The Synthesis of 4-(3,3-Dimethyl-3*H*-pyrrolo[2,3-*f*] quinolin-2-yl)pyrazoles and 4-(3,3-Dimethyl-3*H*-pyrrolo[3,2-*h*] quinolin-2-yl)pyrazoles

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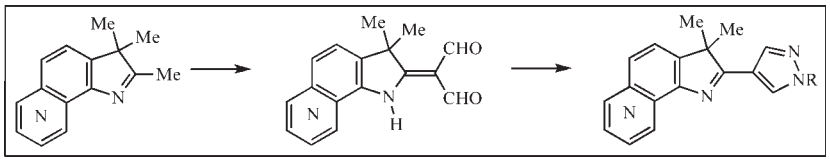

5-Hydrazinoquinoline and 8-hydrazinoquinoline were converted *via* Fischer syntheses with 3-methylbutan-2-one into pyrido-indolenines 2,3,3-trimethyl-3*H*-pyrrolo[2,3-*f*]quinoline **7** and 2,3,3-trimethyl-3*H*-pyrrolo[3,2-*h*]quinoline **11**, respectively. Exposure of the indolenines to the Vilsmeier reagent produced aminomethylene-malondialdehydes **8** and **12**, which reacted with hydrazine or arylhydrazines to give 4-(3*H*-pyrrolo[2,3-*f*]quinolin-2-yl)- and 4-(3*H*-pyrrolo[3,2-*h*]quinolin-2-yl)-pyrazoles, **9** and **13**.

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INTRODUCTION

We recently described the reaction of 2,3,3-trimethylindolenines (3*H*-indoles) **1** with the Vilsmeier reagent formed from dimethylformamide and phosphorus oxychloride to produce aminomethylene malondi-aldehydes **2** [1,2]. Additionally, we showed that these intriguing polyfunctional compounds reacted well with hydrazine or arylhydrazines to produce 4-(3,3-dimethyl-3*H*-indol-2-yl)-substituted pyrazoles, **3**, with migration of the double bond into the dihydropyrrole ring thus restoring the indolenine structure from which the sequence started [2] (Scheme 1). We have now been able to show that the principles embodied in these transformations can be incorporated into more complex heterocyclic systems and thus have prepared several 4-(3,3-dimethyl-3*H*-pyrrolo[2,3-*f*]quinolin-2-yl)pyrazoles and 4-(3,3-dimethyl-3*H*-pyrrolo[3,3-*h*]quinolin-2-yl)pyrazoles.

For the mechanism of formation of the aminomethylene malondialdehydes, we suggested that a small equilibrium concentration of an enamine tautomer **4** is successively *C*-substituted and thus, before hydrolysis during work-up, species **5** is present (Scheme 2). We suggest that a comparable mechanism operates in the work described herein.

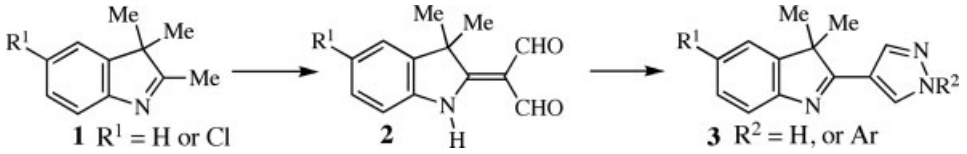
RESULTS AND DISCUSSION

Reduction of 5-nitroquinoline [3] with hydrazine and iron(III) chloride gave 5-aminoquinoline, diazotization of which, then reduction of the diazonium salt with tin(II) chloride, produced the corresponding 5-hydrazino-quinoline **6** [4] dihydrochloride. Reaction of compound **6** with isopropyl methyl ketone in a Fischer reaction [5] produced the pyrido-indolenine (2,3,3-trimethyl-3*H*-pyrrolo[2,3-*f*]quinoline) **7** in acceptable yield (Scheme 3). Similarly, 8-hydrazinoquinoline, prepared by prolonged heating of 8-hydroxyquinoline with hydrazine hydrate [6], reacted with isopropyl methyl ketone in hot acetic acid to give the isomeric pyrido-indolenine (2,3,3-trimethyl-3*H*-pyrrolo[3,2-*h*]quinoline [7]) **11** in 60% yield (Scheme 4). The structures of the two key pyrido-indolenines were evident from their molecular formulae, the six-hydrogen singlets for the geminal methyl groups, at δ 1.35 and 1.37 ppm for **7** and **11**, and singlet signals for the imine-methyl groups, resonating at δ 2.38 and 2.41 ppm, respectively. Each compound had an AB system for the *ortho*-related benzene ring protons, in addition to the three pyridine ring signals in normal positions. Each of the pyrido-indolenines was now reacted with the Vilsmeier reagent and, in yields of 94% and 81%, respectively, aminomethylene malondialdehydes **8** and **12** were obtained (Schemes 3 and 4).

The structures of the aminomethylene malon-dialdehydes rests on the observation of two one-hydrogen singlets at δ 9.83 and δ 9.86 for **8** and δ 9.82 and δ 9.90 for **12** corresponding to aldehyde protons. Absorptions at 3164 cm^{-1} and 3160 cm^{-1} for **8** and **12**, respectively, were evidence for the presence of N—H bonds, further confirmed by ^1H NMR one-hydrogen signals for the *N*-hydrogens appearing at δ 14.03 (**8**) and δ 14.45 (**12**), respectively.

As in our previous work [2], the aminomethylene malondialdehydes reacted smoothly with hydrazine and various arylhydrazines to give pyrazoles, with migration

Scheme 1



of the double bond to reform the imine unit (Schemes 3 and 4). For pyrazoles **9a–g**, the newly formed five-membered heterocyclic ring protons resonated in the range δ 8.30–9.70 and for the isomers, **13a–e**, in the range δ 8.30–9.10.

EXPERIMENTAL

Melting points were recorded on a Philip Harris C4954718 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AQS 300 MHz spectrometer, at 300 MHz and 75 MHz, respectively. Chemical shifts δ are in parts per million (ppm) measured in $CDCl_3$ as solvent and relative to TMS as the internal standard. Infrared spectra were recorded on a Thermonicolet-Nexus 670 FTIR instrument and elemental analyses were carried out on an Exeter analytical model CE440 C, H and N elemental analyzer. High resolution mass spectra were recorded on an Agilent Technology (HP), MS Model: 5973 Network Mass, selective detector ion source: electron impact (EI) 70 eV, ion source temperature: 230 °C, Analyzer: quadrupole, analyzer temperature: 150 °C, and relative abundances of fragments are quoted in parentheses after the *m*/*z* values.

5-Aminoquinoline. A mixture of 5-nitroquinoline (2.65 g, 15.2 mmol), activated carbon (600 mg), ferric chloride hexahydrate (250 mg), and methanol (50 mL) was refluxed for 10 min with stirring. Hydrazine hydrate (3.75 g, 80%) was added over 30 min to the boiling solution. The mixture was stirred under reflux for an additional 12 h, cooled, and evaporated. The resulting slurry was dissolved in dichloromethane (50 mL), washed with water (2 × 20 mL), and dried ($MgSO_4$). Evaporation of the solvent yielded a yellow solid, which was identified as 5-aminoquinoline. Yield 85%; mp: 108–110 °C (lit. 110 °C); IR: 3196, 1585, 1365, 792 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.22 (bs, 2H), 6.77 (dd, 1H, J = 8.4, 1.2 Hz), 7.26 (dd, 1H, J = 8.4, 4.2 Hz), 7.47 (t, 1H, J = 8.4 Hz), 7.56 (d, 1H, J = 8.4 Hz), 8.14 (dd, 1H, J = 8.4, 1.8 Hz), 8.84 (dd, 1H, J = 4.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$): δ 109.95, 118.69, 119.55, 119.97, 129.60, 130.05, 142.42, 149.10, 150.21.

General procedure for the synthesis of (7) and (11). A mixture of quinolinylhydrazine dihydrochloride (5 g, 21 mmol) and isopropyl methyl ketone (1.85 g, 21 mmol) was refluxed in acetic acid (100 mL) for 3–5 h and then cooled, diluted with water (100 mL), and neutralized with NaOH 2 *M*, then extracted with ethyl acetate (4 × 100 mL). The organic layer was dried over Na_2SO_4. The solvent was evaporated and the resulting viscous oil recrystallized from EtOH to give the quinolinyl-indolenines identified as (**7**) or (**11**).

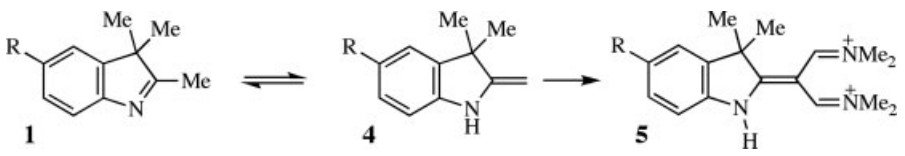
2,3,3-Trimethyl-3H-pyrrolo[2,3-f]quinoline (7). 65% Yield; mp 115–118 °C; IR: 2964, 2928, 1561, 1366 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 6H), 2.38 (s, 3H), 7.44 (dd, 1H, J = 8.4, 4.2 Hz), 7.64 (d, 1H, J = 8.4 Hz), 7.98 (d, 1H, J = 8.4 Hz), 8.84 (dd, 1H, J = 8.4, 1.8 Hz), 8.90 (dd, 1H, J = 4.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$): δ 15.57, 22.50, 54.77, 121.11, 121.87, 122.54, 126.47, 131.80, 142.28, 148.21, 148.67, 149.90, 189.72; *m*/*z*: 210 $[M]^+$, 195 (100), 181, 169, 154, 129, 84. Found: M^+ 210.1158, $C_{14}H_{14}N_2$ requires M^+ 210.1157.

2,3,3-Trimethyl-3H-pyrrolo[3,2-h]quinoline (11). 80% Yield; mp 114–116 °C; IR: 2966, 1686, 1515, 1359 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 6H), 2.41 (s, 3H), 7.38 (dd, 1H, J = 8.4, 4.2 Hz), 7.50 (d, 1H, J = 8.1 Hz), 7.70 (d, 1H, J = 8.1 Hz), 8.17 (dd, 1H, J = 8.4, 1.8 Hz), 9.00 (dd, 1H, J = 4.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$): δ 15.58, 22.43, 55.45, 120.37, 120.97, 125.37, 128.36, 136.59, 140.40, 146.03, 148.64, 150.58, 189.87; *m*/*z*: 210 M^+, 195 (100), 181, 169, 154, 129, 84. Found: M^+ 210.1157, $C_{14}H_{14}N_2$ requires M^+ 210.1157.

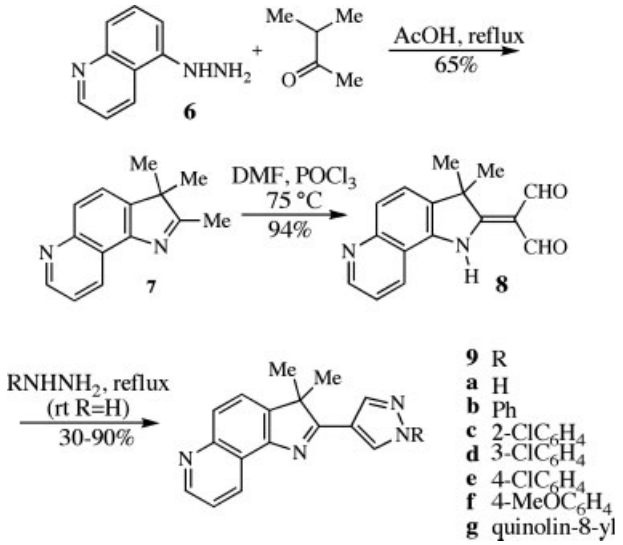
General procedure for the synthesis of (8) and (12). To *N*,*N*-dimethylformamide (10 mL) cooled in an ice bath was added dropwise phosphorus oxychloride (7 mL, 75 mmol) with stirring at below 10 °C. After this addition, a solution of (**7**) or (**11**) (25 mmol, 5.25 g) in DMF (10 mL) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 75 °C for 4–6 h. The resulting solution was added to ice-cooled water and made alkaline with NaOH(aq.) solution. The resulting precipitate was collected by filtration, dried in air, recrystallized from ethanol, and identified as (**8**) or (**12**).

(3,3-Dimethyl-3H-pyrrolo[2,3-f]quinolin-2-ylidene)malondialdehyde (8). 94% Yield; mp 180–183 °C; IR: NH 3164, 2965, 2763, 1679, 1601, 1518, 1363, 1166, 814, 771 cm^{-1}; ^{1}H NMR

Scheme 2



Scheme 3



($CDCl_3$): δ 1.86 (s, 6H), 7.55 (dd, 1H, J = 8.4, 4.2 Hz), 7.72 (d, 1H, J = 8.70 Hz), 8.06 (d, 1H, J = 8.70 Hz), 8.34 (dd, 1H, J = 8.4, 1.8 Hz), 9.02 (dd, 1H, J = 4.2, 1.8 Hz), 9.83 (s, 1H), 9.86 (s, 1H,), 14.03 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ 22.84, 52.43, 110.17, 115.82, 121.79, 122.74, 127.55, 129.20, 134.34, 137.27, 148.08, 150.98, 180.33, 187.62, 192.68. Found: % C 72.02; H 5.38; N 10.63. $C_{16}H_{14}N_2O_2$ requires % C 72.16; H 5.30; N 10.52.

(3,3-Dimethyl-3H-pyrrolo[3,2-h]quinolin-2-ylidene)malondialdehyde (12). 81% Yield; mp 166–168 °C; IR: NH 3160, 2966, 2763,1673, 1602, 1504, 1325, 1161, 816, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.87 (s, 6H), 7.50 (dd, 1H, J = 8.4, 4.2 Hz), 7.54 (d, 1H, J = 8.1 Hz), 7.73 (d, 1H, J = 8.1 Hz), 8.23 (dd, 1H, J = 8.4, 1.5 Hz), 8.97 (dd, 1H, J = 4.2, 1.5 Hz), 9.82 (s, 1H), 9.90 (s, 1H), 14.45 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ 22.75, 53.05, 110.03, 120.02, 121.87, 125.34, 128.26, 135.85, 136.08, 139.95, 150.94, 150.95, 179.05, 187.99, 192.21. Found: % C 71.98; H; 5.31; N 10.44. $C_{16}H_{14}N_2O_2$ requires % C 72.16; H 5.30; N 10.52.

General procedure for the synthesis of (9a) and (13a). A mixture of the malondialdehyde (**8**) or (**12**) (0.5 mmol) and hydrazine monohydrate (0.05 g, 1 mmol) in absolute ethanol (1 mL) was stirred at room temperature for 24 h (R = H). After concentrating the solution, the resulting crystals were collected by filtration and recrystallized from EtOH to give the (**9a**) and (**13a**).

4-(3,3-Dimethyl-3H-pyrrolo[2,3-f]quinolin-2-yl)pyrazole (9a). 60% Yield; mp 130–132 °C; IR: 3137, 2969, 2926, 1570, 1486, 1330, 1062, 924, 832, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 6H), 3.50 (bs, 1H, NH), 7.51 (dd, 1H, J = 8.4, 4.3 Hz), 7.74 (d, 1H, J = 8.4 Hz), 8.04 (d, 1H, J = 8.4 Hz), 8.35 (s, 2H), 8.95–9.01 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 24.28, 54.34, 116.24, 119.55, 121.07, 122.15, 122.28, 126.47, 132.12, 134.22, 142.77, 148.45, 150.12, 179.96. Found: % C 73.07; H 5.32; N 21.49. $C_{16}H_{14}N_4$ requires % C 73.26; H 5.38; N 21.36.

4-(3,3-Dimethyl-3H-pyrrolo[3,3-h]quinolin-2-yl)pyrazole (13a). 65% Yield; mp 135–139 °C; IR: 3163, 2965, 2927, 1566, 1512, 1466, 1326, 1068, 940, 832, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.62 (s, 6H), 4.10 (bs, 1H, NH), 7.49 (dd, 1H, J = 8.4, 3.75 Hz), 7.60 (d, 1H, J = 8.1 Hz), 7.74 (d, 1H, J = 8.1 Hz), 8.28 (d, 1H, J = 8.4 Hz), 8.73 (s, 2H), 9.18 (d, 1H, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$): δ 24.26, 54.34, 116.25, 121.07, 122.16, 122.30, 126.44, 132.16, 134.21, 142.80, 148.42, 149.28, 150.08, 179.99. Found: % C 73.29; H 5.41; N 21.19. $C_{16}H_{14}N_4$ requires % C 73.26; H 5.38; N 21.36.

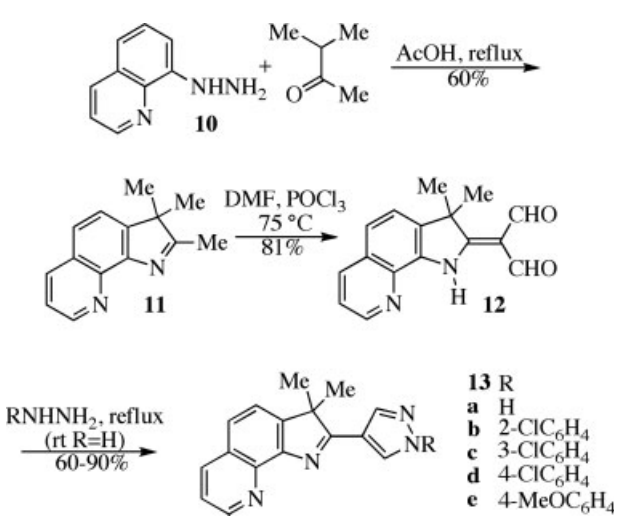
General procedure for the synthesis of (9b–g) and (13b–g). A mixture of the malondialdehyde (**8**) or (**12**) (0.5 mmol) and the arylhydrazine (0.55 mmol) in absolute ethanol (15 mL) was heated with stirring at reflux for 2–3 h. After cooling and concentrating the solution, the resulting crystals were collected by filtration and recrystallized from EtOH to give the corresponding pyrazoles.

1-Phenyl-4-(3,3-dimethyl-3H-pyrrolo[2,3-f]quinolin-2-yl)-pyrazole (9b). 70% Yield; mp 168–170 °C; IR: 3059, 2968, 2928, 2576, 1572, 1561, 1497, 1377, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.61 (s, 6H), 7.34 (dd, 1H, J = 8.4, 4.5 Hz), 7.43–7.51 (m, 3H), 7.70 (d, 1H, J = 8.4 Hz), 7.77 (m, 2H), 8.07 (d, 1H, J = 8.4 Hz), 8.38 (s, 1H), 8.68 (s, 1H), 8.94 (dd, 1H, J = 4.5, 1.8 Hz), 9.00 (dt, 1H, J = 8.4, 0.9 Hz); ^{13}C NMR ($CDCl_3$): δ 24.18, 54.36, 118.06, 119.52, 121.15, 122.18, 122.74, 125.56, 127.22, 127.43, 129.48, 129.61, 133.06, 139.42, 140.75, 143.14, 147.25, 149.35, 179.77. Found: % C 78.29; H 5.26; N 16.41. $C_{22}H_{18}N_4$ requires % C 78.08; H 5.36; N 16.56.

1-(2-Chlorophenyl)-4-(3,3-dimethyl-3H-pyrrolo[2,3-f]quinolin-2-yl)pyrazole (9c). 90% Yield; mp 100–103 °C; IR: 2958, 2927, 1580, 1559, 1491, 1451, 1365, 940, 816, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 6H), 7.36–7.41 (m, 2H), 7.53–7.58 (m, 2H), 7.65 (dd, 1H, J = 7.5, 1.8 Hz), 7.76 (d, 1H, J = 8.4 Hz), 8.14 (d, 1H, J = 8.4 Hz), 8.45 (s, 1H), 8.59 (s, 1H), 8.95 (dd, 1H, J = 4.2, 1.5 Hz), 9.10 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 24.21, 54.48, 117.25, 121.04,122.27, 123.28, 124.90, 127.66, 127.92, 128.24, 129.78, 130.81, 131.81, 134.12, 137.43, 140.77, 143.47, 146.27, 148.67, 149.26, 179.90. Found: % C 70.71; H 4.68; Cl 9.41; N 15.16. $C_{22}H_{17}ClN_4$ requires % C 70.87; H 4.60; Cl 9.51; N 15.03.

1-(3-Chlorophenyl)-4-(3,3-dimethyl-3H-pyrrolo[2,3-f]quinolin-2-yl)pyrazole (9d). 90% Yield; mp 151–153 °C; IR: 2961, 2928, 1578, 1563, 1488, 1415, 1365, 1033, 959, 839, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 6H), 7.30 (dt, 1H, J =

Scheme 4



8.1, 0.9 Hz), 7.40 (t, 1H, J = 8.1 Hz), 7.47 (dd, 1H, J = 8.4, 4.2 Hz), 7.66 (t, 1H, J = 0.9 Hz), 7.70 (d, 1H, J = 8.4 Hz), 7.83–7.84 (m, 1H), 8.03 (d, 1H, J = 8.4 Hz), 8.39 (s, 1H), 8.63 (s, 1H), 8.95 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$): δ 24.17, 54.31, 117.29, 118.73, 119.73, 119.74, 121.15, 122.19, 126.83, 126.86, 127.28, 130.65, 131.95, 135.43, 140.39, 141.07, 142.84, 148.49, 149.18, 150.20, 179.02. Found: % C 70.93; H 4.61; Cl 9.43; N 14.91. $C_{22}H_{17}ClN_4$ requires % C 70.87; H 4.60; Cl 9.51; N 15.03.

1-(4-Chlorophenyl)-4-(3,3-dimethyl-3H-pyrrolo[2,3-f]quinolin-2-yl)pyrazole (9e). 90% Yield; mp 176–177 °C; IR: 2967, 2927, 1577, 1562, 1492, 1421, 1067, 948, 824, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.62 (s, 6H), 7.48–7.52 (m, 3H), 7.75 (t, 3H, J = 8.4), 8.05 (d, 1H, J = 8.40 Hz), 8.40 (s, 1H), 8.64 (s, 1H), 8.95–8.96 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 24.18, 54.30, 118.65, 120.60, 121.12, 122.17, 126.80, 126.85, 129.70, 131.92, 132.89, 138.05, 140.88, 142.81, 148.52, 149.21, 150.19, 179.11. Found: % C 70.81; H 4.50; Cl 9.56; N 15.10. $C_{22}H_{17}ClN_4$ requires % C 70.87; H 4.60; Cl 9.51;N 15.03.

1-(4-Methoxyphenyl)-4-(3,3-dimethyl-3H-pyrrolo[2,3-f]-quinolin-2-yl)pyrazole (9f). 75% Yield; mp 139–141 °C; IR: 2964, 2931, 1575, 1560, 1518, 1502, 1259, 1250, 1038, 958, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 6H), 3.80 (s, 3H), 6.93–6.97 (m, 2H), 7.44 (dd, 1H, J = 8.4, 4.2 Hz), 7.64–7.69 (m, 3H), 8.00 (d, 1H, J = 8.4 Hz), 8.33 (s, 1H), 8.56 (s, 1H), 8.9 (dd, 1H, J = 4.1, 1.8 Hz), 8.94 (d, 1H, J = 9 Hz); ^{13}C NMR ($CDCl_3$): δ 24.25, 54.25, 55.55, 114.62, 117.92, 121.05, 121.12, 122.11, 122.23, 126.52, 127.04, 132.04, 133.15, 140.28, 142.78, 148.42, 149.28, 150.09, 158.82, 179.55. Found: % C 74.71; H 5.39; N 15.29. $C_{23}H_{20}N_4O$ requires % C 74.98; H 5.47; N 15.21.

4-(3,3-Dimethyl-3H-pyrrolo[2,3-f]quinolin-2-yl)-1-(quinolin-8-yl)pyrazole (9g). 30% Yield; mp 186–188 °C; IR: 3055, 2969, 2926, 1580, 1561, 1471, 1409, 1050, 942, 825, 786 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.62 (s, 6H), 7.55–7.59 (m, 2H), 7.71 (t, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 8.4 Hz), 7.87–7.90 (m, 1H), 8.13 (d, 1H, J = 8.4 Hz), 8.29–8.38 (m, 2H), 8.57 (s, 1H), 8.97–8.99 (m, 1H), 9.07–9.09 (m, 1H), 9.13 (d, 1H, J = 8.4 Hz), 9.67 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 24.46, 54.45, 117.18, 120.88, 121.76, 122.25, 122.94, 123.79, 125.39, 126.53, 127.43, 129.27, 133.54, 134.25, 136.23, 136.61, 140.46, 140.67, 143.27, 147.18, 149.16, 149.55, 150.60, 180.26. Found: % C 76.92; H 4.81; N 17.93. $C_{25}H_{19}N_5$ requires % C 77.10; H 4.92; N 17.98.

1-(2-Chlorophenyl)-4-(3,3-dimethyl-3H-pyrrolo[3,3-h]-quinolin-2-yl)pyrazole (13b). 75% Yield; mp 97–100 °C; IR: 2965, 2926, 1571, 1488, 1444, 1073, 940, 834, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 6H), 7.36–7.46 (m, 3H), 7.56–7.60 (m, 2H), 7.68 (dd, 1H, J = 8.1, 1.8 Hz), 7.75 (d, 1H, J = 8.1 Hz), 8.23 (d, 1H, J = 8.4 Hz), 8.57 (s, 1H), 8.73 (s, 1H), 9.08 (dd, 1H, J = 4.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$): δ 24.28, 54.60, 117.63, 119.82, 120.88, 125.52, 127.62, 127.86, 128.11, 128.64, 129.54, 130.84, 132.04, 136.30, 137.62, 141.03, 141.33, 146.75, 149.66, 150.85, 179.05. Found: % C 70.69; H 4.53; Cl 9.61; N 15.12. $C_{22}H_{17}ClN_4$ requires % C 70.87;H 4.60; Cl 9.51; N 15.03.

1-(3-Chlorophenyl)-4-(3,3-dimethyl-3H-pyrrolo[3,3-h]-quinolin-2-yl)pyrazole (13c). 80% Yield; mp 110–113 °C; IR: 2962, 2926, 1594, 1570, 1488, 1458, 1074, 940, 833, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 6H), 7.30–7.41 (m, 3H), 7.57–7.80 (m, 4H), 8.21–8.24 (m, 1H), 8.40 (s, 1H), 8.87 (s, 1H), 9.06–9.08 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 24.11, 54.62, 117.11, 118.72, 119.75, 119.95, 120.94, 125.67, 127.21, 127.88, 128.88, 130.67, 135.47, 136.72, 140.43, 140.83, 141, 146.89, 149.22, 150.68, 178.98. Found: % C 70.78; H 4.66; Cl 9.67; N 14.94. $C_{22}H_{17}ClN_4$ requires % C 70.87; H 4.60; Cl 9.51 N 15.03.

1-(4-Chlorophenyl)-4-(3,3-dimethyl-3H-pyrrolo[3,3-h]-quinolin-2-yl)pyrazole (13d). 85% Yield; mp 128–131 °C; IR: 2967, 2930, 1573, 1496, 1378, 1267, 1076, 950, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.65 (s, 6H), 7.48 (d, 1H, J = 8.7 Hz), 7.56 (dd, 1H, J = 8.1, 4.2 Hz), 7.67 (d, 1H, J = 8.1 Hz), 7.77–7.83 (m, 4H), 8.36–8.38 (m, 1H), 8.39 (s, 1H), 9.07 (s, 1H), 9.17 (d, 1H, J = 4.2, Hz); ^{13}C NMR ($CDCl_3$): δ 24.00, 54.76, 118.13, 120.51, 120.67, 120.99, 125.72, 127.75, 128.27, 128.66, 129.58, 132.69, 137.85, 138.35, 138.78, 140.82, 147.77, 149.42, 179.55. Found: % C 70.83; H 4.61; Cl 9.50; N 15.08. $C_{22}H_{17}ClN_4$ requires % C 70.87; H 4.60; Cl 9.51; N 15.03.

1-(4-Methoxyphenyl)-4-(3,3-dimethyl-3H-pyrrolo[3,3-h]-quinolin-2-yl)pyrazole (13e). 75% Yield; mp 187–189 °C; IR: 2964, 2929, 1572, 1519, 1495, 1257, 1032, 953, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.64 (s, 6H), 3.88 (s, 3H), 7.03 (d, 2H, J = 9.0 Hz), 7.45 (dd, 1H, J = 8.4, 4.2 Hz), 7.60 (d, 1H, J = 8.1 Hz), 7.69–7.76 (m, 3H), 8.23 (dd, 1H, J = 8.4, 1.2 Hz), 8.39 (s, 1H), 8.83 (s, 1H), 9.09 (dd, 1H, J = 4.2, 1.2 Hz); ^{13}C NMR ($CDCl_3$): δ 24.27, 54.55, 55.61, 114.71, 118.01, 119.86, 120.88, 120.98, 125.40, 128.01, 128.67, 133.29, 136.39, 140.26, 141.16, 146.70, 149.53, 150.78, 158.81, 179.40. Found: % C 75.06; H 5.40; N 15.25. $C_{23}H_{20}N_4O$ requires % C 74.98; H 5.47; N 15.21.

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