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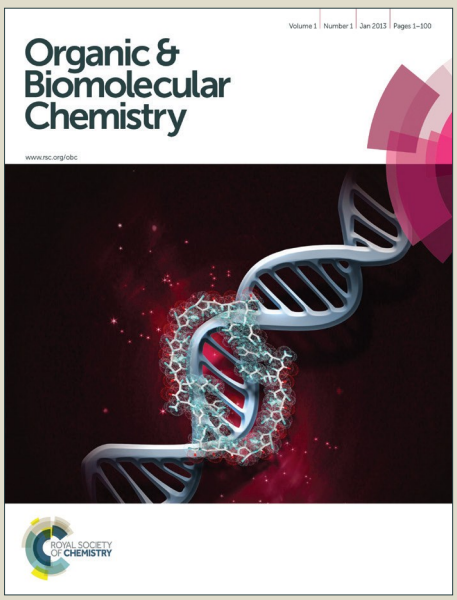

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Synthesis of Indolo[1,2-*f*]phenanthridines by Pd-catalyzed Domino C-N Coupling/Hydroamination/C-H Arylation Reactions

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Dedicated to Professor Dietmar Seyferth

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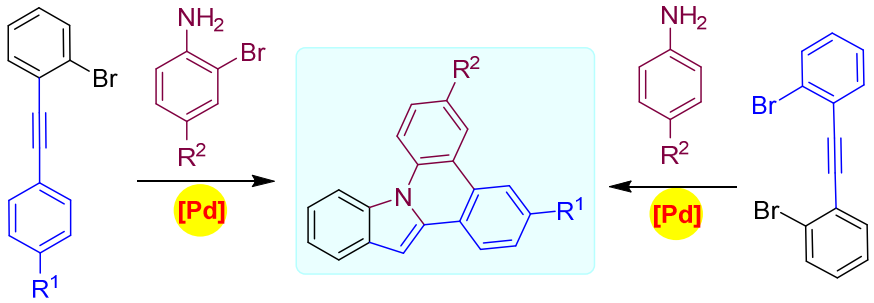


Abstract: A new and convenient method for the synthesis of indolo[1,2-*f*]phenanthridines via palladium-catalyzed domino C-N coupling/hydroamination/C-H arylation reactions was developed. The reactions allow for the synthesis of various phenanthridines in good yields from easily accessible starting materials using a single palladium catalyst.

Introduction

Nitrogen-containing polycyclic compounds are of interest in medicinal chemistry and materials science, owing to their biological and physical properties. A large number of nitrogen-containing

fused heterocycles have been discovered in nature with remarkable bioactivities, some of them have been used as leading compounds in drug discovery.[1] Moreover, fused phenanthridines also found applications in medicinal chemistry. For example, natural alkaloids (manitidine, fagaronine, and coralyne) containing the benzo[*c*]phenanthridine moiety possess interesting antitumor activity and are important targets for total syntheses and biological evaluations.[2] In addition, benzo[*c*]phenanthridines have been considered as important materials for developing new semiconductors and organic light-emitting diodes (OLEDs), due to their large π-conjugated electron system.[3] In particular, recent studies showed that fused phenanthridines possess interesting optical and electronic properties. For instance, phenanthridines fused with *N*-heterocycles are potential candidates for the development of new blue-emitting materials.[4,9] Furthermore, organic dyes, that contain an indolo[1,2-*f*]phenanthridine moiety, exhibit broad and intense visible absorptions, which are promising new sensitizers for dye-sensitized solar cells.[5]

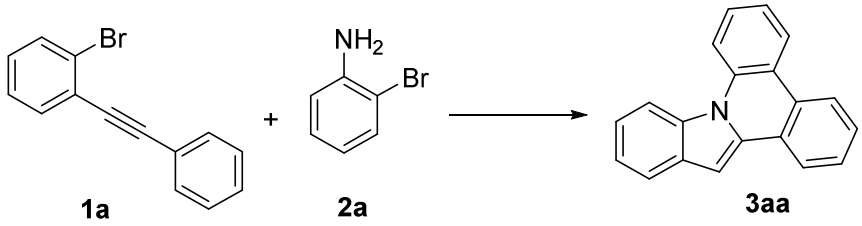
Although many methods for the synthesis of phenanthridines were developed in recent years, most of them require many steps and/or harsh conditions.[6] Therefore, the development of new and efficient methods is important and necessary for the development of new bioactive molecules and organic materials. In recent years, the advances in transition-metal-catalyzed reactions have facilitated considerably the approach to complex structures. Palladium-catalyzed domino reactions proved to be a useful tool for the synthesis of fused heterocyclic compounds with high atom economy.[7] In 2007, Zhang and coworkers published a convenient method to synthesize indolo[1,2-*f*]phenanthridines by reaction of arynes with 1-(2-bromophenyl)-1*H*-indole in the presence of a Pd catalyst.[8] However, the preparation of the starting materials proved to be difficult and requires many synthetic steps. In 2012, Mirua *et al.* and later in 2013, You *et al.* independently reported an interesting Pd-catalyzed domino N–H/C–H arylation for the regioselective synthesis of *N*-heterocyclic fused phenanthridines.[9,10] These authors used readily available 2-arylindoles and 1,2-dibromobenzene as the starting materials, however, they did not study the scope of their methodology and only two derivatives have been reported in their paper. A similar cascade process involving C-H arylations followed by an intramolecular *N*-arylation reaction to prepare benzimidazole-fused phenanthridines in moderate to good yields was published by Peng *et al.* in 2014.[11] More recently, Wang and Lv reported a one-pot tandem approach to indolo[1,2-*f*]phenanthridines employing 2-alkynylanilines and boronic acids via Cu-catalyzed C-N coupling/hydroamination and Pd-catalyzed C-H arylation.[12]

In addition to our continuous contributions to develop new synthetic methods for the synthesis of fused heterocycles,[13] we wish to report two new domino reactions which provide an efficient approach to various indolo[1,2-*f*]phenathridines. The transformations proceed through three sequential steps in a one-pot reaction: C-N coupling, hydroamination, and C-H arylation reactions with employment of a single Pd catalyst.

Results and discussion

For the purpose of studying the reaction, 1-bromo-2-(phenylethynyl)benzene **1a** and 2-bromoaniline **2a** were chosen as model substrates. Initially, the reaction was carried out in DMF at 120 °C using Cs_2CO_3 as the base in the absence of catalyst and ligand. However, the reaction did not give the desired product **3aa**. When we introduced 10 mol% $Pd(OAc)_2$ as the catalyst source in the presence of 20 mol% PPh_3 to the reaction mixture, the product was isolated in 34% yield after 24h. In order to improve the yield, we examined a series of monodentate and bidentate phosphine ligands. Consequently, Xantphos (10 mol%) and $PCy_3 \cdot HBF_4$ (20 mol%) were found to be the best ligands as the reaction resulted in 75% and 74% yields of **3aa**, respectively. For further investigation, we used Xantphos and applied other palladium precursors. No product could be isolated when $Pd_2(dba)_3$ was used, while 70% yield of the desired product was obtained when $Pd(PPh_3)_4$ was employed. It proved to be important to use Cs_2CO_3 as the base. Only trace amounts of product were detected when other bases were used, such as K_2CO_3 and KO*t*Bu. Variation of solvent and temperature did not lead to improved yields.

Table 1: Optimization for the synthesis of **3aa**



Entry	catalyst	ligand	base	Yield (%)[a]
1	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	34
2	$Pd(OAc)_2$	BINAP	Cs_2CO_3	34
3	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	75
4	$Pd(OAc)_2$	DPEphos	Cs_2CO_3	70
5	$Pd(OAc)_2$	DPPE	Cs_2CO_3	38
6	$Pd(OAc)_2$	DPPF	Cs_2CO_3	41
7	$Pd(OAc)_2$	Xphos	Cs_2CO_3	45
8	$Pd(OAc)_2$	SPhos	Cs_2CO_3	34
9	$Pd(OAc)_2$	RuPhos	Cs_2CO_3	38
10	$Pd(OAc)_2$	Davphos	Cs_2CO_3	64
11	$Pd(OAc)_2$	$PCy_3 \cdot HBF_4$	Cs_2CO_3	74
12	$Pd(OAc)_2$	$P(t\text{Bu})_3 \cdot HBF_4$	Cs_2CO_3	5
13	$Pd(Ph_3P)_4$	Xantphos	Cs_2CO_3	70
14	$Pd_2(dba)_3$	Xantphos	Cs_2CO_3	trace
15	$Pd(OAc)_2$	Xantphos	K_2CO_3	trace
16	$Pd(OAc)_2$	Xantphos	KO*t*Bu	5

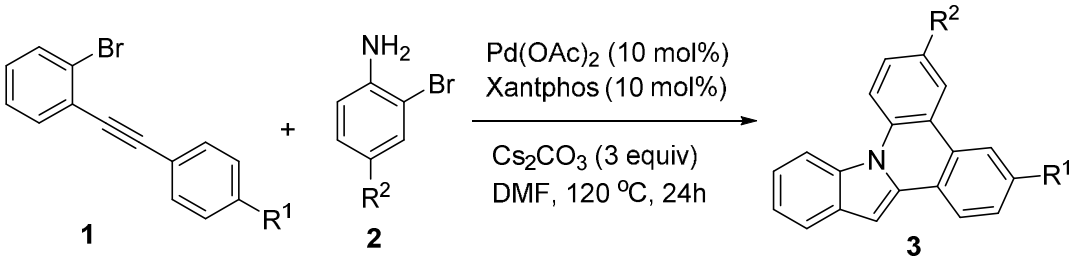
Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (0.01 mmol), ligand (10% with monodentate ligands, 20% with bidentate ligands), Cs_2CO_3 (0.3 mmol), DMF (1 mL), 120 °C, 24 h.

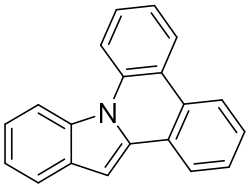
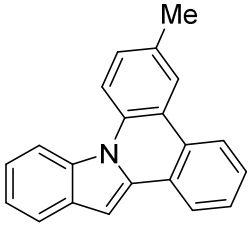
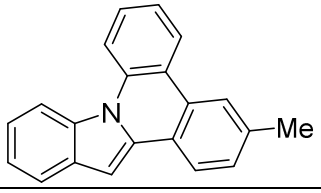
[a] Isolated yield

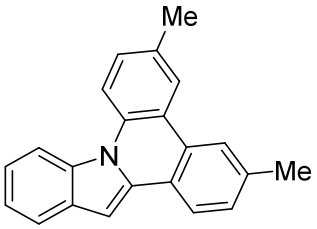
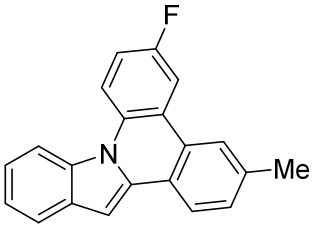
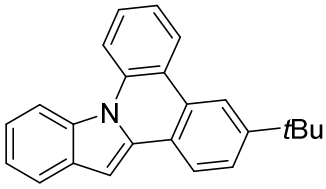
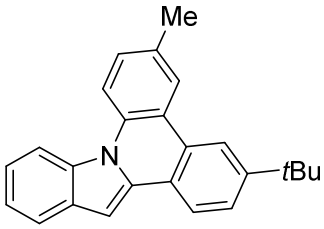
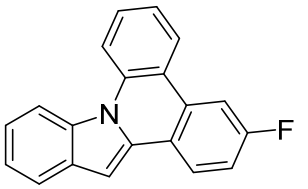
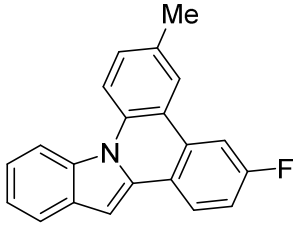
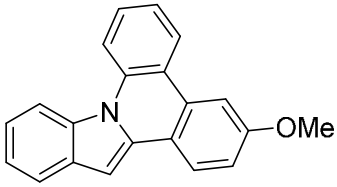
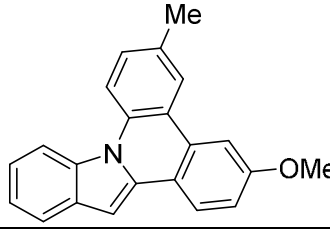
With the optimized conditions in hand, we extended the scope of the reaction by modifying both substrates to prepare a series of indolo[1,2-*f*]phenanthridines. A number of alkynes **1a-e** were synthesized by chemoselective Sonogashira coupling reactions of 2-bromo-iodobenzene with 1.1 equiv of various phenylacetylenes, including electron-withdrawing and -donating substituents. These compounds were obtained in nearly quantitative yield when using a reported procedure.[14] The reaction of **1a-e** with 2-bromoanilline **2a**, 2-bromo-4-methylaniline **2b**, and 2-bromo-4-

fluoroaniline **2c** afforded various indolo[1,2-*f*]phenathridines **3** (Table 2). In general, 1-bromo-2-(phenylethynyl)benzene or 2-bromoaniline derivatives, bearing electron-donating or -withdrawing groups, afforded the corresponding products in moderate to good yields under optimized conditions. The presence of substituents located at the aryl group of the 1-bromo-2-(phenylethynyl)benzene had no pronounced effect on the yield. In contrast, the structure of the 2-bromoaniline derivative had a greater impact, but did not follow a clear trend. The best yields were obtained for **3da** and **3ea** (Table 2). The structure of **3db** was unambiguously confirmed by X-ray crystallography.

Table 2: Synthesis of indolo[1,2-*f*]phenathridines



Entry	R^1	R^2	Products	Yield (%)[a]
1	H (**1a**)	H (**2a**)	 **3aa**	75
2	H (**1a**)	Me (**2b**)	 **3ab**	66
3	Me (**1b**)	H (**2a**)	 **3ba**	52

4	Me (**1b**)	Me (**2b**)	 **3bb**	45
5	Me (**1b**)	F (**2c**)	 **3bc**	55
6	*t*Bu (**1c**)	H (**2a**)	 **3ca**	65
7	*t*Bu (**1c**)	Me (**2b**)	 **3cb**	67
8	F (**1d**)	H (**2a**)	 **3da**	77
9	F (**1d**)	Me (**2b**)	 **3db**	54
10	MeO (**1e**)	H (**2a**)	 **3ea**	78
11	MeO (**1e**)	Me (**2b**)	 **3eb**	73

Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), $Pd(OAc)_2$ (0.03 mmol), Xantphos (0.03 mmol), Cs_2CO_3 (0.9 mmol), DMF (4 mL), 120 °C, 24 h.

[a] Isolated yield

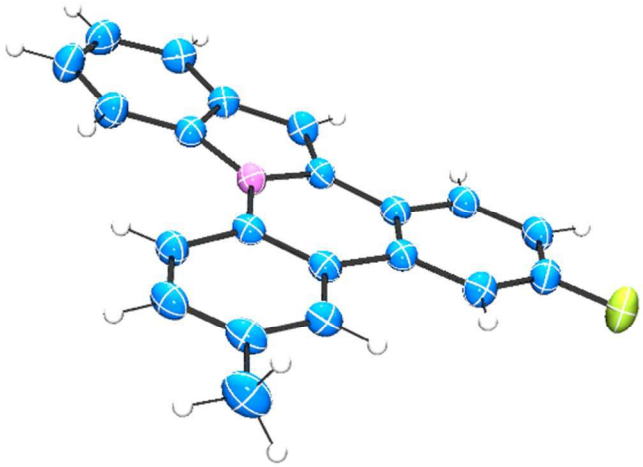
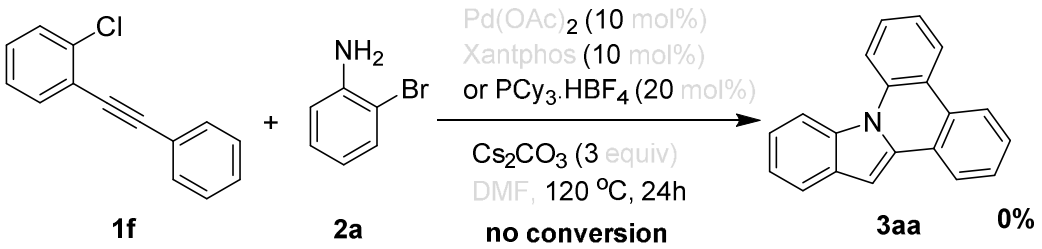


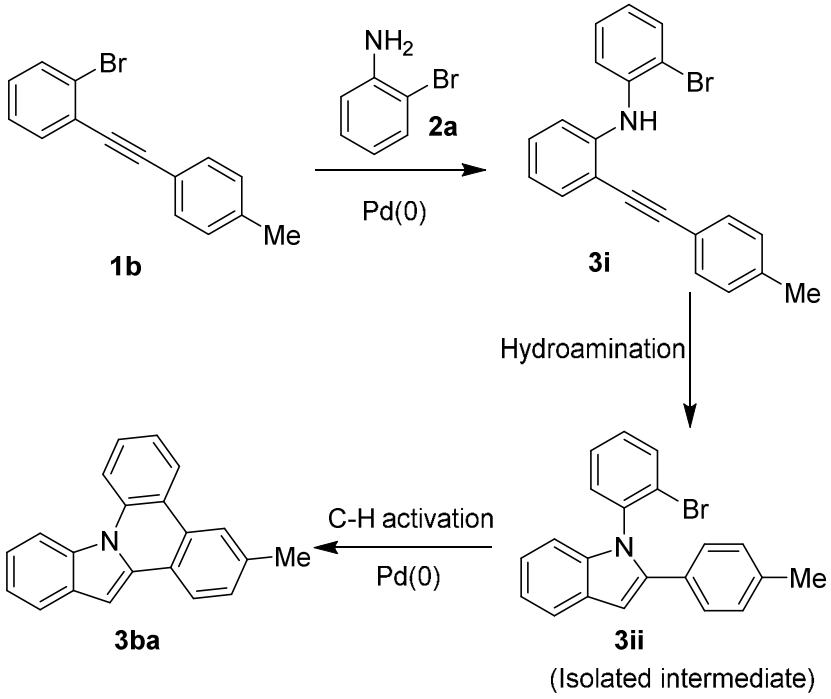
Figure 1: X-ray crystal structure analysis of **3db**

Moreover, we conducted additional experiments to study the applicability of less reactive chlorine substitutents in the reaction. We realized that the bromine substituent in acetylene **1** played a crucial role in the reaction, since no conversion of 1-chloro-2-(phenylethynyl)benzene **1f** was observed when reacting with 2-bromoaniline under our optimized conditions.



Scheme 1: Reaction of 1-chloro-2-(phenylethynyl)benzene **1f** with 2-bromoaniline

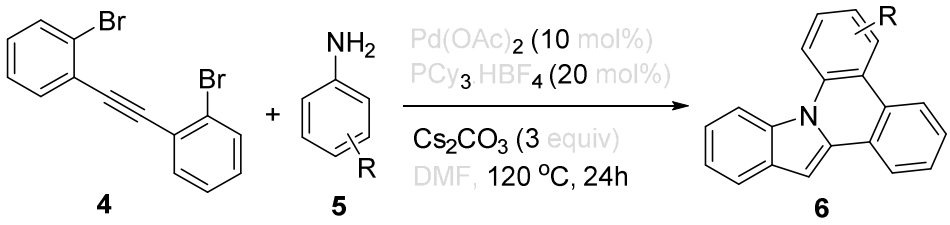
A possible mechanistic pathway of the formation of indolo[1,2-*f*]phenanthridines is proposed in Scheme 2. First, a Buchwald-Hartwig reaction of **1b** with 2-bromoaniline **2a** gave intermediate **3i**. Intramolecular hydroamination of **3i** subsequently formed intermediate **3ii** (which could be isolated and structurally confirmed by NMR spectroscopy). Finally, an intramolecular C-H activation took place to give indolo[1,2-*f*]phenanthridine **3ba.**



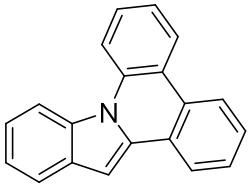
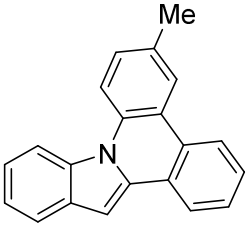
Scheme 2: Proposed pathway for the reaction

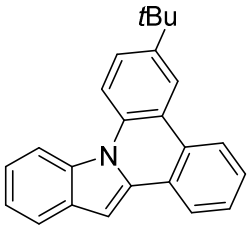
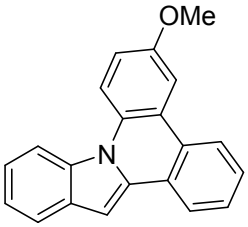
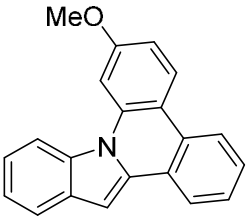
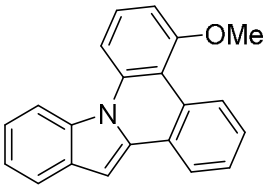
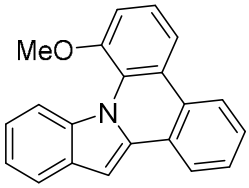
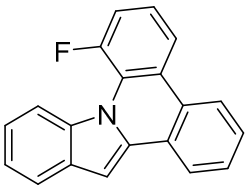
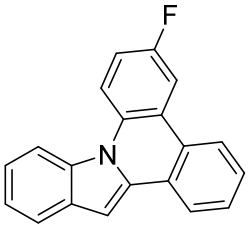
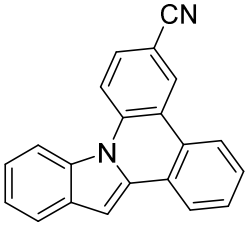
Encouraged by the successful isolation of intermediate **3ii**, we considered the application of 1,2-bis(2-bromophenyl)ethyne **4** as a suitable alternative starting material for our reaction. This would allow the employment of simple anilines as educts and would widely broaden the scope of our methodology. To our delight, the reaction of 1,2-bis(2-bromophenyl)ethyne **4** with various anilines proceeded smoothly and produced the desired products **6a-j** in moderate to good yields (Table 3). Anilines containing a fluoro substituent gave very good results with 72% and 75% isolated yields (entries 7, 8). When employing an unsymmetrical aniline (entry 5), a mixture of two inseparable isomers **6e1** and **6e2** with 1:3 ratio was formed. In the case of anilines with strong electron donating substitutes (entries 4, 5, 6, Table 3), only trace amounts of dehalogenated side products (**3ii**) were detected by GS-MS during the reaction.

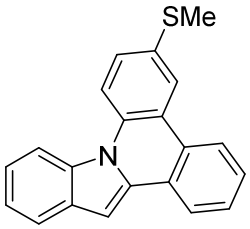
Table 3: Reaction of 1,2-bis(2-bromophenyl)ethyne **4** with amines



4 **5** **6**

Entry	R	Products	Yield (%)[a]
1	H (**5a**)	 **6a (3aa)**	52
2	4-Me (**5b**)	 **6b (3ba)**	55

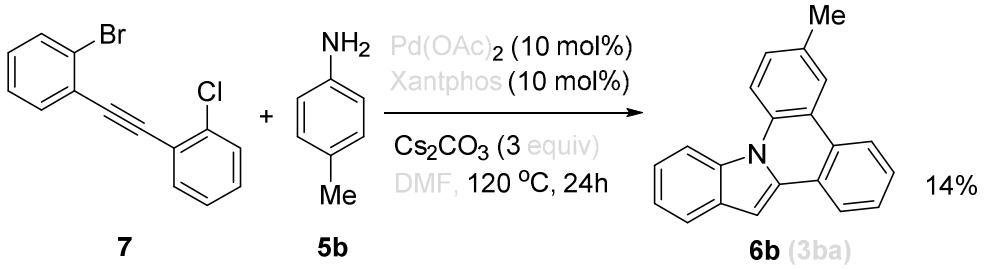
3	4-*t*Bu (**5c**)	 **6c**	43
4	4-MeO (**5d**)	 **6d**	49
5	3-MeO (**5e**)	 **6e1**  **6e2**	43[b]
6	2-MeO (**5f**)	 **6f**	49
7	2-F (**5g**)	 **6g**	72
8	4-F (**5h**)	 **6h**	75
9	4-CN (**5i**)	 **6i**	44

10	4-MeS (**5j**)	 **6j**	56

Reaction conditions: **4** (0.3 mmol), **5** (0.36 mmol), $Pd(OAc)_2$ (0.03 mmol), ($PCy_3 \cdot HBF_4$ 0.06 mmol), Cs_2CO_3 (0.9 mmol), DMF (4 mL), 120 °C, 24 h.

[a] Isolated yield
[b] inseparable mixture (ratio 1:3 determined by NMR)

It is clear that employment of unsymmetrical acetylenes **4** would result in a selectivity issue. In order to address this problem, we investigated the reaction of 1-bromo-2-((2-chlorophenyl)ethynyl)benzene **7** containing two different halides. The reaction of **7** with *p*-toluidine afforded, using our optimized conditions, the desired product **3ba** in only 14% yield. As mentioned before, no conversion takes place in the reaction of 1-chloro-2-(phenylethynyl)benzene with 2-bromoaniline under the same conditions. Therefore, we assume that our reactions proceed by Buchwald Hartwig reaction at the C-Br bond, followed by hydroamination and intramolecular C-H arylation at the C-Cl bond.



Scheme 3: Reaction of 1-bromo-2-((2-chlorophenyl)ethynyl)benzene with *p*-toluidine

In conclusion, we have developed two Pd-catalyzed three-step tandem reactions comprising of the three sequential reactions: C-N coupling, hydroamination and C-H arylation reaction. Our

methods offer a straightforward synthesis of indolo[1,2-*f*]phenanthridines under mild conditions with good yields which are interesting for further applications in the synthesis of new organic materials and bioactive molecules. Our starting materials, 1-halo-2-(phenylethynyl)benzenes and 1-bromoanilines, are readily available. In addition, our methodology is broadly applicable and a wide range of products could be successfully prepared in moderate to good yields. As mentioned in the introduction,[9] You and coauthors prepared two similar products in good yields by Pd catalyzed domino reaction of readily available 2-arylindoles and 1,2-dibromobenzene as the starting materials. However, they did not study the scope of their methodology and reported the synthesis of only two derivatives.

Experimental Section

General information. 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. Compounds **1a**, **1b**, **1c**, **1d**, **1e**, **4**, **7** were prepared according to procedure described in literature.[15,16,17] The synthesis of 3aa has been previously reported.[18]

General procedure for synthesis of Indolo[1,2-*f*]phenanthridines: 1-bromo-2-(phenylethynyl)benzene **1** (0.3 mmol), 2-bromoaniline **2** (0.33 mmol), $Pd(OAc)_2$ (0.03 mmol, 10%), Xantphos (0.03 mmol, 10%), and Cs_2CO_3 (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 heptane. For compounds **6c**, **6d**, **6h**, **6i**, **6j**, **6g**, **6f**, 20% of $PCy_3 \cdot HBF_4$ was used instead of Xantphos.

1-Bromo-2-(phenylethynyl)benzene (1a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.52 (m, 4H), 7.41 – 7.34 (m, 3H), 7.30 (td, ^3J = 7.6, ^4J = 1.2 Hz, 1H), 7.18 (td, 3J = 7.8, ^4J = 1.7 Hz, 1H). ^{13}C-NMR (63 MHz, $CDCl_3$) δ 133.37, 132.60, 131.85 (2C), 129.51, 128.79, 128.52 (2C), 127.17, 125.79, 125.57, 123.07, 94.07, 88.16.

1-Bromo-2-(*p*-tolylethynyl)benzene (1b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, ^3J = 8.0, ^4J = 1.2 Hz, 1H), 7.55 (dd, ^3J = 7.7, ^4J = 1.7 Hz, 1H), 7.48 (d, ^3J = 8.1 Hz, 2H), 7.33 – 7.24 (m, 1H), 7.22 – 7.12 (m, 3H), 2.38 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 139.00, 133.28, 132.56, 131.74 (2C), 129.31, 129.29 (2C), 127.14, 125.76, 125.71, 119.99, 94.34, 87.57, 21.70.

1-Bromo-2-((4-(*tert*-butyl)phenyl)ethynyl)benzene (1c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.47 (m, 4H), 7.39 (d, ^3J = 8.5 Hz, 2H), 7.33 – 7.24 (m, 1H), 7.17 (td, ^3J = 7.9, ^4J = 1.7 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 152.15, 133.31, 132.57, 131.59 (2C), 129.32, 127.13, 125.80, 125.78, 125.54 (2C), 120.04, 94.31, 87.57, 34.99, 31.32 (3C).

1-Bromo-2-((4-fluorophenyl)ethynyl)benzene (1d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 4H), 7.29 (td, ^3J = 7.6, ^4J = 1.3 Hz, 1H), 7.18 (td, ^3J = 7.8, ^4J = 1.7 Hz, 1H), 7.11 – 7.02 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.26. ^{13}C NMR (63 MHz, $CDCl_3$) δ 162.90 (d, ^1J = 250.1 Hz), 133.77 (d, ^3J = 8.4 Hz, 2C), 133.31, 132.63, 129.59, 127.20, 125.74, 125.40, 119.17 (d, ^4J = 3.5 Hz), 115.86 (d, ^2J = 22.1 Hz, 2C), 92.97, 87.86.

1-Bromo-2-((4-methoxyphenyl)ethynyl)benzene (1e). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.0, ^4J = 1.1 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.28 (td, ^3J = 7.6, ^4J = 1.3 Hz, 1H), 7.20 – 7.11 (m, 1H), 6.93 – 6.85 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 160.09, 133.33 (2C), 133.15, 132.53, 129.15, 127.13, 125.87, 125.58, 115.16, 114.19 (2C), 94.22, 86.99, 55.46.

1,2-Bis(2-bromophenyl)ethyne (4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 4H), 7.31 (td, ^3J = 7.6, ^4J = 1.3 Hz, 2H), 7.24 – 7.16 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 133.77 (2C), 132.67 (2C), 129.88 (2C), 127.17 (2C), 125.67 (2C), 125.27 (2C), 92.39 (2C).

Synthesis of indolo[1,2-*f*]phenanthridine (3aa). Yellowish solid, 75%. M.p.: 150-151 °C. IR (ATR): 3054.8, 1938.2, 1594.9, 1562.1, 1550.6, 1485, 1452.2, 1434.9, 1355.8, 1334.6, 1251.6, 1199.6, 1107.0, 1041.4, 956.6, 788.8, 754.1, 742.5, 711.6, 613.3, 574.7 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.55 (dd, $^3J = 8.5$, $^4J = 0.8$ Hz, 1H), 8.45 – 8.35 (m, 1H), 8.32 (dd, $^3J = 8.1$, $^4J = 1.4$ Hz, 1H), 8.27 – 8.18 (m, 1H), 8.18 – 8.09 (m, 1H), 7.90 – 7.80 (m, 1H), 7.63 – 7.52 (m, 1H), 7.53 – 7.44 (m, 2H), 7.44 – 7.31 (m, 3H), 7.26 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 136.26, 135.52, 134.18, 130.64, 129.00, 128.46, 128.09, 127.13, 126.43, 124.42, 124.28, 123.31, 122.68, 122.37, 122.31, 122.06, 121.32, 116.60, 114.50, 96.49. MS (EI,70 eV): m/z (%) = 267 (M+, 100), 239(8), 134(11), 120(4), 106(3). HRMS (EI, 70 eV): calcd for $C_{20}H_{13}N_1$ ($[M]^+$): 267.10425, found: 267.10431.

Synthesis of 6-methylindolo[1,2-*f*]phenanthridine (3ab). Yellowish solid, 66%. M.p.: 170-171 °C. IR (ATR): 3120.4, 3043.3, 2914.1, 1930.0, 51593.0, 1562.1, 1550.6, 1488.8, 1446.4, 1355.8, 1332.6, 1251.6, 1195.7, 1112.8, 1043.4, 958.5, 788.8, 754.1, 736.7, 713.6, 615.2, 578.6 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2) δ 8.46 (d, $^3J = 8.6$ Hz, 1H), 8.38 (d, $^3J =$ Hz, 1H), 8.32 – 8.24 (m, 1H), 8.22 – 8.13 (m, 2H), 7.88 – 7.79 (m, 1H), 7.57 – 7.48 (m, 2H), 7.47 – 7.42 (m, 1H), 7.42 – 7.30 (m, 2H), 7.29 (d, $^4J = 0.7$ Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (63 MHz, CD_2Cl_2) δ 135.73, 134.43, 134.38, 133.33, 130.83, 130.29, 128.75, 128.46, 127.46, 126.72, 124.89, 124.72, 123.01, 122.50, 122.46, 122.19, 121.50, 116.76, 114.70, 96.39, 21.39. MS (EI,70 eV): m/z (%) = 281 (M+, 100), 252(3), 139(12). HRMS (+ESI): calcd for $C_{21}H_{16}N_1$ ($[M+H]^+$): 282.12773, found: 282.12775.

Sythesis of 3-methylindolo[1,2-f]phenanthridine (3ba). Yellowish solid, 52%. M.p.: 135-136 °C. IR (ATR): 3114.6, 3043.3, 2912.1, 2854.3, 1907.3, 1598.8, 1564.1, 1556.3, 1494.6, 1440.6, 1351.9, 1340.4, 1253.6, 1199.6, 1112.8, 1035.6, 958.5, 781.1, 757.9, 740.6, 713.6, 615.2, 578.6, 532.3 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.56 (dd, $^3J = 8.5$, $^4J = 0.9$ Hz, 1H), 8.43 – 8.30 (m, 2H), 8.08 – 8.01 (m, 2H), 7.88 – 7.80 (m, 1H), 7.64 – 7.53 (m, 1H), 7.44 – 7.30 (m, 4H), 7.22 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 137.87, 136.27, 135.67, 133.99, 130.65, 129.69, 128.78, 126.99, 124.32, 124.13, 123.90, 123.13, 122.73, 122.29, 121.93, 121.89, 121.05, 116.51, 114.33, 95.65, 22.04. MS (EI,70 eV): m/z (%) = 281 (M^+, 100), 252 (3), 139 (10), 126 (4). HRMS (EI, 70 eV): calcd for $C_{21}H_{15}N_1$ ($[M]^+$): 281.11990, found: 281.12033.

Synthesis of 3,6-dimethylindolo[1,2-*f*]phenanthridine (3bb). Yellowish solid, 45%. M.p.: 185-186 °C. IR (ATR): 3106.9, 3054.8, 2912.1, 2850.4, 2725.1, 1917.0, 1729.9, 1598.8, 1562.1, 1498.5, 1444.5, 1350.0, 1251.6, 1201.5, 1112.8, 1033.7, 960.4, 867.9, 823.5, 784.9, 756.0, 736.7, 713.6, 655.7, 613.3, 574.7, 538.1 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.40 (d, ^{3}J = 8.6 Hz, 1H), 8.37 – 8.29 (m, 1H), 8.07 (d, ^{4}J = 1.2 Hz, 1H), 8.04 – 7.95 (m, 2H), 7.87 – 7.77 (m, 1H), 7.42 – 7.24 (m, 4H), 7.18 (s, 1H), 2.51 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 137.67, 135.55, 134.10, 133.83, 132.38, 130.50, 129.53, 129.46, 126.93, 124.29, 124.26, 123.89, 122.62, 122.07, 121.70, 121.63, 120.95, 116.27, 114.23, 95.27, 22.00, 21.25. MS (EI,70 eV): m/z (%) = 295 (M^+, 100), 278 (13), 139 (9). HRMS (EI, 70 eV): calcd for $C_{22}H_{17}N_1$ ($[M]^+$): 295.13555, found: 295.13567.

Synthesis of 6-fluoro-3-methylindolo[1,2-*f*]phenanthridine (3bc). Yellowish solid, 55%. M.p.: 165-166°C. IR (ATR): 3106.9, 3049.1, 2917.9, 2856.2, 2736.6, 1917.0, 1729.9, 1606.5, 1567.9, 1496.6, 1448.4, 1429.1, 1353.9, 1276.7, 1249.7, 1203.4, 1172.6, 1116.6, 1068.4, 1041.4, 960.4, 948.9, 867.9, 823.5, 788.8, 754.1, 734.8, 713.6, 655.7, 611.4, 572.8, 536.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (dd, ^{3}J = 9.2, ^{4}J = 4.9 Hz, 1H), 8.26 (dd, ^{3}J = 6.5, ^{4}J = 2.6 Hz, 1H), 7.96 (d, ^{3}J = 8.1 Hz, 1H), 7.89 (dd, ^{3}J = 10.2, ^{4}J = 2.9 Hz, 1H), 7.86 – 7.73 (m, 2H), 7.43 – 7.27 (m, 3H), 7.27 – 7.10 (m, 1H), 2.49 (s, 3H) (signal of one H could not be detected). ^{19}F NMR (282 MHz, $CDCl_3$) δ -119.57. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.70 (d, ^{1}J = 241.8 Hz), 137.93, 135.21, 133.73, 132.61 (d, ^{4}J = 2.2 Hz), 130.43, 130.25, 126.08 (d, ^{4}J = 2.5 Hz), 124.27, 124.17 (d, ^{3}J = 7.6 Hz), 124.09, 122.83, 122.08, 121.89, 121.17, 117.68 (d, ^{4}J = 8.2 Hz), 115.51 (d, ^{2}J = 23.0 Hz), 113.85, 110.20 (d, ^{2}J = 23.8 Hz), 95.70, 21.94. MS (EI,70 eV): m/z (%) = 299 (M^+, 100), 270 (3), 148 (6). HRMS (EI, 70 eV): calcd for $C_{21}H_{14}N_1F_1$ ($[M]^+$): 299.11048, found: 299.11053.

Synthesis of 3-(*tert*-butyl)indolo[1,2-*f*]phenanthridine (3ca). Yellowish solid, 65%. M.p.: 151-152 °C. IR (ATR): 3122.3, 3043.3, 2950.7, 2863.9, 2742.4, 2331.6, 1917.0, 1731.8, 1606.5, 1562.1, 1490.8, 1448.4, 1440.6, 1417.5, 1348.1, 1276.7, 1259.4, 1197.6, 1172.6, 1112.8, 1072.3, 1053.0, 1020.2, 958.5, 875.6, 831.2, 788.8, 754.1, 734.8, 723.2, 661.5, 611.4, 588.2, 541.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, ^{3}J = 8.4 Hz, 1H), 8.41 – 8.31 (m, 2H), 8.25 (d, ^{4}J = 1.7 Hz, 1H), 8.06 (d, ^{3}J = 8.4 Hz, 1H), 7.86 – 7.76 (m, 1H), 7.61 – 7.47 (m, 2H), 7.41 – 7.28 (m, 3H), 1.45 (s, 9H) (signal of one H could not be detected). ^{13}C NMR (63 MHz, $CDCl_3$) δ 136.19,

135.43, 133.91, 130.60, 130.52, 128.64, 126.49, 126.20, 124.12, 123.97, 123.79, 123.04, 122.53, 121.84, 121.78, 120.96, 118.65, 116.45, 114.27, 95.67, 35.19, 31.41 (3C). MS (EI,70 eV): m/z (%) = 323 (M^+,100), 308 (70), 293 (34), 267 (13), 140 (23). HRMS (EI, 70 eV): calcd for $C_{24}H_{21}N_1$ ($[M]^+$): 323.16685, found: 323.16687.

Sythesis of 3-(*tert*-butyl)-6-methylindolo[1,2-*f*]phenanthridine (3cb). Yellowish solid, 67%. M.p.: 195-196 °C. IR (ATR): 3124.3, 3049.1, 2950.7, 2863.9, 2732.8, 2331.6, 1913.1, 1731.8, 1606.5, 1564.1, 1488.8, 1446.4, 1421.4, 1351.9, 1280.6, 1261.3, 1195.7, 1114.7, 1066.5, 1045.3, 1024.1, 960.4, 875.6, 831.2, 788.8, 757.9, 736.7, 727.1, 657.6, 632.6, 611.4, 588.2, 555.4 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2) δ 8.46 (d, ^3J = 8.5 Hz, 1H), 8.38 (d, ^3J = 8.2 Hz, 1H), 8.30 (d, ^4J = 1.7 Hz, 1H), 8.22 (s, 1H), 8.11 (d, ^3J = 8.4 Hz, 1H), 7.83 (dd, ^3J = 6.8, ^4J = 1.9 Hz, 1H), 7.61 (dd, ^3J = 8.4, ^4J = 1.8 Hz, 1H), 7.49 – 7.28 (m, 3H), 7.24 (s, 1H), 2.55 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (63 MHz, CD_2Cl_2) δ 151.65, 135.87, 134.54, 134.30, 133.18, 130.98, 130.06, 126.96, 126.66, 124.69, 124.52, 124.23, 122.78, 122.22, 122.11, 121.35, 119.26, 116.79, 114.66, 95.75, 35.64, 31.68 (3C), 21.42. MS (EI,70 eV): m/z (%) = 337 (M^+, 100), 322 (59), 307 (32), 278 (10), 161 (5), 147 (17). HRMS (EI, 70 eV): calcd for $C_{25}H_{23}N_1$ ($[M]^+$): 337.1825, found: 337.18270.

Synthesis of 3-fluoroindolo[1,2-*f*]phenanthridine (3da). Yellowish solid, 77%. M.p.: 129-130 °C. IR (ATR): 3054.8, 2952.6, 2850.4, 2734.7, 2331.6, 1928.6, 1884.2, 1731.8, 1602.6, 1558.3, 1490.8, 1440.6, 1350.0, 1280.6, 1272.9, 1195.7, 1120.5, 1076.1, 1049.1, 1024.1, 958.5, 887.1, 835.1, 777.2, 754.1, 736.7, 729.0, 651.9, 630.6, 615.2, 597.9, 555.4, 534.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.42 – 8.31 (m, 1H), 8.26 – 8.17 (m, 1H), 8.00 (dd, ^3J = 8.1, ^4J = 1.3 Hz, 1H), 7.90 (dd, ^3J = 8.8, ^4J = 5.7 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.51 – 7.39 (m, 1H), 7.33 – 7.13 (m, 3H), 7.12 – 7.01 (m, 1H), 7.00 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.61. ^{13}C NMR (63 MHz, $CDCl_3$) δ 162.51 (d, ^1J = 246.4 Hz), 136.15, 134.55, 133.72, 130.33, 129.38, 128.87 (d, ^3J = 8.2 Hz), 126.21 (d, ^3J = 8.7 Hz), 124.14, 123.04, 122.53 (d, ^4J = 2.5 Hz), 122.03, 121.89, 121.19 (d, ^4J = 3.1 Hz), 120.97, 116.29, 116.13 (d, ^2J = 23.0 Hz), 114.16, 108.41 (d, ^2J = 23.2 Hz), 95.84 (d, ^6J = 1.5 Hz). MS (EI,70 eV): m/z (%) = 285 (M^+, 100), 257 (7), 143 (10). HRMS (EI, 70 eV): calcd for $C_{20}H_{12}N_1F_1$ ($[M]^+$): 285.09483, found: 285.09458.

Synthesis of 3-fluoro-6-methylindolo[1,2-*f*]phenanthridine (3db). Yellowish solid, 54%. M.p.: 203-204 °C. IR (ATR): 3108.8, 3051.0, 2917.9, 2850.4, 2732.8, 2325.8, 1928.6, 1895.8,

1731.8, 1614.2, 1554.4, 1486.9, 1438.7, 1350.0, 1280.6, 1274.8, 1189.9, 1120.5, 1076.1, 1041.4, 1024.1, 960.4, 900.6, 844.7, 784.9, 736.7, 653.8, 632.6, 615.2, 607.5, 574.7, 530.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 – 8.21 (m, 2H), 8.01 (dd, ^{3}J = 8.8, ^{4}J = 5.7 Hz, 1H), 7.87 (s, 1H), 7.84 – 7.64 (m, 2H), 7.43 – 7.28 (m, 3H), 7.21 – 6.99 (m, 2H), 2.46 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.82. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.63 (d, ^{1}J = 246.2 Hz), 134.63, 134.17, 133.75, 132.58, 130.35, 129.03 (d, ^{3}J = 8.2 Hz), 126.33 (d, ^{3}J = 8.7 Hz), 124.48, 122.72 (d, ^{4}J = 2.4 Hz), 122.00, 121.82, 121.17 (d, ^{4}J = 3.0 Hz), 121.05, 116.26, 116.11 (d, ^{2}J = 22.7 Hz) (one signal of the doublet is overlapped with the signal at 116.26), 114.22, 108.49 (d, ^{2}J = 23.3 Hz), 95.61, 21.16 (signal of one C could not be detected). MS (EI,70 eV): m/z (%) = 299 (M^+, 100), 149 (8). HRMS (EI, 70 eV): calcd for $C_{21}H_{14}N_1F_1$ ($[M]^+$): 299.11048, found: 299.10984.

Sythesis of 3-methoxyindolo[1,2-*f*]phenanthridine (3ea). Yellowish solid, 78%. M.p.: 143-144 °C. IR (ATR): 3108.8, 3043.3, 2919.8, 2850.4, 2732.8, 2323.9, 2057.8, 1918.9, 1891.9, 1731.8, 1610.3, 1558.3, 1492.7, 1427.1, 1348.1, 1286.4, 1199.6, 1120.5, 1078.1, 1037.6, 1024.1, 958.5, 910.3, 835.1, 777.2, 740.6, 653.8, 638.4, 607.5, 565.1, 538.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (dd, ^{3}J = 8.5, ^{4}J = 0.9 Hz, 1H), 8.37 – 8.28 (m, 1H), 8.18 (dd, ^{3}J = 8.1, ^{4}J = 1.4 Hz, 1H), 7.97 (d, ^{3}J = 8.8 Hz, 1H), 7.84 – 7.73 (m, 1H), 7.60 – 7.49 (m, 2H), 7.41 – 7.27 (m, 3H), 7.03 (dd, ^{3}J = 8.8, ^{4}J = 2.5 Hz, 1H), 3.92 (s, 3H). (Signal of one H could not be detected). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.54, 136.31, 135.56, 133.77, 130.75, 128.91, 128.38, 125.85, 124.04, 122.92, 121.96, 121.81, 121.56, 120.78, 119.84, 116.40, 116.13, 114.23, 105.76, 94.74, 55.49. MS (EI, 70 eV): m/z (%) = 297 (M^+, 100), 282 (19), 254 (56), 226 (4), 149 (12), 126 (12). HRMS (EI, 70 eV): calcd for $C_{21}H_{15}N_1O_1$ ($[M]^+$): 297.11482, found: 297.11474.

Synthesis of 3-methoxy-6-methylindolo[1,2-*f*]phenanthridine (3eb). Yellowish solid, 73%. M.p.: 188-189 °C. IR (ATR): 3108.8, 3045.2, 2910.2, 2840.8, 2725.1, 2325.8, 2055.8, 1918.9, 1888.1, 1731.8, 1608.4, 1556.3, 1488.8, 1431.0, 1350.0, 1286.4, 1201.5, 1130.1, 1072.3, 1037.6, 1024.1, 958.5, 919.9, 838.9, 781.1, 736.7, 655.7, 609.4, 565.1, 547.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 – 8.21 (m, 2H), 8.06 – 7.91 (m, 2H), 7.86 – 7.72 (m, 1H), 7.57 (d, ^{4}J = 2.3 Hz, 1H), 7.43 – 7.28 (m, 3H), 7.04 (dd, ^{3}J = 8.8, ^{4}J = 2.4 Hz, 2H), 3.94 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.53, 135.52, 134.22, 133.68, 132.28, 130.63, 129.79, 128.43, 125.88, 124.27, 121.81, 121.62, 121.42, 120.74, 119.95, 116.26, 116.05, 114.15, 105.74, 94.41, 55.57,

21.21. MS (EI, 70 eV): m/z (%) = 311 (M^+, 100), 296 (13), 268 (42), 156 (10), 133 (10). HRMS (EI, 70 eV): calcd for $C_{22}H_{17}N_1O_1$ ($[M]^+$): 311.13047, found: 311.13016.

Synthesis of 6-(*tert*-butyl)indolo[1,2-*f*]phenanthridine (6c). Yellowish solid, 43%. M.p.: 146-168 °C. IR (ATR): 3065.8, 3043.2, 2955.5, 2898.7, 2859.4, 1953.0, 1921.3, 1881.4, 1593.0, 1552.4, 1487.5, 1448.4, 1408.1, 1357.5, 1255.0, 1228.8, 1206.2, 1120.3, 1019.2, 945.7, 877.9, 802.3, 755.3, 732.5, 624.4, 526.5 cm^{-1}. ^1H NMR (250 MHz, Acetone) δ 8.62 (d, ^3J = 8.8 Hz, 1H), 8.57 – 8.47 (m, 3H), 8.33 – 8.24 (m, 1H), 7.84 (dd, ^3J = 7.1, ^4J = 1.5 Hz, 1H), 7.76 (dd, ^3J = 8.8, ^4J = 2.3 Hz, 1H), 7.64 – 7.49 (m, 2H), 7.48 – 7.25 (m, 3H), 1.48 (s, 9H). ^{13}C NMR (63 MHz, Acetone) δ 146.99, 135.98, 134.83, 134.68, 131.44, 129.32, 129.10, 128.09, 127.52, 127.08, 125.27, 123.75, 123.14, 122.71, 122.48, 122.00, 121.78, 117.13, 115.21, 97.23, 35.41 (3C), 31.84. MS (EI, 70 eV): m/z (%) = 323 (M^+, 100), 308 (90), 293 (28), 267 (16), 239 (3), 140 (22). HRMS (EI, 70 eV): calcd for $C_{24}H_{21}N_1$ ($[M]^+$): 323.16685, found: 323.16686.

Synthesis of 6-methoxyindolo[1,2-*f*]phenanthridine (6d). Yellowish solid, 49%. M.p.: 154-155 °C. IR (ATR): 3105.0, 3043.3, 2910.2, 2836.9, 2325.8, 2053.9, 1917.0, 1890.0, 1731.8, 1620.0, 1562.1, 1488.8, 1438.7, 1357.7, 1288.3, 1197.6, 1130.1, 1070.4, 1041.4, 1026.0, 958.5, 919.9, 838.9, 790.7, 734.8, 655.7, 607.5, 563.1 cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2) δ 8.38 (d, ^3J = 9.2 Hz, 1H), 8.23 (d, ^3J = 8.4 Hz, 1H), 8.15 (dd, ^3J = 6.2, ^4J = 3.1 Hz, 1H), 8.10 – 7.93 (m, 1H), 7.74 (d, ^4J = 2.8 Hz, 1H), 7.70 – 7.57 (m, 1H), 7.46 – 7.26 (m, 2H), 7.27 – 6.95 (m, 4H), 3.80 (s, 3H). ^{13}C NMR (63 MHz, CD_2Cl_2) δ 156.19, 135.25, 134.13, 130.68, 130.60, 129.00, 128.41, 127.18, 126.82, 124.69, 123.83, 123.31, 122.47, 121.97, 121.49, 117.99, 115.83, 114.38, 108.86, 96.29, 55.74. MS (EI,70 eV): m/z (%) = 297 (M^+, 100), 282 (25), 254 (53), 226 (5), 148 (11), 127 (14). HRMS (EI, 70 eV): calcd for $C_{21}H_{15}N_1O_1$ ($[M]^+$): 297.13047, found: 297.13000.

Synthesis of 8-methoxyindolo[1,2-*f*]phenanthridine (6f). Yellowish solid, 49%. ^1H NMR (250 MHz, Acetone) δ 8.39 – 8.31 (m, 1H), 8.25 (dd, ^3J = 6.4, ^4J = 2.6 Hz, 1H), 8.05 (d, ^3J = 7.9 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.56 – 7.48 (m, 2H), 7.40 (m, 2H), 7.35 – 7.21 (m, 3H), 3.95 (d, ^3J = 5.1 Hz, 3H). ^{13}C NMR (63 MHz, Acetone) δ 150.70, 137.22, 136.62, 130.80, 129.64, 128.84, 127.96, 127.61, 126.21, 125.58, 125.00, 124.68, 124.14, 122.00, 121.37, 120.89, 118.31, 116.87, 112.88, 98.31, 55.81. MS (EI,70 eV): m/z (%) = 297 (M^+,100), 282 (56), 252 (13), 141

(12), 126 (10), 113 (4).). HRMS (EI, 70 eV): calcd for $C_{21}H_{15}N_1O_1$ ($[M]^+$): 297.11482, found: 297.11451.

Synthesis of 8-fluoroindolo[1,2-*f*]phenanthridine (6g). Yellowish solid, 72%. M.p.: 115-116 °C. IR (ATR): 3041.3, 2923.7, 1901.6, 1604.6, 1552.5, 1494.6, 1475.3, 1442.6, 1436.8, 1346.1, 1288.3, 1251.6, 1213.1, 1184.1, 1134.0, 1074.2, 1018.3, 954.6, 912.2, 781.1, 759.9, 736.7, 551.6 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.02 (m, 3H), 8.02 – 7.87 (m, 1H), 7.85 – 7.74 (m, 1H), 7.59 – 7.41 (m, 2H), 7.41 – 7.27 (m, 5H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.04. ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.30 (d, $J = 249.6$ Hz), 135.64 (d, $J = 1.2$ Hz), 135.51, 130.08, 129.01, 127.97, 126.84, 126.49 (d, $J = 2.7$ Hz), 126.20 (d, $J = 3.0$ Hz), 124.04, 123.95 (d, $J = 8.5$ Hz), 123.21 (d, $J = 11.1$ Hz), 123.02, 121.99, 121.71 (d, $J = 4.1$ Hz), 120.45, 119.45 (d, $J = 2.9$ Hz), 116.04 (d, $J = 22.3$ Hz), 115.77 (d, $J = 26.6$ Hz), 98.01. MS (EI, 70 eV): m/z (%) = 285 (M^+, 100), 264 (12), 142 (9). HRMS (EI, 70 eV): calcd for $C_{20}H_{12}N_1F_1$ ($[M]^+$): 285.09483, found: 285.09470.

Synthesis of 6-fluoroindolo[1,2-*f*]phenanthridine (6h). Yellowish solid, 75%. M.p.: 169-170 °C. IR (ATR): 3049.1, 2140.7, 1918.9, 1729.9, 1621.9, 1567.9, 1488.8, 1448.4, 1357.7, 1276.7, 1247.8, 1197.6, 1180.3, 1139.8, 1066.5, 1041.4, 1024.1, 960.4, 921.9, 838.9, 796.5, 734.8, 659.6, 611.4, 565.1 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2) δ 8.39 (dd, $^3J = 9.2$, $^4J = 4.9$ Hz, 1H), 8.29 – 8.18 (m, 1H), 8.13 – 7.97 (m, 2H), 7.89 (dd, $^3J = 10.3$, $^4J = 2.9$ Hz, 1H), 7.85 – 7.75 (m, 1H), 7.54 – 7.41 (m, 2H), 7.41 – 7.30 (m, 2H), 7.30 – 7.20 (m, 1H), 7.19 (s, 1H). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -120.10. ^{13}C NMR (63 MHz, CD_2Cl_2) δ 159.15 (d, $^1J = 241.2$ Hz), 135.33, 134.21, 132.90 (d, $^4J = 2.2$ Hz), 130.74, 129.40, 128.46, 126.83, 126.47 (d, $^4J = 2.5$ Hz), 124.62, 124.51 (d, $^3J = 7.7$ Hz), 123.13, 122.77, 122.35, 121.65, 118.18 (d, $^3J = 8.2$ Hz), 116.03 (d, $^2J = 23.1$ Hz), 114.31, 110.60 (d, $^2J = 23.9$ Hz), 96.78. MS (EI, 70 eV): m/z (%) = 285 (M^+, 100), 257 (8), 143 (10), 128 (4). HRMS (EI, 70 eV): calcd for $C_{20}H_{12}N_1F_1$ ($[M]^+$): 285.09483, found: 285.09477.

Synthesis of indolo[1,2-*f*]phenanthridine-6-carbonitrile (6i). Yellowish solid, 44%. M.p.: 217-218 °C. IR (ATR): 3068.3, 2221.7, 1593.0, 1556.3, 1490.8, 1446.4, 1409.8, 1353.9, 1288.3, 1251.6, 1207.3, 1182.2, 1145.6, 1068.4, 1045.3, 1024.1, 958.5, 919.9, 877.5, 833.1, 798.4, 734.8, 657.6, 611.4, 565.1 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2) δ 8.45 (d, $^4J = 1.8$ Hz, 1H), 8.42 (d,

^{3}J = 8.8 Hz, 1H), 8.20 (dd, ^{3}J = 6.4, ^{4}J = 2.5 Hz, 1H), 8.14 – 7.97 (m, 2H), 7.85 – 7.77 (m, 1H), 7.73 (dd, ^{3}J = 8.8, ^{4}J = 1.9 Hz, 1H), 7.59 – 7.45 (m, 2H), 7.45 – 7.32 (m, 2H), 7.22 (s, 1H). ^{13}C NMR (63 MHz, CD_2Cl_2) δ 138.96, 135.43, 134.46, 132.28, 131.24, 129.93, 128.90, 128.77, 126.69, 125.54, 124.68, 123.48, 123.32, 123.21, 122.97, 121.92, 119.42, 117.23, 114.75, 106.79, 98.41. MS (EI,70 eV): m/z (%) = 292 (M^+, 100), 264 (10), 146 (8), 132 (9), 118 (3). HRMS (EI, 70 eV): calcd for $C_{21}H_{12}N_2$ ($[M]^+$): 292.0995, found: 292.09960.

Synthesis of 6-(methylthio)indolo[1,2-*f*]phenanthridine (6j). Yellowish solid, 56%. M.p.: 143-144 °C. IR (ATR): 3043.3, 2917.9, 1915.1, 1591.1, 1546.7, 1490.8, 1448.4, 1398.2, 1353.9, 1288.3, 1253.6, 1203.4, 1188.0, 1164.9, 1114.7, 1024.1, 954.6, 916.1, 864.0, 790.7, 734.8, 613.3, 582.4 cm^{-1}. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.38 (d, ^{3}J = 8.8 Hz, 1H), 8.24 (d, ^{3}J = 8.2 Hz, 1H), 8.20 – 8.09 (m, 2H), 8.09 – 7.98 (m, 1H), 7.79 – 7.63 (m, 1H), 7.50 – 7.33 (m, 3H), 7.33 – 7.20 (m, 2H), 7.18 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (63 MHz, CD_2Cl_2) δ 135.33, 134.23, 134.17, 133.33, 130.82, 129.03, 128.43, 128.30, 126.70, 126.66, 124.61, 123.15, 123.05, 123.04, 122.61, 122.24, 121.50, 117.35, 114.58, 96.79, 16.65. MS (EI,70 eV): m/z (%) = 313 (M^+, 100), 298 (47), 265 (12), 254 (25), 156 (9), 132 (5). HRMS (EI, 70 eV): calcd for $C_{21}H_{15}N_1S_1$ ($[M]^+$): 313.09197, found: 313.09196.

1-(2-Bromophenyl)-2-(*p*-tolyl)-1*H*-indole (3ii). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 2H), 7.30 – 7.03 (m, 7H), 6.95 (d, ^{3}J = 8.0 Hz, 2H), 6.90 – 6.83 (m, 1H), 6.71 (d, ^{4}J = 0.7 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.47, 138.88, 138.40, 137.43, 133.81, 131.54, 129.80, 129.66, 129.12 (2C), 128.51 (3C), 128.45, 124.19, 122.34, 120.87, 120.59, 111.00, 103.06, 21.32. MS (EI, 70 eV): m/z (%) = 361 (M^+,100), 281 (51), 267 (74), 190 (5), 165 (6), 133 (50). HRMS (EI, 70 eV): calcd for $C_{21}H_{16}N_1Br_1$ ($[M]^+$): 361.04606, found: 361.04591.

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