A facile, metal-free, oxidative coupling of new 6-(hetero)aryl-[1,2,5]-oxadiazolo[3,4-*b*]pyrazines with pyrroles, indoles and carbazoles

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Abstract
A facile, transition metal free, one-pot oxidative coupling reaction between 6-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines and pyrroles, indoles or carbazoles is reported. This atom-economic C-H functionalization procedure requires only stoichiometric amounts of reacting heterocycles and an appropriate Lewis acid, as catalyst. The structures of representative new 5,6-di(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines were confirmed by X-ray crystallography. The redox and optical measurements for new compounds, bearing carbazole units, have also been performed.

Keywords: Furazano[3,4-*b*]pyrazines, pyrroles, indoles, carbazoles, C-H functionalization

Introduction

The C-C cross-coupling reactions of azaaromatic compounds, in particular, of diazines, with pyrroles and indoles, are of importance for organic synthesis to prepare new derivatives of this family possessing a potential biological activity.[1,2] Also, the analogous transformations of diazines by action of carbazoles lead to C-C coupling products, demonstrating promising optical and electronic properties.[3] [1,2,5]Oxadiazolo[3,4-*b*]pyrazines (furazano[3,4-*b*]-pyrazines belong to one of the important classes of fused diazines.[4] Indeed, [1,2,5]-oxadiazolo[3,4-*b*]-pyrazines have attracted considerable attention of chemists, as heat-resistant explosive materials (for example, see Figure 1).[5]

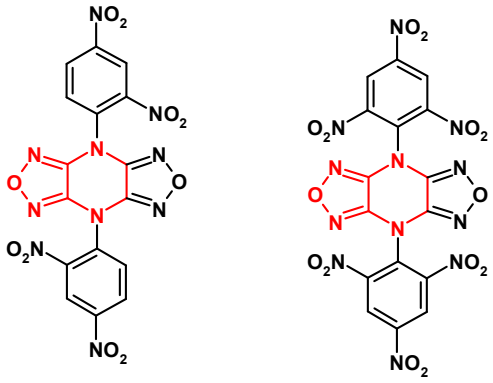
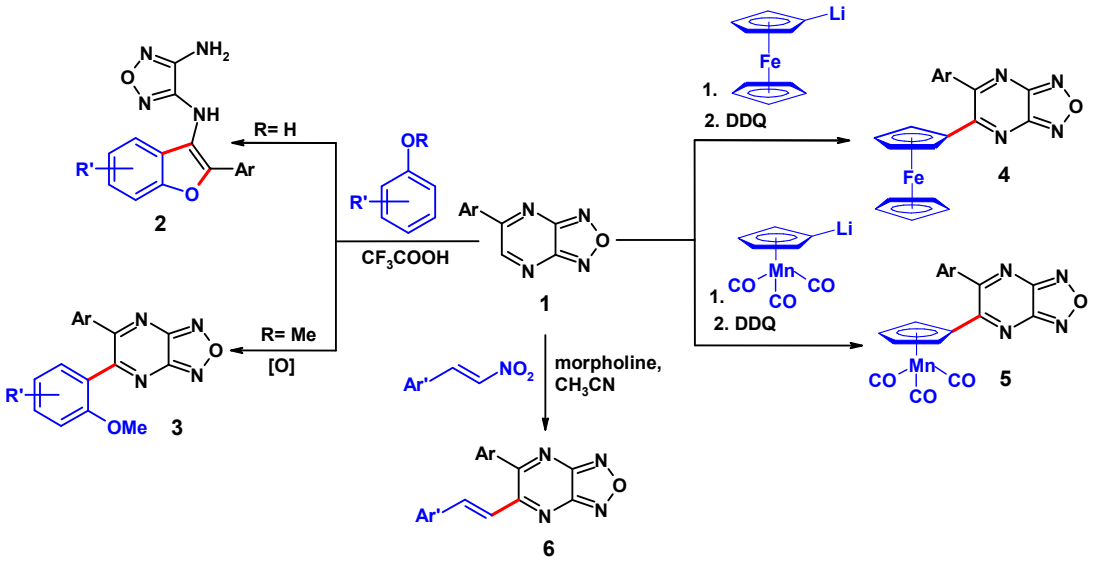


Figure 1. Furazano[3,4-*b*]pyrazines used as heat-resistant explosive materials.

[1,2,5]Oxadiazolo[3,4-*b*]pyrazines proved to exhibit a variety of physiological properties, such as anticancer,[6] anti-HIV,[7] and antibacterial activities.[8] For this reason the syntheses of 6-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine - pyrrole (indole or carbazole) hybrid molecules appear to be rather interesting for elucidation of their biological, photophysical and electrochemical properties. In spite of broad use of furazano[3,4-*b*]pyrazines, there are only few reports in the literature, concerning direct functionalization of this heterocyclic system based on nucleophilic aromatic substitution of hydrogen (S_N^H).[9] An enhanced tendency of pyrazines to undergo a nucleophilic attack at the unsubstituted carbon of the pyrazine ring has been well established.[9] For instance, the synthesis of 3-amino-2-(hetero)arylbenzo[*b*]furans **2** and 5,6-disubstituted furazano[3,4-*b*]pyrazines **3** through the reaction of electrophilic furazanopyrazines **1** with phenols or their methyl ethers in the presence of trifluoroacetic acid, followed by recyclization (in case of phenols) or oxidation, has been reported (Scheme 1).[10] Also, the addition of ferrocenyl lithium or cymantryl lithium at C(6) of furazano[3,4-*b*]pyrazines **1**, followed by oxidation of the intermediate σ^H-adducts, affords the corresponding metallocene derivatives **4** and **5** (Scheme 1).[11] Finally, 6-styryl-5-(hetero)aryl-furazano[3,4-*b*]pyrazines **6** have been obtained according to the same S_N^H-protocol, by reacting **1** with the corresponding α-nitro-β-arylalkenes.[12]



Scheme 1. The S_NH-reactions of [1,2,5]oxadiazolo[3,4-*b*]pyrazines.

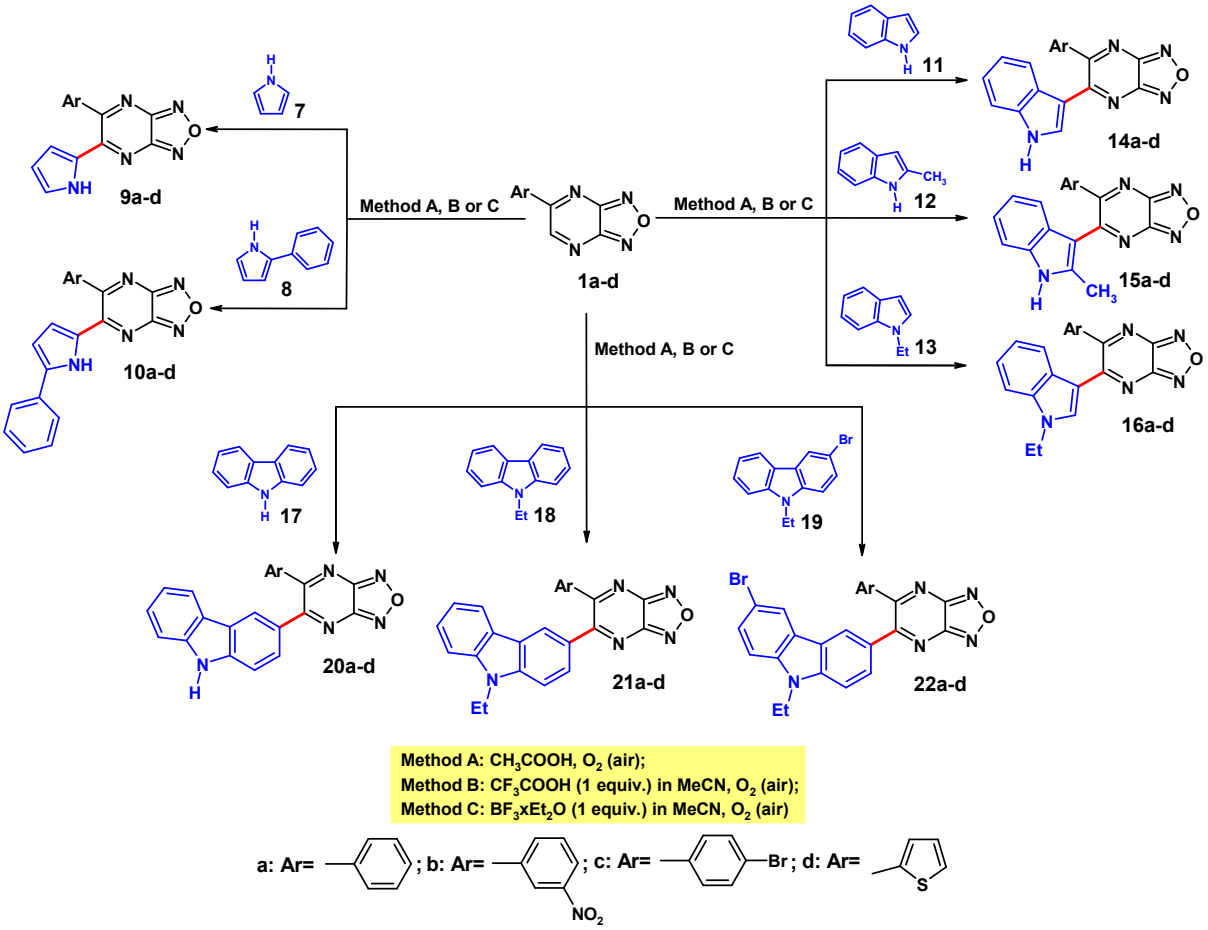
In this communication we wish to report a convenient synthesis and characterization of novel (pyrrol-2-yl)-, (indol-3-yl)- and (9*H*-carbazol-3-yl)-substituted 5-(hetero)aryl-[1,2,5]-oxadiazolo[3,4-*b*]pyrazines, by using the methodology of nucleophilic aromatic substitution of hydrogen.

Results and Discussion

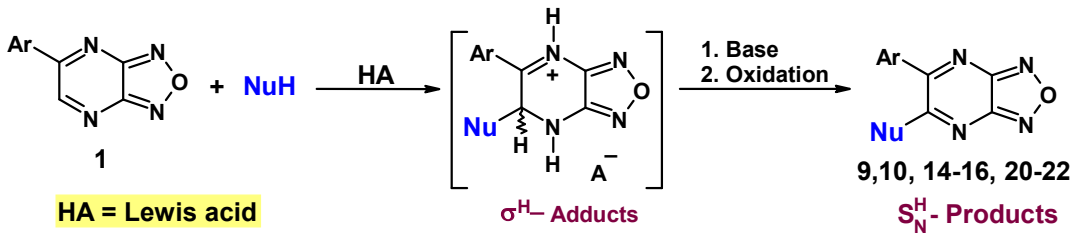
Synthesis

We have studied the direct C-H functionalization of a number of 5-(hetero)aryl substituted [1,2,5]-oxadiazolo[3,4-*b*]pyrazines **1a-d** with pyrroles **7** and **8**, indoles **11-13**, and carbazoles **17-19** (Scheme 2). The reactions proved to proceed as a classical nucleophilic aromatic substitution of hydrogen (S_NH) via the intermediacy of σ^H-adducts, 5-(hetero)aryl-6-substituted-4,5-dihydro-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-4-ium salts, and subsequent oxidation of these dihydro compounds by air oxygen (Scheme 3). While some pyrazine derivatives[10,13-17] tend to form stable crystalline adducts, no intermediate σ^H-adducts have been isolated from 5-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines. Since the S_NH-reactions usually take place in the presence of acidic catalysis, we have tried to use the Lewis acids, such as boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$), acetic and trifluoroacetic acids. To optimize the reaction conditions a number of experiments have been performed, by reacting 5-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1a)** with pyrrole **(7)**, indole **(11)**, 1-ethyl-1*H*-indole **(13)** and carbazole **(17)** in the presence of various catalysts (Table 1). It has been established that the best yeild of the S_NH-product derived from the reaction **1a** with pyrroles is reached on using CF_3COOH, whereas use of $BF_3 \cdot Et_2O$ and CH_3COOH leads to a complex multi-component mixture with a large amount of tar. For the S_NH reactions with indoles all acids proved to be suitable, however application of acetic acid gave the best results

(yields 71-83%). In contrast, 5-phenyl-[1,2,5]-oxadiazolo[3,4-*b*]pyrazine **(1a)** reacts with carbazole **(17)** only in the presence $BF_3 \cdot Et_2O$, while no S_N^H-product **20a** is observed after 48 hours on use of other acidic catalysts (on the basis of TLC data). These facts are in good agreement with the decrease in electrophilicity over the series from pyrrole to indole to carbazole with increasing benzoannulation.[18]



Scheme 2. The S_N^H reactions of 5-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines with pyrroles, indoles and carbazoles.



Scheme 3. A plausible mechanism for the S_N^H process.

Table 1. Optimization of the C-H/C-H coupling 5-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1a)** with pyrroles, indoles and carbazoles

Entry	Reaction	Conditions[a]	Time (hours)	Isolated yield (%)
1	**1a+7**	A	24	30
2		B	24	47
3		C	24	n.i.
4	**1a+11**	A	24	83
5		B	24	59
6		C	24	60
7	**1a+13**	A	24	71
8		B	24	61
9		C	24	68
10	**1a+17**	A	48	n.d.
11		B	48	n.d.
12		C	24	59

n.i.– The product was not isolated; n.d. – The product was not detected by TLC. [a]Method A: [**1**]:[**Heterocycles**]:[CH_3COOH] = 1:1:excess (in mmol); Method B: [**1**]:[**Heterocycles**]:[CF_3COOH] = 1:1:1 (in mmol); Method C: [**1**]:[**Heterocycles**]:[$BF_3 \cdot Et_2O$] = 1:1:1 (in mmol).

The optimal conditions, found for the reaction of 5-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1a)** with pyrroles, indoles and carbazoles, have been applied for the C-C coupling of 5-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines **(1b-d)** with the same nucleophiles. Highly electrophilic azines **(1a-d)** have been found to react smoothly with pyrroles **(7,8)**, indoles **(11-13)** and carbazoles **(17-19)** at room temperature to give the corresponding products **9-10**, **14-16** and **20-22** in 71% , 87% and 76% yields, respectively. It is worth noting that structures of the S_NH-products **9a**, **10d**, **14a**, **21a**, **22a** and **22c** have been established unequivocally by X-ray crystallography (Figs. 2-5, S1 and S2, Table S1, see *Supporting Information*).

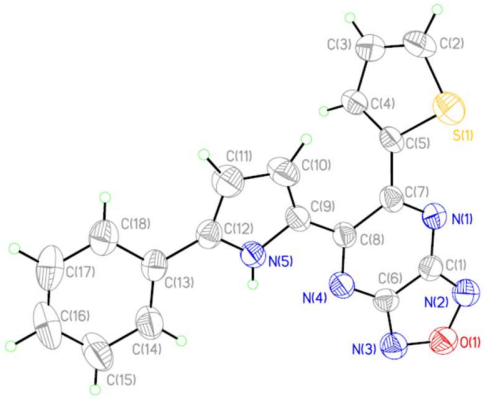


Figure 2. X-ray structure of **10d**.

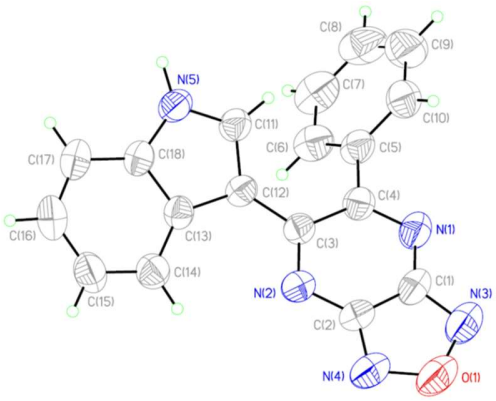


Figure 3. X-ray structure of **14a**.

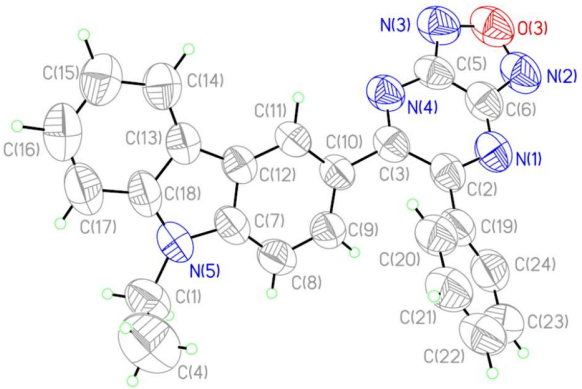


Figure 4. X-ray structure of **21a**.

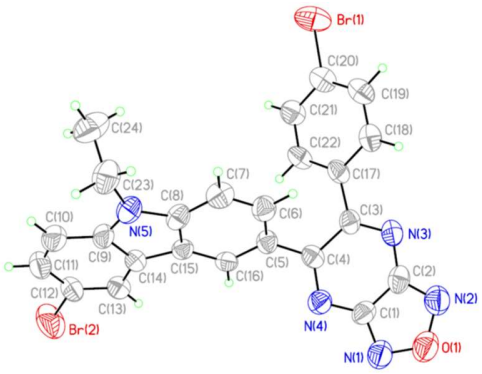


Figure 5. X-ray structure of **22c**.

Compound **21a** is non-planar; the phenyl and carbazole rings are turned towards the pyrazine unit with the angles 46º and 39º, correspondingly. As for compound **22c**, the tetrameric π-stacked "sandwiches" are observed in crystals. Compound **22c** is crystallized in the centro-symmetric space group. 4-Bromophenyl and *N*-ethylcarbazole moieties are turned toward the pyrazine ring with the angles 43º and 44º, correspondingly. The ethyl substituent in the carbazole ring is turned to the side of 4-bromophenyl substituent. In crystals, these molecules form "sandwiches" with π-π interaction between two furazanopyrazine and two carbazole rings (Fig. 6). In these tetramers the nearest C-C distances in π-stacked moieties is 3.212 Å (0.188 Å less then the sum of van der Waals radii), and some additional C-C contacts with distances less then 3.3 Å are observed. The feature of the crystal packing has to be taken into attention, when considering the spectral data of this compound.

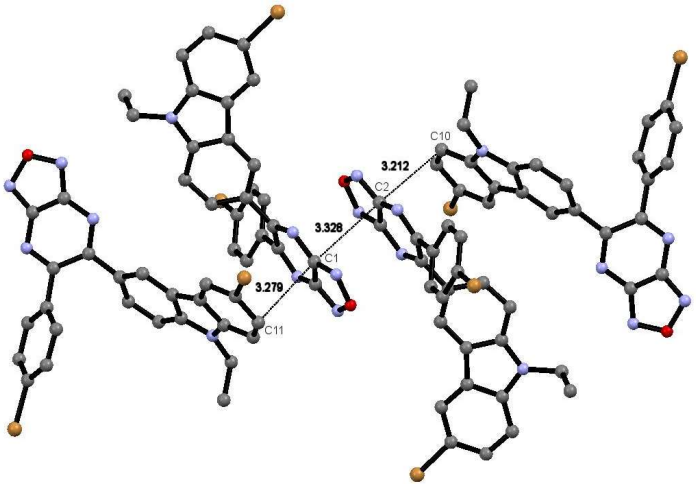


Figure 6. The tetrameric π-stacked "sandwiches" in the molecular packing for **22c**. The interfacial distances are also given. Distances are presented in Å.

Compound **21c** is a structural analogue of **22c**. However, this compound demonstrates significant conformational features. In particular, unlike the compound **22c**, the ethyl substituent in the carbazole moiety is turned from the plane of 4-bromophenyl substituent. 4-Bromophenyl and *N*-ethyl-substituted carbazole moieties are turned toward the pyrazine ring with the angles 45° and 42°, correspondingly. The significantly shortened contacts in the crystal packing of **21c** are not observed.

In the crystals of **9a** and **10d** the conformations of these molecules are ordered by intramolecular H-bonds between NH-group of the pyrrole ring and N-atom of the pyrazine ring. As a result, pyrrole and pyrazine fragments proved to form a planar system, and the second (hetero)aryl substituent in the azine ring is turned toward the plane of the pyrazine ring. In particular, in the crystals of **10d** the phenyl, pyrrole-2-yl and pyrazine moieties are placed in the plane with deviations of atoms from this plane in the limits of 0.24 Å. The thien-2-yl substituent is turned toward the pyrazine ring with the angle 56°. The crystal packing is characterized by π-π interaction between furazano and pyrrole moieties with interatomic distance of 3.35-3.17 Å.

The formation of the intramolecular H-bond in **14a** is not possible due to a strong sterical interaction between the benzene ring of indole and the aryl substituent in the pyrazine ring. As a result, only weak intermolecular H-bonds between N-atoms of the pyrazine ring and H-donating groups are observed in the crystals. The presence of many intermolecular H-bonds does not permit one to assume any efficient π-π-interactions.

Optical and electrochemical properties

Organic semiconductors based on carbazole derivatives have extensively been studied as carrier-transport or host materials for optoelectronic devices, such as photoreceptors, phosphorescent organic light-emitting diodes and organic thin-film transistors.[19-26] On the basis of these

considerations, we have decided to investigate the photophysical and electrochemical properties of carbazole-substituted furazano[3,4-*b*]pyrazines **20a-d** and **21a-d**.
UV-vis absorption spectra of **20a-d** and **21a-d** have been carried out, and the results obtained are summarized in Table 2 and Figures 7 and S4.

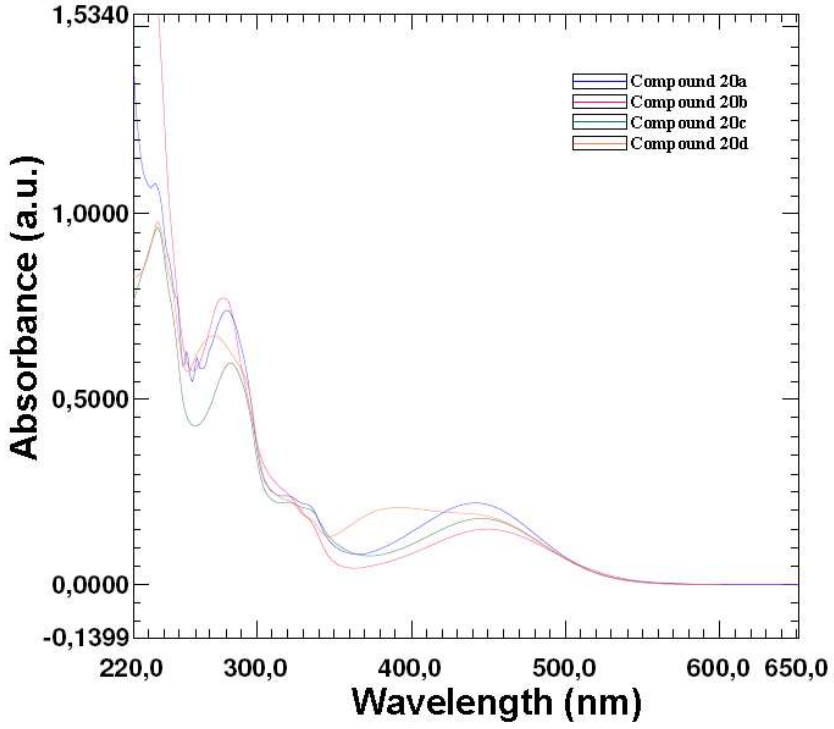


Figure 7. UV–vis absorption spectra of **20a-d**.

Carbazolyl substituted [1,2,5]oxadiazolo[3,4-*b*]pyrazines show a long-wave absorption band in the range of 440-460 nm, which is assigned to the intramolecular charge transfer (ICT) excitation from electron-donating fragment (carbazole) to electron acceptor (the pyrazine ring). In general, these maxima are shifted bathochromically in the following sequence: **20a (21a)**, **20c (21c)**, **20b (21b)**, **20d (21d)**. The bathochromic shift suggests an introduction of a bromine atom [**20c (21c)** compared with **20c** and **21c**]. The bathochromic shift implies an increased degree of conjugation, resulting from thiophene unit relative to phenyl substituents [**20d (21d)** compared with **20a-c (21a-c)**] or influence of NO_2-group [**20b (21b)** compared with **20a (21a)** and **20c (21c)**]. The bathochromic shift in the absorption maxima from non-alkylated **20a-d** to *N*-ethyl carbazole derivatives **21a-d** is attributed to the donor-acceptor character of the molecules **20** and **21** arising with addition of the ethyl-group into the carbazole moiety. Compounds **20a-d** and **21a-d** visual exhibited fluorescence in the acetonitrile solution which could not be detected and the fluorescence quantum yields of these compounds were below 1.00 % in the solution.

For this reason both absorption and fluorescence of [1,2,5]oxadiazolo[3,4-*b*]pyrazine derivatives **20a-d** and **21a-d** in poly(methyl methacrylate) (PMMA) thin film are measured. Relevant photophysical data are summarized in Table 2, and excitation and fluorescence spectra of [1,2,5]oxadiazolo[3,4-*b*]pyrazines **20a-d** and **21a-d** are shown in Figs. S4-S11. The absorption maxima of the four dyes **21a-d** in the solid state were red-shifted (Table 2) by 2-5 nm compared with those for the corresponding dyes in CH_3CN. For D-π-A fluorescent dyes, in general, the red-shifts of absorption or fluorescence maxima by changing from solution to the solid state are quite common and explained in terms of the formation of intermolecular π-π interactions[27] or continuous intermolecular hydrogen bonding[28] in the crystalline state leading to delocalization of excitons or eximers.

The most impressive solid state fluorescence for powder of dyes **20d** and **21d** under daylight and UV irradiation are shown in Figure 8.

Figure 8. Photographs of (*1*) compound **20d** and (*2*) compound **21d** under daylight (*top*) and under UV irradiation (λ_{ex} 365 nm) (*bottom*) in the solid state.

Table 2. Electrochemical and optical properties of carbazole-substituted [1,2,5]oxadiazolo[3,4-*b*]pyrazines **20a-c** and **21 a-d**

Compound	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{elc} (eV)	Absorption λ_{max} (nm)/ε (10^3 M^{-1} cm^{-1})	Solid State Absorption	Solid State Fluorescence	
								Excitation λ_{max} (nm)	Emission λ_{max} (nm)
20a	0.97	-0.79	-5.69	-3.93	1.76	441 / 22.43 333 / 22.06 320 / 24.59 280 / 75.22	442 258 229	462	562
20b	0.98	-0.72	-5.70	-4.00	1.70	450 / 19.70 280 / 85.36	447 306 253 218	460	567
20c	0.98	-0.70	-5.70	-4.02	1.68	445 / 23.14 335 / 26.40 321 / 29.18 283 / 78.18 236 / 12.81	-	461	566
20d	0.97	-0.71	-5.69	-4.01	1.68	446 / 10.13 394 / 11.23 334 / 9.66 322 / 12.04 272 / 36.41 236 / 53.08	384 220	468	572
21a	0.90	-0.67	-5.65	-4.02	1.63	456 / 9.25 342 / 9.32 329 / 10.00 282 / 32.96 237 / 41.44	459 272	477	596
21b	0.93	-0.70	-5.65	-4.02	1.63	464 / 17.19 282 / 69.47	466 224	491	600
21c	0.93	-0.81	-5.65	-3.91	1.74	458 / 9.19 334 / 11.38 330 / 12.35 284 / 32.10 237 / 49.42	449 269	477	586

Table 2(continued)

Compound	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{elc} (eV)	Absorption λ_{max} (nm)/ε (10^3 M^{-1} cm^{-1})	Solid State Absorption	Solid State Fluorescence	
21d	0.90	-0.70	-5.62	-4.02	1.60	452 / 7.82 388 / 9.17 345 / 9.61 278 / 31.17 238 / 46.21	457 386 270	486	599

In order to determine electrochemical behavior and calculate HOMO–LUMO energy gap of any organic compound, cyclic voltammetry (CV) is one of the useful methods. In the cathodic scan regime of the cyclic voltammogram of compound **20** and **21**, it exhibits one characteristic irreversible reduction peak with a onset wave potential (E_{red}^{onset}) in a range from −0.70 to −0.80 V, which probably is attributed to furazano moiety reduction (Fig. S12-S19). Similarly, two consistent oxidation peaks with onset wave potential in a range from 0.90 to 0.98 V were observed for radical anion formation (Fig. S3-S10) emanating from carbazole moiety. The electrochemical HOMO–LUMO band gap of all molecules were calculated from the onset potentials of their oxidation and reduction peaks and these values are presented in Table 2.

This finding suggests that the further tuning of these compounds could lead to very narrow band gap and may be a useful strategy for the design of electron-donating (*p*-type) semiconductors and chromophores.

Conclusions

The S_N^H methodology has proven to be an effective approach to modify 6-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines, derivatives of a highly reactive electron-deficient heterocyclic system, through nucleophilic displacement of hydrogen by aromatic C-nucleophiles, such as pyrroles, indoles or carbazoles, proceeding via the intermediacy of the C^5-adducts. The X-ray crystallography data for a number of new 5,6-di(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines have been presented.

On a base of the redox and optical studies for derivatives bearing carbazole units it is legitimate to say that these compounds can be potentially used for organic electronic applications, but additional modifications are required in order to do so. It should be noted that the *N*-ethyl derivatives **21** and **22** are more realistic prospects for organic electronic applications than the other products with free N-H moieties which are redox liabilities.

Experimental Section

General. All reagents and solvents were obtained from commercial sources and dried by using standard procedures before use. 5-Phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1a)** and 5-(4-bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1c)** were prepared according to the earlier reported method.[10,29] ^{1}H and ^{13}C NMR spectra were recorded on a AVANCE-500 instruments using Me_4Si as an internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. Melting points were determined on Boetius combined heating stages and were not corrected. Flash-column chromatography was carried out using Alfa Aesar silica gel 0.040-0.063 mm (230–400 mesh), eluting with ethyl acetate-hexane. The progress of reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia), in which the spots were visualized with UV light (λ 254 or 365 nm).

Single crystals were investigated on a Xcalibur E diffractometer on standard procedure (graphite-monochromated MoK-irradiation, ω-scans with 1° step). Empirical absorption correction vas applied. Using SHELXTL, the structures were solved with the ShelXS structure solution program by direct methods and refined with the ShelXL refinement package using Least Squares minimization in anisotropic approximation for non-hydrogen atoms. The mean crystallographic data and results of the refinements are presented in the Table S1. The X-ray crystallography data for structures reported in this paper have been deposited with Cambridge Crystallography Data Centre as supplementary publications CCDC 1498293 for **9a**, CCDC 1498294 for **10d**, CCDC 1498295 for **14a**, CCDC 1498296 for **21a**, CCDC 1498297 for **21c** and CCDC 1498298 for **22c**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cyclic voltammetry was carried out on a Metrohm μAutolab type III potentiostat with a standard three-electrode configuration. Typically, a three electrodes cell equipped with a platinum working electrode, a $Ag/AgNO_3$ (0.01 M $AgNO_3$ in acetonitrile) reference electrode and a glassy carbon rod counter electrode were employed. The measurements were performed in anhydrous CH_3CN solution containing the present compound (5×10^{-3} M) and $LiClO_4$ (0.1 M) as the supporting electrolyte at a scan rate of 100 mV/s. The potential of reference electrode was calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+), which has a known oxidation potential of +4.8 eV. The electrochemical energy gap was determined as the difference between the onsets of the oxidation and the reduction potentials ($E_g^{elc} = E_{ox}^{onset} - E_{red}^{onset}$). The HOMO and LUMO energy values were estimated from the onset potentials of the first independent oxidation and reduction process, respectively. After calibration of the measurements against Fc/Fc^+, the HOMO and LUMO energy levels were calculated according to the following equations:

E_{HOMO} (eV) = – [$E_{ox}^{onset} - E_{1/2}(Fc/Fc^+) + 4.8$]

E_{LUMO} (eV) = – [$E_{red}^{onset} - E_{1/2}(Fc/Fc^+) + 4.8$]

where $E_{1/2}(Fc/Fc^+)$ is the half-wave potential of the Fc/Fc^+ couple (the oxidation potential of which is assumed at 4.8 eV) against the Ag/Ag+ electrode.

UV–vis spectra were recorded for a 1×10^{-5} M acetonitrile solution with Shimadzu UV-2401PC spectrophotometer. Fluorescence spectra measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

Preparation of polymeric-fluorescent dye thin film. PMMA thin films were prepared as follows: **20a-d** and **21a-d** (0.20 mg) was dissolved in 200 μL of a PMMA–$CHCl_3$ solution (10%, w/w). A film was obtained by spin coating a 0.2 mL PMMA–$CHCl_3$ solution on quartz glass (size: 2.5 cm × 1.2 cm), and dried in air at room temperature. The concentration of **20a-d** and **21a-d** in PMMA thin film is ca 0.1%, 0.2% and 0.4% (w/w).

General procedure for the synthesis of 5-(3-nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (1b) and (5-thien-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (1d). The solution of 3,4-diaminofurazan (1 g, 10 mmol) and 3-nitrophenylglyoxal [or 2-thienylglyoxal] (10 mmol) in a mixture of EtOH (5 mL) and CH_3COOH (5 mL) was refluxed for 1 h. After that, the mixture was cooled, and the precipitate was filtered and washed with ethanol and then air dried. The desired products **1b** (or **1d**) were obtained as crystalline powders.

5-(3-Nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (1b). Yield 1.65 g, 68%, yellow powder, mp 161-163 °C. δ_H (500 MHz, DMSO-d_6) 9.91 (s, 1H), 9.11 (t, *J* 1.9 Hz, 1H), 8.87-8.78 (m, 1H), 8.53 (ddd, *J* 8.2, 2.2, 0.8 Hz, 1H), 7.97 (t, *J* 8.0 Hz, 1H); δ_C (126 MHz, DMSO-d_6) 158.1, 155.7, 152.1, 151.7, 148.4, 135.8, 135.1, 131.0, 127.0, 123.4. Calcd. for $C_{10}H_5N_5O_3$ (243.18): C 49.03, H 2.07, N 28.80. Found: C 49.08, H 2.10, N 28.94.

(5-Thien-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (1d). Yield 1.43 g, 70%, yellow powder, mp 188 °C. δ_H (500 MHz, DMSO-d_6) 9.77 (s, 1H), 8.55 (d, *J* 3.7 Hz, 1H), 8.15 (d, *J* 4.9 Hz, 1H), 7.47-7.31 (m, 1H); δ_C (126 MHz, DMSO-d_6) 155.1, 154.5, 152.1, 151.5, 140.6, 136.4, 134.7, 129.8. Calcd. for $C_8H_4N_4OS$ (204.21): C 47.05, H 1.97, N 27.44. Found: C 47.15, H 2.03, N 27.64.

General procedure for the synthesis of 5-(hetero)aryl-6-(5-R-1*H*-pyrrol-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine derivatives (9a-d and 10a-d). To a stirred mixture of 5-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1a, 1b, 1c** or **1d)** (0.5 mmol) and pyrrole **(7)** (35 μL, 0.5 mmol) [or 2-phenyl-1*H*-pyrrole **(8)** (72 mg, 0.5 mmol)] in MeCN (4 mL) was added CF_3COOH (38 μL, 0.5 mmol). The reaction mixture was stirred at room temperature for 24 h. The solvent was distilled off *in vacuo*, and the residual semisolid was washed with aqueous Na_2CO_3 and air dried. Purification by flash column chromatography (hexane/ethyl acetate, 1:5) to afford the desired S_N^H-products **(9a-d** or **10a-d)**.

5-Phenyl-6-(1*H*-pyrrol-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (9a). Yield 62 mg, 47%, bright orange powder, mp 194-196 °C. δ_H (500 MHz, DMSO-d_6) 12.38 (s, 1H), 7.67-7.63 (m, 3H), 7.59-7.55 (m, 2H), 7.20 (t, *J* 3.1 Hz, 1H), 6.05 (dt, *J* 4.3, 2.3 Hz, 1H), 5.50-5.38 (m, 1H); δ_C (126 MHz, DMSO-d_6) 164.0, 151.8, 151.7, 150.7, 138.4, 130.3, 129.0, 128.6, 128.2, 128.1, 120.0, 111.3. Calcd. for $C_{14}H_9N_5O$ (263.26): C 63.87, H 3.45, N 26.60. Found: C 63.62, H 3.31, N 26.69.

5-(3-Nitrophenyl)-6-(1*H*-pyrrol-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (9b). Yield 72 mg, 47%, bright orange powder, mp 216 °C. δ_H (500 MHz, DMSO-d_6) 12.43 (s, 1H), 8.57-8.55 (m,

1H), 8.48 (ddd, *J* 8.3, 2.3, 0.9 Hz, 1H), 8.14-8.09 (m, 1H), 7.87 (t, *J* 8.0 Hz, 1H), 7.24-7.18 (m, 1H), 6.05 (dt, *J* 4.3, 2.3 Hz, 1H), 5.45 (ddd, *J* 3.9, 2.5, 1.2 Hz, 1H); δ_C (126 MHz, DMSO-*d*$_6$) 162.1, 151.8, 151.6, 150.7, 147.4, 139.8, 135.3, 130.1, 128.7, 128.2, 125.1, 123.8, 120.0, 111.6. Calcd. for $C_{14}H_8N_6O_3$ (308.26): C 54.55, H 2.62, N 27.26. Found: C 54.30, H 2.50, N 27.25.

5-(4-Bromophenyl)-6-(1*H*-pyrrol-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (9c). Yield 74 mg, 43%, orange powder, mp 217 °C. δ_H (500 MHz, DMSO-*d*$_6$) 12.40 (s, 1H), 7.79 (dd, *J* 8.7, 2.0 Hz, 2H), 7.63 (dd, *J* 8.7, 2.1 Hz, 2H), 7.22 (d, *J* 3.0 Hz, 1H), 6.11 (dt, *J* 4.3, 2.3 Hz, 1H), 5.55-5.52 (m, 1H). δ_C (126 MHz, DMSO-*d*$_6$) 163.1, 151.7, 151.7, 150.7, 137.6, 131.3, 130.9, 128.8, 128.2, 124.0, 120.0, 111.4. Calcd. for $C_{14}H_8BrN_5O$ (342.16): C 49.15, H 2.36, N 20.47. Found: C 49.33, H 2.11, N 20.49.

5-(1*H*-Pyrrol-2-yl)-(6-thien-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (9d). Yield 61 mg, 45%, russet powder, mp 163 °C. δ_H (500 MHz, DMSO-*d*$_6$) 12.36 (s, 1H), 7.99 (d, *J* 4.5 Hz, 1H), 7.63 (d, *J* 2.4 Hz, 1H), 7.24 (s, 1H), 7.22-7.15 (m, 1H), 6.26 (s, 1H), 6.16 (s, 1H); δ_C (126 MHz, DMSO-*d*$_6$) 157.1, 152.0, 151.4, 150.7, 139.8, 133.0, 132.5, 128.8, 127.9, 127.6, 119.7, 110.9. Calcd. for $C_{12}H_7N_5OS$ (269.29): C 53.52, H 2.62, N 26.01. Found: C 53.39, H 2.74, N 25.88.

5-Phenyl-6-(5-phenyl-1*H*-pyrrol-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (10a). Yield 92 mg, 54%, orange powder, mp 225 °C. δ_H (500 MHz, DMSO-*d*$_6$) 12.47 (s, 1H), 7.96 (d, *J* 7.4 Hz, 2H), 7.71-7.63 (m, 3H), 7.58 (t, *J* 7.4 Hz, 2H), 7.42 (t, *J* 7.5 Hz, 2H), 7.34 (t, *J* 7.3 Hz, 1H), 6.58 (d, *J* 2.4 Hz, 1H), 5.56 (d, *J* 3.0 Hz, 1H); δ_C (126 MHz, DMSO-*d*$_6$) 164.1, 151.7, 151.3, 150.7, 140.7, 138.5, 130.8, 130.44, 130.37, 128.8, 128.7, 128.3, 126.0, 121.8, 110.1. Calcd. for $C_{20}H_{13}N_5O$ (339.36): C 70.79, H 3.86, N 20.64. Found: C 70.34, H 3.77, N 20.39.

5-(3-Nitrophenyl)-6-(5-phenyl-1*H*-pyrrol-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (10b). Yield 136 mg, 71%, red powder, mp 236 °C. δ_H (500 MHz, DMSO-*d*$_6$) 12.55 (s, 1H), 8.61 (d, *J* 1.5 Hz, 1H), 8.51 (dd, *J* 8.3, 1.3 Hz, 1H), 8.16 (d, *J* 7.7 Hz, 1H), 7.97 (d, *J* 7.7 Hz, 2H), 7.89 (t, *J* 8.0 Hz, 1H), 7.43 (t, *J* 7.5 Hz, 2H), 7.34 (t, *J* 7.3 Hz, 1H), 6.60 (dd, *J* 4.1, 2.5 Hz, 1H), 5.60 (dd, *J* 4.0, 2.3 Hz, 1H); δ_C (126 MHz, DMSO-*d*$_6$) 162.3, 151.8, 151.0, 150.7, 147.5, 140.9, 139.9, 135.4, 130.4, 130.3, 130.1, 128.7, 128.3, 126.0, 125.2, 123.9, 121.9, 110.3. Calcd. for $C_{20}H_{12}N_6O_3$ (384.36): C 62.50, H 3.15, N 21.87. Found: C 62.71, H 3.03, N 21.63.

5-(4-Bromophenyl)-6-(5-phenyl-1*H*-pyrrol-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (10c). Yield 132 mg, 63%, red powder, mp 257 °C. δ_H (500 MHz, DMSO-*d*$_6$) 12.50 (s, 1H), 7.96 (d, *J* 7.5 Hz, 2H), 7.80 (d, *J* 8.4 Hz, 2H), 7.67 (d, *J* 8.4 Hz, 2H), 7.43 (t, *J* 7.5 Hz, 2H), 7.34 (t, *J* 7.3 Hz, 1H), 6.64 (dd, *J* 4.0, 1.9 Hz, 1H), 5.66 (dd, *J* 4.0, 1.6 Hz, 1H). δ_C (126 MHz, DMSO-*d*$_6$) 163.2, 151.7, 151.1, 150.7, 140.8, 137.7, 131.4, 131.0, 130.6, 130.4, 128.7, 128.3, 126.0, 124.1, 121.8, 110.2. Calcd. for $C_{20}H_{12}BrN_5O$ (418.26): C 57.43, H 2.89, N 16.74. Found: C 57.23, H 3.04, N 16.48.

5-(5-Phenyl-1*H*-pyrrol-2-yl)-(6-thien-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (10d). Yield 116 mg, 67%, dark red powder, mp 244 °C. δ_H (500 MHz, DMSO-*d*$_6$) 12.54 (s, 1H), 8.03 (dd, *J* 5.0, 1.1 Hz, 1H), 8.01-7.94 (m, 2H), 7.70 (dd, *J* 3.8, 1.1 Hz, 1H), 7.45 (dd, *J* 10.6, 4.8 Hz, 2H), 7.34 (dd, *J* 11.5, 4.1 Hz, 1H), 7.21 (dd, *J* 5.0, 3.8 Hz, 1H), 6.72 (dd, *J* 4.1, 2.5 Hz, 1H), 6.42 (dd, *J* 4.1, 2.2 Hz, 1H); δ_C (126 MHz, DMSO-*d*$_6$) 157.2, 151.4, 151.4, 150.8, 140.5, 140.1, 133.26, 132.9,

130.5, 130.5, 128.8, 128.2, 127.7, 125.8, 121.5, 109.6. Calcd. for $C_{18}H_{11}N_5OS$ (345.39): C 62.60, H 3.21, N 20.28. Found: C 62.42, H 3.30, N 20.14.

General procedure for the synthesis of 6-(hetero)aryl-5-(1*H*-indol-3-yl)-[1,2,5]oxadiazolo-[3,4-*b*]pyrazine (14a-d), 6-(hetero)aryl-5-(2-methyl-1*H*-indol-3-yl)-[1,2,5]oxadiazolo[3,4-*b*]-pyrazine (15a-d) and 6-(hetero)aryl-5-(1-ethyl-1*H*-indol-3-yl)-[1,2,5]oxadiazolo[3,4-*b*]-pyrazine (16a-d) derivatives. To a stirred solution of 5-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1a, 1b, 1c** or **1d)** (0.5 mmol) in CH_3COOH (5 mL) was added indole **(11)** (59 mg, 0.5 mmol) [2-methyl-1*H*-indole **(12)** (66 mg, 0.5 mmol) or 1-ethyl-1*H*-indole **(13)** (73 mg, 0.5 mmol)]. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed *in vacuo*, and the residual semisolid was washed with aqueous Na_2CO_3 and air dried. The residue was recrystallized from isopropyl alcohol or methanol to afford the desired S_N^H-products **(14a-d**, **15a-d** or **16a-d)**.

5-(1*H*-Indol-3-yl)-6-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (14a). Yield 130 mg, 83%, dark red powder, mp 128-130 °C. δ_H (500 MHz, DMSO-d_6) 11.91 (s, 1H), 8.61-8.57 (m, 1H), 7.71-7.62 (m, 3H), 7.56 (t, *J* 7.5 Hz, 2H), 7.46 (dd, *J* 5.8, 3.0 Hz, 1H), 7.34-7.23 (m, 2H), 6.59 (d, *J* 3.2 Hz, 1H); δ_C (126 MHz, DMSO-d_6) 164.7, 157.9, 151.9, 150.3, 138.9, 136.3, 134.2, 130.5, 129.0, 128.4, 126.2, 123.7, 122.7, 122.2, 113.5, 112.4. Calcd. for $C_{18}H_{11}N_5O$ (313.32): C 69.00, H 3.54, N 22.35. Found: C 69.22, H 3.63, N 22.51.

5-(1*H*-Indol-3-yl)-6-(3-nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (14b). Yield 142 mg, 79%, orange powder, mp 279 °C. δ_H (500 MHz, DMSO-d_6) 11.85 (s, 1H), 8.60-8.58 (m, 1H), 8.57-8.54 (m, 1H), 8.48 (ddd, *J* 8.3, 2.3, 0.9 Hz, 1H), 8.14-8.04 (m, 1H), 7.82 (t, *J* 8.0 Hz, 1H), 7.54-7.42 (m, 1H), 7.39-7.24 (m, 2H), 6.81 (d, *J* 2.7 Hz, 1H); δ_C (126 MHz, DMSO-d_6) 162.9, 157.6, 152.0, 150.3, 147.7, 140.2, 136.4, 135.7, 134.6, 130.0, 126.1, 125.2, 124.2, 123.8, 122.5, 122.2, 113.2, 112.5. Calcd. for $C_{18}H_{10}N_6O_3$ (358.32): C 60.34, H 2.81, N 23.45. Found: C 60.17, H 2.92, N 23.17.

5-(4-Bromophenyl)-6-(1*H*-indol-3-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (14c). Yield 171 mg, 87%, red powder, mp 309-310 °C. δ_H (500 MHz, DMSO-d_6) 11.91 (s, 1H), 8.60-8.51 (m, 1H), 7.77 (d, *J* 8.4 Hz, 2H), 7.63 (d, *J* 8.4 Hz, 2H), 7.52-7.44 (m, 1H), 7.33- 7.24 (m, 2H), 6.76 (s, 1H); δ_C (126 MHz, DMSO-d_6) 163.8, 157.7, 151.9, 150.3, 138.0, 136.3, 134.3, 131.5, 131.3, 126.1, 124.2, 123.7, 122.5, 122.1, 113.3, 112.5. Calcd. for $C_{18}H_{10}BrN_5O$ (392.22): C 55.12, H 2.57, N 17.86. Found: C 54.91, H 2.54, N 17.77.

5-(1*H*-Indol-3-yl)-(6-thien-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (14d). Yield 125 mg, 78%, dark red powder, mp 258 °C. δ_H (500 MHz, DMSO-d_6) 12.02 (s, 1H), 8.24 (d, *J* 7.6 Hz, 1H), 7.98 (dd, *J* 5.0, 0.7 Hz, 1H), 7.57 (d, *J* 3.1 Hz, 1H), 7.55-7.47 (m, 2H), 7.32-7.17 (m, 2H), 7.11 (dd, *J* 4.8, 4.0 Hz, 1H); δ_C (126 MHz, DMSO-d_6) 157.82, 157.77, 151.6, 150.6, 141.0, 136.5, 133.7, 133.4, 133.3, 127.9, 126.0, 123.4, 121.9, 121.8, 113.5, 112.5. Calcd. for $C_{16}H_9N_5OS$ (319.35): C 60.18, H 2.84, N 21.93. Found: C 59.99, H 2.76, N 21.74.

5-(2-Methyl-1*H*-indol-3-yl)-6-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (15a). Yield 113 mg, 69%, dark red powder, mp 237 °C. δ_H (500 MHz, DMSO-d_6) 11.69 (s, 1H), 7.65-7.53 (m, 2H), 7.42 (dd, *J* 13.7, 7.6 Hz, 2H), 7.35-7.27 (m, 3H), 7.11-7.00 (m, 1H), 6.96-6.86 (m, 1H), 2.08 (s,

3H); δ_C (126 MHz, DMSO-*d*$_6$) 164.1, 159.6, 151.7, 151.2, 140.2, 138.1, 135.2, 130.5, 129.5, 127.9, 126.9, 121.6, 120.2, 119.5, 111.6, 111.0, 12.9. Calcd. for $C_{19}H_{13}N_5O$ (327.35): C 69.72, H 4.00, N 21.39. Found: C 69.67, H 3.93, N 21.51.

5-(2-Methyl-1*H*-indol-3-yl)-6-(3-nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (15b). Yield 102 mg, 55%, dark red powder, mp 251 °C. δ_H (500 MHz, DMSO-*d*$_6$) 11.79 (s, 1H), 8.38 (t, *J* 1.8 Hz, 1H), 8.21 (dd, *J* 8.1, 2.1 Hz, 1H), 7.94 (d, *J* 7.8 Hz, 1H), 7.55 (t, *J* 8.0 Hz, 1H), 7.28 (d, *J* 8.1 Hz, 1H), 7.17 (d, *J* 8.0 Hz, 1H), 6.99 (t, *J* 7.5 Hz, 1H), 6.80 (t, *J* 7.5 Hz, 1H), 2.28 (s, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 162.4, 159.3, 151.9, 151.2, 147.0, 140.7, 139.4, 135.7, 135.2, 129.5, 126.3, 124.9, 124.3, 121.7, 120.2, 119.3, 111.1, 110.9, 12.9. Calcd. for $C_{19}H_{12}N_6O_3$ (372.35): C 61.29, H 3.25, N 22.57. Found: C 61.24, H 3.24, N 22.61.

5-(4-Bromophenyl)-6-(2-methyl-1*H*-indol-3-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (15c). Yield 140 mg, 69%, dark red powder, mp 142 °C. δ_H (500 MHz, DMSO-*d*$_6$) 11.74 (s, 1H), 7.61-7.45 (m, 4H), 7.33 (t, *J* 7.6 Hz, 2H), 7.06 (t, *J* 7.6 Hz, 1H), 6.91 (t, *J* 7.9 Hz, 1H), 2.17 (s, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 163.3, 159.4, 151.8, 151.2, 140.3, 137.3, 135.2, 131.4, 131.0, 126.7, 124.4, 121.7, 120.2, 119.4, 111.4, 111.1, 13.0. Calcd. for $C_{19}H_{12}BrN_5O$ (406.24): C 56.18, H 2.98, N 17.24. Found: C 56.12, H 2.97, N 17.19.

5-(2-Methyl-1*H*-indol-3-yl)-(6-thien-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (15d). Yield 70 mg, 42%, dark red powder, mp 251 °C. δ_H (500 MHz, DMSO-*d*$_6$) 11.83 (s, 1H), 7.88 (d, *J* 4.8 Hz, 1H), 7.36 (dd, *J* 16.1, 8.1 Hz, 2H), 7.18 (d, *J* 3.6 Hz, 1H), 7.09 (t, *J* 7.5 Hz, 1H), 6.95 (dd, *J* 8.6, 6.1 Hz, 2H), 2.29 (s, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 158.9, 156.9, 151.5, 151.1, 141.1, 140.0, 135.2, 134.3, 133.3, 128.4, 127.1, 121.7, 120.3, 119.3, 111.3, 111.2, 12.8. Calcd. for $C_{17}H_{11}N_5OS$ (333.37): C 61.25, H 3.33, N 21.01. Found: C 61.18, H 3.29, N 21.09.

5-(1-Ethyl-1*H*-indol-3-yl)-6-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (16a). Yield 116 mg, 68%, orange powder, mp 216 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.59 (dt, *J* 7.2, 3.2 Hz, 1H), 7.71-7.64 (m, 3H), 7.63-7.55 (m, 3H), 7.39-7.29 (m, 2H), 6.60 (s, 1H), 4.04 (q, *J* 7.2 Hz, 2H), 1.13 (t, *J* 7.2 Hz, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 164.8, 157.6, 151.9, 150.4, 138.8, 136.1, 135.9, 130.5, 129.1, 128.4, 126.7, 123.7, 122.8, 122.5, 112.6, 110.9, 40.9, 14.7. Calcd. for $C_{20}H_{15}N_5O$ (341.38): C 70.37, H 4.43, N 20.52. Found: C 70.12, H 4.37, N 20.48.

5-(1-Ethyl-1*H*-indol-3-yl)-6-(3-nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (16b). Yield 99 mg, 51%, orange powder, mp 245 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.64-8.53 (m, 2H), 8.53-8.44 (m, 1H), 8.07 (dd, *J* 8.9, 1.1 Hz, 1H), 7.81 (t, *J* 8.0 Hz, 1H), 7.67-7.53 (m, 1H), 7.40-7.25 (m, 2H), 6.85 (s, 1H), 4.09 (q, *J* 7.1 Hz, 2H), 1.12 (t, *J* 7.2 Hz, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 162.9, 157.3, 152.0, 150.4, 147.7, 139.9, 136.3, 136.0, 135.8, 129.9, 126.7, 125.3, 124.3, 123.8, 122.7, 122.5, 112.3, 110.9, 40.9, 15.1. Calcd. for $C_{20}H_{14}N_6O_3$ (386.37): C 62.17, H 3.65, N 21.75. Found: C 62.24, H 3.77, N 21.65.

5-(4-Bromophenyl)-6-(1-ethyl-1*H*-indol-3-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (16c). Yield 92 mg, 44%, orange powder, mp 238 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.55-8.51 (m, 1H), 7.77 (d, *J* 8.4 Hz, 2H), 7.66-7.59 (m, 3H), 7.37-7.31 (m, 2H), 6.79 (s, 1H), 4.11 (q, *J* 7.2 Hz, 2H), 1.18 (t, *J* 7.2 Hz, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 163.9, 157.4, 151.9, 150.4, 137.8, 136.1, 135.9, 131.4,

131.4, 126.6, 124.3, 123.7, 122.6, 122.5, 112.5, 110.9, 40.9, 14.8. Calcd. for $C_{20}H_{14}BrN_5O$ (420.27): C 57.16, H 3.36, N 16.66. Found: C 57.14, H 3.34, N 16.84.

5-(1-Ethyl-1*H*-indol-3-yl)-(6-thien-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (16d). Yield 125 mg, 72%, orange, mp 237 °C. δ_H (500 MHz, DMSO-d_6) 8.23 (d, *J* 7.8 Hz, 1H), 8.01 (d, *J* 4.8 Hz, 1H), 7.68 (s, 1H), 7.65 (d, *J* 8.1 Hz, 1H), 7.53 (d, *J* 3.4 Hz, 1H), 7.33 (t, *J* 7.5 Hz, 1H), 7.28 (t, *J* 7.4 Hz, 1H), 7.13 (t, *J* 4.3 Hz, 1H), 4.23 (q, *J* 7.2 Hz, 2H), 1.31 (t, *J* 7.2 Hz, 3H); δ_C (126 MHz, DMSO-d_6) 157.7, 157.4, 151.5, 150.6, 140.9, 136.1, 135.7, 133.6, 133.5, 127.9, 126.5, 123.4, 122.1, 112.6, 111.0, 110.9, 41.0, 15.2. Calcd. for $C_{18}H_{13}N_5OS$ (347.40): C 62.23, H 3.77, N 20.16. Found: C 62.14, H 3.81, N 20.19.

General procedure for the synthesis of 3-[6-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9*H*-carbazole (20a-d), **9-ethyl-3-[6-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9*H*-carbazole (21a-d) and 3-bromo-9-ethyl-3-[6-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9*H*-carbazole (22a-d) derivatives.** To a stirred mixture of 5-(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazine **(1a, 1b, 1c** or **1d)** (0.5 mmol) and carbazole **(17)** (0.5 mmol) [9-ethyl-9*H*-carbazole **(18)** or 3-bromo-9-ethyl-9*H*-carbazole **(18)**] in MeCN (4 mL) was added $BF_3{\cdot}Et_2O$ (62 μL, 0.5 mmol). The solvent was removed *in vacuo*, and the residual semisolid was washed with aqueous Na_2CO_3 and air dried. The residue was recrystallized from isopropyl alcohol to afford the desired S_N^H-products **(20a-d**, **21a-d** or **22a-d)**.

3-(6-Phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl)-9*H*-carbazole (20a). Yield 107 mg, 59%, red powder, mp 296 °C. δ_H (500 MHz, DMSO-d_6) 11.63 (s, 1H), 8.34 (s, 1H), 8.00 (d, *J* 7.7 Hz, 1H), 7.54-7.35 (m, 9H), 7.20 (t, *J* 7.5 Hz, 1H); δ_C (126 MHz, DMSO-d_6) 163.2, 162.8, 150.6, 150.2, 139.9, 139.1, 137.1, 129.3, 128.6, 127.0, 126.9, 126.4, 125.2, 122.0, 121.2, 120.9, 119.0, 118.4, 110.3, 109.1. Calcd. for $C_{22}H_{13}N_5O$ (363.38): C 72.72, H 3.61, N 19.27. Found: C 72.58, H 3.57, N 19.35.

3-[6-(3-Nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9*H*-carbazole (20b). Yield 116 mg, 57%, red powder, mp 285 °C. δ_H (500 MHz, DMSO-d_6) 11.62 (s, 1H), 8.40 (d, *J* 9.9 Hz, 2H), 8.31 (dd, *J* 8.2, 1.4 Hz, 1H), 8.06 (d, *J* 7.8 Hz, 1H), 7.83 (d, *J* 7.9 Hz, 1H), 7.62 (t, *J* 8.0 Hz, 1H), 7.51 (d, *J* 8.1 Hz, 1H), 7.45-7.37 (m, 3H), 7.18 (t, *J* 7.4 Hz, 1H); δ_C (126 MHz, DMSO-d_6) 162.6, 161.5, 150.7, 150.2, 146.1, 140.0, 139.1, 138.5, 135.0, 128.5, 127.1, 125.7, 125.3, 123.8, 123.5, 122.3, 121.12, 121.07, 119.2, 118.4, 110.3, 109.3. Calcd. for $C_{22}H_{12}N_6O_3$ (408.38): C 64.71, H 2.96, N 20.58. Found: C 64.74, H 2.94, N 20.60.

3-[6-(4-Bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9*H*-carbazole (20c). Yield 168 mg, 76%, orange powder, mp 302 °C. δ_H (500 MHz, DMSO-d_6) 11.65 (s, 1H), 8.40 (s, 1H), 8.07 (d, *J* 7.8 Hz, 1H), 7.61 (d, *J* 8.5 Hz, 2H), 7.54 (d, *J* 8.1 Hz, 1H), 7.48-7.41 (m, 4H), 7.38 (dd, *J* 8.5, 1.7 Hz, 1H), 7.22 (t, *J* 7.3 Hz, 1H); δ_C (126 MHz, DMSO-d_6) 163.8, 163.4, 151.7, 151.3, 141.1, 140.3, 137.3, 131.8, 131.1, 128.1, 127.3, 126.3, 124.3, 123.1, 122.3, 122.2, 120.2, 119.5, 111.5, 110.3. Calcd. for $C_{22}H_{12}BrN_5O$ (442.28): C 59.75, H 2.73, N 15.83. Found: C 59.65, H 2.69, N 15.81.

3-(6-Thien-2-yl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl)-9*H*-carbazole (20d). Yield 150 mg, 68%, orange powder, mp 302 °C. δ_H (500 MHz, DMSO-*d*$_6$) 11.69 (s, 1H), 8.51 (d, *J* 1.4 Hz, 1H), 8.15 (d, *J* 7.8 Hz, 1H), 7.93 (dd, *J* 5.0, 0.9 Hz, 1H), 7.64 (dd, *J* 8.4, 1.7 Hz, 1H), 7.58 (dd, *J* 8.1, 6.3 Hz, 2H), 7.50-7.43 (m, 1H), 7.22 (t, *J* 7.5 Hz, 1H), 6.96 (dd, *J* 4.9, 4.1 Hz, 1H), 6.81 (dd, *J* 3.9, 0.9 Hz, 1H); δ_C (126 MHz, DMSO-*d*$_6$) 163.9, 156.6, 151.3, 151.2, 141.5, 141.1, 140.3, 134.6, 134.4, 128.4, 127.9, 127.3, 126.4, 122.3, 122.1, 122.1, 120.5, 119.4, 111.4, 110.5. Calcd. for $C_{20}H_{11}N_5OS$ (369.41): C 65.03, H 3.00, N 18.96. Found: C 64.94, H 3.12, N 18.82.

9-Ethyl-3-(6-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl)-9*H*-carbazole (21a). Yield 86 mg, 44%, dark red powder, mp 177 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.35 (d, *J* 1.6 Hz, 1H), 8.02 (d, *J* 7.7 Hz, 1H), 7.62 (d, *J* 8.2 Hz, 1H), 7.55-7.43 (m, 6H), 7.35 (t, *J* 7.7 Hz, 2H), 7.21 (t, *J* 7.3 Hz, 1H), 4.41 (q, *J* 7.1 Hz, 2H), 1.28 (t, *J* 7.1 Hz, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 164.3, 163.7, 151.7, 151.3, 140.8, 140.1, 138.2, 130.4, 129.7, 128.2, 128.0, 127.7, 126.4, 123.2, 122.1, 121.7, 120.3, 119.7, 109.7, 108.4, 37.2, 13.7. Calcd. for $C_{24}H_{17}N_5O$ (391.44): C 73.64, H 4.38, N 17.89. Found: C 73.54, H 4.34, N 17.83.

9-Ethyl-3-[6-(3-nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9*H*-carbazole (21b). Yield 131 mg, 60%, dark red powder, mp 167 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.43 (s, 2H), 8.33 (dd, *J* 8.1, 2.0 Hz, 1H), 8.12 (d, *J* 7.5 Hz, 1H), 7.86 (d, *J* 7.8 Hz, 1H), 7.65 (dd, *J* 16.0, 8.0 Hz, 2H), 7.57 (d, *J* 8.8 Hz, 1H), 7.54-7.44 (m, 2H), 7.25 (t, *J* 7.5 Hz, 1H), 4.45 (q, *J* 7.1 Hz, 2H), 1.30 (t, *J* 7.1 Hz, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 163.6, 162.6, 151.8, 151.3, 147.3, 140.8, 140.1, 139.5, 136.2, 129.6, 128.4, 127.0, 126.6, 124.9, 124.7, 123.4, 122.1, 121.9, 120.5, 119.8, 109.7, 108.6, 37.2, 13.6. Calcd. for $C_{24}H_{16}N_6O_3$ (436.43): C 66.05, H 3.70, N 19.26. Found: C 66.14, H 3.84, N 19.35.

3-[6-(4-Bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9-ethyl-9*H*-carbazole (21c). Yield 125 mg, 53%, dark red powder, mp 281 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.42 (d, *J* 1.5 Hz, 1H), 8.10 (d, *J* 7.8 Hz, 1H), 7.68 (d, *J* 8.2 Hz, 1H), 7.61 (dd, *J* 8.6, 3.3 Hz, 3H), 7.52 (t, *J* 7.6 Hz, 1H), 7.47 (d, *J* 8.5 Hz, 3H), 7.26 (t, *J* 7.5 Hz, 1H), 4.47 (q, *J* 7.1 Hz, 2H), 1.32 (t, *J* 7.1 Hz, 2H); δ_C (126 MHz, DMSO-*d*$_6$) 163.7, 163.5, 151.7, 151.3, 140.8, 140.1, 137.4, 131.8, 131.1, 128.2, 127.5, 126.5, 124.3, 123.2, 122.1, 121.9, 120.4, 119.8, 109.7, 108.6, 37.2, 13.7. Calcd. for $C_{24}H_{16}BrN_5O$ (470.33): C 61.29, H 3.43, N 14.89. Found: C 61.24, H 3.47, N 14.86.

9-Ethyl-3-(6-thien-2-yl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl)-9*H*-carbazole (21d). Yield 111 mg, 56%, dark red powder, mp 163 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.55 (d, *J* 1.4 Hz, 1H), 8.20 (d, *J* 7.7 Hz, 1H), 7.93 (dd, *J* 5.0, 1.0 Hz, 1H), 7.77-7.68 (m, 3H), 7.56-7.51 (m, 1H), 7.26 (t, *J* 7.4 Hz, 1H), 6.96 (dd, *J* 4.9, 4.0 Hz, 1H), 6.83 (dd, *J* 3.9, 1.0 Hz, 1H), 4.53 (q, *J* 7.1 Hz, 2H), 1.38 (t, *J* 7.1 Hz, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 163.8, 156.6, 151.3, 151.2, 141.5, 140.8, 140.2, 134.6, 134.4, 128.4, 128.1, 127.4, 126.5, 122.2, 122.1, 121.8, 120.7, 119.7, 109.7, 108.7, 37.3, 13.7. Calcd. for $C_{22}H_{15}N_5OS$ (397.46): C 66.48, H 3.80, N 17.62. Found: C 66.64, H 3.94, N 17.59.

3-Bromo-9-ethyl-3-(6-phenyl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl)-9*H*-carbazole (22a). Yield 87 mg, 37%, dark red powder, mp 222 °C. δ_H (500 MHz, DMSO-*d*$_6$) 8.46 (d, *J* 1.4 Hz, 1H), 8.31 (d, *J* 1.6 Hz, 1H), 7.64 (d, *J* 8.7 Hz, 1H), 7.60 (dd, *J* 8.7, 1.4 Hz, 1H), 7.55 (d, *J* 8.7 Hz, 1H), 7.52-7.43 (m, 4H), 7.37 (t, *J* 7.7 Hz, 2H), 4.42 (q, *J* 7.0 Hz, 2H), 1.27 (t, *J* 7.1 Hz, 3H); δ_C (126 MHz, DMSO-*d*$_6$) 164.2, 163.6, 151.7, 151.4, 141.1, 138.9, 138.0, 130.5, 129.8, 128.9, 128.8,

128.3, 128.1, 124.0, 123.7, 123.0, 120.8, 111.9, 111.8, 108.7, 37.4, 13.6. Calcd. for $C_{24}H_{16}BrN_5O$ (470.33): C 61.29, H 3.43, N 14.89. Found: C 61.24, H 3.44, N 14.79.

3-Bromo-9-ethyl-3-[6-(3-nitrophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9*H*-carbazole (22b). Yield 88 mg, 34%, dark red powder, mp 275 °C. δ_H (500 MHz, DMSO-d_6) 8.54 (d, *J* 1.6 Hz, 1H), 8.44 (d, *J* 1.7 Hz, 1H), 8.41 (t, *J* 2.0 Hz, 1H), 8.34 (dd, *J* 8.0, 2.4 Hz, 1H), 7.85 (d, *J* 7.8 Hz, 1H), 7.69-7.62 (m, 3H), 7.59 (d, *J* 8.7 Hz, 1H), 7.47 (dd, *J* 8.7, 1.7 Hz, 1H), 4.45 (q, *J* 7.1 Hz, 2H), 1.28 (t, *J* 7.1 Hz, 3H); δ_C (126 MHz, DMSO-d_6) 163.5, 162.5, 151.8, 151.3, 147.3, 141.1, 139.4, 138.9, 136.2, 129.6, 129.0, 128.9, 127.6, 125.0, 124.7, 124.03, 123.98, 123.3, 121.0, 112.0, 111.8, 108.9, 37.4, 13.6. Calcd. for $C_{24}H_{15}BrN_6O_3$ (515.33): C 55.94, H 2.93, N 16.31. Found: C 55.72, H 2.94, N 16.22.

3-Bromo-6-[6-(4-Bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl]-9-ethyl-9*H*-carbazole (22c). Yield 85 mg, 31%, dark red powder, mp 217 °C. δ_H (500 MHz, DMSO-d_6) 8.53 (d, *J* 1.5 Hz, 1H), 8.41 (d, *J* 1.6 Hz, 1H), 7.69-7.60 (m, 5H), 7.47-7.44 (m, 3H), 4.46 (q, *J* 7.1 Hz, 2H), 1.30 (t, *J* 7.1 Hz, 3H); δ_C (126 MHz, DMSO-d_6) 163.5, 163.3, 151.7, 151.3, 141.1, 138.9, 137.2, 131.9, 131.1, 128.9, 128.0, 124.3, 124.1, 123.7, 123.1, 120.9, 111.9, 111.8, 108.8, 37.4, 13.6. Calcd. for $C_{24}H_{15}Br_2N_5O$ (549.23): C 52.49, H 2.75, N 12.75. Found: C 52.34, H 2.84, N 12.68.

3-Bromo-9-ethyl-3-(6-thien-2-yl-[1,2,5]oxadiazolo[3,4-*b*]pyrazin-5-yl)-9*H*-carbazole (22d). Yield 83 mg, 35%, orange powder, mp 226 °C. δ_H (500 MHz, DMSO-d_6) 8.61 (d, *J* 1.0 Hz, 1H), 8.46 (d, *J* 1.8 Hz, 1H), 7.92 (dd, *J* 5.0, 0.9 Hz, 1H), 7.71 (dt, *J* 8.6, 5.1 Hz, 2H), 7.66 (d, *J* 8.7 Hz, 1H), 7.61 (dd, *J* 8.7, 1.9 Hz, 1H), 6.94 (dd, *J* 4.9, 4.0 Hz, 1H), 6.78 (dd, *J* 3.9, 0.9 Hz, 1H), 4.48 (q, *J* 7.1 Hz, 2H), 1.33 (t, *J* 7.1 Hz, 3H); δ_C (126 MHz, DMSO-d_6) 163.5, 156.4, 151.3, 151.1, 141.4, 141.1, 138.9, 134.7, 134.4, 128.9, 128.6, 128.4, 128.3, 124.0, 123.3, 122.7, 120.9, 111.8, 111.7, 109.1, 37.5, 13.7. Calcd. for $C_{22}H_{14}BrN_5OS$ (476.36): C 55.47, H 2.96, N 14.70. Found: C 55.32, H 2.94, N 14.59.

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