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Synthesis of 2-Azapyrenes and their Photophysical and Electrochemical Properties

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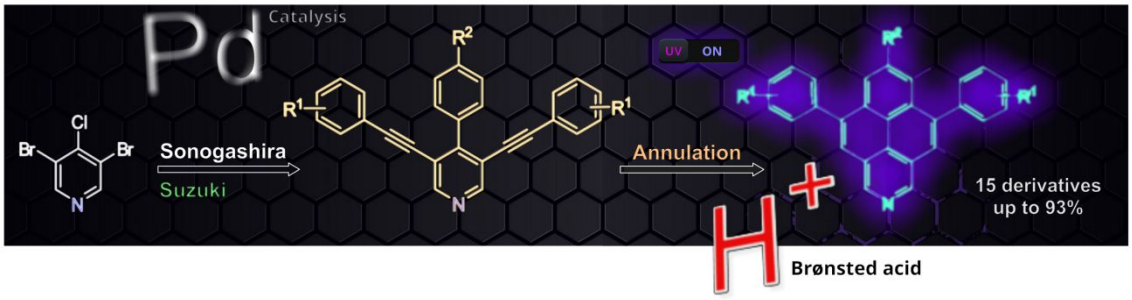
Keywords

Catalysis, cross-coupling, cycloisomerisation, heterocycles, palladium

Graphical abstract



ABSTRACT: A series of 5,7,9-substituted 2-azapyrenes were synthesized for the first time. The synthesis relies on Brønsted acid promoted benzannulation of alkyne precursors prepared by palladium-catalyzed cross-coupling reactions. The synthetic strategy is efficient and the scope covers a variety of functional groups. The electrochemical behavior and photophysical properties of the products were investigated by UV-Vis and fluorescence spectroscopy, cyclic voltammetry and DFT calculations.

Introduction

In the search for attractive and versatile organic materials, the employment of π-conjugated polycyclic (hetero)aromatic hydrocarbons has become a hot topic in materials science.[1,2] In particular, *peri*-fused heteroarenes, isostructural or isoelectronic to pyrene, are of high interest, since this 16π-conjugated polycyclic hydrocarbon exhibits unique electronic and photophysical properties. Hence, pyrene has become a prominent component in organic electronics[3-13] and biomedical chemistry[14-21].

Varying the molecular architecture of the pyrene core by doping with heteroatoms like electronegative nitrogen into the framework is an effective strategy for tuning the photoelectronic properties. For example, it has been reported that the incorporation of nitrogen atoms significantly affects the HOMO-LUMO energy levels, lower the HOMO-LUMO gap and enhances the electron-acceptor ability.[27] These results have intensified the interest in azapyrenes as potential materials for applications in organic semiconductor devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs).[23-27] Moreover, azapyrenes are promising candidates for self-assembled molecules[28,29], main building units in molecular machines[30,31] and DNA intercalators[32-34].

Synthetic strategies for the construction of azapyrenes have been previously reported based on multi-step procedures with a set of drawbacks, e.g., harsh conditions, expensive or complex starting materials, low selectivity and only low functionalization potential.[35-37] With regard to 2-azapyrenes (naphtho[2,1,8-*def*]isoquinolines), only the unsubstituted parent compound has been reported in the literature so far. This compound has been prepared by thermal cyclization[38], by using a lengthy nine step-sequence,[39] and by PPA (polyphosphoric acid) induced Beckmann rearrangement,[40] and by *peri*-annulation with *sym*-triazines[41]. In the course of the development of Pd-catalyzed cross-coupling reactions,[23,42-50] a number of di- and triazapyrenes and related molecules have been published.[25,51-62]. Recently, the group of Kozaki published an intramolecular Cu(I) catalyzed C–H functionalization approach,[63] while Han *et al*. applied the classical Bischler-Napieralski cyclization of amide precursors.[27]

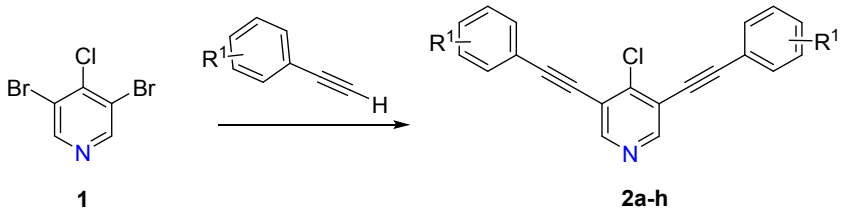
Despite the importance of aza-analogous pyrenes in the field of materials sciences, many azapyrene core structures remain essentially unknown, due to the lack of general methods for their synthesis. Herein, we report what is, to the best of our knowledge, the first synthesis of a series of substituted 2-azapyrenes. Our synthesis is based on Brønsted acid promoted cycloisomerization of substituted pyridines which were prepared by regioselective cross-coupling reactions. In addition, we report, for the first time, a detailed study of the photophysical and electrochemical properties of the products by UV-Vis and fluorescence spectroscopy, cyclic voltammetry and DFT calculations.

Results and Discussion

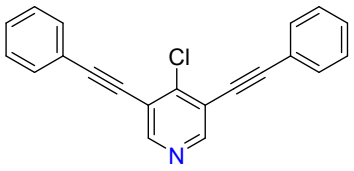
Synthesis

As starting material, we used 3,5-dibromo-4-chloropyridine **1**, which is easily accessible from 4-pyridone in two steps in 77% overall yield.[64] Next, double Sonogashira reactions of pyridine **1** was studied (for optimization details see SI, Table S1). Finally, the employment of $Pd(PPh_3)_4$ (5 mol%), CuI (5 mol%), diisopropylamine along with 2.2 equiv. alkyne at 50°C in acetonitrile proved to be appropriate reaction conditions and various 3,5-alkynyl-4-chloro pyridines **2a-h** could be prepared in good to very good yields with high chemoselectivity (Table 1).

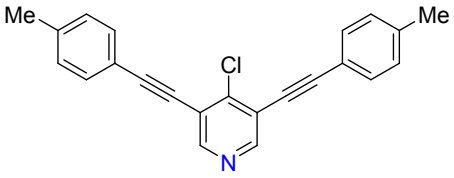
Table 1. Scope of the Sonogashira cross-coupling reaction[a]



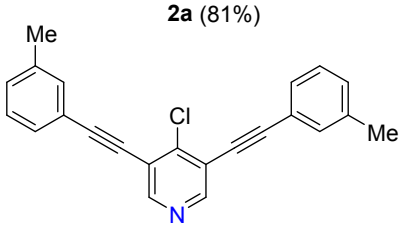
1 **2a-h**



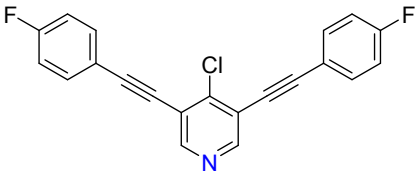
2a (81%)



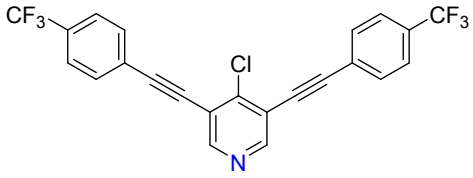
2b (87%)



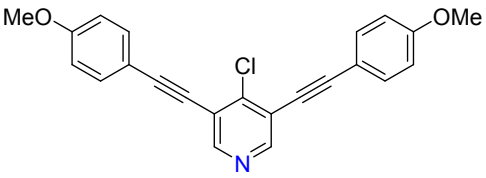
2c (80%)



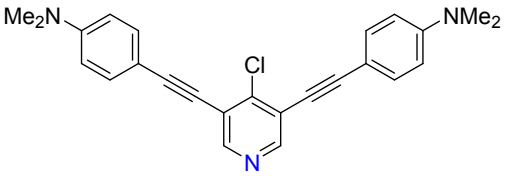
2d (74%)



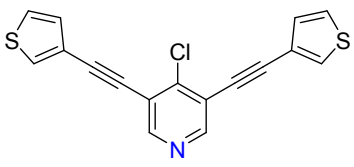
2e (75%)



2f (88%)[b]



2g (80%)

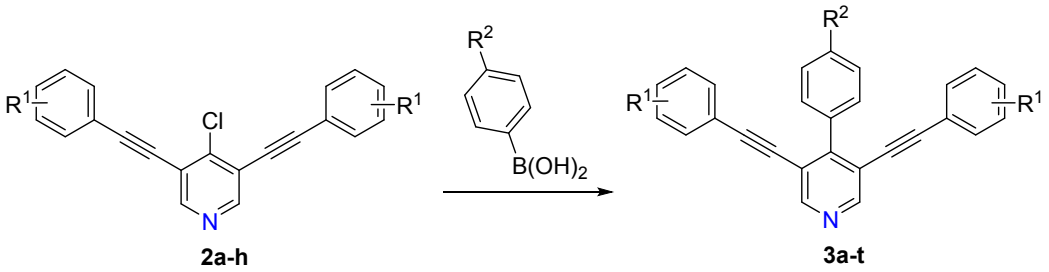


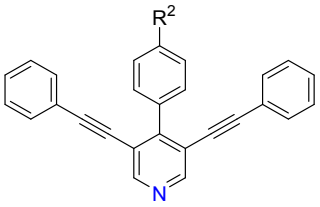
2h (78%)

[a] Reaction conditions: **1** (0.37 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (5 mol%), CuI (5 mol%), alkyne (2.2 eq.), HN^iPr_2, MeCN, 50°C 24h. [b] 2.6 eq. of the alkyne were used.

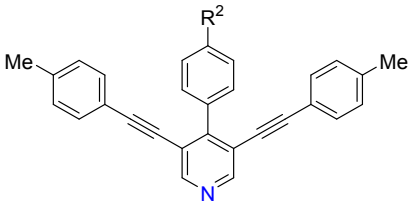
Subsequent Suzuki reactions (for optimization see SI, Table S2) with *para*-substituted aryl boronic acids afforded the key precursors **3a-t** in up to 85% yield (Table 2).

Table 2. Scope of the Suzuki cross-coupling reaction[a]

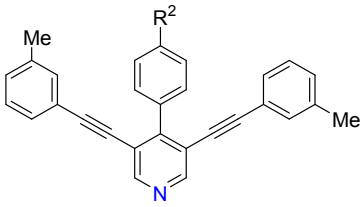




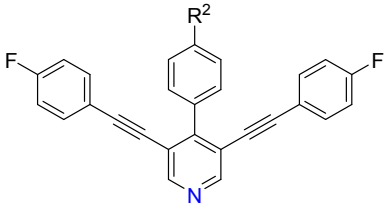
3a R^2 = H 75%
3b R^2 = Me 85%
3c R^2 = OMe 62%
3d R^2 = CF_3 55%



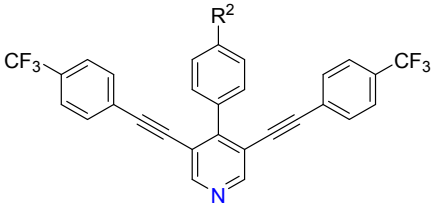
3e R^2 = H 80%
3f R^2 = Me 79%
3g R^2 = OMe 64%
3h R^2 = CF_3 55%



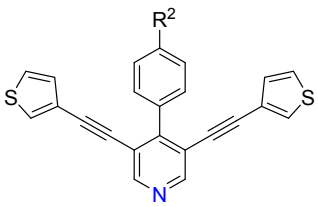
3i R^2 = H 63%
3j R^2 = Me 64%
3k R^2 = OMe 55%



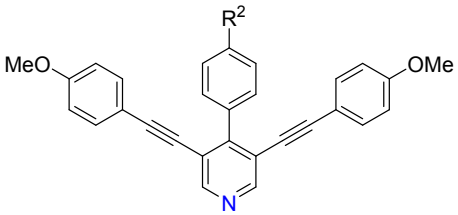
3l R^2 = H 74%
3m R^2 = Me 78%
3n R^2 = OMe 62%



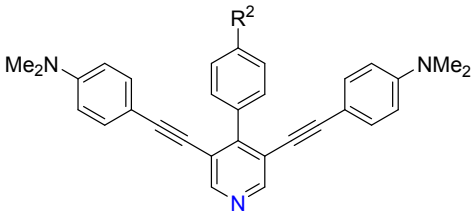
3o R^2 = H 71%
3p R^2 = Me 77%
3q R^2 = OMe 57%



3r R^2 = H 71%



3s R^2 = H 69%



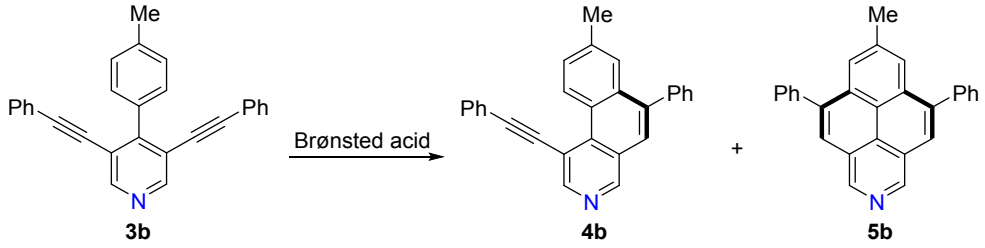
3t R^2 = H 72%

[a] Reaction conditions: **2a-h** (100 mg, 1.0 eq.), arylboronic acid (2.0 eq.), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (2.0 eq.), 1,4-dioxane at 90°C for 24h.

With precursors **3a–q** in hand, the Brønsted acid mediated benzannulation reaction was studied. The optimization was carried out with **3b** as model compound in the presence of *para*-toluenesulfonic acid monohydrate (*p*TsOH) or methanesulfonic acid (MsOH) at 120°C, respectively (Table 3). These conditions were previously employed by us for the construction of various N-PAHs.[65-67] As summarized in Table 3, both Brønsted acids performed equally well using a high excess of the employed acid, providing bis-annulated compound **5b** in very good yields in sub-millimolar (entries 2 and 3) and gram-

scale synthesis (entry 7). Reduction of the amount of *p*TsOH resulted in exclusive formation of mono-cyclized isomer **4b**, whereas **5b** was not formed at all (entry 4). Finally, optimization of the reaction time gave complete conversion and formation of **4b** within 1h at room temperature or, alternatively, formation of **5b** at 120°C for 12h. Thus, we developed two protocols which are suitable for the selective preparation of mono- and bis-annulated isomers.

Table 3. Optimization of the Brønsted acid mediated benzannulation reaction[a]



3b **4b** **5b**

Entry	Acid	Solvent	t [h]	T [°C]	Yield **4b** [%]	Yield **5b** [%]
1	-	Xylene	24	120	-	-
2	MsOH [60 eq.]	-	24	120	-	86
3	*p*TsOH [60 eq.]	-	24	120	-	85
4	*p*TsOH [30 eq.]	-	24	120	88	-
5	MsOH [60 eq.]	-	12	120	-	86
6	MsOH [30 eq.]	Xylene	1	r.t.	89	-
7	MsOH [60 eq.]	-	12	120	-	87[b]

[a] Reaction conditions for 0.27 mmol (100 mg) of **3b**. [b] Reaction conditions for 2.7 mmol (1.0 g) of **3b**.

The optimized reaction conditions were applied for the synthesis of various substituted benzo[*f*]isoquinolines **4a-k** (Table 4) and 2-azapyrenes **5a-o** (Table 5)**.** Very good to excellent yields were obtained for mono-annulated benzo[*f*]isoquinolines and moderate to excellent yields for bis-annulated 2-azapyrenes, respectively. Various functional groups were tolerated which did not impact the yields. A notable decrease in yield was observed for arylalkynes bearing methyl groups in *meta*-position which might be explained by steric effects. More significantly, distinct electronic effects on the yields were observed for the benzannulation during the course of our studies. The strongly electron-withdrawing trifluoromethyl group located at the arylpyridyl moiety of **3d** and **3g** resulted in rapid conversion to give the mono-annulated isomers **4c** and **4f** in 10 and 5 minutes, respectively. On the other hand, the cyclization completely failed at room temperature in case of **3o** and **3p**, where also CF_3-substituents are located at the arylalkynyl moiety. However, efficient annulation of these electron-deficient alkynes proved to be possible when the reaction was performed at elevated temperatures (80°C). Thereby the corresponding mono-annulated products **4i** and **4j** could be obtained within 2h in very good yields.

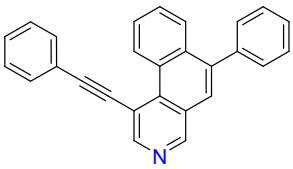
In contrast, employment of our double annulation procedure for CF_3-containing derivatives **3o, 3p** and **3q** resulted in rapid decomposition of the starting material, most likely due to less stabilization of positively charged intermediates during the reaction. Decomposition was also observed for derivative **3s**, containing the strongly electron-donating methoxy group, and for **3r** bearing a thiophene system. Fortunately, a switch from MsOH to *p*TsOH smoothly delivered the desired thiophene-substituted 2-

azapyrene **5o** in very good yield. In comparison, the reactions of **3o** and **3p** with *p*TsOH resulted in formation of mono-annulated products accompanied by traces of the double annulated derivatives, even after prolonged reaction time of 48h.

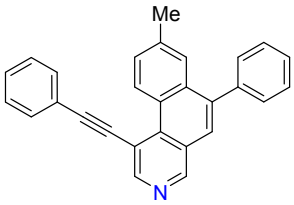
Further changes of the temperature and type of acid as well as the addition of various solvents proved to be not successful. However, twofold annulation of highly reactive **3s** was possible by using less acidic trifluoroacetic acid (TFA) and employing a lower reaction temperature of 60°C. Using these conditions, it was possible to isolate *p*-methoxyphenyl-substituted 2-azapyrene **5m**, albeit, in only 20% yield. Reduction to 30 eq. of acid or performing the reaction at room temperature resulted in a drop of yield to 10%. Finally, we have found, that the use of 3 eq. of TfOH (trifluoromethanesulfonic acid) in CH_2Cl_2 at 0°C and 20 °C provided product **5m** in 66% yield.

The presence of substituents located at the aryl moiety (attached to the pyridine) have a less pronounced impact on the reaction outcome. Accordingly, CF_3 containing products **5d** and **5i** were obtained in good yield, however, an increased reaction time of 24 h was necessary. Employment of starting material **3n**, containing a methoxy group, resulted in formation of product **5l**, albeit, in only 35% yield. This product contains a free hydroxyl group, due to acid induced ether cleavage during the reaction. However, lowering the amount of acid to 30 eq. of MsOH gave the bis-annulated methoxy derivative **5c** in a yield of 33%. Employment of the highly boiling fluorinated alcohol octafluoropentanol (OFPO) gave **5c** at 120°C using 15 eq. of MsOH. However, formation of the corresponding hydroxy-derivative could not be suppressed completely which, thus, resulted in only a slightly improved yield (40%).

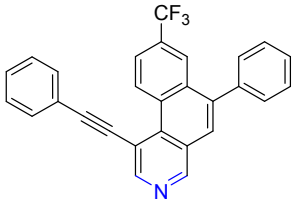
Table 4. Synthesized benzo[*f*]isoquinolines



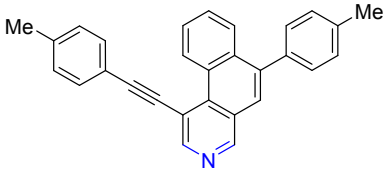
4a (87%)



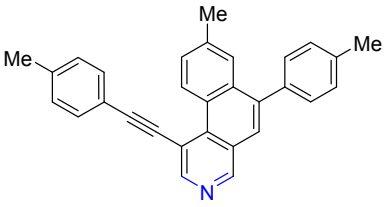
4b (89%)



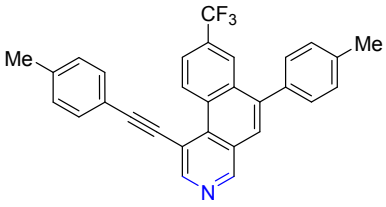
4c (96%)[a]



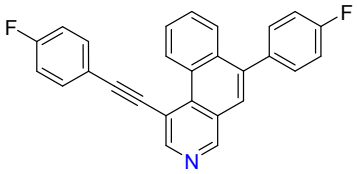
4d (94%)



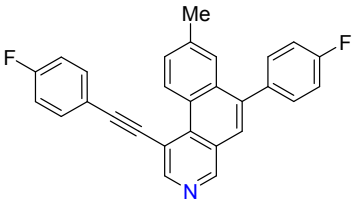
4e (93%)



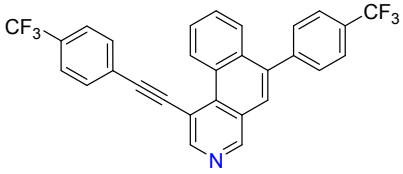
4f (92%)[b]



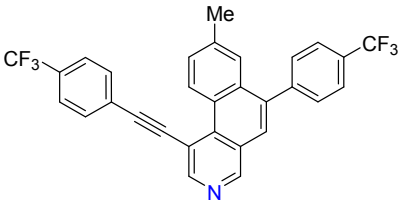
4g (94%)



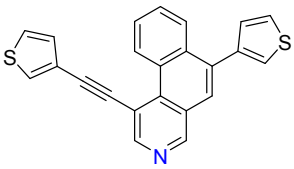
4h (91%)



4i (86%)[c]



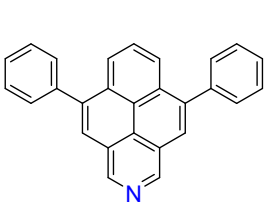
4j (89%)[c]



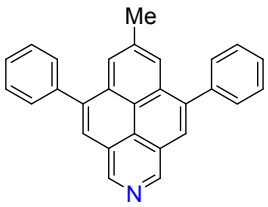
4k (79%)

[a] 10 min reaction time. [b] 5 min reaction time. [c] 2h reaction time at 80°C.

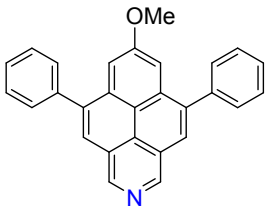
Table 5. Synthesized 2-azapyrenes



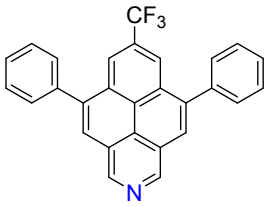
5a (93)%



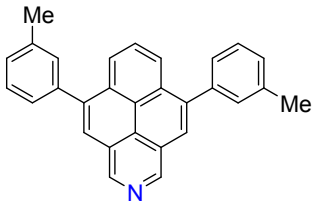
5b (86%)



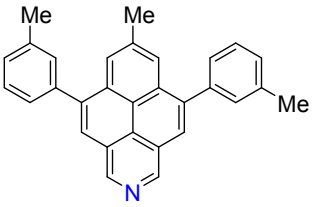
5c (40%)[a]



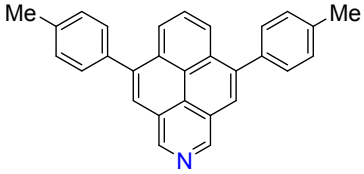
5d (75%)[b]



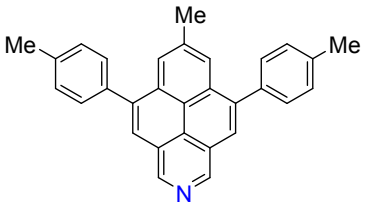
5e (78%)



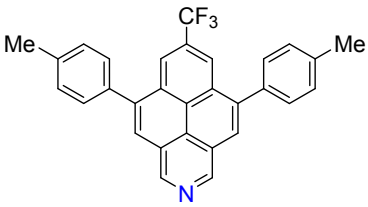
5f (63%)



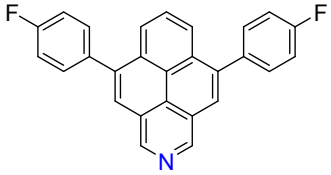
5g (80%)



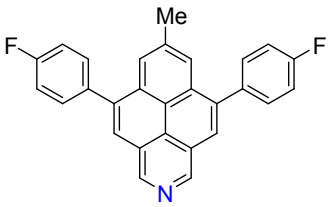
5h (82%)



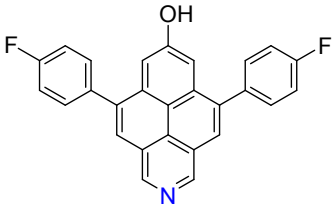
5i (75%)[b]



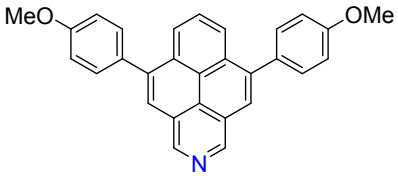
5j (79%)



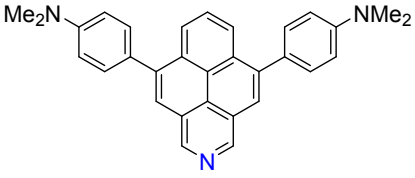
5k (80%)



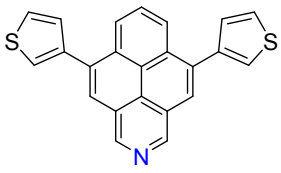
5l (35%)



5m (66%)[c]



5n (75%)



5o (86%)[d]

[a] Reaction carried out with 15 eq. MsOH in OFPO. [b] 24h reaction time. [c] Reaction carried out with 3 eq. TfOH in CH_2Cl_2. [d] Reaction carried out with 60 eq. *p*TsOH.

The structures of **4j** and **5b** were independently confirmed by X-ray crystal structure analysis. For crystal structures and crystallographic data see supporting information. According to the structure analysis of compound **5b**, the phenyl rings are twisted out of plane from the planar core structure with dihedral angles of 51° and 48°.

Physical properties

To gain insights into the photophysical properties, steady state absorption and photoluminescence spectra (PL) for selected 2-azapyrenes were recorded. The key optical data are summarized in Table 6. As depicted in Figure 1, the absorption and emission spectra (except for **5n**) are characterized by well-resolved bands with vibrational progression, highlighting the maintained pyrene-like nature of transitions in the 2-azapyrene, in which the weak L_b band of the transition dipole forbidden $S_1 \leftarrow S_0$ electronic excitation in pyrene, represented by the configuration interaction of HOMO-1 → LUMO and HOMO → LUMO+1 (vide infra), significantly increases upon the incorporation of nitrogen.[68,77] In line with symmetrical 4,10-substituted phenyl[70] and –pyridyl[71] analogues of pyrene, functionalized aryl groups located at the 5,9-position on the 2-azapyrene core have only a small effect on the absorption and emission properties, thus, showing similar overall spectral features. This can be explained by their poor conjugation of the phenyl groups with the 2-azapyrene core because of their twisted orientation.

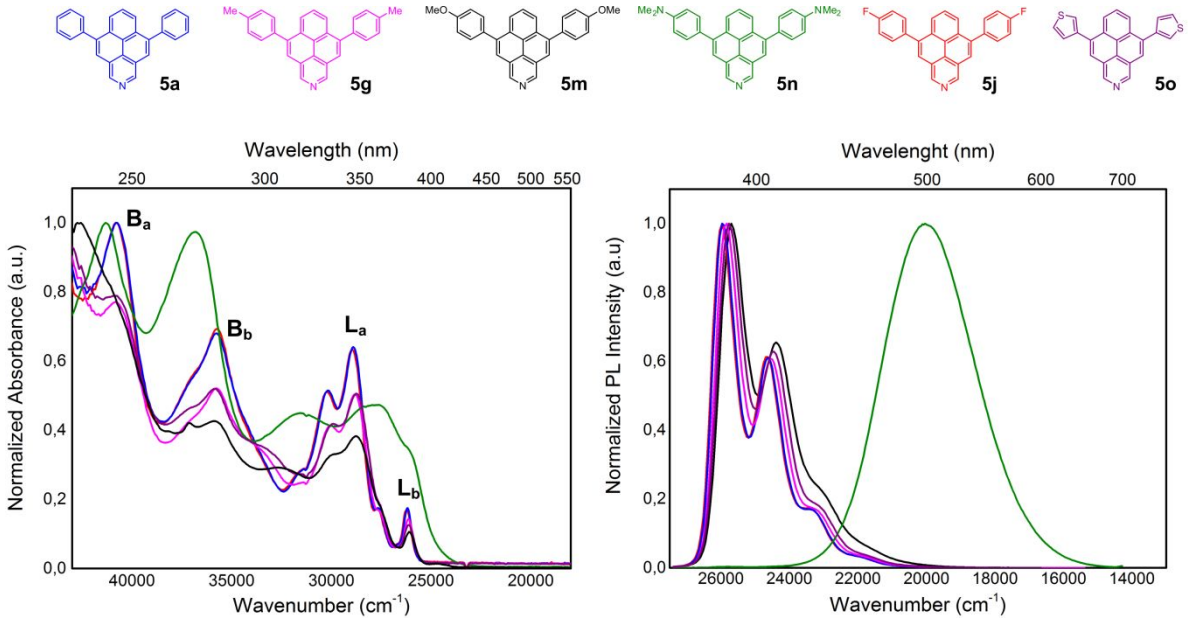


Figure 1. UV-Vis (left) and emission (right, λ_{ex} = 350 nm) spectra of 5,9-diaryl-2-azapyrenes in CH_2Cl_2 (c = 10^{-5} M) at 20°C. Absorption band names are given according to the Platt nomenclature.[72]

However, strong π-donor substituents located at the phenyl groups, like in case of **5m**, show a tendency of band broadening which becomes most prominent for the NMe_2-containing product **5n.** The latter compound exhibits a blue-shifted strongly allowed B_b band (ε = 50244 M^{-1} cm^{-1}), followed by a bathochromically shifted broad absorption with loss of fine structure covering the L_a and L_b band regions. Those are indicative of an extensive conjugation over the whole molecule, and the large

broad unstructured red-shifted emission in the PL spectrum ($\lambda_{em,max}$ = 499 nm) emphasizes an intramolecular charge-transfer (ICT) transition, which has been previously reported for amino substituted pyrenes.[73-76] Comparable emission spectra in CH_2Cl_2 were also observed for alkyl-substituted 4,10-diazapyrenes upon protonation of the nitrogen atoms. In these cases the intensity of the structured initial spectrum decreases with increasing amount of acid and is finally replaced by a new broad red-shifted emission spectrum which results from an enhanced charge transfer transition.[27] In contrast, such a pronounced acid response is not observed for alkyl-substituted 2,7-diazapyrenes where the nitrogen atoms are doped at the nodal plane positions.[26] This highlights the number and position-property relation of nitrogen doping on the photophysical properties beside the substituent position effect at the core structure. This also agrees with the different results between our system and the symmetrical 5,9-*p*-tolyl-substituted di- and tri-azapyrenes[63] investigated by Kozaki and co-workers. The latter compounds are characterized by bathochromically shifted broad absorption and emission spectra, suggesting increased conjugation and charge transfer properties. This is supported by their solvatomchromic and theoretical studies and is most evident for their tetra-azazpyrene derivative which furthermore implies extensive conjugation of aryl groups at position 2 and/or 7 by adjacent doping of nitrogen atoms.

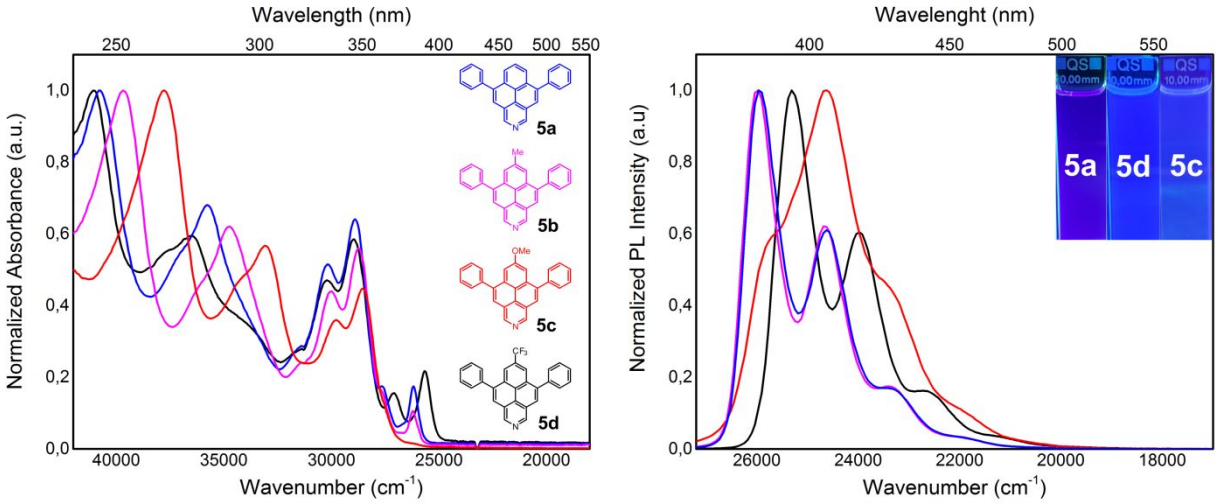


Figure 2. UV-Vis (left) and Emission (right, λ_{ex} = 350 nm) spectra of 7-substituted-5,9-diphenyl-2-azapyrenes in CH_2Cl_2 (c = 10^{-5} M) at 20°C.

In 2-azapyrene, additional functionalization of the nodal plane position 7 shows only a weak effect, which is, however, more significant as compared to the 5,9-substituted derivatives (Figure 2 and Figure S3). The higher lying B_b / B_a as well as the L_b band of the $S_1 \leftarrow S_0$ transition are influenced by the substituent in a reverse manner from higher to lower transitions with increasing electron donating character of the functional groups. In contrast, the L_a band of the $S_2 \leftarrow S_0$ transition is insignificantly influenced by the substituents, consistent with observations for 2- and 2,7-substituted pyrenes.[69,71,77] Taking the highest peak into account, both σ-acceptor and π-donor show a notable bathochromic shift in their emission from **5a** by 10 and 21 nm, respectively, whereby the emission of **5c** is characterized by band broadening with loss of vibrational progression. In the overall comparison to parent 2-azapyrene (λ_{em} = 374 nm)[78] all investigated compounds show a bathochromic shift in their emission

maxima ranging from 11 to 125 nm and a minor 5 nm when **5a** is compared with 4,10-diphenylpyrene (λ_{em} = 380 nm).[70]

The 2-azapyrene derivatives show intense fluorescence at 10^{-5} M concentrations in the blue region of the spectra, except for compound **5n** which exhibits blue-greenish emission in CH_2Cl_2. The quantum yields in dichloromethane range from 0.08 to 0.38 and are generally higher for 5,9-substituted 2-azapyenes, indicating a position and substituent depending quenching effect (Table 6).

Table 6. Spectroscopic data of selected 2-azapyrenes in dichloromethane (c = 10^{-5} M) at 20°C.

	5a	**5b**	**5c**	**5d**	**5g**	**5j**	**5m**	**5n**	**5o**
$\lambda_{1,abs}$ [nm]	228	230	229	229	229	228	234	240	229
log $\varepsilon_{\lambda1}$	4.52	4.51	4.48	4.42	4.52	4.56	4.67	4,70	4.55
$\lambda_{2,abs}$ [nm]	246	252	264	243	245	245	278	271	245
log $\varepsilon_{\lambda2}$	4.53	4.64	4.69	4.43	4.40	4.60	4.29	4,70	4.45
$\lambda_{3,abs}$ [nm]	280	288	302	274	280	280	306	317	279
log $\varepsilon_{\lambda3}$	4.36	4.43	4.45	4.21	4.23	4.44	4.13	4.36	4.27
$\lambda_{4,abs}$ [nm]	332	333	335	331	333	331	332	361	334
log $\varepsilon_{\lambda4}$	4.24	4.28	4.25	4.10	4.13	4.30	4.17	4.39	4.17
$\lambda_{5,abs}$ [nm]	346	348	350	345	347	345	348		348
log $\varepsilon_{\lambda5}$	4.34	4.39	4.34	4.20	4.22	4.40	4.25		4.26
$\lambda_{6,abs}$ [nm]	382	381		369	383	381	383		383
log $\varepsilon_{\lambda6}$	3.75	3.63		3.60	3.65	3.81	3.69		3.62
$\lambda_{7,abs}$ [nm]				389					
log $\varepsilon_{\lambda7}$				3.75					
$\lambda_{1,em}^{350}$ [nm]	385	385	389[b]	395	387	385	389	499	388
$\lambda_{2,em}^{350}$ [nm]	406	405	406	417	407	406	410		408
$\lambda_{3,em}^{350}$ [nm]	427[b]	427[b]	426[b]	440[b]	428[b]	429[b]	434[b]		432[b]
ϕ[a]	0.34	0.31	0.08	0.23	0.38	0.31	0.36	0.33	0.15

[a] Fluorescence standard: quinine hemi sulfate salt monohydrate in 0.05 M H_2SO_4 (ϕ = 0.52).[79] [b] Indicates shoulder.

To investigate the nature of transitions from the ground to excited states, solvatochromic studies were performed for **5b** and **5n**. As shown in Figure 3, the spectral features of **5b** are only weakly affected by the solvent polarity, indicating a strong stabilization of the ground state and a low dipole moment in the excited state, which is consistent with a $\pi \rightarrow \pi^*$ transition without ICT character. Furthermore, no obvious hydrogen-bonding effects in ethanol were detected. In contrast, the small solvatochromism in the absorption spectra of **5n** and the pronounced blue shift of 87 nm in the emission spectra with decreasing polarity from dichloromethane (λ_{em} = 499 nm) to cyclohexane (λ_{em} = 412 nm) indicates a highly polarized excited state with a large dipole moment, which further supports ICT characteristic during excitation. As apparent from the simulated spectra of **5n**, the general trends observed in the experimental absorption spectrum are somewhat reproduced even though the predicted spectrum is generally underestimated particularly in the lowest absorption area. However, the λ_{max} of the lowest absorption band falls into the intersection point of the experimental absorption and emission spectra,

thus the predicted S_1 vertical excitation energy is in accord to the experimentally determined optical gap value (Table 7). On the other hand, the calculated emission wavelength of 496 nm very well reproduces the experimental value of 499 nm (Table 6 and Table S24).

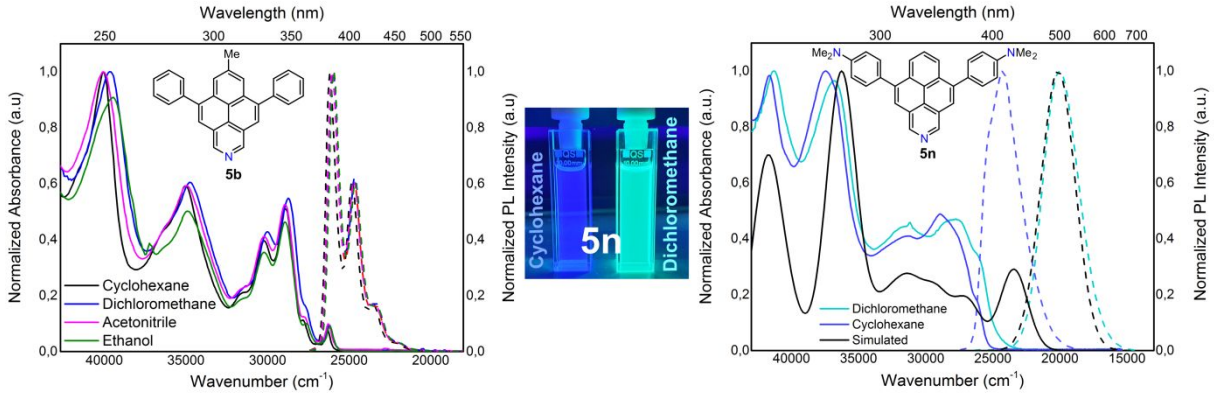


Figure 3. UV-Vis (solid lines) and emission (dashed lines, λ_{ex} = 350 nm) spectra of **5b** (left) and **5n** (right) (c = 10^{-5} M) at 20°C. Picture (middle): Emission color of **5n** in cyclohexane (left) and CH_2Cl_2 (right) solution subjected to ultraviolet (UV) irradiation at 366 nm. Normalized absorption and emission spectra of **5n** simulated at the B3LYP/6-31+G(p) level of theory within IEFPCM of dichloromethane, Half-Width at Half Height = 1200 cm^{-1}.

Next, the electrochemical properties of **5a** and **5n** were characterized by cyclic voltammetry (CV) in terms of their oxidation behavior (Figure 4). The voltammogram of compound **5a** shows two distinct oxidation peaks, while the CV of **5n** displays two broad oxidation events. Furthermore, **5a** shows three oxidation potentials in acetonitrile (Figure S1). The CV scans of both compounds exhibit irreversible oxidation waves, which was also observed for diazapyrenes.[27] The first oxidation onset potential of **5n** (0.26 V vs. Fc/Fc^+) is three times lower than that of **5a** (0.82 V vs. Fc/Fc^+), reflecting an easier oxidation by installing strong donor *N,N*-dimethylaniline units. Both voltammograms consist of a small reduction peak for **5a** (-1.28 V vs. Fc/Fc^+) and for **5n** (-1.23 V vs. Fc/Fc^+). Assuming that the HOMO level of ferrocene[80] is 4.80 eV below the vacuum level, the calculated HOMO-LUMO values (Table 7) of **5a** and **5n** show close LUMO levels, but a much higher HOMO level for **5n**. Hence, a smaller HOMO-LUMO gap is estimated for **5n** (3.39 eV) as compared to **5a** (3.83 eV).

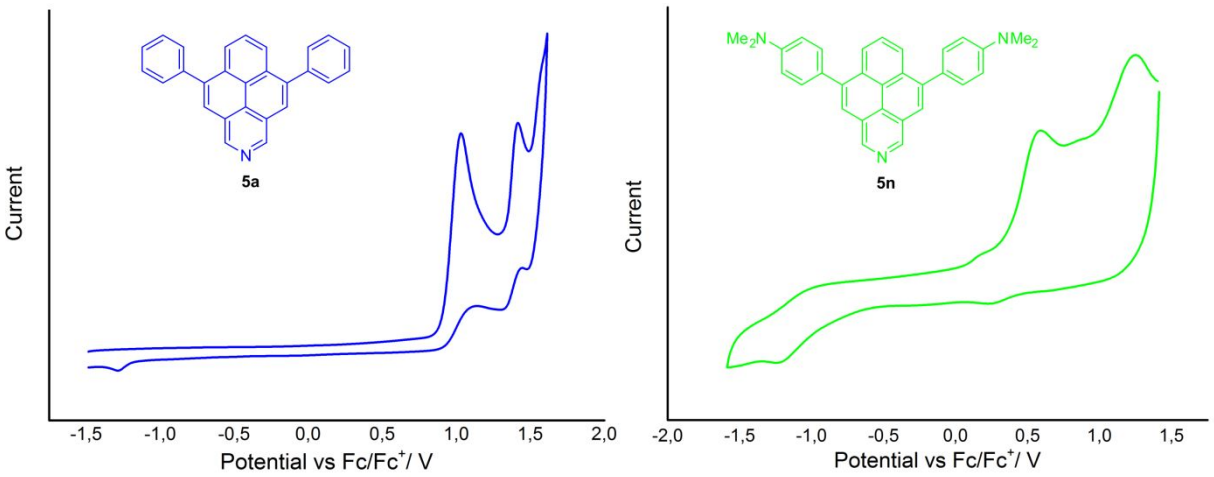


Figure 4. Cyclic voltammograms of **5a** (left) and **5n** (right) measured in CH_2Cl_2 with 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte, glassy carbon working electrode, ANE2 as reference electrode and Pt counter-electrode with ferrocene as standard at a scan rate of 100 mV s^{-1}.

To get deeper insight into the electronic structures and transition characters, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were carried out. Calculations were performed with Gaussian09[81] using the B3LYP and CAM-B3LYP functionals in combination with the 6-31G(p) basis set and a polarizable continuum model (PCM) of dichloromethane using the integral equation formalism variant (IEFPCM) to include solvent effects.

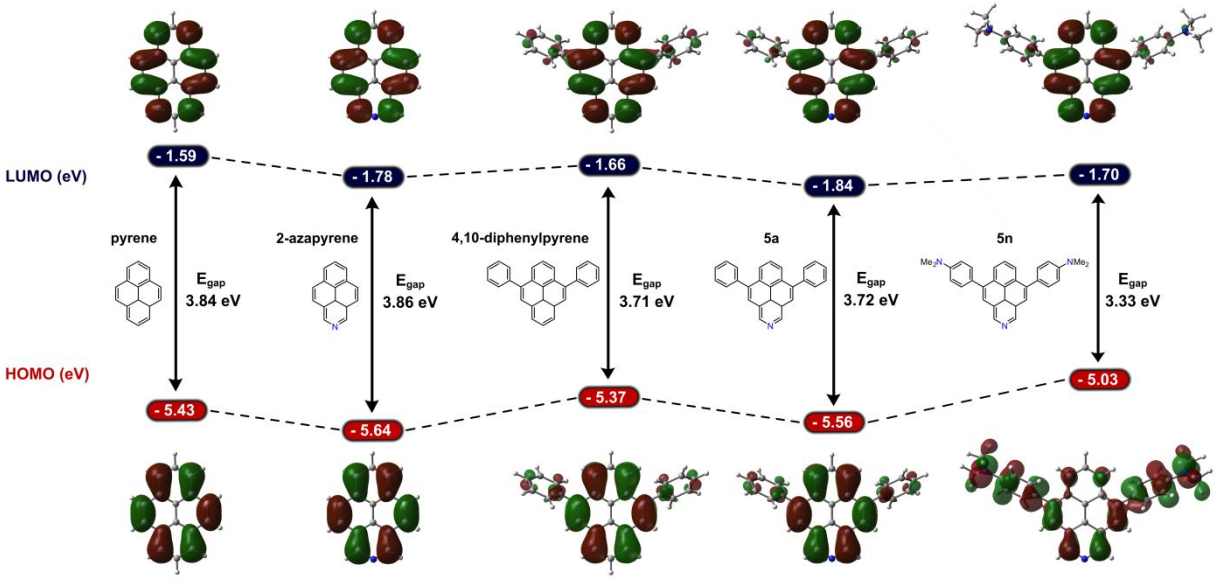


Figure 5. Calculated frontier molecular orbitals and energy levels at the B3LYP/6-31G(p) level of theory within IEFPCM of dichloromethane (isovalue = 0.02 a.u.).

As visualized in Figure 5, the HOMO and LUMO of **5a** are mainly located on the 2-azapyrene frame, while the LUMO of **5n** primarily resides on the core structure and the HOMO is distributed over the outside edges of the 2-azapyrene skeleton with a large proportion on the *N*,*N*-dimethylaniline units, which is similarly predicted for methoxy-containing **5m** (Figure S4). The calculated HOMO and LUMO energy levels of **5a** and **5n** are in very good agreement with the CV data confirming the experimental results (Table 7). Compared to the parent 2-azapyrene, compound **5a** shows only slightly higher HOMO and lower LUMO levels, but significantly lower HOMO and LUMO levels as compared to pyrene and 4,10-diphenylpyrene. This exemplifies that the incorporation of nitrogen in position 2 significantly stabilizes both the HOMO and LUMO levels in pyrene, although to less extent than multiple doped azapyrenes.[42,63] Strong π-donor groups on the phenyl fragments located at the 5,9-position significantly lower the HOMO-LUMO gap. Additional terminal groups at position 7 located at the 2-azapyrene core have only a minor effect on the frontier orbitals and, thus, on the HOMO-LUMO energy gap, due to the nodal plane stated before (Figure S4 and Figure S5). However, as compared to **5a**, bearing in mind that the $S_1 \leftarrow S_0$ transition involves HOMO-1 → LUMO and HOMO → LUMO+1, the non-zero contributed HOMO-1 and LUMO+1 levels of donor OMe-substituted **5c** are destabilized

by 0.38 and 0.15 eV, respectively raising the HOMO-1 orbital energy above that of **5a**, whereas the HOMO and LUMO energy levels remain unaffected. On the other hand, the LUMO+1 and LUMO levels of acceptor CF_3-substituted 2-azapyrene **5d** are stabilized by 0.34 and 0.17 eV respectively, consequently switching the energetic order of these two orbitals with that of **5a**, which is consistent with the observed trend in the experimental absorption and emission spectra.

The first excited state S_1 (L_b) of pyrene is a result of a strongly coupling configuration interaction of HOMO-1 → LUMO and HOMO → LUMO+1 processing the same symmetry, so that the S_1 state is one of the mixed states with symmetric linear combination which in turn lower the energy in this state compared to the state involving HOMO → LUMO excitation S_2 (L_a).[82,83] Similar situation arise in lower symmetry (C_{2v}) classified 2-azapyrene[68,84] (Pyrene: D_{2h} symmetry), which is specified by the obtained TD-DFT results. In accordance to pyrene, the order of excited states in 2-azapyrene is more accurately predicted using the range-separated CAM-B3LYP functional rather than B3LYP.[69] Hence, the $S_1 \leftarrow S_0$ transition with a low oscillator strength (f = 0.0250) derived from HOMO-1 → LUMO and HOMO → LUMO+1 with a dominant proportion of the latter. This, thus, differs from the equal mix in pyrene, while the $S_2 \leftarrow S_0$ excitation with a high oscillator strength (f = 0.3504) is derived from HOMO → LUMO with some admixture of HOMO-1 → LUMO+1 (Table S5). Both $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions predicted to be strongly influenced by the substitution pattern at the 5,9 and 7-position. Electron withdrawing groups located at the phenyl groups or directly attached at the 7-position of the 2-azapyrene core retain the order of excited states, while donor groups reverse the order. Their lowest energy excitations with a high oscillator strength in both B3YLP and CAM-B3YLP mainly derive from HOMO → LUMO, while the weak $S_2 \leftarrow S_0$ transitions originate from the configuration interaction of HOMO-1 → LUMO and HOMO → LUMO+1. In contrast, the first excitation of **5n** using the B3LYP functional is described by a pure HOMO-1 → LUMO transition and the $S_2 \leftarrow S_0$ transition primarily arises from HOMO → LUMO. For CAM-B3LYP, the order of the first and second excited states of **5n** is reversed (Table S20 and S21). Thus, the B3LYP functional provides a better overall agreement with the experimental data of the investigated compounds, but a more accurate ordering of excited states is obtained using the CAM-B3LYP functional. Consequently, the $S_1 \leftarrow S_0$ transition of **5n** is dominated by HOMO → LUMO in order that the S_1 state of **5n** is featured by efficient ICT from the *N,N*-dimethylaniline side groups to the 2-azapyrene moiety, supported by the DFT calculated dipole moments for the S_0 ground-state μ_{gs} = 6.90 D and S_1 excited-state μ_{es} = 25.78 D. These results explain the observed variation in the absorption and emission spectra and verify that the represented spectral red shift of **5n** is derived from the conversion of π→π* to ICT transitions.

Table 7. Optical, electrochemical and theoretical data for compounds **5a** and **5n**.

	UV/Vis - Fluorescence	**Cyclic Voltammetry**		**DFT**		**TD-DFT (B3LYP)**
Structure	$E_g^{opt.}$ [eV][a]	HOMO[cv] [eV][b]	LUMO[cv] [eV][c]	HOMO [eV][d]	LUMO [eV][d]	ΔE [eV][e]
5a	3.30	-5.62	-1.79	-5.56	-1.84	3.46 (0.3886)
5n	2.92	-5.09	-1.70	-5.03	-1.70	2.92 (0.1420)

[a] Estimated from the intersection of normalized absorption and emission spectra. [b] Calculated using the equation: E(HOMO) = -e[E_{Ox}^{onset} vs. Fc/Fc^{+})+4.80]. [c] Estimated using correction factor: E(LUMO) = 1.16E_g^{opt} - E(HOMO)^{cv}.[85] [d] Calculated DFT energy levels at the B3LYP/6-31G(p) level of theory within IEFPCM. [e] Calculated TD-DFT excitation energies (ΔE) at the B3LYP/6-31+G(p) level of theory within IEFPCM (considering the reverse order of excited states), oscillator strength (*f*) in parenthesis.

Finally, nucleus independent chemical shift (NICS) as a magnetic criteria of aromaticity[86,87] were performed on B3LYP/6-31G(p) optimized gas phase structures at the GIAO-B3LYP/6-311+G(p) level of theory. The $NICS_{\pi,zz}$ values were obtained employing the σ-only model[88] and the respective NICS-XY-scans[89,90] are presented in Figure 6.

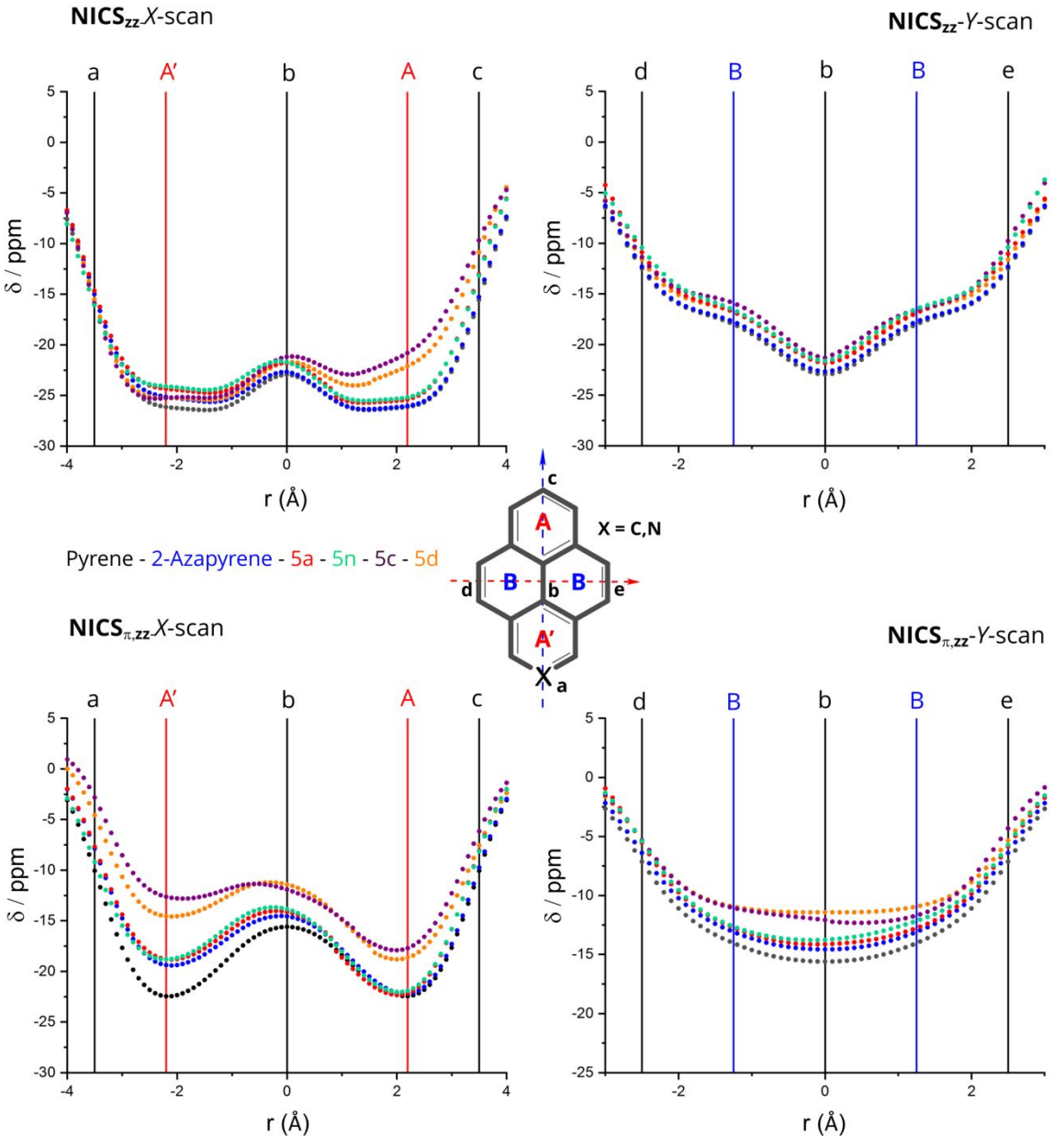


Figure 6. NICS-XY-scans. X-Scans (left). Y-Scans (right). Black letters indicate atoms and center of bonds. Red

and blue capital letters indicate center of rings. Blue dashed arrow – X-scan trajectory direction. Red dashed arrow – *Y*-scan trajectory direction. All scans were performed at a height of 1.7 Å.

As discussed in detail by Gershoni-Poranne and Stanger[88], pyrene can be characterized by a global ring current enclosing the naphthalene and biphenyl unit, and two local diatropic ring currents within the respective A rings. The resulting current density is inhomogeneous at the perimeter in such, increased density arise across the edges of the A rings, were the local currents sum up to the global component. Aza replacement decreases the local current in the A' ring, which result in a small effect on the global component but induce insignificant alterations on the local benzenic current in the opposite A ring. Substituents in 5,9 position have a negligible effect on the overall tropicity picture compared to 2-azapyrene, whereas CF_3-acceptor and OMe-donor groups in position 7 at the 2-azapyrene core significantly decrease the currents in both local and global components with a greater strength in the A' ring of the pyridine unit and the minimum of the induced magnetic field, which is centrally located at the long axis in pyrene (maximum in the X-scan trajectory direction), is shifted from the geometric center.

Conclusion

In summary, a Brønsted acid mediated benzannulation was developed and used to produce a series of hithero unreported 2-azapyrenes and benzo[*f*]isoquinolines in up to excellent yields. Theoretical and experimental investigations verify, that the incorporation of nitrogen in position 2 significantly stabilizes both the HOMO and LUMO levels of pyrene, whereby the terminal functional groups and their respective position at the 2-azapyrene framework play a crucial role for the modulation of the photophysical and electrochemical properties, and thus for adjusting the HOMO-LUMO gap. Introduction of strong donor *N,N*,-dimethylaniline side groups in 5,9 position lead to tunable emission from blue to blue-greenish color which is attributed to the conversion of π→π* to ICT transitions, as validated by solvatochromism and DFT/TD-DFT studies. Furthermore, in comparison to 4,10-diazapyrene (ϕ = 0.11), 1,4,10-triazapyrene (ϕ = 0.092) and 2,4,10-triazapyrene (ϕ = 0.12), bearing the same terminal groups in 5,9 position,[63] 2-azapyrene **5g** shows an up to four times higher quantum yield (ϕ = 0.38). These results provide new information about the effect of functionalized nitrogen doped pyrenes.

EXPERIMENTAL SECTION

General Information

The nuclear magnetic resonance spectra ($^1H/^{13}C/^{19}F$ NMR) were recorded on a Bruker AVANCE 300 III, 250 II or 500. The analyzed chemical shifts δ are referenced to residual solvents signals of the deuterated solvents $CDCl_3$ (δ = 7.26 ppm/77.0 ppm), or TFA-d (δ = 11.50 ppm/164.2 ppm). Multiplicities due to spin-spin correlation are reported as follows: s = singlet, d = doublet, dd = double

doublet, t = triplet, pt = pseudo triplet, m = multiplet and further described through their coupling constants J. Infrared spectra (IR) were measured as attenuated total reflection (ATR) experiments with a Nicolet 380 FT-IR spectrometer. The signals have been characterized through their wave numbers ṽ and their corresponding absorption as very strong (vs), strong (s), medium (m), weak (w) or very weak (vw). UV/VIS spectra were recorded on a Cary 60 UV-VIS spectrophotometer and emission spectra with an Agilent Cary Eclipse Fluorescence spectrophotometer. Cyclovoltammetry (CV) was measured in CH_2Cl_2 and MeCN with 0.1M Bu_4NPF_6 as supporting electrolyte, glassy carbon working electrode, ANE2 (Ag/AgNO3 0.01M in MeCN) as reference electrode and Pt counter electrode with ferrocene as external standard (1 mM in MeCN). The potential is given vs. Fc/Fc^+. The potentiostat used was an AMETEK PARSTAT 4000. Basic and high resolution mass spectra (MS/HRMS) were measured on instruments which are paired with a preceding gas chromatograph (GC) or liquid chromatograph (LC). The samples have been ionized through electron impact ionization (EI) on an Agilent 6890/5973 or Agilent 7890/5977 GC-MS equipped with a HP-5 capillary column using helium carrier gas or by applying electron spray ionization (ESI) on an Agilent 1200/6210 Time-of-Flight (TOF) LC-MS. Melting points (mp) were determined by a Micro-Hot-Stage GalenTM III Cambridge Instruments and are not corrected.

Materials

The applied solvents Acetonitrile, 1,4-Dioxane, Xylene and Dichloromethane were obtained as dry solvents through commercial sources and employed without further purification. Solvents for extraction and column chromatography were available after previous distillation. Other reagents, catalysts, ligands, acids and bases have been utilized in purchased purity. Column chromatography was performed using Merck Silica gel 60 (particle size 63–200 µm).

3,5-dibromo-4-chloropyridine (1)

A mixture of Pyridin-4(1*H*)-one (5.14 g, 54 mmol) and KOH (6.08 g, 108 mmol) dissolved in 100 ml distilled water was cooled to 0 °C. Then, bromine (17.3 g, 108 mmol) was added dropwise and the resulting mixture was stirred for 30 min., filtered, washed with distilled water and dried in vacuo. The residue was dissolved in 50 ml $POCl_3$ (82.92 g, 54 mmol) and stirred under reflux (oil bath) for 12h. The yellow solution was quenched with ice, neutralized with K_2CO_3 and extracted with dichloromethane (3 times). The organic phase was dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (hepatan/EtOAc = 10/1) to obtain **1** as a colorless solid (11.23 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 150.8 (CH), 144.1 (C), 121.8 (C).

General procedure (A) for the synthesis of 3,5-bis(alkynyl)-4-chloropyridines (2a-h)

A pressure tube charged with 100 mg **1** (1 eq., 0.37 mmol), CuI (0.05 eq., 3.5 mg) and $Pd(PPh_3)_4$ (0.05 eq., 21.3 mg) was evacuated and backfilled with argon for 3 times. Then, degased diisopropylamine (1 ml) and dry acetonitrile (2 ml) were added followed by 2.2 eq. (2.6 eq. for **2f**) of the respective alkyne (alkynes that were solids at room temperature were added with **1**, CuI and

catalyst). The pressure tube was sealed with a teflon cap and stirred in a stainless steel heating block at 50 °C for 24h. After cooling to room temperature, the reaction mixture was quenched with distilled water and extracted with ethyl acetate (3 times). The organic phase was dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (heptane/ethyl acetate) to obtain the desired alkynylated products **2a-h**.

General procedure (B) for the synthesis of 4-aryl-3,5-bis(alkynyl)pyridines (3a-t)

A pressure tube charged with **2a-h** (100 mg, 1 eq.), K_3PO_4 (2 eq.), $Pd(PPh_3)_4$ (0.05 eq.) and the respective boronic acid (2.0 eq.) was evacuated and backfilled with argon for 3 times. Then, dry 1,4-dioxane (3 ml) was added and the pressure tube was sealed with a teflon cap. The reaction mixture was stirred in a stainless steel heating block at 90 °C for 24h. After cooling to room temperature, the reaction was quenched with distilled water and extracted with ethyl acetate (3 times). The organic phase was dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (heptane/ethyl acetate) to obtain precursors **3a-t**.

General procedure (C) for the synthesis of 1-alkynyl-6-arylbenzo[*f*]isoquinolines (4a-k)

A pressure tube charged with 100mg (1 eq.) of the respective 4-aryl-3,5-bis(alkynyl)pyridine dissolved in 3 ml Xylene was treated with 30 eq. MsOH. The pressure tube was sealed with a teflon cap and stirred at room temperature for 1h, 10 min (**3d**), 5min (**3h**) or in a stainless steel heating block at 90 °C for 2 h (**3o,p**). The reaction mixture was neutralized with a saturated aqueous solution of $NaHCO_3$ and extracted with ethyl acetate (3 times). The organic phase was dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (heptane/ethyl acetate) to obtain compounds **4a-k**.

General procedure (D) for the synthesis of 5,9-diaryl-naphtho[2,1,8-*def*]isoquinolines (5a-o)

If not otherwise stated, a pressure tube is charged with 100mg (1.0 eq.) of the respective 4-aryl-3,5-bis(alkynyl)pyridine and treated with 60 eq. MsOH. The pressure tube was sealed with a teflon cap and stirred in a stainless steel heating block at 120 °C for 12h or 24h (**3d,h**). After cooling to room temperature, the reaction was neutralized with a saturated aqueous solution of $NaHCO_3$ and extracted with ethyl acetate (3 times). The organic phase was dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (heptane/ethyl acetate) to obtain compounds **5a-o**.

Gram-scale procedure for the synthesis of 7-methyl-5,9-diphenylnaphtho[2,1,8-*def*]isoquinoline (5b)

A 100 ml round bottom flask charged with 1g of **3b** (1 eq., 2.7 mmol) was treated with 60 eq. MsOH. The reaction mixture was placed in an oil bath and stirred at 120 °C for 12h. After cooling to room temperature, the reaction was neutralized with a saturated aqueous solution of $NaHCO_3$ and extracted with ethyl acetate (3 times). The organic phase was dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (heptane/EtOAc = 1/1) to obtain compound **5b** in 87% yield (0.874 g).

Analytical Data

4-chloro-3,5-bis(phenylethynyl)pyridine (2a)

According to general procedure A, title compound **2a** was obtained as a colorless solid in 81% yield (95.6 mg) (heptane/EtOAc = 10/1); mp 110–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 2H), 7.59–7.63 (m, 4H), 7.37–7.43 (m, 6H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 150.7, 146.4, 131.9, 129.4, 128.5, 121.9, 121.1, 98.3, 82.5. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 729 (s), 754 (vs), 896 (m), 911 (m), 966 (m), 1026 (m), 1072 (m), 1201 (m), 1311 (m), 1420 (m), 1490 (s), 1556 (m), 1597 (m), 2211 (m), 3048 (w). MS (EI, 70 eV): m/z (%) = 315 (M^+, 34), 314 (23), 313 (M^+, 100), 277 (10), 250 (29), 249 (10), 248 (14), 157 (16), 150 (7), 126 (21), 125 (28), 77 (13). HRMS (EI) m/z: [M^+] Calcd for $C_{21}H_{12}ClN$ 313.0653; Found 313.0652, [M^+] Calcd for $C_{21}H_{12}{}^{37}ClN$ 315.0623; Found 315.0623.

4-chloro-3,5-bis(*p*-tolylethynyl)pyridine (2b)

According to general procedure A, title compound **2b** was obtained as a colorless solid in 87% yield (109.5 mg) (heptane/EtOAc = 10/1); mp 135–137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 2H), 7.49 (d, J = 8.0 Hz, 4H), 7.20 (d, J = 7.9 Hz, 4H), 2.39 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 150,7, 145,9, 139,7, 131,8, 129,2, 121,1, 118,9, 98,4, 82,1, 21,6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 705 (m), 729 (m), 773 (m), 818 (vs), 888 (m), 1181 (w), 1403 (m), 1418 (m), 1508 (m), 1556 (m), 1605 (w), 2211 (m), 2920 (w), 2978 (vw), 3031 (w). MS (EI, 70 eV): m/z (%) = 344 (8), 343 (M^+, 34), 342 (29), 341 (M^+, 100), 170 (22), 139 (16), 138 (11), 115 (17), 39 (15). HRMS (EI) m/z: [M^+] Calcd for $C_{23}H_{16}ClN$ 341.0966; Found 341.0962, [M^+] Calcd for $C_{23}H_{16}{}^{37}ClN$ 343.0936; Found 343.0939.

4-chloro-3,5-bis(*m*-tolylethynyl)pyridine (2c)

According to general procedure A, title compound **2c** was obtained as a colorless solid in 80% yield (100.6 mg) (heptane/EtOAc = 10/1); mp 114–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 2H), 7.40–7.44 (m, 4H), 7.28 (pt, J = 7.6 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 2.38 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 151.4, 145.7, 138.2, 132.4, 130.2, 129.0, 128.4, 121.9, 120.9, 98.1, 82.4, 21.2. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 713 (m), 771 (m), 795 (vs), 890 (m), 1086 (w), 1208 (w), 1337 (w), 1401 (m), 1428 (m), 1482 (m), 1599 (w), 2217 (m), 2918 (w). MS (EI, 70 eV): m/z (%) = 344 (8), 343 (M^+, 35), 342 (26), 341 (M^+, 100), 276 (11), 263 (11), 170 (14), 139 (19), 138 (11), 115 (17), 39 (11). HRMS (EI) m/z: [M^+] Calcd for $C_{23}H_{16}ClN$ 341.0966; Found 341.0963, [M^+] Calcd for $C_{23}H_{16}{}^{37}ClN$ 343.0940; Found 343.0940.

4-chloro-3,5-bis((4-fluorophenyl)ethynyl)pyridine (2d)

According to general procedure A, title compound **2d** was obtained as a colorless solid in 74% yield (95.2 mg) (heptane/EtOAc = 8/1); mp 141–142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 2H), 7.59 (dd, J = 8.6 Hz, J = 5.4 Hz, 4H), 7.09 (pt, J = 8.6 Hz, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 163.2 (J = 251.7 Hz), 150.8, 146.1, 133.9 (J = 8.8 Hz), 120.9, 118.0 (J = 3.6 Hz), 115.9 (J = 22.2 Hz), 97.2,

82.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.8. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 703 (m), 781 (m), 830 (vs), 1014 (w), 1090 (m), 1137 (m), 1154 (s), 1216 (s), 1401 (m), 1424 (m), 1504 (vs), 1558 (m), 1599 (m), 1888 (w), 2219 (m). MS (EI, 70 eV): m/z (%) = 352 (6), 351 (M^+, 34), 350 (23), 349 (M^+, 100), 286 (22), 174 (13), 144 (22), 143 (20), 75 (10), 57 (12). HRMS (EI) m/z: [M^+] Calcd for $C_{21}H_{10}ClF_2N$ 349.0464; Found 349.0462, [M^+] Calcd for $C_{21}H_{10}{}^{37}ClF_2N$ 351.0435; Found 351.0443.

4-chloro-3,5-bis((4-(trifluoromethyl)phenyl)ethynyl)pyridine (2e)

According to general procedure A, title compound **2e** was obtained as a yellow solid in 75% yield (123.7 mg) (heptane/EtOAc = 8/1); mp 175–177 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.70 (s, 2H), 7.71 (d, *J* = 8.5 Hz, 4H), 7.65 (d, *J* = 8.5 Hz, 4H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 151.8, 146.5, 132.2, 131.1 (*J* = 32.4 Hz), 125.7, 125.5 (*J* = 3.8 Hz), 123.7 (*J* = 272.5 Hz), 120.5, 96.5, 84.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.0. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 723 (s), 767 (m), 837 (vs), 898 (m), 1016 (s), 1063 (vs), 1107 (vs), 1156 (s), 1319 (vs), 1403 (m), 1426 (m), 1545 (w), 1613 (m), 1729 (w), 1797 (vw), 1921 (w), 2221 (w), 2854 (w), 2924 (w), 3066 (w). MS (EI, 70 eV): m/z (%) = 452 (8), 451 (M^+, 35), 450 (25), 449 (M^+, 100), 430 (10), 318 (13), 224 (12), 193 (10). HRMS (EI) m/z: [M^+] Calcd for $C_{23}H_{10}ClF_6N$ 449.0400; Found 449.0406, [M^+] Calcd for $C_{23}H_{10}{}^{37}ClF_6N$ 451.0371; Found 451.0383.

4-chloro-3,5-bis((4-methoxyphenyl)ethynyl)pyridine (2f)

According to general procedure A, but utilizing 2.6 eq. of 4-ethynylanisole gave title compound **2f** as a yellow solid in 88% yield (121.6 mg) (heptane/EtOAc = 3/1); mp 121°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.60 (s, 2H), 7.49–7.57 (m, 4H), 6.85–6.95 (m, 4H), 3.84 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 160.4, 151.0, 145.2, 133.4, 121.0, 114.2, 114.1, 98.0, 81.8, 55.3. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 773 (s), 830 (vs), 884 (m), 1018 (s), 1107 (m), 1168 (s), 1247 (s), 1290 (m), 1422 (m), 1506 (s), 1556 (m), 1601 (m), 2209 (m), 2840 (w), 2936 (w). MS (EI, 70 eV): m/z (%) = 376 (10), 375 (M^+, 34), 374 (24), 373 (M^+, 100), 358 (17), 251 (10), 224 (10), 187 (14), 143 (12), 99 (10), 39 (14). HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{23}H_{16}ClNO_2$ 374.0948; Found 374.0947.

4,4'-((4-chloropyridine-3,5-diyl)bis(ethyne-2,1-diyl))bis(*N,N*-dimethylaniline) (2g)

According to general procedure A, title compound **2g** was obtained as a yellow solid in 80% yield (117.6 mg) (heptane/EtOAc = 2/1); mp 209–211°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.55 (s, 2H), 7.47 (d, *J* = 8.8 Hz, 4H), 6.67 (d, *J* = 8.9 Hz, 4H), 3.01 (s, 12H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 150.6, 150.3, 144.4, 133.1, 121.4, 111.7, 108.7, 99.5, 81.4, 40.1. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 750 (m), 810 (vs), 944 (m), 1028 (m), 1224 (s), 1362 (s), 1519 (s), 1556 (m), 1603 (s), 2201 (m), 2802 (m), 2908 (m). MS (EI, 70 eV): m/z (%) = 402 (13), 401 (M^+, 37), 400 (30), 399 (M^+, 100), 398 (37), 382 (13), 281 (12), 207 (12), 200 (24), 199 (15), 191 (10), 125 (11). HRMS (EI) m/z: [M^+] Calcd for $C_{25}H_{22}N_3Cl_1$ 399.1497; Found 399.1488, [M^+] Calcd for $C_{25}H_{22}N_3{}^{37}Cl$ [M^+] 401.1467; Found 401.1470.

4-chloro-3,5-bis(thiophen-3-ylethynyl)pyridine (2h)

According to general procedure A, title compound **2h** was obtained as a colorless solid in 78% yield (94.4 mg) (heptane/EtOAc = 8/1); mp 105–107 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.61 (s, 2H). 7.65 (dd, J = 3.0 Hz, J = 1.2 Hz, 2H), 7.34 (dd, J = 5.0 Hz, J = 3.0 Hz, 2H), 7.25 (dd, J = 5.0 Hz, J = 1.2 Hz, 2H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 150.8, 145.9, 130.4, 129.8, 125.8, 121.1, 93.4, 82.2. (Signal of one quaternary carbon is absent, which may relate to signal overlap.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 762 (s), 775 (vs), 806 (s), 863 (m), 894 (m), 999 (m), 1084 (m), 1131 (w), 1173 (w), 1214 (m), 1290 (m), 1356 (m), 1395 (m), 1430 (w), 1562 (w), 1752 (w), 1834 (vw), 2213 (m), 3062 (m). MS (EI, 70 eV): m/z (%) = 328 (8), 327 (M$^+$, 43), 326 (20), 325 (M$^+$, 100), 219 (11), 162 (13), 132 (12), 93 (10), 69 (15), 58 (16), 45 (57). HRMS (EI) m/z: [M$^+$] Calcd for $C_{17}H_8ClNS_2$ 324.9781; Found 324.9775, [M$^+$] Calcd for $C_{17}H_8{}^{37}ClNS_2$ 326.9752; Found 326.9744.

4-phenyl-3,5-bis(phenylethynyl)pyridine (3a)

According to general procedure B, title compound **3a** was obtained as a yellow solid in 75% yield (84.8 mg) (heptane/EtOAc = 10/1); mp 138–140 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.76 (s, 2H), 7.66–7.72 (m, 2H), 7.47–7.57 (m, 3H), 7.24–7.33 (m, 10H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 152.4, 151.0, 136.1, 131.5, 129.7, 128.9, 128.8, 128.3, 127.7, 122.4, 119.6, 95.8, 85.3. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 750 (vs), 787 (m), 903 (m), 915 (m), 1026 (w), 1133 (m), 1306 (w), 1401 (m), 1440 (m), 1488 (m), 1597 (w), 2213 (w), 3000 (w), 3048 (w), 3079 (w). MS (EI, 70 eV): m/z (%) = 356 (26), 355 (M$^+$, 100), 354 (98), 352 (24), 326 (21), 278 (27), 277 (23), 176 (26), 162 (21), 77 (51), 51 (25). HRMS (EI) m/z: [M$^+$] Calcd for $C_{27}H_{17}N$ 355.1356; Found 355.1346.

3,5-bis(phenylethynyl)-4-(*p*-tolyl)pyridine (3b)

According to general procedure B, compound **3b** was obtained as a yellow solid in 85% (100 mg) (heptane/EtOAc = 10/1); mp 94–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, 2H), 7.61–7.66 (m, 2H), 7.27–7.37 (m, 12H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.8, 138.8, 133.1, 131.5, 129.7, 128.7, 128.3, 122.6, 119.3, 95.3, 85.7, 21.5. (Signals of one quaternary and one aromatic carbon are absent, which may relate to signal overlap.) IR (ATM, cm-1): $\tilde{\nu}$ = 750 (vs), 822 (s), 892 (m), 1269 (w), 1399 (m), 1488 (m), 1597 (w), 1725 (w), 2207 (vw), 2852 (w), 2920 (w), 3023 (w). MS (EI, 70 eV): m/z (%) = 370 (27), 369 (M$^+$, 100), 368 (55), 354 (42), 352 (20), 176 (36), 162 (19), 77 (57), 51 (26). HRMS (EI) m/z: [M$^+$] Calcd for $C_{28}H_{19}N$ 369.1512; Found 369.1500.

4-(4-methoxyphenyl)-3,5-bis(phenylethynyl)pyridine (3c)

According to general procedure B, title compound **3c** was obtained as a yellow solid in 62% yield (76.6 mg) (heptane/EtOAc = 8/1); mp 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.28–7.37 (m, 10H), 7.06 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.2, 151.8, 151.1, 131.5, 131.4, 128.8, 128.3, 128.1, 122.5, 119.5, 113.1, 95.6, 85.6, 55.4. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 752 (vs), 808 (m), 832 (m), 1020 (m), 1249 (s), 1294 (m), 1401 (m), 1488 (m),

1513 (m), 1603 (m), 2209 (w), 2840 (w), 2930 (w), 3029 (w), 3054 (w). MS (EI, 70 eV): m/z (%) = 386 (22), 385 (M^+, 100), 384 (29), 354 (29), 342 (24), 341 (33), 340 (35), 338 (15), 77 (27). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{19}NO$ 385.1461; Found 385.1462.

3,5-bis(phenylethynyl)-4-(4-(trifluoromethyl)phenyl)pyridine (3d)

According to general procedure B, title compound **3d** was obtained as a colorless solid in 55% yield (74.4 mg) (heptane/EtOAc = 8/1); mp 117–119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (s, 2H), 7.70–7.74 (m, 4H), 7.20–7.27 (m, 6H), 7.17 (dd, J = 8.0 Hz, J = 1.7 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.7, 150.3, 140.0, 131.4, 130.8 (J = 32.4 Hz), 130.3, 129.0, 128.4, 124.7 (J = 3.7 Hz), 124.1 (J = 272.3 Hz), 122.1, 119.2, 96.3, 84.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 734 (s), 750 (vs), 841 (s), 892 (m), 911 (m), 1026 (s), 1069 (vs), 1107 (vs), 1166 (s), 1325 (s), 1442 (m), 1488 (m), 1554 (w), 2209 (w), 2852 (w), 2924 (w), 3027 (w), 3060 (w). MS (EI, 70 eV): m/z (%) = 424 (29), 423 (M^+, 100), 422 (77), 354 (14), 352 (13), 351 (15), 346 (12), 176 (12), 77 (24). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{16}F_3N$ 423.1229; Found 423.1217.

4-phenyl-3,5-bis(*p*-tolylethynyl)pyridine (3e)

According to general procedure B, title compound **3e** was obtained as a yellow solid in 80% yield (89.7 mg) (heptane/EtOAc = 10/1); mp 119–121 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.64–7.74 (m, 2H), 7.46–7.58 (m, 3H), 7.18 (d, J = 8.2 Hz, 4H), 7.10 (d, J = 8.0 Hz, 4H), 2.34 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 152.2, 150.6, 139.1, 136.1, 131.4, 129.8, 129.1, 128.9, 127.6, 119.9, 119.3, 96.1, 84.8, 21.5. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 701 (s), 742 (vs), 812 (vs), 890 (m), 1020 (m), 1183 (m), 1304 (m), 1440 (m), 1504 (m), 1537 (m), 1554 (m), 1601 (w), 1644 (w), 1824 (w), 2211 (m), 2862 (w), 2916 (w), 3025 (m). MS (EI, 70 eV): m/z (%) = 384 (32), 383 (M^+, 100), 382 (53), 368 (36), 290 (13), 277 (12), 183 (31), 176 (28), 91 (27), 65 (23). HRMS (EI) m/z: [M^+] Calcd for $C_{29}H_{21}N$ 383.1669; Found 383.1665.

4-(*p*-tolyl)-3,5-bis(*p*-tolylethynyl)pyridine (3f)

According to general procedure B, title compound **3f** was obtained as a yellow solid in 79% yield (91.2 mg) (heptane/EtOAc = 10/1); mp 155–157 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 8.2 Hz, 4H), 7.11 (d, J = 8.0 Hz, 4H), 2.47 (s, 3H), 2.35 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 151.8, 150.8, 139.0, 138.8, 133.1, 131.4, 129.7, 129.1, 128.3, 119.8, 119.5, 95.8, 85.1, 21.5, 21.4. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 760 (s), 810 (vs), 888 (m), 1020 (w), 1177 (w), 1399 (w), 1440 (m), 1508 (m), 1535 (w), 1554 (w), 1607 (w), 2209 (w), 2858 (w), 2914 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 398 (28), 397 (M^+, 100), 396 (38), 383 (13), 382 (48), 290 (13), 182 (36), 176 (36), 91 (27), 65 (22). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{23}N$ 397.1825; Found 397.1817.

4-(4-methoxyphenyl)-3,5-bis(*p*-tolylethynyl)pyridine (3g)

According to general procedure B, title compound **3g** was obtained as a yellow solid in 64% yield (77.8 mg) (heptane/EtOAc = 8/1); mp 133–136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.1 Hz, 4H), 7.12 (d, J = 7.9 Hz, 4H), 7.04 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 2.35 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 160.0, 151.5, 150.9, 138.9, 131.4, 129.1, 128.5, 119.6, 113.0, 95.5, 85.4, 55.3, 21.5. (Signals of one quaternary and one aromatic carbon are absent, which may relate to signal overlap.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 767 (s), 806 (vs), 820 (s), 892 (m), 1022 (s), 1039 (s), 1135 (m), 1177 (s), 1253 (s), 1294 (m), 1399 (m), 1440 (s), 1506 (s), 1607 (m), 1892 (w), 2211 (w), 2833 (w), 2918 (w), 3027 (w). MS (EI, 70 eV): m/z (%) = 414 (30), 413 (M$^+$, 100), 412 (24), 398 (14), 382 (15), 191 (15), 183 (30), 177 (23), 176 (24), 91 (20). HRMS (EI) m/z: [M$^+$] Calcd for $C_{30}H_{23}NO$ 413.1774; Found 413.1762.

3,5-bis(*p*-tolylethynyl)-4-(4-(trifluoromethyl)phenyl)pyridine (3h)

According to general procedure B, title compound **3h** was obtained as a colorless solid in 55% yield (72.1 mg) (heptane/EtOAc = 8/1); mp 174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 2H), 7.75–7.81 (m, 4H), 7.14 (d, J = 8.2 Hz, 4H), 7.11 (d, ^3J = 8.1 Hz, 4H), 2.35 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.4, 150.0, 140.1, 139.3, 131.3, 130.8 (q, J = 32.4 Hz), 130.3, 129.2, 124.7 (q, J = 3.7 Hz), 124.1 (q, J = 272.2 Hz), 119.4, 119.1, 96.5, 84.3, 21.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 721 (m), 769 (m), 816 (vs), 841 (m), 892 (m), 1026 (m), 1069 (vs), 1117 (vs), 1325 (vs), 1401 (m), 1442 (w), 1506 (m), 1605 (w), 2209 (w), 2920 (w), 3029 (w). MS (EI, 70 eV): m/z (%) = 452 (32), 451 (M$^+$, 100), 450 (32), 436 (13), 382 (13), 365 (12), 91 (10). HRMS (EI) m/z: [M$^+$] Calcd for $C_{30}H_{20}F_3N$ 451.1542; Found 451.1536.

4-phenyl-3,5-bis(*m*-tolylethynyl)pyridine (3i)

According to general procedure B, title compound **3i** was obtained as a yellow solid in 63% yield (70.3 mg) (heptane/EtOAc = 10/1); mp 75–78 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.64–7.74 (m, 2H), 7.47–7.58 (m, 3H), 7.06–7.22 (m, 8H), 2.31 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 151.8, 151.6, 138.0, 136.3, 132.0, 129.8, 129.6, 128.7, 128.6, 128.2, 127.6, 122.3, 119.4, 95.7, 85.2, 21.2. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 736 (s), 775 (s), 894 (m), 1041 (w), 1090 (w), 1401 (m), 1442 (m), 1482 (m), 1601 (w), 2207 (w), 2854 (w), 2916 (w), 3023 (w). MS (EI, 70 eV): m/z (%) = 384 (27), 383 (M$^+$, 100), 382 (59), 369 (13), 368 (46), 367 (17), 366 (11), 364 (12), 352 (10), 91 (18). HRMS (EI) m/z: [M$^+$] Calcd for $C_{29}H_{21}N$ 383.1669; Found 383.1658.

4-(*p*-tolyl)-3,5-bis(*m*-tolylethynyl)pyridine (3j)

According to general procedure B, title compound **3j** was obtained as a yellow solid in 64% yield (74.1 mg) (heptane/EtOAc = 10/1); mp 117–119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.16–7.22 (m, 2H), 7.10–7.16 (m, 6H), 2.48 (s, 3H), 2.32 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.8, 151.7, 138.6, 138.0, 133.2, 132.1, 129.8, 129.6, 128.6,

128.3, 128.2, 122.4, 119.4, 95.5, 85.4, 21.5, 21.2. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 762 (s), 787 (vs), 888 (m), 1016 (s), 1090 (s), 1259 (m), 1397 (w), 1445 (w), 1484 (w), 1556 (w), 1599 (w), 2918 (w), 2961 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 398 (29), 397 (M^+, 100), 396 (43), 383 (15), 382 (50), 381 (14), 380 (12), 365 (12), 364 (12), 182 (16), 91 (17). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{23}N$ 397.1825; Found 397.1814.

4-(4-methoxyphenyl)-3,5-bis(*m*-tolylethynyl)pyridine (3k)

According to general procedure B, title compound **3k** was obtained as a yellow solid in 55% yield (66.2 mg) (heptane/EtOAc = 8/1); mp 113–115 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.66–7.75 (m, 2H), 7.10–7.24 (m, 8H), 7.01–7.09 (m, 2H), 3.91 (s, 3H), 2.32 (s, 6H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ 160.0, 151.8, 151.2, 138.0, 132.0, 131.4, 129.6, 128.6, 128.4, 128.2, 122.4, 119.3, 113.0, 95.5, 85.5, 55.3, 21.2. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 777 (vs), 1020 (vs), 1088 (s), 1181 (m), 1253 (s), 1296 (m), 1445 (m), 1515 (m), 1605 (m), 2207 (w), 2918 (w), 2961 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 414 (30), 413 (M^+, 100), 412 (24), 398 (17), 382 (19), 369 (13), 354 (11), 340 (10), 176 (12), 91 (10), 65 (11). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{23}NO$ 413.1774; Found 413.1766.

3,5-bis((4-fluorophenyl)ethynyl)-4-phenylpyridine (3l)

According to general procedure B, title compound **3l** was obtained as a yellow solid in 74% yield (83.0 mg) (heptane/EtOAc = 8/1); mp 105–107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 2H). 7.66 (dd, J = 7.8 Hz, J = 1.6 Hz, 2H), 7.50–7.56 (m, 3H), 7.25 (dd, J = 8.8 Hz, J = 5.4 Hz, 4H), 6.98 (pt, J = 8.7 Hz, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.8 (d, J = 250.9 Hz), 152.4, 150.9, 136.1, 133.5 (d, J = 8.4 Hz), 129.7, 129.0, 127.7, 119.5, 118.5 (d, J = 3.4 Hz), 115.7 (d, J = 22.4 Hz), 94.8, 85.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 736 (s), 828 (vs), 892 (m), 1043 (m), 1090 (m), 1154 (m), 1230 (s), 1403 (m), 1440 (m), 1500 (s), 1537 (m), 1601 (m), 1743 (m), 1885 (w), 2213 (w), 2854 (w), 2914 (w), 2986 (w), 3025 (w), 3054 (w). MS (EI, 70 eV): m/z (%) = 392 (27), 391 (M^+, 100), 390 (74), 389 (22), 388 (21), 387 (20), 369 (15), 362 (16), 296 (18), 295 (17), 95 (17). HRMS (EI) m/z: [M^+] Calcd for $C_{27}H_{15}F_2N$ 391.1167; Found 391.1157.

3,5-bis((4-fluorophenyl)ethynyl)-4-(*p*-tolyl)pyridine (3m)

According to general procedure B, title compound **3m** was obtained as a yellow solid in 78% yield (90.2 mg) (heptane/EtOAc = 8/1); mp 149–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.27–7.34 (m, 6H), 6.94–7.04 (m, 4H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$) δ 162.8 (d, J = 250.8 Hz), 152.2, 151.0, 139.1, 133.5 (d, J = 8.5 Hz), 132.9, 129.7, 128.4, 119.5, 118.6 (d, J = 3.4 Hz), 115.7 (d, J = 22.1 Hz), 94.6, 85.2, 21.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.7. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 758 (s), 816 (s), 826 (vs), 886 (m), 1012 (m), 1090 (m), 1150 (m), 1224 (s), 1292 (w), 1401 (m), 1442 (m), 1502 (s), 1535 (m), 1599 (m), 1877 (w), 2213 (w), 2856 (w), 2918 (w), 3023 (w). MS (EI, 70 eV): m/z (%) = 406 (31), 405 (M^+, 100), 404 (47), 390 (39), 389 (15), 388 (15), 94 (23), 185 (16), 95 (13), 75 (13). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{17}F_2N$ 405.1324; Found 405.1312.

3,5-bis((4-fluorophenyl)ethynyl)-4-(4-methoxyphenyl)pyridine (3n)

According to general procedure B, title compound **3n** was obtained as a yellow solid in 62% yield (74.1 mg) (heptane/EtOAc = 8/1); mp 148–149 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.68 (d, J = 8.7 Hz, 2H), 7.32 (dd, J = 8.7 Hz, J = 5.4 Hz, 4H), 6.98–7.06 (m, 6H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.8 (d, J = 250.7 Hz), 160.3, 151.9, 150.9, 133.5 (d, J = 8.4 Hz), 131.3, 128.1, 119.5, 118.5 (d, J = 3.2 Hz), 115.7 (d, J = 22.3 Hz), 113.1, 94.6, 85.2, 55.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 767 (m), 830 (vs), 892 (w), 1041 (m), 1090 (m), 1150 (s), 1181 (s), 1226 (s), 1253 (s), 1294 (m), 1401 (w), 1445 (m), 1502 (vs), 1537 (m), 1601 (m), 1890 (vw), 2215 (w), 2835 (w), 2901 (w), 2936 (w), 3044 (w). MS (EI, 70 eV): m/z (%) = 422 (32), 421 (M$^+$, 100), 420 (19), 390 (19), 378 (23), 377 (33), 376 (31), 349 (18), 188 (22), 179 (25), 164 (22), 95 (19). HRMS (EI) m/z: [M$^+$] Calcd for $C_{28}H_{17}F_2NO$ 421.1273; Found 421.1274.

4-phenyl-3,5-bis((4-(trifluoromethyl)phenyl)ethynyl)pyridine (3o)

According to general procedure B, title compound **3o** was obtained as a yellow solid in 71% yield (77.6 mg) (heptane/EtOAc = 8/1); mp 156 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (s, 2H), 7.65 (dd, J = 7.7 Hz, J = 1.9 Hz, 2H), 7.51–7.57 (m, 7H), 7.36 (d, J = 8.0 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.7, 152.1, 135.9, 131.7, 130.4 (q, J = 32.7 Hz), 129.6, 129.1, 127.8, 126.2, 125.3 (q, J = 3.7 Hz), 123.8 (q, J = 272.2 Hz), 118.9, 94.2, 87.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 725 (m), 738 (m), 837 (s), 896 (m), 1016 (m), 1065 (vs), 1105 (vs), 1166 (s), 1321 (s), 1405 (m), 1556 (w), 1611 (w), 1797 (w), 1850 (vw), 3023 (w), 3052 (w). MS (EI, 70 eV): m/z (%) = 492 (23), 491 (M$^+$, 100), 490 (65), 422 (36), 201 (20), 200 (19), 176 (20), 162 (19), 69 (60), 51 (19). HRMS (EI) m/z: [M$^+$] Calcd for $C_{29}H_{15}F_6N$ 491.1103; Found 491.1095.

4-(*p*-tolyl)-3,5-bis((4-(trifluoromethyl)phenyl)ethynyl)pyridine (3p)

According to general procedure B, title compound **3p** was obtained as a yellow solid in 77% yield (85.8 mg) (heptane/EtOAc = 8/1); mp 170 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.2 Hz, 4H), 7.41 (d, J = 8.1 Hz, 4H), 7.34 (d, J = 7.9 Hz, 2H), 2.49 (s, 3H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 153.1, 151.5, 139.4, 132.7, 131.7, 130.5 (q, J = 32.7 Hz), 129.6, 128.5, 126.2, 125.3 (q, J = 3.8 Hz), 123.8 (q, J = 272.4 Hz), 119.2, 94.3, 87.5, 21.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 723 (m), 762 (m), 816 (s), 837 (s), 898 (m), 1014 (s), 1065 (vs), 1100 (vs), 1166 (m), 1181 (m), 1317 (s), 1442 (w), 1513 (w), 1609 (m), 2920 (w), 3044 (w). MS (EI, 70 eV): m/z (%) = 506 (28), 505 (M$^+$, 100), 504 (47), 490 (33), 436 (25), 200 (15), 183 (20), 176 (20), 168 (16), 69 (42). HRMS (EI) m/z: [M$^+$] Calcd for $C_{30}H_{17}F_6N$ 505.1260; Found 505.1249.

4-(4-methoxyphenyl)-3,5-bis((4-(trifluoromethyl)phenyl)ethynyl)pyridine (3q)

According to general procedure B, title compound **3q** was obtained as a yellow solid in 57% yield (65.7 mg) (heptane/EtOAc = 8/1); mp 164–166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.2 Hz, 4H), 7.43 (d, J = 8.0 Hz, 4H), 7.06 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.3, 152.4, 152.0, 131.7, 131.3, 130.4 (q, J = 32.9 Hz), 128.0, 126.3, 125.3 (q, J = 3.6 Hz), 123.8 (q, J = 272.3 Hz), 118.8, 113.1, 93.8, 87.9, 55.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 725 (m), 767 (m), 804 (m), 826 (s), 835 (s), 1016 (m), 1045 (m), 1065 (s), 1102 (vs), 1164 (m), 1181 (s), 1251 (s), 1296 (m), 1321 (s), 1403 (w), 1445 (m), 1515 (m), 1611 (m), 2215 (vw), 2837 (w), 2924 (w), 2996 (w). MS (EI, 70 eV): m/z (%) = 522 (32), 521 (M^+, 100), 520 (17), 409 (17), 408 (21), 195 (15), 176 (18), 169 (17), 145 (14), 69 (46). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{17}F_6NO$ 521.1209; Found 521.1204.

4-phenyl-3,5-bis(thiophen-3-ylethynyl)pyridine (3r)

According to general procedure B, title compound **3r** was obtained as a yellow solid in 71% yield (79.8 mg) (heptane/EtOAc = 8/1); mp 106–109 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.62–7.70 (m, 2H), 7.45–7.55 (m, 3H), 7.33 (dd, J = 3.0 Hz, J = 1.1 Hz, 2H), 7.24 (dd, J = 5.0 Hz, J = 3.0 Hz, 2H), 6.97 (dd, J = 5.0 Hz, J = 1.2 Hz, 2H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 151.7, 151.4, 136.2, 129.7, 129.5, 129.3, 128.8, 127.6, 125.5, 121.6, 119.4, 90.8, 85.1. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 740 (s), 769 (vs), 859 (m), 903 (w), 997 (m), 1078 (m), 1210 (w), 1261 (w), 1356 (w), 1395 (w), 1442 (m), 1556 (w), 2207 (w), 3095 (w). MS (EI, 70 eV): m/z (%) = 369 (10), 368 (31), 367 (M^+, 100), 366 (68), 365 (14), 364 (10), 333 (13), 322 (15), 320 (16), 45 (37). HRMS (EI) m/z: [M^+] Calcd for $C_{23}H_{13}NS_2$ 367.0484; Found 367.0474.

3,5-bis((4-methoxyphenyl)ethynyl)-4-phenylpyridine (3s)

According to general procedure B, title compound **3s** was obtained as a yellow solid in 69% yield (76.5 mg) (heptane/EtOAc = 3/1); mp 153–155 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.71 (s, 2H), 7.64–7.71 (m, 2H), 7.45–7.56 (m, 3H), 7.18–7.25 (m, 4H), 6.77–6.85 (m, 4H), 3.80 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 160.0, 151.3, 151.1, 136.5, 133.0, 129.8, 128.6, 127.6, 119.6, 114.7, 114.0, 95.6, 84.5, 55.3. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 740 (m), 804 (m), 824 (vs), 1026 (s), 1170 (s), 1245 (s), 1288 (m), 1438 (m), 1504 (s), 1605 (m), 2205 (m), 2835 (w), 2961 (w). MS (EI, 70 eV): m/z (%) = 416 (33), 415 (M^+, 100), 414 (13), 400 (12), 329 (12), 328 (19), 327 (11), 164 (11), 163 (11), 44 (15). HRMS (EI) m/z: [M^+] Calcd for $C_{29}H_{21}NO_2$ 415.1567; Found 415.1567.

4,4'-((4-phenylpyridine-3,5-diyl)bis(ethyne-2,1-diyl))bis(*N,N*-dimethylaniline) (3t)

According to general procedure B, title compound **3t** was obtained as a yellow solid in 72% yield (79.1 mg) (heptane/EtOAc = 2/1); mp 196–198 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 2H), 7.69–7.72 (m, 2H), 7.43–7.53 (m, 3H), 7.13–7.17 (m, 4H), 6.57–6.60 (m, 4H), 2.96 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.4, 150.4, 150.3, 136.7, 132.6, 130.0, 128.4, 127.4, 120.0, 111.6, 109.3, 96.9, 84.0, 40.1. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 746 (s), 816 (vs), 968 (m), 1059 (m), 1181 (m), 1222 (m), 1354 (m), 1440 (m),

1515 (m), 1603 (m), 2195 (m), 2809 (w), 2893 (m). MS (EI, 70 eV): m/z (%) = 441 (M^+, 12), 341 (15), 327 (11), 282 (14), 281 (49), 208 (21), 207 (100), 73 (20). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{27}N_3$ 442.228; Found 442.228.

6-phenyl-1-(phenylethynyl)benzo[*f*]isoquinoline (4a) d

According to general procedure C, title compound **4a** was obtained as a yellow oil in 87% yield (87.3 mg) (heptane/EtOAc = 2/1); R_f 0.25 (heptane/EtOAc 3:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 10.42 (dd, J = 8.4 Hz, J = 1.3 Hz, 1H), 9.15 (s, 1H), 9.01 (s, 1H), 7.99 (dd, J = 8.2 Hz, J = 1.4 Hz, 1H), 7.65–7.80 (m, 5H), 7.44–7.57 (m, 8H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 151.7, 151.2, 141.2, 139.8, 133.4, 133.2, 131.5, 129.9, 129.5, 128.9, 128.8, 128.7, 128.5, 127.9, 127.0, 126.8, 126.5, 125.4, 123.1, 114.3, 97.3, 89.3. (Signal of one quaternary carbon is absent, which may relate to signal overlap.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 727 (vs), 752 (vs), 771 (s), 824 (m), 900 (m), 1026 (m), 1069 (m), 1133 (m), 1160 (m), 1208 (m), 1335 (m), 1401 (m), 1442 (m), 1490 (m), 1562 (m), 1597 (m), 1731 (w), 2203 (w), 2850 (w), 2922 (m), 3023 (w), 3052 (w). MS (EI, 70 eV): m/z (%) = 356 (26), 355 (M^+, 100), 354 (67), 353 (12), 352 (17), 351 (12), 278 (14), 277 (14), 77 (16). HRMS (EI) m/z: [M^+] Calcd for $C_{27}H_{17}N$ 355.1356; Found 355.1356.

8-methyl-6-phenyl-1-(phenylethynyl)benzo[*f*]isoquinoline (4b)

According to general procedure C, title compound **4b** was obtained as a yellow solid in 89% yield (89.3 mg) (heptane/EtOAc = 2/1); mp 143–145 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 10.30 (d, J = 8.7 Hz, 1H), 9.12 (s, 1H), 8.98 (s, 1H), 7.66–7.81 (m, 4H), 7.42–7.63 (m, 9H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 151.6, 151.1, 140.9, 140.0, 139.1, 133.6, 133.3, 131.5, 129.9, 128.9, 128.6, 128.5, 128.2, 127.8, 127.3, 126.7, 126.6, 126.4, 125.6, 123.1, 114.1, 97.1, 89.4, 21.8. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 684 (vs), 705 (s), 752 (vs), 822 (m), 900 (m), 1072 (w), 1205 (m), 1313 (w), 1442 (m), 1490 (m), 1560 (m), 1618 (w), 1739 (w), 2852 (w), 2918 (w), 3015 (w). MS (EI, 70 eV): m/z (%) = 370 (31), 369 (M^+, 100), 368 (25), 355 (10), 354 (39), 353 (16), 352 (25), 351 (13), 176 (17), 77 (23). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{19}N$ 369.1512; Found 369.1507.

6-phenyl-1-(phenylethynyl)-8-(trifluoromethyl)benzo[*f*]isoquinoline (4c)

According to general procedure C, title compound **4c** was obtained as a yellow solid in 96% yield (95.8 mg) (heptane/EtOAc = 2/1); mp 128–131 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 10.55 (d, J = 8.9 Hz, 1H), 9.20 (s, 1H), 9.05 (s, 1H), 8.28 (s, 1H), 7.95 (dd, J = 8.9 Hz, J = 1.8 Hz, 1H), 7.70–7.74 (m, 2H), 7.51–7.60 (m, 5H), 7.44–7.51 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.1, 151.3, 141.2, 138.8, 133.1, 132.3, 131.6, 131.5, 130.3 (q, J = 32.9 Hz), 129.8, 129.2, 128.8, 128.7, 128.3, 127.6, 127.1, 126.8, 124.0 (q, J = 4.0 Hz), 124.0 (q, J = 272.8 Hz), 122.4 (q, J = 3.2 Hz), 122.6, 114.7, 98.1, 88.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 729 (m), 756 (s), 835 (m), 851 (m), 900 (m), 1084 (s), 1117 (vs), 1158 (s), 1286 (m), 1315 (s), 1442 (w), 1492 (w), 1562 (w), 1597 (w), 2852 (w), 2922 (w),

3023 (w). MS (EI, 70 eV): m/z (%) = 424 (26), 423 (M^+, 100), 422 (37), 354 (15), 352 (12), 351 (11), 77 (15). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{16}F_3N$ 423.1229; Found 423.1218.

6-(*p*-tolyl)-1-(*p*-tolylethynyl)benzo[*f*]isoquinoline (4d)

According to general procedure C, title compound **4d** was obtained as a yellow solid in 94% yield (94.5 mg) (heptane/EtOAc = 2/1); mp 175–178 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 10.34 (dd, J = 8.4 Hz, ^4J = 1.2 Hz, 1H), 9.05 (s, 1H), 8.91 (s, 1H), 7.92 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 7.55–7.70 (m, 3H), 7.52 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.1 Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 151.5, 150.9, 141.2, 139.2, 137.6, 136.9, 133.6, 133.1, 131.4, 129.7, 129.6, 129.4, 129.2, 128.7, 127.0, 126.8, 126.4, 125.3, 120.0, 97.5, 88.7, 21.6, 21.3. (Signals of two quaternary carbons are absent, which may relate to signal overlap.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 729 (vs), 767 (s), 810 (s), 909 (m), 1109 (w), 1208 (w), 1403 (w), 1447 (m), 1508 (m), 1560 (w), 1607 (w), 2852 (w), 2918 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 384 (29), 383 (M^+, 100), 382 (31), 368 (27), 367 (9), 183 (16), 176 (12). HRMS (EI) m/z: [M^+] Calcd for $C_{29}H_{21}N$ 383.1669; Found 383.1660.

8-methyl-6-(*p*-tolyl)-1-(*p*-tolylethynyl)benzo[*f*]isoquinoline (4e)

According to general procedure C, title compound **4e** was obtained as a yellow solid in 93% yield (92.6 mg) (heptane/EtOAc = 2/1); mp 178–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.31 (d, J = 8.7 Hz, 1H), 9.10 (s, 1H), 8.96 (s, 1H), 7.78 (s, 1H), 7.55–7.64 (m, 3H), 7.68 (s, 1H), 7.40–7.45 (m, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.25–7.29 (m, 2H), 2.51 (s, 3H),), 2.50 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.4, 150.9, 140.8, 139.1, 139.0, 137.5, 137.1, 133.7, 133.1, 131.4, 129.7, 129.4, 129.2, 128.1, 127.4, 126.7, 126.5, 126.5, 125.5, 120.1, 114.2, 97.3, 88.8, 21.8, 21.6, 21.3. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 736 (s), 783 (s), 814 (vs), 900 (s), 1109 (m), 1203 (w), 1436 (m), 1508 (m), 1560 (w), 1618 (w), 1737 (w), 2199 (w), 2852 (w), 2916 (m), 3017 (w). MS (EI, 70 eV): m/z (%) = 398 (30), 397 (M^+, 100), 396 (19), 383 (11), 382 (34), 183 (22), 169 (11). HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{30}H_{23}N$ 398.1909; Found 398.1904.

6-(*p*-tolyl)-1-(*p*-tolylethynyl)-8-(trifluormethyl)benzo[*f*]isoquinoline (4f)

According to general procedure C, title compound **4f** was obtained as a yellow solid in 92% yield (91.6 mg) (heptane/EtOAc = 2/1); mp 177–179 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.56 (d, J = 8.9 Hz, 1H), 9.17 (s, 1H), 9.03 (s, 1H), 8.30 (s, 1H), 7.93 (dd, J = 8.9 Hz, J = 1.9 Hz, 1H), 7.81 (s, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.50 (s, 3H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.9, 151.1, 141.2, 139.6, 138.2, 135.9, 133.2, 132.2, 131.7, 131.4, 130.6 (q, J = 32.5 Hz), 129.6, 129.5, 127.6, 127.2, 126.7, 124.1 (q, J = 4.2 Hz), 122.3 (q, J = 272.7 Hz), 122.2 (q, J = 3.1 Hz), 119.6, 114.9, 98.3, 88.1, 21.6, 21.3. (Signal of one aromatic carbon is absent, which may relate to signal overlap.) ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.3. IR

(ATM, cm^{-1}): $\tilde{\nu}$ = 736 (m), 816 (s), 855 (m), 903 (s), 1084 (s), 1121 (vs), 1170 (s), 1286 (m), 1315 (s), 1372 (w), 1453 (w), 1510 (m), 1566 (w), 1611 (w), 1908 (vw), 2201 (w), 2852 (w), 2918 (w), 3031 (w). MS (EI, 70 eV): m/z (%) = 452 (32), 451 (M^+, 100), 450 (18), 436 (20), 382 (8), 182 (12). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{20}F_3N$ 451.1542; Found 451.1532.

6-(4-fluorophenyl)-1-((4-fluorophenyl)ethynyl)benzo[*f*]isoquinoline (4g)

According to general procedure C, title compound **4g** was obtained as a yellow solid in 94% yield (93.8 mg) (heptane/EtOAc = 2/1); mp 127–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.32–10.38 (m, 1H), 9.14 (s, 1H), 8.99 (s, 1H), 7.89–7.96 (m, 1H), 7.61–7.79 (m, 5H), 7.42–7.54 (m, 2H), 7.11–7.26 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.9 (d, J = 250.9 Hz), 162.5 (d, J = 247.2 Hz), 151.7, 151.2, 140.1, 135.7 (d, J = 3.4 Hz), 133.4 (d, J = 8.4 Hz), 133.4, 133.2, 131.5 (d, J = 8.1 Hz), 129.5, 128.9, 126.8, 126.7, 126.6, 126.6, 125.6, 19.1 (d, J = 3.5 Hz), 116.0 (d, J = 22.3 Hz), 115.5 (d, J = 21.4 Hz), 114.1, 96.2, 88.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.1, -109.5. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 727 (vs), 762 (s), 826 (vs), 911 (m), 1012 (m), 1090 (m), 1154 (s), 1220 (s), 1504 (s), 1599 (m), 2854 (w), 2922 (w), 3044 (w). MS (EI, 70 eV): m/z (%) = 392 (26), 391 (M^+, 100), 390 (63) 389 (10), 388 (11), 185 (13). HRMS (EI) m/z: [M^+] Calcd for $C_{27}H_{15}F_2N$ 391.1167; Found 391.1158.

6-(4-fluorophenyl)-1-((4-fluorophenyl)ethynyl)-8-methylbenzo[*f*]isoquinoline (4h)

According to general procedure C, title compound **4h** was obtained as a yellow solid in 91% yield (91.3 mg) (heptane/EtOAc = 2/1); mp 138–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.24 (d, J = 8.6 Hz, 1H), 9.11 (s, 1H), 8.96 (s, 1H), 7.64–7.72 (m, 4H), 7.59 (dd, J = 8.7 Hz, J = 1.7 Hz, 1H), 7.45–7.52 (m, 2H), 7.12–7.27 (m, 4H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.9 (d, J = 250.8 Hz), 162.5 (d, J = 247.1 Hz), 162.5, 151.6, 151.1, 139.8, 139.3, 135.9 (d, J = 3.4 Hz), 133.6, 133.3, 133.4 (d, J = 8.5 Hz), 131.4 (d, J = 7.9 Hz), 128.3, 127.3, 126.6, 126.4, 126.3, 125.7, 119.2 (d, J = 3.6 Hz), 116.0 (d, J = 22.2 Hz), 115.5 (d, J = 21.4 Hz), 113.9, 96.1, 89.0, 21.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.3, -109.7. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 736 (s), 781 (s), 822 (vs), 1010 (m), 1090 (m), 1154 (s), 1222 (s), 1504 (s), 1562 (w), 1599 (m), 1702 (w), 2852 (w), 2916 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 406 (29), 405 (M^+, 100), 404 (22), 390 (33), 389 (12), 388 (12), 194 (11). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{17}F_2N$ 405.1324; Found 405.1314.

6-(4-(trifluoromethyl)phenyl)-1-((4-(trifluoromethyl)phenyl)ethynyl)benzo[*f*]isoquinoline (4i)

According to general procedure C, title compound **4i** was obtained as a yellow solid in 86% yield (86.1 mg) (heptane/EtOAc = 2/1); mp 174–176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (d, J = 8.4 Hz, 1H), 9.20 (s, 1H), 9.04 (s, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 8.0 Hz, 4H), 7.78 (d, J = 8.3 Hz, 1H), 7.71–7.76 (m, 4H), 7.67 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.2, 151.8, 143.4, 139.9, 133.5, 133.0, 131.7, 130.8 (q, J = 32.8 Hz), 130.2, 130.2 (q, J = 32.4 Hz), 129.4, 129.3, 126.9, 126.7, 126.7, 126.5, 125.7, 125.6 (q, J = 3.7 Hz), 125.5 (q, J = 3.8 Hz), 124.1 (q, J = 272.2 Hz), 123.8 (q, J = 272.2 Hz), 113.7, 95.8, 91.3. (Signal of one aromatic carbon is absent, which may relate to

signal overlap.) ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.8, -62.5. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 727 (s), 767 (s), 828 (s), 845 (s), 903 (m), 1012 (s), 1065 (vs), 1102 (vs), 1156 (s), 1323 (s), 1407 (w), 1564 (w), 1611 (m), 2852 (w), 2924 (w), 3046 (w). MS (EI, 70 eV): m/z (%) = 493 (5), 492 (29), 491 (M^+, 100), 490 (35), 422 (21), 421 (8), 176 (8). HRMS (EI) m/z: [M^+] Calcd for $C_{29}H_{15}F_6N$ 491.1103; Found 491.1097.

8-methyl-6-(4-(trifluoromethyl)phenyl)-1-((4-(trifluoromethyl)phenyl)ethynyl)benzo[*f*]isoquinoline (4j)

According to general procedure C, title compound **4j** was obtained as a yellow solid in 89% yield (88.7 mg) (heptane/EtOAc = 2/1); mp 200–203 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.21 (d, J = 8.6 Hz, 1H), 9.16 (s, 1H), 9.01 (s, 1H), 7.78–7.84 (m, 4H), 7.70–7.74 (m, 3H), 7.60–7.68 (m, 4H), 2.53 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.2, 151.8, 143.6, 139.7, 139.6, 133.6, 133.2, 131.7, 130.8 (q, J = 32.9 Hz), 130.2, 130.1 (q, J = 32.6 Hz), 128.6, 127.2, 126.8, 126.6, 126.3, 126.2, 125.9, 125.6 (q, J = 3.8 Hz), 125.5 (q, J = 3.6 Hz), 124.2 (q, J = 272.2 Hz), 123.9 (q, J = 273.9 Hz), 113.4, 95.6, 91.5, 21.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.83, -62.44. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 734 (m), 781 (m), 824 (s), 839 (s), 898 (m), 1014 (s), 1063 (s), 1100 (vs), 1158 (s), 1319 (s), 1403 (w), 1459 (w), 1510 (w), 1562 (w), 1609 (m), 2201 (w), 2852 (w), 2918 (w). MS (EI, 70 eV): m/z (%) = 507 (11), 506 (79), 505 (M^+, 100), 504 (32), 491 (15), 490 (59), 486 (12), 436 (18), 40 (12), 32 (16). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{17}F_6N$ 505.1260; Found 505.1273.

6-(thiophen-3-yl)-1-(thiophen-3-ylethynyl)benzo[*f*]isoquinoline (4k)

According to general procedure C, title compound **4k** was obtained as a yellow solid in 79% yield (79.1 mg) (heptane/EtOAc = 2/1); mp 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.32–10.37 (m, 1H), 9.12 (s, 1H), 8.97 (s, 1H), 8.09–8.14 (m, 1H), 7.78 (s, 1H), 7.69–7.76 (m, 3H), 7.48–7.53 (m, 2H), 7.42 (dd, J = 5.0 Hz, J = 2.9 Hz, 1H), 7.37 (dd, J = 5.1 Hz, J = 1.3 Hz, 1H), 7.33 (dd, J = 4.7 Hz, J = 1.5 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.6, 151.0, 140.1, 136.0, 133.4, 133.1, 129.5, 129.5, 129.3, 129.2, 128.9, 126.7, 126.6, 126.5, 125.9, 125.8, 125.5, 124.2, 122.1, 114.3, 92.7, 88.7. (Signal of one quaternary carbon is absent, which may relate to signal overlap.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 723 (vs), 760 (s), 783 (s), 820 (m), 845 (s), 900 (m), 1078 (m), 1197 (m), 1311 (w), 1356 (w), 1405 (m), 1510 (w), 1566 (m), 1613 (w), 1706 (w), 2197 (w), 2920 (w), 3041 (w), 3089 (w). MS (EI, 70 eV): m/z (%) = 369 (12), 368 (30), 367 (M^+, 100), 366 (54), 365 (9), 322 (14), 320 (12). HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{23}H_{13}NS_2$ 368.0568; Found 368.0564.

5,9-diphenylnaphtho[2,1,8-*def*]isoquinoline (5a)

According to general procedure D, title compound **5a** was obtained as a yellow solid in 93% yield (93.0 mg) (heptane/EtOAc = 1/1); mp 196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 2H), 8.27 (d, J = 7.9 Hz, 2H), 8.08 (s, 2H), 8.00 (t, J = 7.9 Hz, 1H), 7.65–7.69 (m, 4H), 7.56–7.61 (m, 4H), 7.51–7.55 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.6, 141.3, 140.2, 131.7, 130.0, 128.5, 127.9, 127.7, 126.6,

125.1, 124.8, 124.8, 123.9. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 703 (vs), 727 (s), 773 (s), 839 (m), 898 (s), 989 (w), 1135 (m), 1228 (m), 1360 (m), 1409 (m), 1442 (m), 1467 (m), 1488 (m), 1543 (m), 1581 (m), 2852 (w), 2922 (w), 3019 (m). MS (EI, 70 eV): m/z (%) = 356 (28), 355 (M^+, 100), 354 (27), 352 (10), 351 (8), 176 (12). HRMS (EI) m/z: [M^+] Calcd for $C_{27}H_{17}N$ 355.1356; Found 355.1359.

7-methyl-5,9-diphenylnaphtho[2,1,8-*def*]isoquinoline (5b)

According to general procedure D, title compound **5b** was obtained as a yellow solid in 86% yield (85.8 mg) (heptane/EtOAc = 1/1); mp 220–225 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 2H), 8.09 (s, 2H), 8.05 (s, 2H), 7.65–7.68 (m, 4H), 7.58–7.63 (m, 4H), 7.53–7.57 (m, 2H), 2.66 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.5, 141.4, 140.2, 138.5, 131.8, 130.0, 128.6, 127.9, 126.8, 125.7, 125.2, 124.7, 122.0, 22.7. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 705 (vs), 736 (m), 762 (s), 816 (w), 874 (m), 900 (m), 985 (w), 1069 (w), 1137 (w), 1234 (w), 1356 (w), 1442 (w), 1494 (w), 1548 (w), 1595 (w), 1626 (w), 1733 (w), 3046 (w). MS (EI, 70 eV): m/z (%) = 370 (25), 369 (M^+, 100), 368 (14), 354 (14), 353 (10), 352 (12), 177 (12), 77 (11). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{19}N$ 369.1512; Found 369.1508.

7-methoxy-5,9-diphenylnaphtho[2,1,8-*def*]isoquinoline (5c)

According to general procedure D, but utilizing 15 eq. MsOH in 3 ml octafluoro-1-pentanol provide title compound **5c** as a yellow solid in 40% yield (39.8 mg) (heptane/EtOAc = 1/1); mp 170–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (s, 2H), 8.05 (s, 2H), 7.79 (s, 2H), 7.64–7.69 (m, 4H), 7.49–7.62 (m, 6H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.3, 144.9, 140.7, 140.2, 133.5, 129.9, 128.7, 127.9, 126.5, 125.8, 124.1, 119.2, 110.5, 77.0, 55.6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 707 (vs), 734 (s), 762 (s), 859 (s), 898 (s), 1053 (s), 1137 (s), 1234 (s), 1302 (m), 1422 (m), 1442 (m), 1545 (m), 1591 (m), 2850 (w), 292 0(m), 3017 (w). MS (EI, 70 eV): m/z (%) = 386 (31), 385 (M^+, 100), 341 (13), 340 (19), 185 (17), 176 (21), 170 (28), 156 (22), 143 (10). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{19}ON$ 385.1461; Found 385.1458.

5,9-diphenyl-7-(trifluoromethyl)naphtho[2,1,8-*def*]isoquinoline (5d)

According to general procedure D, title compound **5d** was obtained as a yellow solid in 75% yield (74.9 mg) (heptane/EtOAc = 1/1); mp 196–198 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 2H), 8.51 (s, 2H), 8.16 (s, 2H), 7.54–7.70 (m, 10H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.4, 141.3, 139.3, 132.1, 129.9, 129.2 (q, J = 32.5 Hz), 128.9, 128.3, 126.4, 125.9, 125.4, 125.0, 124.4 (q, J = 273.2 Hz), 120.9 (q, J = 3.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.0. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 699 (vs), 736 (s), 758 (s), 863 (s), 888 (s), 1102 (vs), 1162 (s), 1228 (m), 1271 (m), 1319 (s), 1385 (w), 1434 (m), 1471 (w), 1578 (w), 2850 (w), 2920 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 424 (29), 423 (M^+, 100), 422 (19), 201 (10), 176 (12). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{16}F_3N$ 423.1229; Found 423.1226.

5,9-di-*m*-tolylnaphtho[2,1,8-*def*]isoquinoline (5e)

According to general procedure D, title compound **5e** was obtained as a yellow solid in 78% yield (77.7 mg) (heptane/EtOAc = 1/1); mp 148–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 2H), 8.29 (d, J = 7.9 Hz, 2H), 8.06 (s, 2H), 8.00 (t, J = 7.9 Hz, 1H), 7.44–7.51 (m, 6H), 7.32–7.37 (m, 2H), 2.51 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.5, 141.4, 140.1, 138.2, 131.7, 130.6, 128.6, 128.4, 127.7, 127.1, 126.5, 125.0, 124.8, 123.8, 21.5. (Signal of one quaternary carbon is absent, which may relate to signal overlap.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 701 (vs), 725 (s), 775 (s), 787 (m), 839 (m), 882 (m), 1090 (w), 1135 (w), 1241 (w), 1358 (m), 1409 (m), 1482 (w), 1545 (w), 1601 (w), 2852 (w), 2912 (w), 3027 (w). MS (EI, 70 eV): m/z (%) = 384 (37), 383 (M$^+$, 100), 382 (15), 368 (13), 183 (20), 176 (12). HRMS (EI) m/z: [M$^+$] Calcd for $C_{29}H_{21}N$ 383.1669; Found 383.1673.

7-methyl-5,9-di-*m*-tolylnaphtho[2,1,8-*def*]isoquinoline (5f)

According to general procedure D, title compound **5f** was obtained as a yellow solid in 63% yield (63.3 mg) (heptane/EtOAc = 1/1); mp 171–174 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (s, 2H), 8.08 (s, 2H), 8.03 (s, 2H), 7.43–7.52 (m, 6H), 7.33–7.40 (m, 2H), 2.66 (s, 3H), 2.52 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.4, 141.2, 140.3, 138.3, 138.1, 131.8, 130.6, 128.5, 128.4, 127.1, 126.5, 125.5, 125.1, 124.6, 122.1, 22.7, 21.6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 705 (vs), 736 (s), 775 (vs), 861 (s), 919 (m), 1034 (m), 1088 (m), 1135 (m), 1230 (m), 1358 (m), 1469 (m), 1548 (m), 1597 (m), 2850 (w), 2916 (m), 3017 (w). MS (EI, 70 eV): m/z (%) = 398 (32), 397 (M$^+$, 100), 382 (7), 183 (13), 176 (6). HRMS (EI) m/z: [M$^+$] Calcd for $C_{30}H_{23}N$ 397.1825; Found 397.1825.

5,9-di-*p*-tolylnaphtho[2,1,8-*def*]isoquinoline (5g)

According to general procedure D, title compound **5g** was obtained as a yellow solid in 80% (80.0 mg) (heptane/EtOAc = 1/1); mp 244–246 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.42 (s, 2H), 8.29 (d, J = 7.9 Hz, 2H), 8.05 (s, 2H, CH), 7.98 (t, J = 7.9 Hz, 1H), 7.56 (d, J = 8.0 Hz, 4H), 7.39 (d, J = 8.0 Hz, 4H), 2.52 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.4, 141.3, 137.6, 137.3, 131.8, 129.9, 129.2, 127.6, 126.5, 125.0, 124.9, 124.8, 123.9, 21.3. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 727 (vs), 783 (m), 810 (vs), 839 (m), 909 (m), 991 (w), 1109 (w), 1181 (m), 1228 (w), 1360 (m), 1412 (m), 1510 (m), 2916 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 385 (5), 384 (34), 383 (M$^+$, 100), 382 (12), 368 (10), 367 (7), 366 (4), 364 (4), 352 (4), 351 (4), 191 (5), 190 (4), 183 (8), 182 (12), 176 (10), 169 (5). HRMS (EI) m/z: [M$^+$] Calcd for $C_{29}H_{21}N$ 383.1669; Found 383.1663.

7-methyl-5,9-di-*p*-tolylnaphtho[2,1,8-*def*]isoquinoline (5h)

According to general procedure D, title compound **5h** was obtained as a yellow solid in 82% yield (82.1 mg) (heptane/EtOAc = 1/1); mp 285–288 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 2H), 8.10 (s, 2H), 8.02 (s, 2H), 7.56 (d, J = 8.0 Hz, 4H), 7.41 (d, J = 7.7 Hz, 4H), 2.66 (s, 3H), 2.53 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.4, 140.9, 138.0, 137.5, 137.4, 131.9, 129.9, 129.2, 126.4, 125.4, 125.1, 124.6, 122.1, 22.6, 21.3. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 740 (s), 779 (m), 808 (vs), 872 (m), 911 (vs), 1111 (m), 1183 (m), 1234 (m), 1356 (m), 1449 (m), 1508 (m), 1595 (w), 1626 (w), 2920 (m), 3023

(w). MS (EI, 70 eV): m/z (%) = 399 (6), 398 (38), 397 (M^+, 100), 382 (10), 183 (15), 176 (7). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{23}N$ 397.1825; Found 397.1822.

5,9-di-*p*-tolyl-7-(trifluoromethyl)naphtho[2,1,8-*def*]isoquinoline (5i)

According to general procedure D, title compound **5i** was obtained as a yellow solid in 75% yield (75.2 mg) (heptane/EtOAc = 1/1); mp 214–216 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.47 (s, 2H), 8.54 (s, 2H), 8.12 (s, 2H), 7.54 (d, J = 7.9 Hz, 4H), 7.42 (d, J = 7.9 Hz, 4H), 2.53 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 145.1, 141.3, 138.1, 136.3, 132.2, 129.7, 129.5, 129.0 (q, J = 32.2 Hz), 126.2, 125.7, 125.4, 125.0, 124.4 (q, J = 273.1 Hz), 120.9 (q, J = 3.8 Hz), 21.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.9. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 738 (m), 802 (s), 865 (m), 890 (m), 1105 (vs), 1162 (s), 1230 (w), 1269 (m), 1321 (s), 1383 (w), 1436 (w), 1515 (w), 2856 (w), 2922 (w), 3025 (w). MS (EI, 70 eV): m/z (%) = 452 (32), 451 (M+, 100), 436 (11), 225 (6), 183 (8). HRMS (EI) m/z: [M^+] Calcd for $C_{30}H_{20}F_3N$ 451.1542; Found 451.1537.

5,9-bis(4-fluorophenyl)naphtho[2,1,8-*def*]isoquinoline (5j)

According to general procedure D, title compound **5j** was obtained as a yellow solid in 79% yield (78.7 mg) (heptane/EtOAc = 1/1); mp 211–213 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.45 (s, 2H), 8.22 (d, J = 7.9 Hz, 2H), 7.98–8.07 (m, 3H), 7.58–7.66 (m, 4H), 7.23–7.32 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.6 (d, J = 247.2 Hz), 144.8, 140.2, 136.1 (d, J = 3.5 Hz), 131.8, 131.6 (d, J = 8.1 Hz), 127.9, 126.6, 125.4, 124.6, 123.9, 115.6 (d, J = 21.5 Hz). (Signal of one quaternary carbon is absent, which may relate to signal overlap.) ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.1. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 729 (vs), 787 (m), 818 (vs), 837 (s), 905 (m), 1016 (m), 1098 (m), 1158 (s), 1218 (s), 1296 (w), 1360 (w), 1414 (m), 1500 (s), 1601 (m), 3031 (w). MS (EI, 70 eV): m/z (%) = 392 (28), 391 (M^+, 100), 390 (25), 194 (7), 185 (14). HRMS (EI) m/z: [M^+] Calcd for $C_{27}H_{15}F_2N$ 391.1167; Found 391.1168.

5,9-bis(4-fluorophenyl)-7-methylnaphtho[2,1,8-*def*]isoquinoline (5k)

According to general procedure D, title compound **5k** was obtained as a yellow solid in 80% yield (79.7 mg) (heptane/EtOAc = 1/1); mp 263–266 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (s, 2H), 7.89–7.94 (m, 4H), 7.48–7.57 (m, 4H), 7.15–7.24 (m, 4H), 2.58 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.6 (d, J = 247.0 Hz), 144.7, 139.9, 138.2, 136.2 (d, J = 3.4 Hz), 131.8, 131.6 (d, J = 8.1 Hz), 126.6, 125.5, 125.3, 124.4, 122.1, 115.6 (d, J = 21.4 Hz), 22.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.2. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 740 (s), 789 (m), 816 (s), 841 (vs), 905 (m), 1016 (w), 1090 (w), 1158 (s), 1220 (s), 1356 (m), 1471 (m), 1508 (s), 1601 (m), 1628 (w), 2918 (w), 3054 (w). MS (EI, 70 eV): m/z (%) = 406 (30), 405 (M^+, 100), 390 (10), 389 (7), 388 (6), 194 (11), 185 (9). HRMS (EI) m/z: [M^+] Calcd for $C_{28}H_{17}F_2N$ 405.1324; Found 405.1324.

5,9-bis(4-fluorophenyl)naphtho[2,1,8-*def*]isoquinolin-7-ol (5l)

According to general procedure D, title compound **5l** was obtained as a yellow solid in 35% yield (34.8 mg) (heptane/EtOAc = 1/1); mp 350–354 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.47 (s, 2H), 8.28 (s, 2H), 7.95 (s, 2H), 7.58–7.66 (m, 4H), 7.29–7.36 (m, 4H), 1.26 (s, 1H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 163.32 (d, J = 249.4 Hz), 158.7, 144.3, 135.5, 133.9 (d, J = 3.5 Hz), 133.5, 131.5 (d, J = 8.3 Hz), 129.1, 125.8, 125.1, 117.7, 116.2 (d, J = 21.8 Hz), 114.8, 77.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.1. (Spectra were recorded in $CDCl_3$ with TFA-*d* as additive.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 738 (s), 826 (vs), 903 (m), 1129 (s), 1158 (s), 1216 (vs), 1241 (s), 1306 (s), 1364 (m), 1426 (s), 1504 (s), 1589 (s), 1739 (w), 2850 (w), 2918 (w). MS (EI, 70 eV): m/z (%) = 408 (41), 407 (M^+, 100), 406 (29), 376 (8), 194 (22), 193 (9), 184 (9), 32 (25). HRMS (EI) m/z: [M^+] Calcd for $C_{27}H_{15}F_2NO$ 407.1116; Found 407.1110.

5,9-bis(4-methoxyphenyl)naphtho[2,1,8-*def*]isoquinoline (5m)

According to general procedure D, but utilizing 3 eq. TfOH in 3 ml CH_2Cl_2 for 3h at 0°C and 5h at room temperature provide title compound **5m** as a yellow solid in 66% yield (65.8 mg) (heptane/EtOAc = 1/1); mp 240–242 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.44 (s, 2H), 8.31 (d, J = 7.9 Hz, 2H), 8.06 (s, 2H), 7.99–8.05 (m, 1H), 7.57–7.64 (m, 4H), 7.10–7.16 (m, 4H), 3.95 (s, 6H). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$) δ 159.5, 143.9, 141.2, 132.5, 132.1, 131.1, 127.8, 126.5, 125.0, 124.9, 124.0, 114.0, 55.4. (Signal of one quaternary carbon is absent, which may relate to signal overlap.) IR (ATM, cm^{-1}): $\tilde{\nu}$ = 732 (vs), 806 (vs), 900 (s), 1028 (vs), 1166 (s), 1249 (vs), 1510 (s), 1607 (m), 2840 (m), 2922 (m), 3015 (w). MS (EI, 70 eV): m/z (%) = 419 (18), 416 (38), 415 (M^+, 100), 400 (12), 328 (10), 312 (19), 163 (13), 135 (84). HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{29}H_{21}NO_2$ 416.1650; Found 416.1656.

4,4'-(naphtho[2,1,8-*def*]isoquinoline-5,9-diyl)bis(*N,N*-dimethylaniline) (5n)

According to general procedure D, title compound **5n** was obtained as a yellow solid in 75% yield (74.9 mg) (heptane/EtOAc = 1/1); mp 268–271 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (s, 2H), 8.39 (d, J = 7.9 Hz, 2H), 8.04 (s, 2H),), 8.00 (t, J = 7.9 Hz, 1H), 7.56–7.59 (m, 4H), 6.94 (d, J = 8.7 Hz, 4H), 3.08 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.2, 144.1, 141.5, 132.2, 130.8, 128.2, 127.4, 126.1, 125.2, 124.8, 124.5, 124.1, 112.3, 40.6. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 729 (s), 814 (vs), 907 (s), 944 (m), 1059 (m), 1164 (s), 1224 (s), 1354 (s), 1445 (m), 1519 (s), 1607 (s), 2796 (m), 2852 (m), 2920 (m). MS (EI, 70 eV): m/z (%) = 442 (28), 441 (M^+, 100), 440 (5), 425 (8), 220 (18), 219 (9), 32 (18). HRMS (EI) m/z: [M^+] Calcd for $C_{31}H_{27}N_3$ 441.2200; Found 441.2202.

5,9-di(thiophen-3-yl)naphtho[2,1,8-*def*]isoquinoline (5o)

According to general procedure D but utilizing 60 eq. *p*TsOH provide title compound **5o** as a yellow solid in 86% yield (85.9 mg) (heptane/EtOAc = 1/1); mp 178–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.42 (s, 2H), 8.42 (d, J = 7.9 Hz, 2H), 8.13 (s, 2H), 8.02–8.10 (m, 1H), 7.61 (dd, J = 3.0 Hz, J = 1.3 Hz, 2H), 7.57 (dd, J = 4.9 Hz, J = 3.0 Hz, 2H), 7.47 (dd, J = 4.9 Hz, J = 1.3 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.7, 140.6, 136.0, 131.8, 129.4, 127.9, 126.5, 125.9, 125.2, 124.8, 124.6, 124.3, 123.9. IR (ATM, cm^{-1}): $\tilde{\nu}$ = 727 (vs), 777 (s), 853 (m), 898 (m), 1080 (m), 1199 (m), 1348 (w), 1403

(m), 2848 (w), 2918 (w), 3015 (w), 3099 (w). MS (EI, 70 eV): m/z (%) = 369 (12), 368 (27), 367 (M^+, 100), 366 (21), 365 (5), 322 (10), 183 (5), 161 (6). HRMS (EI) m/z: [M^+] Calcd for $C_{23}H_{13}NS_2$ 367.0484; Found 367.0489.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: .

Supplementary experimental data: ^{1}H-, ^{13}C-NMR, spectra of isolated compounds; crystallographic data; optimization tables; CV spectra; computational details;

Single crystal X-ray data of **5b** (CIF)

Single crystal X-ray data of **4j** (CIF)

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Notes

The authors declare no competing financial interest.

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