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Synthesis of 3-Aminoimidazo[1,2-*a*]pyridines from *α*-Aminopyridynyl Amides

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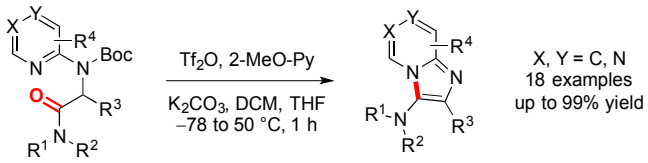


ABSTRACT

3-Aminoimidazo[1,2-*a*]pyridines are rapidly synthesized via a facile and mild cyclodehydration-aromatization reaction starting from readily available amides. The cyclodehydration step is mediated by the activation of *N*-Boc-protected 2-aminopyridine-containing amides by triflic anhydride (Tf_2O) in the presence of 2-methoxypyridine (2-MeO-Py). Subsequently, the addition of K_2CO_3 in THF ensured a clean deprotection-aromatization sequence to afford the desired heterocycle. A wide variety of functional groups and substitution patterns were tolerated under the optimized procedure, and good to excellent yields were obtained for the fused bicyclic 3-aza-heterocycles. In addition, the reaction is found to be scalable to gram-scale and could be performed with unprotected acyclic amide precursors. We also found that the resulting products were valuable intermediates for both Pd- and Ru-catalyzed C−H arylation reactions, allowing for the elaboration to diversely functionalized building blocks.

INTRODUCTION

Nitrogen-containing heterocycles are omnipresent in contemporary medicinal chemistry.[1] They encompass a large number of natural and commercialized synthetic products, exhibiting a remarkably diverse array of biological activities. For instance, the bicyclic imidazo[1,2-*a*]pyridine scaffold, a pertinent nitrogen-containing heterocycle, is increasingly reported to be a valuable drug template and building block.[2] Notably, it is present in various clinically approved drugs, such as zolpidem,[3] alpidem,[4] olprinone,[5] and zolimidine.[6] Moreover, imidazo[1,2-*a*]pyridines are ideal and well-known precursors of both abnormal *N*-heterocyclic carbene (NHC) ligands[7] and organic functional material, playing a critical role in the properties of certain optoelectronic materials.[8]

The C-3 position of imidazo[1,2-*a*]pyridines is an adjustable and metabolically important branching point for several therapeutics, whereby the judicious choice of a substituent at this position has been shown to determine whether a clinical candidate is poorly active or a lead molecule.[9] Consequently, imidazo[1,2-*a*]pyridines substituted at C-3 with an amino group have attracted increasing interest from the pharmaceutical industry. They are included in the structure of potent anti-inflammatory (**I**)[10] anti-cancer (**II**),[11] and anti-fibrosis **(III**)[12] targets (examples highlighted in blue, **Figure 1**). In parallel to medicinal chemistry, recent discoveries in material sciences showcase a different flavour to the potential applications of 3-aminoimidazo[1,2-*a*]pyridines, as they were implicated in the design of a class of fluorescent dyes.[13]

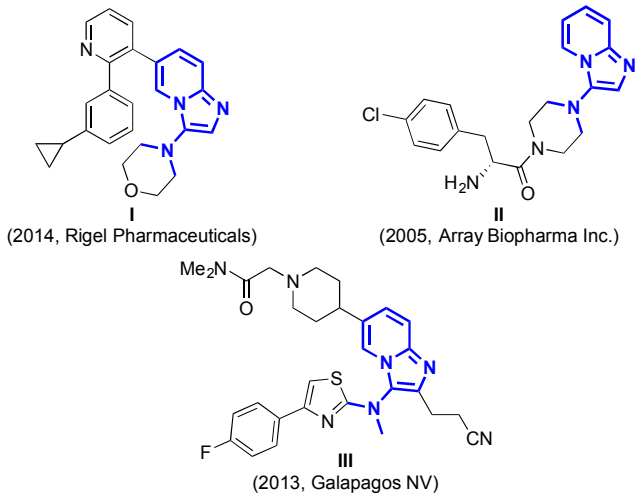
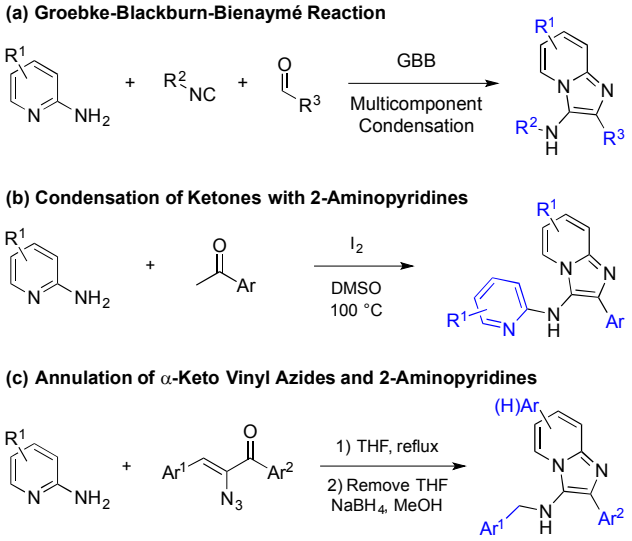


Figure 1. Bioactive pharmaceutical leads bearing substituted 3-aminoimidazo[1,2-*a*]pyridines.

Given the existence of a variety of functions of 3-aminoimidazo[1,2-*a*]pyridines, there comes a need for new and convergent synthetic methods applicable toward the elaboration of these heterocyclic derivatives. [14] Many contemporary approaches rely on the Groebke-Blackburn-Bienaymé (GBB) multicomponent condensation (**Scheme 1a**).[15] This three-component reaction consists of a one-pot coupling of aldehydes, 2-aminopyridines (or amidines) and isocyanides. The transformation of these

reagents to the titled heterocycles is often catalyzed by Brønsted acids (e.g. NH_4Cl,[16] AcOH,[15a] $HClO_4$,[15b] or PTSA[17]) or Lewis acids (e.g. $Sc(OTf)_3$,[15c,18] $BiCl_3$,[19] $ZnCl_2$,[20] or $SnCl_2 \cdot 2H_2O$[21]). Recent improvements to GBB heterocyclizations have disclosed the ability to use water,[22] ionic liquids,[23] solvent-free conditions,[24] as well as microwave irradiation, which increasingly provide shorter and cleaner reactions overall.[18a,25] Multicomponent condensations often constitute attractive synthetic strategies for the rapid and efficient combinatorial generation of libraries of nitrogen-containing heterocycles. However, this advantage is not necessarily well represented with GBB heterocyclization methods, as they suffer from various drawbacks. For instance, they are limited to toxic, costly and/or scarcely available isocyanide partners, which classically exhibit short half-lives at ambient temperatures.[26] Additionally, the scope of these methods is somewhat limited; the synthesis of trisubstituted amines at the C-3 position can be troublesome; and C-2 unsubstituted 3-aminoimidazo[1,2-*a*]pyridines are rarely synthesized following typical GBB procedures.[15-25,27]

Scheme 1. Strategies for the Synthesis of 3-Aminoimidazo[1,2-*a*]pyridines

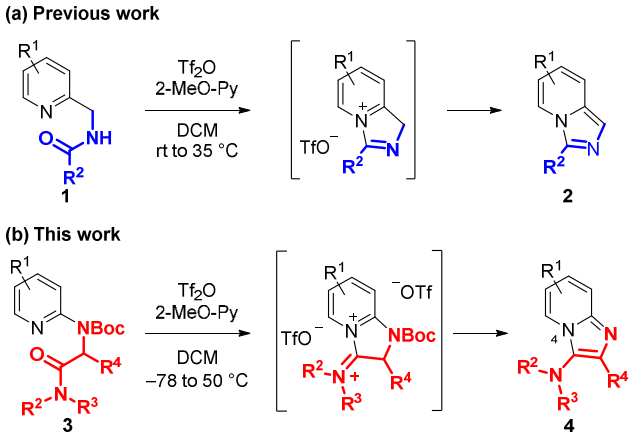


An alternative method for the synthesis 3-aminoimidazo[1,2-*a*]pyridines relies on the condensation of aromatic ketones with 2 equivalents of 2-aminopyridines (**Scheme 1b**).[28] This strategy is also not general, and the scope is inherently limited to preparing 2-aminopyridyls with substituents at the C-3 position and the use of acetophenone precursors. A complementary strategy for the synthesis of 3-aminoimidazo[1,2-*a*]pyridines is reported to proceed via sequential annulation of α-keto vinyl azide units and 2-aminopyridines followed by reduction of the corresponding imine, allowing for the formation of products with mono-substituted C-3-amino groups (**Scheme 1c**). The methodology is practical, but the scope is limited to aryl substitutions on the α-keto vinyl azide partner.[29] The development of a robust, general synthetic method for synthesising structurally diverse imidazo[1,2-*a*]pyridines with high levels of chemoselectivity is a desirable, yet currently unrealized goal. Our previous work with triflic anhydride

(Tf_2O) mediated activation of amides inspired us to pursue a complementary strategy towards these heterocycles.[30] We aimed to develop an operationally simple conditions that may be used to introduce a wide variety of substitution patterns within the 3-aminoimidazo[1,2-*a*]pyridines scaffold.

Various methods based on the chemoselective electrophilic activation of amides in the presence of Tf_2O have found broad applications in the synthesis of valuable building blocks.[30,31] An example of such strategy can be found in our recently reported intramolecular cyclodehydration-aromatization work towards the synthesis of imidazo[1,5-*a*]pyridines (**2**), a constitutional isomer, from activated secondary amides (**1**) (**Scheme 2a**).[32] In these earlier studies, we determined that the use of 2-methoxypyridine (2-MeO-Py), a slightly basic additive, is required for the activation step in order to obtain an efficient conversion to the desired target.[33,30a] Inspired by these results, we envisioned developing an analogous route that would allow the synthesis of 3-aminoimidazo[1,2-*a*]pyridines (**4**) from both tertiary and secondary amides (**3**) (**Scheme 2b**).

Scheme 2. Synthesis of Imidazo[1,5-*a*]azines and 3-Aminoimidazo[1,2-*a*]pyridines by Tf_2O-Mediated Activation of Amides

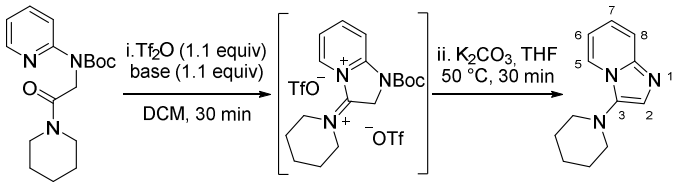


RESULTS AND DISCUSSION

We initially investigated the synthesis of **4a** by applying the previously reported activation conditions to **3a**, a simple amide bearing a *tert*-butoxycarbonyl (Boc) protecting group accessed in two steps from commercially available 2-Boc-aminopyridine. In the presence of 2-MeO-Py in DCM (DCM) at ambient temperature, the desired product **4a** was obtained in 85% yield before optimization (**Table 1**, entry 1). Based on our previous experience with heterocycles, such as **2**, we rapidly and efficiently optimized the overall transformation towards **4a** by fine-tuning various parameters of the reaction. Improved conditions for the activation-cyclodehydration sequence were readily obtained by employing 1.1 equiv of 2-MeO-Py in DCM (0.6 M) while warming the reaction mixture from –78 °C to room temperature (rt) over 30 min. to ensure complete activation of the amide. As exemplified in different methodologies involving Tf_2O-mediated electrophilic activation of amides, the addition of 2-substituded pyridines as non-nucleophilic and slightly basic additives in the reaction was found to be crucial to achieve an appreciable

level of efficiency.[34] Commonly used 2-F-Py also works well in the activation step, although less expensive 2-MeO-Py was the base of choice in this methodology. Consecutively, we screened different acidic and basic conditions for the deprotection-aromatization step and found that the transformation was very clean when performed in the presence of K_2CO_3 in tetrahydrofuran (THF) at 50 °C for an additional 30 min. Both transformations were run in the same pot, facilitating both the work-up and purification procedures.

Table 1. Optimization of the Activation-Cyclodehydration Reaction Sequence



3a **4a**

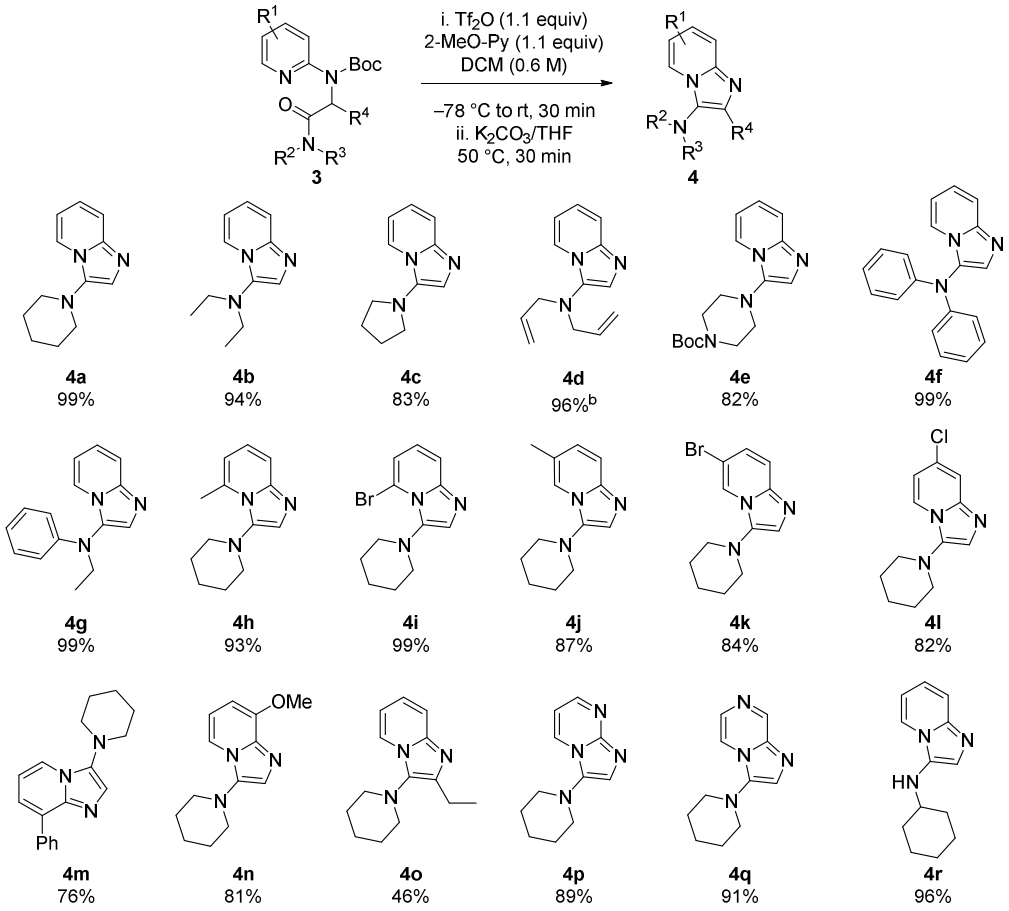
entry	base	temp. (°C)	time (h)	Conc (M)	yield **4a** (%)[a]
1	2-MeO-Py	rt	1	0.2	85
2	2-MeO-Py	rt	0.5	0.6	80
3	2-MeO-Py	0 °C to rt	0.5	0.6	86
4	2-MeO-Py	–78 °C to rt	0.5	0.6	99
5	2-F-Py	rt	0.5	0.6	90
6	None	rt	0.5	0.6	53

[a] Yields determined from the crude reaction mixture by ^{1}H NMR analysis using Ph_3CH as an internal standard.

To explore the scope of the cyclodehydration-aromatization sequence, various amides (**3**) were evaluated under the optimized conditions (Scheme 3). All of these amides can be obtained similarly to **3a**, from commercially available *N*-Boc-aminopyridines, bromoacetyl bromide and an equivalent of amine. To our delight, the overall process towards the synthesis of 3-aminoimidazo[1,2-*a*]pyridines **4** was shown to be effective in the presence of a variety of tertiary amide substrates, tolerating different substitution patterns on both the pyridine and amide components. More precisely, cyclic and acyclic amines can be incorporated at the C-3 position of the imidazo[1,2-*a*]pyridines while consistently affording high yields (**Scheme 3**, **4a**–**4e**). *N*-Aryl substituted 3-aminoimidazo[1,2-*a*]pyridines **4f** and **4g** are also efficiently synthesized in excellent yields. The variation of the electronic and steric properties in all positions of the aminoimidazo[1,2-*a*]pyridine (C-5, C-6, C-7 and C-8) is also well tolerated, as good to excellent yields were obtained in the presence of various functional groups (compounds **4h**–**4n**). Interestingly, product **4o**, with an alkyl substitution at C-2 position, is accessible in moderate yield under our optimized conditions.

Notably, the described method tolerates the replacement of the pyridine ring by other heterocycles, such as pyrimidine (**4p**) and pyrazine (**4q**). The procedure can be efficiently extended to secondary amides, affording mono-substituted 3-aminoimidazo[1,2-*a*]pyridine **4r** in excellent yield (96%). Finally, the transformation was shown to be amenable to gram-scale, as product **4d** was isolated with 96% yield.

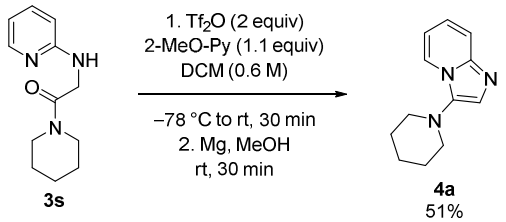
Scheme 3. Synthesis of 3-Aminoimidazo[1,2-*a*]pyridines from the Optimized Cyclodehydration/Aromatization Conditions[a]



[a] Isolated yields. [b] Yield obtained from 4.2 mmol of the corresponding amide precursor.

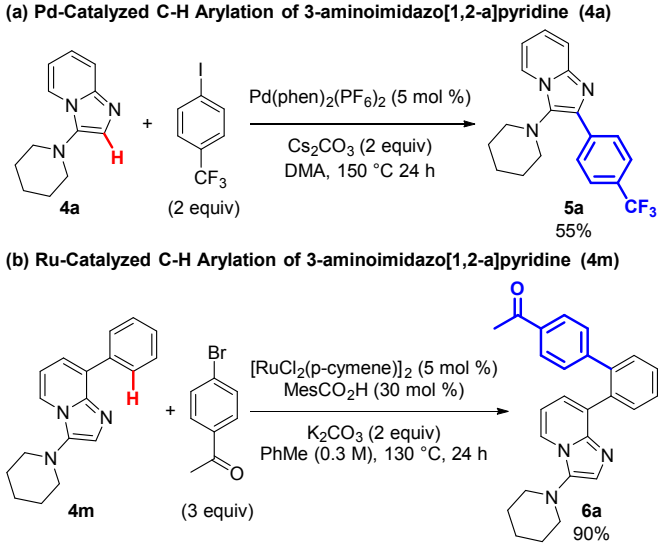
Following our success with Boc-protected substrates, we decided to further expand the scope of the current methodology by starting from an unprotected amide (**Scheme 4**). The treatment of amide **3s** with 2.0 equiv of Tf_2O instead of 1.0 equiv under the optimized conditions led to the corresponding 3-aminoimidazo[1,2-a]pyridine (**4a**) in a reasonable 51% yield following full conversion of starting amide. In this case, the additional equivalent of Tf_2O is required because of initial triflation of the N-1 moiety, which is ultimately cleaved in the presence of Mg(0) in MeOH at the aromatization step.

Scheme 4. Synthesis of 3-Aminoimidazo[1,2-*a*]pyridine from an Unprotected Amide (**3s)**



Inspired by the plethora of methodologies that exploit nitrogen-based directing groups for transition metal-catalyzed C–H arylations,[35] we sought to take advantage of the nitrogen atom at the *N*-1 position of 3-aminoimidazo[1,2-*a*]pyridine **4a** to perform divergent Pd- and Ru-catalyzed C–H functionalization reactions. The introduction of an aryl substituent at the C-2 position was achieved by an intermolecular Pd-catalyzed direct C–H arylation reaction (**Scheme 5a**). Using reported conditions developed by the Murai group with 4-iodobenzotrifluoride as the coupling partner, this C–H activation reaction provided the desired polysubstituted 3-aminoimidazo[1,2-*a*]pyridine **5a** in 55% yield.[36] While our approach to 3-aminoimidazo[1,2-*a*]pyridine (**Scheme 2**) allows the incorporation of an alkyl group at the C-2 position of these scaffolds (**Scheme 3**, compound **4o**), this Pd-catalyzed post-functionalization complements the initial strategy by allowing the addition of aryl groups at the same position at later stage. The latter approach may be advantageous for generating various C-2-substituted heterocycles using a combinatorial approach.

Scheme 5. Novel Metal-Catalyzed C−H Functionalization of 3-Aminoimidazo[1,2-*a*]pyridines



Considering the ability of the nitrogen atom at N-1 position to chelate palladium species, we further pursued the polyfunctionalization of the 3-aminoimidazo[1,2-*a*]pyridine scaffold by performing a Ru-catalyzed C–H arylation at the *ortho* position of the phenyl group in **4m** (**Scheme 5b**).[37] When imidazo[1,2-*a*]pyridine **4m** was subjected to non-optimized Ackermann C–H arylation conditions,

employing $[RuCl_2(p\text{-cymene})]_2$ complex as the catalyst in the presence of 4-bromoacetophenone, the monoarylated product **6a** was obtained in 90% yield with the remaining 10% stemming from the diarylated product. A distinguished feature of such ruthenium catalyzed transformation is exemplified by its site-selectivity being complementary to traditional Pd-catalyzed C–H bond arylation reactions.

Overall, we have successfully developed a mild cyclodehydration-aromatization process that is effective using short reaction times while using minimal amounts of an activating reagent. These conditions were applied to a large panel of tertiary amides with various substitution patterns. The methodology is also shown to be effective in the presence of an unprotected substrate (**3s**) or with a secondary amide (**3r**). The 3-aminoimidazo[1,2-*a*]pyridine products readily engage in versatile transition metal-catalyzed C–H arylation reactions for the synthesis of more complex scaffolds. These include intermolecular Pd- and Ru-catalyzed C–H functionalizations, demonstrating the efficiency of the 3-aminoimidazo[1,2-*a*]pyridine motif as a directing group under contemporary C–H arylation methodologies. We expect this methodology and post-modification strategies to be useful in medicinal chemistry towards the synthesis of novel drug candidates.

EXPERIMENTAL SECTION

General Information

Unless otherwise stated, all glassware was stored in the oven and/or was flame-dried prior to use. All reactions were set up under an argon atmosphere[38] while adding reagents and were run with the exclusion of moisture. All reaction flasks were kept closed with a septum during the reaction time. Anhydrous solvents were obtained either by filtration through drying columns (THF, DCM, toluene) or by distillation over CaH_2 (MeOH) or BaO (DMA). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel. Visualization of the developed chromatogram was performed by UV absorbance (254nm), UV fluorescence (350nm) or aqueous potassium permanganate ($KMnO_4$). Flash column chromatography was performed on an automatic purification system. Prepacked normal phase silica gel columns (12 g, 24 g, 40 g, 80 g and 120 g) were used for separation of products. Melting points were obtained on a melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded on 400 MHz and 500 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of chloroform ($CHCl_3$) (δ = 7.26 ppm), MeOH (δ = 3.31 ppm) or HDO (δ = 4.79 ppm) as the internal standard. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of $CDCl_3$ (δ = 77.23 ppm), as the internal standard. All ^{13}C NMR spectra were obtained with complete proton decoupling. Chemical shifts for ^{19}F NMR spectra are recorded in parts per million from trichlorofluoromethane using the central peak of trifluorotoluene (δ = -63.72 ppm) as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant in Hz and integration. Infrared spectra

are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra were performed by positive electrospray ionization on a TOF analyzer.

Reagents

Unless otherwise stated, commercial reagents were used without purification. Trifluoromethanesulfonic anhydride (Tf_2O) was made by heating TfOH on P_4O_{10}, distilled and kept under argon in a Schlenk flask before use. 2-Methoxypyridine was distilled over 4Å molecular sieves and kept under argon before use. $[Pd(phen)_2][PF_6]_2$[39] was synthesized according to previously reported procedures.

Experimental Procedure and Characterization Data

Synthesis of Carbamates

Procedure A: To a 50-mL round bottom flask equipped with a magnetic stirrer was added 2-aminopyridine (25 mmol; 1 equiv.) in THF (12.5 mL; 2M). Boc_2O (27.5 mmol; 1.1 equiv) was added in one portion and the resulting mixture was stirred at rt for 16 h. Solvents were then removed under reduced pressure and the residue was dissolved in DCM and washed with sat. $NaHCO_3$ and brine. The combined organic layers were dried on Na_2SO_4, filtered and concentrated under reduced pressure. The residue thus obtained was purified by automated flash chromatography over high performance silica gel (40-g column) using a gradient of 0% to 30% EtOAc/Hexanes with a flow of 45 mL/min. The crude amide was injected using a dry pack of silica gel. Fractions containing the carbamate were concentrated to dryness.

Procedure B: To a flame dried 50-mL round bottom flask equipped with a magnetic stirrer was added NaHMDS (4.2 mmol; 2.1 equiv) and THF (10 mL; 0.2M). The aminopyridine was added slowly at 0 °C and the resulting mixture was stirred at this temperature for 30 minutes before the dropwise addition of Boc_2O (2.4 mmol; 1.2 equiv). The reaction mixture was then allowed to warm up to rt and was stirred for 16h. Excess NaHMDS was quenched with methanol at 0°C and the solvents were removed under reduced pressure. DCM was added and the mixture was washed with sat. $NaHCO_3$ and brine. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue thus obtained was purified by automated flash chromatography over high performance silica gel (40 g column) using a gradient of 0% to 30% EtOAc/Hexanes with a flow of 45 mL/min. The crude amide was injected using a dry pack of silica gel. Fractions containing the carbamate were concentrated to dryness.

Characterization Data of Carbamates

tert-Butyl (3-methoxypyridin-2-yl)carbamate: Following general **procedure B**. The crude aminopyridine was purified by flash chromatography over silica gel using a gradient of 0% to 30% EtOAc/Hexanes. The crude amide was injected using a dry pack of silica gel over a 24 g column and a flow of 35 mL/min was used. Fractions containing **A** was obtained as a yellow oil (1.5 mmol; 334 mg; 37% yield). **Rf**: 0.30 (30% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.06 (d, J=4.8 Hz, 1 H), 7.37 (br. s, 1 H), 7.09 (dd, J=8.0, 1.2 Hz, 1 H), 6.93 (dd, J=8.0, 5.0 Hz, 1 H), 3.88 (s, 3 H), 1.54 (s, 9 H);

^{13}C NMR ($CDCl_3$, 126MHz): δ 150.8, 143.7, 142.3, 139.3, 118.0, 116.6, 80.9, 55.5, 28.2; **HRMS** (ESI, Pos): calc. for $C_{11}H_{17}N_2O_3$ [M+H]+: 225.1234 m/z, found: 225.1224 m/z; **FTIR** (cm^{-1}) (neat) 3435, 2977, 2934, 1743, 1597, 1499, 1147, 1120, 1017, 727.

tert-Butyl (5-methylpyridin-2-yl)carbamate: Following general **procedure A**. The crude aminopyridine was purified by flash chromatography over silica gel using a gradient of 0% to 30% EtOAc/Hexanes. The crude amide was injected using a dry pack of silica gel over a 24 g column and a flow of 35 mL/min was used. Fractions containing **B** was obtained as a white solid (9.6 mmol; 2 g; 96% yield). **Rf** = 0.46 (20% Ether/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.19 (br. s., 1 H), 8.07 (d, J=2.2 Hz, 1 H), 7.91 (d, J=8.6 Hz, 1 H), 7.54 (dd, J=8.6, 2.2 Hz, 1 H), 2.29 (s, 3 H), 1.54 (s, 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 152.4, 149.6, 146.1, 139.8, 127.6, 112.2, 81.1, 28.3, 17.6; **HRMS** (ESI, Pos): calcd for $C_{11}H_{17}N_2O_2$ [M+H]+: 209.1285 m/z, found: 209.1291 m/z; **mp**: 138-140 °C; **FTIR** (cm^{-1}) (neat): 3169, 2973, 2924, 1716, 1523, 1155, 1053, 1026, 766.

tert-Butyl pyrazin-2-ylcarbamate: Following general **procedure A**. The crude aminopyridine was purified by flash chromatography over silica gel using a gradient of 0% to 30% EtOAc/Hexanes. The crude amide was injected using a dry pack of silica gel over a Gold 24 g column and a flow of 35 mL/min was used. Fractions containing **C** was obtained as a white solid (6.7 mmol; 1.31 g; 67% yield). **Rf** = 0.43 (30% EtOAc/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 9.33 (s, 1 H), 8.27 (d, J=2.6 Hz, 1 H), 8.22 - 8.25 (m, 1 H), 8.20 (br. s., 1 H), 1.57 (s, 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 151.8, 148.8, 141.6, 138.8, 135.9, 81.9, 28.2; **HRMS** (ESI, Pos): calcd for $C_9H_{14}N_3O_2$ [M+H]+: 196.1081 m/z, found: 196.1084 m/z; **mp** : 112-114 °C; **FTIR** (cm^{-1}) (neat): 3208, 2976, 1726, 1554, 1417, 1243, 1151, 1078, 1011.

Other carbamates used for the synthesis of amides **3a-r** are commercially available.

General Procedures for the Synthesis of Amides 3a-r

To a 50-mL round bottom flask equipped with a magnetic stirrer was added the boc-protected aminopyridine (21mmol; 1 equiv) in THF (106 mL; 0.2 M). The mixture was cooled to 0 °C and NaH (23.3 mmol; 1.1 equiv) was added. The reaction mixture was stirred at this temperature for 30 min and the amide (21 mmol; 1 equiv) was added slowly. The mixture was then stirred at rt for another 16 h before quenching the excess NaH with MeOH at 0 °C. Solvents were removed under reduced pressure and the residue was dissolved in DCM. The resulting solution was washed with sat. $NaHCO_3$ and brine. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue thus obtained was purified by automated flash chromatography over high performance silica gel (24 g column) using a gradient of 0% to 30% EtOAc/Hexanes with a flow of 35 mL/min. The crude amide was injected using a dry pack of silica gel. Fractions containing amide (**3**) were concentrated to dryness.

Characterization Data of Amides 3a-r

tert-Butyl (2-oxo-2-(piperidin-1-yl)ethyl)(pyridin-2-yl)carbamate (3a): Following **general procedure**, **3a** was obtained as a white solid (12.2 mmol; 3.9 g; 62% yield). **Rf** = 0.27 (30% EtOAc/Hexanes); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.28 (ddd, J=4.9, 2.0, 0.8 Hz, 1 H), 7.82 (br. s., 1 H), 7.55 - 7.70 (m, 1 H), 6.96 (ddd, J=7.3, 4.9, 1.0 Hz, 1 H), 4.82 (s, 2 H), 3.30 - 3.68 (m, 4 H), 1.42 - 1.75 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.7, 154.3, 154.0, 147.0, 136.9, 119.2, 81.4, 47.6, 45.7, 43.1, 28.2, 26.3, 25.5, 24.5; **HRMS** (ESI, Pos): calcd for $C_{17}H_{25}N_3O_3$ [M+H]+: 320.1969 m/z, found: 320.1984 m/z; **mp** : 84-86 °C; **FTIR** (cm^{-1}) (neat): 2973, 2929, 2855, 1712, 1659, 1385, 1240, 1153, 786.

tert-Butyl (2-(diethylamino)-2-oxoethyl)(pyridin-2-yl)carbamate (3b): Following **general procedure**, **3b** was obtained as an off-white solid (7.2 mmol; 2.2 g; 46% yield). **Rf** = 0.56 (30% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.28 (ddd, J=4.9, 2.0, 0.8 Hz, 1 H), 7.86 (br. s., 1 H), 7.56 - 7.71 (m, 1 H), 6.97 (ddd, J=7.3, 4.9, 1.0 Hz, 1 H), 4.82 (s, 2 H), 3.37 (dd, J=14.6, 7.2 Hz, 4 H), 1.51 (s, 9 H), 1.01 - 1.35 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 167.6, 154.4, 154.0, 147.0, 137.0, 119.2, 81.5, 47.5, 41.3, 40.6, 28.2, 14.3, 13.1; **HRMS** (ESI, Pos): calcd for $C_{16}H_{25}N_3O_3$ [M+H]+: 308.1969 m/z, found: 308.1981 m/z; **mp** : 68-70 °C; **FTIR** (cm^{-1}) (neat): 2971, 2931, 1715, 1645, 1470, 1363, 1226, 1144, 781.

tert-Butyl (2-oxo-2-(pyrrolidin-1-yl)ethyl)(pyridin-2-yl)carbamate (3c): Following **general procedure**, **3c** was obtained as a pink oil (1.62 mmol; 495 mg; 65% yield). **Rf** = 0.39 (30% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.31 (ddd, J=5.0, 1.9, 0.8 Hz, 1 H), 7.84 (br. s., 1 H), 7.68 (t, J=7.1 Hz, 1 H), 6.92 - 7.10 (m, 1 H), 4.79 (s, 2 H), 3.49 (dt, J=10.0, 6.9 Hz, 4 H), 1.75 - 2.09 (m, 4 H), 1.51 (s, 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.5, 153.7, 153.3, 146.5, 136.4, 118.6, 80.8, 47.7, 45.2, 44.9, 27.6, 25.6, 23.4; **HRMS** (ESI, Pos): calcd for $C_{16}H_{24}N_3O_3$ [M+H]+: 306.1812 m/z, found: 306.1823 m/z; **FTIR** (cm^{-1}) (neat): 2973, 2874, 1708, 1656, 1435, 1366, 1226, 1148, 1061.

tert-Butyl (2-(diallylamino)-2-oxoethyl)(pyridin-2-yl)carbamate (3d): Following **general procedure**, **3d** was obtained as a colorless oil (1.34 mmol; 445 mg; 67% yield). **Rf** = 0.28 (30% EtOAc/Hexanes); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.21 - 8.33 (m, 1 H), 7.83 (br. s., 1 H), 7.54 - 7.66 (m, 1 H), 6.94 (ddd, J=7.2, 4.9, 0.9 Hz, 1 H), 5.63 - 5.94 (m, 2 H), 5.05 - 5.35 (m, 4 H), 4.82 (s, 2 H), 3.85 - 4.08 (m, 4 H), 1.50 (s, 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 168.5, 154.2, 153.9, 146.9, 136.9, 133.1, 132.5, 119.2, 119.1, 117.3, 116.9, 81.5, 48.5, 48.3, 47.4, 28.1; **HRMS** (ESI, Pos): calcd for $C_{18}H_{26}N_3O_3$ [M+H]+: 332.1969 m/z, found: 332.1971 m/z; **FTIR** (cm^{-1}) (neat): 2978, 1712, 1664, 1590, 1469, 1367, 1223, 1151, 730.

tert-Butyl 4-(N-(tert-butoxycarbonyl)-N-(pyridin-2-yl)glycyl)piperazine-1-carboxylate (3e): Following **general procedure**, **3e** was obtained as a white solid (2.16 mmol; 911 mg; 89% yield). **Rf** = 0.25 (10% Acetone/Petroleum ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.22 - 8.34 (m, 1 H), 7.82 (br. s., 1 H), 7.64 (td, J=7.8, 1.9 Hz, 1 H), 6.99 (dd, J=6.8, 5.3 Hz, 1 H), 4.85 (s, 2 H), 3.35 - 3.67 (m, 8 H), 1.50 (d, J=16.5 Hz, 18 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 167.2, 154.3, 153.9, 153.6, 146.9, 136.9, 119.0, 119.0, 81.5, 80.1, 47.3, 44.4, 41.6, 28.2, 28.0; **HRMS** (ESI, Pos): calcd for $C_{21}H_{32}N_4O_5$ [M+H]+: 421.2446 m/z, found: 421.2448 m/z; **mp** : 124-126 °C; **FTIR** (cm^{-1}) (neat): 2973, 2931, 1682, 1413, 1365, 1235, 1151, 1019, 779.

tert-Butyl (2-(diphenylamino)-2-oxoethyl)(pyridin-2-yl)carbamate (3f): Following **general procedure**, **3f** was obtained as a white solid (1.02 mmol; 410 mg; 51% yield). **Rf** = 0.29 (30% EtOAc/Hexanes); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.34 (dd, J=4.9, 1.0 Hz, 1 H), 7.84 (br. s., 1 H), 7.57 - 7.68 (m, 1 H), 7.31 (br. s, 10 H), 6.98 (ddd, J=7.2, 4.9, 0.7 Hz, 1 H), 4.65 (s, 2 H), 1.56 (s, 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 168.6, 154.0, 153.8, 147.0, 141.9, 136.9, 129.4, 128.8, 125.7, 119.1, 119.0, 81.6, 49.5, 28.2; **HRMS** (ESI, Pos): calcd for $C_{24}H_{26}N_3O_3$ [M+H]+: 404.1969 m/z, found: 404.1987 m/z; **mp** : 46-52 °C; **FTIR** (cm^{-1}) (neat): 2974, 1687, 1589, 1469, 1366, 1227, 1147, 755, 692.

tert-Butyl (2-(ethyl(phenyl)amino)-2-oxoethyl)(pyridin-2-yl)carbamate (3g): Following **general procedure**, **3g** was obtained as an off-white solid (2.25 mmol; 800 mg, 99% yield). **Rf** = 0.40 (30% EtOAc/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.30 (d, J=3.5 Hz, 1 H), 7.80 (br. s., 1 H), 7.57 - 7.67 (m, 1 H), 7.42 - 7.51 (m, 2 H), 7.34 - 7.41 (m, 1 H), 7.29 (d, J=7.3 Hz, 2 H), 6.93 - 7.01 (m, 1 H), 4.44 (s, 2 H), 3.77 (q, J=7.2 Hz, 2 H), 1.53 (s, 9 H), 1.13 (t, J=7.2 Hz, 3 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 168.0, 154.2, 153.8, 146.9, 141.2, 137.1, 129.8, 128.5, 128.2, 119.4, 119.2, 81.5, 48.9, 44.2, 28.2, 13.1; **HRMS** (ESI, Pos): calcd for $C_{20}H_{26}N_3O_3$ [M+H]+: 356.1969 m/z, found: 356.1976 m/z; **mp** : 118-120 °C; **FTIR** (cm^{-1}) (neat): 3058, 2971, 2930, 1713, 1666, 1376, 1149, 786, 697.

tert-Butyl (6-methylpyridin-2-yl)(2-oxo-2-(piperidin-1-yl)ethyl)carbamate (3h): Following **general procedure**, **3h** was obtained as a white solid (3.6 mmol; 1.2 g; 75% yield). **Rf** = 0.30 (30% EtOAc/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.59 (br. s., 1 H), 7.47 - 7.55 (m, 1 H), 6.83 (d, J=7.3 Hz, 1 H), 4.81 (s, 2 H), 3.24 - 3.74 (m, 4 H), 2.44 (s, 3 H), 1.39 - 1.8 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.9, 155.9, 154.1, 153.6, 137.4, 118.7, 116.8, 81.3, 47.7, 45.8, 43.1, 30.9, 28.2, 26.3, 25.5, 24.6, 24.1; **HRMS** (ESI, Pos): calcd for $C_{18}H_{28}N_3O_3$ [M+H]+: 334.2125 m/z, found: 334.2135 m/z; **mp** : 78 - 80 °C; **FTIR** (cm^{-1}) (neat): 2974, 2933, 2856, 1710, 1657, 1455, 1364, 1223, 1152.

tert-Butyl (6-bromopyridin-2-yl)(2-oxo-2-(piperidin-1-yl)ethyl)carbamate (3i): Following **general procedure**, **3i** was obtained as an off-white solid (0.74 mmol; 294 mg; 74% yield). **Rf** = 0.28 (30% EtOAc/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.86 (br. s., 1 H), 7.46 (dd, J=8.3, 7.7 Hz, 1 H), 7.12 (dd, J=7.5, 0.6 Hz, 1 H), 4.78 (s, 2 H), 3.30 - 3.73 (m, 4 H), 1.38 - 1.91 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.3, 154.2, 153.5, 139.2, 138.2, 122.7, 117.3, 82.1, 47.3, 46.0, 43.3, 28.1, 26.2, 25.5, 24.6; **HRMS** (ESI, Pos): calcd for $C_{17}H_{25}BrN_3O_3$ [M+H]+: 398.1074 m/z, found: 398.1090 m/z; **mp** : 96 - 100 °C; **FTIR** (cm^{-1}) (neat): 2974, 2934, 2856, 1654, 1437, 1364, 1229, 1149, 1127.

tert-Butyl (5-methylpyridin-2-yl)(2-oxo-2-(piperidin-1-yl)ethyl)carbamate (3j): Following **general procedure**, **3j** was obtained as an off-white solid (1.43 mmol; 477 mg, 72% yield). **Rf** = 0.47 (30% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.08 (dd, J=1.7, 0.7 Hz, 1 H), 7.66 (br. s., 1 H), 7.35 - 7.50 (m, 1 H), 4.77 (s, 2 H), 3.23 - 3.68 (m, 4 H), 2.24 (s, 3 H), 1.39 - 1.77 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.7, 154.0, 152.1, 146.9, 137.7, 128.6, 119.3, 81.1, 47.7, 45.6, 43.0, 28.1, 26.2, 25.4, 24.4, 17.6; **HRMS** (ESI, Pos): calcd for $C_{18}H_{28}N_3O_3$ [M+H]+: 334.2125 m/z, found: 334.2112 m/z; **mp** : 82-84 °C; **FTIR** (cm^{-1}) (neat): 2975, 2921, 2857, 1702, 1651, 1482, 1384, 1229, 1154.

tert-Butyl (5-bromopyridin-2-yl)(2-oxo-2-(piperidin-1-yl)ethyl)carbamate (3k): Following **general procedure**, **3k** was obtained as an off-white solid (0.50 mmol; 200 mg, 50% yield). **Rf** = 0.43 (30% EtOAc/Hexanes); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.23 - 8.40 (m, 1 H), 7.80 (br. s., 1 H), 7.72 (m, 2.5 Hz, 1 H), 4.81 (s, 2 H), 3.27 - 3.71 (m, 4 H), 1.43 - 1.80 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.4, 153.6, 153.0, 147.6, 139.6, 82.0, 47.5, 45.8, 43.2, 28.2, 26.3, 25.5, 24.5; **HRMS** (ESI, Pos): calcd for $C_{17}H_{25}BrN_3O_3$ [M+H]+: 398.1074 m/z, found: 398.1077 m/z; **mp** : 104-108 °C; **FTIR** (cm^{-1}) (neat): 2934, 2855, 1702, 1652, 1464, 1365, 1223, 1152, 836.

tert-Butyl (4-chloropyridin-2-yl)(2-oxo-2-(piperidin-1-yl)ethyl)carbamate (3l): Following **general procedure**, **3l** was obtained as a yellow oil (0.70 mmol; 248 mg, 64% yield). **Rf** = 0.28 (30% EtOAc/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.16 (d, J=5.3 Hz, 1 H), 7.99 (br. s., 1 H), 6.96 (dd, J=5.5, 1.8 Hz, 1 H), 4.84 (s, 2 H), 3.33 - 3.68 (m, 4 H), 1.46 - 1.83 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.4, 155.2, 153.6, 147.5, 144.5, 119.4, 118.8, 82.1, 47.3, 45.8, 43.2, 28.1, 26.3, 25.5, 24.5; **HRMS** (ESI, Pos): calcd for $C_{17}H_{25}ClN_3O_3$ [M+H]+: 354.1579 m/z, found: 354.1593 m/z; **FTIR** (cm^{-1}) (neat): 2975, 2936, 2851, 1703, 1645, 1384, 1233, 1149, 843.

tert-Butyl (2-oxo-2-(piperidin-1-yl)ethyl)(3-phenylpyridin-2-yl)carbamate (3m): Following **general procedure**, **3m** was obtained as a colorless oil (0.71 mmol; 281 mg, 99% yield). **Rf** = 0.51 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.35 (dd, J=4.7, 1.6 Hz, 1 H), 7.63 - 7.94 (m, 3 H), 7.43 (t, J=7.6 Hz, 2 H), 7.32 (d, J=7.0 Hz, 1 H), 7.19 (dd, J=7.5, 4.8 Hz, 1 H), 4.59 - 5.11 (m, 2 H), 3.38 - 3.74 (m, 4 H), 1.52 - 1.71 (m, 6 H), 0.99 (br. s., 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.7, 153.8, 152.1, 146.5, 139.3, 139.2, 133.6, 128.6, 128.4, 127.4, 121.5, 81.1, 49.4, 46.1, 43.1, 27.4, 26.3, 25.5, 24.6; **HRMS** (ESI, Pos): calcd for $C_{23}H_{30}N_3O_3$ [M+H]+: 396.2287 m/z, found: 396.2283 m/z; **FTIR** (cm^{-1}) (neat): 3059,2978, 2934, 2856, 1657, 1365, 1236, 1153, 701.

tert-Butyl (3-methoxypyridin-2-yl)(2-oxo-2-(piperidin-1-yl)ethyl)carbamate (3n): Following **general procedure**, **3n** was obtained as a brown oil (1.06 mmol; 371 mg, 72% yield). **Rf** = 0.30 (30% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.92 (dd, J=4.8, 1.5 Hz, 1 H), 7.16 (dd, J=8.2, 1.4 Hz, 1 H), 7.07 (dd, J=8.3, 4.8 Hz, 1 H), 4.64 (s, 2 H), 3.87 (s, 3 H), 3.31 - 3.55 (m, 4 H), 1.43 - 1.68 (m, 6 H), 1.37 (s, 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.4, 153.8, 150.6, 145.0, 138.7, 122.1, 118.8, 80.4, 55.4, 53.3, 49.1, 45.7, 42.9, 27.9, 26.1, 25.3, 24.4; **HRMS** (ESI, Pos): calcd for $C_{18}H_{28}N_3O_4$ [M+H]+: 350.2074 m/z, found: 350.2080 m/z; **FTIR** (cm^{-1}) (neat): 2977, 2935, 2856, 1699, 1659, 1451, 1365, 1157, 727.

tert-Butyl (1-oxo-1-(piperidin-1-yl)butan-2-yl)(pyridin-2-yl)carbamate (3o): Following **general procedure**, **3o** was obtained as a colorless oil (0.36 mmol; 126 mg, 36% yield). **Rf** = 0.63 (30% Acetone/Petroleum ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.34 - 8.45 (m, 1 H), 7.59 - 7.69 (m, 1 H), 7.40 (d, J=8.3 Hz, 1 H), 7.08 (ddd, J=7.3, 4.8, 0.9 Hz, 1 H), 5.16 (t, J=7.2 Hz, 1 H), 3.34 - 3.68 (m, 4 H), 1.70 - 2.06 (m, 2 H), 1.45 - 1.67 (m, 6 H), 1.41 (s, 9 H), 0.92 (t, J=7.4 Hz, 3 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 168.8, 154.1, 153.0, 147.9, 137.1, 122.2, 121.1, 81.2, 58.0, 46.2, 43.4, 28.1, 26.2, 25.5, 24.6, 24.0, 11.0;

HRMS (ESI, Pos): calcd for $C_{19}H_{30}N_3O_3$ [M+H]+: 348.2282 m/z, found: 348.2296 m/z; **FTIR** (cm^{-1}) (neat): 2974, 2934, 2855, 1698, 1649, 1367, 1243, 1153, 730.

tert-Butyl (2-oxo-2-(piperidin-1-yl)ethyl)(pyrimidin-2-yl)carbamate (3p): Following **general procedure**, **3p** was obtained as an off-white solid (1.42 mmol; 456 mg, 79% yield). **Rf** = 0.36 (50% Acetone/Hexanes); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.57 (d, J=4.8 Hz, 2 H), 6.91 (t, J=4.8 Hz, 1 H), 4.75 (s, 2 H), 3.28 - 3.76 (m, 4 H), 1.40 - 1.83 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.2, 160.4, 157.4, 153.0, 115.8, 81.7, 48.4, 45.7, 43.1, 28.0, 26.2, 25.5, 24.4; **HRMS** (ESI, Pos): calcd for $C_{16}H_{25}N_4O_3$ [M+H]+: 321.1921 m/z, found: 321.1935 m/z; **mp** : 134-136 °C; **FTIR** (cm^{-1}) (neat): 2978, 2963, 2936, 2861, 1731, 1657, 1413, 1152, 794.

tert-Butyl (2-oxo-2-(piperidin-1-yl)ethyl)(pyrazin-2-yl)carbamate (3q): Following **general procedure**, **3q** was obtained as a white solid (1.97 mmol; 631 mg, 98% yield). **Rf** = 0.28 (30% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 9.19 (br. s., 1 H), 8.02 - 8.40 (m, 2 H), 4.77 (s, 2 H), 3.20 - 3.76 (m, 4 H), 1.44 - 1.82 (m, 15 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 166.0, 153.2, 151.1, 141.2, 140.9, 138.2, 82.6, 46.9, 45.8, 43.2, 28.1, 26.3, 25.5, 24.5; **HRMS** (ESI, Pos): calcd for $C_{16}H_{25}N_4O_3$ [M+H]+: 321.1921 m/z, found: 321.1913 m/z; **mp** : 98 - 100 °C; **FTIR** (cm^{-1}) (neat): 2974, 2933, 2859, 1714, 1650, 1408, 1238, 1154, 1006.

tert-Butyl (2-(cyclohexylamino)-2-oxoethyl)(pyridin-2-yl)carbamate (3r): Following **general procedure**, **3r** was obtained as a white solid (4.05 mmol; 1.35 g, 79% yield). **Rf** = 0.56 (30% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.32 - 8.40 (m, 1 H), 7.68 - 7.74 (m, 1 H), 7.61 - 7.67 (m, 1 H), 7.10 (ddd, J=7.2, 5.0, 1.1 Hz, 1 H), 6.93 (d, J=6.6 Hz, 1 H), 4.37 (s, 2 H), 3.74 - 3.94 (m, 1 H), 1.55 - 1.95 (m, 5 H), 1.51 (s, 9 H), 1.07 - 1.44 (m, 5 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 169.1, 154.4, 153.8, 147.6, 137.6, 120.5, 119.8, 82.3, 52.2, 47.8, 32.9, 28.1, 25.5, 24.5; **HRMS** (ESI, Pos): calcd for $C_{18}H_{28}N_3O_3$ [M+H]+: 334.2125 m/z, found: 334.2130 m/z; **mp** : 102-104 °C; **FTIR** (cm^{-1}) (neat): 3296, 2976, 2930, 2854, 1713, 1655, 1366, 1224, 1149.

General Procedure for the Synthesis of 3-Aminoimidazo[1,2-*a*]pyridines 4a-r

To a flame-dried and argon-flushed 10-mL glass microwave vial equipped with a magnetic stirrer and a rubber septum was added the amide (0.3 mmol, 1.0 equiv) in anhydrous DCM (0.5 mL, 0.60 M). 2-methoxypyridine (2-MeOPyr) (35 µL, 0.33 mmol, 1.1 equiv) was added via syringe and the reaction mixture was cooled to –78 °C. Triflic anhydride (55 µL, 0.33 mmol, 1.1 equiv) was added dropwise via syringe and the reaction mixture was stirred at –78 °C for 10 min and at rt for another 20 min. The reaction was quenched by the addition of K_2CO_3 (3.0 mmol, 10.0 equiv) and THF (2.0 mL, 0.15 M) and then stirred at 50°C for 30 min. The residue thus obtained was purified by automated flash chromatography over high performance silica gel (24 g column) using a gradient of 0% to 50% Acetone/Hexanes with a flow of 35 mL/min. The crude amide was injected using a dry pack of silica gel. Fractions containing 3-aminoimidazo[1,2-a]pyridines (**3**) were concentrated to dryness.

Characterization Data of 3-Aminoimidazo[1,2-*a*]pyridines

3-(Piperidin-1-yl)imidazo[1,2-*a*]pyridine (4a): Following general **procedure**, **4a** was obtained as a pale brown solid (0.25 mmol; 50 mg, 99% yield). **Rf** = 0.31 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.96 (dt, J=6.8, 1.2 Hz, 1 H), 7.55 (dt, J=9.0, 1.0 Hz, 1 H), 7.24 (s, 1 H), 7.12 (ddd, J=9.1, 6.6, 1.3 Hz, 1 H), 6.79 (td, J=6.7, 1.0 Hz, 1 H), 2.87 - 3.06 (m, 4 H), 1.57 - 1.91 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 141.6, 136.4, 123.4, 122.4, 120.5, 117.8, 111.6, 53.0, 26.1, 24.1; **HRMS** (ESI, Pos): calcd for $C_{12}H_{16}N_3$ [M+H]+: 202.1339 m/z, found: 202.1330 m/z; **mp** : 68-70 °C; **FTIR** (cm^{-1}) (neat): 3035, 2945, 2913, 2793, 1503, 1304, 1250, 750, 739.

N,N-Diethylimidazo[1,2-*a*]pyridin-3-amine (4b): Following general **procedure**, **4b** was obtained as a brown oil (47 mg, 83% yield). **Rf** = 0.33 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.10 (d, J=7.0 Hz, 1 H), 7.57 (d, J=9.0 Hz, 1 H), 7.35 (s, 1 H), 7.15 (ddd, J=9.1, 6.6, 1.3 Hz, 1 H), 6.81 (td, J=6.7, 1.0 Hz, 1 H), 3.08 (q, J=7.2 Hz, 4 H), 1.03 (t, J=7.1 Hz, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 141.7, 133.1, 124.1, 123.9, 122.7, 117.5, 111.8, 48.5, 12.6; **HRMS** (ESI, Pos): calcd for $C_{11}H_{16}N_3$ [M+H]+: 190.1339 m/z, found: 190.1330 m/z; **FTIR** (cm^{-1}) (neat): 2969, 2932, 2870, 1545, 1304, 1251, 1134, 1077, 739.

3-(Pyrrolidin-1-yl)imidazo[1,2-*a*]pyridine (4c): Following general **procedure**, [1,2- *a*]pyridine g column and a flow of 35 mL/min was used. Fractions containing **4c** was obtained as a brown oil (0.43 mmol; 81 mg, 94% yield). **Rf** = 0.28 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.00 (d, J=7.0 Hz, 1 H), 7.57 (d, J=9.0 Hz, 1 H), 7.23 (s, 1 H), 7.12 (ddd, J=9.0, 6.6, 1.2 Hz, 1 H), 6.80 (td, J=6.7, 0.8 Hz, 1 H), 3.15 - 3.27 (m, 4 H), 2.0 (dt, J=6.9, 3.2 Hz, 4 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 141.2, 134.8, 123.6, 122.9, 118.4, 117.4, 111.8, 52.1, 24.5; **HRMS** (ESI, Pos): calcd for $C_{11}H_{14}N_3$ [M+H]+: 188.1182 m/z, found: 188.1185 m/z; **FTIR** (cm^{-1}) (neat): 2963, 2927, 2873, 2826, 1548, 1299, 1132, 745, 733.

N,N-Diallylimidazo[1,2-*a*]pyridin-3-amine (4d): Following general **procedure**, **4d** was obtained as a colorless oil (4.06 mmol; 867 mg, 96% yield). **Rf** = 0.36 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.08 (dd, J=6.8, 1.1 Hz, 1 H), 7.59 (d, J=9.2 Hz, 1 H), 7.33 (s, 1 H), 7.10 - 7.22 (m, 1 H), 6.83 (t, J=6.8 Hz, 1 H), 5.85 (ddt, J=17.0, 10.3, 6.3 Hz, 2 H), 5.09 - 5.31 (m, 4 H), 3.64 (d, J=6.2 Hz, 4 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 141.8, 134.0, 133.1, 124.8, 123.2, 122.4, 118.2, 117.8, 111.5, 56.2; **HRMS** (ESI, Pos): calcd for $C_{13}H_{16}N_3$ [M+H]+: 214.1339 m/z, found: 214.1339 m/z; **FTIR** (cm^{-1}) (neat): 3080, 2979, 2924, 2849, 1261, 1150, 1030, 753, 636.

tert-Butyl 4-(imidazo[1,2-*a*]pyridin-3-yl)piperazine-1-carboxylate (4e): Following general **procedure**, **4e** was obtained as a yellow oil (0.27 mmol; 82 mg, 82% yield). **Rf** = 0.38 (20% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.99 (dt, J=6.9, 1.1 Hz, 1 H), 7.50 - 7.60 (m, 1 H), 7.29 (s, 1 H), 7.14 (ddd, J=9.1, 6.6, 1.3 Hz, 1 H), 6.81 (td, J=6.8, 0.9 Hz, 1 H), 3.57 - 3.71 (m, 4 H), 2.93 - 3.07 (m, 4 H), 1.50 (s, 9 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 154.6, 142.2, 134.8, 123.5, 122.1, 121.7, 118.1, 111.8, 80.0, 51.7, 44.0, 28.4; **HRMS** (ESI, Pos): calcd for $C_{16}H_{22}N_4O_2$ [M+H]+: 303.1816 m/z, found: 303.1824 m/z; **FTIR** (cm^{-1}) (neat): 2975, 2928, 2829, 1688, 1418, 1244, 1165, 1125, 729.

N,N-Diphenylimidazo[1,2-*a*]pyridin-3-amine (4f): Following general **procedure**, **4f** was obtained as a brown solid (0.38 mmol; 108 mg, 99% yield). **Rf** = 0.42 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ

7.77 - 7.89 (m, 1 H), 7.72 (d, J=9.2 Hz, 1 H), 7.58 (s, 1 H), 7.20 - 7.35 (m, 5 H), 6.99 - 7.14 (m, 5 H), 6.79 (td, J=6.8, 0.9 Hz, 1 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 145.5, 142.8, 129.5, 129.1, 127.6, 124.8, 123.1, 122.4, 120.8, 118.1, 112.7; **HRMS** (ESI, Pos): calcd for $C_{19}H_{16}N_3$ [M+H]+: 286.1339 m/z, found: 286.1326 m/z; **mp** : 136-140 °C; **FTIR** (cm^{-1}) (neat): 3059, 3033, 1585, 1548, 1481, 1288, 1137, 752, 690.

N-Ethyl-N-phenylimidazo[1,2-*a*]pyridin-3-amine (4g): Following general **procedure**, **4g** was obtained as a yellow oil (0.74 mmol; 175 mg, 99% yield). **Rf** = 0.2 (50% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.73 (dt, J=6.8, 1.2 Hz, 1 H), 7.66 (d, J=8.8 Hz, 1 H), 7.55 (s, 1 H), 7.16 - 7.24 (m, 3 H), 6.82 (tt, J=7.3, 1.0 Hz, 1 H), 6.77 (td, J=6.7, 0.9 Hz, 1 H), 6.52 - 6.62 (m, 2 H), 3.77 (q, J=7.2 Hz, 2 H), 1.29 (t, J=7.2 Hz, 3 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 146.5, 143.1, 129.4, 129.2, 127.4, 124.4, 122.5, 118.8, 118.2, 113.3, 112.1, 46.1, 13.3; **HRMS** (ESI, Pos): calcd for $C_{15}H_{15}N_3$ [M+H]+: 238.1339 m/z, found: 238.1340 m/z; **FTIR** (cm^{-1}) (neat): 2972, 2932, 1596, 1494, 1344, 1254, 1138, 738, 692.

5-Methyl-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4h): Following general **procedure**, **4h** was obtained as a brown oil (0.32 mmol; 68 mg, 93% yield). **Rf** = 0.29 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.31 - 7.41 (m, 2 H), 6.96 (dd, J=9.0, 6.6 Hz, 1 H), 6.40 (d, J=6.8 Hz, 1 H), 3.18 (dt, J=11.2, 3.5 Hz, 2 H), 2.89 (s, 3 H), 2.70 - 2.81 (m, 2 H), 1.59 - 1.92 (m, 5 H), 1.27 - 1.45 (m, 1 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 143.3, 139.1, 136.4, 124.3, 123.5, 115.9, 112.9, 56.1, 25.6, 23.9, 19.3; **HRMS** (ESI, Pos): calcd for $C_{13}H_{18}N_3$ [M+H]+: 216.1495 m/z, found: 216.1502 m/z; **FTIR** (cm^{-1}) (neat): 2931, 2850, 2805, 1507, 1290, 1251, 1143, 774, 732.

5-Bromo-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4i): Following general **procedure**, **4i** was obtained as a brown oil (0.42 mmol; 119 mg, 99% yield). **Rf** = 0.47 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.49 (dd, J=8.7, 1.4 Hz, 1 H), 7.37 (s, 1 H), 6.79 - 7.03 (m, 2 H), 3.14 - 3.39 (m, 2 H), 2.73 (td, J=11.5, 2.7 Hz, 2 H), 1.58 - 1.94 (m, 5 H), 1.28 - 1.49 ppm (m, 1 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 144.0, 139.3, 124.5, 123.5, 118.5, 117.2, 112.4, 55.5, 25.3, 23.9; **HRMS** (ESI, Pos): calcd for $C_{12}H_{15}BrN_3$ [M+H]+: 280.0444 m/z, found: 280.0433 m/z; **FTIR** (cm^{-1}) (neat): 2932, 2849, 2803, 1543, 1477, 1275, 1250, 1148, 770.

6-Methyl-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4j): Following general **procedure**, **4j** was obtained as a brown oil (0.22 mmol; 47 mg, 87% yield). **Rf** = 0.24 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.72 (s, 1 H), 7.46 (d, J=9.4 Hz, 1 H), 7.20 (s, 1 H), 6.97 (dd, J=9.2, 1.7 Hz, 1 H), 2.90 - 3.07 (m, 4 H), 2.35 (s, 3 H), 1.57 - 1.8 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 139.5, 136.2, 128.7, 122.6, 120.2, 117.7, 116.1, 53.0, 26.0, 24.0, 18.4; **HRMS** (ESI, Pos): calcd for $C_{13}H_{18}N_3$ [M+H]+: 216.1495 m/z, found: 216.1506 m/z; **FTIR** (cm^{-1}) (neat): 2934, 2852, 2811, 1653, 1525, 1250, 894, 796, 725.

6-Bromo-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4k): Following general **procedure**, **4k** was obtained as a yellow oil (0.21 mmol; 59 mg, 84% yield). **Rf** = 0.30 (50% Acetone/Hexanes); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.07 (dd, J=1.8, 0.7 Hz, 1 H), 7.45 (dd, J=9.5, 0.7 Hz, 1 H), 7.25 (s, 1 H), 7.17 (dd, J=9.4, 1.9 Hz, 1 H), 2.89 - 3.05 (m, 4 H), 1.52 - 1.86 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 140.0, 136.6, 126.8, 122.5, 121.7, 118.5, 106.7, 53.0, 26.1, 24.0; **HRMS** (ESI, Pos): calcd for $C_{12}H_{14}BrN_3$ [M+H]+: 280.0444 m/z, found: 280.0455 m/z; **FTIR** (cm^{-1}) (neat): 2935, 2851, 2811, 2185, 1381, 1155, 901, 791, 727.

7-Chloro-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4l): Following general **procedure**, **4l** was obtained as a colorless oil (0.12 mmol; 27 mg, 82% yield). **Rf** = 0.35 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.88 (d, J=7.2 Hz, 1 H), 7.53 (d, J=1.1 Hz, 1 H), 7.24 (br. s., 1 H), 6.76 (dd, J=7.2, 1.7 Hz, 1 H), 2.92 - 3.02 (m, 4 H), 1.58 - 1.82 ppm (m, 6 H); **^{13}C NMR** ($CDCl_3$, 176MHz): δ 148.9, 136.9, 132.5, 123.0, 118.5, 115.8, 114.6, 53.0, 26.0, 23.9; **HRMS** (ESI, Pos): calcd for $C_{12}H_{15}ClN_3$ [M+H]+: 236.0949 m/z, found: 236.0939 m/z; **FTIR** (cm^{-1}) (neat): 2936, 2852, 2817, 1650, 1626, 1443, 1281, 793, 731.

8-Phenyl-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4m): Following general **procedure**, **4m** was obtained as an off-white solid (0.48 mmol; 134 mg, 76% yield). **Rf** = 0.32 (30% EtOAc/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.92 - 8.03 (m, 3 H), 7.45 - 7.55 (m, 2 H), 7.37 - 7.44 (m, 1 H), 7.31 (s, 1 H), 7.23 (dd, J=6.9, 1.2 Hz, 5 H), 6.88 (t, J=6.9 Hz, 1 H), 2.95 - 3.09 (m, 4 H), 1.60 - 1.89 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 140.5, 136.7, 136.7, 130.6, 128.9, 128.4, 128.0, 121.7, 121.4, 121.2, 111.6, 53.1, 26.2, 24.2; **HRMS** (ESI, Pos): calcd for $C_{18}H_{19}N_3$ [M+H]+: 278.1652 m/z, found: 278.1663 m/z; **mp** : 96-98 °C; **FTIR** (cm^{-1}) (neat): 2929, 2829, 1450, 1367, 1300, 1147, 748, 693, 573.

8-Methoxy-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4n): Following general **procedure 4n** was obtained as an off-white solid (0.28 mmol; 64 mg, 81% yield). **Rf** = 0.37 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.60 (dd, J=6.8, 0.7 Hz, 1 H), 7.17 (s, 1 H), 6.67 (t, J=7.2 Hz, 1 H), 6.33 - 6.43 (m, 1 H), 3.99 (s, 3 H), 2.90 - 3.05 (m, 4 H), 1.54 - 1.83 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 149.3, 137.3, 136.1, 120.0, 115.4, 111.3, 99.3, 55.7, 53.1, 26.1, 24.1; **HRMS** (ESI, Pos): calcd for $C_{13}H_{18}N_3O$ [M+H]+: 232.1444 m/z, found: 232.1453 m/z; **mp** : 106-110 °C; **FTIR** (cm^{-1}) (neat): 3038, 2927, 2915, 2847, 2805, 1542, 1275, 1069, 737.

2-Ethyl-3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (4o): Following general **procedure**, **4o** was obtained as a brown (0.17 mmol; 38 mg, 46% yield). **Rf** = 0.32 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.02 (dt, J=6.8, 1.2 Hz, 1 H), 7.47 (d, J=9.0 Hz, 1 H), 7.08 (ddd, J=9.0, 6.7, 1.4 Hz, 1 H), 6.74 (td, J=6.7, 1.0 Hz, 1 H), 3.00 - 3.15 (m, 4 H), 2.84 (q, J=7.6 Hz, 2 H), 1.74 (br. s., 6 H), 1.36 (t, J=7.5 Hz, 3 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 140.8, 140.0, 129.8, 123.3, 122.4, 116.7, 111.1, 52.4, 27.2, 24.1, 21.6, 14.7; **HRMS** (ESI, Pos): calcd for $C_{14}H_{19}N_3$ [M+H]+: 230.1652 m/z, found: 230.1654 m/z; **FTIR** (cm^{-1}) (neat): 2932, 2850, 2812, 1557, 1501, 1347, 1223, 753, 738.

3-(Piperidin-1-yl)imidazo[1,2-*a*]pyrimidine (4p): Following general **procedure**, **4p** was obtained as a dark green solid (0.27 mmol; 54 mg, 89% yield). **Rf** = 0.29 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.48 (dd, J=3.9, 2.1 Hz, 1 H), 8.25 (dd, J=6.8, 2.0 Hz, 1 H), 7.40 (s, 1 H), 6.84 (dd, J=6.8, 4.0 Hz, 1 H), 2.86 - 3.12 (m, 4 H), 1.55 - 1.89 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 148.4, 144.7, 134.6, 130.0, 122.7, 107.7, 52.9, 26.0, 24.0; **HRMS** (ESI, Pos): calcd for $C_{11}H_{15}N_4$ [M+H]+: 203.1291 m/z, found: 203.1301 m/z; **mp** : 112-116 °C; **FTIR** (cm^{-1}) (neat): 3060, 2929, 2856, 2793, 2755, 1496, 839, 779, 762.

3-(Piperidin-1-yl)imidazo[1,2-*a*]pyrazine (4q): Following general **procedure**, **4q** was obtained as a brown solid (0.17 mmol; 34 mg, 91% yield). **Rf** = 0.29 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.99 (d, J=1.1 Hz, 1 H), 7.75 - 7.94 (m, 2 H), 7.41 (s, 1 H), 2.93 - 3.10 (m, 4 H), 1.56 - 1.91 (m, 6 H); **^{13}C NMR** (CDCl3, 126MHz): δ 143.8, 137.2, 137.1, 128.6, 123.5, 115.4, 52.5, 25.9, 23.9; **HRMS** (ESI, Pos):

calcd for $C_{11}H_{15}N_4$ [M+H]+: 203.1291 m/z, found: 203.1301 m/z; **mp** : 64-66 °C; **FTIR** (cm^{-1}) (neat): 2935, 2844, 2805, 1528, 1315, 1242, 891, 792, 610.

N-Cyclohexylimidazo[1,2-*a*]pyridin-3-amine (4r): Following general **procedure**, **4r** was obtained as a brown solid (0.29 mmol; 62 mg, 96% yield). **Rf** = 0.18 (10% MeOH/DCM); **^{1}H NMR** ($CDCl_3$, 400MHz): δ 8.03 (d, J=7.0 Hz, 1 H), 7.51 (d, J=9.0 Hz, 1 H), 7.21 (s, 1 H), 7.09 (ddd, J=9.0, 6.7, 1.1 Hz, 1 H), 6.70 - 6.86 (m, 1 H), 2.88 - 3.08 (m, 1 H), 1.98 (d, J=9.7 Hz, 2 H), 1.55 - 1.85 (m, 3 H), 1.07 - 1.39 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 140.3, 130.2, 124.9, 122.9, 118.6, 116.3, 112.5, 56.1, 33.5, 25.7, 24.8; **HRMS** (ESI, Pos): calcd for $C_{13}H_{18}N_3$ [M+H]+: 216.1495 m/z, found: 216.1486 m/z; **mp** : 100-106 °C; **FTIR** (cm^{-1}) (neat): 3174, 2995, 2921, 2852, 1565, 1365, 1120, 735, 724.

General Procedure for the Pd-Catalyzed C-H Arylation of 3-aminoimidazo[1,2-a]pyridine 4a

To a flame-dried 10-mL microwave vial equipped with a magnetic stirrer was added dry cesium carbonate (0.8 mmol; 2 equiv). The vial was dried in a vacuum oven at 200 °C for 16 h. After cooling of the said vial, 3-(piperidin-1-yl)imidazo[1,2-*a*]pyridine (0.4 mmol; 1 equiv) was added in the glovebox. The vial was sealed in the glovebox and 1-iodo-4-(trifluoromethyl)benzene (0.8 mmol; 2 equiv) and freshly distilled DMA (1 mL; 0.5M) were added to the reaction vessel. The resulting mixture was then heated to 150 °C for 24 h, after which the reaction was cooled down to rt and the solids were filtered over a pad of celite. The residue was purified using flash chromatography (0 – 50% Acetone/Hexanes, 24g column) to afford 3-(piperidin-1-yl)-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (**5a**) (75 mg; 55% yield) as a bright yellow oil. **Rf** = 0.49 (40% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 8.11 (d, J=7.0 Hz, 1 H), 8.06 (d, J=7.9 Hz, 2 H), 7.65 - 7.77 (m, 3 H), 7.23 - 7.31 (m, 1 H), 6.90 (t, J=6.7 Hz, 1 H), 3.14 (t, J=5.0 Hz, 4 H), 1.55 - 1.88 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 141.6, 138.3, 135.2, 130.9, 130.1, 129.6, 128.5, 125.1, 124.5, 123.3, 117.9, 111.9, 51.2, 26.9, 24.0; **^{19}F NMR** ($CDCl_3$, 471MHz): δ -62.5; **HRMS** (ESI, Pos): calcd for $C_{19}H_{18}F_3N_3$ [M+H]+: 346.1526 m/z, found: 346.1530 m/z; **FTIR** (cm^{-1}) (neat): 2937, 2851, 1319, 1162, 1115, 1063, 847, 753, 730.

General Procedure for the Ru-Catalyzed C-H Arylation of 3-aminoimidazo[1,2-a]pyridine 4m

To a flame-dried 10-mL microwave vial equipped with a magnetic stirrer and charged with **2m** (0.1 mmol; 1 equiv) was added, in the glovebox, dry potassium carbonate (0.2 mmol; 2 equiv), 2,4,6-trimethylbenzoic acid (0.03 mmol; 0.3 equiv), $[RuCl_2(p\text{-cymene})]_2$ (0.005 mmol, 0.05 equiv) and 4-bromoacetophenone (0.3 mmol; 3 equiv). The vial was sealed with a septum and toluene (0.5 mL; 0.2 M) was added. The resulting mixture was then heated at 150 °C for 15h, after which ethyl acetate was added and the mixture was filtered over a pad of celite and concentrated under reduced pressure. The residue was purified using flash chromatography (0 – 50% EtOAc/Hexanes, 24-g column) to afford 1-(2'-(3-(piperidin-1-yl)imidazo[1,2-*a*]pyridin-8-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (**6a**) (0.091 mmol; 36 mg; 91% yield) as a brown solid. **Rf** = 0.41 (40% Acetone/Petroleum Ether); **^{1}H NMR** ($CDCl_3$, 500MHz): δ 7.86 (dd, J=6.1, 1.9 Hz, 1 H), 7.69 - 7.80 (m, 3 H), 7.45 - 7.55 (m, 3 H), 7.27 - 7.32 (m, 2 H), 7.24 (s, 1 H), 6.28 - 6.82 (m, 2

H), 2.94 - 3.09 (m, 4 H), 2.54 (s, 3 H), 1.55 - 1.89 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 126MHz): δ 197.9, 146.5, 140.9, 140.2, 136.5, 135.1, 135.0, 131.2, 130.3, 130.0, 129.5, 128.4, 127.9, 127.9, 124.9, 121.3, 121.0, 111.3, 53.0, 26.5, 26.1, 24.1; **HRMS** (ESI, Pos): calcd for $C_{26}H_{25}N_3O$ [M+H]+: 396.2070 m/z, found: 396.2074 m/z; **mp** : 70-72 °C; **FTIR** (cm^{-1}) (neat): 2931, 2853, 2810, 2214, 1677, 1259, 917, 721, 594.

ASSOCIATED CONTENT

Supporting Information

NMR spectra, and compound characterization data. 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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