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MeOTf- and TBD-Mediated Carbonylation of *ortho*-Arylanilines with CO_2 Leading to Phenanthridinones

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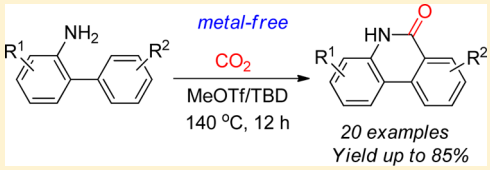
Supporting Information

ABSTRACT: Carbonylation of *o*-arylanilines utilizing CO_2 as a carbonyl source for the synthesis of important phenanthridinones with a free (NH)-lactam motif has been described under metal-free condition. A range of *o*-arylanilines were transformed to the corresponding phenanthridinones in high yields.



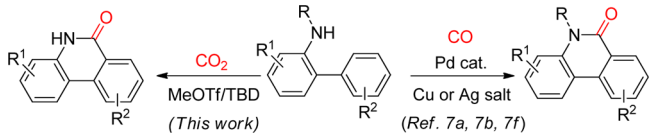
INTRODUCTION

CO_2 is a green, abundant, and inexpensive one-carbon source, which has attracted a great attention in organic synthesis.[1] However, inertia in kinetics and stability in thermodynamics restrict its utilization. On the other hand, as a waste material of combustion, CO_2 emitted to the atmosphere is also threatening the balance of carbon cycle. As a result, research focused on activation and transformation of CO_2 fulfilling the demand of sustainable development is necessary. Recently, utilization of CO_2 for synthesis of carboxylic acid,[2] carbonate,[3] formamide[4] and aldehyde[5] have been well studied. However, carbonylation reaction employing CO_2 has been rarely reported.[6] Compared with CO,[7] which was extensively utilized in transition metal-catalyzed C−H carbonylation reaction, CO_2 seems to be a more promising carbonyl source in organic synthesis considering safety and feasibility. Consequently, application of CO_2 in the carbonylation reactions may provide a better choice for the synthesis of lactam and lactone.

Phenanthridinone is a significant scaffold widely existing in natural product[8a] and valuable compounds with biological activities, such as antitumor,[8b,c] anti-HIV,[8d] and antileukemic.[8e] Traditionally, the phenanthridinone could be obtained from several paths, such as Beckmann rearrangement of oxime, intramolecular C−C formation of *N*-arylbenzamide,[9] and intermolecular C−C and C−N formation between benzoamide and arene[10] or aryne.[11] Recently, transition metal-catalyzed directly C−H activation to obtain phenanthridinones has been reported. In 2013, Zhu,[7a] Zhang,[7b] and Chuang's group,[7f] independently described the carbonyl reaction of *ortho*-arylaniline catalyzed by palladium catalyst using CO as carbonyl source in the presence of copper or silver salts to yield the phenanthridinones (Scheme 1, right).

As part of our ongoing project on CO_2,[12] we herein reported a metal-free method to synthesize the phenanthridinones from *ortho*-arylaniline using atmospheric CO_2 as the carbonyl source with the assistance of MeOTf and TBD (Scheme 1, left), which extend the utilization of CO_2 as C1 synthons.

Scheme 1. Approach to Phenanthridinones Using C1 Synthons



RESULTS AND DISCUSSION

At the outset, we used *o*-phenylaniline **1a** as a starting material to react with CO_2 in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in dichloroethane (DCE) at 140 °C, the reaction did not proceed after 12 h (Table 1, entry 1). As part of our ongoing project using MeOTf,[13] two equivalents of MeOTf was added under the same reaction condition and the desired phenanthridinone **2a** was obtained in 30% yield (entry 2). When three equivalents of MeOTf was added, the yield of **2a** was increased to 63% (entry 3), while addition of four equivalents of MeOTf reduced the yield of **2a** to 58% (entry 4). Then different bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), K_2CO_3, Cs_2CO_3, and ^{t}BuOK, were screened (entries 5−8). TBD showed an excellent performance as a base in this reaction (entry 3). The solvents were also evaluated in the reaction. 1,2-Dichlorobenzene (*o*-DCB) was superior to DCE, PhCl, and toluene (entries 3, 9−11). The reaction showed a dependence on the temperature. When the reaction was treated at 160 °C, 130 °C, and 120 °C, respectively, the yield of **2a** was obtained in 79%, 58%, and 22% (entries 12−14). Notably, the reaction was treated at 160 °C for 3 and 8 h, the yield of product **2a** was obtained in 65% and 45%, respectively.

With optimized reaction condition in hand, we used a range of *o*-arylanilines to investigate substrate scope, and the representative results are summarized in Table 2. Electronic property of

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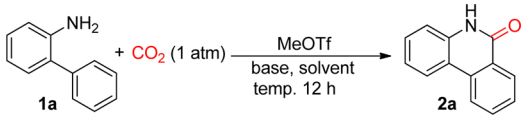
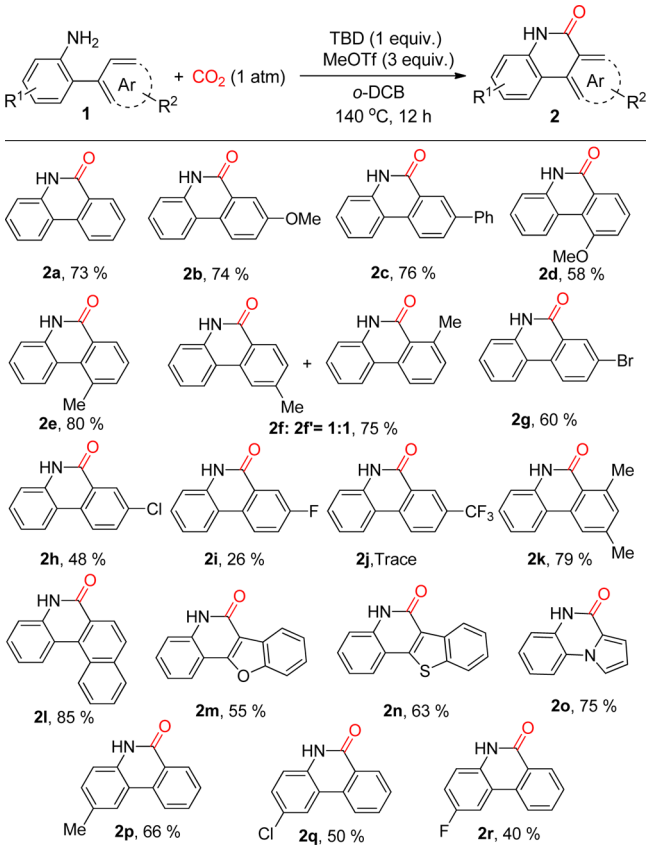
Table 1. Optimization of Reaction of *o*-Phenylaniline 1a with CO_2[a]



entry	MeOTf (*x* equiv)	base	solvent	temp (°C)	yield (%)[b]
1		TBD	DCE	140	0
2	2	TBD	DCE	140	30
3	3	TBD	DCE	140	63
4	4	TBD	DCE	140	58
5	3	DBU	DCE	140	5
6	3	K_2CO_3	DCE	140	0
7	3	Cs_2CO_3	DCE	140	0
8	3	^tBuOK	DCE	140	0
9	3	TBD	PhCl	140	59
10	**3**	**TBD**	***o*-DCB**	**140**	**80** (73)
11	3	TBD	Toluene	140	27
12	3	TBD	*o*-DCB	160	79
13	3	TBD	*o*-DCB	130	58
14	3	TBD	*o*-DCB	120	22
15[c]	3	TBD	*o*-DCB	160	65
16[d]	3	TBD	*o*-DCB	160	45

[a]Reactions were carried out with 0.1 mmol *o*-phenylaniline. [b]NMR yield was detected using dibromomethane as internal standard, isolated yield in parentheses. [c]Reaction time 3 h. [d]Reaction time 8 h.

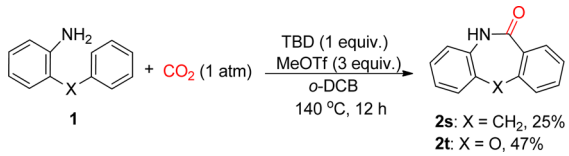
Table 2. Carbonylation of *o*-Arylanilines with CO_2[a]



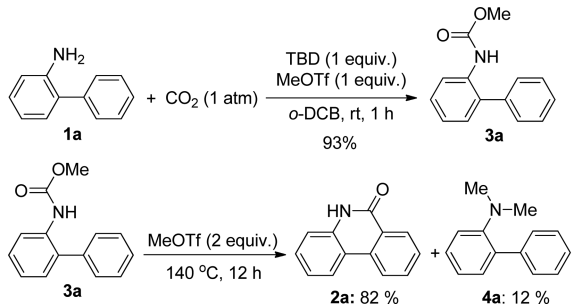
[a]Reactions were carried out with 0.3 mmol *o*-arylaniline. All yields are isolated yields.

substituents is the determinate factor in the reaction. Substrates with electron-donating group in aryl moiety, such as **1b**−**1f** and **1k**, demonstrated higher reactivity and afforded the corresponding products **2** in high yields, while electron-withdrawing group decreased the yield dramatically, such as formation of the corresponding products **2g**−**2j**. The steric effect is unobvious in this reaction, *ortho*-substituted substrates, such as **1d** and **1e**, could react with CO_2 smoothly to give the desired product **2d** and **2e** in 58% and 80% yield, respectively. When *meta*-substituted substrate as **1f** was used, mixture of two isomers (**2f**, **2f′**) in 1:1 ratio were isolated. When two methyl groups located in the *meta*-position of aryl moiety, the product **2k** was obtained in 79% yield. Notably, 2-(naphthalen-1-yl)aniline **1l** and 2-heteroarylanilines, such as **1m**, **1n**, and **1o**, were well subjected in this reaction and delivered the corresponding products **2l**, **2m**, **2n**, and **2o** in good yields, respectively. In addition, substituents such as −Me, −Cl, and, −F could also be tolerated in the aniline ring to afford phenanthridinones **2p**, **2q**, and **2r** in moderate yields.

Furthermore, we have tried to extend this method to synthesis of seven-membered lactams, and the products were isolated in low yield (eq 1).



To gain more information for the reaction mechanism, more experiments were conducted. Initially, *o*-phenylaniline **1a** was treated with CO_2 in the presence of one equivalent TBD and one equivalent of MeOTf at room temperature for 1 h, and *o*-methyl [1,1′-biphenyl]-2-ylcarbamate **3a** was isolated in 93% yield (eq 2). Undoubtly, CO_2 was fixated in the first step to generate the



carbamate **3a**. Then the product **3a** was treated by two equivalents of MeOTf at 140 °C for 12 h, and the phenanthridinone **2a** was obtained in 82% yield with *N*,*N*-dimethyl-[1,1′-biphenyl]-2-amine **4a** in 12% yield (eq 3). The formation of dimethylated product **4a** indicated that the carbamate **3a** could be converted into **1a** under high temperature. Namely, the reaction of **1a** with CO_2 to form carbamate **3a** in the presence of TBD and MeOTf at 140 °C is a reversible reaction. In addition, when the carbamate **3a** was tested by GC-MS, 2-isocyanato-1,1′-biphenyl **5** was observed. This result supported the possibility of isocynate as a key intermediate in this reaction.

On the basis of the experimental results as well as the known reports,[14] the reaction mechanism was proposed as follows (Scheme 2). First, the *o*-arylaniline **1** attacks adduct of TBD and CO_2 to generate the carbamate **3** with the aid of MeOTf. Then,

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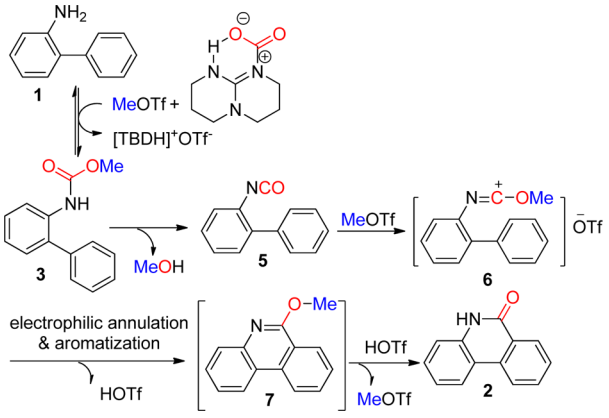
Scheme 2. Plausible Reaction Mechanism



the carbamate **3** tends to lose MeOH to produce isocynate **5** at high temperature.[14b] Next, cyclization occurs in the presence of MeOTf to form the 6-methoxyphenanthridine **7** via intermediate **6**. Finally, the intermediate **7** is hydrolyzed *in situ* to afford phenanthridinone **2**. Addition of excess MeOTf may be attributed to interactions with product.

CONCLUSION

In conclusion, we have developed a carbonylation reaction of *o*-arylanilines applying CO_2 as the ideal carbonyl source to synthesize phenanthridinones containing a free (NH)-lactam motif under metal-free conditions. A range of functionalized phenanthridinone products are obtained in high yields.

EXPERIMENTAL SECTION

General information. DMF (*N*,*N*-dimethylformamide), *o*-DCB (*ortho*-dichlorobenzene), DCM (dichloromethane), and DCE (1,2-dichloroethane) were dried by 4 Å molecular sieves. Unless otherwise mentioned, all reagents commercially available were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded utilizing 600 MHz spectrometer and 400 MHz spectrometer and d_6-DMSO was selected as the solvent. Chemical shifts (δ), recorded in ppm, were referenced using the residual proton resonance of d_6-DMSO (2.50) in ^{1}H NMR and carbon resonance of d_6-DMSO (39.5) in ^{13}C NMR. Coupling constants (J) were obtained in Hertz (Hz). The terms s, d, t, and m represent singlet, doublet, triplet, and multiplet. HRMS were obtained with ESI in positive ion mode on IT-TOF instrument.

General Procedure for Synthesis of 2-Arylaniline ***1***. Sealed tube with 2-bromoaniline (3 mmol), aryboronic acid (4.5 mmol), K_2CO_3 (9 mmol), and $PdCl_2(PPh_3)_2$ (0.3 mmol) was evacuated and backfilled with N_2. DMF/H_2O (15 mL/3 mL) was added under N_2 flow. The tube was closed and the mixture was stirred for 24 h at 90 °C. Then, the reaction was cooled to room temperature, diluted with H_2O and extracted with EtOAc three times. The combined organic layer was washed with saturated NaCl solution two times, dried by Na_2SO_4, evaporated, and purified by flash chromatography (petroleum ether/EtOAc).

*Synthesis of 2-(1H-Pyrrol-1-yl)aniline (**1o**).* 1-Fluoro(chloro)-2-nitrobenzene (10 mmol), pyrrole (10 mmol), and NaOH (10 mmol) in 10 mL DMSO were stirred vigorously at room temperature for 1.5 h. After completion of the reaction, the mixture was cooled to room temperature, diluted by H_2O, and extracted by EtOAc three times. The combined organic layer was washed with saturated NaCl solution two times and dried by Na_2SO_4. The solution was evaporated and used for the next step without purification. To the solution of crude product in 50 mL EtOAc was added 50 mmol SnCl·$2H_2O$ at room temperature, and the solution was stirred for 18 h. The reaction was quenched by NaOH and extracted by EtOAc three times. The organic layer was dried by Na_2SO_4, evaporated, and purified by flash chromatography (petroleum ether/EtOAc).

*Synthesis of 2-Benzylaniline (**1s**).* Sealed tube containing 1-(bromomethyl)-2-nitrobenzene (5 mmol), phenylboronic acid (15 mmol), $Pd(OAc)_2$ (0.15 mmol), PPh_3 (0.3 mmol), and K_3PO_4 (20 mmol) was evacuated and backfilled with N_2. Under N_2 flows, degassed toluene (30 mL) was added. The tube was closed and stirred vigorously at 80 °C for 18 h. Then, the mixture was cooled to room temperature, diluted by H_2O and extracted by EtOAc three times. The combined organic layer was dried by Na_2SO_4. The solution was evaporated and used for the next step without purification. To the solution of crude product in 25 mL EtOAc was added 25 mmol $SnCl_2{\cdot}2H_2O$ at room temperature for 18 h. The reaction was quenched by NaOH and extracted by EtOAc three times. The organic layer was dried over Na_2SO_4, evaporated, and purified by flash chromatography (petroleum ether/EtOAc).

2-Phenoxyaniline (**1t**) was synthesized according to reported literature.[15]

General Procedure for the Carbonylation of 2-Arylaniline with CO_2. TBD (41.7 mg, 0.3 mmol) and aniline (0.3 mmol) were added into sealed tube. The tube was evacuated and backfilled under CO_2 flow three times, and *o*-DCB was added into system under CO_2 flow. The solution was stirred vigorously under atmospheric CO_2 at room temperature for 1 h. Then, MeOTf (147.6 mg, 0.9 mmol) was added into solution under CO_2 flow and the sealed tube was closed and heated in 140 °C for 12 h. Hydrolyzed by 1 M HCl 5 mL and extracted with EtOAc (5 × 5 mL), the combined organic solution was dried by Na_2SO_4, evaporated, and purified by flash chromatography (petroleum ether/EtOAc).

*Phenanthridin-6(5H)-one (**2a**).*[7b] White solid, 41 mg, yield: 73%, mp: > 300 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ 11.69 (br s, 1H), 8.50 (d, J = 8.2 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.32 (dd, J = 7.9, 1.0 Hz, 1H), 7.88−7.83 (m, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.51−7.46 (m, 1H), 7.38−7.35 (m, 1H), 7.29−7.24 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ 161.0, 136.6, 134.4, 133.0, 129.7, 128.1, 127.6, 125.7, 123.4, 122.7, 122.5, 117.7, 116.3; IR (neat) ν_{max} cm^{-1}: 1659.

*8-Methoxyphenanthridin-6(5H)-one (**2b**).*[7b] White solid, 50 mg, yield: 74%, mp: 262−264 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (br s, 1H), 8.43 (d, J = 8.9 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 2.7 Hz, 1H), 7.43 (dt, J = 11.2, 5.5 Hz, 2H), 7.34 (d, J = 7.9 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.7, 159.1, 135.5, 128.5, 127.7, 127.1, 124.7, 122.7, 122.4, 121.7, 117.8, 116.1, 108.7, 55.5; IR (neat) ν_{max} cm^{-1}: 1662.

*8-Phenylphenanthridin-6(5H)-one (**2c**).* White solid, 62 mg, yield: 76%, mp: > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.77 (br s, 1H), 8.61−8.55 (m, 2H), 8.42 (d, J = 7.9 Hz, 1H), 8.17 (dd, J = 8.4, 2.1 Hz, 1H), 7.84−7.80 (m, 2H), 7.57−7.48 (m, 3H), 7.46−7.37 (m, 2H), 7.32−7.26 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.9, 139.4, 138.9, 136.6, 133.4, 131.1, 129.7, 129.2, 128.1, 126.8, 126.2, 124.9, 123.6, 123.4, 122.4, 117.4, 116.2; IR (neat) ν_{max} cm^{-1}: 1662; HRMS (ESI): calcd for $C_{19}H_{13}NO$ [M + H] $^+$ 272.1070, found: 272.1072.

10-Methoxyphenanthridin-6(5*H*)-one (2d).[7a] Pale gray solid, 39 mg, yield: 58%, mp: 228−230 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (br s, 1H), 9.07 (d, J = 7.8 Hz, 1H), 8.02 (dd, J = 7.8, 1.2 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.51 (dd, J = 8.1, 1.0 Hz, 1H), 7.43−47 (m, 1H), 7.37 (dd, J = 8.1, 1.3 Hz, 1H), 7.20−7.24 (m, 1H), 4.06 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.6, 157.7, 136.4, 128.8, 128.5, 128.3, 127.8, 123.4, 122.1, 119.7, 117.3, 115.9, 115.4, 56.2; IR (neat) ν_{max} cm^{-1}: 1654.

*10-Methylphenanthridin-6(5H)-one (**2e**).*[7b] White solid, 50 mg, yield: 80%, mp: 294−296 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (br s, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.31 (dd, J = 7.9, 1.4 Hz, 1H), 7.73−7.70 (m, 1H), 7.56−7.46 (m, 2H), 7.40 (dd, J = 8.1, 1.4 Hz, 1H), 7.24−7.28 (m, 1H), 2.93 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.0, 137.1, 137.0, 135.2, 133.3, 128.8, 127.5, 127.4, 127.3, 126.1, 121.8, 118.8, 116.3, 25.7; IR (neat) ν_{max} cm^{-1}: 1649.

*9-Methylphenanthridin-6(5H)-one (**2f**).*[16] White solid, 23 mg yield: 37.5%, mp: 254−256 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.57 (s, 1H), 8.36 (d, J = 7.8 Hz, 1H), 8.31 (s, 1H), 8.20 (d, J = 8.1 Hz, 1H), 7.49−7.43 (m, 2H), 7.35 (dd, J = 8.2, 1.0 Hz, 1H), 7.27−7.22 (m, 1H),

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2.53 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.8, 143.0, 136.7, 134.2, 129.4, 129.1, 127.5, 123.4, 123.2, 122.5, 122.1, 117.5, 116.1, 21.5. IR (neat) ν_{max} cm^{-1}: 1652.

*7-Methylphenanthridin-6(5H)-one (**2f′**).*[16] White solid, 23 mg yield: 37.5%, mp: 249−251 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.41 (s, 1H), 8.33 (dd, J = 11.1, 8.2 Hz, 2H), 7.66 (t, J = 7.8 Hz, 1H), 7.46−7.41 (m, 1H), 7.38 (d, J = 7.4 Hz, 1H), 7.33−7.30 (m, 1H), 7.22−7.17 (m, 1H), 2.86 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.0, 141.2, 136.7, 135.8, 131.9, 131.2, 129.4, 123.8, 123.5, 121.9, 120.7, 117.7, 115.4, 23.7. IR (neat) ν_{max} cm^{-1}:1650.

*8-Bromophenanthridin-6(5H)-one (**2g**).* White solid, 49 mg, yield: 60%, mp: > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.83 (br s, 1H), 8.44 (d, J = 8.8 Hz, 1H), 8.38−8.33 (m, 2H), 7.98 (dd, J = 8.7, 2.2 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.29−7.24 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.8, 136.6, 135.8, 133.6, 130.3, 129.8, 127.5, 125.5, 123.6, 122.8, 121.3, 117.1, 116.49; IR (neat) ν_{max} cm^{-1}: 1669; HRMS (ESI): calcd for $C_{13}H_8BrNO$ [M + H] $^+$ 273.9862, found: 273.9860

*8-Chlorophenanthridin-6(5H)-one (**2h**).*[7b] White solid, 33 mg, yield: 48%, mp: 292−294 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.84 (br s, 1H), 8.52 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 7.5 Hz, 1H), 8.22 (d, J = 2.4 Hz, 1H), 7.86 (dd, J = 8.7, 2.6 Hz, 1H), 7.48−7.52 (m, 1H), 7.35−7.37 (m, 1H), 7.25−7.29 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.8, 136.5, 133.2, 132.9, 132.8, 130.1, 127.2, 126.7, 125.3, 123.5, 122.7, 117.0, 116.4; IR (neat) ν_{max} cm^{-1}: 1670.

*8-Fluorophenanthridin-6(5H)-one (**2i**).*[7b] White solid, 17 mg, yield: 26%, mp: 282−284 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.82 (br s, 1H), 8.58−8.53 (m, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.95 (dd, J = 9.3, 2.9 Hz, 1H), 7.68−7.73 (m, 1H), 7.51−7.45 (m, 1H), 7.34−7.38 (m, 1H), 7.24−7.29 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.73 (d, J = 246.7 Hz), 160.19 (d, J = 2.2 Hz), 136.13, 131.24, 129.72 (d, J = 4.2 Hz), 127.73 (d, J = 7.4 Hz), 126.07 (d, J = 6.7 Hz), 123.44 (d, J = 4.1 Hz), 122.80 (d, J = 7.4 Hz), 121.23 (d, J = 20.3 Hz), 117.26, 116.40 (d, J = 7.1 Hz), 112.68 (d, J = 22.4 Hz); IR (neat) ν_{max} cm^{-1}: 1680.

*7,9-Dimethylphenanthridin-6(5H)-one (**2k**).*[16] White solid, 53 mg, yield: 79%, mp: 276−278 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.31 (br s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.16 (s, 1H), 7.45−7.40 (m, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.22−7.16 (m, 2H), 2.80 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 162.1, 142.1, 141.2, 136.9, 135.9, 132.6, 129.5, 123.6, 122.0, 121.6, 120.9, 117.8, 115.5, 23.7, 21.4; IR (neat) ν_{max} cm^{-1}: 1671.

*Benzo[k]phenanthridin-6(5H)-one (**2l**).* Pale yellow solid, 62 mg, yield: 85%, mp: 285−287 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (br s, 1H), 8.91−8.96 (m, 1H), 8.61 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 8.6 Hz, 1H), 8.13−8.17 (m, 1H), 8.09 (d, J = 8.6 Hz, 1H), 7.74−7.79 (m, 2H), 7.54−7.58 (m, 1H), 7.49−7.52 (m, 1H), 7.33−7.37 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.0, 137.4, 135.9, 133.0, 129.4, 129.1, 128.7, 128.4, 128.3, 128.0, 127.5, 127.4, 124.6, 122.9, 122.2, 117.6, 116.5; IR (neat) ν_{max} cm^{-1}: 1645; HRMS (ESI): calcd for $C_{17}H_{11}NO$ [M + H] $^+$ 246.0913, found: 246.0916.

*Benzofuro[3,2-c]quinolin-6(5H)-one (**2m**).*[17] Pale yellow solid, 39 mg, yield: 55%, mp: > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.02 (br s, 1H), 8.08−8.12 (m, 1H), 8.03−8.07 (m, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.59−7.64 (m, 1H), 7.45−7.54 (m, 3H), 7.32−7.36 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.2, 158.0, 154.9, 138.5, 131.0, 126.5, 124.8, 123.9, 122.6, 121.4, 121.3, 116.3, 112.0, 110.9, 110.1.

*Benzo[4,5]thieno[3,2-c]quinolin-6(5H)-one (**2n**).* White solid, 47 mg, yield: 63%, 225 °C decomposed. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.01 (br s, 1H), 8.77−8.80 (m, 1H), 8.15 (dd, J = 7.0, 1.5 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.49−7.61 (m, 4H), 7.30−7.34 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.9, 148.0, 137.5, 136.9, 136.6, 130.7, 126.4, 125.9, 124.7, 124.30, 123.4, 123.0, 122.7, 116.3, 116.0; IR (neat) ν_{max} cm^{-1}: 1665; HRMS (ESI): calcd for $C_{15}H_9NOS$ [M+H] $^+$ 252.0478, found: 252.0482.

*Pyrrolo[1,2-a]quinoxalin-4(5H)-one (**2o**).*[17] Pale yellow solid, 41 mg, yield: 75%, mp: 257−259 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.27 (br s, 1H), 8.16−8.19 (m, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.28 (d, J = 6.0 Hz, 2H), 7.18−7.23 (m, 1H), 7.01−7.04 (m, 1H), 6.66−6.70 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.1, 128.6, 125.8, 123.3, 122.7, 122.7, 118.2, 116.6, 115.1, 112.9, 111.5; IR (neat) ν_{max} cm^{-1}: 1652.

*2-Methylphenanthridin-6(5H)-one (**2p**).*[7b] White solid, 41 mg, yield: 66%, mp: 259−261 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.60 (br s, 1H), 8.45 (d, J = 8.1 Hz, 1H), 8.30 (dd, J = 8.0, 1.2 Hz, 1H), 8.16 (s, 1H), 7.80−7.84 m, 1H), 7.59−7.64 (m, 1H), 7.24−7.31 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 1601.0, 134.5, 134.4, 133.0, 131.6, 130.8, 128.0, 127.7, 125.8, 123.2, 122.7, 117.6, 116.2, 20.9; IR (neat) ν_{max} cm^{-1}: 1647.

*2-Chlorophenanthridin-6(5H)-one (**2q**).*[17] Pale yellow solid, 34 mg, yield: 50%, mp: > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.77 (br s, 1H), 8.46 (d, J = 8.1 Hz, 1H), 8.39 (d, J = 8.7 Hz, 1H), 8.30 (dd, J = 7.9, 1.3 Hz, 1H), 7.83−7.87 (m, 1H), 7.63.7.67 (m, 1H), 7.38 (d, J = 2.2 Hz, 1H), 7.28 (dd, J = 8.6, 2.2 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.9, 137.7, 133.8, 133.6, 133.1, 128.4, 127.6, 125.5, 125.3, 122.9, 122.2, 116.6, 115.4; IR (neat) ν_{max} cm^{-1}: 1664.

*2-Fluorophenanthridin-6(5H)-one (**2r**).*[17] White solid, 26 mg, yield: 40%, mp: > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (br s, 1H), 8.49 (d, J = 8.1 Hz, 1H), 8.31 (dd, J = 7.9, 1.2 Hz, 1H), 8.21−8.26(m, 1H), 7.82−7.88 (m, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.35−7.39 (m, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.7, 158.0 (d, J = 237.7 Hz), 133.7, 133.2, 133.1, 128.8, 127.6, 125.9, 123.3 (d, J = 6.4 Hz), 119.0 (d, J = 8.2 Hz), 118.0 (d, J = 7.3 Hz), 117.4 (d, J = 24.1 Hz), 109.3 (d, J = 24.0 Hz); IR (neat) ν_{max} cm^{-1}: 1687.

*5H-Dibenzo[b,e]azepin-6(11H)-one (**2s**).* White solid, 16 mg, yield: 25%, mp: 200−202 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.45 (br s, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.29−7.38 (m, 3H), 7.04−7.19 (m, 3H), 3.89 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.2, 141.5, 136.8, 133.1, 132.3, 132.2, 130.1, 128.2, 127.2, 127.2, 126.9, 124.6, 121.0, 37.9; IR (neat) ν_{max} cm^{-1}: 1668; HRMS (ESI): calcd for $C_{14}H_{11}NO$ [M + H] $^+$ 210.0913, found: 210.0910.

*Dibenzo[b,f][1,4]oxazepin-11(10H)-one (**2t**).*[18] White solid, 30 mg, yield: 47%, mp: 214−216 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.53 (br s, 1H), 7.77 (dd, J = 7.7, 1.7 Hz, 1H), 7.58−7.63 (m, 1H), 7.29−7.35 (m, J = 7.9 Hz, 3H), 7.09−7.18 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.9, 159.0, 150.5, 134.5, 131.4, 131.2, 126.0, 125.8, 125.5, 125.3, 121.7, 121.4, 120.7; IR (neat) ν_{max} cm^{-1}: 1666

*Methyl [1,1′-biphenyl]-2-ylcarbamate (**4**).*[19] White solid, 63 mg, yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 7.3 Hz, 2H), 7.43−7.36 (m, 4H), 7.22 (dd, J = 7.6, 1.6 Hz, 1H), 7.16−7.11 (m, 1H), 6.67 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 138.2, 134.9, 131.5, 130.2, 129.4, 129.2, 128.6, 128.0, 123.4, 119.6, 52.4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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