



HAL
open science

One-Pot Synthesis of Pyrrolo[1,2-f]phenanthridines From 1-Arylpyrroles via Successive Palladium-Catalyzed Direct Arylations

Jian Zhang, Xinzhe Shi, Henri Doucet

► **To cite this version:**

Jian Zhang, Xinzhe Shi, Henri Doucet. One-Pot Synthesis of Pyrrolo[1,2-f]phenanthridines From 1-Arylpyrroles via Successive Palladium-Catalyzed Direct Arylations. *European Journal of Organic Chemistry*, 2021, 2021 (35), pp.4974-4983. 10.1002/ejoc.202100766 . hal-03414079

HAL Id: hal-03414079

<https://hal.science/hal-03414079>

Submitted on 10 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

One pot synthesis of pyrrolo[1,2-*f*]phenanthridines from 1-arylpyrroles *via* successive palladium-catalyzed direct arylations

Jian Zhang,^[a] Xinzhe Shi,^[a] and Henri Doucet*^[a]

[a] Mr J. Zhang, Dr. X. Shi, Dr. H. Doucet
Univ Rennes, CNRS, ISCR-UMR 6226
F-35000 Rennes
France
E-mail: henri.doucet@univ-rennes1.fr

Supporting information for this article is given via a link at the end of the document.

Abstract: The Pd-catalyzed annulative π -extension reaction of 1-arylpyrroles using 1,2-dihalobenzenes as the coupling partners was investigated. The higher reactivity of pyrrole C2-H bond compared to C-H bonds of the aryl unit of 1-arylpyrroles allows the selective synthesis of pyrrolo[1,2-*f*]phenanthridines *via* successive palladium-catalyzed direct intermolecular followed by intramolecular direct arylation steps. From 1-bromo-2-iodobenzenes bearing substituents at C4- or C5-positions and *ortho*-, *meta*- or *para*-substituted 1-arylpyrroles, the access to pyrrolo[1,2-*f*]phenanthridines containing substituents at C5, C6, C7, C8, C10 and/or C11 positions is possible.

Introduction

Pyrrolo[1,2-*a*]quinoline derivatives including pyrrolo[1,2-*f*]phenanthridine units (Fig. 1), have a wide range of applications in organic functional materials or pharmaceuticals.^[1] Therefore, the discovery of simple, but general routes to pyrrolo[1,2-*f*]phenanthridine allowing to introduce useful functional groups at the desired positions has potential for both organic material and pharmaceutical chemistry.

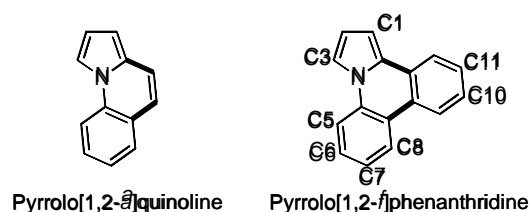
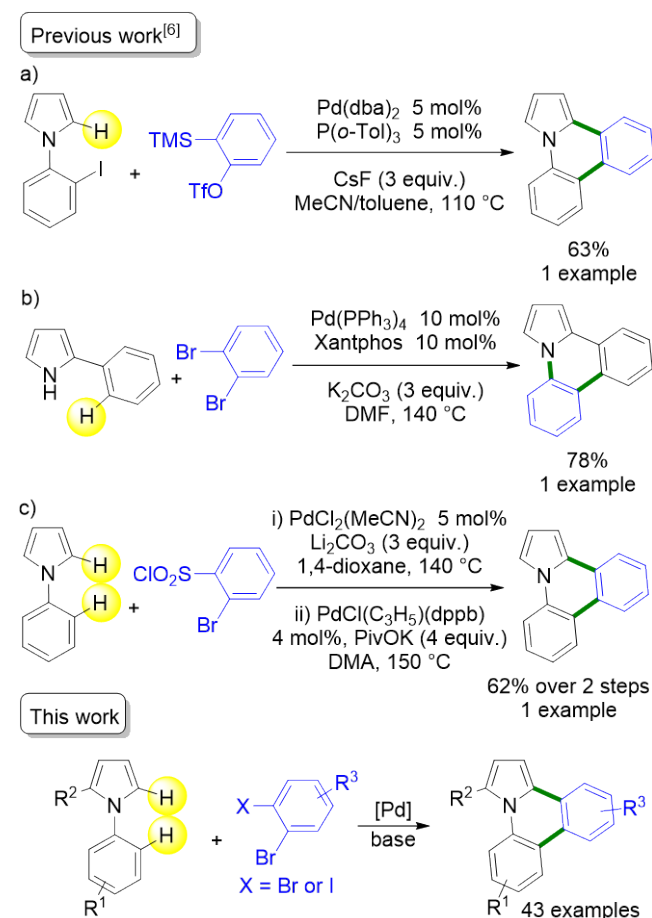


Figure 1. Structures of pyrrolo[1,2-*a*]quinoline and pyrrolo[1,2-*f*]phenanthridine.

Over the past two decades, the Pd-catalyzed arylation of a wide variety of 5-membered heteroarenes *via* a C-H bond activation step led to a revolution in the preparation of bi(hetero)aryls.^[2] In addition, this methodology represents a convenient method to build π -extended (hetero)polyaromatic structures by combining palladium-catalyzed intermolecular C-H arylation with an intramolecular C-H arylation. Such one pot successive couplings are very attractive, compared to the more classical methods to prepare π -extended (hetero)polyaromatic, as they do not require the preliminary synthesis of organometallic derivatives.^[3,4]

Several examples of Pd-catalyzed arylations at the C2/C5-positions of pyrroles *via* a C-H bond functionalization have been described.^[5] However, to the best of our knowledge, only a few examples of preparation of pyrrolo[1,2-*f*]phenanthridines from

pyrroles *via* C-H bond functionalization steps have been reported.^[6,7] In 2007, Liu and Larock prepared pyrrolo[1,2-*f*]phenanthridine in 63% yield from 1-(2-iodophenyl)pyrrole and 2-(trimethylsilyl)phenyltrifluoromethanesulfonate using a Pd-catalyst (Scheme 1, a).^[6a] In 2013, the use of 2-phenylpyrrole and 1,2-dibromobenzene as the reaction partners with 10 mol% Pd(PPh₃)₄/Xantphos catalyst allowed to prepare pyrrolo[1,2-*f*]phenanthridine in 78% yield (Scheme 1, b).^[6b] Two years later, our group described the use of 2-bromobenzenesulfonyl chloride as the aryl source for the two steps Pd-catalyzed preparation of pyrrolo[1,2-*f*]phenanthridine (Scheme 1, c).^[6c] It should be mentioned that with this three methods, no examples of preparation of substituted pyrrolo[1,2-*f*]phenanthridines were reported.



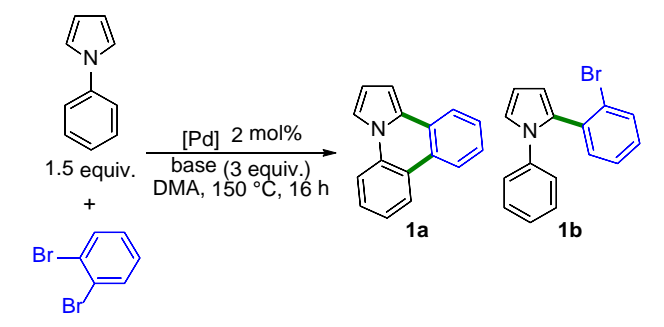
Scheme 1. Metal-catalyzed direct arylation for the synthesis of pyrrolo[1,2-*f*]phenanthridines.

As the discovery of an effective method, for the synthesis of pyrrolo[1,2-*f*]phenanthridine containing useful functional groups at the desired positions, especially using easily available substrates, catalyst and base is highly desirable, the annulative π -extension of diversely functionalized 1-arylpyrroles by 1,2-dihalobenzenes in the presence of palladium catalysts needed to be investigated. Here, we report (i) conditions for the one pot synthesis of pyrrolo[1,2-*f*]phenanthridine from 1-arylpyrroles and 1,2-dihalobenzenes *via* successive palladium-catalyzed direct arylations; (ii) on the regioselectivity of the intramolecular C-H arylation with *meta*-substituted 1-arylpyrroles and (iii) on the functional group tolerance on both coupling partners.

Results and Discussion

1-Phenylpyrrole (1.5 equiv.) and 1,2-dibromobenzene (1 equiv.) were employed as model substrates for our study (Table 1). We initially examined the influence of the nature of the base on the products distribution using 2 mol% Pd(OAc)₂ catalyst and DMA as the solvent. We had previously observed that this catalyst precursor associated with this solvent was very effective to promote the coupling of several heteroarenes with aryl bromides.^[6] Cs₂CO₃ or K₂CO₃ were completely ineffective bases, and NaOAc or CsOAc gave the desired product **1a** in trace amount (Table 1, entries 1-4). By contrast, the use of KOAc afforded **1a** in higher yields of 61-63%. This difference might arise from the dual role of the base for such reactions which certainly proceed *via* a concerted metalation deprotonation pathway, as the base is also a ligand which promotes the C-H bond cleavage.^[9] With KOAc base, a complete conversion of 1,2-dibromobenzene was observed, but the product **1b** was also obtained in low yield when the reaction was stopped after 6 h (Table 1, entry 5). The use of longer reaction times (16 or 48 h) gave **1a** with very high or complete conversion (Table 1, entries 6 and 7). PivOK was found to be a less effective base for this reaction, as **1a** was obtained in only 22% yield (Table 1, entry 8). A palladium catalyst bearing a diphosphine ligand gave **1a** in similar yield (Table 1, entry 9).^[10] The use of DMF or NMP as solvents did not allowed to improve the yield in **1a**; whereas xylene only gave product **1b** in trace amount (Table 1, entries 10-12). A reaction performed with only 1 equiv. of KOAc led to a **1a**:**1b** ratio of 62:38 with a large amount of unreacted 1,2-dibromobenzene revealing that the intramolecular arylation step is quite fast compared to the intermolecular arylation (Table 1, entry 13). The use of 120 °C instead of 150 °C as the reaction temperature gave **1a** in a lower yield due to a partial conversion of the 1,2-dibromobenzene (Table 1, entry 14). When we employed 1-bromo-2-iodobenzene instead of 1,2-dibromobenzene afforded **1a** and **1b** with a similar ratio and reaction yield (Table 1, entry 15); whereas, no formation of 2-(2-iodophenyl)-1-phenylpyrrole intermediate was detected by GC/MS analysis of the crude mixture.

Table 1. Influence of the reaction conditions on the Pd-catalyzed reaction of 1-phenylpyrrole with 1,2-dibromobenzene.^[a]

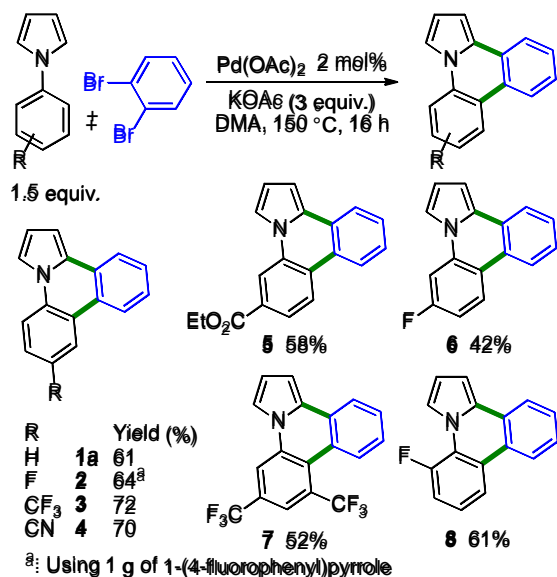


Entry	Catalyst	Solvent	Base	Ratio 1a : 1b	Yield in 1a (%)
1	Pd(OAc) ₂	DMA	Cs ₂ CO ₃	nd	0
2	Pd(OAc) ₂	DMA	K ₂ CO ₃	nd	0
3	Pd(OAc) ₂	DMA	NaOAc	54:46	<12
4	Pd(OAc) ₂	DMA	CsOAc	66:34	<3
5	Pd(OAc) ₂	DMA	KOAc	92:8	57 ^[b]
6	Pd(OAc) ₂	DMA	KOAc	96:4	61
7	Pd(OAc) ₂	DMA	KOAc	100:0	63 ^[c]
8	Pd(OAc) ₂	DMA	KOPiv	63:37	22
9	PdCl(C ₃ H ₅)(dppb)	DMA	KOAc	91:9	58
10	Pd(OAc) ₂	DMF	KOAc	69:31	52
11	Pd(OAc) ₂	NMP	KOAc	84:16	60
12	Pd(OAc) ₂	xylene	KOAc	0:100	0
13	Pd(OAc) ₂	DMA	KOAc ^[d]	62:38	nd
14	Pd(OAc) ₂	DMA	KOAc	80:20	41 ^[e]
15	Pd(OAc) ₂	DMA	KOAc	95:5	60 ^[f]

[a] [Pd] (0.02 equiv.), 1-phenylpyrrole (1.5 equiv.), 1,2-dibromobenzene (1 equiv.), base (3 equiv.), 16 h, 150 °C, isolated yields. [b] 6 h, [c] 48 h. [d] KOAc (1 equiv.). [e] Reaction performed at 120 °C. [f] Reaction performed with 1-bromo-2-iodobenzene instead of 1,2-dibromobenzene.

Then, 1,2-dibromobenzene was coupled with a set of 1-arylpyrroles in the presence of 2 mol% Pd(OAc)₂, KOAc as the base in DMA (Scheme 2). A fluoro-*para*-substituent on the 1-arylpyrrole was well tolerated giving rise to the C7-fluoro-substituted pyrrolo[1,2-*f*]phenanthridine **2** in 64% yield. Good yields in the expected pyrrolo[1,2-*f*]phenanthridines **3** and **4** were also obtained with trifluoromethyl and nitrile *para*-substituted 1-arylpyrroles. Conversely, the use of the electron-donating NMe₂ *para*-substituent on 1-arylpyrrole gave no trace of the desired pyrrolo[1,2-*f*]phenanthridine. Then, the regioselectivity of the reaction of 1-arylpyrroles containing ester or fluoro-substituents at *meta*-position was investigated. In both cases, the annulation reaction occurred regioselectively at the less hindered position of the *meta*-substituted aryl ring providing the C6-substituted pyrrolo[1,2-*f*]phenanthridines **5** and **6** in 58% and 42% yield, respectively. With 1-(3,5-bis(trifluoromethyl)phenyl)pyrrole, the desired 6,8-

bis(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine **7** was obtained in 52% yield. Finally, an *ortho*-substituted 1-arylpyrrole were employed. 1-(2-Fluorophenyl)pyrrole and 1,2-dibromobenzene gave 5-fluoropyrrolo[1,2-*f*]phenanthridine **8** in 61% yield.



Scheme 2. Scope of the pyrrole *N*-aryl substituent.

The one pot synthesis of C10-substituted pyrrolo[1,2-*f*]phenanthridines from 4-substituted 2-bromo-1-iodobenzenes was then examined (Scheme 3). The use of 4-substituted 2-bromo-1-iodobenzene reagents allows to selectively introduce a substituent at the C10-position of the pyrrolo[1,2-*f*]phenanthridines, as the oxidative addition of 2-bromo-1-iodobenzenes to palladium is generally faster for the C-I bond than for the C-Br bond. The first step involves intermolecular C-I/pyrrole-C2-H bond coupling (Fig. 2). Oxidative addition of the 2-bromo-1-iodobenzenes gives intermediate **A**. Then, after a concerted metallation deprotonation, the complex **C** is obtained. Reductive elimination affords the 2-(2-bromoaryl)-1-arylpyrrole **b**. This first catalytic cycle is followed by a second one which involves an intramolecular C-Br/C-H bond coupling of the pyrrolyl aryl ring to give the pyrrolo[1,2-*f*]phenanthridines **a**.

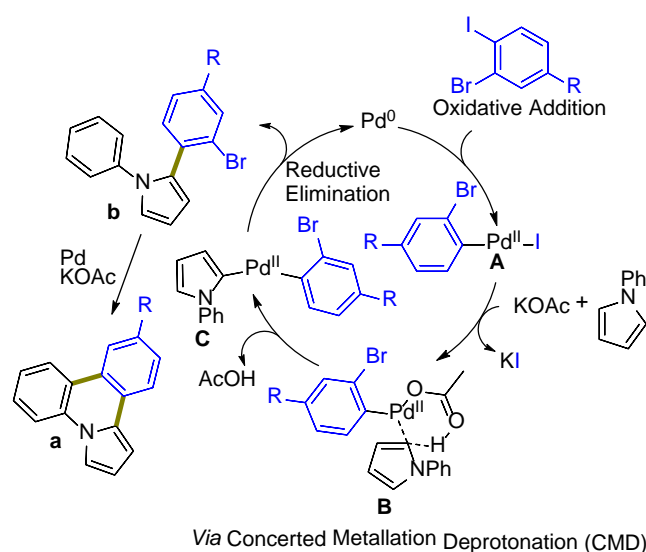
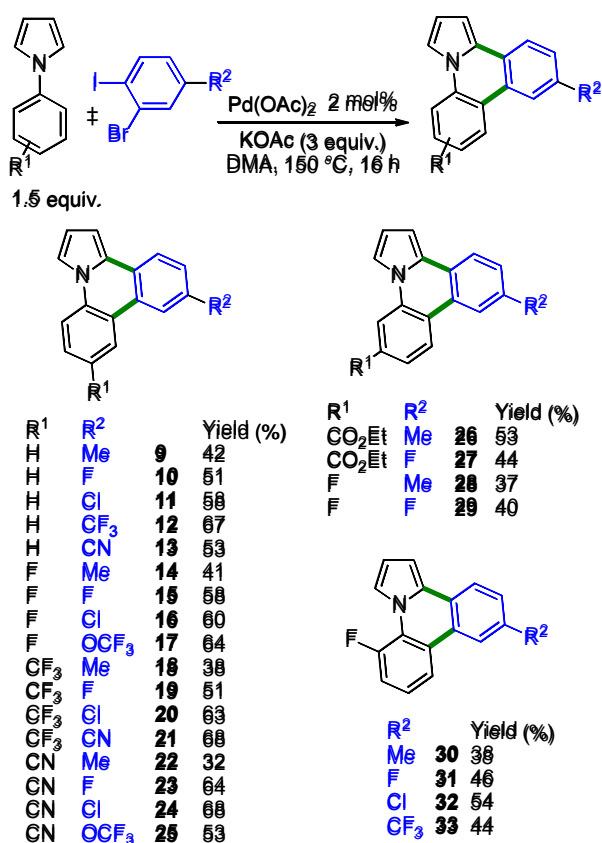


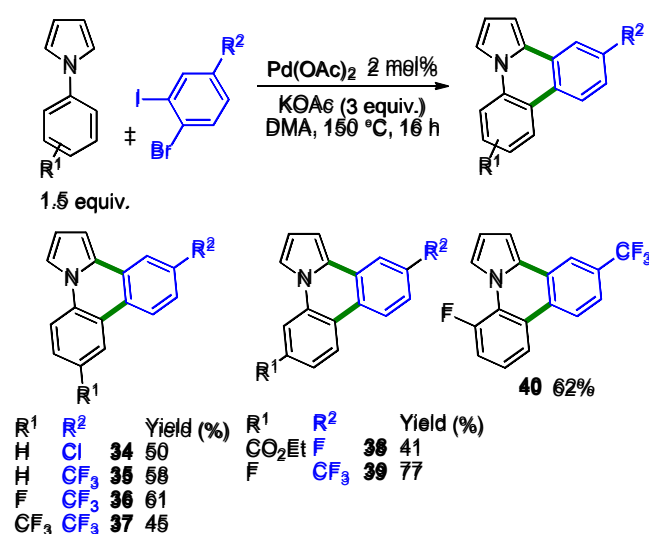
Figure 2. Plausible mechanism.

2-Bromo-1-iodobenzenes bearing methyl, fluoro, chloro, trifluoromethyl or nitrile C4-substituents using 1-phenylpyrrole as the reaction partner gave the corresponding C10-substituted pyrrolo[1,2-*f*]phenanthridines **9-13** in 42-67% yields (Scheme 3). For the reaction with 2-bromo-4-chloro-1-iodobenzene, the C-Cl bond remained untouched potentially allowing for further functionalizations. These 4-substituted 2-bromo-1-iodobenzenes were also reacted with 1-arylpyrroles bearing fluoro, trifluoromethyl or nitrile groups at *para*-position in order to prepare pyrrolo[1,2-*f*]phenanthridines with functional groups at both C7 and C10 positions. In all cases, the desired compounds **14-25** were obtained in moderate to good yields. For example, 10-chloropyrrolo[1,2-*f*]phenanthridine-7-carbonitrile **24** which contain the synthetically useful chloro and nitrile substituents was obtained in 68% yield. Then, the regioselectivity of the intramolecular arylation reaction with *meta*-substituted 1-arylpyrroles was examined. Again, from both ester- and fluoro-*meta*-substituted 1-arylpyrroles, the annulation reaction occurred regioselectively at the less hindered position of the aryl ring, providing the C6,C10-disubstituted pyrrolo[1,2-*f*]phenanthridines **26-29** in moderate yields. From 1-(2-fluorophenyl)pyrrole and a variety of 4-substituted 2-bromo-1-iodobenzenes, the preparation to the pyrrolo[1,2-*f*]phenanthridines **30-33** containing substituents at C5 and C10 was also successful.



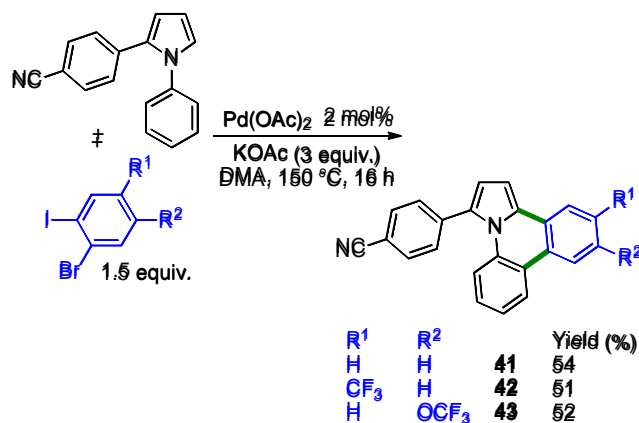
Scheme 3. Scope of the reaction with 4-substituted 2-bromo-1-iodobenzenes.

Then, in order to prepare pyrrolo[1,2-*f*]phenanthridines with a substituent at C11-position, the reactivity of 5-substituted 2-bromo-1-iodobenzenes was studied (Scheme 4). Similar yields compared with the 4-substituted 2-bromo-1-iodobenzenes were obtained, and using 1-phenylpyrrole, the pyrrolo[1,2-*f*]phenanthridines **34** and **35** containing chloro or trifluoromethyl C11-substituents were obtained in 50% and 58% yield, respectively. From these 5-substituted 2-bromo-1-iodobenzenes, we also prepared pyrrolo[1,2-*f*]phenanthridines containing substituents at C7,C11-positions (products **36** and **37**), C6,C11-positions (products **38** and **39**), and C5,C11-positions (product **40**) demonstrating the potential of this methodology to introduce the desired substituents at the appropriate position.



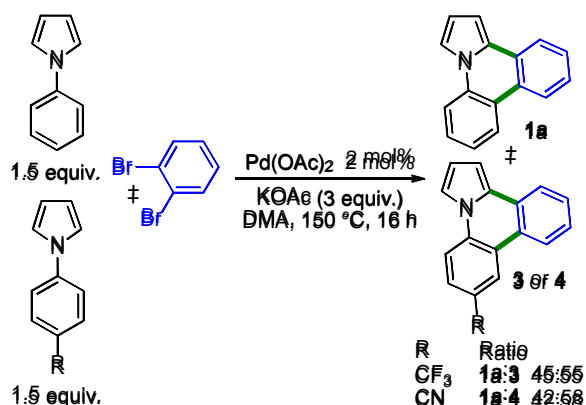
Scheme 4. Scope of the reaction with 5-substituted 2-bromo-1-iodobenzenes.

The reaction is not limited to the use of unsubstituted 1-arylpyrroles. The reaction of 1-phenylpyrrole bearing a benzonitrile substituent at C2-position with 1,2-dibromobenzene and substituted 2-bromo-1-iodobenzenes was also studied (Scheme 5). As expected, a regioselective arylation at C5-position of the pyrrole ring was observed affording after the intramolecular arylation, the corresponding pyrrolo[1,2-*f*]phenanthridines **41-43** bearing a benzonitrile at the C3-position. In addition, compounds **42** and **43** contain OCF₃ or CF₃ substituents at C10 or C11-positions.

Scheme 5. Scope of the pyrrole *N*-aryl substituent.

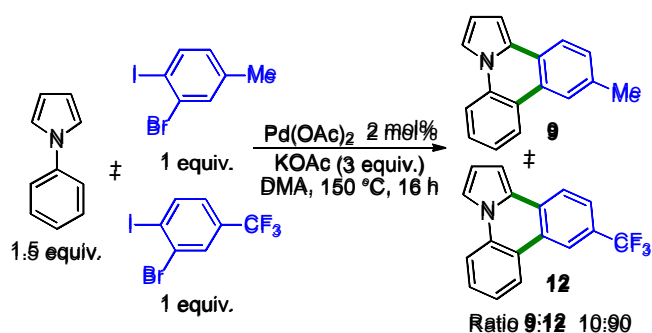
We performed two competition reactions to probe the substitution preference on the aryl ring of 1-arylpyrroles for this synthetic pathway (Scheme 6). From an equimolar mixture of 1-phenylpyrrole and 1-(4-(trifluoromethyl)phenyl)pyrrole using 1,2-dibromobenzene as the aryl source, in the presence of 2 mol% Pd(OAc)₂ associated to KOAc as base, the formation of the pyrrolo[1,2-*f*]phenanthridines **1a** and **3** in 45:55 ratio was obtained. A similar trend was observed using 1-phenylpyrrole and 4-(pyrrol-1-yl)benzonitrile, with the formation of **1a** and **4** in

42:58 ratio. These results indicate that the presence of an electron-withdrawing substituent on the aryl ring of 1-arylpyrrole has a positive effect, even if this effect is not very significant.



Scheme 6. Competition reactions to probe the substitution preference.

Finally, a competition reaction using an equimolar mixture of 4-methyl- and 4-trifluoromethyl-substituted 1-iodo-2-bromobenzenes using 1-phenylpyrrole (1.5 equiv.) in the presence of 2 mol% Pd(OAc)₂ associated to KOAc gave the products **9** and **12** in 10:90 ratio (Scheme 7). This result is consistent with a faster oxidative addition of 2-bromo-1-iodo-4-(trifluoromethyl)benzene than 2-bromo-1-iodo-4-methylbenzene to palladium.



Scheme 7. Competition reactions to probe the substitution preference.

Conclusion

In summary, we demonstrated that using a Pd-catalyzed intermolecular associated to intramolecular double C–H bond arylation of 1-arylpyrroles, a wide variety of the π -extended pyrrolo[1,2-*f*]phenanthridines can be obtained with high regioselectivities and good yields. This procedure tolerates a variety of useful substituents on the 1-arylpyrrole and aryl dihalide. Therefore, with this inedited synthetic scheme, the introduction of desired functional groups at positions 5, 6, 7, 8, 10 and 11 of pyrrolo[1,2-*f*]phenanthridines is possible. Our procedure employs commercially available compounds and only 2 mol% of easily available Pd(OAc)₂ catalyst precursor and KOAc as inexpensive base. Such simple reaction conditions should be very attractive for synthetic chemists, giving a robust access to pyrrolo[1,2-*f*]phenanthridines.

Experimental Section

General procedure for palladium-catalyzed synthesis of pyrrolo[1,2-*f*]phenanthridines:

The reaction of the aryl dihalide (1 mmol), 1-arylpyrrole (1.5 mmol) and KOAc (0.294 g, 3 mmol) in the presence of Pd(OAc)₂ (2.4 mg, 0.02 mmol) at 150 °C during 16 h in DMA (4 mL) under argon affords the coupling products **1a** and **2-43** after evaporation of the solvent and purification on silica gel. Eluent heptane for compounds **1a**, **1b**, **2**, **7**, **9-11**, **28**, **29**, **34**. Eluent heptane:ethyl acetate 95:5 for compounds **3**, **12**, **18-20**, **39**. Eluent heptane:ethyl acetate 9:1 for compounds **4**, **5**, **13**, **17**, **21-24**, **25**, **26**, **27**, **38**, **41-43**. Eluent heptane:ethyl acetate 99:1 for compound **6**. Eluent heptane:CH₂Cl₂ 95:5 for compounds **8**, **14-16**, **30-33**, **35-37**, **40**. HRMS (ESI) were performed using a Bruker Maxis 4G apparatus.

Pyrrolo[1,2-*f*]phenanthridine (1a)^[6a] From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 1,2-dibromobenzene (0.236 g, 1 mmol), product **1a** was obtained in 61% yield (0.132 g) as a white solid: mp 152–154 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.36 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.28 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.81 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.58–7.38 (m, 4H), 6.99 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.76 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 133.2, 129.3, 128.5, 128.1, 126.3, 126.0, 124.8, 124.0, 123.9, 122.8, 122.5, 121.7, 115.0, 113.1, 112.2, 102.0. HRMS calcd for [M+H]⁺ C₁₆H₁₂N 218.0964, found: 218.0966. Intermediate **1b** was also isolated in an impure form:^[11] ¹H NMR (400 MHz, CDCl₃): 7.53 (d, *J* = 7.0 Hz, 1H), 7.30–7.15 (m, 5H), 7.13–7.08 (m, 3H), 7.02 (dd, *J* = 2.0, 2.5 Hz, 1H), 6.45–6.40 (m, 2H).

7-Fluoropyrrolo[1,2-*f*]phenanthridine (2) From 1-(4-fluorophenyl)pyrrole (1 g, 6.2 mmol) and 1,2-dibromobenzene (0.975 g, 4.1 mmol) and KOAc (1.214 g, 12.4 mmol) in the presence of Pd(OAc)₂ (9.9 mg, 0.083 mmol) product **2** was obtained in 64% yield (0.620 g) as a yellow solid: mp 118–120 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 8.1 Hz, 1H), 8.00 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.95 (dd, *J* = 7.3, 2.8 Hz, 1H), 7.77 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.72–7.69 (m, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.24–7.19 (m, 1H), 6.96 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.74 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 159.4 (d, *J* = 242.0 Hz), 129.7 (d, *J* = 2.2 Hz), 129.0, 128.7, 126.6, 126.0, 124.0 (d, *J* = 2.8 Hz), 123.4 (d, *J* = 7.8 Hz), 122.8, 122.7, 116.4 (d, *J* = 8.6 Hz), 115.8 (d, *J* = 23.9 Hz), 113.1, 112.2, 109.8 (d, *J* = 23.8 Hz), 102.2. HRMS calcd for [M+H]⁺ C₁₆H₁₁FN 236.0870, found: 236.0870.

7-(Trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (3) From 1-(4-(trifluoromethyl)phenyl)pyrrole (0.317 g, 1.5 mmol) and 1,2-dibromobenzene (0.236 g, 1 mmol), product **3** was obtained in 72% yield (0.205 g) as a yellow solid: mp 138–140 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.58 (s, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.02 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.79 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.76 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.80 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 135.2, 129.5, 129.0, 126.5, 126.3, 125.8 (q, *J* = 32.5 Hz), 125.0 (q, *J* = 3.5 Hz), 124.2 (q, *J* = 271.8 Hz), 123.8, 122.9, 122.6, 121.8, 121.4 (q, *J* = 4.0 Hz), 115.5, 113.6, 113.1, 102.9. HRMS calcd for [M+H]⁺ C₁₇H₁₁F₃N 286.0838, found: 286.0841.

Pyrrolo[1,2-*f*]phenanthridine-7-carbonitrile (4) From 4-(pyrrol-1-yl)benzotrile (0.252, 1.5 mmol) and 1,2-dibromobenzene (0.236 g, 1 mmol), product **4** was obtained in 70% yield (0.169 g) as a yellow solid: mp 78–80 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.59 (s, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.78 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.75–7.65 (m, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 3.8 Hz, 1H), 6.81 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 135.7, 131.2, 129.5, 129.4, 128.7, 126.6, 126.5, 123.1, 123.0, 122.5, 122.4, 118.9, 115.8, 113.8 (m), 107.3, 103.4. HRMS calcd for [M+H]⁺ C₁₇H₁₁N₂ 243.0917, found: 243.0922.

Ethyl pyrrolo[1,2-*f*]phenanthridine-6-carboxylate (5)⁷¹ From ethyl 3-(pyrrol-1-yl)benzoate (0.322 g, 1.5 mmol) and 1,2-dibromobenzene (0.236 g, 1 mmol), product **5** was obtained in 58% yield (0.168 g) as a white solid: mp 132-134 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 8.02-7.94 (m, 2H), 7.86 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 6.96 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.76 (t, *J* = 3.5 Hz, 1H), 4.49 (q, *J* = 7.6 Hz, 2H), 1.50 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 132.9, 129.9, 129.1, 127.1, 126.0, 125.5, 124.3, 123.9, 123.8, 123.1, 122.8, 116.3, 113.7, 112.5, 102.5, 61.4, 14.4. HRMS calcd for [M+H]⁺ C₁₉H₁₆NO₂ 290.1175, found: 290.1173.

6-Fluoropyrrolo[1,2-*f*]phenanthridine (6) From 1-(3-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 1,2-dibromobenzene (0.236 g, 1 mmol), product **6** was obtained in 42% yield (0.099 g) as a yellow solid: mp 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.74 (ddd, *J* = 8.3, 3.0, 1.2 Hz, 1H), 8.07 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.76 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.56-7.40 (m, 3H), 7.13 (dd, *J* = 13.0, 8.1 Hz, 1H), 6.99 (dd, *J* = 4.3, 1.3 Hz, 1H), 6.77 (t, *J* = 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.9 (d, *J* = 252.1 Hz), 135.1 (d, *J* = 7.1 Hz), 129.5, 128.5 (d, *J* = 11.5 Hz), 128.3 (d, *J* = 2.2 Hz), 127.6 (d, *J* = 26.1 Hz), 126.5, 126.4 (d, *J* = 2.7 Hz), 122.7 (d, *J* = 5.0 Hz), 122.5, 113.5, 112.8, 111.5, 111.4 (d, *J* = 25.4 Hz), 110.8 (d, *J* = 3.4 Hz), 102.2. HRMS calcd for [M+H]⁺ C₁₆H₁₁FN 236.0870, found: 236.0870.

6,8-Bis(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (7) From 1-(3,5-bis(trifluoromethyl)phenyl)pyrrole (0.418 g, 1.5 mmol) and 1,2-dibromobenzene (0.236 g, 1 mmol), product **7** was obtained in 52% yield (0.183 g) as a white solid: mp 160-162 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 8.02 (s, 1H), 7.82-7.78 (m, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.81 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 144.0, 135.2, 131.8, 130.2, 130.1-128.0 (m), 125.7, 125.1 (q, *J* = 271.0 Hz), 125.0 (q, *J* = 271.0 Hz), 122.9, 120.4 (m), 115.4, 113.9, 103.2. HRMS calcd for [M+H]⁺ C₁₈H₁₀F₆N 354.0712, found: 354.0711.

5-Fluoropyrrolo[1,2-*f*]phenanthridine (8) From 1-(2-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 1,2-dibromobenzene (0.236 g, 1 mmol), product **8** was obtained in 61% yield (0.143 g) as a white solid: mp 102-104 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.22 (dd, *J* = 3.0, 1.5 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.14-8.09 (m, 1H), 8.02 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.34-7.26 (m, 2H), 7.02 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.77 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 153.2 (d, *J* = 247.0 Hz), 129.5, 128.7, 126.6, 126.0, 125.0 (d, *J* = 2.3 Hz), 124.0 (d, *J* = 2.6 Hz), 123.4 (d, *J* = 8.8 Hz), 122.9, 122.8, 119.6, 119.4, 119.2 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 22.3 Hz), 112.1 (d, *J* = 4.9 Hz), 101.7 (d, *J* = 1.6 Hz). HRMS calcd for [M+H]⁺ C₁₆H₁₁FN 236.0870, found: 236.0870.

10-Methylpyrrolo[1,2-*f*]phenanthridine (9) From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 2-bromo-1-iodo-4-methylbenzene (0.297 g, 1 mmol), product **9** was obtained in 42% yield (0.097 g) as a white solid: mp 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.33 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.06 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.76 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 9.0, 1.5 Hz, 1H), 6.90 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.72 (dd, *J* = 3.8, 3.0 Hz, 1H), 2.52 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 135.5, 133.3, 129.5, 129.4, 128.4, 124.8, 124.0, 123.9, 123.7, 122.8, 122.6, 121.7, 115.0, 112.7, 112.1, 101.3, 21.8. HRMS calcd for [M+H]⁺ C₁₇H₁₄N 232.1121, found: 232.1123.

10-Fluoropyrrolo[1,2-*f*]phenanthridine (10) From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **10** was obtained in 51% yield (0.120 g) as a white solid: mp 120-122 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.24 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.00 (dd, *J* = 8.7, 5.7 Hz, 1H), 7.94-7.86 (m, 2H), 7.79 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.58 (td, *J* = 7.1, 1.4 Hz, 1H), 7.41 (td, *J* = 7.3, 1.2 Hz, 1H), 7.23 (td, *J* = 8.6, 2.5 Hz, 1H), 6.92 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.75 (dd, *J* =

3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.3 (d, *J* = 244.0 Hz), 133.5, 129.3, 128.8, 126.7 (d, *J* = 7.9 Hz), 124.7 (d, *J* = 8.4 Hz), 124.2, 123.9, 122.9 (d, *J* = 2.4 Hz), 121.0 (d, *J* = 3.2 Hz), 116.2 (d, *J* = 23.1 Hz), 115.1, 112.9, 112.3, 108.5 (d, *J* = 23.1 Hz), 101.6. HRMS calcd for [M]⁺ C₁₆H₁₁FN 235.0792, found: 235.0791.

10-Chloropyrrolo[1,2-*f*]phenanthridine (11) From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 2-bromo-4-chloro-1-iodobenzene (0.317 g, 1 mmol), product **11** was obtained in 58% yield (0.146 g) as a yellow solid: mp 120-122 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.28 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.80 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.48-7.38 (m, 2H), 6.96 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.76 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 133.4, 131.7, 129.2, 128.6, 128.3, 126.3, 124.8, 124.2, 124.1, 124.0, 122.4, 120.6, 115.1, 113.4, 112.4, 102.4. HRMS calcd for [M+H]⁺ C₁₆H₁₁ClN 252.0574, found: 252.0576.

10-(Trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (12) From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 2-bromo-1-iodo-4-(trifluoromethyl)benzene (0.350 g, 1 mmol), product **12** was obtained in 67% yield (0.191 g) as a white solid: mp 150-152 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (s, 1H), 8.35 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.84 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.70 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.59 (td, *J* = 8.0, 2.0 Hz, 1H), 7.44 (td, *J* = 8.0, 1.2 Hz, 1H), 7.08 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.79 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 133.3, 129.4, 128.8, 128.2, 127.5 (q, *J* = 32.5 Hz), 124.7, 124.3 (q, *J* = 3.5 Hz), 124.2 (q, *J* = 271.8 Hz), 124.1, 124.0, 123.2, 120.8, 119.8 (q, *J* = 4.2 Hz), 115.1, 114.2, 112.7, 103.9. HRMS calcd for [M]⁺ C₁₇H₁₀F₃N 285.0760, found: 285.0763.

Pyrrrolo[1,2-*f*]phenanthridine-10-carbonitrile (13) From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 3-bromo-4-iodobenzonitrile (0.308 g, 1 mmol), product **13** was obtained in 53% yield (0.128 g) as a white solid: mp 190-192 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (s, 1H), 8.20 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.87-7.80 (m, 2H), 7.64-7.55 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.80 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 133.2, 130.2, 129.7, 129.2, 127.7, 127.2, 124.9, 124.4, 123.9, 123.2, 119.9, 119.4, 115.1, 114.9, 113.0, 108.7, 105.0. HRMS calcd for [M]⁺ C₁₇H₁₀N₂ 242.0838, found: 242.0843.

7-Fluoro-10-methylpyrrolo[1,2-*f*]phenanthridine (14) From 1-(4-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-4-methylbenzene (0.297 g, 1 mmol), product **14** was obtained in 41% yield (0.102 g) as a white solid: mp 77-79 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (dd, *J* = 10.3, 2.8 Hz, 1H), 7.94 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.82 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.71 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.26-7.20 (m, 1H), 6.92 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.73 (t, *J* = 3.5 Hz, 1H), 2.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 159.4 (d, *J* = 242.0 Hz), 135.7, 130.1, 129.8 (d, *J* = 2.1 Hz), 129.2, 124.3, 124.1 (d, *J* = 2.7 Hz), 123.4 (d, *J* = 7.8 Hz), 122.8 (d, *J* = 19.7 Hz), 116.5 (d, *J* = 8.5 Hz), 115.7 (d, *J* = 23.8 Hz), 112.7, 112.2, 109.8 (d, *J* = 23.7 Hz), 101.4, 21.7. HRMS calcd for [M+H]⁺ C₁₇H₁₃FN 250.1027, found: 250.1028.

7,10-Difluoropyrrolo[1,2-*f*]phenanthridine (15) From 1-(4-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **15** was obtained in 58% yield (0.147 g) as a white solid: mp 152-154 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.88-7.78 (m, 2H), 7.75 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.72 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.33-7.21 (m, 2H), 6.90 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.74 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 160.2 (d, *J* = 244.6 Hz), 159.3 (d, *J* = 242.6 Hz), 130.0 (d, *J* = 1.9 Hz), 128.5, 125.8 (dd, *J* = 7.9, 2.7 Hz), 124.8 (d, *J* = 8.4 Hz), 123.2 (d, *J* = 2.3 Hz), 122.6 (d, *J* = 11.6 Hz), 117.0, 116.7 (m), 112.9, 112.4, 110.0 (d, *J* = 23.80 Hz), 108.6 (d, *J* = 23.2 Hz), 101.8. HRMS calcd for [M+H]⁺ C₁₆H₁₀F₂N 254.0776, found: 254.0780.

10-Chloro-7-fluoropyrrolo[1,2-f]phenanthridine (16) From 1-(4-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-4-chloro-1-iodobenzene (0.317 g, 1 mmol), product **16** was obtained in 60% yield (0.161 g) as a white solid: mp 142-144 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.84 (dd, *J* = 10.0, 2.8 Hz, 1H), 7.77 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.69 (bs, 1H), 7.43 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.74 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 159.4 (d, *J* = 242.0 Hz), 131.7, 129.8 (d, *J* = 2.1 Hz), 128.9, 128.2, 125.3 (d, *J* = 2.8 Hz), 125.0, 124.2, 122.5, 122.2 (d, *J* = 7.8 Hz), 116.6 (d, *J* = 8.5 Hz), 116.5 (d, *J* = 23.8 Hz), 113.4, 112.5, 109.8 (d, *J* = 23.9 Hz), 102.5. HRMS calcd for [M+H]⁺ C₁₆H₁₀ClFN 270.0480, found: 270.0476.

7-Fluoro-10-(trifluoromethoxy)pyrrolo[1,2-f]phenanthridine (17) From 1-(4-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-4-(trifluoromethoxy)benzene (0.367 g, 1 mmol), product **17** was obtained in 64% yield (0.204 g) as a white solid: mp 108-110 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 8.7 Hz, 1H), 7.89 (bs, 1H), 7.84 (dd, *J* = 10.0, 2.8 Hz, 1H), 7.78 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.71 (bs, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.31-7.24 (m, 1H), 6.94 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.75 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 159.4 (d, *J* = 242.0 Hz), 147.2 (q, *J* = 1.8 Hz), 129.9 (d, *J* = 2.1 Hz), 128.0, 125.4 (d, *J* = 2.8 Hz), 125.3, 122.3 (d, *J* = 7.8 Hz), 121.8, 120.6 (d, *J* = 253.0 Hz), 116.9, 116.8 (d, *J* = 23.8 Hz), 116.7 (d, *J* = 8.5 Hz), 115.1, 113.5, 112.6, 110.0 (d, *J* = 23.9 Hz), 102.7. HRMS calcd for [M]⁺ C₁₇H₉F₄NO 319.0614, found: 319.0607.

10-Methyl-7-(trifluoromethyl)pyrrolo[1,2-f]phenanthridine (18) From 1-(4-(trifluoromethyl)phenyl)pyrrole (0.317 g, 1.5 mmol) and 2-bromo-1-iodo-4-methylbenzene (0.297 g, 1 mmol), product **18** was obtained in 38% yield (0.114 g) as a white solid: mp 158-160 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.58 (s, 1H), 8.05 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.78 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.37 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.94 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.78 (t, *J* = 3.5 Hz, 1H), 2.55 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 136.1, 135.3, 130.3, 129.7, 125.8 (q, *J* = 32.5 Hz), 124.1 (q, *J* = 271.8 Hz), 124.8 (q, *J* = 3.5 Hz), 124.2, 123.8, 122.9, 122.6, 121.9, 121.4 (q, *J* = 8.5 Hz), 115.5, 113.2, 113.1, 102.2, 21.7. HRMS calcd for [M+H]⁺ C₁₈H₁₃F₃N 300.0995, found: 300.0993.

10-Fluoro-7-(trifluoromethyl)pyrrolo[1,2-f]phenanthridine (19) From 1-(4-(trifluoromethyl)phenyl)pyrrole (0.317 g, 1.5 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **19** was obtained in 51% yield (0.154 g) as a white solid: mp 130-132 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.44 (s, 1H), 8.00 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.82-7.76 (m, 2H), 7.25 (td, *J* = 7.0, 3.5 Hz, 1H), 6.93 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.79 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.4 (d, *J* = 244.0 Hz), 135.5, 129.0, 126.2, 125.7 (m), 125.0, 124.9, 123.1 (d, *J* = 2.3 Hz), 122.8, 121.6 (q, *J* = 4.0 Hz), 121.1 (d, *J* = 3.1 Hz), 117.1 (d, *J* = 23.1 Hz), 115.7, 113.4, 113.3, 108.5 (d, *J* = 23.3 Hz), 102.5. HRMS calcd for [M+H]⁺ C₁₇H₁₀F₄N 304.0744, found: 304.0741.

10-Chloro-7-(trifluoromethyl)pyrrolo[1,2-f]phenanthridine (20) From 1-(4-(trifluoromethyl)phenyl)pyrrole (0.317 g, 1.5 mmol) and 2-bromo-4-chloro-1-iodobenzene (0.317 g, 1 mmol), product **20** was obtained in 63% yield (0.201 g) as a yellow solid: mp 196-198 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.50 (s, 1H), 8.20 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.83-7.75 (m, 2H), 7.50 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.98 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.81 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 135.5, 132.2, 129.3, 128.7, 126.0 (q, *J* = 32.5 Hz), 125.9 (q, *J* = 3.5 Hz), 125.3, 124.9, 124.4, 124.1 (q, *J* = 271.8 Hz), 122.5, 121.5 (q, *J* = 4.1 Hz), 120.8, 115.7, 113.9, 113.4, 103.2. HRMS calcd for [M+H]⁺ C₁₇H₁₀ClF₃N 320.0448, found: 320.0448.

7-(Trifluoromethyl)pyrrolo[1,2-f]phenanthridine-10-carbonitrile (21) From 1-(4-(trifluoromethyl)phenyl)pyrrole (0.317 g, 1.5 mmol) and 3-bromo-4-iodobenzonitrile (0.308 g, 1 mmol), product **21** was obtained in 68% yield (0.211 g) as a yellow solid: mp 240-242 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.53 (s, 2H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.6 Hz,

1H), 7.90 (s, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.75 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.15 (dd, *J* = 3.8, 1.2 Hz, 1H), 6.88 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 135.2, 131.2, 129.5, 127.9, 127.3, 126.4 (q, *J* = 32.5 Hz), 126.3 (q, *J* = 3.5 Hz), 124.0, 123.9 (q, *J* = 272.0 Hz), 123.5, 121.5 (q, *J* = 4.1 Hz), 120.2, 118.9, 115.8, 115.4, 114.1, 109.4, 105.9. HRMS calcd for [M+H]⁺ C₁₈H₁₀F₃N₂ 311.0791, found: 311.0796.

10-Methylpyrrolo[1,2-f]phenanthridine-7-carbonitrile (22) From 4-(pyrrol-1-yl)benzocarbonitrile (0.252, 1.5 mmol) and 2-bromo-1-iodo-4-methylbenzene (0.297 g, 1 mmol), product **22** was obtained in 32% yield (0.082 g) as a white solid: mp 174-176 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, *J* = 1.8 Hz, 1H), 7.98 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.78-7.70 (m, 2H), 7.39 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.95 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.79 (t, *J* = 3.5 Hz, 1H), 2.55 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 136.4, 135.8, 131.1, 130.7, 129.8, 128.7, 124.2, 123.1, 122.9, 122.6, 122.4, 119.0, 115.9, 113.7, 113.4, 107.1, 102.6, 21.8. HRMS calcd for [M+H]⁺ C₁₈H₁₃N₂ 257.1073, found: 257.1077.

10-Fluoropyrrolo[1,2-f]phenanthridine-7-carbonitrile (23) From 4-(pyrrol-1-yl)benzocarbonitrile (0.252, 1.5 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **23** was obtained in 64% yield (0.166 g) as a white solid: mp 184-186 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.40 (d, *J* = 1.7 Hz, 1H), 7.95 (dd, *J* = 8.7, 5.7 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.79-7.66 (m, 3H), 7.25 (td, *J* = 8.6, 2.5 Hz, 1H), 6.92 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.80 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.3 (d, *J* = 244.0 Hz), 135.7, 131.7, 128.9, 128.7, 124.9 (d, *J* = 8.4 Hz), 124.7 (d, *J* = 7.9 Hz), 122.9 (d, *J* = 2.4 Hz), 121.4 (d, *J* = 3.1 Hz), 118.6, 117.5 (d, *J* = 23.1 Hz), 115.8, 113.9, 113.5, 108.4 (d, *J* = 22.5 Hz), 107.3, 103.0 (d, *J* = 1.5 Hz). HRMS calcd for [M+H]⁺ C₁₇H₁₀FN₂ 261.0822, found: 261.0820.

10-Chloropyrrolo[1,2-f]phenanthridine-7-carbonitrile (24) From 4-(pyrrol-1-yl)benzocarbonitrile (0.252, 1.5 mmol) and 2-bromo-4-chloro-1-iodobenzene (0.317 g, 1 mmol), product **24** was obtained in 68% yield (0.188 g) as a yellow solid: mp 196-198 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, *J* = 1.8 Hz, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.84-7.75 (m, 2H), 7.52 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.00 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.83 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 135.9, 132.5, 131.9, 129.7, 128.8, 125.0, 124.5, 124.4, 122.5, 121.4, 120.7 (q, *J* = 257.5 Hz), 118.6, 116.1, 114.1, 114.0, 107.6, 103.8. HRMS calcd for [M+H]⁺ C₁₇H₁₀ClN₂ 277.0527, found: 277.0527.

10-(Trifluoromethoxy)pyrrolo[1,2-f]phenanthridine-7-carbonitrile (25) From 4-(pyrrol-1-yl)benzocarbonitrile (0.252, 1.5 mmol) and 2-bromo-1-iodo-4-(trifluoromethoxy)benzene (0.367 g, 1 mmol), product **25** was obtained in 53% yield (0.173 g) as a yellow solid: mp 194-196 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, *J* = 1.8 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 8.03-7.99 (m, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.84-7.75 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.01 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.83 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 147.7 (q, *J* = 1.8 Hz), 136.0, 132.1, 128.9, 128.6, 125.2, 124.8, 124.5, 122.6, 121.5, 118.6, 116.1, 115.1, 114.2, 114.1, 107.7, 104.0. HRMS calcd for [M+H]⁺ C₁₈H₁₀F₃N₂O 327.0740, found: 327.0743.

Ethyl 10-methylpyrrolo[1,2-f]phenanthridine-6-carboxylate (26) From ethyl 3-(pyrrol-1-yl)benzoate (0.322 g, 1.5 mmol) and 2-bromo-1-iodo-4-methylbenzene (0.297 g, 1 mmol), product **26** was obtained in 53% yield (0.161 g) as a white solid: mp 146-148 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, *J* = 1.5 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 8.01 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.92 (d, *J* = 8.1, 1H), 7.87 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.36 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.93 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.76 (t, *J* = 3.5 Hz, 1H), 4.49 (q, *J* = 7.6 Hz, 2H), 2.53 (s, 3H), 1.49 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 135.8, 133.1, 130.6, 129.9, 129.4, 125.6, 124.8, 124.2, 124.0, 123.9, 123.2, 122.9, 116.4, 113.4, 112.4, 101.8, 61.4, 21.7, 14.4. HRMS calcd for [M+H]⁺ C₂₀H₁₈NO₂ 304.1332, found: 304.1332.

Ethyl 10-fluoropyrrolo[1,2-*f*]phenanthridine-6-carboxylate (27) From ethyl 3-(pyrrol-1-yl)benzoate (0.322 g, 1.5 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **27** was obtained in 44% yield (0.135 g) as a white solid: mp 186-188 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (d, *J* = 1.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.02-7.92 (m, 2H), 7.88-7.80 (m, 2H), 7.24 (td, *J* = 8.6, 2.5 Hz, 1H), 6.89 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.75 (dd, *J* = 3.8, 3.0 Hz, 1H), 4.49 (q, *J* = 7.6 Hz, 2H), 1.49 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.8, 161.3 (d, *J* = 244.0 Hz), 133.2, 130.7, 128.6, 125.7 (d, *J* = 8.0 Hz), 124.8 (d, *J* = 18.4 Hz), 124.6 (d, *J* = 3.4 Hz), 124.3, 124.1, 123.6 (d, *J* = 2.3 Hz), 117.3 (d, *J* = 23.1 Hz), 116.5, 113.5, 112.6, 109.0 (d, *J* = 23.1 Hz), 102.1 (d, *J* = 1.0 Hz), 61.5, 14.4. HRMS calcd for [M+H]⁺ C₁₉H₁₅FNO₂ 308.1081, found: 308.1085.

6-Fluoro-10-methylpyrrolo[1,2-*f*]phenanthridine (28) From 1-(3-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-4-methylbenzene (0.297 g, 1 mmol), product **28** was obtained in 37% yield (0.092 g) as a white solid: mp 62-64 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.55 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.74 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.50-7.42 (m, 1H), 7.36 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.12 (dd, *J* = 13.0, 8.1 Hz, 1H), 6.92 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.75 (t, *J* = 3.5 Hz, 1H), 2.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 161.9 (d, *J* = 242.0 Hz), 136.0, 135.2, 129.7, 129.6 (d, *J* = 2.1 Hz), 128.4 (d, *J* = 11.6 Hz), 127.7 (d, *J* = 25.4 Hz), 124.1, 122.8 (d, *J* = 5.1 Hz), 122.5, 113.1, 112.7, 111.6, 111.4 (d, *J* = 22.3 Hz), 110.8 (d, *J* = 3.7 Hz), 101.5, 22.0. HRMS calcd for [M]⁺ C₁₇H₁₂FN 249.0948, found: 249.0947.

6,10-Difluoropyrrolo[1,2-*f*]phenanthridine (29) From 1-(3-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **29** was obtained in 40% yield (0.101 g) as a white solid: mp 138-140 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.45-8.38 (m, 1H), 8.02 (dd, *J* = 8.9, 6.0 Hz, 1H), 7.74 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.56-7.47 (m, 1H), 7.30-7.24 (m, 1H), 7.13 (dd, *J* = 13.0, 8.1 Hz, 1H), 6.92 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.76 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.1 (d, *J* = 244.9 Hz), 159.2 (d, *J* = 242.9 Hz), 130.0 (d, *J* = 2.0 Hz), 128.5, 125.8 (dd, *J* = 7.9, 2.8 Hz), 124.8 (d, *J* = 8.4 Hz), 123.2 (d, *J* = 2.3 Hz), 122.5 (dd, *J* = 7.8, 3.1 Hz), 116.9 (d, *J* = 23.0 Hz), 116.7 (d, *J* = 8.4 Hz), 116.6 (d, *J* = 23.9 Hz), 112.9, 112.4, 110.0 (d, *J* = 23.8 Hz), 108.6 (d, *J* = 23.1 Hz), 101.7 (d, *J* = 1.5 Hz). HRMS calcd for [M]⁺ C₁₆H₉F₂N 253.0698, found: 253.0698.

5-Fluoro-10-methylpyrrolo[1,2-*f*]phenanthridine (30) From 1-(2-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-4-methylbenzene (0.297 g, 1 mmol), product **30** was obtained in 38% yield (0.095 g) as a white solid: mp 108-110 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.20 (dd, *J* = 2.8, 1.3 Hz, 1H), 8.16 (dd, *J* = 4.2, 3.3 Hz, 1H), 8.03 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.38-7.26 (m, 3H), 6.98 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.75 (t, *J* = 3.5 Hz, 1H), 2.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 153.2 (d, *J* = 247.0 Hz), 135.6, 130.1, 129.7, 125.0 (d, *J* = 2.7 Hz), 124.3, 124.0 (d, *J* = 2.3 Hz), 123.3 (d, *J* = 9.1 Hz), 122.8 (d, *J* = 21.5 Hz), 119.3, 119.2, 119.0, 115.3 (d, *J* = 22.2 Hz), 112.0 (d, *J* = 4.9 Hz), 101.0 (d, *J* = 1.6 Hz), 21.7. HRMS calcd for [M]⁺ C₁₇H₁₂FN 249.0948, found: 249.0947.

5,10-Difluoropyrrolo[1,2-*f*]phenanthridine (31) From 1-(2-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **31** was obtained in 46% yield (0.116 g) as a white solid: mp 148-150 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.17 (dd, *J* = 3.0, 1.5 Hz, 1H), 8.00-7.94 (m, 2H), 7.80 (dd, *J* = 10.7, 2.5 Hz, 1H), 7.38-7.26 (m, 2H), 7.22 (td, *J* = 8.0, 2.6 Hz, 1H), 6.93 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.74 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.3 (d, *J* = 244.2 Hz), 153.1 (d, *J* = 247.0 Hz), 129.0, 125.8 (d, *J* = 2.6 Hz), 125.7 (d, *J* = 2.7 Hz), 124.7 (d, *J* = 8.4 Hz), 124.1 (d, *J* = 2.8 Hz), 124.0 (d, *J* = 2.6 Hz), 123.5 (d, *J* = 8.8 Hz), 123.1 (m), 119.5, 119.4, 119.2, 116.8 (d, *J* = 23.1 Hz), 116.1 (d, *J* = 23.2 Hz). HRMS calcd for [M+H]⁺ C₁₆H₁₀F₂N 254.0776, found: 254.0780.

10-Chloro-5-fluoropyrrolo[1,2-*f*]phenanthridine (32) From 1-(2-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-4-chloro-1-

iodobenzene (0.317 g, 1 mmol), product **32** was obtained in 54% yield (0.145 g) as a yellow solid: mp 172-174 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.18 (dd, *J* = 3.0, 1.5 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.43 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.36-7.26 (m, 2H), 6.98 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.75 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 153.1 (d, *J* = 247.0 Hz), 131.7, 128.9, 128.7, 125.3 (d, *J* = 2.7 Hz), 125.0, 124.1, 123.8 (d, *J* = 2.3 Hz), 123.5 (d, *J* = 8.9 Hz), 123.0 (d, *J* = 8.5 Hz), 122.7, 119.7 (d, *J* = 24.0 Hz), 119.3 (d, *J* = 3.5 Hz), 116.1 (d, *J* = 22.3 Hz), 112.4 (d, *J* = 4.9 Hz), 102.1 (d, *J* = 1.6 Hz). HRMS calcd for [M]⁺ C₁₆H₉ClFN 269.0402, found: 269.0400.

5-Fluoro-10-(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (33) From 1-(2-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-4-(trifluoromethyl)benzene (0.350 g, 1 mmol), product **33** was obtained in 44% yield (0.133 g) as a yellow solid: mp 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (s, 1H), 8.24 (dd, *J* = 3.0, 1.2 Hz, 1H), 8.14-8.10 (m, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.40-7.32 (m, 2H), 7.10 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.79 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 153.1 (d, *J* = 247.0 Hz), 129.0, 128.4, 127.6 (q, *J* = 32.4 Hz), 124.9 (q, *J* = 3.5 Hz), 124.2 (q, *J* = 271.0 Hz), 124.0 (d, *J* = 2.3 Hz), 123.9, 123.8, 123.2, 123.0 (d, *J* = 2.5 Hz), 120.6 (d, *J* = 23.0 Hz), 120.3 (q, *J* = 4.0 Hz), 119.4 (d, *J* = 3.5 Hz), 116.3 (d, *J* = 22.3 Hz), 112.6 (d, *J* = 4.9 Hz), 103.7 (d, *J* = 1.6 Hz). HRMS calcd for [M]⁺ C₁₇H₉F₄N 303.0666, found: 303.0661.

11-Chloropyrrolo[1,2-*f*]phenanthridine (34) From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 2-bromo-5-chloro-1-iodobenzene (0.317 g, 1 mmol), product **34** was obtained in 50% yield (0.126 g) as a yellow solid: mp 118-120 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.29 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 7.87 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.81 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.97 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.76 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 134.0, 133.1, 128.8, 128.1, 127.6, 126.1, 124.2, 124.1, 123.9, 123.2, 122.3, 121.0, 115.1, 113.7, 112.5, 102.9. HRMS calcd for [M]⁺ C₁₆H₁₀ClN 251.0496, found: 251.0497.

11-(Trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (35) From 1-phenylpyrrole (0.214 g, 1.5 mmol) and 2-bromo-1-iodo-5-(trifluoromethyl)benzene (0.350 g, 1 mmol), product **35** was obtained in 58% yield (0.165 g) as a yellow solid: mp 90-92 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.35 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.33 (d, *J* = 8.3 Hz, 1H), 8.25 (s, 1H), 7.89 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.83 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.65-7.57 (m, 2H), 7.43 (td, *J* = 8.0, 1.2 Hz, 1H), 7.06 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.79 (dd, *J* = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 133.7, 129.8 (q, *J* = 32.2 Hz), 129.7, 128.3, 127.4, 126.3, 124.4, 124.2, 124.1 (q, *J* = 271.8 Hz), 123.2, 121.9 (q, *J* = 3.5 Hz), 120.6, 119.9 (q, *J* = 4.2 Hz), 115.2, 113.8, 112.6, 103.2. HRMS calcd for [M+H]⁺ C₁₇H₁₁F₃N 286.0838, found: 286.0841.

7-Fluoro-11-(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (36) From 1-(4-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-5-(trifluoromethyl)benzene (0.350 g, 1 mmol), product **36** was obtained in 61% yield (0.185 g) as a yellow solid: mp 94-96 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.16 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 10.0, 2.7 Hz, 1H), 7.76 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.71 (s, 1H), 7.57 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.31-7.24 (m, 1H), 6.99 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.76 (t, *J* = 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 159.3 (d, *J* = 242.0 Hz), 130.2 (q, *J* = 32.7 Hz), 130.1 (d, *J* = 2.2 Hz), 128.0, 126.6, 126.5, 123.9 (q, *J* = 272.2 Hz), 123.3, 122.1 (d, *J* = 7.8 Hz), 122.0 (q, *J* = 3.6 Hz), 119.9 (q, *J* = 4.0 Hz), 117.1 (d, *J* = 23.9 Hz), 116.7 (d, *J* = 8.5 Hz), 113.8, 112.7, 110.2 (d, *J* = 23.7 Hz), 103.3. HRMS calcd for [M+H]⁺ C₁₇H₁₀F₄N 304.0744, found: 304.0741.

7,11-Bis(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (37) From 1-(4-(trifluoromethyl)phenyl)pyrrole (0.317 g, 1.5 mmol) and 2-bromo-1-iodo-5-(trifluoromethyl)benzene (0.350 g, 1 mmol), product **37** was obtained in 45% yield (0.159 g) as a yellow solid: mp 194-196 °C. ¹H NMR (400

MHz, CDCl₃): δ 8.53 (s, 1H), 8.29 (d, J = 8.3 Hz, 1H), 8.20 (s, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.84-7.77 (m, 2H), 7.63 (d, J = 8.5 Hz, 1H), 7.06 (dd, J = 3.8, 1.4 Hz, 1H), 6.82 (dd, J = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 135.6, 130.8 (q, J = 32.8 Hz), 128.4, 126.5, 126.4, 126.3 (q, J = 32.2 Hz), 126.2 (q, J = 3.8 Hz), 124.1 (q, J = 271.0 Hz), 124.0 (q, J = 271.0 Hz), 123.3, 122.3 (q, J = 3.6 Hz), 121.8 (q, J = 4.0 Hz), 120.7, 120.0 (q, J = 4.0 Hz), 115.7, 114.3, 113.6, 104.1. HRMS calcd for [M]⁺ C₁₈H₉F₆N 353.0634, found: 353.0628.

Ethyl 11-fluoropyrrolo[1,2-*f*]phenanthridine-6-carboxylate (38) From ethyl 3-(pyrrol-1-yl)benzoate (0.322 g, 1.5 mmol) and 2-bromo-5-fluoro-1-iodobenzene (0.301 g, 1 mmol), product **38** was obtained in 41% yield (0.126 g) as a white solid: mp 170-172 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.52 (d, J = 1.5 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.22 (dd, J = 9.0, 5.4 Hz, 1H), 8.00 (d, J = 8.4, 1.6 Hz, 1H), 7.92-7.85 (m, 1H), 7.62 (dd, J = 9.5, 2.7 Hz, 1H), 7.14 (td, J = 8.6, 2.5 Hz, 1H), 6.95 (dd, J = 3.8, 1.4 Hz, 1H), 6.77 (dd, J = 3.8, 3.0 Hz, 1H), 4.48 (q, J = 7.6 Hz, 2H), 1.49 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 163.1 (d, J = 244.0 Hz), 132.5, 129.9, 128.9 (d, J = 9.5 Hz), 128.3 (d, J = 3.6 Hz), 125.7 (d, J = 9.1 Hz), 124.9, 124.5, 123.7, 120.4 (d, J = 2.3 Hz), 116.4, 114.3, 114.1 (d, J = 23.1 Hz), 112.7, 108.3 (d, J = 23.0 Hz), 103.5, 61.4, 14.4. HRMS calcd for [M]⁺ C₁₉H₁₄FNO₂ 307.1003, found: 307.1004.

6-Fluoro-11-(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (39) From 1-(3-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-5-(trifluoromethyl)benzene (0.350 g, 1 mmol), product **39** was obtained in 77% yield (0.233 g) as a yellow solid: mp 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.80 (dd, J = 8.7, 3.9 Hz, 1H), 8.25 (s, 1H), 7.80-7.76 (m, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.57-7.50 (m, 1H), 7.15 (dd, J = 13.0, 8.1 Hz, 1H), 7.04 (dd, J = 3.8, 1.4 Hz, 1H), 6.79 (dd, J = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 161.9 (d, J = 243.5 Hz), 130.3 (q, J = 32.5 Hz), 128.3, 126.4, 126.2, 124.0 (q, J = 272.1 Hz), 123.6 (d, J = 8.8 Hz), 123.5 (m), 123.4, 123.1 (d, J = 8.4 Hz), 121.8 (q, J = 3.5 Hz), 120.1 (d, J = 18.7 Hz), 119.7 (q, J = 4.2 Hz), 119.5 (d, J = 3.6 Hz), 116.4 (d, J = 22.2 Hz), 112.4 (d, J = 4.8 Hz), 103.4. HRMS calcd for [M+H]⁺ C₁₇H₁₀F₄N 304.0744, found: 304.0742.

5-Fluoro-11-(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (40) From 1-(2-fluorophenyl)pyrrole (0.242 g, 1.5 mmol) and 2-bromo-1-iodo-5-(trifluoromethyl)benzene (0.350 g, 1 mmol), product **40** was obtained in 62% yield (0.188 g) as a white solid: mp 140-142 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.16-8.07 (m, 3H), 7.98 (dd, J = 7.2, 2.2 Hz, 1H), 7.52 (d, J = 8.6, 1.8 Hz, 1H), 7.35-7.20 (m, 2H), 7.00 (d, J = 3.8 Hz, 1H), 6.74 (dd, J = 3.8, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 152.9 (d, J = 247.0 Hz), 130.3 (q, J = 32.6 Hz), 128.3, 126.4, 126.2, 124.0 (q, J = 272.0 Hz), 123.6 (m), 123.4, 123.1 (d, J = 8.4 Hz), 121.8 (q, J = 3.5 Hz), 120.1 (d, J = 24.0 Hz), 119.6 (q, J = 4.0 Hz), 119.5 (d, J = 23.5 Hz), 116.4 (d, J = 22.1 Hz), 112.4 (d, J = 4.9 Hz), 102.8 (d, J = 1.6 Hz). HRMS calcd for [M+H]⁺ C₁₇H₁₀F₄N 304.0744, found: 304.0741.

4-(Pyrrolo[1,2-*f*]phenanthridin-3-yl)benzotrile (41) From 4-(1-phenylpyrrol-2-yl)benzotrile (0.244 g, 1 mmol) and 1,2-dibromobenzene (0.354 g, 1.5 mmol), product **41** was obtained in 54% yield (0.172 g) as a yellow solid: mp 86-88 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.37 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.57-7.43 (m, 2H), 7.41-7.33 (m, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 4.0 Hz, 1H), 6.77 (d, J = 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 139.7, 133.4, 133.3, 132.4, 129.5, 128.5, 128.4, 127.3, 126.7, 126.3, 125.7, 124.4, 124.2, 123.3, 122.9, 122.5, 119.3, 119.0, 118.1, 110.3, 103.0. HRMS calcd for [M+H]⁺ C₂₃H₁₅N₂ 319.1230, found: 319.1233.

4-(11-(Trifluoromethyl)pyrrolo[1,2-*f*]phenanthridin-3-yl)benzotrile (42) From 4-(1-phenylpyrrol-2-yl)benzotrile (0.244 g, 1 mmol) and 2-bromo-1-iodo-5-(trifluoromethyl)benzene (0.525 g, 1.5 mmol), product **42** was obtained in 51% yield (0.197 g) as a white solid: mp 218-220 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.41-8.33 (m, 2H), 8.28 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.68 (dd, J = 7.8, 1.9 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.45-

7.35 (m, 2H), 7.32-7.24 (m, 1H), 7.16 (d, J = 4.0 Hz, 1H), 6.79 (d, J = 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 139.4, 133.8, 132.5, 132.2, 130.2 (q, J = 32.2 Hz), 130.1, 128.7, 128.5, 128.2, 126.4, 124.8, 124.5, 124.0 (q, J = 271.8 Hz), 123.2, 122.6 (q, J = 3.5 Hz), 122.2, 120.1 (q, J = 4.2 Hz), 119.3, 118.9, 118.2, 110.8, 104.0. HRMS calcd for [M+H]⁺ C₂₄H₁₄F₃N₂ 387.1104, found: 387.1104.

4-(10-(Trifluoromethoxy)pyrrolo[1,2-*f*]phenanthridin-3-yl)benzotrile (43) From 4-(1-phenylpyrrol-2-yl)benzotrile (0.244 g, 1 mmol) and 2-bromo-1-iodo-4-(trifluoromethoxy)benzene (0.550 g, 1.5 mmol), product **43** was obtained in 52% yield (0.209 g) as a white solid: mp 186-188 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 8.2 Hz, 1H), 8.11 (s, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.42-7.36 (m, 3H), 7.29-7.22 (m, 1H), 7.10 (d, J = 4.0 Hz, 1H), 6.78 (d, J = 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 139.5, 133.6, 132.5, 132.3, 129.8, 128.6, 128.2, 127.1, 125.0, 124.7, 124.5, 124.4, 122.3, 121.5, 120.1 (q, J = 257.5 Hz), 119.3, 118.9, 118.2, 114.9, 110.6, 103.4. HRMS calcd for [M]⁺ C₂₄H₁₃F₃N₂O 402.0974, found: 402.0964.

Acknowledgements

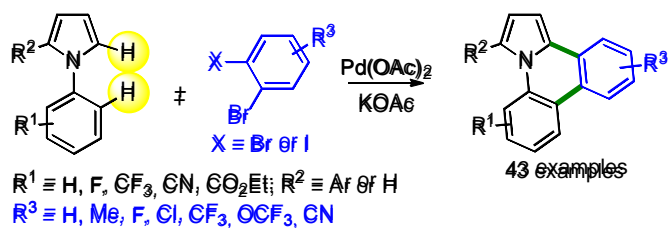
We are grateful to the ANR for a grant to X. S. We thank CNRS and "Rennes Metropole" for providing financial support.

Keywords: Catalysis • C-H Bond functionalization • Direct arylation • Palladium • Pyrrolo[1,2-*f*]phenanthridines

- [1] a) L. Yan, D. Zhao, J. Lan, Y. Cheng, Q. Guo, X. Li, N. Wu, J. You, *Org. Biomol. Chem.* **2013**, *11*, 7966-7966; b) S. Mathew, N. A. Astani, B. F. E. Curchod, J. H. Delcamp, M. Marszalek, J. Frey, U. Rothlisberger, M. K. Nazeeruddin, M. Gratzel, *J. Mater. Chem. A* **2016**, *4*, 2332-2339; c) D. Wu, L. Chen, S. Ma, H. Luo, J. Cao, R. Chen, Z. Duan, F. Mathey, *Org. Lett.* **2018**, *20*, 4103-4106; d) A. S. Patel, V. Jain, V. N. Rao, Y.-W. Lin, A. Shah, K.-C. Lai, T.-L. Su, T.-C. Lee, *Eur. J. Med. Chem.* **2020**, *202*, 112516.
- [2] For reviews on metal-catalyzed C-H bond functionalization: a) T. Satoh, M. Miura, *Chem. Lett.* **2007**, *36*, 200-205; b) L. Ackermann, R. Vicente, A. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792-9826; c) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094-5115; d) G. P. Chiusoli, M. Catellani, M. Costa, E. Mottì, N. Della Ca, G. Maestri, *Coord. Chem. Rev.* **2010**, *254*, 456-469; e) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236-10254; f) R. Rossi, F. Bellina, M. Lessi, C. Manzini, *Adv. Synth. Catal.* **2014**, *356*, 17-117; g) S. Agasti, A. Dey, D. Maiti, *Chem. Commun.* **2017**, *53*, 6544-6556; h) T. Gensch, M. J. James, T. Dalton, F. Glorius, *Angew. Chem. Int. Ed.* **2018**, *57*, 2296-2306; i) J. Kalepu, P. Gandeepan, L. Ackermann, L. T. Pilarski, *Chem. Sci.* **2018**, *9*, 4203-4216; j) S. Mao, H. Li, X. Shi, J.-F. Soulé, H. Doucet, *ChemCatChem* **2019**, *11*, 269-286; k) S. Rej, Y. An, N. Chatani, *Chem. Rev.* **2020**, *120*, 1788-1887; l) H.-Y. Huang, A. Benzai, X. Shi, H. Doucet, *Chem. Rec.* **2021**, *21*, 343-356.
- [3] W. Hagui, H. Doucet, J.-F. Soulé, *Chem* **2019**, *5*, 2006-2078.
- [4] For the preparation of π -extended polyheteroaromatics via Pd-catalyzed C-H bond functionalization of pyrrolo[2,3-*d*]pyrimidines or indoles: a) C. Baik, D. Kim, M.-S. Kang, K. Song, S. O. Kang, J. Ko, *Tetrahedron* **2009**, *65*, 5302-5307; b) D. Takeda, K. Hirano, T. Satoh, M. Miura, *Heterocycles* **2012**, *86*, 487-496; c) J. Dodonova, S. Tumkevicius, *Synthesis* **2017**, *49*, 2523-2534; d) L. Kong, Q. Yao, M. Wang, R. Sun, Y. Li, *ChemistrySelect* **2018**, *3*, 456-460.
- [5] For selected Pd-catalyzed intermolecular direct arylations of pyrroles: a) B. B. Toure, B. S. Lane, D. Sames, *Org. Lett.* **2006**, *8*, 1979-1982; b) D. T. Gryko, O. Vakuliuk, D. Gryko, B. Koszarna, *J. Org. Chem.* **2009**, *74*, 9517-9520; c) Y. Xu, L. Zhao, Y. Li, H. Doucet, *Adv. Synth. Catal.* **2013**, *355*, 1423-1432; d) P. Ehlers, A. Petrosyan, J. Baumgard, S. Jopp, N. Steinfeld, T. V. Ghochikyan,

- A. S. Saghyan, C. Fischer, P. Langer, *ChemCatChem* **2013**, *5*, 2504-2511; e) H. Kitano, W. Matsuoka, H. Ito, K. Itami, *Chem. Sci.* **2018**, *9*, 7556-7561.
- [6] For the preparation of pyrrolo[1,2-f]phenanthridine via Pd-catalyzed C-H bond functionalization: a) Z. Liu, R. C. Larock, *J. Org. Chem.* **2007**, *72*, 223-232; b) L. Yan, D. Zhao, J. Lan, Y. Cheng, Q. Guo, X. Li, N. Wu, J. You, *Org. Biomol. Chem.* **2013**, *11*, 7966-7977; c) W. Hagui, K. Yuan, N. Besbes, E. Srasra, J.-F. Soule, H. Doucet, *ChemCatChem* **2015**, *7*, 3544-3554.
- [7] For an example of preparation of pyrrolo[1,2-f]phenanthridine via Pd-catalyzed Decarboxylative Annulation: Z. Ye, Y. Li, K. Xu, N. Chen, F. Zhang, *Org. Lett.* **2019**, *21*, 9869-9873.
- [8] J. Roger, H. Doucet, *Adv. Synth. Catal.* **2009**, *351*, 1977-1990.
- [9] a) D. García-Cuadrado, A. A. C. Braga, F. Maseras, A. M. Echavarren, *J. Am. Chem. Soc.* **2006**, *128*, 1066-1067; b) S. I. Gorelsky, D. Lapointe, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 10848-10849.
- [10] T. Cantat, E. Génin, C. Giroud, G. Meyer, A. Jutand, *J. Organomet. Chem.* **2003**, *687*, 365-376.
- [11] N. Yasukawa, M. Kuwata, T. Imai, Y. Monguchi, H. Sajiki, Y. Sawama, *Green Chem.* **2018**, *20*, 4409-4413.

Entry for the Table of Contents



From commercially available compounds using only 2 mol% of easily available $\text{Pd}(\text{OAc})_2$ catalyst precursor and KOAc as inexpensive base, a wide variety of pyrrolo[1,2-*f*]phenanthridines can be obtained. With this synthetic scheme, the introduction of desired functional groups at positions 5, 6, 7, 8, 10 and 11 of pyrrolo[1,2-*f*]phenanthridines is possible.