Supporting Information

**Sodium sulphide promoted synthesis of fused quinoline at room temperature.**

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Experimental Section:

**General Procedure** - $^1$HNMR spectra were recorded on JEOL Resonance ECX-500II (500 MHz); Chemical shifts (in ppm) and coupling constant (J in Hz) are calibrated either relative to internal solvent tetramethylsilane TMS ($\delta$H = 0.00ppm) or CDCl$_3$ ($\delta$H = 7.256 ppm). In the $^1$H NMR data, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, dd = double doublets, dt = double triplets, and brs = broad singlet. $^{13}$C NMR spectra were recorded on Jeol Resonance ECX-500II (125 MHz) in CDCl$_3$; chemical shifts are calibrated relative to CDCl$_3$ ($\delta$C = 77.0 ppm). IR spectra were recorded on Perkin Elmer FT-IR spectrometer -spectrum two. The reactions were monitored by Thin Layer Chromatography (TLC) using Merck silica gel plates (Merck® 60F254). The 2-(alkynyl) quinoline-3-carbonitriles were prepared according to literature procedure.$^{[1-2]}$ Na$_2$S.9H$_2$O was purchased from Sigma Aldrich. Solvents were purified prior to its use. Melting points of the compounds was measured by Buchi melting-point apparatus and are uncorrected.

**General procedure for the synthesis of compound 2 and 3:** Solution of 2-chloroquinoline-3-carbonitrile (0.25 mmol), phenyl acetylene (0.26 mmol), PdCl$_2$ (4 mol %), CH$_3$CN (4 ml) and TEA (0.5 mmol) was stirred under N$_2$ at 80°C for 1.5-6 h (as monitored by TLC). The reaction mixture was concentrated in vacuo and residue obtained was purified by column chromatography hexane: ethyl acetate to afford. The Starting material of compound 2c and 3e is A, 2k and 3j is B, 3k is C and 3i is D respectively.

**Analytical data of the Products**

**8-methyl-2-(p- tolylethynyl)quinoline-3-carbonitrile (A):** Light Brown color solid, (88%), mp: 165°C. IR (4000-600cm$^{-1}$): $\nu_{max}$ = 2226, 2214 cm$^{-1}$. $^1$HNMR (CDCl$_3$, 500MHz): 8.47(s,1H), 7.68(dd,$J$=14.9,6.8Hz,3H), 7.55-7.51(m, 1H), 7.50-7.42(m,1H), 7.21(d,$J$=8.0Hz,2H), 2.93(m,3H), 2.60(s,3H). $^{13}$CNMR (CDCl$_3$,125MHz): $\delta$147.90, 142.24, 140.49, 138.01, 133.35, 132.70, 132.43, 132.34, 131.68, 129.42, 128.45, 126.03, 125.08, 118.41, 116.90,109.57, 95.67, 86.54, 21.84, 18.07. HRMS (ESI) for C20H14N2 m/z [M+H]$^+$ calculated:283.12, found:283.119.
2-((4-fluorophenyl)ethynyl)-6-methoxyquinoline-3-carbonitrile (B): Black color solid, (88%), mp: 185°C. IR (4000-600 cm⁻¹): ν max = 2220, 2210 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 8.39 (s, 1H), 8.04-8.02 (d, J=9.1 Hz, 1H), 7.72–7.65 (m, 2H), 7.55–7.46 (m, 2H), 7.11–7.08 (m, 2H), 3.95 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 164.55, 162.54, 159.52, 145.01, 140.36, 134.74, 131.09, 126.41, 117.55, 116.71, 116.16, 115.98, 109.95, 105.14, 93.67, 86.12, 55.96. HRMS (ESI) for C₁₉H₁₂N₂O m/z [M+H]⁺ calculated: 303.0934, found: 303.0893.

7-chloro-2-(p-tolylethynyl)quinoline-3-carbonitrile (C): Brown color solid, (88 %), mp: 179°C. IR (4000-600 cm⁻¹): ν max = 2223, 2213 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz) δ 8.49-8.48 (d, J = 8.6 Hz, 1H), 7.81–7.78 (1H), 7.63–7.57 (m, 3H), 7.22–7.21 (d, J = 6.1 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ 149.05, 144.31, 141.81, 141.00, 139.61, 132.82, 129.75, 129.50, 129.23, 128.62, 123.38, 117.90, 116.30, 109.98, 97.30, 85.85, 21.87. HRMS (ESI) for C₁₉H₁₁N₂Cl m/z [M+H]⁺ calculated: 303.0689, found: 303.0644.

2-((2-methoxyphenyl)ethynyl)quinoline-3-carbonitrile (D): Black color solid, (88%), mp: 186°C. IR(4000-600 cm⁻¹): ν max=2224, 2210 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 8.52 (s, 1H), 8.14 (d, J=84 Hz, 1H), 7.94–7.81 (m, 2H), 7.70 (d, J=55 Hz 2H), 7.68–7.56 (m, 2H), 3.95 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ 160.24, 147.84, 142.42, 141.15, 133.59, 132.30, 128.65, 127.15, 124.00, 115.71, 113.43, 112.24, 108.72, 95.60, 84.79, 76.43, 76.17, 75.92, 54.55. HRMS (ESI) for C₁₉H₁₂N₂O m/z [M+H]⁺ calculated: 285.1085, found: 285.1008.

7-methylquinoline-3-carboxamide: White color sticky solid, (88%), IR(4000-600 cm⁻¹): ν max=1680, 1690 cm⁻¹. ¹H NMR (DMSO, 500 MHz): δ 9.22 (d, J= 1.9 Hz, 1H), 8.74 (d, J=1.8 Hz, 1H), 7.92 (d, J= 8.2 Hz 1H), 7.82 (s, 1H), 7.47 (d, J= 8.8 1H), 2.50 (s, 3H). ¹³C NMR (DMSO, 125 MHz) δ 166.67, 149.17, 141.42, 135.48, 129.50, 128.77, 127.69, 127.54, 126.16, 124.49, 21.53.
Representative procedure for the synthesis of 3-phenyl-1H-thiopyran[4,3-b]quinolin-1-one and (E)-3-benzylidene-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one:

**Reaction conditions:** 2-(phenylethynyl)quinoline-3-carbonitrile (1a) (1 mmol), Na$_2$S.9H$_2$O (3 mmol) and DMSO (2 mL) at room temperature under air stirred for 15h and 30 h consequently h (as monitored by TLC). Chilled water was added to work up reaction. The reaction mixture was then extracted with EtOAC. Organic phase was washed with water, brine and dried over Na$_2$SO$_4$. Solvent was then removed under reduced pressure and residue obtained was purified by column chromatography (hexane: ethyl acetate) to afford (2a-2m and 3a-3p).

3-phenyl-1H-thiopyran[4,3-b]quinolin-1-one(2a): Brown color solid, (84 %), mp: 186 °C.

IR (4000-600 cm$^{-1}$): $\nu_{\text{max}}$ = 1688, 1615, 1580 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta_H$(ppm) 9.13 (s, 1H), 8.15 (d, 1H, $J = 8.5$ Hz), 8.09 (d, 1H, $J = 8.0$ Hz), 7.90 (t, 1H, $J = 6.5$ Hz), 7.82 (s, 1H), 7.71-7.77 (m, 2H), 7.63 (t, 1H, $J = 7.0$ Hz), 7.46-7.53 (m, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta c$(ppm) 187.8, 153.8, 151.1, 142.6, 136.7, 136.4, 133.4, 130.2, 130.0, 129.4, 129.2, 127.6, 127.1, 126.9, 122.3, 121.5. HR-MS (ESI) for C$_{18}$H$_{11}$NOS m/z [M+H]$^+$ calculated.: 290.0639, found: 290.0615.

3-(4-fluorophenyl)-1H-thiopyran[4,3-b]quinolin-1-one (2b): Brown color solid, (88 %), mp: 248 °C. IR (4000-600 cm$^{-1}$): $\nu_{\text{max}}$ = 1651, 1617, 1604 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta_H$(ppm) 9.15 (s, 1H), 8.16 (d, 1H, $J = 8.5$ Hz), 8.05 (d, 1H, $J = 8.0$ Hz), 7.92 (t, 1H, $J = 7.5$ Hz), 7.78 (s, 1H),, 7.65-7.73 (m, 2H), 7.64 (t, 1H, $J = 7.5$ Hz), 7.20 (t, 2H, $J = 8.5$ Hz). $^{13}$C NMR (CDCl$_3$, with few drops of DMSO-d$_6$, 125 MHz): $\delta c$(ppm) 187.1, 164.7, 162.6, 153.4, 150.8, 141.0, 136.2, 133.3, 132.6, 132.6, 129.7, 128.9, 128.6, 128.5, 127.4, 126.8, 121.9, 121.3, 116.3, 116.1. $^{19}$F NMR (CDCl$_3$, 500 MHz): $\delta$-110.09, HR-MS (ESI) for C$_{18}$H$_{10}$NFOS m/z [M+ H]$^+$ calculated.: 308.0545, found: 308.0512.

6-methyl-3-(p-tolyl)-1H-thiopyran[4,3-b]quinolin-1-one (2c): Yellow color solid, (86%), mp: 211 °C. IR (4000-600 cm$^{-1}$): $\nu_{\text{max}}$ = 1650, 1610, 1508 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta_H$(ppm) 9.04 (s, 1H), 7.79-7.89 (m, 2H), 7.48 (t, 1H, $J = 8.0$ Hz), 7.70 (d, 1H, $J = 7.0$ Hz), 7.62 (d, 2H, $J = 8.0$ Hz), 7.29 (d, 2H, $J = 8.0$ Hz), 2.85 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta c$(ppm) 188.5, 153.0, 150.01, 141.8, 140.4, 137.5, 136.3, 134.0, 133.0, 130.0, 127.9, 127.3, 127.1, 126.7, 122.1, 121.6, 21.3, 18.8. HR-MS (ESI) for C$_{29}$H$_{15}$NOS m/z [M+H]$^+$ calculated: 318.0952, found: 318.0929.
7-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2d): Brown color solid, (94%), mp: 166 °C. IR (4000-600 cm⁻¹): ν_max = 1649, 1577 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ_H (ppm) 9.12 (s, 1H), 8.01 (s, 1H), 7.73 (d, 2H, J = 7.0 Hz), 7.63 (d, 1H, J = 8.0 Hz), 7.56 (t, 1H, J = 8.0 Hz), 7.45-7.52 (m, 3H), 7.23 (d, 1H, J = 7.5 Hz), 4.17 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ_c (ppm) 188.1, 154.1, 152.7, 143.1, 141.9, 136.5, 136.0, 129.9, 129.1, 128.1, 127.6, 122.5, 121.8, 121.4, 110.5, 56.3. HR-MS (ESI) for C₁₉H₁₃NO₂S m/z [M+H]+ calculated: 320.0745, found: 320.0710.

3-(thiophen-3-yl)-1H-thiopyrano[4,3-b]quinolin-1-one (2e): Black color solid, (90%), mp: 195 °C. IR (4000-600 cm⁻¹): ν_max = 1642, 1555, 1576 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ_H (ppm) 9.09 (s, 1H), 8.13 (d, 1H, J = 8.6 Hz), 8.01 (d, 1H, J = 8.0 Hz), 7.91-7.87 (m, 1H), 7.80 (s, 1H), 7.68-7.65 (m, 1H), 7.63-7.59 (m, 1H), 7.52-7.50 (m, 1H), 7.47 (dd, J = 48.29 Hz, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ_c (ppm) 187.0, 153.7, 151.1, 137.9, 136.9, 136.5, 133.5, 130.0, 129.1, 127.6, 127.5, 127.0, 125.1, 122.6, 120.2. HR-MS (ESI) for C₁₉H₁₃NO₂S m/z [M+H]+ calculated: 296.0204, found: 296.0172.

7-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2f): Light green color solid, (84%), mp: 182 °C. IR (4000-600 cm⁻¹): ν_max = 1624, 1586, 1492 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ_H (ppm) 9.09 (s, 1H), 7.93 (d, J = 7.4 Hz, 2H), 7.81 (s, 1H), 7.73 (d, J = 6.8 Hz, 2H), 7.48 (dd, J = 16.0, 8.0 Hz, 4H), 2.63 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ_c (ppm) 187.49, 154.10, 153.97, 151.39, 144.36, 142.53, 136.80, 136.03, 130.16, 129.62, 129.36, 128.01, 126.89, 125.37, 121.90, 121.69, 22.38. HR-MS (ESI) for C₁₉H₁₃NOS m/z [M+H]+ calculated: 304.0796, found: 304.0752.

6-ethyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2g): Yellow color solid, (82%), mp: 188 °C. IR (4000-600 cm⁻¹): ν_max = 1646, 1608, 1561 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ_H (ppm) 9.08 (s, 1H), 7.84-7.90 (m, 2H), 7.70-7.77 (m, 3H), 7.44-7.58 (m, 4H), 3.37 (q, 2H, J = 7.5 Hz), 1.42 (t, 3H, J = 7.5 Hz).

¹³C NMR (CDCl₃, 125 MHz): δ_c (ppm) 188.0, 152.6, 149.6, 143.1, 141.4, 136.8, 136.2, 131.3, 129.9, 129.1, 127.7, 127.4, 127.1, 126.8, 122.3, 121.9, 24.5, 14.9. HR-MS (ESI) for C₂₀H₁₅NOS m/z [M+H]+ calculated: 318.0953, found: 318.0933.

6-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2h): Light green color solid, (83 %), mp: 176 °C. IR (4000-600 cm⁻¹): ν_max = 1651, 1598, 1578 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ_H (ppm) 9.09 (s, 1H), 7.86-7.90 (m, 2H), 7.71-7.77 (m, 3H), 7.46-7.54 (m, 4H), 2.87 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ_c (ppm) 188.19, 152.90, 150.36, 141.77, 137.56, 136.89, 136.36, 133.08, 130.06, 129.31, 127.91, 127.39, 127.18, 126.95, 122.34, 122.14, 18.29. HR-MS (ESI) for C₁₉H₁₃NOS m/z [M+H]+ calculated: 318.0953, found: 318.0933.
8-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2i): Light green color solid, (90% ), mp: 198°C. IR (4000-600 cm\(^{-1}\)): \(\nu_{\text{max}} = 1650,1622, 1575 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta_{\text{H}} (\text{ppm})\) 9.03 (s, 1H), 8.05 (d, 1H, \(J = 8.5 \text{ Hz}\)), 7.80 (m, 2H), 7.70-7.75 (m, 3H), 7.45-7.53 (m, 3H), 2.59 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta_{\text{C}} (\text{ppm})\) 187.96, 153.01, 149.72, 141.85, 137.75, 136.68, 135.96, 135.32, 130.05, 129.29, 128.35, 127.12, 126.77, 122.30, 121.50, 21.81. HR-MS (ESI) for C\(_{19}\)H\(_{13}\)NOS m/z [M+H]\(^+\) calculated: 304.0796, found: 304.0776.

8-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2j): Light green color solid, (92%), mp: 220°C. IR (4000-600 cm\(^{-1}\)): \(\nu_{\text{max}} = 1639, 1620, 1578 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta_{\text{H}} (\text{ppm})\) 8.97 (s, 1H), 8.03 (d, 1H, \(J = 9.5 \text{ Hz}\)), 7.78 (s, 1H), 7.67-7.73 (m, 2H), 7.54 (dd, 1H, \(J = 8.5 \text{ Hz}, J = 2.5 \text{ Hz}\)), 7.43-7.52 (m, 3H), 7.21 (d, 1H, \(J = 2.5 \text{ Hz}\)), 4.00 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta_{\text{C}} (\text{ppm})\) 188.0, 158.6, 151.8 147.7, 141.0, 136.8, 134.2, 130.6, 130.0, 129.3, 128.3, 127.4, 126.8, 122.5, 121.5, 106.1, 55.9. HR-MS (ESI) for C\(_{19}\)H\(_{13}\)NO\(_2\) S m/z [M+H]\(^+\) calculated: 320.0745, found: 320.0723.

3-(4-fluorophenyl)-8-methoxy-1H-thiopyrano[4,3-b]quinolin-1-one (2k): Light green color solid, (91%), mp: 263°C. IR (4000-600 cm\(^{-1}\)): \(\nu_{\text{max}} = 1650, 1625, 1573 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta_{\text{H}} (\text{ppm})\) 9.04 (s, 1H), 8.09 (d, \(J = 9.2 \text{ Hz}, 1\text{H}\)), 7.74 (dd, \(J = 15.6, 10.3 \text{ Hz}, 2\text{H}\)), 7.60 (dd, \(J = 9.2, 2.2 \text{ Hz}, 1\text{H}\)), 7.30–7.20 (m, 4H), 4.02 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta_{\text{C}} (\text{ppm})\) 187.73, 164.86, 162.87, 158.71, 151.75, 147.79, 139.97, 134.29, 133.05, 130.71, 128.80, 128.74, 128.43, 127.54, 122.45, 121.65, 116.57, 116.39, 105.91, 77.41, 55.95. \(^{19}\)F NMR (CDCl\(_3\), 500 MHz): \(\delta_{\text{F}}\) -110.50. HR-MS (ESI) for C\(_{19}\)H\(_{13}\)FNO\(_2\) S m/z [M+H]\(^+\) calculated: 338.0651, found: 338.0638.

3-(p-toly)-1H-thiopyrano[4,3-b]quinolin-1-one (2l): Yellow color solid, (88%), mp: 175°C. IR (4000-600 cm\(^{-1}\)): \(\nu_{\text{max}} = 1645, 1617, 1600 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta_{\text{H}} (\text{ppm})\) 9.14 (s, 1H), 8.17 (d, 1H, \(J = 9.0 \text{ Hz}\)), 8.04 (d, 1H, \(J = 8.0 \text{ Hz}\)), 7.91 (t, 1H, \(J = 7.0 \text{ Hz}\)), 7.82 (s, 1H), 7.60-7.65 (m, 3H), 7.31 (d, 2H, \(J = 7.5 \text{ Hz}\)), 2.43 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\) in few drops of DMSO-d6, 125 MHz): \(\delta_{\text{C}} (\text{ppm})\) 187.6, 153.7, 150.7, 140.6, 136.5, 133.6, 133.5, 129.9, 129.9, 128.8, 127.4, 126.9, 126.5, 122.1, 120.4, 21.2. HR-MS (ESI) for C\(_{19}\)H\(_{13}\)NOS m/z [M + H]\(^+\) calculated: 304.0796, found: 304.0765

3-(4-methoxyphenyl)-1H-thiopyrano[4,3-b]quinolin-1-one (2m): Light green color solid, (86%), mp: 242°C. IR (4000-600 cm\(^{-1}\)): \(\nu_{\text{max}} = 1633, 1615, 1588 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta_{\text{H}} (\text{ppm})\) 9.07 (s, 1H), 8.09 (d, 1H, \(J = 9.0 \text{ Hz}\)), 7.99 (d, 1H, \(J = 8.5 \text{ Hz}\)), 7.62 (d, 2H, \(J = 8.5 \text{ Hz}\)), 7.57 (t, 1H, \(J = 8.0 \text{ Hz}\)), 7.71 (s, 1H), 7.85 (t, 1H, \(J = 8.0 \text{ Hz}\)), 6.97 (d, 2H, \(J = 9.0 \text{ Hz}\)), 3.83 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\) with few drops of DMSO-d6, 125 MHz): \(\delta_{\text{C}} (\text{ppm})\) 187.4, 161.3, 154.0, 151.0, 142.3, 136.3, 133.4, 129.9, 128.9, 128.1, 127.3, 126.9, 122.1, 119.9, 114.7, 55.8. HR-MS (ESI) for C\(_{19}\)H\(_{13}\)NO\(_2\) S m/z [M+H]\(^+\) calculated: 320.0745, found: 320.0776.
(E)-3-benzylidene-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3a): Brown color solid, (82 %), mp: 262°C. IR (4000-6000 cm⁻¹): νmax= 1708, 1626, 1504 cm⁻¹. ¹H NMR (CDCl₃ with few drops of DMSO-d6, 500 MHz): δH(ppm) 9.43 (brs, NH), 8.69 (s, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 7.5 Hz, 1H), 7.63 (dd, J = 19.7, 7.4 Hz, 3H), 7.46 (t, J = 7.3 Hz, 2H), 7.34 (d, J = 4.6 Hz, 1H), 7.22 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 166.51, 155.35, 150.84, 133.25, 132.23, 132.15, 130.04, 129.88, 129.48, 128.87, 128.27, 127.89, 127.35, 107.10. HR-MS (ESI) for C₁₃H₁₂N₂O m/z [M+H]+ calculated: 273.1028, found: 273.1016.

(E)-3-benzylidene-5-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3b): Light green color solid, (84%), mp: 270°C. IR (4000-6000 cm⁻¹): νmax = 1716, 1630, 1505 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.65 (s, 1H), 8.24 (s, 1H), 7.86 (d, 1H, J = 8.0 Hz), 7.72 (d, 1H, J = 6.5 Hz), 7.50-7.56 (m, 3H), 7.48 (t, 2H, J = 7.5 Hz), 7.35 (t, 1H, J = 7.0 Hz), 7.27 (m, 1H), 2.94 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 166.9, 154.2, 149.4, 137.5, 134.4, 132.5, 132.2, 131.6, 128.9, 128.8, 127.5, 127.4, 126.5, 120.1, 106.0, 18.5. HR-MS (ESI) for C₁₅H₁₄N₂O m/z [M+H]+ calculated: 287.1184, found: 287.1171.

(E)-3-benzylidene-7-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3c): Light green color solid, (83%), mp: 268 °C. IR (4000-6000 cm⁻¹): νmax = 1704, 1688, 1494 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.87 (brs, NH), 8.57 (s, 1H), 8.14 (d, 1H, J = 8.5 Hz), 7.75 (s, 1H), 7.68 (d, 1H, J = 8.5 Hz), 7.54 (d, 2H, J = 7.5 Hz), 7.43 (t, 2H, J = 7.5 Hz), 7.30 (t, 1H, J = 7.5 Hz), 7.21 (s, 1H), 2.56 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 166.7, 154.6, 149.5, 137.5, 135.0, 134.6, 132.4, 132.3, 129.4, 128.8, 128.8, 128.2, 128.0, 120.8, 106.7, 21.7. HR-MS (ESI) for C₁₅H₁₄N₂O m/z [M+H]+ calculated: 287.1184, found: 287.1148.

(E)-3-benzylidene-5-ethyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3d): Yellow color solid, (88%), mp: 238 °C. IR (4000-6000 cm⁻¹): νmax = 1718, 1629, 1505 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.65 (s, 1H), 8.24 (brs, NH), 7.86 (d, 1H, J = 8.0 Hz), 7.72 (d, 1H, J = 7.0 Hz), 7.51-7.60 (m, 3H), 7.48 (t, 2H, J = 7.5 Hz), 7.35 (t, 1H, J = 7.5 Hz), 7.23 (s, 1H), 3.44 (q, 2H, J = 7.0 Hz), 1.45 (t, 2H, J = 7.5 Hz). ¹³C NMR (CDCl₃ with few drops of DMSO-d6, 125 MHz): δc (ppm) 166.7, 154.2, 148.9, 143.4, 134.7, 132.5, 132.5, 132.4, 130.0, 128.8, 128.8, 127.6, 127.4, 126.6, 120.1, 105.9, 24.4, 14.8. HR-MS (ESI) for C₂₀H₁₆N₂O m/z [M+H]+ calculated: 301.1341, found: 301.1321.

(E)-5-methyl-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3e): Brown color solid, (84%), mp: 241 °C. IR (4000-6000 cm⁻¹): νmax = 17011, 1635, 1507 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.63 (s, 1H), 8.40 (brs, NH), 7.84 (d, 1H, J = 8.5 Hz), 7.70 (d, 1H, J = 7.0 Hz), 7.50 (t, 1H, J = 7.5 Hz), 7.44 (d, 2H, J = 8.0 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.22 (s, 1H), 2.92 (s, 3H), 2.41 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 166.6, 154.2,
149.8, 138.1, 137.9, 133.0, 132.0, 131.9, 131.8, 130.0, 128.6, 127.8, 127.6, 126.8, 120.1, 106.6, 21.4, 18.2. HR-MS (ESI) for C20H16N2O m/z [M+H]+ calculated: 301.1341, found: 301.1299.

(E)-3-benzylidene-6-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3f): Light brown color solid, (85 %), mp: 242 °C. IR (4000-600 cm⁻¹): νmax = 1707, 1688, 1502 cm⁻¹. ¹H NMR (CDCl₃, with few drops of DMSO-d₆, 500 MHz): δH (ppm) 9.26 (brs, NH), 8.45 (s, 1H), 7.78 (d, 1H, J = 9.0 Hz), 7.49 (d, 2H, J = 5.0 Hz), 7.42 (s, 1H), 7.34 (t, 2H, J = 8.0 Hz), 7.21 (t, 1H, J = 7.5 Hz), 7.16 (dd, 1H, J = 9.5 Hz, J = 3.0 Hz), 7.04 (s, 1H), 3.91 (s, 3H).

(E)-3-(4-methoxybenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3g): Light green color solid, (90%), mp: 222 °C. IR (4000-600 cm⁻¹): νmax = 1709, 1626, 1600 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.84 (brs, NH), 8.67 (s, 1H), 8.22 (d, 1H, J = 8.5 Hz), 8.00 (d, 1H, J = 8.0 Hz), 7.85 (t, 1H, J = 7.5 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.53 (d, 2H, J = 8.5 Hz), 7.18 (s, 1H), 6.99 (d, 2H, J = 8.5 Hz), 3.86 (s, 3H).

(E)-3-benzylidene-6-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3h): Yellow color solid, (86 %), mp: 272 °C. IR (4000-600 cm⁻¹): νmax = 1711, 1620, 1507 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.63 (s, 1H), 8.37 (brs, NH), 8.03 (s, 1H), 7.91 (d, 1H, J = 8.5 Hz), 7.54 (d, 2H, J = 7.5 Hz), 7.47 (t, 3H, J = 7.5 Hz), 7.34 (t, 1H, J = 7.0 Hz), 7.21 (s, 1H), 2.63 (s, 3H).

(E)-3-((4-methoxybenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3i): Brown color solid, (91 %), mp: 218 °C. IR (4000-600 cm⁻¹): νmax = 1712, 1625, 1490 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.95 (brs, NH), 8.92 (s, 1H), 8.25 (d, 1H, J = 9.0 Hz), 8.02 (d, 1H, J = 8.0 Hz), 7.86 (t, 1H, J = 7.0 Hz), 7.62 (t, 1H, J = 8.0 Hz), 7.49 (d, 1H, J = 7.5 Hz), 7.35 (t, 1H, J = 8.0 Hz), 7.23-7.26 (m, 1H), 7.07 (t, 1H, J = 7.5 Hz), 7.02 (d, 1H, J = 8.5 Hz), 2.63 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 165.8, 156.5, 155.6, 150.7, 133.0, 132.8, 132.4, 129.7, 129.6, 129.5, 128.9, 128.2, 126.0, 120.1, 106.8, 22.3. HR-MS (ESI) for C₁₉H₁₄N₂O m/z [M+H]+ calculated: 303.1134, found: 303.1103.
Brown color solid, (90 %), mp: 257 °C. IR (4000-600 cm⁻¹): υmax = 1711, 1627, 1507 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH δ 8.52 (s, 1H), 7.57 (d, J = 9.3 Hz, 1H), 7.21 (dd, J = 8.1, 5.3 Hz, 2H), 7.09 (dd, J = 9.2, 2.2 Hz, 1H), 6.82 – 6.66 (m, 4H), 3.51 (s, 3H). (ppm). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) ¹³C NMR (125 MHz, ) δ 166.66, 158.08, 146.73, 131.96, 130.77, 130.45, 130.39, 128.79, 124.61, 120.96, 115.94, 115.77, 106.75, 104.49, 101.89, 55.30. ¹⁹F NMR (CDCl₃, 500 MHz): δ-112.57. HR-MS (ESI) for C₁₉H₁₃FN₂O₅ m/z [M + H]+ calculated: 321.1039, found: 321.1034

(E)-6-chloro-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3k): Light green color solid, (92%), mp: 265 °C. IR (4000-600 cm⁻¹): υmax = 1715, 1623, 1603 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm). δ 8.69 (s, 1H), 8.30 (d, J = 17.3 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 7.9 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.24 (s, 1H), 2.44 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 165.7, 155.8, 150.8, 138.3, 137.8, 132.6, 131.4, 130.8, 130.6, 129.8, 128.5, 127.9, 125.7, 120.5, 107.3, 20.9. HR-MS (ESI) for C₁₉H₁₃ClN₂O m/z [M+H]+ calculated: 321.0794, found: 321.0762.

(E)-3-(thiophen-3-ylmethylene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3l): Black color solid, (81 %), mp: 279 °C. IR (4000-600 cm⁻¹): υmax = 1708, 1628, 1506 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.70 (s, 1H), 8.40 (brs, NH), 8.23 (d, 1H, J = 8.5 Hz), 8.02 (d, 1H, J = 8.0 Hz), 7.87 (t, 1H, J = 8.0 Hz), 7.64 (t, 1H, J = 7.5 Hz), 7.45-7.51 (m, 2H), 7.33 (d, 1H, J = 4.5 Hz), 7.20-7.24 (m 1H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 166.4, 161.0, 156.7, 155.4, 150.9, 135.8, 133.3, 132.1, 130.1, 129.9, 127.8, 127.6, 127.4, 127.3, 124.9, 101.7. HR-MS (ESI) for C₁₈H₁₀N₂O₅ m/z [M+H]+ calculated: 279.0592, found: 279.0542.

(E)-3-(pyridine-3-ylmethylene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3m): Brown color solid, (94 %), mp: 196 °C. IR (4000-600 cm⁻¹): υmax = 1732, 1665, 1587 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 11.43 (brs, NH), 8.68 (s, 1H), 8.64 (d, 1H, J = 4.5 Hz), 8.25 (d, 1H, J = 9.0 Hz), 8.03 (d, 1H, J = 8.0 Hz), 7.87 (dt, 1H, J = 7.0 Hz, J = 1.5 Hz), 7.72 (dt, 1H, J = 7.5 Hz, J = 1.5 Hz), 7.65 (t, 1H, J = 7.0 Hz), 7.42 (d, 1H, J = 7.5 Hz), 7.14-7.19 (m, 1H), 6.99 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 166.2, 155.7, 155.7, 150.6, 149.3, 137.2, 137.0, 133.1, 132.0, 130.1, 129.9, 128.1, 127.5, 125.3, 121.7, 121.6, 102.8. HR-MS (ESI) for C₁₈H₁₂N₂O m/z [M+H]+ calculated: 274.0980, found: 274.1062.

(E)-3-(3-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3n): Brown color solid, (83%), mp: 256 °C. IR (4000-600 cm⁻¹): υmax = 1709, 1623, 1506 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm). δ 8.70 (s, 1H), 8.39–8.32 (m, 1H), 8.26 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.18 (dd, J = 22.0, 14.9 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (CDCl₃ with few drops of DMSO d₆, 125
MHz): δc (ppm) 166.70, 155.47, 150.43, 142.15, 140.77, 138.59, 134.36, 132.55, 131.73, 131.63, 129.69, 129.47, 129.44, 128.80, 128.64, 127.88, 127.75, 127.67, 127.54, 126.85, 126.23, 125.31, 124.36, 120.67, 106.87, 21.26.

HR-MS (ESI) for C20H15NO m/z [M + H]+ calculated: 287.1184, found: 287.1154.

(E)-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3o): Light green color solid, (88 %), mp: 268 °C. IR (4000-600 cm⁻¹): v_max = 1709, 1623, 1506 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.69 (s, 1H), 8.42 (s, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.64 (t, J = 7.1 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.22 (s, 1H), 2.41 (s, 3H). ¹³C NMR (CDCl₃ with few drops DMSO-d₆, 125 MHz): δc (ppm) 166.66, 155.49, 150.47, 137.95, 132.67, 132.62, 131.68, 131.61, 131.22, 129.73, 129.47, 128.92, 127.54, 126.86, 120.65, 106.98, 21.25. HRMS (ESI) for C₁₉H₁₄N₂O m/z [M + H]+ calculated: 287.1184, found: 287.1154.

(E)-3-benzylidene-7-methoxy-2, 3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3p): Light brown color solid, (88 %), mp: 242 °C. IR (4000-600 cm⁻¹): v_max = 1710, 1634, 1508 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δH (ppm) 8.41 (s, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.73 (s, 3H), 7.54–7.51 (m, 1H), 7.44 – 7.39 (m, 4H), 7.09 (s, 1H), 3.97 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δc (ppm) 166.68, 158.44, 153.22, 147.05, 135.02, 132.33, 131.48, 131.11, 129.44, 129.14, 128.80, 128.09, 121.07, 106.92, 106.39, 55.89. HR-MS (ESI) for C₁₉H₁₄N₂O m/z [M+H]+ calculated: 303.1134, found: 303.1097.

Crystal data of the product:

Crystal data were recorded on an Bruker single crystal X-ray diffractometer using graphite monochromatized Mo Ka radiation (0.71073Å) at 298 K. The structures were solved by direct methods and refined by full matrix least square method using SHELXL-2014 and winGX version 2014. All the non-hydrogen atoms were located from the difference Fourier map and refined anisotropically.

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1. Copies of $^1$H & $^{13}$C NMR and HRMS spectra of the Products:

3-phenyl-$^1$H-thiopyrano[4,3-b]quinolin-1-one (2a):
3-(4-fluorophenyl)-1*H*-thiopyrano[4,3-b]quinolin-1-one (2b):
6-methyl-3-(p-tolyl)-1H-thiopyrano[4,3-b]quinolin-1-one(2c):
7-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2d):
3-(thiophen-3-yl)-1H-thiopyrano[4,3-b]quinolin-1-one (2e):
7-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2f):
6-ethyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2g):
6-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2h):
8-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2i):

Parameter | Value
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5 Owner | 
6 Site | 
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8-methyl-3-phenyl-1H-thiopyran-4,3-b[quinolin-1-one (2i):
8-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2j):
3-(4-fluorophenyl)-8-methoxy-1H-thiopyran[4,3-b]quinolin-1-one (2k):
3-(p-tolyl)-1H-thiopyran[4,3-b]quinolin-1-one (2l):
3-(4-methoxyphenyl)-1H-thiopyrano[4,3-b]quinolin-1-one (2m):
(E)-3-benzylidene-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3a):
(E)-3-benzylidene-5-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3b):
(E)-3-benzyldene-7-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3c):
S37

(E)-3-benzylidene-5-ethyl-2,3-dihydro-1\textsubscript{H}\text{-pyrrolo}\[3,4-b\text{-}quinolin-1-one (3d):\]

\begin{equation}
\text{H}_2C
\end{equation}
\begin{equation}
\text{NH}
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\text{O}
\end{equation}

3c
(E)-3-benzylidene-5-ethyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3d):
(E)-5-methyl-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3e):
(E)-3-benzylidene-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3f):
(E)-3-(4-methoxybenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3g):

**Diagram Description:**
- The diagram includes various spectrums and labels indicating chemical shifts and peak assignments.
- The molecule structure is shown with labeled atoms and bonds.
- Additional details such as the chemical formula and molecular weight are provided in the image.
(E)-3-benzylidene-6-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3h):
\((E)-3-(2\text{-methoxybenzylidene})-2,3\text{-dihydro-1H-pyrrolo[3,4-b]quinolin-1\text{-one}}\) (3i):
(E)-3-(4-fluorobenzylidene)-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3j):
(E)-6-chloro-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3k):
(E)-3-(thiophen-3-ylmethylene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3l):
(E)-3-(pyridin-3-ylmethylene)-2,3-dihydro-1H-benzo[f]isoindol-1-one (3m):
(E)-3-(3-methylbenzylidene)-2,3-dihydro-1H-benzo[f]isoindol-1-one (3n):
(E)-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one(3o):
(E)-3-benzylidene-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one(3p):
8-methyl-2-(p-tolylethynyl)quinoline-3-carbonitrile (A):
2-((4-fluorophenyl)ethynyl)-6-methoxyquinoline-3-carbonitrile (B):
7-chloro-2-(p-tolylethynyl)quinoline-3-carbonitrile (C):
Spectrum from 7-Cl 4T (DMSO-d6) Sample 1: 7-Cl 4T, TMS (0) = 10.00 ppm from 0.00 to 10.00 ppm
2-((2-methoxyphenyl)ethynyl)quinoline-3-carbonitrile (D):
7-methylquinoline-3-carboxamide(5)
References:
