Synthesis of 7-aryl-9-methyl-3*h*- pyrazolo[4,3-*f*]quinoline derivatives catalysed by iodine

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A mild and efficient method for the synthesis of 7-aryl-9-methyl-3*H*- pyrazolo[4,3-*f*]quinoline derivatives via a three-component reaction of an aromatic aldehyde, 1*H*-indazol-5-amine and acetone catalysed by iodine is described. This new procedure has the advantages of mild reaction conditions, high yields and a metal-free catalyst.

Keywords: pyrazolo[4,3-*f*]quinoline, 1*H*-indazol-5-amine, iodine

Pyrazoloquinoline derivatives are an important class of heterocycles because they are promising materials for optoelectronic applications.[1–5] In addition, they possess antileishmanial[6] and antimicrobial activities.[7] Some of them are used as modulators of cytokine biosynthesis for treatment of viral and neoplastic diseases,[8] and immune-modulators for inducing cytokine biosynthesis in animals, and in the treatment of diseases, including viral and neoplastic disorders.[9] They are also human A3 adenosine receptor (AR) antagonists.[10,11]

Although a number of useful synthetic procedures to prepare pyrazoloquinolines has been developed,[12–16] several limitations remain. For example, most reported procedures involve several steps, or give low yields. Moreover, the starting materials are not often readily available. Thus, simple and efficient method to synthesise pyrazoloquinolines would be attractive.

Over the past few years, molecular iodine (I_2) has emerged as a powerful catalyst for various organic transformations because of its inexpensive, nontoxic, and eco-friendly nature.[17–22] In view of the importance of pyrazoloquinoline derivatives and as a continuation of our research devoted to the development of new methods for the preparation of heterocycles via multi-component reactions catalysed by iodine,[23,24] we now report the synthesis of 7-aryl-9-methyl-3*H*-pyrazolo[4,3-*f*]quinoline derivatives by the reaction of an aromatic aldehyde, 1*H*-indazol-5-amine and acetone in THF catalysed by iodine.

Results and discussion

Treatment of aromatic aldehyde **1**, 1*H*-indazol-5-amine **2** and acetone **3** in THF in the presence of 5 mol% iodine at reflux condition afforded the corresponding 7-aryl-9-methyl-3*H*-pyrazolo[4,3-*f*]quinoline derivatives **4** in high yields (Scheme 1).

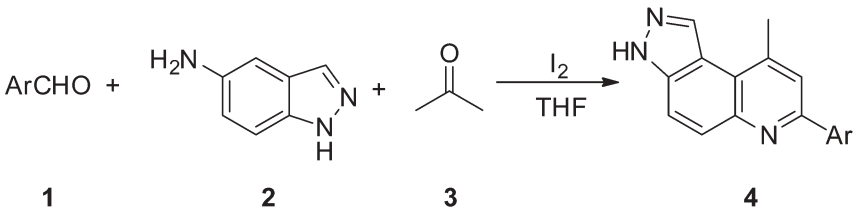
In our initial study, the reaction of 2-chlorobenzaldehyde **1a**, 1*H*-indazol-5-amine **2** and acetone **3** was used as a model reaction to optimise the reaction conditions. The reaction was firstly carried out in THF in the absence of I_2. It was found that no reaction occurred either at room temperature or under reflux (Table 1, entries 1 and 2). Similar reactions were attempted in the presence of 5, 10 and 20 mol% of I_2. The results from Table 1 (entries 5–7) show that 5 mol% I_2 at reflux in THF is sufficient to initiate the reaction. Higher loading of the catalyst had no significant influence on the reaction yield. To find the optimum reaction temperature, the reaction was carried out with 5 mol% of I_2 at room temperature, at 50 °C and at reflux temperature, resulting in the isolation of **4a** in trace amounts, 72% and 90% yields (Table 1, entries 3–5), respectively. Thus, 5 mol% of I_2 and a reaction temperature at reflux were optimal conditions. In addition, CH_3CN, benzene, DMF and $CHCl_3$ (Table 1, entries 8–11) were also tested as the solvents. In these cases, product **4a** was formed in slightly lower yields (Table 1, entries 8–11).

According to the optimised conditions, various aromatic aldehydes **1** were then subjected to reaction with **2** and **3** to generate a library of 7-aryl-9-methyl-3*H*- pyrazolo[4,3-*f*]quinoline derivatives **4** (Table 2). For aldehyde **1**, the yields of **4** were not sensitive to the electronic properties of the aromatic ring in the presence of electron-withdrawing groups (such as halide) or electron-donating groups (such as alkyl or alkoxy group) (Table 2). The structures of the products **4** were characterised by ^{1}H NMR, IR and HRMS, the spectra were all in full agreement with their constitution.

Table 1 Yield optimisation for **4a** under different conditions [a]

Entry	Temp. /°C)	Catalyst /mol %	Solvent	Yields /%[b]
1	r.t.	0	THF	0
2	Reflux	0	THF	0
3	r.t.	5	THF	trace
4	50	5	THF	72
5	Reflux	5	THF	90
6	Reflux	10	THF	89
7	Reflux	20	THF	90
8	Reflux	5	CH_3CN	86
9	Reflux	5	Benzene	78
10	80	5	DMF	82
11	Reflux	5	$CHCl_3$	80

[a]Reagents and conditions: 2-chlorobenzaldehyde **1a** (0.281 g, 2.0 mmol), **2** (0.266 g, 2.0 mmol), **3** (0.232 g, 4 mmol), solvent (10 mL).
[b]Isolated yields.



1 **2** **3** **4**

Scheme 1

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Table 2 Synthetic results of **4a–l** catalysed by iodine in THF[a]

Entry	Ar	Products	Time /h	Yields /%[b]
1	2-ClC_6H_4	**4a**	12	90
2	2-FC_6H_4	**4b**	10	92
3	3-ClC_6H_4	**4c**	13	87
4	3-BrC_6H_4	**4d**	14	83
5	4-FC_6H_4	**4e**	12	88
6	4-ClC_6H_4	**4f**	14	92
7	4-BrC_6H_4	**4g**	14	94
8	4-MeC_6H_4	**4h**	16	88
9	4-$MeOC_6H_4$	**4i**	16	82
10	3,4-$OCH_2OC_6H_3$	**4j**	16	89
11	3,4-$Cl_2C_6H_3$	**4k**	10	90
12	3,4-$Me_2C_6H_3$	**4l**	16	90

[a]Reagents and conditions: **1** (2.0 mmol), **2** (0.266 g, 2.0 mmol), **3** (0.232 g, 4.0 mmol), I_2 (0.1 mmol, 0.026 g), THF (10 mL).
[b]Isolated yields.

Formation of **4** can be considered as an example of the Povarov reaction,[25] which is usually catalysed by various Lewis acids, as documented by Kouznetsov.[26] According to our previous study,[23,24] we suggest that iodine catalyses the reaction as a mild Lewis acid. The mechanism proposed is shown in Scheme 2. In the presence of iodine, acetone is in equilibrium with the enol form **I**.[27] The Schiff base **II** may be formed by the reaction of aromatic aldehyde and 1*H*-indazol-5-amine initially. An imino-Diels–Alder reaction takes place between the iodine-activated Schiff base **III** and enol form **II** to give **IV**. The subsequent dehydration of **IV** results in dihydroquinoline **V**, which is further oxidised by air to give the final aromatised products **4**.

Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Tensor 27 spectrometer in KBr pellet. ^{1}H NMR spectra were obtained from a solution in DMSO-d_6 with Me_4Si as internal standard using a Bruker-400 spectrometer. HRMS analyses were carried out using a Bruker-micro-TOF-Q-MS analyser.

Syntheses of pyrazolo[4,3-f]quinoline derivatives **4a–l***; general procedure*

A dry 50-mL flask was charged with aromatic aldehyde (2.0 mmol), 1*H*-indazol-5-amine (0.266 g, 2.0 mmol), acetone (0.232 g, 4.0 mmol), I_2 (0.026 g, 0.1 mmol) and THF (10 mL). The reaction mixture was stirred at reflux for 10–16 h. After completion of the reaction as indicated by TLC, a little DMF was added to the mixture until all the yellow solid was dissolved. The generated powder was collected by filtration to give **4** when the mixture was cooled to room temperature.

7-(2-Chlorophenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4a**): Pale yellow powder from DMF-THF, m.p. 250–252 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.95 (s, 3H, CH_3), 7.48–7.52 (m, 2H, ArH), 7.60–7.64 (m, 1H, ArH), 7.66–7.69 (m, 1H, ArH), 7.76 (s, 1H, ArH), 7.94–7.99 (m, 2H, ArH), 8.62 (s, 1H, CH), 13.75 (s, 1H, NH). IR (KBr, ν, cm^{-1}): 3193, 3158, 3120, 3002, 2954, 1661, 1576, 1538, 1475, 1442, 1376, 1353, 1334, 1291, 1263, 1179, 1096, 1049, 1010, 940, 875, 845, 792, 756, 730. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}{}^{35}ClN_3$ (M + H$^+$): 294.0798. Found: 294.0811.

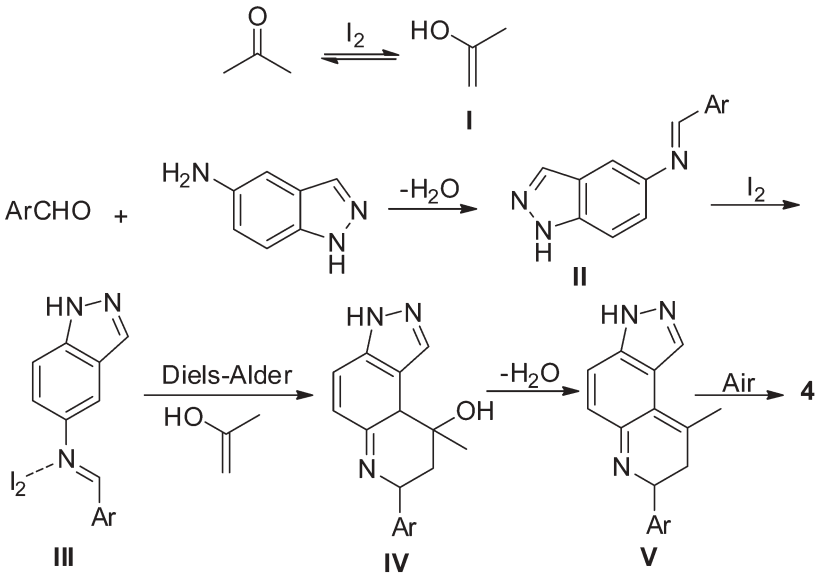
7-(2-Fluorophenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4b**): Pale yellow powder from DMF-THF, m.p. 221–223 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.96 (s, 3H, CH_3), 7.36–7.41 (m, 2H, ArH), 7.51–7.56 (m, 1H, ArH), 7.90 (s, 1H, ArH), 7.95–7.98 (m, 2H, ArH), 8.03–8.07 (m, 1H, ArH), 8.61 (s, 1H, CH), 13.76 (s, 1H, NH). IR (KBr, ν, cm^{-1}): 3199, 3153, 3107, 3000, 2955, 2919, 1619, 1575, 1542, 1494, 1462, 1447, 1376, 1353, 1333, 1213, 1177, 1106, 1086, 942, 875, 839, 820, 787, 756, 734. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}FN_3$ (M + H$^+$): 278.1094. Found: 278.1082.

7-(3-Chlorophenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4c**): White powder from DMF-THF, m.p. 240–242 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.98 (s, 3H, CH_3), 7.52–7.60 (m, 2H, ArH), 7.96–7.80 (m, 2H, ArH), 8.21 (s, 1H, ArH), 8.25 (d, *J* = 7.6 Hz, 1H, ArH), 8.34 (s, 1H, ArH), 8.59 (s, 1H, CH), 13.73 (s, 1H, NH). IR (KBr, ν, cm^{-1}): 3206, 3158, 3116, 3062, 2968, 2918, 1662, 1578, 1568, 1542, 1483, 1448, 1408, 1373, 1350, 1271, 1178, 1097, 1079, 1052, 1009, 946, 908, 840, 808, 735, 692. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}{}^{35}ClN_3$ (M + H$^+$): 294.0798. Found: 294.0800.

7-(3-Bromophenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4d**): White powder from DMF-THF, m.p. 259–261 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.97 (s, 3H, CH_3), 7.50–7.53 (m, 1H, ArH), 7.67 (d, *J* = 8.8 Hz, 1H, ArH). 7.96–8.00 (m, 2H, ArH), 8.21 (s, 1H, ArH), 8.29 (d, *J* = 7.6 Hz, 1H, ArH), 8.48 (s, 1H, ArH), 8.59 (s, 1H, CH), 13.73 (s, 1H, NH). IR (KBr, ν, cm^{-1}): 3198. 3124, 3009, 2954, 1593, 1566, 1540, 1475, 1451, 1377, 1348, 1289, 1175, 1095, 940, 899, 839, 818, 789, 709, 681. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}{}^{79}BrN_3$ (M + H$^+$) 338.0293. Found: 338.0301.

7-(4-Fluorophenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4e**): White powder from DMF-THF, m.p. 258–259 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.96 (s, 3H, CH_3), 7.37 (t, *J* = 8.8 Hz, 2H, ArH), 7.95 (s, 2H, ArH), 8.13 (s, 1H, ArH), 8.30–8.34 (m, 2H, ArH), 8.58 (s, 1H, CH), 13.73 (s, 1H, NH). IR (KBr, ν, cm^{-1}): 3190, 3155, 3123, 3006, 1605, 1573, 1512, 1443, 1411, 1378, 1351, 1290, 1229, 1176, 1158, 1093, 1011, 940, 822, 788, 727. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}FN_3$ (M + H$^+$): 278.1094. Found: 278.1095.

7-(4-Chlorophenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4f**): Pale yellow powder from DMF-THF, m.p. 282–284 °C; ^{1}H NMR



Scheme 2

(DMSO-d_6, δ_H, ppm): 2.97 (s, 3H, CH_3), 7.61 (d, J = 8.4 Hz, 2H, ArH), 7.96 (s, 2H, ArH), 8.17 (s, 1H, ArH), 8.32 (d, J = 8.8 Hz, 2H, ArH), 8.59 (s, 1H, CH), 13.72 (s, 1H, NH). IR (KBr, v, cm^{-1}): 3152, 3116, 3066, 3001, 1581, 1569, 1541, 1493, 1452, 1403, 1375, 1350, 1272, 1174, 1091, 1012, 940, 849, 821, 788, 722. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}{}^{35}ClN_3$ (M + H^+): 294.0798. Found: 294.0814.

7-(4-Bromophenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4g**): Pale yellow powder from DMF-THF, m.p. 295–296 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.97 (s, 3H, CH_3), 7.74 (d, J = 8.4 Hz, 2H, ArH), 7.96 (s, 2H, ArH), 8.17 (s, 1H, ArH), 8.25 (d, J = 8.4 Hz, 2H, ArH), 8.59 (s, 1H, CH), 13.72 (s, 1H, NH). IR (KBr, v, cm^{-1}): 3148, 3105, 2983, 2953, 1579, 1567, 1541, 1490, 1443, 1400, 1349, 1331, 1273, 1174, 1092, 1073, 1008, 941, 848, 820, 788, 721. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}{}^{79}BrN_3$ (M + H^+): 338.0293. Found: 338.0326.

9-Methyl-7-p-tolyl-3H-pyrazolo[4,3-f]quinoline (**4h**): Pale yellow powder from DMF-THF, m.p. 260–261 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.39 (s, 3H, CH_3), 2.96 (s, 3H, CH_3), 7.35 (d, J = 8.0 Hz, 2H, ArH), 7.94 (s, 2H, ArH), 8.10 (s, 1H, ArH), 8.17 (d, J = 8.0 Hz, 2H, ArH), 8.57 (s, 1H, CH), 13.70 (s, 1H, NH). IR (KBr, v, cm^{-1}): 3144, 3097, 3062, 2983, 2866, 1607, 1572, 1543, 1511, 1447, 1376, 1352, 1339, 1271, 1177, 1094, 1012, 980, 933, 824, 792, 730. HRMS (ESI, *m/z*): Calcd for $C_{18}H_{16}N_3$ (M + H^+): 274.1344. Found: 274.1346.

7-(4-Methoxyphenyl)-9-methyl-3H-pyrazolo[4,3-f]quinoline (**4i**): Pale yellow powder from DMF-THF, m.p. 217–218 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.95 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 7.10 (d, J = 8.8 Hz, 2H, ArH), 7.94 (s, 2H, ArH), 8.09 (s, 1H, ArH), 8.23 (d, J = 8.8 Hz, 2H, ArH), 8.59 (s, 1H, CH), 13.69 (s, 1H, NH). IR (KBr, v, cm^{-1}): 3142, 3096, 3096, 2970, 1607, 1571, 1510, 1458, 1417, 1377, 1353, 1306, 1253, 1174, 1135, 1099, 1027, 979, 931, 836, 815, 788, 738. HRMS (ESI, *m/z*): Calcd for $C_{18}H_{16}N_3O$ (M + H^+): 290.1293. Found: 290.1317.

9-Methyl-7-piperonyl-3H-pyrazolo[4,3-f]quinoline (**4j**): Pale yellow powder from DMF-THF, m.p. 247–248 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.95 (s, 3H, CH_3), 6.12 (s, 2H, CH_2), 7.08 (d. J = 8.0 Hz, 1H, ArH), 7.83–7.86 (m, 2H, ArH), 7.93 (s, 2H, ArH), 8.09 (s, 1H, ArH), 8.56 (s, 1H, CH), 13.67 (s, 1H, NH). IR (KBr, v, cm^{-1}): 3151, 3106, 3062, 2994, 1573, 1543, 1503, 1459, 1436, 1344, 1326, 1241, 1211, 1171, 1114, 1042, 942, 872, 858, 818, 769, 725. HRMS (ESI, *m/z*): Calcd for $C_{18}H_{13}N_3O_2$ (M + H^+) 304.1086. Found: 304.1133.

*7-(3,4-Dichlorophenyl)-9-methyl-3H-pyrazolo[4,3-f]quino*line (**4k**): White powder from DMF-THF, m.p. 279–280 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.97 (s, 3H, CH_3), 7.80 (d, J = 8.4 Hz, 1H, ArH), 7.96 (d, J = 5.6 Hz, 2H, ArH), 8.24 (s, 1H, ArH), 8.29 (d, J = 8.8 Hz, 1H, ArH), 8.53 (s, 1H, ArH), 8.59 (s, 1H, CH), 13.74 (s, 1H, NH). IR (KBr, v, cm^{-1}): 3192, 2993, 2959, 2920, 1578, 1560, 1537, 1475, 1456, 1440, 1398. 1373, 1327, 1262, 1178, 1102, 1028, 941, 912, 847, 818, 788, 717. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{12}{}^{35}Cl_2N_3$ (M + H^+): 328.0448. Found: 328.0425.

9-Methyl-7-(3,4-dimethylphenyl)-3H-pyrazolo[4,3-f]quinoline (**4l**): Pale yellow powder from DMF-THF, m.p. 256–258 °C; ^{1}H NMR (DMSO-d_6, δ_H, ppm): 2.30 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.96 (s, 3H, CH_3),7.30 (d, J = 8.0 Hz, 1H, ArH), 7.93 (d, J = 8.8 Hz, 2H, ArH), 7.99 (d, J = 8.0 Hz, 1H, ArH), 8.09 (d, J = 10.8 Hz, 2H, ArH), 8.57 (s, 1H, CH), 13.68 (s, 1H, NH). IR (KBr, v, cm^{-1}): 3146, 2104, 2972, 2917, 1665, 1576, 1536, 1504, 1446, 1376, 1357, 1336, 1267, 1184, 1094, 1009, 927, 875, 827, 786, 726. HRMS (ESI, *m/z*): Calcd for $C_{19}H_{18}N_3$ (M + H^+) 288.1501. Found: 288.1520.

Conclusion

In conclusion, we have developed a mild and efficient method for the synthesis of 7-aryl-9-methyl-3*H*-pyrazolo[4,3-*f*] quinoline derivatives via a three-component reaction of an aromatic aldehyde, 1*H*-indazol-5-amine and acetone catalysed by iodine. The features of this procedure are mild reaction conditions, high yields, operational simplicity and a metal-free catalyst.

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