Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A facile one pot synthesis of thiazolo[3,2-a]benzimidazole and pyran fused polyheterocyclic scaffold

Arumugam Mariappan,[†] Kandasamy Rajaguru,[†] Shanmugam Muthusubramanian,[†,*] and Nattamai Bhuvanesh[#]

[†]*Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai - 625 021, India.*
[#]*X-ray Diffraction Laboratory, Department of Chemistry, Texas A & M University, College Station, TX 77842, USA.*
e-mail:muthumanian2001@yahoo.com
*Corresponding author

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EXPERIMENTAL SECTION

General Remarks:

Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR) spectra were recorded on a 300 MHz, 400 MHz and 500 MHz spectrometer in $CDCl_3$ 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), p (pentet), m (multiplet). ^{13}C NMR spectra were routinely run with broadband decoupling. Pre coated silica gel on aluminium plates (Merck) were used for TLC analysis with a mixture of petroleum ether (60–80 ^{o}C) and ethyl acetate as eluent. Elemental analyses were performed on a Perkin Elmer 2400 Series II Elemental CHNS analyzer.

Procedure for the preparation of 1-aryl-2-(benzo[d]thiazol-2-ylthio)-ethanones 1:

A mixture of phenacyl bromides (1 mol) and 2-mercaptobenzothiazle (1mol) along with triethylamine (1.1 mol) in 10 mL of ethanol was stirred for one hour at room temperature. After the completion of the reaction, the reaction mixture was poured onto crushed ice and filtered off. The product was recrystallised from ethyl alcohol to obtain 1-aryl-2-(benzo[d]thioazol-2-yl thio)ethanones **1** in good yield.

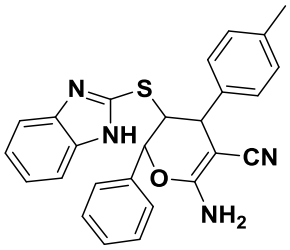
A typical procedure for the synthesis of benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole, 4:

To a mixture of 2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-phenylethan-1-one **1** (1mmol), aryl aldehyde **2** (1mmol) sodium hydroxide (1.5 mmol) after five minutes malononitrile **3** (1mmol) in 10 mL ethanol/ methanol was added and stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into crushed ice and the

solidified compound was filtered and the crude mixture was purified by column chromatography using petroleum ether–ethyl acetate mixture as eluent. The product **4** was recrystallized from dichloromethane and methanol.

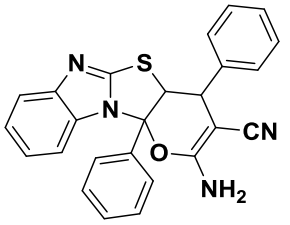
Characterization data

2-Amino-11a-phenyl-4-(*p*-tolyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4a



Isolated as a white solid (372 mg, 85%); mp:125-128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 4H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.20 – 7.16 (m, 5H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.29 (d, *J* = 8.1 Hz, 1H), 4.99 (d, *J* = 5.2 Hz, 1H), 4.81 (s, 2H), 3.97 (d, *J* = 5.2 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 156.4, 148.0, 137.5, 135.9, 133.1, 132.0, 130.8, 129.7, 129.3, 127.9, 126.4, 122.8, 122.2, 120.1, 118.6, 109.5, 93.7, 62.4, 52.2, 36.7, 20.7. Anal. Calcd for $C_{26}H_{20}N_4OS$: C, 71.54; H, 4.62; N, 12.83 %. Found: C, 71.50; H, 4.66; N, 12.86 %.

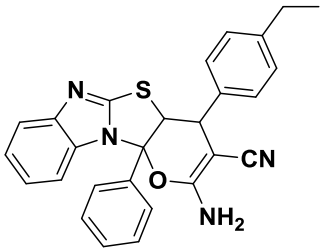
2-amino-4,11a-diphenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-d]thiazole-3-carbonitrile, 4b



Isolated as a white solid (258 mg, 82%); solated as white solid; mp:120-122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 4H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.31 (d, *J* = 6.9 Hz, 2H),

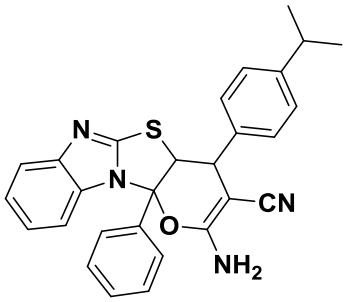
7.18 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 5.01 (d, *J* = 5.2 Hz, 1H), 4.81 (s, 2H), 4.01 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 156.8, 148.2, 137.5, 133.0, 130.5, 130.1, 129.4, 128.6, 128.4, 128.2, 127.5, 125.7, 122.6, 121.8, 119.8, 118.5, 109.7, 94.0, 63.3, 53.2, 36.8. Anal. Calcd for $C_{25}H_{18}N_4OS$: C, 71.07; H, 4.29; N, 13.26%. Found: C, 71.02; H, 4.34; N, 13.22%.

2-Amino-4-(4-ethylphenyl)-11a-phenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4c



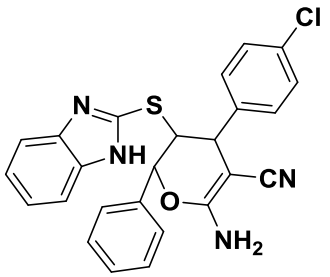
Isolated as a white solid (258 mg, 86%); mp:158-160 ^{o}C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.55 – 7.52 (m, 2H), 7.21 – 7.15 (m, 5H), 7.19 – 7.15 (m, 1H), 6.97 – 6.91 (m, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 5.2 Hz, 1H), 4.82 (s, 2H), 3.98 (d, *J* = 5.2 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 156.2, 148.0, 143.7, 136.0, 133.0, 131.9, 130.7, 129.6, 128.0, 127.8, 126.3, 122.7, 122.0, 119.9, 118.5, 109.3, 93.6, 62.3, 52.2, 36.7, 27.7, 15.3. Anal. Calcd for $C_{27}H_{22}N_4OS$: C, 71.98; H, 4.92; N, 12.44 %. Found: C, 71.94; H, 4.89; N, 12.40 %.

2-Amino-4-(4-isopropylphenyl)-11a-phenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4d



Isolated as a white solid (305 mg, 88%); mp:130-133 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 4H), 7.55 – 7.52 (m, 2H), 7.24 – 7.18 (m, 5H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 5.2 Hz, 1H), 4.82 (s, 2H), 3.98 (d, *J* = 5.2 Hz, 1H), 2.91 (sept, *J* = 7.2 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 149.5, 148.7, 134.3, 133.8, 132.1, 131.1, 130.9, 129.8, 127.7, 127.2, 125.9, 123.2, 122.3, 119.5, 119.2, 109.9, 94.7, 65.8, 64.2, 36.6, 33.8, 23.8. Anal. Calcd for $C_{28}H_{24}N_4OS$: C, 72.39; H, 5.21; N, 12.06 %. Found: C, 72.33; H, 5.26; N, 12.01%.

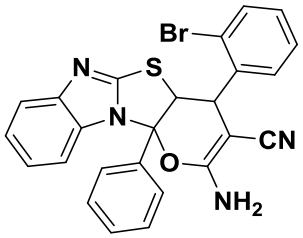
2-Amino-4-(4-chlorophenyl)-11a-phenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4e



Isolated as a white solid (284 mg, 83%); mp:156-158 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 4H), 7.54 – 7.52 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.21 – 7.14 (m, 1H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 4.98 – 4.97 (m, 3H), 3.99 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 156.4, 148.0, 136.0, 133.8, 132.8, 131.7, 130.5, 129.4, 128.9, 128.7,

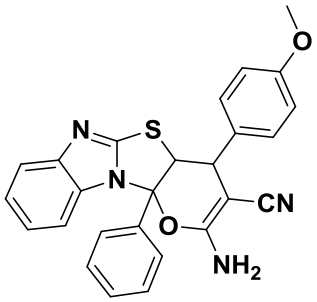
125.6, 122.7, 121.9, 119.4, 118.5, 109.7, 93.9, 62.8, 52.7, 36.2. Anal. Calcd for $C_{25}H_{17}ClN_4OS$: C, 65.71; H, 3.75; N, 12.26 %. Found: C, 65.76; H, 3.70; N, 12.29 %.

2-Amino-4-(2-bromophenyl)-11a-phenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4f



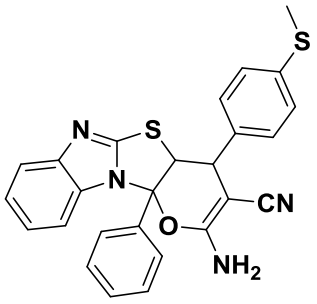
Isolated as a yellow solid (303 mg, 81%); mp: 125-126 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 4H), 7.58 – 7.55 (m, 3H), 7.48 – 7.43 (m, 1H), 7.30 – 7.21 (m, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 5.84 (s, 2H), 5.42 (d, *J* = 5.4 Hz, 1H), 4.50 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (75 MHz,$CDCl_3$) δ 164.1, 155.8, 147.5, 135.6, 132.2, 131.8, 131.3, 130.0, 129.2, 128.8, 128.3, 127.2, 125.1, 123.3, 122.1, 121.3, 119.0, 117.9, 109.1, 93.3, 58.7, 51.5, 35.6. Anal. Calcd for $C_{25}H_{17}BrN_4OS$: C, 59.89; H, 3.42; N, 11.17%. Found: C, 59.84; H, 3.47; N, 11.20%.

2-Amino-4-(4-methoxyphenyl)-11a-phenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-d]thiazole-3-carbonitrile, 4g



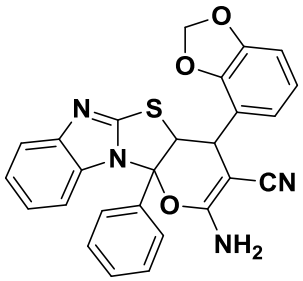
Isolated as a yellow solid (307 mg, 91%); mp: 112-114 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.54 – 7.51 (m, 2H), 7.24 – 7.15 (m, 3H), 6.97 – 6.90 (m, 3H), 6.29 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 5.3 Hz, 1H), 4.87 (s, 2H), 3.96 (d, *J* = 5.2 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz,$CDCl_3$) δ 164.1, 159.2, 156.8, 148.2, 133.1, 131.8, 130.4, 129.4, 129.3, 128.6, 125.6, 122.6, 121.8, 119.7, 118.5, 113.9, 109.7, 94.0, 63.9, 54.8, 53.8, 35.9. Anal. Calcd for $C_{26}H_{20}N_4O_2S$: C, 69.01; H, 4.45; N, 12.38%. Found: C, 69.06; H, 4.41; N, 12.37%.

2-amino-4-(4-(methylthio)phenyl)-11a-phenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4h



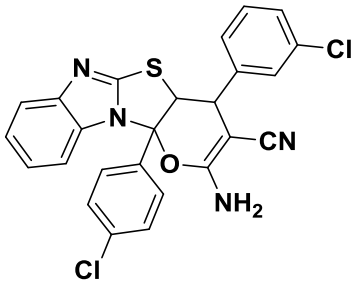
Isolated as a white solid (300 mg, 86%); mp: 116-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 3H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.27 – 7.16 (m, 6H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 8.1 Hz, 1H), 4.99 (d, *J* = 5.2 Hz, 1H), 4.81 (s, 2H), 3.97 (d, *J* = 5.1 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 157.1, 148.7, 139.2, 134.2, 133.5, 132.2, 130.9, 129.8, 128.3, 126.7, 126.0, 123.1, 122.3, 119.8, 119.0, 110.1, 94.5, 63.8, 54.3, 36.6, 15.4. Anal. Calcd for $C_{26}H_{20}N_4OS_2$: C, 66.64; H, 4.30; N, 11.96 %. Found: C, 66.67; H, 4.35; N, 11.93 %.

2-Amino-4-(benzo[*d*][1,3]dioxol-4-yl)-11a-phenyl-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4i



Isolated as a white solid (309 mg, 89 %); mp: 116-118^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.54 – 7.52 (d, *J* = 7.0 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.00 (d, *J* = 1.9 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.83 – 6.76 (m, 3H), 6.28 (d, *J* = 7.9 Hz, 1H), 6.00 (s, 2H), 4.97 (d, *J* = 5.2 Hz, 1H), 4.85 (s, 2H), 3.92 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 157.0, 148.5, 148.0, 147.7, 133.4, 132.0, 131.2, 130.6, 129.6, 125.8,* 122.9, 122.1, 121.2, 118.8, 109.9, 108.4, 107.9, 101.1, 94.3, 63.9, 54.6, 36.7. Anal. Calcd for $C_{26}H_{18}N_4O_3S$: C, 66.94; H, 3.89; N, 12.01%. Found: C, 66.89; H, 3.92; N, 12.06%. * one carbon merged.

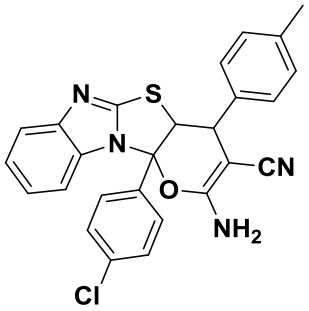
2-Amino-4-(3-chlorophenyl)-11a-(4-chlorophenyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4j



Isolated as a white solid (273 mg, 84 %); mp:146-148^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 3H), 7.49 – 7.46 (m, 2H), 7.38 – 7.37 (m, 2H), 7.27 – 7.18 (m, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 7.9 Hz, 1H), 4.94 – 4.93 (m, 3H),* 3.98 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 156.5, 148.4, 139.4, 136.9, 134.5, 132.1, 132.0, 131.0, 130.0, 128.6, 128.0, 127.4, 125.7,

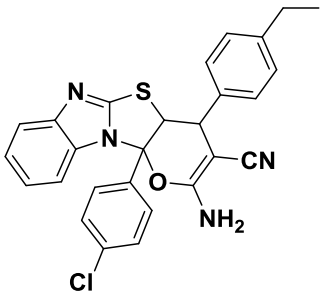
123.0, 122.2, 119.0, 118.9, 109.7, 93.7, 62.7, 53.4, 36.8. Anal. Calcd for $C_{25}H_{16}Cl_2N_4OS$: C, 61.11; H, 3.28; N, 11.40%. Found: C, 61.16; H, 3.24; N, 11.46%. *NH_2 signal merged with the doublet.

2-Amino-11a-(4-chlorophenyl)-4-(*p*-tolyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4k



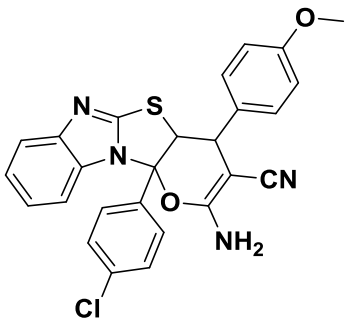
Isolated as a white solid (258 mg, 83%);mp:126-128^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 3H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.19 (bs, 5H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 7.9 Hz, 1H), 4.94 – 4.92* (m, 3H), 3.95 (d, *J* = 5.3 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 157.0, 148.7, 138.7, 137.2, 133.9, 132.3, 131.8, 130.1,** 129.9, 127.7, 127.4, 123.3, 122.5, 119.3, 109.8, 94.2, 64.0, 56.0, 36.5, 21.2. Anal. Calcd for $C_{26}H_{19}ClN_4OS$: C, 66.31; H, 4.07 ; N, 11.90%. Found: C, 66.26; H, 4.11; N, 11.86%. *NH_2 signal merged with the doublet, ** one carbon signal merged.

2-Amino-11a-(4-chlorophenyl)-4-(4-ethylphenyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4l



Isolated as a white solid (272 mg, 85 %); mp:163-165^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 3H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.22 – 7.18 (m, 5H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 5.2 Hz, 1H), 4.83 (bs, 2H), 3.97 (d, *J* = 5.2 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 156.5, 147.9, 143.9, 136.2, 134.2, 131.6, 131.4, 129.4, 127.8, 127.1, 127.1, 122.5, 121.6, 119.3, 118.3, 109.3, 93.2, 63.1, 53.1, 36.1, 27.7, 14.7. Anal. Calcd for $C_{27}H_{21}ClN_4OS$: C, 66.87; H, 4.36; N, 11.55%. Found: C, 66.81; H, 4.32; N, 11.58%

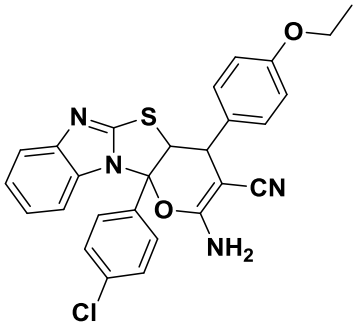
2-Amino-11a-(4-chlorophenyl)-4-(4-methoxyphenyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4m



Isolated as off-white solid; (286 mg, 89 %); mp:168-171^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 3H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.15 (m, 3H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 5.3 Hz, 1H), 4.87 (s, 2H), 3.95 (d, *J* = 5.1 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 159.0, 156.6, 147.9, 136.3, 131.7, 131.5, 129.5,

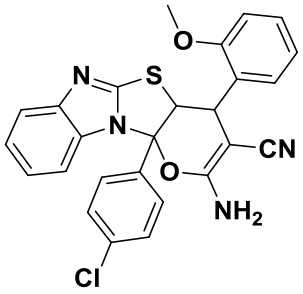
129.1, 128.5, 127.1, 122.6, 121.8, 119.4, 118.4, 113.8, 109.4, 93.3, 63.5, 54.7, 53.4, 35.7. Anal. Calcd for $C_{26}H_{19}ClN_4O_2S$, C, 64.13; H, 3.93; N, 11.51%. Found: C, 64.18; H, 3.96; N, 11.47%.

2-Amino-11a-(4-chlorophenyl)-4-(4-ethoxyphenyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-d]thiazole-3-carbonitrile, 4n



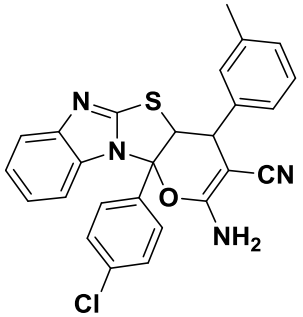
Isolated as white solid; (298mg, 90%); mp: 200-203^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 3H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.18 (m, 3H), 7.01 – 6.96 (m, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.35 (d, *J* = 7.8 Hz, 1H), 4.94 (d, *J* = 5.2 Hz, 1H), 4.80 (s, 2H), 4.04 (q, 7.0 Hz, 2H), 3.95 (d, *J* = 5.2 Hz, 1H), 1.42 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 158.6, 156.8, 148.2, 136.6, 131.9, 131.7, 129.6, 128.9, 128.6, 127.2, 122.7, 121.9, 119.4, 118.6, 114.5, 109.6, 93.5, 63.7, 63.0, 53.9, 35.8, 14.4. Anal. Calcd for $C_{27}H_{21}ClN_4O_2S$: C, 64.73; H, 4.23; N, 11.18%. Found: C, 64.77; H, 4.28; N, 11.14%.

2-Amino-11a-(4-chlorophenyl)-4-(2-methoxyphenyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4o



Isolated as white solid; (280 mg, 87%); mp:146-148^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61– 7.57 (m, 3H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.34 (m, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 5.31 (d, *J* = 5.5 Hz, 1H), 4.93 (bs, 2H), 4.49 (d, *J* = 5.4 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 157.1, 156.9, 148.7, 137.0, 132.4, 132.0, 130.0, 129.3, 129.1, 128.1, 127.5, 125.2, 123.2, 122.4, 121.1, 119.2, 110.5, 109.7, 94.2, 60.8, 56.1, 55.5, 29.9. Anal. Calcd for $C_{26}H_{19}ClN_4O_2S$: C, 64.13; H, 3.93; N, 11.51%. Found: C, 64.19; H, 3.90; N, 11.46%.

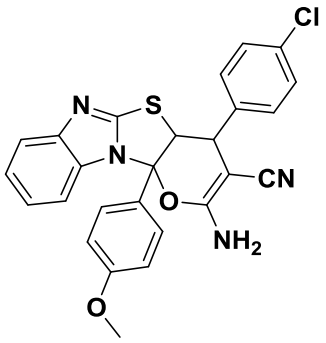
2-Amino-11a-(4-chlorophenyl)-4-(*m*-tolyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4p



Isolated as white solid; (255mg, 82%); mp:130-132^{o}C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 3H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.19 (dd, *J* = 15.2, 7.9 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.08 (s, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 5.3 Hz, 1H), 4.81 (s, 2H), 3.95 (d, *J* = 5.2 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 157.0, 148.4,

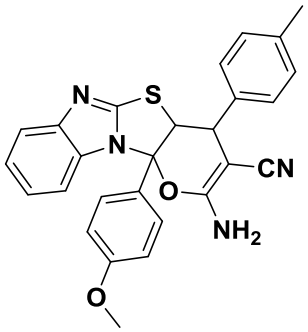
138.7, 137.0, 137.0, 132.1, 131.8, 130.0, 129.4, 128.9, 128.4, 127.4, 124.6, 123.1, 122.3, 119.4, 119.0, 109.8, 93.9, 63.7, 54.7, 36.8, 21.3. Anal. Calcd for $C_{26}H_{19}ClN_4OS$: C, 66.31; H, 4.07; N, 11.90 %; Found: C, 66.26; H, 4.11; N, 11.93%.

2-Amino-4-(4-chlorophenyl)-11a-(4-methoxyphenyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo [2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4q



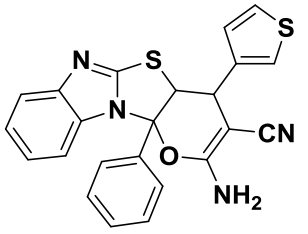
Isolated as white solid; (261 mg, 80%); mp:154-157^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.37 (m, 4H), 7.27 – 7.25 (m, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.92 (d, *J* = 5.1 Hz, 1H), 4.86 (bs, 2H), 4.00 (d, *J* = 5.1 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 161.0, 156.3, 148.2, 136.1, 133.9, 131.8, 129.0, 128.8, 127.1, 124.3, 122.7, 121.9, 119.6, 118.5, 114.7, 109.8, 94.1, 62.9, 55.2, 52.9, 36.4. Anal. Calcd for $C_{26}H_{19}ClN_4O_2S$: C, 64.13; H, 3.93; N, 11.51 %; Found: C, 64.06; H, 3.90; N, 11.54 %.

2-Amino-11a-(4-methoxyphenyl)-4-(*p*-tolyl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-*d*]thiazole-3-carbonitrile, 4r



Isolated as white solid; (256 mg, 82%); mp: 136-138 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.16 (m, 5H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.97 (t, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.95 (d, *J* = 5.1 Hz, 1H), 4.80 (s, 2H), 3.98 (d, *J* = 5.4 Hz, 1H), 3.94 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 161.1, 157.0, 148.4, 138.2, 134.4, 132.0, 129.6, 127.5, 127.2, 124.9, 122.8, 122.0, 119.8, 118.7, 114.9, 109.9, 94.3, 63.9, 55.3, 54.4, 36.5, 20.9. Anal. Calcd for $C_{27}H_{22}N_4O_2S$: C, 69.51; H, 4.75; N, 12.01%. Found: C, 69.47; H, 4.74; N, 11.99%.

2-amino-11a-phenyl-4-(thiophen-3-yl)-4a,11a-dihydro-4*H*-benzo[4,5]imidazo[2,1-*b*]pyrano[2,3-d]thiazole-3-carbonitrile, 4s



Isolated as white solid; (265 mg, 83%); mp: 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 4H), 7.53 (d, *J* = 6.9 Hz, 2H), 7.39 – 7.37 (m, 1H), 7.32 (s, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 4.9 Hz, 1H),. 6.95 (t, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 8.1 Hz, 1H), 5.03 (d, *J* = 5.0 Hz, 1H), 4.78 (s, 2H), 4.17 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 164.7, 157.2, 148.3, 140.0, 133.4,

132.3, 131.4, 130.2, 127.6, 126.7, 124.0, 123.6, 122.8, 120.7, 119.0, 110.2, 94.3, 62.9, 53.1, 32.9. Anal. Calcd for Chemical Formula: $C_{26}H_{20}N_4OS_2$: Elemental Analysis: C, 66.64; H, 4.30; N, 11.96% Found: C, 66.69; H, 4.33; N, 11.92%.

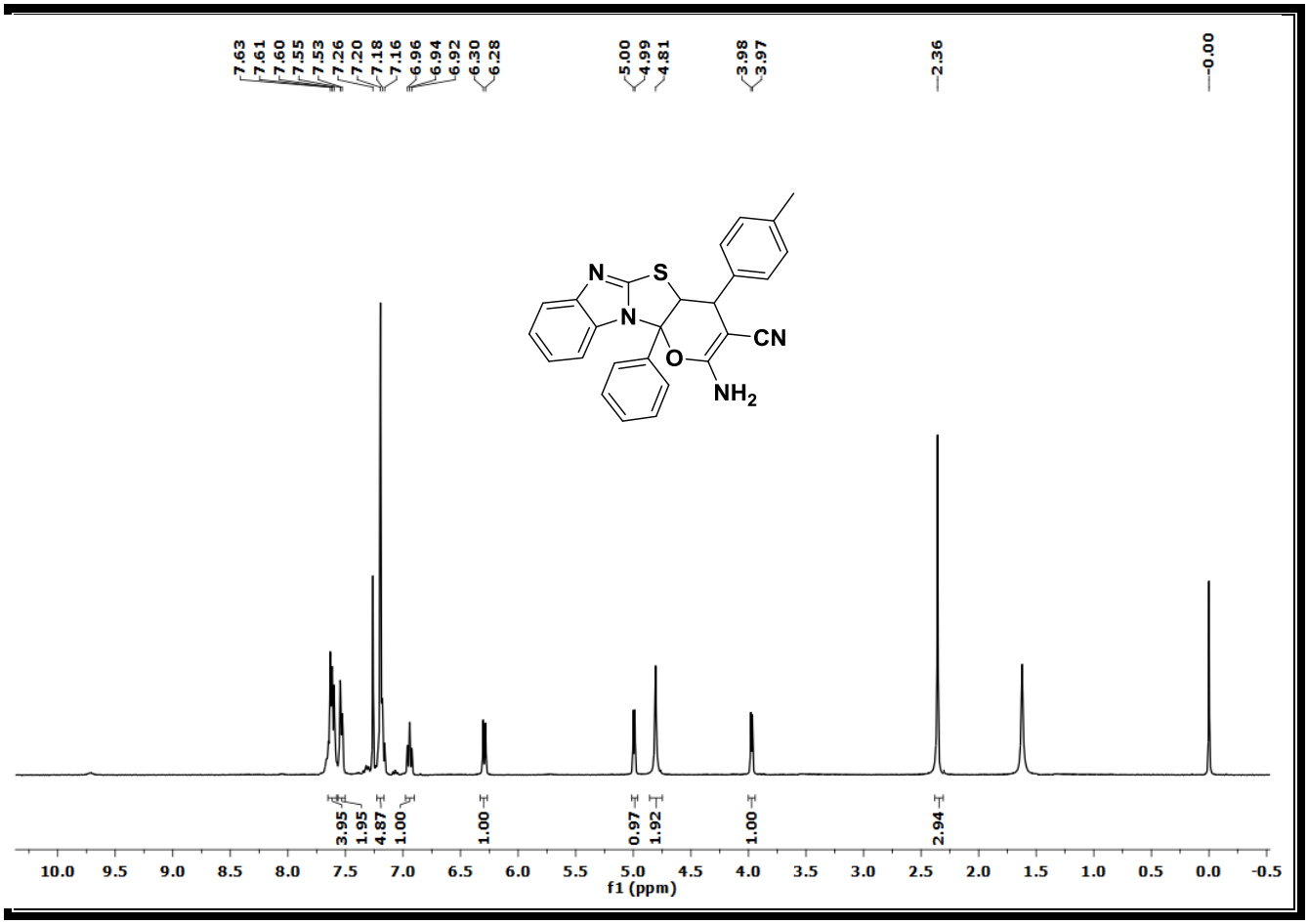


Fig.1. ^{1}H-NMR spectrum of **4a**

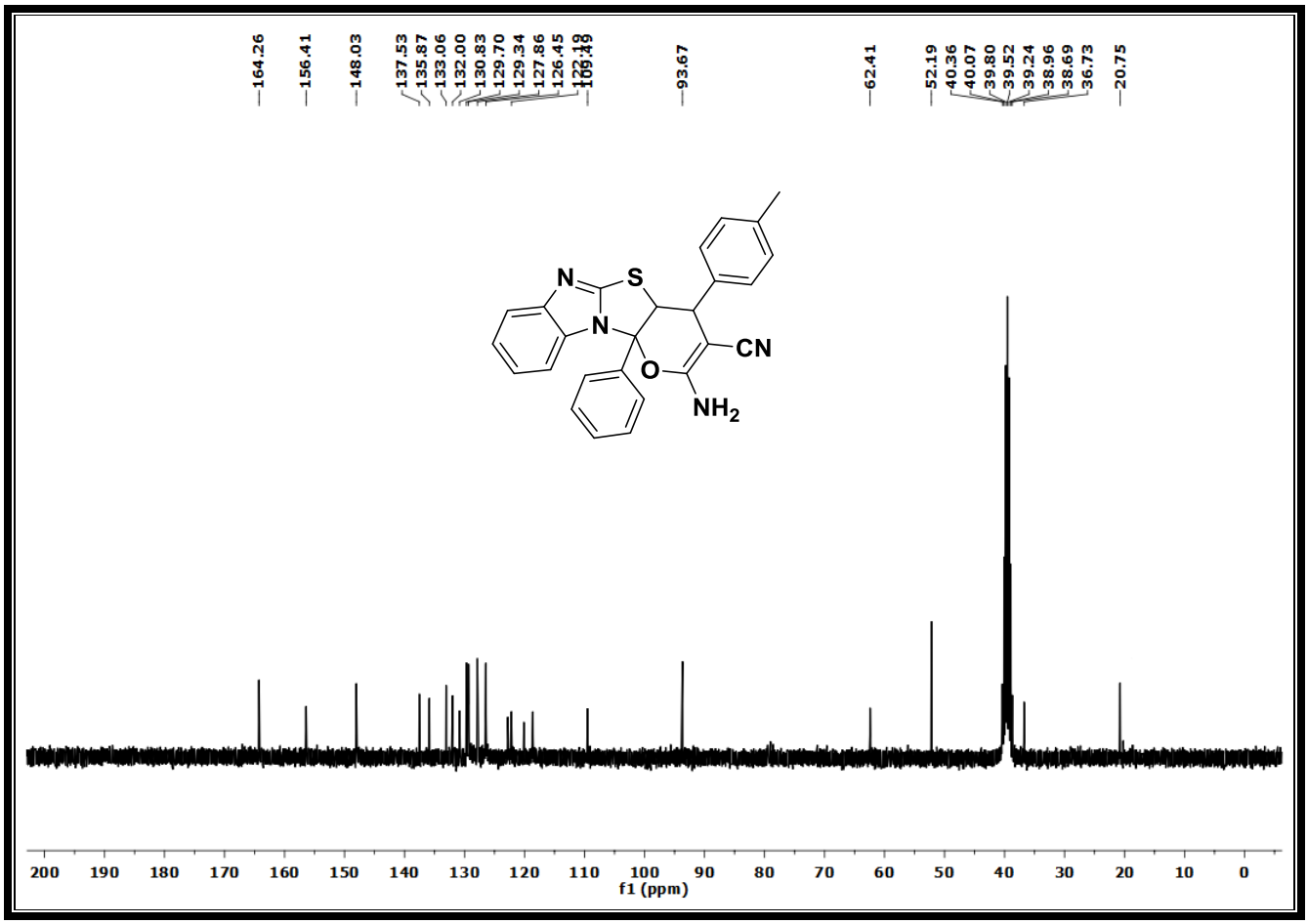


Fig.2. ^{13}C-NMR spectrum of **4a**

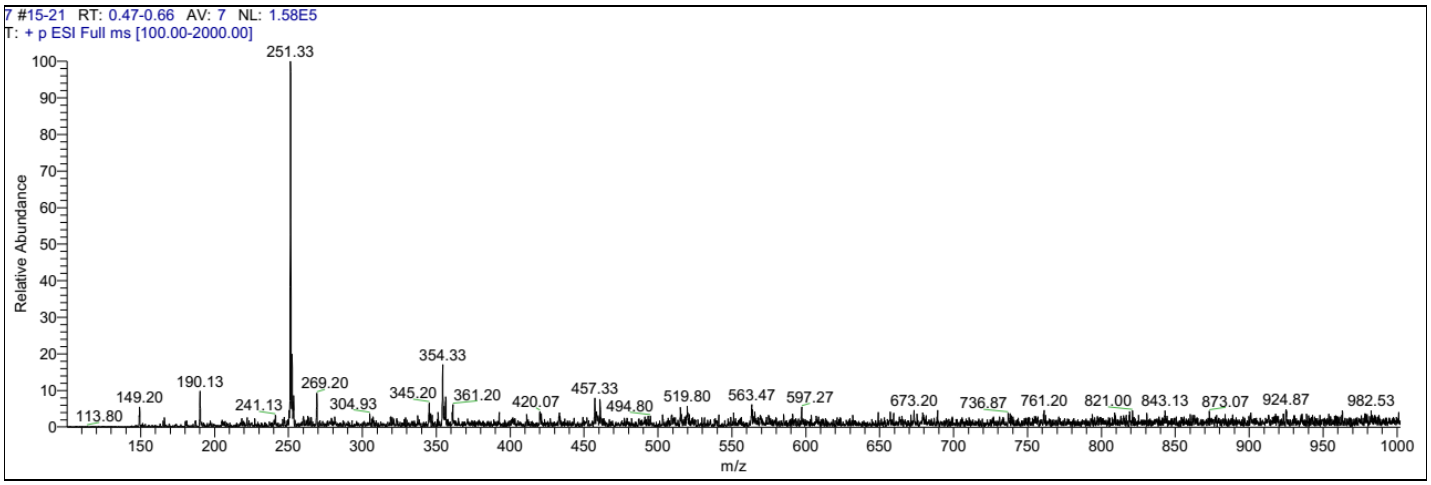


Fig.3. Mass spectrum of **4a**

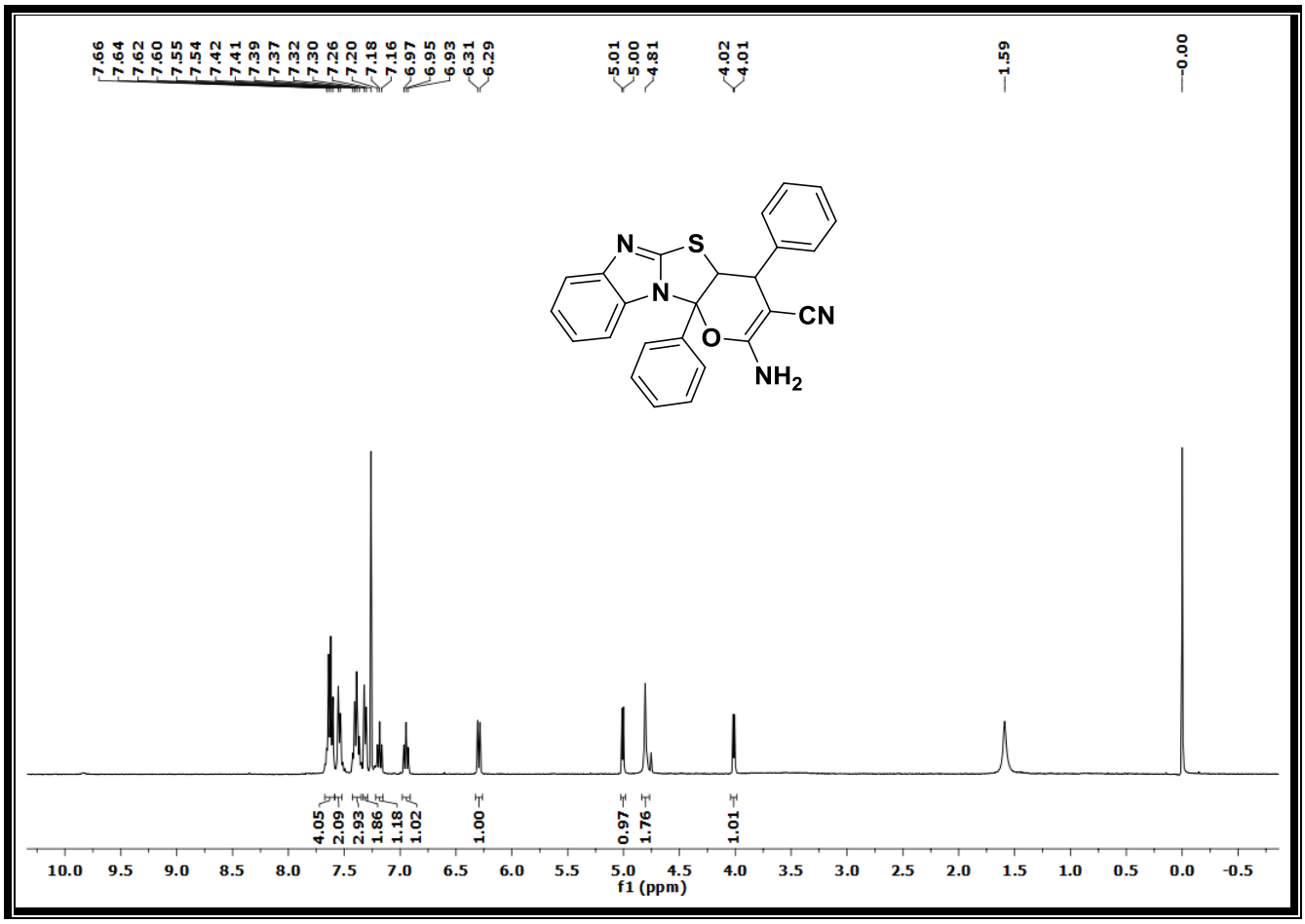


Fig.4. ^{1}H-NMR spectrum of **4b**

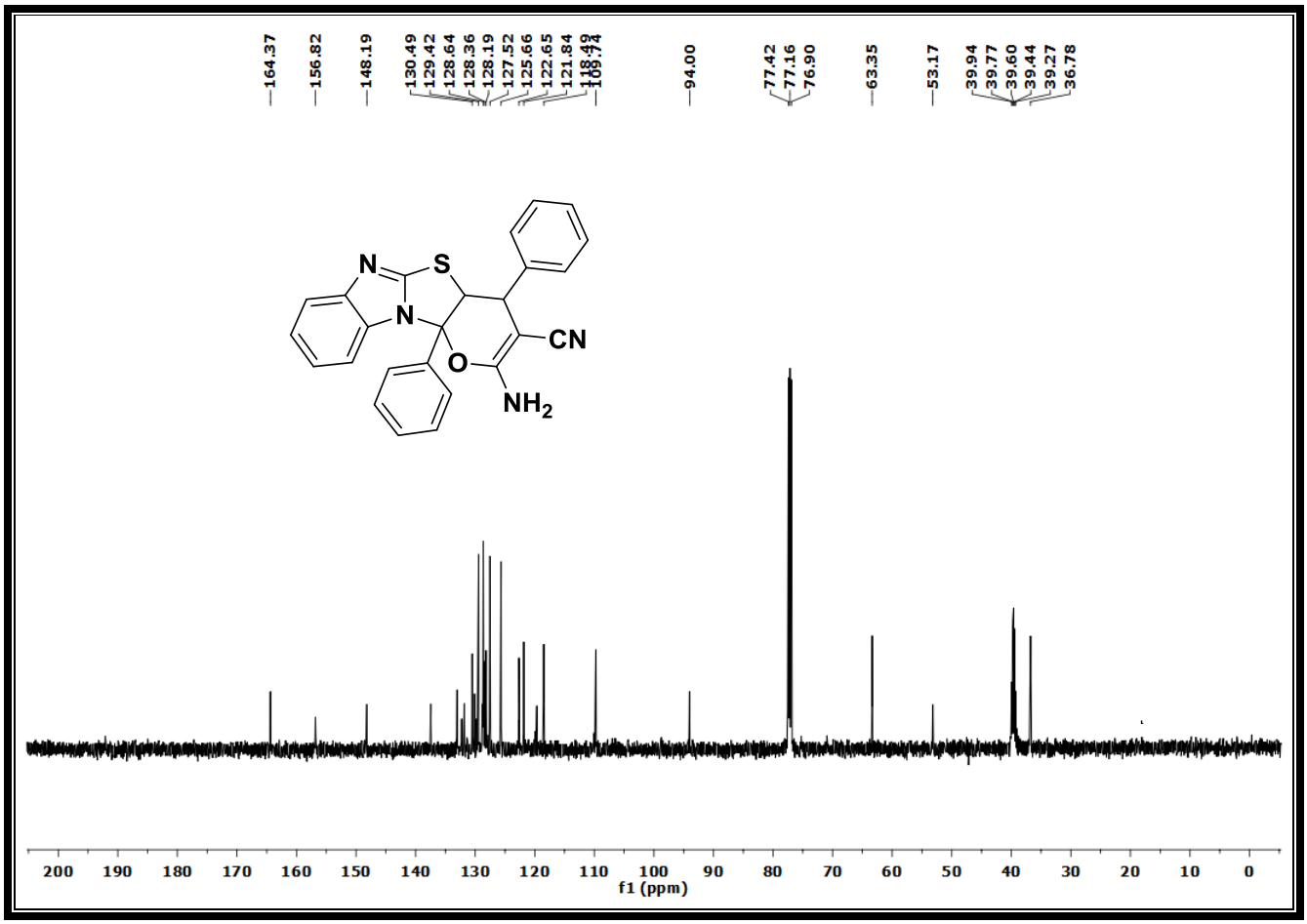


Fig. 5. ^{13}C-NMR spectrum of **4b**

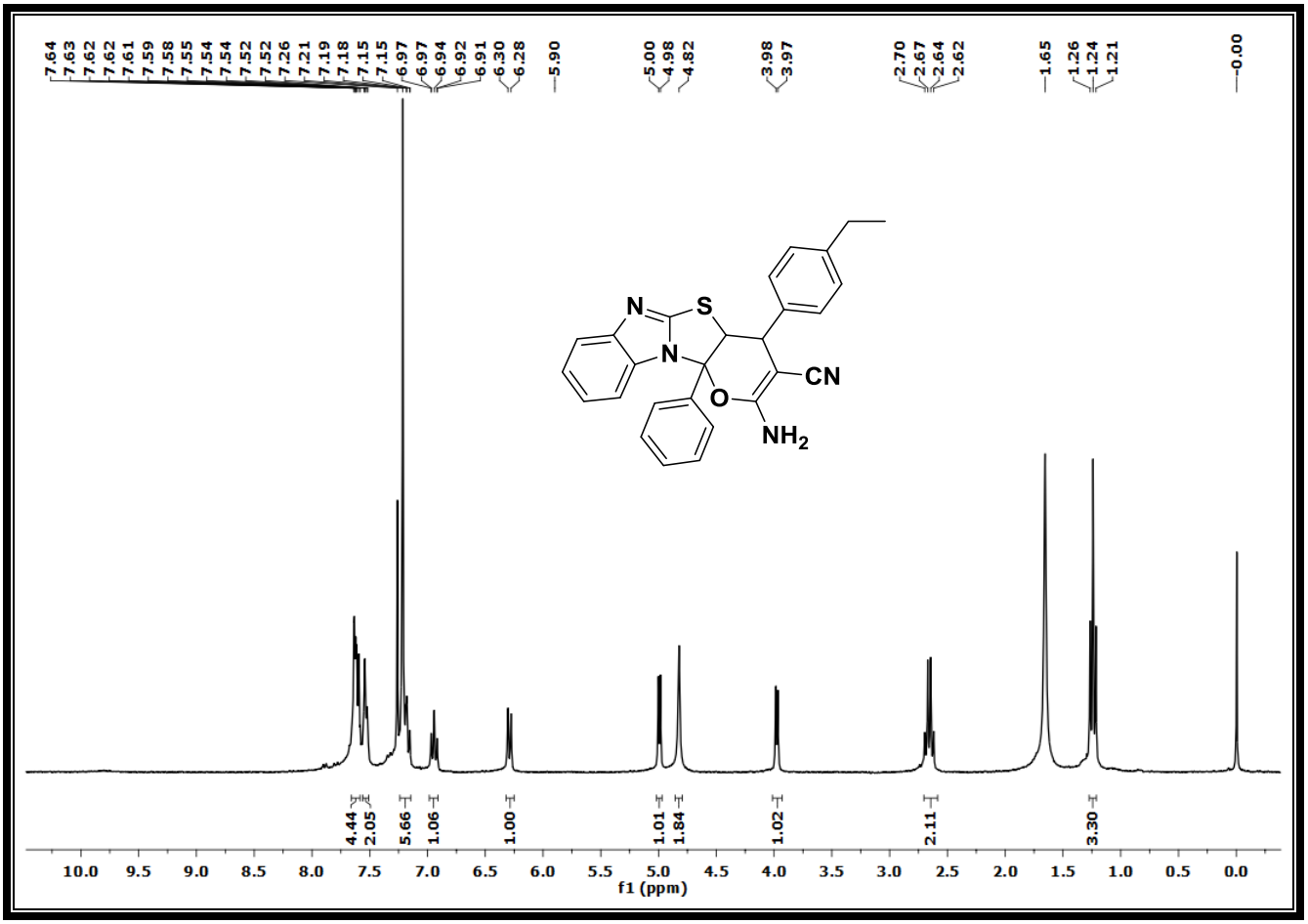


Fig.6. ^{1}H-NMR spectrum of **4c**

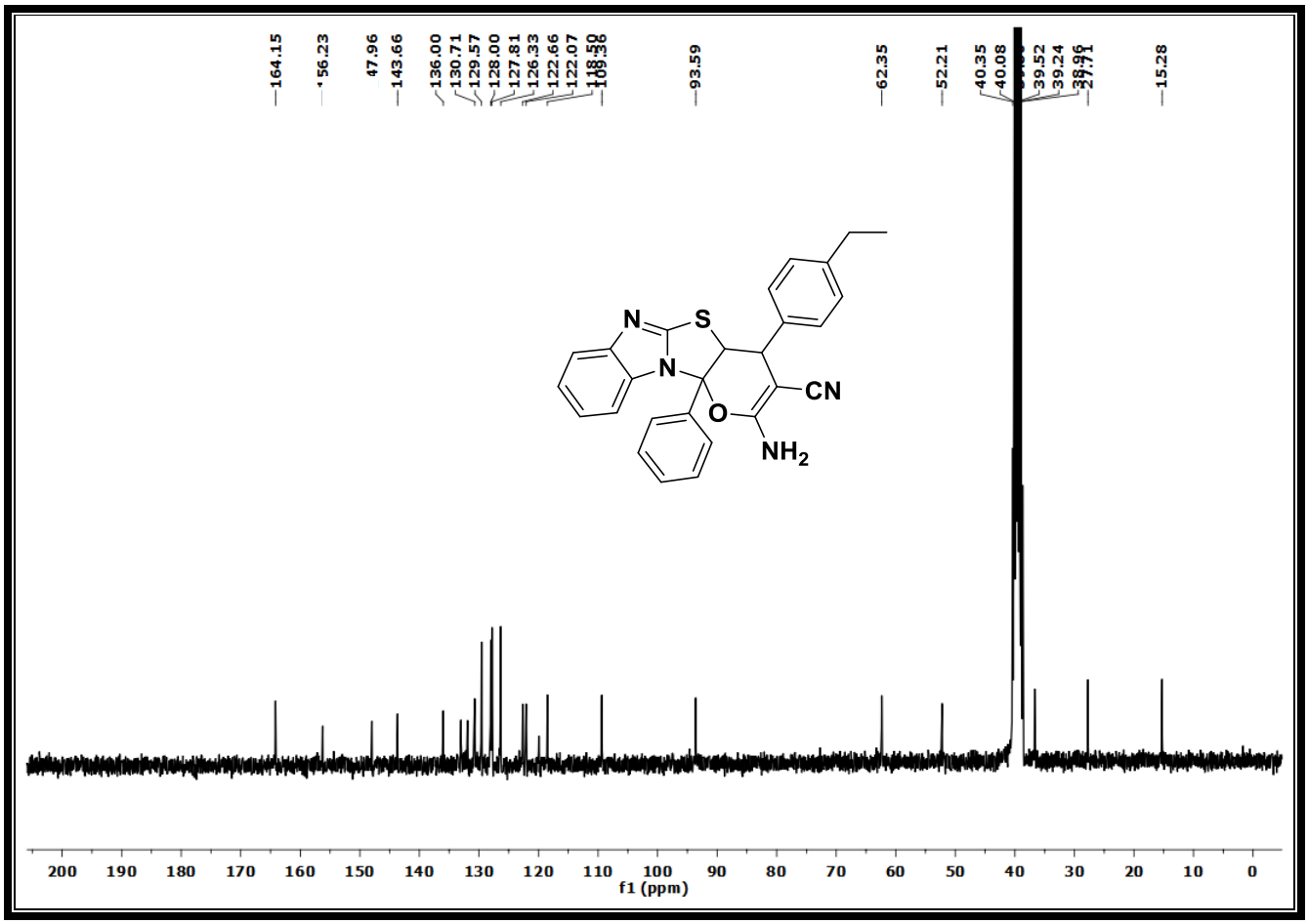


Fig.7. ^{13}C-NMR spectrum of **4c**

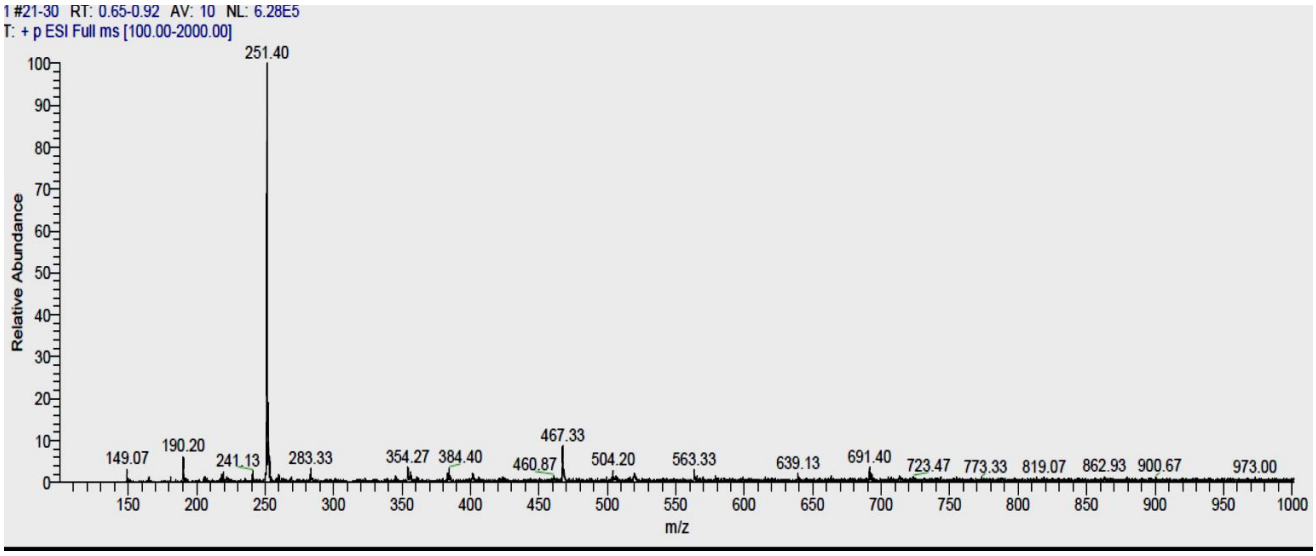


Fig.8. Mass spectrum of **4c**

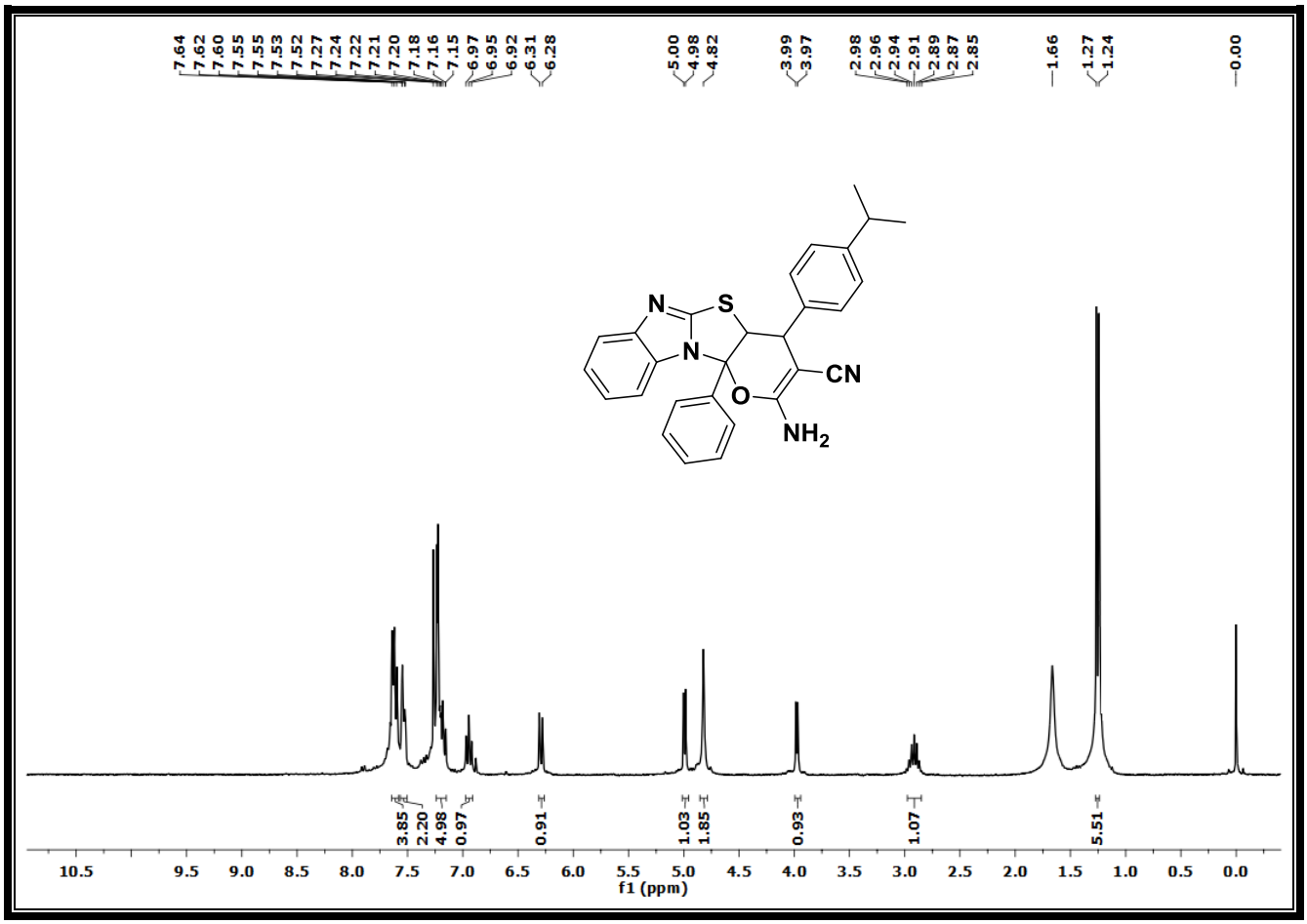


Fig.9. ^{1}H-NMR spectrum of **4d**

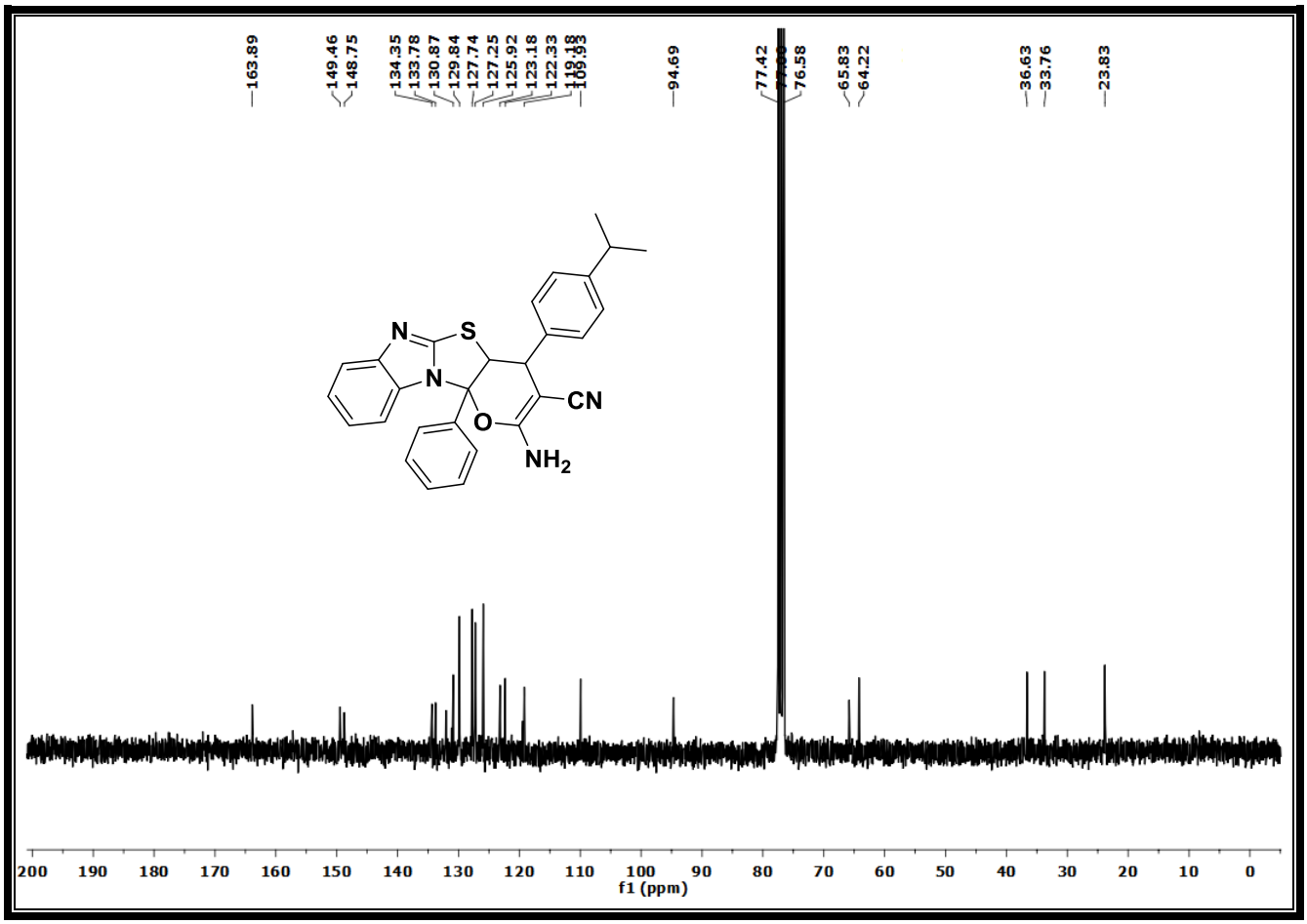


Fig.10. ^{13}C-NMR spectrum of **4d**

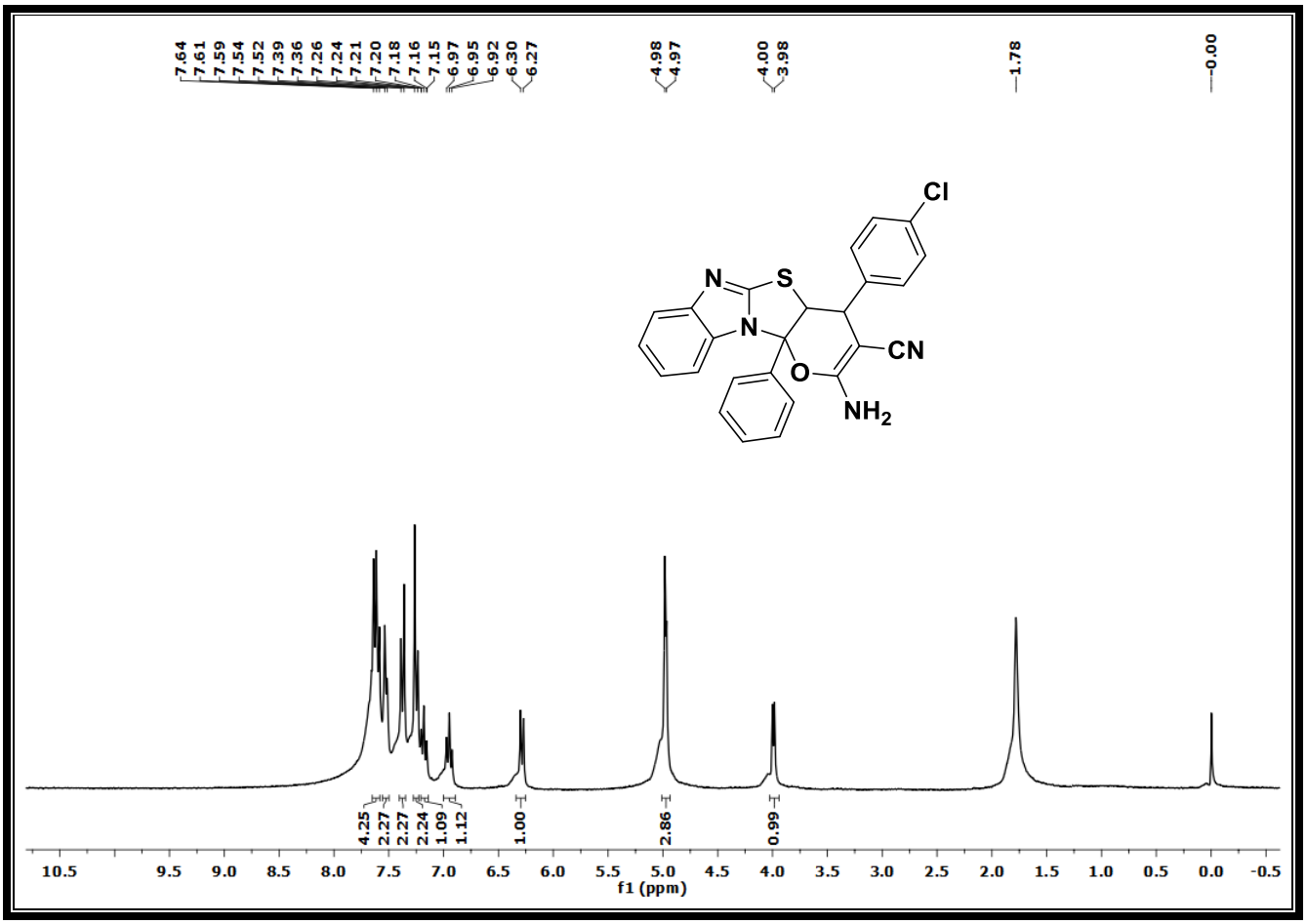


Fig.11. ^{1}H-NMR spectrum of **4e**

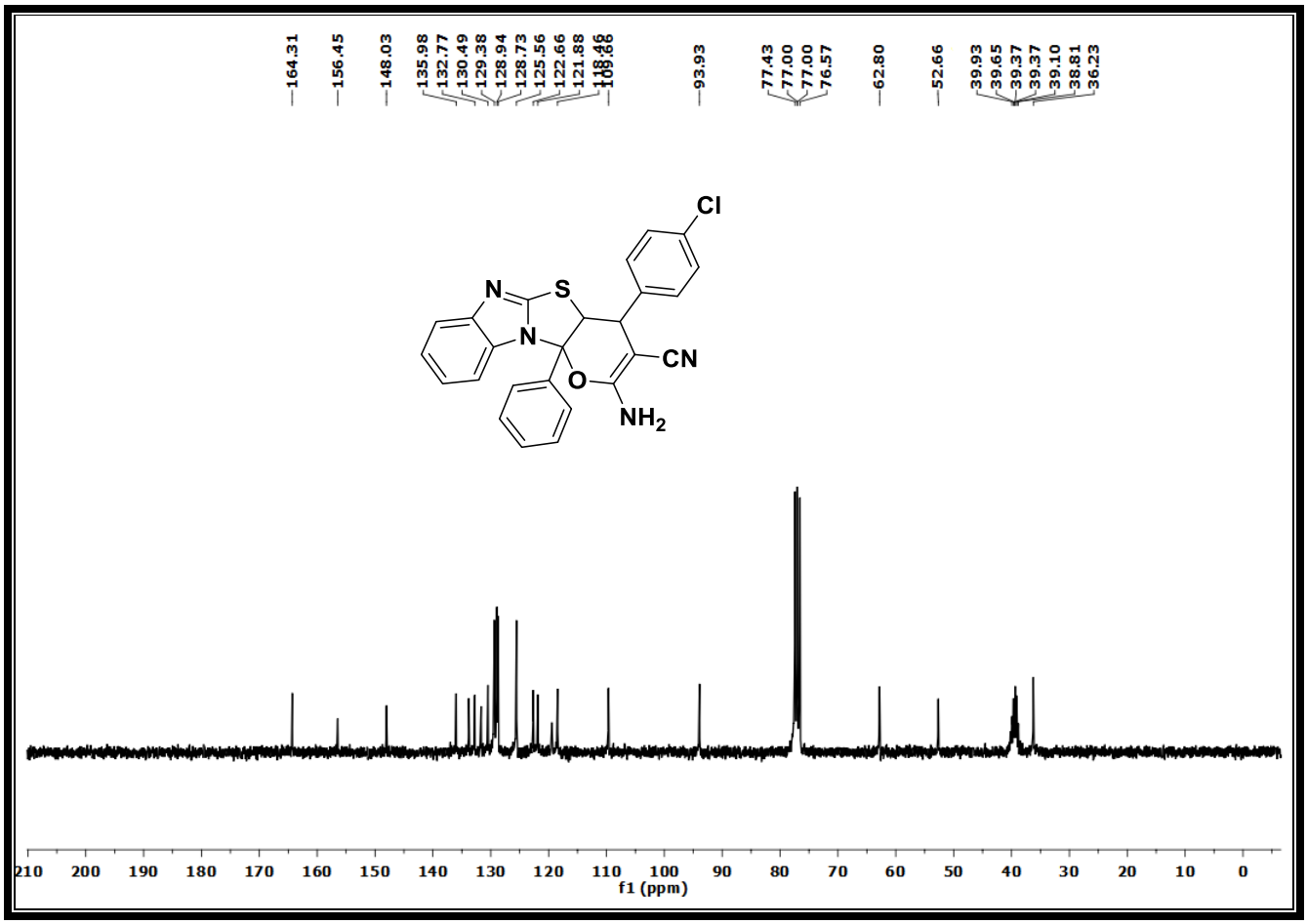


Fig.12. ^{13}C-NMR spectrum of **4e**

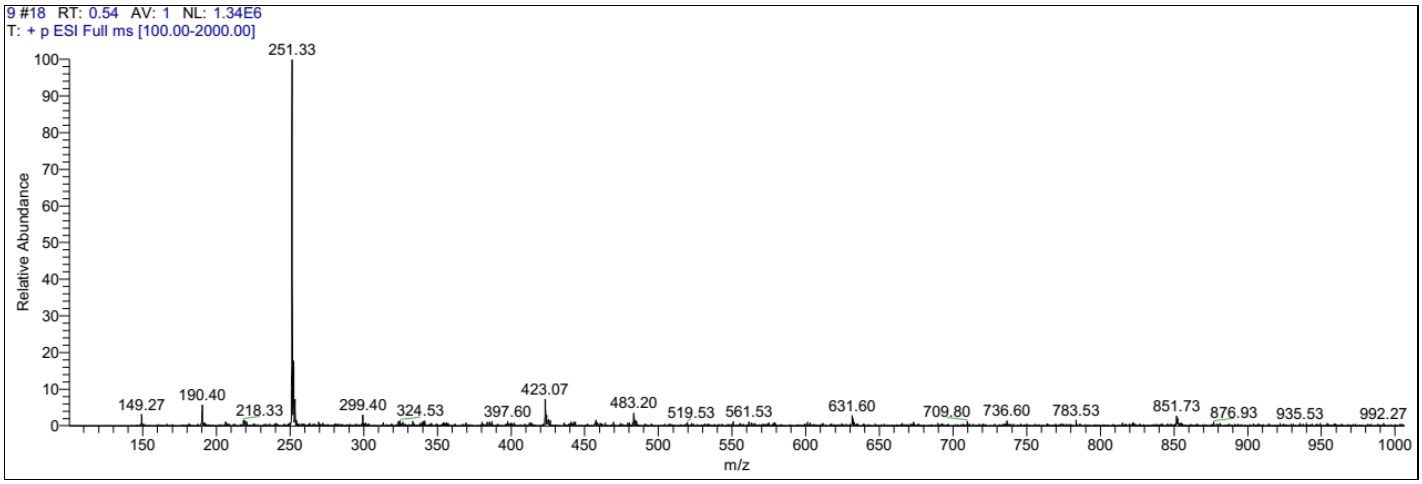


Fig.13. Mass spectrum of **4e**

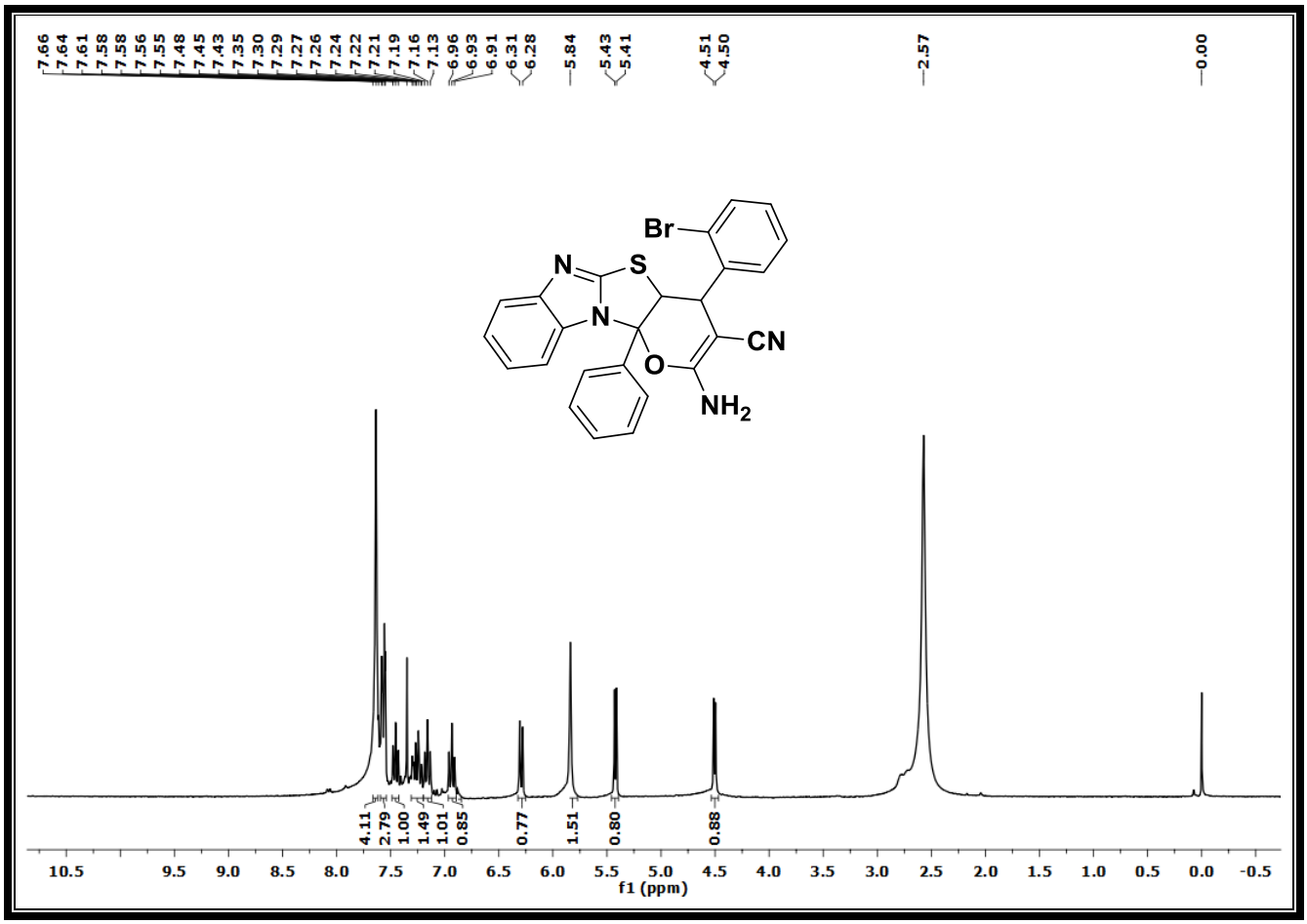


Fig.14. ^{1}H-NMR spectrum of **4f**

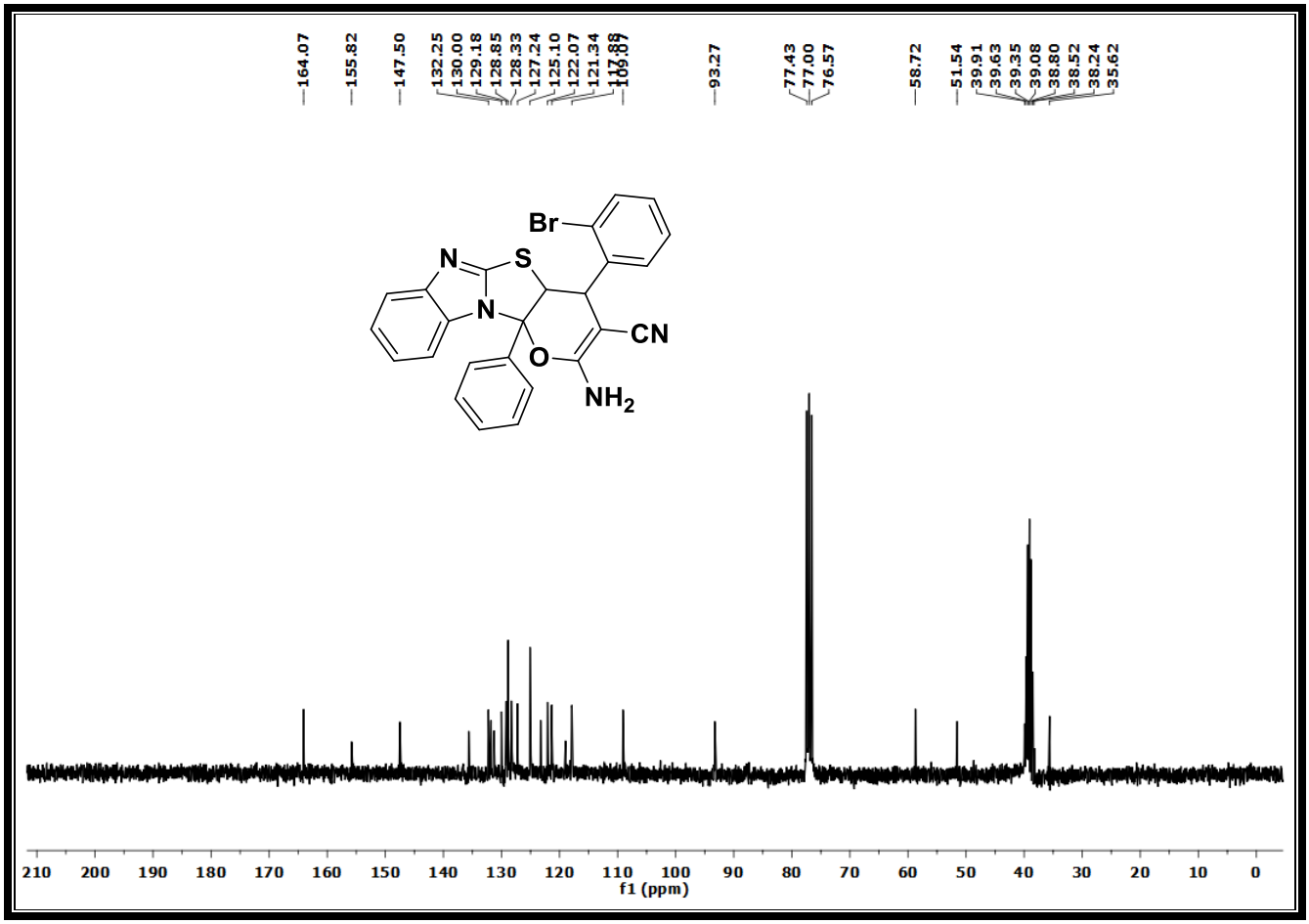


Fig.15. ^{13}C-NMR spectrum of **4f**

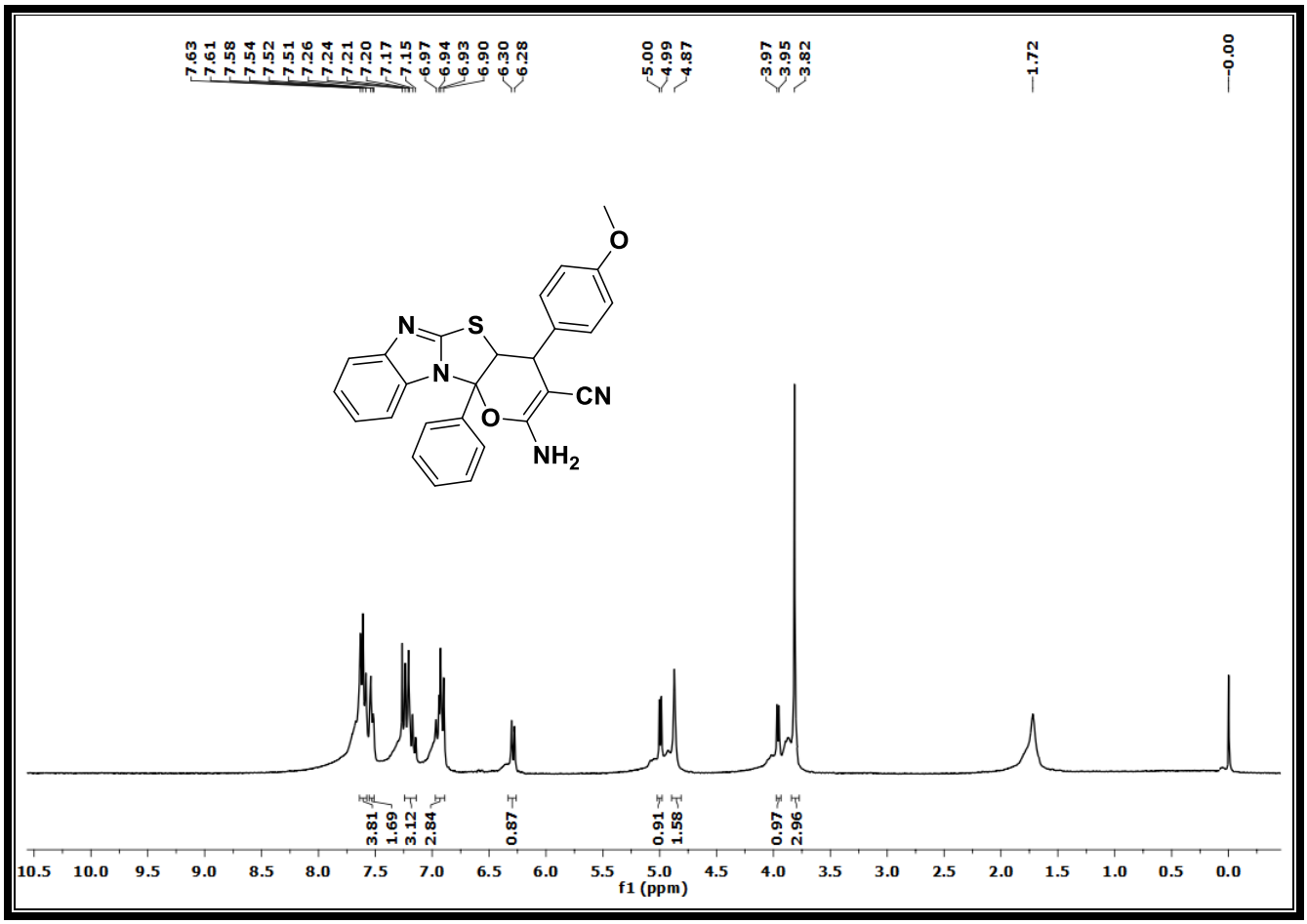


Fig.16. ^{1}H-NMR spectrum of **4g**

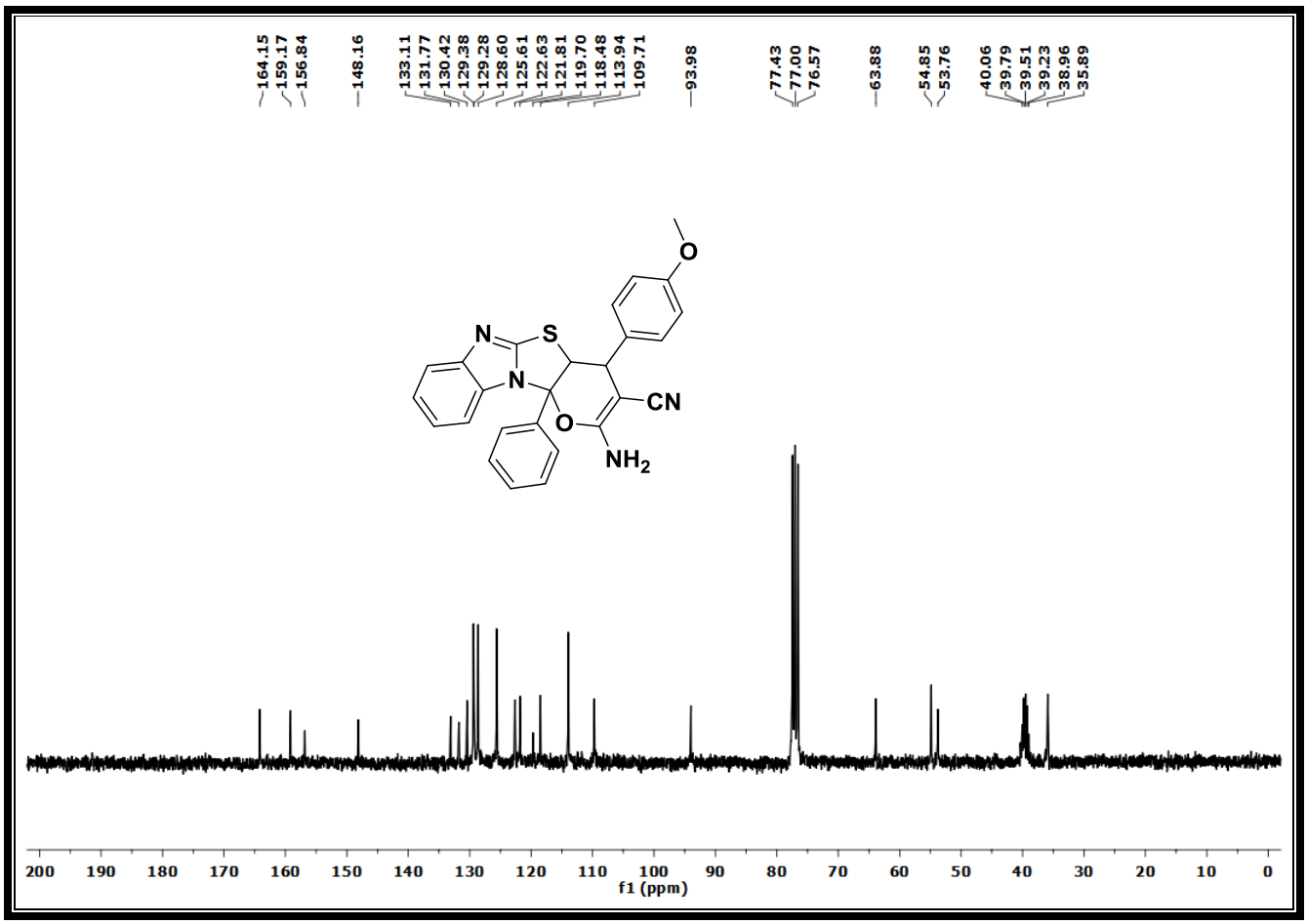


Fig.18. ^{13}C-NMR spectrum of **4g**

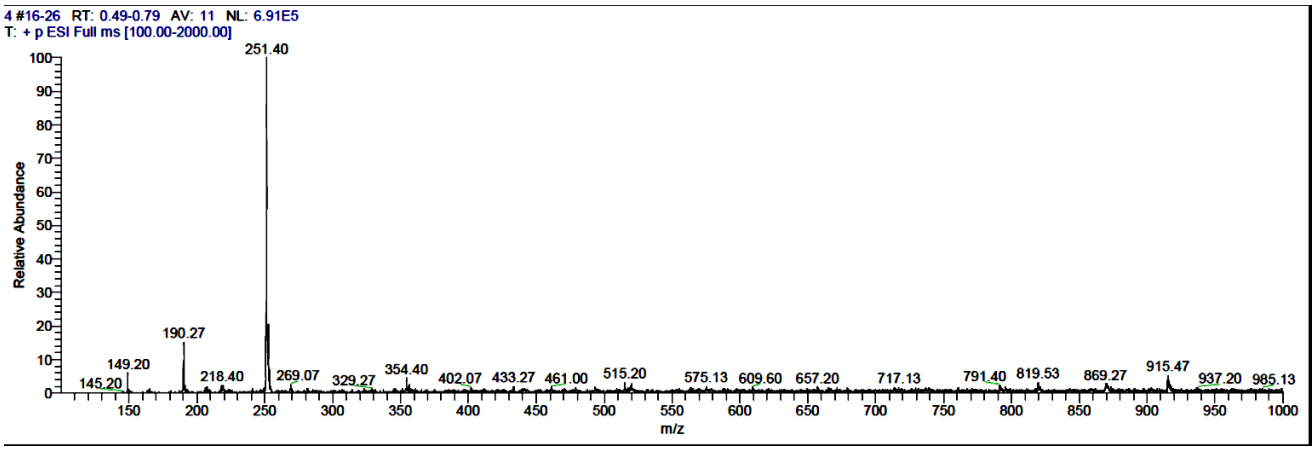


Fig.18. Mass spectrum of **4g**

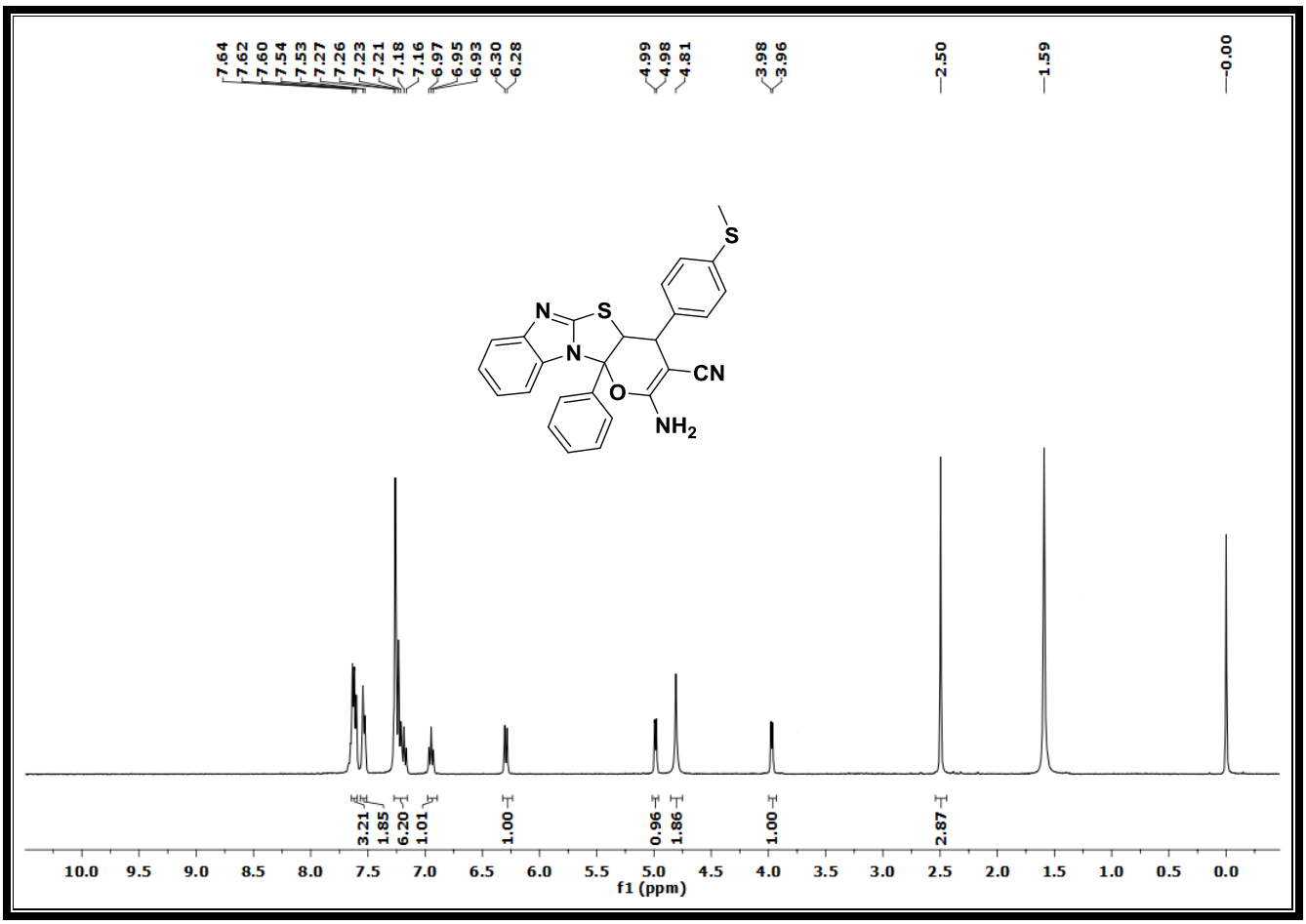


Fig.19. ^{1}H-NMR spectrum of **4h**

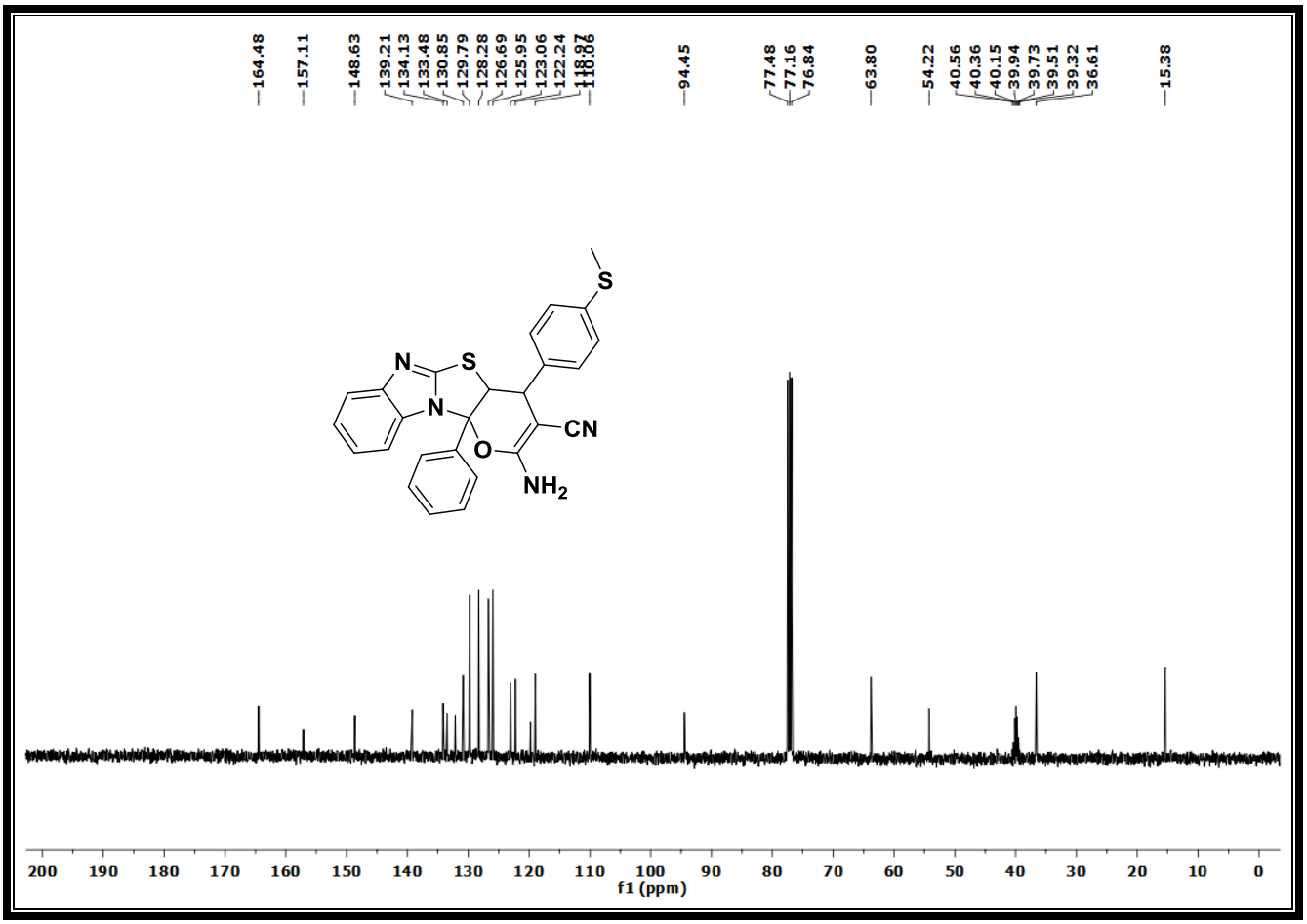


Fig.20. ^{13}C-NMR spectrum of **4h**

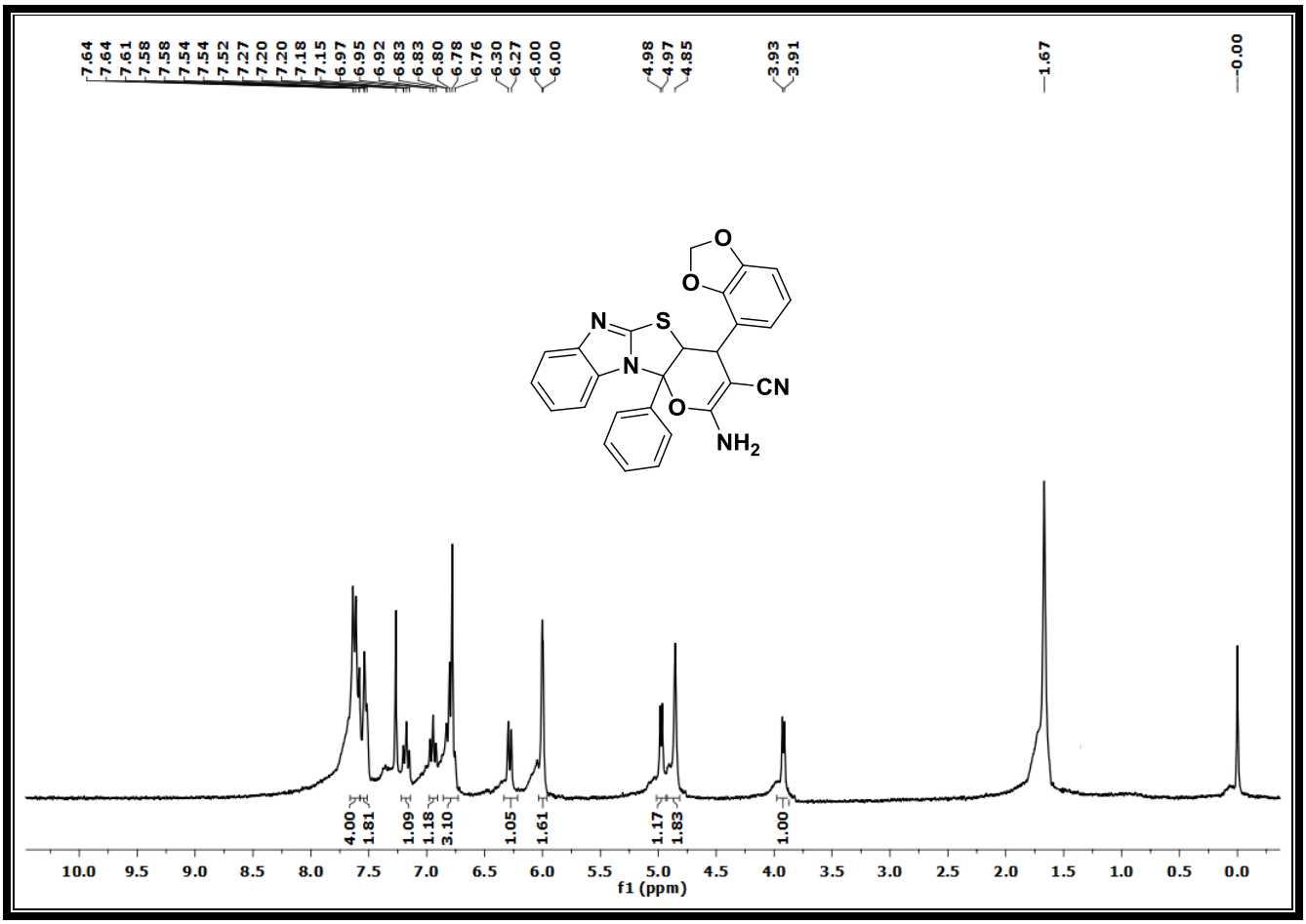


Fig.21. ^{1}H-NMR spectrum of **4i**

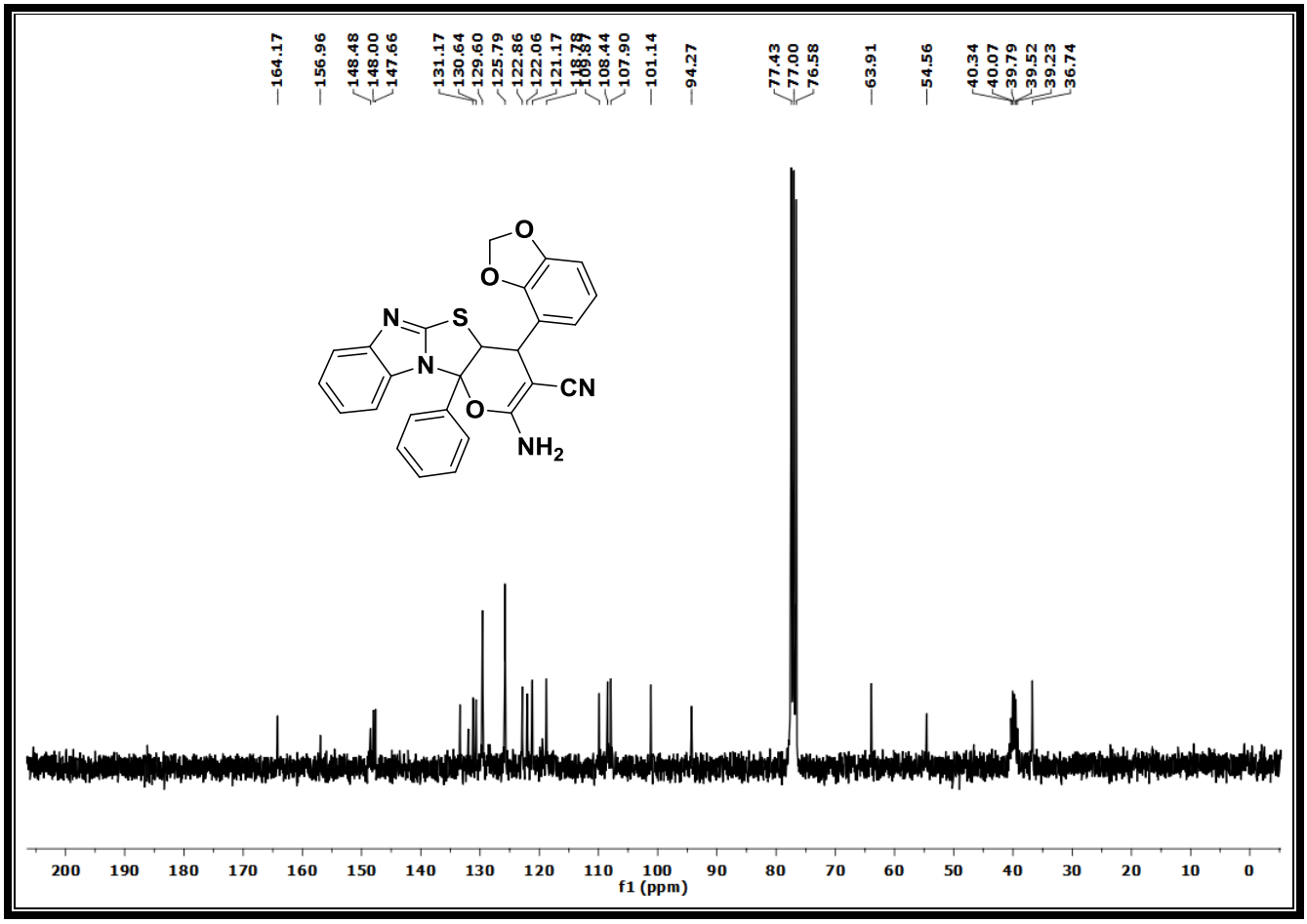


Fig.22. ^{13}C-NMR spectrum of **4i**

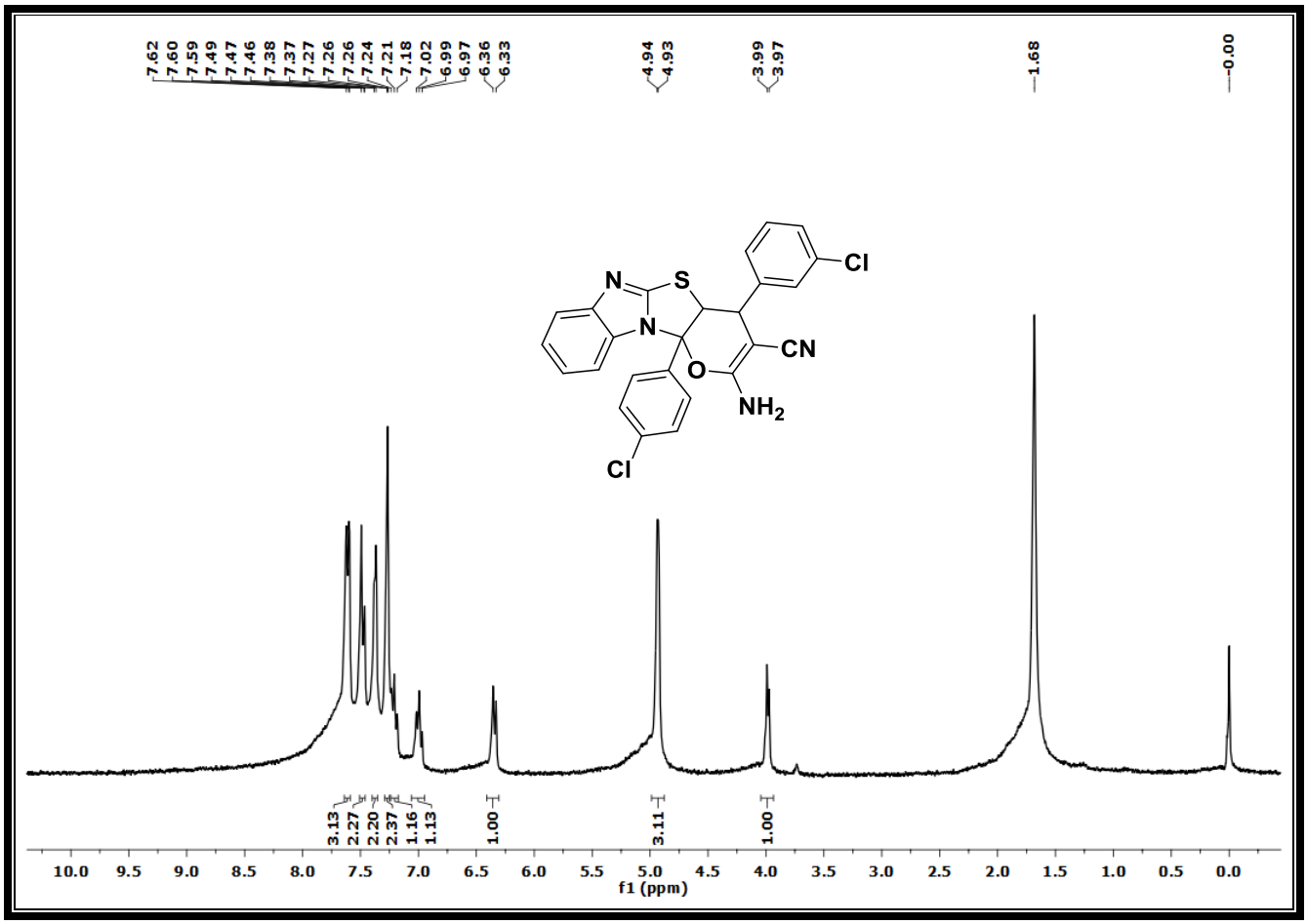


Fig.23. ^{1}H-NMR spectrum of **4j**

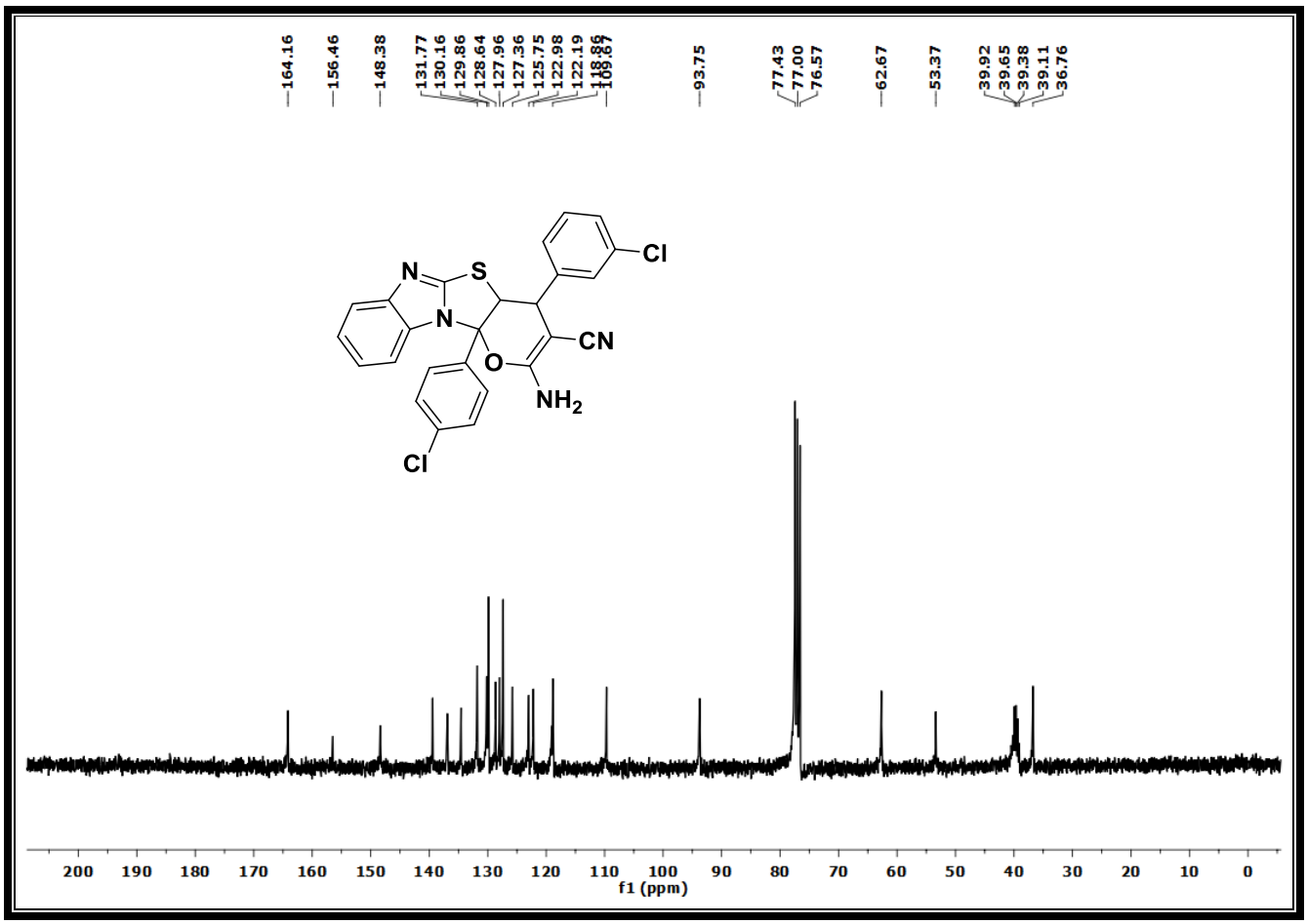


Fig.24. ^{13}C-NMR spectrum of **4j**

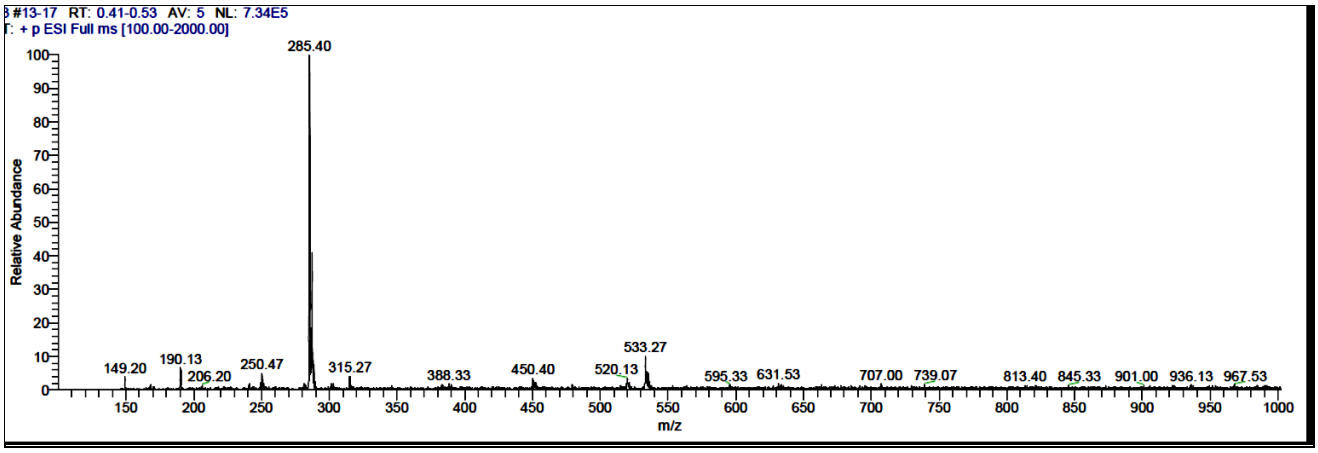


Fig.25. Mass spectrum of **4j**

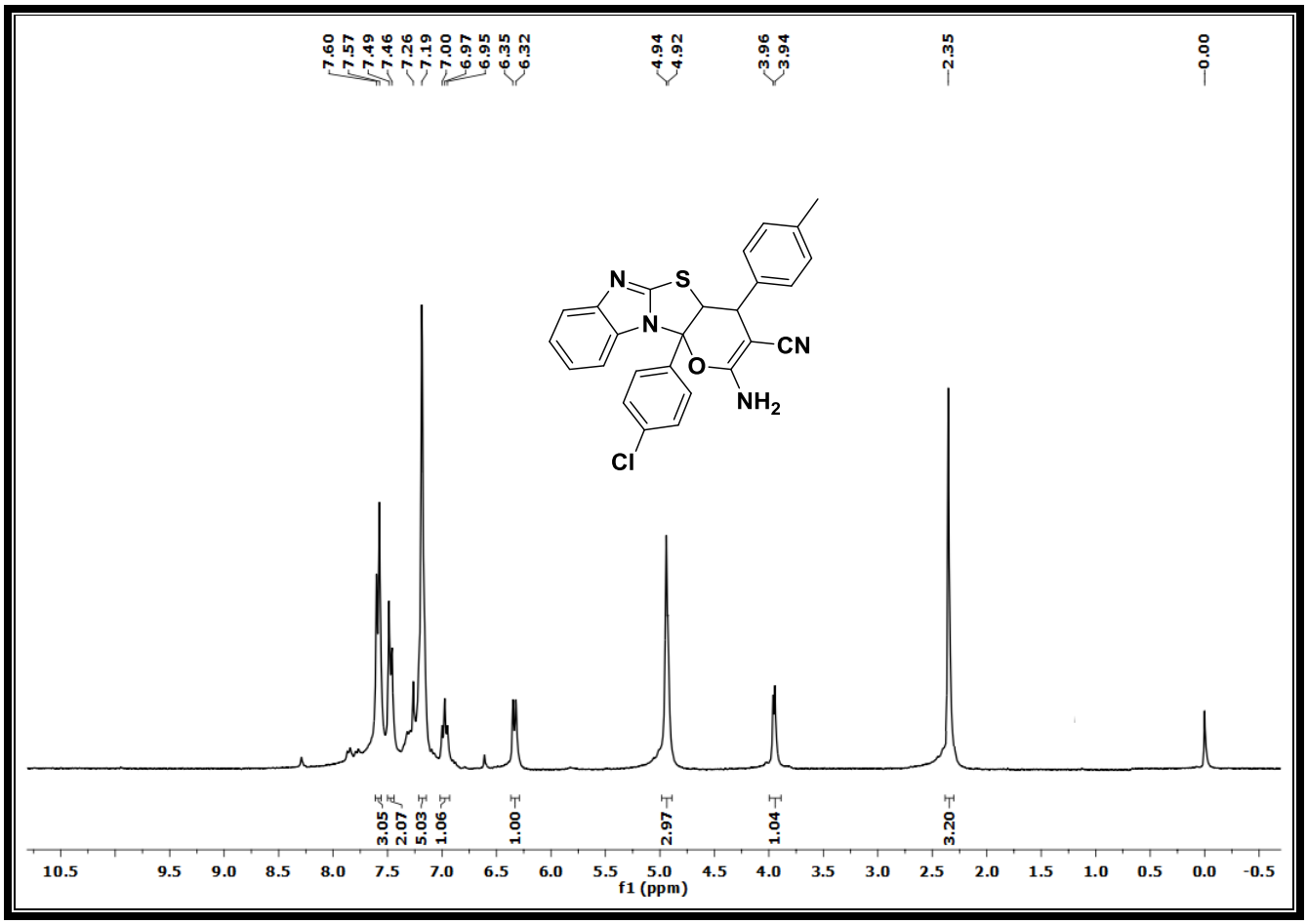


Fig.26. ^{1}H-NMR spectrum of **4k**

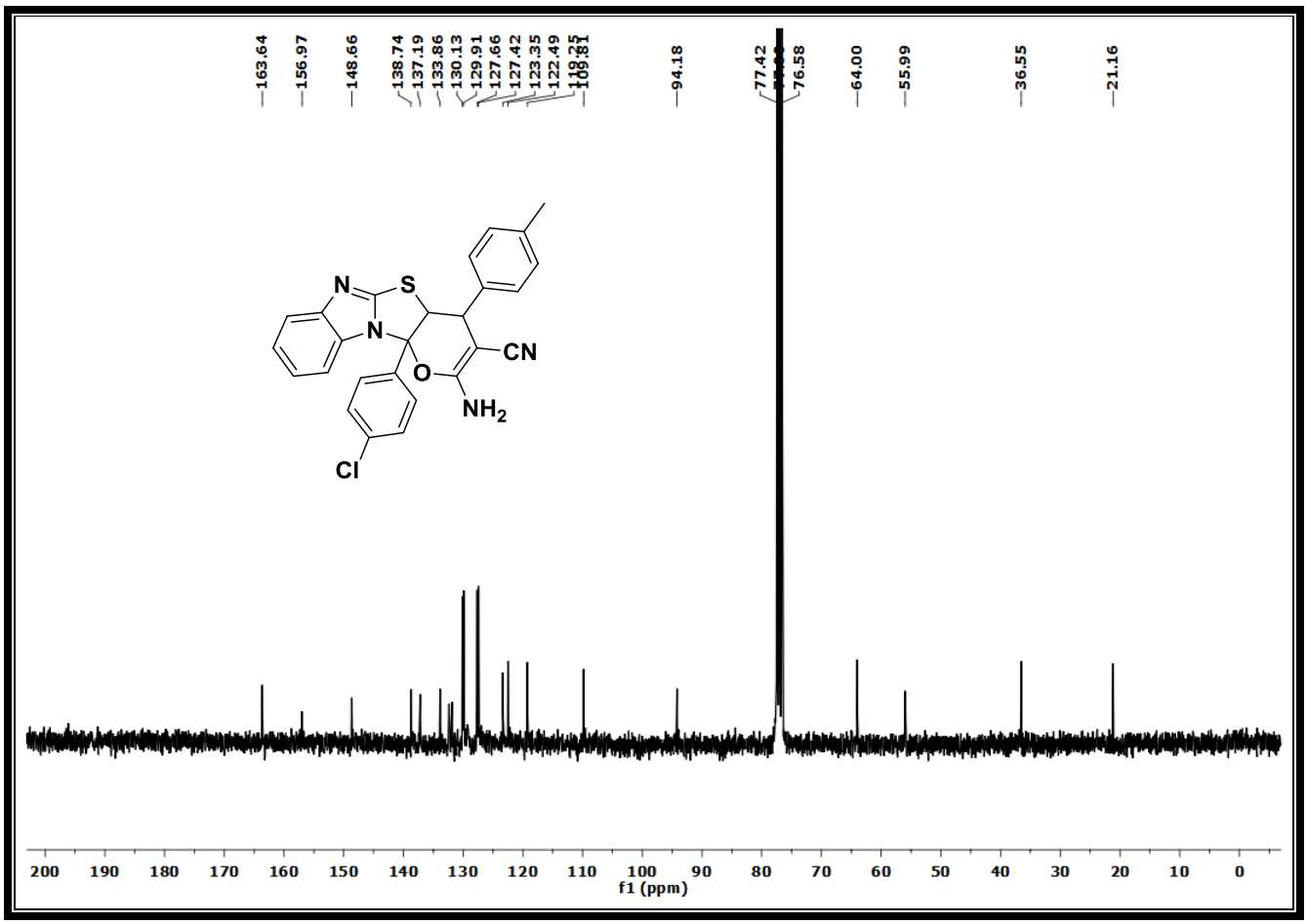


Fig.27. ^{13}C-NMR spectrum of **4k**

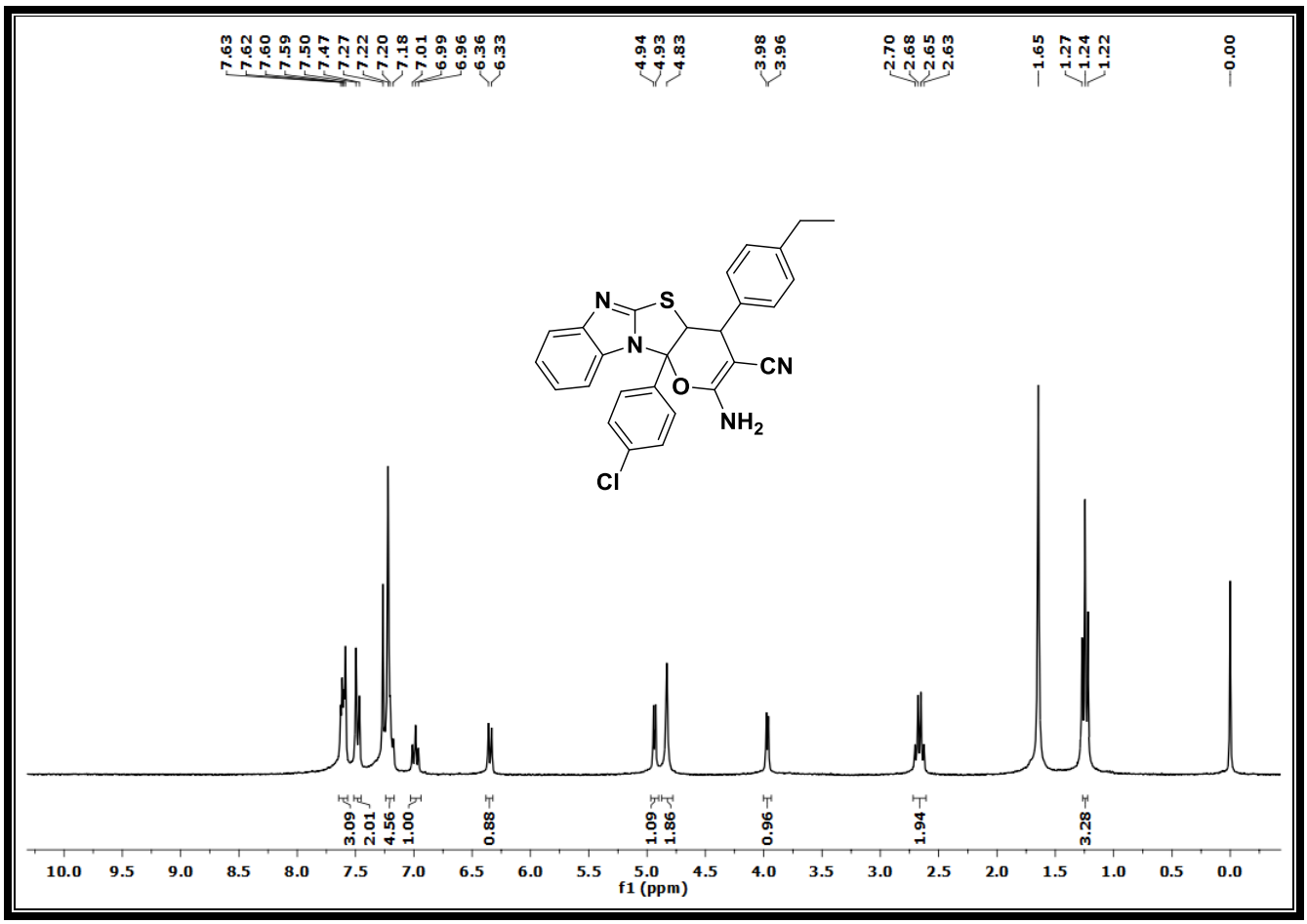


Fig.28. ^{1}H-NMR spectrum of **4l**

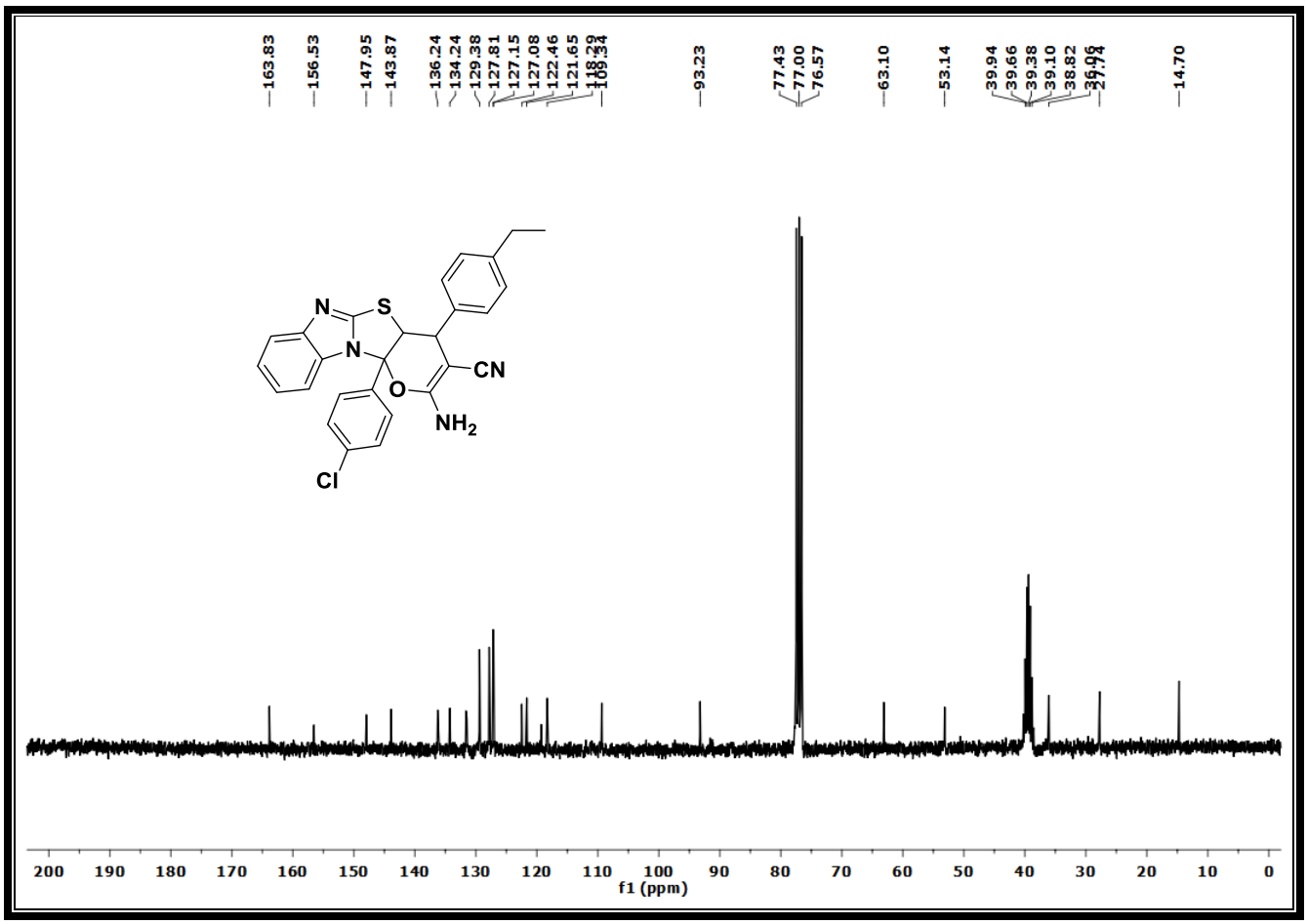


Fig.29. ^{13}C-NMR spectrum of **4l**

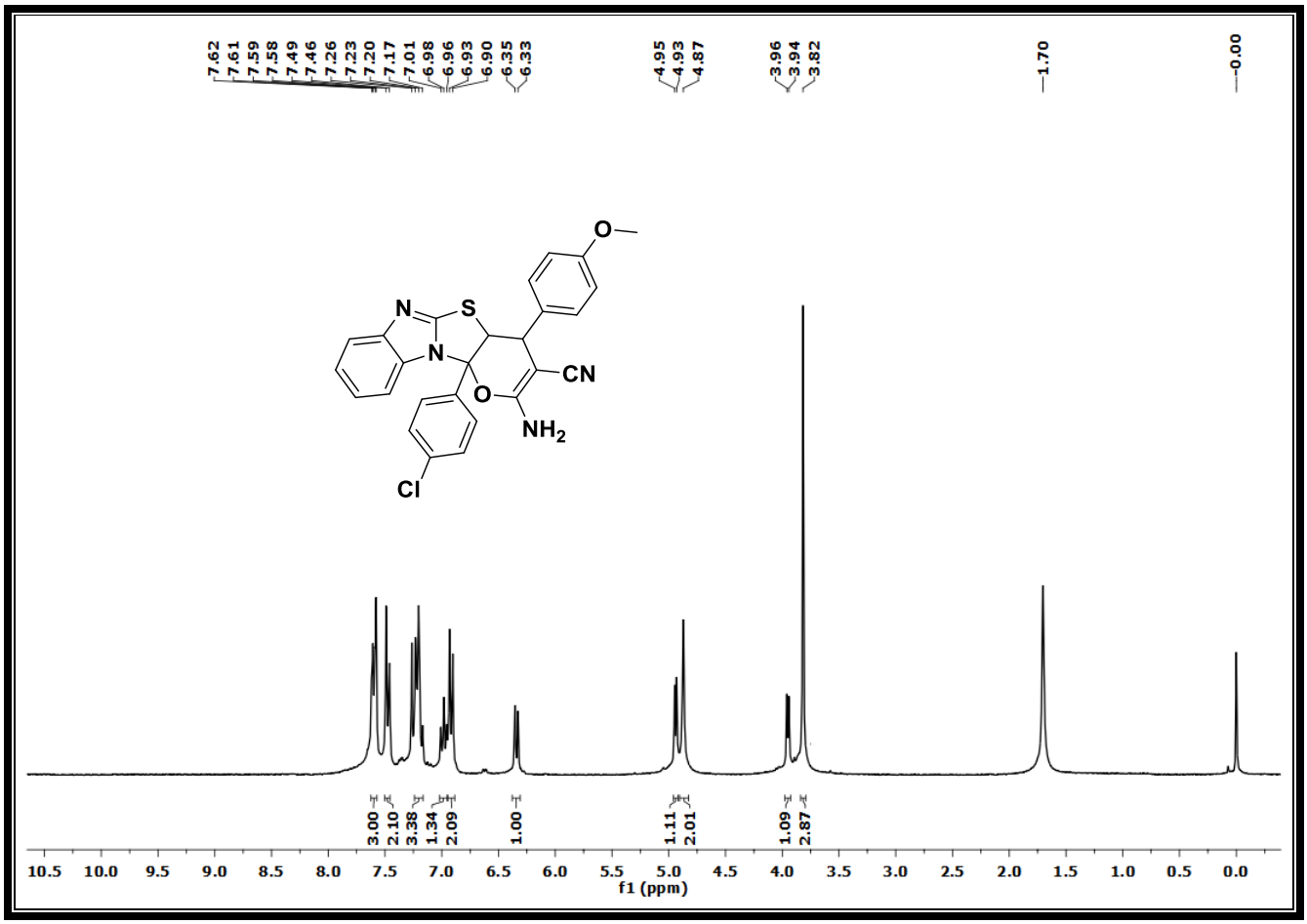


Fig.30. ^{1}H-NMR spectrum of **4m**

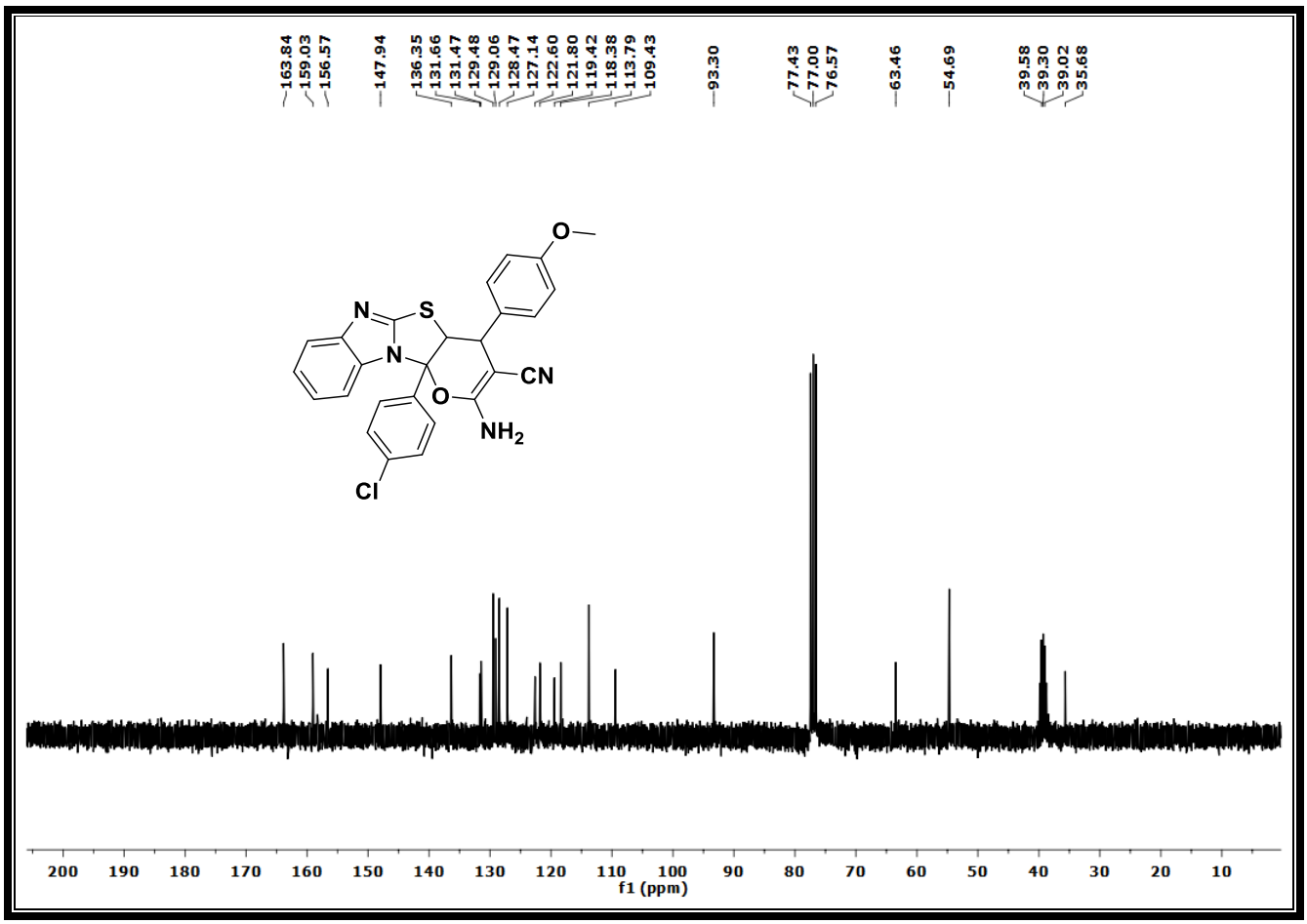


Fig.31. ^{13}C-NMR spectrum of **4m**

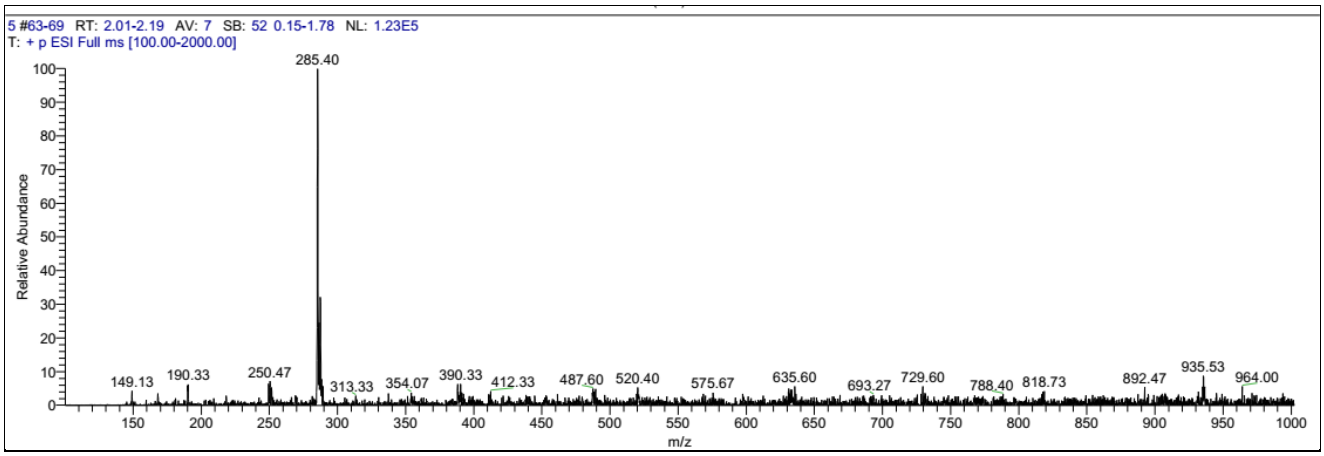


Fig.32. Mass spectrum of **4m**

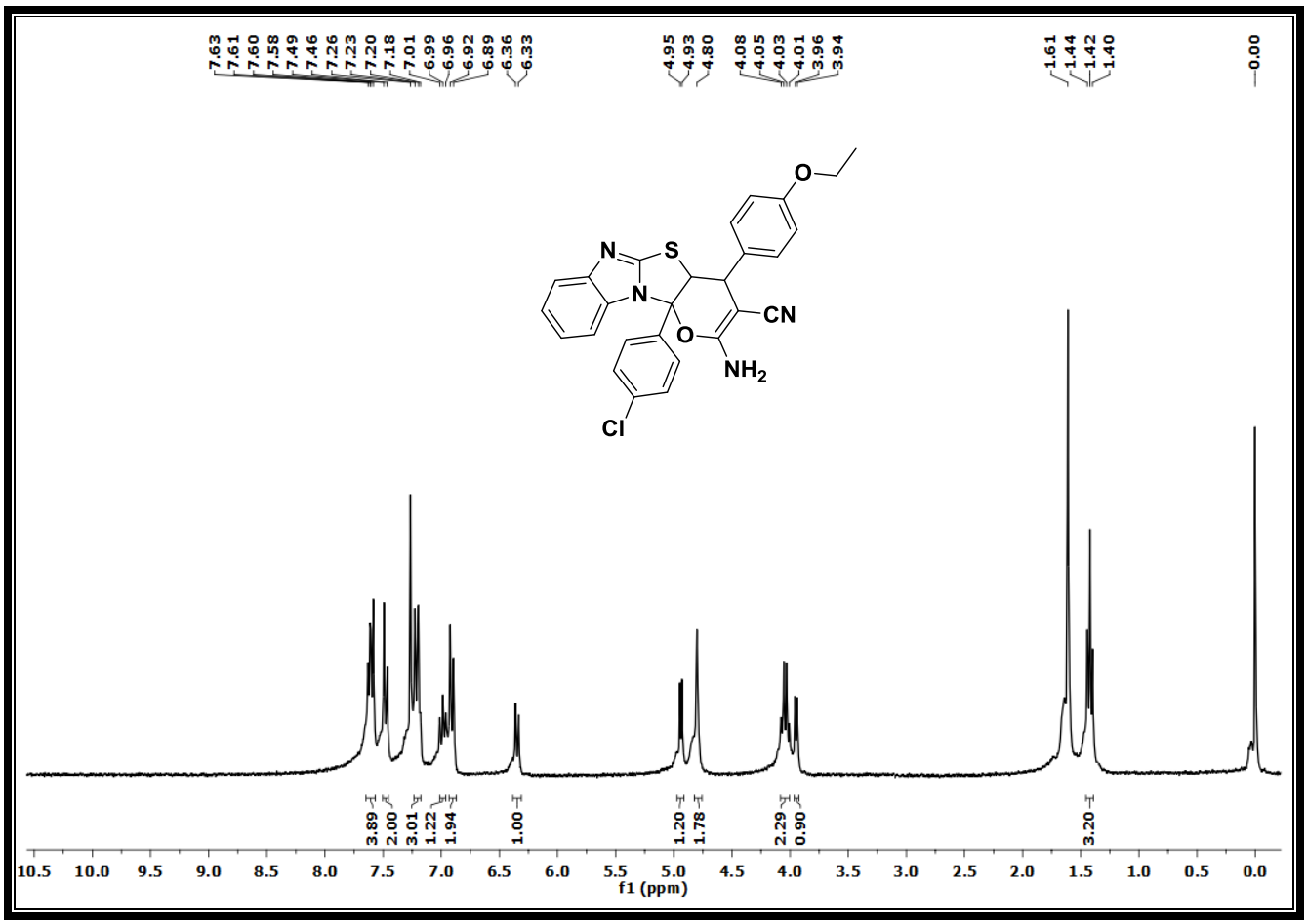


Fig.33. ^{1}H-NMR spectrum of **4n**

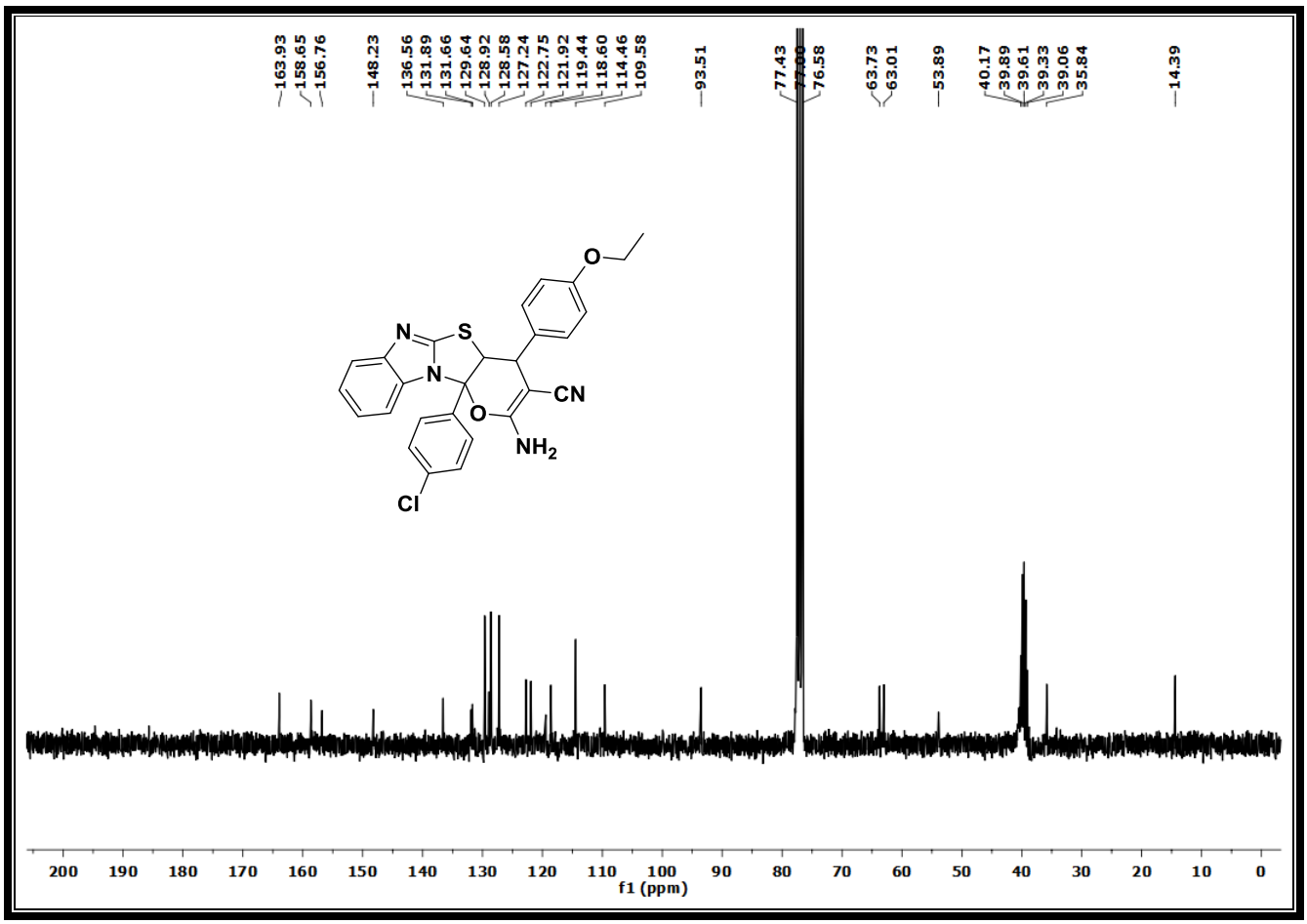


Fig.34. ^{13}C-NMR spectrum of **4n**

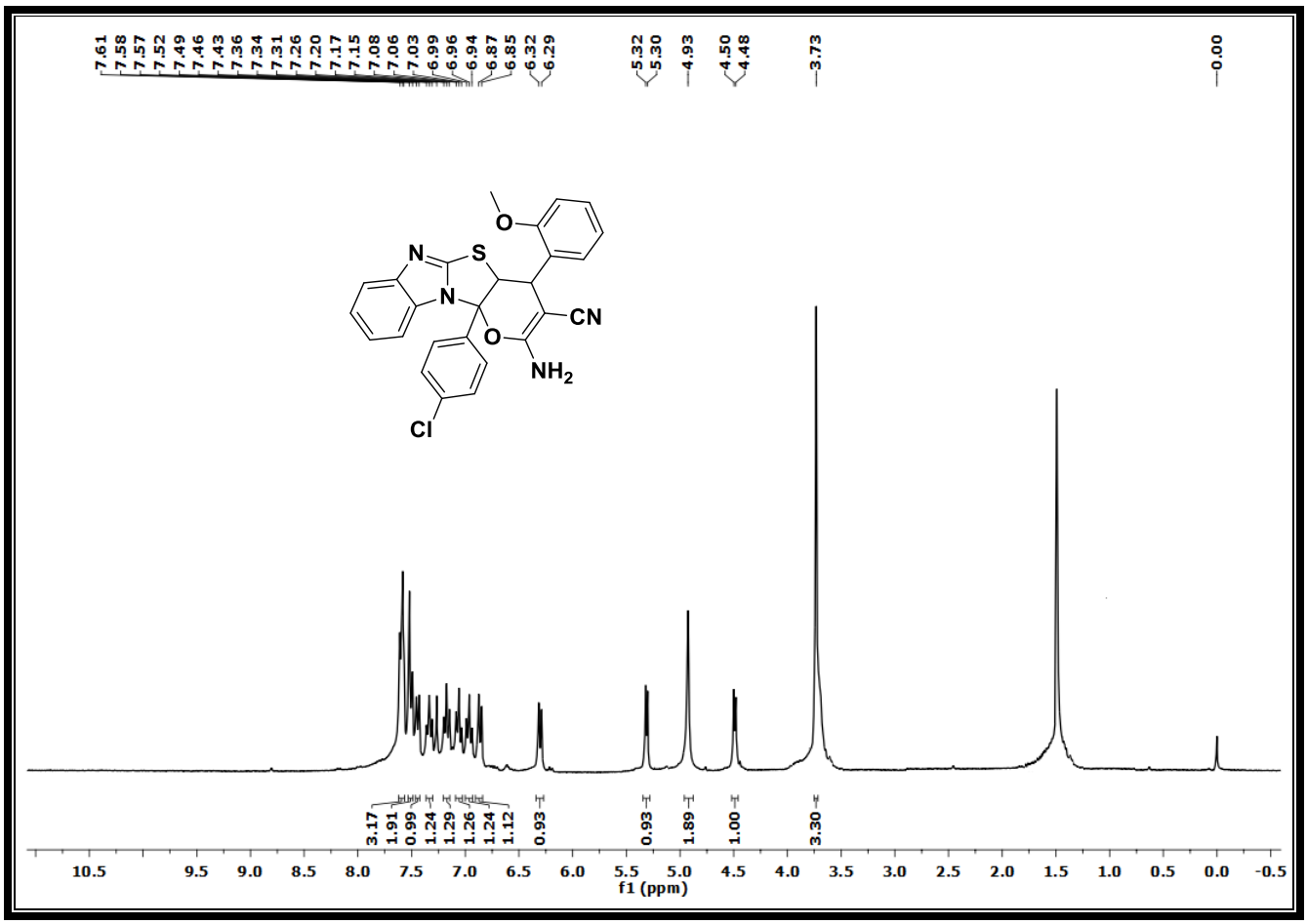


Fig.35. ^{1}H-NMR spectrum of **4o**

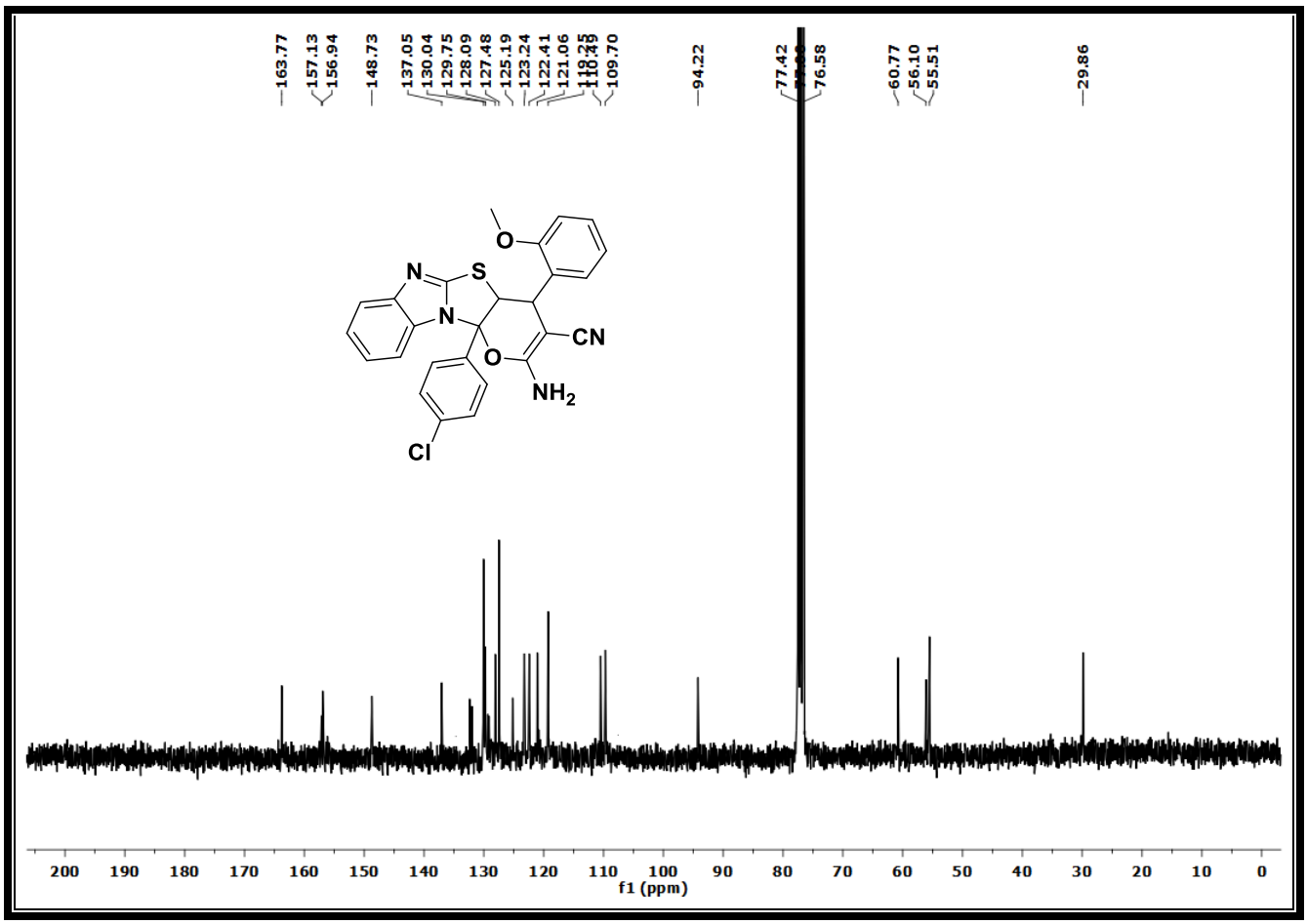


Fig.36. ^{13}C-NMR spectrum of **4o**

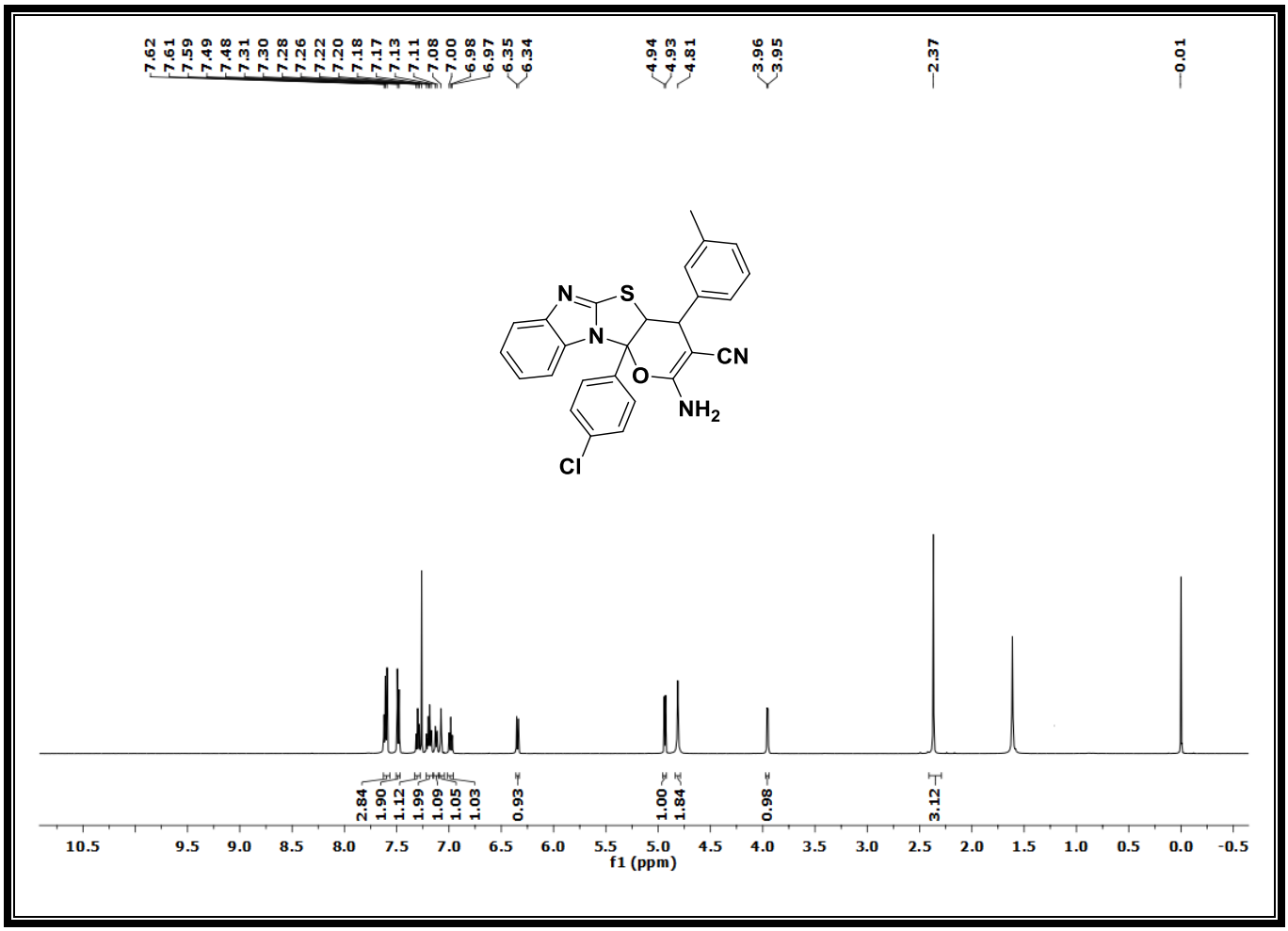


Fig.37. ^{1}H-NMR spectrum of **4p**

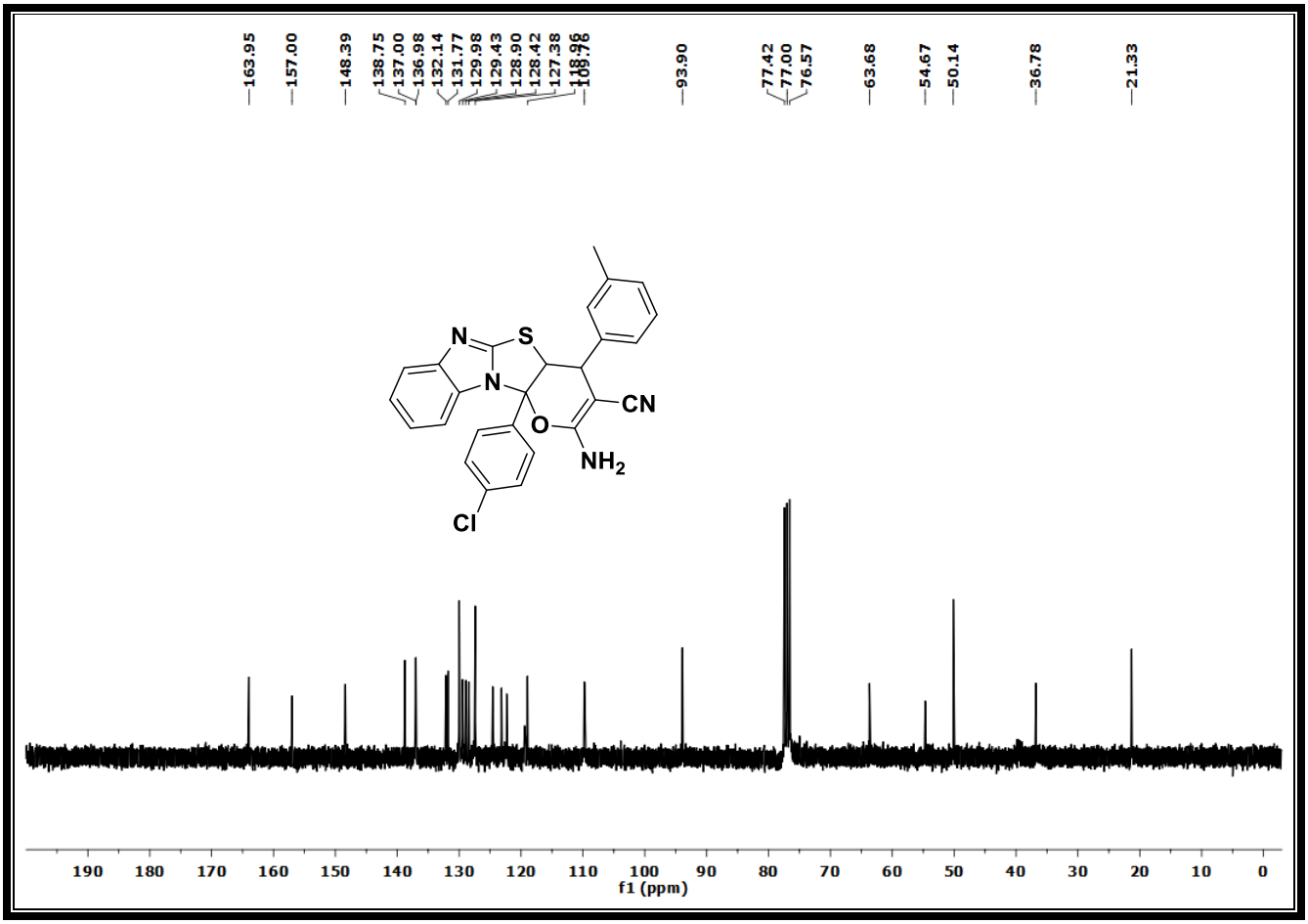


Fig.38. ^{13}C-NMR spectrum of **4p**

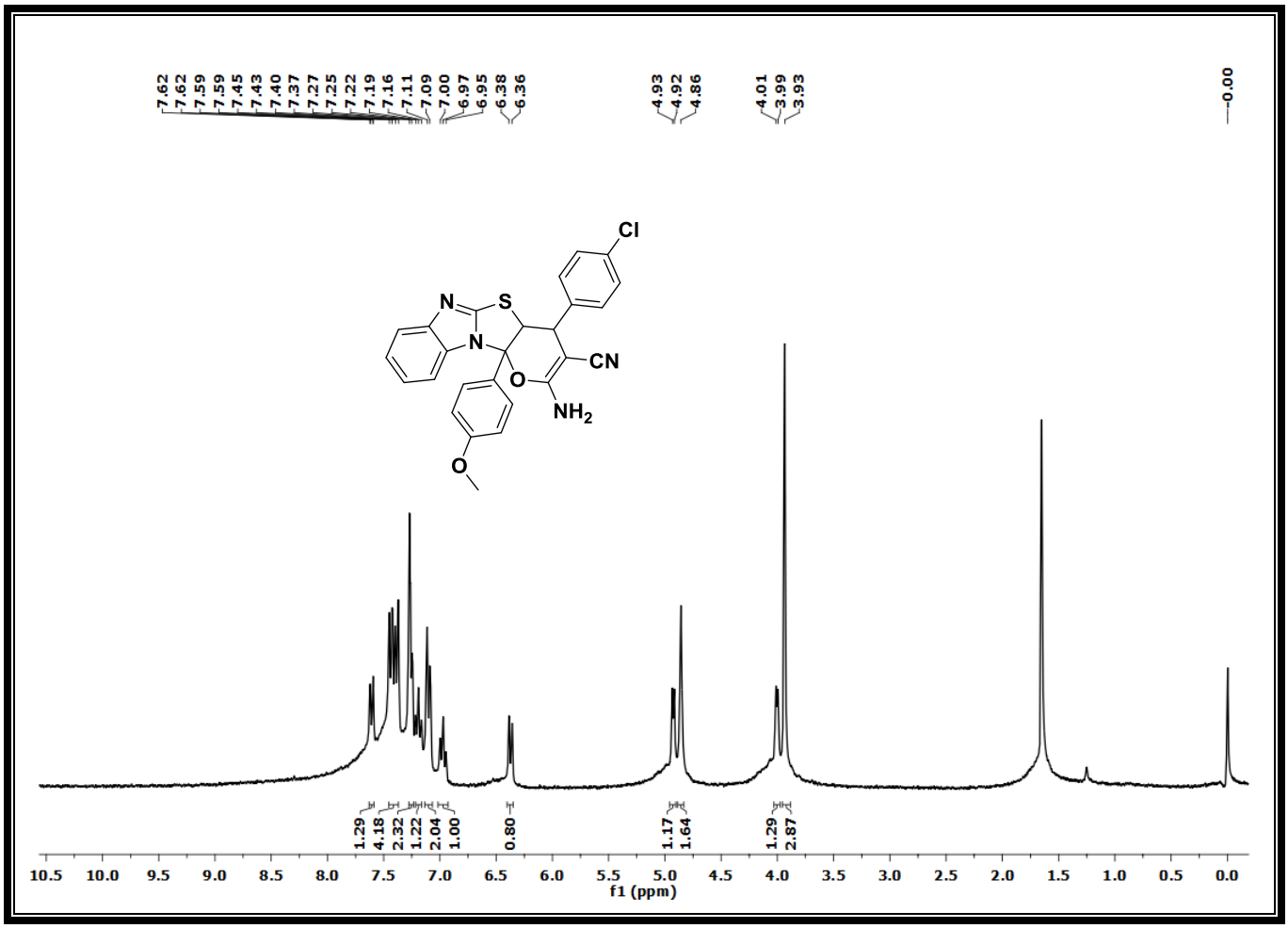


Fig.39. ^{1}H-NMR spectrum of **4q**

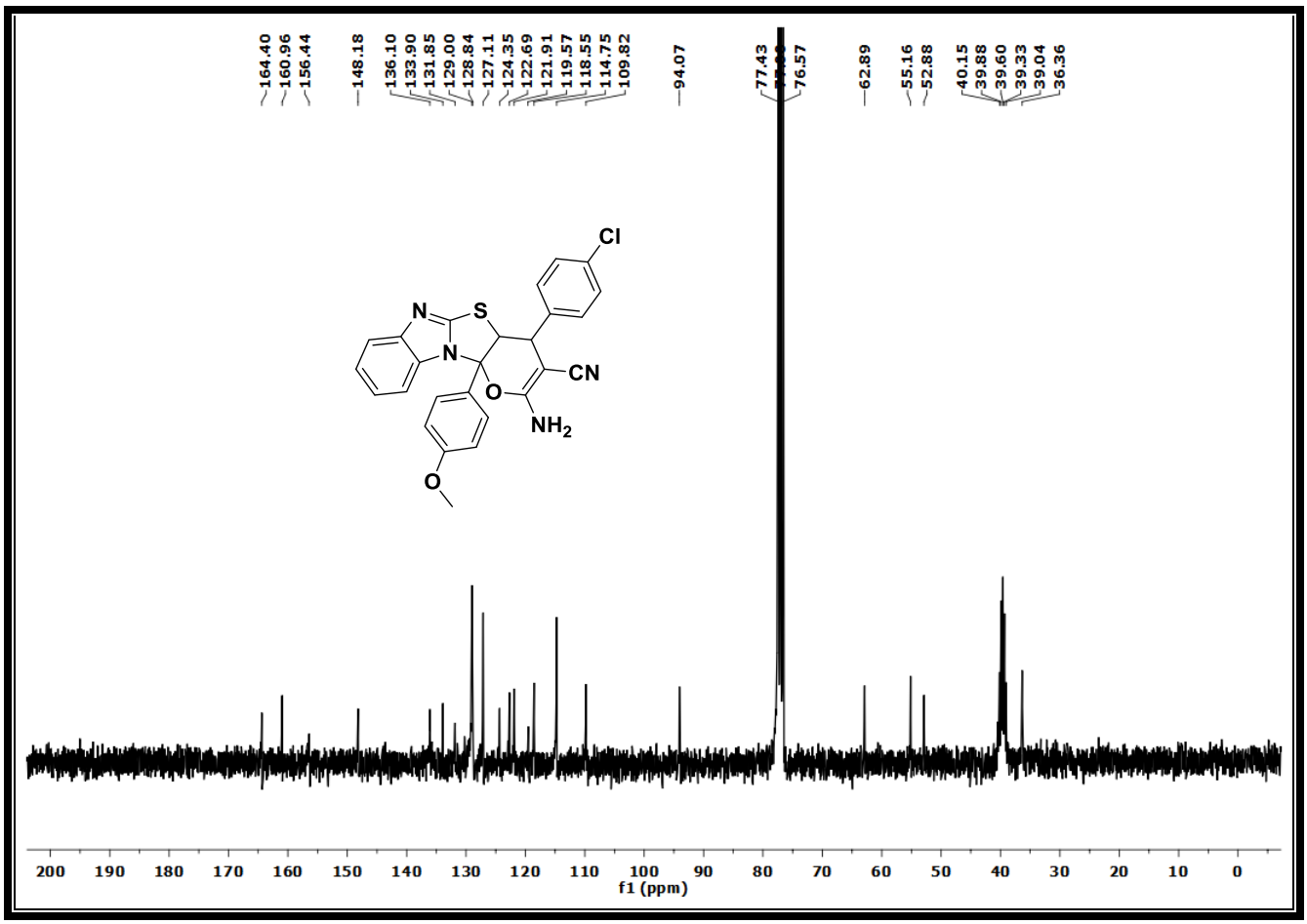


Fig.40. ^{13}C-NMR spectrum of **4q**

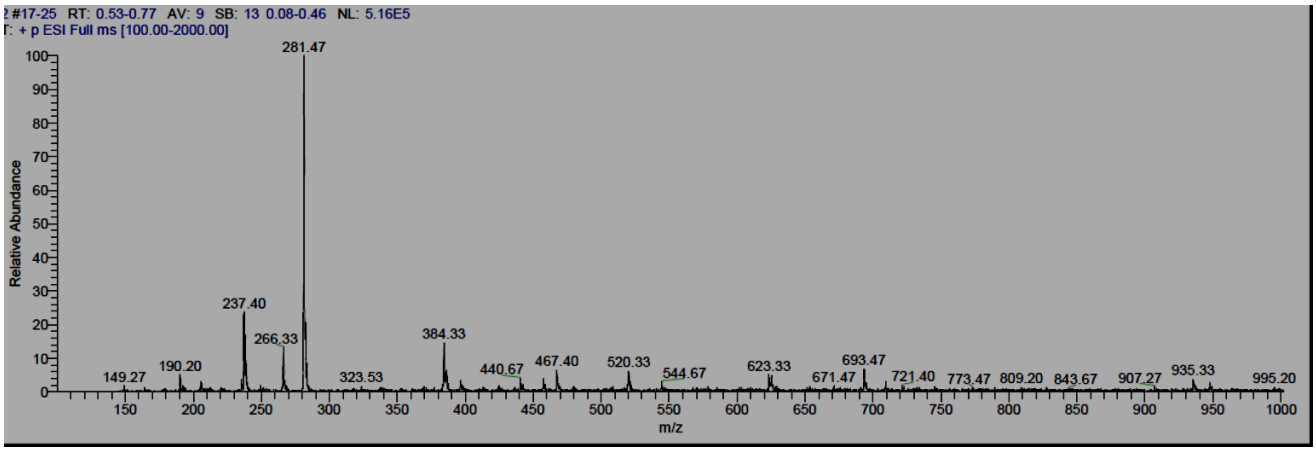


Fig.41. Mass spectrum of **4q**

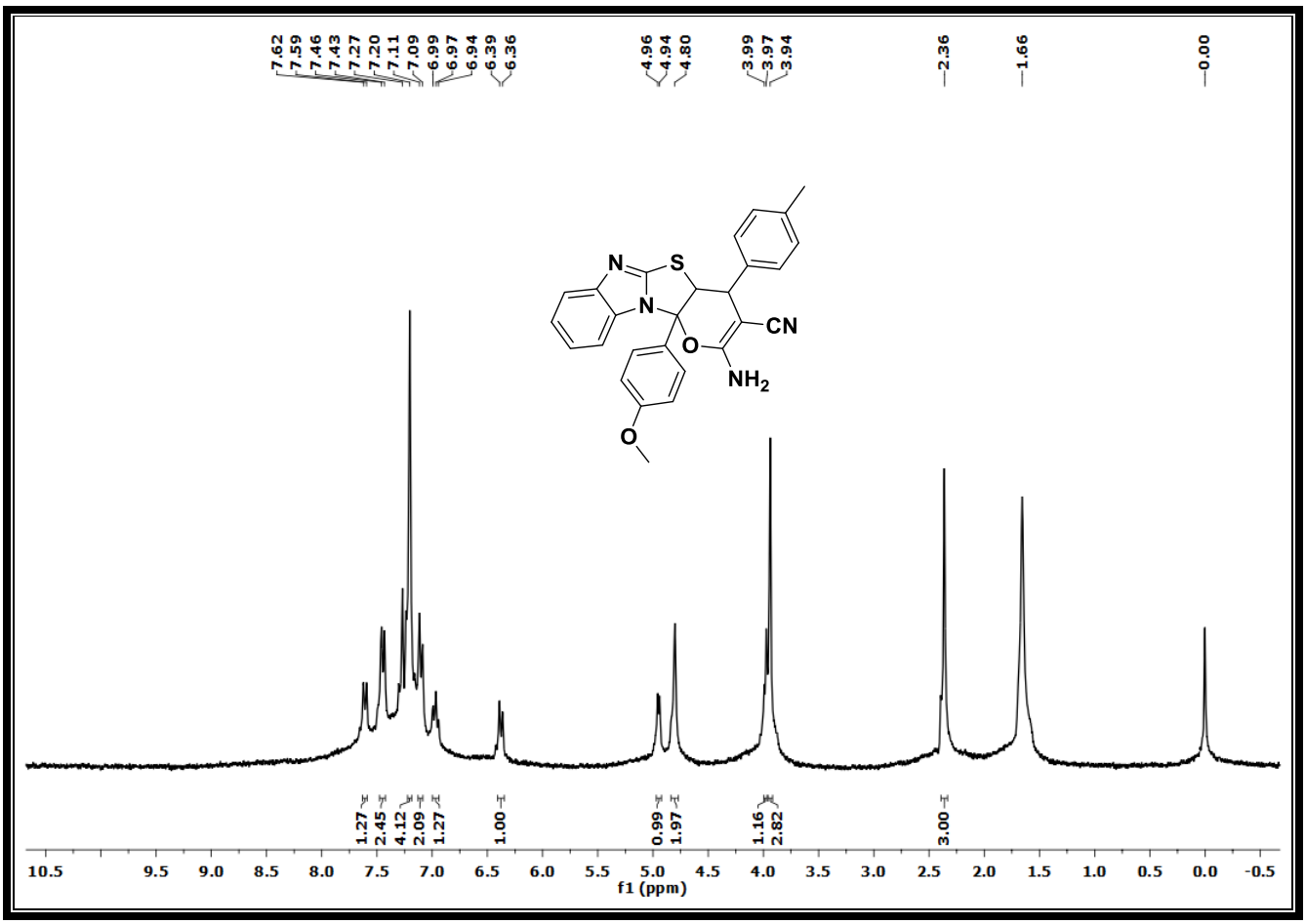


Fig.42. ^{1}H-NMR spectrum of **4r**

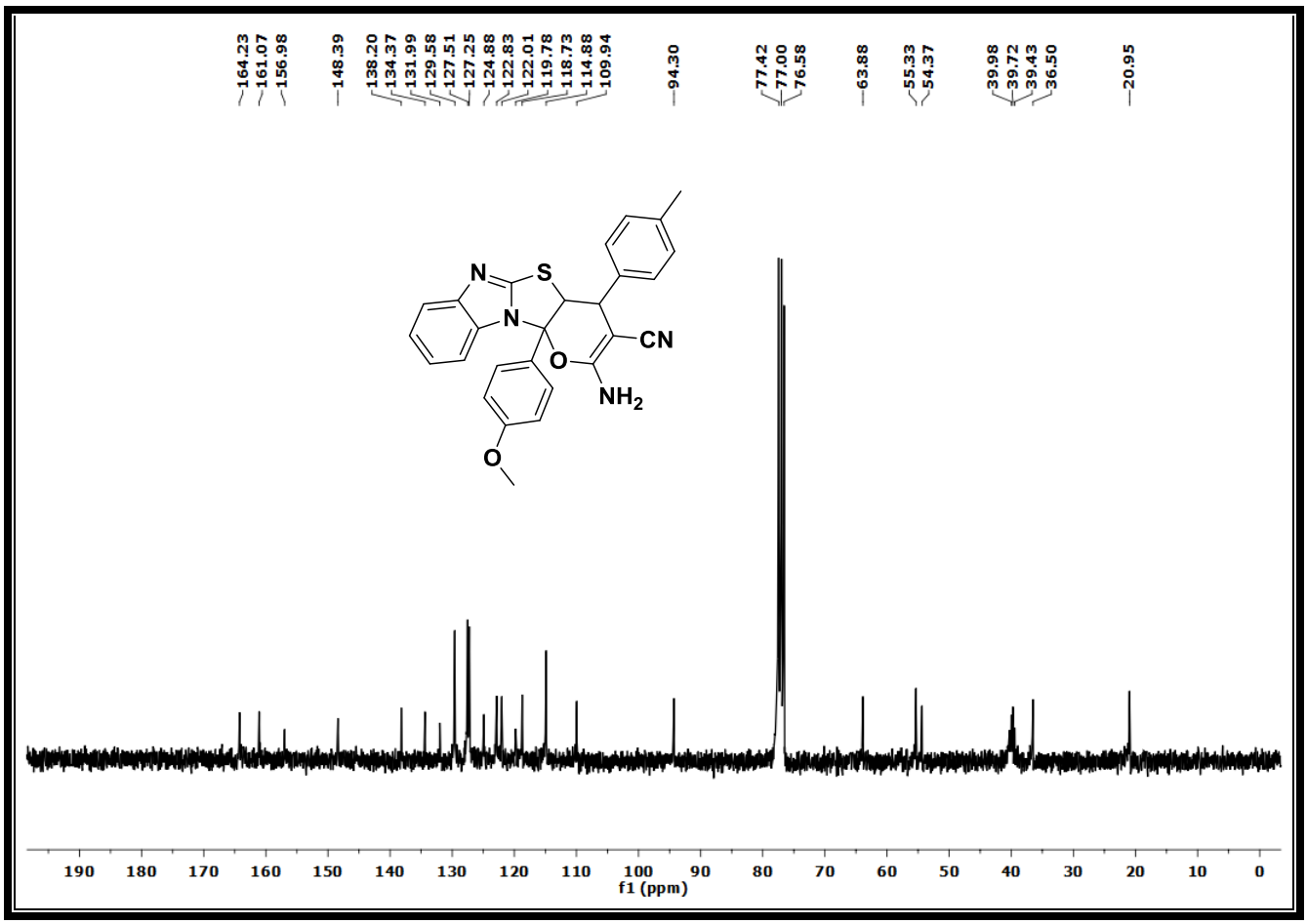


Fig.43.^{13}C-NMR spectrum of **4r**

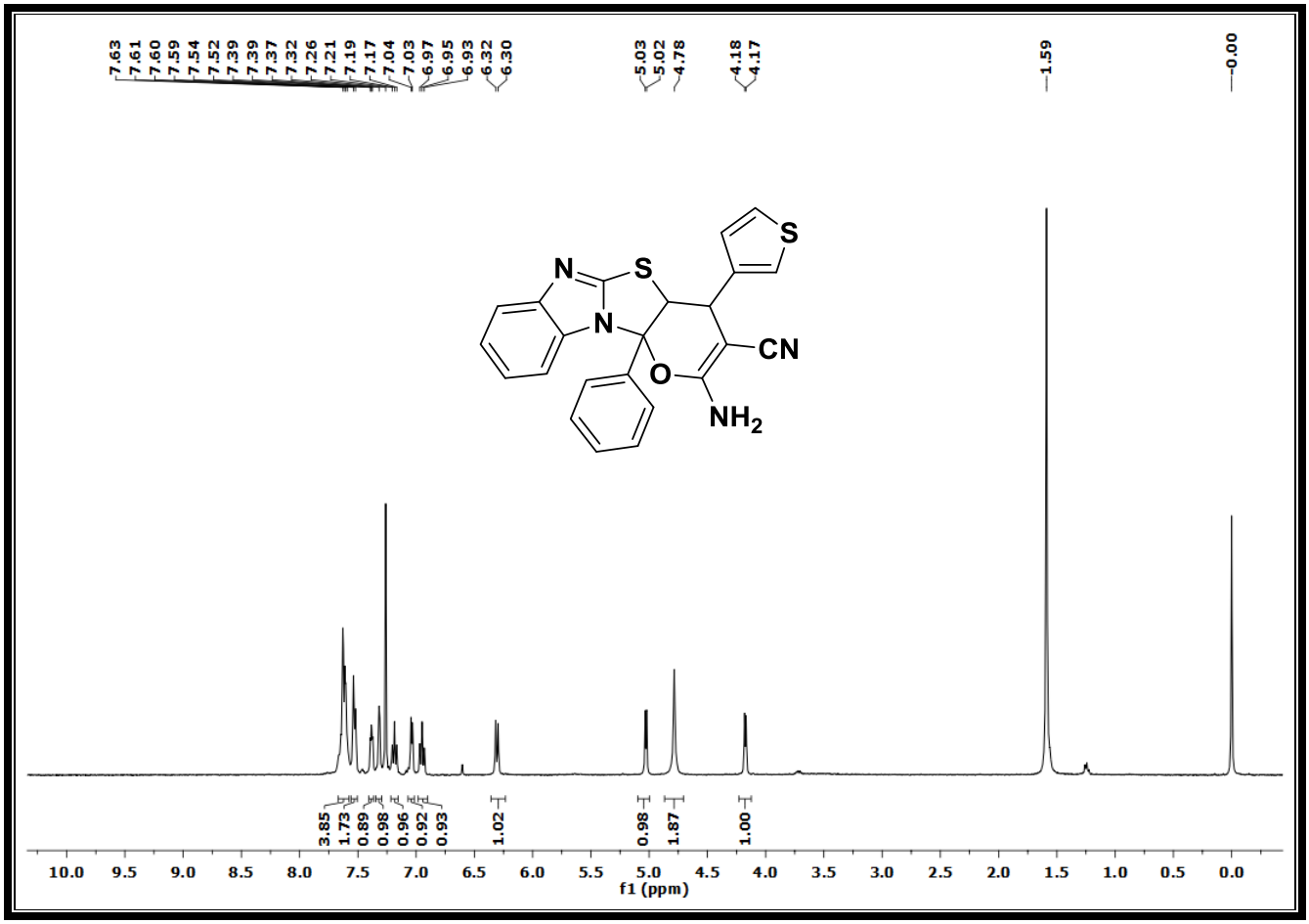


Fig.44. ^{1}H-NMR spectrum of **4s**

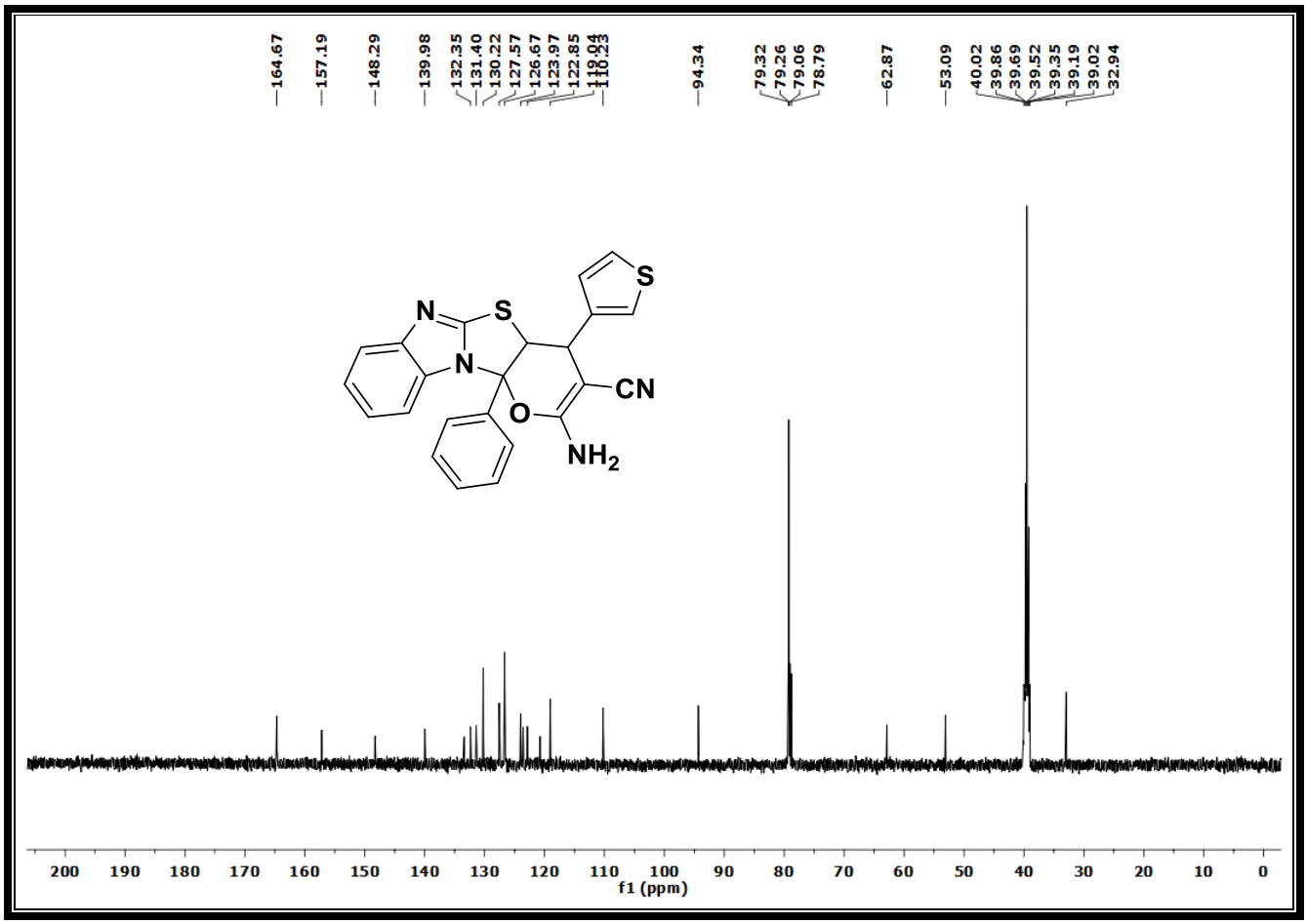


Fig.44.^{13}C-NMR spectrum of **4s**