Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of α, β and γ-Carbolines *via* Pd-mediated C-H activation

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Supplementary Data

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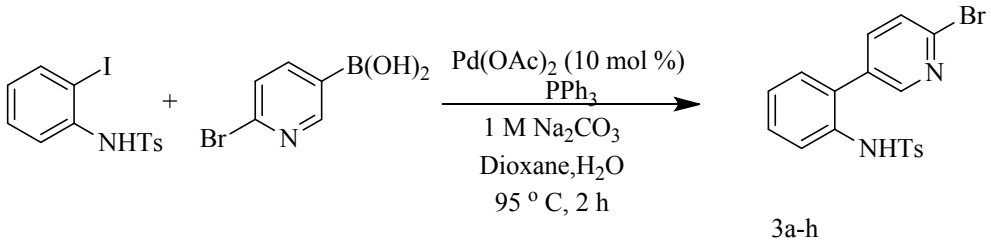
General methods: High quality reagents were purchased from Sigma Aldrich. Analytical grade commercial reagents and solvents were purified by standard procedures prior to use. Chromatographic purification was done with 60-120 mesh silica gel (Merck). For reaction monitoring, pre-coated silica gel 60 F254 sheets (Merck) were used. ^{1}H NMR (200 MHz) spectra were recorded on a BRUCKER-AC 200 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, brs = broad singlet), coupling constant (Hz). ^{13}C NMR (50 MHz) spectra were recorded on a BRUKER-AC 200 MHz. Spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.23 ppm). HRMS (ESI) spectra were taken using Waters Xevo G2 QTof mass spectrometer.

General method for the 4-methyl-N-(2-(pyridin-3-yl)phenyl)benzenesulfonamide derivatives:



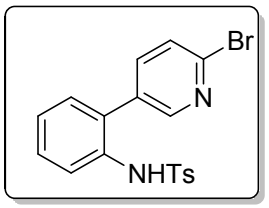
3a-h

In a two necked round bottomed flask N-(2-iodophenyl)-4-methylbenzenesulfonamide (1 mmol), (6-bromopyridin-3-yl)boronic acid (1.2 mmol), PPh_3 (0.25 mmol), $Pd(OAc)_2$ (10 mol %) were taken in 1:1 mixture of 1M Na_2CO_3 and H_2O solvent and it then degasified with N_2. The mixture then heated at 95 ^{o}C temperature for 2-3 h. Completion of the reaction was monitored by checking TLC. The reaction was cooled to room temperature and diluted with

water and extracted with 50 mL of EtOAc. Aqueous layer was acidified with 1M HCL solution and extracted with 2×50mL of EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and solvent was evaporated under reduced pressure. The desired compound was isolated by column chromatography.

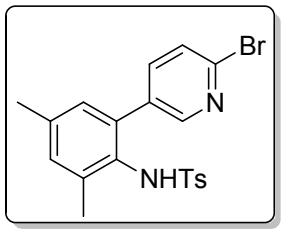
Spectral data of compound:

N-[2-(6-Bromo-pyridin-3-yl)-phenyl]-4-methyl-benzenesulfonamide (3a):



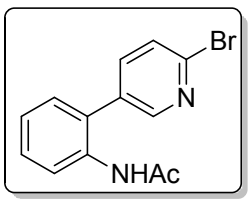
White solid; Yields: 65 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.46 (3H, s), 6.73 (1H, br), 7.13-7.30 (5H, m), 7.38-7.54 (4H, m), 7.63 (1H, dd, J_1 = 1.2 Hz, J_2 = 8.2 Hz), 7.99 (1H, d, J = 2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 21.8, 124.6, 126.5, 127.2 (2C), 128.1, 129.9 (2C), 130.7, 131.1, 133.1, 133.8, 136.5, 139.2, 141.4, 141.8, 144.5, 150.2; Elemental analysis: C, 53.61; H, 3.75; N, 6.95 %; Found: C, 53.53; H, 3.65; N, 6.90 %.

N-(2-(6-bromopyridin-3-yl)-4,6-dimethylphenyl)-4-methylbenzenesulfonamide (3e):



White solid; Yields: 53 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.33 (3H, s), 2.39 (3H, s), 2.44 (3H, s), 6.83 (1H, s), 7.04 (1H, s), 7.10 (2H, m), 7.14 (1H, s), 7.18 (1H, s), 7.24-7.30 (3H, m), 8.10 (1H, s); ^{13}C NMR ($CDCl_3$, 50MHz): 19.4, 21.1, 21.8, 126.8 (2C), 127.3, 128.9, 129.4, 129.5 (2C), 132.5, 135.1, 137.0, 137.6, 138.7, 139.1, 139.9, 140.2, 143.7, 150.1; Elemental Analysis: C, 55.69; H, 4.44; N, 6.49 %; Found: C, 55.62; H, 4.34; N, 6.40 %;

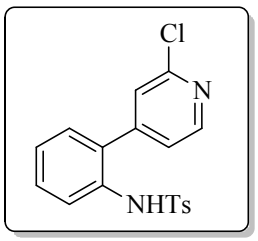
N-(2-(6-bromopyridin-3-yl)phenyl)acetamide (3f):



White solid; Yields: 60 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.10 (3H, s), 7.21-7.30 (2H, m), 7.37-7.45 (1H, m), 7.53-7.62 (3H, m), 7.88 (1H, d, J = 8.4 Hz), 8.27 (1H, s); ^{13}C NMR ($CDCl_3$, 50 MHz): 24.1, 124.0,

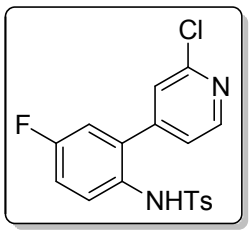
126.0, 128.3, 129.6, 129.8, 130.3, 134.0, 134.7, 139.4, 141.4, 150.0, 169.2; Elemental Analysis: C, 53.63; H, 3.81; N, 9.62 %; Found: C, 53.60; H, 3.71; N, 9.54%;

N-[2-(2-Chloro-pyridin-4-yl)-phenyl]-4-methyl-benzenesulfonamide (5a):



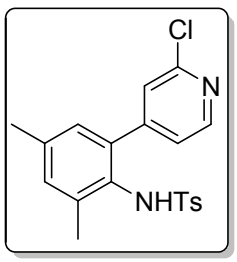
White solid; Yields: 75 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.50 (3H, s); 7.25-7.30 (5H, m), 7.54-7.57 (2H, m), 73.68 (2H, s), 7.72 (1H, s), 8.25 (1H, d, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 21.9, 123.3, 125.1, 129.2 (2C), 129.6 (2C), 129.9, 131.0, 131.8, 132.5, 132.6, 136.0, 140.1, 145.8, 149.2, 149.5, 151.2; Elemental Analysis: C, 60.25; H, 4.21; N, 7.81 %; Found: C, 60.20; H, 4.15; 7.74; %;

N-(2-(2-chloropyridin-4-yl)-4-fluorophenyl)-4-methylbenzenesulfonamide (5b):



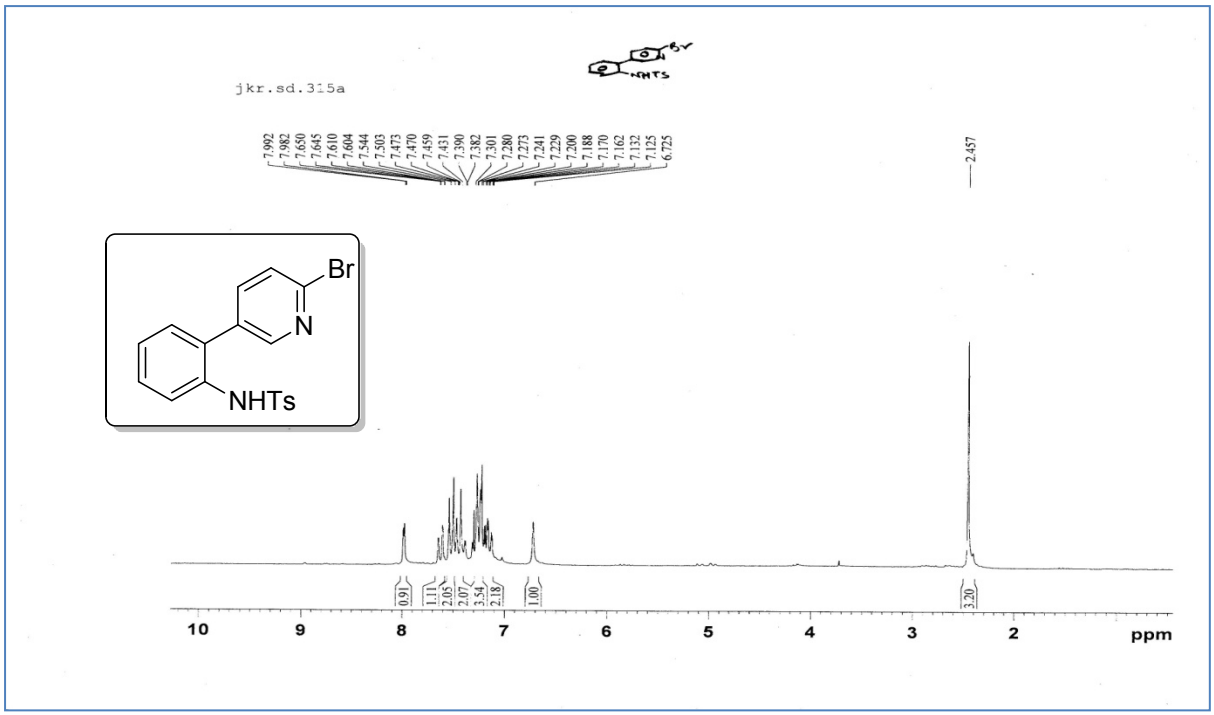
White solid; Yields: 70 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.44 (3H, s), 6.62 (1H, s), 6.80-6.90 (2H, m), 7.10-7.21 (2H, m), 7.33-7.45 (2H, m), 7.55-7.66 (2H, m), 8.31(1H, d, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 21.8, 117.0, 120.4, 122.5, 124.2, 127.2 (2C), 129.0, 130.0 (2C), 135.1, 136.0, 144.6, 148.0, 150.0, 152.1, 158.4, 163.3; Elemental Analysis: C, 57.37; H, 3.74; N, 7.43; %; Found: C, 57.30; H, 3.65; N, 7.36 %;

N-(2-(2-chloropyridin-4-yl)-4,6-dimethylphenyl)-4-methylbenzenesulfonamide (5c):

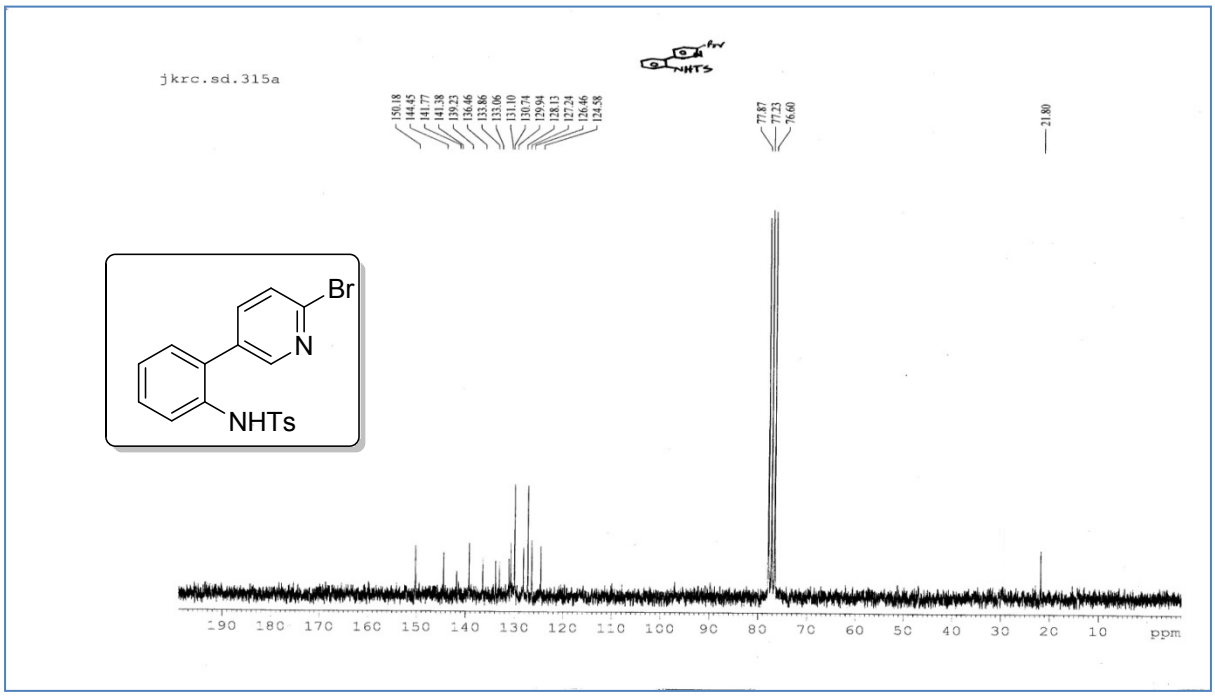


White solid; Yields: 80 %;^{1}H NMR ($CDCl_3$, 200 MHz): 2.32 (3H, s), 2.42 (3H, s), 2.44 (3H, s), 68.0 (1H, s), 6.85 (1H, s), 6.97-7.10 (4H, m), 7.16 (1H, s), 7.25 (1H, s), 8.13 (1H, d, J = 5 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 19.5, 21.1, 21.8, 123.0, 124.3, 127.0 (2C), 128.3, 129.0, 129.6 (2C), 133.1, 136.9, 137.7, 138.7, 140.1, 143.9, 148.9, 150.9, 151.3; Elemental Analysis: C, 62.09; H, 4.95; N, 7.24%; Found: Elemental Analysis: C, 62.00; H, 4.90; N, 7.24%.

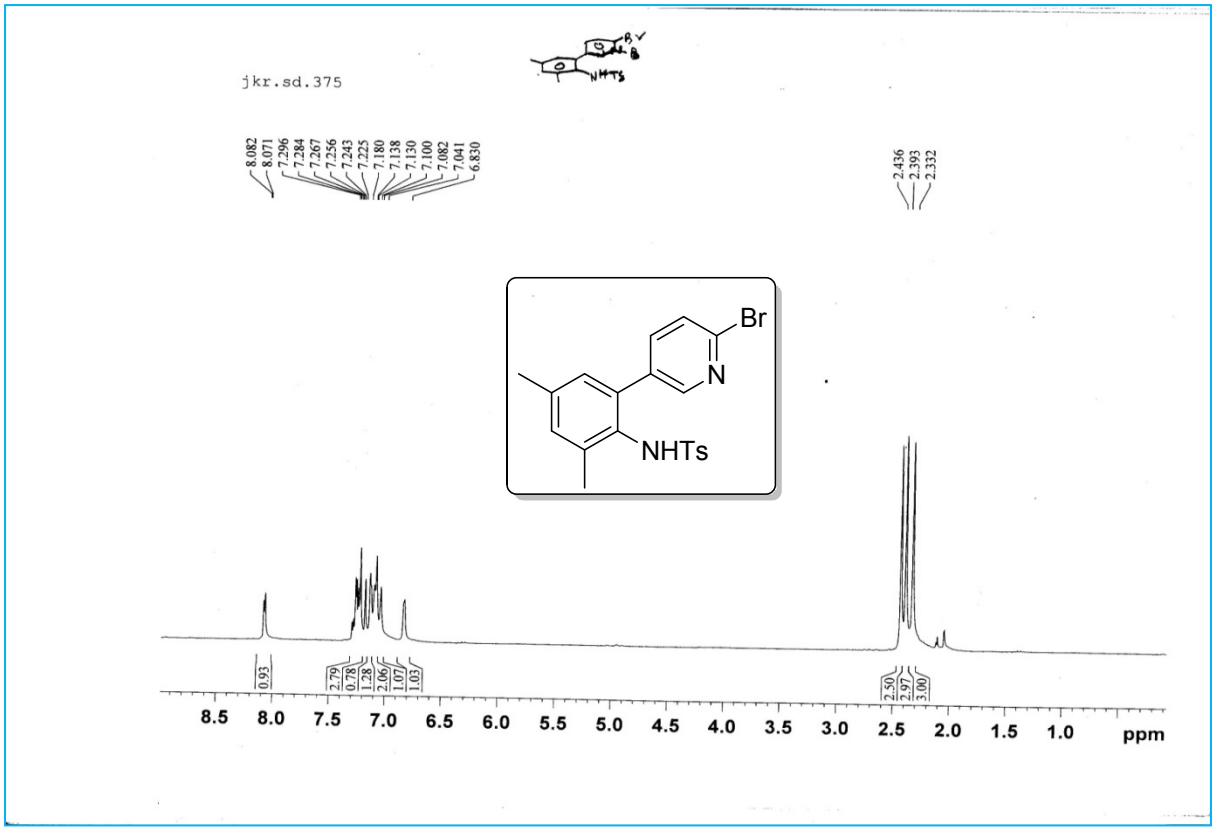
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3a):



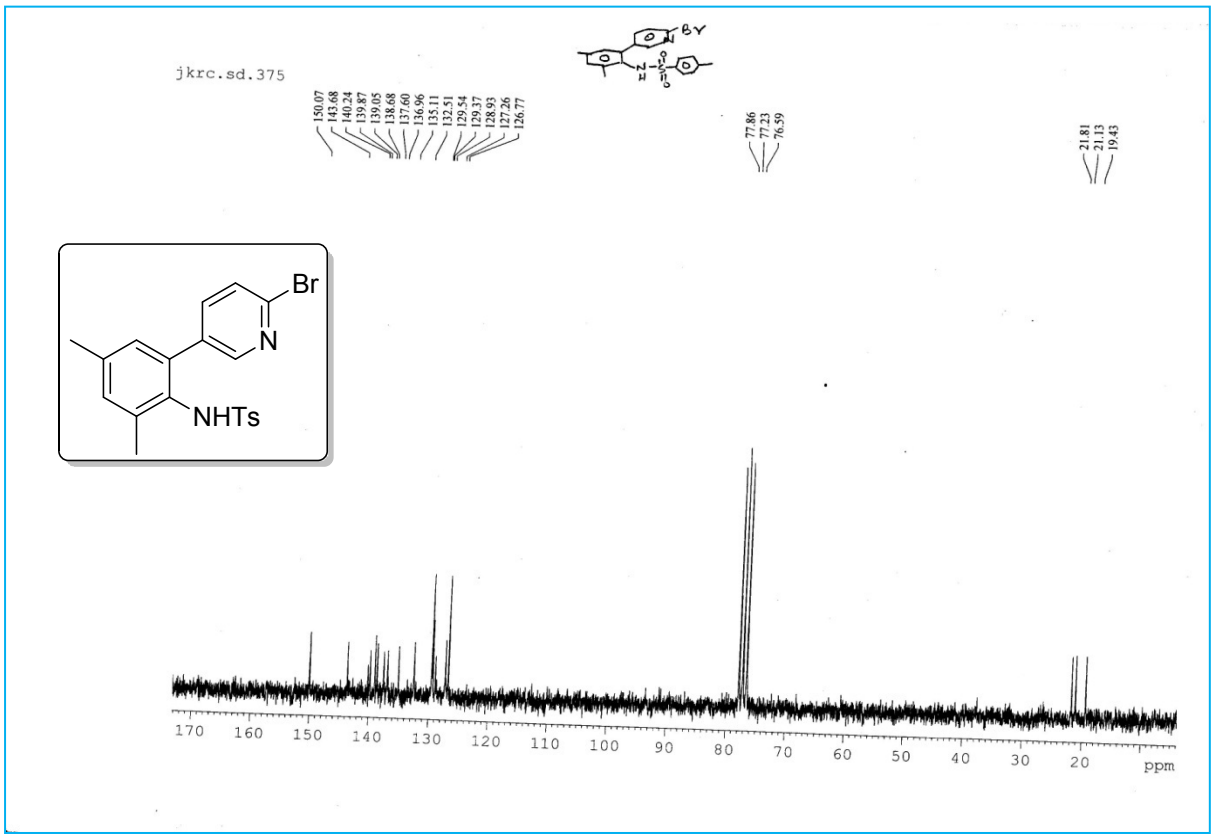
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3a):



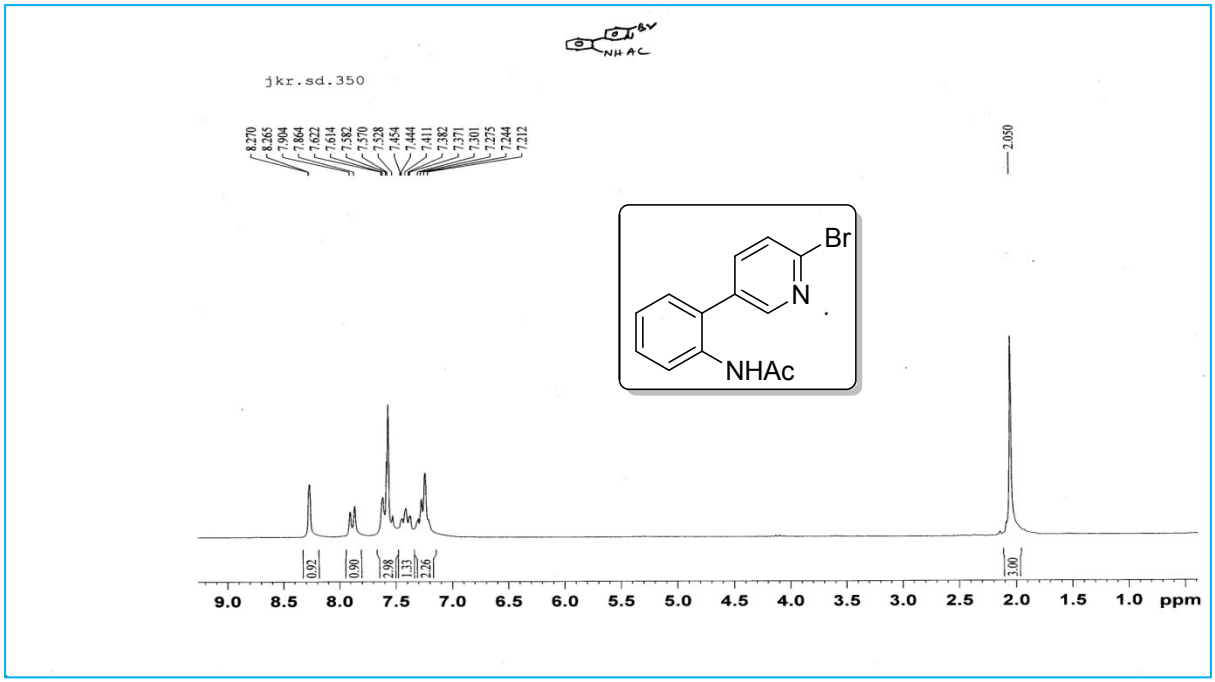
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3e):



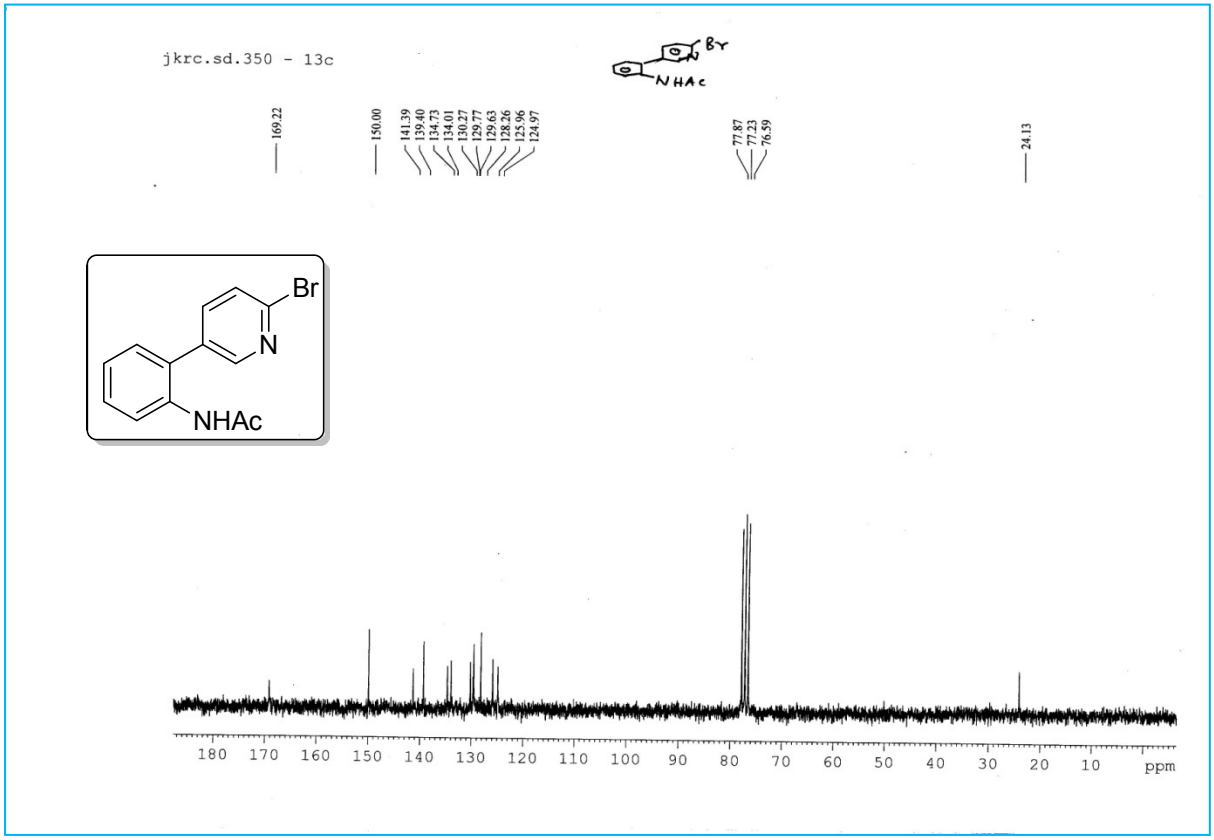
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3e):



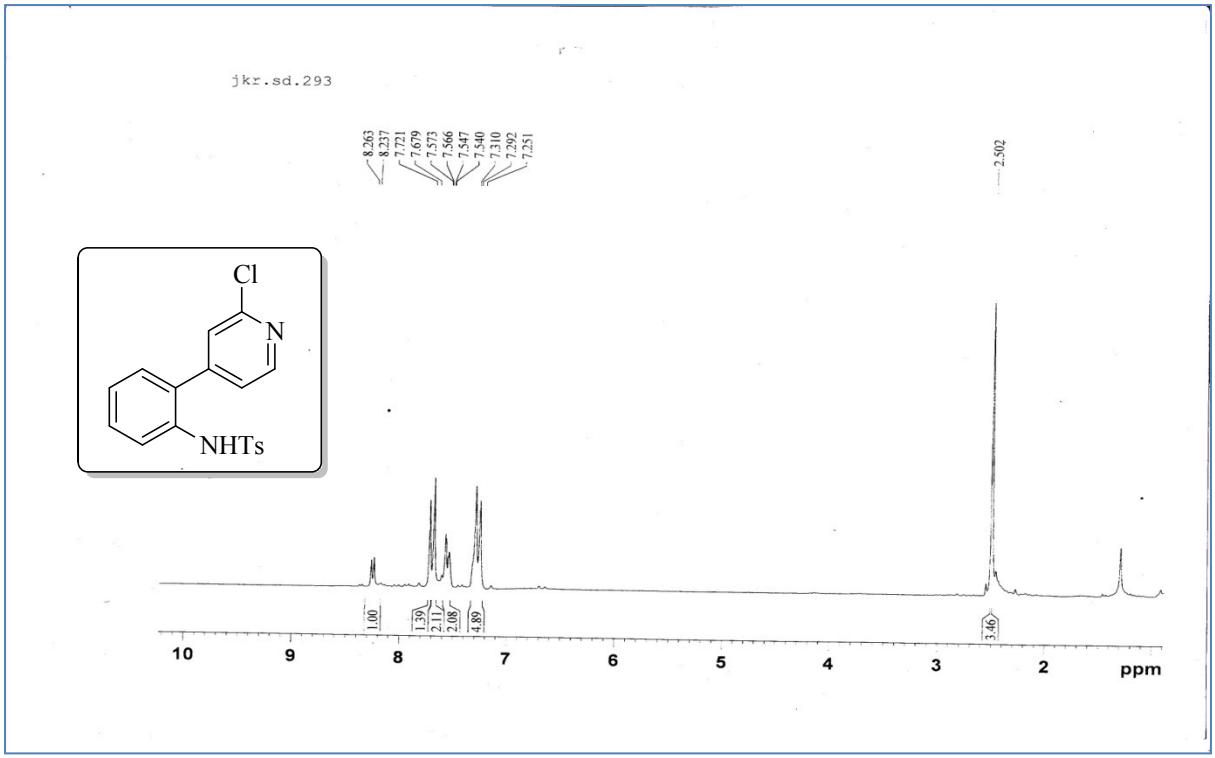
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3f):



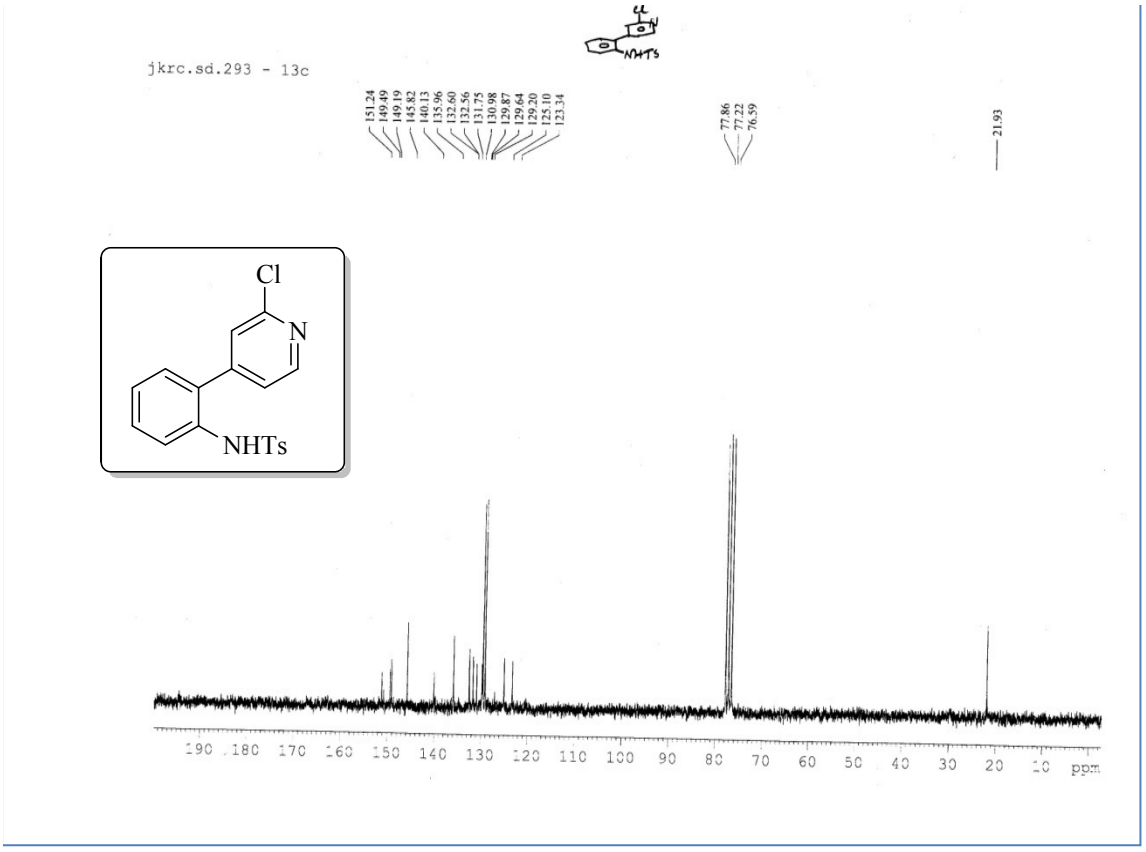
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3f):



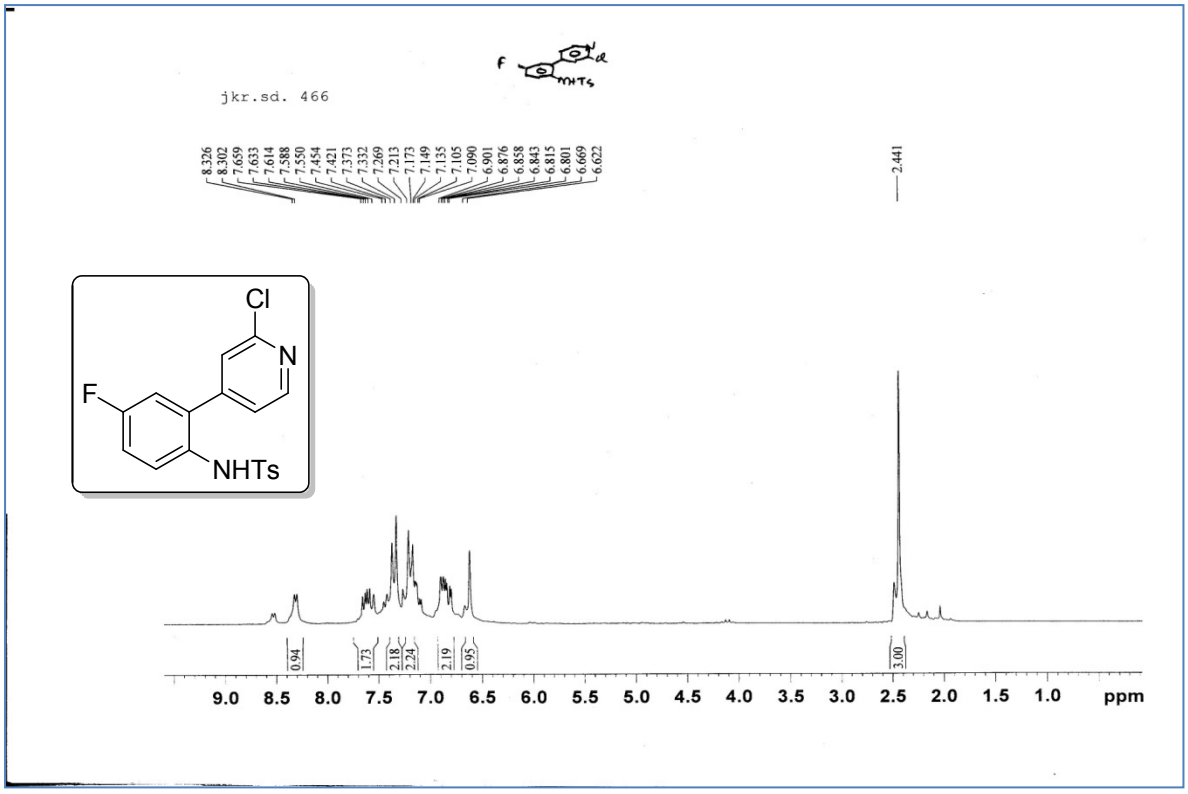
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (5a):



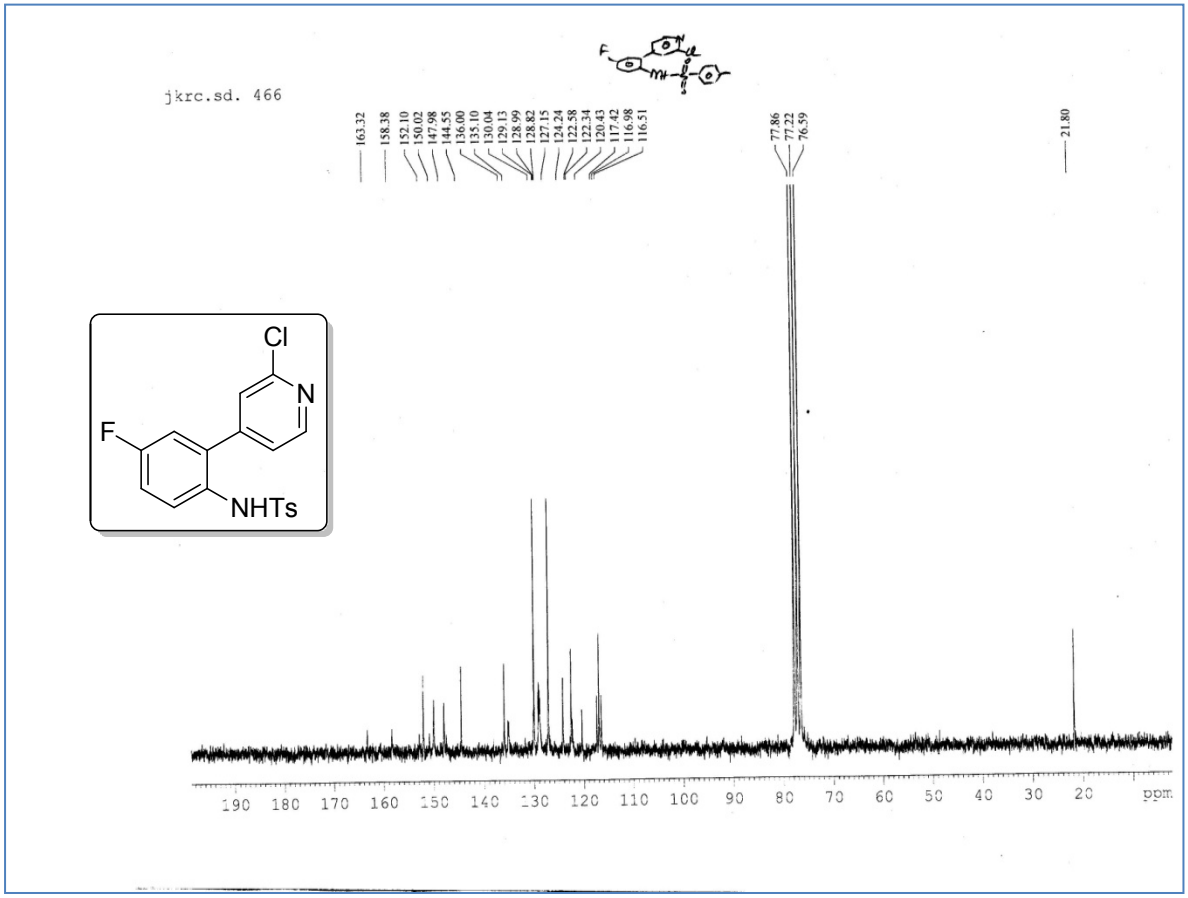
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (5a):



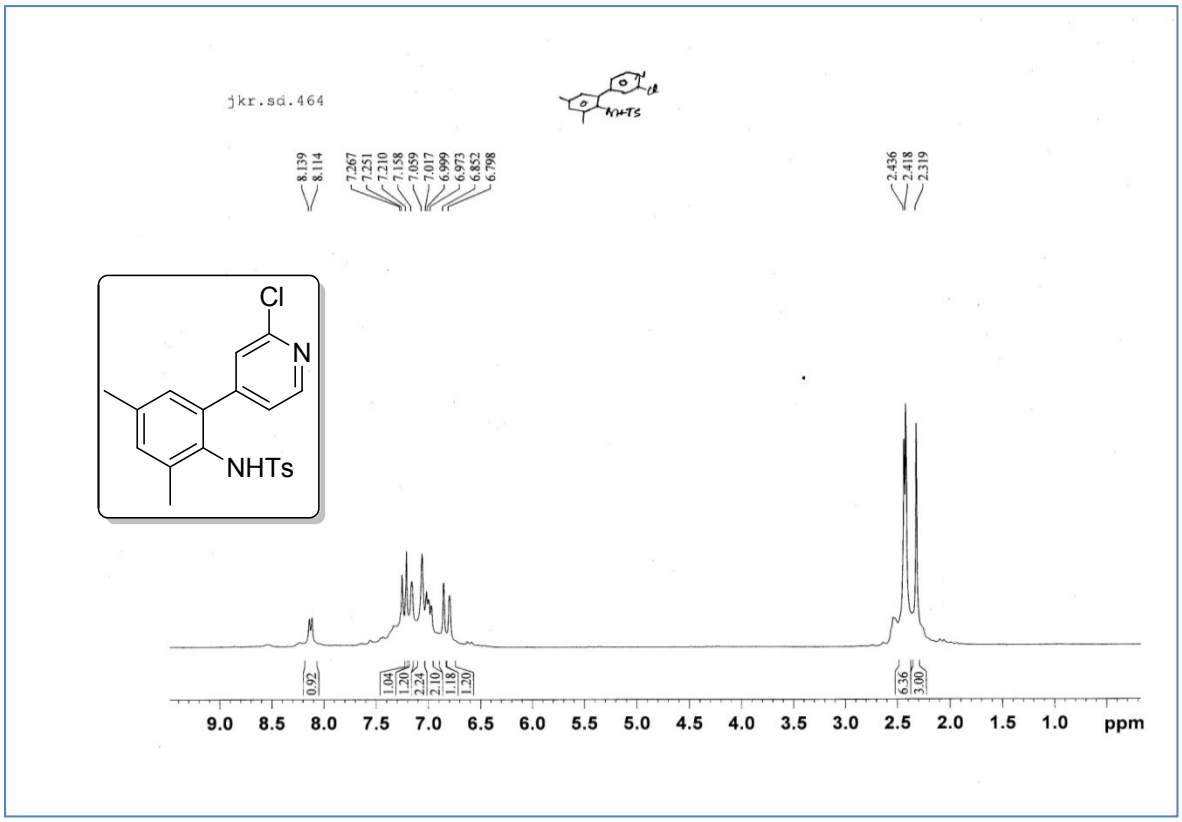
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (5b):



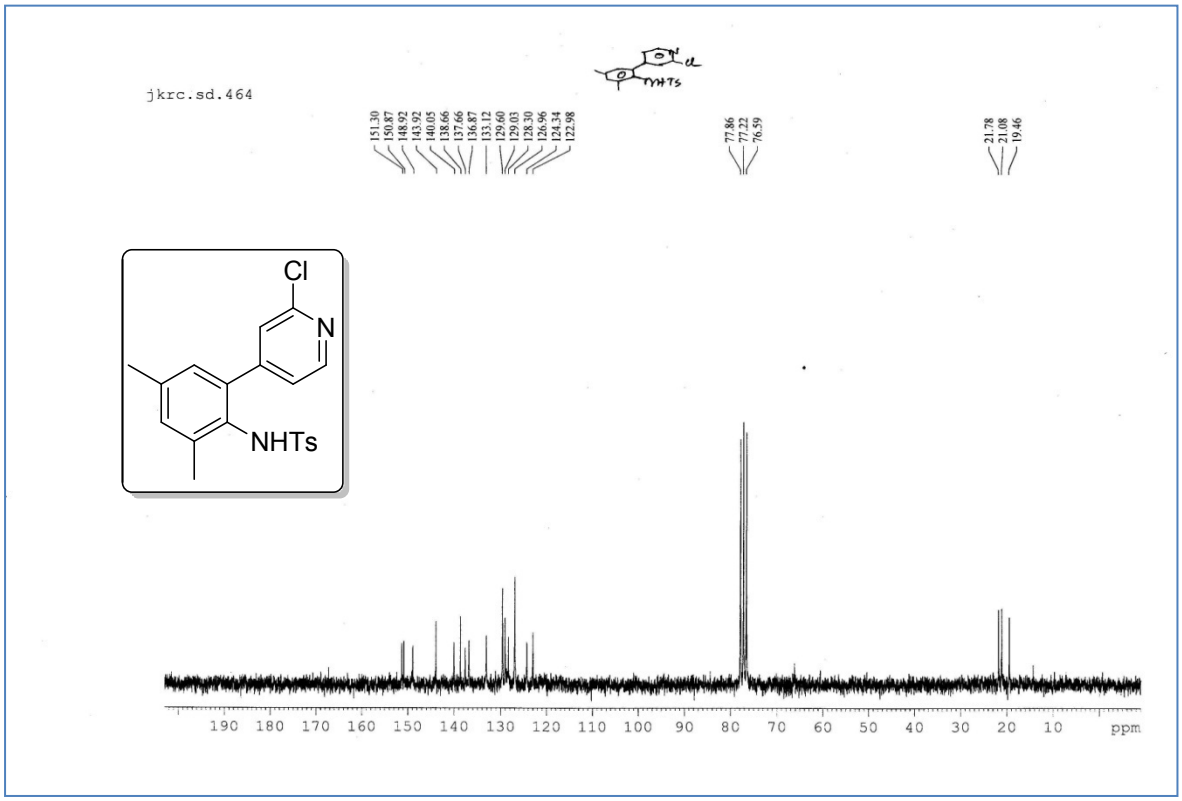
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (5b):



^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (5c):



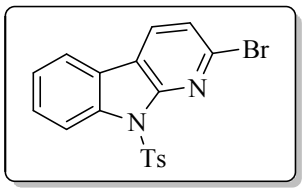
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (5c):



General procedure for the preparation of carboline:

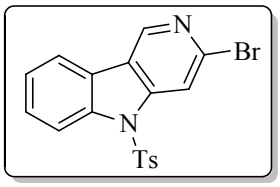
1 mmol of **3a** (N-(2-(6-bromopyridin-3-yl)phenyl)-4-methylbenzenesulfonamide), 10 mol % of $Pd(OAc)_2$, 30 mol % $Cu(OAc)_2$, dry DMSO, 120 ^oC, 3 h. Completion of the reaction was monitored by TLC. The reaction mixture cooled to room temperature, diluted with water and extracted with EtOAc (3× 50 mL). Combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Desired product was isolated by column chromatography.

2-bromo-9-tosyl-9H-pyrido[2,3-b]indole (4aa):



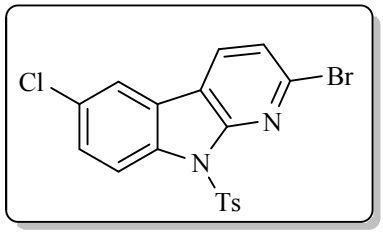
White solid, Yields: 26 %, mp: 202-204 ^oC; ^1H NMR ($CDCl_3$ 400MHz) : 2.35 (3H, s), 7.25 (2H, d, J = 9.6 Hz), 7.38-7.43 (2H, m), 7.60 (1H, q, J_1 = 7.6 Hz, J_2 = 8.0 Hz), 7.90 (1H, d, J = 7.6 Hz), 8.00 (1H, d, J = 8.4 Hz), 8.10 (2H, d, J = 8.4 Hz), 8.50 (1H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 21.8, 115.1, 117.3, 120.8, 122.1, 122.9, 124.1, 128.3 (2C), 128.7, 129.6 (2C), 130.1, 135.5, 137.7, 138.4, 145.5, 149.8; Elemental Analysis: C: 53.88; H: 3.27; N: 6.98 %; Found : C: 53.78; H: 3.21; N: 6.90 %; HRMS (ESI) m/z of $C_{18}H_{14}BrN_2O_2S^+$ $[M+H]^+$: 400.9954; Observed value: 400.9867.

3-bromo-5-tosyl-5H-pyrido[4,3-b]indole (4ab):



White solid, Yields: 73 %, mp: 158-160 ^oC; ^1H NMR ($CDCl_3$, 400MHz) : 2.33 (3H, s), 7.21 (2H, d, J = 8.4 Hz), 7.43 (1H, t, J_1 = 7.2 Hz, J_2 = 7.6 Hz), 7.60 (1H,t, J_1 = 7.6 Hz, J_2 = 8.4 Hz), 7.80 (2H, d, J = 4.0 Hz), 8.0 (1H, d, J = 7.6 Hz), 8.30 (1H, d, J = 8.4 Hz), 8.41 (1H, s), 8.94 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): 21.6, 113.2, 114.7, 120.6, 122.1, 122.9 (2C), 124.8, 126.6, 128.9, 130.1 (2C), 134.3, 138.2, 138.8, 142.2, 144.8, 146.0; Elemental Analysis: C: 53.88; H: 3.27; N: 6.98 %; Found : C: 53.76; H: 3.21; N: 6.91 %.

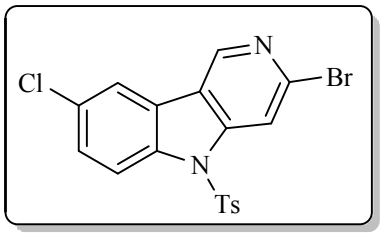
2-bromo-6-chloro-9-tosyl-9H-pyrido[2,3-b]indole (4ba):



White solid, Yields: 36 %;^1H NMR ($CDCl_3$, 400 MHz): 2.37 (3H, s), 7.50 (1H, d, J = 8.0 Hz), 7.55 (2H, t, J = 7.2 Hz), 7.87 (1H, s), 8.00 (1H, d, J = 8.0 Hz), 8.10-8.12 (3H, m), 8.42 (1H, d, J = 9.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 22.6, 116.2, 120.4, 123.1, 123.2, 128.2 (2C), 128.6, 129.5 (2C), 129.6, 129.7, 130.2, 135.0, 135.8, 139.2, 145.6, 149.8; Elemental Analysis: C, 49.62; H, 2.78; N, 6.43 %; Found:

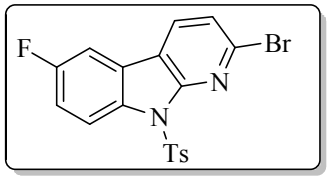
C, 49.58; H, 2.68; N, 6.36%; HRMS (ESI) m/z of $C_{18}H_{13}BrClN_2O_2S^+$ [M+H$^+$]: 434.9564; Observed: 434.9560.

3-bromo-8-chloro-5-tosyl-5H-pyrido[4,3-b]indole (4bb):



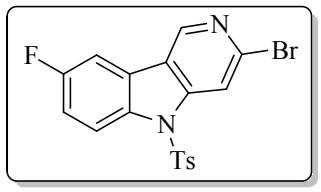
White solid, Yields: 50 %; ^{1}H NMR ($CDCl_3$, 400 MHz): 2.34 (3H, s), 7.22 (2H, d, J = 8.4 Hz), 7.53 (1H, dd, J_1 = 2 Hz, J_2 = 8.8 Hz), 7.74 (2H, d, J = 8.4 Hz), 7.93 (1H, s), 8.21 (1H, d, J = 9.2 Hz), 8.39 (1H, s), 8.90 (1H, s); ^{13}C NMR ($CDCl_3$, 400 MHz): 21.9, 113.6, 116.1, 120.7, 121.4, 123.4, 124.6, 126.9 (2C), 129.2, 130.5 (2C), 134.3, 136.8, 139.8, 142.7, 145.4, 146.6; Elemental Analysis: C, 49.62; H, 2.78; N, 6.43 %; Found: C, 49.56; H, 2.70; N, 633 %; HRMS (ESI) m/z for $C_{18}H_{13}BrClN_2O_2S^+$ [M+H$^+$]: 434.9564; Observed value: 434.9560.

2-bromo-6-fluoro-9-tosyl-9H-pyrido[2,3-b]indole (4ac):



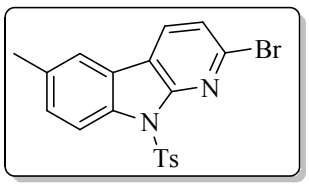
White solid, Yields: 40 %, mp: 212-214 ^{o}C;^{1}H NMR ($CDCl_3$, 400 MHz) : 2.40 (3H, s), 7.25-7.34 (3H, m), 7.44 (1H, d, J = 8.0 Hz), 7.55 (1H, dd, J_1 = 5.6 Hz, J_2 = 8.0 Hz), 8.00 (1H, d, J = 8.4 Hz), 8.10 (2H, d, J = 8.4 Hz), 8.44 (1H, dd, J_1 = 4.4 Hz, J_2 = 9.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) : 21.9, 107.0, 116.3, 116.6, 116.9, 123.2, 128.4 (2C), 129.8 (2C), 130.5, 134.0, 135.4, 139.3, 145.8, 150.4, 158.7, 161.1; Elemental Analysis: C: 51.56; H: 2.88; N: 6.68 %; Found : C: 51.49; H: 2.80; N: 6.58 %; HRMS (ESI) m/z of $C_{18}H_{13}BrFN_2O_2S^+$ [M+H]$^+$: 418.9860; Found: 418.9841.

3-bromo-8-fluoro-5-tosyl-5H-pyrido[4,3-b]indole (4bc):



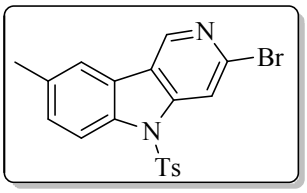
White solid, Yields: 58 %, mp: 174-176 ^{o}C;^{1}H NMR ($CDCl_3$, 400 MHz) : 2.24 (3H, s), 7.21-7.35 (3H, m), 7.62 (1H, dd, J1 =2.8 Hz, J_2 = 8.0 Hz), 7.74 (2H, d, J = 8.4 Hz), 8.24 (1H, dd, J_1 = 4.4 Hz, J_2 = 9.2 Hz), 8.40 (1H, s), 8.90 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) : 21.9, 107.1, 113.7, 116.3, 116.8, 121.9, 126.8 (2C), 130.4 (2C), 134.3, 134.6, 139.7, 142.7, 145.8, 146.5, 159.2, 161.6; Elemental Analysis: C: 51.56; H: 2.88; N: 6.68 %; Found : C: 51.49; H: 2.80; N: 6.58 %;

2-bromo-6-methyl-9-tosyl-9H-pyrido[2,3-b]indole (4ad):



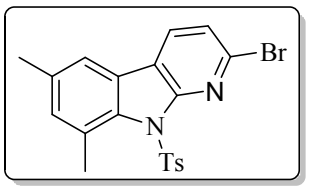
White solid, Yields: 35 %, mp: 188-190 ^{o}C;^{1}H NMR ($CDCl_3$ 400MHz) : 2.35 (3H, s), 2.50 (3H, s), 7.23 (2H, J = 8.0 Hz), 7.39 (2H, t, J = 8.0 Hz), 7.68 (1H, s), 7.95 (1H, d, J = 8.0 Hz), 8.10 (2H, d, J = 8.0 Hz), 8.40 (1H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 21.2, 21.6, 114.7, 117,2, 120.6, 122.0, 122.7, 128.1 (2C), 129.4 (2C), 129.8 (2C), 133.7, 135.4, 135.7, 138.0, 145.2, 149.8; Elemental Analysis: C: 54.95; H: 3.64; N: 6.75 %; Found : C: 54.92; H: 3.54; N: 6.70 %.

3-bromo-8-methyl-5-tosyl-5H-pyrido[4,3-b]indole (4bd):



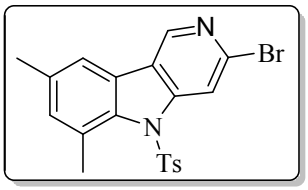
White solid, Yields: 54 %, mp: 164-166 ^{o}C; ^{1}H NMR ($CDCl_3$ 400MHz) : 2.32 (3H, s), 249 (3H, s), 7.20 (2H, d, *J* = 8.8 Hz), 7.40 (1H, d, *J* = 8.8 Hz), 7.80 (3H, d, *J* = 8.2 Hz), 8.13 (1H, d, *J* = 8.8 Hz), 8.38 (1H, s), 8.90 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): 21.5, 21.8, 113.5, 114.7, 120.9, 122.4, 123.4, 126.8 (2C), 130.3 (2C), 130.4, 134.6, 135.0, 136.6, 139.0, 142.3, 145.3, 146.1; Elemental Analysis: C: 54.95; H: 3.64; N: 6.75 %; Found: C: 54.90; H: 3.51; N: 6.72 %; HRMS (ESI) m/z of $C_{19}H_{16}BrN_2O_2S^+$ $[M+H]^+$: 415.0110; Observed: 415.0132.

2-bromo-6,8-dimethyl-9-tosyl-9H-pyrido[2,3-b]indole (4ae):



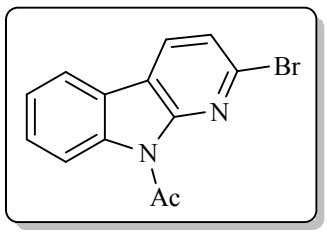
White solid, Yields: 30 %; ^{1}H NMR ($CDCl_3$, 200 MHz) : 2.34 (3H, s), 2.45 (3H, s), 2.75 (3H, s), 7.13 (1H, s), 7.19 (2H, d, *J* = 6.4 Hz), 7.32 (1H, d, *J* = 8 Hz), 7.44 (1H, s), 7.70-7.82 (3H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) : 21.3, 21.8, 22.5, 118.3, 119.2, 120.4, 123.9, 126.2, 128.4 (2C), 129.3 (2C), 129.8 (2C), 133.5, 135.4, 135.5, 137.2, 137.9, 144.9; Elemental Analysis: C: 55.95; H: 3.99; N: 6.52 %; Found: C: 55.90; H: 3.89; N: 6.45 %; HRMS (ESI) m/z for $C_{20}H_{18}BrN_2O_2S$ $[M+ H^+]$: 429.0267; Observed: 429.0279.

3-bromo-6,8-dimethyl-5-tosyl-5H-pyrido[4,3-b]indole (4be):



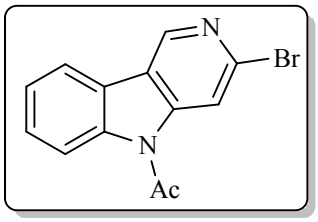
White solid, Yields: 52 %;^{1}H NMR ($CDCl_3$, 200 MHz): 2.29 (3H, s), 2.44 (3H, s), 2.72 (3H, s), 7.04 (2H, d, *J* = 8.0 Hz), 7.30 (1H, s), 7.3 (2H, d, *J* = 2.2 Hz), 7.50 (1H, s), 8.31 (1H, s), 8.71 (1H, s); ^{13}C NMR ($CDCl_3$, 50 MHz): 21.2, 21.8, 22.2, 117.2, 118.3, 124.8, 126.8 (3C), 129.4, 129.7 (2C), 133.7, 134.1, 136.2, 137.9, 138.8, 141.9, 145.3, 148.9; Elemental Analysis: C:55.95; H: 3.99; N: 6.52 %; Found: C: 55.90; H: 3.89; N: 6.45 %; HRMS (ESI) m/z for $C_{20}H_{18}BrN_2O_2S^+$ $[M+ H^+]$: 429.0267; Observed: 429.0279.

1-(2-bromo-9H-pyrido[2,3-b]indol-9-yl)ethanone (4af):



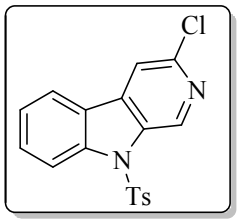
White solid, Yields: 35 %; ^{1}H NMR ($CDCl_3$, 400 MHz): 3.12 (3H, s), 7.34-7.62 (3H, m), 7.95 (1H, d, *J* = 7.6 Hz), 8.12 (1H, d, *J* = 8.0 Hz), 8.71 (1H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 22.9, 118.1, 120.3, 122.3, 123.0, 124.2, 124.6, 129.2, 130.3, 137.6, 138.3, 150.6, 171.2; Elemental Analysis: C, 54.00; H, 3.14; N, 9.69; Found: C, 54.00; H, 3.14; N, 9.69; HRMS (ESI) m/z of $C_{13}H_{10}BrN_2O^+[M+H]^+$: 288.9971; Observed value: 288.9977.

1-(3-bromo-5H-pyrido[4,3-b]indol-5-yl)ethanone (4bf):



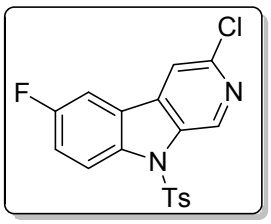
White solid, Yields: 56 %; ^{1}H NMR ($CDCl_3$, 600 MHz): 2.93 (3H, s), 7.50 (1H, t, J_1 = 7.2 Hz, J_2 = 7.8 Hz), 7.61 (1H, t, J_1 = 8.4 Hz, J_2 = 7.8 Hz), 8.12 (2H, dd, J_1 = 7.8 Hz, J_2 = 16.8 Hz), 8.44 (1H, s), 9.04 (1H, s); ^{13}C NMR ($CDCl_3$, 150 MHz): 22.7, 115.1, 115.9, 120.7, 122.2, 123.5, 124.7, 128.8, 138.6, 139.5, 141.9, 145.1, 169.8; Elemental Analysis: C, 54.00; H, 3.14; N, 9.69; Found: C, 53.94; H, 3.10; N, 9.61 %;

3-chloro-9-tosyl-9H-pyrido[3,4-b]indole (5a):



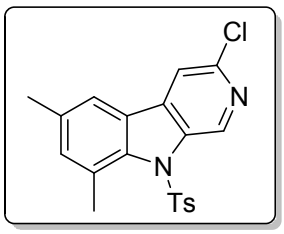
White solid, Yields: 68 %; ^{1}H NMR ($CDCl_3$ 400MHz): 2.29 (3H, s), 7.15 (2H, d, J = 4.0 Hz), 7.43 (1H, t, J_1 = 3.8 Hz, J_2 = 7.6 Hz), 7.65-7.73 (3H, m), 7.81 (1H, s), 7.94 (1H, d, J = 4.0 Hz), 8.35 (1H, d, J = 4.2 Hz), 9.37 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): 21.8, 114.8, 115.6, 122.0, 123.6, 124.8, 126.8(2C), 129.8, 130.2(2C), 131.1, 134.4, 136.0, 136.8, 140.0, 145.3, 146.0; Elemental Analysis: C: 53.88; H: 3.27; N: 6.98 %; Found : C: 53.78; H: 3.20; N, 6.93 %.

3-chloro-6-fluoro-9-tosyl-9H-pyrido[3,4-b]indole (5b):



White solid, Yields: 51 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.31 (3H, s), 7.14 (1H, s), 7.184 (1H, s), 7.36-7.46 (1H, m), 7.60 (1H, dd, J_1 = 2.6 Hz, J_2 = 7.6 Hz), 7.70 (1H, s), 7.71 (1H, s), 7.80 (1H, s), 8.33 (1H, q, J_1 = 4.2 Hz, J_2 = 9.2 Hz), 9.40 (1H, s); ^{13}C NMR ($CDCl_3$, 50 MHz): 21.8, 108.8 (d, J = 24.5 Hz), 115.0, 117.1 (d, J = 8.5 Hz), 119.0 (d, J = 25 Hz), 124.8 (d, J = 9.5 Hz), 126.8 (2C), 130.3 (2C), 134.2, 135.0, 135.4, 136.3, 137.2, 145.8, 157.8, 162.5; HRMS (ESI) m/z of $C_{18}H_{13}ClFN_2O_2S^+$ $[M+H]^+$: 375.0365; Observed: 375.0359; Elemental Analysis: C, 57.68; H, 3.23; N, 7.47 %; Found: C, 57.52; H, 3.13; N, 7.40%;

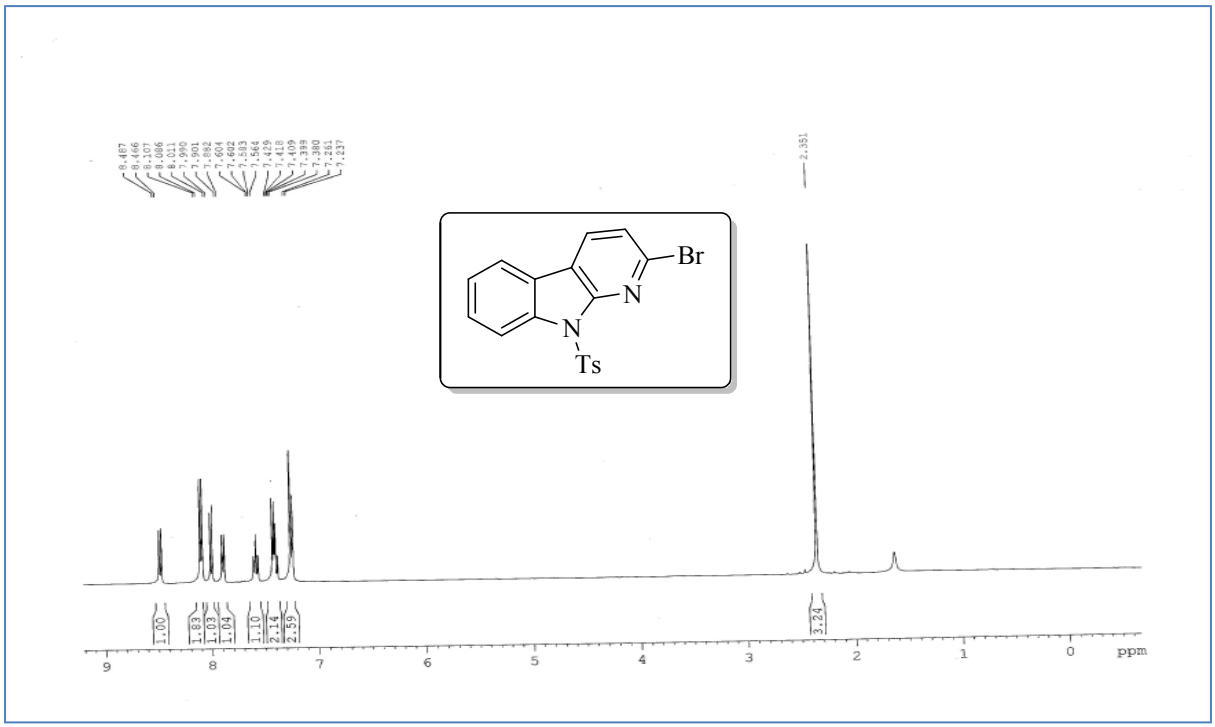
3-chloro-6,8-dimethyl-9-tosyl-9H-pyrido[3,4-b]indole (5c):



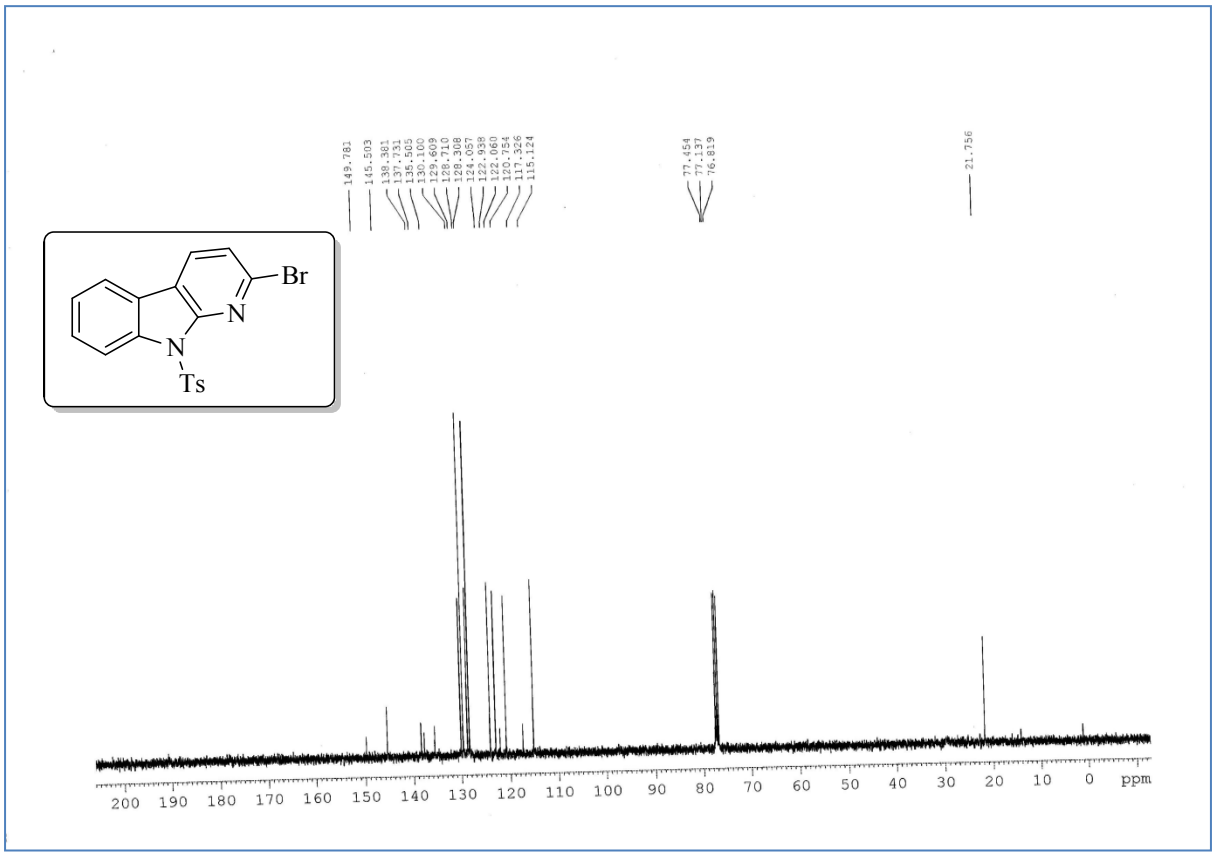
White solid, Yields: 74 %; ^{1}H NMR ($CDCl_3$, 200 MHz) : 2.25 (3H, s), 2.44 (3H, s), 2.80 (3H, s), 6.92 (1H, s), 7.00 (1H, s), 7.11 (1H, s), 7.20 (1H, s), 7.28 (1H, s), 7.40 (1H, s), 7.53 (1H, s), 9.21 (1H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) : 21.0, 21.5, 21.7, 114.1, 119.1, 126.9 (2C), 127.7, 129.2 (2C), 130.6, 132.4, 135.6, 136.1, 137.3, 139.1, 139.5, 140.3, 144.8, 146.5; HRMS (ESI) m/z [M+H]+ for $C_{20}H_{18}ClN_2O_2S^+$: 385.0772; Observed: 385.0768; Elemental Analysis: C, 62.41; H, 4.45; N, 7.28 %; Found: C, 62.30; H, 4.40; N, 7.22 %;

^{1}H and ^{13}C NMR Spectra of synthesized compounds:

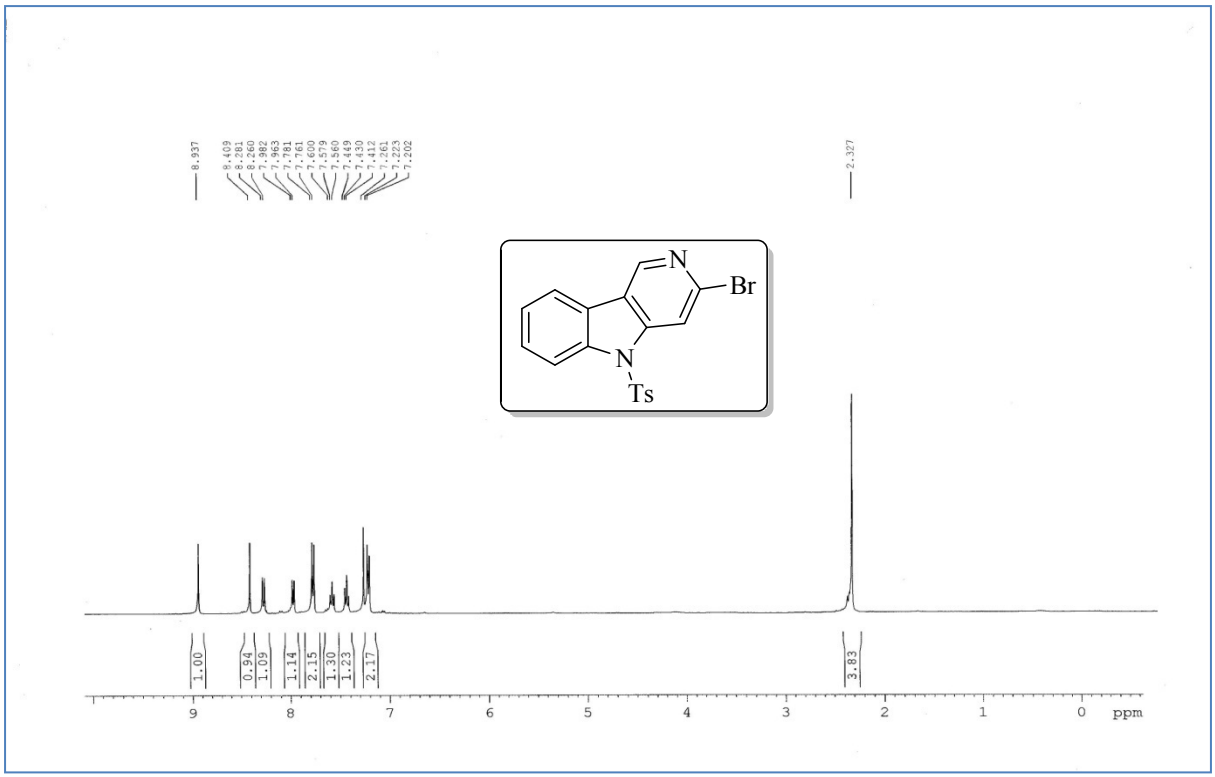
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4aa:



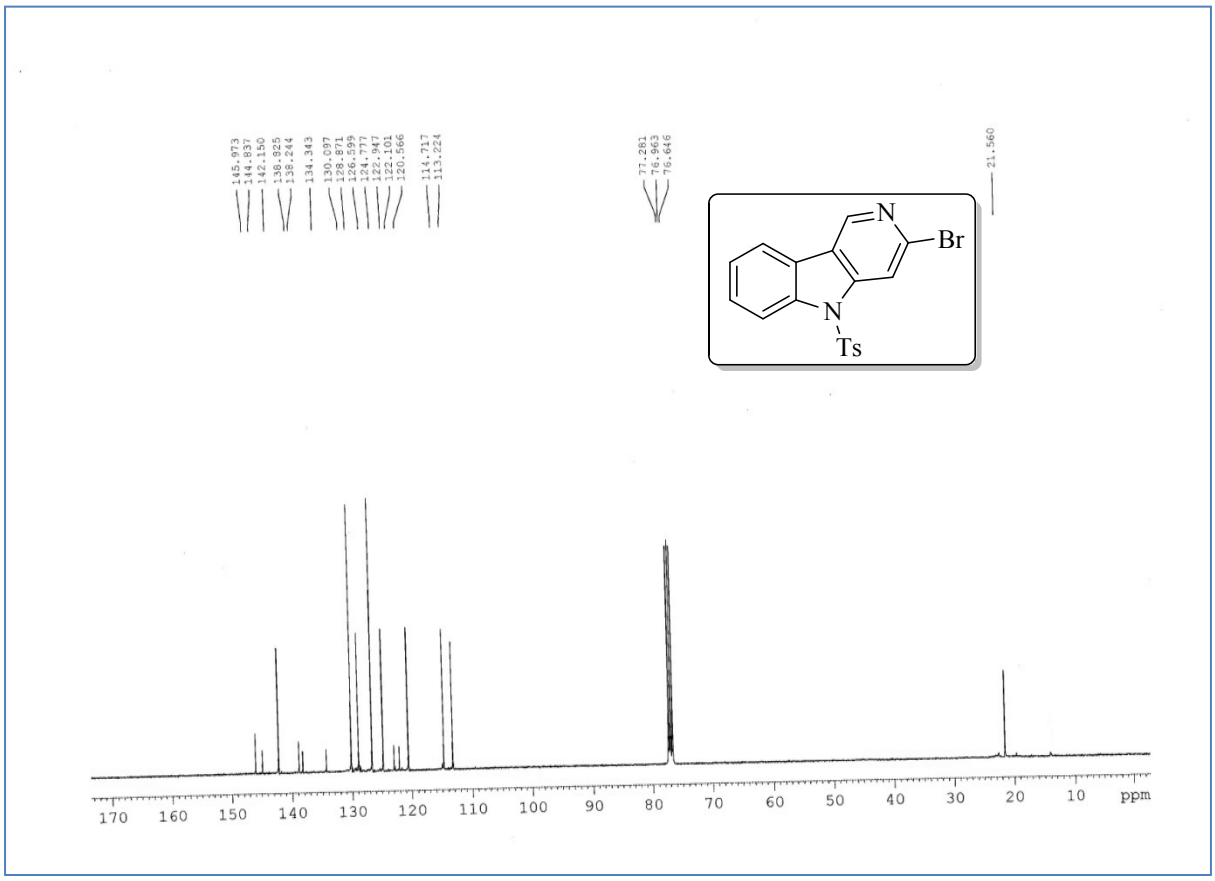
^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4aa:



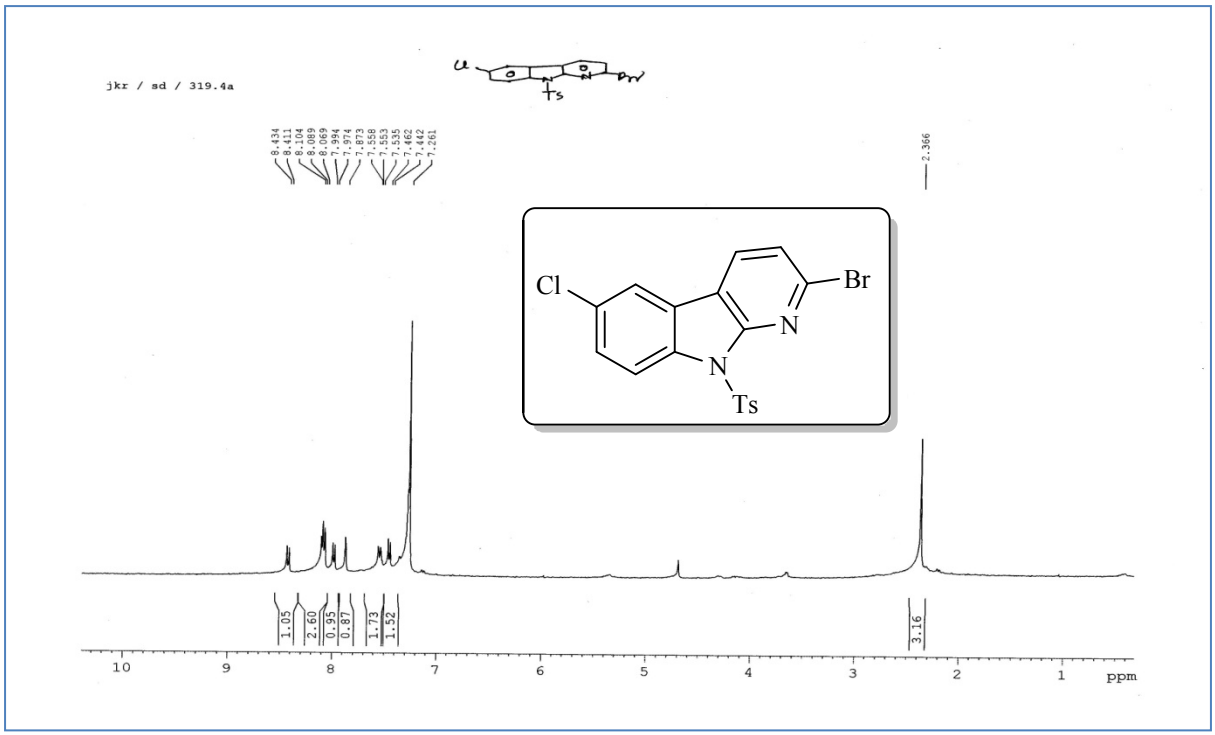
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4ab:



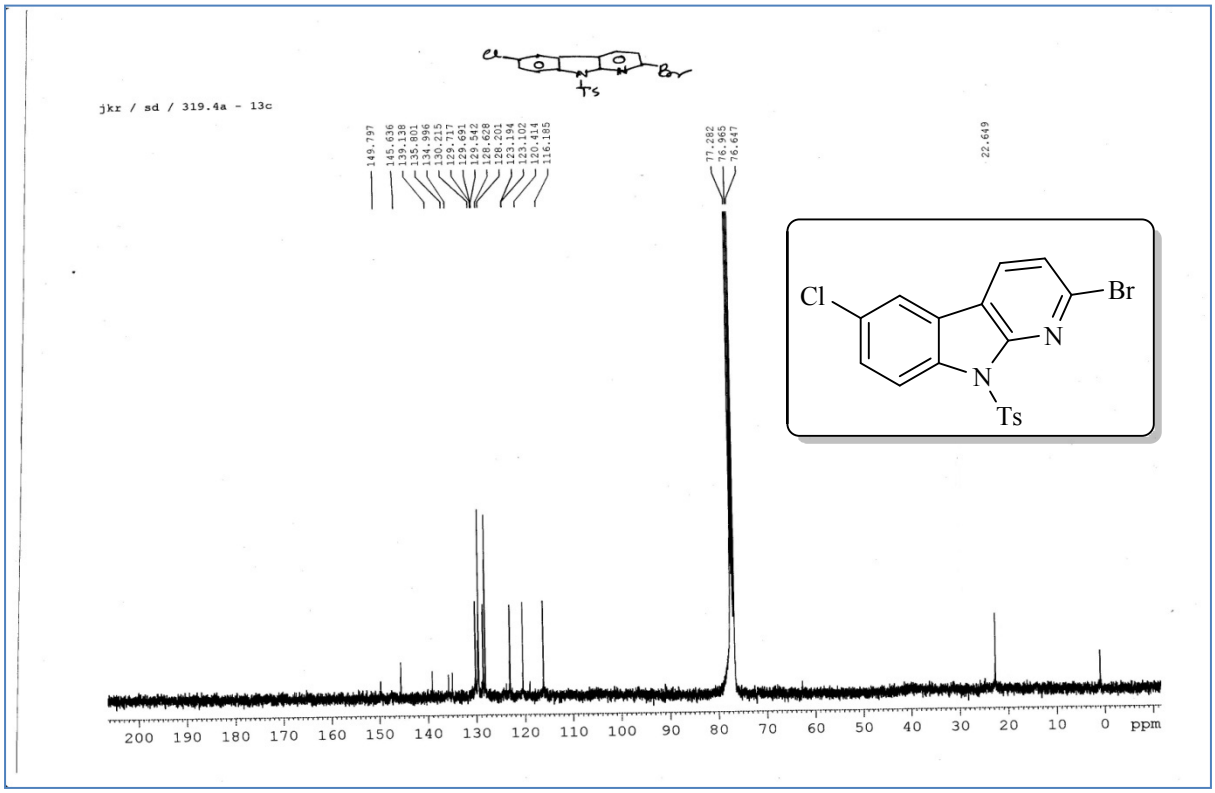
^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4ab:



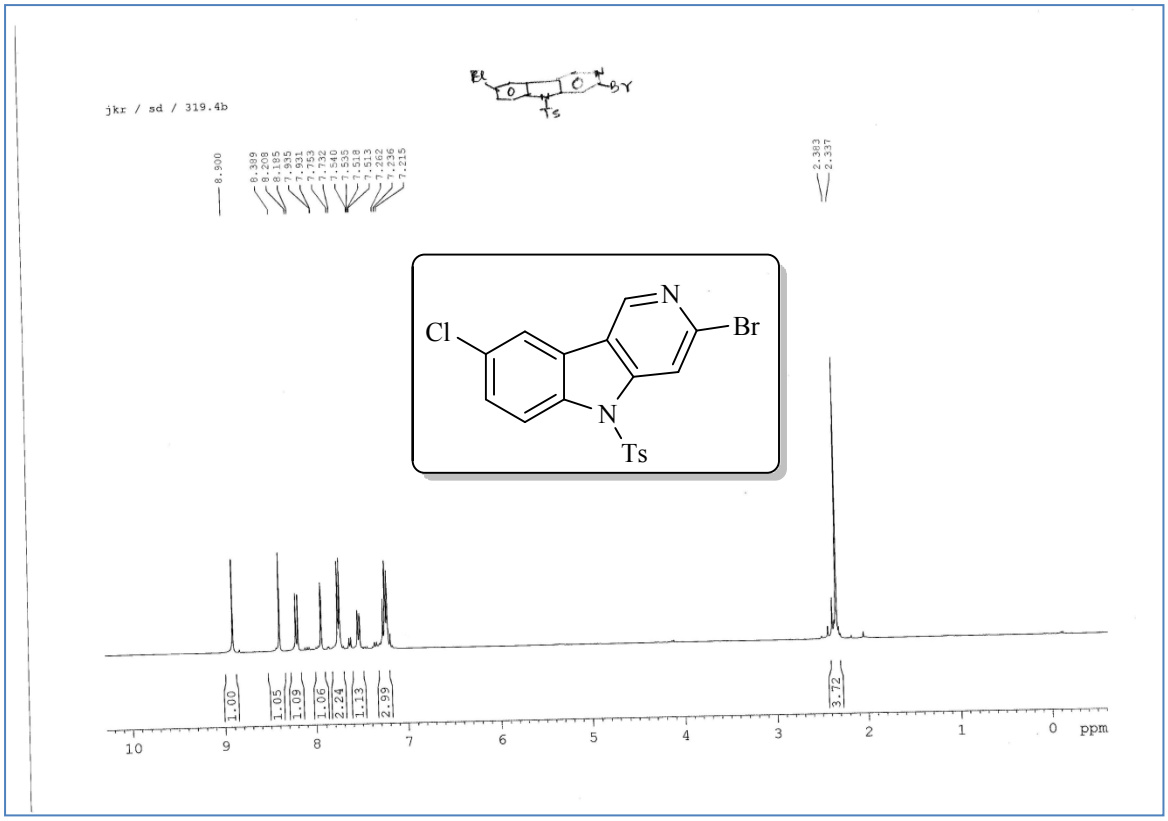
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4ba:



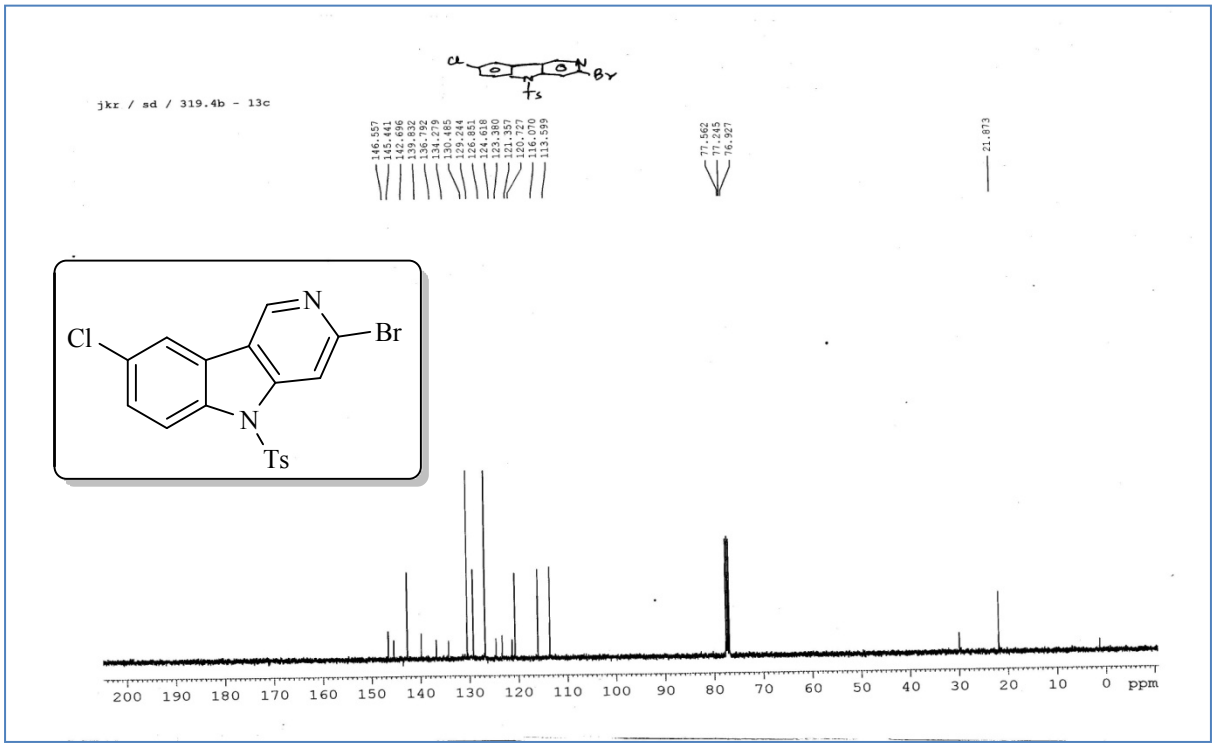
^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4ba:



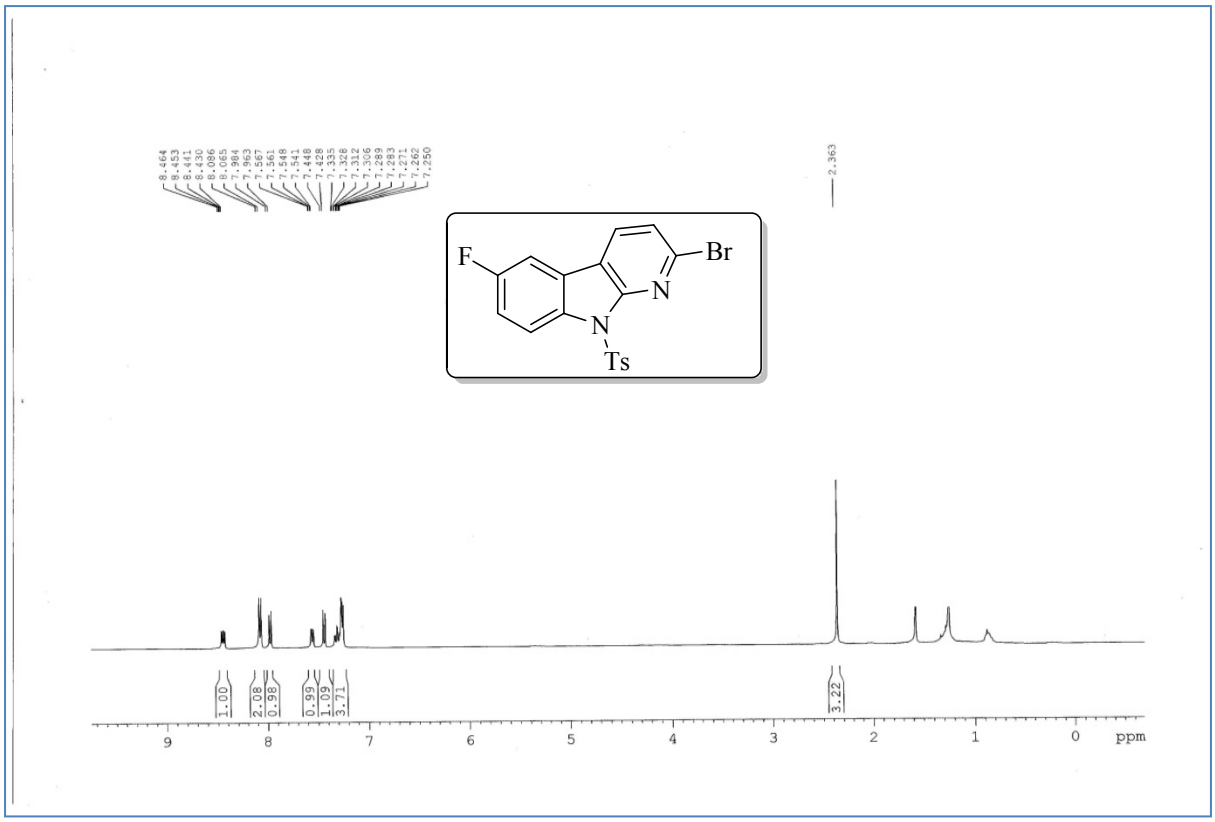
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4bb:



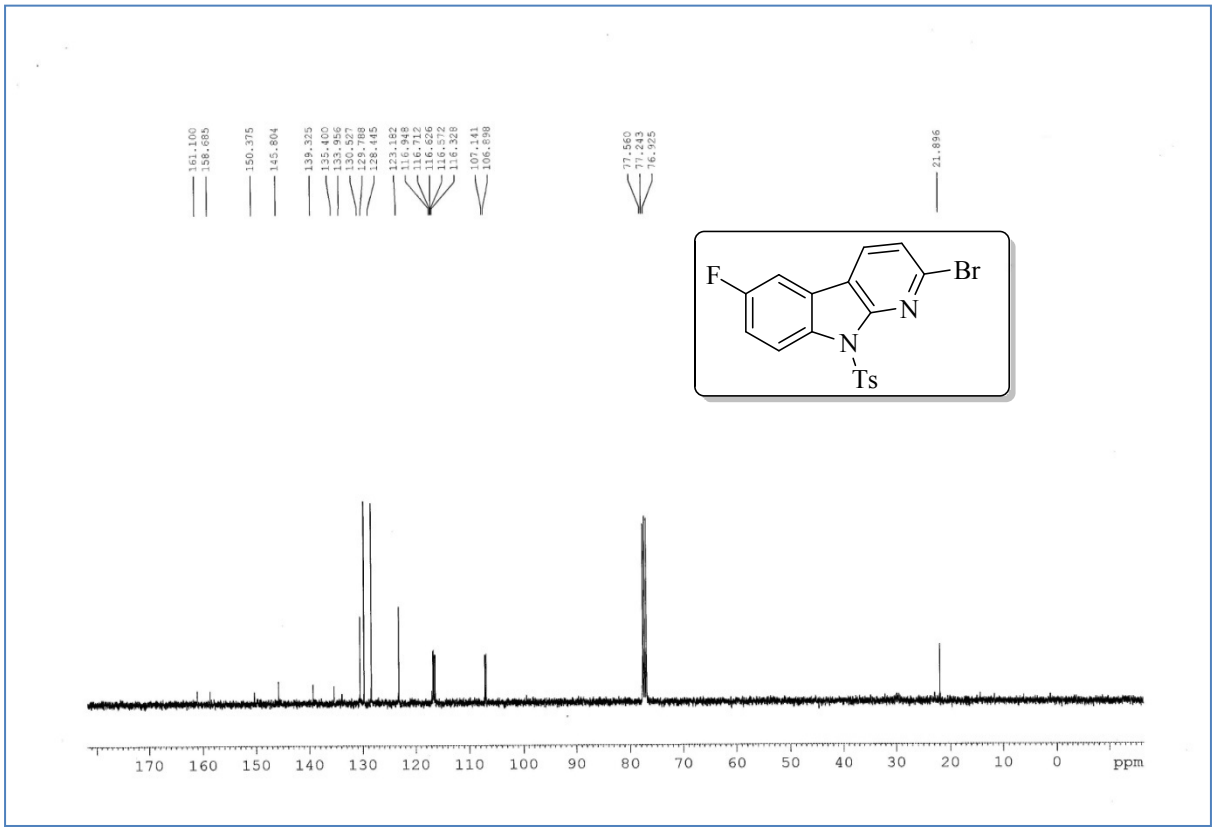
^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4bb:



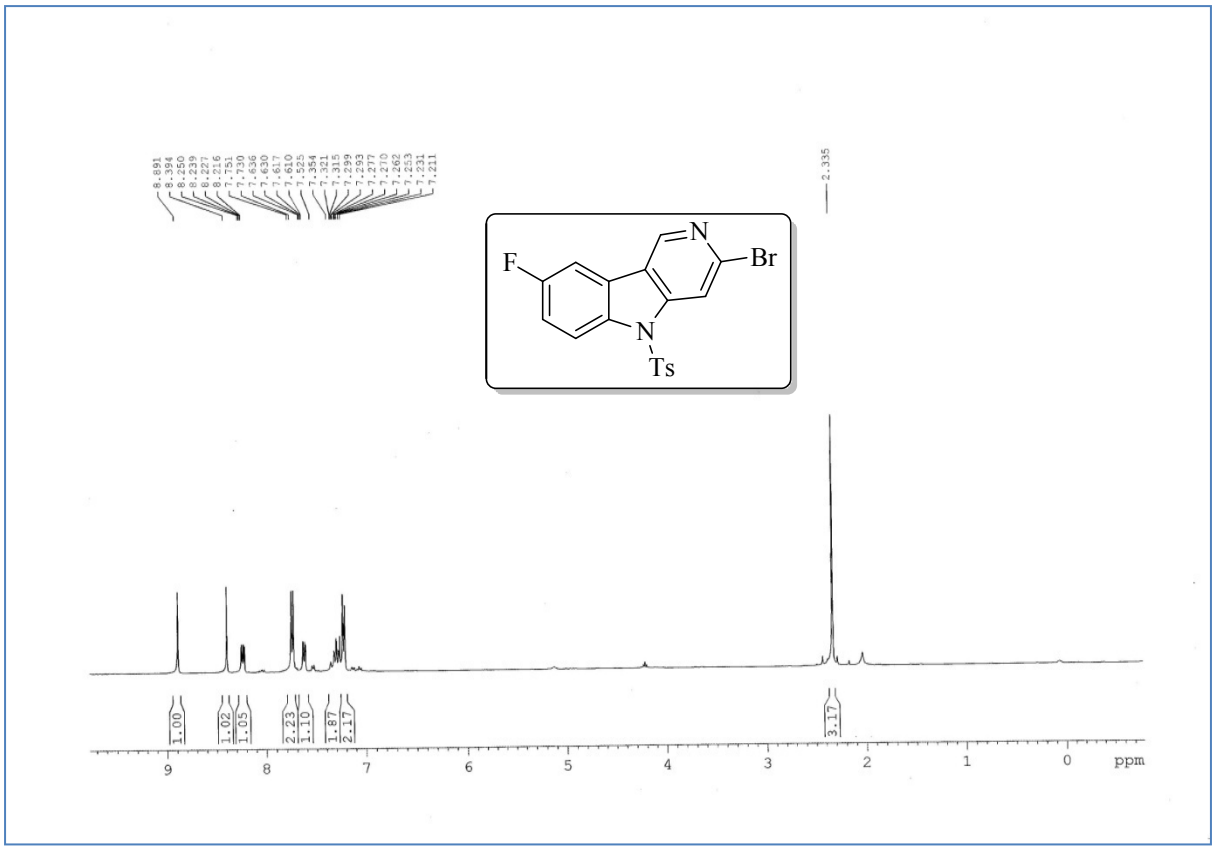
^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4ac:



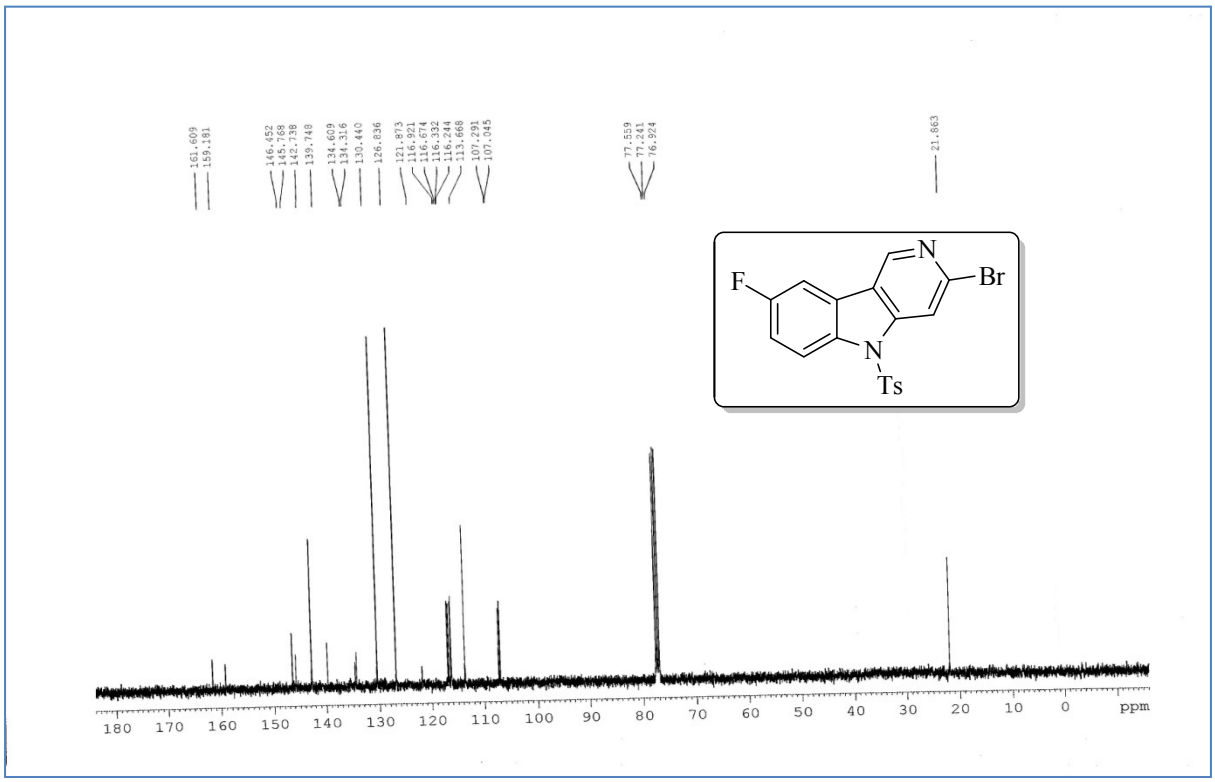
^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4ac:



^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4bc:

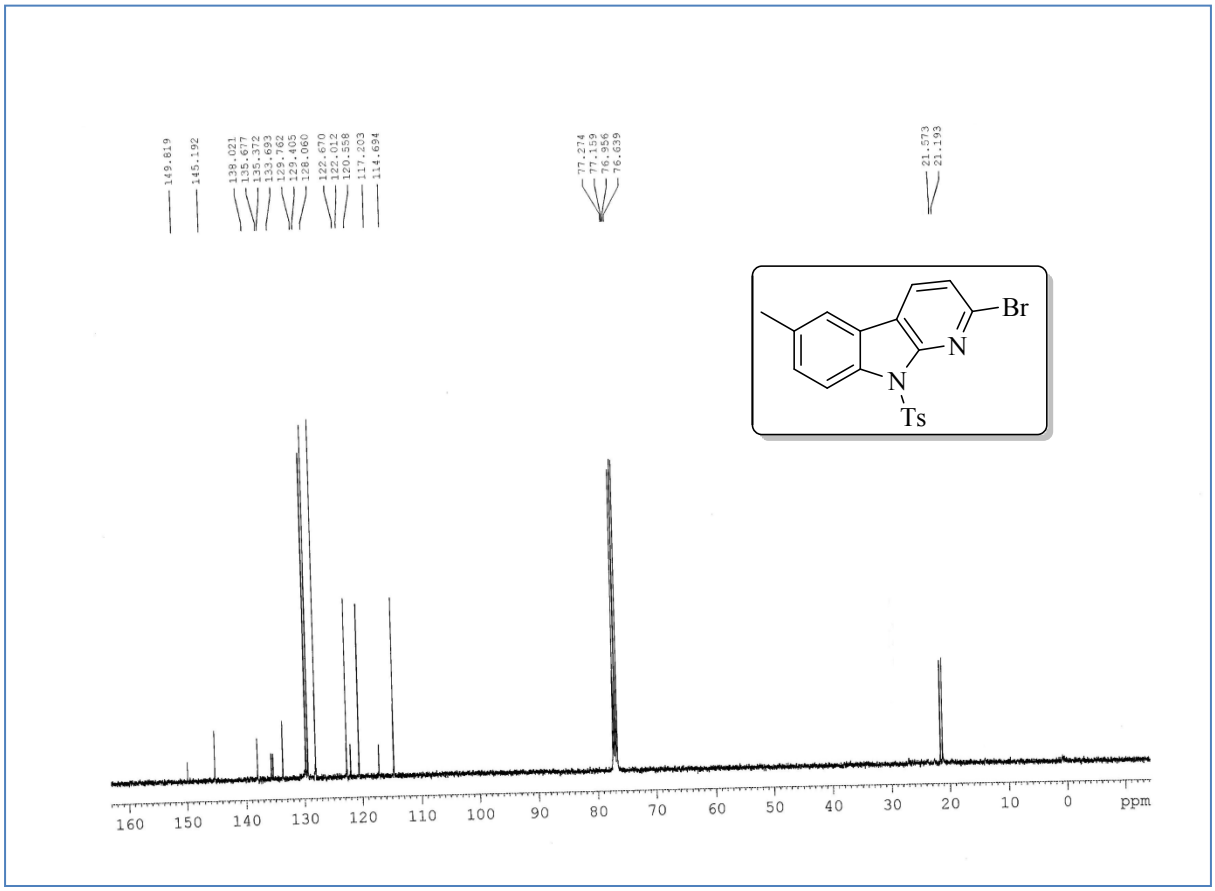


^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4bc:

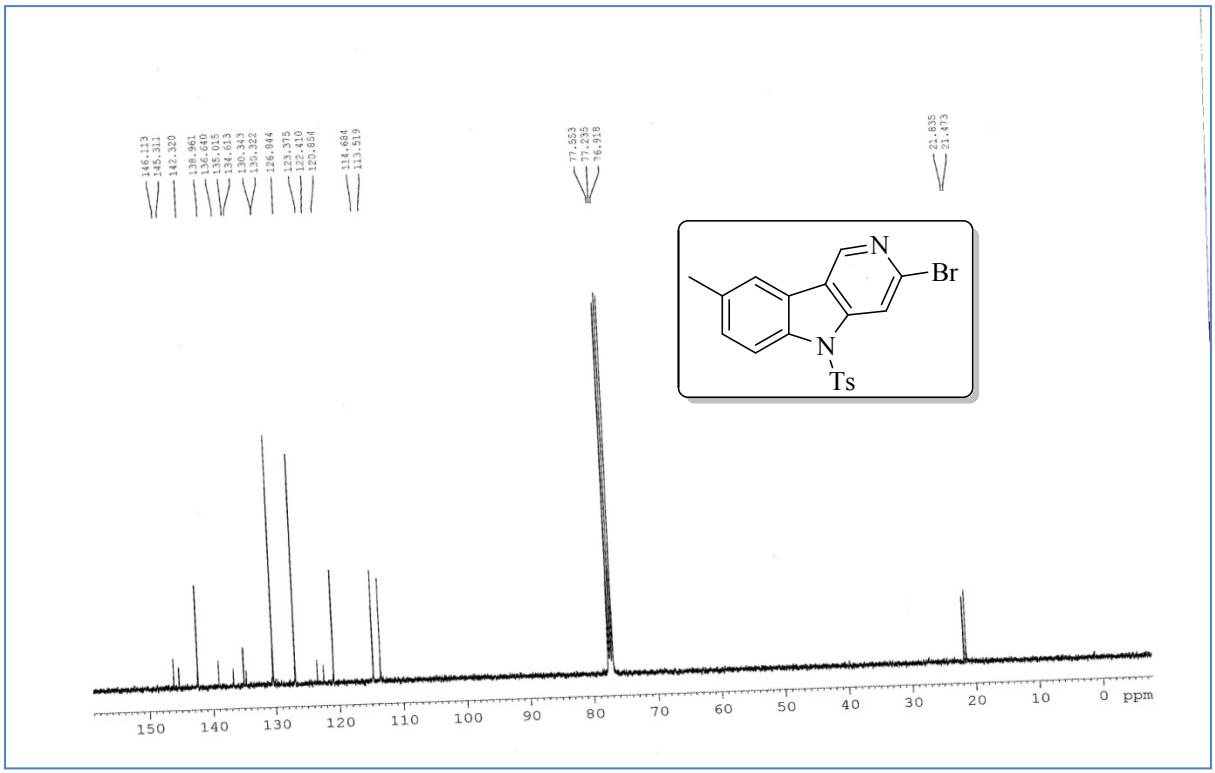


^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 4ad:

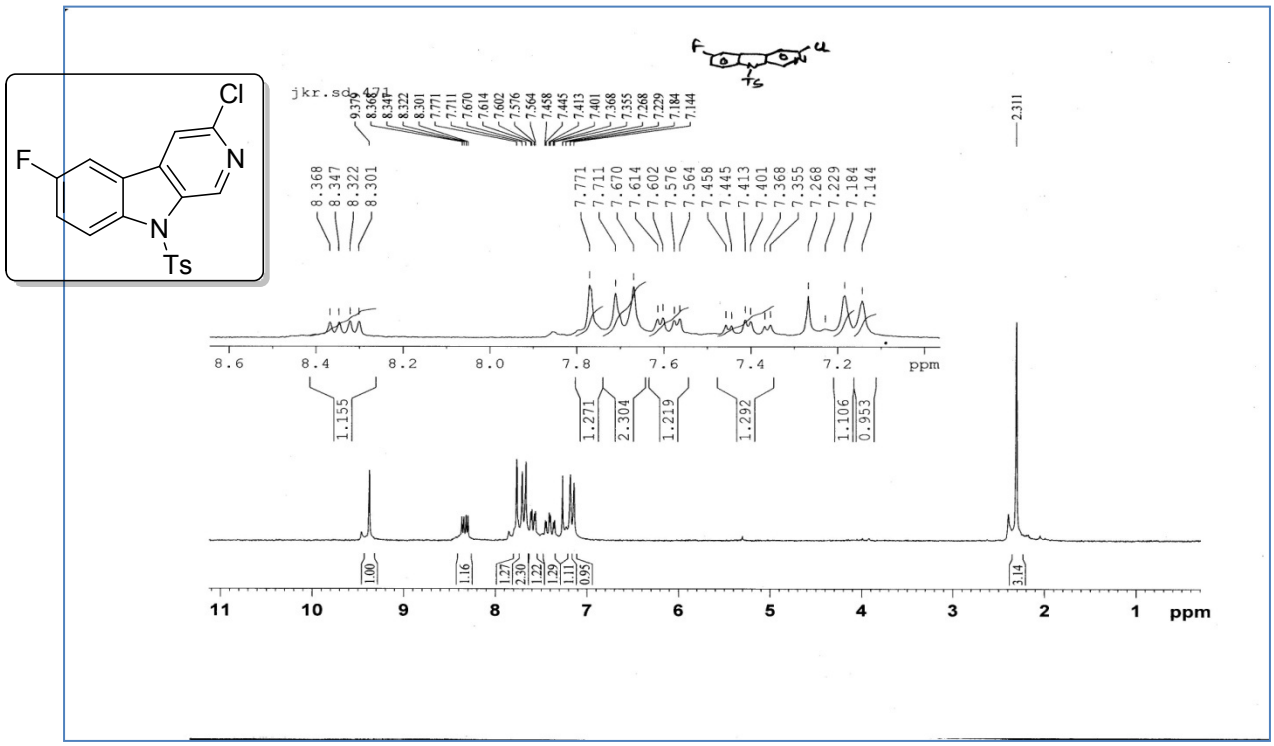
^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4ad:



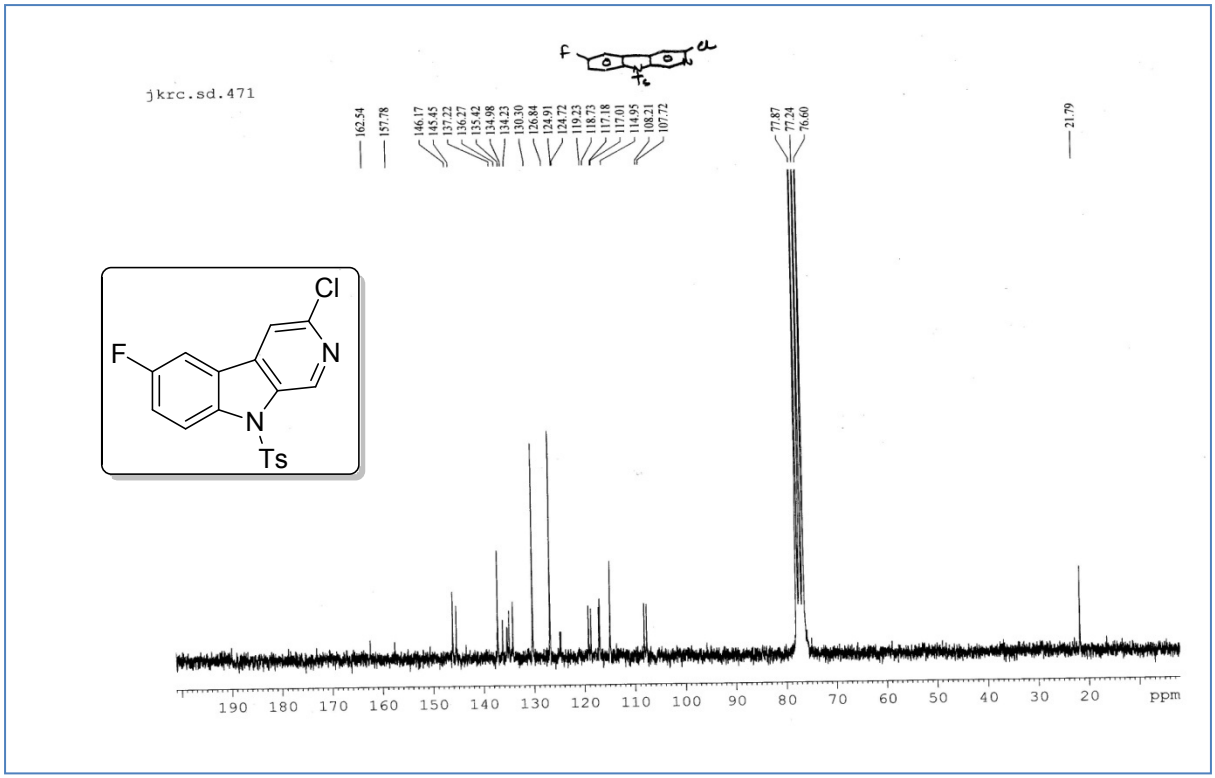
^{13}C NMR ($CDCl_3$, 100 MHz) Spectrum of 4bd:



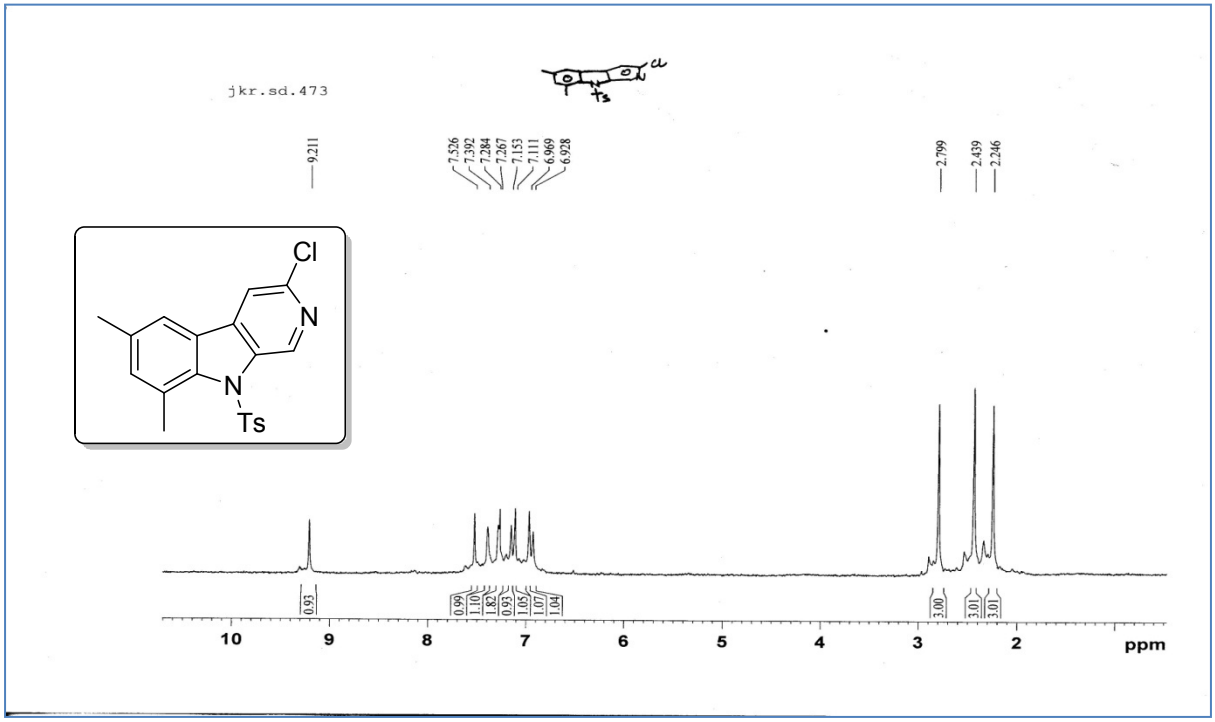
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (5b):



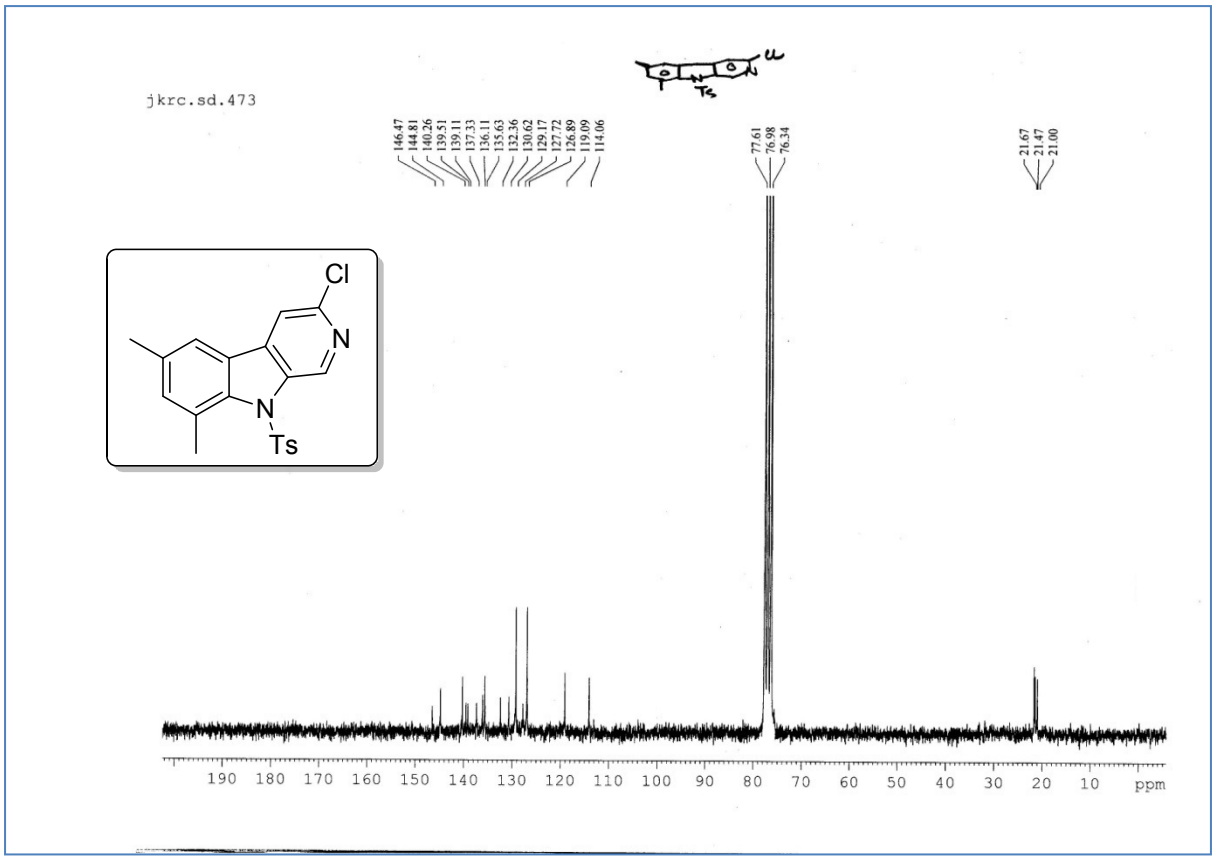
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (5b):



^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (5c):



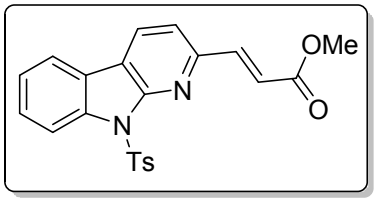
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (5c):



Procedure for Heck Coupling:

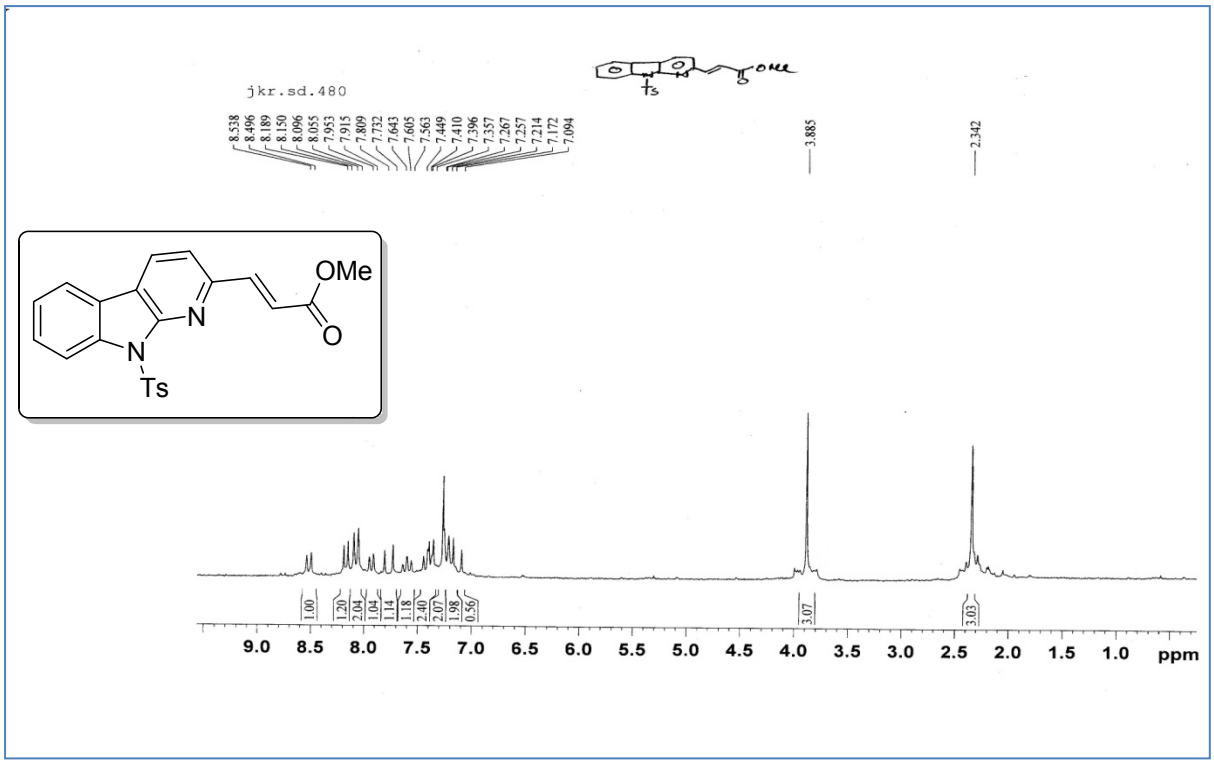
In a two necked round bottomed flask compound **4aa** (0.08 mmol, 30 mg), methyl acrylate (1 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (0.25 mmol, 6 mg), Na_2CO_3 (2.5 mmol, 22 mg) were taken in 3 mL of DMF argon atmosphere and the mixture was heated to 85 ^oC for 3 h. After completion of the reaction usual workup and column chromatography was carried out to get the desired product.

(E)-methyl-3-(9-tosyl-9H-pyrido[2,3-b]indol-2-yl)acrylate (6a):

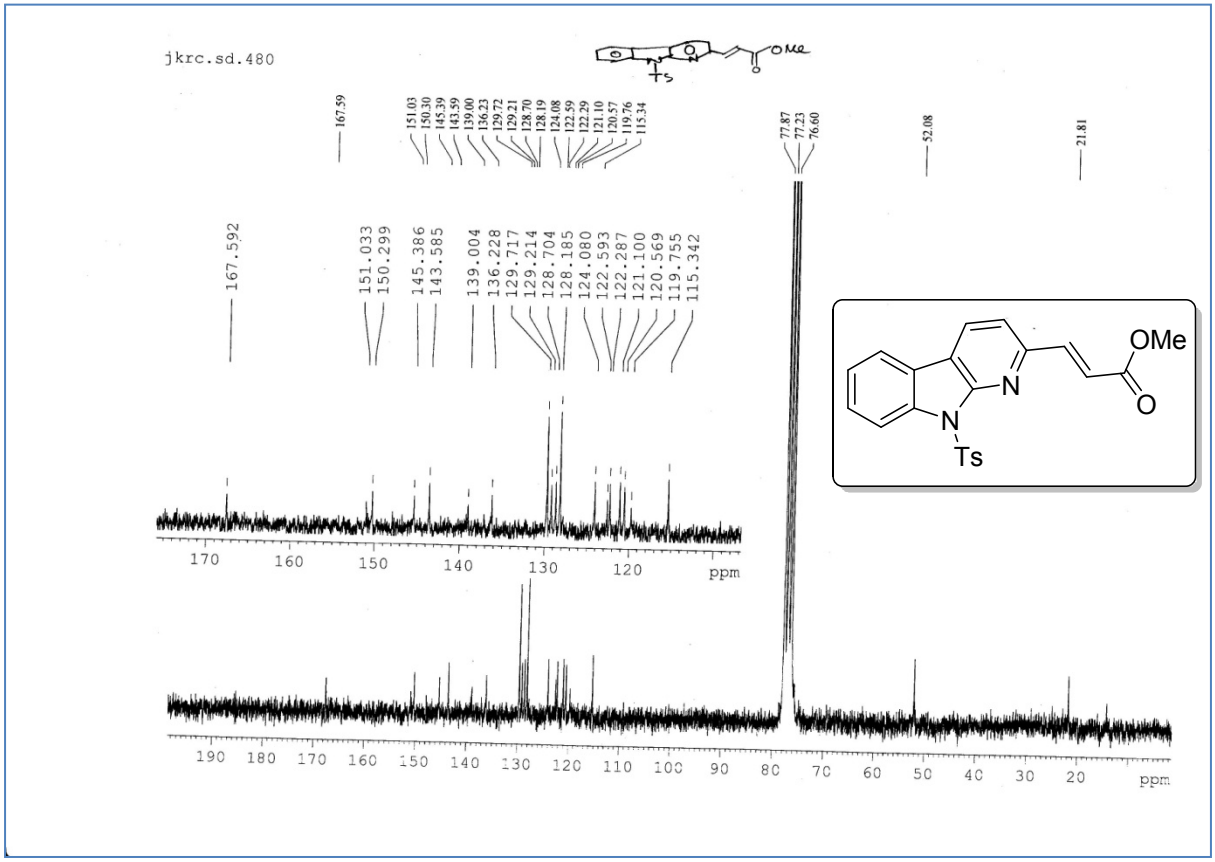


Yellow liquid, Yields: 70 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.34 (3H, s), 3.90 (3H, s), 7.20 (2H, d, J = 8.4 Hz), 7.26 (1H, s), 7.36-7.45 (2H, m), 7.61 (1H, m), 7.81 (1H, s), 7.93 (1H, d, J = 7.6 Hz), 8.10 (2H, d, J = 8.2 Hz), 8.20 (1H, d, J = 7.8 Hz), 8.50 (1H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 21.8, 52.1, 115.3, 119.8, 120.5, 121.1, 122.3, 122.6, 124.1, 128.2 (2C), 128.7, 129.2, 129.7 (2C), 136.2, 139.0, 143.6, 145.4, 150.3, 151.0, 167.6; Elemental Analysis: C, 65.01; H, 4.46; N, 6.89 %; Found: C, 64.95; H, 4.40; N, 6.82%; HRMS (ESI) m/z $[M+H]^+$ for $C_{22}H_{19}N_2O_4S^+$: 407.1060; Observed: 407.1064.

^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (6a):



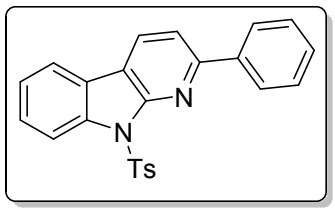
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (6a):



Procedure for Suzuki Coupling:

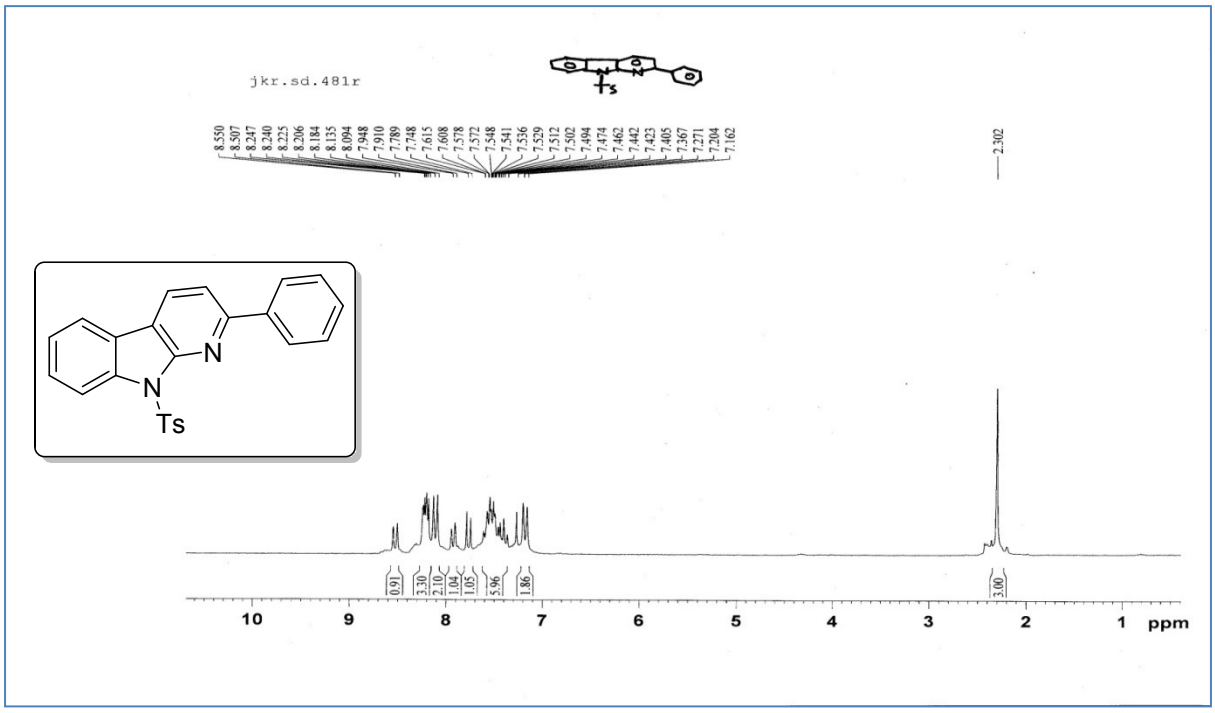
In a two necked round bottomed flask compound **4aa** (0.08 mmol, 30 mg), phenylboronic acid (1.2 mmol, 12 mg), $Pd(PPh_3)_4$ (5 mol %), Na_2CO_3 (3 mmol, 26 mg) were taken in 3 mL of DMF argon atmosphere and it was degassed for 10 min, then the mixture was heated to 85 ^oC for 3 h. After completion of the reaction usual workup and column chromatography was carried out to get the desired product.

2-phenyl-9-tosyl-9H-pyrido[2,3-b]indole (6b):

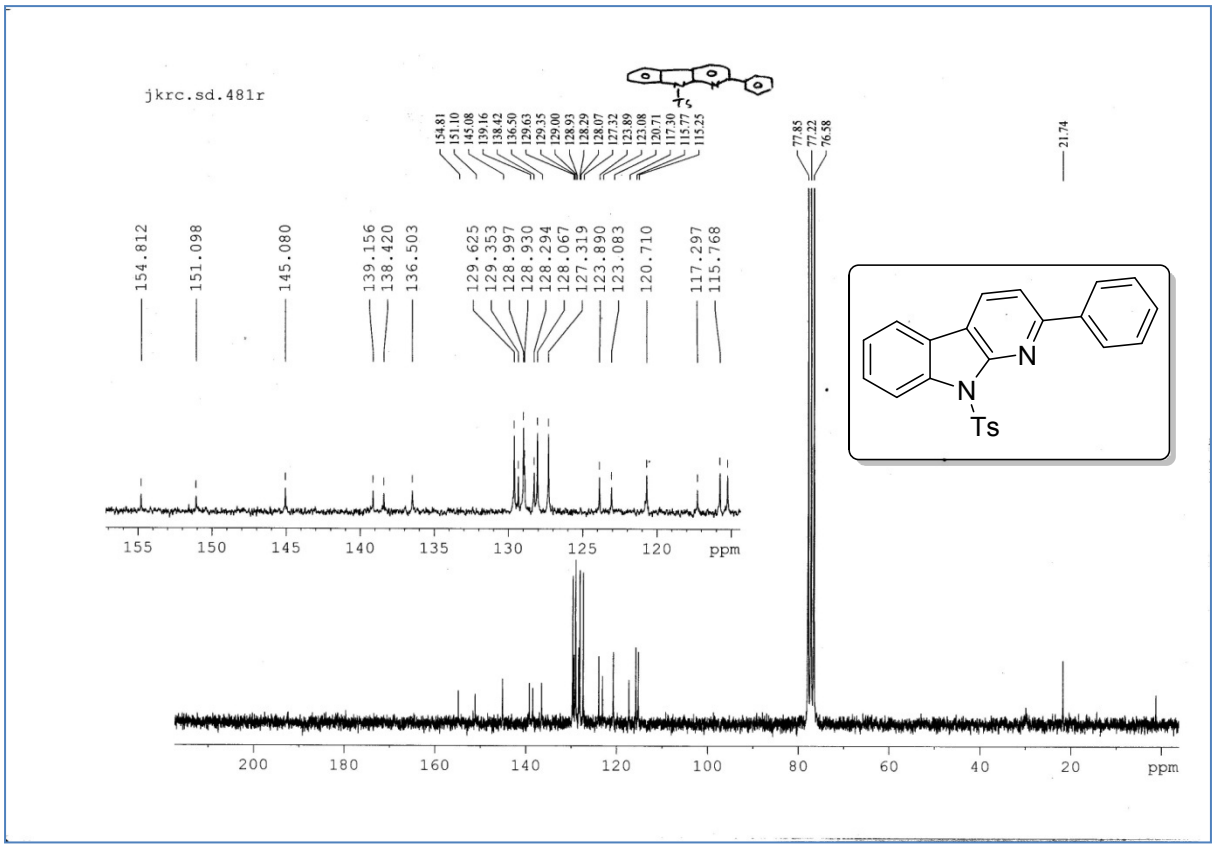


Yellow liquid, Yields: 65 %; ^1H NMR ($CDCl_3$, 200 MHz): 2.30 (3H, s), 7.16 (2H, d , J = 8.4 Hz), 7.37-7.62 (5H, m), 7.80 (1H, d, J = 8.2 Hz), 7.93 (1H, d, J = 7.6 Hz), 8.12 (2H, d, J = 8.2 Hz), 8.18-8.24 (3H, m), 8.52 (1H, d J = 8.6 Hz) ; ^{13}C NMR ($CDCl_3$, 50 MHz): 21.7, 115.3, 115.8, 117.3, 120.7, 123.1, 123.9, 127.3 (2C), 128.1 (2C), 128.3, 128.9, 129.0 (2C), 129.4, 129.6 (2C), 136.5, 138.4, 139.2, 145.1, 151.1, 154.8; Elemental Analysis: C, 72.34; H, 4.55; N, 7.03; Found: C, 72.28; H, 4.45; N, 7.00%; HRMS (ESI) m/z $[M + H]^+$ for $C_{24}H_{19}N_2O_2S^+$: 399.1162; Found: 399.1158.

^1H NMR ($CDCl_3$, 200 MHz) Spectrum of (6b):



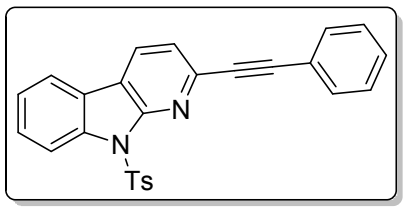
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (6b):



Procedure for Sonogashira Coupling:

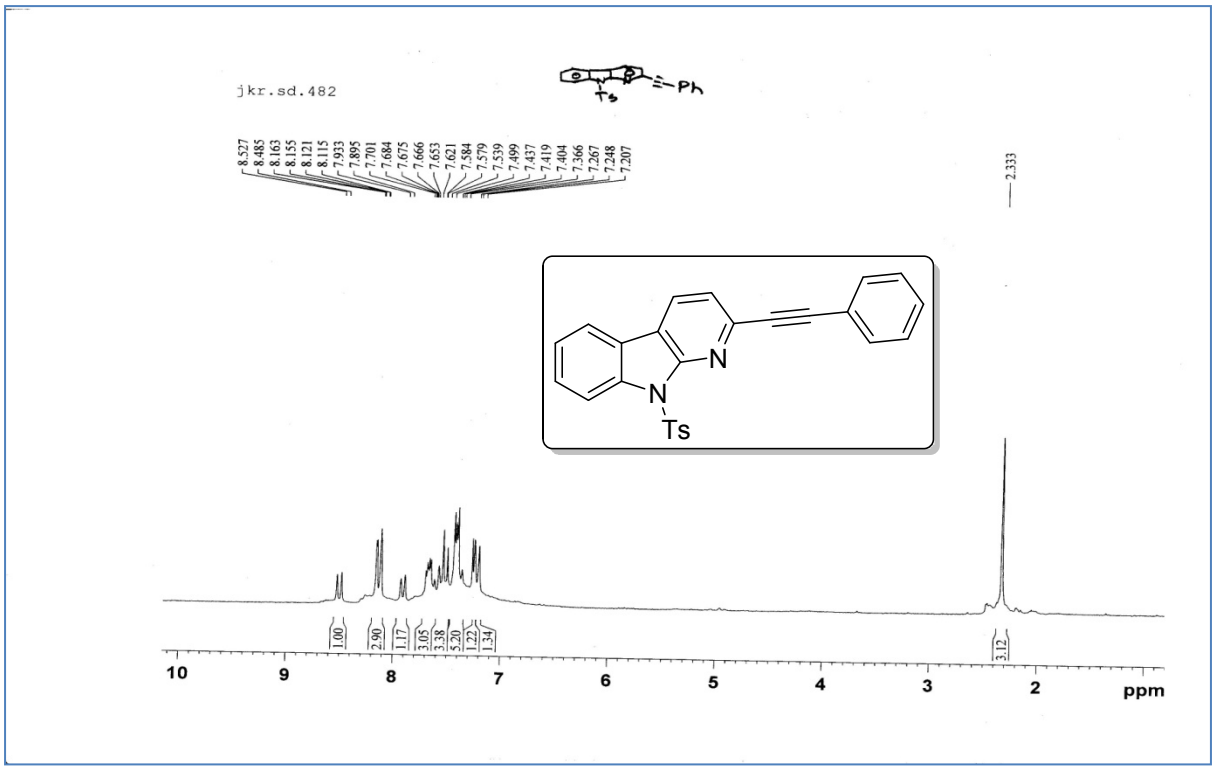
In a two necked round bottomed flask compound **4aa** (0.08 mmol, 30 mg), acetylene (1 mmol) were taken in 3 mL of Et_3N argon atmosphere and it was degassed for 10 min. To the mixture $Pd(PPh_3)_2Cl_2$ (5 mol %), CuI (5 mol %) were added and then the mixture was heated to 85 ^oC for 3 h. After completion of the reaction usual workup and column chromatography was carried out to get the desired product.

2-(phenylethynyl)-9-tosyl-9H-pyrido[2,3-b]indole (6c):

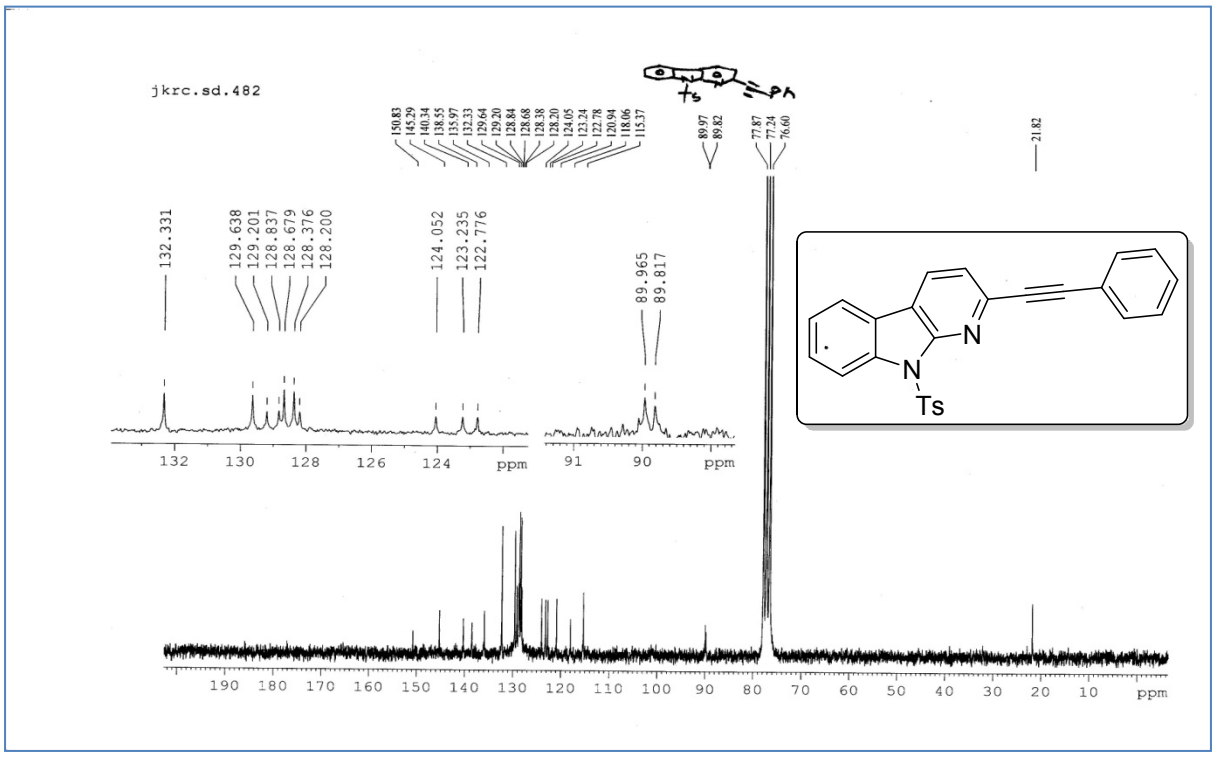


Brown stiky solid, Yields 56 %; ^{1}H NMR ($CDCl_3$, 200 MHz): 2.33 (3H, s), 7.23 (1H, d, *J* = 8.2 Hz), 7.36- 7.44 (4H, m), 7.50-7.58 (3H, m), 7.62-7.70 (3H, m), 7.90 (1H, d, *J* = 7.6 Hz), 8.12-8.16 (2H, m), 8.50 (1H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 21.8, 89.8, 90.0, 115.4, 118.1, 120.9, 122.8, 123.2, 124.1, 128.2, 128.4 (2C), 128.7 (2C), 128.8, 129.2, 129.6 (2C), 132.3 (2C), 136.0, 138.6, 140.3, 145.3, 151.0, (one carbon missing due to overlap); Elemental Analysis: C, 73.74; H, 4.52; N, 6.61; Found: C, 73.70; H, 4.44; N, 6.55%; HRMS (ESI) m/z $[M+H]^+$ for $C_{26}H_{19}N_2O_2S^+$: 423.1162; Observed : 423.1160.

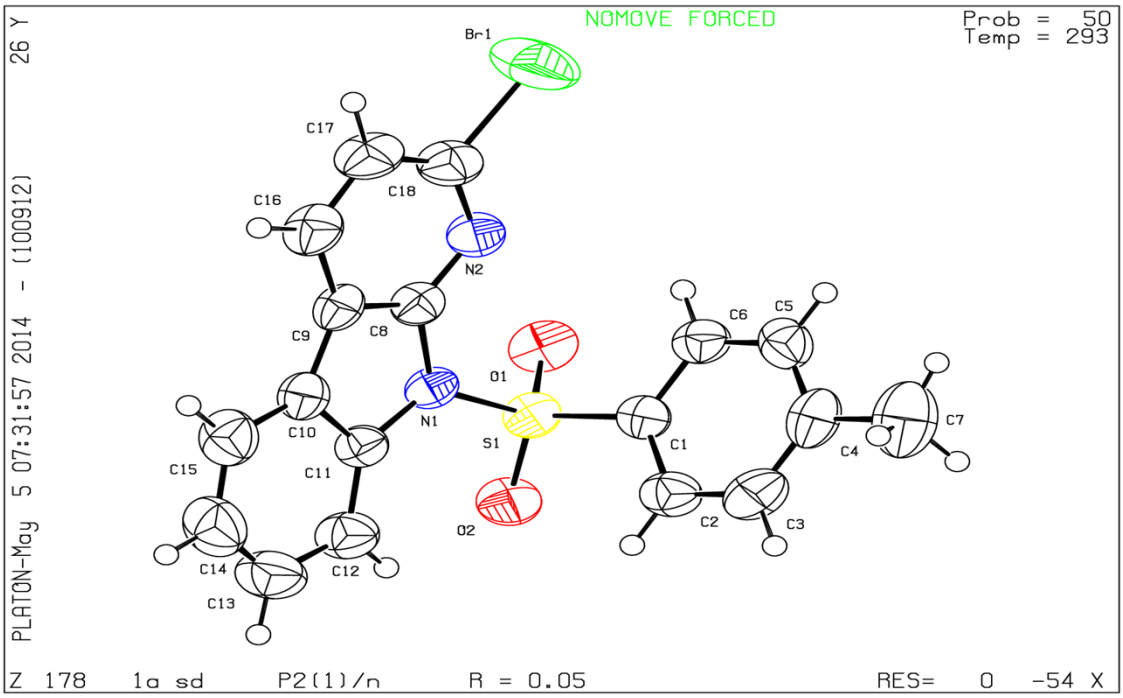
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (6c):



^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (6c):



Single crystal structure of α-Carboline:



Single crystal structure of γ-Carboline:

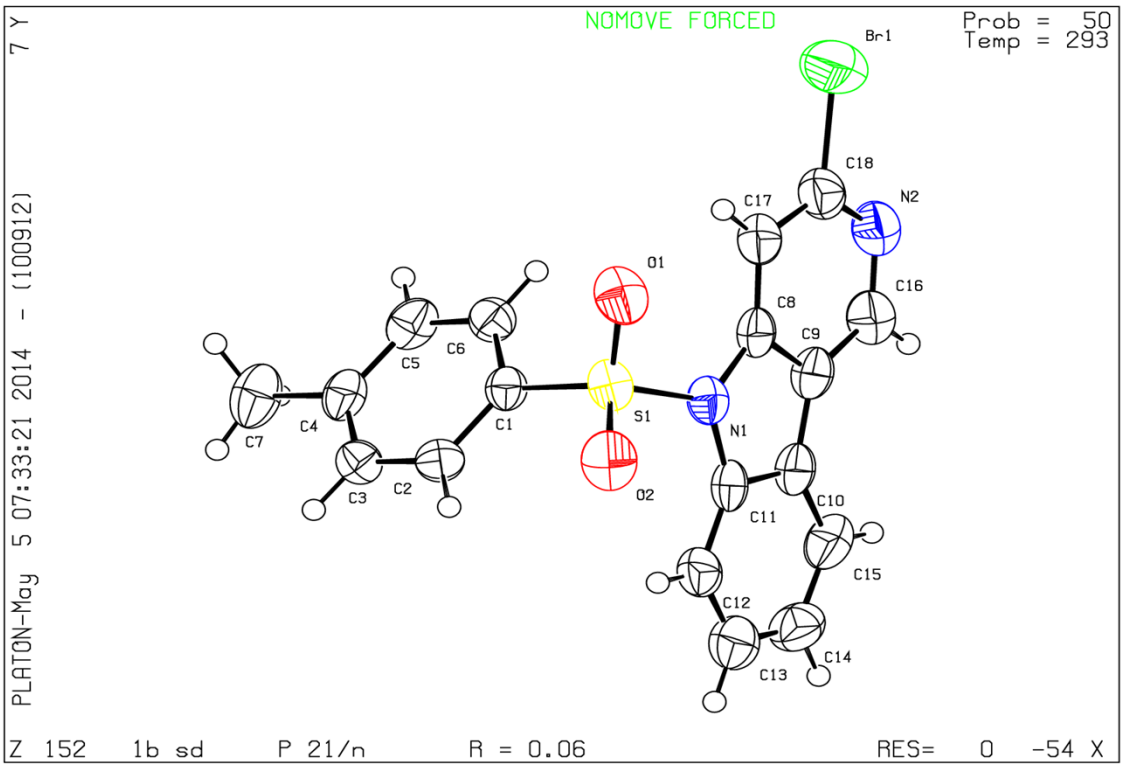


Table 1: Crystallographic Data and Refinement Parameters of compound **1a**, and **1b**

Compound	**1a(α-Carboline)**	**1b (γ-Carboline)**
Formula	$C_{18}H_{13}BrN_2O_2S$	$C_{18}H_{13}BrN_2O_2S$
M g mol^{-1}	401.27	401.27
space group	*P*2(1)/*n*	*P*2(1)/*n*
cryst syst	Monoclinic	Monoclinic
a/Å	13.675(4)	11.494(3)
b/Å	8.025(2)	8.262(2)
c/Å	15.703(4)	17.581(4)
α/deg	90.00	90.00
β/deg	100.008(8)	103.742(8)
γ/deg	90.00	90.00
V/$Å^3$	1697.2(8)	1621.7(7)
T/K	293	293
Z	4	4
D_c/g cm^{-3}	1.570	1.644

F(000)	808	808
μ(Mo-Kα)/cm^{-1}	25.58	26.77
Cryst dimens (mm^3)	0.23×0.19×0.09	0.27×0.15×0.11
No.of reflns collected	19731	18788
No. of unique reflns	2996	2845
No. of params	217	217
R1; wR2 (I > 2σ(I))	0.0504;	0.0566; 0.1971
R(int)	0.0773	0.0771
GOF (F^2)	1.061	0.635
CCDC NO.	953972	953973