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Regioselective Multi-component Synthesis of 7-Aryl-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-diones Catalyzed by *n*-Propylsulfonated γ-Al_2O_3

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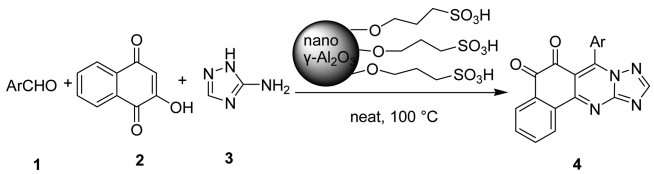
Naphthoquinones constitute a major class of naturally occurring compounds, and interests in their chemistry continues unabated because of their wide range of biological and therapeutic properties such as antioxidant,[1] antifungal,[2] anti-inflammatory,[3] antiallergic,[4] antiviral,[5] and anticancer activity.[6]

Triazoloquinazolines are 'privileged medicinal scaffolds' which are used for the development of pharmaceutical agents of various applications. Compounds with these motif show a wide range of pharmacological activities such as anticonvulsant,[18] anti-inflammatory,[8] antimicrobial,[9] and antiviral.[10] Considering the above reports, development of new and simple synthetic methods for efficient preparation of new *ortho*-naphthoquinones involving the "triazoloquinazoline" synthons are therefore an interesting challenge.

In continuation of our efforts to develop novel reaction methodologies using nano *n*-propylsulfonated γ-Al_2O_3,[11] we now report herein a highly regioselective procedure for the preparation of 7-aryl-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-diones using nano *n*-propylsulfonated γ-Al_2O_3 as an efficient and versatile catalyst under solvent-free conditions (Scheme 1).

First, to achieve suitable conditions for the synthesis of 7-arylbenzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-diones, we tested the three-component reaction of benzaldehyde, 2-hydroxy-1,4-naphthoquinone, and 3-amino-1,2,4-triazole as a simple model system at 100 °C under solvent free conditions using various catalysts (Table 1). As shown in Table 1, the best result was obtained with 100 mg/mmol of nano *n*-propylsulfonated γ-Al_2O_3 as the catalyst at 100 °C under solvent free conditions (Table 1, entry 3). Using less catalyst resulted in lower yields, whereas higher amounts of catalyst did not affect the reaction times and yields. When this reaction was carried out without nano *n*-propylsulfonated γ-Al_2O_3 or with other catalysts such as $FeCl_3$, $AlCl_3$, and nano γ-Al_2O_3, the yield of the expected product was much lower (< 30%). In the presence of *p*-TsOH, $Fe(HSO_4)_3$, or other nano *n*-propyl-sulfonated metal oxide such as nano *n*-propyl-sulfonated SiO_2, nano *n*-propylsulfonated ZnO the product was obtained still in lower yield (52-70%).



Scheme 1. Synthesis of 7-aryl-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-diones using nano *n*-propylsulfonated γ-Al_2O_3.

Table 1. Catalyst optimization for the synthesis 7-phenyl-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione[a]

Entry	Catalyst	Mg/mmol	Time/h	Yield/%
1	-	-	24	12
2	nano *n*-propylsulfonated γ-Al_2O_3	50	2	82
3	nano *n*-propylsulfonated γ-Al_2O_3	100	1	92
4	nano *n*-propylsulfonated γ-Al_2O_3	150	1	92
5	nano *n*-propylsulfonated γ-Al_2O_3	200	1	90
6	$AlCl_3$	100	12	23
7	nano γ-Al_2O_3	100	12	28
8	$FeCl_3$	100	12	20
9	*p*-TsOH	100	2	69
10	$Fe(HSO_4)_3$	100	2	52
11	nano *n*-propylsulfonated SiO_2	100	2	63
12	nano *n*-propylsulfonated ZnO	100	2	70

[a]Reaction conditions: benzaldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol); 3-amino-1,2,4-triazole (1 mmol); 100 °C; neat.

After the successful preparation of **4a**, we decided to introduce more diversity in the benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione scaffolds. With the optimized reaction conditions in hand we examined a variety of aldehydes and 2-hydroxy-1,4-naphthoquinone with 3-amino-1,2,4-triazole and found that nano *n*-propylsulfonated γ-Al_2O_3 is an excellent catalyst system for the synthesis of a large spectrum of benzo[*h*][1,2,4]-triazolo[5,1-*b*] quinazoline-5,6-diones (Table 2). Clearly, these reactions proceeded very cleanly under mild reaction conditions and no *para*-quinone isomeric systems were observed. It is worthwhile to mention that aromatic aldehydes with electron-donating and electron-withdrawing groups as well as heterocyclic aldehydes afforded the correspond products in excellent yields. The structure of the *ortho*-quinone structures **4** is in full agreement with ^{1}H NMR, ^{13}C NMR, MS and elemental analysis as illustrated below for a representative example (compound **4c**). The

Table 2. Preparation of 7-aryl-benzo[*h*][1,2,4]-triazolo[5,1-*b*] quinazoline-5,6-diones[a]

Entry	Ar	Time/h	Product	Yield/%[b]
1	C_6H_5	1	**4a**	92
2	2,4-Cl_2-C_6H_3	1.5	**4b**	88
3	4-Cl-C_6H_4	1	**4c**	90
4	4-F-C_6H_4	1	**4d**	86
5	3-NO_2-C_6H_4	1.5	**4e**	89
6	3,4,5-$(MeO)_3$-C_6H_2	1	**4f**	95
7	4-MeO-C_6H_4	1	**4g**	92
8	2-thiophenyl	1	**4h**	96
9	4-NO_2-C_6H_4	1	**4i**	89
10	4-Me-C_6H_4	1	**4j**	85

[a]Reaction conditions: aldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol); 3-amino-1,2,4-triazole (1 mmol); nano *n*-propylsulfonated γ-Al_2O_3 (100 mg); 100 °C; neat. [b]Isolated yield.

ESI-MS spectrum of **4c** displayed a peak at *m/z* 361 for $[M+H]^+$ and a peak at 1685 cm^{-1} was observed for C=O stretching in the IR spectrum. The ^1H NMR spectrum contained a characteristic single peak at δ 8.58 (s, 1H) for -CH=N. Two peak appeared at δ 178.6 and 178.2 in ^{13}C NMR for C=O of *ortho*-quinone structure. These spectral data are consistent with the structure of **4c**.

While the very close chemical shifts for the carbonyl ^{13}C NMR signals suggested an *ortho*-quinone structure,[12] only marginal differences in the ^1H and ^{13}C chemical shifts are expected for **4** and its regioisomer **5** in simulated spectra (Figure 1). So, we considered it desirable to obtain independent chemical evidence for the presence of *ortho*- or *para*-quinone units in **4**. To this end, we reacted **4c** with *o*-phenylenediamine for 30 min under solvent-free conditions, affording compound **6c** in almost quantitative yield, confirming the *ortho*-quinone structure (Scheme 2). The structure of **6c** was fully characterized by spectroscopic data and elemental analysis, The H-5 and H-8 occur as a multiplet at 9.25-9.31 ppm, more downfield than expected of aromatic protons. This is explicable by the close proximity of these protons to

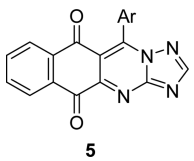


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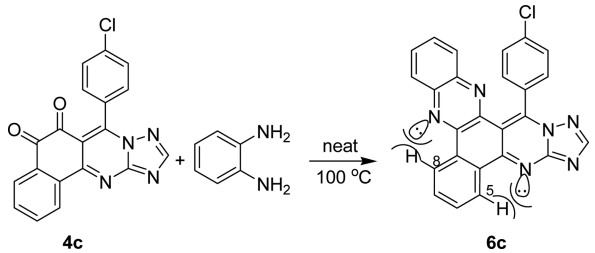
Figure 1. Structures of isomeric systems.



4c 6c

Scheme 2. Synthesis of **6c**.

Table 3. Recyclability of catalyst

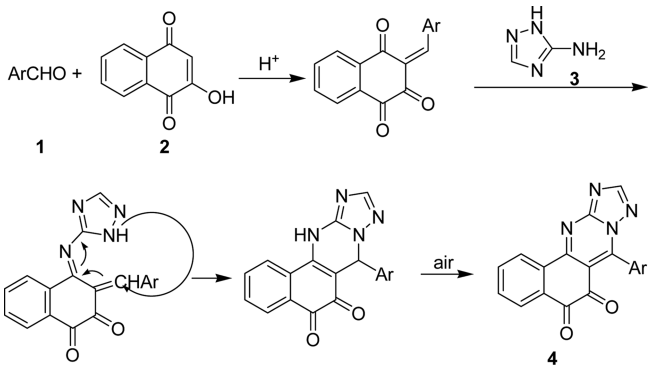
Entry	Cycles	Yield/%	Catalyst recovered/%
1	native	92	95
2	1	88	92
3	2	86	90
4	3	83	88
5	4	80	86
6	5	80	84
7	6	78	82

the lone pairs of the neighboring nitrogens and the consequent anisotropic and van de Waals deshielding. The lack of any carbonyl signal and the presence of two imine carbon signals at 154.6 and 154.4 ppm in ^{13}C NMR spectrum of **6c**, and the fact that **6c** is formed by the reaction of one molecule of **4c** with one molecule of *o*-phenylenediamine clearly support the structure of **6c**, which, in turn, confirms the structure of **4** and the regiochemistry of its formation.

The reusability of the catalyst was tested in the synthesis of **4a**. The catalyst was recovered after each run, washed with EtOH, dried in an oven at 100 °C for 30 min prior to use, and tested for its activity in the subsequent run with no fresh catalyst added. The catalyst was tested for seven runs. It was seen that the catalyst displayed very good reusability (Table 3).

A plausible mechanism for the formation of the *ortho*-naphthoquinone is proposed in Scheme 3. We believe that the transformations proceed *via* the initial formation of α,β-unsaturated carbonyl compounds, which undergo nucleophilic attack by the amine. This step is then followed by cyclization and *in-situ* aromatization to yield to product **4**.

In summary, we have developed a straightforward method for the synthesis of 7-aryl-benzo[*h*][1,2,4]-triazolo[5,1-*b*] quinazoline-5,6-dione derivatives by nano *n*-propylsulfonated γ-Al_2O_3 catalyzed three-component reaction of aldehyde, 2-hydroxy-1,4-naphthoquinone and 3-amino-1,2,4-triazole. A series of 7-aryl-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione derivatives have been synthesized in excellent yield (85-96%). The catalyst can be recycled up to six cycles without much decrease in catalytic activity. Environment



Scheme 3. A plausible mechanism for the formation of the *ortho*-naphthoquinone.

friendly catalyst, high regioselectivity and good yield are the advantages of the method. To the best of our knowledge this is the first report on synthesis of 7-aryl-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione derivatives. We are evaluating anticancer activity of **4**, which will be published elsewhere.

Experimental

Synthesis of Sulfonic Acid Functionalized Nano γ-Al_2O_3. *n*-Propylsulfonated γ-Al_2O_3 is prepared by the reported procedure.[22] Nano γ-Al_2O_3 (6 g) were suspended in 600 mL of 0.1 M toluene solution of 1,3-propane- sultone and the colloidal solution was refluxed for 48 h. The sulfonated nano γ-Al_2O_3 were solated and purified by repeated washing and centrifugation.

General Procedure for the Synthesis of Compounds 4. To a mixture of aldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol); 3-amino-1,2,4-triazole (1 mmol), nano *n*-propylsulfonated γ-Al_2O_3 (100 mg) was added. The mixture was stirred at 100 °C for an appropriate time (Table 2). After completion of the reaction (TLC), the reaction mixture was treated with with CH_2Cl_2 20 mL and EtOAc 20 mL, filtered and the solvent evaporated in vacuo. Solvent was evaporated and the crude product puried by silica gel column chromatography using chloroform: ethyl acetate (*v*:*v* = 1:5) as eluent to afford the pure product **4**.

7-Phenyl-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4a): Pink powder, mp 270-271 ºC; IR (KBr): *v* 3066, 2926, 1679, 1584, 1568, 1520, 1473, 1343, 1306, 1267, 1230, 1070, 1003, 742, 719, 709, 611 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, 1H, *J* = 8.0 Hz, ArH), 8.57 (s, 1H, CH=N), 8.25 (d, 1H, *J* = 8.0 Hz, ArH), 7.94 (d, 1H, *J* = 8.0 Hz, ArH), 7.76-7.52 (m, 6H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 178.2, 159.3, 157.3, 155.8, 154.1, 136.6, 135.0, 133.4, 132.1, 131.6, 129.6, 129.0, 128.7, 128.2, 128.1, 114.0; MS (ESI): *m/z* 327 $[M+H]^+$; Anal. Calc. for $C_{19}H_{10}N_4O_2$: C 69.93, H 3.09, N 17.17; found: C 70.05, H 3.02, N 17.20.

7-(2,4-Dichlorophenyl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4b): Yellow powder, mp 220-221 ºC; IR (KBr): *v* 3072, 2925, 1692, 1596, 1584, 1538, 1516, 1470, 1360, 1342, 1309, 1271, 1231, 1004, 801, 724, 627 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, 1H, *J* = 8.0 Hz, ArH), 8.61 (s, 1H, CH=N), 8.28 (d, 1H, *J* = 7.6 Hz, ArH), 7.96 (t, 1H, *J* = 7.6 Hz, ArH), 7.79 (t, 1H, *J* = 7.6 Hz, ArH), 7.67 (d, 1H, *J* = 7.6 Hz, ArH), 7.52 (dd, 1H, *J* = 1.6, 8.0 Hz, ArH), 7.30 (d, 1H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 177.4, 159.6, 157.0, 155.8, 152.5, 138.1, 136.7, 134.7, 133.6, 133.2, 132.3, 130.3, 130.0, 129.9, 128.1, 128.0, 126.9, 114.6; MS (ESI): *m/z* 395 $[M+H]^+$; Anal. Calc. for $C_{19}H_8Cl_2N_4O_2$: C 57.74, H 3.09, N 14.18; found: C 57.56, H 3.15, N 14.12.

7-(4-Chlorophenyl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4c): Yellow powder, mp 245-246 ºC; IR (KBr): *v* 3074, 2923, 1685, 1598, 1586, 1512, 1478, 1449, 1296, 1283, 1228, 1093, 766, 650 cm-^{1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, 1H, *J* = 8.0 Hz, ArH), 8.58 (s, 1H, CH=N), 8.25 (d, 1H, *J* = 7.6 Hz, ArH), 7.94 (t, 1H, *J* = 8.0 Hz, ArH), 7.70 (t, 1H, *J* = 7.6 Hz, ArH), 7.61 (d, 2H, *J* = 8.4 Hz, ArH), 7.50 (d, 2H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 178.2, 159.3, 157.3, 155.6, 152.9, 138.2, 136.7, 134.9, 133.5, 132.1, 130.4, 129.6, 129.3, 128.1, 126.4, 114.0; MS (ESI): *m/z* 361 $[M+H]^+$; Anal. Calc. for $C_{19}H_9ClN_4O_2$: C 63.26, H 2.51, N 15.53; found: C 63.20, H 2.60, N 15.49.

7-(4-Fluorophenyl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4d): Gray powder, mp 252-253 ºC; IR (KBr): *v* 3032, 2928, 1686, 1601, 1582, 1513, 1496, 1296, 1276, 1229, 1164, 842, 769, 649, 565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, 1H, *J* = 8.0 Hz, ArH), 8.61 (s, 1H, CH=N), 8.28 (d, 1H, *J* = 8.0 Hz, ArH), 7.91 (t, 1H, *J* = 7.6 Hz, ArH), 7.79 (t, 1H, *J* = 7.6 Hz, ArH), 7.62-7.59 (m, 2H, ArH), 7.50 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 178.2, 165.8, 159.3, 157.3, 155.8, 153.1, 136.7, 134.9, 133.5, 132.1, 131.6, 131.5, 129.6, 128.1, 124.0, 123.9, 116.5, 116.3, 114.0; MS (ESI): *m/z* 345 $[M+H]^+$; Anal. Calc. for $C_{19}H_9FN_4O_2$: C 66.28, H 2.63, N 16.27; found: C 66.19, H 2.71, N 16.19.

7-(3-Nitrophenyl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4e): Yellow powder, mp 288-289 ºC; IR (KBr): *v* 3067, 2963, 1687, 1664, 1586, 1518, 1352, 1297, 1262, 1092, 1021, 801, 770, 705, 658 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.83-8.82 (m, 2H, ArH), 8.58 (s, 1H, CH=N), 8.52 (d, 1H, *J* = 8.0 Hz, ArH), 8.18-7.84 (m, 5H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.8, 176.8, 159.0, 157.1, 155.4, 149.3, 148.1, 136.3, 136.0, 135.0, 133.5, 133.3, 131.9, 130.7, 128.9, 127.2, 125.7, 124.9, 116.1; MS (ESI): *m/z* 372 $[M+H]^+$; Anal. Calc. for $C_{19}H_9N_5O_2$: C 61.46, H 2.44, N 18.86; found: C 61.40, H 2.38, N 18.93.

7-(3,4,5-trimethoxyphenyl)-5-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4f): Pink powder, mp 340-342 ºC; IR (KBr): *v* 3092, 2971, 1687, 1512, 1498, 1419, 1326, 1294, 1273, 1248, 1124, 1088, 998, 776, 727, 658 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.80-8.79 (m, 2H, ArH + CH=N), 8.16 (d, 1H, *J* = 7.6 Hz, ArH), 8.01(t, 1H, *J* = 7.6 Hz, ArH), 7.84 (t, 1H, *J* = 7.6 Hz, ArH), 6.99 (s, 2H, ArH), 3.81 (s, 3H, OMe), 3.75 (s, 6H, OMe); ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.3, 177.1, 158.8, 157.1, 155.5, 153.4, 152.0, 140.0, 136.0, 135.2, 133.3, 133.2, 128.8, 127.2, 125.2, 115.9, 107.7, 60.7, 56.8; MS (ESI): *m/z* 417 $[M+H]^+$; Anal. Calc. for $C_{22}H_{16}N_4O_5$: C 63.46, H 3.87, N 13.46; found: C 63.40, H 3.74, N 13.56.

7-(4-Methoxyphenyl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4g): Pink powder, mp 250-251 ºC; IR (KBr): *v* 3075, 2968, 1684, 1604, 1585, 1490, 1453, 1297, 1276, 1186, 1024, 770, 653, 577 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.81-8.78 ((m, 2H, ArH+CH=N), 8.14 (d, 1H, *J* = 7.6 Hz, ArH), 7.99 (t, 1H, *J* = 7.6 Hz, ArH), 7.83 (t, 1H, *J* = 7.6 Hz, ArH), 7.65 (d, 2H, *J* = 8.8 Hz, ArH), 7.15 (d, 2H, *J* = 8.8 Hz, ArH), 3.90 (s, 3H, OMe); ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.4, 177.4, 161.7, 158.7, 157.2, 155.4, 152.2, 135.9, 135.3, 133.2, 133.1, 132.2, 128.7, 127.2, 121.6, 115.7, 114.0, 55.9; MS (ESI): *m/z* 357 $[M+H]^+$; Anal. Calc. for $C_{20}H_{12}N_4O_3$: C 67.41, H 3.39, N 15.72; found: C 67.32, H

3.36, N 15.62.

7-(Thiophen-2-yl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4h): Brown powder, mp 305-306 °C; IR (KBr): *v* 3106, 2953, 1698, 1675, 1581, 1511, 1481, 1451, 1409, 1298, 1282, 1232, 1187, 1089, 764, 723, 473 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 1H, CH=N), 8.78 (d, 1H, *J* = 8.0 Hz, ArH), 8.15 (d, 2H, *J* = 6.4 Hz, ArH), 7.99 (t, 1H, *J* = 7.2 Hz, ArH), 7.85-7.78 (m, 2H, ArH), 7.33 (d, 1H, *J* = 4.4 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.4, 177.4, 159.0, 157.1, 155.3, 146.0, 136.0, 135.5, 135.3, 133.8, 133.3, 133.0, 128.6, 127.8, 127.7, 127.3, 116.4; MS (ESI): *m/z* 333 $[M+H]^+$; Anal. Calc. for $C_{17}H_8N_4O_2S$: C 61.44, H 2.43, N 16.86, S 9.65; found: C 61.52, H 2.50, N 16.56, S 9.52.

7-4-Nitrophenyl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4i): Yellow powder, mp 265-266 °C; IR (KBr): *v* 3101, 3041, 1687, 1585, 1523, 1489, 1356, 1298, 1275, 1244, 1228, 1181, 1088, 846, 775, 740, 659 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, 1H, *J* = 8.0 Hz, ArH), 8.61 (s, 1H, CH=N), 8.52 (d, 2H, *J* = 8.8 Hz, ArH), 8.29 (d, 1H, *J* = 7.6 Hz, ArH), 7.99 (t, 1H, *J* = 7.6 Hz, ArH), 7.82 (t, 1H, *J* = 7.6 Hz, ArH), 8.29 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 177.8, 159.6, 157.3, 155.8, 151.3, 149.4, 136.9, 134.6, 134.5, 133.8, 132.1, 130.0, 129.9, 128.1, 124.2, 114.0; MS (ESI): *m/z* 372 $[M+H]^+$; Anal. Calc. for $C_{19}H_9N_5O_2$: C 61.46, H 2.44, N 18.86; found: C 61.52, H 2.39, N 18.95.

7-(4-Methylphenyl)-benzo[*h*][1,2,4]-triazolo[5,1-*b*]quinazoline-5,6-dione (4j): Brown powder, mp 268-269 °C; IR (KBr): *v* 3072, 2921, 1690, 1585, 1497, 1296, 1275, 771, 749, 649 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.81-8.77 (m, 2H, ArH+CH=N), 8.14 (d, 1H, *J* = 7.2 Hz, ArH), 7.99 (t, 1H, *J* = 7.6 Hz, ArH), 7.83 (t, 1H, *J* = 7.6 Hz, ArH), 7.52 (d, 2H, *J* = 8.0 Hz, ArH), 7.40 (d, 2H, *J* = 8.0 Hz, ArH), 2.46 (s, 3H, Me); ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.3, 177.3, 158.8, 157.2, 155.4, 152.4, 140.8, 136.0, 135.2, 133.3, 133.2, 129.7, 129.2, 128.7, 127.2, 127.1, 115.8, 21.7; MS (ESI): *m/z* 341 $[M+H]^+$; Anal. Calc. for $C_{20}H_{12}N_4O_2$: C 70.58, H 3.55, N 16.46; found: C 70.52, H 3.58, N 16.39.

Typical Procedure for the Synthesis of Compounds 6c. A mixture of 7-(4-chlorophenyl)-benzo[*h*][1,2,4]-triazolo [5,1-*b*]quinazoline-5,6-dione (1 mmol) and *o*-phenyl-enediamine (1.2 mmol) was heated at 100 °C for an appropriate time and monitored by TLC until the final conversion. The reaction mixture was then cooled to room temperature and diluted with cold water (40 mL). The solid product was collected by filtration and was purified by recrystallization from 95% EtOH to afford the desired pure products **6c** as a pale yellow solid.

15-(4-Chlorophenyl)-benzo[*a*][1,2,4]-triazolo[5',1':5,6] pyrimido-[2,3-*c*]phenazine (6c): Yellow powder, mp > 400 °C; IR (KBr): *v* 3059, 1593, 1471, 1355, 1280, 1186, 1118, 1089, 768, 471 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, 1H, *J* = 7.6 Hz, ArH), 9.25 (d, 1H, *J* = 7.6 Hz, ArH), 8.65 (s, 1H, CH=N), 8.22 (d, 1H, *J* = 8.0 Hz, ArH), 7.94-7.90 (m, 2H, ArH), 7.82 (t, 1H, *J* = 7.2 Hz, ArH), 7.74-7.68 (m, 3H, ArH), 7.53 (d, 2H, *J* = 8.0 Hz, ArH), 7.34 (d, 1H, *J* = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 154.6, 154.4, 148.0, 142.4, 141.6, 140.6, 140.4, 136.0, 133.2, 132.5, 131.4, 131.3, 131.2, 131.1, 130.5, 130.2, 129.2, 127.1, 125.7, 113.3; MS (ESI): *m/z* 433 $[M+H]^+$; Anal. Calc. for $C_{25}H_{13}ClN_6$: C 69.37, H 3.03, N 19.41; found: C 69.43, H 3.08, N 19.57.

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Supporting Information. Copy of IR, ^1H NMR and ^{13}C NMR of all compounds are available on request form the correspondence author (wliq1974@sohu.com).

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