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Developing Bis(imino)acenaphthene-Supported *N*-Heterocyclic Carbene Palladium Precatalysts for Direct Arylation of Azoles

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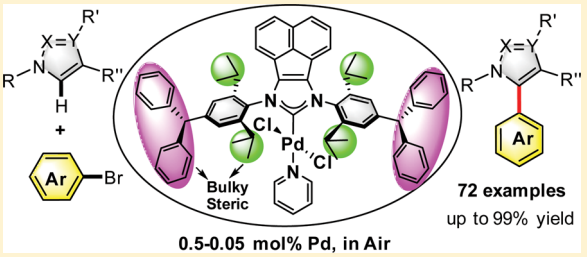
Supporting Information

ABSTRACT: On the basis of the strategy of developing highly efficient protocol for Pd-catalyzed cross-coupling reactions, a series of bulky bis(imino)acenaphthene (BIAN)-supported Pd-PEPPSI complexes were synthesized, characterized, and applied in direct arylation of azoles. The effect of backbone and *N*-moieties on NHCs was evaluated, and the reaction conditions were optimized. It was found that the bulky Pd-PEPPSI complexes could be successfully employed in cross-coupling of (hetero)aryl bromides with azoles at a low palladium loading of 0.5−0.05 mol % under aerobic conditions, demonstrating the ease of manipulation without glovebox and handling of solvents.

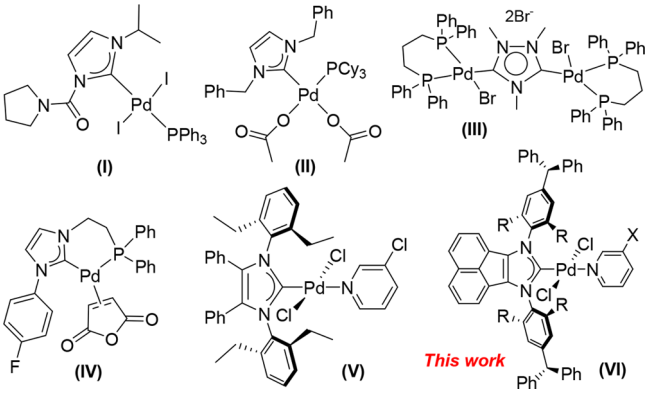


INTRODUCTION

Arylated azoles, especially for imidazoles, are important structural scaffolds found in a large number of pharmaceuticals, bioactive compounds, and natural products, as well as functional materials.[1] The direct C−H bond arylation of imidazoles with aryl halides emerged as a straightforward and environmentally friendly approach,[2] since it avoided the use of organometallic reagents in established traditional cross-coupling reactions. Unfortunately, the cleavage of the C−H bond in imidazole substrates is notoriously difficult, which requires high energy,[3] and the facile binding ability of the nitrogen atoms often led to poison of the catalytic species, which further limited practical applications.[4]

The development of highly efficient palladium/ligand catalytic systems, is an attractive area for both academic research and industrial applications.[2g,5] In this context, sterically demanding and electron-rich phosphines, such as PPh_3,[6] PCy_3,[7] $P(2\text{-furyl})_3$,[8] $P(n\text{-Bu})Ad_2$,[9] dppb,[5g,10] X-phos,[11] and Xant-phos,[12] have been extensively studied. However, it requires high loading of palladium (generally performed in 5−10 mol % palladium sources associated with 10−20 mol % phosphines). In contrast, *N*-heterocyclic carbenes (NHCs), with stronger σ-donor electronic ability, fine-tuning steric as well as lower toxicity compared to those of the phosphines ligands, remain less explored with respect to the application in palladium/ligand catalytic systems. Sames and co-workers[13] first reported the NHCs-Pd complexes in combination with PPh_3 as anciliary ligands for the cross-coupling of imidazoles with aryl halides in moderate yields (Scheme 1, type **I**). Subsequently, a seminal report by Lee and Huynh[14] independently demonstrated that imidazoles could readily couple with aryl bromides as well as activated aryl chlorides with the choice of NHCs/phosphine-supported palladium catalyst (Scheme 1, type **II**−**IV**). Despite their promising utility in cross-coupling reactions, these catalytic systems suffered from several drawbacks with respect to the low reactivities and limited substrate scope. Therefore, high reaction temperature (≥140 °C) and relatively high palladium loading of 2.5−5 mol % were generally required. Moreover, the extreme susceptibility of the LPd(0) species toward oxygen and moisture was commonly occurred, while the reaction proceeded under aerobic reaction conditions has remained elusive.

Scheme 1. Well-Defined NHC−Pd Complexes for Direct C−H Bond Arylation of Imidazoles



Since the pioneering report of Organ, Pd-PEPPSI (pyridine-enhanced precatalyst preparation stabilization and initiation), the mixed coordination of NHCs with monodentate nitrogen was well-developed, which exhibited more air-stable and robust

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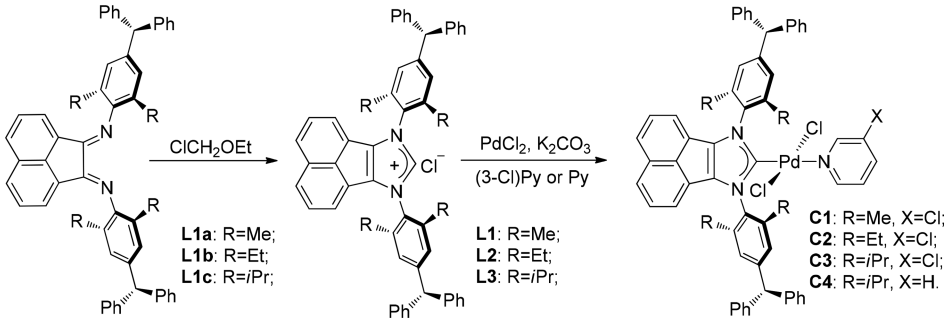
Scheme 2. Synthesis Route for Pd-PEPPSI Complexes of C1−C4



ability than that of the NHCs/phosphines.[15] Recently, we have succeeded in developing Pd-catalyzed direct arylation reaction by utilizing bulky encumbered Pd-PEPPSI precatalysts (Scheme 1, type **V**).[16a] It was shown that the NHCs ligands containing 2,6-diethyl on *N*-moieties and diphenyl groups on backbones could readily promote the cross-coupling in the presence of 1 mol % palladium loading under aerobic conditions. Moreover, we have also developed a series of bulky α-diimine palladium complexes, which exhibited high reactivities toward thiazoles at a palladium loading of 0.2 mol %.[16b] Although significant progress has been achieved in the catalyst design, the substitution on *N*-aryl moieties was mainly focused on the *ortho*-position, which we would expect to protect the axial site of the metal center directly. Very recently, Holland demonstrated that the bulky remote substitution (*para*-position) on NHCs also played positive influence on Suzuki−Miyaura cross-coupling.[17] Considering that the catalytic efficiency of this reaction was correlated to the electronic character and steric environment on NHCs, it is rational that a combination of σ-rich backbone and readily tunable *N*-aryl moieties on NHCs could lead to a systematical investigation. In this regard, we envisioned that the ancenaphthyl backbone-based NHCs with bulky substitution on both *ortho*- and *para*-*N*-aryl moieties might allow a new insight of catalyst structure design (Scheme 1, type **VI**). The strong σ-donor nature of the NHCs could furnish adequate electron donation to the palladium center for promoting the oxidative addition, while the increase of bulky steric on NHCs could stabilize the LPd(0) species and favor the reductive elimination process.[18] Therefore, a further improvement in catalytic activities could be achieved in despite of exposure to air. Herein, we report the synthesis of a type of Pd-PEPPSI complexes and their structural characterization and describe the catalytic properties of these precatalysts for direct arylation of imidazoles with aryl bromides in aerobic conditions.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Imidazolium Salts and the Corresponding Pd-PEPPSI Complexes. A convenient synthetic approach to imidazolinium salts was devised starting from readily available α-diimine compounds of Ar-BIAN, where Ar = 4-benzhydryl-2,6-dimethyl (**L1a**), 4-benzhydryl-2,6-diethyl (**L1b**), and 4-benzhydryl-2,6-diisopropylphenyl (**L1c**). As can be seen in Scheme 2, cyclization of the α-diimine compounds with chloromethyl ethyl ether gave the imidazolinium salts **L1**-**L3** as gray solids in moderate yields (48−67%). The imidazolinium salts were characterized by mass spectrometry (ESI-MS) and ^{1}H and ^{13}C NMR studies. In the ^{1}H NMR spectra, the appearance of chemical shift of imidazolium C−H protons at δ = 11.54−11.27 ppm certified formation of the imidazolium C−H protons (NC*H*N).

Then treatment of the imidazolinium salts **L1**−**L3** with $PdCl_2$ in the presence of K_2CO_3 in 3-chloropyridine or pyridine at 90 °C readily afforded the crude palladium complexes. After purification by chromatograph on silica gel, desired Pd-PEPPSI compounds, **C1**−**C4**, were isolated in 48−68% yields as yellowish solids. All these synthesized palladium complexes are highly moisture- and air-stable both in the solid states and in solutions and could be stored at ambient temperature for months without obvious decline in catalytic efficiency. These palladium complexes were fully characterized by means of ESI-MS and ^{1}H and ^{13}C NMR studies, as well as elemental analysis. For ^{1}H NMR spectra of **C1**−**C4**, the resonances of C−H protons (NC*H*N) in imidazolium salts disappeared, and chemical shifts for other protons changed slightly, when compared with those of the corresponding precursors. As can be seen in the ^{13}C NMR spectra, signals of the Pd−C_{NHC} in **C1**−**C4** appeared at 160.8−156.6 ppm, which were comparable with the ^{13}C NMR data of ancenahphthyl-based Pd-PEPPSI^{An} complexes.[19] Nevertheless, it is noteworthy that the chemical shifts of Pd−C_{NHC} shifted downfield by 7.3 to 3.1 ppm, in comparison with the analogous signals of classical Pd-PEPPSI-IPr,[20] which indicated increased σ-donor properties by the introduction of bulky planar ancenaphthyl backbones.

Moreover, the structures of all these complexes were unambiguously determined by single-crystal X-ray diffraction (XRD). The molecular structures were illustrated in Figures 1−4, respectively. The structural features of the four Pd-PEPPSI complexes are almost identical, which adopts a slightly distorted square planar geometry. Pd−C_{NHC}, Pd−N as well as Pd−Cl bond distances are all within the expected range of reported values. The *N*-aryl moieties were found to be roughly perpendicular to the coordination plane with the dihedral angles of 89.05 (87.81), 76.30 (75.47), 89.26 (81.00), and 76.08° (76.10°), for complexes **C1**−**C4**, respectively. These can be attributed to the much steric repulsion between the alkyl substituents on *N*-aryl moieties and bulky ancenaphthyl backbone, demonstrating an effective shielding on the axial positions of the palladium center and enhancement of the stability of the catalytic species in the course of following transformations.

Direct C−H Bond Arylation Catalyzed by Pd-PEPPSI Complexes. One of the current challenges in direct arylation of imidazoles is to achieve the cross-coupling of aryl halides at low catalyst loadings under aerobic conditions. In order to evaluate the best choice of the palladium precatalyst, the direct arylation of 1-methyl-1*H*-imidazole (**1a**) with 1-bromo-4-chlorobenzene (**2a**) was selected as a model reaction with

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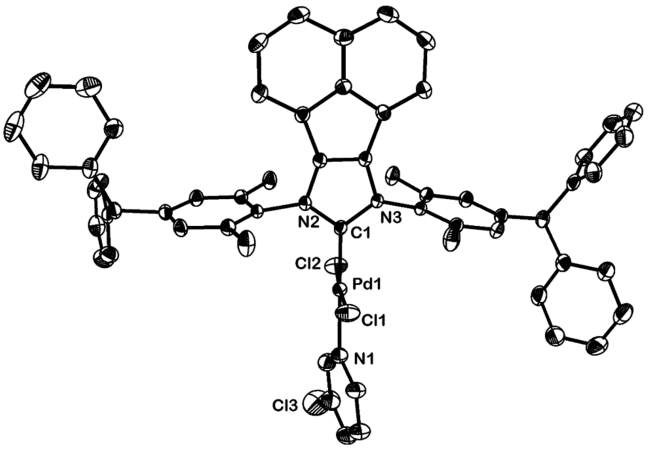

Figure 1. Molecular structure of **C1**·CH_2Cl_2 depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.958(2), Pd(1)−N(1) 2.149(2), Pd(1)−Cl(1) 2.3083(7), Pd(1)−Cl(2) 2.2993(8), N(1)−Pd(1)−C(1) 178.55(10), N(1)−Pd(1)−Cl(1) 91.44(7), C(1)−Pd(1)−Cl(1) 87.13(7), N(1)−Pd(1)−Cl(2) 91.50(7), C(1)−Pd(1)−Cl(2) 89.91(7), Cl(1)−Pd(1)−Cl(2) 176.21(3).

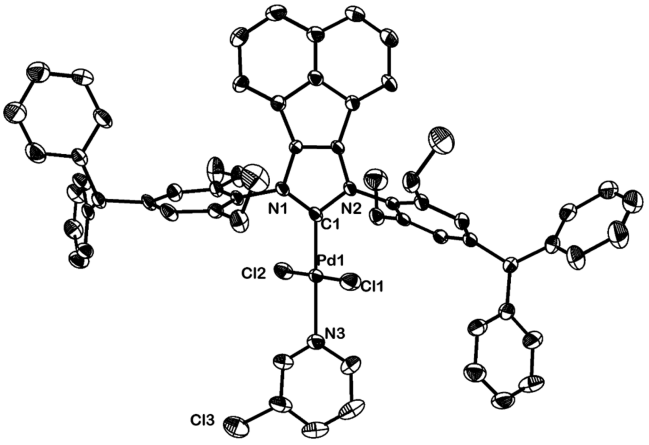

Figure 2. Molecular structure of **C2** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.9533(2), Pd(1)−N(3) 2.1059(2), Pd(1)−Cl(1) 2.2944(2), Pd(1)−Cl(2) 2.2817(2), N(3)−Pd(1)−C(1) 179.663(7), N(3)−Pd(1)−Cl(1) 89.916(6), C(1)−Pd(1)−Cl(1) 89.798(6), N(3)−Pd(1)−Cl(2) 89.827(5), C(1)−Pd(1)−Cl(2) 90.451(6), Cl(1)−Pd(1)−Cl(2) 177.581(7).

N,*N*-dimethylacetamide (DMAc) as solvent, K_2CO_3 as base, and pivalic acid (PivOH) as acid addictive. Initially, 0.25 mol % Pd-PEPPSI complexes was examined, and the reaction proceeded at 130 °C for 12 h. Under the reaction conditions, the desired cross-coupling product of **3a** was obtained in 46% yield when **C1** was selected as precatalyst (entry 1, Table 1). To our delight, high regioselective arylation at the C-5 site of 1-methyl-1*H*-imidazole occurred, which indicated the easier cleavage of C−H bond at the C-5 site than that of C-2 and C-4.[3,21] Comparatively, the sterically bulky **C2** and **C3** were applied instead under the same reaction conditions, affording the product in the yields of 57 and 86%, respectively (entries 2−3, Table 1). Apparently, the significant improvement could be resulted from the structure of the palladium precatalysts. Considering **C2** and **C3** bearing the same ancenaphthyl backbone and 4-benzhydryl on *N*-aryl moieties of these

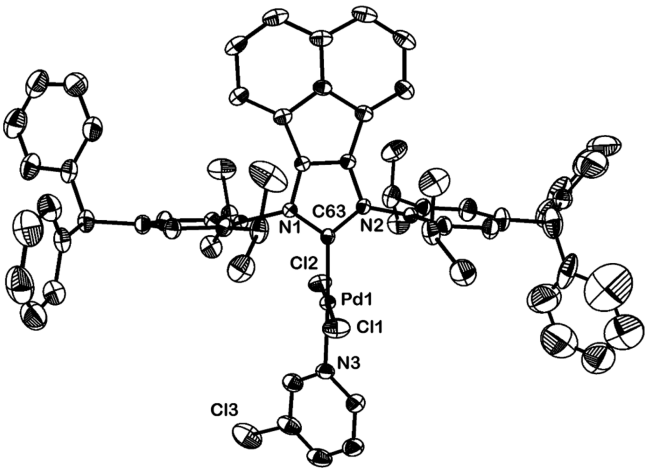

Figure 3. Molecular structure of **C3** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(63) 1.965(4), Pd(1)−N(3) 2.111(4), Pd(1)−Cl(1) 2.2900(14), Pd(1)−Cl(2) 2.2803(14), N(3)−Pd(1)−C(63) 176.80(17), N(3)−Pd(1)−Cl(1) 88.58(12), C(63)−Pd(1)−Cl(1) 94.07(12), N(3)−Pd(1)−Cl(2) 89.33(12), C(63)−Pd(1)−Cl(2) 88.01(12), Cl(1)−Pd(1)−Cl(2) 177.91(5).

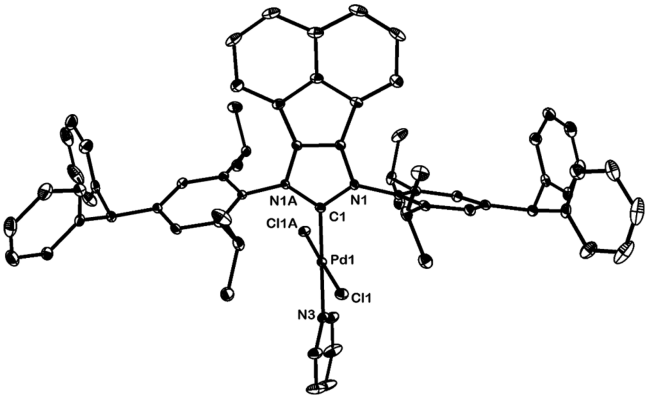

Figure 4. Molecular structure of **C4** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.956(3), Pd(1)−N(3) 2.106(3), Pd(1)−Cl(1) 2.2927(7), Pd(1)−Cl(1A) 2.2927(7), N(3)−Pd(1)−C(1) 180.00, N(3)−Pd(1)−Cl(1) 91.25(2), C(1)−Pd(1)−Cl(1) 88.75(2), N(3)−Pd(1)−Cl(1A) 91.25(2), C(1)−Pd(1)−Cl(1A) 88.75(2), Cl(1)−Pd(1)−Cl(1A) 177.50(3).

palladium complexes, the more efficient performance of **C3** suggested the increase of bulky steric on 2,6-position of the *N*-aryl moieties would stabilize the LPd(0) species when exposure to air and promote reductive elimination process in the transformations.

To further understand the influences of backbone and *para*-substituted *N*-aryl moieties on NHCs, the classical Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An} were also utilized for comparison. As can be seen in Table 1, it was found that Pd-PEPPSI-IPr was much less efficient than that of **C3** under the identical reaction conditions, leading to the formation of **3a** in 54% yield (entry 4). Obviously, the investigation exhibited that the introduction of bulky ancenaphthyl backbone would facilitate the cross-coupling compared to that of less hindered Pd-PEPPSI-IPr with hydrogen atoms on backbone.[19] Moreover, it was noteworthy that the benzhydryl on the *para*-position of the *N*-aryl moieties promoted the reaction significantly, whereas the Pd-PEPPSI-

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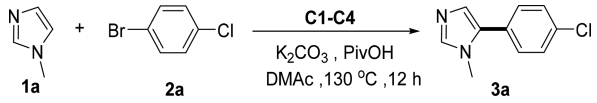
Table 1. Screening of Palladium Complexes for the Direct Arylation Reaction of 1-Methyl-1*H*-imidazole with 1-Bromo-4-chlorobenzene[a]



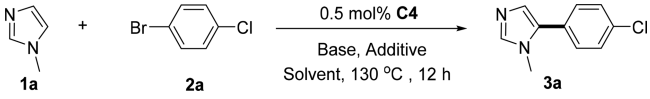
entry	precatalyst	Pd (mol %)	yield (%)[b]	selectivity (%)[d]
1	**C1**	0.25	46	97
2	**C2**	0.25	57	97
3	**C3**	0.25	86	97
4	Pd-PEPPSI-IPr	0.25	54	97
5	Pd-PEPPSI-IPr^{An}	0.25	60	97
6	**C4**	0.25	90	97
7	**C4**	0.5	**97** (97)[c]	98
8	**C4**	0.1	78	98

[a]Reaction conditions: 1-methyl-1*H*-imidazole (2.0 mmol), 1-bromo-4-chlorobenzene (1.0 mmol), palladium source (0.5−0.1 mol %), PivOH (0.3 mmol), K_2CO_3 (2 mmol), DMAc (4 mL), 130 °C, 12 h, under aerobic conditions. [b]GC yield using (trifluoromethyl)benzene as an internal standard. [c]Isolated yields in parentheses. [d]Percent yield of the C5-arylated product (there is a trace amount of C2- and C4-arylated products).

IPr^{An} without remote substitution only afforded moderate yield of 60% (entry 5, Table 1). To further distinguish the effect of the remote benzhydryl, a hand of heteroarenes were performed. As shown in Table S1, in most cases, **C3** and **C4** were superior to PEPPSI-IPr^{An} in the presence of 0.1−0.5 mol % palladium loading. Probably, the catalytic behavior could result from an extra attractive π-stacking interaction between the 4-benzhydryl groups and the substrate of aryl halide, which would further accelerate the oxidative addition step in the cross-coupling reaction.[22] In addition, the ancillary nitrogen-based ligand was also evaluated, and it turned out that **C4** bearing pyridine was the optimal choice, providing the desired product in 90% yield (entry 6, Table 1). To improve the reaction efficiency further, we found that a slightly higher palladium loading of 0.5 mol % would afforded **3a** in almost quantitative yields (entry 7, Table 1).

With the preliminary result in hand, subsequent optimization studies were performed. As shown in Table 2, different combinations of solvents, bases and acid additives were explored in the presence of 0.5 mol % **C4**. Among the solvents screened (entries 1, 17−21, Table 2), DMAc was most effective and gave product **3a** in high yield of 97% (entry 1, Table 2). The bases also had a profound influence on the reaction, due to its involvement in key step of catalytic cycle.[23] NaOAc was comparable with Na_2CO_3, but the use of K_2CO_3 dramatically improved the yield. Other bases, such as K_3PO_4, Cs_2CO_3, and KO^{t}Bu, all led to inferior yields (entries 2, 4, and 5, Table 2). We continued to screen acid additives, and found that HOAc and CF_3COOH gave relatively moderate yields of 50 and 67%, respectively (entries 13 and 15, Table 2). On the contrary, PivOH gave the best effectiveness (entry 1, Table 2). These investigations revealed that the acid additives were crucial for the reaction efficiency. The yield declined sharply to 14% in the absence of any acid additives (entry 16, Table 2), which suggested the acid might function as a proton shuttle in the process of the C−H bond cleavage step.[7b,24] In addition, we observed that the phase transfer agent TBAB afforded no benefit, and a notable decrease in yield of 66% was observed, which was opposite the investigation by Roy and co-workers'.[25]

Table 2. Condition Optimization in Direct Palladium-Catalyzed Cross-Coupling Reaction[a]



entry	solvent	base	additives	yield (%)[b]	selectivity (%)[c]
1	DMAc	K_2CO_3	PivOH	**97**	98
2	DMAc	K_3PO_4	PivOH	7	88
3	DMAc	KOAc	PivOH	60	89
4	DMAc	Cs_2CO_3	PivOH	8	85
5	DMAc	KO^{t}Bu	PivOH	5	91
6	DMAc	NaO^{t}Bu	PivOH	11	87
7	DMAc	KOH	PivOH	19	94
8	DMAc	LiO^{t}Bu	PivOH	22	93
9	DMAc	NaOAc	PivOH	75	95
10	DMAc	Na_2CO_3	PivOH	80	90
11	DMAc	NaOH	PivOH	21	92
12	DMAc	$NaHCO_3$	PivOH	35	97
13	DMAc	K_2CO_3	HOAc	50	93
14	DMAc	K_2CO_3	PhCOOH	3	95
15	DMAc	K_2CO_3	CF_3COOH	67	94
16	DMAc	K_2CO_3	none	14	91
17	DMF	K_2CO_3	PivOH	70	92
18	NMP	K_2CO_3	PivOH	75	98
19	toluene	K_2CO_3	PivOH	11	96
20	dioxane	K_2CO_3	PivOH	25	93
21	xylene	K_2CO_3	PivOH	5	86
22	DMAc	K_2CO_3	PivOH + TBAB	66	91

[a]Reaction conditions: 1-methyl-1*H*-imidazole (2.0 mmol), 1-bromo-4-chlorobenzene (1.0 mmol), **C4** (0.5 mol %), PivOH (0.3 mmol), K_2CO_3 (2 mmol), DMAc (4 mL), 130 °C, 12 h, under aerobic conditions. [b]GC yield using (trifluoromethyl)benzene as an internal standard. [c]Percent yield of the C5-arylated product.

In view of the above analysis, we obtained the optimized catalytic conditions for direct arylation: DMAc as solvent, K_2CO_3 as base, PivOH as acid additive, 0.5 mol % **C4**, and at 130 °C for 12 h.

To confirm the scope of established protocol and the feasibility of employing Pd-PEPPSI complex of **C4**, an array of imidazoles and (hetero)aryl bromides were explored. It was found that the aryl bromides bearing electron-withdrawing groups, such as chloro, fluoro-, cyano-, nitro-, and aldehyde, were successfully coupled with 1-methyl-1*H*-imidazole (**1a**) and excellent yields of 90−97% were achieved in **3a**-**3f**. The robust palladium complex of **C4** was further featured by the rapid access to some important biologically active intermediates and function materials. For instance, 5-(4-chlorophenyl)-1-methyl-1*H*-imidazole (**3a**),[26] 1-methyl-5-phenyl-1*H*-imidazole (**3i**),[27] and 1-methyl-5-(naphthalen-1-yl)-1*H*-imidazole (**3h**)[28] as well as photoactive material intermediate of 4-(1-methyl-1*H*-imidazol-5-yl)benzonitrile (**3d**)[29] were readily prepared under standard conditions. However, the electronic effect of the electrophilic reagents were shown to be significant, and only moderate yields were obtained with regard to aryl bromides bearing electron-donating groups (**3i**−**3k**). Gratifyingly, other challenging substrates of imidazoles, such as 1,2-dimethyl-1*H*-imidazole (**1b**), 1-phenyl-1*H*-imidazole (**1c**), and especially 2-methyl-1-phenyl-1*H*-imidazole (**1d**), were compatible with current standard conditions, furnishing the desired cross-coupling products in moderate to excellent yields of 38−99%

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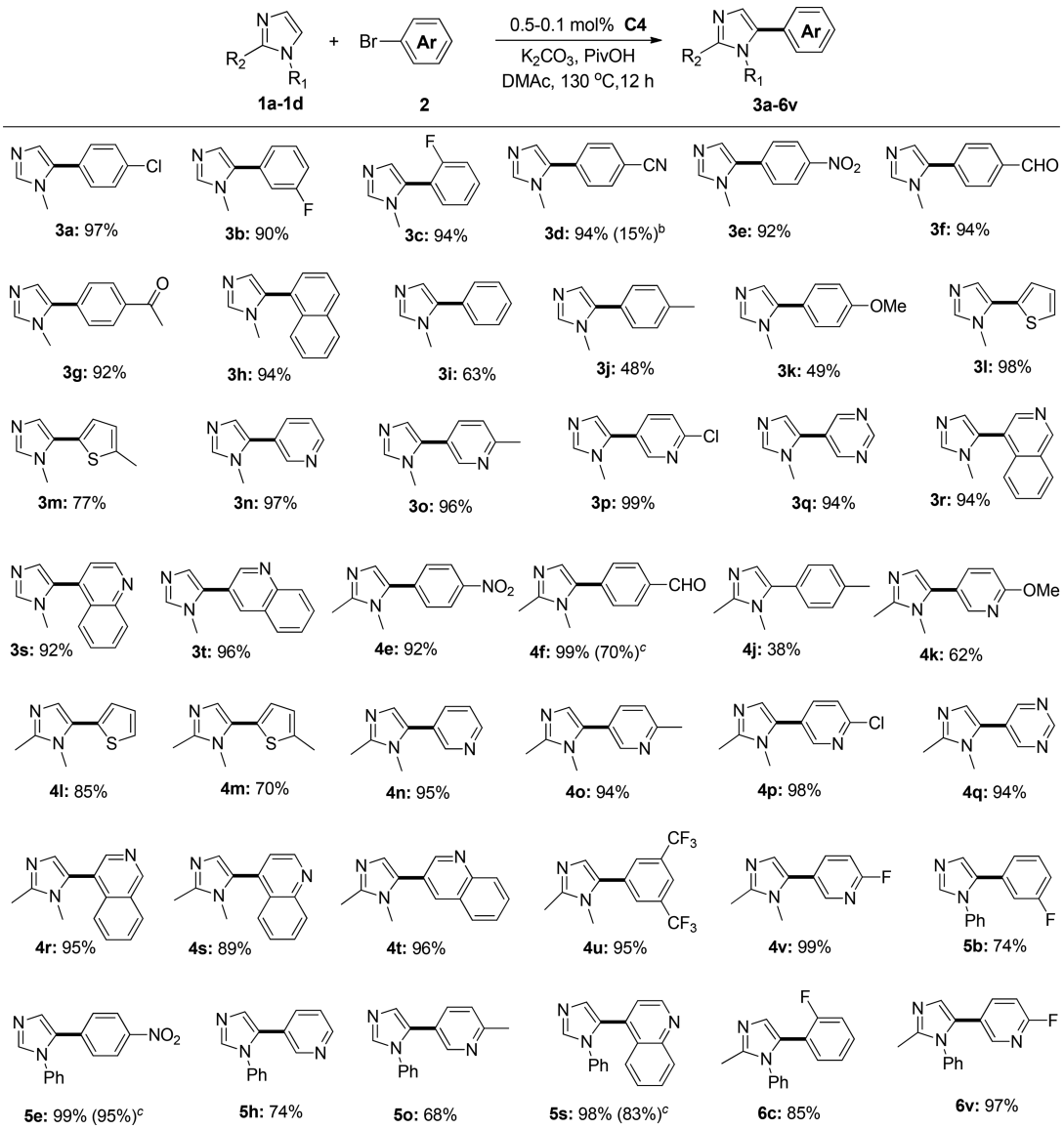
Table 3. Palladium-Catalyzed Direct Arylation of Imidazoles with (Hetero)aryl Bromides[a]



[a]Reaction conditions: imidazoles (2.0 mmol), (hetero)aryl bromides (1.0 mmol), **C4** (0.5 mol %), PivOH (0.3 mmol), K_2CO_3(2 mmol), DMAc (4 mL), 130 °C, 12 h, under aerobic conditions. [b]Isolated yield in parentheses was obtained when 4-chlorobenzonitrile was used as substrate. [c]The reaction was performed at 0.1 mol % palladium loading, and other parameters were the same as reaction conditions described in footnote [a].

(**4e**−**4j**, **4u**, **5b**−**5e**, **6c**). Nevertheless, when aryl chloride such as 4-chlorobenzonitrile was selected as coupling candidate, the desired product of **3d** was afforded in low yield of 15% under the identical reaction conditions. This result suggested that only aryl bromides were limited to the current Pd-catalyzed cross-coupling reaction.

Encouraged by these promising results aforementioned, we next proceeded to evaluate challenging heteroaryl bromides, since the heteroatoms tend to coordinate and subsequently poison the catalytic species.[4] As can be seen in Table 3, a wide range of heteroaryl bromides, such as thiophene, pyridine, pyrimidine, isoquinoline, and quinoline, were suitable cross-coupling partners and moderate to excellent yields of products were obtained under optimized reaction conditions (**3l**−**3t**, **4k**−**4t**, **4v**, **5h**−**5s**, **6v**). To our delight, 1-phenyl-1*H*-imidazole could be smoothly arylated with 4-bromoquinoline to give **5s** in a high yield of 83%, even in the presence of 0.1 mol % palladium loading. It is noteworthy that the heteroarylated compounds of **3p** and **4q**,[30] as the key intermediates of pharmaceutically active compounds against male erectile dysfunction (MED), were afforded in excellent yields of 99 and 94%, respectively.

To further demonstrate the application of this protocol, thiazoles were selected as the coupling partners (Table 4). To our delight, at a low palladium loading of 0.1−0.05 mol %, thiazoles bearing both 2- and/or 4-substituents could smoothly afford the desired products in high yields (**7a**−**10n**). In addition, the catalytic system was tolerable to a variety of functional groups such as chloro, nitrile, aldehyde and acyl groups on aryl bromides. It is significant that **C4** exhibited catalytic ability superior than that of the camphyl-based α-diimine palladium complex,[16b] which demonstrated that the bulky steric NHCs exhibited higher efficiency. The construction of arylated azoles with pyrazoles and isoxazoles were also evaluated, furnishing the corresponding cross-coupling compounds in high efficiency in the presence of 0.1 mol %

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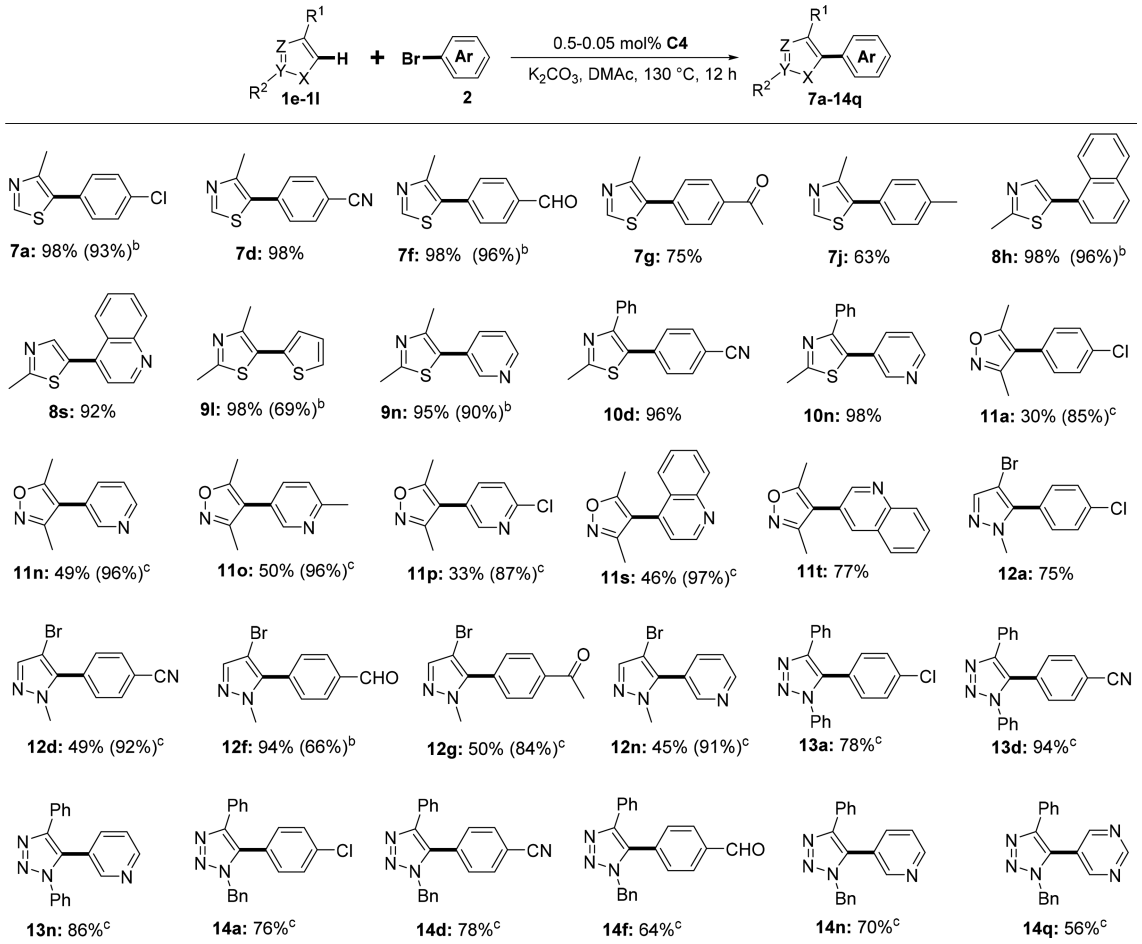
Table 4. Palladium-Catalyzed Direct Arylation of Azoles with (Hetero)aryl Bromides[a]



[a]Reaction conditions: azoles (2.0 mmol), (hetero)aryl bromides (1.0 mmol), **C4** (0.1 mol %), PivOH (0.3 mmol), K_2CO_3 (2 mmol), DMAc (4 mL), 130 °C, 12 h, under aerobic conditions. [b]The reaction was performed at 0.05 mol % palladium loading. [c]The reaction was performed at 0.5 mol % palladium loading.

palladium. Importantly, the introduction of a bromo group at C-4 position of the pyrazole did not affect the cross-coupling reaction, which would enable the opportunity of these products to be used in further transformations. Inspired by the fact that the palladium preceatalyst has been remarkably successful in catalyzing C−H direct cross-coupling reactions, we next explored the most challenging substrates of 1,2,3-triazoles. To our delight, the reaction proceeded smoothly to afford the desired cross-coupling products in moderate to excellent yields (56−94%), in the presence of slightly higher palladium loading of 0.5 mol %.

CONCLUSION

In summary, a type of bis(imino)acenaphthene (BIAN)-supported Pd-PEPPSI complexes have been designed, synthesized, and utilized for direct arylation of imidazoles. It revealed that the NHCs ligands with bulky ancenaphthyl backbone as well as bulky *ortho*- and *para*-steric on *N*-aryl moieties, played a crucial role in the catalytic efficiency. Under the optimized conditions, the direct C−H arylation efficiently proceeded in high to excellent yields in the presence of 0.5−0.05 mol % palladium under aerobic reaction conditions. The reaction displayed excellent functional group tolerance and a wide range of (hetero)aryl bromides and various azoles were compatible. This study highlights a simply employed protocols without the need of glovebox and strict moisture- and air-free reaction conditions. This strategy of catalyst design would provide technical support for the synthesis of important bioactive compounds and functional materials.

EXPERIMENTAL SECTION

Physical Measurements and Materials. Acenaphthenequinone, pyridine, 3-chloropyridine, diphenylmethanol, 1-methyl-1*H*-imidazole, 1,2-dimethyl-1*H*-imidazole, aryl and heteroaromatic bromides, chloromethyl ethyl ether, palladium chloride, all solvents, and inorganic bases were used as received. 2,6-Dimethylaniline, 2,6-diethylaniline, and 2,6-diisopropylaniline were distilled under reduced pressure before being used. 4-Substituted anilines were synthesized according to the literature method.[31] *α*-Diimine compounds, imidazolium salts, and Pd-PEPPSI-IPr compounds were prepared according to literature method.[19,20]

The NMR data of compounds were obtained on a Varian Mercury-Plus 400 MHz spectrometer at ambient temperature with the decoupled nucleus, using $CDCl_3$ as solvent and referenced versus TMS as standard. Elemental analyses were determined with a Vario EL Series Elemental Analyzer from Elementar. The X-ray diffraction data of single crystals were obtained with the ω-2θ scan mode on a Bruker SMART 1000 CCD diffractiometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K for **C1**−**C4**. The structure was solved using direct methods, and further refinement with full-matrix least-squares on F^2 was obtained with the SHELXTL program package.[32] All non-hydrogen atoms were refined anisotropically.

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Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

General Procedures for the Synthesis of Anilines. A 100 mL Schlenk flask was charged with diphenylmethanol (9.58 g, 52 mmol) and aniline (50 mmol) and stirred at 80 °C under a nitrogen atmosphere. After the solid was dissolved, the prepared solution of $ZnCl_2$/concentrated HCl (5 g/8 mL) was added. The temperature of reaction was elevated to 140 °C for 5 h. After completion of the reaction, the reaction mixture was cooled to room temperature, dissolved in 100 mL of dimethyl chloride, and transferred to a beaker. The pH was adjusted to 7−8 with saturated $NaHCO_3$ solution. The zinc salt was removed by filtration. The organic phases were combined, dried over anhydrous sodium sulfate and filtered, and solvent was removed in vacuum. The remaining products were added into a large amount of anhydrous ethanol and stirred to obtain white powders.

4-Benzhydryl-2,6-dimethylaniline (**A1**) was obtained as white powder in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, Ar−H, 4H), 7.26−7.20 (m, Ar−H, 2H), 7.17 (d, J = 7.2 Hz, Ar−H, 4H), 6.74 (s, Ar−H, 2H), 5.46 (s, C*H*Ph$_2$, 1H), 3.47 (s, N*H*$_2$, 2H), 2.15 (s, C*H*$_3$, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 140.9, 133.3, 129.4, 129.2, 128.1, 126.0, 121.6, 56.1, 17.7.

4-Benzhydryl-2,6-diethylaniline (**A2**) was obtained as white powder in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.27 (m, Ar−H, 4H), 7.25−7.19 (m, Ar−H, 2H), 7.17 (d, J = 7.2 Hz, Ar−H, 4H), 6.75 (s, Ar−H, 2H), 5.48 (s, C*H*Ph$_2$, 1H), 3.60 (s, N*H*$_2$, 2H), 2.51 (q, J = 7.5 Hz, C*H*$_2$CH$_3$, 4H), 1.21 (t, J = 7.5 Hz, CH$_2$C*H*$_3$, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 139.7, 133.5, 129.4, 128.1, 127.6 127.2, 125.9, 56.4, 24.4, 13.1.

4-Benzhydryl-2,6-diisopropylaniline (**A3**) was obtained as white powder in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (m, Ar−H, 4H), 7.28−7.22 (m, Ar−H, 2H), 7.18 (d, J = 7.1 Hz, Ar−H, 4H), 6.84 (s, Ar−H, 2H), 5.52 (s, C*H*Ph$_2$, 1H), 3.71 (s, N*H*$_2$, 2H), 2.95 (hept, J = 6.8 Hz, C*H*(CH$_3$)$_2$, 2H), 1.24 (d, J = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 138.4, 133.4, 132.3, 129.4, 128.0, 125.9, 124.0, 56.7, 28.0, 22.4.

General Procedures for the Synthesis of α-Diimine Compounds. A 100 mL Schlenk flask was charged with acenaphthoquinone (1.82 g, 10 mmol), followed with acetonitrile (35 mL). The mixture was stirred at 80 °C for 15 min, then glacial acetic acid (HOAc) (13 mL) was added, and we then slowly added a prepared solution of aniline/acetonitrile (22 mmol/30 mL) into the flask with a syringe. The reaction was carried out at 80 °C under nitrogen protection for 5 h. After the end of the reaction, the reaction mixture was cooled to room temperature, filtrated, and washed with *n*-hexane to give the products.

[4-CH(C$_6$H$_5$)$_2$-2,6-(CH$_3$)$_2$-C$_6$H$_2$−N═C]$_2$C$_{10}$H$_6$ (**L1a**) was obtained as orange powder in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, Ar−H, 2H), 7.41−7.29 (m, Ar−H, 10H), 7.25−7.20 (m, Ar−H, 10H), 7.06 (dd, J = 27.1, 3.7 Hz, Ar−H, 2H), 6.87 (d, J = 25.3 Hz, Ar−H, 4H), 6.77−6.67 (m, Ar−H, 2H), 5.58 (d, J = 14.4 Hz, C*H*Ph$_2$, 2H), 2.04 (s, CH$_3$, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 147.7, 144.4, 139.8, 139.0, 132.1, 130.9, 129.5, 129.4, 128.9, 128.3, 126.2, 124.7, 122.5, 122.2, 56.5, 17.9. ESI-MS m/z: 720.6, [**L1a**]$^+$ (C$_{54}$H$_{44}$N$_2^+$, calcd 720.4).

[4-CH(C$_6$H$_5$)$_2$-2,6-(CH$_2$CH$_3$)$_2$-C$_6$H$_2$−N═C]$_2$C$_{10}$H$_6$ (**L1b**) was obtained as orange powder in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.0 Hz, Ar−H, 2H), 7.52−7.20 (m, Ar−H, 20H), 7.17−6.69 (m, Ar−H, 8H), 5.66 (s, C*H*Ph$_2$, 2H), 2.53 (d, J = 11.0 Hz, C*H*$_2$CH$_3$, 8H), 1.06 (s, CH$_2$C*H*$_3$, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 147.0, 144.5, 139.2, 130.7, 129.7, 129.5, 129.4, 128.7, 128.2, 128.0, 127.7, 127.6, 126.2, 122.9, 56.7, 24.9, 13.9. ESI-MS m/z: 776.7, [**L1b**]$^+$ (C$_{58}$H$_{52}$N$_2^+$, calcd 776.4).

{4-CH(C$_6$H$_5$)$_2$-2,6-[CH(CH$_3$)$_2$]$_2$-C$_6$H$_2$−N═C}$_2$C$_{10}$H$_6$ (**L1c**) was obtained as orange powder in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, Ar−H, 2H), 7.44−7.31 (m, Ar−H, 10H), 7.27−7.19 (m, Ar−H, 12H), 7.00 (s, Ar−H, 4H), 6.64 (d, J = 7.0 Hz, Ar−H, 2H), 5.64 (s, C*H*Ph$_2$, 2H), 3.07−2.85 (m, C*H*(CH$_3$)$_2$, 4H), 1.13 (d, J = 6.5 Hz, CH(C*H*$_3$)$_2$, 12H), 0.86 (d, J = 6.6 Hz, CH(C*H*$_3$)$_2$, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 145.9, 144.7, 140.7, 139.4, 135.2, 131.1, 129.6, 129.5, 128.8, 128.2, 127.7, 126.1, 124.8, 123.3, 56.9, 28.7, 23.3, 23.1. ESI-MS m/z: 832.9, [**L1c**]$^+$ (C$_{62}$H$_{60}$N$_2^+$, calcd 832.5).

General Procedures for the Synthesis of Imidazolium Salts. α-Diimine compounds (2 mmol) and chloromethyl ethyl ether (4 mL) were mixed into a thick-walled pressure flask at ambient temperature. The flask was vacuumized, filled with nitrogen, and heated at 100 °C for 24 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature, washed, and stirred with anhydrous Et_2O three times to give a suspension of solids. The products were obtained by filtration and washing with anhydrous Et_2O.

[4-CH(C$_6$H$_5$)$_2$-2,6-(CH$_3$)$_2$-C$_6$H$_2$−NC]$_2$C$_{10}$H$_6$CH$_2^+$Cl$^-$ (**L1**) was obtained as gray powder in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (s, NC*H*N, 1H), 8.01 (d, J = 8.3 Hz, Ar−H, 2H), 7.67−7.56 (m, Ar−H, 2H), 7.48−7.35 (m, Ar−H, 8H), 7.34−7.17 (m, Ar−H, 15H), 7.10 (s, Ar−H, 3H), 5.64 (s, C*H*Ph$_2$, 2H), 2.31 (s, CH$_3$,12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 142.9, 136.5, 134.4, 130.5, 130.5, 130.2, 129.8, 129.5, 129.2, 128.6, 128.2, 126.7, 124.7, 123.4, 122.8, 56.5, 18.2. ESI-MS m/z: 733.4, [**L1** − Cl]$^+$ (C$_{55}$H$_{45}$N$_2^+$, calcd 733.4).

[4-CH(C$_6$H$_5$)$_2$-2,6-(CH$_2$CH$_3$)$_2$-C$_6$H$_2$−NC]$_2$C$_{10}$H$_6$CH$_2^+$Cl$^-$ (**L2**) was obtained as gray powder in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.44 (s, NC*H*N, 1H), 7.93 (d, J = 8.3 Hz, Ar−H, 2H), 7.54−7.47 (m, Ar−H, 2H), 7.35−7.25 (m, Ar−H, 8H), 7.20 (d, J = 7.2 Hz, Ar−H, 3H), 7.18−7.09 (m, Ar−H, 11H), 7.05 (s, Ar−H, 4H), 5.59 (s, C*H*Ph$_2$, 2H), 2.64−2.40 (m, C*H*$_2$CH$_3$, 8H), 1.00 (t, J = 7.2 Hz, CH$_2$C*H*$_3$, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 143.0, 140.1, 137.2, 130.5, 130.3, 130.2, 129.9, 129.6, 129.4, 128.8, 128.6, 128.2, 126.7, 123.3, 122.9, 56.7, 24.7, 14.6. ESI-MS m/z: 789.5, [**L2** − Cl]$^+$ (C$_{59}$H$_{53}$N$_2^+$, calcd 789.4).

{4-CH(C$_6$H$_5$)$_2$-2,6-[CH(CH$_3$)$_2$]$_2$-C$_6$H$_2$−NC}$_2$C$_{10}$H$_6$CH$_2^+$Cl$^-$ (**L3**) was obtained as gray powder in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, NC*H*N, 1H), 8.00 (d, J = 8.3 Hz, Ar−H, 2H), 7.64−7.54 (m, Ar−H, 2H), 7.42−7.29 (m, Ar−H, 8H), 7.25−7.17 (m, Ar−H, 14H), 7.14 (s, Ar−H, 4H), 5.67 (s, C*H*Ph$_2$, 2H), 2.72 (hept, J = 8.0 Hz, C*H*(CH$_3$)$_2$, 4H), 1.24 (d, J = 5.0 Hz, CH(C*H*$_3$)$_2$, 12H), 1.00 (d, J = 6.4 Hz, CH(C*H*$_3$)$_2$, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 144.6, 143.1, 137.6, 130.6, 130.5, 130.1, 129.5, 128.6, 128.5, 128.3, 127.4, 126.6, 126.1, 123.1, 122.8, 56.9, 29.4, 24.5, 23.5. ESI-MS m/z: 845.8, [**L3** − Cl]$^+$ (C$_{63}$H$_{61}$N$_2^+$, calcd 845.5).

General Procedures for the Synthesis of Pd-PEPPSI Complexes. Imidazolium salts (1 mmol), palladium chloride (195.1 mg, 1.1 mmol), potassium carbonate (1.38 g, 10 mmol), 3-chloropyridine or pyridine (6 mL) was added in a flask, and reacted at 90 °C under nitrogen protection for 24 h. After completion of the reaction, the mixture was cooled to ambient temperature, and 3-chloropyridine or pyridine was distilled off under reduced pressure. Then, 15 mL of dichloromethane was added, and the silica gel column was passed over using dichloromethane as eluent. Distillation of the filtrate gave the fulvous solid. The solid was recrystallized with dichloromethane/*n*-hexane. The turbid mixture solution was filtered to give yellowish products.

[4-CH(C$_6$H$_5$)$_2$-2,6-(CH$_3$)$_2$-C$_6$H$_2$−NC]$_2$C$_{10}$H$_6$CH-Pd(Cl$_2$)(3-ClPy) (**C1**) was obtained as yellowish powder in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 2.3 Hz, Ar−H, 1H), 8.53 (dd, J = 5.5, 1.1 Hz, Ar−H, 1H), 7.80 (d, J = 8.3 Hz, Ar−H, 2H), 7.72−7.64 (m, Ar−H, 1H), 7.52−7.36 (m, Ar−H, 11H), 7.35−7.25 (m, Ar−H, 12H), 7.15 (d, J = 9.5 Hz, Ar−H, 4H), 7.01 (d, J = 6.9 Hz, Ar−H, 2H), 5.71 (s, C*H*Ph$_2$, 2H), 2.44 (s, CH$_3$,12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 150.4, 149.5, 145.0, 143.7, 138.6, 137.6, 136.5, 134.4, 132.1, 129.8, 129.7, 129.5, 129.1, 128.4, 128.2, 127.6, 126.4, 125.5, 124.4, 120.8, 56.6, 19.3. Anal. Calcd for C$_{60}$H$_{48}$Cl$_3$N$_3$Pd: C, 70.39; H, 4.73; N, 4.10. Found: C, 70.56; H, 4.79; N, 4.06. ESI-MS m/z: 908.3, [**C1**-(3ClPy)]$^+$ (C$_{55}$H$_{44}$Cl$_2$N$_2$Pd$^+$, calcd 908.2); 873.4, [**C1** − (3ClPy + Cl)]$^+$ (C$_{55}$H$_{44}$ClN$_2$Pd$^+$, calcd 873.2); 733.3, [**L1** − Cl]$^+$ (C$_{55}$H$_{45}$N$_2^+$, calcd 733.4).

[4-CH(C$_6$H$_5$)$_2$-2,6-(CH$_2$CH$_3$)$_2$-C$_6$H$_2$−N═C]$_2$C$_{10}$H$_6$CH-Pd(Cl$_2$)-(3-ClPy) (**C2**) was obtained as yellowish powder in 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 2.3 Hz, Ar−H, 1H), 8.44 (dd, J = 5.4, 1.2 Hz, Ar−H, 1H), 7.75 (d, J = 8.3 Hz, Ar−H, 2H), 7.61 (d, J = 8.3 Hz, Ar−H, 1H), 7.45−7.32 (m, Ar−H, 10H), 7.28−7.22 (m,

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Ar−H, 12H), 7.16 (d, J = 3.1 Hz, Ar−H, 4H), 7.11 (dd, J = 8.2, 5.5 Hz, Ar−H, 1H), 6.98 (dd, J = 6.9, 2.5 Hz, Ar−H, 2H), 5.72 (s, CHPh$_2$, 2H), 2.97−2.82 (m, CH_2CH$_3$, 4H), 2.79−2.64 (m, CH_2CH$_3$, 4H), 1.07−0.96 (m, CH$_2$CH_3, 12H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 157.6, 150.4, 149.5, 145.3, 143.9, 142.0, 139.2, 137.5, 133.1, 132.0, 129.6, 129.5, 129.2, 129.0, 128.4, 128.1, 127.6, 126.4, 125.8, 124.3, 121.1, 56.9, 24.9, 14.3. Anal. Calcd for $C_{64}H_{56}Cl_3N_3Pd$: C, 71.18; H, 5.23; N, 3.89. Found: C, 71.09; H, 5.27; N, 3.82. ESI-MS m/z: 789.5, [**L2** − Cl]$^+$ ($C_{59}H_{53}N_2^+$, calcd 789.4).

{4-CH(C_6H_5)$_2$-2,6-[CH(CH_3)$_2$]$_2$-C_6H_2−N═C}$_2C_{10}H_6$CH-Pd-(Cl$_2$)(3-ClPy) (**C3**) was obtained as yellowish powder in 67% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.64 (dd, J = 31.1, 3.4 Hz, Ar−H, 2H), 7.76−7.59 (m, Ar−H, 4H), 7.42−7.33 (m, Ar−H, 11H), 7.28 (d, J = 8.5 Hz, Ar−H, 8H), 7.25 (s, Ar−H, 3H), 7.20 (s, Ar−H, 3H), 7.14 (dd, J = 8.2, 5.5 Hz, Ar−H, 1H), 6.83−6.66 (m, Ar−H, 2H), 5.71 (s, CHPh$_2$, 2H), 3.41−3.22 (m, CH(CH$_3$)$_2$, 4H), 1.29 (d, J = 6.5 Hz, CH(CH_3)$_2$, 12H), 0.83 (d, J = 6.9 Hz, CH(CH_3)$_2$, 12H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.0, 150.6, 149.6, 147.0, 145.7, 143.9, 140.5, 137.5, 132.1, 131.0, 129.6, 129.5, 128.4, 128.0, 127.5, 127.3, 126.4, 126.1, 125.9, 124.4, 121.9, 57.0, 28.8, 25.7, 24.1. Anal. Calcd for $C_{68}H_{64}Cl_3N_3Pd$: C, 71.89; H, 5.68; N, 3.70. Found: C, 71.87; H, 5.76; N, 3.73. ESI-MS m/z: 845.4, [**L3** − Cl]$^+$ ($C_{63}H_{61}N_2^+$, calcd 845.5).

{4-CH(C_6H_5)$_2$-2,6-[CH(CH_3)$_2$]$_2$-C_6H_2−N═C}$_2C_{10}H_6$CH-Pd-(Cl$_2$)(Py) (**C4**) was obtained as yellowish powder in 68% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.72−8.63 (m, Ar−H, 2H), 7.74 (d, J = 8.3 Hz, Ar−H, 2H), 7.67−7.59 (m, Ar−H, 1H), 7.43−7.35 (m, Ar−H, 10H), 7.32−7.27 (m, Ar−H, 12H), 7.24−7.17 (m, Ar−H, 6H), 6.78 (d, J = 6.9 Hz, Ar−H, 2H), 5.74 (s, CHPh$_2$, 2H), 3.40 (hept, J = 8.0 Hz, CH(CH$_3$)$_2$, 4H), 1.33 (d, J = 6.6 Hz, CH(CH_3)$_2$, 12H), 0.86 (d, J = 6.9 Hz, CH(CH_3)$_2$, 12H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 160.8, 151.5, 147.0, 145.6, 143.9, 140.4, 137.4, 132.2, 129.5, 129.2, 128.3, 128.0, 127.2, 126.5, 126.4, 126.2, 125.9, 124.1, 121.9, 57.0, 28.8, 25.7, 24.1. Anal. Calcd for $C_{68}H_{65}Cl_2N_3Pd$: C, 74.14; H, 5.95; N, 3.81. Found: C, 73.97; H, 6.00; N, 3.78. ESI-MS m/z: 985.6, [**C4** − (Py + Cl)]$^+$ ($C_{63}H_{60}ClN_2Pd^+$, calcd 985.3); 845.6, [**L3** − Cl]$^+$ ($C_{63}H_{61}N_2^+$, calcd 845.5).

General Procedures for the Synthesis of *N*-Substituted Imidazoles. A 150 mL three-necked flask was charged with 1*H*-imidazole or 2-methyl-1*H*-imidazole (22 mmol), phenyl boronic acid (2.44g, 20 mmol), anhydrous potassium carbonate (5.53g, 40 mmol), copper(I) iodide (0.5 g), and 50 mL of DMAc. Reaction mixture was stirred with a mechanical stirrer. Reaction was carried out at 130 °C for 36 h and monitored by thin layer chromatography (TLC) with a solution of *n*-hexane/ethyl acetate (v/v, 5/1) as a developer. After end of the reaction, the reaction mixture was cooled to ambient temperature. 100 mL of dichloromethane and 100 mL of water were added. The mixture was stirred for 15 min, followed by two rounds of extraction (2 × 30 mL) with dichloromethane. The organic layer was decolored with activated carbon, dried with anhydrous sodium sulfate, filtered, and condensed under reduce pressure. The crude products were purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (v/v, 5/1) as eluent. The filtrate with target product was collected and evaporated under reduced pressure.

1-Phenyl-1*H*-imidazole (**1c**)[33] was obtained as light yellow oil liquid in 60% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (s, Ar−H, 1H), 7.52−7.45 (m, Ar−H, 2H), 7.42−7.34 (m, Ar−H, 3H), 7.29 (s, Ar−H, 1H), 7.21 (s, Ar−H, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.3, 135.5, 130.2, 129.9, 127.5, 121.5, 118.3.

2-Methyl-1-phenyl-1*H*-imidazole (**1d**)[34] was obtained as light yellow oil liquid in 54% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51−7.44 (m, Ar−H, 2H), 7.43 (dd, J = 5.0, 3.7 Hz, Ar−H, 1H), 7.30−7.28 (m, Ar−H, 1H), 7.28−7.27 (m, Ar−H, 1H), 7.01 (dd, J = 7.6, 1.4 Hz, Ar−H, 2H), 2.36 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.6, 138.0, 129.4, 128.1, 127.6, 125.5, 120.6, 13.7.

General Procedures for Direct Arylation Promoted by Palladium Complexes. The direct arylation reactions were carried out with no need of special inert and anhydrous atmosphere. (Hetero)Aryl bromide (1.0 mmol), azoles (2.0 mmol), Pd-PEPPSI complexes (0.05−0.5 mol %), base (2 mmol), acid additive (0.3 mmol), and 4 mL of solvent were added into a parallel reactor. After stirring at 130 °C for 12 h, the mixture was cooled to room temperature. Then, 25 mL of water and 20 mL of dichloromethane were added into the reactor, and the mixture was stirred for minutes, followed by extraction twice with dichloromethane (2 × 5 mL). The organic layer was combined, dried with anhydrous sodium sulfate, and filtered. The remaining product was concentrated and purified by silica-gel column chromatography using methanol/dichloromethane (1/15) as eluent. The isolated yield of product was obtained based on the amount of (hetero)aryl bromide.

5-(4-Chlorophenyl)-1-methyl-1H-imidazole (***3a***).[5j] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (s, Ar−H, 1H), 7.45−7.37 (m, Ar−H, 2H), 7.35−7.30 (m, Ar−H, 2H), 7.09 (s, Ar−H, 1H), 3.65 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 139.2, 133.7, 132.1, 129.5, 128.8, 128.1, 128.1, 32.4.

5-(3-Fluorophenyl)-1-methyl-1H-imidazole (***3b***). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (s, Ar−H, 1H), 7.38 (dd, J = 16.0, 4.0 Hz, Ar−H, 1H), 7.19−7.00 (m, Ar−H, 4H), 3.67 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.9 (d, J = 246.0 Hz), 139.4, 132.2, 131.7 (d, J = 8.0 Hz), 130.3 (d, J = 9.0 Hz), 128.3, 124.0 (d, J = 3.0 Hz), 115.2 (d, J = 22.0 Hz), 114.8 (d, J = 20.0 Hz), 32.6. EI-MS. m/z: 176.2, [**3b**]$^+$ ($C_{10}H_9FN_2^+$, calcd 176.1).

5-(2-Fluorophenyl)-1-methyl-1H-imidazole (***3c***).[35] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (s, Ar−H, 1H), 7.38−7.27 (m, Ar−H, 2H), 7.20−7.08 (m, Ar−H, 2H), 7.06 (s, Ar−H, 1H), 3.54 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 160.9 (d, J = 246.0 Hz), 138.9, 131.7 (d, J = 3.0 Hz), 130.3 (d, J = 8.0 Hz), 129.1, 127.5, 124.3 (d, J = 4.0 Hz), 117.5 (d, J = 16.0 Hz), 115.9 (d, J = 22.0 Hz), 32.0 (d, J = 5.1 Hz).

4-(1-Methyl-1H-imidazol-5-yl)benzonitrile (***3d***).[5k] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71 (d, J = 8.5 Hz, Ar−H, 2H), 7.55 (s, Ar−H, 1H), 7.51 (d, J = 8.5 Hz, Ar−H, 2H), 7.18 (s, CH$_3$, 1H), 3.71 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 140.4, 134.3, 132.5, 131.6, 129.7, 128.2, 118.5, 111.1, 32.8.

1-Methyl-5-(4-nitrophenyl)-1H-imidazole (***3e***).[36] ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.31 (d, J = 8.9 Hz, Ar−H, 2H), 7.63−7.54 (m, Ar−H, 3H), 7.27 (s, Ar−H, 1H), 3.76 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 146.9, 140.8, 136.3, 131.4, 130.3, 128.3, 124.2, 33.0.

4-(1-Methyl-1H-imidazol-5-yl)benzaldehyde (***3f***).[13a] ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.99 (d, J = 4.8 Hz, CHO, 1H), 7.97−7.83 (m, Ar−H, 2H), 7.59−7.47 (m, Ar−H, 3H), 7.18 (d, J = 4.2 Hz, Ar−H, 1H), 3.70 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.3, 140.3, 135.6, 135.1, 132.1, 130.0, 129.6, 128.1, 32.8.

1-(4-(1-Methyl-1H-imidazol-5-yl)phenyl)ethanone (***3g***).[37] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 8.2 Hz, Ar−H, 2H), 7.51 (s, Ar−H, 1H), 7.46 (d, J = 8.2 Hz, Ar−H, 2H), 7.16 (s, Ar−H, 1H), 3.69 (s, C(O)CH$_3$, 3H), 2.58 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 197.3, 140.0, 135.9, 134.3, 132.3 129.2, 128.7, 127.8, 32.7, 26.5.

1-Methyl-5-(naphthalen-1-yl)-1H-imidazole (***3h***).[38] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98−7.87 (m, Ar−H, 2H), 7.65 (d, J = 8.7 Hz, Ar−H, 2H), 7.56−7.41 (m, Ar−H, 4H), 7.15 (s, Ar−H, 1H), 3.40 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.4, 133.6, 132.9, 131.1, 129.4, 129.2, 129.0, 128.3, 127.2, 126.7, 126.1, 125.4, 125.2, 31.9.

1-Methyl-5-phenyl-1H-imidazole (***3i***).[39] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 (s, Ar−H, 1H), 7.46−7.33 (m, Ar−H, 5H), 7.09 (s, Ar−H, 1H), 3.66 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 139.0, 133.4, 129.7, 128.7, 128.4, 127.9, 127.8, 32.5.

1-Methyl-5-(p-tolyl)-1H-imidazole (***3j***).[40] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (s, Ar−H, 1H), 7.29 (d, J = 8.3 Hz, Ar−H, 2H), 7.25 (d, J = 8.1 Hz, Ar−H, 2H), 7.07 (s, Ar−H, 1H), 3.65 (s, Ar−H, 3H), 2.40 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.8, 137.8, 133.4, 129.4, 128.4, 127.8, 126.9, 32.4, 21.2.

5-(4-Methoxyphenyl)-1-methyl-1H-imidazole (***3k***).[40] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 (s, Ar−H, 1H), 7.32 (d, J = 8.8 Hz, Ar−H, 2H), 7.03 (s, Ar−H, 1H), 6.98 (d, J = 8.8 Hz, Ar−H, 2H), 3.85 (s, OCH$_3$, 3H), 3.62 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.4, 138.6, 133.2, 129.9, 127.6, 122.2, 114.1, 55.3, 32.3.

1-Methyl-5-(thiophen-2-yl)-1H-imidazole (***3l***).[41] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (s, Ar−H, 1H), 7.36 (dd, J = 4.9, 1.1 Hz, Ar−H,

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1H), 7.17 (s, Ar−H, 1H), 7.13−7.05 (m, Ar−H, 2H), 3.71 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 130.4, 129.0, 127.6, 126.7, 126.2, 126.0, 32.6.

*1-Methyl-5-(5-methylthiophen-2-yl)-1H-imidazole (**3m**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, Ar−H, 1H), 7.15 (s, Ar−H, 1H), 6.86 (d, J = 3.5 Hz, Ar−H, 1H), 6.77−6.72 (m, Ar−H, 1H), 3.69 (s, CH_3, 3H), 2.51 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 138.8, 128.5, 127.9, 126.9, 126.1, 125.6, 32.4, 15.1. ESI-MS m/z: 178.2, $[\mathbf{3m}]^+$ ($C_9H_{10}N_2S^+$, calcd 178.1).

*3-(1-Methyl-1H-imidazol-5-yl)pyridine (**3n**).*[42] ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 2.2, 0.7 Hz, Ar−H, 1H), 8.62 (dd, J = 4.9, 1.6 Hz, Ar−H, 1H), 7.75−7.69 (m, Ar−H, 1H), 7.58 (s, Ar−H, 1H), 7.41−7.35 (m, Ar−H, 1H), 7.18 (s, Ar−H, 1H), 3.69 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 139.7, 135.3, 129.7, 128.8, 125.7, 123.4, 123.3, 32.4.

*2-Methyl-5-(1-methyl-1H-imidazol-5-yl)pyridine (**3o**).* ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 1.5 Hz, Ar−H, 1H), 7.62−7.46 (m, Ar−H, 2H), 7.19 (d, J = 8.0 Hz, Ar−H, 1H), 7.07 (s, Ar−H, 1H), 3.62 (s, CH_3, 3H), 2.55 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 148.2, 139.5, 136.0, 130.0, 128.5, 123.1, 122.8, 32.4, 24.1. ESI-MS m/z: 173.3, $[\mathbf{3o}]^+$ ($C_{10}H_{11}N_3^+$, calcd 173.1).

*2-Chloro-5-(1-methyl-1H-imidazol-5-yl)pyridine (**3p**).*[30] ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, J = 2.5, 0.6 Hz, Ar−H, 1H), 7.61 (dd, J = 8.3, 2.5 Hz, Ar−H, 1H), 7.50 (s, Ar−H, 1H), 7.33 (dd, J = 8.3, 0.7 Hz, Ar−H, 1H), 7.07 (d, J = 1.0 Hz, Ar−H, 1H), 3.61 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 148.3, 140.0, 138.0, 129.0 128.5, 124.6, 124.1, 32.4.

*5-(1-Methyl-1H-imidazol-5-yl)pyrimidine (**3q**).*[40] ^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, Ar−H, 1H), 8.78 (s, Ar−H, 2H), 7.59 (s, Ar−H, 1H), 7.23 (s, CH_3, 1H), 3.70 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 155.3, 140.6, 129.9, 126.4, 124.4, 32.6.

*4-(1-Methyl-1H-imidazol-5-yl)isoquinoline (**3r**).*[43] ^1H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, Ar−H, 1H), 8.47 (s, Ar−H, 1H), 8.06 (d, J = 8.0 Hz, Ar−H, 1H), 7.77−7.63 (m, Ar−H, 4H), 7.21 (s, Ar−H, 1H), 3.47 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 144.4, 139.2, 135.3, 131.3, 130.4, 128.3, 128.0, 127.7, 124.4, 121.0, 32.1.

*4-(1-Methyl-1H-imidazol-5-yl)quinolone (**3s**).* ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 4.4 Hz, Ar−H, 1H), 8.19 (d, J = 8.4 Hz, Ar−H, 1H), 7.82−7.74 (m, Ar−H, 2H), 7.69 (s, Ar−H, 1H), 7.60−7.54 (m, Ar−H, 1H), 7.34 (d, J = 4.4 Hz, Ar−H, 1H), 7.26 (s, Ar−H, 1H), 3.52 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 148.6, 139.7, 136.0, 130.6, 130.0, 129.9, 128.6, 127.4, 127.4, 125.4, 122.5, 32.4. ESI-MS. m/z: 209.3, $[\mathbf{3s}]^+$ ($C_{13}H_{11}N_3^+$, calcd 209.1).

*3-(1-Methyl-1H-imidazol-5-yl)quinolone (**3t**).*[36] ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 2.3 Hz, Ar−H, 1H), 8.15−8.08 (m, Ar−H, 2H), 7.83 (dd, J = 8.1, 1.3 Hz, Ar−H, 1H), 7.76−7.69 (m, Ar−H, 1H), 7.62−7.55 (m, Ar−H, 2H), 7.25 (d, J = 0.8 Hz, Ar−H, 1H), 3.73 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 147.2, 139.9, 134.3, 129.9, 129.4, 129.2, 127.8, 127.5, 127.3, 123.0, 120.0, 32.6.

*1,2-Dimethyl-5-(4-nitrophenyl)-1H-imidazole (**4e**).*[36] ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.9 Hz, Ar−H, 2H), 7.53 (d, J = 8.9 Hz, Ar−H, 2H), 7.12 (s, Ar−H, 1H), 3.61 (s, CH_3, 3H), 2.48 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 146.4, 136.9, 131.4, 128.2, 128.0, 124.0, 31.7, 13.6.

*4-(1,2-Dimethyl-1H-imidazol-5-yl)benzaldehyde (**4f**).*[13a] ^1H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, CHO, 1H), 7.95−7.82 (m, Ar−H, 2H), 7.50 (d, J = 8.2 Hz, Ar−H, 2H), 7.05 (s, Ar−H, 1H), 3.57 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 147.4, 136.3, 134.9, 132.3, 130.1, 128.1, 127.5, 31.7, 13.6.

*1,2-Dimethyl-5-(p-tolyl)-1H-imidazole (**4j**).*[40] ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, Ar−H, 4H), 6.91 (s, Ar−H, 1H), 3.49 (s, CH_3, 3H), 2.43 (s, CH_3, 3H), 2.38 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 137.5, 133.5, 129.3, 128.5, 127.6, 125.5, 31.2, 21.2, 13.7.

*5-(1,2-Dimethyl-1H-imidazol-5-yl)-2-methoxypyridine (**4k**).* ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 2.4, 0.6 Hz, Ar−H, 1H), 7.51 (dd, J = 8.5, 2.5 Hz, Ar−H, 1H), 6.88 (s, Ar−H, 1H), 6.78 (dd, J = 8.5, 0.7 Hz, Ar−H, 1H), 3.93 (s, OCH_3, 3H), 3.45 (s, CH_3, 3H), 2.41 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 146.5, 146.1, 139.0, 129.9, 125.9, 119.6, 110.8, 53.5, 31.0, 13.6. ESI-MS m/z: 203.3, $[\mathbf{4k}]^+$ ($C_{11}H_{13}N_3O^+$, calcd 203.1).

*1,2-Dimethyl-5-(thiophen-2-yl)-1H-imidazole (**4l**).*[36] ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 5.2, 1.2 Hz, Ar−H, 1H), 7.07 (dd, J = 5.2, 3.6 Hz, Ar−H, 1H), 7.02−6.99 (m, Ar−H, 2H), 3.54 (s, CH_3, 3H), 2.41 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 131.3, 127.4, 127.1, 126.2, 125.7, 124.6, 31.1, 13.6.

*1,2-Dimethyl-5-(5-methylthiophen-2-yl)-1H-imidazole (**4m**).* ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, Ar−H, 1H), 6.81 (d, J = 3.5 Hz, Ar−H, 1H), 6.75−6.72 (m, Ar−H, 1H), 3.54 (s, N−CH_3, 3H), 2.50 (s, CH_3, 3H), 2.42 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 140.6, 128.9, 126.8, 126.7, 126.4, 125.6, 31.1, 15.2, 13.6. ESI-MS m/z: 192.1, $[\mathbf{4m}]^+$ ($C_{10}H_{12}N_2S^+$, calcd 192.1).

*3-(1,2-Dimethyl-1H-imidazol-5-yl)pyridine (**4n**).*[5f] ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, J = 2.2, 0.8 Hz, Ar−H, 1H), 8.59 (dd, J = 4.9, 1.6 Hz, Ar−H, 1H), 7.69−7.64 (m, Ar−H, 1H), 7.39−7.33 (m, Ar−H, 1H), 7.01 (s, Ar−H, 1H), 3.53 (s, CH_3, 3H), 2.46 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.7, 146.9, 135.6, 129.9, 126.7, 126.5, 123.4, 31.3, 13.5.

*5-(1,2-Dimethyl-1H-imidazol-5-yl)-2-methylpyridine (**4o**).* ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 2.0 Hz, Ar−H, 1H), 7.51 (dd, J = 8.0, 2.3 Hz, Ar−H, 1H), 7.18 (d, J = 8.0 Hz, Ar−H, 1H), 6.93 (s, Ar−H, 1H), 3.47 (s, CH_3, 3H), 2.55 (s, CH_3, 3H), 2.40 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 148.4, 146.5, 136.1, 130.0, 126.5, 123.6, 123.0, 31.2, 24.1, 13.6. ESI-MS m/z: 187.3, $[\mathbf{4o}]^+$ ($C_{11}H_{13}N_3^+$, calcd 187.1).

*2-Chloro-5-(1,2-dimethyl-1H-imidazol-5-yl)pyridine (**4p**).* ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.3 Hz, Ar−H, 1H), 7.61 (dd, J = 8.2, 2.5 Hz, Ar−H, 1H), 7.37 (d, J = 8.2 Hz, Ar−H, 1H), 6.99 (s, Ar−H, 1H), 3.50 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 148.6, 147.3, 138.2, 128.7, 127.3, 125.6, 124.2, 31.3, 13.6. ESI-MS m/z: 207.2, $[\mathbf{4p}]^+$ ($C_{10}H_{10}ClN_3^+$, calcd 207.1).

*5-(1,2-Dimethyl-1H-imidazol-5-yl)pyrimidine (**4q**).*[40] ^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, Ar−H, 1H), 8.75 (s, Ar−H, 2H), 7.08 (s, Ar−H, 1H), 3.56 (s, CH_3, 3H), 2.46 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 155.5, 148.0, 128.0, 126.4, 125.1, 31.5 13.7.

*4-(1,2-dimethyl-1H-imidazol-5-yl)isoquinoline (**4r**).*[40] ^1H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, Ar−H, 1H), 8.44 (s, Ar−H, 1H), 8.08−7.98 (m, Ar−H, 1H), 7.73−7.60 (m, Ar−H, 3H), 7.06 (s, Ar−H, 1H), 3.30 (s, CH_3, 3H), 2.49 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 144.4, 135.3, 131.1, 130.8, 128.7, 128.2, 128.2, 128.0, 127.6, 124.5, 121.8, 31.1, 13.6.

*4-(1,2-Dimethyl-1H-imidazol-5-yl)quinolone (**4s**).* ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 4.4 Hz, Ar−H, 1H), 8.17 (d, J = 8.4 Hz, Ar−H, 1H), 7.83 (d, J = 8.4 Hz, Ar−H, 1H), 7.79−7.72 (m, Ar−H, 1H), 7.59−7.51 (m, Ar−H, 1H), 7.30 (d, J = 4.4 Hz, Ar−H, 1H), 7.11 (s, Ar−H, 1H), 3.38 (s, CH_3, 3H), 2.52 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 148.6, 147.0, 136.6, 130.0, 129.8, 128.6, 128.5, 127.3, 127.2, 125.5, 122.3, 31.5, 13.7. ESI-MS m/z: 223.3, $[\mathbf{4s}]^+$ ($C_{14}H_{13}N_3^+$, calcd 223.1).

*3-(1,2-Dimethyl-1H-imidazol-5-yl)quinolone (**4t**).*[5g] ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 2.2 Hz, Ar−H, 1H), 8.10 (dd, J = 10.0, 5.4 Hz, Ar−H, 2H), 7.83 (d, J = 8.3 Hz, Ar−H, 1H), 7.75−7.65 (m, Ar−H, 1H), 7.63−7.52 (m, Ar−H, 1H), 7.11 (s, Ar−H, 1H), 3.59 (s, CH_3, 3H), 2.47 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 147.1, 134.3, 130.2, 129.7, 129.2, 127.8, 127.6, 127.3, 127.3, 126.8, 123.8, 31.5, 13.7.

*5-(3,5-Bis(trifluoromethyl)phenyl)-1,2-dimethyl-1H-imidazole (**4u**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, Ar−H, 1H), 7.78 (s, Ar−H, 2H), 7.08 (s, Ar−H, 1H), 3.56 (s, CH_3, 3H), 2.46 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 132.7, 132.4, 132.0, 131.7, 130.7, 128.0 (t, J = 5.1 Hz), 127.1 (q, J = 272.7 Hz), 121.1 (q, J = 4 Hz), 31.4, 13.7. ESI-MS m/z: 308.3, $[\mathbf{4u}]^+$ ($C_{13}H_{10}F_6N_2^+$, calcd 308.1).

*5-(1,2-Dimethyl-1H-imidazol-5-yl)-2-fluoropyridine (**4v**).* ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 2.4 Hz, Ar−H, 1H), 7.78−7.70 (m, Ar−H, 1H), 6.99 (dd, J = 8.4, 3.0 Hz, Ar−H, 1H), 6.95 (s, Ar−H, 1H), 3.48 (s, CH_3, 3H), 2.42 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (d, J = 240.7 Hz), 147.0, 146.9 (d, J = 3.9 Hz), 141.2 (d, J = 8.1 Hz), 128.7, 126.9, 124.6 (d, J = 4.7 Hz), 109.8 (d, J = 37.6 Hz), 31.2, 13.6. ESI-MS m/z: 191.2, $[\mathbf{4v}]^+$ ($C_{10}H_{10}FN_3^+$, calcd 191.1).

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*5-(3-Fluorophenyl)-1-phenyl-1H-imidazole (**5b**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, Ar−H, 1H), 7.49−7.35 (m, Ar−H, 3H), 7.29 (s, Ar−H, 1H), 7.25−7.10 (m, Ar−H, 3H), 6.99−6.86 (m, Ar−H, 2H), 6.86−6.78 (m, Ar−H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J = 246.1 Hz), 139.3, 136.3, 131.8, 131.4 (d, J = 8.5 Hz), 130.0 (d, J = 8.6 Hz), 129.6, 129.4, 128.4, 125.6, 123.6 (d, J = 2.9 Hz), 114.8 (d, J = 22.8 Hz), 114.3 (d, J = 21.1 Hz). ESI-MS m/z: 238.3, [**5b**]$^+$ ($C_{15}H_{11}FN_2^+$, calcd 238.1).

*5-(4-Nitrophenyl)-1-phenyl-1H-imidazole (**5e**).*[44] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.07 (m, Ar−H, 2H), 7.77 (s, Ar−H, 1H), 7.50−7.42 (m, Ar−H, 4H), 7.29−7.27 (m, Ar−H, 1H), 7.26 (s, Ar−H, 1H), 7.23−7.18 (m, Ar−H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 140.5, 136.0, 135.8, 131.1, 131.0, 129.9, 128.9, 127.9, 125.6, 123.9.

*3-(1-Phenyl-1H-imidazol-5-yl)pyridine (**5h**).*[45] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49−8.43 (m, Ar−H, 2H), 7.75 (d, J = 0.6 Hz, Ar−H, 1H), 7.44−7.38 (m, Ar−H, 3H), 7.38−7.32 (m, Ar−H, 2H), 7.22−7.14 (m, Ar−H, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 148.5, 139.6, 136.0, 135.0, 129.7, 129.6, 128.6, 125.6, 123.1.

*2-Methyl-5-(1-phenyl-1H-imidazol-5-yl)pyridine (**5o**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 2.0 Hz, Ar−H, 1H), 7.73 (s, Ar−H, 1H), 7.41 (dd, J = 5.2, 2.0 Hz, Ar−H, 3H), 7.30 (s, Ar−H, 1H), 7.28−7.26 (m, Ar−H, 1H), 7.21−7.16 (m, Ar−H, 2H), 7.03 (d, J = 8.1 Hz, Ar−H, 1H), 2.52 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 148.0, 139.4, 136.2, 135.5, 129.9, 129.7, 129.3, 128.5, 125.7, 122.8, 122.7, 24.2. ESI-MS m/z: 235.4, [**5o**]$^+$ ($C_{15}H_{13}N_3^+$, calcd 235.1).

*4-(1-Phenyl-1H-imidazol-5-yl)quinolone (**5s**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 4.5 Hz, Ar−H, 1H), 8.16−8.08 (m, Ar−H, 1H), 8.03 (dd, J = 8.5, 0.8 Hz, Ar−H, 1H), 7.91 (d, J = 0.9 Hz, Ar−H, 1H), 7.76−7.65 (m, Ar−H, 1H), 7.55−7.41 (m, Ar−H, 2H), 7.31−7.26 (m, Ar−H, 3H), 7.12−7.05 (m, Ar−H, 2H), 7.00 (d, J = 4.5 Hz, Ar−H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 148.6, 139.3, 135.9, 135.5, 132.3, 129.8, 129.6, 129.5, 128.2, 127.9, 127.0, 126.7, 125.4, 124.7, 122.2. ESI-MS m/z: 271.3, [**5s**]$^+$ ($C_{18}H_{13}N_3^+$, calcd 271.1).

*5-(2-Fluorophenyl)-2-methyl-1-phenyl-1H-imidazole (**6c**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, Ar−H, 3H), 7.17−7.09 (m, Ar−H, 4H), 7.04−6.98 (m, Ar−H, 1H), 6.97−6.88 (m, Ar−H, 2H), 2.31 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, J = 248.8 Hz), 146.5, 136.8, 130.9 (d, J = 2.7 Hz), 129.2 (d, J = 8.1 Hz), 129.1, 128.4 (d, J = 3.5 Hz), 128.3, 127.3, 127.2, 123.7 (d, J = 3.7 Hz), 118.2 (d, J = 14.8 Hz), 115.7 (d, J = 22.1 Hz), 14.1. ESI-MS m/z: 252.3, [**6c**]$^+$ ($C_{16}H_{13}FN_2^+$, calcd 252.1).

*2-Fluoro-5-(2-methyl-1-phenyl-1H-imidazol-5-yl)pyridine (**6v**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 2.2 Hz, Ar−H, 1H), 7.45 (dd, J = 5.1, 1.8 Hz, Ar−H, 3H), 7.41−7.35 (m, Ar−H, 1H), 7.19 (s, Ar−H, 1H), 7.17−7.11 (m, Ar−H, 2H), 6.75 (dd, J = 8.5, 2.9 Hz, Ar−H, 1H), 2.31 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (d, J = 240.2 Hz), 147.5, 146.2 (d, J = 14.9 Hz), 139.9 (d, J = 8.0 Hz), 136.3, 130.9, 129.8, 129.1, 127.6, 127.3, 124.4 (d, J = 4.8 Hz), 109.4 (d, J = 37.6 Hz), 14.1. ESI-MS m/z: 253.3, [**6v**]$^+$ ($C_{15}H_{12}FN_3^+$, calcd 253.1).

*5-(4-Chlorophenyl)-4-methylthiazole (**7a**).*[23b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, Ar−H, 1H), 7.41−7.32 (m, Ar−H, 4H), 2.50 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 148.8, 133.9, 130.6, 130.4, 130.3, 128.9, 16.0.

*4-(4-Methylthiazol-5-yl)benzonitrile (**7d**).*[46] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, Ar−H, 1H), 7.73−7.68 (m, Ar−H, 2H), 7.58−7.52 (m, Ar−H, 2H), 2.55 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 150.0, 136.8, 132.4, 130.0, 129.7, 118.4, 111.4, 16.3.

*4-(4-Methylthiazol-5-yl)benzaldehyde (**7f**).*[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, C*H*O, 1H), 8.74 (s, Ar−H, 1H), 7.95−7.90 (m, Ar−H, 2H), 7.64−7.58 (m, Ar−H, 2H), 2.57 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 151.4, 149.8, 138.2, 135.3, 130.7, 130.0, 129.6, 16.4.

*1-(4-(4-Methylthiazol-5-yl)phenyl)ethanone (**7g**).*[16b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, Ar−H, 1H), 8.02−7.92 (m, Ar−H, 2H), 7.54−7.46 (m, Ar−H, 2H), 2.59 (s, C(O)CH_3, 3H), 2.53 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 151.1, 149.4, 136.7, 136.0, 130.7, 129.1, 128.6, 26.5, 16.2.

*4-Methyl-5-(p-tolyl)thiazole (**7j**).*[47] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, Ar−H, 1H), 7.36−7.30 (m, Ar−H, 2H), 7.25−7.20 (m, Ar−H, 2H), 2.53 (s, CH_3, 3H), 2.39 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 148.1, 137.8, 131.9, 129.3, 129.1, 128.9, 21.1, 16.0.

*2-Methyl-5-(naphthalen-1-yl)thiazole (**8h**).*[16b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.12 (m, Ar−H, 1H), 7.92−7.84 (m, Ar−H, 2H), 7.74 (s, Ar−H, 1H), 7.56−7.44 (m, Ar−H, 4H), 2.80 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 141.0, 135.6, 133.6, 131.8, 128.7, 128.7, 128.4, 128.3, 126.6, 126.0, 125.1, 125.1, 19.1.

*2-Methyl-5-(quinolin-4-yl)thiazole (**8s**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 4.4 Hz, Ar−H, 1H), 8.21−8.10 (m, Ar−H, 2H), 7.83 (s, Ar−H, 1H), 7.78−7.68 (m, Ar−H, 1H), 7.62−7.50 (m, Ar−H, 1H), 7.38 (d, J = 4.4 Hz, Ar−H, 1H), 2.80 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 149.7, 148.6, 142.1, 137.6, 133.0 130.0, 129.7, 127.3, 126.3, 124.9, 121.9, 19.2. ESI-MS m/z: 226.0, [**8s**]$^+$ ($C_{13}H_{10}N_2S^+$, calcd 226.1).

*2,4-Dimethyl-5-(thiophen-2-yl)thiazole (**9l**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 5.0, 1.3 Hz, Ar−H, 1H), 7.06−7.00 (m, Ar−H, 2H), 2.63 (s, CH_3, 3H), 2.50 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 147.6, 133.6, 127.4, 126.5, 125.5, 124.8, 18.9, 16.3. ESI-MS m/z: 195.1, [**9l**]$^+$ ($C_9H_9NS_2^+$, calcd 195.0).

*2,4-Dimethyl-5-(pyridin-3-yl)thiazole (**9n**).*[48] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 1.8 Hz, Ar−H, 1H), 8.55 (dd, J = 4.8, 1.5 Hz, Ar−H, 1H), 7.73−7.67 (m, Ar−H, 1H), 7.37−7.30 (m, Ar−H, 1H), 2.69 (s, CH_3, 3H), 2.45 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 149.4, 148.4, 148.2, 136.0, 128.4, 127.2, 123.2, 19.0, 15.8.

*4-(2-Methyl-4-phenylthiazol-5-yl)benzonitrile (**10d**).*[23b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.52 (m, Ar−H, 2H), 7.47−7.42 (m, Ar−H, 2H), 7.40−7.36 (m, Ar−H, 2H), 7.32−7.27 (m, Ar−H, 3H), 2.75 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 150.9, 136.8, 134.0, 132.1, 130.0, 129.7, 128.8, 128.3, 128.1, 118.2, 111.0, 19.1.

*2-Methyl-4-phenyl-5-(pyridin-3-yl)thiazole (**10n**).*[48] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, Ar−H, 1H), 8.51 (dd, J = 4.8, 1.6 Hz, Ar−H, 1H), 7.63−7.54 (m, Ar−H, 1H), 7.51−7.42 (m, Ar−H, 2H), 7.34−7.24 (m, Ar−H, 3H), 7.23−7.16 (m, Ar−H, 1H), 2.76 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 150.8, 149.8, 148.7, 136.4, 134.1, 128.8, 128.4, 128.4, 128.1, 127.9, 123.2, 19.1.

*4-(4-Chlorophenyl)-3,5-dimethylisoxazole (**11a**).*[49] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.36 (m, Ar−H, 2H), 7.21−7.14 (m, Ar−H, 2H), 2.38 (s, CH_3, 3H), 2.24 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 158.4, 133.5, 130.3, 129.0, 128.8, 115.6, 11.5, 10.7.

*3,5-Dimethyl-4-(pyridin-3-yl)isoxazole (**11n**).*[50] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, J = 4.8, 1.5 Hz, Ar−H, 1H), 8.48 (s, Ar−H, 1H), 7.59−7.51 (m, Ar−H, 1H), 7.38−7.30 (m, Ar−H, 1H), 2.36 (s, CH_3, 3H), 2.21 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 158.3, 149.6, 148.6, 136.2, 126.4, 123.5, 113.3, 11.4, 10.5.

*3,5-Dimethyl-4-(6-methylpyridin-3-yl)isoxazole (**11o**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, Ar−H, 1H), 7.48−7.41 (m, Ar−H, 1H), 7.21 (d, J = 8.0 Hz, Ar−H, 1H), 2.56 (s, CH_3, 3H), 2.37 (s, CH_3, 3H), 2.22 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 158.5, 157.6, 148.9, 136.6, 123.4, 123.2, 113.3, 24.1, 11.4, 10.6. ESI-MS m/z: 188.1, [**11o**]$^+$ ($C_{11}H_{12}N_2O^+$, calcd 188.1).

*4-(6-Chloropyridin-3-yl)-3,5-dimethylisoxazole (**11p**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, Ar−H, 1H), 7.62−7.55 (m, Ar−H, 1H), 7.44 (d, J = 8.2 Hz, Ar−H, 1H), 2.43 (s, CH_3, 3H), 2.28 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 158.2, 150.6, 149.5, 138.9, 125.4, 124.4, 112.3, 11.5, 10.6. ESI-MS m/z: 208.0, [**11p**]$^+$ ($C_{10}H_9ClN_2O^+$, calcd 208.0).

*3,5-Dimethyl-4-(quinolin-4-yl)isoxazole (**11s**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 4.4 Hz, Ar−H, 1H), 8.15 (d, J = 8.4 Hz, Ar−H, 1H), 7.75−7.67 (m, Ar−H, 1H), 7.61−7.48 (m, Ar−H, 2H), 7.22 (d, J = 4.3 Hz, Ar−H, 1H), 2.25 (s, CH_3, 3H), 2.08 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 159.0, 149.9, 148.5, 136.7, 130.0, 129.7, 127.1, 127.0, 124.9, 122.6, 112.9, 11.5, 10.4. ESI-MS m/z: 224.1, [**11s**]$^+$ ($C_{14}H_{12}N_2O^+$, calcd 224.1).

*3,5-Dimethyl-4-(quinolin-3-yl)isoxazole (**11t**).*[50] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, Ar−H, 1H), 8.13 (d, J = 8.5 Hz, Ar−H, 1H), 8.03 (s, Ar−H, 1H), 7.85 (d, J = 8.1 Hz, Ar−H, 1H), 7.80−7.71 (m, Ar−H, 1H), 7.64−7.56 (m, Ar−H, 1H), 2.47 (s, CH_3, 3H), 2.32 (s,

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CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 158.6, 150.6, 147.2, 135.6, 129.9, 129.3, 127.7, 127.6, 127.3, 123.7, 113.6, 11.6, 10.8.

4-Bromo-5-(4-chlorophenyl)-1-methyl-1H-pyrazole (**12a**). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, Ar−H, 1H), 7.50−7.48 (m, Ar−H, 1H), 7.48−7.46 (m, Ar−H, 1H), 7.37−7.34 (m, Ar−H, 1H), 7.34−7.32 (m, Ar−H, 1H), 3.80 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 139.3, 135.4, 131.0, 129.0, 126.8, 93.6, 38.3. ESI-MS m/z: 272.0, $[\mathbf{12a}]^+$ ($C_{10}H_8BrClN_2^+$, calcd 270.0).

4-(4-Bromo-1-methylpyrazol-5-yl)benzonitrile (**12d**).[51] ^1H NMR (400 MHz, $CDCl_3$) δ 7.82−7.77 (m, Ar−H, 2H), 7.57−7.53 (m, Ar−H, 3H), 3.83 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 139.2, 132.9, 132.4, 130.4, 118.1, 113.0, 94.1, 38.5.

4-(4-Bromo-1-methylpyrazol-5-yl)benzaldehyde (**12f**).[51] ^1H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, C*H*O, 1H), 8.08−7.97 (m, Ar−H, 2H), 7.60 (d, J = 8.2 Hz, Ar−H, 2H), 7.55 (s, Ar−H, 1H), 3.84 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 139.8, 139.5, 136.3, 134.2, 130.4, 129.8, 94.0, 38.5.

1-(4-(4-Bromo-1-methyl-1H-pyrazol-5-yl)phenyl)ethanone (**12g**). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09−8.03 (m, Ar−H, 2H), 7.55−7.48 (m, Ar−H, 3H), 3.82 (s, C(O)CH_3, 3H), 2.64 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 140.0, 139.4, 137.2, 132.8, 129.9, 128.5, 93.8, 38.4, 26.6. ESI-MS m/z: 280.0, $[\mathbf{12g}]^+$ ($C_{12}H_{11}BrN_2O^+$, calcd 278.0).

3-(4-Bromo-1-methyl-1H-pyrazol-5-yl)pyridine (**12n**).[51] ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 10.5 Hz, Ar−H, 2H), 7.75 (d, J = 7.7 Hz, Ar−H, 1H), 7.55 (s, Ar−H, 1H), 7.44 (s, Ar−H, 1H), 3.83 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 139.4, 137.9, 137.1, 124.7, 123.4, 94.3, 38.4.

5-(4-Chlorophenyl)-1,4-diphenyl-1H-1,2,3-triazole (**13a**).[23b] ^1H NMR (400 MHz, $CDCl_3$) δ 7.63−7.54 (m, Ar−H, 2H), 7.46−7.37 (m, Ar−H, 3H), 7.37−7.27 (m, Ar−H, 7H), 7.17−7.10 (m, Ar−H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 136.3, 135.6, 132.5, 131.4, 130.5, 129.4, 129.3, 129.2, 128.6, 128.1, 127.4, 126.1, 125.2.

4-(1,4-Diphenyl-1H-1,2,3-triazol-5-yl)benzonitrile (**13d**).[23b] ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.54 (m, Ar−H, 2H), 7.48−7.43 (m, Ar−H, 2H), 7.40−7.33 (m, Ar−H, 3H), 7.31−7.27 (m, Ar−H, 3H), 7.25−7.18 (m, Ar−H, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 135.9, 132.7, 132.4, 131.8, 130.8, 130.0, 129.6, 129.5, 128.7, 128.5, 127.6, 125.2, 118.0, 113.2.

3-(1,4-Diphenyl-1H-1,2,3-triazol-5-yl)pyridine (**13n**).[23b] ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, Ar−H, 1H), 8.46 (s, Ar−H, 1H), 7.59−7.49 (m, Ar−H, 3H), 7.45−7.27 (m, Ar−H, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 150.3, 145.6, 137.4, 136.0, 130.5, 130.1, 129.4, 129.4, 128.7, 128.3, 127.4, 125.3, 124.1, 123.6.

1-Benzyl-5-(4-chlorophenyl)-4-phenyl-1H-1,2,3-triazole (**14a**).[52] ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.49 (m, Ar−H, 2H), 7.46−7.34 (m, Ar−H, 2H), 7.33−7.20 (m, Ar−H, 6H), 7.13−6.97 (m, Ar−H, 4H), 5.39 (s, CH_2Ph, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 135.8, 135.1, 132.6, 131.3, 130.5, 129.4, 128.7, 128.4, 128.2, 127.8, 127.3, 126.6, 126.2, 52.0.

4-(1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)benzonitrile (**14d**).[53] ^1H NMR (400 MHz, $CDCl_3$) δ 7.78−7.65 (m, Ar−H, 2H), 7.56−7.44 (m, Ar−H, 2H), 7.37−7.24 (m, Ar−H, 8H), 7.12−6.93 (m, Ar−H, 2H), 5.47 (s, CH_2Ph, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 134.8, 132.8, 132.7, 131.9, 130.8, 130.0, 128.9, 128.6, 128.4, 128.2, 127.2, 126.9, 117.9, 113.6, 52.4.

4-(1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)benzaldehyde (**14f**).[52] ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, C*H*O, 1H), 7.88−7.80 (m, Ar−H, 2H), 7.46−7.39 (m, Ar−H, 2H), 7.29−7.22 (m, Ar−H, 2H), 7.22−7.13 (m, Ar−H, 6H), 6.96−6.89 (m, Ar−H, 2H), 5.38 (s, CH_2Ph, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 145.1, 136.8, 134.9, 134.0, 132.5, 130.8, 130.3, 130.2, 128.8, 128.6, 128.3, 128.1, 127.3, 126.9, 52.4.

3-(1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)pyridine (**14n**).[7b] ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 4.8, 1.7 Hz, Ar−H, 1H), 8.41 (dd, J = 2.2, 0.8 Hz, Ar−H, 1H), 7.55−7.45 (m, Ar−H, 2H), 7.43−7.36 (m, Ar−H, 1H), 7.04−6.96 (m, Ar−H, 1H), 7.29−7.23 (m, Ar−H, 6H), 7.03−6.96 (m, Ar−H, 2H), 5.45 (s, CH_2Ph, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 150.4, 145.7, 137.6, 134.8, 130.4, 130.2, 128.9, 128.6, 128.4, 128.1, 127.3, 126.8, 124.4, 123.7, 52.4.

5-(1-Benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)pyrimidine (**14q**). ^1H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, Ar−H, 1H), 8.38 (s, Ar−H, 2H), 7.45−7.36 (m, Ar−H, 2H), 7.26−7.17 (m, Ar−H, 6H), 6.98−6.89 (m, Ar−H, 2H), 5.43 (s, CH_2Ph, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 157.5, 146.7, 134.4, 129.6, 129.2, 128.9, 128.8, 128.5, 127.2, 127.0, 123.3, 52.8. ESI-MS m/z: 313.2, $[\mathbf{14q}]^+$ ($C_{19}H_{15}N_5^+$, calcd 313.1).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00784.

NMR spectra (PDF)

Accession Codes

CCDC 1561110−1561113 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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