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One-Pot Tandem Amidation, Knoevenagel Condensation and Palladium-Catalyzed Wacker Type Oxidation/C-O Coupling: Synthesis of Chromeno-Annulated Imidazopyridines

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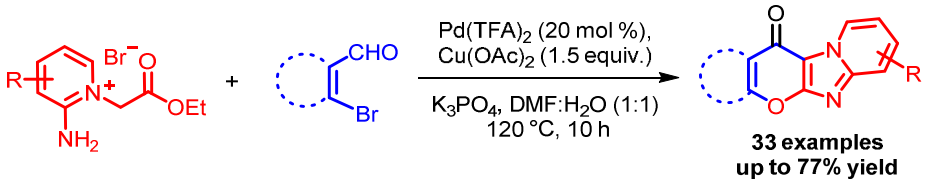


Abstract: A direct one-pot synthesis of chromeno-annulated imidazo[1,2-*a*]pyridines is achieved by the reaction of 2-amino-1-(2-ethoxy-2-oxoethyl)pyridinium salts with 2-bromoarylaldehydes using $Pd(TFA)_2$ as catalyst and $Cu(OAc)_2$ as an oxidant. The overall strategy involves tandem base-mediated amidation and Knoevenagel condensation, followed by palladium-catalyzed Wacker type oxidation and intramolecular C-O coupling reaction. The method is simple, tolerates different functional groups and gives moderate to good yields of chromeno[2',3':4,5]imidazo[1,2-*a*]pyridin-12-one derivatives. The developed tandem reaction was also successfully applied for the synthesis of pyrano-fused imidazo[1,2-*a*]pyridines by using 3-bromo-3-arylacrylaldehydes.

Introduction

Imidazo[1,2-*a*]pyridine is one of the most prominent class of *N*-fused heterocycles which is extensively found in diverse biologically active molecules and organometallics.[1-3] Imidazo[1,2-*a*]pyridine moiety is core structure of several drugs such as alpidem,[4] zolpidem,[5] olprinone,[6] and zolimidine[7] (Figure 1) which are currently available in the market. Due to their wide range of pharmaceutical, biological, and medicinal applications, imidazo[1,2-*a*]pyridine heterocycles

have drawn special attention of organic chemists.[8] Similarly, chromones/chroman-4-ones are oxygen-containing heterocyclic scaffolds classified as privileged structures due to wide range of biological activities displayed by the compounds based on these scaffolds.[9-12] The annulated aromatic systems containing two or more heterocycles are frequently encountered in numerous natural and non-natural drug like products.[9,13,14] The unique architecture of these molecules benefits in their fundamental applications in pharmaceutical fields and development of organic materials. In light of potential biological and functional properties associated with above mentioned two moieties, it is reasonable to prospect that the hybrid of these two privileged structures might be endowed with potent and unique biological activities. Thus synthesis of a heterocyclic system incorporating these 'privileged' fragment is the subject of considerable interest. For example, Proenca and Costa have synthesized chromeno-annulated imidazo[1,2-*a*]pyridines by a domino one-pot reaction of 2-(cyanomethyl)-pyridinium chlorides and salicylaldehydes in aqueous sodium carbonate solution.[15,16] Voskressensky *et al* have synthesized chromeno-annulated imidazo-pyrrolopyridines and imidazocarboline derivatives by base-promoted domino reaction of *o*-hydroxy aryl aldehydes with azaindole-6-cyanomethyl chloride and N^2-(cyanomethyl)-β-carbolinium bromide, respectively.[17,18] They also achieved imidazo[2,1-*a*]isoquinolines-fused chromene derivatives by the base-catalyzed reaction of *N*-cyanomethyl-isoquinolinium salts with *o*-hydroxy aryl aldehydes in a DMF/water mixture.[19,20] Taran and Zou groups have independently prepared imidazo[1,2-*a*]pyridines from 1-(2-ethoxy-2-oxoethyl)-pyridinium salts.[21,22] Although these methods proved successful and allowed facile access to chromeno-annulated imidazoheterocycles, but they suffer from one or more limitations such as narrow substrate scope, moderate yields and longer reaction time. Thus the development of a new protocol for efficient access to chromeno-annulated imidazoheterocycles is highly desirable.

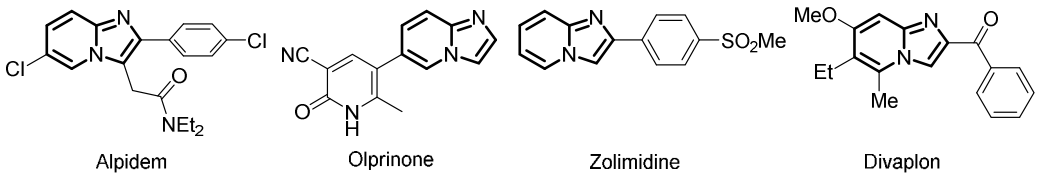


Figure 1: Selected drugs containing imidazo[1,2-*a*]pyridine scaffold.

On the other hand, domino processes also known as cascade or tandem reactions that involve simultaneous formation of multiple new C-C/C-heteroatom bond and generate high levels of diversity and complexity under the same reaction conditions have become very attractive and highly desirable in organic synthesis.[23-25] These methods reduce generation of chemical waste and reaction time. Transition metal catalyzed tandem reactions and in particular, palladium-catalyzed domino transformations are an elegant approach to synthesize complex molecular scaffolds.[26]

As part of our ongoing interest in developing synthetic methods for the preparation of fused imidazo[1,2-*a*]pyridines[27-30] and on exploration of 2-aminopyridinium salts in the synthesis of fused-heterocycles,[31] we envisioned that a tandem reaction of 2-amino-1-(2-ethoxy-2-oxoethyl)pyridin-1-ium bromide with 2-bromoarylaldehydes in the presence of a base and palladium catalyst could give less explored chromene-annulated imidazo[1,2-*a*]pyridine derivatives (Figure 2). Herein, we report our results for a one-pot synthesis of chromeno-annulated imidazo[1,2-*a*]pyridine *via* tandem amidation, Knoevenagel condensation, palladium catalyzed Wacker type oxidation and C-O coupling reactions.

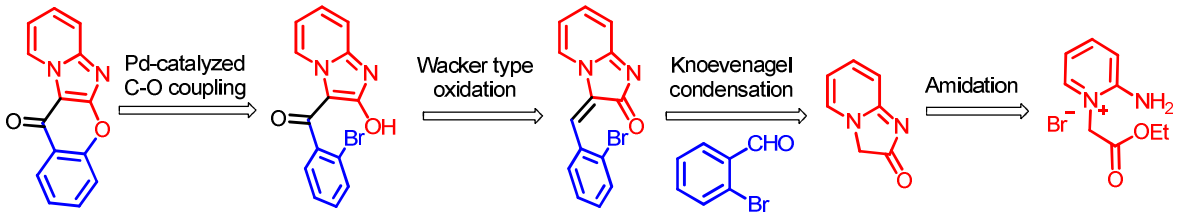


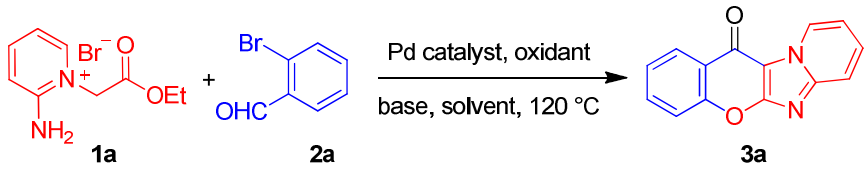
Figure 2. Schematic representation of the domino reactions for the synthesis of chromeno-annulated imidazo[1,2-*a*]pyridine

Results and discussion

We initiated our study with a model reaction of **1a** and **2a** in the presence of $Pd(OAc)_2$ (10 mol %) and $Cu(OAc)_2$ (2 equiv.) and K_2CO_3 (2.5 equiv.) in DMF at 120 °C for 10 h under air. To our satisfaction, the 12*H*-chromeno[2',3':4,5]imidazo[1,2-*a*]pyridin-12-one **(3aa)** was obtained in 48% isolated yield (Table 1, entry 1). This encouraging result indicated the feasibility of the envisioned tandem reaction. Thus, we went on to optimize the reaction conditions by varying different catalysts, oxidants, bases, and solvents, *etc*. for the model reaction (Table 1). The replacement of K_2CO_3 base with various other inorganic (KOH, Cs_2CO_3, *t*-BuOK) and organic (DBU) bases demonstrated somewhat lower efficiency compared with K_2CO_3 (entries 2−5). However, improved yield (61%) of **3aa** was observed when the reaction was carried out with K_3PO_4 (entry 6). We further examined the performance of the reaction with a series of palladium catalysts such as $PdCl_2$, $Pd(TFA)_2$ and $PdCl_2(dppf)_2$ in the presence of $Cu(OAc)_2$ and K_3PO_4 (entries 7-9) and to our satisfaction slightly better yield (67%) was obtained with $Pd(TFA)_2$ as compared to $Pd(OAc)_2$. A sharp decrease in the yield of **3aa** was observed when the reaction was performed in the presence of other oxidants such as IBD, oxone, $AgNO_3$, AgOAc and Ag(TFA) (entries 10-14). In other polar solvents like DMA, DMF: H_2O and PEG-400 moderate yields of **3aa** (48-69%) were obtained, whereas poor yield of **3aa** was obtained in DMSO (entries 15-18), Desired transformation did not occur in non-polar solvents such as toluene and dioxane (entry 19-20). It is also worth mentioning that the yield of **3aa** decreased when the reaction was performed under inert atmosphere (entry 21). Decreasing the loading of $Cu(OAc)_2$ lead to decrease in the yield of **3aa** (entries 22-23). In the absence of $Pd(TFA)_2$, no reaction was observed (entry 24) while in the absence of $Cu(OAc)_2$ only 10% of **3aa** was formed (entry 25). This observation showed that presence of both $Cu(OAc)_2$ and $Pd(TFA)_2$ is necessary for the success of this reaction. Finally, the best yield of **3aa** (77%) was obtained from the reaction of **1a**

(2 equiv.) with **2a** (1 equiv.) in the presence of $Pd(TFA)_2$ (10 mol %), $Cu(OAc)_2$ (2.0 equiv.) in DMF: H_2O (1: 1 *v/v*) at 120 °C for 10 h under air (entry 26).

Table 1: Optimization of the reaction condition.[a]



1a **2a** **3a**

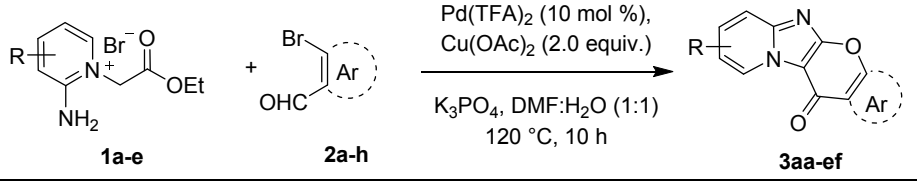
Entry	Pd catalyst	Oxidant	Base	Solvent	% Yield of **3a**[b]
1.	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	DMF	48
2.	$Pd(OAc)_2$	$Cu(OAc)_2$	KOH	DMF	36
3.	$Pd(OAc)_2$	$Cu(OAc)_2$	Cs_2CO_3	DMF	38
4.	$Pd(OAc)_2$	$Cu(OAc)_2$	DBU	DMF	15
5.	$Pd(OAc)_2$	$Cu(OAc)_2$	*t*-BuOK	DMF	36
6.	$Pd(OAc)_2$	$Cu(OAc)_2$	K_3PO_4	DMF	61
7.	$PdCl_2$	$Cu(OAc)_2$	K_3PO_4	DMF	32
8.	$PdCl_2(dppf)_2$	$Cu(OAc)_2$	K_3PO_4	DMF	30
9.	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	DMF	67
10.	$Pd(TFA)_2$	IBD	K_3PO_4	DMF	5
11.	$Pd(TFA)_2$	Oxone	K_3PO_4	DMF	8
12.	$Pd(TFA)_2$	$AgNO_3$	K_3PO_4	DMF	Trace
13.	$Pd(TFA)_2$	AgOAc	K_3PO_4	DMF	30
14	$Pd(TFA)_2$	Ag(TFA)	K_3PO_4	DMF	10
15.	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	DMA	48
16.	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	DMF: H_2O[c]	69
17.	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	PEG-400	50
18.	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	DMSO	25
19.	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	Dioxane	NR
20	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	Toluene	Trace
21.	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	DMF	52[d]
22	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	DMF	27[e]
23	$Pd(TFA)_2$	$Cu(OAc)_2$	K_3PO_4	DMF	50[f]
24	-	$Cu(OAc)_2$	K_3PO_4	DMF	NR
25	$Pd(TFA)_2$	-	K_3PO_4	DMF	10
26.	**$Pd(TFA)_2$**	**$Cu(OAc)_2$**	**K_3PO_4**	**DMF: H_2O[c]**	**77[g]**

[a]Reaction conditions: **1a** (0.54 mmol), **2a** (0.54 mmol) Pd catalyst (10 mol %), oxidant (2.0 equiv.), base (2.5 equiv.), solvent (8 mL), 120 °C, 10 h under open air; [b]Isolated yields; [c]DMF: H_2O (1: 1 *v/v*); [d]Reaction performed under N_2 atm; [e]1.0 equiv. of $Cu(OAc)_2$ was used; [f]1.5 equiv. of $Cu(OAc)_2$ was used; [g]2.0 equiv. of **1a** was used.

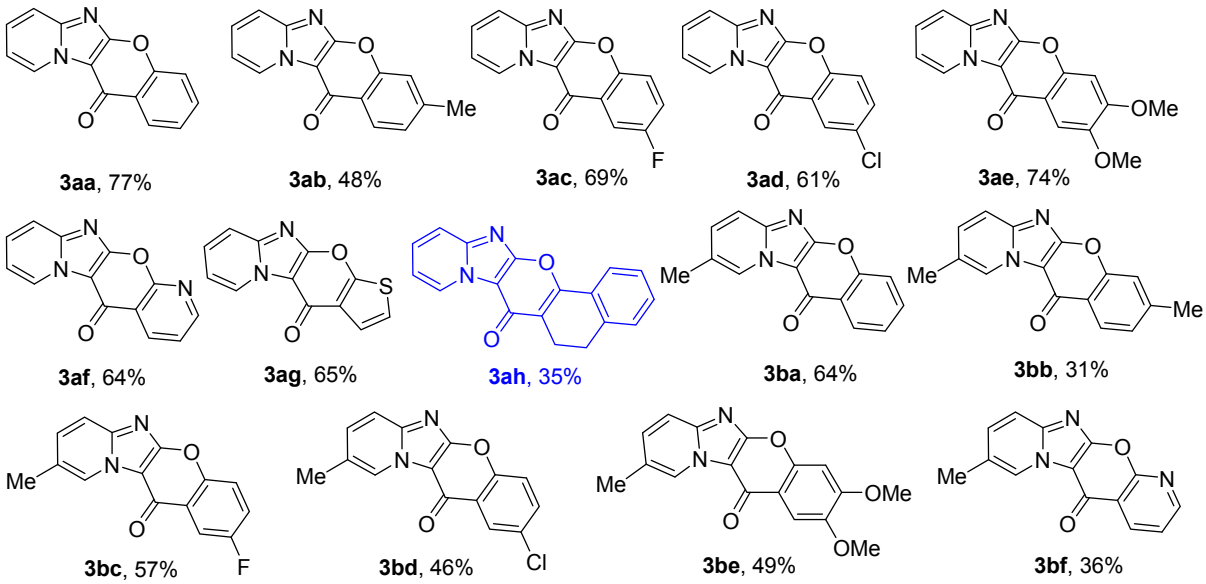
With the optimized condition in hand, we embarked on investigation of the scope and limitation of the methodology. As shown in table 2, different substituted 2-aminopyridinium salts (**1**) reacted smoothly with 2-bromoarylaldehydes (**2**) to give corresponding chromeno-annulated imidazo[1,2-*a*]pyridines (**3**) in moderate to good yield (28-77%) under standardized conditions. First scope of the tandem process was evaluated by using different 2-bromo-arylaldehydes (**2a-e**) having substituents such as methyl, fluoro, chloro, *etc.* No significant electronic influence was observed on the yield of **3aa**. Interestingly, heteroaromatic aldehydes 2-bromopyridine-3-carbaldehyde (**2f**) and 2-bromothiophene-3-carbaldehyde (**2g**) also reacted to furnish corresponding chromeno-fused imidazo[1,2-*a*]pyridines **3af** and **3ag** in 64% and 65% yields, respectively. Finally, 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde (**2h**) was reacted with 2-aminopyridinium salts **1a** to give corresponding 5,6-dihydro-7H-benzo[7',8']chromeno[2',3':4,5]imidazo[1,2-*a*]pyridin-7-ones (**3ah**) in 35% yield. Next, scope of 2-aminopyridinium salts was examined. It was found that the substituents on the pyridine ring of 2-aminopyridinium salts significantly influenced the reaction outcome. For example, slightly lower yields of the desired product were obtained from the C-5 substituted 2-aminopyridinium salts as compared to the unsubstituted or C-3-substituted 2-aminopyridinium salts. Along with formation of the desired chromeno-annulated imidazo[1,2-*a*]pyridines, cleavage of salts leading to *N*-acetyl-2-aminopyridine derivatives (**7d** and **7e**) was observed in case of the 5-substituted 2-aminopyridinium salts (**3d** and **3e**). On the other hand, 5-nitro-2-aminopyridinium salt failed to give desired product under these conditions. Structures of all the synthesized compounds were elucidated by IR, ^{1}H NMR, ^{13}C NMR and HRMS data (See supporting information). The exact structure of the product **3cd** (CCDC 1585320) was unambiguously determined by single X-ray diffraction analysis (Figure 3). The molecular structure of **3cd** is planar in nature with all four

fused rings including the substituted atoms such as chlorine, oxygen atom of the carbonyl group and the carbon atom of the methyl group.

Table 2: Substrate scope for synthesis of chromeno-annulated imidazo[1,2-*a*]pyridines.[a,b]



1a-e **2a-h** **3aa-ef**



3aa, 77% **3ab**, 48% **3ac**, 69% **3ad**, 61% **3ae**, 74%

3af, 64% **3ag**, 65% **3ah**, 35% **3ba**, 64% **3bb**, 31%

3bc, 57% **3bd**, 46% **3be**, 49% **3bf**, 36%

3ca, 62% **3cb**, 34% **3cc**, 65% **3cd**, 59% **3ce**, 58%

3cf, 68% **3cg**, 63% **3ch**, 37% **3da**, 48%

3db, 28% **3ea,** 55% **3ef**, 50%

[a]Reaction conditions: **1** (1.08 mmol), **2** (0.54 mmol), $Pd(TFA)_2$ (18 mg, 0.054 mmol), $Cu(OAc)_2$ (216 mg, 1.08 mmol), K_3PO_4 (286 mg, 1.351 mmol), DMF: H_2O (8 mL, *v/v*), 120 °C, 10 h under open air; [b]Isolated yields.

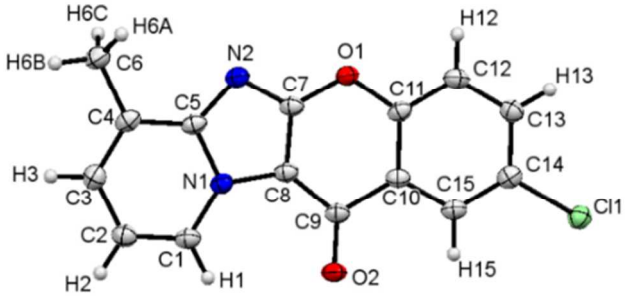
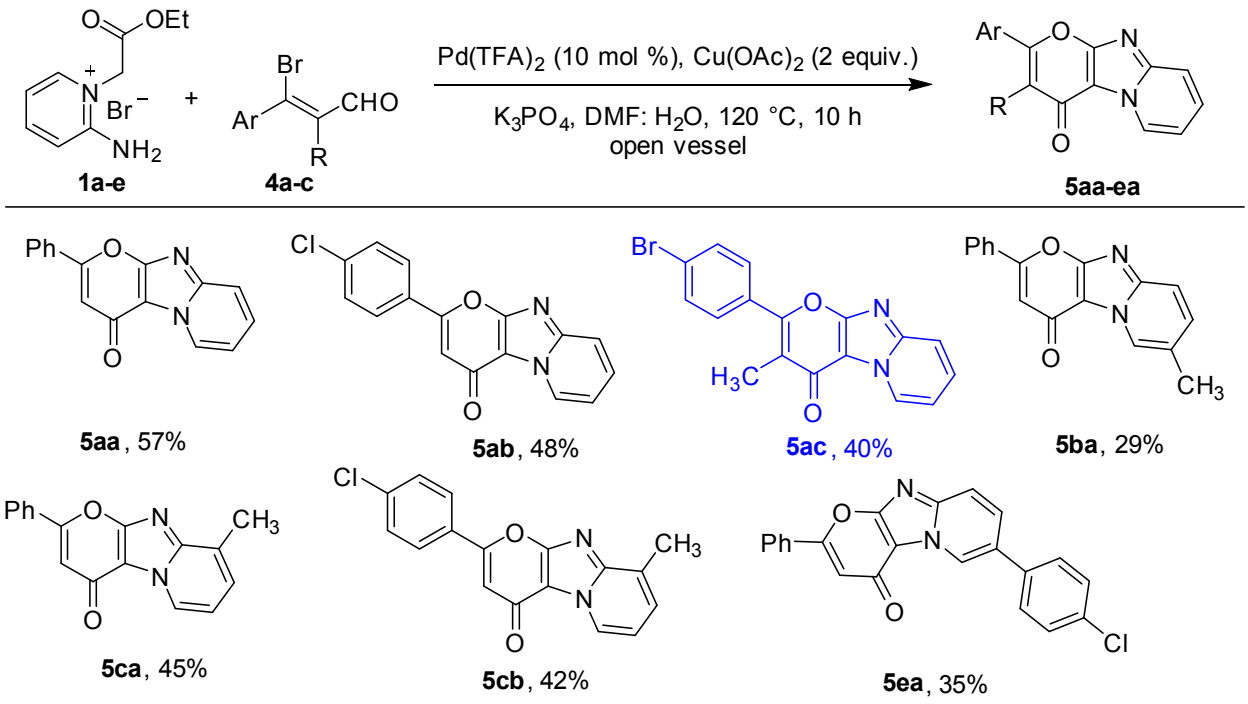


Figure 3: ORTEP diagram of **3cd**. The displacement ellipsoids are drawn at 50% probability level.

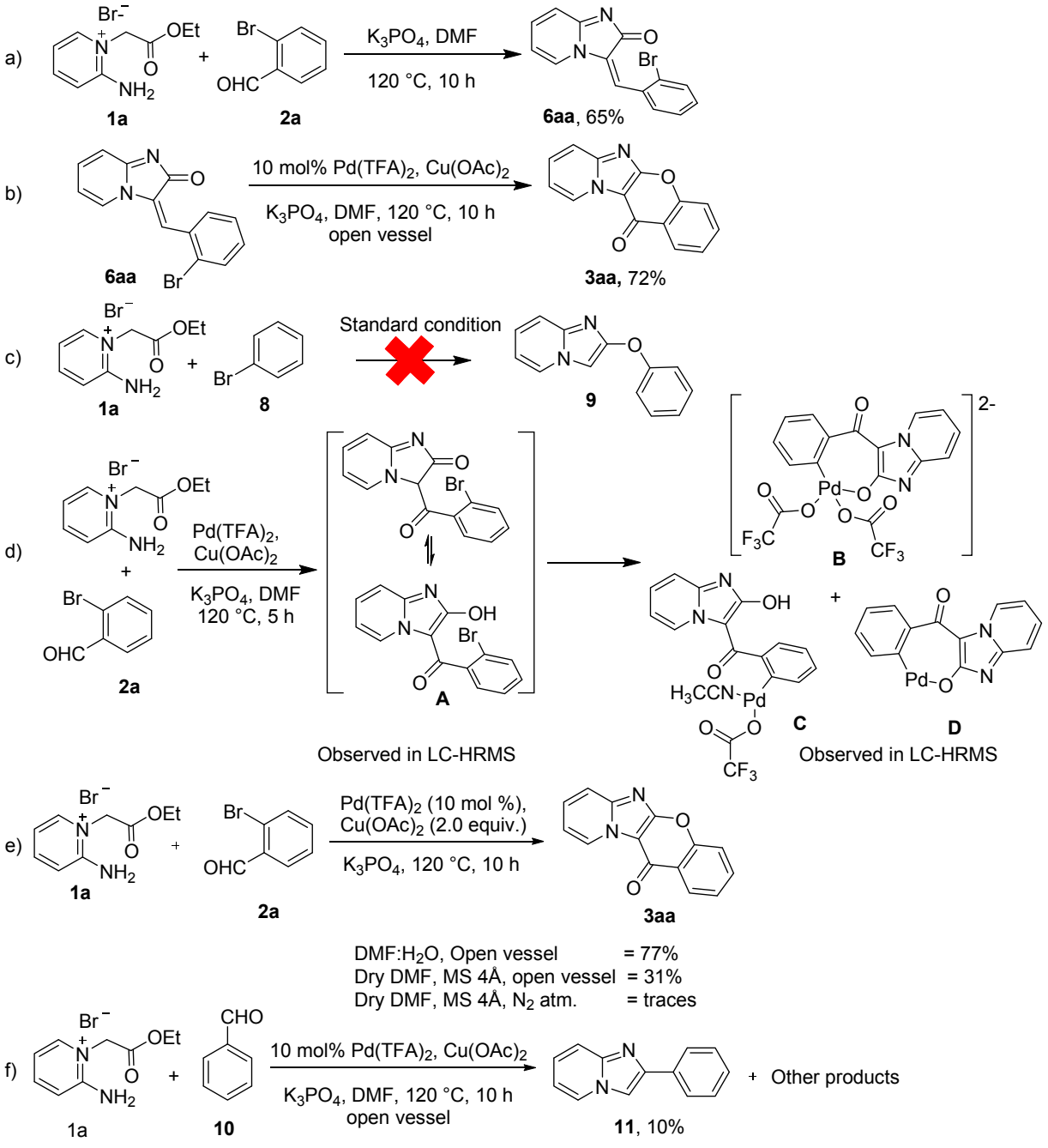
The compatibility of the method was further explored by reacting 2-amino-1-(2-ethoxy-2-oxoethyl)pyridinium salts (**1a-e**) with 3-bromo-3-arylacrylaldehydes (**4a-b**) and 3-bromo-3-(4-bromophenyl)-2-methylacrylaldehyde (**4c**) (Table 3). The tandem reaction worked successfully to give pyrano[2',3':4,5]imidazo[1,2-*a*]pyridin-4-ones (**5aa-ea**) in moderate (29-57%) yields.

Table 3: Synthesis of pyrano[2',3':4,5]imidazo[1,2-*a*]pyridin-4-ones (**5**).[a,b]



[a]Reaction conditions: **1** (1.08 mmol), **2** (0.54 mmol), $Pd(TFA)_2$ (18 mg, 0.054 mmol), $Cu(OAc)_2$ (216 mg, 1.08 mmol), K_3PO_4 (286 mg, 1.351 mmol), DMF: H_2O (8 mL, *v/v*),120 °C, 10 h under open air; [b]Isolated yields.

Some controlled experiments were carried out in order to gain better understanding of the mechanism and are presented in Scheme 1. Initially, reaction of **1a** and **2a** under standard reaction conditions without the addition of palladium catalyst resulted in the formation of 3-(2-bromobenzylidene)imidazo[1,2-*a*]pyridin-2(3H)-one (**6aa**) in 65% yield (Scheme 1, a).

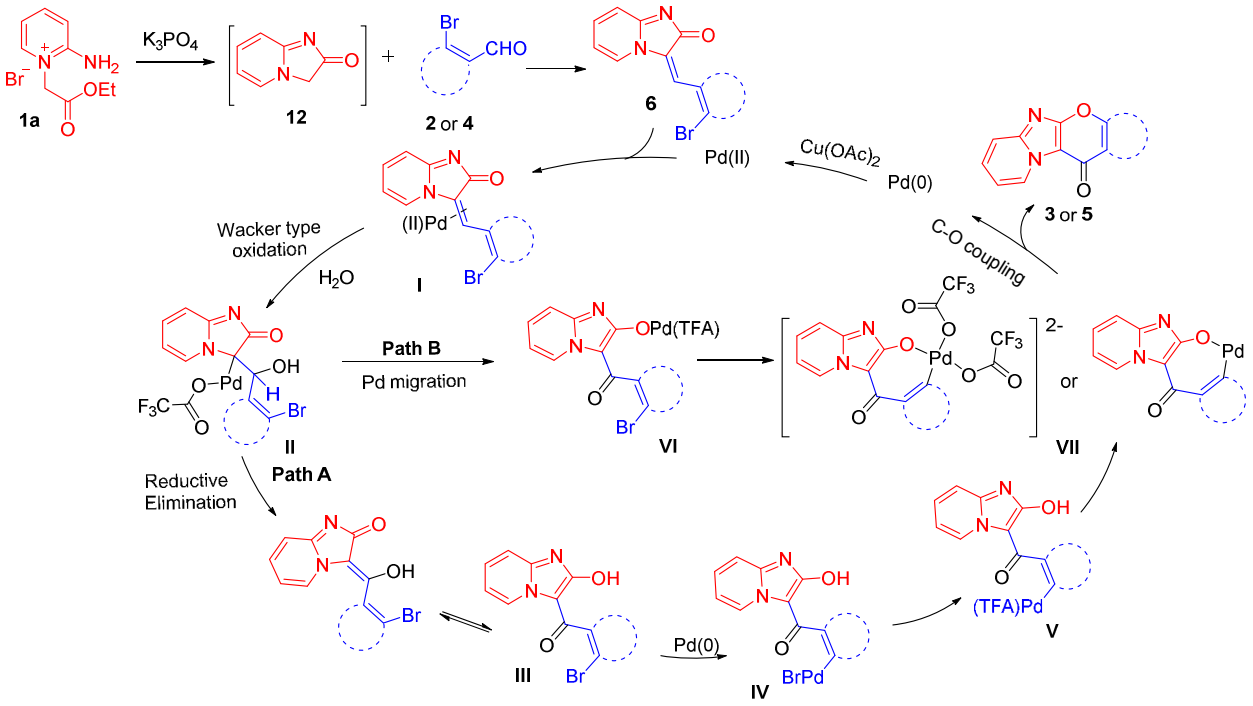


Scheme 1 Controlled experiments

Next, treatment of isolated **6aa** with $Pd(TFA)_2$ under the standard reaction conditions resulted in the formation of **3aa** in 72% yield (Scheme 1, b). This indicated that the reaction proceeds through **6aa**. Reaction of **1a** and bromobenzene (**8**) under optimized reaction condition did not occur to give 2-phenoxyimidazo[1,2-*a*]pyridine (**9**) which indicated that *O*-arylation is not taking place in the tandem reaction (Scheme 1, c). Further, aliquots of reaction between **1a** and **2a** under standard reaction conditions at different time intervals were diluted with acetonitrile and analyzed by LC-HRMS isocratic method using acetonitile-water as eluent. Peaks corresponding to the mass of intermediates **A**, **B**, **C** and **D** were observed at *m/z* 316.9921 (clcd for $C_{14}H_{10}BrN_2O_2$ 316.9926), 568.9393 (clcd for $C_{18}H_9F_6N_2O_6Pd$ 568.9400), 497.9824 (clcd for $C_{18}H_{12}F_3N_3O_4Pd$ 497.9893) and 364.9524 (clcd for $C_{14}H_8N_2O_2PdNa$ 364.9518), respectively in HRMS spectrum (Scheme 1, d) indicating that the tandem reaction might be proceeding through these intermediates. Finally, reaction of **1a** and **2a** under optimized reaction conditions using i) anhydrous DMF in the presence of molecular sieves (MS 4Å) and ii) anhydrous DMF in the presence of MS 4Å under nitrogen atmosphere led to drastic decrease in the yield of **3aa** (Scheme 1, e). This indicates that oxygen and H_2O play very important role in the tandem reaction. Reaction of **1a** with benzaldehyde (**10**) resulted in the formation of 2-phenylimidazo[1,2-*a*]pyridine (**11**) in 10% yield along with other unidentified products (Scheme 1, f). Formation of **11** from **1a** may be proceeding in a similar fashion as reported by Katritzky group from 2-amino-1-[α-benzotriazol-1-ylmethyl]pyridinium chlorides.[32]

Although exact mechanism for the tandem reaction is unclear, based on the experimental results and literature a plausible pathway for the formation of **3** or **5** from **1** is proposed in scheme 2. Initially, base catalyzed intramolecular amidation of 2-aminopyridinium salt **1** gives imidazo[1,2-*a*]pyridin-2(3H)-one (**12**) which on Knoevenagel condensation with 2-bromoaldehyde (**2** or **4**) affords intermediate **6**.[33] The intermediate **6** then coordinates with Pd(II)

to give **I** which then on reaction with water produces **II** via Wacker type oxidation.[34-37] Intermediate **II** may lead to formation of palladacycle **VII** either through **path A** or **path B**. In path B, palladium migrates to give intermediate **VI** which then results in the formation of **VII** (observed in HRMS, Scheme 1, d). In path A, reductive elimination of **II** lead to formation of **III**. Oxidative addition to Pd(0) leads to formation of intermediate **IV** which on exchange of bromide with trifluroacetate leads to formation of **V** (observed in HRMS, Scheme 1, d). Intermediate **V** converts to intermediate **VII** which on reductive elimination leads to the formation of C-O bond and gives cyclized product **3** or **5**.[38]



Scheme 2. Proposed mechanism

CONCLUSION

In summary, we have developed a new synthetic methodology to access less explored chromeno annulated imidazo[1,2-*a*]pyridines through a one-pot tandem reaction of 2-amino-1-(2-ethoxy-2-oxoethyl)pyridinium salts with 2-bromoarylaldehydes. The reaction involves tandem intramolecular amidation, Knoevenagel condensation followed by palladium-catalyzed Wacker

type oxidation and intramolecular C-O coupling reactions. Compared with previously reported methods, this protocol is versatile, tolerates different functional groups and gives moderate to good yields of chromeno[2',3':4,5]imidazo[1,2-*a*]pyridin-12-one derivatives.

EXPERIMENTAL SECTION

General. All reagents and solvents were purchased from commercial sources and used without further purification. Melting points were measured using an automatic capillary point apparatus and are uncorrected. The thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60-F_{254} and a UV-lamp was used as visualizing agent. Column chromatography was performed using silica gel (100-200 mesh) and hexane and ethyl acetate were used as eluents. The ^{1}H and ^{13}C NMR spectra were obtained on 400 MHz and 100 MHz spectrometer. Coupling constant and chemical shifts were reported in hertz (Hz) and parts per million (ppm) respectively, relative to the internal standard of tetramethylsilane (TMS). IR spectroscopy was performed as a neat sample on a FT-IR instrument and values are expressed in cm^{-1}. The HRMS were analyzed by electrospray ionization (ESI) method in positive mode on a Q-TOF LC-MS spectrometer. Synthesis of β-bromo-α,β-unsaturated aldehydes (**2h**, **4a-c**) was achieved from the reaction of corresponding ketones and $POBr_3$ following literature method.[39]

General Procedure for the Synthesis of 2-Aminopyridinium Bromides (1): An oven dried round bottom (RB) flask was charged with 2-aminopyridine (0.500 g, 5.31 mmol) and tetrahydrofuran (15 mL). The RB flask was capped with rubber septum and after purging N_2 gas, ethyl bromoacetate (1.33 g, 7.96 mmol) was added *via* syringe and stirred the reaction mixture under N_2 gas atmosphere at 0 °C. The temperature of the reaction mixture was slowly raised to room temperature and stirred for 8 h to obtain pink colored precipitate. After complete consumption of 2-aminopyridine as monitored by thin layer chromatography, reaction mixture was filtered and residue was washed with diethyl ether to provide pure solid compound.

2-Amino-1-(2-ethoxy-2-oxoethyl)pyridin-1-ium bromide ***1a***. Pink solid (1.3 g, 93%); mp. Decomposed after 200 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.74 (s, 1H), 8.08-8.07 (m, 1H), 7.99 – 7.75 (m, 1H), 7.20 (d, J = 8.1 Hz, 1H), 7.01 – 6.75 (m, 1H), 5.22 (s, 2H), 4.17 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 155.1, 143.3, 140.8, 115.4, 113.1, 62.4, 54.2, 14.4. FT-IR ν_{max} (neat) 3286, 3062, 1739, 1651, 1577, 1338, 1126, 1099, 771 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_9H_{13}N_2O_2^+$ $[M\text{-}Br]^+$ 181.0972, found 181.0970.

2-Amino-5-methyl-1-(2-ethoxy-2-oxoethyl)pyridin-1-ium bromide ***1b***. Pink solid (1.2 g, 96%); mp. 280-282 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 1H), 7.89 (s, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.09 (d, J = 9.1 Hz, 1H), 5.12 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.15 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 153.7, 145.5, 138.2, 122.3, 115.2, 62.4, 54.0, 16.8, 14.4; FT-IR ν_{max} (neat) 3329, 3290, 3124, 1743, 1658, 1523, 1373, 1211, 1022, 759 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{10}H_{15}N_2O_2^+$ $[M\text{-}Br]^+$ 195.1128, found 195.1135.

2-Amino-3-methyl-1-(2-ethoxy-2-oxoethyl)pyridin-1-ium bromide ***1c***. Pink solid (1.2 g, 96%); mp. 296-298 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.35 (s, 2H), 8.04 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.04 – 6.77 (m, 1H), 5.32 (s, 2H), 4.20 (q, J = 7.7 Hz, 2H), 2.26 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 154.2, 142.2, 138.9, 124.0, 112.8, 62.4, 54.8, 18.0, 14.4; FT-IR ν_{max} (neat) 3286, 3070, 1743, 1666, 1585, 1342, 1219, 1022, 767 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{10}H_{15}N_2O_2^+$ $[M\text{-}Br]^+$ 195.1128, found 195.1128.

2-Amino-1-(2-ethoxy-2-oxoethyl)-5-phenylpyridin-1-ium bromide ***1d***. Pink solid (0.90 g, 90%); mp. 285-287 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.79 (s, 2H), 8.53 (s, 1H), 8.36 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.2 Hz, 2H), 7.44 (d, J = 7.0 Hz, 1H), 7.25 (d, J =

9.2 Hz, 1H), 5.25 (s, 1H), 4.23 (q, *J*= 6.7 Hz, 2H), 1.27 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 154.1, 142.0, 138.1, 134.2, 129.7, 128.9, 126.3, 125.3, 115.8, 62.5, 54.5, 14.4; ; FT-IR ν_{max} (neat) 3271, 3244, 3074, 1751, 1662, 1346, 1288, 1095, 759 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{17}N_2O_2^+$ $[M\text{-}Br]^+$ 257.1287, found 257.1306.

2-Amino-5-(4-chlorophenyl)-1-(2-ethoxy-2-oxoethyl)pyridin-1-ium bromide ***1e***. Off white solid, (0.86 g, 95%); mp. 180-182 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 2H), 8.57 (d, *J* = 1.6 Hz, 1H), 8.35 (dd, *J* = 9.3, 1.8 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 9.3 Hz, 1H), 5.23 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 154.2, 141.7, 138.3, 133.7, 133.1, 129.7, 128.1, 125.2, 124.0, 115.8, 62.5, 54.5, 14.4; FT-IR ν_{max} (neat) 3271, 3244, 3074, 1747, 1662, 1539, 1342, 1207, 1161, 1095, 813,752 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{16}ClN_2O_2^+$ $[M\text{-}Br]^+$ 291.0895 found 291.0878.

2-Amino-1-(2-ethoxy-2-oxoethyl)-5-nitropyridin-1-ium bromide ***1f***. Off white solid, (0.25 g, 23%); mp. 135-138 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (bs, 1H), 9.42 (s, 1H), 8.55 (d, *J* = 9.4 Hz, 1H), 7.27 (d, *J* = 9.8 Hz, 1H), 5.31 (s, 2H), 4.23 (q, *J* = 6.7 Hz, 2H), 1.27 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 156.6, 141.8, 136.3, 135.4, 115.8, 62.6, 55.0, 14.4; FT-IR ν_{max} (neat) 3325, 3147, 1762, 1658, 1543, 1361, 1215, 1168, 1053, 991,783 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_9H_{12}N_3O_4^+$ $[M\text{-}Br]^+$ 226.0822, found 226.0809.

General procedure for the synthesis of β-bromo-α,β-unsaturated aldehydes[39]: A dry round bottom flask was charged with $POBr_3$ (3 equiv.) in $CHCl_3$ at 0 °C under N_2 atmosphere. To this cooled solution, *N,N*-dimethylformamide (6 equiv.) was added drop wise over 10 min. and stirred at room temperature for 45-60 min. Over the time, white precipitate was observed. To this mixture, ketone (1 equiv.) dissolved in $CHCl_3$ was added at 0 °C and then the resulting reaction mixture was stirred for 10-15 h at 60 °C. After complete consumption of ketone as monitored by

thin layer chromatography, reaction mass was poured in ice-cold water and the aqueous layer was neutralized with solid K_2CO_3 and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $NaSO_4$, filtered, and concentrated in rotatory evaporator. The crude product obtained was subjected to column chromatography using SiO_2 and EA: hexane (5: 95 *v/v*) as eluting mixture to afford the β-bromo-α,β-unsaturated aldehydes.

1-Bromo-3,4-dihydronaphthalene-2-carbaldehyde ***2h***. Yellow solid (0.580 g, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.92 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.43 – 7.31 (m, 2H), 7.22 (ddd, *J* = 5.9, 2.1, 1.0 Hz, 1H), 2.86 (dd, *J* = 9.2, 6.7 Hz, 2H), 2.71 – 2.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.14, 139.07, 138.95, 134.56, 133.03, 131.36, 128.75, 127.61, 127.15, 27.20, 22.91; FT-IR ν_{max} (neat): 2864, 1682, 1570, 1500, 1220, 1149, 1040, 847, 712 cm^{-1}; HRMS (APCI-TOF, *m/z*): calcd for $C_{11}H_{10}BrO$ $[M + H]^+$ 236.9910, 238.9890; found 236.9901, 238.9881.

3-Bromo-3-(4-bromophenyl)-2-methylacrylaldehyde ***4c*****.** Yellow liquid (0.550 g, 76%); ^{1}H NMR (400 MHz, $CDCl_3$: 10:1 mixture of (E)/(Z)-isomers) signals of (E)-isomer: δ 9.42 (s, 1 H, CHO), 7.74–7.48 (m, 2 HAr), 7.38–7.04 (m, 2 HAr), 2.11 (s, 3 H, Me); additional signals of (Z)-isomer: δ = 10.21 (s, CHO), 1.80 (s, Me); ^{13}C NMR (100 MHz, $CDCl_3$; 10:1 mixture of (E)/(Z)-isomers): δ = 193.95 (Z), 188.34 (E), 146.12 (E), 139.84 (E), 138.23 (Z), 137.61 (Z), 136.54 (E), 135.05 (Z), 131.78 (Z), 131.72 (E), 131.44 (E), 129.99 (Z), 124.65 (E), 124. 10 (Z), 16.43 (E), 14.85 (Z); FT-IR ν_{max} (neat): 2862, 1673, 1598, 1504, 1229, 1159, 1027, 906, 872, 835, 702 cm^{-1}; HRMS (APCI-TOF, *m/z*): calcd for $C_{10}H_9Br_2O$ $[M + H]^+$ 302.9015, 304.8994; found 302.8998, 304.8976.

Representative Procedure for the Synthesis of Chromeno/pyrano-Annulated Imidazo[1,2-*a*]pyridine (3 & 5). An oven-dried 10 mL round bottom flask was charged with 2-amino-1-(2-

ethoxy-2-oxoethyl)pyridin-1-ium bromide (0.282 g, 1.081 mmol), 2–bromoaldehyde (0.100 g, 0.540 mmol), K_3PO_4 (0.286 g, 1.351 mmol), $Cu(OAc)_2$ (0.216 g, 1.08 mmol), and $Pd(TFA)_2$ (0.018 g, 0.054 mmol) in DMF: H_2O (8 mL, *v/v*). The resulting reaction mixture was heated at 120 °C for 10 h. The reaction was monitored by TLC over the time. On completion, the reaction mass was cooled to ambient temperature, diluted with ice cold water (20 mL), extracted with ethyl acetate (2 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude residue was subjected to column chromatography (30% EtOAc: hexane) to afford **3aa** in 77% (98 mg) yield.

12H-Chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3aa***. Cream colored solid (0.098 g, 77%); MP 289 – 291 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, *J* = 6.6 Hz, 1H), 8.43 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.70-7.67 (m, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 161.3, 154.6, 145.3, 133.3, 131.0, 128.7, 125.9, 124.5, 123.8, 118.3, 116.8, 114.3, 107.6; FT-IR ν_{max} (neat) 3093, 1643, 1604, 1442, 1249, 1111, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{14}H_9N_2O_2$ $[M + H]^+$ 237.0659, found 237.0660.

3-Methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ab.*** Cream colored solid (0.060 g, 48%); MP 266 – 268 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 – 9.41 (m, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 7.81- 7.78 (m, 1H), 7.71 – 7.63 (m, 1H), 7.49 (s, 1H), 7.31 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.21 (td, *J* = 6.9, 1.1 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.3, 152.9, 145.5, 133.3, 131.4, 130.5, 128.8, 125.5, 125.0, 119.9, 116.9, 114.5, 107.5, 21.8; FT-IR ν_{max} (neat) 1643, 1612, 1442, 1381, 1249, 1111, 762 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{11}N_2O_2$ $[M + H]^+$ 251.0815, found 251.0815.

2-Fluoro-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ac.*** Cream colored solid (0.086 g, 69%); MP 234-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (dt, *J* = 6.7, 1.1 Hz, 1H),

8.06 (dd, *J* = 8.4, 3.1 Hz, 1H), 7.80 (dt, *J* = 9.0, 1.0 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.46 (ddd, *J* = 9.1, 7.4, 3.2 Hz, 1H), 7.24 (td, *J* = 6.9, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1 (d, *J* = 2.2 Hz), 161.4, 160.4, 158.0, 150.6, 145.5, 131.3, 128.8, 125.1 (d, *J* = 7.2 Hz), 121.0 (d, *J* = 25.1 Hz), 120.1 (d, *J* = 8.1 Hz), 115.7 (d, *J* = 242.7 Hz), 111.2 (d, *J* = 24.3 Hz), 107.3; FT-IR ν_{max} (neat) 3060, 1643, 1620, 1450, 1319, 1242, 1134, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{14}H_8FN_2O_2$ $[M + H]^+$ 255.0564, found 255.0566.

2-Chloro-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ad.*** Cream colored solid (0.075 g, 61%); MP 261 – 263 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 6.4 Hz, 1H), 8.38 (s, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.25 (t, *J* = 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.3, 152.9, 145.5, 133.3, 131.4, 130.5, 128.8, 125.5, 125.0, 119.9, 116.9, 114.5, 107.5; FT-IR ν_{max} (neat) 2916, 1635, 1612, 1442, 1372, 1249, 1026, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{14}H_8ClN_2O_2$ $[M + H]^+$ 271.0269, found 271.0271.

2,3-Dimethoxy-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ae.*** Cream colored solid (0.089 g, 74%); MP 280 – 282 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 6.6 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.76 (s, 1H), 7.69 – 7.62 (m, 1H), 7.21 (dd, *J* = 10.2, 3.5 Hz, 1H), 7.13 (s, 1H), 4.06 (s, 3H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 161.0, 153.8, 150.3, 146.8, 144.8, 130.5, 128.6, 116.7, 116.5, 114.0, 105.0, 100.4, 56.5, 56.41; FT-IR ν_{max} (neat) 2916, 1635, 1612, 1442, 1372, 1249, 1026, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{16}H_{13}N_2O_4$ $[M + H]^+$ 297.0870, found 297.0866.

Pyrido[2'',3'':5,6]-5H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-5-one ***3af.*** Yellow solid (0.081 g, 64%); MP >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, *J* = 6.6 Hz, 1H), 8.82 (dd, *J* = 7.7, 1.7 Hz, 1H), 8.78 (dd, *J* = 4.4, 1.7 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H),

7.56 (dd, *J* = 7.6, 4.7 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 161.2, 159.0, 152.2, 145.9, 136.6, 131.5, 128.7, 121.3, 118.9, 117.2, 114.8, 107.6; FT-IR ν_{max} (neat) 3063, 1635, 1620, 1519, 1458, 1327, 1257, 1111, 1041, 763 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{13}H_8N_3O_2$ $[M + H]^+$ 238.0611, found 238.0612.

4H-Thieno[3'',2'':5',6']pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***3ag***. Yellow solid (0.082 g, 65%); MP 202 – 204 °C; ^{1}H NMR (400 MHz, $CDCl_3$ δ 9.40 (d, *J* = 6.6 Hz, 1H), 7.79 (dd, *J* = 6.8, 4.5 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 5.4 Hz, 1H), 7.21 (t, *J* = 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 161.6, 156.0, 144.7, 131.3, 130.5, 128.5, 123.8, 118.1, 116.9, 114.2, 107.8; FT-IR ν_{max} (neat) 3074, 2954, 2920, 1624, 1512, 1458, 1307, 1249, 1145, 1029, 763 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{12}H_7N_2O_2S$ $[M + H]^+$ 243.0223, found 243.0228.

5,6-Dihydro-7H-benzo[7',8']chromeno[2',3':4,5]imidazo[1,2-a]pyridin-7-one ***3ah.*** Yellow solid (0.042, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (dt, *J* = 6.7, 1.3 Hz, 1H), 8.08 (dd, *J* = 5.6, 3.5 Hz, 1H), 7.77 (dt, *J* = 9.1, 1.2 Hz, 1H), 7.63 (ddd, *J* = 8.9, 7.0, 1.4 Hz, 1H), 7.42 (dd, *J* = 5.6, 3.3 Hz, 2H), 7.32 (dd, *J* = 5.4, 3.4 Hz, 1H), 7.17 (td, *J* = 6.9, 1.2 Hz, 1H), 3.03-3.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 160.3, 155.2, 144.4, 138.6, 130.6, 130.2, 128.4, 128.4, 128.0, 127.1, 123.9, 118.8, 116.8, 113.8, 27.2, 18.9; FT-IR ν_{max} (neat): 3093, 2935, 1647, 1600, 1450, 1258, 1100, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{18}H_{13}N_2O_2$ $[M + H]^+$ 289.0972 found 289.0979.

9-Methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ba.*** Cream colored solid (0.086 g, 64%); MP 215 – 217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 0.8 Hz, 1H), 8.43 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.75 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.53 (dd, *J* = 9.2, 1.7 Hz, 1H), 7.52 – 7.47 (m, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 161.2, 154.6, 144.1, 133.8, 133.2, 126.8, 125.9, 124.4, 124.4, 123.8, 118.3, 116.1, 107.4, 18.2; FT-IR

ν_{max} (neat) 3093, 3039, 2916, 1643, 1519, 1458, 1317, 1248, 1188, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{11}N_2O_2$ $[M + H]^+$ 251.0815, found 251.0813.

3,9-Dimethyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3bb.:*** Off white solid (0.041 g, 31%); MP 207 – 209 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 0.8 Hz, 1H), 8.29 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.50 (dd, *J* = 9.1, 1.6 Hz, 1H), 7.46 (s, 1H), 7.30 - 7.28 (m, 1H), 2.55 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.2, 152.8, 144.3, 134.2, 133.2, 130.3, 126.8, 125.5, 125.0, 124.8, 119.8, 116.2, 107.4, 18.2; FT-IR ν_{max} (neat) 3032, 2929, 2854, 1620, 1519, 1465, 1303, 1234, 1118, 1041, 817, 763 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{16}H_{13}N_2O_2$ $[M + H]^+$ 265.0972, found 265.0980.

2-Fluoro-9-methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3bc.*** Cream colored solid (0.075 g, 57%); MP 230 – 232 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.33 – 9.17 (m, 1H), 8.07 (dd, *J* = 8.4, 3.1 Hz, 1H), 7.71 (d, *J* = 9.5 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.56 (dd, *J* = 9.1, 1.7 Hz, 1H), 7.46 (ddd, *J* = 9.1, 7.4, 3.2 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 161.4, δ 159.2 (d, *J* = 245.5 Hz), 157.8, 150.6, 144.3, 134.2, 126.8, 125.2 (d, *J* = 7.2 Hz), 124.7, 120.9 (d, *J* = 25.1 Hz), 120.0 (d, *J* = 8.1 Hz), 116.2, 111.2 (d, *J* = 24.3 Hz), 107.2, 18.2; FT-IR ν_{max} (neat) 3063, 1635, 1519, 1465, 1303, 1234, 1118, 1041, 817, 763 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{10}FN_2O_2$ $[M + H]^+$ 269.0721, found 269.0722.

2-Chloro-9-methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3bd.*** Off white solid (0.060 g, 46%); MP 248 – 249 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.38 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.69-7-67 (m, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.56 (dd, *J* = 9.1, 1.6 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.2, 152.8, 144.3, 134.2, 133.2, 130.3, 126.8, 125.5, 125.0, 124.8, 119.8, 116.2, 107.4, 18.2; FT-IR ν_{max} (neat) 3063, 1635,

1519, 1465, 1303, 1234, 1118, 1041, 817, 763 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{10}ClN_2O_2$ $[M + H]^+$ 285.0425, found 285.0422.

2,3-Dimethoxy-9-methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3be.*** Yellow viscous liquid (0.062 g, 49%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.76 (s, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.50 (dd, *J* = 9.1, 1.5 Hz, 1H), 7.12 (s, 1H), 4.06 (s, 6H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 160.9, 153.7, 150.3, 146.7, 143.6, 133.4, 126.6, 124.1, 116.6, 116.0, 107.1, 105.1, 100.4, 56.5, 56.4, 18.2; FT-IR ν_{max} (neat) 2958, 2924, 1631, 1612, 1504, 1462, 1427, 1261, 1222, 1111, 1020, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{17}H_{15}N_2O_4$ $[M + H]^+$ 311.1026, found 311.1031.

8-Methyl-pyrido[2'',3'':5',6']-5H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-5-one ***3bf.*** White solid (0.048 g, 36%); MP 271 – 273 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.82 (dd, *J* = 7.7, 2.0 Hz, 1H), 8.77 (dd, *J* = 4.6, 2.0 Hz, 1H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.56 – 7.52 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 161.1, 159.0, 152.1, 144.7, 136.7, 134.45, 126.7, 125.0, 121.2, 118.9, 116.5, 107.4, 18.2; FT-IR ν_{max} (neat) 3085, 2927, 1637, 1519, 1458, 1340, 1240, 1020, 757 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{14}H_{10}N_3O_2$ $[M + H]^+$ 252.0768, found 252.0770.

7-Methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ca.*** Cream colored solid (0.083 g, 62%); MP 253 – 254 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 6.5 Hz, 1H), 8.44 (d, *J* = 7.9 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 6.9 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 154.6, 133.2, 130.1, 126.9, 126.42, 125.9, 124.5, 123.9, 118.3, 114.3, 107.9, 16.8; FT-IR ν_{max} (neat) 3063, 2916, 1643, 1512, 1450, 1381, 1257, 1056, 779 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{11}N_2O_2$ $[M + H]^+$ 251.0815, found 251.0816.

3,7-Dimethyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3cb.*** Cream colored solid (0.045 g, 34%); MP 256 – 258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 6.6 Hz, 1H), 8.30 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.46 (s, 1H), 7.31 (d, *J* = 9.1 Hz, 1H), 7.12 (t, *J* = 6.9 Hz, 1H), 2.72 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 160.9, 154.7, 145.2, 144.6, 129.9, 126.8, 126.3, 125.8, 125.7, 121.5, 118.2, 114.2, 107.8, 21.8, 16.8; FT-IR ν_{max} (neat) 3117, 2916, 1651, 1620, 1519, 1450, 1381, 1272, 1111, 771 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{16}H_{13}N_2O_2$ $[M + H]^+$ 265.0972, found 265.0980.

2-Fluoro-7-methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3cc.*** Cream colored solid (0.085 g, 65%); MP 227 – 228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 6.5 Hz, 1H), 8.07 (dd, *J* = 8.3, 3.0 Hz, 1H), 7.67 (dd, *J* = 9.1, 4.1 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.15 (t, *J* = 6.9 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 161.1, 160.4, 158.0, 150.6, 145.6, 130.5, 127.0, 126.4, 125.1, δ 120.9 (d, *J* = 25.1 Hz), 120.0 (d, *J* = 8.1 Hz), 114.5, 111.2 (d, *J* = 24.3 Hz), 16.8; FT-IR ν_{max} (neat) 3063, 1658, 1612, 1450, 1373, 1257, 1056, 779 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{10}FN_2O_2$ $[M + H]^+$ 269.0721, found 269.0722.

2-Chloro-7-methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3cd.*** Cream colored solid (0.076 g, 59%); MP 273 – 275 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 6.6 Hz, 1H), 8.37 (d, *J* = 2.5 Hz, 1H), 7.68 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 6.9 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 160.9, 152.9, 145.6, 133.2, 130.51, 130.4, 127.1, 126.4, 125.4, 125.0, 119.8, 114.6, 107.8, 16.8; FT-IR ν_{max} (neat) 3063, 1658, 1612, 1450, 1373, 1257, 1056, 779 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{15}H_{10}ClN_2O_2$ $[M + H]^+$ 285.0425, found 285.0430.

2,3-Dimethoxy-7-methyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ce.*** Cream colored solid (0.073 g, 58%); MP 250 – 252 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 6.6 Hz, 1H), 7.77 (s, 1H), 7.46 (d, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 6.9 Hz, 1H), 7.10 (s, 1H), 4.06 (s, 3H), 4.05 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 160.7, 153.7, 150.3, 147.2, 146.8, 131.1, 129.6, 126.8, 126.3, 116.6, 114.1, 105.1, 100.4, 56.5, 56.4, 16.9; FT-IR ν_{max} (neat) 2924, 2850, 1666, 1635, 1612, 1504, 1458, 1438, 1257, 1226, 1114, 1026, 740 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{17}H_{15}N_2O_4$ $[M + H]^+$ 311.1026, found 311.1028.

10-Methyl-pyrido[2'',3'':5',6']-5H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-5-one ***3cf.*** White solid (0.091 g, 68%); MP 238 – 239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 6.5 Hz, 1H), 8.82 (dd, *J* = 7.7, 1.9 Hz, 1H), 8.78 (dd, *J* = 4.6, 1.9 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.54 – 7.50 (m, 1H), 7.17 (t, *J* = 6.9 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 160.9, 159.0, 152.1, 145.9, 136.6, 130.7, 127.4, 126.3, 121.2, 119.0, 114.8, 107.9, 16.9; FT-IR ν_{max} (neat) 3085, 1640, 1609, 1519, 1458, 1357, 1240, 1109, 1041, 757 cm^{-1}; HRMS (+ESI-TOF, m/z): calcd for $C_{14}H_{10}N_3O_2$ $[M + H]^+$ 252.0768, found 252.0767

9-Methyl-4H-thieno[3'',2'':5',6']pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***3cg.*** Yellow solid (0.084 g, 63%); MP 248 – 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$δ 9.25 (d, *J* = 6.6 Hz, 1H), 7.76 (d, *J* = 5.4 Hz, 1H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 5.4 Hz, 1H), 7.11 (t, *J* = 6.9 Hz, 1H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 161.2, 156.0, 144.81, 131.15, 129.52, 127.00, 126.20, 123.81, 118.11, 114.22, 108.16, 16.88; FT-IR ν_{max} (neat) 3097, 2954, 2920, 1654, 1620, 1512, 1450, 1381, 1253, 1161, 1053, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{13}H_9N_2O_2S$ $[M + H]^+$ 257.0379, found 257.0381.

12-Methyl-5,6-dihydro-7H-benzo[7',8']chromeno[2',3':4,5]imidazo[1,2-a]pyridin-7-one ***3ch***. Red solid (0.047, 37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 6.7 Hz, 1H), 8.15 – 8.01 (m,

1H), 7.53 – 7.36 (m, 2H), 7.35 – 7.27 (m, 1H), 7.08 (t, *J* = 6.9 Hz, 1H), 3.03-2.99 (m, 4H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 159.9, 155.1, 144.5, 138.6, 130.5, 129.3, 128.5, 127.9, 127.1, 126.8, 126.1, 123.9, 118.7, 113.9, 27.2, 18.9, 16.9; FT-IR ν_{max} (neat): 3093, 2854, 1650, 1604, 1420, 1250, 1149, 1040, 847, 712, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{19}H_{15}N_2O_2$ $[M + H]^+$ 303.1128 found 303.1148.

9-Phenyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3da.*** Off white solid (0.080 g, 48%); MP 248 – 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.78 (t, *J* = 7.0 Hz, 1H), 7.74 – 7.65 (m, 3H), 7.57 (s, 1H), 7.56 – 7.51 (m, 2H), 7.50 – 7.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 161.5, 154.6, 144.5, 136.1, 133.3, 131.2, 129.3, 129.0, 128.5, 127.1, 126.0, 125.9, 124.5, 123.8, 118.3, 116.6, 107.8; FT-IR ν_{max} (neat) 3063, 1635, 1519, 1458, 1327, 1257, 1080, 1018, 802, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{20}H_{13}N_2O_2$ $[M + H]^+$ 313.0972, found 313.0974.

3-Methyl-9-phenyl-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3db.*** Off white solid (0.045 g, 28%); MP 260 – 262 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 7.93 (dd, *J* = 9.3, 1.8 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.50 (s, 1H), 7.50 – 7.45 (m, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 161.4, 154.8, 144.7, 144.3, 136.1, 131.0, 129.3, 128.9, 128.4, 127.1, 125.9, 125.9, 125.7, 121.5, 118.3, 116.6, 107.7, 21.8; FT-IR ν_{max} (neat) 3063, 1635, 1620, 1519, 1458, 1327, 1257, 1111, 1041, 763 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{21}H_{15}N_2O_2$ $[M + H]^+$ 327.1128, found 327.1137.

9-(4-Chlorophenyl)-12H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-12-one ***3ea.*** Off white solid (0.102 g, 55%); MP 261 – 263 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 2H), 8.44 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.93 – 7.83 (m, 2H), 7.82 – 7.75 (m, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.59 (m,

2H), 7.55 – 7.52 (m, 2H), 7.52 – 7.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 161.5, 154.6, 144.4, 134.8, 134.6, 133.5, 130.8, 129.5, 128.4, 127.8, 126.00, 125.8, 124.6, 123.8, 118.4, 116.8, 107.9; FT-IR ν_{max} (neat) 3097, 3062, 1666, 1635, 1519, 1465, 1334, 1257, 1095, 1010, 810, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{20}H_{12}ClN_2O_2$ $[M + H]^+$ 347.0582, found 347.0594.

8-(4-Chlorophenyl)-pyrido[2",3":5',6']-5H-chromeno[2',3':4,5]imidazo[1,2-a]pyridin-5-one ***3ef.*** Sticky white compound (0.093 g, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.83 (dd, *J* = 7.7, 2.0 Hz, 1H), 8.80 (dd, *J* = 4.6, 2.0 Hz, 1H), 7.95-7.89 (m, 2H), 7.65 – 7.60 (m, 2H), 7.58 (dd, *J* = 7.7, 4.7 Hz, 1H), 7.55 – 7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 161.4, 159.0, 152.3, 145.0, 136.7, 134.9, 134.3, 131.4, 129.6, 128.4, 128.3, 125.8, 121.4, 118.9, 117.2, 107.8; FT-IR ν_{max} (neat) 2948, 1640, 1519, 1460, 1320, 1223, 1020, 815, 757 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{19}H_{11}ClN_3O_2$ $[M + H]^+$ 348.0534, found 348.0531.

2-Phenyl-4H-pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***5aa.*** Brown viscous liquid (0.070 g, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 6.0 Hz, 1H), 8.05 – 7.89 (m, 2H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.59 – 7.49 (m, 3H), 7.18 (t, *J* = 6.2 Hz, 1H), 6.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 161.1, 160.8, 150.4, 144.5, 131.4, 131.2, 130.5, 129.1, 128.5, 126.3, 116.9, 114.1, 109.7; FT-IR ν_{max} (neat) 3063, 1653, 1600, 1439, 1249, 1109, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{16}H_{11}N_2O_2$ $[M + H]^+$ 263.0815, found 263.0822.

2-(4-Chlorophenyl)-4H-pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***5ab.*** Viscous liquid (0.058 g, 48%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 6.7 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.79 (d, *J* = 9.1 Hz, 1H), 7.71 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H), 7.20 (td, *J* = 6.9, 1.0 Hz, 1H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 161.0, 159.7, 144.6, 137.5, 131.4, 130.7, 129.9, 129.4, 128.5, 127.5, 116.9, 114.2, 109.8; FT-IR ν_{max} (neat) 3020, 2920, 2850, 1643, 1627,

1524, 1450, 1257, 1114, 1091, 1006, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{16}H_{10}ClN_2O_2$ $[M + H]^+$ 297.0425, 299. 0401 found 297.0427 and 299.0399.

2-(4-Bromophenyl)-3-methyl-4H-pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***5ac.*** Viscous solid (0.054, 40%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 6.7 Hz, 1H), 7.77 (d, *J* = 9.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.18 (t, *J* = 6.9 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 160.6, 156.6, 153.9, 131.9, 131.7, 130.8, 130.5, 130.5, 128.4, 124.6, 119.6, 116.8, 113.9, 11.7; FT-IR ν_{max} (neat): 3035, 2839, 1656, 1600, 1389, 1250, 1111, 756, 715 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{17}H_{12}BrN_2O_2$ $[M + H]^+$ 355.0077, found 355.0065 and 357.0044.

7-Methyl-2-phenyl-4H-pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***5ba.*** Cream solid (0.038 g, 29%); MP 284 – 286 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.06 – 7.90 (m, 2H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.49 (d, *J* = 9.1 Hz, 1H), 6.89 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 161.0, 160.6, 143.4, 133.5, 131.5, 131.1, 129.0, 126.5, 126.2, 124.2, 116.2, 109.6, 18.1; FT-IR ν_{max} (neat) 3093, 1650, 1604, 1420, 1256, 1111, 756 cm^{-1}; HRMS (ESI-TOF, m/z): calcd for $C_{17}H_{13}N_2O_2$ [M + H]+ 277.0972, found 277.0969.

9-Methyl-2-phenyl-4H-pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***5ca.*** Cream solid (0.059 g, 45%); δ 9.18 (d, *J* = 6.5 Hz, 1H), 8.00 (d, *J* = 3.5 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.10 (t, *J* = 6.9 Hz, 1H), 6.91 (s, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$δ 170.4, 160.7, 151.3, 144.7, 131.5, 131.2, 129.6, 129.0, 126.9, 126.3, 126.2, 114.1, 109.7, 16.9; FT-IR ν_{max} (neat) 3097, 2924, 2854, 1627, 1573, 1446, 1253, 1161, 1111, 867, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{17}H_{13}N_2O_2$ $[M + H]^+$ 277.0972, found 277.0979.

2-(4-Chlorophenyl)-9-methyl-4H-pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***5cb.*** Cream colored solid (0.053 g, 42%); MP 284 – 286 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 6.7 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.79 (d, *J* = 9.1 Hz, 1H), 7.71 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H),

7.20 (td, J = 6.9, 1.0 Hz, 1H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 160.6, 159.5, 144.7, 137.4, 129.9, 129.7, 129.4, 127.5, 127.0, 126.2, 114.2, 109.8, 16.9; FT-IR ν_{max} (neat) 3084, 1656, 1608, 1434, 1256, 1111, 1056, 756 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{17}H_{12}ClN_2O_2$ $[M + H]^+$ 311.0582, found 311.0586.

7-(4-Chlorophenyl)-2-phenyl-4H-pyrano[2',3':4,5]imidazo[1,2-a]pyridin-4-one ***5ea.*** Viscous liquid (0.060 g, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 3H), 8.00 (d, J = 2.7 Hz, 1H), 7.98 (d, J = 3.3 Hz, 1H), 7.86 (d, J = 1.6 Hz, 2H), 7.62 (d, J = 8.5 Hz, 3H), 7.59 – 7.55 (m, 3H), 7.52 (d, J = 8.5 Hz, 2H), 6.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 161.3, 161.0, 146.6, 143.6, 134.7, 134.6, 134.6, 131.3, 130.5, 129.5, 129.1, 128.4, 127.6, 126.3, 125.6, 116.9, 109.7; FT-IR ν_{max} (neat) 3062, 2924, 2854, 1643, 1631, 1577, 1465, 1261, 1091, 817, 694 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{22}H_{14}ClN_2O_2$ $[M + H]^+$ 373.0738, found 373.0744.

N-(5-Phenylpyridin-2-yl)acetamide ***7d***.[40] Cream solid (0.021 g, 18%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.52 (s, 1H), 8.32 (d, J = 8.5 Hz, 1H), 7.95 (dd, J = 8.6, 2.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.44 – 7.35 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 145.9, 141.0, 132.6, 132.2, 128.1, 124.3, 123.0, 122.0, 109.2, 20.0; FT-IR ν_{max} (neat) 3240, 3039, 2924, 1658, 1527, 1373, 1303, 1018, 763 cm^{-1}.

N-(5-(4-Chlorophenyl)pyridin-2-yl)acetamide ***7e.*** Cream solid (0.020 g, 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.32 (s, 1H), 8.30 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.67, 150.71, 145.75, 136.72, 135.85, 133.99, 131.73, 129.26, 127.99, 113.79, 24.79; FT-IR ν_{max} (neat) 3242, 3037, 2923, 1657, 1524, 1371, 1305, 1011, 761 cm^{-1}; HRMS (ESI-TOF, *m/z*): calcd for $C_{13}H_{11}ClN_2O$ $[M + H]^+$ 246.0560, found 246.0558.

2-Phenylimidazo[1,2-a]pyridine ***11***.[41] Cream coloured solid (0.018, 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dt, J = 6.8, 1.2 Hz, 1H), 8.02 – 7.95 (m, 2H), 7.87 (s, 1H), 7.65 (dq, J = 9.1, 1.1

Hz, 1H), 7.51 – 7.41 (m, 2H), 7.39 – 7.32 (m, 1H), 7.18 (ddd, J = 9.1, 6.7, 1.3 Hz, 1H), 6.78 (td, J = 6.7, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 145.7, 133.8, 128.7, 127.9, 126.0, 125.5, 124.6, 117.5, 112.4, 108.1.

Conflict of interest

The authors declare no conflict of interest

Supporting information

Supporting information (copies of NMR data for **1a-f**, **2h**, **4c**, **3aa-3ef**, **5aa-5ea** and **7d-e,** HRMS analysis of reaction mixture) for this article is available.

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