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Boric acid-catalyzed synthesis of fused 1,2,4-triazine derivatives: a new class of red fluorescent organic compounds

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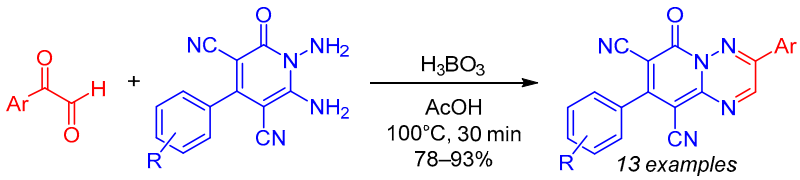

Ar = Ph, 4-MeC_6H_4, Naphth; R = H, 4-Me, 4-OMe, 3-NO_2, 4-NO_2, 4-Cl, 3-Cl

Pyrido[1,2-*b*][1,2,4]triazines have been synthesized in good to excellent yields by condensation reaction between 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitriles and arylglyoxals in the presence of boric acid. The synthesized compounds have considerable red light emission in 650 nm range.

Keywords: arylglyoxals, pyrido[1,2-*b*][1,2,4]triazin-6-ones, red fluorescent dyes.

1,2,4-Triazine derivatives are an important class of nitrogen-containing heterocycles. Intramolecular Diels–Alder reaction of 1,2,4-triazine core with a large number of dienophiles is a convenient synthetic route toward wide range of condensed heterocyclic ring systems.[1] Triazine moiety plays an important role as a core-defining structural unit of commercial dyes, herbicides, insecticides, and, in recent years, pharmaceutical compositions.[2] 1,2,4-Triazine derivatives show interesting and unique biological activities, for example, anticancer, muscle relaxant, hypnotic, anti-inflammatory, diuretic, antiHIV, and antihypertensive.[3–6] In addition, it has been established that fused heterocyclic systems containing pyridine,[7] triazole,[8] and 1,2,4-triazine[9] moieties have an extensive spectrum of biological activities. Nitrogen-containing fused heterocyclic systems also exhibit fluorescent activity[10] and have wide application as light-emitting diodes (LEDs), semiconductor lasers, probes, and fluorescent sensors. In the development of organic LED (OLED) technologies, trends are mainly focused on the optimization of the existing devices and developing new emitting materials.[11,12]

Fused heterobicyclic systems containing 1,2,4-triazinopyridinone moiety are synthesized *via* heterocyclization reaction between *N*-amino-2-pyridones and different reagents.[13] Reactions of some active carbonyl compounds with 4-aryl-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile derivatives have also been reported in the recent literature,[14] yet still, the development of efficient synthetic methods of fused nitrogen-containing heterobicyclic systems remains an important task for organic chemists. Versatile and widely applicable methods for their preparation are of considerable interest.

Therefore we decided to combine 1,2,4-triazine and pyridinone rings using 1,6-diaminopyridinone derivatives as starting compounds for building new fused heterobicyclic systems with potentially enhanced biocidal properties and high fluorescence emission. The key starting 1,6-diaminopyridinone derivatives were obtained in a cyclocondensation reaction of cyanoacetohydrazide with arylbenzilidenemalononitriles by a literature reported method.[15] Arylglyoxal derivatives were prepared by SeO_2-oxidation of the related aryl methyl ketones.[16]

Pyrido[1,2-*b*][1,2,4]triazin-6-one-7,9-dicarbonitrile derivatives **1**–**13** were easily prepared from the readily available 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile derivatives in a reaction with arylglyoxals in the presence of boric acid as a catalyst and acetic acid as a solvent (Scheme 1). We did not observe the substituent effect by changing electron-withdrawing or electron-donating groups in the arylglyoxals and 1,6-diamino-2-oxo-

Scheme 1. Synthesis of pyrido[1,2-*b*][1,2,4]triazin-6-one derivatives **1–13**

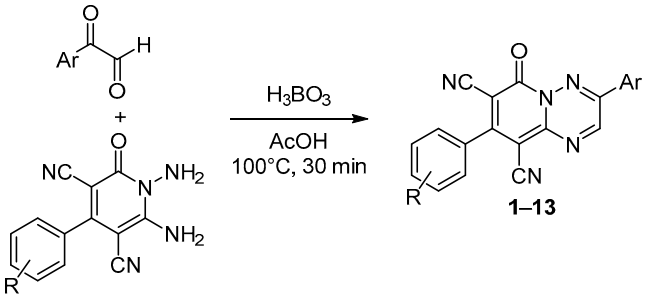

Table 1. Yields of pyrido[1,2-*b*][1,2,4]triazin-6-one derivatives **1–13**

Compound	R	Ar	Yield,%
1	H	Ph	86
2	4-Me	Ph	93
3	4-OMe	Ph	81
4	4-Cl	Ph	78
5	4-NO_2	Ph	85
6	3-NO_2	Ph	84
7	3-Cl	Ph	92
8	4-Me	4-MeC_6H_4	85
9	4-OMe	4-MeC_6H_4	87
10	4-Cl	4-MeC_6H_4	88
11	4-NO_2	4-MeC_6H_4	87
12	3-NO_2	4-MeC_6H_4	83
13	4-NO_2	2-Naphth	85

1,2-dihydropyridine-3,5-dicarbonitriles. In all cases the reactions were clean and provided the desired pyrido[1,2-*b*]-[1,2,4]triazin-6-one derivatives **1–13** in good to excellent yields. The scope and generality of the process is illustrated in Table 1.

All products were fully characterized and their structure confirmed by ^{1}H and ^{13}C NMR, IR spectra and elemental analysis. For example, the IR spectrum of compound **2** show absorption bands at 1685 and 2219 cm^{-1} assigned to C=O and CN groups, respectively. The ^{1}H NMR spectrum of compound **2** showed two singlet signals for the CH_3 and N=CH protons at 2.47 and 9.92 ppm, respectively. Doublets

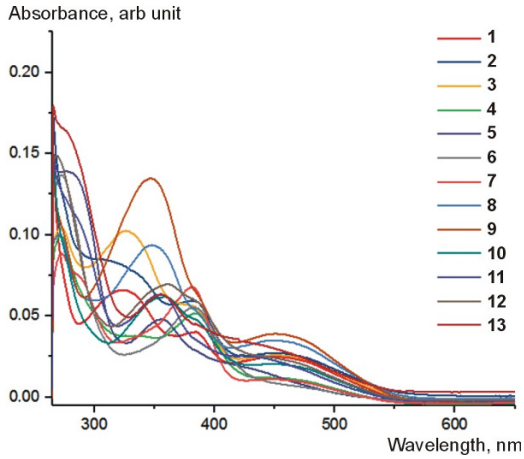

Figure 1. Absorption spectra of compounds **1–13**.

at 8.55, 7.58, and 7.49, triplets at 7.88 and 7.78 ppm correspond to the other nine protons present in the molecule. The ^{13}C NMR spectrum of compound **2** displays a downfield signal at 172.5 ppm for the carbonyl and at 21.5 ppm for the methyl carbon. Two signals at 89.5 and 96.8 ppm correspond to CN groups.

A plausible mechanism of the reaction is outlined in Scheme 2. The amino group at the C-6 atom is more reactive than the one attached to the ring nitrogen N-1. Attack of the primary amino group in the C-6 position of 1,6-diaminopyridinone on the activated aldehyde carbonyl group of the aryglyoxal can account for the formation of intermediate **A**, followed by a nucleophilic attack of a second NH_2 group present in the system to the other carbonyl group to yield the final products **1–13**.

The photophysical properties of products **1–13** were studied by UV-Vis and fluorescence spectroscopy. The absorption spectra of 5 × 10^{-5} M solutions of the compounds in DMF at 25°C are shown in Figure 1. The emission spectra of 2 × 10^{-3} M solutions of the compounds in DMF at 25°C are shown in Figure 2 (excitation wavelengths 460 nm). Excitation and emission maxima, molar extinction coefficients, and Stokes shifts of compounds **1–13** are listed in Table 2. The absorption behavior of all samples is quite similar meaning that the optical band gap of the molecules originates from a unit structure.

Figure 2 indicates that the synthesized compounds can be classified in four categories according to the photoluminescence (PL) intensity. Compound **1** has the lowest

Scheme 2. A plausible mechanism of pyrido[1,2-*b*][1,2,4]triazin-6-one derivatives **1–13** synthesis

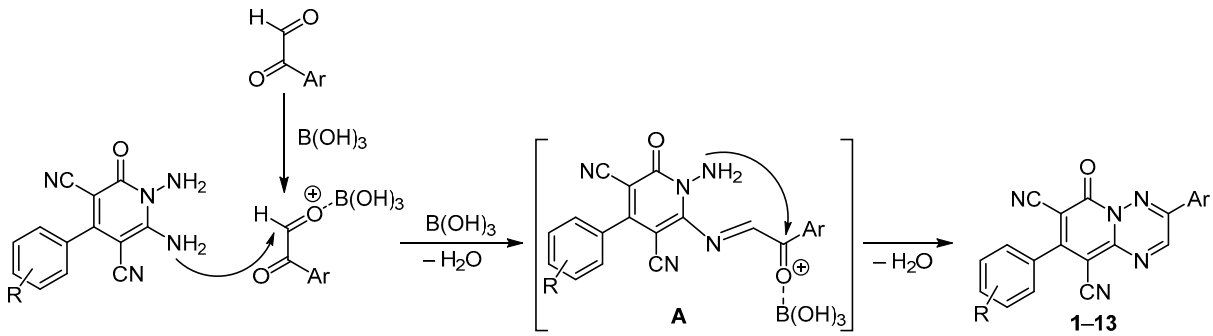

Table 2. UV-Vis spectra absorption data

Compound	λ_{max}, nm (ε_{max})	Fluorescence emission, λ_{max}, nm	Stokes shift, nm
1	324 (14780), 383 (8885), 451 (4994)	656	332
2	299 (19800), 383 (12818), 458 (6476)	656	357
3	271 (21831), 326 (22170), 452 (6099)	658	332
4	383 (19370), 272 (10161)	660	277
5	275 (29910), 356 (10645)	656	381
6	272 (27930), 383 (11366)	658	386
7	272 (19400), 384 (14298)	656	384
8	268 (18495), 350 (19020), 450 (7545)	656	306
9	346 (27000), 451 (7991)	658	312
10	358 (13670), 450 (5096)	656	298
11	356 (26880), 435 (5610)	656	300
12	268 (26880),362 (14283)	656	388
13	275 (28990), 355 (11690)	658	383

PL emission, compounds **2**–**7** have almost the same emission intensity, the emission intensities of compounds **8**–**12** are located very close to each other with a considerable gap, that divides them from the second category, and finally, compound **13** has the highest emission intensity. It should be mentioned that the wavelength of PL emission does not change from compound to compound, only the intensity is influenced which is expected from the absorption spectra as well. It is also interesting to note how the different functional groups affect the intensity of fluorescence due to the facilitated electron flow which can increase under excitation with light and relax back to the ground state as a result of red light emission. A closer look to these categories confirms the proposed mechanism. Compounds **2**–**7**, which are 2nd category, have one donor or acceptor group (Me, MeO, NO_2, Cl) in comparison to compound **1**. Compounds **8**–**12** as 3rd category have two functional groups on two benzene moieties on the both sides of the molecule and thus have higher emission intensity. Finally, compound **13**, containing naphthalene ring, has the highest emission due

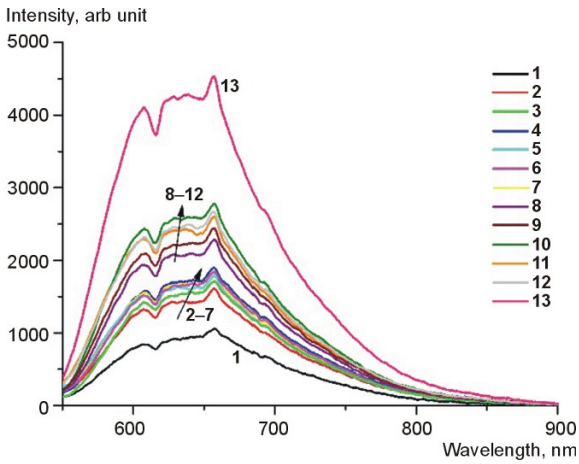

Figure 2. Fluorescence emission spectra of compounds **1**–**13**.

the better π-conjugation compared to compounds **1**–**12**, which can readily incorporate in electron excitation of the central part of the molecule. In general, the synthesized molecules have considerable red light emission located around 650 nm, making them promising targets for application in diagnostic purposes.

In conclusion, an efficient, general, and simple methodology for the synthesis of fluorescent 6-oxo-3-phenyl-6*H*-pyrido[1,2-*b*][1,2,4]triazin-6-one-7,9-dicarbonitrile derivatives from 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitriles and arylglyoxals in the presence of boric acid is reported. The procedure offers several advantages including clean reaction profile, excellent yields, short reaction time, and easy work-up procedure of pure product. Because of their red light emissions, the synthesized compounds could be interesting for diagnostic purposes and as a core structures in new light-emitting material design.

Experimental

IR spectra were obtained on a Matson-1000 FT-IR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer (400 and 100 MHz, respectively) in DMSO-d_6 with TMS as internal standard. Elemental analyses were performed on a Eurovector EuroEA3000 CHNS-O analyzer. Melting points were determined on a Melt-Tem II melting point apparatus and are uncorrected. UV-Vis and photoluminescence spectra were measured using PerkinElmer and Avantes AvaSpec-2048 TEC spectrometers, respectively.

All chemicals and solvents were purchased from commercial sources and used without further purification unless otherwise stated.

Synthesis of compounds 1–13 (General method). In a typical experimental procedure, 50-ml round-bottom flask was charged with acetic acid (15 ml), boric acid (0.012 g, 0.2 mmol), a glyoxal derivative (2 mmol), and a 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile derivative (2 mmol). The mixture was stirred at room temperature for 30 min. Completion of the reaction (about 30 min) monitored by TLC (eluent EtOAc–*n*-hexane, 3:1). The precipitate was filtered off, washed with water, and dried in air.

6-Oxo-3,8-diphenyl-6*H*-pyrido[1,2-*b*][1,2,4]triazine-7,9-dicarbonitrile (1). Yield 0.300 g (86%), orange solid, mp 326–329°C (decomp.). IR spectrum, ν, cm^{-1}: 1677, 2224. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.94 (1H, s, N=CH); 8.57 (2H, d, *J* = 7.6, H Ph); 7.88 (1H, t, *J* = 7.6, H Ph); 7.81–7.69 (7H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 89.5 (CN); 96.9 (CN); 114.8; 115.8; 128.8; 129.4; 129.7; 130.1; 130.2; 130.5; 130.8; 131.5; 131.8; 134.1; 136.1; 141.9; 151.7; 156.0; 157.7; 160.5. Found, %: C 72.06; H 3.12; N 19.98. $C_{21}H_{11}N_5O$. Calculated, %: C 72.20; H 3.17; N 20.05.

8-(4-Methylphenyl)-6-oxo-3-phenyl-6*H*-pyrido[1,2-*b*]-[1,2,4]triazine-7,9-dicarbonitrile (2). Yield 0.337 g (93%), orange solid, mp 327–331°C (decomp.). IR spectrum, ν, cm^{-1}: 1685, 2219. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.92 (1H, s, N=CH); 8.55 (2H, d, *J* = 7.2, H Ph); 7.88 (2H, t, *J* = 7.6,

H Ph); 7.78 (1H, t, *J* = 7.6, H Ph); 7.58 (2H, d, *J* = 8.0, H Ar); 7.49 (2H, d, *J* = 8.0, H Ar); 2.47 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 21.5 (CH_3); 89.5 (CN); 96.8 (CN); 114.9; 115.9; 128.8; 130.0; 130.1; 130.4; 131.2; 131.8; 136.0; 141.6; 141.8; 151.6; 156.0; 157.6; 160.5; 172.5. Found, %: C 72.65; H 3.45; N 19.13. $C_{22}H_{13}N_5O$. Calculated, %: C 72.72; H 3.61; N 19.27.

8-(4-Methoxyphenyl)-6-oxo-3-phenyl-6*H*-pyrido[1,2-*b*]-[1,2,4]triazine-7,9-dicarbonitrile (3). Yield 0.307 g (81%), orange solid, mp 320–324°C (decomp.). IR spectrum, ν, cm^{-1}: 1677, 2228. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.91 (1H, s, N=CH); 8.56 (2H, d, *J* = 7.6, H Ph); 7.88 (1H, t, *J* = 7.2, H Ph); 7.78 (2H, t, *J* = 8.0, H Ph); 7.66 (2H, d, *J* = 8.0, H Ar); 7.24 (2H, d, *J* = 8.0, H Ar); 3.93 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 56.0 (OCH_3); 89.5 (CN); 96.6 (CN); 114.8; 115.0; 116.1; 125.9; 130.1; 130.4; 130.9; 131.8; 136.0; 141.7; 151.6; 156.0; 157.6; 160.1; 161.9. Found, %: C 69.52; H 3.36; N 18.31. $C_{22}H_{13}N_5O_2$. Calculated, %: C 69.65; H 3.45; N 18.46.

8-(4-Chlorophenyl)-6-oxo-3-phenyl-6*H*-pyrido[1,2-*b*]-[1,2,4]triazine-7,9-dicarbonitrile (4). Yield 0.298 g (78%), orange solid, mp 331–335°C (decomp.). IR spectrum, ν, cm^{-1}: 1685, 2226. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.95 (1H, s, N=CH); 8.57 (2H, d, *J* = 7.2, H Ph); 7.88 (1H, t, *J* = 7.2, H Ph); 7.81–7.77 (4H, m, H Ph, H Ar); 7.74–7.71 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 89.4 (CN); 96.9 (CN); 114.7; 115.6; 129.7; 130.2; 130.5; 130.8; 131.8; 132.9; 136.1; 136.5; 142.1; 151.7; 155.9; 157.8; 159.3. Found, %: C 65.46; H 2.72; N 18.28. $C_{21}H_{10}ClN_5O$. Calculated, %: C 65.72; H 2.63; N 18.25.

8-(4-Nitrophenyl)-6-oxo-3-phenyl-6*H*-pyrido[1,2-*b*]-[1,2,4]triazine-7,9-dicarbonitrile (5). Yield 0.290 g (85%), orange solid, mp 340–345°C (decomp.). IR spectrum, ν, cm^{-1}: 1707, 2226. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.98 (1H, s, N=CH); 8.58 (2H, d, *J* = 7.2, H Ph); 8.53 (2H, d, *J* = 8.0, H Ar); 7.99 (2H, d, *J* = 8.0, H Ar); 7.89 (1H, t, *J* = 7.6, H Ph); 7.79 (2H, t, *J* = 7.6, H Ph). ^{13}C NMR spectrum, δ, ppm: 89.2 (CN); 96.9 (CN); 114.5; 115.4; 124.7; 130.3; 130.5; 130.6; 131.7; 136.2; 140.1; 142.3; 149.4; 151.7; 155.7; 158.0; 158.5. Found, %: C 63.87; H 2.76; N 21.38. $C_{21}H_{10}N_6O_3$. Calculated, %: C 63.96; H 2.56; N 21.31.

8-(3-Nitrophenyl)-6-oxo-3-phenyl-6*H*-pyrido[1,2-*b*]-[1,2,4]triazine-7,9-dicarbonitrile (6). Yield 0.331 g (84%), orange solid, mp 301–304°C (decomp.). IR spectrum, ν, cm^{-1}: 1699, 2225. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.98 (1H, s, N=CH); 8.60–8.53 (4H, m, H Ph, H Ar); 8.19–8.17 (1H, m, H Ph(Ar)); 8.02 (1H, t, *J* = 8.0, H Ph(Ar)); 7.89 (1H, t, *J* = 7.6, H Ph(Ar)); 7.79 (2H, t, *J* = 8.0, H Ph(Ar)). ^{13}C NMR spectrum, δ, ppm: 89.5 (CN); 97.3 (CN); 114.6; 115.5; 123.8; 126.2; 130.3; 130.5; 131.5; 131.7; 135.4; 135.5; 136.2; 142.4; 148.2; 151.7; 155.8; 158.0; 158.1. Found, %: C 63.87; H 2.65; N 21.45. $C_{21}H_{10}N_6O_3$. Calculated, %: C 63.96; H 2.56; N 21.31.

8-(3-Chlorophenyl)-6-oxo-3-phenyl-6*H*-pyrido[1,2-*b*]-[1,2,4]triazine-7,9-dicarbonitrile (7). Yield 0.352 g (92%), orange solid, mp 321–326°C (decomp.). IR spectrum, ν, cm^{-1}: 1682, 2230. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.97 (1H, s, N=CH); 8.57 (2H, d, *J* = 8.8, H Ph(Ar)); 7.89 (1H, t, *J* = 7.8, H Ph(Ar)); 7.87–7.74 (3H, m, H Ph(Ar)); 7.72–7.62 (3H, m, H Ph(Ar)). ^{13}C NMR spectrum, δ, ppm: 90.0 (CN); 97.7 (CN); 114.1; 115.0; 128.6; 130.2; 130.4; 130.5; 130.6; 131.2; 131.7; 132.9; 133.3; 136.2; 142.2; 151.7; 155.7; 157.9; 158.4. Found, %: C 65.68; H 2.57; N 18.34. $C_{21}H_{10}ClN_5O$. Calculated, %: C 65.72; H 2.63; N 18.25.

3,8-Bis(4-methylphenyl)-6-oxo-6*H*-pyrido[1,2-*b*][1,2,4]-triazine-7,9-dicarbonitrile (8). Yield 0.320 g (85%), orange solid, mp 298–302°C (decomp.). IR spectrum, ν, cm^{-1}: 1686, 2226. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.88 (1H, s, N=CH); 8.47 (2H, d, *J* = 8.0, H Ar); 7.60 (2H, d, *J* = 8.0, H Ar); 7.57 (2H, d, *J* = 8.0, H Ar); 7.49 (2H, d, *J* = 8.0, H Ar); 2.52 (3H, s, CH_3); 2.47 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 21.5 (CH_3); 22.1 (CH_3); 89.3 (CN); 96.4 (CN); 114.9; 115.9; 128.8; 129.1; 130.0; 130.2; 131.1; 131.2; 141.5; 141.9; 147.5; 151.7; 156.0; 157.3; 160.5; 172.5. Found, %: C 73.34; H 3.86; N 18.63. $C_{23}H_{15}N_5O$. Calculated, %: C 73.20; H 4.01; N 18.56.

8-(4-Methoxyphenyl)-3-(4-methylphenyl)-6-oxo-6*H*-pyrido[1,2-*b*][1,2,4]triazine-7,9-dicarbonitrile (9). Yield 0.342 g (87%), orange solid, mp 299–301°C (decomp.). IR spectrum, ν, cm^{-1}: 1685, 2225. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.87 (1H, s, N=CH); 8.48 (2H, d, *J* = 8.0, H Ar); 7.65 (2H, d, *J* = 8.0, H Ar); 7.60 (2H, t, *J* = 8.0, H Ar); 7.23 (2H, d, *J* = 8.0, H Ar); 3.19 (3H, s, OCH_3); 2.50 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 22.1 (CH_3); 56.0 (OCH_3); 89.3 (CN); 96.2 (CN); 114.8; 115.1; 116.1; 125.9; 129.1; 130.2; 130.8; 131.1; 141.6; 147.5; 151.7; 156.1; 157.3; 160.1; 161.8. Found, %: C 70.14; H 3.56; N 17.66. $C_{23}H_{15}N_5O_2$. Calculated, %: C 70.22; H 3.84; N 17.80.

8-(4-Chlorophenyl)-3-(4-methylphenyl)-6-oxo-6*H*-pyrido[1,2-*b*][1,2,4]triazine-7,9-dicarbonitrile (10). Yield 0.350 g (88%), orange solid, mp 326–330°C (decomp.). IR spectrum, ν, cm^{-1}: 1687, 2228. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.91 (1H, s, N=CH); 8.48 (2H, d, *J* = 8.0, H Ar); 7.80–7.77 (2H, m, H Ar); 7.73–7.70 (2H, m, H Ar); 7.61 (2H, d, *J* = 8.0, H Ar); 2.50 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 22.1 (CH_3); 89.2 (CN); 96.6 (CN); 114.8; 115.7; 129.1; 129.6; 130.3; 130.8; 131.2; 132.9; 136.4; 141.9; 147.7; 151.7; 155.9; 157.5; 159.3; 172.5. Found, %: C 66.23; H 3.15; N 17.54. $C_{22}H_{12}ClN_5O$. Calculated, %: C 66.42; H 3.04; N 17.60.

3-(4-Methylphenyl)-8-(4-nitrophenyl)-6-oxo-6*H*-pyrido-[1,2-*b*][1,2,4]triazine-7,9-dicarbonitrile (11). Yield 0.355 g (87%), orange solid, mp 336–340°C (decomp.). IR spectrum, ν, cm^{-1}: 1698, 2227. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.94 (1H, s, N=CH); 8.53 (2H, d, *J* = 8.0, H Ar); 8.49 (2H, d, *J* = 8.0, H Ar); 8.00–7.97 (2H, m, H Ar); 7.62 (2H, d, *J* = 8.0, H Ar); 2.50 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 22.1 (CH_3); 89.0 (CN); 96.5 (CN); 114.5; 115.4; 124.7; 129.1; 130.4; 130.6; 131.2; 140.2; 142.2; 147.8; 149.4; 151.8; 155.8; 157.7; 158.5. Found, %: C 64.56; H 2.78; N 20.43. $C_{22}H_{12}N_6O_3$. Calculated, %: C 64.71; H 2.96; N 20.58.

3-(4-Methylphenyl)-8-(3-nitrophenyl)-6-oxo-6*H*-pyrido-[1,2-*b*][1,2,4]triazine-7,9-dicarbonitrile (12). Yield 0.338 g (83%), orange solid, mp 298–302°C (decomp.). IR spectrum, ν, cm^{-1}: 1691, 2228. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.94 (1H, s, N=CH); 8.58–8.53 (2H, m, H Ar); 8.49 (2H, d, *J* = 8.0, H Ar); 8.18–8.16 (1H, m, H Ar); 8.02 (1H, t,

J = 8.0, H Ar); 7.61 (2H, d, *J* = 8.4, H Ar); 2.50 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 22.1 (CH_3); 89.2 (CN); 96.9 (CN); 114.6; 115.5; 123.8; 126.2; 129.1; 130.4; 131.2; 131.5; 135.5; 142.3; 147.8; 148.2; 151.8; 155.8; 157.7; 158.1. Found, %: C 64.55; H 2.85; N 20.52. $C_{22}H_{12}N_6O_3$. Calculated, %: C 64.71; H 2.96; N 20.58.

3-(Naphthalen-2-yl)-8-(4-nitrophenyl)-6-oxo-6*H*-pyrido-[1,2-*b*][1,2,4]triazine-7,9-dicarbonitrile (13). Yield 0.386 g (85%), orange solid, mp 313–318°C (decomp.). IR spectrum, ν, cm^{-1}: 1697, 2225. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.10 (1H, s, N=CH); 9.39 (1H, s, H Ar); 8.54 (2H, d, *J* = 8.8, H Ar); 8.50 (1H, dd, *J* = 8.8, *J* = 2.0, H Ar); 8.28 (1H, d, *J* = 8.8, H Ar); 8.23 (1H, d, *J* = 8.0, H Ar); 8.12 (1H, d, *J* = 8.0, H Ar); 8.00 (2H, d, *J* = 8.8, H Ar); 7.83 (1H, dt, *J* = 8.0, *J* = 1.2, H Ar); 7.77 (1H, dt, *J* = 8.0, *J* = 1.2, H Ar). ^{13}C NMR spectrum, δ, ppm: 89.2 (CN); 96.9 (CN); 115.4; 124.0; 124.7; 125.0; 127.4; 128.4; 128.6; 129.2; 130.5; 130.6; 131.0; 132.9; 133.9; 136.5; 140.2; 142.4; 149.4; 151.8; 155.8; 157.8; 158.5. Found, %: C 67.43; H 2.57; N 18.76. $C_{25}H_{12}N_6O_3$. Calculated, %: C 67.57; H 2.72; N 18.91.

The Supplementary information file containing ^{1}H and ^{13}C NMR spectra and UV-Vis spectra of all synthesized compounds is available at the journal website at http://link.springer.com/journal/10593.

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