (3:7 EtOAc/pet. ether); mp 180–182 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.12 (m, 10H), 6.94 – 6.84 (m, 2H), 4.87 (s, 1H), 3.91 – 3.84 (m, 3H), 3.47 (d, *J* = 13.8 Hz, 1H), 1.14 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.4, 157.0, 145.1, 145.0, 137.9, 136.2, 130.9, 129.8, 129.3, 129.3, 129.1, 126.9, 126.6, 120.8, 120.6, 112.9, 99.2, 63.8, 57.9, 33.0, 30.1, 14.9; ESI Calcd *m/z* 480, Found 479 $[(M-1)]^+$; Anal. Calcd for: $C_{28}H_{24}N_4O_2S$: C, 69.98; H, 5.03; N, 11.66; O, 6.66%; Found C, 69.95; H, 5.06; N, 11.69%; One of the –SCH_2 proton was merged with –CH_2 of –OEt peak.



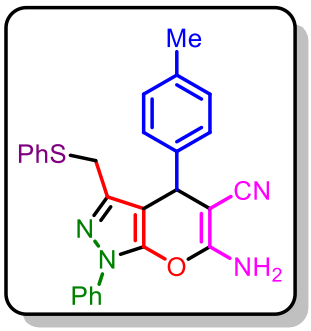
6-amino-4-(4-chlorophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6b). Isolated as white solid; R_f = 0.42 (3:7 EtOAc/pet. ether); mp 200–202 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.73 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.29 – 7.16 (m, 9H), 4.68 (s, 1H), 3.91 (d, *J* = 13.8 Hz, 1H), 3.42 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.2, 145.7, 145.0, 143.1, 138.1, 136.3, 132.7, 130.6, 130.2, 129.8, 129.4, 127.5, 127.1, 121.2, 120.6, 99.0, 58.6, 37.2, 30.7; Anal. Calcd for: $C_{26}H_{19}ClN_4OS$: C, 66.31; H, 4.07; N, 11.90%; Found C, 66.34; H, 4.04; N, 11.93%.



6-amino-4-(4-methoxyphenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6c). Isolated as white solid; R_f = 0.37 (3:7 EtOAc/pet. ether); mp 196–198 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.73 (d, *J* = 8.1 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.13 (m, 12H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.60 (s, 1H), 3.90 (d, *J* = 14.1 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.0, 159.2, 145.8, 144.9, 138.1, 136.3, 136.0, 130.2, 129.8, 127.5, 127.1, 121.2, 120.7, 114.8, 99.7, 59.4, 55.9, 37.0, 30.7; ESI Calcd *m/z* 466, found 465 $[(M-1)]^+$; Anal. Calcd for: $C_{27}H_{22}N_4O_2S$: C, 69.51; H, 4.75; N, 12.01%; Found C, 69.54; H, 4.73; N, 12.04%; One of the –SCH_2 proton was merged with water peak.

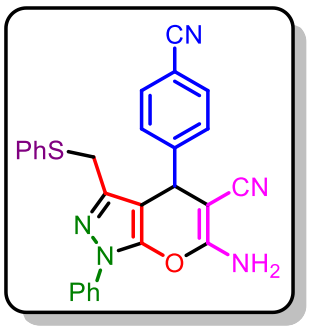


6-amino-1-phenyl-3-((phenylthio)methyl)-4-(p-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6d). Isolated as white solid; R_f = 0.46 (3:7 EtOAc/pet. ether); mp 178–180 °C; ^{1}H NMR



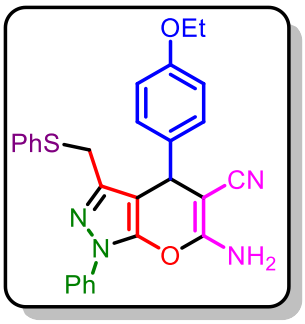
(300 MHz, DMSO-d_6) δ: 7.73 (d, *J* = 8.1 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.21 (m, 10H), 7.11 (s, 2H), 4.60 (s, 1H), 3.90 (d, *J* = 13.8 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.0, 145.7, 144.9, 141.0, 138.1, 137.2, 136.3, 130.2, 130.0, 129.8, 128.6, 127.4, 127.1, 121.2, 120.7, 99.6, 59.2, 37.4, 30.7, 21.6; ESI Calcd *m/z* 450, found 451 $[(M+1)]^+$; Anal. Calcd for: $C_{27}H_{22}N_4OS$: C, 71.98; H, 4.92; N, 12.44%; Found: C, 71.95; H, 4.95; N, 12.47%; One of the –SCH_2 proton was merged with water peak.

6-amino-4-(4-cyanophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6e). Isolated as white solid; R_f = 0.30 (3:7 EtOAc/pet. ether); mp 194–196 °C; ^{1}H NMR



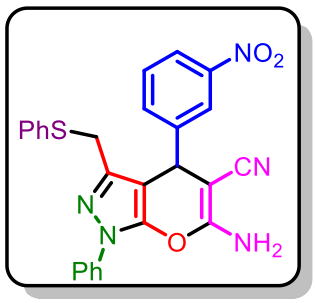
(300 MHz, DMSO-d_6) δ: 7.79 – 7.72 (m, 4H), 7.52 – 7.45 (m, 4H), 7.40 – 7.18 (m, 8H), 4.80 (s, 1H), 3.91 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.4, 149.6, 145.6, 145.2, 138.0, 136.2, 133.5, 130.2, 129.9, 129.8, 127.6, 127.1, 121.3, 120.5, 119.6, 110.9, 98.5, 58.0, 37.8, 30.7; ESI Calcd *m/z* 461, found 460 $[(M-1)]^+$; Anal. Calcd for: $C_{27}H_{19}N_5OS$: C, 70.26; H, 4.15; N, 15.17%; Found C, 70.28; H, 4.19; N, 15.20%; One of the –SCH_2 proton was merged with water peak.

6-amino-4-(4-ethoxyphenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6f). Isolated as white solid; R_f = 0.44 (3:7 EtOAc/pet. ether); mp 188–190 °C; ^{1}H



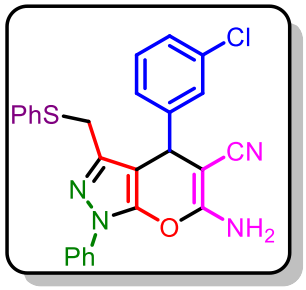
NMR (300 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.11 (m, 10H), 6.84 (d, *J* = 8.1 Hz, 2H), 4.58 (s, 1H), 3.98 – 3.87 (m, 3H), 1.29 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.0, 158.5, 145.8, 144.9, 138.1, 136.3, 135.9, 130.3, 129.8, 127.5, 127.1, 121.2, 115.2, 99.7, 39.5, 37.0, 30.7, 15.5; Anal. Calcd for: $C_{28}H_{24}N_4O_2S$: C, 69.98; H, 5.03; N, 11.66%; Found C, 69.95; H, 5.06; N, 11.69%; One of the ethyl –SCH_2 proton was merged with ethyl –CH_2 and another one –SCH_2 proton was merged with water peak.

6-amino-4-(3-nitrophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6g). Isolated as white solid; R_f = 0.32 (3:7 EtOAc/pet. ether); mp 192–194 °C; ^{1}H NMR



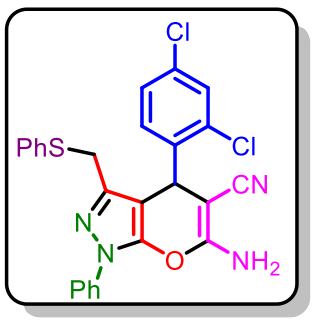
(300 MHz, DMSO-d_6) δ: 8.12 (d, *J* = 9.6 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 3H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.26 – 7.15 (m, 5H), 4.93 (s, 1H), 3.92 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.4, 148.8, 146.4, 145.6, 145.2, 138.0, 136.2, 135.8, 131.1, 130.2, 129.7, 127.6, 127.0, 123.3, 121.3, 120.5, 98.5, 58.1, 37.4, 30.7; Anal. Calcd for: $C_{26}H_{19}N_5O_3S$: C, 64.85; H, 3.98; N, 14.54%; Found C, 64.89; H, 4.01; N, 14.56%; One of the –SCH_2 proton was merged with water peak.

6-amino-4-(3-chlorophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6h). Isolated as white solid; R_f = 0.37 (3:7 EtOAc/pet. ether); mp 178–180 °C; ^{1}H

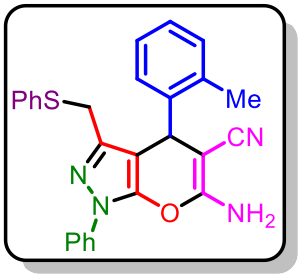


NMR (300 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.40 (m, 1H), 7.37 – 7.16 (m, 11H), 5.19 (s, 1H), 3.90 (d, *J* = 13.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 164.6, 149.5, 144.6, 142.1, 140.3, 137.4, 136.0, 134.7, 134.3, 133.9, 133.8, 132.7, 131.6, 131.1, 125.3, 124.4, 102.5, 61.6, 39.1, 34.7; ESI Calcd *m/z* 470, Found 471 $[(M+1)]^+$; Anal. Calcd for: $C_{26}H_{19}ClN_4OS$: C, 66.31; H, 4.07; Cl, 7.53; N, 11.90%; Found C, 66.35; H, 4.10; N, 11.89%; One of the –SCH_2 proton was merged with water peak.

6-amino-4-(2,4-dichlorophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6i). Isolated as white solid; R_f = 0.40 (3:7 EtOAc/pet. ether); mp 204–206 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.56-7.47 (m, 4H), 7.36 (s, 4H), 7.28 – 7.16 (m, 5H), 5.20 (s, 1H), 3.90 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 164.7, 149.5, 149.4, 143.9, 142.1, 140.3, 138.3, 137.5, 137.4, 134.3, 133.7, 133.6, 132.9, 131.7, 131.4, 125.3, 124.3, 102.1, 61.2, 38.7, 34.7; Anal. Calcd for: $C_{26}H_{18}Cl_2N_4OS$: C, 61.79; H, 3.59; N, 11.09%; Found C, 61.82; H, 3.62; N, 11.13%; One of the –SCH_2 proton was merged with water peak.

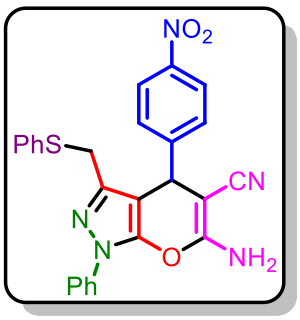


6-amino-1-phenyl-3-((phenylthio)methyl)-4-(o-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6j). Isolated as white solid; R_f = 0.40 (3: EtOAc/pet. ether); mp 170–172 °C; ^{1}H NMR



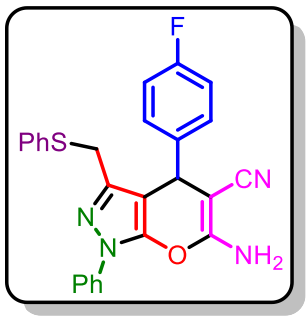
(300 MHz, DMSO-d_6) δ: 7.76 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.39 – 7.10 (m, 12H), 5.02 (s, 1H), 3.90 (d, *J* = 13.5 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 159.3, 144.8, 140.9, 137.4, 135.5, 129.5, 123.0, 128.8, 127.2, 126.9, 126.8, 126.3, 120.5, 120.0, 98.7, 58.0, 33.4, 30.0, 19.1; Anal. Calcd for: $C_{27}H_{22}N_4OS$: C, 71.98; H, 4.92; N, 12.44%; Found C, 71.96; H, 4.95; N, 12.47%; One of the –SCH_2 proton was merged with water peak.

6-amino-4-(4-nitrophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6k). Isolated as white solid; R_f = 0.32 (3:7 EtOAc/pet. ether); mp 208–210 °C; ^{1}H NMR



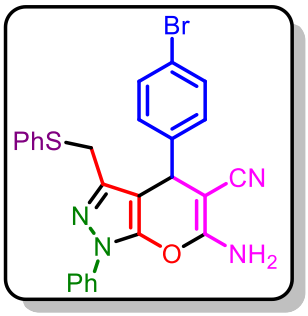
(300 MHz, DMSO-d_6) δ: 8.16 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.48 (m, 5H), 7.41 – 7.34 (m, 2H), 7.28 – 7.16 (m, 5H), 4.88 (s, 1H), 3.92 (d, *J* = 13.8 Hz, 1H), 3.50 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 159.7, 151.0, 146.9, 145.0, 144.5, 137.4, 135.6, 129.5, 129.1, 126.9, 129.1, 124.0, 120.7, 119.7, 97.7, 57.4, 36.9, 30.1; Anal. Calcd for: $C_{26}H_{19}N_5O_3S$: C, 64.85; H, 3.98; N, 14.54%; Found C, 64.88; H, 3.96; N, 14.57%.

6-amino-4-(4-fluorophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6l). Isolated as white solid; R_f = 0.43 (3:7 EtOAc/pet. ether); mp 180–182 °C; ^{1}H

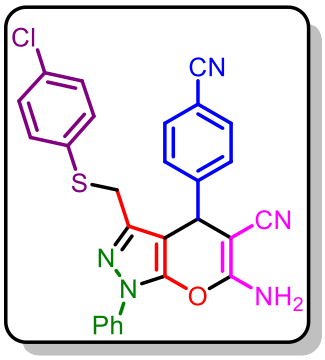


NMR (300 MHz, DMSO-d_6) δ: 7.73 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.24 (m, 10H), 7.21 – 7.10 (m, 3H), 4.69 (s, 1H), 3.91 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 159.4, 145.0, 144.3, 139.6, 137.4, 135.6, 130.0, 129.9, 129.5, 129.1, 126.8, 126.4, 120.5, 119.9, 115.6, 15.3, 98.6, 58.2, 36.4, 30.0; ESI Calcd *m/z* 454, Found 453 $[(M-1)]^+$; Anal. Calcd for: $C_{26}H_{19}FN_4OS$: C, 68.71; H, 4.21; N, 12.33%; Found C, 68.75; H, 4.24; N, 12.36%; One of the –SCH_2 proton was merged with water peak.

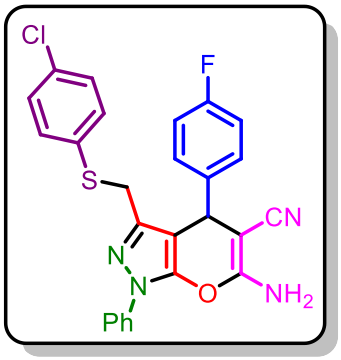
6-amino-4-(4-bromophenyl)-1-phenyl-3-((phenylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6m). Isolated as white solid; R_f = 0.43 (3:7 EtOAc/pet. ether); mp 196–198 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.73 (d, *J* = 8.1 Hz, 2H), 7.49 (t, *J* = 6.6 Hz, 3H), 7.37 – 7.20 (m, 10H), 4.67 (s, 1H), 3.91 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 159.5, 145.0, 144.3, 142.8, 137.4, 135.6, 131.7, 130.3, 129.5, 129.1, 126.8, 126.4, 120.6, 119.9, 98.3, 57.9, 36.6, 30.1; Anal. Calcd for: $C_{26}H_{19}BrN_4OS$: C, 60.59; H, 3.72; N, 10.87%; Found C, 60.62; H, 3.75; N, 10.85%; One of the –SCH_2 proton was merged with water peak.



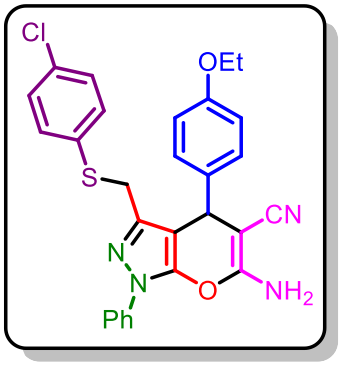
6-amino-3-(((4-chlorophenyl)thio)methyl)-4-(4-cyanophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6n). Isolated as white solid; R_f = 0.31 (3:7 EtOAc/pet. ether); mp 200–202 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.79 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.56 – 7.50 (m, 4H), 7.41 – 7.34 (m, 5H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.87 (s, 1H), 3.95 (d, *J* = 14.1 Hz, 1H), 3.53 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 159.6, 149.0, 144.5, 137.3, 134.6, 132.8, 131.1, 130.6, 129.5, 129.2, 128.9, 126.9, 120.7, 119.8, 118.9, 110.2, 97.7, 57.3, 37.0, 29.9; ESI Calcd *m/z* 495, Found 494 $[(M-1)]^+$; Anal. Calcd for: $C_{27}H_{18}ClN_5OS$: C, 65.38; H, 3.66; N, 14.12%; Found C, 65.41; H, 3.69; N, 14.15%.



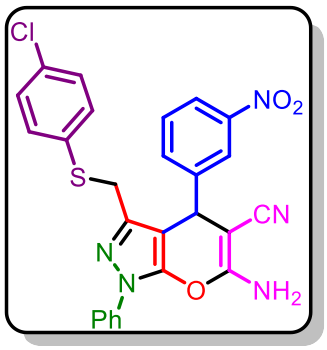
6-amino-3-(((4-chlorophenyl)thio)methyl)-4-(4-fluorophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6o). Isolated as white solid; R_f = 0.40 (3:7 EtOAc/pet. ether); mp 182–184 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.25 (m, 10H), 7.14 (t, *J* = 8.7 Hz, 2H), 4.73 (s, 1H), 3.92 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 159.4, 144.7, 144.3, 139.6, 137.4, 134.7, 131.1, 130.6, 130.0, 129.9, 129.5, 128.9, 126.8, 120.6, 119.9, 115.6, 115.4, 98.6, 58.2, 36.3, 30.0; Anal. Calcd for: $C_{26}H_{18}ClFN_4OS$: C, 63.87; H, 3.71; N, 11.46%; Found C, 63.89; H, 3.74; N, 11.44%; One of the –SCH_2 proton was merged with water peak.



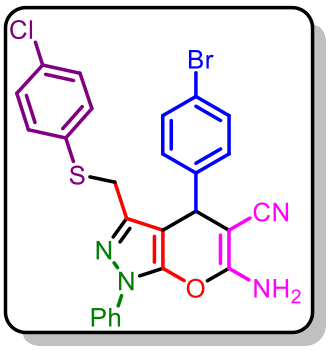
6-amino-3-(((4-chlorophenyl)thio)methyl)-4-(4-ethoxyphenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6p). Isolated as white solid; R_f = 0.43 (3:7 EtOAc/pet. ether); mp 184–186 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.20 (m, 9H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.62 (s, 1H), 4.01 – 3.88 (m, 3H), 1.30 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.0, 158.5, 145.5, 144.9, 138.1, 135.8, 135.5, 131.7, 131.3, 130.2, 129.7, 127.5, 121.2, 120.7, 115.2, 99.7, 63.8, 59.4, 37.0, 30.7, 15.5; Anal. Calcd for: $C_{28}H_{23}ClN_4O_2S$: C, 65.30; H, 4.50; N, 10.88%; Found C, 65.32; H, 4.54; N, 10.86%; One of the ethyl –SCH_2 proton was merged with ethyl –CH_2 and another one –SCH_2 proton was merged with water peak.



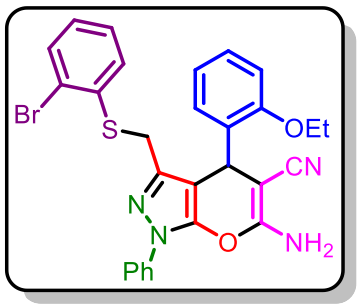
6-amino-3-(((4-chlorophenyl)thio)methyl)-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6q). Isolated as white solid; R_f = 0.31 (3:7 EtOAc/pet. ether); mp 186–188 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.14 (s, 1H), 7.78 (t, *J* = 9.6 Hz, 3H), 7.65 (t, *J* = 8.7 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.44 (s, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.01 (s, 1H), 3.97 (d, *J* = 13.8 Hz, 1H), 3.61 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 158.7, 147.1, 144.7, 143.6, 143.5, 136.3, 134.0, 133.6, 130.1, 129.6, 129.4, 128.5, 127.8, 125.9, 121.6, 121.5, 119.7, 118.7, 96.8, 56.5, 35.7, 29.0; ESI Calcd *m/z* 515, found 514 $[(M-1)]^+$; Anal. Calcd for: $C_{26}H_{18}ClN_5O_3S$: C, 60.52; H, 3.52; N, 13.57%; Found C, 60.56; H, 3.50; N, 13.61%.



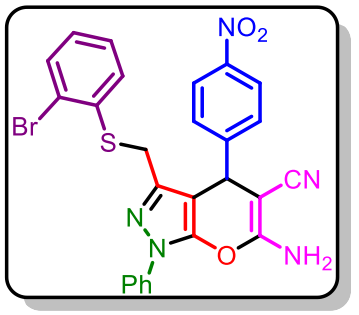
6-amino-4-(4-bromophenyl)-3-(((4-chlorophenyl)thio)methyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6r). Isolated as white solid; R_f = 0.45 (3:7 EtOAc/pet. ether); mp 208–210 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.72 (d, *J* = 6.9 Hz, 2H), 7.50 (d, *J* = 6.3 Hz, 5H), 7.34 – 7.21 (m, 8H), 4.71 (s, 1H), 3.92 (d, *J* = 13.8 Hz, 1H), 3.46 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ: 160.2, 145.4, 145.1, 143.5, 132.4, 131.8, 131.4, 131.0, 130.2, 129.7, 127.6, 121.3, 120.6, 99.0, 58.6, 37.3, 30.7; ESI Calcd *m/z* 548, found 549 $[(M+1)]^+$; Anal. Calcd for: $C_{26}H_{18}BrClN_4OS$: C, 56.79; H, 3.30; N, 10.19%; Found C, 56.82; H, 3.34; N, 10.21%.



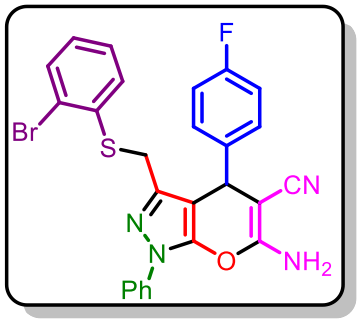
6-amino-3-(((2-bromophenyl)thio)methyl)-4-(2-ethoxyphenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6s). Isolated as white solid; R_f = 0.38 (3:7 EtOAc/pet. ether); mp 184–186 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.75 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.48 (m, 4H), 7.35 – 7.08 (m, 8H), 6.94 – 6.84 (m 2H), 4.94 (s, 1H), 3.96 – 3.86 (m, 3H), 1.15 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.9, 157.3, 145.4, 144.6, 138.2, 133.4, 131.1, 130.2, 130.3, 130.2, 129.5, 129.5, 128.9, 128.6, 127.7, 127.4, 122.6, 121.3, 121.0, 113.2, 99.7, 64.1, 58.0, 29.5, 15.3; Anal. Calcd for: $C_{28}H_{23}BrN_4O_2S$: C, 60.11; H, 4.14; Br, N, 10.01%; Found C, 60.14; H, 4.18; Br, N, 10.03%; One of the ethyl –SCH_2 proton was merged with ethyl –CH_2 and another one –SCH_2 proton was merged with water peak.



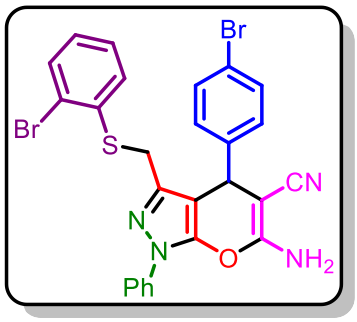
6-amino-3-(((2-bromophenyl)thio)methyl)-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6t). Isolated as white solid; R_f = 0.30 (3:7 EtOAc/pet. ether); mp 192–194 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.11 (d, J = 8.4 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.555 – 7.38 (m, 10H), 7.06 (t, *J* = 6.0 Hz, 1H), 4.93 (s, 1H), 3.96 (d, *J* = 13.8 Hz, 1H), 3.70 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.4, 151.7, 147.6, 145.3, 144.9, 138.0, 197.8, 133.4, 130.2, 130.1, 128.9, 127.8, 127.7, 124.7, 122.7, 121.4, 120.3, 98.6, 58.0, 37.6, 29.7; ESI Calcd *m/z* 559, found 558 $[(M-1)]^+$; Anal. Calcd for: $C_{26}H_{18}BrN_5O_3S$: C, 55.72; H, 3.24; N, 12.50%; Found C, 55.75; H, 3.21; N, 12.54%.



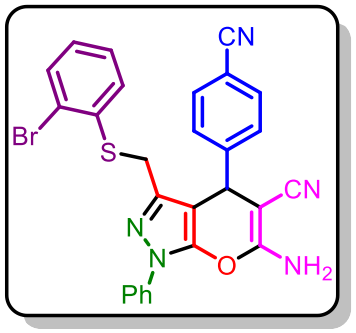
6-amino-3-(((2-bromophenyl)thio)methyl)-4-(4-fluorophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6u). Isolated as white solid; R_f = 0.43 (3:7 EtOAc/pet. ether); mp 180–182 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.74 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.48 (m, 4H), 7.35 – 7.28 (m, 6H), 7.14 – 7.06 (m, 3H), 4.73 (s, 1H), 3.95 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.1, 145.0, 144.9, 140.2, 138.1, 137.9, 133.5, 130.7, 130.3, 130.0, 129.0, 127.9, 127.6, 122.9, 121.4, 120.7, 116.4, 116.1, 112.9, 99.5, 58.9, 37.1, 29.8; Anal. Calcd for: $C_{26}H_{18}BrFN_4OS$: C, 58.54; H, 3.40; N, 10.50%; Found C, 58.57; H, 3.44; N, 10.52%; One of the –SCH_2 proton was merged with water peak.



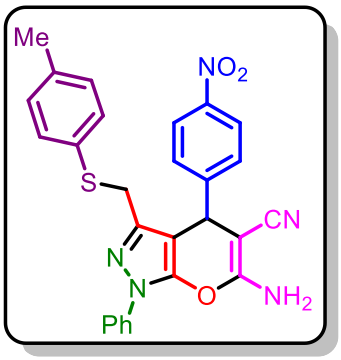
6-amino-4-(4-bromophenyl)-3-(((2-bromophenyl)thio)methyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6v). Isolated as white solid; R_f = 0.38 (3:7 EtOAc/pet. ether); mp 196—198 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.74 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 3.6 Hz, 2H), 7.53 – 7.46 (m, 4H), 7.37 – 7.31 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.11 – 7.06 (m, 1H), 4.71 (s, 1H), 3.96 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.2, 145.0, 144.8, 143.4, 138.0, 137.8, 135.9, 133.4, 132.4, 130.9, 130.2, 130.0, 128.9, 128.2, 127.9, 127.6, 122.8, 121.3, 120.6, 112.9, 99.1, 58.5, 37.3, 29.7; ESI Calcd *m/z* 592, found 593 $[(M+1)]^+$; Anal. Calcd for: $C_{26}H_{18}Br_2N_4OS$: C, 52.54; H, 3.05; N, 9.43%; Found C, 52.52; H, 3.09; N, 9.47%; One of the –SCH_2 proton was merged with water peak.



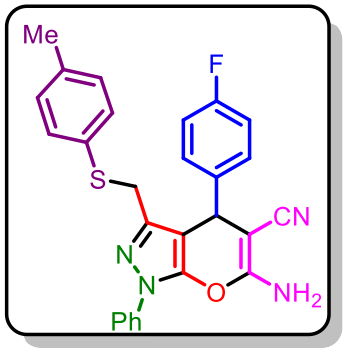
6-amino-3-(((2-bromophenyl)thio)methyl)-4-(4-cyanophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6w). Isolated as white solid; R_f = 0.30 (3:7 EtOAc/pet. ether); mp 194–196 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.76 – 7.72 (m, 4H), 7.57 – 7.45 (m, 5H), 7.38 – 7.32 (m, 4H), 7.10 – 7.05 (m, 1H), 4.84 (s, 1H), 3.95 (d, *J* = 13.8 Hz, 1H), 3.65 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.4, 149.6, 145.3, 144.9, 138.0, 137.8, 133.5, 130.2, 129.8, 129.1, 129.0, 127.9, 127.7, 122.9, 121.5, 120.3, 119.6, 111.0, 98.7, 58.1, 37.8, 29.8; ESI Calcd *m/z* 539, found 538 $[(M-1)]^+$; Anal. Calcd for: $C_{27}H_{18}BrN_5OS$: C, 60.01; H, 3.36; N, 12.96%; Found C, 60.04; H, 3.38; N, 12.94%.



6-amino-4-(4-nitrophenyl)-1-phenyl-3-((p-tolylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6x). Isolated as white solid; R_f = 0.29 (3:7 EtOAc/pet. ether); mp 210–212 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.16 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.54 – 7.47 (m, 4H), 7.40 – 7.35 (m, 3H), 7.12 (d, J=8.1 Hz, 2H), 7.06 (d, J=8.4 Hz, 2H), 4.80 (s, 1H), 3.85 (d, *J* = 13.8 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 160.4, 151.7, 147.5, 145.8, 145.1, 138.0, 137.0, 132.3, 130.7, 130.4, 130.2, 130.1, 127.6, 124.7, 121.3, 120.4, 98.4, 57.9, 37.5, 31.4, 21.4; ESI Calcd *m/z* 495, found 494 $[(M-1)]^+$; Anal. Calcd for: $C_{27}H_{21}N_5O_3S$: C, 65.44; H, 4.27; N, 14.13%; Found C, 65.48; H, 4.31; N, 14.09%; One of the –SCH_2 proton was merged with water peak.

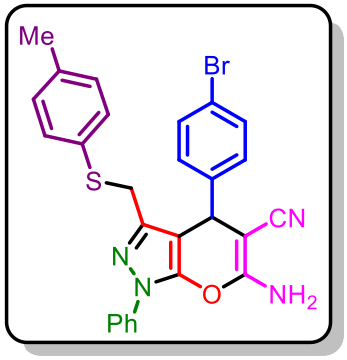


6-amino-4-(4-fluorophenyl)-1-phenyl-3-((p-tolylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6y). Isolated as white solid; R_f = 0.34 (3:7 EtOAc/pet. ether); mp 186–188 °C; ^{1}H NMR



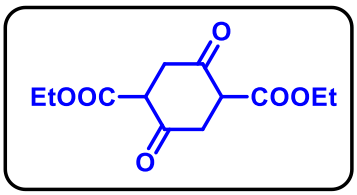
(300 MHz, DMSO-d$_6$) δ: 7.71 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.25 (m, 6H), 7.16 – 7.07 (m, 5H), 4.60 (s, 1H), 3.83 (d, *J* = 13.2 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ: 160.1, 145.8, 144.9, 140.3, 138.1, 137.0, 132.4, 130.8, 130.4, 130.2, 127.5, 121.2, 120.6, 116.3, 116.0, 99.3, 59.0, 37.0, 31.5, 21.4; ESI Calcd m/z 468, found 467 $[(M-1)]^+$; Anal. Calcd for: $C_{27}H_{21}FN_4OS$: C, 69.21; H, 4.52; N, 11.96%; Found C, 69.25; H, 4.56; N, 11.98%; One of the –SCH_2 proton was merged with water peak.

6-amino-4-(4-bromophenyl)-1-phenyl-3-((p-tolylthio)methyl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (6z). Isolated as white solid; R_f = 0.34 (3:7 EtOAc/pet. ether); mp 206–208 °C; ^{1}H

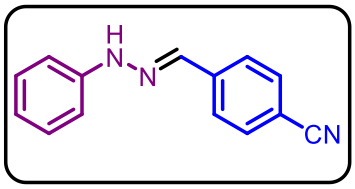


NMR (300 MHz, DMSO-d$_6$) δ: 7.71 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.36 – 7.29 (m, 3H), 7.20 – 7.07 (m, 7H), 4.59 (s, 1H), 3.84 (d, *J* = 13.8 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ: 160.2, 145.8, 145.0, 143.6, 138.1, 137.0, 132.4, 131.0, 130.9, 130.5, 130.2, 127.5, 121.2, 120.6, 98.9, 58.6, 37.2, 31.5, 21.4; ESI Calcd *m/z* 528, found 527 $[(M-1)]^+$; Anal. Calcd for: $C_{27}H_{21}BrN_4OS$: C, 61.25; H, 4.00; N, 10.58%; Found C, 61.28; H, 4.04; N, 10.61%; One of the –SCH_2 proton was merged with water peak.

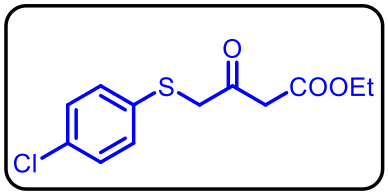
Diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (A_1). Isolated as yellowish crystalline solid; R_f = 0.88 (3:7 EtOAc/pet. ether); mp 126–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.21 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 4H), 3.18 (s, 4H), 1.32 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.3, 168.4, 93.2, 60.7, 28.5, 14.2; HRMS (ESI) m/z calcd for $C_{12}H_{16}O_6$ 257.1025 $[M + H]^+$, found 257.1026 $[M + H]^+$.



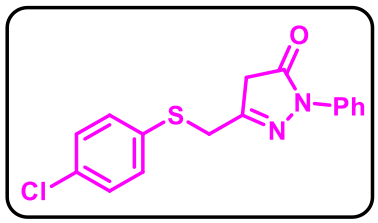
(E)-4-((2-phenylhydrazono)methyl)benzonitrile (B). Isolated as yellowish solid; R_f = 0.58 (3:7 EtOAc/pet. ether); mp 152–154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.01 (s, 1H), 7.67 (d, *J* = 6.3 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 3H), 7.27 (d, *J* = 7.1 Hz, 2H), 7.11 (d, *J* = 6.7 Hz, 2H), 6.91 (t, *J* = 6.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.2, 140.3, 134.7, 132.8, 129.8, 126.6, 121.4, 119.6, 113.4, 111.1; HRMS (ESI) m/z calcd for $C_{14}H_{11}N_3$ 222.1031 $[M + H]^+$, found 221.1028 $[M + H]^+$.



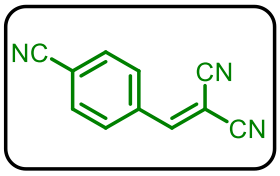
Ethyl 4-((4-chlorophenyl)thio)-3-oxobutanoate (I). Isolated as yellowish liquid; R_f = 0.75 (3:7 EtOAc/pet. ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.29 – 7.26 (m, 4H), 4.21 (q, *J*= 7.1 Hz, 2H), 3.80 (s, 2H), 3.62 (s, 2H), 1.28 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.9, 167.3, 133.8, 132.9, 131.7, 129.8, 62.0, 46.9, 44.4, 14.4.



5-(((4-chlorophenyl)thio)methyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (II). Isolated as brown solid; R_f = 0.81 (3:7 EtOAc/pet. ether); mp 89–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 3.90 (s, 2H), 3.54 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.6, 155.8, 138.1, 134.0, 132.7, 132.2, 129.9, 129.3, 125.8, 119.4, 40.8, 34.8; HRMS (ESI) m/z calcd for $C_{16}H_{13}ClN_2OS$ 317.0515 $[M + H]^+$, found 317.0514 $[M + H]^+$.



2-(4-cyanobenzylidene)malononitrile (III). Isolated as white solid; R_f = 0.85 (3:7 EtOAc/pet. ether); mp 154–156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ: 158.6, 134.8, 133.4, 133.3, 131.2, 131.1, 117.8, 117.1, 113.3, 112.2, 86.5. One of the proton was merged with aromatic proton.



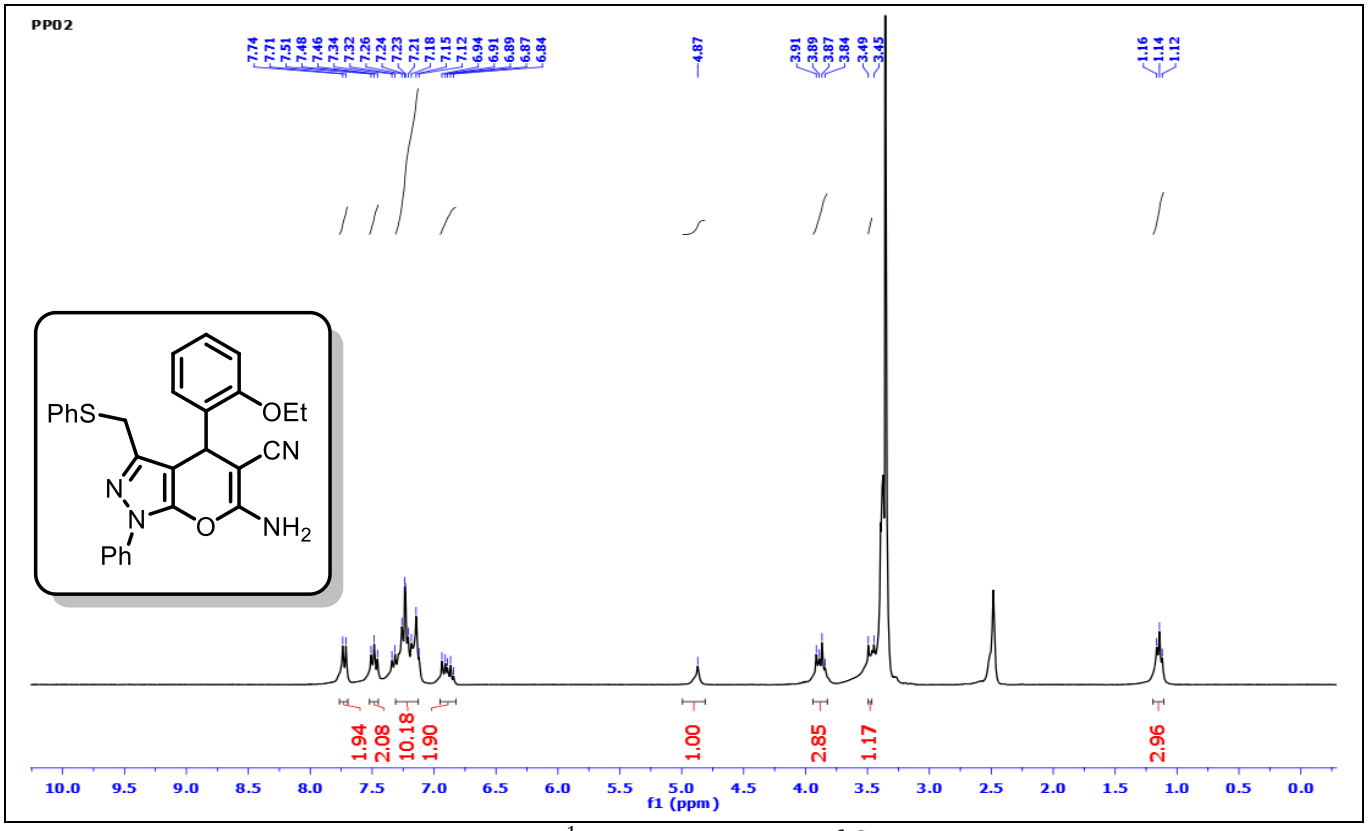


Fig.1. ^{1}H-NMR spectrum of **6a**

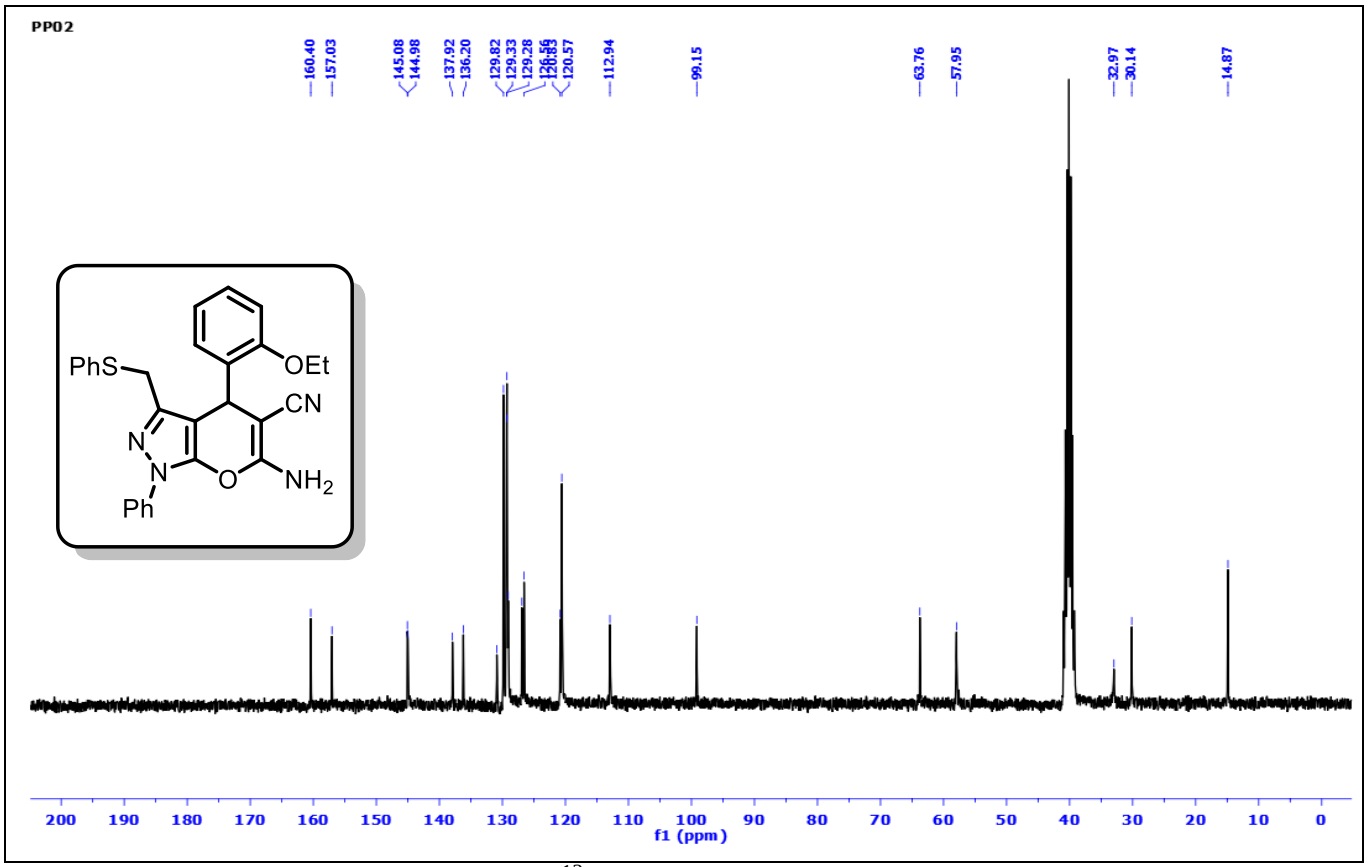


Fig.2. ^{13}C-NMR spectrum of **5a**

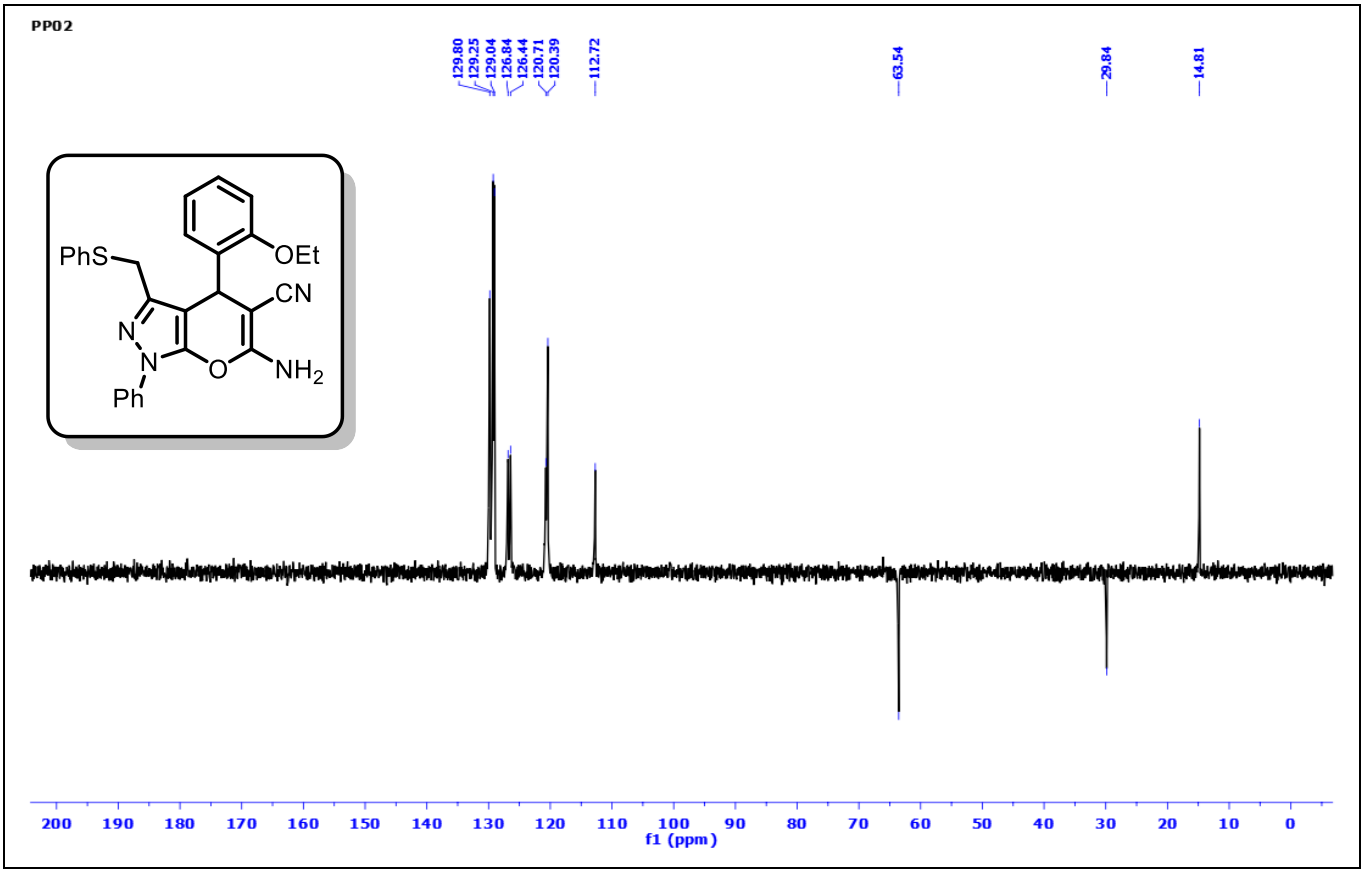


Fig.3. DEPT-135 spectrum of **6a**

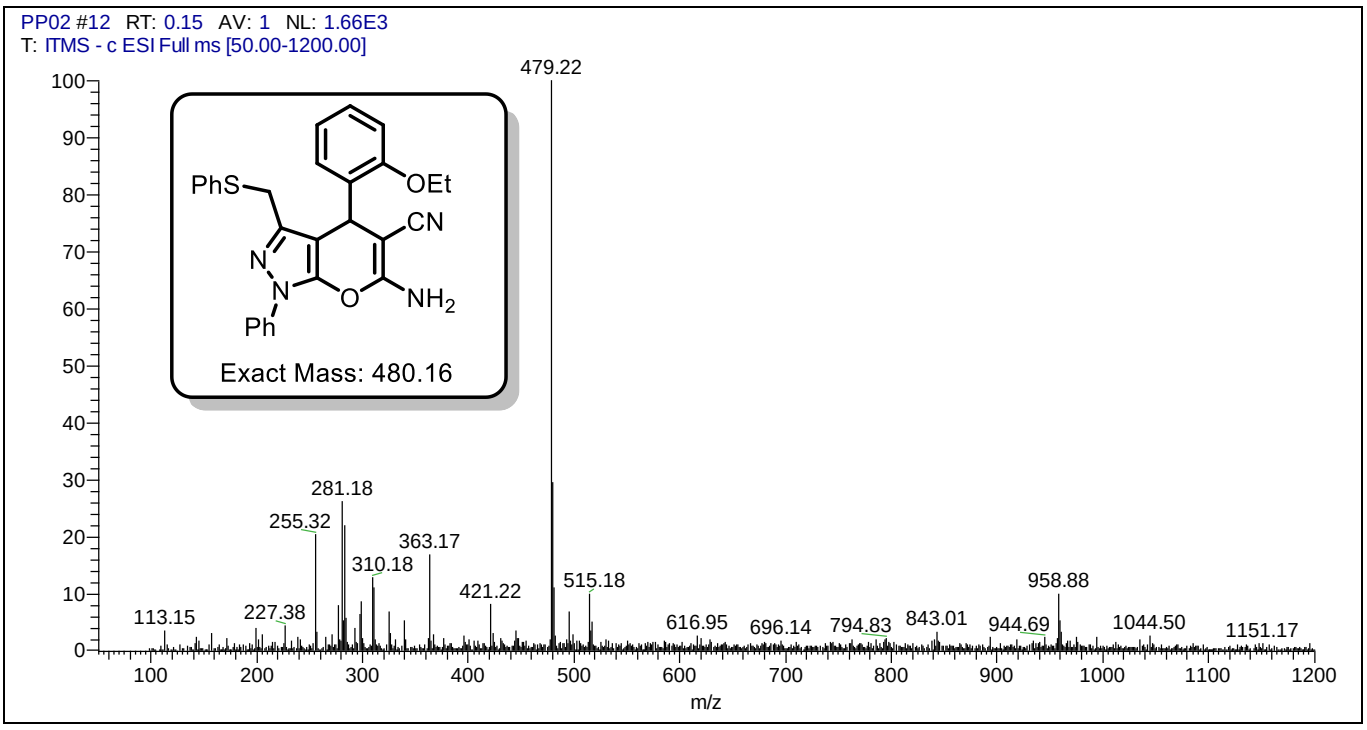


Fig.4. ESI Mass spectra of compound **6a**

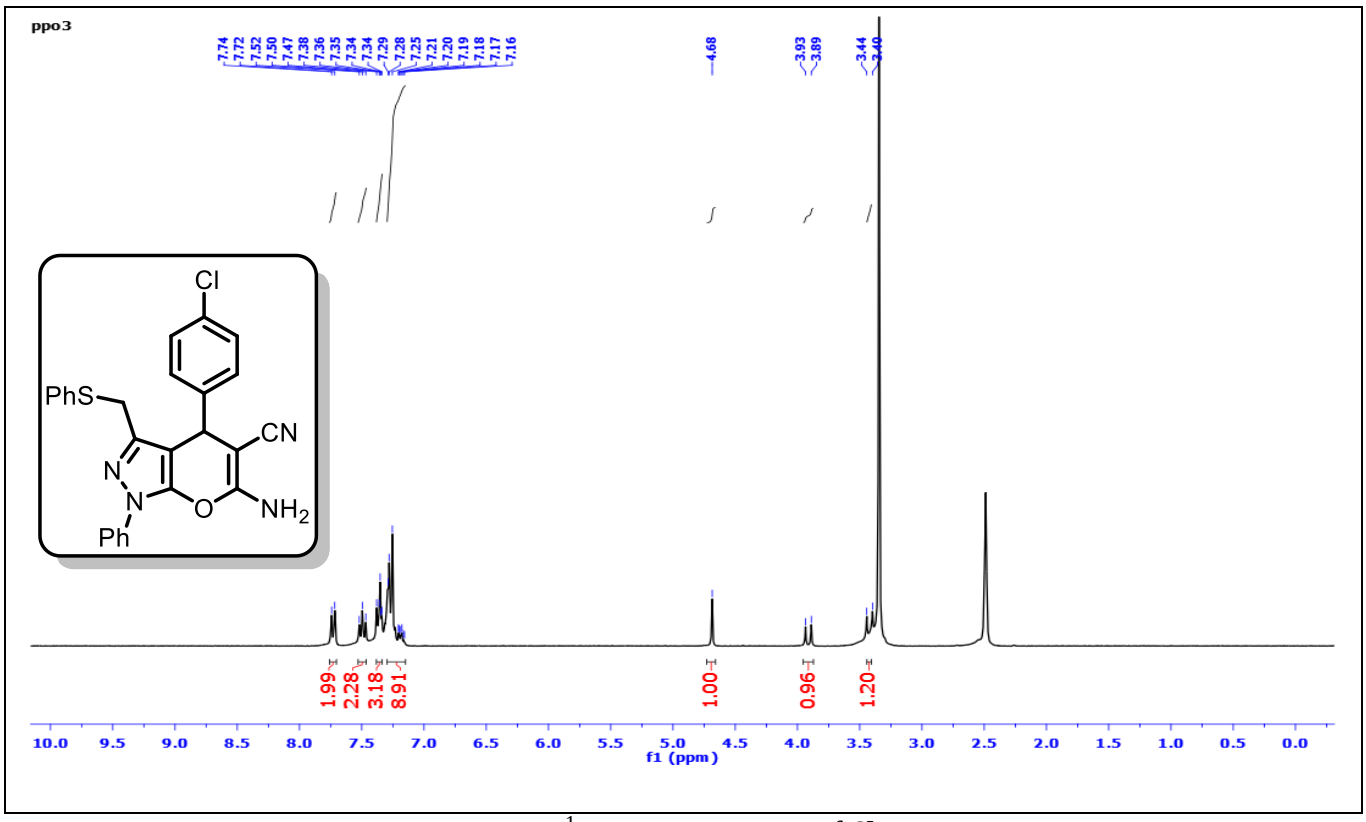


Fig.5. ^{1}H-NMR spectrum of **6b**

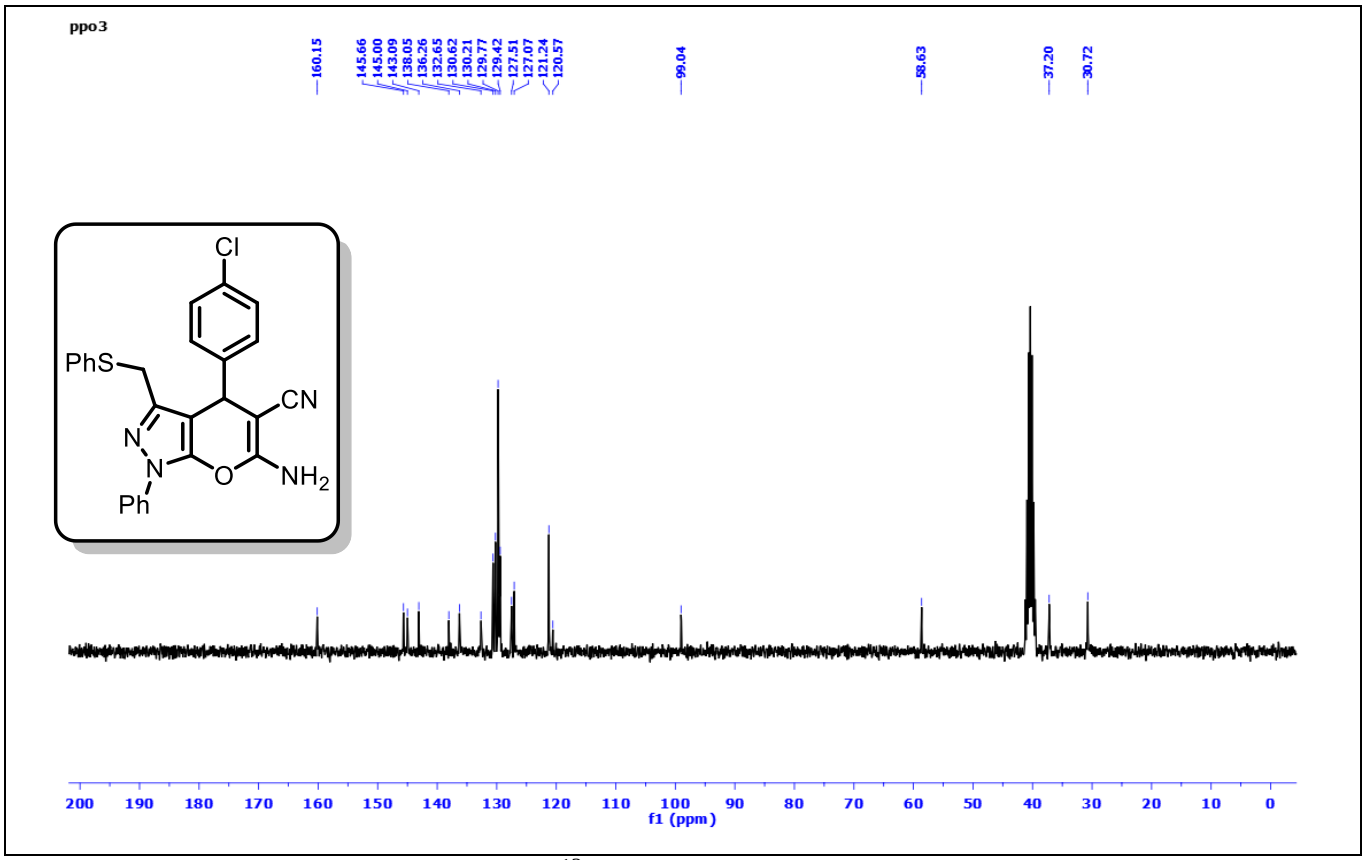


Fig.6. ^{13}C-NMR spectrum of **6b**

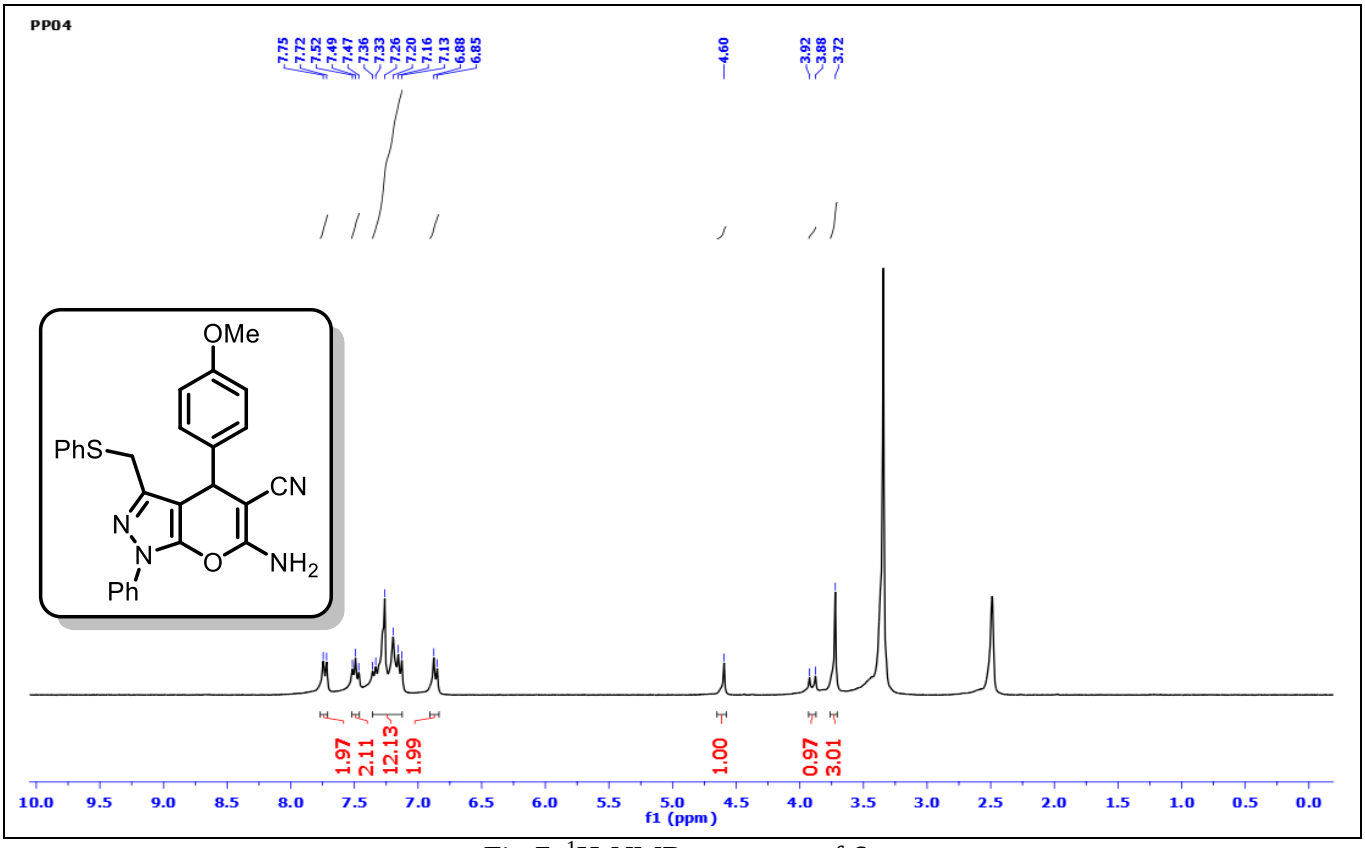


Fig.7. ^{1}H-NMR spectrum of **6c**

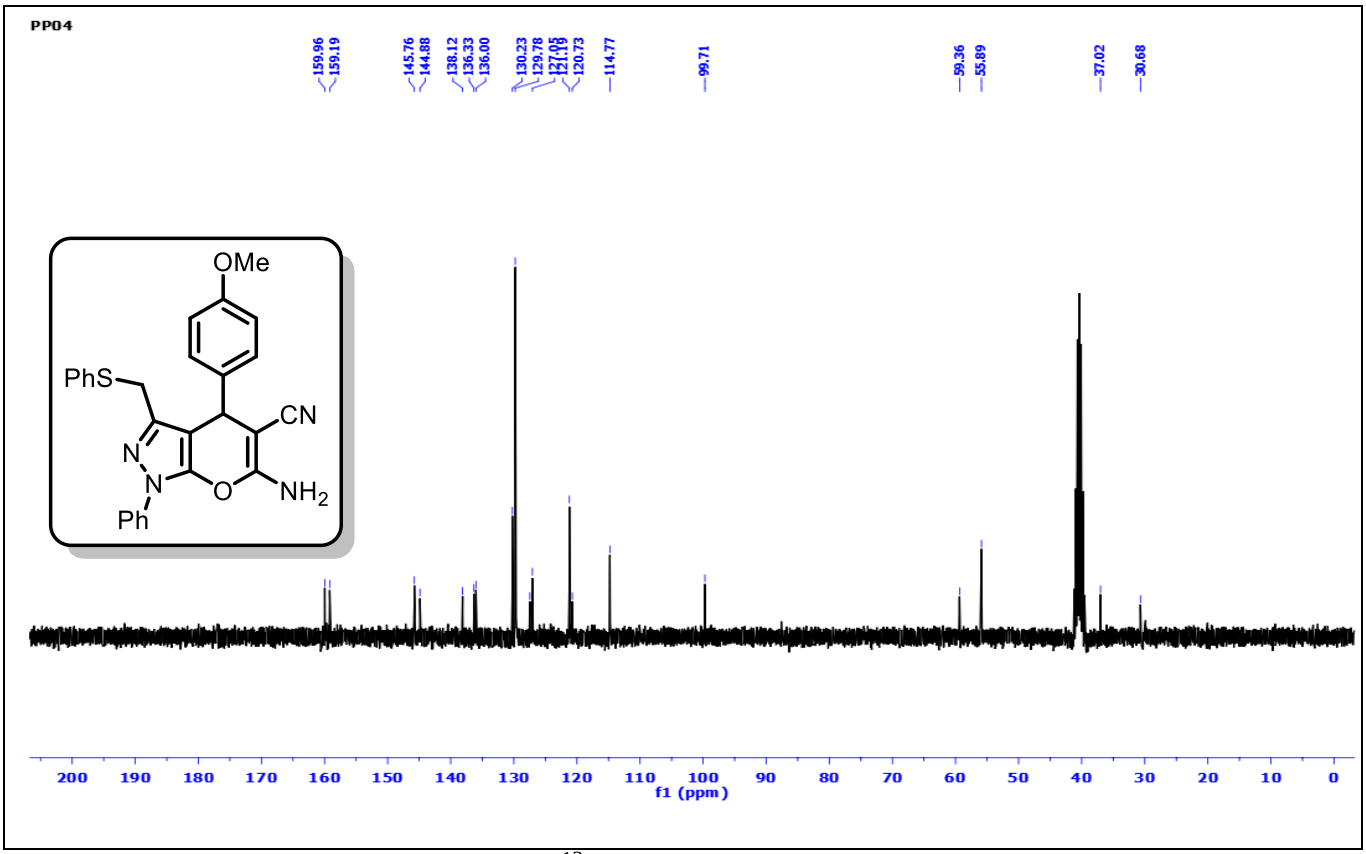


Fig.8. ^{13}C-NMR spectrum of **6c**

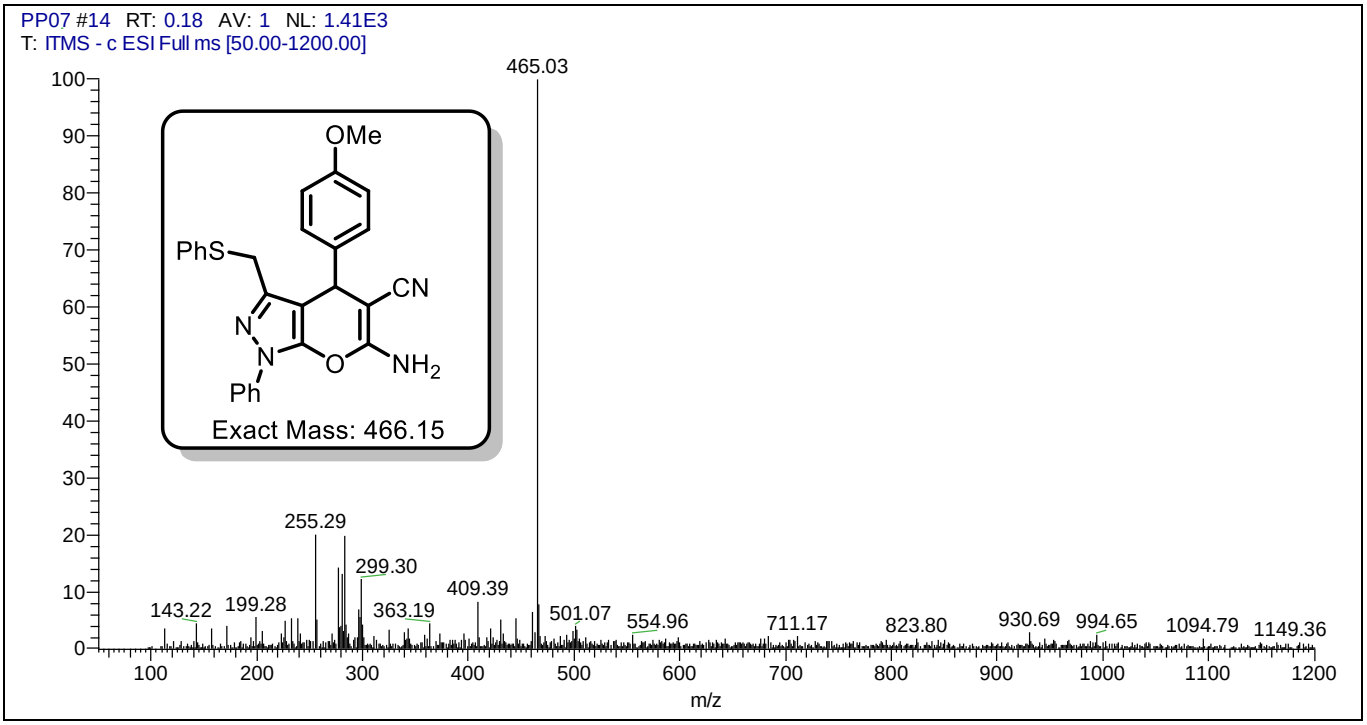


Fig.9. ESI Mass spectra of compound **6c**

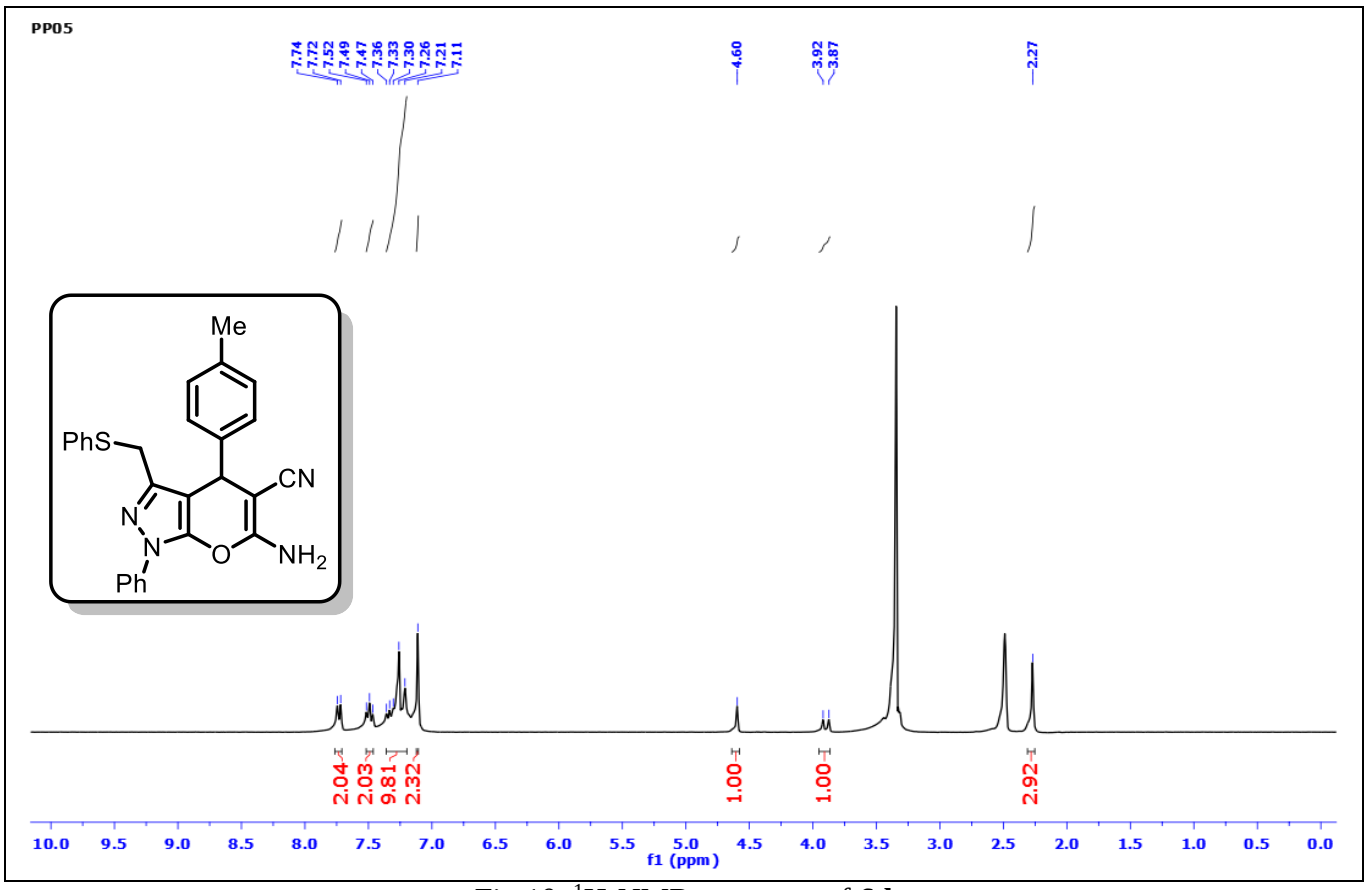


Fig.10. ^{1}H-NMR spectrum of **6d**

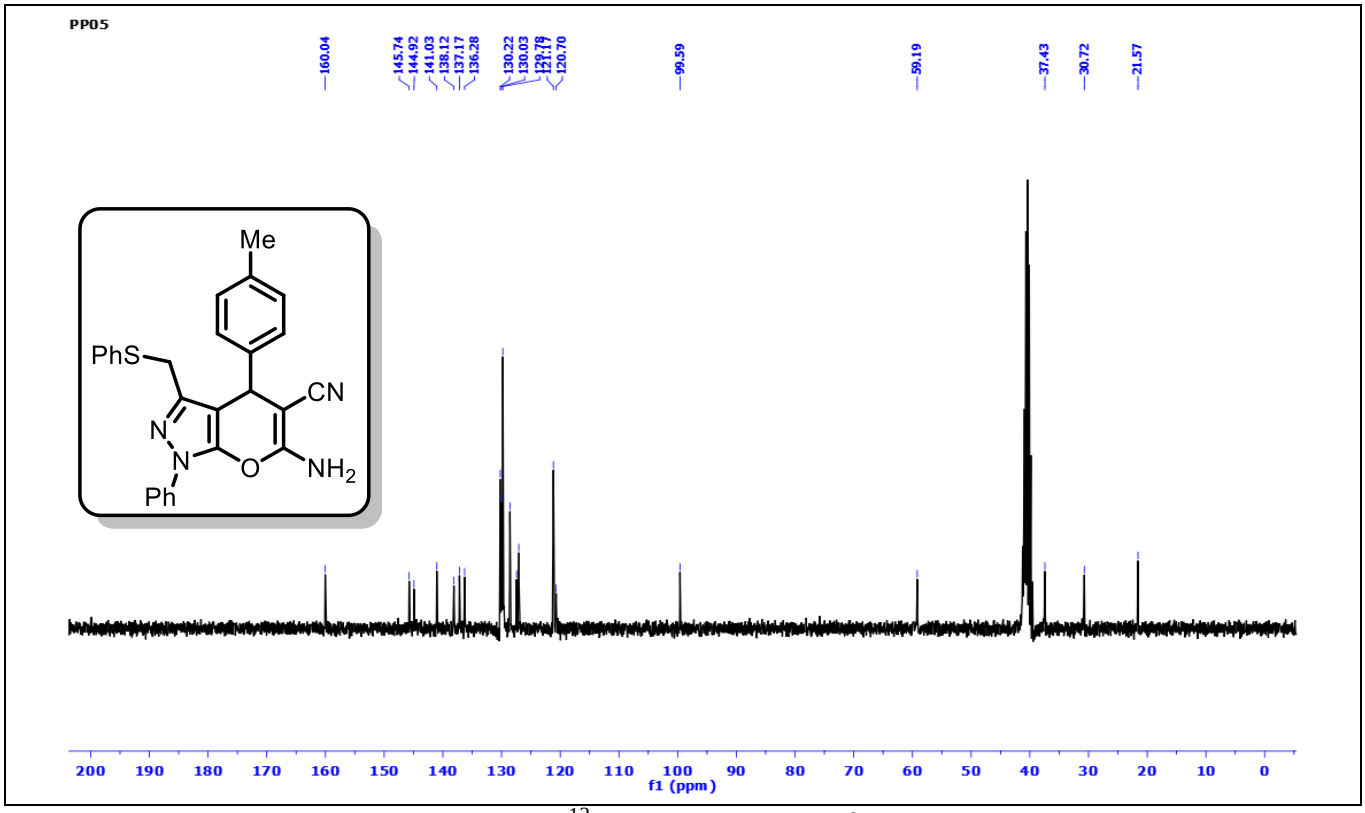


Fig.11. ^{13}C-NMR spectrum of **6d**

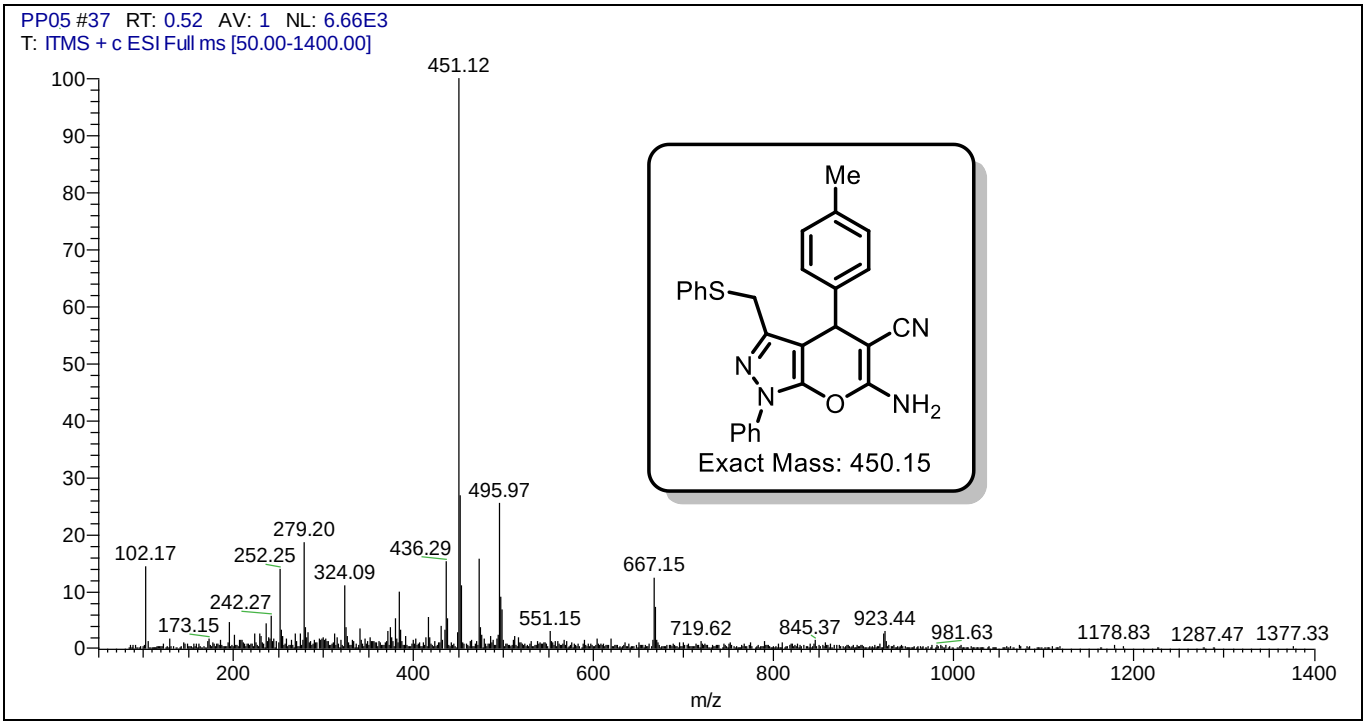


Fig.12. ESI Mass spectra of compound **6d**

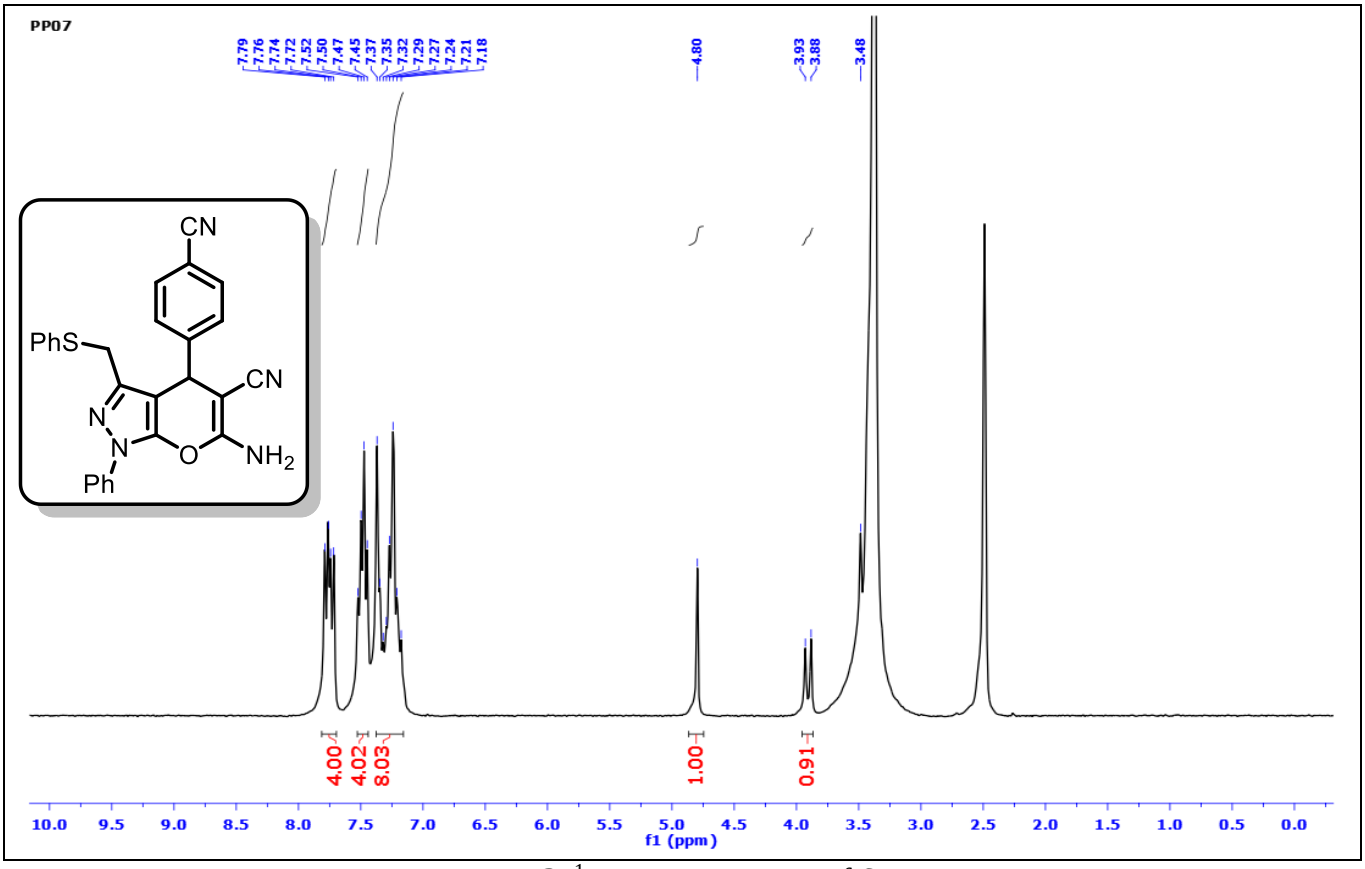


Fig.13. ^{1}H-NMR spectrum of **6e**

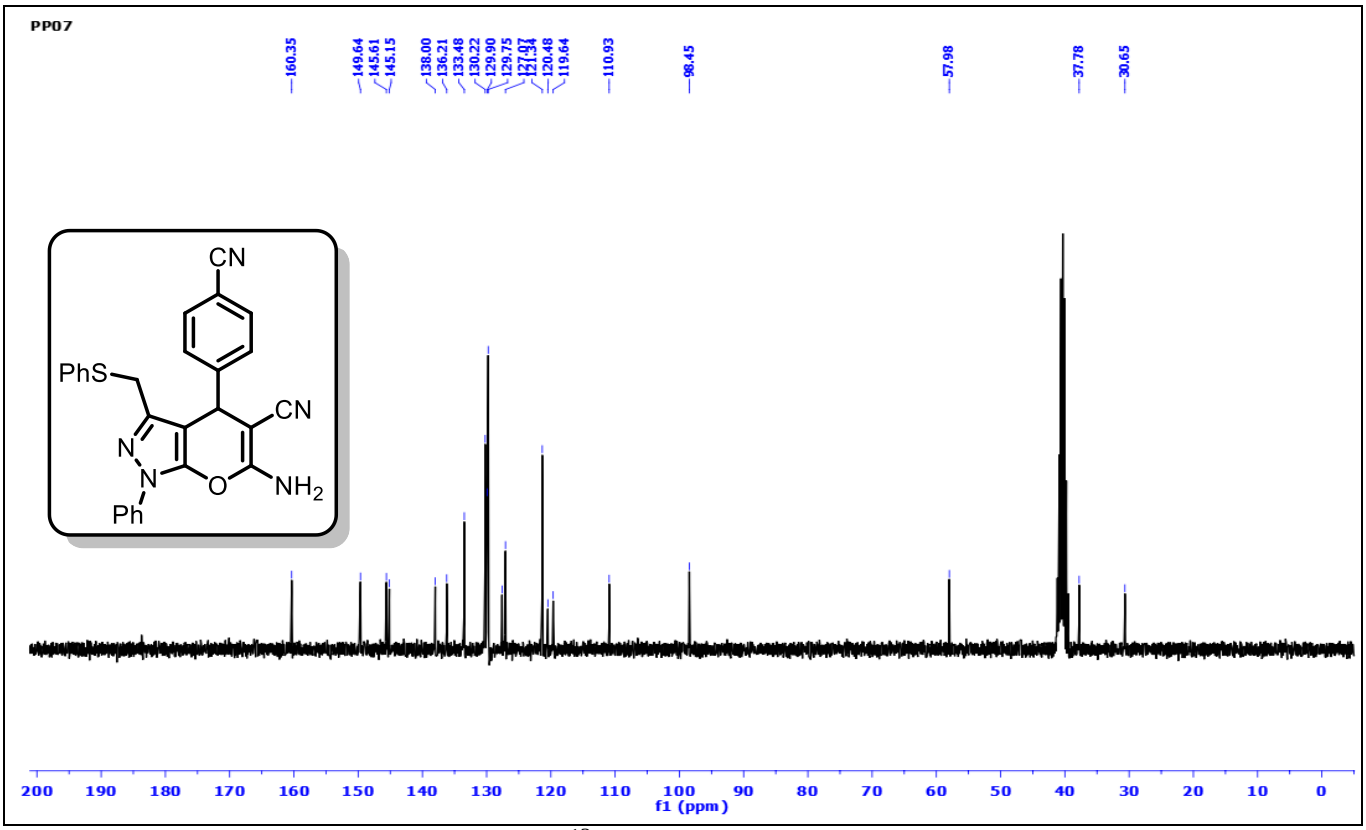


Fig.14. ^{13}C-NMR spectrum of **6e**

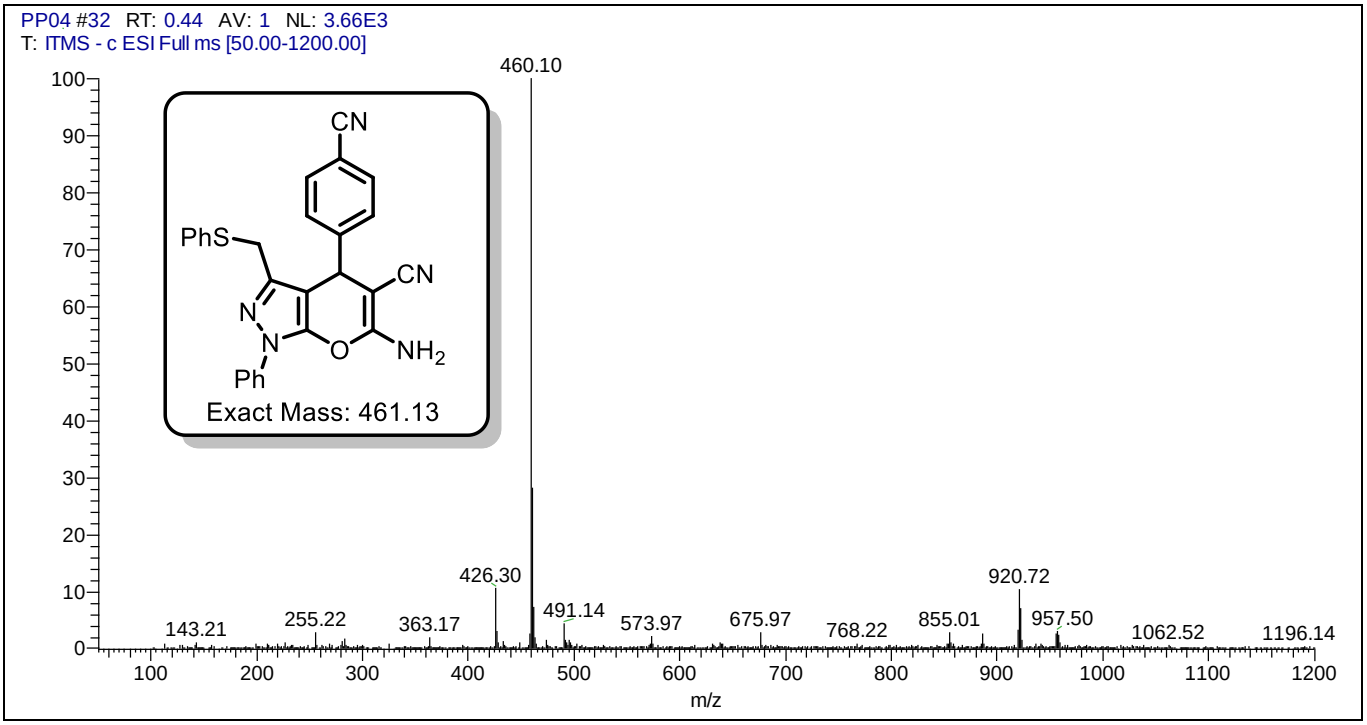


Fig.15. ESI Mass spectra of compound **6e**

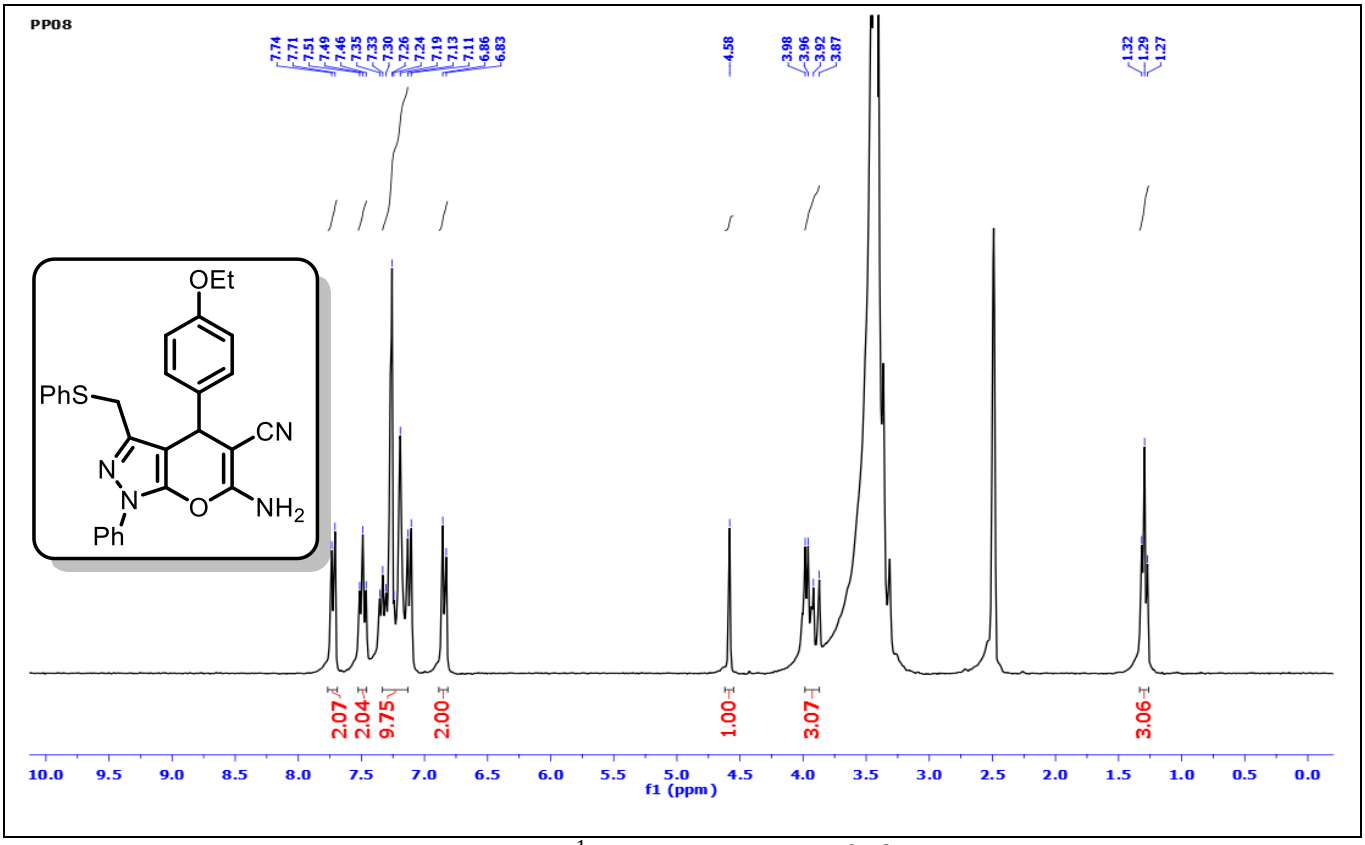


Fig.16. ^{1}H-NMR spectrum of **6f**

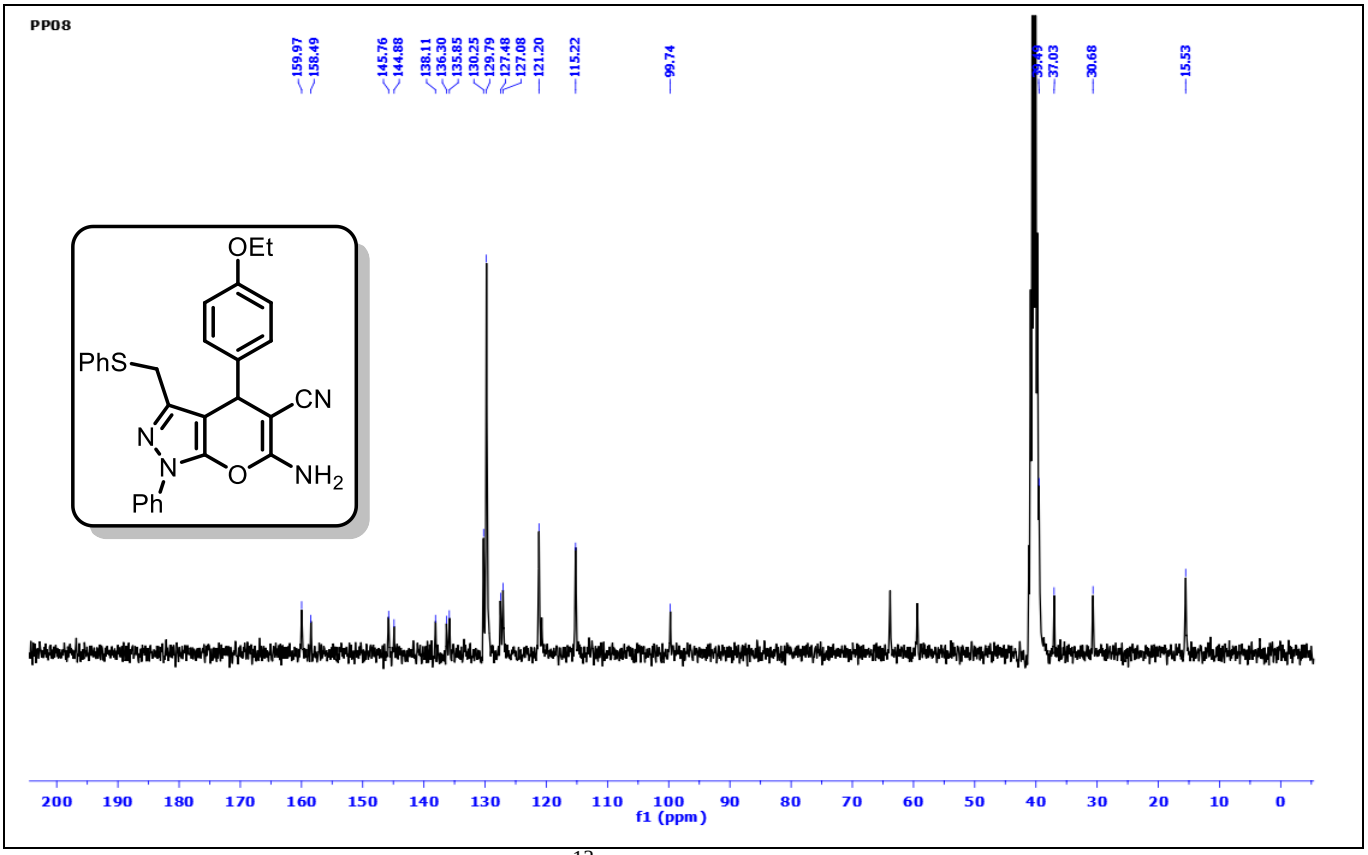


Fig.17. ^{13}C-NMR spectrum of **6f**

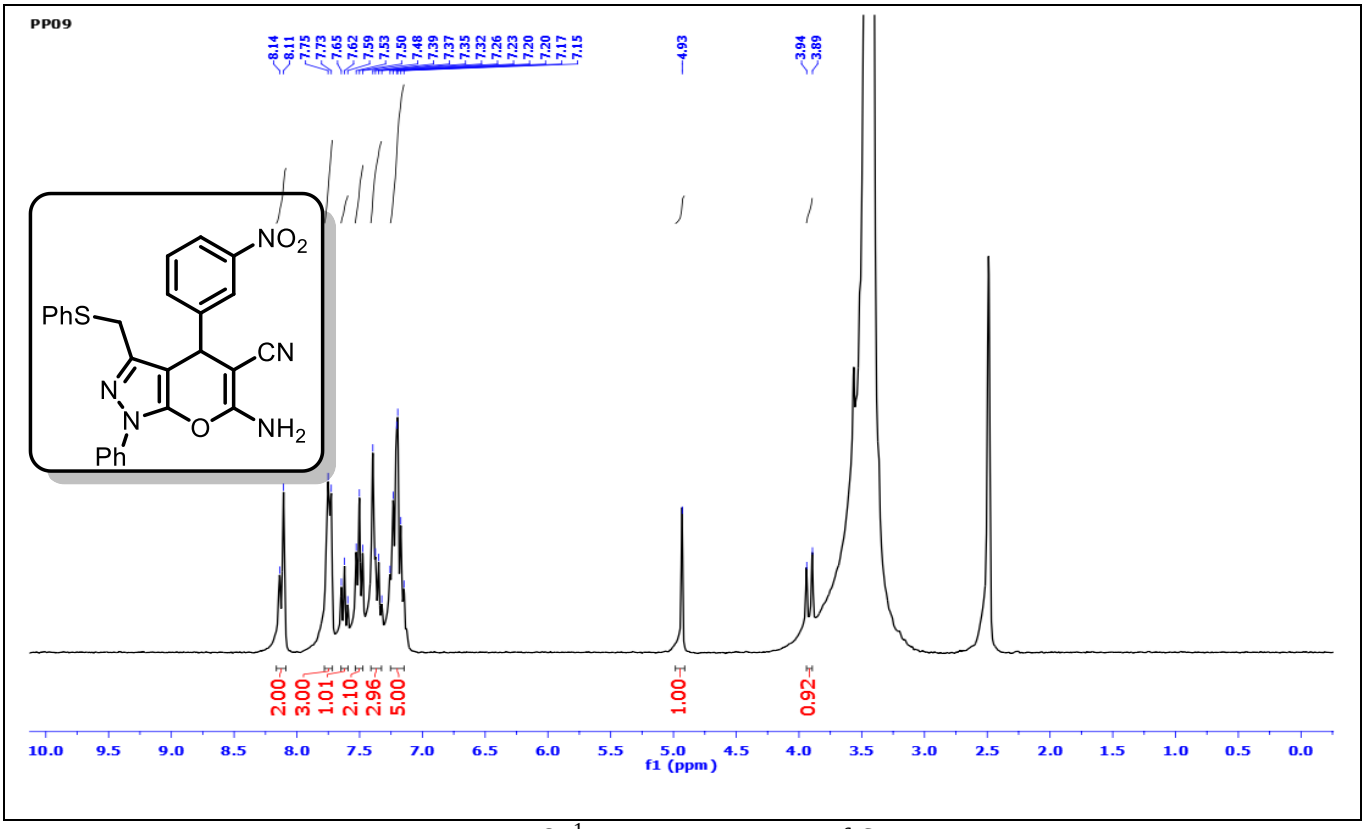


Fig.18. ^{1}H-NMR spectrum of **6g**

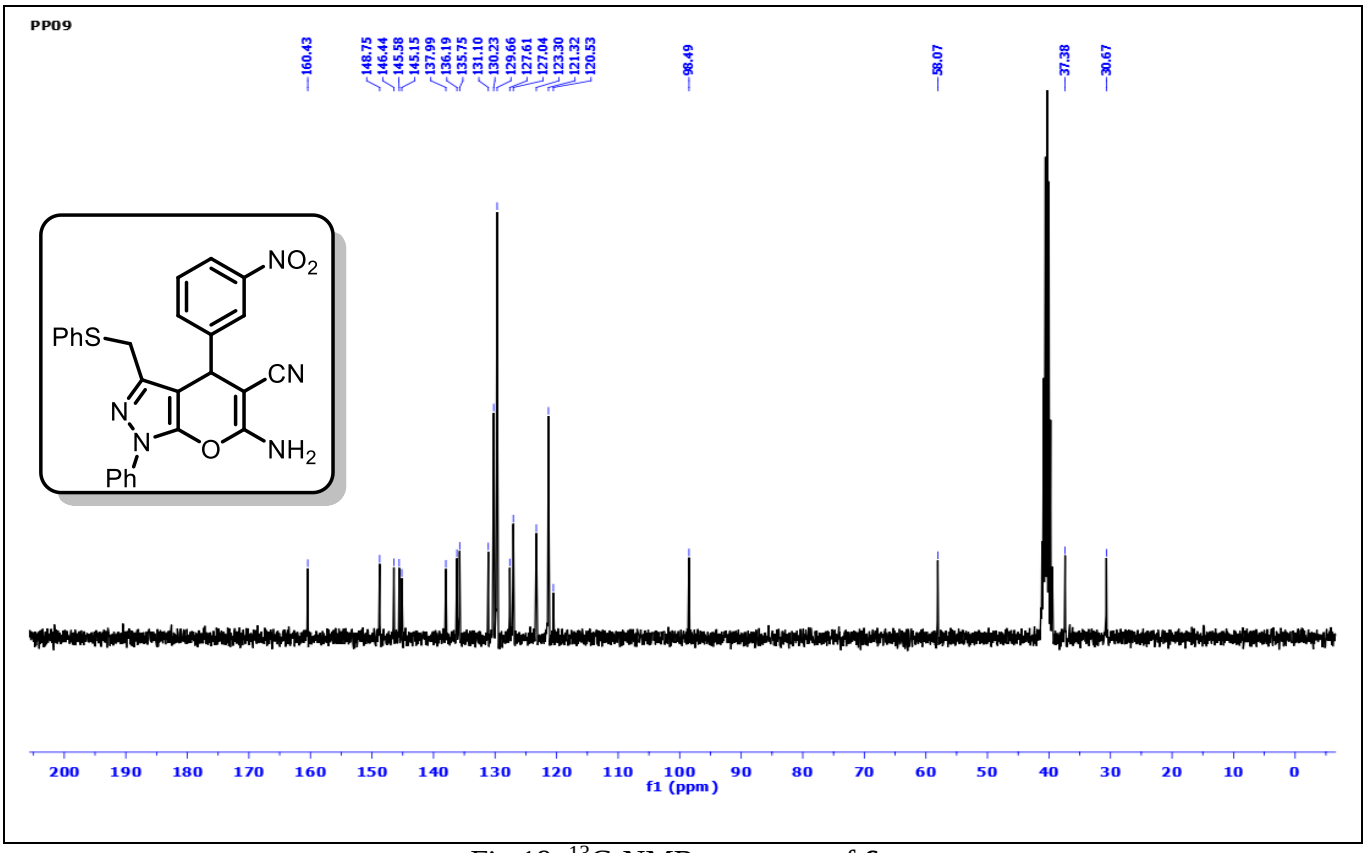


Fig.19. ^{13}C-NMR spectrum of **6g**

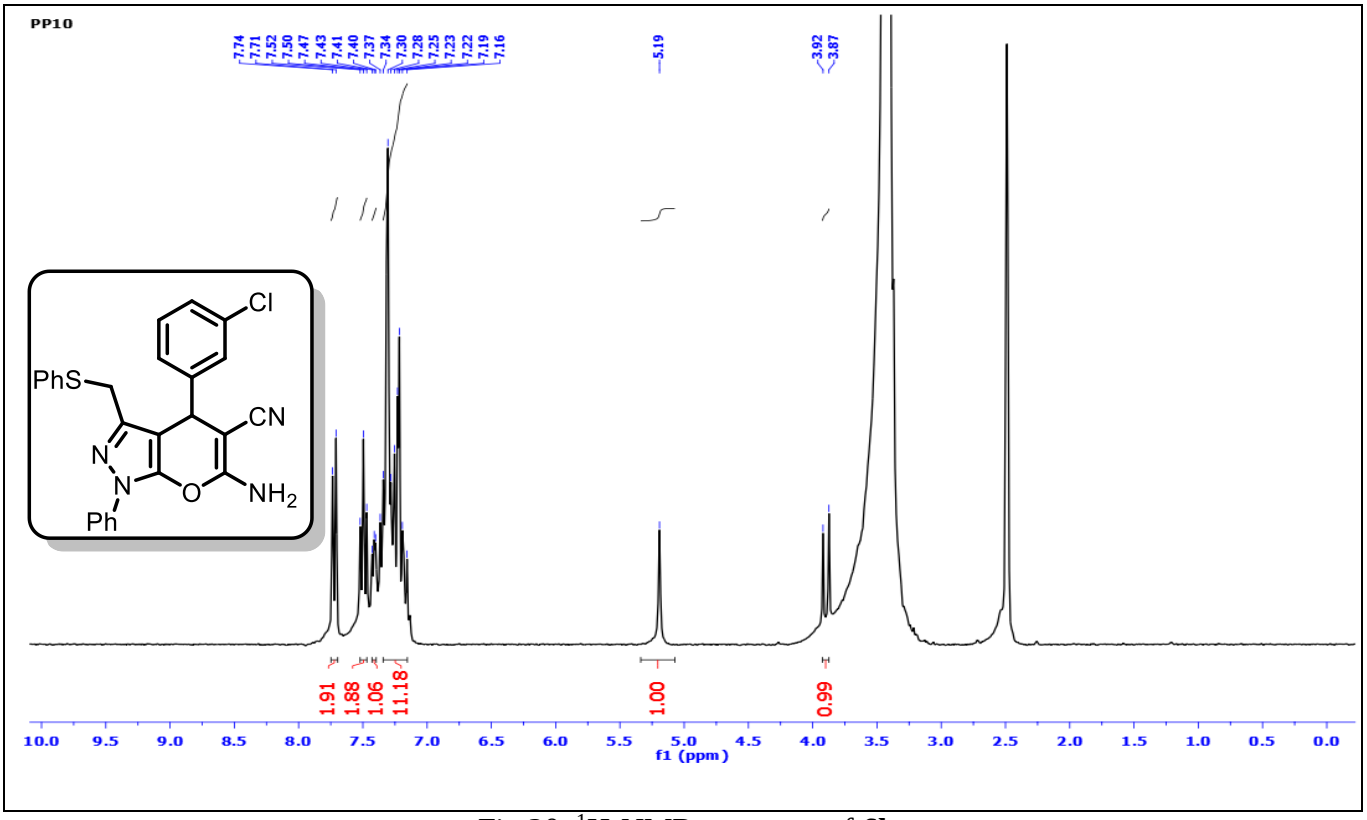


Fig.20. ^{1}H-NMR spectrum of **6h**

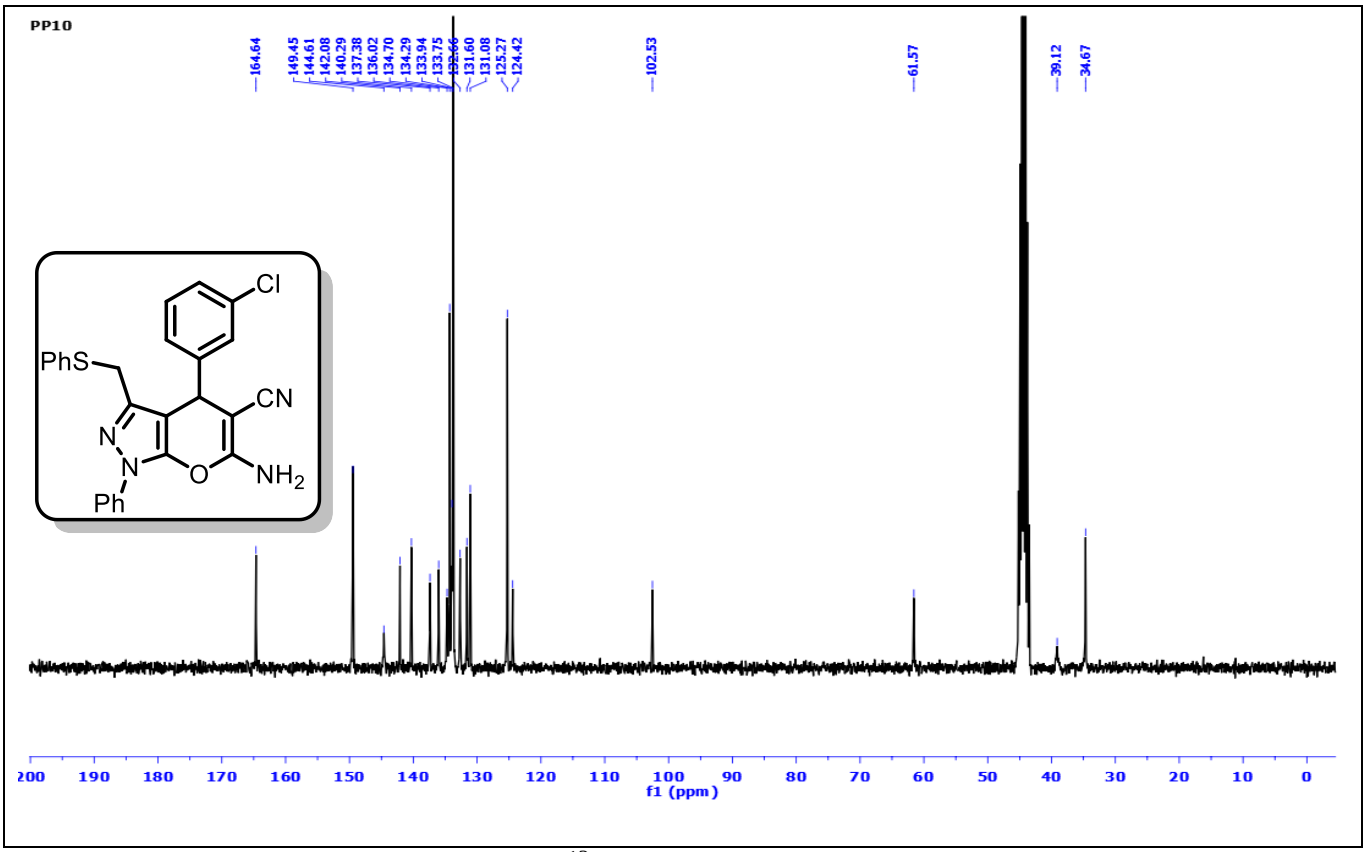


Fig.21. ^{13}C-NMR spectrum of **6h**

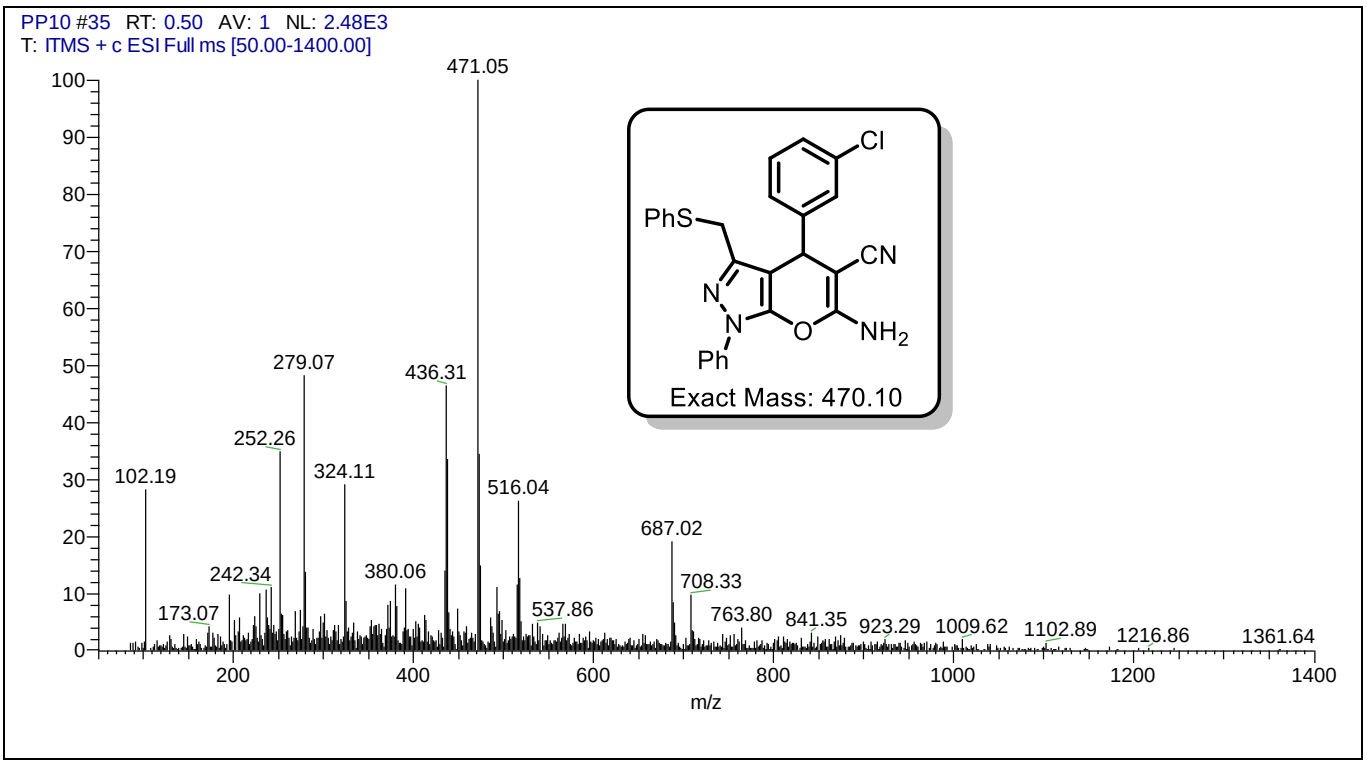


Fig.22. ESI Mass spectra of compound **6h**

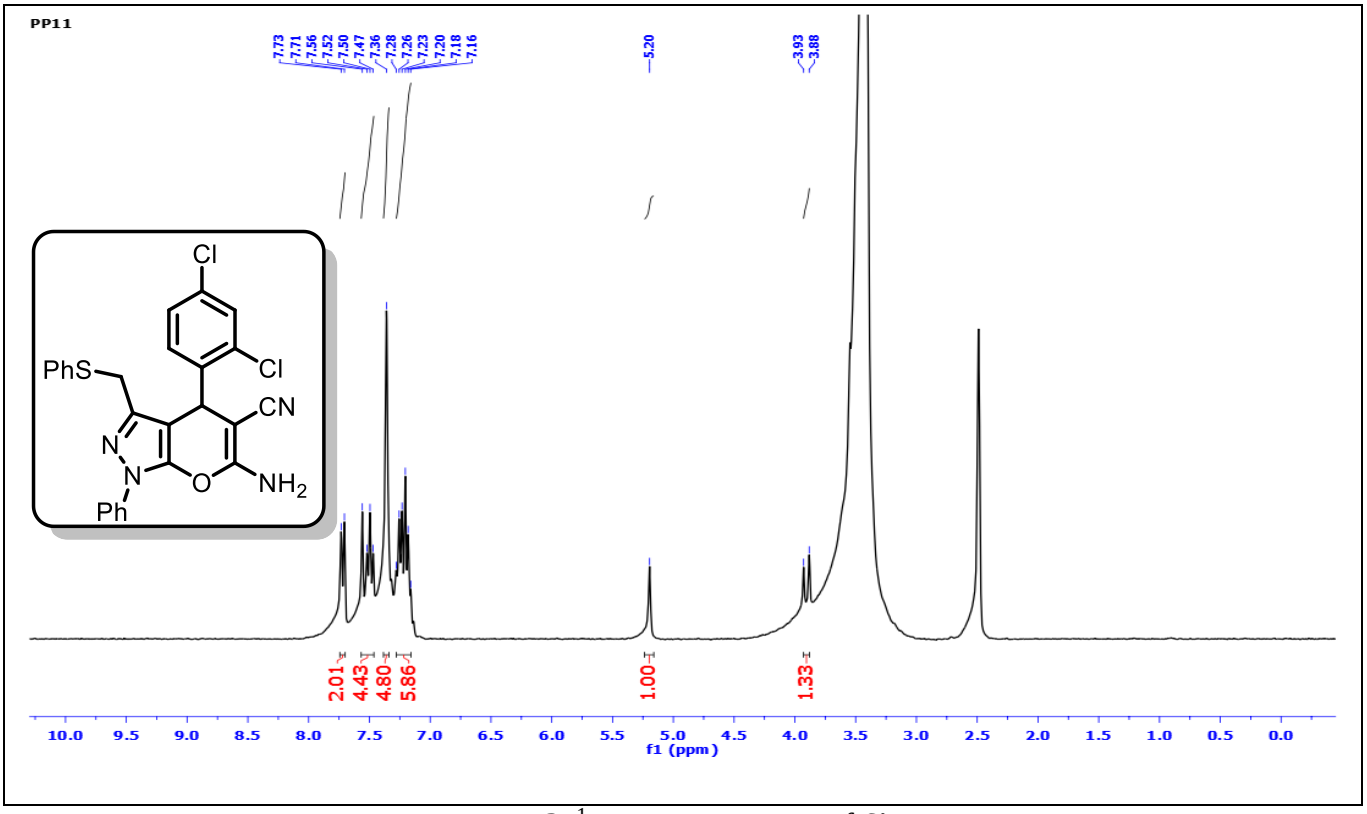


Fig.23. ^{1}H-NMR spectrum of **6i**

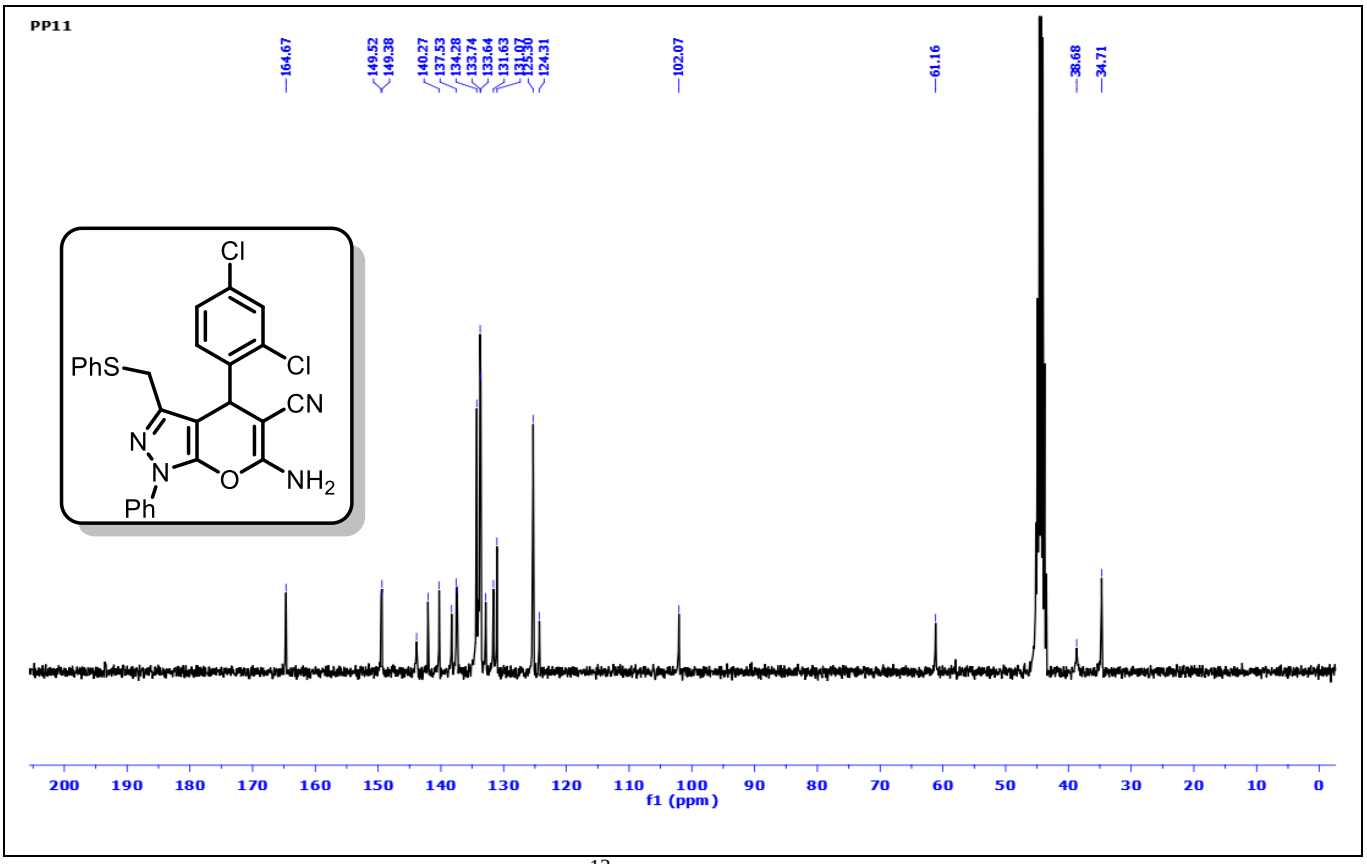


Fig.24. ^{13}C-NMR spectrum **6i**

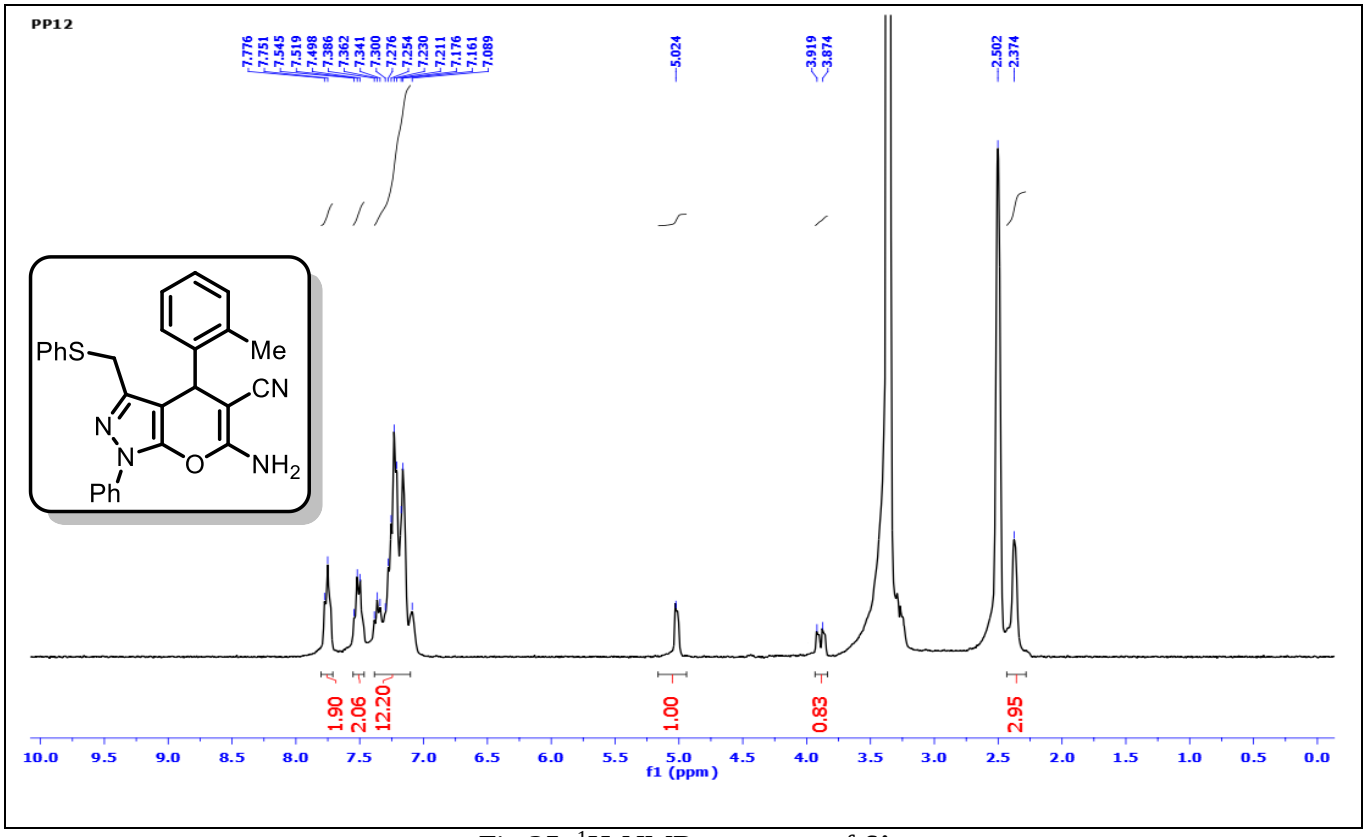


Fig.25. ^{1}H-NMR spectrum of **6j**

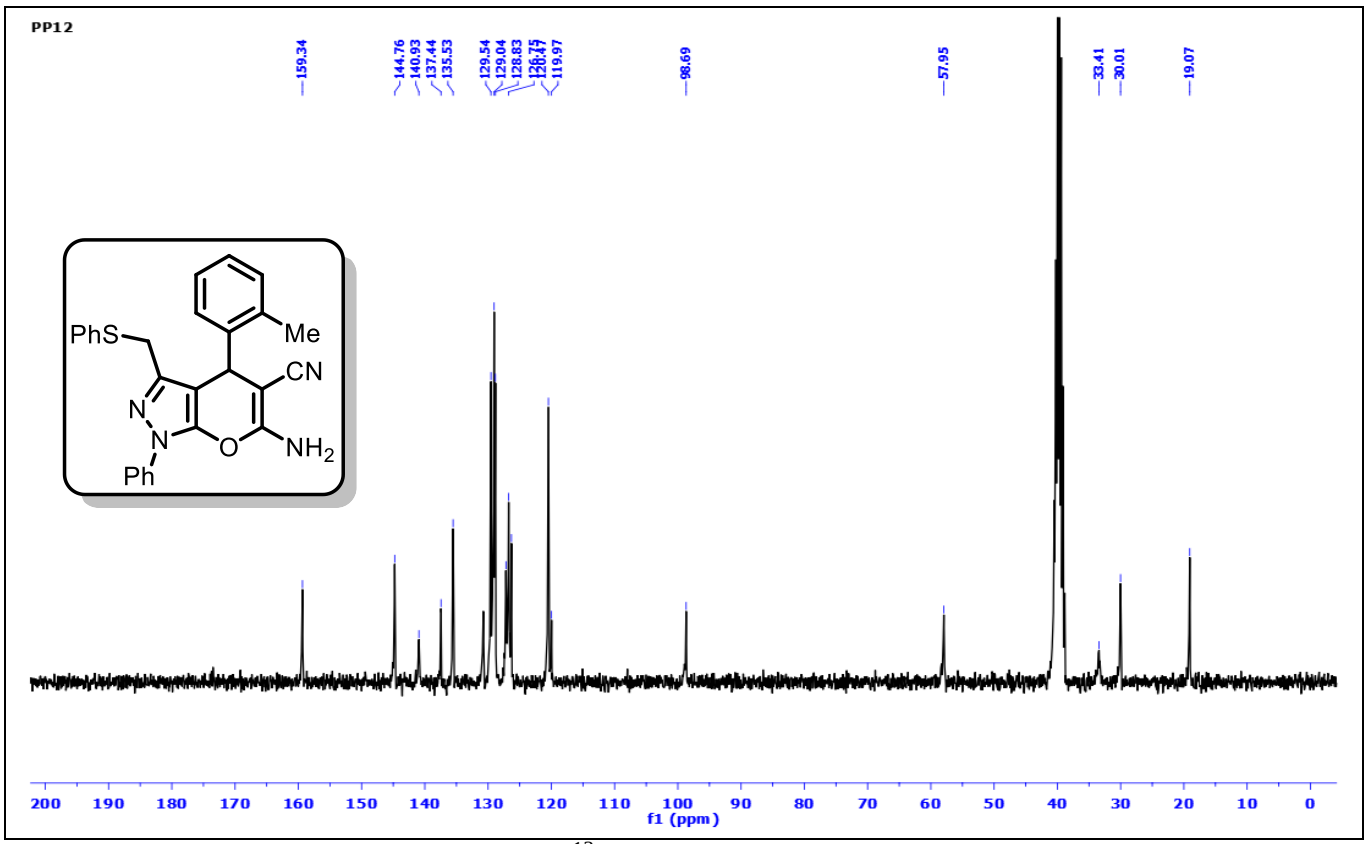


Fig.26. ^{13}C-NMR spectrum of **6j**

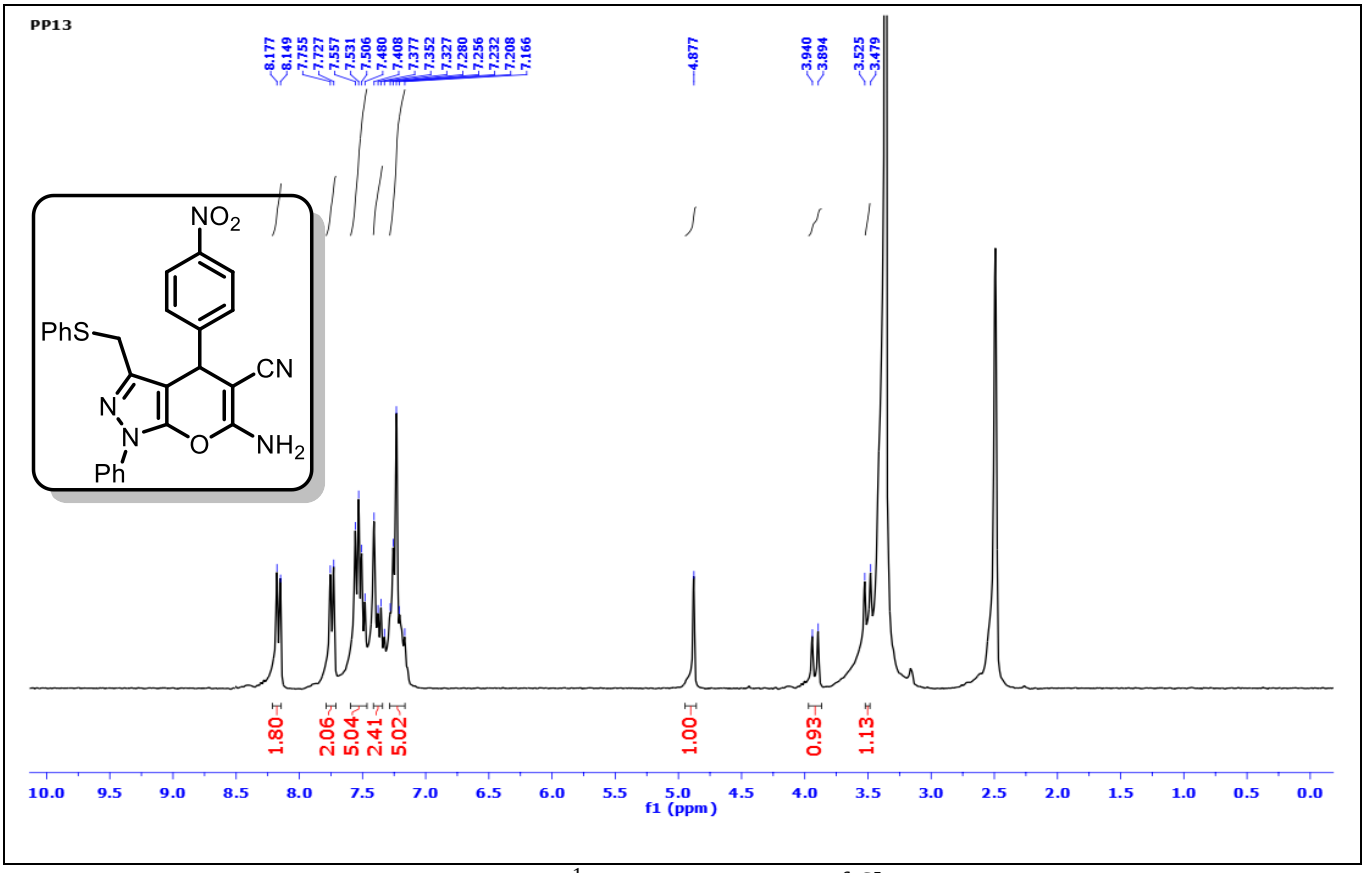


Fig.27. ^{1}H-NMR spectrum of **6k**

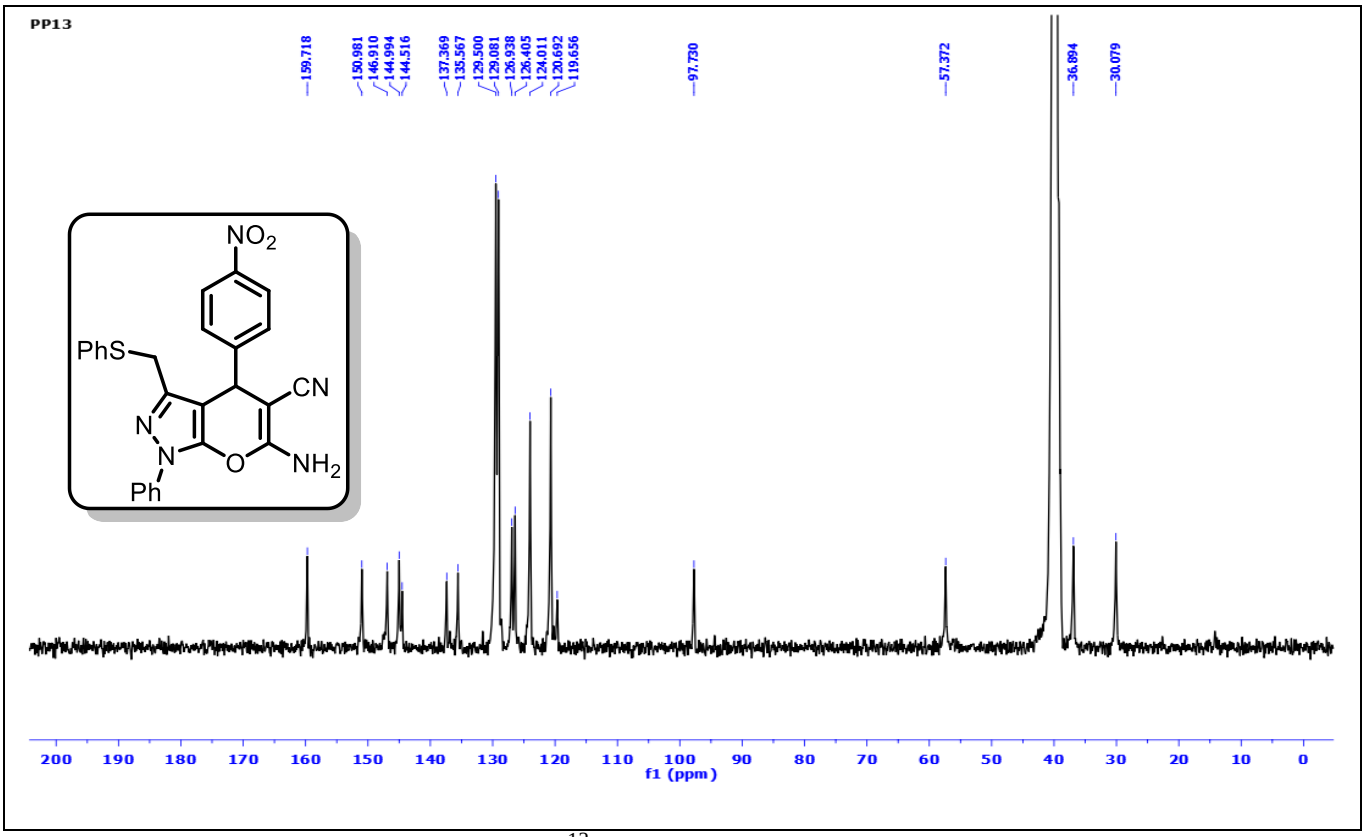


Fig.28. ^{13}C-NMR spectrum of **6k**

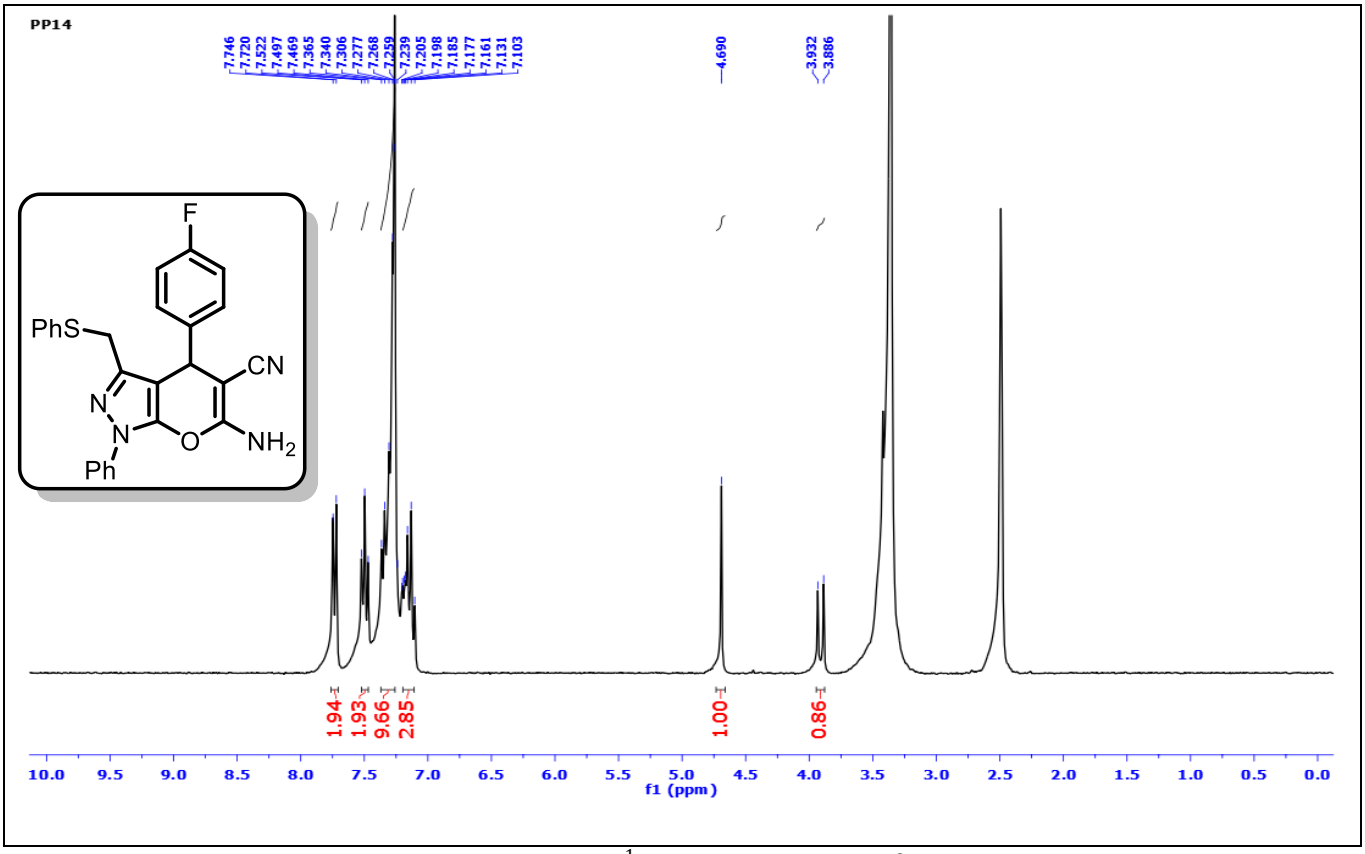


Fig.29. ^{1}H-NMR spectrum of **6l**

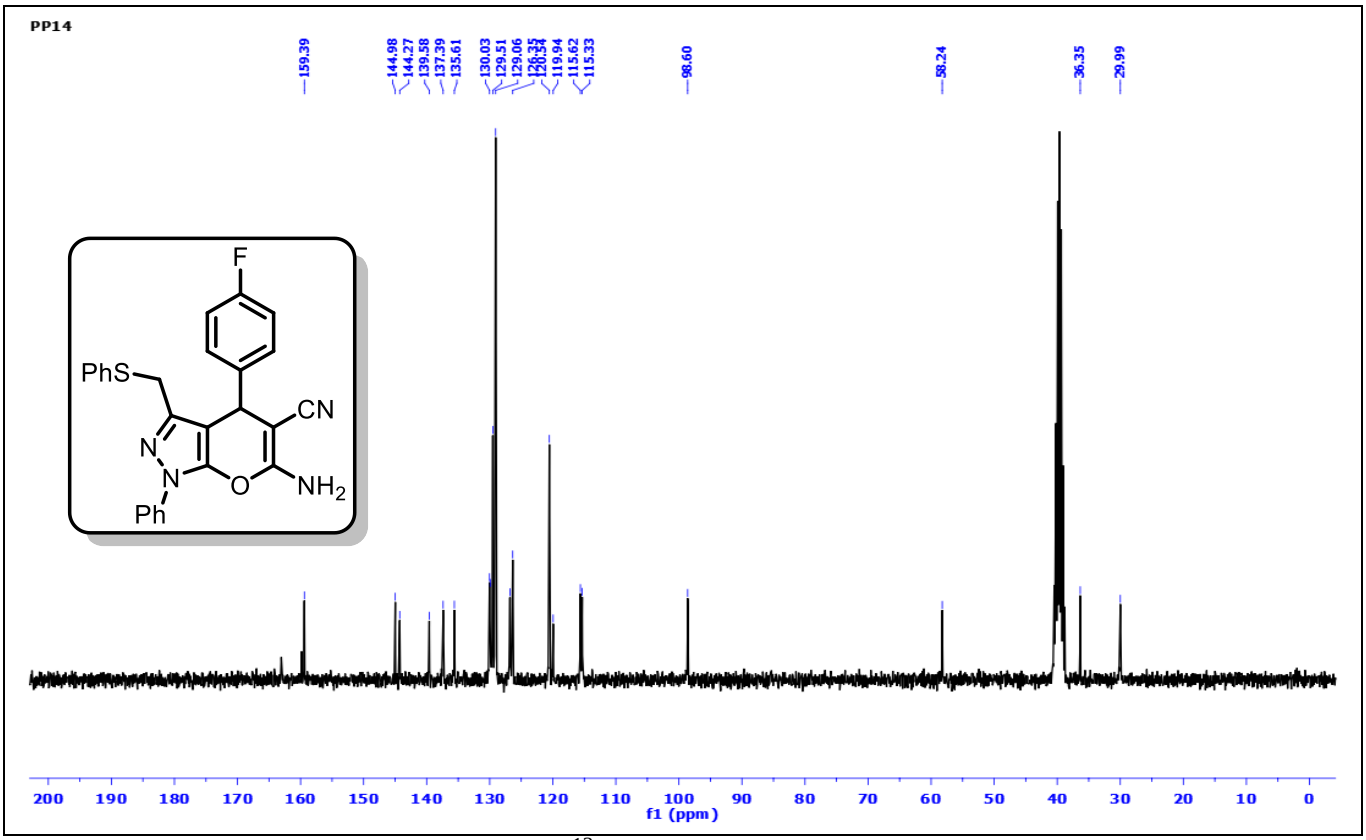


Fig.30. ^{13}C-NMR spectrum of **6l**

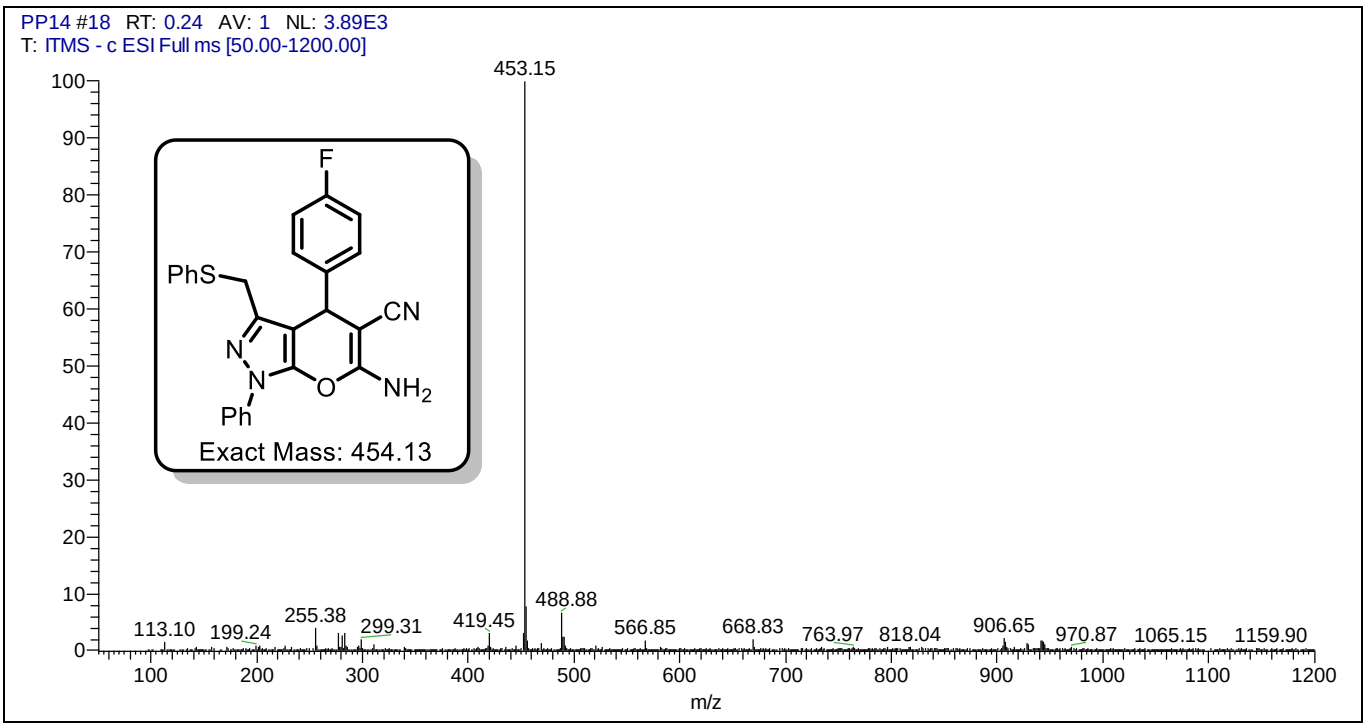


Fig.31. ESI Mass spectra of compound **6l**

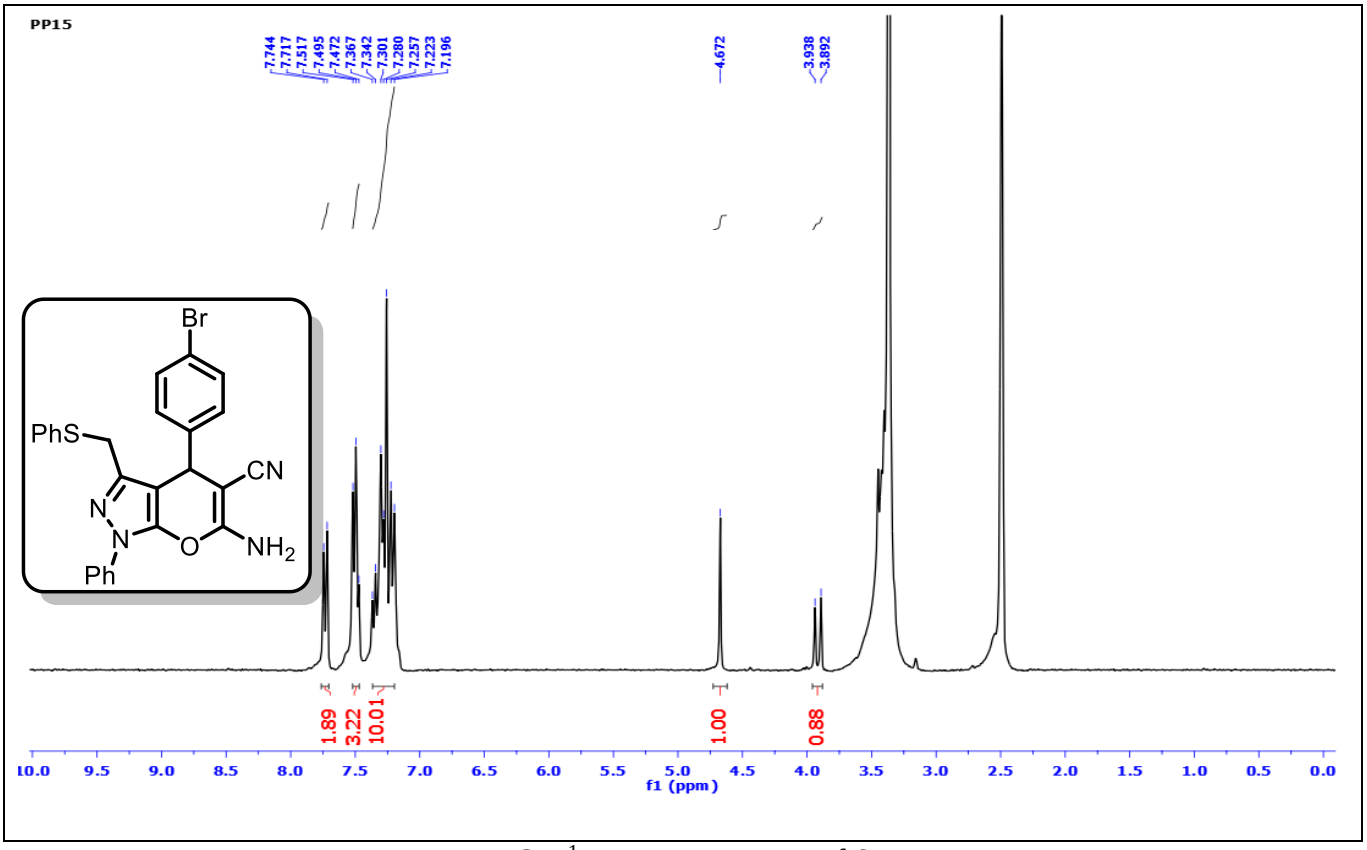


Fig.32. ^{1}H-NMR spectrum of **6m**

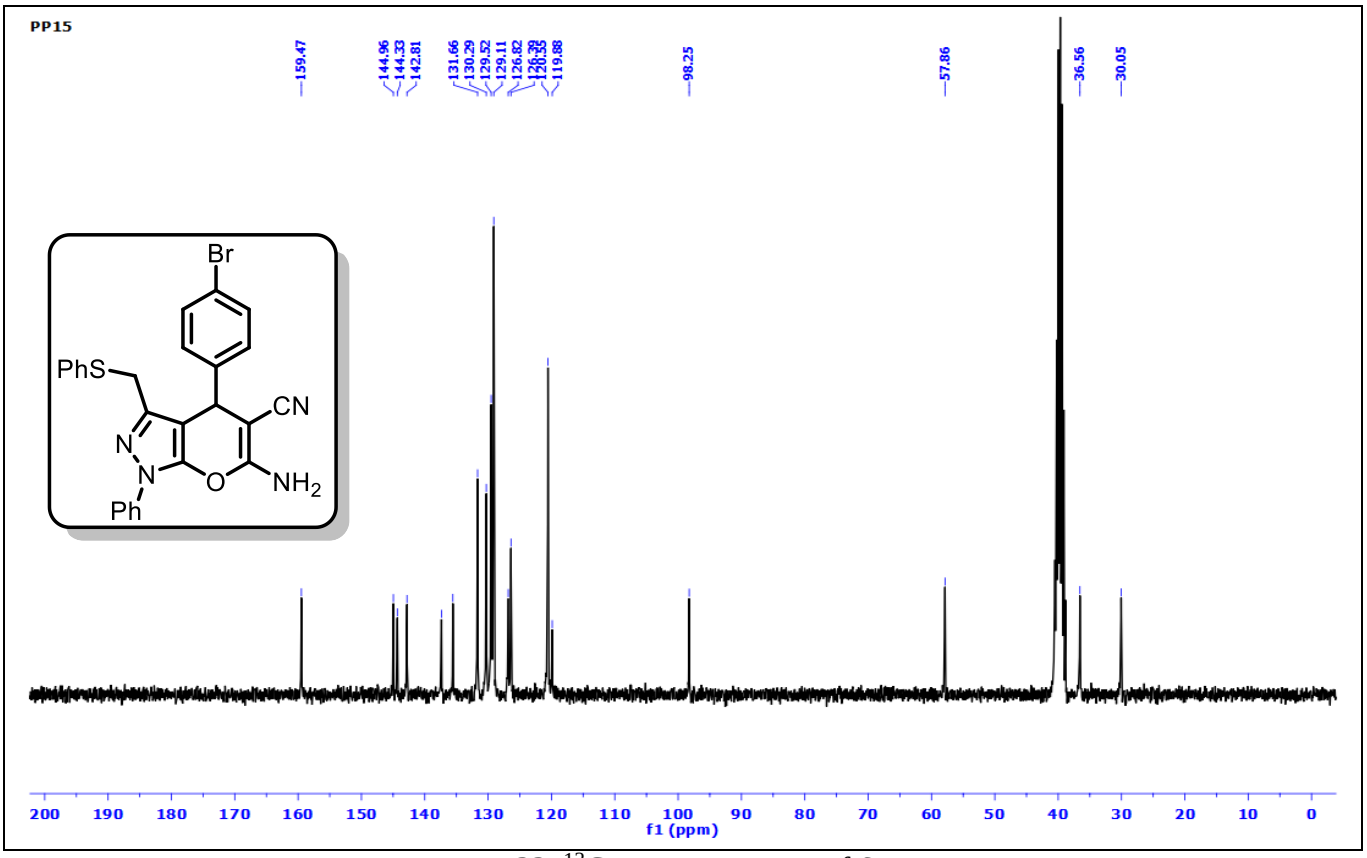


Fig.33. ^{13}C-NMR spectrum of **6m**

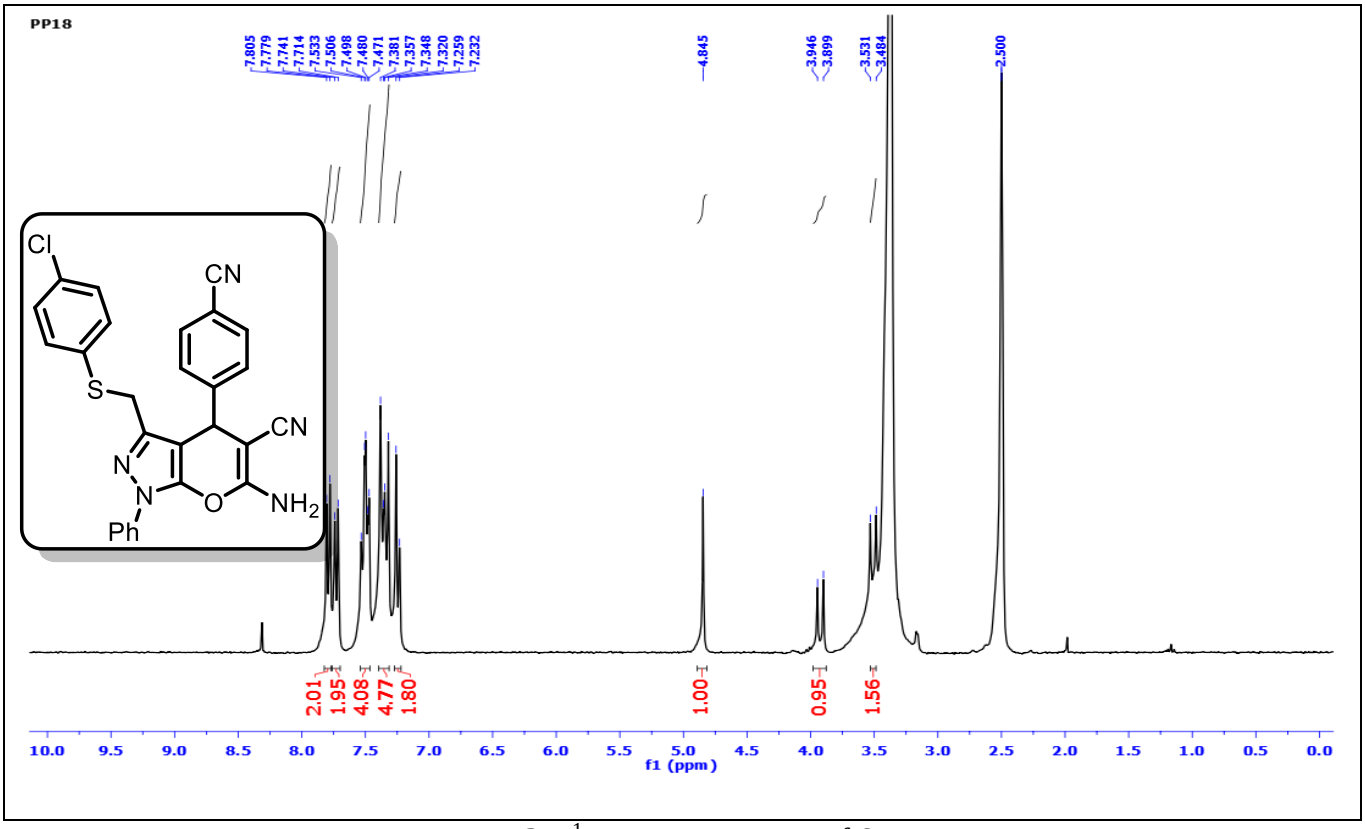


Fig.34. ^{1}H-NMR spectrum of **6n**

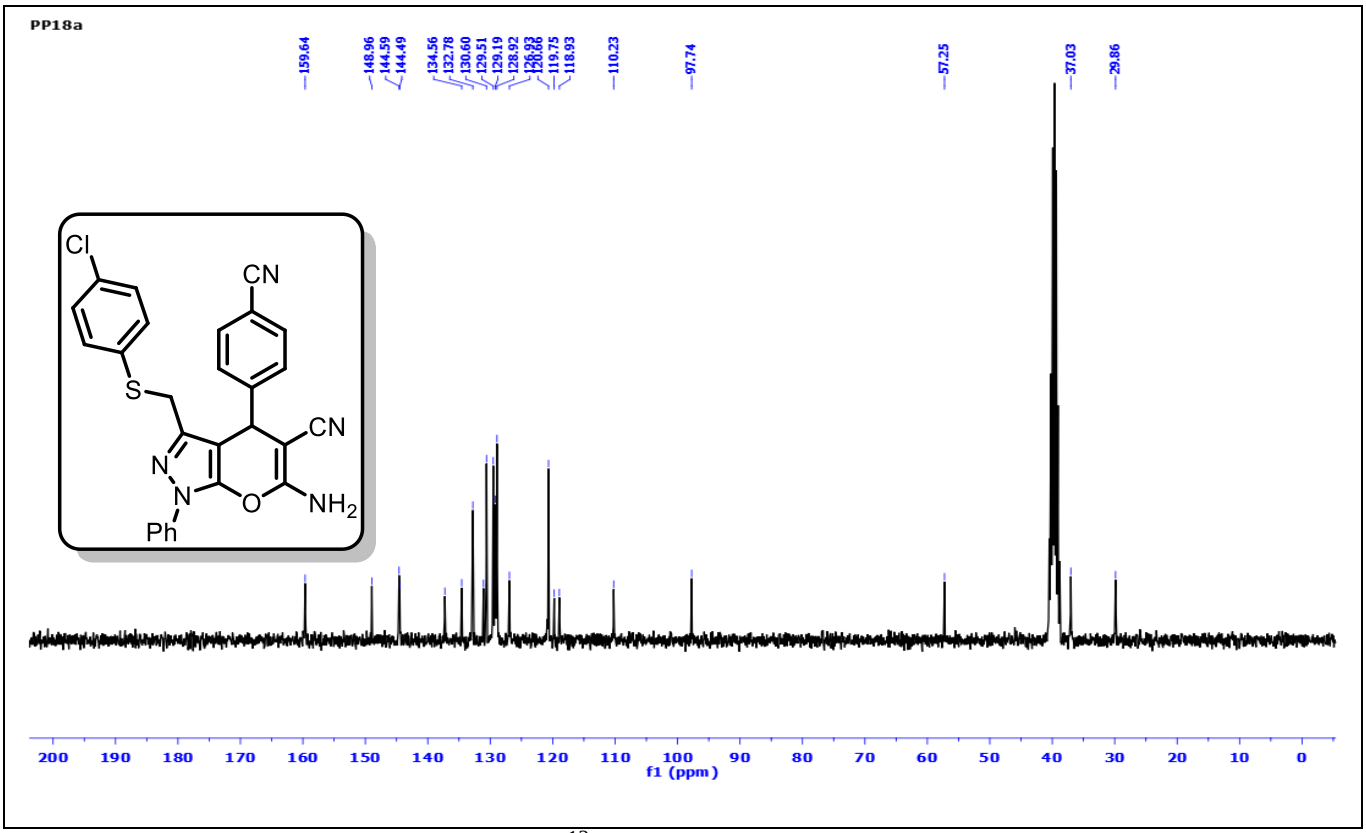


Fig.35. ^{13}C-NMR spectrum of **6n**

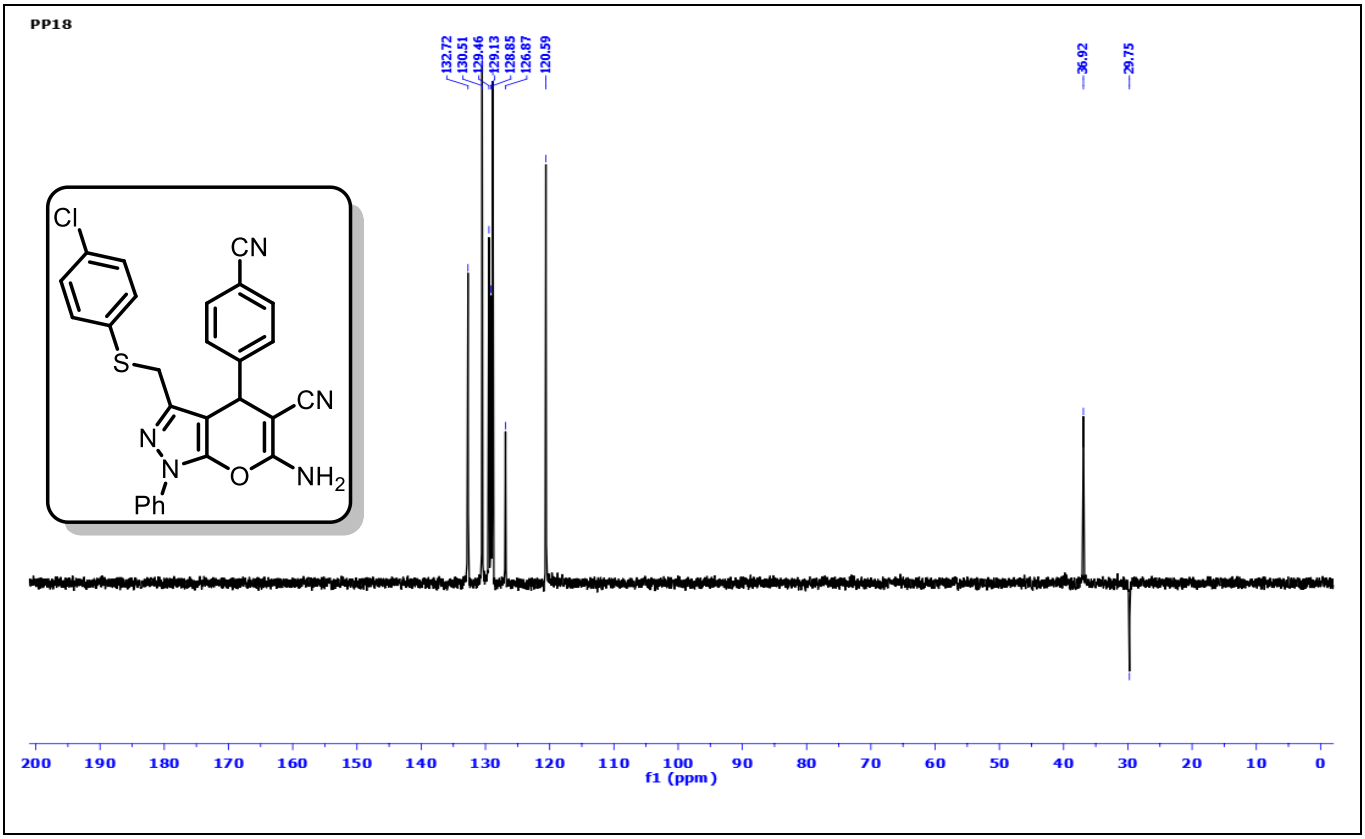


Fig.36. DEPT-135 spectrum of **6n**

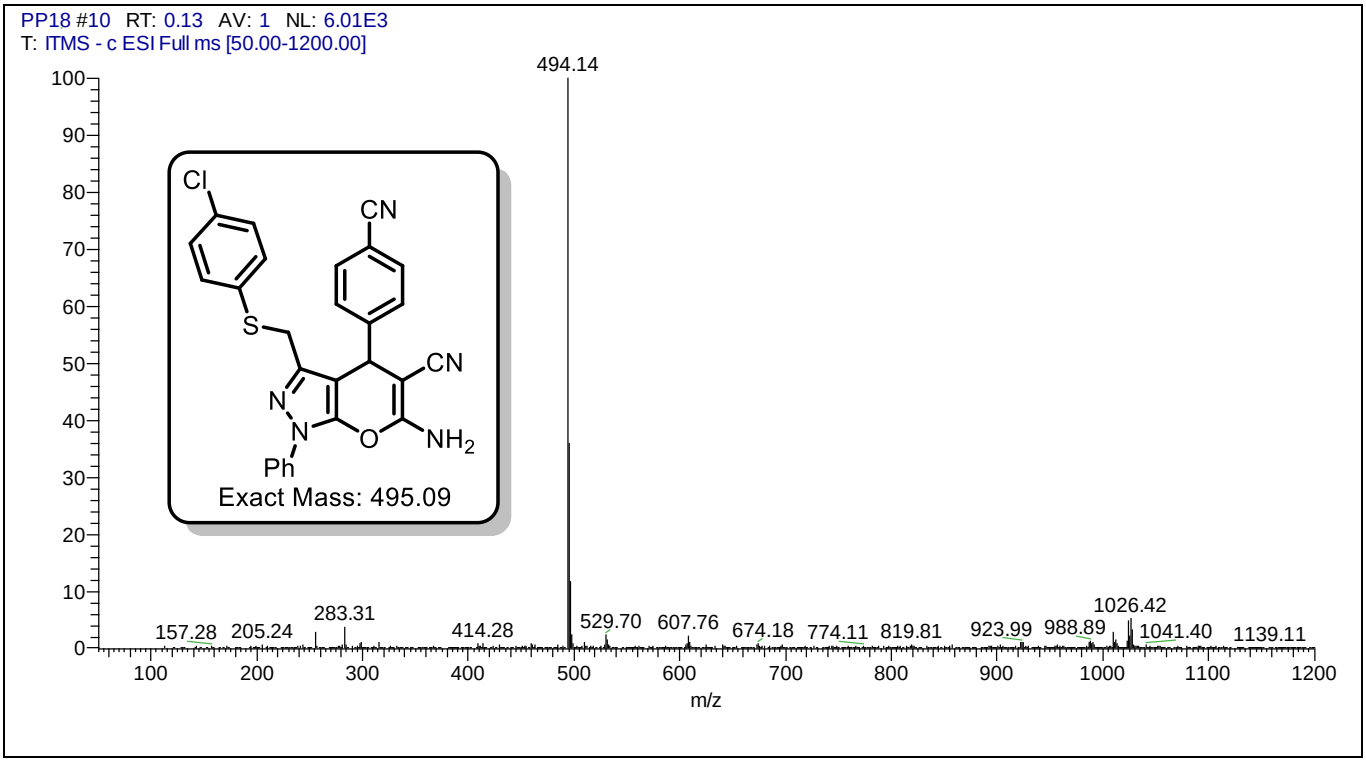


Fig.37. ESI Mass spectra of compound **6n**

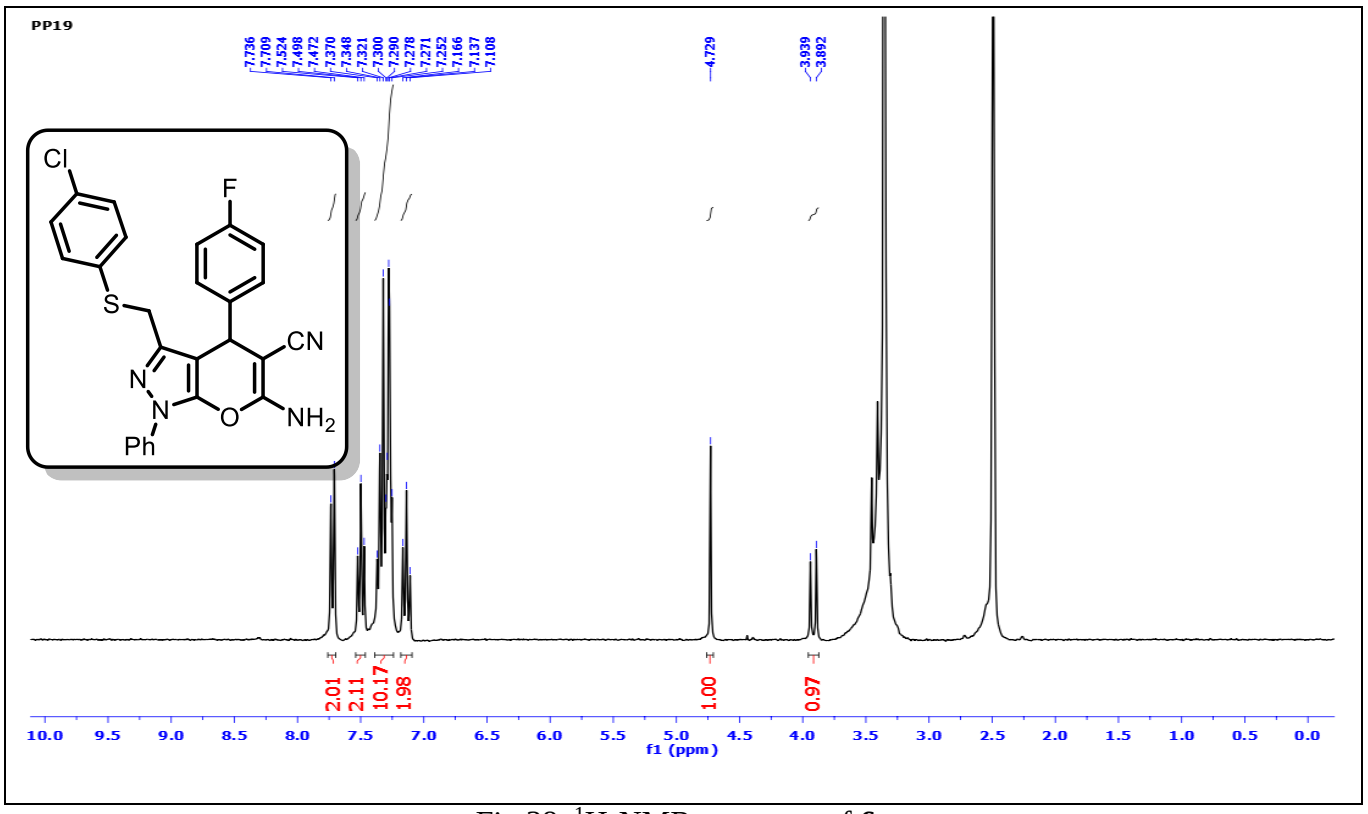


Fig.38. ^{1}H-NMR spectrum of **6o**

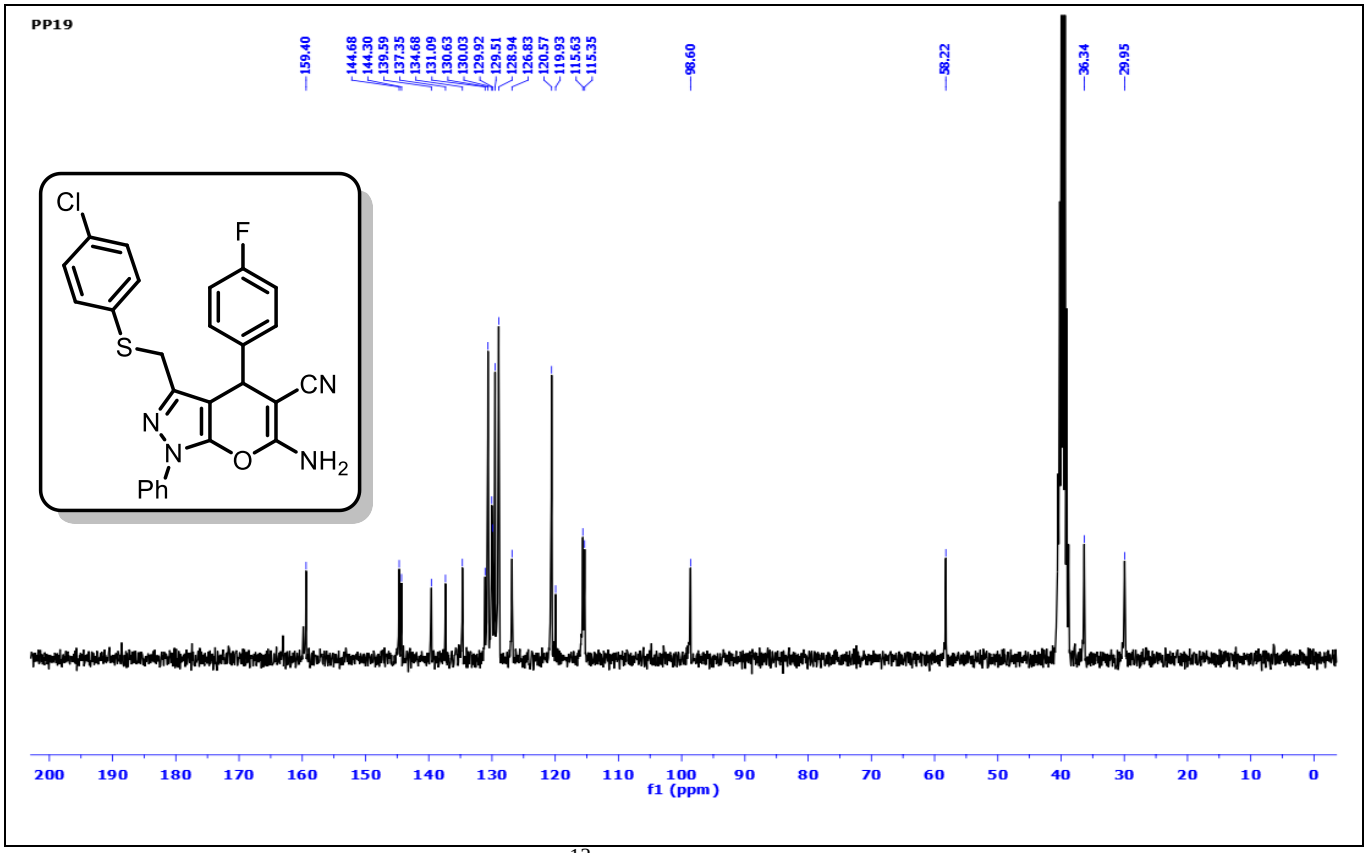


Fig.39. ^{13}C-NMR spectrum of **6o**

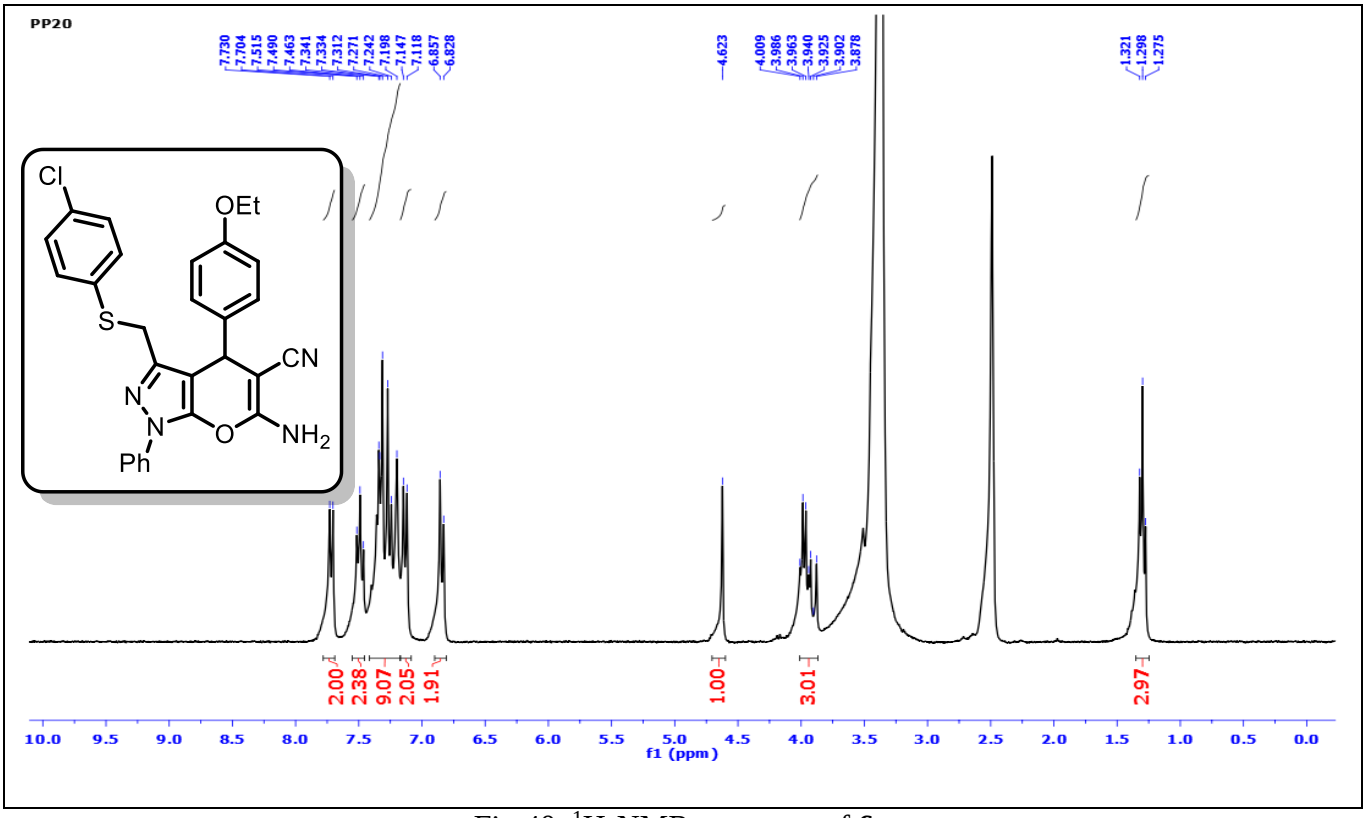


Fig.40. ^{1}H-NMR spectrum of **6p**

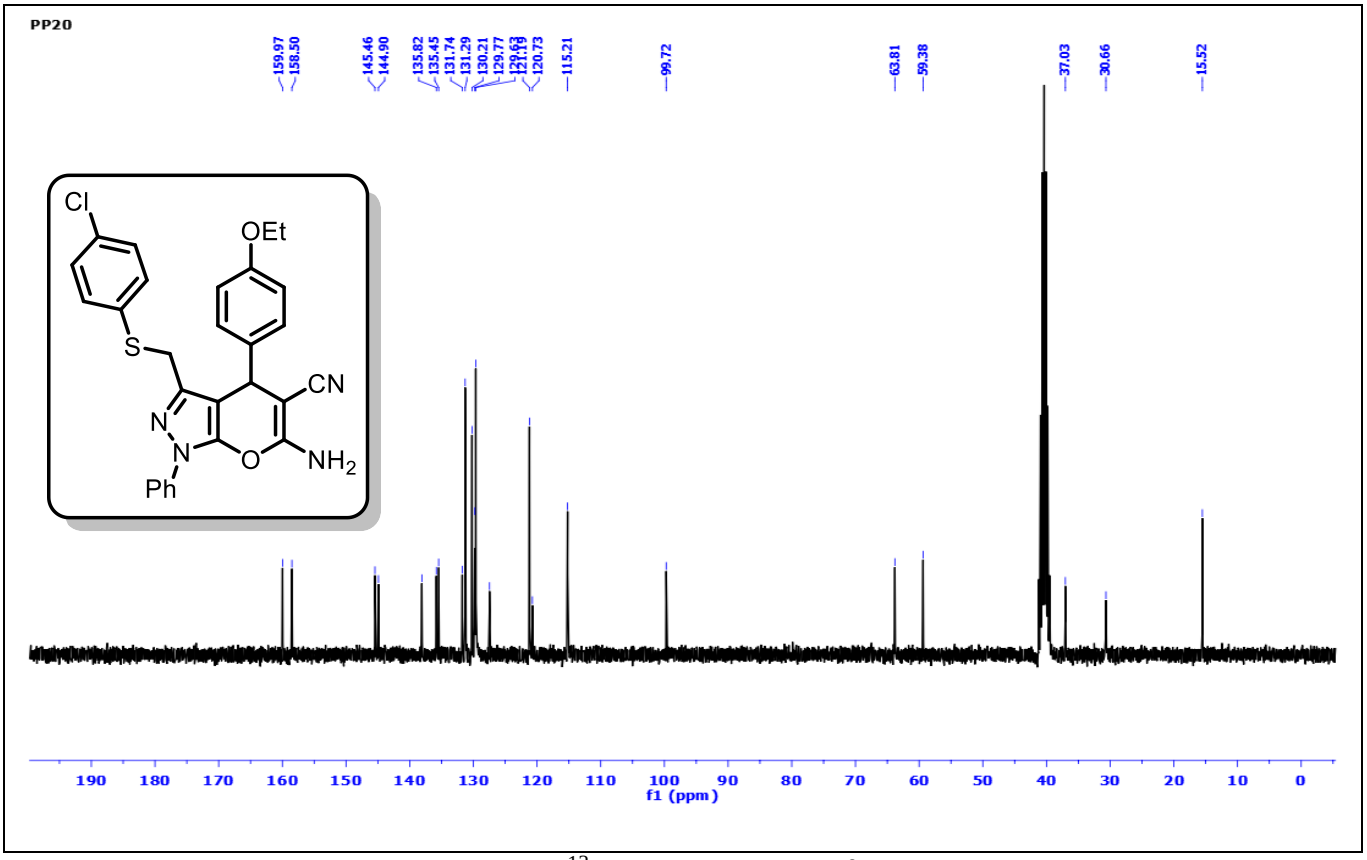


Fig.41. ^{13}C-NMR spectrum of **6p**

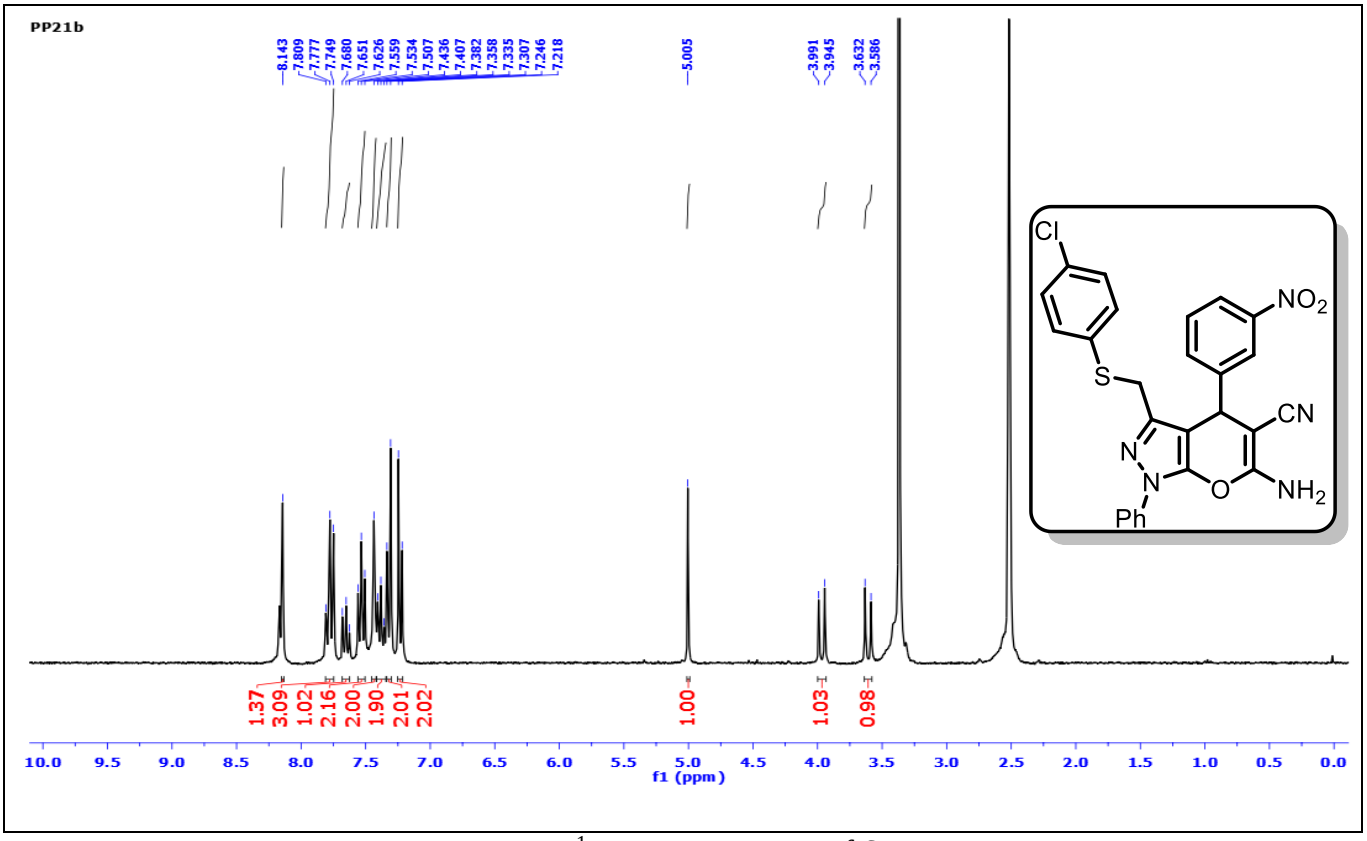


Fig.42. ^{1}H-NMR spectrum of **6q**

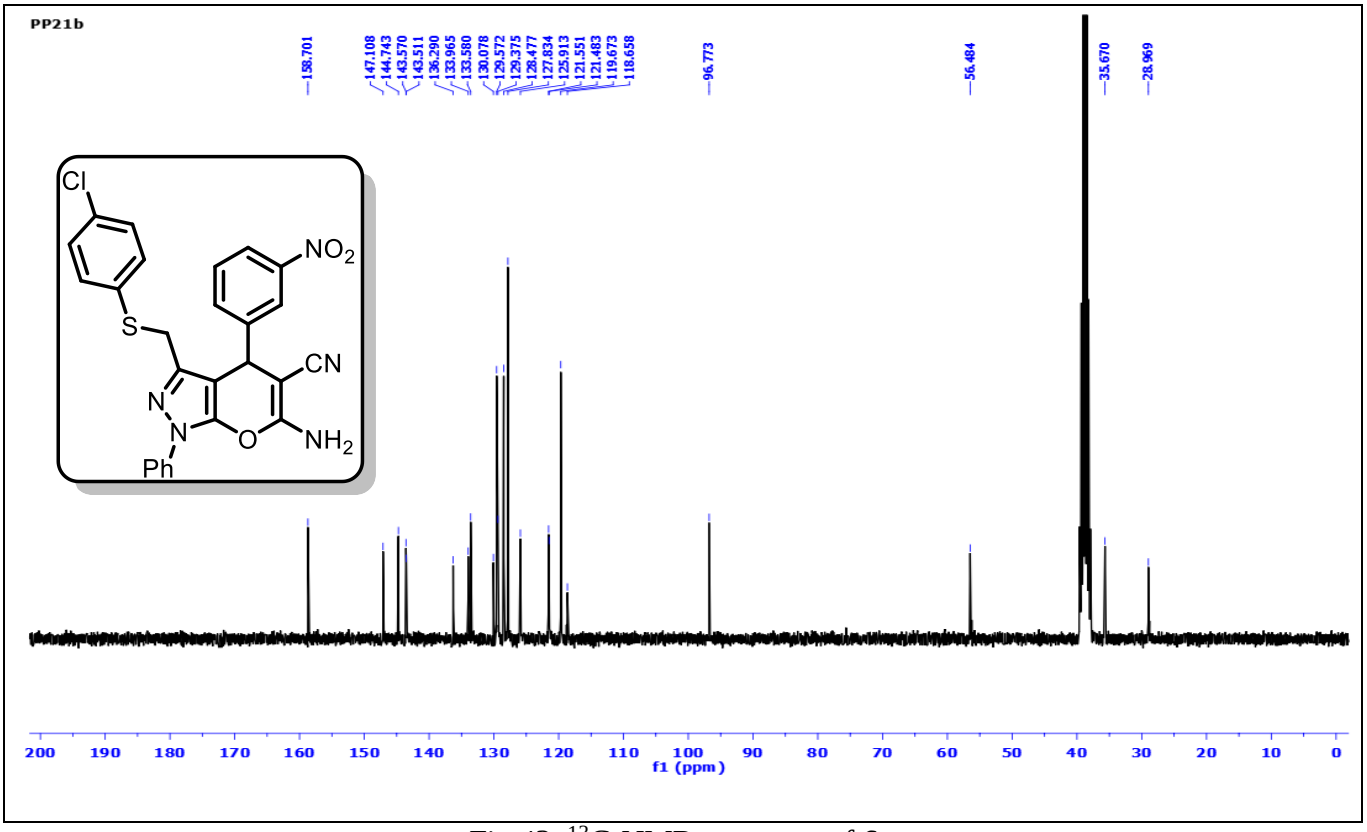


Fig.43. ^{13}C-NMR spectrum of **6q**

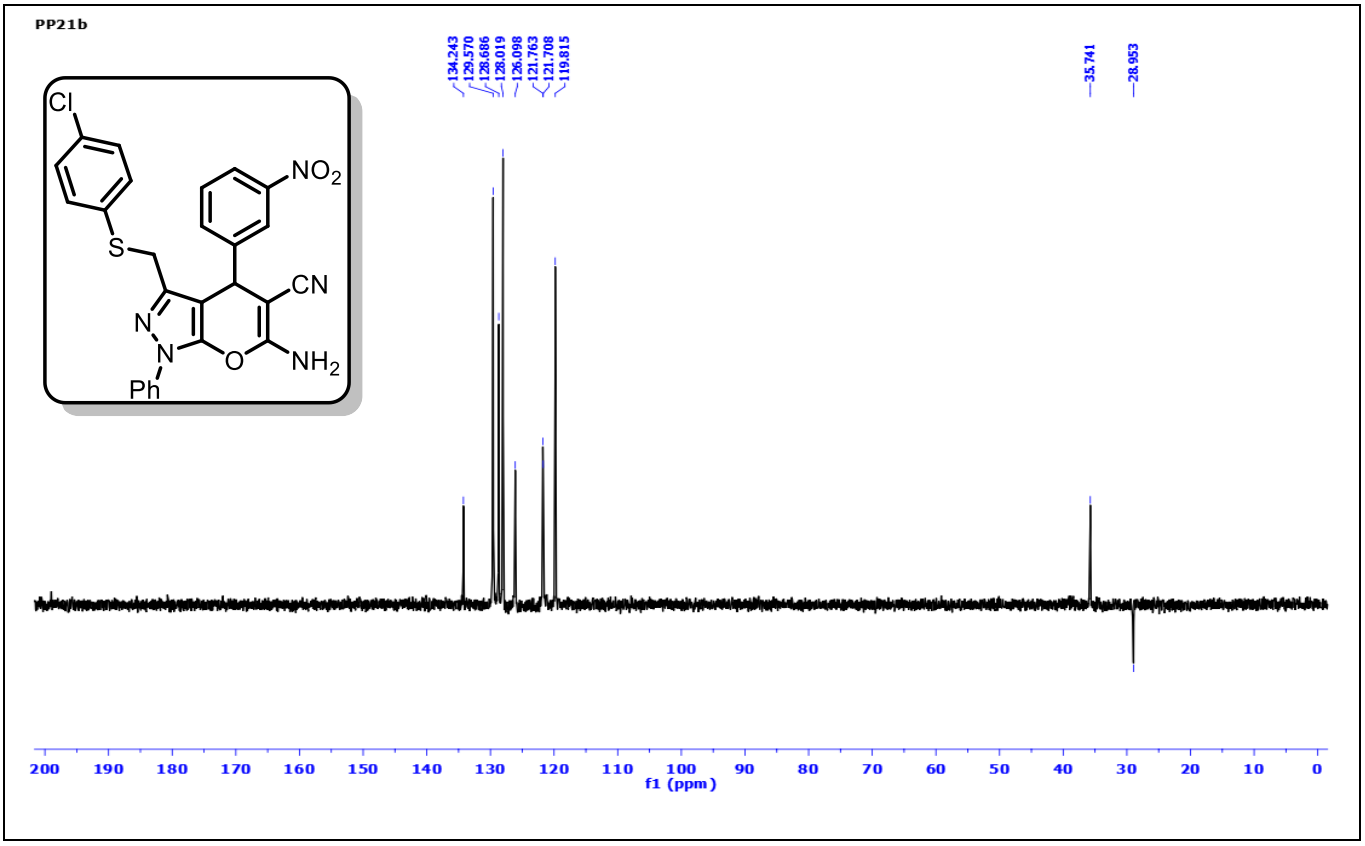


Fig.44. DEPT-135 spectrum of **6q**

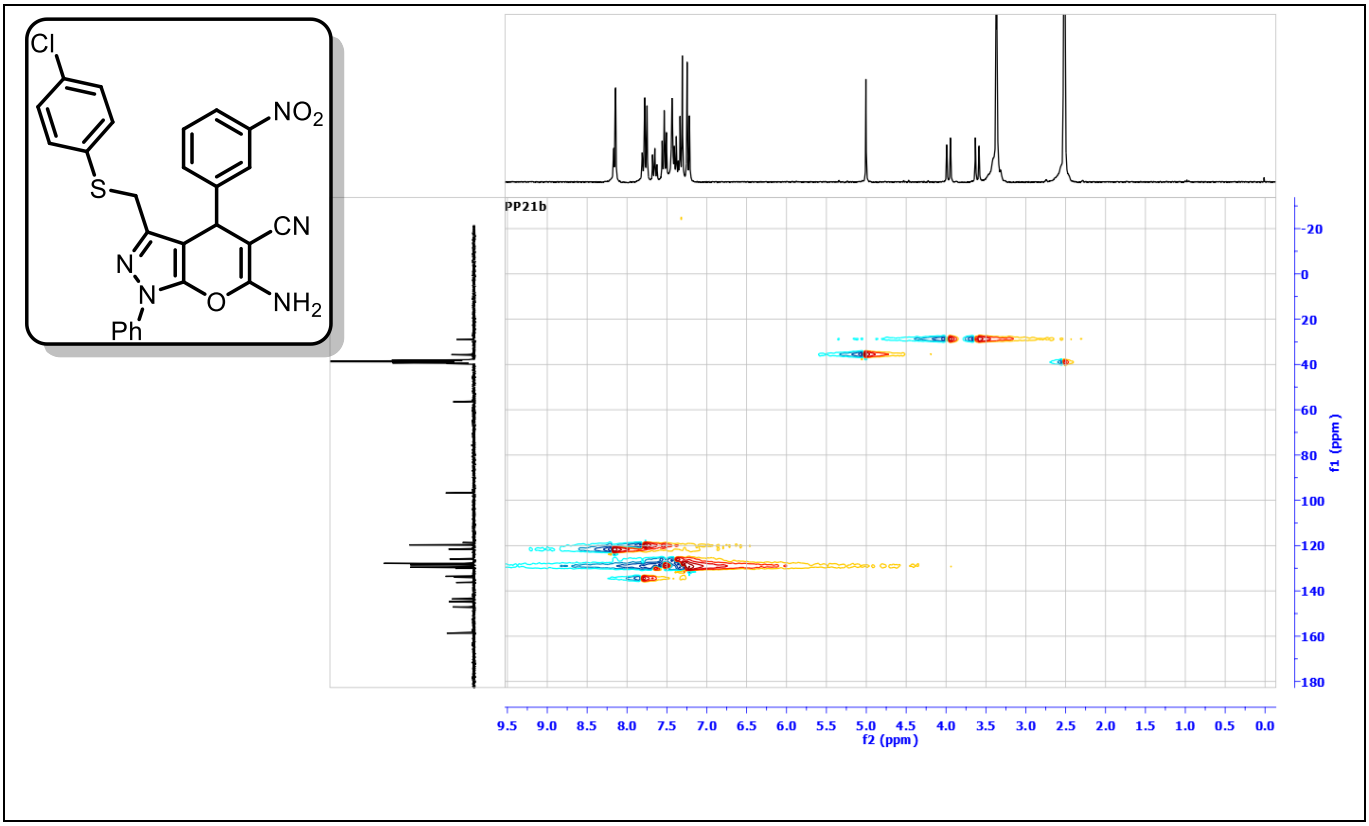


Fig.45. C-H COSY spectrum of **6q**

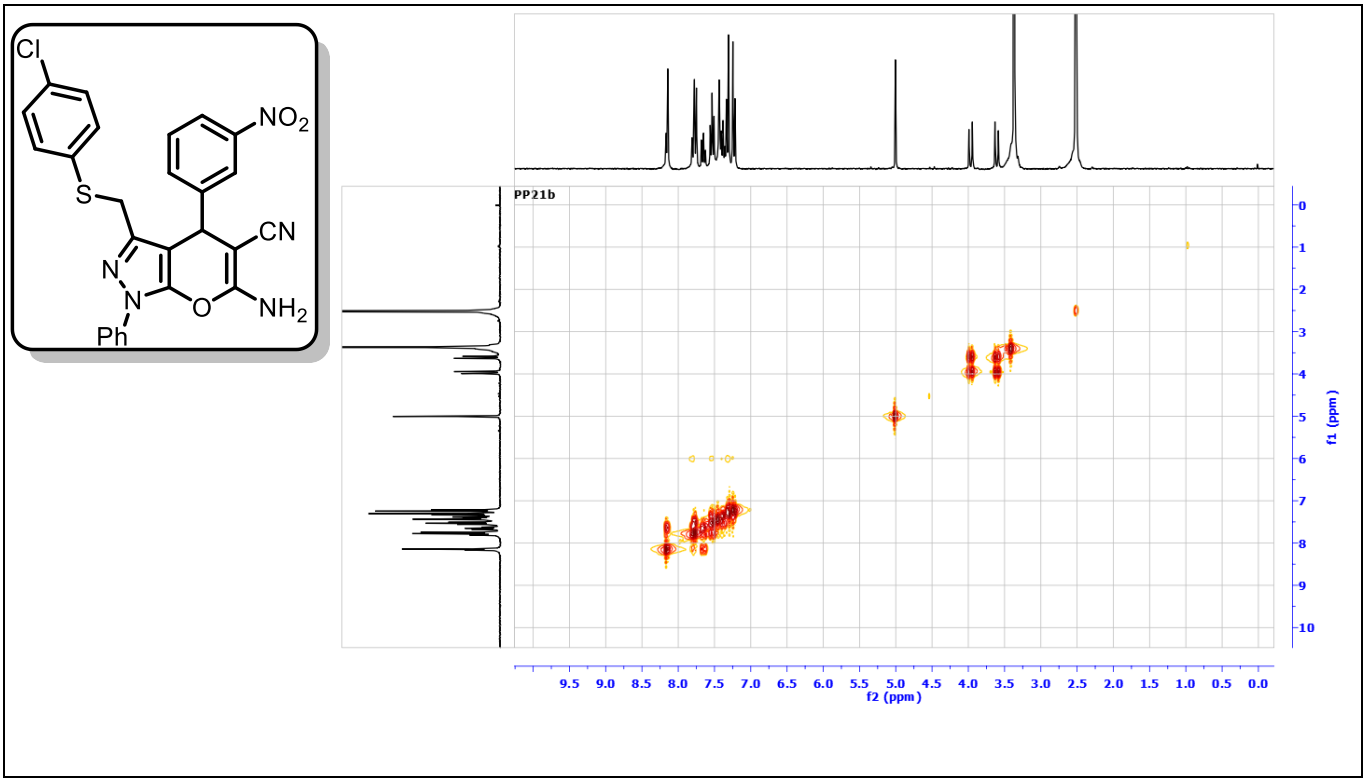


Fig.46. H-H COSY spectrum of **6q**

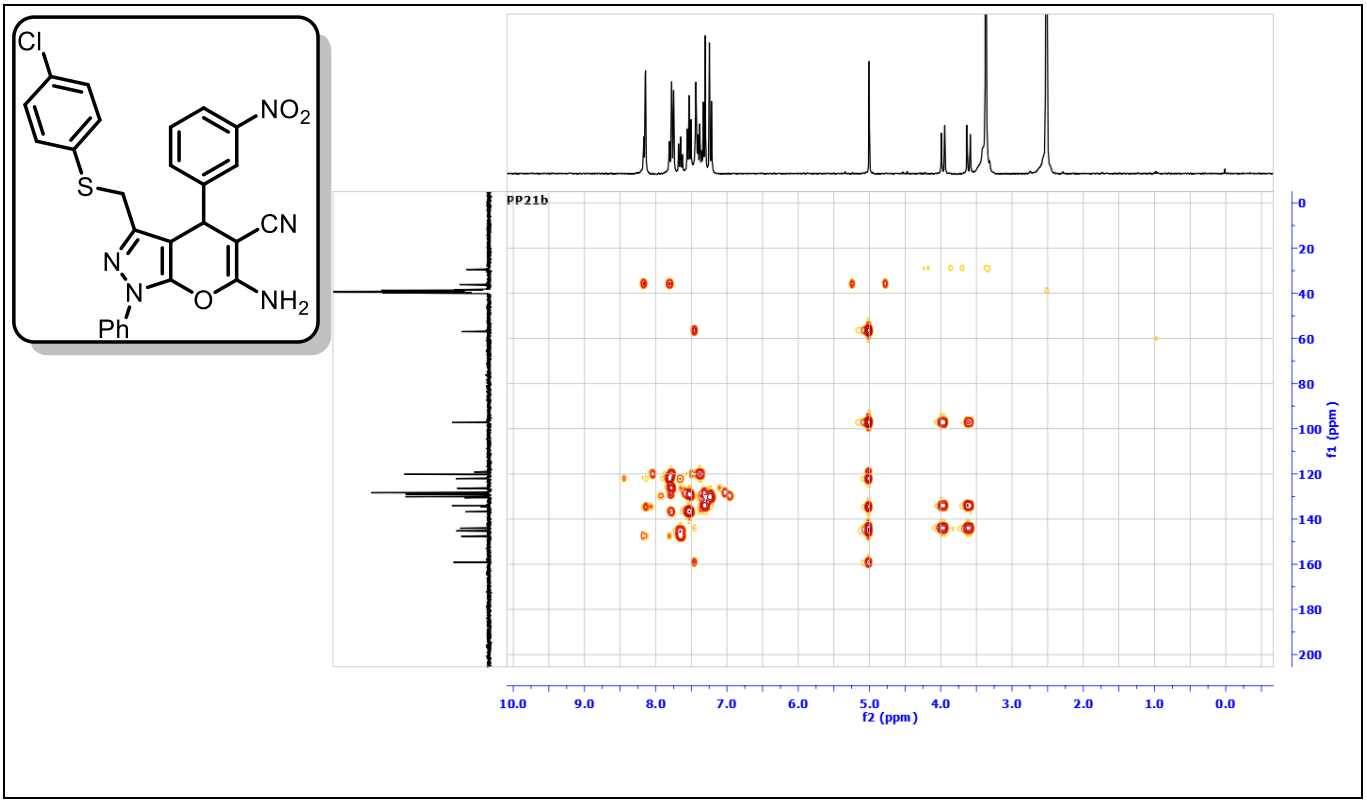


Fig.47. HMBC spectrum of **6q**

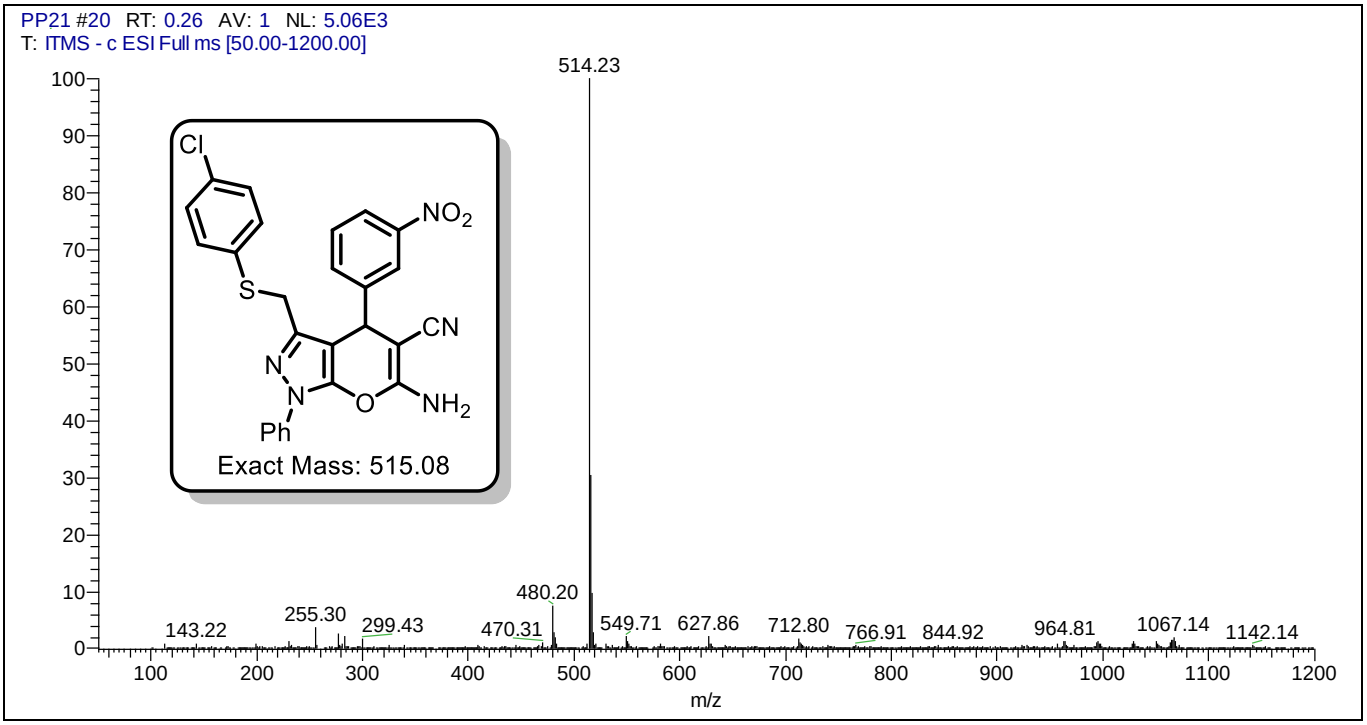


Fig.48. ESI Mass spectra of compound **6q**

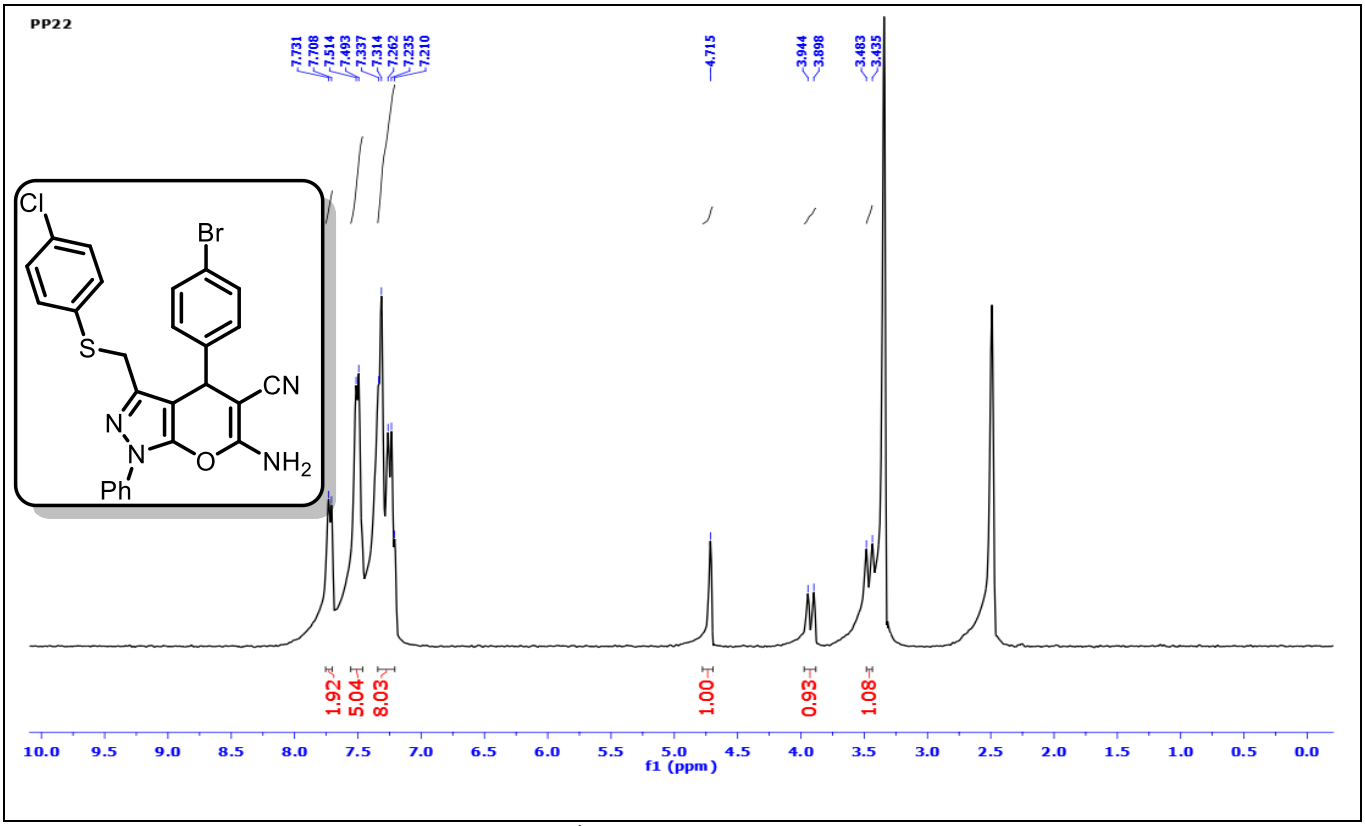


Fig.49. ^{1}H-NMR spectrum of **6r**

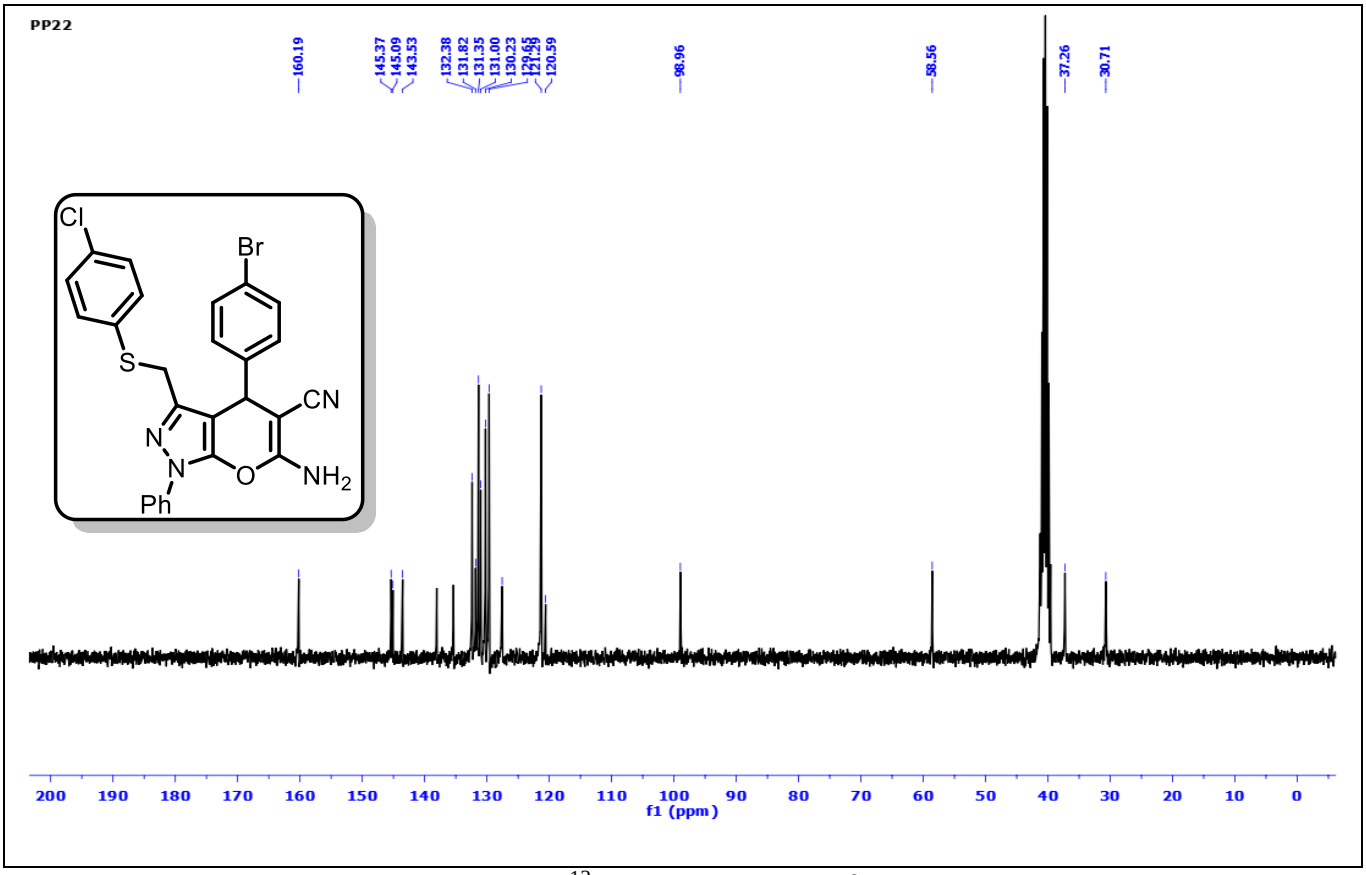


Fig.50. ^{13}C-NMR spectrum of **6r**

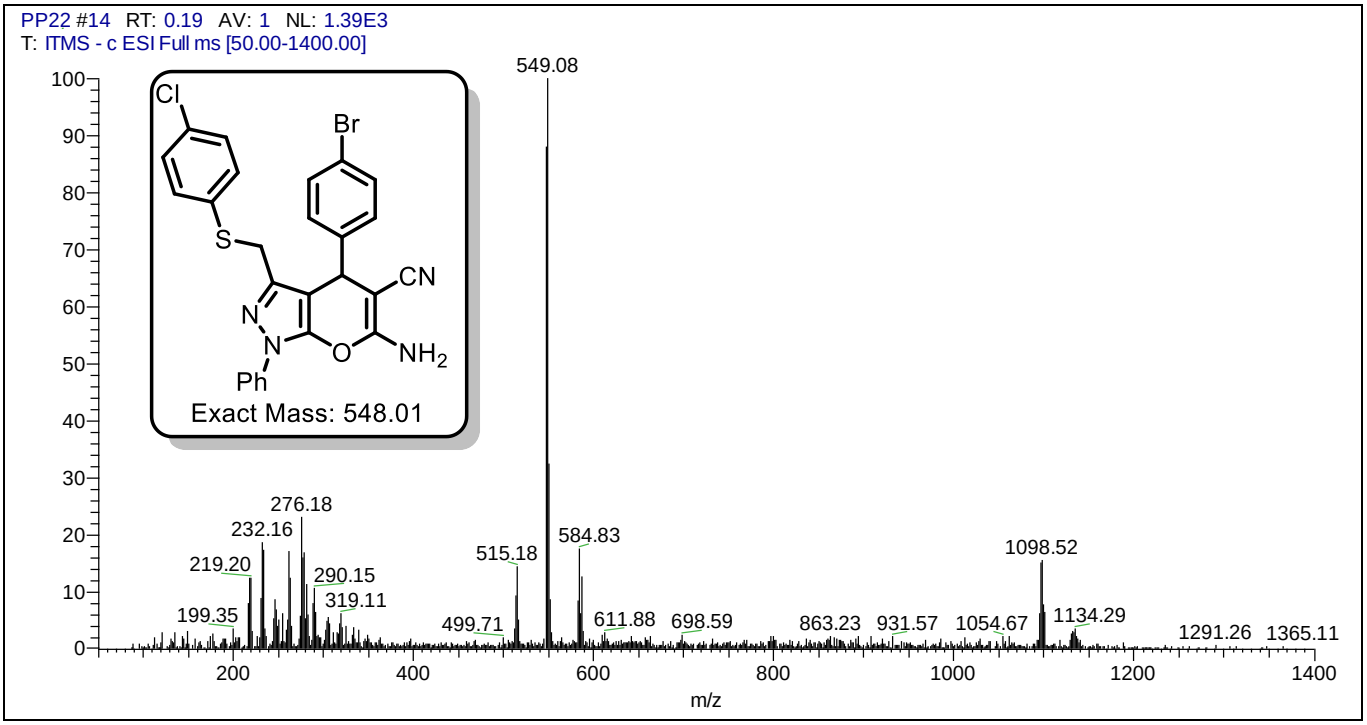


Fig.51. ESI Mass spectra of compound **6r**

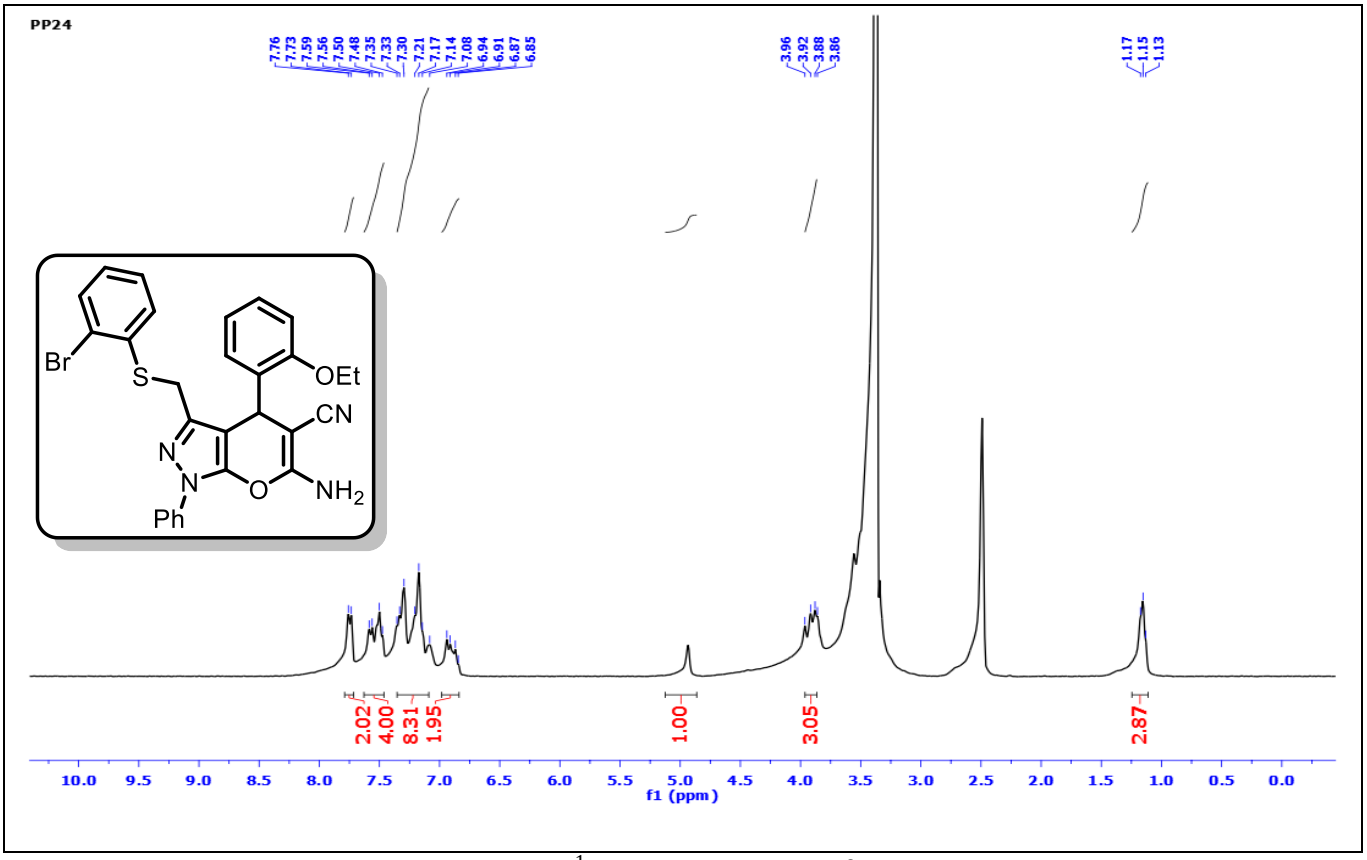


Fig.52. ^{1}H-NMR spectrum of **6s**

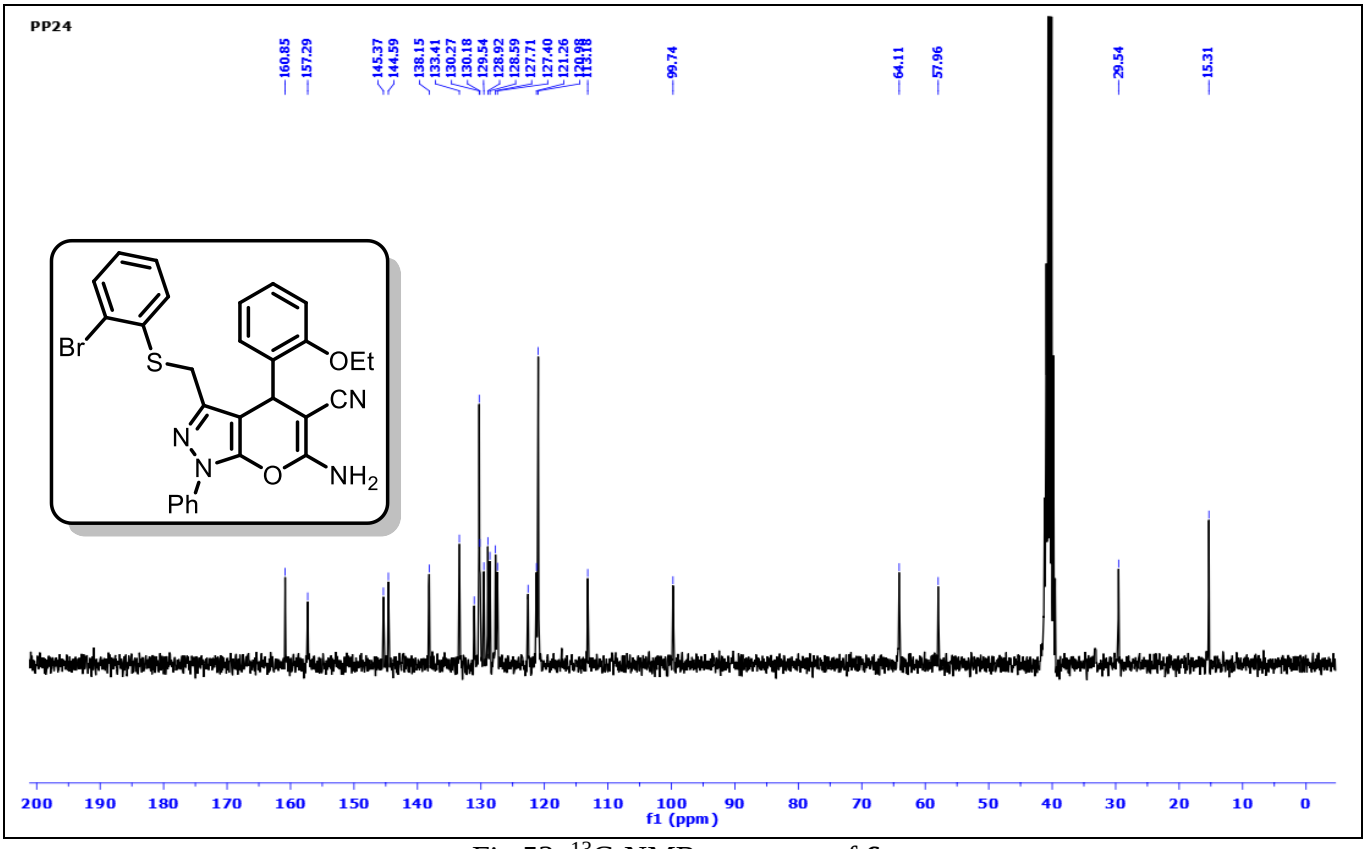


Fig.53. ^{13}C-NMR spectrum of **6s**

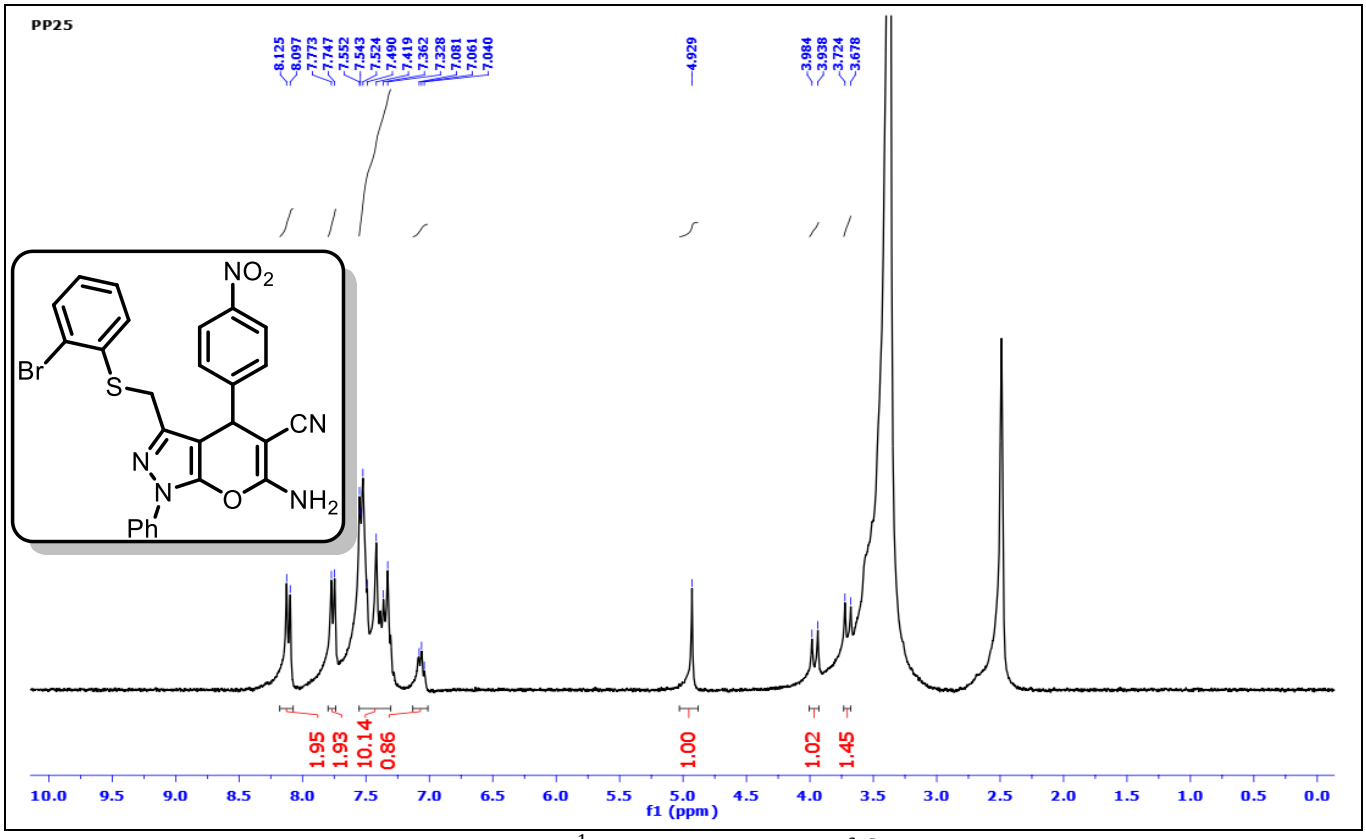


Fig.54. ^{1}H-NMR spectrum of **6t**

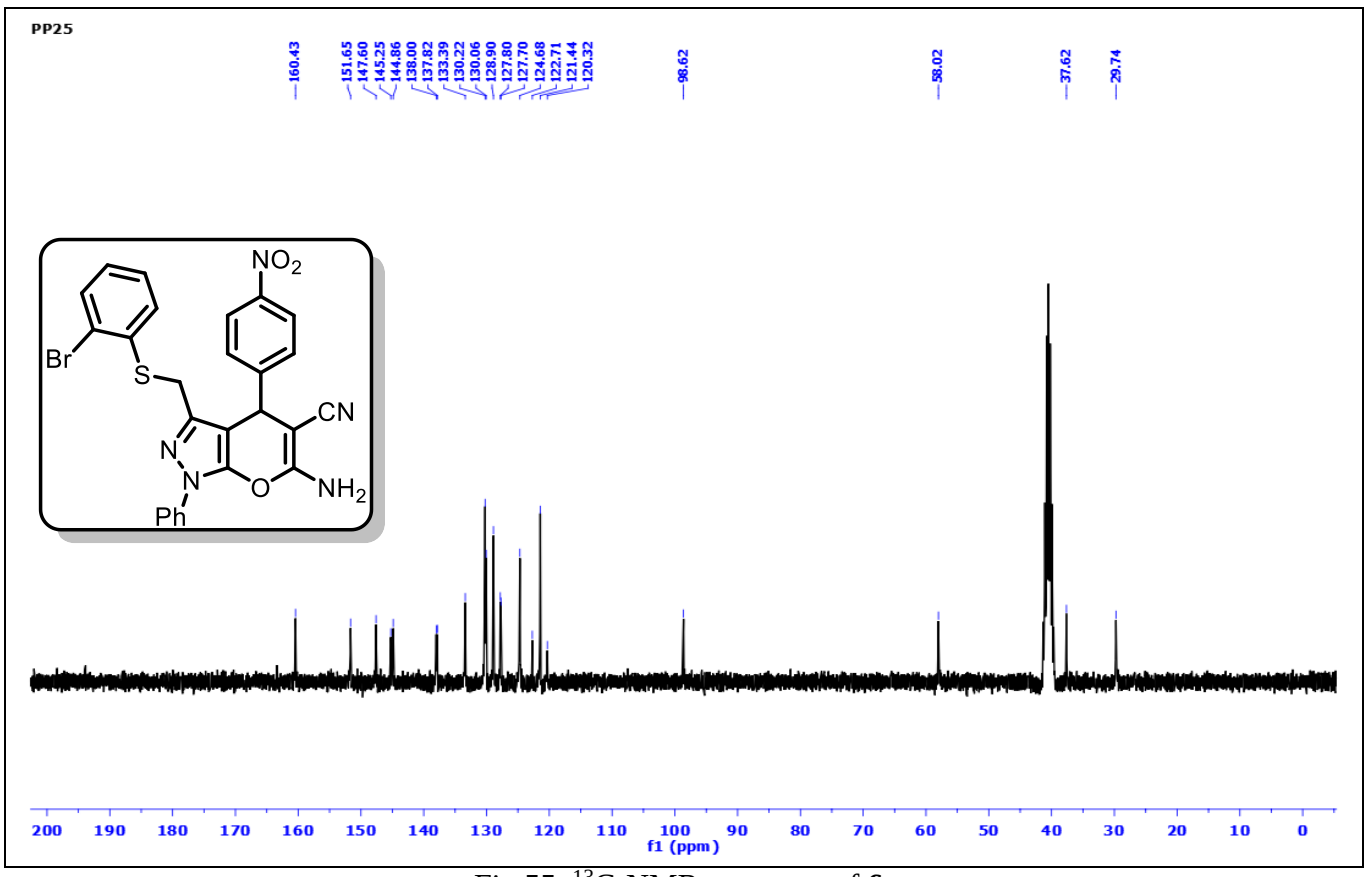


Fig.55. ^{13}C-NMR spectrum of **6t**

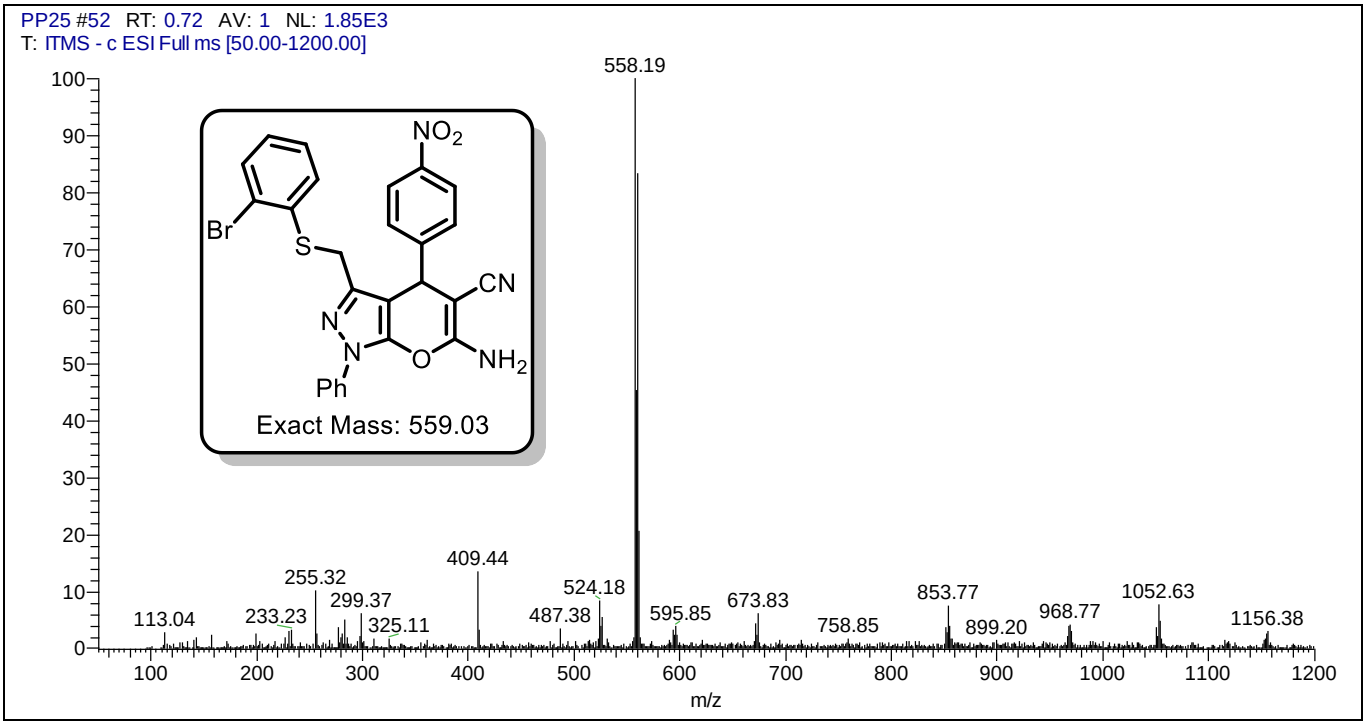


Fig.56. ESI Mass spectra of compound **6t**

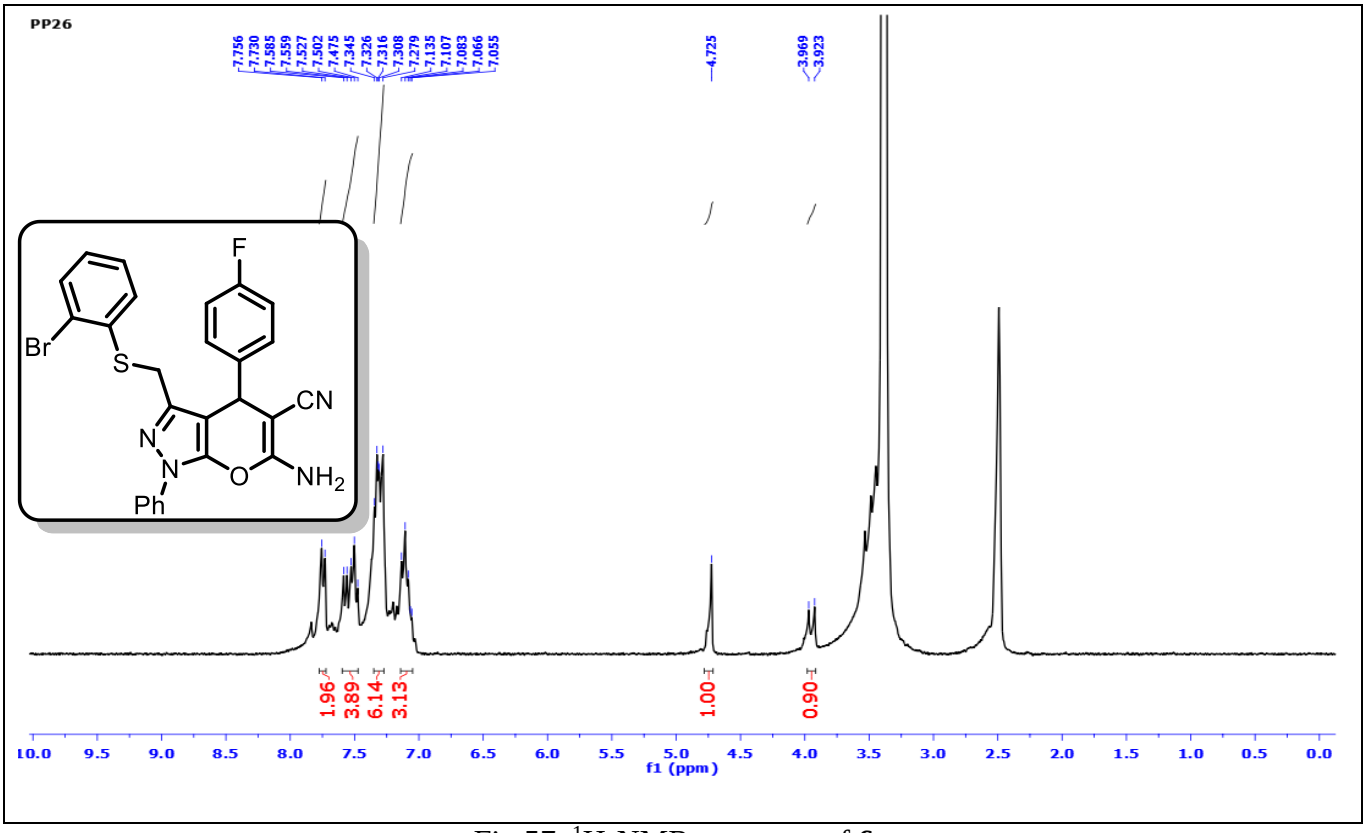


Fig.57. ^{1}H-NMR spectrum of **6u**

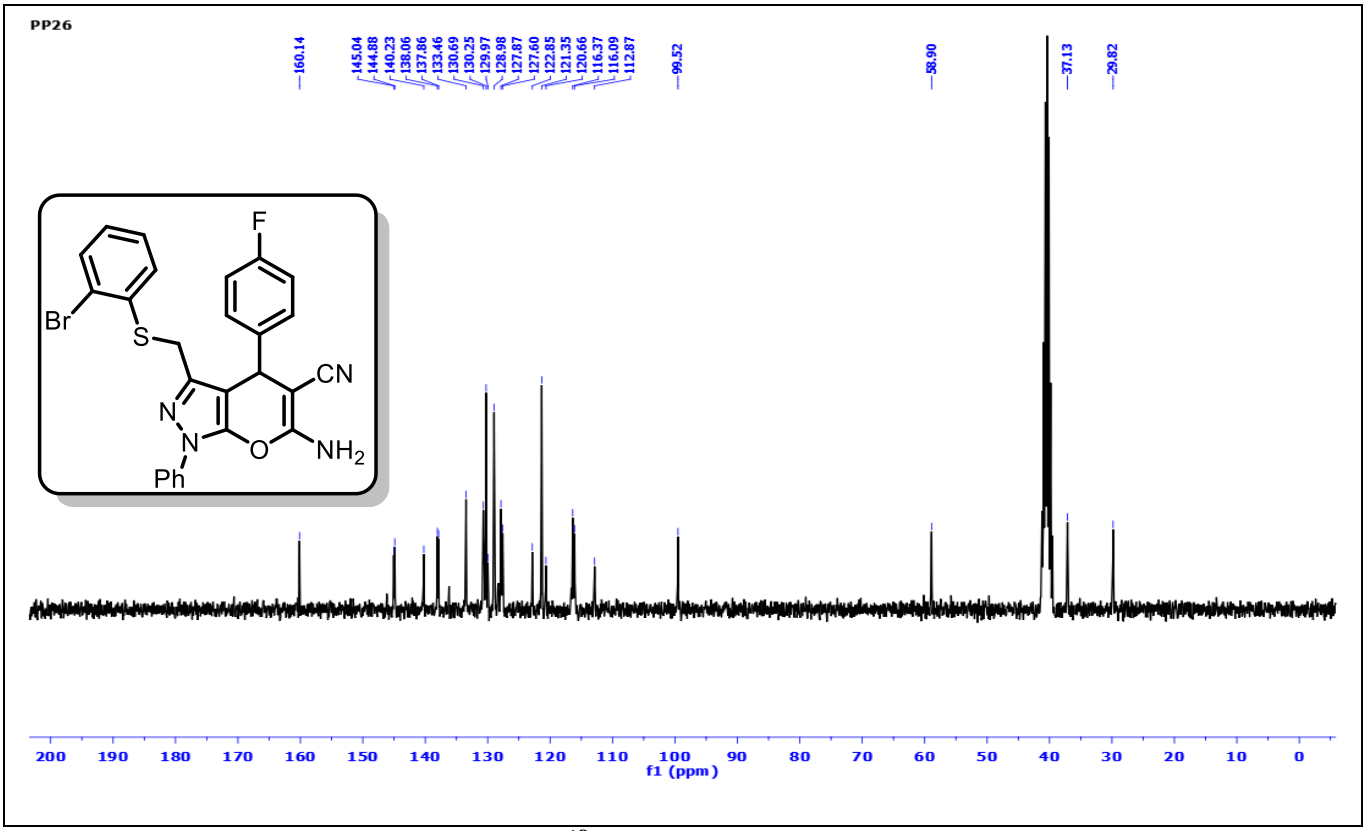


Fig.58. ^{13}C-NMR spectrum of **6u**

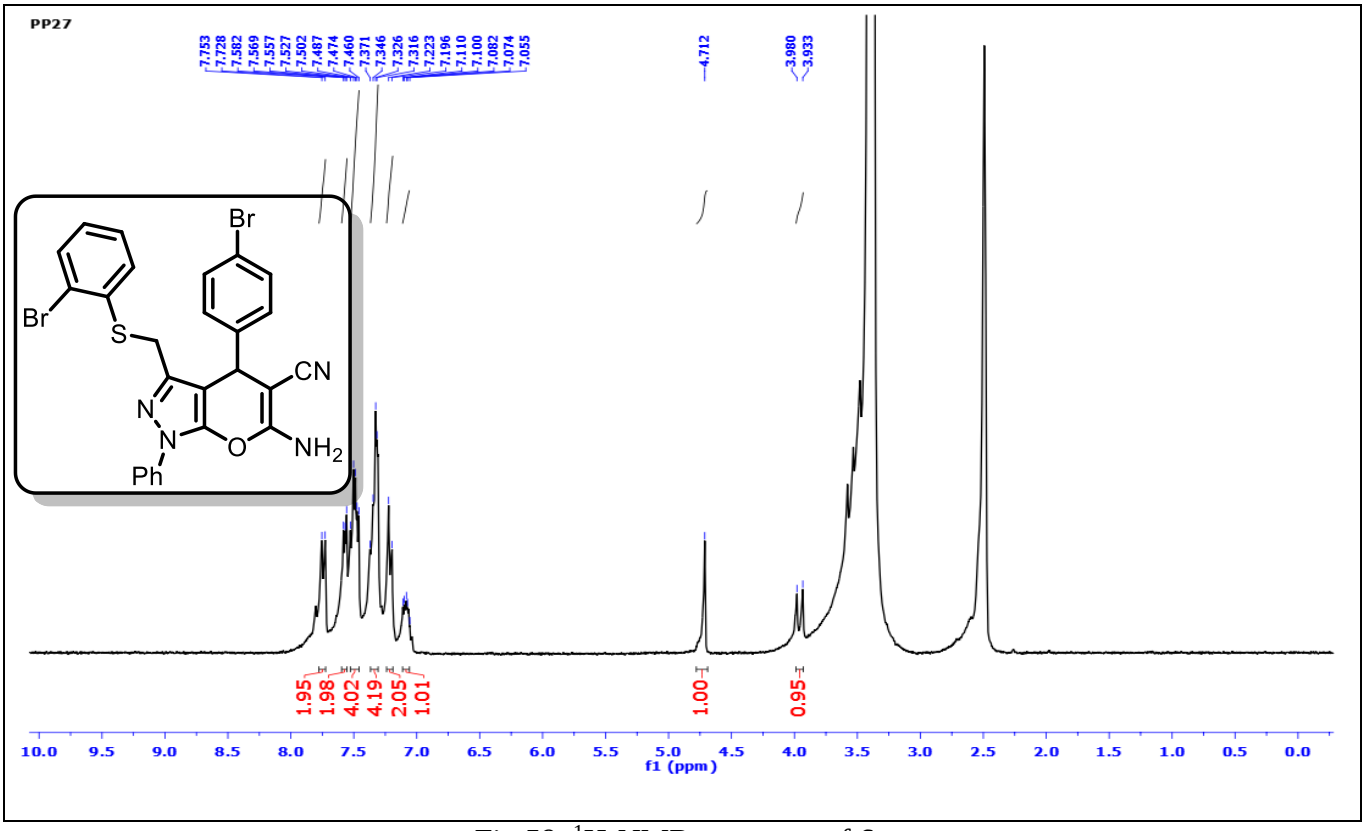


Fig.59. ^{1}H-NMR spectrum of **6v**

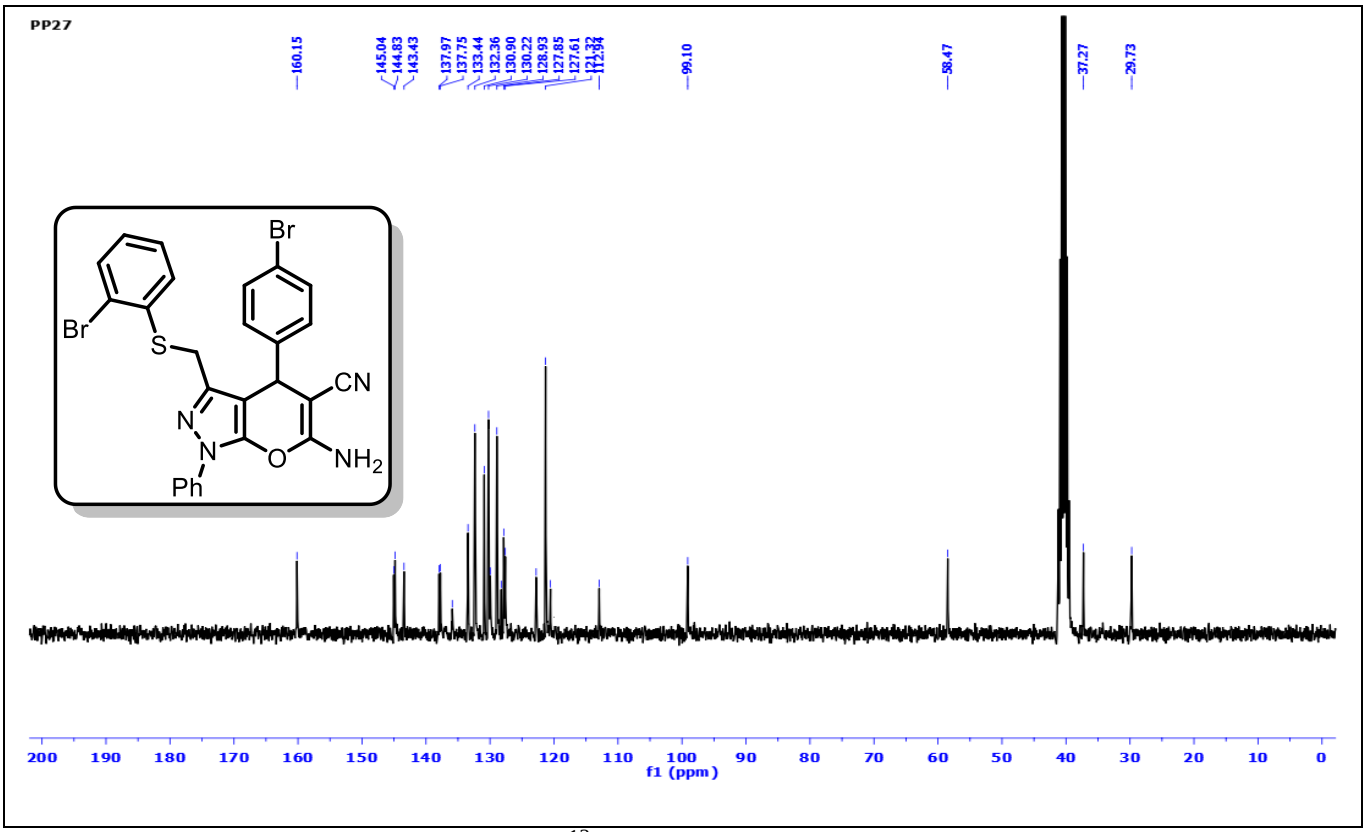


Fig.60. ^{13}C-NMR spectrum of **6v**

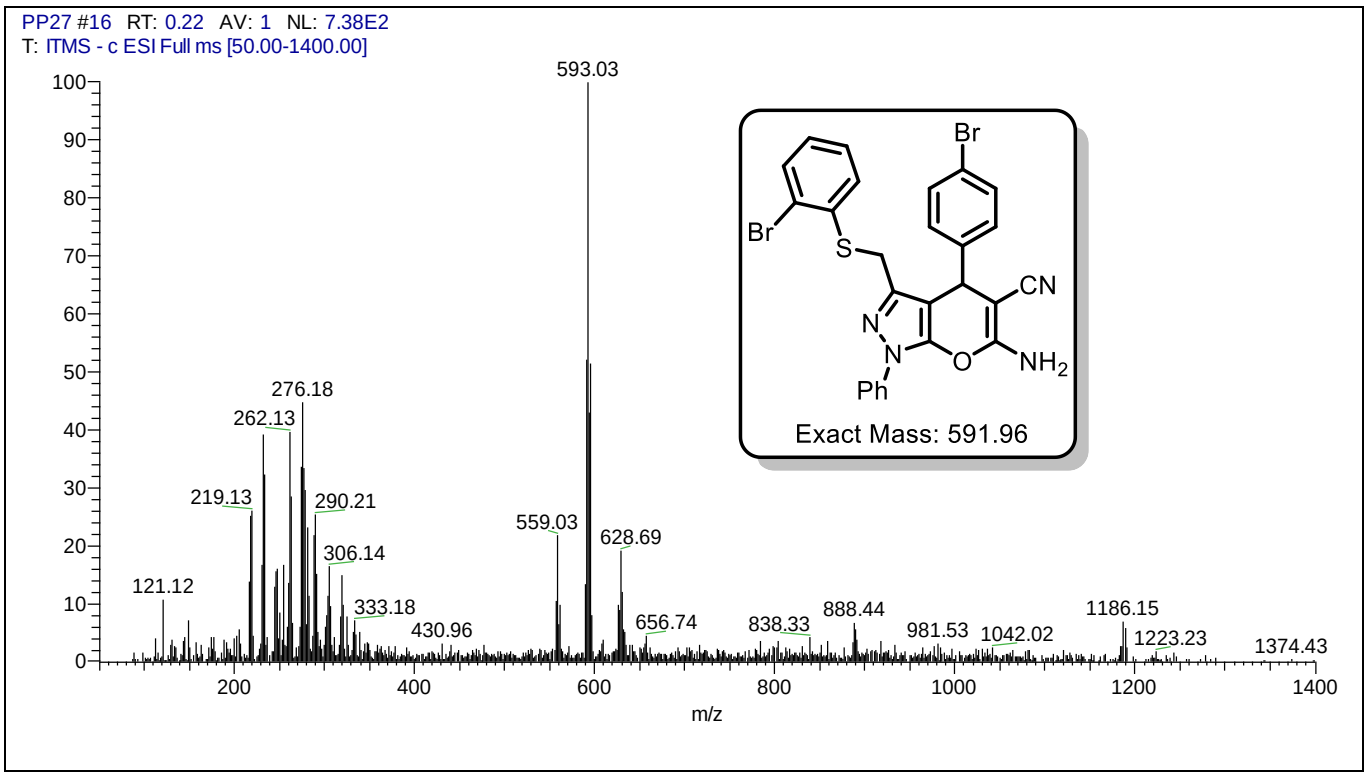


Fig.61. ESI Mass spectra of compound **6v**

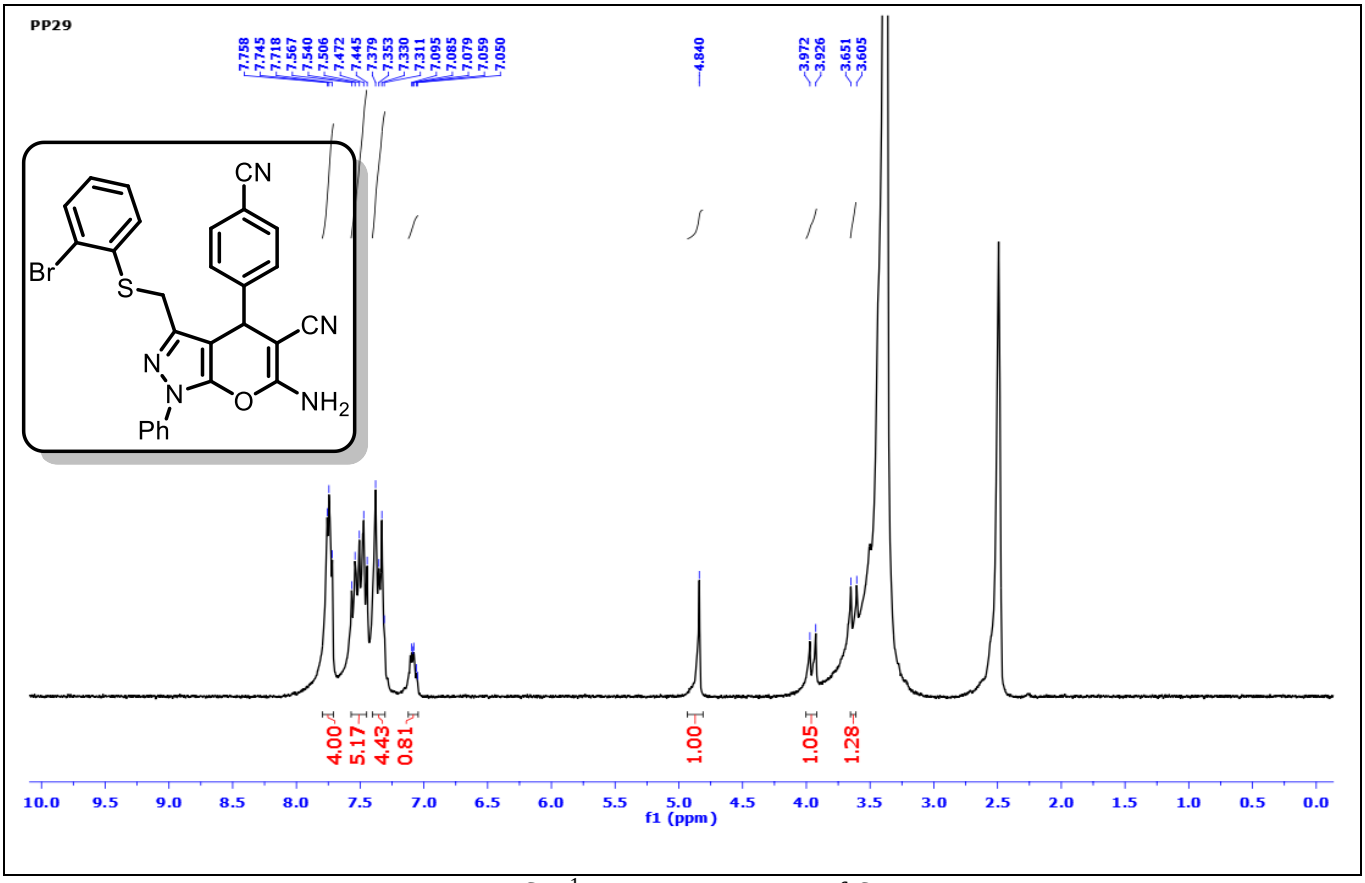


Fig.62. ^{1}H-NMR spectrum of **6w**

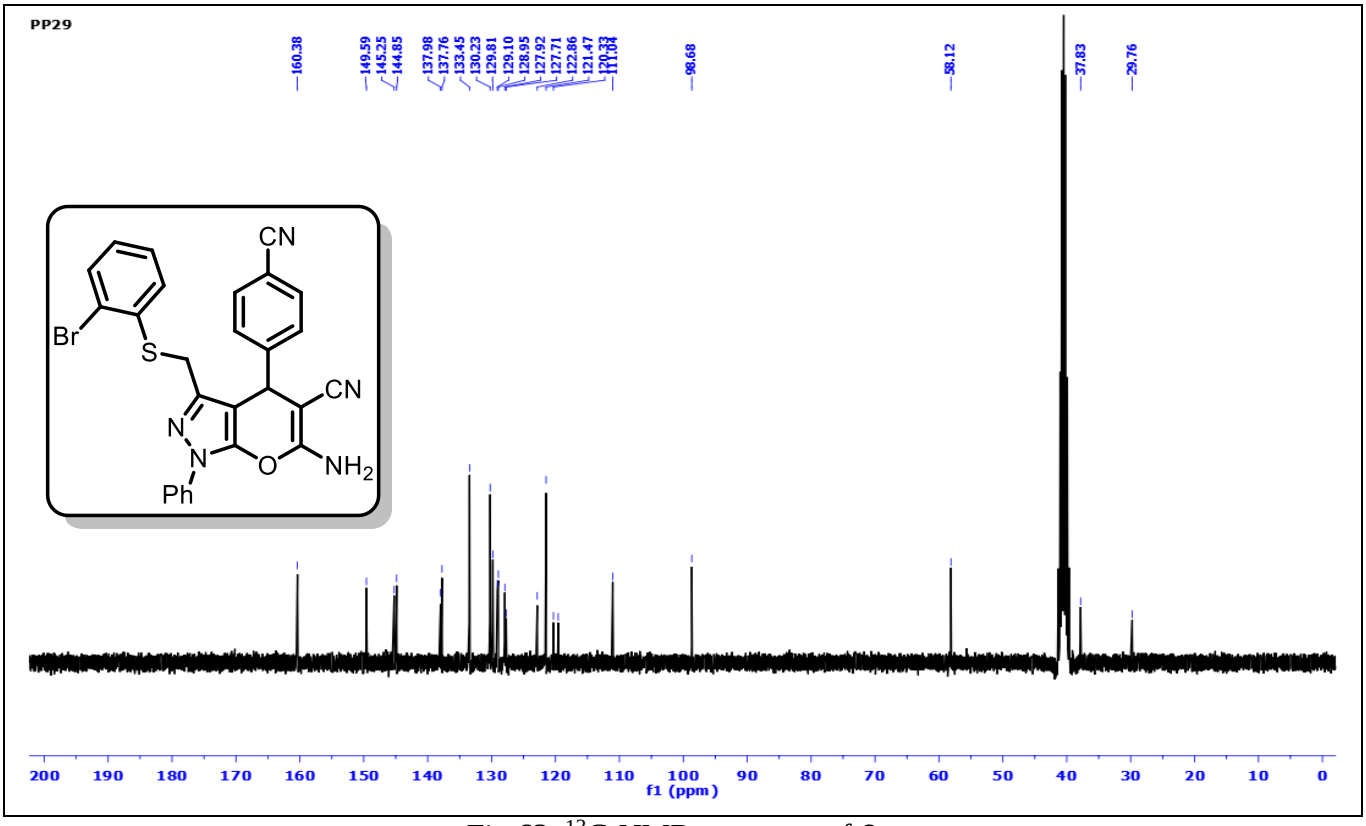


Fig.63. ^{13}C-NMR spectrum of **6w**

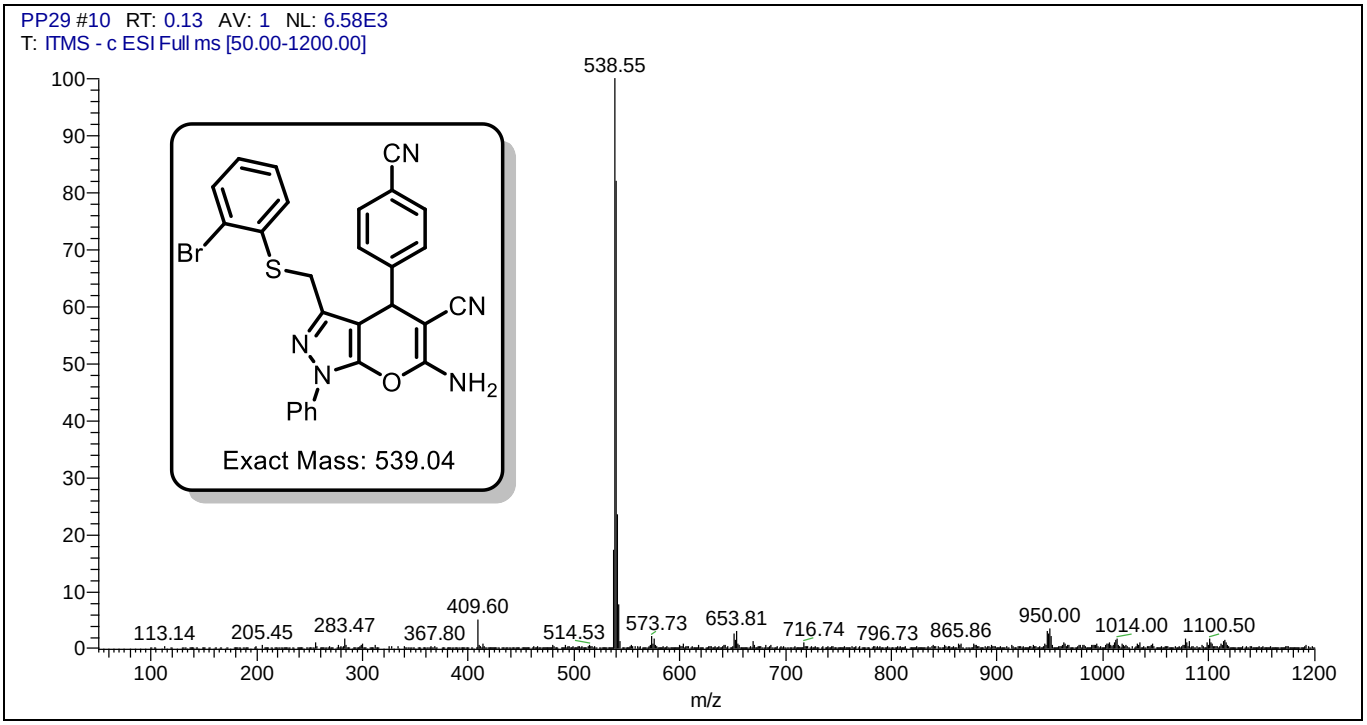


Fig.64. ESI Mass spectra of compound **6w**

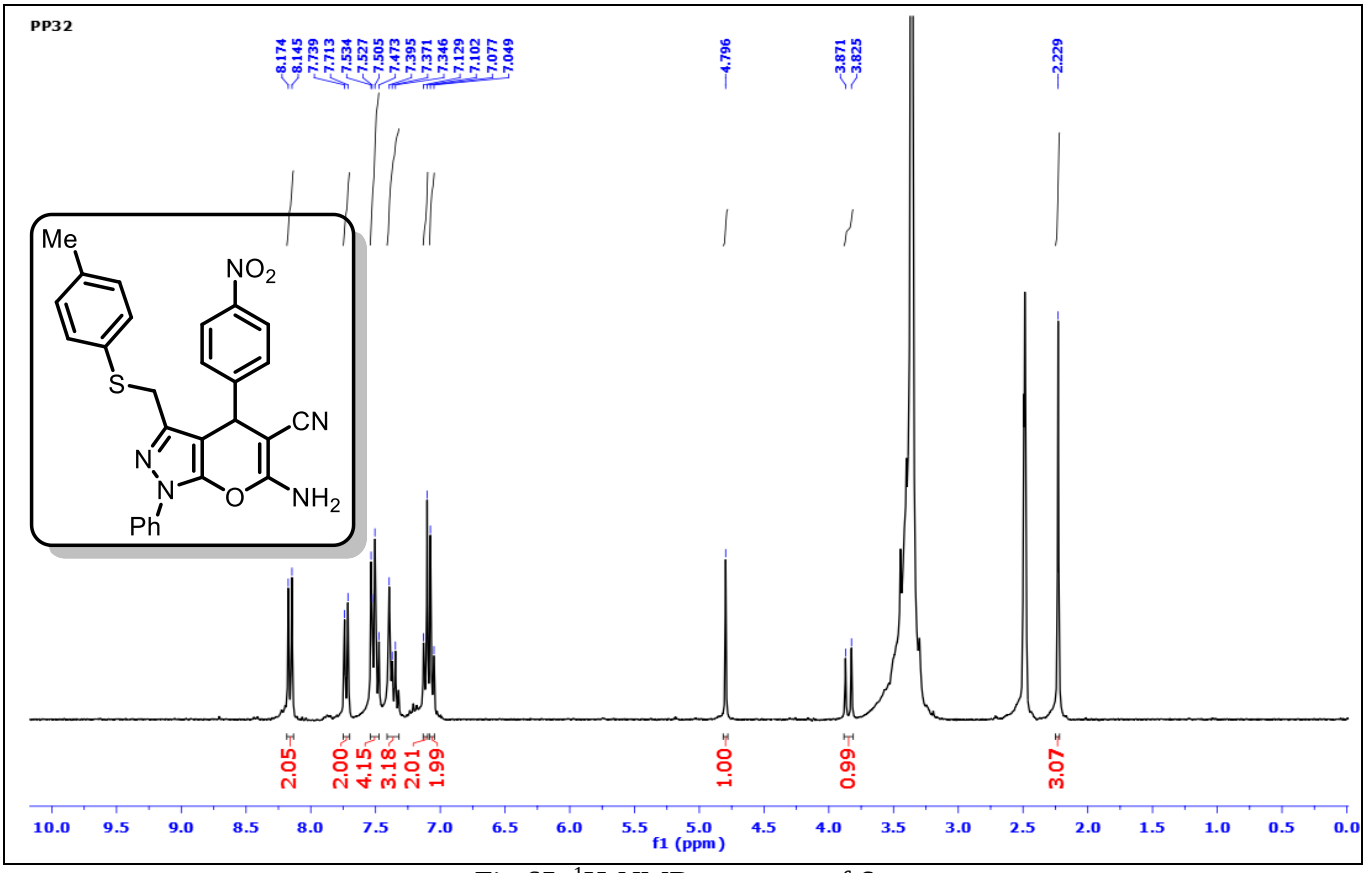


Fig.65. ^{1}H-NMR spectrum of **6x**

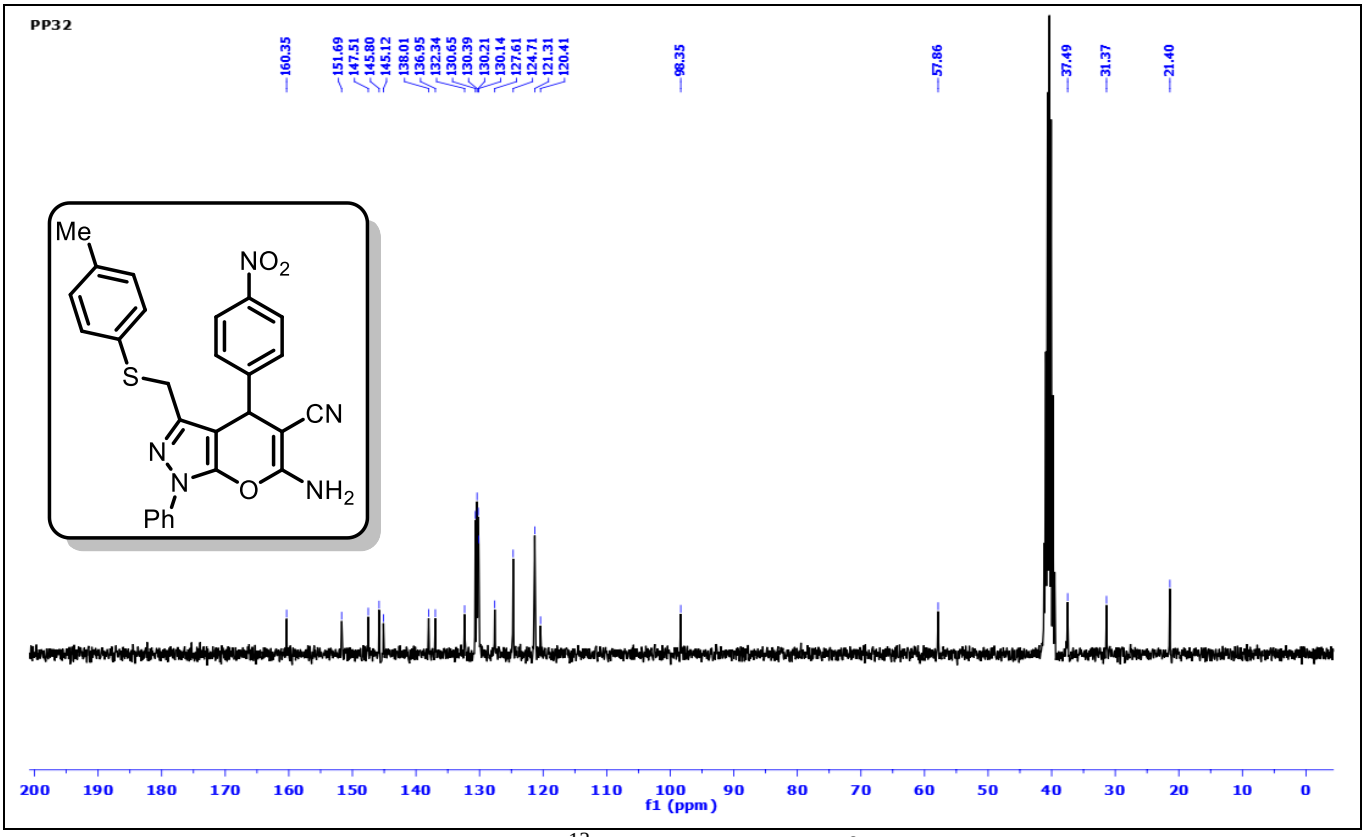


Fig.66. ^{13}C-NMR spectrum of **6x**

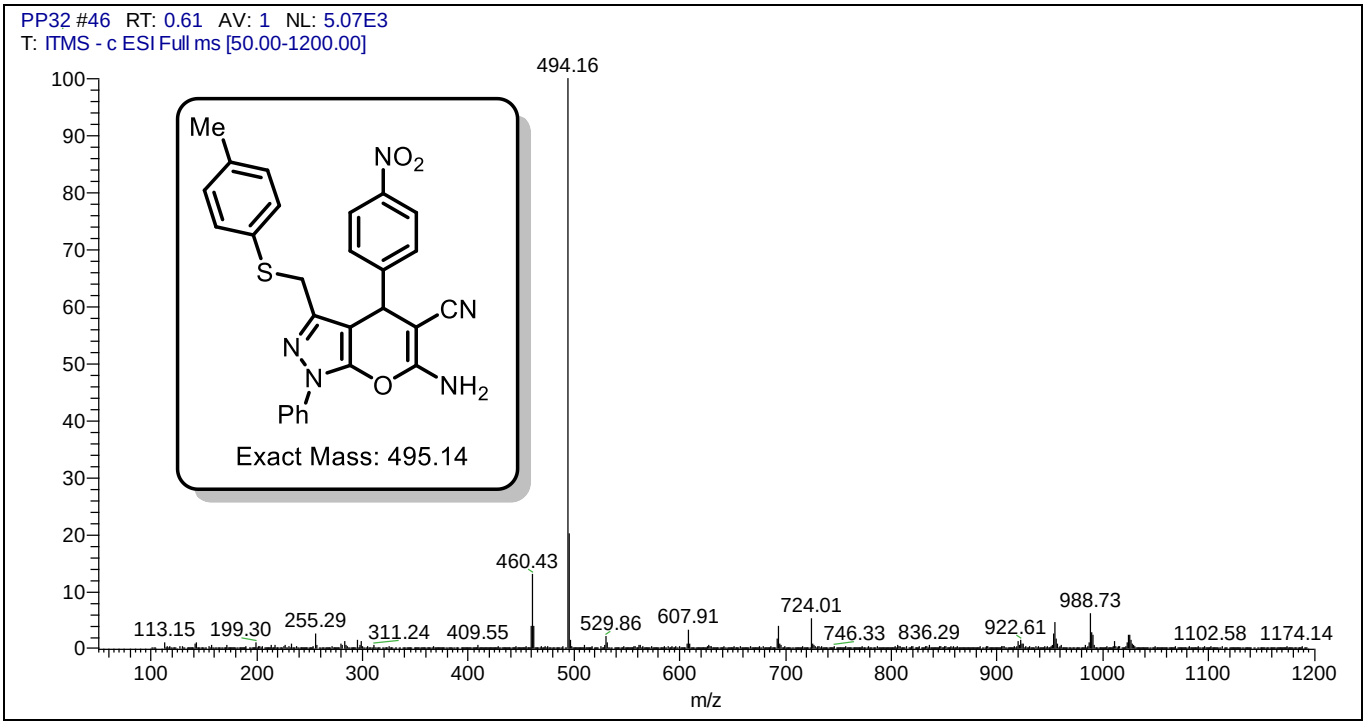


Fig.67. ESI Mass spectra of compound **6x**

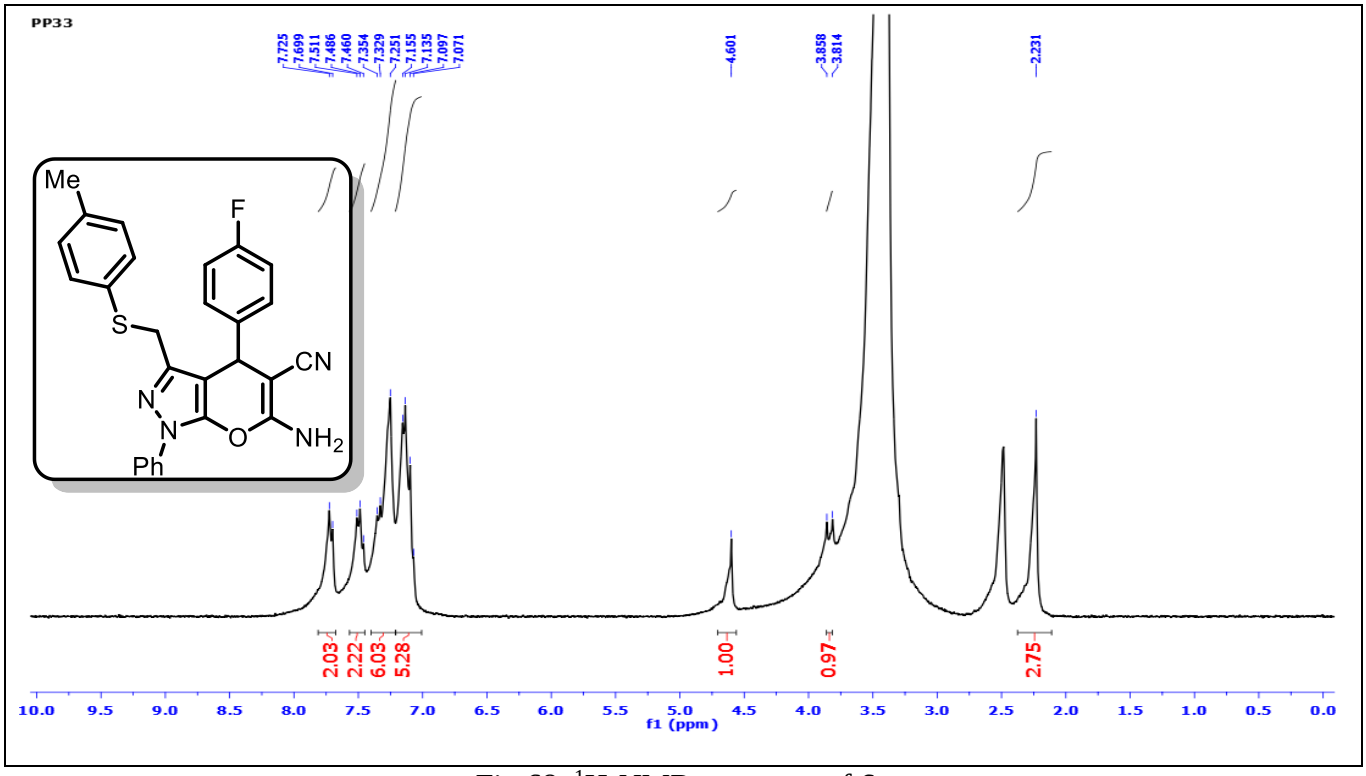


Fig.68. ^{1}H-NMR spectrum of **6y**

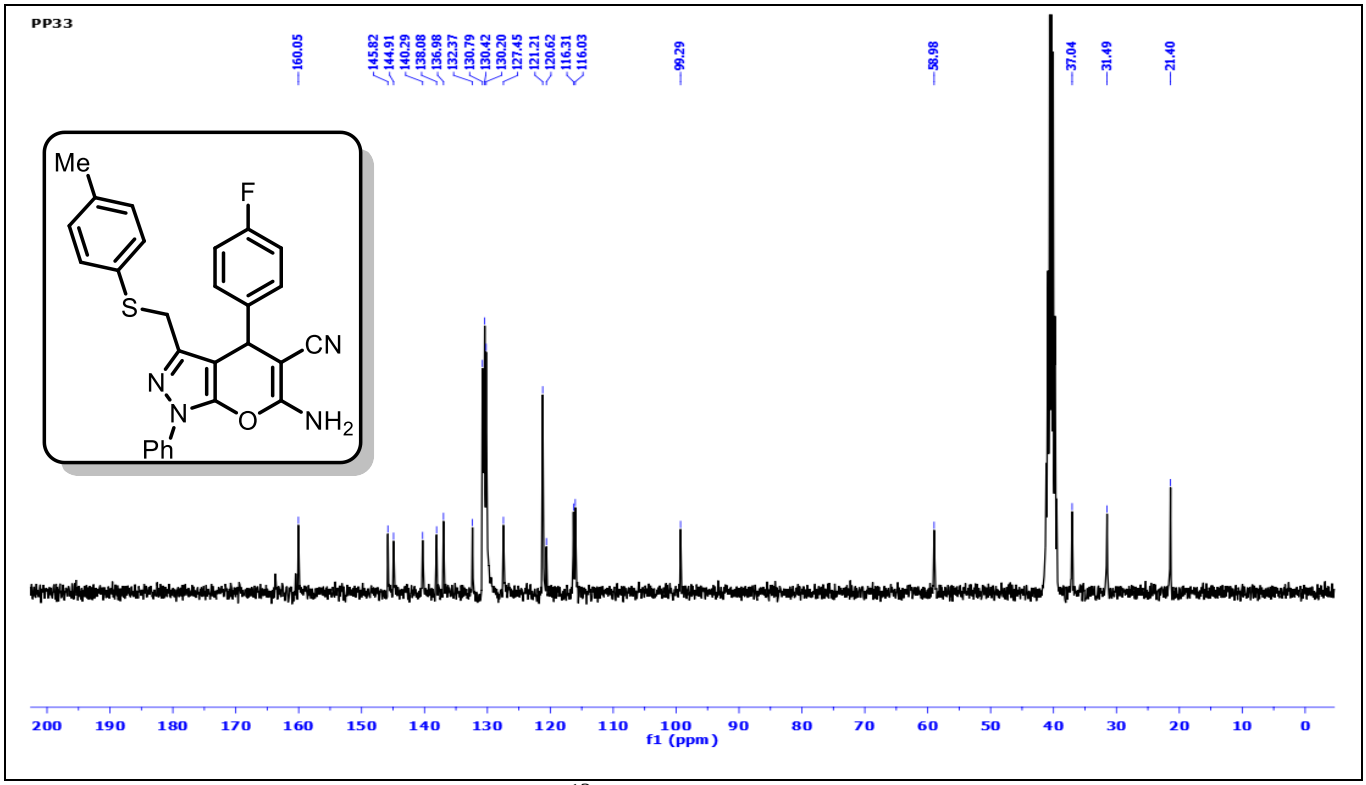


Fig.69. ^{13}C-NMR spectrum of **6y**

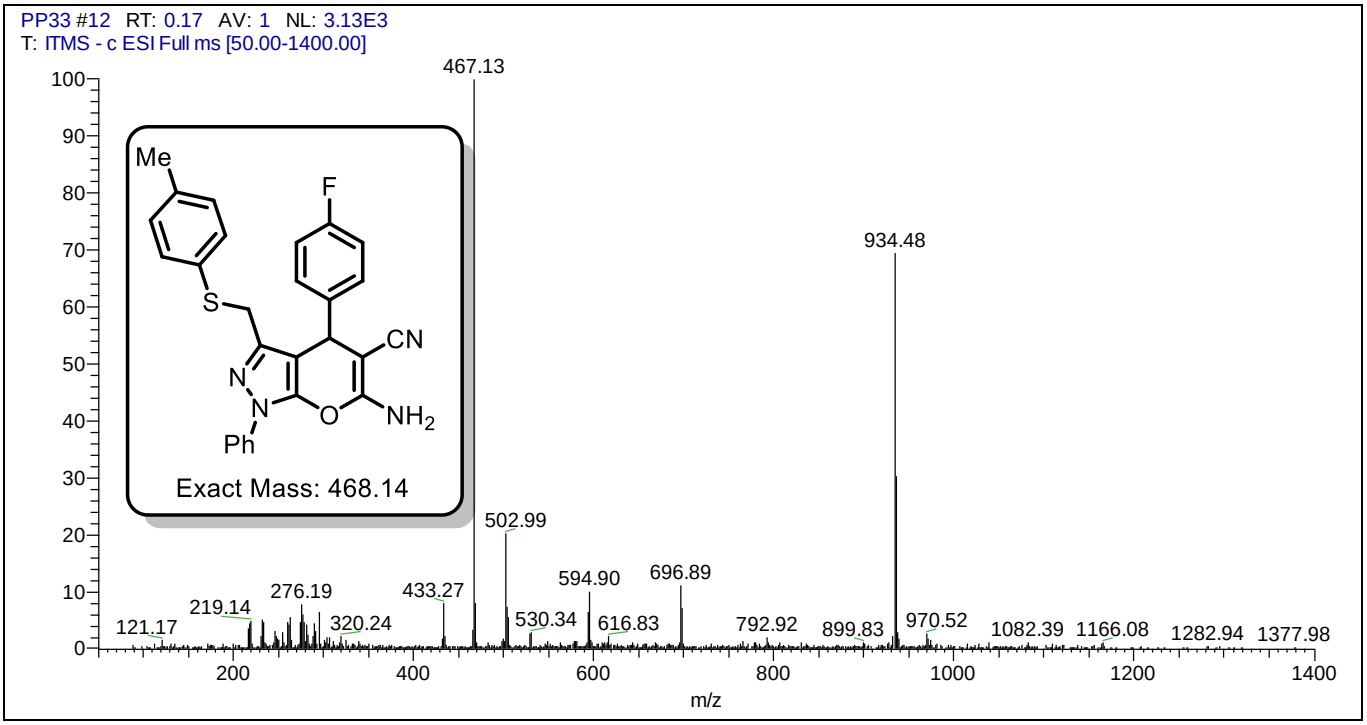


Fig.70. ESI Mass spectra of compound **6y**

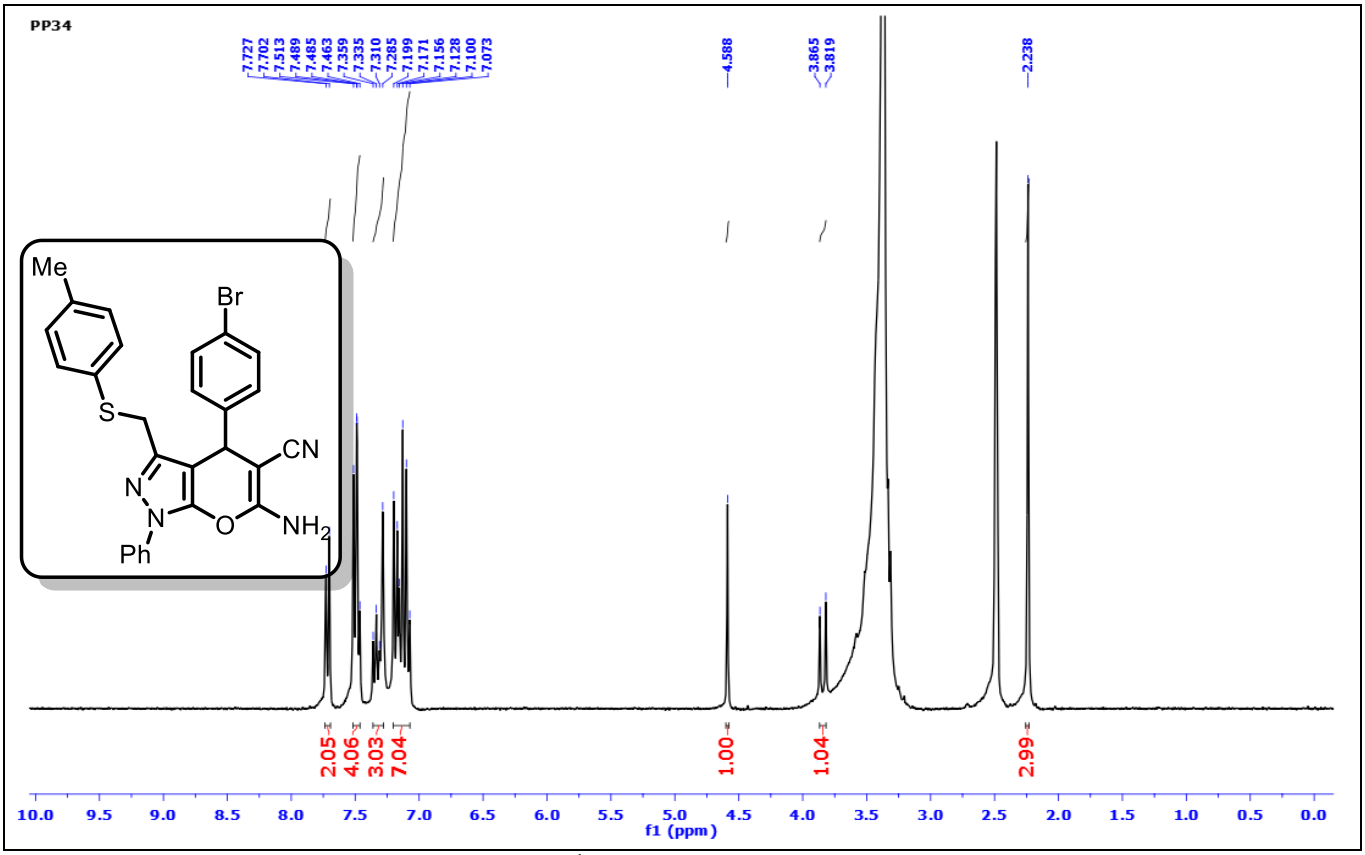


Fig.71. ^{1}H-NMR spectrum of **6z**

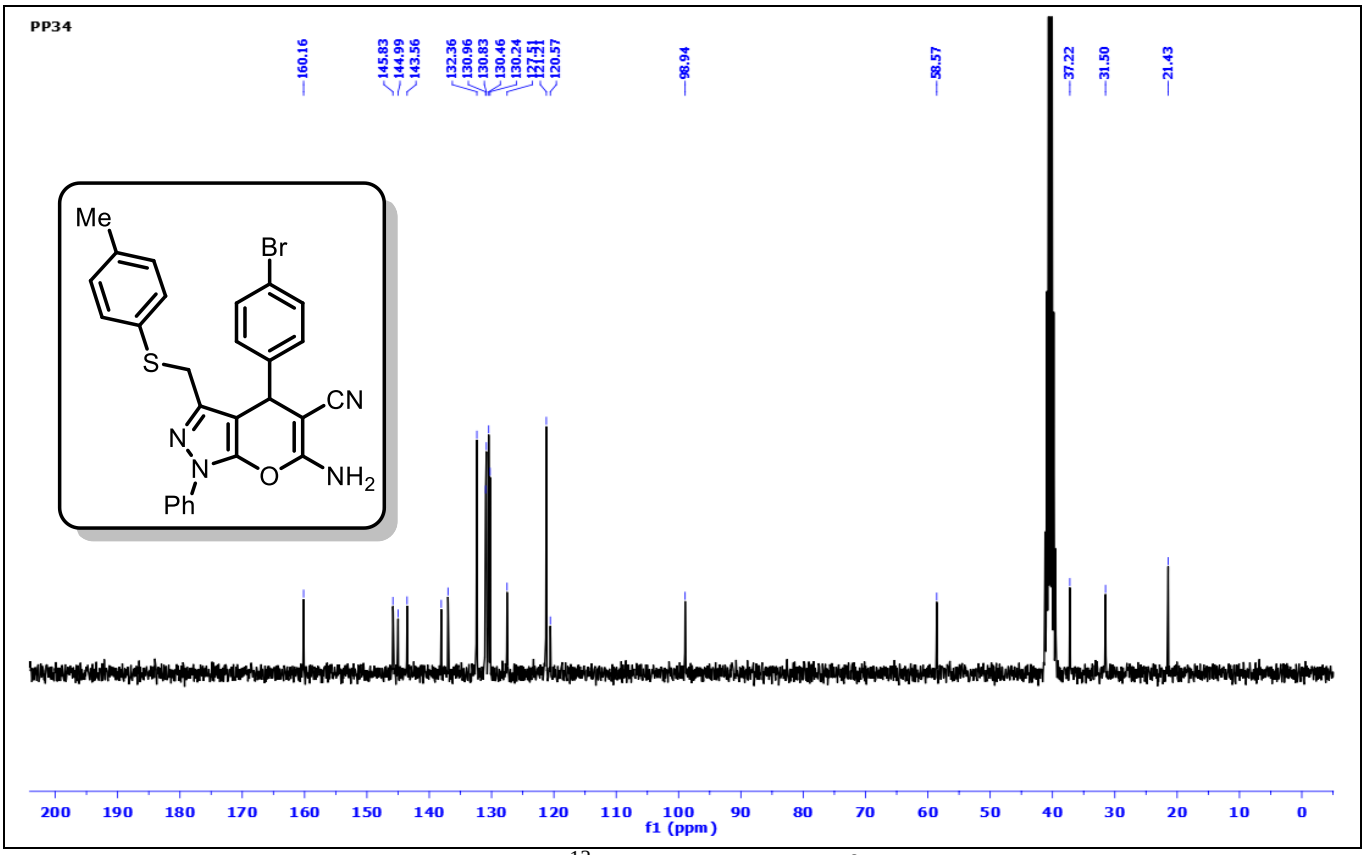


Fig.72. ^{13}C-NMR spectrum of **6z**

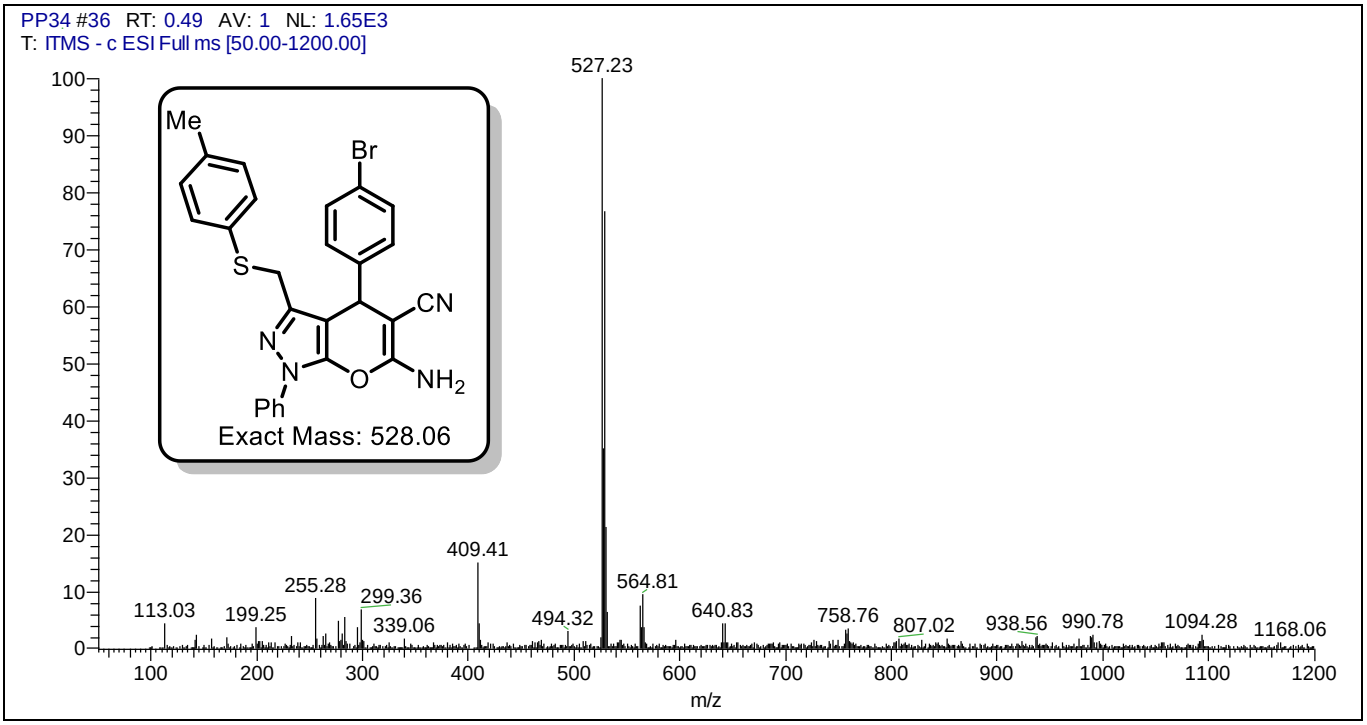


Fig.73. ESI Mass spectra of compound **6z**

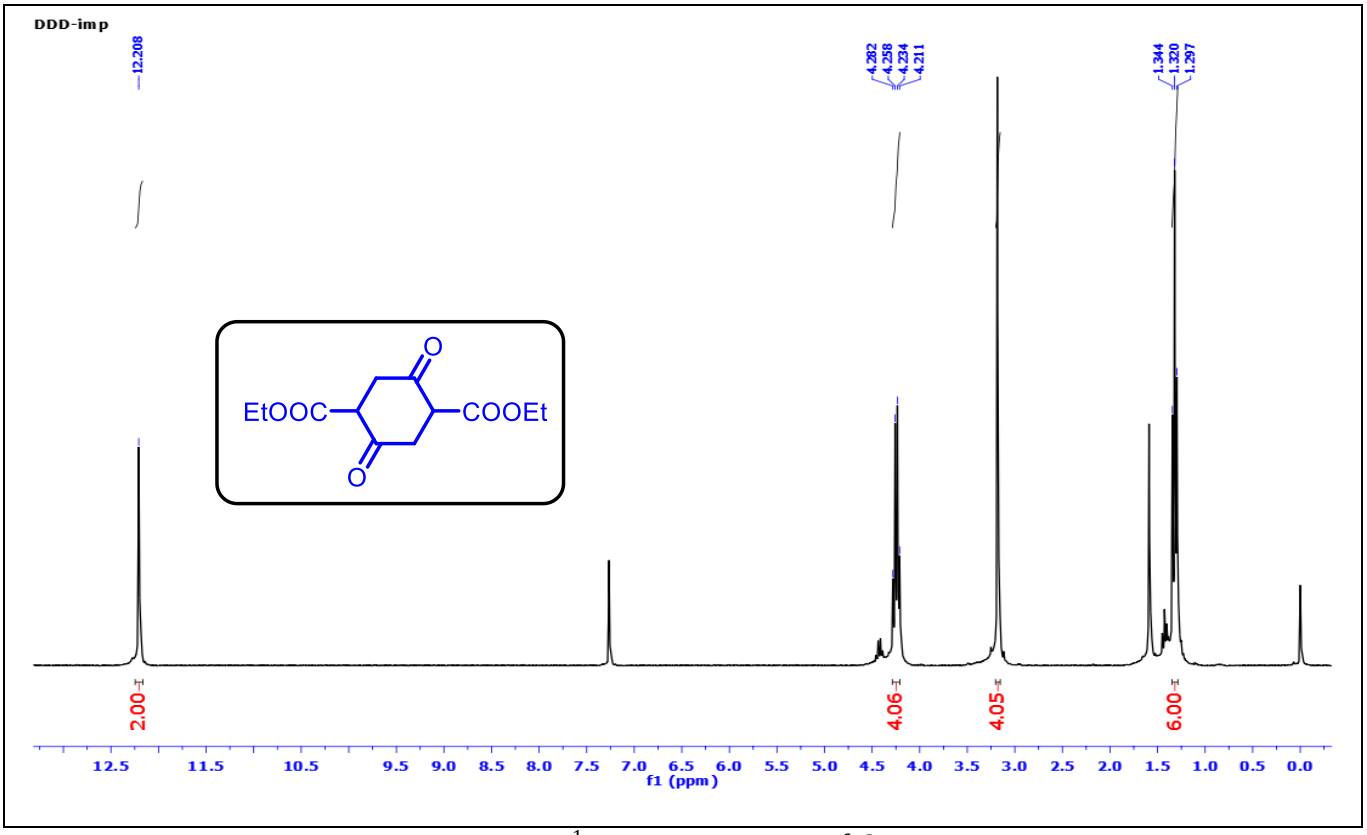


Fig.74. ^{1}H-NMR spectrum of **A_1**

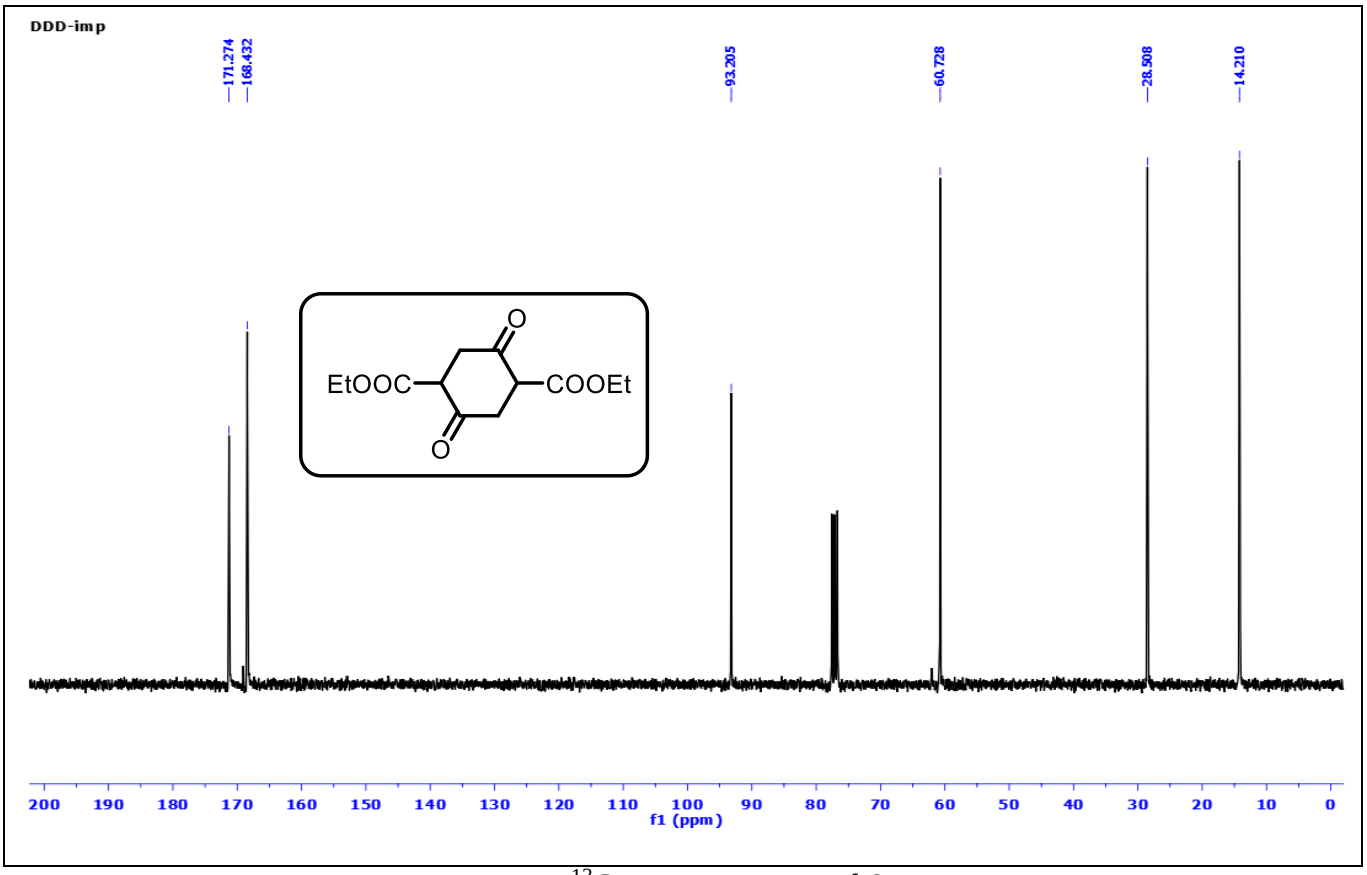


Fig.75. ^{13}C-NMR spectrum of **A_1**

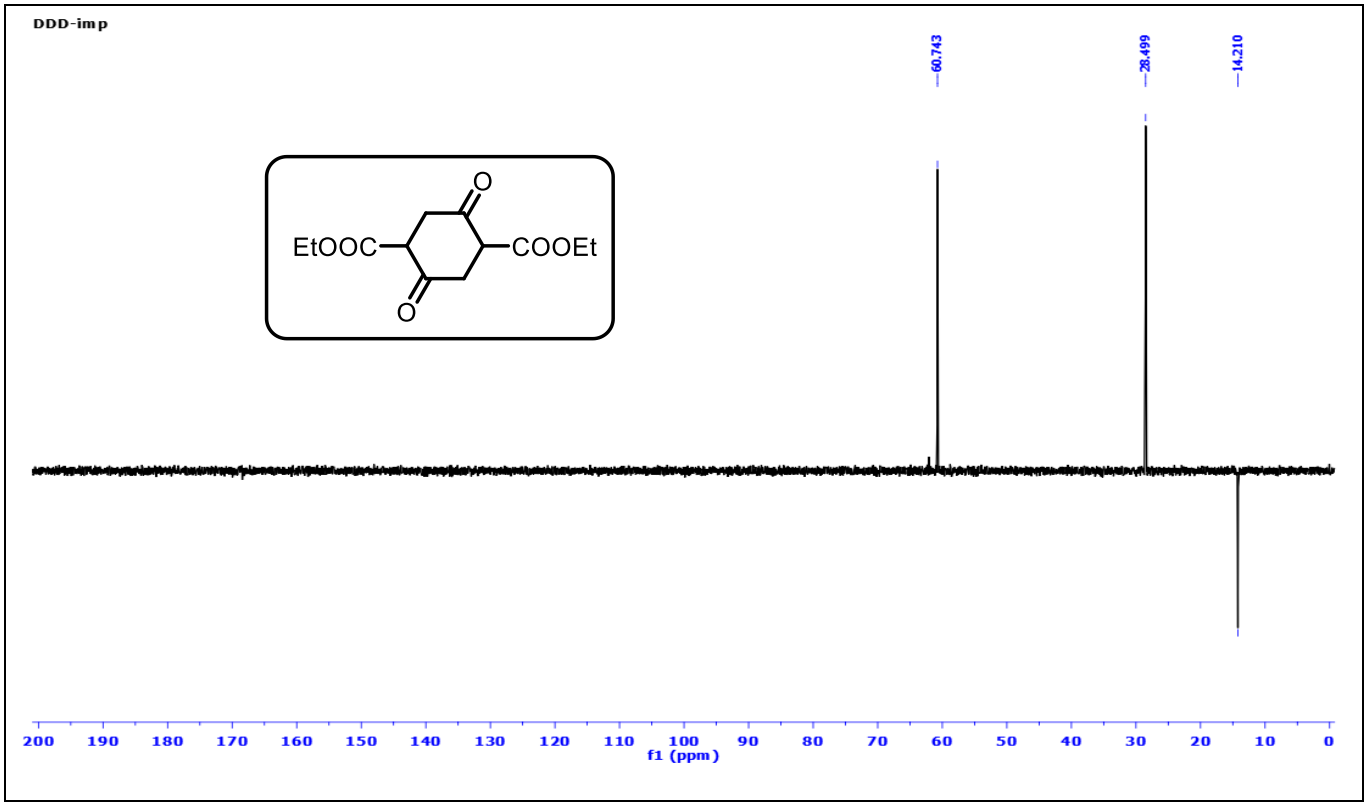


Fig.76. DEPT-135 spectrum of **A_1**

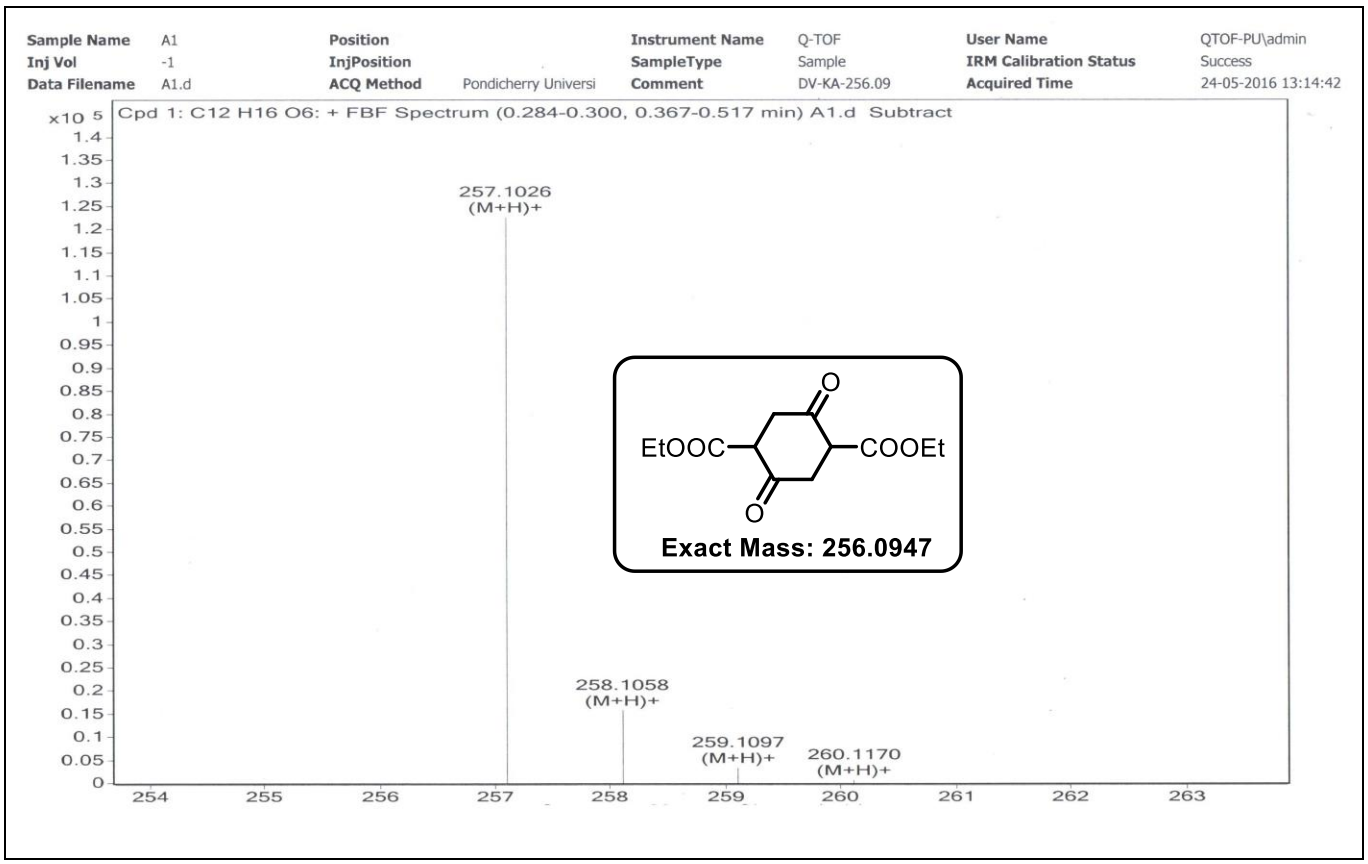


Fig.77. HRMS spectrum of **A_1**

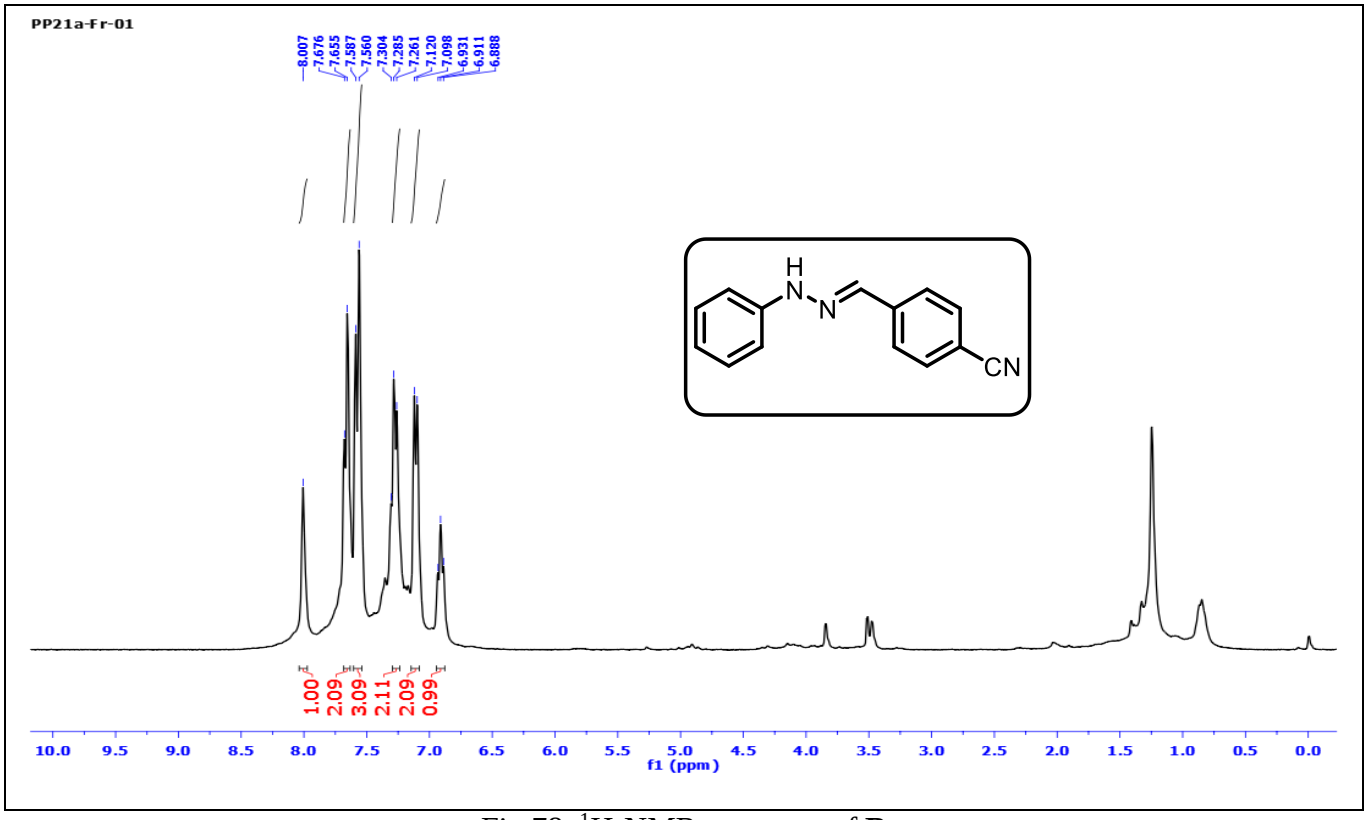


Fig.78. ^{1}H-NMR spectrum of **B**

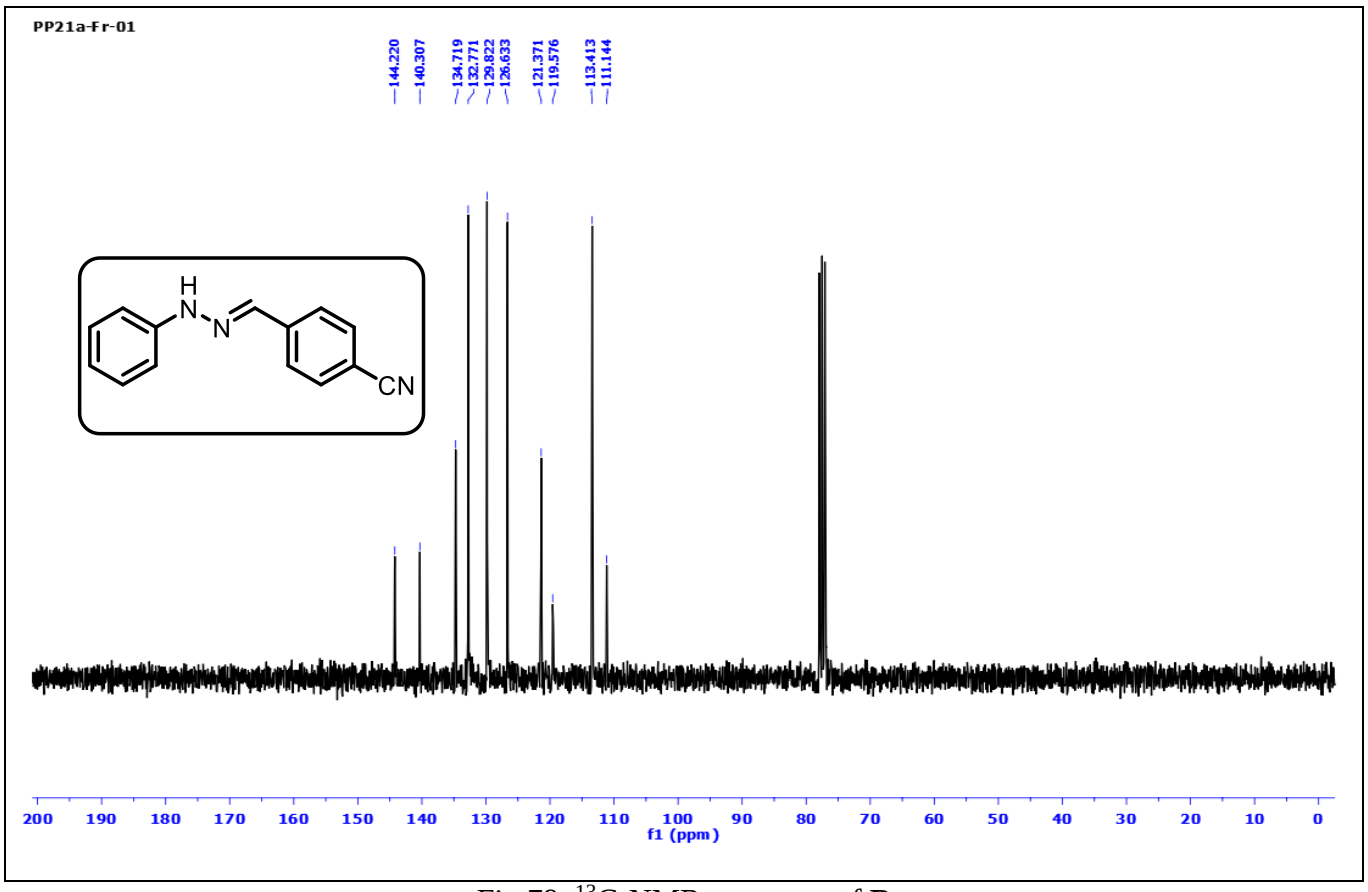


Fig.79. ^{13}C-NMR spectrum of **B**

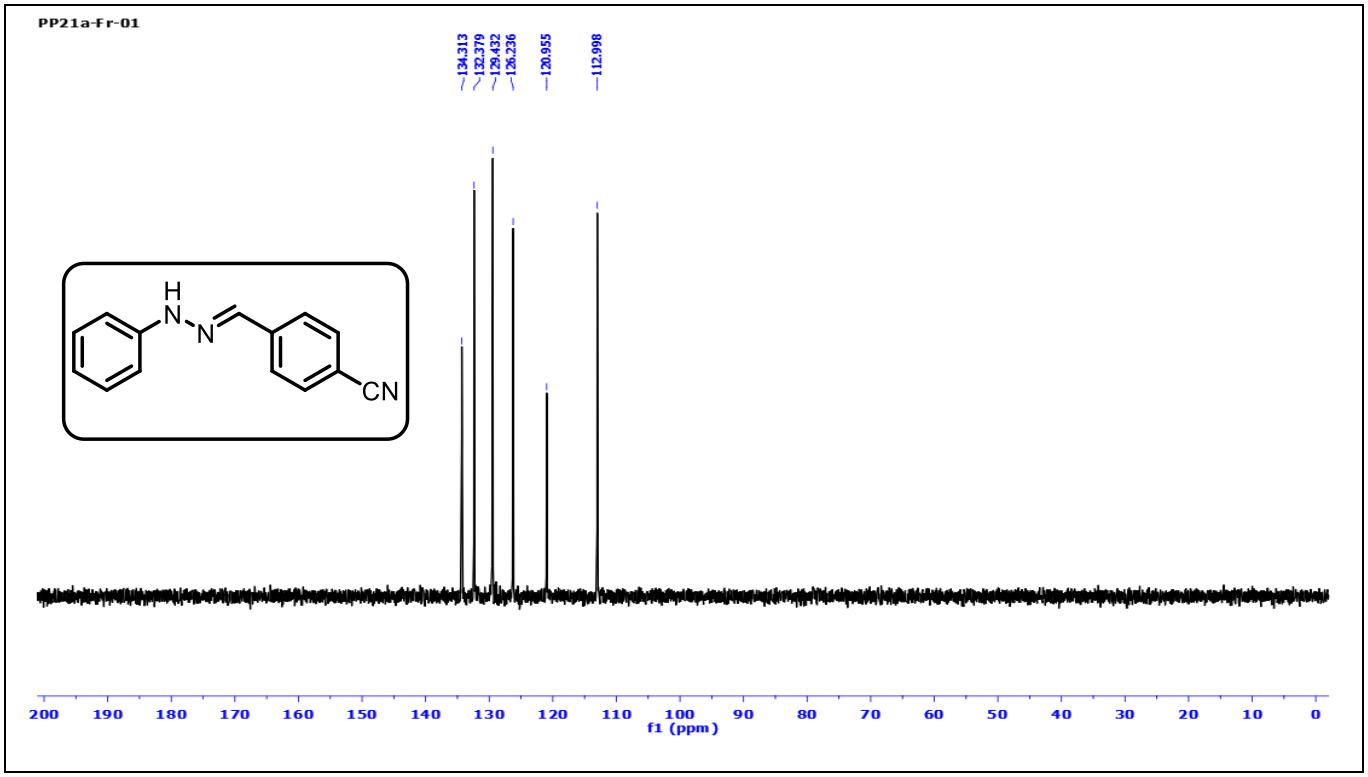


Fig.80. DEPT-135 spectrum of **B**

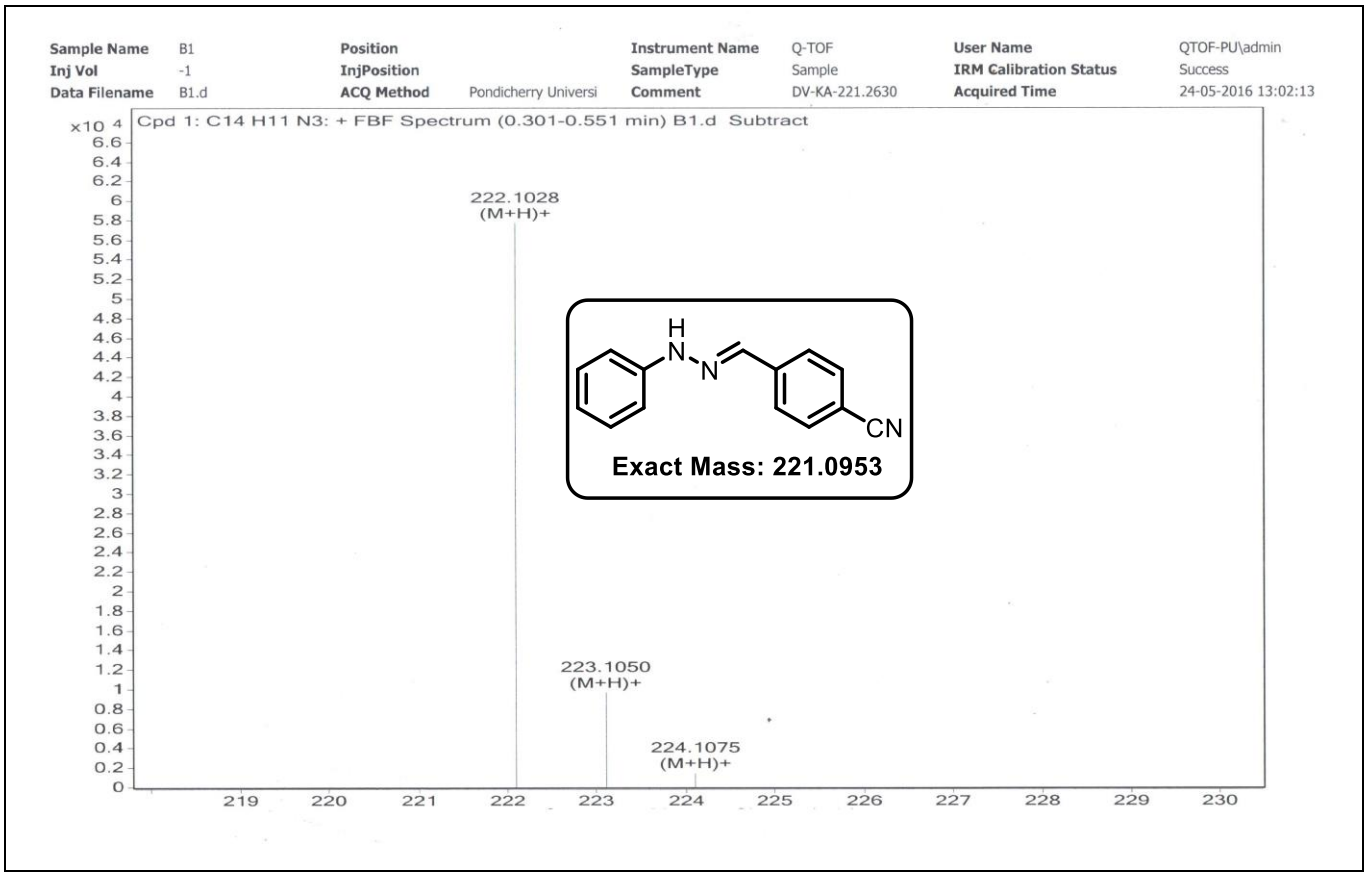


Fig.81. HRMS spectrum of **B**

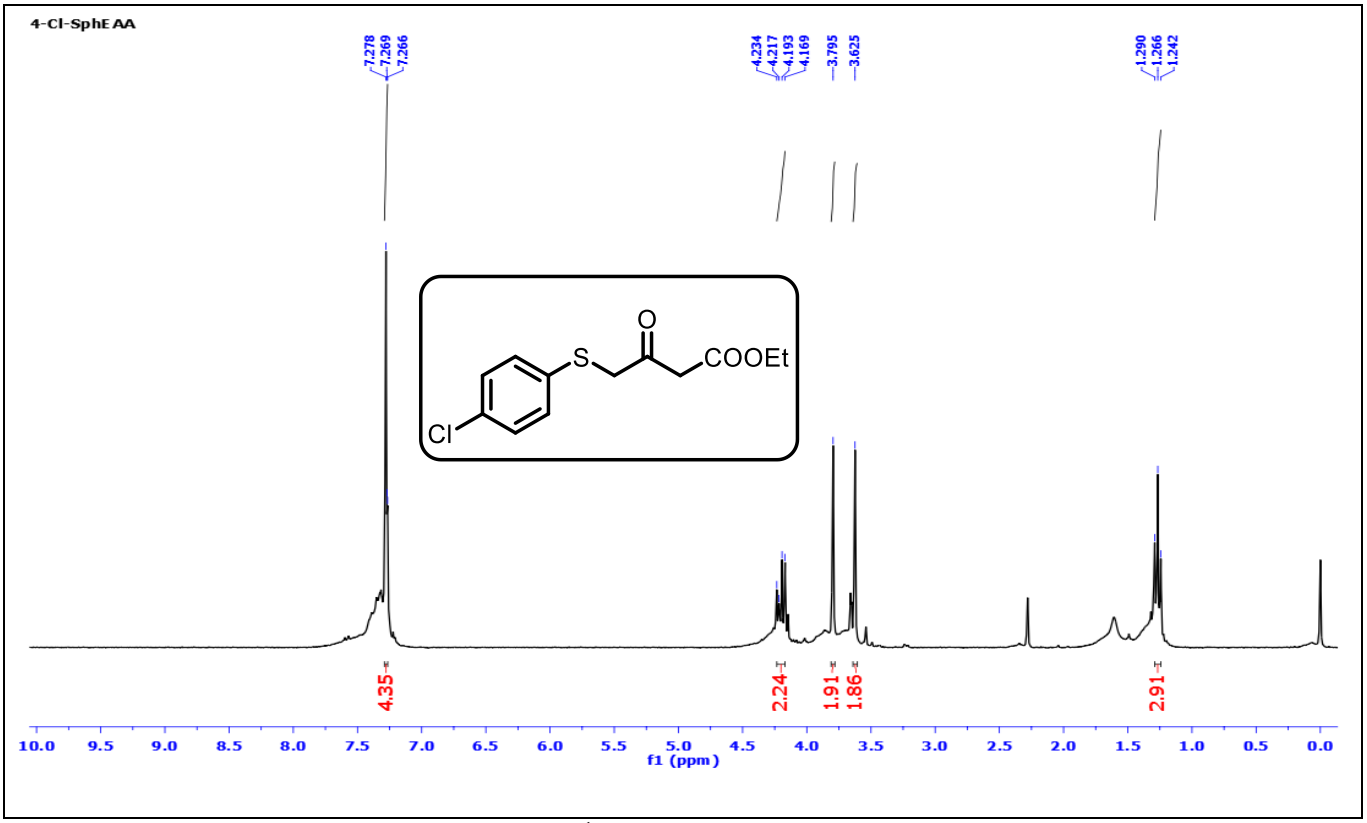


Fig.82. ^{1}H-NMR spectrum of **I**

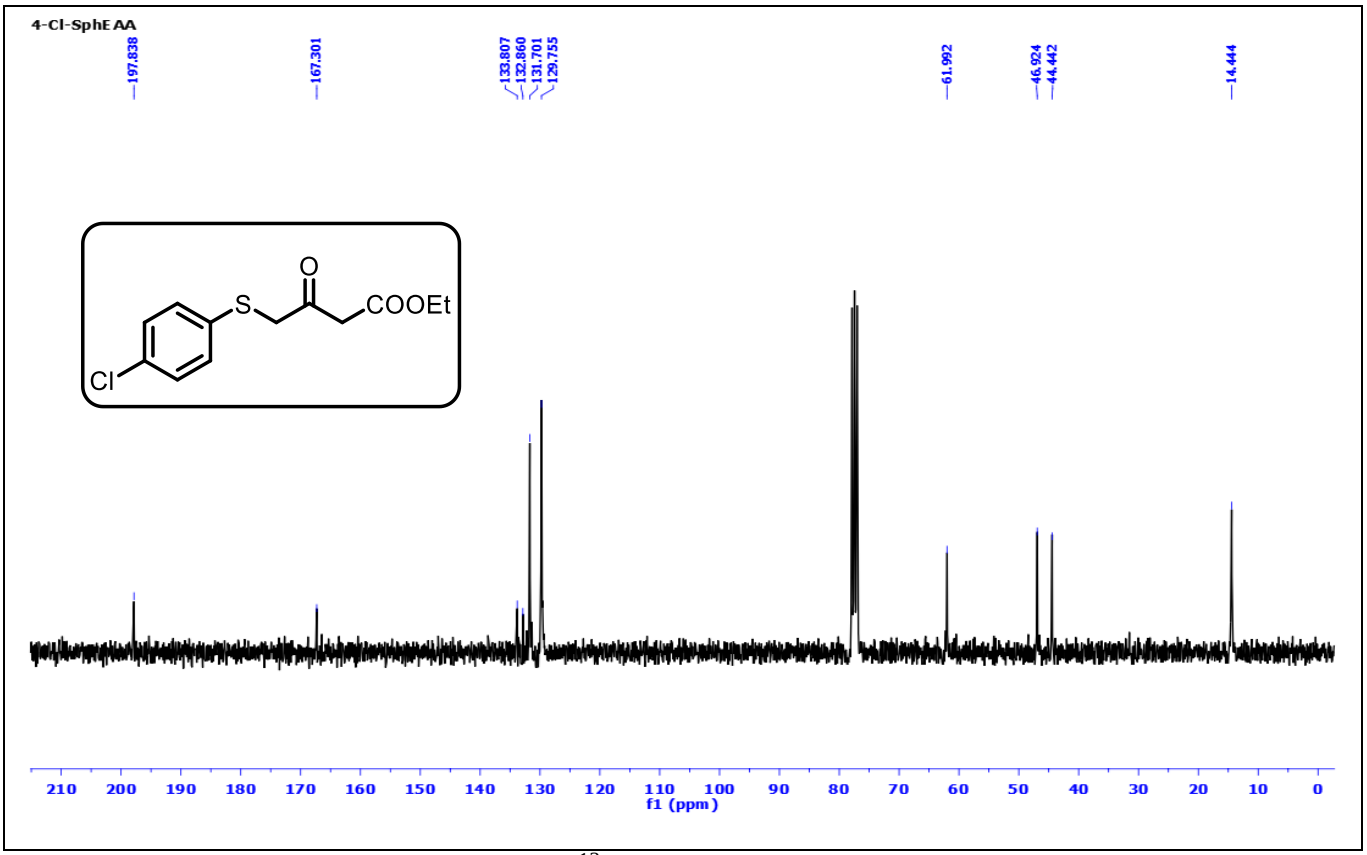


Fig.83. ^{13}C-NMR spectrum of **I**

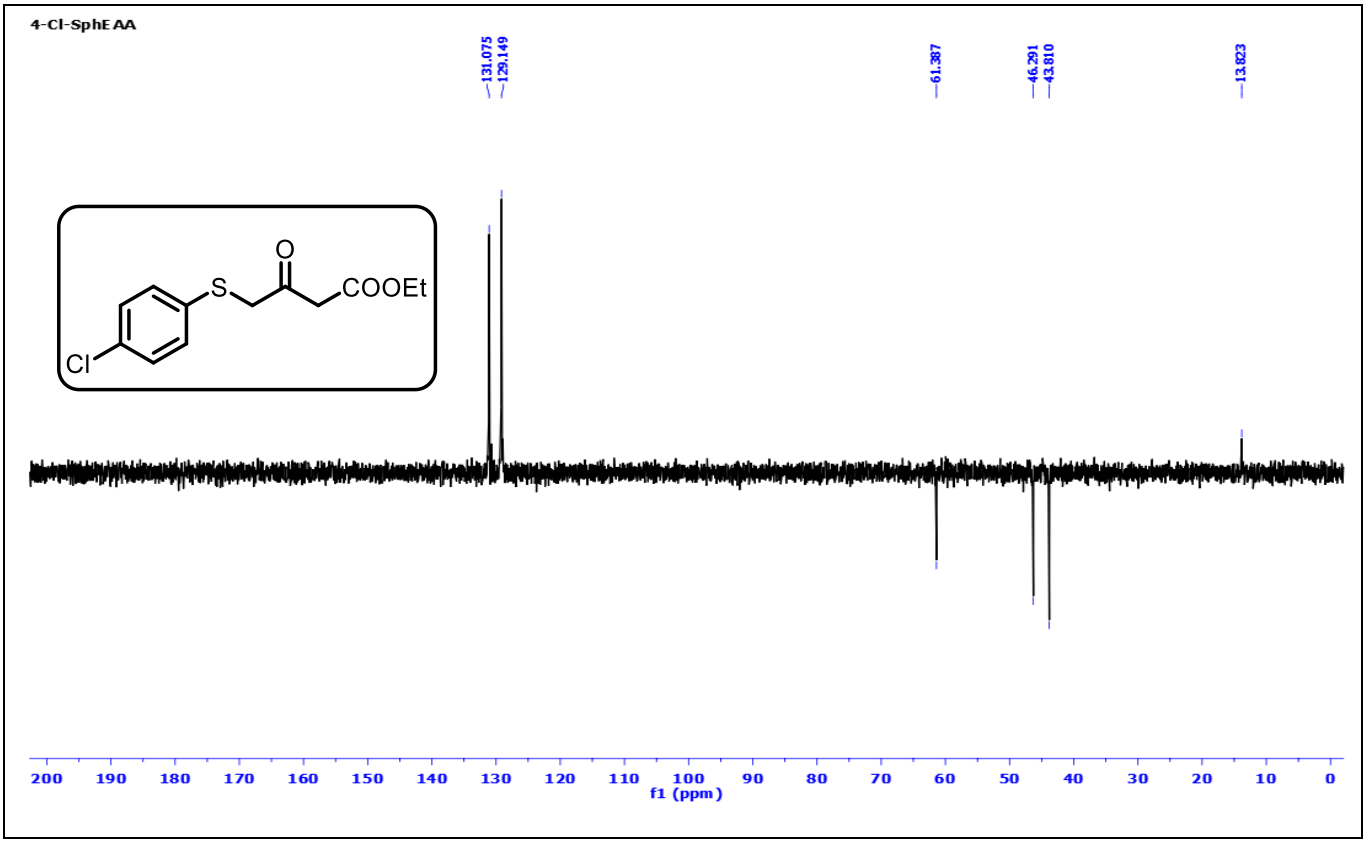


Fig.84. DEPT-135 spectrum of **I**

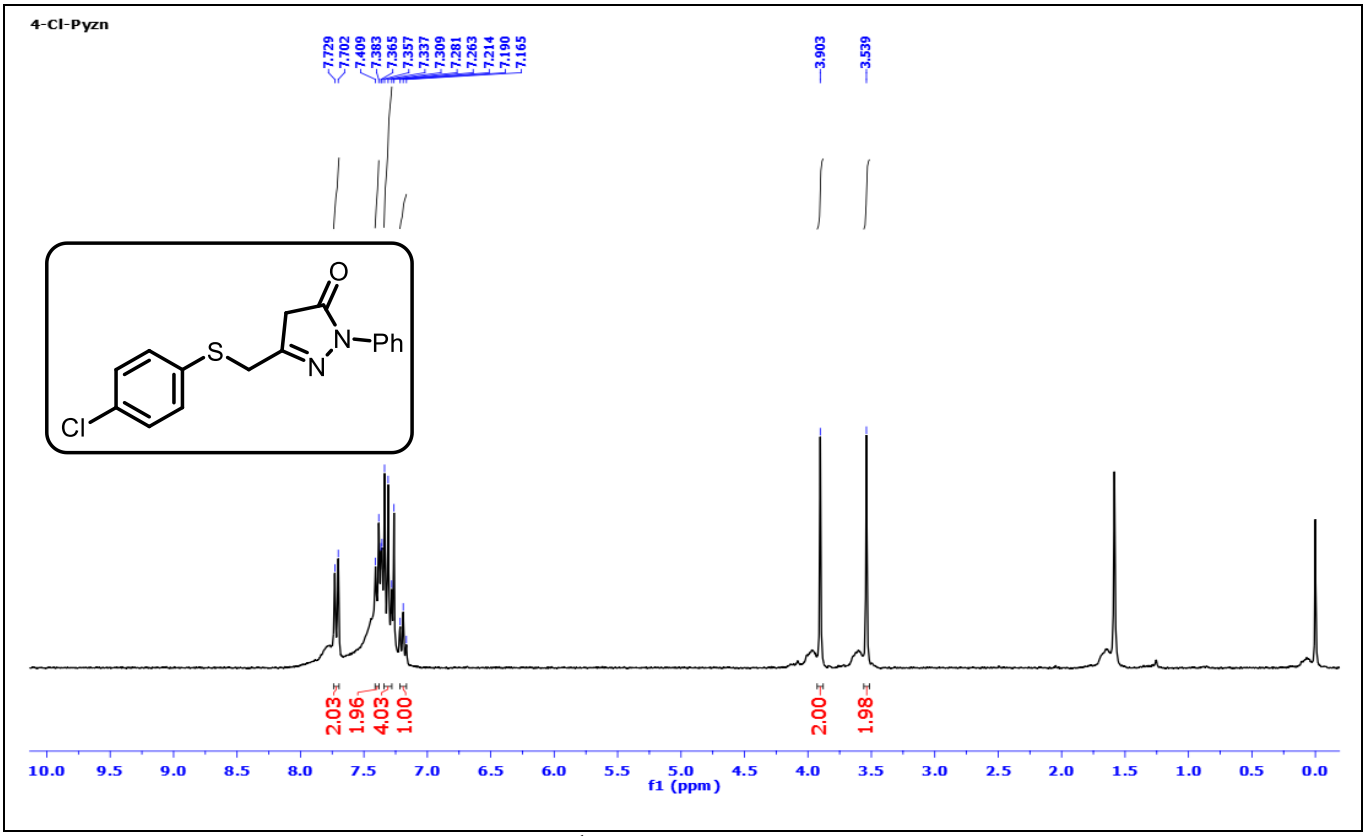


Fig.85. ^{1}H-NMR spectrum of **II**

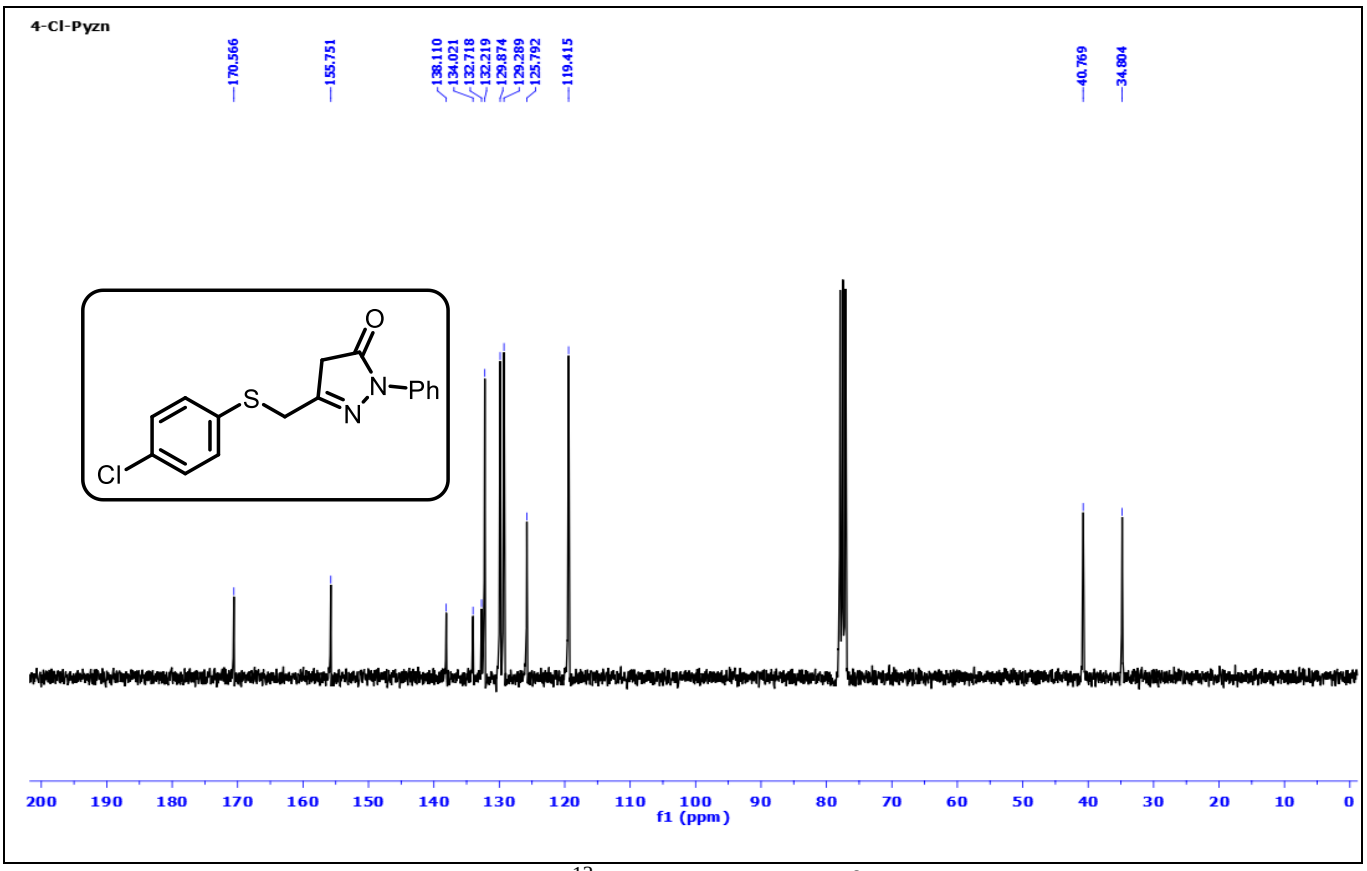


Fig.86. ^{13}C-NMR spectrum of **II**

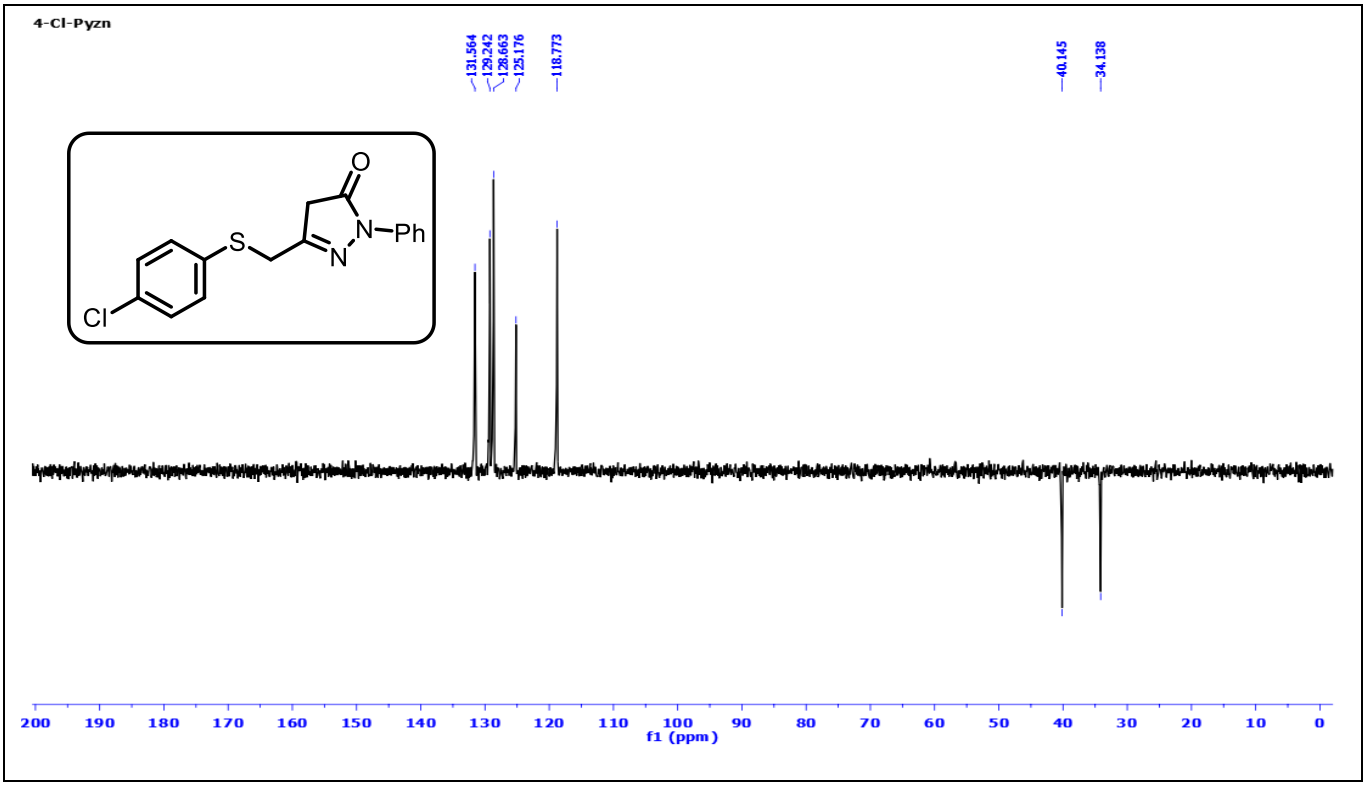


Fig.87. DEPT-135 spectrum of **II**

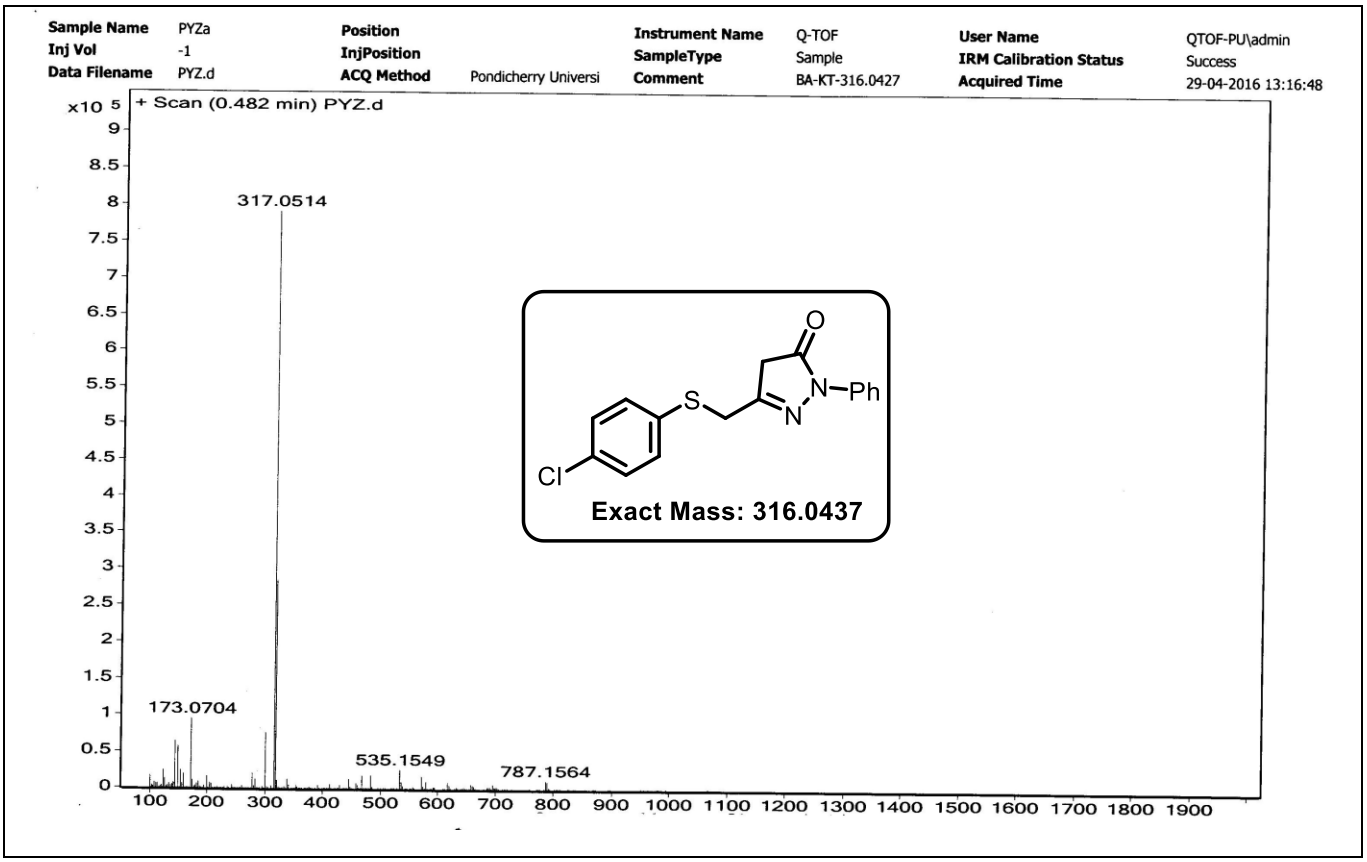


Fig.88. HRMS spectrum of **II**

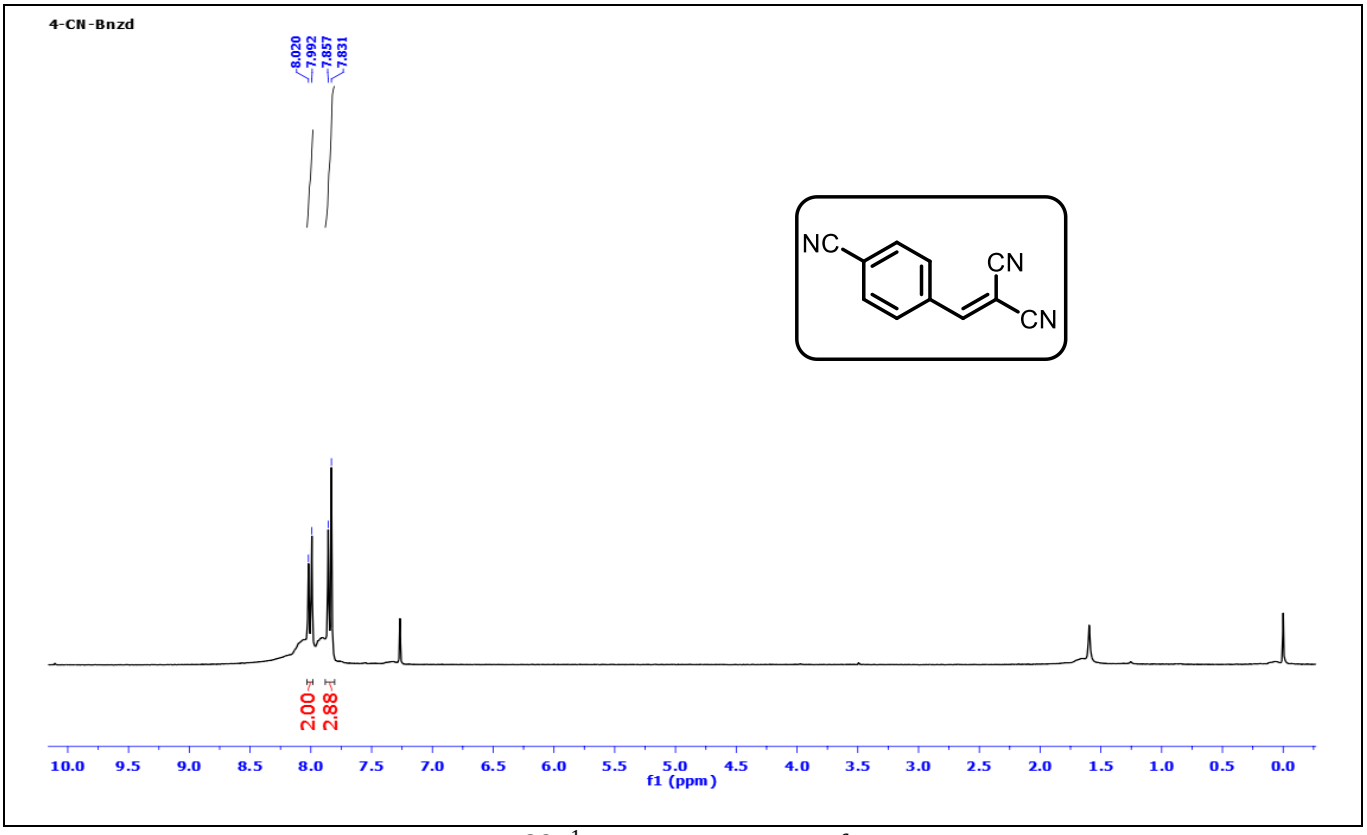


Fig.89. ^{1}H-NMR spectrum of **III**

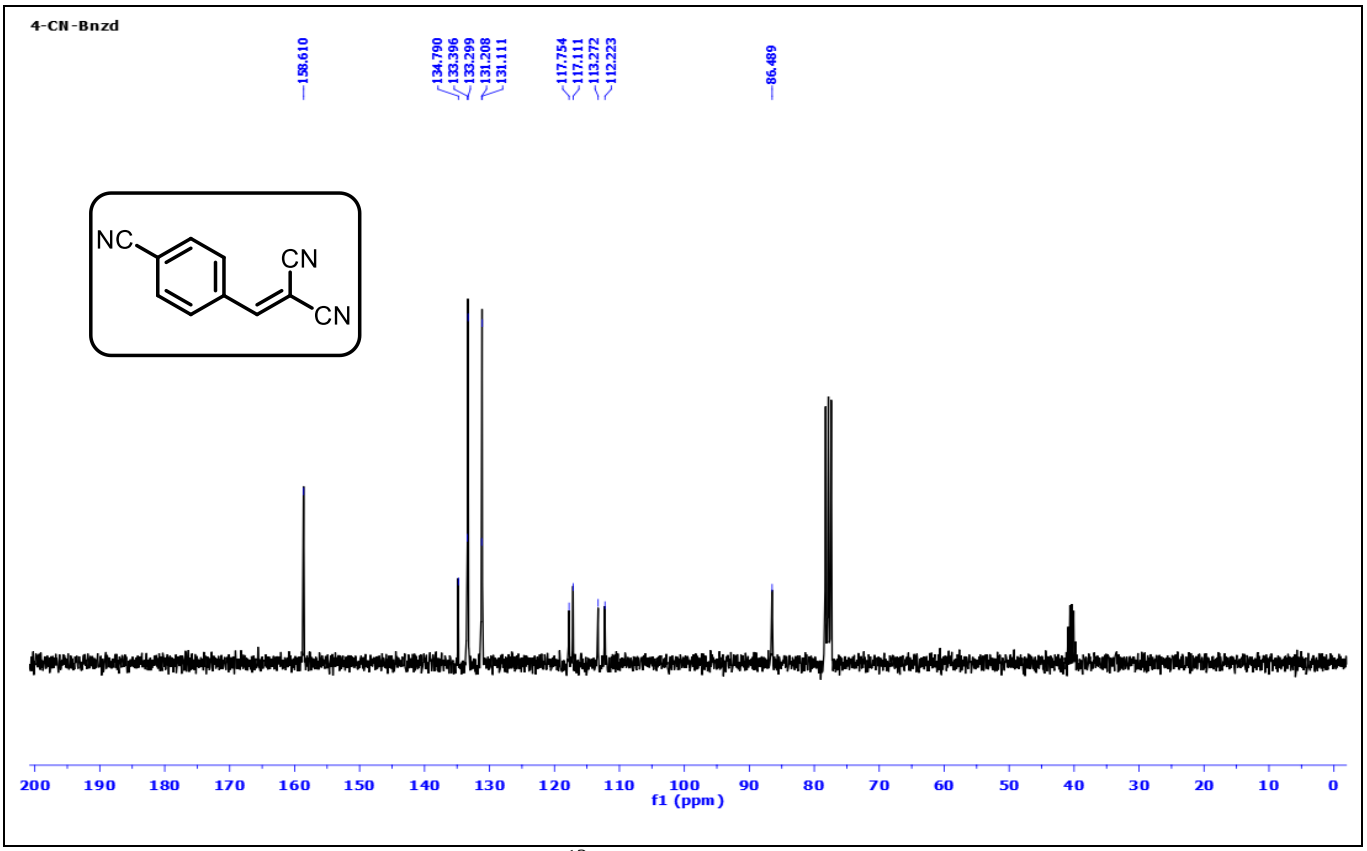


Fig.90. ^{13}C-NMR spectrum of **III**

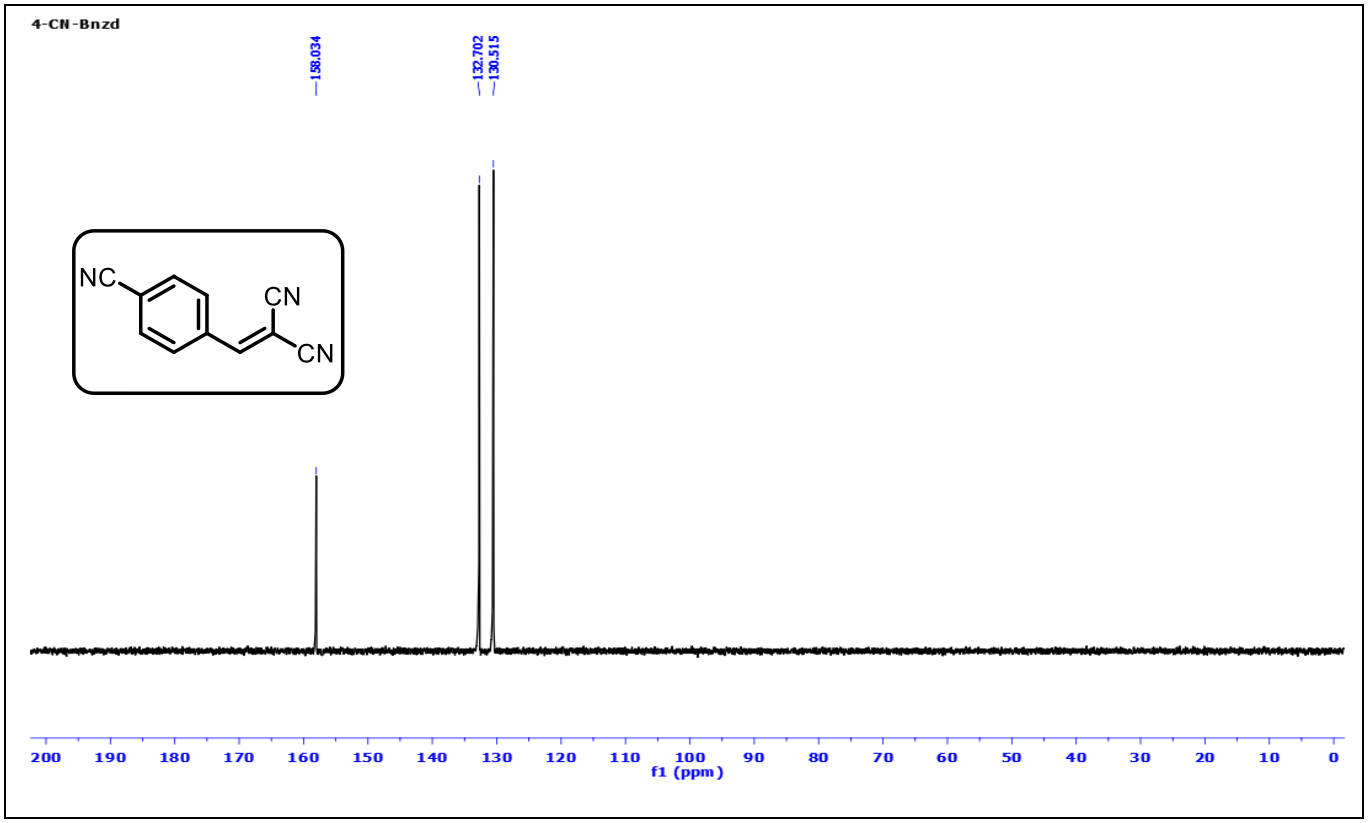


Fig.91. DEPT-135 spectrum of **III**