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Copper-Catalyzed Aerobic Oxidative C–H and C–C Functionalization of 1-[2-(Arylamino)aryl]ethanones Leading to Acridone Derivatives

Jipan Yu,[a] Haijun Yang,[a] Yuyang Jiang,[b] and Hua Fu*[a, b]

Abstract: Efficient copper-catalyzed aerobic oxidative C–H and C–C functionalization of 1-[2-(arylamino)aryl]ethanones leading to acridones has been developed. The procedure involves cleavage of aromatic C–H and acetyl C–C bonds with intramolecular formation of a diarylketone bond. The protocol uses inexpensive $Cu(O_2CCF_3)_2$ as catalyst, pyridine as additive, and economical and environmentally friendly oxygen as the oxidant, and the corresponding acridones with various functional groups were obtained in moderate to good yields.

Keywords: C–C activation · C–H activation · cyclization · nitrogen heterocycles · synthetic methods

Introduction

Transition metal catalyzed selective C–H and C–C functionalization (cleavage) has attracted much attention because of its potential application in organic synthesis.[1] Over the past decade, transition metal catalyzed C–H functionalization reactions have become the subject of intensive studies.[2] In these reactions, organic or inorganic oxidants were often required. Molecular oxygen is the ideal oxidant because of its abundance, low cost, and lack of toxic byproducts,[3] but aerobic oxidation methods often meet great challenges with respect to selectivity and scope. Recently, advances have been made in selective transition metal catalyzed aerobic oxidative formation of bonds,[3,4] and some N heterocycles, such as carbazoles,[5] *N*-methoxylactams,[6] indazoles,[7] indolines,[8] and benzimidazoles,[9] have been synthesized by this strategy. Transition metal catalyzed C–C bond cleavage has also become a hot field and emerged as a tremendous challenge in recent years.[10] In previous selective C–H and C–C functionalization, expensive palladium-, rhodium-, and ruthenium-based catalysts are often required. Recently, great progress has been made in copper-catalyzed cross-coupling with inexpensive and low-toxicity copper catalysts, and the methods exhibit wide applicability and good functional-group tolerance.[11,12] Furthermore, efficient copper-catalyzed aerobic oxidative synthesis of heterocycles has been developed by us[13] and others.[14]

On the other hand, acridones widely occur in natural products and biologically active molecules. For example, they have been used as important antifungal, antileishmanial, antitumor, and DNA-intercalating anticancer drugs[15] and as fluorescent labels.[16] Therefore, it is highly desirable to develop a new and practical approach to acridones, although some efficient methods have been developed.[17, 24] Herein, we report on copper-catalyzed aerobic oxidative C–H and C–C functionalization of 1-[2-(arylamino)aryl]-ethanones leading to acridones (Figure 1).

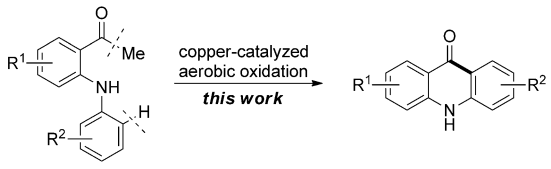

Figure 1. Copper-catalyzed aerobic oxidative C–H and C–C functionalization of 1-[2-(arylamino)aryl]ethanones leading to acridones.

Results and Discussion

First, copper-catalyzed aerobic oxidation of 1-[2-(phenylamino)phenyl]ethanone (**1a**) leading to acridin-9(10*H*)-one (**2a**) was chosen as model to optimize reaction conditions including catalysts, additives, solvents, and temperature. As shown in Table 1 (entries 1–4), various additives were screened with 10 mol% $Cu(OAc)_2$ as catalyst (relative to amount of **1a**), DMF as solvent, and oxygen as oxidant at 130 °C, and pyridine gave the best result (Table 1, entry 1). Only a trace amount of product was observed in the absence of additive (Table 1, entry 5). The amount of pyridine was increased (Table 1, entries 6 and 7), and 84% yield was obtained in the presence of five equivalents of pyridine (Table 1, entry 7). The yield decreased to 43% when Na_2CO_3 was

[a] J. Yu, Dr. H. Yang, Prof. Dr. H. Fu
Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education)
Department of Chemistry
Tsinghua University, Beijing 100084 (P.R. China)
Fax: (+86) 10-62781695
E-mail: fuhua@mail.tsinghua.edu.cn

[b] Prof. Dr. Y. Jiang, Prof. Dr. H. Fu
Key Laboratory of Chemical Biology (Guangdong Province)
Graduate School of Shenzhen
Tsinghua University, Shenzhen 518057 (P.R. China)

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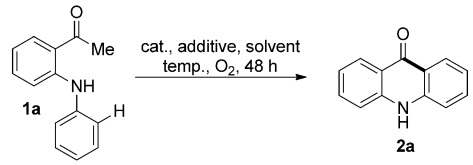
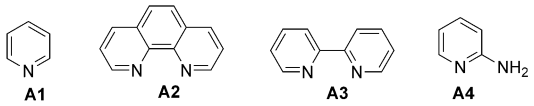
Table 1. Copper-catalyzed aerobic oxidation of 1-(2-(phenylamino)phenyl)ethanone (**1a**) leading to acridin-9(10*H*)-one (**2a**): optimization of conditions.[a]



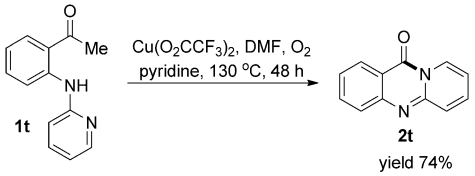


Entry	Catalyst[b]	Additive (equiv)	Solvent	*T* [°C]	Yield [%][c]
1	$Cu(OAc)_2$	A1 (0.1)	DMF	130	70
2	$Cu(OAc)_2$	A2 (0.1)	DMF	130	58
3	$Cu(OAc)_2$	A3 (0.1)	DMF	130	55
4	$Cu(OAc)_2$	A4 (0.1)	DMF	130	66
5	$Cu(OAc)_2$	–	DMF	130	trace
6	$Cu(OAc)_2$	A1 (1.0)	DMF	130	74
7	$Cu(OAc)_2$	A1 (5.0)	DMF	130	84
8	$Cu(OAc)_2$	Na_2CO_3 (5.0)	DMF	130	43
9	CuI	A1 (5.0)	DMF	130	82
10	CuBr	A1 (5.0)	DMF	130	78
11	CuCl	A1 (5.0)	DMF	130	74
12	Cu_2O	A1 (5.0)	DMF	130	84
13	$CuCl_2$	A1 (5.0)	DMF	130	81
14	$CuSO_4$	A1 (5.0)	DMF	130	75
15	CuO	A1 (5.0)	DMF	130	46
16	$Cu(OTf)_2$	A1 (5.0)	DMF	130	74
17	$Cu(TFA)_2$	A1 (5.0)	DMF	130	88
18	–	A1 (5.0)	DMF	130	0
19	$Cu(TFA)_2$	A1 (5.0)	DMSO	130	77
20	$Cu(TFA)_2$	A1 (5.0)	dioxane	130	28
21	$Cu(TFA)_2$	A1 (5.0)	*o*-xylene	130	43
22	$Cu(TFA)_2$	A1 (5.0)	DMF	120	79
23	$Cu(TFA)_2$	A1 (5.0)	DMF	80	0
24	$Cu(TFA)_2$	A1 (5.0)	DMF	130	65[d]

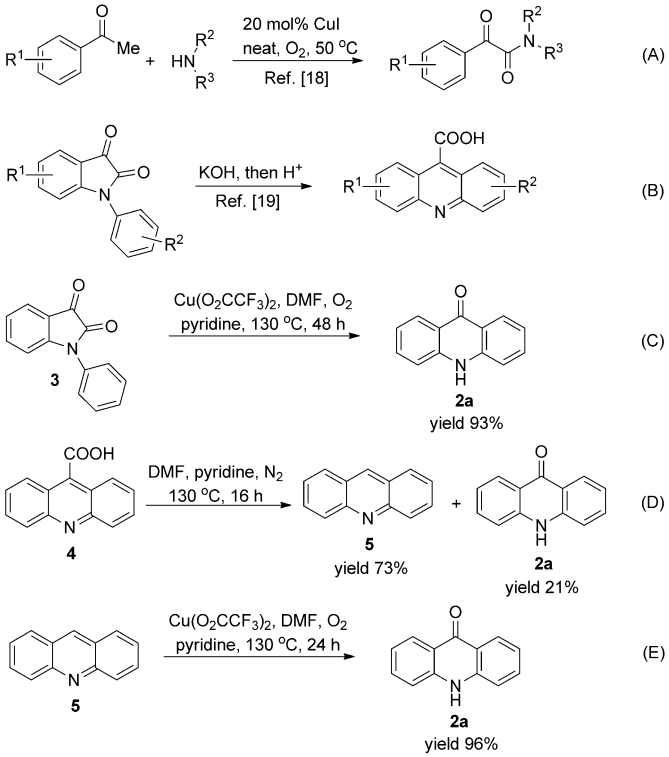
[a] Reaction conditions: under oxygen (1 atm), 1-[2-(phenylamino)phenyl]ethanone (**1a**) (0.20 mmol), catalyst (0.02 mmol), additive (0.02–1.0 mmol), solvent (2 mL), reaction temperature (80–130 °C), reaction time (48 h). [b] Tf = $CF_3SO_2^-$, TFA = CF_3COO^-. [c] Yield of isolated product. [d] Under air.

used as additive (Table 1, entry 8). We used different copper salts as catalyst (Table 1, entries 9–17), and $Cu(O_2CCF_3)_2$ exhibited the highest activity (Table 1, entry 17). The reaction did not work in the absence of copper catalyst (Table 1, entry 18). Other solvents were inferior to DMF (cf Table 1, entries 17 and 19–21). We changed the reaction temperature, and 130 °C was more suitable (cf. Table 1, entries 17, 22, and 23). When the reaction was performed under air, the efficiency was lower (cf. Table 1, entries 17 and 24). Therefore, the optimum conditions are 10 mol % $Cu(O_2CCF_3)_2$ as catalyst, 5 equiv of pyridine as additive, and DMF as solvent at 130 °C under oxygen atmosphere (1 atm).

With the optimum reaction conditions in hand, we investigated the scope of copper-catalyzed aerobic oxidative C–H and C–C functionalization of 1-[2-(arylamino)aryl]ethanones leading to acridone derivatives. As shown in Table 2, the examined substrates provided moderate to good yields. For substrates with substituent R^2 *ortho* or *para* to the NH group, only one product was obtained. Two isomers were observed for substrates with electron-donating *meta* substituents, and acylation primarily occurred at the position *ortho* to the NH group and R^2 (Table 2, entries 4, 7, and 11). No evident difference was observed due to the electronic effect of the examined substrates. The copper-catalyzed aerobic oxidative reactions could tolerate some functional groups in the substrates, including ethers (Table 2, entries 6, 7, and 16–19), C–F bonds (Table 2, entries 8 and 9), C–Cl bonds (Table 2, entries 10, 11, 15, and 19), C–Br bonds (Table 2, entries 13–15) and nitriles (Table 2, entry 12). We extended this copper-catalyzed aerobic oxidative reaction to 1-[2-(pyridylamino)phenyl]ethanone (**1t**) under our standard conditions and obtained 11*H*-pyrido[2,1-*b*]quinazolin-11-one (**2t**) in 74 % yield (Scheme 1).

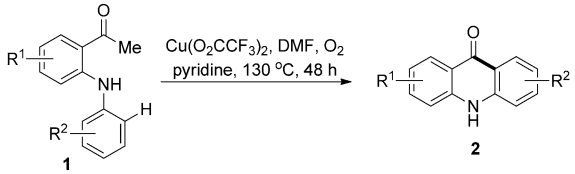


Scheme 1. Copper-catalyzed aerobic oxidative reaction of 1-[2-(pyridylamino)phenyl]ethanone (**1t**) leading to 11*H*-pyrido[2,1-*b*]quinazolin-11-one (**2t**).



Scheme 2. A) Copper-catalyzed aerobic oxidative synthesis of α-ketoamides. B) Synthesis of acridine-9-carboxylic acids from isatins. C) Treatment of 1-phenylindoline-2,3-dione (**3**) under the standard conditions. D) Reaction of acridine-9-carboxylic acid (**4**) under nitrogen atmosphere and heating. E) Oxidation of acridine (**5**) under oxygen atmosphere.

Table 2. Copper-catalyzed aerobic oxidation of 1-[2-(arylamino)aryl]ethanones **1** leading to acridin-9(10*H*)-ones **2**.[a]



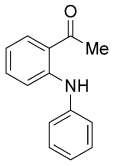
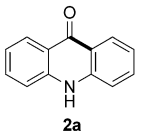
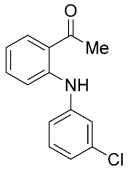
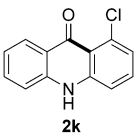
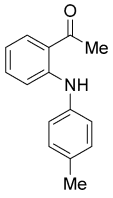
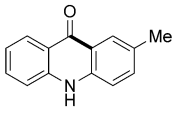
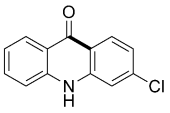
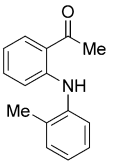
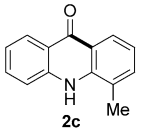
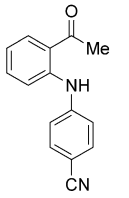
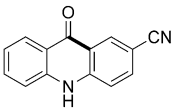
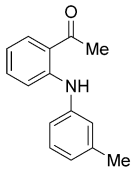
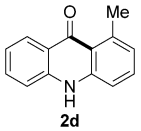
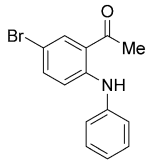
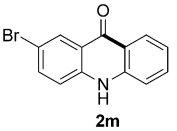
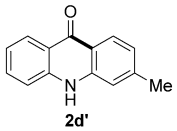
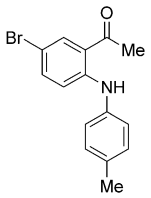
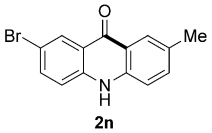
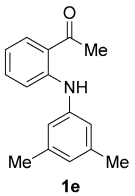
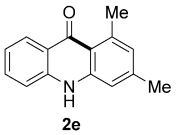
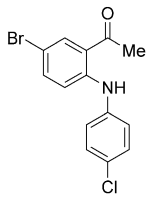
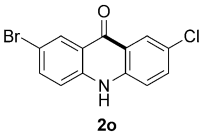
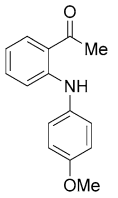
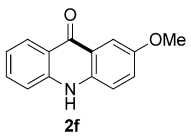
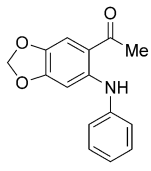
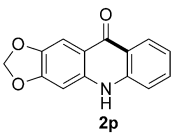
Entry	1	2	Yield [%][b]	Entry	1	2	Yield [%][b]
1	 **1a**	 **2a**	88	11	 **1k**	 **2k**	55
2	 **1b**	 **2b**	72			 **2k'**	trace
3	 **1c**	 **2c**	31	12	 **1l**	 **2l**	75
4	 **1d**	 **2d**	54	13	 **1m**	 **2m**	91
		 **2d'**	38	14	 **1n**	 **2n**	67
5	 **1e**	 **2e**	75	15	 **1o**	 **2o**	61
6	 **1f**	 **2f**	42	16	 **1p**	 **2p**	85

Table 2. (Continued)

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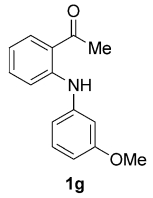
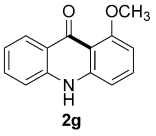
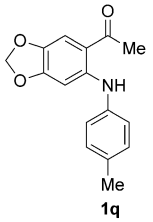
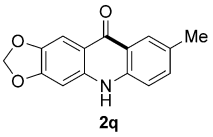
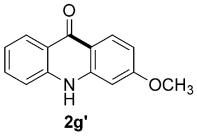
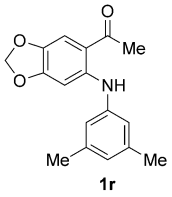
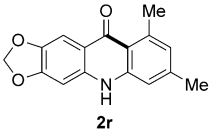
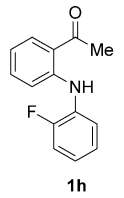
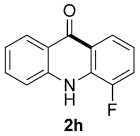
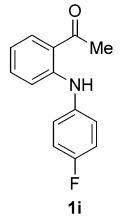
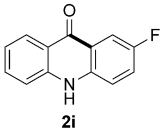
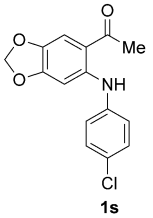
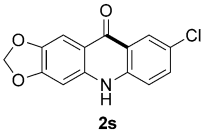
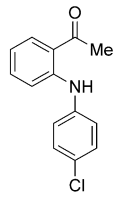
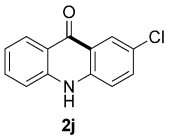
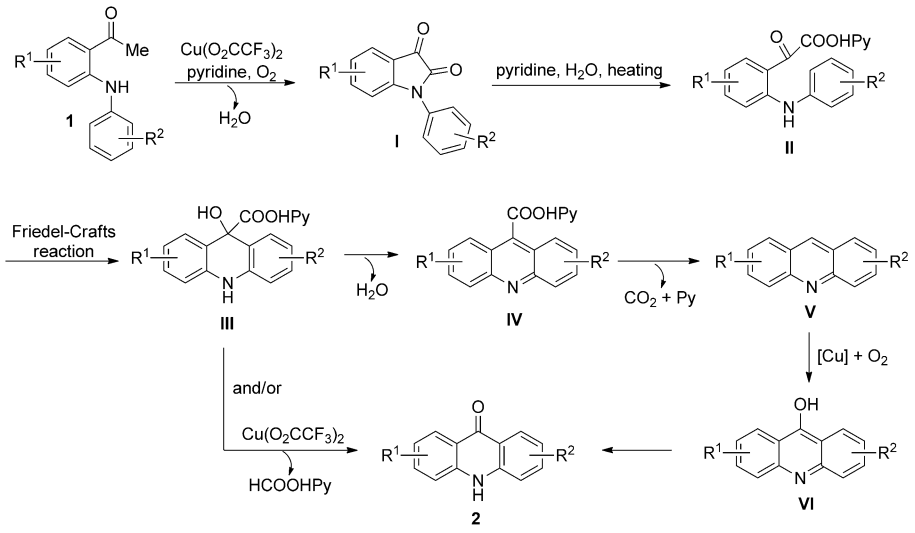
7	 1g	 2g	67	17	 1q	 2q	71
		 2g'	trace	18	 1r	 2r	59
8	 1h	 2h	51				
9	 1i	 2i	65	19	 1s	 2s	54
10	 1j	 2j	68				

[a] Reaction conditions: under oxygen (1 atm), 1-[2-(arylamino)aryl]ethanone **1** (0.20 mmol), $Cu(O_2CCF_3)_2$ (0.02 mmol), pyridine (1.0 mmol), DMF (2 mL), reaction temperature (130 °C), reaction time (48 h). [b] Yield of isolated product.

We explored the mechanism of copper-catalyzed aerobic oxidative C–H and C–C functionalization of 1-[2-(arylamino)aryl]ethanones leading to acridones (Scheme 2). In previous research by Ji and Du, copper-catalyzed reactions of aryl methyl ketones with amines led to α-ketoamides under oxygen atmosphere and neat conditions (Scheme 2A).[18] Isatins could transformed into acridine-9-carboxylic acids by sequential treatment with base and acid (Scheme 2B).[19] We investigated reactions of 1-phenylindoline-2,3-dione (**3**) under our standard conditions (Scheme 2C), and acridone (**2a**) was obtained in 93% yield, which implied that 1-arylindoline-2,3-diones could be key intermediates during formation of acridones. Treatment of acridine-9-carboxylic acid (**4**) under nitrogen atmosphere and heating led to acridine (**5**) in 73% yield with a small amount of **2a** (Scheme 2D), and oxidation of **5** under oxygen atmosphere provided **2a** in 96% yield (Scheme 2E). Therefore, a possible mechanism for copper-catalyzed aerobic oxidative reactions is proposed in Scheme 3. First, copper-catalyzed aerobic oxidation of 1-[2-(arylamino)aryl]ethanones gives 1-arylindoline-2,3-dione (**I**) with elimination of water,[18] and **I** transforms into **II** in the presence of pyridine and water under heating. Friedel–Crafts reaction of **II** provides **III**, and dehydration of **III** gives **IV**.[19] Decarboxylation of **IV** leads to **V**, oxidation of **V** produces **VI**, and isomerization of **VI** affords the target product **2**. Elimination of pyridinium formate from **III** to give **2** under heating is also a possible pathway.



Scheme 3. Possible mechanism for copper-catalyzed aerobic oxidative synthesis of acridones.

Conclusion

We have developed novel and efficient copper-catalyzed aerobic oxidative C–H and C–C functionalization of 1-[2-(arylamino)aryl]ethanones leading to acridones. The protocol uses inexpensive $Cu(O_2CCF_3)_2$ as catalyst, pyridine as additive, and economical and environmentally friendly oxygen as oxidant, and the corresponding acridones were obtained in moderate to good yields. The procedure involves cleavage of aromatic C–H and acetyl C–C bonds with intramolecular formation of a diarylketone bond. Interestingly, the reaction of 1-[2-(pyridylamino)phenyl]ethanone under the standard conditions provided 11*H*-pyrido[2,1-*b*]quinazolin-11-one in good yield. Therefore, this inexpensive, convenient and efficient method should attract much attention in academic and industrial research. Investigations on further applications of this reaction are in progress.

Experimental Section

General: All reactions were carried out under oxygen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded with TMS in [D$_6$]DMSO (^{1}H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 40.0 ppm).

General procedure for synthesis of compounds 2a–t: A 25 mL Schlenk tube was charged with a magnetic stirrer and DMF (2.0 mL). 1-[2-(Arylamino)aryl]ethanone or 1-[2-(pyridylamino)phenyl]ethanone **1** (0.2 mmol), $Cu(O_2CCF_3)_2$ (0.02 mmol, 6.0 mg), and pyridine (1.0 mmol, 79 mg) were added to the tube. The mixture was stirred at 130 °C for 48 h under oxygen atmosphere (1 atm). The resulting mixture was cooled to room temperature, the solvent was removed by rotary evaporator, and the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the desired target product. Further crystallization was performed from ethyl acetate for some impure products.

Acridin-9(10*H*)-one (2a):[20] Eluent: petroleum ether/ethyl acetate (3/1). Yield 34 mg (88%). Light yellow solid, m.p. >300 °C (lit.[20] 344 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.73 (s, 1H), 8.25 (d, 2H, J = 8.0 Hz), 7.74 (t, 2H, J = 7.6 Hz), 7.56 (d, 2H, J = 8.3 Hz), 7.26 ppm (t, 2H, J = 7.5 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 177.3, 141.4, 134.0, 126.6, 121.5, 121.0, 117.9 ppm; ESI-MS: $[M+H]^+$ m/z 196.2.

2-Methylacridin-9(10*H*)-one (2b):[20] Eluent: petroleum ether/ethyl acetate (3/1). Yield 30 mg (72%). Light yellow solid, m.p. >300 °C (lit.[20] 335 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.63 (s, 1H), 8.20 (d, 1H, J = 8.1 Hz), 8.00 (s, 1H), 7.67 (t, 1H, J = 7.7 Hz), 7.55–7.41 (m, 3H), 7.20 (t, 1H, J = 7.5 Hz), 2.39 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 177.1, 141.3, 139.5, 135.5, 133.8, 130.6, 126.6, 125.6, 121.3, 120.9, 117.9, 117.8, 21.1 ppm; ESI-MS: $[M+H]^+$ m/z 210.3.

4-Methylacridin-9(10*H*)-one (2c):[20] Eluent: petroleum ether/ethyl acetate (3/1). Yield 13 mg (31%). Light yellow solid, m.p. >300 °C (lit.[20] 345 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 10.56 (s, 1H), 8.19 (dd, 1H, J = 8.1 Hz, J = 1.4 Hz), 8.10 (d, 1H, J = 7.9 Hz), 7.89 (d, 1H, J = 8.4 Hz), 7.70 (td, 1H, J = 7.7 Hz, J = 1.6 Hz), 7.56 (d, 1H, J = 7.1 Hz), 7.24 (td, 1H, J = 7.5 Hz, J = 1.0 Hz), 7.14 (d, 1H, J = 7.9 Hz), 2.57 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 177.6, 141.6, 140.1, 134.7, 133.8, 126.3, 125.8, 124.5, 121.8, 121.3, 121.2, 120.9, 118.7, 18.4 ppm; ESI-MS: $[M+H]^+$ m/z 210.3.

1-Methylacridin-9(10*H*)-one (2d):[21] Eluent: petroleum ether/ethyl acetate (3/1). Yield 23 mg (54%). Light yellow solid, m.p. 304–306 °C (lit.[21] 302–304 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.50 (s, 1H), 8.14 (d, 1H, J = 8.1 Hz), 7.64 (td, 1H, J = 7.6 Hz, J = 1.4 Hz), 7.52–7.43 (m, 2H), 7.32 (d, 1H, J = 8.3 Hz), 7.17 (td, 1H, J = 7.0 Hz, J = 1.0 Hz), 6.92 (d, 1H, J = 7.2 Hz), 2.84 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 179.4, 143.1, 141.0, 140.7, 133.6, 133.0, 126.7, 124.1, 122.3, 121.3, 119.5, 117.3, 116.0, 24.23 ppm; ESI-MS: $[M+H]^+$ m/z 210.3.

3-Methylacridin-9(10*H*)-one (2d′):[20] Eluent: petroleum ether/ethyl acetate (3/1). Yield 16 mg (38%). Light yellow solid, m.p. >300 °C (lit.[20] 334 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.58 (s, 1H), 8.18 (d, 1H, J = 8.1 Hz), 8.09 (d, 1H, J = 8.3 Hz), 7.67 (td, 1H, J = 8.3 Hz, J = 1.3 Hz), 7.49 (d, 1H, J = 8.4 Hz), 7.27 (s, 1H), 7.20 (t, 1H, J = 7.5 Hz), 7.05 (d, 1H, J = 8.3 Hz), 2.43 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 177.0, 144.4, 141.6, 141.4, 133.8, 126.6, 126.5, 123.4, 121.4, 121.1, 119.1, 117.8, 117.1, 22.1 ppm; ESI-MS: $[M+H]^+$ m/z 210.2.

1,3-Dimethylacridin-9(10*H*)-one (2e):[22] Eluent: petroleum ether/ethyl acetate (3/1). Yield 34 mg (75%). Light yellow solid, m.p. 303–306 °C (lit.[22] 301–306 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.36 (s, 1H), 8.12 (dd, 1H, J = 8.1 Hz, J = 1.5 Hz), 7.62 (td, 1H, J = 7.6 Hz, J = 1.5 Hz), 7.42 (d, 1H, J = 8.2 Hz), 7.15 (td, 1H, J = 7.5 Hz, J = 1.0 Hz), 7.09 (s, 1H) 6.76 (s, 1H), 2.80 (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 179.0, 143.3, 143.2, 140.9, 140.7, 133.4, 126.7, 125.9, 122.4, 121.1, 117.6, 117.2, 115.3, 24.08, 21.83 ppm; ESI-MS: $[M+H]^+$ m/z 224.1.

2-Methoxyacridin-9(10*H*)-one (2f):[20] Eluent: petroleum ether/ethyl acetate (3/1). Yield 19 mg (42%). Light yellow solid, m.p. 280–282 °C (lit.[20] 272 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.74 (s, 1H), 8.28 (d, 1H, J = 8.1 Hz), 7.74 (t, 1H, J = 7.6 Hz), 7.68 (d, 1H, J = 2.7 Hz), 7.58 (d, 1H, J = 2.3 Hz), 7.56 (s, 1H), 7.44 (dd, 1H, J = 9.0 Hz, J = 2.8 Hz), 7.27 (t, 1H, J = 7.5 Hz), 3.90 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.7, 154.5, 141.0, 136.3, 133.5, 126.5, 124.8, 121.6, 121.2, 120.2, 119.7, 117.8, 105.5, 55.9 ppm; ESI-MS: $[M+H]^+$ m/z 226.1.

1-Methoxyacridin-9(10*H*)-one (2g):[23] Eluent: petroleum ether/ethyl acetate (3/1). Yield 30 mg (67%). Light yellow solid, m.p. >300 °C (lit.[23] > 320 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.59 (s, 1H), 8.18 (dd, 1H, J = 8.0 Hz, J = 1.1 Hz), 8.11 (d, 1H, J = 8.9 Hz), 7.65 (td, 1H, J = 7.1 Hz, J = 1.3 Hz), 7.45 (d, 1H, J = 8.2 Hz), 7.19 (t, 1H, J = 7.4 Hz), 6.86 (d, 1H, J = 2.3 Hz), 6.82 (dd, 1H, J = 8.9 Hz, J = 2.3 Hz), 3.86 ppm (s, 3H);

^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.4, 163.9, 143.4, 141.5, 133.6, 128.6, 126.5, 121.5, 121.2, 117.6, 115.6, 112.0, 98.5, 56.0 ppm; ESI-MS: $[M+H]^+$ m/z 225.9.

4-Fluoroacridin-9(10*H*)-one (2h):[24] Eluent: petroleum ether/ethyl acetate (3/1). Yield 22 mg (51%). Light yellow solid, m.p. > 300 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.68 (s, 1H), 8.24 (dd, 1H, J = 8.1 Hz, J = 1.2 Hz), 8.05 (d, 1H, J = 8.0 Hz), 7.84–7.73 (m, 2H), 7.68 (ddd, 1H, J = 7.8 Hz, J = 7.8 Hz, J = 1.2 Hz), 7.30 (td, 1H, J = 7.5 Hz, J = 1.3 Hz), 7.24 ppm (td, 1H, J = 8.0 Hz, J = 4.9 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.6, 153.3, 150.1, 141.3, 134.3, 132.4, 132.0, 131.0, 130.8, 126.5, 123.0, 123.0, 122.3, 121.1, 120.8, 120.7, 118.6, 118.4, 118.2 ppm; ESI-MS: $[M+H]^+$ m/z 214.1.

2-Fluoroacridin-9(10*H*)-one (2i):[25] Eluent: petroleum ether/ethyl acetate (3/1). Yield 28 mg (65%). Light yellow solid, m.p. > 300 °C (lit.[25] > 347 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.88 (s, 1H), 8.24 (d, 1H, J = 7.9 Hz), 7.89 (dd, 1H, J = 9.3 Hz, J = 2.5 Hz), 7.76 (t, 1H, J = 7.2 Hz), 7.67–7.60 (m, 2H), 7.56 (d, 1H, J = 8.3 Hz), 7.28 ppm (t, 1H, J = 7.5 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.7, 159.0, 155.8, 141.3, 138.2, 134.2, 126.4, 123.1, 122.8, 121.8, 121.5, 121.4, 120.6, 120.5, 120.1, 118.0, 110.4, 110.1 ppm; ESI-MS: $[M+H]^+$ m/z 214.2.

2-Chloroacridin-9(10*H*)-one (2j):[20] Eluent: petroleum ether/ethyl acetate (3/1). Yield 31 mg (68%). Light yellow solid, m.p. > 300 °C (lit.[20] 329 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.87 (s, 1H), 8.20 (d, 1H, J = 8.1 Hz), 8.11 (d, 1H, J = 2.1 Hz), 7.72 (dd, 2H, J = 8.5 Hz, J = 1.8 Hz), 7.54 (t, 2H, J = 9.6 Hz), 7.27 ppm (t, 1H, J = 7.8 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.3, 141.3, 140.0, 134.4, 134.0, 126.6, 125.9, 125.3, 122.1, 121.8, 120.8, 120.4, 118.1 ppm; ESI-MS: $[M+H]^+$ m/z 230.2.

1-Chloroacridin-9(10*H*)-one (2k):[26] Eluent: petroleum ether/ethyl acetate (3/1). Yield 25 mg (55%). Light yellow solid, m.p. > 300 °C (lit.[26b] > 360 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.84 (s, 1H), 8.19 (d, 2H, J = 8.6 Hz), 7.73 (t, 1H, J = 7.7 Hz), 7.54 (d, 1H, J = 1.9 Hz), 7.51 (d, 1H, J = 8.3 Hz), 7.29–7.22 ppm (m, 2H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.8, 142.2, 141.4, 138.6, 134.4, 128.9, 126.6, 122.2, 121.9, 121.2, 119.7, 118.0, 116.9 ppm; ESI-MS: $[M+H]^+$ m/z 230.2.

9-Oxo-9,10-dihydroacridine-2-carbonitrile (2l): Eluent: petroleum ether/ethyl acetate (3/1). Yield 33 mg (75%). Light yellow solid, m.p. > 300 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 12.09 (s, 1H), 8.50 (s, 1H), 8.18 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 8.7 Hz), 7.76 (t, 1H, J = 7.6 Hz), 7.60–7.51 (m, 2H), 7.30 ppm (t, 1H, J = 7.4 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.4, 143.6, 141.2, 135.4, 134.9, 132.6, 126.6, 123.0, 121.5, 120.5, 119.5, 119.4, 118.4, 103.4 ppm; HRMS (ESI) calcd for $[C_{14}H_8N_2O+H]^+$: 221.0709; found: 221.0711.

2-Bromoacridin-9(10*H*)-one (2m):[27] Eluent: petroleum ether/ethyl acetate (3/1). Yield 50 mg (91%). Light yellow solid, m.p. > 300 °C (lit.[27] > 300 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.88 (s, 1H), 8.26 (d, 1H, J = 2.1 Hz), 8.19 (d, 1H, J = 8.0 Hz), 8.12 (dd, 1H, J = 8.8 Hz, J = 2.3 Hz), 7.73 (t, 1H, J = 7.7 Hz), 7.51 (t, 2H, J = 8.0 Hz), 7.26 ppm (t, 1H, J = 7.5 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.2, 141.3, 140.3, 136.5, 134.4, 128.5, 126.6, 122.3, 122.1, 120.9, 120.6, 118.1, 113.7 ppm; ESI-MS: $[M+H]^+$ m/z 274.1.

2-Bromo-7-methylacridin-9(10*H*)-one (2n): Eluent: petroleum ether/ethyl acetate (3/1). Yield 39 mg (67%). Light yellow solid, m.p. > 300 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.81 (s, 1H), 8.25 (d, 1H, J = 3.3 Hz), 7.98 (s, 1H), 7.80 (dd, 1H, J = 8.9 Hz, J = 2.3 Hz), 7.56 (dd, 1H, J = 8.5 Hz, J = 1.7 Hz), 7.48–7.42 (m, 2H), 2.39 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.0, 140.2, 139.4, 136.3, 135.9, 131.3, 128.5, 125.6, 122.2, 120.8, 120.5, 118.1, 113.4, 21.1 ppm; HRMS (ESI) calcd for $[C_{14}H_{10}BrNO+H]^+$: 288.0019; found: 288.0021.

2-Bromo-7-chloroacridin-9(10*H*)-one (2o): Eluent: petroleum ether/ethyl acetate (3/1). Yield 38 mg (61%). Light yellow solid, m.p. > 300 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 12.13 (s, 1H), 8.32 (d, 1H, J = 2.2 Hz), 8.18 (d, 1H, J = 2.4 Hz), 7.93 (dd, 1H, J = 8.9 Hz, J = 2.3 Hz), 7.83 (dd, 1H, J = 9.0 Hz, J = 2.4 Hz), 7.63 (d, 1H, J = 8.9 Hz), 7.57 ppm (d, 1H, J = 8.9 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 175.3, 140.3, 140.0, 137.0, 134.5, 128.6, 126.6, 125.4, 122.2, 121.8, 120.9, 120.7, 114.3 ppm; HRMS (ESI) calcd for $[C_{13}H_7BrClNO+H]^+$: 307.9472; found: 307.9468.

[1,3]Dioxolo[4,5-*b*]acridin-10(5*H*)-one (2p):[28] Eluent: petroleum ether/ethyl acetate (3/1). Yield 41 mg (85%). Light yellow solid, m.p. > 300 °C (lit.[28] > 300 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.64 (s, 1H), 8.16 (d, 1H, J = 8.1 Hz), 7.64 (td, 1H, J = 7.6 Hz, J = 1.3 Hz), 7.49 (s, 1H), 7.46 (d, 1H, J = 8.3 Hz), 7.20 (td, 1H, J = 7.0 Hz, J = 0.8 Hz), 6.94 (s, 1H), 6.12 ppm (s, 2H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 175.6, 153.2, 144.3, 140.8, 139.0, 133.1, 126.3, 121.5, 120.5, 117.6, 115.9, 102.6, 102.5, 96.3 ppm; ESI-MS: $[M+H]^+$ m/z 240.1.

8-Methyl[1,3]dioxolo[4,5-*b*]acridin-10(5*H*)-one (2q): Eluent: petroleum ether/ethyl acetate (3/1). Yield 36 mg (71%). Light yellow solid, m.p. > 300 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.56 (s, 1H), 7.95 (s, 1H), 7.48 (s, 1H), 7.46 (d, 1H, J = 1.7 Hz), 7.38 (d, 1H, J = 8.4 Hz), 6.92 (s, 1H), 6.12 (s, 2H), 2.38 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 175.4, 153.0, 144.1, 138.9, 134.6, 130.6, 125.4, 120.4, 117.6, 115.8, 102.6, 102.5, 96.2, 21.2 ppm; HRMS (ESI) calcd for $[C_{15}H_{11}NO_3+H]^+$: 254.0812; found: 254.0814.

7,9-Dimethyl[1,3]dioxolo[4,5-*b*]acridin-10(5*H*)-one (2r): Eluent: petroleum ether/ethyl acetate (3/1). Yield 32 mg (59%). Light yellow solid, m.p. 308–310 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.33 (s, 1H), 7.46 (s, 1H), 7.06 (s, 1H), 6.88 (s, 1H), 6.76 (s, 1H), 6.12 (s, 2H), 2.82 (s, 3H), 2.36 ppm (s, 3H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 177.4, 152.7, 144.0, 142.7, 142.3, 140.5, 138.0, 125.9, 117.2, 117.1, 115.1, 103.0, 102.3, 95.8, 24.1, 21.8 ppm; HRMS (ESI) calcd for $[C_{16}H_{13}NO_3+H]^+$: 268.0968; found: 268.0973.

8-Chloro[1,3]dioxolo[4,5-*b*]acridin-10(5*H*)-one (2s): Eluent: petroleum ether/ethyl acetate (3/1). Yield 29 mg (54%). Light yellow solid, m.p. > 300 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.93 (s, 1H), 8.08 (d, 1H, J = 2.3 Hz), 7.67 (dd, 1H, J = 8.9 Hz, J = 2.4 Hz), 7.52 (d, 1H, J = 8.8 Hz), 7.48 (s, 1H), 6.97 (s, 1H), 6.15 ppm (s, 2H); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 174.5, 153.5, 144.7, 139.3, 139.1, 133.1, 125.9, 125.0, 121.3, 120.1, 115.9, 102.7, 102.5, 96.4 ppm; HRMS (ESI) calcd for $[C_{14}H_8ClNO_3+H]^+$: 274.0271; found: 274.0275.

11*H*-Pyrido[2,1-*b*]quinazolin-11-one (2t):[29] Eluent: petroleum ether/ethyl acetate (3/1). Yield 29 mg (74%). Light yellow solid, m.p. 207–210 °C (lit.[29] 210–212 °C). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.72 (d, 1H, J = 6.2 Hz), 8.24 (d, 1H, J = 7.1 Hz), 7.84 (t, 1H, J = 6.6 Hz), 7.66 (t, 2H, J = 7.4 Hz), 7.44 (d, 2H, J = 8.2 Hz), 7.00 ppm (t, 1H, J = 6.0 Hz); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 158.8, 148.7, 147.9, 135.7, 135.5, 127.2, 127.0, 126.4, 125.5, 116.2, 113.7 ppm; ESI-MS: $[M+H]^+$ m/z 197.3.

Acridine (5):[30] From reaction of 1 mmol of acridine-9-carboxylic acid (**4**) under nitrogen atmosphere with heating. Eluent: petroleum ether/ethyl acetate (5/1). Yield 131 mg (73%). White crystal, m.p. 105–108 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.79 (s, 1H), 8.25 (d, 2H, J = 8.8 Hz), 8.01 (d, 2H, J = 8.5 Hz), 7.79 (td, 2H, J = 7.6 Hz, J = 1.3 Hz), 7.55 ppm (t, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 149.2, 136.2, 130.4, 129.5, 128.3, 126.7, 125.8 ppm; ESI-MS: $[M+H]^+$ m/z 180.2.

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