Tetrahedron 64 (2008) 8963–8973

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Facile synthesis of 6-aryl-3-pyridyl-1,2,4-triazines as a key step toward highly fluorescent 5-substituted bipyridines and their Zn(II) and Ru(II) complexes

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ARTICLE INFO

Article history:
Received 4 February 2008
Received in revised form 26 May 2008
Accepted 12 June 2008
Available online 14 June 2008

Keywords:
2,2′-Bipyridines
1,2,4-Triazines
Luminescence

ABSTRACT

A wide series of substituted bipyridines were obtained through the synthesis of 1,2,4-triazines and their aza Diels–Alder reactions. The reported method facilitates the synthesis of functionally diverse bipyridines that provides fine-tuning of photophysical properties of new ligands and their Zn(II) and Ru(II) complexes. Some of substituted bipyridines exhibit 'off–on' fluorescence response toward Zn^{2+} cations.

1. Introduction

2,2′-Bipyridines (bpy) are undoubtedly among the most widely used ligands in coordination and supramolecular chemistry.[1] The photophysical properties of their metal complexes are of special interest. In particular, electroluminescent chelate complexes have been shown to be useful in organic light emitting diodes (OLEDs).[2] Ruthenium complexes of functionalized bipyridines are presently the most effective sensitizers for dye-sensitized solar cells (DSSCs).[3]

A critical element in designing and fabricating materials for OLEDs is the control of their emission wavelength.[4] One of the approaches for controlling the emitted color of organic materials is to append fluorescent chromophores to a polymeric backbone or to blend such dyes into inert polymeric matrices.[5,20] Ideally, one would like to utilize one family of modular chromophores and tune their photophysical characteristics as required.[6] The parent oligopyridines (2,2′-bipyridine, 2,2′:6′,2″-terpyridine, and 1,10-phenanthroline) possess extremely low fluorescence quantum yields and undesirable short emission wavelengths. Introduction of conjugated electron donor moieties, e.g., pyrrolylethenyl,[7] phenylethynyl,[11c] aminophenyl,[8] or manisyl (4-methoxy-2,6-dimethylphenyl)[9] leads to an increase in quantum yields and a shift in emission wavelength in the visible area. Since the most intense electronic transition of the 2,2′-bipyridine skeleton is polarized along the 5,5′ positions,[9] the 5 position of bipyridines is considered the best for introduction of aromatic substituents. As an example 5-manisyl-2,2′-bipyridines have been previously shown to exhibit higher emission quantum yields compared with the 2- and 4-manisyl analogs.[9] In addition, an aryl moiety at the β-position does not affect the coordination behavior of the ligand. DSSCs are in principle the opposite of OLEDs, producing electrical energy from photonic energy. However, since a sensitizer in DSSC must effectively absorb sunlight, conjugated aromatic substituents in bipyridine are desirable at position 4 or 5. The position 5 is more preferable due to the reasons mentioned above. Although existing methods for the synthesis of symmetrically functionalized 2,2-bipyridines permit the elaboration of many different derivatives, the synthesis of bipyridines with differently functionalized pyridine subunits is still not common. Only a very few examples of the synthesis of unsymmetrically substituted 5-arylbipyridines are known.[9,10] They involve a sequence of the cross-coupling reactions and/or require not easily accessible starting materials. Therefore, it is of no surprise that most researchers focus their interest on the use of more readily accessible 4,4′-disubstituted 2,2′-bipyridines.

2. Results and discussion

One of the most promising pathways toward unsymmetrically substituted bipyridines is the [4+2] cycloaddition of tailor-made 1,2,4-triazines.[11] Based on this strategy, we report here an efficient

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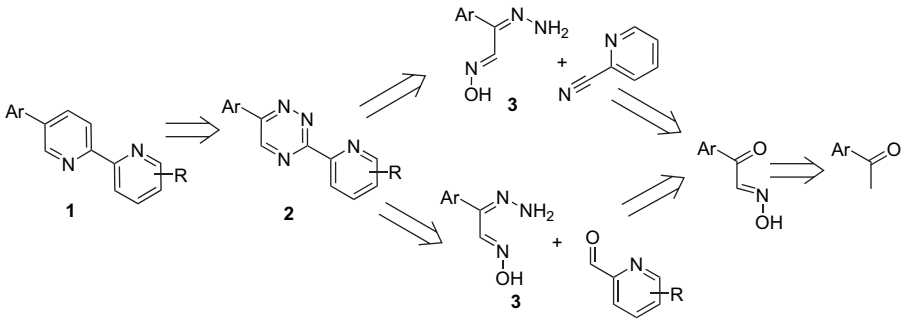
doi:10.1016/j.tet.2008.06.040



Scheme 1. Retrosynthetic analysis of arylbipyridines **1**.

method for the synthesis of 5-(hetero)aryl-2,2′-bipyridines **1**. The key idea is as follows: if suitable 2-pyridyl-substituted 1,2,4-triazines were readily accessible starting materials, the cycloaddition reaction with 2,5-norbornadiene would accomplish two goals. First, the triazine ring could be transformed into the desired pyridine core. Secondly, the position of an aryl substituent in the pyridine ring can be controlled by the structure of the 1,2,4-triazine starting material. The synthesis of bipyridine **1** was planned as shown in Scheme 1.

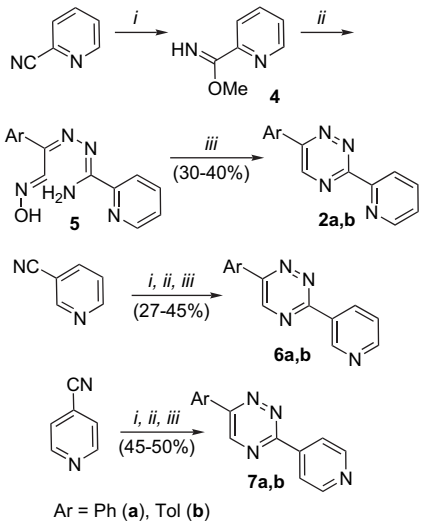
A potential problem arises for 1,2,4-triazines bearing a pyridine residue at the position 3, a (hetero)aromatic substituent at position 6, but no substituent at position 5. Double condensation of the appropriate carbamidrazones with 1,2-dicarbonyl compounds provides one of the most straightforward syntheses of 1,2,4-triazines. In this procedure, α-ketoaldehydes normally give 5-substituted 1,2,4-triazines.[12] The obvious reason for such regioselectivity is that the first condensation of the amino group of the amidrazone proceeds on the more reactive aldehyde group of the α-ketoaldehyde followed by the second condensation on the ketone carbonyl. To change this regioselectivity one can substitute the formyl group with a less active substituent. Recently a method for the synthesis of 6-phenyl-3-(2-pyridyl)-1,2,4-triazine has been reported, where α-hydroxyacetophenone was used for the condensation with the pyridylamidrazone.[13] In this case, the formyl group was formed by the oxidation of the hydroxyl group after the first condensation. Earlier we communicated an alternative strategy for the synthesis of 3-pyridyl-6-aryl-1,2,4-triazines.[14] We decided to use 1-aryl-1-hydrazono-2-oximinoethanes as the starting material. The oximinohydrazones were obtained from readily available acyl(hetero)arenes through nitrosation with ^{i}PrONO and reaction of the oximinoketones with hydrazine hydrate. This sequence of reactions determines unambiguously the position of the aromatic substituent in the assembled 1,2,4-triazine.

Herein we describe two methods for the synthesis of triazines **2** starting from oximinohydrazones **3**: [4+2] cycloaddition with cyanopyridines (four atoms of the triazine ring, N-2, N-1, C-6, C-5 fragments, are introduced with the oximinohydrazone and two atoms, C-3, N-4 fragments—with the nitrile group of the cyanopyridine) and [5+1] cycloaddition with pyridinecarboxaldehydes (five atoms of the triazine ring, N-2, N-1, C-6, C-5, N-4 fragments, are introduced with the oximinohydrazone and one atom, C-3—with the aldehyde group of the pyridinecarboxaldehyde). However, 2-cyanopyridine itself did not react with the oximinohydrazones **3**. Thus we decided to use methoxyimidate **4** obtained in situ from 2-cyanopyridine in MeOH in the presence of MeONa. Addition of the oximinohydrazones **3** to the mixture obtained resulted in an open-chain product **5**. The latter was used without purification and gave after refluxing in AcOH the desired aryltriazines **2a**,**b** in moderate yields. By following an identical procedure with 3- and 4-cyanopyridine the triazines **6a**,**b** and **7a**,**b** were obtained in 27–50% yields (Scheme 2).

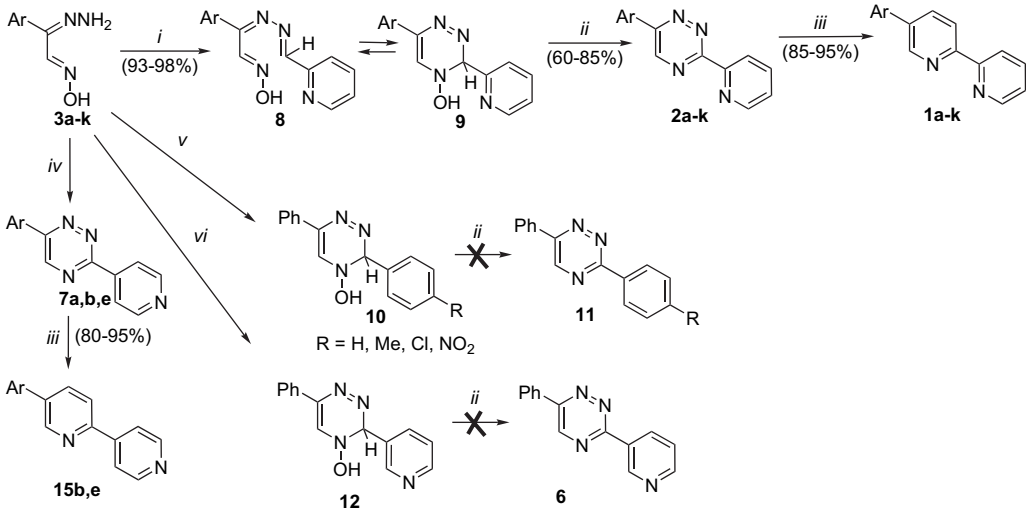
The suggested [5+1] cycloaddition was found to be more effective. Condensation of oximinohydrazones **3** with pyridine-2-carboxaldehyde gave 1-aryl-2-oximino-1-(2-pyridylmethylenehydrazono)ethanes **8** in excellent yields. Open-chain hydrazones **8** exist in solutions in equilibrium with the cyclic 6-aryl-4-hydroxy-3-(2-pyridyl)-3,4-dihydro-1,2,4-triazines **9** (according to NMR spectroscopic data), which is typical for 4-hydroxy-3,4-dihydro-1,2,4-triazines.[15] In spite of the ratio of open-chain and cyclic isomers in the mixture, dehydration of **9** should lead to the desired triazines **2**.

Indeed, heating the mixture of isomers in acetic acid for a short time gave pyridyltriazines **2** in good yields (Scheme 3). Isolation of the intermediates **8** and **9** from the reaction mixtures can be omitted to make the synthetic procedure easier. Keeping in mind that acetylarenes are quite accessible starting materials one can realize that the approach allows an easy synthesis of a series of pyridyltriazines with a variety of aromatic substituents. The same procedure was applied to the reaction of hydrazones **3** with pyridine-4-carboxaldehyde to give 3-(4-pyridyl)-1,2,4-triazines **7** in good yields (Scheme 3).

It should be noted that oxidative aromatization of dihydrotriazines like **9** is a useful method for the synthesis of 3,6-susbtituted 1,2,4-triazine 4-oxides,[15] while the dehydration of **9** has not been previously observed. Indeed, we found that prolonged heating of 3-aryl-4-hydroxy-3,4-dihydro-1,2,4-triazines **10** in acetic acid did not result in aromatic 1,2,4-triazines **11**, only starting materials were isolated. Furthermore, when the product of condensation of hydrazone **3** with pyridine-3-carboxaldehyde—dihydrotriazine **12** was heated in acetic acid, 3-(3-pyridyl)-1,2,4-triazine **6** did not



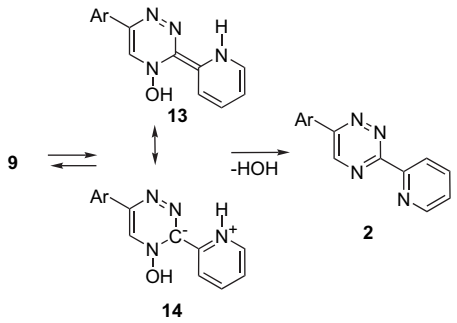
Scheme 2. Reagents and conditions: (i) MeONa/MeOH, 23 °C, 1 h; (ii) hydrazone **3**, MeOH, 23 °C, 1 h; (iii) AcOH, refluxing, 0.5 h.



Ar = Ph (**a**), 4-Me-C_6H_4 (**b**), 4-MeO-C_6H_4 (**c**), 4-Cl-C_6H_4 (**d**), 4-Br-C_6H_4 (**e**), 3,4-Cl_2-C_6H_3 (**f**), 4-NO_2-C_6H_4 (**g**), 2-pyridyl (**h**), 4-pyridyl (**i**), thienyl-2 (**j**), naphthyl-2 (**k**)

Scheme 3. Reagents and conditions: (i) pyridyl-2-carboxaldehyde, EtOH; (ii) AcOH, 90 °C, 1 h; (iii) 2,5-norbornadiene, *o*-xylene, reflux, 24 h; (iv) pyridyl-4-carboxaldehyde, AcOH, rt, 1 h then 90 °C, 1 h; (v) R–C_6H_4–CHO, EtOH; (vi) pyridyl-3-carboxaldehyde, EtOH.

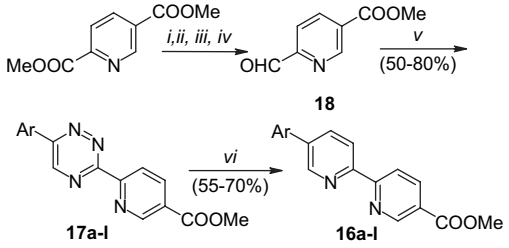
form. Thus aromatization of 4-hydroxy-3,4-dihydro-1,2,4-triazines via dehydration is possible under the following conditions: (1) the pyridine residue is at position 3 of the triazine ring; (2) a nitrogen atom is in α- and γ-position of the pyridyl group. Such selectivity in the dehydration step can be explained by the formation of en-amine **13** from dihydrotriazine **9** as the first step of the reaction. The en-amine **13** can be represented as Zwitterion **14**, which under acidic conditions loses the hydroxyl group to give aromatic triazine **2**. This process can be considered as an E1cb elimination of water (2-pyridyl as an internal base) (Scheme 4).



Scheme 4. Mechanism of the cyclization of 1,2,4-triazines.

With the desired 1,2,4-triazines now readily available, the aza Diels–Alder reactions planned with 2,5-norbornadiene were carried out under forcing conditions (8–15 h reflux in *o*-xylene) to give the desired 2,2′-bipyridines **1** and 2,4′-bipyridines **15** in 80–95% yields (Scheme 3). It is noteworthy that the reactions are easily scaled up to produce multi-gram quantities of bipyridines **1** (we obtained 5 g of bipyridine **1b** from a single operation). The forcing conditions did not affect the yields or purities of bipyridines **1**.

Encouraged by these results, we investigated the synthesis of unsymmetrically substituted 2,2′-bipyridines by the method. Using substituted pyridinecarboxaldehydes is an additional means of providing diverse arylbipyridines. We decided to explore this by the synthesis of arylbipyridines bearing a carboxylate group, because of the importance of bipyridinecarboxylic acids as building blocks for supramolecular chemistry.[16] 5-Aryl-5′-methoxycarbonyl-2,2′-bipyridines **16a–l** were synthesized by the same route through formation of intermediate 6-aryl-3-(5′-methoxycarbonyl-2-pyridyl)-1,2,4-triazines **17a–l** (Scheme 5). The key reagent in this case is 5-methoxycarbonylpyridine-2-carboxaldehyde **18**, which was obtained from pyridine-2,5-dicarboxylic acid by esterification, mono reduction of α-carboxylate and oxidation using SeO_2.

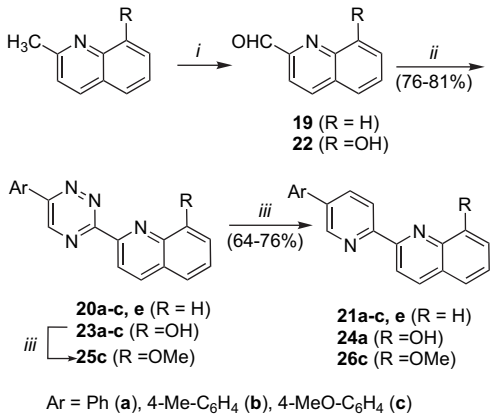


Ar = Ph (**a**), 4-Me-C_6H_4(**b**), 4-MeO-C_6H_4(**c**), 4-Cl-C_6H_4(**d**), 4-Br-C_6H_4(**e**), 4-pyridyl (**i**), 2-naphthyl (**k**), 1-naphthyl (**l**)

Scheme 5. Reagents and conditions: (i) $SOCl_2$; (ii) MeOH, reflux; (iii) $NaBH_4$, MeOH/THF, 0 °C; (iv) MnO_2, $CHCl_3$, reflux, 3–4 h; (v) hydrazone **3**, AcOH, 23 °C, 1 h then 90 °C, 1 h; (vi) 2,5-norbornadiene, *o*-xylene, reflux, 20 h.

Unsymmetrically substituted quinoline analogs of bipyridines can be obtained by the reported method. In this case, quinoline-2-carboxaldehyde **19** (available from quinaldine) was used as the starting material. The reaction of **19** with oximinohydrazones **3** afforded 3-quinolyl-1,2,4-triazines **20a–c** (Scheme 6). Refluxing triazines **20a–c** with norbornadiene in xylene gave 2-(5-aryl-2-pyridyl)quinolines **21a–c** in 50–70% total yield. However, it was interesting to apply the described method to the synthesis of analogs of the widely used ligand 8-hydroxyquinoline. Starting from 8-hydroxyquinoline-2-carboxaldehyde, **21** was obtained by allylic oxidation of the accessible 8-hydroxy-2-methylquinoline using SeO_2.[17] The cyclization reactions of **21** with hydrazones **3** gave hydroxyquinolyltriazines **23** in high yields. The following aza Diels–Alder reactions of triazine **23a** with 2,5-norbornadiene afforded the desired 2-(5-aryl-2-pyridyl)-8-hydroxyquinoline **24a** (Scheme 6).

Table 1 summarizes the photophysical data of new bipyridines in acetonitrile solutions. Lowest energy absorption maxima of 2,2′-bipyridines **1**, **16** are not affected by the nature of the aryl



Scheme 6. i) SeO_2, dioxane, 80 °C, 16–20 h; (ii) hydrazone **3**, AcOH, 23 °C, 1 h, then 90 °C, 1 h; (iii) 2,5-norbornadiene, *o*-xylene, reflux, 20 h.

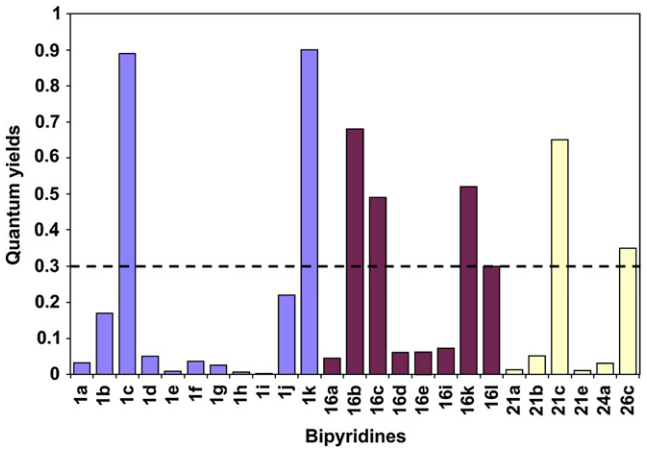


Figure 1. Quantum yields of new aryl-2,2′-bipyridines.

substituents and lie in the interval of wavelength of 298–326 nm. On the other hand, the substituents control the emission maxima (298–438 nm) and quantum yields (0.002–0.90) (Table 1). All new bipyridines can be divided into two groups: exhibiting weak fluorescence (Φ_F<0.20) with short Stoke's shifts (50–60 nm) and bright emitting (Φ_F>0.30) with large Stoke's shifts (80–130 nm) (Fig. 1). Increasing polarization along 5,5′-axis of the bipyridine moiety (introduction of electron-donating aryl substituents at the position 5 and/or electron-withdrawing ester group at the position 5′) results in red shifts of emission maxima and increasing fluorescence quantum efficiency. Observing difference in luminescence means that a difference in the nature of the excited states of these two groups of bipyridines is observed. It was considered to be n–π*, π–π*, and intraligand charge transfer (ICT) excited states. DFT calculation (B3LYP/6-31G**) was carried out on bipyridine **1b** (from the first group) and **16b** (from the second group). The results for **1b** show that both HOMO and LUMO having π character are delocalized over the whole conjugated system and can be denoted as π and π*, respectively (Fig. 2). Apparently, lone pairs of nitrogen atoms substantially contribute to the second HOMO (HOMO-1), which can be denoted as *n*-orbital. This shows competition between n–π* and π–π* excited states, and there is no ICT from HOMO to LUMO. Contrary to that, excitation of **16b** leads to the ICT from the HOMO localized on the aryl substituent and the central pyridine to the LUMO localized on the pyridine and ester group (Fig. 2).

The lowest energy absorbance maxima of bipyridines of both groups display a very small red shift upon increasing solvent polarity. Solvent polarity has little influence on the emission maxima of bipyridines of the first group. For example, **1a** and **21a** exhibit a very weak emission. Fluorescence maxima of phenyl derivatives **1a** and **21a** undergo slight red shifts upon increasing solvent polarity (8–12 nm on comparing emission maxima in toluene and methanol). This behavior can be explained by close proximity of the

Table 1
Photophysical data for new arylbipyridines

Compound	Ar	λ_{max}[a] [nm]	λ_{em}[b] [nm]	(Φ_F)[c]	λ_{max} (Zn^{2+})[d] [nm]	λ_{em} (Zn^{2+})[e] [nm]
1a	Ph	298	357	0.032	322	378, $430_{sh.}$
1b	Tol	302	360	0.17	326	403, $423_{sh.}$
1c	4-MeO–C_6H_4	309	399	0.89	339	460, 512_{sh}
1d	4-Cl–C_6H_4	301	354	0.050	326	401
1e	4-Br–C_6H_4	299	355	0.008	322	397
1f	3,4-Cl_2–C_6H_3	300	357	0.036	320	380
1g	4-NO_2–C_6H_4	320	377	0.025	322	396, 435
1h	2-Pyridyl	305	365	0.006	319	371
1i	4-Pyridyl	298	385	0.002	316	354
1j	2-Thienyl	322	375	0.22	344	437
1k	2-Naphthyl	312	378	0.90	326	467, 517
16a	Ph	312	380	0.045	328	410, 430
16b	Tol	317	395, $430_{sh.}$	0.68	339	438
16c	4-MeO–C_6H_4	326	438, $510_{sh.}$	0.49	355	520
16d	4-Cl–C_6H_4	313	376	0.061	333	434
16e	4-Br–C_6H_4	313	378	0.062	332	432
16i	4-Pyridyl	308	350	0.072	324	352, 364
16k	2-Naphthyl	322	435	0.52	335	520
16l	1-Naphthyl	306	438	0.30	344	530
21a	Ph	$315_{sh.}$, 324, $340_{sh.}$	370	0.012	359	400, 430
21b	Tol	$315_{sh.}$, 326, $342_{sh.}$	377, $429_{sh.}$	0.051	360	436, $510_{sh.}$
21c	4-MeO–C_6H_4	$318_{sh.}$, 328, $342_{sh.}$	432	0.65	367	520
21e	4-Br–C_6H_4	$315_{sh.}$, 326, $340_{sh.}$	367	0.010	358	434
24a	Ph	295, 326	377	0.030	312, 358	—
26c	4-MeO–C_6H_4	335	434	0.35	375	525

[a] Absorption maxima in MeCN.
[b] Emission maxima in MeCN.
[c] Fluorescence quantum yields were measured using anthracene as the standard (Φ=0.27 in EtOH[20]).
[d] Absorption maxima in MeCN after addition of excess $Zn(ClO_4)_2$.
[e] Emission maxima in MeCN after addition of excess $Zn(ClO_4)_2$.

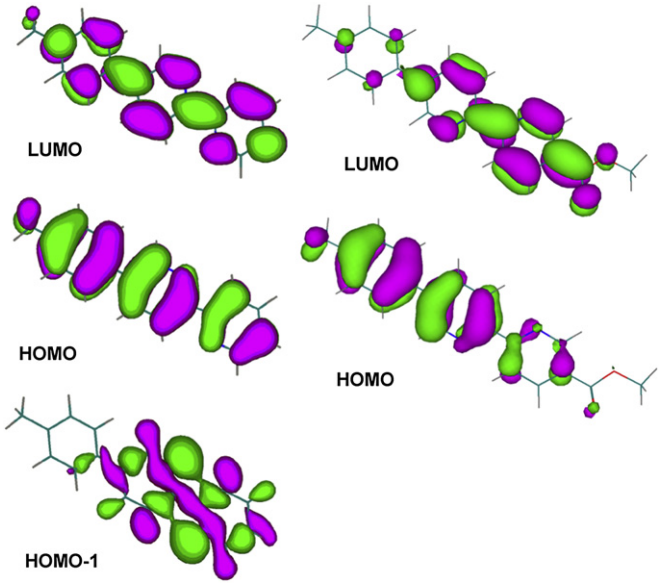


Figure 2. Pictorial presentation of HOMO and LUMO of **1b** (left) and **16b** (right) calculated at the B3LYP/6-31G** .

n–π* and π–π* excited states. Greater contribution of the n–π* excited state in fluorescence leads to low emission quantum yield, since the n–π* excited state often decays through nonradiative pathways. In contrast, emission maxima of bipyridines of the second group are affected considerably by solvent polarity. For example, large red shifts were observed for bright fluorescence of **16b** upon increasing solvent polarity (60 nm on comparing emission maxima in benzene and methanol) (Fig. 3). This indicates great contribution of the ICT excited state to emission of **16b**. Fluorescent spectra of **16b** recorded in different solvents can be split into two overlapping components: the short-wavelength band of emission from the π–π* excited state, and the long-wavelength band of emission from ICT excited state. The latter increases with increasing solvent polarity (Fig. 3).

Co-ordination metal ion, e.g., Zn^{2+}, involves the lone pairs of the nitrogen atoms of bipyridines and excludes n–π* transitions, resulting in intensive fluorescence from π–π* excited states.[18] Indeed, addition of excess $Zn(ClO_4)_2$ to the solutions of bipyridines of the first group leads to moderate red shifts of the emission maxima (20–60 nm) and significant enhanced emission intensity. Titrating

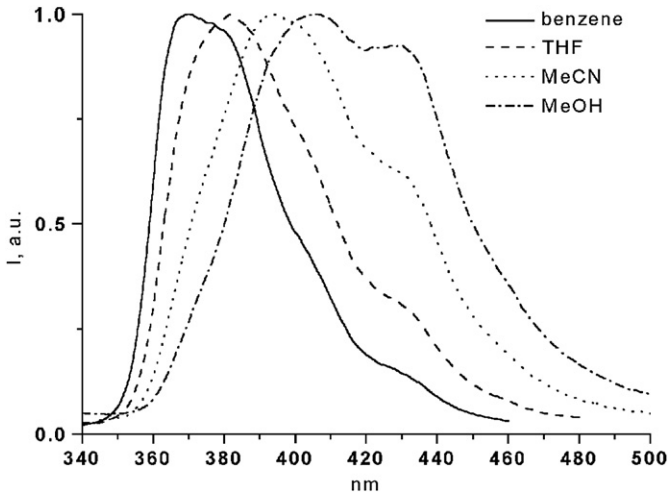


Figure 3. Fluorescence spectra of **16b** recorded in different solvents.

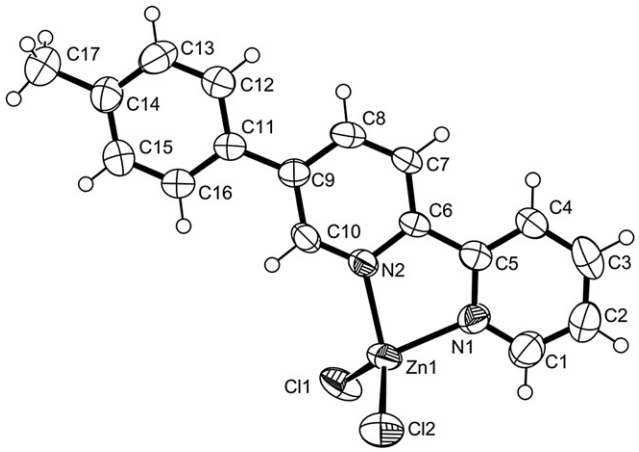


Figure 4. ORTEP view of [Zn(**1b**)Cl_2]. Selected bond lengths, (Å): Zn(1)–N(1) 2.093, Zn(1)–N(2) 2.078, Zn(1)–Cl(1) 2.243, Zn(1)–Cl(2) 2.232.

$Zn(ClO_4)_2$ into solutions of bipyridines of the second group resulted in larger red shifts of the emission maxima (60–100 nm) and somewhat decreasing fluorescence intensity (Table 1).

We isolated complex [Zn(**1b**)Cl_2] from the reaction of **1b** with $ZnCl_2$. Single crystals of [Zn(**1b**)Cl_2] suitable for X-ray diffraction were grown from acetonitrile. The molecular structure of the complex [Zn(**1b**)Cl_2] is shown in Figure 4, and selected bond distances are given in the caption. The bipyridine fragment is planar (torsion angle is 5.26°), the torsion angle between the pyridine ring and the aromatic substituent is 10.43°. The Zn atom adopts a tetrahedral coordination geometry. Complex face-to-face π–π stacking interactions between the phenylbipyridine ligands are also evident, the interplanar separations are in the range 3.5 Å, and the glide-related complexes are linked in a head-to-tail fashion to generate a supramolecular architecture of infinite chains (see Supplementary data).

Many of the bipyridines of the first group can be assumed as potential 'off–on' fluorescent probes for Zn(II) ions. For example, titrating $Zn(ClO_4)_2$ into a 1 μM solution of pyridylquinoline **21a** in acetonitrile shows increasing emission intensity by a factor 200 (excitation at the isobestic point 333 nm) measured at the complex emission maximum (430 nm) (Fig. 5). Other transition metal ions (Ni^{2+}, Cu^{2+}, Co^{2+}) quench the emission of **21a** and any other new bipyridines.

Reactions of new bipyridines **1**, **16** with $Ru(bpy)_2Cl_2$ followed by treatment of the reaction mixtures with NH_4PF_6 resulted in the formation of the corresponding complexes [$Ru(bpy)_2$(**1a**–**e**,**i**)]$(PF_6)_2$ and [$Ru(bpy)_2$(**16a**–**c**)]$(PF_6)_2$. These complexes exhibit typical for polypyridine-Ru(II) complexes photophysical properties (Table 1). Lowest energy absorption bands for the complexes are centered around 450 nm that is very similar to absorption of parent [$Ru(bpy)_3$]$(PF_6)_2$.[19] Fluorescence maxima of new complexes are red shifted in comparison with those of [$Ru(bpy)_3$]$(PF_6)_2$. The presence of the electron-withdrawing ester group in bipyridines **16a**–**c** stabilizes MLCT excited states and causes larger red shifts (56–60 nm).

3. Conclusions

The relatively simple synthesis and availability of numerous precursors enable the preparation of 5-aryl-2,2′-bipyridines. Structural diversity leads to fine-tunable chromophores with diverse photophysical properties, where changes in the substitution patterns, solvation, and co-ordination are translated into dramatic spectral changes. Unique selective responses allow new ligands to be considered as sensitive probes for zinc(II).

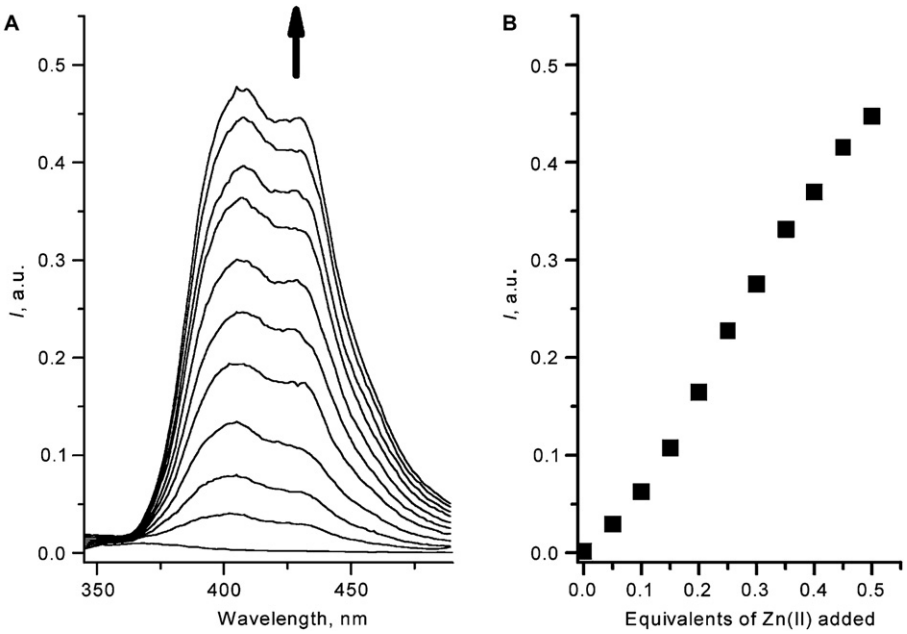


Figure 5. (A) Fluorescence enhancement of **21a** as a function of Zn^{2+} concentration. Spectra were acquired in MeCN solutions. Compound **21a** (1 μM) was titrated with 0.05 μM aliquots of $Zn(ClO_4)_2$ (0–0.5 μM). (B) Fluorescence as a function of added Zn(II) monitored at 430 nm (molar ratio plot).

4. Experimental section

4.1. General

All solvents were purified by standard methods prior to use. Melting points are uncorrected. NMR spectra were recorded on a 400 MHz Bruker Avance DRX spectrometer. Electronic absorption spectra were recorded on a Varian Cary 50 Bio UV–visible spectrophotometer and the emission spectra were measured on a Varian Cary Eclipse fluorescence spectrophotometer. Fluorescence quantum yields were determined in EtOH using optically matching solutions of anthracene (Φ_{std} 0.27 in EtOH)[20] for new bipyridines or $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (Φ_{std} 0.042 in deaerated water)[21] for new Ru complexes as the standard and the quantum yields were calculated using Eq. 1.

$$\Phi_F = \Phi_{std}\left(A_{std}F\eta^2\right)\Big/\left(AF_{std}\eta_{std}^2\right) \quad (1)$$

where, A and A_{std} are the absorbance of the sample and standard solutions, respectively, at the excitation wavelength, F and F_{std} are relative integrated fluorescence intensities of the sample and standard solutions correspondingly, η and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).

All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The C, H, and N analyses were carried out with a Perkin–Elmer PE 2400 microanalyzer. Mass spectra were determined with a Varian CH-5 mass spectrometer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H) or 75.4 MHz (^{13}C), using $SiMe_4$ (^{1}H and ^{13}C NMR) as standard.

4.2. X-ray crystallography for complex [Zn(1b)Cl$_2$]

A solution of bipyridine **1b** (50 mg, 0.13 mmol) in acetonitrile (30 mL) was added to a solution of $ZnCl_2$ (19 mg, 0.13 mmol) in acetonitrile (30 mL). The resulting colorless solution was kept for 13 days at rt for slow evaporation to yield crystals suitable for X-ray diffraction. Crystal data for [Zn(**1b**)Cl_2] were measured with an *Xcalibur 3 CCD* (graphite monochromator, Mo Kα): $C_{17}H_{14}Cl_2N_2Zn$, FW=382.57, needle, a=20.978(6), b=8.436(2), c=9.792(3) Å, α=90.00°, β=96.24(2)°, γ=90.00°, V=1722.7(8) Å^3, T=295(2) K, space group-*P*2*ybc*, Z=4, 3427 reflections were used in all calculations. R=0.0402. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 668968. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.3. Typical procedure for the synthesis of hydrazones 3

Corresponding acetophenone (0.5 mol) was added to the solution prepared by dissolving Na (11.5 g) in EtOH (200 mL) at 10 °C. After 2 min *iso*-propylnitrite was added, and the resulting mixture was stirred at 10–15 °C for 2 h and kept at room temperature overnight. The precipitate of the sodium salt of *iso*-nitrosoacetophenone was filtered off, dried in vacuo, and dissolved in water (100–200 mL) at room temperature. Acetic acid (21 mL, 0.35 mol) was added to the solution, mixture was cooled by adding of ice (50 g), the crystals of the *iso*-nitrosoacetophenone were filtered off, and dried under reduced pressure. The latter was dissolved in the mixture of EtOH (100 mL) and hydrazone hydrate (25 mL, 0.5 mol) at 40–50 °C and the mixture was kept for 1 h at room temperature. Water (300–500 mL) was added, appeared crystals were filtered off and dried. The crude hydrazone **3** was used directly in the next step.

4.4. Typical procedure for the synthesis of 1,2,4-triazines 2 and 7 starting from pyridinecarboxaldehydes

To solution of 1-hydrazono-2-oximino-1-arylethanes **3a–k** (8.4 mmol) in EtOH (50 mL) was added 2-pyridinecarboxaldehyde or 4-pyridinecarboxaldehyde (8.4 mmol). The mixture was stirred at 23 °C for 12 h. Appeared crystals were filtered off, then dissolved in AcOH at 90 °C, heated at this temperature for 1 h, allowed to cool

to room temperature, and then diluted with water (10 mL). The resulting precipitate was filtered off, washed with water and ethanol. The crude triazine was used directly in the next step.

*4.4.1. 6-Phenyl-3-(2-pyridyl)-1,2,4-triazine (**2a**)*

Yield 1.36 g, 69%, mp 148–150 °C. ^{1}H NMR (DMSO-d_6) δ: 7.58 (m, 4H, Ph+H-5′), 8.03 (ddd, 1H, *J* 7.8, 7.8, 1.2 Hz, H-4′), 8.31 (m, 2H, Ph), 8.54 (d, 1H, *J* 7.8 Hz, H-3′), 8.83 (dd, 1H, *J* 4.7, 1.2 Hz, H-6′), 9.50 (s, 1H, H-5).

*4.4.2. 6-Tolyl-3-(2-pyridyl)-1,2,4-triazine (**2b**)*

Yield 1.50 g, 72%, mp 164–166 °C. ^{1}H NMR (DMSO-d_6) δ: 2.50 (s, 3H, CH_3), 7.41 (d, 2H, *J* 8.2 Hz, Tol), 7.57 (ddd, 1H, *J* 7.8, 4.7, 1.2 Hz, H-5′), 8.02 (ddd, 1H, *J* 7.8, 7.8, 1.2 Hz, H-4′), 8.18 (d, 2H, *J* 8.2 Hz, Tol), 8.50 (d, 1H, *J* 7.8 Hz, H-3′), 8.81 (dd, 1H, *J* 4.7, 1.2 Hz, H-6′), 9.43 (s, 1H, H-5). EIMS *m*/*z* (*I* (%)) 248 (5) [M^+], 220 (10) [$M-N_2$], 116 (100).

*4.4.3. 6-(4-Methoxyphenyl)-3-(2-pyridyl)-1,2,4-triazine (**2c**)*

Yield 1.24 g, 56%, mp 184–186 °C. ^{1}H NMR (DMSO-d_6) δ: 3.88 (c, 3H, OCH_3), 7.12 (d, 2H), 7.55 (ddd, 1H, *J* 7.8, 4.7, 1.2 Hz, H-5′), 7.99 (ddd, 1H, *J* 7.8, 7.8, 1.2 Hz, H-4′), 8.25 (d, 2H), 8.47 (dd, 1H, *J* 4.7, 0.7 Hz, H-3′), 8.80 (dd, 1H, J 4.7, 1.2 Hz, H-6′), 9.42 (s, 1H, H-5). MS *m*/*z* (*I* (%)) 264 (8) [M^+], 236 (8) [$M-N_2$], 132 (100).

*4.4.4. 6-(4-Chlorophenyl)-3-(2-pyridyl)-1,2,4-triazine (**2d**)*

Yield 1.92 g, 85%, mp 187–189 °C. ^{1}H NMR (DMSO-d_6) δ: 7.59 (m, 2H), 7.68 (ddd, 1H, *J* 7.80, 4.75, 1.25 Hz), 8.05 (ddd, 1H, *J* 7.80, 7.80, 1.25 Hz), 8.34 (d, 2H), 8.50 (dd, 1H, *J* 4.25, 1.5 Hz), 8.83 (ddd, 1H, *J* 4.75, 0.75 Hz), 9.54 (s, 1H). EIMS *m*/*z* (*I* (%)): 270 (2) [M^+], 268 (5) [M^+], 136 (100).

*4.4.5. 6-(4-Bromophenyl)-3-(2-pyridyl)-1,2,4-triazine (**2e**)*

Yield 1.92 g, 73%, mp 118–120 °C. ^{1}H NMR (DMSO-d_6) δ: 7.48 (m, 2H), 7.65 (ddd, 1H, *J* 7.80, 4.75, 1.25 Hz), 8.00 (ddd, 1H, *J* 7.80, 7.80, 1.25 Hz), 8.31 (d, 2H), 8.48 (dd, 1H, *J* 4.25, 1.5 Hz), 8.79 (ddd, 1H, *J* 4.75, 0.75 Hz), 9.52 (s, 1H).

*4.4.6. 6-(3,4-Dichlorophenyl)-3-(2-pyridyl)-1,2,4-triazine (**2f**)*

Yield 2.06 g, 81%, mp 215–216 °C. ^{1}H NMR (DMSO-d_6) δ: 7.60 (ddd, 1H, *J* 7.9, 4.7, 1.2 Hz, H-5′), 7.85 (d, 1H, *J* 8.5 Hz, H-5″), 8.05 (ddd, 1H, *J* 7.9, 7.9, 1.7 Hz, H-4′), 8.30 (dd, 1H, *J* 8.5, 2.0 Hz, H-6″), 8.52 (ddd, 1H, *J* 7.9, 1.2, 0.7 Hz, H-3′), 8.54 (d, 1H, *J* 2.0 Hz, H-2″), 8.83 (ddd, 1H, *J* 4.7, 1.2, 0.7 Hz, H-6′), 9.60 (s, 1H, H-5).

*4.4.7. 6-(4-Nitrophenyl)-3-(2-pyridyl)-1,2,4-triazine (**2g**)*

Yield 1.92 g, 82%, mp>220 °C. ^{1}H NMR (DMSO-d_6) δ: 7.61 (m, 1H), 8.05 (ddd, 1H, *J* 7.80, 4.75, 1.25 Hz), 8.45 (ddd, 2H, *J* 7.80, 7.80, 1.25 Hz), 8.60 (m, 3H), 8.85 (dd, 1H, *J* 4.25, 1.5 Hz), 9.65 (s, 1H).

*4.4.8. 3,6-Bis(2-pyridyl)-1,2,4-triazine (**2h**)*

Yield 1.32 g, 67%, mp 155–157 °C. ^{1}H NMR (DMSO-d_6) δ: 7.58 (ddd, 2H, *J* 7.6, 4.7, 1.2 Hz), 8.05 (ddd, 2H, *J* 7.6, 7.6, 1.8 Hz), 8.61 (ddd, 2H, *J* 7.9, 1.0, 1.0 Hz), 8.78 (ddd, 1H, *J* 4.7, 1.6, 1.0 Hz), 8.81 (m, 1H), 9.69 (s, 1H).

*4.4.9. 3-(2-Pyridyl)-6-(4-pyridyl)-1,2,4-triazine (**2i**)*

Yield 1.74 g, 88%, mp 193–194 °C. ^{1}H NMR (DMSO-d_6) δ: 7.64 (ddd, 1H, *J* 7.5, 4.7, 1.1 Hz), 8.09 (ddd, 1H, *J* 7.8, 7.8, 1.8 Hz), 8.26 (m, 2H), 8.52 (d, 1H, *J* 7.9 Hz), 8.85 (m, 3H), 9.65 (s, 1H).

*4.4.10. 6-Thienyl-3-(2-pyridyl)-1,2,4-triazine (**2j**)*

Yield 1.31 g, 65%, mp 189–190 °C. ^{1}H NMR (DMSO-d_6) δ: 7.28 (dd, 1H, *J* 5.0, 3.7 Hz), 7.56 (m, 1H), 7.82 (dd, 1H, *J* 5.0, 1.0 Hz), 8.00 (ddd, 1H, *J* 7.80, 7.80, 1.25 Hz), 8.14 (dd, 1H, *J* 3.7, 1.0 Hz), 8.47 (dd, 1H, *J* 4.25, 1.5 Hz), 8.8 (dd, 1H, *J* 4.75, 0.75 Hz), 9.48 (s, 1H). EIMS *m*/*z* (*I* (%)): 240 (7) [M^+], 212 (8) [$M-N_2$], 108 (100).

*4.4.11. 6-(2-Naphthyl)-3-(2-pyridyl)-1,2,4-triazine (**2k**)*

Yield 1.69 g, 71%, mp 143–145 °C. ^{1}H NMR (DMSO-d_6) δ: 7.55 (m, 3H), 7.9–8.1 (m, 4H), 8.41 (dd, 1H, *J* 7.8, 1.0 Hz), 8.52 (ddd, 1H, *J* 7.9, 1.2, 0.7 Hz, H-3′), 8.82 (m, 2H), 9.62 (s, 1H, H-5).

*4.4.12. 6-Phenyl-3-(4-pyridyl)-1,2,4-triazine (**7a**)*

Yield 1.48 g, 75%, mp 166–168 °C. ^{1}H NMR (DMSO-d_6) δ: 7.64 (m, 3H), 8.32 (m, 4H), 8.86 (m, 2H, H-3′,5′), 9.52 (s, 1H, H-6). EIMS *m*/*z* (*I* (%)): 234 (4) [M^+], 206 (2) [$M-N_2$], 102 (100).

*4.4.13. 6-(4-Methylphenyl)-3-(4-pyridyl)-1,2,4-triazine (**7b**)*

Yield 1.75 g, 84%, mp 192–194 °C. ^{1}H NMR (DMSO-d_6) δ: 2.51 (s, 3H), 7.44 (m, 2H, H_{Ar}), 8.20 (m, 2H, H_{Ar}), 8.35 (m, 2H, H-2′,6′), 8.85 (m, 2H, H-3′,5′), 9.43 (s, 1H, H-6). EIMS *m*/*z* (*I* (%)): 248 (6) [M^+], 220 (8) [$M-N_2$], 116 (100).

*4.4.14. 6-(4-Bromophenyl)-3-(4-pyridyl)-1,2,4-triazine (**7e**)*

Yield 2.10 g, 80%, mp 208–210 °C. ^{1}H NMR (DMSO-d_6) δ: 7.84 (m, 2H, H_{Ar}), 8.30 (m, 4H), 8.84 (m, 2H, H-3′,5′), 9.57 (s, 1H, H-6).

4.5. Typical procedure for the synthesis of triazines 6

3-Cyanopyridine (0.06 mol) was dissolved in the solution of sodium methoxide obtained from sodium (20 mg) and MeOH (20 mL). The resulting solution was stirred at 23 °C for 1 h and corresponding hydrazone **3** (0.06 mol) was added, and the mixture was stirred at room temperature for additional 1 h. The solvent was removed under reduced pressure, and the residue (oil) was refluxed in acetic acid (20 mL) for 0.5 h. The resulting mixture was diluted with water (40 mL), crystals appeared were filtered off, and recrystallized from ethanol.

*4.5.1. 3-(3-Pyridyl)-6-phenyl-1,2,4-triazine (**6a**)*

Yield: 45%, mp 155–156 °C. ^{1}H NMR (DMSO-d_6) δ: 7.58 (m, 4H), 8.28 (m, 2H, C_6H_5), 8.76 (m, 2H), 9.47 (s, 1H), 9.60 (m, 1H). Found, %: C, 71.86; H, 4.14; N, 24.08. $C_{14}H_{10}N_4$. Calculated, %: C, 71.78; H, 4.30; N, 23.92.

*4.5.2. 6-(4-Methylphenyl)-3-(3-pyridyl)-1,2,4-triazine (**6b**)*

Yield 27%, mp 159–160 °C. ^{1}H NMR (DMSO-d_6) δ: 2.48 (m, 3H), 7.40 (m, 2H), 7.57 (m, 1H), 8.17 (m, 2H), 8.78 (m, 2H), 9.42 (s, 1H, H-5), 9.57 (m, 1H). Found, %: C, 72.62; H, 4.78; N, 22.54. $C_{15}H_{12}N_4$. Calculated, %: C, 72.56; H, 4.87; N, 22.57 for $C_{15}H_{12}N_4$ (248.29).

4.6. Typical procedure for the synthesis of bipyridines (1) and (15)

Triazines **2a–l** (3.1 mmol), bicyclo[2.2.1]hepta-2,5-diene (1.58 mL, 15.5 mmol), and *o*-xylene (30 mL) were refluxed for 24 h and cooled to room temperature. The solvent was removed under reduced pressure, residue was purified by column chromatography (silica gel, CH_2Cl_2) to give arylbipyridines **1a–l**. Analytical sample of **1** was recrystallized from ethanol.

*4.6.1. 5-Phenyl-2,2′-bipyridine (**1a**)*

Yield 0.53 g, 73%, mp 83–85 °C. ^{1}H NMR (DMSO-d_6) δ: 7.33–7.53 (m, 4H, Ph+H-5′), 7.72 (m, 2H, Ph), 7.89 (ddd, 1H, *J* 7.6, 7.6, 1.7 Hz, H-4′), 8.11 (dd, 1H, *J* 7.6, 2.5 Hz, H-4), 8.48 (m, 2H, H-3,3′), 8.64 (ddd, 1H, *J* 7.6, 1.7, 1.2 Hz, H-6′), 8.90 (d, 1H, *J* 2.5 Hz, H-6). Found, %: C, 82.77; H, 5.16; N, 11.98. Calculated, %: C, 82.73; H, 5.21; N, 12.06 for $C_{16}H_{12}N_2$ (232.29).

*4.6.2. 5-(4-Methylphenyl)-2,2′-bipyridine (**1b**)*

Yield 0.63 g, 82%, mp 90–92 °C. ^{1}H NMR (DMSO-d_6) δ: 2.49 (s, 3H), 7.28 (m, 2H), 7.37 (ddd, 1H, *J* 7.6, 4.9, 1.2 Hz, H-5′), 7.57 (m, 2H), 7.85 (ddd, 1H, *J* 7.6, 7.6, 1.7 Hz, H-4′), 8.07 (dd, 1H, *J* 7.6, 2.5 Hz, H-4),

8.48 (m, 2H, H-3,3′), 8.63 (ddd, 1H, *J* 7.6, 1.7, 1.2 Hz, H-6′), 8.85 (d, 1H, *J* 2.5 Hz, H-6). EIMS *m*/*z* (*I* (%)): 246 (100) $[M]^+$. Found, %: C, 82.87; H, 5.76; N, 11.42. Calculated, %: C, 82.90; H, 5.73; N, 11.37 for $C_{17}H_{14}N_2$ (246.31).

*4.6.3. 5-(4-Methoxyphenyl)-2,2′-bipyridine (**1c**)*

Yield 0.69 g, 85%, mp 124–126 °C. ^{1}H NMR (DMSO-d_6) δ: 3.84 (s, 3H), 7.02 (m, 2H), 7.35 (ddd, 1H, *J* 7.6, 4.9, 1.2 Hz, H-5′), 7.65 (m, 2H), 7.86 (ddd, 1H, *J* 7.6, 7.6, 1.7 Hz, H-4′), 8.05 (dd, 1H, *J* 7.6, 2.5 Hz, H-4), 8.42 (m, 2H, H-3,3′), 8.62 (ddd, 1H, *J* 7.6, 1.7, 1.2 Hz, H-6′), 8.81 (d, 1H, *J* 2.5 Hz, H-6). Found, %: C, 77.91; H, 5.42; N, 10.57. Calculated, %: C, 77.84; H, 5.38; N, 10.68 for $C_{17}H_{14}N_2O$ (262.31).

*4.6.4. 5-(4-Chlorophenyl)-2,2′-bipyridine (**1d**)*

Yield 0.79 g, 95%, mp 143–145 °C. ^{1}H NMR (DMSO-d_6) δ: 7.38 (m, 1H), 7.51 (m, 2H), 7.75 (m, 2H), 7.88 (ddd, 1H, *J* 7.6, 7.6, 1.75 Hz), 8.13 (dd, 1H, *J* 8.25, 2.5 Hz), 8.46 (m, 2H), 8.65 (m, 1H), 8.90 (dd, 1H, *J* 2.5, 1.0 Hz). EIMS *m*/*z* (*I* (%)): 266 (100) and 268 (33) $[M]^+$. Found, %: C, 72.11; H, 4.10; N, 10.54. Calculated, %: C, 72.05; H, 4.16; N, 10.50 for $C_{16}H_{11}ClN_2$ (266.73).

*4.6.5. 5-(4-Bromophenyl)-2,2′-bipyridine (**1e**)*

Yield 0.77 g, 89%, mp 215–217 °C. ^{1}H NMR (DMSO-d_6) δ: 7.38 (ddd, 1H, *J* 7.6, 4.75, 1.25 Hz), 7.67 (m, 4H), 7.88 (ddd, 1H, *J* 7.6, 7.6, 1.75 Hz), 8.13 (dd, 1H, *J* 8.25, 2.5 Hz), 8.47 (m, 2H), 8.65 (m, 1H), 8.90 (dd, 1H, *J* 2.5, 1.0 Hz). ^{1}H NMR ($CDCl_3$), δ: 121.0, 121.1, 122.6, 123.9, 128.7, 132.3, 135.0, 135.4, 136.5, 137.0, 147.4, 149.3, 155.3, 155.7. EIMS *m*/*z* (*I* (%)): 310 (99) and 312 (100) $[M]^+$. Found, %: C, 61.91; H, 3.50; N, 9.18. Calculated, %: C, 61.76; H, 3.56; N, 9.00 for $C_{16}H_{11}BrN_2$ (311.18).

*4.6.6. 5-(3,4-Dichlorophenyl)-2,2′-bipyridine (**1f**)*

Yield 0.85 g, 91%, mp 192–194 °C. ^{1}H NMR (DMSO-d_6) δ: 7.40 (ddd, 1H, *J* 7.8, 5.0, 1.2 Hz, H-5′), 7.64 (d, 1H, *J* 8.5 Hz, H-5″), 7.72 (dd, 1H, *J* 8.5, 2.0 Hz, H-6″), 7.89 (ddd, 1H, *J* 7.8, 7.8, 1.7 Hz, H-4′), 7.97 (d, 1H, *J* 2.0 Hz, H-2″), 8.19 (dd, 1H, *J* 7.6, 2.5 Hz, H-4), 8.44 (ddd, 1H, *J* 7.9, 1.2, 0.7 Hz, H-3′), 8.49 (d, 1H, *J* 8.5 Hz), 8.65 (ddd, 1H, *J* 5.0, 1.2, 0.7 Hz, H-6′), 8.94 (d, 1H, *J* 2.5 Hz, H-6). Found, %: C, 63.67; H, 3.30; N, 9.17. Calculated, %: C, 63.81; H, 3.35; N, 9.30 for $C_{16}H_{10}Cl_2N_2$ (301.18).

*4.6.7. 5-(4-Nitrophenyl)-2,2′-bipyridine (**1g**)*

Yield 0.75 g, 87%, mp 218–220 °C. ^{1}H NMR (DMSO-d_6) δ: 7.48 (ddd, 1H, *J* 7.6, 4.75, 1.25 Hz), 7.97 (ddd, 1H, *J* 7.6, 7.6, 1.75 Hz), 8.12 (d, 2H), 8.38 (m, 2H), 8.50 (m, 2H), 8.72 (m, 1H), 9.13 (dd, 1H, *J* 2.5, 1.0 Hz). Found, %: C, 69.27; H, 3.90; N, 15.01. Calculated, %: C, 69.31; H, 4.00; N, 15.15 for $C_{16}H_{11}N_3O_2$ (277.28).

*4.6.8. 2,2′:5′,2″-Terpyridine (**1h**)*

Yield 0.62 g, 86%, mp 182–184 °C. ^{1}H NMR (DMSO-d_6) δ: 7.33–7.42 (m, 2H), 7.90 (m, 2H), 8.03 (m, 1H), 8.45–8.56 (m, 3H), 8.64–8.71 (m, 2H), 9.30 (m, 1H). Found, %: C, 77.20; H, 4.61; N, 18.06. Calculated, %: C, 77.23; H, 4.75; N, 18.01 for $C_{15}H_{11}N_3$ (233.28).

*4.6.9. 2,2′:5′,4″-Terpyridine (**1i**)*

Yield 0.64 g, 88%, mp 183–185 °C. ^{1}H NMR (DMSO-d_6) δ: 7.31 (m, 1H), 7.62 (d, 2H, *J* 7.6 Hz), 7.95 (m, 1H), 8.14 (dd, 1H, *J* 2.25, 8.25 Hz), 8.37 (dd, 1H, *J* 2.25, 2.25 Hz), 8.55 (m, 3H), 8.92 (s, 1H). Found, %: C, 77.25; H, 4.68; N, 17.96. Calculated, %: C, 77.23; H, 4.75; N, 18.01 for $C_{15}H_{11}N_3$ (233.28).

*4.6.10. 5-(2-Thienyl)-2,2′-bipyridine (**1j**)*

Yield 0.64 g, 87%, mp 96–98 °C. ^{1}H NMR (DMSO-d_6) δ: 7.16 (m, 1H), 7.35 (m, 1H), 7.51 (dd, 1H, *J* 5.2, 1.2 Hz), 7.60 (dd, 1H, *J* 5.2, 1.2 Hz), 7.88 (ddd, 1H, *J* 7.9, 7.9, 1.8 Hz), 8.10 (dd, 1H, *J* 8.5, 2.44 Hz), 8.42 (m, 2H), 8.63 (m, 1H), 8.92 (m, 1H). Found, %: C, 70.48; H, 4.19; N, 11.86. Calculated, %: C, 70.56; H, 4.23; N, 11.75 for $C_{14}H_{10}N_2S$ (238.31).

*4.6.11. 5-(2-Naphthyl)-2,2′-bipyridine (**1k**)*

Yield 0.73 g, 84%, mp 130–132 °C. ^{1}H NMR (DMSO-d_6) δ: 7.38 (ddd, 1H, *J* 7.8, 5.0, 1.2 Hz, H-5′), 7.52 (m, 2H), 7.8–8.0 (m, 5H), 8.27 (m, 2H), 8.48 (ddd, 1H, *J* 7.8, 1.2, 0.7 Hz, H-3′), 8.52 (dd, 1H, *J* 8.5, 1.0 Hz), 8.64 (ddd, 1H, *J* 4.8, 1.7, 1.2 Hz, H-6′), 9.06 (d, 1H, *J* 2.3 Hz, H-6). Found, %: C, 70.48; H, 4.19; N, 11.86. Calculated, %: C, 85.08; H, 5.00; N, 9.92 for $C_{20}H_{14}N_2$ (282.35).

*4.6.12. 5-(4-Methylphenyl)-2,4′-bipyridine (**15b**)*

Yield 0.64 g, 84%, mp 156–158 °C. ^{1}H NMR (DMSO-d_6) δ: 2.39 (s, 3H, CH_3), 7.29 (m, 2H, H_{Ar}), 7.61 (m, 2H, H_{Ar}), 8.00–8.21 (m, 4H, H-2′,6′,3,4), 8.66 (m, 2H, H-3′,5′), 8.95 (dd, 1H, *J* 2.1, 1.1 Hz, H-6). Found, %: C, 82.75; H, 5.71; N, 11.21. Calculated, %: C, 82.90; H, 5.73; N, 11.37 for $C_{17}H_{14}N_2$ (246.31).

*4.6.13. 5-(4-Bromophenyl)-2,4′-bipyridine (**15e**)*

Yield 0.73 g, 76%, mp 160–161 °C. ^{1}H NMR (DMSO-d_6) δ: 7.60–7.75 (m, 4H, H_{Ar}), 8.04 (m, 2H, H-2′,6′), 8.10 (dd, 1H, *J* 8.2, 0.9 Hz, H-3), 8.16 (dd, 1H, *J* 8.2, 2.1 Hz, H-4), 8.67 (m, 2H, H-3′,5′), 8.99 (dd, 1H, *J* 2.1, 0.9 Hz, H-6). Found, %: C, 61.85; H, 3.69; N, 8.81. Calculated, %: C, 61.76; H, 3.56; N, 9.00 for $C_{16}H_{11}BrN_2$ (311.18).

4.7. 5-Methoxycarbonylpyridine-2-carboxaldehyde (18)

To the stirring mixture of dimethyl pyridine-2,5-dicarboxylate (20 g, 102.4 mmol), ethanol (200 mL), and THF (70 mL) was added $NaBH_4$ (7.8 g, 204 mmol) at 0 °C. The mixture was stirred at this temperature for 8 h. Then, ice (100 g) and water (300 mL) were added and resulting mixture was extracted with DCM (4×200 mL). Combined organic extracts were dried over Na_2SO_4, the solvent was removed under reduced pressure. So obtained crude methyl 2-hydroxymethylpyridine-2-carboxylate (10 g, 60 mmol) was dissolved in 1,4-dioxane (80 mL), SeO_2 (5 g, 43 mmol) was added, and the mixture was refluxed for 2 h. Solids were filtered off and the solvent was removed under reduced pressure. The residue was extracted with hot hexane (6×100 mL). Removing the solvent from combined extracts gave crude aldehyde **18**, which was used on the next step without additional purification. Yield 7.2 g, 43%.

4.8. Typical procedure for the synthesis of 5-methoxycarbonylpyridyltriazines (17a–l)

Mixture of aldehyde **18** (1.83 g, 12 mmol), hydrazones **3a–l** (12 mmol) and acetic acid (50 mL) was stirred at 23 °C for 1 h. Resulting mixture was heated at 90 °C for 1 h, then cooled to room temperature. Crystals of triazine **17** were filtered off and washed with ethanol. The crude triazine **17** was used directly in the next step.

*4.8.1. 3-(5-Methoxycarbonyl-2-pyridyl)-6-phenyl-1,2,4-triazine (**17a**)*

Yield 48%, mp>250 °C. ^{1}H NMR (DMSO-d_6) δ: 3.97 (s, 3H, OCH_3), 7.58–7.66 (m, 3H, Ph), 8.32 (m, 2H, Ph), 8.54 (dd, 1H, *J* 8.3, 2.1 Hz, H-4′), 8.66 (d, 1H, *J* 8.3 Hz, H-3′), 9.31 (d, 1H, *J* 0.9 Hz, H-6′), 9.54 (c, 1H, H-5).

*4.8.2. 3-(5-Methoxycarbonyl-2-pyridyl)-6-(4-methylphenyl)-1,2,4-triazine (**17b**)*

Yield 43%, mp 240–242 °C. ^{1}H NMR (DMSO-d_6) δ: 2.49 (s, 3H, CH_3), 3.97 (s, 3H, OCH_3), 7.42 (m, 2H, H_{Ar}), 8.21 (m, 2H, H_{Ar}), 8.52 (dd, 1H, *J* 8.3, 2.3 Hz, H-4′), 8.64 (d, 1H, *J* 8.3 Hz, H-3′), 9.30 (dd, 1H, *J* 2.3 Hz, H-6′), 9.50 (s, 1H, H-5).

*4.8.3. 3-(5-Methoxycarbonyl-2-pyridyl)-6-(4-methoxyphenyl)-1,2,4-triazine (**17c**)*

Yield 40%, mp 254–256 °C. ^{1}H NMR (DMSO-d_6) δ: 3.90 (s, 3H, OCH_3), 3.98 (s, 3H, COOMe), 7.15 (m, 2H, H_{Ar}), 8.27 (m, 2H, H_{Ar}), 8.49 (dd, 1H, *J* 8.1, 2.4 Hz, H-4′), 8.63 (d, 1H, *J* 8.1 Hz, H-3′), 9.30 (d, 1H, *J* 2.4 Hz, H-6′), 9.49 (c, 1H, H-5).

*4.8.4. 6-(4-Chlorophenyl)-3-(5-methoxycarbonyl-2-pyridyl)-1,2,4-triazine (**17d**)*

Yield 55%, mp>250 °C. ^{1}H NMR (DMSO-d_6) δ: 3.97 (s, 3H, COOMe), 7.66 (m, 2H, H_{Ar}), 8.35 (m, 2H, H_{Ar}), 8.53 (dd, 1H, *J* 8.1, 1.9 Hz, H-4′), 8.66 (d, 1H, *J* 8.1 Hz, H-3′), 9.31 (d, 1H, *J* 1.9 Hz, H-6′), 9.58 (s, 1H, H-5).

*4.8.5. 6-(4-Bromophenyl)-3-(5-methoxycarbonyl-2-pyridyl)-1,2,4-triazine (**17e**)*

Yield 51%, mp>250 °C. ^{1}H NMR (CF_3COOD) δ: 4.28 (s, 3H, COOMe), 7.89 (m, 2H, H_{Ar}), 8.06 (m, 2H, H_{Ar}), 9.46 (d, 1H, *J* 8.6 Hz, H-3′), 9.51 (dd, 1H, *J* 8.6, 1.6 Hz, H-4′), 9.56 (s, 1H, H-5), 9.74 (d, 1H, *J* 1.6 Hz, H-6′).

*4.8.6. 3-(5-Methoxycarbonyl-2-pyridyl)-6-(4-pyridyl)-1,2,4-triazine (**17i**)*

Yield 36%, mp>250 °C. ^{1}H NMR (DMSO-d_6) δ: 3.97 (s, 3H, COOMe), 8.26 (m, 2H, H-2″,6″), 8.55 (dd, 1H, *J* 8.8, 2.0 Hz, H-4′), 8.68 (d, 1H, *J* 8.8 Hz, H-3′), 8.84 (m, 2H, H-3″,5″), 9.32 (d, 1H, *J* 2.0 Hz, H-6′), 9.68 (s, 1H, H-5).

*4.8.7. 3-(5-Methoxycarbonyl-2-pyridyl)-6-(2-naphthyl)-1,2,4-triazine (**17k**)*

Yield 22%, mp>250 °C. ^{1}H NMR (DMSO-d_6) δ: 3.97 (s, 3H, COOMe), 7.63 (m, 2H, H_{Ar}), 8.07 (m, 3H, H_{Ar}), 8.45 (m, 1H, H_{Ar}), 8.55 (dd, 1H, *J* 8.1, 2.1 Hz, H-4′), 8.67 (d, 1H, *J* 8.1 Hz, H-3′), 8.93 (m, 1H, H_{Ar}), 9.33 (d, 1H, *J* 2.1 Hz, H-6′), 9.73 (s, 1H, H-5).

*4.8.8. 3-(5-Methoxycarbonyl-2-pyridyl)-6-(1-naphthyl)-1,2,4-triazine (**17l**)*

Yield 33%, mp 207–209 °C. ^{1}H NMR (DMSO-d_6) δ: 3.99 (s, 3H, COOMe), 7.57–7.74 (m, 3H, H_{Ar}), 7.88 (m, 1H, H_{Ar}), 8.02–8.21 (m, 3H, H_{Ar}), 8.54 (dd, 1H, *J* 8.1, 2.1 Hz, H-4′), 8.72 (d, 1H, *J* 8.1 Hz, H-3′), 9.26 (s, 1H, H-5), 9.34 (d, 1H, *J* 2.1 Hz, H-6′).

4.9. Typical procedure for the synthesis of 5′-methoxycarbonyl-2,2′-bipyridines (16)

Suspension of the triazine **17** (5 mmol) and 2,5-norbornadiene (1.5 mL, 15 mmol) in *o*-xylene (60 mL) were refluxed 16 h. Hexane (40 mL) was added and the resulting mixture was kept for 0.5 h at room temperature. Appeared crystals were filtered off and washed with hexane.

*4.9.1. 5′-Methoxycarbonyl-5-phenyl-2,2′-bipyridine (**16a**)*

Yield 82%, mp 183–185 °C. ^{1}H NMR (DMSO-d_6) δ: 3.94 (s, 3H, OCH_3), 7.20–7.60 (m, 3H, Ph), 7.72 (m, 2H, Ph), 8.15 (dd, 1H, *J* 8.2, 2.4 Hz, H-4), 8.38 (dd, 1H, *J* 8.2, 2.1 Hz, H-4′), 8.55 (d, 1H, *J* 8.1 Hz, H-3), 8.58 (d, 1H, *J* 8.2 Hz, H-3′), 8.94 (d, 1H, *J* 2.4 Hz, H-6), 9.16 (d, 1H, *J* 2.1 Hz, H-6′). EIMS *m*/*z* (*I* (%)): 290 (100) $[M]^+$. Found, %: C, 74.29; H, 4.58; N, 9.53. $C_{18}H_{14}N_2O_2$. Calculated, %: C, 74.47; H, 4.86; N, 9.65.

*4.9.2. 5′-Methoxycarbonyl-5-(4-methylphenyl)-2,2′-bipyridine (**16b**)*

Yield 84%, mp 187–189 °C. ^{1}H NMR (DMSO-d_6) δ: 2.40 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 7.31 (m, 2H, H_{Ar}), 7.64 (m, 2H, H_{Ar}), 8.17 (dd, 1H, *J* 8.3, 2.5 Hz, H-4), 8.40 (dd, 1H, *J* 8.4, 2.1 Hz, H-4′), 8.51 (d, 1H, *J* 8.3 Hz, H-3), 8.55 (d, 1H, *J* 8.4 Hz, H-3′), 8.94 (d, 1H, *J* 2.5 Hz, H-6), 9.16 (d, 1H, *J* 2.1 Hz, H-6′). ^{13}C NMR ($CDCl_3$) δ: 21.2, 52.4, 120.4, 121.8, 125.5, 127.0, 129.9, 134.4, 135.0, 137.2, 138.0, 138.5, 147.7, 150.6, 153.5, 159.3, 165.9. Found, %: C, 74.98; H, 5.39; N, 9.31. $C_{19}H_{16}N_2O_2$. Calculated, %: C, 74.98; H, 5.30; N, 9.20.

*4.9.3. 5′-Methoxycarbonyl-5-(4-methoxyphenyl)-2,2′-bipyridine (**16c**)*

Yield 84%, mp 208–210 °C. ^{1}H NMR (DMSO-d_6) δ: 3.85 (s, 3H, OCH_3), 3.95 (s, 3H, COOMe), 7.04 (m, 2H, H_{Ar}), 7.68 (m, 2H, H_{Ar}), 8.11 (dd, 1H, *J* 8.3, 2.0 Hz, H-4), 8.38 (dd, 1H, *J* 8.5, 2.0 Hz, H-4′), 8.51 (d, 1H, *J* 8.3 Hz, H-3), 8.54 (d, 1H, *J* 8.5 Hz, H-3′), 8.92 (d, 1H, *J* 2.0 Hz, H-6), 9.16 (d, 1H, *J* 2.0 Hz, H-6′). ^{13}C NMR ($CDCl_3$) δ: 31.0, 52.4, 55.4, 114.7, 120.4, 121.9, 125.6, 128.3, 129.7, 134.7, 138.0, 147.5, 150.6, 160.1, 165.9. EIMS *m*/*z* (*I* (%)): 320 $[M]^+$. Found, %: C, 71.16; H, 4.86; N, 8.89. $C_{19}H_{16}N_2O_3$. Calculated, %: C, 71.24; H, 5.03; N, 8.74.

*4.9.4. 5-(4-Chlorophenyl)-5′-methoxycarbonyl-2,2′-bipyridine (**16d**)*

Yield 75%, mp 209–211 °C. ^{1}H NMR (DMSO-d_6) δ: 3.94 (s, 3H, COOMe), 7.53 (m, 2H, H_{Ar}), 7.82 (m, 2H, H_{Ar}), 8.23 (dd, 1H, *J* 8.5, 2.0 Hz, H-4), 8.41 (dd, 1H, *J* 8.3, 1.8 Hz, H-4′), 8.54 (d, 1H, *J* 8.5 Hz, H-3), 8.57 (d, 1H, *J* 8.3 Hz, H-3′), 9.00 (d, 1H, *J* 2.0 Hz, H-6), 9.17 (d, 1H, *J* 1.8 Hz, H-6′). Found, %: C, 66.58; H, 3.84; N, 8.55. $C_{18}H_{13}N_2O_2Cl$. Calculated, %: C, 66.57; H, 4.03; N, 8.63.

*4.9.5. 5-(4-Bromophenyl)-5′-methoxycarbonyl-2,2′-bipyridine (**16e**)*

Yield 63%, mp 206–208 °C. ^{1}H NMR (DMSO-d_6) δ: 3.95 (s, 3H, COOMe), 7.66 (m, 2H, H_{Ar}), 7.72 (m, 2H, H_{Ar}), 8.19 (dd, 1H, *J* 8.4, 2.1 Hz, H-4), 8.40 (dd, 1H, *J* 8.3, 2.0 Hz, H-4′), 8.54 (d, 1H, *J* 8.4 Hz, H-3), 8.57 (d, 1H, *J* 8.3 Hz, H-3′), 8.97 (d, 1H, *J* 2.1 Hz, H-6), 9.17 (d, 1H, *J* 2.0 Hz, H-6′). Found, %: C, 58.50; H, 3.29; N, 7.63. $C_{18}H_{13}N_2O_2Br$. Calculated, %: C, 58.56; H, 3.55; N, 7.59.

*4.9.6. 5-Methoxycarbonyl-2,2′:5′,4″-terpyridine (**16i**)*

Yield 74%, mp 210–212 °C. ^{1}H NMR (DMSO-d_6) δ: 3.95 (s, 3H, COOMe), 7.76 (m, 2H, H-3″,5″), 8.30 (dd, 1H, *J* 8.5, 1.8 Hz, H-4′), 8.39 (dd, 1H, *J* 8.5, 1.8 Hz, H-4), 8.57 (d, 1H, *J* 8.5 Hz, H-3′), 8.58 (d, 1H, *J* 8.5 Hz, H-3), 8.67 (m, 2H, H-2″,6″), 9.07 (d, 1H, *J* 1.8 Hz, H-6′), 9.17 (d, 1H, *J* 1.8 Hz, H-6). Found, %: C, 70.22; H, 4.60; N, 14.23. $C_{17}H_{13}N_3O_2$. Calculated, %: C, 70.09; H, 4.50; N, 14.42.

*4.9.7. 5′-Methoxycarbonyl-5-(2-naphthyl)-2,2′-bipyridine (**16k**)*

Yield 71%, mp 211–213 °C. ^{1}H NMR (DMSO-d_6) δ: 3.95 (s, 3H, COOMe), 7.54 (m, 2H, H_{Ar}), 7.88–8.05 (m, 4H, H_{Ar}), 8.32–8.44 (m, 3H, $H_{Ar,}$ H-4,4′), 8.59 (d, 2H, *J* 8.5 Hz, H-3,3′), 9.14 (d, 1H, *J* 1.5 Hz, H-6), 9.18 (d, 1H, *J* 1.3 Hz, H-6′). Found, %: C, 77.48; H, 4.80; N, 8.17. $C_{22}H_{16}N_2O_2$. Calculated, %: C, 77.63; H, 4.74; N, 8.23.

*4.9.8. 5′-Methoxycarbonyl-5-(1-naphthyl)-2,2′-bipyridine (**16l**)*

Yield 71%, mp 151–153 °C. ^{1}H NMR (DMSO-d_6) δ: 3.96 (s, 3H, COOMe), 7.45–7.65 (m, 4H, H_{Ar}), 7.84 (m, 1H, H_{Ar}), 7.98 (m, 2H, H_{Ar}), 8.05 (dd, 1H, *J* 7.9, 2.4 Hz, H-4), 8.43 (dd, 1H, *J* 8.4, 2.1 Hz, H-4′), 8.62 (m, 2H, H-3,3′), 8.79 (d, 1H, *J* 2.4 Hz, H-6), 9.20 (d, 1H, *J* 2.1 Hz, H-6′). Found, %: 77.77; H, 4.81; N, 7.99. $C_{22}H_{16}N_2O_2$. Calculated, %: C, 77.63; H, 4.74; N, 8.23.

4.10. Typical procedure for the synthesis of quinolinyltriazines (20)

To solution of hydrazone **3** (10 mmol) in AcOH (10 mL) was added 2-quinolinecarboxaldehyde **22** (1.57 g, 10 mmol). The mixture was stirred at room temperature for 1 h, heated at 90 °C for 1 h, allowed to cool to room temperature, and then diluted with water (10 mL). The resulting precipitate was filtered off, washed with water and ethanol. The crude triazines **20a–c** were used directly in the next step.

*4.10.1. 6-Phenyl-3-(2′-quinolyl)-1,2,4-triazine (**20a**)*

Yield 2.30 g, 81%, ^{1}H NMR (DMSO-d_6) δ: 7.73–7.62 (m, 4H, Ph+H-7′), 7.86 (ddd, 1H, *J* 8.2, 7.9, 1.5 Hz, H-6′), 8.08 (dd, 1H, *J* 7.9, 1.5 Hz, H-5′), 8.22 (dd, 1H, *J* 7.9, 1.5 Hz, H-8′), 8.33 (m, 2H, Ph), 8.58 (d, 1H, *J* 8.7 Hz, H-4′), 8.64 (d, 1H, *J* 8.7 Hz, H-3′), 9.58 (s, 1H, H-5).

*4.10.2. 6-Tolyl-3-(2′-quinolyl)-1,2,4-triazine (**20b**)*

Yield 2.55 g, 86%, ^{1}H NMR (DMSO-d_6) δ: 2.49 (s, 3H, Me), 7.38 (m, 2H), 7.64 (ddd, 1H, *J* 8.2, 7.9, 1.2 Hz, H-7′), 7.80 (ddd, 1H, *J* 8.2, 7.9, 1.5 Hz, H-6′), 7.99 (dd, 1H, *J* 7.9, 1.5 Hz, H-5′), 8.21 (m, 3H, Tol+H-8′), 8.48 (d, 1H, *J* 8.5 Hz, H-4), 8.62 (d, 1H, *J* 8.5 Hz, H-3), 9.45 (s, 1H, H-5).

*4.10.3. 6-(4″-Methoxyphenyl)-3-(2′-quinolyl)-1,2,4-triazine (**20c**)*

Yield 2.42 g, 77%, ^{1}H NMR (DMSO-d_6) δ: 3.89 (s, 3H, OMe), 7.14 (m, 2H), 7.67 (ddd, 1H, *J* 8.2, 7.9, 1.2 Hz, H-7′), 7.83 (ddd, 1H, *J* 8.2, 7.9, 1.5 Hz, H-6′), 8.04 (d, 1H, *J* 7.9 Hz, H-5′), 8.21 (d, 1H, *J* 7.9 Hz, H-8′), 8.28 (m, 2H), 8.57 (d, 1H, *J* 8.5 Hz, H-4′), 8.62 (dd, 1H, *J* 8.5 Hz, H-3′), 9.48 (s, 1H, H-5).

*4.10.4. 6-(4″-Bromophenyl)-3-(2′-quinolyl)-1,2,4-triazine (**20e**)*

Yield 2.35 g, 65%, ^{1}H NMR ($CDCl_3$) δ: 7.62 (ddd, 1H, *J* 8.2, 7.9, 1.2 Hz, H-7′), 7.73 (m, 2H, H_{Ar}), 7.80 (ddd, 1H, *J* 8.2, 7.9, 1.2 Hz, H-6′), 7.93 (dd, 1H, *J* 7.9, 1.2 Hz, H-5′), 8.09 (m, 2H, H_{Ar}), 8.41 (m, 2H, H-4′, H-8′), 8.82 (dd, 1H, *J* 8.5 Hz, H-3′), 9.25 (s, 1H, H-5).

4.11. Typical procedure for the synthesis of pyridylquinolines (21)

Quinolinyltriazine **20** (3.1 mmol), bicyclo[2.2.1]hepta-2,5-diene (1.58 mL, 15.5 mmol), and *o*-xylene (30 mL) were refluxed for 6–12 h and cooled to room temperature. The solvent was removed under reduced pressure, residue was recrystallized from ethanol to give title arylpyridylquinolines **7a–c**.

*4.11.1. 2-(5-Phenyl-2-pyridyl)quinoline (**21a**)*

Yield 612 mg, 70%, mp 145–146 °C. ^{1}H NMR (DMSO-d_6) δ: 7.4–7.6 (m, 4H), 7.7–7.8 (m, 3H), 7.95 (dd, 1H, *J* 8.2, 1.5 Hz, H-8), 8.09 (ddd, 1H, *J* 8.2, 1.2, 0.9 Hz, H-5), 8.19 (dd, 1H, *J* 8.2, 2.4 Hz, H-4′), 8.40 (dd, 1H, *J* 8.5, 0.6 Hz, H-3′), 8.62 (d, 1H, *J* 8.5 Hz, H-3), 8.72 (dd, 1H, *J* 8.2, 0.9 Hz, H-4), 8.98 (dd, 1H, *J* 2.4, 0.6 Hz, H-6′). Found, %: C, 85.19; H, 4.88; N, 9.99. $C_{20}H_{14}N_2$. Calculated, %: C, 85.08; H, 5.00; N, 9.92.

*4.11.2. 2-(5-Tolyl-2-pyridyl)quinoline (**21b**)*

Yield 698 mg, 76%, mp 157–158 °C. ^{1}H NMR (DMSO-d_6) δ: 2.41 (s, 3H, Me), 7.32 (m, 2H), 7.58 (ddd, 1H, *J* 8.2, 7.0, 1.2 Hz, H-7), 7.62 (m, 2H), 7.77 (ddd, 1H, *J* 8.2, 7.0, 1.5 Hz, H-6), 7.96 (dd, 1H, *J* 8.2, 1.5 Hz, H-8), 8.09 (ddd, 1H, *J* 8.2, 1.2, 0.9 Hz, H-5), 8.17 (dd, 1H, *J* 8.2, 2.4 Hz, H-4′), 8.42 (dd, 1H, *J* 8.5, 0.6 Hz, H-3′), 8.61 (d, 1H, *J* 8.5 Hz, H-3), 8.69 (dd, 1H, *J* 8.2, 0.9 Hz, H-4), 8.96 (dd, 1H, *J* 2.4, 0.6 Hz, H-6′). Found, %: C, 85.22; H, 5.38; N, 9.51. $C_{21}H_{16}N_2$. Calculated, %: C, 85.11; H, 5.44; N, 9.45.

*4.11.3. 2-[5-(4-Methoxyphenyl)-2-pyridyl]quinoline (**21c**)*

Yield 620 mg, 64%, mp 181–182 °C. ^{1}H NMR (DMSO-d_6) δ: 3.85 (s, 3H, OMe), 7.04 (m, 2H), 7.57 (ddd, 1H, *J* 8.2, 7.0, 1.2 Hz, H-7), 7.69 (m, 2H), 7.75 (ddd, 1H, *J* 8.2, 7.0, 1.5 Hz, H-6), 7.94 (dd, 1H, *J* 8.2, 1.5 Hz, H-8), 8.09 (ddd, 1H, *J* 8.2, 1.2, 0.9 Hz, H-5), 8.12 (dd, 1H, *J* 8.2, 2.4 Hz, H-4′), 8.38 (dd, 1H, *J* 8.5, 0.6 Hz, H-3′), 8.61 (d, 1H, *J* 8.5 Hz, H-3), 8.69 (dd, 1H, *J* 8.2, 0.9 Hz, H-4), 8.93 (dd, 1H, *J* 2.4, 0.6 Hz, H-6′). Found, %: C, 80.77; H, 5.08; N, 9.02. $C_{21}H_{16}N_2O$. Calculated, %: C, 80.75; H, 5.16; N, 8.97.

*4.11.4. 2-[5-(4-Bromophenyl)-2-pyridyl]quinoline (**21e**)*

Yield 940 mg, 84%, mp 187–189 °C. ^{1}H NMR ($CDCl_3$) δ: 7.5–7.6 (m, 3H, H-7′, H_{Ar}), 7.65 (m, 2H, H_{Ar}), 7.74 (ddd, 1H, *J* 8.2, 7.8, 1.5 Hz, H-6′), 7.87 (dd, 1H, *J* 7.8, 1.5 Hz, H-5′), 8.04 (dd, 1H, *J* 8.2, 2.5 Hz, H-4), 8.20 (d, 1H, *J* 8.2 Hz, H-8′), 8.31 (d, 1H, *J* 8.5 Hz, H-4′), 8.60 (d, 1H, *J* 8.5 Hz, H-3′), 8.73 (dd, 1H, *J* 8.2, 0.8 Hz, H-3), 8.93 (dd, 1H, *J* 2.5, 0.8 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 118.9, 121.9, 122.7, 126.9, 127.7, 128.3, 128.7, 129.7, 129.8, 132.3, 135.1, 135.7, 136.5, 136.9, 147.4, 148.0, 155.5, 155.7. EIMS *m*/*z* (*I* (%)): 360 (100) and 362 (99) $[M]^+$. Found, %: C, 66.67; H, 3.58; N, 7.70. $C_{20}H_{13}BrN_2$. Calculated, %: C, 66.50; H, 3.63; N, 7.75.

4.12. Typical procedure for the synthesis of hydroxyquinolinyl-1,2,4-triazines (23a–c)

To solution of 1-hydrazono-2-oximino-1-arylethanes **3a–c** (13 mmol) in EtOH (30 mL) was added 8-hydroxyquinolin-2-carboxaldehyde **25** (2.28 g, 13.2 mmol) in EtOH (20 mL). The mixture was kept at room temperature overnight. Appeared crystals were filtered off, dried, and dissolved in AcOH (40 mL). The mixture was heated at 80 °C for 30 min and allowed to cool to room temperature. The resulting precipitate was filtered off and washed with ethanol. The crude triazine was used directly in the next step.

*4.12.1. 3-(8-Hydroxyquinolin-2-yl)-6-phenyl-1,2,4-triazine (**23a**)*

Yield 2.25 g (63%), mp 187–190 °C. ^{1}H NMR (DMSO-d_6) δ: 7.22 (dd, 1H, *J* 7.6, 1.2 Hz, H-7′), 7.52 (dd, 2H, *J* 7.6, 1.2 Hz, H-5′), 7.56 (dd, 2H, *J* 7.6, 7.6 Hz, H-6′), 7.67 (m, 3H, Ph), 8.34 (m, 2H, Ph), 8.56 (d, 1H, *J* 8.4 Hz, H-3′), 8.60 (d, 1H, *J* 8.4 Hz, H-4′), 9.63 (s, 1H, H-5), 9.95 (br s, 1H, OH).

*4.12.2. 3-(8-Hydroxyquinolin-2-yl)-6-(4-methylphenyl)-1,2,4-triazine (**23b**)*

Yield 2.37 g (58%), mp 155–157 °C. ^{1}H NMR (DMSO-d_6) δ: 2.44 (s, 3H, CH_3), 7.21 (dd, 1H, *J* 7.6, 1.4 Hz, H-7′), 7.47 (d, 2H, Tol), 7.50 (dd, 2H, *J* 7.6, 1.4 Hz, H-5′), 7.54 (dd, 2H, *J* 7.6, 7.6 Hz, H-6′), 8.25 (m, 2H, Tol), 8.56 (d, 1H, *J* 8.6 Hz, H-3′), 8.59 (d, 1H, *J* 8.6 Hz, H-4′), 9.61 (s, 1H, H-5), 9.98 (br s, 1H, OH).

*4.12.3. 3-(8-Hydroxyquinolin-2-yl)-6-(4-methoxyphenyl)-1,2,4-triazine (**23c**)*

Yield 2.45 g (57%), mp 158–160 °C. ^{1}H NMR (DMSO-d_6) δ: 3.89 (s, 3H, OCH_3), 7.21 (m, 3H, H-7′, H-3″), 7.52 (dd, 2H, *J* 7.6, 1.2 Hz, H-5′), 7.56 (dd, 2H, *J* 7.6, 7.6 Hz, H-6′), 8.32 (m, 2H), 8.55 (d, 1H, *J* 8.4 Hz, H-3′), 8.58 (d, 1H, *J* 8.4 Hz, H-4′), 9.58 (s, 1H, H-5), 9.97 (br s, 1H, OH).

4.13. 2-(8-Hydroxyquinolin-2-yl)-5-phenylpyridine (24a)

Triazine **23a** (1.5 g, 5 mmol), bicyclo[2.2.1]hepta-2,5-diene (2.52 mL, 25 mmol), and *o*-xylene (50 mL) were refluxed for 24 h and cooled to room temperature. The solvent was removed under reduced pressure, residue was purified by column chromatography (silica gel, CH_2Cl_2). Analytical sample of **24a–c** was recrystallized from ethanol. Yield 1.06 g (71%), mp 197–200 °C. ^{1}H NMR (DMSO-d_6) δ: 7.16 (dd, 1H, *J* 7.2, 1.6 Hz, H-7′), 7.4–7.6 (m, 5H, Ph, H-5′ H-6′), 7.88 (m, 2H, Ph), 8.31 (dd, 1H, *J* 8.4, 2.4 Hz, H-4), 8.46 (d, 1H, *J* 8.6 Hz, H-4′), 8.63 (d, 1H, *J* 8.6 Hz, H-3′), 9.07 (dd, 1H, *J* 2.4, 0.8 Hz, H-6), 9.21 (dd, 1H, *J* 8.4, 0.8 Hz, H-3), 9.88 (br s, 1H, OH). Found, %: C, 80.50; H, 4.84; N, 9.30. $C_{20}H_{14}N_2O$. Calculated, %: C, 80.52; H, 4.73; N, 9.39.

4.14. 6-(4-Methoxyphenyl)-3-(8-methoxyquinolin-2-yl)-1,2,4-triazine (25c)

Mixture of hydroxyquinolinyltriazine **26c** (660 mg, 2 mmol), K_2CO_3 (2.02 g, 20 mmol), and MeI (0.14 mL, 2.2 mmol) in DMF (30 mL) was stirred overnight at room temperature, then diluted with water (80 mL), and appeared crystals were filtered off. The crude triazine was used directly in the next step. Yield 520 mg (73%), mp 150–153 °C. ^{1}H NMR (DMSO-d_6) δ: 3.89 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 7.21 (m, 2H), 7.31 (dd, 1H, *J* 6.5, 2.2 Hz, H-7′), 7.62

(m, 2H, H-5′, H-6′), 8.32 (m, 2H, H-2″), 8.56 (d, 1H, *J* 8.4 Hz, H-4′), 8.61 (d, 1H, *J* 8.4 Hz, H-3′), 9.58 (c, 1H, H-5). Found, %: C, 69.81; H, 4.69; N, 16.09. $C_{20}H_{16}N_4O_2$. Calculated, %: C, 69.76; H, 4.68; N, 16.27.

4.15. 5-(4-Methoxyphenyl)-2-(8-methoxyquinolin-2-yl)-pyridine (26c)

Triazine **25c** (500 mg, 1.4 mmol), bicyclo[2.2.1]hepta-2,5-diene (0.73 mL, 7 mmol), and *o*-xylene (20 mL) were refluxed for 24 h and cooled to room temperature. The solvent was removed under reduced pressure, residue was purified by column chromatography (silica gel, CH_2Cl_2). Analytical sample of **29c** was recrystallized from ethanol. Yield 343 mg (71%), mp 185–190 °C. ^{1}H NMR (DMSO-d_6) δ: 3.83 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 7.12 (m, 2H, H-3″, H-5″), 7.25 (m, 1H, H-7′), 7.56 (m, 2H, H-5′, H-6′), 7.79 (m, 2H), 8.26 (dd, 1H, *J* 8.2, 2.2 Hz, H-4), 8.45 (d, 1H, *J* 8.4 Hz, H-3′), 8.59 (d, 1H, *J* 8.4 Hz, H-3′), 8.65 (d, 1H, *J* 8.4 Hz, H-3), 9.03 (d, 1H, *J* 2.2 Hz, H-6). Found, %: C, 77.05; H, 5.50; N, 7.91. $C_{22}H_{18}N_2O_2$. Calculated, %: C, 77.17; H, 5.30; N, 8.18.

4.16. Typical procedure for the synthesis of complexes $[Ru(L)(bpy)_2](PF_6)_2$

Arylbipyridine **1** or **19** (0.11 mmol) and $Ru(bpy)_2Cl_2\cdot 2H_2O$ (0.052 g, 0.1 mmol) were refluxed 10 h in 10 mL of methanol/water (2:1) mixture. Water (20 mL) was added and the mixture was treated with CH_2Cl_2 (2×30 mL). Water solution of NH_4PF_6 (10%, 2 mL) was added to the water layer and resulting mixture was extracted with CH_2Cl_2 (3×30 mL). Organic layer was dried over Na_2SO_4, the solvent was removed under reduced pressure, the residue was treated with methanol, and crystals were filtered off.

4.16.1. $[Ru(\mathbf{1a})(bpy)_2](PF_6)_2$

Yield 75%. ^{1}H NMR (CD_3CN) δ: 7.37–7.46 (m, 10H), 7.73–7.81 (m, 5H), 7.83 (ddd, 1H, *J* 5.0, 1.2, 0.7 Hz, H-6′), 8.02–8.10 (m, 5H), 8.30 (dd, 1H, *J* 8.5, 2.1 Hz, H-4), 8.50 (m, 5H), 8.55 (d, 1H, *J* 8.5 Hz, H-3).

4.16.2. $[Ru(\mathbf{1b})(bpy)_2](PF_6)_2$

Yield 84%. ^{1}H NMR (CD_3CN) δ: 2.35 (s, 3H, CH_3), 7.28 (m, 4H, H_{Ar}), 7.40 (m, 5H), 7.70–7.80 (m, 5H), 7.84 (ddd, 1H, *J* 5.0, 1.2, 0.7 Hz, H-6′), 8.05 (m, 5H), 8.27 (dd, 1H, *J* 8.5, 2.2 Hz, H-4), 8.50 (m, 5H), 8.55 (d, 1H, *J* 8.5 Hz, H-3).

4.16.3. $[Ru(\mathbf{1c})(bpy)_2](PF_6)_2$

Yield 73%. ^{1}H NMR (CD_3CN) δ: 3.80 (s, 3H, OCH_3), 6.97 (m, 2H, H_{Ar}), 7.32 (m, 2H, H_{Ar}), 7.35–7.45 (m, 6H), 7.70–7.80 (m, 5H), 7.84 (ddd, 1H, *J* 5.0, 1.1, 0.7 Hz, H-6′), 8.00–8.10 (m, 5H), 8.23 (dd, 1H, *J* 8.5, 2.2 Hz, H-4), 8.45–8.54 (m, 6H).

4.16.4. $[Ru(\mathbf{1d})(bpy)_2](PF_6)_2$

Yield 80%. ^{1}H NMR (CD_3CN) δ: 7.36–7.48 (m, 9H), 7.68–7.80 (m, 5H), 7.84 (ddd, 1H, *J* 5.0, 1.2, 0.7 Hz, H-6′), 8.06 (m, 5H), 8.27 (dd, 1H, *J* 8.5, 2.2 Hz, H-4), 8.48–8.52 (m, 5H), 8.56 (d, 1H, *J* 8.5 Hz, H-3).

4.16.5. $[Ru(\mathbf{1e})(bpy)_2](PF_6)_2$

Yield 70%. ^{1}H NMR (CD_3CN) δ: 7.30 (m, 2H, H_{Ar}), 7.40 (m, 5H), 7.60 (m, 2H, H_{Ar}), 7.70–7.80 (m, 5H), 7.85 (ddd, 1H, *J* 5.0, 1.1, 0.7 Hz, H-6′), 8.05 (m, 5H), 8.27 (dd, 1H, *J* 8.5, 1.9 Hz, H-4), 8.50 (m, 5H), 8.55 (d, 1H, *J* 8.5 Hz, H-3).

4.16.6. $[Ru(\mathbf{16a})(bpy)_2](PF_6)_2$

Yield 64%. ^{1}H NMR (CD_3CN) δ: 3.81 (s, 3H, $COOCH_3$), 7.38–7.48 (m, 9H), 7.72–7.88 (m, 5H), 8.0–8.15 (m, 5H), 8.33 (dd, 1H, *J* 8.5, 1.9 Hz, H-4), 8.43–8.57 (m, 6H), 8.62 (d, 1H, *J* 8.5 Hz, H-3).

4.16.7. $[Ru(\mathbf{16b})(bpy)_2](PF_6)_2$

Yield 76%. ^{1}H NMR (CD_3CN) δ: 2.33 (s, 3H), 3.78 (s, 3H, $COOCH_3$), 7.2–7.3 (m, 4H, H_{Ar}), 7.35–7.45 (m, 4H), 7.71–7.83 (m, 5H), 8.00–8.12 (m, 5H), 8.29 (dd, 1H, *J* 8.5, 1.9 Hz, H-4), 8.44–8.62 (m, 6H), 8.58 (d, 1H, *J* 8.5 Hz, H-3).

4.16.8. $[Ru(\mathbf{16c})(bpy)_2](PF_6)_2$

Yield 69%. ^{1}H NMR (CD_3CN) δ: 3.79 (s, 6H, $COOCH_3$), 3.81 (s, 3H, OCH_3), 6.98 (m, 2H, H_{Ar}), 7.33 (m, 2H, H_{Ar}), 7.38–7.48 (m, 5H), 7.79 (m, 4H), 7.84 (ddd, 1H, *J* 5.0, 1.1, 0.7 Hz, H-6′), 8.00–8.09 (m, 4H), 8.11 (ddd, 1H, *J* 7.8, 7.8, 1.7 Hz, H-4′), 8.29 (dd, 1H, *J* 8.5, 1.9 Hz, H-4), 8.45–8.60 (m, 7H).

Acknowledgements

We thank the RFBR, the DAAD (M.M.U.) and the CRDF (O.V.S.) for funding. We thank Dr. Pavel A. Slepukhin for collecting X-ray crystallography data.

Supplementary data

Supplementary data contain changes in the absorbance and emission spectra of **21a** as a function of Zn^{2+} concentration and crystal packing of the complex [Zn(**1b**)Cl_2]. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.06.040.

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