Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Eosin Y-Yb(OTf)$_3$ catalyzed visible light mediated electrocyclization/indole ring opening towards the synthesis of heterobiaryl-pyrazolo[3,4-*b*]pyridines

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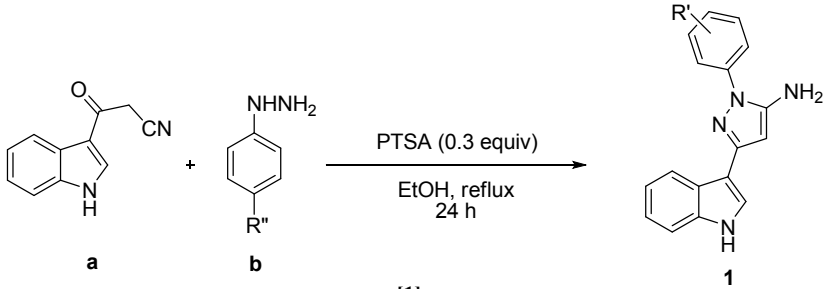
1. General Information:

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 using DMSO-d6 as solvent and tetramethylsilane as internal reference. Splitting patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). IR spectra were recorded on a FT-IR spectrophotometer and melting points were determined on melting point apparatus and are uncorrected. Electrospray ionization mass spectrometry (ESI-MS) was obtained on Thermo LCQ Advantage Max Spectrometer and HRMS was recorded on Agilent 6520 Q-TOF. Reactions were monitored on silica gel TLC plates (coated with TLC grade silica gel, obtained from Merck). All glass apparatus were oven dried prior to use. Column chromatography was performed over silica gel (230-400 Mesh) by using Smart flash EPCLC AI-700X YAMAZEN with minimal amount of solvent. All chemicals and reagents were obtained from Aldrich (USA) and Alfa Aesar (England) and were used without further purification.

2. Experimental Section:

2.1 General Procedure for the Synthesis of 1-Aryl-3-indolyl-5-amino pyrazoles (1):



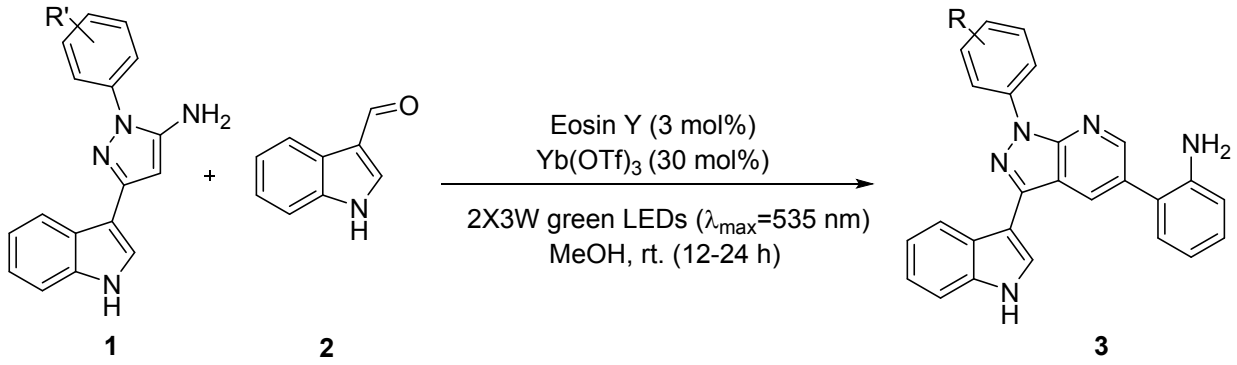
a **b** **1**

On the basis of available literature,[1] various substituted 1-Aryl-3-indolyl-5-amino pyrazoles were synthesized as follows:

To a solution of 3-(cyanoacetyl)indole **a** (1.0 equiv) in EtOH (20 mL) was added substituted phenylhydrazine hydrochloride (1.1 equiv) and PTSA (0.3 equiv). The reaction mixture was refluxed for 2-10 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was neutralized with a saturated $NaHCO_3$ solution, extracted with EtOAc (3 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Desired 1-aryl-3-indolyl-5- amino pyrazole solid products (**1a-1h**) were obtained after recrystallization in EtOH (20 mL).

[1] D. Anand, P. K. Yadav, O. P. S. Patel, N. Parmar, R. K. Maurya, P. Vishwakarma, K. S. R. Raju, I. Taneja, M. Wahajuddin, S. Kar, P. P . Yadav, *J. Med. Chem.* **2017**, *60*, 1041-1059.

2.2 General procedure for the synthesis of product (3):



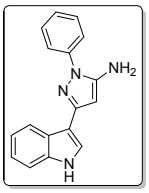
1 **2** **3**

To a solution of 1-Aryl-3-indolyl-5-aminopyrazole **1** (1.0 mmol) and 1*H*-indole-3-carbaldehyde (1.2 mmol) in MeOH (10 mL), Eosin Y (3 mol%) and $Yb(OTf)_3$ (30 mol%) was added. The mixture was irradiated with green light (LED, λ_{max} = 535 nm, 2X 3W) and stirred at room temperature in an open air atmosphere for 12-24 hours. After completion of the reaction (monitored by TLC), solvent was evaporated under reduced pressure and reaction crude was added saturated $NaHCO_3$ solution. The aqueous layer was extracted with ethyl acetate (3×20 mL). The organic layer was further dried over sodium sulphate (anhydrous) and removed under reduced pressure to give crude product, which was further purified by column chromatography over silica gel afforded the desired product **3**.

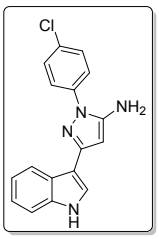
General reaction set-up

3. Analytical Data:

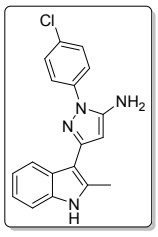
3.1 Characterization of Substrates (1):



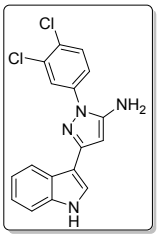
4-(1H-indol-3-yl)-1-phenyl-1H-pyrrol-2-amine (1a): brown solid, yield 69%, mp 230-233°C; FT-IR (KBr, ν_{max}/cm^{-1}) 3684, 3415, 1623, 1510, 1447, 758, 670; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 5.36 (s, 2H), 5.86 (s, 1H), 7.05-7.15 (m, 2H), 7.31 (t, J =7.4 Hz, 1H), 7.40 (d, J =7.9 Hz, 1H),7.52 (t, J =7.5 Hz, 2H), 7.68 (d, J =1.9 Hz, 1H), 7.72-7.75 (m, 2H), 8.18 (d, J =7.6 Hz, 1H), 11.19 (s,1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 88.1, 110.2, 111.0, 119.7, 121.7, 121.8, 122.7, 123.9, 125.5, 125.9, 129.5, 136.9, 140.2, 147.7,148.1;**ESI-HRMS** calcd for $C_{17}H_{14}N_4$ $[M+H]^+$: 275.1291; found: 275.1287.



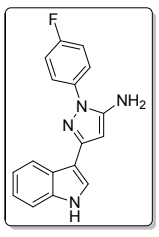
1-(4-chlorophenyl)-3-(1H-indol-3-yl)-1H-pyrazol-5-amine (1b): brown solid, yield 62%, mp 284-289 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3425, 1620, 1510, 1384,1069, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 5.45 (s, 2H), 5.86 (s, 1H), 7.05-7.14 (m, 2H), 7.39 (d, J =8.1 Hz, 1H),7.56 (d, J =8.6 Hz, 2H), 7.70 (d, J =2.2 Hz, 1H), 7.77(d, J =8.7 Hz, 2H), 8.17 (d, J =7.7 Hz, 1H),11.2 (s, 1H) ; **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C88.5, 109.9,111.9, 119.8, 121.7, 121.9, 124.1, 124.2, 125.5,129.5, 129.8, 136.9, 139.1, 148.0, 148.5; **ESI-HRMS** calcd for $C_{17}H_{13}ClN_4$ $[M+H]^+$: 309.0907; found: 309.0902.



1-(4-chlorophenyl)-3-(2-methyl-1H-indol-3-yl)-1H-pyrazol-5-amine (1c): Off white solid, yield 86%, mp 277-280 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3369, 3020, 1646, 1215, 759, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 2.60 (s, 3H), 5.45 (s, 2H), 5.84 (s, 1H), 7.00-7.08 (m, 2H), 7.29-7.32 (m, 1H), 7.55-7.58 (m, 2H), 7.77-7.80 (m, 2H), 7.97-7.99 (m, 1H), 11.10 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 13.8 , 89.9, 105.9, 109.9, 119.6, 120.3, 120.9, 124.1, 127.3, 129.5, 129.9, 134.1, 135.6, 139.1, 147.9, 148.3; **ESI-HRMS** calcd for $C_{18}H_{15}ClN_4$ $[M+H]^+$: 323.1058; found: 323.1056.

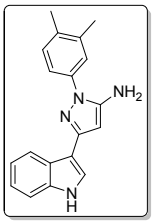


1-(3,4-dichlorophenyl)-4-(1H-indol-3-yl)-1H-pyrrol-2-amine (1d): brown solid, yield 57%, mp 265-270 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3685, 3338, 3021, 2407, 1424, 928, 768, 671; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 5.56 (s, 2H), 5.89 (s, 1H), 7.08-7.15 (m, 2H), 7.41 (d, J =7.9 Hz, 1H), 7.73-7.82 (m, 3H), 8.01 (d, J =2.4 Hz, 1H),8.16 (d, J =7.5 Hz, 1H),11.26 (s,1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 89.1, 109.6, 112.0, 119.9, 121.6, 121.9, 122.3, 123.4, 124.6, 125.97, 128.50 131.4, 131.8, 136.9, 140.1, 148.4, 149.1; **ESI-HRMS** calcd for $C_{17}H_{12}Cl_2N_4$ $[M+H]^+$: 343.0512; found: 343.0510.

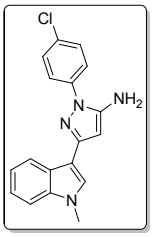


1-(4-fluorophenyl)-4-(1H-indol-3-yl)-1H-pyrrol-2-amine (1e): brown solid, yield 55%, mp 221-224 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3391, 3019, 2400, 1646, 1385, 757, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 5.35 (s, 2H), 5.84 (s, 1H), 7.03-7.13 (m, 2H), 7.32-7.40 (m, 3H),

7.68 (s, 1H), 7.72-7.76 (m, 2H), 8.18 (d, *J* =7.7 Hz, 1H) 11.19 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 88.1, 110.1, 111.9, 116.2 (d, *J* = 22 Hz, 2XCH), 119.7, 121.7 (d, *J* = 15 Hz, CH), 124.0, 124.8 (d, *J* = 8 Hz, 2XCH), 125.5, 136.6 , 136.9, 147.8, 148.1, 160.3 (d, *J* = 241 Hz, C-F); **ESI-HRMS** calcd for $C_{17}H_{14}FN_4$ $[M+H]^+$: 293.1197; found: 293.1193.



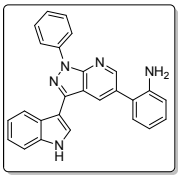
1-(3,4-dimethylphenyl)-3-(1H-indol-3-yl)-1H-pyrazol-5-amine (1f): brown solid, yield 66%, mp 268-271 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3688, 3418, 2416, 1474, 758, 670; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 2.28 (s, 3H), 2.31 (s, 3H), 5.27 (s, 2H), 5.82 (s, 1H), 7.04-7.13 (m, 2H), 7.26 (d, *J* =8.1 Hz, 1H), 7.39 (d, *J* =7.9 Hz, 2H), 7.47 (s, 1H), 7.66 (d, *J* =2.4 Hz, 2H), 8.15 (d, *J* =7.7 Hz, 1H), 11.18 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 19.5 , 20.0 , 87.6, 110.3, 111.9, 119.6, 120.5, 121.6, 121.8, 123.7, 124.1, 125.5, 130.4, 134.2, 136.9, 137.4, 137.9, 147.5, 147.6; ESI-HRMS calcd for $C_{19}H_{18}N_4$ $[M+H]^+$: 303.1604; found: 303.1603.



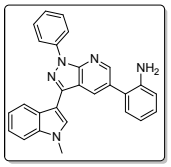
1-(4-chlorophenyl)-3-(1-methyl-1H-indol-3-yl)-1H-pyrazol-5-amine (1g): Off white solid, yield 86%, mp 219-222 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3684, 3368, 3020, 2400, 1340, 759, 670; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 3.82 (s,3H), 5.46 (s,2H), 5.84 (s,1H), 7.09-7.13 (m, 1H), 7.18-7.22 (m, 1H), 7.44 (d, *J*=8.2 Hz, 1H), 7.54-7.58 (m, 2H), 7.70 (s, 1H), 7.76-7.79 (m, 2H), 8.18-(d, *J*=7.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 32.9, 88.4,

109.1, 110.2, 119.9, 121.8, 121.9, 124.1, 125.8, 128.4, 129.5, 129.9, 137.4, 139.1, 148.1, 148.1; **ESI-HRMS** calcd for $C_{18}H_{15}ClN_4$ $[M+H]^+$: 323.1058; found: 323.1055.

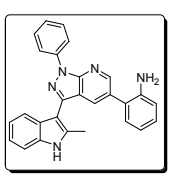
3.2 Compound Characterization Data of Product 3:



2-(3-(1H-indol-3-yl)-1-phenyl-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3a): Yellow solid, yield 66%, mp 256-259 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3400, 3080, 2927, 1503, 1216, 769, 669; **^{1}H NMR** (400 MHz, DMSO-d_6): δ_H 5.00 (s, 2H), 6.71 (t, *J* =14.7Hz, 1H) 6.83 (d, *J* =8.0 Hz, 1H), 7.11-7.18 (m, 2H), 7.21-7.26 (m, 2H), 7.34 (t, *J* =14.7 Hz, 1H), 7.50-7.53 (m, 1H), 7.64 (t, *J* =15.8 Hz, 2H), 8.43 (d, *J* =2.6 Hz, 1H) , 8.49-8.53 (m, 3H), 8.71 (dd, *J*1 =6.2 Hz, *J*2=1.8 Hz, 2H),11.66 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ_C107.8, 112.3, 115.8, 115.9, 117.2, 120.2 , 120.7, 121.9, 122.7, 123.1, 125.6, 126.6, 129.2, 129.7 , 130.3, 131.5 , 136.9 , 140.1, 142.2, 146.6, 149.9, 150.5; **ESI-HRMS** calcd for $C_{26}H_{20}N_5$ $[M+H]^+$: 402.1713; found: 402.1712.

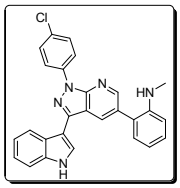


2-(3-(1-methyl-1H-indol-3-yl)-1-phenyl-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline(3b): Yellow solid, yield 68%, mp 218-223 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3385, 3017, 1596, 1412, 1115, 763, 670; **^{1}H NMR** (400 MHz, DMSO-d_6): δ_H 3.93 (s, 3H), 5.00 (s, 2H), 6.70-6.74 (m,1H), 6.84 (d, *J* =7.4 Hz, 1H), 7.13-7.17 (m, 2H), 7.27-7.37 (m, 3H), 7.57 (dd, *J*1 =6.8 Hz, *J*2=1.1 Hz, 1H),7.63 (t, *J* =7.6 Hz, 2H) , 8.49-8.55 (m, 4H), 8.71 (dd, *J*1 =12 Hz, *J*2=1.9 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C33.2 , 106.8, 110.6, 115.7, 115.8 , 117.1, 120.2, 120.9, 122.2, 122.8, 123.2, 125.6, 125.9,129.3, 130.4 , 130.5, 131.5 , 137.4, 140.0, 141.8, 146.6, 149.8, 150.5; **ESI-HRMS** calcd for $C_{27}H_{22}N_5$ $[M+H]^+$: 416.1870; found: 416.1874.

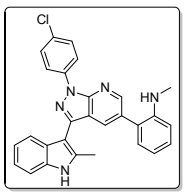


2-(3-(2-methyl-1H-indol-3-yl)-1-phenyl-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline(3c):

Yellow solid, yield 69%, mp 221-226 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3385, 3012, 2920, 1426, 756, 669; **^{1}H NMR** (400 MHz, DMSO-d_6): δ_H 2.66 (s, 3H), 4.98 (s, 2H), 6.66-6.69 (m,1H), 6.79 (dd, *J*1 =8.4 Hz, *J*2=1.0 Hz, 1H), 7.04-7.15 (m, 4H), 7.36 (t, *J* =7.4 Hz, 1H), 7.42 (d, *J* =7.9 Hz, 1H), 7.63 (t, *J* =7.5 Hz, 2H), 7.75 (d, *J* =7.8 Hz, 1H), 8.24 (d, *J* =2.0 Hz, 1H), 8.44 (d, *J* =8.6 Hz, 2H), 8.71 (d, *J* =2.0 Hz, 1H), 11.51 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 13.4, 104.2,111.5, 115.9, 116.8,117.3, 119.1, 120.1, 120.6 , 121.5 , 123.0, 125.9, 127.6, 129.2, 129.7 , 129.9, 131.2, 131.3, 135.9, 136.0, 139.9, 141.6, 146.5, 150.0, 150.6; **ESI-HRMS** calcd for $C_{27}H_{22}N_5$ $[M+H]^+$: 416.1870; found: 416.1874.

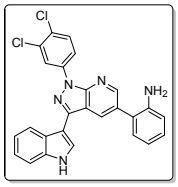


2-(1-(4-chlorophenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)-N-methylaniline (3d): Yellow solid, yield 67%, mp 213-216 °C; FT-IR (KBr, ν_{max}/cm^{1}) 3403, 3019, 1592, 1401, 1116, 765, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 2.66 (d, *J* =4.7 Hz, 3H), 5.12 (d, *J* =4.8 Hz, 1H), 6.66 (d, *J* =8.1 Hz, 1H), 6.73 (t, *J* =7.2 Hz, 1H), 7.15 (d, *J* =7.0 Hz, 1H), 7.23-7.29 (m, 3H), 7.50-7.52 (m, 1H), 7.69 (d, *J* =8.8 Hz, 2H), 8.45-8.51 (m, 2H), 8.58-8.69 (m, 4H), 11.68 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 30.7, 107.5, 110.2, 112.3, 116.2, 116.4, 120.7, 121.4 , 121.9, 122.7, 123.9, 125.6, 126.9, 129.4, 129.7, 130.2, 131.3, 132.2, 136.9, 138.9, 142.6, 147.7, 150.01, 150.8; **ESI-HRMS** calcd for $C_{27}H_{21}ClN_5$ $[M+H]^+$: 450.1480; found: 450.1498.

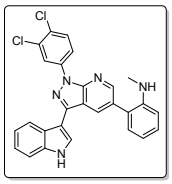


2-(1-(4-chlorophenyl)-3-(2-methyl-1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)-N-methylaniline (3e): Off white solid, yield 72%, mp 186-189 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3402, 3012, 1596, 1457, 1260, 1117, 758, 668; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 2.64 (s, 3H), 2.65 (s, 3H), 5.17 (s, 1H), 6.64 (d, *J*=8.2 Hz, 1H), 6.69 (t, *J*=7.3 Hz, 1H),7.03-7.14 (m,

3H), 7.24 (t, *J*=7.24 Hz, 1H), 7.41 (d, *J*=7.9 Hz, 1H), 7.68 (d, *J*=8.9 Hz, 2H), 7.75 (d, *J*=7.8 Hz, 1H), 8.20 (d, *J*=1.9 Hz, 1H), 8.51 (d, *J*=8.9 Hz, 2H), 8.66 (d, *J*=1.9 Hz, 1H), 11.5 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 13.4 30.7, 103.9, 110.3, 111.5, 116.6 , 117.2 119.2, 120.2, 121.6, 121.8, 123.8, 127.5, 129.7 129.9, 130.9, 132.0 , 136.0, 136.1 138.8 142.1, 147.7, 150.2, 150.9; **ESI-HRMS** calcd for $C_{28}H_{23}ClN_5$ $[M+H]^+$: 464.1636; found: 464.1631.

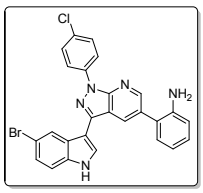


2-(1-(3,4-dichlorophenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3f) : Yellow solid, yield 71%, mp 265-269 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3432, 2933, 1636, 1214, 1119, 757, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 5.02 (s, 2H), 6.71 (t, *J* =6 Hz, 1H), 6.82 (d, *J*=7.9 Hz, 1H), 7.12-7.18 (m, 2H), 7.25-7.27(m, 2H), 7.51-7.53 (m, 1H), 7.88 (d, *J*=8.8 Hz, 1H), 8.45-8.54 (m, 3H), 8.73 (s, 2H), 8.89 (d, *J*=2.4 Hz, 1H), 11.7 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 107.4,112.4, 115.8, 116.5,117.2, 119.5, 120.5, 120.9, 121.9, 122.9, 125.5, 127.0, 127.3, 129.3, 130.9, 131.5, 131.8, 131.9, 132.0, 136.9, 139.8, 143.2, 146.6, 150.0, 150.8 ; **ESI-HRMS** calcd for $C_{26}H_{18}C_{l2}N_5$ $[M+H]^+$: 470.0934; found: 470.0937.

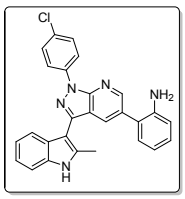


2-(1-(3,4-dichlorophenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)-N-methylaniline(3g): Yellow solid, yield 74%, mp 273-276 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3432, 2933, 1626, 1210, 1109, 758, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H2.64 (d, *J* =4.8 Hz, 3H), 5.11 (d, *J* =4.9 Hz, 1H)6.65 (d, *J* =8.2 Hz, 1H), 6.72 (t, *J* =7.3 Hz, 1H), 7.13 (d, *J* =8.2 Hz, 1H), 7.22-7.28 (m,3H), 7.48-7.52 (m, 1H), 7.87 (d, *J* =8.9 Hz, 1H),8.44-8.46 (m, 1H), 8.52 (dd, *J*1 =8.9 Hz, *J*2=2.4 Hz, 1H) ,8.67 (dd, *J*1 =16.3 Hz, *J*2=1.6 Hz, 2H), 8.88 (d, *J* =2.5 Hz, 2H), 11.69 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 30.7 , 107.3, 110.2, 112.4, 116.4, 116.5, 119.5, 120.5, 120.9, 121.8, 122.8, 123.8, 125.5, 127.0, 127.3, 129.8,

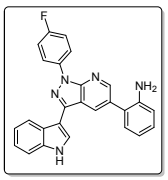
130.6, 131.3, 131.8, 132.1, 132.5, 136.9, 139.7, 147.7, 150.2, 151.1; **ESI-HRMS** calcd for $C_{27}H_{20}C_{l2}N_5$ $[M+H]^+$: 484.1090; found: 484.1094.



2-(3-(5-bromo-1H-indol-3-yl)-1-(4-chlorophenyl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3h): Yellow solid, yield 73%, mp 278-282 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3400, 3029, 1631, 1520, 1395, 773, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 5.22 (s, 2H), 6.77 (d, *J* =8.8 Hz, 1H),7.23-7.31 (m, 4H), 7.51-7.53 (m, 1H), 7.69 (d,*J* = 9.2 Hz, 2H), 8.49 (d, *J* =2.3 Hz, 2H), 8.58 (d, *J* =8.8 Hz, 2H), 8.69 (d, *J* =1.7 Hz, 1H), 8.75 (d, *J* =1.6 Hz, 1H), 11.70 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 107.5,112.3, 116.1,117.5, 120.8, 121.4, 121.9, 122.8, 125.1, 125.5, 127.1, 129.2, 129.4, 129.7, 131.7, 132.0, 133.4, 136.9, 138.8, 142.7, 146.2, 149.9, 150.4; **ESI-HRMS** calcd for $C_{26}H_{18}BrClN_5$ $[M+H]^+$: 514.0429; found: 514.0435.

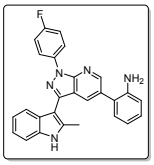


2-(1-(4-chlorophenyl)-3-(2-methyl-1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3i): Yellow solid, yield 68%, mp 236-241 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3395, 3014, 2923, 1498, 1214, 753, 667; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H2.66 (s, 3H), 4.99 (s, 2H), 6.67 (t, *J* =14.7 Hz, 1H), 6.79 (d, *J* =8.1 Hz, 1H), 7.04-7.15 (m, 4H), 7.42 (d, *J* =7.9 Hz, 1H), 7.68 (d, *J* =8.9 Hz, 2H), 7.74 (d, *J* =7.8 Hz, 1H), 8.25 (d, *J* =2 Hz, 1H), 8.52 (d, *J* =8.9 Hz, 2H), 8.72 (d, *J* =2.0 Hz, 1H), 11.53 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 13.4 , 104.2, 111.5, 115.9, 117.1, 117.4, 119.1, 120.2, 121.6, 121.8, 122.9, 127.5, 129.3, 129.7, 129.8, 130.2, 131.2, 131.5, 136.0, 136.1, 138.8, 142.1, 146.5, 150.0, 150.7; **HR-MS (ESI)** calcd for $C_{27}H_{21}ClN_5$ $[M+H]^+$: 450.1480; found: 450.1491.

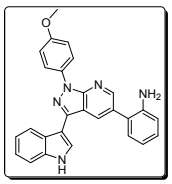


2-(1-(4-fluorophenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline(3j):

Yellow solid, yield 69%, mp 265-269 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3684, 3352, 3019, 2400, 1415, 1385, 757, 626; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H5.00 (s, 2H), 6.72 (t, *J* =7.3 Hz, 1H), 6.83 (d, *J* =8.0 Hz, 1H), 7.12-7.18 (m, 2H), 7.21-7.27 (m,2H), 7.47-7.53 (m, 3H), 8.44 (d, *J* =8.0 Hz, 1H), 8.48-8.54 (m, 3H), 8.71 (dd, *J*1 =10 Hz, *J*2 =1.5 Hz, 2H), 11.66 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 107.7, 112.3, 115.7, 115.8, 116.4, 116.6, 117.2, 120.7, 121.9, 122.1, 122.7, 123.1, 125.6, 126.6, 129.2, 130.3, 131.5, 131.6, 136.5, 136.9, 142.2, 146.6, 149.7, 150.6, 159.8 (d, *J* =241 Hz, C-F); **ESI-HRMS** calcd for $C_{26}H_{19}FN_5$ $[M+H]^+$: 420.1619; found: 420.1620.



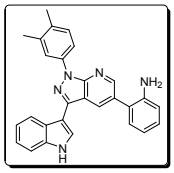
2-(1-(4-fluorophenyl)-3-(2-methyl-1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3k): brown solid, yield 72%, mp 232-237 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3684, 3352, 3019, 2400, 1415, 1385, 757, 626; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H2.66 (s, 3H), 5.00 (s, 2H), 6.67 (t, *J* =7.4 Hz, 1H), 6.79 (d, *J* =8.1 Hz, 1H), 7.04-7.15 (m, 4H), 7.42 (d, *J* =7.9 Hz, 1H), 7.46-7.50 (m,2H), 7.74 (d, *J* =7.7 Hz, 1H), 8.24 (d, *J* = 2 Hz, 1H), 8.42-8.46 (m, 2H), 8.71 (d, *J*= 2 Hz, 1H), 11.53 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 13.5 , 104.2, 111.6, 116.0, 116.4, 116.7, 116.9, 117.4, 119.2, 120.2, 121.7, 122.6, 123.1, 127.6, 129.3, 130.1, 131.2, 131.5, 136.1 ,136.5, 141.8, 146.6, 149.9, 150.8, 160.2 (d, *J* =321 Hz, C-F); **ESI-HRMS** calcd for $C_{27}H_{21}FN_5$ $[M+H]^+$: 434.1776; found: 434.1805.



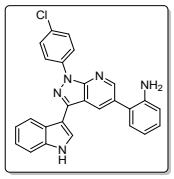
2-(3-(1H-indol-3-yl)-1-(4-methoxyphenyl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline(3l):

Yellow solid, yield 73%, mp 286-290 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3694, 3342, 3019, 2410, 1425, 1395, 757, 626; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H3.86 (s, 3H), 4.98 (s, 2H), 6.69-6.74 (m, 1H), 6.82-6.84 (m, 1H), 7.11-7.26 (m, 6H), 7.52 (dd, *J*1 =6.1 Hz, *J*2=1.7 Hz, 1H), 8.32-8.34 (m, 2H), 8.38 (d, *J* =2.7 Hz, 1H), 8.46-8.48 (m, 1H), 8.67 (dd, *J*1 =5.3 Hz, *J*2

=2.0 Hz, 2H), 11.62 (d, *J* =2.0 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 55.8, 107.9, 112.3, 114.8, 115.3, 115.8, 117.2, 120.6, 121.9, 122.1, 122.7, 123.3, 125.6, 126.2, 129.2, 129.9, 131.3, 131.5, 133.4, 136.9, 141.5, 146.5, 149.5, 150.4, 157.3; **ESI-HRMS** calcd for $C_{27}H_{22}N_5O$ $[M+H]^+$: 432.1819; found: 432.1814.

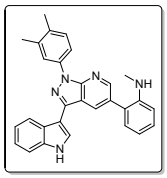


2-(1-(3,4-dimethylphenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline(3m): Yellow solid, yield 71%, mp 236-239 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3397, 3352, 2925, 1611, 1414, 1267, 754, 616; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H2.33 (s, 3H), 2.41 (s, 3H), 5.00 (s, 2H), 6.72 (t, *J* =7.3 Hz, 1H), 6.83 (d, *J* =7.9 Hz, 1H), 7.11-7.18 (m, 2H), 7.21-7.26 (m, 2H), 7.38 (d, *J* =8.2 Hz, 1H), 7.49-7.52 (m, 1H), 8.18 (d, *J* =8.2 Hz, 1H), 8.26 (s, 1H), 8.39 (d, *J* =2.4 Hz, 1H), 8.47-8.49 (m, 1H), 8.68 (d, *J* =1.9 Hz, 2H), 11.63 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 19.5 , 20.5 , 108.0, 112.4, 115.7, 115.9, 117.3, 118.1, 120.7, 121.5, 122.0, 122.7, 123.3, 125.7,126.5, 129.3, 130.1, 130.6, 131.4, 131.6, 133.8, 137.0, 137.6, 138.1, 141.8, 146.7, 149.8, 150.5; **ESI-HRMS** calcd for $C_{28}H_{24}N_5$ $[M+H]^+$: 430.2026; found: 430.2018.



2-(1-(4-chlorophenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline(3n): Yellow solid, yield 67%, mp 244-247 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3397, 3352, 2925, 1611, 1414, 1267, 754, 616; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H5.02 (s, 2H),6.70- 6.72 (m, 1H), 6.84 (d, *J* =7.6 Hz, 1H), 7.12-7.19 (m, 2H), 7.23-7.28 (m, 2H), 7.52-7.54 (m, 1H), 7.69-7.72 (m, 2H), 8.46 (d, *J* =2.7 Hz, 1H), 8.49-8.52 (m, 1H), 8.59-8.61 (m, 2H), 8.73 (dd, *J*1=8.4 Hz, *J*2=1.9 Hz 2H), 11.69 (d, *J* =1.4 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 107.6, 112.3, 115.8, 116.1, 117.2, 120.8, 121.4, 121.9, 122.8, 123.0, 125.6, 126.8, 129.3, 129.4,

129.7, 130.5, 131.5, 131.7, 136.9, 138.9, 142.6, 146.6, 149.9, 150.6; **ESI-HRMS** calcd for $C_{26}H_{19}ClN_5$ $[M+H]^+$: 436.1323; found: 436.1328



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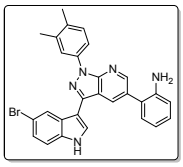
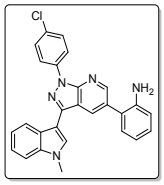
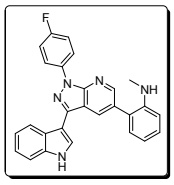
2-(1-(3,4-dimethylphenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)-N-methylaniline (3o): Yellow solid, yield 72%, mp 221-236 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3400, 3019, 1621, 1510, 1385, 771, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 2.29 (s, 3H), 2.37 (s, 3H), 2.64 (d, *J* =4.8 Hz, 3H), 5.09 (d, *J* =5.0 Hz, 1H), 6.64 (d, *J* =8.2 Hz, 1H), 6.71 (t, *J* =7.3 Hz, 1H), 7.12 (d, *J* =7.3 Hz, 1H), 7.18-7.26 (m,3H), 7.35 (d, *J* =8.3 Hz, 1H),7.47-7.49 (m, 1H), 8.15 (d, *J* =8.2 Hz, 1H) , 8.23 (s, 1H), 8.36 (d, *J* =2.6 Hz, 1H), 8.44-8.46 (m, 1H), 8.59 (dd, *J*1 =11.4 Hz, *J*2=1.8 Hz, 2H), 11.59 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 19.4, 20.4 , 30.7 , 107.8, 110.1, 112.3, 115.7, 116.4, 117.9, 120.6, 121.4, 121.9, 122.6, 124.1, 125.6, 126.4, 129.6, 129.7, 130.5, 131.3, 131.8, 133.7, 136.8, 137.5, 137.9, 141.7, 147.7, 149.8, 150.7; **ESI-HRMS** calcd for $C_{29}H_{26}N_5$ $[M+H]^+$: 444.2183; found: 444.2186.



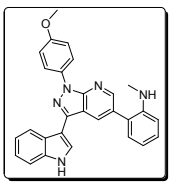
2-(3-(5-bromo-1H-indol-3-yl)-1-(3,4-dimethylphenyl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3p) : Yellow solid, yield 68%, mp 264-269 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3400, 3012, 1619, 1502, 1379, 771, 669; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 2.31 (s, 3H), 2.39 (s, 3H), 5.20 (s, 2H), 6.77 (d, *J* =8.6 Hz, 1H), 7.20-7.27 (m, 3H), 7.31 (d, *J* =2.4 Hz, 1H), 7.37 (d, *J* =6.9 Hz, 1H), 7.49-7.52 (m, 1H), 8.16 (dd, *J*1 =8.2 Hz, *J*2=2.1 Hz, 1H), 8.25 (d, *J* =1.8 Hz, 1H), 8.43 (d, *J* =2.7 Hz, 1H), 8.47-8.49 (m, 1H), 8.68 (dd, *J*1 =10.9 Hz, *J*2=2.0 Hz, 2H), 11.6 (d, *J* =1.8 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 19.5 , 20.4 , 107.5, 107.8, 112.3, 115.6, 117.5, 118.0, 120.7, 121.4, 121.9, 122.6, 125.3, 125.6, 126.5, 128.6, 130.5, 131.5, 131.6, 133.3, 133.8, 136.9, 137.5, 137.9, 141.8, 146.2, 149.8, 150.2; **ESI-HRMS** calcd for $C_{28}H_{23}BrN_5$ $[M+H]^+$: 508.1131; found: 508.1132.



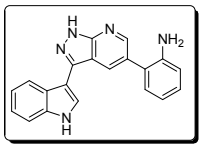
2-(1-(4-chlorophenyl)-3-(1-methyl-1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3q) : Yellow solid, yield 67%, mp 229-231 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3406, 3336, 3019, 1587, 1489, 1397, 756, 668; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 3.93 (s, 3H), 5.00 (s, 2H), 6.73 (t, *J* =14.4 Hz, 1H), 6.84(d, *J* =7.8 Hz, 1H), 7.13-7.17 (m, 2H), 7.27-7.34 (m, 2H), 7.58 (d, *J* =7.4 Hz, 1H), 7.70 (d, *J* =8.5 Hz, 2H), 8.53 (s, 2H), 8.59 (d, *J* =8.5 Hz, 2H), 8.73 (d, *J* =14.4 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 33.2 , 106.6, 110.6, 115.7, 116.0, 117.1, 121.0, 121.4, 122.2, 122.8, 123.1, 125.8, 129.3, 129.7, 130.6, 130.8, 131.5, 131.7, 137.4, 138.9, 142.2, 146.6, 149.9, 150.6; **ESI-HRMS** calcd for $C_{27}H_{21}ClN_5$ $[M+H]^+$: 450.1480; found: 450.1491.



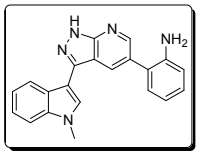
2-(1-(4-fluorophenyl)-3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)-N-methylaniline (3r): Yellow solid, yield 69%, mp 265-269 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3684, 3352, 3019, 2400, 1415, 1385, 757, 626; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H2.64 (s, 3H), 5.01 (s, 1H), 6.66 (d, *J* =8.2 Hz, 1H), 6.73 (t, *J* =14.6 Hz, 1H), 7.11 (d, *J* =7.3 Hz, 1H),7.19-7.27 (m, 3H), 7.44(t, *J* =8.7 Hz, 2H), 7.52 (d, *J* =7.3 Hz, 1H), 8.33 (d, *J* =2.4 Hz, 1H), 8.41-8.45 (m, 3H), 8.58 (d, *J* =4.9 Hz, 2H), 11.58 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 30.7 , 107.7, 110.3, 112.3, 115.7, 116.3, 116.5, 116.7, 120.8, 121.8, 122.2, 122.4, 122.8, 123.9, 125.5, 126.4, 129.8, 129.9, 131.2, 131.8, 136.3, 136.8, 142.1, 147.6, 149.7,150.8, 159.9 (d, *J* =241 Hz, C-F); **ESI-HRMS** calcd for $C_{27}H_{21}FN_5$ $[M+H]^+$: 434.1776; found: 434.1775.



2-(3-(1H-indol-3-yl)-1-(4-methoxyphenyl)-1H-pyrazolo[3,4-b]pyridin-5-yl)-N-methylaniline (3s): Yellow solid, yield 68%, mp 287-292 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3682, 3342, 3008, 2430, 1425, 1395, 757, 626; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ_H2.67 (s, 3H), 3.86 (s, 3H), 5.12(d, *J* =4.9 Hz, 1H), 6.67 (d, *J* =8.2 Hz, 1H), 6.74 (t, *J* =7.4 Hz, 1H), 7.15 (d, *J* =7.2 Hz, 1H), 7.20-7.29 (m, 5H), 7.51 (d, *J* =6.9 Hz, 1H), 8.34 (d, *J* =9.1 Hz, 2H), 8.40 (d, *J* =2.6 Hz, 1H), 8.47-8.49 (m, 1H), 8.59-8.60 (m, 1H), 8.65 (d, *J* =1.9 Hz, 1H), 11.62 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ_C 30.7 , 55.9 , 107.9, 110.1, 112.2, 114.9, 115.4, 116.4, 120.6, 121.9, 122.1, 124.2, 125.6, 126.3, 129.6, 131.3, 131.8, 133.4, 136.9, 141.6, 147.8, 149.6, 150.7, 157.4; **ESI-HRMS** calcd for $C_{28}H_{24}N_5O$ $[M+H]^+$: 446.1975; found: 446.1977.

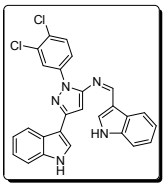


2-(3-(1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3t): Yellow solid, yield 39%, mp 243-249 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3684, 3352, 3019, 2400, 1415, 1385, 757, 626; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ_H4.91 (s, 2H), 7.09 (t, *J* =7.9 Hz, 1H), 7.12 (d, *J* = 4.0 Hz, 1H), 7.13-7.21 (m, 4H), 7.47 (d, *J* = 7.9 Hz, 1H), 8.21 (d, *J* = 2.5 Hz, 1H), 8.35 (d, *J* =7.7 Hz, 1H), 8.52 (d, *J* =1.8 Hz, 2H), 11.45 (s, 1H), 13.47 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ_C 108.9, 112.1, 112.9, 115.8, 117.3, 120.2, 121.8, 122.4, 123.8, 125.1, 125.7,128.6, 128.9, 130.4, 131.5, 136.8, 141.1, 146.4, 149.9, 152.1; **ESI-HRMS** calcd for $C_{20}H_{16}N_5$ $[M+H]^+$: 326.1400; found: 326.1403.



2-(3-(1-methyl-1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-5-yl)aniline (3u): Yellow solid, yield 42%, mp 265-269 °C; FT-IR (KBr, ν_{max}/cm^{-1}) 3688, 3359, 3021, 2420, 1415, 1395, 757, 626; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ_H 3.88 (s, 3H), 4.90 (s, 2H), 6.67-6.72 (m, 1H), 6.82 (dd, *J*1 =8.4 Hz, *J*2= 1.0 Hz, 1H), 7.10-7.13 (m, 2H), 7.16-7.20 (m, 1H), 7.24-7.28 (m, 1H), 7.51 (d, *J* = 2.5 Hz, 1H), 8.29 (s, 1H), 8.38 (d, *J* =7.8 Hz, 1H), 8.54 (dd, *J*1 = 9.0 Hz, *J*2= 1.6 Hz, 2H), 13.48 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ_C 33.0 , 108.1,

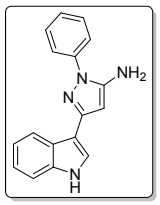
110.3, 112.8, 115.6, 117.1, 120.4, 122.1, 122.5, 123.9, 126.1, 128.7, 128.9, 129.2, 130.4, 131.5, 137.3, 140.8, 146.5, 149.9, 152.1; **ESI-HRMS** calcd for $C_{21}H_{18}N_5$ $[M+H]^+$: 340.1557; found: 340.1587.

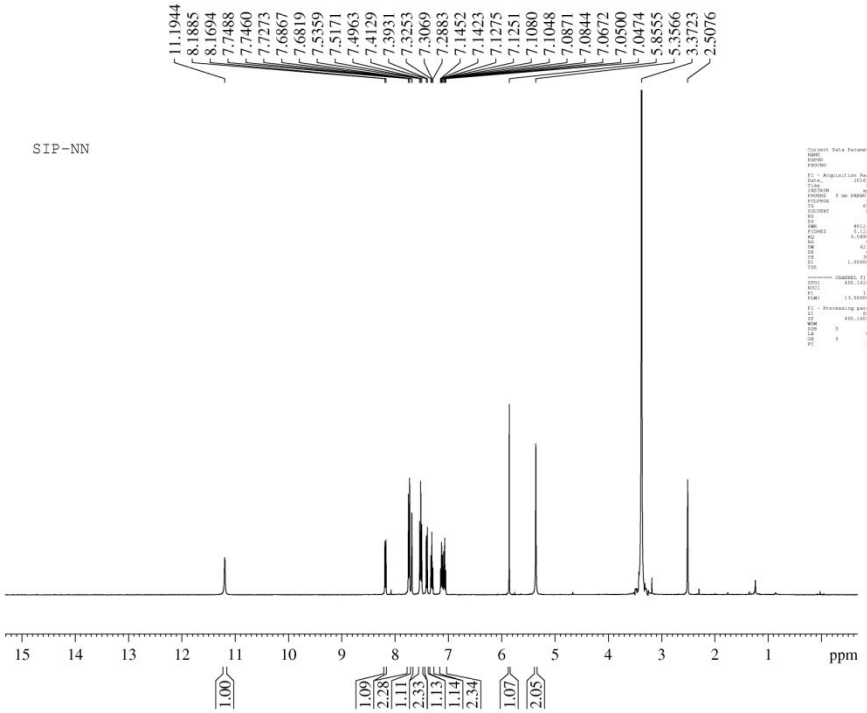


N-((1H-indol-3-yl)methylene)-1-(3,4-dichlorophenyl)-3-(1H-indol-3-yl)-1H-pyrazol-5-amine (4) : Yellow solid, mp 244-251 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ_H 6.93 (s, 1H), 7.15-7.20 (m, 2H), 7.24-7.31 (m, 2H), 7.46 (d, J = 5.8 Hz, 1H), 7.55 (d, J = 6.3 Hz, 1H), 7.84 (d, J = 7.0 Hz, 1H), 7.89 (d, J = 2.0 Hz, 1H), 8.09 (dd, $J1$ =7.0 Hz, $J2$= 1.9 Hz, 1H), 8.18 (s, 1H), 8.29 (d, J = 5.8 Hz, 1H), 8.35 (d, J = 5.9 Hz, 1H), 8.57 (d, J = 1.9 Hz, 1H), 9.07 (s, 1H), 11.38 (s, 1H), 12.05 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C 90.9, 109.4, 112.2, 112.9, 115.33, 120.2, 121.5, 121.9, 122.2, 122.2, 122.6, 123.9, 124.1, 124.8, 124.9, 125.3, 127.9, 131.3, 131.5, 136.6, 137.1, 137.97, 140.1, 149.2, 153.5, 158.1;**ESI-HRMS** calcd for $C_{26}H_{18}C_{l2}N_5$ $[M+H]^+$: 470.0934; found: 470.0990.

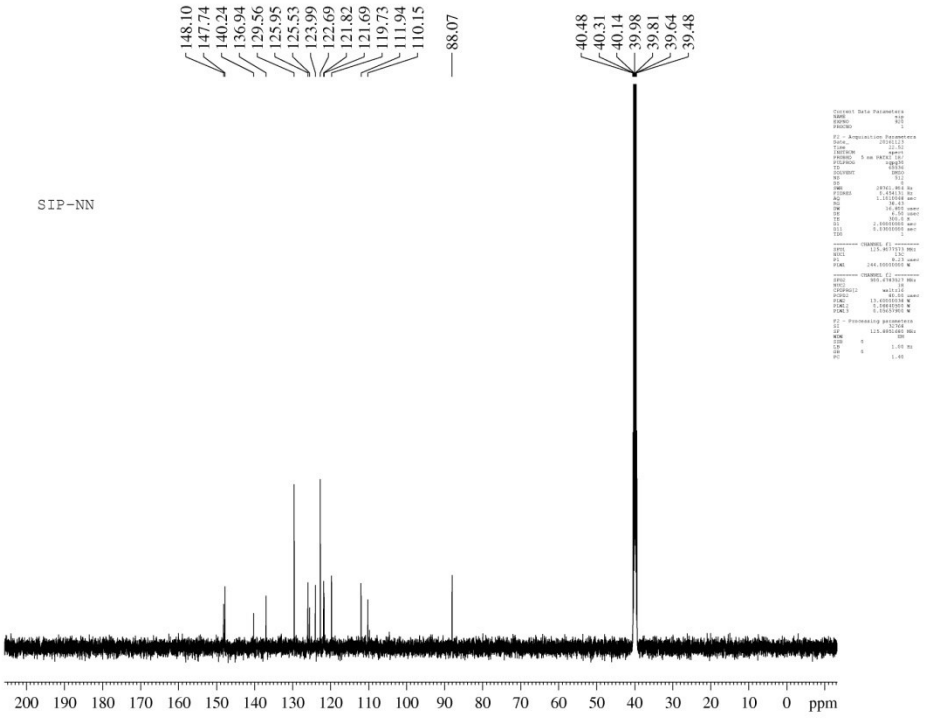
3. NMR and HRMS Spectra

4.1 NMR Spectra of Substrates (1a-1g)

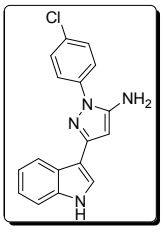


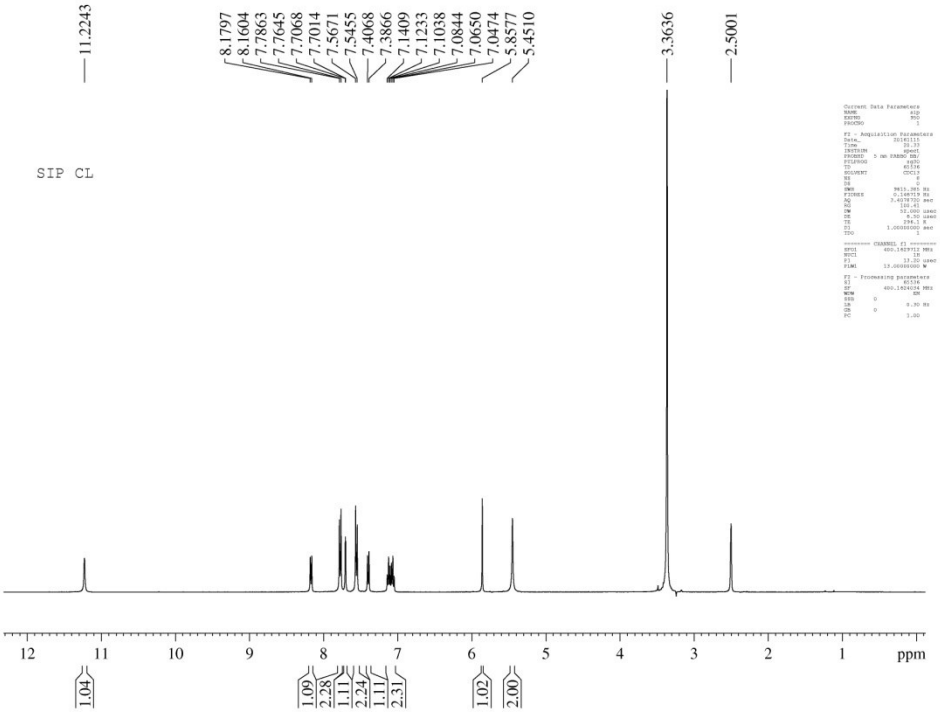


^{1}H NMR Spectra of (**1a)** (400 MHz, DMSO-d6)

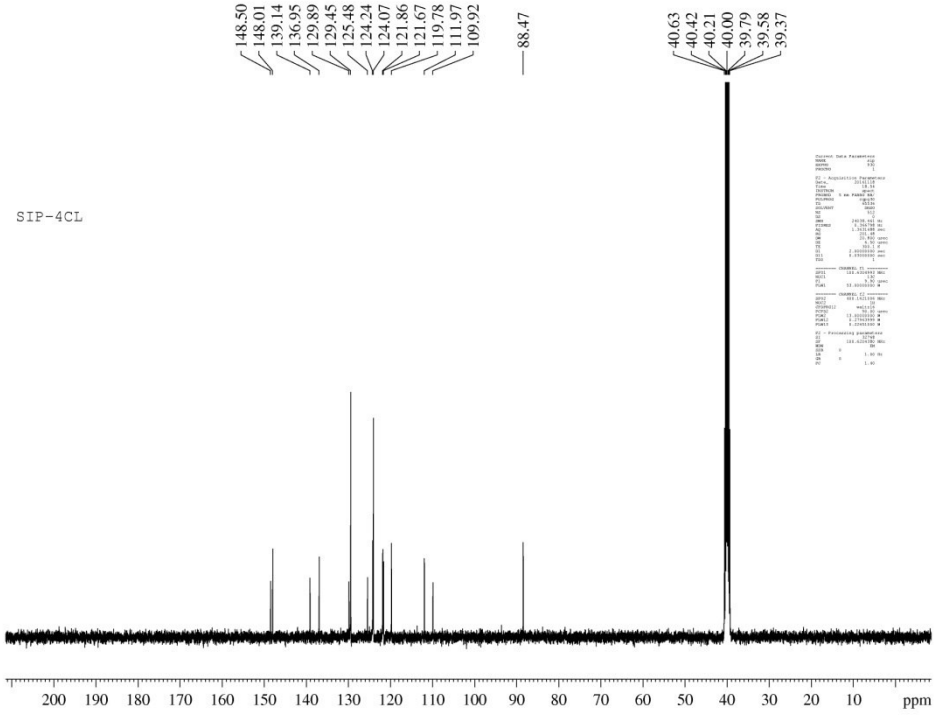


^{13}C NMR Spectra of (**2a)** (100 MHz, DMSO-d6)

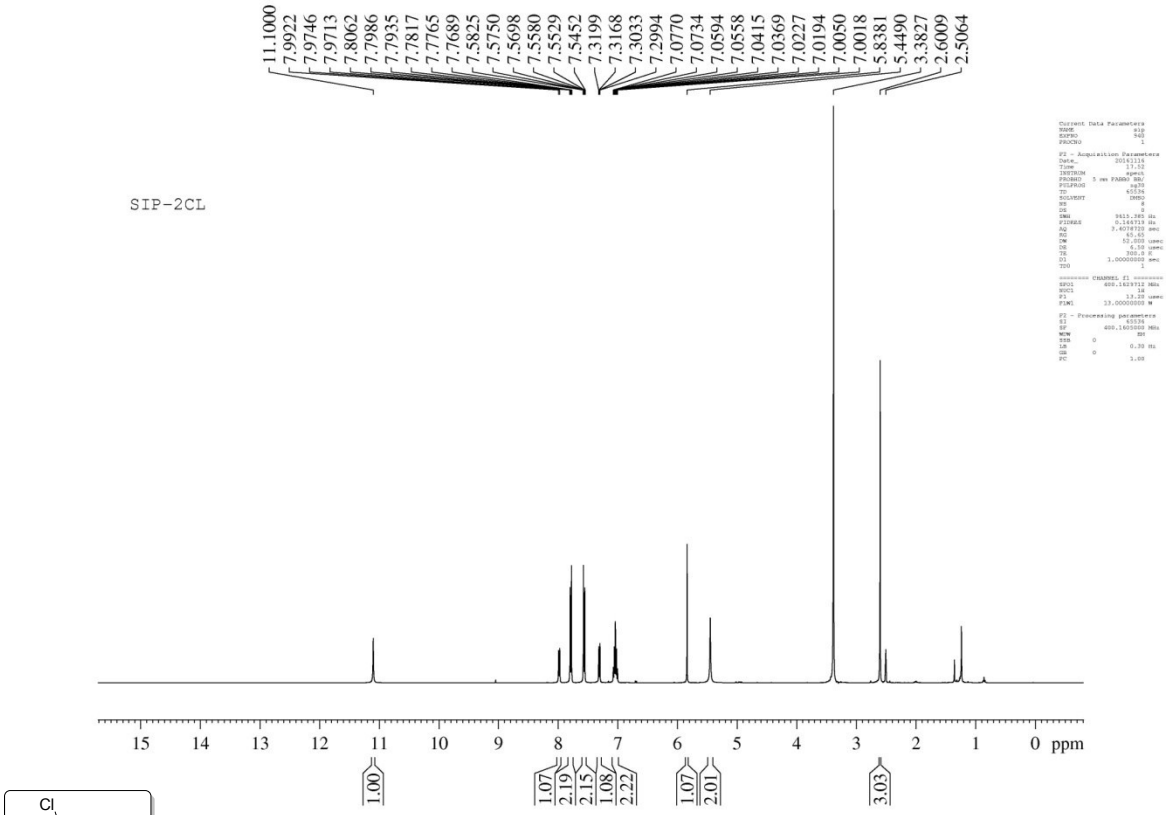


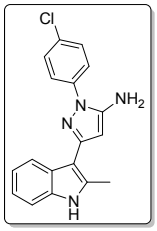


^{1}H NMR Spectra of (**1b)** (400 MHz, DMSO-d_6)

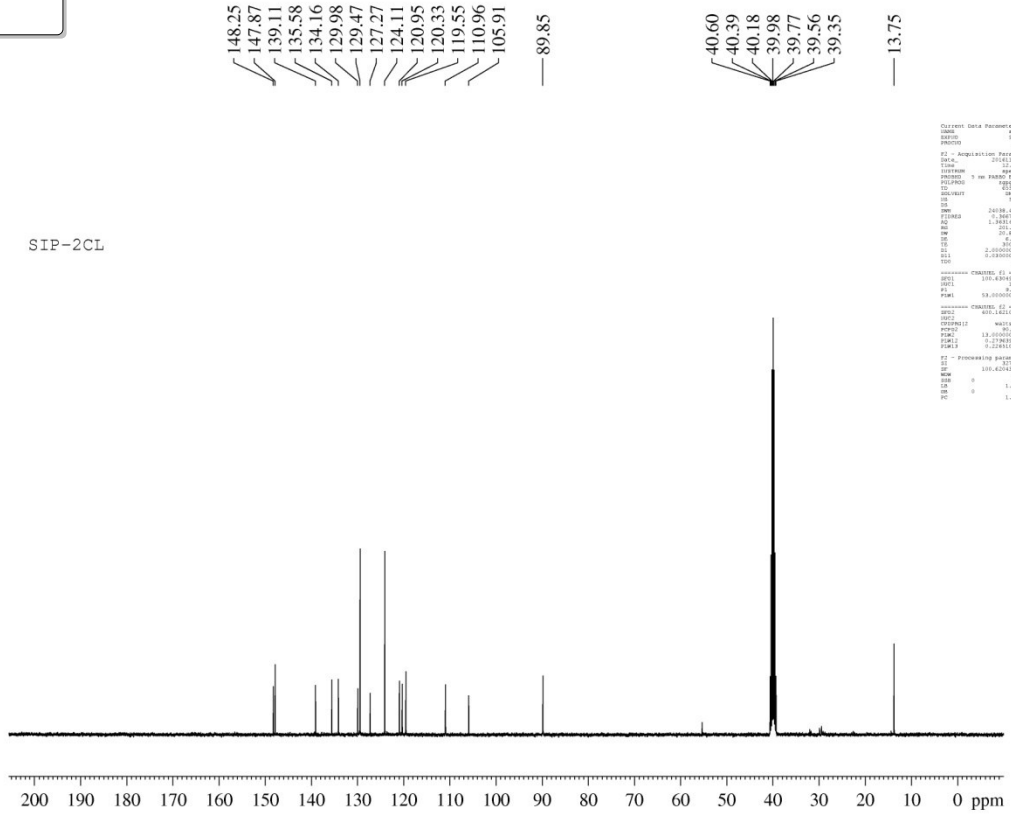


^{13}C NMR Spectra of (**1b)** (100 MHz, DMSO-d6)

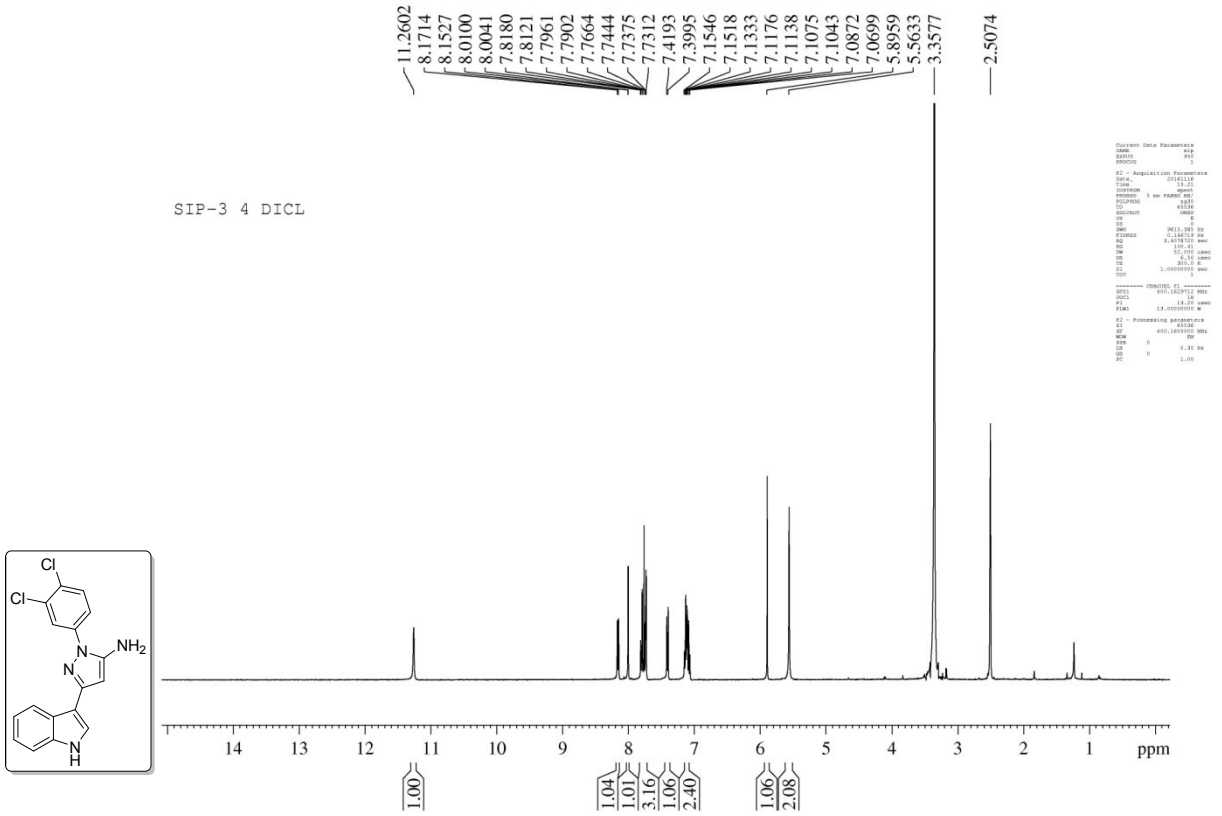




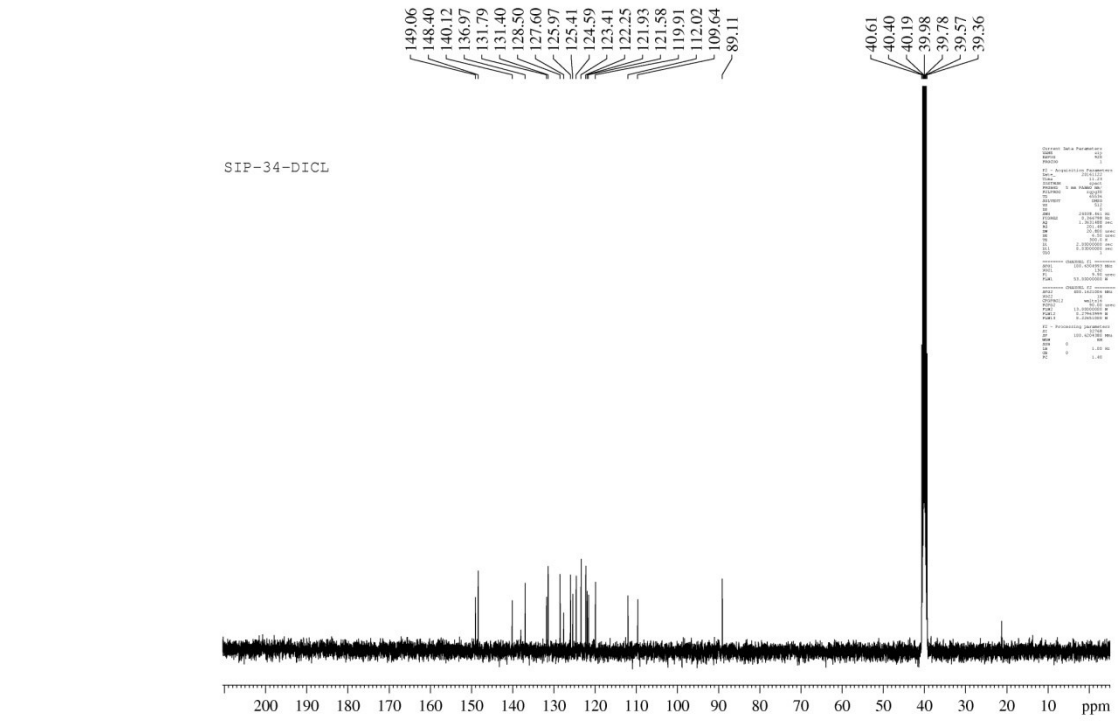
^{1}H NMR Spectra of (**1c)** (400 MHz, DMSO-d_6)



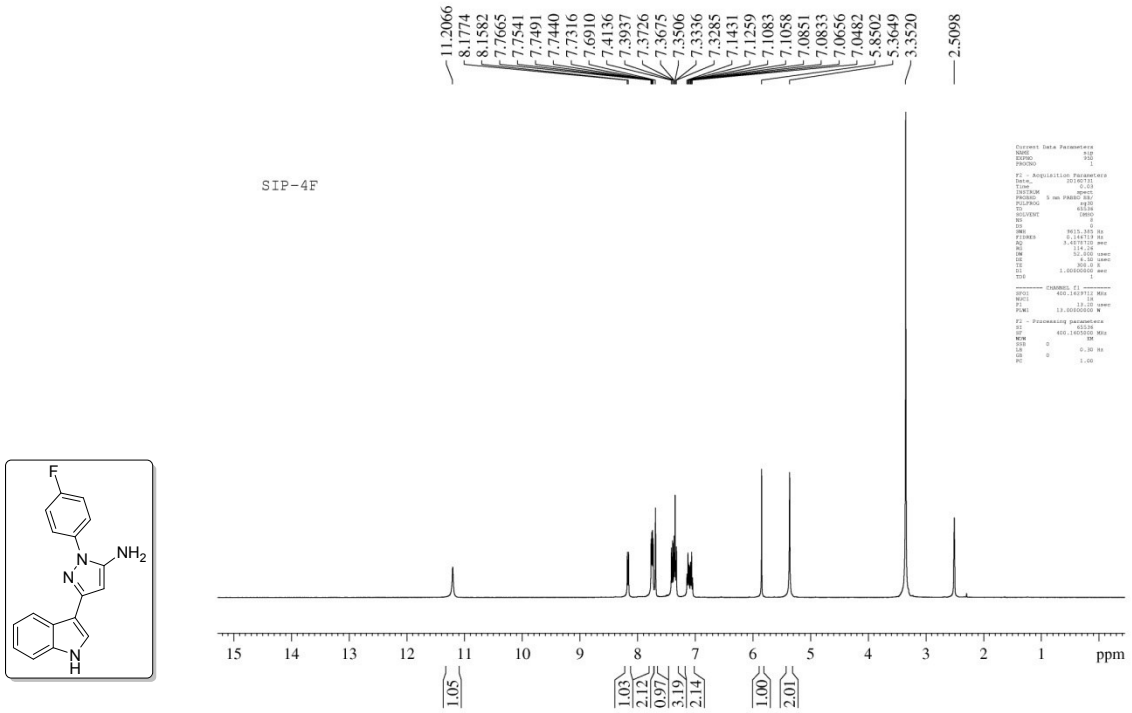
^{13}C NMR Spectra of (**1c)** (100 MHz, DMSO-d6)



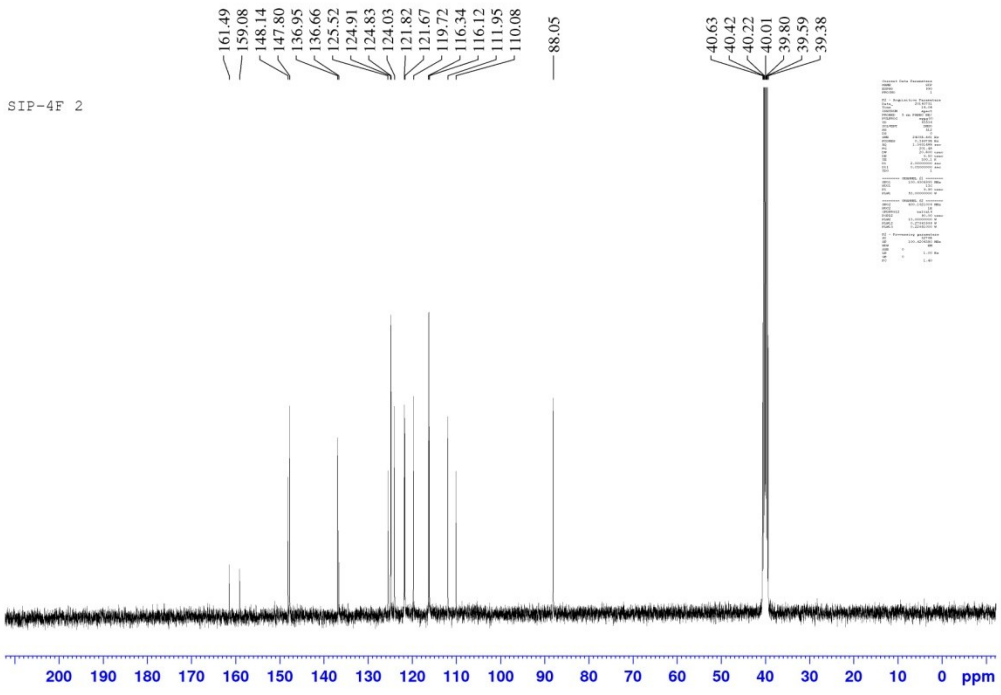
^{1}H NMR Spectra of (**1d)** (400 MHz, DMSO-d_6)



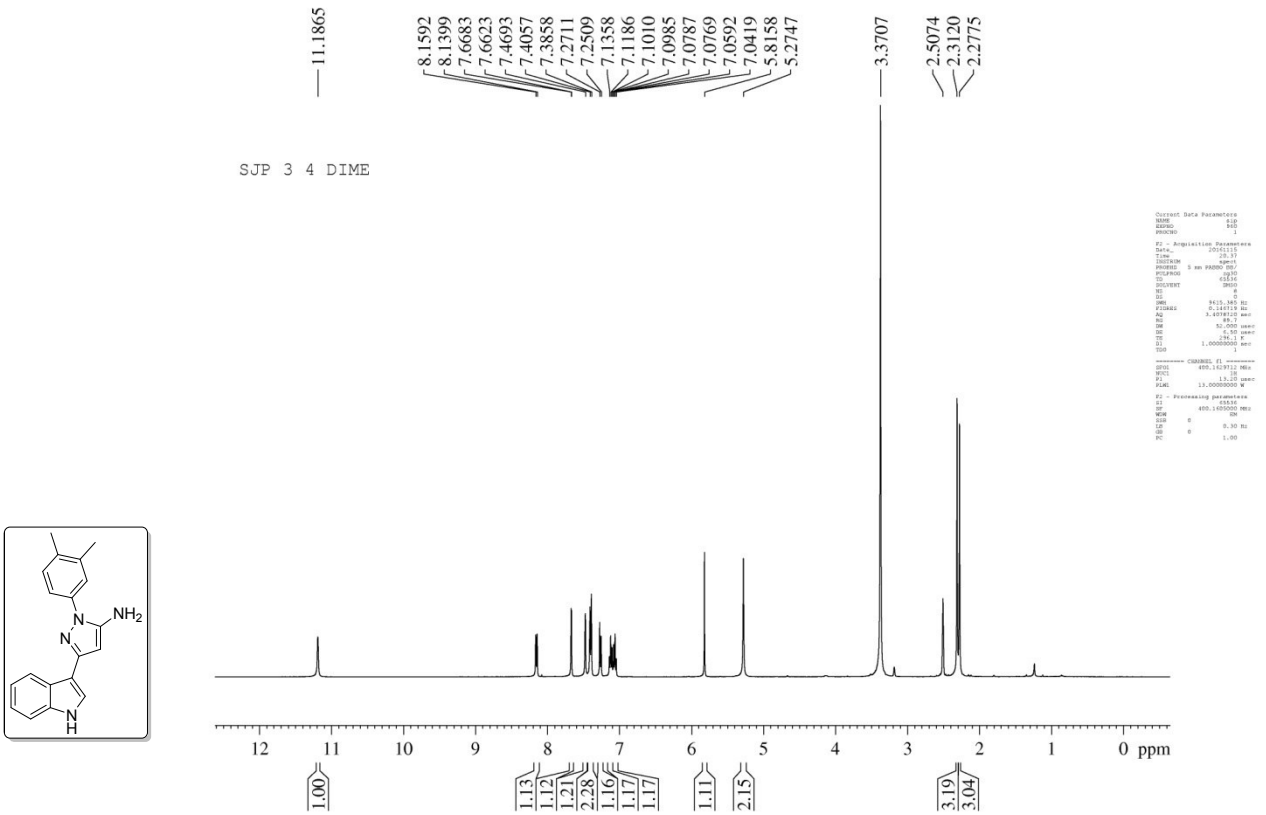
^{13}C NMR Spectra of (**1d)** (100 MHz, DMSO-d6)



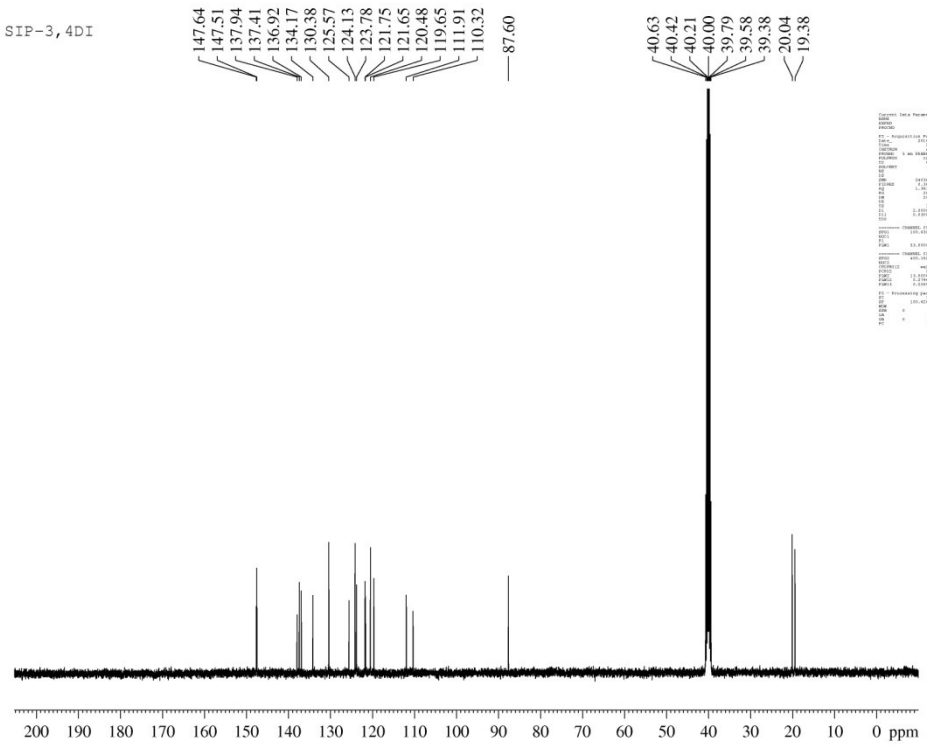
^{1}H NMR Spectra of (**1e)** (400 MHz, DMSO-d_6)



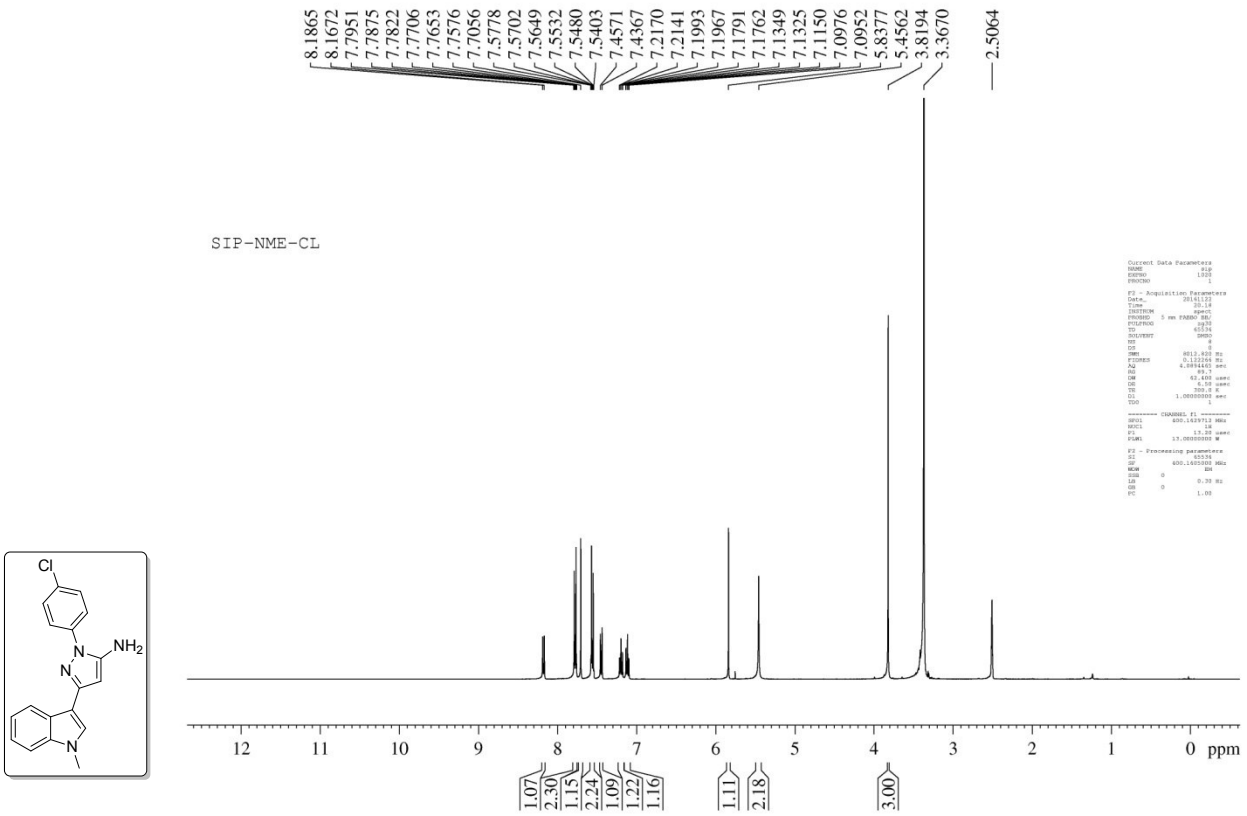
^{13}C NMR Spectra of (**1e)** (100 MHz, DMSO-d6)



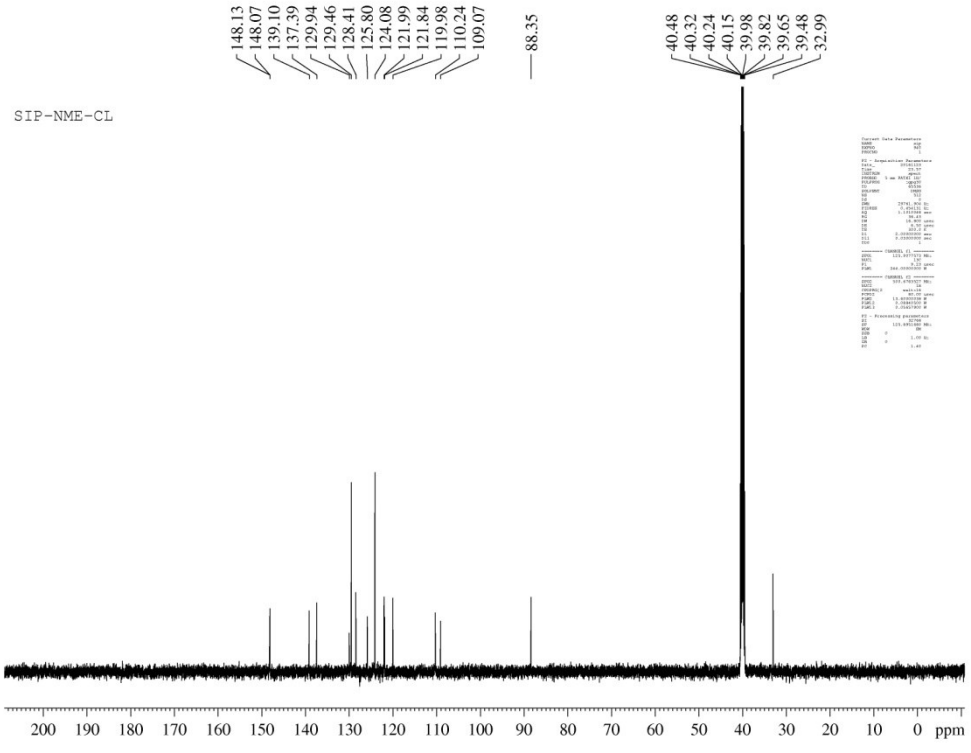
^{1}H NMR Spectra of (**1f)** (400 MHz, DMSO-d_6)



^{13}C NMR Spectra of (**1f)** (100 MHz, DMSO-d6)

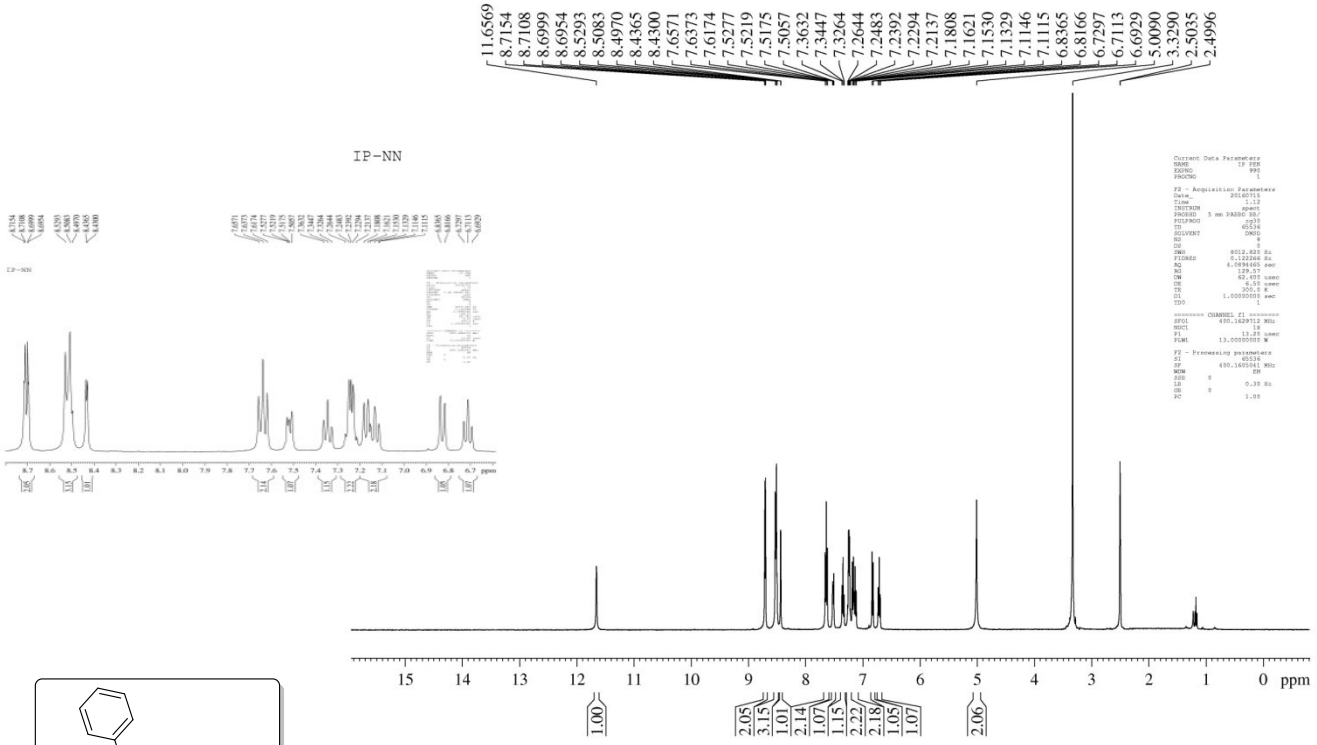


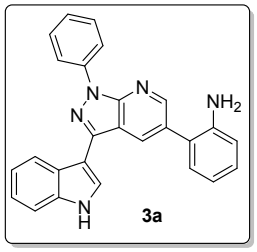
^{1}H NMR Spectra of (**1g**) (400 MHz, DMSO-d_6)



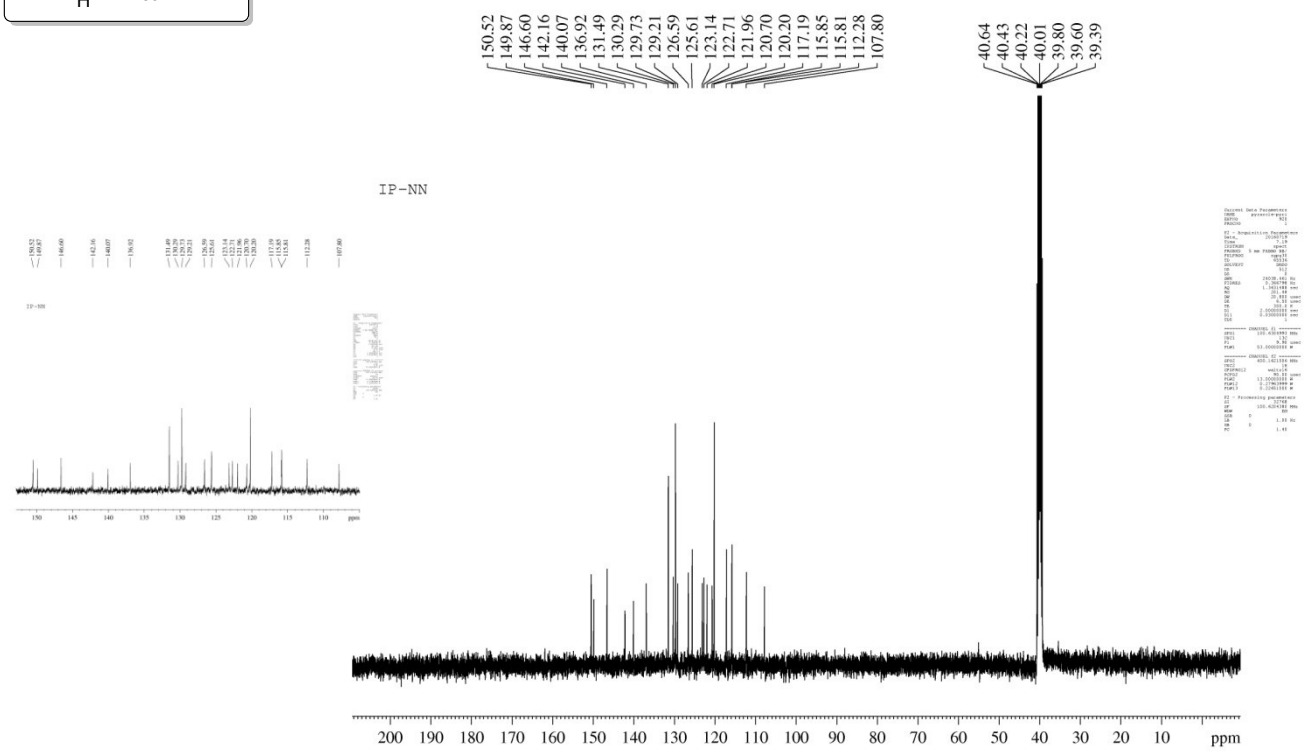
^{13}C NMR Spectra of (**1g**) (100 MHz, DMSO-d6)

4.2 NMR and HRMS Spectra of Products (3a-3u)

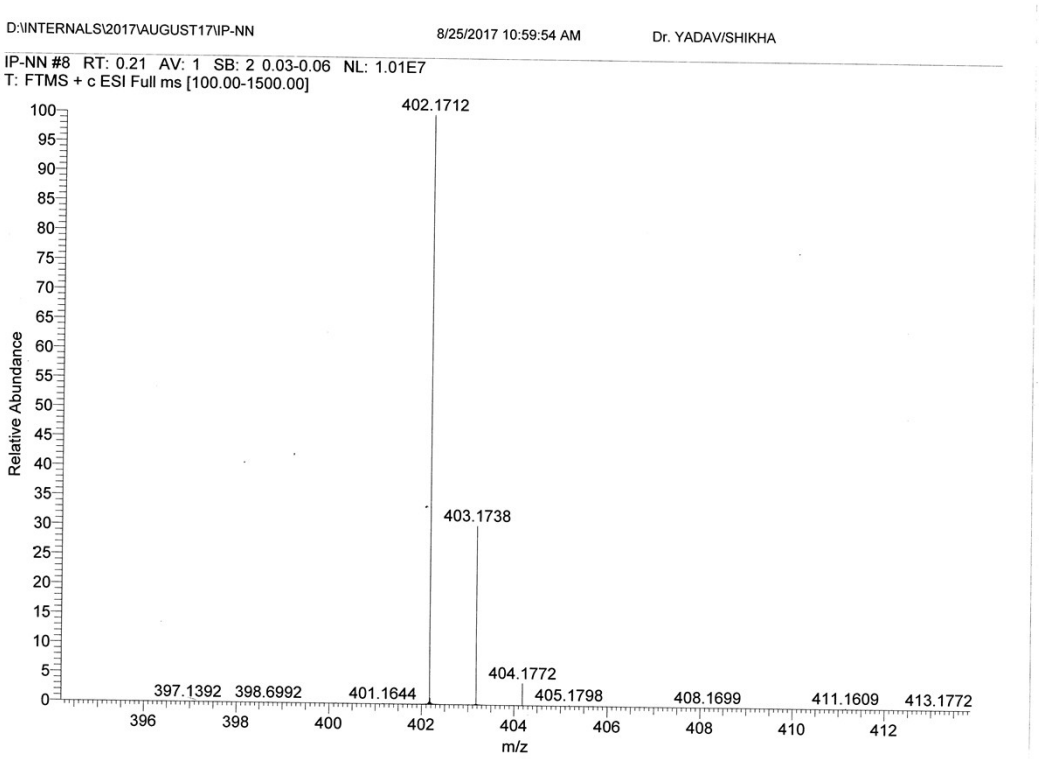




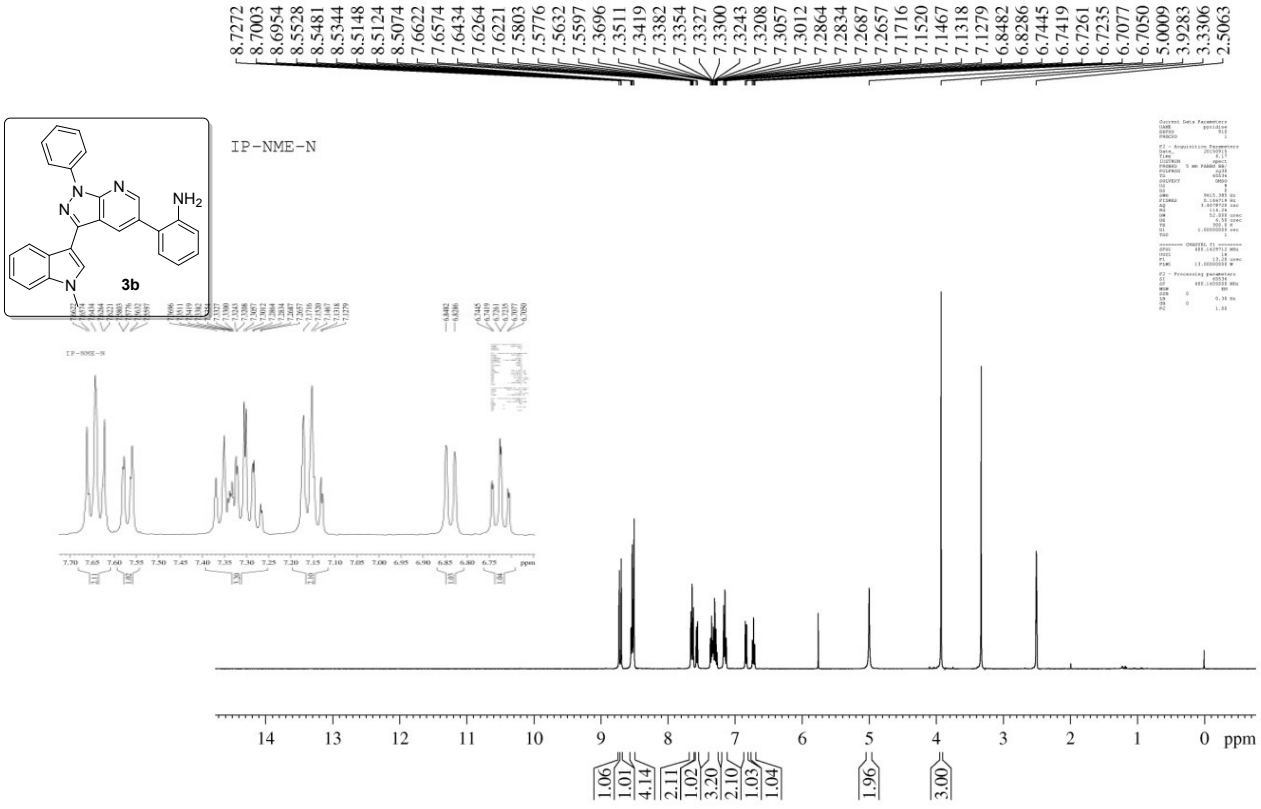
^{1}H NMR Spectra of (**3a)** (400 MHz, DMSO-d6)



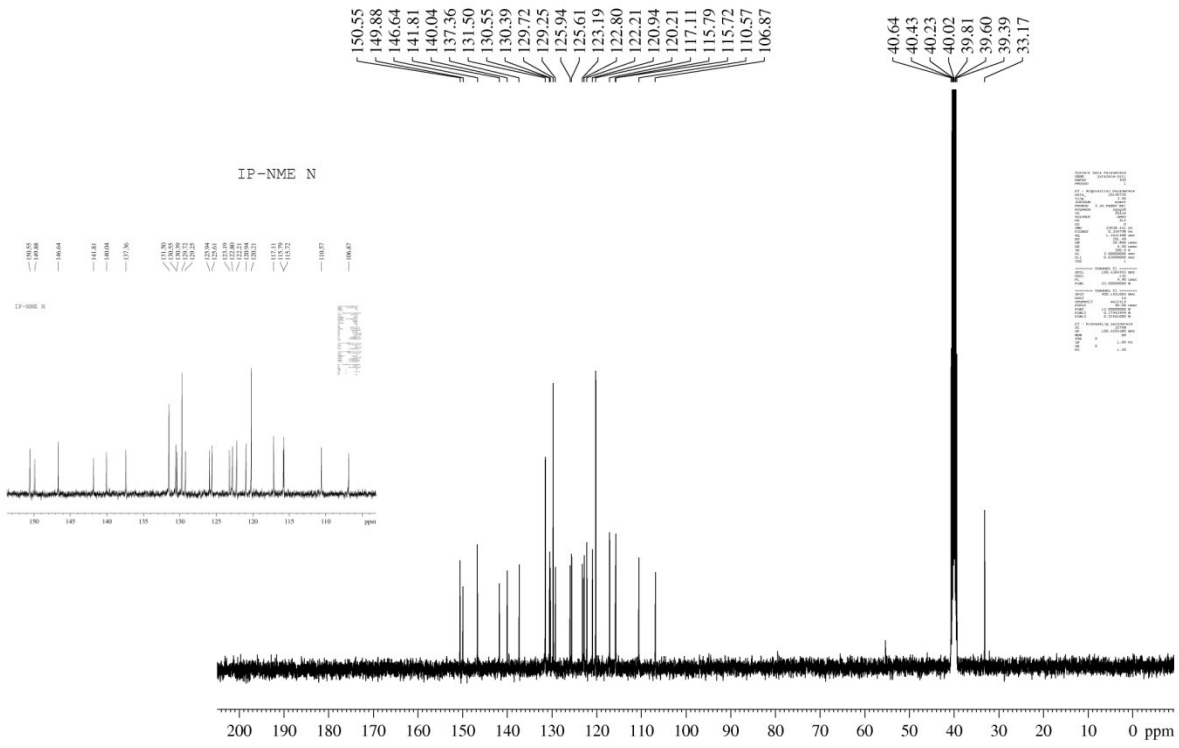
^{13}C NMR Spectra of (**3a)** (100 MHz, DMSO-d6)



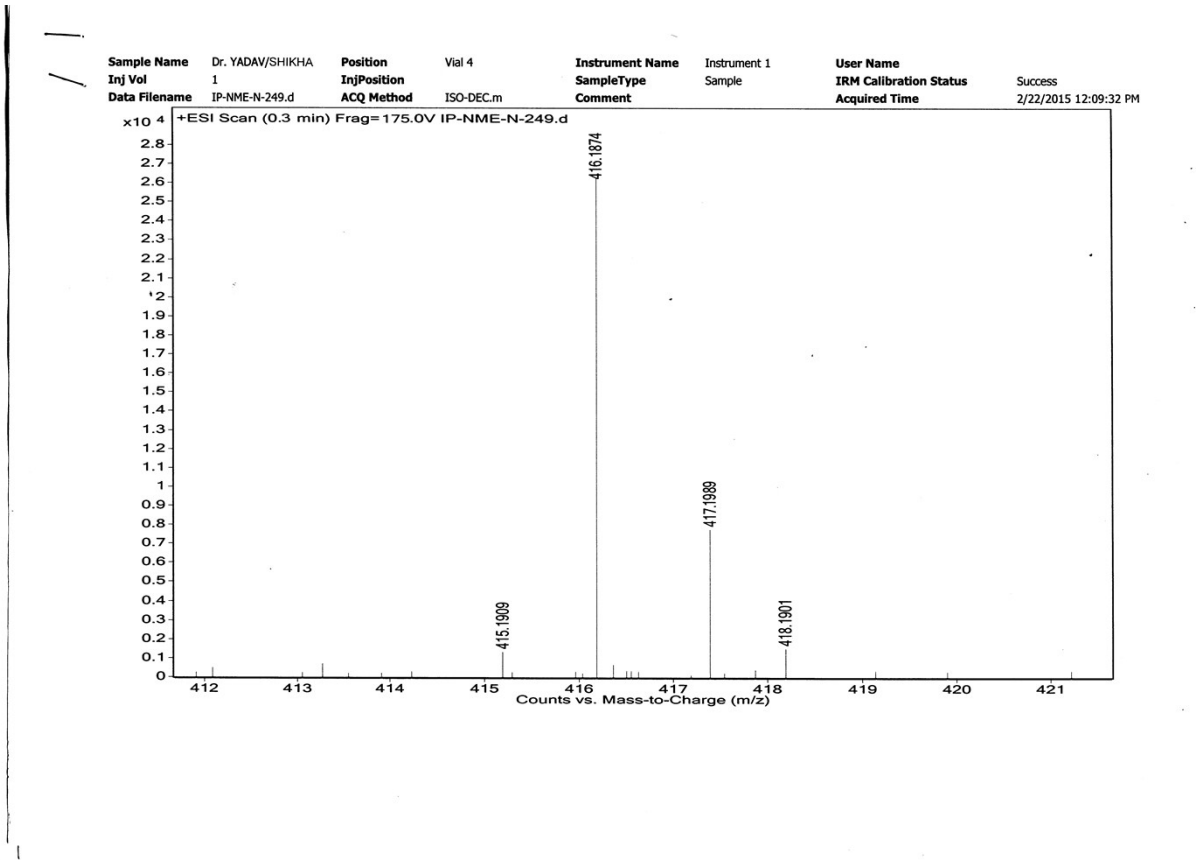
HRMS-**3a**



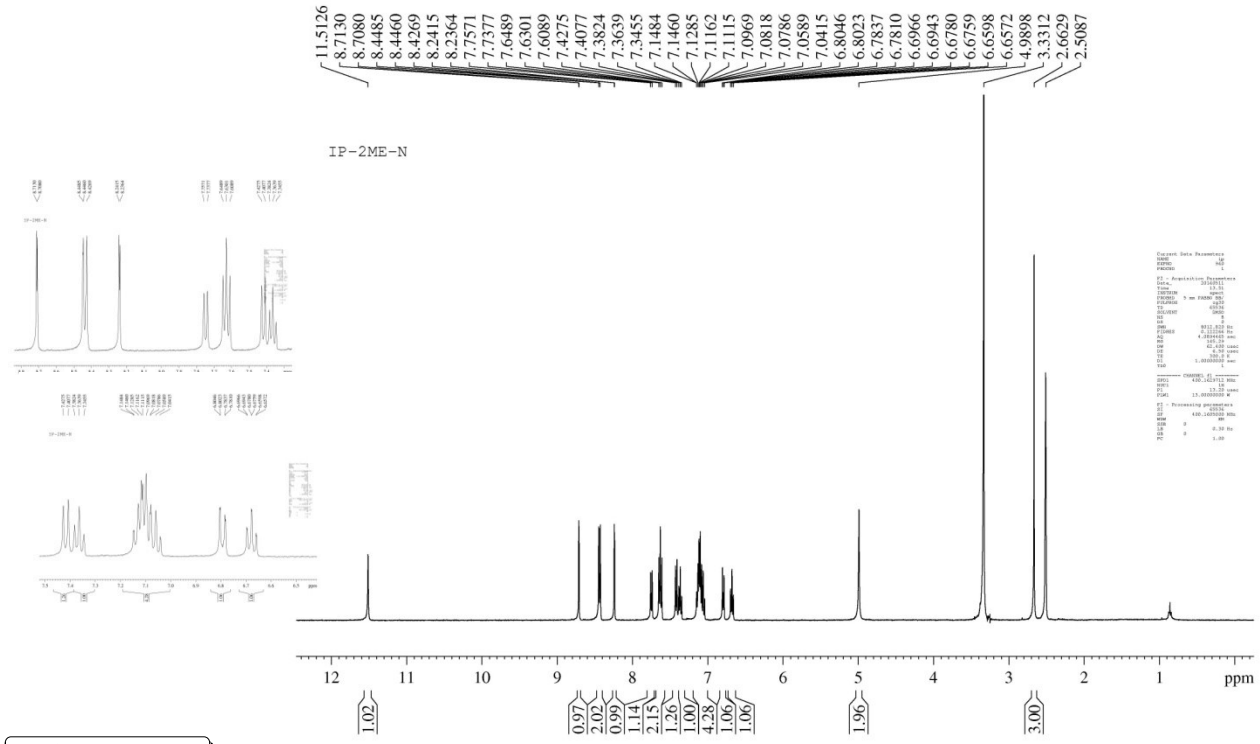
[1]H NMR Spectra of (**3b)** (400 MHz, DMSO-d6)

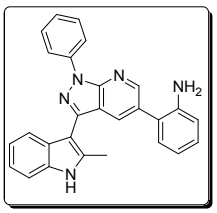


^{13}C NMR Spectra of (**3b)** (100 MHz, DMSO-d6)

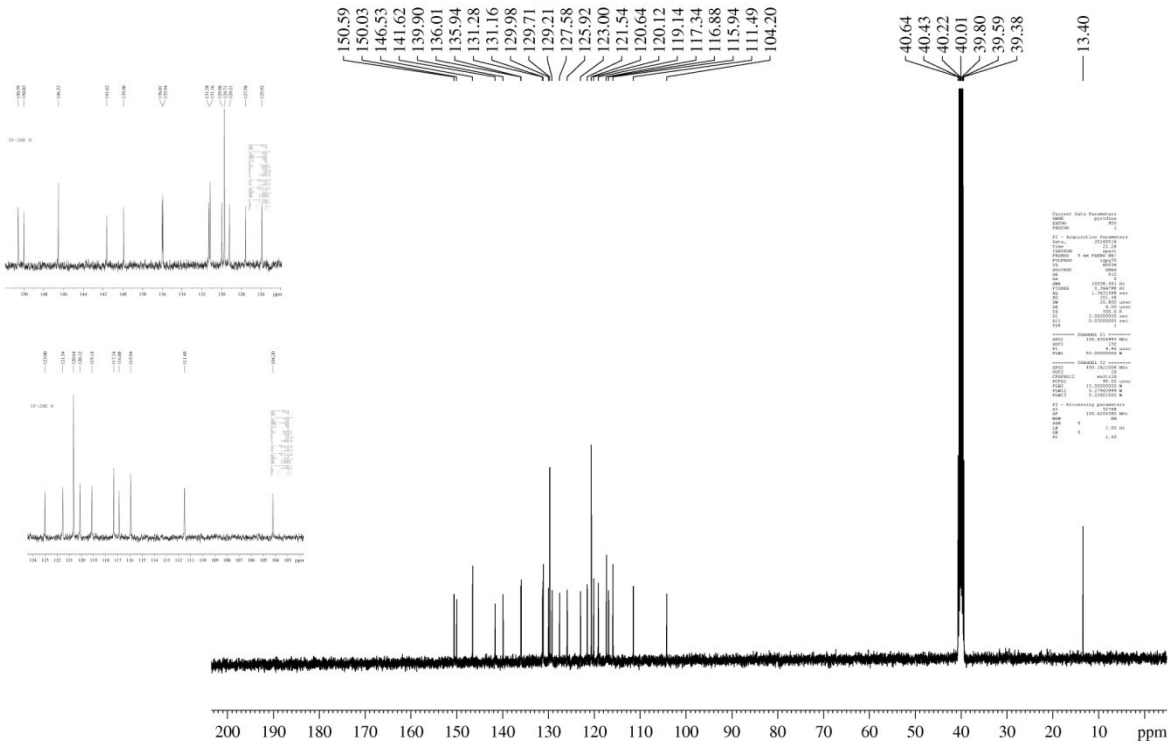


HRMS-**3b**

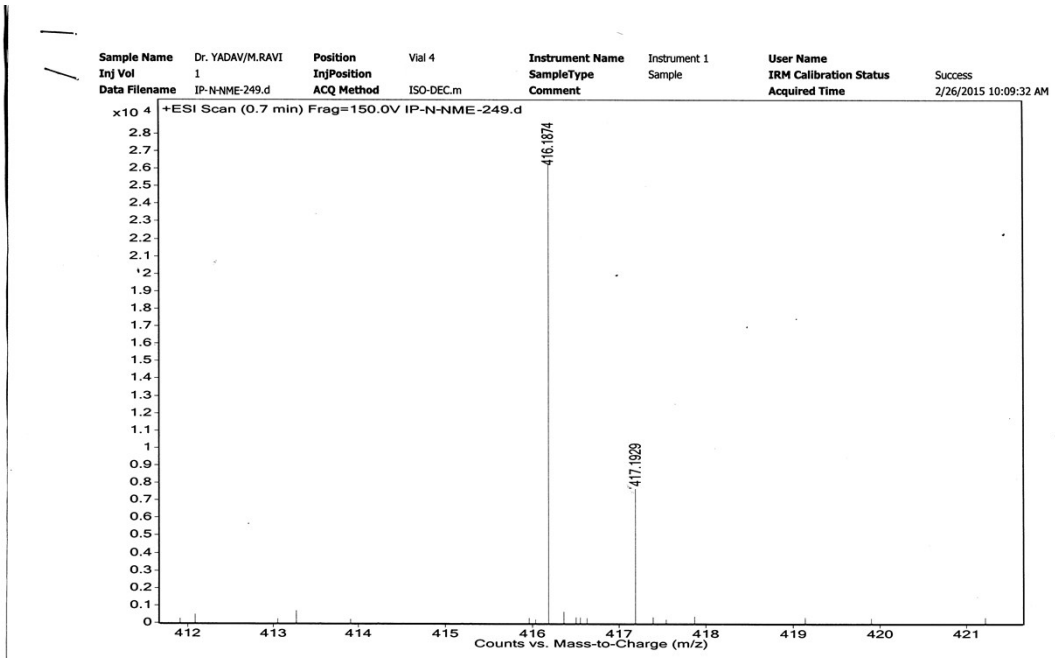




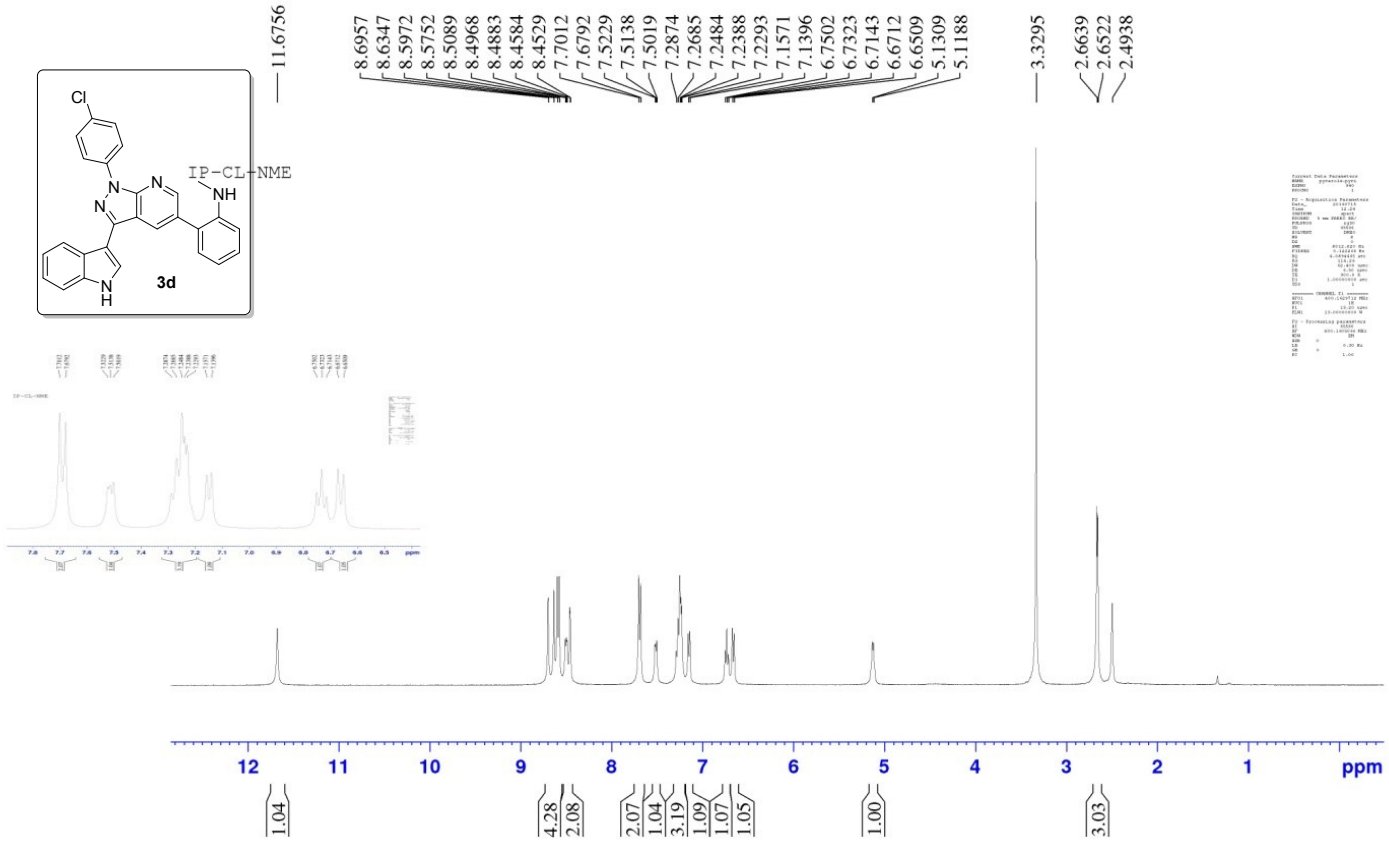
^{1}H NMR Spectra of (**3c)** (400 MHz, DMSO-d6)



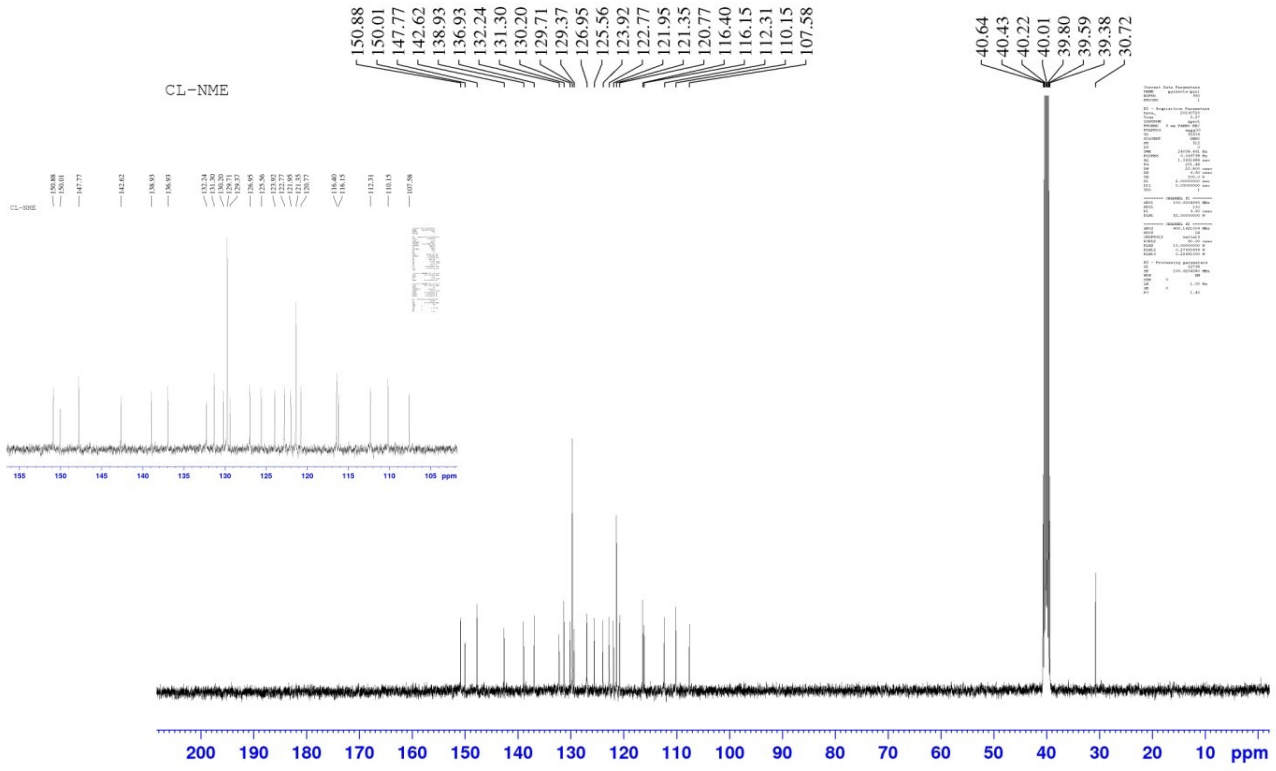
^{13}C NMR Spectra of (**3c)** (100 MHz, DMSO-d6)



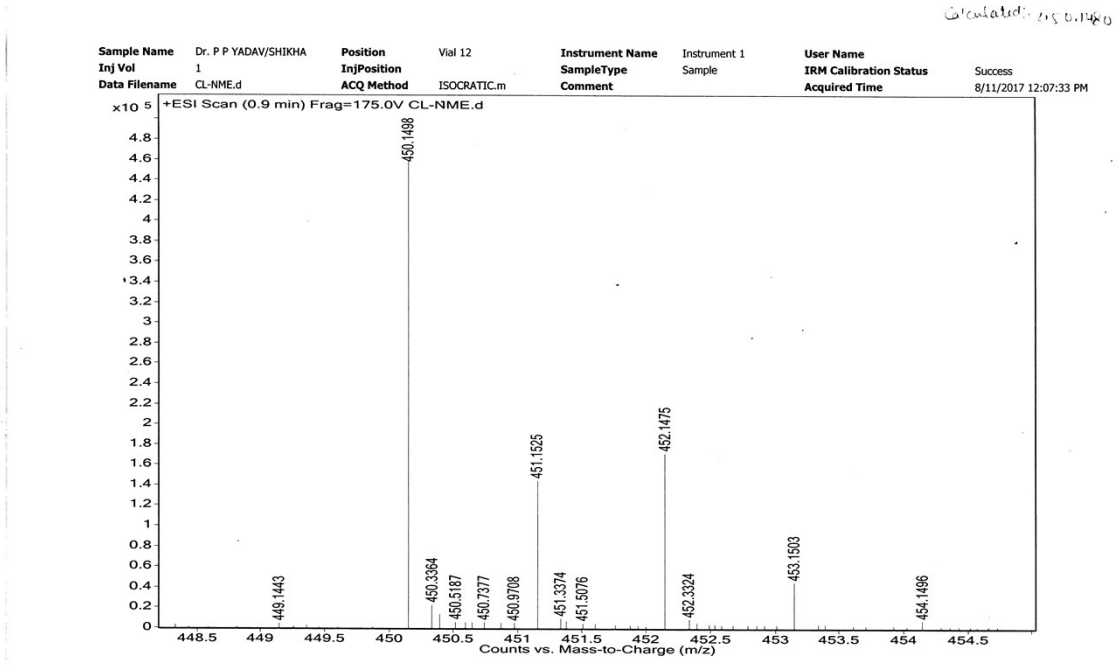
HRMS-**3c**



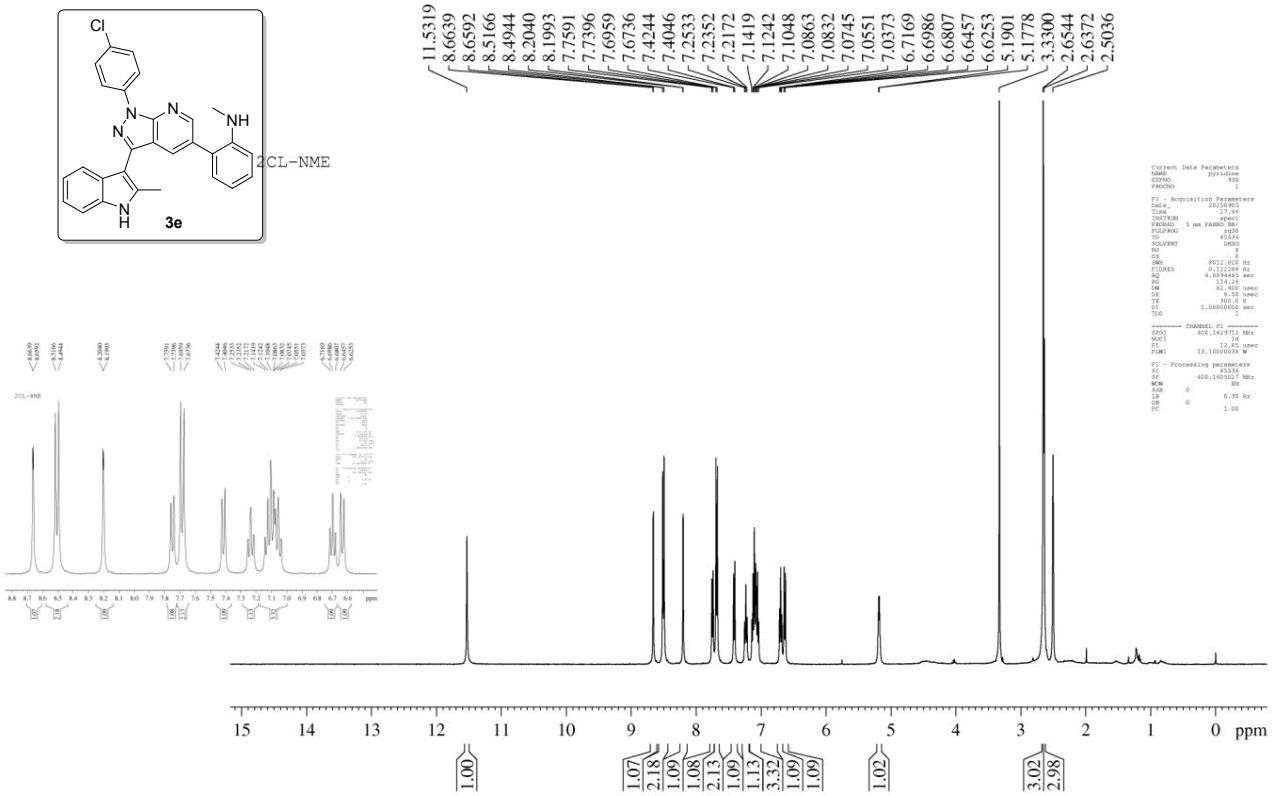
^{1}H NMR Spectra of (**3d)** (400 MHz, DMSO-d6)



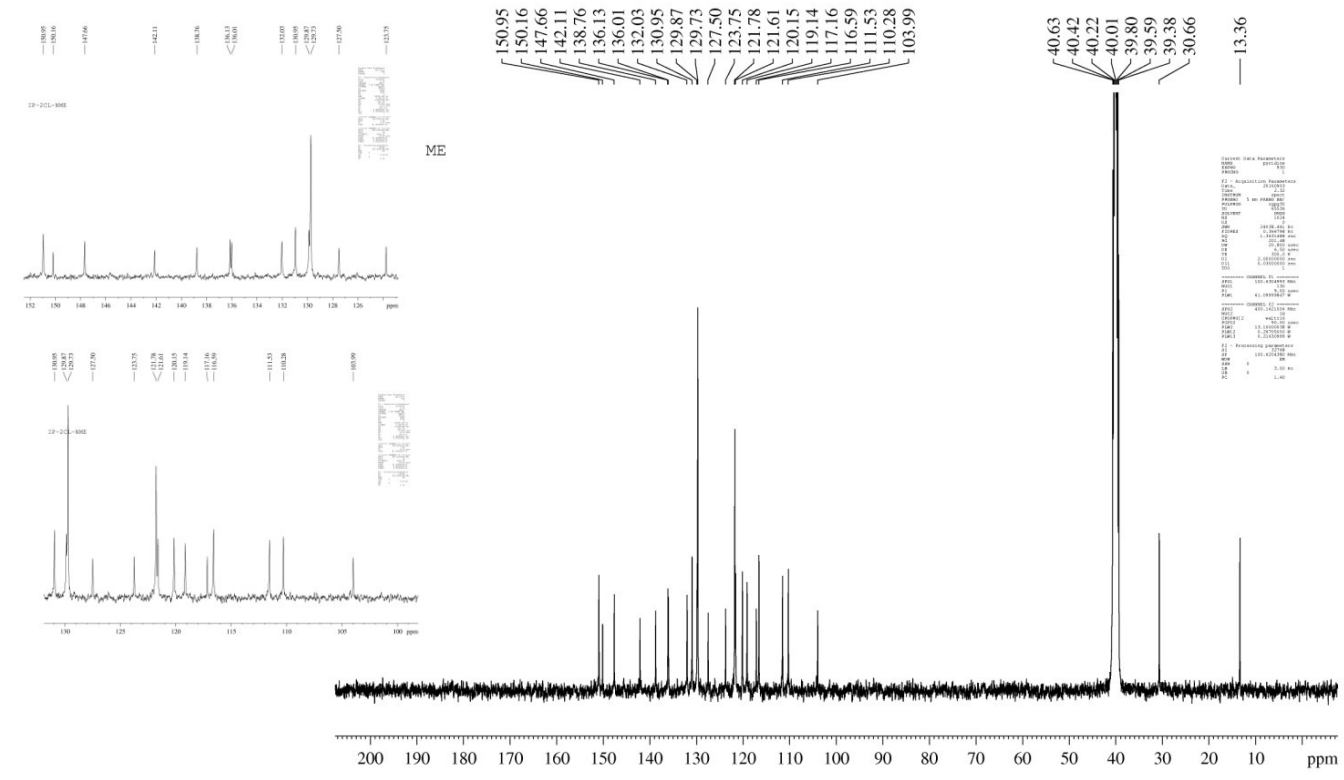
^{13}C NMR Spectra of (**3d)** (100 MHz, DMSO-d6)



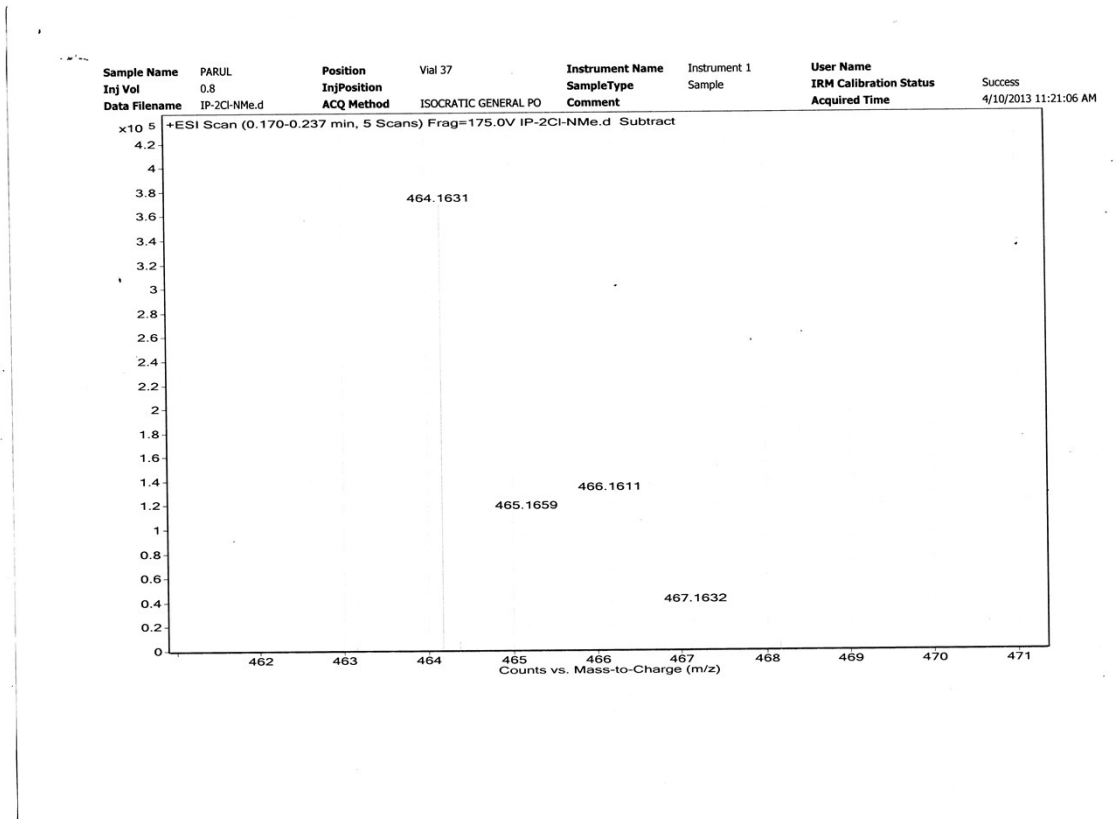
HRMS-**3d**



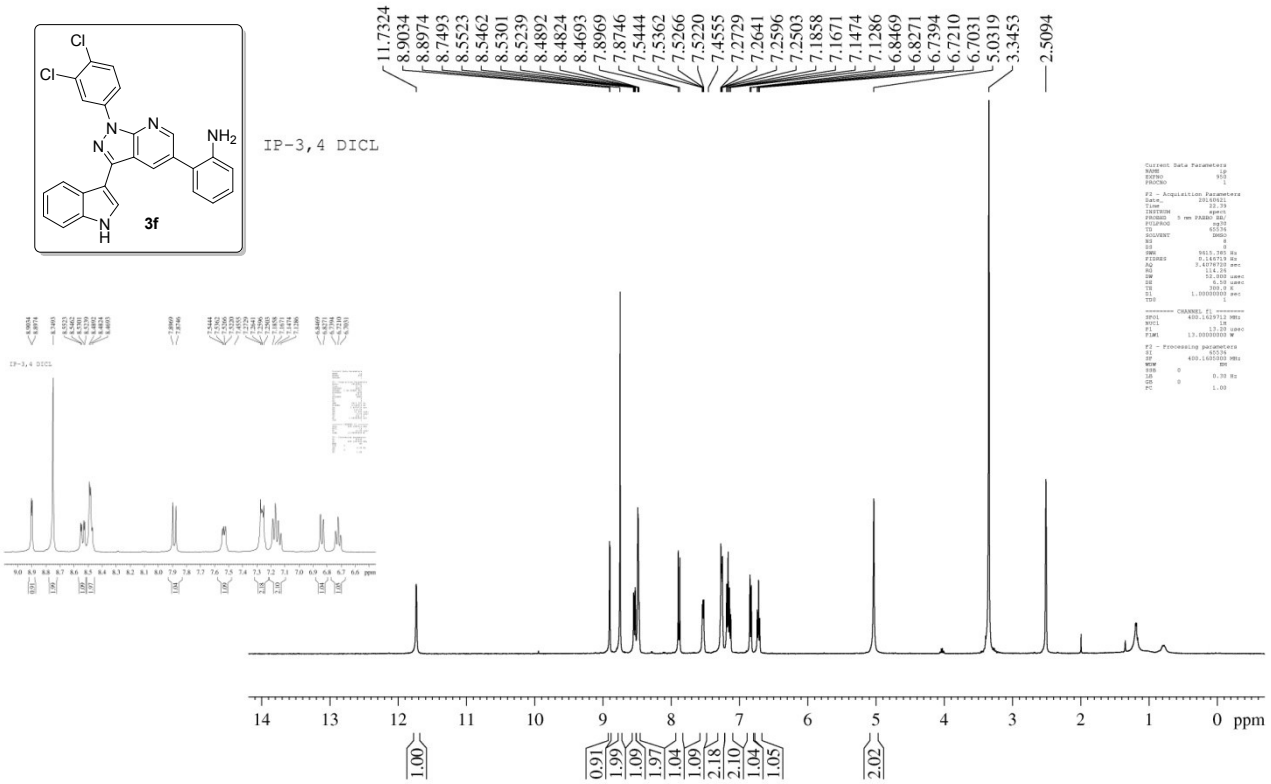
^{1}H NMR Spectra of (**3e)** (400 MHz, DMSO-d6)



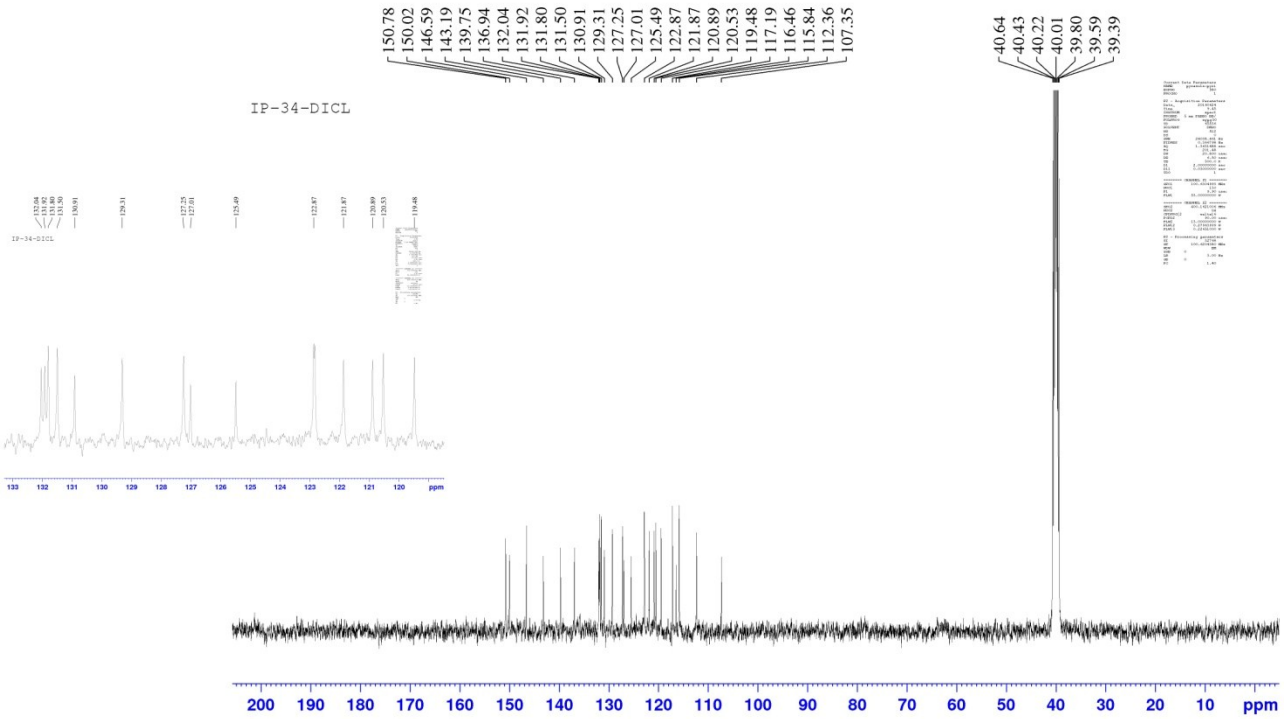
^{13}C NMR Spectra of (**3e)** (100 MHz, DMSO-d6)



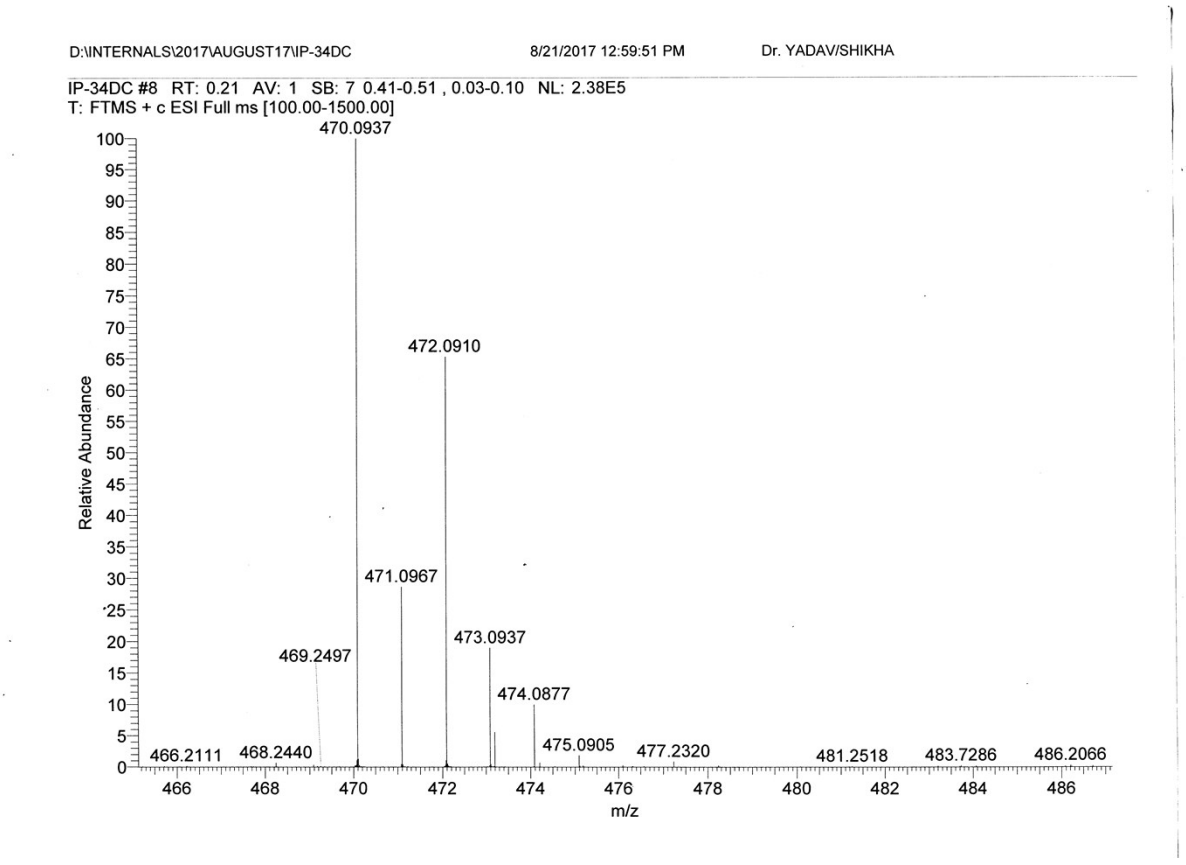
HRMS-**3e**



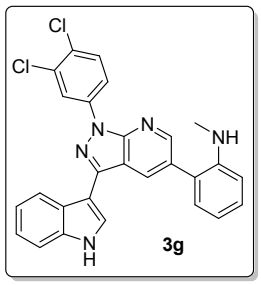
^{1}H NMR Spectra of (**3f)** (400 MHz, DMSO-d6)



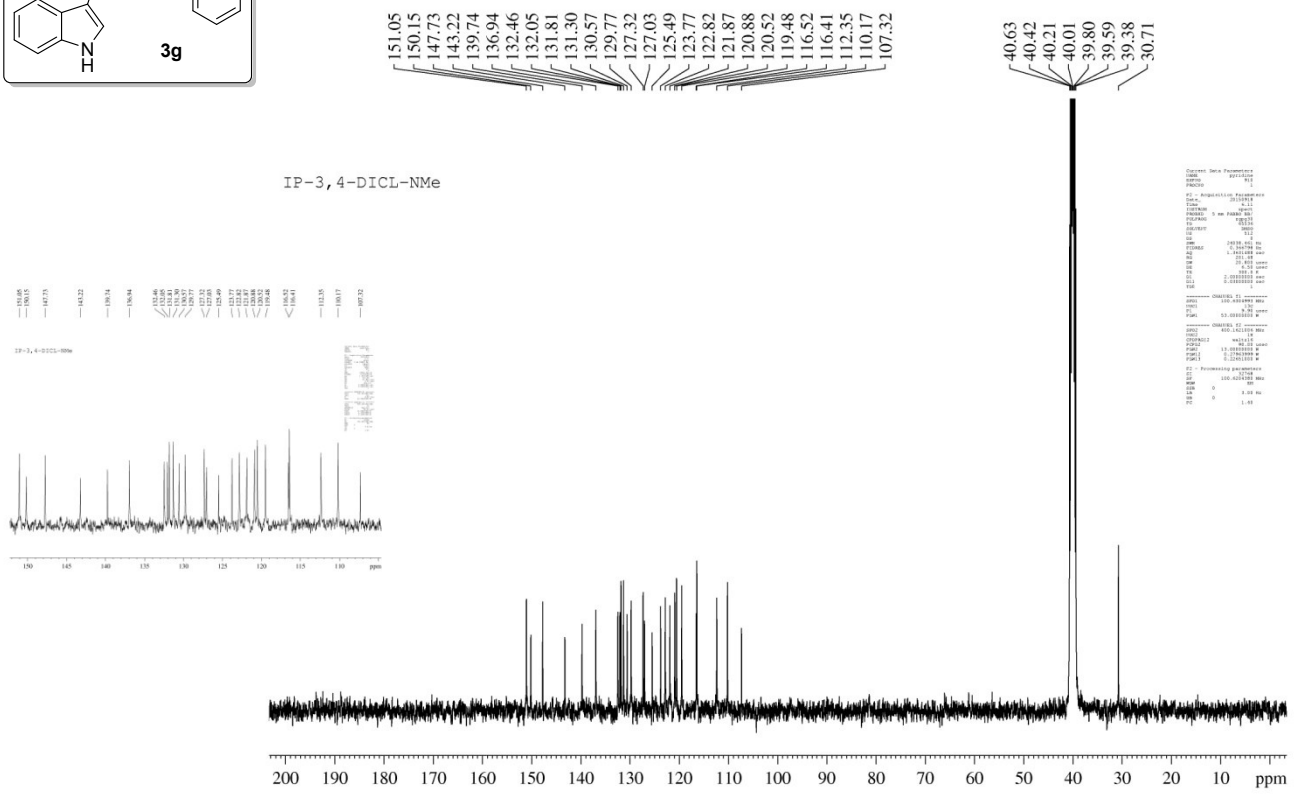
^{13}C NMR Spectra of (**3f)** (100 MHz, DMSO-d6)



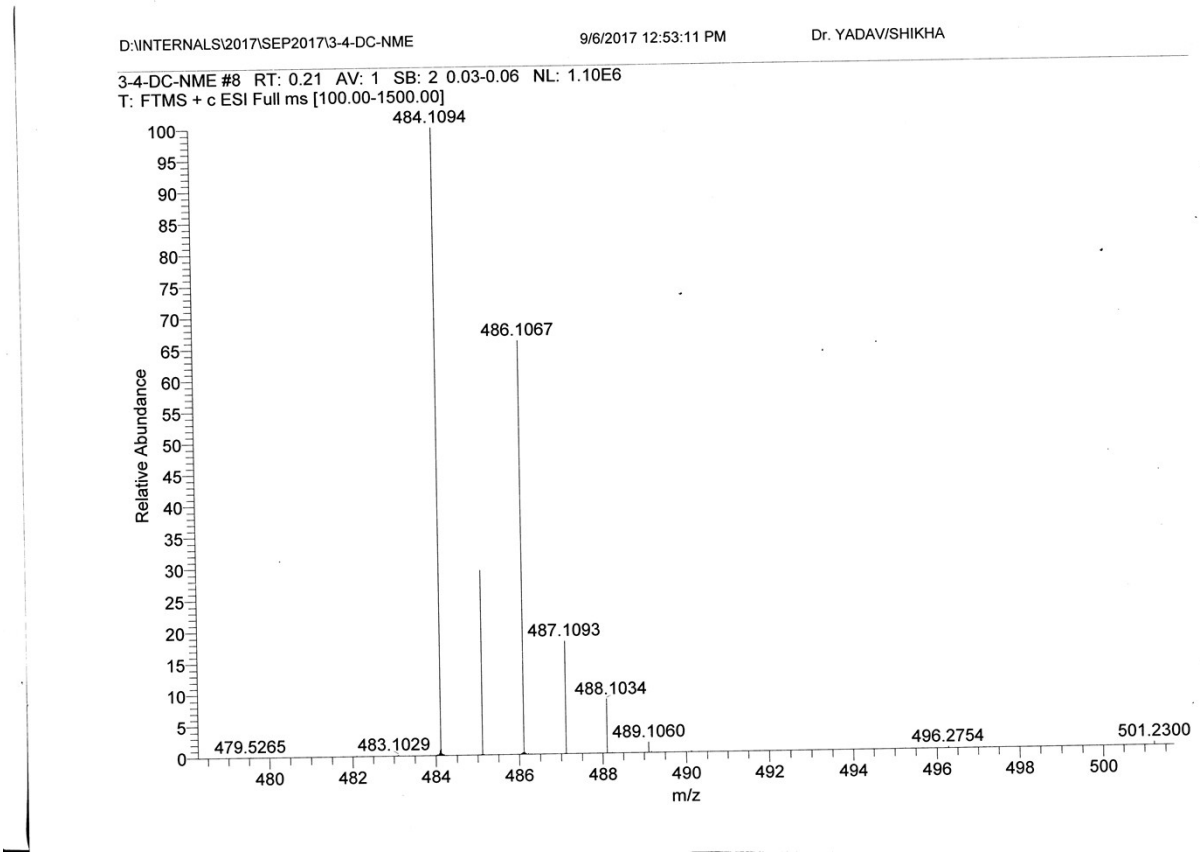
HRMS-**3f**



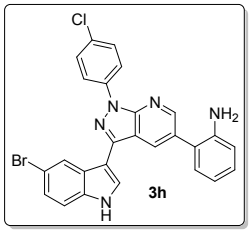
^{1}H NMR Spectra of (**3g**) (400 MHz, DMSO-d6)



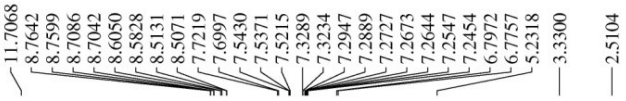
^{13}C NMR Spectra of (**3g**) (100 MHz, DMSO-d6)

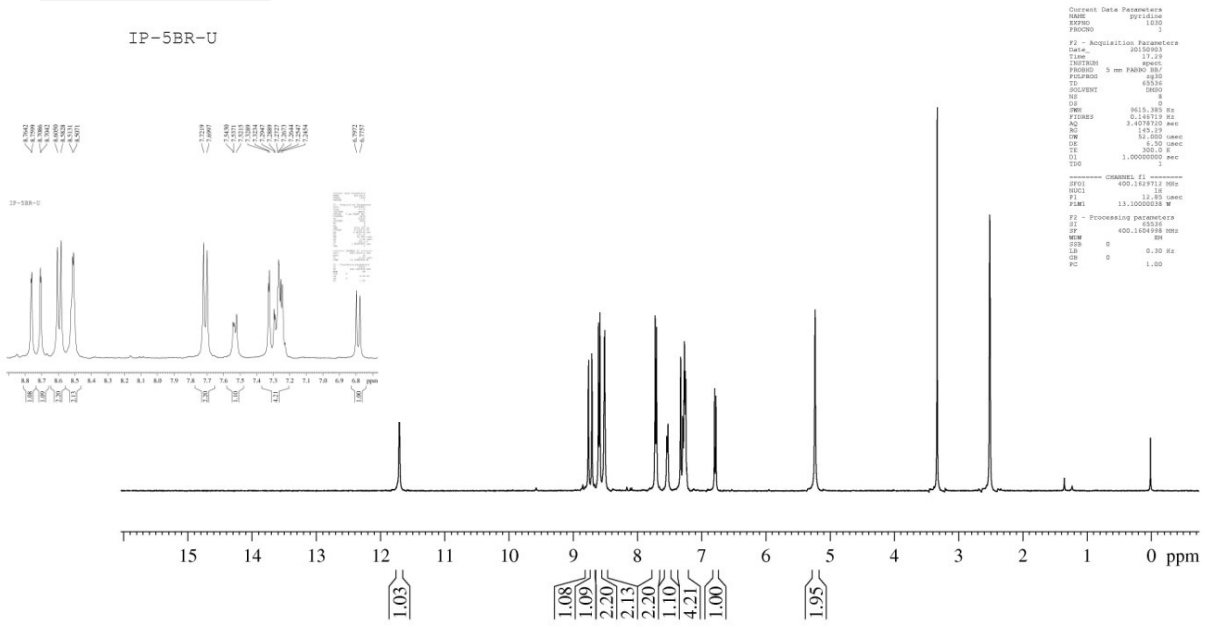


HRMS-**3g**

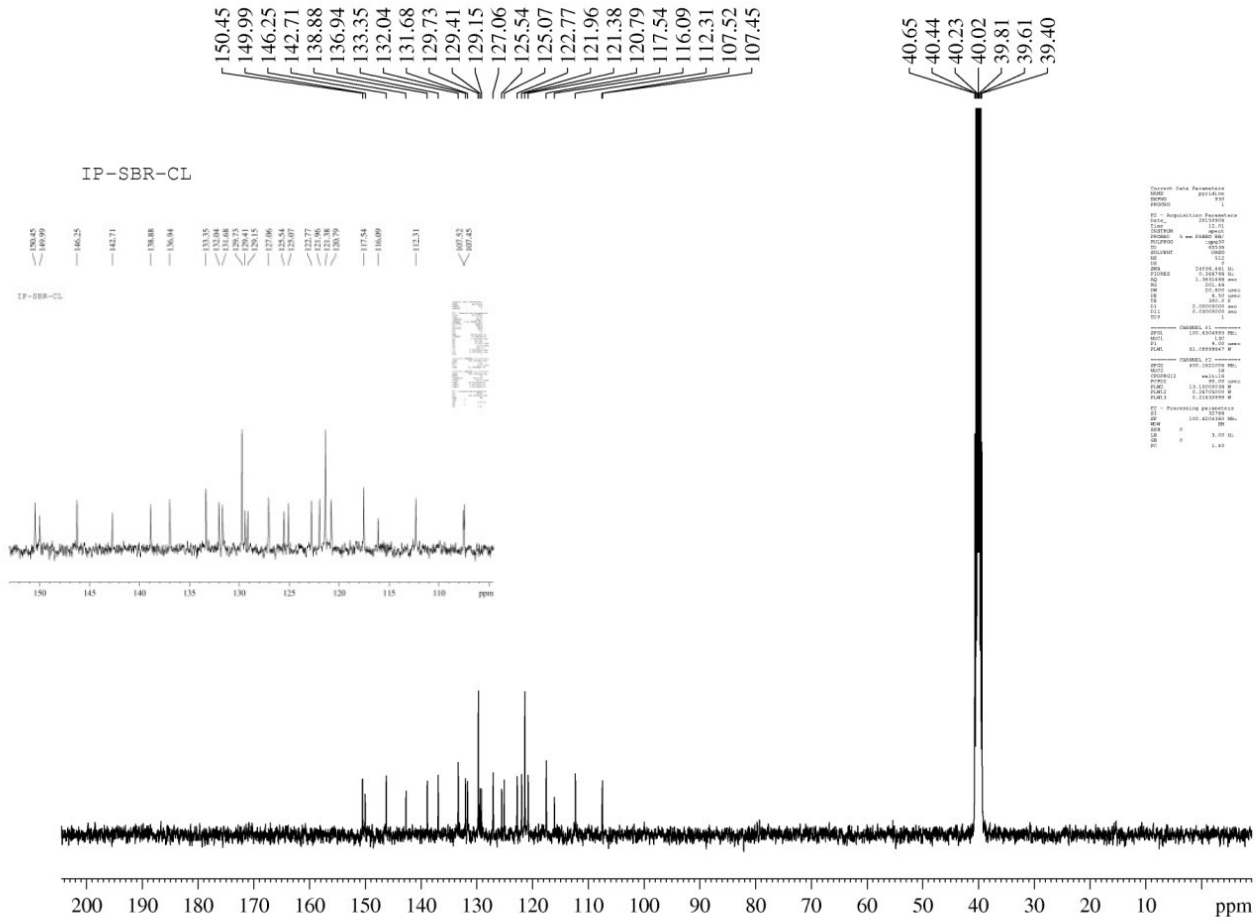


IP-5BR-U

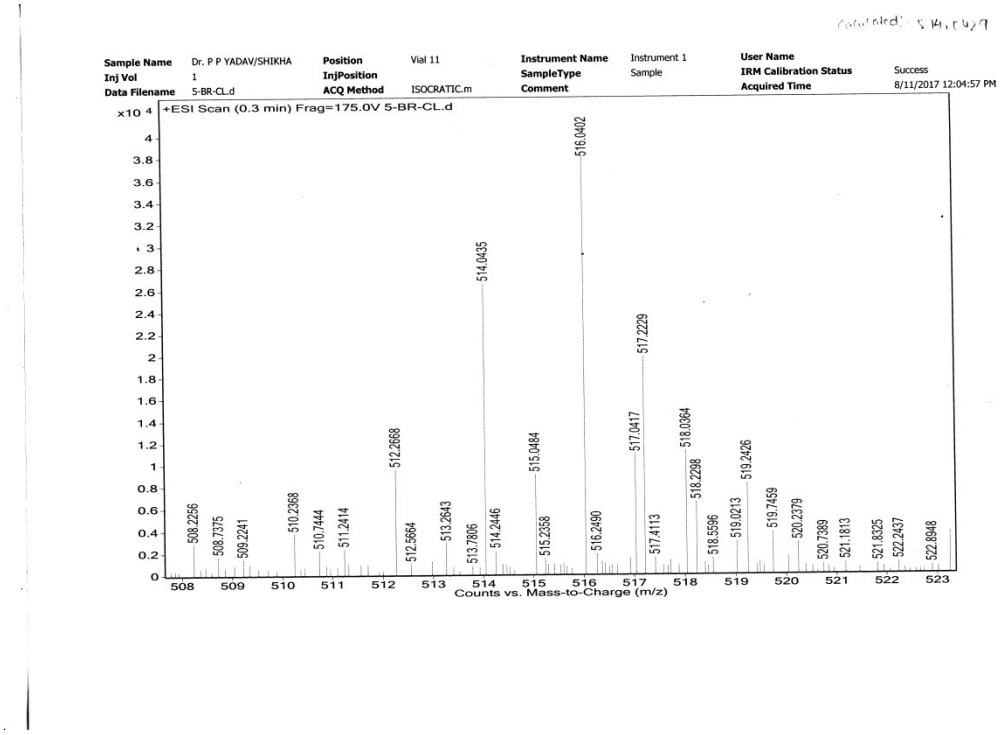




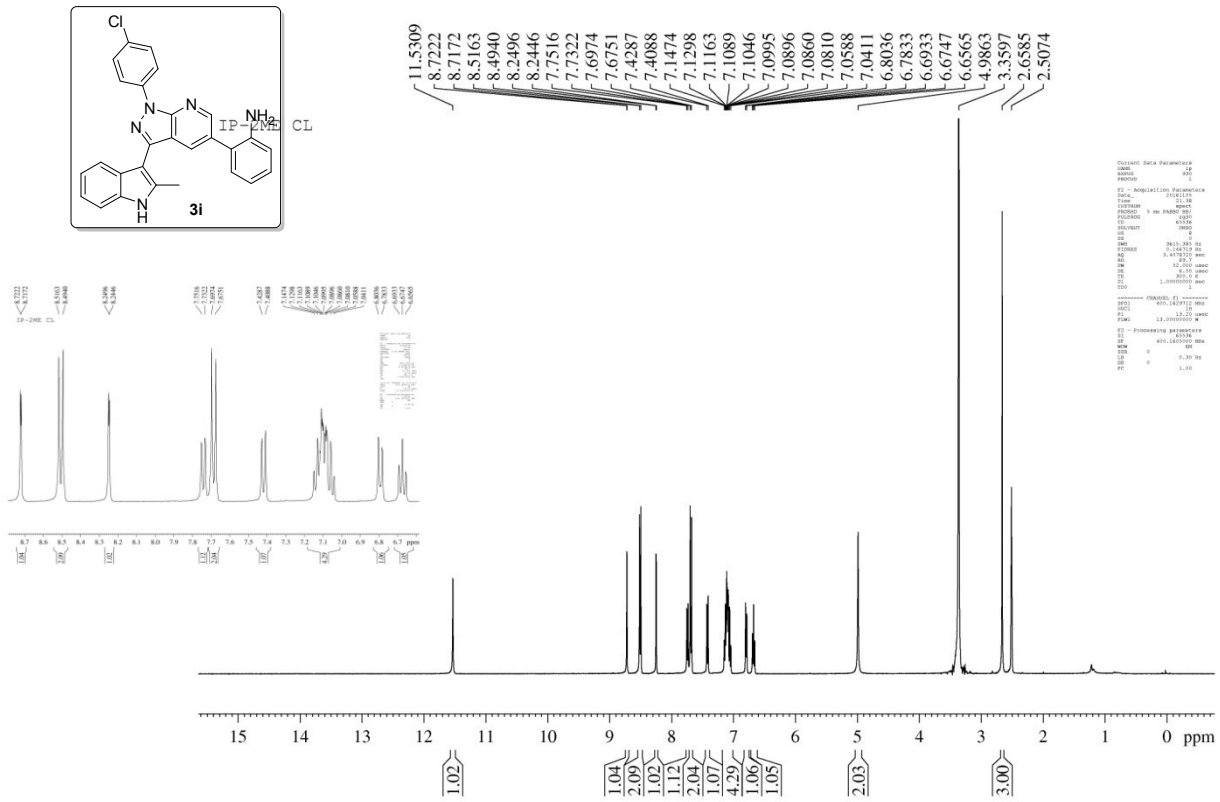
^{1}H NMR Spectra of (**3h)** (400 MHz, DMSO-d6)



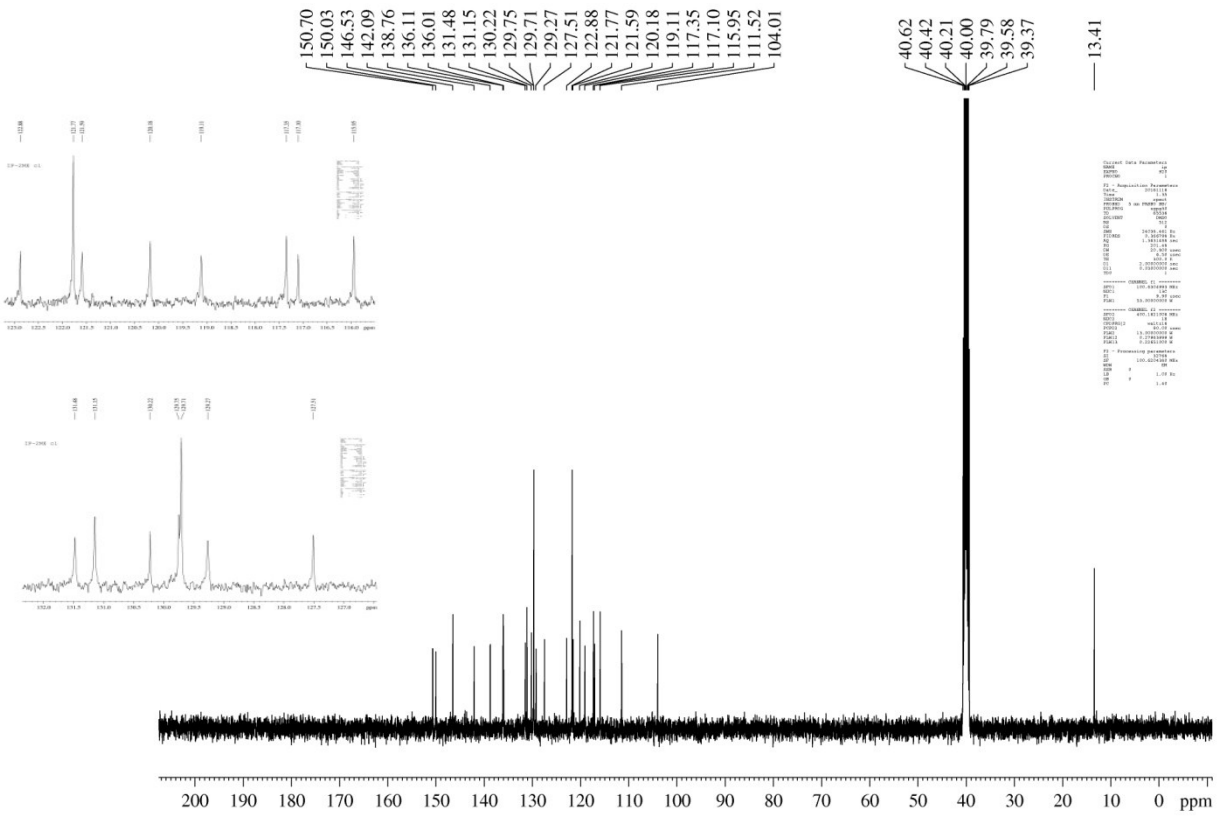
^{13}C NMR Spectra of (**3h)** (100 MHz, DMSO-d6)



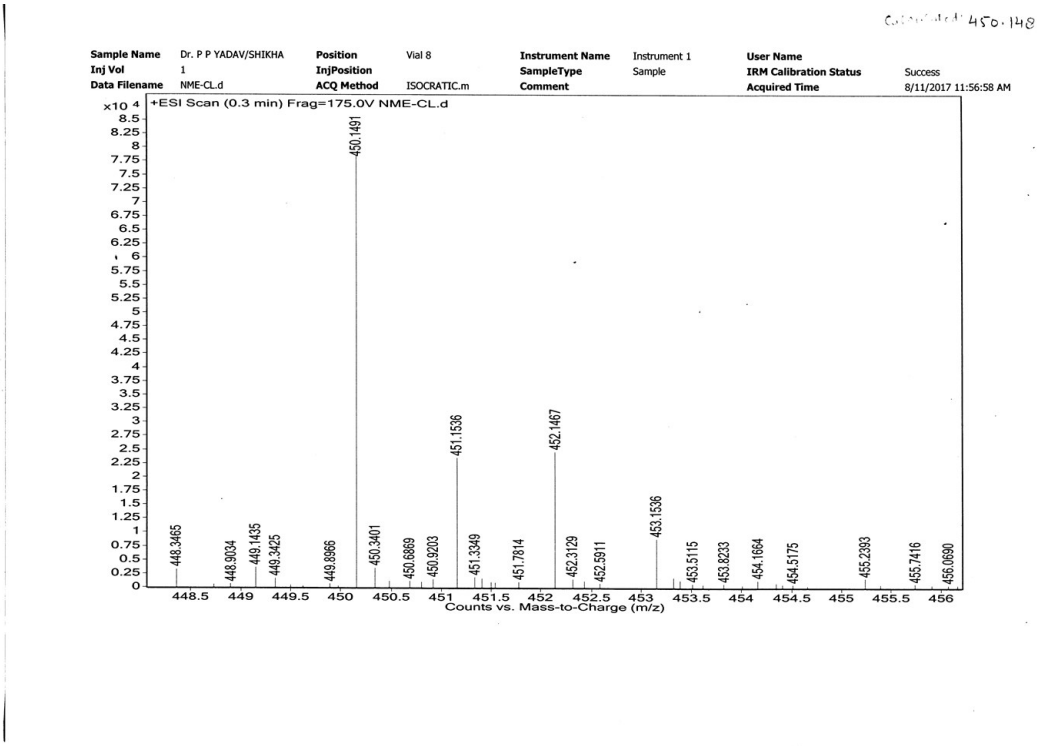
HRMS-**3h**



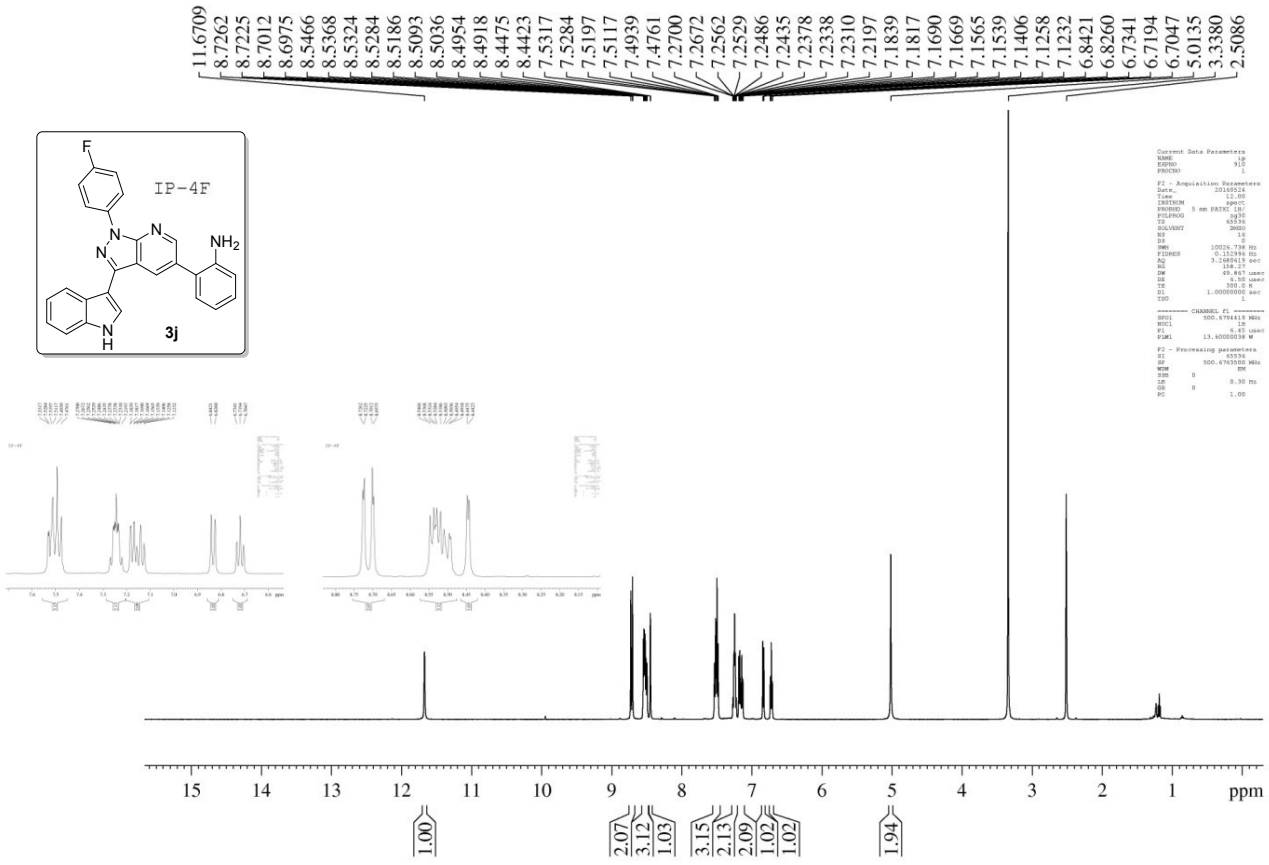
^{1}H NMR Spectra of (**3i)** (400 MHz, DMSO-d6)



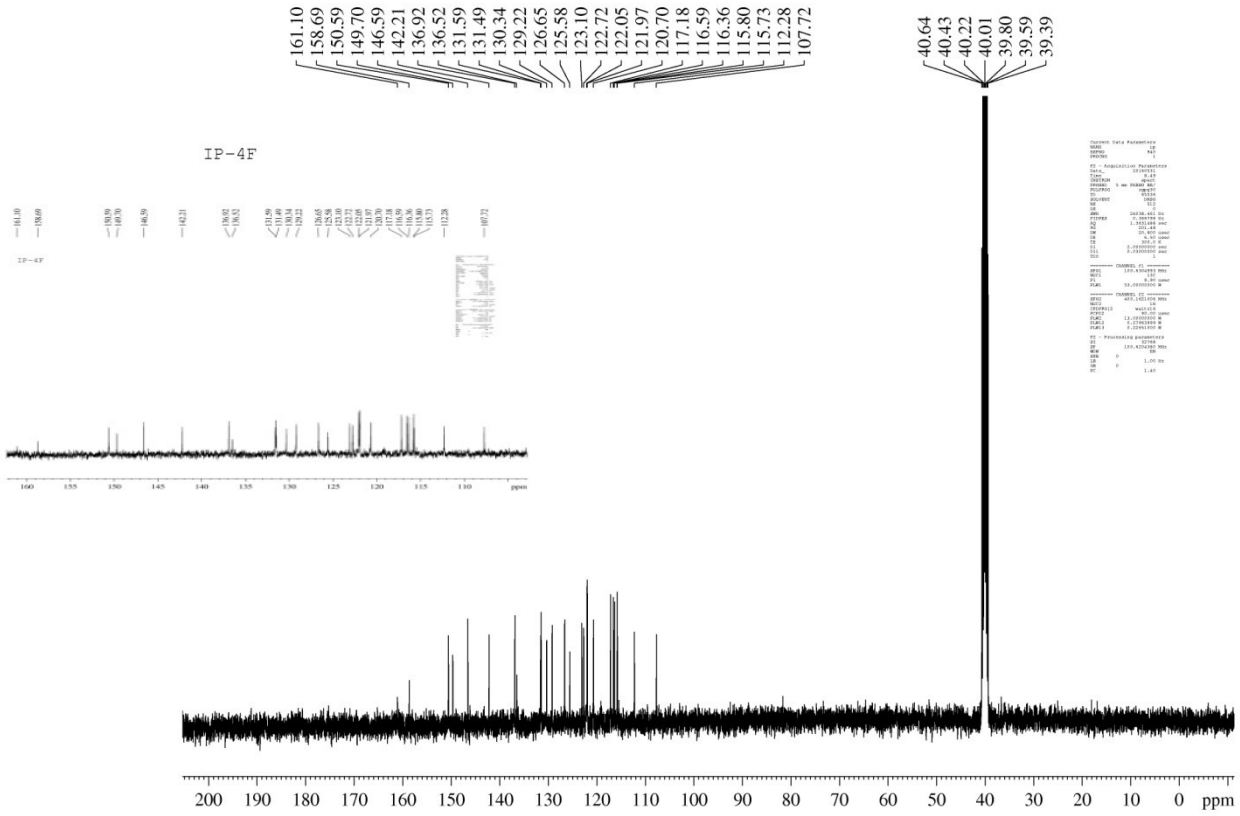
^{13}C NMR Spectra of (**3i)** (100 MHz, DMSO-d6)



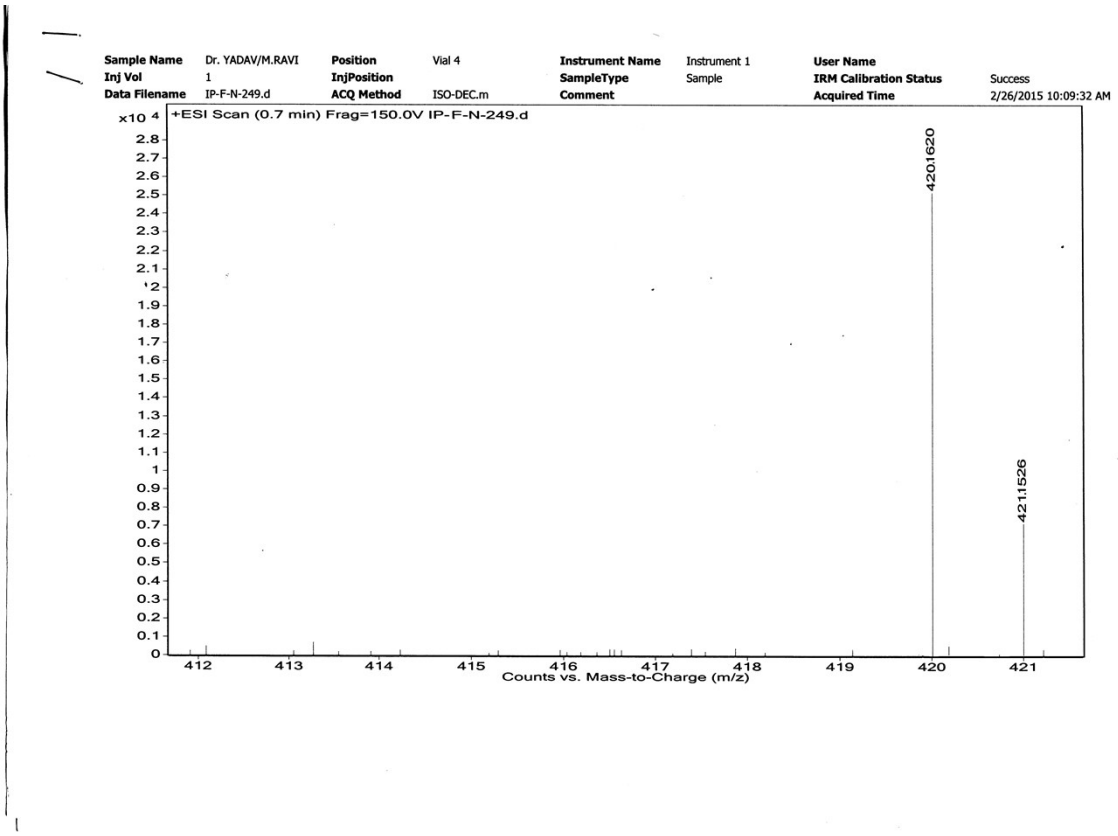
HRMS-**3i**



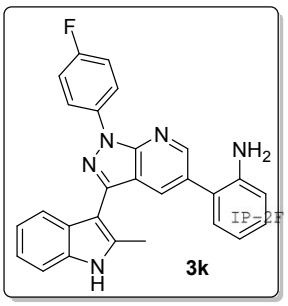
^{1}H NMR Spectra of (**3j)** (400 MHz, DMSO-d6)

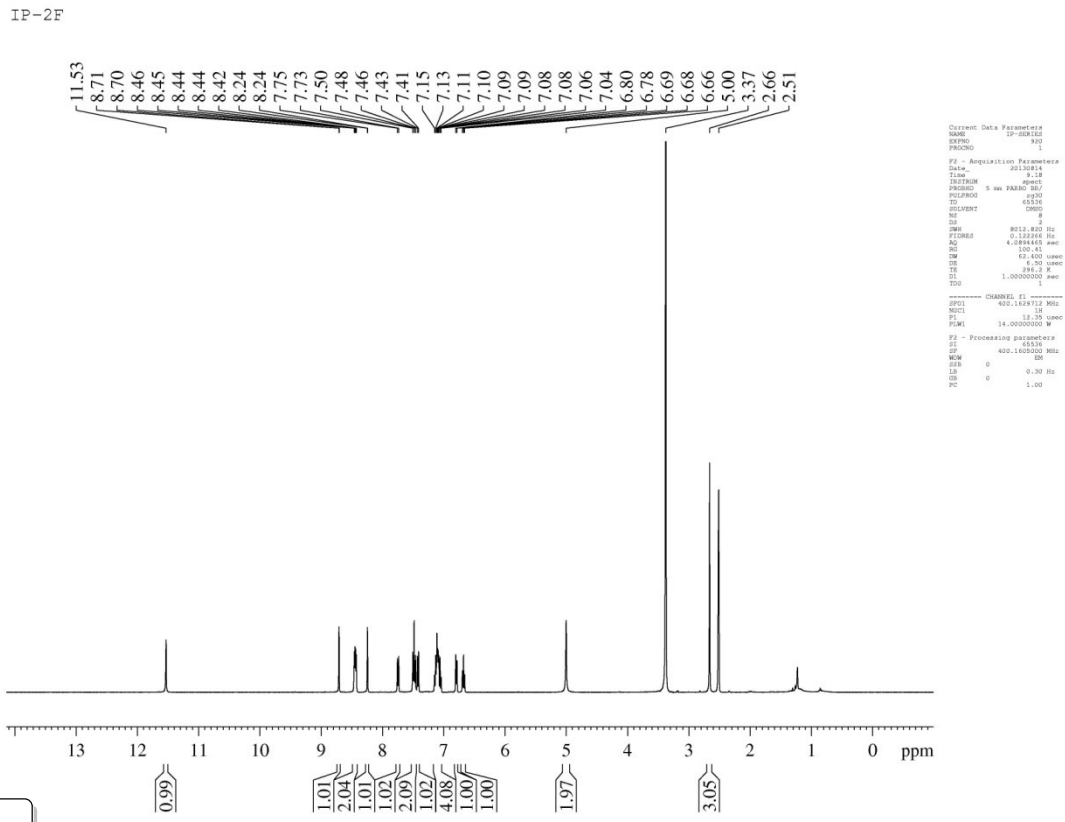


^{13}C NMR Spectra of (**3j)** (100 MHz, DMSO-d6)

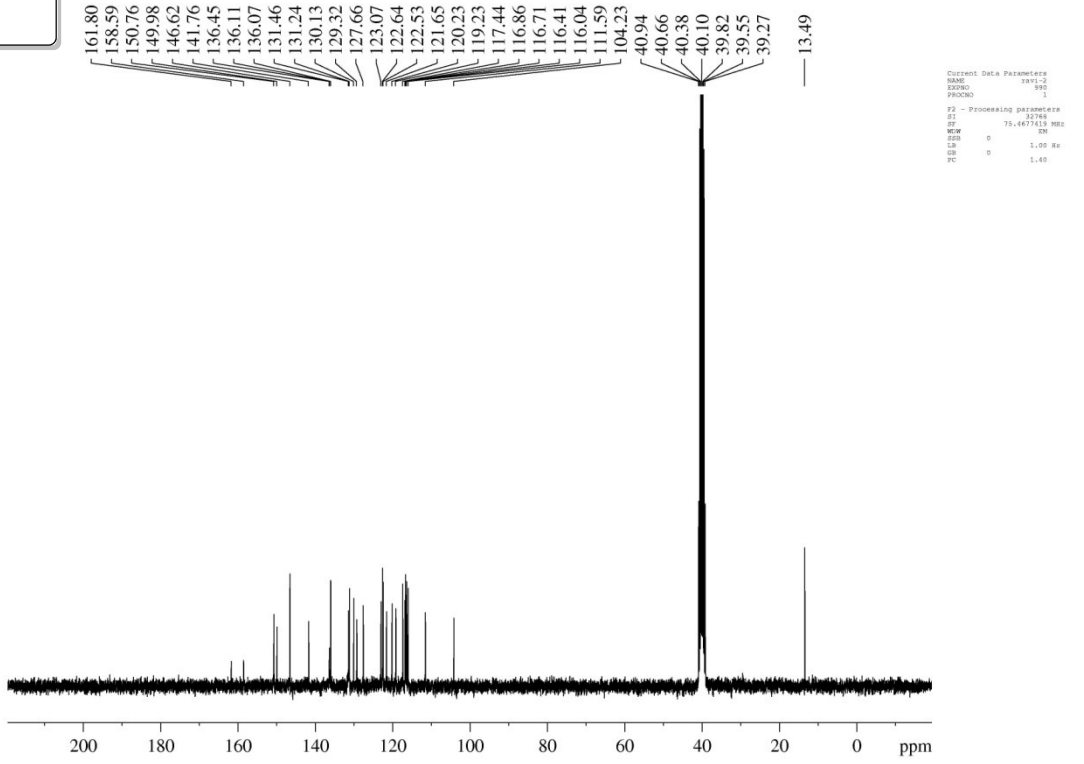


HRMS-**3j**

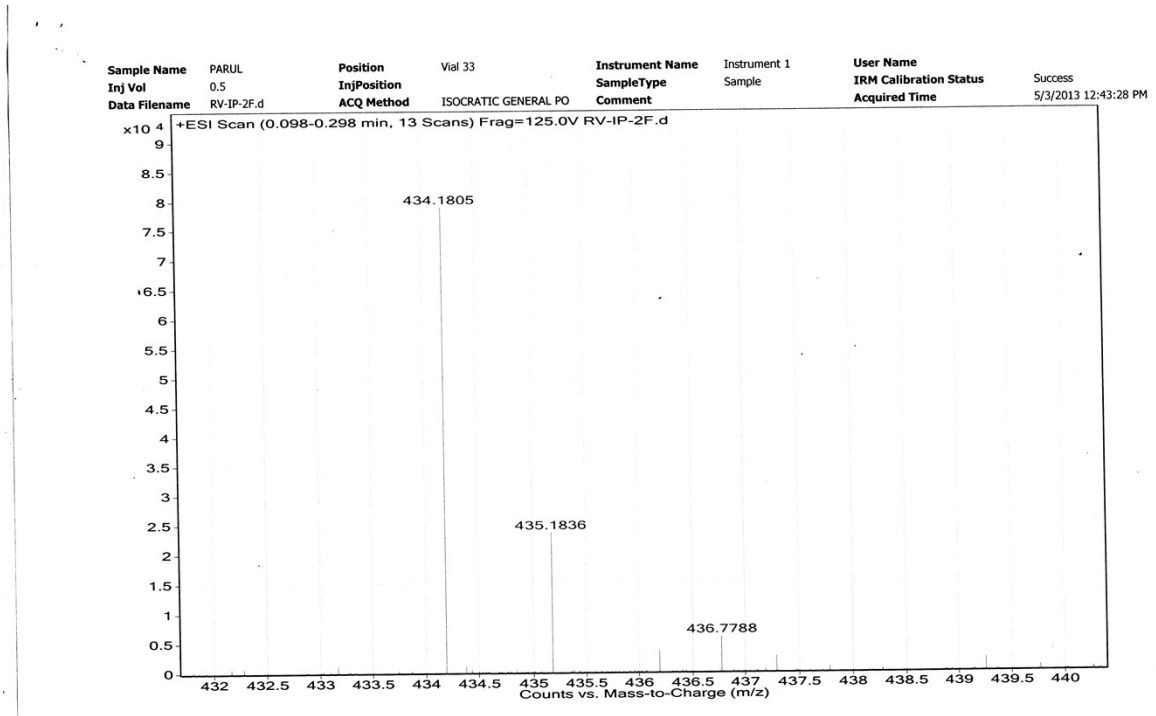




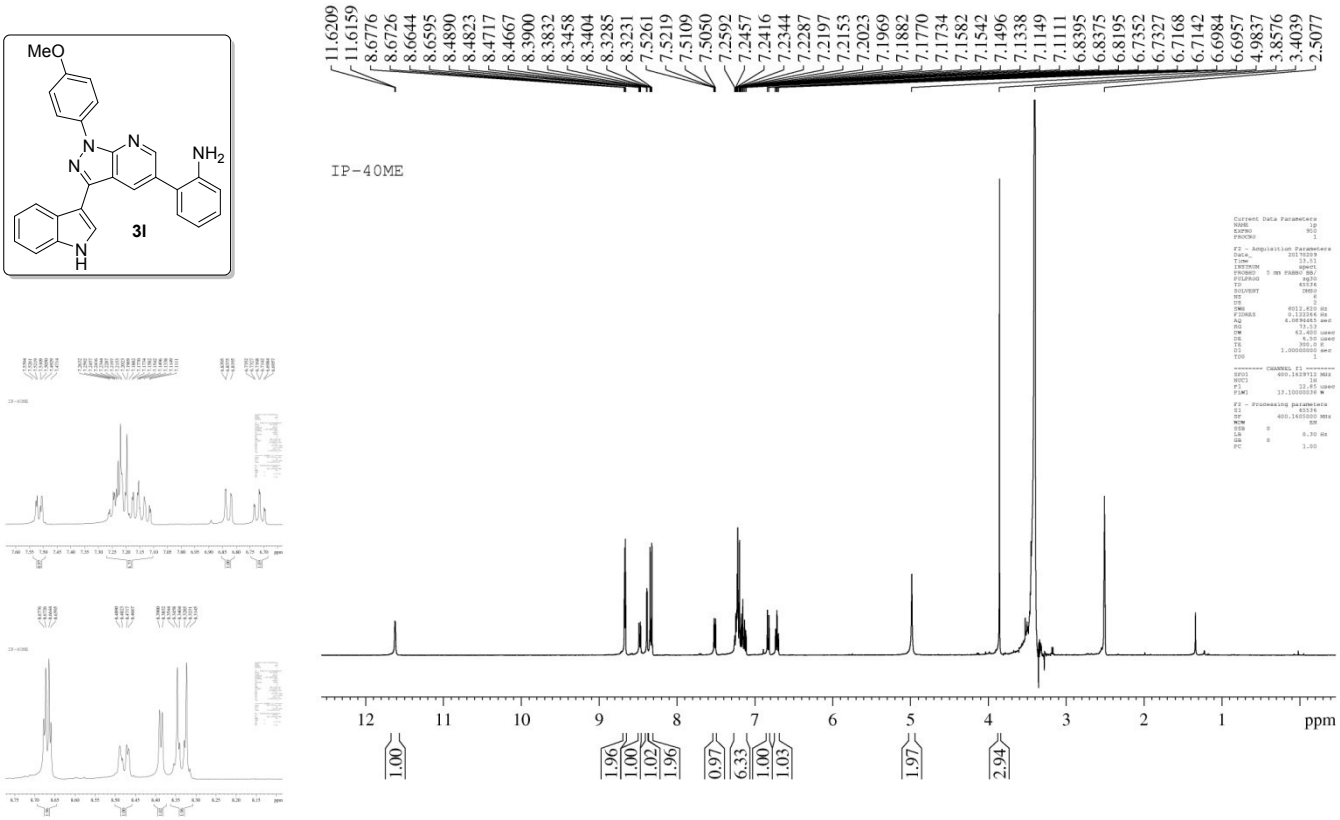
^{1}H NMR Spectra of (**3k)** (400 MHz, DMSO-d6)



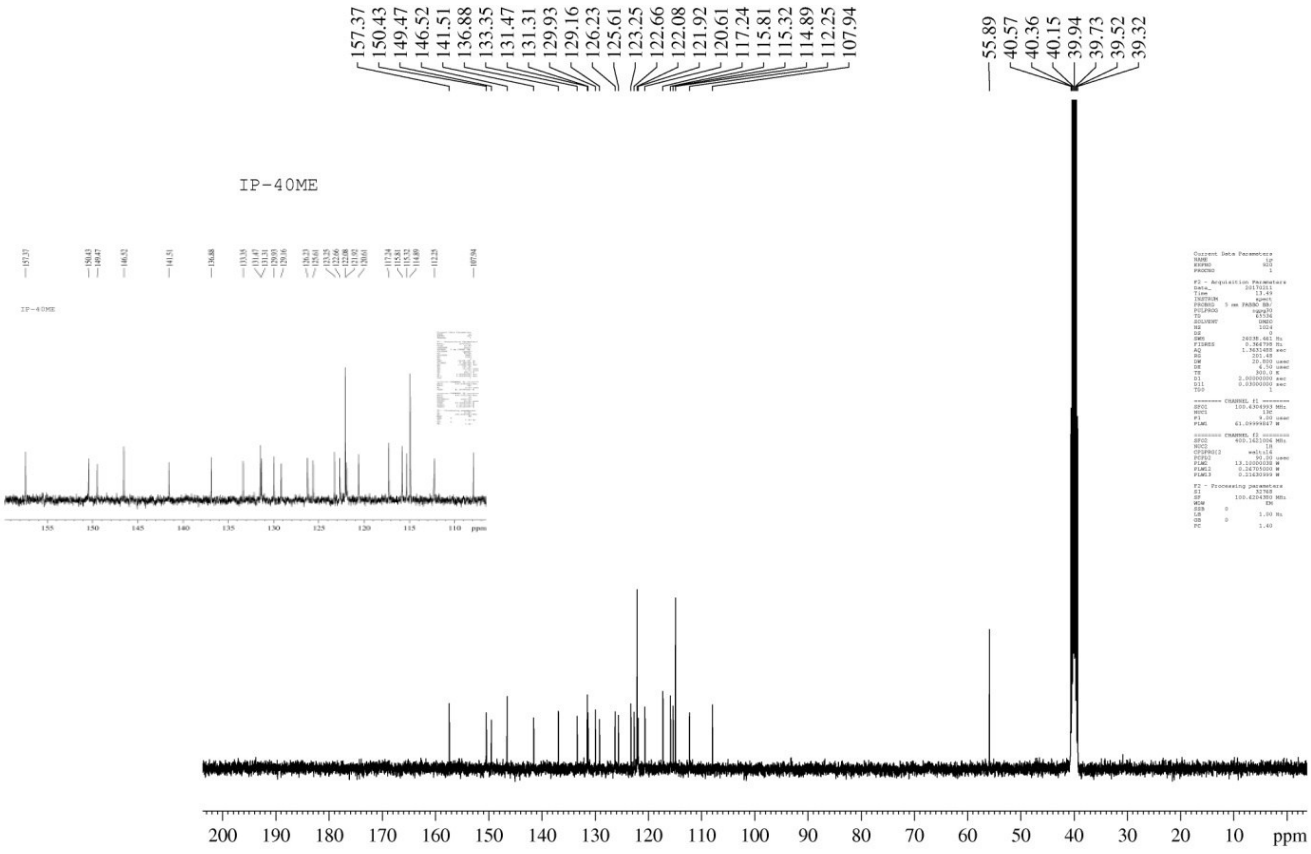
^{13}C NMR Spectra of (**3k)** (100 MHz, DMSO-d6)



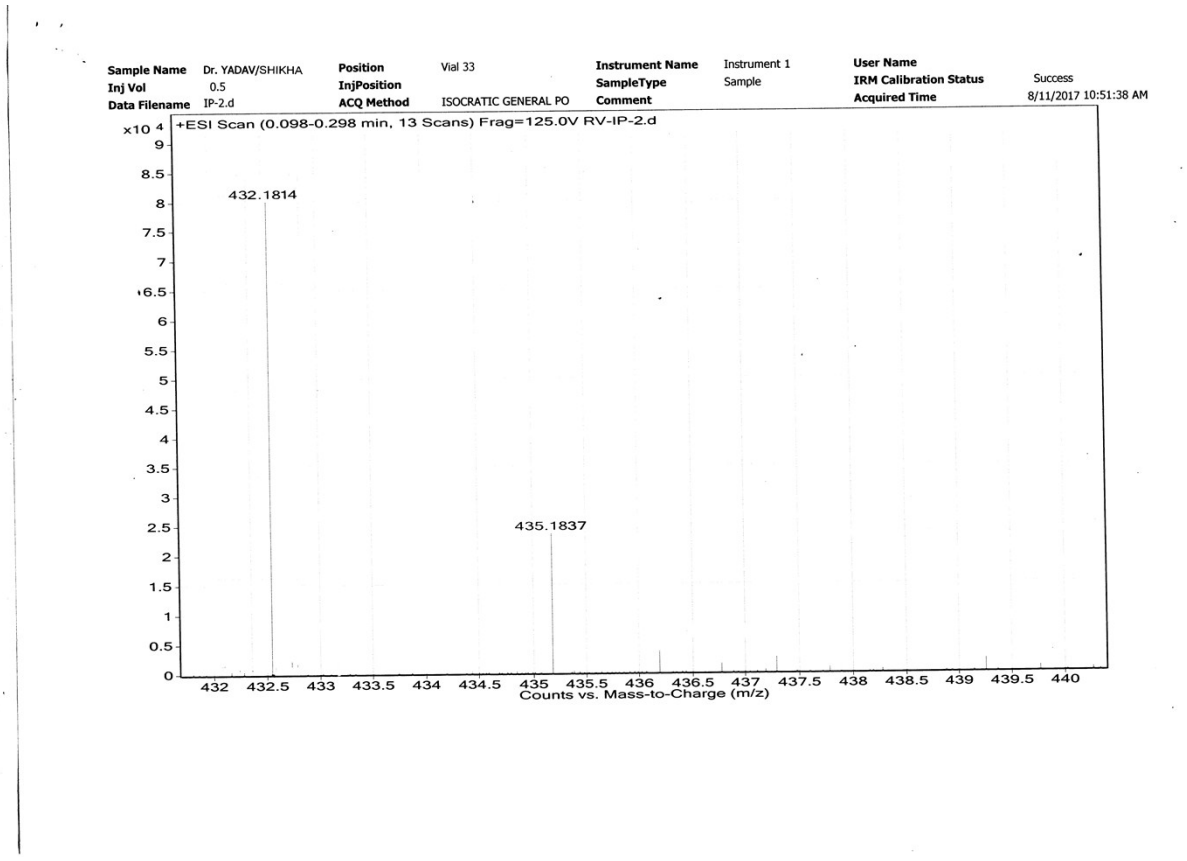
HRMS-**3k**



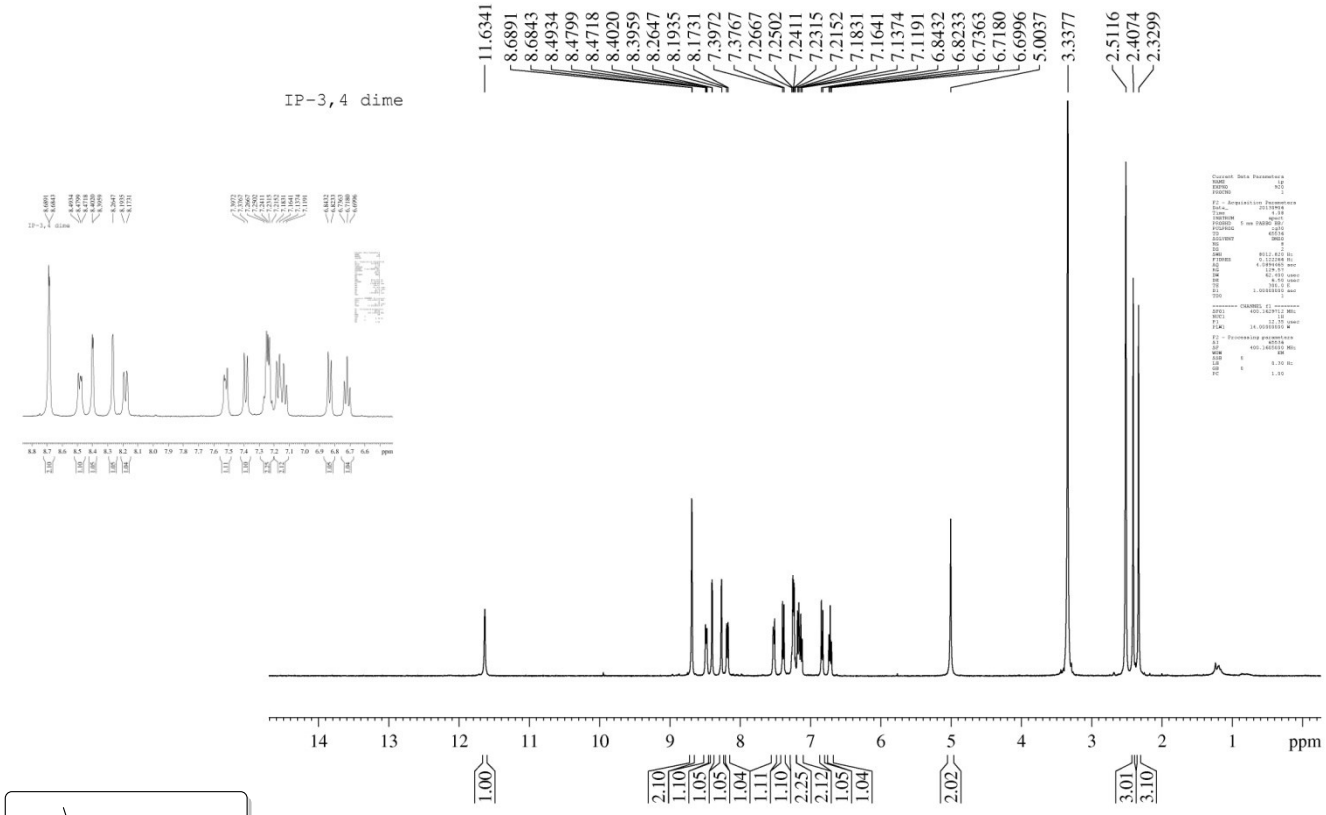
^{1}H NMR Spectra of (**3l**) (400 MHz, DMSO-d6)

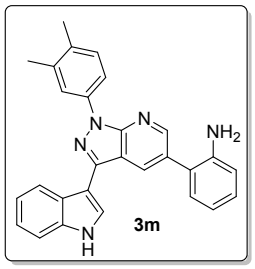


^{13}C NMR Spectra of (**3l)** (100 MHz, DMSO-d6)

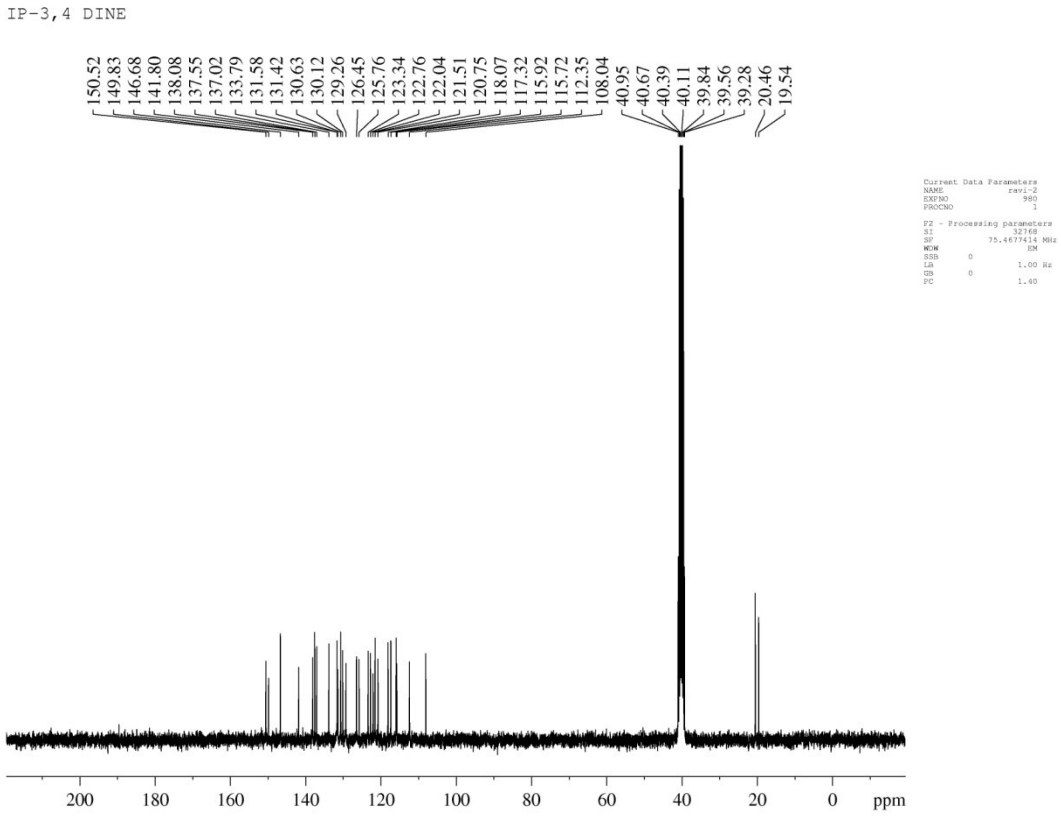


HRMS-**3l**

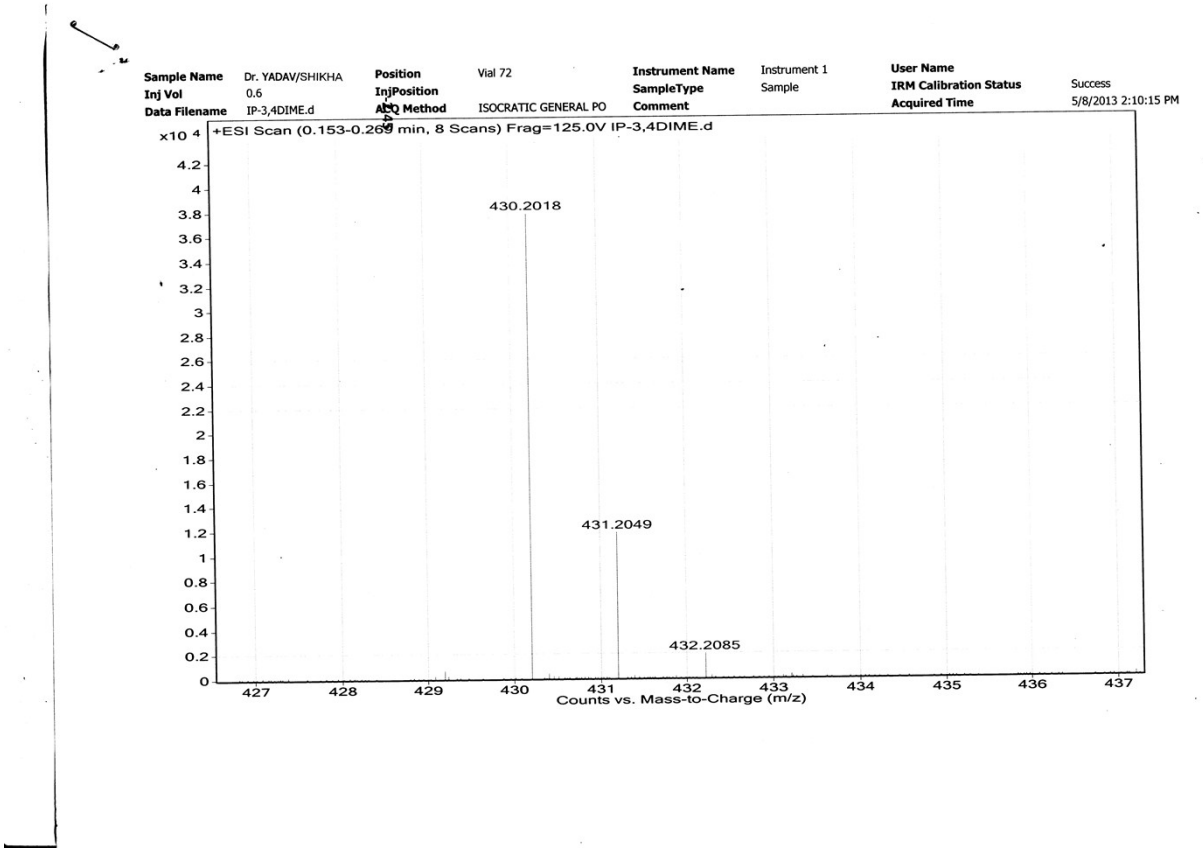




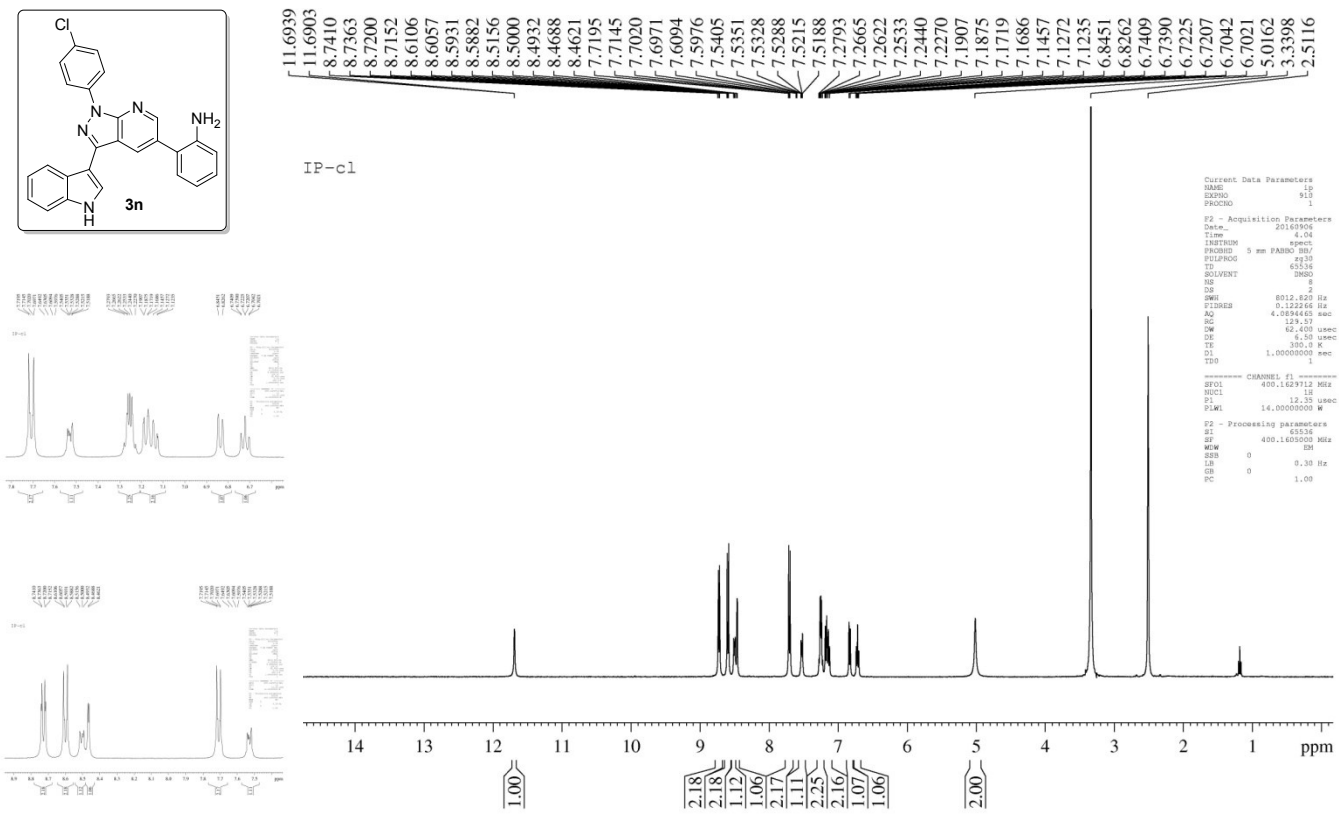
^{1}H NMR Spectra of (**3m)** (400 MHz, DMSO-d6)



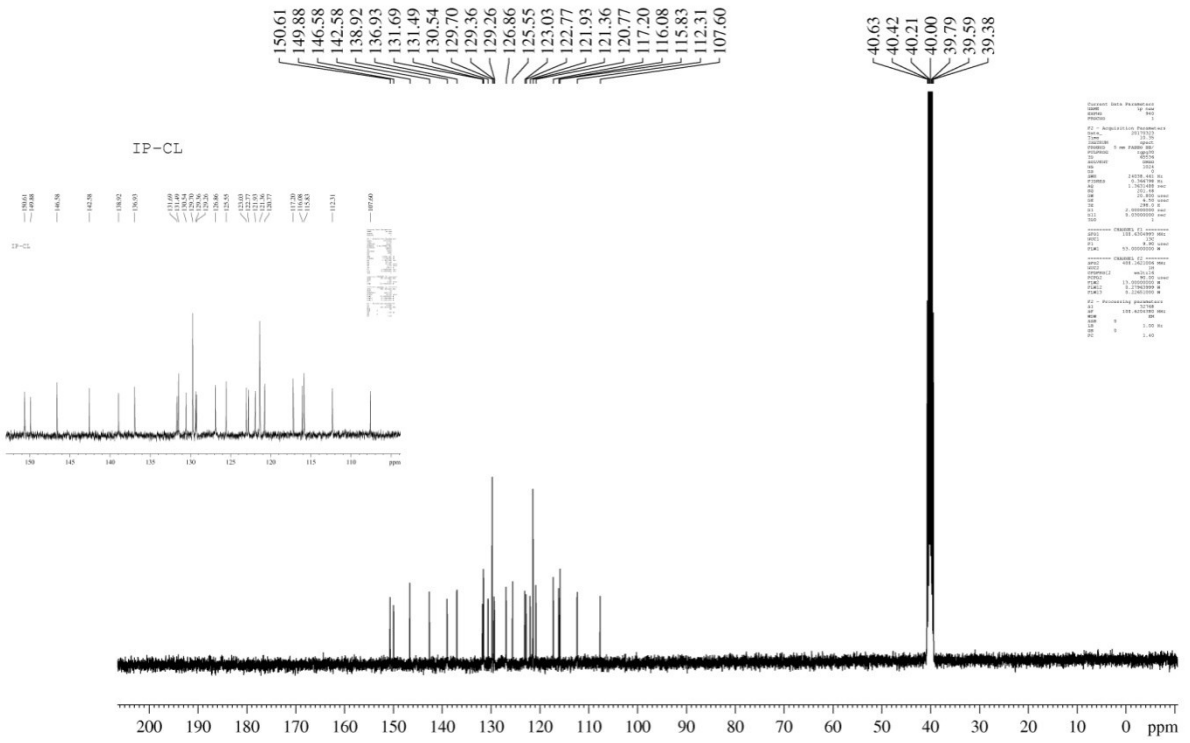
^{13}C NMR Spectra of (**3m)** (100 MHz, DMSO-d6)



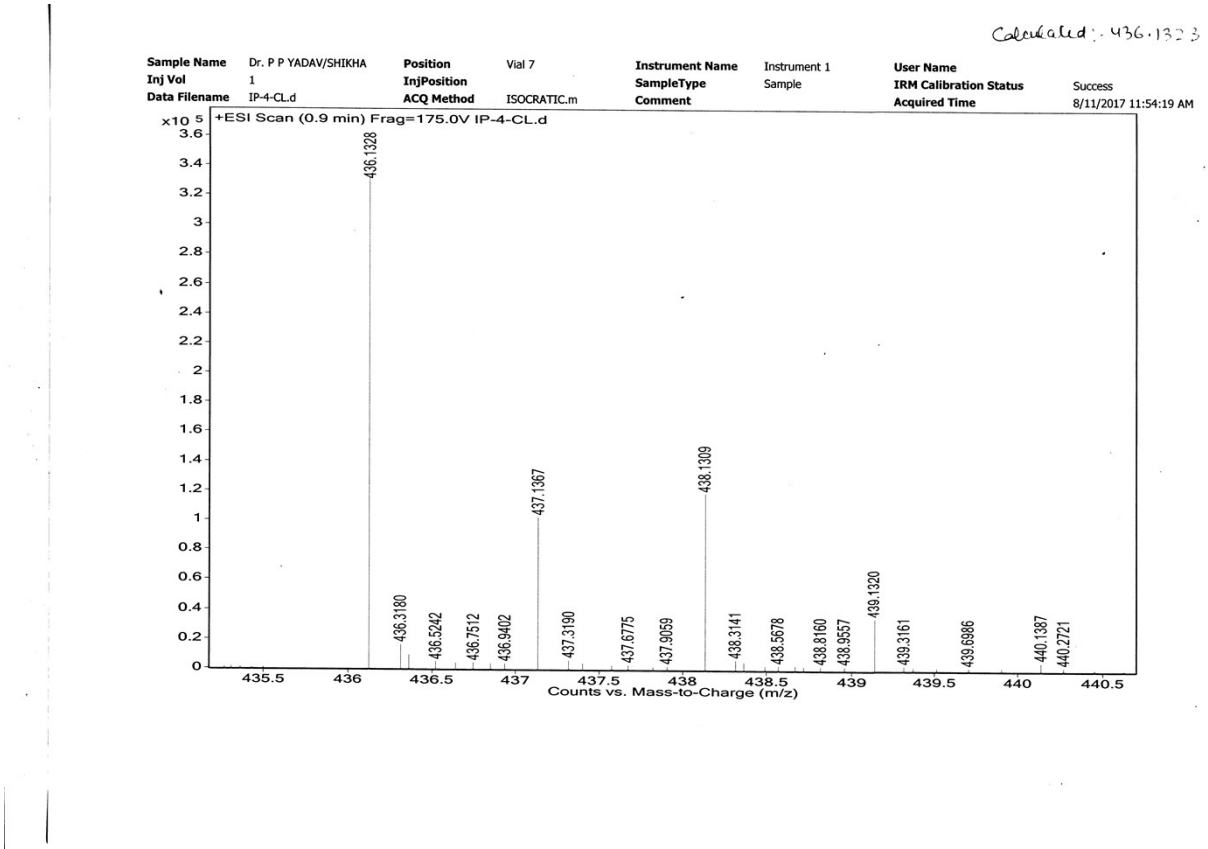
HRMS-**3m**



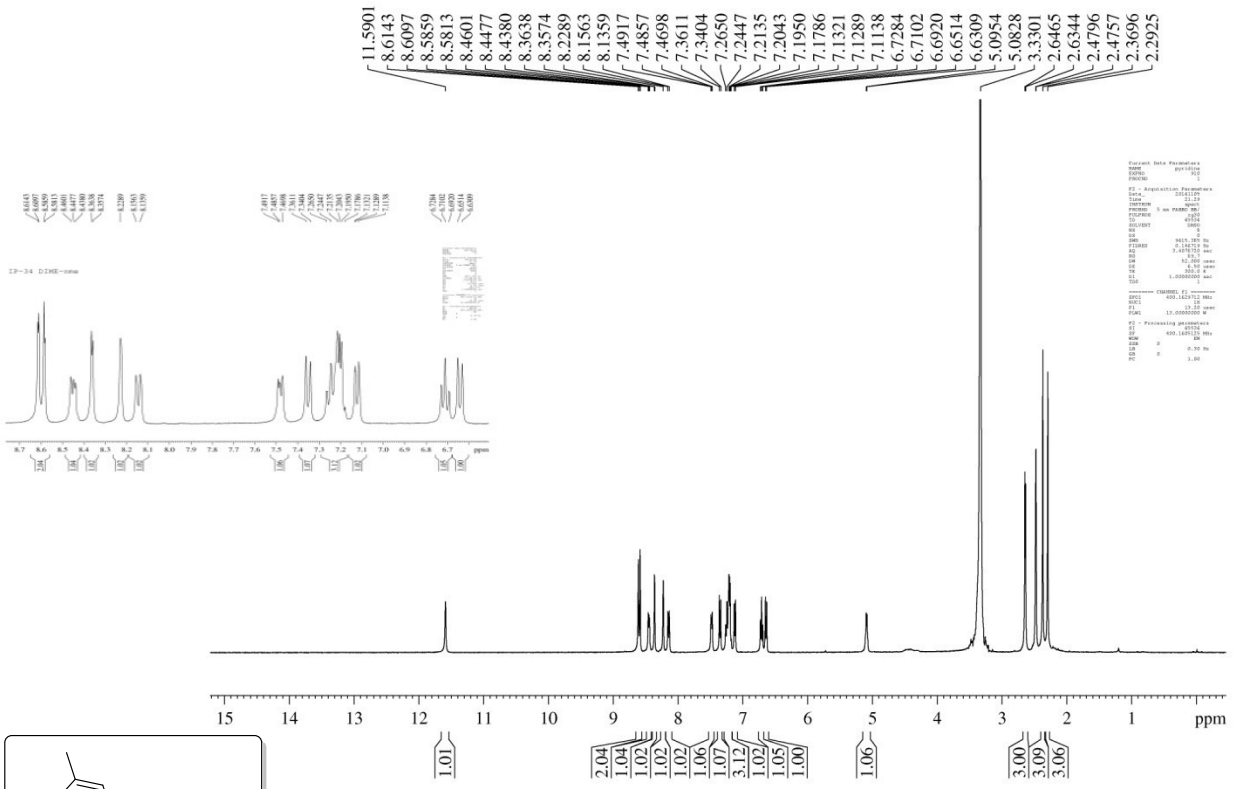
^{1}H NMR Spectra of (**3n)** (400 MHz, DMSO-d6)

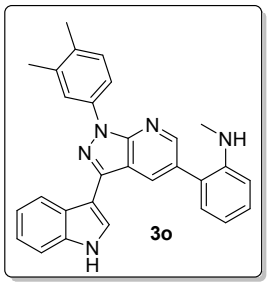


^{13}C NMR Spectra of (**3n)** (100 MHz, DMSO-d6)

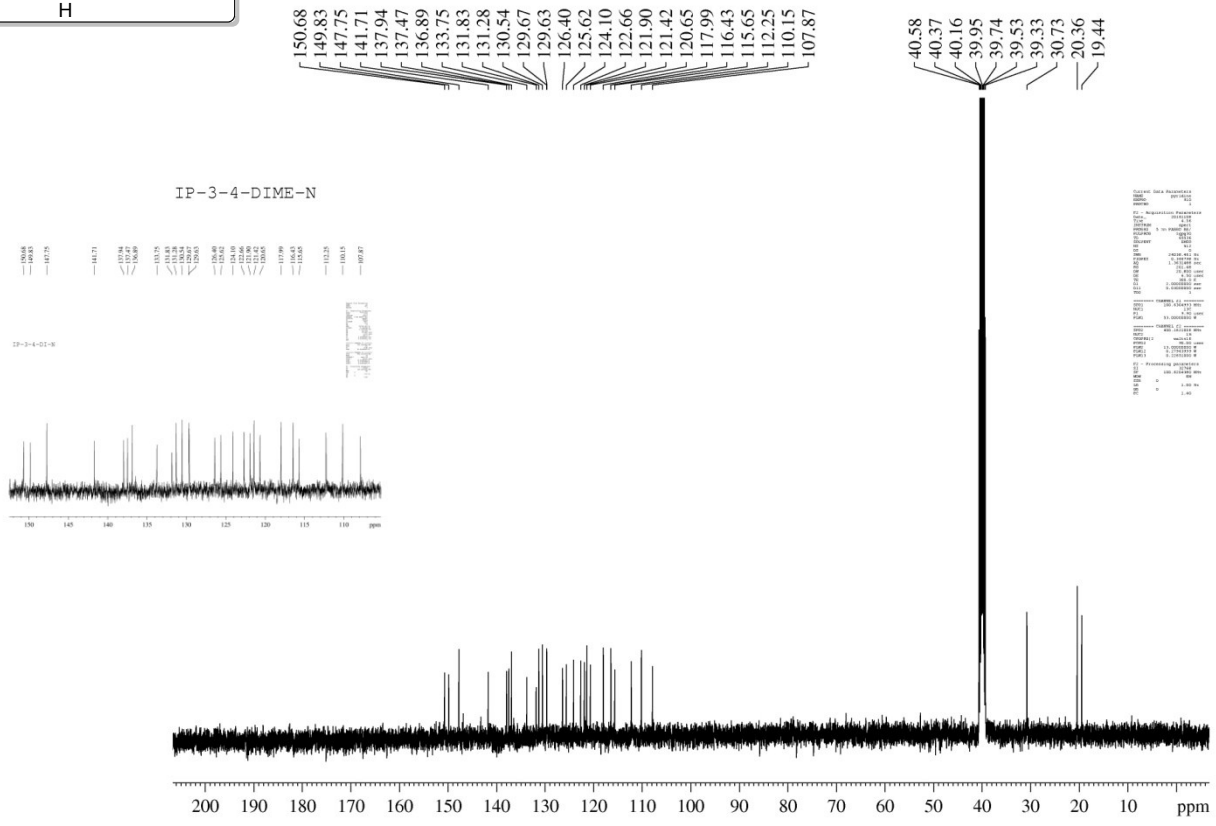


HRMS-**3n**

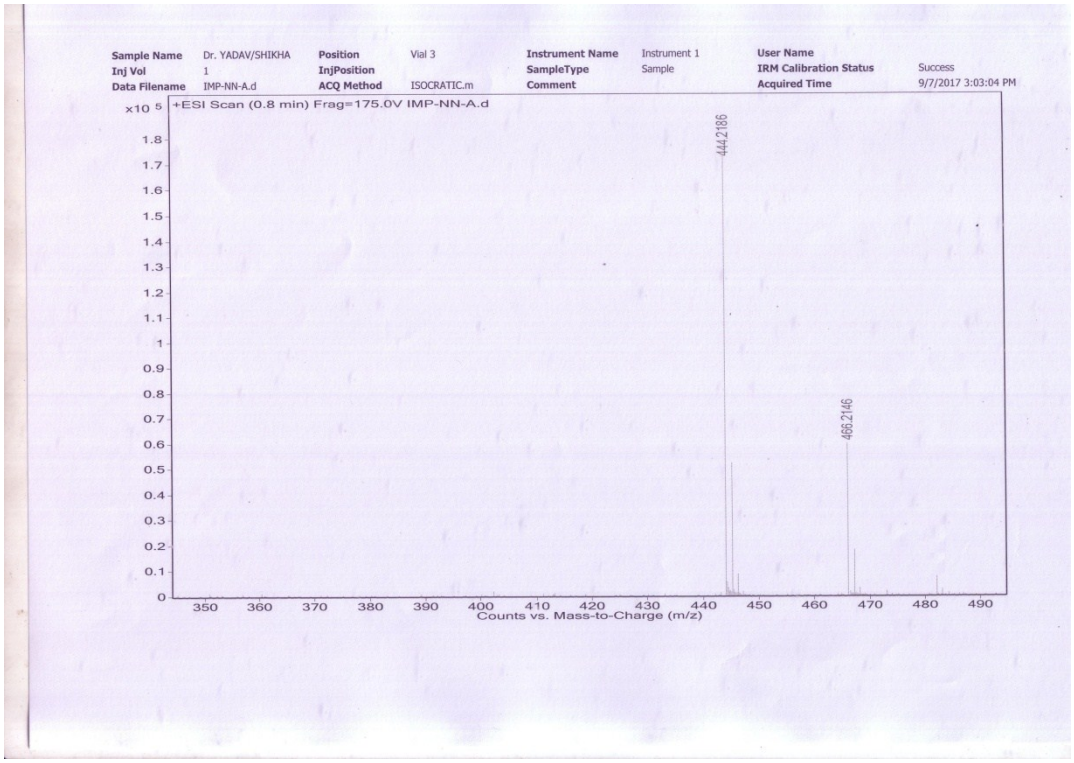




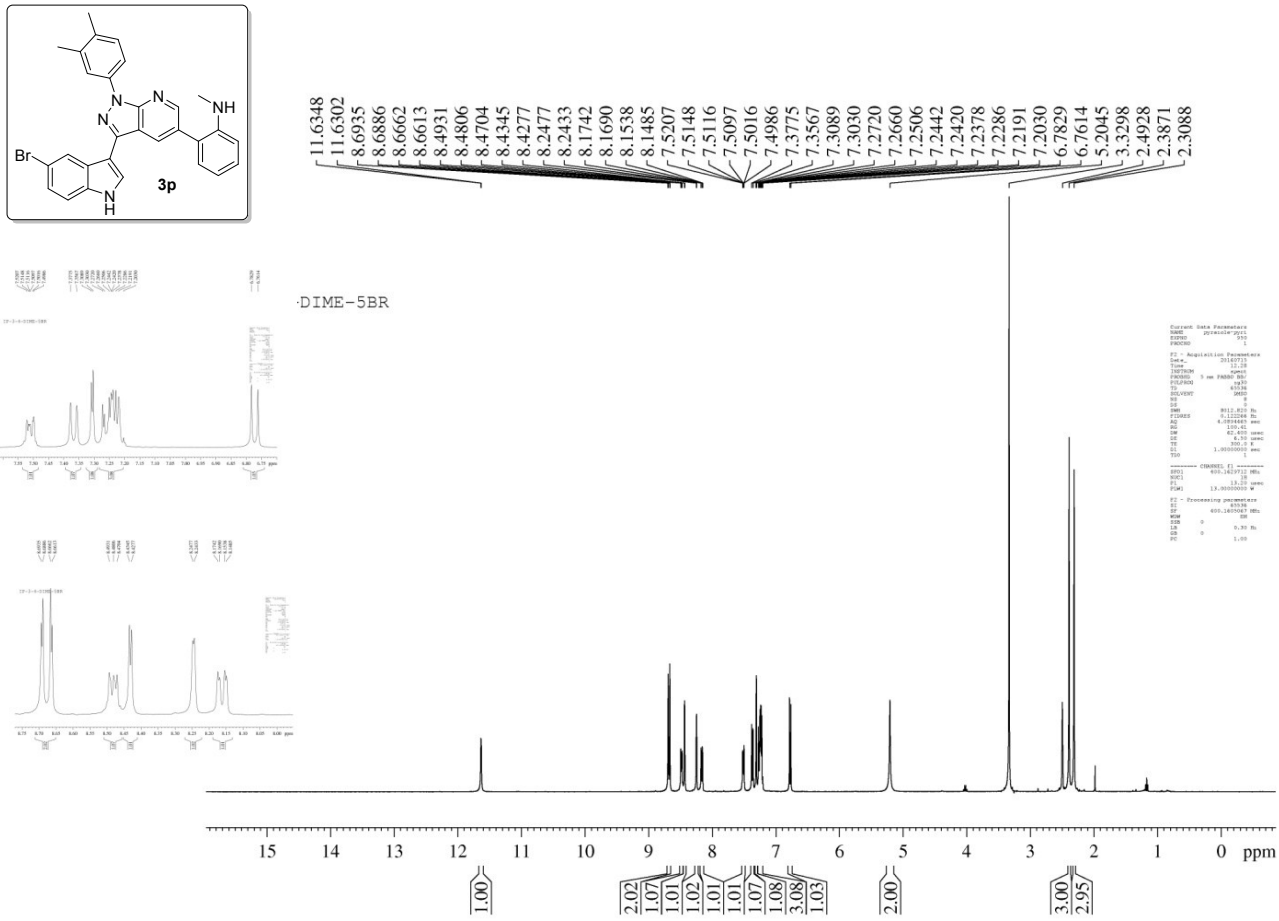
^{1}H NMR Spectra of (**3o)** (400 MHz, DMSO-d6)



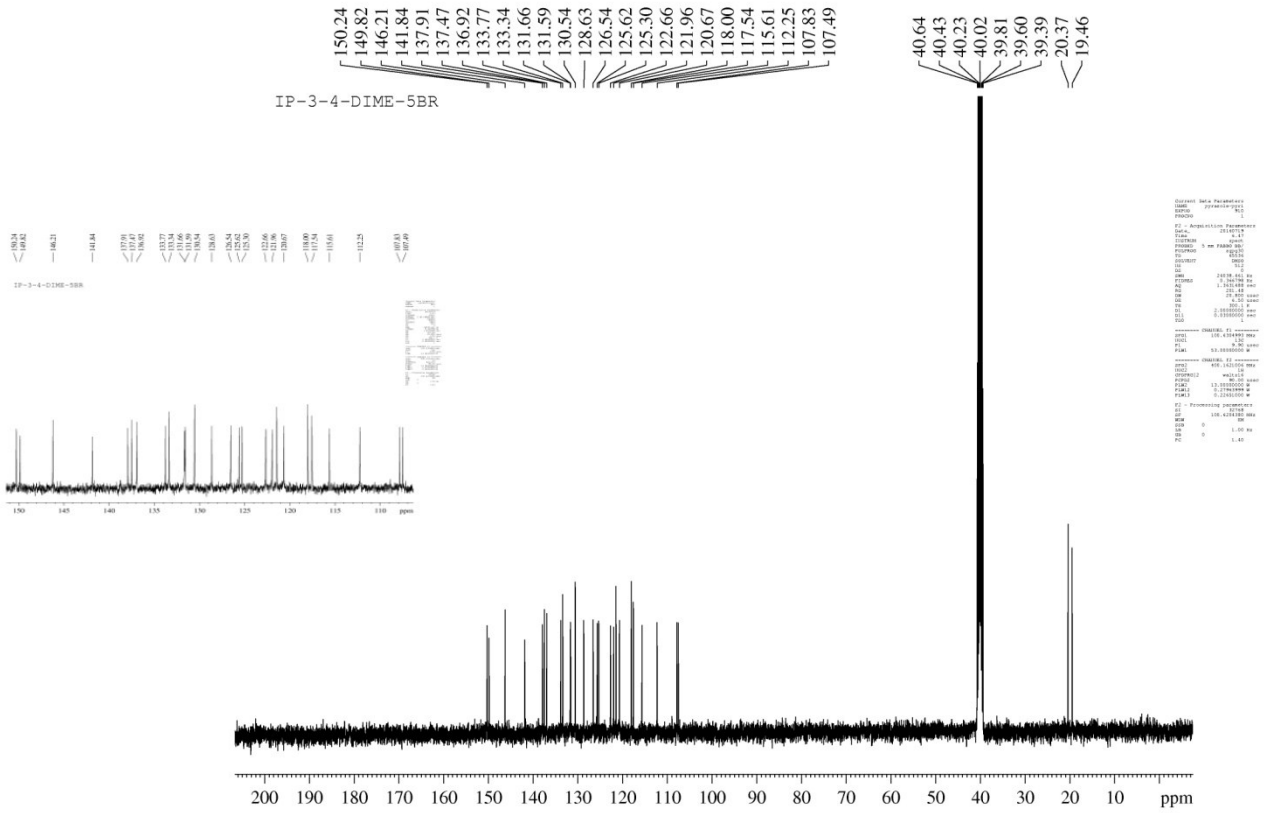
^{13}C NMR Spectra of (**3o)** (100 MHz, DMSO-d6)



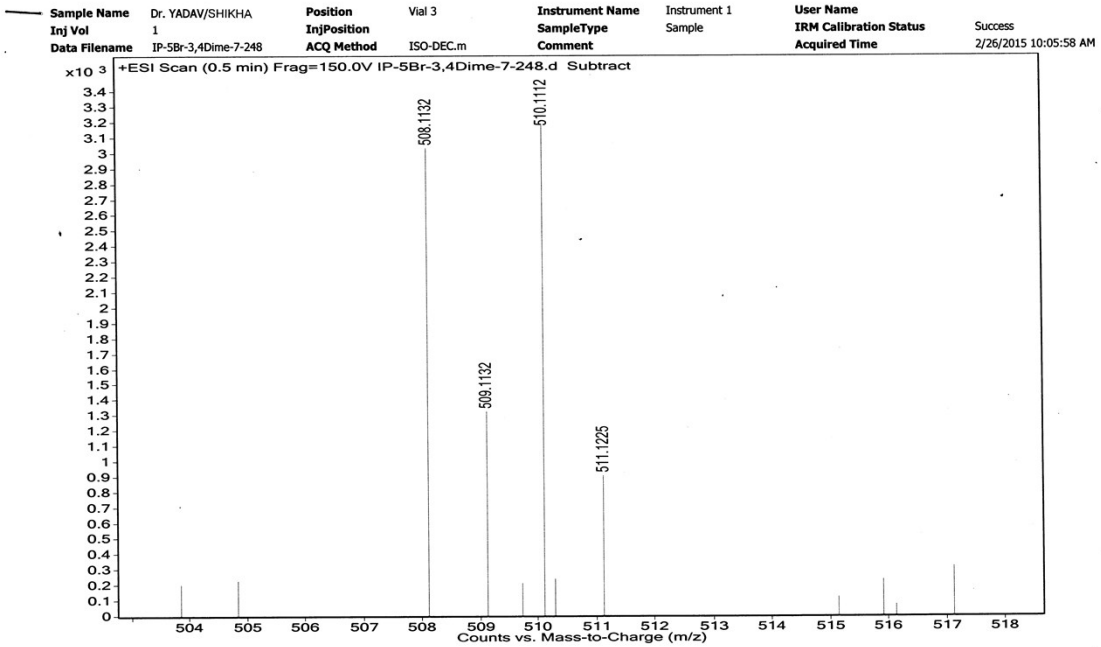
HRMS-**3o**



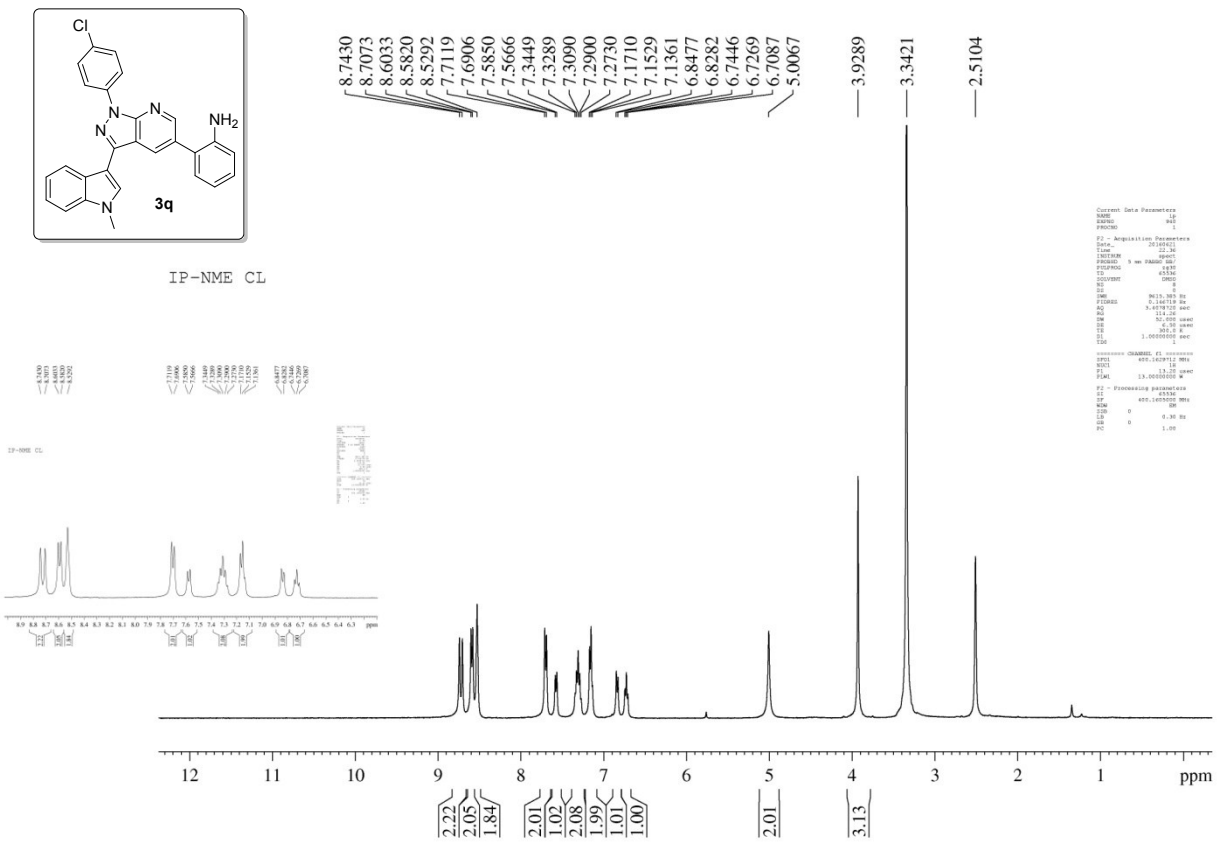
^{1}H NMR Spectra of (**3p)** (400 MHz, DMSO-d6)



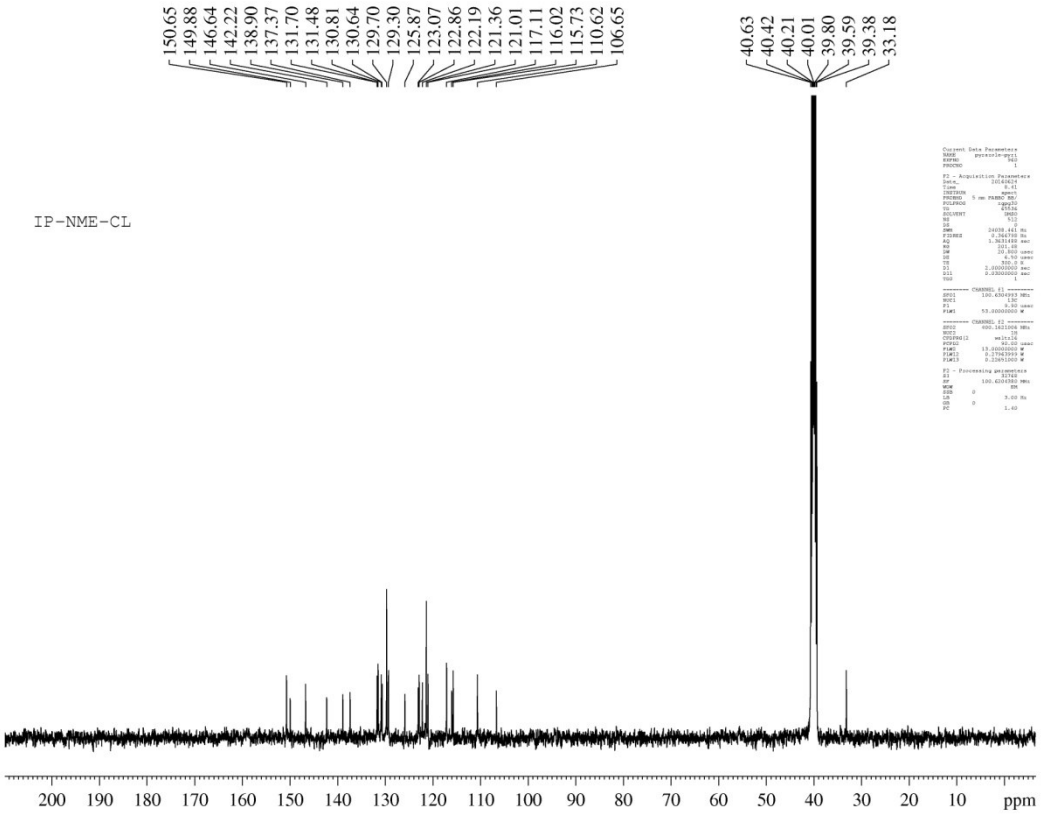
^{13}C NMR Spectra of (**3p)** (100 MHz, DMSO-d6)



HRMS-**3p**

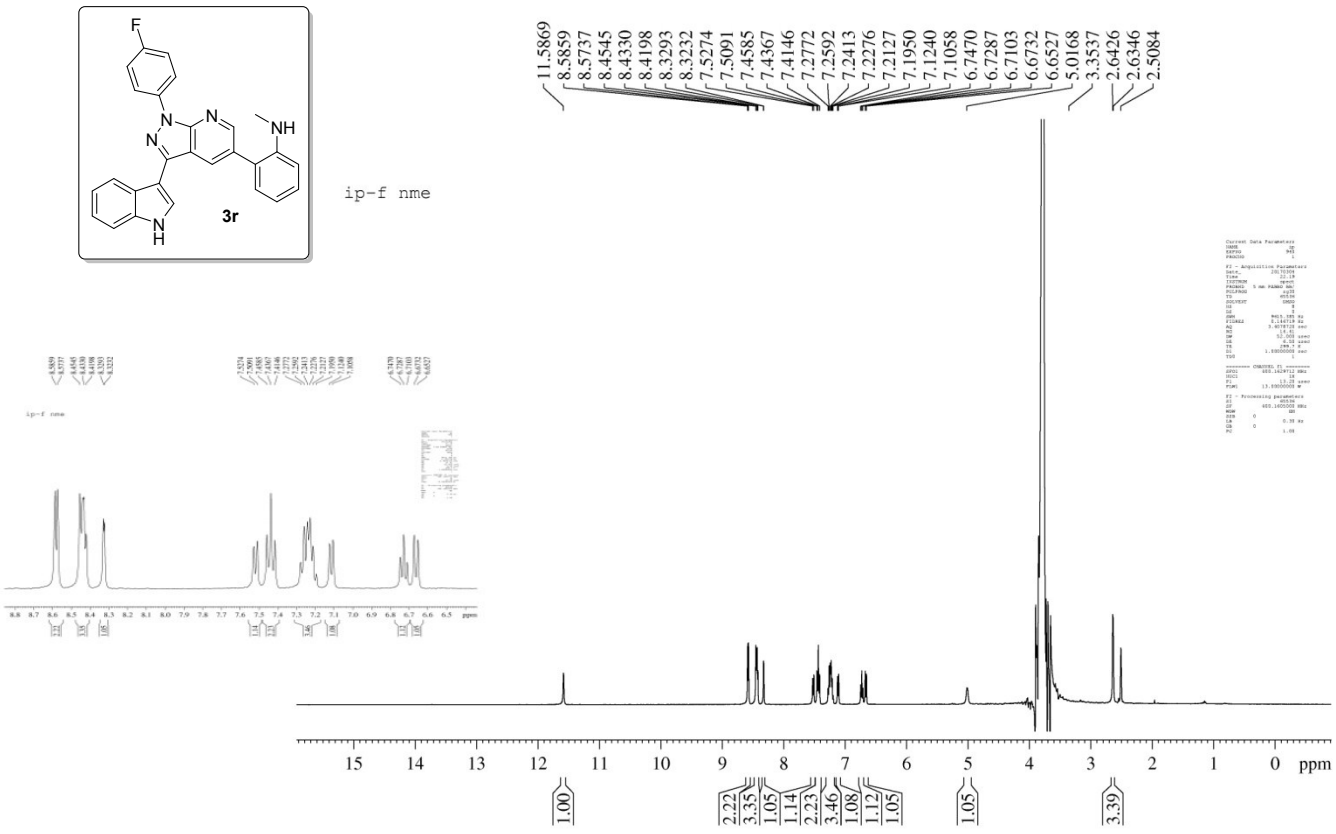


^{1}H NMR Spectra of (**3q)** (400 MHz, DMSO-d6)

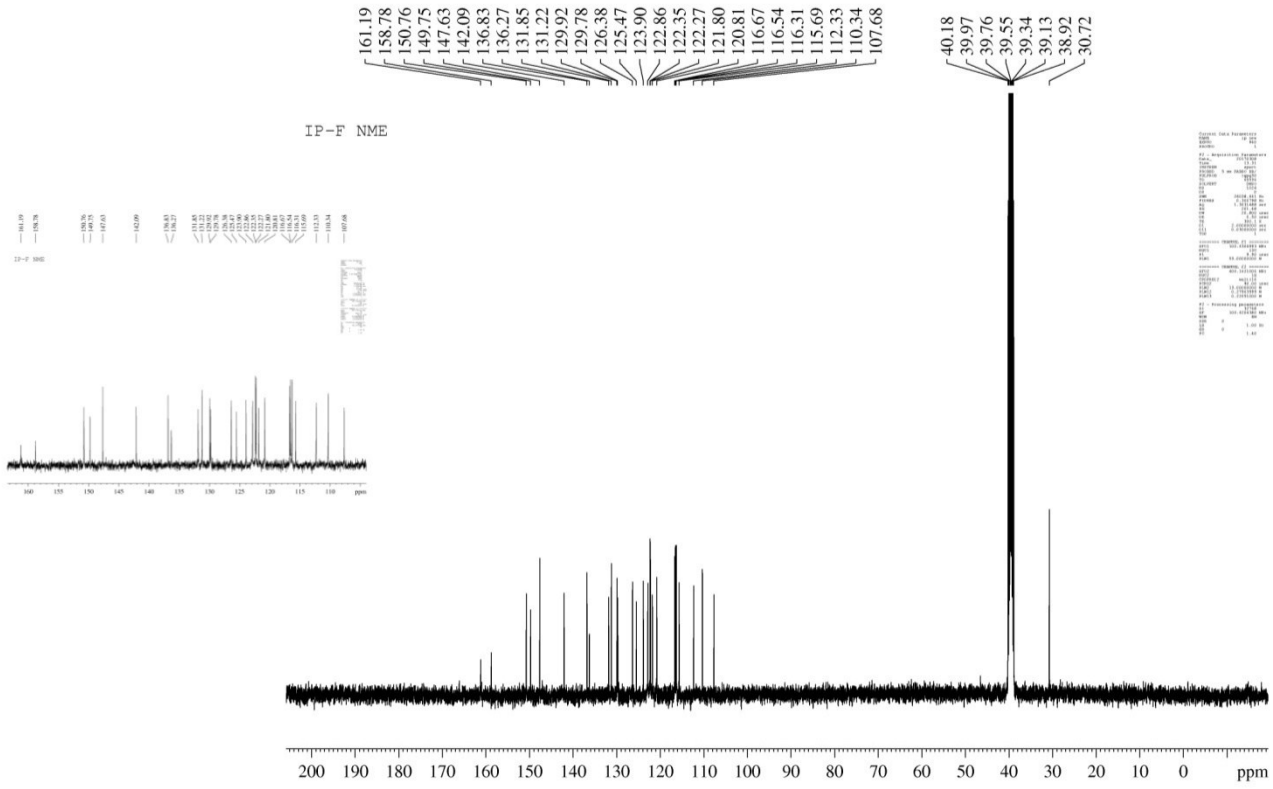


^{13}C NMR Spectra of (**3q)** (100 MHz, DMSO-d6)

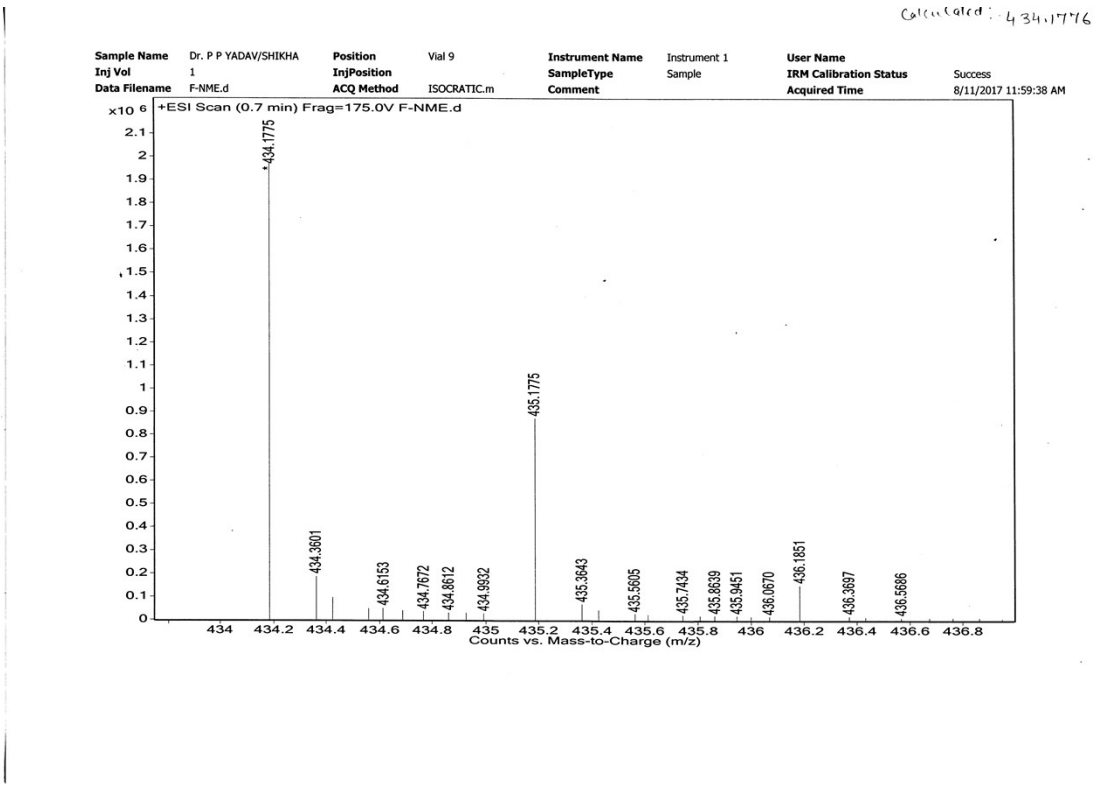
HRMS-**3q**



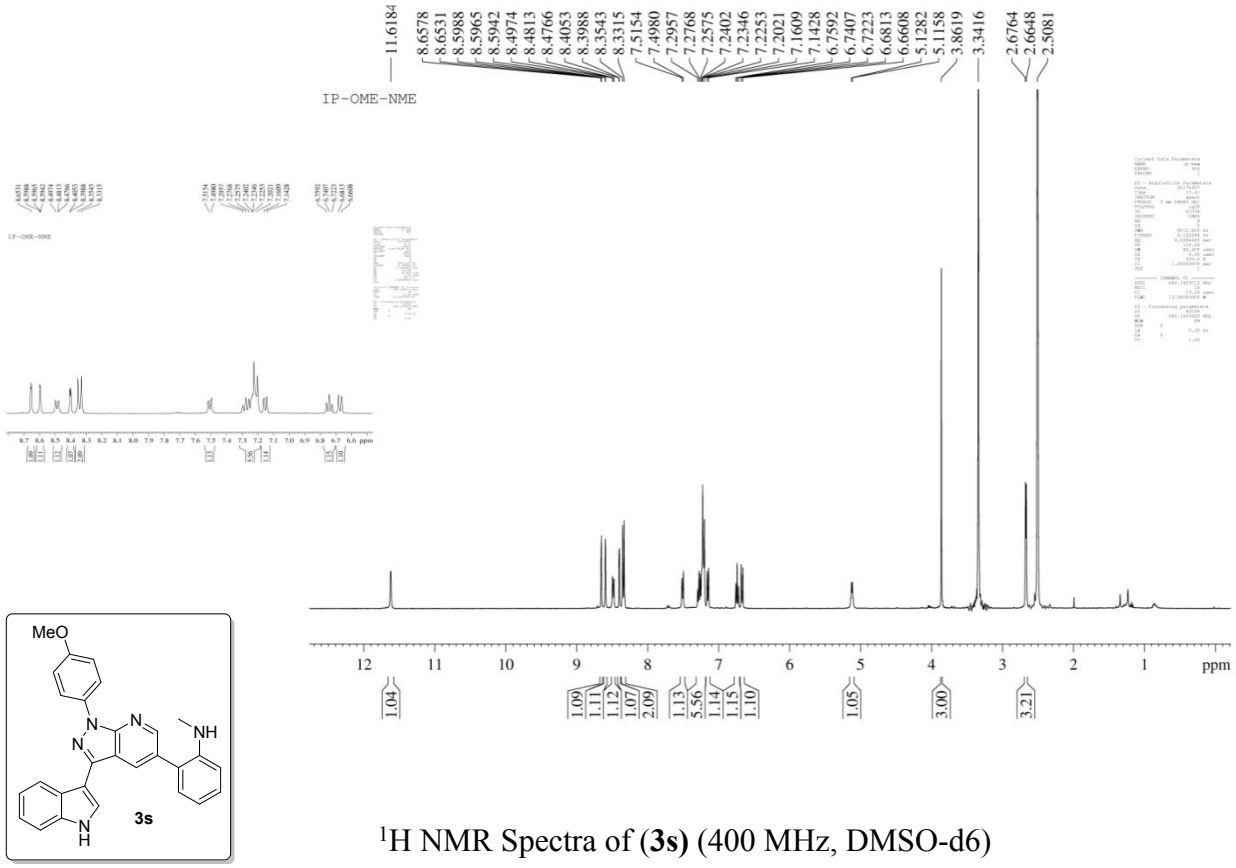
^{1}H NMR Spectra of (**3r)** (400 MHz, DMSO-d6)



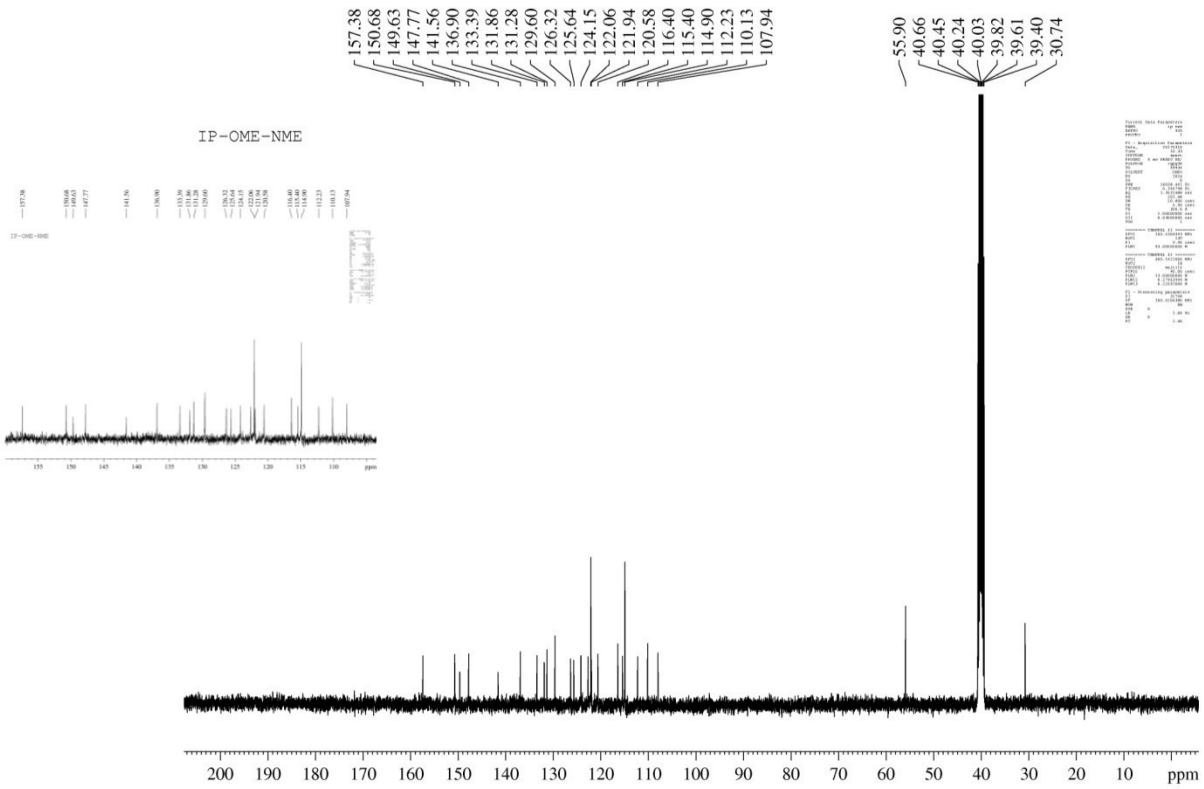
^{13}C NMR Spectra of (**3r)** (100 MHz, DMSO-d6)



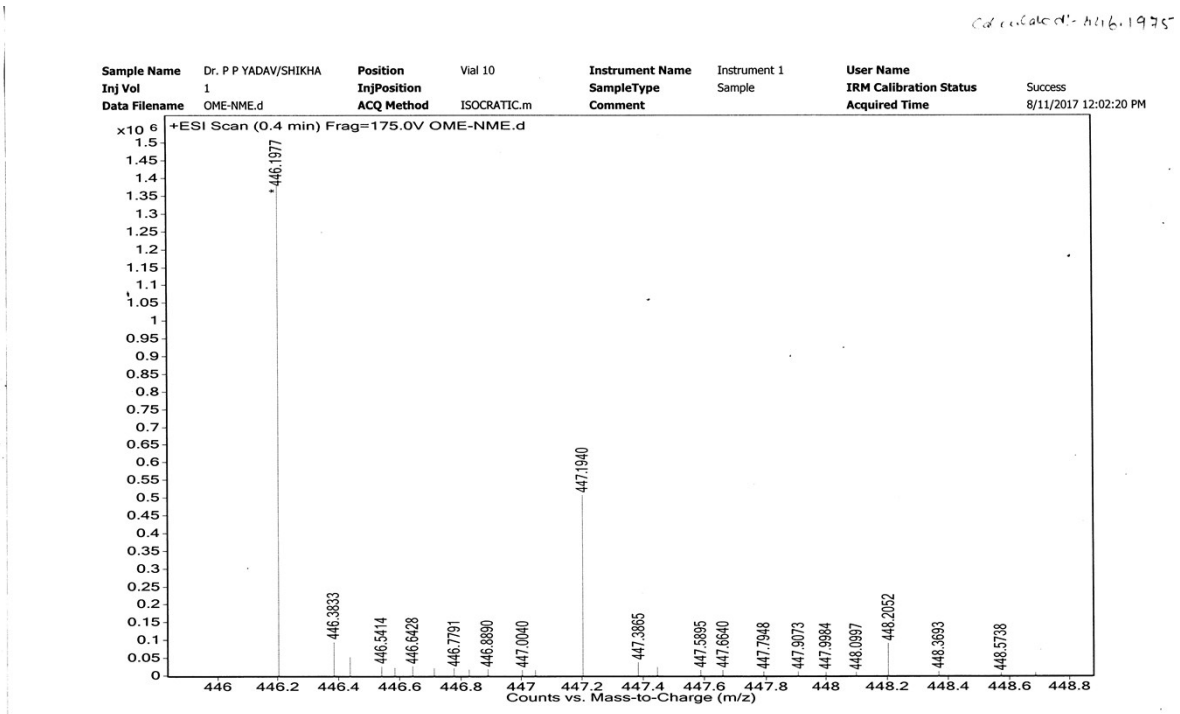
HRMS-**3r**



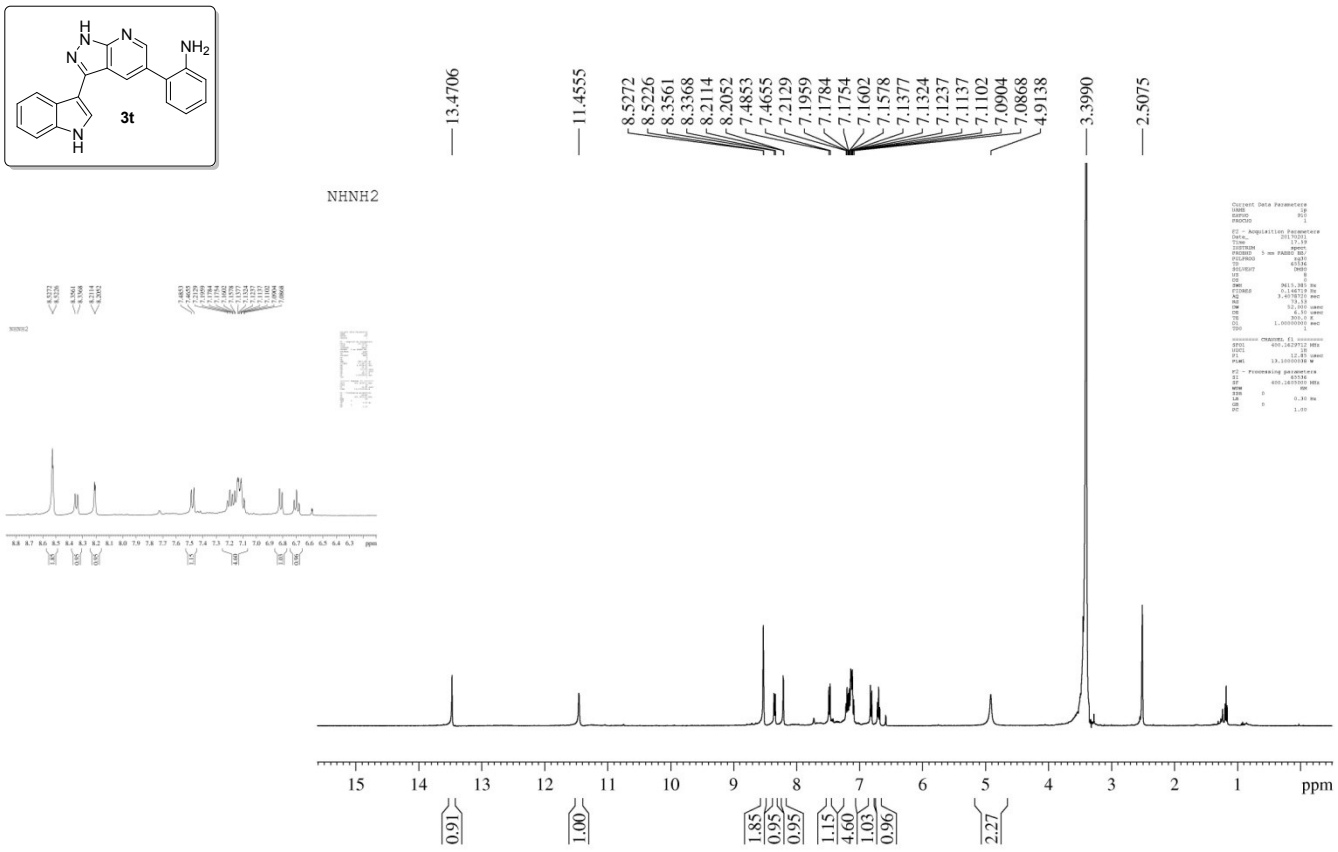
^{1}H NMR Spectra of (**3s)** (400 MHz, DMSO-d6)



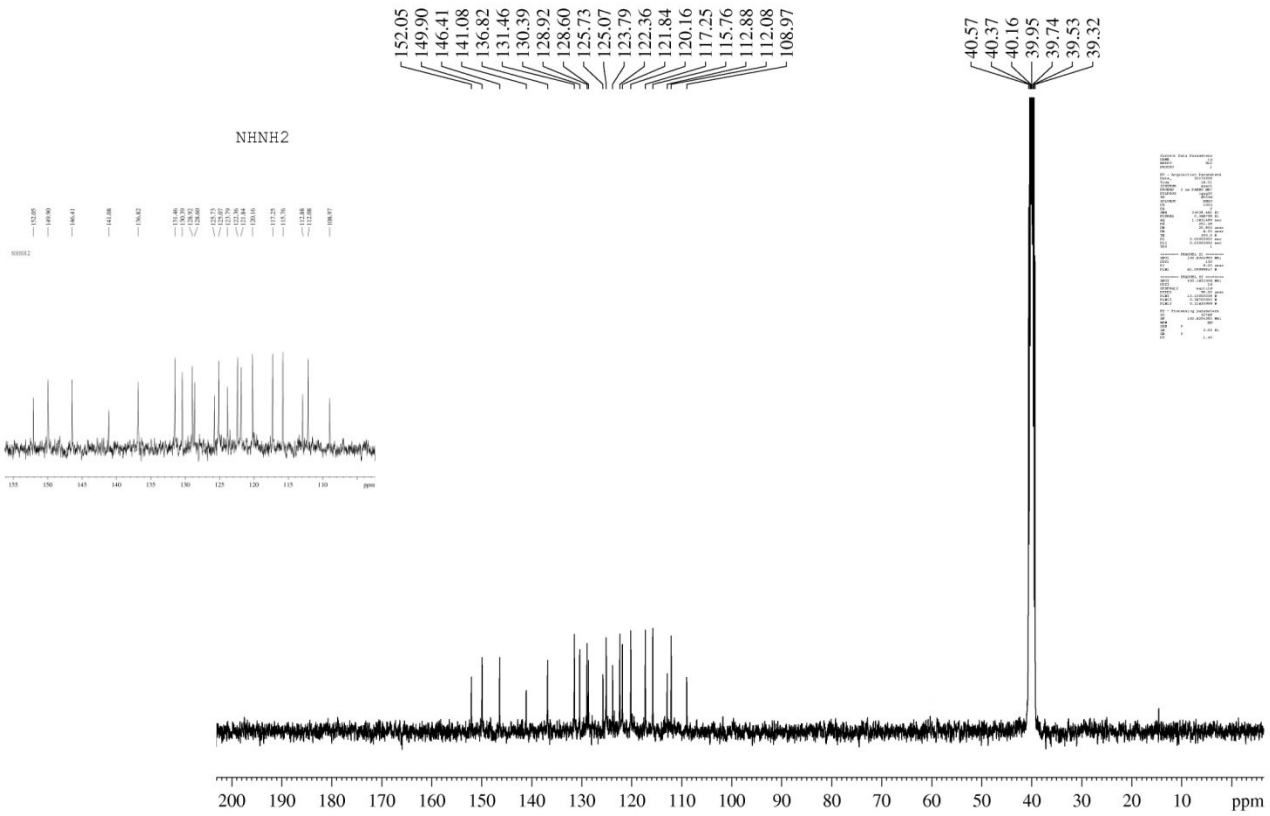
^{13}C NMR Spectra of (**3s)** (100 MHz, DMSO-d6)



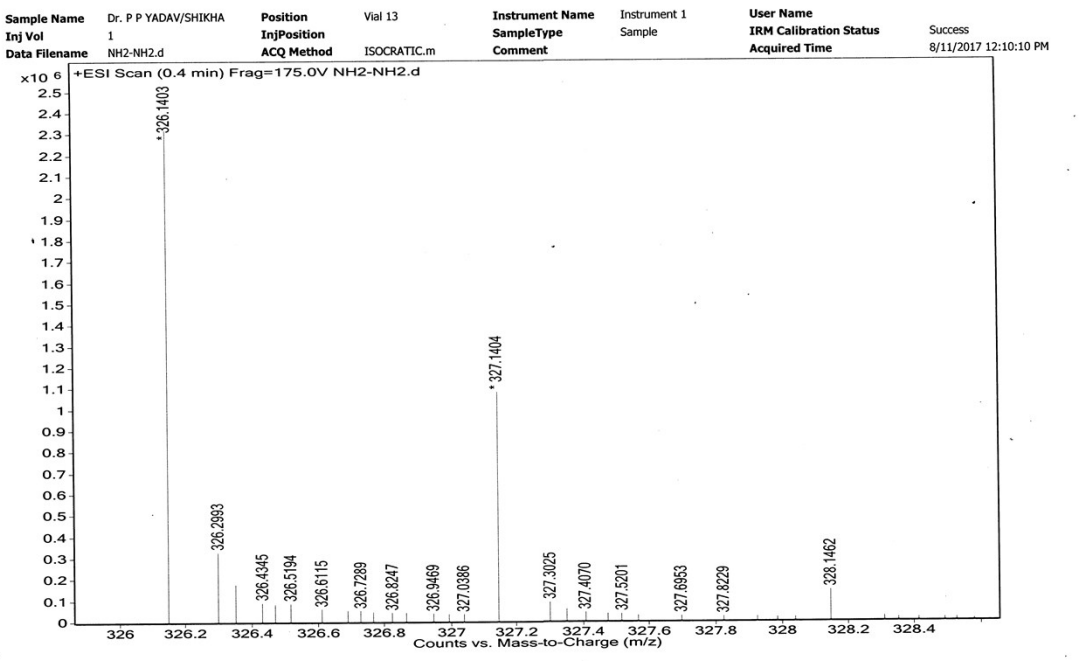
HRMS-**3s**



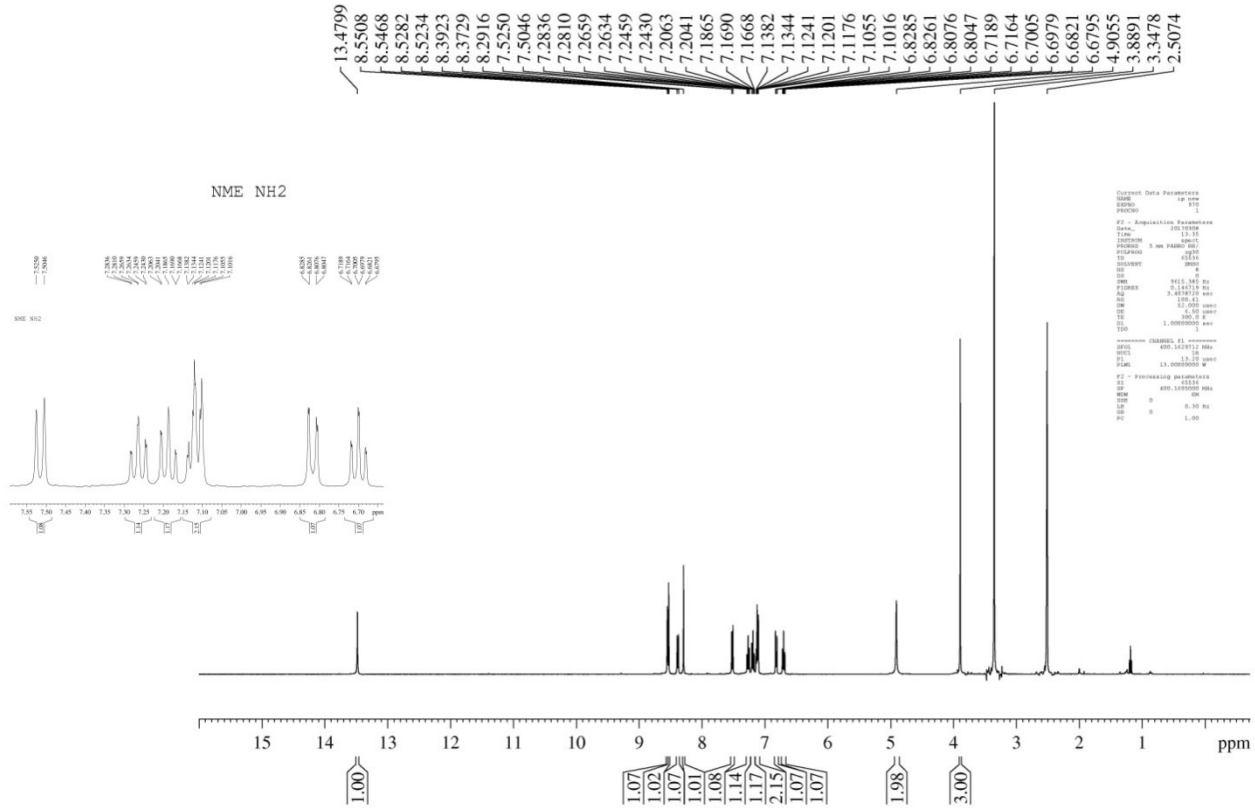
^{1}H NMR Spectra of (**3t)** (400 MHz, DMSO-d6)

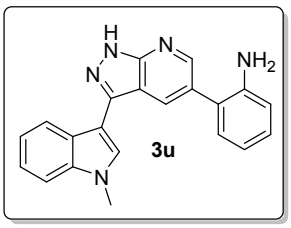


^{13}C NMR Spectra of (**3t**) (100 MHz, DMSO-d6)

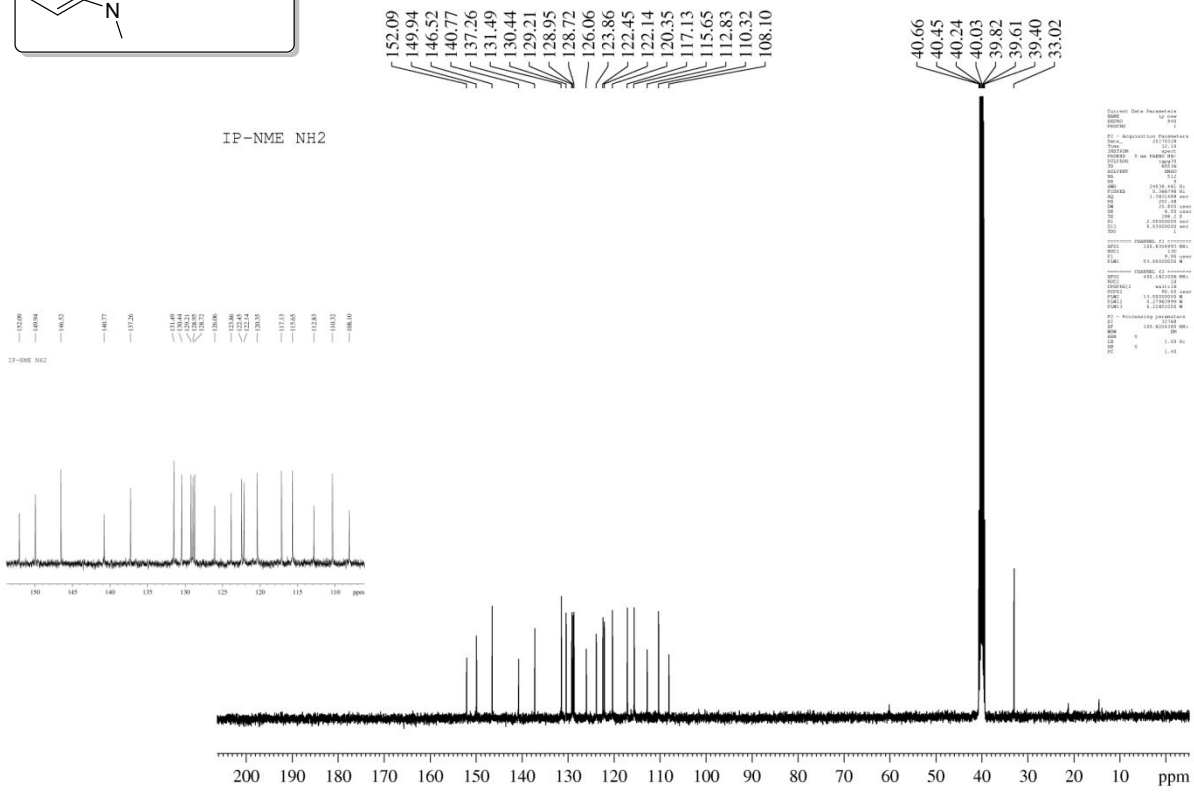


HRMS-**3t**

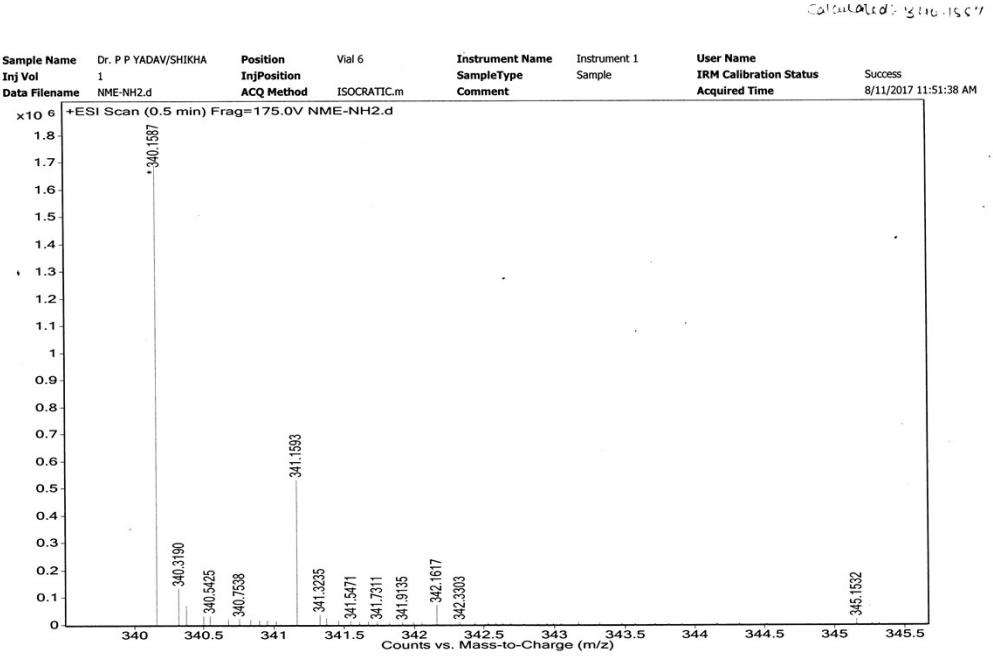




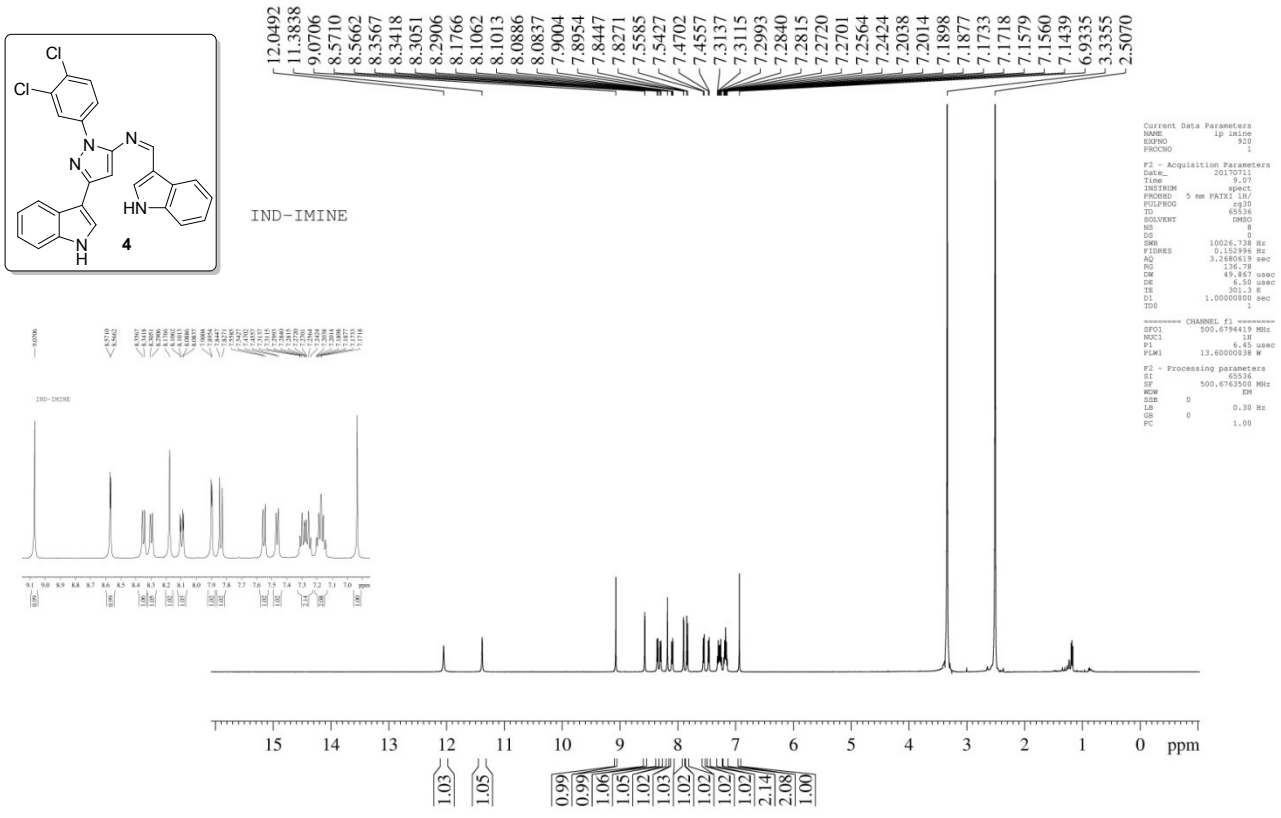
^{1}H NMR Spectra of (**3u)** (400 MHz, DMSO-d6)



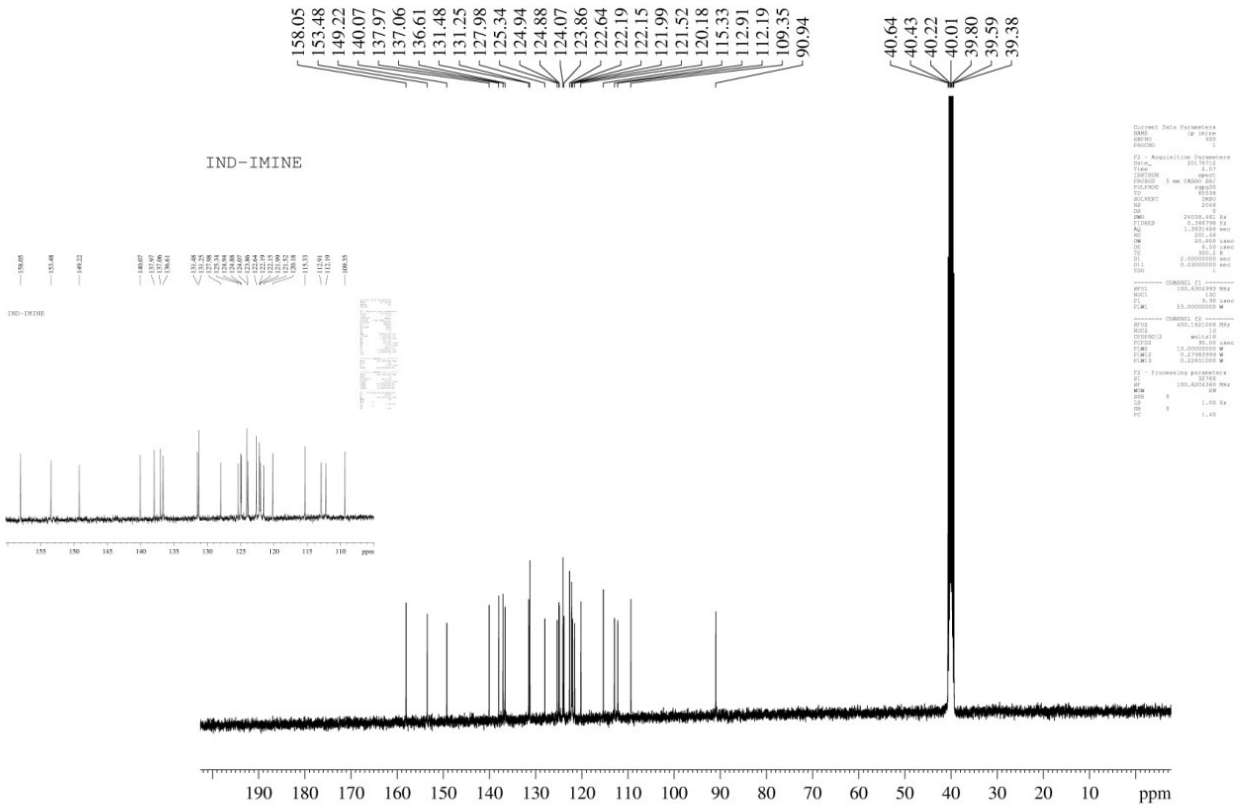
^{13}C NMR Spectra of (**3u)** (100 MHz, DMSO-d6)



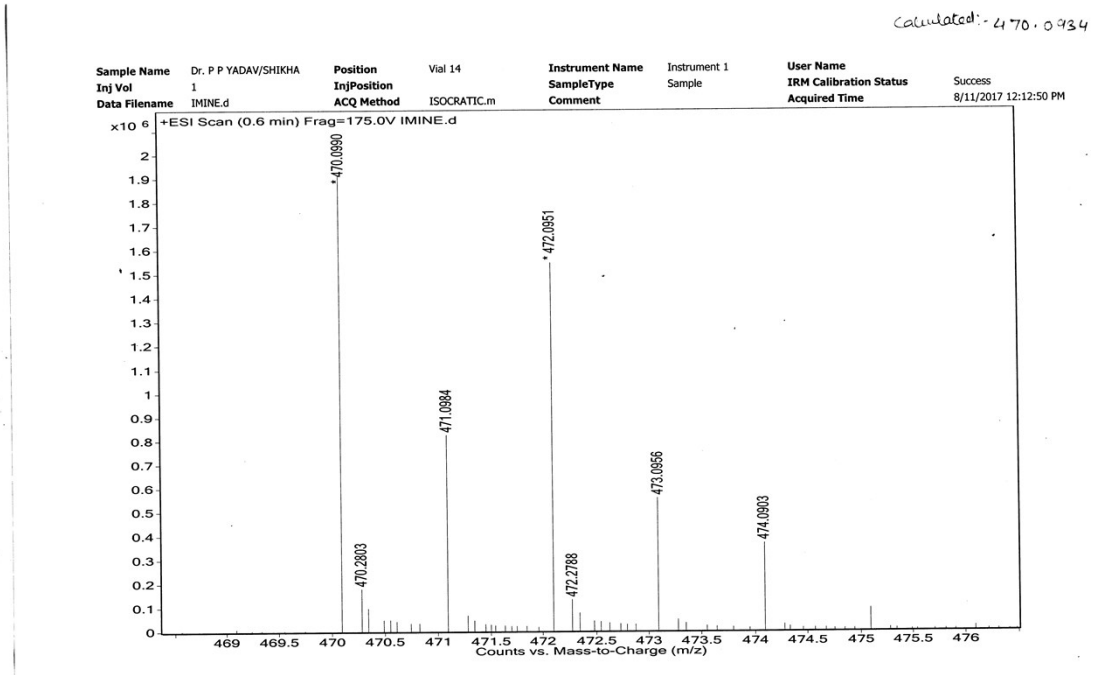
HRMS-**3u**



^{1}H NMR Spectra of (**4**) (400 MHz, DMSO-d6)



^{13}C NMR Spectra of (**4**) (100 MHz, DMSO-d6)



HRMS-**4**