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Base-Promoted Transition metal-free Arylation of Imidazo fused Heterocycles with Diaryliodonium salts

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Abstract: Potassium tert-butoxide promoted arylation of imidazo heterocycles with diaryliodonium salts under transition metal-free conditions has been described. The

reactions proceed through radical pathway without additives and oxidants with good to excellent yields and functional group tolerance of arylated products.

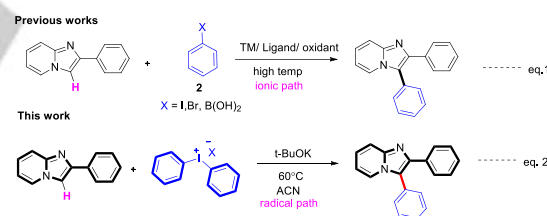
Introduction

Pyridine fused heterocycles such as imidazo[1,2-*a*]pyridines, imidazo[1, 5-*a*]pyridines, imidazo[1,2-*a*]pyrazines, indolizines, imidazo[2,1-*a*]isoquinolines and pyrazolo[1, 5-*a*]pyridines are important intermediate in both medicinal chemistry and drug development.^[1] Imidazo[1,2-*a*]pyridine scaffolds are widely distributed in many natural products pharmacologically important compounds.^[2] Particularly, alpidem, zolpidem, olprinone (the treatment of acute heart failure), minodronic acid,^[3] zolimidine (peptic ulcer), necopidem, saripidem (sedative and anxiolytic),^[4] optically active GSK812397 candidate (HIV infection) and as well as CXCR-chemokine receptor (CXCR4) antagonists are derived from imidazo[1,2-*a*]pyridine cores.^[5] Recently imidazo[1,2-*a*]pyridines are recognized as NO synthases, GABA inhibitors, L-Dopa and Dopamine pro-drugs.^[6] In addition, they received considerable attention as core ligands in the field of electronic devices, and abnormal N-heterocyclic carbenes.^[7]

The functionalized heterocycles through C-C, C-hetero bond formations exhibit their enhanced biological activities compared to their basic moiety. Although, these methods are efficient, but often required the expensive transition metal precursors such as platinum, palladium, rhodium, gold, ruthenium, cobalt, copper, etc.^[8] In particular C3-aryl imidazo[1,2-*a*]pyridine showed diverse biological activities.^[4-7] Different synthetic methods have been developed for the preparation of C3-arylated imidazo[1,2-*a*]pyridines using various transition metal catalysts and different aryl sources such as haloarenes and phenylboronic acids.^[9] The development of metal-free conditions for the arylation of imidazo[1,2-*a*]pyridines is desirable due to the milder reaction

impurities in the final products. Recently, some transition metal-free methods for the preparation of 3-arylated imidazo[1,2-*a*]pyridines have been reported,^[10] but they requires activated starting materials, such as bromoalkynes, bromoketones, bromoaldehydes, and iodonium salts, keto aldehydes.^[10]

To the best of our knowledge the direct C3-arylation of imidazo[1,2-*a*]pyridines under metal-free conditions has not been reported. In continuation of our research on the functionalization of imidazo[1,2-*a*]pyridines,^[11] we describe herein arylation of imidazo[1,2-*a*]pyridines and imidazo thiazoles under transition metal-free conditions using diphenyl iodonium salts as aryl source (Scheme 1).



Scheme 1. Arylation of imidazo[1,2-*a*]pyridine

Results and Discussion

The combination of diphenyl iodonium salts and base plays a crucial role as alternate to transition metals for the arylation of imidazoheterocycles in the present work. To optimize the reaction conditions, we initiated the arylation of 2-phenylimidazo[1,2-*a*]pyridine (0.25 mmol) **1a** with diphenyliodonium chloride (0.25 mmol) **2a** using Cs₂CO₃ (0.5 mmol) as a base at 60°C in DMF as solvent for 24h, the desired product 2, 3-diphenylimidazo[1, 2-*a*]pyridine **3a** was isolated in 18 % yield (Table 1, entry 1). With the same conditions, reaction was performed in other solvents like DCE, MeOH and ACN; in these solvents, the desired product **3a** was obtained in 26%, 22% and 30% yield respectively (Table 1, entry 2–4). Under the same conditions with ACN as solvent, the reaction was screened with different bases such as Na₂CO₃, K₂CO₃, NaHCO₃, NaOH, KOH, CsOH, t-BuONa, DBU and t-BuOK (entries 5-13), among these bases the good yield (56%) of

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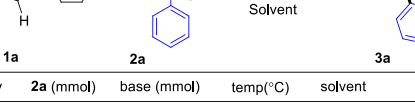
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conditions, less expensive reagents, and lack of residual metallic

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3a was isolated with t-BuOK (Table 1, entry 13). Further to improve the yield, diphenyliodonium chloride **2a** was increased from 0.25 mmol to 0.3 - 0.5 mmol with respect to **1a**, (entries 14-16) to our surprise, the desired product **3a** yield was increased to 86% at 0.5 mmol of **2a** (Table 1, entry 16). To see the effect temperature, when the reaction was conducted at room temperature and at 45° C, the yield of the product **3a** was declined (Table 1, entries 17 and 18). The yield of the desired product was further dropped by decreasing the amount of base (Table 1, entries 19–21). The reaction was failed in yield the desired product in absence of base (Table 1, entry 22).

Table 1. Optimization of the reaction conditions ^[a]



entry	2a (mmol)	base (mmol)	temp(°C)	solvent	3a (%) ^b
1	0.25	Cs ₂ CO ₃ (0.5)	60°C	DMF	18
2	0.25	Cs ₂ CO ₃ (0.5)	60°C	DCE	26
3	0.25	Cs ₂ CO ₃ (0.5)	60°C	MeOH	22
4	0.25	Cs ₂ CO ₃ (0.5)	60°C	ACN	30
5	0.25	Na ₂ CO ₃ (0.5)	60°C	ACN	43
6	0.25	K ₂ CO ₃ (0.5)	60°C	ACN	Traces
7	0.25	NaHCO ₃ (0.5)	60°C	ACN	nr
8	0.25	NaOH (0.5)	60°C	ACN	41
9	0.25	KOH (0.5)	60°C	ACN	39
10	0.25	CsOH (0.5)	60°C	ACN	29
11	0.25	t-BuONa (0.5)	60°C	ACN	49
12	0.25	DBU (0.5)	60°C	ACN	30
13	0.25	t-BuOK (0.5)	60°C	ACN	56
14	0.30	t-BuOK (0.5)	60°C	ACN	63
15	0.40	t-BuOK (0.5)	60°C	ACN	71
16	0.5	t-BuOK (0.5)	60°C	ACN	86
17	0.5	t-BuOK (0.5)	RT	ACN	51
18	0.5	t-BuOK (0.5)	45°C	ACN	64
19	0.5	t-BuOK (0.05)	60°C	ACN	Traces
20	0.5	t-BuOK (0.10)	60°C	ACN	Traces
21	0.5	t-BuOK (0.20)	60°C	ACN	15
22	0.5	--	60°C	ACN	nr

^[a] Reaction conditions: **1a** (0.25 mmol) and **2a** (0.5 mmol) were heated in 1 mL solvent at 60°C, 24 h. ^[b] Isolated products.

We then verified the reactivity of other diphenyl iodonium salts **2b–e** (Table 2) as arylation sources for the arylation of **1a** under the optimized reaction conditions (Table 1, entry 16) in place of **2a**. Among, these diaryliodonium salts (such as diphenyliodonium nitrate **2b**, diphenyliodonium hexafluorophosphates **2c**, Diphenyliodonium Trifluoromethanesulfonate **2d**, and diphenyliodonium tetrafluoroborates **2e**), comparable yield (81%) of **3a** was obtained with **2d** (Table 2, entries 1–5). However, the best yield of **3a** was observed with diphenyliodonium chloride **2a** under the present conditions. Hence the optimum conditions were set as 0.25 mmol of **1a**, 0.5 mmol of **2**, and 0.5 mmol of t-BuOK in 1.0 mL of acetonitrile at 60° C for 24 h.

With the optimized conditions in hand (Table 1, entry 16), we examined the versatility of C-3 arylation of imidazo[1, 2-*a*]pyridines and as well as diaryliodonium chlorides (Scheme 2).

First, we examined C-3 arylation of para substituted 2-phenyl imidazo[1, 2-*a*]pyridines with diaryliodonium chloride.

To our delight, the protocol was found to be broadly pertinent to presence of electron rich and electron deficient groups (Me, Et, Cl, Br, and CN) underwent smoothly to the optimized conditions and gave good yields (60–86%) of selective C-3 arylated products **3a-f**. Also the presence of cyanide and methyl-sulfanedione groups at meta and para position of phenyl ring of 2-phenyl imidazo[1, 2-*a*]pyridines gave the C-3 arylated products 3-(3-phenylimidazo[1,2-*a*]pyridin-2-yl)benzonitrile (**3g**) and 2-(4-(methylsulfonyl)phenyl)-3-phenylimidazo[1,2-*a*]pyridine (**3h**) in 60% and 65% yields respectively.

Table 2. Screening of the counter anions^[a]

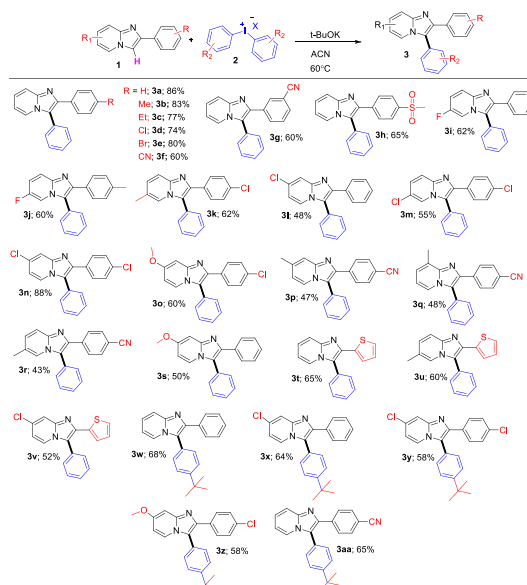
Reaction scheme showing the synthesis of 3a from 1a and 2a-e. Reagents: t-BuOK, ACN, 60 °C.

Entry	X (2)	Yield
1	Cl; (2a)	86
2	NO ₂ ; (2b)	60
3	PF ₆ ; (2c)	60
4	CF ₃ SO ₂ ⁻ ; (2d)	81
5	BF ₄ ⁻ ; (2e)	66

[a] Reaction conditions: **1a** (0.25 mmol) and **2a** (0.5 mmol) were heated in 1 mL solvent at 60°C, 24h. Yields are of isolated products.

Further, the presence of electron-rich or electron-deficient groups (Me, OMe, Cl, F and CN) at different positions on the phenyl as well as pyridyl ring of 2-phenyl imidazo[1, 2-a]pyridines were reacted smoothly with diaryliodonium chloride and afford the corresponding C-3 arylated imidazo[1, 2-a]pyridines **3i-s** in moderate to good yields (48-88%). The present conditions also

Scheme 2. Scope of various imidazo[1,2-*a*]pyridines^[a]



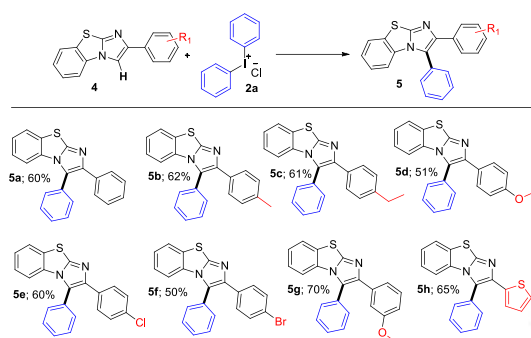
^[a]Reaction conditions: **1** (0.25 mmol) and **2** (0.5 mmol) were heated in 1 mL ACN at 60°C. 24h. isolated yields.

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amenable to the 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine derivatives and successfully obtained the C-3 arylated products **3t-v** in moderate to good yields. Similarly, the reaction of substituted imidazo[1, 2-*a*]pyridines with bis(4-(tert-butyl)phenyl)iodonium chloride was examined under the optimized conditions and the desired arylated products (**3w-3aa**) were obtained in good to excellent yields (52-91%).

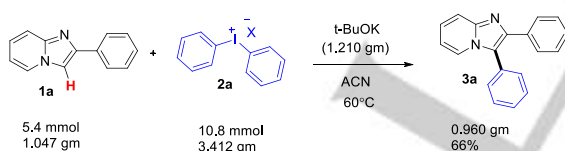
Subsequently, to ascertain the scope of the present methodology, C-3 arylation of different heterocycles was tested (Scheme 3). Various substituted 2-aryl benzo[d]imidazo[2,1-*b*]thiazoles, including 2-(thiophen-2-yl)benzo[d]imidazo[2,1-*b*]thiazole underwent to this arylation procedure and provided the corresponding products **5a-h** with moderate to good yields (50–70%).

Scheme 3. Scope of fused imidazo heterocycles^[a]



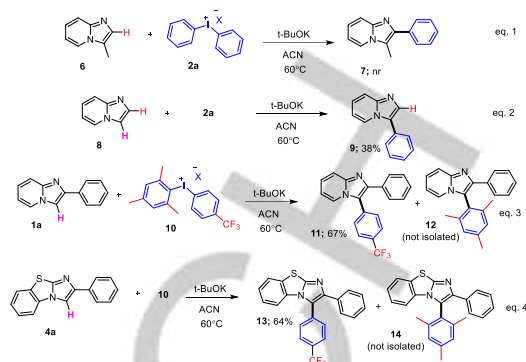
^[a]Reaction conditions: **1** (0.25 mmol) and **2** (0.5 mmol) were heated in 1 mL ACN at 60°C, 24h, isolated yields.

Additionally, to validate the present protocol, the reaction of **1a** was carried out at gram scale using 5.4 mmol of **1a** and 10.8 mmol of **2a** and **3a** was obtained in 66% yield (Scheme 4). This study indicates the feasibility of the method for industrial/commercial preparation of such products.



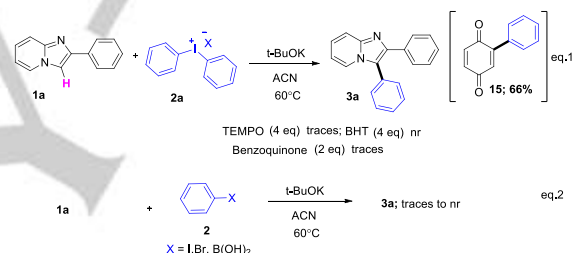
Scheme 4. Gram scale reaction

Next, we checked the selectivity of present reaction (Scheme 5). Reaction was performed with C-3 substituted imidazopyridine that is 3-methylimidazo[1,2-*a*]pyridine **6** under the optimized conditions (Scheme 5 eq.1). With this substrate no desired product **7** formation was observed. In the same way reaction with simple unsubstituted imidazo[1,2-*a*]pyridine **8**, the major C3 arylated product **9** was isolated in 38% yield along with a mixture of products (Scheme 5, eq.2). These selectivity studies indicates that the reaction may proceed in both ionic as well as radical pathway.



Scheme 5. Selectivity experiments

Further, the reaction of **1a** and **4a** with iodonium salt containing different arene rings **10** was conducted under the optimized conditions, the arylated product **11** and **13** were isolated in 67% and 64% respectively. In both reactions, the selective electron withdrawing group (CF₃) containing arene substituted product was observed instead of **12** and **14** (Scheme 5, eq.3 & 4).



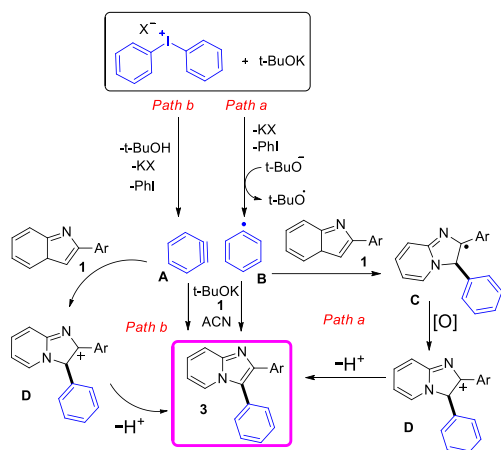
Scheme 6. Control experiments

To gain insights into the reaction mechanism, we performed some control experiments with radical scavengers (Scheme 6). Neither desired product nor adduct formation was observed with radical scavengers TEMPO and BHT (Scheme 6, eq.1).

Further, the reaction with benzoquinone, the adduct **15** was isolated in 66% (Scheme 6, eq. 1). On the basis of these experimental results, and previous reports,^[12] the reaction may proceed both ionic and radical pathway. Also the optimized reaction conditions were applied to other aryl source like iodobenzene, bromobenzene and phenyl boronic acid, in these cases only trace to no product formation was observed (Scheme 6, eq.2).

Based on the control experiments and the literature reports,^[12] a plausible reaction mechanism has been proposed for the present transformation (Scheme 7). Initially (*path-a*), the reaction of diaryliodonium salt **2a** with *t*-BuOK generates aryl radical **B**, via the formation of benzene carbocation. The aryl radical **B** reacts with imidazopyridine **1** and generates another radical intermediate **C**. Subsequently, the oxidation of **C** through intermediate **D**, yield the desired product **3**. Alternately, the reaction may also proceed through aryne ^[12f-h] intermediate **A** (*path-b*).

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Scheme 7. Probable mechanism

Conclusions

In summary, we have developed a novel and efficient protocol for the arylation of imidazo[1, 2-a]pyridine mediated by K-OtBu under mild reaction conditions without transition metal catalyst. The method also applicable to the imidazo thiazoles, which were reacted smoothly and delivered desired products in good yields. We also demonstrated the efficacy of the present strategy for the gram-scale synthesis of arylated imidazo[1, 2-a]pyridine including with good functional group tolerance in all cases studied.

Experimental Section

General: All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^1H and ^{13}C NMR spectra were recorded at 500, and 125 MHz, respectively. The spectra were recorded in CDCl_3 as solvent. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of ^1H NMR (7.2), and ^{13}C NMR (77.0) are correspond to deuterated solvent chloroform respectively. Mass spectra were obtained using electron impact (EI) ionization method. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane/ethyl acetate as eluent unless otherwise indicated.

General procedure for 3a

A clean washed boiling tube equipped with a magnetic stir bar was charged with 2-phenylimidazo[1,2-a]pyridine **1a** (0.0485 g, 0.25 mmol), diphenyliodonium chloride **2a** (0.157 g, 0.5 mmol), 0.5 mmol of *t*-BuOK and acetonitrile (1mL), the above mixture was stirred for 24h at 60°C temperature. After completion of the reaction, the mixture was poured into 10mL of NaHCO_3 solution. The product was extracted with ethyl acetate (10 mL $\times$ 3) and dried with anhydrous Na_2SO_4 . Removal of the solvent

under reduced pressure, the left out residue was purified through column chromatography using silica gel (20% EtOAc/hexane) to obtain 2,3-diphenylimidazo[1,2-a]pyridine **3a** in 86 % yield (0.0584g).

Characterization data

2, 3-diphenylimidazo[1,2-a]pyridine **3a**^[13]

(Eluent: 20% EtOAc/hexane); 86% yield (58.1 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, J = 7.2 Hz, 1H), 7.68-7.64 (M 3H), 7.51 (t, J = 7.2 Hz, 2H), 7.84-7.43 (m, 3H), 7.28-7.23 (m, 3H), 7.20 (t, J = 7.8 Hz, 1H), 6.73 (t, J = 6.6 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.7, 142.3, 134.0, 130.7, 129.8, 129.5, 128.8, 128.2, 128.0, 127.4, 124.6, 123.2, 117.5, 112.2.

3-phenyl-2-(p-tolyl)imidazo[1,2-a]pyridine **3b**

(Eluent: 20% EtOAc/hexane); 83% yield (58.9 mg); white solid; ^1H NMR (600 MHz, CDCl_3) δ 7.94 (d, J = 6.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.54-7.49 (m, 4H), 7.47-7.43 (m, 3H), 7.19 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.72 (t, J = 6.6 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.7, 142.4, 137.2, 131.1, 130.7, 129.9, 129.4, 128.9, 128.7, 127.9, 120.7, 117.4, 112.1, 21.2. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{Na}$: 307.1206, found:307.1206.

(4-ethylphenyl)-3-phenylimidazo[1,2-a]pyridine **3c**

(Eluent: 15% EtOAc/hexane); 77% yield (57.3 mg); white solid; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 6.6 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.48-7.44 (m, 3H), 7.19 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 6.72 (t, J = 6.6 Hz, 1H), 2.63 (q, J = 6.6 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 143.5, 142.1, 130.7, 129.5, 128.8, 127.9, 127.7, 124.5, 123.1, 117.3, 112.1, 28.5, 15.2. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2$: 299.1543, found:299.1545.

2-(4-chlorophenyl)-3-phenylimidazo[1,2-a]pyridine **3d**^[13]

(Eluent: 20% EtOAc/hexane); 74% yield (56.2 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 9.6 Hz, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 8.4 Hz, 2H), 7.49-7.48 (M, 1H), 7.42 (d, J = 7.2 Hz, 2H), 7.24-7.19 (m, 3H), 6.74 (t, J = 6.6 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.8, 141.1, 133.3, 132.5, 130.6, 129.6, 129.4, 129.2, 129.0, 128.4, 124.9, 123.2, 121.2, 117.4, 112.4.

2-(4-bromophenyl)-3-phenylimidazo[1,2-a]pyridine **3e**^[13]

(Eluent: 20% EtOAc/hexane); 80% yield (69.6 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.54-7.47 (m, 5H), 7.43 (d, J = 8.4 Hz, 2H), 7.40-7.38 (m, 2H), 7.21 (dd, J = 8.8, 7.2 Hz, 1H), 6.73 (t, J = 6.8 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 131.51, 130.74, 129.76, 129.66, 129.20, 125.06, 123.41, 117.63, 112.55, 77.29, 77.08, 76.87

4-(3-phenylimidazo[1,2-a]pyridin-2-yl)benzonitrile **3f**^[14]

(Eluent: 20% EtOAc/hexane); 60% yield (44.2 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.91 (s, 1H), 7.76 (s, 2H), 7.67 (s, 1H), 7.54 (d, J = 5.4 Hz, 5H), 7.43 (s, 2H), 7.25 (s, 1H), 6.77 (s, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.10, 140.24, 138.90, 132.19, 130.72, 129.96, 129.62, 129.16, 128.34, 125.60, 123.58, 122.63, 119.16, 117.83, 112.96, 110.76.

3-(3-phenylimidazo[1,2-a]pyridin-2-yl)benzonitrile **3g**

(Eluent: 20% EtOAc/hexane); 60% yield (44.2 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.97 (s, 1H), 7.93 (d, J = 6.6 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.67

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(d, $J = 9.0$ Hz, 1H), 7.55 – 7.48 (m, 4H), 7.42 (d, $J = 7.2$ Hz, 2H), 7.35 (t, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 6.6$ Hz, 1H), 6.77 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 132.10, 131.47, 130.88, 130.65, 129.97, 129.63, 129.14, 125.45, 123.58, 117.78, 112.85, 102.23. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3$: 296.1182 found: 296.1179

2-(4-(methylsulfonyl)phenyl)-3-phenylimidazo[1,2-a]pyridine 3h

(Eluent: 20% EtOAc/hexane); 65% yield (56.5 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, $J = 7.2$ Hz, 1H), 7.84 (q, $J = 7.8$ Hz, 4H), 7.69 (d, $J = 9.6$ Hz, 1H), 7.56 – 7.52 (m, 3H), 7.43 (d, $J = 7.2$ Hz, 2H), 7.25 – 7.22 (m, 1H), 6.78 (t, $J = 7.2$ Hz, 1H), 3.02 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.0, 140.0, 139.7, 138.7, 130.6, 129.8, 129.5, 129.0, 128.5, 127.3, 125.5, 123.5, 122.6, 117.7, 112.8, 44.4. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$: 349.1005 found: 349.1005.

6-fluoro-2,3-diphenylimidazo[1,2-a]pyridine 3i^[15]

(Eluent: 20% EtOAc/hexane); 62% yield (44.6 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 2.4$ Hz, 1H), 7.66 – 7.61 (m, 4H), 7.54 (t, $J = 6.6$ Hz, 2H), 7.50 (d, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 6.0$ Hz, 2H), 7.27 – 7.24 (m, 2H), 7.13 – 7.10 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 143.71, 130.55, 130.11, 129.79, 129.63, 129.29, 129.10, 128.41, 128.07, 127.76, 125.87, 118.12.

6-fluoro-3-phenyl-2-(p-tolyl)imidazo[1,2-a]pyridine 3j

(Eluent: 20% EtOAc/hexane); 60% yield (45.3 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, $J = 1.8$ Hz, 1H), 7.65 (dd, $J = 9.7$, 5.1 Hz, 1H), 7.54 – 7.47 (m, 5H), 7.42 (d, $J = 7.2$ Hz, 2H), 7.11 – 7.07 (m, 3H), 2.31 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 137.60, 130.56, 129.76, 129.22, 129.16, 127.95, 119.42, 117.97, 116.51, 115.65, 110.07, 77.30, 77.09, 76.88, 21.31. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{F}$: 303.1292 found: 303.1293.

2-(4-chlorophenyl)-6-methyl-3-phenylimidazo[1,2-a]pyridine 3k

(Eluent: 20% EtOAc/hexane); 62% yield (49.2 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.68 (s, 1H), 7.56 – 7.52 (m, 5H), 7.50 (dd, $J = 8.5$, 6.4 Hz, 1H), 7.42 (d, $J = 7.3$ Hz, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 9.2$ Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 130.8, 129.7, 129.2, 129.0, 128.9, 128.5, 128.1, 123.8, 120.9, 120.0, 116.9, 110.1, 77.3, 77.0, 76.8, 18.4. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_2\text{Na}$: 341.0816 found: 341.0812.

7-chloro-2,3-diphenylimidazo[1,2-a]pyridine 3l^[15]

(Eluent: 20% EtOAc/hexane); 48% yield (36.4 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, $J = 6.6$ Hz, 1H), 7.66 (s, 1H), 7.62 (d, $J = 5.4$ Hz, 2H), 7.52 – 7.49 (m, 3H), 7.42 (s, 2H), 7.2 (d, $J = 10.2$ Hz, 4H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.58, 143.23, 133.73, 131.20, 130.72, 129.75, 129.36, 129.27, 128.42, 128.12, 127.84, 123.70, 116.37, 113.99.

6-chloro-2-(4-chlorophenyl)-3-phenylimidazo[1,2-a]pyridine 3m^[13]

(Eluent: 20% EtOAc/hexane); 55% yield (46.4 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (s, 1H), 7.61 (d, $J = 9.3$ Hz, 1H), 7.56 (dd, $J = 18.0$, 6.9 Hz, 5H), 7.41 (d, $J = 7.1$ Hz, 2H), 7.24 (s, 2H), 7.17 (d, $J = 9.4$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 143.22, 140.57, 130.63, 129.96, 129.60, 129.29, 128.96, 128.66, 126.41, 121.24, 117.99.

7-chloro-2-(4-chlorophenyl)-3-phenylimidazo[1,2-a]pyridine 3n

(Eluent: 20% EtOAc/hexane); 88% yield (74.3 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.84 (d, $J = 7.1$ Hz, 1H), 7.64 (s, 1H), 7.56 – 7.50 (m, 5H), 7.41 (d, $J = 7.4$ Hz, 2H), 7.24 (d, $J = 2.2$ Hz, 2H), 6.72 (dd, $J = 6.9$, 2.2 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 133.74, 131.87, 131.44, 130.65, 129.88, 129.48, 129.29, 128.65, 124.96, 123.73, 116.39, 114.15. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{19}\text{H}_{13}\text{N}_2\text{Cl}_2$: 339.0450 found: 339.0445.

2-(4-chlorophenyl)-7-methoxy-3-phenylimidazo[1,2-a]pyridine 3o

(Eluent: 20% EtOAc/hexane); 60% yield (50.1 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 7.8$ Hz, 1H), 7.55 – 7.54 (m, 2H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.46 (d, $J = 6.6$ Hz, 1H), 7.40 – 7.38 (m, 2H), 7.22 – 7.20 (m, 2H), 6.96 (d, $J = 2.2$ Hz, 1H), 6.46 (dd, $J = 7.9$, 2.3 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 158.35, 146.37, 142.53, 140.51, 133.16, 133.03, 132.81, 132.42, 130.77, 130.47, 129.69, 129.39, 129.12, 129.03, 128.71, 128.52, 127.73, 123.93, 107.63, 94.56, 55.67. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{ClO}$: 335.0946 found: 335.0943.

4-(7-methyl-3-phenylimidazo[1,2-a]pyridin-2-yl)benzonitrile 3p

(Eluent: 20% EtOAc/hexane); 47% yield (36.3 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, $J = 7.1$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.58 – 7.50 (m, 5H), 7.41 (d, $J = 8.1$ Hz, 3H), 6.60 (d, $J = 6.8$ Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.45, 139.80, 139.01, 136.53, 132.02, 130.59, 129.77, 129.34, 129.25, 128.14, 122.66, 122.01, 119.10, 115.94, 115.49, 110.43, 21.34. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3$: 310.1339 found: 310.1342.

4-(8-methyl-3-phenylimidazo[1,2-a]pyridin-2-yl)benzonitrile 3q

(Eluent: 20% EtOAc/hexane); 48% yield (37.0 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 7.6$ Hz, 3H), 7.59 – 7.47 (m, 5H), 7.41 (d, $J = 6.4$ Hz, 2H), 7.02 (d, $J = 5.9$ Hz, 1H), 6.68 (t, $J = 6.4$ Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.62, 139.29, 132.16, 130.73, 129.85, 129.55, 129.44, 128.46, 127.88, 124.12, 122.97, 121.42, 119.28, 112.94, 110.53, 17.14. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3$: 310.1339 found: 310.1343.

4-(6-methyl-3-phenylimidazo[1,2-a]pyridin-2-yl)benzonitrile 3r

(Eluent: 20% EtOAc/hexane); 43% yield (33.2 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.66 (s, 1H), 7.59 – 7.51 (m, 6H), 7.42 (d, $J = 7.0$ Hz, 2H), 7.09 (d, $J = 9.1$ Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.21, 139.10, 132.15, 130.77, 129.93, 129.52, 128.79, 128.20, 122.69, 121.08, 119.21, 117.13, 110.56, 18.42. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3$: 310.1339 found: 310.1335.

7-methoxy-2,3-diphenylimidazo[1,2-a]pyridine 3s^[15]

(Eluent: 20% EtOAc/hexane); 50% yield (37.5 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (s, 1H), 7.62 (d, $J = 7.8$ Hz, 2H), 7.48 (d, $J = 7.0$ Hz, 2H), 7.41 (s, 3H), 7.27 – 7.23 (m, 2H), 7.23 – 7.16 (m, 1H), 6.97 (d, $J = 2.2$ Hz, 1H), 6.46 – 6.42 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 158.19, 146.31, 141.63, 134.25, 130.84, 129.56, 128.80, 128.29, 127.94, 127.34, 123.89, 120.11, 107.41, 94.62, 55.64.

3-phenyl-2-(thiophen-2-yl)imidazo[1,2-a]pyridine 3t

(Eluent: 20% EtOAc/hexane); 65% yield (44.8 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 6.9$ Hz, 1H), 7.64 (d, $J = 9.0$ Hz, 1H), 7.56 (d, $J = 7.0$ Hz, 2H), 7.54 – 7.48 (m, 3H), 7.21 (d, $J = 5.3$ Hz, 1H), 7.17 (d, $J = 7.9$ Hz, 1H), 7.08 (d, $J = 3.4$ Hz, 1H), 6.91 (dd, $J = 5.2$, 3.9 Hz, 1H), 6.70

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(s, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.76, 137.72, 131.13, 129.69, 129.48, 129.22, 127.50, 125.30, 124.95, 124.61, 123.33, 117.36, 112.46, 30.99. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{S}$: 277.0794 found: 277.0795.

6-methyl-3-phenyl-2-(thiophen-2-yl)imidazo[1,2-a]pyridine 3u

(Eluent: 20% EtOAc/hexane); 60% yield (43.5 mg); liquid, ^1H NMR (600 MHz, CDCl_3) δ 7.58-7.52 (m, 5H), 7.50 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 4.2 Hz, 1H), 7.03 (d, J = 10.2 Hz, 2H), 6.90 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 143.84, 137.94, 137.58, 131.19, 129.67, 129.39, 128.11, 127.46, 125.04, 124.33, 122.15, 120.95, 116.69, 18.35. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{S}$: 291.0950 found: 291.095.

7-chloro-3-phenyl-2-(thiophen-2-yl)imidazo[1,2-a]pyridine 3v

(Eluent: 20% EtOAc/hexane); 52% yield (40.3 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, J = 7.1 Hz, 1H), 7.63 (s, 1H), 7.61 – 7.51 (m, 3H), 7.49 (d, J = 6.9 Hz, 2H), 7.27 – 7.19 (m, 1H), 7.07 (s, 1H), 6.91 (s, 1H), 6.69 (d, J = 7.0 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 144.47, 138.58, 137.18, 131.39, 131.03, 129.82, 129.77, 128.64, 127.58, 125.66, 124.90, 123.64, 120.17, 116.10, 114.07. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{17}\text{H}_{12}\text{ClN}_2\text{S}$: 311.0404 found: 311.0401.

3-(4-(tert-butyl)phenyl)-2-phenylimidazo[1,2-a]pyridine 3w^[9e]

(Eluent: 20% EtOAc/hexane); 68% yield (55.4 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.96 (d, J = 6.8 Hz, 1H), 7.67 (t, J = 7.8 Hz, 3H), 7.52 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.7 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.23 (dd, J = 12.6, 5.9 Hz, 1H), 7.19 – 7.15 (m, 1H), 6.70 (t, J = 6.6 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 151.91, 144.70, 142.19, 134.26, 130.27, 128.19, 128.06, 127.33, 126.66, 126.39, 124.53, 123.44, 121.15, 117.43, 112.08, 34.80, 31.29.

3-(4-(tert-butyl)phenyl)-7-chloro-2-phenylimidazo[1,2-a]pyridine 3x

(Eluent: 20% EtOAc/hexane); 64% yield (57.6 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 6.6 Hz, 1H), 7.65 (s, 3H), 7.58 (d, J = 7.1 Hz, 2H), 7.34 (d, J = 6.9 Hz, 2H), 7.29 (dd, J = 15.8, 8.9 Hz, 3H), 6.70 (d, J = 7.1 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 137.13, 130.30, 128.39, 128.11, 127.73, 127.65, 126.64, 126.52, 126.18, 123.90, 118.27, 116.29, 113.81, , 29.78. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{23}\text{H}_{22}\text{ClN}_2$: 361.1466 found: 361.1466.

3-(4-(tert-butyl)phenyl)-7-chloro-2-(4-chlorophenyl)imidazo[1,2-a]pyridine 3y

(Eluent: 20% EtOAc/hexane); 58% yield (57.1 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, J = 7.1 Hz, 1H), 7.64 (d, J = 1.9 Hz, 1H), 7.57 (d, J = 8.9 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 6.71 – 6.69 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 152.56, 144.44, 141.84, 133.52, 132.34, 131.24, 130.14, 129.19, 128.52, 126.67, 126.31, 125.76, 123.82, 121.53, 116.17, 114.86, 113.90, 34.88, 31.27. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{23}\text{H}_{21}\text{Cl}_2\text{N}_2$: 395.1076 found: 395.1078.

3-(4-(tert-butyl)phenyl)-2-(4-chlorophenyl)-7-methoxyimidazo[1,2-a]pyridine 3z

(Eluent: 20% EtOAc/hexane); 58% yield (56.5 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 6.6 Hz, 1H), 7.65 (s, 3H), 7.52 (d, J = 7.1 Hz, 2H), 7.34 (d, J = 6.9 Hz, 2H), 7.27 (dd, J = 15.8, 8.9 Hz, 3H), 6.69 (d, J =

7.1 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 137.13, 130.30, 128.39, 128.11, 127.73, 127.65, 126.64, 126.52, 126.18, 123.90, 118.27, 116.29, 113.81, 29.78. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{24}\text{H}_{24}\text{ClN}_2\text{O}$: 391.1572 found: 391.1575

4-(3-(4-(tert-butyl)phenyl)imidazo[1,2-a]pyridin-2-yl)benzonitrile 3aa

(Eluent: 20% EtOAc/hexane); 65% yield (57.0 mg); solid, ^1H NMR (600 MHz, CDCl_3) δ 7.92 (t, J = 7.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.65 (s, 1H), 7.55 (t, J = 7.5 Hz, 4H), 7.34 (d, J = 8.0 Hz, 2H), 7.25 (s, 1H), 1.39 (s, 9H). ^{13}C NMR δ 152.81, 132.17, 130.31, 128.31, 126.84, 125.44, 123.77, 117.77, 112.76, 31.37. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{24}\text{H}_{22}\text{N}_3$: 352.1808 found: 352.1804.

2,3-diphenylbenzo[d]imidazo[2,1-b]thiazole 5a^[16]

(Eluent: 20% EtOAc/hexane); 60% yield (48.9 mg); solid, ^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, J = 7.6 Hz, 1H), 7.55 (s, 7H), 7.24 (t, J = 7.7 Hz, 3H), 7.19 (d, J = 6.6 Hz, 1H), 7.13 (t, J = 6.6 Hz, 1H), 6.82 (d, J = 7.9 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 148.21, 147.76, 133.88, 132.25, 130.39, 128.82, 127.62, 126.28, 125.28, 124.97, 124.49, 112.73, 106.94, 31.02.

3-phenyl-2-(p-tolyl)benzo[d]imidazo[2,1-b]thiazole 5b

(Eluent: 20% EtOAc/hexane); 62% yield (52.7 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.65 (d, J = 6.5 Hz, 1H), 7.54 (s, 5H), 7.45 (d, J = 7.8 Hz, 2H), 7.24 (dd, J = 6.6 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 151.6, 147.1, 129.5, 129.4, 128.7, 128.4, 128.2, 126.7, 125.5, 124.2, 117.6, 113.2, 113.6, 105.6. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{SNa}$: 363.0926 found: 363.0926.

2-(4-ethylphenyl)-3-phenylbenzo[d]imidazo[2,1-b]thiazole 5c

(Eluent: 20% EtOAc/hexane); 61% yield (53.9 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 8.21 (d, J = 6.5 Hz, 1H), 8.12 (d, J = 7.5 Hz, 2H), 8.06 (d, J = 9.0 Hz, 2H), 7.79 (d, J = 9.0 Hz, 1H), 7.45-7.37 (m, 4H), 7.08 (d, J = 9.0 Hz, 2H), 6.94 (t, J = 6.5 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 152.3, 147.6, 146.0, 144.9, 132.7, 129.0, 128.5, 128.2, 127.2, 125.1, 124.5, 124.0, 118.0, 113.6, 103.5. HRMS(ESI-TOF) m/z : calcd for $\text{C}_{23}\text{H}_{19}\text{N}_2\text{S}$: 355.1263 found: 355.1259.

2-(4-methoxyphenyl)-3-phenylbenzo[d]imidazo[2,1-b]thiazole 5d

(Eluent: 20% EtOAc/hexane); 51% yield (45.3 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 8.51 (d, J = 7.0 Hz, 1H), 8.28 (t, J = 7.0 Hz, 2H), 7.67 (d, J = 9.0 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.43 (quin, J = 7.5 Hz, 1H), 7.33-7.29 (m, 1H), 7.17 (q, J = 6.0 Hz, 1H), 7.04 (q, J = 6.0 Hz, 1H), 6.94 (q, J = 7.0 Hz, 1H), 6.88 (q, J = 9.0 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 150.1, 146.5, 133.3, 129.9, 129.4, 128.5, 128.3, 127.8, 127.5, 126.5, 124.3, 117.6, 113.0, 109.1. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{OS}$: 357.1056 found: 357.1062.

2-(4-chlorophenyl)-3-phenylbenzo[d]imidazo[2,1-b]thiazole 5e

(Eluent: 10% EtOAc/hexane); 60% yield (54.0 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, J = 8.4 Hz, 1H), 7.58-7.52 (m, 5H), 7.48 (d, J = 9.0 Hz, 2H), 7.25-7.22 (m, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.14-7.11 (m, 1H), 6.28 (d, J = 7.8 Hz, 17.48 (d, J = 9.0 Hz, 2H), H), ^{13}C NMR (150 MHz, CDCl_3) δ 139.6, 137.4, 135.0, 129.7, 128.6, 125.6, 124.6, 122.5, 120.4, 119.6, 109.6, 100.3, 33.0. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{21}\text{H}_{14}\text{ClN}_2\text{S}$: 361.0561, found: 361.0557.

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2-(4-bromophenyl)-3-phenylbenzo[d]imidazo[2,1-b]thiazole 5f

(Eluent: 5% EtOAc/hexane); 50% yield (50.3 mg); liquid; ^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, J = 7.8 Hz, 1H), 7.58–7.55 (m, 3H), 7.53–7.52 (m, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H), 7.25–7.22 (m, 1H), 7.14 (t, J = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 136.5, 134.4, 129.9, 128.8, 128.6, 127.9, 126.9, 125.6, 124.6, 122.7, 120.6, 119.8, 110.2, 101.3, 50.4. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{21}\text{H}_{14}\text{BrN}_2\text{S}$: 405.0056; found: 405.0053.

2-(3-methoxyphenyl)-3-phenylbenzo[d]imidazo[2,1-b]thiazole 5g

(Eluent: 10% EtOAc/hexane); 70% yield (62.3 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, J = 8.4 Hz, 1H), 7.56 (s, 5H), 7.24 (t, J = 8.4 Hz, 1H), 7.13 (t, J = 7.2 Hz, 4H), 6.82 (d, J = 8.4 Hz, 1H), 6.74–7.73 (m, 1H), 3.64 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 139.1, 136.4, 130.6, 129.0, 128.6, 125.7, 124.7, 123.0, 120.8, 119.6, 111.5, 102.7. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{OS}$: 357.1056; found: 357.1051.

2-(3-methoxyphenyl)-3-phenylbenzo[d]imidazo[2,1-b]thiazole 5h

(Eluent: 10% EtOAc/hexane); 65% yield (53.9 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.65 (t, J = 7.2 Hz, 1H), 7.60–7.59 (m, 5H), 7.25–7.22 (m, 1H), 7.14–7.11 (m, 2H), 6.95–6.94 (m, 1H), 6.89–6.87 (m, 1H), 6.82 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 140.0, 139.3, 135.4, 130.2, 128.6, 125.4, 124.4, 122.1, 120.6, 118.9, 110.5, 93.3, 12.1. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{19}\text{H}_{13}\text{N}_2\text{S}_2$: 333.0515; found: 333.0523.

3-phenylimidazo[1,2-a]pyridine 9

(Eluent: 15% EtOAc/hexane); 38% yield (18.2 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 8.34 (d, J = 7.2 Hz, 1H), 7.69 (t, J = 9.0 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 6.6 Hz, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 6.81 (t, J = 6.6 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 132.4, 129.3, 128.2, 128.1, 124.3, 123.4, 118.3, 112.6.

2-phenyl-3-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine 11

(Eluent: 15% EtOAc/hexane); 67% yield (56.4 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 9.0 Hz, 1H), 7.60–7.57 (m, 4H), 7.31–7.26 (m, 3H), 7.24–7.21 (m, 1H), 6.78–6.76 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.2, 143.4, 133.6, 128.4, 127.8, 126.4, 125.1, 122.9, 199.4, 117.4, 112.7. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{20}\text{H}_{13}\text{F}_3\text{N}_2\text{Na}$: 361.0923; found: 361.0916.

2-phenyl-3-(4-(trifluoromethyl)phenyl)benzo[d]imidazo[2,1-b]thiazole 13

(Eluent: 15% EtOAc/hexane); 64% yield (62.5 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 8.4 Hz, 3H), 7.49 (d, J = 7.8 Hz, 2H), 7.29–7.24 (m, 3H), 7.22–7.17 (m, 2H), 6.87 (d, J = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 148.0, 144.3, 133.7, 132.9, 131.7, 130.6, 128.4, 127.4, 127.3, 126.3, 125.9, 124.8, 124.5, 113.2. HRMS (ESI-TOF) m/z : calcd for $\text{C}_{22}\text{H}_{14}\text{F}_3\text{N}_2\text{S}$: 395.0824; found: 395.0818.

[1,1'-biphenyl]-2,5-dione 15

Eluent: 5% EtOAc/hexane); 66% yield (30.4 mg); solid; ^1H NMR (600 MHz, CDCl_3) δ 7.47–7.46 (m, 3H), 7.45–7.43 (m, 2H), 6.87 (t, J = 7.2 Hz, 2H), 6.83 (d, J = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 186.7, 146.0, 137.1, 136.3, 132.7, 130.2, 129.3, 128.6.

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Keywords: • metal-free • potassium tert-butoxide • arylation • regioselectivity.

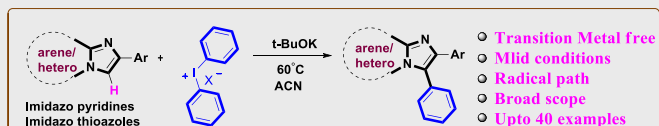
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C–H Arylation

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Base-Promoted Transition metal-free Arylation of Imidazo fused Heterocycles with Diaryliodonium salts

The arylation of imidazo[1,2-a]pyridine and phenylbenzo[d]imidazo[2,1-b]thiazoles using Diaryliodonium salts as aryl source under metal-free conditions were described.