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SILVER-CATALYZED CONVERSION OF CO_2 AND 2-ETHYNYLANILINES INTO 4-HYDROXYQUINOLIN-2(1*H*)-ONES IN PROTIC IONIC LIQUID AT ATMOSPHERIC PRESSURE

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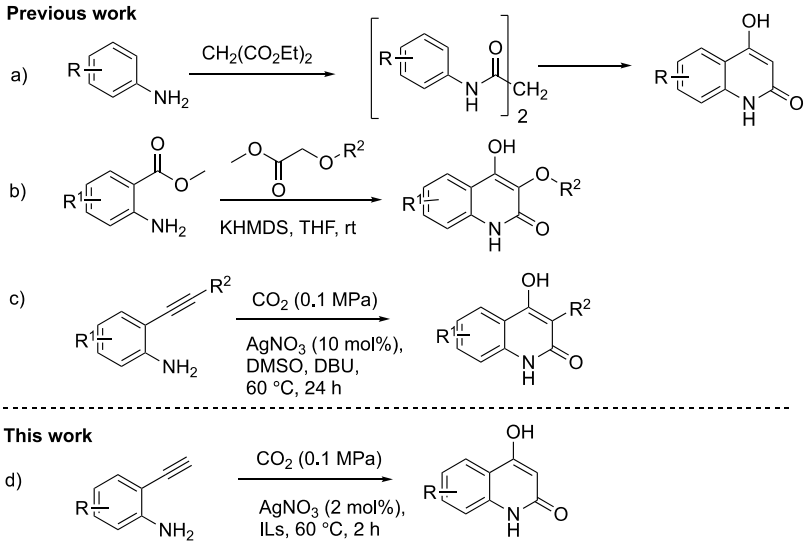
Abstract – 4-Hydroxyquinolin-2(1*H*)-ones are core structural subunits frequently found in many pharmacological compounds and the synthesis of this kind of compounds is highly desirable. An efficient protic ionic liquid and $AgNO_3$ catalytic system was developed for the preparation of various 4-hydroquinolin-2(1*H*)-ones from CO_2 and 2-ethynylanilines in moderate to excellent yields (65-94%). It was found that [HTMG][Im], a simple and easily prepared protic ionic liquid comprising a 1,1,3,3-tetramethylguanidinium cation and a imidazolide anion, could act as both the solvent and reaction promoter, and that the reaction could be efficient carried out with a mount of 2 mol% $AgNO_3$ under atmospheric pressure of CO_2 at 60 ℃. This method provides a new approach for the synthesis of 4-hydroxyquinolin-2(1*H*)-ones.

Due to the environmental advantage of CO_2 as a C1 building block, as well as the importance of CO_2 emission reduction in mitigate climate change, chemical conversion of CO_2 has paid much attention in recent decades. In this field, ionic liquids (IL), because of their unique properties, have showed outstanding performance in CO_2 capture and utilization processes. Many value-added chemicals have been synthesized from CO_2, using ILs as solvents and/or catalysts, such as quinazoline-2,4-(1*H*,3*H*)-diones,[1-6] cyclic carbonates,[7] 2-benzimidazolones,[8] carbamates,[9] oxazolidinones,[10] ureas,[11] and so on. Although much progress has been made, expanding the scope of the chemical conversion of CO_2 in ILs, especially under mild conditions is still a challenge.

4-Hydroxyquinolin-2(1*H*)-one derivatives are important intermediates due to their pharmacological activities,[12] including antitubercular potency,[13] anti-HIV activity,[14] antibacterial activity,[15] and anticancer

activity.[16] The traditional preparations of 4-hydroxyquinolin-2(1*H*)-ones mostly require multistep reactions or relatively harsh conditions, as shown in **Scheme 1**.[17-21] These methods have been based on cyclization of malondianilides under high temperature (**Scheme 1 a**), or nucleophilic addition-elimination reactions (**Scheme 1 b**). An alternative method of 4-hydroxyquinolin-2(1*H*)-one synthesis is based on the DBU-promoted preparation from *o*-alkynylaniline derivatives and CO_2 in DMSO or acetonitrile in the presence of silver nitrate (**Scheme 1 c**).[22,23] We were inspired by this method and envisioned that 4-hydroxyquinolin-2(1*H*)-ones could be obtained using CO_2 and *o*-alkynylanilines under IL-promoted conditions in the presence of $AgNO_3$. Herein, a series of protic ILs were synthesized and utilized for the preparation of various 4-hydroxyquinolin-2(1*H*)-ones (**Figure 1**). It was found that these simple and easily prepared ILs could act as both the solvent and promoter, and the reactions could be carried out efficiently at atmospheric pressure of CO_2 with a smaller amount of $AgNO_3$ (**Scheme 1 d**).



Scheme 1. Synthesis of 4-hydroxyquinolin-2(1*H*)-one derivatives

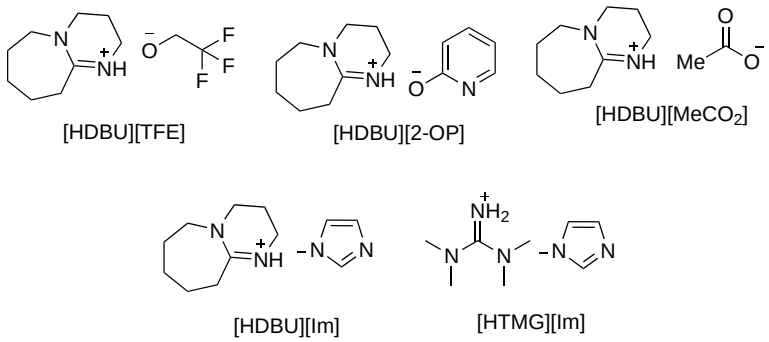
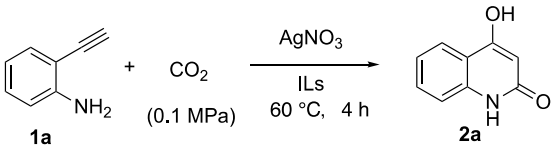


Figure 1. The protic ILs prepared in current study

Initially, 2-ethynylaniline was selected as a model substrate, and the reaction with CO_2 catalyzed by $AgNO_3$ was carried out in the presence of different protic ILs as solvents at ambient conditions (**Table 1**). Based on the important catalytic role of DBU in previous synthesis of 4-hydroxyquinolin-2(1*H*)-one,[22] the DBU-typed protic ILs were examined at first. In general, the differences in their chemical structures may be responsible for their activities. [HDBU][Im], having the same cation as [HDBU][TFE], afforded a much higher product yield (78%), which indicated the anions of the protic ILs influence the activities of the catalysts. The promising results encourage us to further investigate the effect of cation on the catalytic activity. As can be seen from entries 4-5, the catalytic activity followed the order of [HTMG][Im]>[HDBU][Im]. This catalytic sequence may be related with the strength of hydrogen-bond between the substrate 2-ethynylaniline and the cation of protic ILs.

Table 1. Examination of ILs



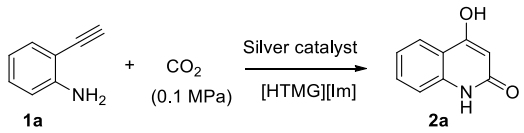
Entry [a]	Protic ILs	Yield(%)[b]
1	[HDBU][TFE]	46
2	[HDBU][2-OP]	69
3	[HDBU][OAc]	67
4	[HDBU][Im]	78
5	[HTMG][Im]	87

[a] Starting material **1a** (1.0 mmol) and $AgNO_3$ (10 mol%) in protic IL (3.0 mmol) at 60 ℃ under atmospheric pressure of CO_2. [b] Isolated yields.

The amount of ILs and Ag catalyst as well as the reaction temperature and reaction time was then finely tuned (**Table 2**). It was found that within 2-6 hours, the reaction time have little effect on the yield (entries 1-3). Further shortening reaction time resulted in an uncompetitive product yield (entry 4). Additionally, this reaction can be proceeded under a low temperature of 30 ℃, affording a promising yield of 80% (entry 5). Meanwhile, a lower yield of 30% was obtained, probably due to the decomposition of 2-ethynylaniline under a higher temperature of 80 ℃ (entry 6). Intrigued by these results, we attempted to reduce the amount of Ag catalyst and [HTMG][Im] for the sake of low cost of the reaction. To our delight, with the amount of 2 mol% and 1 mol% $AgNO_3$, the reaction could still afford 4-hydroxyquinolin-2(1*H*)-one in a yield of 89% (entry 7) and 83% respectively. Nevertheless, because of low solubility of 2-ethynylaniline, a low yield could be generated with 1 equiv. [HTMG][Im] (entry 11). Notably, it was found that 2 mol% of AgI as

catalyst gave the same yield as $AgNO_3$ (entry 8), and the reaction afforded a slightly lower yield with 2 mol% AgOAc (entry 9). These proved that both soluble silver salt and insoluble silver salt could effectively catalyze the reaction, and relatively cheap $AgNO_3$ is the first choice for reaction catalyst. It is noteworthy that the reaction without any silver catalyst gave no product (entry 12). These clearly certified the catalytic role of silver salt. Summarily, the optimal reaction conditions were as follows: 2 mol% $AgNO_3$, 3 equiv. [HTMG][Im], 0.1 MPa CO_2, 60 ℃ for 2 hours.

Table 2. Condition optimization



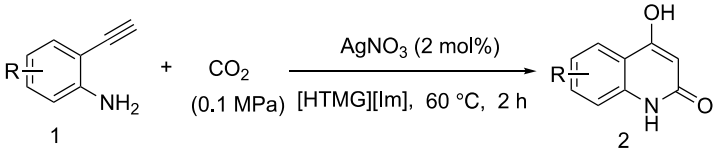
Entry [a]	Silver catalyst (mol%)	Temperature(℃)	Time (h)	Yield(%)[b]
1	$AgNO_3$ (10)	60	4	87
2	$AgNO_3$ (10)	60	6	90
3	$AgNO_3$ (10)	60	2	88
4	$AgNO_3$ (10)	60	1	80
5	$AgNO_3$ (10)	30	18	80
6	$AgNO_3$ (10)	80	2	30
7	$AgNO_3$ (2)	60	2	89
8	AgI (2)	60	2	89
9	AgOAc (2)	60	2	86
10	$AgNO_3$ (1)	60	2	83
11	$AgNO_3$ (2) [c]	60	2	63
12	$AgNO_3$ (0)	60	2	0

[a] Conditions: starting material **1a** (1.0 mmol) and $AgNO_3$ in [HTMG][Im] (3.0 mmol) under atmospheric pressure of CO_2. [b] Isolated yields. [c] [HTMG][Im] (1.0 mmol) was used.

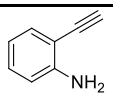
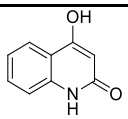
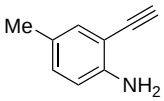
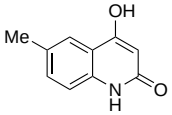
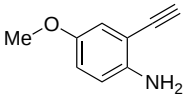
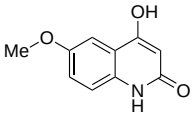
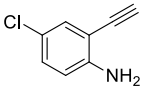
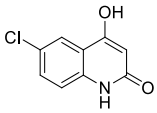
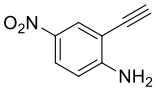
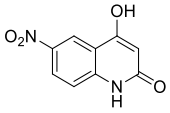
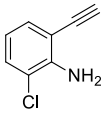
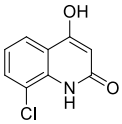
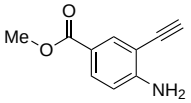
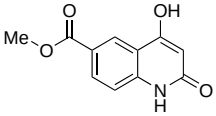
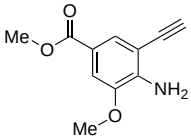
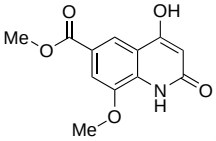
Under the optimized reaction conditions, the [HTMG][Im] and $AgNO_3$-catalyzed system could be applied to various 2-ethynylanilines reacting with CO_2 at atmospheric pressure (**Table 3**). It was demonstrated that both electron-withdrawing and –donating groups at the phenyl ring can proceed smoothly to produce the corresponding 4-hydroxyquinolin-2(1*H*)-ones (entries 1-5). The positions of substituents do not affect the yields dramatically (entries 4 and 6). When there is methoxy at the *para* position of phenyl ring, this catalytic system give the corresponding product in excellent yield (94%, entry 3). Probably owing to the instability of methoxycarbonyl group, relatively low yields were obtained in entry 7 and 8. The present

catalytic system was also successfully applied to 2-((trimethylsilyl)ethynyl)anilines with carbon dioxide in moderate yield (78%), though trimethylsilyl group was removed (**Scheme 2**).

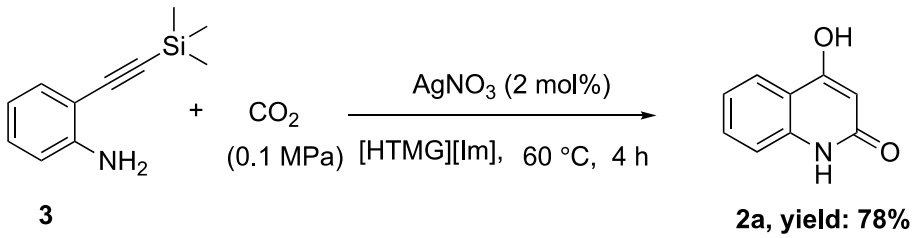
Table 3. Synthesis of various 4-hydroxyquinolin-2(1*H*)-ones



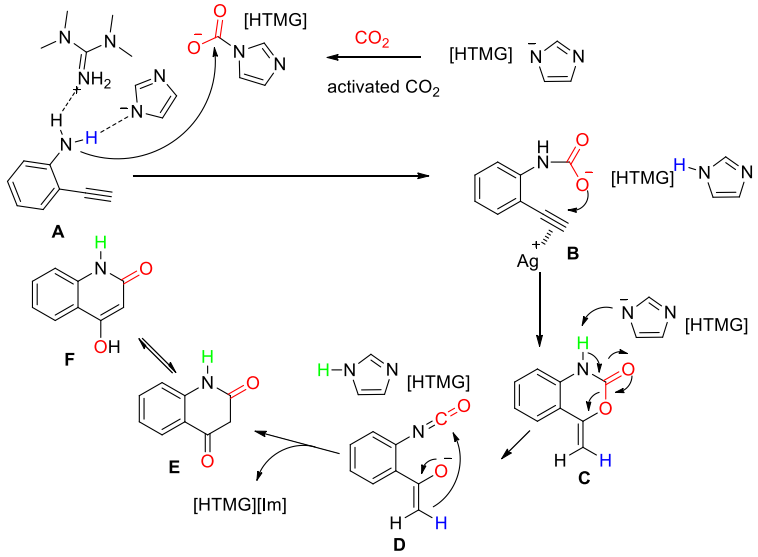
1 2

Entry [a]	Substrate	Product	Yield(%)[b]
1	 **1a**	 **2a**	90
2	 **1b**	 **2b**	91
3	 **1c**	 **2c**	94
4	 **1d**	 **2d**	90
5	 **1e**	 **2e**	80
6	 **1f**	 **2f**	88
7	 **1g**	 **2g**	65
8	 **1h**	 **2h**	69

[a] Conditions: starting material **1** (1.0 mmol) and $AgNO_3$ in [HTMG][Im] (3.0 mmol) at 60 °C under atmospheric pressure of CO_2. [b] Isolated yields.



Scheme 2. Synthesis of 4-hydroxyquinolin-2(1*H*)-one from 2-((trimethylsilyl)ethynyl)aniline



Scheme 3. Plausible reaction mechanism

On the basis of the above experimental results and previous reports,[2,22] we proposed a plausible mechanism as shown in **Scheme 3**. Initially, CO_2 was activated by the [Im] anion, and this kind of interactions between [HTMG][Im] and CO_2 were confirmed by previous report.[6] Meanwhile, the substrate of 2-ethynylaniline was activated by [HTMG][Im] through hydrogen bonds (**A**). Then, the electron-rich nitrogen of **A** facilely conducted a nucleophilic attack at the activated CO_2 to produce an oxyanion intermediate **B**. The oxygen anion of the intermediate **B** attacked the triple bond activated by $AgNO_3$, thus generating benzoxazin-2-one **C**. Subsequently, the benzoxazine would immediately be deprotonated with [Im] anion to generate the isocyanate and the enolate from C-O bond cleavage of the carbamate functionality (**D**). The enolate would then attack the carbon atom of the isocyanate to afford the 1, 3-diketone intermediate **E**, which would afford 4-hydroxyquinolin-2(1*H*)-one (**F**) after enolization.

In conclusion, a strategy of simple employing $AgNO_3$ and [HTMG][Im] as a highly efficient catalytic system for the transformation of 2-ethynylanilines into 4-hydroquinolin-2(1*H*)-ones with CO_2 was developed. We found that both the cations and anions of this IL played important role in this reaction. Various substrates could be converted into the desired compounds in moderate to excellent yields under

atmospheric pressure of CO_2 even when the silver loading was decreased to the lowermost level of 2 mol%. Further investigation of the application of the reaction to the synthesis of more complex molecules are underway.

EXPERIMENTAL

All reagents, including 2-ethynylaniline, were purched from Energy Chemistry Co. Ltd., and used without further purification. CO_2 and Ar were purchased from Hangzhou Jinggong Special Gas Co. Ltd. ^{1}H NMR and ^{13}C NMR studies were carried out with a Bruker AVANCE III 500 (500 MHz, 125 MHz) spectrometer or Bruker AVANCE III HD 600 (600 MHz, 150 MHz) with $CDCl_3$, D_2O or DMSO-d_6 as the solvent.

The Preparation of Protic ILs. According to the reported procedures,[1,2] the protic ILs were synthesized via the neutralization of corresponding based and proton donors respectively. In a typical process, equimolar imidazole (50 mmol) was added to the 1,1,3,3-tetramethylguanidine (50 mmol), then the mixture was stirred at 30 ℃ for 10 h under Ar atmosphere. The product [HTMG][Im] thus obtained in quantitative yield was then stored over 4 Å molecular sieves before use. Other protic ILs were prepared similarly. The structures of them were confirmed by NMR.

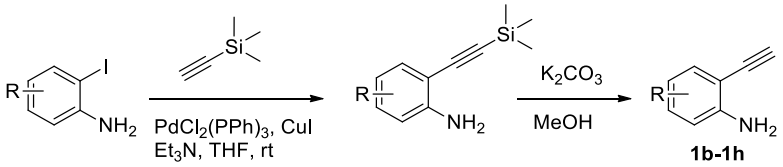
1,1,3,3-Tetramethylguanidinium imidazolide [HTMG][Im]: ^{1}H NMR (600 MHz, D_2O) δ 7.62 (s, 1H), 7.00 (s, 2H), 2.76 (s, 12H). ^{13}C NMR (150 MHz, D_2O) δ 163.57, 136.62, 122.04, 38.74.

1,8-Diazabicyclo[5.4.0]-7-undecenium imidazolide [HDBU][Im]: ^{1}H NMR (600 MHz, D_2O) δ 7.62 (s, 1H), 7.00 (s, 2H), 3.39-3.37 (m, 2H), 3.34 (t, 2H), 3.15 (t, 2H), 2.45-2.43 (m, 2H), 1.85-1.82 (m, 2H), 1.62-1.49 (m, 6H). ^{13}C NMR (150 MHz, D_2O) δ 165.87, 136.26, 121.88, 49.78, 45.79, 37.90, 36.15, 29.88, 29.05, 27.32, 22.58.

1,8-Diazabicyclo[5.4.0]-7-undecenium 2,2,2-trifluoroethanolate [HDBU][TFE]: ^{1}H NMR (600 MHz, D_2O) δ 3.82-3.77 (m, 2H), 3.43-3.42 (m, 2H), 3.38 (t, 2H), 3.18 (t, 2H), 2.49-2.48 (m, 2H), 1.89-1.85 (m, 2H), 1.62-1.53 (m, 6H). ^{13}C NMR (150 MHz, D_2O) δ 165.93, 125.95 (q), 60.90 (q), 54.07, 48.16, 38.04, 32.83, 28.42, 25.87, 23.32, 18.95.

1,8-Diazabicyclo[5.4.0]-7-undecenium pyridin-2-olate [HDBU][2-OP]: ^{1}H NMR (600 MHz, D_2O) δ 7.65 (dd, 1H), 7.40-7.38 (m, 1H), 6.41 (t, 1H), 6.33 (d, 1H), 3.39-3.37 (m, 2H), 3.34 (t, 2H), 3.15 (t, 2H), 2.45-2.43 (m, 2H), 1.85-1.82 (m, 2H), 1.60-1.50 (m, 6H). ^{13}C NMR (150 MHz, D_2O) δ 169.43, 165.81, 144.01, 140.45, 115.04, 110.28, 54.03, 48.09, 37.94, 32.74, 28.37, 23.26, 18.87.

1,8-Diazabicyclo[5.4.0]-7-undecenium acetate [HDBU][OAc]: ^{1}H NMR (600 MHz, D_2O) δ 3.46-3.45 (m, 2H), 3.41 (t, 2H), 3.21 (t, 2H), 2.52-2.50 (m, 2H), 1.92-1.89 (m, 2H), 1.80 (s, 3H), 1.64-1.57 (m, 6H). ^{13}C NMR (150 MHz, D_2O) δ 181.23, 165.94, 54.12, 48.19, 37.94, 32.77, 23.29, 23.25, 18.90.



Scheme 4. Synthesis of 2-ethynylanilines

The Preparation of 2-Ethynylanilines. The substrates 2-ethynylanilines were synthesized according to the literature (**Scheme 4**), and confirmed by ^{1}H NMR and ^{13}C NMR.[24,25] 2-Ethynyl-4-methylaniline (**1b**), brown oil, yield 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (s, 1H, Ar-H), 6.95 (dd, 1H, ^{4}J= 1.8 Hz, J= 8.3 Hz, Ar-H), 6.61 (d, 1H, J= 8.5 Hz, Ar-H), 4.12 (br s, 2H, NH2), 3.35 (s, 1H, CH), 2.20 (s, 3H, CH3). ^{13}C NMR (125 MHz, $CDCl_3$) 146.19, 132.64, 130.98, 127.06, 114.53, 106.63, 82.14, 80.80, 20.20.

2-Ethynyl-4-methoxyaniline (**1c**), brown oil, yield 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (d, 1H, ^{4}J=2.5 Hz, Ar-H), 6.78 (dd, 1H, ^{4}J= 2.8 Hz, J= 8.8 Hz, Ar-H), 6.65 (d, 1H, J= 8.5 Hz, Ar-H), 3.73 (s, 3H, CH3). 3.38 (s, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 150.68, 141.76, 116.82, 115.24, 114.93, 106.18, 81.41, 79.64, 54.76.

2-Ethynyl-4-chloroaniline (**1d**), brown solid, mp 57-58 ℃, yield 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, 1H, ^{4}J=2.5 Hz, Ar-H), 7.09 (dd, 1H, ^{4}J= 2.5 Hz, J= 8.5 Hz, Ar-H), 6.62 (d, 1H, J= 8.5 Hz, Ar-H), 4.25 (s, 2H, NH2), 3.41 (s, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 146.11, 130.75, 129.13, 120.92, 114.42, 106.83, 82.47, 78.34.

2-Ethynyl-4-nitroaniline (**1e**), yellow solid, mp 116-117 ℃, yield 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, 1H, ^{4}J=3.0 Hz, Ar-H), 8.05 (dd, 1H, ^{4}J= 3.0 Hz, J= 9.0 Hz, Ar-H), 6.68 (d, 1H, J= 9.0 Hz, Ar-H), 4.96 (s, 2H, NH2), 3.47 (s, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 152.56, 137.25, 128.31, 125.40, 111.95, 104.70, 83.24, 77.13.

2-Ethynyl-6-chloroaniline (**1f**), brown solid, mp 39-41 ℃, yield 90%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (d, 2H, J= 7.8 Hz, Ar-H), 6.60 (t, 1H, J= 7.8 Hz, Ar-H), 4.64 (s, 2H, NH2), 3.42 (s, 1H, CH). ^{13}C NMR (150 MHz, $CDCl_3$): 145.15, 131.06, 130.21, 118.71, 117.64, 107.71, 83.19, 79.91.

2-Ethynyl-4-methoxycarbonylaniline (**1g**), orange solid, mp 105-106 ℃, yield 85%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, 1H, ^{4}J=1.8 Hz, Ar-H), 7.82 (dd, 1H, ^{4}J= 1.8 Hz, J= 8.4 Hz, Ar-H), 6.67 (d, 1H, J= 8.4 Hz, Ar-H), 4.69 (s, 2H, NH2), 3.85 (s, 3H, OCH3), 3.40 (s, 1H, CH). ^{13}C NMR (150 MHz, $CDCl_3$): 166.48, 152.17, 134.94, 131.86, 119.29, 113.28, 105.81, 82.99, 79.51, 51.77.

2-Ethynyl-4-methoxycarbonyl-8-methoxyaniline (**1h**), orange solid, mp 86-87 ℃, yield 90%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, 1H, ^{4}J=1.8 Hz, Ar-H), 7.41 (d, 1H, ^{4}J=1.8 Hz, Ar-H), 4.84 (s, 2H, NH_2), 3.91 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 3.39 (s, 1H, CH). ^{13}C NMR (150 MHz, $CDCl_3$): 166.74, 145.62, 143.42, 127.28, 118.35, 111.08, 82.82, 79.53, 55.82, 51.85.

Typical Procedure for the Preparation of Products 4-Hydroxyquinolin-2(1*H*)-ones. Substrate 2-ethylnylaniline (1.0 mmol), $AgNO_3$ (2 mol%), and [HTMG][Im] (3.0 mmol) were loaded in a 20 mL Schlenk flask equipped with a magnetic stirrer, connecting with a CO_2 balloon. Then, the reaction mixture was stirred at the desired temperature for desired time. After cooling to room temperature, 10 mL water was added into the reactor. The resulting solution was filtered to remove insoluble matter. Then the pH of the mixture was adjusted to 2 by 2 mol/L nitric acid. The product precipitated from the mixture and was separated by filtration. Then the filter cake was washed with water and methyl *tert*-butyl ether, respectively, and dried under an infrared lamp for 4 hours. The product was further identified by NMR spectra. 4-Hydroxyquinolin-2(1*H*)-one (**2a**), white solid, mp >300 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.36 (s, 1H, OH), 11.20 (s, 1H, NH), 7.78 (d, 1H, *J*= 8.0 Hz, Ar-H), 7.49 (t, 1H, *J*= 8.0 Hz, Ar-H), 7.26 (d, 1H, *J*= 8.5 Hz, Ar-H), 7.14 (t, 1H, *J*= 7.3 Hz, Ar-H), 5.74 (s, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 163.49, 162.39, 139.17, 130.78, 122.61, 120.97, 115.06, 114.97, 98.21.

A similar procedure was used to prepare the other 4-hydroxyquinolin-2(1*H*)-ones, and the physical data of **2a-c** and **2 e-g** were identical with those reported in literatures.[26,27] Compounds **2d** and **2h** were confirmed by NMR and HRMS.

6-Methyl-4-hydroxyquinolin-2(1*H*)-one (**2b**), white solid, mp 258-259 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.94 (s, 1H, NH), 7.58 (s, 1H, Ar-H), 7.28 (d, 1H, *J*= 8.5 Hz, Ar-H), 7.14 (d, 1H, *J*= 8.5 Hz, Ar-H), 5.65 (s, 1H, CH), 2.33 (s, 3H, CH_3). 13C NMR (125 MHz, DMSO-d_6): 163.77, 163.71, 137.20, 131.54, 129.49, 122.40, 114.94, 114.89, 97.83, 20.62.

6-Methoxy-4-hydroxyquinolin-2(1*H*)-one (**2c**), white solid, mp >300 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.93 (s, 1H, NH), 7.25 (d, 1H, ^4J= 2.0 Hz, Ar-H), 7.18 (d, 1H, ^3J= 8.5 Hz, Ar-H), 7.11 (dd, 1H, ^4J= 3.0 Hz, ^3J= 9.0 Hz, Ar-H), 5.66 (s, 1H, CH), 3.77 (s, 3H, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6): 163.16, 162.19, 153.70, 133.65, 120.01, 116.53, 115.54, 103.89, 98.46, 55.30.

6-Chloro-4-hydroxyquinolin-2(1*H*)-one (**2d**), white solid, mp >300 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.54 (s, 1H, OH), 11.34 (s, 1H, NH), 7.72 (d, 1H, ^4J= 2.5 Hz, Ar-H), 7.54 (dd, 1H, ^4J= 2.5 Hz, *J*= 9.0 Hz, Ar-H), 7.27 (d, 1H, *J*= 8.5 Hz, Ar-H), 5.76 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6): 163.24, 161.26, 137.87, 130.75, 125.10, 121.71, 117.07, 116.20, 99.11. HRMS (ESI) $[M+H]^+$ calculated for $C_9H_7ClNO_2$: 196.0160 , found: 196.0158.

6-Nitro-4-hydroxyquinolin-2(1*H*)-one (**2e**), yellow solid, mp >300 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.23 (s, 1H, OH), 11.74 (s, 1H, NH), 8.59 (d, 1H, ^4J= 2.5 Hz, Ar-H), 8.33 (dd, 1H, ^4J= 2.5 Hz, *J*= 9.0 Hz, Ar-H), 7.39 (d, 1H, *J*= 9.0 Hz, Ar-H), 5.79 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6): 163.65, 162.43, 143.50, 140.89, 125.50, 119.26, 116.04, 115.06, 99.18.

8-Chloro-4-hydroxyquinolin-2(1*H*)-one (**2f**), gray solid, mp >300 ℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.67 (s, 1H, OH), 10.40 (s, 1H, NH), 7.79 (d, 1H, *J*= 8.4 Hz, Ar-H), 7.66 (d, 1H, *J*= 7.8 Hz, Ar-H), 7.12

(t, 1H, *J*= 8.1 Hz, Ar-H), 5.81 (s, 1H, CH). ^{13}C NMR (150 MHz, DMSO-d_6): 163.59, 162.67, 136.00, 131.52, 122.46, 122.19, 118.85, 117.48, 99.27.

6-Methoxycarbonyl-4-hydroxyquinolin-2(1*H*)-one (**2g**), white solid, mp 288-290 ℃. 1H NMR (600 MHz, DMSO-d_6): δ 11.56 (s, 1H, NH), 8.40 (d, 1H, ^4J= 1.8 Hz, Ar-H), 8.04 (dd, 1H, ^4J= 2.1 Hz, *J*= 8.7 Hz, Ar-H), 7.33 (d ,1H, *J*= 8.7 Hz, Ar-H), 5.79 (s, 1H, CH), 3.87 (s, 3H, OCH_3). 13C NMR (150 MHz, DMSO-d_6): 166.20, 164.10, 162.71, 142.87, 131.60, 125.25, 122.58, 115.90, 115.16, 99.28, 52.53.

6-Methoxycarbonyl-8-methoxy-4-hydroxyquinolin-2(1*H*)-one (**2h**), white solid, mp 291-292 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.75 (s, 1H, OH), 10.60 (s, 1H, NH), 8.06 (d, 1H, ^4J= 1.2 Hz, Ar-H), 7.53 (d, 1H, ^4J= 1.2 Hz, Ar-H), 5.79 (s, 1H, CH), 3.94 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3). ^{13}C NMR (150 MHz, DMSO-d_6): 166.30, 163.56, 163.03, 146.20, 133.41, 131.94, 122.45, 115.62, 110.79, 99.66, 56.66, 52.64. HRMS (ESI) $[M+H]^+$ calculated for $C_{12}H_{12}NO_5$: 250.0716, found: 250.0708.

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