A Facile Synthesis of Furo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5(7*H*)-one Derivatives via Three-Component Reaction in Ionic Liquid without Any Catalyst

Da-Qing Shi,[a,b]* Fang Yang,[b] and Sai-Nan Ni[b]

[a]College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215123, People's Republic of China
[b]College of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou 221116, People's of Republic of China
*E-mail: dqshi@suda.edu.cn
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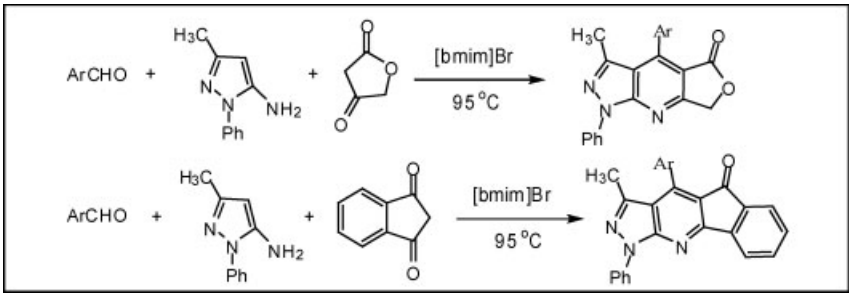

A series of furo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5(7*H*)-one and indeno[2,1-*e*]pyrazolo[3,4-*b*]pyridine-5(1*H*)-one derivatives were synthesized via the three-component reaction of an aldehyde, 5-aminopyrazole and either tetronic acid or 1,3-indanedione in ionic liquid without any catalyst. The structures of the products have been established by spectroscopic data and further confirmed by X-ray diffraction analysis. This method has the advantages of easier work-up, mild reaction conditions, high yields and an environmentally benign procedure.

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INTRODUCTION

Multicomponent reactions (MCRs) are of increasing importance in organic and medical chemistry. The first MCR was described by Strecker in 1850 for the synthesis of amino acids [1]. However, in the past decade there have tremendous developments in three- and four-component reactions and great efforts continue to be made to develop new MCRs [2]. Recently, there has been considerable interest in the use of ionic liquids as an environmentally benign reaction media because of its unique properties such as a wide liquid range, good solvating ability, tunable polarity, high-thermal stability, negligible vapor pressure, and ease of recyclablity [3]. Numerous chemical reactions, such as polymerization [4], hydrogenation [5], regioselective alkylation [6], Friedel–Crafts reactions [7], dimerization of alkenes [8], Diels–Alder reactions [9], Michael reactions [10], cross-coupling reactions [11], and some enzymic reactions [12] can be carried out in ionic liquids. Recently, some MCRs in ionic liquids have been reported [13].

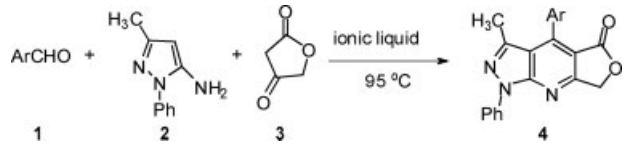
Furopyridines is one of the ''privileged medicinal scaffolds'' which are used for the development of pharmaceutical agents of various applications. Compounds with this motif show a wide range of pharmacological activities such as antipsychotic [14], antiproliferative [15], anticonvulsant [16], antianaphylactic [17], and anthelmintic [18] activities and can be used as calcium influx promoters [19], HIV-1 non-nucleoside reverse transcriptase inhibitors [20], and acetylcholinesterase inhibitors [21]. Pyrazole derivatives have been reported in the literature to be versatile building blocks for the synthesis of a wide range of the heterocyclic motifs, such as pyrazolopyridines [22], pyrazoloquinolines [23], and pyrzolopyrazoles [24]. The pyrazolo[3,4-*b*]pyridine system has interesting biological and pharmacological properties [25], such as adrenocorticotropic hormone (ACTH)-releasing factor antagonist activity [26].

Furopyridines and pyrazolo[3,4-*b*]pyridines have been reported widely in the literature. However, the synthesis of the compounds with both pyrazolo[3,4-*b*]pyridine and furo[3,4-*b*]pyridine motifs was neglected. We herein described a facile three-component reaction consisting of aldehyde **1**, 5-amino-3-methyl-1-phenylpyrazole **2**, and tetronic acid **3** in ionic liquid to synthesize the furo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5(7*H*)-one derivatives **4** (Scheme 1).

RESULTS AND DISCUSSION

Choosing an appropriate solvent is of crucial importance for the successful organic synthesis. To search for

Scheme 1



the optimal solvent, the three-component reaction of 4-bromobenzaldehyde **1a**, 5-amino-3-methyl-1-phenylpyrazole **2**, and tetronic acid **3** was examined using ionic liquid such as [bmim]Br, [bmim]BF_4, [pmim]Br, water, glacial acetic acid, acetone, and ethanol as solvent, respectively, at different temperature for the synthesis of **4a**.

It can be seen from Table 1 that the reactions using ionic liquids as the solvent resulted in higher yields and shorter reaction times than those using organic solvents. Using water can also give the higher yields, but the reaction time is very long. On the basis of the obtained results, [bmim]Br was found to be superior in terms of cheap and yield. Under these optimized reaction conditions, a series of furo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5(7*H*)-one derivatives **4** were synthesized. The results are summarized in Table 2. The products were different from those in ethanol in the presences of L-proline [27]. The structures of the products may be affected by catalyst and solvents.

To expand the scope of the present method, the replacement of tetronic acid **3** with 1,3-indanedione **5** was examined. This is particularly attractive because compounds with indenopyridine motifs show a wide range of biological activities such as calcium antagonistic [28], antioxidant [29], antihistamine and antidepressant [30], and also act as phosphodiesterase inhibitors

Table 1

Solvent optimization for the synthesis of **4a**.[a]

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	[bmim]Br	95	2	98
2	[bmim]BF_4	95	2	94
3	[pmim]Br	95	2	93
4	H_2O/TEBAC	95	20	97
5	AcOH	95	4	92
6	CH_3COCH_3	Reflux	7	75
7	EtOH	Reflux	4	80

[a] 4-Bromobenzaldehyde (2 mmol), 5-amino-3-methyl-1-phenylpyrazole (2 mmol), tetronic acid (2 mmol), and 2 mL solvent.

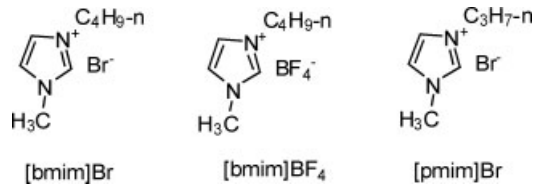


Table 2

The synthesis of **4** in [bmim]Br.

Entry	Ar	Time (h)	Yield (%)
4a	4-BrC_6H_4	2	98
4b	4-$CH_3OC_6H_4$	2	92
4c	4-FC_6H_4	2	88
4d	4-ClC_6H_4	2	96
4e	4-$NO_2C_6H_4$	3	87
4f	4-HOC_6H_4	3	92
4g	4-$(CH_3)_2NC_6H_4$	3	75
4h	3-$NO_2C_6H_4$	4	86
4i	2,4-$Cl_2C_6H_3$	3	95
4j	3,4-$(CH_3)_2C_6H_3$	2	91
4k	3,4-$(CH_3O)_2C_6H_3$	2	91
4l	2-NO_2-5-ClC_6H_3	3	95
4m	3,4-$OCH_2OC_6H_3$	3	85
4n	Thiophen-2-yl	5	80
4o	Pyridin-3-yl	5	62
4p	Pyridin-4-yl	5	72

[31], NK-1, and dopamine receptor ligands [32]. To our delight, under the earlier-optimized conditions, the reactions proceeded smoothly. A series of indeno[2,1-*e*]pyrazolo[3,4-*b*] pyridine-5(1*H*)-one derivatives **6** were obtained (Scheme 2) in excellent yields. The products were agreed with those in ethanol [27] or DMF [33]. The results are summarized in Table 3.

As shown in Tables 2 and 3, this method can be applied not only to the aromatic aldehydes with either electron-withdrawing groups (such as nitro and halide groups) or electron-donating groups (such as hydroxyl and alkoxyl groups), but also to heterocyclic aldehydes with excellent yields under same conditions. Therefore, we concluded that the electronic nature of the substituents has no significant effect on this reaction.

Apart from the mild conditions of the process and its excellent results, the simplicity of product isolation and the possibility to recycle the [bmim]Br offer a significant advantage. Because [bmim]Br is miscible with water and the desired products are insoluble in water, the products can be directly separated by adding water into the synthetic system after the reaction is complete. The remaining [bmim]Br can then be recycled after removal of water under vacuum. Studies using **1a**, **2**, and **3** as model substrates showed that the recovered ionic liquid could be successively recycled in subsequent reactions without almost any decrease in its efficiency (Table 4). An overall process for the one-pot synthesis

Scheme 2

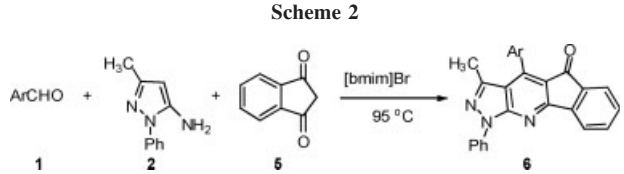


Table 3

The synthesis of **6** in [bmim]Br.

Entry	Ar	Time (°C)	Yield (%)
6a	4-$CH_3C_6H_4$	4	91
6b	4-$CH_3OC_6H_4$	2	90
6c	4-FC_6H_4	2	94
6d	4-ClC_6H_4	2	95
6e	4-BrC_6H_4	2	96
6f	4-$NO_2C_6H_4$	2	91
6g	4-HOC_6H_4	3	90
6h	3-$NO_2C_6H_4$	3	89
6i	3-ClC_6H_4	3	88
6j	4-$(CH_3)_2NC_6H_4$	4	92
6k	2,4-$Cl_2C_6H_3$	3	85
6l	3,4-$(CH_3)_2C_6H_3$	3	92
6m	3,4-$(CH_3O)_2C_6H_3$	3	90
6n	3,4-$OCH_2OC_6H_3$	3	93
6o	3,4-$Cl_2C_6H_3$	3	87
6p	Thiophen-2-yl	4	80
6q	Pyridin-4-yl	5	79

of furo[3,4-*e*]pyrazolo [3,4-*b*]pyridine-5(7*H*)-one derivatives can be envisaged as shown in Figure 1.

All the products **4** and **6** were characterized by mp, IR, and ^{1}H NMR spectra as well as HRMS. The structure of **4l** was further confirmed by X-ray diffraction analysis [34]. The molecular structure **4l** is shown in Figure 2.

Although the detailed mechanism of the above reaction remains to be fully clarified the formation of furo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5(7*H*)-one derivatives **4** could be explained by a reaction sequence presented in Scheme 3. We proposed that the reaction proceeded via a reaction sequence of condensation, addition, cyclization, dehydration, and aromatization. First, the condensation of aldehyde **1** and tetronic acid **3** gave the intermediate product **7**. The addition of **7** to 5-amino-3-methyl-1-phenylpyrazole **2** then furnished the intermediate product **9**, which on intermolecular cyclization and dehydration gave rise to **11**. In the last step, the intermediate product **11** aromatized to product **4**.

Evidence supporting this proposed mechanism came from the observation that when **7a** and **2** were treated under same conditions, the expected product **4a** was obtained in a yield similar to that obtained in the one-pot reaction (Scheme 4).

In conclusion, we have developed a simple three-component reaction of an aldehyde, 5-amino-3-methyl-1-phenylpyrazole and either tetronic acid or 1,3-indanedione for the synthesis of furo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5(7*H*)-one and indeno[2,1-*e*]pyrazolo[3,4-*b*]pyridine-5(1*H*)-one derivatives in ionic liquid without any catalyst. This method has the advantages of good yields, convenient procedure, and environmentally friendly reaction conditions.

Table 4

Studies on the reuse of [bmim]Br in the preparation of **4a**.

Round	1	2	3	4	5	6
Yield (%)	97	98	97	97	96	97

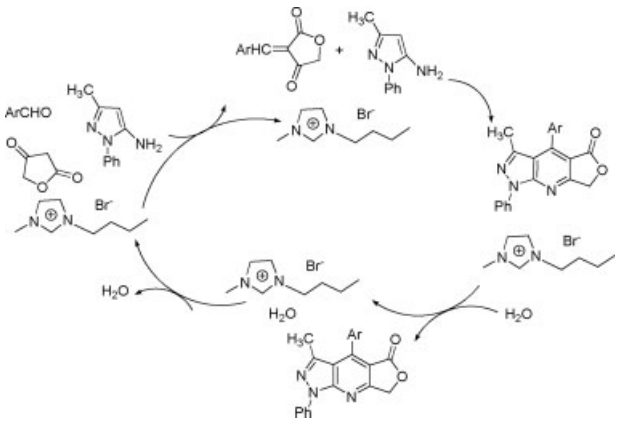


Figure 1. Reaction-isolation-recycle process for the one-pot synthesis of 4 in [bmim]Br.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded on a Tensor 27 spectrometer in KBr with absorption in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a

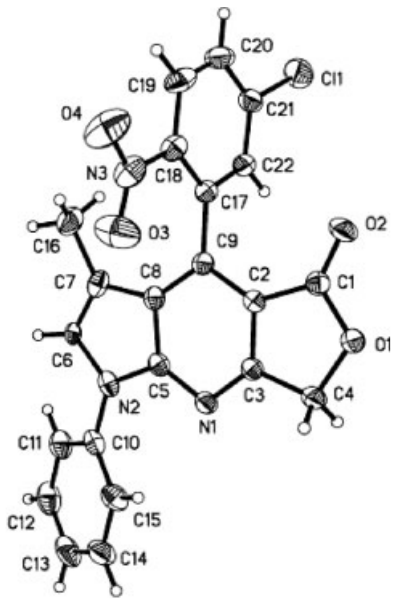
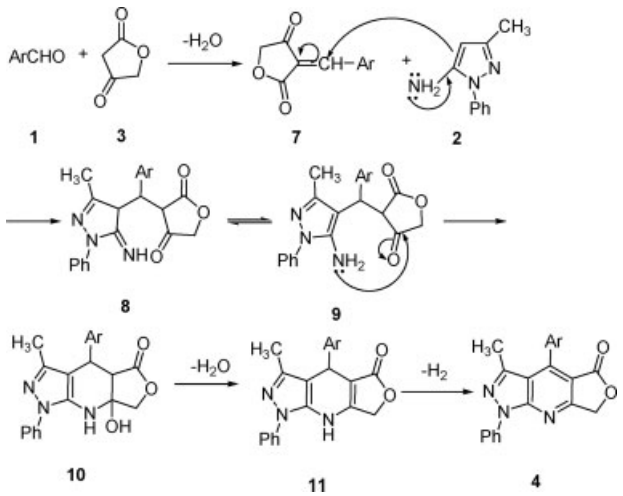


Figure 2. The structure of 4l showing 40% probability displacement ellipsoids.

Scheme 3



Bruker DPX 400-MHz or Inova 300-MHz spectrometer as DMSO-d_6 solution. J values are in hertz (Hz). Chemical shifts are expressed in δ downfield from internal tetramethylsilane. HRMS were obtained using TOF-MS instrument. X-ray crystallographic analysis was performed with a Smart-1000 CCD diffractometer.

General procedure for the synthesis of furo[3,4-*e*]pyrazolo[3,4-*b*]pyridine-5(7*H*)-one derivatives 4 and indeno[2,1-*e*]pyrazolo[3,4-*b*]pyridine-5(1*H*)-one derivatives 6 in ionic liquid. Aldehyde 1 (2 mmol), 5-amino-3-methyl-1-phenylpyrazole 2 (2 mmol), tetronic acid 3 or 1,3-indanedione 5 (2 mmol) were added to a 10 mL round bottom flask containing 2 mL [bmim]Br. The mixture was then stirred at 95°C for given times. After completion of the reaction, the reaction mixture was added with 5 mL water. The precipitate was collected by suction and purified by recrystallization from EtOH to give products 4 or 6. The filtrate was concentrated under reduced pressure and dried at 100°C to recover the ionic liquid for subsequent use.

4-(4-Bromophenyl)-3-methyl-1-phenyl-1H-furo[3,4-e]-pyrazolo[3,4-b]pyridine-5(7H)-one (4a). This compound was obtained as solid with mp 226–227°C; IR (potassium bromide): 3058, 2965, 2929, 1764, 1578, 1557, 1505, 1439, 1386, 1356, 1313, 1210, 1140, 1070, 1048, 1027, 1011, 847, 821, 798, 759, 720 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.13 (s, 3H, CH_3), 5.51 (s, 2H, CH_2), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.55 (d, J = 8.4 Hz, 2H, ArH), 7.62 (t, J = 7.6 Hz, 2H, ArH), 7.79 (d, J = 8.0 Hz, 2H, ArH), 8.19 (d, J = 8.8 Hz, 2H, ArH). HRMS [Found: m/z 421.0236 (M^+); Calcd for $C_{21}H_{14}{}^{79}BrN_3O_2$: M 421.0249].

3-Methyl-4-(4-methoxyphenyl)-1-phenyl-1H-furo[3,4-e] pyrazolo[3,4-b]pyridine-5(7H)-one (4b). This compound was obtained as solid with mp 190–192°C; IR (potassium bromide): 3046, 2971, 2924, 1765, 1608, 1579, 1561, 1509, 1458, 1445, 1426, 1384, 1358, 1309, 1294, 1259, 1208, 1176, 1140, 1071, 1048, 1036, 1019, 824, 797, 758, 692 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.16 (s, 3H, CH_3), 3.88 (s, 3H, CH_3O), 5.47 (s, 2H, CH_2), 7.13 (d, J = 8.4 Hz, 2H, ArH), 7.40 (t, J = 7.2 Hz, 1H, ArH), 7.53 (d, J = 8.4 Hz, 2H, ArH), 7.61 (t, J = 8.0 Hz, 2H, ArH), 8.20 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: m/z 371.1255 (M^+); Calcd for $C_{22}H_{17}N_3O_3$: M 371.1270].

4-(4-Fluorophenyl)-3-methyl-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4c). This compound was obtained as solid with mp 235–237°C; IR (potassium bromide): 3070, 2929, 1756, 1597, 1578, 1513, 1490, 1449, 1437, 1422, 1392, 1360, 1315, 1221, 1167, 1137, 1068, 1042, 1028, 830, 798, 757 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.12 (s, 3H, CH_3), 5.49 (s, 2H, CH_2), 7.39–7.45 (m, 3H, ArH), 7.59–7.67 (m, 4H, ArH), 8.19 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: m/z 359.1055 (M^+); Calcd for $C_{21}H_{14}FN_3O_2$: M 359.1070].

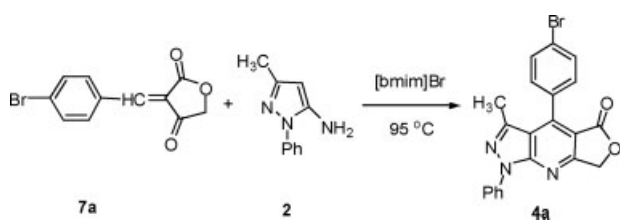
4-(4-Chlorophenyl)-3-methyl-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4d). This compound was obtained as solid with mp 223–225°C; IR (potassium bromide): 3062, 2934, 1763, 1598, 1580, 1562, 1505, 1488, 1459, 1442, 1421, 1386, 1358, 1313, 1269, 1211, 1144, 1124, 1089, 1071, 1048, 1027, 1015, 915, 848, 825, 799, 760, 723 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.12 (s, 3H, CH_3), 5.50 (s, 2H, CH_2), 7.39–7.43 (m, 1H, ArH), 7.59–7.67 (m, 6H, ArH), 8.19 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ 15.62, 69.66, 111.48, 116.50, 121.74, 127.26, 128.64, 129.98, 130.74, 131.92, 135.14, 138.84, 145.41, 146.51, 153.11, 168.02, 168.33. HRMS [Found: m/z 375.0768 (M^+); Calcd for $C_{21}H_{14}{}^{35}Cl\ N_3O_2$: M 375.0775].

3-Methyl-4-(4-nitrophenyl)-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4e). This compound was obtained as solid with mp 288–289°C; IR (potassium bromide): 3068, 2929, 1763, 1580, 1517, 1439, 1388, 1350, 1314, 1293, 1213, 1142, 1108, 1073, 1050, 1022, 838, 802, 754, 709, 692 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.11 (s, 3H, CH_3), 5.54 (s, 2H, CH_2), 7.43 (t, J = 7.6 Hz, 1H, ArH), 7.63 (t, J = 7.6 Hz, 2H, ArH), 7.90 (d, J = 8.4 Hz, 2H, ArH), 8.20 (d, J = 8.0 Hz, 2H, ArH), 8.44 (d, J = 8.4 Hz, 2H, ArH). HRMS [Found: m/z 386.1012 (M^+); Calcd for $C_{21}H_{14}N_4O_4$: M 386.1015].

4-(4-Hydroxyphenyl)-3-methyl-1-phenyl-1H-furo[3,4-e] pyrazolo[3,4-b]pyridine-5(7H)-one (4f). This compound was obtained as solid with mp >300°C; IR (potassium bromide): 3312, 1744, 1614, 1591, 1573, 1511, 1490, 1438, 1388, 1360, 1317, 1276, 1214, 1173, 1146, 1082, 1051, 1026, 854, 826, 802, 758 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.17 (s, 3H, CH_3), 5.45 (s, 2H, CH_2), 6.93 (d, J = 8.0 Hz, 2H, ArH), 7.40 (d, J = 8.0 Hz, 3H, ArH), 7.60 (t, J = 7.6 Hz, 2H, ArH), 8.19 (d, J = 7.6 Hz, 2H, ArH), 9.97 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 15.88, 69.34, 111.13, 115.27, 116.72, 121.66, 121.96, 127.08, 129.90, 132.04, 138.96, 145.61, 148.82, 153.18, 159.48, 168.14, 168.45. HRMS [Found: m/z 357.1092 (M^+); Calcd for $C_{21}H_{15}N_3O_3$: M 357.1113].

4-(4-Dimethylaminophenyl)-3-methyl-1-phenyl-1H-furo [3,4-e] pyrazolo[3,4-b]pyridine-5(7H)-one(4g). This compound was obtained as solid with mp 246–248°C; IR (potassium bromide): 2926, 1760, 1615, 1593, 1571, 1531, 1515, 1457, 1441, 1390, 1362, 1311, 1294, 1272, 1213, 1191, 1139, 1070, 1044, 1029,

Scheme 4



943, 850, 813, 796, 759 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.23 (s, 3H, CH_3), 3.04 (s, 6H, $(CH_3)_2N$), 5.43 (s, 2H, CH_2), 6.86 (d, J = 8.4 Hz, 2H, ArH), 7.37–7.45 (m, 3H, ArH), 7.60 (t, J = 7.6 Hz, 2H, ArH), 8.20 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ 16.31, 69.25, 110.81, 111.29, 116.57, 118.08, 121.78, 121.82, 127.12, 129.94, 132.13, 132.18, 139.05, 145.72, 149.45, 151.78, 153.34, 168.39, 168.65. HRMS [Found: *m/z* 384.1585 (M^+); Calcd for $C_{23}H_{20}N_4O_2$: M 384.15 86].

3-Methyl-4-(3-nitrophenyl)-1-phenyl-1H-furo[3,4-e]pyrazolo [3,4-b]pyridine-5(7H)-one (4h). This compound was obtained as solid with mp 259–261°C; IR (potassium bromide): 3069, 2934, 1773, 1589, 1535, 1516, 1491, 1460, 1439, 1387, 1345, 1315, 1212, 1156, 1125, 1073, 1048, 1029, 875, 800, 755, 738, 713, 702, 692 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.12 (s, 3H, CH_3), 5.53 (s, 2H, CH_2), 7.42 (t, J = 7.6 Hz, 1H, ArH), 7.62 (t, J = 7.6 Hz, 2H, ArH), 7.90 (t, J = 8.0 Hz, 1H, ArH), 8.10 (d, J = 7.6 Hz, 1H, ArH), 8.20 (d, J = 8.0 Hz, 2H, ArH), 8.47 (d, J = 8.8 Hz, 1H, ArH), 8.51 (s, 1H, ArH); ^{13}C NMR (DMSO-d_6): δ 14.34, 68.57, 108.77, 110.48, 115.22, 120.58, 123.76, 126.07, 128.73, 132.23, 135.37, 135.39, 137.58, 143.49, 143.99, 146.68, 151.99, 166.68, 167.10. HRMS [Found: *m/z* 386.1031 (M^+); Calcd for $C_{21}H_{14}N_4O_4$: M 386.1015].

4-(2,4-Dichlorophenyl)-3-methyl-1-phenyl-1H-furo[3,4-e]pyrazolo [3,4-b]pyridine-5(7H)-one (4i). This compound was obtained as solid with mp 206–208°C; IR (potassium bromide): 3064, 2930, 1762, 1585, 1506, 1490, 1475, 1441, 1470, 1389, 1376, 1361, 1316, 1274, 1210, 1180, 1150, 1127, 1100, 1078, 1050, 1024, 893, 853, 821, 801, 757, 689 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.10 (s, 3H, CH_3), 5.54 (d, J = 16.0 Hz, 1H, CH), 5.61 (d, J = 16.0 Hz, 1H, CH), 7.43 (t, J = 7.6 Hz, 1H, ArH), 7.60–7.65 (m, 3H, ArH), 7.68 (d, J = 8.4 Hz, 1H, ArH), 7.95 (s, 1H, ArH), 8.19 (d, J = 8.4 Hz, 2H, ArH). HRMS [Found: *m/z* 409.0385 (M^+); Calcd for $C_{21}H_{13}{}^{35}Cl_2N_3O_2$: M 409.0385].

4-(3,4-Dimethylphenyl)-3-methyl-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4j). This compound was obtained as solid with mp 231–233°C; IR (potassium bromide): 2926, 2861, 1768, 1577, 1513, 1458, 1434, 1386, 1355, 1268, 1228, 1210, 1182, 1128, 1070, 1042, 1027, 852, 818, 808, 798, 758, 719 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.11 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 5.48 (s, 2H, CH_2), 7.28 (d, J = 8.0 Hz, 1H, ArH), 7.32–7.35 (m, 2H, ArH), 7.41 (t, J = 7.6 Hz, 1H, ArH), 7.61 (t, J = 7.6 Hz, 2H, ArH), 8.20 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ 15.62, 19.98, 69.47, 111.34, 116.68, 121.82, 127.18, 127.47, 129.31, 129.56, 129.95, 130.93, 136.33, 138.43, 138.97, 145.61, 148.48, 153.17, 168.11, 168.31. HRMS [Found: *m/z* 369.1480 (M^+); Calcd for $C_{23}H_{19}N_3O_2$: M 369.1477].

3-Methyl-4-(3,4-dimethoxyphenyl)-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4k). This compound was obtained as solid with mp 203–205°C; IR (potassium bromide): 3059, 3018, 2930, 1768, 1589, 1570, 1512, 1460, 1438, 1412, 1355, 1325, 1309, 1259, 1234, 1203, 1174, 1130, 1070, 1045, 1027, 843, 795, 761, 701 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.19 (s, 3H, CH_3), 3.79 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 5.47 (s, 2H, CH_2), 7.10–7.17 (m, 2H, ArH), 7.20 (s, 1H, ArH), 7.41 (t, J = 7.6 Hz, 1H, ArH), 7.61 (t, J = 7.6 Hz, 2H, ArH), 8.19 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ 20.44, 60.97, 74.11, 116.36, 119.99, 121.51, 126.54, 127.86, 128.63, 131.88, 134.65, 134.73, 143.71, 150.39, 153.01, 153.34, 155.29, 157.96, 172.81, 173.03. HRMS [Found: *m/z* 401.1386 (M^+); Calcd for $C_{23}H_{19}N_3O_4$: M 401.1376].

4-(2-Chloro-5-nitrophenyl)-3-methyl-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4l). This compound was obtained as solid with mp 253–255°C; IR (potassium bromide): 3081, 1771, 1587, 1568, 1527, 1507, 1459, 1437, 1422, 1370, 1338, 1325, 1214, 1152, 1124, 1108, 1082, 1054, 1025, 947, 867, 853, 820, 757, 709 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.13 (s, 3H, CH_3), 5.54 (d, J = 16.0 Hz, 1H, CH), 5.64 (d, J = 16.0 Hz, 1H, CH), 7.44 (t, J = 7.6 Hz, 1H, ArH), 7.64 (t, J = 7.6 Hz, 2H, ArH), 7.96 (s, 1H, ArH), 8.01 (d, J = 8.8 Hz, 1H, ArH), 8.21 (d, J = 8.0 Hz, 2H, ArH), 8.45 (d, J = 8.8 Hz, 1H, ArH). HRMS [Found: *m/z* 420.0621 (M^+); Calcd for $C_{21}H_{13}{}^{35}ClN_4O_4$: M 420.0625].

3-Methyl-4-(3,4-methylinenedioxophenyl)-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4m). This compound was obtained as solid with mp 248–249°C; IR (potassium bromide): 3070, 2903, 1764, 1577, 1508, 1490, 1445, 1387, 1364, 1341, 1313, 1240, 1207, 1166, 1119, 1071, 1051, 1031, 924, 796, 758 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.19 (s, 3H, CH_3), 5.47 (s, 2H, CH_2), 6.18 (s, 2H, OCH_2O), 7.04 (d, J = 8.0 Hz, 1H, ArH), 7.12 (d, J = 8.0 Hz, 1H, ArH), 7.18 (s, 1H, ArH), 7.40 (t, J = 7.6 Hz, 1H, ArH), 7.61 (t, J = 7.6 Hz, 2H, ArH), 8.19 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ 15.67, 69.45, 102.22, 108.51, 110.70, 111.51, 116.80, 121.71, 124.38, 125.22, 127.15, 129.92, 138.93, 145.56, 147.48, 147.82, 149.03, 153.19, 168.02, 168.27. HRMS [Found: *m/z* 385.1065 (M^+); Calcd for $C_{22}H_{15}N_3O_4$: M 385.1063].

3-Methyl-4-(thiophen-2-yl)-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4n). This compound was obtained as solid with mp 248–250°C; IR (potassium bromide): 3098, 1761, 1579, 1541, 1515, 1490, 1438, 1384, 1360, 1340, 1311, 1266, 1225, 1201, 1181, 1131, 1116, 1076, 1050, 1028, 852, 817, 794, 762, 732, 716, 720 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.25 (s, 3H, CH_3), 5.48 (s, 2H, CH_2), 7.32 (t, J = 8.0 Hz, 1H, ArH), 7.40–7.46 (m, 2H, ArH), 7.61 (t, J = 8.0 Hz, 2H, ArH), 7.97 (d, J = 5.2 Hz, 1H, ArH), 8.18 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ 19.95, 74.20, 117.01, 122.03, 126.62, 132.01, 132.56, 134.64, 135.02, 135.44, 136.22, 143.56, 145.58, 150.10, 157.81, 172.63, 172.70. HRMS [Found: *m/z* 347.0745 (M^+); Calcd for $C_{19}H_{13}N_3O_2S$: M 347.0728].

3-Methyl-4-(pyridin-3-yl)-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4o). This compound was obtained as solid with mp 223–225°C; IR (potassium bromide): 3032, 2971, 2947, 1753, 1593, 1579, 1510, 1487, 1440, 1421, 1389, 1357, 1336, 1312, 1293, 1269, 1213, 1194, 1146, 1125, 1071, 1050, 1026, 908, 848, 813, 795, 760, 717, 701 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.14 (s, 3H, CH_3), 5.53 (s, 2H, CH_2), 7.42 (t, J = 7.6 Hz, 1H, ArH), 7.60–7.65 (m, 3H, ArH), 8.08 (dd, J_1 = 1.5 Hz, J_2 = 7.6 Hz, 1H, ArH), 8.20 (d, J = 8.0 Hz, 2H, ArH), 8.79 (d, J = 2.0 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ 20.39, 74.46, 116.48, 121.39, 126.52, 128.22, 132.00, 132.72, 134.66, 142.47, 155.85, 157.87, 172.67, 173.11. HRMS [Found: *m/z* 342.1136 (M^+); Calcd for $C_{20}H_{14}N_4O_2$: M 342.1117].

3-Methyl-4-(pyridin-4-yl)-1-phenyl-1H-furo[3,4-e]pyrazolo[3,4-b]pyridine-5(7H)-one (4p). This compound was obtained as solid with mp 223–225°C; IR (potassium bromide): 3032, 2976, 2939, 1769, 1583, 1543, 1510, 1491, 1438, 1419, 1388, 1361, 1340, 1314, 1273, 1212, 1178, 1148, 1126, 1072, 1051,

1029, 989, 812, 797, 759 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.11 (s, 3H, CH_3), 5.53 (s, 2H, CH_2), 7.42 (t, J = 7.6 Hz, 1H, ArH), 7.60–7.70 (m, 4H, ArH), 8.18 (d, J = 8.0 Hz, 2H, ArH), 8.80 (d, J = 5.2 Hz, 2H, ArH). HRMS [Found: m/z 342.1099 (M^+); Calcd for $C_{20}H_{14}N_4O_2$: M 342.1117].

3-Methyl-1-phenyl-4-p-tolylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6a). This compound was obtained as solid with mp 219–221°C (Lit. [32] 217–218°C); IR (potassium bromide): 3028, 2916, 1712, 1592, 1572, 1555, 1498, 1461, 1437, 1383, 1326, 1310, 1278, 1246, 1198, 1178, 1159, 1119, 1083, 1022, 995, 869, 767, 726, 698 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.02 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 7.36 (d, J = 7.2 Hz, 2H, ArH), 7.41–7.47 (m, 3H, ArH), 7.60–7.67 (m, 4H, ArH), 7.77 (t, J = 7.2 Hz, 1H, ArH), 8.01 (d, J = 7.6 Hz, 1H, ArH), 8.29 (d, J = 7.6 Hz, 2H, ArH). HRMS [Found: m/z 401.1533 (M^+); Calcd for $C_{27}H_{19}N_3O$: M 401.1528].

4-(4-Methoxyphenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6b). This compound was obtained as solid with mp 222–224°C (Lit. [32] 224–225°C); IR (potassium bromide): 2995, 2932, 2834, 1710, 1608, 1560, 1511, 1463, 1439, 1384, 1327, 1311, 1292, 1246, 1201, 1178, 1152, 1122, 1035, 996, 952, 834, 787, 770, 757, 727, 690 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.01 (s, 3H, CH_3), 3.88 (s, 3H, CH_3O), 7.12 (d, J = 7.6 Hz, 2H, ArH), 7.42 (t, J = 7.6 Hz, 1H, ArH), 7.51 (d, J = 7.6 Hz, 2H, ArH), 7.57–7.65 (m, 4H, ArH), 7.74 (t, J = 7.6 Hz, 1H, ArH), 7.96 (d, J = 7.2 Hz, 1H, ArH), 8.30 (d, J = 8.4 Hz, 2H, ArH). HRMS [Found: m/z 417.1474 (M^+); Calcd for $C_{27}H_{19}N_3O_2$: M 417.1477].

4-(4-Fluorophenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6c). This compound was obtained as solid with mp 256–258°C (Lit. [32] 255–257°C); IR (potassium bromide): 3068, 3019, 1715, 1605, 1596, 1561, 1509, 1462, 1437, 1383, 1324, 1209, 1248, 1226, 1201, 1160, 1121, 1096, 1085, 1015, 995, 911, 872, 839, 803, 763, 730, 697 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.99 (s, 3H, CH_3), 7.37–7.44 (m, 3H, ArH), 7.57–7.64 (m, 6H, ArH), 7.74 (t, J = 7.6 Hz, 1H, ArH), 7.98 (d, J = 7.6 Hz, 1H, ArH), 8.28 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: m/z 405.1276 (M^+); Calcd for $C_{26}H_{16}FN_3O$: M 405.1277].

4-(4-Chlorophenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6d). This compound was obtained as solid with mp 265–267°C (Lit. [32] 269–270°C); IR (potassium bromide): 3054, 2924, 1710, 1597, 1572, 1558, 1503, 1461, 1438, 1383, 1325, 1311, 1294, 1270, 1246, 1179, 1153, 1120, 1084, 1015, 996, 953, 867, 835, 767, 728 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.01 (s, 3H, CH_3), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.56–7.65 (m, 8H, ArH), 7.75 (t, J = 7.2 Hz, 1H, ArH), 7.98 (d, J = 7.2 Hz, 1H, ArH), 8.28 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: m/z 421.0976 (M^+); Calcd for $C_{26}H_{16}{}^{35}ClN_3O$: M 421.0982].

4-(4-Bromophenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6e). This compound was obtained as solid with mp 272–274°C (Lit. [32] 274–276°C); IR (potassium bromide): 1712, 1595, 1570, 1503, 1460, 1438, 1383, 1326, 1311, 1293, 1270, 1246, 1201, 1180, 1153, 1120, 1083, 1012, 767, 728 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.99 (s, 3H, CH_3), 7.42 (t, J = 7.6 Hz, 1H, ArH), 7.53 (d, J = 8.0 Hz, 2H, ArH), 7.56–7.64 (m, 4H, ArH), 7.73–7.77 (m, 3H, ArH), 7.98 (d, J = 7.6 Hz, 1H, ArH), 8.27 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: m/z 465.0479 (M^+); Calcd for $C_{26}H_{16}{}^{79}BrN_3O$: M 465.0477].

3-Methyl-4-(4-nitrophenyl)-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6f). This compound was obtained as solid with mp >300°C (Lit. [26] 318–319°C); IR (potassium bromide): 3065, 1709, 1592, 1566, 1510, 1503, 1462, 1439, 1384, 1347, 1325, 1311, 1290, 1246, 1201, 1180, 1154, 1121, 1084, 1016, 997, 949, 865, 838, 768, 752, 729, 719, 703, 691 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.99 (s, 3H, CH_3), 7.44 (t, J = 7.2 Hz, 1H, ArH), 7.61–7.66 (m, 4H, ArH), 7.78 (t, J = 7.6 Hz, 1H, ArH), 7.90 (d, J = 8.4 Hz, 2H, ArH), 8.03 (d, J = 7.2 Hz, 1H, ArH), 8.28 (d, J = 8.0 Hz, 2H, ArH), 8.42 (d, J = 8.4 Hz, 2H, ArH). HRMS [Found: m/z 432.1220 (M^+); Calcd for $C_{26}H_{16}N_4O_3$: M 432.1222].

4-(4-Hydroxyphenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6g). This compound was obtained as solid with mp >300°C (Lit. [26] 316–318°C); IR (potassium bromide): 3233, 3067, 3031, 1695, 1614, 1593, 1557, 1510, 1489, 1456, 1436, 1418, 1383, 1332, 1323, 1309, 1293, 1275, 1247, 1232, 1201, 1176, 1157, 1121, 1083, 768, 756, 730 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.04 (s, 3H, CH_3), 6.91 (d, J = 8.4 Hz, 2H, ArH), 7.35–7.41 (m, 3H, ArH), 7.53–7.62 (m, 4H, ArH), 7.72 (t, J = 7.6 Hz, 1H, ArH), 7.94 (d, J = 8.0 Hz, 1H, ArH), 8.27 (d, J = 8.0 Hz, 2H, ArH), 9.90 (s, 1H, OH). HRMS [Found: m/z 403.1317 (M^+); Calcd for $C_{26}H_{17}N_3O_2$: M 403.1321].

3-Methyl-4-(3-nitrophenyl)-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6h). This compound was obtained as solid with mp 269–271°C; IR (potassium bromide): 3086, 1710, 1605, 1593, 1564, 1525, 1503, 1437, 1417, 1384, 1349, 1326, 1311, 1285, 1247, 1204, 1188, 1156, 1123, 1083, 909, 770, 760, 741, 728, 706, 690 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.99 (s, 3H, CH_3), 7.43 (t, J = 7.2 Hz, 1H, ArH), 7.60–7.65 (m, 4H, ArH), 7.77 (t, J = 7.2 Hz, 1H, ArH), 7.88 (t, J = 8.0 Hz, 1H, ArH), 8.02 (d, J = 7.2 Hz, 1H, ArH), 8.08 (d, J = 7.6 Hz, 1H, ArH), 8.29 (d, J = 8.0 Hz, 2H, ArH), 8.46 (d, J = 8.4 Hz, 1H, ArH), 8.51 (s, 1H, ArH). HRMS [Found: m/z 432.1237 (M^+); Calcd for $C_{26}H_{16}N_4O_3$: M 432.1222].

4-(3-Chlorophenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6i). This compound was obtained as solid with mp 243–245°C; IR (potassium bromide): 3065, 1715, 1593, 1561, 1503, 1474, 1461, 1436, 1382, 1325, 1309, 1293, 1276, 1245, 1203, 1180, 1153, 1119, 1024, 998, 955, 907, 889, 766, 754, 726, 702 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.01 (s, 3H, CH_3), 7.43 (t, J = 7.6 Hz, 1H, ArH), 7.52–7.67 (m, 7H, ArH), 7.70 (s, 1H, ArH), 7.77 (t, J = 7.6 Hz, 1H, ArH), 8.01 (d, J = 7.6 Hz, 1H, ArH), 8.28 (d, J = 7.6 Hz, 2H, ArH). HRMS [Found: m/z 421.0963 (M^+); Calcd for $C_{26}H_{16}{}^{35}ClN_3O$: M 421.0982].

4-(4-Dimethylaminophenyl)2-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6j). This compound was obtained as solid with mp 242–244°C (Lit. [26] 241–242°C); IR (potassium bromide): 2892, 1706, 1617, 1561, 1531, 1504, 1481, 1462, 1441, 1384, 1370, 1325, 1310, 1292, 1244, 1233, 1206, 1194, 1182, 1168, 1156, 1125, 1085, 1059, 1020, 992, 945, 815, 768, 729, 690 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.14 (s, 3H, CH_3), 3.05 (s, 6H, $(CH_3)_2N$), 6.80 (d, J = 8.4 Hz, 2H, ArH), 7.40–7.43 (m, 3H, ArH), 7.56–7.64 (m, 4H, ArH), 7.74 (t, J = 7.2 Hz, 1H, ArH), 7.97 (d, J = 7.6 Hz, 1H, ArH), 8.29 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: m/z 430.1783 (M^+); Calcd for $C_{28}H_{22}N_4O$: M 430.1794].

4-(2,4-Dichlorophenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6k). This compound was

obtained as solid with mp 179–181°C (Lit. [26] 182–184°C); IR (potassium bromide): 3076, 2990, 1716, 1593, 1561, 1504, 1473, 1464, 1435, 1383, 1321, 1306, 1261, 1246, 1197, 1158, 1124, 1102, 1084, 1055, 995, 946, 872, 829, 791, 772, 760, 728 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.99 (s, 3H, CH_3), 7.43 (t, J = 7.6 Hz, 1H, ArH), 7.60–7.68 (m, 6H, ArH), 7.78 (t, J = 7.6 Hz, 1H, ArH), 7.93 (s, 1H, ArH), 8.03 (d, J = 7.6 Hz, 1H, ArH), 8.27 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: *m/z* 455.0585 (M^+); Calcd for $C_{26}H_{15}{}^{35}Cl_2N_3O$: M 455.0592].

4-(3,4-Dimethylphenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6l). This compound was obtained as solid with mp 200–202°C; IR (potassium bromide): 3046, 2969, 2921, 1709, 1591, 1558, 1506, 1456, 1437, 1378, 1326, 1311, 1291, 1280, 1245, 1207, 1187, 1154, 1123, 1084, 1023, 807, 769, 758, 726, 691 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.00 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.26 (d, J = 7.6 Hz, 1H, ArH), 7.30–7.32 (m, 2H, ArH), 7.42 (t, J = 7.6 Hz, 1H, ArH), 7.56–7.64 (m, 4H, ArH), 7.74 (t, J = 7.2 Hz, 1H, ArH), 7.98 (d, J = 7.6 Hz, 1H, ArH), 8.28 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: *m/z* 415.1686 (M^+); Calcd for $C_{28}H_{21}N_3O$: M 415.1685].

4-(3,4-Dimethoxyphenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6m). This compound was obtained as solid with mp 224–226°C (Lit. [26] 230–231°C); IR (potassium bromide): 3054, 2959, 2938, 1703, 1606, 1550, 1510, 1488, 1463, 1444, 1381, 1355, 1328, 1309, 1287, 1275, 1262, 1247, 1232, 1195, 1168, 1158, 1138, 1123, 1086, 1022, 801, 763, 729 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.09 (s, 3H, CH_3), 3.79 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 7.12 (s, 1H, ArH), 7.21 (s, 1H, ArH), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.58–7.65 (m, 4H, ArH), 7.76 (t, J = 7.6 Hz, 1H, ArH), 8.00 (d, J = 7.2 Hz, 1H, ArH), 8.29 (d, J = 8.4 Hz, 2H, ArH). HRMS [Found: *m/z* 447.1599 (M^+); Calcd for $C_{28}H_{21}N_3O_3$: M 447.1583].

4-(3,4-Methylienedioxyphenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6n). This compound was obtained as solid with mp 220–222°C (Lit. [32] 223–224°C); IR (potassium bromide): 3075, 3016, 2880, 1714, 1594, 1561, 1503, 1483, 1462, 1440, 1383, 1354, 1324, 1308, 1282, 1239, 1196, 1160, 1138, 1118, 1106, 1081, 1044, 1029, 996, 942, 918, 805, 768, 730, 701 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.04 (s, 3H, CH_3), 6.17 (s, 2H, OCH_2O), 7.01 (d, J = 8.0 Hz, 1H, ArH), 7.08 (d, J = 8.0 Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.41 (t, J = 7.2 Hz, 1H, ArH), 7.55–7.62 (m, 4H, ArH), 7.72 (t, J = 7.2 Hz, 1H, ArH), 7.93 (d, J = 7.6 Hz, 1H, ArH), 8.26 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: *m/z* 431.1264 (M^+); Calcd for $C_{27}H_{17}N_3O_3$: M 431.1270].

4-(3,4-Dichlorophenyl)-3-methyl-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6o). This compound was obtained as solid with mp 194–196°C (Lit. [26] 192–194°C); IR (potassium bromide): 3065, 2985, 2927, 1713, 1596, 1566, 1546, 1503, 1471, 1436, 1416, 1376, 1323, 1307, 1244, 1202, 1180, 1154, 1135, 1118, 1034, 998, 953, 895, 831, 775, 766, 751, 726 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.06 (s, 3H, CH_3), 7.43 (t, J = 7.2 Hz, 1H, ArH), 7.60–7.66 (m, 5H, ArH), 7.77 (t, J = 7.2 Hz, 1H, ArH), 7.85 (d, J = 8.4 Hz, 1H, ArH), 7.95 (s, 1H, ArH), 8.01 (d, J = 7.2 Hz, 1H, ArH), 8.28 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: *m/z* 455.0586 (M^+); Calcd for $C_{26}H_{15}{}^{35}Cl_2N_3O$: M 455.0592].

3-Methyl-4-(thiophen-2-yl)-1-phenylindeno[2,1-e]pyrazolo[3,4-b]pyridine-5(1H)-one (6p). This compound was obtained as solid with mp 231–233°C (Lit. [26] 232–233°C); IR (potassium bromide): 3076, 2993, 1705, 1593, 1562, 1510, 1499, 1460, 1434, 1381, 1336, 1320, 1306, 1291, 1247, 1220, 1192, 1170, 1155, 1117, 1082, 1030, 991, 860, 806, 770, 752, 720 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.12 (s, 3H, CH_3), 7.30 (t, J = 8.0 Hz, 1H, ArH), 7.41–7.45 (m, 2H, ArH), 7.60–7.67 (m, 4H, ArH), 7.76 (t, J = 7.6 Hz, 1H, ArH), 7.92 (d, J = 5.2 Hz, 1H, ArH), 8.00 (d, J = 7.2 Hz, 1H, ArH), 8.27 (d, J = 8.0 Hz, 2H, ArH). HRMS [Found: *m/z* 393.0917 (M^+); Calcd for $C_{24}H_{15}N_3OS$: M 393.09 36].

3-Methyl-4-(pyridin-4-yl)-1-phenylindeno[2,1-e]pyrazolo-[3,4-b]pyridine-5(1H)-one (6q). This compound was obtained as solid with mp >300°C; IR (potassium bromide): 3021, 2986, 1707, 1590, 1568, 1541, 1504, 1462, 1437, 1412, 1385, 1327, 1312, 1249, 1203, 1181, 1157, 1123, 1085, 1068, 996, 950, 831, 772, 763, 732, 691 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.02 (s, 3H, CH_3), 7.44 (t, J = 7.2 Hz, 1H, ArH), 7.61–7.67 (m, 6H, ArH), 7.79 (t, J = 7.2 Hz, 1H, ArH), 8.04 (d, J = 8.0 Hz, 1H, ArH), 8.28 (d, J = 8.0 Hz, 2H, ArH), 8.79 (d, J = 8.8 Hz, 2H, ArH). HRMS [Found: *m/z* 388.1326 (M^+); Calcd for $C_{25}H_{16}N_4O$: M 388.1324].

The preparation of 4a from 7a. 3-(4-Bromobenzylidene)-furan-2,4(3*H*,5*H*)-dione **7a** (2 mmol) and 5-amino-3-methyl-1-phenylpyrazole **2** (2 mmol) were added to a 10 mL round flask containing 2 mL [bmim]Br. The mixture was then stirred at 95°C for 2 h. After completion of the reaction, the reaction mixture was added with 5 mL water. The precipitate was collected by suction and purified by recrystallization from ethanol to give **4a** in 96% yield.

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[34] The single-crystal growth was carried out in EtOH solutions at r.t. X-ray crystallographic analysis was performed with a Smart-1000 CCD diffractometer (graphite monochromator, MoKα radiation, $\lambda = 0.71073$ Å). Crystal data for 4l: Empirical formula $C_{21}H_{13}ClN_4O_4$, yellow, crystal dimension $0.57 \times 0.52 \times 0.34$ mm^3, monoclinic, space group $P2_1/c$, $a = 9.923(4)$ Å, $b = 22.070(8)$ Å, $c = 9.319(3)$ Å, $\alpha = 90°$, $\beta = 112.894(3)°$, $\gamma = 90°$. $V = 1880.1(12)$ Å^3, $M_r = 419.81$, $Z = 4$, $D_c = 1.483$ Mg/m^3, μ(MoKα) $= 0.240$ mm^{-1}, $F(000) = 864$, $S = 1.054$, $R_1 = 0.0605$, $wR_2 = 0.1478$.