PAPER

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Synthesis and properties of thienonaphtho[*bc*]pyridines and thienonaphtho[*bc*]quinolines†

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The incorporation of heteroatoms within polycyclic aromatic compounds has gained significant interest due to its potential to effectively alter the inherent physicochemical properties of compounds without the need for profound structural changes. We herein report the development of a modular synthesis of hitherto unknown thienonaphtho[*bc*]pyridines and thienonaphtho[*bc*]quinolines in very good yields by Brønsted acid mediated cycloisomerization, permitting selective access to two isomeric products that are isoelectronic to the parent dibenzopyrene. The photophysical and electrochemical properties of the desired compounds were extensively studied and further complemented by DFT calculations.

Over the past decades, the development of efficient opto-electronic materials based on polycyclic aromatic hydrocarbons (PAHs) has attracted wide attention and has been extensively investigated.[1–8] The π-expansion of PAHs is a powerful approach to improve their photophysical and electrochemical properties. Therefore, the development of new and modular methods for the synthesis and derivatization of PAHs is of considerable current interest.[9–12] In this context, the annulation and replacement of benzene rings by heterocycles is an efficient strategy to modulate the intrinsic physicochemical properties, such as band gap, redox properties, aromaticity and chemical stability of PAHs, giving rise to new and wide applications in materials science.[13–17] Thus, thiophene-fused π-conjugated molecules have received significant interest as promising building blocks for the development of high-performance π-conjugated materials in diverse scientific fields, such as organic photovoltaic materials (OPVs), organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs).[18–24]

Today, one of the most studied PAHs is undoubtedly pyrene, due to its unique optical and electronic properties.[7,25–29] However, the incorporation of heterocycles such as electron-rich thiophene or electron-deficient pyridines into the pyrene scaffold is still in its infancy. The present synthetic methods often suffer from multi-step synthetic procedures, requirement of complex, not readily available starting materials, harsh reaction conditions, low selectivity and/or poor overall yields.[30–40] For instance, the group of Otsubo obtained phenalenothiophene by flash vacuum pyrolysis. Later, Höger and coworkers used Pd-catalyzed CH-activation to obtain related benzotetracenothiophenes, which upon functionalization with certain alkynyl side chains self-assemble to ribbon- and ziggurat-like superstructures in the solid state. Diazaphenalenothiophenes were obtained by Aksenov and coworkers by the electrolysis of benzoylperimidines in the presence of H_2S or its condensation with elemental sulfur at high temperature. We recently reported the synthesis of S,N-doped thienonaphthopyridines (**TNP**) by Brønsted acid mediated cycloisomerisation (Fig. 1).[41] Incorporation of heteroatoms and alteration of the ring size within the pyrene scaffold led to substantial changes of the inherent photophysical properties.

Thus, as an extension of our previous work, we were interested in the selective N-doping of the respective thienophenalenes and its impact on their photophysical and electrochemical properties. The newly developed methodology reported herein is highly modular and is based on Brønsted acid mediated cycloisomerisation, giving access to various TNP isomers including their π-expanded derivatives.

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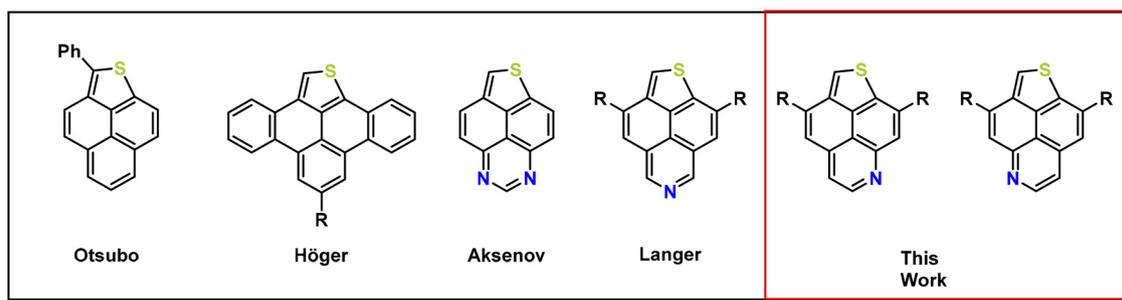*Org. Biomol. Chem.*, 2024, **22**, 8631–8648 | **8631**

Fig. 1 Structures of (aza)thienophenalenes.

Results and discussion

Synthesis

The starting materials **1a–j** and **2a–c** were obtained in 41–92% isolated yields by palladium catalyzed Suzuki–Miyaura and Sonogashira reactions, respectively, adapting previously reported procedures for the respective phenyl derivatives (ESI, Scheme S1†).[40]

Subsequently, the Brønsted acid mediated cycloisomerisation reaction was studied, utilizing **1a** as a representative substrate to optimize the reaction conditions. It is important to note that direct treatment of precursor **1a** with a high excess of methanesulfonic acid (MsOH) at elevated temperatures resulted in complete conversion of the starting material to give an inseparable mixture of the bis-annulated regioisomers **5a** and **6a** (Table 1, entries 1 and 2). Further investigations showed that employing the less acidic trifluoroacetic acid (TFA) resulted in the formation of the mono-annulated isomers **3a** and **4a** in moderate to very good overall yields with

varying selectivities for the two products (Table 1, entries 5–9). Performing the reaction at room temperature (entry 6) resulted in an improved selectivity for the isolated isomers, but at the same time in a reduced overall yield. Hence, applying the reaction conditions at 40 °C provided the best overall results in terms of yield and selectivity of products **3a** and **4a**. Decreasing the amount of TFA from 120 eq. to 30 eq. proved to be ineffective as no conversion of the starting material was observed.

In all optimization reactions, the cyclization proceeded selectively at the α-position of thiophene and no formation of the isomeric product derived from the reaction at the β-position was observed. Single crystal structures were obtained for both isomers by slow evaporation of heptane/dichloromethane solutions, which unambiguously confirmed the configuration of both isomers (ESI, Fig. S1, Table S1†). Moreover, the characteristic NMR shift of the singlet of the central benzene proton allowed for the assignment of the respective regioisomers (~8.0 ppm for **3a** and ~7.5 ppm for **4a**).

Afterwards, the preparative scope was studied and the respective mono-annulated thieno[*f*]quinolines **3a–j** and thieno[*h*]isoquinolines **4a–h** were obtained in moderate to very good yields (Scheme 1). Both electron-poor and electron-rich systems gave good yields regardless of the substitution pattern. Surprisingly, in the case of **1b**, the formation of the bis-annulated isomer **5b** instead of the expected mono-annulated product **4b** was observed, albeit in only 15% yield. The reaction of **1j**, containing a strongly donating dimethylamino (DMA) group, behaved differently from all other starting materials employed and provided an isomeric mixture of products derived from cyclization at the α-position and β-position of the thiophene ring. This could be explained by the formation of highly reactive charged species. The strongly acidic reaction conditions may protonate the DMA functional group and transform it into an acceptor, leading to a less stabilized vinyl carbocation upon protonation of the triple bond. In the case of **1i**, an inseparable mixture of products was obtained due to the formation of phenolic by-products caused by the cleavage of the methoxy group. The use of **1f** and **1g**, containing electron withdrawing trifluoromethyl and cyano groups, resulted in rapid decomposition of the starting materials, most likely due to the low stability of the positively charged intermediates
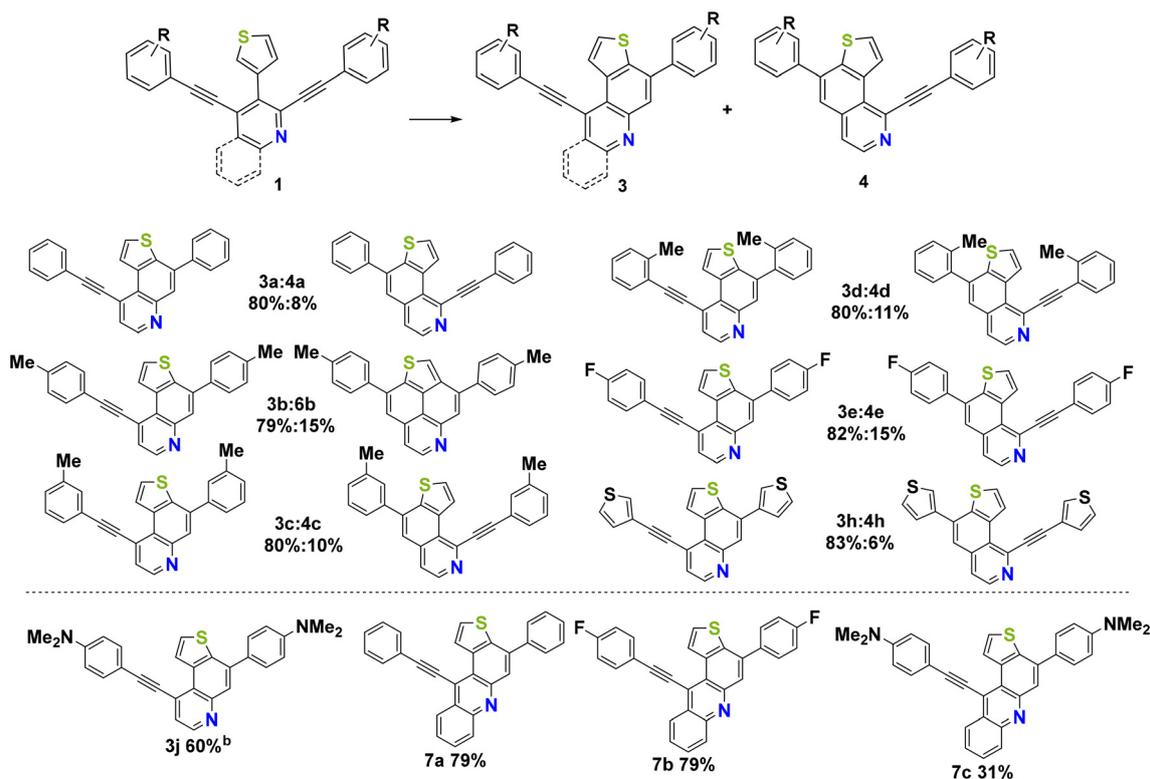
Table 1 Optimization of the cycloisomerization reaction of **1a**
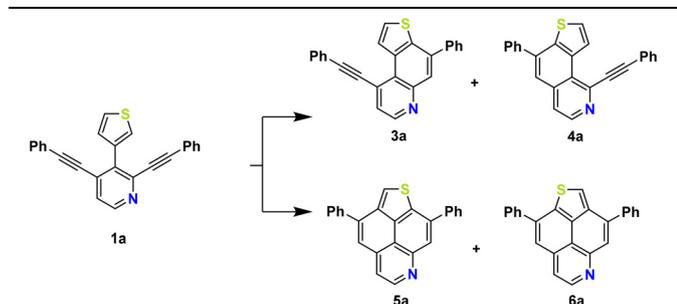
Entry	Acid (eq.)	Solvent	T, °C	t, h	Yield[a] (%)	Ratio 3a : 4a : 5a : 6a
1	MsOH (30)	—	120	3	24 : 24	0 : 0 : 1 : 1
2	MsOH (60)	—	120	24	27 : 27	0 : 0 : 1 : 1
3	MsOH (60)	—	20	24	25 : 49	1 : 2 : 0 : 0
4	MsOH (60)	—	20	3	28 : 43	1 : 1.5 : 0 : 0
5	TFA (120)	—	70	24	81 : 11	7 : 1 : 0 : 0
6	TFA (120)	—	20	24	50 : 4	11 : 1 : 0 : 0
7	**TFA (120)**	**—**	**40**	**30**	**80 : 8**	**10 : 1 : 0 : 0**
8	TFA (30)	—	40	30	—	—
9	TFA (30)	DCE	70	30	Traces	—

[a] Yields of isolated products.

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Scheme 1 Synthesis [a] of **3a–j**, **4a–h**, **7a–c**; [a] yields of isolated products; [b] mixture of isomers.

during the reaction. It is noteworthy that the reaction could be successfully extended to benzannulated derivatives **2a–c**, resulting in the selective formation of products **7a–c** as single isomers in moderate to good yields.

With precursors **3a–j**, **4a–h** and **7a–c** in hand, optimizations were carried out for the acid mediated cycloisomerization for the synthesis of the desired thienonaphtho[*bc*]pyridines and thienonaphtho[*bc*]quinolines (Table 2). The reaction was optimized for the transformation of the mono-cyclized precursor **3a** into the bis-cyclized product **5a**. The best yield of **5a** (82%) was obtained using *p*-toluenesulfonic acid (*p*TsOH·H$_2$O, 30 eq.) as the acid and xylene as the solvent at an elevated temperature (140 °C), while the use of methanesulfonic acid (MsOH) gave lower yields (Table 2, entries 1–3). Application of these optimized conditions to the mono-cyclized precursor **7a** resulted in only 42% yield of the desired bis-cyclized 3,11-diphenylthieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]quinoline **8a** (Table 2, entry 4). Hence, we tested the transformation of the non-cyclized precursor **2a** into **8a** using MsOH at 140 °C (Table 2, entry 6). To our delight, the desired bis-annulated product **8a** was formed in an improved yield (68%) directly from precursor **2a**. The yield is even higher as compared to the step-wise protocol described above and avoids the tedious purification of intermediates. It is noteworthy that only one single isomer of **8a** was formed.

The optimized conditions were successfully applied to various precursors **3a–j**, **4a–h** and **2a–c** and the desired products **5a–j**, **6a–b** and **8a–c** were formed in moderate to very

Table 2 Optimization of the cycloisomerisation reaction

Entry	Precursor	Acid (eq.)	Solvent	T, °C	t, h	Yield (%)
1	**3a**	MsOH (30)	—	120	24	*53*
2	**3a**	*p*TsOH·H$_2$O (30)	Xylene	140	24	*82*
3	**3a**	*p*TsOH·H$_2$O (60)	Xylene	140	24	76
4	**7a**	*p*TsOH·H$_2$O (30)	Xylene	140	24	*42*
5	**2a**	*p*TsOH·H$_2$O (30)	Xylene	140	24	*30*
6	**2a**	MsOH (30)	Xylene	140	24	*68*

Yields of isolated products.

good yields, respectively (Fig. 2). The best yield (98%) was obtained for product **5e** containing an electron withdrawing fluorine substituent located at the *para* position of the phenyl group. Using the DMA-substituted precursor **3j** (used as a mixture of two isomers) afforded product **5j**, albeit in only 24% yield. For comparison, an equally low yield (32%) was
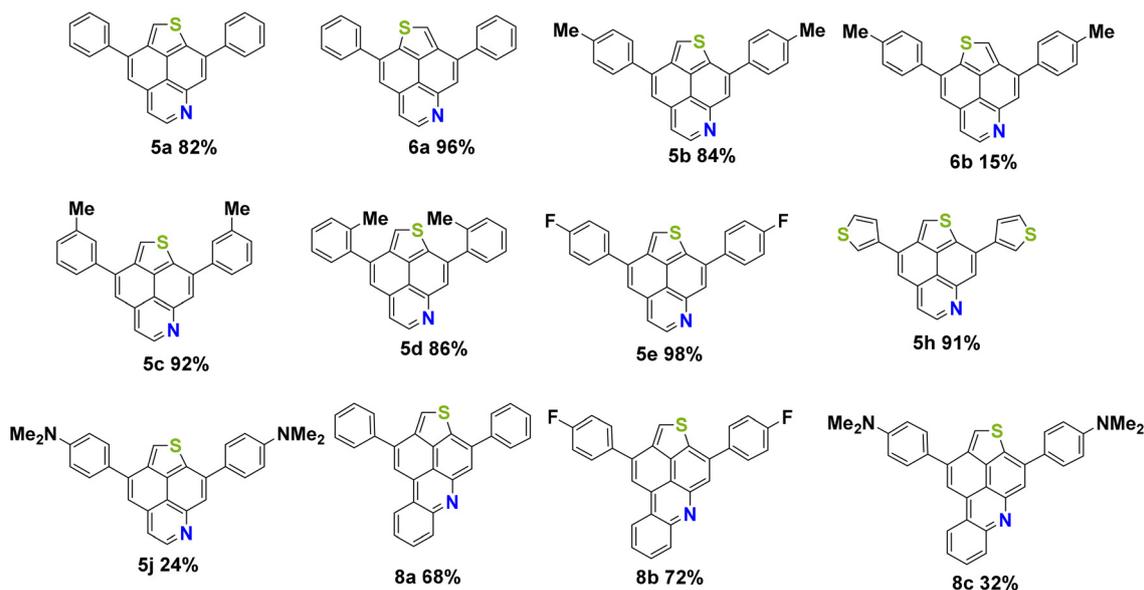
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5a 82% **6a 96%** **5b 84%** **6b 15%**

5c 92% **5d 86%** **5e 98%** **5h 91%**

5j 24% **8a 68%** **8b 72%** **8c 32%**

Fig. 2 Synthesis of **5a–j**, **6a–b** and **8a–c**; yields of isolated products.

observed for the DMA-substituted product **8c**. The reduced yield of both compounds might be explained by the protonation of the amine during the reaction and its transformation from a donor to an acceptor group. Additionally, purification by column chromatography was hampered by the low solubility of DMA-substituted products.

The structure of **8a** was independently confirmed by X-ray crystal structure analysis. Crystals were grown from mixtures of heptane and CH$_2$Cl$_2$ by slow evaporation at room temperature (Fig. 3; ESI, Table S1†). Compound **8a** crystallizes in a triclinic system with the space group $P\bar{1}$. The phenyl substituents are twisted out of the plane of the core structure and adopt a

slipped antiparallel orientation to each other with a centroid-to-centroid distance of 3.43 Å. Furthermore, adjacent molecules form N–H hydrogen bonds with a distance of 2.70 Å.

Physical properties

Steady-state absorption and photoluminescence (PL) spectra in CH$_2$Cl$_2$ were recorded to obtain improved insights into the photophysical properties of the selected compounds. The key photophysical data of compounds **5a**, **5j**, **6a**, **8a** and **8c** are shown in Fig. 4 and Table 3. Emission spectra were recorded at excitation wavelengths of 360 nm (**5a** and **6a**), 400 nm (**5j** and **8a**) and 450 nm (**8c**). The photophysical data are generally con-
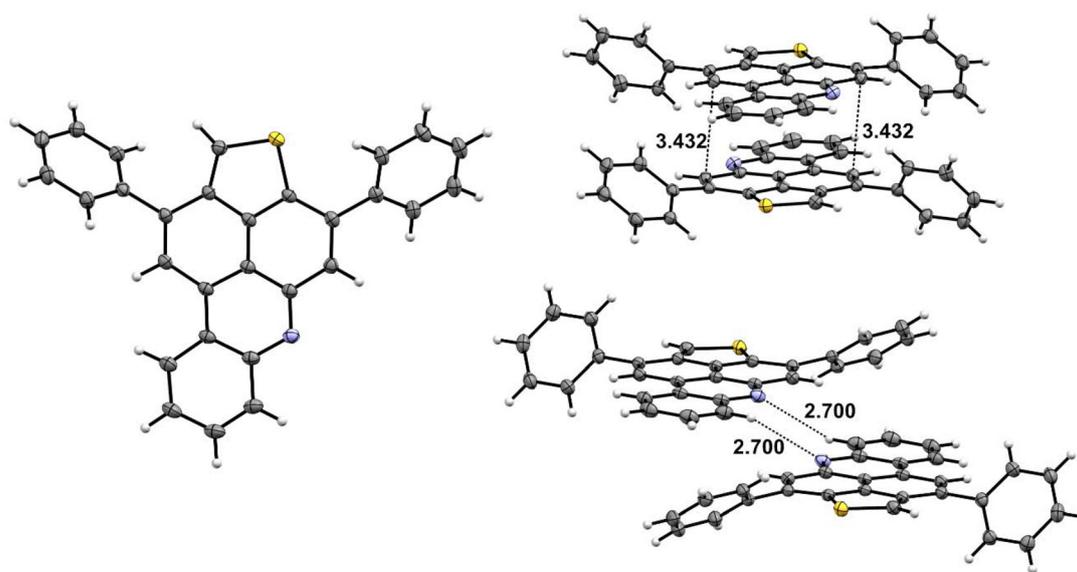

Fig. 3 X-ray crystal structures of **8a** and intermolecular packing of **8a** (determined at 123 K; thermal ellipsoids are drawn at the 50% probability level).

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Table 3 Spectroscopic data of selected compounds in CH_2Cl_2 ($c = 10^{-5}$ M) at 20 °C

	5a [a]	5j [b]	6a [a]	8a [b]	8c [c]
$\lambda_{1,abs}$ [nm]	373	—	374	436	483
$\log \varepsilon_{\lambda_1}$	4.30	—	3.85	4.21	3.83
$\lambda_{2,abs}$ [nm]	390	396	390	460	509
$\log \varepsilon_{\lambda_2}$	4.25	4.05	3.86	4.18	3.81
$\lambda_{3,abs}$ [nm]	—	501	—	512	595
$\log \varepsilon_{\lambda_3}$	—	3.71	—	3.30	3.49
$\lambda_{1,em}$ [nm]	413	547	408	483	600
$\lambda_{2,em}$ [nm]	430		427	512	
$\phi^{d,e}$ [nm]	0.08	0.13	0.10	0.51	0.09

[a] λ_{em}^{360} [nm]. [b] λ_{em}^{400} [nm]. [c] λ_{em}^{450} [nm]. [d] Fluorescence standard: quinine hemisulfate monohydrate in 0.05 M H_2SO_4 ($\phi = 0.52$). [e] Fluorescence standard: coumarin 153 in EtOH ($\phi = 0.38$).

sistent with earlier studies on related compounds, revealing the absorption features of azapyrene and thienonaphthopyridine (TNP) with well-resolved vibrational progression bands.[40,42–45]

The lowest energy absorption band of **5a** shows remarkably higher extinction coefficients ($\varepsilon = 2.3 \times 10^4$ M^{-1} cm^{-1}) in comparison with **6a**, which also possesses more than half of the absorptivity as compared to **TNP**. However, the variation in the position of N-doping only has a negligible impact on the absorption edge of all three TNP derivatives. TD-DFT calculations at the B3LYP level suggest that for all three compounds, the S1 ← S0 transition originates from HOMO → LUMO with a reasonable oscillator strength and are in good agreement with experimental results (ESI, Tables S11 and S13†).[46] The extension of conjugation by fusion of an additional benzene ring (**8a**) leads to bathochromically shifted absorption bands in comparison with **5a**. Compounds **5j** and **8c**, containing DMA as a strong donor, show substantially altered absorption and emission spectra. In particular, **5j** and **8c** display a strongly red-shifted lowest energy band with loss of its absorption fine structure. The emission spectra of both compounds exhibit notable bathochromic shifts from two-band emission to a single very broad emission band, indicating the presence of intramolecular charge-transfer (ICT) features, which were also observed in previously reported amino-substituted pyrenes, 1- and 2-azapyrenes and **TNP**.[40,42,43] Quantum yields (QYs) were determined in reference to quinine hemisulfate monohydrate in 0.05 M H_2SO_4 ($\phi = 0.52$) and coumarin 153 in ethanol ($\phi = 0.38$) as fluorescence standards (ESI, Table S2†).[47] The highest fluorescence QY of 0.51 in dichloromethane was detected for derivative **8a**, while derivatives **5a**, **5e** and **6a** showed relatively low QYs of 0.08, 0.08 and 0.13, respectively. The fluorescence QY of **5j** (0.13) is slightly higher than that of its unsubstituted counterpart **5a**, whereas derivative **8c** exhibits a decrease in QY (0.09) more than 5 times in comparison with **8a**.

Hence, variation of the relative position of nitrogen and sulfur in TNP has negligible effects on the absorption edges and absorption fine structure. In comparison, benzannulation on the pyridine ring leads to strong alteration of the absorption features of the respective TNP derivatives.

To investigate the potential ICT properties, the emission spectra of derivatives **5j** and **8c** were measured in various solvents of different polarities (Fig. 5). The emission in acetonitrile is bathochromically shifted by 110 nm ($\lambda_{em,max}$ = 605 nm **5j**) and 117 nm ($\lambda_{em,max}$ = 653 nm **8c**) in comparison with nonpolar toluene. It is noteworthy that changing the solvent from acetonitrile to the polar and protic solvent ethanol leads to a blue shift of the emission maximum by 14 nm ($\lambda_{em,max}$ = 591 nm **5j**) and 18 nm ($\lambda_{em,max}$ = 635 nm **8c**). The emission intensities of **5j** and **8c** varied with changes in the solvent polarity. Nonpolar solvents cause intensity enhancements as compared to polar solvents. These results clearly suggest a certain ICT for **5j** and **8c**, which is characterized by stabilization of the excited state in polar environments, due to a large dipole moment in the excited state.[48] Hence, the dipole moments of **5j** and **8c** have been calculated for their S_0 and excited S_1 states, confirming the experimental results. In particular, TNP **5j** shows an increase in its calculated dipole moment upon excitation from 7.7 to 23.9 Debye, while for benzo-TNP **8c**, the dipole moment is increased from 8.3 to 22.3 Debye.

Furthermore, the impact of protonation on the optical properties was studied and the changes in the absorption and emission spectra upon protonation are clearly shown in Fig. 6 for **5a** and in Fig. S2 (ESI†) for **6a** and **8a**. All studied compounds showed red shifted absorption and emission spectra when trifluoroacetic acid (TFA) was added to a CH_2Cl_2 solution of **5a**, **6a** or **8a**. For all compounds, the intensity of the low energy band is strongly enhanced, while the shape of the emission band is roughly the same. However, the intensity of the second emission band is reduced with respect to the first emission band. The bathochromic shift of both spectra might be explained by improved ICT properties from the electron-rich thiophene to the positively charged pyridinium.

The redox behavior of compounds **5a**, **5j**, **6a**, **8a** and **8c** in comparison with the recently reported **TNP** was investigated by cyclic voltammetry experiments (Table 4; ESI, Fig. S3†). In comparison with the voltammogram of **TNP** (one irreversible oxidation peak at 0.92 V vs. Fc^+/Fc), the voltammograms of isomers **5a** and **6a** display two irreversible oxidations events. However, compound **5j**, bearing strong π-donating NMe_2-substituents, displays a broad oxidation potential accompanied by a shoulder at a less positive potential (0.62 V vs. Fc^+/Fc), which exemplifies the electron donating ability of the dimethylaniline substituents. The fusion of an additional benzene ring to the core structure results in three irreversible oxidations events (compounds **8a** and **8c**). Interestingly, the presence of NMe_2-groups in **8c** does not lead to a more facile oxidation as compared to its unsubstituted analogue **8a**.

To rationalize the observed experimental results and to obtain additional insight into the intrinsic electronic characteristics of π-conjugated thienonaphtho[bc]pyridines and thienonaphtho[bc]quinolines, density functional theory (DFT) calculations were performed.[46] Calculations were carried out for
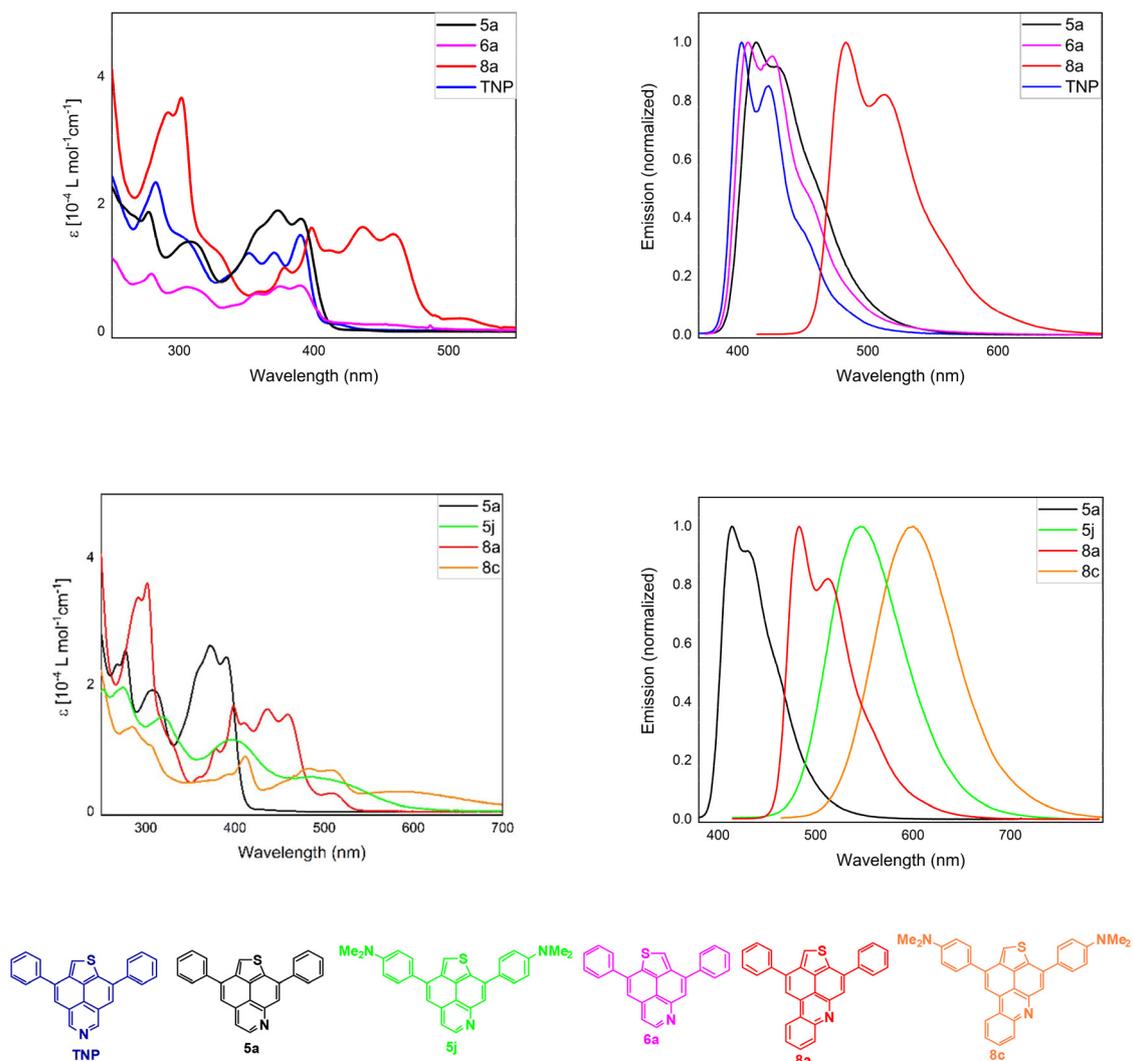
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Fig. 4 Absorption (solid lines) and emission (dashed lines) spectra of selected compounds.
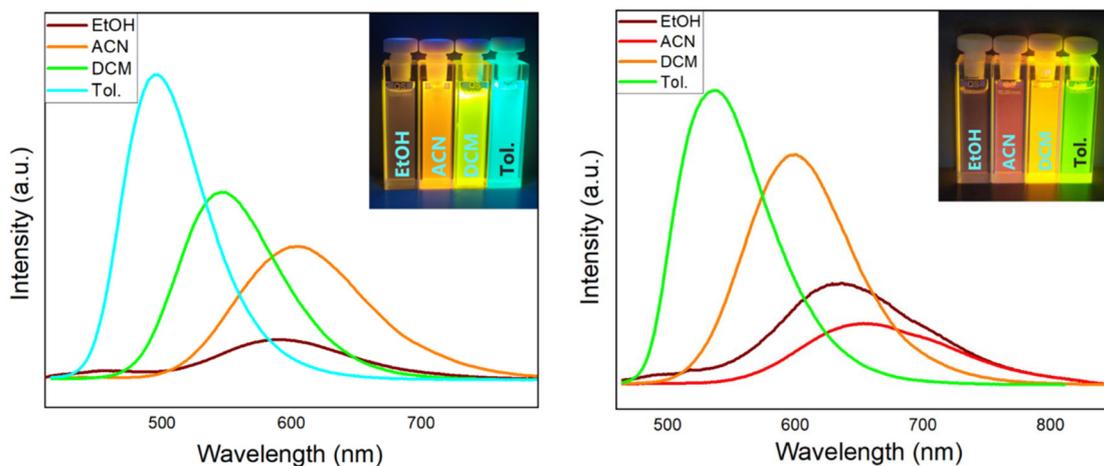
Fig. 5 Emission spectra of **5j** (left) and **8c** (right) ($c = 10^{-5}$ M) at 20 °C.

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Table 4 Cyclic voltammograms of **5a** and **5j** and CV data for **5a**, **5j**, **6a**, **8a**, and **8c** [a]

	5a	**5j**	**6a**	**8a**	**8c**
E_1^{Ox}	1.02	0.62	1.01	0.68	0.99
E_2^{Ox}	1.67	1.62	1.74	1.47	1.50
E_3^{Ox}				1.83	1.86
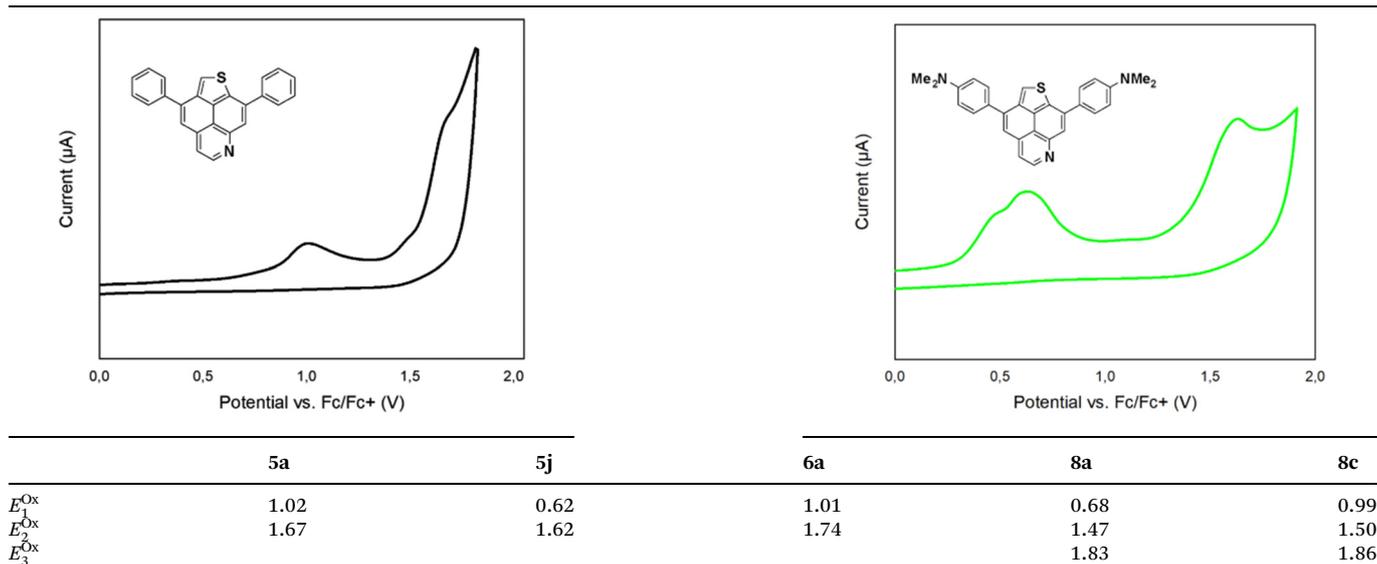
[a] Measured in CH_2Cl_2 with 0.1 M n-Bu$_4$NPF$_6$ as a supporting electrolyte, glassy carbon working electrode, ANE2 as a reference electrode and Pt counter-electrode with ferrocene as a standard at a scan rate of 50 mV s^{-1}.

5a, **5j**, **6a**, **8a** and **8c** as well as for **TNP**, utilizing the B3LYP functional in combination with the 6-311G(d,p) basis set and a polarizable continuum model (PCM) of dichloromethane using the integral equation formalism variant (IEFPCM) (Scheme 2, ESI, Scheme S2†).

In comparison with **TNP**, the HOMO and LUMO energy levels of regioisomeric **5a** and **6a** are reduced, with **5a** slightly more stabilized as compared to **6a**. However, the calculated band gap remains constant. The expansion of the π-conjugated system leads to even more stabilized HOMO and LUMO levels
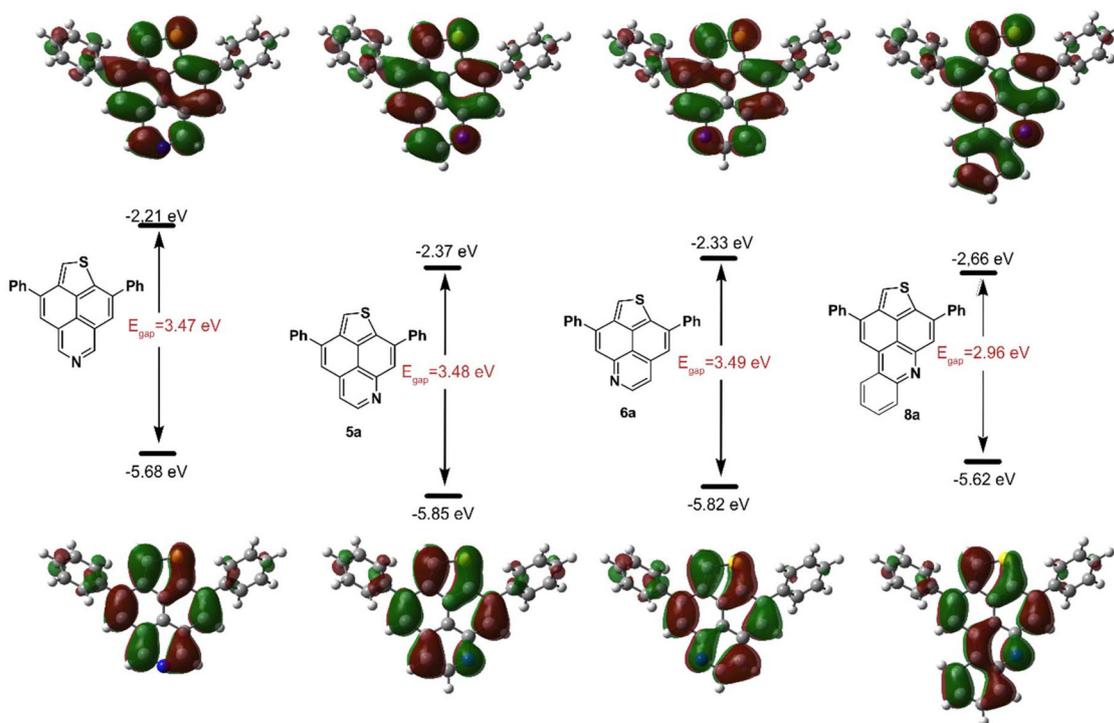
Scheme 2 Calculated frontier molecular orbitals and energy levels at the B3LYP/6-311G(d,p) level of theory within IEFPCM of dichloromethane (isovalue = 0.02 a.u.).
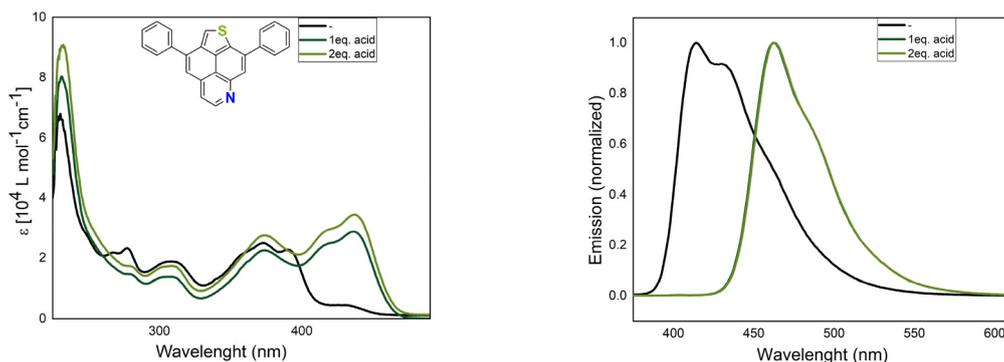
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Fig. 6 Absorption (left) and normalized emission spectra (right) of **5a** in CH_2Cl_2 ($c = 10^{-5}$ M) at 20 °C with different equivalents of TFA.

for **8a**, as corroborated by its red-shifted absorption and emission bands and consequently, its optical band gap. The DMA functional group as a strong donor leads to energetically elevated frontier molecular orbitals (**5j** and **8c**) accompanied by reduced band gaps due to greater destabilization of the HOMO energies (ESI, Fig. S2†). Moreover, the presence of the DMA group (**5c**) leads to altered electron density distribution of the HOMO but does not affect the LUMO. In **5j**, the electron density is mainly located on the DMA group and the edges of the **TNP** framework, whereas in **TNP**, **5a** and **6a**, it is mainly distributed across the polycyclic scaffold. However, for **8c**, this effect is diminished, and the electron density is distributed across the entire molecule, which might explain why the DMA group has less impact on the oxidation behavior of **8c** compared to **5j**. In general, the calculated HOMO and LUMO energies correlate very well with experimental results.

To investigate the aromatic behavior, we performed nuclear-independent chemical shift (NICS) calculations and visualized the bond currents using the NICS2BC program developed by Gershoni-Poranne *et al.*[49–52] The calculations were performed for the unsubstituted core structures **5′**, **6′** and **8′** and the results were compared with those of **TNP** (Fig. 7). As shown in the depictions, all compounds exhibit a global diatropic ring current with strong variation in current density along the edges. However, the global ring currents depend on the relative position of the heteroatoms within the structure. Thus, stronger ring currents can be observed on the molecular side where the sulfur atom is located. However, it does not depend on the position of the nitrogen, as reflected by the determined NICS values of the central naphthalene unit. Each compound exhibits a semiglobal ring current of its inherent thienoquinoline or thienoacridine moiety. Local ring currents are observed for the thiophene, pyridine or quinoline rings. The central naphthalene moiety shows no semiglobal ring current and exhibits significantly different NICS values for both central benzene rings. The aryl ring involved in the semiglobal ring current of the thienoquinoline or thienoacridine moiety possesses high aromaticity, while the aromaticity of the aryl ring located outside this semiglobal ring current is strongly decreased. Thus, **6′** shows a significant difference as compared to **5′** and **8′**, since the sulfur is located opposite to
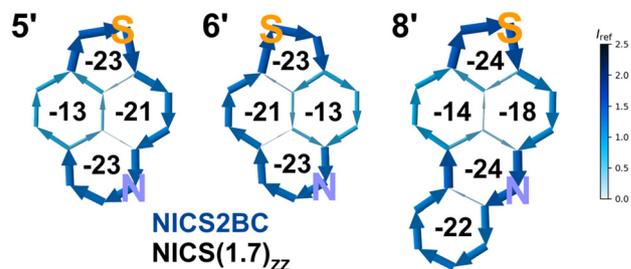

Fig. 7 NICS calculations for thieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]pyridine (**5′**); thieno[4′,3′,2′:4,5]naphtho[1,8-*bc*]pyridine (**6′**); and thieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]quinoline (**8′**). NICS2BC bond current graphs with NICS(1.7)$_{ZZ}$ values marked in black. Current was calculated from NICS(1.25)$_{ZZ}$ strength relative to I_{ref} (ring current of benzene, 11.5 nA T^{-1}).[51]

the nitrogen. When comparing **5′** with the π-expanded compound **8′**, only slight differences in the NICS values are observed. Finally, **TNP** reveals almost identical NICS values as compared to **5′** and **6′**.[41]

Conclusions

In conclusion, we have successfully developed an efficient and broadly applicable protocol for the synthesis of hitherto unknown thienonaphtho[*bc*]pyridines and thienonaphtho[*bc*]quinolines in very good yields by Brønsted acid mediated cycloisomerization. This methodology allows for selective access to regioisomeric products. The photophysical and electrochemical properties of the desired compounds were extensively studied and the experimental data were compared with theoretical results. Our studies revealed that the incorporation of the thiophene ring into the core structure plays a crucial role in the stabilization of the energy levels of the HOMO and LUMO. The orientation of the sulfur and nitrogen atoms within the structure has a negligible effect on the inherent optical and electrochemical properties of the parent TNP structure. Expansion of the π-conjugated system by the introduction of an additional benzene ring in the core structure however leads to significant effects on electronic struc-

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tures, stabilizing the frontier molecular orbitals by reducing the HOMO–LUMO gap. It is noteworthy that the strong π-donating DMA unit of compounds **5j** and **8c** leads to strongly red-shifted, structureless absorption and emission properties and produces a large positive solvatochromism, suggestive of the strong ICT character of these compounds due to certain push–pull characteristics. Our findings are expected to have a significant impact on future investigations on the development and application of S- and N-doped PAHs.

Experimental section

General information

Nuclear magnetic resonance spectra (^{1}H/^{13}C/^{19}F NMR) were recorded on a Bruker AVANCE 300 III, 250 II, or 500 instrument. The analyzed chemical shifts (δ) are referenced to residual solvent signals from the deuterated solvents CDCl$_3$ (δ = 7.26 ppm/77.16 ppm) or p-xylene-d$_{10}$ (δ = 2.1 ppm/ 18.75 ppm). Multiplicities due to spin–spin correlation are reported as follows: s = singlet, d = doublet, dd = double doublet, and 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 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 were recorded using an Agilent Cary Eclipse fluorescence spectrophotometer. Cyclovoltammetry (CV) experiments were performed at room temperature in a three-electrode cell with CH$_2$Cl$_2$ as the solvent, 0.1 M nBu$_4$NPF$_6$ as the supporting electrolyte, a glassy carbon working electrode, ANE2 (Ag/AgNO$_3$ 0.01 M in CH$_3$CN) as the reference electrode, and Pt as the counter electrode (0.5 mm diameter platinum wire, 6.35 mm outer diameter). Ferrocene was used as the external standard (1 mM in CH$_3$CN), with potentials reported $vs.$ Fc$^+$/Fc. The potentiostat used was a PalmSense EmStat3 blue. The working electrode is a 3 mm diameter (length 80 mm, 6.35 mm outer diameter) glassy carbon disk electrode with a KeI-F coating that was polished on a polishing pad with an aqueous alumina slurry (0.03 micro alumina powder). Basic and high-resolution mass spectra (MS/HRMS) were measured on instruments that were paired with a preceding gas chromatograph (GC) or liquid chromatograph (LC). The samples were 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. X-ray single-crystal structure analysis was performed on a Bruker Apex Kappa-II CCD diffractometer. The solvents used, acetonitrile, dioxane, toluene and xylene, were obtained as dry solvents from commercial sources and employed without further purification. Solvents for extraction and column chromatography were distilled prior to use. Other reagents,

catalysts, ligands, acids and bases were utilized in purchased purity. Column chromatography was performed using Merck Silica gel 60 (particle size 40–63 μm).

Synthesis of 2,4-dichloro-3-(thiophen-3-yl)quinoline. An argon flushed pressure tube was loaded with 3-bromo-2,4-dichloroquinoline (130 mg, 0.47 mmol), 1.0 eq. of 3-thienyl-boronic acid, 3.0 eq. of K$_3$PO$_4$, Pd(dppf)Cl$_2$ (0.05 eq.), 4.5 ml of dioxane and 1 ml of H$_2$O. The pressure tube was sealed with a Teflon cap and the reaction mixture was stirred in a stainless-steel heating block for 5 h at 100 °C. After cooling to room temperature, the reaction was quenched with distilled water and extracted three times with ethyl acetate. The combined organic phases were dried over Na$_2$SO$_4$ and filtered, and the solvent was distilled in $vacuo$. After purification by column chromatography (heptane/DCM 2 : 1), the desired product was isolated as a white solid in 51% yield (67 mg, 0.24 mmol); mp 69–71 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 8.23 (dd, ^3J = 8.4 Hz, ^5J = 0.6 Hz, 1H, CH$_{Ar}$), 8.06 (ddd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, ^5J = 0.7 Hz, 1H, CH$_{Ar}$), 7.79 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH$_{Ar}$), 7.66 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.48 (dd, ^3J = 4.9 Hz, ^4J = 3.0 Hz, 1H, CH$_{Ar}$), 7.42 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.16 (dd, ^3J = 4.9 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 150.7, 146.9, 143.7, 134.9 (C), 131.4, 129.0 (CH$_{Ar}$), 128.9 (C), 128.3, 126.4 (CH$_{Ar}$), 125.7 (C), 125.6, 125.0 (CH$_{Ar}$) ppm. MS (EI, 70 eV): m/z (%) = 283 (16), 281 (83), 280 (19), 278 ([M]$^+$, 100), 244 (30), 209 (63), 164 (25), 45 (26). HRMS (ESI) m/z: [M + H]$^+$ calcd for: C$_{13}$H$_8$Cl$_2$NS 279.9754; found 279.9757. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1475 (s), 1412 (m), 1337 (m), 1296 (s), 1107 (m), 1010 (m), 841 (s), 756 (vs), 732 (s), 653 (s), 598 (s), 470 (m).

Synthesis of 4,4′-((3-chloropyridine-2,4-diyl)bis(ethyne-2,1-diyl))dibenzonitrile and 3-chloro-2,4-bis(thiophen-3-ylethynyl)pyridine. An argon flushed pressure tube was loaded with 1 eq. of 3-chloropyridine-2,4-diyl bis(trifluoromethanesulfonate) (200 mg, 0.49 mmol), CuI (0.05 eq., 4.6 mg), Pd(PPh$_3$)$_4$ (0.025 eq., 14.2 mg), 1 ml of HNiPr$_2$, 2.2 eq. of the respective alkyne and 2 ml of dry acetonitrile. The pressure tube was sealed with a Teflon cap and the reaction mixture was stirred for 24 h at 25 °C. The reaction was quenched with distilled water and extracted three times with ethyl acetate. The combined organic phases were dried over Na$_2$SO$_4$ and filtered, and the solvent was distilled in $vacuo$. After purification by column chromatography (heptane/EtOAc 5 : 1), the desired alkynylated products were isolated.

4,4′-[(3-Chloropyridine-2,4-diyl)bis(ethyne-2,1-diyl)]dibenzonitrile was obtained as a beige solid in 38% yield (67 mg, 0.19 mmol) (heptane/EtOAc 4 : 1); mp 245–250 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.53 (d, ^3J = 4.9 Hz, 1H, CH$_{Ar}$), 7.77–7.72 (m, 2H, CH$_{Ar}$), 7.71–7.69 (m, 6H, CH$_{Ar}$), 7.69–7.66 (m, 1H, CH$_{Ar}$), 7.63 (d, ^3J = 3.7 Hz, 1H, CH$_{Ar}$), 7.44 (d, ^3J = 4.9 Hz, 1H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 147.7 (CH$_{Ar}$), 142.1 (C), 133.2, 132.9, 132.7, 132.4, 132.3 (CH$_{Ar}$), 131.3, 126.7, 126.4 (C), 126.3 (CH$_{Ar}$), 118.3, 118.2, 113.4, 113.1 (C), 97.7, 93.1, 89.3, 87.2 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 366 (8), 365 (35), 364 (28), 363 ([M]$^+$, 100), 328 (6), 327 (9), 300 (11), 182 (10), 175 (5). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{23}$H$_{10}$N$_3$Cl

363.0558; found 363.0555. Calcd for $C_{23}H_{10}N_3{}^{37}Cl$ ([M]$^+$) 365.0528; found 365.0539. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2225 (m), 1601 (m), 1564 (s), 1390 (m), 1271 (m), 1038 (m), 832 (vs), 550 (vs), 469 (m).

3-Chloro-2,4-bis[(thiophen-3-yl)ethynyl]pyridine was obtained as a brown solid in 90% yield (143 mg, 0.44 mmol) (Hep/EtOAc 4 : 1); mp 112–115 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.44 (s, 1H, CH$_{Ar}$), 7.73–7.68 (m, 2H, CH$_{Ar}$), 7.37–7.32 (m, 3H, CH$_{Ar}$), 7.32–7.29 (m, 1H, CH$_{Ar}$), 7.27–7.24 (m, 1H, CH$_{Ar}$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 147.3 (CH$_{Ar}$), 142.7, 134.4, 132.0 (C), 131.2, 131.2, 130.2, 130.0, 126.1, 125.8, 125.4 (CH$_{Ar}$), 121.2, 121.0 (C), 95.1, 90.4, 85.8, 83.8 (C$_{Alkyn}$) ppm. MS (EI, 70eV): m/z (%) = 328 (10), 327 (41), 326 (21), 324 ([M]$^+$, 100), 133 (16), 69 (10), 58 (15), 45 (41). HRMS (ESI) m/z: [M + H]$^+$ calcd for: $C_{17}H_9ClNS_2$ 325.9865; found 325.9867. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3101 (w), 2209 (m), 1564 (s), 1445 (m), 1366 (m), 1115 (m), 826 (m), 773 (vs), 682 (m), 618 (s), 552 (s).

General procedure (A) for the synthesis of 2,4-bis(arylethynyl)-3-(thiophen-3-yl)pyridines 1a–j

An argon flushed pressure tube was loaded with 1.0 eq. of 3-chloro-2,4-bis(arylethynyl)pyridine, 2.0 eq. of K$_3$PO$_4$, Pd$_2$(dba)$_3$ (0.05 eq.), SPhos (0.1 eq.), 2.0 eq. of 3-thienylboronic acid and 2 ml of dry toluene. The pressure tube was sealed with a Teflon cap and the reaction mixture was stirred in a stainless-steel heating block for 24 h at 110 °C. After cooling to room temperature, the reaction was quenched with distilled water and extracted three times with ethyl acetate. The combined organic phases were dried over Na$_2$SO$_4$ and filtered, and the solvent was distilled *in vacuo*. After purification by column chromatography (Hep/EtOAc 4 : 1), the desired products 1a–j were isolated.

2,4-Bis(phenylethynyl)-3-(thiophen-3-yl)pyridine (1a). According to general procedure A, the title compound 1a was obtained as a brown solid in 80% yield (102 mg, 0.28 mmol) (heptane/EtOAc 4 : 1); mp 115–119 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.55 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.74 (dd, ^4J = 2.9 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.52 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.45 (dd, ^3J = 5.0 Hz, ^4J = 2.9 Hz, 1H, CH$_{Ar}$), 7.43 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.41–7.38 (m, 2H, CH$_{Ar}$), 7.37–7.30 (m, 8H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 148.4 (CH$_{Ar}$), 142.8, 136.4, 136.2 (C), 132.1, 131.9 (CH$_{Ar}$), 131.4 (C), 129.8, 129.4, 129.1, 128.6, 128.5, 126.5, 125.2, 124.2 (CH$_{Ar}$), 122.4, 122.2 (C), 97.5, 92.8, 88.7, 86.7 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 362 (20), 361 (70), 360 ([M]$^+$, 100), 359 (37), 358 (12). HRMS (EI) m/z: [M]$^+$ calcd for: $C_{25}H_{15}NS$ 360.0841; found 360.0834. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2921 (vs), 2851 (s), 2213 (w), 1559 (m), 1717 (m), 838 (m), 752 (s), 688 (s), 653 (s), 523 (m).

3-(Thiophen-3-yl)-2,4-bis(p-tolylethynyl)pyridine (1b). According to general procedure A, the title compound 1b was obtained as a brown oil in 73% yield (183 mg, 0.47 mmol) (heptane/EtOAc 4 : 1). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.52 (d, ^3J = 5.1 Hz, 1H, CH$_{Ar}$), 7.73 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.51 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.43 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH$_{Ar}$), 7.39 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.32–7.26 (m, 3H, CH$_{Ar}$), 7.25–7.23 (m, 1H, CH$_{Ar}$), 7.16–7.09 (m, 4H, CH$_{Ar}$), 2.36 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 148.4 (CH$_{Ar}$), 142.9, 139.8, 139.4, 136.5, 135.9 (C), 132.0, 131.9 (CH$_{Ar}$), 131.5 (C), 129.9, 129.4, 129.2, 126.5, 124.9, 124.1 (CH$_{Ar}$), 119.4, 119.2 (C), 97.8, 93.1, 88.3, 86.3 (C$_{Alkyn}$), 21.7 (CH$_3$) ppm. MS (EI, 70eV): m/z (%) = 390 (30), 389 ([M]$^+$, 100), 388 (81), 387 (16), 386 (12), 375 (11), 374 (49), 373 (28), 372 (12), 359 (12), 91 (10). HRMS (ESI) m/z: [M + H]$^+$ calcd for: $C_{27}H_{20}NS$ 390.1316; found 390.1316. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2209 (m), 1559 (s), 1508 (s), 1417 (s), 1176 (m), 960 (m), 811 (vs), 768 (s), 677 (m), 653 (s), 525 (s).

3-(Thiophen-3-yl)-2,4-bis(m-tolylethynyl)pyridine (1c). According to general procedure A, the title compound 1c was obtained as a brown oil in 86% yield (216 mg, 0.56 mmol) (heptane/EtOAc 4 : 1). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.53 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.74 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.53 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.45 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH$_{Ar}$), 7.40 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.24–7.11 (m, 8H, CH$_{Ar}$), 2.33 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 148.3 (CH$_{Ar}$), 142.8, 138.3, 138.1, 136.4, 136.0 (C), 132.6, 132.4 (CH$_{Ar}$), 131.4 (C), 130.3, 130.0, 129.9, 129.2, 129.0, 128.4, 128.3, 126.5, 125.1, 124.1 (CH$_{Ar}$), 122.2, 122.0 (C), 97.7, 93.0, 88.4, 86.4 (C$_{Alkyn}$), 21.3, 21.3 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 390 (30), 389 ([M]$^+$, 100), 388 (79), 387 (15), 374 (43), 373 (28), 372 (15), 359 (15), 187 (16), 140 (24), 91 (39), 89 (17), 65 (36), 45 (20), 39 (26). HRMS (EI) m/z: [M]$^+$ calcd for: $C_{27}H_{19}NS$ 389.1232; found 389.1220. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2206 (m), 1559 (s), 1483 (m), 1417 (s), 1090 (m), 836 (m), 780 (vs), 653 (s), 544 (s), 517 (m).

3-(Thiophen-3-yl)-2,4-bis(o-tolylethynyl)pyridine (1d). According to general procedure A, the title compound 1d was obtained as a brown oil in 92% yield (443 mg, 1.14 mmol) (heptane/EtOAc 4 : 1). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.57 (d, ^3J = 5.1 Hz, 1H, CH$_{Ar}$), 7.61 (dd, ^4J = 2.8 Hz, ^4J = 1.5 Hz, 1H, CH$_{Ar}$), 7.43 (d, ^3J = 5.1 Hz, 1H, CH$_{Ar}$), 7.42–7.40 (m, 1H, CH$_{Ar}$), 7.40–7.37 (m, 2H, CH$_{Ar}$), 7.35–7.31 (m, 1H, CH$_{Ar}$), 7.25–7.21 (m, 1H, CH$_{Ar}$), 7.21–7.18 (m, 1H, CH$_{Ar}$), 7.18–7.09 (m, 4H, CH$_{Ar}$), 2.22 (s, 6H, CH$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 148.6 (CH$_{Ar}$), 143.3, 141.0, 140.9, 136.9, 136.1 (C), 132.8, 132.5 (CH$_{Ar}$), 132.0 (C), 129.7, 129.6, 129.4, 129.1, 125.9, 125.8, 125.6, 125.0, 124.9 (CH$_{Ar}$), 122.2, 122.0 (C), 96.6, 92.2, 91.8, 90.2 (C$_{Alkyn}$), 20.4, 20.4 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 390 (30), 389 ([M]$^+$, 100), 388 (97), 387 (29), 386 (19), 374 (27), 356 (29), 355 (32), 354 (38), 353 (15), 342 (23), 341 (32), 340 (24), 298 (22), 297 (16). HRMS (ESI) m/z: [M + H]$^+$ calcd for: $C_{27}H_{20}NS$ 390.1316; found 390.1312. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2206 (m), 1559 (s), 1485 (m), 1415 (s), 1110 (w), 836 (m), 754 (vs), 712 (s), 655 (s), 546 (m), 457 (m).

2,4-Bis((4-fluorophenyl)ethynyl)-3-(thiophen-3-yl)pyridine (1e). According to general procedure A, the title compound 1e was obtained as a yellow solid in 66% yield (131 mg, 0.33 mmol) (heptane/EtOAc 4 : 1); mp 124–126 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 8.54 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.70 (dd, ^4J = 2.8 Hz, ^4J = 1.5 Hz, 1H, CH$_{Ar}$), 7.47 (dd, ^3J = 5.0 Hz, ^4J = 2.1 Hz, 2H, CH$_{Ar}$), 7.41 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.39–7.29 (m, 4H, CH$_{Ar}$), 7.06–6.96 (m, 4H, CH$_{Ar}$) ppm. ^{19}F NMR (282 MHz, CDCl$_3$) δ = −108.82 (s, 1F, CF), −109.33 (s, 1F, CF) ppm. ^{13}C

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NMR (63 MHz, CDCl$_3$) δ = 165.2 (d, $^1J_{C,F}$ = 251.5 Hz), 163.1 (d, $^1J_{C,F}$ = 250.9 Hz, C), 148.5 (CH$_{Ar}$), 142.7, 136.4, 136.2 (C), 134.2 (d, $^3J_{C,F}$ = 8.5 Hz), 134.0 (d, $^3J_{C,F}$ = 8.5 Hz, CH$_{Ar}$), 131.3 (C), 129.8, 126.4, 125.0, 124.3 (CH$_{Ar}$), 118.5 (d, $^4J_{C,F}$ = 3.5 Hz), 118.3 (d, $^4J_{C,F}$ = 3.6 Hz, C), 116.2 (d, $^2J_{C,F}$ = 22.2 Hz), 115.9 (d, $^2J_{C,F}$ = 22.2 Hz, CH$_{Ar}$), 96.5, 91.8, 88.4, 86.4 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 398 (20), 397 (84), 396 ([M]$^+$, 100), 395 (29), 75 (11). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{25}$H$_{13}$NSF$_2$ 396.0653; found 396.0646. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2211 (m), 1559 (m), 1504 (s), 1228 (s), 1153 (s), 830 (vs), 764 (s), 653 (s), 647 (s), 527 (s).

3-(Thiophen-3-yl)-2,4-bis((4-(trifluoromethyl)phenyl)ethynyl) pyridine (1f). According to general procedure A, the title compound **1f** was obtained as a yellow solid in 54% yield (96 mg, 0.19 mmol) (heptane/EtOAc 4 : 1); mp 154–156 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.59 (d, ^3J = 5.0 Hz, 1H, CH$_{Ar}$), 7.70 (qt, ^4J = 2.1 Hz, 1H, CH$_{Ar}$), 7.63–7.54 (m, 4H, CH$_{Ar}$), 7.51–7.41 (m, 7H, CH$_{Ar}$) ppm. ^{19}F NMR (282 MHz, CDCl$_3$) δ = −62.96 (s, 3F, CF$_3$), −62.99 (s, 3F, CF$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 148.7 (CH$_{Ar}$), 142.4, 136.9, 136.1 (C), 132.3, 132.2 (CH$_{Ar}$), 131.0 (q, $^2J_{C,F}$ = 32.3 Hz, C), 129.6 (CH$_{Ar}$), 126.6 (CH$_{Ar}$), 126.1 (d, $^4J_{C,F}$ = 1.4 Hz), 125.9 (d, $^4J_{C,F}$ = 1.4 Hz, C), 125.7 (C), 125.6 (q, $^3J_{C,F}$ = 4.2 Hz), 125.5 (q, $^3J_{C,F}$ = 3.9 Hz, CH$_{Ar}$), 124.7 (CH$_{Ar}$), 122.1, 122.0 (C), 95.9, 91.2, 90.5, 88.4 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 498 (34), 497 ([M]$^+$, 100), 496 (99), 495 (18), 478 (23), 429 (21), 428 (74), 427 (47), 426 (24), 69 (47), 45 (17). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{27}$H$_{13}$NSF$_6$ 497.0667; found 497.0655. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1611 (w), 1561 (m), 1318 (s), 1164 (s), 1102 (vs), 1063 (vs), 1013 (s), 836 (vs), 801 (s), 593 (s).

4,4′-((3-(Thiophen-3-yl)pyridine-2,4-diyl)bis(ethyne-2,1-diyl)) dibenzonitrile (1g). According to general procedure A, the title compound **1g** was obtained as a brown solid in 41% yield (116 mg, 0.28 mmol) (heptane/EtOAc 4 : 1); mp 224–226 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.61 (d, ^3J = 5.1 Hz, 1H, CH$_{Ar}$), 7.69 (dd, ^4J = 2.9 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.66–7.58 (m, 4H, CH$_{Ar}$), 7.55–7.39 (m, 7H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 148.3 (CH$_{Ar}$), 143.8, 141.6, 137.2, 135.7 (C), 132.6, 132.5, 132.3, 132.2 (CH$_{Ar}$), 131.2 (C), 129.5 (CH$_{Ar}$), 126.9 (C), 126.8 (CH$_{Ar}$), 126.7 (C), 125.9, 125.0 (CH$_{Ar}$), 118.4, 118.3, 113.0, 112.7 (C), 96.0, 89.9 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 413 (7), 412 (20), 411 (70), 410 ([M]$^+$, 100), 409 (18), 408 (7), 102 (6), 75 (5), 45 (7). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{27}$H$_{13}$N$_3$S 410.0746; found 410.0743. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2225 (m), 1603 (m), 1559 (m), 1502 (m), 834 (vs), 762 (s), 649 (m), 552 (vs).

3-(Thiophen-3-yl)-2,4-bis(thiophen-3-ylethynyl)pyridine (1h). According to general procedure A, the title compound **1h** was obtained as a brown solid in 75% yield (120 mg, 0.32 mmol) (heptane/EtOAc 4 : 1); mp 97–100 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 8.53 (d, ^3J = 5.1 Hz, 1H, CH$_{Ar}$), 7.73 (dd, ^4J = 2.9 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.51 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.49–7.46 (m, 1H, CH$_{Ar}$), 7.47–7.37 (m, 3H, CH$_{Ar}$), 7.32–7.21 (m, 2H, CH$_{Ar}$), 7.11–7.02 (m, 2H, CH$_{Ar}$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.2 (CH$_{Ar}$), 142.6, 136.2, 135.8, 131.4 (C), 130.4, 129.9, 129.8, 129.7, 126.5, 125.9, 125.6, 124.9, 124.1 (CH$_{Ar}$), 121.5, 121.3 (C), 93.0, 88.4, 88.2, 86.4 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 375 (11), 374 (35), 373 ([M]$^+$, 90), 372 (100), 371 (25), 340 (18), 339 (14), 328 (17), 327 (10), 69

(12), 58 (14), 45 (68). HRMS (ESI) m/z: [M + H]$^+$ calcd for: C$_{21}$H$_{12}$NS$_3$ 374.0132; found 374.0132. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2204 (m), 1561 (m), 1024 (s), 989 (s), 780 (vs), 690 (m), 622 (vs), 554 (s).

2,4-Bis((4-methoxyphenyl)ethynyl)-3-(thiophen-3-yl)pyridine (1i). According to general procedure A, the title compound **1i** was obtained as a yellow solid in 92% yield (130 mg, 0.31 mmol) (heptane/EtOAc 4 : 1); mp 116–122 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 8.50 (d, ^3J = 5.1 Hz, 1H, CH$_{Ar}$), 7.72 (dd, ^4J = 2.9 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.51 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.43 (dd, ^3J = 5.0 Hz, ^4J = 2.9 Hz, 1H, CH$_{Ar}$), 7.39–7.33 (m, 2H, CH$_{Ar}$), 7.33–7.26 (m, 3H, CH$_{Ar}$), 6.89–6.79 (m, 4H, CH$_{Ar}$), 3.81 (s, 3H, OMe), 3.80 (s, 3H, OMe) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 160.5, 160.3 (C), 148.3 (CH$_{Ar}$), 143.0, 136.6, 135.6 (C), 133.7, 133.6 (CH$_{Ar}$), 131.6 (C), 130.0, 126.4, 124.6, 124.0 (CH$_{Ar}$), 114.5, 114.3 (C), 114.3, 114.2 (CH$_{Ar}$), 97.9, 93.1, 87.8, 85.8 (C$_{Alkyn}$), 55.5, 55.4 (OMe) ppm. MS (EI, 70 eV): m/z (%) = 422 (31), 421 ([M]$^+$, 100), 420 (17), 406 (21), 377 (17), 335 (21), 334 (33), 333 (15). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{27}$H$_{19}$NSO$_2$ 421.1131; found 421.1123. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2209 (m), 1603 (s), 1561 (s), 1506 (s), 1390 (m), 1246 (s), 1020 (m), 826 (vs), 550 (s).

4,4′-((3-(Thiophen-3-yl)pyridine-2,4-diyl)bis(ethyne-2,1-diyl)) bis(*N,N*-dimethylaniline) (1j). According to general procedure A, the title compound **1j** was obtained as a brown solid in 74% yield (140 mg, 0.31 mmol) (heptane/EtOAc 4 : 1); mp 120–125 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 8.43 (d, ^3J = 5.3 Hz, 1H, CH$_{Ar}$), 7.75 (dd, ^4J = 3.0, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.54 (dd, ^3J = 5.0, ^4J = 1.3 Hz, 1H, CH$_{Ar}$), 7.43 (dd, ^3J = 5.0, ^4J = 3.0 Hz 1H, CH$_{Ar}$), 7.36–7.28 (m, 3H, CH$_{Ar}$), 7.25–7.19 (m, 2H, CH$_{Ar}$), 6.65–6.56 (m, 4H, CH$_{Ar}$), 3.00 (s, 6H, CH$_3$), 2.99 (s, 6H, CH$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 150.8, 150.7 (C), 147.7 (CH$_{Ar}$), 142.9, 136.8, 134.8 (C), 133.4, 133.3 (CH$_{Ar}$), 132.3 (C), 130.2, 126.4, 123.8, 123.7, 111.8 (CH$_{Ar}$), 109.0, 108.7 (C), 99.9, 95.3, 87.4, 85.7 (C$_{Alkyn}$), 40.2, 40.2 (CH$_3$) ppm. MS (EI, 70°eV): m/z (%) = 448 (33), 447 ([M]$^+$, 100), 446 (18), 201 (27), 69 (28), 57 (19), 44 (57), 43 (22). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{29}$H$_{25}$N$_3$S 447.1763; found 447.1750. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2206 (m), 1599 (m), 1559 (s), 1504 (s), 1226 (s), 960 (m), 828 (vs), 647 (s), 527 (s).

General procedure (B) for the synthesis of 2,4-bis(arylethynyl)-3-(thiophen-3-yl)quinolines 2a–c

An argon flushed pressure tube was loaded with 1.0 eq. of 2,4-dichloro-3-(thiophen-3-yl)quinoline (352 mg), 0.06 eq. of PdCl$_2$(CH$_3$CN)$_2$, 0.04 eq. of CuI, 0.12 eq. of XPhos, 4 eq. of HN^{i}Pr$_2$ and 2 ml of dioxane. Then 4.0 eq. of the respective alkyne was added to the solution with stirring. The pressure tube was sealed with a Teflon cap and the reaction mixture was stirred in a stainless-steel heating block for 24 h at 100 °C. After cooling to room temperature, the reaction was quenched with distilled water and extracted three times with ethyl acetate. The combined organic phases were dried over Na$_2$SO$_4$ and filtered, and the solvent was distilled *in vacuo*. After purification by column chromatography (heptane/EtOAc 5 : 1 (1 : 1 for **2c**)), the desired products **2a–c** were isolated.

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2,4-Bis(phenylethynyl)-3-(thiophen-3-yl)quinoline (2a). According to general procedure B, the title compound **2a** was obtained as a yellow solid in 70% yield (97 mg, 0.24 mmol) (heptane/EtOAc 4:1); mp 167–169 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.40 (d, ^{3}J = 8.2 Hz, 1H, CH$_{Ar.}$), 8.18 (d, ^{3}J = 8.4 Hz, 1H, CH$_{Ar.}$), 7.80–7.74 (m, 2H, CH$_{Ar}$), 7.66 (qt, ^{3}J = 7.6 Hz, 1H, CH$_{Ar}$), 7.57 (dd, ^{3}J = 4.9 Hz, ^{4}J = 0.7 Hz, 1H, CH$_{Ar}$), 7.50 (dd, ^{3}J = 4.9 Hz, ^{4}J = 3.0 Hz, 1H, CH$_{Ar}$), 7.48–7.41 (m, 4H, CH$_{Ar}$), 7.40–7.30 (m, 6H, CH$_{Ar}$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 147.1, 143.2, 137.2, 134.1 (C), 132.3, 132.0, 130.3, 130.2, 129.6, 129.5, 129.3 (CH$_{Ar.}$), 128.9 (C), 128.7, 128.5, 128.1 (CH$_{Ar.}$), 126.8 (C), 126.7, 126.4, 124.2 (CH$_{Ar.}$), 122.4, 122.3 (C), 102.6, 93.5, 89.3, 85.0 (C$_{Alkyn}$). MS (EI, 70 eV): m/z (%) = 412 (28), 411 (80), 410 ([M]$^+$, 100), 409 (17), 408 (18), 378 (6), 334 (10), 77 (14). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{29}$H$_{17}$NS 410.0998; found 410.0993. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1492 (m), 1346 (m), 837 (m), 748 (vs), 723 (m), 684 (s), 664 (s), 610 (m), 525 (s), 495 (m).

2,4-Bis((4-fluorophenyl)ethynyl)-3-(thiophen-3-yl)quinoline (2b). According to general procedure B, the title compound **2b** was obtained as a yellow solid in 72% yield (283 mg, 0.63 mmol) (heptane/EtOAc 4:1); mp 190–194 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 8.34 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.5 Hz, 1H, CH$_{Ar.}$), 8.20–8.13 (m, 1H, CH$_{Ar.}$), 7.81–7.72 (m, 2H, CH$_{Ar}$), 7.65 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.3 Hz, 1H, CH$_{Ar.}$), 7.51 (dd, ^{3}J = 5.0 Hz, ^{4}J = 1.4 Hz, 1H, CH$_{Ar.}$), 7.49 (dd, ^{3}J = 5.0 Hz, ^{4}J = 2.8 Hz, 1H, CH$_{Ar.}$), 7.46–7.34 (m, 4H, CH$_{Ar}$), 7.11–6.95 (m, 4H, CH$_{Ar}$) ppm. ^{19}F NMR (471 MHz, CDCl$_3$) δ = −108.6 (s, 1F, CF), −108.9 (s, 1F, CF), ^{13}C NMR (63 MHz, CDCl$_3$) δ = 163.3 (d, $^{1}J_{C,F}$ = 251.7 Hz). 163.2 (d, $^{1}J_{C,F}$ = 251.3 Hz, C), 147.0, 143.0, 137.2 (C), 134.3 (d, $^{3}J_{C,F}$ = 8.6 Hz), 134.0 (d, $^{3}J_{C,F}$ = 8.5 Hz, CH$_{Ar}$), 130.4, 130.2, 129.6 (CH$_{Ar}$), 128.8 (C) 128.2 (CH$_{Ar}$), 126.7 (C), 126.6, 126.3, 124.3 (CH$_{Ar}$), 118.5 (d, $^{4}J_{C,F}$ = 3.5 Hz), 118.3 (d, $^{4}J_{C,F}$ = 3.5 Hz, C), 116.2 (d, $^{2}J_{C,F}$ = 22.2 Hz), 115.8 (d, $^{2}J_{C,F}$ = 22.2 Hz, CH$_{Ar}$), 101.5, 92.5 (C$_{Alkyn}$), 88.9 (d, $^{5}J_{C,F}$ = 1.3 Hz), 84.8 (d, $^{5}J_{C,F}$ = 1.4 Hz, C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 449 (7), 448 (28), 447 ([M]$^+$, 96), 446 (100), 445 (14), 444 (9), 223 (8), 222 (10), 213 (8). HRMS (ESI) m/z: [M + H]$^+$ calcd for: C$_{29}$H$_{15}$F$_2$NS 448.0971; found 448.0971. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1504 (s), 1214 (s), 1152 (s), 830 (vs), 808 (s), 758 (vs), 528 (s), 499 (s), 453 (s).

4,4′-((3-(Thiophen-3-yl)quinoline-2,4-diyl)bis(ethyne-2,1-diyl))bis(N,N-dimethylaniline) (2c). According to general procedure B, the title compound **2c** was obtained as a brown solid in 76% yield (345 mg, 0.69 mmol) (heptane/EtOAc 4:1); mp 112–114 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.39 (d, ^{3}J = 8.1 Hz, 1H, CH$_{Ar.}$), 8.12 (d, ^{3}J = 8.4 Hz, 1H, CH$_{Ar.}$), 7.79–7.75 (m, 1H, CH$_{Ar.}$), 7.71 (qt, ^{3}J = 7.1 Hz, 1H, CH$_{Ar}$), 7.62–7.57 (m, 2H, CH$_{Ar}$), 7.46 (dd, ^{3}J = 5.0 Hz, ^{4}J = 3.0 Hz, 1H, CH$_{Ar.}$), 7.34–7.29 (m, 4H, CH$_{Ar}$), 6.65–6.59 (m, 4H, CH$_{Ar}$), 2.99 (s, 6H, CH$_3$), 2.98 (s, 6H, CH$_3$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 150.8, 150.7, 147.1, 143.8, 137.7 (C), 133.7, 133.4 (CH$_{Ar}$), 132.7 (C), 130.6, 129.9 (CH$_{Ar}$), 129.5 (C), 129.2, 127.2, 126.6 (CH$_{Ar}$), 126.4 (C), 123.6, 111.8, 111.7 (CH$_{Ar}$), 109.0, 108.8 (C), 104.9, 95.8, 88.4, 84.1 (C$_{Alkyn}$), 40.2 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 497 ([M]$^+$, 45), 449 (52), 367 (100), 278 (91), 214 (94), 97 (66), 83 (55), 57 (53), 55 (79). HRMS (EI) m/z: [M]$^+$ calcd for C$_{33}$H$_{27}$N$_3$S 497.1920; found 497.1923. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2186 (s), 1601

General procedure (C) for the synthesis of 4-aryl-9-(arylethynyl)thieno[3,2-f]quinolines (3a–j)

6-Aryl-1-(arylethynyl)thieno[2,3-h]isoquinolines (4a–h) and 4-aryl-11-(arylethynyl)thieno[3,2-a]acridines (7a–c). A degassed and argon flushed Schlenk tube was charged with 100 mg of **1a–j** and **2a–c**, 30 eq. of p-TsOH·H$_2$O and 3 ml of xylene. The reaction mixture was stirred in an oil bath at 100 °C for 5 h. After cooling to room temperature, the reaction mixture was washed with saturated NaHCO$_3$ solution and extracted with dichloromethane. The combined organic layers were dried over Na$_2$SO$_4$ and filtered, and the solvent was distilled *in vacuo*. Column chromatographic purification (heptane/EtOAc 4:1) afforded the desired derivatives **3a–j**, **4a–h** and **7a–c** as pure compounds.

4-Phenyl-9-(phenylethynyl)thieno[3,2-f]quinoline (3a). According to general procedure C, the title compound **3a** was obtained as a yellow solid in 80% yield (160 mg, 0.44 mmol) (heptane/EtOAc 4:1); mp 149–150 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.26 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 8.91 (d, ^{3}J = 4.6 Hz, 1H, CH$_{Ar}$), 8.07 (s, 1H, CH$_{Ar}$), 7.87–7.80 (m, 2H, CH$_{Ar}$), 7.76–7.69 (m, 4H, CH$_{Ar}$), 7.61–7.44 (m, 6H, CH$_{Ar}$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.6 (C), 148.2 (CH$_{Ar}$), 140.0, 139.9, 139.3, 135.7 (C), 131.8, 129.6, 129.1, 128.9, 128.9, 128.6 (CH$_{Ar}$), 127.5 (C), 126.9, 126.0, 125.8, 125.7 (CH$_{Ar}$), 122.7, 122.6 (C), 98.8, 89.2 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 363 (5), 362 (20), 361 (100), 360 ([M]$^+$, 69), 359 (29), 358 (12), 357 (6). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{25}$H$_{15}$NS 360.0842; found 360.0834. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2197 (w), 1556 (m), 1334 (m), 875 (m), 810 (vs), 743 (s), 626 (m), 495 (s).

4-(p-Tolyl)-9-(p-tolylethynyl)thieno[3,2-f]quinoline (3b). According to general procedure C, the title compound **3b** was obtained as a yellow solid in 79% yield (158 mg, 0.41 mmol) (heptane/EtOAc 4:1); mp 193–196 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.39 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 9.02 (d, ^{3}J = 4.6 Hz, 1H, CH$_{Ar}$), 8.19 (s, 1H, CH$_{Ar}$), 7.89 (s, 1H, CH$_{Ar}$), 7.88–7.80 (m, 1H, CH$_{Ar}$), 7.74 (d, ^{3}J = 7.8 Hz, 1H, CH$_{Ar}$), 7.51 (d, ^{3}J = 8.1 Hz, 1H, CH$_{Ar}$), 7.41 (d, ^{3}J = 7.5 Hz, 1H, CH$_{Ar}$), 2.62 (s, 3H, CH$_3$), 2.58 (s, 3H, CH$_3$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.4 (C), 147.9 (CH$_{Ar}$), 140.0, 139.3, 138.8, 136.9, 135.6 (C), 131.7, 129.8, 129.6, 128.5 (CH$_{Ar}$), 127.8 (C), 126.8, 125.7, 125.5 (CH$_{Ar}$), 122.6, 119.5 (C), 99.3, 88.7 (C$_{Alkyn}$), 21.8, 21.5 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 391 (11), 390 (37), 389 ([M]$^+$, 100), 387 (9), 386 (7), 374 (14), 373 (18), 372 (9), 359 (10), 186 (23). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{27}$H$_{19}$NS 389.1232; found 389.1224. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2200 (w), 1555 (m), 1327 (m), 886 (m), 811 (vs), 743 (s), 694 (s), 616 (m), 498 (s).

4-(m-Tolyl)-9-(m-tolylethynyl)thieno[3,2-f]quinoline (3c). According to general procedure C, the title compound **3c** was obtained as a yellow solid in 80% yield (130 mg, 0.33 mmol) (heptane/EtOAc 4:1); mp 135–137 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.25 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 8.89 (d, ^{3}J = 4.3 Hz, 1H, CH$_{Ar}$), 8.06 (s, 1H, CH$_{Ar}$), 7.73–7.61 (m, 4H, CH$_{Ar}$), 7.57–7.50 (m, 2H, CH$_{Ar}$), 7.49–7.41 (m, 1H, CH$_{Ar}$), 7.40–7.28

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(m, 3H, CH_{Ar}), 2.49 (s, 3H, CH_3), 2.44 (s, 3H, CH_3) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.5 (C), 148.1 (CH$_{Ar}$), 139.9, 139.8, 139.3, 138.7, 138.6, 135.6 (C), 132.2, 130.5, 129.6, 129.3, 128.9, 128.7 (CH$_{Ar}$), 127.4 (C), 126.7, 125.9, 125.6 (CH$_{Ar}$), 122.6, 122.4 (C), 99.0, 88.8 (C$_{Alkyn}$), 21.7, 21.4 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 390 (30), 389 ([M]$^+$, 100), 388 (21), 374 (14), 373 (17), 359 (11), 186 (18). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{27}$H$_{19}$NS 389.1232; found 389.1225. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1555 (m), 1481 (m), 1329 (m), 1088 (m), 873 (m), 735(s), 677 (s), 548 (m), 434 (m).

4-(*o*-Tolyl)-9-(*o*-tolylethynyl)thieno[3,2-*f*]quinoline (3d). According to general procedure C, the title compound 3d was obtained as a beige solid in 80% yield (280 mg, 0.72 mmol) (heptane/EtOAc 4:1); mp 135–137 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 9.26 (d, ^3J = 5.6 Hz, 1H, CH$_{Ar}$), 8.92 (d, ^3J = 4.6 Hz, 1H, CH$_{Ar}$), 7.97 (s, 1H, CH$_{Ar}$), 7.77 (d, ^3J = 4.6 Hz, 1H, CH$_{Ar}$), 7.73–7.65 (m, 2H, CH$_{Ar}$), 7.48–7.27 (m, 7H, CH$_{Ar}$), 2.65 (s, 3H, CH$_3$), 2.22 (s, 3H, CH$_3$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 147.6, 141.7, 140.8, 139.4, 139.1, 136.2, 135.0 (C), 132.3, 130.7, 130.1, 129.7, 129.5, 128.8, 127.3, 126.1, 126.1, 125.8, 125.7 (CH$_{Ar}$), 122.7, 122.3 (C), 92.7 (C$_{Alkyn}$), 21.1, 20.0 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 390 (29), 389 ([M]$^+$, 100), 388 (61), 387 (18), 386 (10), 374 (11), 372 (10), 298 (14), 297 (11), 91 (13). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{27}$H$_{19}$NS 389.1232; found 389.1222. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2198 (w), 1555 (m), 1327 (m), 96 (m), 836 (m), 754 (vs), 729 (s), 688 (s), 560 (m), 453 (m).

4-(4-Fluorophenyl)-9-((4-fluorophenyl)ethynyl)thieno[3,2-*f*]quinoline (3e). According to general procedure C, the title compound 3e was obtained as a white solid in 82% yield (245 mg, 0.62 mmol) (heptane/EtOAc 4:1); mp 167–169 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.19 (d, ^3J = 5.6 Hz, 1H, CH$_{Ar}$), 8.90 (d, ^3J = 4.6 Hz, 1H, CH$_{Ar}$), 8.03 (d, ^3J = 2.1 Hz, 1H, CH$_{Ar}$), 7.84–7.75 (m, 2H, CH$_{Ar}$), 7.75–7.65 (m, 4H, CH$_{Ar}$), 7.30–7.12 (m, 4H, CH$_{Ar}$) ppm. ^{19}F NMR (282 MHz, CDCl$_3$) δ = −108.50 (s, 1F, CF), −112.73 (s, 1F, CF) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 163.4 (d, $^1J_{C,F}$ = 251.8 Hz), 163.2 (d, $^1J_{C,F}$ = 248.3 Hz, C), 148.2 (C), 148.1 (CH$_{Ar}$), 140.0, 138.4 (C), 135.7 (d, $^4J_{C,F}$ = 3.4 Hz, C), 135.6 (C), 133.8 (d, $^3J_{C,F}$ = 8.6 Hz), 130.4 (d, $^3J_{C,F}$ = 8.2 Hz, CH$_{Ar}$) 127.5 (C), 127.0, 125.8, 125.6 (CH$_{Ar}$), 122.7 (C), 118.6 (d, $^4J_{C,F}$ = 3.6 Hz, C), 116.34 (d, $^2J_{C,F}$ = 22.2 Hz), 116.10 (d, $^2J_{C,F}$ = 21.6 Hz, CH$_{Ar}$), 98.0, 88.8 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 399 (7), 398 (27), 397 ([M]$^+$, 100), 396 (47), 395 (26), 198 (5), 75 (4). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{25}$H$_{13}$NSF$_2$ 397.0731; found 397. 0725. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2206 (w), 1599 (m), 1557 (m), 1506 (s), 1221 (s), 1156 (s), 828 (vs), 805 (s), 735 (s), 496 (s).

4-(Thiophen-3-yl)-9-(thiophen-3-ylethynyl)thieno[3,2-*f*]quinoline (3h). According to general procedure C, the title compound 3h was obtained as a yellow solid in 83% yield (186 mg, 0.50 mmol) (heptane/EtOAc 4:1); mp 80–82 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.13 (d, ^3J = 5.5 Hz, 1H, CH$_{Ar}$), 8.83 (d, ^3J = 4.3 Hz, 1H, CH$_{Ar}$), 8.11 (s, 1H, CH$_{Ar}$), 7.86 (s, 1H, CH$_{Ar}$), 7.74–7.58 (m, 4H, CH$_{Ar}$), 7.53–7.30 (m, 3H, CH$_{Ar}$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.2 (C), 148.1 (CH$_{Ar}$), 140.1, 139.1, 135.7, 133.6 (C), 130.2, 129.5, 127.8 (CH$_{Ar}$), 127.3 (C), 126.5, 126.4, 126.2, 125.5, 125.2, 124.0 (CH$_{Ar}$), 122.4, 121.6 (C), 94.2,

88.7 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 375 (13), 374 (28), 373 ([M]$^+$, 100), 372 (42), 371 (19), 339 (7), 328 (8), 45 (16). HRMS (ESI) m/z: [M + H]$^+$ calcd for: C$_{21}$H$_{12}$NS$_3$ 374.0132; found 374.0132. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2202 (w), 1555 (s), 1314 (m), 869(m), 778 (vs), 731 (vs), 622 (s), 556 (s).

4-(9-((4-(Dimethylamino)phenyl)ethynyl)thieno[3,2-*f*]quinolin-4-yl)-*N*,*N*-dimethylaniline (3j). According to general procedure C, the title compound 3j was obtained as a brown solid in 60% yield (154 mg, 0.34 mmol) (heptane/EtOAc 4:1); mp 246–249 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.32 (d, ^3J = 5.6 Hz, 1H, CH$_{Ar}$), 8.80 (d, ^3J = 4.9 Hz, 1H, CH$_{Ar}$), 8.09 (s, 1H, CH$_{Ar}$), 7.81–7.74 (m, 2H, CH$_{Ar}$), 7.73 (d, ^3J = 5.6 Hz, 1H, CH$_{Ar}$), 7.65 (d, ^3J = 4.9 Hz, 1H, CH$_{Ar}$), 7.62–7.56 (m, 2H, CH$_{Ar}$), 6.90–6.84 (m, 2H, CH$_{Ar}$), 6.78–6.71 (m, 2H, CH$_{Ar}$), 3.06 (s, 6H, CH$_3$), 3.06 (s, 6H, CH$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 151.1, 150.9, 140.3, 135.7 (C), 133.3, 129.5 (CH$_{Ar}$), 127.2 (C), 126.9, 125.8, 124.4 (CH$_{Ar}$), 122.3 (C), 112.5, 112.0 (CH$_{Ar}$), 108.7 (C), 88.3 (C$_{Alkyn}$), 40.5, 40.3 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 450 (7), 449 (38), 448 (85), 447 ([M]$^+$, 100), 433 (12), 432 (11), 431 (26), 430 (19), 224 (13), 223 (34). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{29}$H$_{25}$N$_3$S 447.1763; found 447.1758.

6-Phenyl-1-(phenylethynyl)thieno[2,3-*h*]isoquinoline (4a). According to general procedure C, the title compound 4a was obtained as a brown solid in 8% yield (16 mg, 0.04 mmol) (heptane/EtOAc 4:1); mp 155–157 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.35 (d, ^3J = 5.6 Hz, 1H, CH$_{Ar}$), 8.67 (d, ^3J = 5.4 Hz, 1H, CH$_{Ar}$), 7.82–7.73 (m, 6H, CH$_{Ar}$), 7.69 (s, 1H, CH$_{Ar}$), 7.61–7.50 (m, 3H, CH$_{Ar}$), 7.50–7.43 (m, 3H, CH$_{Ar}$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 143.3 (CH$_{Ar}$), 141.0, 140.5, 140.2, 139.7, 136.4, 135.2 (C), 132.1, 129.5, 129.1, 128.8, 128.6, 127.4, 125.7 (CH$_{Ar}$), 124.3 (C), 122.9 (CH$_{Ar}$), 122.6 (C), 121.7 (CH$_{Ar}$), 94.0, 91.2 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 363 (8), 362 (27), 361 (100), 360 ([M]$^+$, 52), 359 (31), 358 (6), 357 (5). HRMS (ESI) m/z: [M + H]$^+$ calcd for: C$_{25}$H$_{16}$NS 361.1003; found 361.1006. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2200 (w), 1532 (m), 1256 (m), 870 (s), 681 (vs), 565 (s), 43 (m).

6-(*m*-Tolyl)-1-(*m*-tolylethynyl)thieno[2,3-*h*]isoquinoline (4c). According to general procedure C, the title compound 4c was obtained as a yellow oil in 10% yield (16 mg, 0.04 mmol) (heptane/EtOAc 4:1). ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.35 (d, ^3J = 5.6 Hz, 1H, CH$_{Ar}$), 8.66 (d, ^3J = 5.5 Hz, 1H, CH$_{Ar}$), 7.82–7.74 (m, 2H, CH$_{Ar}$), 7.69 (s, 1H, CH$_{Ar}$), 7.64–7.56 (m, 4H, CH$_{Ar}$), 7.49–7.41 (m, 1H, CH$_{Ar}$), 7.40–7.27 (m, 3H, CH$_{Ar}$), 2.49 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 142.9 (CH$_{Ar}$), 141.1, 140.6, 140.3, 139.6, 138.9, 138.5, 136.5, 135.2 (C), 132.7, 130.5, 129.9, 129.3, 129.3, 129.0, 128.7, 127.5, 125.7 (CH$_{Ar}$), 124.2 (C), 122.8 (CH$_{Ar}$), 122.3 (C), 121.7 (CH$_{Ar}$), 90.6 (C$_{Alkyn}$), 21.7, 21.5 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 390 (30), 389 ([M]$^+$, 100), 388 (26), 374 (15), 373 (19), 359 (11), 187 (18), 186 (13). HRMS (EI) m/z: [M]$^+$ calcd for: C$_{27}$H$_{19}$NS 389.1232; found 389.1226. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2206 (w), 1584 (m), 1522 (m), 1483 (m), 1333 (m), 1273 (m), 877 (s), 783(s), 686 (vs), 560 (s), 434 (m).

4-Phenyl-11-(phenylethynyl)thieno[3,2-*a*]acridine (7a). According to general procedure C, the title compound 7a was obtained as a yellow solid in 79% yield (68 mg, 0.17 mmol)

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(heptane/EtOAc 4 : 1); mp 156–159 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.42 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 8.67 (d, ^{3}J = 8.6 Hz, 1H, CH$_{Ar}$), 8.26 (d, ^{3}J = 8.6 Hz, 1H, CH$_{Ar}$), 8.10 (s, 1H, CH$_{Ar}$), 7.90–7.85 (m, 2H, CH$_{Ar}$), 7.85–7.75 (m, 3H, CH$_{Ar}$), 7.71–7.47 (m, 8H, CH$_{Ar}$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 149.2, 147.2, 140.0, 139.7, 139.6, 135.5 (C), 131.8, 130.0, 129.7, 129.7, 129.0, 129.0, 128.6 (CH$_{Ar}$), 127.1 (C), 126.9, 126.6, 126.5, 126.2, 126.0 (CH$_{Ar}$), 124.4, 122.7, 122.0 (C), 105.8, 87.7 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 413 (10), 412 (32), 411 ([M]$^{+}$, 100), 410 (28), 409 (21), 205 (17), 204 (12). HRMS (EI) m/z: [M]$^{+}$ calcd for: C$_{29}$H$_{17}$NS 411.1076; found 411.1077. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1498 (m), 1440 (m), 1341 (m), 878 (m), 746 (vs), 696 (s), 684 (s), 666 (s), 600 (m), 571 (m), 509 (m), 441 (m).

4-(4-Fluorophenyl)-11-((4-fluorophenyl)ethynyl)thieno[3,2-*a*]acridine (7b). According to general procedure C, the title compound **7b** was obtained as a yellow solid in 70% yield (64 mg, 0.14 mmol) (heptane/EtOAc 4 : 1); mp 210–212 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.36 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 8.63 (ddd, ^{3}J = 8.6 Hz, ^{4}J = 1.4 Hz, ^{5}J = 0.7 Hz, 1H, CH$_{Ar}$), 8.27 (d, ^{3}J = 8.6 Hz, 1H, CH$_{Ar}$), 8.07 (s, 1H, CH$_{Ar}$), 7.86–7.75 (m, 5H, CH$_{Ar}$), 7.72–7.64 (m, 2H, CH$_{Ar}$), 7.29–7.18 (m, 4H, CH$_{Ar}$) ppm. ^{19}F NMR (282 MHz, CDCl$_3$) δ = −108.19 (s, 1F, CF), −112.56 (s, 1F, CF) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 163.5 (d, $^{1}J_{C,F}$ = 252.3 Hz), 163.2 (d, $^{1}J_{C,F}$ = 248.6 Hz, C), 148.8, 146.9, 139.4, 138.9 (C), 135.6 (d, $^{4}J_{C,F}$ = 3.3 Hz, C), 135.4 (C), 133.8 (d, $^{3}J_{C,F}$ = 8.6 Hz, CH$_{Ar}$), 130.3 (d, $^{3}J_{C,F}$ = 8.2 Hz, CH$_{Ar}$), 130.1, 129.5, 127.0 (CH$_{Ar}$), 127.0 (C), 126.5, 126.3, 126.2, 125.8 (CH$_{Ar}$), 124.3, 121.8 (C), 118.7 (d, $^{4}J_{C,F}$ = 3.5 Hz, C), 116.4 (d, $^{2}J_{C,F}$ = 22.3 Hz, CH$_{Ar}$), 116.0 (d, $^{2}J_{C,F}$ = 21.6 Hz, CH$_{Ar}$), 104.7, 87.3 (C$_{Alkyn}$) ppm. MS (EI, 70 eV): m/z (%) = 448 (31), 447 ([M]$^{+}$, 100), 446 (29), 445 (19), 223 (13), 222 (8), 83 (9), 55 (9), 43 (11), 41 (7). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{29}$H$_{16}$F$_2$NS 448.0971; found 448.0966. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1508 (vs), 1228 (s), 1156 (s), 826 (vs), 806 (s), 750 (vs), 705 (s), 670 (s), 600 (m), 523 (s), 480 (s), 457 (m).

4-(11-((4-(Dimethylamino)phenyl)ethynyl)thieno[3,2-*a*]acridin-4-yl)-*N,N*-dimethylaniline (7c). According to general procedure C, the title compound **7c** was obtained as a brown solid in 31% yield (31 mg, 0.06 mmol) (heptane/EtOAc 4 : 1); mp 124–126 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 9.55 (d, ^{3}J = 5.5 Hz, 1H, CH$_{Ar}$.), 8.73 (d, ^{3}J = 8.5 Hz, 1H, CH$_{Ar}$), 8.27 (d, ^{3}J = 8.6 Hz, 1H, CH$_{Ar}$), 8.09 (s, 1H, CH$_{Ar}$), 7.85–7.78 (m, 3H, CH$_{Ar}$), 7.74–7.68 (m, 3H, CH$_{Ar}$), 7.67–7.62 (m, 1H, CH$_{Ar}$), 6.89 (d, ^{3}J = 8.6 Hz, 2H, CH$_{Ar}$), 6.77 (d, ^{3}J = 8.5 Hz, 2H, CH$_{Ar}$), 3.07 (s, 6H, CH$_3$), 3.07 (s, 6H, CH$_3$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 150.9, 150.7, 139.6, 135.6 (C), 133.2, 133.0, 129.7, 129.4 (CH$_{Ar}$), 127.4 (C), 126.8, 126.7 (CH$_{Ar}$), 126.6 (C), 126.6, 126.0, 125.7 (CH$_{Ar}$), 121.3, 120.2 (C), 112.3, 111.9 (CH$_{Ar}$), 109.0, 86.7 (C$_{Alkyn}$), 40.4, 40.1 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 499 (21), 498 (43), 497 ([M]$^{+}$, 100), 483 (16), 481 (17), 248 (39), 247 (15), 204 (18), 118 (32), 57 (19), 58 (18), 44 (31), 43 (21). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{33}$H$_{27}$N$_3$S 498.2004; found 498.2003.

General procedure (D) for the synthesis of diarylthieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]pyridines (5a–j)

3,9-Diarylthieno[4′,3′,2′:4,5]naphtho[1,8-*bc*]pyridines (6a–b) and 3,11-diarylthieno[2′,3′,4′:4,5]-naphtho[1,8-*bc*]quinolines

(8a–c). If not otherwise stated, a degassed and argon flushed Schlenk tube was charged with 100 mg of **3a–j**, **4a–h** and **7a–c**, 30 eq. of *p*-TsOH·H$_2$O and 3 ml of xylene. The reaction mixture was stirred in an oil bath at 140 °C for 24 h. After cooling to room temperature, the reaction mixture was washed with a saturated NaHCO$_3$ solution and extracted with dichloromethane. The combined organic layers were dried over Na$_2$SO$_4$ and filtered, and the solvent was distilled *in vacuo*. Column chromatographic purification (Hep/EtOAc 3 : 1) afforded products **5a–j**, **6a–b** and **8a–c**.

3,9-Diphenylthieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]pyridine (5a). According to general procedure D, the title compound **5a** was obtained as a yellow solid in 82% yield (82 mg, 0.23 mmol) (heptane/EtOAc 4 : 1); mp 160–163 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.17 (d, ^{3}J = 5.0 Hz, 1H, CH$_{Ar}$), 8.39 (s, 1H, CH$_{Ar}$), 8.21 (s, 1H, CH$_{Ar}$), 8.03–7.98 (m, 2H, CH$_{Ar}$), 7.84–7.78 (m, 2H, CH$_{Ar}$), 7.79–7.72 (m, 1H, CH$_{Ar}$), 7.68–7.51 (m, 7H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 148.9 (CH$_{Ar}$), 147.3, 140.7, 139.8, 139.4, 136.9, 133.1, 132.9, 132.7 (C), 129.4, 129.1, 128.9, 128.8, 128.5, 124.2, 124.2, 123.7 (CH$_{Ar}$), 118.3 (C), 116.2 (CH$_{Ar}$) ppm. MS (EI, 70 eV): m/z (%) = 363 (7), 362 (26), 361 ([M]$^{+}$, 100), 360 (29), 359 (23), 358 (5), 357 (5), 180 (15). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{25}$H$_{16}$NS 362.1003; found 362.1003. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1578 (m), 1467 (m), 1372 (m), 1075 (m), 877 (m), 760 (s), 692 (vs), 597 (s), 465 (m).

3,9-Di-*p*-tolylthieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]pyridine (5b). According to general procedure D, the title compound **5b** was obtained as a yellow solid in 84% yield (84 mg, 0.22 mmol) (heptane/EtOAc 4 : 1); mp 221–225 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.15 (d, ^{3}J = 5.0 Hz, 1H, CH$_{Ar}$), 8.34 (s, 1H, CH$_{Ar}$), 8.19 (s, 1H, CH$_{Ar}$), 7.90 (d, ^{3}J = 8.1 Hz, 2H, CH$_{Ar}$), 7.76–7.68 (m, 3H, CH$_{Ar}$), 7.62 (s, 1H, CH$_{Ar}$), 7.47–7.34 (m, 4H, CH$_{Ar}$), 2.50 (s, 3H, CH$_3$), 2.49 (s, 3H, CH$_3$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.9 (CH$_{Ar}$), 147.5, 140.6, 139.3, 138.8, 138.8, 137.0, 136.9, 136.6, 133.1, 132.9, 132.8 (C), 130.0, 129.8, 128.7, 128.4, 124.0, 124.0, 123.4 (CH$_{Ar}$), 118.2 (C), 116.0 (CH$_{Ar}$), 21.5 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 391 (7), 390 (25), 389 ([M]$^{+}$, 100), 388 (7), 373 (7), 187 (6), 186 (6). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{27}$H$_{20}$NS 390.1316; found 390.1325. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2901 (m), 1667 (m), 1518 (m), 1370 (s), 1162 (s), 1088(s), 842 (s), 766 (s), 712 (s), 556 (vs).

3,9-Di-*m*-tolylthieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]pyridine (5c). According to general procedure D, the title compound **5c** was obtained as a yellow solid in 92% yield (92 mg, 0.24 mmol) (heptane/EtOAc 4 : 1); mp 164–168 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 9.14 (d, ^{3}J = 4.9 Hz, 1H, CH$_{Ar}$), 8.34 (s, 1H, CH$_{Ar}$), 8.17 (s, 1H, CH$_{Ar}$), 7.80 (s, 2H, CH$_{Ar}$), 7.71 (d, ^{3}J = 4.9 Hz, 1H, CH$_{Ar}$), 7.64–7.58 (m, 3H, CH$_{Ar}$), 7.53–7.42 (m, 2H, CH$_{Ar}$), 7.33 (qt, ^{3}J = 7.2 Hz, 2H, CH$_{Ar}$), 2.52 (s, 3H, CH$_3$), 2.50 (s, 3H, CH$_3$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.4 (CH$_{Ar}$), 146.9, 140.9, 139.6, 139.3, 139.1, 138.8, 137.0, 133.1, 132.7, 132.7 (C), 129.6, 129.6, 129.4, 129.3, 129.2, 128.9, 125.9, 125.6, 124.4, 123.7, 123.5 (CH$_{Ar}$), 118.1 (C), 116.0 (CH$_{Ar}$), 21.7, 21.7 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 391 (9), 390 (31), 389 ([M]$^{+}$, 100), 388 (17), 374 (10), 373 (16), 359 (11), 187 (5), 186 (7), 179 (6), 39 (5). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{27}$H$_{20}$NS 390.1316; found

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390.1315. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1582 (m), 1475 (m), 1397 (m), 1090 (m), 873 (m), 778 (s), 725 (s), 698 (vs), 560 (m).

3,9-Di-o-tolylthieno[2′,3′,4′:4,5]naphtho[1,8-bc]pyridine (5d). According to general procedure D, the title compound **5d** was obtained as a yellow solid in 86% yield (86 mg, 0.22 mmol) (heptane/EtOAc 4:1); mp 166–171 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.22 (d, ^{3}J = 5.0 Hz, 1H, CH$_{Ar}$), 8.20 (s, 1H, CH$_{Ar}$), 7.78 (d, ^{3}J = 5.0 Hz, 1H, CH$_{Ar}$), 7.76 (s, 1H, CH$_{Ar}$), 7.57 (d, ^{3}J = 5.9 Hz, 2H, CH$_{Ar}$), 7.50–7.30 (m, 7H, CH$_{Ar}$), 2.34 (s, 3H, CH$_3$), 2.31 (s, 3H, CH$_3$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 149.0 (CH$_{Ar}$), 147.1, 140.7, 139.3, 139.2, 138.6, 136.7, 136.2, 136.2, 134.7, 133.6, 132.0 (C), 130.9, 130.7, 129.8, 129.7, 128.7, 128.5, 126.2, 126.0, 125.3, 124.4, 124.2 (CH$_{Ar}$), 118.3 (C), 116.2 (CH$_{Ar}$), 20.4, 20.3 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 390 (31), 389 ([M]$^{+}$, 100), 388 (61), 387 (16), 374 (15), 372 (12), 356 (11), 341 (10), 298 (14), 187 (15). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{27}$H$_{20}$NS 390.1316; found 390.1311. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1584 (m), 1465 (m), 1399 (m), 1046 (m), 890 (m), 758 (s), 725 (vs), 605 (s), 544 (m).

3,9-Bis(4-Fluorophenyl)thieno[2′,3′,4′:4,5]naphtho[1,8-bc]pyridine (5e). According to general procedure D, the title compound **5e** was obtained as a yellow solid in 98% yield (98 mg, 0.25 mmol) (heptane/EtOAc 4:1); mp 246–250 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.16 (d, ^{3}J = 5.0 Hz, 1H, CH$_{Ar}$), 8.32 (s, 1H, CH$_{Ar}$), 8.16 (s, 1H, CH$_{Ar}$), 8.02–7.91 (m, 2H, CH$_{Ar}$), 7.83–7.73 (m, 3H, CH$_{Ar}$), 7.62 (s, 1H, CH$_{Ar}$), 7.36–7.23 (m, 4H, CH$_{Ar}$) ppm. ^{19}F NMR (471 MHz, CDCl$_3$) δ = −112.58 (s, 1F, CF) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 165.2, 161.3 (C), 148.9 (CH$_{Ar}$), 147.1, 139.7, 138.4, 136.8 (C), 135.7 (d, $^{4}J_{C,F}$ = 3.4 Hz), 135.4 (d, $^{4}J_{C,F}$ = 3.4 Hz, C), 133.1, 132.8, 132.8 (C), 130.5 (d, $^{3}J_{C,F}$ = 8.1 Hz), 130.2 (d, $^{3}J_{C,F}$ = 8.2 Hz, CH$_{Ar}$), 124.2, 124.1, 123.8 (CH$_{Ar}$), 118.2 (C), 116.4 (d, $^{2}J_{C,F}$ = 21.6 Hz, CH$_{Ar}$), 116.3 (CH$_{Ar}$), 116.2 (d, $^{2}J_{C,F}$ = 21.5 Hz, CH$_{Ar}$) ppm. MS (EI, 70 eV): m/z (%) = 399 (12), 398 (44), 397 ([M]$^{+}$, 100), 396 (48), 395 (33), 393 (5), 368 (5), 198 (9). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{25}$H$_{14}$F$_2$NS 398.0815; found 398.0821. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1603 (m), 1504 (vs), 1224 (vs), 1153 (s), 1098 (s), 830 (vs), 731 (s), 531 (s), 502 (vs).

3,9-Di(thiophen-3-yl)thieno[2′,3′,4′:4,5]naphtho[1,8-bc]pyridine (5h). According to general procedure D, the title compound **5h** was obtained as a yellow solid in 91% yield (91 mg, 0.24 mmol) (heptane/EtOAc 4:1); mp 179–185 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.06 (d, ^{3}J = 5.0 Hz, 1H, CH$_{Ar}$), 8.34 (s, 1H, CH$_{Ar}$), 8.17 (s, 1H, CH$_{Ar}$), 7.94 (dd, ^{4}J = 2.9 Hz, ^{4}J = 1.4 Hz, 1H, CH$_{Ar}$), 7.76–7.69 (m, 2H, CH$_{Ar}$), 7.59 (d, ^{3}J = 5.1 Hz, 1H, CH$_{Ar}$), 7.57 (s, 1H, CH$_{Ar}$), 7.56–7.51 (m, 3H, CH$_{Ar}$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.7 (CH$_{Ar}$), 146.8, 140.3, 140.1, 136.5, 134.8, 133.5, 132.7, 132.3, 132.2 (C), 127.9, 127.4, 126.9, 126.7, 124.0, 123.6, 123.5, 123.2, 122.9 (CH$_{Ar}$), 117.8 (C), 116.0 (CH$_{Ar}$) ppm. MS (EI, 70 eV): m/z (%) = 375 (15), 374 (26), 373 ([M]$^{+}$, 100), 372 (22), 371 (16), 339 (6), 328 (5), 326 (5), 164 (6), 45 (12). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{21}$H$_{12}$NS$_3$ 374.0132; found 374.0131. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1621 (w), 1584 (m), 1465 (m), 859 (s), 774 (vs), 721 (s), 651 (vs), 533 (m).

4,4′-(Thieno[2′,3′,4′:4,5]naphtho[1,8-bc]pyridine-3,9-diyl)bis(N,N-dimethylaniline) (5j). According to general procedure D,

the title compound **5j** was obtained as a yellow solid in 24% yield (24 mg, 0.05 mmol) (heptane/EtOAc 4:1); mp 185–190 °C. ^{1}H NMR (250 MHz, CDCl$_3$) δ = 9.08 (d, ^{3}J = 5.1 Hz, 1H, CH$_{Ar}$), 8.32 (s, 1H, CH$_{Ar}$), 8.27 (s, 1H, CH$_{Ar}$), 7.99–7.91 (m, 2H, CH$_{Ar}$), 7.74 (d, ^{3}J = 8.8 Hz, 2H, CH$_{Ar}$), 7.67 (d, ^{3}J = 5.1 Hz, 1H, CH$_{Ar}$), 7.58 (s, 1H, CH$_{Ar}$), 6.98–6.85 (m, 4H, CH$_{Ar}$), 3.08 (s, 6H, CH$_3$), 3.07 (s, 6H, CH$_3$) ppm. ^{13}C NMR (63 MHz, CDCl$_3$) δ = 150.9, 133.1 (C), 129.7, 129.4 (CH$_{Ar}$), 127.5, 127.3, 124.4 (C), 122.0 (CH$_{Ar}$), 117.7 (C), 115.2, 112.8, 112.6 (CH$_{Ar}$), 40.6, 40.6 (CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 448 (31), 447 ([M]$^{+}$, 100), 431 (13), 223 (23), 222 (12), 82 (12). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{29}$H$_{26}$N$_3$S 448.1847; found 448.1841. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1605 (vs), 1580 (s), 1510 (s), 1357 (vs), 1193 (vs), 813 (vs), 595 (s), 517 (s).

3,9-Diphenylthieno[4′,3′,2′:4,5]naphtho[1,8-bc]pyridine (6a). According to general procedure D, the title compound **6a** was obtained as a brown solid in 96% yield (96 mg, 0.27 mmol) (heptane/EtOAc 4:1); mp 162–168 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.99 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 8.25 (s, 1H, CH$_{Ar}$), 8.03 (s, 1H, CH$_{Ar}$), 8.00–7.93 (m, 3H, CH$_{Ar}$), 7.91 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 7.86 (d, ^{3}J = 7.4 Hz, 2H, CH$_{Ar}$), 7.65–7.50 (m, 6H, CH$_{Ar}$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 150.7 (C), 145.2 (CH$_{Ar}$), 140.4, 140.1, 139.6, 139.4, 134.5, 134.1, 133.6, 132.0 (C), 129.4, 129.1, 129.1, 128.9, 128.7, 128.6, 126.7, 124.5, 121.5 (CH$_{Ar}$), 118.6 (C), 117.3 (CH$_{Ar}$) ppm. MS (EI, 70 eV): m/z (%) = 363 (9), 362 (35), 361 ([M]$^{+}$, 100), 360 (41), 359 (28), 358 (5), 357 (6), 180 (8). HRMS (ESI) m/z: [M + H]$^{+}$ calcd for: C$_{25}$H$_{16}$NS 362.1003; found 362.1000. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1578 (m), 1403 (m), 1300 (m), 1075 (m), 873 (m), 760 (s), 690 (vs), 597 (m), 562 (m).

3,9-Di-p-tolylthieno[4′,3′,2′:4,5]naphtho[1,8-bc]pyridine (6b). According to general procedure D, the title compound **6b** was obtained as a yellow solid in 15% yield (30 mg, 0.08 mmol) (heptane/EtOAc 4:1); mp 182–186 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 9.35 (d, ^{3}J = 5.6 Hz, 1H, CH$_{Ar}$), 8.64 (d, ^{3}J = 5.4 Hz, 1H, CH$_{Ar}$), 7.80 (dd, ^{2}J = 11.6 Hz, ^{3}J = 5.5 Hz, 2H, CH$_{Ar}$), 7.75–7.67 (m, 5H, CH$_{Ar}$), 7.38 (d, ^{3}J = 7.8 Hz, 2H, CH$_{Ar}$), 7.27 (d, ^{3}J = 8.0 Hz, 2H, CH$_{Ar}$), 2.48 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 141.3, 140.2, 139.3, 136.8, 136.6, 135.3 (C), 132.2, 129.8, 129.6, 128.5, 127.8, 125.6 (CH$_{Ar}$), 124.0 (C), 122.6, 121.7 (CH$_{Ar}$), 119.2 (C) ppm. MS (EI, 70 eV): m/z (%) = 391 (9), 390 (30), 389 ([M]$^{+}$, 100), 388 (23), 387 (9), 386 (7), 374 (12), 373 (15), 372 (6), 359 (9), 195 (5), 187 (12), 186 (7). HRMS (EI) m/z: [M]$^{+}$ calcd for C$_{27}$H$_{19}$NS 389.1232; found 389.1225. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 220 (w), 1510 (m), 1020 (m), 816 (vs), 739 (s), 692(s), 605 (m), 519 (s), 461 (s).

3,11-Diphenylthieno[2′,3′,4′:4,5]naphtho[1,8-bc]quinoline (8a). According to general procedure D, utilizing 30 eq. of MsOH in 3 ml of xylene for 24 h at 140 °C, the title compound **8a** was obtained as a yellow solid in 68% yield (35 mg, 0.09 mmol) (heptane/EtOAc 2:1); mp 230–235 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.69 (d, ^{3}J = 8.4 Hz, 1H, CH$_{Ar}$), 8.48–8.43 (m, 2H, CH$_{Ar}$), 8.36 (s, 1H, CH$_{Ar}$), 8.28 (s, 1H, CH$_{Ar}$), 8.05–8.00 (m, 2H, CH$_{Ar}$), 7.91–7.85 (m, 3H, CH$_{Ar}$), 7.71–7.67 (m, 1H, CH$_{Ar}$), 7.65–7.60 (m, 4H, CH$_{Ar}$), 7.58–7.53 (m, 2H, CH$_{Ar}$) ppm.

^{13}C NMR (63 MHz, CDCl$_3$) δ = 148.6, 148.0, 140.4, 140.3, 139.9, 139.6, 133.4, 133.1, 132.9, 131.9 (C), 130.3, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.6, 125.6, 124.4, 123.5, 123.0 (CH$_{Ar}$), 121.7 (C), 120.0 (CH$_{Ar}$), 116.0 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 413 (14), 412 (34), 411 ([M]$^+$, 100), 410 (47), 409 (22), 407 (10), 205 (95), 204 (26). HRMS (ESI) *m/z*: [M + H]$^+$ calcd for: C$_{29}$H$_{18}$NS 412.1160; found 412.1165. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1453 (m), 1438 (m), 1385 (m), 1177 (m), 868 (m), 754 (s), 742 (vs), 696 (vs), 608 (s), 573 (s).

3,11-Bis(4-fluorophenyl)thieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]quinoline (8b). According to general procedure D, but utilizing 30 eq. of MsOH in 3 ml of xylene for 24 h at 140 °C, the title compound **8b** was obtained as a yellow solid in 72% yield (69 mg, 0.15 mmol) (heptane/EtOAc 2 : 1); mp 303–306 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.13 (s, 1H, CH$_{Ar}$), 9.01 (d, ^3J = 8.3 Hz, 1H, CH$_{Ar}$), 8.81 (s, 1H, CH$_{Ar}$), 8.43–8.18 (m, 3H, CH$_{Ar}$), 8.06–7.95 (m, 5H, CH$_{Ar}$), 7.48–7.38 (m, 4H, CH$_{Ar}$) ppm. ^{19}F NMR (471 MHz, CDCl$_3$) δ = −109.4 (s, 1F, CF), −109.6 (s, 1F, CF) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 164.7 (d, $^1J_{C,F}$ = 252.7 Hz, C), 164.5 (d, $^1J_{C,F}$ = 252.4 Hz, C), 147.9, 147.5, 141.5, 140.2, 137.7 (C), 137.4, 135.4 (CH$_{Ar}$), 134.0 (d, $^4J_{C,F}$ = 3.4 Hz, C), 133.4, 133.4, 132.8, 132.0 (C), 131.5 (d, $^3J_{C,F}$ = 8.6 Hz, CH$_{Ar}$), 131.0 (d, $^3J_{C,F}$ = 8.8 Hz, CH$_{Ar}$), 128.1, 124.7 (CH$_{Ar}$), 121.1 (C), 120.7 (CH$_{Ar}$), 120.2, 117.2 (d, $^2J_{C,F}$ = 22.1 Hz, CH$_{Ar}$), 117.1 (d, $^2J_{C,F}$ = 22.0 Hz, CH$_{Ar}$), 115.2 (C), 113.8 (CH$_{Ar}$) ppm. MS (EI, 70 eV): *m/z* (%) = 448 (29), 447 ([M]$^+$, 71), 446 (100), 445 (17), 444 (11), 223 (40), 221 (23), 213 (17), 207 (21). HRMS (EI) *m/z*: [M]$^+$ calcd for: C$_{29}$H$_{15}$F$_2$NS 447.0883; found 447.0888. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1500 (s), 1385 (m), 1335 (m), 1226 (s), 1156 (s), 1098 (m), 828 (vs), 808 (s), 746 (vs), 606 (m), 560 (s), 513 (s).

4,4′-(Thieno[2′,3′,4′:4,5]naphtho[1,8-*bc*]quinoline-3,11-diyl)bis(*N,N*-dimethylaniline) (8c). According to general procedure D, but utilizing 30 eq. of MsOH in 3 ml of xylene for 24 h at 140 °C, the title compound **8c** was obtained as a brown solid in 32% yield (32 mg, 0.06 mmol) (heptane/EtOAc 2 : 1); mp 209–212 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.74 (d, ^3J = 8.4 Hz, 1H, CH$_{Ar}$), 8.47 (d, ^3J = 8.6 Hz, 1H, CH$_{Ar}$), 8.43 (s, 1H, CH$_{Ar}$), 8.37 (s, 1H, CH$_{Ar}$), 8.33 (s, 1H, CH$_{Ar}$), 7.98 (d, ^3J = 8.7 Hz, 2H, CH$_{Ar}$), 7.87–7.81 (m, 1H, CH$_{Ar}$), 7.82 (d, ^3J = 8.7 Hz, 2H, CH$_{Ar}$), 7.70–7.66 (m, 1H, CH$_{Ar}$), 6.95–6.90 (m, 4H, CH$_{Ar}$), 3.08 (s, 3H, CH$_3$), 3.07 (s, 3H, CH$_3$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ = 150.9, 150.9, 148.9, 148.0, 140.7, 140.5, 133.7, 133.4, 133.3, 132.1 (C), 130.1, 130.0, 129.4, 129.1 (CH$_{Ar}$), 127.8, 127.4 (C), 124.9, 123.6, 123.1, 122.6 (CH$_{Ar}$), 121.5 (C), 118.4 (CH$_{Ar}$), 115.5 (C), 112.7, 112.7 (CH$_{Ar}$), 40.6, 40.5 (CH$_3$). MS (EI, 70 eV): *m/z* (%) = 512 (19), 511 (47), 498 (23), 497 ([M]$^+$, 56), 483 (25), 248 (18), 126 (21), 56 (23), 44 (100). HRMS (ESI) *m/z*: [M + H]$^+$ calcd for: C$_{33}$H$_{28}$N$_3$S 498.2004; found 498.2010. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1605 (vs), 1520 (s), 1357 (s), 1195 (s), 943 (m), 818 (s), 741 (vs), 607 (m).

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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