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ARTICLE

Metal-free site-selective C–N bond-forming reaction of polyhalogenated pyridines and pyrimidines

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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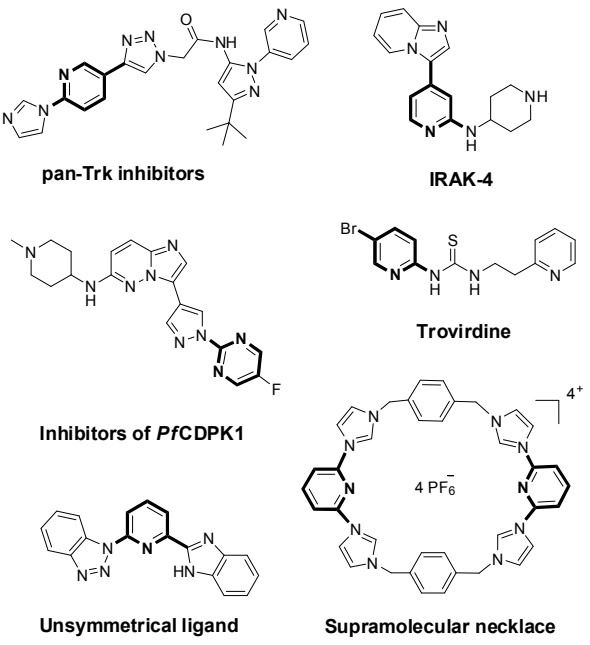
This paper presents a metal-free method for highly site-selective C–N bond-forming reaction of polyhalogenated pyridines and pyrimidines. The preferred coupling site can be tuned from the fluorine group bearing the *N*-heterocyclic ring to the chlorine group when changing from the pyridine ring to the pyrimidine ring. A wide array of halogenated pyridines preferentially reacted with amines at the fluorine group of the pyridine ring to generate monosubstituted halogenated pyridines with high selectivities. Different halogen atoms at various positions were produced by the pyridine ring that performed well under mild conditions. Halogenated pyrimidines underwent highly selective coupling at the chloride group with a wide range of amines having broad substrate applicability and moderate to good yields. The selectivity of the polyfluoropyridines in the developed reaction system was also tested, and the result indicated that the reaction occurred site-selectively at the *ortho*-position of the nitrogen ring. This reaction accommodated a wide range of halogenated groups. Thus, a wide range of chloro-, bromo-, iodo-, and fluoropyridines were generated, which have a wide utility for organic synthesis.

Introduction

Polysubstituted heteroarenes are important building blocks for bioactive medicinal molecules, advanced materials and organometallic catalysts.[1] In particular, polysubstituted pyridines and pyrimidines are used as inhibitors of anti-HIV (e.g., Trovirdine),[2] enzymes (e.g., IRAK-4),[3] pan-Trk-inhibitors,[4] and PfCDPK1.[5] These compounds are also key in the construction of supramolecular frame[6] and dye-sensitized solar cells,[7] as well as precursors of organometallic catalysts (Scheme 1).[8]

The substituents bearing *N*-heterocycles often differ. Therefore, controlling the selectivity of halogen atoms on *N*-heterocycles is crucial to construct polysubstituted *N*-heteroarenes.[9] Yu et al.[10] were the first to prepare 2-bromo-6-(pyrazol-1-yl)pyridines from 2,6-dibromopyridine and pyrazoles through palladium-catalyzed Buchwald–Hartwig coupling (Scheme 2, method a). We have recently found a low-cost and environment-friendly copper catalyst and developed a copper-catalyzed synthesis method to prepare 2-bromo-6-substituent-pyridines (Scheme 2, method b).[11] A metal-free method is an alternative strategy to access these key compounds. Meanwhile, Frech et al.[12] have developed a metal-free method to prepare 6-bromopyridine-2-amines (Scheme 2, method c). However, these methods are currently limited to 2,6-dibromopyridine.



Scheme 1. Example of application.

Considering the importance of pyridines with substituents at other positions, Bryce et al.[13] have reported a method to prepare brominated *N*-heterocyclic substituted pyridines or

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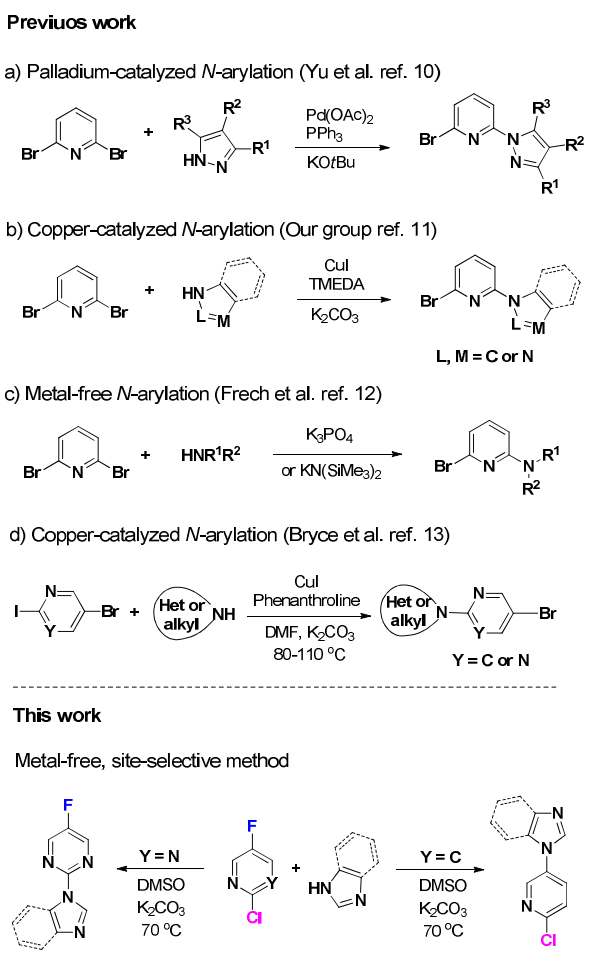
† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

pyrimidines through a copper-catalyzed C–N bond-forming reaction (Scheme 2, method d). However, in a copper-catalyzed system, the selectivity of halogens bearing the *N*-heteroaromatic ring cannot be regulated by the type of *N*-heteroaromatic ring. Imidazole prefers to react with the iodine atom of either 5-bromo-2-iodopyridine or 5-bromo-2-iodopyrimidine.



Scheme 2. Synthetic method for substituted pyridines or pyrimidines.

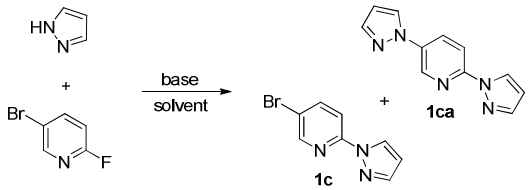
Selective C–F bond activation has become a current area of interest.[14] In this paper, we report a metal-free method for the highly site-selective coupling of halogenated pyridines or pyrimidines with amines through C–F bond activation (Scheme 2). Changing the type of the N-heteroaromatic ring switches the preferred coupling site from the fluorine atom to the chlorine atom. Products are generated because an active halide site has a wide functionality for organic synthesis through a series of subsequent transformations.

Results and Discussion

Substituted halogenated pyridines are key structural units in a multitude of pharmaceuticals, agrochemicals and advanced materials.[15]

The coupling reaction between 5-bromo-2-fluoropyridine and pyrazole was chosen as the model reaction to optimize the reaction conditions. A range of reaction conditions, including temperature, solvent, and base, was investigated (Table 1).

Table 1. Optimization of 5-bromo-2-fluoropyridine coupling[a]



Entry	T (°C)	Solvent	Base	Yield (%)
1	50	DMSO	K_2CO_3	39 (0)
2	60	DMSO	K_2CO_3	67 (0)
3	70	DMSO	K_2CO_3	95 (trace)
4	90	DMSO	K_2CO_3	93 (6)
5	110	DMSO	K_2CO_3	53 (45)
6	70	DMF	K_2CO_3	58 (trace)
7	70	DMA	K_2CO_3	67 (7%)
8	70	NMP	K_2CO_3	47 (trace)
9	70	DMSO	$K_3PO_4{\cdot}3H_2O$	77 (11)
10	70	DMSO	KOH	26 (40)
11	70	DMSO	KO*t*Bu	0 (53)
12	70	DMSO	$NaHCO_3$	68 (12)
13	70	DMSO	Na_2CO_3	70 (19)
14	70	DMSO	NaOH	11 (68)
15	70	DMSO	NaO*t*Bu	0 (33)
16	70	DMSO	Cs_2CO_3	21 (45)

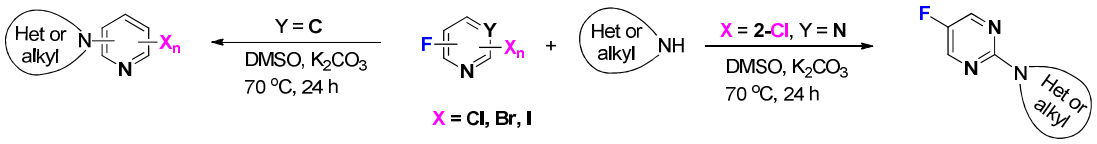
[a] Reaction conditions: 5-bromo-2-fluoropyridine (0.5 mmol), pyrazole (1.0 mmol), base (1.0 mmol) in solvent (2 mL), 24 h. DMSO = dimethylsulfoxide, DMA = *N,N*-dimethylacetamide, DMF = *N,N*-dimethylformamide, NMP = *N*-methyl-2-pyrrolidone. Isolated yield, data in parentheses correspond to isolated yield of **1ca**.

The effect of temperature on the coupling of 5-bromo-2-fluoropyridine with pyrazole was first examined. The reaction rate increased at reaction temperatures ranging from 50 °C to 70 °C (Table 1, entries 1-3). However, the monosubstituted product underwent second coupling and conversion into the disubstituted product at temperatures above 70 °C (Table 1, entries 4 and 5). Evaluation of various solvents showed that DMSO was superior to DMF, DMA, and NMP (Table 1, entries 3, and 6-8). Evaluation of bases exhibited that weak bases (Table 1, entries 3, 9, 12, and 13) had better selectivity than strong bases (Table 1, entries 10, 11, and 14-15), with K_2CO_3 exhibiting the best results (Table 1, entry 3). Despite being a weak base, Cs_2CO_3 still yielded disubstituted products (Table 1, entry 16). Inorganic base combined with dipolar aprotic solvents such as DMSO, form a superbasic media.[16] The extraordinary basicity of Cs_2CO_3/DMSO may accelerate the

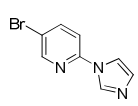
deprotonation of azole. However, other weak bases exhibit different catalytic effects from Cs_2CO_3, which indicates that base acts not only as a deprotonation agent but also exerts additional effects on reaction rates.[14b]

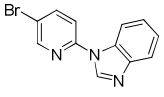
A reaction system using di- or multihalogenated pyridine and a range of amines was explored under the optimized reaction conditions (Table 2).

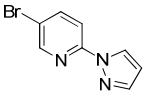
Table 2. Substrate scope of halogenated pyridine and pyrimidine[a]

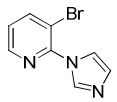


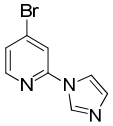
Pyridine ring

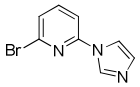

1a, 95% (0)

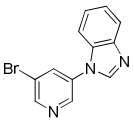

1b, 89% (0)

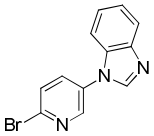

1c, 95% (0)

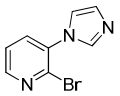

1d, 96% (0)

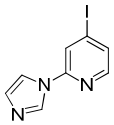

1e, 68%

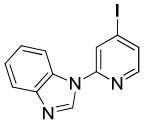

1f, 76%

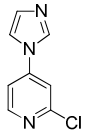

1g, 84% (trace)

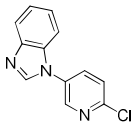

1h, 43%

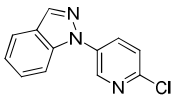

1i, 28%

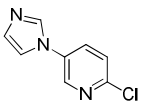

1j, 97% (0)

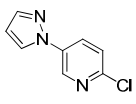

1k, 95% (0)

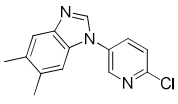

1l, 94% (0)

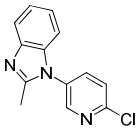

1m, 65%[b] (0)

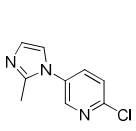

1n, 43%[b]

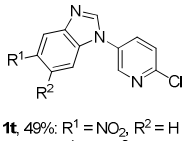

1o, 36%[b]

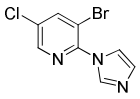

1p, 51%[b]


1q, 37%[b]

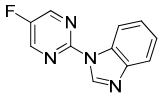

1r, 42%[b]

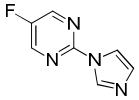

1s, 33%[b]

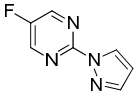

1t, 49%: R^1 = NO_2, R^2 = H
1u, 8%: R^1 = H, R^2 = NO_2

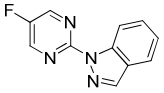

1v, 85% (trace)

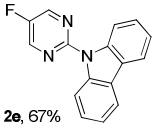
Pyrimidine ring

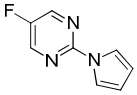

2a, 97%

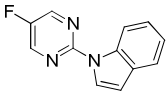

2b, 86%

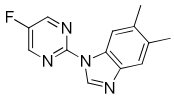

2c, 66%

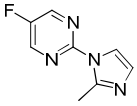

2d, 51%

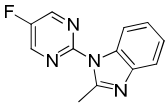

2e, 67%

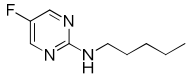

2f, 87%

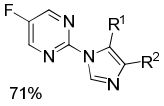

2g, 81%

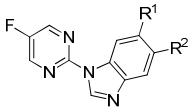

2h, 96%

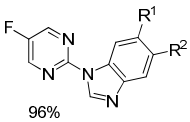

2i, 86%

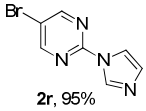

2j, 71%

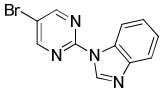

2k, 96%

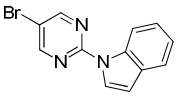

71%
2l, R^1 = H, R^2 = Me
2m, R^1 = Me, R^2 = H

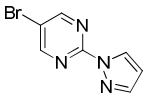

2n, 41%[c]: R^1 = H, R^2 = NO_2
2o, 47%: R^1 = NO_2, R^2 = H


96%
2p, R^1 = H, R^2 = Me
2q, R^1 = Me, R^2 = H


2r, 95%


2s, 97%


2t, 56%


2u, 92%

2v, 46%

2w, 90%

2x, 95%

[a] Reaction conditions: halogenated pyridine and pyrimidine (0.5 mmol), amine (1.0 mmol), K_2CO_3 (1.0 mmol) in DMSO (2 mL), 70 °C, 24 h. Isolated yield, data in parentheses correspond to isolated yield of 2,6-disubstituted pyridine. [b] 90 °C. [c] NMR yield.

Halogen atom substituted position on the pyridine ring showed evident effectd on the reaction rate. The 2-fluoropyridine with bromide substitution at the *meta* position to the nitrogen ring showed higher reactivity than that with

bromide substitution at the *para* or *ortho* position to the nitrogen ring. Thus, 5-bromo-2-fluoropyridine and 3-bromo-2-fluoropyridine easily reacted with amines to provide the corresponding products in excellent yield (Table 2, 1a-d). However, 4-bromo-2-fluoropyridine and 2-bromo-6-fluoropyridine were weakly reactive in this system and provided moderate product yields (Table 2, 1e and 1f). The electronic effect of the bromide group bearing the 3-fluoropyridine ring was also observed. The 3-fluoropyridine with bromide substitution at the *meta* position to the nitrogen ring showed higher reactivity than those with bromide substitution at the *ortho* position to the nitrogen ring. Therefore, 5-bromo-3-fluoropyridine successfully converted them into the desired product in high yields (Table 2, 1g). However, 2-bromo-5-fluoropyridine and 2-bromo-3-fluoropyridine produced low conversion (Table 2, 1h and 1i). This result suggests that the position of the bromide group on the pyridine ring is crucial to the reactivity of fluorinated pyridine.

The iodinated and chlorinated fluoropyridines were also investigated for their reactivity in the developed metal-free system. This method showed high selectivity and reactivity, and the nucleophilic substitution occurred site-selectively at the fluorine substituent of the pyridine ring (Table 2, 1j-s).

The electronic effect of the nitro-substituent of benzimidazole on regioselectivity was examined. The nitro-substituent evidently affected regioselectivity and produced a 6:1 mixture of 1t/1u.

Trihalogenated pyridines were also examined for selectivity and reactivity in the developed metal-free reaction system. For example, 3-bromo-5-chloro-2-fluoropyridine underwent high conversion and produced satisfactory results with minimal amounts of by-products (Table 2, 1v).

The type of *N*-heterocyclic ring was also examined to extend the scope of the reaction system. Interestingly, replacing the pyridine ring with a pyrimidine ring resulted in reversed selectivity. The chlorine atom on the pyrimidine ring had evidently higher reactive activity than the fluorine atom.

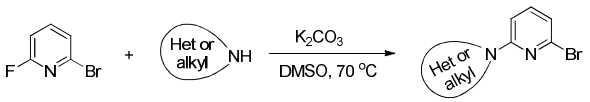
The scope of the reaction system using 5-fluoro-2-chloropyrimidine and a range of amines was explored.

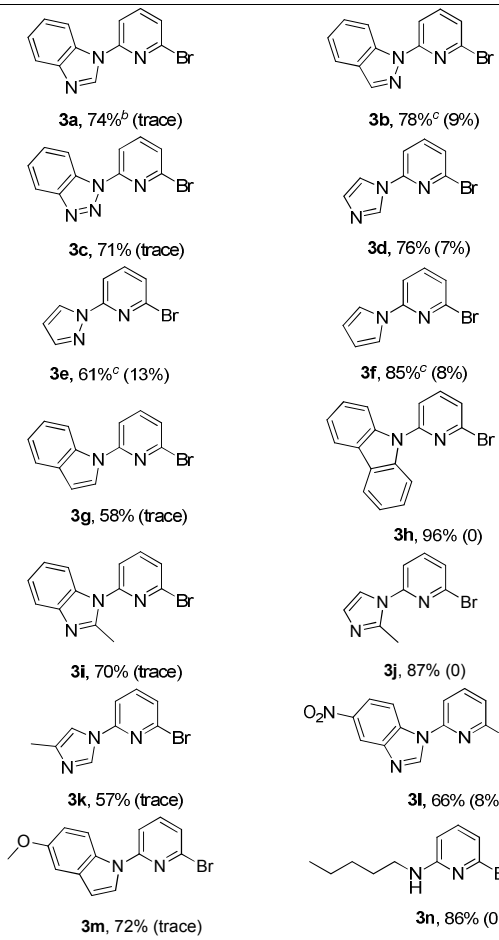
The coupling of 5-fluoro-2-chloropyrimidine with a range of azole and indole derivatives proceeded smoothly to produce moderate to good yields (Table 2, 2a-h). Steric hindrance was not evident in the developed metal-free system. 2-Methylbenzimidazole and 2-methylimidazole successfully reacted with 5-fluoro-2-chloropyrimidine to provide good results (Table 2, 2i and 2j). 5-Fluoro-2-chloropyrimidine easily reacted with *n*-pentylamine to generate the desired product with a 96% yield (Table 2, 2k).

Some starting materials are tautomeric compounds. Thus, their regioselectivity on the coupling reaction was examined. The electronic effect of the methyl- and nitro-substituents only slightly affected regioselectivity, resulting in an approximately 1:1 mixture of 2n/2o or 2p/2q. By contrast, 5-methylimidazole showed high regioselectivity and 5-methyl-substituted products were predominantly formed, producing 1:5 mixtures of 2l/2m.

The main factors responsible for the high site-selectivity of the chloride group bearing pyrimidine were investigated by employing 5-bromo-2-chloropyrimidine instead of 5-fluoro-2-chloropyrimidine (Table 2, 2q-v). The preferred reaction site was also the chloride group, which is consistent with the obtained result when 5-fluoro-2-chloropyrimidine was employed. The reactivity of 2-chloropyrimidine was investigated to eliminate the interference of halogen on the pyridine ring. 2-Chloropyrimidine readily reacted to yield the desired product (Table 2, 2x). Thus, the selectivity of the reaction was dominated by two nitrogen bearing pyrimidine rings rather than by the halide group–bearing the pyrimidine ring.

Table 3. Coupling of 2-bromo-6-fluropyridine and amines[a]





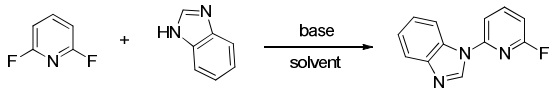
[a] Reaction conditions: 2-bromo-6-fluoropyridine (0.5 mmol), amine (1.0 mmol), K_2CO_3 (1.0 mmol) in DMSO (2 mL), 70 °C, 24 h. Isolated yield, data in parentheses correspond to isolated yield of 2,6-disubstituted pyridine. [b] 60 °C. [c] 90 °C.

6-Substituted 2-bromopyridines are important core structures of various agrochemical and pharmaceutical intermediates. They are generally synthesized using 2,6-dibromopyridine.[10-12] Herein, the developed metal-free method was applied to synthesize 6-substituted 2-bromopyridines using 2-bromo-6-fluropyridine (Table 3).

The developed metal-free method exhibited higher selectivity than our previously reported copper-catalyzed approach[11] and yielded a monosubstituted product with minimal amounts of disubstituted products. Steric and electronic effects on the amines were not evident on reactivity and regioselectivity in the developed reaction system.

We explored the C–N coupling of 2,6-difluoropyridine with benzimidazole under metal-free reaction conditions because it is less costly and more readily available than that of 2-bromo-6-fluoropyridine. The selectivity of the pyridine fluorine atom was efficiently controlled.

Table 4. Optimization of 2,6-difluoropyridine coupling[a]



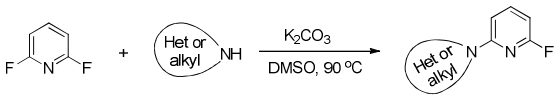
Entry	T (°C)	Solvent	Base	Yield (%)
1[b]	90	DMSO	K_2CO_3	34 (57)
2[c]	90	DMSO	K_2CO_3	49 (29)
3	**90**	**DMSO**	**K_2CO_3**	**85 (11)**
4[d]	90	DMSO	K_2CO_3	83 (9)
5	70	DMSO	K_2CO_3	51 (trace)
6	110	DMSO	K_2CO_3	70 (26)
7	90	DMF	K_2CO_3	68 (13)
8	90	DMA	K_2CO_3	75 (19)
9	90	NMP	K_2CO_3	73 (22)
10	90	DMSO	$K_3PO_4·3H_2O$	54 (7)
11	90	DMSO	KOH	52 (25)
12	90	DMSO	KO*t*Bu	65 (34)
13	90	DMSO	$NaHCO_3$	70 (17)
14	90	DMSO	Na_2CO_3	69 (13)
15	90	DMSO	HCOONa	59 (16)
16	90	DMSO	NaOH	57 (27)
17	90	DMSO	NaO*t*Bu	37 (43)
18	90	DMSO	Cs_2CO_3	66 (38)

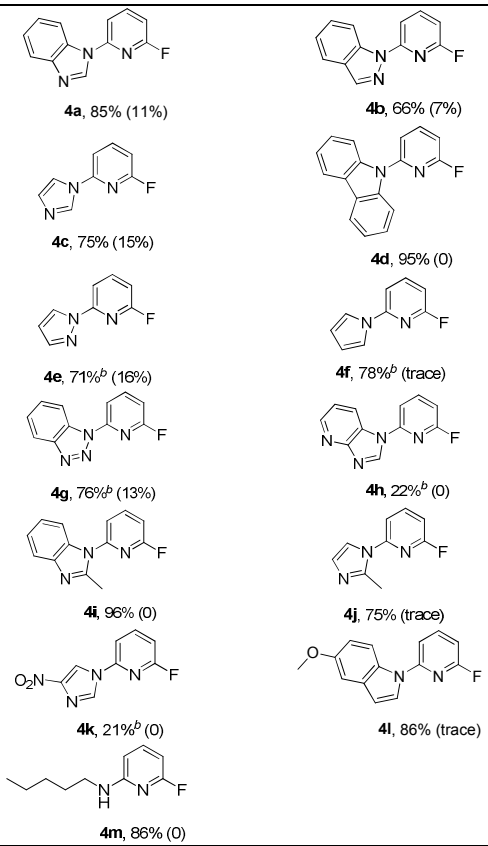
[a] Reaction conditions: 2,6-difluropyridine (0.75 mmol), benzimidazole (0.5 mmol), base (1.0 mmol) in solvent (4 mL), 6 h. Isolated yield, data in parentheses correspond to isolated yield of 2,6-di(benzimidazol-1-yl)pyridine. [b] Molar ratio of 2,6-difluropyridine:benzimidazole = 0.5:0.75. [c] Molar ratio of 2,6-difluropyridine:benzimidazole = 0.5:0.5. [d] Molar ratio of 2,6-difluropyridine:benzimidazole = 1.0:0.5.

The *N*-arylation of 2,6-difluoropyridine with benzimidazole was selected as the model reaction to optimize the reaction conditions, in which a range of reaction conditions, including solvent, temperature, base, and molar ratio of substrates, was evaluated. The optimal reaction conditions for the *N*-arylation of 2,6-difluoropyridine with benzimidazole were found to be a 1.5:1 molar ratio of 2,6-difluoropyridine and benzimidazole, 2.0 equiv. K_2CO_3 in DMSO at 90 °C.

Azole and indole derivatives were tested and afforded the corresponding products in good to excellent yields (Table 5, 4a-g). 4-Azabenzimidazole showed less reactivity and produced a lower yield than other azole (Table 5, 4h). The steric effect of azole in the developed reaction system was not observed and 2-methylbenzimidazole and 2-methylimidazole afforded good to excellent product yields (Table 5, 4i and 4j).

Table 5. Coupling of 2,6-difluoropyridine and amines[a]





[a] Reaction conditions: 2,6-difluoropyridine (0.75 mmol), amine (0.5 mmol), K_2CO_3 (1.0 mmol) in DMSO (4 mL), 90 °C, 6 h. Isolated yield, data in parentheses correspond to isolated yield of 2,6-disubstituted pyridine.[b] 110 °C.

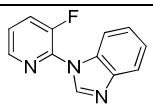
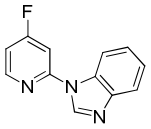
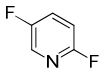
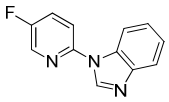
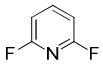
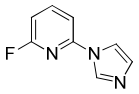
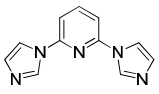
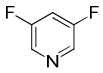
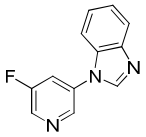
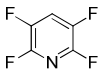
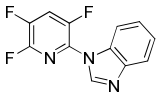
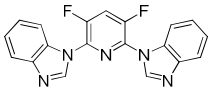
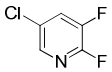
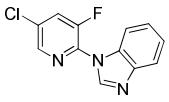
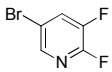
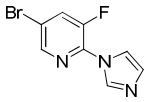
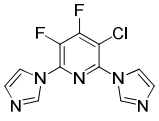
The electronic effect of imidazole and indole significantly influenced the reaction rate. The 5-methoxy-1*H*-indole bearing electron-donating group afforded high conversion with a good product yield (Table 5, 4l). However, the 4-nitro-1*H*-imidazole bearing electron-withdrawing group was less reactive and afforded a low product yield, even after the reaction temperature was increased to 110 °C (Table 5, 4k). *n*-Pentylamine was successfully coupled with 2,6-

difluoropyridine to afford the desired product in 86% yield (Table 5, 4m).

Fluorinated heteroaromatic molecules are extremely important building blocks in organic chemistry,[17] especially with fluorinated substituted pyridine compounds, which are important molecular scaffolds for drug discovery.[18]

The site-selectivities of difluoro and multifluoropyridine were investigated. The reaction occurred site-selectively at the *ortho* position of the nitrogen ring and exclusively produced *ortho*-substituted pyridine in good to excellent yields (Table 6).

Table 6. Coupling of polyfluorogenated pyridines[a]

Entry	Substrates	Monoproducts	Dimerisation product
1		 **5a**, 90%	none
2		 **5b**, 96%	none
3		 **5c**, 61%	none
4[b]		 **4c**, 73%	 **6a**, 15%
5		 **5d**, 97%	none
6		 **5e**, 32%	 **6b**, 30%
7		 **5f**, 85%	none
8		 **5g**, 95%	none
9		trace	 **6c**, 32%

[a] Reaction conditions: halogenated pyridine (0.5 mmol), amine (1.0 mmol), K_2CO_3 (1.0 mmol) in DMSO (2 mL), 90 °C, 24 h. Isolated yield.

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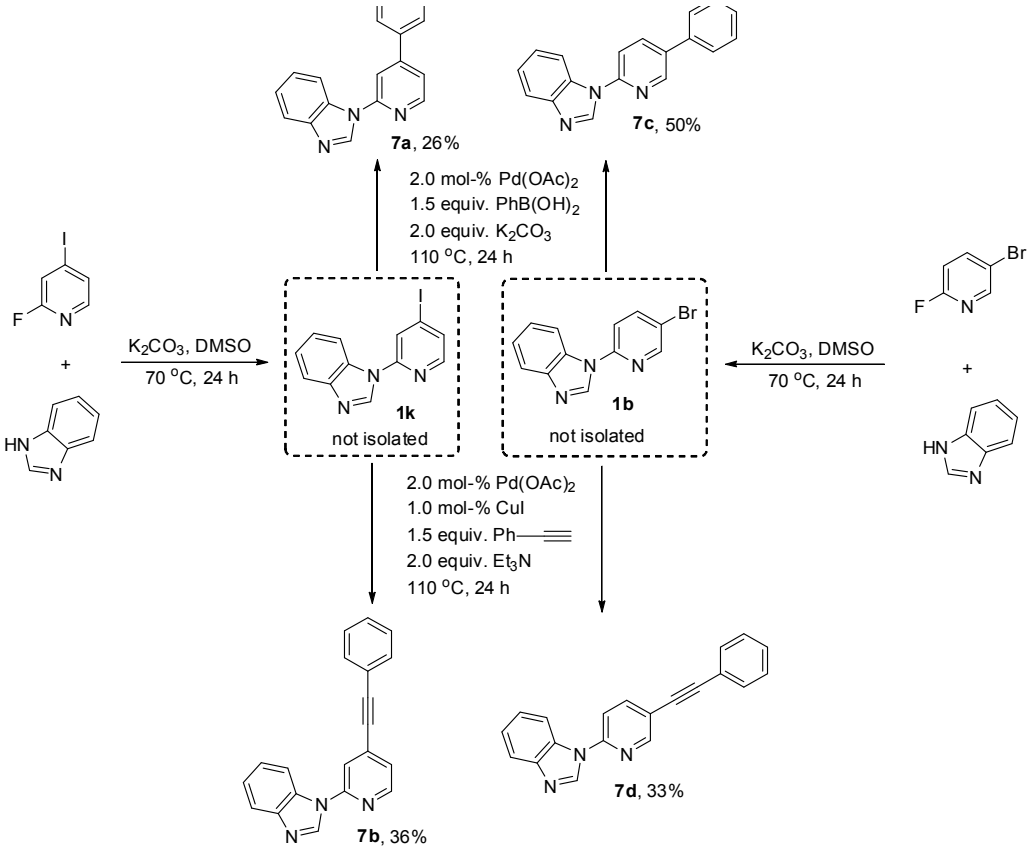
Halogens, such as chlorine, bromine, and iodine, on the *N*-heteroaromatic ring are well tolerated in this metal-free *N*-arylation. Thus, this system provides an opportunity to functionalize halogenated pyridines or pyrimidines further and convert them into useful pharmaceutical, agrochemical, and advanced material intermediates through a series of chemical transformations. In this study, we chose 4-iodo-2-fluoropyridine and 5-bromo-2-fluoropyridine as model substrates to explore their efficiency and selectivity through successive SNAr substitution reactions and transition-metal-catalyzed cross-coupling reaction without an intervening purification step. 4-Iodo-2-fluoropyridine and 5-bromo-2-fluoropyridine successively reacted in one-pot with benzimidazole and phenylboronic acid or phenylacetylene through nucleophilic substitution reaction palladium-catalyzed Suzuki coupling or Sonogashira coupling, resulting in valuable intermediates (Scheme 3).



Scheme 3. Functionalization of halogenated substituted pyridines.

Conclusions

We developed a metal-free method for highly site-selective synthesis of substituted pyridines and pyrimidines. The proposed reaction system showed high selectivity and reactivity for halogenated pyridines. Moreover, nucleophilic substitution site-selectively occurred at the fluorine substituent bearing the pyridine ring. A wide range of substituted pyridines bearing mono-halogen or multi-halogen group was obtained. The effect of the position of the bromine group on the pyridine ring was evident. Fluorinated pyridines bearing bromine group at the 3-position to the nitrogen ring were much more reactive than those bearing bromine group

at the 2- and 4-position to the nitrogen ring. The preferred coupling site was switched from the fluorine atom to the chlorine atom when changing from the pyridine ring to pyrimidine ring. The developed metal-free reaction system was highly efficient and selective for the coupling of 5-fluoro-2-chloropyrimidine with a range of amines bearing various functional groups. Site-selectivity was also observed with the coupling reaction between the polyfluoropyridines and amines in the developed reaction system. The reaction was found to occur preferentially at the ortho-position of the nitrogen ring. The major advantage of this process is that the selectivity of halogen atoms on N-heteroaromatic ring for C–N coupling reaction could be completely controlled. This characteristic provides a range of substituted pyridines and pyrimidines bearing fluorine, chloride, bromide, and iodine groups. The resulting halogenated N-heteroaromatic compounds could be converted into valuable intermediates through classical transition-metal-catalyzed Suzuki coupling and Sonogashira coupling.

Experimental

General Experimental Methods

All reactions were performed in glass tubes under air atmosphere. All reagents were purchased from commercial sources used without additional purification. All solvents were AR grade. NMR spectra were recorded on a Bruke Avance III HD 400 spectrometer using TMS as internal standard (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR). The Mass data of the compounds were collected on a Bruker ultrafleXtreme mass spectrometer.

General Procedure for Metal-Free N-Arylation

A mixture of halogenated pyridines, amines, and base in solvent was allowed to react under air atmosphere. The reaction mixture was heated to 70 °C or 90 °C for 24 h. After reaction, the reaction mixture was added to brine (15 mL) and extracted three times with dichloromethane (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

5-Bromo-2-(1*H*-imidazol-1-yl)pyridine (1a)[5]**.** Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (106 mg, 95%), mp = 145-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, J = 2.4 Hz, J = 0.4 Hz, 1H), 8.37 (s, 1H), 7.95 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.62 (t, J = 1.6 Hz, 1H), 7.31 (dd, J = 8.8 Hz, J = 0.8 Hz, 1H), 7.23 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.09, 147.67, 141.46, 134.94, 130.89, 117.71, 116.09, 113.45, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6BrN_3$ $[M+H]^+$ 223.9818, found 223.9825.

1-(5-Bromopyridin-2-yl)-1*H*-benzo[*d*]imidazole (1b)[13]. Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (122 mg, 89%), mp = 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 2.4 Hz, 1H), 8.57 (s, 1H), 8.05-7.99 (m, 2H), 7.89-7.87 (m, 1H), 7.50 (J = 8.4 Hz, J = 0.4 Hz, 1H), 7.43-7.37 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.42, 148.51, 144.57, 141.46, 141.05, 131.87, 124.50, 123.60, 120.77, 117.64, 115.24, 112.67, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8BrN_3$ $[M+H]^+$ 273.9974, found 273.9972.

5-Bromo-2-(1*H*-pyrazol-1-yl)pyridine (1c)[19]. Purification by flash chromatography (petroleum ether/EtOAc = 10:1): a white solid (106 mg, 95%), mp = 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, J = 2.8 Hz, J = 0.8 Hz, 1H), 8.47 (dd, J = 2.0 Hz, J = 1.2 Hz, 1H), 7.93-7.92 (m, 2H), 7.76 (s, 1H), 6.49 (dd, J = 2.4 Hz, J = 1.6 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.25, 148.88, 142.39, 141.17, 127.10, 117.02, 113.80, 108.17, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6BrN_3$ $[M+H]^+$ 223.9818, found 223.9825.

2,5-Di(1*H*-pyrazol-1-yl)pyridine (1ca). Purification by flash chromatography (petroleum ether/EtOAc = 10:1): a white solid, mp = 162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 2.4 Hz, 1H), 8.59 (d, J = 2.8 Hz, 1H), 8.19 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 2.4 Hz, 1H), 7.81-7.78 (m, 2H), 6.56 (t, J = 2.0 Hz, 1H), 6.52 (t, J = 2.0 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.61, 142.25, 141.88, 138.57, 134.83, 129.58, 127.11, 126.79, 112.81, 108.39, 108.07, ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_9N_5$ $[M+H]^+$ 212.0931, found 212.0932.

3-Bromo-2-(1*H*-imidazol-1-yl)pyridine (1d). Purification by flash chromatography (EtOAc): a white solid (111 mg, 99%), mp = 89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 8.18 (s, 1H), 8.10 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.57 (t, J = 1.6 Hz, 1H), 7.25 (dd, J = 8.0 Hz, J = 4.8 Hz, 1H), 7.21 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.80, 147.45, 143.65, 137.15, 129.18, 124.15, 119.22, 113.01, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6BrN_3$ $[M+H]^+$ 223.9818, found 223.9820.

4-Bromo-2-(1*H*-imidazol-1-yl)pyridine (1e). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (76 mg, 68%), mp = 62-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 1.6 Hz, 1H), 7.62-7.61 (m, 1H), 7.43 (dd, J = 5.2 Hz, J = 1.6 Hz, 1H), 7.25 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.72, 135.05, 134.84, 130.88, 130.86, 125.26, 116.08, 115.6, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6BrN_3$ $[M+H]^+$ 223.9818, found 223.9816.

2-Bromo-6-(1*H*-imidazol-1-yl)pyridine (1f). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (85 mg, 76%), mp = 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.61 (s, 1H), 7.41 (dd, J = 8.0 Hz, 1H), 7.31 (dd, J = 8.0 Hz, 1H), 7.19 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.81, 141.01, 140.91, 134.99, 131.01, 126.04, 116.12, 110.60, ppm; HRMS (EI): *m/z* calcd for $C_8H_6BrN_3$ $[M]^+$ 222.9740, found 222.9737.

1-(5-Bromopyridin-3-yl)-1*H*-benzo[*d*]imidazole (1g). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (115 mg, 84%), mp = 169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 2H), 8.17 (s, 1H), 8.08 (t, J = 2.4 Hz, 1H), 7.95-7.91 (m, 1H), 7.57-7.53 (m, 1H), 7.44-7.40 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.26, 144.03, 143.11, 141.54, 133.78, 133.73, 133.13, 124.56, 123.64, 121.13, 121.08, 109.86, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8BrN_3$ $[M+H]^+$ 273.9974, found 273.9972.

1-(6-Bromopyridin-3-yl)-1*H*-benzo[*d*]imidazole (1h). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (59 mg, 43%), mp = 214 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (dd, J = 2.4 Hz, J = 0.8 Hz, 1H), 8.14 (s, 1H), 7.95-7.90 (m, 1H), 7.79-7.73 (m, 2H), 7.51-7.48 (m, 1H), 7.43-7.38 (m, 2H), ppm; ^{13}C NMR (100 MHz,

$CDCl_3$): δ 145.29, 143.98, 141.54, 140.94, 133.75, 133.24, 132.62, 129.27, 124.53, 123.57, 121.04, 109.79, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8BrN_3$ $[M+H]^+$ 273.9974, found 273.9970.

2-Bromo-3-(1*H*-imidazol-1-yl)pyridine (1i). Purification by flash chromatography (EtOAc): a white solid (32 mg, 28%), mp = 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (dd, *J* = 4.8 Hz, *J* = 2.0 Hz, 1H), 7.73 (s, 1H), 7.68 (dd, *J* = 7.6 Hz, *J* = 4.8 Hz, 1H), 7.26 (s, 1H), 7.18 (t, *J* = 1.2 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.95, 139.81, 137.46, 135.87, 134.42, 129.99, 123.38, 120.43, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6BrN_3$ $[M+H]^+$ 223.9818, found 223.9814.

2-(1*H*-Imidazol-1-yl)-4-iodopyridine (1j). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (131 mg, 97%), mp = 116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.14 (d, *J* = 5.2 Hz, 1H), 7.75 (s, 1H), 7.61-7.60 (m, 2H), 7.21 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.24, 135.03, 131.05, 131.02, 121.45, 116.02, 107.15, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6IN_3$ $[M+H]^+$ 271.9679, found 271.9675.

1-(4-Iodopyridin-2-yl)-1*H*-benzo[*d*]imidazole (1k). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (128 mg, 95%), mp = 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.30 (d, *J* = 5.2 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 8.01 (s, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.70 (dd, *J* = 5.2 Hz, *J* = 1.6 Hz, 1H), 7.46-7.38 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.06, 149.47, 144.59, 141.08, 131.82, 130.86, 124.52, 123.65, 123.18, 120.78, 112.75, 107.14, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8IN_3$ $[M+H]^+$ 321.9836, found 321.9831.

2-Chloro-4-(1*H*-imidazol-1-yl)pyridine (1l). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (84 mg, 94%), mp = 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 5.6 Hz, 1H), 8.06 (s, 1H), 7.42-7.39 (m, 2H), 7.32-7.28 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.34, 151.38, 145.49, 134.94, 131.88, 116.77, 114.75, 113.33, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6ClN_3$ $[M+H]^+$ 180.0323, found 180.0314.

2-Chloro-5-(1*H*-benzimidazol-1-yl)pyridine (1m). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (75 mg, 65%), mp = 200-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 2.4 Hz, 1H), 8.13 (s, 1H), 7.96-7.91 (m, 1H), 7.87 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 7.60 (d, *J* = 8.8 Hz), 7.51-7.48 (m, 1H), 7.44-7.39 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.71, 144.89, 143.93, 141.58, 134.07, 133.31, 132.17, 125.48, 124.51, 123.57, 121.03, 109.78, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8ClN_3$ $[M+H]^+$ 230.0480, found 230.0473.

1-(6-Chloropyridin-3-yl)-1*H*-indazole (1n). Purification by flash chromatography (petroleum ether/EtOAc = 10:1): a white solid (50 mg, 43%), mp = 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (dd, *J* = 2.8 Hz, *J* = 0.4 Hz,1H), 8.27 (d, *J* = 1.2 Hz,1H), 8.09 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz,1H), 7.85 (dt, *J* = 8.4 Hz, *J* = 0.8 Hz,1H), 7.74 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz,1H), 7.54-7.50 (m, 2H), 7.33-7.29 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.42, 142.76, 138.70, 137.03, 136.12, 132.32, 128.05, 125.71, 124.87, 122.31, 121.75, 109.81, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8ClN_3$ $[M+H]^+$ 230.0480, found 230.0483.

2-Chloro-5-(1*H*-imidazol-1-yl)pyridine (1o). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (32 mg, 36%), mp = 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 2.8 Hz, 1H), 7.90 (s, 1H), 7.73 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz,1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.29 (s, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.10, 142.43, 135.52, 133.01, 131.7, 131.38, 125.22, 118.09, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6ClN_3$ $[M+H]^+$ 180.0323, found 180.0320.

2-Chloro-5-(1*H*-pyrazol-1-yl)pyridine (1p). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (46 mg, 51%), mp = 110-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 2.8 Hz,1H), 8.05 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz,1H), 7.95 (d, *J* = 2.4 Hz,1H), 7.78 (d, *J* = 1.6 Hz,1H), 7.44 (dd, *J* = 8.8 Hz, *J* = 0.8 Hz,1H), 6.54 (t, *J* = 2.0 Hz,1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.49, 142.24, 139.84, 135.74, 129.36, 126.82, 124.72, 108.79, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6ClN_3$ $[M+H]^+$ 180.0323, found 180.0323.

1-(6-Chloropyridin-3-yl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1q). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (48 mg, 37%), mp = 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 2.8 Hz, 1H), 7.99 (s, 1H), 7.84 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz,1H), 7.64 (s, 1H), 7.56 (d, *J* = 8.4 Hz,1H), 7.25 (s, 1H), 2.40 (s, 3H), 2.38 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.26, 144.64, 144.63, 142.54, 140.75, 133.82, 132.57, 132.47, 131.74, 125.39, 120.87, 109.92, 20.64, 20.26, ppm; HRMS (MALDI): *m/z* calcd for $C_{14}H_{12}ClN_3$ $[M+H]^+$ 258.0793, found 258.0788.

1-(6-Chloropyridin-3-yl)-2-methyl-1*H*-benzo[*d*]imidazole (1r). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (51 mg, 42%), mp = 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 2.8 Hz,1H), 7.78 (d, *J* = 8.0 Hz,1H), 7.74 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz,1H), 7.61 (d, *J* = 8.4 Hz,1H), 7.35-7.24 (m, 2H), 7.11 (d, *J* = 8.0 Hz,1H), 2.55 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.60, 151.05, 147.92, 142.56, 137.10, 136.03, 131.93, 125.48, 123.35, 123.16, 119.44, 109.30, 14.36, ppm.

2-Chloro-5-(2-methyl-1*H*-imidazol-1-yl)pyridine (1s)[20]. Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (32 mg, 33%), mp = 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 2.8 Hz,1H), 7.65 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz,1H), 7.50 (d, *J* = 8.4 Hz,1H), 7.10 (d, *J* = 1.2 Hz,1H), 7.02 (d, *J* = 1.2 Hz,1H), 2.40 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.01, 146.22, 144.82, 135.48, 133.62, 128.62, 124.96, 120.46, 13.65, ppm.

1-(6-Chloropyridin-3-yl)-5-nitro-1*H*-benzo[*d*]imidazole (1t). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a pale yellow solid (67 mg, 49%), mp = 286-287 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.97 (s, 1H), 8.89 (dd, *J* = 2.8 Hz, *J* = 0.8 Hz,1H), 8.49 (d, *J* = 2.0 Hz, 1H), 8.36 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz,1H), 8.24 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz,1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_7ClN_4O_2$ $[M+H]^+$ 275.0330, found 275.0328.

1-(6-Chloropyridin-3-yl)-6-nitro-1*H*-benzo[*d*]imidazole (1u). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a pale yellow solid (11 mg, 8%), mp = 236-238 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.91 (s, 1H), 8.86 (d, *J* = 2.8 Hz, 1H), 8.68 (d, *J* = 2.0 Hz, 1H), 8.31 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz,1H), 8.25 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz,1H), 7.85 (t, *J* = 8.0 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.09, 147.78, 145.99, 144.00, 143.57, 137.86, 136.16, 132.00,

125.85, 119.67, 116.56, 111.99, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_7ClN_4O_2$ $[M+H]^+$ 275.0330, found 275.0328.

3-Bromo-5-chloro-2-(1*H*-imidazol-1-yl)pyridine (1v). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (110 mg, 85%), mp = 106-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 2.0 Hz, 1H), 8.17 (s, 1H), 8.13 (d, *J* = 2.4 Hz, 1H), 7.55 (t, *J* = 1.2 Hz, 1H), 7.23 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.59, 145.95, 142.73, 137.13, 131.08, 129.52, 119.16, 112.89, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_5BrClN_3$ $[M+H]^+$ 257.9428, found 257.9428.

1-(5-Fluoropyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (2a). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (103 mg, 97%), mp = 192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.64 (s, 2H), 8.52 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.46-7.38 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.67, 154.08, 152.26, 146.26, 146.04, 144.76, 141.75, 131.62, 124.75, 123.89, 120.43, 115.14, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.10, ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_7FN_4$ $[M+H]^+$ 215.0728, found 215.0734.

5-Fluoro-2-(1*H*-imidazol-1-yl)pyrimidine (2b). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (71 mg, 86%), mp = 155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59-8.58 (m, 1H), 7.86 (t, *J* = 1.2 Hz, 1H), 7.20 (t, *J* = 1.2 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.33, 154.73, 146.53, 146.31, 136.17, 130.82, 116.75, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -141.36, ppm; HRMS (MALDI): *m/z* calcd for $C_7H_5FN_4$ $[M+H]^+$ 165.0571, found 165.0571.

5-Fluoro-2-(1*H*-pyrazol-1-yl)pyrimidine (2c). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (54 mg, 66%), mp = 93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 2H), 8.51 (d, *J* = 2.4 Hz, 1H), 7.82 (s, 1H), 6.49 (dd, *J* = 2.4 Hz, *J* = 1.6 Hz,1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.33, 154.74, 152.07, 146.56, 146.34, 143.75, 129.25, 108.84, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.21, ppm; HRMS (MALDI): *m/z* calcd for $C_7H_5FN_4$ $[M+H]^+$ 165.0571, found 165.0571.

1-(5-Fluoropyrimidin-2-yl)-1*H*-indazole (2d). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (55 mg, 51%), mp = 136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72-8.69 (m, 3H), 8.33 (d, *J* = 0.8 Hz, 1H), 7.82 (dt, *J* = 8.0 Hz, *J* = 1.2 Hz,1H), 7.61-7.56 (m, 1H), 7.38-7.34 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.39, 154.09, 154.06, 153.80, 146.35, 146.13, 139.20, 138.98, 128.51, 126.37, 123.28, 121.09, 115.11, ppn; ^{19}F NMR (376 MHz, $CDCl_3$): δ -143.95, ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_7FN_4$ $[M+H]^+$ 215.0728, found 215.0730.

9-(5-Fluoropyrimidin-2-yl)-9*H*-carbazole (2e). Purification by flash chromatography (petroleum ether): a white solid 88 mg, 67%), mp = 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.8 Hz, 2H), 8.69 (s, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.56-7.51 (m, 2H), 7.43-7.39 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.38, 155.22, 155.19, 145.54, 145.32, 139.02, 126.67, 125.65, 122.39, 119.59, 115.74, ^{19}F NMR (376 MHz, $CDCl_3$): δ -145.43, ppm; HRMS (MALDI): *m/z* calcd for $C_{16}H_{10}FN_3$ $[M+H]^+$ 264.0932, found 264.0931.

5-Fluoro-2-(1*H*-pyrrol-1-yl)pyrimidine (2f). Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (71 mg, 87%), mp = 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 2H), 7.73 (t, *J* = 2.4 Hz,2H), 6.36 (d, *J* = 2.4 Hz,2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.59, 154.02, 150.32, 146.04, 145.82, 119.26, 112.14, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -145.17, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6FN_3$ $[M+H]^+$ 164.0619 found 164.0620.

1-(5-Fluoropyrimidin-2-yl)-1*H*-indole (2g). Purification by flash chromatography (petroleum ether): a white solid (86 mg, 81%), mp = 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 8.4 Hz,1H), 8.59 (s, 2H), 8.21 (d, *J* = 3.6 Hz,1H), 7.65 (d, *J* = 7.6 Hz,1H), 7.39-7.35 (m, 1H), 7.29-7.25 (m, 1H), 6.72 (d, *J* = 3.6 Hz,1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.80, 154.06, 153.24, 145.79, 145.57, 135.20, 131.17, 126.00, 123.75, 122.20, 120.89, 115.74, 107.02, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -146.18, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8FN_3$ $[M+H]^+$ 214.0775, found 214.0772.

1-(5-Fluoropyrimidin-2-yl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (2h). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (116 mg, 96%), mp = 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, *J* = 3.2 Hz,1H), 863-8.61 (m, 2H), 8.26 (d, *J* = 4.8 Hz,1H), 7.61 (s, 1H), 2.46 (s, 3H), 2.42 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.49, 153.91, 152.31, 152.28, 146.08, 145.86, 143.30, 141.00, 133.80, 132.71, 130.02, 120.45, 115.23, 20.60, 20.20, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.81, ppm; HRMS (MALDI): *m/z* calcd for $C_{13}H_{11}FN_4$ $[M+H]^+$ 243.1041, found 243.1041.

5-Fluoro-2-(2-methyl-1*H*-imidazol-1-yl)pyrimidine (2i). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (77 mg, 86%), mp = 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 2H), 7.81 (d, *J* = 1.6 Hz,1H), 6.99 (d, *J* = 1.6 Hz,1H), 2.81 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.84, 154.23, 152.30, 146.43, 146.13, 145.91, 127.68, 118.68, 17.82, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.28, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_7FN_4$ $[M+H]^+$ 179.0728, found 179.0734.

1-(5-Fluoropyrimidin-2-yl)-2-methyl-1*H*-benzo[*d*]imidazole (2j). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (81 mg, 71%), mp = 110-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 2H), 8.19-8.16 (m, 1H), 7.76-7.73 (m, 1H), 7.36-7.31 (m, 2H), 2.95 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.67, 154.06, 153.06, 153.03, 152.47, 146.22, 146.00, 142.46, 133.83, 123.65, 123.62, 119.11, 113.88, 18.31, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -141.52, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_9FN_4$ $M+H]^+$ 229.0884, found 229.0881.

5-Fluoro-*N*-pentylpyrimidin-2-amine (2k). Purification by flash chromatography (petroleum ether/EtOAc = 10:1): a white solid (88 mg, 96%), mp = 39-40 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 2H), 5.23 (br, 1H), 3.36 (dd, *J* = 12.8 Hz, *J* = 6.8 Hz, 2H), 1.65-1.57 (m, 2H), 1.41-.132 (m, 4H), 0.93-0.90 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.59, 159.58, 153.06, 150.61, 145.50, 145.29, 42.03, 29.19, 29.09, 22.40, 13.96, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -156.65 — -156.67, ppm; HRMS (MALDI): *m/z* calcd for $C_9H_{14}FN_3$ $[M+H]^+$ 184.1245, found 184.1246.

5-Fluoro-2-(4- or 5-methyl-1*H*-imidazol-1-yl)pyrimidine (2l/2m). Compounds of 2l and 2m are tautomers and difficult to isolated by the chromatography. Molar ratio of 2m and 2n in NMR spectrum is

1.0:4.7. Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (63 mg, 71%), mp = 129-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, $2H_{2l}$), 8.54 (s, $2H_{2m}$), 8.45 (d, J = 0.8 Hz, $1H_{2m}$), 7.54 (d, J = 1.2 Hz, $1H_{2m}$), 7.28 (s, $1H_{2l}$), 6.87 (br, $1H_{2l}$), 2.57 (d, J = 1.2 Hz, $3H_{2l}$), 2.31 (d, J = 1.2 Hz, $3H_{2m}$), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.09, 154.50, 150.88, 150.85, 146.40, 146.21, 146.18, 145.99, 140.09, 137.49, 135.48, 129.57, 112.90, 13.72, 12.87, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -141.78 (2m), 142.13 (2n), ppm; HRMS (MALDI): *m/z* calcd for $C_8H_7FN_4$ $[M+H]^+$ 179.0728 found 179.0726.

1-(5-Fluoropyrimidin-2-yl)-5-nitro-1*H*-benzo[*d*]imidazole (2n). Compound of 2n is difficult to isolated by chromatography. NMR yield is 41%.

1-(5-Fluoropyrimidin-2-yl)-6-nitro-1*H*-benzo[*d*]imidazole (2o). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (61 mg, 47%), mp = 256-258 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, 1H), 8.77 (d, J = 2.4 Hz, 1H), 8.74 (s, 2H), 8.69 (d, J = 8.8 Hz, 1H), 8.37 (dd, J = 9.2 Hz, J = 2.4 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.25, 154.64, 151.68, 146.74, 146.52, 144.76, 144.60, 135.73, 120.28, 116.91, 115.40, 112.25, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -139.93, ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_6FN_5O_2$ $[M+H]^+$ 260.0578, found 260.0578.

1-(5-Fluoropyrimidin-2-yl)-5- or 6-methyl-1*H*-benzo[*d*]imidazole (2p/2q). Compounds of 2o and 2p are tautomers and difficult to isolated by the chromatography. Molar ratio of 2k and 2l in the spectrum is 1:1.3. Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (109 mg, 96%), mp = 183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, $1H_{2p}$), 8.95 (s, $1H_{2q}$), 8.65 (s, $2H_{2p}$), 8.64 (s, $2H_{2q}$), 8.38 (d, J = 8.4 Hz, $1H_{2p}$), 8.33 (s, $1H_{2q}$), 7.73 (d, J = 8.4 Hz, $1H_{2p}$), 7.65 (s, $1H_{2q}$), 7.25 (dd, J = 8.4 Hz, J = 1.2 Hz, $1H_{2p}$), 7.22 (dd, J = 8.4 Hz, J = 1.2 Hz, $1H_{2q}$), 2.57 (s, $1H_{2p}$), 2.53 (s, $1H_{2q}$), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.60, 154.01, 152.33, 152.26, 146.20, 145.98, 145.07, 142.87, 141.71, 141.32, 134.83, 133.70, 131.81, 129.63, 126.07, 125.30, 120.29, 119.88, 115.04, 114.61, 21.97, 21.47, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.45 (2k), 142.53 (2l), ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_9FN_4$ $[M+H]^+$ 229.0884, found 229.0883.

5-Bromo-2-(1*H*-imidazol-1-yl)pyrimidine (2r). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (107 mg, 95%), mp = 235-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 2H), 8.59 (s, 1H), 7.85 (s, 1H), 7.19 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.30, 153.09, 136.22, 130.93, 116.60, 116.42, ppm; HRMS (MALDI): *m/z* calcd for $C_7H_5BrN_4$ $[M+H]^+$ 224.9770, found 224.9763.

1-(5-Bromopyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (2s). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (133 mg, 97%), mp = 193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.78 (s, 2H), 8.50 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.45-7.37 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.01, 154.45, 144.88, 141.64, 131.55, 124.88, 124.07, 120.53, 115.47, 115.41, ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_7BrN_4$ $[M+H]^+$ 274.9927, found 274.9929.

1-(5-Bromopyrimidin-2-yl)-1*H*-indole (2t). Purification by flash chromatography (petroleum ether): a white solid (77 mg, 56%), mp = 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74-8.71 (m, 3H), 8.20 (d, J = 4.0 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.40-7.35 (m, 1H), 7.30-7.26 (m, 1H), 6.73 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.48, 155.95, 135.22, 131.36, 125.74, 123.89, 122.44, 120.95, 116.20, 113.10, 107.54, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8BrN_3$ $[M+H]^+$ 273.9974, found 273.9975.

5-Bromo-2-(1*H*-pyrazol-1-yl)pyrimidine (2u). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (104 mg, 92%), mp = 138-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 2H), 8.53 (d, J = 2.8 Hz, 1H), 7.84 (s, 1H), 6.51 (dd, J = 2.8 Hz, J = 1.6 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.30, 154.29, 144.09, 129.31, 116.24, 109.11, ppm; HRMS (MALDI): *m/z* calcd for $C_7H_5BrN_4$ $[M+H]^+$ 224.9770, found 224.9763.

5-Bromo-2-(1*H*-pyrrol-1-yl)pyrimidine (2v). Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (52 mg, 46%), mp = 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 2H), 7.73 (t, J = 2.4 Hz, 2H), 6.37 (t, J = 2.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.81, 119.21, 114.32, 112.48, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6BrN_3$ $[M+H]^+$ 223.9818, found 223.9820.

5-Bromo-*N*-pentylpyrimidin-2-amine (2w). Purification by flash chromatography (petroleum ether/EtOAc = 10:1): a white solid (110 mg, 90%), mp = 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H), 5.33 (br, 1H), 3.40-3.35 (m, 2H), 1.65-1.57 (m, 2H), 1.40-1.32 (m, 4H), 0.93-0.90 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.70, 158.17, 105.89, 41.74, 29.12, 29.06, 22.41, 14.00, ppm; HRMS (MALDI): *m/z* calcd for $C_9H_{14}BrN_3$ $[M+H]^+$ 244.0444, found 244.0437.

1-(Pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (2x)[21]. Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (93 mg, 95%), mp = 154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.75 (d, J = 4.8 Hz, 2H), 8.61-8.59 (m, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.45-7.36 (m, 2H), 7.19 (t, J = 4.8 Hz, 1H), ppm.

1-(6-Bromopyridin-2-yl)-1*H*-benzo[*d*]imidazole (3a)[11]**.** Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (102 mg, 74%), mp = 145-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 7.45-7.37 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.60, 144.66, 141.15, 140.92, 140.84, 131.79, 125.75, 124.63, 123.72, 120.79, 112.88, 112.14, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8BrN_3$ $[M+H]^+$ 273.9974, found 273.9977.

1-(6-Bromopyridin-2-yl)-1H-indazole (3b)[11]**.** Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (107 mg, 78%), mp = 102-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 4.0 Hz, 1H), 7.98 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.31-7.27 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.69, 140.25, 139.29, 138.75, 137.64, 128.42, 126.10, 123.40, 122.98, 120.79, 115.33, 111.52, ppm; HRMS (EI): *m/z* calcd for $C_{12}H_8BrN_3$ $[M]^+$ 272.9896, found 272.9890.

1-(6-Bromopyridin-2-yl)-1*H*-benzo[*d*][1,2,3]triazole(3c)[11]**.** Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (98 mg, 71%), mp = 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.12

(d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.51-7.46 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.08, 146.74, 140.83, 140.02, 131.24, 129.28, 126.14, 125.25, 119.91, 114.70, 112.58, ppm; HRMS (EI): *m/z* calcd for $C_{11}H_7BrN_4$ $[M]^+$ 273.9849, found 273.9841.

2-Bromo-6-(1*H*-imidazol-1-yl)pyridine (3d)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (85 mg, 76%), mp = 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.32 (s, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.41 (dd, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.81, 141.01, 140.91, 134.99, 131.01, 126.04, 116.12, 110.60, ppm; HRMS (EI): *m/z* calcd for $C_8H_6BrN_3$ $[M]^+$ 222.9740, found 222.9737.

2-Bromo-6-(1*H*-pyrazol-1-yl)pyridine (3e)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (68 mg, 61%), mp = 55-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.53 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 6.46 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.39, 142.66, 140.68, 139.86, 127.52, 125.19, 110.83, 108.19, ppm; HRMS (EI): *m/z* calcd for $C_8H_6BrN_3$ $[M]^+$ 222.9740, found 222.9737.

2-Bromo-6-(1*H*-pyrrol-1-yl)pyridine (3f)[11]. Purification by flash chromatography (petroleum ether): a white solid (95 mg, 85%), mp = 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.56 (t, *J* = 8.0 Hz, 1H), 7.47-7.46 (m, 2H), 7.25 (dd, *J* = 12.0 Hz, *J* = 8.0 Hz, 2H), 6.35 (s, 2H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.58, 140.39, 127.03, 123.87, 118.21, 111.90, 109.40, ppm; HRMS (EI): *m/z* calcd for $C_9H_7BrN_2$ $[M]^+$ 221.9787, found 221.9789.

1-(6-Bromopyridin-2-yl)-1H-indole (3g)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white viscous solid (79 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.27 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 4.0 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.18, 140.47, 140.32, 134.97, 130.60, 125.44, 123.63, 123.55, 121.82, 121.15, 113.50, 112.04, 106.58, ppm; HRMS (EI): *m/z* calcd for $C_{13}H_9BrN_2$ $[M]^+$ 271.9944, found 271.9939.

9-(6-Bromopyridin-2-yl)-9*H*-carbazole (3h). Purification by flash chromatography (petroleum ether/EtOAc = 40:1): a white solid (155 mg, 96%), mp = 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.13 (dq, *J* = 8.0 Hz, *J* = 0.8 Hz, 2H), 7.92 (dt, *J* = 8.0 Hz, *J* = 0.8 Hz, 2H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.63 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.51-7.47 (m, 3H), 7.39-7.35 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.60, 140.92, 140.39, 139.13, 126.50, 124.93, 124.63, 121.56, 120.26, 116.83, 111.43, ppm; HRMS (MALDI): *m/z* calcd for $C_{17}H_{11}BrN_2$ $[M+H]^+$ 323.0178, found 323.0169.

1-(6-Bromopyridin-2-yl)-2-methyl-1*H*-benzo[*d*]imidazole (3i)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (101 mg, 70%), mp = 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.80 (t, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31-7.23 (m, 2H), 2.71 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.35, 149.46, 142.67, 141.33, 140.69, 134.48, 127.18, 123.23, 123.12, 119.39, 118.05, 110.15, 15.54, ppm; HRMS (MALDI): *m/z* calcd for $C_{13}H_{10}BrN_3$ $[M+H]^+$ 288.0131, found 288.0140.

2-Bromo-6-(2-methyl-1*H*-imidazol-1-yl)pyridine (3j)[11]. Purification by flash chromatography (EtOAc): a white solid (104 mg, 87%), mp = 98-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.70 (t, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.30-7.28 (m, 2H), 7.01 (d, *J* = 1.6 Hz, 1H), 2.63 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.30, 145.12, 140.69, 140.62, 128.23, 126.36, 118.68, 115.07, 15.67, ppm; HRMS (MALDI): *m/z* calcd for $C_9H_8BrN_3$ $[M+H]^+$ 237.9974, found 237.9973.

2-Bromo-6-(4-methyl-1*H*-imidazol-1-yl)pyridine (3k)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (68 mg, 57%), mp = 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 (d, *J* = 1.6 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.31 (t, *J* = 1.2 Hz, 1H), 7.24 (dd, *J* = 8.0 Hz, *J* = 0.4 Hz, 1H), 2.28 (d, *J* = 4.0 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.85, 140.92, 140.80, 140.27, 134.24, 125.54, 112.34, 110.19, 13.74, ppm; HRMS (MALDI): *m/z* calcd for $C_9H_8BrN_3$ $[M+H]^+$ 237.9974, found 237.9980.

1-(6-Bromopyridin-2-yl)-5-nitro-1*H*-benzo[*d*]imidazole (3l)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a pale yellow solid (105 mg, 66%), mp = 201-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.77 (d, *J* = 2.0 Hz, 1H), 8.68 (s, 1H), 8.36 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ*148.79, 144.58, 144.17, 143.72, 141.50, 141.24, 135.93, 126.94, 120.23, 117.19, 113.62, 112.46, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_7BrN_4O_2$ $[M+H]^+$ 318.9825, found 318.9830.

1-(6-Bromopyridin-2-yl)-5-methoxy-1*H*-indole (3m)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a pale brown solid (109 mg, 72%), mp = 59-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 4.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 4.0 Hz, 1H), 6.96 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 1H), 6.64 (d, *J* = 4.0 Hz, 1H), 3.87 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 155.31, 152.18, 140.38, 140.25, 131.34, 130.02, 125.69, 123.14, 114.67, 112.98, 111.35, 106.45, 103.13, 55.72, ppm; HRMS (MALDI): *m/z* calcd for $C_{14}H_{11}BrN_2O$ $[M]^+$ 302.0049, found 302.0054.

6-Bromo-*N*-pentylpyridin-2-amine (3n)[11]. Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a pale brown oil (105 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.24 (t, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 4.72 (br, 1H), 3.19 (t, *J* = 8.0 Hz, 2H), 1.63-1.56 (m, 2H), 1.38-1.32 (m, 4H), 0.92-0.89 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.02, 140.24, 139.50, 115.43, 103.89, 42.26, 29.09, 28.95, 22.39, 14.00, ppm; HRMS (MALDI): *m/z* calcd for $C_{10}H_{15}BrN_2$ $[M+H]^+$ 243.0491, found 243.0490.

1-(6-Fluoropyridin-2-yl)-1*H*-benzo[*d*]imidazole (4a). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (91 mg, 85%), mp = 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.57 (s, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 8.01-7..95 (m, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.47-7.35 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 163.90, 161.48, 148.32, 148.17, 144.67, 143.63, 143.55, 141.03, 131.79, 124.55, 123.66, 120.77, 112.90, 110.25, 106.93, 106.58, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -65.55, ppm;

HRMS (MALDI): *m/z* calcd for $C_{12}H_8FN_3$ $[M+H]^+$ 214.0775, found 214.0777.

1-(6-Fluoropyridin-2-yl)-1*H*-indazole (4b). Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (70 mg, 66%), mp = 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, J = 8.0 Hz, 1H), 8.20 (s, 1H), 7.93-7.86 (m, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.27, 160.88, 142.74, 142.66, 138.82, 137.61, 128.32, 126.08, 122.93, 120.81, 115.36, 109.66, 109.61, 104.18, 103.82, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.63, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8FN_3$ $[M+H]^+$ 214.0775, found 214.0779.

2-Fluoro-6-(1*H*-imidazol-1-yl)pyridine (4c). Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (61 mg, 75%), mp = 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.93 (q, J = 8.0 Hz, 1H), 7.61 (s, 1H), 7.25-7.20 (m, 2H), 6.88 (dd, J = 8.0 Hz, J = 2.4 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.88, 161.46, 147.49, 143.72, 143.64, 135.09, 131.08, 116.15, 108.68, 108.63, 107.22, 106.87, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6FN_3$ $[M+H]^+$ 164.0619, found 164.0619.

9-(6-Fluoropyridin-2-yl)-9*H*-carbazole (4d). Purification by flash chromatography (petroleum ether/EtOAc = 80:1): a white solid (125 mg, 95%), mp = 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dq, J = 7.6 Hz, J = 0.8 Hz, 2H), 8.03 (q, J = 8.4 Hz, 1H), 7.96 (dq, J = 8.4 Hz, J = 0.8 Hz, 2H), 7.58 (ddd, J = 8.0 Hz, J = 2.0 Hz, J = 0.8 Hz, 1H), 7.51-7.47 (m, 2H), 7.39-7.35 (m, 2H), 6.96-6.93 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.13, 161.72, 150.30, 150.16, 143.00, 142.92, 139.19, 126.45, 124.61, 121.49, 120.24, 115.15, 115.10, 111.54, 106.18, 105.82, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.84, ppm; HRMS (MALDI): *m/z* calcd for $C_{17}H_{11}FN_2$ $[M+H]^+$ 263.0979, found 263.0978.

2-Fluoro-6-(1*H*-pyrazol-1-yl)pyridine (4e). Purification by flash chromatography (petroleum ether/EtOAc = 10:1): a pale yellow oil (58 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (dd, J = 2.8 Hz, J = 0.8 Hz, 1H), 7.91 (q, J = 8.0 Hz, 1H), 7.88-7.85 (m, 1H), 7.76 (d, J = 1.2 Hz, 1H), 6.81 (ddd, J = 7.6 Hz, J = 2.4 Hz, J = 0.8 Hz, 1H), 6.48 (dd, J = 2.8 Hz, J = 1.6 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.42, 161.02, 150.00, 143.37, 143.29, 142.64, 127.44, 108.88, 108.84, 108.20, 106.14, 105.78, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.29, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_6FN_3$ $[M+H]^+$ 164.0619, found 164.0619.

2-Fluoro-6-(1*H*-pyrrol-1-yl)pyridine (4f). Purification by flash chromatography (petroleum ether/EtOAc = 40:1): a brown oil (63 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (q, J = 8.0 Hz, 1H), 7.51 (t, J = 2.4 Hz, 2H), 7.18 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 6.74-6.71 (m, 1H), 6.38 (t, J = 2.4 Hz, 2H), ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.19, ppm; HRMS (MALDI): *m/z* calcd for $C_9H_7FN_2$ $[M+H]^+$ 163.0666, found 163.0671.

1-(6-Fluoropyridin-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (4g). Purification by flash chromatography (petroleum ether/EtOAc = 20:1): a white solid (81 mg, 76%), mp = 166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 8.8 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.04 (q, J = 8.0 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 6.96 (dd, J = 8.0 Hz, J = 2.4 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.50, 161.08, 146.74, 143.54, 143.46, 131.33, 129.22, 125.22, 119.96, 114.69, 110.87, 110.83, 107.23, 106.88, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.39, ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_7FN_4$ $[M+H]^+$ 215.0728, found 215.0728.

1-(6-Fluoropyridin-2-yl)-1*H*-imidazo[4,5-*b*]pyridine (4h). Purification by flash chromatography (EtOAc): a white solid (24 mg, 22%), mp = 210-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.66 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 8.59 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 8.06 (q, J = 8.0 Hz, 1H), 7.50 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.38 (q, J = 3.6 Hz, 1H), 6.98 (dd, J = 8.0 Hz, J = 2.8 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.96, 161.53, 156.84, 146.18, 144.01, 143.93, 142.64, 122.25, 119.71, 109.78, 109.73, 107.49, 107.14, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.25, ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_7FN_4$ $[M+H]^+$ 215.0728, found 215.0730.

1-(6-Fluoropyridin-2-yl)-2-methyl-1*H*-benzo[*d*]imidazole (4i). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a pale yellow oil (109 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-7.96 (m, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.34-7.31 (m, 1H), 7.28-7.20 (m, 2H), 7.01-6.97 (m, 1H), 2.68 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.97, 161.54, 147.83, 147.68, 143.49, 143.41, 142.62, 123.21, 123.07, 119.28, 116.43, 116.38, 110.30, 108.73, 108.37, 15.52, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.11, ppm; HRMS (MALDI): *m/z* calcd for $C_{13}H_{10}FN_3$ $[M+H]^+$ 228.0932, found 228.0929.

2-Fluoro-6-(2-methyl-1*H*-imidazol-1-yl)pyridine (4j). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a pale yellow solid (66 mg, 75%), mp = 100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (q, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.02 (s, 1H), 6.92 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 2.65 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.53, 161.11, 148.83, 145.14, 143.29, 143.21, 128.24, 118.72, 113.19, 113.14, 107.62, 107.27, 15.79, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.72, ppm; HRMS (MALDI): *m/z* calcd for $C_9H_8FN_3$ $[M+H]^+$ 178.0775, found 178.0767.

2-Fluoro-6-(4-nitro-1*H*-imidazol-1-yl)pyridine (4k). Purification by flash chromatography (petroleum ether/EtOAc = 10:1): a pale yellow solid (22 mg, 21%), mp = 174-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 1.6 Hz, 1H), 8.31 (d, J = 1.6 Hz, 1H), 8.09 (q, J = 8.0 Hz, 1H), 7.42 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.08 (dd, J = 8.0 Hz, J = 2.8 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.94, 161.48, 144.55, 144.47, 133.55, 115.99, 109.80, 109.45, 109.32, 109.27, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.39, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_5FN_4O_2$ $[M+H]^+$ 209.0469, found 209.0472.

1-(6-Fluoropyridin-2-yl)-5-methoxy-1*H*-indole (4l). Purification by flash chromatography (petroleum ether/EtOAc = 5:1): a pale yellow oil (104 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 9.2 Hz, 1H), 7.86 (q, J = 8.0 Hz, 1H), 7.68 (d, J = 3.6 Hz, 1H), 7.30 (dd, J = 8.0 Hz, J = 2.4 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 6.99 (ddd, J = 9.2 Hz, J = 2.4 Hz, J = 0.4 Hz, 1H), 6.74 (ddd, J = 8.0 Hz, J = 2.8 Hz, J = 0.4 Hz, 1H), 6.66 (dd, J = 3.6 Hz, J = 0.8 Hz, 1H), 3.90 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.72, 161.32, 155.32, 151.11, 150.96, 142.90, 142.82, 131.38, 130.08, 125.90, 114.76, 112.95, 109.50, 109.46, 106.38, 104.07, 103.71, 103.16, 55.72, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.89, ppm; HRMS (MALDI): *m/z* calcd for $C_{14}H_{11}FN_2O$ $[M+H]^+$ 243.0928, found 243.0928.

6-Fluoro-*N*-pentylpyridin-2-amine (4m). Purification by flash chromatography (petroleum ether/EtOAc = 40:1): a pale yellow oil (78 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 1H), 6.17 (dd, J = 8.0 Hz, J = 2.4 Hz, 1H), 6.09 (d, J = 7.6 Hz, 1H), 468 (br, 1H), 3.22 (t, J = 7.2 Hz, 2H), 1.63-1.56 (m, 2H), 1.38-1.31 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.36, 162.02, 158.31, 158.14, 141.71, 141.62, 102.11, 102.07, 95.25, 94.88, 42.16, 29.11, 28.97, 22.39, 13.95, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -70.06, ppm; HRMS (MALDI): *m/z* calcd for $C_{10}H_{15}FN_2$ $[M+H]^+$ 183.1292, found 183.1288.

1-(3-Fluoropyridin-2-yl)-1*H*-benzo[*d*]imidazole (5a). Purification by flash chromatography (EtOAc): a white solid (96 mg, 90%), mp = 85-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50-8,41 (m, 2H), 8.00-7.85 (m, 2H), 7.71-7.64 (m, 1H), 7.40-7.27 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.84, 149.24, 144.54, 144.48, 143.53, 141.95, 141.84, 138.67, 138.57, 132.58, 125.85, 125.66, 124.25, 123.50, 123.26, 123.22, 120.35, 113.31, 113.28, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -126.98, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8FN_3$ $[M+H]^+$ 214.0775, found 214.0775.

1-(4-Fluoropyridin-2-yl)-1*H*-benzo[*d*]imidazole (5b). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (102 mg, 96%), mp = 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 5.6 Hz, 1H), 8.27 (s, 1H), 7.95-7.91 (m, 1H), 7.73-7.69 (m, 1H), 7.48-7.42 (m, 3H), 7.20 (t, J = 1.6 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.02, 163.63, 149.87, 149.70, 147.70, 147.59, 144.52, 141.13, 132.11, 124.85, 124.02, 121.26, 114.86, 114.81, 110.61, 102.93, 102.52, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.75, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8FN_3$ $[M+H]^+$ 214.0775, found 214.0770.

1-(5-Fluoropyridin-2-yl)-1*H*-benzo[*d*]imidazole (5c). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (65 mg, 61%), mp = 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.50 (dd, J = 3.2 Hz, J = 0.8 Hz, 1H), 8.01 (dd, J = 6.4 Hz, J = 1.6 Hz, 1H), 7.90 (dd, J = 6.4 Hz, J = 1.6 Hz, 1H), 7.71-7.66 (m, 1H), 7.61 (ddd, J = 8.8 Hz, J = 3.6 Hz, J = 0.8 Hz, 1H), 7.44-7.37 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.08, 156.54, 145.93, 145.90, 144.46, 141.26, 137.42, 137.16, 132.09, 126.13, 125.93, 124.34, 123.40, 120.69, 115.38, 115.33, 112.23, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -129.13, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8FN_3$ $[M+H]^+$ 214.0775, found 214.0775.

1-(5-Fluoropyridin-3-yl)-1*H*-benzo[*d*]imidazole (5d). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (103 mg, 97%), mp = 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.75 (s, 1H), 8.65 (s, 1H), 8.20-8.18 (m, 1H), 7.95-7.92 (m, 1H), 7.70-7.67 (m, 1H), 7.58-7.54 (m, 1H), 7.45-7.40 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.05, 158.05, 144.09, 141.59, 140.73, 140.69, 137.75, 137.52, 133.84, 133.79, 133.10, 124.55, 123.63, 121.09, 118.41, 118.21, 109.87, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -123.41, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_8FN_3$ $[M+H]^+$ 214.0775, found 214.0775.

1-(3,5,6-Trifluoropyridin-2-yl)-1*H*-benzo[*d*]imidazole (5e). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (40 mg, 32%), mp = 114-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 2.8 Hz, 1H), 8.02-7.98 (m, 1H), 7.91-7.87 (m, 1H), 7.77-7.71 (m, 1H), 7.46-7.40 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.06, 148.03, 148.01, 147.98, 147.04, 147.02, 146.88, 146.86, 145.47, 145.44, 145.42, 145.39, 144.63, 144.61, 144.47, 144.45, 144.01, 143.96, 143.71, 143.66, 143.34, 141.37, 141.31, 141.25, 141.13, 141.07, 141.01, 132.13, 124.72, 124.02, 120.61, 118.56, 118.52, 118.36, 118.32, 118.28, 118.12, 118.09, 112.95, 112.93, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -87.44 (dd, J = 30.1, J = 24.1, 1F), -126.79 (dd, J = 30.1, J = 3.8, 1F), 136.29 (dd, J = 22.6, J = 3.8, 1F), ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_6F_3N_3$ $[M+H]^+$ 250.0587, found 250.0587.

1-(5-Chloro-3-fluoropyridin-2-yl)-1H-benzo[d]imidazole (5f). Purification by flash chromatography (petroleum ether/EtOAc = 1:1): a white solid (105 mg, 85%), mp = 142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 2.8 Hz, 1H), 8.46 (d, J = 2.0 Hz, 1H), 8.02-7.97 (m, 1H), 7.93-7.88 (m, 1H), 7.78 (dd, J = 10.0 Hz, J = 2.0 Hz, 1H), 7.44-7.39 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.06, 148.41, 143.53, 143.40, 143.35, 141.58, 141.47, 137.22, 137.12, 132.38, 129.88, 129.86, 126.16, 125.95, 124.47, 123.77, 120.54, 113.20, 113.18, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.26, ppm; HRMS (MALDI): *m/z* calcd for $C_{12}H_7ClFN_3$ $[M+H]^+$ 248.0385, found 248.0385.

5-Bromo-3-fluoro-2-(1*H*-imidazol-1-yl)pyridine (5g). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (115 mg, 95%), mp = 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 2H), 7.82-7.73 (m, 2H), 7.20 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.87, 147.22, 145.34, 145.29, 136.88, 136.78, 136.17, 136.07, 130.18, 130.16, 128.91, 128.70, 117.38, 117.32, 116.92, 116.90, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -125.59, ppm; HRMS (MALDI): *m/z* calcd for $C_8H_5BrFN_3$ $[M+H]^+$ 241.9724, found 241.9722.

2,6-Bis(1*H*-benzo[*d*]imidazol-1-yl)pyridine (6a)[6b]. Purification by flash chromatography (EtOAc): a white solid (23 mg, 15%), mp = 124-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 2H), 7.98 (t, J = 8.0 Hz, 1H), 7.68 (s, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.24 (s, 2H), ppm.

1,1'-(3,5-Difluoropyridine-2,6-diyl)*bis*(1*H*-benzo[*d*]imidazole) (6b). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (52 mg, 30%), mp = 234-235 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 2H), 7.95 (t, J = 7.2 Hz, 4H), 7.90 (t, J = 8.8 Hz, 1H), 7.46-7.36 (m, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.86, 148.81, 146.21, 146.16, 143.50, 141.39, 141.33, 141.27, 133.35, 133.31, 133.24, 133.20, 132.18, 124.87, 124.16, 120.75, 117.69, 117.46, 117.23, 113.15, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.29, ppm; HRMS (MALDI): *m/z* calcd for $C_{19}H_{11}F_2N_5$ $[M+H]^+$ 348.1055, found 348.1054.

3-Chloro-4,5-difluoro-2,6-di(1*H*-imidazol-1-yl)pyridine (6c). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (45 mg, 32%), mp = 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.84 (s, 1H), 7.74 (d, J = 1.2 Hz, 1H), 7.35 (s, 1H), 7.28-7.27 (m, 1H), 7.25 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.68, 154.65, 152.27, 152.24, 142.21, 142.15, 139.60, 139.54, 137.10, 137.07, 136.92, 136.88, 136.78, 136.74, 136.24, 136.14, 134.08, 133.96, 133.93, 133.80, 131.05, 131.03, 130.64, 119.52, 119.50, 117.37, 117.30, 110.81, 110.78, 110.44, 110.41, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.83 (d, J = 26.3, 1F), -139.49 (d, J = 26.3, 1F), ppm; HRMS (MALDI): *m/z* calcd for $C_{11}H_6ClF_2N_5$ $[M+H]^+$ 282.0353, found 282.0352.

1-(4-Phenylpyridin-2-yl)-1*H*-benzo[*d*]imidazole (7a). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (35 mg, 26%), mp = 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68-8.66 (m, 2H), 8.13-8.11 (m, 1H), 7.93-7.91 (m, 1H), 7.78 (q, J = 0.8 Hz, 1H), 7.74-7.71 (m, 2H), 7.60-7.51 (m, 4H), 7.46-7.38 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.87, 150.57, 149.84, 144.72, 141.46, 137.39, 132.23, 129.77, 129.38, 127.11, 124.26, 123.34, 120.74, 120.13, 112.62, 112.32, ppm; HRMS (MALDI): *m/z* calcd for $C_{18}H_{13}N_3$ $[M+H]^+$ 272.1182, found 272.1182.

1-(4-(Phenylethynyl)pyridin-2-yl)-1*H*-benzo[*d*]imidazole (7b). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a yellow solid (53 mg, 36%), mp = 184-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.61 (d, J = 5.2 Hz, 1H), 8.13 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 6.8 Hz, 1H), 7.70 (s, 1H), 7.65-7.60 (m, 2H), 7.48=7.38 (m, 6H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.12, 149.41, 144.69, 141.25, 134.47, 132.04, 132.02, 129.64, 128.62, 124.36, 123.62, 123.46, 121.61, 120.72, 115.88, 112.83, 95.42, 86.08, ppm; HRMS (MALDI): *m/z* calcd for $C_{20}H_{13}N_3$ $[M+H]^+$ 296.1182, found 296.1182.

1-(5-Phenylpyridin-2-yl)-1*H*-benzo[*d*]imidazole (7c). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (68 mg, 50%), mp = 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (dd, J = 2.4 Hz, J = 0.4 Hz, 1H), 8.67 (s, 1H), 8.15-8.11 (m, 2H), 7.93 (d, J = 7.2 Hz, 1H), 7.69-7.65 (m, 3H), 7.57-7.53 (m, 2H), 7.49-7.39 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.81, 147.62, 144.54, 141.30, 137.24, 136.67, 135.00, 132.15, 129.28, 128.43, 126.97, 124.33, 123.41, 120.66, 114.09, 112.79, ppm; HRMS (MALDI): *m/z* calcd for $C_{18}H_{13}N_3$ $[M+H]^+$ 272.1182, found 272.1182.

1-(5-(Phenylethynyl)pyridin-2-yl)-1*H*-benzo[*d*]imidazole (7d). Purification by flash chromatography (petroleum ether/EtOAc = 2:1): a white solid (49 mg, 33%), mp = 157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J = 1.6 Hz, 1H), 8.65 (s, 1H), 8.12 (d, J = 7.6 Hz, 1H), 8.03 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.62-7.58 (m, 3H), 7.44-7.38 (m, 5H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.91, 148.51, 144.44, 141.30, 141.15, 131.92, 131.72, 129.02, 128.53, 124.53, 123.67, 122.31, 120.68, 118.59, 113.42, 112.97, 93.41, 85.15, ppm; HRMS (MALDI): *m/z* calcd for $C_{20}H_{13}N_3$ $[M+H]^+$ 296.1182, found 296.1187.

Acknowledgements

The authors thank the financial support from the National Natural Science Foundation of China (grant number 21466033).

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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