Supporting Information

InCl₃ promoted Synthesis of pyrazolyl substituted quinolines in green media

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General procedure for the synthesis of pyrazolyl substituted benzo[h]quinolines/quinolines:

The respective hydrazinylquinoline (**1(a-c)** & **6(a-c)**, 0.001 m), trifluoro acetyl acetone / acetyl acetone / ethyl acetoacetate / ethyl benzoylacetate (0.0012 m) and 15 mol % InCl₃ was taken in a microwave vessel (5 mL capacity) and subjected to microwave irradiation (Biotage microwave oven, 80 °C, 2 bar pressure) for 5 minutes. After completion of the reaction (as indicated by TLC), the reaction mixture was cooled to room temperature. The obtained solid was dissolved with dichloromethane and filtered. The catalyst was recovered during the filtration. The filtrate was concentrated and dried. The crude product was washed with ethanol and recrystallization from the same to obtain the respective pure product (**2 / 3 / 4 / 5(a-c) & 7 / 8 / 9 / 10(a-c)**).

Synthesis of 2-chloro-4-(3',5'-disubstituted-pyrazol-1'-yl)benzo[h]quinoline / quinolines and synthesis of 2-chloro-4-(3'-methyl-/phenyl-5'-oxo-pyrazol-1'-yl)benzo[h]quinoline / quinolines

2-Chloro-4-(5'-methyl-3'-trifluoromethyl-1H-pyrazol-1'-yl)benzo[h]quinoline (**2a**)

Yellow solid; M.p. 90-92 °C; Yield: 0.300 g, 83 %; IR (KBr, cm⁻¹) ν_{max} : 1583, 1109; ¹H NMR (CDCl₃, 400 MHz) (ppm) δ : 2.07 (s, 3H, C₅'-CH₃), 6.49 (s, 1H, C₄'-H), 7.14 (t, *J*=6.8 Hz,

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1H, C₈-H), 7.49-7.67 (m, 5H, C₃-, C₅-, C₆-, C₇-, C₉-H), 8.99 (dd, $J=7.6$ Hz, 2.4 Hz, 1H, C₁₀-H); Anal. Calcd. for: C₁₅H₁₄ClN₃: C, 59.76; H, 3.06; N, 11.62. Found: C, 59.82; H, 3.02; N, 11.54 %.

2-Chloro-8-methyl-4-(5'-methyl-3'-trifluoromethyl-1*H*-pyrazol-1'-yl)quinoline (2b)

Yellow crystals; M.p. 79-81 °C; Yield: 0.280 g, 86 %; IR (KBr, cm⁻¹) $\nu_{\max}$: 1579, 1111; ¹H NMR (CDCl₃, 400 MHz) (ppm) δ : 2.19 (s, 3H, C₅'-CH₃), 2.80 (s, 3H, C₈-CH₃), 6.56 (s, 1H, C₄'-H), 7.20 (d, $J=7.6$ Hz, 1H, C₇-H), 7.43 (s, 1H, C₃-H), 7.47 (t, $J=7.2$ Hz, 1H, C₆-H), 7.65 (d, $J=6.8$ Hz, 1H, C₅-H); ¹³C NMR (CDCl₃, 100 MHz) (ppm) δ : 11.77, 18.50, 104.98, 117.18, 119.85, 120.81, 122.53, 123.69, 128.41, 132.01, 137.60, 142.86, 144.15, 144.91, 148.28; Anal. Calcd. for: C₁₅H₁₁ClF₃N₃: C, 55.31; H, 3.40; N, 12.90. Found: C, 55.35; H, 3.39; N, 12.87 %.

2,6-Dichloro-4-(5'-methyl-3'-trifluoromethyl-1*H*-pyrazol-1'-yl)quinoline (2c)

Yellow solid; M.p. 85-87 °C; Yield: 0.301 g, 87 %; IR (KBr, cm⁻¹) $\nu_{\max}$: 1588, 1119; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.27 (s, 3H, C₅'-CH₃), 6.46 (s, 1H, C₄'-H), 7.31 (s, 1H, C₃-H), 7.59 (dd, $J=8.5$ Hz, 1.5 Hz, 1H, C₇-H), 7.61 (d, $J=8.5$ Hz, 1H, C₈-H), 7.86 (d, $J=8.5$ Hz, 1H, C₅-H); Anal. Calcd. for: C₁₄H₈Cl₂F₃N₃: C, 48.58; H, 2.33; N, 12.14. Found: C, 48.53; H, 2.31; N, 12.19 %.

2-Chloro-4-(3',5'-dimethyl-1*H*-pyrazol-1'-yl)benzo[*h*]quinoline (3a)

White solid; M.p. 99-101 °C; Yield: 0.267 g, 87 %; IR (KBr, cm⁻¹) $\nu_{\max}$: 1561, 1123; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.16 (s, 3H, C₅'-CH₃), 2.36 (s, 3H, C₃'-CH₃), 6.14 (s, 1H, C₄'-H), 7.44 (d, $J=9.0$ Hz, 1H, C₆-H), 7.50 (s, 1H, C₃-H), 7.73-7.78 (m, 2H, C₈-, C₉-H), 7.82 (d, $J=9.0$ Hz, 1H, C₅-H), 7.90 (dd, $J=8.5$ Hz, 2.0 Hz, 1H, C₇-H), 9.26 (dd, $J=9.0$ Hz, 2.0 Hz, 1H, C₁₀-H); ¹³C NMR (CDCl₃, 125 MHz) (ppm) δ : 11.75, 13.60, 107.24, 120.15, 120.58, 122.10, 125.12, 127.67, 127.81, 129.15, 129.30, 130.30, 133.92, 141.48, 145.65, 147.99, 149.40, 150.76; Anal. Calcd. for: C₁₈H₁₄ClN₃: C, 70.24; H, 4.58; N, 13.65. Found: C, 70.20; H, 4.59; N, 13.69 %.

2-Chloro-4-(3',5'-dimethyl-1*H*-pyrazol-1'-yl)-8-methylquinoline (**3b**)

White solid; M.p. 89-91 °C; Yield: 0.239 g, 88 %; IR (KBr, cm⁻¹) ν_{max} : 1576, 1121; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.18 (s, 3H, C₅'-CH₃), 2.44 (s, 3H, C₃'-CH₃), 2.88 (s, 3H, C₈-CH₃), 6.00 (s, 1H, C₄'-H), 6.96 (s, 1H, C₃-H), 7.27 (t, *J* = 7.50 Hz, 1H, C₆-H), 7.51 (d, *J* = 7.50 Hz, 1H, C₇-H), 7.92 (d, *J* = 8.50 Hz, 1H, C₅-H); ¹³C NMR (CDCl₃, 125 MHz) (ppm) δ : 11.92, 13.85, 18.47, 100.25, 116.68, 121.19, 124.23, 128.58, 130.36, 133.19, 135.56, 135.97, 146.36, 150.65, 151.43; Anal. Calcd. for: C₁₅H₁₄ClN₃: C, 66.30; H, 5.19; N, 15.46. Found: C, 66.27; H, 5.19; N, 15.48 %.

2,6-Dichloro-4-(3',5'-dimethyl-1*H*-pyrazol-1'-yl)quinoline (**3c**)

White solid; M.p. 92-94 °C; Yield: 0.260 g, 89 %; IR (KBr, cm⁻¹) ν_{max} : 1578, 1120; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.48 (s, 3H, C₅'-CH₃), 2.85 (s, 3H, C₃'-CH₃), 6.76 (s, 1H, C₄'-H), 7.39 (s, 1H, C₃-H), 7.45 (dd, *J*=8.5 Hz, 2.5 Hz, 1H, C₇-H), 7.56 (d, *J*=8.5 Hz, 1H, C₈-H), 7.92 (s, 1H, C₅-H); ¹³C NMR (CDCl₃, 125 MHz) (ppm) δ : 14.28, 18.65, 108.97, 121.92, 123.29, 123.85, 124.58, 130.38, 131.03, 134.75, 135.47, 144.48, 146.29, 152.41; Anal. Calcd. for: C₁₄H₁₁Cl₂N₃: C, 57.55; H, 3.79; N, 14.38. Found: C, 57.58; H, 3.77; N, 14.39 %.

2-Chloro-4-(3'-methyl-5'-oxo-1*H*-pyrazol-1'-yl)benzo[*h*]quinoline (**4a**)

White solid; M.p. 128-130 °C; Yield: 0.278 g, 90 %; IR (KBr, cm⁻¹) ν_{max} : 1731; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.18 (s, 3H, C₃'-CH₃), 3.50 (s, 2H, C₄'-CH₂), 7.52 (s, 1H, C₃'-H), 7.53 (d, *J*=9.5 Hz, 1H, C₆-H), 7.70-7.73 (m, 2H, C₈-, C₉-H), 7.78 (d, *J*=9.0 Hz, 1H, C₅-H), 7.89 (d, *J*=9.0 Hz, 1H, C₇-H), 9.23 (dd, *J*=9.0 Hz, 1.5 Hz, 1H, C₁₀-H); ¹³C NMR (CDCl₃, 125 MHz) (ppm) δ : 13.78, 27.29, 109.38, 119.18, 121.13, 124.92, 125.70, 127.71, 128.56, 129.37, 130.00, 134.44, 143.20, 146.08, 149.85, 155.34, 175.98; Anal. Calcd. for: C₁₇H₁₂ClN₃O: C, 65.92; H, 3.90; N, 13.57. Found: C, 65.86; H, 3.91; N, 13.59 %.

2-Chloro-8-methyl-4-(3'-methyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (**4b**)

White solid; M.p. 113-115 °C ; Yield: 0.240 g, 88 %; IR (KBr, cm⁻¹) ν_{max} : 1728; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.15 (s, 3H, C₃'-CH₃), 2.48 (s, 3H, C₈-CH₃), 3.42 (s, 2H, C₄'-CH₂), 7.39 (s, 1H, C₃-H), 7.47-7.54 (m, 2H, C₆, C₇-H), 8.07 (d, *J*=8.0 Hz, 1H, C₅-H); ¹³C NMR (CDCl₃, 125 MHz) (ppm) δ : 13.64, 18.52, 27.24, 99.88, 116.72, 120.12, 125.79, 131.30, 136.36, 142.99, 146.91, 150.54, 151.59, 175.44; Anal. Calcd. for: C₁₄H₁₂ClN₃O: C, 61.43; H, 4.42; N, 15.35. Found: C, 61.47; H, 4.40; N, 15.32 %.

2,6-Dichloro-4-(3'-methyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (**4c**)

White solid; M.p. 122-124 °C; Yield: 0.264 g, 90 %; IR (KBr, cm⁻¹) ν_{max} : 1733; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.21 (s, 3H, C₃'-CH₃), 3.46 (s, 2H, C₄'-CH₂), 7.33 (s, 1H, C₃'-H), 7.55 (d, *J* = 8.40 Hz, 1H, C₈'-H), 7.66 (d, *J* = 8.80 Hz, 1H, C₇'-H), 7.97 (s, 1H, C₅'-H); Anal. Calcd. for: C₁₃H₉Cl₂N₃O: C, 53.08; H, 3.08; N, 14.29. Found: C, 53.02; H, 3.09; N, 14.33 %.

2-Chloro-4-(3'-phenyl-5'-oxo-1*H*-pyrazol-1'-yl)benzo[*h*]quinoline (**5a**)

White solid; M.p. 154-156 °C; Yield: 0.309 g, 83 %; IR (KBr, cm⁻¹) ν_{max} : 1689; ¹H NMR (CDCl₃, 400 MHz) (ppm) δ : 4.01 (s, 2H, C₄'-CH₂), 7.26-7.50 (m, 3H, C₃"-, C₄"-, C₅"-H), 7.61 (s, 1H, C₃-H), 7.68-7.71 (m, 2H, C₈-, C₉-H), 7.82-7.90 (m, 3H, C₅-, C₆-, C₇-H), 7.96 (d, *J*=7.2 Hz, 2H, C₂"-, C₆"-H), 9.23 (dd, *J*=7.2 Hz, 1.6 Hz, 1H, C₁₀-H); ¹³C NMR (CDCl₃, 100 MHz) (ppm) δ : 34.23, 103.99, 113.46, 117.06, 125.42, 126.45, 126.92, 127.35, 127.72, 128.58, 128.90, 129.68, 131.06, 133.78, 137.19, 143.12, 146.95, 149.32, 151.38, 169.82; Anal. Calcd. for: C₂₂H₁₄ClN₃O: C, 71.07; H, 3.80; N, 11.30. Found: C, 71.12; H, 3.83; N, 11.26 %.

2-Chloro-8-methyl-4-(3'-phenyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (**5b**)

White solid; M.p. 139-141 °C; Yield: 0.279 g, 83 %; IR (KBr, cm⁻¹) ν_{max} : 1687; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.72 (s, 3H, C₈-CH₃), 3.91 (s, 2H, C₄'-CH₂), 7.35 (t, *J*=7.5 Hz, 1H,

C₆-H), 7.44 (s, 1H, C₃-H), 7.47-7.56 (m, 4H, C₃"-, C₄"-, C₅"-, C₇-H), 7.59 (d, *J*=8.5 Hz, 1H, C₅-H), 7.90-7.94 (m, 2H, C₂"-, C₆"-H); Anal. Calcd. for: C₁₉H₁₄ClN₃O: C, 67.96; H, 4.20; N, 12.51. Found: C, 67.92; H, 4.21; N, 12.53 %.

2,6-Dichloro-4-(3'-phenyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (5c)

White solid; M.p. 146-148 °C; Yield: 0.292 g, 82 %; IR (KBr, cm⁻¹) *v*_{max}: 1689; ¹H NMR (CDCl₃, 400 MHz) (ppm) δ: 3.90 (s, 2H, C₄'-CH₂), 7.41-7.53 (m, 5H, C₃-, C₃"-, C₄"-, C₅"-, C₇-H), 7.61 (d, *J*=6.4 Hz, 1H, C₈-H), 7.85 (d, *J*=8.4 Hz, 1H, C₅-H), 7.93-7.97 (m, 2H, C₂"-, C₆"-H); Anal. Calcd. for: C₁₈H₁₁Cl₂N₃O: C, 60.69; H, 3.11; N, 11.80. Found: C, 60.65; H, 3.12; N, 11.84 %.

Synthesis of 4-chloro-2-(3',5'-disubstituted-pyrazol-1'-yl)benzo[*h*]quinoline / quinolines and synthesis of 4-chloro-2-(3'-methyl-/phenyl-5'-oxo-pyrazol-1'-yl)benzo[*h*]quinoline / quinolines

4-Chloro-2-(5'-methyl-3'-trifluoromethyl-1*H*-pyrazol-1'-yl)benzo[*h*]quinoline (7a)

Yellow solid; M.p. 85-87 °C ; Yield: 0.307 g, 85 %; IR (KBr, cm⁻¹) *v*_{max}: 1607, 1159; ¹H NMR (CDCl₃, 400 MHz) (ppm) δ: 1.92 (s, 3H, C₅'-CH₃), 6.32 (s, 1H, C₄'-H), 6.93 (t, *J*=7.2 Hz, 1H, C₈-H), 7.45-7.62 (m, 5H, C₃-, C₅-, C₆-, C₇-, C₉-H), 8.96 (dd, *J*=7.2 Hz, 2.4 Hz, 1H, C₁₀-H); ¹³C NMR (CDCl₃, 100 MHz) (ppm) δ: 11.83, 105.12, 110.61, 117.22, 119.89, 120.95, 125.25, 128.16, 129.79, 130.16, 134.04, 142.92, 143.91, 144.29, 144.65, 145.05, 148.22, 148.48; Anal. Calcd. for: C₁₈H₁₁ClF₃N₃: C, 59.76; H, 3.06; N, 11.62. Found: C, 59.72; H, 3.08; N, 11.65 %.

4-Chloro-8-methyl-2-(5'-methyl-3'-trifluoromethyl-1*H*-pyrazol-1'-yl)quinoline (7b)

Yellow crystals; M.p. 69-71 °C; Yield: 0.277 g, 85 %; IR (KBr, cm⁻¹) *v*_{max}: 1604, 1143; ¹H NMR (CDCl₃, 400 MHz) (ppm) δ: 2.14 (s, 3H, C₅'-CH₃), 2.74 (s, 3H, C₈-CH₃), 6.49 (s, 1H, C₄'-H), 7.02 (d, *J*=7.2 Hz, 1H, C₇-H), 7.34 (s, 1H, C₃-H), 7.49 (t, *J*=7.2 Hz, 1H, C₆-H), 7.69 (d,

$J=7.6$ Hz, 1H, C₅-H); Anal. Calcd. for: C₁₅H₁₁ClF₃N₃: C, 55.31; H, 3.40; N, 12.90. Found: C, 55.35; H, 3.39; N, 12.86 %.

4,6-Dichloro-2-(5'-methyl-3'-trifluoromethyl-1*H*-pyrazol-1'-yl)quinoline (7c)

Yellow solid; M.p. 76-78 °C; Yield: 0.298 g, 86 %; IR (KBr, cm⁻¹) ν_{max} : 1600, 1149; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.23 (s, 3H, C₅'-CH₃), 6.39 (s, 1H, C₄'-H), 7.31 (s, 1H, C₃-H), 7.61 (d, $J = 8.5$ Hz, 1H, C₈-H), 7.62 (dd, $J = 8.5$ Hz, 1.5 Hz, 1H, C₇-H), 7.88 (d, $J = 8.5$ Hz, 1H, C₅-H); Anal. Calcd. for: C₁₄H₈Cl₂F₃N₃: C, 48.58; H, 2.33; N, 12.14. Found: C, 48.54; H, 2.34; N, 12.16 %.

4-Chloro-2-(3',5'-dimethyl-1*H*-pyrazol-1'-yl)benzo[*h*]quinoline (8a)

White solid; M.p. 93-95 °C; Yield: 0.261 g, 87 %; IR (KBr, cm⁻¹) ν_{max} : 1603, 1121; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.38 (s, 3H, C₅'-CH₃), 3.01 (s, 3H, C₃'-CH₃), 6.13 (s, 1H, C₄'-H), 7.73-7.75 (m, 2H, C₈-, C₉-H), 7.87 (d, $J=9.0$ Hz, 1H, C₆-H), 7.95 (dd, $J=8.0$ Hz, 3.0 Hz, 1H, C₇-H), 8.13 (d, $J=9.0$ Hz, 1H, C₅-H), 8.39 (s, 1H, C₃-H), 9.11 (d, $J=5.5$ Hz, 1H, C₁₀-H); Anal. Calcd. for: C₁₈H₁₄ClN₃: C, 70.24; H, 4.58; N, 13.65. Found: C, 70.27; H, 4.59; N, 13.62 %.

4-Chloro-2-(3',5'-dimethyl-1*H*-pyrazol-1'-yl)-8-methylquinoline (8b)

White solid; M.p. 82-84 °C; Yield: 0.244 g, 90 %; IR (KBr, cm⁻¹) ν_{max} : 1607, 1125; ¹H NMR (CDCl₃, 400 MHz) (ppm) δ : 2.11 (s, 3H, C₅'-CH₃), 2.32 (s, 3H, C₅'-CH₃), 2.78 (s, 3H, C₈-CH₃), 6.09 (s, 1H, C₄'-H), 7.34 (s, 1H, C₃-H), 7.38-7.44 (m, 2H, C₆-, C₇-H), 7.59 (d, 1H, C₅-H, $J=6.4$ Hz); ¹³C NMR (CDCl₃, 100 MHz) (ppm) δ : 11.78, 13.63, 18.22, 107.21, 120.09, 121.82, 124.24, 127.70, 131.53, 137.13, 141.54, 146.33, 148.27, 149.07, 150.71; Anal. Calcd. for: C₁₅H₁₄ClN₃: C, 66.30; H, 5.19; N, 15.46. Found: C, 66.27; H, 5.20; N, 15.49 %.

4,6-Dichloro-2-(3',5'-dimethyl-1*H*-pyrazol-1'-yl)quinoline (**8c**)

White solid; M.p. 87-89 °C; Yield: 0.251 g, 86 %; IR (KBr, cm⁻¹) $\nu_{\max}$: 1605, 1122; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.36 (s, 3H, C_{5'}-CH₃), 2.64 (s, 3H, C_{3'}-CH₃), 6.25 (s, 1H, C_{4'}-H), 7.36 (s, 1H, C₃-H), 7.58 (dd, *J*=8.5 Hz, 2.5 Hz, 1H, C₇-H), 7.69 (d, *J*=8.5 Hz, 1H, C₈-H), 7.92 (d, *J*=8.5 Hz, 1H, C₅-H); Anal. Calcd. for: C₁₄H₁₁Cl₂N₃: C, 57.55; H, 3.79; N, 14.38. Found: C, 57.59; H, 3.78; N, 14.35 %.

4-Chloro-2-(3'-methyl-5'-oxo-1*H*-pyrazol-1'-yl)benzo[*h*]quinoline (**9a**)

White solid; M.p. 124-126 °C; Yield: 0.272 g, 88 %; IR (KBr, cm⁻¹) $\nu_{\max}$: 1721; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.23 (s, 3H, C_{3'}-CH₃), 3.58 (s, 2H, C_{4'}-CH₂), 7.40 (s, 1H, C_{3'}-H), 7.65 (d, *J*=8.5 Hz, 1H, C₆-H), 7.73-7.79 (m, 2H, C₈, C₉-H), 7.86 (d, *J*=8.0 Hz, 1H, C₅-H), 7.93 (d, *J*=8.5 Hz, 1H, C₇-H), 9.17 (dd, *J*=8.5 Hz, 2.5 Hz, 1H, C₁₀-H); Anal. Calcd. for: C₁₇H₁₂ClN₃O: C, 65.92; H, 3.90; N, 13.57. Found: C, 65.97; H, 3.88; N, 13.55 %.

4-Chloro-8-methyl-2-(3'-methyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (**9b**)

White solid; M.p. 107-109 °C; Yield: 0.243 g, 89 %; IR (KBr, cm⁻¹) $\nu_{\max}$: 1718; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.12 (s, 3H, C_{3'}-CH₃), 2.56 (s, 3H, C₈-CH₃), 3.34 (s, 2H, C_{4'}-CH₂), 7.41 (s, 1H, C₃-H), 7.47 (t, 1H, C₆-H, *J*=7.5 Hz), 7.65 (d, 1H, C₇-H, *J*=7.0 Hz), 7.93 (d, 1H, C₅-H, *J*=8.5 Hz); ¹³C NMR (CDCl₃, 125 MHz) (ppm) δ : 13.69, 17.78, 37.09, 112.52, 121.91, 123.00, 125.65, 131.70, 135.53, 143.99, 145.01, 151.15, 159.53, 170.30; Anal. Calcd. for: C₁₄H₁₂ClN₃O: C, 61.43; H, 4.42; N, 15.35. Found: C, 61.37; H, 4.45; N, 15.32 %.

4,6-Dichloro-2-(3'-methyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (**9c**)

White solid; M.p. 113-115 °C; Yield: 0.261 g, 89 %; IR (KBr, cm⁻¹) $\nu_{\max}$: 1720; ¹H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.30 (s, 3H, C_{3'}-CH₃), 3.40 (s, 2H, C_{4'}-CH₂), 6.68 (s, 1H, C_{3'}-H), 7.60-7.74 (m, 2H, C_{7'}, C_{8'}-H), 8.05 (s, 1H, C_{5'}-H), 9.83 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 125

MHz) (ppm) δ : 13.78, 35.21, 100.10, 116.89, 121.66, 128.43, 133.36, 135.96, 141.83, 146.47, 150.91, 153.19, 175.49; Anal. Calcd. for: $C_{13}H_9Cl_2N_3O$: C, 53.08; H, 3.08; N, 14.29. Found: C, 53.14; H, 3.06; N, 14.26 %.

4-Chloro-2-(3'-phenyl-5'-oxo-1*H*-pyrazol-1'-yl)benzo[*h*]quinoline (**10a**)

White solid; M.p. 141-143 °C; Yield: 0.297 g, 80 %; IR (KBr, cm^{-1}) ν_{max} : 1685; 1H NMR (DMSO-*d*₆, 500 MHz) (ppm) δ : 3.80 (s, 2H, C_{4'}-CH₂), 6.92-6.98 (m, 3H, C_{4''}-, C_{5''}-, C_{6''}-H), 7.27 (t, *J*=7.5 Hz, 1H, C₈-H), 7.37 (d, *J*=8.0 Hz, 1H, C₆-H), 7.40 (s, 1H, C₃-H), 7.58 (t, *J*=8.0 Hz, 1H, C₉-H), 7.70 (d, *J*=9.0 Hz, 2H, C_{2''}-, C_{6''}-H), 7.82 (m, 2H, C₅-, C₇-H), 9.12 (dd, *J*=8.0 Hz, 2.0 Hz, 1H, C₁₀-H); Anal. Calcd. for: $C_{22}H_{14}ClN_3O$: C, 71.07; H, 3.80; N, 11.30. Found: C, 71.15; H, 3.77; N, 11.26 %.

4-Chloro-8-methyl-2-(3'-phenyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (**10b**)

White solid; M.p. 126-128 °C; Yield: 0.272 g, 81 %; IR (KBr, cm^{-1}) ν_{max} : 1689; 1H NMR (CDCl₃, 500 MHz) (ppm) δ : 2.65 (s, 3H, C₈-CH₃), 3.95 (s, 2H, C_{4'}-CH₂), 7.31 (t, *J*=7.5 Hz, 1H, C₆-H), 7.41 (s, 1H, C₃-H), 7.47-7.54 (m, 4H, C_{3''}-, C_{4''}-, C_{5''}-, C₇-H), 7.59 (d, *J*=8.5 Hz, 1H, C₅-H), 7.88-7.91 (m, 2H, C_{2''}-, C_{6''}-H); Anal. Calcd. for: $C_{19}H_{14}ClN_3O$: C, 67.96; H, 4.20; N, 12.51. Found: C, 67.92; H, 4.21; N, 12.53 %.

4,6-Dichloro-2-(3'-phenyl-5'-oxo-1*H*-pyrazol-1'-yl)quinoline (**10c**)

White solid; M.p. 131-133 °C; Yield: 0.299 g, 84 %; IR (KBr, cm^{-1}) ν_{max} : 1685; 1H NMR (CDCl₃, 400 MHz) (ppm) δ : 3.97 (s, 2H, C_{4'}-CH₂), 7.39-7.48 (m, 5H, C₃-, C_{3''}-, C_{4''}-, C_{5''}-, C₇-H), 7.53 (d, *J*=6.4 Hz, 1H, C₈-H), 7.81 (d, *J*=8.4 Hz, 1H, C₅-H), 7.93 (d, *J*=7.2 Hz, 2H, C_{2''}-, C_{6''}-H); ^{13}C NMR (CDCl₃, 100 MHz) (ppm) δ : 36.12, 102.33, 116.87, 117.61, 125.50, 126.40, 128.84, 129.64, 130.59, 137.13, 137.33, 143.15, 147.56, 149.18, 151.21, 169.72; Anal. Calcd. for: $C_{18}H_{11}Cl_2N_3O$: C, 60.69; H, 3.11; N, 11.80. Found: C, 60.63; H, 3.13; N, 11.83 %.

Crystallographic data for compound **2b** and **3b**:

Data was collected at -173 °C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 40 mm and exposure time was 5 seconds per frame for all sets. The scan width was 0.5°. Data was integrated and scaled with the APEX2 software package by Bruker. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

Compound	3b	2b
Empirical formula	C15 H11 Cl F3 N3	C15 H14 Cl N3
Formula weight	325.72	271.74
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 2 ₁ /n
Unit cell dimensions	a = 8.2493(12) Å	a = 8.5943(6) Å
	α = 91.476(7)°.	α = 90°
	b = 8.9265(12) Å	b = 7.4120(5) Å
	β = 90.292(7)°.	β = 100.550(3)°.
	c = 9.9313(14) Å	c = 20.9738(15) Å
	γ = 110.776(4)°.	γ = 90°
Volume	683.45(17) Å ³	1313.47(16) Å ³
Z	2	4
Density (calculated)	1.583 Mg/m ³	1.374 Mg/m ³
Absorption coefficient	0.313 mm ⁻¹	0.280 mm ⁻¹
F(000)	332	568
Crystal size (mm ³)	0.17 x 0.10 x 0.08	0.18 x 0.17 x 0.17
Theta range for data collection	2.05 to 28.43°.	2.92 to 28.40°.
Index ranges (h, k, l)	±11, ±11, ±13-,	±11, ±9, ±28,
Reflections collected	38008	68492
R(int)	0.0290	0.0291
Completeness to theta = 25.00°	99.7 %	99.6 %
Max. /min. transmission	0.9754 / 0.9487	0.9540 / 0.9514
Data / restraints / parameters	3396 / 0 / 201	3280 / 0 / 175
Goodness-of-fit on F ²	1.051	1.051
R1, wR2 [I > 2σ(I)]	0.0292, 0.0775	0.0295, 0.0779
R1, wR2 (all data)	0.0321, 0.0800	0.0316, 0.0796
Largest diff. peak /hole e.Å ⁻³	0.451 / -0.274	0.393 / -0.231

¹H NMR spectrum of the compound **2b**

¹³C NMR spectrum of the compound **2b**

¹H NMR spectrum of the compound **3a**

¹³C NMR spectrum of the compound **3a**

¹H NMR spectrum of the compound **5b**

¹³C NMR spectrum of the compound **5b**

¹H NMR spectrum of the compound **6a**

¹³C NMR spectrum of the compound **6a**

¹H NMR spectrum of the compound 7a

¹³C NMR spectrum of the compound 7a

¹H NMR spectrum of the compound **8a**

¹³C NMR spectrum of the compound **8a**

¹H NMR spectrum of the compound **9b**

¹³C NMR spectrum of the compound **9b**

¹H NMR spectrum of the compound **10c**

¹³C NMR spectrum of the compound **10c**