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ACCESS TO FUNCTIONALIZED PYRROLOPHENANTHRIDINE VIA AN *ortho* C-H AMINATION/INTERANNULAR C-H ARYLATION CASCADE OF *N*-ARYLPYRROLES

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Abstract – An expeditious access to pyrrolophenanthridine scaffold enabled by a Catellani strategy from *N*-arylpyrroles and *O*-benzoylhydroxylamines is disclosed. This reaction proceeds smoothly involving an *ortho* C-H amination/interannular C-H arylation cascade and well tolerates a number of pyrrole and amine substrates. Furthermore, the potential of this protocol has been highlighted by the easily accessible scale-up synthesis and a plausible mechanism of this reaction was also proposed.

INTRODUCTION

Pd/NBE (palladium/norbornene) cooperative catalysis, which was originally developed by Catellani in 1997,[1] has been extensively explored since then for arene/alkene functionalization via *ortho* C-H activation and *ipso* cross-coupling reaction to construct multiple chemical bonds in one pot, by accomplishing diverse *ortho* C-H functionalizations utilizing a variety of electrophiles.[2-14] Among them, *O*-benzoylhydroxylamines, which was employed by Dong's group for the first time in 2013,[15] has showed high reactivity serving as *ortho*-aminated electrophile by merging various *ipso* functionalizations.[16-29] In particular, the annulative Catellani reaction using *O*-benzoylhydroxylamines for *ortho*-amination has been emerging as a powerful tool for the construction of aminated cyclic compounds.[30-47] For instance, Lautens and coworkers have disclosed the amination-triggered synthesis of 3,4-dihydroquinolin-2(1*H*)-ones and phenanthridinones in 2017 and 2020, respectively. In 2017, Luan's group has developed a Catellani system for the rapid assembly of diversely functionalized spiroindenes via a C-H amination/phenol dearomatization

cascade. By combining the Catellani strategy and C(sp^3)-H activation, the access to several aminated cyclic scaffolds, such as indolines, 2,3-dihydro-1*H*-indenes and phenanthrenes, with *O*-benzoylhydroxylamines was achieved. Despite of those significant progresses, we asserted that exploring the application potential of the amination/cyclization Catellani reaction for the construction of functional molecules should be given the priority. Therefore, the development of efficient annulative Catellani strategies to synthesize aminated π-extended heterocycles, which might present special photophysical properties that benefiting from the electron-donating feature of amine towards aromatic rings, would be of great importance and also be highly desirable.

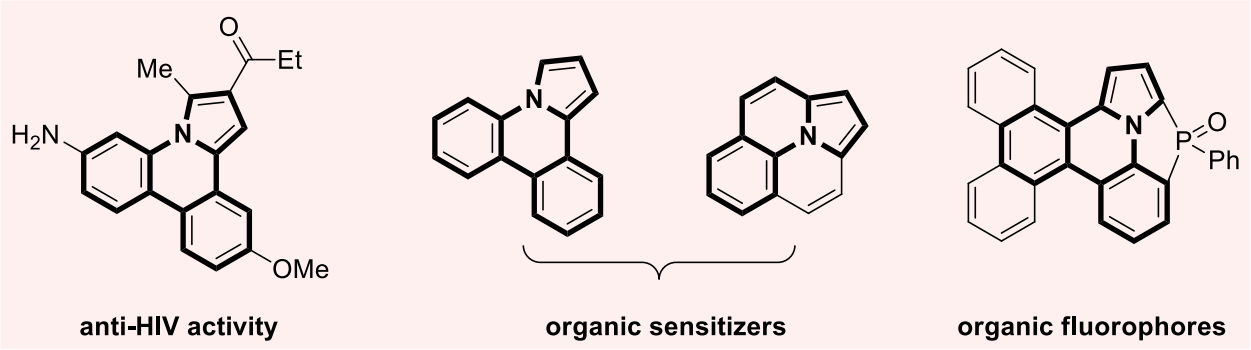


Figure 1. Examples of important pyrrolophenanthridine derivatives

Pyrrolophenanthridines, representing as a kind of highly privileged structural motif, are found ubiquitously in biologically relevant compounds and functional materials, such as blue-emitting luminophores in OLEDs (Figure 1).[48-50] Thus, to achieve a straightforward access to these valuable compounds with structural diversity has been a subject of great interest in organic chemistry (Figure 2). A Pd(0)-catalyzed cross-coupling of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate and 1-(2-iodophenyl)-1*H*-pyrrole was reported by Larock in 2006, in which a benzyne intermediate was involved to deliver pyrrolophenanthridine.[51] In 2013, You's group accomplished the construction of pyrrolophenanthridine core from 1,2-dibromobenzene and 2-phenyl-1*H*-pyrrole via C-C and C-N formation.[52] Alternatively, the iterative C-H arylation between 2-bromobenzene-1-sulfonyl chloride and 1-phenyl-1*H*-pyrrole was disclosed by Doucet and coworkers, thereby furnishing the desired valuable heterocycle.[53] However, these previous synthetic methods always limited with narrow substrate scope due to their involvement of simple coupling reaction, which might be extremely unfavorable for the further investigation of their structure-determined nature, such as photophysical properties. Herein, we disclosed a concise protocol enabled by Catellani strategy to access structurally diverse pyrrolophenanthridines from *N*-arylpyrroles and *O*-benzoylhydroxylamines, in which the installed amine group might lead to an push−pull effect for the photoluminescence of the synthesized molecules.

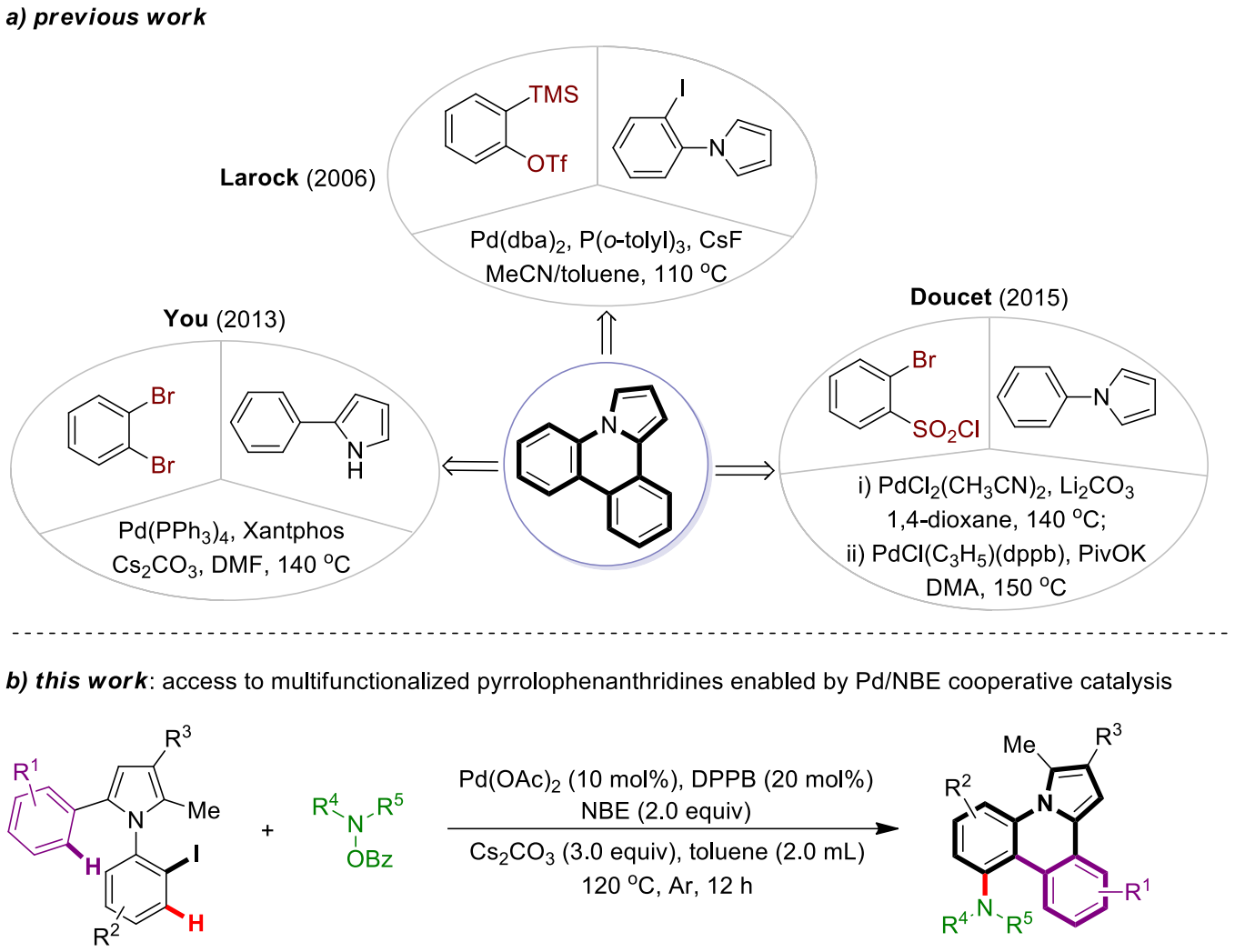


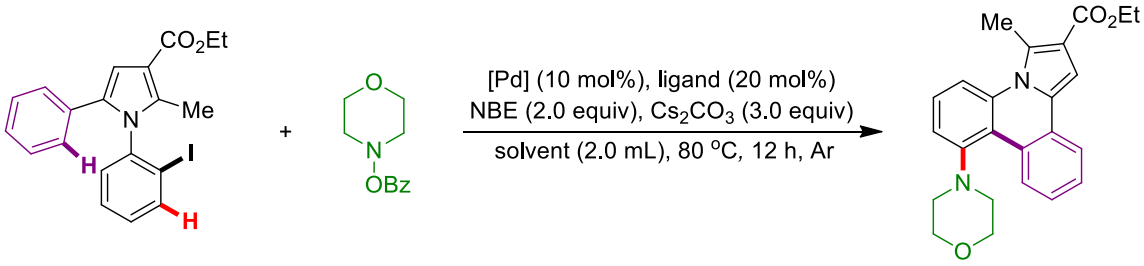
Figure 2. Strategies for accessing pyrrolophenanthridines

RESULTS AND DISCUSSION

Initially, the substrate ethyl 1-(2-iodophenyl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (**1a**) was readily synthesized via a condensation reaction of 1,4-dicarbonyl compound and 2-iodoaniline.[54] We then investigated the reaction using **1a** and morpholino benzoate (**2a**) as the model substrates in the presence of $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), Cs_2CO_3 (3.0 equiv.), in toluene (2.0 mL) at 80 ℃ under Ar atmosphere for 12 h (more details, see Optimization of Reaction Conditions and Table S1 in the Supporting Information). Gratifyingly, the desired product **3aa** could be isolated in 21% yield (Table 1, entry 1). Subsequently, a large number of phosphine ligands were tested and superior efficiency was obtained by the use of 1,4-bis(diphenylphosphino)butane (DPPB) to give **3aa** in 35% yield (Table 1, entries 2-6). However, the variation of solvents did not lead to better results (Table 1, entries 7-10). To our delight, when the reaction temperature was elevated to 120 ℃, the reaction efficiency was improved remarkably, by affording the desired product **3aa** in 74% yield (Table 1, entry 11). Other palladium catalysts, such as $PdCl_2$,

$Pd(TFA)_2$, $[PdCl(C_3H_5)]_2$, were less effective for this transformation to furnish the desired product **3aa** in depressing yields (Table 1, entries 12-14). Additionally, decreasing the loading of NBE led to a lower efficiency (Table 1, entry 15). No desired product **3aa** was observed in the absence of NBE, and only the intramolecular arylation via C-H/C-I cross-coupling happened, which proceeded similarly to Knochel's work.[55,56]

Table 1. Optimization of the reaction conditions[a]



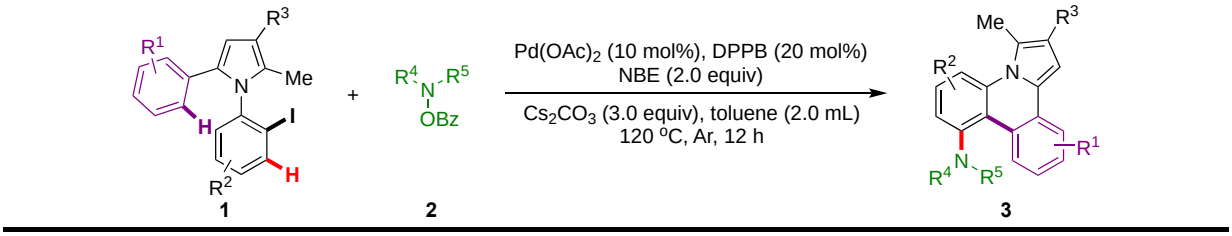
1a **2a** **3aa**

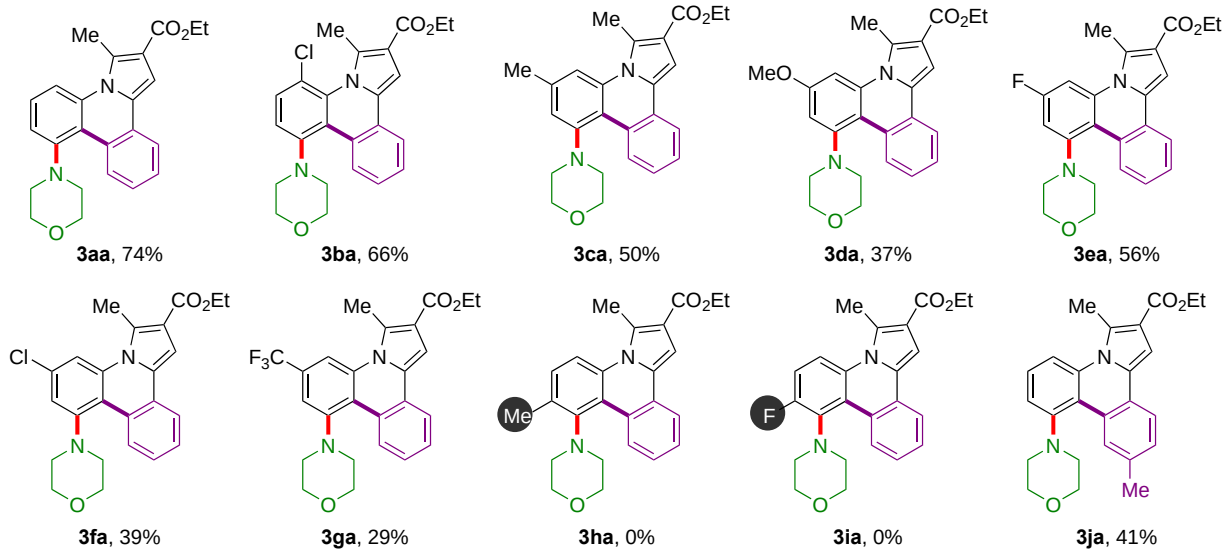
entry	[Pd]	ligand	solvent	**3aa**, yield (%)[b]
1	$Pd(OAc)_2$	PPh_3	toluene	21
2	$Pd(OAc)_2$	S-Phos	toluene	trace
3	$Pd(OAc)_2$	DPPE	toluene	11
4	$Pd(OAc)_2$	DPPP	toluene	16
5	$Pd(OAc)_2$	DPPM	toluene	trace
6	$Pd(OAc)_2$	DPPB	toluene	35
7	$Pd(OAc)_2$	DPPB	1,4-dioxane	21
8	$Pd(OAc)_2$	DPPB	HFIP	0
9	$Pd(OAc)_2$	DPPB	*o*-xylene	23
10	$Pd(OAc)_2$	DPPB	*p*-xylene	17
11[c]	$Pd(OAc)_2$	DPPB	toluene	74
12[c]	$PdCl_2$	DPPB	toluene	26
13[c]	$Pd(TFA)_2$	DPPB	toluene	19
14[c]	$[PdCl(C_3H_5)]_2$	DPPB	toluene	32
15[d]	$Pd(OAc)_2$	DPPB	toluene	39
16[e]	$Pd(OAc)_2$	DPPB	toluene	0

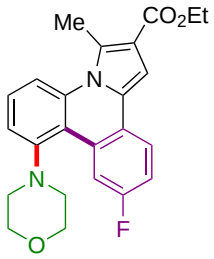
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Pd] (0.02 mmol), ligand (0.04 mmol), NBE (0.4 mmol), Cs_2CO_3 (0.6 mmol), solvent (2.0 mL), 80 °C, 12 h. [b]Isolated yield by flash column chromatography based on **1a**. [c]The reaction was performed at 120 °C. [d]1.0 equiv NBE was used. [e]In the absence of NBN. NBE = norbornene.

With the optimal conditions in hand, we began to examine the generality of this method by investigating the scope of *N*-arylpyrroles and amines. As shown in Table 2, several kinds of functional groups bearing in the *N*-arene rings could be well tolerated in the reaction to afford the desired products (**3aa**-**3fa**) in moderate to good yields, and the structure of **3aa** was further confirmed based on X-ray crystallographic analysis. Notably, the CF_3 substituted *N*-arylpyrrole was also compatible with the reaction conditions to generate the corresponding product (**3ga**) in 29% yield. Obviously, the reaction presented steric hindrance effect, as ethyl 2-methyl-5-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate and ethyl 1-(4-fluorophenyl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate could not conduct this reaction to give the corresponding products (**3ha** and **3ia**), in which it was not favourable to form the five-membered aryl-norbornyl-palladacycle (ANP) via C-H activation at the ortho position of methyl or fluoro group. Besides, different aromatic C-H coupling partners were also explored, and the desired pyrrolophenanthridine products (**3ja**-**3ra**) could be generated in all the cases. Next, we evaluated the reactivity of amine species in this transformation. It was found that kinds of cyclic amines, such as piperazine, piperidine and even azepane, could be tolerated in the reaction to construct the C-N bond. However, current methodology did not allow the acyclic amine reagent to participate in the reaction and only intramolecular arylation happened.[52,53] It should be point out that the generally lower yields obtained in this transformation were due to both the low conversion and undesired side-reaction of direct intramolecular C-H arylation.

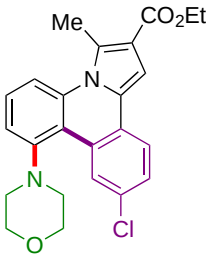
Table 2. Substrate scope[a,b]



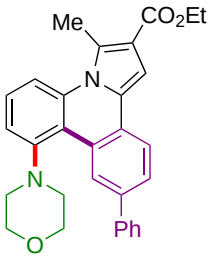




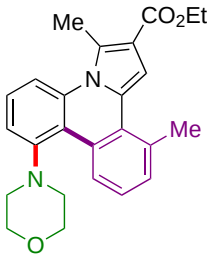
3ka, 25%



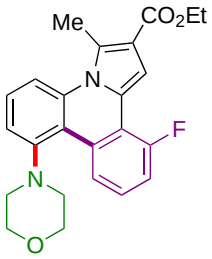
3la, 33%



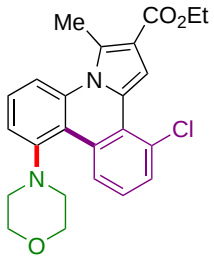
3ma, 40%



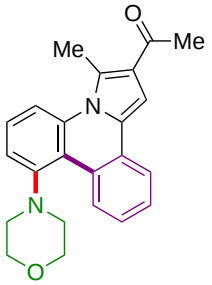
3na, 20%



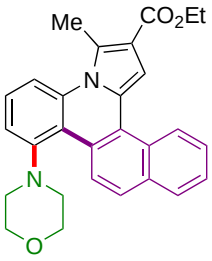
3oa, 33%



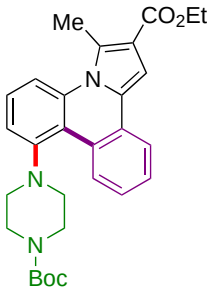
3pa, 25%



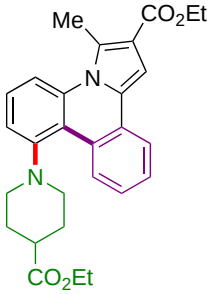
3qa, 40%



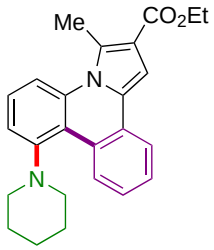
3ra, 18%



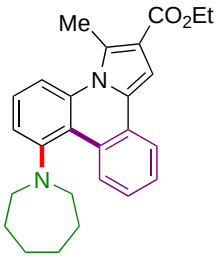
3ab. 41%



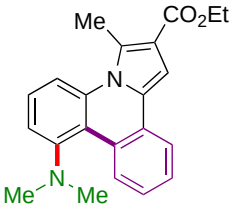
3ac. 32%



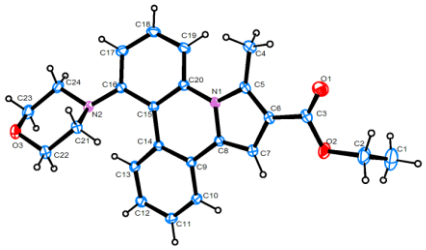
3ad, 23%



3ae, 11%

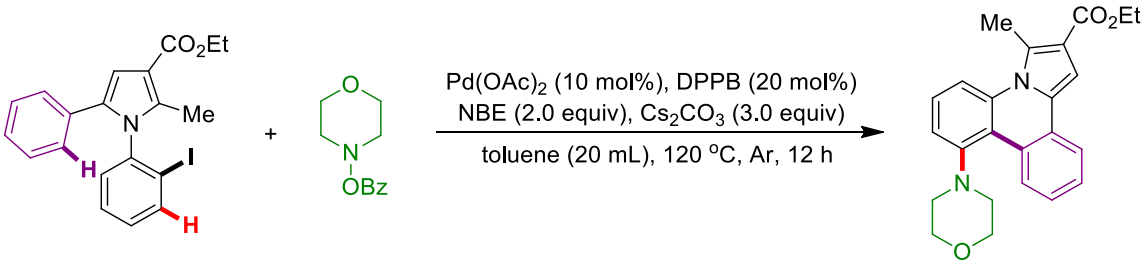


3af, 0%



***X-ray structure of* 3aa, CCDC 2063259**

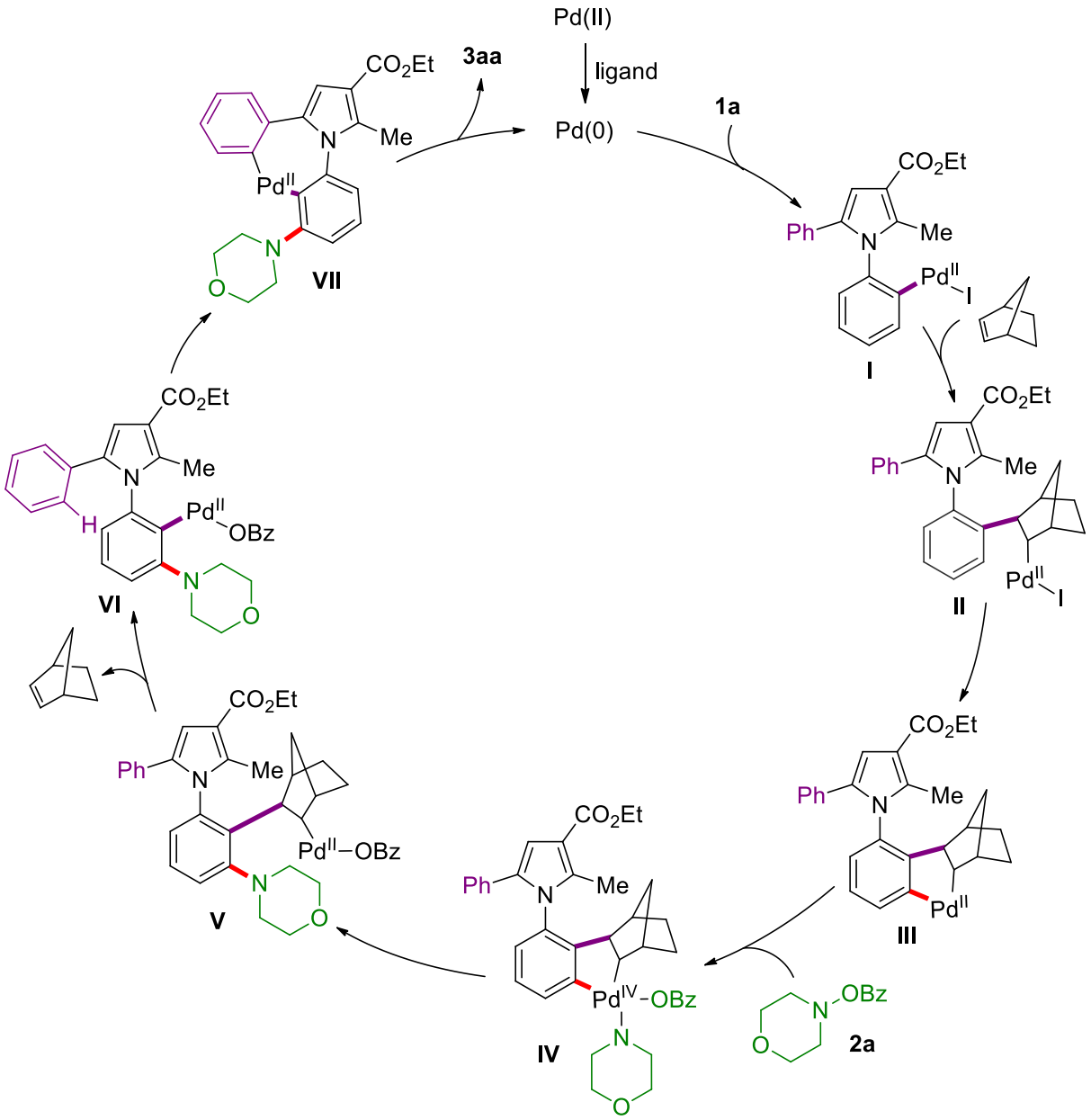
[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), [Pd] (0.02 mmol), DPPB (0.04 mmol), NBE (0.4 mmol), Cs_2CO_3 (0.6 mmol), toluene (2.0 mL), 80 °C, 12 h. [b]Isolated yield by flash column chromatography based on **1a**.



1a, 5 mmol **2a**, 7.5 mmol **3aa**, 60%, 1.16 g

Scheme 1. Gram-scale synthesis of **3aa**

To demonstrate the practicality of this reaction, a scale-up reaction was performed (Scheme 1). Gratifyingly, when conducted at 5 mmol scale under standard conditions, the desired product **3aa** was isolated in 60% yield (1.16 g).



Scheme 2. Proposed mechanism

Finally, based on our study and previous literatures,[57] a plausible reaction mechanism was proposed (Scheme 2). The reaction started with the oxidation of substrate **1a** to the in-situ generated active Pd(0) species to give a Pd(II) intermediate **I**, which conducted the insertion of norbornene and sequential *ortho* C-H activation to form the palladacycle **III**. Then, the oxidation of **2a** to intermediate **III** would afford a Pd(IV) complex **IV**, which could transform to the aminated palladium complex **VI** via a cascade of reductive elimination and NBE release. At last, the intramolecular C-H activation happened to afford the seven-membered palladacycle **VII**, and the following reductive elimination could furnish the desired product **3aa**, by regenerating the active Pd(0) catalyst.

In conclusion, we have demonstrated an entry for the concise synthesis of a series of functionalized pyrrolophenanthridines enabled by a Catellani strategy from *N*-arylpyrroles and *O*-benzoylhydroxylamines. In this method, various functional groups and kinds of amines are tolerated to accomplish the synthesis of desired products. Moreover, the further investigation of photophysical properties of the synthesized pyrrolophenanthridine products with different kinds of substituents and possible design for the optoelectronic devices are ongoing in our laboratory.

EXPERIMENTAL

$Pd(OAc)_2$ (Energy Chemical) were purchased from above mentioned company and used without additional purification. Other chemical reagents were commercially available and directly used without any further purification.^{1}H-NMR spectra were recorded at 400 MHz and 500 MHz NMR spectrometers using TMS as an internal standard, ^{13}C-NMR spectra were recorded at 100 MHz and 125 MHz NMR spectrometers using TMS as an internal standard, and were fully decoupled by broad band proton decoupling. Data for ^{1}H-NMR are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Mass spectra were obtained on a Bruker Apex IV RTMS.

General procedure for the preparation of substrate 1.

At 0 ℃, we add the tetrahydrofuran (THF) solution of active methylene compound dropwise to the anhydrous THF suspension of sodium hydride. After stirring for 30 min, add dropwise the THF solution of 2-bromoacetophenone. The slower the better in this step. The solution was stirred at 0 ℃ for 2 h and then at room temperature for 8 h. The reaction was quenched with HCl solution and extracted with Et_2O (3×80 mL). The organic layers were combined, dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with PE/EA, to give 1,4-dicarbonyl compound **A**.

Subsequently, 0.1 equivalent of *p*-toluenesulfonic acid was added to the ethanol solution of 1,4-dicarbonyl compound **A** (1.1 equiv) and 2-iodoaniline. After refluxing for 24 h, the solvent was removed in vacuo, the resulting mucus was dissolved in water, and extraction with CH_2Cl_2 for three times, remove excess water with anhydrous sodium sulfate, concentrate and purify by fast silica gel column chromatography (PE/EA) to obtain reaction material **1**.

General procedure for palladium/norbornene catalyzed C-H amination/cyclization cascade of *N*-arylpyrrole. To an oven-dried 25 mL Schlenk tube were added substrate **1** (0.2 mmol), **2** (0.4 mmol), $Pd(OAc)_2$ (0.02 mmol), DPPB (0.04 mmol), NBE (0.4 mmol), Cs_2CO_3 (0.6 mmol), and toluene (2.0 mL). The mixture was stirred in Ar for 12 h at 120 ℃ followed by cooling. The resulting mixture was quenched by filtered through a celite pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using PE/EA as the eluent to afford the product **3**.

Ethyl 3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3aa). White solid. 74% yield; mp: 178-179 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.88-9.86 (m, 1H), 8.01-7.99 (m, 1H), 7.89-7.87 (m, 1H), 7.46-7.34 (m, 4H), 7.14-7.11 (m, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.02-3.96 (m, 4H), 3.29-3.24 (m, 2H), 3.16 (s, 3H), 3.02-2.96 (m, 2H), 1.45 (t, *J* = 6.9 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 166.1, 152.2, 136.8, 133.6, 129.7, 128.4, 127.7, 126.3, 126.2, 126.2, 126.0, 123.0, 117.7, 117.0, 115.1, 114.2, 102.9, 67.2, 60.3, 53.0, 17.1, 14.9. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{25}N_2O_3$ $(M+H)^+$: 389.1860, found: 389.1854.

Ethyl 5-chloro-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ba). White solid. 66% yield; mp: 140-142 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.68-9.66 (m, 1H), 7.96-7.94 (m, 1H), 7.49-7.45 (m, 1H), 7.38-7.33 (m, 3H), 7.00 (d, *J* = 8.6 Hz, 1H), 4.43-4.36 (m, 2H), 4.14-3.87 (m, 4H), 3.37-3.29 (m, 3H), 2.85-2.78 (m, 4H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.5, 148.9, 138.0, 132.0, 130.0, 128.9, 128.7, 126.3, 126.1, 125.7, 124.2, 122.3, 121.8, 119.7, 116.8, 114.7, 104.1, 66.7, 59.9, 55.3, 50.2, 17.0, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{24}ClN_2O_3$ $(M+H)^+$: 423.1470, found: 423.1471.

Ethyl 3,6-dimethyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ca).

White solid. 50% yield; mp: 186-187 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.81-9.79 (m, 1H), 7.99-7.97 (m, 1H), 7.68 (s, 1H), 7.43-7.32 (m, 3H), 6.93 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.02-3.94 (m, 4H), 3.26-3.22 (m, 2H), 3.15 (s, 3H), 3.02-2.93 (m, 2H), 2.49 (s, 3H), 1.45 (t, *J* = 7.2, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.8, 151.6, 137.4, 136.4, 133.0, 129.4, 127.5, 125.9, 125.6, 125.6, 125.5, 116.5, 115.8, 114.8, 114.4, 102.4, 66.9, 59.9, 52.7, 22.0, 16.8, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{25}H_{27}N_2O_3$ $(M+H)^+$: 403.2016, found: 403.2019.

Ethyl 6-methoxy-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3da). White solid. 37% yield; mp: 190-191 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.69-9.67 (m, 1H), 7.98-7.95 (m, 1H), 7.41-7.31 (m, 4H), 6.69 (d, *J* = 2.5 Hz, 1H), 4.40 (q, *J* = 7.1 Hz), 4.01-3.93 (m, 7H), 3.26-3.23 (m, 2H), 3.17 (s, 3H), 2.99-2.91 (m, 2H),1.45 (t, *J* = 7.1Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.7, 158.7, 153.1, 137.4, 132.5, 129.6, 126.9, 126.0, 125.7, 125.0, 124.9, 122.5, 116.8, 110.7, 102.3, 102.3, 98.7, 66.8, 59.9, 55.4, 52.6, 16.6, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{25}H_{27}N_2O_4$ $(M+H)^+$: 419.1965, found: 419.1959.

Ethyl 6-fluoro-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ea). White solid. 56% yield; mp: 175-176 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.71-9.68 (m, 1H), 8.00-7.97 (m, 1H), 7.64-7.61 (m, 1H), 7.45-7.41 (m, 1H), 7.39-7.33 (m, 2H), 6.88-6.85 (m, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.01-3.94 (m, 4H), 3.28-3.24 (m, 2H), 3.16 (s, 3H), 2.98-2.91 (m, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.6, 161.5 (d, *J* = 244.4 Hz), 153.5 (d, *J* = 9.4 Hz), 137.2 (d, *J* = 12.1 Hz), 132.9, 129.4, 127.8, 125.8, 125.4 (d, *J* = 2.9 Hz), 125.2, 122.7, 117.1, 113.5 (d, *J* = 3.3 Hz), 102.7, 102.6, 102.4, 100.6 (d, *J* = 27.2 Hz), 66.6, 60.0, 52.5, 16.5, 14.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.68. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{24}FN_2O_3$ $(M+H)^+$: 407.1765, found: 407.1771.

Ethyl 6-chloro-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3fa).
White solid. 39% yield; mp: 160-161 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.70-9.68 (m, 1H), 7.97-7.95 (m, 1H), 7.81 (d, J = 2.1 Hz, 1H), 7.46-7.42 (m, 1H), 7.38-7.33 (m, 1H), 7.31 (s, 1H), 7.05 (d, J = 2.1 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.97-3.92 (m, 4H), 3.26-3.22 (m, 2H), 3.12 (s, 3H), 2.98-2.91 (m, 2H), 1.45 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.5, 152.5, 136.8, 133.0, 133.0, 129.3, 128.2, 125.8, 125.7, 125.5, 125.1, 122.6, 117.0, 115.8, 115.0, 113.5, 102.8, 66.6, 60.0, 52.4, 16.6, 14.5. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{24}ClN_2O_3$ $(M+H)^+$: 423.1470, found: 423.1474.

Ethyl 3-methyl-8-morpholino-6-(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ga). White solid. 29% yield; mp: 175-177 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.80-9.78 (m, 1H), 8.10 (s, 1H), 8.01-7.99 (m, 1H), 7.52-7.48 (m, 1H), 7.41-7.36 (m, 2H), 7.30 (s, 1H), 4.40 (q, J = 7.1 Hz, 2H), 4.01-3.94 (m, 4H), 3.32-3.29 (m, 2H), 3.15 (s, 3H), 3.06-2.98 (m, 2H), 1.45 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.5, 152.1, 136.2, 133.2, 129.2, 129.1, 128.7 (q, J = 32.6 Hz), 126.4, 125.9, 125.8, 124.8, 123.9 (q, J = 270.7 Hz), 122.8, 120.0, 117.3, 110.6 (q, J = 3.5 Hz), 110.3 (q, J = 4.3 Hz), 103.1, 66.6, 60.1, 52.4, 16.5, 14.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.78. **HRMS** *m/z* (ESI) calcd for $C_{25}H_{24}F_3N_2O_3$ $(M+H)^+$: 457.1734, found: 457.1732.

Ethyl 3,10-dimethyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ja). White solid. 41% yield; mp: 152-153 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.89-7.84 (m, 2H), 7.39-7.35 (m, 1H), 7.28-7.25 (m, 2H), 7.10-7.08 (m, 1H), 4.40 (q, J = 7.1 Hz, 2H), 4.00-3.94 (m, 4H), 3.28-3.24 (m, 2H), 3.14 (s, 3H), 3.03-2.95 (m, 2H), 1.45 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.8, 151.7, 136.5, 135.1, 132.8, 129.5, 129.2, 127.2, 125.8, 125.8, 123.5, 122.5, 117.3, 116.5, 114.6, 113.8, 101.7, 67.0, 59.9, 52.7, 21.9, 16.7, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{25}H_{27}N_2O_3$ $(M+H)^+$: 403.2016, found: 403.2015.

Ethyl 10-fluoro-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ka). White solid. 25% yield; mp: 151-153 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.75-9.71 (m, 1H), 7.95-7.92 (m, 1H), 7.88-7.86 (m, 1H), 7.43 (t, J = 8.3 Hz, 1H), 7.25 (s, 1H), 7.19-7.13 (m, 2H), 4.39 (q, J = 7.2 Hz, 2H), 4.05-3.96 (m, 4H), 3.25-3.21 (m, 2H), 3.13 (s, 3H), 3.04-2.97 (m, 2H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.7, 161.0 (d, J = 240.0 Hz), 152.1, 136.7, 133.0, 128.7, 128.0, 127.3 (d, J = 9.6 Hz), 124.2 (d, J = 8.5 Hz), 122.5 (d, J = 2.2 Hz), 116.7, 116.6 (d, J = 3.0 Hz), 116.1, 115.8, 115.0, 114.0, 111.9, 111.7, 102.0, 66.7, 60.0, 52.8, 16.7, 14.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.15. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{24}FN_2O_3$ $(M+H)^+$: 407.1765, found: 407.1761.

Ethyl 10-chloro-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3la). White solid. 33% yield; mp: 172-173 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.02 (d, 2.2 Hz, 1H), 7.87-7.84 (m, 2H), 7.42 (t, J = 8.2 Hz, 1H), 7.38-7.35 (m, 1H), 7.28 (s, 1H), 7.14-7.11 (m, 1H), 4.39 (q, J = 7.2 Hz, 2H), 4.07-3.96 (m, 4H), 3.23-3.20 (m, 2H), 3.13 (s, 3H), 3.03-2.97 (m, 2H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.6, 152.0, 136.6, 133.4, 131.4, 128.5, 128.0, 128.0, 126.8, 125.6, 124.3, 123.7, 116.8,

116.2, 115.1, 113.9, 66.8, 60.0, 52.7, 16.7, 14.5. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{24}ClN_2O_3$ $(M+H)^+$: 423.1470, found:423.1476.

Ethyl 3-methyl-8-morpholino-10-phenylpyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ma). White solid. 40% yield; mp: 169-171 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.29 (d, J = 1.8 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.89-7.87 (m, 1H), 7.76-7.74 (m, 2H), 7.72-7.69 (m, 1H), 7.54-7.50 (m, 2H), 7.43-7.38 (m, 2H), 7.36 (s, 2H), 7.16-7.14 (m, 1H), 4.41 (q, J = 7.2 Hz, 2H), 3.89-3.76 (m, 4H), 3.28-3.25 (m, 2H), 3.16 (s, 3H), 3.01-2.95 (m, 2H), 1.47 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.7, 152.0, 140.9, 138.1, 136.6, 133.3, 129.1, 129.0, 127.4, 127.3, 126.8, 126.8, 126.1, 124.9, 124.4, 123.1, 117.5, 116.8, 115.0, 114.0, 102.7, 66.8, 60.0, 52.8, 16.8, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{30}H_{29}N_2O_3$ $(M+H)^+$: 465.2173, found: 465.2182.

Ethyl 3,12-dimethyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3na). White solid. 20% yield; mp: 145-146 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.81 (d, J = 7.5 Hz, 1H), 7.73-7.70 (m, 1H), 7.42 (s, 1H), 7.40-7.34 (m, 2H), 7.31-7.27 (m, 1H), 7.08-7.06 (m, 1H), 4.41 (q, J = 7.1 Hz, 2H), 4.00-3.93 (m, 4H), 3.31-3.27 (m, 2H), 3.11 (s, 3H), 3.01-2.93 (m, 2H), 2.82 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.8, 151.1, 135.7, 133.4, 133.0, 131.2, 138.4, 127.7, 127.0, 125.0, 122.9, 117.7, 116.3, 114.2, 113.8, 108.4, 66.8, 59.9, 52.4, 25.1, 16.8, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{25}H_{27}N_2O_3$ $(M+H)^+$: 403.2016, found: 403.2019.

Ethyl 12-fluoro-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3oa). White solid. 33% yield; mp: 148-149 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.71 (d, J = 8.3 Hz, 1H), 7.82-7.80 (m, 1H), 7.58 (d, J = 4.8 Hz, 1H), 7.41 (t, J = 8.2 Hz, 1H), 7.33-7.28 (m, 1H), 7.22-7.17 (m, 1H), 7.12-7.10 (m, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.98-3.92 (m, 4H), 3.26-3.23 (m, 2H), 3.14 (s, 3H), 3.00-2.95 (m, 2H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.7, 158.5 (d, J = 248.3 Hz), 151.8, 136.4, 133.3, 128.5 (d, J = 3.4 Hz), 127.8, 125.5 (d, J = 9.0 Hz), 123.7 (d, J = 2.8 Hz), 121.1 (d, J = 3.6 Hz), 117.1 (d, J = 3.0 Hz), 116.6 (d, J = 2.8 Hz), 115.3 (d, J = 12.4 Hz), 114.7, 114.2 (d, J = 21.1 Hz), 113.9, 108.3 (d, J = 17.6 Hz), 66.8, 60.0, 52.6, 16.7, 14.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.82. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{24}FN_2O_3$ $(M+H)^+$: 407.1765, found: 407.1768.

Ethyl 12-chloro-3-methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3pa). White solid. 25% yield; mp: 168-169 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.88-9.86 (m, 1H), 8.21 (s, 1H), 7.72-7.70 (m, 1H), 7.55-7.53 (m, 1H), 7.40 (t, J = 8.1 Hz, 1H), 7.26 (t, J = 8.1 Hz, 1H), 7.10-7.07 (m, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.98-3.89 (m, 4H), 3.27-3.23 (m, 2H), 3.10 (s, 3H), 3.01-2.94 (m, 2H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.6, 151.3, 135.9, 133.7, 130.7, 129.5, 129.2, 127.8, 126.0, 125.3, 123.6, 116.8, 116.5, 114.5, 113.9, 109.9, 66.8, 60.0, 52.4, 16.8, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{24}H_{24}ClN_2O_3$ $(M+H)^+$: 423.1470, found: 423.1472.

1-(3-Methyl-8-morpholinopyrrolo[1,2-*f*]phenanthridin-2-yl)ethanone (3qa). White solid. 40% yield; mp: 169-170 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.88 (d, J = 8.4 Hz, 1H), 8.00-7.98 (m, 1H), 7.86-7.83 (m, 1H), 7.48-7.44 (m, 1H), 7.42-7.36 (m, 2H), 7.26 (s, 1H), 7.14-7.12 (m, 1H), 4.02-3.95 (m, 4H), 3.28-3.24 (m, 2H), 3.13 (s, 3H), 3.02-2.95 (m, 2H), 2.63 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 196.2, 151.8, 136.1, 132.4, 129.3, 128.1, 127.3, 125.9, 125.9, 125.8, 125.8, 124.4, 122.4, 117.5, 114.9, 114.1, 102.7, 66.8, 52.6, 29.5, 17.2. **HRMS** *m/z* (ESI) calcd for $C_{23}H_{23}N_2O_2$ $(M+H)^+$: 359.1754, found: 359.1750.

Ethyl 13-methyl-4-morpholinobenzo[*i*]pyrrolo[1,2-*f*]phenanthridine-12-carboxylate (3ra). White solid. 18% yield; mp: 151-152 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.83 (d, J = 9.1 Hz, 1H), 9.01 (d, J = 8.5 Hz, 1H), 7.93-7.91 (m, 1H), 7.84-7.75 (m, 3H), 7.70-7.66 (m, 1H), 7.62-7.58 (m, 1H), 7.45 (t, J = 8.1 Hz, 1H), 7.18-7.16 (m, 1H), 4.43 (q, J = 7.1 Hz, 2H), 4.04-3.92 (m, 4H), 3.32-3.17 (m, 5H), 3.00-2.93 (m, 2H), 1.46 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.8, 151.2, 135.2, 133.5, 133.3, 128.8, 128.3, 128.1, 127.3, 126.6, 126.4, 126.2, 125.2, 124.9, 123.6, 122.8, 118.2, 117.0, 115.3, 114.3, 108.1, 66.9, 60.0, 52.7, 16.6, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{28}H_{27}N_2O_3(M+H)^+$: 439.2016, found: 439.2017.

Ethyl 8-(4-(*tert*-butoxycarbonyl)piperazin-1-yl)-3-methylpyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ab). White solid. 41% yield; mp: 196-197 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.86-9.84 (m, 1H), 8.00-7.98 (m, 1H), 7.88-7.86 (m, 1H), 7.45-7.32 (m, 4H), 7.10-7.08 (m, 1H), 4.39 (q, J = 7.1 Hz, 2H), 4.15-4.10 (m, 2H), 3.36-3.30 (m, 2H), 3.15 (s, 3H), 2.82-2.77 (m, 2H), 1.51 (s, 9H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 166.7, 154.9, 151.8, 136.4, 133.1, 129.3, 128.1, 127.3, 126.0, 125.9, 125.8, 125.6, 122.6, 117.5, 116.6, 115.1, 113.9, 102.5, 80.0, 59.9, 52.3, 28.6, 16.8, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{29}H_{34}N_3O_4$ $(M+H)^+$: 488.2544, found: 488.2548.

Ethyl 8-(4-(ethoxycarbonyl)piperidin-1-yl)-3-methylpyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ac). White solid. 32% yield; mp: 153-154 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.82-9.80 (m, 1H), 8.01-7.98 (m, 1H), 7.86-7.84 (m, 1H), 7.46-7.33 (m, 4H), 7.14-7.11 (m, 1H), 4.39 (q, J = 7.1 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.52-3.48 (m, 2H), 3.32-3.09 (m, 4H), 2.76-2.67 (m, 2H), 2.45-2.37 (m, 1H), 2.13-2.03 (m, 4H), 1.45 (t, J = 7.1 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 175.1, 165.8, 152.6, 136.3, 133.1, 129.4, 128.0, 127.1, 126.0, 125.9, 125.8, 125.8, 122.4, 117.7, 116.5, 115.2, 113.7, 102.4, 60.6, 59.9, 52.6, 41.3, 28.5, 16.8, 14.6, 14.3. **HRMS** *m/z* (ESI) calcd for $C_{28}H_{31}N_2O_4$ $(M+H)^+$: 459.2278, found: 459.2276.

Ethyl 3-methyl-8-(piperidin-1-yl)pyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ad). White solid. 23% yield; mp: 79-80 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.90 (d, J = 8.4 Hz, 1H), 8.01-7.99 (m, 1H), 7.83-7.81 (m, 1H), 7.46-7.42 (m, 1H), 7.39-7.36 (m, 3H), 7.15-7.13 (m, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.43-3.39 (m, 2H), 3.15 (s, 3H), 2.73-2.67 (m, 2H), 1.95-1.90 (m, 2H), 1.80-1.75 (m, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.42-1.29 (m, 2H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.9, 153.4, 136.2, 133.0, 129.4, 127.8, 127.1, 126.3, 126.1,

125.6, 125.6, 122.3, 127.6, 116.5, 115.2, 113.2, 102.2, 59.9, 53.9, 26.0, 24.1, 16.7, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{25}H_{27}N_2O_2$ $(M+H)^+$: 387.2067, found: 387.2073.

Ethyl 8-(azepan-1-yl)-3-methylpyrrolo[1,2-*f*]phenanthridine-2-carboxylate (3ae). White solid. 11% yield; mp: 76-77 ℃; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.21-9.19 (m, 1H), 7.98-7.96 (m, 1H), 7.70-7.68 (m, 1H), 7.43-7.39 (m, 1H), 7.36-7.31 (m, 3H), 7.19-7.16 (m, 1H), 4.39 (q, J = 7.1 Hz, 2H), 3.52-3.46 (m, 2H), 3.38-3.32 (m, 2H), 3.14 (s, 3H), 1.82-1.67 (m, 8H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.9, 152.8, 136.2, 133.0, 129.4, 127.3, 126.8, 126.5, 125.7, 125.4, 125.4, 122.3, 116.8, 116.5, 116.3, 111.9, 102.2, 59.8, 55.3, 28.5, 28.5, 16.5, 14.6. **HRMS** *m/z* (ESI) calcd for $C_{26}H_{29}N_2O_2$ $(M+H)^+$: 401.2224, found: 401.2229.

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