Synthesis R. Adam et al. Paper

Synthesis of Novel Polyazinyl-Substituted Triazolopyridines from [1,2,3]Triazolo[1,5-*a*]pyridines

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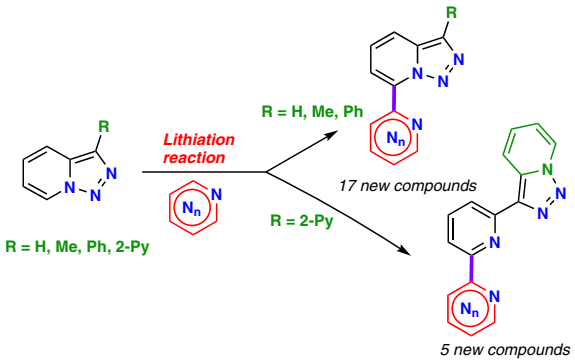

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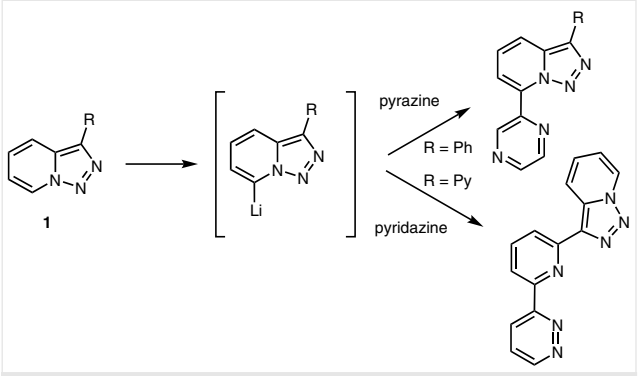
Abstract A series of 7-azinyl-substituted triazolopyridines and 3-(6-azinyl-substituted 2-pyridyl)triazolopyridines were synthesized by addition of the corresponding 3-substituted 7-lithiotriazolopyridine to pyrimidine, pyrazine, pyridazine, and 1,3,5-triazine respectively, followed by hydrolysis and oxidation.

Key words triazolopyridines, diazines, triazines, lithiation reactions, polynitrogenated ligands

Nitrogenated compounds containing two or three azines in their structure are highly relevant scaffolds in different fields.[1] The location of nitrogen atoms in the azide determines different applications for these compounds. For example 2,2′-bipyridine has interesting properties in coordination chemistry or as a catalyst,[2] whereas 4,4′-bipyridine is also applied in photochemistry.[3] Another relevant example is terpyridine with applications in a large variety of domains.[4]

In recent years, our research has focused on the chemistry and potential applications of [1,2,3]triazolo[1,5-*a*]pyridines and their derivatives.[5] 1,2,3-Triazole moieties are considered privileged scaffolds in medicinal chemistry,[6,7] as these structures are present in molecules described to have antibiotic,[8,9] antineoplastic,[10,11] anti-HIV,[12] or antifungal activities.[13] Furthermore, some molecules containing 1,2,3-triazole structure have been described as antileishmanial agents.[14–17] Recently, we reported the first [1,2,3]triazolo[1,5-*a*]pyridine derivatives with leishmanicidal activity.[18] On the other hand, triazolopyridines and derivatives are also very good ligands in supramolecular chemistry. Hence, several of these molecules have been described as fluorescent sensors and compounds with interesting magnetic properties.[19]

Remarkably [1,2,3]triazolo[1,5-*a*]pyridines **1** give regioselective lithiation in the 7-position,[20] and the corresponding 7-lithiotriazolopyridines can react with different electrophiles. Using this methodology we have recently reported the synthesis of two new triazolopyridines containing diazine rings that are fluorescent tridentate ligands[21] (Scheme 1).



Scheme 1

With the aim of obtaining new triazolopyridine derivatives, potentially active against leishmaniasis, and/or with interesting coordination properties, we have applied the same methodology to the synthesis of 22 novel polyazinyl triazolopyridines. In this study we present the reaction of lithio derivatives of [1,2,3]triazolo[1,5-*a*]pyridines **1** using four different azines as electrophiles.[22]

Bi- or terheterocycles of the azinyl-substituted triazolopyridine-type have been synthesized by nucleophilic addition of 7-lithiotriazolopyridines to azines. The identity and purity of all these new compounds were confirmed by HRMS, ^{1}H and ^{13}C NMR.

The 7-lithio derivatives of triazolopyridines **1a–d** were obtained by regioselective lithiation using *n*BuLi in toluene at –40 °C. Addition of lithium derivatives of **1a–c** to the azines shown in Figure 1 occurs in the most electrophilic position of the azine, i.e. the position *ortho* to nitrogen. These adducts were hydrolyzed and oxidized by aqueous $KMnO_4$ solution and finally afforded azinyl derivatives **2** (Scheme 2).

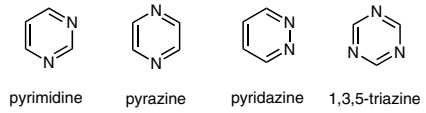
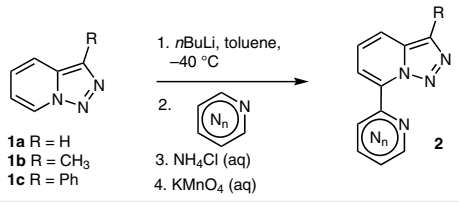


Figure 1 Selected azines



Scheme 2

Compounds **3a–c**, **4a–c**, **5a–c**, and **6a–c** were obtained in low to moderate yields (Figure 2). All products, except **3b**,**c** and **5b**,**c**, precipitated when the crude product was treated with ethyl acetate.

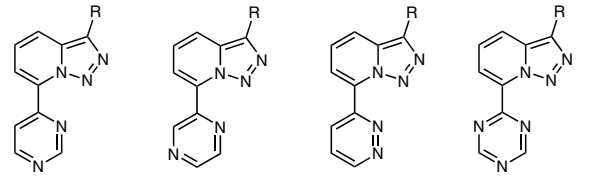


Figure 2 Azinyl-substituted triazolopyridines **3–6**

In the reactions with pyrimidine and pyridazine, except in the reaction of **1c** with pyridazine, traces of secondary products **7a–c** and **8a**,**b** were obtained originating from the attack of the corresponding 7-lithiotriazolopyridine at the 2- and 4-positions of the pyrimidine and pyrazine, respectively. In addition, reaction of 3-methyltriazolopyridine **1b** with pyrimidine also afforded traces of compound **9** (2.5%). When triazolopyridine **1a** was reacted with 1,3,5-triazine, amide **10**, arising from the opening of the triazine ring, was obtained in very low yield (Figure 3).

Ring-chain isomerization is a well-known property of 3-(2-pyridyl)triazolopyridine **1d** (R = 2-pyridyl). This effect is observed when compound **1d** is substituted in the 7-position providing **A**-type structures when electron-donating

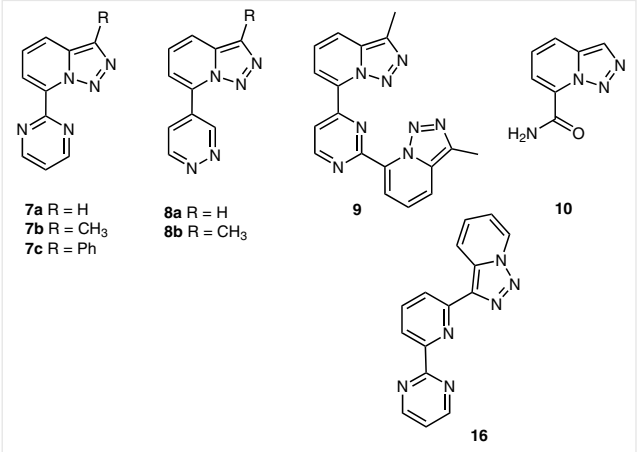
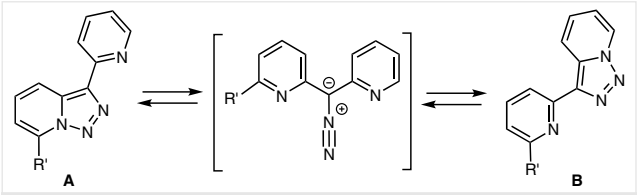


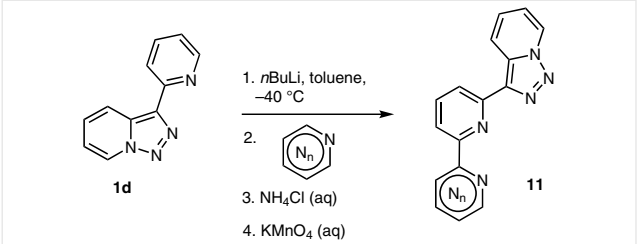
Figure 3 Secondary products

substituents R′ are present and **B**-type structures when electron-withdrawing substituents R′ are present (Scheme 3).[23]



Scheme 3 Tautomeric equilibrium of **1d** derivatives

Hence, when azines were reacted with the 7-lithio derivative of **1d** (Scheme 4), in all cases the ring-chain-ring tautomeric equilibrium resulted in compounds of structure **B**. Thus, 3-(6-azinyl-substituted 2-pyridyl)triazolopyridines **12–15** were obtained, as the electron-withdrawing nature of the azines made the diazo compound intermediate cyclize with the less electron-deficient pyridine (Figure 4). All compounds, except **14**, precipitated pure when the crude product was treated with ethyl acetate. In the reaction with pyrimidine, traces of compound **16** were obtained (Figure 3). It is interesting to note that these compounds have terpyridine-like structures which implies a great capacity to coordinate with metals.[19b]



Scheme 4 3-(6-Azinyl-substituted 2-pyridyl)triazolopyridine synthesis

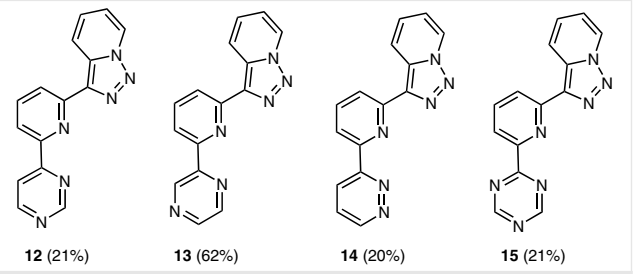


Figure 4 3-(6-Azinyl-substituted 2-pyridyl)triazolopyridine **12–15**

In conclusion, a series of 7-azinyl-triazolopyridines **3a–c**, **4a–c**, **5a–c**, and **6a–c** were synthesized by addition of corresponding 7-lithiotriazolopyridine to pyrimidine, pyrazine, pyridazine, and 1,3,5-triazine, respectively, followed by hydrolysis and oxidation. Furthermore, similar reactions with 7-lithio-3-(2-pyridyl)triazolopyridine gave 3-(6-azinyl-substituted 2-pyridyl)triazolopyridines **12–15**. These new class of polynitrogenated compounds meet the structural requirements for use in coordination chemistry. Moreover, based on previous experience with structurally related derivatives, they are potential leishmanicidal compounds. These promising applications are currently being studied.

Melting points were determined on a Büchi B-545. NMR spectra were recorded on a Bruker AC 300 MHz or 500 MHz in $CDCl_3$ or DMSO-d_6 as solvent; COSY experiments were performed for all compounds. HRMS (EI) determinations were made using a VG Autospec Trio 1000 (Fisons) and Q-TOF spectrometer 5600 system (Applied Biosystems-MDS Sciex with ESI+. IR spectra were recorded using FT-IR ATR. All the lithiation reactions were done under inert atmosphere and dry solvents.[24] All reagents used were from a commercial source (Aldrich).

[1,2,3]Triazolo[1,5-*a*]pyridine (**1a**),[25] 3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (**1b**),[25] 3-phenyl-[1,2,3]triazolo[1,5-*a*]pyridine (**1c**),[26] and 3-(2-pyridyl)-[1,2,3]triazolo[1,5-*a*]pyridine (**1d**)[27] were prepared by literature procedures.

Lithiation of [1,2,3]Triazolo[1,5-*a*]pyridines 1a–d and Reactions with Azines; General Procedure

To a solution of the corresponding [1,2,3]triazolo[1,5-*a*]pyridine **1** in anhydrous toluene at –40 °C under an argon current, a solution of 1.6 *n*BuLi in hexane (1.1 equiv) was added with stirring; a deep red color developed. The mixture was kept at –40 °C for 4 h. The azine (1.1 equiv) in dry toluene solution was added and the mixture was kept in the cold bath at –40 °C for 2 h. The solution was treated with a saturated solution of NH_4Cl followed by aq $KMnO_4$ solution for 30 min at r.t. The mixture was filtered over Celite, the organic and aqueous layers were separated, the aqueous layer was extracted with CH_2Cl_2, the combined organic extracts were dried (Na_2SO_4), and the solution was filtered and concentrated to give the crude product.

7-(Pyrimidin-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (3a) and 7-(Pyrimidin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (7a)

Following the general procedure using **1a** (0.2 g), 1.6 M *n*BuLi (1.4 mL), toluene (85 mL), pyrimidine (0.4 mL), and $KMnO_4/H_2O$ (0.29 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **3a** (40 mg). The filtrate was concentrated and purified by chromatotron (hexane/EtOAc) to give **1a** (14 mg), an additional amount of **3a** (31 mg), and finally **7a** (13 mg).

7-(Pyrimidin-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (3a)

Yellow solid; yield: 71 mg (21%); mp 168–169 °C (EtOAc).

IR: 3121, 1577, 1460, 1396, 1321, 1202, 1001, 838, 791, 732, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.50 (d, *J* = 1.3 Hz, 1 H), 9.35 (dd, *J* = 5.4, 1.4 Hz, 1 H), 9.12 (d, *J* = 5.4 Hz, 1 H), 8.42 (dd, *J* = 7.1, 1.2 Hz, 1 H), 8.37 (s, 1 H), 8.05 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.59 (dd, *J* = 8.7, 7.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9 (CH), 158.8 (CH), 155.6 (C), 135.3 (C), 134.4 (C), 126.7 (CH), 125.5 (CH), 121.5 (CH), 120.3 (CH), 118.3 (CH).

MS: *m*/*z* (%) = 170 (12), 143 (69), 116 (100), 102 (2).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_8N_5$: 198.0774; found: 198.0770.

7-(Pyrimidin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (7a)

Orange oil; yield: 13 mg (4%).

IR: 3072, 2925, 2855, 2357, 2339, 1564, 1409, 1383, 1352, 1205, 1091, 1029, 789, 729, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.03 (d, *J* = 4.9 Hz, 2 H), 8.23 (s, 1 H), 7.89 (dd, *J* = 8.8, 1.25 Hz, 1 H), 7.75 (dd, *J* = 7.0, 1.3 Hz, 1 H), 7.43 (dd, *J* = 4.9, 4.9 Hz, 1 H), 7.39 (dd, *J* = 8.8, 7.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5 (C), 157.8 (CH), 136.5 (C), 126.4 (CH), 125.1 (CH), 120.9 (CH), 120.1 (C), 119.7 (CH), 118.8 (CH).

MS: *m*/*z* (%) = 197 (30), 171 (22), 169 (100), 157 (11), 143 (12), 116 (10), 73 (15).

HRMS: *m*/*z* [M$^+$] calcd for $C_{10}H_7N_5$: 197.0701; found: 197.0689.

3-Methyl-7-(pyrimidin-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (3b), 7,7′-(Pyrimidin-2,4-diyl)bis(3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (9), and 3-Methyl-7-(pyrimidin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (7b)

Following the general procedure using **1b** (0.2 g), 1.6 M *n*BuLi (1.3 mL), toluene (75 mL), pyrimidine (0.4 mL), and $KMnO_4/H_2O$ (0.26 g/50 mL). The crude was purified by chromatotron (hexane/EtOAc) to give **1b** (20 mg), then **3b** (79 mg), and by increasing the polarity **9** (2 mg), and finally **7b** (47 mg).

3-Methyl-7-(pyrimidin-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (3b)

Yellow solid; yield: 79 mg (25%); mp 137–138 °C (EtOAc).

IR: 3314, 3081, 2920, 2853, 1574, 1521, 1463, 1410, 1379, 1335, 1302, 1199, 1121, 1046, 1010, 849, 794, 724, 702, 666 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.33 (d, *J* = 1.4 Hz, 1 H), 9.20 (dd, *J* = 5.4, 1.4 Hz, 1 H), 8.96 (dd, *J* = 5.4, 0.3 Hz, 1 H), 8.23 (dd, *J* = 7.1, 1.3 Hz, 1 H), 7.78 (dd, *J* = 8.7, 1.3 Hz, 1 H), 7.35 (dd, *J* = 8.8, 7.1 Hz, 1 H), 2.67 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.7 (CH), 158.7 (CH), 155.6 (C), 135.4 (C), 133.9 (C), 133.1 (C), 123.8 (CH), 121.3 (CH), 119.8 (CH), 118.1 (CH), 10.5 (CH_3).

MS: *m*/*z* (%) = 212 (12), 184 (100), 167 (8), 157 (17), 142 (8), 131 (55), 104 (10).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{10}N_5$: 212.0931; found: 212.0926.

7,7′-(Pyrimidin-2,4-diyl)bis(3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (9)

White solid; yield: 2 mg (3%); mp 215–216 °C (EtOAc).

IR: 3023, 2357, 2328, 1569, 1468, 1424, 1380, 1293, 1163, 1091, 1050, 988, 853, 799, 758, 707 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.36 (d, *J* = 5.3 Hz, 1 H), 9.21 (d, *J* = 5.3 Hz, 1 H), 8.68 (dd, *J* = 7.1, 1.3 Hz, 1 H), 7.93 (dd, *J* = 6.9, 1.3 Hz, 1 H), 7.84 (dd, *J* = 8.7, 1.3 Hz, 1 H), 7.82 (dd, *J* = 8.8, 1.3 Hz, 1 H), 7.45 (dd, *J* = 8.8, 7.1 Hz, 1 H), 7.37 (dd, *J* = 8.8, 6.9 Hz, 1 H), 2.73 (s, 3 H), 2.72 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7 (CH), 159.6 (C), 156.2 (C), 147.2 (C), 145.6 (C), 140.7 (C), 138.5 (C), 135.1 (C), 133.3 (C), 124.3 (CH), 123.6 (CH), 120.3 (CH), 120.2 (CH), 119.6 (CH), 119.6 (CH), 118.9 (CH), 10.67 (CH_3), 10.63 (CH_3).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}N_8$: 343.1420; found: 343.1429.

3-Methyl-7-(pyrimidin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (7b)

Orange solid; yield: 47 mg (15%); mp 165–166 °C (EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.02 (d, *J* = 4.9 Hz, 2 H), 7.77 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.71 (dd, *J* = 6.9, 1.2 Hz, 1 H), 7.42 (dd, *J* = 4.9, 4.9 Hz, 1 H), 7.32 (dd, *J* = 8.8, 6.9 Hz, 1 H), 2.69 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2 (C), 157.7 (CH), 135.5 (C), 135.0 (C), 133.1 (C), 123.6 (CH), 120.8 (CH), 119.3 (CH), 118.7 (CH), 10.6 (CH_3).

MS: *m*/*z* (%) = 211 (20), 183 (88), 182 (100), 157 (60), 149 (17), 129 (26), 104 (37), 79 (20), 57 (18).

HRMS: *m*/*z* [M$^+$] calcd for $C_{11}H_9N_5$: 211.0858; found: 211.0852.

3-Phenyl-7-(pyrimidin-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (3c) and 3-Phenyl-7-(pyrimidin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (7c)

Following the general procedure using **1c** (0.2 g), 1.6 M *n*BuLi (0.9 mL), toluene (50 mL), pyrimidine (0.2 mL), and $KMnO_4$/H_2O (0.17 g/40 mL). The crude was purified by chromatotron (hexane/EtOAc) to give **1c** (120 mg), **3c** (42 mg), and finally **7c** (11 mg).

3-Phenyl-7-(pyrimidin-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (3c)

Yellow solid; yield: 42 mg (15%); mp 166–167 °C (EtOAc).

IR: 3472, 3406, 3084, 2917, 2848, 1565, 1465, 1385, 1257, 1129, 1071, 1008, 855, 805, 733, 696, 663 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.40 (d, *J* = 1.3 Hz, 1 H), 9.25 (dd, *J* = 5.4, 1.4 Hz, 1 H), 9.02 (dd, *J* = 5.3, 0.3 Hz, 1 H), 8.32 (dd, *J* = 7.1, 1.2 Hz, 1 H), 8.19 (dd, *J* = 8.9, 1.2 Hz, 1 H), 8.00–7.97 (m, 2 H), 7.58–7.41 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9 (CH), 158.8 (CH), 157.8 (C), 155.6 (C), 139.0 (C), 134.6 (C), 131.2 (C), 129.3 (CH), 128.5 (CH), 127.3 (CH), 125.8 (CH), 121.6 (CH), 120.7 (CH), 118.5 (CH).

MS: *m*/*z* (%) = 274 (8), 245 (50), 219 (16), 193 (19), 167 (100).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{12}N_5$: 274.1087; found: 274.1088.

3-Phenyl-7-(pyrimidin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (7c)

Yellow solid; yield: 11 mg (4%); mp 158–159 °C (EtOAc).

IR: 3049, 2933, 2845, 1566, 1411, 1401, 1122, 1011, 784, 735 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.04 (d, *J* = 4.9 Hz, 2 H), 8.15 (dd, *J* = 8.9, 1.2 Hz, 1 H), 8.02–7.95 (m, 2 H), 7.72 (dd, *J* = 6.9, 1.2 Hz, 1 H), 7.58–7.50 (m, 2 H), 7.49–7.40 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2 (C), 157.8 (CH), 138.6 (C), 135.7 (C), 131.9 (C), 131.5 (C), 129.1 (CH), 128.1 (CH), 127.2 (CH), 125.5 (CH), 121.0 (CH), 120.0 (CH), 118.8 (CH).

MS: *m*/*z* (%) = 273 (3), 245 (100), 192 (27), 164 (6), 122 (2), 63 (2).

HRMS: *m*/*z* [M$^+$] calcd for $C_{16}H_{11}N_5$: 273.1014; found: 273.1002.

3-[6-(Pyrimidin-4-yl)pyridin-2-yl]-[1,2,3]triazolo[1,5-*a*]pyridine (12) and 3-[6-(Pyrimidin-2-yl)pyridin-2-yl]-[1,2,3]triazolo[1,5-*a*]pyridine (16)

Following the general procedure using **1d** (0.2 g), 1.6 M *n*BuLi (0.9 mL), toluene (50 mL), pyrimidine (0.2 mL), and $KMnO_4$/H_2O (0.17 g/40 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **12** (21 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1d** (25 mg), an additional amount of **12** (37 mg), then **16** (3 mg).

3-[6-(Pyrimidin-4-yl)pyridin-2-yl]-[1,2,3]triazolo[1,5-*a*]pyridine (12)

Yellow solid; yield: 58 mg (21%); mp 254–255 °C (EtOAc).

IR: 3089, 2925, 2856, 1576, 1524, 1415, 1385, 1313, 1202, 1116, 1007, 844, 794, 727, 696 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.37 (d, *J* = 1.3 Hz, 1 H), 9.23 (d, *J* = 7.0 Hz, 1 H), 9.07 (d, *J* = 5.3 Hz, 1 H), 8.79 (d, *J* = 8.9 Hz, 1 H), 8.56 (dd, *J* = 5.2, 1.4 Hz, 1 H), 8.47–8.41 (m, 2 H), 8.18 (dd, *J* = 7.9, 7.9 Hz, 2 H), 7.71 (ddd, *J* = 8.9, 6.7, 0.9 Hz, 1 H), 7.37 (ddd, *J* = 6.9, 6.9, 1.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9 (CH), 158.7 (CH), 152.1 (CH), 149.6 (C), 141.6 (C), 138.9 (CH), 128.5 (CH), 126.3 (C), 125.0 (C), 121.9 (CH), 120.9 (C), 119.9 (CH), 119.8 (CH), 117.4 (CH), 116.9 (CH).

MS: *m*/*z* (%) = 247 (100), 230 (4), 220 (12), 194 (53), 167 (7).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{12}N_5$: 275.1040; found: 275.1043.

3-[6-(Pyrimidin-2-yl)pyridin-2-yl]-[1,2,3]triazolo[1,5-*a*]pyridine (16)

Yellow solid; yield: 3 mg (1%); mp 173–174 °C (EtOAc).

IR: 3077, 2922, 2858, 2364, 2331, 1561, 1525, 1429, 1386, 1313, 1241, 1122, 1094, 1021, 990, 815, 735, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.10 (ddd ap., *J* = 8.9, 1.2, 1.2 Hz, 1 H), 8.97 (d, *J* = 4.8 Hz, 2 H), 8.77 (ddd ap., *J* = 7.0, 1.0, 1.0 Hz, 1 H), 8.47 (dd, *J* = 7.9, 1.0 Hz, 1 H), 8.40 (dd, *J* = 7.8, 1.0 Hz, 1 H), 7.98 (dd, *J* = 7.8, 7.8 Hz, 1 H), 7.46 (ddd, *J* = 8.9, 6.7, 1.0 Hz, 1 H), 7.35 (dd, *J* = 4.8, 4.8 Hz, 1 H), 7.07 (ddd, *J* = 6.9, 6.9, 1.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2 (C), 157.8 (CH), 154.5 (C), 152.3 (C), 143.5 (C), 137.9 (CH), 132.7 (C), 127.0 (CH), 125.3 (CH), 122.1 (CH), 122.0 (CH), 121.7 (CH), 120.5 (CH), 116.3 (CH).

MS: *m*/*z* (%) = 274 (15), 246 (100), 193 (26), 169 (5), 156 (4), 142 (3), 123 (3), 78 (10).

HRMS: *m*/*z* [M$^+$] calcd for $C_{15}H_{10}N_6$: 274.0967; found: 274.0965.

7-(Pyrazin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (4a)

Following the general procedure using **1a** (0.5 g), 1.6 M *n*BuLi (3.6 mL), toluene (50 mL), pyrazine/toluene (1 g/5 mL), and $KMnO_4/H_2O$ (0.66 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **4a** (129 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1a** (42 mg) and an additional amount of **4a** (21 mg); yellow solid; yield: 150 mg (17%); mp 209–210 °C (EtOAc).

IR: 3850, 3733, 3645, 3563, 2153, 1507, 1453, 1101, 1019 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 10.28 (d, *J* = 1.5 Hz, 1 H), 8.80–8.70 (m, 2 H), 8.25 (s, 1 H), 7.98 (dd, *J* = 7.1, 1.2 Hz, 1 H), 7.89 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.46 (dd, *J* = 8.8, 7.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.2 (CH), 145.4 (C), 145.3 (CH), 144.4 (CH), 135.1 (C), 134.4 (C), 126.5 (CH), 125.6 (CH), 119.1 (CH), 117.6 (CH).

MS: *m*/*z* (%) = 198 (3), 170 (5), 143 (72), 116 (100), 102 (7).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_8N_5$: 198.0774; found: 198.0774.

3-Methyl-7-(pyrazin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (4b)

Following the general procedure using **1b** (0.3 g), 1.6 M *n*BuLi (1.9 mL), toluene (165 mL), pyrazine/toluene (0.55 g/5 mL), and $KMnO_4/H_2O$ (0.39 g/100 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **4b** (45 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1b** (84 mg) and an additional amount of **4b** (98 mg); yellow solid; yield: 143 mg (30%); mp 136–137 °C (EtOAc).

IR: 3078, 3050, 2917, 1526, 1463, 1413, 1382, 1321, 1216, 1121, 1043, 1013, 849, 788, 724, 674 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 10.30 (d, *J* = 1.5 Hz, 1 H), 8.78–8.68 (m, 2 H), 7.95 (dd, *J* = 7.0, 1.2 Hz, 1 H), 7.77 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.38 (dd, *J* = 8.8, 7.1 Hz, 1 H), 2.71 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.1 (CH), 145.5 (C), 145.2 (CH), 144.4 (CH), 133.1 (C), 129.6 (C), 124.1 (CH), 123.7 (C), 118.7 (CH), 117.4 (CH), 10.65 (CH_3).

MS: *m*/*z* (%) = 212 (10), 184 (100), 156 (72), 142 (10), 129 (53), 104 (35).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{10}N_5$: 212.0931; found: 212.0927.

3-Phenyl-7-(pyrazin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (4c)[21]

Following the general procedure using **1c** (0.5 g), 1.6 M *n*BuLi (2.2 mL), toluene (50 mL), pyrazine/toluene (0.62 g/5 mL), and $KMnO_4/H_2O$ (0.40 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **4c** (66 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1c** (71 mg) and an additional amount of **4c** (360 mg); yellow solid; yield: 426 mg (61%); mp 141–142 °C (EtOAc). The structure of this compound was confirmed by powder X-diffraction data.

IR: 3108, 3031, 1540, 1458, 1394, 1264, 1127, 1058, 998, 918, 853, 722, 689 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 10.32 (d, *J* = 0.9 Hz, 1 H), 8.78–8.72 (m, 2 H), 8.15 (dd, *J* = 8.8, 0.9 Hz, 1 H), 8.02–7.99 (m, 3 H), 7.58–7.43 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.3 (CH), 145.4 (C), 145.3 (CH), 144.5 (CH), 138.8 (C), 134.6 (C), 131.9 (C), 131.3 (C), 129.2 (CH), 128.4 (CH), 127.2 (CH), 126.0 (CH), 119.5 (CH), 117.8 (CH).

MS: *m*/*z* (%) = 245 (54), 218 (13), 191 (13), 167 (100), 139 (3).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{12}N_5$: 274.1087; found: 274.1086.

3-[6-(Pyrazin-2-yl)pyridin-2-yl]-[1,2,3]triazolo[1,5-*a*]pyridine (13)

Following the general procedure using **1d** (0.5 g), 1.6 M *n*BuLi (2.2 mL), toluene (50 mL), pyrazine/toluene (0.62 g/5 mL), and $KMnO_4/H_2O$ (0.40 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **13** (283 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1d** (63 mg) and an additional amount of **13** (136 mg); yellow solid; yield: 419 mg (62%); mp 218–219 °C (EtOAc).

IR: 3085, 2920, 2842, 2359, 1525, 1380, 1114, 1089, 1032, 804, 737 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.78 (d, *J* = 1.3 Hz, 1 H), 8.83–8.80 (m, 2 H), 8.70–8.61 (m, 2 H), 8.48 (dd, *J* = 7.9, 0.9 Hz, 1 H), 8.33 (d, *J* = 7.8, 0.9 Hz, 1 H), 7.98 (dd, *J* = 7.9, 7.9 Hz, 1 H), 7.48 (dd, *J* = 9.2, 6.8 Hz, 1 H), 7.11 (ddd, *J* = 6.8, 6.8, 1.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8 (C), 152.0 (C), 151.6 (C), 144.6 (CH), 144.0 (CH), 143.3 (CH), 138.1 (CH), 137.2 (C), 132.2 (C), 127.0 (CH), 125.6 (CH), 121.5 (CH), 121.1 (CH), 120.0 (CH), 116.2 (CH).

MS: *m*/*z* (%) = 247 (100), 220 (22), 193 (5), 168 (5).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}N_6$: 274.1087; found: 275.1037.

7-(Pyridazin-3-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (5a) and 7-(Pyridazine-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (8a)

Following the general procedure using **1a** (0.5 g), 1.6 M *n*BuLi (3.6 mL), toluene (50 mL), pyridazine/toluene (1 g/5 mL), and $KMnO_4/H_2O$ (0.66 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **5a** (64 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1a** (76 mg) and an additional amount of **5a** (25 mg), and finally **8a** (14 mg).

7-(Pyridazin-3-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (5a)

Yellow solid; yield: 89 mg (14%); mp 179–180 °C (EtOAc).

IR: 3139, 1546, 1456, 1318, 1207, 1089, 1039, 949, 853, 779, 722 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.30 (dd, *J* = 5.0, 1.6 Hz, 1 H), 9.21 (dd, *J* = 8.8, 1.6 Hz, 1 H), 8.25 (s, 1 H), 8.20 (dd, *J* = 7.1, 1.2 Hz, 1 H), 7.93 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.72 (dd, *J* = 8.8, 5.0 Hz, 1 H), 7.50 (dd, *J* = 8.8, 7.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5 (C), 151.3 (CH), 135.1 (C), 134.1 (C), 128.2 (CH), 126.6 (CH), 126.4 (CH), 125.8 (CH), 119.4 (CH), 117.6 (CH).

MS: *m*/*z* (%) = 170 (17), 153 (3), 143 (37), 129 (4), 116 (100), 102 (8).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_8N_5$: 198.0774; found: 198.0770.

7-(Pyridazine-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (8a)

Orange solid; yield: 14 mg (2%); mp 333–334 °C (EtOAc).

IR: 3142, 1548, 1373, 1308, 1197, 1091, 1052, 998, 970, 828, 742 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.75 (dd, *J* = 2.4, 1.2 Hz, 1 H), 9.44 (dd, *J* = 5.5, 1.2 Hz, 1 H), 8.53 (dd, *J* = 5.5, 2.5 Hz, 1 H), 8.25 (s, 1 H), 7.91 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.44 (dd, *J* = 8.8, 7.0 Hz, 1 H), 7.35 (dd, *J* = 7.0, 1.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.6 (CH), 151.5 (C), 149.6 (CH), 133.6 (C), 130.4 (C), 127.0 (CH), 125.6 (CH), 125.4 (CH), 119.8 (CH), 116.8 (CH).

MS: *m*/*z* (%) = 169 (5), 153 (5), 142 (20), 116 (100).

HRMS (Q-TOF): *m*/*z* [M^+ + H – N_2] calcd for $C_{10}H_8N_3$: 170.0713; found: 170.0710.

3-Methyl-7-(pyridazin-3-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (5b) and 3-Methyl-7-(pyridazine-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (8b)

Following the general procedure using **1b** (0.5 g), 1.6 M *n*BuLi (3.2 mL), toluene (50 mL), pyridazine/toluene (0. 90 g/5 mL), and $KMnO_4/H_2O$ (0.59 g/50 mL). The crude was purified by chromatotron (hexane/EtOAc) to give **1b** (43 mg), **5b** (167 mg), and finally **8b** (34 mg).

3-Methyl-7-(pyridazin-3-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (5b)

Yellow solid; yield: 167 mg (21%); mp 191–192 °C (EtOAc).

IR: 3077, 2953, 2917, 2847, 2353, 1566, 1530, 1373, 1246, 1197, 1163, 1096, 1032, 812, 737, 693 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.26 (dd, *J* = 5.0, 1.6 Hz, 1 H), 9.18 (dd, *J* = 8.8, 1.6 Hz, 1 H), 8.13 (dd, *J* = 7.0, 1.1 Hz, 1 H), 7.78 (dd, *J* = 8.8, 1.2 Hz, 1 H), 7.69 (dd, *J* = 8.8, 5.0 Hz, 1 H), 7.39 (dd, *J* = 8.8, 7.1 Hz, 1 H), 2.69 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5 (C), 151.2 (CH), 135.4 (C), 133.7 (C), 133.0 (C), 128.0 (CH), 126.4 (CH), 124.3 (CH), 119.0 (CH), 117.4 (CH), 10.6 (CH_3).

MS: *m*/*z* (%) = 212 (4), 184 (100), 157 (4), 130 (42), 104 (10).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{10}N_5$: 212.0931; found: 212.0938.

3-Methyl-7-(pyridazine-4-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (8b)

Oil; yield: 34 mg (4%).

IR: 3442, 3374, 3250, 2927, 2865, 2362, 2334, 1540, 1450, 1429, 1360, 1254, 1215, 1135, 905, 784, 727 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.74 (dd, *J* = 2.3, 1.1 Hz, 1 H), 9.41 (dd, *J* = 5.5, 1.1 Hz, 1 H), 8.54 (dd, *J* = 5.5, 2.4 Hz, 1 H), 7.78 (dd, *J* = 8.3, 1.7 Hz, 1 H), 7.39–7.29 (m, 2 H), 2.69 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.6 (CH), 149.5 (CH), 135.9 (C), 132.8 (C), 132.2 (C), 130.5 (C), 125.5 (CH), 123.8 (CH), 119.4 (CH), 116.7 (CH), 10.6 (CH_3).

MS: *m*/*z* (%) = 184 (58), 167 (53), 157 (100), 144 (63), 130 (38), 117 (5), 104 (7).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{10}N_5$: 212.0931; found: 212.0938.

3-Phenyl-7-(pyridazin-3-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (5c)

Following the general procedure using **1c** (0.5 g), 1.6 M *n*BuLi (2.2 mL), toluene (50 mL), pyridazine/toluene (0.90 g/5 mL), and $KMnO_4/H_2O$ (0.40 g/50 mL). The crude was purified by chromatotron (hexane/EtOAc) to give **1c** (202 mg) and then **5c** as an orange solid; yield: 77 mg (11%); mp 191–192 °C (EtOAc).

IR: 3095, 2158, 1571, 1442, 1417, 1269, 1225, 1140, 1065, 1001, 851, 786, 735, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.30 (dd, *J* = 5.0, 1.6 Hz, 1 H), 9.22 (dd, *J* = 8.8, 1.6 Hz, 1 H), 8.23–8.15 (m, 2 H), 8.03–7.96 (m, 2 H), 7.73 (dd, *J* = 8.8, 5.0 Hz, 1 H), 7.59–7.50 (m, 3 H), 7.47–7.40 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5 (C), 151.3 (CH), 138.9 (C), 134.3 (C), 131.9 (C), 131.3 (C), 129.3 (CH), 128.4 (CH), 128.3 (CH), 127.2 (CH), 126.4 (CH), 126.2 (CH), 119.9 (CH), 117.8 (CH).

MS: *m*/*z* (%) = 245 (41), 229 (25), 219 (48), 205 (19), 191 (100), 167 (98), 139 (38).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{12}N_5$: 274.1087; found: 274.1088.

3-[6-(Pyridazin-3-yl)pyridin-2-yl]-[1,2,3]triazolo[1,5-*a*]pyridine (14)[21]

Following the general procedure using **1d** (0.5 g), 1.3 M *n*BuLi (2.2 mL), toluene (50 mL), pyridazine/toluene (0.62 g/5 mL), and $KMnO_4/H_2O$ (0.40 g/50 mL). The crude was purified by chromatotron (hexane/EtOAc) to give **1d** (108 mg) and then **14** as a yellow solid; yield: 140 mg (20%); mp 232–233 °C (EtOAc). The structure of this compound was confirmed by powder X-diffraction data.

IR: 3086, 3025, 1529, 1438, 1402, 1368, 1113, 1035, 741, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.26 (dd, *J* = 4.9, 1.7 Hz, 1 H), 8.81 (ddd, *J* = 7.0, 1.0, 1.0 Hz, 1 H), 8.69 (ddd, *J* = 8.9, 1.2, 1.2 Hz, 1 H), 8.63 (dd, *J* = 7.8, 1.0 Hz, 1 H), 8.60 (dd, *J* = 8.5, 1.7 Hz, 1 H), 8.49 (dd, *J* = 7.9, 1.0 Hz, 1 H), 8.01 (dd, *J* = 7.9, 7.9 Hz, 1 H), 7.69 (dd, *J* = 8.6, 4.9 Hz, 1 H), 7.45 (ddd, *J* = 8.9, 6.7, 1.0 Hz, 1 H), 7.10 (ddd, *J* = 6.9, 6.9, 1.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0 (C), 153.2 (C), 152.0 (C), 151.3 (CH), 138.2 (CH), 137.3 (C), 132.1 (C), 127.2 (CH), 126.8 (CH), 125.7 (CH), 124.4 (CH), 121.9 (CH), 120.8 (CH), 120.3 (CH), 116.0 (CH).

MS: *m*/*z* (%) = 247 (100), 230 (5), 220 (22), 193 (55), 167 (56), 140 (9).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}N_6$: 275.1040; found: 275.1037.

7-(1,3,5-Triazin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (6a) and [1,2,3]Triazolo[1,5-*a*]pyridine-7-carboxamide (10)

Following the general procedure using **1a** (0.5 g), 1.3 M *n*BuLi (2.9 mL), toluene (50 mL), 1,3,5-triazine/toluene (1.02 g/5 mL), and $KMnO_4/H_2O$ (0.66 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **6a** (36 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1a** (175 mg), then traces of **10** (9 mg), and finally an additional amount of **6a** (47 mg).

7-(1,3,5-Triazin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (6a)

Yellow solid; yield: 83 mg (10%); mp 183–185 °C (EtOAc).

IR: 1683, 1628, 1559, 1507, 1450, 1411, 1365, 1019, 740 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.49 (s, 2 H), 8.29 (s, 1 H), 8.12 (dd, *J* = 7.0, 1.3 Hz, 1 H), 8.01 (dd, *J* = 8.8, 1.3 Hz, 1 H), 7.44 (dd, *J* = 8.8, 7.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9 (CH), 150.7 (C), 140.9 (C), 131.9 (C), 127.0 (CH), 124.8 (CH), 122.1 (CH), 121.2 (CH).

MS: *m*/*z* (%) = 199 (11), 171 (2), 144 (100), 117 (13).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_9H_7N_4$: 199.0727; found: 199.0726.

[1,2,3]Triazolo[1,5-*a*]pyridine-7-carboxamide (10)

Oil; yield: 9 mg (1%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.80 (s_a, 2 H), 8.25 (s, 1 H), 8.15 (dd, *J* = 7.0, 1.3 Hz, 1 H), 7.98 (dd, *J* = 8.8, 1.3 Hz, 1 H), 7.46 (dd, *J* = 8.8, 7.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6 (C=O), 129.9 (C), 129.5 (C), 126.9 (CH), 125.6 (CH), 121.6 (CH), 121.2 (CH).

MS: *m*/*z* (%) = 163 (18), 120 (15), 107 (100).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_7H_7N_4$: 163.0614; found: 163.0612.

3-Methyl-7-(1,3,5-triazin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (6b)

Following the general procedure using **1b** (0.5 g), 1.3 M *n*BuLi (2.6 mL), toluene (50 mL), 1,3,5-triazine/toluene (0.91 g/5 mL), and $KMnO_4/H_2O$ (0.59 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **6b** (145 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1b** (43 mg) and an additional amount of **6b** (189 mg); yellow solid; yield: 334 mg (42%); mp 161–163 °C (EtOAc).

IR: 3308, 3153, 3031, 2923, 1546, 1518, 1421, 1390, 1343, 1318, 1221, 1202, 1105, 1146, 985, 952, 824, 780, 735, 721, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.47 (s, 2 H), 8.09 (dd, *J* = 7.0, 1.3 Hz, 1 H), 7.88 (dd, *J* = 8.8, 1.3 Hz, 1 H), 7.36 (dd, *J* = 8.8, 7.0 Hz, 1 H), 2.71 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8 (CH), 135.8 (C), 133.3 (C), 132.8 (C), 123.2 (CH), 121.7 (CH), 121.3 (CH), 10.6 (CH_3).

MS: *m*/*z* (%) = 131 (71), 104 (100), 103 (6).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_9N_6$: 213.0810; found: 213.0883.

3-Phenyl-7-(1,3,5-triazin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (6c)

Following the general procedure using **1c** (0.5 g), 1.3 M *n*BuLi (1.8 mL), toluene (50 mL), 1,3,5-triazine/toluene (0.62 g/5 mL), and $KMnO_4/H_2O$ (0.40 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **6c** (46 mg). The filtrate was purified by chromatotron (hexane/EtOAc) to give **1c** (63 mg) and an additional amount of **6c** (101 mg); yellow solid; yield: 147 mg (21%); mp 174–175 °C (EtOAc).

IR: 3039, 1546, 1448, 1422, 1386, 1362, 1220, 1150, 1014, 776, 740, 707 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.49 (s, 2 H), 8.25 (dd, *J* = 8.9, 1.2 Hz, 1 H), 8.07 (dd, *J* = 7.0, 1.2 Hz, 1 H), 8.01–7.97 (m, 2 H), 7.58–7.41 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9 (CH), 152.5 (C), 145.2 (C), 132.1 (C), 131.2 (C), 129.3 (CH), 128.5 (CH), 127.4 (CH), 125.0 (CH), 122.4 (CH), 121.2 (CH).

MS: *m*/*z* (%) = 275 (7), 247 (13), 220 (4), 193 (100), 166 (32), 139 (5).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}N_6$: 275.1040; found: 275.0978.

3-[6-(1,3,5-Triazin-2-yl)pyridin-2-yl]-[1,2,3]triazolo[1,5-*a*]pyridine (15)

Following the general procedure using **1d** (0.5 g), 1.3 M *n*BuLi (1.8 mL), toluene (50 mL), 1,3,5-triazine/toluene (0.62 g/5 mL), and $KMnO_4/H_2O$ (0.40 g/50 mL). The crude was treated with EtOAc, the yellow solid that precipitated was filtered and identified as **15** (90 mg). The filtrated was purified by chromatotron (hexane/EtOAc) to give **1d** (74 mg) and then an additional amount of **15** (73 mg); yellow solid; yield: 163 mg (21%); mp 252–253 °C (EtOAc).

IR: 3124, 3039, 1553, 1535, 1453, 1435, 1414, 1386, 1334, 1262, 1194, 1174, 1117, 1037, 985, 804, 753, 688 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.42 (s, 2 H), 9.09 (ddd, *J* = 8.9, 1.2, 1.2 Hz, 1 H), 8.80 (ddd, *J* = 7.0, 1.1, 1.1 Hz, 1 H), 8.56 (dd, *J* = 8.0, 1.0 Hz, 1 H), 8.51 (dd, *J* = 7.8, 1.0 Hz, 1 H), 8.03 (dd, *J* = 7.9, 7.9 Hz, 1 H), 7.51 (ddd, *J* = 8.9, 6.7, 1.0 Hz, 1 H), 7.11 (ddd, *J* = 6.9, 6.7, 1.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6 (C), 167.0 (CH), 152.9 (C), 152.1 (C), 138.1 (CH), 137.1 (C), 132.8 (C), 127.4 (CH), 125.4 (CH), 123.4 (CH), 123.0 (CH), 121.8 (CH), 116.3 (CH).

MS: *m*/*z* (%) = 248 (20), 194 (100), 167 (32).

HRMS (Q-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}N_7$: 276.0992; found: 276.0997.

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Supporting Information

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