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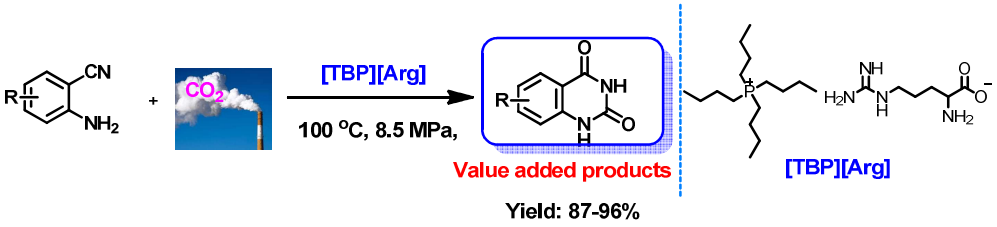
Xian-Dong Lang, Shuai Zhang, Qing-Wen Song and Liang-Nian He*



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An easily prepared amino acid ionic liquid (AAIL) i.e. [TBP][Arg] comprising *tetra*-butylphosphonium cation and arginine anion was found to be an efficient and recyclable catalyst for the synthesis of quinazoline-2,4(1H, 3H)-diones from 2-aminobenzonitriles and CO_2 under solvent-free conditions. As a result, various 2-aminobenzonitriles bearing electron-withdrawing or electron-donating substituents worked well to afford quinazoline-2,4(1H, 3H)-diones in excellent yields. Notably, this type of AAIL showed good stability, and could be easily recovered and reused for five times without significant loss of its catalytic activity. This process represents an alternative approach for greener chemical fixation of CO_2 to afford valuable compounds.

Introduction

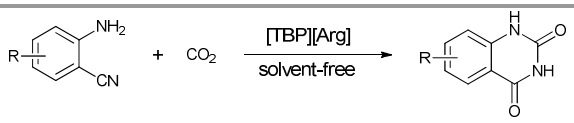
The detrimental influences of increasing accumulation of CO_2 in the atmosphere have received more and more attention. Nevertheless, CO_2 can also be regarded as a sustainable feedstock with several characteristics such as low cost, nontoxicity, nonflammability, renewable and so on.[1] To date, numerous valuable chemicals such as formic acids,[2] methanol,[3] dimethyl carbonate,[4] cyclic carbonate,[5] polycarbonates,[6] ureas,[7] urethanes,[8] α, β-unsaturated carbonyl compounds,[9] carbon monoxide[10] have been prepared from CO_2.

Quinazoline-2,4(1H, 3H)-diones and their derivatives have found widespread applications in pharmaceutical industry.[11] Traditionally, quinazoline-2,4(1H, 3H)-diones are synthesized through the reaction of anthranilamides with phosgene or anthranilic acids with urea, potassium cyanate and chlorosulfonyl isocyanate, respectively.[12] However, most of those methods generally suffer from tedious workup procedures, use of toxic reactants and low efficiency. Therefore, development of more efficient, simple and green approaches using environmentally benign reagents would be highly desirable. Since a promising process for the synthesis of quinazoline-2,4(1H, 3H)-diones from CO_2 and 2-aminobenonitriles was developed for the first time by Mizuno[13], a diverse library of catalysts such as 1,1,3,3-*tetra*-methylguanidine (TMG),[14] Cs_2CO_3,[15] poly(amidine),[16] MgO/ZrO_2,[17] monomeric tungstate,[18] 1-butyl-3-methylimidazolium hydroxyl ([BMIm]OH),[19] [BMIm]OAc,[20] amine-functionalized MCM-41,[21] mesoporous smectites,[22] TBD-functionalized Fe_3O_4,[23] and protic ionic liquids (ILs)[24] have been proved to be effective catalysts. In this context, development of more convenient and efficient catalytic systems with ease of recyclability remains a challenge.

As organic salts with melting point of lower than 100 ^oC, ILs have attracted much attention in recent years.[25-27] ILs containing cations such as imidazolium, pyridinium, ammonium and anions e.g. chloride, dicyanamide, bis(trifluoromethylsulfonyl)amide, tetra-fluoroborate, hexa-fluorophosphate are most common ILs. Notably, phosphonium-based AAILs have been explored with a number of advantages, for example, tetra-alkylphosphonium-based AAILs displayed lower viscosity and higher decomposition temperature than traditional ammonium-based AAILs.[28] Additionally, application of anion-functionalized ionic liquids including AAILs have been extended to CO_2 capture and fixation.[29] Zhang and co-workers found that the porous silica gel-supported *tetra*-butylphosphonium AAILs were used for fast and reversible CO_2 absorption.[30] Moreover, ILs, i.e. phosphonium-based ILs could also act as reaction media for the transesterification reaction and gave higher efficiency than traditional organic solvents.[31] Recently, our group also showed that 1-butyl-3-methylimidazolium alanine-based AAILs i.e. [Bmim][Ala] could act as an effective catalyst for the cycloaddition of epoxides with CO_2 to produce cyclic carbonates in excellent yields under solvent-free conditions.[32]

It was also worth mentioning that phosphonium-based AAILs are low-toxic, environmentally benign, and biodegradable. As known, ionic liquids with *tetra*-alkylphosphonium as cation can be more easily detected by ^{31}P NMR technique. On the other hand, CO_2 can be fixed and

activated by guanidines, which is a kinetically reversible process.[33] In this aspect, carboxylic group is able to form hydrogen bond with N-H, thus weakening the N-H bond and facilitating nucleophilicity of the NH_2 group.[20,34] These inspired us to design the reactive arginine-based ionic liquid with the guanidine motif denoted as [TBP][Arg] as a multifunctional base for CO_2 activation and carboxylic anion for N-H bond activation. In this work, we found that the carbonylation of 2-aminobenzonitriles with CO_2 performed smoothly to give a series of quinazoline-2,4(1H, 3H)-diones in excellent yields by using [TBP][Arg] as a catalyst as depicted in Scheme 1. This phosphonium arginine-based IL featured numbers of advantages such as high catalytic activity, lower toxicity, environmentally benign characters, along with ease of detection by ^{31}P NMR technique. Moreover, the catalyst could be easily recovered and reused for five times without appreciable loss of its catalytic activity.



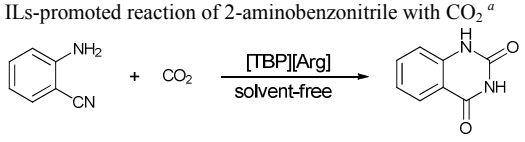
Scheme 1 Cyclization of 2-aminobenzonitrile with CO_2 catalyzed by [TBP][Arg].

Results and discussion

At the start of this work, we prepared the bifunctional phosphonium arginine ([TBP][Arg]) ILs through the neutralization of *tetra*-butylphosphonium hydroxide ([TBP][OH]) aqueous solution with arginine at room temperature[28] (For detailed characterization of [TBP][Arg], see Experimental Section). It was worth mentioning that [TBP][Arg] is more stable than traditional ILs.[28] 2-Aminobenzonitrile (**1a**) was selected as a model substrate to evaluate catalytic activity of [TBP][Arg] as listed in Table 1. Gratifyingly, quinazoline-2,4(1H, 3H)-dione **2a** was obtained in 60% isolated yield by employing 1 equiv. [TBP][Arg] under 10 MPa CO_2 at 120 ^oC employing DMF as solvent (entry 1). It is particularly worth mentioning that none of any byproduct was detected. As a result, the [TBP][Arg-cyclization of 2-aminobenzonitrile with CO_2 performed effectively with perfect chemoselectivity.

Encouraged by such results, a series of ILs including *tetra*-butylammonium arginine ([TBN][Arg]), *tetra*-butylphosphonium alanine ([TBP][Ala]), 1-butyl-3-methylimidazolium arginine [Bmim][Arg], Na[Arg], *tetra*-butylphosphonium hydroxide aqueous solution ([TBP][OH]), and *tetra*-butylammonium hydroxide aqueous solution ([TBN][OH]) were further examined for the reaction. As a result, [TBN][Arg] and [Bmim][Arg] promoted the reaction with moderate yields (entries 2-3). While [TBP][Ala] and Na[Arg] showed inactivity at 120 ^oC with full recovery of the starting material under neat conditions (entries 4-5). This is probably because [TBP][Ala] with weak basicity is unable to activate **1a** and CO_2.

Table 1 ILs-promoted reaction of 2-aminobenzonitrile with CO_2 [a]



1a **2a**

Entry	Catalyst	Amount (equiv.)	DMF (mL)	Yield[b] (%)
1	[TBP][Arg]	1	2	60
2	[TBN][Arg]	1	2	45
3	[Bmim][Arg]	1	2	50
4	[TBP][Ala]	1	2	0
5	Na[Arg]	1	2	0
6	[TBP][Arg]	1	-	85
7[c]	[TBP][OH]	1	-	48
8[d]	[TBN][OH]	1	-	52
9	[TBP][Arg]	0.5	-	84
10	[TBP][Arg]	0.3	-	96
11	[TBP][Arg]	0.1	-	95
12	[TBP][Arg]	0.05	-	88

[a]Reaction conditions: **1a** (1 mmol, 0.118 g), CO_2 (10 MPa), 120 ^oC, 24 h. [b]Isolated yield. [c]*tetra*-butylphosphonium hydroxide (40% in water). [d]*tetra*-butylammonium hydroxide (25% in water).

On the other hand, poor solubility of Na[Arg] in DMF could account for activity. In addition, [TBP][OH] and [TBN][OH] were also evaluated for this reaction. As a consequence, the desired product **2a** can also be attained in moderate yields (entries 7-8). Interestingly, the [TBP][Arg]-promoted reaction performed more efficiently without additional organic solvent compared with that in DMF (entry 6 vs. 1). Meanwhile, the influence of catalyst loading on the reaction was further investigated under identical reaction conditions (entries 9-12). Notably, [TBP][Arg] performed well even in the presence of 5 mol% catalyst relative to **1a**, presumably due to synergistic effect of such dual activation of [TBP][Arg] consisting of two functional sites: carboxylic group and guanidine structure on the cyclization reaction. Carboxylic group is able to activate N-H bond through hydrogen bond interaction, thus improves the nucleophilicity of the NH_2 group. At the same time, CO_2 can be activated by guanidine structure as detected in ref. 33.

Subsequently, the influences of the reaction parameters including CO_2 pressure, reaction temperature and time on the reaction were investigated in detail. The results are summarized in Table 2. As easily seen, **2a** yield was closely related to CO_2 pressure (entries 1-6). With CO_2 pressure decrease from 8.5 to 0.1 MPa, a sharp drop in **2a** yield was observed from 95% to 16%, presumably because appropriate amount of CO_2 is beneficial for the reaction involving CO_2. Furthermore, temperature effect was also evaluated under 8.5 MPa CO_2. It was found that comparative yields were obtained at 120 ^oC and 100 ^oC (entries 2, 7). However, **2a** yield was reduced as further decrease in the reaction temperature to 60 ^oC (entry 8, 9). Finally, we examined the effect of the reaction time under 8.5 MPa CO_2 at 100 ^oC. To be delighted, 70% **2a** yield was obtained for 4 h. Further improved result (91%) was received after 12 h. With a longer time than 12 h, unchanged yield was acquired (entries 10-13).

Table 2 Effects of reaction parameters on chemical fixation of CO_2 with **1a**[a]

Entry	P_{CO2} (MPa)	T (°C)	Time (h)	Yield[b] (%)
1	10	120	24	95
2	8.5	120	24	93
3	7.5	120	24	62
4	7	120	24	32
5	4	120	24	25
6	0.1	120	24	16
7	8.5	100	24	91
8	8.5	80	24	79
9	8.5	60	24	65
10	8.5	100	16	91
11	8.5	100	12	91
12	8.5	100	8	83
13	8.5	100	4	70
14[c]	8.5	100	12	0
15[d]	8.5	100	12	0
16[e]	8.5	100	12	0
17[f]	8.5	100	12	7
18[g]	8.5	100	12	16

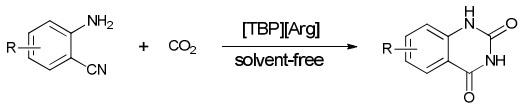
[a]All the reactions were carried out with **1a** (1 mmol, 0.118 g) and [TBP][Arg] (0.1 mmol, 0.0433 g) unless otherwise specifically notified. [b]Isolated yield. [c]without any catalyst. [d]KF instead of [TBP][Arg]. [e]Cs_2CO_3 instead of [TBP][Arg]. [f]Et_3N instead of [TBP][Arg]. [g]Melamine instead of [TBP][Arg].

In addition, several typical inorganic and organic bases were also tested by employing 8.5 MPa CO_2 at 100 °C for 12 h. Obviously, no reaction occurred without any catalyst (entry 14). Inorganic bases such as Cs_2CO_3 and KF showed inactive under the given conditions (entries 15-16), presumably being ascribed to the poor insolubility. On the other hand, organic bases such as Et_3N and melamine, being difficult to activate both **1a** and CO_2, only showed low activity (entries 17, 18). Consequently, suitable basicity and good solubility are crucial to promoting the cyclization of 2-aminobenzonitrile with CO_2.

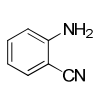
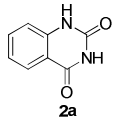
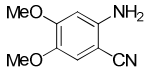
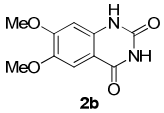
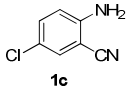
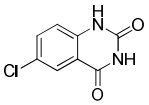
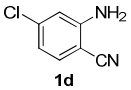
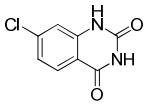
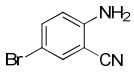
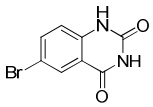
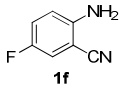
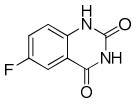
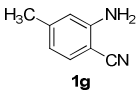
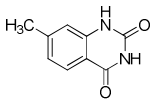
With the optimized reaction conditions in hand, the generality and the utility of this protocol were then examined using different 2-aminobenzonitriles bearing various substituents as listed in Table 3. As expected, 2-aminobenzonitrile derivatives with electron-withdrawing or electron-donating groups at benzene worked well to afford quinazoline-2,4(1H, 3H)-diones **2** in excellent yields under the given reaction conditions. The target product **2b** and **2g** were obtained in 87% and 91% isolated yield from the dimethoxy substituted **1b** and *para*-methyl substituted **2g**, respectively (entries 2, 7). Notably, both the *meta* and *para*-halogen substituted 2-aminobenzonitriles could almost quantitatively be converted into the corresponding quinazoline-2,4(1H, 3H)-diones (entries 3-6).

The reusability of the catalyst i.e. [TBP][Arg] was also studied by performing the reaction of 2-aminobenzonitrile and CO_2 under the optimum reaction conditions. After the reaction, the catalyst was recovered through adding water, filtration, and desiccation in vacuo for 24 h, which can be reused directly for the next run. As seen from Figure 1, the catalyst could be reused for five times without appreciable loss of its catalytic activity.

Table 3 Synthesis of quinazoline-2,4(1H, 3H)-diones **2** from various substrates **1** and CO_2[a]



1 2

Entry	Substrate	Product	Yield[b] (%)
1	 1a	 2a	91
2	 1b	 2b	87
3	 1c	 2c	96
4	 1d	 2d	94
5	 1e	 2e	96
6	 1f	 2f	95
7	 1g	 2g	91

[a]Reaction conditions: **1** (1 mmol), [TBP][Arg] (0.1 mmol, 0.0433 g), CO_2 (8.5 MPa), 100 °C, 12 h. [b]Isolated yield.

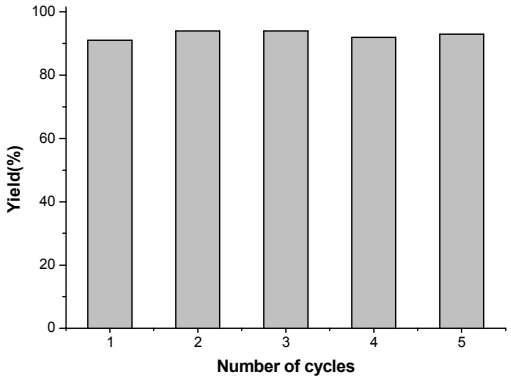
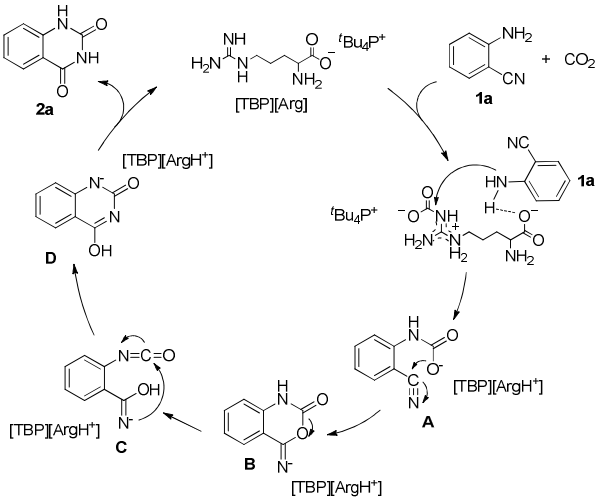


Figure 1 Catalyst reusability.

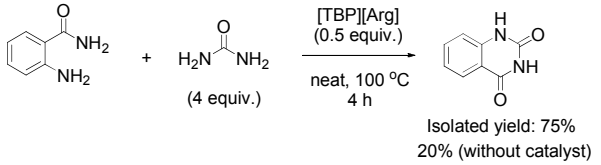
^{1}H NMR, ^{13}C NMR and ^{31}P NMR examination displayed that change of structure was not observed for the recovered catalyst in comparison with the fresh one (For the details, see Supporting Information).

A tentative mechanism for the present [TBP][Arg]-catalyzed chemical fixation of CO_2 with 2-aminobenzonitrile is illustrated in Scheme 2. Both amino group in **1a** and CO_2 are initially activated by the bifunctional anion (carboxyl group and guandine group, respectively) in [TBP][Arg], which facilitates the nucleophilic attack of **1a** at CO_2 to generate the carbamate salt **A**. Subsequently, a cyclization occurs resulting in the formation of the intermediate **B**, followed by a ring opening to generate a crucial isocyanate intermediate **C**. **C** undergoes further ring-closing pathway to afford the species **D**. Finally, the final product **2a** can be obtained through proton transfer of **D** with catalyst regeneration. Additionally, the formation of the isocyanate intermediate **C** assisted by the *o*-cyano group seems to be of great importance.[35]



Scheme 2 Possible pathway for the reaction of 2-aminobenzonitrile with CO_2 catalyzed by [TBP][Arg].

To further investigate the effectiveness of the present simultaneous activation of N-H bond, we explored the [TBP][Arg]-catalyzed chemical transformations via different nucleophiles such as anthranilamide and urea as a CO_2 equivalent (Scheme 3). In general, the reaction of anthranilamide and urea[36,37] afford low yield of quinazoline-2,4(1H, 3H)-dione even under harsh reaction conditions (e.g. 190 ^{o}C). Interestingly, the [TBP][Arg]-promoted reaction of anthranilamide with urea afforded the target product with a good yield even at milder conditions Yet, in the absence of any catalyst, the reaction only gave 20% yield.



Scheme 3 The reaction of anthranilamide with CO_2 catalyzed by [TBP][Arg].

Conclusions

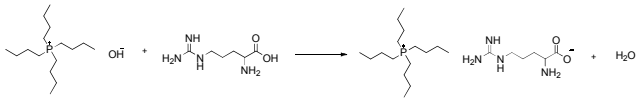
In conclusion, *tetra*-butylphosphonium arginine-based IL [TBP][Arg] able to activate amino-group and CO_2 was proved to be a very efficient and recyclable catalyst for the synthesis of quinazoline-2,4(1H, 3H)-diones from 2-aminobenzonitriles and CO_2 under solvent-free conditions. The catalyst [TBP][Arg] works well with a range of 2-aminobenzonitrile with electron-donating or electron withdrawing groups at the ring of benzene. Moreover, easy recovery and excellent reusability of the catalyst render this protocol to have much potential application for the catalytic conversion of CO_2 into valuable compounds and materials in industry.

Experimental

Materials and methods

Experiments using compressed gases CO_2 are potentially hazardous and must only be carried out by using appropriate equipment and under rigorous safety precautions. CO_2 with a purity of 99.999 % was commercially available. All starting materials were obtained from TCI, Aladdin or Alfa Aesar Company and used as received. ^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as solvent referenced to $CHCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm). ^{13}C NMR spectra were recorded at 100.6 MHz in $CDCl_3$ (or DMSO-d_6) using $CDCl_3$ (77.0 ppm) (or DMSO-d_6, 39.5 ppm) as as internal reference. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. High resolution mass spectrometry was conducted using a Varian 7.0 T FTICR-MS by ESI technique. Melting points were measured on an X4 apparatus and uncorrected. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. All the products were characterized by ^{1}H, ^{13}C NMR, ESI-MS and IR analysis here and were identified by comparison of their characterized data with those reported in the literature.

Typical procedure for the synthesis of [TBP][Arg]



[TBP][Arg] was synthesized according to the reported procedure.[28] In a typical process, an [TBP][OH] 40% aqueous solution (20 mmol, 13.8 g) was added dropwise to a aqueous solution of slightly excess amino acid (22 mmol, 4.0 g,). After stirring for 24 h at room temperature, water was removed by evaporation in vacuum. A mixture (30 mL) of acetonitrile and methanol at the percentage of 9:1 was added to the reaction mixture. Then the mixture was agitated intensely for 2 h to deposit the excess amino acid. Then excess amino acid was removed by filtration. The target product was obtained with a yield of 80% by evaporation and then dried in vacuo for 1 d at 70 ^{o}C. Other AAILs such as [TBN][Arg], [Bmim][Arg] and [TBP][Ala] was prepared similarly.

General procedure for the reaction of 2-aminobenzonitrile and CO_2

All of the reactions were conducted in a 50 mL stainless steel reactor with a magnetic bar. In a typical experiment, 2-aminobenzonitrile (1 mmol, 0.118 g) and [TBP][Arg] (0.1 mmol, 0.0433 g) were introduced into the inner glass tube successively. Afterwards, CO_2 with an appropriate pressure was charged. The reaction mixture was stirred for desired time at pre-set temperature. When the reaction finished, the reactor was cooled in ice-water and CO_2 was ejected slowly. After addition of 20 mL water, the residue was filtrated to yield the crude product with recovery of the catalyst. The crude product was washed with water and *t*-BuOMe, respectively and then dried in vacuo at 70 °C for 24 h. The product was further identified by NMR, IR and ESI-MS.

Characterization data of the products

Quinazoline-2,4(1H, 3H)-dione (2a). Mp > 300 °C; IR (KBr) ν/cm^{-1} 3253, 3054, 2846, 1702, 1670, 1618, 1443, 755; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.29 (s, 1H), 11.14 (s, 1H), 7.87 (dd, J = 8.3, 1.4 Hz, 1H), 7.63-7.59 (m, 1H), 7.15 (t, J = 7.4 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ 163.10, 150.57, 141.11, 135.23, 127.21, 122.59, 115.57, 114.58 ppm; ESI-MS calcd for $[C_8H_6N_2O_2]^-$ 161.13, found 161.17 (M-H)$^-$.

6,7-**Dimethoxyquinazoline-2,4(1H, 3H)-dione (2b).** Mp > 300 °C; IR (KBr) ν/cm^{-1} 3471, 3379, 3294, 3175, 1704, 1627, 1427, 1436, 1269, 1103; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.11 (s, 1H), 10.93 (s, 1H), 7.25 (s, 1H), 6.67 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ 162.31, 154.89, 150.40, 145.02, 136.54, 107.13, 106.19, 97.75, 55.80, 55.70 ppm; ESI-MS calcd for $[C_{10}H_9N_2O_4]^-$ 221.05, found 221.07 (M-H)$^-$.

6-Chloroquinazoline-2,4(1H, 3H)-dione (2c). Mp > 300 °C; IR (KBr) ν/cm^{-1} 3210, 3060, 1728, 1668, 1482, 1431, 1284, 877; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.35 (s, 2H), 7.81 (s, 1H), 7.67 (s, 1H), 7.17 (d, J = 8.8 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ 161.83, 150.05, 139.75, 134.76, 126.27, 125.84, 117.54, 115.71 ppm; ESI-MS calcd for $[C_8H_4ClN_2O_2]^-$ 195.58, found 195.17 (M-H)$^-$.

7-Chloroquinazoline-2,4(1H, 3H)-dione (2d). Mp > 300 °C; IR (KBr) ν/cm^{-1} 3306, 3171, 3050, 1744, 1687, 1617, 1430, 1286, 862; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.31 (s, 2H), 7.86 (d, J = 7.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.17 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ 162.05, 150.21, 142.03, 139.27, 129.04, 122.46, 114.71, 113.34 ppm; ESI-MS calcd for $[C_8H_4ClN_2O_2]^-$ 195.58, found 195.21 (M-H)$^-$.

6-Bromoquinazoline-2,4(1H, 3H)-dione (2e). Mp > 300 °C; IR (KBr) ν/cm^{-1} 3193, 3066, 1742, 1701, 1613, 1480, 1433, 1286, 836; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.33 (s, 2H), 7.93 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ 161.75, 150.09, 140.16, 137.48, 128.90, 117.82, 116.22, 113.78 ppm; HRMS calcd for $C_8H_5BrN_2O_2$ (M-H)$^-$ 238.9462, found 238.9455.

6-Fluoroquinazoline-2,4(1H, 3H)-dione (2f). Mp > 300 °C; IR (KBr) ν/cm^{-1} 3236, 3054, 1718, 1678, 1500, 1439, 1378, 1287, 884; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.19 (m, 1H), 7.52-7.60 (m, 2H), 11.29 (s, 2H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ (111.7, 112.0), (115.2, 115.3), (117.4, 117.5), (122.7, 122.9), 137.4, 150.0, (156.0, 158.4), (162.05, 162.07) ppm; HRMS calcd for $C_8H_5FN_2O_2$ (M-H)$^-$ 179.0262, found 179.0255.

7-Methylquinazoline-2,4(1H, 3H)-dione (2g). Mp > 300 °C; IR (KBr) ν/cm^{-1} 3193, 3066, 2950. 1742, 1701, 1613, 1480, 1433, 1286, 836; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.12 (s, 2H), 7.75 (d, 1H), 6.98 (t, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ 162.68, 150.44, 145.57, 140.93, 126.89, 123.63, 115.04, 112.04, 21.42 ppm; HRMS calcd for $C_8H_5BrN_2O_2$ (M-H)$^-$ 175.0586, found 175.0583.

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