

Highly efficient synthesis of 7-aryl-pyrano[3,4-*c*]pyrazolo[4,3-*f*]quinoline derivatives catalyzed by iodine

Wei Wang, Yu-Ling Li, and Xiang-Shan Wang *

School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, Jiangsu 221116, P.R. China

E-mail: xswang1974@yahoo.com

Abstract

A mild and efficient method for the synthesis of 7-arylpyrano[3,4-*c*]pyrazolo[3,4-*f*]quinoline derivatives via a three-component reaction of aromatic aldehyde, 1*H*-Indazol-5-amine and tetrahydropyran-4-one catalyzed by iodine is described. This new procedure has the advantages of mild reaction condition, high yields, one-pot and metal-free catalyst.

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

Introduction

Pyranoquinoline derivatives are found to possess a wide spectrum of biological activities, such as psychotropic, anti-allergenic, anti-inflammatory and estrogenic activities.¹ Pyrazoloquinoline derivatives are also an important class of heterocycles due to their promising materials for optoelectronic applications.² In addition, they are reported to possess anti-leishmanial and antimicrobial activities.³ Some of them are used as modulators of cytokine biosynthesis for treatment of viral and neoplastic diseases,⁴ and immuno modulators for inducing cytokine biosynthesis in animals.⁵

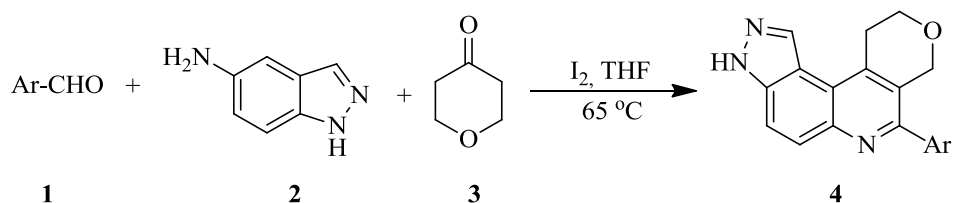
Although a number of useful synthetic procedures to prepare pyranoquinoline⁶ and pyrazoloquinoline⁷ derivatives have been developed, to the best of our knowledge, there is no literature about the synthesis of fused heterocycle containing both pyran, pyrazole and quinoline rings, this novel skeleton may possess potential bioactive for screening. Thus, simple and efficient method to synthesize pyranopyrazoloquinolines would be attractive,

Over the past few years, molecular iodine (I₂) has emerged as a powerful catalyst for various organic transformations due to several advantages such as its inexpensive, nontoxic, and eco-friendly nature.⁸ As a continuation of our research devoted to the development of new methods for the preparation of heterocycles via multi-component reactions catalyzed by iodine,⁹ herein,

we would like to report the synthesis of 7-aryl-pyrano[3,4-*c*]pyrazolo[3,4-*f*]quinoline derivatives by a reaction of aromatic aldehyde, 1*H*-indazol-5-amine and tetrahydropyran-4-one in THF catalyzed by iodine.

Results and Discussion

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



Scheme 1. The reaction of **1a-1**, **2** and cyclopentanone **3**.

Table 1. Synthetic results of **4a** under different reaction conditions^a

Entry	Temp. (°C)	Cat. (mol %)	Solvent	Time (h)	Yields (%) ^b
1	r.t.	-	THF	24	0
2	Reflux	-	THF	24	0
3	r.t.	I ₂ (5)	THF	24	trace
4	50	I ₂ (5)	THF	24	84
5	Reflux	I ₂ (5)	THF	12	93
6	Reflux	I ₂ (10)	THF	12	92
7	Reflux	I ₂ (20)	THF	12	93
8	Reflux	I ₂ (5)	CH ₃ CN	12	82
9	Reflux	I ₂ (5)	Benzene	10	78
10	80	I ₂ (5)	DMF	10	85
11	Reflux	I ₂ (5)	CHCl ₃	12	77
12	Reflux	TsOH(5)	THF	10	78
13	Reflux	ZnCl ₂ (5)	THF	18	0
14	Reflux	Yb(OTf) ₃ (5)	THF	12	69
15	Reflux	Sc(OTf) ₃ (5)	THF	10	82

^a Reagents and conditions: 2-chlorobenzaldehyde **1a** (0.281 g, 2.0 mmol), **2** (0.266 g, 2.0 mmol), **3** (0.200 g, 2.0 mmol), solvent (10 mL). ^b Isolated yields.

Using the conversion of 2-chlorobenzaldehyde **1a**, **2** and **3** as a model, several parameters were explored as shown in Table 1. The **4a** was not detected by TLC at room temperature and reflux in the absence of iodine (Table 1, Entries 1 and 2), and much greater in the presence of various quantities of the catalyst (I_2), reaching a maximum of 93 % yield with 5 mol% iodine (Table 1, entries 5-7). The yield of **4a** was also dependent on temperature (entries 3~5), proceeding smoothly at reflux in high yield. Different solvents were also tested, and THF appeared to be the best medium for this transformation (entry 5 vs. 8-11). In addition, other Lewis acids, such as TsOH, $ZnCl_2$, $Yb(OTf)_3$ and $Sc(OTf)_3$, were selected as catalysts to this reaction in 5 mol%, they all gave slightly lower yields.

These optimized conditions were applied to the conversion of various kinds of aromatic aldehydes **1a-l** into the corresponding 7-aryl-pyrano[3,4-*c*]pyrazolo[3,4-*f*]quinoline analogues **4a-l**. Reactions using aldehydes containing electron-withdrawing groups (such as halide) or electron-donating groups (such as alkyl and alkoxy group) all proceeded smoothly within a few hours, giving **4a-l** in high yields. It should be noted that only 7-aryl-pyrano[3,4-*c*]pyrazolo[3,4-*f*]quinolines were obtained in high region-chemistry. The best reason is that the 4-position is not only the *ortho*-position to amino group, but also the α -position of the benzene ring in 1*H*-indazol-5-amine, which is more active than 6-position.

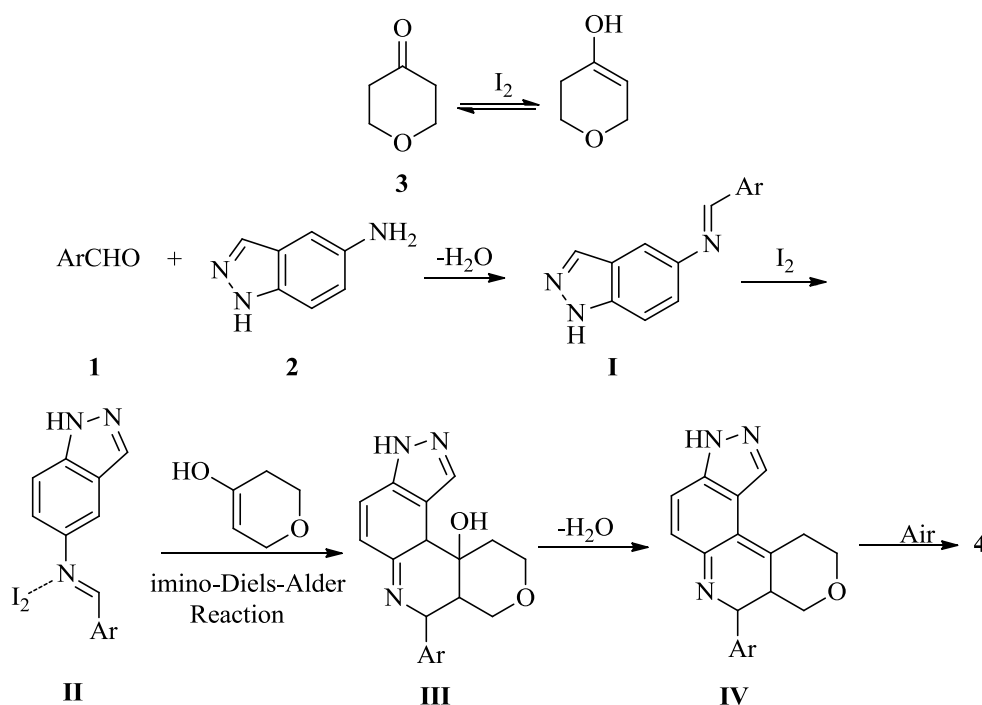
Table 2. Synthetic results of **4a-l** catalyzed by iodine ^a

Entry	Ar	time (h)	products	yields (%) ^b
1	2-ClC ₆ H ₄	12	4a	93
2	4-ClC ₆ H ₄	14	4b	90
3	4-BrC ₆ H ₄	14	4c	92
4	4-MeOC ₆ H ₄	18	4d	87
5	4-MeC ₆ H ₄	14	4e	83
6	3-ClC ₆ H ₄	14	4f	90
7	4-FC ₆ H ₄	10	4g	88
8	3,4-Cl ₂ C ₆ H ₃	12	4h	89
9	3-BrC ₆ H ₄	14	4i	90
10	3,4-(MeO) ₂ C ₆ H ₃	16	4j	84
11	3,4-Me ₂ C ₆ H ₃	18	4k	87
12	Piperonyl	16	4l	90

^a Reagents and conditions: benzaldehyde **1a-l** (2.0 mmol), **2** (0.266 g, 2.0 mmol), **3** (0.200 g, 2.0 mmol), THF (10 mL). ^b Isolated yields.

According to the literatures,¹⁰ we think that iodine catalyzes the reaction as a mild Lewis acid. The mechanism was tentatively proposed as shown in Scheme 2. In the presence of iodine, tetrahydropyran-4-one is in equilibrium with its enol form.^{10b} The Schiff base **I** may be formed by the reaction of aromatic aldehyde and 1*H*-indazol-5-amine firstly. And then imino-Diels-

Alder reaction between the iodine-activated Schiff base **II** and enol takes place selectively to form the intermediate **III** for its stability. The dehydration of **III** results in dihydro pyrano[3,4-*c*]pyrazolo[3,4-*f*]quinoline **IV**, which is further oxidized by air to afford aromatized final products **4**.



Scheme 2. The possible mechanism for the formation of products **4**.

Conclusions

In conclusion, we found a mild and efficient method for the synthesis of 7-aryl-pyrano[3,4-*c*]pyrazolo[3,4-*f*]quinoline derivatives via three-component reactions of aromatic aldehyde, 1*H*-indazol-5-amine and tetrahydropyran-4-one catalyzed by iodine. The features of this procedure are mild reaction conditions, high yields, operational simplicity, one-pot and metal-free catalyst.

Experimental Section

General. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Tensor 27 spectrometer in KBr pellet. 1H NMR spectra and ^{13}C NMR was obtained from a solution in $CDCl_3$ or $DMSO-d_6$ with Me_4Si as internal standard using a Bruker-400 spectrometer. HRMS analyses were carried out using a Bruker-micro-TOF-Q-MS analyzer.

General procedure for the syntheses of 7-aryl-pyrano[3,4-*c*]pyrazolo[3,4-*f*]quinoline derivatives 4a-l

A dry 50 mL flask was charged with aromatic aldehyde (2.0 mmol), 1*H*-indazol-5-amine (0.266 g, 2.0 mmol), tetrahydropyran-4-one (0.200 g, 2.0 mmol), I₂ (0.026 g, 0.1 mmol) and THF (10 mL). The reaction mixture was stirred at reflux for 10-18 h. After completion of the reaction as indicated by TLC, a little DMF was added to the mixture until the yellow precipitate was dissolved. The generated crystals were collected by filtration to give **4** when the mixture was cooled to room temperature.

7-(2-Chlorophenyl)-3,8,10,11-tetrahydropyrano[3,4-*c*]pyrazolo[4,3-*f*]quinoline (4a). Mp 281-283 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ_H 3.43~3.46 (m, 2H, CH₂), 4.01~4.13 (m, 2H, CH₂), 4.51 (s, 2H, CH₂), 7.45~7.56 (m, 3H, ArH), 7.63 (d, *J* 7.6 Hz, 1H, ArH), 7.88 (d, *J* 9.2 Hz, 1H, ArH), 7.95 (d, *J* 8.8 Hz, 1H, ArH), 8.61 (s, 1H, CH), 13.76 (s, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ_C 28.4, 64.3, 65.9, 113.2, 115.2, 116.3, 121.7, 127.8, 128.0, 129.4, 129.9, 130.8, 132.0, 135.9, 138.2, 138.7, 139.3, 144.0, 151.8. IR (KBr): ν 3207, 3150, 3113, 3054, 2892, 1662, 1608, 1574, 1531, 1478, 1435, 1368, 1321, 1234, 1180, 1162, 1079, 1051, 980, 886, 844, 790, 708 cm⁻¹. HRMS (ESI, *m/z*): Calcd for C₁₉H₁₅ClN₃O [M+H]⁺ 336.0904, found 336.0928.

7-(4-Chlorophenyl)-3,8,10,11-tetrahydropyrano[3,4-*c*]pyrazolo[4,3-*f*]quinoline (4b). Mp > 300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ_H 3.43 (s, 2H, CH₂), 4.15~4.18 (m, 2H, CH₂), 4.80 (s, 2H, CH₂), 7.57 (d, *J* 8.4 Hz, 2H, ArH), 7.64 (d, *J* 8.4 Hz, 2H, ArH), 7.88~7.96 (m, 2H, ArH), 8.59 (s, 1H, CH), 13.72 (s, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz): 28.2, 63.9, 66.3, 114.7, 115.7, 120.8, 127.1, 128.3, 129.0, 130.7, 133.2, 135.5, 138.0, 138.2, 139.1, 143.6, 152.0. IR (KBr): ν 3195, 3156, 3105, 3047, 2880, 1588, 1564, 1529, 1493, 1431, 1400, 1353, 1323, 1241, 1119, 1093, 1017, 978, 952, 886, 823, 790, 739 cm⁻¹. HRMS (ESI, *m/z*): Calcd for C₁₉H₁₅ClN₃O [M+H]⁺ 336.0904, found 336.0897.

7-(4-Bromophenyl)-3,8,10,11-tetrahydropyrano[3,4-*c*]pyrazolo[4,3-*f*]quinoline (4c). Mp > 300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ_H 3.42 (s, 2H, CH₂), 4.16 (t, *J* 5.2 Hz, 2H, CH₂), 4.81 (s, 2H, CH₂), 7.57 (d, *J* 8.0 Hz, 2H, ArH), 7.72 (d, *J* 8.0 Hz, 2H, ArH), 7.90~7.95 (m, 2H, ArH), 8.60 (s, 1H, CH), 13.74 (s, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ_C 28.7, 64.4, 66.8, 101.4, 115.3, 116.2, 122.4, 127.6, 129.5, 131.5, 131.7, 135.96, 136.03, 138.9, 139.7, 144.2, 153.6. IR (KBr): ν 3190, 3153, 3103, 3047, 2887, 1665, 1587, 1528, 1489, 1395, 1353, 1322, 1240, 1136, 1100, 1072, 1012, 977, 952, 866, 849, 821, 790, 737 cm⁻¹. HRMS (ESI, *m/z*): Calcd for C₁₉H₁₅BrN₃O [M+H]⁺ 380.0398, found 380.0394.

7-(4-Methoxyphenyl)-3,8,10,11-tetrahydropyrano[3,4-*c*]pyrazolo[4,3-*f*]quinoline (4d). Mp 267-269 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ_H 3.42 (s, 2H, CH₂), 3.84 (s, 3H, OCH₃), 4.15~4.18 (m, 2H, CH₂), 4.81 (s, 2H, CH₂), 7.06 (d, *J* 8.8 Hz, 2H, ArH), 7.55 (d, *J* 8.8 Hz, 2H, ArH), 7.87~7.93 (m, 2H, ArH), 8.58 (s, 1H, CH), 13.71 (s, 1H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ_C 28.2, 55.1, 63.9, 66.6, 113.5, 114.5, 115.8, 120.4, 127.1, 129.1, 130.2, 131.6, 135.4, 138.1, 138.8, 143.7, 153.1, 159.3. IR (KBr): ν 3251, 2930, 2860, 1608, 1590, 1561, 1509, 1460, 1441, 1348, 1322, 1242, 1181, 1119, 1079, 1033, 988, 949, 889, 832, 816, 801, 787, 733 cm⁻¹. HRMS (ESI, *m/z*): Calcd for C₂₀H₁₈N₃O₂ [M+H]⁺ 332.1399, found 332.1414.

7-(4-Methylphenyl)-3,8,10,11-tetrahydropyrano[3,4-c]pyrazolo[4,3-f]quinoline (4e). Mp 281~283 °C; ^1H NMR (DMSO- d_6 , 400 MHz): δ_{H} 2.40 (s, 3H, CH₃), 3.42 (s, 2H, CH₂), 4.15~4.17 (m, 2H, CH₂), 4.79 (s, 2H, CH₂), 7.32 (d, J 8.0 Hz, 2H, ArH), 7.49 (d, J 7.2 Hz, 2H, ArH), 7.87~7.96 (m, 2H, ArH), 8.58 (s, 1H, CH), 13.72 (s, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ_{C} 20.8, 28.2, 63.9, 66.5, 114.5, 115.8, 120.6, 127.1, 128.66, 128.75, 129.1, 135.4, 136.5, 137.7, 138.1, 138.8, 143.7, 153.4. IR (KBr): ν 3187, 3131, 3093, 3037, 2980, 1670, 1592, 1561, 1530, 1510, 1451, 1428, 1384, 1365, 1349, 1322, 1237, 1160, 1099, 1034, 984, 938, 889, 826, 791, 741 cm^{-1} . HRMS (ESI, m/z): Calcd for C₂₀H₁₈N₃O [M+H]⁺ 316.1450, found 316.1464.

7-(3-Chlorophenyl)-3,8,10,11-tetrahydropyrano[3,4-c]pyrazolo[4,3-f]quinoline (4f). Mp 277~279 °C; ^1H NMR (DMSO- d_6 , 400 MHz): δ_{H} 3.42 (s, 2H, CH₂), 4.15~4.18 (m, 2H, CH₂), 4.79 (s, 2H, CH₂), 7.56 (s, 3H, ArH), 7.67 (s, 1H, ArH), 7.88~7.95 (m, 2H, ArH), 8.59 (s, 1H, CH), 13.75 (s, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ_{C} 28.6, 64.3, 66.7, 115.3, 116.2, 121.5, 127.6, 127.9, 128.8, 129.1, 129.5, 130.6, 133.5, 136.0, 138.7, 139.7, 141.7, 144.1, 152.2. IR (KBr): ν 3272, 3163, 3038, 2958, 2852, 1669, 1595, 1556, 1531, 1475, 1417, 1357, 1320, 1298, 1237, 1094, 1033, 979, 946, 885, 836, 823, 789, 721, 706 cm^{-1} . HRMS (ESI, m/z): Calcd for C₁₉H₁₅ClN₃O [M+H]⁺ 336.0904, found 336.0924.

7-(4-Fluorophenyl)-3,8,10,11-tetrahydropyrano[3,4-c]pyrazolo[4,3-f]quinoline (4g). Mp > 300 °C; ^1H NMR (DMSO- d_6 , 400 MHz): δ_{H} 3.42 (s, 2H, CH₂), 4.15~4.17 (m, 2H, CH₂), 4.79 (s, 2H, CH₂), 7.34 (t, J 8.8 Hz, 2H, ArH), 7.64~7.67 (m, 2H, ArH), 7.87~7.94 (m, 2H, ArH), 8.59 (s, 1H, CH), 13.74 (s, 1H, NH). IR (KBr): ν 3191, 3157, 3108, 3053, 2942, 2879, 1665, 1603, 1588, 1531, 1510, 1434, 1351, 1322, 1217, 1182, 1156, 1100, 1036, 979, 953, 885, 845, 789, 740 cm^{-1} . HRMS (ESI, m/z): Calcd for C₁₉H₁₅FN₃O [M+H]⁺ 320.1199, found 320.1205.

7-(3,4-Dichlorophenyl)-3,8,10,11-tetrahydropyrano[3,4-c]pyrazolo[4,3-f]quinoline (4h). Mp > 300 °C; ^1H NMR (DMSO- d_6 , 400 MHz): δ_{H} 3.44 (s, 2H, CH₂), 4.17 (t, J 4.2 Hz, 2H, CH₂), 4.84 (s, 2H, CH₂), 7.62 (d, J 8.8 Hz, 1H, ArH), 7.80 (d, J 8.4 Hz, 1H, ArH), 7.89~7.96 (m, 3H, ArH), 8.61 (s, 1H, CH), 13.77 (s, 1H, NH). IR (KBr): ν 3187, 3147, 3101, 2992, 2951, 2877, 1670, 1585, 1526, 1471, 1434, 1391, 1349, 1312, 1280, 1241, 1118, 1140, 1105, 1033, 978, 952, 884, 847, 820, 788, 747, 705 cm^{-1} . HRMS (ESI, m/z): Calcd for C₁₉H₁₄Cl₂N₃O [M+H]⁺ 370.0514, found 370.0515.

7-(3-Bromophenyl)-3,8,10,11-tetrahydropyrano[3,4-c]pyrazolo[4,3-f]quinoline (4i). Mp 288~290 °C; ^1H NMR (DMSO- d_6 , 400 MHz): δ_{H} 3.42 (s, 2H, CH₂), 4.17 (t, J 9.6 Hz, 2H, CH₂), 4.81 (s, 2H, CH₂), 7.48 (t, J 8.0 Hz, 1H, ArH), 7.61 (d, J 8.0 Hz, 1H, ArH), 7.70 (d, J 8.0 Hz, 1H, ArH), 7.80 (s, 1H, ArH), 7.89~7.96 (m, 2H, ArH), 8.60 (s, 1H, CH), 13.75 (s, 1H, NH). IR (KBr): ν 3193, 3152, 3104, 3050, 2953, 2874, 1664, 1587, 558, 1528, 1475, 1431, 1348, 1318, 1238, 1180, 1119, 1101, 1073, 979, 952, 86, 843, 788, 736, 707 cm^{-1} . HRMS (ESI, m/z): Calcd for C₁₉H₁₅BrN₃O [M+H]⁺ 380.0398, found 380.0401.

7-(3,4-Dimethoxyphenyl)-3,8,10,11-tetrahydropyrano[3,4-c]pyrazolo[4,3-f]quinoline (4j). Mp 239~241 °C; ^1H NMR (DMSO- d_6 , 400 MHz): δ_{H} 3.17~3.26 (m, 1H, CH), 3.72 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.92 (d, J 11.2 Hz, 1H, CH), 4.27~4.39 (m, 2H, CH₂), 5.99 (s, 1H, CH), 6.39 (s, 1H, CH), 6.84 (d, J 8.8 Hz, 1H, ArH), 6.91~6.92 (m, 2H, ArH), 7.08 (s, 1H, ArH),

7.24 (d, J 8.8 Hz, 1H, ArH), 8.18 (s, 1H, CH), 12.86 (s, 1H, NH). IR (KBr): ν 3351, 3262, 2987, 2966, 2869, 2828, 1634, 1591, 1515, 1491, 1460, 1420, 1387, 1372, 1334, 1271, 1232, 1144, 1024, 943, 888, 825, 805, 692 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ 362.1505, found 362.1527

7-(3,4-Dimethylphenyl)-3,8,10,11-tetrahydropyrano[3,4-*c*]pyrazolo[4,3-*f*]quinoline (4k). M.p > 300 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO-}d_6$, 400 MHz): δ_{H} 2.31 (s, 6H, 2 CH_3), 3.41 (s, 2H, CH_2), 4.15 (t, J 5.6 Hz, 2H, CH_2), 4.79 (s, 2H, CH_2), 7.25~7.31 (m, 2H, ArH), 7.37 (s, 1H, ArH), 7.86~7.93 (m, 2H, ArH), 8.58 (s, 1H, CH), 13.72 (s, 1H, NH). IR (KBr): ν 3187, 3131, 3094, 3036, 2934, 2870, 1670, 1592, 1561, 1529, 1452, 1426, 1383, 1351, 1320, 1237, 1159, 1099, 1032, 983, 939, 918, 887, 825, 793, 735, 719 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 330.1606, found 330.1627.

7-Piperonyl-3,8,10,11-tetrahydropyrano[3,4-*c*]pyrazolo[4,3-*f*]quinoline (4l). Mp 289~290 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO-}d_6$, 400 MHz): δ_{H} 3.41 (s, 2H, CH_2), 4.16 (t, J 5.6 Hz, 2H, CH_2), 4.81 (s, 2H, CH_2), 6.12 (s, 2H, CH_2), 7.03~7.07 (m, 2H, ArH), 7.18 (s, 1H, ArH), 7.86~7.96 (m, 2H, ArH), 8.57 (s, 1H, CH), 13.72 (s, 1H, NH). IR (KBr): ν 3191, 3159, 3107, 3050, 2932, 2872, 1606, 1588, 1571, 1530, 1500, 1438, 1377, 1351, 1327, 1254, 1233, 1180, 1125, 1088, 1039, 979, 953, 915, 883, 856, 816, 739, 725 cm^{-1} . HRMS (ESI, m/z): Calcd for $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 346.1192, found 346.1218.

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