Supplementary Information

An object oriented synthetic approach towards angular and linear fused pyrazoloquinolines of biological importance with InCl₃ catalyst

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I. Experimental

General Methods

Chemistry

All reagents and solvents used in this paper were commercially available and the major chemicals were purchased from sigma Aldrich. Microwave experiments were carried out in a CEM Discover microwave synthesizer (Model No: 908010) operating at 180/264 V and 50/60 Hz with microwave power maximum level of 300 W and microwave frequency of 2455 MHz was employed. The reaction courses were monitored by TLC on silica gel precoated F254 Merck plates. Developed plates were examined with UV lamps (254nm). IR were recorded on a FT-IR (Bruker). Melting point were recorded on METTLER FP 51 apparatus in open capillary tubes and these are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker spectrometer in CDCl_3 . Chemical shifts are given in parts per million (δ -scale) and coupling constants are given in Hertz. The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). Elemental analyses were performed on a Perkin Elmer 2400 series II Elemental CHNS analyser. Mass spectra were obtained on a GC mass spectrometer.

α -Glucosidase inhibition assay

The commercially available α -glucosidase from baker's yeast (Sigma, G5003) was selected as the target protein using p-nitrophenyl- α -D-glucopyranoside (pNGP, Sigma, N1377) as the substrate. The enzyme and the substrate were dissolved in 0.05 M potassium phosphate buffer with pH 6.8. The enzymatic reaction mixture composed of 20 μL α -glucosidase (0.06 U), 30 μL of 1 mM substrate, 10 μL of test compound (dissolved in DMSO) and 140 μL of potassium phosphate buffer was incubated at 37 $^\circ\text{C}$ for 30 min. The enzymatic activity was detected by spectrophotometer at the wavelength of 405 nm. The test compound replaced by DMSO as control. Acarbose used as the standard inhibitor. Results are the average of three independent experiments, each performed in duplicate.

General procedure for the synthesis of pyrazoloquinolines (**3a-3p**) and (**6a-6h**)

Method 1: (Microwave Irradiation)

A mixture of 3-acyl quinolin-2-one **1** (0.30 mmol), Phenylhydrazine **2** (0.60 mmol) and InCl₃ (0.03mmol) in ethanol 5 mL was sealed and subjected to microwave irradiation, programmed at 80 °C and 110 W for 3-7 mins. The completion of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature, and the crude product recrystallized from ethanol to obtain pure products.

Method 2: (Conventional)

To a mixture of 3-acyl quinolin-2-one **1** (0.30 mmol) and Phenylhydrazine **2** (0.60 mmol), InCl₃ (0.03) ethanol 5mL was refluxed using a water bath 1-3h. The reaction was monitored by TLC (MeOH : CHCl₃ = 1:9). After completion of reaction, the mixture bring to the room temperature, the solid was appeared and filtered off, subsequently washed with methanol and crude product recrystallized from ethanol to obtained pure products.

II. Spectroscopic and Analytical Data of products

3-Methyl-4-phenyl-1-(4-fluorophenyl)-1H-pyrazolo[3,4-b]quinoline (3a)

Pale yellow solid, mp 200 °C; IR (KBr) $\nu_{\max}$ 2921, 1571, 1507, 1439, 1380 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.47-8.31 (m, 2H, ArH), 8.29-8.17 (m, 1H, ArH), 7.81-7.61 (m, 2H, ArH), 7.62 (s, 2H, ArH), 7.50 (s, 2H, ArH), 7.40 (q, 2H, $J = 7.2$ Hz, ArH), 7.28 (t, 1H, $J = 6$ Hz, ArH), 7.16 (s, 1H, ArH), 2.14 (s, 3H, CH_3); ^{13}C (100MHz, CDCl_3): δ 151.2, 146.1, 144.1, 130.8, 130.7, 129.6, 129.4, 128.9, 128.8, 128.3, 127.0, 124.1, 124.0, 123.6, 122.4, 122.1, 116.4, 115.7, 14.7; Mass (ESI) m/z ; 353.1 $[\text{M}+\text{H}]^+$; Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{FN}_3$: C, 78.17; H, 4.56; N, 11.89 %; Found. C, 78.12; H, 4.60; N, 11.94 %.

3-Methyl-4-phenyl-1-(4-chlorophenyl)-1H-pyrazolo[3,4-b]quinoline (3b)

Pale yellow solid, mp 210 °C; IR (KBr) $\nu_{\max}$ 3054, 1584, 1492, 1439, 1380 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.50 (d, 2H, $J = 8.8$ Hz, ArH), 8.18 (d, 1H $J = 10$ Hz, ArH), 7.71-7.68 (m, 2H, ArH), 7.63 (t, 3H, $J = 3.2$ Hz, ArH), 7.60 (t, 2H, $J = 7.2$ Hz, ArH), 7.48-7.46 (m, 2H), 7.33 (t, 1H, $J = 7.6$ Hz, ArH), 2.15 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 150.0, 146.7, 143.8, 143.7, 139.7, 134.2, 131.3, 130.5, 129.6, 129.0, 128.4, 125.3, 125.2, 124.1, 120.4, 116.7, 14.8; Mass (ESI) m/z ; 369.1 $[\text{M}+\text{H}]^+$; Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{ClN}_3$: C, 74.69; H, 4.36; N, 11.36 %; Found. C, 74.64; H, 4.39; N, 11.41 %.

3-Methyl-4-phenyl-1-(4-methoxyphenyl)-1H-pyrazolo[3,4-b]quinoline (3c)

Light green solid, mp 180 °C; IR (KBr) $\nu_{\max}$ 2880, 1586, 1512, 1440 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, 3H, $J = 9.6$ Hz, ArH), 7.77 (q, 2H, $J = 9.6$ Hz, ArH), 7.62 (t, 3H, $J = 3.2$ Hz, ArH), 7.50-7.49 (m, 2H, ArH), 7.40 (t, 1H, $J = 7.2$ Hz, ArH), 7.12 (d, 2H, $J = 9.2$ Hz, ArH), 3.93 (s, 3H, OCH_3), 2.16 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 150.5, 144.6, 143.7, 143.4, 139.2, 134.9, 130.6, 129.6, 128.8, 128.3, 127.0, 123.9, 123.4, 122.6, 114.40, 55.6, 14.7; Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}$: C, 78.88; H, 5.24; N, 11.50 %; Found. C, 78.83; H, 5.19; N, 11.54 %.

1-(4-Bromo-phenyl)-3-methyl-4-phenyl-1H-pyrazolo[3,4-b]quinoline (3d)

Brown solid, mp 190 °C; IR (KBr) $\nu_{\max}$ 2905, 1579, 1488, 1400 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.50 (d, 2H, $J = 8$ Hz, ArH), 8.28 (d, 1H, $J = 9.2$ Hz, ArH), 7.80 (t, 1H, $J = 7.2$ Hz, ArH), 7.75 (d, 1H, $J = 8.8$ Hz, ArH), 7.69 (d, 2H, $J = 7.2$ Hz, ArH), 7.63-7.61 (m, 3H, ArH), 7.48-7.46

(2H, m, ArH) 7.41 (t, 1H, $J=7.2$ Hz, ArH) 2.14 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): δ 150.2, 146.3, 144.1, 139, 134, 132, 131, 129, 128, 128.2, 127, 126, 123, 122, 121, 14.0; Mass (ESI) m/z : 413.1 [M+H]⁺; Anal. Calcd for C₂₃H₁₆BrN₃: C, 66.68; H, 3.89; N, 10.14 %; Found. C, 68.63; H, 3.92; N, 10.21 %.

1-(4-bromophenyl)-3-methyl-6-chloro-4-phenyl-1H-pyrazolo[3,4-b]quinoline (3e)

Pale Yellow solid, mp 160 °C; IR (KBr) $\nu_{\max}$ 3057, 1588, 1488, 1393 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.48 (d, 2H, $J = 8.8$ Hz, ArH), 8.18 (d, 1H, $J = 9.6$ Hz, ArH), 7.72-7.63 (m, 7H, ArH), 7.47 (q, 2H, $J=4$ Hz, ArH), 2.15 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): 149.8, 146.7, 144.3, 144.1, 132.0, 131.5, 130.5, 129.4, 129.6, 129.1, 128.5, 125.4, 121.5, 117.9, 106.7, 14.9; Anal. Calcd for C₂₃H₁₅BrClN₃: C, 61.56; H, 3.37; N, 9.36 %; Found: C, 61.51; H, 3.41; N, 9.31 %.

6-chloro-3-Methyl-4-phenyl-1-(4-chlorophenyl)-1H-pyrazolo [3, 4-b] quinoline (3f)

Light green solid, mp 165 °C; IR (KBr) $\nu_{\max}$ 3057, 1589, 1493, 1440, 1395 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.44 (d, 2H, $J = 8.8$ Hz, ArH), 8.23 (d, 1H, $J = 8.8$ Hz, ArH), 7.73 (dd, 1H, $J = 9.2, 2.4$ Hz, ArH), 7.69 (d, 1H, $J = 2.4$ Hz, ArH), 7.65 (t, 3H, $J = 2.8$ Hz, ArH), 7.55 (d, 2H, $J = 8.8$ Hz, ArH), 7.47 (q, 2H, $J = 4$ Hz, ArH), 2.15 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): δ 151.0, 146.4, 144.5, 138.0, 133.9, 131.9, 130.6, 129.9, 129.5, 129.3, 129.2, 128.6, 125.5, 124.2, 121.7, 14.77; Anal. Calcd for C₂₃H₁₅Cl₂N₃: C, 68.33; H, 3.74; N, 10.39 %; Found: C, 68.38; H, 3.68; N, 10.33 %.

1-(4-trifluoromethylphenyl)-3-methyl-6-chloro-4-phenyl-1H-pyrazolo[3,4-b]quinoline (3g)

Light brown solid, mp 110 °C; IR (KBr) $\nu_{\max}$ 3054, 1580, 1527, 1442, 1399 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.76 (d, 2H, $J = 8.4$ Hz, ArH), 8.20 (d, 1H, $J = 9.2$ Hz, ArH), 7.82 (d, 2H, $J = 8.8$ Hz, ArH), 7.75-7.70 (m, 2H, ArH), 7.65 (t, 3H, $J = 2.4$ Hz, ArH), 7.46 (q, 2H, $J = 2.4$ Hz, ArH) 2.15 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): δ 150.9, 146.7, 145.0, 134.0, 132.9, 131.7, 130.54, 130.1, 129.6, 129.2, 128.6, 126.2, 125.4, 124.4, 119.4, 15.0; Mass (ESI) m/z : 403.1 [M+H]⁺; Anal. Calcd for C₂₄H₁₅ClF₃N₃: C, 65.84; H, 3.45; N, 9.60 %; Found. C, 65.79; H, 3.51; N, 9.65 %.

6-chloro-3-methyl-1,4-diphenyl-1H-Pyrazolo[3,4-b]quinoline (3h)

Light brown solid, mp 170 °C; IR (KBr) $\nu_{\max}$ 2965, 1588, 1488, 1439, 1393 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, 2H, $J = 9.6$ Hz, ArH), 8.27 (d, 1H, $J = 8.4$ Hz, ArH), 7.80 (t, 1H, $J = 8$

Hz, ArH), 7.75 (d, 1H, J = 8.8 Hz, ArH), 7.62 (t, 3H, J = 3.2 Hz, ArH), 7.55 (d, 2H, J = 9.6 Hz, ArH), 7.48 (q, 2H, J = 2.4 Hz, ArH), 7.41 (t, 1H, J = 8.8 Hz, ArH), 2.16 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): δ 149.5, 146.7, 144.4, 133.1, 131.4, 130.7, 130.3, 129.6, 129.1, 128.9, 128.7, 128.3, 127.0, 124.3, 121.3, 14.7; Anal. Calcd for C₂₃H₁₆ClN₃: C, 74.69; H, 4.36; N, 11.36 %; Found. C, 74.75; H, 4.31; N, 11.41 %.

1-(4-fluorophenyl)-3-methyl-6-chloro-4-phenyl-1H-pyrazolo [3,4-b]quinoline (3i)

Brown solid, mp 160 °C; IR (KBr) $\nu_{\max}$ 2921, 1589, 1506, 1442, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.46 (q, 2H, J = 4 Hz, ArH), 8.16 (d, 1H, J = 10 Hz, ArH), 7.71-7.69 (m, 2H), 7.63 (t, 3H, J = 3.6 Hz), 7.47 (q, 2H, J = 4 Hz, ArH), 7.26 (d, 2H, J = 6.8 Hz, ArH), 2.14 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): δ 149.9, 146.8, 143.85, 135.9, 134.2, 131.4, 130.4, 129.7, 129.6, 129.1, 128.5, 125.4, 124.1, 122.0, 121.9, 116.6, 115.8, 115.6, 14.7; Mass (ESI) m/z ; 387.1 [M+H]⁺; Anal. Calcd for C₂₃H₁₅ClFN₃: C, 71.23; H, 3.90; N, 10.83 %; Found. C, 71.19; H, 3.95; N, 10.87 %.

1-(4-bromophenyl)-3-methyl-6-nitro-4-phenyl-1H-Pyrazolo[3,4-b]quinoline (3j)

Light green solid, mp 230 °C; IR (KBr) $\nu_{\max}$ 2994, 1587, 1489, 1441, 1336 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, 1H, J = 2.4 Hz, ArH), 8.54 (dd, 1H, J = 9.2 Hz, ArH), 8.46 (d, 2H, J = 8.8 Hz, ArH), 8.31 (d, 1H, J = 9.6 Hz, ArH), 7.72-7.67 (m, 5H, ArH), 7.50-7.48 (m, 2H, ArH), 2.18 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): δ 151.2, 150.2, 147.8, 144.9, 143.8, 138.4, 133.1, 130.4, 129.8, 129.5, 128.8, 124.8, 123.7, 121.8, 118.6, 15.0; Anal. Calcd for C₂₃H₁₅BrN₄O₂: C, 60.15; H, 3.29; N, 12.20 %; Found. C, 60.21; H, 3.24; N, 12.15 %.

3-Methyl-6-nitro-1,4-diphenyl-1H-pyrazolo[3,4-b]quinoline (3k)

Pale yellow solid, mp 185 °C; IR (KBr) $\nu_{\max}$ 2982, 1589, 1502, 1438, 1379 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.74 (d, 1H, J = 2.8 Hz), 8.52 (dd, 1H, J = 9.2 Hz, 2.8 Hz, ArH), 8.49 (d, 2H, J = 8 Hz, ArH), 8.31 (d, 1H, J = 9.2 Hz, ArH), 7.69-7.67 (m, 3H, ArH), 7.60 (t, 2H, J = 8.8 Hz, ArH), 7.51 (q, 2H, J = 3.2 Hz, ArH), 7.36 (t, 1H, J = 7.2 Hz, ArH), 2.20 (s, 3H, ArH); ¹³C (100 MHz, CDCl₃): δ 150.2, 147.6, 144.4, 143.7, 139.3, 133.3, 130.5, 129.7, 129.5, 129.1, 128.7, 125.8, 124.8, 123.5, 122.0, 120.8, 14.9; Mass (ESI) m/z ; 380.1 [M+H]⁺; Anal. Calcd for C₂₃H₁₆N₄O₂: C, 72.62; H, 4.24; N, 14.73 %; Found. C, 72.57; H, 4.30; N, 14.78 %.

1-(4-methoxyphenyl)-3-methyl-6-nitro-4-phenyl-1H-pyrazolo[3,4-b]quinoline (3l)

Brown solid, mp 190 °C; IR (KBr) $\nu_{\max}$ 3315, 1511, 1332, 1246 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.73 (d, 1H, $J = 2.4$ Hz, ArH), 8.51-8.48 (m, 1H, ArH), 8.31-8.26 (m, 3H, ArH), 7.69-7.54 (m, 3H, ArH), 7.51-7.49 (m, 2H, ArH), 7.14 (d, 2H, $J = 8.8$ Hz), 3.92 (s, 3H, OCH_3), 2.19 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 150.3, 145.9, 144.4, 132.18, 131.5, 130.0, 129.8, 129.5, 129.2, 128.8, 128.6, 124.9, 123.7, 122.9, 121.8, 116.7, 114.4, 55.6, 14.8; Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_3$: C, 70.23; H, 4.42; N, 13.65%; Found. C, 70.28; H, 4.37, N, 13.60 %.

1-(4-trifluoromethylphenyl)-3-methyl-6-nitro-4-phenyl-1H-pyrazolo[3,4-b]quinoline (3m)

Light green solid, mp 190 °C; IR (KBr) $\nu_{\max}$ 2976, 1591, 1522, 1251, 1161 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.74 (t, 3H, $J = 8$ Hz, ArH), 8.56 (dd, 1H, $J = 9.2$ Hz, ArH), 8.34 (d, 1H, $J = 9.2$ Hz, ArH), 7.86 (d, 2H, $J = 8.8$ Hz, ArH), 7.72-7.68 (m, 3H, ArH), 7.51-7.50 (m, 2H, ArH), 2.1 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 151.5, 150.2, 147.9, 145.5, 144.0, 142.0, 133.0, 130.5, 129.9, 128.8, 126.3, 124.6, 123.9, 122.4, 119.9, 118.0, 15.0; Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{F}_3\text{N}_4\text{O}_2$: C, 64.69; H, 3.37; N, 12.49 %; Found. C, 64.73; H, 3.33; N, 12.54 %.

1-(4-fluorophenyl)-3-methyl-6-nitro-4-phenyl-1H-pyrazolo[3,4-b]quinoline (3n)

Light brown solid, mp 215 °C; IR (KBr) $\nu_{\max}$ 2875, 1657, 1527, 1484, 1341 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.74 (d, 1H, $J = 2.4$ Hz, ArH), 8.53 (dd, 1H, $J = 9.6$ Hz, 2.8 Hz, ArH), 8.46-8.43 (m, 2H, ArH), 8.27 (d, 1H, $J = 9.6$ Hz), 7.70-7.68 (m, 3H, ArH), 7.51-7.48 (m, 2H, ArH), 7.29 (t, 2H, $J = 8.4$ Hz), 2.1 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 151.0, 150.3, 147.8, 144.5, 143.7, 133.2, 130.44, 129.4, 129.5, 128.8, 124.8, 123.7, 122.5, 122.1, 117.5, 116.0, 115.8, 14.9; Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{FN}_4\text{O}_2$: C, 69.34; H, 3.80; N, 14.06 %; Found. C, 69.29; H, 3.86; N, 14.01 %.

1-(4-Methoxy-phenyl)-3,4-dimethyl-1H-pyrazolo[3,4-b]quinoline (3o)

Light brown solid, mp 150 °C; IR (KBr) $\nu_{\max}$ 2918, 1603, 1509, 1446 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.26 (dd, 4H, $J = 9.2$ Hz, 8.4 Hz, ArH), 7.78 (t, 1H, $J = 7.2$ Hz), 7.51 (t, 1H, $J = 7.2$ Hz, ArH), 7.11 (d, 2H, $J = 9.2$ Hz, ArH), 3.9 (s, 3H, OCH_3), 3.1 (s, 3H, CH_3), 2.9 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 154.0, 150.36, 145.6, 135.3, 132.2, 131.5, 129.0, 124.5, 123.1, 122.7, 114.5, 92.17, 55.61, 36.55, 16.5, 14.2; Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}$: C, 75.23; H, 5.65; N, 13.85 %. Found. C, 75.27; H, 13.79; N, 13.91 %.

1-(4-Bromo-phenyl)-3,4-dimethyl-1H-pyrazolo[3,4-b]quinoline (3p)

Pale white solid, mp 145 °C; IR (KBr) $\nu_{\max}$ 2918, 1585, 1373, 1253 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.49 (d, 2H, J = 8.8 Hz, ArH), 8.23 (d, 1H, J = 8.8 Hz, ArH), 8.18 (d, 1H, J = 8.8 Hz, ArH), 7.79 (t, 1H, J = 8 Hz, ArH), 7.67 (d, 2H, J = 8.8 Hz, ArH), 7.53 (t, 1H, J = 8 Hz, ArH), 3.1 (s, 3H, CH_3), 2.9 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 151.7, 149.3, 144.8, 133.7, 132.4, 131.9, 129.3, 124.4, 124.0, 123.6, 122.5, 121.5, 16.5, 14.5; Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{BrN}_3$: C, 61.38; H, 4.01; N, 11.93 %; Found. C, 61.33; H, 4.04; N, 11.95 %.

*1,5-dihydro-1-(4-bromophenyl)-3-methyl-4H-Pyrazolo[4,3-*c*]quinolin-4-one (6a)*

White solid, mp 270 °C; IR (KBr) $\nu_{\max}$ 2884, 1679, 1496, 1348 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.30 (s, 1H, Q-NH), 7.77 (d, 2H, J = 8.4 Hz), 7.48-7.45 (m, 3H, ArH), 7.30 (s, 1H, ArH), 7.25 (d, 1H, J = 8.8 Hz, ArH), 7.04 (t, 1H, J = 7.6 Hz, ArH), 2.8 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 160.0, 149.7, 141.7, 139.4, 137.8, 133.0, 130.4, 128.9, 123.8, 122.7, 111.4, 13.22; Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{BrN}_3\text{O}$: C, 57.65; H, 3.41; N, 11.86 %; Found. C, 57.71; H, 3.37; N, 11.85 %.

*1,5-dihydro-1-(4-methoxyphenyl)-3-methyl-4H-Pyrazolo[4,3-*c*]quinolin-4-one (6b)*

Light white solid, mp 220 °C; IR (KBr) $\nu_{\max}$ 2884, 1669, 1603, 1517, 1425 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.5 (s, 1H, Q-NH), 7.49 (s, 1H, ArH), 7.47 (d, 2H, J = 2.4 Hz, ArH), 7.42 (d, 1H, J = 7.6 Hz), 7.23 (d, 1H, J = 7.6 Hz), 7.12 (d, 2H, J = 10 Hz), 7.06 (t, 1H, J = 7.2 Hz), 3.96 (s, 3H, OCH_3), 2.78 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 160.3, 146.7, 143.6, 139.1, 135.5, 130.1, 128.4, 123.4, 122.6, 117.11, 114.9, 55.8, 13.2; Mass (ESI) m/z : 305.1 $[\text{M}+\text{H}]^+$; Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_2$: C, 70.81; H, 4.95; N, 10.48 %; Found C, 70.80; H, 4.97; N, 10.45 %.

*1,5-dihydro-1-(4-fluorophenyl)-3-methyl-4H-Pyrazolo[4,3-*c*]quinolin-4-one. (6c)*

White solid, mp 255 °C; IR (KBr) $\nu_{\max}$ 2889, 1679, 1515, 1231 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.9 (s, 1H, Q-NH), 7.58 (q, 2H, J = 5.2 Hz, ArH), 7.47 (t, 2H, J = 2.8 Hz, ArH), 7.31 (t, 2H, J = 8.8 Hz, ArH), 7.18 (d, 1H, J = 8.4 Hz, ArH), 7.03-6.99 (m, 1H, ArH) 2.83 (s, 3H, CH_3); ^{13}C (100 MHz, CDCl_3): δ 160.9, 149.3, 142.0, 138.3, 136.4, 130.0, 129.2, 122.4, 122.2, 117.0, 116.8, 116.6, 111.18, 13.2; Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{FN}_3\text{O}$: C, 69.60; H, 4.12; N, 14.33 %. Found. C, 69.54; H, 4.15; N, 14.37 %.

*1,5-dihydro-3,5-dimethyl-1-phenyl-4H-Pyrazolo[4,3-*c*]quinolin-4-one (6d)*

Brown solid, mp 185 °C; IR (KBr) $\nu_{\max}$ 3279, 1615, 1497, 1403, 1307 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.26 (d, 1H, $J = 8$ Hz, ArH), 7.61 (t, 1H, $J = 7.2$ Hz, ArH), 7.33 (m, 3H, ArH), 7.25 (d, 1H, $J = 8$ Hz), 7.05 (d, 2H, $J = 8.4$ Hz, ArH), 6.99 (t, 1H, $J = 7.2$ Hz, ArH), 3.69 (s, 3H, N-CH₃) 2.75 (s, 3H, CH₃). ^{13}C (100 MHz, CDCl_3): δ 162.8, 144.2, 139.7, 132.2, 129.6, 125.2, 121.7, 121.4, 117.5, 113.8, 113.3, 103.8, 29.3, 15.7; Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}$: C, 74.72; H, 5.23; N, 14.52 %; Found. C, 74.75; H, 5.20; N, 14.50 %.

1-(4-chlorophenyl)-1,5-dihydro-3,5-dimethyl-4H-Pyrazolo[4,3-c]quinolin-4-one (6e)

Light white solid, mp 200 °C; IR (KBr) $\nu_{\max}$ 2922, 1655, 1488, 1260 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.60-7.57 (m, 2H, ArH), 7.52-7.50 (m, 3H, ArH), 7.45 (d, 1H, $J = 8.8$ Hz, ArH) 7.30 (t, 1H, $J = 8$ Hz, ArH), 7.05 (t, 1H, $J = 8$ Hz, ArH), 3.78 (s, 3H, N-CH₃), 2.78 (s, 3H, CH₃); ^{13}C (100 MHz, CDCl_3): δ 159.5, 149.8, 140.5, 139.8, 138.9, 135.6, 130.1, 128.5, 123.0, 121.7, 115.7, 111.9, 29.1, 13.2; Mass (ESI) m/z ; 323.1 $[\text{M}+\text{H}]^+$; Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{ClN}_3\text{O}$: C, 66.77; H, 4.36; N, 12.98 %; Found. C, 66.73; H, 4.40; N, 12.88 %.

1-(4-(trifluoromethyl)phenyl)-1,5-dihydro-3,5-dimethyl-4H-Pyrazolo[4,3-c]quinolin-4-one (6f)

Light brown solid, mp 180 °C; IR (KBr) $\nu_{\max}$ 3259, 1617, 1583, 1324 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.23 (d, 1H, $J = 7.6$ Hz, ArH), 7.65-7.58 (m, 3H, ArH), 7.35 (t, 2H, $J = 8.8$ Hz, ArH), 7.10 (d, 2H, $J = 8.8$ Hz); 3.70 (s, 3H, N-CH₃) 2.7 (s, 3H, CH₃); ^{13}C (100 MHz, CDCl_3): δ 162.4, 146.6, 139.6, 135.0, 132.4, 127.0, 126.2, 125.2, 122.0, 113.9, 112.3, 29.0, 15.8; Mass (ESI) m/z ; 357.1 $[\text{M}+\text{H}]^+$; Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3\text{N}_3\text{O}$: C, 63.86; H, 3.95; N, 11.76 %; Found. C, 63.90; H, 3.90; N, 11.74 %.

1-(4-methoxyphenyl)-1,5-dihydro-3,5-dimethyl-4H-Pyrazolo[4,3-c]quinolin-4-one (6g)

Light brown solid, mp 210 °C; IR (KBr) $\nu_{\max}$ 2921, 1654, 1518, 1553 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.52 (t, 1H, $J = 8.8$ Hz, ArH), 7.46 (d, 3H, $J = 8.8$ Hz, ArH), 7.29 (d, 1H, $J = 8$ Hz, ArH); 7.11 (d, 2H, $J = 6.8$ Hz); 7.0 (t, 1H, $J = 8\text{Hz}$), 3.95 (s, 3H, OCH₃), 3.78 (s, 3H, N-CH₃), 2.79 (s, 3H, CH₃); ^{13}C (100 MHz, CDCl_3): δ 160.5, 149.0, 144.4, 139.8, 132.8, 130.0, 128.5, 123.1, 121.7, 115.6, 114.9, 55.8, 28.9, 13.22; Mass (ESI) m/z ; 319.1 $[\text{M}+\text{H}]^+$; Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$: C, 71.46; H, 5.37; N, 13.16 %; Found. C, 71.45; H, 5.39; N, 13.11 %.

1-(4-bromophenyl)-1,5-dihydro-3,5-dimethyl-4H-Pyrazolo[4,3-c]quinolin-4-one (6h)

Brown solid, mp 210⁰C; IR (KBr) $\nu_{\max}$ 2924, 1656, 1490, 1340 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, 2H, J = 8.8 Hz, ArH), 7.54 (t, 1H, J = 8.4 Hz, ArH), 7.46 (d, 3H, J = 8.4 Hz, ArH), 7.33 (d, 1H, J = 7.6 Hz, ArH), 7.05 (t, 1H, J = 7.2 Hz, ArH), 3.77 (s, 3H, N-CH₃), 2.77 (s, 3H, CH₃); ¹³C (100 MHz, CDCl₃): δ 159.5, 149.8, 140.4, 139.8, 139.5, 132.9, 130.1, 128.7, 123.5, 123.0, 121.6, 115.7, 111.9, 111.6, 29.1, 13.2; Mass (ESI) m/z ; 367.0 [M+H]⁺; Anal. Calcd for C₁₈H₁₄BrNO₃: C, 58.71; H, 3.83; N, 11.41 %; Found. C, 58.67; H, 3.87; N, 11.42 %.

III. Spectral Copies of pyrazoloquinolines

Figure 1 IR Spectrum of 1a

Figure 2 ^1H NMR Spectrum of 1a

Figure 3 ¹³C NMR Spectrum of 1a

Figure 4 IR Spectrum of 3b

Figure 5 ^1H NMR Spectrum of **3b**

Figure 6 ^1H NMR expand Spectrum of **3b**

Figure 7 ¹³C NMR Spectrum of **3b**

File :C:\msdchem\Sam F48\150324 AV POLY8.D
Operator :
Acquired : 7 May 2015 16:42 using AcqMethod 3206.M
Instrument : 7890A 5975C GCMS
Sample Name: 6Cl4PQ
Misc Info :
Vial Number: 1

Mass Spectrum of 3b

Figure 8 Mass Spectrum of 3b

Figure 9 IR Spectrum of **3i**

Figure 10 ^1H NMR Spectrum of **3i**

Figure 11 ^{13}C NMR Spectrum of 3i

File :C:\msdchem\Sam F48\150324 AV POLY13.D
Operator :
Acquired : 7 May 2015 20:17 using AcqMethod 3206.M
Instrument : 7890A 5975C GCMS
Sample Name: 6Cl4PQ
Misc Info :
Vial Number: 1

Figure 12 Mass Spectrum of 3i

Figure 13 ^1H NMR Spectrum of **3k**

Figure 14 ^{13}C NMR Spectrum of 3k

File :C:\msdchem\Sam F48\150324 AV POLY11.D
Operator :
Acquired : 7 May 2015 19:09 using AcqMethod 3206.M
Instrument : 7890A 5975C GCMS
Sample Name: 6N4PC
Misc Info :
Vial Number: 1

Mass Spectrum of 3k

Figure 15 Mass Spectrum of 3k

Figure 16 ^1H NMR Spectrum of 6h

Figure 17 ^1H NMR expand Spectrum of **6h**

Figure 18 ^{13}C NMR Spectrum of 6h

File :C:\msdchem\Sam F48\150324 AV POLY20.D
Operator :
Acquired : 9 May 2015 16:33 using AcqMethod 3206.M
Instrument : 7890A 5975C GCMS
Sample Name: N-MeQ+4Br PH
Misc Info :
Vial Number: 1

Figure 19 Mass Spectrum of 6h