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Novel synthetic approach to pyrrolo[1,2-*b*]cinnolines

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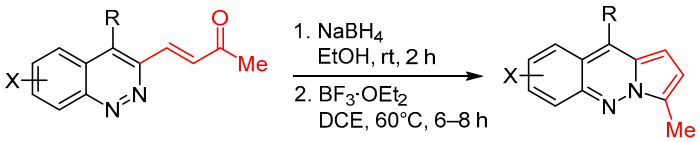


R = H, 5-methylfuran-2-yl, Ar
X = H, Cl, Br, MeO

- *12 examples*, up to 73% yield
- Readily available starting materials
- No metal catalysts

Straightforward method for the synthesis of pyrrolo[1,2-*b*]cinnolines starting from 2-nitrobenzaldehydes and 2-methylfurans has been elaborated. The key steps of the process are oxidative furan ring opening with diazonium cation and intramolecular alkylation of azo group of the resulted cinnoline with secondary allyl alcohol.

Keywords: aza-heterocycles, cinnolines, pyrrolo[1,2-*b*]cinnolines, furan ring opening.

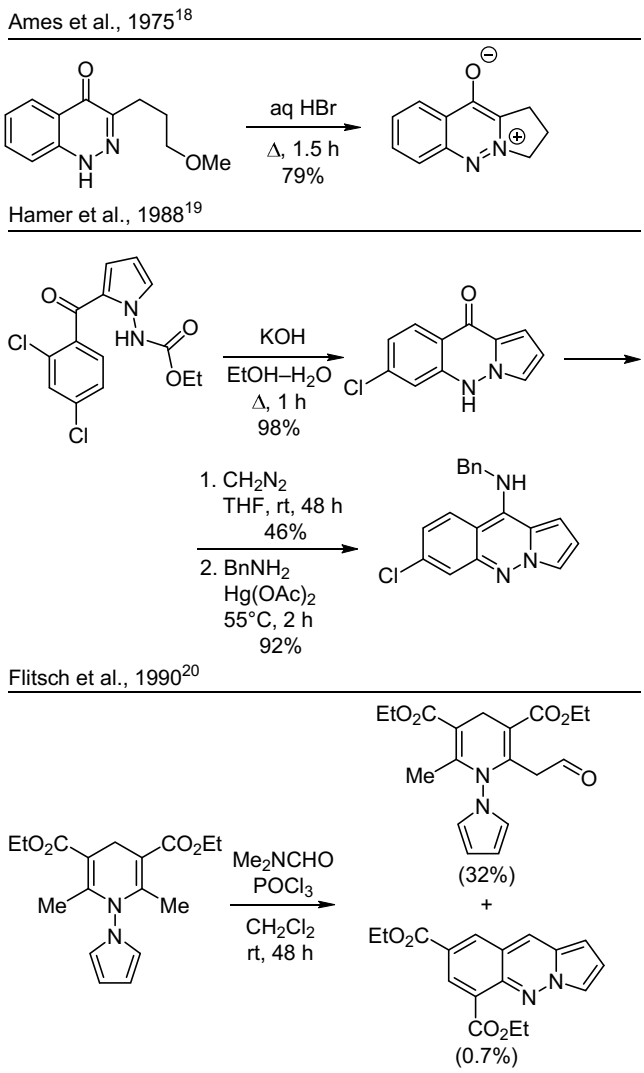
In the last decade, pyrrolo[1,2-*b*]pyridazines enjoy ever-growing use in medicine due to the wide spectrum of biological activity they possess including anticancer,[1] antibacterial,[2] antioxidant,[3–5] anti-inflammatory,[6] Janus kinase (JAKs)[7–9] and IRAK4 inhibiting activity.[10] No less attention is paid to the photophysical properties of this class of compounds. Their fluorescent properties made them popular materials in the constructing different optical devices, lasers, OLED screens.[11–15] Some representatives of pyrrolo[1,2-*b*]cinnolines display prominently high luminescence level with quantum efficiencies up to 90%.[12]

General methods of assembling pyrrolo[1,2-*b*]pyridazine framework are numerous and mainly based on condensation and cycloaddition approaches.[16,17] The number of synthetic routes to access pyrrolo[1,2-*b*]cinnolines is considerably lower. Thus, the first derivative of rare pyrrolo[1,2-*b*]cinnoline ring system was reported by Ames in 1975.[18] The corresponding 2-aminovalerophenone was diazotized under conditions of Borsche–Koelsch cinnoline synthesis, and resulting 3-methoxypropylcinnolinone was refluxed with concentrated HBr (Scheme 1). Later on pyrrolo[1,2-*b*]cinnolinone derivative was prepared from 2-benzoyl-1*H*-pyrrol-1-ylcarbamate employing aromatic nucleophilic substitution.[19] Methylation with diazomethane produced *O*-methyl ether and further reaction with benzylamine allowed for obtaining 10-amino derivative of pyrrolo[1,2-*b*]cinnoline. Pyrrolo[1,2-*b*]cinnoline derivative accompanied anticipated product of the Hantzsch 1,4-dihydropyridine Vilsmeier formylation. Its formation was rationalized by unusual dihydropyridine ring recyclization (Scheme 1).[20] In 2003, the synthesis of pyrrolo[1,2-*b*]-cinnolines directly from cinnolines under the action of dimethyl acetylenedicarboxylate (DMAD) in MeOH at low temperature was developed. Alternatively, cinnolines were *N*-alkylated with *tert*-butyl bromoacetate before the reaction with DMAD.[12]

We developed a novel approach for the synthesis of pyrrolo[1,2-*b*]cinnolines starting from *o*-nitrobenzaldehydes or *o*-azidobenzhydrols.

Cinnolines **4a**–**h**,**l** which were employed as precursors for the synthesis of pyrrolo[1,2-*b*]cinnolines were easily obtained from 2-nitrobenzaldehydes **1a**–**h**,**l** (Scheme 2) as was reported earlier.[21–30] At the first step, condensation of benzaldehydes with 2-methylfuran in the presence of $HClO_4$ gave rise to the corresponding difurylmethanes **2a**–**h**,**l** which were reduced with $NaBH_4$ in the presence of palladium on charcoal. Diazotisation under mild conditions with *tert*-butyl nitrite in MeCN resulted in electrophilic attack of diazonium cation onto furan ring, its opening and furnished the desired cinnolines **4a**–**h**,**l** in good yields.

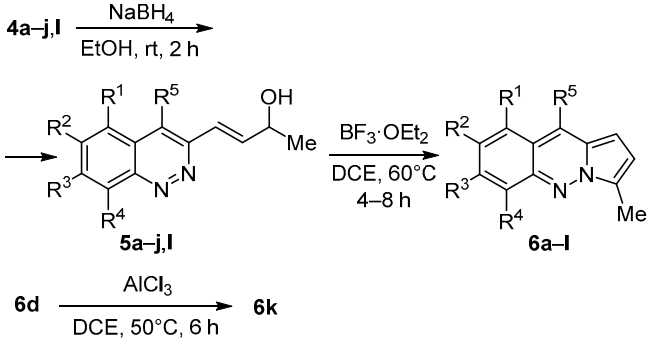
Scheme 1. Reported synthetic approaches to pyrrolo[1,2-*b*]cinnoline ring system



Cinnolines with phenyl substituent in position 4 **4i**,**j** were obtained from the corresponding amines **3i**,**j** which were available *via* condensation of 2-azidobenzhydrols with sylvan and subsequent Staudinger reaction followed by hydrolysis.

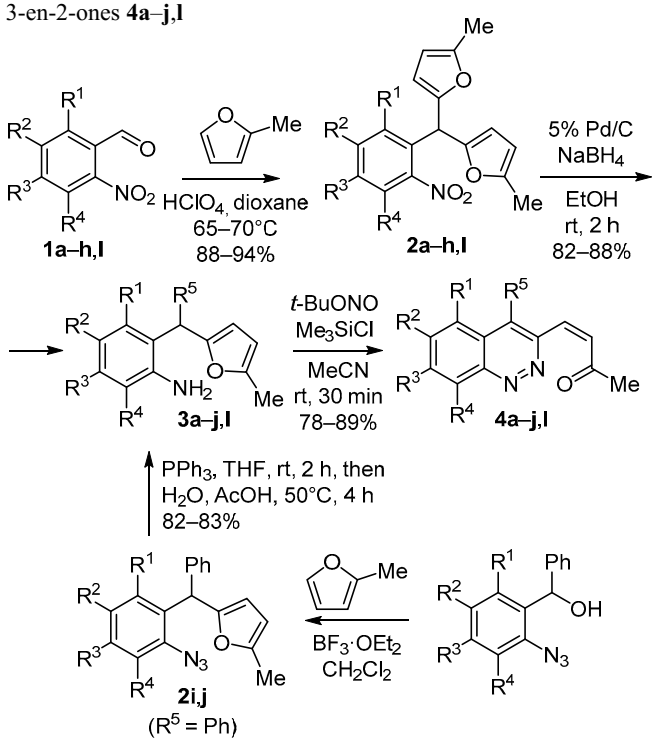
Having a set of cinnolines **4a**–**j**,**l** in hand, we reduced carbonyl group with $NaBH_4$ to get alcohols **5a**–**j**,**l**. Interestingly that during workup, initial cinnoline *cis*-enones **4a**–**j**,**l** underwent complete isomerization and alcohols **5a**–**j**,**l** were obtained exclusively in the *trans* form. Obviously, this thermodynamically driven process occurs *via* reversible addition to enone double bond of nucleophile, more likely hydroxide ion. Alternatively, isomerization can be self-catalyzed and cinnoline ring can act as nucleophile by analogy with 4-dimethylaminopyridine in the related isomerization process in acylvinylindoles.[27] Next, pyrrolocinnolines **6a**–**j** were obtained by the intramolecular alkylation with $BF_3 \cdot Et_2O$ which appeared to be an appropriate reagent. Depending on the nature of the substituents cyclization was completed in 4–8 h in refluxing dichloroethane in 62–73% yields (Table 1).

Table 1. Synthesis of pyrrolo[1,2-*b*]cinnolines **6a**–**l** from (*Z*)-4-(cinnolin-3-yl)but-3-en-2-ones **4a**–**j**,**l**



Compound	R^1	R^2	R^3	R^4	R^5	Isolated yield, %
6a	H	H	H	H	5-MeFu	68
6b	H	OMe	OMe	H	5-MeFu	64
6c	OMe	H	H	OMe	5-MeFu	72
6d	H	H	H	OMe	5-MeFu	62
6e	OMe	Me	H	OMe	5-MeFu	65
6f	OMe	OMe	H	Br	5-MeFu	68
6g	OMe	OMe	H	Cl	5-MeFu	70
6h	H	OMe	OMe	H	H	61
6i	H	Cl	H	H	Ph	73
6j	H	OMe	OMe	H	Ph	74
6k	H	H	H	OH	5-MeFu	98
6l	H	NO_2	H	H	5-MeFu	–

Scheme 2. Synthesis of starting (*Z*)-4-(cinnolin-3-yl)but-3-en-2-ones **4a**–**j**,**l**



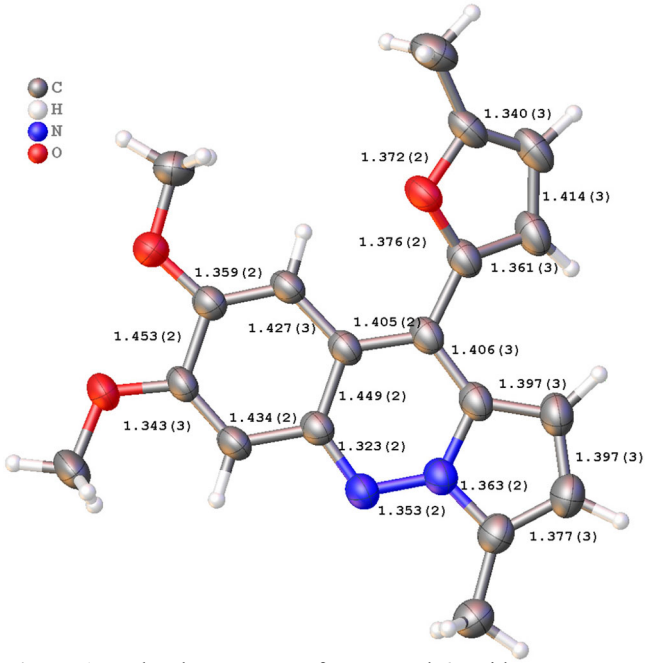


Figure 1. Molecular structure of compound **6b** with atoms represented as thermal vibration ellipsoids of 50% probability.

Unfortunately, conjugation of cinnoline azo fragment with nitro group retarded the reaction and precluded the formation of pyrrolocinnoline **6l**.

For the unambiguous proof of structure of obtained compounds, a single crystal of representative compound **6b** was grown from the EtOAc – petroleum ether mixture and characterized using X-ray structural analysis (Fig. 1).

As it is known from the literature data, benzannulation enhances aromaticity of pyrrolopyridazine which is evidenced by increased bond equalization.[12] Thus, the length of N–N bond equals to 1.375 Å in 3-ethyl 1,2-dimethyl pyrrolo[2,1-*a*]phthalazine-1,2,3-tricarboxylate (PPH), while in trimethyl pyrrolo[1,2-*b*]cinnoline-1,2,3-tricarboxylate (PC) it is much shorter: 1.343 Å. Meanwhile the N=C double bond in PPH (1.294 Å) is sufficiently shorter than N=C bond in PC (1.343 Å) (Fig. 2).[12]

For the synthesized compound **6b**, N–N and N=C bond lengths equal to 1.353 and 1.323 Å, respectively, which are medium values between PPH and PC. As can be seen from Figure 3, the π-planes of the molecules do not stack up unlike PPH, PP, and PC where π-stacking interactions are reflected in the distances between π-planes: 3.39, 3.34, and 3.31 Å, respectively.

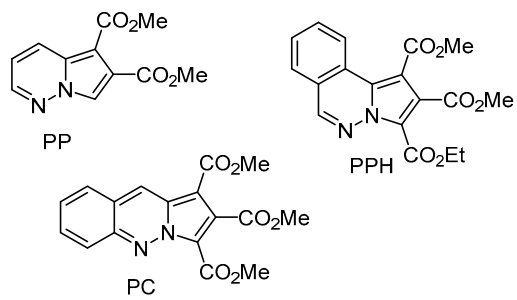


Figure 2. Structures of PP, PPH, and PC.

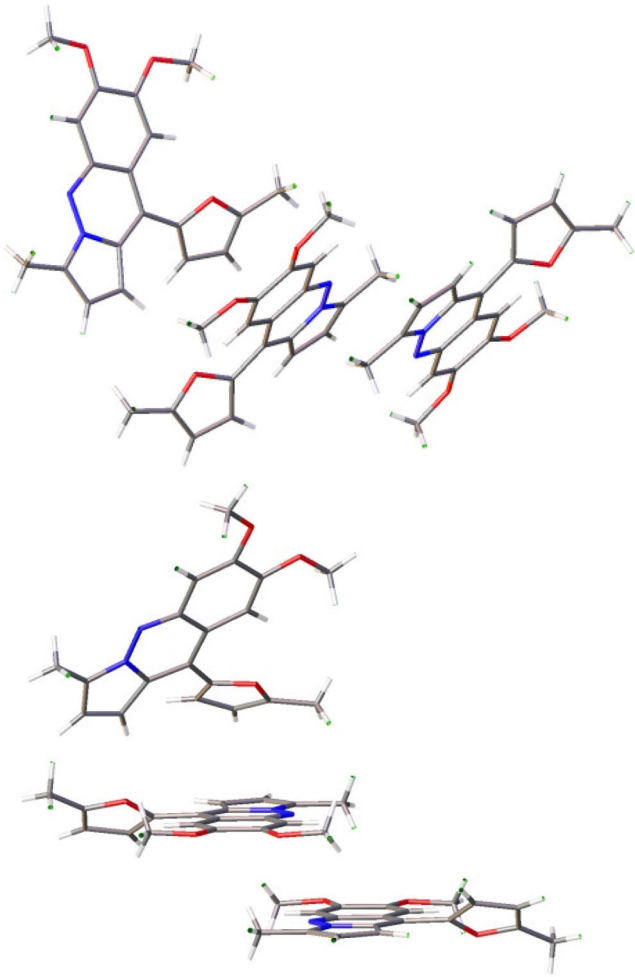


Figure 3. π-Stacking diagram of compound **6b**.

From another point of view (Fig. 4), the relatively small distance of 3.892 Å between centroids of furan and pyridazine rings may be indicative of their donor–acceptor interaction.

Next, optical properties of the synthesized compounds were studied. The absorption spectra of compounds **6a**–**i** were recorded in DMSO, MeOH, CH_2Cl_2, and hexane solutions at room temperature.

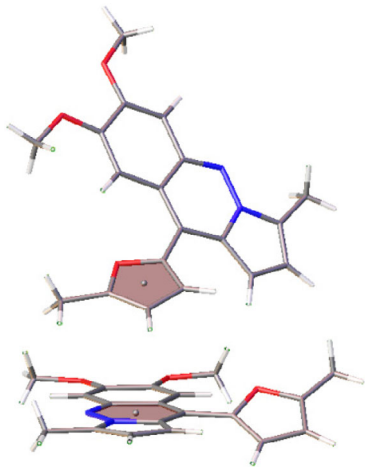


Figure 4. Plane centroid – plane centroid distance for compound **6b**.

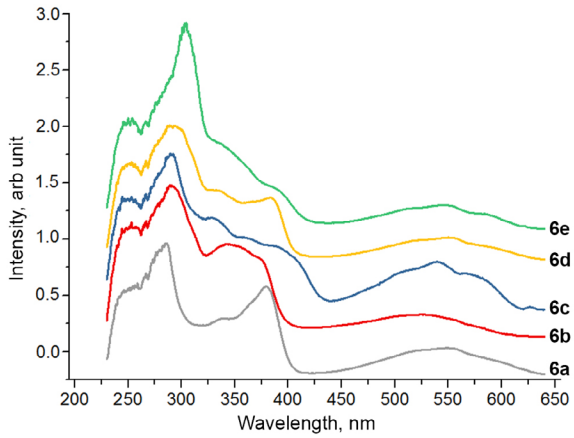


Figure 5. The UV absorption spectra of compounds **6a**,**b**,**c**,**d**,**e** in CH_2Cl_2.

Table 2. Absorption spectra of compounds PC, **6a–i** (λ_{max}, nm)

Compound	Solvent			
	DMSO	MeOH	CH_2Cl_2	Hexane
PC[12]	437	435	440	448
6a	550	547	549	548
6b	529	522	525	517
6c	543	539	539	536
6d	550	547	541	547
6e	546	545	547	542
6f	577	570	572	564
6h	494	494	495	497
6i	534	531	534	535

As it can be seen from Figure 5 and Table 2, absorption peaks of compounds **6a**–**i** are sufficiently shifted to long wave region in comparison with PC – displaying a difference of 100 nm in hexane and even more (113 nm) in more polar DMSO.

In general, if substituents R^{1-4} in pyrrolo[1,2-*b*]-cinnolines bearing 5-methylfuryl as R^5 substituent are methoxy groups then absorption peaks are shifted to blue region (compounds **6b**,**c**,**d**,**e**), and oppositely, in the case of acceptor bromine substituent in R^4 position of compound **6f**, absorption peaks shifted red in comparison to unsubstituted compound **6a** (Table 2).

Noteworthy that the π-system extension with furan (compound **6a**) or benzene ring (compound **6i**) as R^5 substituent in comparison with compound **6h**, lacking R^5 substituent is in accordance with electrochemical data below. For compound **6h**, strong shift to blue region is observed (497 nm), then follows absorption peak of compound **6i** (535 nm), and finally red-shifted absorbance band of compound **6a** (548 nm). Although here λ_{max} are presented for hexane, the same tendency was observed for other solvents.

Further, electrochemical studies of the synthesized compounds were performed. Cyclic voltammetry is well-known tool for measurement of reduction and oxidation potentials of organic compounds, which correlate with HOMO and LUMO energies, constituting substantial interest in prediction of stabilities of materials for opto-electronic devices.

In the paper published in 2003 on the synthesis and properties of high fluorescent pyrrolopyridazine derivatives,[12] electrochemical behavior of pyrrolo[1,2-*b*]cinnoline containing various electron-withdrawing substituents in the pyrrole ring was described. Along with noted surprisingly large red shift (about 100 nm), its HOMO and LUMO energy levels are characterized as ideally appropriate for the employment in the development of materials for optical devices.[31–34] With the series of synthesized pyrrolo[1,2-*b*]-cinnolines incorporating electron-donating substituents in hand, we were interested in their electrochemical properties evaluation for revealing high signal reversibility in the cathode region, similarly to PC. All of the explored compounds possess high electrochemical activity, though the nature of the redox processes is in direct accordance with the presence of R^{1-4} substituents. The cyclic voltammetry reduction and oxidation potentials for the examined pyrrolo[1,2-*b*]cinnolines are given in Table 3. Figure 6 depicts voltammetric curves for pyrrolo[1,2-*b*]-cinnoline **6a**, without R^{1-4} substituents on the aryl ring.

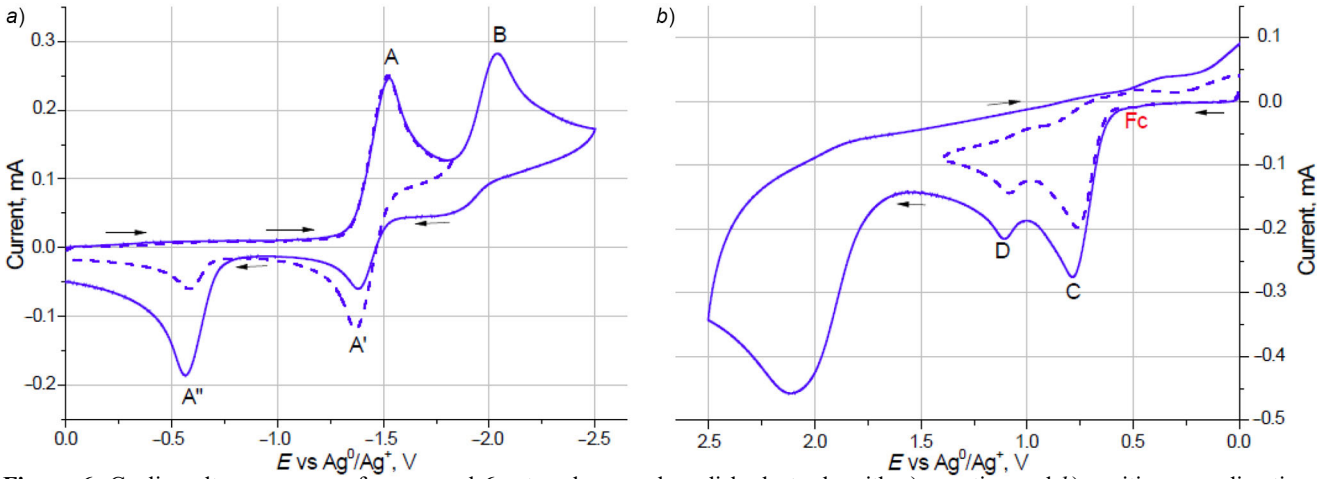


Figure 6. Cyclic voltammograms of compound **6a** at a glassy carbon disk electrode with *a*) negative and *b*) positive scan directions; 1 mM solution in MeCN containing 0.1 M TBAP; *v* 0.2 V/s.

Table 3. Electrochemical properties of compounds **6a**–**k***

Compound	Reduction		Oxidation	
	E_{pk}, V	E_{pa},V	E_{pa}, V	E_{pk},V
6a	–1.51 (A)**	–0.61 (A")	+0.72 (C)	–
	–2.09 (B)	–1.42 (A')	+1.08 (D)	–
		–2.19	+1.95	
6b	–1.67	–0.80	+0.52	–
	–2.24	–1.61	+0.86	–
		–2.31	+1.76	–
			+1.88	–
			+2.23	–
6c	–1.56	–0.59	+0.69	–
	–2.25	–1.47	+0.94	–
		–2.22	+1.71	–
			+2.15	–
6d	–1.60	–0.71	+0.63	–
	–2.24	–1.47	+0.99	–
		–2.27	+1.84	–
			+1.98	–
			+2.29	–
6e	–1.53	–0.63	+0.75	–
	–2.12	–1.43	+1.01	–
		–1.91	+1.39	–
			+1.75	–
			+2.10	–
6f	–1.49	–0.62	+0.74	–
	–1.67	–0.78	+0.97	–
	–2.27	–1.37	+1.75	–
		–1.64	+2.09	–
		–2.27		
6g	–1.40	–0.54	+0.72	–
	–1.96	–1.31	+0.95	–
		–1.98	+1.72	–
			+2.06	–
6h	–1.80	–1.04	+0.66	–
		–1.68	+0.92	–
			+1.78	–
			+2.28	–
			+2.45	–
6i	–1.55	–0.59	+0.84	–
	–2.06	–1.47	+1.08	–
		–1.67	+1.67	–
			+2.17	–
6j	–1.72	–0.64	+0.75	–
	–2.22	–1.61	+0.97	–
		–1.96	+1.64	–
			+1.82	–
			+2.33	–
6k	–1.35	–0.08	+0.82	–
	–1.88	–0.38	+1.10	–
		–1.86	+1.67	–
			+1.94	–
Fc***	–	–	+0.61	+0.47

* Solvent: MeCN, containing 0.1 M TBAP; *v* 0.2 V/s.
** Letters A–D correspond to the peaks on Figures 6–8.
*** Ferrocene was used as an internal reference redox electrode.

It is legitimate that the lowest first-stage reduction potentials (Table 3) belong to bromo **6f** (–1.49 V), chloro **6g** (–1.40 V), and hydroxy derivatives **6k** (–1.35 V), which is accounted by the presence of an electron-withdrawing substituent (Fig. 7). Apparently in the case of compound **6k** the negative inductive effect of the hydroxy group oxygen at R^4 position tends to be stronger than the positive mesomeric effect. Compounds **6b**,**c**,**d**,**e**,**h** having electron-donating substituents in the benzene ring are capable of adding electrons at more negative potentials in contrast to compound **6a** (Fig. 8).

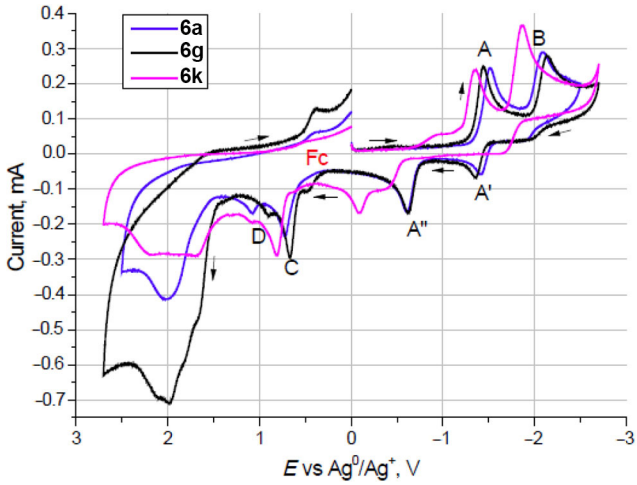


Figure 7. Cyclic voltammograms of compounds **6a**,**g**,**k** at a glassy carbon disk electrode with negative and positive scan directions; 1 mM solution in MeCN containing 0.1 M TBAP; *v* 0.2 V/s.

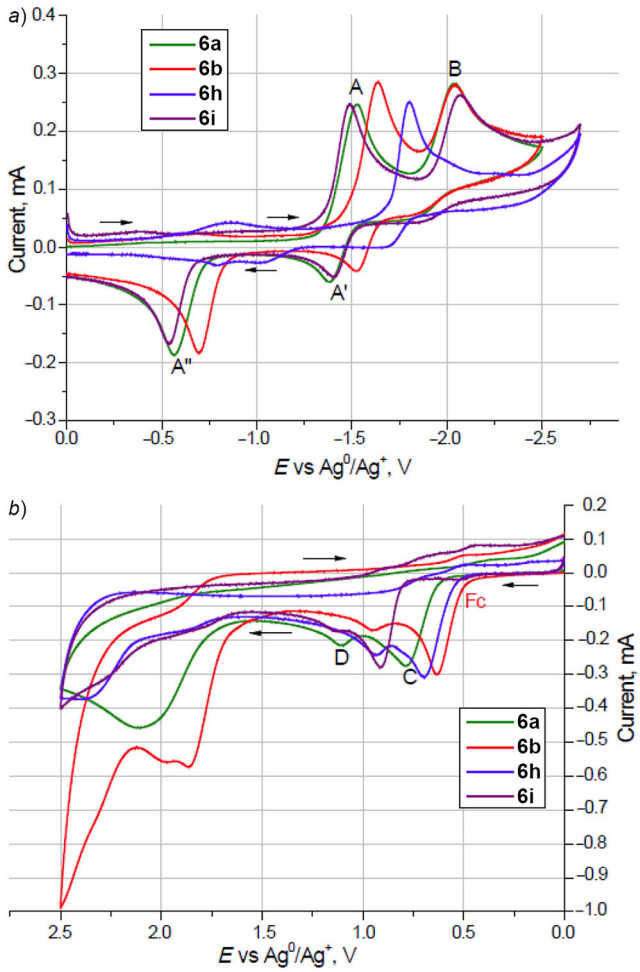
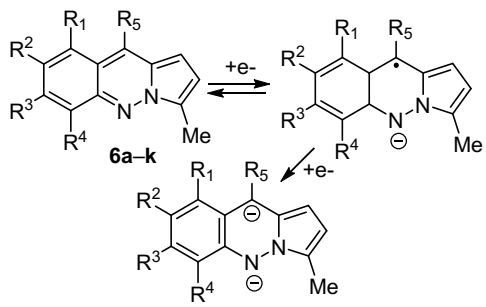


Figure 8. Cyclic voltammograms of compounds **6a**,**b**,**h**,**i** at a glassy carbon disk electrode with *a*) negative and *b*) positive scan directions; 1 mM solution in MeCN containing 0.1 M TBAP; *v* 0.2 V/s.

As it is evident from Figures 6–8, the electrochemical reduction of the synthesized pyrrolo[1,2-*b*]cinnolines proceeds in two steps, with the first one being reversible to large extent, while the second is only partially reversible. It

is also worth noting that the first reduction signal on the *E* curve produces an extra peak A" (Figs. 6, 7, and 8). We assume the formation of a stable anion radical at the first step (peak A), which upon addition of an electron is converted to a dianion (peak B), capable of being oxidized at negative potentials (Scheme 3). Seemingly, from the two anion radicals a dimer-dianion is chemically formed with the involvement of one of $R^{1–4}$ positions. Peak A' is considered the dimer-dianion oxidation signal. The existence of some correlation between the dimer-dianion stability and the height of the peak A" is also presumed. As Figure 6 indicates, the maximal magnitude of this signal is observed for compound **6a** in which the electron density of the pyrrolocinnoline nucleus is additionally stabilized by the furan ring. For compound **6h** which is lacking an additional stabilizing factor, such a signal is absent.

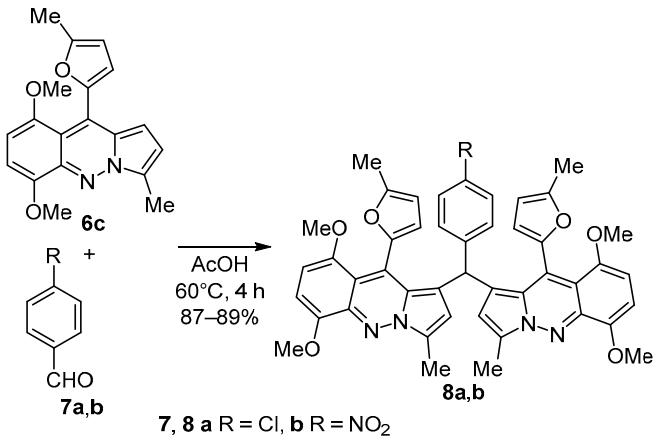
Scheme 3. Electrochemical reduction of compounds **6a**–**k** at a glassy carbon disk electrode



The influence of a more extended π-system in comparison to PC can be conveniently viewed considering examples **6a**,**i** involving a 5-methylfuryl and phenyl groups at position 10, and compound **6h**, which is unsubstituted at this position. As the data from Table 3 and Figure 6 implies, the strongest stabilizing effect on the anion radical formed at the first stage is provided by the methylfuryl substituent in compound **6a** (–1.51 V), while the potential for the first stage of reduction of compound **6i** is slightly more negative (–1.55 V). In the case of absence of substituents at position 10, the signal shifts to the region of more negative magnitudes and is –1.80 V for compound **6h**. The effect of the extended π-system on the reversibility of signals of the first stage of oxidation is lower, than it is for reduction. All the synthesized compounds have significantly lower oxidation potentials than PC. First stage of oxidation proceeds with the greatest facility in the case of compound **6b** (+0.52 V), which incorporates methoxy substituents at positions 7, 8 and the methylfuryl group at position 10. It may also be outlined that, in general, the presence of an electron-accepting halogen substituent at position 6, compensated in terms of electronic effects by the presence of two donating methoxy substituents at positions 8 and 9, has no considerable influence on the E_{ox} magnitude: it equals to +0.72 V for the model compound **6a**, +0.74 V and +0.72 V for compounds **6f** and **6g**, respectively. An interesting effect of the influence of donating substituent position on the first stage potential can be observed if one compares the redox behavior of compounds **6c**, **6d**, and **6e**. All of the three compounds have more positive E_{ox} magnitudes compared to that of compound **6b** (+0.52 V): +0.69, +0.63, and +0.75 V, respectively. Most likely, the presence of donating groups at positions 8 and 9 obstructs the first step of oxidation. Note that the current description is generally in a good agreement with the data in literature; oxidation of 1,2-dimethoxybenzene is known to be impeded in contrast to that of 1,4-dimethoxybenzene.[35]

For elongation of conjugation and modulation of photophysical properties of pyrrolo[1,2-*b*]cinnolines, few test reactions were performed. First we considered that electrophilic activation of the ring should lead to enhanced acidity of pyrrole-bound methyl group rendering it suitable for condensation with benzaldehydes. Unexpectedly, treatment of pyrrolocinnoline **6c** with benzaldehydes **7a**,**b** gave rise to dihetarylmethanes **8a**,**b** rather than styryl compounds (Scheme 4). Structure of compound **8a** has been proved by X-ray crystallography (Fig. 9). The crystal of compound **8a** contains two nonequivalent molecules which differ in the side chain conformation (methoxy group) and the relative angles of aromatic cycles around a pseudoasymmetric carbon atom.

Scheme 4. Synthesis of dihetarylmethanes **8a**,**b**



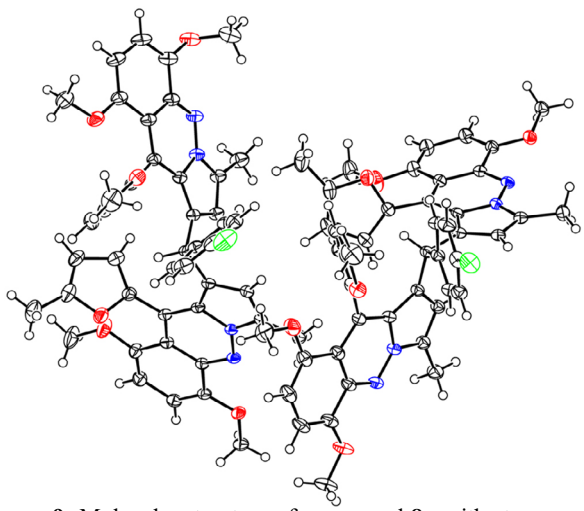


Figure 9. Molecular structure of compound **8a** with atoms represented as thermal vibration ellipsoids of 50% probability.

Eleven new heterocycles, based on the pyrrolo[1,2-*b*]-cinnoline unit, have been prepared and their electrochemical properties, as well as their crystal structures, have been studied. We have shown that the molecules of the synthesized pyrrolo[1,2-*b*]cinnolines, which involve two nucleophilic fragments – furan and pyrrole rings – possess strongly polarized character, which is demonstrated by their condensation reactions with suitable benzaldehydes, where pyrrolo[1,2-*b*]cinnolines act as donor aromatic compounds.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance HD 400 (400 and 101 MHz, respectively) spectrometer at room temperature in $CDCl_3$ or DMSO-d_6. Solvent signals were used as internal standard ($CDCl_3$: 7.26 ppm for ^{1}H nuclei, 77.2 ppm for ^{13}C nuclei; DMSO-d_6: 2.50 ppm for ^{1}H nuclei, 39.5 ppm for ^{13}C nuclei). Mass spectra were recorded on a Bruker UHR-TOF Maxis™ Impact mass spectrometer (ESI). Melting points were determined with a Stuart SMP 30 and are uncorrected.

All the reactions were carried out using freshly distilled and dry solvents from solvent stills.

The starting 2-nitrobenzaldehyde (**1a**), 2-methylfuran, benzaldehydes **7a**,**b** were commercial reagents. Other aldehydes were synthesized according to the published procedures.[21–24] 5,5'-[(2-Nitrophenyl)methylene]bis(2-methylfuran) (**2a**),[25] 5,5'-[(4,5-dimethoxy-2-nitrophenyl)-methylene]bis(2-methylfuran) (**2b**),[25] 5,5'-[(3,6-dimethoxy-2-nitrophenyl)methylene]bis(2-methylfuran) (**2c**),[25] 5,5'-[(2,5-dimethoxy-3-methyl-6-nitrophenyl)methylene]bis-(2-methylfuran) (**2e**),[25] 5,5'-[(3-bromo-5,6-dimethoxy-2-nitrophenyl)methylene]bis(2-methylfuran) (**2f**),[25] 5,5'-[(3-chloro-5,6-dimethoxy-2-nitrophenyl)methylene]bis(2-methylfuran) (**2g**),[25] (4,5-dimethoxy-2-nitrophenyl)(5-methylfuran-2-yl)methanone (**2h**),[26] 2-[(2-azido-5-chlorophenyl)-(phenyl)methyl]-5-methylfuran (**2i**),[27] 2-[(2-azido-4,5-dimethoxyphenyl)(phenyl)methyl]-5-methylfuran (**2j**),[27] 5,5'-[(2-azido-5-nitrophenyl)methylene]bis(2-methylfuran) (**2l**),[27] 2-[bis(5-methylfuran-2-yl)methyl]aniline (**3a**),[28] 2-[bis(5-methylfuran-2-yl)methyl]-4,5-dimethoxyaniline (**3b**),[29] 4,5-dimethoxy-2-[(5-methylfuran-2-yl)methyl]aniline (**3h**)[26] were prepared according to the published procedures.

2,2'-[(3-Methoxy-2-nitrophenyl)methanediyl]bis(5-methylfuran) (2d). $HClO_4$ (0.1 ml) was added to a solution of *o*-nitrobenzaldehyde **1d** (10 mmol) and 2-methylfuran (3 ml, 33.4 mmol) in 1,4-dioxane (15 ml). The reaction mixture was stirred overnight, poured into H_2O, and extracted with warm PhH (3×30 ml). Combined organic fractions were dried over Na_2SO_4 and concentrated *in vacuo*. The oily residue was dissolved in hot hexane, passed through a thin pad of Al_2O_3, and left overnight. The crystalline product was filtered off and dried on air. Yield 2.68 g (82%), white solid, mp 129–132°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.37 (1H, t, *J* = 8.2, H Ar); 6.97–6.93 (2H, m, H Ar); 5.96 (2H, d, *J* = 2.9, H Ar); 5.90 (2H, d, *J* = 2.1, H Ar); 5.45 (1H, s, CH); 3.89 (3H, s, OCH_3); 2.25 (6H, s, $2CH_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.0 (2C); 150.8; 150.1 (2C); 141.0; 132.7; 130.8; 121.3; 111.2; 109.0 (2C); 106.2 (2C); 56.4; 39.6; 30.9; 13.6. Found, *m*/*z*: 350.0999 $[M+Na]^+$. $C_{18}H_{17}NNaO_5$. Calculated, *m*/*z*: 350.1008.

Preparation of compounds 3c–g (General method). The compounds were prepared according to the literature method.[29,30]

2-[Bis(5-methylfuran-2-yl)methyl]-3,6-dimethoxyaniline (3c). Yield 2.61 g (88%), beige solid, mp 147–149°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.70 (1H, d, *J* = 8.7, H-5 Ar); 6.30 (1H, d, *J* = 8.7, H-4 Ar); 6.19 (1H, s, CH); 6.05 (2H, d, *J* = 2.8, H-3 furan); 5.91 (2H, d, *J* = 2.8, H-4 furan); 4.17 (2H, br. s, NH_2); 3.82 (3H, s, OCH_3); 3.80 (3H, s, OCH_3); 2.28 (6H, s, $2CH_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.0; 151.6 (2C); 151.3 (2C); 142.3; 137.0; 112.4; 108.8; 108.1 (2C); 106.0 (2C); 99.0; 56.5; 55.9; 34.9; 13.8 (2C). Found, *m*/*z*: 350.1363 $[M+Na]^+$. $C_{19}H_{21}NNaO_4$. Calculated, *m*/*z*: 350.1352.

2-[Bis(5-methylfuran-2-yl)methyl]-6-methoxyaniline (3d). Yield 2.58 g (87%), beige solid, mp 71–73°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.78 (2H, d, *J* = 4.2, H-3,5 Ar); 6.65–6.58 (1H, m, H-4 Ar); 5.96 (2H, d, *J* = 2.3, H-3 furan); 5.92 (2H, s, H-4 furan); 5.51 (1H, s, CH); 4.29 (2H, br. s, NH_2); 3.87 (3H, s, OCH_3); 2.27 (6H, s, $2CH_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.7; 151.5 (2C); 148.0; 148.1; 121.1; 119.0; 118.7; 109.1 (2C); 108.7 (2C); 106.1 (2C); 55.7; 40.6; 13.7 (2C). Found, *m*/*z*: 296.1292 $[M–H]^-$. $C_{18}H_{18}NO_3$. Calculated, *m*/*z*: 296.1295.

2-[Bis(5-methylfuran-2-yl)methyl]-3,6-dimethoxy-4-methylaniline (3e). Yield 2.68 g (82%), pale-yellow solid, mp 111–114°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.58 (1H, s, H-5 Ar); 6.07 (2H, d, *J* = 2.6, H-3 furan); 6.06 (1H, s, CH); 5.90 (2H, d, *J* = 2.6, H-4 furan); 4.01 (2H, br. s, NH_2); 3.81 (3H, s, OCH_3); 3.70 (3H, s, OCH_3); 2.28 (3H, s, CH_3); 2.26 (6H, s, $2CH_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.3 (4C); 150.3; 143.8; 134.5; 118.1; 117.2; 111.5; 108.3 (2C); 106.0 (2C); 61.2; 55.7; 36.1; 16.0; 13.7 (2C). Found, *m*/*z*: 342.1700 $[M+H]^+$. $C_{20}H_{24}NO_4$. Calculated, *m*/*z*: 342.1699.

2-[Bis(5-methylfuran-2-yl)methyl]-6-bromo-3,4-dimethoxyaniline (3f). Yield 3.41 g (84%), yellow solid, mp 89–91°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.04 (1H, s, H-5); 6.19 (1H, s, CH); 6.09 (2H, d, *J* = 2.7, H-4 furan); 5.92 (2H, d, *J* = 2.7, H-3 furan); 4.12 (2H, br. s, NH_2); 3.83 (3H, s, OCH_3); 3.82 (3H, s, OCH_3); 2.27 (6H, s, $2CH_3$). ^{13}C NMR ($CDCl_3$), δ, ppm: 151.5; 150.5 (2C); 147.5; 145.1; 137.9; 119.7; 116.4; 108.5 (2C); 106.1 (2C); 104.7 (2C); 61.2; 56.6; 36.1; 13.7 (2C). Found, *m*/*z*: 428.0468 $[M+Na]^+$. $C_{19}H_{20}BrNNaO_4$. Calculated, *m*/*z*: 428.0489.

2-[Bis(5-methylfuran-2-yl)methyl]-6-chloro-3,4-dimethoxyaniline (3g). Yield 3.1 g (86%), yellow solid, mp 85–87°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.89 (1H, s, H-5 Ar); 6.17 (1H, s, CH); 6.09 (2H, d, *J* = 2.7, H-3 furan); 5.92 (2H, d, *J* = 2.7, H-4 furan); 4.08 (2H, br. s, NH_2); 3.83 (3H, s, OCH_3); 3.82 (3H, s, OCH_3); 2.27 (6H, s, $2CH_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.6 (2C); 150.5 (2C); 146.8; 144.8; 136.7; 119.7; 114.7; 113.3; 108.5 (2C); 106.1 (2C); 61.3; 56.5; 36.0; 13.7 (2C). Found, *m*/*z*: 384.0973 $[M+Na]^+$. $C_{19}H_{20}ClNNaO_4$. Calculated, *m*/*z*: 384.0971.

Preparation of compounds 3i,j (General method). PPh_3 (10 mmol) was added to a solution of compound **2i**,**j** (10 mmol) in THF (30 ml). The reaction mixture was stirred at room temperature for 2 h, after which H_2O (8 ml) and AcOH (2 ml) were added, followed by stirring at 50°C for 4 h (TLC control, petroleum ether – EtOAc, 4:1).

4-Chloro-2-[(5-methylfuran-2-yl)(phenyl)methyl]aniline (3i). Yield 2.44 g (82%), pale-yellow solid, mp 95–97°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.41–7.25 (3H, m, H Ph); 7.21 (2H, d, *J* = 7.0, H Ph); 7.07 (1H, dd, *J* = 8.4, *J* = 2.3, H-5 Ar); 6.77 (1H, d, *J* = 2.2, H-3 furan); 6.63 (1H, d, *J* = 8.4, H-6 Ar); 5.92 (1H, d, *J* = 1.9, H-3 Ar); 5.78 (1H, d, *J* = 2.8, H-4 furan); 5.35 (1H, s, CH); 3.55 (2H, br. s, NH_2); 2.30 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.9; 152.1; 142.8; 139.7; 129.1; 128.8 (4C); 127.6 (2C); 127.3; 123.6; 117.5; 109.8; 106.2; 46.3; 13.7. Found, *m*/*z*: 320.0821. $[M+Na]^+$. $C_{18}H_{16}ClNNaO$. Calculated, *m*/*z*: 320.0818.

4,5-Dimethoxy-2-[(5-methylfuran-2-yl)(phenyl)methyl]-aniline (3j). Yield 2.68 g (83%), pale-yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.37–7.20 (5H, m, H Ph); 6.38 (1H, s, H-6 Ar); 6.31 (1H, s, H-3 Ar); 5.91 (1H, s, H-3 furan); 5.77 (1H, d, *J* = 2.5, H-4 furan); 5.38 (1H, s, CH); 3.84 (3H, s, OCH_3); 3.68 (3H, s, OCH_3); 3.36 (2H, s,); 2.28 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 154.1; 151.7; 148.7; 141.9; 140.8; 138.1; 128.8 (2C); 128.6 (2C); 127.0; 118.7; 114.2; 109.3; 106.0; 101.6; 56.6; 55.8; 46.0; 13.7. Found, *m*/*z*: 346.1414 $[M+Na]^+$. $C_{20}H_{21}NNaO_3$. Calculated, *m*/*z*: 346.1411.

2-[Bis(5-methylfuran-2-yl)methyl]-4-nitroaniline (3l). Yield 2.68 g (86%), yellow solid, mp 153–155°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.04 (1H, dd, *J* = 8.8, *J* = 2.5, H-5 Ar); 7.86 (1H, d, *J* = 2.5, H-3 Ar); 6.66 (1H, d, *J* = 8.8, H-4 Ar); 6.00 (2H, d, *J* = 2.9, H-3 furan); 5.96 (2H, d, *J* = 2.9, H-4 furan); 5.34 (1H, s, CH); 4.45 (2H, br. s, NH_2); 2.29 (6H, s, $2CH_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.4; 150.6; 149.7; 139.3; 132.2; 132.1; 128.6; 128.5; 126.0; 124.8; 123.6; 115.1; 109.4; 106.5; 41.0; 13.7 (2C). Found, *m*/*z*: 335.1002 $[M+Na]^+$. $C_{17}H_{16}N_2NaO_4$. Calculated, *m*/*z*: 335.0998.

Preparation of compounds 4a–j,l (General method).[29] Me_3SiCl (2 ml, 16 mmol) and *t*-BuONO (1.1 ml, 11 mmol) were added to a solution of compound **3a–j,l** (10 mmol) in MeCN (15 ml). The mixture was stirred for 30 min, poured into H_2O (200 ml), and neutralized with dry $NaHCO_3$. The product was extracted with EtOAc (3×50 ml), combined organic fractions were dried over Na_2SO_4 and concentrated *in vacuo*. The product was isolated by column chromatography, eluent petroleum ether – EtOAc, 4:1.

4(*E*)-4-[4-(5-Methylfuran-2-yl)cinnolin-3-yl]but-3-en-2-one (4a). Yield 2.30 g (83%), yellow-green solid, mp 94–96°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.61 (1H, d, *J* = 8.4, H-8 Ar); 8.27 (1H, d, *J* = 8.4, H-5 Ar); 8.01 (1H, d, *J* = 15.6, CH=); 7.89 (1H, t, *J* = 7.6, H-6 Ar); 7.87–7.81 (2H, m, H-7 Ar, CH=); 6.75 (1H, d, *J* = 3.2, H-3 furan); 6.35 (1H, d, *J* = 2.7, H-4 furan); 2.52 (3H, s, CH_3); 2.45 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.4; 155.9; 149.9; 145.8; 144.0; 137.6; 131.9; 131.5; 130.8; 130.5; 125.8; 124.2; 123.6; 118.0; 108.6; 29.1; 14.0. Found, *m*/*z*: 279.1128 $[M+H]^+$. $C_{17}H_{15}N_2O_2$. Calculated, *m*/*z*: 279.1122.

(*E*)-4-[6,7-Dimethoxy-4-(5-methylfuran-2-yl)cinnolin-3-yl]but-3-en-2-one (4b). Yield 2.90 g (86%), yellow-orange solid, mp 150–152°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.93 (2H, s, H-8 Ar, CH=); 7.91 (1H, d, *J* = 15.7, CH=); 7.69 (1H, d, *J* = 15.7, H-7 Ar); 7.51 (1H, s, H-5 Ar); 6.76 (1H, d, *J* = 3.1, H-3 furan); 6.36 (1H, d, *J* = 3.1, H-4 furan); 4.16 (3H, s, OCH_3); 4.04 (3H, s, OCH_3); 2.51 (3H, s, CH_3); 2.42 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.2; 155.8; 154.4; 154.1; 147.1; 145.3; 144.3; 137.3; 131.0; 124.2; 121.5; 117.8; 108.8; 106.5; 102.3; 56.8; 56.3; 29.2; 14.0. Found, *m*/*z*: 339.1339 $[M+H]^+$. $C_{19}H_{19}N_2O_4$. Calculated, *m*/*z*: 339.1329.

(*E*)-4-[5,8-Dimethoxy-4-(5-methylfuran-2-yl)cinnolin-3-yl]but-3-en-2-one (4c). Yield 2.70 g (80%), yellow solid, mp 95–97°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.78 (2H, s, H-6,7 Ar); 7.11 (1H, d, *J* = 15.2, CH=); 7.03 (1H, d, *J* = 15.2, CH=); 6.38 (1H, d, *J* = 2.7, H-3 furan); 6.21 (1H, d, *J* = 2.7, H-4 furan); 4.15 (3H, s, OCH_3); 3.70 (3H, s, OCH_3); 2.42 (3H, s, CH_3); 2.39 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.5; 153.3; 150.6; 148.8; 148.7; 144.9; 142.6; 136.9; 131.8; 123.1; 118.4; 113.0; 111.6; 109.3; 107.2; 56.9; 56.6; 28.7; 13.7. Found, *m*/*z*: 361.1159 $[M+Na]^+$. $C_{19}H_{18}N_2NaO_4$. Calculated, *m*/*z*: 361.1141.

(*E*)-4-[8-Methoxy-4-(5-methylfuran-2-yl)cinnolin-3-yl]-but-3-en-2-one (4d). Yield 2.59 g (84%), yellow-green solid, mp 175–177°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.98 (1H, d, *J* = 15.6, CH=); 7.84–7.75 (2H, m, H-7 Ar, CH=); 7.71 (1H, t, *J* = 8.1, H-6 Ar); 7.18 (1H, d, *J* = 7.6, H-5 Ar); 6.73 (1H, d, *J* = 3.0, H-3 furan); 6.34 (1H, d, *J* = 3.0, H-4 furan); 4.21 (3H, s, OCH_3); 2.51 (3H, s, CH_3); 2.45 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.5; 156.6; 155.6; 146.5; 144.1; 142.6; 137.8; 132.6; 131.7; 125.0; 124.0; 117.7; 116.9; 108.8; 108.5; 56.5; 28.9; 14.0. Found, *m*/*z*: 331.1053 $[M+Na]^+$. $C_{18}H_{16}N_2NaO_3$. Calculated, *m*/*z*: 331.1055.

(*E*)-4-[5,8-Dimethoxy-6-methyl-4-(5-methylfuran-2-yl)-cinnolin-3-yl]but-3-en-2-one (4e). Yield 2.78 g (84%), yellow-green solid, mp 134–137°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.75 (1H, d, *J* = 15.7, CH=); 7.66 (1H, d, *J* = 15.7, CH=); 6.99 (1H, s, C-7 Ar); 6.45 (1H, d, *J* = 3.0, H-3 furan); 6.22 (1H, d, *J* = 2.2, H-4 furan); 4.15 (3H, s, OCH_3); 3.30 (3H, s, OCH_3); 2.48 (3H, s, CH_3); 2.43 (3H, s, CH_3); 2.38 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.5; 153.5; 152.7; 149.1; 145.8; 144.7; 142.2; 137.0; 135.5; 132.0; 122.2; 121.1; 113.2; 112.5; 107.2; 61.5; 56.5; 28.6; 17.3; 13.7. Found, *m*/*z*: 353.1496 $[M+H]^+$. $C_{20}H_{21}N_2O_4$. Calculated, *m*/*z*: 353.1493.

(*E*)-4-[8-Bromo-5,6-dimethoxy-4-(5-methylfuran-2-yl)-cinnolin-3-yl]but-3-en-2-one (4f). Yield 3.58 g (86%), yellow-green solid, mp 183–185°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.99 (1H, s, H-7 Ar); 7.80 (1H, d, *J* = 15.7, CH=); 7.68 (1H, d, *J* = 15.7, CH=); 6.43 (1H, d, *J* = 2.6, H-4 furan); 6.21 (1H, d, *J* = 2.6, H-4 furan); 4.07 (3H, s, OCH_3); 3.54 (3H, s, OCH_3); 2.41 (3H, s, CH_3); 2.37 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.3; 153.6; 153.7; 148.3; 144.2; 142.8; 141.9; 136.3; 132.3; 122.7; 122.3; 121.9; 112.9 (2C); 107.2; 61.4; 57.0; 28.8;

13.7. Found, *m/z*: 417.0444 $[M+H]^+$. $C_{19}H_{18}BrN_2O_4$. Calculated, *m/z*: 417.0443.

(*E*)-4-[8-Chloro-5,6-dimethoxy-4-(5-methylfuran-2-yl)-cinnolin-3-yl]but-3-en-2-one (4g). Yield 3.31 g (89%), yellow-green solid, mp 126–128°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.77 (1H, s, H-7 Ar); 6.85 (1H, d, *J* = 15.7, CH=); 6.46–6.39 (2H, m, H-3 furan, CH=); 6.19 (1H, d, *J* = 3.0, H-4 furan); 4.07 (3H, s, OCH_3); 3.53 (3H, s, OCH_3); 2.41 (3H, s, CH_3); 2.39 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 202.4; 153.5; 153.1; 150.0; 144.9; 142.0; 140.9; 135.4; 131.8; 130.2; 122.5; 120.2; 119.0; 113.1; 107.0; 61.4; 56.9; 30.6; 13.7. Found, *m/z*: 373.0950 $[M+H]^+$. $C_{19}H_{18}ClN_2O_4$. Calculated, *m/z*: 373.0964.

(*E*)-4-(6,7-Dimethoxycinnolin-3-yl)but-3-en-2-one (4h). Yield 2.0 g (78%), white solid, mp 215–218°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.83 (1H, d, *J* = 16.5, CH=); 7.80 (1H, s, H-4 Ar); 7.73 (1H, s, H-8 Ar); 7.33 (1H, d, *J* = 16.4, CH=); 6.98 (1H, s, H-5 Ar); 4.10 (3H, s, OCH_3); 4.06 (3H, s, OCH_3); 2.46 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.4; 154.1; 148.9; 148.4; 140.3; 129.8; 123.2; 122.3; 121.0; 107.1; 103.2; 56.6; 56.5; 28.1. Found, *m/z*: 259.1077 $[M+H]^+$. $C_{14}H_{15}N_2O_3$. Calculated, *m/z*: 259.1077.

(*E*)-4-(6-Chloro-4-phenylcinnolin-3-yl)but-3-en-2-one (4i). Yield 2.53 g (82%), yellow solid, mp 198–200°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.57 (1H, d, *J* = 9.0, H-8 Ar); 7.81 (1H, d, *J* = 15.7, CH=); 7.79 (1H, dd, *J* = 8.9, *J* = 2.1, H-7 Ar); 7.65–7.61 (3H, m, H-2,4,6 Ph); 7.58 (1H, d, *J* = 1.7, H-5 Ar); 7.49 (1H, d, *J* = 15.6, CH=); 7.35 (2H, dd, *J* = 6.5, *J* = 2.9, H-3,5 Ph); 2.33 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.1; 147.0; 138.3; 136.2 (2C); 134.6; 132.0 (2C); 131.8; 131.7; 129.9 (2C); 129.7; 129.2 (2C); 124.5 (2C); 29.0. Found, *m/z*: 331.0609 $[M+Na]^+$. $C_{18}H_{13}ClN_2NaO$. Calculated, *m/z*: 331.0607.

(*E*)-4-(6,7-Dimethoxy-4-phenylcinnolin-3-yl)but-3-en-2-one (4j). Yield 2.94 g (88%), brown solid, mp 225–227°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.92 (1H, s, H-8 Ar); 7.69 (1H, d, *J* = 15.6, CH=); 7.64–7.58 (3H, m, H-2,4,6 Ph); 7.45 (1H, d, *J* = 15.6, CH=); 7.38–7.34 (2H, m, H-3,5 Ph); 6.75 (1H, s, H-5 Ar); 4.15 (3H, s, OCH_3); 3.84 (3H, s, OCH_3); 2.31 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.2; 154.2; 154.1; 147.3; 145.9; 136.7; 132.8; 130.7; 129.7 (2C); 129.4; 129.1 (2C); 122.9; 106.6; 101.9; 56.8; 56.3; 31.0; 28.9. Found, *m/z*: 335.1390 $[M+H]^+$. $C_{20}H_{19}N_2O_3$. Calculated, *m/z*: 335.1318.

(*E*)-4-[4-(5-Methylfuran-2-yl)-6-nitrocinnolin-3-yl]but-3-en-2-one (4l). Yield 2.52 g (78%), yellow solid, mp 205–207°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.25 (1H, d, *J* = 1.8, H-5 Ar); 8.69 (1H, d, *J* = 9.2, H-8 Ar); 8.51 (1H, dd, *J* = 9.2, *J* = 2.0, H-7 Ar); 7.97 (1H, d, *J* = 15.5, CH=); 7.77 (1H, d, *J* = 15.5, CH=); 6.82 (1H, d, *J* = 3.3, H-3 furan); 6.36 (1H, d, *J* = 3.1, H-4 furan); 2.49 (3H, s, CH_3); 2.40 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 198.0; 157.7; 149.8; 148.6; 146.8; 143.2; 136.4; 132.8; 132.6; 124.6; 124.1; 123.7; 122.6; 120.1; 109.6; 29.4; 14.2. Found, *m/z*: 346.0798 $[M+Na]^+$. $C_{17}H_{13}N_3NaO_4$. Calculated, *m/z*: 346.0760.

Preparation of compounds 5a–j,l (General method). $NaBH_4$ (10 mmol) was added in portions to a suspension of compound **4a–j,l** (10 mmol) in EtOH (30 ml). The reaction mixture was stirred at room temperature for 2 h until the full conversion of the starting material (TLC control, petroleum ether – EtOAc, 2:1). The reaction mixture was poured into H_2O (150 ml), extracted with EtOAc (3×50 ml), combined organic fractions were dried over Na_2SO_4 and concentrated *in vacuo*. The obtained compounds were used further without purification.

(*E*)-4-[6,7-Dimethoxy-4-(5-methylfuran-2-yl)cinnolin-3-yl]but-3-en-2-ol (5b). Yield 3.33 g (98%), beige solid, mp 149–151°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.71 (1H, s, H-8 Ar); 7.50 (1H, s, H-8 Ar); 6.75–6.68 (2H, m, H-3 furan, CH=); 6.29 (1H, s, H-4 furan); 6.14 (1H, dd, *J* = 11.6, *J* = 7.4, CH=); 4.76–4.67 (1H, m, C<u>H</u>–OH); 4.11 (3H, s, OCH_3); 4.02 (3H, s, OCH_3); 2.48 (3H, s, CH_3); 1.44 (3H, d, *J* = 6.4, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 154.7; 154.1; 153.1; 148.4; 147.3; 145.2; 141.4; 126.8; 122.2; 121.4; 116.9; 108.2; 106.9; 101.9; 63.4; 56.4; 56.2; 22.4; 13.9. Found, *m/z*: 341.1496 $[M+H]^+$. $C_{19}H_{21}N_2O_4$. Calculated, *m/z*: 41.1485.

Preparation of compounds 6a–j,l (General method). $BF_3{\cdot}OEt_2$ (1.10 ml) was added dropwise to a solution of compound **5a–j,l** (3 mmol) in 1,2-dichloroethane (20 ml). The reaction mixture was stirred at 60°C for 4–8 h until the full conversion of the starting material (TLC control, petroleum ether – EtOAc, 4:1), poured into H_2O (100 ml), and extracted with 1,2-dichloroethane (3×50 ml). Combined organic fractions were dried over Na_2SO_4 and concentrated *in vacuo*. The products were isolated by column chromatography, eluent petroleum ether – EtOAc, 9:1.

3-Methyl-10-(5-methylfuran-2-yl)pyrrolo[1,2-*b*]cinnoline (6a). Yield 0.53 g (68%), purple solid, mp 72–74°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.19 (1H, d, *J* = 8.9, H-6 Ar); 7.76 (1H, d, *J* = 9.0, H-9 Ar); 7.41 (1H, br. dd, *J* = 9.0, *J* = 6.8, H-8 Ar); 7.15 (2H, s, H-7 Ar, H-1 Ar); 7.08–7.05 (2H, m, H-2 Ar, H-3 furan); 6.33 (1H, d, *J* = 2.5, H-4 furan, H-2 Ar); 2.82 (3H, s, CH_3); 2.55 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 154.6; 147.1; 146.0; 129.0; 125.8; 125.1 (3C); 124.1; 122.3; 117.0; 116.1; 113.1; 108.3; 99.6; 14.1; 12.0. Found, *m/z*: 263.1179 $[M+H]^+$. $C_{17}H_{15}N_2O$. Calculated, *m/z*: 263.1190.

7,8-Dimethoxy-3-methyl-10-(5-methylfuran-2-yl)pyrrolo-[1,2-*b*]cinnoline (6b). Yield 0.61 g (64%), purple-red solid, mp 150–152°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.44 (1H, s, H-6 Ar); 7.01 (1H, d, *J* = 3.0, H-3 furan); 6.96–6.97 (2H, m, H Ar); 6.93 (1H, d, *J* = 4.4, H-2 Ar); 6.32 (1H, d, *J* = 3.0, H-4 furan); 4.04 (3H, s, OCH_3); 3.97 (3H, s, OCH_3); 2.74 (3H, s, CH_3); 2.52 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 153.8; 153.2; 148.2; 147.5; 144.4; 124.3; 123.1; 122.6; 114.9; 114.6; 110.0; 108.2; 101.7; 101.6; 97.5; 56.1; 55.7; 14.0; 11.9. Found, *m/z*: 323.1390 $[M+H]^+$. $C_{19}H_{19}N_2O_3$. Calculated, *m/z*: 323.1391.

6,9-Dimethoxy-3-methyl-10-(5-methylfuran-2-yl)pyrrolo-[1,2-*b*]cinnoline (6c). Yield 0.69 g (72%), purple solid, mp 165–167°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.08 (1H, d, *J* = 4.5, H-8 Ar); 6.86 (1H, d, *J* = 4.5, H-7 Ar); 6.65 (1H, d, *J* = 3.1, H-3 furan); 6.59 (1H, d, *J* = 8.2, H-1 Ar); 6.24–6.20 (2H, m, H-2 Ar, H-4 furan); 4.05 (3H, s, OCH_3); 3.70 (3H, s, OCH_3); 2.84 (3H, s, CH_3); 2.44 (3H, s,

CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.6; 150.0; 147.6; 146.6; 140.3; 127.4; 125.3 (2C); 117.1; 111.6; 109.0; 107.0; 105.0; 99.9; 99.2; 56.2; 56.0; 13.8; 11.9. Found, *m*/*z*: 323.1390 $[M+H]^+$. $C_{19}H_{19}N_2O_3$. Calculated, *m*/*z*: 323.1383.

6-Methoxy-3-methyl-10-(5-methylfuran-2-yl)pyrrolo-[1,2-*b*]cinnoline (6d). Yield 0.54 g (62%), purple solid, mp 131–133°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.78 (1H, d, *J* = 8.7, H-9); 7.12 (2H, q, *J* = 4.7, H-7,8 Ar); 7.04 (1H, d, *J* = 3.3, H-3 furan); 6.98 (1H, dd, *J* = 9.0, *J* = 7.4, H-1 Ar); 6.70 (1H, d, *J* = 7.4, H-2 Ar); 6.32 (1H, d, *J* = 3.3, H-4 furan); 4.10 (3H, s, OCH_3); 2.85 (3H, s, CH_3); 2.53 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 154.5; 152.3; 147.1; 139.8; 125.1; 124.9 (2C); 121.7; 117.8; 117.0; 116.2; 113.9; 108.3; 105.0; 99.4; 56.1; 14.0; 11.9. Found, *m*/*z*: 315.1104 $[M+Na]^+$. $C_{18}H_{16}N_2NaO_2$. Calculated, *m*/*z*: 315.1107.

6,9-Dimethoxy-3,8-dimethyl-10-(5-methylfuran-2-yl)-pyrrolo[1,2-*b*]cinnoline (6e). Yield 0.65 g (65%), purple solid, mp 146–148°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.08 (1H, d, *J* = 4.5, H-1 Ar); 6.80 (1H, d, *J* = 4.5, H-2 Ar); 6.69 (1H, d, *J* = 3.0, H-3 furan); 6.48 (1H, s, H-7 Ar); 6.23 (1H, d, *J* = 3.0, H-4 furan); 4.06 (3H, s, OCH_3); 3.28 (3H, s, OCH_3); 2.83 (3H, s, CH_3); 2.46 (3H, s, CH_3); 2.33 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.8; 148.6; 147.3; 145.8; 140.0; 127.8; 124.6; 123.6; 121.5; 117.0; 112.3; 110.7; 108.7; 107.0; 99.0; 60.6; 56.2; 16.4; 13.9; 11.8. Found, *m*/*z*: 359.1366 $[M+Na]^+$. $C_{20}H_{20}N_2NaO_3$. Calculated, *m*/*z*: 359.1358.

6-Bromo-8,9-dimethoxy-3-methyl-10-(5-methylfuran-2-yl)pyrrolo[1,2-*b*]cinnoline (6f). Yield 0.81 g (68%), purple solid, mp 123–125°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.74 (1H, s, H-7 Ar); 7.15 (1H, d, *J* = 4.5, H-1 Ar); 6.83 (1H, d, *J* = 4.6, H-2 Ar); 6.67 (1H, d, *J* = 3.1, H-3 furan); 6.23 (1H, d, *J* = 3.1, H-4 furan); 3.95 (3H, s, OCH_3); 3.57 (3H, s, OCH_3); 2.82 (3H, s, CH_3); 2.44 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.9; 146.9; 144.6; 142.8; 140.6; 128.3; 125.8; 125.0; 124.1; 118.2; 114.4; 111.8; 111.3; 107.0 (2C); 61.1; 58.1; 13.8; 11.7. Found, *m*/*z*: 401.0495 $[M+H]^+$. $C_{19}H_{18}BrN_2O_3$. Calculated, *m*/*z*: 401.0512.

6-Chloro-8,9-dimethoxy-3-methyl-10-(5-methylfuran-2-yl)pyrrolo[1,2-*b*]cinnoline (6g). Yield 0.75 g (70%), purple solid, mp 121–123°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.53 (1H, s, H-7 Ar); 7.15 (1H, d, *J* = 4.6, H-1 Ar); 6.83 (1H, d, *J* = 4.6, H-2 Ar); 6.67 (1H, d, *J* = 3.6, H-3 furan); 6.23 (1H, d, *J* = 3.6, H-4 furan); 3.95 (3H, s, OCH_3); 3.56 (3H, s, OCH_3); 2.81 (3H, s, CH_3); 2.45 (3H, s, OCH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.9; 147.0; 144.1; 142.1; 140.1; 128.2; 124.8; 124.4; 124.0; 122.0; 118.1; 111.8; 111.3; 107.0; 99.1; 61.1; 58.0; 13.8; 11.7. Found, *m*/*z*: 357.1000 $[M+H]^+$. $C_{19}H_{18}ClN_2O_3$. Calculated, *m*/*z*: 357.1003.

7,8-Dimethoxy-3-methylpyrrolo[1,2-*b*]cinnoline (6h). Yield 0.44 g (61%), orange solid, sublimates over 180°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.89 (1H, s, H Ar); 6.86 (1H, d, *J* = 4.4, H pyrrol); 6.84 (1H, s, H Ar); 6.59 (1H, s, H Ar); 6.57 (1H, d, *J* = 4.4, H pyrrol); 3.92 (3H, s, OCH_3); 3.87 (3H, s, OCH_3); 2.63 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 153.9; 147.8; 144.1; 127.0; 123.0; 122.1; 114.8; 113.6; 103.2; 101.2; 96.8; 56.1; 55.9; 11.8. Found, *m*/*z*: 243.1128 $[M+H]^+$. $C_{14}H_{15}N_2O_2$. Calculated, *m*/*z*: 243.1125.

8-Chloro-3-methyl-10-phenylpyrrolo[1,2-*b*]cinnoline (6i). Yield 0.64 g (73%), red-pink solid, mp 118–121°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.69 (1H, d, *J* = 9.5, H-6 Ar); 7.55–7.47 (5H, m, H Ph); 7.40 (1H, d, *J* = 2.1, H-9 Ar); 7.23 (1H, dd, *J* = 9.5, *J* = 2.1, H-7 Ar); 7.03 (1H, s, H-1 Ar); 6.57 (1H, s, H-2 Ar); 2.73 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 144.1; 137.2; 133.8; 130.9; 129.9 (2C); 129.3; 128.8 (2C); 127.6; 127.2; 126.2; 125.3; 123.8; 118.1; 114.6; 100.5; 12.0. Found, *m*/*z*: 293.0840 $[M+H]^+$. $C_{18}H_{14}ClN_2$. Calculated, *m*/*z*: 293.0835.

7,8-Dimethoxy-3-methyl-10-phenylpyrrolo[1,2-*b*]-cinnoline (6j). Yield 0.70 g (74%), red solid, mp 126–128°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.65–7.54 (5H, m, H Ph); 7.06 (1H, s, H-6 Ar); 6.92 (1H, s, H-9 Ar); 6.69 (1H, s, H-1 Ar); 6.45 (1H, s, H-2 Ar); 4.04 (3H, s, OCH_3); 3.77 (3H, s, OCH_3); 2.78 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 153.8; 147.9; 144.4; 135.1; 135.0; 129.7 (2C); 128.8; 128.7 (2C); 127.0; 123.5; 114.9; 111.4; 101.2; 101.1; 97.7; 56.2; 55.7; 11.9. Found, *m*/*z*: 319.1449 $[M+H]^+$. $C_{20}H_{19}N_2O_2$. Calculated, *m*/*z*: 319.1441.

3-Methyl-10-(5-methylfuran-2-yl)pyrrolo[1,2-*b*]cinnolin-6-ol (6k). $AlCl_3$ (665 mg) was added to a solution of compound **6d** (1 mmol) in 1,2-dichloroethane (5 ml). The reaction mixture was stirred at 50°C for 6 h (TLC control, petroleum ether – EtOAc, 4:1), poured into H_2O (150 ml), and extracted with EtOAc (3×15 ml). Combined organic fractions were dried over Na_2SO_4 and concentrated *in vacuo*. The product was separated by column chromatography, eluent petroleum ether – EtOAc, 50:1. Yield 0.27 g (97%), purple solid, mp 90–92°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.59 (1H, s, OH); 7.64 (1H, d, *J* = 8.9, H-9 Ar); 7.28–7.20 (2H, m, H-1 Ar, H-3 furan); 7.11 (1H, d, *J* = 4.5, H-2 Ar); 6.99 (1H, dd, *J* = 8.9, *J* = 7.4, H-8 Ar); 6.79 (1H, d, *J* = 6.8, H-7); 6.51 (1H, d, *J* = 3.2, H-4 furan); 3.33 (3H, s, CH_3, overlapped with H_2O); 2.75 (3H, s, CH_3). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.75 (1H, d, *J* = 9.0, H-9 Ar); 7.13 (1H, s, H-7 Ar); 7.11 (1H, d, *J* = 3.3, H-3 furan); 7.04 (1H, dd, *J* = 9.0, *J* = 7.2, H-8 Ar); 6.94 (1H, d, *J* = 7.2, H-2 Ar); 6.35 (1H, d, *J* = 3.3, H-4 furan); 2.80 (3H, s, CH_3); 2.55 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 155.3; 148.0; 146.8; 137.7; 126.4; 125.7; 125.2; 123.0; 117.6; 117.4; 116.8; 113.1; 109.0; 108.7; 14.1; 12.1. Found, *m*/*z*: 279.1129 $[M+H]^+$. $C_{17}H_{15}N_2O_2$. Calculated, *m*/*z*: 279.1133.

Preparation of compounds 8a,b (General method). A solution of compound **6c** (3 mmol) and benzaldehyde **7a**,**b** (1,5 mmol) in AcOH (10 ml) was stirred at 60°C for 4 h until the full conversion of the starting material **6c** (TLC control, petroleum ether – EtOAc, 4:1). The reaction mixture was poured into H_2O (50 ml), neutralized with $NaHCO_3$ solution, extracted with EtOAc (3×20 ml). Combined organic fractions were dried over Na_2SO_4 and evaporated to dryness. The product was isolated by column chromatography, eluent petroleum ether – EtOAc, 4:1.

1,1'-[(4-Chlorophenyl)methylene]bis[6,9-dimethoxy-3-methyl-10-(5-methylfuran-2-yl)pyrrolo[1,2-*b*]cinnoline] (8a).

Yield 1.02 g (89%), violet solid, mp 230–231°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.02 (2H, d, *J* = 8.4, H-3,5 C_6H_4Cl); 6.60–6.47 (4H, m, H-3 furan); 6.24 (2H, s, H-1 Ar); 6.12 (2H, d, *J* = 8.4, H-2,6 C_6H_4Cl); 5.98 (2H, br. s, H-2 Ar); 5.86 (2H, d, *J* = 2.1, H-4 furan); 5.79 (1H, s, CH); 4.04 (6H, s, OCH_3); 3.50 (6H, s, OCH_3); 2.70 (6H, s, CH_3); 1.98 (6H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.4 (2C); 150.3 (2C); 146.4 (2C); 145.3 (2C); 144.0 (2C); 139.4; 130.4; 130.1 (2C); 127.4 (4C); 126.3 (2C); 123.5 (2C); 122.6 (2C); 120.9 (2C); 118.6 (2C); 110.9 (2C); 106.6 (2C); 105.1 (2C); 99.4 (2C); 56.6 (2C); 56.3 (2C); 42.8; 13.2 (2C); 11.9 (2C). Found, *m*/*z*: 789.2457 $[M+Na]^+$. $C_{45}H_{39}ClN_4NaO_6$. Calculated, *m*/*z*: 789.2450.

1,1'-[(4-Nitrophenyl)methylene]bis[6,9-dimethoxy-3-methyl-10-(5-methylfuran-2-yl)pyrrolo[1,2-*b*]cinnoline] (8b). Yield 1.01 g (87%), violet solid, mp 248–250°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.91 (2H, d, *J* = 8.4, H-3,5 $C_6H_4NO_2$); 6.75 (2H, d, *J* = 7.2, H-2,6 C_6H_4NO); 6.57 (2H, d, *J* = 8.0, H-8 Ar); 6.25 (2H, s, H-2 Ar); 6.13 (2H, d, *J* = 8.0, H-7 Ar); 5.99 (2H. br. s, H-3 furan); 5.89 (3H, d, *J* = 10.6, H-4 furan, CH); 4.04 (6H, s, OCH_3); 3.50 (6H, s, OCH_3); 2.71 (6H, s, CH_3); 1.94 (6H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 153.1 (2C); 151.4 (2C); 150.1 (2C); 146.5; 145.5; 145.2 (2C); 139.5 (2C); 129.6 (2C); 129.1 (2C); 126.0 (2C); 123.7 (2C); 122.7 (2C); 122.4 (2C); 120.7 (2C); 117.1 (2C); 111.2 (2C); 106.8 (2C); 105.2 (2C); 99.6 (2C); 56.5 (2C); 56.3 (2C); 43.3; 13.2 (2C); 11.6 (2C). Found, *m*/*z*: 800.2691 $[M+Na]^+$. $C_{45}H_{39}N_5NaO_8$. Calculated, *m*/*z*: 800.2695.

Optical properties studies. The absorption spectra of the studied solutions were recorded using an SF-2000 spectrophotometer with a step of 0.1 nm in the spectral range 200–1100 nm. UNICO Q-104 quartz cuvettes, transparent in the UV spectral region were used. The graphs were built on several (1–15) series of measurements to average values. As the number of accumulations increases, the error decreases to the square root of the number of registrations, which in our case can be 4 times. The processing of the results of spectral measurements was carried out after exporting the data array to the Origin and Mathlab programs.

Cyclic voltammetry was performed with a three-electrode cell in an MeCN solution of 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) at a scan rate (*v*) of 200 mV/s. A Pt wire was used as counter electrode, glassy carbon disk was used as working electrode, and an Ag wire was used as reference electrode.

X-ray structural study of compounds 6b, 8a. X-ray analysis of a single crystal of compound **6b** ($C_{19}H_{18}N_2O_3$) was performed on an Agilent SuperNova automated four-circle diffractometer (Dual, Cu at zero, Atlas S2 CCD detector) at 301.4(6) K. The structure was solved by the direct method implemented in Olex2[36] and ShelXS[37] and was refined against F^2 by the full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms using the SHELXL program set.[38] Monoclinic crystal system, space group $P2_1/n$, *M* 322.35; unit cell parameters: *a* 9.1839(6), *b* 8.6480(4), *c* 20.5307(10) Å; β 99.246(6)°; *V* 1609.40(16) Å^3; *Z* 4; d_{calc} 1.330 g/cm^3; μ(CuKα) 0.740 mm^{-1}; *F*(000) 680.0; 8.728° ≤ 2Θ ≤ 148.342°; –11 ≤ *h* ≤ 11, –5 ≤ *k* ≤ 10, –25 ≤ *l* ≤ 19. Total of 5711 reflection intensities were measured, including 3092 independent reflections (R_{int} 0.0295, R_σ 0.0322); final probability factors: R_1 0.0476 ($I > 2\sigma(I)$) and wR_2 was 0.1412 (all data). The X-ray diffraction data for compound **6b** were deposited to the Cambridge Crystallographic Data Center (deposit CCDC 1955393).

Single crystals of compound **8a** were obtained in the form of dark-violet blocks by slow evaporation of CH_2Cl_2 from DMSO/CH_2Cl_2 solution. The single crystals of compound **8a** grown by slow evaporation of CH_2Cl_2 from DMSO/CH_2Cl_2 solution at room temperature. Crystal data for $C_{45}H_{39}ClN_4O_6$ (*M* 767.25): monoclinic, space group $P2_1/n$; *a* 16.6668(2), *b* 24.1507(2), *c* 20.8315(2) Å; β 93.2160(10)°; *V* 8371.78(15) Å^3; *Z* 8. The crystal was kept at 100.00(10) K during data collection, μ(Cu*K*α) 1.226 mm^{-1}; d_{calc} 1.217 g/cm^3; 105174 reflections measured (6.986° ≤ 2Θ ≤ 152.92°), 17466 unique (R_{int} 0.0403, R_σ 0.0264) which were used in all calculations. The final R_1 was 0.0472 ($I > 2\sigma(I)$) and wR_2 was 0.1270 (all data). The collection of reflections, determination and refinement of unit cell parameters were performed by using the specialized CrysAlisPro 1.171.38.41 software suite.[39] The structures were solved by using the ShelXT program,[37] structure refinement was also performed with ShelXL program.[38] The complete X-ray diffraction dataset was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1978825).

Supplementary information file containing ^{1}H and ^{13}C NMR spectra of the synthesized compounds and X-ray data of compounds **6b** and **8a** is available at the journal website at http://link.springer.com/journal/10593.

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