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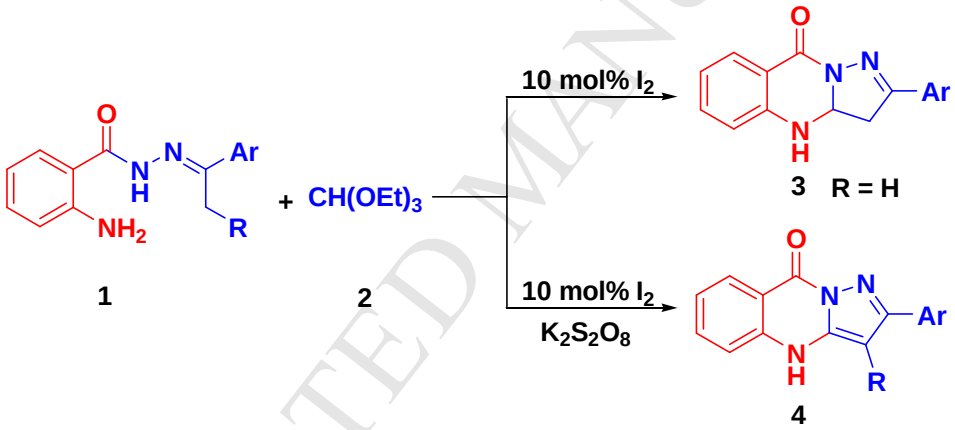
The Domino reaction of (*E*)-2-amino-*N*'-(1-arylethylidene)benzohydrazide and triethyl orthoformate in ionic liquids catalyzed by 10 mol% iodine gave 3*a*,4-dihydro-2-arylpyrazolo[5,1-*b*]quinazolin-9(3*H*)-one derivatives unexpectedly. In the presence of $K_2S_2O_8$, it could be oxidized to aromatized products in good yields.



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Iodine-Catalyzed Synthesis of 2-Arylpyrazolo[5,1-*b*]quinazolin-9(3*H*)-one Derivatives in Ionic Liquids via Domino Reaction

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Abstract. The Domino reaction of (*E*)-2-amino-*N*'-(1-arylethylidene)benzohydrazide and triethyl orthoformate in ionic liquids catalyzed by 10 mol% iodine gave 3*a*,4-dihydro-2-arylpyrazolo [5,1-*b*]quinazolin-9(3*H*)-one derivatives unexpectedly. In the presence of $K_2S_2O_8$, it could be oxidized to aromatized products in good yields.

Keywords: pyrazoloquinazoline; Domino reaction; iodine; synthesis

Introduction

Pyrazoloquinazoline moiety is a fused tricyclic heterocycle, and its derivatives are an important class of molecules with physiological significance and pharmaceutical utility. A well-known example is 7-(benzolylamino)-4,9-dihydro-4-methyl-9-oxo pyrazolo[5,1-*b*]quinazoline-2-carboxylic acid (Figure 1), which was reported to be an effective nerve growth factor antagonist.[1] Its derivatives are usually used as various kinds of inhibitors, such as PDE10A enzyme inhibitors,[2] MPS1 kinase inhibitors,[3] phosphodie-sterase 10A inhibitors,[4] PDK1 inhibitors,[5] and orally polo-like kinase 1

inhibitors.[6] They are also used in treating diseases caused by dysregulated protein kinase activity and PIM kinases,[7] or used in the treatment of mesothelioma as ATP-competitive CDK inhibitor.[8] Therefore, much attention has been devoted to the synthesis of these bioactive pyrazoloquinazoline derivatives.[9-13] The existing methods for these derivatives are three-component condensation of 5-aminopyrazoles, dimedone, and aldehydes,[9] the reaction of 2-(1-hydropolyfluoro-1-alkenyl)-4*H*-3,1-benzoxin-4-ones with hydrazine hydrate and phenylhydrazine,[10] or the condensation of α-cyanoketones and 2-hydrazinobenzoic acids.[11]

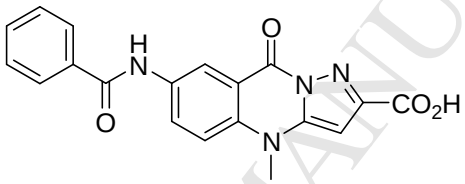
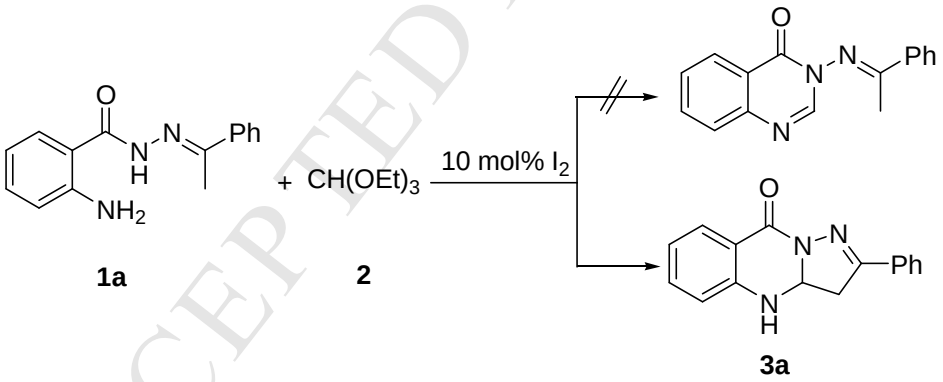


Figure 1. The active molecule containing pyrazoloquinazoline moiety

In our previous study, quinazolin-4(3*H*)-ones were obtained by the known reaction of triethyl orthoformate and 2-aminobenzamide catalyzed by iodine in ionic liquids.[14] In order to get structurally diversified quinazolin-4(3*H*)-ones, the reactant of 2-aminobenzamide was replaced by 2-amino-*N*'-(1-phenylethylidene)benzohydrazide **1a** which reacts with triethyl orthoformate **2**. It was found that a distinctly different product of 3*a*,4-dihydro-2-phenylpyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3a** was obtained unexpectedly rather than 3-(1-phenylethylideneamino)quinazolin-4(3*H*)-one (Scheme 1) with ring-closure. Herein, we would like to report the new Domino ring-closure reaction catalyzed by iodine to build potentially bioactive pyrazolo[5,1-*b*]quinazoline moiety.

Results and Discussion

We repeated this novel reaction to optimize the conditions. Several parameters including catalysts and solvents were explored as shown in Table 1. No desired product was obtained when the reaction was carried out in the absence of iodine (Table 1, Entry 1), and 52 % of the product was obtained with 5 mol% of iodine. A maximum of 89 % yield was reached with 10 mol% iodine (Table 1, entries 2, 3, and 4). Other metal Lewis acids, such as AgOTf, $Yb(OTf)_3$, TsOH were also tested in this reaction (Table 1, entries 6–8), and no product of **3a** was found by TLC. In addition, different imidazoliums in ionic liquids and organic solvents, such as toluene, CH_3CN, THF DMF and DME were also tested, and [PMIm]Br appeared to be the best medium for this transformation (entries 3 vs. 9-16).



Scheme 1. The model reaction

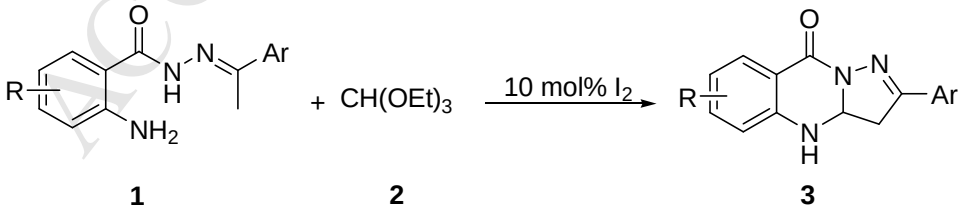
Table 1. Synthesis of **3a** under different reaction conditions [a]

Entry	Cat.	Solvent[b]	Yields[c]/%
1	-	[PMIm]Br	0
2	I_2(5)	[PMIm]Br	52
3	I_2(10)	[PMIm]Br	89
4	I_2(20)	[PMIm]Br	88

5	CuI(10)	[PMIm]Br	0
6	AgOTf(10)	[PMIm]Br	0
7	$Yb(OTf)_3$(10)	[PMIm]Br	0
8	TsOH(10)	[PMIm]Br	0
9	I_2(10)	[EMIm]Br	62
10	I_2(10)	[BMIm]Br	82
11	I_2(10)	[PMIm][BF_4]	80
12	I_2(10)	Toluene[d]	trace
13	I_2(10)	CH_3CN[d]	trace
14	I_2(10)	THF[d]	trace
15	I_2(10)	DMF[e]	41
16	I_2(10)	DME[e]	39

[a] Reagents and conditions: **1a** (0.253 g, 1.0 mmol), **2** (0.222 g, 1.5 mmol), organic solvent (10 mL). [b] BMIm = 1-butyl-3-methylimidazolium; EMIm = 1-ethyl-3-methyl imidazolium; PMIm = 1-methyl-3-propylimidazolium, ionic liquids 2 mL, 80 °C. [c] Isolated yields. [d] reflux, [e] 100 °C.

Similarly, various kinds of **1** were submitted to react with **2** to give structurally diversified 3*a*,4-dihydro-2-arylpyrazolo[5,1-*b*]quinazolin-9(3*H*)-one derivatives **3a-o** in good yields (Scheme 2). The results are summarized in Table 2. It can be observed that the process tolerates both electron-donating (such as alkyl and alkoxy) and electron-withdrawing (such as halogen and nitro) substituents in the **1**. In all cases, the reactions proceeded efficiently at 80 °C under mild conditions to afford the corresponding products in good to high yields. The structure of **3h** was confirmed by X-ray diffraction analysis, and its crystal structure is shown in Figure 2.



1 **2** **3**

Scheme 2. Synthetic route of **3**

Table 2. The synthetic results for the products **3**[a]

Products	Ar	R	Time /h	Yields [b] /%
3a	Ph	H	12	89
3b	4-ClC_6H_4	H	10	85
3c	3-BrC_6H_4	H	10	85
3d	4-$CH_3C_6H_4$	H	15	90
3e	4-BrC_6H_4	H	12	83
3f	2-$NH_2C_6H_4$	H	15	78
3g	4-$NO_2C_6H_4$	H	10	86
3h	4-$MeOC_6H_4$	H	14	84
3i	3,4-$Cl_2C_6H_3$	H	10	89
3j	4-*n*-BuC_6H_4	H	13	80
3k	4-*i*-BuC_6H_4	H	13	85
3l	2-Thienyl	H	12	78
3m	Ph	5-Me	12	89
3n	Ph	5-Br	10	86
3o	Ph	5-Cl	10	82

[a] Reagents and conditions: **1** (1.0 mmol), **2** (0.222 g, 1.5 mmol), I_2 (25 mg, 0.1 mmol), [PMIm]Br (2.0 mL). [b] Isolated yields.

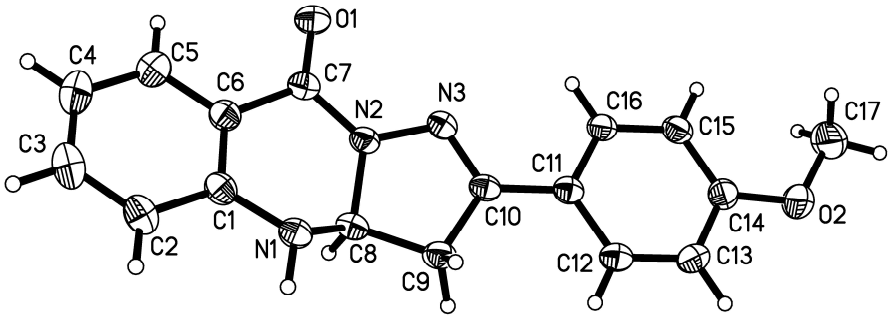
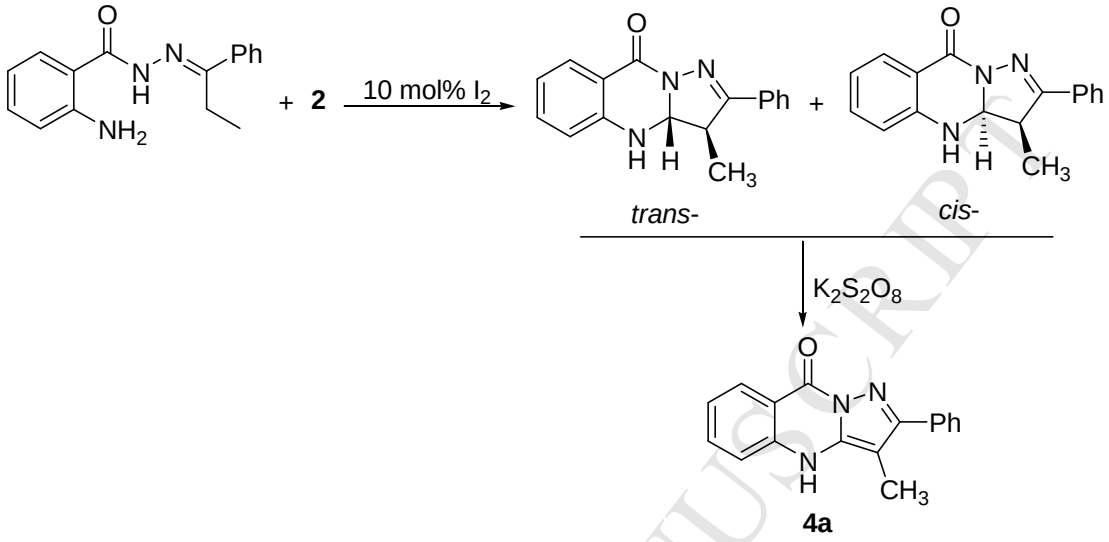


Figure 2. The crystal structure of the product **3h**

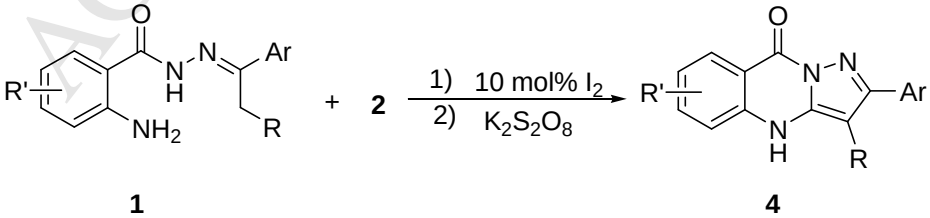
2-Amino-*N*'-(1-phenylpropylidene)benzohydrazide was also chosen as starting material to react with triethyl orthoformate under the same reaction conditions. As we expected, the designed reaction occurred smoothly but gave a mixture of *cis*- and *trans*-3*a*,4-dihydro-3-methyl-2-phenylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one in 90 % yield (31 : 69, Scheme 3), which was determined by ^{1}H NMR. However, it should be

noted that the mixture of *cis*- and *trans*-isomers was hard to separate although column chromatography of silica gel was used.



Scheme 3. Synthetic route of **4a**

Subsequently, in order to obtain aromatized products, different oxidants, such as DDQ, $PhI(OAc)_2$ and $K_2S_2O_8$, were used to promote dehydrogenation (Scheme 3). It was found that $K_2S_2O_8$ gave the best result in total of 79 % yield for **4a**. In our continued study, the product **4a** could be obtained in 82 % by a one-pot reaction without separation of intermediate. And then, different reactants of **1** were applied to this first ring-closure reaction and then dehydrogenation reaction (Scheme 4), which all reacted well to give **4a-k** in good yields (Table 3).



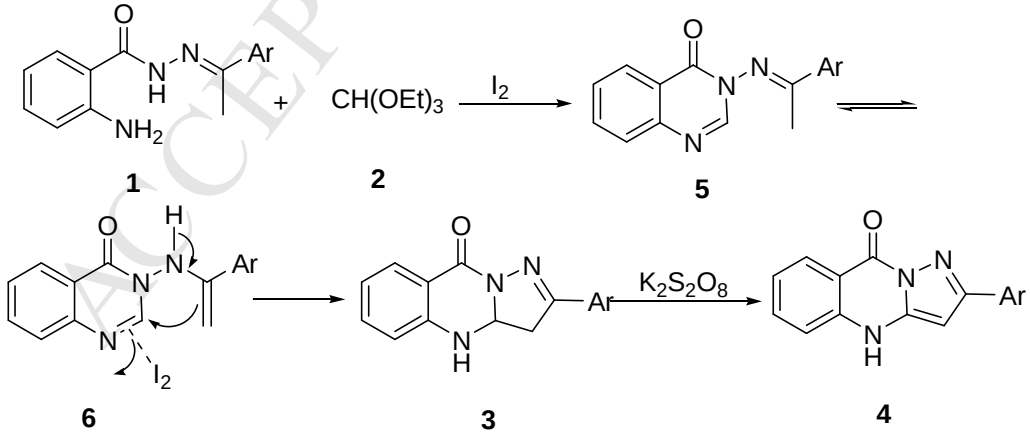
Scheme 4. Synthetic route of **4**

Table 3. The synthetic results for the products **4**[a]

Prodocts	Ar	R	R'	Time /h	Yields [b] /%
4a	Ph	CH_3	H	18	82
4b	3-ClC_6H_4	CH_3	H	20	75
4c	4-ClC_6H_4	CH_3	H	21	76
4d	4-$CH_3C_6H_4$	CH_3	H	20	85
4e	4-FC_6H_4	CH_3	H	19	75
4f	4-$OMeC_6H_4$	CH_3	H	25	86
4g	4-$CH_3C_6H_4$	H	H	21	79
4h	Ph	Et	H	23	80
4i	Ph	Et	5-Me	24	76
4j	Ph	*n*-Pr	5-Br	22	76
4k	4-ClC_6H_4	*n*-Pr	H	20	81

[a] Reagents and conditions: **1** (1.0 mmol), **2** (0.222g, 1.5 mmol), I_2 (25 mg, 0.1 mmol), $K_2S_2O_8$ (0.405g, 1.5 mmol), [PMIm]Br (2.0 mL). [b] Isolated yields.

According to the product structures, we think that the intermediate product **5** may form by a condensation reaction first; and then, **5** is in equilibrium with its enamine form **6** in the presence of iodine; the intra-molecular nucleophilic addition takes place along with cyclization reaction at last to give final product **3**. In the presence of $K_2S_2O_8$, it could be oxidized to aromatized product **4**. The possible mechanism was proposed as shown in Scheme 5.



Scheme 5. The possible mechanism

Conclusion

In conclusion, we found a novel and efficient method for the Domino synthesis of 2-arylpyrazolo[5,1-*b*]quinazolin-9(3*H*)-one derivatives catalyzed by iodine in ionic liquids. The subsequent dehydrogenation took place to give aromatized ones in good yields using $K_2S_2O_8$ as an oxidant.

Experimental Section

General procedure for the syntheses of 3*a*,4-dihydro-2-arylpyrazolo [5,1-*b*]quinazolin-9(3*H*)-one derivatives 3

2-Amino-*N*'-(1-arylethylidene)benzohydrazide (1.0 mmol), triethyl orthoformate (222 mg, 1.5 mmol), I_2 (25 mg), and [PMIm]Br (2 mL) were added into a 25 mL flask. The reaction mixture was stirred at 80 °C for 10-15 h before completion, which was monitored by TLC. A small amount of water (5 mL) was added to the mixture, and the generated yellow solid was filtered off. The water in the filtrate was removed by distillation under reduced pressure, and the ionic liquids in the residue could be reusable by evaporating at 80 °C for 4 hours *in vacuo*. The crude yellow products were washed with water and purified by recrystallization from 95 % EtOH to give **3**.

2-Phenyl-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3a**: Yield 89 % (234 mg). Pale yellow solid, m.p.: 272~274 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.30 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.73 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 5.42 (t, *J* = 10.0 Hz, 1H), 6.88~6.94 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.51~7.52 (m, 3H), 7.55 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.83~7.84 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 69.6, 115.4, 116.5, 118.9, 126.8, 128.0, 128.8, 130.6, 131.1, 133.3, 147.9, 156.7,

157.1. IR (KBr): ν 3300, 3052, 3031, 2095, 1651, 1578, 1559, 1481, 1440, 1415, 1330, 1315, 1302, 1258, 1239, 1196, 1177, 1153, 1116, 1050, 887, 858, 755, 688 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{13}N_3ONa$ $[M + Na]^+$ 286.0956, found 286.0953.

2-(4-Chlorophenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3b**: Yield 85 % (253 mg). Pale yellow solid, m.p.: 269~271 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.30 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 3.74 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 5.41 (t, *J* = 10.0 Hz, 1H), 6.88~6.93 (m, 2H), 7.33~7.40 (m, 3H), 7.60 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.87~7.91 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 70.2, 115.9, 116.3, 116.5, 117.0, 119.4, 128.5, 129.7, 129.8, 133.8, 148.4, 156.8, 157.1. IR (KBr): ν 3300, 3060, 3022, 2712, 1650, 1608, 1564, 1512, 1483, 1443, 1423, 1329, 1306, 1227, 1196, 1179, 1152, 1117, 1096, 1049, 1031, 1012, 982, 947, 886, 836, 811, 758, 686 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{12}ClN_3ONa$ $[M + Na]^+$ 320.0567, found 320.0562.

2-(3-Bromophenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3c**: Yield 85 % (291 mg). Pale yellow solid, m.p.: 280~282 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.31 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.74 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 5.42 (t, *J* = 10.0 Hz, 1H), 6.88~6.94 (m, 2H), 7.37~7.41 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.79~7.84 (m, 2H), 7.98 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 70.3, 116.0, 116.8, 119.48, 119.52, 122.6, 126.3, 128.6, 129.6, 131.5, 133.6, 134.0, 148.5, 156.5, 157.2. IR (KBr): ν 3265, 3036, 2955, 2926, 2856, 1658, 1632, 1575, 1495, 1481, 1434, 1325, 1271, 1265, 1162, 1115,

1030, 936, 862, 831, 757, 690cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{12}BrN_3ONa$ [M + Na]$^+$ 364.0061, found 364.0048.

2-(*p*-Tolyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3d**: Yield 90 % (249 mg). Pale yellow solid, m.p.: 250~252 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.37 (s, 3H), 3.27 (dd, *J* = 17.0 Hz, *J'* = 10.0 Hz, 1H), 3.70 (dd, *J* = 17.0 Hz, *J'* = 10.0 Hz, 1H), 5.90 (t, *J* = 10.0 Hz, 1H), 6.87~6.93 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.36~7.40 (m, 1H), 7.55 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 21.0, 39.5, 69.6, 115.4, 116.6, 118.9, 126.8, 128.0, 128.3, 129.4, 133.2, 140.5, 147.9, 156.6, 157.1. IR (KBr): ν 3270, 3032, 2978, 2899, 2858, 1661, 1608, 1494, 1434, 1324, 1271, 1256, 1238, 1175, 1162, 1114, 1030, 935, 861, 816, 754, 688cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{15}N_3ONa$ [M + Na]$^+$ 300.1113, found 300.1122.

2-(4-Bromophenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3e**: Yield 83 % (284 mg). Pale yellow solid, m.p.: 280~282 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.30 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 3.71 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 5.41 (t, *J* = 10.0 Hz, 1H), 6.88~6.93 (m, 2H), 7.37~7.41 (m, 1H), 7.59 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.76~7.80 (m, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.6, 70.3, 115.9, 116.9, 119.5, 124.5, 128.5, 129.2, 130.8, 132.3, 133.9, 148.4, 156.8, 157.2. IR (KBr): ν 3296, 3064, 2905, 2850, 1650, 1610, 1482, 1441, 1417, 1326, 1308, 1258, 1239, 1195, 1178, 1152, 1117, 1071, 1008, 861, 821, 756, 690 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{12}BrN_3ONa$ [M + Na]$^+$ 364.0061, found 364.0057.

2-(2-Aminophenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3f**: Yield 78 % (217 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.38 (dd, *J* = 16.4 Hz, *J'* = 9.6 Hz, 1H), 3.42 (brs. 2H), 3.85 (dd, *J* = 16.4 Hz, *J'* = 9.6 Hz, 1H), 5.40 (t, *J* = 9.6 Hz, 1H), 6.66~6.70 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.93~6.99 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.42~7.46 (m, 1H), 7.61 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 41.0, 68.6, 112.0, 115.5, 115.8, 115.9, 117.1, 119.4, 128.4, 130.6, 131.6, 133.7, 148.4, 148.6, 156.7, 159.3. IR (KBr): ν 3419, 3308, 3199, 3078, 3035, 1662, 1612, 1573, 1541, 1498, 1479, 1441, 1342, 1327, 1270, 1197, 1161, 1011, 1032, 985, 934, 881, 823, 761, 745, 686 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{13}N_4O$ $[M - H]^-$ 277.1089, found 277.1104.

2-(4-Nitrophenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3g**: Yield 86 % (265 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.36 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 3.79 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 5.47 (t, *J* = 10.0 Hz, 1H), 6.89~6.94 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.64 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 8.08~8.08 (m, 2H), 8.32(d, *J* = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 70.6, 116.0, 116.7, 119.5, 124.4, 128.4, 128.6, 134.2, 137.7, 148.5, 148.6, 156.0, 157.4. IR (KBr): ν 3272, 3069, 3000, 2950, 2850, 1656, 1613, 1561, 1509, 1484, 1440, 1343, 1317, 1232, 1185, 1163, 1109, 1033, 938, 847, 789, 760, 689cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{11}N_4O_3Na$ $[M + Na]^+$ 331.0807, found 331.0799.

2-(4-Methoxyphenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3h**: Yield 84 % (246 mg). Pale yellow solid, m.p.: 234~236 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.25 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.69 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.83 (s, 3H), 5.37 (t, *J* = 10.0 Hz, 1H), 6.87~6.90 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.36~7.40 (m, 1H), 7.55 (s, 1H), 7.77~7.80 (m, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.8, 55.8, 70.0, 114.7, 115.8, 117.1, 119.4, 124.0, 128.5, 129.0, 133.7, 148.3, 157.0, 157.3, 161.6. IR (KBr): ν 3257, 3000, 2954, 2907, 2833, 1642, 1606, 1515, 1486, 1437, 1331, 1304, 1255, 1173, 1117, 1032, 1017, 834, 794, 757, 690 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{15}N_3O_2Na$ $[M + Na]^+$ 316.1062, found 316.1066.

2-(3,4-Dichlorophenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3i**: Yield 89 % (295 mg). Pale yellow solid, m.p.: 251~253 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.31 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 3.74 (dd, *J* = 17.2 Hz, *J'* = 10.0 Hz, 1H), 5.43 (t, *J* = 10.0 Hz, 1H), 6.88~6.94 (m, 2H), 7.37~7.41 (m, 1H), 7.61 (s, 1H), 7.72~7.81 (m, 3H), 8.00~8.01 (m, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 70.4, 116.0, 116.8, 119.5, 127.2, 128.6, 128.9, 131.6, 132.2, 132.3, 133.4, 134.0, 148.5, 155.8, 157.3. IR (KBr): ν 3443, 3293, 2933, 2915, 1655, 1559, 1504, 1445, 1416, 1392, 1317, 1301, 1257, 1188, 1167, 1149, 1105, 1050, 894, 829, 757, 727, 688 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{10}Cl_2N_3O$ $[M - H]^-$ 330.0201, found 330.0197.

2-(4-*n*-Butylphenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3j**: Yield 80 % (255 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 0.88~0.93 (m, 3H), 1.26~1.36 (m, 2H), 1.53~1.61 (m, 2H), 2.63 (t, *J* = 7.6 Hz, 2H),

3.27 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.70 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 5.38 (t, *J* = 10.0 Hz, 1H), 6.88~6.93 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.36~7.40 (m, 1H), 7.56 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 14.2, 22.2, 33.4, 35.2, 39.5, 70.0, 115.9, 117.1, 119.4, 126.8, 127.3, 128.5, 129.2, 133.7, 145.8, 148.4, 157.1, 157.6. IR (KBr): ν 3266, 3071, 3027, 2927, 2854, 1661, 1612, 1501, 1439, 1406, 1321, 1305, 1275, 1191, 1164, 1150, 1122, 1070, 1030, 995, 945, 887, 778, 749, 688cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{20}H_{20}N_3O$ $[M - H]^-$ 318.1606, found 318.1603.

2-(4-*iso*-Butylphenyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3k**: Yield 85 % (271 mg). Pale yellow solid, m.p.: 273~275 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 0.87~0.90 (m, 8H), 1.82~1.92 (m, 1H), 3.28 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.71 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 5.39 (t, *J* = 10.0 Hz, 1H), 6.88~6.93 (m, 2H), 7.28~7.30 (m, 2H), 7.36~7.42 (m, 1H), 7.56 (s, 1H), 7.74~7.77 (m, 2H), 7.79 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 22.6, 30.1, 39.5, 44.9, 70.1, 115.9, 117.1, 119.4, 126.7, 127.2, 128.5, 129.9, 133.7, 144.6, 148.4, 157.1, 157.6. IR (KBr): ν 3269, 3141, 3070, 3039, 2952, 2912, 2867, 1659, 1630, 1608, 1578, 1553, 1495, 1481, 1433, 1407, 1325, 1295, 1271, 1174, 1161, 1115, 936, 863, 843, 795, 784, 758 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{20}H_{20}N_3O$ $[M - H]^-$ 318.1606, found 318.1611.

2-(2-Thienyl)-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3l**: Yield 78 % (210 mg). Pale yellow solid, m.p.: 251~253 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.23 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.61 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 5.37 (t,

J = 10.0 Hz, 1H), 6.71~6.72 (m, 1H), 6.87~6.92 (m, 2H), 7.11~7.12 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.55 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 69.7, 112.9, 114.8, 115.9, 117.0, 119.5, 128.5, 133.8, 146.5, 146.8, 148.3, 148.7, 157.1. IR (KBr): ν 3423, 3273, 3117, 3080, 2907, 2856, 1663, 1613, 1498, 1481, 1426, 1394, 1321, 1272, 1245, 1161, 1117, 1035, 1004, 939, 884, 760 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{14}H_{10}SN_3O$ $[M - H]^-$ 268.0545, found 268.0551.

7-Methyl-2-phenyl-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3m**: Yield 89 % (246 mg). Pale yellow solid, m.p.: 279~281 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.32 (s, 3H), 3.34 (dd, *J* = 17.0 Hz, *J'* = 10.0 Hz, 1H), 3.77 (dd, *J* = 17.0 Hz, *J'* = 10.0 Hz, 1H), 5.41 (t, *J* = 10.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.40~7.42 (m, 1H), 7.56~7.57 (m, 3H), 7.66 (s, 1H), 7.87~7.89 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 20.6, 39.5, 70.3, 116.0, 117.0, 127.3, 128.3, 128.34, 129.3, 131.0, 131.6, 134.7, 146.2, 157.2, 157.5. IR (KBr): ν 3443, 3424, 3293, 2933, 2915, 1655, 1504, 1445, 1416, 1392, 1332, 1317, 1257, 1188, 1167, 1149, 1105, 1050, 912, 894, 829, 757, 727, 688cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{14}N_3O$ $[M - H]^-$ 276.1137, found 276.1146.

7-Bromo-2-phenyl-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3n**: Yield 89 % (294 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.33 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.75 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 5.44 (t, *J* = 10.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 7.51~7.54 (m, 4H), 7.82~7.84 (m, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 70.0, 110.4, 118.2, 118.7, 127.4, 129.3, 130.4,

131.3, 131.4, 136.3, 147.5, 155.9, 158.3. IR (KBr): ν 3263, 3061, 2920, 2850, 1654, 1607, 1559, 1491, 1448, 1435, 1333, 1302, 1273, 1240, 1189, 1173, 1126, 1073, 858, 810, 755, 685 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{11}BrN_3O$ $[M - H]^-$ 340.0085, found 340.0074.

5-Chloro-2-phenyl-3*a*,4-dihydropyrazolo[5,1-*b*]quinazolin-9(3*H*)-one **3o**: Yield 82 % (244 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.30 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 3.75 (dd, *J* = 16.8 Hz, *J'* = 10.0 Hz, 1H), 5.44 (t, *J* = 10.0 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 7.42~7.44 (m, 1H), 7.51~7.53 (m, 3H), 7.72~7.73 (m, 1H), 7.79 (s, 1H), 7.83~7.85 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 39.5, 70.1, 117.9, 118.3, 123.1, 127.4, 127.5, 129.3, 131.2, 131.4, 133.5, 147.2, 156.0, 158.3. IR (KBr): ν 3291, 3188, 3151, 3066, 2963, 2907, 1653, 1585, 1560, 1494, 1446, 1411, 1362, 1333, 1255, 1205, 1166, 1139, 1119, 1100, 1076, 1051, 998, 969, 945, 901, 861, 821, 760, 727, 688 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{16}H_{11}ClN_3O$ $[M - H]^-$ 296.0591, found 296.0590.

General procedure for the syntheses of 2-arylpyrazolo[5,1-*b*] quinazolin-9(4*H*)-one derivatives 4

2-Amino-*N*'-(1-arylethylidene)benzohydrazide (1.0 mmol), triethyl orthoformate (222 mg, 1.5 mmol), I_2 (25 mg), and [PMIm]Br (2 mL) was added into a 25 mL flask. The reaction mixture was stirred at 80 °C for 18-25 h before completion, which was monitored by TLC. Then $K_2S_2O_8$ (0.405g, 1.5 mmol) were added to the reaction, and it was kept at the same reaction temperature until all the intermediates were consumed. A small amount of water (5 mL) was added to the mixture, and the generated yellow

solid was filtered off. The water in the filtrate was removed by distillation under reduced pressure, and the ionic liquids in the residue could be reusable by evaporating at 80 °C for 4 hours *in vacuum*. The crude yellow products were washed with water and purified by recrystallization from 95 % EtOH to give **4**.

3-Methyl-2-phenylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4a**: Yield 82 % (225 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.33 (s, 3H), 7.25 (t, J = 7.6 Hz, 1H), 7.47~7.55 (m, 4H), 7.34~7.78 (m, 1H), 7.82 (d, J = 7.2 Hz, 2H), 8.20 (d, J = 8.0 Hz, 1H), 11.90 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 8.6, 93.8, 112.0, 116.4, 121.6, 128.0, 128.4, 129.07, 129.11, 133.5, 135.0, 140.4, 141.0, 154.8, 156.0. IR (KBr): ν 3285, 3207, 3132, 3092, 3059, 3007, 2976, 2929, 2885, 1639, 1578, 1509, 1492, 1474, 1439, 1428, 1337, 1308, 1271, 1224, 1208, 1181, 1125, 1015, 946, 775, 749, 701 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{12}N_3O$ $[M - H]^-$ 274.0980, found 274.0983.

2-(3-Chlorophenyl)-3-methylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4b**: Yield 75 % (232 mg). Pale yellow solid, m.p.: 285~287 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.34 (s, 3H), 7.25~7.28 (m, 1H), 7.50~7.57 (m, 3H), 7.75~7.84 (m, 3H), 8.20 (d, J = 8.0 Hz, 1H), 11.99 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 8.5, 94.1, 111.9, 116.5, 121.7, 127.0, 127.8, 128.0, 129.0, 131.1, 133.9, 135.2, 135.5, 140.4, 141.2, 153.2, 156.0. IR (KBr): ν 3290, 3214, 3134, 3074, 3007, 2938, 1667, 1651, 1568, 1492, 1474, 1438, 1406, 1328, 1274, 1222, 1209, 1178, 1082, 948, 785, 749, 693 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{11}ClN_3O$ $[M - H]^+$ 308.0591, found 308.0603.

2-(4-Chlorophenyl)-3-methylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4c**: Yield 76 % (235 mg). Pale yellow solid, m.p.: 266~268 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.32 (s, 3H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.74~7.78 (m, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 11.94 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 8.6, 93.9, 111.9, 116.4, 121.6, 128.0, 129.2, 130.1, 132.3, 133.9, 135.1, 140.4, 141.1, 153.5, 156.0. IR (KBr): ν 3286, 3215, 3136, 3070, 3029, 3007, 2937, 1666, 1646, 1581, 1567, 1508, 1493, 1473, 1436, 1401, 1327, 1268, 1222, 1207, 1176, 1157, 1091, 1010, 945, 843, 748, 695 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{11}ClN_3O$ $[M - H]^-$ 308.0591, found 308.0608.

3-Methyl-2-(*p*-tolyl)pyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4d**: Yield 85 % (246 mg). Pale yellow solid, m.p.: 278~280 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.32 (s, 3H), 2.38 (s, 3H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.74~7.77 (m, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 11.87 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 8.7, 21.4, 93.6, 111.9, 116.4, 121.5, 128.0, 128.3, 129.6, 130.6, 135.0, 138.6, 140.4, 141.0, 154.7, 156.0. IR (KBr): ν 3289, 3241, 3125, 3066, 3029, 1666, 1643, 1581, 1506, 1491, 1470, 1434, 1330, 1306, 1270, 1222, 1206, 1175, 1158, 1112, 1011, 943, 824, 751 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{18}H_{14}N_3O$ $[M - H]^-$ 288.1137, found 288.1149.

2-(4-Fluorophenyl)-3-methylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4e**: Yield 75 % (220 mg). Pale yellow solid, m.p.: 275~277 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.32 (s, 3H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.34~7.38 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.74~7.78 (m, 1H), 7.85~7.88 (m, 2H), 8.20 (d, *J* = 8.0 Hz, 1H), 11.92 (s, 1H). ^{13}C

NMR (DMSO-d_6, 100 MHz): δ_c 8.6, 93.7, 111.9, 116.1 (d, J_{F-C} = 21.4 Hz), 116.4, 121.6, 128.0, 129.9 (d, J_{F-C} = 3.0 Hz), 130.5 (d, J_{F-C} = 8.4 Hz), 135.1, 140.4, 141.1, 153.8, 156.0, 163.4 (d, J_{F-C} = 127.1 Hz). IR (KBr): ν 3276, 3208, 3131, 3069, 3007, 2961, 2933, 2856, 1672, 1652, 1607, 1582, 1525, 1508, 1472, 1435, 1330, 1270, 1232, 1209, 1155, 1125, 980, 945, 837, 745 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{11}FN_3O$ $[M - H]^+$ 292.0886, found 292.0894.

2-(4-Methoxyphenyl)-3-methylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4f**: Yield 86 % (262 mg). Pale yellow solid, m.p.: 280~282 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.32 (s, 3H), 3.83 (s, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.23~7.26 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.73~7.78 (m, 3H), 8.19 (d, *J* = 8.0 Hz, 1H), 11.85 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 8.7, 55.6, 93.4, 112.0, 114.5, 116.4, 121.5, 125.8, 128.0, 129.7, 134.9, 140.4, 140.9, 154.6, 156.0, 160.1. IR (KBr): ν 3280, 3217, 3141, 3075, 3009, 2938, 2870, 1666, 1612, 1582, 1531, 1510, 1493, 1474, 1437, 1347, 1333, 1303, 1291, 1250, 1222, 1174, 1112, 1019, 1006, 982, 838, 751 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{18}H_{14}N_3O_2$ $[M - H]^-$ 304.1086, found 304.1094.

2-(*p*-Tolyl)pyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4g**: Yield 79 % (217 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.37 (s, 3H), 6.55 (s, 1H), 7.26~7.32 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 12.37 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 21.4, 84.5, 112.1, 116.4, 121.8, 126.8, 128.0, 129.8, 129.9, 135.1, 139.2, 140.2, 143.7, 155.4, 156.0. IR (KBr): ν 3280, 3222, 3138, 3088, 3060, 3025, 2926, 2921, 1678, 1636, 1561, 1501, 1487, 1454, 1423, 1344, 1325, 1246, 1180, 1001, 940,

870, 826, 759 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{12}N_3O$ $[M - H]^-$ 274.0980, found 274.0992.

3-Ethyl-2-phenylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4h**: Yield 80 % (231 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.17 (t, *J* = 7.2 Hz, 3H), 2.80 (q, *J* = 7.2 Hz, 2H), 7.24~7.28 (m, 1H), 7.46~7.49 (m, 1H), 7.52~7.55 (m, 3H), 7.75~7.78 (m, 3H), 8.21 (d, *J* = 8.0 Hz, 1H), 11.87 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 15.3, 15.7, 100.7, 112.0, 116.5, 121.7, 128.0, 128.4, 129.1, 133.6, 135.1, 140.4, 140.6, 154.5, 156.1. IR (KBr): ν 3283, 3232, 3131, 3057, 3007, 2961, 2927, 2870, 1661, 1641, 1578, 1506, 1490, 1475, 1444, 1357, 1263, 1217, 1203, 1172, 1151, 1113, 1078, 1053, 1025, 943, 750, 718, 694 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{18}H_{14}N_3O$ $[M - H]^-$ 288.1137, found 288.1137.

3-Ethyl-7-methyl-2-phenylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4i**: Yield 76 % (230 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.16 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 2.80 (q, *J* = 7.2 Hz, 2H), 7.45~7.49 (m, 2H), 7.52~7.55 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 8.00 (s, 1H), 11.80 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 15.3, 15.7, 20.8, 100.4, 111.8, 116.5, 121.0, 128.3, 129.1, 130.9, 133.7, 136.5, 138.5, 140.7, 154.4, 156.0. IR (KBr): ν 3281, 3228, 3096, 3055, 3021, 2958, 2925, 2871, 1662, 1643, 1574, 1514, 1475, 1450, 1355, 1335, 1265, 1217, 1174, 1130, 1079, 1054, 1028, 952, 838, 773, 718, 700 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{19}H_{16}N_3O$ $[M - H]^-$ 302.1293, found 302.1292.

7-Bromo-2-phenyl-3-propylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4j**: Yield 76 % (290 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.16 (t, *J*

= 7.2 Hz, 3H), 1.97 (s, 2H), 2.78~2.83 (m, 2H), 7.49~7.56 (m, 4H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 1H), 8.26 (s, 1H), 12.06 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 15.3, 15.7, 21.9, 101.2, 112.9, 113.7, 119.1, 128.4, 129.2, 129.3, 129.8, 133.4, 137.6, 139.5, 140.4, 154.9, 155.0. IR (KBr): ν 3276, 3225, 3098, 3062, 3012, 2961, 2933, 2874, 1666, 1641, 1574, 1498, 1470, 1447, 1403, 1350, 1336, 1254, 1214, 1184, 1140, 1080, 1053, 1026, 952, 839, 769, 702 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{19}H_{15}N_3OBr$ $[M - H]^-$ 380.0398, found 380.0395.

2-(4-Chlorophenyl)-3-propylpyrazolo[5,1-*b*]quinazolin-9(4*H*)-one **4k**: Yield 81 % (273 mg). Pale yellow solid, m.p.: > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 0.90 (t, *J* = 7.2 Hz, 3H), 1.47~1.57 (m, 2H), 2.74~2.78 (m, 2H), 7.25~7.29 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.57~7.60 (m, 2H), 7.75~7.80 (m, 3H), 8.19~8.22 (m, 1H), 11.84 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ_c 14.1, 23.4, 24.2, 99.2, 112.0, 116.5, 121.7 128.0, 129.2, 130.2, 132.6, 133.9, 135.1, 140.5, 141.1, 153.5, 156.0. IR (KBr): ν 3366, 3092, 3071, 3008, 2966, 2932, 2838, 1671, 1589, 1529, 1456, 1432, 1372, 1345, 1316, 1300, 1273, 1255, 1205, 1159, 1095, 1059, 1000, 929, 836, 778, 724 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{19}H_{15}ClN_3O$ $[M - H]^-$ 336.0904, found 336.0903.

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