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Synthesis and Characterization of New Blue-Greenish Electroluminescent Materials Based on 1,3,4-Oxadiazole-triazolopyridinone Hybrids

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ABSTRACT: *New functionalized oxadiazole-triazolopyridinone derivatives were synthesized via arcycloaddition. With the chromophores of triazolopyridinone, the photoluminescence spectra of these compounds in dichloromethane solution showed emission peaks between 430 and 520 nm. Following the spectroscopic studies, and the measurements of cyclic voltammogram, 1,3,4-oxadiazole-triazolopyridinone hybrids possess a great potential as highly efficient, blue-greenish, organic light-emitting devices materials.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:212–219, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20285

INTRODUCTION

Organic light-emitting devices have been an important subject in recent years because of their applications in displays and electronic industries [1–3]. Furthermore, blue light-emitting materials have been essential because of their wild applicability [4–7].

In 1990, Adachi et al. reported 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) as an excellent electron transport material in an organic multilayer electroluminescent (EL) diode [8]. After this report, 1,3,4-oxadiazole derivatives have been widely exploited as electron-transporting, hole-blocking materials in EL devices because of their electron-deficient nature, high thermal stability, and high photoluminescence quantum yield (PLQL) [9–10]. 1,3,4-Oxadiazole-based heterocyclic compounds were also enthusiastically investigated. For example, 1,3,4-oxadiazole-pyridine hybrids [11], 1,3,4-oxadiazole-pyrimidine hybrids [11],1,3,4-oxadiazole-carbazole [12], and 1,3,4-oxadiazole-spirobifluorene [13] were well studied. The heterocyclic moieties on the molecular structure can provide the improved hole injection, transport properties, and confer rigidity.

In this work, novel 1,3,4-oxadiazole-triazolopyridinone derivatives were synthesized to explore the effect of modification of the

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triazolopyridinone moiety [14]. We synthesized a series of 6-(1,3,4-oxadiazol-2-yl)-[1,2,4]triazodone derivatives (**5a–5i**) in which *N*1-phenyl group and C-10 of 1,3,4-oxadiazole ring were modified in several ways. Following the spectroscopic studies and the measurements of cyclic voltammogram, 1,3,4-oxadiazole-triazolopyridinone derivatives were highly efficient, blue-greenish EL.

RESULTS AND DISCUSSION

Synthesis of 1,3,4-oxadiazol-2-yl-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one Derivatives (*5a–5i*).

The synthetic route of 3-(5-phenyl-1,3,4-oxadiazol-2-yl)pyridine derivatives (**4a–4c**) is shown in Scheme 1. Isonicotinyl chloride **1** reacted with hydrazine monohydrhydrate to generate isonicotinyl hydrazine **2** [15]. Then various benzoyl chloride (para-$R^1 = H$, Me, and Cl) were treated with isonicotinyl hydrazine **2** to give the corresponding 1-isonicotinyl-2-nicotinyl hydrazines **3a–3c** [16]. 1-Isonicotinyl-2-nicotinyl hydrazines **3a–3c** were subjected to dehydration–cyclization by using fresh $POCl_3$ to produce 1,3,4-oxadiazol-2-ylpyridine derivatives **4a–4c**.

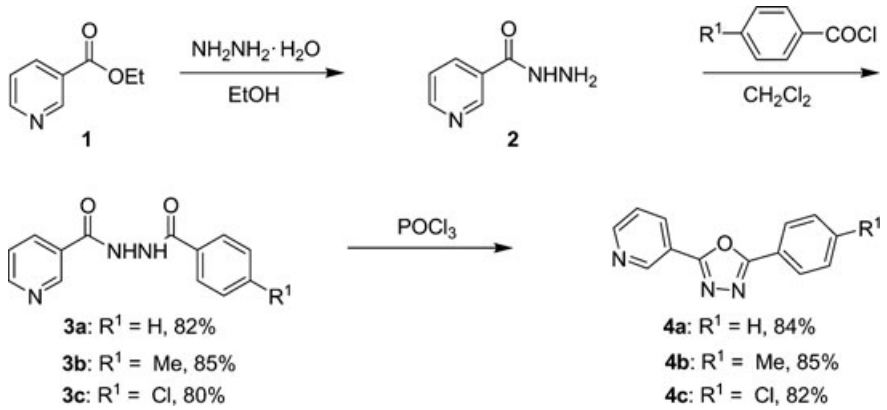
α-Chloroformylarylhydrazines hydrochloride were synthesized through our previous published procedures [17]. 1,3,4-Oxadiazol-2-ylpyridine derivatives **4a–4c** reacted with α-chloroformylarylhydrazine in *i*-PrOH at 80°C for 2 h to generate 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i** in 65–72% yields (see Scheme 2).

Photophysical Properties

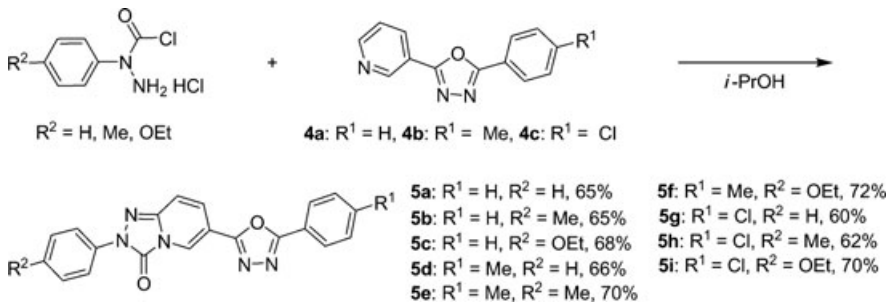
The ultraviolet-visible (UV-vis) spectra of 1,3,4-oxadiazol-2-ylpyridine **4a–4c** and 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i** were measured in CH_2Cl_2 and $CHCl_3$ solutions. UV-vis absorption maxima of **4a–4c** are between 286 and 292 nm. 1,3,4-Oxadiazole-triazolopyridinone derivatives **5a–5i** with the moiety of triazolopyridinone have gradual red shifts to 291–305 nm because of the extension of conjugation (see Table 1). The photoluminescence (PL) spectra of 1,3,4-oxadiazol-2-ylpyridine derivatives **4a–4c** and 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i** were shown in Table 1. The emission wavelengths for **4a–4c** are between 356 and 360 nm in CH_2Cl_2 or $CHCl_3$ solution. The λ_{max}s of photoluminescence are around 465–477 nm of 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i** with the moiety of triazolopyridinone exhibiting blue fluorescence in CH_2Cl_2 or $CHCl_3$ solution. The long range of substitution effects on R^1 and R^2 positions is clearly not a function for absorption and emission spectra (see Table 1). The solution fluorescence quantum yields (Φ_f) of **5a–5i**, all of which fall in the range 0.68–0.76, were determined relative to that of 2-phenyl-5-(4-biphenyl)-1,3,4-oxzdiazole in benzene ($\Phi_f = 0.80$, see Table 1) [18]. The PL spectra **5c, 5f**, and **5i** of the vacuum evaporated films on quartz substrates, with a maximum at 498 nm, show a red-shift (~30 nm), with respect to the solution spectrum as shown in Fig. 1.

Cyclic Voltammetry Measurements

The electrochemical behavior of 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i** was investigated by cyclic voltammetry. The measurements were carried out with a platinum electrode in CH_2Cl_2 containing tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The potential was measured against Ag/AgCl as reference electrode, and each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system [19–20].



SCHEME 1



SCHEME 2

The data were summarized in Table 2, and the HOMO energy (*Ip*) for 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i** were calculated on the basis of the value of −4.8 eV for Fc with respect to zero vacuum level [19]. Upon the anodic sweep, **5a–5i** showed irreversible reduction processes. As an example, the cyclic voltammogram of **5f** is shown in Fig. 2. In the case of **5f**, the reversibility of oxidation was estimated and the HOMO value is −5.60 eV with respect to Ag/AgCl (−5.66 eV with respect to Fc). The bandgap energies (3.68–3.70 eV) of 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i** were estimated from the onset wavelength (λ_{onset}) of the UV-vis absorption. The substitution effects on R^1 and R^2 positions do not promote the electronic properties characterization of 1,3,4-oxadiazole-triazolopyridinone derivatives **5a–5i**. From the high electron affinities, **5a–5i** possess the potential of electron-transporting and highly efficient, blue-greenish, EL materials.

We successfully prepared a series of new blue EL materials on the basis of 1,3,4-oxadiazole-triazolopyridinone moiety by using 1,3,4-oxadiazole-pyridine derivatives with α-chloroformylarylhydrazine hydrochloride. Triazolopyridinone moiety plays an excellent assistant role in controlling fundamental photolytic process.

EXPERIMENTAL

General

Nicotinohydrazide [14] and α-chloroformylaryl-hydrazines hydrochloride [21] were synthesized according to literature procedures. All chemicals were reagent grade and used as purchased. All reactions were carried out under nitrogen atmosphere and monitored by thin-layer chromatography (TLC) analysis. Flash column chromatography was carried out on silica gel (230–400 mesh). Commercially available reagents were used without further purification unless otherwise noted. Ethyl acetate, dimethyl sulfoxide, diisopropyl ether, hexanes, glacid acetic acid, and methanol were purchased from Mallinckrodt Chemical Co. Tetrahydrofuran (reagent grade) was purchased from Aldrich. The following compounds were purchased from Acoros Chemical Co: Benzoyl chloride, *p*-toluoyl chloride, 4-chlorobenzoyl

TABLE 1 UV-Vis Absorption Maxima and Photoluminescence Peak Wavelength of 1,3,4-Oxadiazole-Triazolopyridinone Derivatives **5a–5i**

			λ_{max}/nm of UV-Vis		λ_{max}/nm of PL		
Compound	R^1	R^2	$CHCl_3$	CH_2Cl_2	$CHCl_3$	CH_2Cl_2	Φ_f^a
4a	H	–	288	286	356	358	–
4b	Me	–	288	285	356	358	–
4c	Cl	–	292	290	358	361	–
5a	H	H	296	294	469	465	0.75
5b	H	Me	295	294	470	468	0.72
5c	H	OEt	293	291	471	468	0.68
5d	Me	H	298	295	470	469	0.76
5e	Me	Me	297	295	468	466	0.69
5f	Me	OEt	295	291	472	471	0.74
5g	Cl	H	305	301	476	475	0.65
5h	Cl	Me	301	298	477	472	0.68
5i	Cl	OEt	300	297	475	470	0.69

[a] Φ_f: Fluorescence quantum efficiency, relative to 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole in benzene ($\Phi_f = 0.8$).

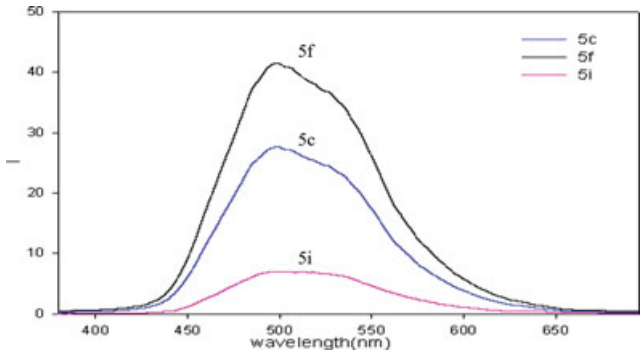


FIGURE 1 Normalized photoluminescence spectra of **5c, 5f**, and **5i** (vacuum evaporated film).

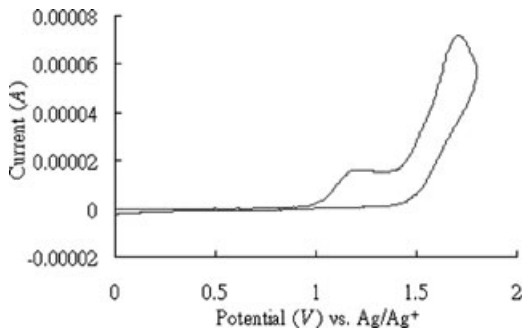


FIGURE 2 Cyclic voltammogram of **5f** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at a scan rate.

chloride, sodium hydrogen carbonate, sodium hydroxide, and tributyl amine.

Analytical TLC was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Purification by gravity column chromatography was carried out by use of Merck Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wave numbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. UV-vis spectra were measured with an HP 8452A diode-array spectrophotometer. PL spectra were obtained on a Perkin-Alemer fluorescence spectrophotometer (LS 55). Proton NMR spectra were obtained on a Varian Unity-400 (400 MHz) or a Bruker-300 (400 MHz) spectrometer by use of chloroform-*d*/DMSO-*d6* as solvent. Carbon-13 NMR spectra were obtained on a Varian Unity-400 (100 MHz) spectrometer or a Bruker-400 (100 MHz) spectrometer by use of chloroform-*d* as solvent. Carbon-13 chemical shifts are referenced to the center of the $CDCl_3$ triplet (δ 77.0 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; J, coupling constant (hertz). Elemental analyses were carried out on a Heraeus CHN–O RAPID element analyzer.

Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on a PGSTAT 20 electrochemical analyzer. The oxidation and reduction measurements were carried out, respectively, in anhydrous CH_2Cl_2 and anhydrous THF containing 0.1 M tetrabutylammonium

TABLE 2 Electrochemical Properties of 1,3,4-Oxadiazole-Triazolopyridinone Derivatives **5a–5i**

Compound	*E onset*[a] *(v)*	*E′ onset*[b] *(v)*	*Ip*[c,d] $= E_{HOMO}$ *(eV)*	*Eg*[d,f] *= Bandgap energy (eV)*	*Ea*[e,f] $= E_{LUMO}$ *(eV)*
5a	1.27	1.08	–5.88	3.67	–2.21
5b	1.17	0.98	–5.78	3.68	–2.10
5c	0.98	0.79	–5.59	3.68	–1.91
5d	1.07	0.88	–5.68	3.68	–2.00
5e	1.04	0.85	–5.63	3.69	–1.96
5f	0.99	0.80	–5.60	3.70	–1.90
5g	1.12	0.93	–5.93	3.68	–2.05
5h	1.46	1.27	–6.07	3.68	–2.39
5i	1.41	1.22	–6.02	3.69	–2.33

[a]Measured vs. ferrocene/ferrocenium.
[b]*E′* onset = *E* onset − 0.19 eV (Measured vs. Ag/AgCl).
[c]*Ip* = −(*E′* onset + 4.8) [19].
[d]*Eg*: the bandgap energy estimated from the onset wavelength of UV-vis absorption.
[e]*Ea* = *Ip* + *Eg*.
[f] 1 eV = 96.5 kJ/mol.

hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at a scan rate of 50 mV s^{-1}. The potentials were measured against an Ag/Ag^+ (0.01 M AgCl) reference electrode using ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram [19].

Standard Procedure for Acylation [16]

A solution of nicotinohydrazide and pyridine was mixed and stirred in CH_2Cl_2 solution at room temperature. Benzoyl chloride was added dropwise into the reaction mixture and stirred at room temperature for 3 h. After the reaction was completed, the reaction mixture was filtered and washed with CH_2Cl_2. The filtrate solid was dried in vacuum oven overnight and crystallized from CH_2Cl_2 to give the desired product (**3a–3c**).

Benzoic acid(pyridine-3-carbonyl)hydrazide (3a). A solution of nicotinohydrazide (**2**, 2.50 g, 18.2 mmol, 1.0 equivalent) and pyridine (126 mg, 20.1 mmol, 1.1 equivalent) was mixed and stirred in CH_2Cl_2 (50.0 mL) solution at room temperature. Benzoyl chloride (156 mg, 20.3 mmol, 1.1 equivalent) was added dropwise into the reaction mixture and stirred at room temperature for 3 h. After the reaction was completed, the reaction mixture was filtered and washed with CH_2Cl_2 (150 mL). The filtrate solid was dried in vacuum oven overnight and crystallized from CH_2Cl_2 to give the pure **3a** as white powder in 82% yield (3.60 g, 14.9 mmol): ^{1}H NMR (DMSO-d6, 200 MHz) δ 7.60–7.51 (m, 3H, ArH), 7.82 (t, J = 4.0 Hz, 1H), 7.92 (d, J = 4.4 Hz, 2H, ArH), 8.54 (d, J = 4.0 Hz, 1H), 8.89 (d, J = 3.2 Hz, 1H), 9.19 (s, 1H), 10.69 (s, 1H, NH), 10.96 (s, 1H, NH).

4-Methylbenzoic acid(pyridine-3-carbonyl)hydrazide (3b). The standard procedure was followed, and the desired product **3b** was obtained as white powder in 85% yield: ^{1}H NMR (DMSO-d6, 200 MHz) δ 2.49 (s, 3H, CH_3), 7.33 (d, J = 3.8 Hz, 2H, ArH), 7.86–7.78 (m, 3H), 8.57 (d, J = 3.9 Hz, 1H), 8.91 (d, J = 3.5 Hz, 1H), 9.20 (s, 1H), 10.60 (s, 1H, NH), 10.93 (s, 1H, NH).

4-Chlorobenzoic acid(pyridine-3-carbonyl)hydrazide (3c). The standard procedure was followed, and the desired product **3c** was obtained as white powder in 85% yield: ^{1}H NMR (DMSO-d6, 200 MHz) δ 7.40 (d, J = 3.9 Hz, 2H), 7.92–7.80 (m, 3H), 8.60 (d, J = 4.1 Hz, 1H), 8.88 (d, J = 3.8 Hz, 1H), 9.22 (s, 1H), 10.58 (s, 1H, NH), 10.95 (s, 1H, NH).

Standard Procedure for Dehydroxyl-cyclolization [16]

A solution of benzoic acid(pyridine-3-carbonyl)-hydrazide compounds **3a–3c** in $POCl_3$ (15 mL) was stirred at 100°C for 2–4 h. After the reaction was completed, the reaction mixture was added with cold water (50 mL) and neutralized with NaOH aqueous solution (50 mL) to precipitate. The product was washed with cold water, filtrated, and dried in vacuum oven overnight to give the desired product (**4a–4c**).

3-(5-Phenyl-1,3,4-oxadiazol-2-yl)pyridine (4a). A solution of benzoic acid(pyridine-3-carbonyl)-hydrazide (**2a**, 3.40 g, 14.1 mmol, 1.0 equivalent) in $POCl_3$ (15 mL) was stirred at 100°C for 2–4 h. After the reaction was completed, the reaction mixture was added with cold water (50 mL) and neutralized with NaOH aqueous solution (50 mL) to precipitate. The product was washed with cold water, filtrated, and dried in vacuum oven overnight to obtain a pure **4a** (2.64 g, 11.8 mmol) as white solid in 84% isolated yield: ^{1}H NMR (DMSO-d6, 200 MHz) δ 7.68–7.60 (m, 4H), 8.15 (d, J = 4.1 Hz, 2H, ArH), 8.49 (d, J = 4.2 Hz, 1H), 8.82 (d, J = 4.5, 1H), 9.30 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz): δ 120.45, 122.26, 124.22, 127.18, 130.62, 142.66, 147.73, 152.78, 162.35, 164.66.

3-(5-(4-Methylpheny)l-1,3,4-oxadiazol-2-yl)pyridine (4b). The standard procedure was followed, and the desired product **4b** was obtained as white powder in 84% yield: ^{1}H NMR (DMSO-d6, 200 MHz) δ 2.39 (s, 3H, CH_3), 7.42 (d, J = 3.8 Hz, 2H, ArH), 7.65 (t, J = 6.1 Hz, 1H), 8.02 (d, J = 3.3 Hz, 2H, ArH), 8.46 (d, J = 3.7 Hz, 1H), 8.80 (d, J = 4.7 Hz, 1H), 9.27 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 21.57, 120.43, 120.79, 124.73, 127.18, 130.38, 134.60, 142.85, 147.73, 152.84, 162.45, 164.89.

3-(5-(4-Chloropheny)l-1,3,4-oxadiazol-2-yl)pyridine (4c). The standard procedure was followed, and the desired product **4b** was obtained as white powder in 82% yield: ^{1}H NMR (DMSO-d6, 200 MHz) δ 7.72–7.65 (m, 3H), 8.15 (d, J = 4.1 Hz, 2H, ArH), 8.48 (d, J = 3.9 Hz, 1H), 8.80 (d, J = 4.2 Hz, 1H), 9.29 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 120.21, 122.44, 124.75, 129.02, 130.02, 134.71, 137.29, 147.84, 152.99, 162.96, 164.08.

Standard Procedure for Arcycloaddition [16]

A solution of 3-phenyl-1,3,4-oxadiazolpyridine (**4a–4c**) was stirred in *i*-PrOH (15 mL) and triethylamine (1.0 mL) solution. The reaction mixture was heated up to 80°C. α-Chloroformylarylhydrazine hydrochloride (0.29 g, 1.47 mmol, 1.1 equivalent) was added into the reaction mixture. After the reaction was completed, hot filtration was performed and washed with cold ethanol (10 mL) to isolate the solid crude product. The crude product was dried and crystallized from CH_2Cl_2 to give pure **5a–5i** as light yellow solids in 65–72% yields.

2-Phenyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)-[1,2,4]-triazolo[4,3-a]pyridin-3(2H)-one (5a). A solution of 3-(5-phenyl-1,3,4-oxadiazol-2-yl)pyridine (**4a**, 0.30 g, 1.34 mmol, 1.0 equivalent) was stirred in *i*-PrOH (15 mL) and triethylamine (1.0 mL) solution. The reaction mixture was heated up to 80°C. α-Chloroformylarylhydrazine hydrochloride (0.29 g, 1.47 mmol, 1.1 equivalent) was added into the reaction mixture. After the reaction was completed, hot filtration was performed and washed with cold ethanol (10 mL) to isolate the solid crude product. The crude product was dried and crystallized from CH_2Cl_2 to give pure **5a** as a light yellow solid in 65% yield (339 mg, 0.956 mmol): mp 187–189°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 7.35 (t, $J = 4.1$ Hz, 1H, ArH), 7.67–7.48 (m, 6H), 7.86 (d, $J = 3.9$ Hz, 1H), 8.08 (d, $J = 3.8$ Hz, 2H, ArH), 8.24 (d, $J = 4.0$ Hz, 2H, ArH), 8.81 (s, 1H);^{13}C NMR (DMSO-d6, 50 MHz) δ 120.12, 120.79, 124.31, 125.47, 126.22, 127.18, 130.21, 134.60, 142.85, 146.23, 147.72, 155.21, 157.34, 160.21, 167.36, 168.21; IR (KBr) 1605 (m, C=N), 1725 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 356 (M + 1, 27), 278 (69), 77 (100). Anal. Calcd for $C_{20}H_{13}N_5O_2$: C, 67.60; H, 3.69; N, 19.71. Found: C, 67.66; H, 3.60; N, 19.63.

2-(4-Methylphenyl)-6-(5-phenyl-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one (5b). The standard procedure was followed, and the desired product **5b** was obtained as a light yellow in 65% yield: mp 178–180°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 2.18 (s, 3H, CH_3), 7.60–7.48 (m, 4H), 7.72 (d, $J = 4.1$ Hz, 2H, ArH), 7.90 (d, $J = 3.2$ Hz, 1H), 8.07 (d, $J = 3.5$ Hz, 2H, ArH), 8.26 (d, $J = 3.8$ Hz, 2H, ArH), 8.81 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 22.80, 120.12, 124.31, 125.47, 126.22, 128.53, 135.36, 135.47, 141.25, 147.72, 155.25, 158.25, 163.34, 168.52, 169.35; IR (KBr) 1602 (m, C=N), 1730 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 372 (M + 1, 30), 148 (100), 91 (40). Anal. Calcd for $C_{21}H_{15}N_5O_2$: C, 68.28; H, 4.09; N, 18.96. Found: C, 68.19; H, 4.09; N, 19.02.

2-(4-Ethoxyphenyl)-6-(5-phenyl-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2 H)-one (5c). The standard procedure was followed, and the desired product **5c** was obtained as a light yellow solid in 68% yield: mp 214–216°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 1.31 (t, $J = 6.9$ Hz, 3H, CH_3), 4.01 (q, $J =$ 5.18 Hz, 2H, CH_2), 4.01 (q, $J =$ 5.18 Hz, 2H, CH_2), 7.60–7.47 (m, 4H), 7.72 (d, $J = 3.2$ Hz, 2H, ArH), 7.78 (d, $J = 3.7$ Hz, 1H), 8.02 (d, $J = 4.0$ Hz, 2H, ArH), 8.30 (d, $J = 3.6$ Hz, 2H, ArH), 8.81 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 14.60, 64.50, 120.12, 120.79, 123.31, 124.49, 126.60, 132.28, 136.90, 143.26, 146.72, 148.23, 153.21, 159.34, 161.21, 166.36, 167.56; IR (KBr) 1608 (m, C=N), 1726 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 400 (M + 1, 28), 354 (100), 77 (33). Anal. Calcd for $C_{22}H_{17}N_5O_3$: C, 66.16; H, 4.29; N, 17.53. Found: C, 66.16; H, 4.26; N, 17.50.

2-Phenyl-6-(5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2 H)-one (5d). The standard procedure was followed, and the desired product **5d** was obtained as a light yellow solid in 66% yield: mp 180–182°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 2.07 (s, 3H, CH_3), 7.72 (d, $J = 3.4$ Hz, 2H, ArH), 7.58–7.48 (m, 3H), 7.33 (t, $J = 4.1$ Hz, 1H, ArH), 7.83 (d, $J = 4.1$ Hz, 1H), 8.06 (d, $J = 3.4$ Hz, 2H, ArH), 8.24 (d, $J = 4.3$ Hz, 2H, ArH), 8.81 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 21.57, 120.80, 124.76, 125.92, 126.46, 127.25, 130.98, 134.35, 142.49, 147.76, 155.67, 157.11, 160.65, 167.59, 168.11; IR (KBr) 1602 (m, C=N), 1726 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 370 (M + 1, 21), 292 (100), 91 (60). Anal. Calcd for $C_{21}H_{15}N_5O_2$: C, 68.28; H, 4.09; N, 18.96. Found: C, 68.20; H, 4.05; N, 18.95.

2-(4-Methylphenyl)-6-(5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2 H)-one (5e). The standard procedure was followed, and the desired product **5e** was obtained as a light yellow solid in 70% yield: mp 189–191°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 2.18–2.05 (m, 6H), 7.65–7.57 (m, 3H), 7.72 (d, $J =$ 3.7 Hz, 2H, ArH), 7.86 (d, $J = 4.0$ Hz, 1H), 8.08 (d, $J = 4.0$ Hz, 2H, ArH), 8.24 (d, $J = 3.8$, 2H, ArH), 8.82 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 21.57, 25.67, 120.60, 120.80, 124.92, 126.46, 129.25, 132.98, 136.35, 143.49, 146.23, 157.67, 159.11, 163.64, 168.29, 169.25; IR (KBr) 1600 (m, C=N), 1720 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 384 (M + 1, 50), 292 (80), 91

(100). Anal. Calcd for $C_{22}H_{17}N_5O_2$: C, 68.92; H, 4.47; N, 18.27. Found: C, 68.86; H, 4.50; N, 18.30.

2-(4-Ethoxyphenyl)-6-(5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one (5f). The standard procedure was followed, and the desired product **5f** was obtained as a light yellow solid in 72% yield: mp 216–218°C; ^{1}H NMR (DMSO-d6, 200 MHz) 1.31 (t, $J = 6.9$ Hz, 3H, CH_3), 2.07 (s, 3H, CH_3), 4.00 (q, $J = 6.9$ Hz, 2H, CH_2), 7.67–7.54 (m, 3H), 7.68 (d, $J = 4.1$ Hz, 2H, ArH), 7.84 (d, $J = 3.7$ Hz, 1H), 8.02 (d, $J = 3.5$ Hz, 2H, ArH), 8.27 (d, $J = 3.2$ Hz, 2H, ArH), 8.80 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 15.03, 21.60, 65.22, 120.80, 124.76, 125.92, 126.46, 127.65, 132.98, 134.35, 142.49, 146.23, 147.76, 155.21, 157.64, 160.21, 167.49, 168.35; IR (KBr) 1610 (m, C=N), 1715 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 414 (M + 1, 17), 121 (100), 77 (41). Anal. Calcd for $C_{23}H_{19}N_5O_3$: C, 66.82; H, 4.63; N, 16.94. Found: C, 66.86; H, 4.60; N, 16.88.

2-Phenyl-6-(5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2 H)-one (5g). The standard procedure was followed, and the desired product **5g** was obtained as a light yellow solid in 60% yield: mp 243–245°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 7.33 (t, $J = 4.1$ Hz, 1H, ArH), 7.64–7.54 (m, 3H), 7.70 (d, $J = 3.9$ Hz, 2H, ArH), 7.81 (d, $J = 3.9$ Hz, 1H), 8.05 (d, $J = 4.0$ Hz, 2H, ArH), 8.25 (d, $J = 4.1$ Hz, 2H, ArH), 8.81 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 120.25, 120.86, 124.25, 125.53, 126.98, 127.56, 131.98, 136.35, 142.26, 146.95, 147.46, 155.35, 157.69, 159.21, 166.89, 167.11; IR (KBr) 1600 (m, C=N), 1710 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 490 (M + 1, 11), 179 (100), 111 (36). Anal. Calcd for $C_{20}H_{12}N_5O_2$: C, 61.63; H, 3.10; N, 17.97. Found: C, 61.68; H, 3.08; N, 17.92.

2-(4-Methylphenyl)-6-(5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one (5h). The standard procedure was followed, and the desired product **5h** was obtained as a light yellow solid in 62% yield: mp 202–204°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 2.18 (s, 3H, CH_3), 7.60–7.50 (m, 3H), 7.68 (d, $J = 3.4$ Hz, 2H, ArH), 7.76 (d, $J = 3.0$ Hz, 1H), 8.08 (d, $J = 3.8$ Hz, 2H, ArH), 8.26 (d, $J = 4.0$ Hz, 2H, ArH), 8.82 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 25.57, 120.69, 120.88, 124.56, 125.72, 126.48, 127.26, 130.98, 134.33, 142.49, 146.23, 147.76, 156.67, 159.26, 160.26, 167.57, 168.12; IR (KBr) 1602 (m, C=N), 1732 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 404 (M + 1, 25), 312 (40), 91 (100). Anal. Calcd for $C_{21}H_{14}N_5O_2$: C, 62.46; H, 3.49; N, 17.34. Found: C, 62.52; H, 3.49; N, 17.32.

2-(4-Ethoxyphenyl)-6-(5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one (5i). The standard procedure was followed, and the desired product **5i** was obtained as a light yellow solid in 70% yield: mp 210–212°C; ^{1}H NMR (DMSO-d6, 200 MHz) δ 1.30 (t, $J = 6.9$ Hz, 3H, CH_3), 4.00 (q, $J = 6.9$ Hz, 2H, CH_2), 7.68–7.52 (m, 3H), 7.78 (d, $J = 4.1$ Hz, 2H, ArH), 7.85 (d,$J = 3.6$ Hz, 1H), 8.10 (d, $J = 4.0$ Hz, 2H, ArH), 8.30 (d, $J = 3.9$ Hz, 2H, ArH), 8.79 (s, 1H); ^{13}C NMR (DMSO-d6, 50 MHz) δ 14.25, 21.57, 65.22, 120.50, 124.22, 126.46, 127.55, 130.58, 134.15, 142.69, 146.83, 147.26, 155.37, 157.51, 160.15, 167.29, 168.18; IR (KBr) 1608 (m, C=N), 1718 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity): 434 (M + 1, 6), 312 (100), 179 (36). Anal. Calcd for $C_{22}H_{16}N_5O_3$: C, 60.91; H, 3.72; N, 16.14. Found: C, 60.98; H, 3.69; N, 16.10.

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