

General procedure for the preparation of [1.2.4]triazino[6,5-*f*]quinolines and/or 1(3)H-pyrazolo[3,4-*f*]quinolines: A mixture of 6-nitroquinoline (0.30 g), aromatic hydrazone (1.2 eq), sodium hydride (4.0 eq) and DMF (15mL) was stirred at $-10\text{ }^{\circ}\text{C}$. After 3-4 h, the mixture was diluted with water (100 mL) and the organic phase was extracted with EtOAc (3 x 50 mL). The combined extracts were evaporated and chromatographed on silica gel using a mixture of EtOAc and hexane as the eluent to give the corresponding pyrazole and/or [1.2.4]triazine derivatives in the yields shown in Tables 1 and 2.

[1.2.4]triazino[6,5-*f*]quinolines

3-Phenyl[1.2.4]triazino[6,5-*f*]quinoline. (5b) Mp. 178 – 179 $^{\circ}\text{C}$. ^1H HMR (CDCl_3) δ 7.55-7.65 (m 3H), 7.81 (dd, 1H, $J = 4.4, 8.4$), 8.44 (d, 1H, $J = 10.0$), 8.62 (dd, 2H, $J = 1.6, 7.2$), 8.67 (dd, 1H, $J = 10.0$), 9.19 (dd, 1H, $J = 1.6, 4.4$), 9.69 (dd, 1H, $J = 1.6, 8.4$). MS m/z (CI) 259 ($\text{M}^+ + 1, 100$), 149 (27).

3-(4-Methylphenyl)[1.2.4]triazino[6,5-*f*]quinoline. (5c) Mp. 199 – 201 $^{\circ}\text{C}$. ^1H HMR (CDCl_3) δ 2.50 (s, 3H), 7.43 (d 2H, $J = 8.0$), 7.81 (dd, 1H, $J = 4.4, 8.4$), 8.15 (d, 1H, $J = 9.2$), 8.48 (d, 1H, $J = 9.2$), 8.69 (dd, 2H, $J = 8.0$), 9.16 (dd, 1H, $J = 1.6, 4.4$), 9.77 (dd, 1H, $J = 1.6, 8.4$). MS m/z (CI) 273 ($\text{M}^+ + 1, 100$), 244 (7).

3-(4-Methoxyphenyl)[1.2.4]triazino[6,5-*f*]quinoline. (5d) Mp. 236 - 238 $^{\circ}\text{C}$. ^1H NMR ($\text{DMSO-}d_6$) δ 3.79 (s, 3H), 7.01 (d, 2H, $J = 8.8$), 7.43 (d, 1H, $J = 9.2$), 7.60 (d, 2H, $J = 8.8$), 7.64 (dd, 1H, $J = 4.4, 8.8$), 8.06 (d, 1H, $J = 9.2$), 8.99 (d, 1H, $J = 4.4$), 9.31 (d, 1H, $J = 8.8$). MS m/z (CI) 289 ($\text{M}^+ + 1, 100$), 263 (14), 190 (32), 136 (41).

3-(4-Chlorophenyl)[1.2.4]triazino[6,5-*f*]quinoline. (5e) Mp. 254 - 255 $^{\circ}\text{C}$. ^1H HMR (CDCl_3) δ 7.59 (d, 2H, $J = 8.0$), 7.83 (dd, 1H, $J = 4.4, 8.4$), 8.15 (d, 1H, $J = 9.2$), 8.50 (d, 1H, $J = 9.2$), 8.75 (d, 1H, $J = 8.0$), 9.18 (dd, 1H, $J = 1.6, 4.4$), 9.77 (dd, 1H, $J = 1.6, 8.4$). MS m/z (CI) 295 ($\text{M}^+ + 2, 3.3$), 293 ($\text{M}^+, 10.7$) 266 (27), 264 (82), 132 (34), 127 (100).

3-(4-Fluorophenyl)[1.2.4]triazino[6,5-*f*]quinoline. Mp. ?? $^{\circ}\text{C}$. ^1H HMR (CDCl_3) δ 7.30 (dd, 2H, $J = 8.8, 8.8$), 7.83 (dd, 1H, $J = 4.4, 8.4$), 8.15 (d, 1H, $J = 9.2$), 8.50 (d, 1H, $J = 9.2$), 8.82 (dd, 2H, $J = 5.6, 8.8$), 9.18 (dd, 1H, $J = 1.6, 4.4$), 9.77 (dd, 1H, $J = 1.6, 8.4$). MS m/z (CI) 277 ($\text{M}^+ + 1, 100$), 251 (22), 190 (30).

1(3)H-pyrazolo[3,4-*f*]quinolines

3-Phenyl-1(3)H-pyrazolo[3,4-*f*]quinoline. (4b) Mp. 225 - 226 °C. ¹H NMR (DMSO-*d*₆) δ 7.46-7.49 (m, 3H), 7.80 (dd, 1H, *J* = 4.4, 8.6), 9.15 (dd, 1H, *J* = 1.6, 4.4), 8.14 (d, 1H, *J* = 9.6), 8.47 (d, 1H, 9.6), 9.75 (dd, 1H, *J* = 1.6, 8.6), 12.59 (s, 1H). MS *m/z* (CI) 245 (M⁺, 46), 189 (35), 170 (100).

3-(4-Chlorophenyl)-1(3)H-pyrazolo[3,4-*f*]quinoline. (4e) Mp 262 - 263 °C. ¹H NMR (DMSO-*d*₆) δ 7.48-7.53 (m, 3H), 7.60-7.67(m, 3H), 8.03 (d, 1H, *J* = 9.2), 8.99 (d, 1H, *J* = 4.3), 9.15 (d, 1H, *J* = 8.8), 11.66 (s, 1H). MS *m/z* (CI) 281 (M⁺+2, 12), 279 (M⁺, 59), 277 (85), 140 (100).

3-(4-Nitrophenyl)-1(3)H-pyrazolo[3,4-*f*]quinoline. (4f) Mp. 281-282 °C. ¹H NMR (DMSO-*d*₆) δ 7.51 (dd, 1H, *J* = 4.4, 8.0), 7.93 – 7.99 (m, 2H), 8.05 (d, 2H, *J* = 8.8), 8.40 (d, 1H, *J* = 1.3, 8.0), 8.43 (dd, 1H, *J* = 8.8), 8.83 (dd, 1H, *J* = 1.3, 4.4), 14.03 (s, 1H). MS *m/z* (CI) 290 (M⁺, 100), 244 (39), 190 (51).

9-(4-Nitrophenyl)-7H-pyrazolo-[3,4-*h*]quinoline. Mp. 244 – 246 °C. ¹H NMR (DMSO-*d*₆) δ 7.64 (d, H, *J* = 8.8), 7.71 (d, H, *J* = 4.4), 8.05 (d, 2H, *J* = 8.4), 8.29 (d, 2H, *J* = 8.8), 8.30 (d, 1H, *J* = 8.4), 8.91 (d, 1H, *J* = 8.4), 9.04 (d, 1H, *J* = 4.4), 11.73 (s, 1H). MS *m/z* (CI) 291 (M⁺+1, 100), 261 (72), 175 (42), 145 (46).

Benzopyrazoles

6-Chloro-3-(4-nitrophenyl)benzopyrazole. Mp. 219 – 220 °C. ¹H NMR (DMSO-*d*₆) δ 7.47 (dd, 1H, *J* = 1.6, 8.8), 7.69 (d, 1H, *J* = 8.8), 8.25 (d, 1H, *J* = 1.6), 8.30 (d, 2H, *J* = 8.8), 8.34 (dd, 2H, *J* = 8.8), 13.83 (s, 1H). MS *m/z* (CI) 276 (M⁺+3, 38), 274 (M⁺+1, 100), 246 (11), 244 (37).

5-Nitro-3-(4-nitrophenyl)benzopyrazole. Mp. 259 – 261 °C (dec.). ¹H NMR (CDCl₃) δ 8.06 (dd, 1H, *J* = 2.0, 9.0), 8.31(d, 2H, *J* = 8.8), 8.37(dd, 2H, *J* = 8.8), 8.39(d, 1H, *J* = 9.0), 8.54(d, 1H, *J* = 2.0), 14.30(s, 1H). MS *m/z* (CI) 285 (M⁺+1, 100), 255 (34).

6-Nitro-3-(4-nitrophenyl)benzopyrazole. Mp. 230 – 231 °C. ¹H NMR (CDCl₃) δ 7.45

(dd, 1H, $J = 1.6, 8.8$), 8.02 (d, 1H, $J = 1.6$), 8.13 (d, 2H, $J = 8.4$), 8.16 (d, 1H, $J = 8.8$), 8.39 (d, 2H, $J = 8.4$), 14.24 (s, 1H). MS m/z (CI) 285 (M^{+1} , 15), 194 (56), 164 (46), 140 (100).