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Химия гетероциклических соединений

In memory of Dr. Prof. H. Neunhoeffer (1936–2018)

2,5-Di(het)arylpyridines: synthesis by "1,2,4-triazine" methodology and photophysical properties

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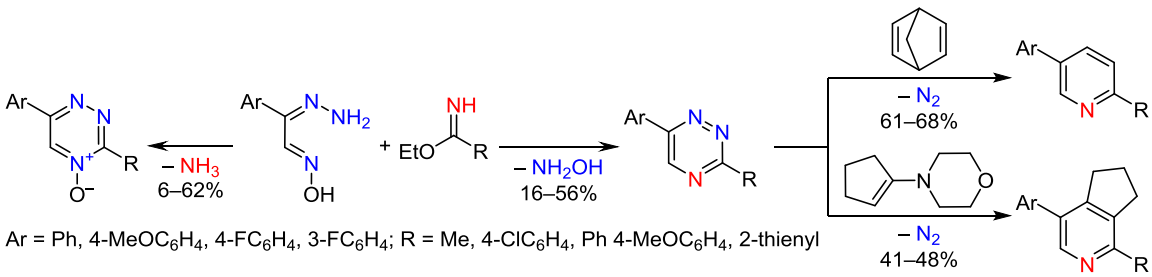

The method for the preparation of 3,6-disubstituted 1,2,4-triazines based on condensation reaction between easily available α-imino esters and isonitrosoacetophenone hydrazones was reported. The significant differences in reaction conditions, ratio of products, and yields between the developed method and the earlier reported approach were demonstrated. The corresponding 2,5-disubstituted pyridines were synthesized from the prepared 1,2,4-triazines, and their photophysical properties were studied. Studies of the photophysical properties revealed low and moderate luminescence quantum yields, and negligible solvatochromic behavior in case of 4-methoxyphenylpyridine derivative due to the role of donating methoxy group, however, with a low linearity of a Lippert–Mataga plot. Nevertheless, 2,5-disubstituted pyridines are of interest due to simple protocols of synthesis, moderate photophysical properties, and potential applicability in different scientific and industrial areas.

Keywords: imino ester, pyridine, 1,2,4-triazine, 1,2,4-triazine 4-oxide, aza-Diels–Alder reaction, fluorescence, synthesis.

Pyridine is one of the most common, widespread, and applicable N-heterocycle that could be found in natural products[1] and pharmaceuticals.[2] It also can be applied as a ligand for different metal cations. Particularly, 2,5-disubstituted pyridines can find their application as ligands in platinum[3] and iridium[4] complexes, including the ones for the production of white OLEDs,[5] pyridine-boron complexes,[6,7] herbicides,[8,9] and DNA-binding agents.[10] Thus, 2,5-disubstituted pyridines are of significant practical interest.

One of the methods for the synthesis of substituted pyridines is the transformation of the 1,2,4-triazine ring into a pyridine one in an aza-Diels–Alder reaction with various dienophiles.[11–13] Previously, 2,5-diaryl-substituted pyridines were synthesized using this method.[14,15] The starting substrates in this case should be 3,6-disubstituted 1,2,4-triazines; the approaches to their synthesis were considered by us earlier.[16] Among these methods, our attention was drawn to condensations using readily available isonitrosoacetophenone hydrazones. The second substrate for the condensation reaction can be aldehyde[17,18] or ortho ester.[19] In addition, there is a known protocol that describes the use of α-imino esters derived from the corresponding nitriles. This method is attractive because nitriles are often more accessible than the corresponding aldehydes and ortho esters. However, despite the attractiveness of this method, it has been developed to an insignificant extent and is only presented in a few works.[14,20–23] In some cases, this method leads to the production of 1,2,4-triazine 4-oxides. As for 1,2,4-triazines, this method has been used to prepare compounds containing various pyridyl residues or its aza/fused analogs,

Scheme 1. The synthesis of 1,2,4-triazines **3b–j**, *N*-oxides **4a–j**, and 2,5-disubstituted pyridines **5b–j** and **6c**,**f**

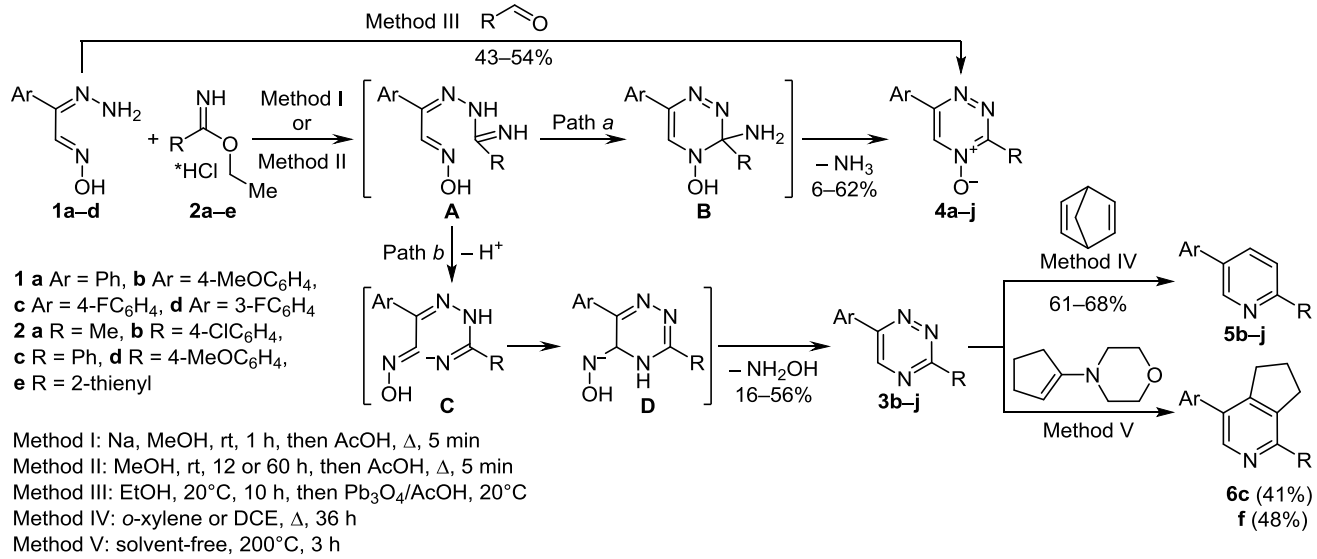

Table 1. Yields of 1,2,4-triazines **3a–j**, 1,2,4-triazine 4-oxides **4a–j**, and pyridines **5b–j**

Ar	R	Product	Yield, % (method)	Product	Yield, % (method)	Ratio of products **3**/**4**	Product	Yield, %
Ph	Me	**3a**	0 (I)	**4a**	62 (I)	0:100	**5a**	–
Ph	4-ClC_6H_4	**3b**	54 (I)	**4b**	6 (I)	90:10	**5b**	63
4-$MeOC_6H_4$	Ph	**3c**	50 (I)	**4c**	12 (I) 43 (III)	80:20	**5c**	65
4-FC_6H_4	Ph	**3d**	41 (I) 20 (II)	**4d**	26 (I) 50 (II) 50 (III)	61:39 30:70	**5d**	63
4-FC_6H_4	4-$MeOC_6H_4$	**3e**	47 (I)	**4e**	11 (I)	81:19	**5e**	65
4-FC_6H_4	2-Thienyl	**3f**	16 (I)	**4f**	40 (I) 54 (III)	29:71	**5f**	61
4-FC_6H_4	4-ClC_6H_4	**3g**	54 (I)	**4g**	10 (I)	84:16	**5g**	68
3-FC_6H_4	Ph	**3h**	56 (I) 31 (II)	**4h**	6 (I) 31 (II)	90:10 50:50	**5h**	61
3-FC_6H_4	4-$MeOC_6H_4$	**3i**	40 (I)	**4i**	17 (I)	70:30	**5i**	61
3-FC_6H_4	2-Thienyl	**3j**	21 (I)	**4j**	43 (I)	33:67	**5j**	64

as well as di- or trichloromethyl group at the C-3 position. In this work, we have proposed a convenient approach for the preparation of 1,2,4-triazines functionalized at the C-3 position with different (hetero)aromatic or aliphatic substituents.

α-Imino esters **2a–e** were obtained as hydrochlorides from the corresponding nitriles (Scheme 1).[24] During the heterocyclization reaction, α-imino esters were released in free form *in situ* as a result of interaction with sodium methoxide. The further reaction was carried out according to the previously reported procedure.[14] As a result, two products were found in the reaction mixture in almost all cases: the corresponding 1,2,4-triazines **3** and their *N*-oxides **4**. These two products could be separated using column chromatography (Scheme 1, paths *a* and *b*, intermediates **A**–**D** are shown according to the previously published mechanism).[19] 1,2,4-Triazines **3b–j** were obtained with the yields of 16–56%, while 1,2,4-triazine 4-oxides **4a–j** were obtained in 6–62% yields. When α-imino esters **2b–d** with an aromatic substituent were used, triazines **3b–e**,**g–i** predominated in the products mixture, while the corresponding *N*-oxides **4b–e**,**g–i** were only byproducts (Table 1). The situation changed when the aromatic fragment was replaced by an electron-donating 2-thienyl. In this case, the amount of triazine 4-oxides **4f**,**j** increased significantly (yield up to 43%), and they actually became the main reaction products. When methyl-containing α-imino ester **2a** was used, *N*-oxide **4a** was generally the only product.

Previously, a similar pattern was studied that describes the influence of the electron-withdrawing ability of a substituent in an α-imino ester on the course of the reaction in the series of mono-, di-, and trichloromethyl-substituted esters.[21] Obviously, if an α-imino ester contains the methyl group, which is significantly more electron-donating than chloromethyl group, the exclusive formation of the triazine 4-oxide **4** occurs.

It should be noted that similar heterocyclization with aromatic α-imino esters was previously reported in a single publication,[23] where the corresponding 1,2,4-triazine 4-oxides were the only products obtained with yields of 16–54%. In this case, the authors used α-imino esters derived from substituted benzonitriles that contained both an electron-donating methoxy group and an electron-

withdrawing nitro group in the *para* position. Perhaps, the reason for the exclusive formation of *N*-oxides was different reaction conditions, specifically without preliminary removal of the hydrochloride, as well as with a much longer reaction time. Thus, the authors dissolved two starting compounds in absolute methanol and kept them for 12 h to 3 days at room temperature or at –20°C. The resulting precipitate was purified by recrystallization (in some cases repeated) from various solvents such as $CHCl_3$, DMSO, or a mixture of DMF–H_2O, 8:1. Authors also tested different molar ratios of hydrazone and α-imino ester (from 1:1 to 1:2.5).[23]

We attempted to reproduce this technique in the reaction of isonitroso-4(3)-fluoroacetophenone hydrazones **1c**,**d** with α-imino ester hydrochloride **2c**. However, after keeping the solution of the substrates in methanol at room temperature for 1 day or 3 days, we did not detect the formation of products **3d**,**h** or **4d**,**h**. The analysis of the reaction mixture by NMR revealed only mixtures of unidentifiable products, likely nonaromatized intermediates **A**–**D** (Scheme 1). Their brief refluxing in AcOH resulted in a mixture of the corresponding 1,2,4-triazines **3d**,**h** and their *N*-oxides **4d**,**h** in ratios of 30/70 and 50/50, respectively. The yields of *N*-oxides **4d**,**h** were 50 and 31%, respectively. In this case, prolonged exposure of the reagents increased the proportion of triazine 4-oxides **4d**,**h** in the product mixture. However, triazines **3d**,**h**, were still formed. In other words, the formation of a mixture of 1,2,4-triazine and 1,2,4-triazine 4-oxide occurs in all cases, even including the one described in the publication.[23] Thus, it is likely that the authors of article[23] misinterpreted the results of this reaction. At the same time, the following facts attract attention: in their procedure there is no stage of aromatization of products, and they also use recrystallization (often multiple) to isolate products. That is, perhaps, at the recrystallization stage, aromatization of the triazine ring occurs as a result of increasing the temperature, as well as separation of the second product (i.e., 1,2,4-triazine, the nature of which was not analyzed by the authors). Repeating this procedure multiple times is probably required to completely separate the triazine.

The structure of 1,2,4-triazines **3b**–**j** and their *N*-oxides **4a**–**j** was confirmed based on the ^{1}H, ^{19}F, and ^{13}C NMR data, mass spectrometry, and elemental analysis. It should be noted that the ^{1}H NMR spectra of products **3b**–**j** and **4a**–**j** are quite similar, and the mass spectroscopy and elemental analysis data are especially necessary to establish their structure accurately. In addition, in a number of cases, the structure of triazine 4-oxides (in particular, **4c**,**d**,**f**) were confirmed by an alternative method based on the condensation of isonitrosoacetophenone hydrazones **1** with aldehydes followed by oxidative aromatization (Scheme 1, method III).[17] 1,2,4-Triazine **3b** was described previously[25] (the synthesis was performed by an alternative method), and the spectral data obtained by us coincided with the published ones.

Additionally, the structure of products **3b** and **4e** was confirmed by X-ray diffraction analysis. According to the crystallography data, two independent molecules of compound **3b** are crystallized in the centrosymmetric space

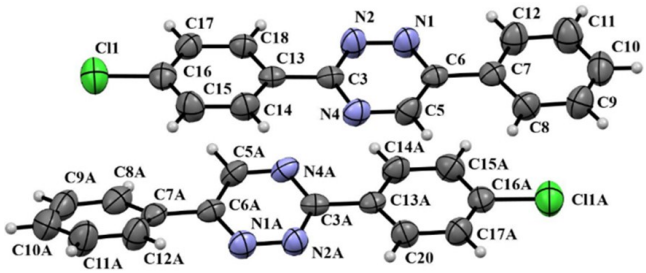

Figure 1. Molecular structure of compound **3b** in the thermal ellipsoids of the 50% probability level.

group of the monoclinic system (Fig. 1). The molecules are distinguished by torsion angles between phenyl substituent and triazine ring and demonstrate nonsignificant deviations in the bond distance and interatomic angles. In general, the geometry of the molecules is near to standard. Any significantly shortened intermolecular contacts in the molecules were not observed.

Compound **4e** crystallized in the centrosymmetric space group of the monoclinic system. The bond distances and angles in the molecule are near to expectation (Fig. 2). The molecule is nonplanar, the torsion angles N(4)–C(3)–C(13)–C(18) 14.7(5)°, N(1)–C(6)–C(7)–C(8) 14.1(5)°. The O atom of the NO group forms the weak H-bonds with C(5)–H(5) and C(12)–H(12) atoms of the nearest molecule ($1.5 - x$, $y - 0.5$, $0.5 - z$) (Fig. 3). The π–π interactions are observed in the crystal between the triazine ring and the 4-$MeOC_6H_4$ moiety of the nearest molecule (x, $y - 1$, z) (Fig. 4).

Further aza-Diels–Alder reaction of 1,2,4-triazines **3b**–**j** with 2,5-norbornadiene where carried out in accordance with the previously described procedure,[12] this allowed us

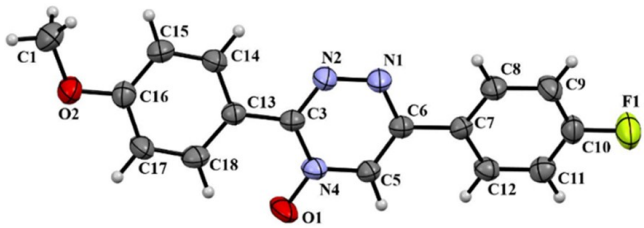

Figure 2. Molecular structure of compound **4e** in the thermal ellipsoids of the 50% probability level.

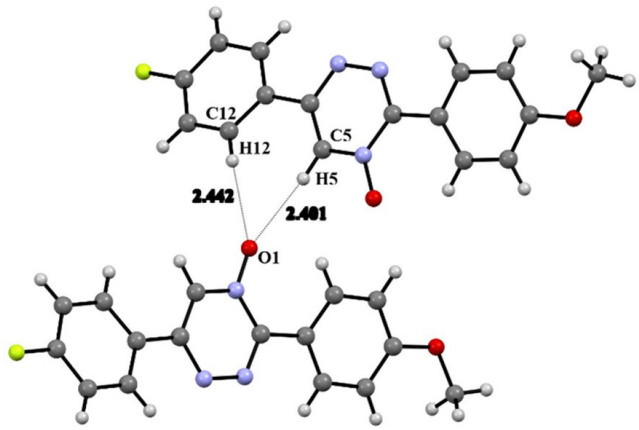

Figure 3. The shortened contacts in the single crystal of molecule **4e** (in Å).

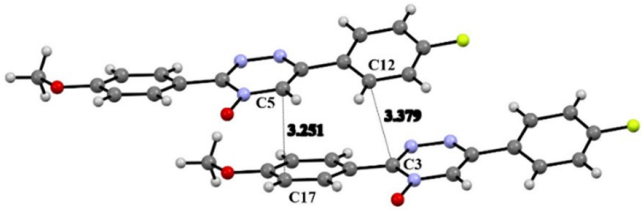

Figure 4. The π–π interactions in a single crystal of molecule **4e** (in Å).

to obtain the target 2,5-disubstituted pyridines **5b–j** in yields up to 68% (Scheme 1). In addition to 2,5-norbornadiene, we also used another well-known dienophile – 1-morpholinocyclopentene, that provided respective cyclopentane-annulated pyridines **6c**,**f** under solvent-free conditions[26] with the yield up to 48%. The structures of the obtained compounds **5b–j** and **6c**,**f** were confirmed by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. In particular, in the ^{1}H NMR spectra of compounds **5b–j** one can note the appearance of signals from the protons of the ABX system of the new pyridine ring in the form of two doublets and a doublet of doublets with the corresponding coupling constants, as well as a high-field shift of the signals of a number of protons in the substituents of the former triazine ring. For annulated pyridines **6c**,**f**, one can note the appearance of signals of the cyclopentane fragment in the resonance region of aliphatic protons and carbons in the ^{1}H and ^{13}C NMR spectra, respectively. In the case of compound **5d**, one can note the coincidence of the previously published[27] spectral data with those obtained by us. Also, the structure of compound **5g** was confirmed by X-ray diffraction analysis. According to X-ray diffraction data, compound **5g** is crystallized in the centrosymmetric space group of the orthorhombic system. The structure is nonplanar (Fig. 5), the bond distances and angles in the molecules are near to expectations. In the crystal, the shortened T-like contacts C–H···C_{Ar} are observed (Fig. 6).

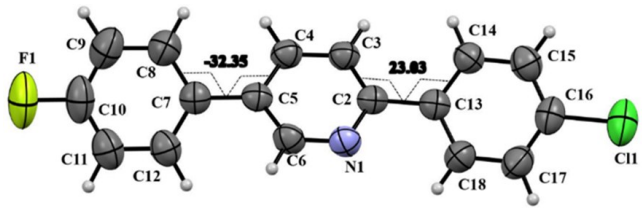

Figure 5. Molecular structure of compound **5g** in the thermal ellipsoids of the 50% probability level. The figure shows torsion angles in degrees.

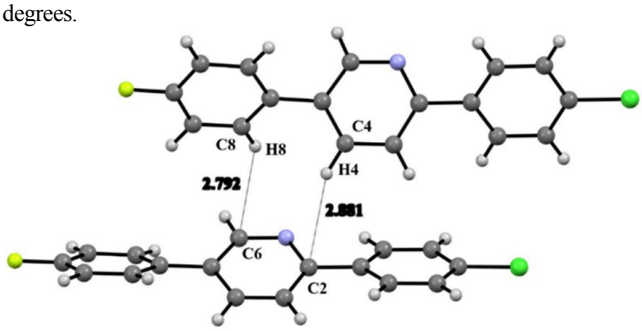

Figure 6. The shortened contacts in the single crystal of molecule **5g** (in Å).

Table 2. Photophysical properties of compounds **5b–j** and **6c**,**f** in MeCN solution at concentration 10^{-5}·M

Compound	λ_{abs}, nm	ε_M, 10^4 M^{-1} cm^{-1}	λ_{em}, nm	Stokes shift, nm	Φ*, %
5b	273 sh, 294	1.68	338 sh, 350	56	0.6
5c	301	2.42	372	71	<0.1
5d	270 sh, 287	1.62	335 sh, 347	60	<0.1
5e	276 sh, 298	2.72	362	64	52.3
5f	265 sh, 320	1.14	371	51	14.0
5g	273 sh, 289	1.65	338 sh, 350	61	<0.1
5h	272 sh, 291	2.22	347	56	<0.1
5i	306	2.31	375	69	<0.1
5j	268 sh, 321	2.02	372	51	16.8
6c	292	1.63	364	72	26.4
6f	264 sh, 316	1.30	365	49	26.9

* Absolute quantum yield of luminescence was obtained using an integrating sphere of Horiba-Fluoromax-4 spectrophotometer at room temperature in MeCN solution according the procedure.[31]

The photophysical properties for the synthesized compounds were studied (Table 2, Fig. 7). In acetonitrile solution, the absorption spectrum maxima are in the range

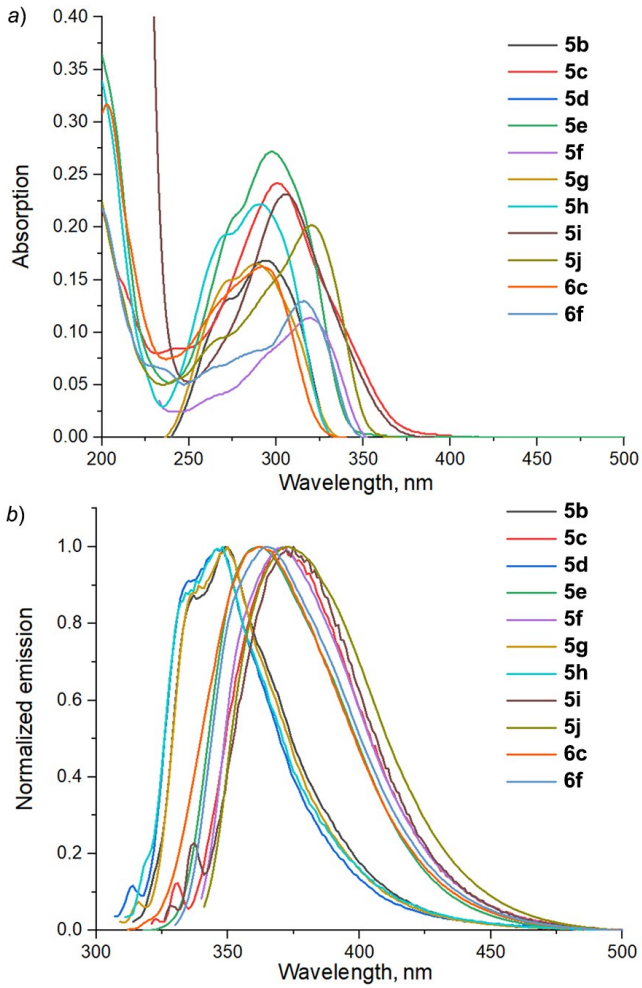

Figure 7. *a*) UV/Vis absorption spectra and *b*) normalized emission spectra of compounds **5b–j** and **6c**,**f** in MeCN at room temperature at concentration 10^{-5} M.

of 287–321 nm, the fluorescence maxima are in the range of 347–375 nm, the Stokes shift is 49–72 nm, and the luminescence quantum yields vary in the range from less than 0.1 to 52.3% depending on the type and positions of substituents. For example, the highest Stokes shift was found for compound **6c**, containing a single methoxy group in the phenyl substituent in cyclopentene-annulated pyridine, and the highest quantum yield of luminescence was found in case of compound **5e**, functionalized with 4-methoxyphenyl and 4-fluorophenyl moieties. Pyridines **6c**,**f** were chosen as model compounds for solvatochromism studies (Fig. S1 and Table S2, Fig. S2 and Table S3, respectively, Supplementary information file). It was found that in the case of pyridine **6c** the difference in the emission maxima between the least and most polar solvents was 25 nm (due to a donating nature of the methoxy group[28]), while in the case of pyridine **6f** – 4 nm. Both values are low, as evidenced by the low linearity of the Lippert–Mataga plot ($r^2 < 0.14$), as well as in comparison with 2,2'-bipyridine analogs, which have been previously described by our scientific group in many works.[29,30] However, pyridines **5b–j** and **6c**,**f** are compare favorably in terms of ease of synthesis, good product yields, and moderate/high quantum yields of luminescence (depending on the nature and positions of the substituents).

In summary, the method for preparation of 3,6-disubstituted 1,2,4-triazines and their *N*-oxides based on condensation reaction between easily available α-imino esters and isonitrosoacetophenone hydrozones has been reported. A comparison between the developed method and the one reported earlier in literature was conducted. The ratios of the yields of the synthesized 1,2,4-triazines and their corresponding 1,2,4-triazine 4-oxides were determined, and the course of reaction of the developed method and the one reported in literature was discussed. 2,5-Disubstituted pyridines and their cyclopentene-annulated analogs were synthesized from the obtained 1,2,4-triazines in aza-Diels–Alder reaction in good yields. Despite unremarkable photophysical properties (except high quantum yield of luminescence for one substituted pyridine) and low solvatochromic behavior, some 2,5-disubstituted pyridines could find a promising application due to simple synthetic protocols of their preparation.

Experimental

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance-400 spectrometer (400, 101, and 376 MHz, respectively), 298K, digital resolution ± 0.01 ppm, using as internal standards TMS (for ^{1}H, ^{13}C NMR spectra) and $CFCl_3$ (for ^{19}F NMR spectra) and C_6F_6 as internal standard for ^{19}F spectrum of compound **5i**. UV-Vis spectra were recorded on a Shimadzu UV1800 spectrophotometer. Luminescence spectra were recorded on a Horiba-Fluoromax-4 spectrofluorometer equipped with integrated sphere. Mass spectrometric studies were performed on an Agilent 6545 Q-TOF LC/MS (Agilent Technologies, USA) quadrupole time-of-flight mass spectrometer with an electrospray ionization source in the positive (negative) ion mode. An Agilent 1290 Infinity II chromatographic system was used to inject the sample. Elemental analysis was performed on a PE 2400 II CHN-analyzer (PerkinElmer).

All reagents were purchased from commercial sources and used without further purification. Silica gel 60 (Kieselgel 60, 230–400 mesh) was used for the column chromatography.

The starting hydrazones **1a–c**[18] and α-imino ester hydrochlorides[24] were synthesized as described in literature. The starting hydrazine **1d** was synthesized according to method described in the literature for similar compounds.[18] 1,2,4-Triazine 4-oxides **4a**[17] and **4b**,[25] as well as 1,2,4-triazines **3b**,[25] **3c**,[32] **3d**,[32] **3f**,[33] **5b**,[27] **5c**,[34] **5d**[34] are known compounds; all of these compounds were synthesized in the course of this research work and characterized by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

Synthesis of triazines 3b–j and *N*-oxides 4a–j (General method I). The corresponding hydrochloride of imino ester **2** (4.0 mmol) was dissolved in solution of Na (92 mg) in MeOH (20 ml). The resulting mixture was stirred at room temperature for 1 h. The corresponding hydrazone of isonitrosoacetophenone **1** (4.0 mmol) was added and the resulting mixture was stirred at room temperature for 1 h. Solvent was removed under reduced pressure. Glacial AcOH (20 ml) was added to the residue, and the resulting mixture was refluxed for 5–10 min. Solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel ($CHCl_3$ as eluent, R_f 0.7 (for 1,2,4-triazines **3b–j**) and 0.3 (for 1,2,4-triazine 4-oxides **4a–j**)). Analytical samples were obtained by recrystallization from MeCN.

Synthesis of triazines 3d,h and *N*-oxides 4d,h (General method II). Hydrochloride of imino ester **2c** (743 mg, 4.0 mmol) was dissolved in MeOH (20 ml). The solution of corresponding hydrazone of isonitrosoacetophenone **1c** or **1d** (725 mg, 4.0 mmol) in MeOH (20 ml) was added, and the resulting mixture was stirred at room temperature overnight (for compound **1d**) or for 3 days (for compound **1c**). Solvent was removed under reduced pressure. Glacial AcOH (20 ml) was added to the residue, and the resulting mixture was refluxed for 5–10 min. Solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel ($CHCl_3$ as eluent, R_f 0.7 (for triazines **3**) and 0.3 (for *N*-oxides **4**)). Analytical samples were obtained by recrystallization from MeCN.

Synthesis of *N*-oxides 4c,d,f (General method III). The corresponding hydrazone of isonitrosoacetophenone **1** (3.0 mmol) was dissolved in EtOH (30 ml), and the corresponding aldehyde (3.0 mmol) was added to solution. The resulting mixture was kept at room temperature overnight. Solvent was removed under reduced pressure, obtained residue was dissolved in AcOH (10 ml), and Pb_3O_4 (3058 mg, 3.0 mmol) was added by portions during 1 h by stirring at room temperature. The reaction mixture was diluted with H_2O (100 ml), and the precipitate obtained was filtered off and recrystallized from EtOH.

3-Methyl-6-phenyl-1,2,4-triazin-4-ium-4-olate (4a). Yield 466 mg (62%), yellow amorphous solid, mp 181–183°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.72 (3H, s, CH_3);

7.53–7.60 (3H, m, H Ph); 8.12–8.19 (2H, m, H Ph); 9.20 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 17.1; 127.4; 129.6; 131.5; 131.6; 132.7; 156.6; 159.5. Mass spectrum, *m*/*z*: 188 $[M+H]^+$. Found, %: C 64.23; H 4.89; N 22.53. $C_{10}H_9N_3O$. Calculated, %: C 64.16; H 4.85; N 22.45.

3-(4-Chlorophenyl)-6-phenyl-1,2,4-triazine (3b). Yield 578 mg (54%), yellow amorphous solid, mp 174–176°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.51–7.56 (2H, m, C_6H_4Cl); 7.56–7.62 (3H, m, H Ph); 8.13–8.18 (2H, m, H Ph); 8.51–8.56 (2H, m, C_6H_4Cl); 9.05 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 126.7; 129.2; 129.4; 129.5; 131.0; 133.2; 138.1; 146.5; 155.2; 161.6. Mass spectrum, *m*/*z*: 268 $[M+H]^+$. Found, %: C 67.48; H 3.67; N 15.73. $C_{15}H_{10}ClN_3$. Calculated, %: C 67.30; H 3.77; N 15.70.

3-(4-Chlorophenyl)-6-phenyl-1,2,4-triazin-4-ium-4-olate (4b). Yield 63 mg (6%), light-yellow amorphous solid, mp 202–204°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.57–7.63 (5H, m, H Ph, C_6H_4Cl); 8.23–8.28 (2H, m, H Ph); 8.38–8.43 (2H, m, C_6H_4Cl); 9.34 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 127.6; 128.4; 128.8; 129.7; 129.8; 132.0; 132.4; 133.4; 136.7; 155.9; 156.3. Mass spectrum, *m*/*z*: 284 $[M+H]^+$. Found, %: C 63.52; H 3.42; N 14.94. $C_{15}H_{10}ClN_3O$. Calculated, %: C 63.50; H 3.55; N 14.81.

6-(4-Methoxyphenyl)-3-phenyl-1,2,4-triazine (3c). Yield 524 mg (50%), yellow amorphous solid, mp 168–170°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.90 (3H, s, OCH_3); 7.10–7.15 (2H, m, $C_6\underline{H}_4OCH_3$); 7.55–7.60 (3H, m, H Ph); 8.21–8.26 (2H, m, $C_6\underline{H}_4OCH_3$); 8.47–8.53 (2H, m, H Ph); 9.36 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.5; 114.9; 125.7; 128.0; 128.1; 128.9; 131.5; 134.8; 145.9; 154.6; 151.9; 162.0. Mass spectrum, *m*/*z*: 264 $[M+H]^+$. Found, %: C 72.78; H 5.04; N 15.92. $C_{16}H_{13}N_3O$. Calculated, %: C 72.99; H 4.98; N 15.96.

6-(4-Methoxyphenyl)-3-phenyl-1,2,4-triazin-4-ium-4-olate (4c). Yield 131 mg (12%, method I), 360 mg (43%, method III), yellow amorphous solid, mp 216–218°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.90 (3H, s, OCH_3); 7.09–7.13 (2H, m, $C_6\underline{H}_4OCH_3$); 7.54–7.61 (3H, m, H Ph); 8.20–8.23 (2H, m, $C_6\underline{H}_4OCH_3$); 8.28–8.33 (2H, m, H Ph); 9.27 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 56.0; 115.2; 124.6; 128.5; 129.2; 129.7; 130.1; 131.7; 132.5; 155.9; 156.1; 162.5. Mass spectrum, *m*/*z*: 280 $[M+H]^+$. Found, %: C 68.87; H 4.74; N 14.98. $C_{16}H_{13}N_3O_2$. Calculated, %: C 68.81; H 4.69; N 15.05.

6-(4-Fluorophenyl)-3-phenyl-1,2,4-triazine (3d). Yield 408 mg (41%, method I), 200 mg (20%, method II), yellow amorphous solid, mp 135–137°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.34–7.42 (2H, m, C_6H_4F); 7.57–7.62 (3H, m, H Ph); 8.32–8.39 (2H, m, C_6H_4F); 8.50–8.57 (2H, m, H Ph); 9.43 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 116.6 (d, *J* = 21.8); 128.2; 128.7 (d, *J* = 9.2); 129.0; 129.5 (d, *J* = 3.2); 131.7; 134.6; 146.1; 154.2; 162.4; 164.7 (d, *J* = 252.8). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –109.75 (s). Mass spectrum, *m*/*z*: 252 $[M+H]^+$. Found, %: C 71.56; H 4.04; N 16.62. $C_{15}H_{10}FN_3$. Calculated, %: C 71.70; H 4.01; N 16.72.

6-(4-Fluorophenyl)-3-phenyl-1,2,4-triazin-4-ium-4-olate (4d). Yield 273 mg (26%, method I), 530 mg (50%, method II), 401 mg (50%, method III), yellow amorphous solid, mp 223–225°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.32–7.40 (2H, m, C_6H_4F); 7.54–7.65 (3H, m, H Ph); 8.31–8.37 (4H, m, C_6H_4F, H Ph); 9.37 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 116.7 (d, *J* = 21.6); 128.6; 129.0 (d, *J* = 2.8); 129.5; 130.1 (d, *J* = 8.1); 130.2; 131.9; 133.3; 155.2; 158.7; 164.6 (d, *J* = 250.5). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –108.88 (s). Mass spectrum, *m*/*z*: 268 $[M+H]^+$. Found, %: C 67.37; H 3.85; N 15.83. $C_{15}H_{10}FN_3O$. Calculated, %: C 67.41; H 3.77; N 15.72.

6-(4-Fluorophenyl)-3-(4-methoxyphenyl)-1,2,4-triazine (3e). Yield 530 mg (47%), light-yellow amorphous solid, mp 169–171°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.88 (3H, s, OCH_3); 7.15–7.20 (2H, m, $C_6\underline{H}_4OCH_3$); 7.44–7.50 (2H, m, C_6H_4F); 8.30–8.36 (2H, m, C_6H_4F); 8.42–8.48 (2H, m, $C_6\underline{H}_4OCH_3$); 9.44 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 55.9; 115.1; 116.8 (d, *J* = 21.1); 127.2; 129.5 (d, *J* = 8.7); 129.9; 130.3 (d, *J* = 2.8); 147.9; 153.9; 161.7; 162.7; 164.3 (d, *J* = 249.2). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –110.29 (s). Mass spectrum, *m*/*z*: 282 $[M+H]^+$. Found, %: C 68.28; H 4.23; N 14.81. $C_{16}H_{12}FN_3O$. Calculated, %: C 68.32; H 4.30; N 14.94.

6-(4-Fluorophenyl)-3-(4-methoxyphenyl)-1,2,4-triazin-4-ium-4-olate (4e). Yield 134 mg (11%), yellow amorphous solid, mp 234–236°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.88 (3H, s, OCH_3); 7.12–7.16 (2H, m, $C_6\underline{H}_4OCH_3$); 7.43–7.48 (2H, m, C_6H_4F); 8.27–8.31 (2H, m, C_6H_4F); 8.35–8.39 (2H, m, $C_6\underline{H}_4OCH_3$); 9.33 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 56.0; 114.1; 116.7 (d, *J* = 21.5); 121.6; 129.1 (d, *J* = 3.3); 130.7 (d, *J* = 9.1); 132.0; 133.3; 154.6; 156.1; 162.4; 164.6 (d, *J* = 249.7). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –109.43 (s). Mass spectrum, *m*/*z*: 298 $[M+H]^+$. Found, %: C 64.78; H 4.02; N 14.01. $C_{16}H_{12}FN_3O$. Calculated, %: C 64.64; H 4.07; N 14.13.

6-(4-Fluorophenyl)-3-(thiophen-2-yl)-1,2,4-triazine (3f). Yield 165 mg (16%), yellow amorphous solid, mp 154–156°C ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.25–7.30 (1H, m, H thienyl); 7.33–7.40 (2H, m, C_6H_4F); 7.78–7.82 (1H, m, H thienyl); 8.10–8.14 (1H, m, H thienyl); 8.27–8.34 (2H, m, C_6H_4F); 9.34 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 116.6 (d, *J* = 21.8); 128.5 (d, *J* = 8.7); 128.7; 129.5 (d, *J* = 3.7); 130.3; 131.4; 139.4; 146.1; 153.6; 159.9; 164.6 (d, *J* = 252.6). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –109.84 (s). Mass spectrum, *m*/*z*: 258 $[M+H]^+$. Found, %: C 60.77; H 3.23; N 16.45. $C_{13}H_8FN_3S$. Calculated, %: C 60.69, H 3.13, N 16.33.

6-(4-Fluorophenyl)-3-(thiophen-2-yl)-1,2,4-triazin-4-ium-4-olate (4f). Yield 440 mg (40%, method I), 440 mg (54%, method III), yellow amorphous solid, mp 193–195°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.31–7.40 (3H, m, H thienyl, C_6H_4F); 7.90–7.95 (1H, m, H thienyl); 8.28–8.35 (2H, m, C_6H_4F); 8.58–8.62 (1H, m, H thienyl); 9.43 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 116.7 (d, *J* = 21.5); 128.1; 129.1 (d, *J* = 3.2); 129.1; 129.9 (d, *J* = 9.0); 132.2; 132.7; 134.5; 152.8; 153.5; 164.5 (d, *J* = 249.7). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –109.19 (s). Mass spectrum, *m*/*z*: 274 $[M+H]^+$. Found, %: C 57.08; H 3.01; N 15.51. $C_{13}H_8FN_3OS$. Calculated, %: C 57.13; H 2.95; N 15.38.

3-(4-Chlorophenyl)-6-(4-fluorophenyl)-1,2,4-triazine (3g). Yield 612 mg (54%), yellow amorphous solid, mp 170–172°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.33–7.41 (2H, m, C_6H_4F); 7.58–7.63 (2H, m, C_6H_4Cl); 8.32–8.38 (2H, m, C_6H_4F); 8.49–8.54 (2H, m, C_6H_4Cl); 9.44 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 116.6 (d, *J* = 22.2); 128.7 (d, *J* = 8.1); 129.2; 129.4 (d, *J* = 3.1); 129.5; 133.1; 138.2; 146.0; 154.3; 161.6; 164.8 (d, *J* = 252.3). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –109.62 (s). Mass spectrum, *m*/*z*: 286 $[M+H]^+$. Found, %: C 63.16; H 3.24; N 14.81. $C_{15}H_9ClFN_3$. Calculated, %: C 63.06; H 3.18; N 14.71.

3-(4-Chlorophenyl)-6-(4-fluorophenyl)-1,2,4-triazin-4-ium-4-olate (4g). Yield 121 mg (10%), yellow amorphous solid, mp 211–213°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.32–7.41 (2H, m, C_6H_4F); 7.57–7.64 (2H, m, C_6H_4Cl); 8.29–8.36 (2H, m, C_6H_4F); 8.36–8.42 (2H, m, C_6H_4Cl); 9.38 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 116.8 (d, *J* = 22.3); 128.4; 128.8; 129.0 (d, *J* = 3.3); 130.2 (d, *J* = 7.9); 132.0; 133.4; 136.8; 155.5; 156.8; 164.6 (d, *J* = 247.9). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –108.75 (s). Mass spectrum, *m*/*z*: 302 $[M+H]^+$. Found, %: C 59.84, H 3.12, N 13.79. $C_{15}H_9ClFN_3O$. Calculated, %: C 59.71; H 3.01; N 13.93.

6-(3-Fluorophenyl)-3-phenyl-1,2,4-triazine (3h). Yield 559 mg (56%, method I), 309 mg (31%, method II), yellow amorphous solid, mp 178–180°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.24–7.28 (1H, m, C_6H_4F); 7.54–7.60 (4H, m, C_6H_4F, H Ph); 7.91–7.95 (2H, m, C_6H_4F); 8.58–8.61 (2H, m, H Ph); 9.07 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 113.7 (d, *J* = 23.3); 117.8 (d, *J* = 21.2); 122.2 (d, *J* = 3.0); 128.3; 128.9; 131.0 (d, *J* = 8.1); 131.8; 134.5; 135.6 (d, *J* = 8.0); 146.3; 154.0 (d, *J* = 3.0); 162.8; 163.5 (d, *J* = 249.1). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –111.02 (s). Mass spectrum, *m*/*z*: 252 $[M+H]^+$. Found, %: C 71.57; H 4.06; N 16.79. $C_{15}H_{10}FN_3$. Calculated, %: C 71.70; H 4.01; N 16.72.

6-(3-Fluorophenyl)-3-phenyl-1,2,4-triazin-4-ium-4-olate (4h). Yield 59 mg (6%, method I), 329 mg (31%, method II), yellow amorphous solid, mp 208–210°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.27–7.32 (1H, m, C_6H_4F); 7.54–7.58 (3H, m, H Ph); 7.59–7.62 (1H, m, C_6H_4F); 7.79–7.82 (1H, m, C_6H_4F); 7.84–7.87 (1H, m, C_6H_4F); 8.43–8.47 (2H, m, H Ph); 8.62 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 114.1 (d, *J* = 23.7); 118.7 (d, *J* = 20.9); 122.5 (d, *J* = 3.8); 128.3; 128.4; 130.0; 131.2 (d, *J* = 8.9); 132.2 (2C); 133.9 (d, *J* = 8.2); 154.9 (d, *J* = 3.0); 157.0; 163.4 (d, *J* = 248.8). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –111.53 (s). Mass spectrum, *m*/*z*: 268 $[M+H]^+$. Found, %: C 67.53; H 3.89; N 15.61. $C_{15}H_{10}FN_3O$. Calculated, %: C 67.41; H 3.77; N 15.72.

6-(3-Fluorophenyl)-3-(4-methoxyphenyl)-1,2,4-triazine (3i). Yield 450 mg (40%), yellow amorphous solid, mp 197–199°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.92 (3H, s, OCH_3); 7.04–7.10 (2H, m, $C_6\underline{H}_4OCH_3$); 7.21–7.25 (1H, m, C_6H_4F); 7.54–7.58 (1H, m, C_6H_4F); 7.88–7.93 (2H, m, C_6H_4F); 8.53–8.58 (2H, m, $C_6\underline{H}_4OCH_3$); 8.99 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 55.9; 113.7 (d, *J* = 23.9); 115.1; 118.0 (d, *J* = 20.8); 123.1 (d, *J* = 3.0); 127.1; 130.0; 131.8 (d, *J* = 8.0); 136.1 (d, *J* = 8.0); 148.2; 153.5 (d, *J* = 3.0); 162.0; 162.8; 163.2 (d, *J* = 244.2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –111.16 (s). Mass spectrum, *m*/*z*: 282 $[M+H]^+$. Found, %: C 68.48; H 4.27; N 15.03. $C_{16}H_{12}FN_3O$. Calculated, %: C 68.32; H 4.30; N 14.94.

6-(3-Fluorophenyl)-3-(4-methoxyphenyl)-1,2,4-triazin-4-ium-4-olate (4i). Yield 202 mg (17%), yellow amorphous solid, mp 226–228°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.92 (3H, s, OCH_3); 7.03–7.09 (2H, m, $C_6\underline{H}_4OCH_3$); 7.26–7.32 (1H, m, C_6H_4F); 7.51–7.59 (1H, m, C_6H_4F); 7.76–7.81 (1H, m, C_6H_4F); 7.81–7.87 (1H, m, C_6H_4F); 8.56–8.60 (3H, m, $C_6\underline{H}_4OCH_3$, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 55.9; 114.1; 114.2 (d, *J* = 22.3); 118.5 (d, *J* = 22.3); 121.5; 123.6 (d, *J* = 3.0); 130.0; 131.8 (d, *J* = 8.2); 132.1; 133.7; 134.9 (d, *J* = 8.2); 154.2 (d, *J* = 3.0); 156.5; 163.1 (d, *J* = 244.0). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –110.65 (s). Mass spectrum, *m*/*z*: 298 $[M+H]^+$. Found, %: C 64.59; H 4.11; N 14.03. $C_{16}H_{12}FN_3O_2$. Calculated, %: C 64.64; H 4.07; N 14.13.

6-(3-Fluorophenyl)-3-(thiophen-2-yl)-1,2,4-triazine (3j). Yield 219 mg (21%), yellow amorphous solid, mp 166–168°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.26–7.30 (1H, m, H thienyl); 7.32–7.38 (1H, m, C_6H_4F); 7.60–7.67 (1H, m, C_6H_4F); 7.82–7.85 (1H, m, H thienyl); 8.03–8.11 (2H, m, C_6H_4F); 8.13–8.16 (1H, m, H thienyl); 9.38 (1H, s, H-5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 113.8 (d, *J* = 23.5); 118.1 (d, *J* = 21.5); 123.2 (d, *J* = 3.0); 129.6; 130.8; 131.9 (d, *J* = 8.1); 133.0; 136.0 (d, *J* = 8.1); 139.4; 148.5; 153.7 (d, *J* = 3.0); 159.9; 163.2 (d, *J* = 244.8). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –111.58 (s). Mass spectrum, *m*/*z*: 258 $[M+H]^+$. Found, %: C 60.79; H 3.11; N 16.42. $C_{13}H_8FN_3S$. Calculated, %: C 60.69; H 3.13; N 16.33.

6-(3-Fluorophenyl)-3-(thiophen-2-yl)-1,2,4-triazin-4-ium-4-olate (4j). Yield 470 mg (43%), yellow amorphous solid, mp 191–193°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.32–7.40 (2H, m, H thienyl, C_6H_4F); 7.58–7.66 (1H, m, C_6H_4F); 7.92–7.97 (1H, m, H thienyl); 8.03–8.13 (2H, m, C_6H_4F, H thienyl); 8.59–8.63 (1H, m, H thienyl); 9.48 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 113.9 (d, *J* = 21.3); 118.5 (d, *J* = 21.3); 122.2 (d, *J* = 3.0): 127.7; 128.5; 130.7; 131.2 (d, *J* = 8.0); 133.4; 134.0 (d, *J* = 8.0); 134.1; 153.1 (d, *J* = 3.0); 153.5; 163.4 (d, *J* = 248.9). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –111.57 (s). Mass spectrum, *m*/*z*: 274 $[M+H]^+$. Found, %: C 57.20; H 2.92; N 15.23. $C_{13}H_8FN_3OS$. Calculated, %: C 57.13; H 2.95; N 15.38.

Synthesis of pyridines 5b–j (General method IV). The corresponding triazine **3** (0.6 mmol) was suspended in *o*-xylene (for triazines **3d**,**e**,**h**,**j**) or in 1,2-dichlorobenzene (for triazines **3b**,**c**,**f**,**g**,**i**) (25 ml), 2,5-norbornadiene (0.30 ml, 3.0 mmol) was added, and the resulting mixture was refluxed for 36 h with addition of 2,5-norbornadiene (0.15 ml, 1.5 mmol) every 12 h. Solvent was removed under reduced pressure. The product was isolated by column chromatography on silica gel ($CHCl_3$, R_f 0.6). Solvent from fractions containing product was removed under reduced pressure. The residue was recrystallized from EtOH.

2-(4-Chlorophenyl)-5-phenylpyridine (5b). Yield 101 mg (63%), light-yellow crystalline solid, mp 177–179. ^{1}H NMR

spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 7.40–7.46 (1H, m, H Ph); 7.48–7.55 (4H, m, H Ph, C_6H_4Cl); 7.72–7.77 (2H, m, H Ph); 8.02 (1H, d, ^3J = 8.4, H-3); 8.10–8.18 (3H, m, C_6H_4Cl, H-4); 8.94 (1H, d, ^4J = 2.0, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 120.2; 127.0; 128.1; 128.2; 129.0; 129.2; 135.2; 135.2; 135.3; 137.4; 137.5; 148.1; 154.9. Mass spectrum, *m*/*z*: 266 $[M+H]^+$. Found, %: C 76.97; H 4.43; N 5.12. $C_{17}H_{12}ClN$. Calculated, %: C 76.84; H 4.55; N 5.27.

5-(4-Methoxyphenyl)-2-phenylpyridine (5c). Yield 102 mg (65%), yellow amorphous solid, mp 207–208°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.87 (3H, s, CH_3O); 7.00–7.06 (2H, m, $C_6\underline{H}_4OCH_3$); 7.39–7.45 (1H, m, H Ph); 7.46–7.53 (2H, m, H Ph); 7.55–7.61 (2H, m, H Ph); 7.79 (1H, d, ^3J = 8.0, H-3); 7.91 (1H, dd, ^3J = 8.0, ^4J = 2.4, H-4); 8.01–8.07 (2H, m, $C_6\underline{H}_4OCH_3$); 8.91 (1H, d, ^4J = 2.4, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.4; 114.6; 120.3; 126.8; 128.1; 128.8; 128.9; 130.1; 134.6; 139.1; 147.7; 155.6; 159.8. Mass spectrum, *m*/*z*: 262 $[M+H]^+$. Found, %: C 82.61; H 5.85; N 5.24. $C_{18}H_{15}NO$. Calculated, %: C 82.73; H 5.79; N 5.36.

5-(4-Fluorophenyl)-2-phenylpyridine (5d). Yield 95 mg (63%), light-grey amorphous solid, mp 178–180°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.16–7.22 (2H, m, C_6H_4F); 7.40–7.46 (1H, m, Ph); 7.47–7.53 (2H, m, H Ph); 7.57–7.63 (2H, m, C_6H_4F); 7.81 (1H, d, ^3J = 8.0, H-3); 7.91 (1H, dd, ^3J = 8.0, ^4J = 2.4, H-4); 8.02–8.07 (2H, m, H Ph); 8.93 (1H, d, ^4J = 2.4, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 116.1 (d, *J* = 21.1); 120.5; 126.9; 128.7 (d, *J* = 8.1); 128.9; 129.1; 133.7 (d, *J* = 3.1); 134.0; 135.1; 138.8; 147.8; 156.2; 163.0 (d, *J* = 248.4). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –114.24 (s). Mass spectrum, *m*/*z*: 250 $[M+H]^+$. Found, %: C 81.83; H 4.94; N 5.69. $C_{17}H_{12}FN$. Calculated, %: C 81.91; H 4.85; N 5.62.

5-(4-Fluorophenyl)-2-(4-methoxyphenyl)pyridine (5e). Yield 109 mg (65%), yellow amorphous solid, mp 189–191°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.88 (3H, s, OCH_3); 6.99–8.05 (2H, m, $C_6\underline{H}_4OCH_3$); 7.15–7.21 (2H, m, C_6H_4F); 7.55–7.61 (2H, m, C_6H_4F); 7.74 (1H, d, ^3J = 8.0, H-3); 7.88 (1H, dd, ^3J = 8.0, ^4J = 2.4, H-4); 7.97–8.03 (2H, m, $C_6\underline{H}_4OCH_3$); 8.85 (1H, d, ^4J = 2.4, H-6). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 55.7; 114.7; 116.5 (*J* = 21.8); 119.7; 128.3; 129.2 (*J* = 8.2); 131.1; 132.8; 133.9 (*J* = 3.1); 135.4; 147.8; 155.1; 160.7; 162.7 (*J* = 245.6). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –114.43 (s). Mass spectrum, *m*/*z*: 280 $[M+H]^+$. Found, %: C 77.26; H 4.92; N 5.11. $C_{18}H_{14}FNO$. Calculated, %: C 77.40; H 5.05; N 5.01.

5-(4-Fluorophenyl)-2-(thiophen-2-yl)pyridine (5f). Yield 94 mg (61%), light-yellow crystalline solid, mp 169–171°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.12–7.21 (3H, m, H thienyl, C_6H_4F); 7.40–7.44 (1H, m, H thienyl); 7.53–7.60 (2H, m, C_6H_4F); 7.60–7.64 (1H, m, H thienyl); 7.72 (1H, d, ^3J = 8.0, H-3); 7.84 (1H, dd, ^3J = 8.0, ^4J = 2.0, H-4); 8.77 (1H, d, ^4J = 2.0, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 116.1 (d, *J* = 21.3); 118.7; 124.7; 127.8; 128.2; 128.5 (d, *J* = 8.0); 133.6 (d, *J* = 3.7); 133.7; 134.8; 144.5; 147.7; 151.4; 162.9 (d, *J* = 248.2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –114.17 (s). Mass spectrum, *m*/*z*: 256 $[M+H]^+$. Found, %: C 70.51; H 4.08; N 5.34. $C_{15}H_{10}FNS$. Calculated, %: C 70.57; H 3.95; N 5.49.

2-(4-Chlorophenyl)-5-(4-fluorophenyl)pyridine (5g). Yield 116 mg (68%), light-yellow crystalline solid mp 173–175°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 7.25–7.32 (2H, m, C_6H_4F); 7.47–7.53 (2H, m, C_6H_4Cl); 7.75–7.82 (2H, m, C_6H_4F); 8.02 (1H, d, ^3J = 8.4, H-3); 8.11 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-4); 8.12–8.17 (2H, m, C_6H_4Cl); 8.92 (1H, d, ^4J = 2.4, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 116.2 (d, *J* = 21.6); 120.2; 128.1; 128.7 (d, *J* = 8.0); 129.0; 133.3 (d, *J* = 3.1); 134.3; 135.1; 135.2; 137.3; 148.0; 154.9; 163.0 (d, *J* = 248.2). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –114.12 (s). Mass spectrum, *m*/*z*: 284 $[M+H]^+$. Found, %: C 72.08; H 4.02; N 4.81. $C_{17}H_{11}ClFN$. Calculated, %: C 71.96; H 3.91; N 4.94.

5-(3-Fluorophenyl)-2-phenylpyridine (5h). Yield 92 mg (61%), yellow amorphous solid, mp 186–188°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.08–7.14 (1H, m, C_6H_4F); 7.31–7.36 (1H, m, C_6H_4F); 7.40–7.54 (5H, m, C_6H_4F, H Ph); 7.83 (1H, d, ^3J = 8.0, H-3); 7.94 (1H, dd, ^3J = 8.0, ^4J = 2.4, H-4); 8.03–8.08 (2H, m, H Ph); 8.92 (1H, d, ^4J = 2.4, H-6). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 114.0 (d, *J* = 22.6); 115.4 (d, *J* = 21.6); 120.6; 123.3 (d, *J* = 2.1); 127.0; 129.3; 129.7; 131.6 (d, *J* = 8.5); 133.3 (d, *J* = 2.1); 135.8; 138.6; 139.7 (d, *J* = 7.7); 148.2; 155.8; 163.3 (d, *J* = 244.1). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –112.25 (s). Mass spectrum, *m*/*z*: 250 $[M+H]^+$. Found, %: C 82.79; H 4.78; N 5.64. $C_{17}H_{12}FN$. Calculated, %: C 81.91; H 4.85; N 5.62.

5-(3-Fluorophenyl)-2-(4-methoxyphenyl)pyridine (5i). Yield 103 mg (61%), yellow amorphous solid, mp 192–194°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.89 (3H, s, OCH_3); 7.00–7.05 (2H, m, $C_6\underline{H}_4OCH_3$); 7.07–7.13 (1H, m, C_6H_4F); 7.30–7.35 (1H, m, C_6H_4F); 7.39–7.49 (2H, m, C_6H_4F); 7.78 (1H, d, ^3J = 8.0, H-3); 7.93 (1H, dd, ^3J = 8.0, ^4J = 2.4, H-4); 8.00–8.05 (2H, m, $C_6\underline{H}_4OCH_3$); 8.89 (1H, d, ^4J = 2.4, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 55.4; 113.8 (d, *J* = 22.8); 114.3; 114.8 (d, *J* = 21.7); 119.7; 122.6 (d, *J* = 3.0); 128.3; 130.7 (d, *J* = 8.4); 131.1; 133.0 (d, *J* = 2.2); 135.3; 139.9 (d, *J* = 8.4); 147.6; 156.3; 160.8; 163.3 (d, *J* = 247.2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –49.50 (s). Mass spectrum, *m*/*z*: 280 $[M+H]^+$. Found, %: C 77.51; H 5.17; N 5.13. $C_{18}H_{14}FNO$. Calculated, %: C 77.40; H 5.05; N 5.01.

5-(3-Fluorophenyl)-2-(thiophen-2-yl)pyridine (5j). Yield 98 mg (64%), yellow crystalline solid, mp 176–178°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.06–7.16 (2H, m, H thienyl, C_6H_4F); 7.28–7.33 (1H, m, C_6H_4F); 7.36–7.41 (1H, m, C_6H_4F); 7.41–7.49 (2H, m, H thienyl, C_6H_4F); 7.61–7.65 (1H, m, H thienyl); 7.73 (1H, d, ^3J = 8.0, H-3); 7.87 (1H, dd, ^3J = 8.0, ^4J = 2.0, H-4); 8.80 (1H, d, ^4J = 2.0, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 113.7 (d, *J* = 21.9); 114.9 (d, *J* = 21.2); 116.7; 122.5 (d, *J* = 3.1); 124.9; 127.9; 128.2; 130.7 (d, *J* = 8.8); 133.4 (d, *J* = 2.2); 134.9; 139.8 (d, *J* = 7.2); 144.4; 147.8; 152.0; 163.3 (d, *J* = 246.5). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –112.18 (s). Mass spectrum, *m*/*z*: 256 $[M+H]^+$. Found, %: C 70.63; H 3.87; N 5.54. $C_{15}H_{10}FNS$. Calculated, %: C 70.57; H 3.95; N 5.49.

Synthesis of pyridines 6c,f (General method V). The mixture of the corresponding triazine **3c** or **3f** (0.5 mmol)

and 1-morpholinocyclopentene (0.40 ml, 2.5 mmol) was stirred at 200°C for 2 h under argon atmosphere. Then the additional portion of 1-morpholinocyclopentene (0.20 ml, 1.25 mmol) was added and the resulting mixture was stirred for additional 1 h at the same conditions. The reaction mass was cooled to room temperature. The products were separated by flash chromatography on silica gel (DCM as eluent, R_f 0.6) and then were purified by recrystallization (EtOH).

4-(4-Methoxyphenyl)-1-phenyl-5*H*,6*H*,7*H*-cyclopenta-[*c*]pyridine (6c). Yield 62 mg (41%), light-grey crystalline solid, mp 169–171°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.01–2.12 (2H, m, 6-CH_2); 3.05 (2H, t, ^3J = 7.6, 7-CH_2); 3.17 (2H, t, ^3J = 7.6, 5-CH_2); 3.88 (3H, s, OCH_3); 6.99–7.04 (2H, m, $C_6\underline{H}_4OCH_3$); 7.37–7.51 (5H, m, H Ph); 7.81–7.82 (2H, m, $C_6\underline{H}_4OCH_3$); 8.54 (1H, s, H-3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 25.9; 32.9; 33.1; 55.7; 114.7; 128.6; 128.7; 128.7; 129.8; 130.1; 132.2; 137.6; 140.1; 146.9; 151.9; 152.4; 159.4. Mass spectrum, *m*/*z*: 302 $[M+H]^+$. Found, %: C 83.82; H 6.48; N 4.52. $C_{21}H_{19}NO$. Calculated, %: C 83.69; H 6.35; N 4.65.

4-(4-Fluorophenyl)-1-(thiophen-2-yl)-5*H*,6*H*,7*H*-cyclopenta[*c*]pyridine (6f). Yield 71 mg (48%), light-grey crystalline solid, mp 155–157°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.21–2.22 (2H, m, 6-CH_2); 3.02 (2H, t, ^3J = 7.6, 7-CH_2); 3.26 (2H, t, ^3J = 7.6, 5-CH_2); 7.12–7.19 (3H, m, H thienyl, C_6H_4F); 7.39–7.45 (3H, m, H thienyl, C_6H_4F); 7.52–7.55 (1H, m, H thienyl); 8.42 (1H, s, H-3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 25.0; 32.6; 33.2; 115.7 (d, *J* = 21.9); 126.2; 127.4; 128.0; 130.1 (d, *J* = 8.4); 131.4; 133.8 (d, *J* = 3.0); 135.3; 145.1; 146.7; 147.3; 152.7; 162.5 (d, *J* = 247.6). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –114.41 (s). Mass spectrum, *m*/*z*: 296 $[M+H]^+$. Found, %: C 73.32; H 4.89; N 4.61. $C_{18}H_{14}FNS$. Calculated, %: C 73.19; H 4.78; N 4.74.

The X-ray diffraction analyses of compounds 3b, 4e, and 5g were carried out using equipment of the Center for Joint Use "Spectroscopy and Analysis of Organic Compounds" at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch). The experiments were accomplished on the automated X-ray diffractometer Xcalibur 3 with CCD detector on standard procedure (Mo*K*α irradiation, graphite monochromator, ω-scans with 1° step at 295(2)K). Empirical absorption correction was applied. The solution and refinement of the structures were accomplished using the Olex2 program package.[35] The structures were solved by direct method in the ShelXS program and refined by the ShelXL by full-matrix least-squared method in anisotropic approximation for non-hydrogen atoms.[36] The H atoms were placed in the calculated positions and were refined in the isotropic approximation.

Compound 3b. Crystal data for $C_{15}H_{10}ClN_3$ (*M* 267.71 g/mol): monoclinic, space group $P2_1/n$; *a* 11.8295(10), *b* 7.6753(7), *c* 27.459(2) Å; β 95.589(7)°; *V* 2481.3(4) Å^3; *Z* 8, *T* 295(2)K, μ(Mo*K*α) 0.295 mm^{-1}; D_{calc} 1.433 g/cm^3. 16864 Reflections measured (2.76° ≤ Θ ≤ 29.14°), 6240 unique (R_{int} 0.0478, R_{sigma} 0.0942) and 2391 reflections with $I > 2\sigma(I)$ which were used in all calculations. The final R_1 0.0488 ($I > 2\sigma(I)$) and wR_2 0.0804 (all data), *GOOF* 1.007. Largest difference peak/hole 0.240/–0.250 ēÅ^{-3}.

Compound 4e. Crystal data for $C_{16}H_{12}FN_3O_2$ (*M* 297.29 g/mol): monoclinic, space group $P2_1/n$; *a* 12.4029(16), *b* 6.5008(5), *c* 17.2879(17) Å; β 106.773(12)°; *V* 1334.6(2) Å^3; *Z* 4; *T* 295(2)K; μ(Mo*K*α) 0.110 mm^{-1}; D_{calc} 1.480 g/cm^3. 5202 Reflections measured (4.76° ≤ Θ ≤ 54.2°), 2915 unique (R_{int} 0.0515, R_{sigma} 0.1421) and 1141 reflections with $I > 2\sigma(I)$ which were used in all calculations. The final R_1 0.0613 ($I > 2\sigma(I)$) and wR_2 0.1265 (all data), *GOOF* 0.964. Largest difference peak/hole 0.17/–0.20 ēÅ^{-3}.

Compound 5g. Crystal data for $C_{17}H_{11}ClFN$ (*M* 283.72 g/mol): orthorhombic, space group *Pbca*; *a* 10.0665(12), *b* 10.1880(12), *c* 26.244(4) Å; β 90°; *V* 2691.6(6) Å^3; *Z* 8; *T* 295(2)K; μ(Mo*K*α) 0.283 mm^{-1}; D_{calc} 1.400 g/cm^3. 14676 Reflections measured (7.354° ≤ Θ ≤ 56.564°), 3280 unique (R_{int} 0.0571, R_{sigma} 0.0407) and 1943 reflections with $I > 2\sigma(I)$ which were used in all calculations. The final R_1 0.0574 ($I > 2\sigma(I)$) and wR_2 0.1974 (all data), *GOOF* 1.043. Largest difference peak/hole 0.19/–0.29 ēÅ^{-3}.

The final atomic coordinates and crystallographic data for compounds **3b**, **4e**, and **5g** have been deposited at the Cambridge Crystallographic Data Center (deposits CCDC 2298502, CCDC 2309894, and CCDC 2309892, respectively).

Supplementary information file containing ^{1}H, ^{13}C, and ^{19}F NMR spectra of compounds **3b–j**, **4a–j**, **5b–j**, **6c**,**f**, the selected bond distances and angles for compound **3b**, and additional photophysical data for compounds **6c**,**f**, is available at the journal website http://hgs.osi.lv.

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