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PAPER

One-pot synthesis of benzo[*f*]quinolin-3-ones and benzo[*a*]phenanthridein-5-ones by the photoanuulation of 6-chloropyridin-2-ones and 3-chloroisoquinolin-1-ones to phenylacetylene†

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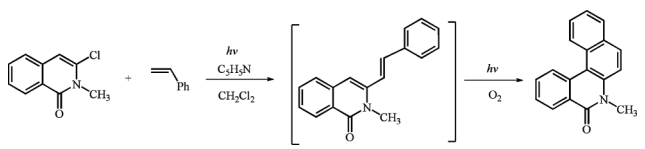
The one-pot synthesis of benzo[*f*]quinolin-3-ones and benzo[*a*]phenanthridein-5-ones was achieved by the inter- and intramolecular photoannulation of 6-chloropyridin-2-ones and 3-chloroisoquinolin-1-ones with phenylacetylene or tethered phenylacetylene. The reactions were proceeded by photoaddition of 6-chloropyridin-2-ones and 3-chloroisoquinolin-1-ones to phenylacetylene to give the chlorine-substituted stilbenoids, and then 6π electrocyclization of the stilbenoids and oxidation aromatization to afford the polycyclic products.

Introduction

The photochemistry of aryl halides has long received great attention due to their values in the organic synthesis and the reaction mechanistic investigation.[1] Among many photochemical reactions, photoinduced addition reactions of aryl halogens with alkenes has become a useful tool for the synthesis of aryl-substituted alkylamines, alkanols, ketones and heterocycles.[2] In addition, photoinduced coupling reactions of aryl halogens with styrenes supply an efficient route to stilbenes or "stilbenoids".[3] Photocyclization reaction of stilbenes has widely used in the synthesis of phenanthrenes.[4] This reaction is equally useful for the synthesis of the heterocyclic analogues of phenanthrenes, the so-called "phenanthrenoids".[5] It is of great interesting to combine these two photoreactions into "one-pot". Recently, we reported that one-pot synthesis of benzo[*c*]carbazole and benzo[*a*]phenanthridein-5-one derivatives by the photoreaction of 2-chloroindole-3-carbaldehydes and 3-chloroisoquinlin-2-ones with styrenes (Scheme 1).[6] These reactions proceeded *via* photoinduced dechlorinative coupling to give 2-heteroarylstyrenes firstly, then 6π electrocyclization and deacylation or oxidative aromatization to afford the polycyclic heterocycles.



Scheme 1 Photoreaction of 3-chloroisoquinlin-2-ones with styrene.

The photoinduced coupling reactions of aryl halogens with alkynes to give the 1-arylalkynes have been reported by several authors,[3c,7] but the photoaddition reactions of aryl halogens to alkynes to give the chloro-substituted 1-phenylalkenes or stilbenes are not found in literature. We report in this paper the first investigation on the inter- and intramolecular photoreactions of 6-chloropyridin-2-ones and 3-chloroisoquinolin-1-ones with phenylacetylene.

Results and discussion

Similarly to the photoreaction of 3-chloroisoquinolin-1-one with styrene,[6b] the intermolecular photoreactions of 6-chloropyridin-2-one (**1a**) and 3-chloroisoquinolin-1-one (**3a–c**) with phenylacetylene were also carried out in dichloromethane (DCM) with quartz tube (for 6-chloropyridin-2-ones) or Pyrex tube (for 3-chloroisoquinolin-1-ones) as reaction vessels because the rate of photoreactions was higher than that in other solvents like acetone and methanol. It was found that 6-chlorobenzo[*f*]quinolin-3-one (**2a**) could be obtained as the main product from the photoreaction of **1a** with phenylacetylene and 8-chlorobenzo[*a*]phenanthridin-5-ones (**4a–c**) were obtained as the main product from the photoreaction of **3a–c** with phenylacetylene under these conditions (Table 1).

Obviously, the products were all derived from two continuous photoreactions. The first was the photoaddition of **1a** or **3a–c** to phenylacetylene to afford the chlorine-substituted "stilbenoids"; the second was the photocyclization of "stilbenoids" and oxidative aromatization to afford **2a** or **4a–c**. it was found that the photoreaction rates and yields of products were higher in the presence of oxygen than those in the absence of oxygen. Thus, oxygen favors the formation of the cyclization products. All these

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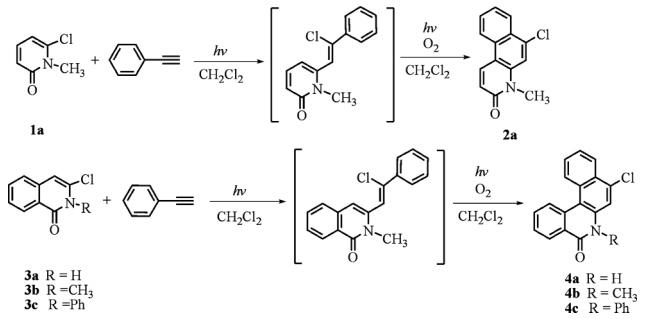
Table 1 Photoreaction of 6-chloropyridin-2-one and 3-chloroisoquinolin-1-one with phenylacetylene



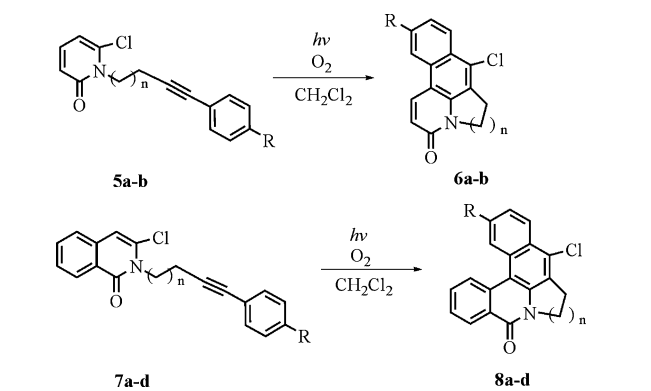
Entry	Substrate	*R*	Time (h)	Convn[a] (%)	Product	Yield[b] (%)
1	**1a**	—	38	95	**2a**	46
2	**3a**	H	40	90	**4b**	53
3	**3b**	CH_3	40	93	**4c**	60
4	**3c**	Ph	40	96	**4d**	56

[a] Conversion were based on the **1a** or **3a–c**. [b] Isolated yields.

photoreactions proceeded smoothly and the results were listed in Table 1.

Based on these promising results, we decided to extend these reactions to intramolecuar mode. Several 6-chloro-*N*-(ω-phenylethynylalkyl)pyridin-2-ones (**5a–b**) and 3-chloro-*N*-(ω-phenylethynylalkyl)isoquinolin-1-ones (**7a–d**) were synthesized and their photoreactions were conducted under the same conditions (Table 2). The photoreactions of these phenylacetylene-tethered 6-chloropyridin-2-one and 3-chloroisoquinolin-1-one all afforded the fused 6-chlorobenzo[*f*]quinolin-3(4*H*)-one (**6a–b**) and 8-chlorobenzo[*a*]phenanthridin-5(6*H*)-ones (**8a–d**) as main products (Table 2). The products were identified by ^{1}H NMR, ^{13}C NMR and HRMS, and the structure of **8d** was further confirmed

Table 2 Photocyclizations of 6-chloro-*N*-(ω-phenylethynylalkyl)pyridin-2-one and 3-chloro-*N*-(ω-phenylethynylalkyl)isoquinolin-1-one



Entry	Substrate	*R*	n	Time (h)	Convn[a] (%)	Product	Yield[b] (%)
1	**5a**	CH_3	2	12	90	**6a**	55
2	**5b**	H	2	12	92	**6b**	60
3	**7a**	CH_3	1	12	95	**8a**	68
4	**7b**	H	1	12	98	**8b**	72
5	**7c**	CH_3	2	12	95	**8c**	70
6	**7d**	H	2	12	98	**8d**	74

[a] Conversion were based on the **1a** or **3a–c**. [b] Isolated yields.

by X-ray analysis as depicted in Fig. 1.[8] Comparatively, the intramolecular reactions of **5a–b** and **7a–d** (Table 2) are more efficient than the intermolecular photoreactions of **1a** or **3a–c** with phenylacetylene (Table 1), not only the yields of products were increased, but the reaction times were decreased greatly. The presence of electron-donating substituents as methyl group on phenylacetylene retarded photoreactions.

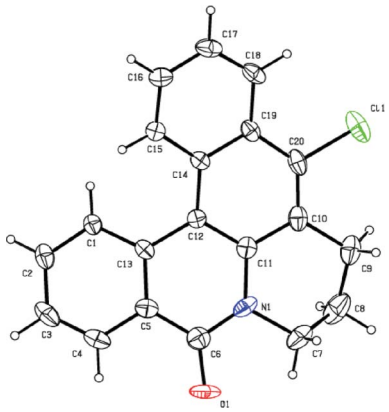


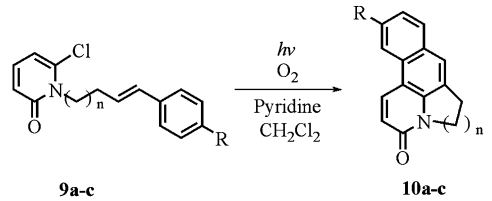
Fig. 1 X-Ray crystal structure of **8d**.

In order to compare the intramolecular photoreactions of phenylacetylene-tethered 6-chloropyridin-2-ones (**5a–b**) or 3-chloroisoquinolin-1-ones (**7a–d**) with styrene-tethered 6-chloropyridin-2-one or 3-chloroisoquinolin-1-one. We synthesized the 6-chloro-*N*-(ω-styrylalkyl)pyridin-2-ones (**9a–c**) or 3-chloro-*N*-(ω-styrylalkyl)isoquinolin-1-ones (**11a–j**) and investigated their photoreaction. All these substrates could also be transformed to fused benzo[*f*]quinolin-3-one (**10a–c**) benzo[*a*]phenanthridin-5-ones (**12a–j**) in high yields after 8–12 h irradiation (Table 3). Differently, no chlorine-retained products were detected. It could be inferred that intermediates "stilbenoids" were produced *via* two step reactions: intramolecular addition of 6-chloropyridin-2-one or 3-chloroisoquinolin-1-one to tethered styrene and subsequent photodehyrochlorination because it was found that the presence of pyridine in solution was helpful to the increase of conversion of reactants and the yields of products.

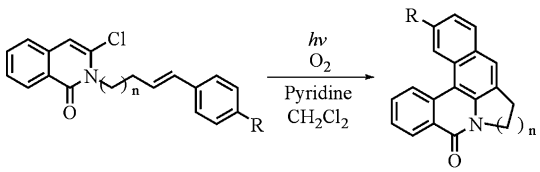
It could be noticed that the substituents on styrene and the length of tethers all had similar influences to the results of photoreactions as to the reactions involving phenylacetylene. The electron-donating groups like methyl (**9a**, **11a**, **11e**) and methoxy group (**11d**) retarded the photoreactions; in contrast, the electron-attracting groups like chlorine (**9c**, **11c**, **11g**) and cyano group (**11h**) accelerated the photoreactions. This influence of substituents to the photocyclizations of 6-chloro-*N*-(ω-styrylalkyl)pyridin-2-ones (**9a–c**) and 3-chloro-*N*-(ω-styrylalkyl)isoquinolin-1-ones (**11a–j**) was consistent with that observed in photocyclizations of stilbenes with different substituents.[9] The conversion of reactants (**11a**, **11c**, **11g**, **11j**) and the yields of products (**12a**, **12c**, **12g**, **12j**) were decreased gradually with the increase of the tether's length (n = 1 to n = 3).

Differently from the photoreactions of **11a–11i**, the photoreaction of substrate **11j** with a tether n = 0 gave only intramolecular coupling product **13** in both Pyrex tube or reaction flask, no normal product **12j** was detected (Scheme 2). Obviously, it was difficult to form the highly strained ring system like **11j** in this

Table 3 Photoreactions of 6-chloro-*N*-(ω-styrylalkyl)pyridin-2-ones and 3-chloro-*N*-(ω-styrylalkyl)isoquinolin-1-ones



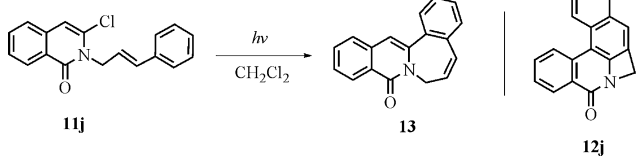
9a-c **10a-c**



11-a-j **12a-j**

Entry	Substrate	n	*R*	Time (h)	Convn[a] (%)	product	Yield[b] (%)
1	**9a**	2	CH_3	16	85	**10a**	50
2	**9b**	2	H	15	88	**10b**	52
3	**9c**	2	Cl	14	90	**10c**	56
5	**11a**	1	CH_3	16	90	**12a**	55
6	**11b**	1	H	14	90	**12b**	60
7	**11c**	1	Cl	12	95	**12c**	63
8	**11d**	2	CH_3	16	90	**12d**	58
9	**11e**	2	OCH_3	16	80	**12e**	54
10	**11f**	2	H	15	91	**12f**	61
11	**11g**	2	Cl	12	95	**12g**	65
12	**11h**	2	CN	12	98	**12h**	67
13	**11i**	3	H	16	80	**12i**	45

[a] Conversion were based on the **1a** or **3a–c**; [b] isolated yields.



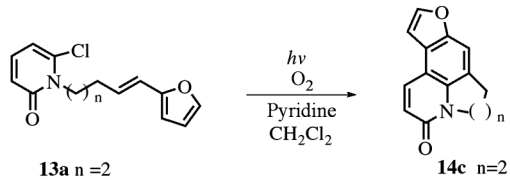
11j **13** **12j**

Scheme 2 Photoreaction of 3-chloro-2-(3-phenylpropenylisoquinolin-2-ones) (**11j**).

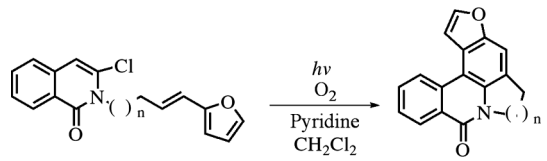
photoreaction. In addition, this result also indicated the homolysis of C–Cl bond in 3-chloroisoquinolin-1-one was feasible under the irradiation of $\lambda > 300$ nm.

Besides the above styrene-tethered 6-chloropyridin-2-ones (**5a–b**) or 3-chloroisoquinolin-1-ones (**7a–d**), three 6-chloro-*N*-(ω-furanylethenylalkyl)isoquinolin-1-one (**13a**) and 3-chloro-*N*-(ω-furanylethenylalkyl)isoquinolin-1-one (**15a–b**) were synthesized and were subjected to photoreactions under the same conditions because styrylfuran is known to undergo photochemical cyclization and oxidative aromatization to afford the polycyclic compounds.[7] As shown in Table 4, the photocyclization of **13a** and **15a–b** could proceed smoothly, but conversion of reactants and the yields of products were relatively lower as compared with styrene-tethered 6-chloropyridin-2-ones or 3-chloroisoquinolin-1-ones. The products were identified by ^{1}H NMR, ^{13}C NMR and HRMS, and the structure of **14a** was further confirmed by X-ray analysis as depicted in Fig. 2.[10]

Table 4 Photoreactions of 6-chloro-*N*-(ω-furanylethenylalkyl)-isoquinolin-1-one and 3-chloro-*N*-(ω-furanylethenylalkyl)isoquinolin-1-one



13a n =2 **14c** n=2



15a n=1
15b n=2

16a n=1
16b n=2

Entry	Substrate	n	Time (h)	Convn[a] (%)	Product	Yield[b] (%)
1	**13a**	2	15	88	**14a**	52
2	**15a**	1	10	90	**16a**	47
3	**15b**	2	10	90	**16b**	58

[a] Conversion were based on the **1a** or **3a–c**. [b] Isolated yields.

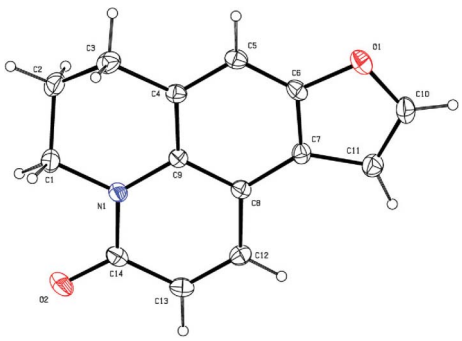


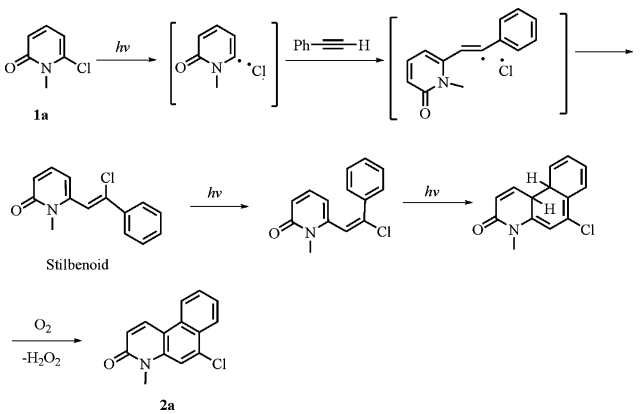
Fig. 2 X-Ray crystal structure of **14a**.

Mechanistic proposal

Similarly to the proposal for the mechanism of photoreactions between 3-chloroisoquinolin-1(2H)-one and styrenes,[6b] the photoreactions between 6-chloropyridin-2-one (**1a**) or 3-chloroisoquinolin-1-ones (**3b**) and phenylacetylene were considered to be also initiated by the homolytic fission of C–Cl bond in excited **1a** or **3b** to give the heteroraryl radical and chlorine atom as reported by Kaneko in his investigation on the photolysis of **3b** in benzene.[11] Then the addition of heteroaryl radicals to the triple bond of phenylacetylene and the combination of the newly-produced radical with chlorine atom to afford the chlorine-substituted "stilbenoid"; photoisomerization of the *trans*-stilbenoid, 6π electrocyclization and oxidative aromatization afforded the product **2a** or **4b** (Scheme 3).

Conclusions

In conclusion, we have developed an efficient one-pot synthesis of benzo[*f*]quinolin-3-ones and benzo[*a*]phenanthridein-5-ones by the photoannulation of 6-chloropyridin-2-ones and 3-chloroisoquinolin-1-ones to phenylacetylene or tethered



Scheme 3 Proposed mechanism for the formation of **2a**.

phenylacetylene. The photoannulations were proceeded by two-step photoreactions containing chlorine atom transfer addition of 6-chloropyridin-2-ones and 3-chloroisoquinolin-1-ones to phenylacetylene to give "chloro-stilbenoid" intermediates and 6π electrocyclization and oxidative aromatization. The intramolecular photoreactions were much more efficient than the intermolecular photoreactions.

Experimental

General information

All reagents were purchased from commercial suppliers and used without further purification. All solvents were dried and redistilled before use. Flash chromatography was carried out with silica gel (200–300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Melting points were determined on a Yanagimoto melting point apparatus and uncorrected. Elementary analyses were carried out on a PERKIN-ELMER 2400 II analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 NMR or a Bruker DRX-300 NMR spectrometers in $CDCl_3$ with TMS as an internal standard. EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The HMRS spectra were measured on a Burker Dattonics APEXII47e spectrometer by ESI.

General procedure for the photochemical reactions of 1a and 5a–b and 9a–c

6-Chloro-1-methylpyridin-2-one (**1a**) (72 mg, 0.5 mmol) was dissolved in 40 mL dry dichloromethane. The solution was distributed into two quartz tubes and the two tubes were irradiated with a medium-pressure mercury lamp (500 W) at ambient temperature for 36 h. The progress of the reaction was monitored by TLC at regular intervals. After almost all substrate **1a** had been consumed, the solvent was removed under reduced pressure and the residue was separated by column chromatography on silica gel eluted by hexane-acetone 10 : 1(v/v) to afford photoreaction product **2a**.

General procedure for the photochemical reactions of 3a–c, 7a–d and 11a–j

6-Chloro-1-(5-phenylpent-4-enyl)pyridin-2-one (**3a**) (90 mg, 0.5 mmol) was dissolved in 40 mL dry dichloromethane and dry pyridine (160 mg) was added. The solution was distributed into two Pyrex tubes and the two tubes were irradiated with a medium-pressure mercury lamp (500 W) at ambient temperature for 40 h. The progress of the reaction was monitored by TLC at regular intervals. After almost all substrate **3a** had been consumed, the solvent was removed under reduced pressure and the residue was separated by column chromatography on silica gel eluted by hexane-acetone 10 : 1(v/v) to afford photoreaction product **4a**.

6-Chloro-4-methylbenzo[*f*]quinolin-3-ones (2a)

Brown solid; mp: 129–130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.50 (d, J = 10 Hz, 1H), 8.35 (t, J = 7.6 Hz, 1H), 7.74 (s, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 10 Hz, 1H), 3.84 (s, 1H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 162.2, 138.8, 136.2, 133.6, 130.7, 128.9, 126.5, 126.3, 125.4, 121.9, 121.0, 115.2, 113.9, 30.3; FT-IR (KBr,cm^{-1})3412, 2924, 1548, 1512, 1220, 756. ESI-HMRS: (m/z) calcd for $C_{14}H_{10}ClNO$ (M+H$^+$): 244.0524, found 244.0529.

8-Chlorobenzo[*a*]phenanthridin-5-ones (4a)

White solid; mp: 205–206 °C; ^{1}H NMR (DMSO,400 MHz) δ 8.83 (d, J = 8.8 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H), 8.43 (dd, J = 8.0 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.92 (td, J = 7.6 Hz, 1H), 7.78 (td, J = 7.6 Hz, 1H), 7.70–7.31 (m, 2H); ^{13}C NMR (DMSO,100 MHz) δ 160.1, 134.7, 133.4, 132.1, 131.8, 129.9, 128.0, 127.1, 127.0, 126.4, 126.3, 126.2, 125.1, 125.0, 124.2, 116.4, 110.2; FT-IR (KBr,cm^{-1}) 3405, 1630, 1324, 1142, 888, 784. ESI-HMRS: (m/z) calcd for $C_{17}H_{10}ClNO$ (M+H$^+$): 280.0524, found 280.0529.

8-Chloro-6-methylbenzo[*a*]phenanthridein-5-ones (4b)

White solid; mp: 255–256 °C; ^{1}H NMR ($CDCl_3$,400 MHz) δ 8.74 (d, J = 8.4 Hz,1H), 8.60 (dd, J = 8.0 Hz, 1H), 8.53 (d, J = 8.4 Hz,1H), 8.36 (d, J = 8.4 Hz,1H), 7.76 (td, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.66–7.58 (m, 3H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 136.8, 136.0, 133.8, 131.4, 130.0, 129.6, 128.6, 126.9, 126.8, 126.7, 126.5, 126.3, 124.6, 115.6, 112.6, 30.5; FT-IR (KBr,cm^{-1}) 3064, 2925, 2864, 1638, 1330, 1150, 890, 786. ESI-HMRS: (m/z) calcd for $C_{18}H_{12}ClNO$ (M+H$^+$): 294.0680, found 294.0684.

8-Chloro-6-phenylbenzo[*a*]phenanthridein-5-ones (4c)

White solid; mp: 260–261 °C; ^{1}H NMR ($CDCl_3$,400 MHz) δ 8.84 (d, J = 8.4 Hz,1H), 8.66 (d, J = 8.0 Hz, 1H), 8.63 (dd, J = 7.6 Hz,1H), 8.34 (dd, J = 8.6 Hz,1H), 7.85 (td, J = 7.6 Hz,1H), 7.72–7.60 (m, 6 H), 7.34 (d, J = 7.2 Hz, 2H), 7.01 (s,1H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 161.6, 137.8, 136.9, 133.3, 132.0, 130.7, 130.4, 129.1, 129.1, 129.0, 128.0, 127.7, 127.6, 127.2, 126.9, 126.3, 125.7, 125.1, 116.9, 113.0; FT-IR (KBr, cm$^{-1)}$ 3070, 145, 1340, 1154, 893, 790. ESI-HMRS: (m/z) calcd for $C_{23}H_{14}ClNO$ (M+H$^+$): 356.0837, found 356.0840.

5,6-Dihydro-7-chloro-11-methylnaphtho[3,2,1-ij]quinolizin-3-one (6a)

White solid; mp:146–147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (d, J = 8.4 Hz,1H), 8.22 (d, J = 8.8 Hz,1H), 8.07 (s,1H), 7.41 (d, J = 8.4 Hz,1H), 6.86 (d, J = 10 Hz,1H), 4.28 (t, J = 5.8 Hz, 2H), 3.23 (t, J = 6.4 Hz, H), 2.59 (s, 3H), 2.20–2.14 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 137.8, 136.9, 134.0, 133.6, 129.2, 128.1, 125.0, 124.8, 122.2, 120.9, 120.0, 113.0, 42.27, 26.7, 22.0, 20.4; FT-IR (KBr,cm^{-1}) 2930, 2848, 1658, 1563, 1508, 1232, 758. ESI-HMRS: (m/z) calcd for $C_{17}H_{14}ClNO$ (M+H$^+$): 284.0837, found 284.0840.

5,6-Dihydro-7-chloronaphtho[3,2,1-ij]quinolizin-3-one (6b)

White solid; mp:162–163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53 (d, J = 10 Hz,1H), 8.34 (dd, J = 8.4 Hz, 2H), 7.66 (t, J = 7.6 Hz,1H), 7.59 (t, J = 7.6 Hz,1H), 6.89 (d, J = 9.6 Hz,1H), 4.30 (t, J = 5.8 Hz, 2H), 3.26 (t, J = 6.2 Hz, 2H), 2.22–2.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 136.8, 134.1, 133.6, 129.1, 127.8, 126.6, 126.1, 125.2, 123.3, 121.4, 120.3, 113.4, 42.2, 26.8, 20.4; FT-IR (KBr,cm^{-1}) 2935, 2852, 1652, 1560, 1501, 1226, 750. ESI-HMRS: (m/z) calcd for $C_{16}H_{12}ClNO$ (M+H$^+$):270.0680, found 270.0684.

6,7-Dihydro-8-chloro-1-methylbenzo[*a*]pyrrolo[3,2,1-*de*]phenanthridin-5-ones (8a)

White solid; mp: 154–155 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.74 (d, J = 8.4 Hz,1H), 8.66 (dd, J = 8.0 Hz,1H), 8.59 (s, 1H), 8.24 (d, J = 7.2 Hz,1H), 7.81 (td, J = 8.4 Hz,1H), 7.62 (t, J = 7.2 Hz,1H), 7.40 (d, J = 8.4 Hz,1H), 4.51 (t, J = 8.0 Hz, 2H), 3.49 (t, J = 8.0 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.1, 139.1, 137.6, 134.7, 132.1, 130.8, 128.7, 128.6, 127.5, 127.0, 126.9, 125.7, 124.8, 124.3, 108.5, 46.2, 26.7, 22.1; FT-IR (KBr,cm^{-1}) 3048, 2917, 2857, 1635, 1336, 1154, 890, 788. ESI-HMRS: (m/z) calcd for $C_{20}H_{14}ClNO$ (M+H$^+$): 320.0837, found 320.0840.

6,7-Dihydro-8-chlorobenzo[*a*]pyrrolo[3,2,1-*de*] phenanthridin-5-ones (8b)

White solid; mp: 249–250 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (d, J = 8.4 Hz,1H), 8.69 (d, J = 8.4 Hz,1H), 8.64 (dd, J = 8.0 Hz,1H), 8.34 (d, J = 7.6 Hz,1H), 7.78 (td, J = 7.6 Hz,1H), 7.65–7.55 (m, 3H), 4.48 (t, J = 8.0 Hz, 2H), 3.47 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 139.0, 134.5, 132.1, 130.6, 129.8, 128.8, 128.7, 128.6, 127.6, 127.5, 127.0, 125.7, 125.1, 125.0, 124.7, 108.9, 46.2, 26.8; FT-IR (KBr,cm^{-1}) 3060, 2928, 2850, 1630, 1328, 1148, 886, 784. ESI-HMRS: (m/z) calcd for $C_{19}H_{12}ClNO$ (M+H$^+$): 306.0680, found 306.0684.

7,8-Dihydro-9-chloro-12-methylbenzo[*a*]pyridine[3,2,1-*de*]phenanthridin-5-ones (8c)

White solid; mp: 155–156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (dd, J = 8.0 Hz,1H), 8.47 (d, J = 8.4 Hz,1H), 8.38 (s,1H), 8.23 (d, J = 8.4 Hz,1H), 7.73 (td, J = 7.6 Hz,1H), 7.59 (t, J = 7.2 Hz,1H), 7.36 (dd, J = 8.4 Hz,1H), 4.30 (td, J = 4 Hz, 2H), 3.22 (t, J = 6.6 Hz, 2H), 2.52 (s, 3H), 2.17–2.11 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0, 136.7, 133.9, 133.4, 132.4, 131.3, 129.3, 128.1, 127.5, 127.4, 127.1, 126.3, 125.6, 125.3, 124.7, 122.0, 112.4, 42.3, 27.0, 21.9, 20.5; FT-IR (KBr,cm^{-1}) 3064, 2914, 2852, 1638, 1334, 1160, 899, 786. ESI-HMRS: (m/z) calcd for $C_{21H16}ClNO$ (M+H$^+$): 334.0993, found334.0997.

7,8-Dihydro-9-chlorobenzo[*a*]pyridine[3,2,1,- *de*]phenanthridin-5-ones (8d)

White solid; mp:176–177 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64 (dd, J = 8.4 Hz,1H), 8.58 (dd, J = 8.0 Hz,1H), 8.50 (d, J = 8.0 Hz,1H), 8.38 (dd, J = 8.0 Hz,1H), 7.75 (td, J = 7.6 Hz,1H), 7.61 (t, J = 7.6 Hz,1H), 7.56 (td, J = 8.4 Hz,1H), 4.32 (td, J = 4 Hz, 2H), 3.26 (t, J = 6.4 Hz, 2H), 2.20–2.14 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0, 133.8, 133.2, 132.4, 131.4, 129.1, 128.1, 127.5, 127.3, 126.8, 126.3, 126.1, 125.5, 124.8, 124.8, 123.1, 112.9, 42.3, 27.1, 20.4; FT-IR (KBr,cm^{-1}) 3068, 2920, 2860, 1633, 1330, 1153, 894, 782. ESI-HMRS: (m/z) calcd for $C_{20}H_{14}ClNO$ (M+H$^+$): 320.0837, found 320.0842.

5,6-Dihydro-10-methylnaphtho[3,2,1-ij]quinolizin-3-one (10a)

White solid; mp:160–161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (d, J = 10.0 Hz, 1H), 8.06 (s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 10.0 Hz, 1H), 4.28 (t, J = 6.0 Hz, 2H), 3.09 (t, J = 6.0 Hz, 2H), 2.57 (s, 3H), 2.13–2.19 (m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.1, 136.9, 136.8, 133.9, 129.6, 129.1, 127.7, 127.3, 126.9, 123.9, 120.6, 119.7, 114.1, 43.2, 28.3, 22.1, 20.9; FT-IR (KBr,cm^{-1}) 3022, 2932, 2860, 1660, 1568, 1508, 838, 790. ESI-HMRS: (m/z) calcd for $C_{17}H_{15}NO$ (M+H$^+$): 250.1227, found 250.1232.

5,6-Dihydronaphtho[3,2,1-ij]quinolizin-3-one (10b)

White solid, mp: 104–105 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (d, J = 9.6 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.57 (td, J = 7.6 Hz), 7.47 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 9.6 Hz, 1H), 4.25 (t, J = 6.0 Hz, 2H), 3.07 (t, J = 6.0 Hz, 2H), 2.11–2.17 (m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.1, 136.7, 133.7, 129.7, 128.9, 128.7, 127.8, 126. 9, 125.2, 124.9, 121.1, 120.1, 114.3, 43.1, 28.3, 20.7; FT-IR (KBr,cm^{-1}) 3035, 2941, 2869, 1652, 1562, 1500, 833, 788. ESI-HMRS: (m/z)calcd for $C_{16}H_{13}NO$ (M+H$^+$): 236.1070, found 236.1074.

5,6-Dihydro-10-chloronaphtho[3,2,1-ij]quinolizin-3-one (10c)

White solid; mp: 156–157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, J = 10 Hz, 1H), 8.17 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.63 (s, 1H), 7.39 (dd, J = 8.4 Hz, 1H), 6.83 (d, J = 9.6 Hz, 1H), 4.25 (t, J = 6.0 Hz, 2H), 3.07 (t, J = 6.0 Hz, 2H), 2.12–2.18(m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.9, 137.2, 133.5, 133.1, 129.8, 129.3, 129.2, 126.9, 125.9, 125.2, 120.6, 120.3, 113.5, 43.1, 28.2, 21.6; FT-IR (KBr,cm^{-1}) 3026, 2928, 2858, 1648, 1560, 1512, 840, 786. ESI-HMRS: (m/z)calcd for $C_{16}H_{12}NOCl$ (M+H$^+$): 260.0680, found 260.0684.

7,8-Dihydro-11-methylbenzo[*a*]pyrrolo[3,2,1- *de*]phenanthridin-5-ones (12a)

White solid; mp: 168–169 °C; ^{1}H NMR ($CDCl_3$,400 MHz) δ 8.75 (d, J = 7.6 Hz, 1H), 8.63 (d, J = 8 Hz, 1H), 8.53 (s, 1H), 7.78 (t, J = 8 Hz, 1H),7.70 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.28 (s, 1H), 4.43 (t, J = 7.6 Hz, 2H), 3.37 (t, J = 6.8 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 139.5, 136.7, 135.1, 131.8, 130.1, 129.4, 129.0, 128.5, 127.5, 126.5, 126.1, 125.6, 124.9,

123.9, 109.4, 46.4, 26.1, 22.2; FT-IR (KBr,cm^{-1}) 3054, 2924, 2848, 1652, 1340, 1150, 890, 788. ESI-HMRS: (*m*/*z*) calcd for $C_{20}H_{15}NO$ (M+H$^+$): 286.1227, found 286.1232.

7,8-Dihydrobenzo[*a*]pyrrolo[3,2,1-*de*]phenanthridin-5-ones (12b)

White solid; mp:142–143 °C; ^{1}H NMR ($CDCl_3$,400 MHz) δ 8.79 (t, J = 4 Hz, 2H), 8.65 (dd, J = 8.0 Hz, 1H), 7.84 (d, J = 8 Hz, 1H), 7.80 (td, J = 8 Hz, 1H), 7.76 (s, 1H), 7.57 (td, J = 8 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 4.74 (t, J = 8.0 Hz, 2H), 3.43 (t, J = 8.0 Hz, 2H);^{13}C NMR ($CDCl_3$,100 MHz) δ 160.1, 139.4, 135.0, 132.0, 131.9, 131.2, 129.3, 129.2, 128.5, 127.5, 126.9, 126.8, 125.7, 125.2, 124.4, 124.3, 109.9, 46.4, 26.3, FT-IR (KBr,cm^{-1}) 3047, 2918, 2850, 1647, 1342, 1118, 887, 784. ESI-HMRS: (*m*/*z*) calcd for $C_{19}H_{13}NO$ (M+H$^+$): 272.1070, found272.1074.

7,8-Dihydro-11-chlorobenzo[*a*]pyrrolo[3,2,1-*de*]phenanthridin-5-ones (12c)

White solid; mp:146–147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.58 (d, J = 8 Hz, 2H), 8.51 (d, J = 8.4 Hz, 1H), 7.75 (td, J = 8.4 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.58 (td, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.36 (dd, J = 8.8 Hz, 1H), 4.40 (t, J = 8.0 Hz, 2H), 3.36 (t,7.6 Hz, 2H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 139.9, 132.9, 132.1, 131.5, 130.1, 129.8, 128.5, 127.4, 127.0, 125.1, 124.7, 123.5, 108.9, 46.4, 26.1; FT-IR (KBr,cm^{-1}) 3030, 2910, 2842, 1640, 1328, 1132, 885, 782. ESI-HMRS: (*m*/*z*) calcd for $C_{19}H_{12}NOCl$ (M+H$^+$): 306.0680, found 306.0683.

8,9-Dihydro-12-methoxybenzo[*a*]pyridino[3,2,1-*de*]phenanthridin-5-ones ((12d)

Yellow syrup; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (d, J = 8.4 Hz, 1H), 8.60 (d, J = 8.0 Hz, 1H), 8.11 (s, 1H), 7.69–7.75 (m, 2H), 7.56–7.59 (m, 2H), 4.32 (t, J = 6.0, 2H), 3.94 (s,3H), 3.09 (t, J = 6.0 Hz, 2H), 2.12–2.17 (m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 158.3, 134.4, 134.1, 131.2, 130.2, 129.3, 128.7, 126.8, 126.3, 125.3, 122.4, 116.0, 112.9, 106.3, 55.4, 43.5, 28.5, 20.9; FT-IR (KBr,cm^{-1}) 3056, 2927, 2846, 1639, 1330, 1157, 896, 788. ESI-HMRS: (*m*/*z*) calcd for $C_{21}H_{17}NO_2$ (M+H$^+$): 316.1332, found 316.1338.

8,9-Dihydro-12-methylbenzo[*a*]pyridino[3,2,1-*de*]phenanthridin-5-ones (12e)

Yellow syrup; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (dt, J = 4 Hz, 2H), 8.43 (s, 1H), 7.73 (td, J = 5.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.57 (td, J = 5.6 Hz, 2H), 7.26 (dd, J = 6.0 Hz, 1H), 4.30 (t, J = 6.0 Hz, 2H), 3.07 (t, J = 6.0 Hz, 2H), 2.53 (s, 3H), 2.08–2.14 (m, 2H);^{13}C NMR ($CDCl_3$,100 MHz) δ 161.3, 135.9, 133.9, 133.9, 131.2, 129.2, 128.6, 128.1, 128.1, 127.6, 127.1, 126.6, 125.1, 123.8, 113.2, 43.4, 28.6,20.9; FT-IR(KBr,cm^{-1}) 3047, 2921, 2852, 1632, 1324, 1152, 893, 785. ESI-HMRS: (*m*/*z*) calcd for $C_{21H17}NO$ (M+H$^+$): 300.1083, found 300.1390.

8,9-Dihydrobenzo[*a*]pyridino[3,2,1-*de*]phenanthridin-5-ones (12f)

White solid; mp 90–91 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.66 (d, J = 8.8 Hz, 1H), 8.60 (d, J = 8 Hz, 2H), 7.79 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.65 (s, 1H),7.59(t, J = 8 Hz, 1H), 7.51 (t, J = 6.0 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 4.32 (t, J = 6.0 Hz, 2 H), 3.11 (t, J = 6.0 Hz, 2H), 2.11–2.13 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 133.8, 133.8, 131.2, 129.9, 129.0, 128.8, 128.1, 127.7, 127.2, 127.0, 126.3, 126.2, 125.8, 124.9, 124.6, 113.7, 43.49, 28.69, 20.68; FT-IR (KBr,cm^{-1}) 3064, 2929, 2860, 1636, 1326, 1155, 891, 785. ESI-HMRS: (*m*/*z*) calcd for $C_{20}H_{15}NO$ (M+H$^+$):286.1226, found 286.1233.

8,9-Dihydro-12-chlorobenzo[*a*]pyridino[3,2,1-*de*]phenanthridin-5-ones (12g)

White solid; mp 150–151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (s, 1H), 8.59 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 5.6 Hz, 1H), 7.38 (dd, J = 8.4 Hz, 1H), 4.31 (t, J = 6.0 Hz, 2H), 3.11 (t, J = 6.0 Hz, 2H), 2.13–2.16 (m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 134.5, 133.4, 132.5, 131.7, 129.7, 129.2, 128.5, 128.3, 128.1, 127.3, 126.7, 126.3, 125.3, 125.3, 124.9, 113.0, 43.5, 28.6, 20.7; FT-IR (KBr,cm^{-1}) 3073, 2922, 2866, 1630, 1330, 1147, 896, 784. ESI-HMRS: (*m*/*z*) calcd for $C_{20}H_{14}NOCl$ (M+H$^+$): 320.0837, found 320.0834.

8,9-Dihydro-12-cyanobenzo[*a*]pyridino[3,2,1-*de*]phenanthridin-5-ones (12h)

White solid; mp: 212–231 °C; ^{1}H NMR($CDCl_3$, 400 MHz) δ 9.01 (s, 1H), 8.62 (dd, J = 8.0 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.86 (td, J = 7.2 Hz, 1H), 7.73 (s, 1H), 7.68 (td, J = 7.2 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 4.35 (t, J = 6.0 Hz, 2H), 3.19 (t, J = 6.0 Hz, 2H), 2.17–2.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.2, 134.8, 132.8, 132.1, 131.8, 131.3, 128.9, 128.7, 128.5, 128.4, 128.2, 128.0, 126.9, 126.6, 125.4, 119.6, 113.8, 109.6, 43.5, 28.9, 20.5; FT-IR (KBr,cm^{-1}) 3035, 2937, 2894, 1645, 1330, 1150, 898, 784. ESI-HMRS: (*m*/*z*) calcd for $C_{21}H_{14}N_2O$ (M+H$^+$): 311.1179, found 311.1184

6,7,8,9-Tetrahydrobenzo[*a*]azepino[3,2,1-*de*]phenanthridin-5-one (12i)

White solid; mp: 40–41 °C; ^{1}H NMR ($CDCl_3$,400 MHz) δ 8.57–8.62 (m, 3H), 7.81 (d, J = 8.4 Hz, 1H), 7.75 (td, J = 7.6 Hz, 1H), 7.65 (s, 1H), 7.59 (td, J = 7.6 Hz, 1H), 7. 54 (td, J = 8.0 Hz, 1H), 7.46 (td, J = 8.0 Hz, 1H), 4.56 (t, J = 5.2 Hz, 2H), 3.31 (t, J = 5.2 Hz, 2H), 2.10–2.15 (m, 2H), 1.99–2.05 (m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.1, 138.9, 134.0, 131.5, 130.8, 130.2, 130.2, 128.5, 128.4, 127.5, 127.2, 127.1, 126.3, 125.9, 125.8, 124.8, 115.6, 44.5, 33.8, 25.7, 23.2; FT-IR (KBr,cm^{-1}) 3072, 2935, 2882, 1647, 1588, 1444, 1172, 819, 748. ESI-HMRS: (*m*/*z*) calcd for $C_{21}H_{17}NO$ (M+H$^+$): 300.1383, found 300.1388.

Benzo[3,4]azepino[1,2-*b*]isoquinolin-9-one (13)

White solid; mp:118–119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (d, J = 8.4 Hz, 1H), 7.74 (dd, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.38–7.51 (m, 4 H), 7.30 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 9.6 Hz, 1H), 6.57 (s, 1H), 6.47 (m, 1H), 5.75 (dd, J = 6.8 Hz, 1H), 3.50 (qd, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.1, 142.8, 136.4, 135.9,135.8, 134.5, 132.0, 129.7, 129.5, 129.0, 128.9, 127.8, 127.8, 126.4, 126.0, 124.2, 108.1, 39.5; FT-IR (KBr,cm^{-1}) 3056, 3025, 2921, 1637, 1588, 1444, 1172, 819, 748. ESI-HMRS: (*m*/*z*) calcd for $C_{18}H_{13}NO$ (M+H$^+$): 260.1070, found 260.1073.

5,6-Dihydrofurano[*1*,*2-f*]pyridino[3,2,1-*de*]quinolin-5-ones (14a)

Brown solid; mp: 203–204 °C; ^{1}H NMR($CDCl_3$, 400 MHz) δ 7.98 (d, J = 9.6 Hz, 1H), 7.69 (s, 1H), 7.47 (s, 1H), 7.01 (s, 1H), 6.80 (d, J = 9.6 Hz, 1H), 4.25 (t, J = 6.0 Hz, 2H), 3.08 (t, J = 6.0 Hz, 2H), 2.11–2.18 (m, 2H);^{13}C NMR($CDCl_3$, 100 MHz) δ 161.8, 149.8, 145.6, 134.9, 133.5, 123.0, 122.2, 121.1, 113.5, 113.3, 104.6, 42.7, 28.5, 20.9; FT-IR(KBr,cm^{-1}) 3134, 3112, 2937, 1649, 1589, 1413, 1130, 837, 783. ESI-HMRS: (m/z) calcd for $C_{17}H_{11}NO_2$ (M+H$^+$) 262.0863, found 262.0868.

6,7-Dihydrofurano[1,2-*f*]pyrrolo[3,2,1-*de*]phenanthridin-5-ones (16a)

Brown solid, mp: 216–217 °C; ^{1}H NMR($CDCl_3$, 400 MHz) δ 8.61 (dd, J = 8.0 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.80 (td, J = 9.2 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.48 (s, 1H), 7.37 (s, 1H), 4.52 (t, J = 8.0 Hz, 2H), 3.46 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 159.7, 152,7, 145.8, 136.5, 134.4, 132.0, 128.5, 128.4, 127.3, 127.2, 124.2, 120.5, 109.3, 106.5, 46.9, 26.8; FT-IR (KBr,cm^{-1}) 3118, 2920, 2868, 1625, 1600, 1342, 1149, 1033, 789. ESI-HMRS: (m/z) calcd for $C_{17}H_{11}NO_2$ (M+H$^+$) 276.1019, found 276.1023.

7,8-Dihydrofurano[1,2-*f*]pyrrolo[3,2,1-*de*]phenanthridin-5-ones (16b)

Brown solid, mp:134–135 °C; ^{1}H NMR($CDCl_3$, 400 MHz) δ 8.61 (dd, J = 8.0 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.74 (s, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.46 (s, 1H), 7.45 (s, 1H), 4.34 (t, J = 6 Hz, 2H), 3.10 (t, J = 6.0 Hz, 2H), 2.10–2.16 (m, 2H);^{13}C NMR ($CDCl_3$,100 MHz) δ 160.9, 150.8, 145.5, 134.2, 132.0, 131.4, 128.5, 127.3, 125.6, 124.4, 123.0, 121.2, 112.8, 112.7, 107.4, 43.5, 29.3, 20.8; FT-IR (KBr,cm^{-1}) 3124, 2929, 2873, 1627, 1602, 1346, 1149, 1035, 790. ESI-HMRS: (m/z) calcd for $C_{18}H_{13}NO_2$ (M+H$^+$) 276.1019, found 276.1023.

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