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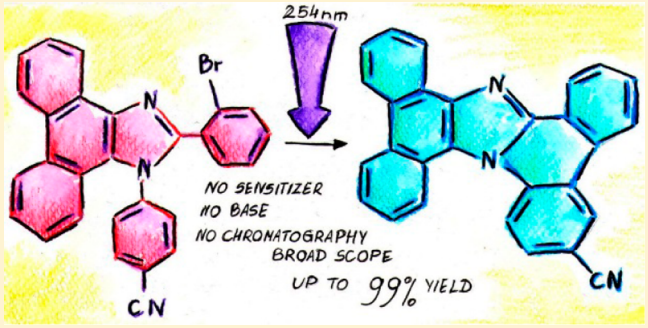
Photochemical Conversion of Phenanthro[9,10-*d*]imidazoles into π-Expanded Heterocycles

Kamil Skonieczny and Daniel T. Gryko*

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Supporting Information

ABSTRACT: We discovered that phenanthro[9,10-*d*]-imidazoles bearing a 2-halogenoaryl substituent at position 2 undergo swift photochemically driven direct arylation, leading to barely known phenanthro[9′,10′:4,5]imidazo[1,2-*f*]-phenanthridines. The reaction is high-yielding, and it does not require any sensitizer or base. The discovered process is tolerant of a variety of substituents present both at positions 1 and 2; i.e., strongly electron-donating and electron-withdrawing substituents are tolerated as well as various heterocyclic units. Steric hindrance does not affect this process. The evidence gathered here indicates that $S_{RN}1$ mechanism is operating in this case with the formation of radical anion as a critical step, followed by heterolytic cleavage of a carbon−halogen bond. Also TfO groups were shown to undergo cyclization, which allows the use of salicylaldehydes in the construction of heterocyclic systems. Efficiency of this photochemically driven direct arylation has been demonstrated by the synthesis of two systems possessing 13 and 17 conjugated rings, respectively. Phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridines are blue-emitters, and they exhibit strong fluorescence in solution and in the solid state in direct contrast to their precursors.



INTRODUCTION

Synthetic photochemistry has undergone a renaissance in recent decades.[1] Striking structural complexity has been achieved, and completely new photodriven reactions have been discovered.[2] Most of the reactions recently reported require the addition of photosensitizers, often as iridium complexes.[3] Photolability of the halogen-arene bond has been known for a long time, but most reactions employing such reactivity require harsh conditions including a strong base.[4] Independently, imidazole[5] derivatives, known since the work of Debus[6] and Radziszewski,[7] have attracted attention due to their intriguing photophysical properties.[8] Triphenylimidazoles played an important role in the discovery of chemiluminescence[7,9] and recently their intriguing photochemistry and photochromism has been extensively studied by Abe and co-workers.[10] Park and co-workers[11] showed that tetraphenylimidazoles, with the proper choice of substituents, can lead to white-light emitting compounds by the combination of excited-state intramolecular proton transfer and restricted energy transfer. One can envision that π-expansion of multisubstituted imidazoles will significantly alter the optical properties, as occurs for many aromatic systems.[12] While phenanthro[9,10-*d*]imidazoles have been known since 1941,[13] analogous imidazo[1,2-*f*]phenanthridines remain elusive. Phenanthro-[9,10-*d*]imidazoles are typically prepared using the Debus−Radziszewski method from fused α-diketones such as phenanthrene-9,10-dione,[14] 1,10-phenanthroline-5,6-dione,[15] or 4,7-phenanthroline-5,6-dione.[16] Among the few known methods[17] leading to imidazo[1,2-*f*]phenanthridines, the most interesting approach was developed by Cronin et al., in which phenanthridinine undergoes a reaction which proceeds via addition of a primary amine to the highly reactive iminium moiety followed by five-membered ring cyclization and an oxidation step.[18] Other heteroaryl-fused phenanthridines were also recently investigated.[19] These procedures are not comprehensive though and they also suffer from limited availability of starting materials. In general, phenanthro[9,10-*d*]heterocycles constitute not only the core of several natural products (cryptopleurine, thyloforine, or anthofine) but also several biological agents which present very interesting pharmacological properties related to the planarity of the system and consequently its DNA-chain intercalating ability[20] and capacity to bind to human telomere derived G-quadruplexes.[21] They were also investigated as violet-blue emitters in organic light emitting diods (OLEDs)[22] and as electron transfer mediators.[23] Phenanthro[9′,10′:4,5]imidazo-[1,2-*f*]phenanthridine was prepared for the first time by Barton and Grinham by decarbonylation of dibenzo[*c*,*e*]phenanthro-[9′,10′:4.5]imidazo[1,2-*a*]azepine-10-one,[24] and very recently by Peng and co-workers,[25a] while larger systems containing this unit were prepared by direct *N*-arylation.[25b] We set ourselves the goal to explore alternative and possibly more versatile

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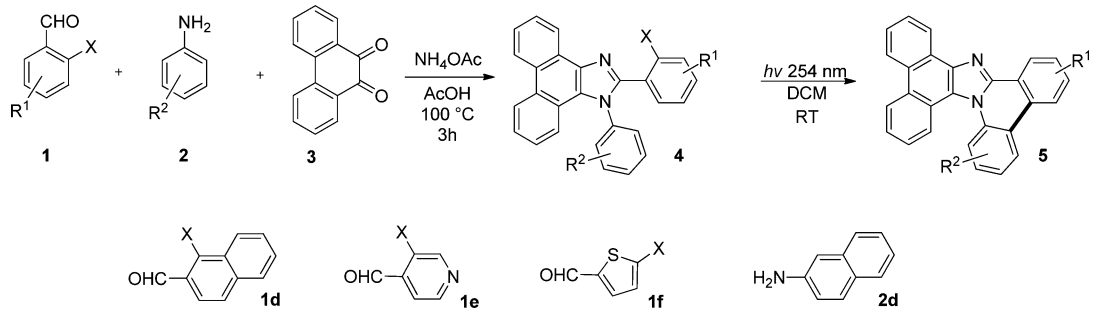
Table 1. Synthesis of Phenanthroimidazoles 4a−4p and their Photochemical Transformation into Dyes 5a−n



aldehyde	R^1	X	amine	R^2	PHI	yield (%)	π-exp PHI	yield (%)
1a	H	Br	**2a**	4-*t*-butyl	**4a**	85	**5a**	92
1b	4-CN	Br	**2a**	4-*t*-butyl	**4b**	86	**5b**	96
1c	4,5-OMe	Br	**2a**	4-*t*-butyl	**4c**	66	**5c**	94
1d	–	Br	**2a**	4-*t*-butyl	**4d**	77	**5d**	95
1e	–	Br	**2b**	3,5-*t*-butyl	**4e**	99	**5e**	95
1f	–	Br	**2c**	4-*n*-octyl	**4f**	81	**5f**	94
1a	H	Br	**2d**	–	**4g**	66	**5g**	87
1a	H	Br	**2e**	4-NO_2	**4h**	62	**5h**	61
1a	H	Br	**2f**	4-SF_5	**4i**	70	**5i**	91
1a	H	Br	**2g**	4-CO_2Et	**4j**	90	**5j**	74
1a	H	Br	**2h**	4-CN	**4k**	72	**5k**	71
1a	H	Br	**2i**	3,4,5-F	**4l**	83	**5l**	96
1g	H	CI	**2j**	3,4,5-OMe	**4m**	79	**5m**	88
1a	H	Br	**2j**	3,4,5-OMe	**4n**	89	**5m**	95
1h	H	I	**2j**	3,4,5-OMe	**4o**	91	**5m**	97
1i	H	OTf	**2j**	3,4,5-OMe	**4q**	91	**5m**	59
1j	6-F	CI	**2j**	3,4,5-OMe	**4p**	61	**5n**	89

strategies for preparation of such compounds via Pd-mediated intramolecular direct arylation.

RESULTS AND DISCUSSION

We have chosen the phenanthroimidazole **4a** as a model system (Table 1). While its preparation via Debus−Radziszewski reaction from 2-bromobenzaldehyde (**1a**) and 4-*t*-butylaniline (**2a**) was straightforward and high-yielding, during TLC plate analysis we observed a rapid and intriguing change of fluorescence. This observation led us to irradiate a solution of imidazole **4a** in CH_2Cl_2. After complete conversion of the substrate (6 h), the reaction was stopped and analysis of the only product readily showed that intramolecular photodirect-arylation had occurred, leading to compound **5a** in 92% yield (Table 1). Exceptionally mild reaction conditions combined with limited availability of these compounds via other methodologies and promising optical properties encouraged us to study the scope and limitations of this reaction. A broad range of phenanthro[9,10-*d*]imidazoles **4a−m** were prepared by the classic Debus−Radziszewski reaction and all of them were purified without chromatography in 62−99% yield (Table 1). Phenanthro[9,10-*d*]imidazoles (PHIs) were designed in such a way that they possessed both electron-withdrawing and electron-donating groups at both aryl substituents. In addition, several heterocyclic derivatives were prepared.

Irradiation (λ = 254 nm) of bromo-PHIs **4a−m** led to the intramolecular direct arylation forming compounds **5a−m** in 61−96% yield (Table 1). The reaction occurred regardless of the type and position of substituents. Both positions 1 and 2 of the imidazole ring may be substituted by any electron-donating and electron-accepting group or substituents. The electronic character of these groups did not affect the qualitative rate of cyclization. The only exception was nitro derivative **4h**, which showed a markedly slower photochemical reaction. In this case, the reaction was terminated after 5 days and the product **5h** was isolated in 61% yield.

It is worth noting that the reaction was very clean. After full conversion of starting material, we observed essentially one product, which often spontaneously crystallized from the reaction mixture. Only in the case of a photochemical cyclization of imidazoles **4j** and **4k**, obtained from substituted anilines bearing the electron withdrawing groups CO_2Et and CN, did we observe byproducts of debromination of these compounds (compounds **5jb** and **5kb** respectively, in the Supporting Information (SI)). The conjugated systems were characterized by reduced solubility, which facilitated their separation by crystallization. Again, no chromatography was used to purify compounds **5a−m**.

It should be noted that the photochemical reaction proceeded readily even with strongly sterically hindered substrates such as **4e**. An exposure to UV irradiation caused a very fast and efficient conversion of **4e** to the corresponding π-expanded imidazole **5e**. Interestingly, we could not prepare this fused compound by palladium direct arylation methods (initially planned in this project), even when we conducted the reaction for a few days at high temperature.

The photochemical reaction was easily observed on the TLC plate. Compounds **4a−n** after a few seconds of light exposure (254 nm) appeared on the TLC as a characteristic fluorescent spot with reduced polarity. Products **5a−m** were therefore isolated by adsorbing the substrates **4a−n** onto a suitable adsorbent, e.g., SiO_2, Al_2O_3, irradiating the immobilized

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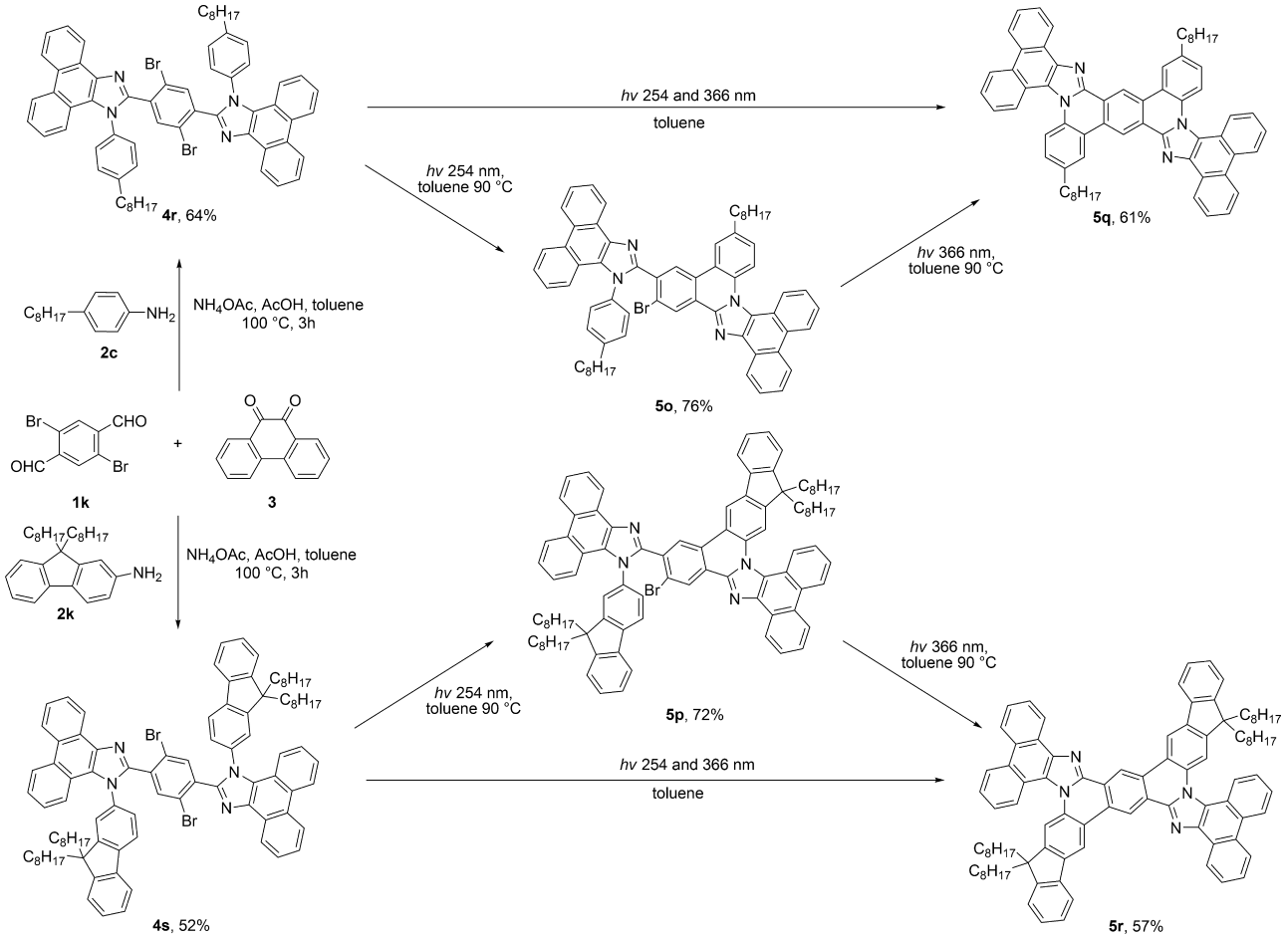
Scheme 1. Synthesis of Bis-phenanthroimidazoles and Their Photochemical Transformation into Dyes 5o−r

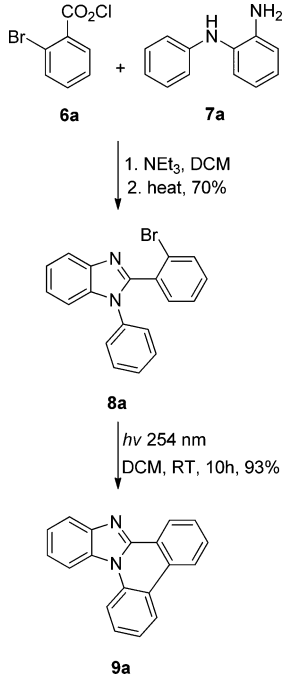


substrate, and then eluting the product with a suitable eluent selected on the basis of its polarity. Performing the reaction on silica gel had no influence in regard to either qualitative reaction rate or the yield of product.

Given the versatility of the method and high yields of both steps (compounds of type **4** and type **5** were isolated from the reaction mixture without chromatography), we extended this methodology to larger aromatic systems (Scheme 1). For this purpose, 2,5-dibromoterephthalaldehyde (**1k**) was obtained,[26] and transformed into imidazoles **4r** and **4s** with 64% and 52% yields, respectively. Because of the steric hindrance of the bromine atoms and the alkyl chain of fluorene, product **4s** was isolated as a mixture of atropoisomers.

After several hours of irradiation (254 nm), we were surprised to observe that the reaction did not lead to a fully conjugated product, but the product of a single cyclization **5p** ("mono", Scheme 1). Only after irradiation at 366 nm did a second cyclization occur, resulting in compounds **5o** and **5p** being converted to the fully coupled systems **5q** and **5r** (see later for details). This phenomenon must be somewhat associated with the π-expansion after first photochemical cyclization although the difference in intensity of absorption of **5o**/**5p** versus **4r**/**4s** at 254 nm is negligible (see SI). The methodology was also successfully extended to benzimidazole derivatives (Scheme 2). Interestingly, compound **8a**, has been described in several literature reports, but its rapid conversion to benzo[4,5]imidazo[1,2-*f*]phenanthridine **9a** under brief UV irradiation had not been previously noted. Such a product had

Scheme 2. Synthesis of Benzimidazole 8a and its Photochemical Transformation into 9a



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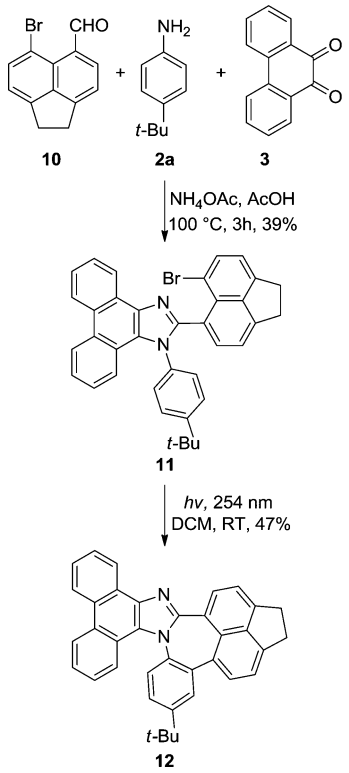
been obtained only through the activation of palladium[27] or by electrochemical methods,[28] which showed lower yields than via irradiation.

The question about mechanism of this intramolecular process is very important and indeed for analogous reactions involving *o*-terphenyl derivatives it was already raised by Sata et al. and Letcher and co-workers.[29] Two mechanistic options have to be considered. One is photolytic reaction of halogenoarene with subsequent intramolecular substitution onto a nearby aromatic ring,[30] and the second one is conrotatory photocyclization of 1,3,5-hexatriene system (6π-electrocyclization) followed by elimination of HX. Photoinduced 6π-electrocyclization is well-known for stilbene derivatives;[31] however, it is much less popular for derivatives and analogues of *o*-terphenyl.[32] Numerous studies have shown that it can occur only if molecule is in singlet π,π^* excited state, and it does not occur if compound possesses low lying nπ^* excited state (such as azodyes and arylideneanilines). Although details of this reaction are well studied for classical stilbene derivatives, in the case of *o*-terphenyl only very recently Bragg and co-workers have shown via time-resolved spectroscopy that cyclization of this compound to form 4a,4b-dihydrotriphenylene is considerably slower than the nonadiabatic process of related diarylethenes.[33] We found it important to start our mechanistic investigation from studying the dependence of the qualitative rate of reaction on the strength of carbon−halogen or carbon−oxygen bond. The PHIs **4m−p** were prepared possessing a variety of leaving groups X (I, Br, Cl, F, OTf). The rate of photochemical reaction was as follows I > OTf > Br > Cl. Fluorine−carbon bond remains intact under irradiation and PHI **2j** derived from 2-chloro-6-fluorobenzaldehyde (**1j**) undergoes selective cyclization (89% yield) into compound **5n**. The iodides (reaction time 2 h) and triflates (reaction time 5 h) reacted most readily. The derivative with the chloride ion was the slowest to react; even after 3 days there was no full conversion of the substrate. However, the best choice seemed to be bromine derivatives (reaction time 10 h), due to the broad commercial availability of aldehydes substituted at the *ortho* position with this halogen. The photochemical cyclization proceeded to a similar degree in different solvents, i.e., toluene, dichloromethane, ethyl acetate, THF. However, the reactions conducted in DCM were the most successful because this solvent gave the best solubility of reactants. Furthermore, the products were readily recovered by addition of hexanes to the irradiated solution.

The presence of radical scavengers, such as TEMPO, did not affect the reaction. In contrast, the addition of an electron acceptor such as *m*-dinitrobenzene (a well-known inhibitor of $S_{RN}1$ reaction)[4h,34] decreased the reaction rate. This result is expected since the radical anion initially formed on the X-substituted ring can either lose X- or transfer an electron to *m*-dinitrobenzene. These two observations indicate that the intramolecular cyclization is very fast. Such phenomenon has been already observed by Rossi and co-workers for intramolecular arylation of *N*-(*ortho*-halobenzyl)arylamines.[4d]

The following additional points argue against the mechanism involving 6π-electrocyclization followed by dehydrohalogenation: (1) The attempts to perform oxidative 6π-electrocyclization for 1-(4-cyanophenyl)-2-phenylphenanthroimidazole (**5kb**) failed to give traces of the corresponding π-expanded phenanthroimidazole, even if conditions optimized by Katz and co-workers (stoichiometric amount of iodine plus propylene oxide in the absence of air)[35] were used (details in SI). (2) Photoinduced 6π-electrocyclization is known not to occur in the presence of either nitro or amino groups because of the nature of lowest energy singlet excited state. Conversly, intramolecular direct arylation does occur in phenanthroimidazole **4h** bearing NO_2. (3) Kim and co-workers clearly proved that cyclization occurs via homolysis of C−Cl bond assisted by with n-complexation of chlorine radical for two somewhat analogous groups of compounds, namely *N*-benzyl-2-halopyridinium salts[36] and 2-chloro-*N*-pyridinylbenzamides.[37] This mechanism was determined by laser flash photolysis and subsequent detection of spectroscopic signatures of radical species. (4) Phenanthroimidazole **11** synthesized from 6-bromo-1,2-dihydroacenaphthylene-5-carboxaldehyde (**10**)[38] smoothly undergoes photoinduced cyclization into **12** (Scheme 3) even though 6π-electrocyclization mechanism is obviously not possible. (5) A small amount of a photodehalogenated product was observed in some cases (see above and data in SI). (6) The reaction is considerably faster in the presence of benzophenone (triplet sensitizer) (details in SI).[1b,39] On the basis of this evidence, the $S_{RN}1$ mechanism is the most plausible one. Full or partial intramolecular electron transfer occurs in the excited state followed by formation of radical-anion/radical-cation pair (Scheme 4). The compound subsequently undergoes heterolytic cleavage to produce X^- anion and an Ar·. Intramolecular cyclization of the latter scenario leads to formation of the product as a cation (Scheme 4).

Scheme 3. Synthesis of Phenanthroimidazole 11 and its Photochemical Transformation into 12



Optical Properties. For each of the structures **4a−4s**, **5a−5r**, **9a** and **11−12**, we analyzed the basic photophysical properties in CH_2Cl_2 as a solvent (Figure 1, Tables 2 and 3).

We analyzed the absorption and emission spectra of the obtained phenanthroimidazoles and π-expanded phenanthroimidazoles, with the aim of understanding the impact of

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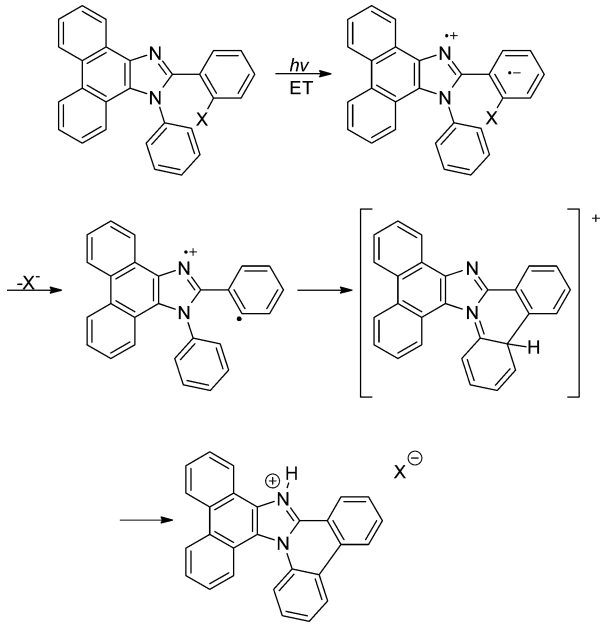
Scheme 4. Plausible Mechanism of Photoinduced Intramolecular Arylation



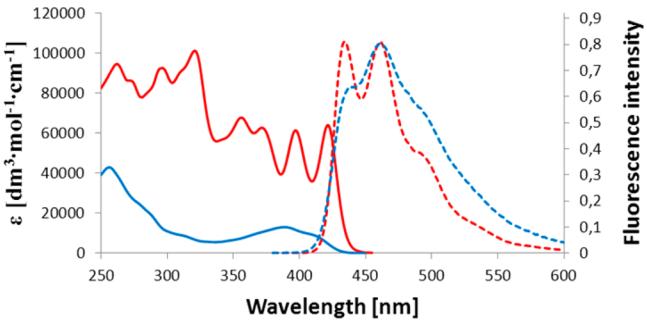


Figure 1. Absorption (solid line) and emission (dotted line) spectra of **5r** (red) and **12** (blue).

enlargement of the chromophore on the electronic properties of the compounds.

Increasing the number of conjugated aromatic ring structures and their planarity to produce systems in which there is the possibility of intramolecular charge transfer (ICT) resulted in large changes in the optical properties as compared to the PHIs **4a–s**.

Absorption maxima of the π-expanded PHI **5a–m** were bathochromically shifted by 20 to 30 nm in comparison with their precursors **4a–n**, and the molar absorption coefficients were much higher relative to the respective nonexpanded systems. In the case of cyclization of compound **4e**, the absorption shift was much larger (90 nm). This is probably related to the formation of push–pull chromophore by forcing electron-deficient pyridine and relatively electron-rich phenanthroimidazole into planarity.

As might be expected for these new rigid polycyclic aromatic heterocycles, the Stokes shift was reduced when compared with compounds **4a–s**. The notable exception was compound **5g**, which was characterized by an unusually large Stokes shift (102 nm) in comparison to the corresponding PHI **4g** (7 nm).

Fluorescence quantum yields of compounds possessing phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridine core were strongly increased in comparison to the precursors **4a–s**. The fluorescence emissions of compounds with a bromine or iodine atom as leaving groups were rudimentary due to the heavy atom effect. In conjugated systems, the fluorescence quantum yield is generally in the range of 30–50%. We did not observe a fluorescence emission for compounds **4h** and **5h** due to the known quenching effect of the nitro group.

Optical properties of compound **12** possessing one seven-membered ring are slightly different than dyes **5a–n**. Its absorption and emission are bathochromically shifted and Φ_{fl} is higher (0.55). We observed the most interesting luminescence results for structures with a multicore imidazole expanded ring.

Table 2. Spectroscopic Properties of Phenanthroimidazoles 4a–s and 11

compd	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm	Φ_{fl}[a]	Stokes shift (nm)
4a	355 (4000)	362, 381, 399	0.17	7
4b	355 (7500)	445	0.05	90
4c	356 (3600)	366, 382	0.04	10
4d	356 (4600)	444	0.03	88
4e	353 (3200)	417	0.03	64
4f	366 (3500)	399	0.01	33
4g	355 (3300)	362, 378	0.05	7
4h	353 (3300)	–	0	–
4i	354 (2800)	360, 377	0	6
4j	354 (3300)	429	0.03	75
4k	399 (3000)	434	0.02	35
4l	353 (3000)	358, 375	0.04	5
4m	355 (3000)	361, 379, 392	0.17	6
4n	355 (3000)	361, 377, 392	0.03	6
4o	355 (3000)	360, 374, 393	0.01	5
4q	356 (7300)	362, 383, 391	0.16	8
4p	353 (3000)	358, 376, 389	0.18	5
4r	354 (13 500)	430	0.01	76
4s	354 (11 500)	434	0.01	80
11	358 (5300)	433, 457	0.01	75

[a]Determined with 2-aminopyridine in H_2SO_4 (0.5 M) as a standard (Φ_{fl} = 0.65 ± 0.04 in H_2SO_4).[40]

Table 3. Spectroscopic Properties of Dyes 5a–r, 9a and 12

compd	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm	Φ_{fl}[a]	Stokes shift (nm)
5a	370 (16 000)	401	0.43	31
5b	390 (21 500)	437	0.69	47
5c	378 (22 200)	388, 406	0.33	10
5d	395 (16 400)	443	0.41	48
5e	440 (19 200)	423, 484	0.47	5
5f	384 (10 800)	425	0.13	41
5g	369 (13 400)	471	0.18	102
5h	365 (20 000)	–	0	–
5i	366 (11 000)	432	0.11	66
5j	370 (13 800)	420	0.29	50
5k	369 (12 500)	427	0.28	58
5l	371 (13 800)	414	0.32	43
5m	370 (17 500)	358, 376, 391	0.39	5
5n	372 (16 800)	402	0.46	30
5q	418 (69 200)	432, 458, 477	0.74[b]	14
5r	422 (64 000)	434, 461, 490	0.89[b]	12
9a	310, 320, 334, 351	356, 372, 388	0.14	5
12	404 (10 000)	438, 461	0.55[b]	34

[a]Determined with 2-aminopyridine in H_2SO_4 (0.5 M) as a standard. [b]Determined with quinine sulfate in H_2SO_4 (0.5 M) as a standard.

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Compounds **5q** and **5r** exhibited very high fluorescence quantum yields (75−90%) and high molar absorption coefficients (>65 000). Absorption and emission maxima were significantly bathochromically shifted from their respective precursors **4r** and **4s**.

CONCLUSIONS

In conclusion, the spatial proximity of the 2-halogenoaryl substituent and an adjacent aryl ring allowed photochemical direct arylation to occur under exceptionally mild conditions; i.e., neither photosensitizers nor base were necessary for this reaction. The efficiency of the new process leading to phenanthro[9′,10′:4,5]imidazo[1,2-*f*]phenanthridine and its analogues depended on the halogen employed and decreased in the order I > Br > Cl. The reaction occurs via $S_{RN}1$ mechanism and the formation of radical-anion seems to be the rate-determining step, while subsequent formation of radical and intramolecular addition are very fast. This conclusion would explain why the process is slowed down by the presence of good electron acceptor but not by a radical scavenger. Because of the high efficiency of the individual steps, compounds may be isolated from the reaction mixture without chromatography. The new method extends the possibilities for producing polyaza-heterocyclic fluorescent materials with precisely defined structures and unique spectroscopic properties. A wide range of functional groups were tolerated, and the corresponding imidazo[1,2-*f*]phenanthridine derivatives were produced in high yields. Because of the very interesting optical properties of multicore imidazoles, these dyes are therefore excellent candidates for purposes such as emitters in organic electroluminescent diodes.

EXPERIMENTAL SECTION

General Remarks. All chemicals were used as received unless otherwise noted. All reported ^{1}H NMR and ^{13}C NMR spectra were recorded on 500 or 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. Mass spectra were obtained via EI, FD or electrospray MS (ESI-MS). For HRMS measurements both quadruple and TOF mass analyzer types were used. UV−Vis and fluorescence spectra were recorded in dichloromethane. For the determination of quantum yields, 2-aminopyridine (or quinine sulfate) in 0.5 M H_2SO_4 was used as a standard. Chromatography was performed on silica (Kieselgel 60, 200−400 mesh). Photoreaction was performed in a quartz flask by irradiating UV light at room temperature using 254 nm lamps or 366 nm lamps (4 W each). 2,5-Dibromoterephthalaldehyde (**1k**),[41] 9,9-dioctyl-9*H*-fluoren-2-amine (**2k**),[42] 2-(2-bromophenyl)-1-phenyl-1*H*-benzo[*d*]imidazole (**8a**),[43] 5,6-dibromo-1,2-dihydroacenaphthylene (**10**)[44] were prepared according to the literature procedures.

Linear Optical Measurements. Steady-state fluorescence measurements were performed with dilute solutions (10^{-6} M, optical density <0.1) contained in standard 1 cm quartz cuvettes at room temperature. Compounds were dissolved in dichloromethane unless otherwise noted. Emission spectra were obtained under excitation at λ = 285, 350, or 400 nm depending on the compound. Fluorescence quantum yields were measured by using either 2-aminopyridine in H_2SO_4 (0.5 M) or quinine hemisulfate monohydrate in H_2SO_4 (0.5 M) as a standards.

General Procedure for the Synthesis of Phenanthro[9,10-*d*]imidazoles (General Procedure 1). Phenanthroquinone (1 equiv) and ammonium acetate (5 equiv) were added to the solution of benzaldehyde (1 equiv) and aniline (1.5 equiv) in glacial acetic acid (15 mL). After the mixture was stirred at 110 °C for 4 h, 10 mL MeOH was added to the hot solution followed by water until the solution became cloudy. The suspension was cooled down to rt to produce a precipitate, which was filtered, washed extensively with water/MeOH 1:1, 50 mL, and dried overnight under a high vacuum to give the expected, pure product. In some cases recrystallization was performed from ethyl acetate/hexanes or ethanol solution.

General Procedure for the Photochemical Direct Arylation (General Procedure 2). Phenanthroimidazole (200 mg) was dissolved in dichloromethane (80 mL) and placed in a 100 mL round-bottom quartz flask. The mixture was irradiated overnight using two lamps of λ = 254 nm (4 W each). When conversion was complete, hexanes was added to the reaction mixture to induce crystallization. The product was filtered, washed with ethanol or EtOAc, and dried overnight under a high vacuum to give the expected, pure product. In some cases recrystallization from chloroform/hexanes was performed.

*2-(2-Bromophenyl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazole (**4a**).* Yield: 830 mg (85%). White solid; mp = 260−261 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.9 Hz, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H), 7.76−7.71 (m, 1H), 7.69−7.62 (m, 1H), 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.55−7.51 (m, 1H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.43−7.36 (m, 3H), 7.32−7.17 (m, 4H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 150.2, 134.6, 132.7, 132.6, 130.9, 129.3, 128.3, 127.8, 127.4, 127.1, 126.7, 126.4, 126.3, 125.6, 125.1, 124.9, 124.0, 123.1, 122.9, 121.0, 34.9, 31.3; HRMS (EI) calcd for $C_{31}H_{25}N_2Br$ 504.1201, found 504.1212 [$M^{+\cdot}$].

*3-(tert-Butyl)phenanthro[9′,10′:4,5]imidazo[1,2-f]-phenanthridine (**5a**).* Prepared from **4a**. Yield: 80 mg (92%). White solid; mp = 285−286 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.28 (d, *J* = 7.9 Hz, 1H), 9.89 (d, *J* = 8.0 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.63 (dd, *J* = 8.1, 3.6 Hz, 2H), 8.59 (d, *J* = 1.9 Hz, 1H), 8.39 (d, *J* = 8.6 Hz, 2H), 8.01−7.95 (m, 1H), 7.92 (t, *J* = 7.5 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.78−7.70 (m, 2H), 7.70−7.60 (m, 2H), 1.55 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 142.9, 133.5, 131.0, 130.9, 130.2, 130.2, 130, 129.3, 129.0, 128.9, 128.4, 127.5, 126.7, 126.3, 126.1, 124.7, 123.5, 123.3, 123.0, 122.5, 122.4, 121.2, 121.0, 120.6, 120.2, 117.2, 35.4, 31.4; HRMS (EI) calcd for $C_{31}H_{24}N_2$ 424.1936, found 424.1939 [$M^{+\cdot}$].

*3-Bromo-4-(1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]-imidazol-2-yl)benzonitrile (**4b**).* Yield: 219 mg (86%). White solid; mp = 236−237 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86−8.76 (m, 2H), 8.72 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 1.4 Hz, 1H), 7.78−7.71 (m, 1H), 7.71−7.62 (m, 1H), 7.60−7.52 (m, 2H), 7.52−7.44 (m, 3H), 7.40−7.33 (m, 2H), 7.32−7.27 (m, 1H), 7.21 (dd, *J* = 8.1, 0.6 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 148.2, 137.5, 137.1, 135.9, 134.2, 133.3, 130.1, 129.5, 128.4, 127.7, 127.5 (2 signals), 127.0, 126.7, 126.4, 125.9, 125.7, 125.4, 124.1, 123.2, 122.7, 121.0, 116.8, 114.7, 35.0, 31.3; HRMS (EI) calcd for $C_{32}H_{25}N_3Br$ 530.1232, found 530.1230 [$M^{+\cdot}$].

*3-(tert-Butyl)phenanthro[9′,10′:4,5]imidazo[1,2-f]-phenanthridine-6-carbonitrile (**5b**).* Prepared from **4b**. Yield: 92 mg (96%). White solid; mp = 291−292 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.1 Hz, 1H), 8.72−8.69 (m, 1H), 8.68−8.64 (m, 2H), 8.50 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.25 (s, 1H), 8.24 (d, *J* = 6.3 Hz, 1H), 7.74−7.67 (m, 2H), 7.67−7.61 (m, 3H), 7.58 (t, *J* = 7.5 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 145.4, 141.4, 131.5, 130.0, 129.6, 129.3 (2 signals), 127.4, 126.7, 126.7, 126.6, 125.9, 125.9, 125.6, 125.4, 124.5, 124.4, 123.4, 123.3, 123.2, 123.0, 120.8 (2 signals), 119.1, 119.0, 112.0, 35.0, 31.5; HRMS (EI) calcd for $C_{32}H_{23}N_3$ 449.1910, found 449.1912 [$M^{+\cdot}$].

*2-(2-Bromo-4,5-dimethoxyphenyl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazole (**4c**).* Yield: 360 mg (66%). White solid; mp = 198−199 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 7.5 Hz, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 8.71 (d, *J* = 8.3 Hz, 1H), 7.72 (t, *J* = 7.1 Hz, 1H), 7.67−7.61 (m, 1H), 7.56−7.49 (m, 1H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.30−7.26 (m, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 6.85 (s, 1H), 3.86 (s, 3H), 3.73 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 150.3, 150.2, 147.7, 134.9, 129.3, 128.3, 127.8, 127.3, 127.1, 126.4, 126.2, 125.6, 125.0, 124.0, 123.1, 122.9, 122.8, 121.0, 115.7, 115.2, 115.0, 56.2, 56.1, 34.9, 31.3; HRMS (EI) calcd for $C_{33}H_{29}N_2O_2Br$ 564.1412, found 564.1400 [$M^{+\cdot}$].

*3-(tert-Butyl)-6,7-dimethoxyphenanthro[9′,10′:4,5]imidazo[1,2-f]phenanthridine (**5c**).* Prepared from **4c**. Yield: 86 mg (94%). White solid; mp = 270−271 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (d, *J* =

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J. Org. Chem. 2015, 80, 5753−5763

7.8 Hz, 1H), 9.50 (s, 1H), 8.76 (d, J = 8.1 Hz, 1H), 8.68 (d, J = 8.2 Hz, 1H), 8.46−8.41 (m, 3H), 7.88 (s, 1H), 7.85 (t, J = 7.4 Hz, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.74−7.69 (m, 2H), 7.66 (t, J = 7.4 Hz, 1H), 4.32 (s, 3H), 4.20 (s, 3H), 1.57 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 151.6, 151.3, 142.8, 130.9, 130.1, 129.8, 128.8, 128.7, 127.9, 127.2, 126.4, 126.3, 126.2, 125.1, 124.8, 123.3, 123.0, 122.1, 121.4, 120.9, 120.4, 120.3, 111.5, 109.5, 103.3, 59.1, 56.5, 35.3, 31.4; HRMS (EI) calcd for $C_{33}H_{28}N_2O_2$ 484.2151, found 484.2149 [$M^{+\cdot}$].

*2-(1-Bromonaphthalen-2-yl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazole (**4d**).* Yield: 205 mg (77%). White solid; mp = 255−256 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (dd, J = 8.0, 1.0 Hz, 1H), 8.80 (d, J = 8.3 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.79−7.70 (m, 2H), 7.69−7.64 (m, 1H), 7.64−7.59 (m, 1H), 7.58−7.56 (m, 1H), 7.55−7.51 (m, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.45−7.38 (m, 4H), 7.31−7.27 (m, 1H), 7.18 (dd, J = 8.2, 0.7 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.7, 151.0, 137.1, 134.8, 134.4, 132.0, 130.9, 129.3, 128.3, 128.2, 127.9, 127.7, 127.4, 127.3 (2 signals), 127.2 (2 signals), 126.5, 126.2 (2 signals), 125.5, 124.9, 124.0, 123.1, 123.0, 122.8, 121.0, 34.8, 31.2; HRMS (EI) calcd for $C_{35}H_{27}N_2Br$ 554.1358, found 554.1368 [$M^{+\cdot}$].

*8-(tert-Butyl)benzo[k]phenanthro[9′,10′:4,5]imidazo[1,2-f]-phenanthridine (**5d**).* Prepared from **4d**. Yield: 87 mg (95%). Yellowish solid; mp = 295−296 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.10 (d, J = 8.6 Hz, 1H), 9.90 (d, J = 7.9 Hz, 1H), 8.97 (d, J = 8.4 Hz, 1H), 8.91 (d, J = 2.0 Hz, 1H), 8.73 (d, J = 7.8 Hz, 1H), 8.65 (d, J = 8.3 Hz, 1H), 8.51 (dd, J = 7.9, 1.1 Hz, 1H), 8.44 (d, J = 8.8 Hz, 1H), 8.21 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.86−7.82 (m, 1H), 7.82−7.74 (m, 3H), 7.72−7.64 (m, 3H), 1.50 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 143.2, 136.1, 131.2, 131.0 (2 signals), 130.1, 129.9, 129.5, 129.0, 128.9, 128.8, 128.6, 128.0 (2 signals), 127.6 (2 signals), 126.9, 126.7, 126.5, 126.0, 124.8, 123.5, 123.3, 123.1, 123.0, 121.8, 120.9, 120.6, 119.9, 116.4, 35.4, 31.3; HRMS (EI) calcd for $C_{35}H_{26}N_2$ 474.2096, found 474.2094 [$M^{+\cdot}$].

*2-(3-Bromopyridin-4-yl)-1-(3,5-di-tert-butylphenyl)-1H-phenanthro[9,10-d]imidazole (**4e**).* Yield: 267 mg (99%). White solid; mp = 197−198 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, J = 7.7 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 7.3 Hz, 2H), 8.50 (d, J = 4.8 Hz, 1H), 7.77−7.72 (m, 1H), 7.71−7.65 (m, 1H), 7.59−7.53 (m, 1H), 7.47 (t, J = 1.7 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 4.8 Hz, 1H), 7.33−7.29 (m, 1H), 7.28−7.24 (m, 2H), 1.26 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 152.0, 147.5, 136.1, 129.5, 128.4, 127.5, 127.0, 126.9, 126.3, 125.9, 125.5, 124.1, 123.2, 122.9, 122.8, 122.7, 121.2, 35.0, 31.1; HRMS (EI) calcd for $C_{34}H_{32}N_3Br$ 474.561.1780, found 561.1776 [$M^{+\cdot}$].

*5,7-Di-tert-butylbenzo[c]phenanthro[9′,10′:4,5]imidazo[2,1-a]-[2,6]naphthyridine (**5e**).* Prepared from **4e**. Yield: 93 mg (95%). Yellow solid; mp = 305−306 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.99 (d, J = 5.9 Hz, 1H), 8.84 (d, J = 8.3 Hz, 1H), 8.74 (d, J = 8.3 Hz, 1H), 8.65 (d, J = 7.8 Hz, 1H), 8.48 (d, J = 6.0 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 8.27 (d, J = 1.6 Hz, 1H), 8.03 (d, J = 1.5 Hz, 1H), 7.74−7.80 (m, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 1.80 (s, 9H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 151.4, 143.2, 141.4, 135.8, 134.2, 130.4, 130.0, 128.1, 128.0, 127.5, 126.6, 125.9, 125.4 (2 signals), 125.0, 124.0, 123.6, 123.4, 122.3, 120.4, 116.4, 116.3, 37.9, 35.7, 33.7, 31.1; HRMS (EI) calcd for $C_{34}H_{31}N_3$ 481.2518, found 481.2524 [$M^{+\cdot}$].

*2-(2-Bromothiophen-3-yl)-1-(4-octylphenyl)-1H-phenanthro-[9,10-d]imidazole (**4f**).* Yield: 440 mg (81%). White solid; mp = 97−98 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (dd, J = 8.0, 1.0 Hz, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 8.3 Hz, 1H), 7.75−7.71 (m, 1H), 7.66−7.63 (m, 1H), 7.54−7.50 (m, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.30 (dd, J = 10.2, 6.8 Hz, 3H), 7.29−7.23 (m, 2H), 6.97 (d, J = 5.4 Hz, 1H), 2.73 (t, J = 7.7 Hz, 2H), 1.74−1.67 (quintet, J = 7.3 Hz, 2H), 1.33−1.27 (m, 10H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.9, 143.4, 137.4, 134.8, 130.4, 129.6, 129.4, 128.5, 128.4, 128.3, 128.0, 127.4, 127.1, 126.9, 126.3, 125.7, 125.2, 124.0, 123.1, 122.8 (2 signals), 121.1, 114.4, 35.6, 31.9, 31.1, 29.4, 29.3, 29.1, 22.7, 14.1; HRMS (EI) calcd for $C_{33}H_{31}N_2SBr$ 566.1391, found 566.1399 [$M^{+\cdot}$].

*5-Octylphenanthro[9′,10′:4,5]imidazo[1,2-a]thieno[3,2-c]-quinoline (**5f**).* Prepared from **4f**. Yield: 71 mg (94%). Yellowish solid; mp = 136−137 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (dd, J = 7.9, 1.2 Hz, 1H), 8.79 (d, J = 7.7 Hz, 1H), 8.73 (d, J = 8.2 Hz, 1H), 8.51 (dd, J = 8.1, 1.1 Hz, 1H), 8.39 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 1.8 Hz, 1H), 7.85 (d, J = 5.2 Hz, 1H), 7.79−7.74 (m, 1H), 7.72−7.69 (m, 1H), 7.68 (d, J = 5.2 Hz, 1H), 7.63−7.60 (m, 1H), 7.59−7.55 (m, 1H), 7.36 (dd, J = 8.6, 1.9 Hz, 1H), 2.83−2.80 (m, 2H), 1.80−1.73 (quintet, 2H), 1.48−1.28 (m, 10H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 141.5, 140.1, 136.4, 131.5, 129.7, 128.8, 128.6, 127.3, 127.0, 126.5, 126.4, 125.2, 124.9, 124.5, 124.3, 123.8, 123.6, 123.4, 122.9, 122.8, 122.3, 121.7, 119.4, 35.7, 31.9, 29.7, 29.5, 29.4, 29.3, 22.7, 14.1; HRMS (EI) calcd for $C_{33}H_{30}N_2S$ 486.2130, found 486.2132 [$M^{+\cdot}$].

*2-(2-Bromophenyl)-1-(naphthalen-2-yl)-1H-phenanthro[9,10-d]-imidazole (**4g**).* Yield: 635 mg (66%). Yellowish solid; mp = 247−248 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (dd, J = 8.0, 1.0 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 8.74 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 1.7 Hz, 1H), 7.94 (dd, J = 8.2, 3.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.78−7.72 (m, 1H), 7.69−7.65 (m, 1H), 7.62−7.53 (m, 3H), 7.53−7.46 (m, 3H), 7.25−7.13 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 137.2, 134.9, 133.1 (2 signals), 132.7, 132.6, 132.5, 131.0, 129.6, 129.3, 128.4, 128.3, 128.0, 127.3 (3 signals), 127.2, 127.1, 126.8, 126.3, 126.0, 125.6, 125.1, 124.9, 124.1, 123.1, 122.9 (2 signals), 121.0; HRMS (EI) calcd for $C_{31}H_{19}N_2Br$ 498.0732, found 498.0732 [$M^{+\cdot}$].

*Benzo[a]phenanthro[9′,10′:4,5]imidazo[1,2-f]phenanthridine (**5g**).* Prepared from **4g**. Yield: 69 mg (87%). Yellowish solid; mp = 281−282 °C; ^{1}H NMR (600 MHz, $CDCl_3$, drop TFA-d) δ 9.13 (d, J = 8.4 Hz, 1H), 9.03 (d, J = 8.4 Hz, 1H), 8.96 (d, J = 7.8 Hz, 1H), 8.75 (d, J = 8.3 Hz, 1H), 8.69 (d, J = 7.5 Hz, 1H), 8.65−8.59 (m, 1H), 8.31 (d, J = 8.9 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 8.11−8.05 (m, 2H), 7.97 (t, J = 7.5 Hz, 1H), 7.93−7.88 (m, 1H), 7.85 (t, J = 7.1 Hz, 1H), 7.80−7.73 (m, 3H), 7.61 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, drop TFA-d) δ 141.6, 133.7, 133.1, 131.0, 130.7, 130.2, 129.9, 129.7 (2 signals), 129.5, 129.4, 129.3, 129.0, 128.9, 128.3, 128.1 (2 signals), 127.1, 126.8, 125.5, 124.9, 123.8, 123.5, 122.7, 122.6, 120.9, 120.8, 119.5, 118.2, 116.5; HRMS (EI) calcd for $C_{31}H_{18}N_2$ 418.470, found 418.1475 [$M^{+\cdot}$].

*2-(2-Bromophenyl)-1-(4-nitrophenyl)-1H-phenanthro[9,10-d]-imidazole (**4h**).* Yield: 220 mg (62%). Yellow solid; mp = 256−257 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (dd, J = 7.9, 0.9 Hz, 1H), 8.80 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 8.3 Hz, 1H), 8.31 (d, J = 9.0 Hz, 2H), 7.78−7.71 (m, 1H), 7.71−7.61 (m, 3H), 7.61−7.52 (m, 2H), 7.46 (dd, J = 7.5, 1.6 Hz, 1H), 7.37−7.26 (m, 3H), 7.18 (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 147.9, 143.1, 137.5, 132.8, 132.7, 131.7, 131.6, 129.6, 129.5, 128.5, 127.6, 127.2, 126.9, 126.7, 126.5, 126.1, 125.5, 124.8, 124.7, 124.4, 123.1, 122.9, 122.2, 120.7; HRMS (EI) calcd for $C_{27}H_{16}N_3O_2Br$ 493.0426, found 493.0438 [$M^{+\cdot}$].

*3-Nitrophenanthro[9′,10′:4,5]imidazo[1,2-f]phenanthridine (**5h**).* Prepared from **4h**. Reaction time: 5 days. Yield: 46 mg (61%). Yellow solid; mp = 320−321 °C; ^{1}H NMR (600 MHz, $CDCl_3$:TFA-d) δ 9.61 (d, J = 2.3 Hz, 1H), 9.00 (d, J = 7.5 Hz, 1H), 8.95 (d, J = 8.3 Hz, 1H), 8.89 (d, J = 9.1 Hz, 2H), 8.82 (d, J = 8.2 Hz, 1H), 8.69 (d, J = 7.5 Hz, 1H), 8.67 (dd, J = 9.2, 2.3 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.22 (t, J = 7.7 Hz, 1H), 8.11 (t, J = 7.1 Hz, 1H), 7.99−7.90 (m, 3H), 7.79 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, TFA-d) δ 148.9, 145.6, 137.4, 136.3, 134.0, 133.4, 132.8, 132.6, 132.2, 131.7, 131.1 (2 signals), 129.2, 127.5, 127.1, 126.0, 125.7, 125.2, 125.0, 124.3, 123.3, 122.4, 121.0, 118.6, 117.3, 115.0; HRMS (EI) calcd for $C_{27}H_{15}N_3O_2$ 413.1164, found 413.1172 [$M^{+\cdot}$].

*Compound **4i**.* Yield: 290 mg (70%). White solid; mp = 262−263 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, J = 7.8 Hz, 1H), 8.80 (d, J = 8.3 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.73 (t, J = 7.3 Hz, 1H), 7.70−7.65 (m, 1H), 7.63−7.55 (m, 4H), 7.45 (d, J = 6.9 Hz, 1H), 7.38−7.27 (m, 3H), 7.17 (d, J = 8.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.1, 154.0, 153.9, 149.9, 140.2, 132.8, 132.7, 131.6, 129.6, 128.9, 128.5, 127.6, 127.4, 127.1, 126.7, 126.6, 126.1, 125.5, 124.7, 124.4, 123.1, 123.0, 122.2, 120.7; HRMS (EI) calcd for $C_{27}H_{16}N_2SBrF_5$ 574.0138, found 574.0147 [$M^{+\cdot}$].

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*Compound **5i***. Prepared from **4i**. Yield: 80 mg (91%). White solid; mp = 226−227 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90−8.84 (m, 2H), 8.82 (d, J = 2.3 Hz, 1H), 8.80 (d, J = 8.0 Hz, 1H), 8.72 (d, J = 8.1 Hz, 1H), 8.45 (d, J = 9.1 Hz, 1H), 8.40−8.35 (m, 1H), 8.33 (dd, J = 8.1, 0.8 Hz, 1H), 7.93 (dd, J = 9.1, 2.4 Hz, 1H), 7.79−7.70 (m, 4H), 7.68−7.63 (m, 1H), 7.63−7.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 150.2, 150.1, 147.6, 141.7, 134.8, 129.9, 129.7, 129.6, 129.2, 128.2, 127.5, 126.8, 126.7, 125.6 (2 signals), 125.5, 124.7, 124.3, 123.9, 123.4, 123.3, 123.1, 123.0, 122.7, 122.3, 119.2; HRMS (EI) calcd for $C_{27}H_{15}N_2SF_5$ 494.0876, found 494.0887 [$M^{+\cdot}$].

*Ethyl 4-(2-(2-bromophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzoate (**4j**)*. Yield: 900 mg (90%). White solid; mp = 222−223 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (dd, J = 7.9, 1.0 Hz, 1H), 8.79 (d, J = 8.3 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 8.6 Hz, 2H), 7.76−7.71 (m, 1H), 7.69−7.64 (m, 1H), 7.58−7.52 (m, 4H), 7.43 (dd, J = 7.5, 1.7 Hz, 1H), 7.32−7.27 (m, 2H), 7.26−7.20 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 150.0, 141.4, 137.3, 132.7 (2 signals), 132.2, 131.6, 131.2, 130.8, 129.4, 128.5, 128.4, 127.4, 127.1, 126.9, 126.4, 125.8, 125.2, 124.8, 124.2, 123.1, 122.9, 122.6, 120.9, 61.5, 14.3; HRMS (EI) calcd for $C_{30}H_{21}N_2O_2Br$ 520.0786, found 520.0795 [$M^{+\cdot}$].

*Ethyl phenanthro[9′,10′:4,5]imidazo[1,2-f]phenanthridine-3-carboxylate (**5j**)*. Prepared from **4j**. Yield: 85 mg (74%). White solid; mp = 278−279 °C; ^{1}H NMR (600 MHz, $CDCl_3$, one drop of TFA-d) δ 9.32 (s, 1H), 9.03 (d, J = 8.0 Hz, 1H), 8.76 (d, J = 8.3 Hz, 1H), 8.72 (d, J = 7.6 Hz, 2H), 8.67 (d, J = 7.8 Hz, 1H), 8.57 (d, J = 8.7 Hz, 1H), 8.39 (d, J = 8.6 Hz, 1H), 8.30 (d, J = 8.1 Hz, 1H), 8.07 (t, J = 7.5 Hz, 1H), 7.96 (t, J = 7.5 Hz, 1H), 7.80−7.72 (m, 3H), 7.66 (t, J = 7.5 Hz, 1H), 4.58 (q, J = 7.1 Hz, 2H), 1.54 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, one drop of TFA-d) δ 165.4, 143.2, 134.4, 132.9, 131.2, 130.5 (2 signals), 130.3, 130.2 (2 signals), 129.6, 129.1, 129.0, 128.2, 127.0, 126.8, 126.2, 125.1, 123.6 (2 signals), 123.5, 123.3, 123.2, 122.9, 120.7 (2 signals), 119.7, 116.8, 62.6, 14.3; HRMS (EI) calcd for $C_{30}H_{20}N_2O_2$ 440.1525, found 440.1519 [$M^{+\cdot}$].

*Ethyl 4-(2-phenyl-1H-phenanthro[9,10-d]imidazol-1-yl)benzoate (**5jb**)*. Prepared from **4j**. Purified by the column chromatography (SiO_2; hexanes/ethyl acetate 4:1). Yield: 22 mg (19%). White solid; mp = 206−207 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, J = 7.9 Hz, 1H), 8.76 (d, J = 8.3 Hz, 1H), 8.70 (d, J = 8.3 Hz, 1H), 8.28−8.24 (m, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.69−7.63 (m, 1H), 7.60−7.55 (m, 2H), 7.55−7.47 (m, 3H), 7.34−7.24 (m, 4H), 7.16 (d, J = 8.3 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 150.8, 142.5, 131.7, 131.3, 129.5, 129.3, 129.2, 129.1, 128.3, 127.8, 127.4, 126.4, 125.8, 125.1, 124.2, 123.1, 122.9, 122.7, 120.7, 61.6, 14.3; HRMS (EI) calcd for $C_{30}H_{22}N_2O_2$ 442.1681, found 442.1692 [$M^{+\cdot}$].

*4-(2-(2-Bromophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)-benzonitrile (**4k**)*. Yield: 1.15 g (72%). Pale orange crystals; mp = 236−238 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85−8.78 (m, 2H), 8.73 (d, J = 8.3 Hz, 1H), 7.77−7.72 (m, 3H), 7.68 (ddd, J = 8.4, 7.1, 1.5 Hz, 1H), 7.62−7.54 (m, 4H), 7.43 (dd, J = 7.5, 1.6 Hz, 1H), 7.36−7.30 (m, 2H), 7.30−7.26 (m, 1H), 7.17 (dd, J = 8.3, 0.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 141.5, 137.6, 133.4, 132.8, 132.7, 131.9, 131.5, 129.5, 129.4, 128.4, 127.5, 127.1, 127.0, 126.7, 126.5, 126.0, 125.4, 124.7, 124.4, 123.1, 122.9, 122.3, 120.7, 117.7, 113.4; HRMS (EI) calcd for $C_{28}H_{16}N_3Br$ 473.0528, found 473.0539 [$M^{+\cdot}$].

*Phenanthro[9′,10′:4,5]imidazo[1,2-f]phenanthridine-3-carbonitrile (**5k**)*. Prepared from **4k**. Yield: 120 mg (71%). White solid; mp = 290−292 °C; ^{1}H NMR (600 MHz, $CDCl_3$, drop TFA-d) δ 9.28 (d, J = 6.7 Hz, 1H), 9.05 (s, 1H), 8.93 (d, J = 7.2 Hz, 1H), 8.86 (d, J = 8.3 Hz, 1H), 8.79 (dd, J = 8.1, 3.8 Hz, 2H), 8.69 (d, J = 7.9 Hz, 1H), 8.33 (d, J = 7.7 Hz, 1H), 8.16 (t, J = 7.3 Hz, 1H), 8.11−8.04 (m, 2H), 7.92−7.82 (m, 3H), 7.74 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, drop TFA-d) δ 143.3, 135.1, 133.0, 132.1, 131.1, 130.9, 130.6, 130.3, 130.1, 129.4, 129.3, 128.7, 127.1, 126.9, 125.4, 124.6, 123.8 (2 signals), 123.5, 123.1, 121.8, 120.5, 119.5, 117.2, 117.0, 115.3, 113.4, 112.1, 111.5; HRMS (EI) calcd for $C_{28}H_{15}N_3$ 393.1266, found 393.1255 [$M^{+\cdot}$].

*4-(2-Phenyl-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (**5kb**)*. Prepared from **4k**. Purified by the column chromatography (SiO_2; hexanes/ethyl acetate 4:1).Yield: 34 mg (20%). White solid; mp = 288−289 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, J = 7.8 Hz, 1H), 8.78 (d, J = 8.3 Hz, 1H), 8.70 (d, J = 8.3 Hz, 1H), 7.89−7.84 (m, 2H), 7.77−7.72 (m, 1H), 7.70−7.64 (m, 1H), 7.63−7.59 (m, 2H), 7.57−7.51 (m, 1H), 7.49−7.44 (m, 2H), 7.39−7.27 (m, 4H), 7.10 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 142.6, 133.9, 130.2, 129.5, 129.4, 129.3, 128.5, 128.3, 127.6, 127.5, 126.5, 126.0, 125.3, 124.4, 123.1, 122.9, 122.4, 120.4, 117.6, 113.8; HRMS (EI) calcd for $C_{28}H_{16}N_3$ 394.1344, found 394.1351 [$M^{+\cdot}$].

*2-(2-Bromophenyl)-1-(3,4,5-trifluorophenyl)-1H-phenanthro-[9,10-d]imidazole (**4l**)*. Yield: 140 mg (83%). White solid; mp = 245−246 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84−8.79 (m, 2H), 8.73 (d, J = 8.3 Hz, 1H), 7.77−7.71 (m, 1H), 7.71−7.66 (m, 1H), 7.64−7.57 (m, 2H), 7.45 (dd, J = 7.5, 1.6 Hz, 1H), 7.43−7.35 (m, 2H), 7.34−7.30 (m, 1H), 7.24 (dd, J = 8.2, 0.6 Hz, 1H), 7.22−7.18 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.0 (m), 150.3 (m), 150.0, 141.5 (m), 139.8 (m), 137.1 (m), 132.9, 132.6, 131.7, 129.5, 128.4, 127.6, 127.2, 126.8, 126.7, 126.7, 126.1, 125.6, 124.7, 124.4, 123.1, 122.9, 122.1, 120.5, 113.9, 113.9, 113.7; HRMS (EI) calcd for $C_{27}H_{14}N_2BrF_3$ 502.0292, found 502.0287 [$M^{+\cdot}$].

*2,3,4-Trifluorophenanthro[9′,10′:4,5]imidazo[1,2-f]-phenanthridine (**5l**)*. Prepared from **4l**. Yield: 74 mg (96%). White solid; mp = 302−303 °C; ^{1}H NMR (500 MHz, $CDCl_3$, drop TFA-d) δ 8.98 (t, J = 7.3 Hz, 2H), 8.91 (d, J = 8.4 Hz, 1H), 8.84 (d, J = 7.8 Hz, 1H), 8.67 (d, J = 7.3 Hz, 1H), 8.40−8.31 (m, 2H), 8.13 (t, J = 7.8 Hz, 1H), 8.05 (t, J = 7.7 Hz, 1H), 7.96−7.87 (m, 3H), 7.78 (t, J = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, drop TFA-d) δ 143.3, 135.1, 131.4, 130.9, 130.6, 130.2, 130.1, 129.4, 128.7, 127.7 (m), 127.5, 127.3, 127.1, 126.2 (m), 125.9, 125.5, 124.0, 123.1, 122.9, 122.9, 120.3, 119.5, 116.5, 112.0 (m), 105.3 (m); HRMS (EI) calcd for $C_{27}H_{13}N_2F_3$ 422.1031, found 422.1022 [$M^{+\cdot}$].

*2-(2-Chlorophenyl)-1-(3,4,5-trimethoxyphenyl)-1H-phenanthro-[9,10-d]imidazole (**4m**)*. Yield: 377 mg (79%). White solid; mp = 168−169 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, J = 7.2 Hz, 1H), 8.79 (d, J = 8.3 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 7.75−7.70 (m, 1H), 7.68−7.63 (m, 1H), 7.59−7.53 (m, 1H), 7.45 (dd, J = 7.5, 1.5 Hz, 1H), 7.43−7.32 (m, 4H), 7.28−7.24 (m, 1H), 6.70 (s, 2H), 3.92 (s, 3H), 3.74 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 149.2, 138.6, 137.0, 135.1, 132.8, 132.5, 131.0, 130.6, 129.5, 129.3, 128.3, 127.3, 127.2, 127.0, 126.4, 126.3, 125.6, 125.2, 124.1, 123.1, 122.8 (2 signals), 121.1, 105.7, 61.1, 56.3; HRMS (EI) calcd for $C_{30}H_{23}N_2O_3Cl$ 494.1397, found 494.1390 [$M^{+\cdot}$].

*2-(2-Bromophenyl)-1-(3,4,5-trimethoxyphenyl)-1H-phenanthro-[9,10-d]imidazole (**4n**)*. Yield: 730 mg (89%). White solid; mp = 194−195 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, J = 7.6 Hz, 1H), 8.80 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.69−7.63 (m, 1H), 7.62−7.53 (m, 2H), 7.46−7.34 (m, 3H), 7.33−7.25 (m, 2H), 6.74 (s, 2H), 3.92 (s, 3H), 3.75 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 150.3, 138.6, 132.6, 131.2, 129.3, 128.3, 127.4, 126.8, 126.5, 125.7, 125.2, 125.0, 124.1, 123.1, 122.9, 122.7, 121.1, 105.7, 61.1, 56.3; HRMS (EI) calcd for $C_{30}H_{23}N_2O_3Br$ 538.0892, found 538.0890 [$M^{+\cdot}$].

*2-(2-Iodophenyl)-1-(3,4,5-trimethoxyphenyl)-1H-phenanthro-[9,10-d]imidazole (**4o**)*. Yield: 320 mg (91%). Pale orange solid; mp = 213-214 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, J = 7.3 Hz, 1H), 8.80 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.76−7.70 (m, 1H), 7.68−7.63 (m, 1H), 7.59−7.54 (m, 1H), 7.42−7.35 (m, 3H), 7.35−7.30 (m, 1H), 7.09 (td, J = 7.9, 1.7 Hz, 1H), 6.77 (s, 2H), 3.92 (s, 3H), 3.76 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 152.3, 138.9, 138.5, 136.7, 132.8, 131.9, 131.0, 129.3, 128.3, 127.5, 127.4, 127.3, 126.8, 126.5, 125.6, 125.1, 124.1, 123.1, 122.8 (2 signals), 121.1, 106.0, 100.4, 61.1, 56.4; HRMS (EI) calcd for $C_{30}H_{23}N_2O_3I$ 586.0753, found 586.0746 [$M^{+\cdot}$].

*2-(1-(3,4,5-Trimethoxyphenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl trifluoromethanesulfonate (**4q**)*. Yield: 331 mg (91%). White solid; mp = 189−190 °C; ^{1}H NMR (500 MHz, cdcl$_3$) δ 8.83 (dd, J = 7.9, 0.9 Hz, 1H), 8.80 (d, J = 8.3 Hz, 1H), 8.72 (d, J = 8.4 Hz, 1H), 7.77−7.70 (m, 1H), 7.70−7.64 (m, 1H), 7.60−7.54 (m, 1H), 7.50−7.30 (m, 6H), 6.73 (s, 2H), 3.96 (s, 3H), 3.74 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 147.7, 145.1, 138.8, 137.5, 132.7, 132.6, 131.1, 129.6, 128.3, 127.9, 127.6, 127.4, 127.1, 126.4, 125.8, 125.4,

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125.1, 124.1, 123.0, 122.8, 122.7, 122.4, 121.2, 119.7, 117.1, 106.1, 61.2, 56.3; HRMS (EI) calcd for $C_{31}H_{23}N_2O_6SF_3$ 608.1229, found 608.1237 [$M^{+\cdot}$].

*2,3,4-Trimethoxyphenanthro[9′,10′:4,5]imidazo[1,2-f]-phenanthridine (**5m**).* Prepared from **4m**. Reaction time: 70 h. Yield 52 mg (88%). Prepared from **4n**. Reaction time: 10 h. Yield 320 mg (95%). Prepared from **4o**. Reaction time: 2 h. Yield 81 mg (97%). Prepared from **4q**. Reaction time: 5 h. Yield 74 mg (59%). White crystals; mp = 195−196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (dd, J = 8.1, 0.9 Hz, 1H), 8.99−8.95 (m, 2H), 8.84−8.80 (m, 1H), 8.74 (d, J = 8.3 Hz, 1H), 8.46−8.41 (m, 1H), 7.81−7.76 (m, 1H), 7.74−7.67 (m, 3H), 7.66 (s, 1H), 7.64−7.57 (m, 2H), 4.08 (s, 3H), 4.07 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 152.3, 148.4, 141.7, 140.6, 130.5, 129.7, 129.6, 128.9, 128.7, 127.5, 127.4, 127.2, 126.5, 126.4, 125.2, 124.9, 124.6, 123.9, 123.7, 123.5, 123.4, 123.0, 111.1, 99.5, 61.3, 60.6, 56.1; HRMS (EI) calcd for $C_{30}H_{22}N_2O_3$ 458.1630, found 458.1628 [$M^{+\cdot}$].

*2-(2-Chloro-6-fluorophenyl)-1-(3,4,5-trimethoxyphenyl)-1H-phenanthro[9,10-d]imidazole (**4p**).* Yield: 793 mg (61%). White solid; mp = 203−204 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, J = 7.1 Hz, 1H), 8.80 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 7.74 (t, J = 7.2 Hz, 1H), 7.70−7.64 (m, 1H), 7.61−7.55 (m, 1H), 6.79 (d, J = 2.2 Hz, 1H), 6.75 (s, 1H), 3.93 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 160.7, 153.7, 153.5, 143.4, 138.9, 136.7, 136.7, 132.3, 129.4, 128.3, 127.5, 127.4, 126.6, 125.9, 125.5, 125.2 (2 signals), 124.1, 123.1, 123.0, 122.5, 121.1, 114.1, 113.9, 105.0, 104.9, 61.1, 56.3 (2 signals); HRMS (EI) calcd for $C_{30}H_{22}N_2O_3ClF$ 512.1303, found 512.1300 [$M^{+\cdot}$].

*8-Fluoro-2,3,4-trimethoxyphenanthro[9′,10′:4,5]imidazo[1,2-f]-phenanthridine (**5n**).* Prepared from **5n**. Reaction time: 70 h. Yield: 67 mg (89%). White solid; mp = 227−228 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, J = 8.4 Hz, 1H), 9.00 (d, J = 7.8 Hz, 1H), 8.83 (d, J = 7.8 Hz, 1H), 8.74 (d, J = 8.2 Hz, 1H), 8.40 (dd, J = 8.0, 1.2 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.74−7.70 (m, 1H), 7.69−7.57 (m, 4H), 7.44−7.39 (m, 1H), 4.06 (s, 3H), 4.04 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 158.7, 153.2, 152.9, 144.9, 144.8, 142.1 (2 signals), 140.7, 130.9, 130.6, 129.9, 129.8, 129.6, 129.3, 127.5, 127.1, 126.6, 125.2, 124.9, 124.7, 124.1, 123.7, 123.4, 123.0, 122.9, 122.3, 122.2, 114.7, 114.5, 112.9, 112.8, 110.5 (2 signals), 99.4, 61.3, 60.6, 56.1; HRMS (EI) calcd for $C_{30}H_{21}N_2O_3F$ 476.1536, found 476.1534 [$M^{+\cdot}$].

*2,2′-(2,5-Dibromo-1,4-phenylene)bis(1-(4-octylphenyl)-1H-phenanthro[9,10-d]imidazole) (**4r**).* Prepared following general procedure 1, but with the use of 0.5 equiv of aldehyde. Yield: 562 mg (64%). White solid; mp = 231−232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78−8.74 (m, 4H), 8.70 (d, J = 8.4 Hz, 2H), 7.73−7.70 (m, 2H), 7.67−7.63 (m, 4H), 7.54−7.50 (m, 2H), 7.35 (q, J = 8.4 Hz, 8H), 7.29−7.25 (m, 2H), 7.13−7.10 (m, 2H), 2.81−2.76 (m, 4H), 1.79 (dt, J = 15.6, 7.7 Hz, 4H), 1.49−1.26 (m, 20H), 0.89 (t, J = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.2, 145.2, 137.0, 136.4, 135.4, 134.4, 130.0, 129.4, 128.4, 128.0, 127.6, 127.3, 127.0, 126.4, 125.7, 125.3, 124.0, 123.3, 123.2, 122.8, 122.6, 121.0, 35.8, 31.9, 30.9, 29.5 (2 signals), 29.3, 22.7, 14.1; HRMS (ESI) calcd for $C_{64}H_{61}N_4Br_2$ [M + H^+] 1043.3263, found 1043.3235.

*7-Bromo-3-octyl-6-(1-(4-octylphenyl)-1H-phenanthro[9,10-d]-imidazol-2-yl)phenanthro[9′,10′:4,5]imidazo[1,2-f]phenanthridine (**5o**).* Prepared from **4r**. The reaction is carried out in toluene at 90 °C. Irradiated with UV light having a wavelength of 254 nm for 12 h. The product purified by column chromatography (SiO_2, ethyl acetate/hexane 1:9). Yield 109 mg (76%). Yellowish solid; mp = 260−261 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.17−8.63 (m, 7H), 8.60−8.26 (m, 3H), 8.14 (s, 1H), 7.78−7.38 (m, 9H), 7.36−7.34 (m, 1H), 7.33−7.26 (m, 2H), 7.21 (d, J = 6.9 Hz, 1H), 7.10 (ddd, J = 27.3, 8.5, 2.5 Hz, 1H), 2.76−2.83 (m, 2H), 2.52−2.59 (m, 2H), 1.70−1.78 (m, 2H), 1.50−1.56 (m, 2H), 1.40−1.20 (m, 20H), 0.85 (t, J = 6.9 Hz, 3H), 0.77 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 138.4, 131.6, 129.7, 129.5, 129.2, 128.4, 128.2, 127.5, 126.6, 125.4, 124.6, 124.4 (2 signals), 124.1, 124.0, 123.5, 123.3, 123.0, 119.1, 35.5, 31.9, 31.7, 31.5, 31.4, 30.8, 30.2, 30.1, 29.7, 29.5, 29.3, 29.1, 22.7, 22.6, 14.1, 14.0; HRMS (ESI) calcd for $C_{64}H_{60}BrN_4$ [M + H^+] 963.4001, found 963.3976.

*2,17-Dioctylphenanthro[10′,9′:4,5]imidazo[1,2-f]phenanthro-[9″,10″:4′,5′]imidazo[1′,2′:1,2]quinolino[4,3-j]phenanthridine (**5q**).* **Method A:** Prepared from **4r**. The reaction is carried out in toluene at 90 °C. Irradiated with UV light having a wavelength of 254 nm for 12 h and then UV light having a wavelength of 366 nm for 20 h. The product purified by recrystallization in a mixture of ethyl acetate/chloroform. Yield 63 mg (61%). **Method B:** Prepared from **5o**. The reaction is carried out in toluene at 90 °C. Irradiated with UV light having a wavelength of 366 nm for 20 h. The product purified by recrystallization in a mixture of ethyl acetate/chloroform. Yield 63 mg (61%). Yellow solid; mp = 344−345 °C; ^{1}H NMR (600 MHz, $CDCl_3$, one drop of TFA-d) δ 10.31 (s, 2H), 8.88 (d, J = 8.3 Hz, 2H), 8.83 (d, J = 8.0 Hz, 2H), 8.76−8.72 (m, 2H), 8.69 (s, 2H), 8.60 (d, J = 8.5 Hz, 4H), 7.98−7.87 (m, 6H), 7.80 (t, J = 7.5 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 3.06−3.01 (m, 4H), 1.86 (dt, J = 15.6, 7.9 Hz, 4H), 1.52 (dt, J = 15.0, 7.3 Hz, 4H), 1.47−1.39 (m, 4H), 1.39−1.28 (m, 12H), 0.90 (t, J = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, one drop of TFA-d) δ 146.1, 140.9, 131.0, 130.9, 130.7, 130.6, 130.1, 129.4, 128.9, 128.8, 127.1, 125.5, 125.2, 124.2, 124.1, 124.0, 122.9, 121.4, 120.8, 120.7, 119.7, 119.4, 115.4, 113.5, 36.0, 31.9, 31.8, 29.5 (2 signals), 29.3, 22.7, 14.0; HRMS (ESI) calcd for $C_{64}H_{59}N_4$ [M + H^+] 883.4740, found 883.4718.

*2,2′-(2,5-Dibromo-1,4-phenylene)bis(1-(9,9-dioctyl-9H-fluoren-2-yl)-1H-phenanthro[9,10-d]imidazole) (**4s**).* Prepared following general procedure 1, but with the use of 0.5 equiv of aldehyde. Because of steric hindrance, the compound is in the form of isomers. Yield: 280 mg (52%). White solid; mp = 264−265 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78−8.74 (m, 3H), 8.70 (d, J = 8.4 Hz, 3H), 7.86 (d, J = 7.5 Hz, 1H), 7.83−7.72 (m, 3H), 7.72−7.61 (m, 6H), 7.60−7.55 (m, 2H), 7.51−7.35 (m, 8H), 7.32 (d, J = 8.3 Hz, 1H), 7.30 (dd, J = 7.8, 1.8 Hz, 1H), 7.27 (d, J = 8.3 Hz, 1H), 7.22 (s, 1H), 7.15 (dt, J = 11.2, 7.6 Hz, 2H), 2.02−1.85 (m, 8H), 1.26−0.58 (m, 48H), 0.56 (t, J = 6.8 Hz, 3H), 0.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.4, 152.3, 151.2, 151.1, 148.2, 148.1, 142.8, 142.8, 139.7, 137.2, 136.3, 136.3, 135.7, 135.6, 135.5, 135.4, 129.4, 128.3, 128.1, 128.0, 127.5, 127.3, 127.3, 127.2, 127.1, 126.5, 126.4, 126.2, 125.7, 125.2, 124.0, 123.4, 123.3, 123.1, 123.0, 122.9 (2 signals), 122.8, 121.2 (2 signals), 121.1, 120.6, 55.5, 40.6, 40.5, 40.2, 31.8 (2 signals), 31.7 (2 signals), 31.6, 30.2 (2 signals), 30.1 (2 signals), 29.5, 29.4 (3 signals), 29.3 (2 signals), 24.1, 24.0 (2 signals), 23.9, 22.7, 22.6 (2 signals), 22.5 (2 signals), 14.1 (2 signals), 13.8 (2 signals); HRMS (ESI) calcd for $C_{94}H_{101}N_4Br_2$ [M + H^+] 1443.6393, found 1443.6396.

*7-Bromo-8-(1-(9,9-dioctyl-9H-fluoren-2-yl)-1H-phenanthro[9,10-d]imidazol-2-yl)-15,15-dioctyl-15H-indeno[1,2-b]phenanthro-[9′,10′:4,5]imidazo[1,2-f]phenanthridine (**5p**).* Prepared from **4s**. The reaction is carried out in toluene of 90 °C. Irradiated with UV light having a wavelength of 254 nm for 12 h. The product purified by column chromatography (SiO_2, ethyl acetate/hexane 1:9). Yield 115 mg (72%). Yellow solid; mp = 269.270 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.94 (d, J = 7.8 Hz, 1H), 8.87 (d, J = 7.2 Hz, 2H), 8.82 (d, J = 8.7 Hz, 1H), 8.78 (d, J = 7.9 Hz, 1H), 8.76−8.68 (m, 3H), 8.35 (s, 1H), 8.32 (s, 1H), 7.94 (d, J = 7.0 Hz, 1H), 7.79−7.64 (m, 6H), 7.57 (ddd, J = 10.2, 7.7, 3.7 Hz, 4H), 7.47−7.37 (m, 5H), 7.25−7.21 (m, 4H), 2.14−2.00 (m, 4H), 1.81−1.69 (m, 4H), 1.44−0.96 (m, 48H), 0.89−0.75 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.2, 151.5, 151.0, 150.5, 150.3, 145.6, 142.4, 141.8, 140.0, 139.6, 139.2, 137.2, 135.9, 133.4, 133.0, 129.7, 129.4, 129.3, 128.7, 128.4, 128.2, 127.9, 127.5, 127.4, 127.3, 127.1, 126.9, 126.6, 126.2, 125.7, 125.3, 125.1, 125.0, 124.6, 124.3, 124.1, 124.0, 123.6, 123.4 (2 signals), 123.2, 123.0, 122.7, 121.2, 120.5, 120.1, 115.1, 114.1, 55.8, 55.4, 40.9, 40.4, 40.2, 31.9, 31.8, 31.7 (2 signals), 31.6, 31.5, 31.4, 30.3, 30.2, 30.0, 29.7, 29.4, 29.3 (2 signals), 29.2 (3 signals), 24.0, 23.5, 22.7, 22.6, 22.5 (2 signals), 14.1 (2 signals), 14.0, 13.8; HRMS (ESI) calcd for $C_{94}H_{100}N_4Br$ [M + H^+] 1363.7108, found 1363.7131.

*Compound **5r**.* **Method A:** Prepared from **4s**. Reaction was carried out in toluene at 90 °C. Irradiated with UV light having a wavelength of 254 nm for 12 h and then UV light having a wavelength of 366 nm for 20 h. The product purified by column chromatography (SiO_2,

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J. Org. Chem. 2015, 80, 5753−5763

toluene). Yield 59 mg (57%). **Method B:** Prepared from **5p**. Reaction was carried out in toluene at 90 °C. Irradiated with UV light having a wavelength of 366 nm for 20 h. The product purified by column chromatography (SiO_2, toluene). Yield 59 mg (57%). Yellow solid; mp = 277−278 °C; ^{1}H NMR (600 MHz, $CDCl_3$, one drop of TFA-d) δ 10.59 (s, 2H), 9.25 (s, 2H), 8.99 (d, J = 8.3 Hz, 2H), 8.92 (d, J = 8.2 Hz, 2H), 8.89 (d, J = 7.7 Hz, 2H), 8.63 (d, J = 8.3 Hz, 2H), 8.61 (s, 2H), 8.25 (d, J = 7.5 Hz, 2H), 8.06 (t, J = 7.2 Hz, 2H), 8.01 (t, J = 7.1 Hz, 2H), 7.96 (t, J = 7.5 Hz, 2H), 7.72 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 7.3 Hz, 2H), 7.54 (t, J = 7.2 Hz, 2H), 7.47 (d, J = 7.3 Hz, 2H), 2.43−1.94 (m, 8H), 1.53−0.89 (m, 48H), 0.89−0.64 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$, drop TFA-d) δ 154.2, 150.4, 143.8, 141.3, 138.6, 131.3, 131.1, 131.0, 130.9, 130.2, 129.8, 129.6, 129.5, 128.8, 128.1, 126.5, 125.4, 124.1, 124.0, 123.9, 123.2, 123.0, 122.6, 121.6, 121.2, 120.0, 119.4, 117.5, 116.3, 115.6, 115.3, 113.7, 111.8, 56.4, 31.7, 29.2, 22.5, 13.9; HRMS (ESI) calcd for $C_{94}H_{99}N_4$ [M + H$^+$] 1283.7870, found 1283.7876.

*Benzo[4,5]imidazo[1,2-f]phenanthridine (**9a**).* Prepared from **8a**. Reaction time: 10 h. Yield: 86 mg (93%). White solid; mp 152−155 °C; ^{1}H NMR (500 MHz, $CDCl_3$, drop TFA-d) δ 9.15 (d, J = 8.0 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 7.9 Hz, 1H), 8.52 (dd, J = 10.7, 5.5 Hz, 2H), 8.32 (dd, J = 6.4, 2.7 Hz, 1H), 8.00 (t, J = 7.5 Hz, 1H), 7.95−7.83 (m, 2H), 7.79−7.70 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, one drop of TFA-d) δ 142.3, 135.0, 131.2, 131.1, 131.0, 130.6, 128.7, 128.5, 128.0, 127.4, 126.9, 124.9, 123.0, 122.1, 117.4, 115.7, 115.6, 115.3, 113.4; HRMS, calcd for $C_{19}H_{13}N_2$ (M + H$^+$) 269.1073, found 269.1071.

*6-Bromo-1,2-dihydroacenaphthylene-5-carbaldehyde (**10**).* *n*-Butyllithium (4.4 mL, 11 mmol, 1.6 M solution in hexane) was added into a solution of 5,6-dibromo-1,2-dihydroacenaphthylene (3.12 g, 10 mmol) in anhydrous Et_2O (120 mL) at −78 °C under argon atmosphere. The resulting reaction mixture was stirred for 24 h (allowing to warm up to to 0 °C), and then for 30 min at rt. Subsequently, the reaction mixture was again cooled to −78 °C, treated with 4 mL of anhydrous DMF, and stirred at −78 °C for 1 h. The cooling bath was removed and the reaction mixture was slowly warmed to room temperature while stirred for 1 h. The reaction was quenched by adding 100 mL of 10% NH_4Cl. The residue was repeatedly extracted with Et_2O and washed with water and brine. The organic extracts were dried with anhydrous $MgSO_4$ and concentrated under a reduced pressure. The product purified by column chromatography (SiO_2, ethyl acetate/hexanes 1:6). Yield: 2.11 g (81%). Yellow solid; mp = 167−170 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 11. 57 (s, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 3.33 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.9, 153.7, 146.9, 141.3, 135.7, 135.1, 132.2, 130.9, 121.1, 120.8, 119.9, 112.6, 30.7, 29.8; HRMS (EI) calcd for $C_{13}H_9BrO$ 259.9837, found 259.9839 [M$^{+\cdot}$].

*2-(6-Bromo-1,2-dihydroacenaphthylen-5-yl)-1-(4-(tert-butyl)-phenyl)-1H-phenanthro[9,10-d]imidazole (**11**).* Purified by the column chromatography (SiO_2; hexanes/ethyl acetate 6:1). Yield: 180 mg (39%). Yellowish solid; mp = 311−312 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.79 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 7.72−7.61 (m, 3H), 7.58 (d, J = 6.8 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.38 (dd, J = 8.3, 2.1 Hz, 1H), 7.32−7.21 (m, 4H), 7.14 (d, J = 8.1 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 3.44−3.24 (m, 4H), 1.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 150.0, 148.9, 146.3, 140.7, 137.0, 135.4, 134.3, 134.2, 129.8, 129.2, 128.5, 128.2, 127.6, 127.4, 127.2, 126.5, 126.1, 125.3, 124.7, 124.0, 123.5, 123.2, 123.0, 122.9, 121.0, 120.6, 119.0, 114.4, 110.0, 34.7, 31.2, 30.5, 29.9; HRMS (EI) calcd for $C_{37}H_{29}BrN_2$ 580.1514, found 580.1511 [M$^{+\cdot}$].

*6-(tert-Butyl)-1,2-dihydroacenaphtho[5,6-cd]benzo[f]-phenanthro[9′,10′:4,5]imidazo [1,2-a]azepine (**12**).* Prepared from **11**. Purified by the column chromatography (SiO_2; toluene). Yield: 26 mg (47%). Yellowish solid; mp = 293−294 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (d, J = 7.3 Hz, 1H), 8.79 (dd, J = 7.9, 1.0 Hz, 1H), 8.75 (d, J = 8.3 Hz, 1H), 8.70 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 7.3 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.75−7.68 (m, 1H), 7.68−7.62 (m, 1H), 7.57−7.50 (m, 1H), 7.46 (dd, J = 7.3, 4.5 Hz, 2H), 7.44−7.40 (m, 1H), 7.38 (d, J = 2.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.28 (dd, J = 8.5, 2.2 Hz, 1H), 3.54−3.37 (m, 4H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 151.2, 148.2, 146.8, 140.3, 139.6, 134.0, 133.6, 132.6, 132.2, 130.7, 129.5, 129.2, 128.9, 128.1, 127.2, 127.1 (2 signals), 127.0, 125.8, 125.7, 124.7, 124.6, 124.1, 123.7, 123.6, 123.5, 123.0, 122.8, 120.5, 120.4, 34.7, 31.3, 30.6, 30.3; HRMS (EI) calcd for $C_{37}H_{28}N_2$ 500.2252, found 500.2249 [M$^{+\cdot}$].

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **4a−s**, **5a−r**, **9a**, **10**, **11** and **12**, as well as optical data and mechanistic data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00714.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dtgryko@icho.edu.pl.

Notes

The authors declare no competing financial interest.

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