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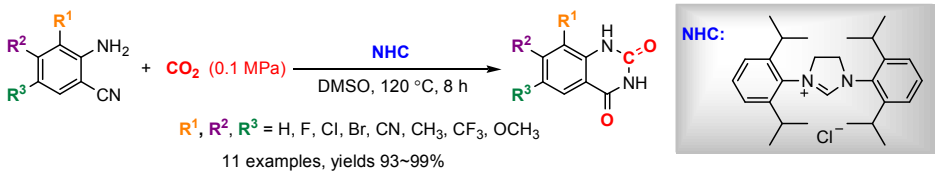

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ARTICLE

Efficient synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO_2 catalyzed by *N*-heterocyclic carbene at atmospheric pressure

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Under atmospheric pressure, quinazoline-2,4(1*H*,3*H*)-diones were obtained from the reaction of 2-aminobenzonitriles with carbon dioxides (0.1 MPa) with a catalytic amount of *N*-heterocyclic carbene in DMSO. It was found that various electron-donating and electron-withdrawing groups such as –OMe, -F, -Cl, -Br, -CH_3, -CF_3 and -CN were well tolerated to give the products in almost quantitative yields.

Introduction

Efficient transformation of CO_2, one of the major green house gases, into value-added chemicals and materials has gained much interest from the viewpoint of the sustainable and green chemistry. Carbon dioxide (CO_2) is a renewable, abundant, low cost, easily available and nontoxic source of functional carbon unit.[1] Recently, utilization of CO_2 as a substrate to prepare a variety of organic compounds, such as cyclic carbonates[2], dimethyl carbonate[3], polycarbonates[4], urethanes[5], formic acids[6], methanol[7], ureas[8], esters[9] and others[10], have been reported.

Quinazoline-2,4(1*H*,3*H*)-diones and their derivatives as one of the important heterocyclic compounds have been widely applied in the pharmaceutical and biotechnology industries.[11] Many strategies for the synthesis of this class of compounds have been developed;[12] however, as an environmentally benign process with 100% atom efficiency, the transformation of CO_2 into quinazoline-2,4(1*H*,3*H*)-diones with 2-aminobenzonitriles has received much attention and a wide range of catalysts have been explored for this transformation, such as DBU, Cs_2CO_3, MgO-ZrO_2, [Bmim]OH, [Bmim]OAc, guanidine and MCM-41 *etc.*.[13] However, most of synthetic protocols reported have many drawbacks such as long reaction times, high pressures of CO_2, expensive catalysts, high reaction temperature, and poor generality, so development of an efficient and general approach for this transformation under mild conditions with cheap and readily available catalyst is still highly desired.

In the recent years, *N*-Heterocyclic carbenes (NHCs) have been successfully applied in catalysis and in coordination chemistry.[14] We have developed an interest in exploring the utility of *N*-heterocyclic carbenes in CO_2 fixation, and observed that NHC is a highly active catalyst for the activation of CO_2 to synthesize cyclic carbonates with epoxides due to its strong σ–donor character to capture CO_2.[15] Herein, we report that NHC as a cheap, readily available and highly active catalyst for the efficient synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO_2 and 2-aminobenzonitriles under mild reaction conditions. The excellent yield, wide substrate scope and various functional group tolerance were found in this catalytic protocol.

Results and Discussion

To test the feasibility of our envisaged approach, we initially examined the reaction of 2-amino-4-chlorobenzonitrile with CO_2 catalyzed by NHC generated from imidazolium chloride (**e**) in the presence of the base K_2CO_3 in DMSO. When the reaction was carried out at 120 ºC and atmospheric pressure of CO_2 (0.1 MPa) for 10 hours, 65% of 7-chloroquinazoline-2,4(1*H*,3*H*)-dione was isolated (Table 1, entry 5). To investigate how the steric and electronic properties of NHCs affect the results of the syntheses of quinazoline derivatives, the different types of NHCs (**a**-**h**) were chosen and a survey of their catalytic activities was performed under the identical conditions (Table 1, entries 1-8). The results showed the most effective catalyst was found to be **a** leading to the highest 93% yield of the product, whereas, and the least effective catalysts are **f** and **g** leading to the lowest 37-39% yield. The reactivity of **d** is moderate and comparable to that of **e** (~65%). Furthermore, the reactivity of **b** and **c** is very similar, but slightly lower (~50%) than that of **d** and **e**. The results suggested that combination the steric hindrance and electron-donating ability plays a role in the reactivity, however, the real reasons behind the difference are not very obvious at this time.

The high activity of **a** prompted us to optimize the reaction further using this catalyst. It is known that the base and solvent are very important parameters determining the reaction efficiency. Firstly, the effect of base was investigated using K_2CO_3, KOH, K_3PO_4, and KO*t*Bu (Table 1, entries 1 and 9-11). The results revealed that only 52% of product was obtained by using stronger base potassium *tert*-butoxide (entry 11), whereas the reaction of using weaker base potassium carbonate occurred in the highest 93% yield (entry 1). The lowest yield of 30% was obtained using K_3PO_4 as base (entry 10) and slightly higher yield (40%) was observed for using KOH (entry 9).

It is known that the reaction could be catalyzed by ionic liquid, such as 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH) as a catalyst under high pressure of CO_2 (3 MPa)[13(l)] or [Bmim]OAc under atmospheric pressure[13(g)]. To understand if the reaction would be catalyzed by imidazolium chloride or imidazolium hydroxide resulting from anion exchange, the hydroxide analogue **i** of imidazolium chloride **a** was prepared. The control reactions were run and the results revealed that no product was observed for both of them without base (Table 1, entries 12-13), implying that NHC generated in situ is an active specie in the reaction, not the precursor imidazolium salt. In addition, the activity of K_2CO_3 in the absence of imidazolium salt was checked as the base used as the catalyst has been reported for the process. The result was illustrated in Table 1 entry 14, showing only 28% of product isolated. The effect of solvents on the reaction was also investigated (Table 1, entries 1 and 15-18). The reaction in DMF gave relatively low yield (45%) comparing to that in DMSO (93%), whereas dioxane, CH_3CN, and water all led to even worse yields (below 10%). To clarify

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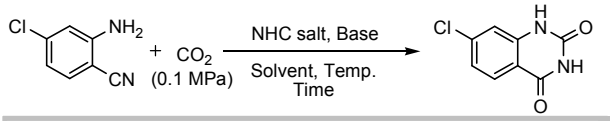
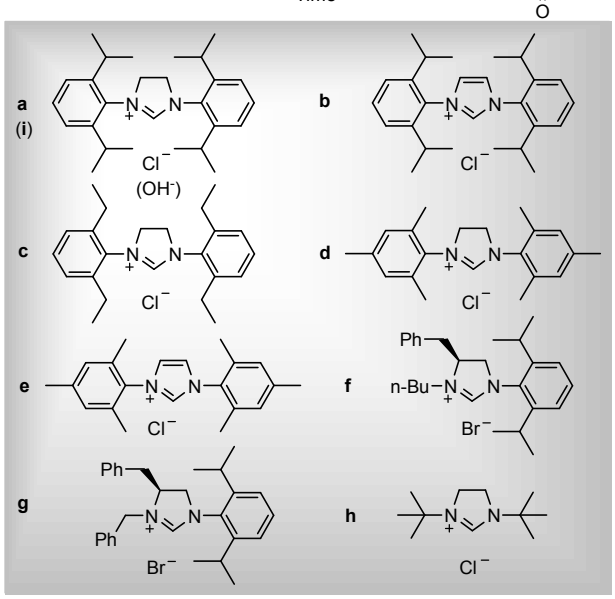
that the lower yield in DMF was not caused by the longer reaction time (10 h), the controlled reaction was carried out in DMF for 8 h (Table 1, entry 19). The result showed shorter reaction time leading to lower yield (37%). Furthermore, the effect of reaction temperature and time on the reaction was investigated (Table 1, entries 20-27). The choice of the reaction temperature is very crucial, both lower and higher temperatures would lead to lower yield, and 120 ºC is the optimal reaction temperature. The lower yield caused by higher temperature is probably due to the decomposing of NHC-CO_2 adduct, which is known in literature.[16] By studying the influence of reaction time on the reaction,

Table 1. Synthesis of 7-chloroquinazoline-2,4(1*H*,3*H*)-dione under different reaction conditions

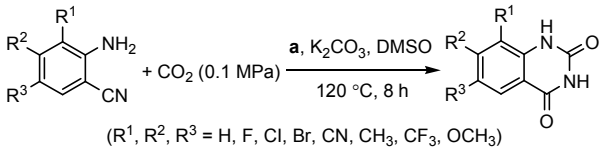




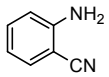
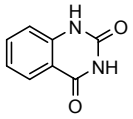
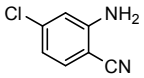
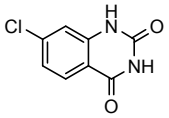
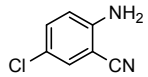
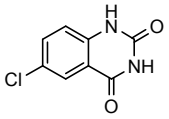
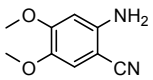
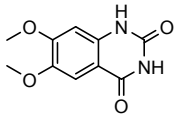
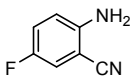
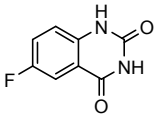
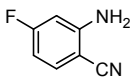
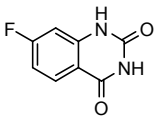
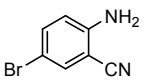
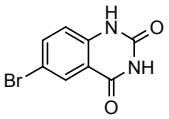
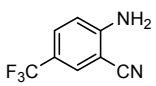
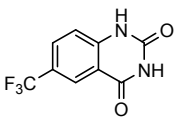
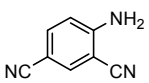
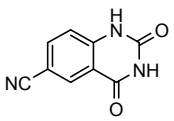
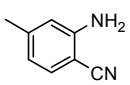
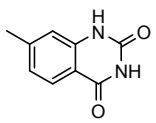
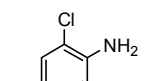
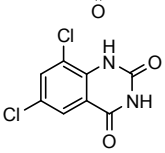
Entry[a]	NHC salt	Base	Solvent	Temp. (ºC)	Time (h)	Yield (%)[b]
1	**a**	K_2CO_3	DMSO	120	10	93
2	**b**	K_2CO_3	DMSO	120	10	53
3	**c**	K_2CO_3	DMSO	120	10	50
4	**d**	K_2CO_3	DMSO	120	10	62
5	**e**	K_2CO_3	DMSO	120	10	65
6	**f**	K_2CO_3	DMSO	120	10	37
7	**g**	K_2CO_3	DMSO	120	10	39
8	**h**	K_2CO_3	DMSO	120	10	59
9	**a**	KOH	DMSO	120	10	40
10	**a**	K_3PO_4	DMSO	120	10	30
11	**a**	KO^{t}Bu	DMSO	120	10	52
12	**a**	-	DMSO	120	10	0
13	**i**	-	DMSO	120	10	0
14	**-**	K_2CO_3	DMSO	120	10	28
15	**a**	K_2CO_3	DMF	120	10	45
16	**a**	K_2CO_3	dioxane	120	10	10
17	**a**	K_2CO_3	CH_3CN	120	10	3
18	**a**	K_2CO_3	H_2O	120	10	3
19	**a**	K_2CO_3	DMF	120	8	37
20	**a**	K_2CO_3	DMSO	40	10	5
21	**a**	K_2CO_3	DMSO	60	10	5
22	**a**	K_2CO_3	DMSO	80	10	10
23	**a**	K_2CO_3	DMSO	100	10	41
24	**a**	K_2CO_3	DMSO	130	10	80
25	**a**	K_2CO_3	DMSO	120	4	77
26	**a**	K_2CO_3	DMSO	120	6	89
27	**a**	K_2CO_3	DMSO	120	8	93

[a]Reaction conditions: 2-amino-4-chlorobenzonitrile (2 mmol), NHC salt (0.4 mmol), base (2 mmol), CO_2 (0.1 MPa) and solvent (3 mL). [b]Isolated yield on average of two runs.

Table 2. Synthesis fo quinazoling-2,4(1*H*,3*H*)diones compounds



(R^1, R^2, R^3 = H, F, Cl, Br, CN, CH_3, CF_3, OCH_3)

Entry[a]	Anline	Product	Yield (%)[b]
1			95
2			93
3			99
4			99
5			99
6			93
7			99
8			98
9			97
10			98
11[c]			98

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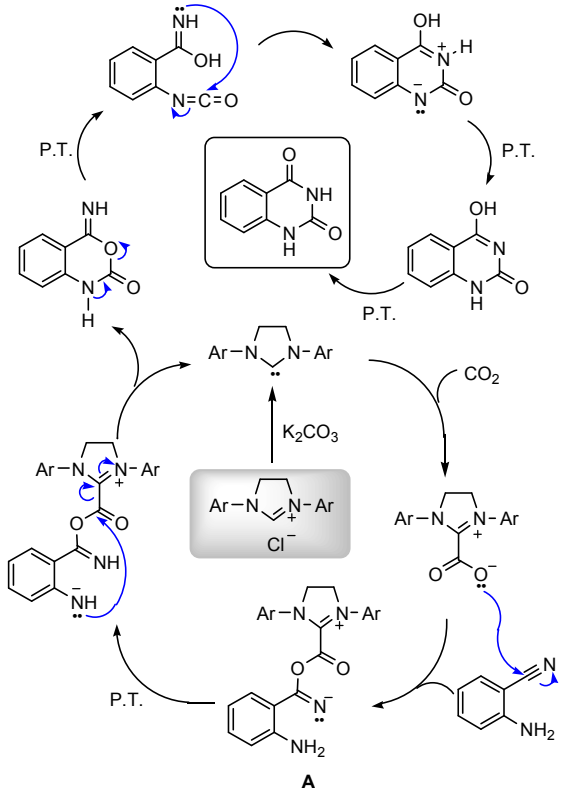
[a]Reaction conditions: 2-aminobenzonitriles (2 mmol), **a** (0.4 mmol), K_2CO_3 (2 mmol), CO_2 (0.1 MPa) and DMSO (3 mL); [b]Isolated yield on average of two runs; [c]15 h.

it was found the reaction actually completed within 8 h when the reaction was carried out at 120 °C under 0.1 MPa CO_2 (Table 1, entries 25-27). Hence in the following studies, all reactions were carried with 20 mol % of **a** as catalyst, K_2CO_3 as base, and DMSO as a solvent at 120 °C and 0.1 MPa CO_2 pressure for 8 h.

To further assess the generality and scope of the reaction, various substituted 2-aminobenzonitrile were chosen and examined in the synthesis of quinozoline-2,4(1*H*, 3*H*)-diones (Table 2). The reactions of 2-aminobenzonitriles bearing the electron-donating group such as OMe group (Table 2, entry 4) went smoothly with the yield of up to 99%. In addition, the reaction of 2-aminobenzonitriles bearing the electron-withdrawing group such as CF_3 (Table 2, entry 8) went well with yields of up to 98%. Various groups, such as –OMe, -F, -Cl, -Br, $-CH_3$, $-CF_3$ and -CN, were well tolerated to give the product in excellent yields. The reactions were very clean and the workup and purification is very simple. The pure quinazoline products were obtained by simply filtration in almost quantitative yields.

From the established mechanism for the reaction of 2-aminobenzonitriles with CO_2 and our current experimental results, the proposed mechanism is shown in Scheme 1. We suggest that NHC is the catalytic active species, NHC generated in situ directly reacts with CO_2 to form the NHC-CO_2 adduct. Then the nucleophilic addition of zwitterionic adduct to the benzonitrile to generate intermediate **A**. Subsequent intramolecular cyclization regenerate NHC. Finally, quinazoling-2,4(1*H*,3*H*)diones is produced via a series of proton transfer, ring opening, and intramolecular nucleophilic addition.



Scheme 1. Plausible reaction mechanism for the reaction of 2-aminobenzonitriles with CO_2

Conclusions

In summary, we have developed an efficient method for the reaction of CO_2 with 2-aminobenzomitriels to synthesize quinazoling-2,4(1*H*,3*H*)diones. In the present work, the fixation of CO_2 can be carried out using readily avaliable NHC as catalyst under atmopheric pressure of CO_2 (0.1 MPa). High conversions and excellent yield were achieved using this catalytic system under mild conditions, and the workup and purification was very simple. Various electron-donating and electron-withdrawing groups such as –OMe, -F, -Cl, -Br, $-CH_3$, $-CF_3$ and -CN were well tolerated in the reaction.

Experimental Section

General information

Imidazolinium bromides **f** and **g** were prepared using literature procedures.[17] Imidazolinium hydroxide **i** was prepared by modified prodecure.[18] All other chemicals were commercially available and used as received unless otherwise stated. DMSO and acetonitrile were distilled from calcium hydride, and dioxane was distilled from sodium benzophenone ketyl prior to use. DMF was stirred over anhydrous $MgSO_4$ overnight, filtered, and then distilled over 4Å molecular sieves under nitrogen atmosphere. CO_2 with a purity of 99.95% was used. ^1H and ^{13}C spectra were recorded on a Bruker AV 400 MHz spectrometer at room temperature and referenced to the residual signals of the solvent. Melting points were detected by microscope melting point apparatus. IR spectra were recorded on KBr pellets on a FTIR-Tensor 27 spectrometer.

Synthesis of 1,3-bis[2,6-bis(1-methylethyl)phenyl]-4,5-dihydro-1*H*-Imidazolium hydroxide (i)

To 15 mL of DCM in a 25 mL round bottom flask, was added imidazolinium chloride **a** (0.854 g, 2 mmol), KOH (0.56 g, 10 mmol). The reaction was stirred at room temperature for 24 h, after which time the solids were removed by filtration. The filtrate was concentrated and the resulting crude was purified by chromatography to give 0.752 g of the product in 92% yield as white solid. (PE:EtOAc = 5:1). IR (KBr) 3647, 3379, 2966, 2869, 2359, 1661, 1590, 1487, 1461, 1403, 1384, 1344, 1267, 1120, 1097, 1054, 992, 930, 861, 843, 811, 799, 758, 676, 621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.09 (s, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.8 Hz, 2H), 7.07-7.00 (m, 3H), 3.87 (t, J = 7.3 Hz, 2H), 3.22-3.01 (m, 6H), 1.25-1.13 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.0, 147.7, 142.4, 135.6, 129.6, 124.6, 123.9, 123.6, 49.0, 48.8, 28.4, 27.9, 25.5, 24.3, 23.6.

General procedure of synthesis of quinazoline

In a typical run, a 10 mL of high pressure autoclave with a stir bas was charged with 2-aminobenzonitrile (2 mmol, 305 mg), **a** (0.4 mmol, 171 mg), K_2CO_3 (2 mmol, 276 mg) in glove box, and the capped autoclave was move out of glove box. DMSO (3 mL) was injected into the autoclave, and it was connected to a CO_2 container. The autoclave was purged with CO_2 for 3 times and its pressure was adjusted to 0.1 MPa. After the autoclave was heated at 120 °C for 8 h with stirring, it was cool to room temperature. The reaction mixture was poured into the water (10 mL), and the solid was collected by filtration and rinsed with water and ether, then dried under vacuum to give the pure product.

Quinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 1) White solid, m.p. > 300 °C, IR (KBr) 3252, 3054, 2845, 1701, 1670, 1617, 1442, 754 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.30 (s, 1H, NH), 11.16 (s, 1H, NH), 7.88 (d, J = 7.6 Hz, 1H, CH), 7.63 (t, J = 8.0 Hz, 1H, CH), 7.17 (t, J = 8.4 Hz, 2H, 2CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.8, 150.3, 140.9, 134.9, 126.9, 122.3, 115.3, 114.3.

7-Chloroquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 2) Light yellow solid, m.p. > 300 °C, IR (KBr) 3305, 3046, 1744, 1682, 1616, 1430, 1283, 862 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.41 (s, 1H, NH), 11.26 (s, 1H, NH), 7.88 (d, J = 8.4 Hz, 1H, CH), 7.22 (d, J = 8.4 Hz, 1H, CH), 7.18 (d, J = 1.6 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.1, 150.2, 141.9, 139.3, 129.0, 122.4, 114.7, 113.3.

6-Chloroquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 3) Light yellow solid, m.p. > 300 °C, IR (KBr) 3199, 3056, 1712, 1668, 1482, 1428, 1283, 876 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.43 (s, 1H, NH), 11.27 (s, 1H, NH), 7.79 (s, 1H, CH), 7.66 (d, J = 8.8 Hz, 1H, CH), 7.17 (d, J = 8.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.0, 150.2, 139.8, 134.9, 126.5, 126.0, 117.6, 115.8.

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6,7-Dimethoxyquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 4) Light yellow solid, m.p. > 300 ºC, IR (KBr) 3470, 3378, 3294, 1708, 1652, 1624, 1466, 1436, 1264, 1098 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.09 (s, 1H, NH), 10.92 (s, 1H, NH), 7.25 (s, 1H, CH), 6.67 (s, 1H, CH), 3.82 (s, 3H, CH_3), 3.78 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.4, 154.9, 150.4, 145.0, 136.5, 107.2, 106.2, 97.8, 55.8, 55.7.

6-Fluoroquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 5) Light yellow solid, m.p. > 300 ºC, IR (KBr) 3198, 3058, 1714, 1676, 1634, 1500, 1438, 1288, 884 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.43 (s, 1H, NH), 11.22 (s, 1H, NH), 7.53-7.59 (m, 2H, 2CH), 7.18-7.21 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 165.9 (d, J = 249.4 Hz), 162.0, 150.4, 143.0 (d, J = 13.1 Hz), 130.2 (d, J = 11.2 Hz), 111.4 (d, J = 1.8 Hz), 110.4 (d, J = 23.0 Hz), 101.6 (d, J = 26.0 Hz).

7-Fluoroquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 6) White solid, m.p. > 300 ºC, ^1H NMR (400 MHz, DMSO-d_6) δ = 11.38 (s, 1H, NH), 11.28 (s, 1H, NH), 7.93-7.96 (m, 1H, CH), 7.03 (t, J = 8.8 Hz, 1H, CH), 6.89 (dd, J = 1.6 Hz, J = 4.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.2 (d, J = 3.0 Hz), 157.3 (d, J = 238.2 Hz), 150.1, 137.6 (d, J = 1.4 Hz), 123.0 (d, J = 24.1 Hz), 117.6 (d, J = 7.8 Hz), 115.4 (d, J = 7.6 Hz), 112.0 (d, J = 23.6 Hz).

6-Bromoquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 7) Yellow solid, m.p. > 300 ºC, ^1H NMR (400 MHz, DMSO-d_6) δ = 11.45 (s, 1H, NH), 11.30 (s, 1H, NH), 7.93 (s, 1H, CH), 7.79 (dd, J = 2.0 Hz, J = 8.8 Hz, 1H, CH), 7.13 (d, J = 8.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 161.8, 150.1, 140.1, 137.5, 128.9, 117.8, 116.2, 113.9.

6-(Trifluoromethyl)quinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 8) White solid, m.p. > 300 ºC, IR (KBr): 3311, 3187, 3066, 2897, 2832, 1702,1634, 1508, 1489, 1441, 1378, 1319, 1289, 1253, 1145, 1112, 1069, 1015, 930, 842, 785, 755, 693, 652, 609, 511 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.56 (s, 1H, NH), 11.52 (s, 1H, NH), 8.08 (s, 1H, CH), 7.95 (dd, J = 8.6 Hz, J = 2.0 Hz, 1H, CH), 7.31 (d, J = 8.6 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.0, 150.2, 143.8, 131.3 (d, J = 3.3 Hz), 124.2 (d, J = 4.1 Hz), 122.6 (d, J = 33 Hz), 122.5 (m), 116.7, 114.5.

2,4-Dioxo-1,2,3,4-tetrahydroquinazoline-6-carbonitrile (Table 2, entry 9) Light yellow solid, m.p. > 300 ºC, IR (KBr): 3224, 3082, 2349, 2229, 1700, 1623, 1505, 1456, 1384, 1340, 1294, 1238, 1193, 1157, 1099, 1018, 943, 861, 806, 723, 670 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.58 (s, 1H, NH), 11.57 (s, 1H, NH), 8.24 (d, J = 2.0 Hz, 1H, CH), 8.00 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H, CH), 7.27 (d, J = 8.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 161.5, 150.0, 144.1, 137.6, 132.1, 118.3, 116.6, 115.0, 104.6.

7-Methylquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 10) White solid, m.p. decomposing at 285 ºC, IR (KBr): 3464, 3252, 3042, 2822, 1702, 1630, 1482, 1429, 1380, 1294, 1180, 1147, 1106, 1036, 954, 866, 824, 764, 722, 700, 685, 622 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.13 (s, 1H, NH), 11.01 (s, 1H, NH), 7.71 (d, J = 8.0 Hz, 1H, CH), 6.93 (d, J = 8.0 Hz, 1H, CH), 6.89 (s, 1H, CH), 2.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.7, 150.5, 145.6, 141.0, 126.9, 123.7, 115.1, 112.1, 21.5.

6,8-Dichloroquinazoline-2,4(1*H*,3*H*)-dione (Table 2, entry 11) Yellow solid, m.p. > 300 ºC, IR (KBr): 3482, 3177, 3072, 2830, 2361, 1695, 1609, 1492, 1461, 1417, 1368, 1315, 1285, 1236, 1164, 1088, 1028, 912, 896, 880, 840, 777, 758, 733, 683, 616 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.66 (s, 1H, NH), 10.87 (s, 1H, NH), 7.94 (d, J = 2.4 Hz, 1H, CH), 7.81 (d, J = 2.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 161.1, 149.7, 137.0, 134.2, 126.3, 125.3, 120.2, 117.4.

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