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Helicenes

Synthesis and Characterization of Azine-[5]Helicene Hybrids

Anna V. Gulevskaya,*[a] Daria I. Tonkoglazova,[a] Andrey S. Guchunov[a] and Alexander D. Misharev[b]

Abstract: Novel azine-helicene hybrids (pyridine-, pyrazine- and quinoxaline-fused along the central ring [5]helicenes) have been prepared in a good overall yields through a five-step synthetic sequence. Commercially available 2,3-dihaloazines were used as starting materials. To discern the effect of merging an azine moiety within a helical skeleton, the X-ray structures, UV-vis absorption spectra, cathodic and anodic electrochemistry of the helicene hybrids were investigated and compared to that of the parent [5]helicene.

Introduction

[*n*]Helicenes are polycyclic aromatic molecules in which *n ortho*-condensed benzene or other aromatic rings give rise to helical chiral and highly conjugated structures. Unique screw shape, helically extended π-system and intriguing electronic and chirooptical properties of these molecules, such as exceptionally high values of optical rotation and large circular dichroism, have attracted scientific interest for decades.[1] The applications of helicenes have now expanded into several fields including material science, nanoscience, biochemistry, supramolecular and polymer chemistry. Helicenes have also been studied with respect to conductivity,[2] nonlinear optics,[3] circularly

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polarized luminescence,[4] organocatalysis,[5] conformational analysis,[6] chirality sensing,[7] chemical sensors,[8] DNA-intercalators,[9] ets.

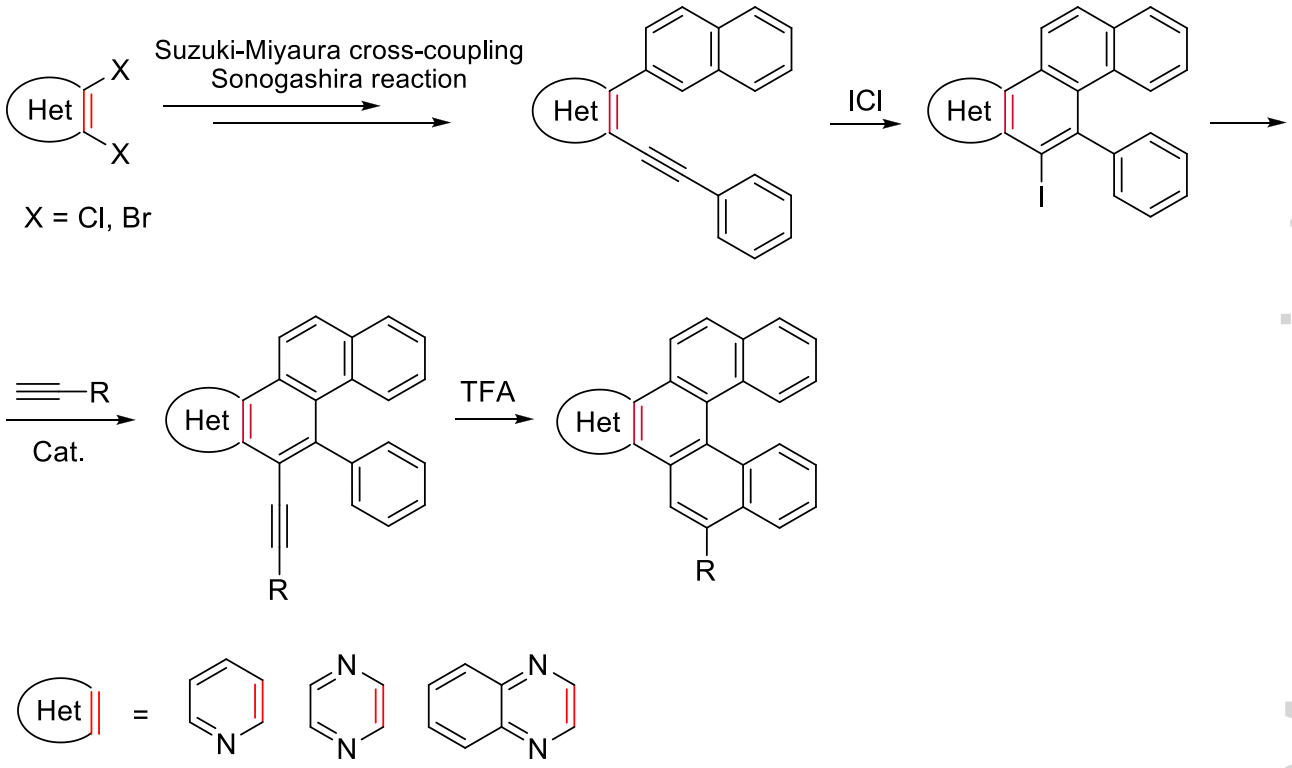
The most common structural modifications of helicenes are the preparation of higher helicenes and incorporation of heteroatoms within the carbon skeleton.[1] Synthesis and investigation of helicene derivatives with extended π-systems resulting from fusion of aromatic or heteroaromatic rings without lengthening of the helix are not numerous.[1] Though these helicene hybrids exhibit even more intriguing physical properties relative to simple helicenes,[1,10] synthetic methods available for their construction are still limited.

The classical synthetic approach for carbohelicenes is oxidative photocyclization of the stilbene derivatives.[1] The latter are generally available by the Wittig reaction or Heck-type cross-coupling between aryl halides and aryl ethenes. Due to this method, even the highest carbohelicenes, including [16]helicene,[1j] were obtained. It is also a helpful way to synthesize heterohelicenes. Unfortunately, this method is not applicable to the synthesis of [5]helicenes because the [5]helicene product, initially formed from 1,2-di(naphthyl)ethene or 1,4-distyrylbenzene, is itself photoreactive and undergoes overannulation to form benzo[*g,h,i*]perylene.[11] To overcome this difficulty, alternative synthetic pathways for [5]helicenes have been developed. Among them are the Diels–Alder reactions of 1,4-divinylbenzenes and benzoquinones[12a-c], [2+2+2]-cycloaddition of arynes and alkynes,[12d] transition-metal catalyzed cycloisomerizations of 2-ethynyl-1,1'-binaphthyl[11e], 3-ethynyl-4-phenylphenanthrenes[12f] and 1,2-bis(2-((Z)-but-1-en-3-ynyl)phenyl)ethyne[12g], double Stille cross-coupling of 2,2'-bis(trimethylstannyl)-1,1'-binaphthyl and 1,2-diiodobenzene[12h], double Suzuki–Miyaura cross-coupling between 2,2′-dibromo-1,1′-binaphthyl and *vic*-bis(pinacolatoboryl)alkene[12i], Heck-type double intramolecular C-H arylation of 1,4-bis(2-bromostyryl)benzenes[12j], ring-closing metathesis of 2,2'-divinyl-1,1'-binaphthyl[12k], Rh(II)-catalyzed cyclization of 1,1'-binaphthyl-2,2'-dicarbaldehyde bis(N-tosylhydrazone)[12l] and some others. Each method is not without drawbacks such as hardly available starting materials, rather expensive catalysts, harsh reaction conditions or low product yields.

Transition metal-catalyzed, electrophile-induced and oxidative radical cyclizations of *ortho*-alkynylated biaryls are widely used for synthesis of polynuclear aromatics.[13] Alkynes are carbon-rich and form aromatic rings via cycloisomerization, which is atom-economic process. In addition, alkyne reactions are highly favorable thermodynamically.[14]

We now report an efficient strategy for the synthesis of azine-[5]helicene hybrids ([5]helicenes heteroannelated along the central nucleus) starting from commercially available *ortho*-dihaloazines

(2,3-dibromopyridine, 2,3-dichloropyrazine and 2,3-dichloroquinoxaline). The method includes two Sonogashira reactions, Suzuki-Miyaura arylation and two electrophile-induced cyclizations of the intermediate *ortho*-alkynylated biaryls (Scheme 1).



Scheme 1. Synthetic strategy for azine-fused [5]helicenes.

It should be noted that [5]helicenes heteroannelated along the central nucleus are rather rare. Most publications are related to [5]helicenes and tetrahydro[5]helicenes condensed with furan-2,5-dione[15a-d] or pyrrole-2,5-dione rings[15d-k]. There are single reports on [5]helicenes fused with pyranone,[15l] indole,[15m] phthalocyanine,[15n,o] triazatruxene,[15p] dihydroimidazole,[15q] pyrrolobenzimidazole,[15r] naphthopyrazine,[15s] phenanthropyrazine,[15s] hexahydroquinoxaline[15q] and pyridine[13i] core.

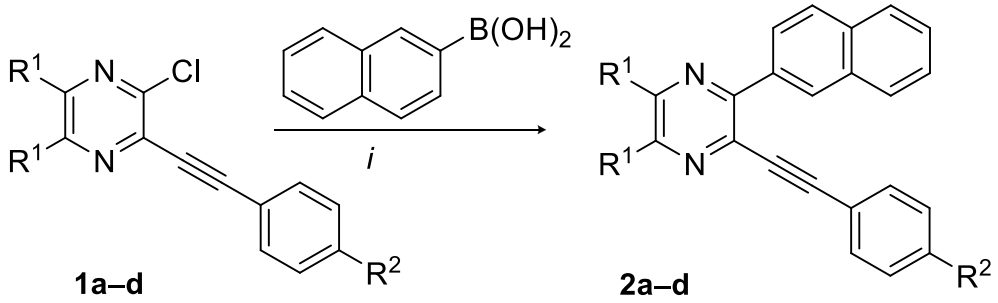
Results and discussions

In accordance with the above strategy, we first synthesized *ortho*-halogen alkynylazines **1a-d** via the Sonogashira reaction of commercially available 2,3-dihaloazines (2,3-dichloroquinoxaline and 2,3-dichloropyrazine) with phenylacetylene and 4-methoxyphenylacetylene using known[13o] procedure.

Coupling of compounds **1a–d** with naphthalen-2-ylboronic acid in the $Pd(PPh_3)_4/K_3PO_4$/THF catalytic system for 24 h under reflux (*method A*) afforded the desired 3-alkynyl-2-naphthylazines

2a–d in 72–85 % yields (Table 1). Another catalytic system with a cheaper catalyst, *e.g.* 5 % Pd/C/PPh_3/K_2CO_3/toluene (*method B*), was just as effective.

Table 1. Suzuki coupling of compounds **1** with naphthalen-2-ylboronic acid.

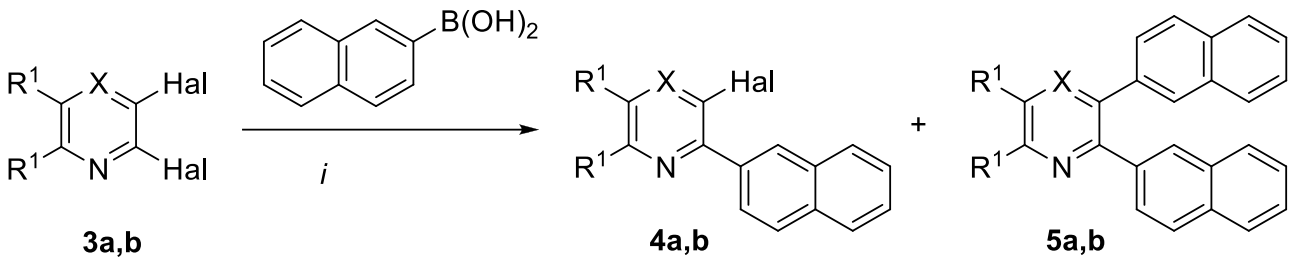


i – *method A*: $Pd(PPh_3)_4$, K_3PO_4, THF, reflux, 24 h, argon
method B: 5 % Pd/C, PPh_3, K_2CO_3, H_2O, toluene, 100 °C, 24 h, argon

Entry	R^1, R^1	R^2	Product	Yield [%] (*method*)
1	-(CH=CH)$_2$-	H	**2a**	72 (*A*) 85 (*B*)
2	-(CH=CH)$_2$-	OMe	**2b**	85 (*A*)
3	H, H	H	**2c**	82 (*A*) 80 (*B*)
4	H, H	OMe	**2d**	85 (*A*)

3-Alkynyl-2-naphthylazines can also be prepared using an alternative synthetic sequence, *i.e.* Suzuki-Miyaura arylation – Sonogashira reaction. For example, coupling of 2,3-dichloroquinoxaline **3a** and 2,3-dibromopyridine **3b** with naphthalen-2-ylboronic acid (1.2 equiv.) in the 5 % Pd/C/PPh_3/K_2CO_3/toluene catalytic system at 100 °C for 24 h gave a mixture of the corresponding mono- and dinaphthyl derivatives **4** (79–80 %) and **5** (9–10 %) (Table 2). The products were easily separated by column chromatography. *ortho*-Halogen naphthylazines **4a,b** were then introduced into Sonogashira reaction with phenylacetylene using the $Pd(PPh_3)_2Cl_2$/CuI/*i*Pr_2NH/DMSO catalytic system giving rise to 3-alkynyl-2-naphthylazines **2a,e** in high yields (Table 3).

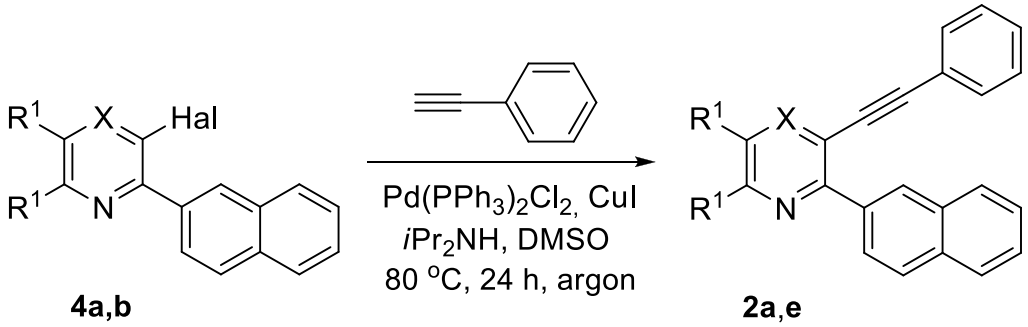
Table 2. Suzuki coupling of 2,3-dihaloazines with naphthalen-2-ylboronic acid.



i – 5 % Pd/C, PPh_3, K_2CO_3, toluene, 100 °C, 24 h, argon

Entry	X	R^1, R^1	Hal	Product	Yield [%]
1	N	-(CH=CH)$_2$-	Cl	**4a**	80
				5a	9
2	CH	H, H	Br	**4b**	79
				5b	10

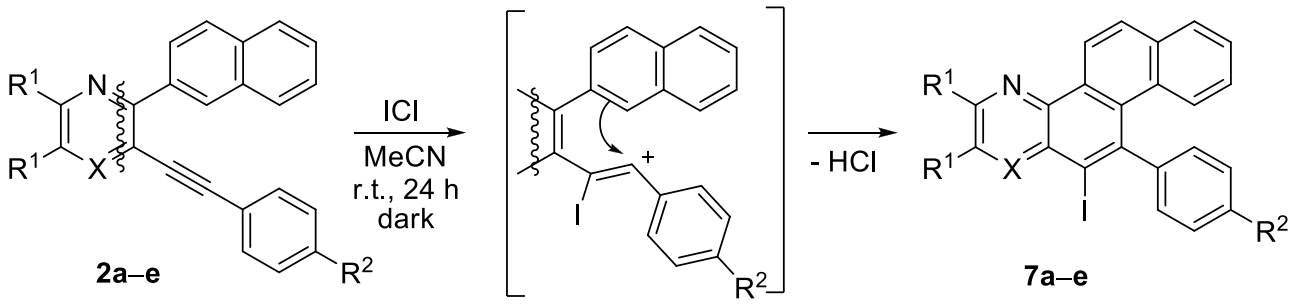
Table 3. Sonogashira coupling of compounds **4** with phenylacetylene.



Entry	X	R^1, R^1	Hal	Product	Yield [%]
1	N	-(CH=CH)$_2$-	Cl	**2a**	83
2	CH	H, H	Br	**2e**	95

Electrophilic cyclizations of 3-alkynyl-2-naphthylazines **2a–e** into phenanthroazines **7a–e** were carried out with a 1.5-fold excess of ICl in dry acetonitrile at room temperature in the dark (Table 4). In all cases, the product yield exceeded 84 %. It should be noted that compounds **7** are derivatives of the little-known heterocyclic systems naphtho[1,2-*h*]quinoline,[16a] naphtho[2,1-*f*]quinoxaline,[13o,16b,c] naphtho[2,1-*a*]phenazine[13n,16d-g]. After reviewing these publications, the synthetic sequence described above seems to be the best method for constructing these heterosystems.

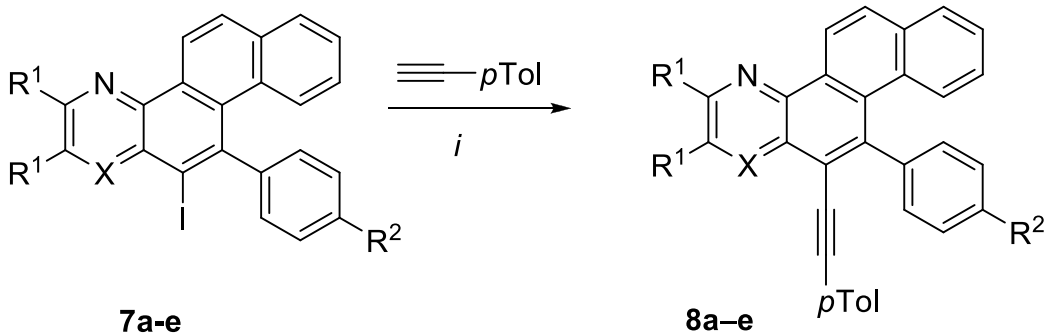
Table 4. ICl-Induced cyclyzation of compounds **2**.



Entry	X	R^1, R^1	R^2	Product	Yield [%]
1	N	-(CH=CH)$_2$-	H	**7a**	84
2	N	-(CH=CH)$_2$-	OMe	**7b**	90
3	N	H, H	H	**7c**	85
4	N	H, H	OMe	**7d**	89
5	CH	H, H	H	**7e**	95

Performing the next stage of the synthesis, namely, Sonogahira coupling of iodides **7** with *p*-tolylacetylene, we encountered some difficulties. In the reaction of **7b**, the $Pd(PPh_3)_2Cl_2$/CuI/*i*Pr_2NH/DMSO catalytic system, which proved to be effective in the synthesis of compounds **2a,e**, made it possible to obtain alkyne **8b** in 76 % yield (Table 5, Entry 2). In case of **7a**, the reaction was less effective producing alkyne **8a** in 51 % yield only (Entry 1). Pyrazine-based substrate **7c** showed even lower reactivity giving rise to the corresponding alkynyl derivative **8c** in 21 % yield (Entry 3). The use of the $Pd(PPh_3)_2Cl_2$/CuI/Et_3N/THF catalytic system has led to a significant increase in the yields of products **8a-d**. In the reaction of iodide **7e** with *p*-tolylacetylene, this catalytic system showed the greatest efficiency, allowing to obtain alkyne **8e** in 91 % yield (Entry 5). In case of substrate **7c**, the $Pd(PPh_3)_4$/CuI/Et_3N catalytic system at 85 °C gave the best result (65–74 %).

Table 5. Sonogashira coupling of compounds **7** with *p*-tolylacetylene.

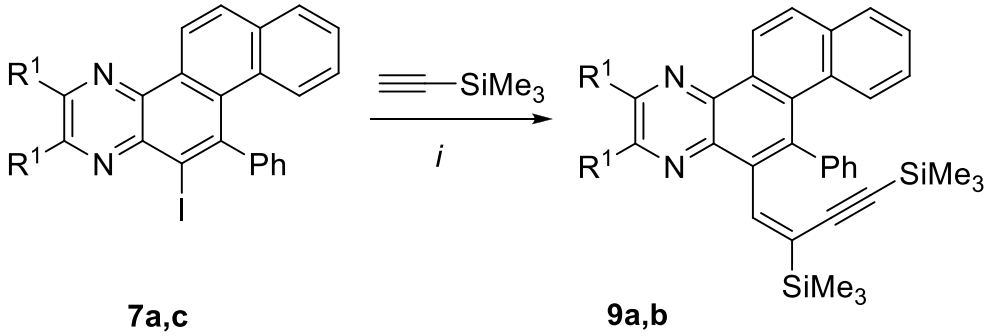


i - $Pd(PPh_3)_2Cl_2$, CuI, base, solvent, 80 °C, 24 h, argon

Entry	X	R^1, R^1	R^2	Base, solvent	Product	Yield [%]
1	N	-(CH=CH)$_2$-	H	*i*Pr$_2$NH, DMSO	**8a**	51
				Et$_3$N, THF		63
2	N	-(CH=CH)$_2$-	OMe	*i*Pr$_2$NH, DMSO	**8b**	76
3	N	H, H	H	*i*Pr$_2$NH, DMSO	**8c**	21
				Et$_3$N, THF		48–52
				Et$_3$N[a]		65–74
4	N	H, H	OMe	Et$_3$N, THF	**8d**	62
5	CH	H, H	H	Et$_3$N, THF	**8e**	91

[a] $Pd(PPh_3)_4$ was used instead of $Pd(PPh_3)_2Cl_2$. The reaction was carried out at 85 °C.

In contrast to the above reaction, the interaction of iodides **7a,c** with trimethylsilylacetylene under the same conditions resulted in the formation of exclusively enynes **9a,b** (Scheme 2). When using a 2-fold excess of alkyne, compound **9a** was obtained in 10 % yield only. The starting iodide **7a** has been recovered by 75 %. The reaction of **7a** with a 7-fold excess of trimethylsilylacetylene gave **9a** in 84 % yield. Similarly, iodide **7c** was transformed into enyne **9b** (64 %). Usually enynes are formed in the Sonogashira reaction as a minor product.[17] Most recently, a mechanism for their formation has been proposed and argued.[17c] It is believed that the intermediate of type **10**, formed at the *trans*-metallation step, coordinates the second trimethylsilylacetylene molecule giving rise to complex **11** (Scheme 3). Then, migratory insertion of the alkyne ligand into the C–X bond affords alkenyl palladium *cis*-complex **12**. Subsequent reductive elimination affords enyne **9**. Only one question remains: why is enyne **9** the only product of the above reaction? Probably, the *peri*-aza group makes reductive elimination of Pd^0 from complex **10** difficult and contributes to the coordination of alkyne in complex **11**. This assumption is supported by the fact that the interaction of the pyridine substrate **7e** with a 7-fold excess of trimethylsilylacetylene gave a mixture of the "normal" Sonogashira product and the corresponding enyne in a 1.5: 1 ratio.

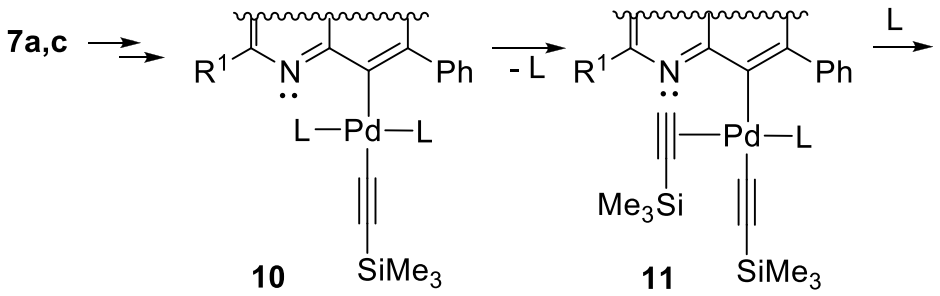


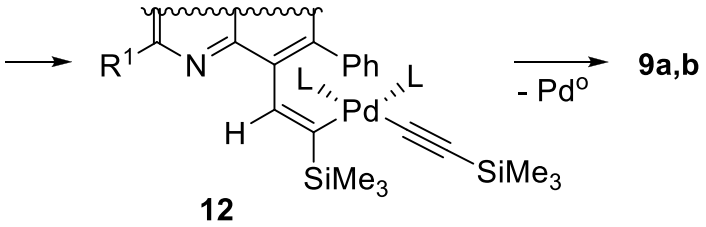
7a,c **9a,b**

i - $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, 75–80 °C, 24 h, argon

9: a R^1,R^1 = -(CH=CH)$_2$-, **b** R^1 = R^1 = H

Scheme 2. Sonogashira coupling of compounds **7** with trimethylsilylacetylene.

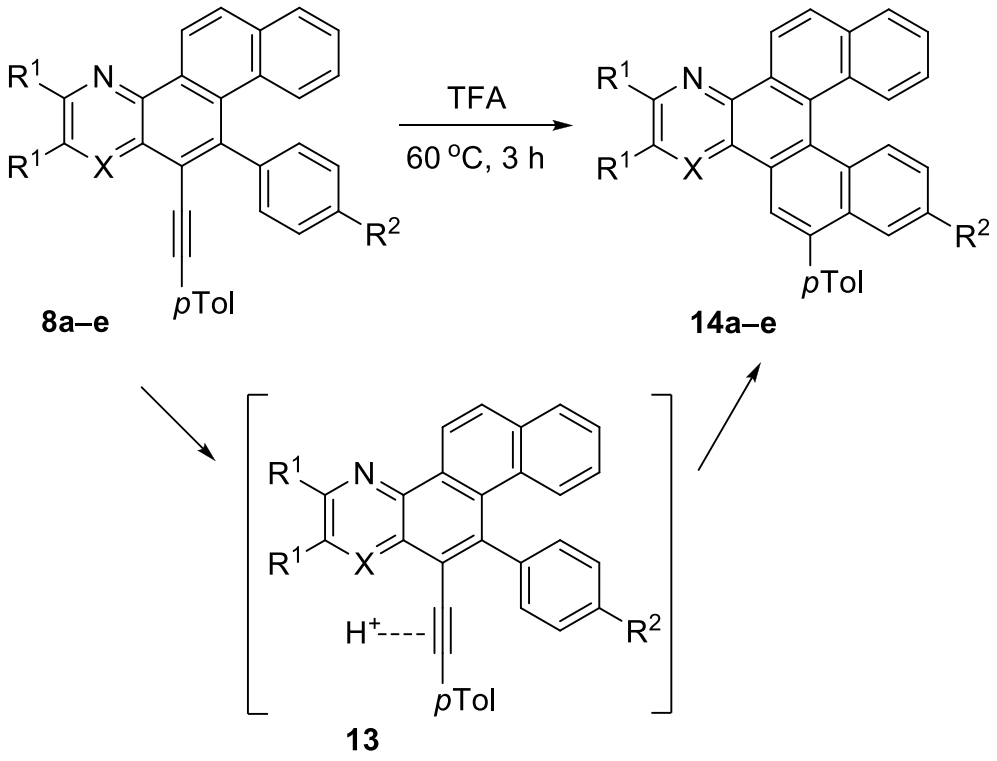




Scheme 3. A reasonable mechanism for the formation of products **9**.

Heating of alkynyl derivatives **8a-e** in trifluoroacetic acid led to their isomerization into the desired [5]helicene hybrids **14a-e** (Table 6). Helicenes **14a,b,e** were obtained in almost quantitative yields (Entries 1,2,5), while pyrazine-fused helicenes **14c,d** were isolated in 31–35 % yield (Entries 3,4). Apparently, the reason for the low yield of these products is the high basicity of the aza group adjacent to the triple bond in compounds **8c,d**. Its protonation makes the formation of intermediate **13** difficult. Fortunately, the treatment of alkynes **8c,d** with triflic acid in CH_2Cl_2 solution at room temperature allowed us to obtain the desired helicenes **14c,d** in quantitative yield.

Table 6. TFA-Induced cyclyzation of compounds **8**.



Entry	X	R^1, R^1	R^2	Product	Yield [%]
1	N	-(CH=CH)$_2$-	H	**14a**	92
2	N	-(CH=CH)$_2$-	OMe	**14b**	98
3	N	H, H	H	**14c**	31[a] 98[b]
4	N	H, H	OMe	**14d**	35[a] 94[b]
5	CH	H, H	H	**14e**	95[a]

[a] Reaction was carried out at 85 °C for 24 h.
[b] Reaction was carried out with TfOH in CH_2Cl_2 at r.t. for 24 h.

We performed single-crystal diffraction studies of helicenes **14b** and **14c** (Figure 1) and compared the solid-state structure of [5]helicene and its benzene- and azine-fused on the central ring hybrids **14** to see the effect of annelation (Table 7). Compound **14c** possesses pronounced polymorphism: orange prisms and pale yellow plates are simultaneously formed under conditions of isothermic crystallization from chloroform - acetonitrile solution. X-ray diffraction studies were carried out for both forms. The orange polymorph seems to be more stable with one independent molecule in the unit cell (Figure 1, *c* and Table 7). Its crystal structure is characterized by a compact arrangement of alternating enantiomeric helicene molecules (Figure 1, *d*). By contrast, there are five independent molecules (40 in total) in the unit cell of the pale yellow polymorph (see Supporting Information, S54). The packing of molecules in a crystal reminds fancy lace (S55).

Torsion and interplanar angles are usually used to describe the extent of distortion of the helical skeleton. The former is dihedral angle between the four adjacent inner helix carbon atoms, the latter is the angle between the two terminal aromatic rings. It is easy to see that benzo[5]helicene[18] is more twisted than [5]helicene itself. The interplanar angle between the two terminal rings *A* and *D* of [5]helicene is equal to 48.3°,[10d] whereas the same value for benzo[5]helicene is 53.9°. Evidently, this extra twisting is the result of the repulsive interaction of the H(9) and H(f) atoms of this molecule. Pyrazine-fused [5]helicene **14c** (orange polymorph) demonstrates intermediate helicity (51.0°). In the case of pale-yellow polymorph, the interplanar angles for five independent molecules range from 49.1 to 53.1°. Quinoxaline-helicene hybrid **14b** depicts a similar twisted helical shape, but the distortion angle of 41.1° was significantly smaller than in the parent [5]helicene and its benzo- and pyrazine-fused analogs. On the one hand, this flattening may originate from the attractive interaction of the aza groups N(f) and N(e) with the H(9) and H(6) atoms, respectively. The short intramolecular contact H(9)….N(f) (2.459 Å) and H(6)….N(e) (2.449 Å) as well as smaller angles in the bay region of molecule **14b** supports this opinion. But the question arises: why is this effect not so noticeable in the case of helicene **14c** ? Thus, it can be assumed that the flattening of helicene **14b** may be a result of packing forces. In accordance with the foregoing, the sum of the inner helix torsion angles in the most twisted benzo[5]helicene is the largest, while in the more planar quinoxaline-helicene this sum is the smallest.

Because of torsion strain, the bond lengths in the helicenes skeletons are different, with different C-C bonds having features of a single bond or a double bond. In comparison with the bond length of benzene (1.393 Å), the bond lengths of the C-C bonds in the inner helix of [5]helicene itself are lengthened to 1.411–1.460 Å, while the outer helix C-C bonds are shortened to 1.342–1.372 Å. Benzo[5]helicene has the shortest inner helix bonds, while quinoxaline-fused [5]helicene has the longest both inner and outer helix bonds. The lengths of the C-C bonds of the central *C* ring are the most deviated from the standard length. This is especially noticeable in the case of quinoxaline-[5]helicene hybrid **14b**, in which the C(b)-C(c) bond length is 1.475 Å, which is very close to the value of the standard single C(sp^2)-C(sp^2) bond (ca. 1.48 Å).

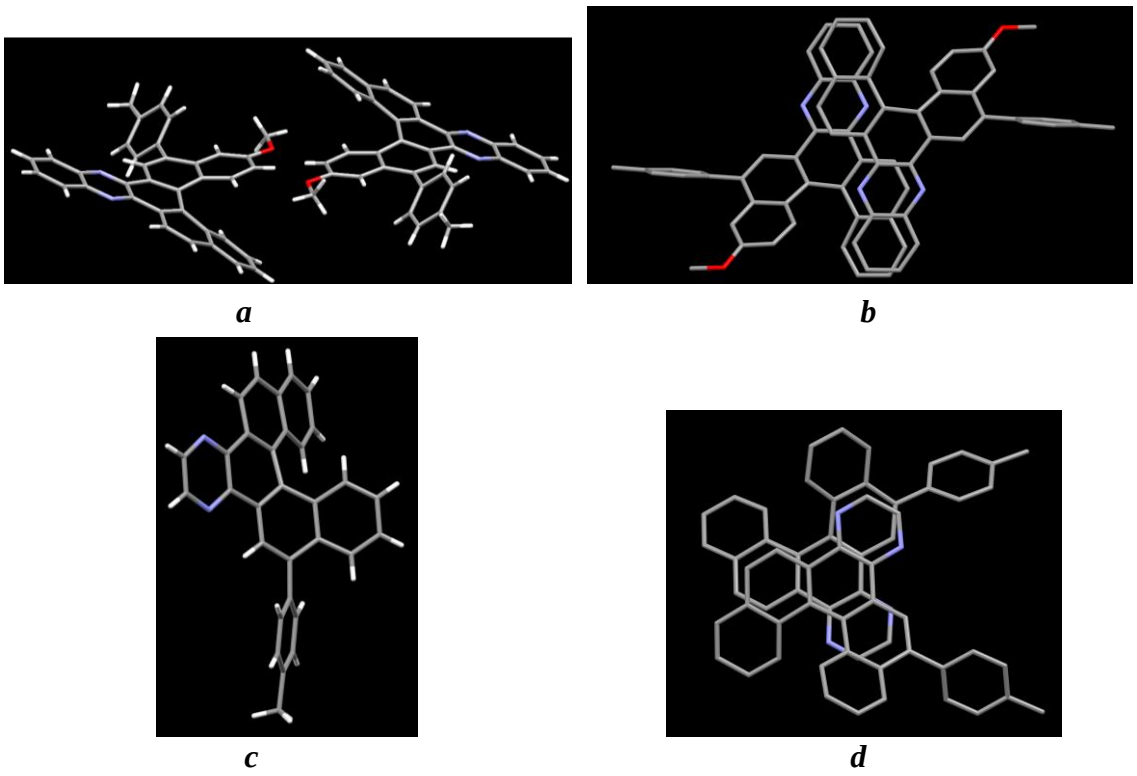
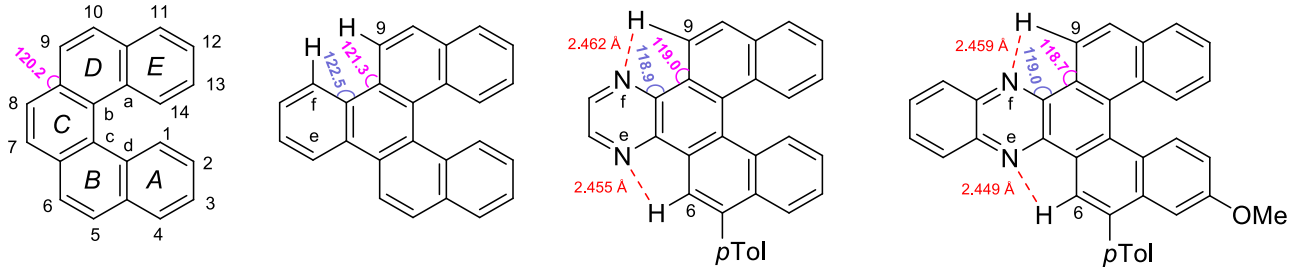


Figure 1. Molecular structure and packing of quinoxaline-fused [5]helicene **14b** (*a*, *b*) and pyrazine-fused [5]helicene **14c** (*c*, *d*) (X-ray data).

Table 7. Comparison of X-ray data of [5]helicene and condensed analogs.



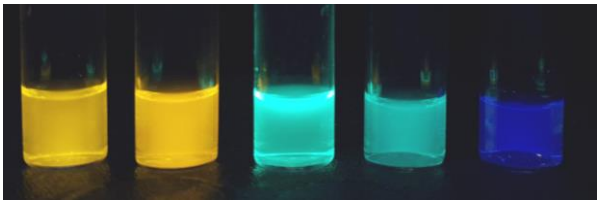
Helicene	Space group	Bond length [Å]			Inner helix angle [°]	Torsion angle [°]	Interplanar angle [°]
		Inner helix	Outer helix	Ring *C*			
		1-d	3-4	b-c	1-d-c	1-d-c-b	*A*/*E*
		d-c	5-6	c-6a	d-c-b	d-c-b-a	
		c-b	7-8	6a-7	c-b-a	c-b-a-14	
		b-a	9-10	7-8	b-a-14		
		a-14	11-12	8-8a			
				8a-b			
[5]Helicene [10d]	$P2_1/c$	1.412	1.372	1.447	123.50	20.20	48.29*
		1.449	1.354	1.414	124.80	29.84	50.17
		1.447	1.359	1.407	124.46	16.41	51.30

		1.460 1.411 (7.179 in total)	1.342 1.360 (6.787 in total)	1.359 1.417 1.417 (8.461 in total)	123.21 (495.97 in total)	(66.45 in total)	
Benzo[5]helicene [18]	P 21/n	1.407 1.455 1.454 1.447 1.410 (7.173 in total)	1.347 1.350 1.414 1.344 1.348 (6.803 in total)	1.454 1.393 1.456 1.414 1.452 1.398 (8.567 in total)	123.40 123.11 122.87 123.42 (492.80 in total)	19.64 32.72 20.52 (72.88 in total)	53.91
Pyrazine-fused [5]helicene **14c** (orange polymorph)	P bca	1.420 1.457 1.462 1.452 1.421 (7.212 in total)	1.370 1.363 1.404 1.354 1.367 (6.858 in total)	1.462 1.402 1.449 1.404 1.450 1.410 (8.527 in total)	121.77 124.79 124.12 123.47 (494.15 in total)	21.39 30.09 15.88 (67.36 in total)	51.00
Quinoxaline-fused [5]helicene **14b**	P 21/c	1.422 1.451 1.475 1.448 1.424 (7.220 in total)	1.375 1.377 1.431 1.359 1.371 (6.913 in total)	1.475 1.400 1.457 1.431 1.458 1.401 (8.622 in total)	122.19 124.48 124.01 123.16 (493.84 in total)	17.76 28.86 17.49 (64.11 in total)	41.09

* There are three independent molecules in the unit cell. All data are of this molecule.

In the crystal packing of **14b**, a pair of enantiomeric helicene molecules are aggregated on the manner of embrace (Figure 1, *a*). The solid structure of azine-helicene hybrids **14b** and **14c** displayed layers of the aromatic molecules. An intermolecular distance of 3.77 Å was found between the centroids of the central benzene ring *C* of one molecule of **14b** and ring *D* of another making π overlap possible. In the case of **14c**, the distance between the centroids of the *C* rings of two adjacent molecules as measured to be 3.75 Å. The layered structures of both hybrids **14b** (Figure 1, *b*) and **14c** (Figure 1, *d*) show increased π overlap (with participation of four aromatic rings of each helicene molecule) when compared to [5]helicene itself (only two aromatic rings of each helicene molecule participate in overlapping).[10d] Co-planar or stacked-like arrangements shown in the solid-state structures of **14c** and **14b** are typically important when developing organic electronic materials.[19]

[5]Helicene is an off-white compound with λ_{max} 350 nm.[10d] Annelation of pyridine or pyrazine ring to the [5]helicene skeleton changed the wavelength of the absorption maximum (Table 8, S56). Pyridine- and pyrazine-fused [5]helicenes **14e** and **14c,d** are off-white (λ_{max} 357 nm, $CHCl_3$) and pale yellow (λ_{max} 396–402 nm), respectively. The absorption of quinoxaline-based [5]helicenes **14a,b** was red-shifted (λ_{max} 415–421 nm). Both compounds are bright yellow. It should be noted that UV-vis spectrum of [7]helicene,[20] which contains as many aromatic rings as compounds **14a,b**, only tails to about 400 nm, whereas these helicene hybrids have a significant absorption band at 415–421 nm and tails up to 500–508 nm. All azine-fused [5]helicenes **14** were nearly non-fluorescent in chloroform solution and showed weak fluorescence in the acetonitrile solution (Figure 2). The optical band gaps (E_g^{opt}), estimated from the onset point of the absorption spectra, were 2.44 eV (**14a**), 2.66 eV (**14c**) and 2.96 eV (**14e**) (Table 8). The E_g^{opt} value of [5]helicene itself estimated from the intersection between the absorption and emission bands was equal to 3.59 eV.[10d] These spectral differences are most likely a result of the extended π-conjugation in the hybrid helicenes **14**, suggesting a higher HOMO and lower oxidation potential, which are typically desired characteristics when designing organic materials. As can also be seen, an increase in the π-deficiency of heteroring fused to [5]helicene leads to a decrease in the optical band gap.



14a **14b** **14d** **14c** **14e**

Figure 2. Acetonitrile solutions of [5]helicenes **14** under UV irradiation (365 nm).

The cathodic and anodic electrochemistry of azine-fused [5]helicenes **14a**, **14c** and **14e** was evaluated by cyclic voltammetry (CV) in dichloromethane solution containing 0.1 M *n*-Bu_4NPF_6 vs. $Ag/AgNO_3$ in the standard three-electrode electrochemical cell (Table 8, S57-S59). All helicenes displayed three irreversible oxidation waves (in cases of **14a** and **14c**, two of them are overlapped), with the little variation of the potentials induced by the fused heteroring. Scanning cathodically, quinoxaline-fused helicene **14a** showed reversible and quasi-reversible reduction waves at $E_{1/2}^{red}$ = -1.57 V (1) and -1.88 V (2) vs. the ferrocenium/ferrocene couple, respectively. The first of them corresponds to the anion-radical specie as confirmed by the EPR spectroscopy data (S57). The

reductions of **14c** were very close to one another. In the case of **14e**, reduction wave was not expressed on CV.

From the first oxidation potentials and $E_{1/2}(Fc^+/Fc)$ = -4.80 eV, highest occupied molecular orbital energies E_{HOMO} of -5.58 (**14a**), -5.67 (**14c**) and -5.69 eV (**14e**) were obtained (Table 8). From the first reduction potential, lowest unoccupied molecular orbital energy and electrochemical band gap of **14a** were calculated as -3.23 eV (E_{LUMO}) and 2.35 eV (E_g^{el}), respectively. LUMO energy levels of **14c** and **14e** were deduced from the corresponding E_{HOMO} and optical band gaps E_g^{opt}.

Table 8. Photophysical properties of azine-fused [5]helicenes **14**.

Com-pound	λ_{max} [nm][a]	λ_{onset} [nm]	E_g^{opt} [eV][b]	$E_{1/2}^{ox}(1)$ [V][c]	$E_{1/2}^{red}(1)$ [V][c]	E_{HOMO}/ E_{LUMO} [eV]	E_g^{el} [eV][f]
14a	415	508	2.44	+0.78	-1.57	-5.58/-3.23[d]	2.35
14c	396	466	2.66	+0.87	-	-5.67/-2.97[e]	-
14e	357	419	2.96	+0.89	-	-5.69[d]/-2.71[e]	-

[a] Absorption maxima measured in $CHCl_3$ solution10^{-5} M. [b] The optical gap was estimated from the onset point of the absorption spectra: $E_g^{opt} = 1240/\lambda_{onset.}$ [c] CV data (vs. Fc^+/Fc).
[d] Estimated from the first oxidation and reduction potential and $E_{1/2}(Fc^+/Fc)$ = -4.80 eV.
[e] Deduced from E_{HOMO} and E_g^{opt}. [f] Electrochemical band gap.

Conclusions

In summary, novel pyridine-, pyrazine- and quinoxaline-[5]helicene hybrids have been prepared from commercially available 2,3-dihaloazines via a five-step synthetic sequence. Two key steps of the method are electrophile-induced *6-endo-dig* cyclizations of *ortho*-alkynylated biaryls. The overall yields of helicenes in five stages of the synthesis exceed 30 %. It seems that the proposed method is more efficient than other currently existing synthetic routes for [5]helicenes.

In addition, the azine-fused helicenes represent novel helicene structures with an increased π surface. Their physical properties were compared to the parent [5]helicene. Spectrophotometric analysis displayed significant absorption red-shifts (7–65 nm) and reduced optical band gaps (by 0.6–1.2 eV) for the azine-helicene hybrids. The obtained compounds showed amphoteric multiredox behavior, which is characteristic for π-expanded molecules. Extending the π surface of the [5]helicene molecule by annelating an azine ring (without lengthening of the helix) led to an increase in the HOMO level and a decrease in the LUMO level resulting in significantly reduced electrochemical band gap. X-Ray crystal structure analysis of pyrazine- and quinoxaline-helicene hybrids revealed greater π overlap and, in the case of quinoxaline-fused helicene, a smaller distortion angle in the "twist" as compared to [5]helicene itself.

Experimental Section

General Information: Reactions were monitored by thin layer chromatography (silica gel 60 F_{254}) and visualized using UV. Flash column chromatography was performed using silica gel (230–400 mesh, grade 60). Commercial alkynes, naphthalene-2-boronic acid, catalysts, ICl, 2,3-dihaloazines, diisopropylamine, triethylamine, PPh_3, TFA, triflic acid, anhydrous DMSO, THF were used as received. ^1H, ^{13}C NMR spectra were recorded on 250, 400 and 600 MHz spectrometers. Chemical shifts were reported in ppm relative to Me_4Si. The IR spectra were recorded on a FT-IR spectrometer. The UV-vis spectra were recorded on Varian Cary 50 Probe spectrophotometer in $CHCl_3$. The HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source.

Crystal Structure Determination: X-Ray measurements were conducted with Bruker APEX II CCD diffractometer and four-circle diffractometer SuperNova, Single source at offset/far, HyPix3000. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 1920988 (**14b**), CCDC 1920968 (**14c**, orange polymorph) and CCDC 1920967 (**14c**, pale yellow polymorph). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2-(Naphthalen-2-yl)-3-(phenylethynyl)quinoxaline (2a): *Method A.* 2-Chloro-3-(phenylethynyl)quinoxaline **1a**[13o] (264 mg, 1.0 mmol), naphthalen-2-ylboronic acid (258 mg, 1.5 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol), K_3PO_4 (424 mg, 2.0 mmol) and dry THF (15 mL) were stirred and refluxed under argon for 24 h. The reaction mixture was then evaporated to dryness. The residue was treated with water (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (3.5 × 50 cm) with CH_2Cl_2 as the eluent. The fraction with R_f 0.7 was the recovered starting compound (5–7 %). The next yellowish fraction with R_f 0.5 gave 258 mg (72 %) of compound **2a**.

Method B. 2-Chloro-3-(phenylethynyl)quinoxaline **1a** (264 mg, 1.0 mmol), naphthalen-2-ylboronic acid (189 mg, 1.1 mmol), 5 % Pd/C (16 mg, 0.015 mmol Pd), PPh_3 (16 mg, 0.6 mmol), toluene (1 mL) and a solution of K_2CO_3 (552 mg, 4 mmol) in water (3 mL) were stirred at 100 °C for 24 h under argon. The reaction mixture was then diluted with water (50 mL) and extracted with

CH_2Cl_2 (3 × 15 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (3.5 × 40 cm) with CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.5 gave 302 mg (85 %) of compound **2a**.

Method C. Compound **2a** was obtained similarly to **2e** starting from 2-chloro-3-(naphthalen-2-yl)quinoxaline **4a** (145 mg, 0.5 mmol). Yield 148 mg (83%).

2-(Naphthalen-2-yl)-3-(phenylethynyl)quinoxaline **2a** was obtained as white needles with m.p. 134–136 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.28–7.40 (m, 3 H), 7.50 (d, J = 7.0 Hz, 2 H), 7.56–7.62 (m, 2 H), 7.79–7.82 (m, 2 H), 7.97 (d, J = 7.4 Hz, 1 H), 8.02 (d, J = 7.4 Hz, 1 H), 8.05 (d, J = 8.6 Hz, 1 H), 8.18–8.21 (m, 2 H), 8.27 (d, J = 8.5, 1.1 Hz, 1 H), 8.73 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 88.6, 95.2, 121.7, 126.5, 126.9, 127.1, 127.81, 127.82, 128.5, 128.80, 128.82, 129.4, 129.6, 129.9, 130.3, 130.7, 132.2, 133.0, 133.9, 135.0, 138.2, 140.9, 141.1, 154.8. HRMS (ESI): *m/z* calcd. for $C_{26}H_{17}N_2^+$ [M+H$^+$]: 357.1386, found 357.1387.

2-((4-Methoxyphenyl)ethynyl)-3-(naphthalen-2-yl)quinoxaline (2b) was obtained similarly to **2a** (*Method A*) starting from 2-chloro-3-((4-methoxyphenyl)ethynyl)quinoxaline **1b** (294 mg, 1.0 mmol). R_f 0.5. Yield 328 mg (85 %). Yellowish needles with m.p. 153–155 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.80 (s, 3 H), 6.83 (d, J = 8.5 Hz, 2 H), 7.42 (d, J = 8.5 Hz, 2 H) 7.56–7.62 (m, 2 H), 7.77–7.80 (m, 2 H), 7.96–8.05 (m, 3 H), 8.17 (dd, J = 8.6, 4.4 Hz, 2 H), 8.27 (d, J = 8.5 Hz, 1 H), 8.73 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.3, 87.9, 95.9, 113.7, 114.2, 126.5, 126.9, 127.1, 127.7, 127.8, 128.7, 128.8, 129.3 (2C), 129.9, 130.2, 130.4, 132.9, 133.9, 135.1, 138.5, 140.7, 141.1, 154.7, 160.7. HRMS (ESI): *m/z* calcd. for $C_{27}H_{19}N_2O^+$ [M+H$^+$]: 387.1492, found 387.1499.

2-(Naphthalen-2-yl)-3-(phenylethynyl)pyrazine (2c) was obtained similarly to **2a** (*Methods A and B*) starting from 2-chloro-3-(phenylethynyl)pyrazine **1c** (214 mg, 1.0 mmol). R_f 0.35. Yield 251 mg (82 %, *Method A*) and 245 mg (80 %, *Method B*). Colorless needles with m.p. 100–102 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.32–7.40 (m, 3 H), 7.49–7.51 (m, 2 H), 7.55–7.61 (m, 2 H), 7.94–8.03 (m, 3 H), 8.22 (dd, J = 8.5, 1.4 Hz, 1 H), 8.59 (d, J = 2.2 Hz, 1 H), 8.65 (d, J = 2.2 Hz, 1 H), 8.71 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 87.7, 94.8, 121.8, 126.5, 127.1, 127.77, 127.83, 128.5, 128.8, 129.47 (2C), 129.52, 132.0, 132.9, 133.8, 134.4, 137.6, 142.4, 142.5, 155.4. HRMS (ESI): *m/z* calcd. for $C_{22}H_{15}N_2^+$ [M+H$^+$]: 307.1230, found 307.1234.

2-((4-Methoxyphenyl)ethynyl)-3-(naphthalen-2-yl)pyrazine (**2d)** was obtained similarly to **2a** *(Method A)* starting from 2-chloro-3-((4-methoxyphenyl)ethynyl)pyrazine **1d** (245 mg, 1.0 mmol). R_f 0.3. Yield 286 mg (85 %). Yellow solid with m.p. 84–85 °C (EtOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 3.78 (s, 3H), 6.82 (d, J = 8.8 Hz, 2 H), 7.39 (d, J = 8.8 Hz, 2 H), 7.52–7.57 (m, 2 H), 7.90 (d, J = 7.8 Hz, 1 H), 7.94 (d, J = 7.8 Hz, 1 H), 7.97 (d, J = 8.5 Hz, 1 H), 8.17 (dd, J = 8.5, 1.7 Hz, 1 H), 8.53 (br s, 1 H), 8.58 (br s, 1 H), 8.66 (br s, 1 H). ^{13}C NMR (150.94 MHz, $CDCl_3$): δ [ppm] = 55.3, 86.8, 95.3, 113.8, 114.2 (2C), 126.4, 126.5, 127.0, 127.7, 128.7, 129.4, 132.9, 133.6, 133.8, 134.5, 137.9, 142.0, 142.3, 155.0, 160.6. IR (Nujol): 2218 (C≡C) cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{23}H_{17}N_2O^+$ [M+H$^+$]: 337.1335, found 337.1338.

2-(Naphthalen-2-yl)-3-(phenylethynyl)pyridine (2e): A mixture of 3-bromo-2-(naphthalen-2-yl)pyridine **4b** (142 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), CuI (4 mg, 0.02 mmol), *i*Pr_2NH (1 mL) and DMSO (5 mL) was stirred at 80 °C for 20 min under argon. Then a solution of phenylacetylene (153 mg, 0.16 mL, 1.5 mmol) in *i*Pr_2NH (2 mL) was added by portions for 1 h. The reaction mixture was stirred at 80 °C for 24 h, evaporated without heating to remove *i*Pr_2NH, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (3.5 × 35 cm) with CH_2Cl_2 as the eluent. The fraction with R_f 0.25 and violet fluorescence gave 145 mg (95 %) of 2-(naphthalen-2-yl)-3-(phenylethynyl)pyridine **2e**. The viscous oily product was crystallized by mashing with EtOH (0.5 mL). Yellowish solid with m.p. 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.28–7.34 (m, 4 H), 7.42–7.45 (m, 2 H), 7.53–7.59 (m, 2 H), 7.93–8.06 (m, 4 H), 8.22 (dd, J = 8.6, 1.5 Hz, 1 H), 8.66 (s, 1 H), 8.74 (dd, J = 4.7, 1.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 87.7, 94.9, 118.2, 121.5, 122.8, 126.1, 126.6, 127.0, 127.5, 127.7, 128.4, 128.69, 128.71, 129.2, 131.5, 133.1, 134.6, 136.8, 141.0, 148.6, 159.4. HRMS (ESI): *m/z* calcd. for $C_{23}H_{16}N^+$ [M+H$^+$]: 306.1277, found 306.1266.

3-Bromo-2-(naphthalen-2-yl)pyridine (4b) and 2,3-di(naphthalen-2-yl)pyridine (5b): A mixture of 2,3-dibromopyridine **3b** (119 mg, 0.5 mmol), naphthalen-2-ylboronic acid (103 mg, 0.6 mmol), 5 % Pd/C (16 mg, 0.015 mmol), PPh_3 (16 mg, 0.06 mmol), 2M aqueous solution K_2CO_3 (2 mL) and toluene (0.5 mL) were stirred at 100 °C under argon for 24 h. The reaction mixture was then extracted with CH_2Cl_2 (3 × 15 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (3.5 × 20 cm) with CH_2Cl_2 as the eluent. The fraction with R_f

0.3 gave compound **4b** 140 mg (98 %). The loadings may be increased 4-fold. In this case, compound **4b** was obtained in 79 % together with 2,3-di(naphthalen-2-yl)pyridine **5b** (10 % yield, R_f 0.2).

3-Bromo-2-(naphthalen-2-yl)pyridine **4b** was obtained as an off-white solid with m.p. 63–66 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.15 (dd, J = 8.1, 4.6 Hz, 1 H), 7.49–7.54 (m, 2 H), 7.80 (dd, J = 8.5, 1.7 Hz, 1 H), 7.88–7.94 (m, 3 H), 8.02 (dd, J = 8.1, 1.4 Hz, 1 H), 8.19 (d, J = 1.1 Hz, 1 H), 8.66 (dd, J = 4.6, 1.4 Hz, 1 H). ^{13}C NMR (150.94 MHz, $CDCl_3$): δ [ppm] = 120.1, 123.3, 126.2, 126.7, 126.8, 127.6, 127.7, 128.6, 129.0, 132.9, 133.3, 137.0, 141.4, 148.1, 158.1. HRMS (ESI): *m/z* calcd. for $C_{15}H_{11}BrN^+$ [M+H$^+$]: 286.0049 (^{81}Br), 284.0069 (^{79}Br); found 286.0056 (^{81}Br), 284.0075 (^{79}Br).

2,3-Di(naphthalen-2-yl)pyridine **5b** was obtained as an off-white solid with m.p. 115–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.22 (dd, J = 8.5, 1.6 Hz, 1 H), 7.41–7.47 (m, 4 H), 7.48–7.52 (m, 2 H), 7.63 (d, J = 8.5 Hz, 1 H), 7.64 (d, J = 8.5 Hz, 1 H), 7.75–7.83 (m, 4 H), 7.88 (s, 1 H), 7.91 (dd, J = 7.7, 1.5 Hz, 1 H), 8.11 (s, 1 H), 8.83 (dd, J = 4.7, 1.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 122.2, 125.9, 126.2, 126.3, 127.3, 127.5, 127.6, 127.71, 127.78, 127.81 (2C), 128.1, 128.3, 128.6, 129.6, 132.4, 132.9, 133.3, 133.5, 136.2, 137.6, 137.7, 139.1, 148.6, 157.0 HRMS (ESI): *m/z* calcd. for $C_{25}H_{19}N^+$ [M+H$^+$]: 332.1434, found 332.1439.

2-Chloro-3-(naphthalen-2-yl)quinoxaline (4a) and 2,3-di(naphthalen-2-yl)quinoxaline (5a): Compounds **4a** and **5a** were obtained similarly to **4b** and **5b** starting from 2,3-dichloroquinoxaline (100 mg, 0.5 mmol). The flash column chromatography was carried out on silica gel (3.5 × 40 cm) with CH_2Cl_2 as the eluent.

2-Chloro-3-(naphthalen-2-yl)quinoxaline **4a** was obtained as white needles with m.p. 153–155 °C (EtOH). Yield 116 mg (80 %). R_f 0.6. ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.54–7.59 (m, 2 H), 7.79–7.82 (m, 2 H), 7.90–8.00 (m, 4 H), 8.07–8.10 (m, 1 H), 8.16–8.19 (m, 1 H), 8.38 (br s, 1 H). ^{13}C NMR (150.94 MHz, $CDCl_3$): δ [ppm] = 126.6, 127.3, 127.7, 127.9, 128.2, 128.8, 129.3 129.9, 130.5, 130.8, 132.9, 133.7, 134.1, 141.0, 141.1, 146.3, 152.9. HRMS (ESI): *m/z* calcd. for $C_{18}H_{12}ClN_2^+$ [M+H$^+$]: 293.0654 (^{37}Cl), 291.0684 (^{35}Cl); found 293.0669 (^{37}Cl), 291.0693 (^{35}Cl).

2,3-Di(naphthalen-2-yl)quinoxaline **5a** was obtained as white needles with m.p. 191–193 °C (EtOH). Yield 17 mg (9 %). R_f 0.5. ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.44–7.50 (m, 2 H), 7.52 (dd, J = 8.5, 1.7 Hz, 1 H), 7.68 (d, J = 8.5 Hz, 1 H), 7.78–7.81 (m, 3 H), 8.22–8.24 (m, 2 H). ^{13}C NMR (150.94 MHz, $CDCl_3$): δ [ppm] = 126.3, 126.8, 127.1, 127.7, 127.8, 128.7, 129.3, 129.8,

130.1, 133.2, 133.3, 136.7, 141.4, 153.4. HRMS (ESI): *m/z* calcd. for $C_{28}H_{19}N_2^+$ [M+H$^+$]: 383.1543, found 383.1550.

6-Iodo-5-phenylnaphtho[2,1-*a*]phenazine (7a): To a suspension of 2-(naphthalen-2-yl)-3-(phenylethynyl)quinoxaline **2a** (71 mg, 0.2 mmol) in dry CH_3CN (10 mL) a solution of ICl (49 mg, 0.3 mmol) in dry CH_3CN (5 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark and evaporated to dryness. The residue was shaken with $CHCl_3$ (10 mL) and $Na_2S_2O_3$ solution (5 mL) and extracted with $CHCl_3$ (3 × 10 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2.5 × 40 cm) with $CHCl_3$ as the eluent. The bright yellow fraction with R_f 0.9 gave 81 mg (84 %) of the cyclization product. 6-Iodo-5-phenylnaphtho[2,1-*a*]phenazine **7a** was obtained as bright yellow needles with m.p. 217–219 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.09–7.13 (m, 1 H), 7.44–7.47 (m, 4 H), 7.62–7.66 (m, 3 H), 7.90–7.92 (m, 3 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.42–8.45 (m, 2 H), 9.60 (d, *J* = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 112.6, 122.6, 125.5, 126.6, 128.33, 128.34, 128.8, 129.1, 129.3, 129.6, 129.97, 130.01, 130.2, 130.50, 130.55, 130.6, 131.1, 135.3, 140.6, 141.4, 142.8, 143.9, 148.3, 149.5. HRMS (ESI): *m/z* calcd. for $C_{26}H_{16}IN_2^+$ [M+H$^+$]: 483.0353, found 483.0355.

6-Iodo-5-(4-methoxyphenyl)naphtho[2,1-*a*]phenazine (7b) was obtained similarly to **7a** starting from 2-((4-methoxyphenyl)ethynyl)-3-(naphthalen-2-yl)quinoxaline **2b** (77 mg, 0.2 mmol). Yield 92 mg (90 %). R_f 0.9. Bright yellow needles with m.p. 244–246 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.00 (s, 3 H), 7.14–7.19 (m, 3 H), 7.34 (d, *J* = 8.6 Hz, 2 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.55 (d, *J* = 8.9 Hz, 1 H), 7.89–7.94 (m, 3 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.42–8.45 (m, 2 H), 9.60 (d, *J* = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.4, 113.2, 114.4, 122.5, 125.6, 126.6, 128.4, 128.8, 129.3, 129.6, 130.0, 130.2, 130.5, 130.6, 130.9, 131.1, 131.3, 135.4, 140.66, 140.73, 141.5, 142.8, 143.8, 149.3, 159.6. HRMS (ESI): *m/z* calcd. for $C_{27}H_{18}IN_2O^+$ [M+H$^+$]: 513.0458, found 513.0462.

12-Iodo-11-phenylnaphtho[2,1-*f*]quinoxaline (7c) was obtained similarly to **7a** starting from 2-(naphthalen-2-yl)-3-(phenylethynyl)pyrazine **2c** (61 mg, 0.2 mmol). Flash column chromatography was carried out on silica gel (2.5 × 30 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.7 gave 73 mg (85 %) of the cyclization product. When using a larger excess of ICl (0.33 mmol), the product **7c** was obtained in near quantitative yield. Off-white needles with m.p. 220–222 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.16 (t, *J* = 7.8 Hz, 1H), 7.39–7.41 (m, 2 H), 7.50–

7.52 (m, 2 H), 7.62–7.64 (m, 3 H), 7.97 (d, *J* = 7.8 Hz, 1 H), 8.15 (d, *J* = 8.9 Hz, 1 H), 8.99 (br s, 1 H), 9.07 (br s, 1 H), 9.44 (d, *J* = 8.9 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 111.8, 122.0, 125.7, 126.8, 128.4, 128.5, 128.9, 129.3, 129.8, 130.1 (2C), 130.7, 131.2, 135.0, 140.4, 141.2, 144.3, 145.7, 148.1, 148.7. HRMS (ESI): *m/z* calcd. for $C_{22}H_{14}IN_2^+$ [M+H$^+$]: 433.0196, found 433.0201.

12-Iodo-11-(4-methoxyphenyl)naphtho[2,1-*f*]quinoxaline (7d) was obtained similarly to **7a** starting from 2-((4-methoxyphenyl)ethynyl)-3-(naphthalen-2-yl)pyrazine **2d** (67 mg, 0.2 mmol). Flash column chromatography was carried out on silica gel (2.5 × 30 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.6 gave 82 mg (89 %) of cyclization product. Light yellow solid with m.p. 196–198 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.98 (s, 3 H), 7.14 (d, *J* = 8.6 Hz, 2 H), 7.16–7.22 (m, 1 H), 7.26 (d, *J* = 8.6 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.56 (d, *J* = 8.9 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 8.04 (d, *J* = 8.9 Hz, 1 H), 8.88 (d, *J* = 1.7 Hz, 1 H), 8.98 (d, *J* = 1.7 Hz, 1 H), 9.31 (d, *J* = 8.9 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.4, 112.6, 114.6, 121.8, 125.6, 126.7, 128.5, 128.8, 129.8, 129.9. 130.9, 131.0, 131.2, 134.9, 140.2, 140.6, 141.1, 144.1, 145.5, 148.3, 159.6. HRMS (ESI): *m/z* calcd. for $C_{23}H_{16}IN_2O^+$ [M+H$^+$]: 463.0302, found 463.0312.

12-Iodo-11-phenylnaphtho[1,2-*h*]quinoline (7e) was obtained similarly to **7a** starting from 2-(naphthalen-2-yl)-3-(phenylethynyl)pyridine **2e** (61 mg, 0.2 mmol). Flash column chromatography was carried out on silica gel (2.5 × 30 cm) with CH_2Cl_2 as the eluent. The fraction with R_f 0.7 gave 57 mg (66 %) of the cyclization product. The use of ICl (65 mg, 0.4 mmol) gave **7e** in 95% yield. Yellowish prisms with m.p. 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.12 (ddd, *J* = 8.7, 6.8, 1.4 Hz, 1 H), 7.35–7.40 (m, 2 H), 7.46–7.50 (m, 2 H), 7.59–7.63 (m, 3 H), 7.65 (dd, *J* = 8.4, 4.2 Hz, 1 H), 7.95 (dd, *J* = 8.2, 1.1 Hz, 1 H), 8.12 (d, *J* = 9.0 Hz, 1 H), 8.80 (dd, *J* = 8.4, 1.5 Hz, 1 H), 9.06 (dd, *J* = 4.2, 1.5 Hz, 1 H), 9.58 (d, *J* = 9.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 108.9, 122.6, 123.4, 125.3, 126.4, 128.2, 128.4, 128.5, 128.8, 129.2, 129.5, 130.0, 130.5, 131.6, 134.8, 142.5, 144.8, 145.5, 149.1, 149.8 (2C). HRMS (ESI): *m/z* calcd. for $C_{23}H_{15}NI^+$ [M+H$^+$]: 432.0244, found 432.0244.

5-Phenyl-6-(*p*-tolylethynyl)naphtho[2,1-*a*]phenazine (8a): 6-Iodo-5-phenylnaphtho[2,1-*a*]phenazine **7a** (97 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), CuI (2 mg, 0.01 mmol) and Et_3N (5 mL) was stirred under argon for 20 min at 80–82 °C. Then a solution of *p*-tolylacetylene (46 mg, 0.4 mmol) in dry THF (5 mL) was added by portions for 3 h. The reaction mixture was stirred

for total 24 h at 80–82 °C. Then it was evaporated to dryness, treated with H_2O (100 mL) and extracted with $CHCl_3$ (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 45 cm) with $CHCl_3$ as the eluent. The first and second fractions were 1,4-di-*p*-tolylbuta-1,3-diyne and traces of the starting compound. The next yellow orange fraction with R_f 0.5 and yellow fluorescence under UV (356 nm) gave 59 mg (63 %) of compound **8a**. Yellow orange solid with m.p. 234–236 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.39 (s, 3 H), 7.14–7.19 (m, 3 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.52 (t, J = 7.3 Hz, 1 H), 7.55–7.65 (m, 5 H), 7.70 (d, J = 8.8 Hz, 1 H), 7.91–7.96 (m, 2 H), 7.99 (d, J = 7.7 Hz, 1 H), 8.19 (d, J = 8.8 Hz, 1 H), 8.44–8.51 (m, 2 H), 9.69 (d, J = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.6, 86.9, 101.3, 120.7, 122.5, 122.6, 125.4, 126.6, 127.9, 128.5, 128.8 (2C), 128.9, 129.7, 129.9, 130.0, 130.12, 130.15, 130.2, 130.3, 130.4, 130.9, 131.7, 135.3, 138.4, 141.0, 141.9, 142.6, 143.1, 143.5, 147.2. UV-vis, λ_{max} nm (lg ε): 264 (4.76), 308 (4.52), 339 (4.47), 353 (4.36), 396 (4.06), 417 (4.15), end absorption up to 471 nm. HRMS (ESI): *m/z* calcd. for $C_{35}H_{23}N_2^+$ [M+H$^+$]: 471.1856, found 471.1844.

5-(4-Methoxyphenyl)-6-(*p*-tolylethynyl)naphtho[2,1-*a*]phenazine (8b): 6-Iodo-5-(4-methoxyphenyl)naphtho[2,1-*a*]phenazine **7b** (102 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol), CuI (2 mg, 0.01 mmol), *i*Pr_2NH (2 mL) and DMSO (6 mL) was stirred under argon for 20 min at 80 °C. Then a solution of *p*-tolylacetylene (35 mg, 0.3 mmol) in *i*Pr_2NH (2 mL) was added by portions for 30–45 min. The reaction mixture was stirred for 24 h at 80 °C. Then it was evaporated without heating to remove *i*Pr_2NH, treated with H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 60 cm) with CH_2Cl_2 as the eluent. The first and second fractions were 1,4-di-*p*-tolylbuta-1,3-diyne and traces of the starting compound. The next bright yellow fraction with R_f 0.7 and bright yellow fluorescence under UV (356 nm) gave 76 mg (76 %) of compound **8b** as bright yellow orange solid with m.p. 214–216 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.40 (s, 3 H), 3.99 (s, 3 H), 7.14–7.23 (m, 5 H), 7.36 (d, J = 8.0 Hz, 2 H), 7.49–7.56 (m, 3 H), 7.77 (d, J = 8.8 Hz, 1 H), 7.90–7.93 (m, 2 H), 7.97 (d, J = 7.8 Hz, 1 H), 8.15 (d, J = 8.8 Hz, 1 H), 8.41–8.49 (m, 2 H), 9.63 (d, J = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.6, 55.5, 87.1, 100.9, 114.2, 120.8, 122.4, 122.6, 125.3, 126.6, 128.5, 128.7, 128.9, 129.7, 129.9, 130.12, 130.17, 130.2 (2C), 130.5, 130.8, 131.4, 131.8, 135.3, 135.4, 138.4, 141.0, 142.0, 142.5, 143.4, 146.8, 159.4. UV-vis, λ_{max} nm (lg ε): 262 (4.71), 268 (4.70), 303 (4.64), 330 (4.73), 389

(4.05), 411 (4.19), 459 (3.96), end absorption up to 501 nm. HRMS (ESI): *m/z* calcd. for $C_{36}H_{25}N_2O^+$ [M+H$^+$]: 501.1961, found 501.1952.

11-Phenyl-12-(*p*-tolylethynyl)naphtho[2,1-*f*]quinoxaline (8c): 12-Iodo-11-phenylnaphtho[2,1-*f*]quinoxaline **7c** (86 mg, 0.2 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol) and Et_3N (5 mL) were stirred under argon for 20 min at 85 °C. Then a solution of *p*-tolylacetylene (46 mg, 0.4 mmol) in Et_3N (5 mL) was added by portions for 3 h. The reaction mixture was stirred for total 24 h at 82–85 °C. Then it was evaporated to dryness, treated with H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 60 cm) with $CHCl_3$ as the eluent. The first and second fractions were 1,4-di-*p*-tolylbuta-1,3-diyne and the starting compound. The next yellow fraction with R_f 0.35 gave 62 mg (74 %) of compound **8c.** Yellow orange solid, decomp. > 210 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.36 (s, 3 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 7.15–7.21 (m, 3 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.56–7.64 (m, 5 H), 7.68 (d, *J* = 8.8 Hz, 1 H), 7.97 (d, *J* = 7.7 Hz, 1 H), 8.12 (d, *J* = 8.9 Hz, 1 H), 9.06 (d, *J* = 1.8 Hz, 1 H), 9.11 (d, *J* = 1.8 Hz, 1 H), 9.41 (d, *J* = 8.9 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.6, 86.8, 101.7, 120.2, 121.8 (2C) 122.5, 125.6, 126.8, 127.9, 128.4, 128.8, 128.9, 129.0, 129.8, 130.0, 130.1, 130.7, 131.9, 134.9, 138.6, 140.3, 141.4, 143.0, 144.1, 145.2, 146.5. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 275 (4.47), 319 (4.50), 338 (4.24), 389 (3.93), end absorption up to 466 nm. HRMS (ESI): *m/z* calcd. for $C_{31}H_{21}N_2^+$ [M+H$^+$]: 421.1699, found 421.1697.

11-(4-Methoxyphenyl)-12-(*p*-tolylethynyl)naphtho[2,1-*f*]quinoxaline (8d) was obtained similarly to **8a** starting from 12-iodo-11-(4-methoxyphenyl)naphtho[2,1-*f*]quinoxaline **7d** (93 mg, 0.2 mmol). Flash column chromatography was carried out on silica gel (3.5 × 45 cm) with CH_2Cl_2 as the eluent. The first and second fractions were 1,4-di-*p*-tolylbuta-1,3-diyne and the starting compound. The next yellow fraction with R_f 0.3 and yellow fluorescence under UV (356 nm) gave 56 mg (62 %) of compound **8d**. Yellow orange solid with m.p. 191–193 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.37 (s, 3 H), 3.98 (s, 3 H), 7.12–7.17 (m, 4 H), 7.21–7.23 (m, 1 H), 7.27 (d, *J* = 8.7 Hz, 2 H), 7.48–7.55 (m, 3 H), 7.80 (d, *J* = 8.8 Hz, 1 H), 7.97 (d, *J* = 7.7 Hz, 1 H), 8.11 (d, *J* = 8.9 Hz, 1 H), 9.03 (d, *J* = 1.7 Hz, 1 H), 9.10 (d, *J* = 1.7 Hz, 1 H), 9.40 (d, *J* = 8.9 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.5, 55.5, 86.7, 100.9, 114.4, 120.5, 121.8, 122.7, 125.5, 126.7, 128.5, 128.7, 128.9, 129.8, 130.1, 130.3, 130.7, 131.3, 131.7, 134.9, 135.3, 138.5, 140.2, 141.5, 143.8,

145.3, 146.2, 159.4. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 267 sh (4.45), 286 sh (4.52), 306 (4.59), 323 (4.47), 376 (4.04), 416 sh (3.97), end absorption up to 466 nm. HRMS (ESI): *m/z* calcd. for $C_{32}H_{23}N_2O^+$ [M+H$^+$]: 451.1805, found 451.1806.

11-Phenyl-12-(*p*-tolylethynyl)naphtho[1,2-*h*]quinoline (8e) was obtained similarly to **8a** starting from 12-iodo-11-phenylnaphtho[1,2-*h*]quinoline **7e** (86 mg, 0.2 mmol). Yield 77 mg (91 %). R_f 0.7. Yellowish solid with m.p. 162–165 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 2.38 (s, 3 H), 7.12–7.20 (m, 5 H), 7.47–7.63 (m, 6 H), 7.68–7.76 (m, 2 H), 7.97 (d, *J* = 7.9 Hz, 1 H), 8.11 (d, *J* = 9.0 Hz, 1 H), 8.94 (dd, *J* = 8.3, 1.5 Hz, 1 H), 9.15 (dd, *J* = 4.1, 1.5 Hz, 1 H), 9.56 (d, *J* = 9.0 Hz, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ [ppm] = 21.6, 86.7, 100.0, 120.2, 120.7, 122.4, 125.1, 125.7, 126.3, 127.6, 128.5, 128.7, 128.8, 129.1, 129.4, 129.6, 130.3, 130.4, 131.4, 134.7, 134.9 (2C), 138.6 (2C), 142.6, 143.7, 145.3, 149.6. HRMS (ESI): *m/z* calcd. for $C_{32}H_{22}N^+$ [M+H$^+$]: 419.1747, found 420.1750.

6-(2,4-Bis(trimethylsilyl)but-1-en-3-ynyl)-5-phenylnaphtho[2,1-*a*]phenazine (9a): 6-Iodo-5-phenylnaphtho[2,1-*a*]phenazine **7a** (97 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol), Et_3N (5 mL) and dry THF (3 mL) was stirred under argon for 20 min at 75–80 °C. Then a solution of trimethylsilylacetylene (118 mg, 0.17 mL, 1.2 mmol) in Et_3N (2 mL) was added by portions for 2 h. The reaction mixture was stirred for total 24 h at 75–80 °C. Then it was evaporated to dryness, treated with H_2O (50 mL) and extracted with $CHCl_3$ (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 55 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.65 gave 92 mg (84 %) of compound **9a.** 6-(2,4-Bis(trimethylsilyl)but-1-en-3-ynyl)-5-phenylnaphtho[2,1-*a*]phenazine **9a** was obtained as yellow solid with m.p. 199–201 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = -0.41 (s, 9 H), 0.15 (s, 9 H), 7.12–7.17 (m, 2 H), 7.44–7.46 (m, 2 H), 7.49–7.52 (m, 4 H), 7.71 (d, *J* = 8.8 Hz, 1 H), 7.85–7.92 (m, 2 H), 8.01 (d, *J* = 7.9 Hz, 1 H), 8.19 (d, *J* = 8.8 Hz 1 H), 8.32 (d, *J* = 7.9 Hz, 1 H), 8.45 (d, *J* = 8.8 Hz, 1 H), 9.74 (d, *J* = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = -2.1, -0.5, 103.2, 106.2, 122.7, 125.2, 126.3, 127.5, 128.4, 128.7, 128.9, 129.1, 129.60, 129.61, 129.85, 129.89, 130.2, 130.7, 130.8, 131.2, 135.3, 136.6, 141.0, 141.1, 141.5, 142.1, 142.5, 143.0, 145.26, 145.33. HRMS (ESI): *m/z* calcd. for $C_{36}H_{35}N_2Si_2^+$ [M+H$^+$]: 551.2339, found 551.2330.

12-(2,4-Bis(trimethylsilyl)but-1-en-3-ynyl)-11-phenylnaphtho[2,1-*f*]quinoxaline (9b): Compound **9b** was obtained similarly to **9a** starting from 12-iodo-11-phenylnaphtho[2,1-*f*]quinoxaline **7c** (86 mg, 0.2 mmol). Yield 64 mg (64 %). R_f 0.3. Yellowish needles with m.p. 145–147 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = –0.23 (s, 9 H), 0.10 (s, 9 H), 7.03 (s, 1 H), 7.14 (t, J = 7.5 Hz, 1 H), 7.32–7.44 (m, 2 H), 7.45–7.57 (m, 4 H), 7.70 (d, J = 8.8 Hz, 1 H), 7.98 (d, J = 7.7 Hz, 1 H), 8.11 (d, J = 8.9 Hz, 1 H), 9.01 (s, 2 H), 9.48 (d, J = 8.9 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = –2.1, 0.2, 102.9, 106.0, 122.0, 125.3, 126.4, 127.5, 128.4, 128.8, 128.9, 129.0, 129.5, 129.8, 130.6(1), 130.6(4), 131.1, 134.9, 136.8, 140.0, 140.3, 140.9, 142.5, 143.1, 144.4, 145.8. HRMS (ESI): *m/z* calcd. for $C_{32}H_{33}N_2Si_2^+$ [M+H$^+$]: 501.2182, found 501.2158.

9-*p*-Tolyldinaphtho[2,1-*a*:1',2'-*c*]phenazine (14a): A purple solution of 5-phenyl-6-(*p*-tolylethynyl)naphtho[2,1-*a*]phenazine **8a** (47 mg, 0.1 mmol) in CF_3COOH (5 mL) was heated at 55–60 °C for 3 h. The reaction mixture was evaporated to dryness, treated with saturated K_2CO_3 (2 mL) and $CHCl_3$ (10 mL), shaked and separated in a separating funnel. The orange $CHCl_3$ phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (3.5 × 40 cm) with $CHCl_3$ as the eluent. The bright yellow fraction with R_f 0.9 gave the cyclization product (43 mg, 92 %). 9-*p*-Tolyldinaphtho[2,1-*a*:1',2'-*c*]phenazine **14a** was obtained as bright yellow plates with m.p. 264–268 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.57 (s, 3 H), 7.32–7.37 (m, 2 H), 7.47 (d, J = 7.7 Hz, 2 H), 7.53 (t, J = 7.5 Hz, 1 H), 7.60 (t, J = 7.4 Hz, 1 H), 7.72 (d, J = 7.7 Hz, 2 H), 7.83–7.89 (m, 2 H), 8.05 (d, J = 8.0 Hz, 1 H), 8.14 (d, J = 8.3 Hz, 1 H), 8.18–8.23 (m, 3 H), 8.33–8.40 (m, 2 H), 9.46 (s, 1 H), 9.49 (d, J = 8.7 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.4, 122.2, 122.5, 124.6, 124.8, 126.4, 126.94, 126.96, 128.1 (2C), 128.4, 128.6, 129.0, 129.2, 129.3, 129.51, 129.53, 129.61, 129.7, 129.8, 129.9, 130.2, 130.8, 131.4 (2C), 132.9, 134.3, 137.3, 137.6, 140.6, 142.28, 142.32, 142.36, 142.5. UV-vis, λ_{max} nm (lg ε): 263 (4.72), 289 (4.61), 300 (4.62), 308 (4.63), 336 (4.56), 352 sh (4.47), 393 (4.14), 415 (4.23), 450 sh (3.63), end absorption up to 508 nm. HRMS (ESI): *m/z* calcd. for $C_{35}H_{23}N_2^+$ [M+H$^+$]: 471.1856, found 471.1849.

2-Methoxy-18-*p*-tolyldinaphtho[2,1-*a*:1',2'-*c*]phenazine (14b) was obtained similarly to **14a** starting from 5-(4-methoxyphenyl)-6-(*p*-tolylethynyl)naphtho[2,1-*a*]phenazine **8b** (50 mg, 0.1 mmol). Yield 49 mg (98 %). R_f 0.7. Yellow solid with m.p. 244–246 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.57 (s, 3 H), 3.93 (s, 3 H), 6.99 (dd, J = 9.3, 2.4 Hz, 1 H), 7.37 (t, J = 7.5 Hz, 1 H), 7.45–7.49 (m, 3 H), 7.60 (t, J = 7.3 Hz, 1 H), 7.72 (d, J = 7.7 Hz, 2 H), 7.84–7.87 (m, 2

H), 8.05 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 9.3 Hz, 1 H), 8.19 (d, *J* = 8.7 Hz, 1 H), 8.24 (d, *J* = 8.6 Hz, 1 H), 8.32–8.40 (m, 2 H), 9.43 (s, 1 H), 9.49 (d, *J* = 8.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.4, 55.3, 105.5, 116.1, 122.3, 123.3, 124.9, 126.5 (2C), 126.9, 127.7, 128.1, 128.5, 128.6, 129.1, 129.3 (2C), 129.50, 129.52, 129.7, 130.0 (2C), 130.9, 131.4, 134.3, 134.6, 137.3, 137.8, 139.7, 142.1, 142.3 (2C), 142.6, 158.4. UV-vis, λ_{max} nm (lg ε): 266 (4.87), 292 (4.55), 307 (4.58), 321 (4.61), 343 sh (4.48), 358 (4.36), 400 (4.15), 421 (4.23), end absorption up to 500 nm. HRMS (ESI): *m/z* calcd. for $C_{36}H_{25}N_2O^+$ [M+H$^+$]: 501.1961, found 501.1947.

1-*p*-Tolyldinaphtho[2,1-*f*:1',2'-*h*]quinoxaline (14c): To a solution of compound **8c** (42 mg, 0.1 mmol) in CH_2Cl_2 (11 mL) CF_3SO_3H (0.1 mL) was added. The dark red reaction mixture was kept at room temperature for 24 h in the dark. Then it was evaporated to dryness without heating. The dark red residue was treated with saturated K_2CO_3 (50 mL) and CH_2Cl_2 (10 mL), shaken in a separating funnel and separated. The yellow CH_2Cl_2 phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 50 cm) with CH_2Cl_2 as the eluent. The bright yellow fraction with R_f 0.7 gave the cyclization product (41 mg, 98 %). Yellowish needles with m.p. 181–183 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.55 (s, 3 H), 7.30–7.37 (m, 2 H), 7.43 (d, *J* = 7.8 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.61 (t, *J* = 7.4 Hz, 1 H), 7.70 (d, *J* = 7.9 Hz, 2 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.3 Hz, 1 H), 8.19 (d, *J* = 8.7 Hz, 1 H), 8.35 (t, *J* = 9.4 Hz, 2 H), 8.96 (d, *J* = 1.9 Hz, 1 H), 8.97 (d, *J* = 1.9 Hz, 1 H), 9.28 (s, 1 H), 9.32 (d, *J* = 8.7 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.3, 121.4, 121.6, 124.6, 124.8, 126.4, 126.92, 126.96, 127.5, 128.10, 128.12, 128.5, 128.9, 129.2, 129.42, 129.49, 129.7, 130.1, 130.6, 131.3, 132.4, 133.9, 137.3, 137.5, 140.5, 141.2, 141.4, 143.52, 143.56. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 305 (4.61), 322 (4.57), 341 (4.50), 375 (3.95), 396 (3.84), end absorption up to 466 nm. HRMS (ESI): *m/z* calcd. for $C_{31}H_{21}N_2^+$ [M+H$^+$]: 421.1699, found 421.1680; *m/z* calcd. for $C_{31}H_{20}N_2Na^+$ [M+Na$^+$]: 443.1519, found 443.1502.

15-Methoxy-1-*p*-tolyldinaphtho[2,1-*f*:1',2'-*h*]quinoxaline (14d): Compound **14d** was obtained similarly to **14c** starting from 11-(4-methoxyphenyl)-12-(*p*-tolylethynyl)naphtho[2,1-*f*]quinoxaline **8d** (45 mg, 0.1 mmol). Flash column chromatography was carried out on silica gel (2.5 × 30 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.5 gave the cyclization product (42 mg, 94 %). Yellow solid with m.p. 204–206 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.54 (s, 3 H), 3.86 (s, 3 H), 6.98 (dd, *J* = 9.3, 2.5 Hz, 1 H), 7.36 (t, *J* = 7.6 Hz, 1 H), 7.43 (d, *J* = 7.7 Hz, 2 H),

7.49 (d, *J* = 2.5 Hz, 1 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.70 (d, *J* = 7.7 Hz, 2 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 8.17 (d, *J* = 8.7 Hz, 1 H), 8.23 (d, *J* = 9.3 Hz, 1 H), 8.37 (d, *J* = 8.5 Hz, 1 H), 8.94 (br s, 2 H), 9.25 (s, 1 H), 9.30 (d, *J* = 8.7 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.4, 55.3, 105.6, 115.8, 121.5, 122.3, 124.8, 126.3, 126.9, 127.3, 127.8, 128.0, 128.1, 128.4, 129.2, 129.3, 129.5, 129.9, 130.7, 131.4, 133.8, 134.2, 137.3, 137.6, 139.7, 141.0, 141.4, 143.1, 143.5, 158.4. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 267 (4.58), 312 (4.51), 340 sh (4.41), 380 (3.87), 402 sh (3.72), end absorption up to 486 nm. HRMS (ESI): *m/z* calcd. for $C_{32}H_{23}N_2O^+$ [M+H$^+$] 451.1805, found 451.1798.

8-*p*-Tolyldinaphtho[2,1-*f*:1',2'-*h*]quinoline (14e): Compound **14e** was obtained similarly to **14a** starting from 11-phenyl-12-(*p*-tolylethynyl)naphtho[1,2-*h*]quinoline **8e** (42 mg, 0.1 mmol). Yield 40 mg (95 %). R_f 0.7. Off-white needles with m.p. 236–238 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 2.60 (s, 3 H), 7.31–7.39 (m, 2 H), 7.48–7.72 (m, 7 H), 8.10 (d, *J* = 8.2 Hz, 2 H), 8.23 (d, *J* = 8.8 Hz, 1 H), 8. 34 (dd, *J* = 8.5, 1.8 Hz, 2 H), 8.61 (s, 1 H), 8.98 (dd, *J* = 8.4, 1.3 Hz, 1 H), 9.10 (dd, *J* = 4.3, 1.5 Hz, 1 H), 9.49 (d, *J* = 8.8 Hz, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ [ppm] = 21.4, 120.5, 121.9, 122.0, 124.6, 124.7, 124.8, 125.6, 126.2, 126.4, 126.6, 127.3, 127.7, 128.1, 128.2, 129.3, 129.5, 130.0, 130.1, 130.6, 130.8, 131.0, 131.4, 131.7, 133.6, 137.5, 137.7, 140.1, 146.5, 149.0. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 283 (4.91), 305 sh (4.98), 312 (4.99), 338 sh (4.64), 357 (4.59), end absorption up to 419 nm. HRMS (ESI): *m/z* calcd. for $C_{32}H_{22}N^+$ [M+H$^+$]: 420.1747, found 420.1728.

Supporting Information: Copies of the ^{1}H and ^{13}C NMR spectra of all compounds, X-ray, UV-vis and CV data (PDF).

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[1] a) Y. Shen, C.-F. Chen, *Chem. Rev*. **2012**, *112*, 1463−1535; b) M. Gingras, *Chem. Soc. Rev*. **2013**, *42*, 968−1006; c) M. Gingras, G. Ferlix, R. Peresuttiab, *Chem. Soc. Rev*. **2013**, *42*, 1007−1050; d) M. Gingras, *Chem. Soc. Rev*. **2013**, *42*, 1051−1095; e) F. Dumitrascu, D. G. Dumitrescu, I. Aron, *Arkivoc* **2010**, (i), 1−32; f) N. Saleh, C. Shen, J. Crassous, *Chem. Sci.* **2014**, *5*, 3680−3694; g) M. Shigeno, Y. Kushida, M. Yamaguchi, *Chem. Commun.* **2016**, *52*, 4955−4970; h) H. Isla, J. Crassous, *C. R. Chimie* **2016**, *19*, 39−49; i) C.-F. Chen, Y. Shen, Helicene Chemistry: From Synthesis to Applications. Springer-Verlag Berlin Heidelberg, 2017, 272 p.; j) K. Mori, T. Murase, M. Fujita, *Angew. Chem. Int. Ed.* **2015**, *54*, 6847−6851; k) M. Rickhaus, M. Mayor, M. Juríček, *Chem. Soc. Rev.* **2016**, *45*, 1542−1556.

[2] a) L. Rulíšek, O. Exner, L. Cwiklik, P. Jungwirth, I. Starý, L. Pospíšil, Z. Havlas, *J. Phys. Chem. C* **2007**, *111*, 14948–14955; b) J. Hrbac, J. Storch, V. Halouzka, V. Cirkva, P. Matejka, J. Vacek, *RSC Adv.* **2014**, *4*, 46102–46105; c) J. Vacek, J. Vacek Chocholoušová, I. G. Stará, I. Starý, Y. Dubi, *Nanoscale* **2015**, *7*, 8793–8802; d) T. Fujikawa, N. Mitoma, A. Wakamiya, A. Saeki, Y. Segawa, K. Itami, *Org. Biomol. Chem.* **2017**, *15*, 4697–4703.

[3] a) T. Verbiest, S. van Elshocht, M. Kauranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T. J. Katz, A. Persoons, *Science* **1998**, *282*, 913–915; b) B. J. Coe, D. Rusanova, V. D. Joshi, S. Sánchez, J. Vávra, D. Khobragade, L. Severa, I. Císařová, D. Šaman, R. Pohl, K. Clays, G. Depotter, B. S. Brunschwig, F. Teplý, *J. Org. Chem.* **2016**, *81*, 1912–1920.

[4] a) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, *J. Am. Chem. Soc.* **2001**, *123*, 11899–11907; b) J. E. Field, G. Muller, J. P. Riehl, D. Venkataraman, *J. Am. Chem. Soc*. **2003**, *125*, 11808−11809; c) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.* **2012**, *134*, 4080−4083; d) M. S. Sundar, H. R. Talele, H. M. Mande, A. V. Bedekar, R. C. Tovar, G. Muller, *Tetrahedron Lett.* **2014**, *55*, 1760−1764; e) K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya, K. Tanaka, *J. Am. Chem. Soc.* **2014**, *136*, 5555−5558; f) Y. Yamamoto, H. Sakai, J. Yuasa, Y. Araki, T. Wada, T. Sakanoue, T. Takenobu, T. Kawai, T. Hasobe, *Chem. Eur. J.* **2016**, *22*, 4263–4273; h) Y. Yamamoto, H.

Sakai, J. Yuasa, Y. Araki, T. Wada, T. Sakanoue, T. Takenobu, T. Kawai, T. Hasobe, *J. Phys. Chem. C* **2016**, *120*, 7421–7427.

[5] a) B. B. Hassine, M. Gorsane, J. Pecher, R. H. Martin, *Bull. Soc. Chim. Belg.* **1986**, *95*, 557−566; b) M. T. Reetz, E. W. Beuttenmüller, R. Goddard, *Tetrahedron Lett*. **1997**, *38*, 3211−3214; c) R. Takenaka, S. Sarangthem, B. Captain, *Angew. Chem. Int. Ed.* **2008**, *47*, 9708−9710; d) P. Aillard, A. Voituriez, A. Marinetti, *Dalton Trans.* **2014**, *43*, 15263−15278; e) D. Dova, L. Viglianti, P. R. Mussini, S. Prager, A. Dreuw, A. Voituriez, E. Licandro, S. Cauteruccio, *Asian J. Org. Chem.* **2016**, *5*, 537−549.

[6] T. Fujikawa, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2016**, *138*, 3587−3595.

[7] Q. Huang, L. Jiang, W. Liang, J. Gui, D. Xu, W. Wu, Y. Nakai, M. Nishijima,G. Fukuhara, T. Mori, Y. Inoue, C. Yang, *J. Org. Chem.* **2016**, *81*, 3430−3434.

[8] M. Tounsi, M. B. Braiek, A. Baraket, M. Lee, N. Zine, M. Zabala, J. Bausells, F. Aloui, B. B. Hassine, A. Maaref, A. Errachid, *Electroanalysis* **2016**, *28*, 2892−2899.

[9] a) Y. Xu, Y. X. Zhang, H. Sugiyama, T. Umano, H. Osuga, K. Tanaka, *J. Am. Chem. Soc.* **2004**, *126*, 6566−6567; b) R. Passeri, G. G. Aloisi, F. Elisei, L. Latterini, T. Caronna, F. Fontana, I. N. Sora, *Photochem. Photobiol. Sci.* **2009**, *8*, 1574−1582.

[10] For selected examples, see: a) Y. Sawada, S. Furumi, A. Takai, A. Takeuchi, K. Noguchi, K. Tanaka. *J. Am. Chem. Soc.* **2012**, *134*, 4080−4083; b) J. Kelber, M.-F. Achard, F. Durola, H. Bock. *Angew. Chem. Int. Ed.* **2012**, *51*, 5200−5203; c) S. Xiao, S. J. Kang, Y. Wu, S. Ahn, J. B. Kim, Y.-L. Loo, T. Siegrist, M. L. Steigerwald, H. Li, C. Nuckolls. *Chem. Sci.* **2013**, *4*, 2018-2023; d) A.-C. Bédard, A. Vlassova, A. C. Hernandez-Perez, A. Bessette, G. S. Hanan, M. A. Heuft, S. K. Collins. *Chem. Eur. J.* **2013**, *19*, 16295−16302.

[11] a) M. Scholz, M. Mühlstädt, F. Dietz. *Tetrahedron Lett.* **1967**, *8*, 665–668; b) D. D. Morgan, S. W. Horgan, M. Orchin. *Tetrahedron Lett.* **1972**, *13*, 1789–1792; c) F. Dietz, M. Scholz. *Tetrahedron* **1968**, *24*, 6845–6849; d) W. H. Laarhoven, Th. J. H. M. Cuppen, R. J. F. Nivard. *Tetrahedron* **1970**, *26*, 1069–1083; e) A. V. Bedekar, A. R. Chaudhary, M. Shyam Sundar, M. Rajappa. *Tetrahedron Lett.* **2013**, *54*, 392–396; f) N. Ito, T. Hirose, K. Matsuda. *Org. Lett.* **2014**, *16*, 2502–2505.

[12] a) L. B. Liu, T. J. Katz. *Tetrahedron Lett.* **1990**, 31, 3983–3986; b) T. J. Katz, L. B. Liu, N. D. Willmore, J. M. Fox, A. L. Rheingold, S. H. Shi, C. Nuckolls, B. H. Rickman. *J. Am. Chem. Soc.* **1997**, *119*, 10054–10063; c) N. D. Willmore, L. B. Liu, T. J. Katz. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1093–1095; d) J. Caeiro, D. Pena, A. Cobas, D. Perez, E. Guitian. *Adv. Synth. Catal.* **2006**, *348*, 2466–2474; e) V. Mamane, P. Hannen, A. Fürstner. *Chem. Eur. J.* **2004**, *10*,

4556–4575; f) K. Yamamoto, M. Okazumi, H. Suemune, K. Usui. *Org. Lett.* **2013**, *15*, 1806–1809; g) F. Teply, I. G. Stara, I. Stary, A. Kollarovic, D. Saman, L. Rulisek, P. Fiedler. *J. Am. Chem. Soc.* **2002**, 124, 9175–9180; h) X. Xue, L. T. Scott. *Org. Lett.* **2007**, *9*, 3937–3940; i) M. Shimizu, I. Nagao, Y. Tomioka, T. Hiyama. *Angew. Chem. Int. Ed.* **2008**, *47*, 8096–8099; j) K. Kamikawa, I. Takemoto, S. Takemoto, H. Matsuzaka. *J. Org. Chem.* **2007**, *72*, 7406–7408; k) S. K. Collins, A. Grandbois, M. P. Vachon, J. Cote. *Angew. Chem. Int. Ed*. **2006**, *45*, 2923–2926; l) Y. Xia, Z. Liu, Q. Xiao, P. Qu, R. Ge, Y. Zhang, J. Wang. *Angew. Chem. Int. Ed.* **2012**, *51*, 5714–5717.

[13] a) G. V. Baryshnikov, P. Gawrys, K. Ivaniuk, B. Witulski, R. J. Whitby, A. Al-Muhammad, B. Minaev, V. Cherpak, P. Stakhira, D. Volyniuk, G. Wiosna-Salyga, B. Luszczynska, A. Lazauskas, S. Tamuleviciush, J. V. Grazuleviciusf, *J. Mater. Chem. C* **2016**, *4*, 5795–5805; b) M. Weimar, R. Correa da Costa, F.-H. Lee, M. J. Fuchter, *Org. Lett.* **2013**, *15*, 1706–1709; c) J. Carreras, M. Patil, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2012**, *134*, 16753–16758; d) M. Frigoli, J. Marrot, P. L. Gentili, D. Jacquemin, M. Vagnini, D. Pannacci, F. Ortica, *ChemPhysChem* **2015**, *16*, 2447–2458; e) Y. Li, J. Waser, *Angew. Chem. Int. Ed.* **2015**, *54*, 5438–5443; f) H. Oyama, K. Nakano, T. Harada, R. Kuroda, M. Naito, K. Nobusawa, K Nozaki, *Org. Lett*. **2013**, *15*, 2104-2107; g) K. Hirano, Y. Inaba, K. Takasu, S. Oishi, Y. Takemoto, N. Fujii, H. Ohno, *J. Org. Chem.* **2011**, *76*, 9068–9080; h) T. Yao, M. A. Campo, R. C. Larock, *J. Org. Chem.* **2005**, *70*, 3511–3517; i) R. K. Mohamed, S. Mondal, J. V. Guerrera, T. M. Eaton, T. E. Albrecht-Schmitt, M. Shatruk, I. V. Alabugin, *Angew. Chem. Int. Ed.* **2016**, *55*, 12054–12058; j) J. Storch, J. Čermák, J. Karban, I. Císařová, J. Sýkora, *J. Org. Chem.* **2010**, *75*, 3137–3140; k) A. K. Mandadapu, M. D. Dathi, R. K. Arigela, B. Kundu, *Tetrahedron* **2012**, *68*, 8207–8215; l) K. S. Kumar, B. Bhaskar, M. S. Ramulu, N. P. Kumar, M. A. Ashfaq, M. Pal, *Org. Biomol. Chem.* **2017**, *15*, 82–87; m) K. Pati, C. Michas, D. Allenger, I. Piskun, P. S. Coutros, G. dos Passos Gomes, I. V. Alabugin, *J. Org. Chem.* **2015**, *80*, 11706–11717; n) A. V. Gulevskaya, *Eur. J. Org. Chem.* **2016**, 4207–4214; o) A.V Gulevskaya, E. A. Shvydkova, D. I. Tonkoglazova. *Eur. J. Org. Chem.* **2018**, 5030–5043.

[14] a) I. V. Alabugin, E. Gonzalez-Rodrigues, *Acc.Chem. Res.* **2018**, *51*, 1206–1219; b) I. V. Alabugin, B. Gold, *J. Org. Chem.* **2013**, *78*, 7777–7784.

[15] a) H. S. Blair, M. Crawford, J. M. Spence, V. R. Supanekar. *J. Chem. Soc.* **1960**, 3313–3318; b) M. Crawford, R. A. M. Mackinnon, V. R. Supanekar. *J. Chem. Soc.* **1959**, 2807–2812; c) M.S. Newman. *J. Chem. Soc.* **1940**, *62*, 1683–1687; d) H. A. Weialich. *Ber.* **1938**, *71B*, 1203–

1209; e) T. P. Bender, Y. Qi, J. P. Gao, Z. Y. Wang. *Macromolecules* **1997**, *30*, 6001–6006; f) M. Li, H.-Y. Lu, C. Zhang, L. Shi, Z. Tang, C.-F. Chen. *Chem. Commun*. **2016**, *52*, 9921–9924; g) C. Zhang, M. Li, H.Y. Lu, C.-F. Chen. *Asian J. Org. Chem*. **2016**, *5*, 1518–1524; h) N. Kaewnok, A. Petdum, J. Sirirak, A. Charoenpanich, W. Panchan, S. Sahasithiwat, T. Sooksimuang, N. Wanichacheva. *New. J. Chem.* **2018**, *42*, 5540–5547; i) D.-C. Yang, M. Li, C.-F. Chen. *Chem. Commun*. **2017**, *53*, 9336–9339; j) L. Minuti, A. Taticchi, A. Marrocchi, E. Gacs-Baitz. *Tetrahedron* **1997**, *53*, 6873–6878; k) Z. Y. Wang, Y. Qi, T. P. Bender, J. P. Gao. *Macromolecules* **1997**, *30*, 764–769; l) G. Pieters, K. Sbargoud, A. Bridoux, A. Gaucher, S. Marque, F. Bourdreux, J. Marrot, D. Flot, G. Wantz, O. Dautel, D. Prim. *Eur. J. Org. Chem.* **2013**, 490–497; m) H. Kitano, W. Matsuoka, H. Ito, K. Itami. *Chem. Sci.* **2018**, *9*, 7556–7561; n) B. K. Mandal, T. Sooksimuang. *J. Phorphyrins Phthalocyanines* **2002**, *6*, 66–72; o) T. Sooksimuang, B. K. Mandal. *J. Org. Chem.* **2003**, *68*, 652–655; p) C.-F. Liu, C. Cheng, Y. Jiang, W.-Y. Lai, W. Huang. *New. J. Chem.* **2017**, *41*, 13619–13624; q) M. Putala, N. Kastner-Pustet, A. Mannschreck. *Tetrahedron: Asymmetry* **2001**, 3333–3342; r) H. Sakai, T. Kubota, J. Yuasa,Y. Araki, T. Sakanoue, T. Takenobu, T. Wada, T. Kawai, T. Hasobe. *Org. Biomol. Chem.* **2016**, *14*, 6738–6743; s) A. Modler-Spreitzer, A. Mannschreck, M. Scholz, G. Gescheidt, H. Spreitzer, J. Daub. *J. Chem. Res., Synopses* **1995**, *(5)*, 180–181.

[16] a) M. J. E. Hewlins, R. Salter. *Synthesis* **2007**, 2164–2174; b) A. Ohta, K. Hasegawa, K. Amano, C. Mori, A. Ohsawa, K. Ikeda,T. Watanabe. *Chem. Pharm. Bull.* **1979**, *27*, 2596–2601; c) D. C. Thang, N. P. Buu-Hoï, N. D. Xuong. *J. Chem. Soc.* **1965**, 4585-4588; d) S. H. Han, A. K. Pandey, H. Lee, S. Kim, D. Kang, Y. H. Jung, H. S. Kim, S. Hong, I. S. Kim. *Org. Chem. Front.* **2018**, *5*, 3210–3218; e) B. C. Raju, K. V. Prasad, G. Saidachary, B. Sridhar. *Org. Lett.* **2014**, *16*, 420–423; f) K. O. Eyong, H. Hussain, G. N. Folefoc, A. E. Nkengfack, M. Saeftel, S. R. Sarife, A. Hoerauf, K. Krohn. *Rasayan J. Chem.* **2011**, *4*, 713–722; g) F. R. Hewgill, R. Slamet, J. M. Stewart. *J. Chem. Soc., Perkin Trans. 1* **1991**, *12*, 3033–3042.

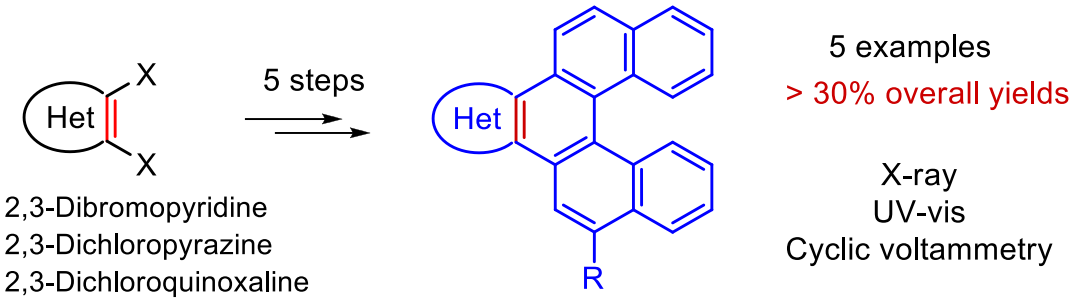
[17] a) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Saman, P. Fiedler. *Tetrahedron* **1998**, *72*, 1547–1557; b) E.A. Filatova, A.V. Gulevskaya, A.F. Pozharskii, V.A. Ozeryanskii. *Tetrahedron* **2016**, *72*, 1547–1557; c) S. Rogalski, M. Kubicki, C. Pietraszuk. *Tetrahedron* **2018**, *74*, 6192–6198; d) K. Nikitin, H. Müller-Bunz, P. J. Guiry, M. J. McGlinchey. *J. Organomet. Chem*. **2019**, *880*, 1–6.

[18] Y.-w. Sun, Q. Xu, M. Shi. *Beilstein J. Org. Chem.* **2013**, *9*, 2224–2232.

[19] J. E. Anthony. *Chem. Rev.* **2006**, *106*, 5028–5048.

[20] R. H. Martin, M. J. Marchant. *Tetrahedron* **1974**, *30*, 343–345.

Graphical Abstract



2,3-Dibromopyridine
2,3-Dichloropyrazine
2,3-Dichloroquinoxaline

A systematic study on the synthesis and properties of novel azine-[5]helicene hybrids is reported. To discern the effect of merging an azine moiety within a helical skeleton, the X-ray structures, UV-vis absorption spectra, cathodic and anodic electrochemistry of the helicene hybrids were investigated and compared to that of the parent [5]helicene.