Convenient one-step synthesis of pyrrolo[3,4-c]quinolin-1-ones via TMSCl-catalyzed cascade reactions of isatins and β-enamino ketones

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1. General Information

All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Bruker Avance 400 (1H: 400 MHz, 13C: 100 MHz) and Bruker DRX500 (1H: 500 MHz, 13C: 125 MHz), chemical shifts (δ) are expressed in ppm, and J values are given in Hz, and deuterated CDCl₃ and DMSO-d₆ were used as solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. The melting points were determined on XT-4A melting point apparatus and are uncorrected. HRMs were performed on a Agilent LC/MS TOF instrument.

All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

The material 4 was purchased from Aldrich Corporation Limited. Compounds 5 were prepared according to the literature.¹

2. General Procedure
2.1 Synthesis of 3-methylene pyrrolo[3,4-c]quinolin-1-ones 6.

Isatins 4 (0.5 mmol) and β-enamino ketones 5 (0.5 mmol), acetonitrile (3.0 mL), TMSCl (2.0 mmol) were placed into a 10 mL round-bottom flask and the mixture was stirred at 60 °C for 1.0 h, and monitored by TLC until the β-enamino ketone substrate was used up. The mixture was cooled to room temperature, neutralized with a saturated solution of Na₂CO₃ to pH 8–9, and then EtOAc (30 mL × 2) were added. The organic phase was washed with water (20 mL), dried over Na₂SO₄, concentrated and purified by flash column chromatography to afford quinoline derivative 6.

2.2 Synthesis of pyrrolo[3,4-c]quinolin-1,3-diones 7.²

The 3-methylene pyrrolo[3,4-c]quinolin-1-one 6d/6f (0.2 mmol) is then dissolved in acetone, and the KMnO₄/Al₂O₃ powder (90 mg supported reagent, 0.3 mmol KMnO₄) added room temperature. After five hours of vigorous stirring, the reaction mixture is filtered and the acetone filtrate condensed. The residue is taken up into EtOAc, washed with dilute hydrochloric acid, dried over Na₂SO₄, concentrated and purified by flash column chromatography to give the product 7a/7b.
3. Characterization of products

2-(4-methoxyphenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6a).

Yellow solid; mp 199–201 ºC; IR (KBr): 1701, 1630, 1511, 1443, 1337, 1253, 1165, 1140, 1033, 844, 787, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.00 (s, 3H, C–CH₃), 3.87 (s, 3H, ArOCH₃), 5.06 (d, J = 2.4 Hz, 1H, C=CH₂), 5.54 (d, J = 2.0 Hz, 1H, C=CH₂), 7.06 (d, J = 8.8 Hz, 2H, ArH), 7.31 (d, J = 8.8 Hz, 1H, ArH), 7.64–7.68 (m, 1H, ArH), 7.76–7.80 (m, 1H, ArH), 8.12 (d, J = 8.4 Hz, 1H, ArH), 9.01 (d, J = 8.4 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 55.7, 97.9, 115.0, 115.0, 122.0, 124.5, 126.6, 127.6, 128.1, 128.8, 129.9, 129.9, 130.6, 131.3, 143.3, 148.2, 153.3, 159.7, 166.4; HRMS (TOF ES⁺): m/z calcd for C₂₀H₁₇N₂O₂ [(M+H)⁺], 317.1285; found, 317.1282.

4-methyl-3-methylene-2-(p-tolyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6b).

Yellow solid; mp 201–203 ºC; IR (KBr): 1721, 1704, 1633, 1515, 1388, 1249, 1153, 1130, 1068, 873, 781, 704 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ = 2.41 (s, 3H, ArCH₃), 2.91 (s, 3H, C–CH₃), 4.97 (d, J = 2.4 Hz, 1H, C=CH₂), 5.65 (d, J = 2.4 Hz, 1H, C=CH₂), 7.32 (d, J = 8.4 Hz, 2H, ArH), 7.40 (d, J = 8.0 Hz, 2H, ArH), 7.70–7.74 (m, 1H, ArH), 7.82–7.86 (m, 1H, ArH), 8.08 (d, J = 8.8 Hz, 1H, ArH), 8.81 (d, J = 8.4 Hz, 1H, ArH); ¹³C NMR (100 MHz, DMSO-d₆): δ = 21.7, 25.6, 99.6, 122.0, 124.3, 128.1, 129.0, 129.5, 129.5, 129.6, 130.9, 130.9, 131.0, 131.5, 132.1, 139.1, 142.9, 148.3, 154.4, 166.1; HRMS (TOF ES⁺): m/z calcd for C₂₀H₁₇N₂O [(M+H)⁺], 301.1335; found, 301.1334.

4-methyl-3-methylene-2-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6c).

Yellow solid; mp 212–215 ºC; IR (KBr): 1712, 1625, 1499, 1384, 1335, 1278, 1244, 1153, 839, 793, 770, 713 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.06 (s, 3H, C–CH₃), 5.15 (d, J = 5.0 Hz, 1H, C=CH₂), 5.62 (d, J = 5.0 Hz, 1H, C=CH₂), 7.46 (d, J = 7.75 Hz, 2H, ArH), 7.51–7.54 (m, 1H, ArH), 7.60–7.63 (m, 2H, ArH), 7.70–7.74 (m, 1H, ArH), 7.82–7.86 (m, 1H, ArH), 8.17–8.19 (m, 1H, ArH), 9.06–9.08 (m, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.6, 98.3, 122.3, 124.8, 128.0, 128.5, 129.0, 129.1, 129.1, 130.9, 131.0, 131.5, 134.4, 143.2, 148.5, 156.3, 166.5; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₅N₂O [(M+H)⁺], 287.1179; found, 287.1178.
2-(2-bromophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6d).

Yellow solid; mp 222–225 °C; IR (KBr): 1713, 1638, 1477, 1383, 1237, 1165, 1058, 1027, 859, 771 cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\(\text{d}_6\)): \(\delta \) =3.10 (s, 3H, C–CH\(_3\)), 4.85 (d, \(J = 3.4 \) Hz, 1H, C=CH\(_2\)), 5.82 (d, \(J = 3.3 \) Hz, 1H, C=CH\(_2\)), 7.57–7.61 (m, 1H, ArH), 7.66–7.71 (m, 2H, ArH), 7.87–7.91 (m, 1H, ArH), 7.96–8.03 (m, 2H, ArH), 8.29 (d, \(J = 8.5 \) Hz, 1H, ArH), 8.94 (d, \(J = 8.0 \) Hz, 1H, ArH); \(^1\)C NMR (125 MHz, DMSO-\(\text{d}_6\)): \(\delta \) = 24.2, 99.7, 121.6, 123.8, 123.9, 127.9, 127.9, 129.2, 129.6, 130.8, 131.8, 131.9, 132.3, 133.4, 133.9, 133.9, 140.9, 154.3, 164.7; HRMS (TOF ES\(^+\)): m/z calcd for C\(_{19}\)H\(_{14}\)BrN\(_2\)O [(M+H\(^+\)], 365.0290; found, 365.0293.

2-(3-bromophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6e).

White solid; mp 211–213 °C; IR (KBr): 1706, 1634, 1477, 1334, 1278, 1148, 1126, 854, 773, 720, 680 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) = 3.02 (s, 3H, C–CH\(_3\)), 5.13 (d, \(J = 2.4 \) Hz, 1H, C=CH\(_2\)), 5.60 (d, \(J = 2.4 \) Hz, 1H, C=CH\(_2\)), 7.37 (d, \(J = 7.6 \) Hz, 1H, ArH), 7.42–7.46 (m, 1H, ArH), 7.60–7.63 (m, 2H, ArH), 7.66–7.70 (m, 1H, ArH), 7.79–7.82 (m, 1H, ArH), 8.14 (d, \(J = 8.4 \) Hz, 1H, ArH), 8.99 (d, \(J = 8.4 \) Hz, 1H, ArH); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) = 25.3, 98.1, 121.9, 123.0, 124.4, 127.5, 127.6, 128.3, 128.9, 130.8, 130.9, 130.9, 131.9, 132.0, 135.4, 142.5, 148.3, 153.3, 166.0; HRMS (TOF ES\(^+\)): m/z calcd for C\(_{19}\)H\(_{14}\)BrN\(_2\)O [(M+H\(^+\)], 365.0284; found, 365.0281.

2-(2-chlorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6f).

White solid; mp 217–219.5 °C; IR (KBr): 1713, 1638, 1595, 1482, 1385, 1250, 1170, 1059, 858, 771, 688 cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\(\text{d}_6\)): \(\delta \) =3.18 (s, 3H, C–CH\(_3\)), 4.94 (d, \(J = 3.4 \) Hz, 1H, C=CH\(_2\)), 5.86 (d, \(J = 3.4 \) Hz, 1H, C=CH\(_2\)), 7.66–7.70 (m, 3H, ArH), 7.83–7.84 (m, 1H, ArH), 7.93–7.96 (m, 1H, ArH), 8.06–8.09 (m, 1H, ArH), 8.44 (d, \(J = 8.6 \) Hz, 1H, ArH), 8.96 (d, \(J = 8.2 \) Hz, 1H, ArH); \(^1\)C NMR (125 MHz, DMSO-\(\text{d}_6\)): \(\delta \) = 23.1, 100.4, 121.7, 124.0, 126.2, 128.2, 129.1, 129.8, 130.8, 131.4, 131.9, 131.9, 132.2, 132.6, 133.1, 140.4, 144.3, 154.5, 164.3; HRMS (TOF ES\(^+\)): m/z calcd for C\(_{19}\)H\(_{14}\)ClN\(_2\)O [(M+H\(^+\)], 321.0795; found, 321.0797.

2-(4-chlorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6g).
White solid; mp 236–238 ºC; IR (KBr): 1708, 1634, 1494, 1390, 1087, 834, 769, 737, 684 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.00 (s, 3H, C–CH₃), 5.09 (d, J = 2.4 Hz, 1H, C=CH₂), 5.57 (d, J = 2.4 Hz, 1H, C=CH₂), 7.36 (d, J = 8.8 Hz, 2H, ArH), 7.53 (d, J = 8.4 Hz, 2H, ArH), 7.65–7.68 (m, 1H, ArH), 7.77–7.81 (m, 1H, ArH), 8.12 (d, J = 8.4 Hz, 1H, ArH), 8.98 (d, J = 8.4 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 97.9, 116.7 (d, J = 22.8 Hz), 116.7 (d, J = 22.8 Hz), 121.9, 124.4, 127.6, 128.3, 128.9, 130.6 (d, J = 8.6 Hz), 130.6 (d, J = 8.6 Hz), 130.7, 131.1, 143.0, 148.3, 153.3, 162.5 (d, J = 247.1 Hz), 166.3; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₄ClN₂O [(M+H)+], 321.0789; found, 321.0789.

2-(4-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6h).

Pink solid; mp 189–191 ºC; IR (KBr): 1698, 1633, 1509, 1385, 1224, 1150, 1097, 833, 773, 726 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.01 (s, 3H, C–CH₃), 5.06 (d, J = 2.8 Hz, 1H, C=CH₂), 5.57 (d, J = 2.4 Hz, 1H, C=CH₂), 7.23–7.27 (m, 2H, ArH), 7.37–7.41 (m, 2H, ArH), 7.65–7.69 (m, 1H, ArH), 7.77–7.82 (m, 1H, ArH), 8.13 (d, J = 8.4 Hz, 1H, ArH), 8.99 (d, J = 8.4 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 97.9, 116.7 (d, J = 22.8 Hz), 116.7 (d, J = 22.8 Hz), 121.9, 124.4, 127.6, 128.3, 128.9, 130.6 (d, J = 3.2 Hz), 130.6 (d, J = 8.6 Hz), 130.6 (d, J = 8.6 Hz), 130.7, 131.1, 143.0, 148.3, 153.3, 162.5 (d, J = 247.1 Hz), 166.3; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₄FN₂O [(M+H)+], 305.1082; found, 305.1082.

2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6i).

White solid; mp 233–235 ºC; IR (KBr): 1706, 1626, 1590, 1497, 1450, 1224, 1145, 849, 808, 771, 748, 715, 687 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.08 (s, 3H, C–CH₃), 5.21 (d, J = 2.8 Hz, 1H, C=CH₂), 5.67 (d, J = 2.8 Hz, 1H, C=CH₂), 7.23–7.31 (m, 3H, ArH), 7.58–7.61 (m, 1H, ArH), 7.73–7.76 (m, 1H, ArH), 7.85–7.89 (m, 1H, ArH), 8.20 (d, J = 8.4 Hz, 1H, ArH), 9.06 (d, J = 8.4 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 98.1, 115.8 (d, J = 20.8 Hz), 116.3 (d, J = 22.9 Hz), 121.9, 124.4, 124.6 (d, J = 3.3 Hz), 127.6, 128.3, 128.9, 130.7, 130.8 (d, J = 9.3 Hz), 130.9, 135.5 (d, J = 9.8 Hz), 142.5, 148.2, 153.3, 163.1 (d, J = 246.7 Hz), 165.9; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₄FN₂O [(M+H)+], 305.1085; found, 305.1086.

N-(4-(4-methyl-3-methylene-1-oxo-1H-pyrrolo[3,4-c]quinolin-2(3H)-yl)phenyl)acetamide (6j).
Pink solid; mp 302.5–304.5 °C; IR (KBr): 1703, 1668, 1532, 1513, 1313, 839, 772, 744, 671 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ = 2.10 (s, 3H, C–CH₃), 2.91 (s, 3H, C–CH₃), 4.98 (s, 1H, C=CH₂), 5.64 (s, 1H, C=CH₂), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.71–7.73 (m, 1H, ArH), 7.79 (d, J = 8.0 Hz, 2H, ArH), 7.82–7.84 (m, 1H, ArH), 8.06 (d, J = 8.0 Hz, 1H, ArH), 8.80 (d, J = 8.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, DMSO-d₆): δ = 25.0, 25.6, 99.6, 120.6, 120.6, 122.0, 124.3, 128.1, 129.0, 129.2, 129.6, 130.1, 130.1, 131.0, 131.5, 140.4, 142.9, 148.3, 154.4, 166.2, 169.6; HRMS (TOF ES⁺): m/z calcd for C₂₁H₁₈N₃O₂ [(M+H)⁺], 344.1394; found, 344.1399.

8-bromo-2-(4-methoxyphenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6k).

Yellow solid; mp 230–232.5 °C; IR (KBr): 1705, 1634, 1518, 1498, 1303, 1256, 1171, 1042, 987, 829, 726 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.98 (s, 3H, C–CH₃), 3.88 (s, 3H, ArOCH₃), 5.11 (d, J = 2.4 Hz, 1H, C=CH₂), 5.58 (d, J = 2.4 Hz, 1H, C=CH₂), 7.06 (d, J = 8.8 Hz, 2H, ArH), 7.29 (d, J = 8.8 Hz, 2H, ArH), 7.82–7.85 (m, 1H, ArH), 7.96 (d, J = 8.8 Hz, 1H, ArH), 9.16 (d, J = 2.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 55.7, 98.7, 115.0, 115.0, 122.6, 123.0, 126.3, 126.8, 128.2, 129.9, 129.9, 130.3, 130.4, 134.1, 143.0, 146.7, 153.8, 159.8, 165.8; HRMS (TOF ES⁺): m/z calcd for C₂₀H₁₆BrN₂O₂ [(M+H)⁺], 395.0390; found, 395.0393.

8-bromo-4-methyl-3-methylene-2-(p-tolyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6l).

White solid; mp 231–233.5 °C; IR (KBr): 1704, 1631, 1514, 1375, 1333, 1264, 1170, 1061, 874, 814, 796, 656 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.45 (s, 3H, ArCH₃), 2.98 (s, 3H, C–CH₃), 5.14 (d, J = 2.4 Hz, 1H, C=CH₂), 5.58 (d, J = 2.4 Hz, 1H, C=CH₂), 7.27 (d, J = 8.0 Hz, 2H, ArH), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.82–7.85 (m, 1H, ArH), 7.97 (d, J = 8.8 Hz, 1H, ArH), 9.17 (d, J = 2.4 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 21.4, 25.2, 98.7, 122.6, 123.0, 126.8, 128.2, 128.4, 130.3, 130.3, 130.4, 131.2, 134.1, 138.8, 142.8, 146.7, 153.8, 165.7; HRMS (TOF ES⁺): m/z calcd for C₂₀H₁₆BrN₂O [(M+H)⁺], 379.0441; found, 379.0440.

8-bromo-4-methyl-3-methylene-2-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6m).
White solid; mp 235–237.5 °C; IR (KBr): 1721, 1634, 1497, 1384, 1335, 1185, 1067, 988, 785, 719 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.99 (s, 3H, C–CH₃), 5.15 (d, J = 2.8 Hz, 1H, C=CH₂), 5.60 (d, J = 2.8 Hz, 1H, C=CH₂), 7.39–7.41 (m, 2H, ArH), 7.46–7.50 (m, 1H, ArH), 7.55–7.58 (m, 2H, ArH), 7.83–7.86 (m, 1H, ArH), 9.16 (d, J = 2.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 98.8, 122.6, 122.9, 126.7, 128.2, 128.7, 128.8, 129.7, 130.2, 130.4, 133.9, 134.1, 142.6, 146.7, 153.8, 165.6; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₄BrN₂O [(M+H)⁺], 365.0284; found, 365.0283.

8-bromo-2-(3-bromophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6n).

White solid; mp 223.5–225.5 °C; IR (KBr): 1707, 1631, 1586, 1476, 1441, 1371, 1333, 1171, 886, 865, 682 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.99 (s, 3H, C–CH₃), 5.17 (d, J = 2.8 Hz, 1H, C=CH₂), 5.64 (d, J = 2.8 Hz, 1H, C=CH₂), 7.37 (d, J = 8.0 Hz, 1H, ArH), 7.42–7.46 (m, 1H, ArH), 7.59–7.63 (m, 2H, ArH), 7.84–7.87 (m, 1H, ArH), 9.14 (d, J = 2.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.3, 98.9, 122.8, 122.9, 123.0, 126.7, 127.4, 128.2, 129.9, 130.5, 130.9, 131.9, 132.0, 134.3, 135.2, 142.2, 146.8, 153.8, 165.4; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₃Br₂N₂O [(M+H)⁺], 442.9389; found, 442.9387.

8-bromo-2-(4-chlorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6o).

White solid; mp 244–246 °C; IR (KBr): 1704, 1634, 1496, 1378, 1333, 1174, 1089, 1016, 863, 830, 774, 736 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.99 (s, 3H, C–CH₃), 5.14 (d, J = 2.8 Hz, 1H, C=CH₂), 5.62 (d, J = 2.8 Hz, 1H, C=CH₂), 7.35 (d, J = 8.8 Hz, 2H, ArH), 7.55 (d, J = 8.8 Hz, 2H, ArH), 7.84–7.87 (m, 1H, ArH), 7.97 (d, J = 9.2 Hz, 1H, ArH), 9.13 (d, J = 2.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.3, 98.7, 122.8, 122.9, 126.7, 128.3, 130.0, 130.0, 130.0, 130.0, 130.5, 132.4, 134.3, 142.4, 146.7, 153.8, 165.5; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₃BrClN₂O [(M+H)⁺], 398.9890; found, 398.9890.

8-bromo-2-(4-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6p).
Pink solid; mp 230.5–233 °C; IR (KBr): 1702, 1633, 1512, 1393, 1222, 1182, 1160, 1061, 865, 831, 733, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.97 (s, 3H, C–CH₃), 5.10 (s, 1H, C=CH₂), 5.60 (s, 1H, C=CH₂), 7.23–7.27 (m, 2H, ArH), 7.36–7.40 (m, 2H, ArH), 7.84 (d, J = 9.2 Hz, 1H, ArH), 7.95 (d, J = 9.2 Hz, 1H, ArH), 9.11 (s, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 98.6, 116.8 (d, J = 22.7 Hz), 122.7, 122.8, 126.6, 128.2, 129.7, 130.0, 130.5 (d, J = 12.3 Hz), 130.5 (d, J = 12.3 Hz), 130.5, 134.2, 142.6, 146.7, 153.8, 162.5 (d, J = 247.2 Hz), 165.7; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₃BrFN₂O [(M+H)⁺], 383.0190; found, 383.0194.

8-bromo-2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6q).

White solid; mp 226.5–230 °C; IR (KBr): 1702, 1629, 1496, 1393, 1334, 1218, 1146, 890, 857, 827, 673 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.99 (s, 3H, C–CH₃), 5.19 (d, J = 2.8 Hz, 1H, C=CH₂), 5.64 (d, J = 2.8 Hz, 1H, C=CH₂), 7.14–7.23 (m, 3H, ArH), 7.51–7.57 (m, 1H, ArH), 7.84–7.87 (m, 1H, ArH), 8.08 (d, J = 9.2 Hz, 1H, ArH), 9.14 (d, J = 2.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 21.3, 25.1, 98.6, 122.4, 123.3, 128.1, 128.3, 130.2, 130.2, 130.3, 130.9 (d, J = 8.7 Hz), 134.3, 135.3 (d, J = 9.8 Hz), 142.2, 146.7, 153.8, 163.1 (d, J = 247.0 Hz), 165.4; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₃BrFN₂O [(M+H)⁺], 383.0190; found, 383.0192.

8-chloro-4-methyl-3-methylene-2-(p-tolyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6r).

White solid; mp 223–225 °C; IR (KBr): 1702, 1626, 1499, 1402, 1340, 1169, 1071, 873, 796, 742 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.50 (s, 3H, ArCH₃), 3.04 (s, 3H, C–CH₃), 5.19 (d, J = 2.4 Hz, 1H, C=CH₂), 5.63 (d, J = 2.4 Hz, 1H, C=CH₂), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.41 (d, J = 8.0 Hz, 2H, ArH), 7.74–7.76 (m, 1H, ArH), 8.08 (d, J = 9.2 Hz, 1H, ArH), 9.03 (d, J = 9.2 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 21.3, 25.1, 98.6, 122.4, 123.3, 128.1, 128.3, 130.2, 130.3, 130.3, 131.0, 131.4, 134.1, 138.7, 142.6, 146.3, 153.5, 165.6; HRMS (TOF ES⁺): m/z calcd for C₂₀H₁₈ClN₂O [(M+H)⁺], 335.0946; found, 335.0946.

8-chloro-4-methyl-3-methylene-2-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6s).
Red solid; mp 231–233 °C; IR (KBr): 1702, 1629, 1388, 1331, 1184, 897, 873, 720, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.00 (s, 3H, C–CH₃), 5.15 (d, J = 2.4 Hz, 1H, C=CH₂), 5.60 (d, J = 2.4 Hz, 1H, C=CH₂), 7.40 (d, J = 7.6 Hz, 2H, ArH), 7.46–7.50 (m, 1H, ArH), 7.55 (d, J = 7.6 Hz, 2H, ArH), 7.69–7.72 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.1, 98.7, 122.4, 123.3, 128.6, 128.6, 128.6, 128.6, 128.6, 128.7, 129.6, 130.2, 131.4, 133.8, 134.2, 142.5, 146.3, 153.5, 165.5; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₄ClN₂O [(M+H)⁺], 321.0789; found, 321.0788.

2-(3-bromophenyl)-8-chloro-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6t).

White solid; mp 193.5–195 °C; IR (KBr): 1704, 1630, 1475, 1369, 1334, 1171, 1075, 865, 782, 748, 684 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.97 (s, 3H, C–CH₃), 5.16 (d, J = 2.4 Hz, 1H, C=CH₂), 5.62 (d, J = 2.4 Hz, 1H, C=CH₂), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.42 (d, J = 8.0 Hz, 1H, ArH), 7.59–7.62 (m, 2H, ArH), 7.68–7.71 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.1, 98.8, 122.2, 122.9, 123.1, 127.3, 128.1, 129.9, 130.3, 130.8, 131.5, 131.7, 131.8, 134.3, 135.0, 142.1, 146.3, 153.5, 165.3; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₃BrClN₂O [(M+H)⁺], 398.9900; found, 398.9904.

8-chloro-2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6u).

Yellow solid; mp 238–240 °C; IR (KBr): 1702, 1630, 1593, 1387, 1333, 1160, 1021, 883, 831, 692 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.06 (s, 3H, C–CH₃), 5.25 (d, J = 2.8 Hz, 1H, C=CH₂), 5.70 (d, J = 2.8 Hz, 1H, C=CH₂), 7.21–7.32 (m, 3H, ArH), 7.57–7.62 (m, 1H, ArH), 7.77–7.79 (m, 1H, ArH), 8.11 (d, J = 8.95 Hz, 1H, ArH), 9.02 (d, J = 2.15 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.5, 99.0, 116.2 (d, J = 20.8 Hz), 116.5 (d, J = 23.0 Hz), 122.7, 123.6, 123.6, 124.8, 128.6, 130.4, 130.6, 131.1 (d, J = 8.9 Hz), 132.0, 134.8, 135.6 (d, J = 5.8 Hz), 142.5, 146.8, 153.9, 163.4 (d, J = 250.6 Hz), 165.7; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₂ClFNO [(M+H)⁺], 339.0695; found, 339.0695.

8-fluoro-2-(4-methoxyphenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6v).
Yellow solid; mp 200–202 °C; IR (KBr): 1703, 1634, 1515, 1387, 1252, 1193, 1036, 873, 867, 810, 786, 662 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.05 (s, 3H, C–CH₃), 3.94 (s, 3H, ArOCH₃), 5.16 (d, J = 2.4 Hz, 1H, C=CH₂), 5.64 (d, J = 2.3 Hz, 1H, C=CH₂), 7.12 (d, J = 8.75 Hz, 2H, ArH), 7.36 (d, J = 8.75 Hz, 2H, ArH), 7.58–7.62 (m, 1H, ArH), 8.16–8.19 (m, 1H, ArH), 8.67–8.69 (m, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.3, 56.0, 98.8, 108.5 (d, J = 23.8 Hz), 115.3, 115.3, 121.0 (d, J = 26.3 Hz), 123.0 (d, J = 11.3 Hz), 126.7, 128.5, 130.2, 130.2, 131.2 (d, J = 6.3 Hz), 131.5 (d, J = 10 Hz), 143.4, 145.6, 152.8, 160.1, 161.5 (d, J = 250.0 Hz), 166.4; HRMS (TOF ES⁺): m/z calcd for C₂₀H₁₈FN₂O [(M+H)⁺], 335.1190; found, 335.1194.

8-fluoro-4-methyl-3-methylene-2-(p-tolyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6w).

Yellow solid; mp 165.5–167 °C; IR (KBr): 1717, 1634, 1514, 1374, 1341, 1243, 1210, 1093, 873, 804, 784, 753 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.45 (s, 3H, ArCH₃), 3.00 (s, 3H, C–CH₃), 5.13 (d, J = 2.8 Hz, 1H, C=CH₂), 5.59 (d, J = 2.4 Hz, 1H, C=CH₂), 7.28 (d, J = 8.4 Hz, 2H, ArH), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.52–7.57 (m, 1H, ArH), 8.10–8.14 (m, 1H, ArH), 8.62–8.65 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 21.4, 25.1, 98.6, 108.2 (d, J = 23.7 Hz), 120.7 (d, J = 25.9 Hz), 122.7 (d, J = 11.6 Hz), 128.2, 128.5, 128.5, 130.4, 130.9 (d, J = 5.8 Hz), 131.2, 131.3, 133.8, 142.9, 145.3, 152.6 (d, J = 2.9 Hz), 161.6 (d, J = 248.5 Hz), 165.9; HRMS (TOF ES⁺): m/z calcd for C₂₀H₁₆FN₂O [(M+H)⁺], 319.1241; found, 319.1245.

8-fluoro-4-methyl-3-methylene-2-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6x).

White solid; mp 204.5–206 °C; IR (KBr): 1702, 1633, 1602, 1512, 1373, 1341, 1270, 1211, 1095, 870, 840, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.00 (s, 3H, C–CH₃), 5.14 (d, J = 2.8 Hz, 1H, C=CH₂), 5.60 (d, J = 2.4 Hz, 1H, C=CH₂), 7.39–7.41 (m, 2H, ArH), 7.48–7.50 (m, 1H, ArH), 7.52–7.58 (m, 3H, ArH), 8.10–8.13 (m, 1H, ArH), 8.61–8.64 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.1, 98.6, 108.2 (d, J = 23.7 Hz), 120.8 (d, J = 25.9 Hz), 122.7 (d, J = 11.6 Hz), 128.3, 128.7, 128.8, 129.7, 129.7, 130.9 (d, J = 6.0 Hz), 131.3 (d, J = 9.4 Hz), 133.9, 142.7, 145.3, 152.6 (d, J = 2.9 Hz), 161.7 (d, J = 248.6 Hz), 165.8; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₄FN₂O [(M+H)⁺], 305.1085; found, 305.1089.

2-(3-bromophenyl)-8-fluoro-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6y).
White solid; mp 197–199 °C; IR (KBr): 1705, 1635, 1514, 1478, 1375, 1340, 1241, 1194, 870, 798, 772, 679 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.99 (s, 3H, C–CH₃), 5.16 (d, J = 1.6 Hz, 1H, C=CH₂), 5.63 (s, 1H, C=CH₂), 7.26–7.36 (m, 1H, ArH), 7.42–7.46 (m, 1H, ArH), 7.53–7.63 (m, 3H, ArH), 8.10–8.13 (m, 1H, ArH), 8.56–8.60 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.1, 98.8, 108.1 (d, J = 23.8 Hz), 120.9 (d, J = 25.9 Hz), 122.6 (d, J = 11.7 Hz), 123.0, 127.5, 128.2, 130.5, 130.9, 131.4 (d, J = 9.4 Hz), 131.9, 131.9, 135.2, 142.3, 145.3, 152.5 (d, J = 2.9 Hz), 161.7 (d, J = 249 Hz), 165.6; HRMS (TOF ES⁺): m/z calcld forC₁₀H₁₃BrFN₂O [(M+H)⁺], 383.0190; found, 383.0187.

8-fluoro-2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6z).

White solid; mp 221–223 °C; IR (KBr): 1700, 1633, 1596, 1514, 1494, 1376, 1344, 1223, 865, 775, 681 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.00 (s, 3H, C–CH₃), 5.18 (d, J = 2.4 Hz, 1H, C=CH₂), 5.63 (d, J = 2.4 Hz, 1H, C=CH₂), 7.15–7.26 (m, 3H, ArH), 7.53–7.57 (m, 2H, ArH), 8.10–8.13 (m, 1H, ArH), 8.57–8.60 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 25.1, 98.7, 108.1 (d, J = 23.7 Hz), 115.9 (d, J = 20.8 Hz), 116.3 (d, J = 23.0 Hz), 120.9 (d, J = 26.0 Hz), 122.6 (d, J = 11.7 Hz), 124.5 (d, J = 3.3 Hz), 128.2, 130.6 (d, J = 6.1 Hz), 130.9 (d, J = 9.0 Hz), 131.4 (d, J = 9.2 Hz), 135.3 (d, J = 9.9 Hz), 142.3, 145.3, 152.5 (d, J = 2.8 Hz), 161.7 (d, J = 248.7 Hz), 163.1 (d, J = 247.0 Hz), 165.3; HRMS (TOF ES⁺): m/z calcld forC₁₀H₁₃F₃N₂O [(M+H)⁺], 323.0990; found, 323.0996.

2-butyl-6-fluoro-4-methyl-3-methylene-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6a')

White solid; mp 90–92 °C; IR (KBr): 1699, 1510, 1469, 1227, 1089, 831, 758, 631 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 0.98–1.01 (m, 3H, CH₃), 1.41–1.48 (m, 2H, CH₂), 1.68–1.75 (m, 2H, CH₂), 3.03 (s, 3H, CH₃), 3.86–3.89 (m, 2H, CH₂), 5.28 (d, J = 2.8 Hz, 1H, C=CH₂), 5.62 (d, J = 2.8 Hz, 1H, C=CH₂), 7.44–7.48 (m, 1H, ArH), 7.57–7.61 (m, 1H, ArH), 8.78 (d, J = 8.5 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 14.1, 20.6, 25.6, 31.0, 39.6, 97.1, 114.9 (d, J = 20.0 Hz), 120.5 (d, J = 5.0 Hz), 123.8, 128.2 (d, J = 8.8 Hz), 128.8, 131.9, 138.2 (d, J = 11.3 Hz), 141.5, 154.0, 157.8 (d, J = 253.8 Hz), 166.3; HRMS (TOF ES⁺): m/z calcld forC₁₇H₁₈FN₂O [(M+H)⁺], 285.1398; found, 285.1399.

2-cyclohexyl-4-methyl-3-methylene-6-(trifluoromethyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6b')
White solid; mp 164–166 °C; IR (KBr): 1691, 1511, 1375, 1303, 1133, 845, 767 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 1.33–1.38 (m, 1H, CH₂), 1.41–1.49 (m, 2H, CH₂), 1.77–1.80 (m, 1H, CH₂), 1.86–1.89 (m, 2H, CH₂), 1.89–1.98 (m, 2H, CH₂), 2.34–2.41 (m, 2H, CH₂), 3.05 (s, 3H, CH₃), 4.12–4.15 (m, 1H, CH), 5.46 (d, J = 2.9 Hz, 1H, C=CH₂), 5.69 (d, J = 2.9 Hz, 1H, C=CH₂), 7.68–7.71 (m, 1H, ArH), 8.11 (d, J = 7.3 Hz, 1H, ArH), 9.26 (d, J = 8.3 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.8, 26.0, 26.8, 26.8, 30.3, 30.3, 53.5, 97.7, 122.8, 124.3 (J = 271.3 Hz), 126.7, 127.8 (J = 30.0 Hz), 128.4, 128.6, 128.9, 131.7, 141.2, 144.4, 154.4, 166.7; HRMS (TOF ESI⁺): m/z calcd for C₂₀H₂₀F₃N₂O [(M+H)+], 361.1522; found, 361.1526.

2-butyl-4-methyl-3-methylene-6-(trifluoromethyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6c')

White solid; mp 113–115 °C; IR (KBr): 1701, 1578, 1510, 1452, 1348, 1300, 1130, 840, 675 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 0.99–1.02 (m, 3H, CH₃), 1.42–1.49 (m, 2H, CH₂), 1.70–1.76 (m, 2H, CH₂), 3.05 (s, 3H, CH₃), 3.88–3.91 (m, 2H, CH₂), 5.30 (d, J = 2.9 Hz, 1H, C=CH₂), 5.65 (d, J = 2.9 Hz, 1H, C=CH₂), 7.69–7.72 (m, 1H, ArH), 8.12 (d, J = 7.3 Hz, 1H, ArH), 9.24 (d, J = 8.2 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 14.2, 20.6, 25.8, 31.0, 39.6, 97.2, 122.8, 124.4 (J = 271.3 Hz), 126.8, 127.8 (J = 28.8 Hz), 128.5, 128.7, 128.8, 131.8, 141.4, 145.8, 154.5, 166.5; HRMS (TOF ESI⁺): m/z calcd for C₁₉H₁₈F₃N₂O [(M+H)+], 335.1366; found, 335.1374.

4-methyl-3-methylene-2-(((tetrahydrofuran-2-yl)methyl)-6-(trifluoromethyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6d')

White solid; mp 115–116 °C; IR (KBr): 1705, 1581, 1395, 1349, 1305, 1120, 1085, 873, 786, 680, 559 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 1.34–1.37 (m, 1H, CH₂), 1.92–1.98 (m, 2H, CH₂), 2.05–2.10 (m, 1H, CH₂), 3.04 (s, 3H, CH₃), 3.76–3.80 (m, 1H, CH₂), 3.91–3.96 (m, 2H, CH₂), 4.03–4.07 (m, 1H, CH₂), 4.28–4.30 (m, 1H, CH), 5.55 (d, J = 2.7 Hz, 1H, C=CH₂), 5.69 (d, J = 2.7 Hz, 1H, C=CH₂), 7.69–7.72 (m, 1H, ArH), 8.12 (d, J = 7.3 Hz, 1H, ArH), 9.23 (d, J = 8.3 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.9, 26.0, 29.7, 44.1, 68.7, 98.6, 122.7, 124.4 (J = 272.5 Hz), 126.8, 127.8 (J = 30.0 Hz), 128.7, 128.7, 128.8, 129.0, 131.5, 141.7, 144.5, 154.6, 166.8; HRMS (TOF ESI⁺): m/z calcd for C₁₉H₁₈F₃N₂O₂ [(M+H)+], 363.1315; found, 363.1314.

2-(furan-2-ylmethyl)-4-methyl-3-methylene-6-(trifluoromethyl)-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-
one (6e′)

White solid; mp 141–143 °C; IR (KBr): 1705, 1630, 1346, 1135, 1083, 771, 676, 642 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.02 (s, 3H, CH₃), 5.08 (s, 2H, CH₂), 5.50 (d, J = 3.0 Hz, 1H, C=CH₂), 5.66 (d, J = 3.0 Hz, 1H, C=CH₂), 6.35 (d, J = 4.2 Hz, 2H, CH), 7.38 (s, 1H, CH), 7.69–7.72 (m, 1H, ArH), 8.12 (d, J = 7.3 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.8, 36.6, 98.2, 108.8, 111.0, 122.7, 124.3 (J = 271.3 Hz), 126.9, 127.8 (J = 28.8 Hz), 128.6, 128.9, 129.0, 131.4, 140.9, 142.9, 144.5, 150.0, 154.6, 166.1; HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₄F₃N₂O₂ [(M+H)+], 359.1002; found, 359.1005.

2-butyl-4-methyl-3-methylene-8-nitro-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6f’)

Yellow solid; mp 203–205 °C; IR (KBr): 1698, 1495, 1395, 1229, 1080, 913, 845, 760, 633, 573 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 0.99–1.02 (m, 3H, CH₃), 1.42–1.49 (m, 2H, CH₂), 1.71–1.77 (m, 2H, CH₂), 3.90–3.93 (m, 2H, CH₂), 5.37 (d, J = 2.9 Hz, 1H, C=CH₂), 5.69 (d, J = 2.9 Hz, 1H, C=CH₂), 8.19 (d, J = 8.3 Hz, 1H, ArH), 8.50–8.52 (m, 1H, ArH), 9.86 (d, J = 2.4 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 14.2, 20.6, 25.7, 31.0, 39.8, 98.1, 121.2, 121.6, 124.1, 129.5, 130.7, 133.4, 141.1, 146.8, 149.9, 157.5, 165.6; HRMS (TOF ES⁺): m/z calcd for C₁₇H₁₈N₃O₃ [(M+H)+], 312.1343; found, 312.1349.

4-methyl-3-methylene-8-nitro-2-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6g’)

Yellow solid; mp 226–228 °C; IR (KBr): 1700, 1528, 1498, 1379, 1337, 1117, 917, 887, 723 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 3.10 (s, 3H, CH₃), 5.27 (d, J = 2.7 Hz, 1H, C=CH₂), 5.73 (d, J = 2.7 Hz, 1H, C=CH₂), 7.43 (d, J = 7.6 Hz, 2H, ArH), 7.51–7.54 (m, 1H, ArH), 7.59–7.62 (m, 2H, ArH), 8.25 (d, J = 9.35 Hz, 1H, ArH), 8.54–8.56 (m, 1H, ArH), 9.90 (d, J = 2.5 Hz, 1H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.8, 100.2, 121.3, 121.6, 124.3, 128.9, 129.3, 129.4, 130.1, 130.1, 130.8, 132.8, 133.9, 142.5, 146.9, 150.1, 157.7, 165.3; HRMS (TOF ES⁺): m/z calcd for C₁₇H₁₈N₃O₃ [(M+H)+], 332.1030; found, 332.1032.

4-methyl-3-methylene-8-(morpholinosulfonyl)-2-phenyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one (6h’)

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Yellow solid; mp 224–226 °C; IR (KBr): 1708, 1631, 1499, 1265, 1163, 1112, 947, 839, 741, 635, 599 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 3.10\) (s, 3H, CH\(_3\)), 3.11–3.13 (m, 4H, CH\(_2\)), 3.74–3.76 (m, 4H, CH\(_2\)), 5.25 (d, \(J = 2.8\) Hz, 1H, C=CH\(_2\)), 5.72 (d, \(J = 2.8\) Hz, 1H, C=CH\(_2\)), 7.43 (d, \(J = 7.5\) Hz, 2H, ArH), 7.50–7.53 (m, 1H, ArH), 7.58–7.61 (m, 2H, ArH), 8.10–8.12 (m, 1H, ArH); \(^1\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 25.7, 46.5, 46.5, 66.5, 66.5, 100.0, 121.6, 125.7, 128.3, 128.9, 128.9, 129.3, 130.1, 130.1, 130.1, 130.5, 130.5, 130.5, 132.2, 133.9, 135.3, 142.7, 149.4, 157.0, 165.6; HRMS (TOF ES\(^{+}\)): m/z calcd for C\(_{23}\)H\(_{21}\)N\(_3\)NaO\(_4\)S [(M+Na)\(^{+}\)], 458.1145; found, 458.1149.

2-(2-bromophenyl)-4-methyl-1\(^{1}\)H-pyrrolo[3,4-c]quinoline-1,3(2\(^{1}\)H)-dione (7a).

White solid; mp 202–204 °C; IR (KBr): 1712, 1625, 1476, 1371, 1126, 1096, 1028, 754, 737, 665 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.10\) (s, 3H, C–CH\(_3\)), 7.38–7.42 (m, 2H, ArH), 7.48–7.52 (m, 1H, ArH), 7.72–7.79 (m, 2H, ArH), 7.89–7.94 (m, 1H, ArH), 8.17 (d, \(J = 8.4\) Hz, 1H, ArH), 8.84 (d, \(J = 8.4\) Hz, 1H, ArH); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 22.3, 120.8, 121.8, 123.4, 125.1, 128.5, 129.2, 129.4, 130.5, 130.8, 130.9, 133.0, 133.7, 135.8, 151.8, 155.4, 166.6, 166.8; HRMS (TOF ES\(^{+}\)): m/z calcd for C\(_{18}\)H\(_{12}\)BrN\(_2\)O\(_2\) [(M+H)\(^{+}\)], 367.0087; found, 367.0085.

2-(2-chlorophenyl)-4-methyl-1\(^{1}\)H-pyrrolo[3,4-c]quinoline-1,3(2\(^{1}\)H)-dione (7b).

White solid; mp 184–186 °C; IR (KBr): 1714, 1624, 1483, 1373, 1115, 1065, 1029, 754, 737, 691 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.10\) (s, 3H, C–CH\(_3\)), 7.40–7.47 (m, 3H, ArH), 7.59–7.61 (m, 1H, ArH), 7.71–7.75 (m, 1H, ArH), 7.89–7.93 (m, 1H, ArH), 8.16 (d, \(J = 8.8\) Hz, 1H, ArH), 8.83 (d, \(J = 8.4\) Hz, 1H, ArH); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 22.3, 120.8, 121.8, 125.1, 128.5, 129.2, 129.4, 130.5, 130.8, 130.9, 133.0, 133.3, 135.9, 151.8, 155.4, 166.6, 166.8; HRMS (TOF ES\(^{+}\)): m/z calcd for C\(_{18}\)H\(_{12}\)ClN\(_2\)O\(_2\) [(M+H)\(^{+}\)], 323.0588; found, 323.0588.
4. X-ray Structure and Data$^3$ of 6p (CCDC 1438897)

![Figure S1](image)

**Figure S1** X-Ray crystal structure of 6p

**Table S1** Crystal data and structure refinement for 6p

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Empirical formula</td>
<td>$C_{19}H_{12}BrFN_2O$</td>
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<tr>
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<td>Temperature</td>
<td>293(2) K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<td>Crystal system, space group</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td></td>
<td>$b = 17.185(3)$ Å, $beta = 108.741(2)$ deg.</td>
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<tr>
<td></td>
<td>$c = 11.370(2)$ Å, $gamma = 90.00$ deg.</td>
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<tr>
<td>Volume</td>
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<td>Z, Calculated density</td>
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<tr>
<td>Absorption coefficient</td>
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<td>F(000)</td>
<td>1536</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.32 x 0.20 x 0.18 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
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<tr>
<td>Limiting indices</td>
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<tr>
<td>Reflection collected/unique</td>
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<tr>
<td>Completeness to theta</td>
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<td>Absorption correction</td>
<td>fine-focus sealed tube</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.9506 and 0.9811</td>
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<tr>
<td>Refinement method</td>
<td>phi and omega scans</td>
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<tr>
<td>Data/restraints/parameters</td>
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Goodness-of-fit on F² 0.919
Final R indices [I>2sigma(I)] R1 = 0.1492, wR2 = 0.1347
R indices (all data) R1 = 0.0480, wR2 = 0.1003
Semi-empirical from equivalents 0.287 and -0.354 e.A^-3

Table S2 Bond lengths [Å] and angles [deg] for 6p

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<th>Length [Å]</th>
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<td>F(2)-C(12)</td>
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<td>N(1)-C(7)</td>
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<td>N(1)-C(15)</td>
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<td>1.378(4)</td>
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<tr>
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<td>1.429(4)</td>
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<tr>
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<tr>
<td>O(1)-C(25)</td>
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<tr>
<td>O(1)-C(16)</td>
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C(14)-H(14) 0.9300
C(16)-H(16) 0.9800
C(18)-C(23) 1.377(5)
C(18)-C(19) 1.382(4)
C(19)-C(20) 1.374(5)
C(19)-H(19) 0.9300
C(20)-C(21) 1.363(5)
C(20)-H(20) 0.9300
C(21)-C(22) 1.383(5)
C(22)-C(23) 1.377(5)
C(22)-H(22) 0.9300
C(23)-H(23) 0.9300
C(24)-H(24A) 0.9600
C(24)-H(24B) 0.9600
C(24)-H(24C) 0.9600
C(25)-C(26) 1.495(6)
C(26)-H(26A) 0.9600
C(26)-H(26B) 0.9600
C(26)-H(26C) 0.9600
5. NMR spectra (\textsuperscript{1}H NMR and \textsuperscript{13}C NMR)
Figure 1. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6a
Figure 2. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6a
Figure 3. $^1$H NMR (400 MHz, DMSO-$d_6$) spectra of compound 6b
Figure 4. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectra of compound 6b
Figure 5. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6c
Figure 6. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6c
Figure 7. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 6d
Figure 8. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 6d
Figure 9. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6e
Figure 10. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6e
Figure 11. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 6f
Figure 12. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 6f
Figure 13. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6g
Figure 14. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6g
Figure 15. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6h
Figure 16. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6h
Figure 17. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6i
Figure 18. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6i
Figure 19. $^1$H NMR (400 MHz, DMSO-$d_6$) spectra of compound 6j
Figure 20. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectra of compound 6j
Figure 21. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6k
Figure 22. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6k
Figure 23. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6l
Figure 24. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6l
Figure 25. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6m
Figure 26. \[^{13}\text{C} NMR (100 \text{ MHz, CDCl}\_3)\) spectra of compound 6m
Figure 27. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6n
Figure 28. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6n
Figure 29. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 60.
Figure 30. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 60
Figure 31. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6p
Figure 32. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6p
Figure 33. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6q
Figure 34. $^1$C NMR (100 MHz, CDCl$_3$) spectra of compound 6q
Figure 35. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6r
Figure 36. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6r
Figure 37. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6s
Figure 38. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6s
Figure 39. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6t
Figure 40. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6t
Figure 41. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6u
Figure 42. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6u
Figure 43. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6v
Figure 44. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6v
Figure 45. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6w
Figure 46. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6w
Figure 47. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6x
Figure 48. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6x
Figure 49. $^1$H NMR (400 MHz, CDCl₃) spectra of compound 6y
Figure 50. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 6y
Figure 51. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 6z
Figure 52. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectra of compound 6z
Figure 53. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6a′

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Figure 54. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6a’
Figure 55. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6b'
Figure 56. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6b'}
Figure 57. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6c'
Figure 58. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6c'
Figure 59. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6d'}
Figure 60. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6d'
Figure 61. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6e$^e$
Figure 62. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6e′
Figure 63. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6f'}
Figure 64. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6f"
Figure 65. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6g'
Figure 66. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound $6g'$
Figure 67. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 6h’
Figure 68. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 6h'
Figure 69. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 7a
Figure 70. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 7a
Figure 71. $^1$H NMR (400 MHz, CDCl$_3$) spectra of compound 7b
Figure 72. $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of compound 7b
6. References and Notes


3. CCDC 1438897 contain the supplementary crystallographic data for compound 6p. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.