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Metal Oxidant Free Cobalt Catalyzed C(sp^2)−H Carbonylation of *ortho*-Arylanilines: An Approach Towards Free (*NH*)-Phenanthridinones

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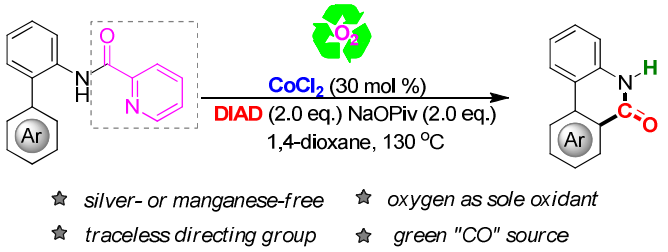


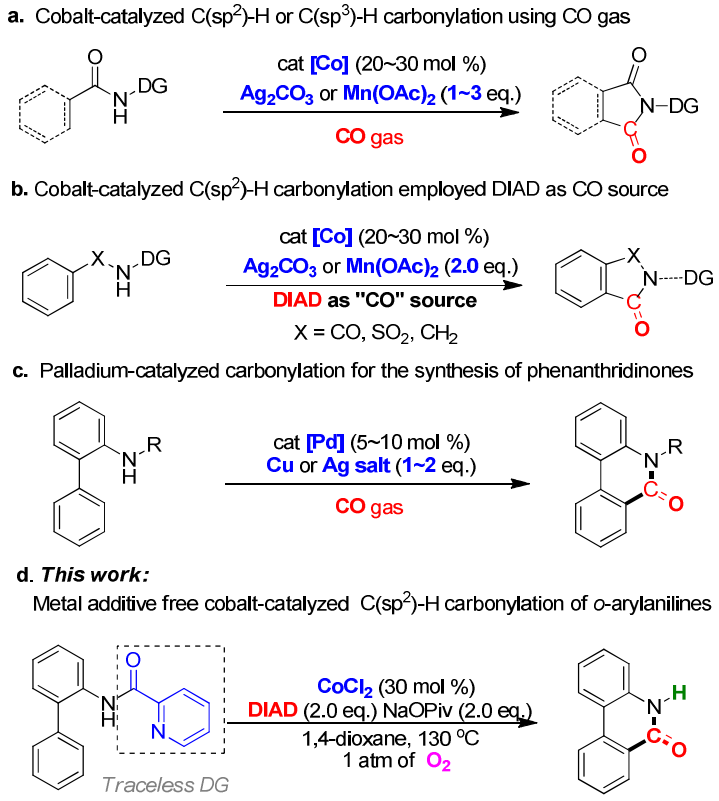
ABSTRACT: A traceless directing group assisted Co-catalyzed C(sp^2)−H carbonylation of *ortho*-arylanilines for the synthesis of free (*NH*)-phenanthridinones in metal based oxidant free fashion was accomplished. This protocol employs diisopropyl azodicarboxylate as CO source and oxygen as the sole oxidant, and provides good yields with various functional tolerance. The methodology has been applied for the total synthesis of PARP inhibitor **PJ-34**. Furthermore, the kinetic isotopic effect experiments reveal the C−H bond cleavage probably occurred in the rate-determining step.

INTRODUCTION:

Transition metal catalyzed carbonylation of inert C(sp^2)−H and C(sp^3)−H bonds represents as a powerful tool for the access of carbonyl-containing compounds, which are widely found in organic and medicinal chemistry.[1] Among these reactions, earth-abundant cobalt catalyzed C−H carbonylation has attracted considerable interest in recent years, owing to its cheap cost and environmentally benign.[2] In this area, pioneered by the studies of Murahashi,[2b] Daugulis and co-wokers,[2c] recent advances have remarkably uncovered the high reactivity and regioselectivity of directing group assisted Co-catalyzed C−H carbonylation reactions for the construction of versatile cyclic amides (Scheme 1a). However, the use of toxic and unsafe CO gas and stoichiometric amount of environmental unfriendly metal oxidant limited their further expansions. A greener process has been achieved by Zhang's group, who firstly employed azodicarboxylate as stoichiometric

carbonyl source instead of CO gas in the Co-catalyzed C(sp^2)−H carbonylation of benzamides, although two equivalents of silver additives still has been used as oxidant (Scheme 1b).[2g] Similarly, Daugulis and co-wokers have developed Co-catalyzed C(sp^2)−H carbonylation of sulfonamide in the presence of diisopropyl azodicarboxylate (DIAD) and stoichiometric $Mn(OAc)_2$.[2h] Very recently, our group disclosed a work of traceless directing group assisted Co-catalyzed C(sp^2)−H carbonylation of benzylamines using diethyl azodicarboxylate (DEAD) as a CO source.[2i] Despite the great success that have been achieved, these transformations still needed stoichiometric amount of metal oxidants to reoxidate Co(I) or Co(II) species to Co(III) species. Thereby, the development of practical and environmentally friendly methodologies in metal based oxidant free fashion for the cobalt catalyzed carbonylation reactions has remained elusive, but highly desirable.

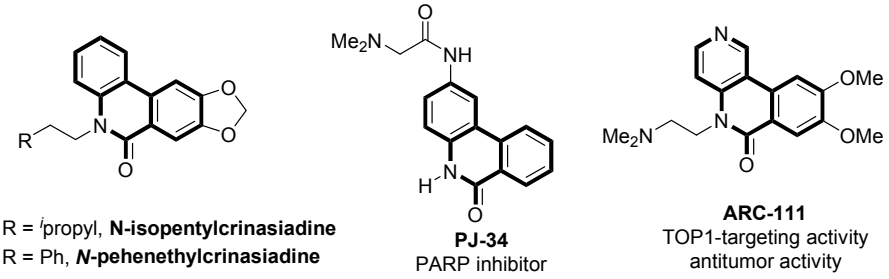
Scheme 1. Selected examples of Co- or Pd-catalyzed C−H carbonylation.



Phenanthridinone is a significant scaffold widely found in biologically active alkaloid natural products[3] and pharmaceuticals (Figure 1) that present broad range of potent biological activities, such as antitumor,[4] anti-HIV,[5] and antileukemic[6]. For example, PJ-34 is demonstrated as a cell-permeable PARP inhibitor.[7] while ARC-111 exhibits TOP1-targeting activity and pronounced antitumor activity.[8] Therefore, synthetic approaches towards penanthridinone derivatives have been intensively pursued during the past decades.[9] In this context,

the Pd-catalyzed carbonylation of *ortho*-arylanilines via C−H bond activation provides more atom-economic and straightforward method to access these compounds (Scheme 1c).[10] In 2013, Chuang,[10a] Zhang,[10b] and Zhu's group,[10c] independently described palladium catalyzed C−H carbonylation of *ortho*-arylaniline using CO as carbonyl source in the presence of copper or silver salts for the preparation of phenanthridinones. Despite its high efficiency, its further expansion is limited by the need for noble metal catalyst, metal oxidant and toxic CO gas. Thus, devising much greener synthetic routes for phenanthridinones though C−H bond activation is urgently-needed. Inspired by our previous work and as our continuing interest in pursuing the green synthetic methodologies for natural products, we report here a protocol of metal based oxidant free Co-catalyzed C(sp^2)−H carbonylation using O_2 as the sole oxidant and DIAD as the CO source, to produce a variety of free (*NH*)-phenanthridinones (Scheme 1d).

Figure 1 Phenanthridinone-Containing Natural Products and Drugs

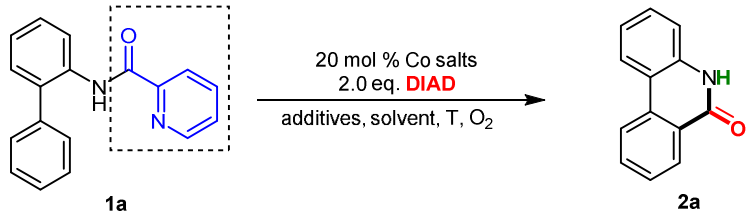


RESULT AND DISCUSSION

At the outset, we used *o*-phenylaniline (**1a**) as a starting material to react with DIAD in the presence of $Co(OAc)_2$•$4H_2O$ and PivOH in TFE (trifluoroethanol) at 130 °C under 1 atm of O_2 for 24 h. Fortunately, the expected phenanthridinone (**2a**) was obtained in 35% isolated yield, albeit in low yield (Table 1, entry 1). Next, a set of cobalt salts were screened, and $CoCl_2$ turned out to be the optimal, while high valent $Co(acac)_3$ only afforded **2a** in 32% yield (Table 1, entries 1~4). In addition, the exploration of reaction solvents indicated that the solvents had a little influence on yield, and 1,4-dioxane gave the best result (Table 1, entries 5~7). It was noteworthy that majority of basic additives delivered relatively higher yield than acidic additives, and NaOPiv was found to the best additive to produce **2a** in 67% yield (Table 1, entries 8~11). Furthermore, changing the temperature did not improve the yield (Table 1, entries 12 and 13). Gratifyingly, increasing the catalyst loading to 30 mol% dramatically promoted the reaction to access **2a** in up-to 97% yield (Table 1, entry 14). In contrast,

no desired product was detected in the absence of Co catalyst, and a sharp decrease in yield was observed when the reaction was carried out under air or N_2 atmosphere or catalytic amount (50 mol %) of NaOPiv (entries 15~18). These blank tests clearly indicated that Co catalyst, O_2 and stoichiometric amount of NaOPiv are required for this reaction.

Table 1. Optimization of Reaction Conditions[a]



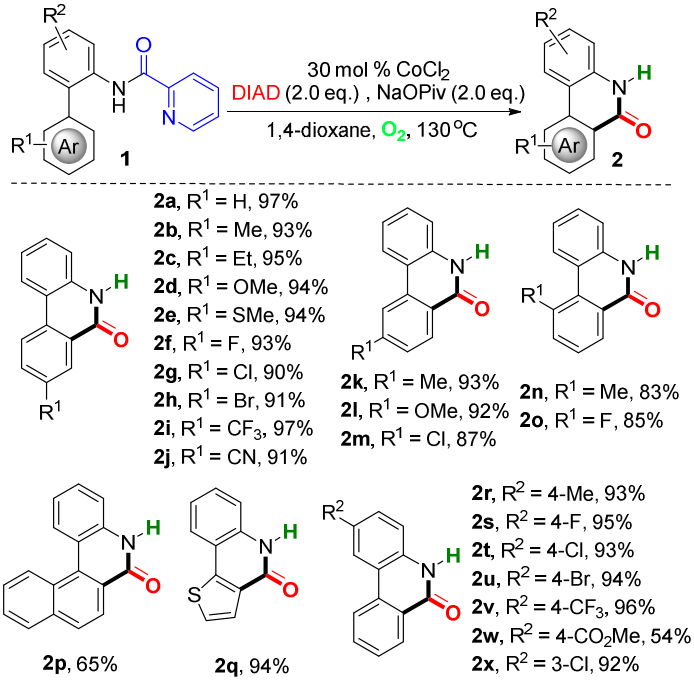
Entry	Cat.	Additive	Solvent	T (□)	Yield (%)
1	$Co(OAc)_2•4H_2O$	PivOH	TFE	130	35
2	$CoCl_2$	PivOH	TFE	130	41
3	$Co(acac)_2$	PivOH	TFE	130	30
4	$Co(acac)_3$	PivOH	TFE	130	32
5	$CoCl_2$	PivOH	DCE	130	35
6	$CoCl_2$	PivOH	1,4-dioxane	130	45
7	$CoCl_2$	PivOH	HFIP	130	37
8	$CoCl_2$	HOAc	1,4-dioxane	130	21
9	$CoCl_2$	$PhCO_2Na$	1,4-dioxane	130	50
10	$CoCl_2$	NaOPiv	1,4-dioxane	130	67
11	$CoCl_2$	KOPiv	1,4-dioxane	130	47
12	$CoCl_2$	NaOPiv	1,4-dioxane	120	51
13	$CoCl_2$	NaOPiv	1,4-dioxane	140	63
14[b]	***$CoCl_2$***	***NaOPiv***	***1,4-dioxane***	130	***97***
15	-	NaOPiv	1,4-dioxane	130	0
16[c]	$CoCl_2$	NaOPiv	1,4-dioxane	130	46
17[d]	$CoCl_2$	NaOPiv	1,4-dioxane	130	14
18[e]	$CoCl_2$	NaOPiv	1,4-dioxane	130	54

[a]Reactions conditions:**1a** (0.4 mmol), Co catalyst (0.08 mmol), DIAD (0.8 mmol), and additive (0.8 mmol) in solvent (4 mL) at 130 □ for 24 h under oxygen atmosphere. [b]Co catalyst (0.12 mmol). [c]Under air. [d]Under N_2. [e]NaOPiv (0.2 mmol).

After identifying the optimum reaction conditions, we next set out to determine the versatility of this reaction system in the carbonylation reaction of various *o*-arylanilines. Upon experimentation, it was found that this developed synthetic methodology offered a broad scope with respect to the selected substrates and it was quite tolerant to a variety of functional groups (Scheme 2). For example, *o*-arylanilines with both electron-withdrawing substituents (**2b**-**2e**) and electron-withdrawing substituents (**2f**-**2j**) on the para position of

the non-aniline rings were well tolerated, leading to the corresponding products in 90−97% yield. In addition, the reaction conditions were compatible with Br and Cl, which are convenient handles for further functionalization (**2h** and **2g**). Besides, methylthio group could also be used in this reaction to give **2e** in excellent yield. It was noteworthy that the current protocol was regioselective for meta substituted substrates where two unsymmetrical C–H bonds could be carbonylated. Only one product generated from carbonylation of the less sterically hindered C–H bond was isolated (**2k**-**2m**). However, the reactions were less efficient for *ortho*-substituted substrates to yield **2n** and **2o** in moderate yields, due to steric effects. Pleasingly, other aromatic rings such as naphthyl ring and thienyl ring, were also tolerated, delivering the expected products **2p** and **2q** in 65% and 94% yields, respectively. On the other hand, the substrate scope with respect to the substituents on the aniline ring was studied. The electronic effect had no influence on the reaction yield, and the desired products were achieved in 92–96% yield. An exception was found when *o*-phenylaniline **1w** bearing ester group was used as substrate, leading to the corresponding product **2w** in moderate yield.

Scheme 2. Substrate Scopes of *o*-Arylanilines 1.[a]

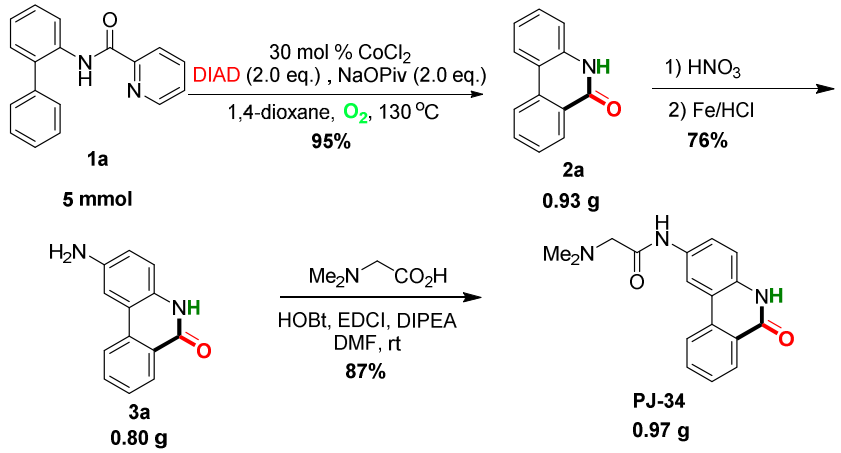


[a]Conditions: **1** (0.4 mmol), $CoCl_2$ (0.12 mmol), DIAD (0.8 mmol), and NaOPiv (0.8 mmol) in 1,4-dioxane (4 mL) at 130 □ for 24 h under 1 atm of O_2.

To demonstrate the scalability and utility of this method, we applied it in the formal synthesis of PARP

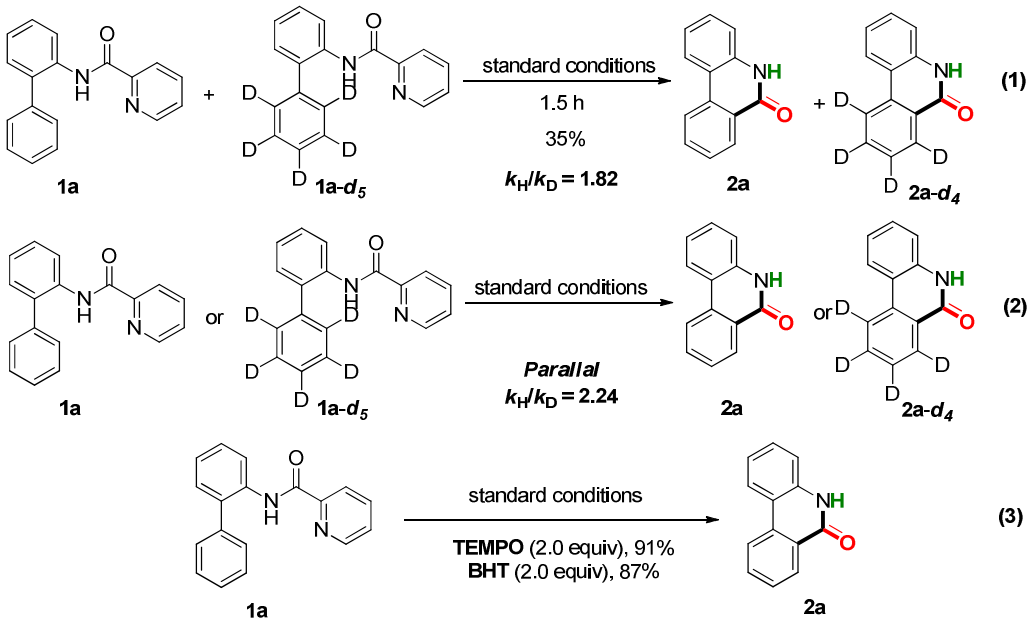
inhibitor **PJ-34** on a gram scale (Scheme 3). The reaction was conducted with 5 mmol scale of **1a** to afford phenanthridin-6(5*H*)-one (**2a**) in 0.93 g, 95% yield. Next, the regioselective nitration of **2a**, followed by reduction of the nitro group to amine group, resulted in the formation of **3a** in 76% yield over two steps. Finally, using EDCI and HOBt as condensing agents, the *N*-acylation of **3a** and *N*,*N*-dimethylglycine underwent smoothly, forming the desired **PJ-34** in 87% yield.

Scheme 3. Total Synthesis of PARP Inhibitor PJ-34.



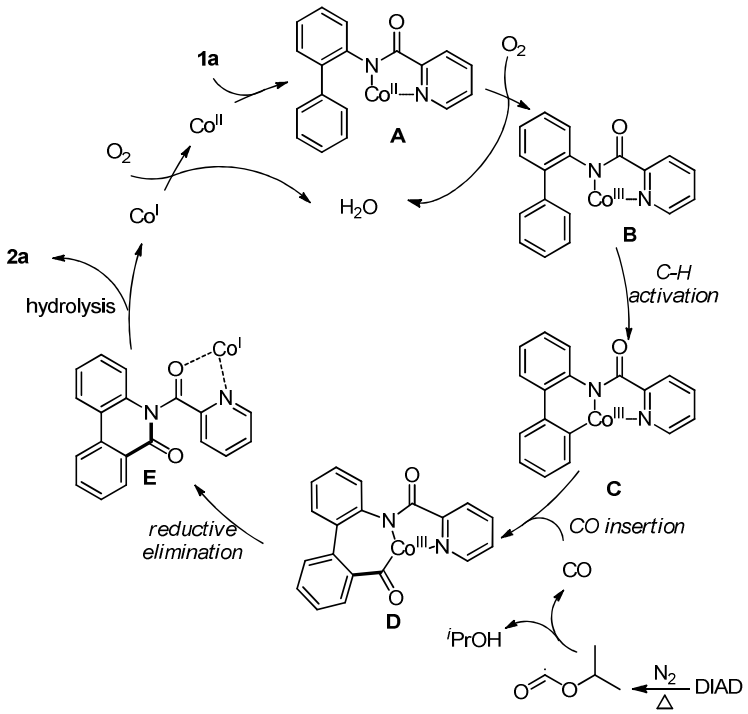
To gain insights into the reaction mechanism, several control experiments were performed. Firstly, the intermolecular competition experiment (Scheme 4, eq 1) gave a kinetic isotope effect (KIE) of k_H/k_D = 1.72, while the k_H/k_D value of 2.24 was obtained by two parallel reactions (Scheme 4, eq 2) using substrates **1a** and **1a-*d5***. These KIE experiments indicated that the C−H bond cleavage probably occurred in the rate-determining step. Secondly, we found that radical scavengers, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-tert-butyl-4-methylphenol (BHT), had little influence on the reaction outcomes, indicating that the alkoxycarbonyl radical, generated from DIAD, might not severe as the active carbonylation species in our C−H carbonylation reaction (Scheme 4, eq 3).

Scheme 4. Control Experiments.



Based on the control experiments and the literature reports on Co catalysis,[2] a plausible reaction mechanism for the cobalt-catalyzed C−H carbonylation is depicted in Scheme 5 with **1a** as the model substrates. The reaction is believed to be initiated by the coordination of Co(II) with benzylpicolinamide (**1a**) to give intermediate **A**, which is then oxidized by oxygen to form a substrate coordinate Co(III) complex **B**. Subsequently, C(sp^2)−H bond activation of *ortho*-phenyl group takes place to generated a cyclic Co(III) complex **C**. In addition, thermal decomposition of DIAD releases the CO gas,[11] which then inserts into the C−Co bond of the complex **C** to afford a cyclic acyl Co(III) species **D.** The reductive elimination of species **D** results in the formation of intermediate **E** and generates Co(I) species. Subsequently hydrolysis of intermediate **E** leads to the expected product **2a** along with the release of picolinic acid derivative, might due to the activation of the amide group by the coordination of Co(I) species with intermediate **E** via *N*,*O*-coordination.[12] Notably, the attempts of recovery of directing group are failed, because picolinic acid is decomposed under standard conditions. The released Co(I) species are reoxidized to active Co(II) species by oxygen to complete the catalytic cycle.

Scheme 5. Plausible Reaction Mechanism



CONCLUSION

In summary, we have developed a metal based oxidant free and highly efficient strategy for the C(sp^2)−H bond carbonylation of *ortho*-arylanilines to synthesize free (*NH*)-Phenanthridinones by using earth-abundant and inexpensive $CoCl_2$ as the catalyst, the commercially available azodicarboxylates as the environmentally benign carbonyl source and oxygen as the sole oxidant. This protocol features a wide substrate scope and various functional group tolerances, thereby providing a facile and efficient method for the formal synthesis of PARP inhibitor **PJ-34**. To the best of our knowledge, the current approach represents the first example of metal based oxidant free cobalt-catalyzed C−H bond carbonylation. Further researches based on this novel approach are currently going on in our laboratory.

EXPERIMENTAL SECTION

General information: All commercial materials were used as received unless otherwise noted. Commercially available chemicals were obtained from Energy Chemical, TCI, Alfa Aesar, J&K. ^{1}H NMR spectra were recorded at 400 MHz, 500 MHz, and 600 MHz using TMS as internal standard, ^{13}C NMR spectra were recorded at 100 MHz, 125 MHz, and 150 MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

General Procedure for the Preparation of Starting Materials 1a. To a stirred solution of phenylboronic acid (0.73 g, 6.00 mmol) in EtOH (30 mL) was added 2-iodoaniline (1.10 g, 5.00 mmol), K_3PO_4 (2.65 g, 12.50 mmol), $Pd(PPh_3)_4$ (0.29 g, 0.25mmol). The reaction was stirred at a reflux for 24 h under argon atmosphere before EtOH was removed by rotary evaporation. The crude product [1,1'-biphenyl]-2-amine was used directly in the next step without further purification.

The crude product [1,1'-biphenyl]-2-amine was dissolved in 8 mL of anhydrous DMF, 2-picolinic acid (740 mg, 6 mmol) was added, followed by addition of EDCI (1.16 g, 6 mmol), HOBt (920 mg, 6 mmol) and DIPEA (2.2 mL, 12.5 mmol). The mixture was stirred at rt for 3 h. The mixture was quenched with water, and extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash chromatography (n-hexane/EtOAc:30:1) to give the desired product **1a**.

*N-([1,1'-Biphenyl]-2-yl)picolinamide (**1a**)*: R_f 0.28 (hexane/EtOAc = 30/1). White solid, 82% yield, m.p. 96-97 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.31 (s, 1H), 8.65 – 8.63 (m, 1H), 8.36 (d, *J* = 4.2 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.51 – 7.46 (m, 4H), 7.44 – 7.42 (m, 2H), 7.37 – 7.35 (m, 1H), 7.33 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.22 – 7.20 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 150.0, 147.9, 138.2, 137.5, 134.9, 132.6, 130.2, 129.5, 128.9, 128.4, 127.8, 126.1, 124.3, 122.3, 120.7. **HRMS-ESI**: calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$: 275.1179; Found: 275.1177.

*N-(4'-Methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1b**)*: R_f 0.30 (hexane/EtOAc = 30/1). White solid, 68% yield, m.p. 107-108 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.34 (s, 1H), 8.64 (dd, *J* = 8.4, 4.8 Hz, 1H), 8.40 (d, *J* = 4.8 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.43 – 7.40 (m, 1H), 7.38 – 7.36 (m, 3H), 7.32 – 7.30 (m, 3H), 7.21 – 7.19 (m, 1H), 2.44 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 150.1, 148.0, 137.5, 137.5, 135.2, 134.9, 132.6, 130.4, 129.6, 129.4, 128.2, 126.1, 124.3, 122.3, 120.7, 21.33. **HRMS-ESI**: calcd for $C_{19}H_{17}N_2O$ $[M + H]^+$: 289.1335; Found: 289.1330.

*N-(4'-Ethyl-[1,1'-biphenyl]-2-yl)picolinamide (**1c**)*: R_f 0.27 (hexane/EtOAc = 30/1). White solid, 65% yield, m.p. 77-78 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.33 (s, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 4.2 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.42 – 7.35 (m, 4H), 7.33 – 7.31 (m, 3H), 7.21 – 7.19 (m, 1H), 2.76 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.8 Hz, 3H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 161.9, 150.1, 147.9, 143.9, 137.5, 135.4, 134.9, 132.6, 130.2, 129.5, 128.4, 128.2, 126.1, 124.2, 122.3, 120.6, 28.70, 15.71. **HRMS-ESI**: calcd for $C_{20}H_{19}N_2O$ $[M + H]^+$: 303.1492; Found: 303.1496.

*N-(4'-Methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1d**)*: R_f 0.28 (hexane/EtOAc = 30/1). White solid, 69%

yield, m.p. 103-104 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 10.31 (s, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 4.5 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.42 – 7.36 (m, 4H), 7.31 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.04 – 7.01 (m, 2H), 3.88 (s, 3H). **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, ppm) δ 161.9, 159.2, 149.9, 147.9, 137.4, 134.8, 132.2, 130.6, 130.3, 130.3, 128.0, 126.1, 124.1, 122.1, 120.6, 114.3, 55.28. **HRMS-ESI**: calcd for $C_{19}H_{17}N_2O_2$ $[M + H]^+$: 305.1285; Found: 305.1286.

*N-(4'-(Methylthio)-[1,1'-biphenyl]-2-yl)picolinamide (**1e**)*: R_f 0.24 (hexane/EtOAc = 30/1). White solid, 69% yield, m.p. 108-109 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 10.28 (s, 1H), 8.62 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 4.5 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.44 – 7.36 (m, 6H), 7.30 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.22 – 7.19 (m, 1H), 2.55 (s, 3H). **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, ppm) δ 162.0, 149.9, 148.0, 138.3, 137.5, 134.8, 132.0, 130.2, 129.9, 128.4, 126.8, 126.2, 124.3, 122.2, 120.9, 15.7. **HRMS-ESI**: calcd for $C_{19}H_{17}N_2OS$ $[M + H]^+$: 321.1056; Found: 321.1061.

*N-(4'-Fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1f**)*: R_f 0.29 (hexane/EtOAc = 30/1). White solid, 65% yield, m.p. 110-111 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 10.22 (s, 1H), 8.62 (dd, J = 9.0, 0.5 Hz, 1H), 8.39 (d, J = 4.0 Hz, 1H), 8.26 (d, J = 7.5 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.45 – 7.40 (m, 3H), 7.40 – 7.37 (m, 1H), 7.29 (dd, J = 7.5, 1.5 Hz, 1H), 7.22 – 7.16 (m, 3H). **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, ppm) δ 163.4 ($J_{C\text{-}F}$ = 245.6 Hz), 161.9, 149.8, 147.9, 137.5, 134.8, 134.1 ($J_{C\text{-}F}$ = 3.3 Hz), 131.5, 131.3 ($J_{C\text{-}F}$ = 8.1 Hz), 131.2, 130.2, 128.6, 126.2, 124.3, 122.2, 120.8, 115.9 ($J_{C\text{-}F}$ = 21.4 Hz). **HRMS-ESI**: calcd for $C_{18}H_{14}FN_2O$ $[M + H]^+$: 293.1085; Found: 293.1085.

*N-(4'-Chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1g**)*: R_f 0.21 (hexane/EtOAc = 30/1). White solid, 67% yield, m.p. 145-146 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.22 (s, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 4.8 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.47 – 7.43 (m, 3H), 7.41 – 7.39 (m, 3H), 7.30 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.23 – 7.20 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 149.8, 148.0, 137.6, 136.7, 134.7, 133.9, 131.5, 130.9, 130.2, 129.1, 128.8, 126.3, 124.5, 122.3, 121.1. **HRMS-ESI**: calcd for $C_{18}H_{14}ClN_2O$ $[M + H]^+$: 309.0789; Found: 309.0779.

*N-(4'-Bromo-[1,1'-biphenyl]-2-yl)picolinamide (**1h**)*: R_f 0.30 (hexane/EtOAc = 30/1). White solid, 69% yield, m.p. 144-145 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.20 (s, 1H), 8.59 (d, *J* = 7.8 Hz, 1H), 8.42 (d, *J* = 4.8 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.62 – 7.60 (m, 2H), 7.45 – 7.42 (m, 1H), 7.41 – 7.39 (m, 1H), 7.35 – 7.33 (m, 2H), 7.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.22 – 7.19 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 149.8, 148.1, 137.6, 137.2, 134.7, 132.1, 131.5, 131.2, 130.1, 128.8, 126.3, 124.5, 122.3, 122.1, 121.2. **HRMS-ESI**: calcd for $C_{18}H_{14}BrN_2O$ $[M + H]^+$: 353.0284; Found: 353.0268.

*N-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)picolinamide (**1i**)*: R_f 0.28 (hexane/EtOAc = 30/1). White solid,

66% yield, m.p. 128-129 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 10.19 (s, 1H), 8.61 – 8.59 (m, 1H), 8.36 – 8.35 (m, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.46 (m, 1H), 7.41 – 7.38 (m, 1H), 7.33 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.26 – 7.23 (m, 1H). **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, ppm) δ 162.0, 149.7, 148.0, 142.0, 137.6, 134.7, 131.3, 130.3 (J_{C-F} = 32.5 Hz), 130.0, 129.9, 129.2, 127.4 (J_{C-F} = 270.4 Hz), 126.3, 125.8 (J_{C-F} = 3.6 Hz), 124.5, 122.3, 121.2. **HRMS-ESI**: calcd for $C_{19}H_{14}F_3N_2O$ [M + H]$^+$: 343.1053; Found: 343.1048.

*N-(4'-Cyano-[1,1'-biphenyl]-2-yl)picolinamide (**1j**)*: R_f 0.26 (hexane/EtOAc = 30/1). White solid, 65% yield, m.p. 157-158 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.13 (s, 1H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.41 (d, *J* = 4.2 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.44 – 7.42 (m, 1H), 7.31 – 7.30 (m, 1H), 7.27 – 7.24(m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 149.6, 148.1, 143.2, 137.7, 134.6, 132.7, 131.0, 130.3, 130.0, 129.6, 126.5, 124.8, 122.4, 121.6, 118.8, 111.6. **HRMS-ESI**: calcd for $C_{19}H_{14}N_3O$ [M + H]$^+$: 300.1131; Found: 300.1129.

*N-(3'-Methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1k**)*: R_f 0.29 (hexane/EtOAc = 30/1). White solid, 62% yield, m.p. 95-96 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.43 (s, 1H), 8.70 – 8.66 (m, 1H), 8.39 (d, *J* = 4.2 Hz, 1H), 8.27 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.36 (m, 2H), 7.35 – 7.32 (m, 2H), 7.28 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 2.43 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.o, 150.1, 147.9, 138.6, 138.0, 137.5, 134.9, 132.5, 130.2, 130.2, 128.9, 128.5, 128.4, 126.6, 126.2, 124.2, 122.3, 120.5, 21.52. **HRMS-ESI**: calcd for $C_{19}H_{17}N_2O$ [M + H]$^+$: 289.1335; Found: 289.1328.

*N-(3'-Methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1l**)*: R_f 0.28 (hexane/EtOAc = 30/1). Yellow solid, 64% yield, m.p. 90-91 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.41 (s, 1H), 8.68 (d, *J* = 7.8 Hz, 1H), 8.39 (d, *J* = 4.8 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.45 – 7.37 (m, 3H), 7.35 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.22 - 7.19 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.02 – 7.01 (m, 1H), 7.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.82 (s, 3H),. **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 159.9, 150.1, 147.9, 139.5, 137.5, 134.9, 132.3, 130.1, 130.0, 128.5, 126.2, 124.2, 122.3, 121.9, 120.6, 114.4, 114.1, 55.30. **HRMS-ESI**: calcd for $C_{19}H_{17}N_2O_2$ [M + H]$^+$: 305.1285; Found: 305.1286.

*N-(3'-Chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1m**)*: R_f 0.26 (hexane/EtOAc = 30/1). White solid, 61% yield, m.p.129-130 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.33 (s, 1H), 8.64 (d, *J* = 7.8 Hz, 1H), 8.41 (d, J = 4.2 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.49 (s, 1H), 7.46 – 7.43 (m, 1H), 7.42 – 7.40 (m, 2H), 7.39 – 7.37 (m, 1H), 7.36 – 7.34 (m, 1H), 7.30 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.22 – 7.19 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 161.9, 149.8, 148.0, 140.0, 137.6, 134.8, 134.8, 131.0, 130.2, 130.1, 129.7, 129.0, 127.9, 127.8,

126.3, 124.4, 122.3, 120.9. **HRMS-ESI**: calcd for $C_{18}H_{14}ClN_2O$ $[M + H]^+$: 309.0789; Found: 309.0785.

*N-(2'-Methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1n**)*: R_f 0.30 (hexane/EtOAc = 30/1). White solid, 66% yield, m.p. 160-161 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 9.93 (s, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 4.2 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.45 – 7.42 (m, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.30 (m, 2H), 7.26 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 2.12 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 161.9, 150.0, 148.0, 137.4, 137.2, 136.9, 135.5, 132.0, 130.5, 130.3, 129.9, 128.4, 128.3, 126.3, 126.1, 123.9, 122.1, 119.9, 19.79. **HRMS-ESI**: calcd for $C_{19}H_{17}N_2O$ $[M + H]^+$: 289.1335; Found: 289.1333.

*N-(2'-Fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1o**)*: R_f 0.26 (hexane/EtOAc = 30/1). White solid, 61% yield, m.p. 45-46 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 10.12 (s, 1H), 8.57 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.35 (d, *J* = 4.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.49 – 7.38 (m, 3H), 7.37 – 7.32 (m, 2H), 7.29 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.26 – 7.20 (m, 2H). **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, ppm) δ 162.0, 160.7 ($J_{C\text{-}F}$ = 245.8 Hz), 149.8, 147.9, 137.4, 135.5, 132.1, 132.0, 130.7, 130.1 ($J_{C\text{-}F}$ = 8.0 Hz), 129.1, 126.8, 126.2, 125.5 ($J_{C\text{-}F}$ = 15.9 Hz), 124.6 ($J_{C\text{-}F}$ = 3.6 Hz), 124.2, 122.2, 121.2, 116.2 ($J_{C\text{-}F}$ = 22.1 Hz). **HRMS-ESI**: calcd for $C_{18}H_{14}FN_2O$ $[M + H]^+$: 293.1085; Found: 293.1083.

*N-(2-(Naphthalen-1-yl)phenyl)picolinamide (**1p**)*: R_f 0.27 (hexane/EtOAc = 30/1). White oily liquid, 64% yield. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 9.93 (s, 1H), 8.75 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 7.5 Hz, 1H), 7.96 – 7.91 (m, 3H), 7.69 – 7.65 (m, 1H), 7.60 – 7.57 (m, 2H), 7.54 – 7.49 (m, 2H), 7.46 – 7.43 (m, 1H), 7.37 – 7.32 (m, 2H), 7.27 – 7.24 (m, 1H), 7.17 – 7.14 (m, 1H). **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, ppm) 162.0, 149.7, 147.7, 137.2, 136.1, 135.4, 134.0, 132.0, 131.0, 130.6, 128.8, 128.6, 128.3, 128.0, 126.6, 126.1, 125.9, 125.8, 125.6, 123.9, 121.9, 120.3. **HRMS-ESI**: calcd for $C_{22}H_{17}N_2O$ $[M + H]^+$: 325.1335; Found: 325.1332.

*N-(2-(Thiophen-2-yl)phenyl)picolinamide (**1q**)*: R_f 0.26 (hexane/EtOAc = 30/1). White solid, 67% yield, m.p. 112-113 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.57 (s, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.48 (d, *J* = 4.2 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.47 – 7.40 (m, 4H), 7.27 (dd, *J* = 3.0, 0.6 Hz, 1H), 7.20 – 7.17 (m, 2H). **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$, ppm) δ 162.0, 149.6, 147.9, 137.5, 136.7, 134.3, 134.0, 132.8, 131.2, 129.3, 129.0, 128.3, 126.3, 122.2, 122.0, 116.8. **HRMS-ESI**: calcd for $C_{16}H_{13}N_2OS$ $[M + H]^+$: 281.0743; Found: 281.0750.

*N-(5-Methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1r**)*: R_f 0.23 (hexane/EtOAc = 30/1). White solid, 68% yield, m.p. 106-107 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.23 (s, 1H), 8.52 – 8.49 (m, 1H), 8.37 (d, *J* = 4.8 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.50 – 7.46 (m, 4H), 7.44 – 7.41 (m, 1H), 7.38 – 7.35 (m, 1H), 7.26 – 7.24 (m, 1H), 7.15 (s, 1H), 2.39 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 161.9, 150.1, 147.9,

138.3, 137.5, 133.9, 132.6, 132.3, 130.9, 129.5, 129.0, 128.9, 127.7, 126.1, 122.2, 120.8, 20.96. **HRMS-ESI**: calcd for $C_{19}H_{17}N_2O$ $[M + H]^+$: 289.1335; Found: 289.1334.

*N-(5-Fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1s**)*: R_f 0.27 (hexane/EtOAc = 30/1). White solid, 64% yield, m.p. 143-144 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.21 (s, 1H), 8.58 (dd, *J* = 9.6, 5.4 Hz, 1H), 8.36 (d, *J* = 4.2 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.51 – 7.49 (m, 2H), 7.46 – 7.44 (m, 3H), 7.38 – 7.36 (m, 1H), 7.14 – 7.11 (m, 1H), 7.06 (dd, *J* = 9.0, 3.0 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 161.9, 159.9 ($J_{C\text{-}F}$ = 242.7 Hz), 149.8, 148.0, 137.5, 137.1, 134.6 ($J_{C\text{-}F}$ = 7.6 Hz), 131.0 ($J_{C\text{-}F}$ = 2.5 Hz), 129.3, 129.0, 128.3, 126.2, 122.6 ($J_{C\text{-}F}$ = 7.9 Hz), 122.3, 116.9 ($J_{C\text{-}F}$ = 22.8 Hz), 114.9 ($J_{C\text{-}F}$ = 21.7 Hz). **HRMS-ESI**: calcd for $C_{18}H_{14}FN_2O$ $[M + H]^+$: 293.1085; Found: 293.1095.

*N-(5-Chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1t**)*: R_f 0.30 (hexane/EtOAc = 30/1). White solid, 67% yield, m.p. 154-155 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.29 (s, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 4.2 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.52 – 7.50 (m, 2H), 7.47 – 7.43 (m, 3H), 7.40 – 7.36 (m, 2H), 7.31 (d, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 149.7, 148.0, 137.5, 136.8, 134.0, 133.6, 130.0, 129.3, 129.1, 129.1, 128.3, 128.3, 126.3, 122.3, 121.8. **HRMS-ESI**: calcd for $C_{18}H_{14}ClN_2O$ $[M + H]^+$: 309.0789; Found: 309.0793.

*N-(5-Bromo-[1,1'-biphenyl]-2-yl)picolinamide (**1u**)*: R_f 0.32 (hexane/EtOAc = 30/1). White solid, 70% yield, m.p. 165-166 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.30 (s, 1H), 8.58 (d, *J* = 9.0 Hz, 1H), 8.36 – 8.31 (m, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.55 – 7.50 (m, 3H), 7.48 – 7.44 (m, 4H), 7.39 – 7.37 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$) δ 162.01, 149.69, 147.99, 137.55, 136.72, 134.34, 134.07, 132.83, 131.24, 129.37, 129.08, 128.35, 126.31, 122.28, 122.06, 116.81, 77.26, 77.05, 76.84. **HRMS-ESI**: calcd for $C_{18}H_{14}BrN_2O$ $[M + H]^+$: 353.0284; Found: 353.0291.

*N-(5-(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)picolinamide (**1v**)*: R_f 0.28 (hexane/EtOAc = 30/1). White solid, 73% yield, m.p. 100-101 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.50 (s, 1H), 8.85 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 4.8 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.50 (d, *J* = 6.6 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.38 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.3, 149.5, 148.0, 138.0, 137.6, 136.7, 132.4, 129.4, 129.2, 128.5, 127.2 ($J_{C\text{-}F}$ = 3.7 Hz), 126.5, 125.9 ($J_{C\text{-}F}$ = 32.4 Hz), 125.5 ($J_{C\text{-}F}$ = 3.7 Hz), 125.1 ($J_{C\text{-}F}$ = 270.0 Hz), 122.4, 120.1. **HRMS-ESI**: calcd for $C_{19}H_{14}F_3N_2O$ $[M + H]^+$: 343.1053; Found: 343.1069.

*N-(4-Chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1x**)*: R_f 0.30 (hexane/EtOAc = 30/1). White solid, 74% yield, m.p. 133-135 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 10.34 (s, 1H), 8.76 (d, *J* = 2.4 Hz, 1H), 8.36 (d, *J* = 4.2 Hz,

1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.52 – 7.50 (m, 2H), 7.47 – 7.42 (m, 3H), 7.39 – 7.37 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.4 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3$, ppm) δ 162.0, 149.6, 148.0, 137.6, 137.1, 135.9, 134.1, 131.1, 130.7, 129.4, 129.1, 128.1, 126.4, 124.1, 122.3, 120.4. **HRMS-ESI**: calcd for $C_{18}H_{14}ClN_2O$ $[M + H]^+$: 309.0789; Found: 309.0792.

Typical procedure for the Preparation of 9-bromo-6H-chromeno[4,3-b]quinolin-6-one (2a): A mixture of **1a** (84.9 mg, 0.4 mmol), DIAD (0.8 mmol, 161.6 mg, 2.0 eq.), $CoCl_2$ (0.12 mmol, 15.6 mg, 30 mol %), NaOPiv (113.7 mg, 0.8 mmol, 2.0 eq.) and 1,4-dioxane (4.0 mL) in a 10 mL tube was heated at 130 ^{o}C under O_2 (1 atm) for 24 hours. The reaction mixture was cooled to room temperature, and then the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (DCM/EtOAc: 10:1 to 6:1) to yield **2a** (75.7 mg, 97%) as a white solid.

*Phenanthridin-6(5H)-one (**2a**)*: R_f 0.30 (DCM/EtOAc = 10/1). White solid, 75.7 mg, 97% yield, m.p. 297-298 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.70 (s, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 7.8 Hz, 1H), 8.34 (d, *J* = 7.8 Hz 1H), 7.86 – 7.83 (m, 1H), 7.66 – 7.63 (m, 1H), 7.50 – 7.47 (m, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.24 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.3, 137.0, 134.7, 133.2, 130.0, 128.4, 127.9, 126.2, 123.7, 123.1, 122.7, 118.0, 116.6. **HRMS-ESI**: calcd for $C_{13}H_8NO$ $[M - H]^-$: 194.0611; Found: 194.0610.

*8-Methylphenanthridin-6(5H)-one (**2b**)*: R_f 0.28 (DCM/EtOAc = 10/1). White solid, 77.8 mg, 93% yield, m.p. 266-267 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.62 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.13 (s, 1H), 7.67 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.22 (m, 1H), 2.48 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.3, 138.0, 136.7, 134.4, 132.3, 129.5, 127.7, 126.1, 123.4, 123.1, 122.6, 118.1, 116.5, 21.40. **HRMS-ESI**: calcd for $C_{14}H_{10}NO$ $[M - H]^-$: 208.0768; Found: 208.0765.

*8-Ethylphenanthridin-6(5H)-one (**2c**)*: R_f 0.27 (DCM/EtOAc = 10/1). White solid, 84.8 mg, 95% yield, m.p. 254-255 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.64 (s, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 8.15 (s, 1H) 7.72 (dd, *J*=6.0, 1.8 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.36 (dd, *J* = 7.8, 0.6 Hz, 1H) , 7.26 – 7.23 (m, 1H) , 2.80 (q, *J* = 7.8 Hz, 2H) , 1.27 (t, *J* = 7.8 Hz, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.3, 144.2, 136.7, 133.4, 132.5, 129.6, 126.4, 126.1, 123.5, 123.2, 122.7, 118.1, 116.5, 28.4, 15.8. **HRMS-ESI**: calcd for $C_{15}H_{12}NO$ $[M - H]^-$: 222.0924; Found: 222.0925.

*8-Methoxyphenanthridin-6(5H)-one (**2d**)*: R_f 0.28 (DCM/EtOAc = 10/1). White solid, 84.7 mg, 94% yield, m.p. 267-268 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.72 (s, 1H), 8.44 (d, *J* = 9.0 Hz, 1H), 8.30 (d, *J* = 7.8

Hz, 1H), 7.77 (d, *J* = 3.0 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.23 (m, 1H) , 3.91 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-*d*$_6$, ppm) δ 161.0, 159.5, 136.0, 128.9, 128.1, 127.6, 125.0, 123.1, 122.7, 122.1, 118.2, 116.4, 109.2, 55.9. **HRMS-ESI**: calcd for $C_{14}H_{10}NO_2$ [M - H]$^-$: 224.0717; Found: 224.0716.

*8-(Methylthio)phenanthridin-6(5H)-one (**2e**):* R_f 0.30 (DCM/EtOAc = 10/1). White solid, 90.7 mg, 94% yield, m.p. 269-270 °C. **^{1}H NMR** (600 MHz, DMSO-*d*$_6$, ppm) δ 11.76 (s, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 2.4 Hz, 1H), 7.72 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.26 – 7.23 (m, 1H), 2.60 (s, 3H). **^{13}C {^{1}H} NMR** (125 MHz, DMSO-*d*$_6$, ppm) δ 160.3, 138.8, 136.1, 131.0, 130.4, 129.2, 126.2, 123.3, 122.9, 122.7, 122.3, 117.4, 116.1, 14.4. **HRMS-ESI**: calcd for $C_{14}H_{10}NOS$ [M - H]$^-$: 240.0489, found: 240.0487.

*8-Fluorophenanthridin-6(5H)-one (**2f**):* R_f 0.23 (DCM/EtOAc = 10/1). White solid, 79.3 mg, 93% yield, m.p. 279-280 °C. **^{1}H NMR** (600 MHz, DMSO-*d*$_6$, ppm) δ 11.84 (s, 1H), 8.58 – 8.56 (m, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 7.96 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.50 - 7.47 (m, 1H), 7.38 – 7.36 (m, 1H), 7.27 – 7.25 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-*d*$_6$, ppm) δ 162.8 ($J_{C\text{-}F}$ = 368.8 Hz), 161.2, 136.5, 131.5 ($J_{C\text{-}F}$ = 2.2 Hz), 129.9, 128.1 ($J_{C\text{-}F}$ = 7.3 Hz), 126.3 ($J_{C\text{-}F}$ = 7.9 Hz), 123.7, 122.9, 121.5 ($J_{C\text{-}F}$ = 22.8 Hz), 117.5, 116.6, 113.0 ($J_{C\text{-}F}$ = 22.3 Hz). **HRMS-ESI**: calcd for $C_{13}H_7FNO$ [M - H]$^-$: 212.0517; Found: 212.0518.

*8-Chlorophenanthridin-6(5H)-one (**2g**):* R_f 0.24 (DCM/EtOAc = 10/1). White solid, 82.7 mg, 90% yield, m.p. 289-290 °C. **^{1}H NMR** (600 MHz, DMSO-*d*$_6$, ppm) δ 11.86 (s, 1H), 8.54 (d, *J* = 9.0 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 2.4 Hz, 1H), 7.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.26 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-*d*$_6$, ppm) δ 160.1, 136.9, 133.5, 133.2, 133.2, 130.4, 127.6, 127.0, 125.6, 123.9, 123.0, 117.3, 116.7. **HRMS-ESI**: calcd for $C_{13}H_7ClNO$ [M - H]$^-$: 228.0222; Found: 228.0199.

*8-Bromophenanthridin-6(5H)-one (**2h**):* R_f 0.28 (DCM/EtOAc = 10/1). White solid, 99.8 mg, 91% yield, m.p. 287-288 °C. **^{1}H NMR** (600 MHz, DMSO-*d*$_6$, ppm) δ 11.85 (s, 1H), 8.48 (d, *J* = 9.0 Hz, 1H), 8.39 – 8.37 (m, 2H), 8.01 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.27 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-*d*$_6$, ppm) δ 160.1, 137.0, 136.0, 133.9, 130.5, 130.1, 127.8, 125.8, 123.9, 123.0, 121.6, 117.4, 116.7. **HRMS-ESI**: calcd for $C_{13}H_7BrNO$ [M - H]$^-$: 271.9717; Found: 271.9707.

*8-(Trifluoromethyl)phenanthridin-6(5H)-one (**2i**):* R_f 0.26 (DCM/EtOAc = 10/1). White solid, 102.1 mg, 97% yield, m.p. 292-293 °C. **^{1}H NMR** (600 MHz, DMSO-*d*$_6$, ppm) δ 11.96 (s, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.54 (s, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.29 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-*d*$_6$, ppm) δ 160.4, 138.0, 137.7, 131.4, 129.1 ($J_{C\text{-}F}$ = 6.6 Hz),

128.7 ($J_{C\text{-}F}$ = 32.3 Hz), 127.1 ($J_{C\text{-}F}$ = 270.5 Hz), 126.3, 124.9 ($J_{C\text{-}F}$ = 3.6 Hz), 124.8 ,124.5, 123.1, 117.0, 116.9. **HRMS-ESI**: calcd for $C_{14}H_7F_3NO$ $[M - H]^-$: 262.0485; Found: 262.0483.

*6-Oxo-5,6-dihydrophenanthridine-8-carbonitrile (**2j**):* R_f 0.28 (DCM/EtOAc = 10/1). White solid, 80.2 mg, 91% yield, m.p. 284-285 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.96 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 1.8 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.23 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.40 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.33 – 7.30 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 160.0, 138.4, 138.0, 135.4, 132.6, 131.8, 126.5, 124.8, 124.7, 123.2, 118.8, 116.9, 110.7. **HRMS-ESI**: calcd for $C_{14}H_7N_2O$ $[M - H]^-$: 219.0564; Found: 219.0562.

*9-Methylphenanthridin-6(5H)-one (**2k**):* R_f 0.27 (DCM/EtOAc = 10/1). White solid, 77.8 mg, 93% yield, m.p. 257-258 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.60 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.30 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.23 (m, 1H), 2.52 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.3, 143.4, 137.2, 134.7, 129.9, 129.6, 127.9, 123.9, 123.6, 122.9, 122.5, 118.0, 116.5, 22.0. **HRMS-ESI**: calcd for $C_{14}H_{10}NO$ $[M - H]^-$: 208.0768; Found: 208.0762.

*9-Methoxyphenanthridin-6(5H)-one (**2l**):* R_f 0.24 (DCM/EtOAc = 10/1). White solid, 82.9 mg, 92% yield, m.p. 248-249 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.53 (s, 1H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 2H), 3.98 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 163.3, 161.1, 137.5, 136.8, 130.1, 130.0, 124.1, 122.4, 119.7, 117.9, 116.7, 116.5, 105.5, 56.2. **HRMS-ESI**: calcd for $C_{14}H_{10}NO_2$ $[M - H]^-$: 224.0717; Found: 224.0716.

*9-Chlorophenanthridin-6(5H)-one (**2m**):* R_f 0.26 (DCM/EtOAc = 10/1). White solid, 79.9 mg, 87% yield, m.p. 330-331 °C. **^{1}H NMR** (400 MHz, DMSO-d_6, ppm) δ 11.79 (s, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 9.0 Hz, 1H), 8.31 (d, *J* = 10.2 Hz, 1H), 7.68 (dd, *J* = 10.2, 1.8 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.38 – 7.36 (m, 1H), 7.29 – 7.25 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 160.6, 138.7, 137.5, 136.5, 130.8, 130.2, 128.5, 124.8, 124.3, 122.9, 117.1, 116.6. **HRMS-ESI**: calcd for $C_{13}H_7ClNO$ $[M - H]^-$: 228.0222; Found: 228.0223.

*10-Methylphenanthridin-6(5H)-one (**2n**):* R_f 0.27 (DCM/EtOAc = 10/1). White solid, 69.5 mg, 83% yield, m.p. 294-296 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 11.71 (s, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 6.6 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.50 – 7.47 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.27 – 7.24 (m, 1H), 2.92 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.4, 137.4, 135.6, 133.7, 129.2, 127.9, 127.8, 127.7, 126.5, 122.1, 119.2, 116.7, 26.1. **HRMS-ESI**: calcd for $C_{14}H_{10}NO$ $[M - H]^-$: 208.0768; Found: 208.0767.

*10-Fluorophenanthridin-6(5H)-one (**2o**):* R_f 0.27 (DCM/EtOAc = 10/1). White solid, 72.5 mg, 85% yield, m.p. 304-305 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.84 (s, 1H), 8.43 (s, 1H), 8.21 (s, 1H), 7.69 – 7.63 (m,

2H), 7.50 (s, 1H), 7.39 (s, 1H), 7.24 (s, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 160.9 (J_{C-F} = 250.0 Hz), 160.1, 137.1, 130.2, 129.2, 128.7, 127.4, 127.3, 124.4, 123.1, 120.6 (J_{C-F} = 24.2 Hz), 116.7, 115.3. **HRMS-ESI**: calcd for $C_{13}H_7FNO$ [M - H]$^-$: 212.0517; Found: 212.0516.

*Benzo[k]phenanthridin-6(5H)-one (**2p**):* R_f 0.28 (DCM/EtOAc = 10/1). White solid, 63.8 mg, 65% yield, m.p. 285-286 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.98 (s, 1H), 8.95 - 8.94 (m, 1H), 8.62 (d, J = 7.8 Hz, 1H), 8.33 (d, J = 9.0 Hz, 1H), 8.16 – 8.15 (m, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.78 – 7.77 (m, 2H), 7.57 – 7.55 (m, 1H), 7.52 – 7.51 (m, 1H), 7.36 – 7.33 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.3, 137.8, 136.2, 133.3, 129.7, 129.4, 129.0, 128.8, 128.6, 128.3, 127.8, 127.7, 125.0, 123.2, 122.5, 117.9, 116.8. **HRMS-ESI**: calcd for $C_{17}H_{10}NO$ [M - H]$^-$: 244.0768; Found: 244.0769.

*Thieno[3,2-c]quinolin-4(5H)-one (**2q**):* R_f 0.23 (DCM/EtOAc = 10/1). White solid, 75.7 mg, 94% yield, m.p. 285-286 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.77 (s, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 4.8 Hz, 1H), 7.60 (d, J = 4.8 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.24 – 7.22 (m, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 158.6, 146.0, 136.6, 131.6, 129.8, 127.1, 125.7, 123.8, 122.9, 116.7, 116.6. **HRMS-ESI**: calcd for $C_{11}H_6NOS$ [M - H]$^-$: 200.0176; Found: 200.0169.

*2-Methylphenanthridin-6(5H)-one (**2r**):* R_f 0.26 (DCM/EtOAc = 10/1). White solid, 77.8 mg, 93% yield, m.p. 258-259 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.61 (s, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.33 – 8.31 (m, 1H), 8.19 (s, 1H), 7.85 – 7.82 (m, 1H) , 7.64 – 7.62 (m, 1H) , 7.32 – 7.30 (m, 1H), 7.27 (d, J = 8.4 Hz, 1H) , 2.41 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.1, 134.9, 134.7, 133.1, 131.7, 131.0, 128.2, 127.9, 126.2, 123.5, 123.0, 117.9, 116.5, 21.2. **HRMS-ESI**: calcd for $C_{14}H_{10}NO$ [M - H]$^-$: 208.0768; Found: 208.0773.

*2-Fluorophenanthridin-6(5H)-one (**2s**):* R_f 0.30 (DCM/EtOAc = 10/1). White solid, 81.0 mg, 95% yield, m.p. 302-303 ^{o}C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.73 (s, 1H), 8.51 (d, J = 7.8 Hz, 1H), 8.33 (d, J = 7.8 Hz, 1H), 8.26 (d, J = 9.6 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.69 – 7.66 (m, 1H), 7.38 – 7.37 (m, 2H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.0, 159.1 (J_{C-F} = 236.0 Hz), 134.0, 133.6, 133.3, 129.0, 127.9, 126.3, 123.6, 119.3 (J_{C-F} = 8.3 Hz), 118.2 (J_{C-F} = 8.4 Hz), 117.7 (J_{C-F} = 23.9 Hz), 109.7 (J_{C-F} = 23.9 Hz). **HRMS-ESI**: calcd for $C_{13}H_7FNO$ [M - H]$^-$: 212.0517; Found: 212.0525.

*2-Chlorophenanthridin-6(5H)-one (**2t**):* R_f 0.21 (DCM/EtOAc = 10/1). White solid, 85.4 mg, 93% yield, m.p. 329-330 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d_6, ppm) δ11.82 (s, 1H), 8.58 (d, J = 6.8 Hz, 1H), 8.48 (d, J = 5.6 Hz, 1H), 8.33 (d, J = 6.0 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.70 – 7.67 (m, 1H), 7.54 (dd, J = 7.2, 2.0 Hz, 1H), 7.38 (d, J = 6.8 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.1, 135.8, 133.6, 133.4, 129.9, 129.1, 127.9, 127.0, 126.3, 123.6, 123.3, 119.6, 118.3. **HRMS-ESI**: calcd for $C_{13}H_7ClNO$ [M - H]$^-$: 228.0222; Found:

228.0217.

*2-Bromophenanthridin-6(5H)-one (**2u**):* R_f 0.28 (DCM/EtOAc = 10/1). White solid, 103.1 mg, 94% yield, m.p. 328-329 °C. **^{1}H NMR** (400 MHz, DMSO-d_6, ppm) δ 11.81 (s, 1H), 8.59 (d, *J* = 5.2 Hz, 2H), 8.32 (s, 1H), 7.86 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 6.4 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.1, 136.2, 133.6, 133.4, 132.6, 129.1, 127.9, 126.3, 126.2, 123.6, 120.1, 118.6, 114.9. **HRMS-ESI**: calcd for $C_{13}H_7BrNO$ [M - H]$^-$: 271.9717; Found: 271.9713.

*2-(Trifluoromethyl)phenanthridin-6(5H)-one (**2v**):* R_f 0.24 (DCM/EtOAc = 10/1). White solid, 101.1 mg, 96% yield, m.p. 294-295 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 12.00 (s, 1H), 8.70 (s, 1H), 8.66 (d, *J* = 7.8 Hz, 1H), 8.34 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.89 – 7.88 (m, 1H), 7.81 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 161.4, 139.7, 133.7, 133.6, 129.3, 127.9, 127.7 ($J_{C\text{-}F}$ = 270.2 Hz), 126.4 ($J_{C\text{-}F}$ = 3.9 Hz), 126.3, 123.6, 123.3 ($J_{C\text{-}F}$ = 32.0 Hz), 121.3 ($J_{C\text{-}F}$ = 3.5 Hz), 118.1, 117.4. **HRMS-ESI**: calcd for $C_{14}H_7F_3NO$ [M - H]$^-$: 262.0485; Found: 262.0486.

*Methyl 6-oxo-5,6-dihydrophenanthridine-2-carboxylate (**2w**):* R_f 0.26 (DCM/EtOAc = 10/1). White solid, 54.7 mg, 54% yield, m.p. 272-273 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 12.00 (s, 1H), 8.83 (s, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 8.01 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.70 – 7.67 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ 166.3, 161.4, 140.5, 133.9, 133.6, 130.4, 129.0, 127.9, 126.1, 125.1, 123.7, 123.1, 117.7, 116.8, 52.5. **HRMS-ESI**: calcd for $C_{15}H_{10}NO_3$ [M - H]$^-$: 252.0666; Found: 252.0665.

*3-Chlorophenanthridin-6(5H)-one (**2x**):* R_f 0.24 (DCM/EtOAc = 10/1). White solid, 84.5 mg, 92% yield, m.p. 312-313 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.77 (s, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.66 – 7.64 (m, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.27 (dd, *J*=8.4, 1.8 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, DMSO-d_6, ppm) δ161.3, 138.1, 134.2, 134.0, 133.5, 128.7, 128.0, 126.0, 125.7, 123.2, 122.6, 117.0, 115.8. **HRMS-ESI**: calcd for $C_{13}H_7ClNO$ [M - H]$^-$: 228.0222; Found: 228.0228.

Typical procedure for the Preparation of PJ-34: 5-*H*-Phenanthridin-6-one **2a** (0.97g, 5.0 mmol) was dissolved in 15 mL nitric acid with stirring for 24 h at room temperature. A thick yellow precipitate formed. The mixture was filtered through a plug of Celite and the residue was washed with cold water (25 mL), ethyl ether (25 mL), dried under vacuum at 55 °C. The crude product was used directly in the next step without further purification. The crude product was dissolved in EtOH (25 mL), water (10 mL) was added, followed by addition of Iron powder (20 mol, 1.12 g) and a drop of concentrated hydrochloric acid. The mixture was stirred at 90 °C for 6 hours under nitrogen, and then cooled to room temperature and filtered through a pad of Celite. The

solvents were evaporated under reduced pressure. The resulting residue was dissolved in diethyl ether and extracted with 2 M hydrochloric acid. The aqueous fraction was basified using concentrated aqueous sodium hydroxide solution and the product amine was extracted with EtOAc (10 mL × 3). The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography with ethyl acetate (EA) as eluent to afford 2-aminophenanthridin-6(5*H*)-one **3a** (0.70 g, 76%).

A solution of 2-aminophenanthridin-6(5*H*)-one **3a** (0.80 g, 3.8 mmol), dimethylglycine (0.47 g, 4.6 mmol), EDCI (0.80 g, 4.2 mmol), HOBt (0.57 g, 4.2 mmol) and DIPEA (1.78 mL, 8.4 mmol) were dissolved in 8 mL of anhydrous DMF. The mixture was stirred at rt for 5 h. The mixture was quenched with water, and extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash chromatography (ethyl acetate/methanol: 10:1) to give the desired product **PJ-34** (0.97 g, 87%).

*2-(Dimethylamino)-N-(6-oxo-5,6-dihydrophenanthridin-2-yl)acetamide (**PJ-34**):* R_f 0.28 (ethyl acetate/methanol = 10/1). White solid, 0.92 g, 89%. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.67 (s, 1H), 9.83 (s, 1H), 8.68 (d, *J* = 1.8 Hz, 1H), 8.34 – 8.30 (m, 2H), 7.89 – 7.86 (m, 1H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 3.11 (s, 2H), 2.32 (s, 6H). **^{13}C {^{1}H} NMR** (100 MHz, DMSO-d_6, ppm) δ 168.6, 160.5, 134.0, 133.6, 132.8, 132.7, 128.0, 127.6, 125.8, 122.3, 122.0, 117.4, 116.2, 113.5, 63.3, 45.5. **HRMS-ESI**: calcd for $C_{17}H_{18}N_3O_2$ $[M + H]^+$: 296.1394; Found: 296.1403.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all starting materials and products. This material is available free of charge *via* the Internet at http:// pubs.acs.org.

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