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PhI(OCOCF$_3$)$_2$-Mediated Intramolecular Oxidative N−N Bond Formation: Metal-Free Synthesis of 1,2,4-Triazolo[1,5-*a*]pyridines

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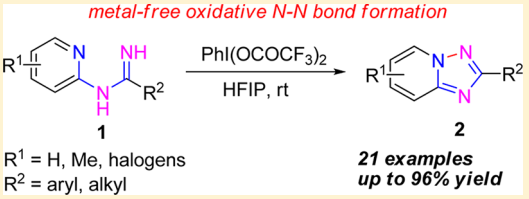
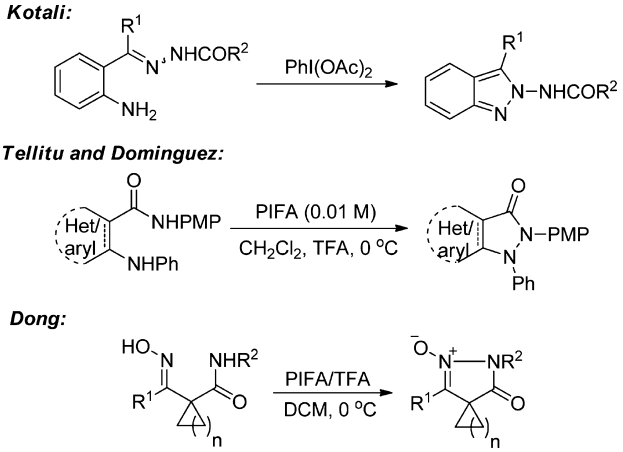
Supporting Information

ABSTRACT: The biologically important 1,2,4-triazolo[1,5-*a*]pyridines were readily synthesized from *N*-(pyridin-2-yl)benzimidamides via phenyliodine bis(trifluoroacetate)-mediated intramolecular annulation. This novel strategy allows for the convenient construction of a 1,2,4-triazolo[1,5-*a*]pyridine skeleton through direct metal-free oxidative N−N bond formation, featuring a short reaction time and high reaction yields.



In the past two decades, hypervalent iodine reagents have emerged as a class of non-metal oxidants with superb oxidizing power and environmental benignity.[1] In particular, hypervalent iodine(III) reagents such as phenyliodine(III) diacetate (PIDA) and phenyliodine(III) bis(trifluoroacetate) (PIFA) have found wide applications in the construction of various heterocyclic compounds.[2] Among these methods, intramolecular carbon−heteroatom[3−5] and carbon−carbon bond formation[6] strategies have been intensively investigated. However, a careful literature survey indicated that there are only a few reports describing the synthesis of heterocycles through the heteroatom−heteroatom bond forming approach,[7−9] although such a strategy may comply well with the atom economy principle and provides the most straightforward access to the desired heterocyclic compounds. In particular, the formation of heterocycles through the I(III)-mediated N−N bond forming reactions was very limited, as shown in Scheme 1.[9] In 1996, Kotali et al. reported a PIDA-mediated oxidative cyclization of *o*-aminoaryl ketone acylhydrazones to afford aminoindazoles, in which the two hydrogens on the aryl amine moiety were dehydrogenatively removed.[9a] Hirota and co-workers applied the same oxidative cyclization strategy to the construction of pyrazolo[3,4-*d*]pyrimidines.[7a] In 2006, Tellitu, Domínguez, and their co-workers described the construction of N,N′-disubstituted indazolones from methyl anthranilates through PIFA-mediated N−N bond formation.[9b,c] During the process, the two hydrogens on the two respective N atoms were oxidatively removed. Subsequently, Malamidou-Xenikaki applied a similar strategy to the synthesis of denocarboxamides.[9d] Dong et al. also reported a synthesis of spiro-fused pyrrazolin-5-one *N*-oxides from 1-carbamoyl-1-oximylcycloalkanes employing a PIFA-mediated N−N bond forming approach.[9e] The hydrogen on the oxime moiety and the hydrogen on the amide moiety can be considered to be oxidatively eliminated during the transformation. Continuing our research into constructing heterocyclic compounds through hypervalent iodine-mediated reactions, we have established and herein disclose a convenient assemblage of the biologically important 1,2,4-triazolo[1,5-*a*]pyridine skeleton[10,11] through PIFA-mediated, intramolecular oxidative N−N bond coupling in *N*-(pyridin-2-yl)benzimidamide compounds, many advantageous features of which identify with those of "click chemistry".[12,13]

Scheme 1. Previously Reported Construction of Heterocycles through I(III)-Mediated N−N Bond Formation



Today, many synthetic routes to 1,2,4-triazolo[1,5-*a*]-pyridines have been explored.[11] Oxidative cyclization of amidine derivatives with various oxidants, such as NaClO/base,[11a] Pb(OAc)$_4$,[11b] or MnO$_2$,[11h] was the most straightforward strategy. However, some disadvantages of the existing methods, including low yields and scope limitations, encouraged us to develop methods that proceed at ambient

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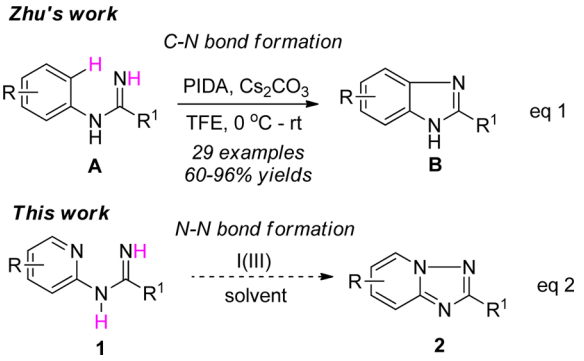
temperature efficiently devoid of transition metal catalysts or metal-containing oxidants.

In 2012, Zhu et al. reported that the *N*-aryl amidines **A** could smoothly undergo direct oxidative C−N bond formation to afford 2-substituted benzimidazoles **B** in satisfactory to high yields (Scheme 2, eq 1).[3b] Inspired by their work as well as some previously reported I(III)-mediated N−N bond forming reactions, we envisaged that the analogous *N*-(pyridin-2-yl)amidines **1** would probably undergo the oxidative N−N bond formation in a similar manner to give 1,2,4-triazolo[1,5-*a*]pyridine product **2**.

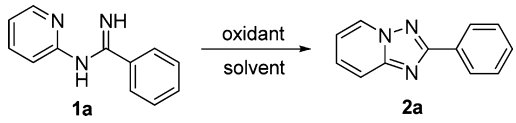
Scheme 2. Proposed Route to Access 1,2,4-Triazolo[1,5-*a*]pyridines Based on the Previously Reported I(III)-Mediated Synthesis of 2-Substituted Benzimidazoles (eq 2), Except That the Two Hydrogens Oxidatively Removed in This Case Are from the Imine and Amine Moieties



N-(Pyridin-2-yl)benzimidamide (**1a**),[11i,14] easily prepared from the corresponding 2-aminopyridine and benzonitrile, was used as a model substrate to test the feasibility of the proposed oxidative cyclization reaction. The initial reaction mixture of **1a** was treated with $PhI(OAc)_2$ in dichloromethane (DCM) at ambient temperature. This set of conditions indeed afforded the desired product in 40% yield with full consumption of the substrate within 30 min (Table 1, entry 1). The other two hypervalent iodine(III) reagents, i.e., $PhI(OCOCF_3)_2$ and PhIO, were also screened in DCM, among which $PhI(OCOCF_3)_2$ provided the best yield (Table 1, entries 1−3). To obtain the desired product (**2a**) in a more desirable yield, various solvents were tested in the follow-up solvent screening experiments (Table 1, entries 3−11). Results showed that the reaction using hexafluoroisopropanol (HFIP)[15] as a solvent afforded the best yield (96%), though other solvents, i.e., 1,2-dichloroethane (DCE), MeCN, DMF, and trifluoroethanol (TFE), also provided moderate to good yields of >70%. Further study indicated that the reaction performance was not improved by varying the dosage of the oxidant (Table 1, entries 11−13), while a higher reaction concentration (0.20 mol/L) proved to have a negative impact on the yield (Table 1, entries 11, 14, and 15).

With the optimized reaction conditions established (Table 1, entry 11), the scope of the newly discovered oxidative N−N bond formation reaction was investigated (Table 2). Because **2a** was afforded in an excellent yield from its corresponding substrate **1a**, the effect of substituents on the pyridine ring (R^1) was first examined. This heterocyclic ring was found to be tolerant of both electron-rich groups such as methyl (**2b**) and electron-deficient groups such as halogens (**2c−e**). Reactions of halogen-containing substrates provided yields slightly lower than that of the methyl-containing substrate, which was probably due to the relatively low nucleophilicity of the pyridines affected by the halogens (Table 2, entries 1−4). The substitution effect of the R^2 group was then examined. It was found that when R^2 is an aryl group, bearing either electron-withdrawing substituents such as halogens and trifluoromethyl group (Table 2, enties 5−11) or electron-donating substituents such as methyl and methoxy groups (Table 2, entries 13−15), it is well tolerated under identical conditions. The reaction was also shown to be compatible with multiple substituents on the aromatic ring (Table 2, entry 10). Reaction of 4-methyl-substituted substrate **1p** showed an obvious decrease in the isolated product yield.[16] When a substrate bearing a nitro group at the *para* position of the phenyl group was subjected to the optimal reaction conditions, although substrate **1m** was completely consumed, the reaction resulted in the formation of some inseparable, polar products, with no detection of the desired cyclized product (Table 2, entry 12). It is worth noting that heterocyclic substituents such as pyridinyl and thienyl ring (**2q** and **2r**, respectively) could also well survive the process (Table 2, entries 16 and 17, respectively). To our delight, the method could also be applied to substrates with R^2 being an alkyl group (Table 2, entries 18−20), which greatly expands the scope of our method. For example, substrate **1s** bearing a benzyl group proceeded smoothly to give cyclized product **2s** in 91% yield (Table 2, entry 18). It was gratifying to know the presence of an alkenyl group in the substrate would not influence the outcome of the cyclization process (Table 2, entry 19).

Table 1. Optimization of Reaction Conditions[a]



entry	oxidant (equiv)	solvent	conc (M)	yield (%)[b]
1	PIDA (1.2)	DCM	0.1	40
2[c]	PhIO (1.2)	DCM	0.1	36
3	PIFA (1.2)	DCM	0.1	68
4	PIFA (1.2)	DCE	0.1	78
5	PIFA (1.2)	MeCN	0.1	84
6	PIFA (1.2)	EtOAc	0.1	70
7	PIFA (1.2)	toluene	0.1	60
8	PIFA (1.2)	DMF	0.1	87
9	PIFA (1.2)	MeOH	0.1	67
10	PIFA (1.2)	TFE	0.1	88
11	PIFA (1.2)	HFIP	0.1	96
12	PIFA (1.0)	HFIP	0.1	85
13	PIFA (1.5)	HFIP	0.1	96
14	PIFA (1.2)	HFIP	0.05	96
15	PIFA (1.2)	HFIP	0.2	90

[a]Reaction conditions: **1a** (0.5 mmol) and oxidant in solvent at ambient temperature for 10 min unless otherwise stated. [b]Isolated yields. [c]Reaction mixture heated under reflux for 3 h.

On the basis of the obtained results, a plausible mechanism for the cyclization process of 1,2,4-triazolo[1,5-*a*]pyridines **2** was suggested. As described in Scheme 3, the entire reaction consists of three simple steps, with intermediate **I** being first formed from the reaction of *N*-(pyridin-2-yl)-imidamide **1** and PIFA by losing one molecule of TFA and then direct intramolecular nucleophilic attack of the N atom of the pyridine ring to generate ammonium ion **II**,[17] which affords the

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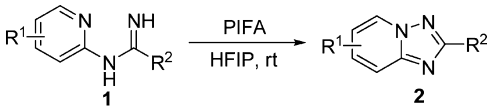
Table 2. Oxidative Cyclization of *N*-(Substituted pyridin-2-yl)imidamides to 1,2,4-Triazolo[1,5-*a*]pyridines[a]



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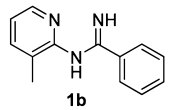
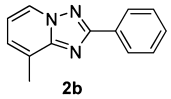
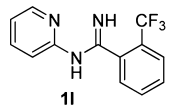
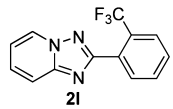
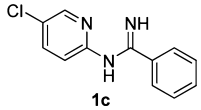
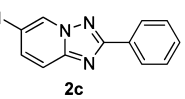
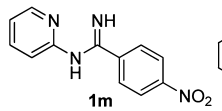
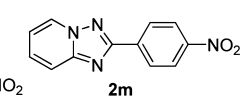
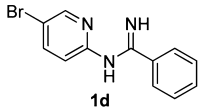
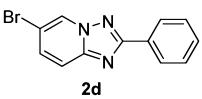
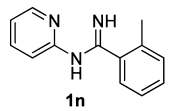
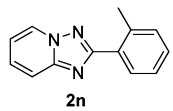
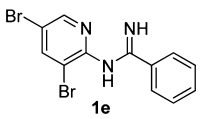
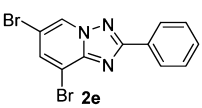
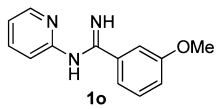
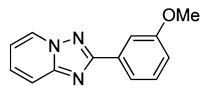
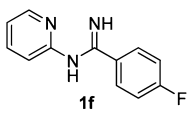
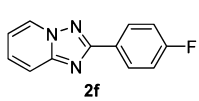
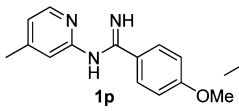
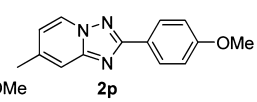
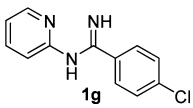
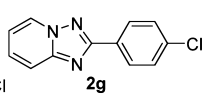
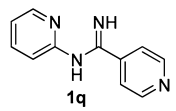
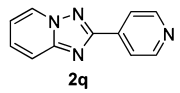
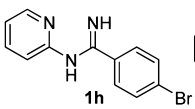
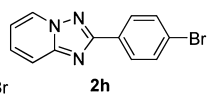
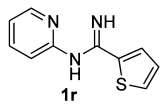
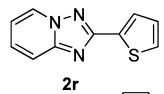
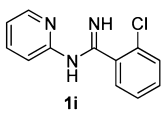
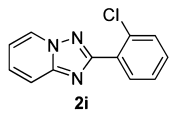
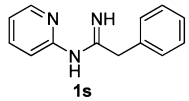
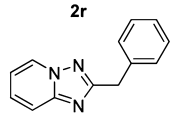
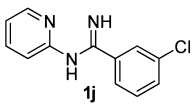
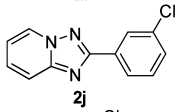
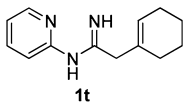
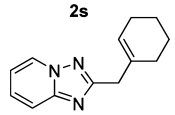
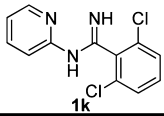
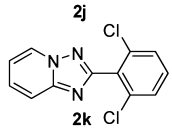
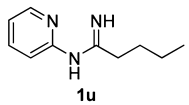
1	 1b	 2b	93	11	 1l	 2l	89
2	 1c	 2c	86	12	 1m	 2m	0
3	 1d	 2d	87	13	 1n	 2n	91
4	 1e	 2e	89	14	 1o	 2o	86
5	 1f	 2f	93	15	 1p	 2p	74
6	 1g	 2g	90	16	 1q	 2q	94
7	 1h	 2h	91	17	 1r	 2r	96
8	 1i	 2i	91	18	 1s	 2s	91
9	 1j	 2j	94	19	 1t	 2t	88
10	 1k	 2k	90	20	 1u	2u	86

[a]General condition: **1** (1.0 mmol) and PIFA (1.2 mmol) in HFIP (10 mL) stirred at room temperature for 10 min unless otherwise stated. [b]Isolated yield.

title compound **2** after rearomatization through the abstraction of a proton. The mechanism offers straightforward explanations to two of our observations: (a) why a strongly electron-withdrawing R^2, i.e., NO_2, impeded the reaction and (b) why electron-donating R^1, i.e., Me, facilitated the reaction. The answers are the greatly reduced nucleophilicity of **1**, which led to the failure of the first step, and the increased nucelophilicity of **I** in facilitating the second step.

In summary, a convenient and efficient synthesis of 1,2,4-triazolo[1,5-*a*]pyridines under mild conditions has been realized from a variety of *N*-(substituted pyridin-2-yl)-imidamides through intramolecular oxidative N−N bond formation. The method signifies a new PIFA-mediated N−N bond formation pattern, and the attractive features such as the wide substrate scope, mild reaction conditions, and high reaction yields qualify its click chemistry efficiency.

EXPERIMENTAL SECTION

General Information. All reactions were conducted at room temperature without precaution of air and mixtures stirred magnetically. ^1H and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer at 25 °C. Chemical shift values are given in parts per million and referred to the internal standard, TMS (tetramethylsilane). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; td, triplet of doublets; br s, broad singlet. The coupling constants (*J*) are reported in hertz. High-resolution mass spectrometry (HRMS) was conducted

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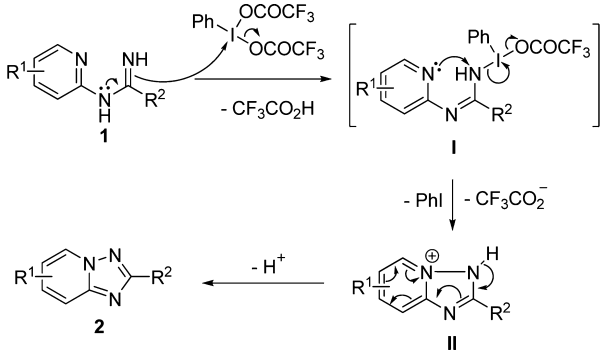
Scheme 3. Proposed Mechanism for the Construction of 1,2,4-Triazolo[1,5-*a*]pyridines



on a Q-TOF micro spectrometer. Elemental (C, H, N) analysis was conducted using a Vario Micro cube analyzer. Melting points were determined with a national micromelting point apparatus without corrections. Reagents and solvents were purchased as reagent grade and were used without further purification. Flash column chromatography was performed over silica gel 200−300 mesh, and the eluent was a mixture of ethyl acetate and petroleum ether.

General Procedure for the Preparation of *N*-Substituted Amidines 1. *General Procedure A.*[11i] To a stirred solution of substituted 2-aminopyridine (10 mmol) in DMF (5.0 mL) was added NaH (60% dispersion in mineral oil, 12 mmol) at 0 °C, and the mixture was stirred at the same temperature for 30 min. Substituted benzonitrile (12 mmol) was then added to the reaction mixture and the mixture stirred at room temperature until TLC indicated the total consumption of the substituted 2-aminopyridine. The reaction was quenched by the addition of 5% aqueous $NaHCO_3$ (10 mL) and the mixture extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. The solvent was then evaporated, and the residue was purified by column chromatography using a mixture of petroleum ether and EtOAc as the eluent to afford the desired *N*-substituted amidine **1**.

General Procedure B.[14] Substituted benzonitrile (10 mmol) was taken in a dry round-bottom flask, and to this was added a substituted 2-aminopyridine (10 mmol). The flask was heated, after fitting a dry condenser along with a guard tube, in an oil bath over a temperature range of 80−90 °C while its contents were being stirred. After 30 min, $SnCl_4$ (1.4 mL, 12 mmol) was added to the flask. After that addition, the temperature was increased to 100−110 °C, and the contents of the flask were heated for 3−4 h. The mixture was cooled to room temperature, and the solid, thus formed, was crushed into powder and dissolved in hot water. The aqueous suspension was made alkaline with 10% NaOH and extracted with CH_2Cl_2 (3 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4. After the solvent had been evaporated under reduced pressure, crude amidine was obtained and purified by column chromatography using a mixture of petroleum ether and EtOAc as the eluent to afford the desired *N*-substituted amidine **1**.

Following procedure A, known N-substituted amidines **1a**,[11i] **1d**,[14] **1g** and **1h**,[14] and **1j**[14] were prepared in 65, 42, 70, 68, and 84% yields, respectively. The properties and ^{1}H NMR data of **1a**, **1d**, **1g**, **1h**, and **1j** were consistent with those in the literature. Novel N-substituted amidines **1b**, **1c**, **1e**, **1f**, **1i**, and **1k**−**u** thus obtained were characterized as follows.

*N-(3-Methylpyridin-2-yl)benzimidamide (**1b**).*[11b] Following general procedure A, **1b** was isolated as a yellow solid: yield 1.20 g, 57%; mp 69−70 °C (lit.[11b] 68−69 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.85 (br s, 1H), 8.18 (d, 1H, J = 4.8), 7.97 (d, 2H, J = 7.2), 7.48 (d, 1H, J = 7.2), 7.46−7.42 (m, 3H), 6.84 (dd, 1H, J = 7.2, 4.8), 6.18 (br s, 1H), 2.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 157.3, 143.6, 138.0, 137.5, 130.6, 130.4, 128.5, 127.1, 117.9, 18.6; HRMS (ESI) calcd for $C_{13}H_{14}N_3^+$ [M + H$^+$] 212.1182, found 212.1185.

*N-(5-Chloropyridin-2-yl)benzimidamide (**1c**).* Following general procedure A, **1c** was isolated as a light pink solid: yield 1.04 g, 45%; mp 157−158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.25 (br s, 1H), 8.27 (d, 1H, J = 3.0), 7.90−7.89 (m, 2H), 7.59 (dd, 1H, J = 8.4, 3.0), 7.48−7.43 (m, 3H), 7.21 (d, 1H, J = 9.0), 5.98 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 159.1, 144.4, 137.4, 137.2, 130.8, 128.7, 126.9, 125.1, 123.5; HRMS (ESI) calcd for $C_{12}H_{11}{}^{35}ClN_3^+$ [M + H$^+$] 232.0636, found 232.0635. Anal. Calcd for $C_{12}H_{10}ClN_3$: C, 62.21; H, 4.35; N, 18.14. Found: C, 62.49; H, 4.29; N, 17.99.

*N-(3,5-Dibromopyridin-2-yl)benzimidamide (**1e**).* Following general procedure A, **1e** was isolated as a white solid: yield 1.56 g, 44%; mp 128−129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (br s, 1H), 8.28 (d, 1H, J = 2.4), 8.04 (d, 1H, J = 2.4), 8.02 (d, 2H, J = 7.8), 7.50 (t, 1H, J = 7.2), 7.45 (t, 2H, J = 7.2), 6.14 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 157.9, 145.6, 143.0, 136.4, 131.3, 128.7, 127.3, 119.1, 112.0; HRMS (ESI) calcd for $C_{12}H_{10}{}^{79}Br_2N_3^+$ [M + H$^+$] 353.9236, found 353.9235. Anal. Calcd for $C_{12}H_9Br_2N_3$: C, 40.60; H, 2.56; N, 11.84. Found: C, 40.89; H, 2.50; N, 11.52.

*4-Fluoro-N-(pyridin-2-yl)benzimidamide (**1f**).* Following general procedure A, **1f** was isolated as a light yellow solid: yield 1.14 g, 53%; mp 163−164 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.52 (br s, 1H), 8.33 (dd, 1H, J = 4.8, 1.8), 7.92 (dd, 2H, J = 8.4, 6.0), 7.65 (td, 1H, J = 7.5, 1.8), 7.26 (d, 1H, J = 7.8), 7.13 (t, 2H, J = 8.7), 6.94 (t, 1H, J = 6.0), 5.97 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.3 (d, J = 247.5), 162.8, 158.0, 146.0, 137.6, 133.6, 129.1 (d, J = 7.5), 122.5, 118.0, 115.6 (d, J = 21.0); HRMS (ESI) calcd for $C_{12}H_{11}FN_3^+$ [M + H$^+$] 216.0932, found 216.0932. Anal. Calcd for $C_{12}H_{10}FN_3$: C, 66.97; H, 4.68; N, 19.52. Found: C, 67.21; H, 4.65; N, 19.17.

*2-Chloro-N-(pyridin-2-yl)benzimidamide (**1i**).* Following general procedure A, **1i** was isolated as a white solid: yield 1.64 g, 71%; mp 104−105 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.72 (br s, 1H), 8.34 (d, 1H, J = 3.6), 7.69−7.67 (m, 1H), 7.64 (td, 1H, J = 7.8, 1.8), 7.43−7.41 (m, 1H), 7.34−7.32 (m, 2H), 7.23 (d, 1H, J = 7.2), 6.95 (t, 1H, J = 6.3), 5.90 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 158.5, 146.0, 137.6, 137.2, 131.4, 130.5, 130.5, 130.2, 127.1, 122.4, 118.2; HRMS (ESI) calcd for $C_{12}H_{11}{}^{35}ClN_3^+$ [M + H$^+$] 232.0636, found 232.0635. Anal. Calcd for $C_{12}H_{10}ClN_3$: C, 62.21; H, 4.35; N, 18.14. Found: C, 62.43; H, 4.39; N, 17.81.

*2,6-Dichloro-N-(pyridin-2-yl)benzimidamide (**1k**).* Following general procedure A, **1k** was isolated as a white solid: yield 1.73 g, 65%; mp 147−148 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.63 (br s, 1H), 8.36−8.35 (m, 1H), 7.65 (t, 1H, J = 7.5), 7.35 (d, 2H, J = 7.8), 7.27−7.22 (m, 2H), 6.97 (t, 1H, J = 6.0), 5.70 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6, 155.9, 146.1, 137.7, 136.4, 133.6, 130.3, 128.3, 122.4, 118.6; HRMS (ESI) calcd for $C_{12}H_{10}{}^{35}Cl_2N_3^+$ [M + H$^+$] 266.0246, found 266.0246. Anal. Calcd for $C_{12}H_9Cl_2N_3$: C, 54.16; H, 3.41; N, 15.79. Found: C, 54.41; H, 3.50; N, 15.45.

*N-(Pyridin-2-yl)-2-(trifluoromethyl)benzimidamide (**1l**).* Following general procedure B, **1l** was isolated as a white solid: yield 1.75 g, 66%; mp 139−140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.61 (br s, 1H), 8.33 (d, 1H, J = 3.6), 7.72 (d, 1H, J = 7.8), 7.68 (d, 1H, J = 7.8), 7.64 (td, 1H, J = 7.8, 1.8), 7.60 (t, 1H, J = 7.5), 7.52 (t, 1H, J = 7.8), 7.20 (d, 1H, J = 8.4), 6.95 (t, 1H, J = 6.0), 5.70 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 158.9, 146.0, 137.7, 137.3, 132.1, 130.0, 129.3, 127.7 (q, J = 31.0), 126.5 (q, J = 5.0), 123.9 (q, J = 272.0), 122.3, 118.4; HRMS (ESI) calcd for $C_{13}H_{11}F_3N_3^+$ [M + H$^+$] 266.0900, found 266.0900. Anal. Calcd for $C_{13}H_{10}F_3N_3$: C, 58.87; H, 3.80; N, 15.84. Found: C, 59.04; H, 3.72; N, 15.61.

*4-Nitro-N-(pyridin-2-yl)benzimidamide (**1m**).* Following general procedure B, **1m** was isolated as a yellow solid: yield 1.28 g, 53%; mp 185−186 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.52 (br s, 1H), 8.38−8.37 (m, 1H), 8.31 (d, 2H, J = 9.0), 8.11 (d, 2H, J = 8.4), 7.70 (td, 1H, J = 7.8, 1.8), 7.30 (d, 1H, J = 7.8), 7.01−6.99 (m, 1H), 6.03 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 156.5, 149.1, 146.1, 143.3, 137.8, 128.1, 123.8, 122.9, 118.7; HRMS (ESI) calcd for $C_{12}H_{11}N_4O_2^+$ [M + H$^+$] 243.0877, found 243.0877. Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.65; H, 4.23; N, 22.98.

*2-Methyl-N-(pyridin-2-yl)benzimidamide (**1n**).* Following general procedure B, **1n** was isolated as a yellow solid: yield: 0.84 g, 40%; mp 98−99 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.58 (br s, 1H), 8.32 (d, 1H, J = 4.2), 7.62 (t, 1H, J = 7.5), 7.46 (d, 1H, J = 7.2), 7.31−7.28 (m, 1H), 7.24−7.19 (m, 3H), 6.93 (t, 1H, J = 6.0), 5.67 (br s, 1H), 2.50 (s,

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3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 161.2, 146.0, 138.4, 137.6, 135.5, 130.9, 129.2, 127.7, 125.9, 122.2, 118.0, 19.6; HRMS (ESI) calcd for $C_{13}H_{14}N_3^+$ [M + H$^+$] 212.1182, found 212.1182. Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.91; H, 6.20; N, 19.89. Found: C, 74.16; H, 6.09; N, 19.63.

*3-Methoxy-N-(pyridin-2-yl)benzimidamide (**1o**).* Following general procedure B, **1o** was isolated as a white solid: yield 1.32 g, 58%; mp 85−86 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.52 (br s, 1H), 8.33 (dd, 1H, J = 5.1, 1.5), 7.64 (td, 1H, J = 7.8, 1.8), 7.50 (s, 1H), 7.43 (d, 1H, J = 7.8), 7.34 (t, 1H, J = 7.8), 7.28 (d, 1H, J = 7.8), 7.01 (dd, 1H, J = 7.8, 2.4), 6.94−6.92 (m, 1H), 6.01 (br s, 1H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 159.8, 159.0, 146.0, 139.0, 137.5, 129.6, 122.5, 119.0, 117.9, 116.7, 112.4, 55.4; HRMS (ESI) calcd for $C_{13}H_{14}N_3O^+$ [M + H$^+$] 228.1131, found 228.1127. Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; N, 18.49. Found: C, 68.95; H, 5.71; N, 18.20.

*4-Methoxy-N-(4-methylpyridin-2-yl)benzimidamide (**1p**).* Following general procedure B, **1p** was isolated as a white solid: yield 1.23 g, 51%; mp 97−98 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (br s, 1H), 8.18 (d, 1H, J = 4.8), 7.87 (d, 2H, J = 9.0), 7.08 (s, 1H), 6.94 (d, 2H, J = 8.4), 6.74 (d, 1H, J = 6.6), 6.09 (br s, 1H), 3.84 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 161.5, 158.5, 148.4, 145.7, 129.9, 128.5, 122.6, 119.0, 113.8, 55.4, 21.0; HRMS (ESI) calcd for $C_{14}H_{16}N_3O^+$ [M + H$^+$] 242.1288, found 242.1283. Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.41. Found: C, 69.80; H, 6.19; N, 17.09.

*N-(Pyridin-2-yl)isonicotinimidamide (**1q**).* Following general procedure A, **1q** was isolated as a light yellow solid: yield 1.50 g, 76%; mp 164−165 °C; ^{1}H NMR (600 MHz, d_6-DMSO) δ 10.25 (br s, 1H), 8.74 (dd, 2H, J = 4.8, 1.5), 8.44 (br s, 1H), 8.39 (dd, 1H, J = 5.1, 1.5), 7.99 (d, 2H, J = 5.4), 7.76 (td, 1H, J = 7.8, 1.8), 7.19 (d, 1H, J = 7.8), 7.06−7.04 (m, 1H); ^{13}C NMR (150 MHz, d_6-DMSO) δ 162.3, 155.8, 149.9, 146.3, 143.6, 137.8, 121.9, 121.3, 118.0; HRMS (ESI) calcd for $C_{11}H_{11}N_4^+$ [M + H$^+$] 199.0978, found 199.0978. Anal. Calcd for $C_{11}H_{10}N_4$: C, 66.65; H, 5.08; N, 28.26. Found: C, 66.77; H, 5.14; N, 27.90.

*N-(Pyridin-2-yl)thiophene-2-carboximidamide (**1r**).* Following general procedure A, **1r** was isolated as a light yellow solid: yield 1.50 g, 74%; mp 133−134 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (dd, 1H, J = 5.1, 1.5), 7.62 (td, 1H, J = 7.8, 1.8), 7.47 (d, 1H, J = 3.6), 7.43 (dd, 1H, J = 5.4, 0.6), 7.23 (d, 1H, J = 7.8), 7.07 (dd, 1H, J = 4.8, 3.6), 6.92−6.90 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6, 153.5, 146.1, 142.2, 137.5, 129.5, 127.5, 126.0, 122.4, 117.9; HRMS (ESI) calcd for $C_{10}H_{10}N_3S^+$ [M + H$^+$] 204.0584, found 204.0589. Anal. Calcd for $C_{10}H_9N_3S$: C, 59.09; H, 4.46; N, 20.67. Found: C, 59.28; H, 4.40; N, 20.43.

*2-Phenyl-N-(pyridin-2-yl)acetimidamide (**1s**).* Following general procedure B, **1s** was isolated as a light yellow solid: yield 1.46 g, 69%; mp 90−91 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.34 (br s, 1H), 8.24 (dd, 1H, J = 5.1, 1.5), 7.63−7.60 (m, 1H), 7.37−7.35 (m, 4H), 7.30−7.28 (m, 1H), 7.16 (d, 1H, J = 7.8), 6.90−6.87 (m, 1H), 5.34 (br s, 1H), 3.77 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 162.1, 145.9, 137.5, 136.1, 129.5, 128.9, 127.3, 121.5, 117.7, 45.0; HRMS (ESI) calcd for $C_{13}H_{14}N_3^+$ [M + H$^+$] 212.1177, found 212.1180. Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.91; H, 6.20; N, 19.89. Found: C, 74.10; H, 6.28; N, 19.58.

*2-Cyclohexenyl-N-(pyridin-2-yl)acetimidamide (**1t**).* Following general procedure B, **1t** was isolated as a light brown liquid: yield 1.18 g, 55%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.21 (br s, 1H), 8.18−8.18 (m, 1H), 7.52 (t, 1H, J = 7.8), 7.05 (d, 1H, J = 7.2), 6.80 (t, 1H, J = 6.0), 5.73 (br s, 1H), 5.61 (s, 1H), 2.98 (s, 2H), 1.99−1.94 (m, 4H), 1.55−1.49 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 162.0, 145.9, 137.5, 134.1, 126.7, 121.3, 117.6, 47.5, 27.9, 25.4, 22.8, 22.1; HRMS (ESI) calcd for $C_{13}H_{18}N_3^+$ [M + H$^+$] 216.1495, found 216.1495. Anal. Calcd for $C_{13}H_{17}N_3$: C, 72.52; H, 7.96; N, 19.52. Found: C, 72.81; H, 7.89; N, 19.17.

*N-(Pyridin-2-yl)pentanimidamide (**1u**).* Following general procedure B, **1u** was isolated as a yellow liquid: yield 1.02 g, 58%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.20 (br s, 1H), 8.57 (d, 1H, J = 4.2), 7.58 (t, 1H, J = 7.5), 7.11 (d, 1H, J = 7.8), 6.86 (t, 1H, J = 6.0), 5.56 (br s, 1H), 2.34 (t, 2H, J = 7.8), 1.72−1.67 (m, 2H), 1.44−1.40 (m, 2H), 0.94 (t, 3H, J = 7.2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.2, 162.9, 145.9, 137.4, 121.2, 117.4, 38.6, 29.8, 22.5, 13.9; HRMS (ESI) calcd for $C_{10}H_{16}N_3^+$ [M + H$^+$] 178.1339, found 178.1339. Anal. Calcd for $C_{10}H_{15}N_3$: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.88; H, 8.48; N, 23.64.

General Procedure for the Preparation of 1,2,4-Triazolo[1,5-*a*]pyridines 2. *General Procedure.* To a stirred solution of *N*-substituted amidine **1** (1.0 mmol) in HFIP (10 mL) was added PIFA (1.2 mmol) at room temperature. The resulting mixture was stirred at the same temperature until TLC indicated the total consumption of the substrate (within 10 min). The reaction was quenched by the addition of 5% aqueous $NaHCO_3$ (50 mL) and the mixture extracted with CH_2Cl_2 (50 mL). The extract was washed with brine and dried over Na_2SO_4. The solvent was then evaporated, and the residue was purified by column chromatography using a mixture of petroleum and EtOAc as the eluent to afford the desired 1,2,4-triazolo[1,5-*a*]pyridine **2**.

Following this general procedure, known 1,2,4-triazolo[1,5-*a*]-pyridines **2a**,[11i] **2f−h**,[11i] **2j**,[11i] and **2o−r**[11i] were prepared in 95, 93, 90, 91, 94, 86, 74, 94, and 96% yields, respectively. The properties and ^{1}H NMR data of **2a**, **2f−h**, **2j**, and **2o−r** were consistent with those in the literature. Novel 1,2,4-triazolo[1,5-*a*]pyridines **2b−e**, **2i**, **2k**, **2l**, **2n**, and **2s−u** thus obtained were characterized as follows.

*2-Phenyl-[1,2,4]triazolo[1,5-a]pyridine (**2a**).*[11i] Following the general procedure, **2a** was isolated as a white solid: yield 185 mg, 95%; mp 138−139 °C (lit.[11b] 138 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, 1H, J = 6.6), 8.30−8.29 (m, 2H), 7.76 (d, 1H, J = 8.4), 7.50−7.45 (m, 4H), 6.9 (td, 1H, J = 6.9, 1.2).

*8-Methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (**2b**).*[11b] Following the general procedure, **2b** was isolated as a white solid: yield 194 mg, 93%; mp 100−101 °C (lit.[11b] 97−98 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, 1H, J = 7.2), 8.30 (d, 2H, J = 7.2), 7.50−7.47 (m, 2H), 7.45−7.43 (m, 1H), 7.21 (d, 1H, J = 6.6), 6.84 (t, 1H, J = 6.9); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 152.2, 131.1, 129.9, 128.7, 128.1, 127.4, 127.0, 125.9, 113.4, 17.0; HRMS (ESI) calcd for $C_{13}H_{12}N_3^+$ [M + H$^+$] 210.1026, found 210.1027.

*6-Chloro-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (**2c**).* Following the general procedure, **2c** was isolated as a white solid: yield 198 mg, 86%; mp 168−169 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.25 (d, 2H, J = 6.6), 7.68 (d, 1H, J = 9.0), 7.49−7.45 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 150.3, 131.0, 130.3, 128.8, 127.3, 126.6, 121.6, 116.4 (one carbon peak was missing because of overlapping); HRMS (ESI) calcd for $C_{12}H_9{}^{35}ClN_3^+$ [M + H$^+$] 230.0480, found 230.0480. Anal. Calcd for $C_{12}H_8ClN_3$: C, 62.76; H, 3.51; N, 18.30. Found: C, 62.85; H, 3.48; N, 18.21.

*6-Bromo-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (**2d**).* Following the general procedure, **2d** was isolated as a white solid: yield 238 mg, 87%; mp 165−166 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, J = 1.2, 1H), 8.27−8.25 (m, 2H), 7.65 (d, 1H, J = 9.0), 7.57 (dd, 1H, J = 9.0, 1.8), 7.51−7.47 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 150.4, 133.1, 130.4, 130.3, 128.8, 127.4, 123.3, 116.8, 107.7; HRMS (ESI) calcd for $C_{12}H_9{}^{79}BrN_3^+$ [M + H$^+$] 273.9974, found 273.9973. Anal. Calcd for $C_{12}H_8BrN_3$: C, 52.58; H, 2.94; N, 15.33. Found: C, 52.70; H, 2.99; N, 15.22.

*6,8-Dibromo-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (**2e**).* Following the general procedure, **2e** was isolated as a white solid: yield 314 mg, 89%; mp 163−165 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, 1H, J = 1.2), 8.28−8.27 (m, 2H), 7.80 (d, 1H, J = 1.2), 7.49−7.47 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 149.7, 134.9. 130.6, 129.8, 128.7, 128.0, 127.6, 110.1, 106.8; HRMS (ESI) calcd for $C_{12}H_8{}^{79}Br_2N_3^+$ [M + H$^+$] 351.9079, found 351.9077. Anal. Calcd for $C_{12}H_7Br_2N_3$: C, 40.83; H, 2.00; N, 11.90. Found: C, 40.92; H, 2.08; N, 11.71.

*2-(4-Fluorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (**2f**).*[11i] Following the general procedure, **2f** was isolated as a yellow solid: yield 198 mg, 93%; mp 181−182 °C (lit.[11i] 173−174 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, 1H, J = 6.6), 8.28 (dd, 2H, J = 8.4, 5.4), 7.75 (d, 1H, J = 9.0), 7.51 (t, 1H, J = 7.8), 7.18 (t, 2H, J = 8.7), 7.01 (t, 1H, J = 6.6).

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*2-(4-Chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (**2g**).*[11i] Following the general procedure, **2g** was isolated as a white solid: yield 206 mg, 90%; mp 225−226 °C (lit.[11i] 220−221 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, 1H, J = 6.6), 8.23 (d, 2H, J = 8.4), 7.75 (d, 1H, J = 9.0), 7.52 (t, 1H, J = 7.8), 7.47 (d, 2H, J = 7.8), 7.02 (t, 1H, J = 6.9).

*2-(4-Bromophenyl)-[1,2,4]triazolo[1,5-a]pyridine (**2h**).*[11i] Following the general procedure, **2h** was isolated as a white solid: yield 249 mg, 91%; mp 234−235 °C (lit.[11i] 229−230 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, 1H, J = 7.2), 8.16 (d, 2H, J = 8.4), 7.76 (d, 1H, J = 9.0), 7.63 (d, 2H, J = 8.4), 7.53 (t, 1H, J = 7.5), 7.03 (t, 1H, J = 6.6).

*2-(2-Chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (**2i**).* Following the general procedure, **2i** was isolated as a white solid: yield 209 mg, 91%; mp 122−123 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, 1H, J = 7.2), 8.02−8.01 (m, 1H), 7.82 (d, 1H, J = 9.0), 7.56−7.53 (m, 2H), 7.41−7.38 (m, 2H), 7.05 (td, 1H, J = 6.6, 1.2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 151.0, 133.2, 132.2, 130.8, 130.7, 130.0, 129.7, 128.5, 126.8, 116.7, 113.9; HRMS (ESI) calcd for $C_{12}H_8{}^{35}ClN_3Na^+$ [M + Na^+] 252.0299, found 252.0298. Anal. Calcd for $C_{12}H_8ClN_3$: C, 62.76; H, 3.51; N, 18.30. Found: C, 62.89; H, 3.45; N, 18.13.

*2-(3-Chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (**2j**).*[11i] Following the general procedure, **2j** was isolated as a white solid: yield 198 mg, 86%; mp 182−184 °C (lit.[11i] 177−178 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, 1H, J = 6.6), 8.29 (s, 1H), 8.17−8.16 (m, 1H), 7.75 (d, 1H, J = 9.0), 7.51 (t, 1H, J = 8.1), 7.43−7.40 (m, 2H), 7.01 (t, 1H, J = 6.9).

*2-(2,6-Dichlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (**2k**).* Following the general procedure, **2k** was isolated as a white solid: yield 238 mg, 90%; mp 109−110 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, 1H, J = 6.6), 7.92 (d, 1H, J = 9.0), 7.63 (t, 1H, J = 7.8), 7.45 (d, 2H, J = 7.8), 7.37 (t, 1H, J = 8.1), 7.14 (t, 1H, J = 6.9); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 150.7, 136.0, 131.3, 130.4, 130.1, 128.7, 128.1, 116.8, 114.6; HRMS (ESI) calcd for $C_{12}H_8{}^{35}Cl_2N_3^+$ [M + H^+] 264.0090, found 264.0090. Anal. Calcd for $C_{12}H_7Cl_2N_3$: C, 54.57; H, 2.67; N, 15.91. Found: C, 54.70; H, 2.61; N, 15.74.

*2-[2-(Trifluoromethyl)phenyl]-[1,2,4]triazolo[1,5-a]pyridine (**2l**).* Following the general procedure, **2l** was isolated as a light brown solid: yield 234 mg, 89%; mp 81−82 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, 1H, J = 7.2), 7.90 (d, 1H, J = 7.8), 7.85 (d, 1H, J = 7.8), 7.81 (d, 1H, J = 9.0), 7.66 (t, 1H, J = 7.2), 7.60 (t, 1H, J = 7.5), 7.57−7.54 (m, 1H), 7.06 (td, 1H, J = 6.9, 1.2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 151.1, 132.4, 131.6, 130.4, 129.7, 129.6, 129.3 (q, J = 31.5), 128.5, 126.7 (q, J = 5.0), 123.8 (q, J = 272.0), 116.8, 114.0; HRMS (ESI) calcd for $C_{13}H_9F_3N_3^+$ [M + H^+] 264.0743, found 264.0746. Anal. Calcd for $C_{13}H_8F_3N_3$: C, 59.32; H, 3.06; N, 15.96. Found: C, 59.39; H, 3.11; N, 15.77.

*2-o-Tolyl-[1,2,4]triazolo[1,5-a]pyridine (**2n**).* Following the general procedure, **2n** was isolated as a white solid: yield 190 mg, 91%; mp 95−96 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, 1H, J = 6.6), 8.07 (d, 1H, J = 7.8), 7.77 (d, 1H, J = 9.0), 7.51−7.48 (m, 1H), 7.36−7.30 (m, 3H), 6.99 (td, 1H, J = 6.9, 1.2), 2.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.2, 150.9, 137.8, 131.3, 130.3, 130.2, 129.5, 129.3, 128.3, 125.9, 116.5, 113.4, 21.7; HRMS (ESI) calcd for $C_{13}H_{12}N_3^+$ [M + H^+] 210.1026, found 210.1031. Anal. Calcd for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.75; H, 5.23; N, 19.90.

*2-(3-Methoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (**2o**).*[11i] Following the general procedure, **2o** was isolated as a white solid: yield 194 mg, 86%; mp 106−108 °C (lit.[11i] 106−108 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, 1H, J = 6.6), 7.90 (d, 1H, J = 7.8), 7.84−7.84 (m, 1H), 7.77 (d, 1H, J = 9.0), 7.54−7.51 (m, 1H), 7.41 (t, 1H, J = 8.1), 7.04−7.01 (m, 2H), 3.93 (s, 3H).

*2-(4-Methoxyphenyl)-7-methyl-[1,2,4]triazolo[1,5-a]pyridine (**2p**).*[11i] Following the general procedure, **2p** was isolated as a white solid: yield 177 mg, 74%; mp 166−167 °C (lit.[11i] 165−166 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, 1H, J = 7.2), 8.20 (d, 2H, J = 8.4), 7.47 (s, 1H), 7.01 (d, 2H, J = 9.0), 6.78 (dd, 1H, J = 7.2, 1.5), 3.87 (s, 3H), 2.47 (s, 3H).

*2-(Pyridin-4-yl)-[1,2,4]triazolo[1,5-a]pyridine (**2q**).*[11i] Following the general procedure, **2q** was isolated as a yellow solid: yield 184 mg, 94%; mp 194−195 °C (lit.[1] 190−192 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, 2H, J = 5.4), 8.64 (d, 1H, J = 7.2), 8.16 (d, 2H, J = 6.6), 7.81 (d, 1H, J = 9.0), 7.58 (t, 1H, J = 7.8), 7.09 (t, 1H, J = 6.9).

*2-(Thiophen-2-yl)-[1,2,4]triazolo[1,5-a]pyridine (**2r**).*[11i] Following the general procedure, **2r** was isolated as a yellow solid: yield 193 mg, 96%; mp 168−169 °C (lit.[18] 165 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, 1H, J = 7.2), 7.90 (dd, 1H, J = 3.6, 1.2), 7.74 (d, 1H, J = 9.0), 7.53−7.50 (m, 1H), 7.46 (dd, 1H, J = 5.1, 4.2), 7.17 (dd, 1H, J = 4.8, 3.6), 7.01 (td, 1H, J = 6.6, 1.2).

*2-Benzyl-[1,2,4]triazolo[1,5-a]pyridine (**2s**).* Following the general procedure, **2s** was isolated as a yellow solid: yield 190 mg, 91%; mp 80−81 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, 1H, J = 6.6), 7.66 (d, 1H, J = 8.4), 7.45 (t, 1H, J = 7.8), 7.41 (d, 2H, J = 7.2), 7.31 (t, 2H, J = 7.8), 7.22 (t, 1H, J = 7.5), 6.94 (t, 1H, J = 6.9), 4.27 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 151.3, 137.7, 129.4, 129.0, 128.6, 128.2, 126.7, 116.2, 113.3, 35.4; HRMS (ESI) calcd for $C_{13}H_{12}N_3^+$ [M + H^+] 210.1026, found 210.1026. Anal. Calcd for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.75; H, 5.37; N, 19.97.

*2-(Cyclohexenylmethyl)-[1,2,4]triazolo[1,5-a]pyridine (**2t**).* Following the general procedure, **2t** was isolated as a light yellow liquid: yield 187 mg, 88%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, 1H, J = 6.6), 7.68 (d, 1H, J = 9.0), 7.46 (t, 1H, J = 8.1), 6.96 (t, 1H, J = 6.9), 5.63 (s, 1H), 3.58 (s, 2H), 2.04−2.03 (m, 4H), 1.65−1.61 (m, 2H), 1.58−1.54 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 151.2, 134.3, 129.2, 128.1, 124.0, 116.1, 113.1, 37.7, 28.2, 25.2, 22.7, 22.1; HRMS (ESI) calcd for $C_{13}H_{16}N_3^+$ [M + H^+] 214.1339, found 214.1339. Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.56; H, 7.14; N, 19.48.

*2-Butyl-[1,2,4]triazolo[1,5-a]pyridine (**2u**).* Following the general procedure, **2u** was isolated as a yellow liquid: yield 150 mg, 86%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, 1H, J = 6.6), 7.56 (d, 1H, J = 9.0), 7.35 (t, 1H, J = 7.8), 6.84 (t, 1H, J = 6.9), 2.84 (t, 2H, J = 7.8), 1.79−1.74 (m, 2H), 1.39−1.33 (m, 2H), 0.87 (t, 3H, J = 7.5); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 151.1, 129.1, 127.9, 115.8, 112.9, 30.4, 28.4, 22.4, 13.7; HRMS (ESI) calcd for $C_{10}H_{14}N_3^+$ [M + H^+] 176.1182, found 176.1182. Anal. Calcd for $C_{10}H_{13}N_3$: C, 68.15; H, 8.01; N, 23.84. Found: C, 68.23; H, 8.06; N, 23.64.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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