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:**

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$_2$CO$_3$ and H$_2$O solvent and it then degasified with N$_2$. The mixture then heated at 95 °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$_2$SO$_4$ 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):**

![Structure](image)

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):**

![Structure](image)

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$_3$, 50 MHz): 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):**

![Structure](image)

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):

\[ \text{Diagram of NMR spectrum with peaks and chemical shifts} \]

$^{13}$C NMR (CDCl$_3$, 50 MHz) Spectrum of (5c):

\[ \text{Diagram of NMR spectrum with peaks and chemical shifts} \]
General procedure for the preparation of carboiline:

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 °C, 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$_2$SO$_4$ and evaporated to dryness under reduced pressure. Desired product was isolated by column chromatography.


White solid, Yields: 26 %, mp: 202-204 °C; $^1$H 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, $J = 7.6$ 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, 121.1, 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 $\text{C}_{18}\text{H}_{14}\text{BrN}_{2}\text{O}_2\text{S}^+$ [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 °C; $^1$H 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, $J = 7.6$ 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 %; $^1$H 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_{2}O_{2}S{^+} [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, 6.33 %; HRMS (ESI) m/z for C\(_{18}\)H\(_{13}\)BrClN\(_{2}\)O\(_{2}\)S{^+} [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 °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, 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\(_{2}\)O\(_{2}\)S{^+} [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 °C; \(^{1}H\) NMR (CDCl\(_{3}\), 400 MHz): 2.24 (3H, s), 7.21-7.35 (3H, m), 7.62 (1H, dd, \(J_{1} = 2.8\) 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, d, \(J = 8.4\) Hz), 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 °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, \(J = 8.0\) 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 °C; 1H NMR (CDCl₃ 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); 13C NMR (CDCl₃, 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 C₁₉H₁₆BrN₂O₂S⁺ [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 %; 1H NMR (CDCl₃, 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); 13C NMR (CDCl₃, 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 C₂₀H₁₈BrN₂O₂S⁺ [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 %; 1H NMR (CDCl₃, 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); 13C NMR (CDCl₃, 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 C₂₀H₁₈BrN₂O₂S⁺ [M+H]⁺: 429.0267; Observed: 429.0279.

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

White solid, Yields: 35 %; 1H NMR (CDCl₃, 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); 13C NMR (CDCl₃, 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 C₁₅H₁₀BrN₂O⁺[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$_2$O$_2$S$^+$ [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$_2$O$_2$S$^+$: 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:
**1H NMR (CDCl₃, 400 MHz) Spectrum of 4ba:**

![1H NMR Spectrum of 4ba]

**13C NMR (CDCl₃, 100 MHz) Spectrum of 4ba:**

![13C NMR Spectrum of 4ba]

**1H NMR (CDCl₃, 400 MHz) Spectrum of 4bb:**

![1H NMR 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:
$\text{^{13}C NMR (CDCl}_3, 100 \text{ MHz})$ Spectrum of 4bd:

$\text{^1H NMR (CDCl}_3, 200 \text{ MHz})$ Spectrum of (5b):

$\text{^{13}C NMR (CDCl}_3, 50 \text{ MHz})$ Spectrum of (5b):
$^1$H NMR (CDCl$_3$, 200 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$_2$CO$_3$ (2.5 mmol, 22 mg) were taken in 3 mL of DMF argon atmosphere and the mixture was heated to 85 °C 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$_2$O$_4$S$: 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(PPh₃)₄ (5 mol %), Na₂CO₃ (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 °C 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 (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₄H₁₉N₂O₂S⁺: 399.1162; Found: 399.1158.

¹H NMR (CDCl₃, 200 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 Et3N argon atmosphere and it was degassed for 10 min. To the mixture Pd(PPh3)2Cl2 (5 mol %), CuI (5 mol %) were added and then the mixture was heated to 85 °C 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 stick solid, Yields 56 %; 1H NMR (CDCl3, 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);

13C NMR (CDCl3, 50 MHz): 21.8, 89.8, 90.0, 115.4, 118.1, 120.9, 122.2, 123.2, 124.1, 128. 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 C26H19N2O2S+: 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:**

![α-Carboline Structure](image1)

**Single crystal structure of γ-Carboline:**

![γ-Carboline Structure](image2)
Table 1: Crystallographic Data and Refinement Parameters of compound 1a, and 1b

<table>
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<tr>
<th>Compound</th>
<th>1a(α-Carboline)</th>
<th>1b (γ-Carboline)</th>
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<tbody>
<tr>
<td>Formula</td>
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<td>C_{18}H_{13}BrN_{2}O_{2}S</td>
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<td>401.27</td>
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<td>space group</td>
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<td>P2(1)/n</td>
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<td>Monoclinic</td>
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<td></td>
<td>Value 1</td>
<td>Value 2</td>
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