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A facile, practical and metal-free microwave-assisted protocol for mono- and bis-[1,2,4]triazolo[1,5-*a*]pyridines synthesis utilizing 1-amino-2-imino-pyridine derivatives as versatile precursors†

Hamada Mohamed Ibrahim, ^{*a} Haider Behbehani^{*b} and Wael Abdelgayed Ahmed Arafa ^{ac}

A facile and effective assembly of several substituted functionalized mono- and bis-[1,2,4]triazolo[1,5-*a*]pyridines from conveniently attainable 1-amino-2-imino-pyridines has been established. Using microwave irradiation speeds up the reaction efficiently, proceeding with a higher rate and yields than with conventional heating. In the presented protocol, a broad variety of carboxylic acids could be employed effectively to synthesize the respective derivatives *via* direct metal-free C–N bond construction. Interestingly, other substrates such as aldehydes (or their arylidene malononitriles), phenyl isothiocyanate, glyoxalic acid, and acrylonitriles could also provide the corresponding 1,2,4-triazolo[1,5-*a*]pyridines successfully. This versatile and convergent approach performs well with both deactivating and activating substrates in an environmentally benign manner compared with other already reported protocols. Other notable merits of the current strategy involve no need for column chromatography, no tedious work-up, and a direct pathway for the fast design of triazolopyridine frameworks. The identity of the newly synthesized compounds was established using several spectroscopic techniques, and X-ray single-crystal tools were employed to authenticate the suggested structures of some representative samples.

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Introduction

N-Fused heteroaromatic frameworks are an essential structural moiety in several effective pharmacological compounds and natural products.¹ Among them, 1,2,4-triazolo[1,5-*a*]pyridines which are considered as a unique category of *N*-bridged 5,6-bicyclic compounds have received substantial consideration for either their potential utility as bioactive precursors or for other industrial applications.^{2,3} For example, they exhibit several pharmaceutical behaviors including, mGlu modulation,⁴ PHD-1 inhibition,⁵ PDE10 inhibition,⁶ and acting as an antioxidant.⁷ In addition examples of these compounds have been utilized as herbicidal agents⁸ and for treatment of diabetes (type-II),^{9,10} cardiovascular disorders,¹¹ and hyperproliferative disorders.¹² Besides, such derivatives have been included in a variety of pharmaceutically effective compounds as dipeptidomimetics¹³

and have been employed as effective ligands for various transition metals.^{14–16} As a consequence of the above-mentioned applications, several approaches for the triazolopyridine assembly have been established over the past decades. The reported synthetic strategies for assembling triazolopyridines could be classified into three approaches depending on the reactants: triazoles, pyridines, and multiple components. The oxidative cyclization of *N*-(2-pyridyl)amidines is amongst the most simple protocols for developing the 1,2,4-triazolo[1,5-*a*]pyridines that have been accomplished *via* employing oxidants including Pb(OAc)₄,¹⁷ NaClO/base¹⁸ and MnO₂.¹⁹ Nonetheless, there are several drawbacks associated with these procedures such as restricted scopes, lower yields, lack of regioselectivity, and multi-step synthetic strategies. Moreover, Ueda and Nagasawa²⁰ developed a method for achieving 2-aryl-1,2,4-triazolo[1,5-*a*]pyridines from a copper-catalyzed cyclization reaction of aryl nitriles and 2-aminopyridines. Similarly, Zhao *et al.*²¹ described a Cu–Zn/Al–Ti reusable catalyst for the same conversion. Further, Jianguang and co-workers successfully synthesized triaryl[1,2,4]triazolo[1,5-*a*]pyridine derivatives *via* copper-catalyzed radical cyclization reaction of benzylidenmalononitriles and azines.²² More recently, Xia *et al.* presented the preparation of triazolopyridines through the copper-catalyzed oxidative cyclization of amidines or 2-aminopyridines with several nitriles.²³ Notwithstanding, these reactions are followed

^aChemistry Department, Faculty of Science, Fayoum University, P.O. Box 63514, Fayoum, Egypt. E-mail: hmi00@fayoum.edu.eg; hamadaaldeb@yahoo.com

^bChemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait. E-mail: drhaider.b@gmail.com

^cChemistry Department, College of Science, Jouf University, P.O. Box 2014, Sakaka, Aljouf, Kingdom of Saudi Arabia

† CCDC 1982378–1982383 and crystal data for compounds **5m** (CIF), **5p** (CIF), **5q** (CIF), **5u** (CIF), **5v** (CIF), **14** (CIF). For crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ra02256j

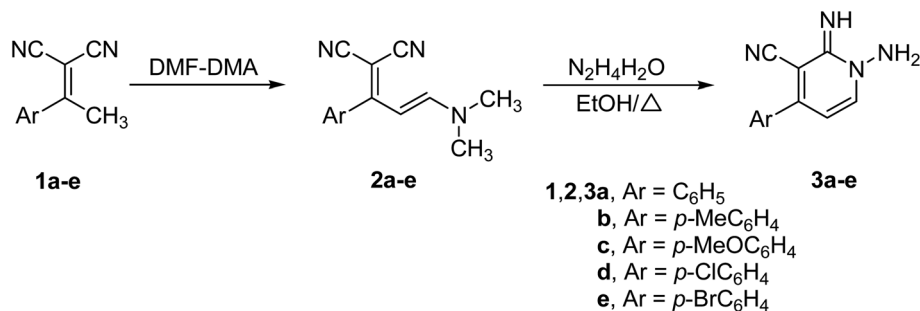

by certain drawbacks, such as using the catalysts in higher loads (5–20 mol%) and not being recyclable or reusable. Moreover, these metal catalysts could be interacted conveniently with the obtained products, since [1,2,4]triazolo[1,5-*a*]pyridines are reported to be coordinated effectively with transition metals producing stable complexes.^{24,25} Such challenges are of particular economic and environmental concerns, limiting the utility of such protocols in large-scale productions, and hence in industrial purposes. Furthermore, access to [1,2,4]triazolo[1,5-*a*]pyridines has also been documented for certain metal-free synthetic procedures. For instance, Alizadeh *et al.* reported the synthesis of [1,2,4]triazolo[1,5-*a*]pyridine derivatives *via* iodine-catalyzed one-pot four-component reaction comprising malononitrile, dimethyl acetylenedicarboxylate, aromatic aldehydes, and benzyldienhydrazines.²⁶ Even though, this approach could be implemented only to alkynes with powerful electron-deficient moieties. Also, Zhao and co-workers²⁷ recorded a PIFA-mediated conversion of amidines into 2-substituted triazolopyridine derivatives. On the other hand, Chang *et al.*²⁸ published a method for the preparation of 1,2,4-triazolo[1,5-*a*]pyridine derivatives employing I₂/KI as a catalyst. Ashish *et al.*²⁹ also recorded the contraction of 1,2,4-triazolo[1,5-*a*]pyridines through oxidative cyclization of trichloroisocyanuric acid and benzamidine derivatives. In addition to more reported protocols,³⁰ however, in one aspect or another, the above reported protocols acquire several disadvantages, including the utility of costly catalysts, a restricted substrates scope, lower regioselectivity, and the isolation of by-products. Consequently, the development of creative and generalized protocols to access these unique heterocyclic categories is still in demand. Following on with our reported works^{31–33} herein we describe an alternative, more effective, and environmentally friendly metal-free approach for assembling 1,2,4-triazolo[1,5-*a*]pyridines from 1-amino-2-imino-4-aryl-1,2-dihydropyridine-3-carbonitrile precursors *via* the formation of C–N bonds employing the microwave irradiation as a sustainable energy source.

Results and discussion

The strategy utilized to construct 1-amino-2-imino-pyridine derivatives **3a–e** includes two sequentially steps that start with the synthesis of enaminonitriles **2a–e**, by reacting dimethylformamide dimethylacetal (DMF-DMA) with the respective

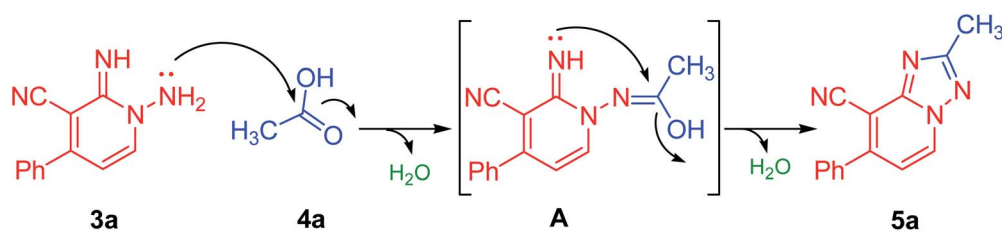
ethylidenemalononitriles **1a–e** (Scheme 1). Enaminonitrile derivatives (**2a–e**) could then be converted to their corresponding targets **3a–e** through thermally mediated reaction with hydrazine hydrate in EtOH (Scheme 1).³³

Our initial investigation commenced by the reaction of 1-amino-2-imino-pyridine derivative (**3a**) with acetic acid (as a solvent and reactant) at reflux for 3 h. Interestingly, the formation of the required product (**5a**) has been detected, albeit in a good yield of 74%, as a preliminary endeavor (Table 1, entry 1). Encouraged by the obtained results, the reaction conditions such as solvents, energy sources, and temperature have been evaluated to improve both reaction rate and yield (Table 1). Thereby, the reaction of **3a** with acetic acid (1 equiv.) was investigated utilizing various solvents such as polar protic (EtOH, MeOH, and propanol), polar aprotic (CH₃CN, and dioxane), and nonpolar (toluene) solvents at different times using various energy sources (heating, US, and MW irradiations). Unfortunately, none of them could afford the required product (Table 1, entries 2–13). Then the model reaction (Table 1) was also examined in 10.0 mL of ethanol comprising 5 equiv. of acetic acid to investigate its efficiency in the production of derivative **5a**. Interestingly, compound **5a** was crystalline out from the reaction mixture in 3 h of refluxing in 80% yield (Table 1, entry 14). Next, the molar ratio of acetic acid employed has also assessed. It was found that employing a mixture of ethanol/acetic acid (10 equiv.), not only improved the reaction yield to 85% but also provided a cleaner and lighter color product (Table 1, entry 15). Increasing the equivalents of acetic acid more than 10 equiv., neither improves the reaction rate nor the yield (Table 1, entry 16). Due to the versatility, efficiency, and selectivity of microwave irradiation, the model reaction (Scheme 1) was also investigated under the microwave irradiation conditions. The required product **5a** was obtained in 89% in 25 min under microwave irradiation at 80 °C (Table 1, entry 17). On reducing the reaction duration to 15 min and increasing the temperature to 100 °C, the isolated yield was enhanced to be 92% (Table 1, entry 18). Increasing the temperature more than 100 °C did not improve the reaction (Table 1, entry 19). Thus, employing the model reaction (Table 1) using 3.0 mmol of derivative **3a** in ethanol (10.0 mL) containing acetic acid (10 equiv.) and irradiation under microwave for 15 min at 100 °C has been identified as the optimal conditions (Table 1, entry 18). A reasonable reaction mechanism for the synthesis of 1,2,4-triazole derivative (**5a**) was described in Table 1, based on experimental evidences



Scheme 1 Synthesis of 1-amino-2-imino-pyridines **3a–e**.³³



Table 1 Optimization of the reaction condition between *N*-aminopyridine **3a** and acetic acid **4a**^a

Entry	Solvent	Method	Time	Yield (%)
1	AcOH	Heating	3 h	74
2	EtOH	Heating	12 h	NR ^b
3	EtOH	MW	45 min	NR
4	MeOH	Heating	12 h	NR
5	MeOH	MW	45 min	NR
6	CH ₃ CN	Heating	12 h	NR
7	CH ₃ CN	MW	45 min	NR
8	Propanol	Heating	12 h	NR
9	Propanol	MW	45 min	NR
10	1,4-Dioxane	Heating	12 h	NR
11	1,4-Dioxane	MW	45 min	NR
12	Toluene	Heating	12 h	NR
13	Toluene	US	45 min (80 °C)	NR
14	EtOH/AcOH (5 equiv.)	Heating	3 h	80
15	EtOH/AcOH (10 equiv.)	Heating	3 h	85
16	EtOH/AcOH (15 equiv.)	Heating	3 h	85
17	EtOH/AcOH (10 equiv.)	MW	25 min (80 °C, 250 W)	89
18	EtOH/AcOH (10 equiv.)	MW	15 min (100 °C, 250 W)	92
19	EtOH/AcOH (10 equiv.)	MW	15 min (120 °C, 250 W)	92

^a Reaction conditions: a mixture of 1-amino-2(1H)-pyridine-2-imine derivatives (**3a**) (3.0 mmol) and acetic acid **4a** (as reported) in solvent (10.0 mL) was heated or irradiated by microwave or ultrasound for the given time. ^b NR: no reaction.

and our reported studies.^{31–33} As outlined in Table 1, the transformation of the non-isolable intermediate (**A**) to the target compound (**5a**) occurred under metal-free conditions.

Now, the limitations and scope of the aforesaid reaction have then investigated. Therefore the reaction of 1-amino-2(1H)-pyridine-2-imines (**3a–d**) with various carboxylic acid derivatives (**4a–g**, 10 equiv.) in EtOH (10.0 mL) was scrutinized under microwave irradiation. It was observed that these reactions did not proceed smoothly without using additives, as in the case of acetic acid. After several optimization trials, the optimal reaction condition for acids (**4b–g**) other than acetic acid was established to be 3.0 mmol of 1-amino-pyridine-2-imines **3a–d** with 4.0 mmol of carboxylic acid derivatives (**4b–g**) in EtOH (10.0 mL) containing acetic acid (5 equiv.) as catalyst, under microwave irradiation (Table 2). It is worth mentioning that, the amount of acetic acid should not exceed 5 equiv., otherwise the reaction between 1-amino-pyridine-2-imines (**3a–d**) and acetic acid will have occurred. As displayed in Table 2, the summarized results demonstrate that all the proposed reactions yielded their corresponding products (**5a–k**) in outstanding isolated yields without detecting by-products. Also, all the reactions were effectively afforded the desired products regardless of the substitution pattern of the aromatic moiety (Ar, Table 2). Further, the influence of the *R*-groups on reaction

efficiency was also been investigated (Table 2). In this regard, electron-donating and electron-deficient groups are both acceptable in the present process. For instance, the substrates comprising cyano groups (Table 2, entries 4–6) were easily converted to the corresponding products in excellent yields. Besides, the current protocol has shown a good tolerance for both aromatic and aliphatic carboxylic acids (Table 2).

Moreover, the proposed approach could also be successfully applied for carboxylic acid esters. For example when the diethyl oxalate (3.0 mmol) allowed to react with *N*-amino-2-iminopyridines (**3a–e**, 3.0 mmol) using 5 equiv. of acetic acid in EtOH (10.0 mL) under microwave irradiation at 100 °C for 15 min, the desired products (**5l–p**) were received in excellent yields (85–93%, Scheme 2). In these cyclization reactions, both electron-deficient and electron-rich Ar groups are also applicable. The cyclization reaction of electron-rich bearing substrates and diethyl oxalate, proceeded smoothly to produce the corresponding products (**5m** and **5n**) in good yields (87 and 85% yield, respectively, Scheme 2). Similarly, in comparison to the unsubstituted aromatic derivative (**5l**), electron-deficient derivatives provided the respective products (**5o** and **5p**) in excellent yields (92 and 93% yield, respectively, Scheme 2, Fig. 1 and 2).



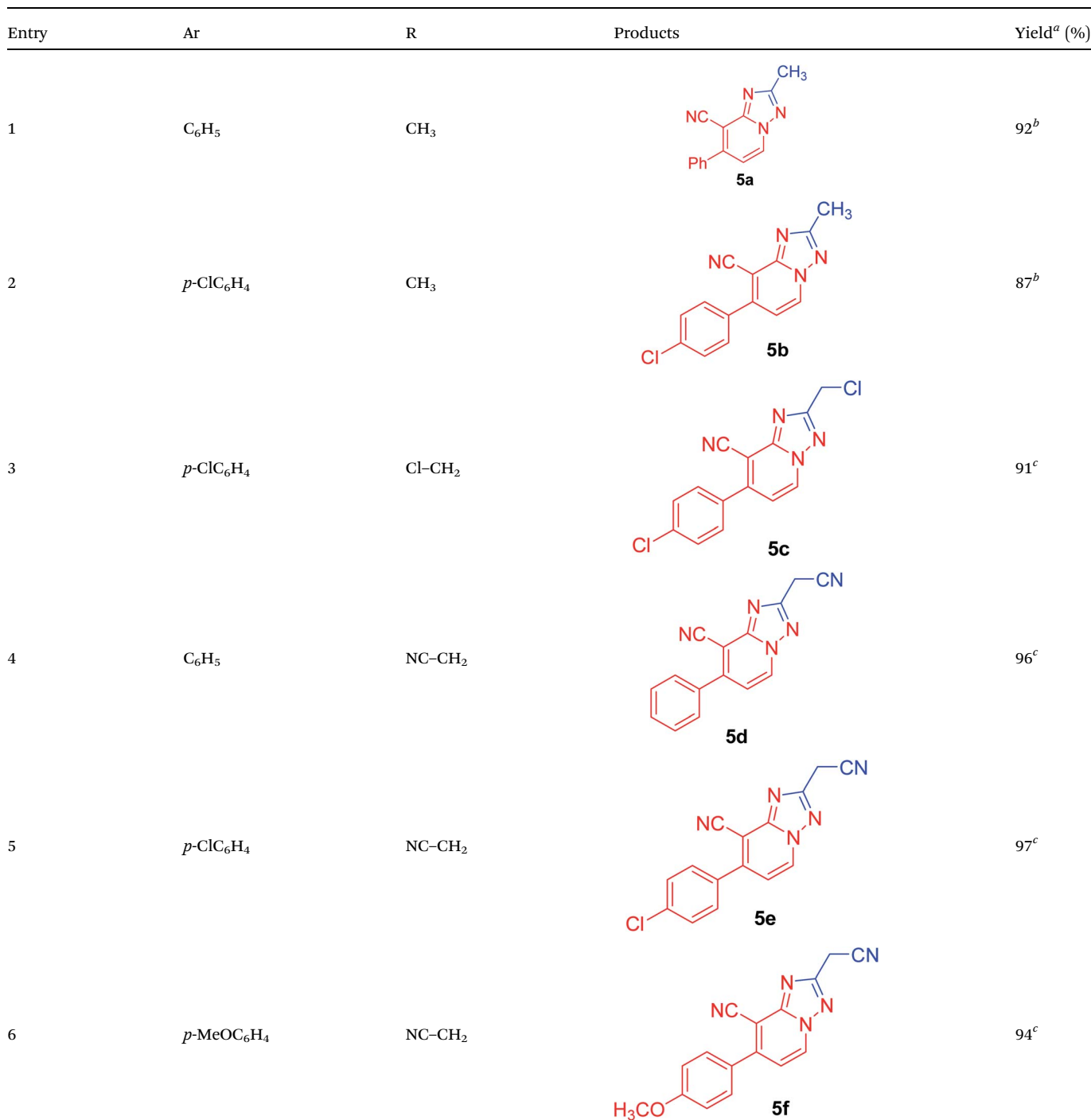
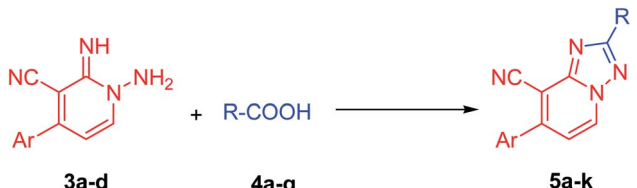
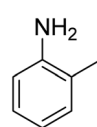
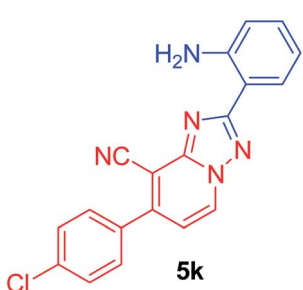


Table 2 (Contd.)

Entry	Ar	R	Products	Yield ^a (%)
7	<i>p</i> -MeOC ₆ H ₄			93 ^c
8	<i>p</i> -MeOC ₆ H ₄	C ₆ H ₅		83 ^c
9	<i>p</i> -ClC ₆ H ₄	C ₆ H ₅		86 ^c
10	<i>p</i> -ClC ₆ H ₄			87 ^c



Table 2 (Contd.)

				
Entry	Ar	R	Products	Yield ^a (%)
11	<i>p</i> -ClC ₆ H ₄			84 ^c

^a Isolated yield. ^b Reaction conditions: a mixture of 1-amino-2(1*H*)-pyridine-2-imine derivatives (**3a–d**) (3.0 mmol) and acetic acid **4a** (10 equiv.) in ethanol (10.0 mL) was charged in the glass tube of the microwave tube and irradiated at 100 °C for 15 min. ^c Reaction conditions: a mixture of 1-amino-2(1*H*)-pyridine-2-imine derivatives (**3a–d**) (3.0 mmol) and different carboxylic acids (**4b–g**) (4.0 mmol) in ethanol (10.0 mL), acetic acid (5 equiv.), was charged in the glass tube of the microwave tube and irradiated at 80 °C for 15 min.

Scheme 2 Substrate scope for the reaction of 1-amino-2-imino-pyridine derivatives (**3a–e**) with diethyl oxalate.

Notably, 1,2,4-triazolo[1,5-*a*]pyridine-8-carbonitrile derivatives (**5**) could also be obtained through the cyclization reaction of derivatives **3c–d** with either the corresponding aldehydes (**6a–**

f) or with their arylidene malononitriles (**7a–f**) (Table 3, Fig. 3 and 4). These reactions were effectively performed with several aromatic aldehydes and their arylidenes comprising electron-

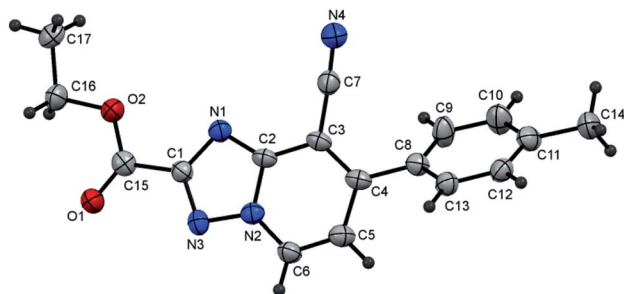
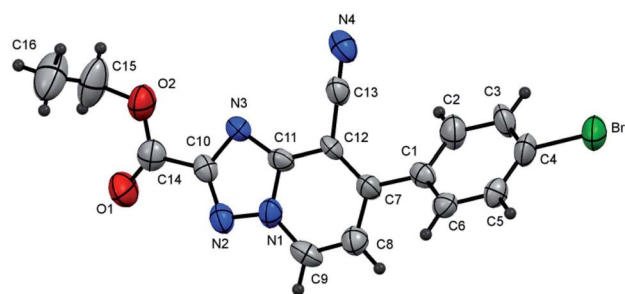
Fig. 1 X-ray single crystal data determined for **5m**.Fig. 2 X-ray single crystal data determined for **5p**.

Table 3 Reaction of 1-amino-2-imino-pyridine derivatives (**3c–d**) with aldehydes (**6**) and arylidene malononitriles (**7**)

Entry	Ar	R	Products	Yield (%)
1	<i>p</i> -ClC ₆ H ₄	Cl-CH ₂		85
2	<i>p</i> -MeOC ₆ H ₄	C ₆ H ₅		91
3	<i>p</i> -ClC ₆ H ₄	C ₆ H ₅		94
4	<i>p</i> -ClC ₆ H ₄			93



Table 3 (Contd.)

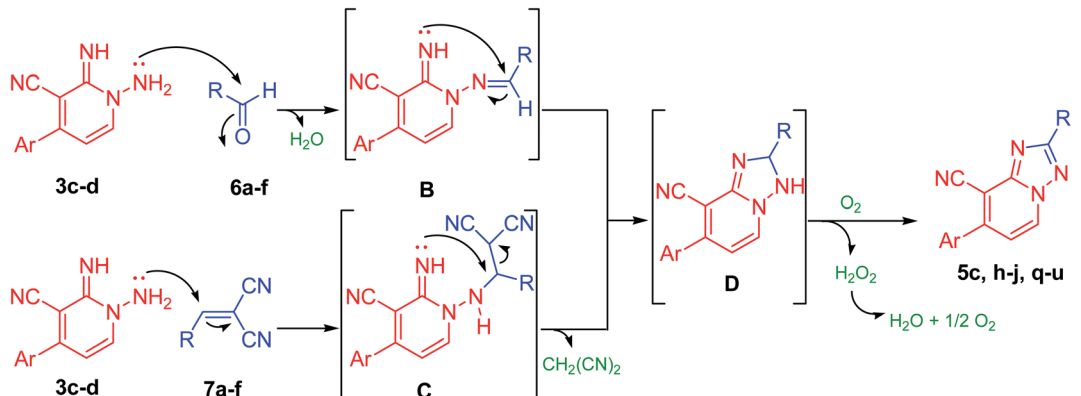
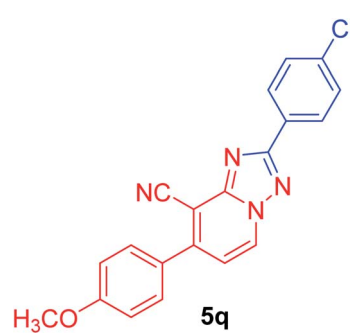
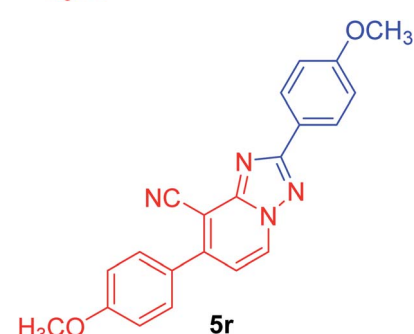
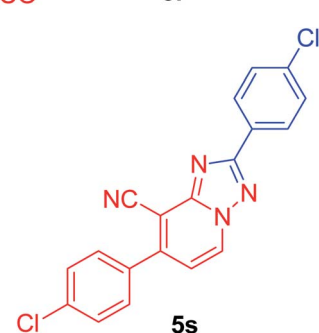
				
Entry	Ar	R	Products	Yield (%)
5	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	 5q	90
6	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄	 5r	93
7	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	 5s	94



Table 3 (Contd.)

Entry	Ar	R	Products	Yield (%)
8	<i>p</i> -ClC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	 5t	91
9	<i>p</i> -ClC ₆ H ₄	Ph-CH=CH	 5u	88

withdrawing or electron-donating groups and afforded the corresponding products in comparable yields (Table 3). Also, aliphatic aldehydes such as chloroacetaldehyde yielded the targeted product in slightly lower yield in parallel to aromatic aldehydes (Table 3, entry 1). In comparison to carboxylic acids, the aldehydes or their arylidene malononitriles underwent the cyclization reaction at a fast rate with much more yields. Moreover, derivative **5t** could be also obtained *via* refluxing of (*E*)-1-methyl-4-(2-nitrovinyl)benzene (**8**) with derivative **3d** in CH₃CN/DMF mixture (Scheme 3).

Likewise, compounds **5d–f** could be also acquired *via* the cyclization reaction of derivatives **3a,c,d** with (*E*)-3-(piperidin-1-yl)acrylonitrile (**9**) or with (*E*)-3-(dimethylamino)acrylonitrile (**10**) in superb yield (Scheme 4). Besides, this active methylene derivatives **5d–f** underwent condensation reaction either with

DMF–DMA or benzaldehyde easily to afford the isolable enamines **11a,b** and arylidenes **12a,b**, respectively (Scheme 4).

Further, the present approach was effectively applied also to isothiocyanate derivatives under moderate conditions. Thus, under microwave irradiation, 1,2-dihydropyridine-3-carbonitrile derivative (**3d**) underwent cyclization reaction when treated with phenyl isothiocyanate providing the unreported [1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile derivative (**5v**) in excellent yield (90%) (Scheme 5). In the course of this reaction, the sulfur of the isothiocyanate moiety gets lost presumably in the form of hydrogen sulfide gas. Therefore, the reaction may be started by the nucleophilic addition of the amino group of derivative **3d** onto azomethine motif of phenyl isothiocyanate. Then, hydrogen sulfide was removed, possibly *via* an addition–elimination reaction, which results in a [1,2,4]



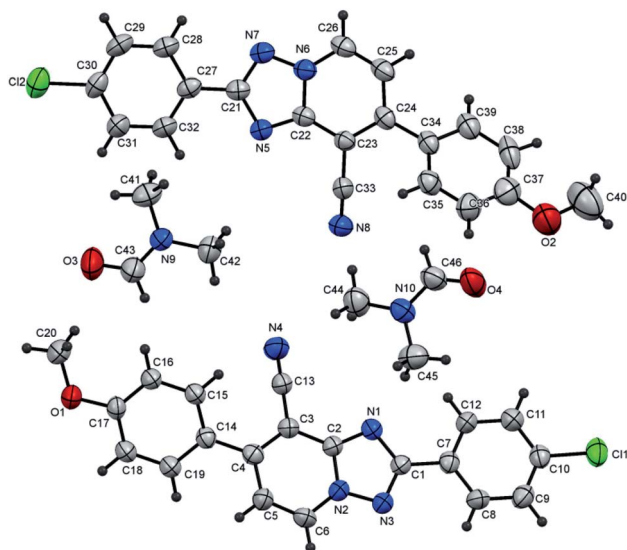


Fig. 3 X-ray single crystal data determined for 5q.

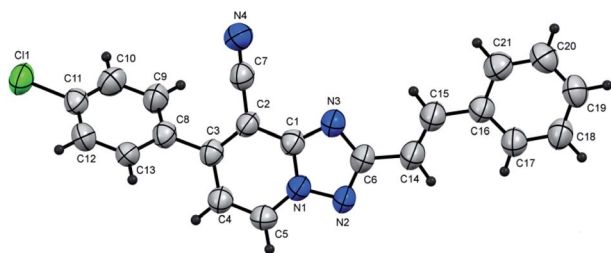


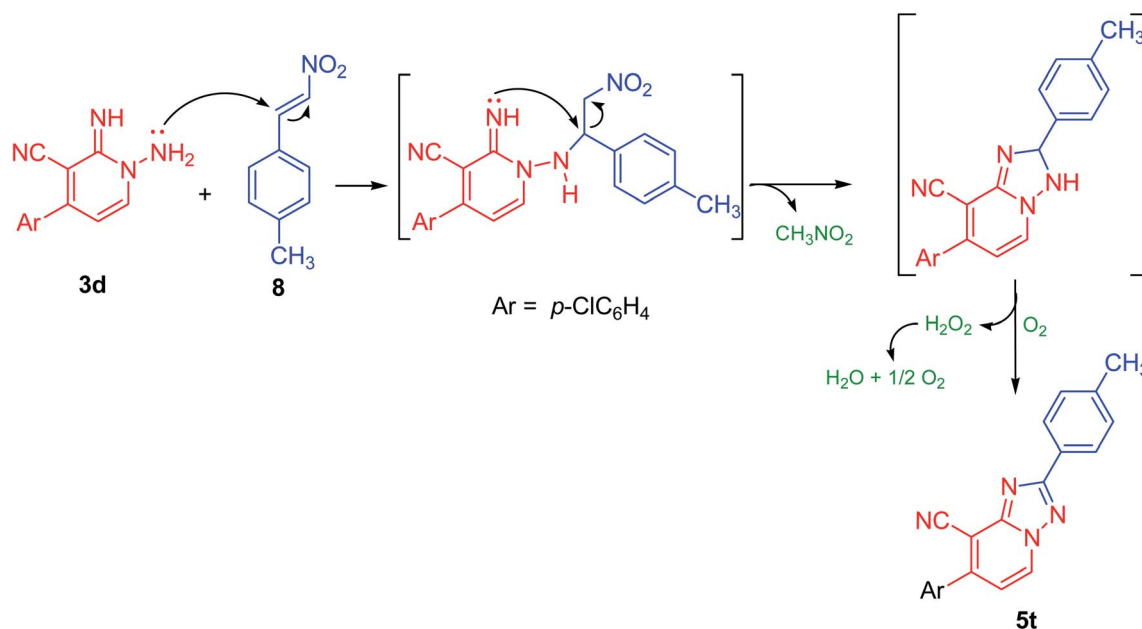
Fig. 4 X-ray single crystal data determined for 5u.

triazolo[1,5-*a*]pyridine ring formation (Scheme 5, Fig. 5). Moreover, by boiling pyridine derivatives (**3a,b,d**) in DMF or glyoxalic acid, the unsubstituted triazole derivatives (**5w–y**) have been achieved in superb yields (89–91%, Scheme 5). In the latter reactions, the aldehydic group might be involved in cyclization reaction followed by the loss of dimethylamine (in case of DMF) or carbon dioxide (in the case of glyoxalic acid).

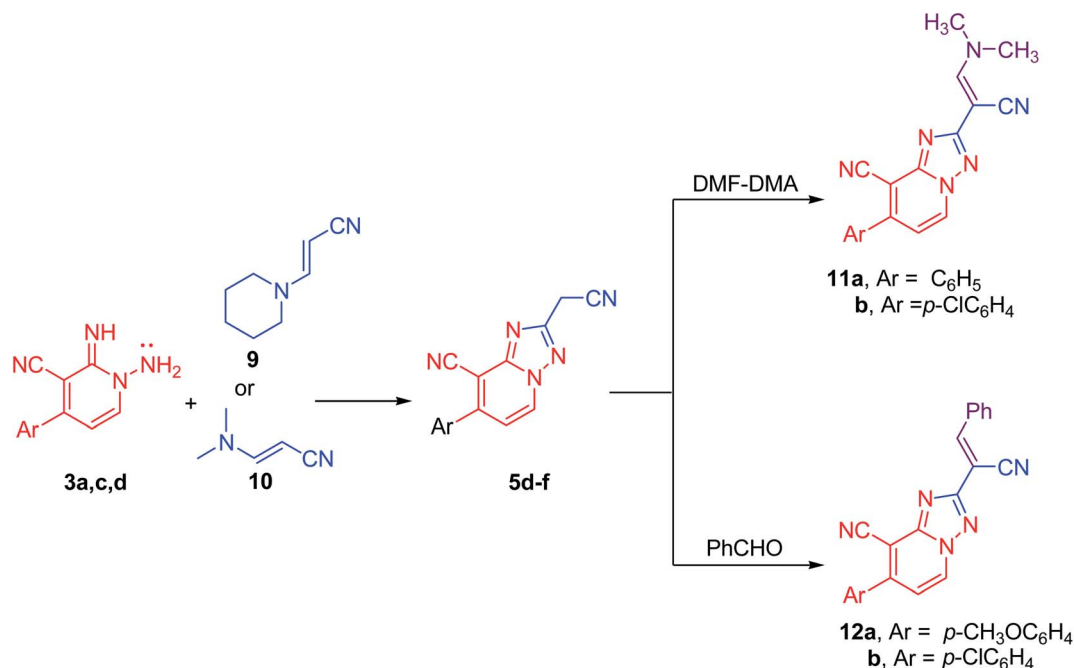
The aforesaid protocol also applied successfully for the bi-function aromatic aldehydic compounds. For example, the synthesis of bis-triazolopyridine derivatives (**13a–c**) was achieved through the cyclization reaction of the commercially available terephthalaldehyde with *N*-amino-2-imino-pyridine derivatives (**3b,d,e**) in 2 : 1 molar ratio (Scheme 6). Whereas, the mono-triazolopyridine derivative (**5z**), could be received on conducting the reaction between terephthalaldehyde and derivative **3d** in 1 : 1 molar ratio (Scheme 6). Interestingly, the bis-derivative (**13b**) could be also synthesized *via* the reaction of the mono-derivative (**5z**), with another batch of **3d** (1.0 mmol) (**13b**, Scheme 6).

Ultimately, the nicotinonitrile derivative (**14**) was produced under microwave irradiation in excellent yield (98%, Scheme 7, Fig. 6) on boiling compound **3d** in EtOH containing a catalytic amount of TEA (triethylamine) or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).

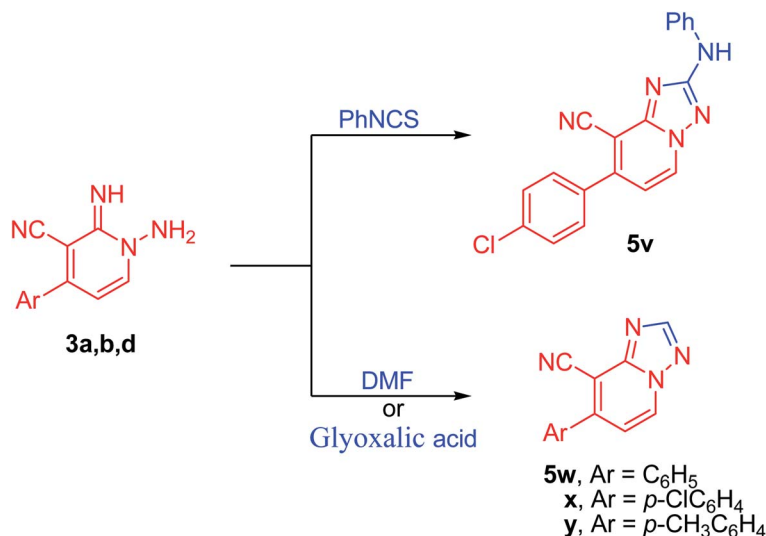
The suggested structures of the synthesized mono- and bis-triazolopyridines have been verified based on several techniques of spectrometric analyses including ^1H NMR and ^{13}C NMR, in addition to the mass and accurate mass assignment. Moreover, the above structures were assured without any doubt through the X-ray single-crystal structure determination in some representative examples.



Scheme 3 Alternative route for 5t.



Scheme 4 Alternative preparation of 5d-f and their reactions with DMF-DMA and PhCHO.



Scheme 5 Reaction of 1-amino-2-imino-pyridine with PhNCS and DMF.

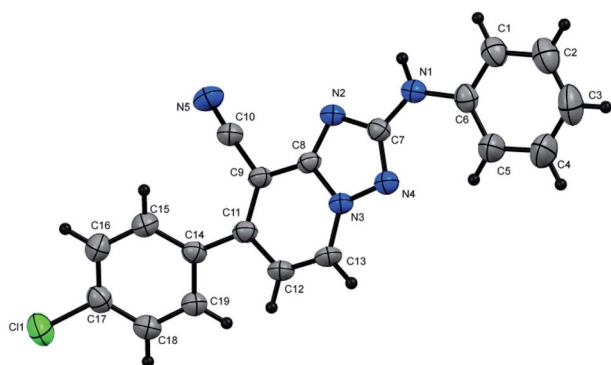
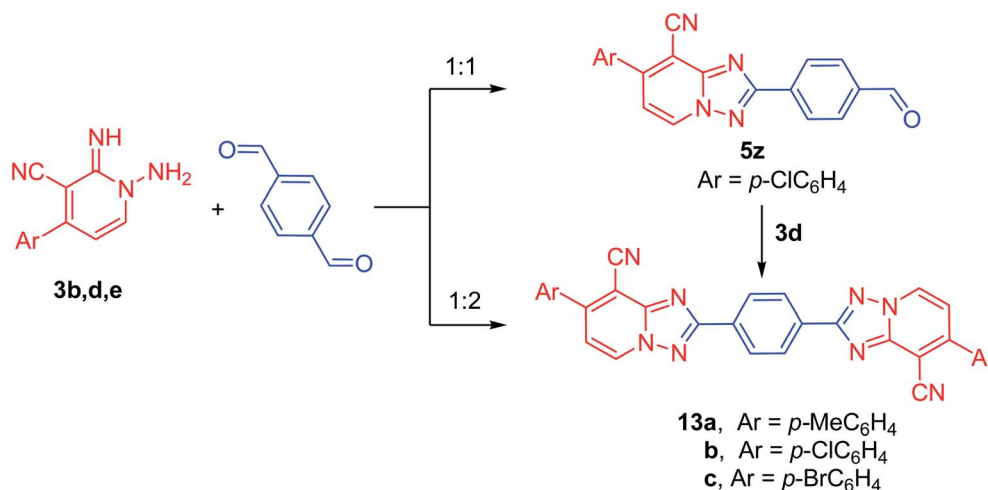


Fig. 5 X-ray single crystal data determined for 5v.

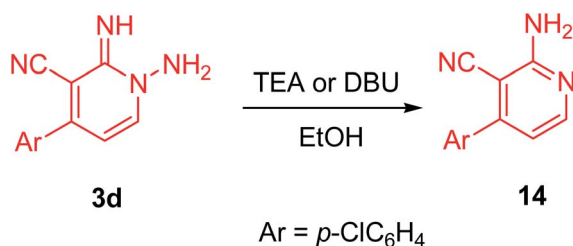
Conclusion

A microwave metal-free protocol towards the assembly of mono- and bis-[1,2,4]triazolo[1,5-*a*]pyridines has been established from the cyclization reaction of 1-amino-2-imino-pyridine derivatives with readily available carboxylic acids and diesters. Moreover, the utility and versatility of the present procedure are also established for a diverse range of other substrates, such as mono-aldehydes, di-aldehydes, phenyl isothiocyanate, acrylonitriles, and glyoxalic acid. The essential strengths of the current procedure are operational efficiency, conveniently accessible substrates, inexpensive reagents, good to excellent





Scheme 6 Reaction of 1-amino-2-imino-pyridines with terephthalaldehyde.



Scheme 7 Conversion 1-amino-2-imino-pyridine derivative (3d) to 2-aminopyridine derivative (14).

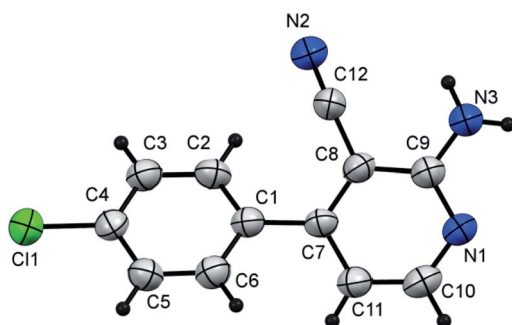


Fig. 6 X-ray single crystal data determined for 14.

yields, broad functional group tolerance, and chromatography-free procedure. Therefore, we believe that such an environmentally friendly strategy paves the way for the design of biologically important scaffolds and provides practical alternatives to the design of these hybrid molecules.

Experimental

General

Melting points were recorded on a Griffin melting point apparatus and are uncorrected. IR spectra were recorded using KBr disks using Jasco FT-IR-6300 spectrophotometer. ¹H NMR (400

MHz) or (600 MHz) and ¹³C NMR (100 MHz) or (150 MHz) spectra were recorded at 25 °C using DMSO-*d*₆ (or CDCl₃) as a solvent with TMS as internal standard on a Bruker DPX 400 or 600 super-conducting NMR spectrometer. Chemical shifts are reported in ppm. Low-resolution electron impact mass spectra [MS (EI)] and high-resolution electron impact mass spectra [HRMS (EI)] were performed using a high-resolution GC-MS (DFS) thermo spectrometer at 70.1 eV and a magnetic sector mass analyzer. Follow up of the reactions and checking homogeneity of the prepared compounds was made by using thin-layer chromatography (TLC). Microwave heating was carried out with a single mode cavity Explorer Microwave synthesizer (CEM Corporation, NC, USA), producing continuous irradiation and equipped with simultaneous external air-cooling system. The X-ray crystal structures were determined by using a Rigaku R-Axis RAPID diffractometer and Bruker X8 Prospector and the collection of single-crystal data was made at room temperature by using Cu-Kα radiation. The structures were solved by using direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The structures were solved and refined using the Bruker SHELXTL Software Package (Structure solution program-SHELXS-97 and Refinement program-SHELXL-97).³⁴ Data were corrected for the absorption effects using the multi-scan method (SADABS). The *N*-amino-2-iminopyridines 3a-e were prepared according to the literature procedure.³³

General procedure for the preparation of 1-amino-2-imino-4-aryl-1,2-dihydropyridine-3-carbonitrile 3a-e.³³ A mixture of the enaminonitriles 2a-e (20.0 mmol) and hydrazine hydrate (1.5 mL, 30.0 mmol) in 60.0 mL of EtOH was stirred at reflux for 1 h. The mixture was concentrated *in vacuo* giving a solid that was crystallized from the appropriate solvent to give 3 as pure product.

1-Amino-2-imino-4-phenyl-1,2-dihydropyridine-3-carbonitrile (3a). Yellow crystals; yield: 3.7 g (89%); m.p. 165–166 °C, IR (KBr): ν/cm^{-1} 3318, 3226 (NH₂), 3137 (NH), 2211 (C≡N); ¹H NMR (400 MHz, DMSO-*d*₆): δ 5.90 (d, *J* = 7.2 Hz, 1H, C-H6), 6.16 (s, 2H, NH₂), 6.53 (brs, 1H, imine NH), 7.52–7.59 (m, 5H, Ar-H),

7.81 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 97.2, 101.6, 117.1, 127.8, 128.8, 130.1, 136.3, 143.1, 154.6, 155.1 ppm; MS (EI): m/z (%) 211 ($\text{M}^+ + 1$, 18.25), 210 (M^+ , 100); HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_{10}\text{N}_4$ (M^+) 210.0899, found 210.0899.

1-Amino-2-imino-4-*p*-tolyl-1,2-dihydropyridine-3-carbonitrile (3b). Yellow crystals; yield: 4.3 g (90%); m.p. 223–224 °C, IR (KBr): ν/cm^{-1} 3315, 3262 (NH_2), 3171 (NH), 2207 ($\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 2.38 (s, 3H, CH_3), 5.88 (d, $J = 7.2$ Hz, 1H, C-H6), 6.13 (s, 2H, NH_2), 6.58 (brs, 1H, imine NH), 7.34 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.48 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.79 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 20.9 (CH_3), 101.6, 117.2, 127.7, 129.3, 133.3, 140.0, 142.6, 143.0, 154.6, 155.0 ppm; MS (EI): m/z (%) 225 ($\text{M}^+ + 1$, 13.19), 224 (M^+ , 72.89); HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{N}_4$ (M^+) 224.1056, found 224.1055.

1-Amino-2-imino-4-(4-methoxyphenyl)-1,2-dihydropyridine-3-carbonitrile (3c). Yellow crystals; yield: 4.2 g (88%); m.p. 225–226 °C, IR (KBr): ν/cm^{-1} 3316, 3248 (NH_2), 3167 (NH), 2206 ($\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 3.83 (s, 3H, OCH_3), 5.89 (d, $J = 6.8$ Hz, 1H, C-H6), 6.11 (s, 2H, NH_2), 6.55 (brs, 1H, imine NH), 7.08 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.56 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.76 ppm (d, $J = 6.8$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 55.84 (OCH_3), 101.99, 102.02, 114.65, 117.83, 128.66, 129.91, 143.27, 155.06, 155.23, 161.23 ppm; MS (EI): m/z (%) 241 ($\text{M}^+ + 1$, 19.27), 240 (M^+ , 100); HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}$ (M^+) 240.1005, found 240.1005.

1-Amino-4-(4-chlorophenyl)-2-imino-1,2-dihydropyridine-3-carbonitrile (3d). Bright yellow crystals; yield: 4.35 g (89%); m.p. 234–235 °C, IR (KBr): ν/cm^{-1} 3314, 3267 (NH_2), 3178 (NH), 2210 ($\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 5.89 (d, $J = 6.8$ Hz, 1H, C-H6), 6.16 (s, 2H, NH_2), 6.61 (brs, 1H, imine NH), 7.61–7.63 (m, 4H, Ar-H), 7.81 ppm (d, $J = 6.8$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 101.3, 116.8, 128.8, 129.7, 134.8, 135.0, 143.1, 153.9, 154.3 ppm; MS (EI): m/z (%) 246 ($\text{M}^+ + 2$, 34.29), 245 ($\text{M}^+ + 1$, 17.94), 244 (M^+ , 100); HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_9\text{N}_4\text{Cl}$ (M^+) 244.0510, found 244.0510.

1-Amino-4-(4-bromophenyl)-2-imino-1,2-dihydropyridine-3-carbonitrile (3e). Yellow crystals; yield: 5.3 g (92%); m.p. 239–240 °C, IR (KBr): ν/cm^{-1} 3311, 3263 (NH_2), 3176 (NH), 2208 ($\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 5.90 (d, $J = 6.8$ Hz, 1H C-H6), 6.17 (s, 2H, NH_2), 6.73 (brs, 1H, imine NH), 7.54 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.82 ppm (d, $J = 6.8$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 102.2, 116.6, 123.7, 130.0, 131.8, 135.3, 143.4, 143.4, 154.2, 154.3 ppm; MS (EI): m/z (%) 290 ($\text{M}^+ + 2$, 97.06), 289 ($\text{M}^+ + 1$, 18.49), 288 (M^+ , 100); HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_9\text{N}_4\text{Br}$ (M^+) 288.0005, found 288.0005.

General procedure for the preparation of triazolo[1,5-*a*]pyridine derivatives 5a–k

For acetic acid. Independent mixtures of 1-amino-2-imino-pyridine 3a,d (3.0 mmol), and acetic acid (10 equiv.) in EtOH (10 mL).

For other acids. Independent mixtures of 1-amino-2-imino-pyridine 3a–d (3.0 mmol), and the appropriate carboxylic acids (4a–g) (4.0 mmol), in EtOH (10.0 mL) containing acetic acid (0.90 g, 5 equiv.), were charged in the glass tube of the microwave tube and irradiated by focused microwave using a single-mode cavity explorer microwave synthesizer (CEM

Corporation, NC, USA) for 15 min at 100 °C, and 250 W. The build-up of pressure in the closed reaction vessel was carefully monitored. After the irradiation, the reaction tube was cooled through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The reaction was controlled by TLC and continued until the starting substrates were completely consumed. The solid products that formed on standing at room temperature were collected by filtration, washed with ethanol and recrystallized from the proper solvent (see below), to give 5a–k as pure products.

Method B for 5d–g. Independent mixtures of 1-amino-2-imino-pyridine (3.0 mmol), cyanoacetic acid or 4-nitrophenylacetic acid (3.0 mmol) in acetic anhydride (8.0 mL) were charged in the glass tube of the microwave tube and irradiated by focused microwave using a single-mode cavity explorer microwave synthesizer (CEM Corporation, NC, USA) for 5 min at 120 °C, the formed solid was collected by filtration and recrystallized from the appropriate solvent (see below).

2-Methyl-7-phenyl[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5a). Recrystallized from EtOH/dioxane mixture (5 : 1), as yellowish white crystals, yield: 0.65 g (92%), m.p. 155–156 °C; IR (KBr): ν/cm^{-1} 2218 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 2.55 (s, 3H, CH_3), 7.37 (d, $J = 6.8$ Hz, 1H, C-H6), 7.59–7.63 (m, 3H, Ar-H), 7.75 (d, $J = 8.4$ Hz, 2H, Ar-H) 9.19 ppm (d, $J = 6.8$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 14.13 (CH_3), 96.41, 114.61, 114.64, 128.78, 128.99, 130.18, 132.45, 135.47, 149.06, 150.30, 165.01 ppm; MS (EI): m/z (%) 235 ($\text{M}^+ + 1$, 26.78), 234 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{10}\text{N}_4$ (M^+) 234.0899, found 234.0898.

7-(4-Chlorophenyl)-2-methyl[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5b). Recrystallized from EtOH/dioxane mixture (3 : 1), as buff crystals, yield: 0.70 g (87%), m.p. 225–226 °C; IR (KBr): ν/cm^{-1} 2223 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 2.54 (s, 3H, CH_3), 7.36 (d, $J = 6.8$ Hz, 1H, C-H6), 7.67 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.76 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.20 ppm (d, $J = 6.8$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 14.1, 96.6, 114.5, 128.7, 129.1, 130.7, 132.6, 134.3, 135.2, 147.8, 150.2, 165.1 ppm; MS (EI): m/z (%) 270 ($\text{M}^+ + 2$, 29.65), 269 ($\text{M}^+ + 1$, 14.89), 268 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{10}\text{ClN}_4$ (M^+) 268.1147, found 268.1147.

2-(Chloromethyl)-7-(4-chlorophenyl)[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5c). Recrystallized from EtOH/dioxane mixture (3 : 1), as beige crystals, yield: 0.80 g (91%) in case of acid, 0.75 g (85% in case of chloroacetaldehyde), m.p. 179–180 °C; IR (KBr): ν/cm^{-1} 2239 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, CDCl_3): δ 4.86 (s, 2H, CH_2), 7.22 (d, $J = 7.2$ Hz, 1H, C-H6), 7.56 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.64 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.77 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 37.36, 99.14, 113.49, 115.25, 129.70, 129.97, 131.50, 133.49, 137.26, 148.92, 151.00, 165.10 ppm; MS (EI): m/z (%) 304 ($\text{M}^+ + 2$, 64.82), 303 ($\text{M}^+ + 1$, 17.68), 302 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_8\text{Cl}_2\text{N}_4$ (M^+) 302.01205, found 302.01205.

2-(Cyanomethyl)-7-phenyl[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5d). Recrystallized from dioxane as buff crystals, yield: 0.75 g (96%), m.p. 245–246 °C; IR (KBr): ν/cm^{-1} 2261, 2231 ($\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 4.56 (s, 2H, CH_2), 7.50 (d, $J = 7.2$ Hz, 1H, C-H6), 7.60–7.64 (m, 3H, Ar-H), 7.74–7.78 (m, 2H, Ar-H), 9.33 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150



MHz, DMSO- d_6): δ 17.86, 97.44, 114.04, 115.70, 116.14, 128.62, 128.96, 130.26, 132.71, 135.39, 150.04, 150.74, 159.59 ppm; MS (EI): m/z (%) 260 ($M^+ + 1$, 20.54), 259 (M^+ , 100). HRMS (EI): m/z calcd for $C_{15}H_9N_5$ (M^+) 259.0852, found 259.0853.

7-(4-Chlorophenyl)-2-(cyanomethyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5e). Recrystallized from dioxane as buff crystals, yield: 0.85 g (97%), m.p. 229–230 °C; IR (KBr): ν/cm^{-1} 2264, 2231 ($2C\equiv N$); 1H NMR (400 MHz, DMSO- d_6): δ 4.56 (s, 2H, CH_2), 7.52 (d, $J = 7.2$ Hz, 1H, C-*H6*), 7.72 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.81 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.36 ppm (d, $J = 7.2$ Hz, 1H, C-*H5*); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO- d_6): δ 17.83, 97.36, 114.26, 115.60, 116.61, 129.12, 130.78, 133.09, 134.08, 135.43, 148.67, 150.56, 159.65 ppm; MS (EI): m/z (%) 295 ($M^+ + 2$, 75.08), 294 ($M^+ + 1$, 61.59), 293 (M^+ , 100). HRMS (EI): m/z calcd for $C_{15}H_8ClN_5$ (M^+) 293.0462, found 293.0462.

2-(Cyanomethyl)-7-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5f). Recrystallized from dioxane as buff crystals, yield: 0.82 g (94%), m.p. 270–271 °C; IR (KBr): ν/cm^{-1} 2261, 2230 ($2C\equiv N$); 1H NMR (600 MHz, DMSO- d_6): δ 3.86 (s, 3H, OCH_3), 4.52 (s, 2H, CH_2), 7.17 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.47 (d, $J = 7.2$ Hz, 1H, C-*H6*), 7.75 (d, $J = 9.0$ Hz, 2H, Ar-H), 9.26 ppm (d, $J = 7.2$ Hz, 1H, C-*H5*); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO- d_6): δ 17.79, 55.47, 96.12, 114.55, 114.70, 115.58, 116.62, 127.25, 130.52, 132.70, 149.60, 150.83, 159.38, 161.06 ppm; MS (EI): m/z (%) 290 ($M^+ + 1$, 17.36), 289 (M^+ , 100). HRMS (EI): m/z calcd for $C_{16}H_{11}N_5O$ (M^+) 289.0958, found 289.289.0957.

2-(4-Nitrobenzyl)-7-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5g). Recrystallized from dioxane as white crystals, yield: 1.05 g (93%), m.p. 159–160 °C; IR (KBr): ν/cm^{-1} 2233 ($C\equiv N$); 1H NMR (600 MHz, DMSO- d_6): δ 3.87 (s, 3H, OCH_3), 4.57 (s, 2H, CH_2), 7.18 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.40 (d, $J = 7.2$ Hz, 1H, C-*H6*), 7.67 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.74 (d, $J = 9.0$ Hz, 2H, Ar-H), 8.21 (d, $J = 9.0$ Hz, 2H, Ar-H), 9.21 ppm (d, $J = 7.2$ Hz, 1H, C-*H5*); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO- d_6): δ 33.99, 55.45, 95.94, 114.51, 114.90, 115.02, 123.56, 127.43, 130.34, 130.46, 132.53, 145.45, 146.36, 149.18, 150.65, 160.95, 166.03 ppm; MS (EI): m/z (%) 386 ($M^+ + 1$, 24.83), 385 (M^+ , 100). HRMS (EI): m/z calcd for $C_{21}H_{15}N_5O_3$ (M^+) 385.1169, found 385.1169.

7-(4-Methoxyphenyl)-2-phenyl-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5h). Recrystallized from EtOH/dioxane mixture (1 : 3), as creamy white crystals, yield: 0.80 g (83%), m.p. 199–200 °C; IR (KBr): ν/cm^{-1} 2221 ($C\equiv N$); 1H NMR (600 MHz, DMSO- d_6): δ 3.88 (s, 3H, OCH_3), 7.18 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.43 (d, $J = 7.2$ Hz, 1H, C-*H6*), 7.56–7.59 (m, 3H, Ar-H), 7.77 (d, $J = 9.0$ Hz, 2H, Ar-H), 8.23–8.25 (m, 2H, Ar-H), 9.28 ppm (d, $J = 7.2$ Hz, 1H, C-*H5*); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO- d_6): δ 55.46, 96.09, 114.50, 114.99, 115.28, 127.03, 129.02, 129.63, 130.50, 130.74, 132.63, 149.15, 151.04, 160.94, 164.13 ppm; MS (EI): m/z (%) 327 ($M^+ + 1$, 23.79), 326 (M^+ , 100). HRMS (EI): m/z calcd for $C_{20}H_{14}N_4O$ (M^+) 326.1162, found 326.1162.

7-(4-Chlorophenyl)-2-phenyl-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5i). Recrystallized from dioxane as creamy white crystals, yield: 0.85 g (86%), m.p. 210–212 °C; IR (KBr): ν/cm^{-1} 2224 ($C\equiv N$); 1H NMR (600 MHz, DMSO- d_6): δ 7.48 (d, $J = 7.2$ Hz, 1H, C-*H6*), 7.57–7.60 (m, 3H, Ar-H), 7.71 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.81 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.25–8.26 (m, 2H, Ar-H),

9.37 ppm (d, $J = 7.2$ Hz, 1H, C-*H5*); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO- d_6): δ 97.29, 114.53, 115.29, 127.10, 129.08, 129.54, 130.73, 130.87, 133.00, 134.25, 135.30, 148.22, 150.81, 164.54 ppm; MS (EI): m/z (%) 332 ($M^+ + 2$, 40.03), 331 ($M^+ + 1$, 30.11), 330 (M^+ , 100). HRMS (EI): m/z calcd for $C_{19}H_{11}ClN_4$ (M^+) 330.0666, found 330.0667.

7-(4-Chlorophenyl)-2-(2-hydroxyphenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5j). Recrystallized from dioxane as yellowish white crystals, yield: 0.90 g (87%), m.p. 244–245 °C; IR (KBr): ν/cm^{-1} 3385 (OH), 2226 ($C\equiv N$); 1H NMR (600 MHz, DMSO- d_6): δ 6.99–7.04 (m, 2H, Ar-H), 7.41 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.53 (d, $J = 7.2$ Hz, 1H, C-*H6*), 7.71 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.81 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.06 (d, $J = 7.8$ Hz, 1H, Ar-H), 9.37 (d, $J = 7.2$ Hz, 1H, C-*H5*), 10.87 ppm (s, 1H, OH); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO- d_6): δ 96.71, 112.76, 113.44, 115.39, 116.85, 119.28, 127.50, 128.65, 130.11, 132.10, 132.29, 133.65, 135.16, 148.29, 149.08, 156.82, 163.16 ppm; MS (EI): m/z (%) 348 ($M^+ + 2$, 34.08), 347 ($M^+ + 1$, 23.17), 346 (M^+ , 100). HRMS (EI): m/z calcd for $C_{19}H_{11}ClN_4O$ (M^+) 346.0615, found 346.0614.

2-(2-Aminophenyl)-7-(4-chlorophenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5k). Recrystallized from EtOH/dioxane mixture (1 : 2), as creamy white crystals, yield: 0.86 g (84%), m.p. 215–216 °C; IR (KBr): ν/cm^{-1} 3364, 3292 (NH_2), 2221 ($C\equiv N$); 1H NMR (600 MHz, DMSO- d_6): δ 5.01 (brs, 2H, NH_2), 6.59 (d, $J = 7.8$ Hz, 1H, Ar-H), 6.73 (d, $J = 7.2$ Hz, 1H, C-*H6*), 6.95 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.32 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.43 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.65 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.95 (d, $J = 7.8$ Hz, 1H, Ar-H), 8.22 ppm (d, $J = 7.2$ Hz, 1H, C-*H5*); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO- d_6): δ 97.10, 110.26, 113.63, 114.80, 120.38, 121.30, 128.39, 129.58, 131.39, 131.89, 131.98, 141.44, 146.24, 147.34, 155.09, 158.35, 168.96 ppm; MS (EI): m/z (%) 347 ($M^+ + 2$, 3.01), 346 ($M^+ + 1$, 1.78), 345 (M^+ , 9.65). HRMS (EI): m/z calcd for $C_{19}H_{12}ClN_5$ (M^+) 345.0775, found 345.0776.

General procedure for the preparation of triazolo[1,5-*a*]pyridine derivatives (5l–z and 11–14). Independent mixtures of 1-amino-2-imino-pyridine **3a–e** (3.0 mmol), and the appropriate reactant (3.0 mmol) in ethanol (10.0 mL) containing acetic acid (0.90 g, 5 equiv.), were charged in the glass tube of the microwave tube and irradiated by focused microwave using a single-mode cavity explorer microwave synthesizer (CEM Corporation, NC, USA) for 15 min at 100 °C, and 250 W. The build-up of pressure in the closed reaction vessel was carefully monitored. After the irradiation, the reaction tube was cooled through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The reaction was controlled by TLC and continued until the starting substrates were completely consumed. The solid products that formed on standing at room temperature were collected by filtration, washed with ethanol and recrystallized from the proper solvent (see below), to give pure products. But in the case of **14** TEA or DBU was added instead of acetic acid.

Ethyl 8-cyano-7-phenyl-[1,2,4]triazolo[1,5-*a*]pyridine-2-carboxylate (5l). Recrystallized from EtOH/dioxane mixture (1 : 1), as white crystals, yield: 0.77 g (88%), m.p. 234–235 °C; IR (KBr): ν/cm^{-1} 2231 ($C\equiv N$), 1722 (CO); 1H NMR (400 MHz, DMSO- d_6): δ 1.39 (t, $J = 7.2$ Hz, 3H, CH_3CH_2), 4.45 (q, $J = 7.2$ Hz, 2H, CH_3CH_2), 7.61–7.66 (m, 4H, pyridine C-*H6* and 3 Ar-H),



7.79–7.82 (m, 2H, Ar-H), 9.42 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (100 MHz, CDCl₃): δ 14.19 (CH₃), 62.79 (CH₂), 100.15, 113.13, 117.18, 128.65, 129.34, 130.86, 131.64, 134.82, 150.81, 151.08, 157.46, 159.49 ppm; MS (EI): m/z (%) 293 ($\text{M}^+ + 1$, 3.24), 292 (M^+ , 16.04). HRMS (EI): m/z calcd for C₁₆H₁₂N₄O₂ (M^+) 292.0954, found 292.0954.

Ethyl 8-cyano-7-*p*-tolyl-[1,2,4]triazolo[1,5-*a*]pyridine-2-carboxylate (5m). Recrystallized from EtOH/dioxane mixture (1 : 1), as white crystals, yield: 0.80 g (87%), m.p. 180–181 °C; IR (KBr): ν/cm^{-1} 2230 (C \equiv N), 1726 (C=O); ^1H NMR (400 MHz, DMSO-*d*₆): δ 1.38 (t, $J = 7.2$ Hz, 3H, CH₃CH₂), 2.43 (s, 3H, CH₃), 4.45 (q, $J = 7.2$ Hz, 2H, CH₃CH₂), 7.45 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.61 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.70 (d, $J = 8.0$ Hz, 2H, Ar-H), 9.38 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (100 MHz, DMSO-*d*₆): δ 14.06, 20.96 (2CH₃), 61.99 (CH₂), 97.99, 114.41, 117.32, 128.86, 129.74, 132.23, 133.47, 140.73, 150.49, 150.60, 156.19, 159.37 ppm; MS (EI): m/z (%) 307 ($\text{M}^+ + 1$, 7.09), 306 (M^+ , 37.28). HRMS (EI): m/z calcd for C₁₇H₁₄N₄O₂ (M^+) 306.1111, found 306.1111. Crystal data, moiety formula: C₁₇H₁₄N₄O₂, $M = 306.32$, monoclinic, $a = 16.043(2)$ Å, $b = 9.9874(9)$ Å, $c = 18.960(2)$ Å, $V = 2972.1(5)$ Å³, $\alpha = \gamma = 90^\circ$, $\beta = 101.956(8)^\circ$, space group: $P2_1/c$ (#14), $Z = 8$, $D_{\text{calc}} = 1.369$ g cm⁻³, no. of reflection measured = 5132, $2\theta_{\text{max}} = 50.10^\circ$, $R1 = 0.0638$ (CCDC 1982378†).³⁵

Ethyl 8-cyano-7-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-2-carboxylate (5n). Recrystallized from EtOH/dioxane mixture (1 : 1), as white crystals, yield: 0.82 g (85%), m.p. 184–185 °C; IR (KBr): ν/cm^{-1} 2231 (C \equiv N), 1732 (C=O); ^1H NMR (400 MHz, DMSO-*d*₆): δ 1.38 (t, $J = 7.2$ Hz, 3H, CH₃CH₂), 3.86 (s, 3H, OCH₃), 4.43 (q, $J = 7.2$ Hz, 2H, CH₃CH₂), 7.17 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.59 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.76 (d, $J = 8.8$ Hz, 2H, Ar-H), 9.32 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (100 MHz, DMSO-*d*₆): δ 14.47, 55.96 (2CH₃), 62.40 (CH₂), 97.66, 115.03, 117.65, 127.45, 131.05, 133.67, 150.61, 150.97, 156.55, 159.77, 161.65 ppm; MS (EI): m/z (%) 323 ($\text{M}^+ + 1$, 8.65), 322 (M^+ , 43.39). HRMS (EI): m/z calcd for C₁₇H₁₄N₄O₃ (M^+) 322.1060, found 322.1060.

Ethyl 7-(4-chlorophenyl)-8-cyano[1,2,4]triazolo[1,5-*a*]pyridine-2-carboxylate (5o). Recrystallized from EtOH/dioxane mixture (1 : 3), as white crystals, yield: 0.90 g (92%), m.p. 218–219 °C; IR (KBr): ν/cm^{-1} 2231 (C \equiv N), 1735 (C=O); ^1H NMR (600 MHz, DMSO-*d*₆): δ 1.38 (t, $J = 7.2$ Hz, 3H, CH₃CH₂), 4.44 (q, $J = 7.2$ Hz, 2H, CH₃CH₂), 7.65 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.72 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.82 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.43 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (150 MHz, DMSO-*d*₆): δ 14.05 (CH₃), 62.03 (CH₂), 98.69, 114.13, 117.23, 129.22, 130.85, 133.68, 133.91, 135.64, 149.33, 150.30, 156.28, 159.30 ppm; MS (EI): m/z (%) 328 ($\text{M}^+ + 2$, 6.34), 327 ($\text{M}^+ + 1$, 3.57), 326 (M^+ , 17.29). HRMS (EI): m/z calcd for C₁₆H₁₁ClN₄O₂ (M^+) 326.0565, found 326.0565.

Ethyl 7-(4-bromophenyl)-8-cyano[1,2,4]triazolo[1,5-*a*]pyridine-2-carboxylate (5p). Recrystallized from EtOH/dioxane mixture (1 : 3), as white crystals, yield: 1.00 g (92%), m.p. 229–230 °C; IR (KBr): ν/cm^{-1} 2231 (C \equiv N), 1733 (C=O); ^1H NMR (400 MHz, DMSO-*d*₆): δ 1.38 (t, $J = 7.2$ Hz, 3H, CH₃CH₂), 4.45 (q, $J = 7.2$ Hz, 2H, CH₃CH₂), 7.65 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.75 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.87 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.43 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (150 MHz, DMSO-*d*₆): δ 14.07

(CH₃), 62.05 (CH₂), 98.66, 114.16, 117.18, 124.48, 131.05, 132.17, 133.72, 134.31, 149.44, 150.33, 156.30, 159.33 ppm; MS (EI): m/z (%) 372 ($\text{M}^+ + 2$, 24.53), 371 ($\text{M}^+ + 1$, 5.12), 370 (M^+ , 24.85). HRMS (EI): m/z calcd for C₁₆H₁₁BrN₄O₂ (M^+) 370.0059, found 370.0058. Crystal data, moiety formula: C₁₆H₁₁BrN₄O₂, $M = 371.19$, orthorhombic, $a = 13.845(2)$ Å, $b = 7.528(1)$ Å, $c = 30.459(4)$ Å, $V = 3174.7(8)$ Å³, $\alpha = \beta = \gamma = 90^\circ$, space group: $Pbca$ (#61), $Z = 8$, $D_{\text{calc}} = 1.553$ g cm⁻³, no. of reflection measured = 2742, $2\theta_{\text{max}} = 49.9^\circ$, $R1 = 0.0807$ (CCDC 1982379†).³⁵

2-(4-Chlorophenyl)-7-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5q). Recrystallized from dioxane/DMF mixture (2 : 1), as creamy white crystals, yield: 0.95 g (90%), m.p. 224–225 °C; IR (KBr): ν/cm^{-1} 2229 (C \equiv N); ^1H NMR (600 MHz, DMSO-*d*₆): δ 3.89 (s, 3H, OCH₃), 7.17 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.39 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.60 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.75 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.22 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.17 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (150 MHz, DMSO-*d*₆): δ 55.10 (OCH₃), 96.03, 114.14, 114.24, 114.98, 127.15, 128.28, 128.40, 128.60, 129.88, 131.97, 135.12, 148.95, 150.75, 160.77, 163.21 ppm; MS (EI): m/z (%) 362 ($\text{M}^+ + 2$, 30.89), 361 ($\text{M}^+ + 1$, 20.56), 360 (M^+ , 100.00). HRMS (EI): m/z calcd for C₂₀H₁₃ClN₄O (M^+) 360.0772, found 360.0772. Crystal data, moiety formula: C₂₀H₁₃ClN₄O, C₃H₇NO, sum formula: C₂₃H₂₀ClN₅O₂, $M = 433.90$, orthorhombic, $a = 22.8101(9)$ Å, $b = 7.5155(3)$ Å, $c = 24.720(2)$ Å, $V = 4237.7(4)$ Å³, $\alpha = \beta = \gamma = 90^\circ$, space group: $Pca2_1$ (#29), $Z = 8$, $D_{\text{calc}} = 1.360$ g cm⁻³, no. of reflection measured = 3817, $2\theta_{\text{max}} = 50.1^\circ$, $R1 = 0.0428$ (CCDC 1982380†).³⁵

2,7-Bis(4-methoxyphenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5r). Recrystallized from dioxane as creamy white crystals, yield: 1.00 g (93%), m.p. 226–227 °C; IR (KBr): ν/cm^{-1} 2232 (C \equiv N); ^1H NMR (600 MHz, DMSO-*d*₆): δ 3.86 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 7.12 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.18 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.40 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.78 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.18 (d, $J = 9.0$ Hz, 2H, Ar-H), 9.25 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (150 MHz, DMSO-*d*₆): δ 55.33, 55.46 (2OCH₃), 95.80, 114.45, 114.51, 114.96, 115.07, 122.05, 127.52, 128.71, 130.45, 132.50, 148.97, 151.07, 160.93, 161.30, 164.36 ppm; MS (EI): m/z (%) 357 ($\text{M}^+ + 1$, 24.09), 356 (M^+ , 100.00). HRMS (EI): m/z calcd for C₂₁H₁₆N₄O₂ (M^+) 356.1267, found 356.1266.

2,7-Bis(4-chlorophenyl)-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5s). Recrystallized from dioxane as creamy white crystals, yield: 1.02 g (94%), m.p. 279–280 °C; IR (KBr): ν/cm^{-1} 2230 (C \equiv N); ^1H NMR (600 MHz, DMSO-*d*₆): δ 7.49 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.66 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.71 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.81 (d, $J = 7.8$ Hz, 2H, Ar-H), 8.26 (d, $J = 7.8$ Hz, 2H, Ar-H), 9.37 ppm (d, $J = 7.2$ Hz, 1H, C-H5); ^{13}C { ^1H } NMR (150 MHz, DMSO-*d*₆): δ 97.22, 113.87, 115.10, 128.24, 128.57, 128.73, 128.82, 130.27, 132.55, 133.96, 135.06, 135.33, 148.10, 150.60, 163.46 ppm; MS (EI): m/z (%) 366 ($\text{M}^+ + 2$, 59.97), 365 ($\text{M}^+ + 1$, 24.36), 364 (M^+ , 100.00). HRMS (EI): m/z calcd for C₂₀H₁₃ClN₄O (M^+) 360.0772, found 360.0774.

7-(4-chlorophenyl)-2-*p*-tolyl-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (5t). Recrystallized from dioxane as creamy white crystals, yield: 0.95 g (91%), m.p. 227–228 °C; IR (KBr): ν/cm^{-1} 2228 (C \equiv N); ^1H NMR (600 MHz, DMSO-*d*₆): δ 2.39 (s, 3H, CH₃),



7.37 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.44 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.71 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.80 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.12 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.32 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 21.05 (CH_3), 97.12, 114.56, 115.12, 126.79, 127.07, 129.08, 129.65, 130.73, 132.92, 134.28, 135.27, 140.73, 148.09, 150.78, 164.66 ppm; MS (EI): m/z (%) 346 ($\text{M}^+ + 2$, 33.47), 345 ($\text{M}^+ + 1$, 27.19), 344 (M^+ , 100.00). HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{13}\text{ClN}_4$ (M^+) 344.0823, found 344.0823.

(*E*)-7-(4-Chlorophenyl)-2-styryl[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**5u**). Recrystallized from dioxane as creamy white crystals, yield: 0.94 g (88%), m.p. 243–244 °C; IR (KBr): ν/cm^{-1} 2231 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 7.39–7.47 (m, 5H, Ar-H), 7.72 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.81–7.89 (m, 5H, Ar-H), 9.29 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 96.83, 114.59, 114.98, 116.97, 127.54, 128.87, 129.08, 129.26, 130.73, 132.78, 134.30, 135.28, 135.43, 137.41, 148.23, 150.43, 164.45 ppm; MS (EI): m/z (%) 358 ($\text{M}^+ + 2$, 17.05), 357 ($\text{M}^+ + 1$, 38.14), 356 (M^+ , 47.89), 355 ($\text{M}^+ - 1$, 100.00). HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{13}\text{ClN}_4$ (M^+) 356.0823, found 356.0823. Crystal data, moiety formula: $\text{C}_{21}\text{H}_{13}\text{ClN}_4$, $M = 356.81$, monoclinic, $a = 7.653(1)$ Å, $b = 6.928(9)$ Å, $c = 32.82(4)$ Å, $V = 1734(4)$ Å³, $\alpha = \gamma = 90^\circ$, $\beta = 94.79(3)^\circ$, space group: $P2_1/n$ (#14), $Z = 4$, $D_{\text{calc}} = 1.367$ g cm⁻³, no. of reflection measured = 3041, $2\theta_{\text{max}} = 50.10^\circ$, $R1 = 0.0800$ (CCDC 1982381†).³⁵

7-(4-Chlorophenyl)-2-(phenylamino)[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**5v**). Recrystallized from EtOH/dioxane mixture (1 : 2), as yellow crystals, yield: 0.95 g (91%), m.p. 216–218 °C; IR (KBr): ν/cm^{-1} 3362 (NH), 2225 ($2\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 6.92 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.17 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.31 (t, $J = 7.8$ Hz, 2H, Ar-H), 7.63 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.68 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.07 (d, $J = 7.2$ Hz, 1H, C-H5), 10.09 ppm (s, 1H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 93.95, 112.72, 114.76, 116.86, 120.75, 128.77, 128.95, 130.52, 131.82, 134.49, 134.98, 140.42, 146.95, 149.72, 163.23 ppm; MS (EI): m/z (%) 347 ($\text{M}^+ + 2$, 33.07), 346 ($\text{M}^+ + 1$, 48.39), 345 (M^+ , 100.00). HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{12}\text{ClN}_5$ (M^+) 345.0775, found 345.0775. Crystal data, moiety formula: $\text{C}_{19}\text{H}_{12}\text{ClN}_5$, $M = 345.79$, triclinic, $a = 8.9886(8)$ Å, $b = 12.8468(10)$ Å, $c = 15.1372(12)$ Å, $V = 1635.2(2)$ Å³, $\alpha = 71.352(4)^\circ$, $\beta = 80.896(4)^\circ$, $\gamma = 86.548(5)^\circ$, space group: $P\bar{1}$, $Z = 4$, $D_{\text{calc}} = 1.405$ g cm⁻³, no. of reflection measured = 5570, $\theta_{\text{max}} = 66.470^\circ$, $R1 = 0.0441$ (CCDC 1982382†).³⁵

7-Phenyl[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**5w**). Recrystallized from EtOH/dioxane mixture (4 : 1), as yellow crystals, yield: 0.55 g (84%), m.p. 159–160 °C; IR (KBr): ν/cm^{-1} 2221 ($\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 7.49 (d, $J = 7.2$ Hz, 1H, C-H6), 7.62–7.67 (m, 3H, Ar-H), 7.79 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.75 (s, 1H, C-H) 9.35 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 97.60, 114.41, 115.56, 128.85, 129.03, 130.28, 133.27, 135.40, 149.60, 149.68, 155.40 ppm; MS (EI): m/z (%) 221 ($\text{M}^+ + 1$, 17.65), 220 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_8\text{N}_4$ (M^+) 220.0743, found 220.0743.

7-(4-Chlorophenyl)[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**5x**). Recrystallized from EtOH/dioxane mixture (3 : 1), as yellow crystals, yield: 0.65 g (85%), m.p. above 300 °C; IR (KBr): ν/cm^{-1} 2226 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 7.48 (d, $J = 7.2$ Hz,

1H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 2H), 8.75 (s, 1H), 9.35 ppm (d, $J = 7.2$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 97.8, 114.4, 115.4, 129.1, 130.8, 133.2, 134.2, 135.3, 148.3, 149.6, 155.5 ppm; MS (EI): m/z (%) 256 ($\text{M}^+ + 2$, 33.19), 255 ($\text{M}^+ + 1$, 16.29), 254 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_7\text{ClN}_4$ (M^+) 254.1147, found 254.1147.

7-*p*-Tolyl-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**5y**). Recrystallized from EtOH/dioxane mixture (3 : 1), as yellowish white crystals, yield: 0.60 g (83%), m.p. 172–173 °C; IR (KBr): ν/cm^{-1} 2224 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 2.40 (s, 3H, CH_3), 7.40 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.42 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.65 (d, $J = 7.8$ Hz, 2H, Ar-H), 8.70 (s, 1H, C-H2), 9.28 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 20.87 (CH_3), 97.15, 114.63, 115.46, 128.73, 129.58, 132.47, 132.94, 140.29, 149.55, 149.73, 155.31 ppm; MS (EI): m/z (%) 235 ($\text{M}^+ + 1$, 13.94), 234 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{10}\text{N}_4$ (M^+) 234.0899, found 234.0898.

7-(4-Chlorophenyl)-2-(4-formylphenyl)[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**5z**). Recrystallized from dioxane/DMF mixture (4 : 1), as orange crystals, yield: 1.00 g (92%), m.p. 276–277 °C; IR (KBr): ν/cm^{-1} 2231 ($\text{C}\equiv\text{N}$), 1695 ($\text{C}=\text{O}$); ^1H NMR (600 MHz, DMSO- d_6): δ 7.54 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.74 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.84 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.12 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.48 (d, $J = 8.4$ Hz, 2H, Ar-H), 9.41 (d, $J = 7.2$ Hz, 1H, C-H5), 10.12 ppm (s, 1H, CHO); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 97.41, 113.55, 115.20, 127.32, 128.56, 129.44, 130.06, 132.40, 133.81, 134.41, 135.01, 137.31, 148.15, 150.54, 163.29, 191.82 ppm; MS (EI): m/z (%) 360 ($\text{M}^+ + 2$, 31.05), 359 ($\text{M}^+ + 1$, 41.58), 358 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{11}\text{ClN}_4\text{O}$ (M^+) 358.0615, found 358.0615.

(*E*)-2-(1-Cyano-2-(dimethylamino)vinyl)-7-phenyl-[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**11a**). Recrystallized from EtOH/dioxane mixture (1 : 3), as yellowish white crystals, yield: 0.85 g (90%), m.p. 279–280 °C; IR (KBr): ν/cm^{-1} 2227, 2202 ($2\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 3.36 (s, 6H, 2CH_3), 7.29 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.60–7.62 (m, 3H, Ar-H), 7.73–7.76 (m, 2H, Ar-H), 7.98 (s, 1H, enamine C-H), 9.14 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 30.55, 49.89 (2CH_3), 65.96, 95.00, 113.45, 114.04, 117.91, 128.11, 128.39, 129.48, 131.31, 135.31, 148.43, 150.07, 153.27, 165.03 ppm; MS (EI): m/z (%) 315 ($\text{M}^+ + 1$, 47.38), 314 (M^+ , 100.00). HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{14}\text{N}_6$ (M^+) 314.1274, found 314.1274.

(*E*)-7-(4-Chlorophenyl)-2-(1-cyano-2-(dimethylamino)vinyl)[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**11b**). Recrystallized from dioxane, as yellowish white crystals, yield: 0.90 g (87%), m.p. 21–292 °C; IR (KBr): ν/cm^{-1} 2228, 2203 ($2\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, DMSO- d_6): δ 3.36 (s, 6H, 2CH_3), 7.31 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.69 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.78 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.99 (s, 1H, enamine C-H), 9.17 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 30.42, 50.07 (2CH_3), 66.32, 95.57, 113.79, 114.40, 118.40, 128.96, 130.49, 131.91, 134.56, 135.19, 147.58, 150.46, 153.78, 165.62 ppm; MS (EI): m/z (%) 350 ($\text{M}^+ + 2$, 31.57), 349 ($\text{M}^+ + 1$, 29.98), 348 (M^+ , 100.00). HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{13}\text{ClN}_6$ (M^+) 348.0884, found 348.0884.



(*E*)-2-(1-Cyano-2-phenylvinyl)-7-(4-methoxyphenyl)[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**12a**). Recrystallized from dioxane/DMF mixture (3 : 1), as yellowish white crystals, yield: 1.00 g (89%), m.p. 257–258 °C; IR (KBr): ν/cm^{-1} 2225, 2208 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 3.88 (s, 3H, OCH_3), 7.20 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.52 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.61–7.62 (m, 3H, Ar-H), 7.79 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.13–8.14 (m, 2H, Ar-H), 8.58 (s, 1H, arylidene C-H), 9.34 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, TFA-*d*): δ 57.46 (OCH_3), 68.17, 95.42, 95.65, 117.90, 122.64, 128.22, 131.88, 133.19, 133.22, 133.58, 135.79, 137.64, 148.82, 157.48, 159.06, 159.79, 165.53 ppm; MS (EI): m/z (%) 378 ($\text{M}^+ + 1$, 53.67), 377 (M^+ , 53.67), 376 ($\text{M}^+ - 1$, 100.00). HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{15}\text{N}_5\text{O}$ (M^+) 377.1271, found 377.1270.

(*E*)-7-(4-Chlorophenyl)-2-(1-cyano-2-phenylvinyl)[1,2,4]triazolo[1,5-*a*]pyridine-8-carbonitrile (**12b**). Recrystallized from DMF as yellowish white crystals, yield: 1.05 g (93%), m.p. 282–283 °C; IR (KBr): ν/cm^{-1} 2226, 2210 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 7.49 (d, $J = 7.2$ Hz, 1H, pyridine C-H6), 7.60–7.61 (m, 3H, Ar-H), 7.69 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.80 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.10–8.11 (m, 2H, Ar-H), 8.57 (s, 1H, arylidene C-H), 9.30 ppm (d, $J = 7.2$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 97.20, 101.09, 113.50, 115.28, 115.43, 128.61, 128.66, 129.48, 130.13, 131.55, 132.09, 132.52, 133.72, 135.12, 148.06, 148.67, 150.25, 160.90 ppm; MS (EI): m/z (%) 383 ($\text{M}^+ + 2$, 62.87), 382 ($\text{M}^+ + 1$, 36.81), 381 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{12}\text{ClN}_5$ (M^+) 381.0775, found 381.0775.

7-(*p*-Tolyl)-2-{4-(7-(*p*-tolyl)-8-cyano[1,2,4]triazolo[1,5-*a*]pyridin-2-yl)phenyl}-8-cyano[1,2,4]triazolo[1,5-*a*]pyridine (**13a**). Recrystallized from DMF as orange crystals, yield: 1.50 g (92%), m.p. above 300 °C; IR (KBr): ν/cm^{-1} 2231, 2175 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, TFA-*d*): δ 2.59 (s, 6H, 2CH_3), 7.60 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.83 (d, $J = 8.4$ Hz, 4H, Ar-H), 8.07 (d, $J = 7.2$ Hz, 2H, C-H5), 8.69 (s, 4H, Ar-H), 9.26 ppm (d, $J = 7.2$ Hz, 2H, C-H6); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, TFA-*d*): δ 21.05 (CH_3), 94.85, 112.61, 122.40, 128.34, 129.79, 130.52, 130.94, 131.79, 135.20, 146.78, 156.93, 160.24 ppm; MS (EI): m/z (%) 543 ($\text{M}^+ + 1$, 37.19), 542 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{34}\text{H}_{22}\text{N}_8$ (M^+) 542.1961, found 542.1961.

7-(4-Chlorophenyl)-2-{4-(7-(4-chlorophenyl)-8-cyano[1,2,4]triazolo[1,5-*a*]pyridin-2-yl)phenyl}-8-cyano[1,2,4]triazolo[1,5-*a*]pyridine (**13b**). Recrystallized from DMF as orange crystals, yield: 1.70 g (97%), m.p. above 300 °C; IR (KBr): ν/cm^{-1} 2231, 2173 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, TFA-*d*): δ 7.68 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.79 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.79 (d, $J = 7.2$ Hz, 2H, C-H5), 8.62 (s, 4H, Ar-H), 9.24 ppm (d, $J = 7.2$ Hz, 2H, C-H6); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, TFA-*d*): δ 95.88, 112.17, 122.16, 128.41, 130.55, 130.99, 131.42, 132.20, 135.56, 141.71, 146.73, 157.40, 158.56 ppm; MS (EI): m/z (%) 584 ($\text{M}^+ + 2$, 71.23), 583 ($\text{M}^+ + 1$, 42.09), 582 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{32}\text{H}_{16}\text{Cl}_2\text{N}_8$ (M^+) 582.0869, found 582.0869.

7-(4-Bromophenyl)-2-{4-(7-(4-bromophenyl)-8-cyano[1,2,4]triazolo[1,5-*a*]pyridin-2-yl)phenyl}-8-cyano[1,2,4]triazolo[1,5-*a*]pyridine (**13c**). Recrystallized from DMF, as orange crystals, yield: 1.90 g (95%), m.p. above 300 °C; IR (KBr): ν/cm^{-1} 2231, 2177 ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, TFA-*d*): δ 7.75 (d, $J = 8.4$ Hz, 4H, Ar-

H), 7.90 (d, $J = 8.4$ Hz, 4H, Ar-H), 8.01 (d, $J = 7.2$ Hz, 2H, C-H5), 8.66 (s, 4H, Ar-H), 9.29 ppm (d, $J = 7.2$ Hz, 2H, C-H6); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, TFA-*d*): δ 95.87, 122.06, 128.48, 129.88, 130.58, 130.97, 132.62, 134.57, 135.56, 146.85, 157.52, 158.68 ppm; MS (EI): m/z (%) 672 ($\text{M}^+ + 2$, 56.78), 671 ($\text{M}^+ + 1$, 15.94), 670 (M^+ , 27.15). HRMS (EI): m/z calcd for $\text{C}_{32}\text{H}_{16}\text{Br}_2\text{N}_8$ (M^+) 669.9859, found 669.9859.

2-Amino-4-(4-chlorophenyl)nicotinonitrile (**14**). Recrystallized from EtOH/dioxane mixture (3 : 1), as yellow crystals, yield: 0.70 g (98%), m.p. 217–218 °C; IR (KBr): ν/cm^{-1} 3462, 3317 (NH_2), 2210 cm^{-1} ($\text{C}\equiv\text{N}$); ^1H NMR (600 MHz, DMSO- d_6): δ 6.70 (d, $J = 5.4$ Hz, 1H, pyridine C-H6), 6.99 (s, 2H, NH_2), 7.60 (s, 4H, Ar-H), 8.23 ppm (d, $J = 5.4$ Hz, 1H, C-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): δ 87.58, 112.26, 116.50, 128.81, 130.05, 134.49, 135.47, 152.56, 152.78, 161.07 ppm; MS (EI): m/z (%) 231 ($\text{M}^+ + 2$, 28.16), 230 ($\text{M}^+ + 1$, 16.32), 229 (M^+ , 100). HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_8\text{ClN}_3$ (M^+) 229.0401, found 229.0401, Crystal data, moiety formula: $\text{C}_{12}\text{H}_8\text{ClN}_3$, $M = 229.67$, monoclinic, $a = 3.8851(9)$ Å, $b = 19.350(4)$ Å, $c = 14.116(3)$ Å, $V = 1055.5(4)$ Å³, $\alpha = \gamma = 90^\circ$, $\beta = 95.964(7)^\circ$, space group: $P2_1/c$ (#14), $Z = 4$, $D_{\text{calc}} = 1.445$ g cm⁻³, no. of reflection measured = 1863, $2\theta_{\text{max}} = 50.0^\circ$, $R1 = 0.0782$ (CCDC 1982383†).³⁵

Conflicts of interest

The authors declare that they have no competing interests.

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