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Full Paper

Palladium-Catalyzed Suzuki Cross-Coupling of 2-Halo-Deazapurines with Potassium Organotrifluoroborate Salts in the Regioselective Synthesis of Imidazo[4,5-*b*]pyridine Analogues

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In this paper, we report the use of potassium organotrifluoroborate salts as nucleophilic organoboron reagents in the Suzuki cross-coupling reactions of 2-halo deazapurines. Regio-isomeric C-2-substituted imidazo[4,5-*b*]pyridine analogues were synthesized by employing this protocol in good to excellent yields. Whereas aryl and heteroaryl trifluoroborates reacted readily to give the coupled products in high yields, alkyltrifluoroborates were found to be less reactive. The utilization of tetrabutylammonium acetate was found to play a substantial role in enhancing the reaction rates of the cross-coupling process. Also, a comparative study was performed between boronic acids and potassium organotrifluoroborate salts.

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Introduction

The palladium-catalyzed cross-coupling reaction of an organoboron compound with an electrophile (Suzuki reaction) is one of the most robust and well explored reactions in organic synthesis for the selective construction of carbon–carbon bonds, especially in the synthesis of biaryls.[1] The biaryl moiety is found in a wide range of pharmaceuticals, natural products, and herbicides, as well as in conducting polymers and liquid-crystalline materials.[2] Owing to these varied applications, the development of improved protocols for Suzuki coupling is essential in organic synthesis.

In general, boronic acids or esters are good nucleophilic organoboron reagents in the Suzuki coupling reaction.[3] However, they have been found to exhibit several drawbacks such as the partial formation of dimeric and cyclic trimeric boroxines[4] (depending on storage water content) owing to which the stoichiometry of boronic acids added to the reaction mixture gets affected. Moreover, the boronic acid functionality is susceptible to a wide range of undesired chemical processes[5,6] including protodeboronation, oxidative homocoupling, and oxidative insertion. Owing to these side reactions, there remains a major limitation in terms of the overall efficacy of the process. Although several strategies have been developed to overcome these problems associated with boronic acids, potassium organotrifluoroborates[7,8] have shown commendable potential as a stable reservoir for the vulnerable boronic acids. Potassium organotrifluoroborate salts[9,10] can be easily prepared and purified, and special care is not required in handling them. Molander et al. have published a range of procedures for the coupling of potassium organotrifluoroborate salts with a wide range of electrophiles[11,12] and have shown the great scope of these reagents and simplified the coupling protocols. The reactions can be performed in methanol or water, in open air using a palladium catalyst and an inorganic base.[12] In 1996, Genet et al. reported the first coupling reactions involving potassium aryl and alkenyltrifluoroborates with arenediazonium tetrafluoroborates. In 1999, Xia et al. applied this method to carry out the coupling with diaryliodonium salts. Recently,

Guy C. Lloyd-Jones and his group investigated the factors that affect the hydrolysis of RBF_3K reagents and classified the trifluoroborate substrates according to their hydrolytic half-life, which allows a prior evaluation of whether the trifluoroborate substrate will engender a slow or fast release.[13] Further, the mechanistic insights of the 'slow-release strategy' of potassium organotrifluoroborate salts were studied in detail by Guy C. Lloyd-Jones et al.[13]

Owing to the importance of the biaryl fragment in the modern field of medicinal chemistry and as a part of our research on palladium-catalyzed cross-coupling reactions,[14] we were interested in the Suzuki cross-coupling reactions of 2-halo-3-alkyl-1-deazapurines with potassium organotrifluoroborate salts. Imidazo[4,5-*b*]pyridines can be considered as structural analogues of purines[15] and are known to have great medicinal relevance.[15,16] The reason why various deazapurines have a broad pharmacological profile lies in their similarity and isosterism to purines. Taking into account the isosterism mentioned above, deazapurines can be used as agonists and antagonists of the corresponding receptors (Fig. 1). Also, Suzuki cross-coupling reactions involving nitrogen-containing heteroaromatics[17–19] are more challenging compared with carbocyclic systems owing to the potential binding nature of these substrates to palladium leading to catalyst deactivation,[20,21] and therefore requiring higher amounts of catalyst to drive the reactions to completion.

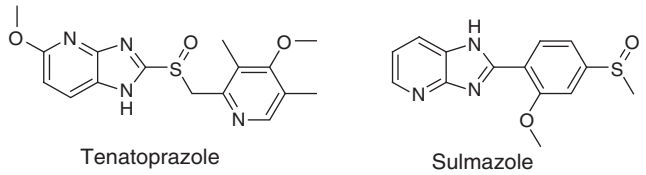
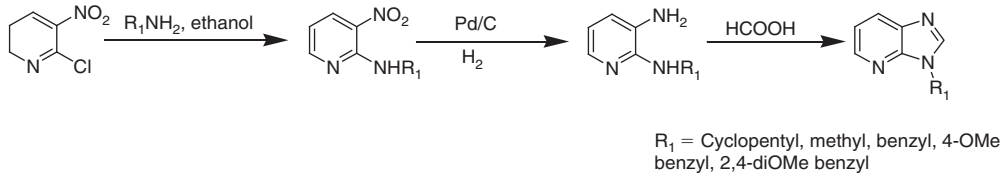


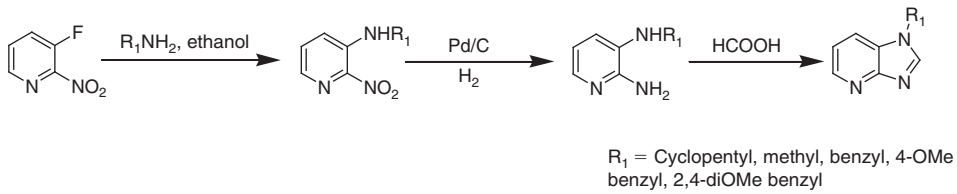
Fig. 1. Pharmacologically relevant imidazo[4,5-*b*]pyridines.

Results and Discussion

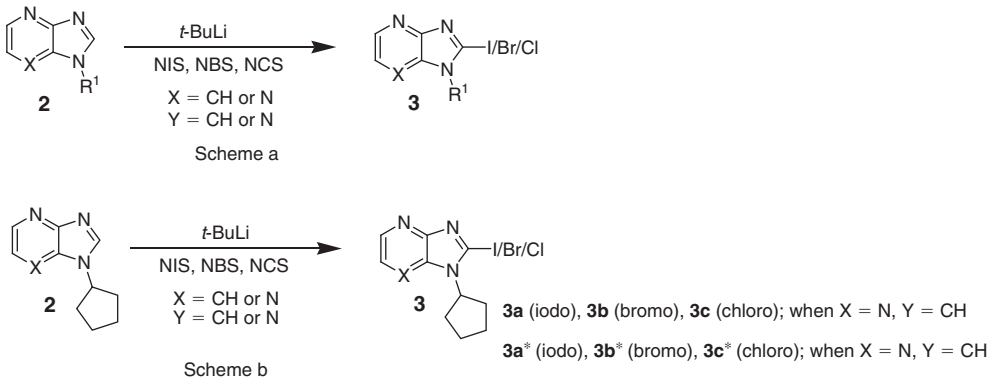
The synthesis of the required intermediate compounds was performed as outlined in Schemes 1 and 2. The potential halo intermediate **3** (Scheme 3) was obtained by treating compound **2** with *t*-BuLi in THF at −78°C, followed by the addition of corresponding electrophilic halide source (N-Iodosuccinimide, N-Bromosuccinimide or N-Chlorosuccinimide) in THF dropwise and stirred at −78°C for additional 2 h (Scheme 3). These halo intermediates were employed for the Suzuki cross-coupling reaction with potassium organotrifluoroborate salts (Scheme 4). We chose the iodo intermediate **3a** (Scheme 3) and potassium naphthalene organotrifluoroborate **4a** to screen the catalyst and to optimize the cross-coupling reaction conditions (Scheme 4). Initially, the trial reaction was performed using acetonitrile as the solvent, Tris(dibenzylideneacetone)dipalladium(0)/Triphenyl phosphine as the catalyst and K_3PO_4 as the base in a sealed



Scheme 1. Synthesis of 3-substituted-3*H*-imidazo[4,5-*b*]pyridine cores.



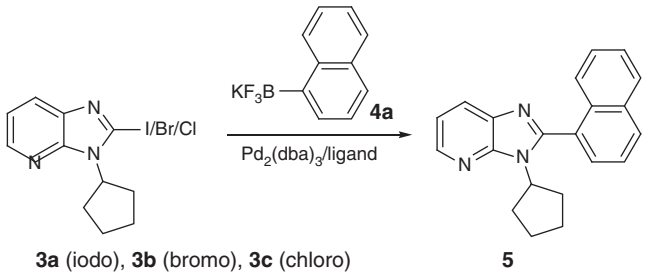
Scheme 2. Synthesis of 1-substituted-1*H*-imidazo[4,5-*b*]pyridine cores.



Scheme 3. Synthesis of halo imidazopyridine cores.

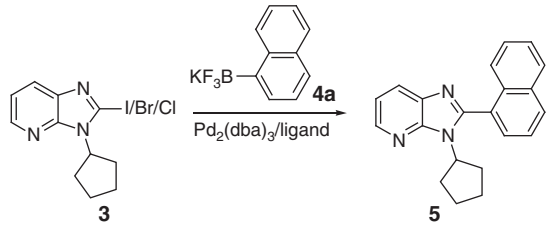
vial at 90°C for 12 h. Unfortunately, only starting material was observed and there was no product formation. The reaction was carried out using different solvents such as ethanol and isopropanol, but this change did not assist in the formation of the required product either. Our subsequent strategy was to use water as a co-solvent along with acetonitrile, and the same reaction was carried out under microwave irradiation and showed only traces of product and mostly the decomposed iodo intermediate **3a**, (dehalogenation). It was observed that changing the solvent or base did not lead to any positive enhancement in the results.

Iodo intermediate **3a** (Scheme 4) was replaced with the corresponding bromo **3b** (Scheme 4) and chloro **3c** (Scheme 4)[21] intermediates to evaluate the effects of the halogens and to tune the reaction for better conversions. The halogen atom flanked by the two nitrogen atoms can be considered as 'activated' and hence more susceptible to oxidative addition, which is often the rate-determining step. The results of cross-coupling of **3** with **4a** are summarized in Table 1. The use of the bromo analogue as a cross-coupling substrate yielded 25 % conversion after 15 h, (Table 1, entry 2; Fig. 2). These results encouraged us to further optimize the reaction conditions in the presence of $Pd_2(dba)_3$ and various ligands using different bases and solvent combinations as well as reaction temperatures. Screening of palladium catalysts and ligands as shown in Table 1, entry 6, indicates that an effective catalytic species was achieved using the $Pd_2(dba)_3$/RuPhos system, which



Scheme 4. Cross-coupling of **3** with **4a**.

Table 1. Cross-coupling of 3 with 4a



Entry	Catalytic system	Yield [%][A,B]
1	$Pd_2(dba)_3$[C]	0
2	$Pd_2(dba)_3/PPh_3$	25
3	$Pd_2(dba)_3$/Xantphos	45
4	$Pd_2(dba)_3$/XPhos	50
5	$Pd_2(dba)_3$/SPhos	50
6	$Pd_2(dba)_3$/RuPhos	62

[A]Isolated yields. [B]Method B: 4 mol-% $Pd_2(dba)_3$, 8 mol-% ligand, K_2CO_3 (2.5 equiv.), **3b** (1 equiv.) **4a** (1.3 equiv.), sealed vial, 90°C, 15 h, ACN/H_2O. [C]Dba = dibenzylideneacetone.

enhanced the coupling yield (Fig. 2). Different inorganic bases like K_3PO_4, NaOAc, KOAc, and CsOAc were explored to find an optimum base for the reaction. Table 2 details the effect of various bases on the cross-coupling of **3** with **4a**.

Aqueous solvent systems were found to be essential for Suzuki cross-coupling reactions using potassium organotrifluoroborate salts.[22,23] This is in accordance with earlier experimental results where it was observed that water was essential in these transformations.[22] It is hypothesized that mixed borates, $[RBF_{3-n}(OH)_n]$[22,23] are the true transmetallating species. Among all the bases explored, caesium acetate was found to be very effective in these transformations (Table 2). Thus, our optimal conditions were 1 equiv. halo intermediate, 1.3 equiv. of **4a**, 3 equiv. of caesium acetate, 4 : 1 acetonitrile/water as solvent, 4 mol-% of $Pd_2(dba)_3$, and 8 mol-% RuPhos ligand, heated to 90°C in a sealed vial for 15 h. Under these optimal conditions, we widened the scope of the reaction by performing the coupling reactions of potassium organotrifluoroborates[21] with **3** (Scheme 5). It was found that the reaction of the bromo analogue **3b** (Scheme 4) with most of the substrates was very efficient, with high yields.

The influence of tetrabutylammonium acetate was also studied (Table 2, entry 6). We speculate that the use of tetrabutylammonium acetate in these reactions stabilized the catalytic species and also acted as a phase-transfer catalyst for the dissolution of both reagents in the aqueous–organic medium.[24] The formation of the products under these optimized conditions was confirmed by ^{1}H NMR and ^{13}C NMR spectral analysis. Various heteroaryl potassium organotrifluoroborate salts were also found to be efficient reagents under these conditions.

The optimized conditions that had been developed for the cross-coupling reactions of aryl and heteroaryl potassium organotrifluoroborates were employed for the cross-coupling of alkyl potassium organotrifluoroborates as well.[25] We conducted a model reaction of bromo analogue **3b** (Scheme 4) with cyclopropyl trifluoroborate **4n** using the conditions that were most successful in the case of naphthalene trifluoroborate. Attempts to perform the reaction under conventional heating did not give any promising results. However, under microwave conditions, we saw 52 % product formation. Among the alkyl potassium trifluoroborate salts studied (**4n**, **4o**, and **4p**; Table 3), only cyclopropyl potassium trifluoroborate (**4n**, Table 3) was found to react successfully.

Under microwave-assisted conditions, vinyltrifluoroborate reacted to give the product in good yields when compared with conventional heating. The increased sp^2 character associated with cyclopropyl trifluoroborates makes them a better cross-coupling substrate when compared with other

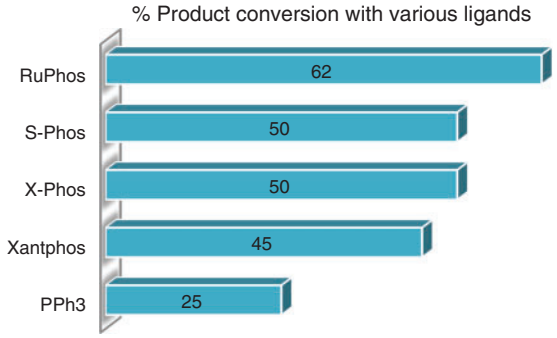
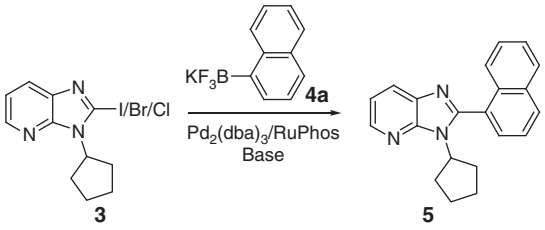


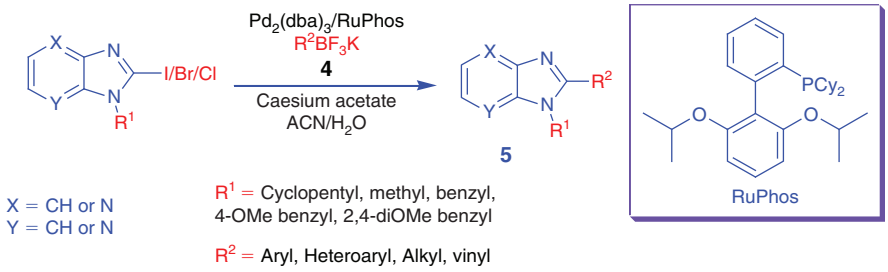
Fig. 2. Effect of ligands on cross-coupling of **3b** with **4a**.

Table 2. Effect of bases on cross-coupling of 3 with 4a



Entry	Catalytic system	Base (3 equiv.)	Conditions	Solvent	Yield [%][A]
1	$Pd_2(dba)_3$/RuPhos	Na_2CO_3	90°C, 15 h	ACN/H_2O	Traces
2	$Pd_2(dba)_3$/RuPhos	KOAc	90°C, 15 h	ACN/H_2O	35
3	$Pd_2(dba)_3$/RuPhos	K_3PO_4	90°C, 15 h	ACN/H_2O	52
4	$Pd_2(dba)_3$/RuPhos	Cs_2CO_3	90°C, 15 h	ACN/H_2O	58
5	$Pd_2(dba)_3$/RuPhos	CsOAc	90°C, 15 h	ACN/H_2O	89[B]
6	$Pd_2(dba)_3$/RuPhos	CsOAc/Bu_4NOAc	90°C, 3 h	ACN/H_2O	81[C]

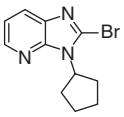
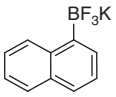
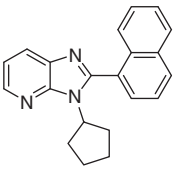
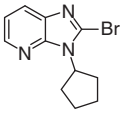
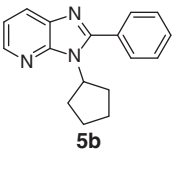
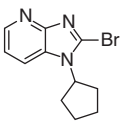
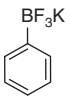
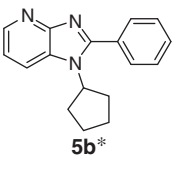
[A]Isolated yields. [B]Method B: 4 mol-% $Pd_2(dba)_3$, 8 mol-% RuPhos, Base (3 equiv.), **3b** (1 equiv.), **4a** (1.3 equiv.), sealed vial, 90°C, 15 h, ACN/H_2O; [C]Method C: 4 mol-% $Pd_2(dba)_3$, 8 mol-% RuPhos, CsOAc (3 equiv.), Bu_4NOAc (1 equiv.), **3b** (1 equiv.), **4a** (1.3 equiv.), sealed vial, 90°C, 3 h, ACN/H_2O.



Scheme 5. Synthesis of substituted imidazo[4, 5-*b*]pyridines.

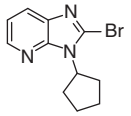
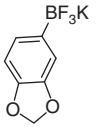
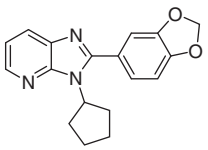
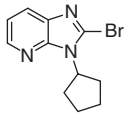
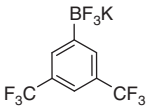
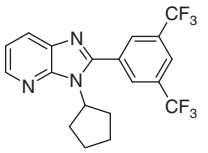
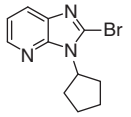
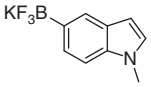
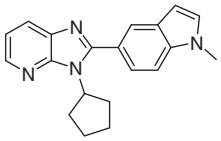
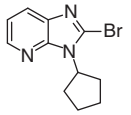
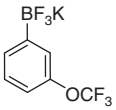
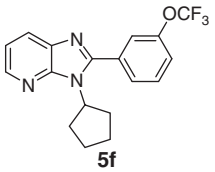
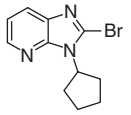
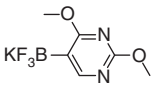
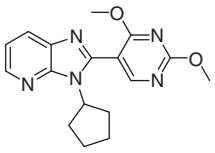
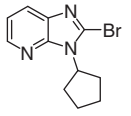
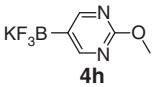
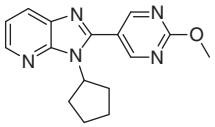
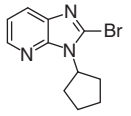
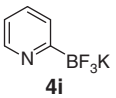
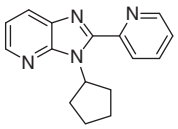
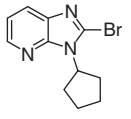
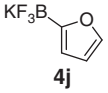
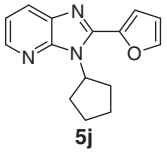
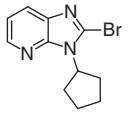
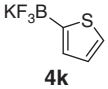
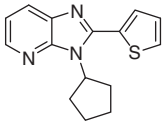
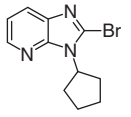
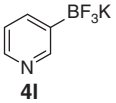
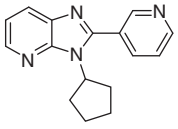
Table 3. Cross-coupling of halo intermediates 3 with trifluoroborates 4

Method C: 4 mol-% $Pd_2(dba)_3$, 8 mol-% RuPhos, CsOAc (3 equiv.), Bu_4NOAc (1 equiv.), **3** (1 equiv.), RBF_3K (1.3 equiv.), sealed vial, 90°C, 6 h, ACN/H_2O

Entry	Halo intermediate **3**	R^2BF_3K salt **4**	Product **5**	Yield [%][A]
1		 **4a**	 **5a**	89
2		 **4b**	 **5b**	88
3		 **4b**	 **5b***	90

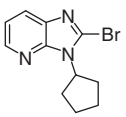
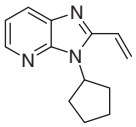
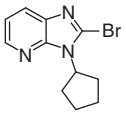
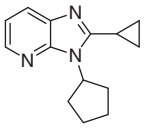
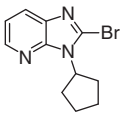
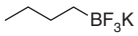
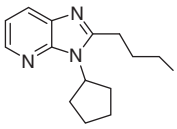
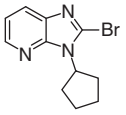
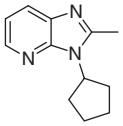
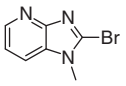
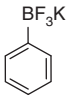
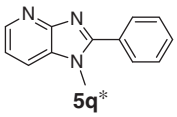
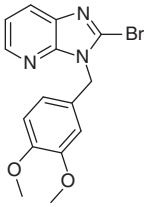
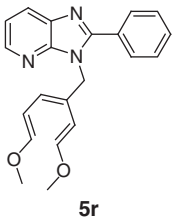
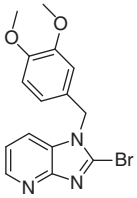
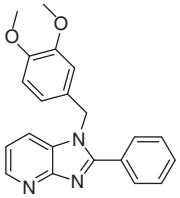
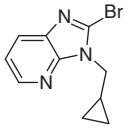
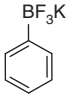
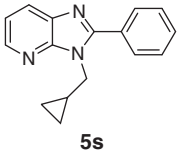
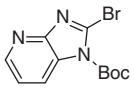
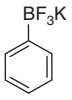
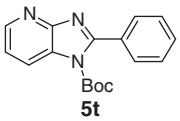
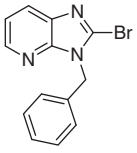
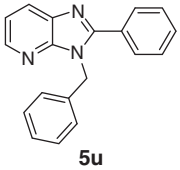
(*Continued*)

Table 3. (Continued)

Entry	Halo intermediate **3**	R^2BF_3K salt **4**	Product **5**	Yield [%][A]
4		 **4c**	 **5c**	92
5		 **4d**	 **5d**	79
6		 **4e**	 **5e**	88
7		 **4f**	 **5f**	84
8		 **4g**	 **5g**	79
9		 **4h**	 **5h**	69
10		 **4i**	 **5i**	25
11		 **4j**	 **5j**	30
12		 **4k**	 **5k**	90
13		 **4l**	 **5l**	92

(*Continued*)

Table 3. (Continued)

Entry	Halo intermediate **3**	R^2BF_3K salt **4**	Product **5**	Yield [%][A]
14		 **4m**	 **5m**	85
15		 **4n**	 **5n**	52
16		 **4o**	 **5o**	0
17		 **4p**	 **5p**	Traces
18		 **4b**	 **5q***	90
19		 **4b**	 **5r**	85
20		 **4b**	 **5r***	88
21		 **4b**	 **5s**	91
22		 **4b**	 **5t**	72
23		 **4b**	 **5u**	86

[A]Isolated yields.

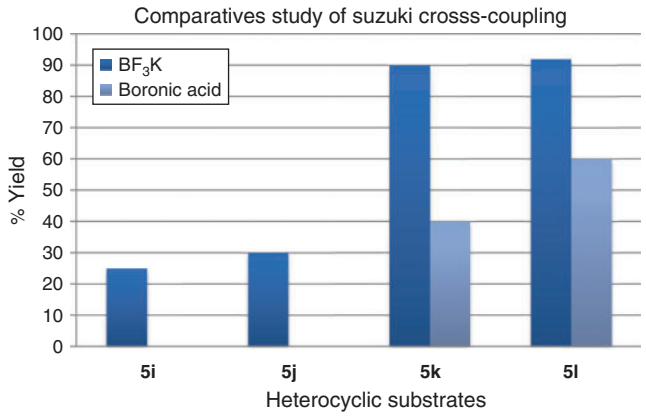


Fig. 3. Comparative study of Suzuki cross-coupling of boronic acids and potassium organotrifluoroborate salts.

alkyltrifluoroborates under these conditions. Table 3 shows the different substrates and optimum conditions that were explored for the Suzuki cross-coupling reactions with potassium organotrifluoroborates.

To establish the difference in reactivity between the trifluoroborate salt and the corresponding boronic acid (Fig. 3), the reaction was carried out under the same conditions using the corresponding boronic acid of **4e** and **3b** (Method B). TLC analysis showed less product formation compared with the corresponding trifluoroborate salt where 88 % product was isolated. Similarly, with cyclopropylboronic acid (Method A), we could not see any product formation. Unfortunately, when the trifluoroborate group was ortho to the heteroatom in furans and pyridines, the Suzuki cross-coupling reaction was found to be sluggish.[26] Using Method A, 25 % product was obtained with pyridine trifluoroborate, **4i** (Table 3, entry 9) and 30 % product with furan trifluoroborate, **4j** (Table 3, entry 10). Table 4 describes the reactivity of boronic acids, which were susceptible to protodeboronation. The use of corresponding potassium organotrifluoroborates resulted in higher yields of the coupled products (Table 5).

The overall efficiency of a cross-coupling process is significantly affected by the structure of the ligand. Therefore, the use of a ligand with appropriate steric and electronic properties is crucial in dealing with problematic and specific substrates in this area. In the present work, we screened various ligands that showed excellent catalytic activity in various cross-coupling reactions involving heteroaromatic substrates (Fig. 4).

The mechanism of the Suzuki reaction involves the generation of 'true catalytic species' from the $Pd_2(dba)_3$/RuPhos system, which is a co-ordinatively unsaturated palladium complex. This then undergoes oxidative addition with the halodeazapurine to give the oxidative adduct complex. The slow release of boronic acid from the trifluoroborate salts results in maintaining a low concentration of boronic acid during the cross-coupling process as the boronic acids are more vulnerable to competitive side reactions. It has been claimed that an aqueous solvent combination is essential for the cross-coupling reaction to proceed and that one or more hydroxyl groups are attached to the boron.[27] This mixed borate species then undergoes a transmetallation,[28] which, followed by reductive elimination, yields the coupled product as shown in Scheme 6.

Conclusion

Aryl and heteroaryl trifluoroborates were found to be excellent reagents for the cross-coupling reactions with 2-halo-3-alkyl deazapurines under palladium catalysis. These cross-couplings are equally comparable with the classical Suzuki cross-coupling reactions with boronic acids. The use of alkyl potassium trifluoroborate salts in the synthesis of alkylated analogues was found to be unsuccessful, as reported in the literature.[29]

Experimental

General information

All experiments were performed under a nitrogen atmosphere. All reagents including palladium catalysts, phosphine ligand, potassium organotrifluoroborate salts, and inorganic bases were purchased from commercial sources and used as received. Acetonitrile was used as such, obtained from commercial sources. Commercially available prepacked silica gel plugs and hexane and ethyl acetate solvents were used for column-chromatographic purification of organic products. Isolated yields correspond to products of greater >90 % purity as determined by liquid chromatography–mass spectrometry (LC-MS) and NMR. All NMR (^{1}H, ^{13}C) chemical shifts are reported in parts per million (ppm) and all coupling constants are reported in hertz (Hz). Microwave-assisted synthesis was performed in a single-mode Biotage Initiator Microwave Synthesizer and temperature was monitored using an infrared probe. The microwave reaction was carried out in a 5-mL glass vial and a high absorption level was maintained. The conditions were maintained till the completion of the reaction.

*Procedure for the Coupling of 2-Halo Imidazo[4,5-*b*] pyridine with Different Potassium Organotrifluoroborates*

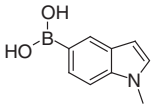
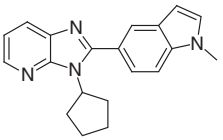
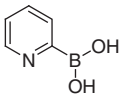
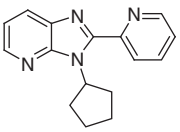
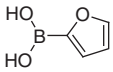
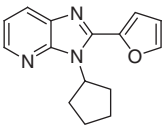
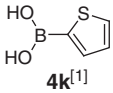
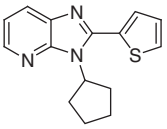
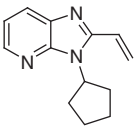
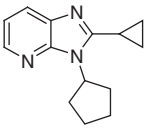
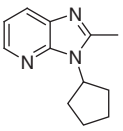
Method A

To a degassed solution of 3-substituted-2-halo imidazo[4,5-*b*]pyridine derivative **3** (1 equiv.) in acetonitrile/water (1 : 2) was added palladium catalyst (4 mol-%) and phosphine ligand (8 mol-%). The solution was again purged with nitrogen and stirred at room temperature for 15 min; at this time, the potassium organotrifluoroborate salts (1.3 equiv.), caesium acetate (3 equiv.), and tetrabutylammonium acetate (1 equiv.) were added. The reaction solution was purged again with nitrogen and then placed in the microwave and heated for 20 to 50 min at 150°C. When TLC and LC-MS showed full consumption of starting materials, the reaction mixture was diluted with ethyl acetate, and the ethyl acetate layer separated, washed with water, followed by a brine wash, dried over anhydrous sodium sulfate, and concentrated to get the crude material. The crude product was directly purified by column chromatography (20–50 % light petroleum ether/EtOAc) to isolate the 3-substituted-2-aryl or heteroaryl imidazo[4,5-*b*] pyridine derivatives.

Method B

To a degassed solution of 3-substituted-2-halo imidazo[4,5-*b*]pyridine derivative (1 equiv.) in acetonitrile/water (1 : 2) in a sealed vial was added palladium catalyst (4 mol-%) and phosphine ligand (8 mol-%). The solution was again purged with nitrogen, stirred at room temperature for 15 min, and potassium organotrifluoroborate salts (1.3 equiv.) and caesium acetate (3 equiv.) were added. The reaction contents were then heated to 90°C for 15 h. When TLC and LC-MS showed complete consumption of the starting materials, the reaction

Table 4. Cross-coupling of 3 with boronic acids

Entry	Halo intermediate **3**	Boronic acid **4**	Product **5**	Method	Yield (%)[C,D]
1	**3b** and **3c**	 **4e**[1]	 **5e**	B and C	**3b** = 40[B] **3c** = 32[C]
2	**3c**	 **4i**[1]	 **5i**	B	No reaction
3	**3b** and **3c**	 **4j**[1]	 **5j**	A, B and C	No reaction
4	**3b**	 **4k**[1]	 **5k**	B	**3c** = 40[B]
5	**3b**	 **4m**[1]	 **5m**	A and B	**3b** = 25[A] **3b** = 20[B]
6	**3b**	 **4n**[1]	 **5n**	A and B	**3b** = 18[A] **3b** = 20[B]
7	**3b**	 **4p**[1]	 **5p**	A, B and C	No reaction

[A]Method A: 4 mol-% $Pd_2(dba)_3$, 8 mol-% RuPhos, CsOAc (3 equiv.), Bu_4NOAc (1 equiv.), **3** (1 equiv.), $RB(OH)_2$ (1.3 equiv.), microwave, 150°C, 50 min, ACN/H_2O; [B]Method B: 4 mol-% $Pd_2(dba)_3$, 8 mol-% RuPhos, CsOAc (3 equiv.), **3** (1 equiv.), $RB(OH)_2$ (1.3 equiv.), sealed vial, 90°C, 15 h, ACN/H_2O; [C]Method C: 4 mol-% $Pd_2(dba)_3$, 8 mol-% RuPhos, CsOAc (3 equiv.), Bu_4NOAc (1 equiv.), **3** (1 equiv.), $RB(OH)_2$ (1.3 equiv.), sealed vial, 90°C, 6 h, ACN/H_2O; decomposing = iodo intermediate **3a** was found to undergo dehalogenation under the reaction conditions. [D]Isolated yields.

mixture was diluted with ethyl acetate, the ethyl acetate layer separated, washed with water, followed by a brine wash, dried over anhydrous sodium sulfate, and concentrated to get the crude material. The crude product was directly purified by column chromatography (0–20 % hexane/EtOAc) to isolate the 3-substituted-2-aryl or heteroaryl imidazo[4,5-*b*]pyridine derivatives.

Method C

The same as that of Method B, except that the reaction contents were heated to 90°C for 3 h.

The synthesis of the halo intermediates **3** (**3a**, **3b**, and **3c**) was done according to the procedures mentioned in ref. [21]. The intermediates were found to be very labile and were found to degrade over time (so they were stored at −20°C and used immediately for the coupling step).

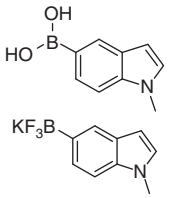
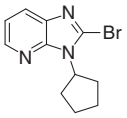
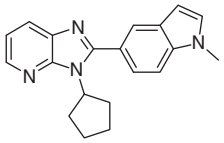
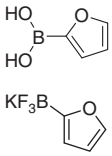
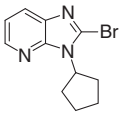
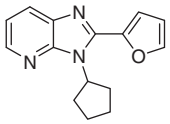
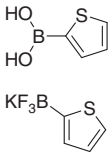
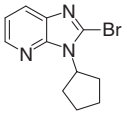
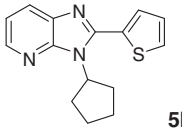
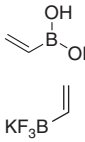
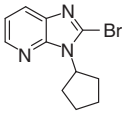
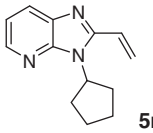
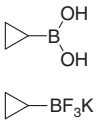
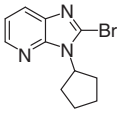
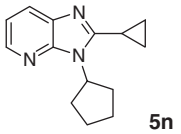
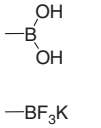
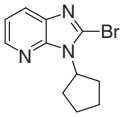
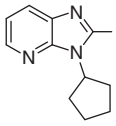
Experimental Results

*3-Cyclopentyl-2-(naphthalen-1-yl)-3*H*-imidazo[4,5-*b*] pyridine (**5a**)*

Prepared from **4a** using the general procedure (Method C). Purification by flash column chromatography (48–53 % ethyl

Table 5. Comparative study of cross-coupling of 3 with boronic acids and potassium trifluoroborate salts

Method C: 4 mol-% $Pd_2(dba)_3$, 8 mol-% RuPhos, CsOAc (3 equiv.), Bu_4NOAc (1 equiv.), **3** (1 equiv.), RBF_3K (1.3 equiv.), sealed vial, 90°C, 6 h, ACN/H_2O

Entry	R^2BX	Halo intermediate **3**	Product **5**	Yield [%][A]
1			 **5e**	32 88
3			 **5j**	No reaction 30
4			 **5k**	40 90
5			 **5m**	25 85
6			 **5n**	20 52
7			 **5p**	No reaction No reaction

[A]Isolated yields.

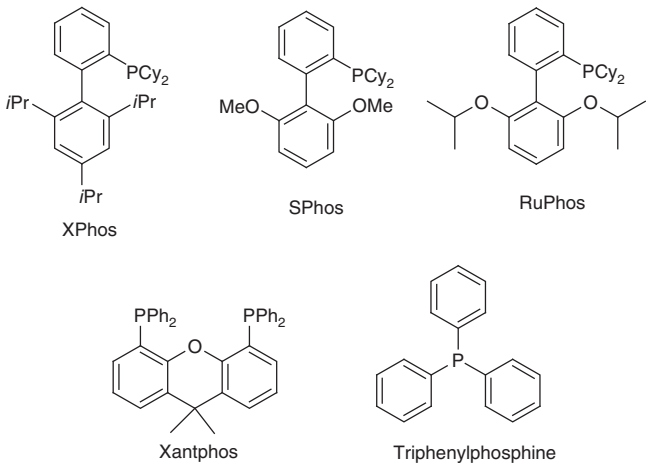
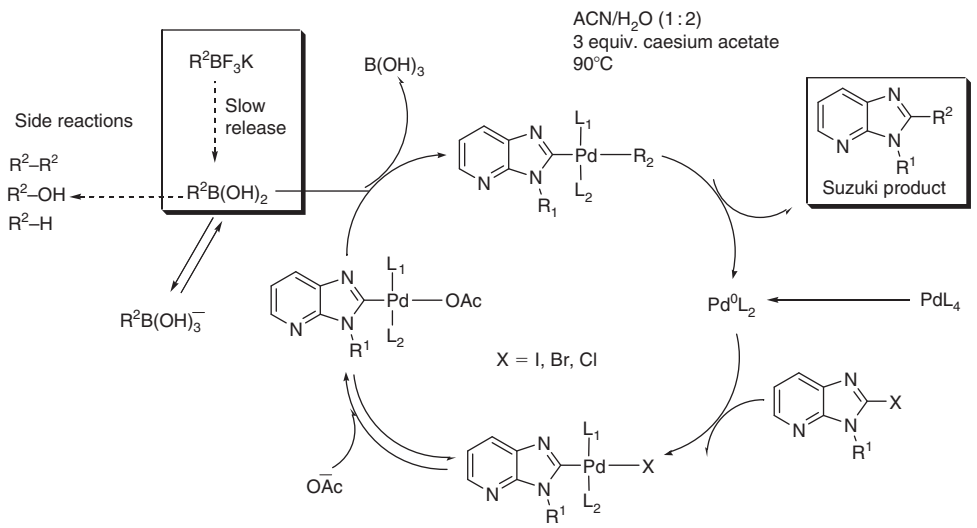


Fig. 4. Ligands used during optimization.

acetate in light petroleum) yielded the product as a white solid (20 mg, 81 %). Mp 135.6–136.7°C. δ_H (300 MHz, $CDCl_3$) 1.44–1.48 (m, 2H), 1.87–1.91 (m, 4H), 2.49–2.51 (m, 2H), 4.36–4.38 (m, 1H), 7.35–7.38 (m, 1H), 7.55–7.59 (m, 3H), 7.61–7.71 (m, 2H), 8.10–8.20 (m, 3H), 8.43–8.45 (m, 1H). δ_C (100 MHz, $CDCl_3$) 24.83, 30.59, 58.06, 119.96, 122.52, 125.46, 125.72, 127.12, 128.07, 129.45, 130.34, 132.72, 134.26, 143.48, 147.06, 156.57. *m/z* 314.12 (M + H). Anal. Calc. for $C_{21}H_{19}N_3$: C 80.48, H 6.11, N 13.41. Found: C 80.55, H 6.39, N 13.78 %.

*3-Cyclopentyl-2-phenyl-3*H*-imidazo[4,5-*b*]pyridine (**5b**)*

Prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (43–48 % ethyl acetate in light petroleum) yielded the product as a white solid (35 mg, 88 %). Mp 124.6–125.7°C. δ_H (300 MHz, $CDCl_3$) 1.67–1.70 (m, 1H), 2.02–2.05 (m, 2H), 2.13–2.15 (m, 2H), 2.15–2.71 (m, 2H), 4.83–4.87 (m, 1H), 7.24–7.27 (m, 1H), 7.38–7.57 (m,



Scheme 6. Mechanism of Suzuki reaction.

3H), 7.69–7.71 (m, 2H), 8.10–8.12 (m, 1H), 8.40–8.41 (m, 1H). δ_C (100 MHz, $CDCl_3$) 24.81, 30.57, 58.03, 119.93, 127.08, 128.03, 128.42, 130.13, 130.56, 133.87, 134.69, 135.09, 135.19, 143.44, 148.02, 156.53. *m/z* 264.12 (M + H). Anal. Calc. for $C_{17}H_{17}N_3$: C 77.54, H 6.51, N 15.96. Found: C 77.49, H 6.73, N 15.90 %.

*1-Cyclopentyl-2-phenyl-1*H*-imidazo[4,5-*b*]pyridine (**5b***)*

The regioisomer of **5b** was prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (43–48 % ethyl acetate in light petroleum) yielded the product as a white solid (36 mg, 90 %). Mp 124.8–125.8°C. δ_H (300 MHz, $CDCl_3$) 1.62–1.66 (m, 1H), 1.97–2.01 (m, 2H), 2.05–2.09 (m, 2H), 2.11–2.67 (m, 2H), 4.77–4.81 (m, 1H), 7.19–7.22 (m, 1H), 7.31–7.52 (m, 3H), 7.62–7.65 (m, 2H), 8.05–8.08 (m, 1H), 8.33–8.36 (m, 1H). δ_C (100 MHz, $CDCl_3$) 24.76, 30.52, 58.01, 119.92, 127.05, 128.01, 128.41, 130.09, 130.53, 133.86, 134.67, 135.04, 135.16, 143.41, 148.01, 156.52. *m/z* 264.12 (M + H). Anal. Calc. for $C_{17}H_{17}N_3$: C 77.54, H 6.51, N 15.96 . Found: C 77.51, H 6.68, N 15.88 %.

*2-(Benzo[*d*][1,3]dioxol-5yl)-3-cyclopentyl-3*H*-imidazo [4,5-*b*]pyridine (**5c**)*

Prepared from **4c** using the general procedure (Method C). Purification by flash column chromatography (33–39 % ethyl acetate in light petroleum) furnished a white solid (15 mg, 88 %). Mp 144.6–145.7°C. δ_H (300 MHz, $CDCl_3$) 1.66–1.72 (m, 2H), 1.93–2.16 (m, 4H), 2.60–2.72 (m, 2H), 4.79–4.90 (m, 1H), 6.05 (s, 2H), 6.93–6.96 (d, *J* 9, 1H), 7.15–7.21 (m, 3H), 7.98–8.01 (dd, J_1 1.5, J_2 8, 1H), 8.32–8.34 (m, 1H). δ_C (100 MHz, $CDCl_3$) 24.74, 30.42, 57.90, 101.54, 108.54, 109.64, 117.98, 123.73, 124.21, 126.74, 135.42, 143.03, 147.89, 148.18, 154.72. *m/z* 308.13 (M + H). Anal. Calc. for $C_{18}H_{17}N_3O_2$: C 70.34, H 5.58, N 13.67. Found: C 70.39, H 5.76, N 13.78 %.

*2-(3,5-Bistrifluoromethyl)phenyl)-3-cyclopentyl-3*H*-imidazo[4,5-*b*]pyridine (**5d**)*

Prepared from **4d** using the general procedure (Method B and Method C). Purification by flash column chromatography (23–27 % ethyl acetate in light petroleum) furnished the product as a white solid (55 mg, 79 %). Mp 134.3–135.7°C. δ_H (300 MHz, $CDCl_3$) 1.72–1.73 (m, 1H), 2.03–2.13 (m, 4H), 2.68–2.75 (m, 2H), 4.71–4.77 (m, 1H), 7.25–7.30 (m, 1H), 8.05–8.10 (m, 2H), 8.19 (s, 2H), 8.42–8.44 (dd, J_1 1.5, J_2 4.7, 1H). δ_C (100 MHz, $CDCl_3$) 24.89, 30.83, 58.37, 117.42, 118.65, 121.04, 123.52, 123.56, 124.66, 127.61, 129.52, 131.63, 135.46, 144.28, 148.03, 151.61. *m/z* 400.12 (M + H). Anal. Calc. for $C_{19}H_{15}F_6N_3$: C 57.15, H 3.79, N 10.52. Found: C 57.25, H 3.93, N 10.90 %.

*3-Cylopentyl-2-(1-methyl-1*H*-indol-5-yl)-3*H*-imidazo [4,5-*b*]pyridine (**5e**)*

Prepared from **4e** using the general procedure (Method B and Method C). Purification by flash column chromatography (43–50 % ethyl acetate in light petroleum) furnished the product as a white solid (55 mg, 74 %). Mp 168.6–169.7°C. δ_H (400 MHz, $CDCl_3$) 1.62–1.67 (m, 2H), 2.01–2.04 (m, 4H), 2.09–2.15 (m, 2H), 3.87 (s, 3H), 4.93–5.02 (m, 1H), 6.61 (d, *J* 4, 1H), 7.16 (d, *J* 4, 1H), 7.20–7.23 (m, 1H), 7.47 (d, *J* 8, 1H), 7.56–7.58 (m, 1H), 7.97 (s, 1H), 8.04–8.06 (m, 1H), 8.36 (dd, J_1 4, J_2 4, 1H). δ_C (100 MHz, $CDCl_3$) 24.79, 30.45, 33.04, 57.99, 101.88, 109.52, 117.86, 12.60, 122.85, 126.58, 128.34, 130.15, 135.70, 137.32, 156.08. *m/z* 317.14 (M + H). Anal. Calc. for $C_{20}H_{20}N_4$: C 75.92, H 6.37, N 17.71. Found: C 75.98, H 5.89, N 17.90 %.

*(4-(3-Cyclopentyl-3*H*-imidazo[4,5-*b*]pyridin-2-yl) phenyl)(pyrrolidin-1-yl)methanone (**5f**)*

Prepared from **4f** using the general procedure (Method C). Purification by flash column chromatography (35–40 % ethyl acetate in light petroleum) yielded the product as a white solid (87 mg, 63 %). Mp 176.3–177.4°C. δ_H (400 MHz, $CDCl_3$) 1.64–1.67 (m, 2H), 1.83–1.92 (m, 4H), 2.03–2.06 (m, 4H), 2.49–2.57 (m, 2H), 3.44–3.53 (m, 4 H), 4.82–4.86 (m, 1 H), 7.31–7.34 (dd, 1H), 7.72–7.80 (m, 4H), 8.09–8.10 (m, 1H), 8.39–8.40 (m, 1H). δ_C (100 MHz, $CDCl_3$) 24.69, 24.78, 30.56, 47.24, 58.03, 119.97, 128.33, 128.72, 130.16, 130.76, 131.22, 133.54, 143.76, 144.22, 149.32, 170.56. *m/z* 361.44 (M + H). Anal. Calc. for $C_{22}H_{24}N_4O$: C 73.31, H 6.71, N 15.54. Found: C 73.59, H 6.44, N 15.80 %.

*3-Cyclopentyl-2-(2,4-dimethoxypyrimidin-5-yl)-3*H*-imidazo[4,5-*b*]pyridine (**5g**)*

Prepared from **4g** using the general procedure (Method B and Method C). Purification by flash column chromatography (38–42 % ethyl acetate in light petroleum) yielded the product as a

yellow solid (55 mg, 79 %). Mp 145.6–146.3°C. δ_H (300 MHz, $CDCl_3$) 1.65–1.73 (m, 2 H), 1.89–2.05 (m, 4 H), 2.60–2.62 (m, 2H), 4.04 (s, 3 H), 4.07 (s, 3 H), 4.39–4.42 (m, 1 H), 7.21–7.25 (m, 1 H), 8.38–8.43 (m, 2H), 8.52 (s, 1H). δ_C (75 MHz, $CDCl_3$) 23.77, 24.68, 29.61, 30.35, 32.59, 54.29, 55.27, 58.42, 118, 127.16, 143.58, 144.13, 160.41, 166.24, 168.76. *m/z* 326.14 (M + H). Anal. Calc. for $C_{17}H_{19}N_5O_2$: C 62.75, H 5.89, N 21.52. Found: C 62.71, H 5.92, N 21.55 %.

*3-Cyclopentyl-2-(2-methoxypyrimidin-5-yl)-3*H-*imidazo[4,5-*b*]pyridine (**5h**)*

Prepared from **4h** using the general procedure (Method B). Purification by flash column chromatography (38–42 % ethyl acetate in light petroleum) yielded product as a white solid (40 mg, 69 %). Mp 139.2–140.3°C. δ_H (400 MHz, $CDCl_3$) 1.55–1.72 (m, 2H), 1.80–2.22 (m, 4H), 2.60–2.72 (m, 2H), 4.10 (s, 3 H), 4.68–4.72 (m, 1H), 7.21–7.26 (m, 1H), 8.02–8.04 (m, 1H), 8.36–8.38 (m, 1H), 8.85 (s, 2H). δ_C (100 MHz, $CDCl_3$) 23.80, 30.78, 55.48, 58.36, 118.49, 127.32, 135.65, 143.86, 148.09, 159.59, 165.94. *m/z* 296.14 (M + H). Anal. Calc. for $C_{16}H_{17}N_5O$: C 65.07, H 5.80, N 23.71. Found: C 65.27, H 5.98, N 23.74 %.

*3-Cyclopentyl-2-(pyridin-2-yl)-3*H-*imidazo[4,5-*b*]pyridine (**5i**)*

Prepared from **4i** using the general procedure (Method B). Purification by flash column chromatography (48–52 % ethyl acetate in light petroleum) yielded the product as a white solid (10 mg, 15 %). Mp 124.6–125.3°C. δ_H (400 MHz, $CDCl_3$) 1.72–1.75 (m, 2H), 2.03–2.06 (m, 2H), 2.16–2.19 (m, 2H), 2.40–2.44 (m, 2H), 5.11–5.20 (m, 1H), 7.15–7.18(q, *J* 5.0, 1H) 7.25–7.27 (dd, J_1 1.0, J_2 5.0, 1H), 7.35–7.37 (d, *J* 8.2, 1H), 7.84–7.91 (m, 2H), 8.27–8.29 (dd, J_1 1.4, J_2 4.9, 1H), 8.40–8.41 (t, *J* 3.3, 1H). δ_C (100 MHz, $CDCl_3$) 24.72, 30.60, 54.67, 113.82, 118.0, 121.57, 125.80, 132.71, 140.19, 141.97, 146.55, 148.52, 154.94, 160.15. *m/z* 265.2 (M + H). Anal. Calc. for $C_{16}H_{16}N_4$: C 72.70, H 6.10, N 21.20. Found: C 72.84, H 6.04, N 21.13 %.

*3-Cyclopentyl-2-(furan-2-yl)-3*H-*imidazo[4,5-*b*]pyridine (**5j**)*

Prepared from **4j** using the general procedure (Method B and Method A). Purification by flash column chromatography (40–45 % ethyl acetate in light petroleum) yielded the product as a pale-yellow solid (50 mg, 77 %). Mp 147.4–148.5°C. δ_H (400 MHz, $CDCl_3$) 1.67–1.71 (m, 2H), 2.01–2.14 (m, 4H), 2.61–2.69 (m, 2H), 5.07–5.13 (m, 1H), 7.13–7.17 (m, 2H), 7.55–7.56 (d, *J* 4.84, 2H), 8.01–8.04 (dd, J_1 1.88, J_2 8.24, 1H), 8.32–8.33 (dd, J_1 1.24, J_2 4.92, 1H). δ_C (100 MHz, $CDCl_3$) 24.89, 30.60, 58.06, 118.42, 126.91, 127.81, 129.14, 131.94, 135.46, 143.76, 148.36, 149.08. *m/z* 254.2 (M + H). Anal. Calc. for $C_{15}H_{15}N_3O$: C 71.13, H 5.97, N 16.59. Found: C 71.22, H 5.91, N 16.53 %.

*3-Cyclopentyl-2-(thiophen-2-yl)-3*H-*imidazo[4,5-*b*]pyridine (**5k**)*

Prepared from **4k** using the general procedure (Method B and Method A). Purification by flash column chromatography (31–36 % ethyl acetate in light petroleum) yielded the product as a yellow solid (55 mg, 80 %). Mp 144.2–145.3°C. δ_H (400 MHz, $CDCl_3$) 1.74–1.78 (m, 2H), 2.07–2.23 (m, 4H), 2.69–2.78 (m, 2H), 5.18–5.22 (m, 1H), 7.24–7.27(m, 2H) 7.62–7.63 (d, *J* 4.6, 2H), 8.08–8.10 (dd, J_1 1.3, J_2 8.0, 1H), 8.39–8.40 (dd, J_1 1.5, J_2 4.8, 1H). δ_C (100 MHz, $CDCl_3$) 24.88, 30.58, 58.05, 118.39, 126.89, 127.80, 129.13, 131.91, 135.41, 143.48, 148.33, 148.93. *m/z* 270.2 (M + H). Anal. Calc. for $C_{15}H_{15}N_3S$: C 66.88, H 5.61, N 15.60. Found: C 66.97, H 5.57, N 15.57 %.

*3-Cyclopentyl-2-(pyridin-3-yl)-3*H-*imidazo[4,5-*b*]pyridine (**5l**)*

Prepared from **4l** using the general procedure (Method B). Purification by flash column chromatography (48–52 % ethyl acetate in light petroleum) yielded the product as a white solid (50 mg, 70 %). Mp 134.2–135.5°C. δ_H (400 MHz, $CDCl_3$) 1.70–1.74 (m, 2H), 2.06–2.21 (m, 4H), 2.68–2.75 (m, 2H), 4.80–4.85 (m, 1H), 7.28–7.31 (q, *J* 5.5, 1H), 7.53–7.57 (dd, J_1 2.5, J_2 4.8, 1H), 8.11–8.15 (t, *J* 7.0, 2H), 8.44–8.45 (d, *J* 4.6, 1H), 8.82 (s,1H), 8.98 (s, 1H). δ_C (100 MHz, $CDCl_3$) 24.82, 30.74, 58.28, 118.45, 123.67, 127.37, 135.65, 137.09, 143.85, 148.16, 149.84, 150.93, 151.98. *m/z* 265.2 (M + H). Anal. Calc. for $C_{16}H_{16}N_4$: C 72.70, H 6.10, N 21.20. Found: C 72.77, H 6.08, N 21.14 %.

*3-Cyclopentyl-2-vinyl-3*H-*imidazo[4,5-*b*]pyridine (**5m**)*

Prepared from **4m** using the general procedure (Method B and Method A). Purification by flash column chromatography (31–36 % ethyl acetate in light petroleum) yielded the product as a white solid (11 mg, 62 %). Mp 115.6–116.3°C. δ_H (400 MHz, $CDCl_3$) 1.80–1.90 (m, 2H), 2.06–2.10 (m, 4H), 2.13–2.18 (m, 2H), 5.11–5.20 (m, 1H), 5.80–5.82 (d, 1H), 6.67–6.71 (m, 1H), 6.90–7.01 (m, 1H), 7.22–7.29 (m, 1H), 8.03–8.04 (d, 1H), 8.35–8.36 (d, 1H). δ_C (100 MHz, $CDCl_3$) 24.83, 30.59, 58.07, 118.64, 119.22, 120.01, 128.13, 129.06, 137.24, 144.24, 146.32. *m/z* 214.14 (M + H). Anal. Calc. for $C_{13}H_{15}N_3$: C 73.21, H 7.09, N 19.70. Found: C 73.27, H 6.98, N 19.79 %.

*3-Cyclopentyl-2-cyclopropyl-3*H-*imidazo[4,5-*b*]pyridine (**5n**)*

Prepared from **4n** using the general procedure (Method B and Method A). Purification by flash column chromatography (31–36 % ethyl acetate in light petroleum) yielded the product as a white solid (14 mg, 40 %). Mp 114.6–115.6°C. δ_H (400 MHz, $CDCl_3$) 1.22–1.27 (m, 4H), 1.71–1.75 (m, 2H), 2.04–2.08 (m, 4H), 2.09–2.11 (m, 4H), 5.21–5.25 (m, 1H), 7.19–7.22 (m, 1H), 7.88–7.90 (d, 1H), 8.25–8.26 (d, 1H). δ_C (100 MHz, $CDCl_3$) 2.82, 9.13, 24.81, 30.55, 58.07, 120.14, 128.08, 129.42, 144.48, 145.33, 150.54. *m/z* 228.14 (M + H). Anal. Calc. for $C_{14}H_{17}N_3$: C 73.98, H 7.54, N 18.49. Found: C 73.77, H 7.78, N 18.64 %.

*1-Methyl-2-phenyl-1*H-*imidazo[4,5-*b*]pyridine (**5q***)*

Prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (40–45 % ethyl acetate in light petroleum) yielded 90 % product as a light-yellow solid (35 mg). Mp 123.8–124.8°C. δ_H (400 MHz, $CDCl_3$) 4.24 (s, 3H), 7.56–7.78 (m, 6H), 7.98 (d, *J* 8.24, 1H), 8.86 (d, *J* 8.64, 1H). δ_C (100 MHz, $CDCl_3$) 29.76, 120.54, 126.11, 126.83, 127.78, 129.27, 130.12, 132.44, 146.34, 150.54, 151.88. *m/z* 210.2 (M + H). Anal. Calc. for $C_{13}H_{11}N_3$: C 74.62, H 5.30, N 20.08. Found: C 74.68, H 5.27, N 20.04 %.

*3-(3,4-Dimethoxybenzyl)-2-phenyl-3*H-*imidazo[4,5-*b*]pyridine (**5r**)*

Prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (55–60 % ethyl

acetate in light petroleum) yielded product as a white solid (33 mg, 85 %). Mp 132.5–133.5°C. δ_H (400 MHz, $CDCl_3$) 3.75 (s, 6H), 5.37 (s, 2H),6.31–6.64 (m, 3H), 7.09–7.13 (m, 1H), 7.36–7.53 (m,6H), 8.56 (s, 1H). δ_C (100 MHz, $CDCl_3$) 44.21, 53.55, 55.48, 104.18, 116.21, 117.97, 118.85, 127.82, 128.81, 129.78, 130.34, 131.93, 145.18, 155.87, 156.52, 157.63, 160.86. *m/z* 346.4 (M + H). Anal. Calc. for $C_{21}H_{19}N_3O_2$: C 73.03, H 5.54, N 12.17. Found: C 73.14, H 5.48, N 12.14 %.

*1-(3,4-Dimethoxybenzyl)-2-phenyl-1*H*-imidazo[4,5-*b*] pyridine (**5r***)*

Prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (58–60 % ethyl acetate in light petroleum) yielded 88 % product as a white solid (35 mg). Mp 132.9–134.3°C. δ_H (400 MHz, $CDCl_3$) 3.71 (s, 6H), 5.32 (s, 2H), 6.28–6.54 (m, 3H), 7.04–7.09 (m, 1H), 7.31–7.48 (m, 6H), 8.48 (s, 1H). δ_C (100 MHz, $CDCl_3$) 44.16, 53.51, 55.38, 104.12, 116.15, 117.91, 118.77, 127.78, 128.79, 129.76, 130.31, 131.88, 145.14, 155.86, 156.51, 157.59, 160.82. *m/z* 346.4 (M + H). Anal. Calc. for $C_{21}H_{19}N_3O_2$: C 73.03, H 5.54, N 12.17. Found: C 73.11, H 5.49, N 12.16 %.

*3-(Cyclopropylmethyl)-2-phenyl-3*H*-imidazo[4,5-*b*] pyridine (**5s**)*

Prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (46–50 % ethyl acetate in light petroleum) yielded 91 % product as an off-white solid (36 mg). Mp 124.7–125.7°C. δ_H (400 MHz, $CDCl_3$) 0.46–0.77 (m, 5H), 3.94 (s, 2H), 7.48–7.81 (m, 6H), 7.97 (d, *J* 7.88, 1H), 8.85 (d, *J* 8.44, 1H). δ_C (100 MHz, $CDCl_3$) 2.78, 5.16, 24.81, 53.59, 120.17, 128.11, 129.47, 130.42, 132.22, 132.35, 133.68, 146.28, 147.36, 151.86. *m/z* 249.3 (M + H). Anal. Calc. for $C_{16}H_{15}N_3$: C 77.08, H 6.06, N 16.85. Found: C 77.17, H 6.01, N 16.80 %.

*(*tert*-Butyl)-2-phenyl-1*H*-imidazo[4,5-*b*]pyridine-1-carboxylate (**5t**)*

Prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (22–27 % ethyl acetate in light petroleum) yielded 72 % product as a white solid (28 mg). Mp 142.6–143.6°C. δ_H (400 MHz, $CDCl_3$) 1.72 (s, 9H), 7.43–7.76 (m, 6H), 7.93 (d, *J* 7.72, 1H), 8.78 (d, *J* 8.24, 1H). δ_C (100 MHz, $CDCl_3$) 26.78, 77.64, 120.24, 128.23, 129.67, 130.74, 131.28, 132.56, 145.45, 146.37, 148.24, 150.98. *m/z* 195.3 (M + H). Anal. Calc. for $C_{17}H_{17}N_3O_2$: C 69.14, H 5.80, N 14.23. Found: C 69.27, H 5.74, N 14.15 %.

*3-(Benzyl)-2-phenyl-3*H*-imidazo[4,5-*b*]pyridine (**5u**)*

Prepared from **4b** using the general procedure (Method C). Purification by flash column chromatography (55–65 % ethyl acetate in light petroleum) yielded 86 % product as an off-white solid (34 mg). Mp 128.4–129.4°C. δ_H (400 MHz, $CDCl_3$) 5.64 (s, 2H), 7.23–7.34 (m, 5H), 7.46–7.76 (m, 6H), 7.93 (d, *J* 7.76, 1H), 8.83 (d, *J* 8.36, 1H). δ_C (100 MHz, $CDCl_3$) 47.26, 120.19, 124.23, 125.86, 126.94, 126.98, 128.32, 129.49, 130.35, 132.46, 133.72, 135.08, 146.33, 147.42, 152.13. *m/z* 286.3 (M + H). Anal. Calc. for $C_{17}H_{17}N_3O_2$: C 79.98, H 5.30, N 14.73. Found: C 80.06, H 5.23, N 14.71 %.

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