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Palladium-catalyzed intramolecular C–H arylation of 2-halo-*N*-Boc-*N*-arylbenzamides for the synthesis of N–H phenanthridinones†

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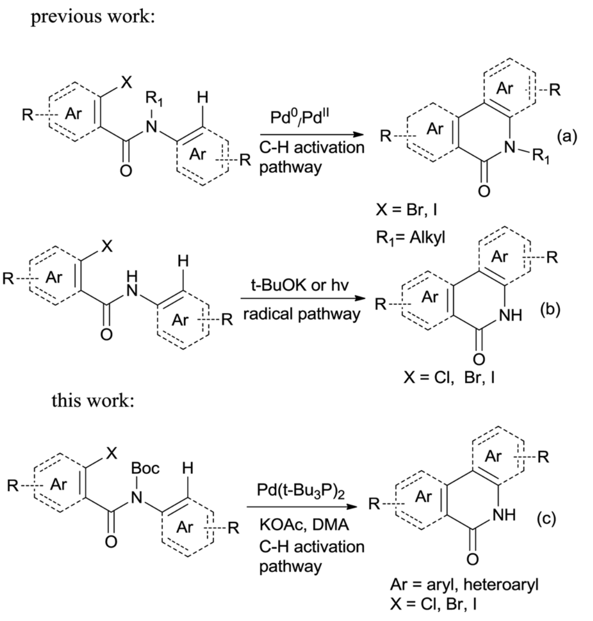
A palladium catalyzed synthesis of N–H phenanthridinones was developed *via* C–H arylation. The protocol gives phenanthridinones regioselectively by one-pot reaction without deprotection. It exhibits broad substrate scope and affords targets in up to 95% yields. Importantly, it could be applied for the less reactive *o*-chlorobenzamides.

Introduction

Palladium-catalyzed direct functionalization of C–H bonds has become one of the most efficient and environmentally friendly mild procedures for building carbon–carbon bonds.[1] It holds a special place among various types of palladium-catalyzed coupling reactions. C–H direct arylation is its typical application, which is catalyzed by Pd(0) or Pd(II) with phosphine ligands operating under a Pd(0)/Pd(II) or Pd(II)/Pd(IV) catalytic cycle with or without the assistance of base.[2] This coupling strategy has been well developed in terms of regioselectivity and efficiency; the tolerance of diverse functional groups makes the C–H arylation particularly versatile for organic synthesis. The starting materials may be easily achieved and thus this strategy has been used for building a variety of aromatic and heteroaromatic systems.[3]

Phenanthridinones are important structural units found in many natural products and pharmaceuticals that exhibit wide range of biological activities.[4] A variety of novel synthetic approaches have been developed to the synthesis of the phenanthridinone cores and related lactams, most of them are based on palladium catalyzed biaryl coupling by the regioselective C–H bond activation (Scheme 1a, synthesis of *N*-alkyl phenanthridinones).[5] Although they are effective for synthesis of *N*-alkyl phenanthridinones, the obvious drawbacks were observed when applied to *N*–H phenanthridinones.[5e,6] Their scope of substrates is quite limited and high reaction temperature is necessary. To the best of our knowledge, only the yields with iodo-substituted anilides are reported. Usually a complex mixture of side-products is observed, decreasing the yield of desired product.[6a,6b] This is possibly resulted from the coordination of nitrogen to palladium in the presence of the NH free amide.[5e] Earlier reported efficient protocols for such analog were mediated by potassium *tert*-butoxide[7] or photochemistry.[8,9] However, those procedures are not regioselective with substituted anilides due to radical cyclization mechanism (Scheme 1b, radical pathway for synthesis of N–H phenanthridinones), limiting application of substrate scopes.[7] So based on those disadvantages researchers reported utilization of protection groups which could be easily cleaved after the ring closure. Sandro Cacchi and co-workers[5e] developed *N*-benzyl derivatives of *N*-benzoyl-*o*-iodoanilides which can be converted



Scheme 1 Synthesis of phenanthridinones *via* intramolecular cyclization.

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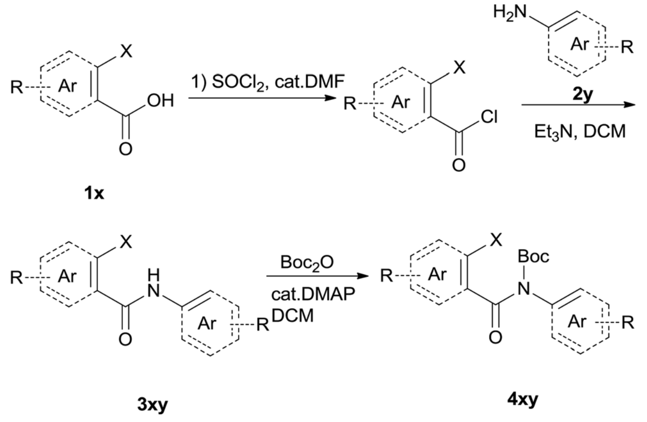
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra02099j



Scheme 2 Synthesis of cyclization substrates.

into the corresponding phenanthridinones in good to high yields, but needed one more deprotection step in TFA. François Tillequin *et al.*[6d] developed Boc as protection and leaving group, however, one equivalent of Pd catalyst and two equivalents of phosphine ligands were involved, and only 26% yield was obtained.

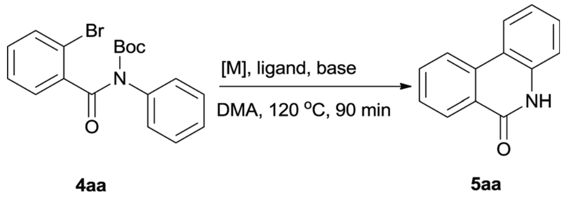
In this account it is important to develop an operationally simple catalyst system for direct intramolecular arylation processes exhibiting broad scope for aryl chlorides, bromides, and iodides. Here we disclosed a palladium catalyzed one pot C–H activation protocol, cyclization and decarboxylation of *N*-Boc protected *o*-halobenzamides to produce phenanthridinones directly, which gave good to excellent yields as high as 95% (Scheme 1c, synthesis of N–H phenanthridinones by C–H activation from Boc protected amide). It can be easily scaled up even with increasing of yield. The reaction was promoted by Pd(t-Bu$_3$P)$_2$ combining together with KOAc, a convenient, commercial available catalyst inexpensive, but highly efficient to produce a broad range of phenanthridinones.

Results and discussion

The synthesis of the amide starting material **4xy** for this investigation is shown in Scheme 2. Ortho-halogen substituted arylcarboxylic acid was easily converted to acyl chloride, which reacted with aniline to give amide **3xy**. Then under catalytic amount of DMAP in DCM, **3xy** was almost quantitatively converted to **4xy**.[10]

In our initial investigation to optimize cyclization conditions of **4xy**, we selected **4aa** as starting point for screening, which is briefly summarized in Table 1. The C–H direct arylation is strongly dependent on the catalyst, the solvent and the base. Firstly we tried most popular coupling catalyst/base system (entries 1–3),[11] but obtained low yields; Pd(OAc)$_2$/Bu$_3$P/Ag$_2$CO$_3$ system[12] gave better yield (38%). After that, we tried Pd(PCy$_3$)$_2$ under various basic conditions, and found the yield can be increased to 48% when KOAc was used. Speculating that different ligand could be used to fine-tune the reaction due to its electronic and steric particularities,[2d] we further screened Pd(t-Bu$_3$P)$_2$ catalyst[13] with different bases and finally identified Pd(t-Bu$_3$P)$_2$/KOAc was the best combination (entry 11, 72% yield). Other bases with different cation or anion were inferior (entries 9, 10). When the optimized condition was utilized with non-Boc protected substrate **3aa** (entry 12), the strategy was not effective, suggesting that unprotected NH completely inhibited

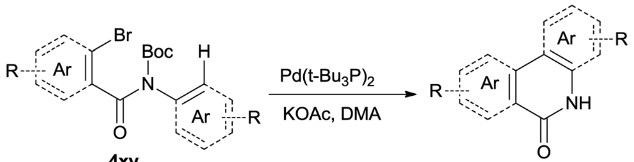
Table 1 Screening of reaction conditions[a]



Entry	Catalyst/ligand (mol%)	Base (equiv.)	Subs. conv. (%)	Yield[b] (%)
1	Pd(PPh$_3$)$_4$ (5)	K$_2$CO$_3$ (2)	100	22
2	Pd(OAc)$_2$/PCy$_3$·HBF$_4$ (5/10)	Cs$_2$CO$_3$ (2)	100	33
3	Pd(OAc)$_2$/Bu$_3$P (5/10)	Ag$_2$CO$_3$ (2)	89	38
4	Pd(PCy$_3$)$_2$ (5)	Cs$_2$CO$_3$ (2)	97	35
5	Pd(PCy$_3$)$_2$ (5)	K$_2$CO$_3$	98	31
6	Pd(PCy$_3$)$_2$ (5)	AgOAc (4)	83	20
7	Pd(PCy$_3$)$_2$ (5)	K$_3$PO$_4$ (2)	88	11
8	Pd(PCy$_3$)$_2$ (5)	KOAc (4)	89	48
9	Pd(t-Bu$_3$P)$_2$ (5)	Cs$_2$CO$_3$ (2)	98	38
10	Pd(t-Bu$_3$P)$_2$ (5)	AgOAc (4)	82	23
11	Pd(t-Bu$_3$P)$_2$ (5)	KOAc (4)	100	72
12[c]	Pd(t-Bu$_3$P)$_2$ (5)	KOAc (4)	18	Trace

[a] Reaction conditions: **4aa** (0.5 mmol), Pd catalyst and base in DMA (5 ml) were heated at 120 °C for 90 min under Ar atmosphere. [b] Yield determined by LCMS. [c] **3aa** was used as substrate.

Table 2 Scope of phenanthridinones formation[a]



4xy **5xy**

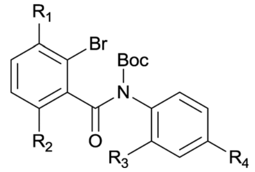
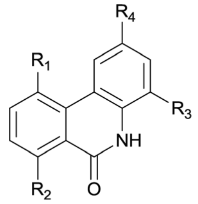
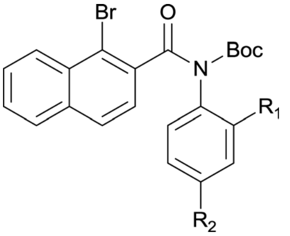
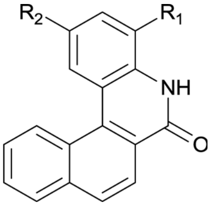
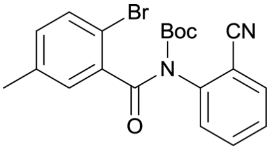
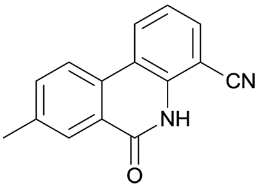
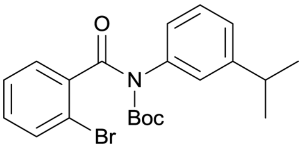
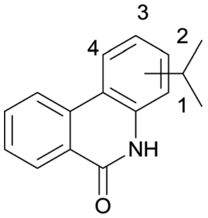
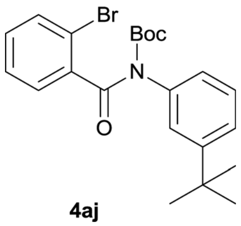
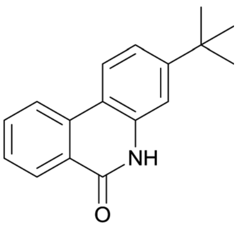
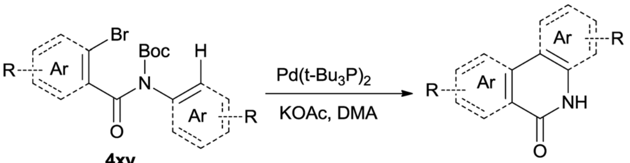
Entry	4xy	5xy	Yield[b] [%]
			
1	**4ab** $R_1 = R_2 = R_3 = H$ $R_4 = OMe$	**5ab** $R_1 = R_2 = R_3 = H$ $R_4 = OMe$	88
2	**4db** $R_1 = Me$ $R_2 = R_3 = H$ $R_4 = OMe$	**5db** $R_1 = Me$ $R_2 = R_3 = H$ $R_4 = OMe$	81
3	**4dc** $R_1 = Me$ $R_2 = H$ $R_3 = Me$ $R_4 = OMe$	**5dc** $R_1 = Me$ $R_2 = H$ $R_3 = Me$ $R_4 = OMe$	87
4	**4ec** $R_1 = H$ $R_2 = OMe$ $R_3 = Me$ $R_4 = OMe$	**5ec** $R_1 = H$ $R_2 = OMe$ $R_3 = Me$ $R_4 = OMe$	92
5	**4hd** $R_1 = H$ $R_2 = F$ $R_3 = Cl$ $R_4 = OMe$	**5hd** $R_1 = H$ $R_2 = F$ $R_3 = Cl$ $R_4 = OMe$	89
			
6	**4lb** $R_1 = H$ $R_2 = OMe$	**5lb** $R_1 = H$ $R_2 = OMe$	91/95[c]
7	**4lg** $R_1 = Cl$ $R_2 = H$	**5lg** $R_1 = Cl$ $R_2 = H$	75
8	 **4jh**	 **5jh**	37[d]
9	 **4ae**	 **5ae-a** 2-isopropyl **5ae-b** 4-isopropyl 2:1	78
10	 **4aj**	 **5aj**	82

Table 2 (*Contd.*)



4xy **5xy**

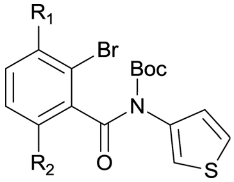
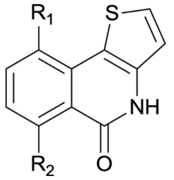
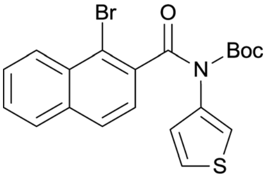
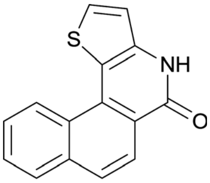
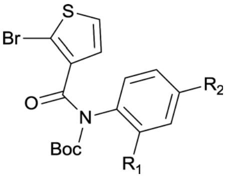
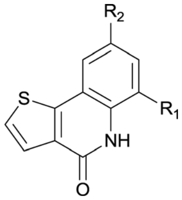
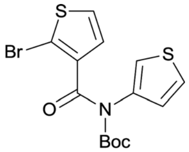
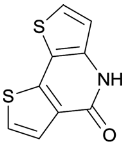
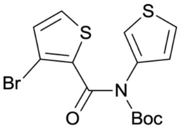
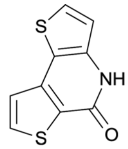
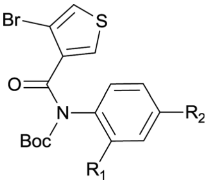
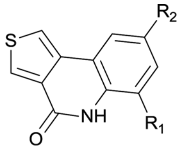
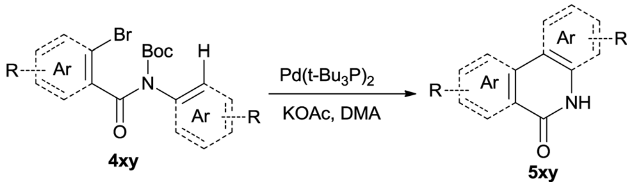
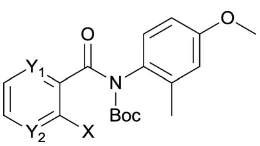
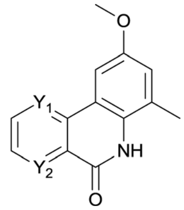
Entry	4xy	5xy	Yield[b] [%]
			
11	**4af** $R_1 = R_2 = H$	**5af** $R_1 = R_2 = H$	84/93[c]
12	**4df** $R_1 = Me$ $R_2 = H$	**5df** $R_1 = Me$ $R_2 = H$	71
13	**4ef** $R_1 = H$ $R_2 = OMe$	**5ef** $R_1 = H$ $R_2 = OMe$	61
14	 **4lf**	 **5lf**	91
			
15	**4kc** $R_1 = Me$ $R_2 = OMe$	**5kc** $R_1 = Me$ $R_2 = OMe$	83/91[c]
16	**4kg** $R_1 = Cl$ $R_2 = H$	**5kg** $R_1 = Cl$ $R_2 = H$	71
17	 **4kf**	 **5kf**	84
18	 **4if**	 **5if**	85
			
19	**4fb** $R_1 = H$ $R_2 = OMe$	**5fb** $R_1 = H$ $R_2 = OMe$	62
20	**4fc** $R_1 = Me$ $R_2 = OMe$	**5fc** $R_1 = Me$ $R_2 = OMe$	58

Table 2 (*Contd.*)



4xy **5xy**

Entry	**4xy**	**5xy**	Yield[b] [%]
			
21	**4rc** $Y_1 = C$ $Y_2 = N$ $X = Br$	**5rc** $Y_1 = C$ $Y_2 = N$	0
22	**4sc** $Y_1 = N$ $Y_2 = C$ $X = Br$	**5sc** $Y_1 = N$ $Y_2 = C$	0
23	**4tc** $Y_1 = N$ $Y_2 = C$ $X = I$	**5tc** $Y_1 = N$ $Y_2 = C$	0

[a] Reaction conditions: 1 mmol of substrate, 4 equiv. of KOAc, and 5% equiv. of Pd (t-Bu$_3$P)$_2$ in 10 ml DMA were heated at 120 °C for 2 h under Ar atmosphere. [b] Isolated yield. [c] Reaction conducted at 20 mmol scale. [d] Reacted at 135 °C.

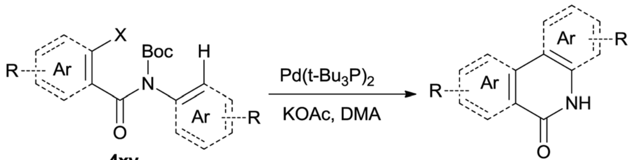
the reaction, presumably resulted by coordination of nitrogen to palladium in the presence of the NH free amide.[5e,14]

After optimization of the reaction condition, we attempted to extend the scope and generality of the intramolecular coupling as shown in Table 2. Various aryl acids and aryl amines were examined. Electron-rich groups (*e.g.* Me and OMe) either on the acid partner or on the aniline partner could smoothly undergo cyclization-decarboxylation which exclusively provided the desired products in 81–92% yields (entries 1–5). Notably, naphthyl-based substrates **4lb** and **4lg** also gave good to excellent yields (75–95%). **4lg** gave lower yield due to slight electron deficiency. When this protocol was subjected to strong electron-deficient substrate such as cyano group (**5jh**, entry 8), the yield reduced sharply. To explore the cyclization position with respect to meta-substituted anilines, we tested meta-isopropyl aniline (entry 9). The reaction gave para and ortho-cyclization mixtures (2 : 1); However when *tert*-butyl analine was tested (entry 10), only para-cyclization was produced, presumably due to stronger steric hindrance. It was worth noting that the 3-amino thiophene also gave moderate to high yields (61–93%, entries 11–14), suggesting it's high C–H activation activity and regioselectivity. NMR confirmed the coupling is at second position. The reaction scope is not limited to benzoic acids, thiophene-carboxylic acids could also go cyclization smoothly (entries 15–20) with aniline or aminothiophene. Similar to early Pd-catalyzated protocol,[15] we found that pyridine ring was not an effective acid partner under our reaction condition (entries 21–23). To further evaluation the protocol's scaling up efficiency, we tested **4lb**/**4af**/**4kc** as substrates for gram scale synthesis. To our delight, the yields increased up from 91%/84%/83% to 95%/93%/91% respectively.

Our above results showed that diverse functional groups, including F, Cl, CN, OMe, alkyl and a variety of aryl carboxylic acids and aryl amines were well tolerated. It leads us to speculate the reaction scope is not limited to bromo-substituted acid, but can also be extended to chloro-substituted acid. So we tested the activity of halogens in Table 3. Firstly, we selected the synthesis of **5aa** as example (entries 1a to 1c). When iodide and bromide were tested, the reaction can be finished at 120 °C, given 77% and 66% yield respectively. When chloride was utilized, the yield decreased to moderate (45%) and must be conducted at higher temperature. After that, we tested electron-donating substitutes on either carboxylic moiety or aniline moiety (entries 2–5) and found yield can be as high as 78%; instead electron-withdrawing substitutes were negative to the reaction (entry 6, 38% yield). When the reaction was extended to strong electron withdrawing substituents, the yield decreased significantly even with iodide (entry 9). Chloro-thiophene carboxylic acid also delivered the corresponding products without a problem (entries 7, 8). Considering both chlorine and bromine were active as acid partner, we subjected **4uc** for the reaction. Just as we predicted, the reaction turned to be quite messy and yielded no desired target (entry 10).

Next we examined the effect of catalyst loading to further optimize the reaction condition. Substrates **4lb** and **4af** were selected as examples which are shown in Table 4. Firstly we tested **4lb**, when the catalyst loading increased from 5 mol% to 6 mol%, the influence was insignificant. However, when it was reduced to 4 mol%, the starting material remained and the yield was reduced by 13%; and only 60% yield was obtained when decreased further to 3 mol%; the same situation was observed with substrate **4af**. Based on research below, 5 mol% catalyst was established as an optimal catalyst loading.

Table 3 Scope of the reaction with respect to halogen-substituted substrates[a]



4xy **5xy**

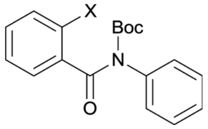
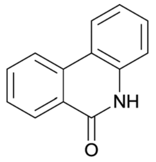
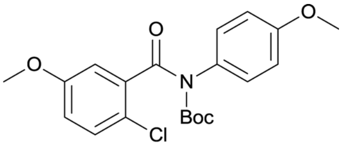
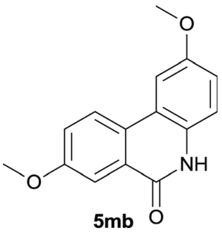
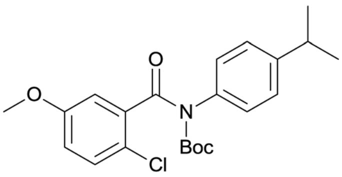
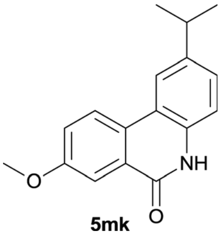
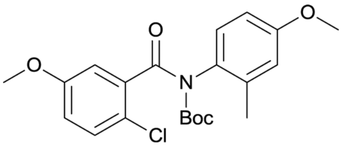
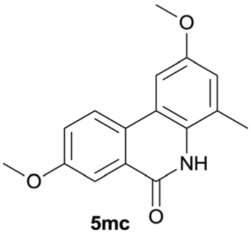
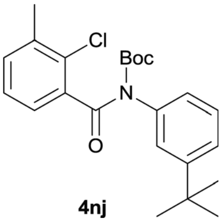
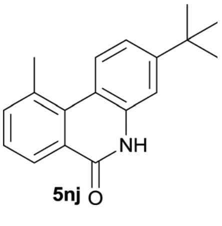
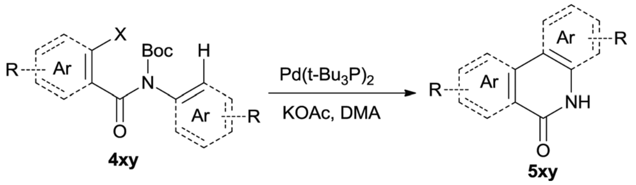
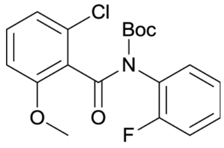
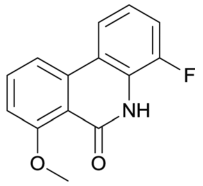
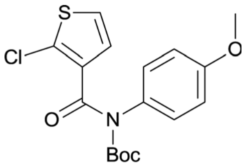
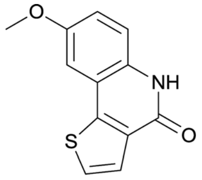
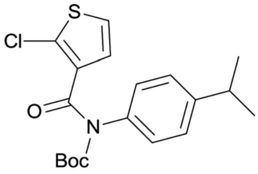
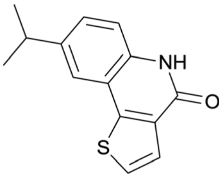
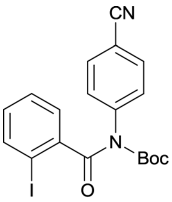
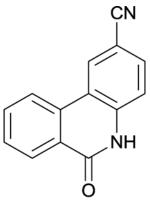
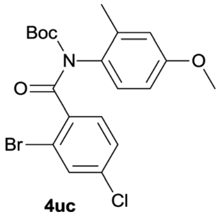
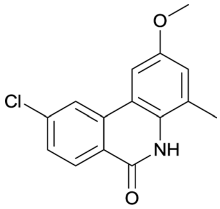
Entry	4xy	5xy	Yield[b] [%]
		 **5aa**	
1a	**4aa1** X = I		77[c]
1b	**4aa2** X = Br		66[c]
1c	**4aa3** X = Cl		45
2	 **4mb**	 **5mb**	68
3	 **4mk**	 **5mk**	45
4	 **4mc**	 **5mc**	67
5	 **4nj**	 **5nj**	78

Table 3 (*Contd.*)



4xy 5xy

Entry	4xy	5xy	Yield[b] [%]
6	 **4pl**	 **5pl**	38
7	 **4ob**	 **5ob**	53
8	 **4ok**	 **5ok**	51
9	 **4ci**	 **5ci**	40
10	 **4uc**	 **5uc**	0

[a] Reaction conditions: 1 mmol of substrate, 4 equiv. of KOAc, and 5% equiv. of (t-Bu$_3$P)$_2$Pd in 10 ml DMA were heated at 135 °C for 2 h under Ar atmosphere. [b] Isolated yield. [c] Reacted at 120 °C.

The directly cleavage of Boc was left for investigation for further exploring of reaction mechanism. We tested another protection group acetyl and used it for cyclization. However acetyl group is extremely unstable and only trace cyclization product was produced. It leaded us to suspect the stability of Boc on such conformationally rigid tricyclic system. So we re-protected the final target **5ec** with Boc again and then heated it in the reaction system at same condition without Pd catalyst (Table 5). To our delight, 26% **5ec** was produced and 69% **6ec** remained. This result revealed that Boc was a fragile spot however just heating the substrate couldn't result full decomposition. Pd catalyst should have played a critical role in catalytic cycle for complete cleavage.

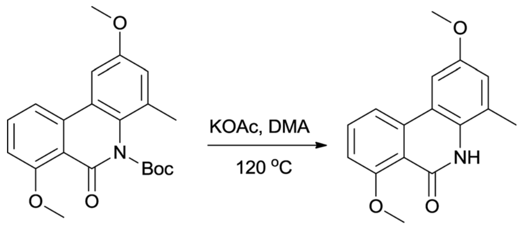
Although additional data are needed to establish the mechanism, the fact that Pd catalyst loading influences the reaction significantly and the base KOAc gives the best yield, Boc group is some extend of fragile suggests their critical roles. It leads us to propose a plausible Pd(0)/Pd(II) catalytic cycle[2] (Scheme 3). A proton abstraction mechanism previously proposed by Echavarren and Maseras,[16] was found to explain our reaction outcomes: (1) the anionic ligand KOAc is directly involved in C–H bond cleaving; (2) the anion ligand must bind to the catalyst, but not block the catalytic cycle by competitive occupation of vacant coordination sites;[17] (3) the arene which interacts with the catalyst weakly must compete for binding to the arylpalladium(II) intermediate with the excess anionic ligand.[18] So initially oxidative addition of polarized Ph–Br bond to the Pd(0) catalyst forms a highly electrophilic arylpalladium intermediate **I**,[18,19] which exchange with KOAc to produce intermediate **II**,[18,20] followed by phosphine dissociation. Secondly Pd(II) interacts with arene at the *ortho* position of aniline in a C–H activation manner which forms intermediate **III**.[20,21] Here HOAc plays a critical role in the stabilized coordination intermediate.[21,22] Next is irreversible deprotonation: Pd(II) inserts into the C–H bond of the arene to give cyclobiarylpalladium intermediate **IV**,[20–22] accompanied by elimination of HOAc. Under the effect of produced HOAc, Pd presumably kicks off Boc and coordinates to nitrogen to give intermediate **V**, which finally undergoes reductive elimination to provide the desired product and regenerates the Pd(0) catalyst.[16,20,22]

Table 4 Effect of catalyst loading[a]

Entry	Substrate	Pd(t-Bu$_3$P)$_2$	Subs. conv. (%)	Yield (%) of 5[b]
1	**4lb**	6%	100	93
2	**4lb**	5%	100	91
3	**4lb**	4%	94	78
4	**4lb**	3%	89	60
5	**4af**	5%	100	84
6	**4af**	4%	93	61
7	**4af**	3%	82	52

[a] Reaction conditions: 1 mmol of substate, 4 equiv. of KOAc, Pd catalyst and 10 ml DMA were heated at 120 °C for 2 h under Ar atmosphere. [b] Isolated yield.

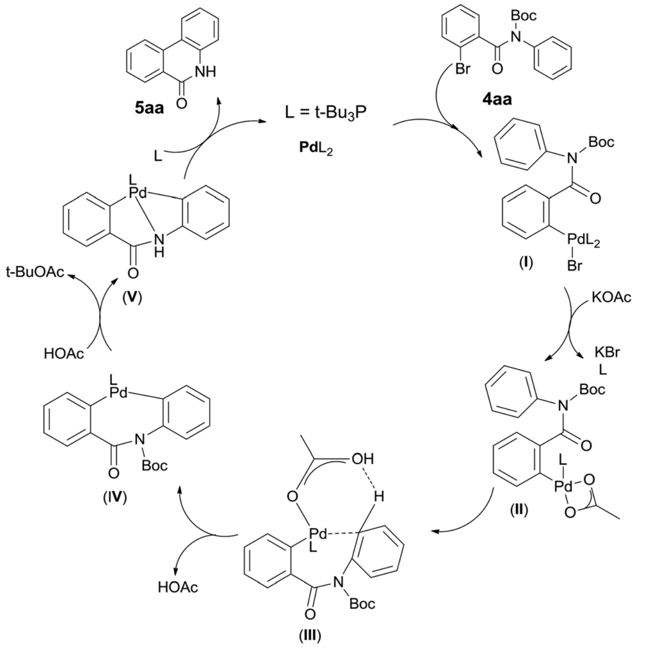
Table 5 Stability testing of **6ec**[a]



6ec **5ec**

Entry	Time (min)	**5ec** (%)[b]	**6ec** (%)[b]
1	60	13	83
2	90	26	69

[a] Reaction conditions: **6ec** (0.5 mmol), 4 equiv. of KOAc in DMA (5 ml) were heated at 120 °C. [b] Determined by LCMS.



Scheme 3 Proposed mechanism for the phenanthridinone synthesis.

Conclusions

In summary, we have developed a palladium catalyzed C–H arylation method for synthesis of N–H phenanthridinones from Boc protected diaryl amide. There are four advantages of using Boc as protection group: (1) the protection stage gives quantitive yield and just simple workup produces pure product; (2) the protection group is stable to some extent compared with acetyl group; (3) the coupling stage directly gives de-protection final targets, additional de-proctection is unnecessary; (3) in contrast to the system of radical pathway without protection reported by Bhakuni *et al.*, the regioisomer is not a concern, only a single desired target was obtained. The catalyst Pd(t-Bu$_3$P)$_2$ is commercial available, inexpensive and the catalyst loading is reasonable; a second phosphine ligand is not required compared to published method.[6d] This practical and convenient method can be easily scaled up, applicable for versatile substrates and produces high yields. Most important of all, it could be applied for the less reactive *o*-chlorobenzamides which greatly extend the substrates scope.

Experimental

General experimental details

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 25 °C using DMSO-d_6 or $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in ppm relative to Me_4Si (internal standard), coupling constants (*J*) are reported in hertz, and peak multiplicity are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br s (broad singlet). High resolution mass analysis is performed on a Waters Q-TOF Premier mass spectrometer with electron spray ionization (ESI). Thin layer chromatography (TLC) was performed on 0.20 mm silica gel F-254 plates (Qingdao Haiyang Chemical, China). Visualization of TLC was accomplished with UV light and/or aqueous potassium permanganate or I_2 in silica gel. Column chromatography was performed using silica gel 60 of 300–400 mesh (Qingdao Haiyang Chemical, China).

General procedure for synthesis of 4xy[10,23]

To suspension of **1x** (5 mmol) in $SOCl_2$ (5 ml) was added with 2 drops of DMF. The mixture was heated under reflux for 3 h. Then the mixture was concentrated and diluted with DCM and concentrated, then diluted and concentrated again to give light brown semi-solid. The residue was dissolved in anhydrous DCM (10 ml), added dropwise to a mixture of **2y** (5 mmol) and Et_3N (12.5 mmol) in DCM (10 ml). The resulting suspension was stirred for another 1 h after addition finished. The mixture was diluted with water, washed with 1 N HCl, 2 N NaOH and brine successively. The organic layer was dried over Na_2SO_4, filtered and concentrated to give the crude amide **3xy** which was used for next step directly.

To the above crude **3xy** was added anhydrous DCM (20 ml), DMAP (0.05 eq., 0.25 mmol), and Boc_2O (1.2 eq., 6 mmol). The suspension was stirred until the bubbling was not observed which indication completion of the reaction. TLC showed a less polar product which was also confirmed by LCMS. The mixture was concentrated, diluted with hexane and water. After stirring for a couple of minutes a precipitate deposited. The solid was filtered, washed with water and hexane, dried under vacuum to give off-white solid **4xy**.

General procedure for synthesis of product 5 (Tables 2 and 3)

To a 50 ml two necked flask equipped with a thermometer was added **4xy** (1 mmol), DMA (10 ml), KOAc (4 eq., 4 mmol), Pd(*t*-$Bu_3P)_2$ (0.05 mmol, 0.05 eq.). The mixture was heated under argon at 120–135 °C for 2 h. It was diluted with H_2O (30 ml), filtered and the solid was washed with H_2O and ethanol successively. The crude product was dissolved in DCM/MeOH (5 : 1), filtered through celite to remove catalyst residue, then concentrated and re-crystallized from hexane/ethyl acetate to give almost pure compound **5xy**.

Most of the final compound can be purified by crystallization easily, for those compounds which has good solubility, a short silica gel column purification is necessary.

Representative gram scale procedure for synthesis of 5

To a three necked 500 ml flask equipped with a thermometer was added **4lb** (9.13 g, 20 mmol, 1 eq.), DMA (200 ml), anhydrous KOAc (azeotroped with toluene prior to use) (7.85 g, 80 mmol, 4 eq.), Pd(*t*-$Bu_3P)_2$ (511.05 mg, 1 mmol, 0.05 eq.). The mixture was heated under argon at 120 °C for 2 h. The mixture was diluted with H_2O (30 ml) to precipitate the product, filtered and the solid was washed with H_2O and ethanol successively. The crude product was dissolved in DCM/MeOH (5 : 1), filtered through celite to remove catalyst residue, then concentrated and re-crystallized from hexane/ethyl acetate to give pure compound **5lb** (5.23 g, 19 mmol, 95% yield).

Phenanthridin-6(5H)-one (5aa). Off-white solid, 129 mg, 66% yield, TLC R_f 0.5 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.69 (s, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 7.6 Hz, 1H), 7.86 (t, J = 7.2 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.8, 136.5, 134.2, 132.8, 129.6, 127.9, 127.5, 125.7, 123.2, 122.6, 122.3, 117.5, 116.1. ESI-HRMS: calculated for $C_{13}H_9NNaO$ $[M + Na]^+$ 218.0576, found 218.0576.

2-Methoxyphenanthridin-6(5H)-one (5ab). Off-white solid, 198 mg, 88% yield, TLC R_f 0.3 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.23 (s, 1H), 8.61 (d, J = 7.6 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.83–7.79 (m, 1H), 7.68–7.62 (m, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.14–7.11 (m, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.3, 154.8, 134.1, 132.5, 130.7, 127.9, 127.5, 125.9, 123.0, 118.3, 117.7, 117.3, 106.2, 55.6; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{11}NNaO_2$ $[M + Na]^+$ 248.0682, found 248.0690.

3-Isopropylphenanthridin-6(5H)-one (5ae-a). Off-white solid, 123 mg 52% yield, TLC R_f 0.5 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.60 (s, 1H), 8.46 (d, J = 8.0 Hz, 1H), 8.31–8.29 (m, 2H), 7.83 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.23 (s, 1H), 7.17 (d, J = 8.4 Hz, 1H), 2.93–3.00 (m, 1H), 1.25 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.9, 150.2, 136.6, 134.3, 132.7, 127.4, 125.3, 123.2, 122.4, 120.9, 115.6, 113.4, 33.3, 23.6; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}NNaO$ $[M + Na]^+$ 260.1046, found 260.1033.

1-Isopropylphenanthridin-6(5H)-one (5ae-b). Off-white solid, 62 mg, 26% yield, TLC R_f 0.5 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.37 (s, 1H), 8.56 (d, J = 7.6 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 6.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 3.98–3.93 (m, 1H), 1.39 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 147.0, 137.2, 134.4, 131.9, 128.8, 127.6, 127.2, 127.0, 121.0, 116.1, 113.8, 30.0, 24.5; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}NNaO$ $[M + Na]^+$ 260.1046, found 260.1046.

Thieno[3,2-*c*]isoquinolin-5(4H)-one (5af). Off-white solid, 169 mg, 84% yield, TLC R_f 0.5 (20 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.01 (s, 1H), 8.27 (d, J = 7.6 Hz, 1H), 7.79–7.75 (m, 3H), 7.54–7.50 (m, 1H), 7.06 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.4, 138.4, 133.1, 133.0, 128.2, 127.7, 126.3, 123.6, 122.4, 117.9, 115.0; HRMS (ESI) *m*/*z* calcd for $C_{11}H_7NNaOS$ $[M + Na]^+$ 224.0141, found 224.0137.

3-*tert*-Butylphenanthridin-6(5H)-one (5aj). Off-white solid, 206 mg, 82% yield, TLC R_f 0.7 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.99 (s, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.20 (d, $J = 8.0$ Hz, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.74–7.69 (m, 1H), 7.54–7.50 (m, 1H), 7.33–7.27 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 153.3, 136.0, 135.0, 132.8, 128.2, 127.4, 125.5, 122.6, 121.9, 120.7, 116.2, 113.4, 35.0, 31.2; HRMS (ESI) m/z calcd for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383, found 252.1395.

6-Oxo-5,6-dihydrophenanthridine-2-carbonitrile (5ci). Brow solid, 88 mg, 40% yield, TLC R_f 0.4 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.07 (s, 1H), 8.98 (d, $J = 1.6$ Hz, 1H), 8.65 (d, $J = 8.0$ Hz, 1H), 8.34–8.32 (m, 1H), 7.93–7.88 (m, 2H), 7.75–7.71 (m, 1H), 7.48 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.9, 139.7, 133.2, 132.9, 132.4, 129.0, 128.6, 127.4, 125.7, 123.2, 119.1, 118.2, 117.1, 104.5; HRMS (ESI) m/z calcd for $C_{14}H_8N_2NaO$ $[M + Na]^+$ 243.0529, found 243.0516.

2-Methoxy-10-methylphenanthridin-6(5H)-one (5db). Grey white solid, 194 mg, 81% yield, TLC R_f 0.4 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.59 (s, 1H), 8.32 (d, $J = 7.6$ Hz, 1H), 7.94 (d, $J = 1.6$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.8$ Hz, 1H), 7.19–7.16 (m, 1H), 3.85 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 153.8, 136.9, 135.1, 133.0, 131.0, 127.5, 127.3, 126.1, 119.4, 117.1, 116.1, 111.3, 55.3, 25.4; HRMS (ESI) m/z calcd for $C_{15}H_{13}NNaO_2$ $[M + Na]^+$ 262.0838, found 262.0842.

2-Methoxy-4,10-dimethylphenanthridin-6(5H)-one (5dc). Off white solid, 220 mg, 87% yield, TLC R_f 0.7 (1 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.77 (s, 1H), 8.51 (d, $J = 7.6$ Hz, 1H), 7.86 (s, 1H), 7.63 (d, $J = 6.8$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 1H), 6.98 (s, 1H), 3.89 (s, 3H), 2.99 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.9, 153.2, 137.1, 135.1, 133.6, 129.2, 127.4, 127.3, 126.1, 125.2, 119.5, 117.6, 109.2, 55.3, 25.6, 18.2; HRMS (ESI) m/z calcd for $C_{16}H_{15}NNaO_2$ $[M + Na]^+$ 276.0995, found 276.1007.

9-Methylthieno[3,2-*c*]isoquinolin-5(4H)-one (5df). Brown solid, 153 mg, 71% yield, TLC R_f 0.7 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.10 (s, 1H), 8.25 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 5.2$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 5.6$ Hz, 1H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.3, 138.2, 134.7, 132.6, 132.1, 128.6, 126.3, 125.6, 124.6, 117.2, 113.9, 22.0; HRMS (ESI) m/z calcd for $C_{12}H_9NNaOS$ $[M + Na]^+$ 238.0297, found 238.0318.

2,7-Dimethoxy-4-methylphenanthridin-6(5H)-one (5ec). Off-white solid, 247 mg, 92% yield, TLC R_f 0.7 (20 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.08 (s, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.73 (t, $J = 8.2$ Hz, 1H), 7.63 (d, $J = 2.4$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 6.99 (d, $J = 2.0$ Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.9, 159.3, 153.9, 137.2, 133.4, 129.7, 125.0, 119.2, 117.8, 114.9, 114.7, 110.8, 104.4, 56.0, 55.5, 17.5; HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_3$ $[M + H]^+$ 270.1125, found 270.1118.

6-Methoxythieno[3,2-*c*]isoquinolin-5(4H)-one (5ef). Brown solid, 141 mg, 61% yield, TLC R_f 0.7 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.63 (s, 1H), 7.73 (d, $J = 5.2$ Hz, 1H), 7.65 (t, $J = 8.2$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.03 (d, $J = 8.4$ Hz, 1H), 6.96 (d, $J = 5.2$ Hz, 1H). 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.3, 160.2, 138.9, 135.6, 134.0, 127.9, 117.5, 114.6, 114.3, 112.5, 108.9, 55.8; HRMS (ESI) m/z calcd for $C_{12}H_9NNaO_2S$ $[M + Na]^+$ 254.0246, found 254.0257.

8-Methoxythieno[3,4-*c*]quinolin-4(5H)-one (5fb). Brown solid, 143 mg, 62% yield, TLC R_f 0.6 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.06 (s, 1H), 8.49–8.47 (m, 2H), 7.66 (d, $J = 2.8$ Hz, 1H), 7.22 (d, $J = 8.8$ Hz, 1H), 7.03–7.00 (m, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.7, 154.7, 136.3, 130.9, 130.2, 129.9, 119.6, 117.3, 117.2, 116.1, 107.5, 55.6; HRMS (ESI) m/z calcd for $C_{12}H_9NNaO_2S$ $[M + Na]^+$ 254.0246, found 254.0246.

8-Methoxy-6-methylthieno[3,4-*c*]quinolin-4(5H)-one (5fc). Brown solid, 142 mg, 58% yield, TLC R_f 0.7 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.08 (s, 1H), 8.52 (d, $J = 2.0$ Hz, 1H), 8.47 (s, 1H), 7.52 (s, 1H), 6.89 (s, 1H), 3.82 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.1, 154.3, 136.6, 130.7, 130.0, 128.5, 125.8, 119.7, 117.5, 117.3, 105.3, 55.4, 17.9; HRMS (ESI) m/z calcd for $C_{13}H_{11}NNaO_2S$ $[M + Na]^+$ 268.0403, found 268.0398.

4-Chloro-7-fluoro-2-methoxyphenanthridin-6(5H)-one (5hd). Light grey solid, 247 mg, 89% yield, TLC R_f 0.5 (1 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.50 (s, 1H), 8.43 (d, $J = 8.0$ Hz, 1H), 7.89–7.85 (m, 2H), 7.45 (dd, $J = 11.6$, 8.4 Hz, 1H), 7.36 (d, $J = 2.0$ Hz, 1H); 3.89 (s. 3H); ^{13}C NMR was not obtained due to low solubility; HRMS (ESI) m/z calcd for $C_{14}H_9ClFNNaO_2$ $[M + Na]^+$ 300.0198, found 300.0208.

Dithieno[3,2-*b*:3′,2′-*d*]pyridin-5(4H)-one (5if). Brown solid, 176 mg, 85% yield, TLC R_f 0.6 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.23 (s, 1H), 8.17 (d, $J = 4.0$ Hz, 1H), 7.79 (d, $J = 4.8$ Hz, 1H), 7.61 (d, $J = 4.4$ Hz, 1H), 7.11 (d, $J = 4.4$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.0, 139.9, 135.3, 127.5, 127.1, 122.6, 117.4, 113.3; HRMS (ESI) m/z calcd for $C_9H_5NNaOS_2$ $[M + Na]^+$ 229.9705, found 229.9718.

8-Methyl-6-oxo-5,6-dihydrophenanthridine-4-carbonitrile (5jh). Brown solid, 87 mg, 37% yield, TLC R_f 0.6 (20 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.42 (d, $J = 8.0$ Hz, 1H), 8.36 (s, 1H), 8.18 (d, $J = 8.0$ Hz, 1H), 7.75–7.68 (m, 2H), 7.36 (t, $J = 7.8$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR was not obtained due to low solubility; HRMS (ESI) m/z calcd for $C_{15}H_{10}N_2NaO$ $[M + Na]^+$ 257.0685, found 257.0696.

8-Methoxy-6-methylthieno[3,2-*c*]quinolin-4(5H)-one (5kc). Brown solid, 204 mg, 83% yield, TLC R_f 0.7 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.73 (s, 1H), 7.78 (d, $J = 5.6$ Hz, 1H), 7.60 (d, $J = 5.2$ Hz, 1H), 7.11 (d, $J = 2.4$ Hz, 1H), 7.01 (d, $J = 2.0$ Hz, 1H), 3.83 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.1, 154.1, 145.8, 131.1, 129.0, 126.7, 126.4, 125.3, 119.3, 116.8, 103.1, 55.4, 17.8; HRMS (ESI) m/z calcd for $C_{13}H_{11}NNaO_2S$ $[M + Na]^+$ 268.0403, found 268.0411.

Dithieno[3,2-*b*:2′,3′-d]pyridin-5(4H)-one (5kf). Brown solid, 174 mg, 84% yield, TLC R_f 0.6 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.15 (s, 1H), 7.79 (d, $J = 5.2$ Hz, 1H), 7.62 (d, $J = 5.2$ Hz, 1H), 7.54 (d, $J = 4.8$ Hz, 1H), 7.09 (d, $J = 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.4, 142.1, 139.4, 128.5, 127.6, 125.3, 124.1, 117.6, 112.2; HRMS (ESI) m/z calcd for $C_9H_6NOS_2$ $[M + H]^+$ 207.9885, found 207.9880.

6-Chlorothieno[3,2-*c*]quinolin-4(5H)-one (5kg). Brown solid, 167 mg, 71% yield, TLC R_f 0.6 (20 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.91 (s, 1H), 7.88–7.86 (m, 2H), 7.66–7.63 (m, 2H), 7.27 (t, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.9, 145.3, 132.5, 131.5, 129.4, 128.0, 125.3, 123.1, 122.6, 119.3, 117.9. ESI-HRMS: calculated for $C_{11}H_6ClNNaOS$ [M + Na]$^+$ 257.9751, found 257.9739.

2-Methoxybenzo[*k*]phenanthridin-6(5H)-one (5lb). Off-white solid, 250 mg, 91% yield, TLC R_f 0.5 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.85 (s, 1H), 9.01 (d, J = 7.2 Hz, 1H), 8.33 (d, J = 8.8 Hz, 1H), 8.17–8.08 (m, 3H), 7.80–7.78 (m, 2H), 7.47 (d, J = 8.8 Hz, 1H), 7.28–7.25 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 154.2, 135.7, 132.5, 131.5, 129.0, 128.6, 128.4, 128.1, 127.4, 126.9, 124.9, 122.9, 118.1, 117.4, 117.2, 111.1, 55.5; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{14}NO_2$ [M + H]$^+$ 276.1019, found 276.1028.

Benzo[f]thieno[3,2-*c*]isoquinolin-5(4H)-one (5lf). Brown solid, 229 mg, 91% yield, TLC R_f 0.7 (20 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.55 (s, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.04–8.01 (m, 2H), 7.90 (t, J = 7.4 Hz, 1H), 7.83 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.2, 140.1, 135.1, 131.8, 129.4, 129.2, 128.4, 127.6, 127.1, 126.8, 125.5, 124.1, 122.1, 117.4, 112.8; HRMS (ESI) *m*/*z* calcd for $C_{15}H_9NNaO$ [M + Na]$^+$ 274.0297, found 274.0314.

4-Chlorobenzo[k]phenanthridin-6(5H)-one (5lg). Grey solid, 210 mg, 75% yield, TLC R_f 0.4 (2 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.08 (s, 1H), 8.89–8.87 (m, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.20–8.15 (m, 2H), 7.83–7.74 (m, 3H), 7.38 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.2, 131.3, 128.2, 127.7, 124.3, 123.9, 123.7, 123.1, 122.2, 122.0, 121.9, 119.6, 118.0, 117.0, 115.1, 114.9, 113.6; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{11}ClNO$ [M + H]$^+$ 276.1019, found 276.1026.

2,8-Dimethoxyphenanthridin-6(5H)-one (5mb). Light yellow solid, 174 mg, 68% yield, TLC R_f 0.4 (1 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.58 (s, 1H), 8.49 (d, J = 9.2 Hz, 1H), 7.80–7.76 (m, 2H), 7.45–7.42 (m, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.08 (dd, J = 8.8, 2.8 Hz, 1H), 3.92 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.1, 159.0, 154.9, 129.6, 127.5, 127.3, 124.9, 121.3, 118.5, 117.1, 116.5, 108.7, 105.7, 55.6, 55.4; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}NNaO_3$ [M + Na]$^+$ 278.0788, found 278.0797.

2,8-Dimethoxy-4-methylphenanthridin-6(5H)-one (5mc). Light yellow solid, 180 mg, 67% yield, TLC R_f 0.5 (1 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.66 (s, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 2.8 Hz, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.31 (dd, J = 8.8, 2.8 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.5, 159.0, 154.3, 128.0, 127.8, 127.0, 125.7, 125.2, 121.7, 118.5, 117.9, 108.4, 103.5, 55.5, 17.7; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}NNaO_3$ [M + Na]$^+$ 292.0944, found 292.0954.

2-Isopropyl-8-methoxyphenanthridin-6(5H)-one (5mk). Off-white solid, 120 mg, 45% yield, TLC R_f 0.6 (1 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, CDCl$_3$): δ 11.16 (s, 1H), 8.27 (d, J = 9.2 Hz, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.99 (s, 1H), 7.42–7.35 (m, 3H), 4.02 (s, 3H), 3.10–3.03 (m, 1H), 1.36 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.3, 143.5, 133.1, 128.6, 127.0, 123.8, 122.6, 119.6, 118.5, 116.7, 108.7, 55.7, 34.1, 24.3; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{17}NNaO_2$ [M + Na]$^+$ 290.1151, found 290.1147.

3-*tert*-Butyl-10-methylphenanthridin-6(5H)-one (5nj). Off-white solid, 207 mg, 78% yield, TLC R_f 0.7 (1 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.58 (s, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 7.2 Hz, 1H), 7.69 (d, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 1.6 Hz, 1H), 7.32 (dd, J = 8.8, 2.0 Hz, 1H), 2.92 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.0, 151.5, 136.9, 136.8, 134.9, 133.2, 127.1, 126.8, 126.0, 119.3, 116.4, 112.7, 34.4, 30.8, 25.5; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{19}NNaO$ [M + Na]$^+$ 288.1359, found 288.1370.

8-Methoxythieno[3,2-*c*]quinolin-4(5H)-one (5ob). Brown solid, 123 mg, 53% yield, TLC R_f 0.7 (10 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.63 (s, 1H), 7.79 (d, J = 5.2 Hz, 1H), 7.58 (d, J = 5.2 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 2.4 Hz, 1H), 7.14 (dd, J = 8.8, 2.8 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.7, 154.6, 145.1, 131.4, 130.4, 126.7, 125.3, 118.2, 117.6, 116.8, 105.2, 55.6; HRMS (ESI) *m*/*z* calcd for $C_{12}H_9NNaO_2S$ [M + Na]$^+$ 254.0246, found 254.0252.

8-Isopropylthieno[3,2-*c*]quinolin-4(5H)-one (5ok). Brown solid, 124 mg, 51% yield, TLC R_f 0.5 (20 : 1, DCM : MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.67 (s, 1H), 7.77 (d, J = 5.2 Hz, 1H), 7.63 (d, J = 2.8 Hz, 1H), 7.58 (d, J = 5.2 Hz, 1H), 7.42–7.35 (m, 2H), 3.04–2.97 (m, 1H), 1.26 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.1, 145.6, 142.7, 134.4, 131.1, 127.9, 126.4, 125.3, 120.3, 116.3, 116.1, 32.9, 23.9; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{13}NNaOS$ [M + Na]$^+$ 266.0610, found 266.0641.

4-Fluoro-7-methoxyphenanthridin-6(5H)-one (5pl). Light yellow solid, 93 mg, 38% yield, TLC R_f 0.5 (1 : 1, petroleum ether : EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.12 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 8.2 Hz, 1H), 7.38–7.34 (m, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.20–7.15 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.0, 159.0, 150.0, 147.6, 136.4, 133.9, 125.8, 125.7, 121.4, 121.3, 119.5, 114.9, 114.8, 114.7, 111.5, 56.0; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}FNNaO_2$ [M + Na]$^+$ 266.0588, found 266.0599.

Conflicts of interest

There are no conflicts of interest to declare.

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