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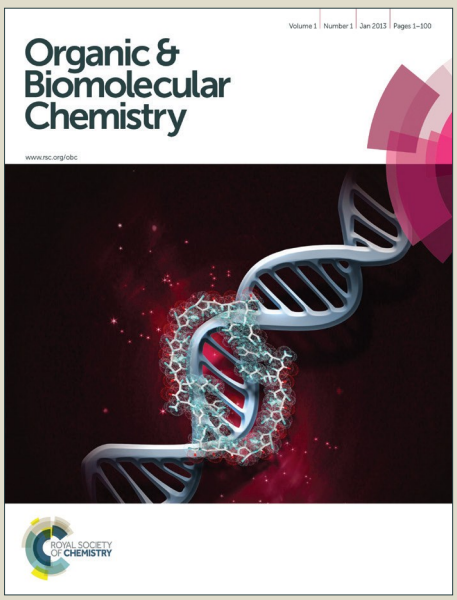

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Pd(0)-catalyzed Domino C-N Coupling/Hydroamination/C-H Arylation Reactions: Efficient Synthesis and Photophysical Properties of Azaindolo[1,2-*f*]phenanthridines

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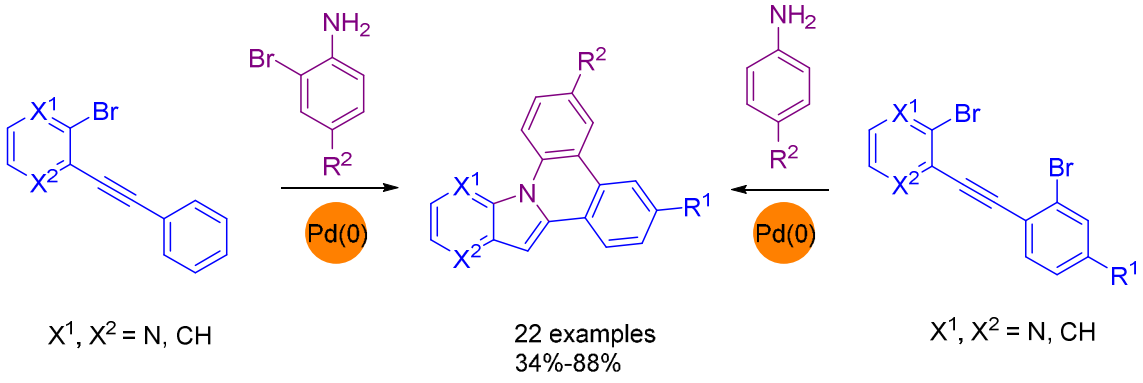
Abstract: A series of new 7- and 4-azaindolo[1,2-*f*]phenanthridines were synthesized by a domino Pd(0)-catalyzed reaction, which involves three sequential steps: C-N coupling, hydroamination, and intramolecular C-H arylation. The products show promising fluorescence properties with high quantum yields (12-65%).

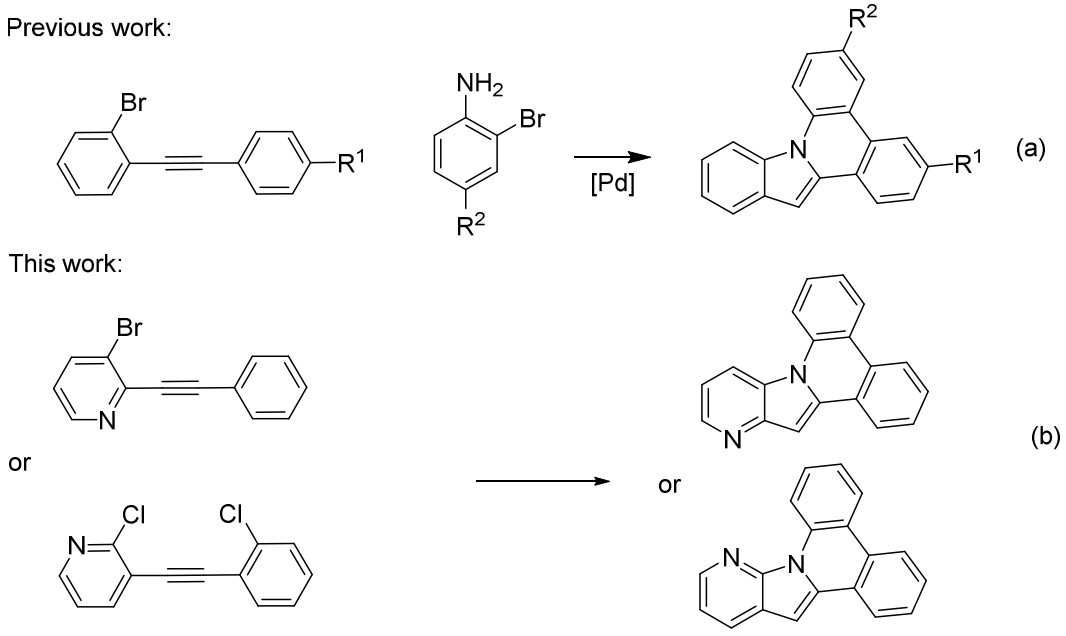


Introduction

Fused phenanthridines have been recognized as an important motif among drug-like molecules and organic materials.[1] A large number of fused phenanthridines exhibit remarkable bioactivities, which arouse the interest for further medicinal studies. For instance, natural and synthetic benzo[*c*]phenanthridine alkaloids, such as nitidine, fagaronin, NK109

are promising antitumor agents and were subjected to clinical studies.[2] Furthermore, the combination of phenanthridine moiety with other heterocycles results in many interesting structures with promising properties. For example, phenanthridine fused with N-heterocycles, such as imidazole, benzoimidazole, indole, and pyrrole, were reported to possess remarkable optical and electronic properties.[3,4,5] Moreover, azaindoles are also considered as important core structures and have been studied for decades.[6] However, the scaffold of phenanthridine fused with azaindole is rarely reported, probably because of difficulties in synthetic approaches. Therefore, developing an efficient synthetic method for this scaffold is compelling for further studies of its properties.

Recently, the advance of transition-metal-catalyzed reactions has provided chemists with a handy tool to approach complex structures via more effective and shorter pathways. Especially for constructing nitrogen containing polycyclic ring systems, transition-metal-catalyzed tandem reactions have been proved to be efficient.[7] Regarding fused phenanthridines, there are some noticeable strategies reported recently, which involve sequential formation of C-N/C-C bonds, or two C-C bonds in a one-pot reaction.[5,8,9,10,11] In 2015, we reported a convenient approach to synthesize indolo[1,2-*f*]phenanthridines.[11] Our strategy consists of three sequential steps in a one-pot reaction: C-N coupling, hydroamination and intramolecular C-H arylation catalyzed by a single Pd catalyst. Our method utilizes easily accessible starting materials and could be efficiently applied to the synthesis of phenanthridines-fused azaindole scaffolds (Scheme 1).

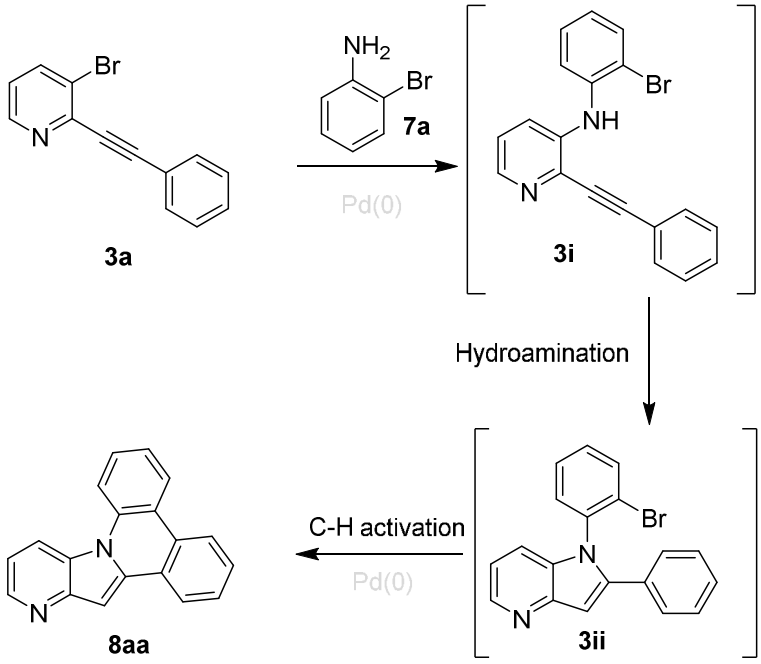


Scheme 1. Synthesis of indolo[1,2-*f*]phenanthridines (a). Our current work (b)

Herein, we report the synthesis of new azaindolo[1,2-*f*]phenanthridines via Pd-catalyzed domino C–N coupling/hydroamination/C–H arylation reactions. In addition, the optical properties of the synthesized azaindo[1,2-*f*]phenanthridine derivatives were studied.

Results and discussion

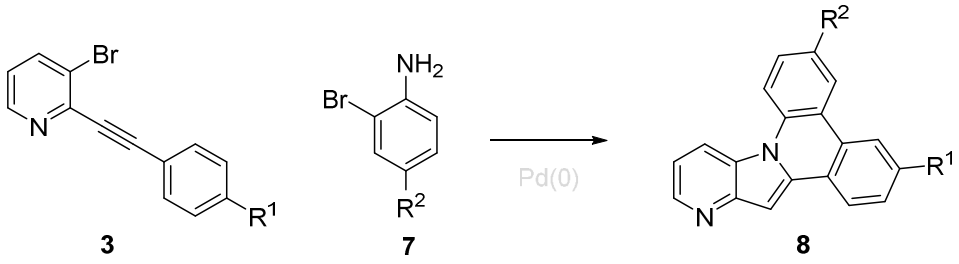
Initially, we chose 3-bromo-2-(phenylethynyl)pyridines **3a** and 2-bromoaniline as model substrates to study the reaction. No desired product was obtained after stirring the mixture of substrates and cesium carbonate in DMF at 120 ºC for 24 h. At the beginning, we applied the reaction conditions from our previous report which utilized $Pd(OAc)_2$/Xantphos as the catalytic system.[11] Interestingly, these conditions produced the desired product with 39% yield. Furthermore, when the reaction time was increased to 48 h, the yield of the reaction raised to 64%. Encouraged by this result, we continued to investigate other combinations of catalytic sources and ligands using the same solvent, base, and temperature conditions. To our delight, Xantphos was the best choice of ligand so far. The combination of $Pd(Ph_3P)_4$ and Xantphos gave the best result with 68% yield. Other attempts to change the solvent and base did not lead to higher yields. Notably, decreasing the reaction temperature also led to a significant decrease of yield. During the reaction, we observed the formation of intermediate **3ii** as a potential intermediate of the reaction pathway which is proposed in Scheme 2.



Scheme 2: Proposed pathway for the reaction

With the optimized conditions in hand, we expanded the scope of the reaction by modifying the starting alkyne and 2-bromoaniline. Both electron-withdrawing and electron-donating substituents were introduced into both substrates. The reaction proceeded smoothly with various starting materials under optimized conditions affording the desired products in moderate to high yields. However, no perspicuous effect of the substituents on the yield was observed. Compound **8da** was obtained with the highest yield (88%) **(Table 1**). Furthermore, the structure of **8ea** was confirmed by X-ray crystallographic analysis.

Table 1: Synthesis of 4-azaindolo[1,2-*f*]phenanthridines



Entry	**8**	**R[1]**	**R[2]**	**Yield (%)[a]**
1	**8aa**	H	H	68
2	**8ab**	H	Me	64
3	**8ac**	H	F	41
4	**8ba**	Me	H	61
5	**8bb**	Me	Me	72
6	**8ca**	*t*Bu	H	69
7	**8cb**	*t*Bu	Me	32
8	**8da**	F	H	88
9	**8db**	F	Me	79
10	**8ea**	MeO	H	85
11	**8eb**	MeO	Me	37

Reaction conditions*:* **3** (0.3 mmol), **7** (0.36 mmol), $Pd(Ph_3P)_4$ (0.03 mmol), Xantphos (0.03 mmol), Cs_2CO_3 (0.9 mmol), DMF (4 mL), 120 °C, 24 h.
[a] Isolated yield

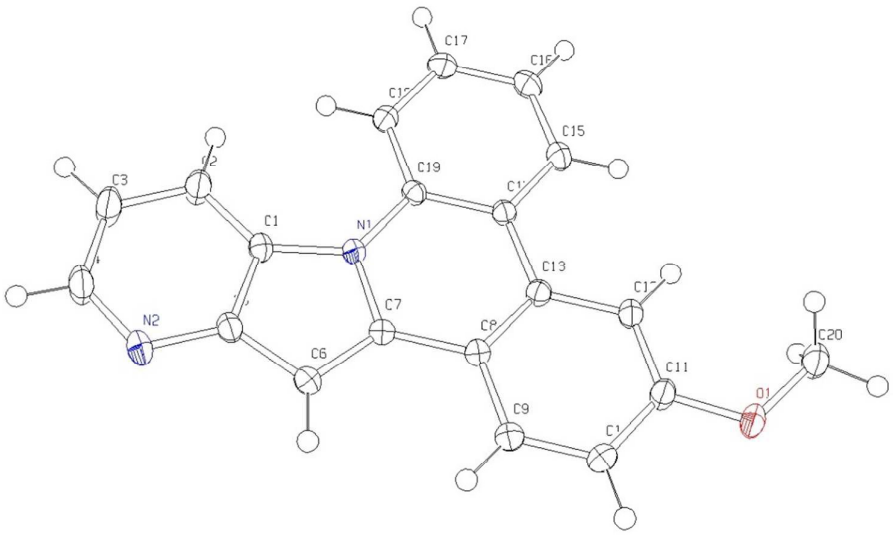
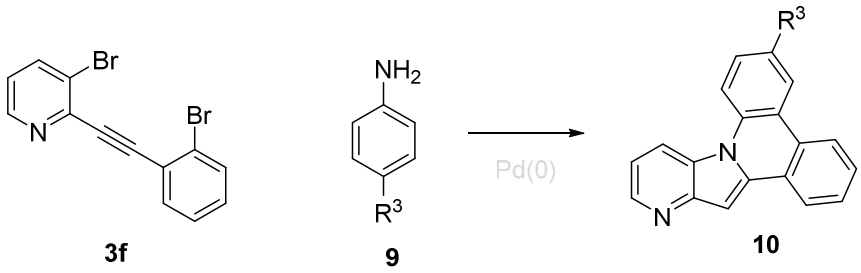


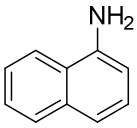
Figure 1: X-ray crystallographic analysis of **8ea**.

Similar to our previous report, we assumed that the position of bromine and hydrogen atom participating in the last step of the reaction could be interchangeable. With this idea in mind, we investigated the reaction of **3f** with various amines to broaden the scope of our strategy.

Table 2. Synthesis of 4-azaindolo[1,2-*f*]phenanthridines



3f **9** **10**

Entry	**10**	**R^3**	**Yield (%)**[a]
1	**10a (8aa)**	H	87
2	**10b**	4-MeO	51
3	**10c**	2-MeO	60
4	**10d**	3-MeO	65 (mixture)
5	**10e (8ac)**	4-F	76
6	**10f (8ab)**	4-CH_3	65
7	**10g**	4-SMe	81
8	**10h**		42

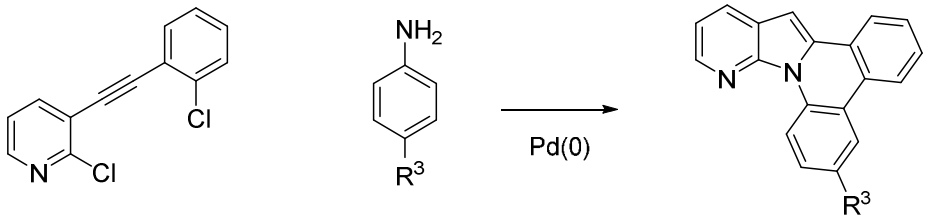
Reaction conditions*:* **3f** (0.3 mmol), **9** (0.36 mmol), $Pd(Ph_3P)_4$ (0.03 mmol), Xantphos (0.03 mmol), Cs_2CO_3 (0.9 mmol), DMF (4 mL), 120 °C, 24 h.
[a]Isolated yield

To our delight, the reaction proceeded without any problem when the same conditions as in the previous reaction were applied, affording desired products in moderate to high yields. Interestingly, compounds **8aa** (**10a**), **8ab** (**10e**), **8ac** (**10f**) could be synthesized by this method with higher yield (87%, entry 1, 5, 6, **table 2**). Besides, other modifications on the aniline ring gave lower yields compared to 2-bromoanline. However, the limitation of this method is the selectivity when meta-substituted amines are used, as demonstrated in entry 4 (**table 2**). In this case using 3-methoxyaniline resulted in a mixture of two products, which we were not able to separate by column chromatography.

Additionally, the selectivity of the Sonogashira reaction on halogenated pyridines gives us the possibility to deliver a higher diversity of products by customizing the starting material. To demonstrate this, we performed the selective Sonogashira mono-coupling reaction of 1-

chloro-2-ethynylbenzene on 3-bromo-2-chloropyridine to afford alkyne **6**. The coupling reaction of 3-bromo-2-chloropyridine is controlled by the chemoselectivity of bromide at position 3 versus the chloride at position 2, compared to 2,3-dibromopyridine in whichreactions at position 2 are more favored. Subsequently, alkyne **6** produced various 7-azaindolo[1,2-*f*]phenanthridines under optimized conditions as shown in **table 3**.

Table 3. synthesis of 7-azaindolo[1,2-*f*]phenanthridines



6 **9** **11**

Entry	**11**	**R^3**	**Yield (%)**[a]
1	**11a**	4-MeO	34
2	**11b**	4-F	51
3	**11c**	4-SMe	36

Reaction conditions*:* **6** (0.3 mmol), **9** (0.36 mmol), $Pd(Ph_3P)_4$ (0.03 mmol), Xantphos (0.03 mmol), Cs_2CO_3 (0.9 mmol), DMF (4 mL), 120 °C, 24 h. (temperature and reaction time were not optimized)
[a] Isolated yield

Absorption and Fluorescence Properties

The optical properties of all synthesized compounds were studied by UV/Vis and fluorescence spectroscopy in CH_2Cl_2 at 25 ºC as summarized in **table 4**. The UV/Vis spectra show an absorption band in the range of 270-300 nm and several weaker bands in the range of 300-400 nm (**figure 2**). In general, introducing electron-donor groups, such as a methyl or methoxy group, at the core structure **8aa** causes a slight red shift of the absorption bands. A stronger redshift was observed for compound **10h** by extending the conjugated system of the core structure. Changing the position of the nitrogen atom in the azaindole moiety (compounds **11a**, **11b**, **11c**) caused also a shift to longer wavelengths. The similar trend was also observed in the emission spectra.

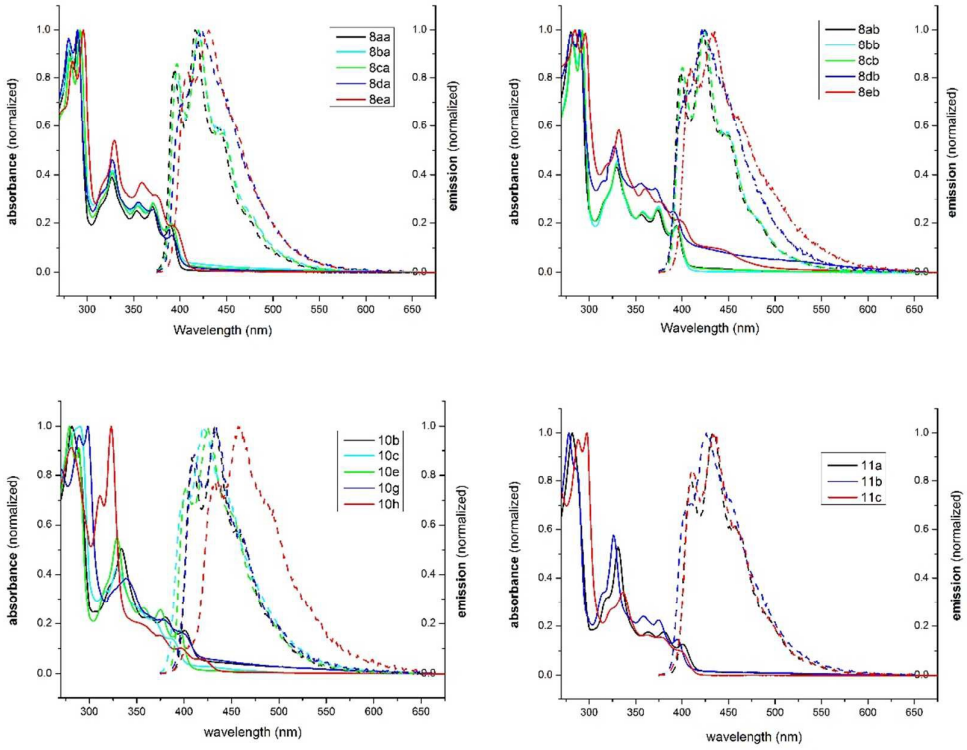


Figure 2. Normalized absorption and corrected emission spectra of azaindolo[1,2-*f*]phenanthridines in CH_2Cl_2.

Table 4. Absorption and emission spectroscopic data of azaindolo[1,2-*f*]phenanthridines

cp	λ_{abs1}	Log $\varepsilon(\lambda_{abs1})$	λ_{abs2} (nm)	Log $\varepsilon(\lambda_{abs2})$	λ_{abs3} (nm)	Log $\varepsilon(\lambda_{abs3})$	λ_{abs4} (nm)	Log $\varepsilon(\lambda_{abs4})$	λ_{abs5} (nm)	Log $\varepsilon(\lambda_{abs5})$	λ_{em} (nm)	max	Φ_{fluo} %
8aa	290	6.347	326	5.937	354	5.744	370	5.777	390	5.623	416		65
8ba	292	6.598	328	6.251	355	6.098	371	6.100	391	5.978	420		42
8ca	292	6.729	327	6.349	354	6.178	371	6.196	390	6.054	420		53
8da	290	6.614	327	6.296	355	6.105	371	6.065	391	5.872	424		28
8ea	296	6.554	329	6.287	359	6.121	373	6.059	391	5.836	431		47
8ab	290	6.576	329	6.214	356	5.953	374	5.984	394	5.860	421		52
8bb	292	6.647	330	6.308	357	6.039	374	6.072	394	5.916	424		56
8cb	292	6.649	330	6.301	375	6.041	374	6.069	394	5.929	425		55
8db	289	6.469	327	6.233	356	6.122	371	6.105	390	6.011	424		14
8eb	296	6.338	332	6.115	360	5.893	375	5.819	396	5.702	435		32
10b	282	6.503	334	6.234	361	5.947	380	5.946	400	5.858	432		28
10c	290	6.645	330	6.288	-	-	368	6.010	385	5.832	420		28
10e	289	6.581	329	6.363	357	6.049	375	6.036	395	5.871	425		38
10g	289	6.567	338	6.203	-	-	375	5.994	-	-	434		12
10h	281	6.646	-	-	374	5.897	396	5.735	418	5.530	459		19
11a	282	6.785	331	6.060	364	6.060	380	6.063	400	5.930	433		40
11b	278	6.649	326	6.416	358	6.056	375	6.027	395	5.858	426		30
11c	288	6.845	337	6.337	363	6.018	376	5.993	400	5.785	436		26

Fluorescence spectra of the compounds were measured in CH_2Cl_2 exciting them at 360 nm. The spectra show maximal emission in the range of 416 nm to 469 nm. Emission quantum yields were determined using a solution of quinine hemisulfate salt monohydrate in 0.05 M H_2SO_4 (Φ= 0.52) as a reference standard.[12] Compound **8aa** which contains no substituent possesses the highest quantum yield of 65%. Noteworthy, the quantum yield of indolo[1,2-*f*]phenanthridine was reported to be only 21%. Therefore, in comparison with indolo[1,2-*f*]phenanthridine, introducing one more nitrogen atom to the scaffold gives a much better result. However, introducing both electron-donor and electron-withdrawing groups to the core structure leads to decreased quantum yields. The poorest quantum yield of 12% was observed in compound **10g** which contains a methylthio group.

Conclusions

In conclusion, we have developed an efficient method for synthesizing a series of new azaindolo[1,2-*f*]phenanthridines. The reaction evolves one-pot three steps: C-N coupling, hydroamination, and C-H arylation reaction. In addition, the starting materials were easily accessible by regioselective Sonogashira cross-coupling reaction, which lead to diverse final products. The absorption and fluorescence properties of all products were studied. This class of compounds shows promising photophysical properties, in particular high quantum yields.

Experimental section

All chemicals used are commercially available and were used without further purification. Column chromatography was performed using Merck Silicagel 60 (0.043-0.06 mm).

NMR data were recorded on a Bruker AC 250, Bruker ARX 300, Bruker ARX 500 spectrometers.

Gas chromatography-mass analysis was carried out on an AgilentHP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column using helium carrier gas. ESI HR-MS measurements were performed on an Agilent 1969A TOF mass-spectrometer. For High Resolution MS (HRMS), a Finnigan MAT95 XP was used. Only the measurements with an average deviation from the theoretical mass of ±2mDa were accounted as correct.

Infrared Spectra were recorded on a Nicolet 550 FT – IR spectrometer with ATR sampling technique.

Absorption spectra were measured with the UV/Vis-spectrophotometer Specord 50 from Analytik Jena and the fluorescence spectra using the spectrofluorometer Fluoromax-4 of Horiba Scientific.

General procedure for synthesis of azaindolo[1,2-*f*]phenanthridines:

3-bromo-2-(phenylethynyl)pyridine **3** (0.3 mmol), 2-bromoaniline **7** (1.1 equiv., 0.33 mmol), $Pd(Ph_3P)_4$ (10 mol%, 0.03 mmol,), Xantphos (10 mol%, 0.03 mmol), and Cs_2CO_3 (3 equiv., 0.9 mmol) were placed in a dried pressure tube equipped with a septum. Then dried and degassed DMF (4 mL) was added under argon. The reaction was back-filled with argon three times and the septum was replaced with a Teflon cap. The reaction mixture was allowed to stir at 120 °C for 24 h. Then the reaction mixture was cooled to room temperature and was filtered through a pad of Celite. The filtrate was dried under reduced pressure, and the product **3** was obtained after flash chromatography on a silica gel column with ethyl acetate.

Pyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8aa

Yellowish solid, 86%. M.p.: 144 - 145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.62 (dd, *J* = 4.6, 1.0 Hz, 1H), 8.50 (d, *J* = 8.6 Hz, 1H), 8.35 – 8.17 (m, 2H), 8.17 – 7.90 (m, 2H), 7.53 – 7.43 (m, 3H), 7.39 – 7.09 (m, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 147.6, 144.9, 138.3, 135.2, 129.0, 128.9, 128.5, 127.0, 126.9, 125.2, 124.9, 124.3, 123.7, 122.4, 121.9, 121.3, 116.2, 116.0, 96.8. IR (ATR, cm^{-1}): = 3123 (w), 3099 (w), 3062 (w), 3034 (w), 1887 (w), 1598 (m), 1580 (w), 1556 (s), 1503 (w), 1488 (w), 1479 (m), 1453 (m), 1440 (s), 1414 (s), 1401 (w), 1378 (m), 1356 (m), 1325 (w), 1311 (w), 1303 (w), 1279 (m), 1236 (m), 1186 (m), 1138 (w), 1127 (w), 1110 (w), 1073 (w), 1051 (w), 1042 (w), 973 (w), 954 (w), 943 (w), 923 (w), 908 (w), 877 (w), 862 (w), 833 (w), 805 (w), 774 (w), 745 (s), 731 (w), 708 (m), 666 (w), 640 (w), 617 (m), 608 (w), 584 (w), 574 (w), 556 (w), 537 (w). MS (EI, 70 eV): m/z(%) = 268 (M^+, 100), 240 (7), 214 (3), 134 (10), 120 (13), 106 (5). HRMS (EI): Calculated for $C_{19}H_{12}N_2$ (M^+): 268.09950, found: 268.09952.

3-methylpyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8ba

Yellowish solid, 61%. M.p.:162 - 164 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.72 – 8.54 (m, 1H), 8.50 – 8.36 (m, 1H), 8.19 (dd, *J* = 10.5, 5.7 Hz, 2H), 7.95 – 7.78 (m, 2H), 7.54 – 7.36 (m, 1H), 7.34 – 7.09 (m, 4H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.9, 144.8, 138.8, 138.5, 135.3, 129.7, 128.8, 126.8, 124.8, 124.1, 123.5, 122.6, 122.5, 121.9, 121.0,

115.9, 115.8, 96.1, 22.0. (Signal of one C tertiary could not be detected). IR(ATR, cm^{-1}): = 3120 (w), 3093 (w), 3061 (w), 3032 (w), 2917 (w), 2851 (w), 1914 (w), 1883 (w), 1613 (w), 1598 (m), 1575 (w), 1557 (m), 1550 (w), 1493 (w), 1481 (w), 1444 (s), 1414 (s), 1375 (m), 1349 (m), 1306 (m), 1283 (m), 1238 (m), 1208 (w), 1189 (m), 1164 (w), 1149 (w), 1127 (w), 1115 (w), 1079 (m), 1039 (m), 956 (m), 943 (w), 923 (m), 913 (w), 903 (w), 873 (m), 834 (w), 810 (s), 772 (m), 755 (s), 734 (s), 714 (w), 660 (w), 651 (w), 623 (m), 610 (m), 578 (s), 545 (w), 532 (s). MS (EI, 70 eV): m/z(%) = 282 (M^+, 100), 266 (4), 140 (10), 128 (2), 126 (5). HR-MS (EI): calculated for $C_{20}H_{14}N_2$ (M^+): 282.11515, found: 282.11477.

3-(*tert*-butyl)pyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8ca

Yellowish solid, 69%. M.p.: 176 – 178 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.63 (d, *J* = 4.1 Hz, 1H), 8.53 (d, *J* = 8.6 Hz, 1H), 8.41 – 8.29 (m, 2H), 8.24 (d, *J* = 1.7 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.48 (m, 2H), 7.42 – 7.32 (m, 2H), 7.22 (dd, *J* = 8.5, 4.6 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.1, 148.0, 144.9, 138.5, 135.5, 128.9, 127.0, 126.6, 126.5, 124.9, 124.2, 123.6, 122.8, 122.4, 121.1, 118.7, 116.1, 116.0, 96.3, 35.4, 31.4 (3C). IR (ATR, cm^{-1}): = 3060 (w), 3025 (w), 2947 (m), 2902 (w), 2860 (w), 1931 (w), 1884 (w), 1732 (w), 1615 (w), 1598 (m), 1578 (w), 1557 (m), 1504 (w), 1494 (m), 1479 (w), 1463 (w), 1443 (s), 1413 (s), 1392 (w), 1357 (w), 1348 (m), 1303 (w), 1275 (m), 1265 (m), 1242 (w), 1205 (w), 1187 (m), 1162 (w), 28 1151 (w), 1127 (w), 1115 (w), 1097 (w), 1070 (w), 1053 (w), 1039 (w), 1021 (w), 970 (w), 956 (m), 925 (w), 913 (w), 875 (m), 832 (w), 813 (m), 788 (s), 769 (m), 756 (s), 738 (s), 710 (w), 657 (w), 648 (w), 623 (s), 608 (w), 584 (m), 542 (s). MS (EI, 70 eV): m/z(%) = 324 (M^+, 100), 309 (98), 294 (28), 290 (4), 281 (12), 268 (15), 240 (4), 154 (4), 146 (4), 140 (24), 132 (6), 126 (4), 41 (3), 39 (3). HR-MS (EI): calculated for $C_{23}H_{20}N_2$ (M^+): 324.16210, found: 324.16196.

3-fluoropyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8da

Yellowish solid, 88%. M.p.: 213 - 215 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 3.6 Hz, 1H), 8.41 (d, *J* = 8.6 Hz, 1H), 8.23 – 8.11 (m, 1H), 8.02 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.95 (dd, *J* = 8.8, 5.7 Hz, 1H), 7.66 (dd, *J* = 10.6, 2.5 Hz, 1H), 7.55 – 7.45 (m, 1H), 7.32 – 7.23 (m, 2H), 7.23 – 7.08 (m, 3H). ^{19}F NMR (63 MHz, CDCl3) δ = 110.77 Hz. ^{13}C NMR (63 MHz, $CDCl_3$) δ = 163.1 (d, *J* = 248.2 Hz), 147.7, 145.1, 137.5, 135.5, 129.7, 129.1 (d, *J* = 8.4 Hz), 127.2 (d, *J* = 8.9 Hz), 126.8, 124.4, 123.7, 121.5 (d, *J* = 2.5 Hz), 121.1, 121.1, 116.5 (d, *J* = 23.2 Hz), 116.2, 116.0, 108.5 (d, *J* = 23.4 Hz), 96.5 (d, *J* = 1.3 Hz). IR (ATR, cm^{-1}): = 3059 (w), 3035 (w), 1616 (m), 1603 (m), 1580 (w), 1558 (m), 1551 (m), 1489 (m), 1443 (s), 1416 (s), 1379 (w), 1349 (m), 1331 (w), 1304 (w), 1272 (m), 1245 (w), 1236 (w), 1180 (s), 1135

(w), 1128 (w), 1106 (w), 1072 (w), 1054 (w), 1032 (w), 957 (m), 933 (w), 915 (w), 892 (m), 854 (w), 819 (w), 810 (m), 784 (w), 763 (s), 755 (m), 733 (s), 706 (w), 652 (m), 631 (m), 621 (m), 606 (w), 599 (m), 583 (w), 545 (w), 533 (m). MS (EI, 70 eV): m/z(%) = 286 (M^+, 100), 258 (7), 232 (3), 195 (2), 143 (10), 129 (11), 115 (3). HR-MS (EI): calculated for $C_{19}H_{11}N_2F_1$ (M^+): 286.09008, found: 286.08980.

3-methoxypyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8ea

Yellowish solid, 85%. M.p.: 200 – 201 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.49 (d, *J* = 4.2 Hz, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.98 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.44 – 7.29 (m, 2H), 7.22 – 7.12 (m, 1H), 7.07 (dd, *J* = 8.5, 4.6 Hz, 1H), 7.02 (s, 1H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.2, 148.0, 144.7, 138.6, 135.5, 129.1, 128.5, 126.8, 126.6, 124.2, 123.5, 121.7, 120.9, 118.6, 116.3, 116.0, 115.6, 105.6, 95.2, 55.5. IR (ATR, cm^{-1}): = 3089 (w), 3032 (w), 2999 (w), 2958 (w), 2930 (w), 2908 (w), 2831 (w), 1609 (s), 1601 (s), 1550 (s), 1493 (s), 1450 (s), 1438 (w), 1428 (w), 1414 (s), 1379 (w), 1347 (m), 1334 (w), 1303 (w), 1278 (s), 1244 (w), 1219 (s), 1190 (m), 1181 (w), 1141 (w), 1130 (w), 1111 (w), 1079 (w), 1073 (w), 1056 (w), 1041 (w), 1033 (w), 1021 (m), 980 (w), 971 (w), 956 (m), 912 (w), 905 (w), 883 (w), 872 (w), 865 (w), 830 (m), 823 (w), 813 (s), 785 (w), 766 (s), 753 (s), 736 (s), 705 (w), 656 (m), 634 (m), 623 (m), 607 (s), 584 (m), 555 (m), 539 (m). MS (EI, 70 eV): m/z(%) = 298 (M^+, 100), 283 (20), 255 (63), 227 (7), 149 (9), 127 (4), 113 (5), 99 (3). HR-MS (EI): calculated for $C_{20}H_{14}N_2O_1$ (M^+): 298.11006, found: 298.10998.

6-methylpyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8ab

Yellow solid, 64%. M.p.: 184 – 186 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.60 (s, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.13 – 7.95 (m, 3H), 7.91 (s, 1H), 7.54 – 7.35 (m, 2H), 7.30 (s, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.2, 144.4, 139.9, 138.3, 133.14 133.0, 129.8, 128.8, 128.3, 127.0, 125.0, 125.0, 124.4, 122.4, 121.7, 121.3, 116.0, 115.7, 96.2, 21.2. IR (ATR, cm^{-1}): = 3124 (w), 3069 (w), 3036 (w), 2954 (w), 2916 (m), 2850 (m), 2746 (w), 1942 (w), 1900 (w), 1877 (w), 1860 (w), 1823 (w), 1795 (w), 1600 (m), 1577 (w), 1569 (m), 1553 (s), 1524 (w), 1496 (m), 1450 (s), 1416 (s), 1387 (w), 1372 (w), 1354 (m), 1324 (w), 1310 (w), 1300 (w), 1279 (m), 1236 (w), 1193 (w), 1182 (m), 1165 (w), 1145 (w), 1124 (m), 1116 (m), 1066 (w), 1042 (w), 999 (w), 972 (w), 955 (m), 937 (w), 910 (m), 883 (w), 866 (m), 853 (m), 828 (w), 801 (m), 790 (s), 772 (m), 748 (s), 730 (w), 720 (w), 710 (w), 694 (w), 660 (w), 643 (m), 620 (w), 576 (s), 540 (m). MS (EI, 70 eV): m/z(%) = 282

(M^+, 100), 266 (4), 252 (3), 140 (16), 126 (5), 113 (2), 100 (2). HRMS (EI): calculated for $C_{20}H_{14}N_2$ (M^+): 282.11515, found: 282.11484.

3,6-dimethylpyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8bb

Yellowish solid, 72%. M.p.: 208 – 210 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.59 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.79 (s, 1H), 7.35 – 6.87 (m, 4H), 2.45 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.71, 144.59, 138.65, 138.40, 133.12, 132.85, 129.55, 129.47, 126.82, 126.71, 124.81, 124.23, 122.63, 122.41, 121.65 (2C), 120.88, 115.63, 95.65, 22.00, 21.15. IR (ATR, cm^{-1}): = 3154 (w), 3115 (w), 3097 (w), 3056 (w), 3025 (w), 3004 (w), 2952 (w), 2917 (m), 2851 (w), 1920 (w), 1898 (w), 1854 (w), 1613 (w), 1601 (m), 1569 (w), 1549 (s), 1491 (m), 1481 (w), 1434 (w), 1416 (s), 1373 (w), 1352 (w), 1300 (w), 1281 (m), 1262 (w), 1237 (m), 1205 (w), 1192 (m), 1152 (w), 1121 (w), 1099 (w), 1069 (w), 1041 (m), 957 (m), 929 (w), 906 (w), 877 (m), 867 (w), 817 (w), 806 (s), 784 (s), 754 (s), 741 (w), 716 (w), 694 (w), 660 (m), 629 (w), 622 (w), 590 (m), 578 (m), 560 (w), 533 (s). MS (EI, 70 eV): m/z(%) = 296 (M^+, 100), 279 (11), 266 (2), 148 (6), 147 (3), 146 (3), 140 (7), 126 (2). HR-MS (EI): calculated for C21H16N2 ($[M+1]^{+1}$): 297.13862, found: 297.13882.

3-(*tert*-butyl)-6-methylpyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8cb

Yellow solid, 32%; M.p. 197 - 199 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 – 8.56 (m, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.23 – 8.07 (m, 4H), 7.63 – 7.57 (m, 1H), 7.36 – 7.29 (m, 2H), 7.20 (dd, *J* = 8.5 Hz, *J* = 4.5 Hz, 1H), 2.51 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.0, 147.9, 144.8, 138.4, 133.4, 133.1, 129.8, 126.7, 126.3, 125.0, 124.3, 122.9, 122.3, 121.0, 118.6, 116.0, 115.8, 96.0, 35.4, 31.5, 21.3 (3C) (one signal of C tertiary could not be detected). IR (ATR, cm^{-1}): = 3033 (w), 2956 (m), 2914 (w), 2864 (w), 1615 (w), 1600 (w), 1569 (w), 1556 (m), 1548 (m), 1489 (w), 1482 (w), 1460 (w), 1444 (w), 1427 (w), 1414 (s), 1391 (w), 1379 (w), 1357 (m), 1353 (m), 1301 (w), 1280 (m), 1263 (m), 1240 (w), 1202 (w), 1187 (w), 1159 (w), 1131 (w), 1121 (w), 1067 (w), 1045 (w), 958 (m), 941 (w), 925 (w), 904 (w), 880 (m), 865 (w), 830 (m), 811 (w), 786 (s), 774 (s), 757 (s), 736 (w), 722 (m), 666 (w), 656 (w), 634 (w), 620 (w), 611 (w), 578 (m), 552 (s), 533 (w). MS (EI, 70 eV): m/z(%) = 338 (M^+, 100), 323 (85), 308 (29), 295 (9), 282 (11) , 266 (3), 161 (7), 153 (4), 152 (3), 147 (23), 140 (8), 139 (5), 133 (4), 41 (5), 39 (4). HR-MS (EI): calculated for $C_{24}H_{22}N_2$ (M^+): 338.17775, found: 338.17773.

3-fluoro-6-methylpyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8db

Yellow solid, 79%. M.p.: 233 – 235 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.68 (s, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 8.11 – 8.01 (m, 2H), 7.84 (s, 1H), 7.76 – 7.69 (m, 1H), 7.35 – 7.22 (m, 3H), 7.19 (dd, *J* = 8.4 Hz, *J* = 2.3 Hz, 1H), 2.48 (s, 3H). ^{19}F NMR (63 MHz, $CDCl_3$) δ = 110.92. ^{13}C NMR (63 MHz, $CDCl_3$) δ = 163.1 (d, *J* = 247.9 Hz), 147.5, 144.9, 137.5, 133.3, 133.3, 130.5, 129.1 (d, *J* = 8.4 Hz), 127.2 (d, *J* = 8.9 Hz), 124.6, 121.6 (d, *J* = 2.4 Hz), 121.0, 120.9 (d, *J* = 3.0 Hz), 116.4 (d, *J* = 23.2 Hz), 116.0, 115.8, 108.5 (d, *J* = 23.4 Hz), 96.1 (s), 21.2 (Signal of one C tertiary could not be detected). IR (ATR, cm^{-1}): = 3033 (w), 2956 (m), 2914 (w), 2864 (w), 1615 (w), 1600 (w), 1569 (w), 1556 (m), 1548 (m), 1489 (w), 1482 (w), 1460 (w), 1444 (w), 1427 (w), 1414 (s), 1391 (w), 1379 (w), 1357 (m), 1353 (m), 1301 (w), 1280 (m), 1263 (m), 1240 (w), 1202 (w), 1187 (w), 1159 (w), 1131 (w), 1121 (w), 1067 (w), 1045 (w), 958 (m), 941 (w), 925 (w), 904 (w), 880 (m), 865 (w), 830 (m), 811 (w), 786 (s), 774 (s), 757 (s), 736 (w), 722 (m), 666 (w), 656 (w), 634 (w), 620 (w), 611 (w), 578 (m), 552 (s), 533 (w). MS (EI, 70 eV): m/z(%) = 338 (M^+, 100), 323 (85), 308 (29), 295 (9), 282 (11), 266 (3), 161 (7), 153 (4), 147 (23), 140 (8), 139 (5), 133 (4), 41 (5), 39 (4). HR-MS (EI): calculated for $C_{24}H_{22}N_2$ (M^+): 338.17775, found: 338.17773.

3-methoxy-6-methylpyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8eb

Yellow solid, 37%, M.p.: 183 – 185 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.57 (s, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.93 (s, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.31 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.24 – 7.13 (m, 2H), 7.07 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.95 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.5, 147.2, 143.7, 139.1, 133.3, 130.2, 128.8, 127.0, 126.9, 124.5, 121.7, 121.4, 118.6, 116.4, 115.9, 115.4, 105.8, 94.5, 55.7, 21.3. (one signal of C tertiary could not be detected). IR (ATR, cm^{-1}): = 3094 (w), 3029 (w), 3005 (w), 2916 (w), 2839 (w), 2054 (m), 1722 (w), 1610 (s), 1572 (w), 1546 (s), 1493 (s), 1467 (w), 1452 (w), 1432 (w), 1418 (s), 1378 (w), 1353 (w), 1333 (w), 1300 (w), 1282 (s), 1243 (w), 1223 (s), 1194 (m), 1188 (m), 1152 (w), 1125 (w), 1074 (w), 1028 (s), 959 (m), 936 (w), 906 (w), 860 (w), 833 (m), 819 (m), 803 (w), 782 (s), 773 (m), 751 (s), 710 (w), 682 (w), 668 (w), 633 (m), 621 (w), 587 (w), 579 (w), 545 (s). MS (EI, 70 eV): m/z(%) = 312 (M^+, 100), 297 (16), 269 (53), 253 (4), 239 (2), 156 (10), 134 (7), 121 (3), 120 (3), 107 (2). HR-MS (EI): calculated for $C_{21}H_{16}N_2O_1$ (M^+): 312.12571, found: 312.12596.

6-fluoropyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 8ac

Yellow solid, 41%. M.p.: 220 – 221 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.65 (d, *J* = 4.0 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.23 (dd, *J* = 9.2, 4.8 Hz, 1H), 8.16 – 8.07 (m, 1H), 8.07 – 8.00

(m, 1H), 7.90 (dd, *J* = 10.0, 2.8 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.36 (s, 1H), 7.28 – 7.16 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -118.20. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.0 (d, *J* = 243.3 Hz), 147.7, 145.3, 137.9, 131.8 (d, *J* = 2.1 Hz), 129.3, 129.0, 126.8, 126.2 (d, *J* = 2.5 Hz), 125.6, 125.1, 124.0 (d, *J* = 7.7 Hz), 122.7, 120.7, 117.5 (d, *J* = 8.1 Hz), 116.5, 116.1 (d, *J* = 23.2 Hz), 110.6 (d, *J* = 23.9 Hz), 97.1. IR (ATR, cm^{-1}): = 3131.1 (w), 3056.8 (w), 3031.7 (w), 2920.8 (w), 2850.5 (w), 1942.2 (w), 1889.7 (w), 1573.4 (m), 1557.6 (s), 1496.3 (m), 1452.2 (m), 1420.5 (s), 1280.2 (m), 1243.7 (m), 1201.1 (m), 1174.1 (m), 1137.7 (m), 1108.0 (w), 1168.8 (m), 957.1 (m), 909.6 (m), 856.1 (m), 806.8 (m), 782.8 (m), 746.5 (s), 577.9 (m). MS (EI, 70 eV): m/z(%) = 286 (M^+, 100), 258 (7), 232 (5), 208 (2), 195 (3), 168 (3), 143 (6), 128 (3), 99 (2), 87 (2), 75 (2), 62 (5), 51 (3), 39 (3). HR-MS (EI): calculated for $C_{19}H_{11}N_2F_1$ (M^+): 286.09008, found: 286.09014.

6-methoxypyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 10b

Yellowish solid, 51%. M.p.: 156 – 157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 4.0 Hz, 1H), 8.41 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 8.10 – 8.00 (m, 2H), 7.64 (d, *J* = 2.8 Hz, 1H), 7.53 – 7.39 (m, 2H), 7.32 (s, 1H), 7.19 (dd, *J* = 8.6, 4.6 Hz, 1H), 7.03 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 155.7, 147.4, 144.7, 137.9, 129.7, 128.8, 128.6, 126.8, 126.7, 125.4, 125.1, 123.3, 122.5, 120.84 117.1, 116.3, 115.3, 108.4, 96.3, 55.7. IR (ATR, cm^{-1}): = 3133.5 (w), 3055.6 (w), 2919.6 (w), 2849.1 (w), 1957.7 (w), 1925.7 (w), 1900.2 (w), 1726.6 (w), 1616.8 (m), 1606.1 (m), 1569.7 (m), 1552.5 (s), 1500.3 (m), 1453.4 (m), 1419.4 (s), 1350.4 (m), 1218.9 (m), 1185.5 (m), 1138.4 (m), 1018.3 (m), 956.6 (m), 850.5 (m), 789.6 (m), 755.3 (s), 694.9 (m), 583.2 (m). MS (EI, 70 eV): m/z (%) = 298 (M^+, 100), 283 (37), 255 (70), 227 (11). 200 (5), 174 (4), 149 (8), 127 (7), 114 (11), 100 (5), 87 (7), 75 (4), 63 (4), 51 (4), 39 (6). HR-MS (EI): calculated for $C_{20}H_{14}N_2O_1$ (M^+): 298.11006, found: 298.10977.

8-methoxypyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 10c

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.59 (dd, *J* = 4.5, 0.9 Hz, 1H), 8.25 – 8.12 (m, 2H), 8.10 – 8.03 (m, 1H), 7.94 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.65 – 7.45 (m, 3H), 7.39 (t, *J* = 8.1 Hz, 1H), 7.22 – 7.07 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 149.5, 146.9, 144.4, 139.1, 129.9, 128.9, 128.8, 127.3, 125.9, 125.4, 124.9, 124.7 (2C), 124.1, 123.1, 116.4, 115.0, 112.1, 97.6, 55.9. MS (EI, 70 eV): m/z (%) = 298 (M^+, 100), 283 (83), 253 (13), 227 (7), 201 (4), 175 (2), 142 (10), 127 (6), 114 (7), 100 (7). HRMS (EI): calculated for $C_{20}H_{14}N_2O_1$ (M^+): 298.11006, found: 298.11014.

6-(methylthio)pyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 10g

Yellow solid, 81%. M.p.: 172 – 173 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.61 (s, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.17 – 7.97 (m, 4H), 7.57 – 7.42 (m, 2H), 7.35 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.31 (s, 1H), 7.22 (dd, *J* = 8.5, 4.6 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.2, 144.6, 138.2, 133.5, 133.0, 129.0, 128.8, 127.9, 126.4, 125.2, 125.1, 122.8, 122.6, 122.4, 121.3, 116.5, 116.2, 96.7, 16.8. (one signal of C-tertiary could not be detected). IR (ATR, cm^{-1}): = 3031.8 (w), 3001.0 (w), 2958.0 (w), 2917.4 (w), 2849.2 (w), 1597.0 (w), 1646.3 (m), 1488.3 (w), 1449.2 (m), 1413.4 (s), 1354.0 (m), 1278.7 (m), 1189.0 (m), 1115.3 (w), 955.0 (m), 855.7 (w), 789.8 (s), 750.4 (s), 580.6 (m). MS (EI, 70 eV): m/z(%) = 314 (M^+, 100), 299 (52), 266 (9), 255 (28), 227 (4), 157 (13), 127 (6), 113 (3), 100 (2). HRMS (EI): calculated for $C_{20}H_{14}N_2S_1$ (M^+): 314.08722, found: 314.08694.

Benzo[c]pyrido[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine 10h

Yellow solid, 42%. M.p.: 231 – 232 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.64 (d, *J* = 4.0 Hz, 1H), 8.34 – 8.11 (m, 4H), 7.96 – 7.84 (m, 2H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.47 (m, 3H), 7.45 (d, *J* = 0.6 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.03 (dd, *J* = 8.5, 4.5 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 147.6, 145.4, 139.8, 134.1, 129.9, 129.2, 129.0, 128.7, 128.3, 127.6, 127.2, 125.9, 125.2, 124.7, 124.6, 124.3, 123.7, 123.0, 122.1, 121.0, 120.5, 114.0, 97.7. IR (ATR, cm^{-1}): = 3096.6 (w), 2958.7 (w), 2850.5 (w), 1954.5 (w), 1915.3 (w), 1808.3, 1713.7 (w), 1621.8 (w), 1576.9 (m), 1543.0 (m), 1416.8 (s), 1389.4 (m), 1274.8 (m), 1029.8 (m), 807 (m), 752.5 (s), 611.2 (m), 566.6 (m). MS (EI, 70 eV): m/z(%) = 318 (M^+, 100), 291 (12), 237 (2), 159 (41), 144 (23), 131 (9), 105 (2), 87 (1). HRMS (EI): calculated for $C_{23}H_{14}N_2$ (M^+): 318.11515, found: 318.11507.

6-methoxypyrido[3',2':4,5]pyrrolo[1,2-*f*]phenanthridine11a

Yellowish solid, 34%. M.p.: 186 – 187 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.15 (d, *J* = 9.3 Hz, 1H), 8.50 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.24 – 7.97 (m, 3H), 7.72 (d, *J* = 2.8 Hz, 1H), 7.57 – 7.39 (m, 2H), 7.34 – 7.16 (m, 2H), 7.08 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 155.8, 146.9, 141.8, 134.6, 129.9, 128.4, 128.3, 128.2, 127.4, 125.8, 124.3, 122.8, 122.7, 122.1, 120.4, 117.5, 115.5, 107.5, 92.4, 55.7. IR (ATR, cm^{-1}): = 3104.4 (w), 2997.7 (w), 2930.7 (w), 2830.5 (w), 2089.0 (w), 1892.9 (w), 1713.5 (w), 1620.3 (w), 1563.3 (m), 1543.8 (s), 1499.5 (m), 1453.9 (m), 1407.9 (m), 1327 (m), 1293.2 (m), 1215.2 (m), 1075.3 (m), 1042.8 (m), 1016.0 (m), 945.9 (w), 855.2 (m), 792.4 (m), 758.9 (m), 729.0 (m), 607.9 (m), 566.3 (m). MS (EI, 70 eV): m/z(%) = 298 (M^+, 100), 283 (34), 255 (61), 227 (7), 201 (3), 175 (2), 149 (15), 127 (16), 113 (4), 100 (5). HRMS (EI): calculated for $C_{20}H_{14}N_2O_1$ (M^+): 298.11066, found: 298.11047

6-fluoropyrido[3',2':4,5]pyrrolo[1,2-*f*]phenanthridine 11b

Yellowish solid, 51%. M.p.: 201 – 202 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.26 (dd, *J* = 9.3, 5.5 Hz, 1H), 8.50 (dd, *J* = 4.5, 1.3 Hz, 1H), 8.25 – 8.03 (m, 3H), 7.91 (dd, *J* = 10.3, 2.7 Hz, 1H), 7.52 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.41 – 7.26 (m, 2H), 7.11 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -118.48. ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.3 (d, *J* = 242.1 Hz), 142.1, 134.6, 131.9, 130.4, 128.9, 128.7, 128.4, 126.8 (d, *J* = 1.9 Hz), 125.8, 124.3, 123.4 (d, *J* = 7.6 Hz), 122.9, 122.2, 121.0 (d, *J* = 7.8 Hz), 117.9, 116.4 (d, *J* = 22.4 Hz), 109.3 (d, *J* = 24.0 Hz), 93.0. IR (ATR, cm^{-1}): = 3122.0 (w), 3054.0 (w), 1920.0 (w), 1884.2 (w), 1798.7 (w), 1661.0 (w), 1620.4 (w), 1567.0 (m), 1497.6 (m), 1454.6 (m), 1409.4 (m), 1329.7 (m), 1267.7 (m), 1174.5 (m), 1141.0 (m), 892.5 (m), 824.2 (m), 752.8 (m), 724.4 (m), 662.7 (w), 593.9 (m), 566.3 (m). MS (EI, 70 eV): m/z(%) = 286 (M^+, 100), 258 (10), 232 (3), 143 (17), 129 (4), 115 (3). HRMS (EI): calculated for $C_{19}H_{11}N_2F_1$ (M^+): 286.09008, found: 286.08990.

6-(methylthio)pyrido[3',2':4,5]pyrrolo[1,2-*f*]phenanthridine 11c

Yellow solid, 36%. M.p.: 168 – 169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.14 (d, *J* = 8.9 Hz, 1H), 8.49 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.27 – 8.11 (m, 2H), 8.10 – 7.99 (m, 2H), 7.57 – 7.41 (m, 3H), 7.26 (dd, *J* = 7.9, 4.7 Hz, 1H), 7.06 (s, 1H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.1, 142.0, 134.7, 133.4, 132.9, 128.5 (2C), 128.4, 128.2, 127.0, 125.7, 124.2, 122.7, 122.3, 122.2, 122.0, 119.8, 117.7, 93.0, 17.2. IR (ATR, cm^{-1}): = 3107.2 (w), 3037.2 (w), 2918.0 (w), 2849.6 (w), 2731.2 (w), 2520.1 8w), 2387.1 (w), 2116.4 (w), 1959.0 (w), 1916.1 (w), 1724.9 (w), 1595.9 (m), 1541.6 (m), 1453.3 (s), 1405.6 (s), 1323.5 (m), 1103.3 (m), 955.8 (m), 818.2 (m), 793.9 (s), 758.7 (s), 730.2 (s), 646.5 (m), 585.3 (m). MS (EI, 70 eV): m/z(%) = 314 (M^+, 100), 299 (59), 266 (7), 255 (29), 227 (3), 201 (1), 157 (14), 133 (5), 113 (2). HRMS (EI): calculated for $C_{20}H_{14}N_2S_1$ (M^+): 314.08722, found: 314.08645.

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References

(1) (a) Slaninová, I.; Pěnčíková, K.; Urbanová, J.; Slanina, J.; Táborská, E. *Phytochem. Rev.* **2013**, *13* (1), 51. (b) Walton, J. C. *Acc. Chem. Res.* **2014**, *47* (4), 1406. (c) Tumir, L.-M.; Radić Stojković, M.; Piantanida, I. *Beilstein J. Org. Chem.* **2014**, *10* (1), 2930.

(d) Ahmed, E.; Briseno, A. L.; Xia, Y.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2008**, *130* (4), 1118. (e) Abet, V.; Nuñez, A.; Mendicuti, F.; Burgos, C.; Alvarez-Builla, J. *J. Org. Chem.* **2008**, *73* (22), 8800. (f) Mishra, A.; Bäuerle, P. *Angew. Chem. Int. Ed. Engl.* **2012**, *51* (9), 2020. (g) Zhu, L.; Kim, E.-G.; Yi, Y.; Ahmed, E.; Jenekhe, S. A.; Coropceanu, V.; Brédas, J.-L. *J. Phys. Chem. C* **2010**, *114* (48), 20401. (h) Bondarev, S. L.; Knyukshto, V. N.; Tikhomirov, S. A.; Pyrko, A. N. *Opt. Spectrosc.* **2006**, *100* (3), 386.

(2) (a) Nakanishi, T.; Suzuki, M.; Saimoto, A.; Kabasawa, T. *J. Nat. Prod.* **1999**, *62* (6), 864. (b) Nakanishi, T.; Masuda, A.; Suwa, M.; Akiyama, Y.; Hoshino-Abe, N.; Suzuki, M. *Bioorg. Med. Chem. Lett.* **2000**, *10* (20), 2321.(c) Nakanishi, T.; Suzuki, M. *J. Nat. Prod.* **1998**, *61* (10), 1263. (d) Phillips, S. D.; Castle, R. N. *J. Heterocycl. Chem.* **1981**, *18* (2), 223.S

(3) Ritchie, C.; Cooper, G. J. T.; Song, Y.-F.; Streb, C.; Yin, H.; Parenty, A. D. C.; MacLaren, D. A.; Cronin, L. *Nat. Chem.* **2009**, *1* (1), 47.

(4) Almerico, A. M.; Mingoia, F.; Diana, P.; Barraja, P.; Montalbano, A.; Lauria, A.; Loddo, R.; Sanna, L.; Delpiano, D.; Setzu, M. G.; Musiu, C. *Eur. J. Med. Chem.* **2002**, *37* (1), 3.

(5) Satoh, T.; Miura, M.; Takeda, D.; Hirano, K. *Heterocycles* **2012**, *86* (1), 487.

(6) (a) Wang, T.; Yin, Z.; Zhang, Z.; Bender, J. A.; Yang, Z.; Johnson, G.; Yang, Z.; Zadjura, L. M.; D'Arienzo, C. J.; DiGiugno Parker, D.; Gesenberg, C.; Yamanaka, G. A.; Gong, Y.-F.; Ho, H.-T.; Fang, H.; Zhou, N.; McAuliffe, B. V; Eggers, B. J.; Fan, L.; Nowicka-Sans, B.; Dicker, I. B.; Gao, Q.; Colonno, R. J.; Lin, P.-F.; Meanwell, N. A.; Kadow, J. F. *J. Med. Chem.* **2009**, *52* (23), 7778. (b) Wang, T.; Yang, Z.; Zhang, Z.; Gong, Y.-F.; Riccardi, K. A.; Lin, P.-F.; Parker, D. D.; Rahematpura, S.; Mathew, M.; Zheng, M.; Meanwell, N. A.; Kadow, J. F.; Bender, J. A. *Bioorg. Med. Chem. Lett.* **2013**, *23* (1), 213. (c) Tanis, S. P.; Plewe, M. B.; Johnson, T. W.; Butler, S. L.; Dalvie, D.; DeLisle, D.; Dress, K. R.; Hu, Q.; Huang, B.; Kuehler, J. E.; Kuki, A.; Liu, W.; Peng, Q.; Smith, G. L.; Solowiej, J.; Tran, K. T.; Wang, H.; Yang, A.; Yin, C.; Yu, X.; Zhang, J.; Zhu, H. *Bioorg. Med. Chem. Lett.* **2010**, *20* (24), 7429. (d) Plewe, M. B.; Butler, S. L.; R. Dress, K.; Hu, Q.; Johnson, T. W.; Kuehler, J. E.; Kuki, A.; Lam, H.; Liu, W.; Nowlin, D.; Peng, Q.; Rahavendran, S. V.; Tanis, S. P.; Tran, K. T.; Wang, H.; Yang, A.; Zhang, J. *J. Med. Chem.* **2009**, *52* (22), 7211.

(7) Tietze, L. F.; Brasche, G.; Gericke, K. M. *Domino Reactions in Organic Synthesis*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2006. (b) L. F. Tietze, *Domino Reactions: Concepts for Efficient Organic Synthesis*, Wiley-VCH, 2013. (c) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1991**, *113* (2), 701. (d) de Meijere, A.; von Zezschwitz, P.; Bräse, S. *Acc. Chem. Res.* **2005**, *38* (5), 413. (e) Liang, J.; Hu, W.; Tao, P.; Jia, Y. *J. Org. Chem.* **2013**, 78, 5810. (f) Tao, P.; Liang, J.; Jia, Y. *Eur. J. Org. Chem.* **2014**, 5735. (g) Pawliczek, M.; Jones, P. G.; Werz, D. B. *Eur. J. Org. Chem.* **2015**, 6278.

(8) Xie, C.; Zhang, Y.; Huang, Z.; Xu, P. *J. Org. Chem.* **2007**, *72* (14), 5431.

(9) Yan, L.; Zhao, D.; Lan, J.; Cheng, Y.; Guo, Q.; Li, X.; Wu, N.; You, J. *Org. Biomol. Chem.* **2013**, *11* (45), 7966.

(10) Chen, C.; Shang, G.; Zhou, J.; Yu, Y.; Li, B.; Peng, J. *Org. Lett.* **2014**, *16* (7), 1872.

(11) Ngo, T. N.; Ehlers, P.; Dang, T. T.; Villinger, A.; Langer, P. *Org. Biomol. Chem.* **2015**, *13* (11), 3321.

(12) Meech, S. R.; Phillips, D. *J. Photochem.* **1983**, *23* (2), 193.