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Cascade synthesis of azoquinazolinones by Cu(I)-catalyzed C–N coupling/C–H activation/C–N formation reactions under O_2

Dingben Chen [a,b,*], Qiufang Chen [a], Miaochang Liu [b], Shuangqun Dai [a], Ling Huang [a], Jianguo Yang [a], Weiliang Bao [c,*]

[a] College of Pharmaceutical and Chemical Engineering, Taizhou University, Linhai, Zhejiang 317000, PR China
[b] Faculty of Chemistry & Material Engineering, Wenzhou University, Wenzhou, Zhejiang 325027 PR China
[c] Department of Chemistry, Xi Xi Campus, Zhejiang University, Hangzhou, Zhejiang 310028, PR China

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ABSTRACT

A 'one-pot' method has been developed for the synthesis of azoquinazolinones from substituted 2-halobenzamides and different *N*-heterocycles via Cu(I)-catalyzed C–N coupling/C–H activation/C–N formation process under O_2. A number of azoquinazolinones containing different azole rings and substituents were obtained in good yields.

1. Introduction

Quinazolinone derivatives have been widely found in numerous biologically active compounds and drug molecules.[1] Azoquinazolinone was a combined structure of quinazolinone and azole, such as imidazole, triazole, pyrazole, benzimidazole, theophylline, and so on. Azoquinazolinones also exhibit various biological and medicinal functions.[2] For example, as shown in Fig. 1, imidazole[1,2-*a*]quinazolinone-7-carboxamide (**1**) was disclosed as matrix metalloproteinase inhibitor. 4-Phenyl-1,2,4-triazolo[4,3-*a*]quinazolin-5(4*H*)-one (**2**) was a class of H_1-antihistaminic agents. Pyrazolo[1,5-*a*]quinazolinone-3-carboxylic acid derivatives (**3**) could be used as anti-inflammatory, anti-allergic, and anti-parasitic agents. As potential antitumor agents, purinoquinazolinone compound (**4**) was able to form a complex with DNA and to inhibit the topoisomerase II. In addition, benzimidazoquinazolinones have also attracted much attention for their application in antitumor agents and potential immunosuppressors.

Some approaches have been developed for the syntheses of azoquinazolinones.[3] For example, mercaptoquinazolones (I) could be used as key intermediates to synthesize 1,2,4-triazolo[4,3-*a*]quinazolin-5(4*H*)-ones via treating with[1] hydrazine and followed by ring closure upon heating in formic acid. Imidazole[1,2-*a*]quinazolinones could also be synthesized from intermediates (I), through chlorinating with $SOCl_2$ and reacting with dimethoxyethylamine, followed by cyclization in acidic media. The other literature had reported that 1,2,4-triazolo[1,5-*a*]quinazolin-5(4*H*)-one and pyrazolo[1,5-*a*]quinazolin-5(4*H*)-one

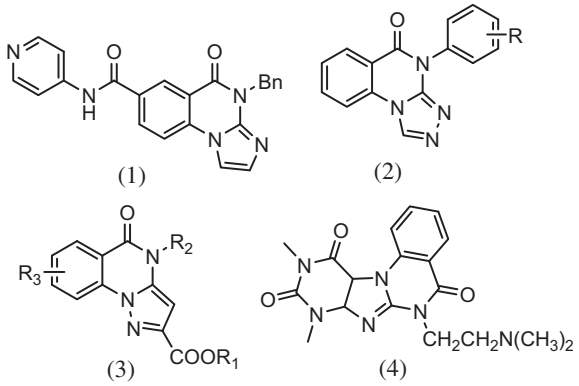

Fig. 1. Structures of some pharmaceutically important azoquinazolinone derivatives.

* Corresponding authors. Tel./fax: +86 571 88273814; e-mail addresses: chendb@tzc.edu.cn (D. Chen), wlbao@css.zju.edu.cn (W. Bao).

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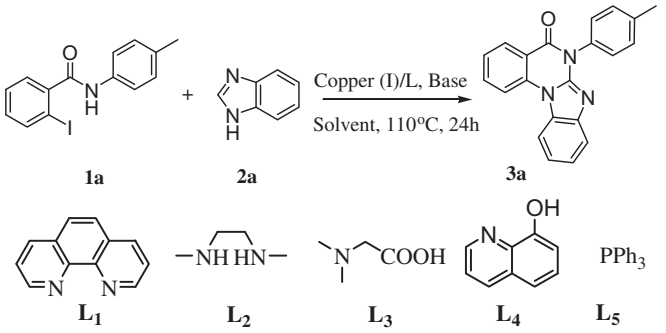
could be synthesized by reacting 2-hydrazinylbenzoic acid with *N*-cyanoformimidate or 3-oxoalkanenitrile. Recently, copper-catalyzed syntheses of azoquinazolinones have been reported. For example, CuBr-catalyzed condensation between 2-halobenzoic acid and 2-amniobenzimidazole or 8-aminotheophylline, could afford benzimidazol- and purino-quinazolinone.[2d,3d] Fu group reported that *N*-alkyl substituted benzimidazol- and imidazol-quinazolinones could be prepared by CuBr/(S)-proline catalyzed intermolecular Ullmann coupling reaction under N_2 for 12 h, then intramolecular C–H amidation under O_2 for 48 h. Although these methods are feasible for the syntheses of some title heterocycles, they have some disadvantages: (i) the expansion of the substrate is limited, for example, it is difficult to synthesize *N*-aryl substituted azoquinazolinones, and there are no common approaches for the syntheses of different azoquinazolinone. (ii) Most of the substituted products were obtained in low yield because of multi-steps. Therefore, it's highly desirable to search for common, convenient and efficient approaches for the title heterocycles, in particular, for *N*-aryl substituted azoquinazolinones.

In recent years, C–H functionalization strategy for C–C and C–heteroatom bond formation has attracted much attention because of its economic, sustainable, and environmentally benign features.[4] Most C–H activations have been implemented on palladium, rhodium, ruthenium, and copper catalysis. Recently, more and more copper-catalyzed/mediated C–H functionalization has been reported, due to the cheapness and relatively low toxicity of copper salts.[5] In addition, in the past decade, considerable progress has been made in the area of copper-catalyzed Ullmann coupling reaction to form C–X (X=C, N, O, S etc.) bond. More Recently, Ullmann coupling has been successfully applied to assemble various heterocyclic compounds by cascade reaction strategies.[6] Our research group has been engaged in copper-catalyzed cascade synthesis of heterocycles and has developed many tandem reactions to synthesize different heterocycles.[7] As the copper salts could catalyze both C–H activation and Ullmann coupling, we hope to develop new cascade methods to construct heterocycle. Herein, we report a reaction of azoles with 2-halo-*N*-ary(alk)benzamides via Cu(I)-catalyzed C–N coupling/C–H activation/C–N formation cyclization tandem process to synthesize azoquinazolinones, which includes different azole rings and substituents in good yield.

In our preliminary experiments, the reaction between 2-iodo-*N*-*p*-tolylbenzamide (**1a**) and 1*H*-benzo[*d*]imidazole (**2a**) was investigated to optimize the reaction conditions, including catalysts, bases, ligands, solvents, and temperature. The results are summarized in Table 1. Initially, the following reaction condition (10 mol % CuI, 20 mol % 1,10-phenanthroline, Cs_2CO_3 in DMF at 110 °C) was adopted to study the synthesis of 6-*p*-tolyl-benzimidazo[1,2-*a*]quinazolin-5(6*H*)-one **3a**. However, the yield of product **3a** was only 48%. Then Cu-catalysts were selected (entries 1–4), the others ($Cu(OAc)_2$, CuBr, $CuCl_2$) were worse than CuI. Different bases were examined, the weak base K_2CO_3 made the yield of **3a** decreased (30%, entry 6), but the strong base NaOEt improved the yield (62%, entry 5). Five ligands ($\mathbf{L_1}$–$\mathbf{L_5}$), including 1,10-phenanthroline, DMEDA, *N*,*N*-dimethylglycine, quinolin-8-ol and PPh_3 were evaluated (entries 7–9); 1,10-phenanthroline $\mathbf{L_1}$ was proved to be the most effective, DMEDA $\mathbf{L_2}$ and quinolin-8-ol $\mathbf{L_4}$ were not suitable for the reaction, only 10% and 12% isolated yield were obtained. In the absence of ligand, the product was obtained in 23% yield (entry 11). The effect of solvent, including PhMe, DMF, DMSO, NMP were tested. The yield was lowest in toluene (only 29%). When the reaction temperature reached 120 °C, the product yield was increased to 81%. However, when the reaction temperature was raised to 130 °C, the yield didn't improve (entry 16). Subsequently, the dosage of copper-catalyst was increased to 20%, the yield of product reached 84%. If the ligand $\mathbf{L_1}$ was also increased to 40%, to our delight, the reaction was enhanced greatly and the highest yield was obtained (97%, entry 18).

Table 1
Optimization of the reaction conditions of synthesis of 6-*p*-tolyl-benzimidazo[1,2-*a*]quinazolin-5(6*H*)-one[a]



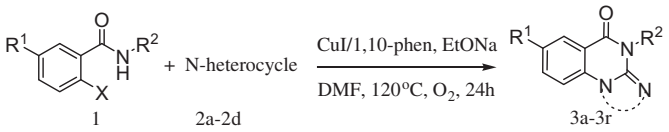
Entry	Cat.	Ligand	Base	Solvent	*T* (°C)	Yield[b] (%)
1	CuI	$\mathbf{L_1}$	Cs_2CO_3	DMF	110	48
2	$Cu(OAc)_2$	$\mathbf{L_1}$	Cs_2CO_3	DMF	110	45
3	CuBr	$\mathbf{L_1}$	Cs_2CO_3	DMF	110	28
4	$CuCl_2$	$\mathbf{L_1}$	Cs_2CO_3	DMF	110	47
5	CuI	$\mathbf{L_1}$	EtONa	DMF	110	62
6	CuI	$\mathbf{L_1}$	K_2CO_3	DMF	110	30
7	CuI	$\mathbf{L_2}$	EtONa	DMF	110	10
8	CuI	$\mathbf{L_3}$	EtONa	DMF	110	27
9	CuI	$\mathbf{L_4}$	EtONa	DMF	110	12
10	CuI	$\mathbf{L_5}$	EtONa	DMF	110	43
11	CuI	—	EtONa	DMF	110	23
12	CuI	$\mathbf{L_1}$	EtONa	PhMe	110	29
13	CuI	$\mathbf{L_1}$	EtONa	DMSO	110	58
14	CuI	$\mathbf{L_1}$	EtONa	NMP	110	40
15	CuI	$\mathbf{L_1}$	EtONa	DMF	120	81
16	CuI	$\mathbf{L_1}$	EtONa	DMF	130	80
17	CuI	$\mathbf{L_1}$	EtONa	DMF	120	84[c]
18	CuI	$\mathbf{L_1}$	EtONa	DMF	120	97[d]

[a] Reaction conditions: 2-iodo-*N*-*p*-tolylbenzamide **1a** (0.5 mmol), 1*H*-benzo[*d*]imidazole **2a** (0.5 mmol), copper source (0.05 mmol), ligand (0.1 mmol), and base (1.0 mmol) in solvent (2.0 mL) under O_2 for 24 h.
[b] Isolated yield.
[c] CuI (0.1 mmol).
[d] CuI (0.1 mmol), $\mathbf{L_1}$ (0.2 mmol).

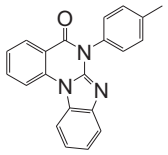
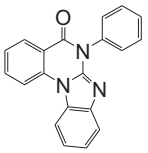
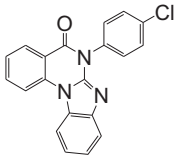
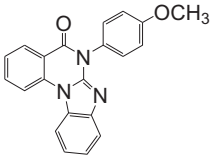
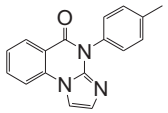
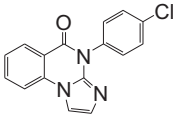
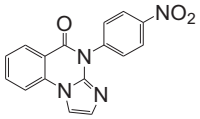
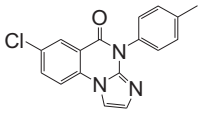
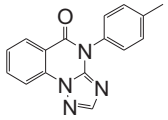
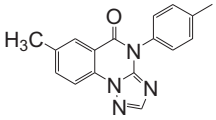
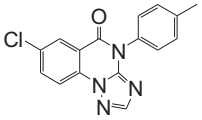
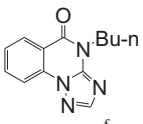
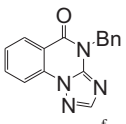
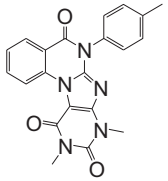
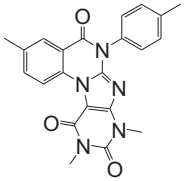
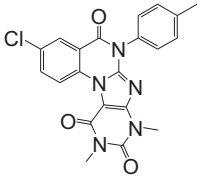
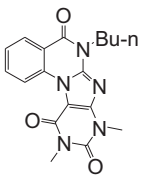
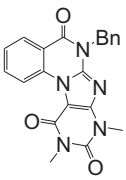
We then investigated the scope of the copper-catalyzed cascade reaction of substituted 2-iodo-benzamides and different azoles (**2a**–**d**) for the synthesis of azoquinazolinones under the optimized conditions determined above (20 mol % CuI and 40 mol % $\mathbf{L_1}$ in the presence of NaOEt as base in DMF under O_2 at 120 °C). As shown in Table 2, most benzimidazoquinazolinones and triazolo-quinazolinones were obtained in higher yield than imidazoloquinazolinones and purinoquinazolinones. The latters must be gained in higher reaction temperature (in between 130 °C and 140 °C). In *N*-aryl benzimidazoquinazolinones, the *p*-chlorophenyl and tolyl exhibited higher reactivity than phenyl and methoxyphenyl (Table 2, **3a**–**d**). We also investigated the influence of R^1 group on the product yield. The product with electron-donating R^1 group (CH_3–) was obtained in lower yield than those with electron-withdrawing group (Cl–) or H atom (Table 2, **3i**–**k**, **3n**–**p**). The cascade reaction also produced *N*-alkyl products, *N*-benzyl and butyl triazoloquinazolinones, and purinoquinazolinones as listed in Table 2. *N*-Alkyl triazoloquinazolinones were obtained in DMF under N_2 for 24 h at 120 °C, then O_2 for 24 h at 140 °C. The molecular structure of **3i** and **3z** were unambiguously elucidated by X-ray crystallography (Fig. 2).

To the best of our knowledge, there was no report about C–H activation/C–N formation of pyrazole. However, in this work, C–H amination of pyrazole could occur in the tandem reaction to synthesize pyrazolo[1,5-*a*]quinazolinone from the reaction of substituted 2-iodo-benzamides with pyrazole. The scope of the reaction was also investigated (Table 3, **3s**–**dd**). Most of pyrazolo

Table 2
CuI-catalyzed one-pot synthesis of azoquinazolinones from 2-iodo-benzamides and *N*-heterocycles[a]



R^1= H, Me, Cl, NO_2 R_2= Aryl or alkyl

Compound no. Yield[b] [%]				
 3a 49%[c]	 3b, 74%	 3c, 90%	 3d, 73%	
 3e, 81%[d]	 3f, 70%[d]	 3g, 68%[d]	 3h, 75%[d]	
 3i, 89%	 3j, 51%	 3k, 80%	 3l, 84%[f]	 3m, 83%[f]
 3n, 67%[e]	 3o, 52%[e]	 3p, 63%[e]	 3q, 62%[e]	 3r, 65%[e]

[a]Reaction conditions: 2-iodo-benzamide **1** (0.5 mmol), *N*-heterocycle **2** (0.5 mmol), CuI (0.1 mmol), 1,10-phen (0.2 mmol), and EtONa (1.0 mmol) in DMF (2.0 mL) under O_2 for 24 h.
[b]Isolated yield.
[c]2-Bromo-*N*-*p*-tolylbenzamide (0.5 mmol).
[d]130 °C.
[e]140 °C.
[f]Under N_2 for 24 h in 120 °C, then O_2 for 24 h in 140 °C.

[1,5-*a*]quinazolinones could be obtained in good yield under the optimized conditions. Among the examination of *N*-aryl group of 2-iodo-benzamides, the *N*-aryl substrate with electron-donating groups (CH_3、OCH_3) gave lower yield of product than the others with electron-withdrawing groups (Cl、NO_2) (Table 3, **3s**–**w**). The products with electron-withdrawing R^1 group (Cl–, NO_2), **3z**, **3aa**, and **3bb** were obtained in higher yield than the others (**3s**, **3x**, **3y**). *N*-Alkyl pyrazolo[1,5-*a*]quinazolinones were also obtained in moderate yield (Table 3, **3cc**,**dd**).

In summary, a method for the assembly of azoquinazolinones has been developed, which relied on copper-catalyzed one-pot reaction of 2-halo-benzamides with azoles via cascade C–N coupling/C–H amination process. Most azoquinazolinones containing different azole rings and substituents were obtained in good yields. This method should be valuable for the construction of these kinds of molecules with biological and medicinal activities, so it may find application in organic synthesis.

2. Experimental section

2.1. Typical experimental procedures for the Cu(I)-catalyzed one-pot synthesis of azoquinazolinones

An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, 2-iodo-benzamides **1** (0.5 mmol), *N*-heterocycle **2** (0.5 mmol), CuI (20 mg, 0.1 mmol, 20 mol %), 1,10-phenanthroline (40 mg, 0.10 mmol, 40 mol %), NaOEt (68 mg, 1.0 mmol), and DMF (2.0 mL). The tube was evacuated and back-filled with O_2 balloon. The mixture was stirred at 120 °C for 24 h. After the reaction was completed, the mixture was extracted with dichloromethane (3×15 mL), and then the organic layer was washed with brine (3×10 mL) and dried with anhydrous Na_2SO_4. Subsequently, the solvent was removed and the product was purified by column chromatography on silica gel to give the pure azoquinazolinone.

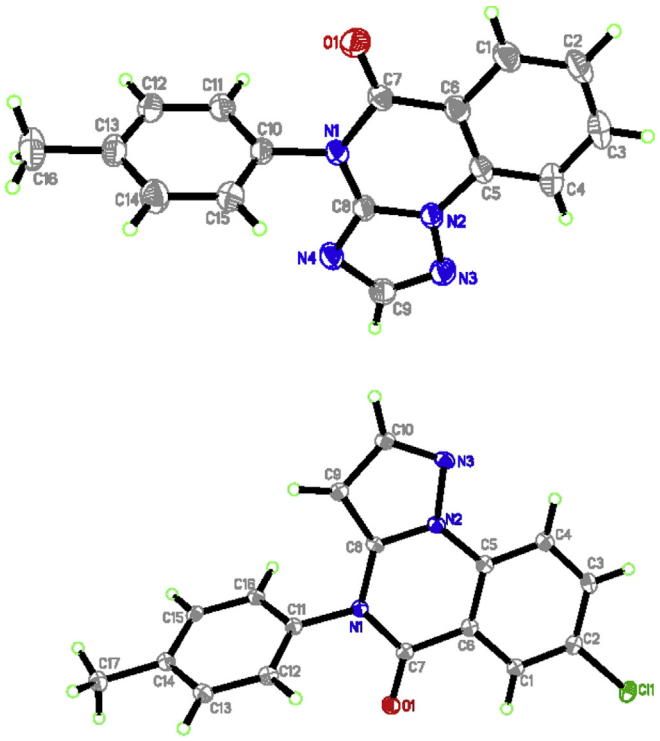


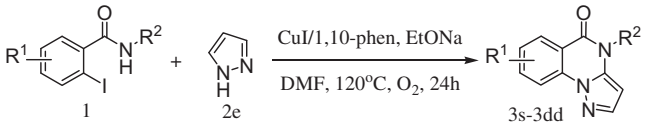
Fig. 2. X-ray crystallographs for **3i** and **3z**.

found: C 77.81, H 4.73, N 12.87; EI-MS: m/z=325 (M^+). HRMS (ESI) for $C_{21}H_{15}N_3O$ $(M+H)^+$: calcd 326.1215, found 326.1219.

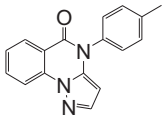
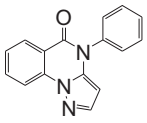
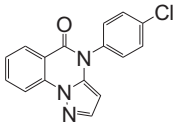
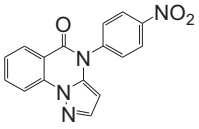
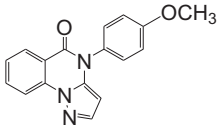
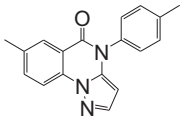
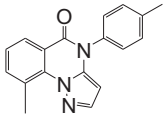
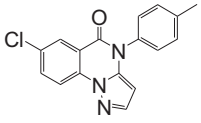
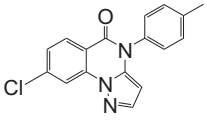
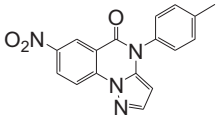
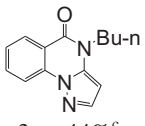
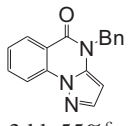
*2.1.2. 6-Phenyl-benzimidazo[1,2-a]quinazolin-5(6H)-one (**3b**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=1:1) to give a light yellow solid (115.1 mg, 74%), mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, J=8.0, 1.0 Hz, 1H), 8.30 (d, J=8.5 Hz, 1H), 8.08–8.06 (m, 1H), 7.94–7.91 (m, 1H), 7.75–7.72 (m, 1H), 7.64–7.61 (m, 2H), 7.57–7.49 (m, 4H), 7.39–7.35 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 147.5, 142.4, 137.2, 135.4, 135.3, 130.5, 129.8, 129.4, 128.5, 125.0, 124.2, 122.5, 119.8, 117.1, 114.5, 112.3. Anal. Calcd for $C_{20}H_{13}N_3O$: C 77.16, H 4.21, N 13.50; found: C 76.98, H 4.30, N 13.67; EI-MS: m/z=311 (M^+). HRMS (ESI) for $C_{20}H_{13}N_3O$ $(M+H)^+$: calcd 312.1059, found 312.1063.

*2.1.3. 6-(4-Chlorophenyl)-benzimidazo[1,2-a]quinazolin-5(6H)-one (**3c**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=1:1) to give a light yellow solid (155.6 mg, 90%); mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (dd, J=8.0, 1.5 Hz, 1H), 8.30 (d, J=8.5 Hz, 1H), 8.08–8.06 (m, 1H), 7.95–7.92 (m, 1H), 7.75–7.73 (m, 1H), 7.59–7.57 (m, 2H), 7.52 (t, J=7.5 Hz, 1H), 7.46–7.43 (m, 2H), 7.40–7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 147.2, 142.3, 137.2, 135.5, 135.4, 133.7, 130.6, 130.1, 129.9, 125.2, 124.3, 122.7, 119.8, 116.9, 114.5, 112.4; Anal. Calcd for $C_{20}H_{12}ClN_3O$: C 69.47, H 3.50, N 12.15; found: C 69.30, H 3.62, N 11.88; EI-MS: m/z=345 (M^+). HRMS (ESI) for $C_{20}H_{12}ClN_3O$ $(M+H)^+$: calcd 346.0669, found 346.0671.

Table 3
CuI-catalyzed one-pot synthesis of pyrazolo[1,5-*a*]quinazolinones from 2-iodo-benzamides and pyrazole[a]



R^1= H, Me, Cl, NO_2 R_2= Aryl or alkyl

Compound no. Yield[b] [%]					
 3s, 67%	 3t, 74%	 3u, 89%	 3v, 82%	 3w, 61%	 3x, 62%
 3y, 59%	 3z, 78%	 3aa, 80%	 3bb, 76%	 3cc, 44%[c]	 3dd, 55%[c]

[a]Reaction conditions: 2-iodo-benzamide **1** (0.5 mmol), pyrazole **2e** (0.5 mmol), CuI (0.1 mmol), 1,10-phen (0.2 mmol), and EtONa (1.0 mmol) in DMF (2.0 mL) under O_2 for 24 h.
[b]Isolated yield.
[c]Under N_2 for 24 h in 120 °C, then O_2 for 24 h in 140 °C.

*2.1.1. 6-p-Tolyl-benzimidazo[1,2-a]quinazolin-5(6H)-one (**3a**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=1:1) to give a light yellow solid (157.6 mg, 97%), mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, J=8.0, 1.5 Hz, 1H), 8.29 (d, J=8.5 Hz, 1H), 8.07–8.05 (m, 1H), 7.93–7.90 (m, 1H), 7.75–7.73 (m, 1H), 7.50 (t, J=7.5 Hz, 1H), 7.42–7.41 (m, 2H), 7.37–7.35 (m, 4H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 147.7, 142.6, 139.3, 137.2, 135.2, 132.7, 130.6, 130.5, 128.1, 128.1, 125.0, 124.1, 122.4, 119.9, 117.1, 114.4, 112.3, 21.4; Anal. Calcd for $C_{21}H_{15}N_3O$: C 77.52, H 4.65, N 12.91;

*2.1.4. 6-(4-Methoxyphenyl)-benzimidazo[1,2-a]quinazolin-5(6H)-one (**3d**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=1:1) to give a light yellow solid (124.4 mg, 73%); mp >300 °C; Yellow solid; mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, J=7.5, 1.5 Hz, 1H), 8.30 (d, J=8.0 Hz, 1H), 8.07–8.06 (m, 1H), 7.94–7.90 (m, 1H), 7.75–7.74 (m, 1H), 7.51 (t, J=7.5 Hz, 1H), 7.41–7.36 (m, 4H), 7.13–7.10 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 159.7, 147.5, 140.7, 137.2, 135.2, 130.5, 129.4, 127.9, 125.0, 124.2, 124.1, 122.4, 119.9, 117.1, 115.1, 114.4, 112.3,

55.5. Anal. Calcd for $C_{21}H_{15}N_3O_2$: C 73.89, H 4.43, N 12.31; found: C 74.15, H 4.51, N 12.14; EI-MS: m/z=341 (M^+). HRMS (ESI) for $C_{21}H_{15}N_3O_2$ $(M+H)^+$: calcd 342.1164, found 342.1168.

*2.1.5. 4-p-Tolyl-imidazo[1,2-a]quinazolin-5(4H)-one (**3e**).* Synthesized according to the typical procedure at 130 °C and purified by column chromatography (dichloromethane/ethyl acetate=3:1) to give a light yellow solid (111.5 mg, 81%); mp 229–231 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (dd, J=8.0, 1.0 Hz, 1H), 7.82–7.79 (m, 1H), 7.63 (d, J=8.5 Hz, 1H), 7.52 (d, J=1.5 Hz, 1H), 7.48 (t, J=7.5 Hz, 1H), 7.38–7.35 (m, 2H), 7.33–7.31 (m, 2H), 7.10 (d, J=1.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 139.1, 135.2, 134.8, 132.6, 130.4, 130.3, 129.1, 128.0, 126.7, 125.6, 117.3, 114.2, 109.2, 21.3; Anal. Calcd for $C_{17}H_{13}N_3O$: C 74.17, H 4.76, N 15.26; found: C 74.05, H 4.79, N 15.48; EI-MS: m/z=275 (M^+). HRMS (ESI) for $C_{17}H_{13}N_3O$ $(M+H)^+$: calcd 276.1059, found 276.1060.

*2.1.6. 4-(4-Chlorophenyl)-imidazo[1,2-a]quinazolin-5(4H)-one (**3f**).* Synthesized according to the typical procedure at 130 °C and purified by column chromatography (dichloromethane/ethyl acetate=3:1) to give a light yellow solid (103.5 mg, 70%); mp 256–258 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, J=7.5 Hz, 1H), 7.83 (t, J=8.0 Hz, 1H), 7.64 (d, J=8.0 Hz, 1H), 7.55–7.48 (m, 4H), 7.42–7.40 (m, 2H), 7.11 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 135.2, 135.1, 133.7, 130.3, 129.9, 129.8, 129.0, 125.8, 117.1, 114.3, 109.5, 107.3; Anal. Calcd for $C_{16}H_{10}ClN_3O$: C 64.98, H 3.41, N 14.21; found: C 64.65, H 3.46, N 13.97; EI-MS: m/z=295 (M+). HRMS (ESI) for $C_{16}H_{10}ClN_3O$ $(M+H)^+$: calcd 296.0512, found 296.0519.

*2.1.7. 4-(4-Nitrophenyl)-imidazo[1,2-a]quinazolin-5(4H)-one (**3g**).* Synthesized according to the typical procedure at 130 °C and purified by column chromatography (dichloromethane/ethyl acetate=3:1) to give a light yellow solid (104.1 mg, 68%); mp 262–264 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44–8.43 (m, 3H), 7.88–7.84 (m, 1H), 7.72–7.70 (m, 2H), 7.66 (d, J=8.0 Hz, 1H), 7.56 (d, J=1.5 Hz, 1H), 7.57–7.50 (m, 1H), 7.11 (d, J=1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 147.8, 142.1, 140.7, 135.5, 135.2, 130.4, 129.8, 128.9, 126.0, 124.8, 116.8, 114.4, 109.8; Anal. Calcd for $C_{16}H_{10}N_4O_3$: C 62.74, H 3.29, N 18.29; found: C 62.81, H 3.34, N 18.11; EI-MS: m/z=306 (M+). HRMS (ESI) for $C_{16}H_{10}N_4O_3$ $(M+H)^+$: calcd 307.0753, found 307.0753.

*2.1.8. 7-Chloro-4-p-tolylimidazo[1,2-a]quinazolin-5(4H)-one (**3h**).* Synthesized according to the typical procedure at 130 °C and purified by column chromatography (dichloromethane/ethyl acetate=3:1) to give a light yellow solid (116.2 mg, 75%); mp 254–256 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J=5.0 Hz, 1H), 7.76 (dd, J=9.0, 2.5 Hz, 1H), 7.58 (d, J=9.0 Hz, 1H), 7.48 (d, J=1.5 Hz, 1H), 7.38–7.37 (m, 2H), 7.32–7.30 (m, 2H), 7.11 (d, J=1.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 139.4, 134.9, 133.7, 132.4, 131.5, 130.5, 129.8, 129.4, 127.9, 118.6, 115.9, 109.3, 21.3; Anal. Calcd for $C_{17}H_{12}ClN_3O$: C 65.92, H 3.90, N 13.57; found: C 65.67, H 4.03, N 13.31; EI-MS: m/z=309 (M+). HRMS (ESI) for $C_{17}H_{12}ClN_3O$ $(M+H)^+$: calcd 310.0669, found 310.0675.

*2.1.9. 4-p-Tolyl-[1,2,4]triazolo[1,5-a]quinazolin-5(4H)-one (**3i**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (122.9 mg, 89%); mp 265–267 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, J=10.0 Hz, 1H), 8.15 (d, J=10.0 Hz, 1H), 7.92–7.89 (m, 2H), 7.55 (t, J=10.0 Hz, 1H), 7.39 (d, J=5.0 Hz, 2H), 7.33 (d, J=5.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 151.5, 149.8, 139.7, 135.6, 135.5, 132.0, 130.5, 129.7, 127.6, 126.6, 116.7, 115.0, 21.3. HRMS (ESI) for $C_{16}H_{12}N_4O$ $(M+H)^+$: calcd 277.1011, found 277.1013.

*2.1.10. 7-Methyl-4-p-tolyl-[1,2,4]triazolo[1,5-a]quinazolin-5(4H)-one (**3j**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (74.0 mg, 51%); mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.03 (d, J=8.5 Hz, 1H), 7.90 (s, 1H), 7.69 (dd, J=8.5, 1.5 Hz, 1H), 7.39 (d, J=8.0 Hz, 2H), 7.32 (d, J=8.0 Hz, 2H), 2.52 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 151.2, 149.5, 139.6, 136.9, 136.6, 133.6, 132.1, 130.5, 129.4, 127.6, 116.5, 114.9, 21.3, 21.1. HRMS (ESI) for $C_{17}H_{14}N_4O$ $(M+H)^+$: calcd 291.1168, found 291.1169.

*2.1.11. 7-Chloro-4-p-tolyl-[1,2,4]triazolo[1,5-a]quinazolin-5(4H)-one (**3k**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (124.3 mg, 80%); mp 227–229 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J=2.0 Hz, 1H), 8.10 (d, J=9.0 Hz, 1H), 7.92 (s, 1H), 7.83 (dd, J=9.0, 2.5 Hz, 1H), 7.39 (d, J=8.5 Hz, 2H), 7.32 (d, J=8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 151.7, 149.7, 139.9, 135.7, 134.1, 132.7, 131.7, 130.5, 129.2, 127.5, 118.0, 116.7, 21.3; Anal. Calcd for $C_{16}H_{11}ClN_4O$: C 61.84, H 3.57, N 18.03; found: C 61.73, H 3.68, N 17.85; EI-MS: m/z=310 (M^+). HRMS (ESI) for $C_{16}H_{11}ClN_4O$ $(M+H)^+$: calcd 311.0621, found 311.0627.

*2.1.12. 4-Butyl-[1,2,4]triazolo[1,5-a]quinazolin-5(4H)-one (**3l**).* Synthesized according to the typical procedure under N_2 for 24 h at 120 °C, then O_2 for 24 h at 140 °C, and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (101.6 mg, 84%); mp 68–70 °C; δ 8.36 (dd, J=8.0, 1.0 Hz, 1H), 8.07 (d, J=8.0 Hz, 1H), 7.99 (s, 1H), 7.84–7.81 (m, 1H), 7.52–7.49 (m, 1H), 4.31 (t, J=7.5 Hz, 2H), 1.85–1.79 (m, 2H), 1.48–1.41 (m, 2H), 0.97 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 151.5, 149.2, 135.4, 135.0, 129.3, 126.4, 116.6, 114.8, 43.9, 29.6, 20.1, 13.7; Anal. Calcd for $C_{13}H_{14}N_4O$: C 64.45, H 5.82, N 23.13; found: C 64.23, H 5.97, N 22.96; EI-MS: m/z=242 (M^+). HRMS (ESI) for $C_{13}H_{14}N_4O$ $(M+H)^+$: calcd 243.1168, found 243.1171.

*2.1.13. 4-Benzyl-[1,2,4]triazolo[1,5-a]quinazolin-5(4H)-one (**3m**).* Synthesized according to the typical procedure under N_2 for 24 h at 120 °C, then O_2 for 24 h at 140 °C, and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (114.5 mg, 83%); mp 250–252 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35–8.32 (m, 1H), 8.03–7.99 (m, 2H), 7.80–7.76 (m, 1H), 7.60 (d, J=7.0 Hz, 2H), 7.48–7.46 (m, 1H), 7.35–7.24 (m, 3H), 5.48 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 151.4, 149.1, 135.6, 135.3, 135.1, 129.3, 129.1, 128.5, 128.1, 126.4, 116.5, 114.8, 47.0. HRMS (ESI) for $C_{16}H_{12}N_4O$ $(M+H)^+$: calcd 277.1011, found 277.1016.

*2.1.14. 8,10-Dimethyl-6-p-tolylpurino[7,8-a]quinazoline-5,9,11(6H,8H,10H)-trione (**3n**).* Synthesized according to the typical procedure at 140 °C and purified by column chromatography (dichloromethane/acetone=30:1) to give a light yellow solid (129.7 mg, 67%); mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (d, J=5.0 Hz, 1H), 8.40 (d, J=5.0 Hz, 1H), 7.89–7.85 (m, 1H), 7.53–7.50 (m, 1H), 7.38 (d, J=5.0 Hz, 2H), 7.29 (d, J=10.0 Hz, 2H), 3.50 (s, 3H), 3.46 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 154.0, 151.1, 150.5, 147.2, 139.4, 135.9, 135.5, 132.1, 130.2, 129.4, 127.9, 126.4, 120.1, 116.9, 104.0, 30.2, 29.0, 21.3; Anal. Calcd for $C_{21}H_{17}N_5O_3$: C 65.11, H 4.42, N 18.08; found: C 65.32, H 4.45, N 17.91; EI-MS: m/z=387 (M^+). HRMS (ESI) for $C_{21}H_{17}N_5O_3$ $(M+H)^+$: calcd 388.1331, found 388.1335.

*2.1.15. 3,8,10-Trimethyl-6-p-tolylpurino[7,8-a]quinazoline-5,9,11(6H,8H,10H)-trione (**3o**).* Synthesized according to the typical procedure at 140 °C and purified by column chromatography

(dichloromethane/acetone=30:1) to give a light yellow solid (104.3 mg, 52%); mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (d, J=9.0 Hz, 1H), 8.18 (s, 1H), 7.67 (t, J=1.5 Hz, 1H), 7.38 (d, J=8.5 Hz, 2H), 7.27 (d, J=8.5 Hz, 2H), 3.49 (s, 3H), 3.45 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 154.0, 151.2, 150.4, 146.9, 139.4, 136.6, 136.5, 133.8, 132.2, 130.2, 129.0, 128.0, 120.1, 116.8, 104.0, 30.2, 29.0, 21.3, 20.9; Anal. Calcd for $C_{22}H_{19}N_5O_3$: C 65.83, H 4.77, N 17.45; found: C 66.06, H 4.75, N 17.36; EI-MS: m/z=401 (M^+). HRMS (ESI) for $C_{22}H_{19}N_5O_3$ $(M+H)^+$: calcd 402.1488, found 402.1489.

*2.1.16. 3-Chloro-8,10-dimethyl-6-p-tolylpurino[7,8-a]quinazoline-5,9,11(6H,8H,10H)-trione (**3p**).* Synthesized according to the typical procedure at 140 °C and purified by column chromatography (dichloromethane/acetone=30:1) to give a light yellow solid (132.6 mg, 63%); mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (d, J=9.5 Hz, 1H), 8.35 (d, J=2.5 Hz, 1H), 7.80 (dd, J=9.0, 2.5 Hz, 1H), 7.38 (d, J=8.0 Hz, 2H), 7.28 (d, J=2.5 Hz, 2H), 3.49 (s, 3H), 3.45 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 154.0, 151.0, 150.5, 147.0, 139.7, 135.5, 134.3, 132.5, 131.8, 130.3, 128.7, 127.8, 122.1, 118.3, 104.0, 30.3, 29.0, 21.3; Anal. Calcd for $C_{21}H_{16}ClN_5O_3$: C 59.79, H 3.82, N 16.60; found: C 60.01, H 3.96, N 16.37; EI-MS: m/z=421 (M^+). HRMS (ESI) for $C_{21}H_{16}ClN_5O_3$ $(M+H)^+$: calcd 422.0942, found 422.0946.

*2.1.17. 6-Butyl-8,10-dimethylpurino[7,8-a]quinazoline-5,9,11(6H,8H,10H)-trione (**3q**).* Synthesized according to the typical procedure at 140 °C and purified by column chromatography (dichloromethane/acetone=30:1) to give a light yellow solid (109.4 mg, 62%); mp 224–226 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (d, J=8.5 Hz, 1H), 8.38 (d, J=8.0 Hz, 1H), 7.84 (t, J=7.0 Hz, 1H), 7.50 (t, J=7.5 Hz, 2H), 4.41 (t, J=7.5 Hz, 2H), 3.66 (s, 3H), 3.51 (s, 3H), 1.85–1.79 (m, 2H), 1.46–1.43 (m, 2H), 1.01 (t, J=7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 154.0, 151.2, 150.7, 146.7, 135.7, 135.1, 129.0, 126.3, 120.0, 116.7, 104.1, 43.7, 30.2, 29.5, 29.0, 20.0, 13.7; Anal. Calcd for $C_{18}H_{19}N_5O_3$: C 61.18, H 5.42, N 19.82; found: C 61.05, H 5.43, N 20.03; EI-MS: m/z=353 (M^+). HRMS (ESI) for $C_{18}H_{19}N_5O_3$ $(M+H)^+$: calcd 354.1488, found 354.1490.

*2.1.18. 6-Benzyl-8,10-dimethylpurino[7,8-a]quinazoline-5,9,11(6H,8H,10H)-trione (**3r**).* Synthesized according to the typical procedure at 140 °C and purified by column chromatography (dichloromethane/acetone=30:1) to give a light yellow solid (125.8 mg, 65%); mp 209–211 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (d, J=8.5 Hz, 1H), 8.40 (dd, J=8.0, 1.5 Hz, 1H), 7.85–7.81 (m, 1H), 7.61–7.60 (m, 2H), 7.51–7.48 (m, 1H), 7.33–7.27 (m, 3H), 5.58 (s, 2H), 3.68 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 153.9, 151.1, 150.5, 146.5, 135.6, 135.3, 129.3, 129.1, 128.5, 128.2, 126.9, 126.3, 120.1, 116.7, 104.2, 46.8, 30.2, 29.0; Anal. Calcd for $C_{21}H_{17}N_5O_3$: C 65.11, H 4.42, N 18.08; found: C 64.98, H 4.46, N 17.82; EI-MS: m/z=387 (M^+). HRMS (ESI) for $C_{21}H_{17}N_5O_3$ $(M+H)^+$: calcd 388.1331, found 388.1331.

*2.1.19. 4-p-Tolylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3s**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=1:1) to give a light yellow solid (92.2 mg, 67%); mp 157–158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (dd, J=8.0, 1.0 Hz, 1H), 8.22 (d, J=8.5 Hz, 1H), 7.84–7.80 (m, 1H), 7.66 (d, J=1.5 Hz, 1H), 7.47–7.44 (m, 1H), 7.37 (d, J=8.0 Hz, 2H), 7.31 (d, J=8.5 Hz, 2H), 5.49 (d, J=2.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 141.7, 139.3, 137.7, 134.9, 134.1, 130.6, 129.4, 127.4, 125.4, 116.3, 114.7, 90.9, 21.3; Anal. Calcd for $C_{17}H_{13}N_3O$: C 74.17, H 4.76, N 15.26; found: C 74.10, H 4.63, N 15.40; EI-MS: m/z=275 (M^+). HRMS (ESI) for $C_{17}H_{13}N_3O$ $(M+H)^+$: calcd 276.1059, found 276.1066.

*2.1.20. 4-Phenylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3t**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (96.6 mg, 74%); mp 154–155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (dd, J=7.5, 1.0 Hz, 1H), 8.23 (d, J=8.0 Hz, 1H), 7.84–7.80 (m, 1H), 7.66 (d, J=2.0 Hz, 1H), 7.59–7.56 (m, 2H), 7.53–7.50 (m, 1H), 7.47–7.44 (m, 3H), 5.49 (d, J=2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 141.7, 141.6, 137.8, 136.8, 135.0, 129.9, 129.4, 129.3, 127.8, 125.5, 116.3, 114.7, 90.9; Anal. Calcd for $C_{16}H_{11}N_3O$: C 73.55, H 4.24, N 16.08; found: C 73.78, H 4.09, N 16.33; EI-MS: m/z=261 (M^+). HRMS (ESI) for $C_{16}H_{11}N_3O$ $(M+H)^+$: calcd 262.0902, found 262.0903.

*2.1.21. 4-(4-Chlorophenyl)pyrazolo[1,5-a]quinazolin-5(4H)-one (**3u**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (131.2 mg, 89%); mp 214–216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J=7.5 Hz, 1H), 8.22 (d, J=8.5 Hz, 1H), 7.83 (t, J=8.0 Hz, 1H), 7.67 (d, J=1.5 Hz, 1H), 7.55 (d, J=9.0 Hz, 2H), 7.46 (t, J=7.5 Hz, 1H), 7.40 (d, J=8.5 Hz, 2H), 5.51 (d, J=2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 141.8, 141.2, 137.8, 135.3, 135.2, 130.3, 129.4, 129.2, 125.6, 116.0, 114.8, 90.8; Anal. Calcd for $C_{16}H_{10}ClN_3O$: C 64.98, H 3.41, N 14.21; found: C 65.10, H 3.43, N 14.40; EI-MS: m/z=295 (M^+). HRMS (ESI) for $C_{16}H_{10}ClN_3O$ $(M+H)^+$: calcd 296.0512, found 296.0515.

*2.1.22. 4-(4-Nitrophenyl)pyrazolo[1,5-a]quinazolin-5(4H)-one (**3v**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (125.5 mg, 82%); mp 223–225 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46–8.44 (m, 2H), 8.34 (dd, J=8.0, 1.0 Hz, 1H), 8.25 (d, J=8.0 Hz, 1H), 7.88–7.85 (m, 1H), 7.71–7.69 (m, 3H), 7.50–7.47 (m, 1H), 5.56 (d, J=2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 147.9, 142.2, 141.8, 140.3, 137.8, 135.6, 129.4, 129.2, 125.9, 125.3, 115.7, 115.0, 90.8; Anal. Calcd for $C_{16}H_{10}N_4O_3$: C 62.74, H 3.29, N 18.29; found: C 63.02, H 3.41, N 18.47; EI-MS: m/z=306 (M^+). HRMS (ESI) for $C_{16}H_{10}N_4O_3$ $(M+H)^+$: calcd 307.0753, found 307.0754.

*2.1.23. 4-(4-Methoxyphenyl)pyrazolo[1,5-a]quinazolin-5(4H)-one (**3w**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (88.7 mg, 61%); mp 179–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (dd, J=8.0, 1.0 Hz, 1H), 8.22 (d, J=8.0 Hz, 1H), 7.83–7.80 (m, 1H), 7.66 (d, J=2.0 Hz, 1H), 7.46–7.43 (m, 1H), 7.36–7.33 (m, 2H), 7.08–7.05 (m, 2H), 5.50 (d, J=2.0 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 158.9, 141.9, 141.7, 137.8, 135.0, 129.4, 128.9, 125.5, 116.3, 115.2, 115.2, 114.7, 90.9, 55.6; Anal. Calcd for $C_{17}H_{13}N_3O_2$: C 70.09, H 4.50, N 14.42; found: C 69.95, H 4.58, N 14.37; EI-MS: m/z=291 (M^+). HRMS (ESI) for $C_{17}H_{13}N_3O_2$ $(M+H)^+$: calcd 292.1008, found 292.1010.

*2.1.24. 7-Methyl-4-p-tolylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3x**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (89.6 mg, 62%); mp 140–142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.10 (d, J=8.0 Hz, 1H), 7.63–7.61 (m, 2H), 7.36 (d, J=8.0 Hz, 2H), 7.30 (d, J=8.5 Hz, 2H), 5.47 (d, J=2.0 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 141.4, 141.3, 139.3, 136.0, 135.7, 135.5, 134.3, 130.6, 129.0, 127.5, 116.1, 114.6, 90.7, 21.3, 21.0; Anal. Calcd for $C_{18}H_{15}N_3O$: C 74.72, H 5.23, N 14.52; found: C 74.67, H 5.06, N 14.67; EI-MS: m/z=289 (M^+). HRMS (ESI) for $C_{18}H_{15}N_3O$ $(M+H)^+$: calcd 290.1215, found 290.1219.

*2.1.25. 9-Methyl-4-p-tolylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3y**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (85.2 mg, 59%); mp 137–139 °C; ^{1}H NMR

(500 MHz, $CDCl_3$) δ 8.28 (d, J=7.5 Hz, 1H), 7.65–7.60 (m, 3H), 7.37–7.29 (m, 5H), 5.48 (s, 1H), 3.01 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 142.2, 140.6, 139.3, 138.5, 136.5, 134.4, 130.6, 127.5, 127.5, 125.0, 117.6, 90.1, 23.3, 21.3; HRMS (ESI) for $C_{18}H_{15}N_3O$ $(M+H)^+$: calcd 290.1215, found 290.1216.

*2.1.26. 7-Chloro-4-p-tolylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3z**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (120.5 mg, 78%); mp 132–134 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.16 (d, J=9.0 Hz, 1H), 7.75 (d, J=8.5 Hz, 1H), 7.65 (s, 1H), 7.37 (d, J=7.5 Hz, 2H), 7.30 (d, J=8.0 Hz, 2H), 5.51 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 142.0, 141.6, 139.6, 136.2, 135.1, 133.9, 131.3, 130.6, 128.8, 127.3, 117.5, 116.5, 91.2, 21.3; Anal. Calcd for $C_{17}H_{12}ClN_3O$: C 65.92, H 3.90, N 13.57; found: C 66.12, H 3.83, N 13.43; EI-MS: m/z=309 (M^+). HRMS (ESI) for $C_{17}H_{12}ClN_3O$ $(M+H)^+$: calcd 310.0669, found 310.0670.

*2.1.27. 8-Chloro-4-p-tolylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3aa**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (123.5 mg, 80%); mp 177–179 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J=8.5 Hz, 1H), 8.22 (d, J=2.0 Hz, 1H), 7.65 (d, J=1.5 Hz, 1H), 7.40–7.36 (m, 3H), 7.30 (d, J=8.5 Hz, 2H), 5.49 (d, J=2.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 142.2, 142.0, 141.6, 139.5, 138.3, 133.8, 130.9, 130.6, 127.3, 125.9, 114.9, 114.6, 91.2, 21.3; HRMS (ESI) for $C_{17}H_{12}ClN_3O$ $(M+H)^+$: calcd 310.0669, found 310.0676.

*2.1.28. 7-Nitro-4-p-tolylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3bb**).* Synthesized according to the typical procedure and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (121.6 mg, 76%); mp 210–212 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, J=2.5 Hz, 1H), 8.64 (dd, J=9.0, 2.5 Hz, 1H), 8.35 (d, J=9.0 Hz, 1H), 7.74 (d, J=2.0 Hz, 1H), 7.39 (d, J=8.0 Hz, 2H), 7.31 (d, J=8.5 Hz, 2H), 5.56 (d, J=2.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 144.9, 143.8, 142.5, 141.1, 139.9, 133.4, 130.8, 129.6, 127.2, 126.0, 116.7, 116.2, 92.0, 21.3; Anal. Calcd for $C_{17}H_{12}N_4O_3$: C 63.75, H 3.78, N 17.49; found: C 63.60, H 3.82, N 17.43; EI-MS: m/z=320 (M^+). HRMS (ESI) for $C_{17}H_{12}N_4O_3$ $(M+H)^+$: calcd 321.0909, found 321.0915.

*2.1.29. 4-Butylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3cc**).* Synthesized according to the typical procedure under N_2 for 24 h at 120 °C, then O_2 for 24 h at 140 °C, and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (53.0 mg, 44%); mp 57–59 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, J=8.0, 1.0 Hz, 1H), 8.17 (d, J=8.5 Hz, 1H), 7.77 (d, J=2.0 Hz, 2H), 7.44–7.41 (m, 1H), 5.94 (d, J=2.0 Hz, 1H), 4.09 (t, J=7.5 Hz, 2H), 1.82–1.75 (m, 2H), 1.46–1.42 (m, 2H), 0.98 (t, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 148.6, 142.0, 140.5, 134.6, 129.0, 125.4, 115.0, 114.6, 89.1, 44.9, 29.7, 20.2, 13.7; Anal. Calcd for $C_{14}H_{15}N_3O$: C 69.69, H 6.27, N 17.41; found: C 69.60, H 6.41, N 17.23; EI-MS: m/z=241 (M^+). HRMS (ESI) for $C_{14}H_{15}N_3O$ $(M+H)^+$: calcd 242.1215, found 242.1217.

*2.1.30. 4-Benzylpyrazolo[1,5-a]quinazolin-5(4H)-one (**3dd**).* Synthesized according to the typical procedure under N_2 for 24 h at 120 °C, then O_2 for 24 h at 140 °C, and purified by column chromatography (petroleum ether/ethyl acetate=2:1) to give a light yellow solid (75.6 mg, 55%); mp 153–155 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (dd, J=8.0, 1.5 Hz, 1H), 8.16 (d, J=8.5 Hz, 1H), 7.77 (d, J=1.0 Hz, 1H), 7.68 (d, J=2.0 Hz, 1H), 7.44–7.41 (m, 1H), 7.36 (d, J=7.5 Hz, 2H), 7.32–7.25 (m, 3H), 5.89 (d, J=2.0 Hz, 1H), 5.29 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 141.9, 140.3, 137.5, 135.2, 134.8, 129.2, 128.7, 127.9, 127.5, 125.4, 115.8, 114.6, 90.0, 48.1; Anal. Calcd for $C_{17}H_{13}N_3O$: C 74.17, H 4.76, N 15.26; found: C 73.89, H 4.68, N 15.47; EI-MS: m/z=275 (M^+). HRMS (ESI) for $C_{17}H_{13}N_3O$ $(M+H)^+$: calcd 276.1059, found 276.1060.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.05.071.

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