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Pd-PEPPSI Complexes Bearing Bulky [(1,2-Di-(*tert*-butyl)acenaphthyl] (DtBu-An) on *N*-Heterocarbene Backbones: Highly Efficient for Suzuki−Miyaura Cross-Coupling under Aerobic Conditions

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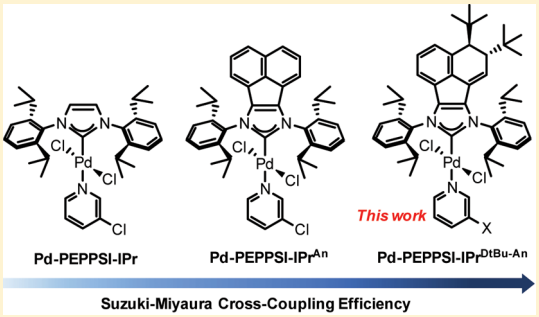
Supporting Information

ABSTRACT: With the goal of achieving highly efficient palladium-catalyzed cross-coupling reactions under mild reaction conditions, the Pd-PEPPSI complexes **C1** and **C2** bearing 1,2-di(*tert*-butyl)acenaphthyl (DtBu-An) backbones were synthesized and characterized, and their use in Suzuki−Miyaura cross-coupling was investigated. The effects of catalyst structure and reaction conditions on the cross-coupling efficiency were evaluated in detail. The significant differences in catalytic activity compared with classical PEPPSI-IPr and PEPPSI-IPr^{An} precatalysts are discussed, where the axial sterics on the backbone play an important role. At low palladium loadings of 0.05−0.1 mol % and upon the addition of the relatively weak base K_3PO_4, the palladium complex **C1** was found to be highly efficient for the coupling of (hetero)aryl chlorides with arylboronic acids under aerobic conditions, affording the corresponding biaryls in excellent yields.

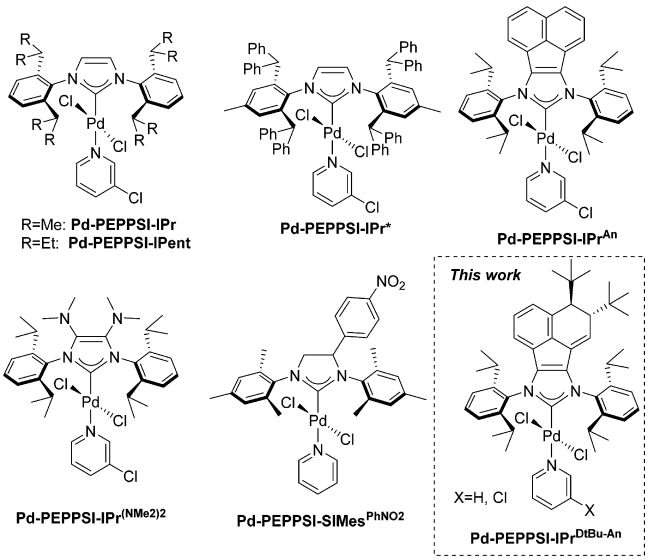


INTRODUCTION

Palladium-catalyzed cross-coupling reactions are now recognized as highly versatile tools for C−C bond formation.[1] In 2010, the Nobel Prize in Chemistry was awarded to Heck,[2] Negishi,[3] and Suzuki[4] for their considerable contributions to the field. Among them, the Suzuki−Miyaura reaction, which involves the cross-coupling of aryl halides with arylboronic acids to construct the respective biaryl structure, has emerged as one of the most valuable synthetic methodologies.[1c,e,4,5] Since the isolation and structural characterization of the first stable free *N*-heterocyclic carbenes (NHCs) by Arduengo in 1991,[6] this class of ligands has been recognized as excellent candidates for palladium-catalyzed cross-coupling reactions.[7] NHCs behave as strong σ-electron donors and are less sensitive to oxidation than alkyl phosphines, leading to greater stability of the precatalysts and the catalytic species. As a result, even sterically hindered substrates have been used as coupling partners with readily available aryl chlorides following these protocols due to the facile cleavage of the carbon−chlorine bond upon employing NHC-Pd species.[8,9]

In view of their increasing popularity in scientific and industrial applications, developing efficient precatalysts with low palladium loadings remains a significant interest.[10] Therefore, considerable effort has been focused on understanding the electronic as well as the steric properties of ligands to guide catalyst design.[11] For PEPPSI (Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation) palladium complexes, it was found that increasing the steric bulk at the *ortho*-position of the *N*-aryl moiety on NHC can benefit the Suzuki−Miyaura reaction.[12] For example, the use of bulky palladium complexes such as Pd-PEPPSI-IPr,[13] particularly in Pd-PEPPSI-IPent[12a] and Pd-PEPPSI-IPr*[12e] precatalysts (Scheme 1), has resulted in significant improvements in

Scheme 1. Bulky Pd-PEPPSI Precatalysts on Backbones and *N*-Aryl Moieties



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catalytic performance.[13] Relative to the extensively studied *N*-aryl moiety, modification of the backbone derived from NHCs has been of less focus and is, therefore, limited in the literature.[14] Nevertheless, this strategy has emerged as a powerful tool because such modification would greatly enhance the steric and electronic ability of the palladium center.[15] Tu revealed that the acenaphthyl-based Pd-PEPPSI-IPr^{An} precatalyst exhibited a much higher efficiency than the classical Pd-PEPPSI-IPr precatalyst.[15a,16] Under a moderate palladium loading of 0.5 mol %, a variety of biaryls including tetra-*ortho*-substituted biaryls can be conveniently synthesized. Moreover, a new type of Pd-PEPPSI-IPr$^{(NMe_2)_2}$ precatalyst developed by César and Lavigne, wherein NMe_2 groups were introduced on the skeleton, showed broad applicability and efficiency toward aryl chlorides in C−N amination.[15f,17] The NHCs-Pd precatalysts were very stable under aerobic conditions; however, their catalytic species Pd(0) was highly air-sensitive,[18] as a low level of dissolved oxygen in commercially available anhydrous solvent would terminate the reaction.[11c] Therefore, most of the NHCs-Pd catalyzed cross-couplings were performed in an environment free of oxygen. Moreover, in these catalytic systems, strong bases (such as KO^{t}Bu, KOH, and NaOH) were indispensable when aryl chlorides were used as substrates, casting limitation on the functional group tolerance.[19] In contrast, relatively weak bases (such as K_3PO_4 and K_2CO_3) generally led to much lower efficiency.[20] Until now, only in rare instances could weaker bases be successfully used in aerobic conditions.[21] An exception is the reaction with Pd-PEPPSI-SIMes^{PhNO_2}, which contained a nitrophenyl group on the backbone (Scheme 1), wherein the catalytic activity was greatly increased.[21d]

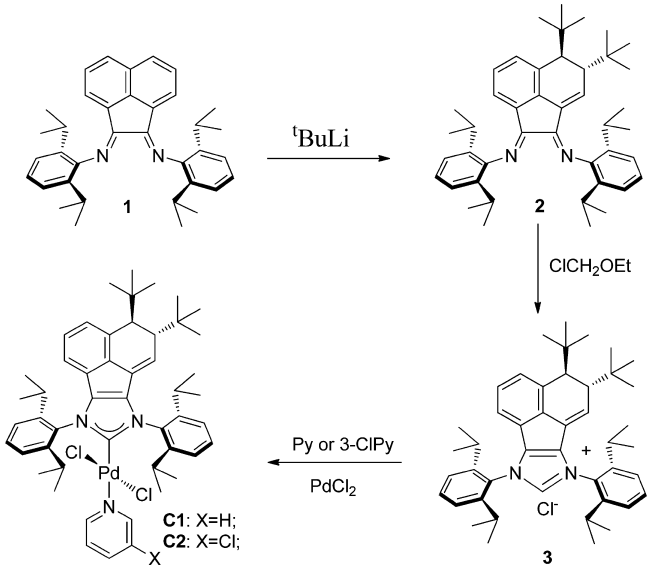
Considering both academic and potential industrial applications, we have focused on the development of highly efficient palladium catalysts that do not necessitate the use of air- and moisture-free techniques.[15o] Taking into account that modifying the backbone is a very useful strategy to elevate the catalytic efficiency, we surmised that bulky substituted acenaphthyl groups combined with sterically hindering *N*-aryl moieties can protect the Pd(0) species effectively. Therefore, a great improvement in the catalytic efficiency could be achieved. Herein, we report the results of 1,2-di(*tert*-butyl)acenaphthyl (DtBu-An)-based Pd-PEPPSI complexes for the Suzuki−Miyaura reaction of aryl chlorides with arylboronic acids using relatively weak bases under aerobic conditions.

RESULTS AND DISCUSSION

Synthesis and Characterization of α-Diimine Palladium Complexes. As an access to bulky Pd-PEPPSI complexes on the backbone, acenaphthyl α-diimine was first synthesized via the acid-catalyzed condensation reaction between acenaphthenequinone and 2,6-diisopropylaniline.[15a] Then, 2 equiv of *tert*-butyllithium was added to a hexane solution of acenaphthyl α-diimine, affording the bulky 1,2-di(*tert*-butyl)acenaphthyl α-diimine, **2**, in high yield (Scheme 2).[22] The desired imidazolium salt of **3** was subsequently obtained by the cyclization of 1,2-di(*tert*-butyl)acenaphthyl α-diimine (**2**) with chloromethyl ethyl ether, giving a moderate yield of 68%. The formation of the NC*H*N bond in the imidazolium salt was confirmed by characteristic signals in the ^{1}H NMR spectrum, in which the resonance of imidazolium C−H protons appeared at δ = 11.71 ppm.

Unlike the synthesis of Pd-PEPPSI-IPr$^{(NMe_2)_2}$, which requires the use of strong bases such as butyllithium (*n*BuLi),[15f] the

Scheme 2. Synthetic Route of Pd-PEPPSI-IPr$^{DtBu-An}$ Complexes



(DtBu-An)-based Pd-PEPPSI complexes in this study were readily prepared from the one-pot reaction between imidazolium salt and $PdCl_2$ in pyridine or 3-chloropyridine. The resulting palladium complexes were purified by silica-gel chromatography in dichloromethane and isolated in satisfactory yields of 73% and 61%, respectively. These two complexes are air- and moisture-stable and were characterized by ^{1}H and ^{13}C NMR. The characteristic signals of Pd−$C_{carbene}$ were observed at δ = 160.6 ppm for **C1** and δ = 159.0 ppm for **C2**, consistent with literature data for Pd-PEPPSI-IPr^{An}.[16]

Single crystals of these synthesized Pd-PEPPSI complexes were obtained by slowly evaporating a concentrated solution of dichloromethane and hexane (v/v = 1/2), and the structures were unambiguously confirmed by X-ray diffraction analysis. Figures 1 and 2 display the molecular structures of **C1** and **C2**, respectively. The palladium complexes are structurally similar, in which palladium is coordinated by two chlorides in a *trans* arrangement, an NHC ligand, and pyridine or 3-chloropyridine as the ancillary ligand in a pseudo-square-planar geometry. The bond lengths lie within the same range as those observed for analogous Pd-PEPPSI complexes.[11] For instance, the lengths of the Pd−$C_{carbene}$ bonds are 1.981(7) Å (for **C1**) and 1.970(6) Å (for **C2**), while those of the Pd−N bonds are 2.090(6) Å (for **C1**) and 2.093(6) Å (for **C2**). Nevertheless, it is noteworthy that the bulky 1,2-di-*tert*-butyl groups on the backbone lie above and below the coordination plane, which retards *N*-aryl rotation. Moreover, the *N*-aryl moiety on NHC is almost perpendicular to the coordination plane, with dihedral angles of 87.60° and 80.00° in **C1** and 86.96° and 82.53° in **C2**. It is reasonable to assume that the steric bulk derived from both the *N*-aryl group and the backbone provides axial protection for the palladium center and is believed to stabilize the Pd(0) species in the process of the catalytic reaction.

Suzuki−Miyaura Cross-Coupling Promoted by Palladium Complexes. The catalytic performance of precatalysts **C1** and **C2** in the Suzuki−Miyaura cross-coupling reaction was then explored. Unless otherwise specified, the reaction was performed under aerobic conditions, and the solvent did not undergo any further purification. We began this study by choosing to examine the coupling between 1-chloro-2-methyl-

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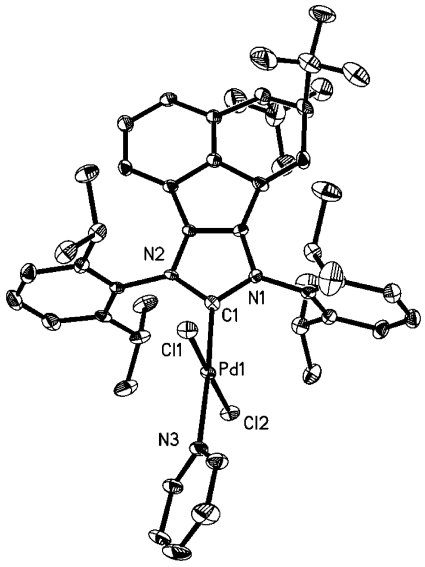

Figure 1. Molecular structure of **C1** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.981(7), Pd(1)−N(3) 2.090(6), Pd(1)−Cl(1) 2.2977(18), Pd(1)−Cl(2) 2.2793(18), N(3)−Pd(1)−C(1) 176.7(3), N(3)−Pd(1)−Cl(1) 90.4(2), C(1)−Pd(1)−Cl(1) 88.97(19), N(3)−Pd(1)−Cl(2) 88.3(2), C(1)−Pd(1)−Cl(2) 92.53(19), Cl(1)−Pd(1)−Cl(2) 177.45(7).

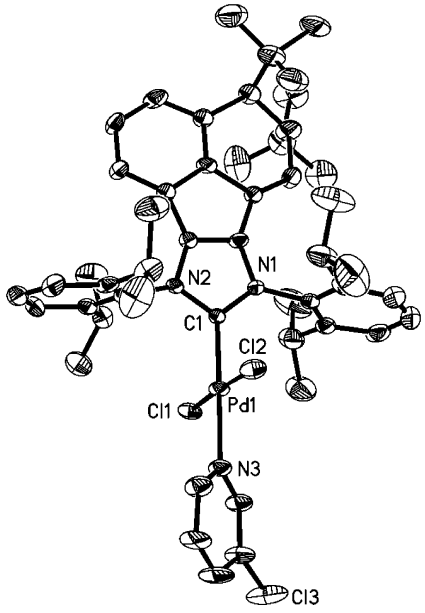

Figure 2. Molecular structure of **C2** depicted with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.970(6), Pd(1)−N(3) 2.093(6), Pd(1)−Cl(1) 2.3223(17), Pd(1)−Cl(2) 2.3054(18), N(3)−Pd(1)−C(1) 178.9(3), N(3)−Pd(1)−Cl(1) 89.55(18), C(1)−Pd(1)−Cl(1) 90.56(18), N(3)−Pd(1)−Cl(2) 87.72(18), C(1)−Pd(1)−Cl(2) 92.21(18), Cl(1)−Pd(1)−Cl(2) 176.86(7).

benzene and phenylboronic acid as a model reaction in the presence of 0.05 mol % **C1**. Initially, a variety of reaction parameters, such as bases and solvents, were screened. As illustrated in Table 1, among the bases screened, the use of K_3PO_4 resulted in near completion, giving quantitative yield of the product (run 2, Table 1). Other bases, such as K_2CO_3, NaOH, KOH, and KO^{t}Bu, were inferior (runs 1, 7−9, Table 1), whereas other bases led to minor yields for this cross-coupling. Considering that K_3PO_4 is readily available, relatively inexpensive, and tolerant toward a variety of functional groups, it was chosen for further study. We next screened the solvents, and a significant acceleration effect was observed when ethanol was used, while THF, MeOH, and *i*PrOH afforded moderate to high yields (runs 13−15, Table 1). Unexpectedly, water, dioxane, and toluene, which are frequently used with NHC-Pd catalytic systems, were totally inactive (runs 10−12, Table 1).

On the basis of the optimized reaction conditions, **C2** was also tested in the cross-coupling reaction for comparison. In a previous report, a chlorine atom at the 3-position of pyridine further favors the dissociation of the Pd(0)−N bond and thereby promotes the oxidation process in the Suzuki−Miyaura reaction.[13] However, in this study, an almost identical result of 98% was obtained with **C2**. In an effort to further understand the effects of "throw away" ligand on the catalytic efficiency, kinetic experiments were performed. As can be seen in Figure 3, the cross-coupling reactions turned over immediately and were complete within 40 min. A comparison of the rate of cross-coupling reaction between **C1** and **C2** demonstrated that they possess very similar catalytic activities, indicating minor differences in performance of the "throw away" ligands in this study. To additionally investigate the backbones on our NHC ligand design, coupling reactions employing classical Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An} were also subjected under the current reaction conditions (also seen in runs 18 and 19 in Table 1). We found that significant, but much lower, yields of 84% and 91% were afforded for Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An}, respectively. Significantly, no induction period was observed for these palladium complexes, and the reaction rates were almost the same in the initial 20 min. These results indicated that backbones derived from the NHCs do not play a key role on their activation as well as activities. However, the classical palladium complexes of Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An} stalled at approximately 25 and 30 min, respectively, with no increased products when extending the reaction time. In contrast, the catalyst lifetime of **C1** and **C2** was much longer than that of these classical palladium complexes, therefore leading to a much higher catalytic efficiency. On accounting the catalytic properties of these Pd-PEPPSI complexes, the stability of the palladium(0) species (catalyst lifetime) would become an important issue in the cross-coupling when exposed to air.

To shed further light onto the performance of these palladium complexes, an extremely low palladium concentration of 0.01 mol % was conducted. The cross-coupling product was obtained in a satisfying yield of 72% and 74% for **C1** and **C2**, respectively (runs 20 and 21, Table 1). In contrast, much lower yields of 43% and 56% were given by Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An}, respectively (runs 22 and 23, Table 1). At this stage, the kinetic experiment of the **C1** and **C2** demonstrated somewhat higher activities than that of Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An}. Nevertheless, on assuming that the palladium(0) species would be easily deactivated at a low palladium concentration in aerobic conditions, we cannot conclude such comparison simply. Therefore, we conducted some other control experiments. It was found that, in the presence of 1 atm of oxygen and at a palladium loading of 0.05 mol %, the reactions were completely shut down and only amount of ca. 20% biphenyl was obtained by these four Pd-PEPPSI complexes. It can be inferred from these investigations that the NHCs-Pd(0) would be captured by oxygen, forming

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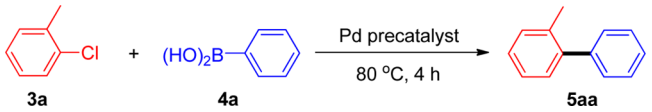
Table 1. Screening of the Palladium Precatalysts on Suzuki−Miyaura Cross-Coupling Reaction[a]



run	Pd	loading (%)	base	solvent	yield (%)[b]
1	**C1**	0.05	K_2CO_3	EtOH	93
2	**C1**	0.05	K_3PO_4	EtOH	100 (98)[c]
3	**C1**	0.05	KOAc	EtOH	NR
4	**C1**	0.05	$NaHCO_3$	EtOH	7
5	**C1**	0.05	Na_2CO_3	EtOH	16
6	**C1**	0.05	Cs_2CO_3	EtOH	8
7	**C1**	0.05	NaOH	EtOH	89
8	**C1**	0.05	KOH	EtOH	98
9	**C1**	0.05	KO^{t}Bu	EtOH	88
10	**C1**	0.05	K_3PO_4	H_2O	NR
11	**C1**	0.05	K_3PO_4	1,4-dioxane	NR
12	**C1**	0.05	K_3PO_4	toluene	NR
13	**C1**	0.05	K_3PO_4	THF	36
14	**C1**	0.05	K_3PO_4	MeOH	86
15	**C1**	0.05	K_3PO_4	*i*PrOH	91
16	**C2**	0.05	K_3PO_4	EtOH	98
17	**$PdCl_2$**	0.05	K_3PO_4	EtOH	NR
18	**PEPPSI-IPr**	0.05	K_3PO_4	EtOH	84
19	**PEPPSI-IPr^{An}**	0.05	K_3PO_4	EtOH	91
20	**C1**	0.01	K_3PO_4	EtOH	72
21	**C2**	0.01	K_3PO_4	EtOH	74
22	**PEPPSI-IPr**	0.01	K_3PO_4	EtOH	43
23	**PEPPSI-IPr^{An}**	0.01	K_3PO_4	EtOH	56

[a]Reaction conditions: 1-chloro-2-methylbenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (1.5 mmol), solvent: 3 mL in aerobic environment. [b]The GC yield was determined by GC-FID using the (trifluoromethyl)benzene as internal standard. Two parallel reactions were performed, and the yield was given in average. [c]Isolated yields in parentheses.

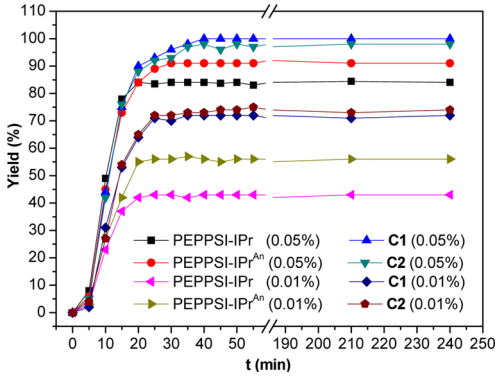


Figure 3. Kinetic profiles for the Suzuki−Miyaura cross-coupling reaction of 1-chloro-2-methylbenzene with phenylboronic acid performing in Table 1.

the unreactive NHCs-Pd(O-O) peroxo complexes.[18c,g,h] Moreover, the cross-coupling reactions were also carried out at lower temperature (25, 60, and 70 °C) in air. Beyond expectation, neither the desired cross-coupling product nor biphenyl was observed. Although the role of the reaction temperature is still not fully understood, Cazin recently revealed that the oxygen binding of peroxo complex IPr-Pd(O-O) is reversible, which would revert back to IPr-Pd(0) at 80 °C (threshold temperature) at a high vacuum.[18f]

With these viewpoints, the catalytic performances of the PEPPSI palladium complexes in this study are discussed below. Because **C1**, **C2**, Pd-PEPPSI-IPr, and Pd-PEPPSI-IPr^{An} bear the same *N*-aryl moiety, the observed differences in catalytic activity can be mostly ascribed to the steric hindrance on the backbones for their protection on Pd(0) species. With only two hydrogen atoms on the backbone, the decreased bulk of Pd-PEPPSI-IPr led to a much less efficient reaction. Although Pd-PEPPSI-IPr^{An} contains a large acenaphthyl backbone, it exists in a planar geometry and thus has less of an effect on protecting the axial site of the metal center. Consequently, the catalytic species NHC-Pd(0) can be captured by oxygen molecules to form NHC-Pd(O-O) complexes, ultimately resulting in catalyst deactivation. In comparison, as seen in the solid structure analysis in Figures 1 and 2, the 1,2-di-*tert*-butyl groups on Pd-PEPPSI-IPr$^{DtBu-An}$ provide steric hindrance to the axial positions above and below the acenaphthyl on the backbone, which retards C_{Ar}−N bond rotation and, therefore, protects the catalytic species from exposure to air. It can be reasonable that sterically encumbered substituents on the backbone would extend the catalyst life and, therefore, improve the efficiency of the cross-coupling reaction. In order to further clarify the bond strength of NHCs-Pd(0) in our study, the poison experiments were performed to determine the possibility of the palladium nanoparticles involved as catalytic species. Upon the addition of one drop of Hg(0) to the reaction mixture, the reaction was not affected and nearly quantitative yield of the product was observed (both for **C1** and **C2**). Obviously, the result indicated a homogeous nature involved in the reaction, and the bulky NHCs ligand would strongly coordinate on the Pd(0). In addition, the formation of the expected biphenyl byproducts, which can be derived from the oxidative homocoupling of

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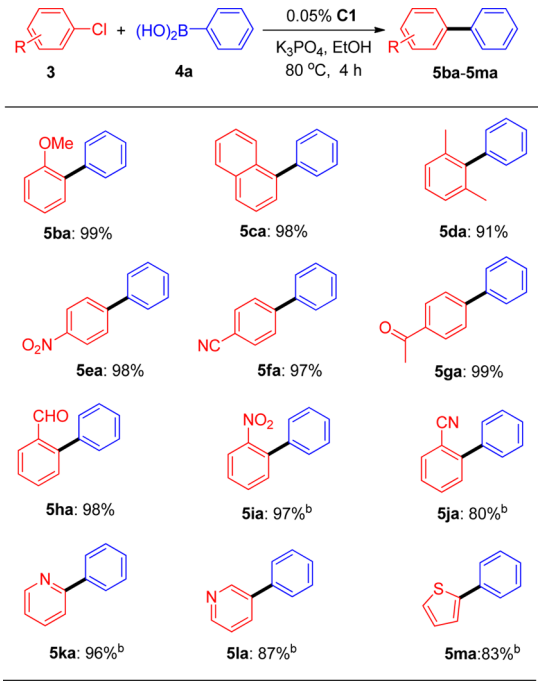
phenylboronic acid, was suppressed under the reaction conditions (<1%). Thus, based on the screening conditions, optimized reaction conditions were obtained at a palladium loading of 0.05 mol %, K_3PO_4 as the base, and EtOH as the solvent in an aerobic environment. Moreover, **C1** was selected as the palladium source for its easily accessible.

With the established optimized reaction conditions, the scope of the aryl chloride substrates was then examined in the cross-coupling reaction with phenylboronic acid. As shown in Table 2, all of the reactions proceeded with excellent yield, and

Table 2. Suzuki−Miyaura Cross-Coupling Reaction of Aryl Chlorides with Phenylboronic Acids[a]

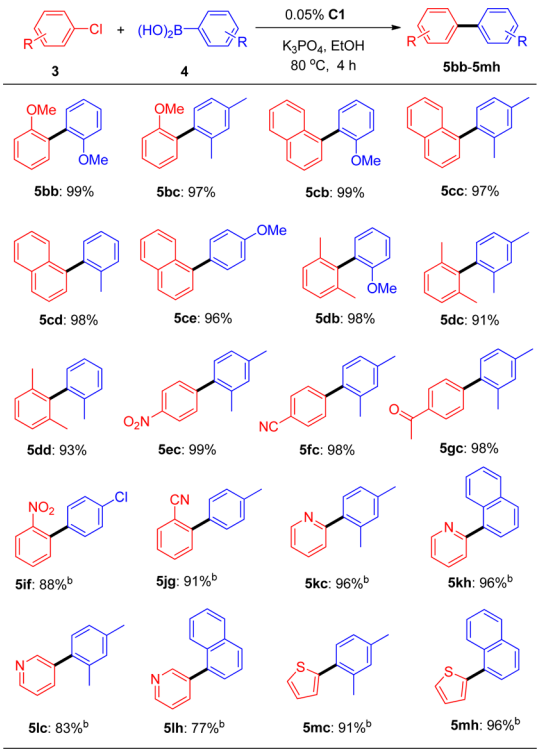


[a]Reaction conditions: aryl chloride (1.0 mmol), phenylboronic acid (1.2 mmol), K_3PO_4 (1.5 mmol); EtOH: 3 mL in aerobic environment, **C1** (0.05 mol %). Isolated yields. [b]Reaction conditions: **C1** (0.1 mol %) was performed.

various functional groups, such as −MeO, −CN, $-NO_2$, $-CH_3CO$, and −CHO, were tolerated under the standard conditions. Meanwhile, neither electron-donating (**5ba−5da**, Table 2) nor electron-withdrawing (**5ea−5ja**, Table 2) groups on the aryl chloride affected the corresponding biaryls and gave good to excellent yields. It is important to note that aryl chlorides with *ortho*-substituents, such as 2-Me, 2-OMe, 2-CN, 2-NO_2, 2-CHO, and even bulky 2,6-dimethyl, were also compatible and furnished the product in good to excellent yields. Encouraged by the excellent performance of the palladium complexes, we set out to explore the synthesis of heterobiaryls, which are commonly found in the structure of pharmaceuticals, natural products, and functional materials.[23] To our delight, heteroaromatic chlorides, such as 2-chloropyridine, 3-chloropyridine, and 2-chlorothiophene, also reacted efficiently to afford **5ka−5ma** in high yields at a palladium loading of 0.1 mol %.

The remarkable activities encouraged us to extend the scope further. We next examined the coupling with various arylboronic acids. As shown in Table 3, the coupling of arylboronic acid with 2-MeO, 2,4-dimethyl, 2-Me, and 4-MeO

Table 3. Suzuki−Miyaura Cross-Coupling Reaction of Aryl Chlorides with Arylboronic Acids[a]



[a]Reaction conditions: aryl chloride (1.0 mmol), arylboronic acid (1.2 mmol), K_3PO_4 (1.5 mmol); EtOH: 3 mL in aerobic environment, **C1** (0.05 mol %). Isolated yields. [b]Reaction conditions: **C1** (0.1 mol %) was performed.

functional groups was successful, giving the corresponding products (**5bb−5gc**) in 91−99% yields. Moreover, challenging cross-couplings involving sterically hindered 2,6-dimethylphenyl chloride with several *ortho*-substituted arylboronic acids were tested. Indeed, 2-MeO, 2-Me, and 2,4-dimethyl phenylboronic acids are readily coupled, affording the tri-*ortho*-substituted biaryls of **5db−5dd** in very high yields of 98, 91, and 93%, respectively. To further gauge the potential application in functional molecule formation, the cross-coupling of 2-nitrochlorobenzene and 4-chlorophenylboronic acids proceeded at a satisfying yield of 88% (**5if**), providing a key intermediate of boscalid, which is used in agricultural chemicals. Furthermore, 2-chlorobenzonitrile and 4-methylphenylboronic acids were also coupled to provide an important intermediate of the Sartan family in 91% yield (**5jg**).

CONCLUSION

In summary, we have developed well-defined and air-stable Pd-PEPPSI-$IPr^{DtBu-An}$ complexes for the Suzuki−Miyaura cross-coupling reaction by incorporating bulky 1,2-di(*tert*-butyl)-acenaphthene (DtBu-An) into the catalyst backbone. Compared with the classical Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An} precatalysts, the introduction of steric bulk to the axial positions on the skeleton provided significant enhancements in Pd-catalyzed cross-coupling. Upon optimizing the reaction conditions, Pd-PEPPSI-$IPr^{DtBu-An}$-(Py) (**C1**) was found to be highly efficient in the presence of the relatively weak base K_3PO_4, allowing the reaction to be performed under aerobic conditions at low palladium loadings of 0.05−0.1 mol %. Notably, substrates with electron-deficient, electron-rich, and

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sterically bulky aryl and heteroaryl chlorides were compatible. This study further illustrated the potential of this synthetic strategy for pharmaceuticals, agrochemicals, and functional materials.

EXPERIMENTAL SECTION

Physical Measurements and Materials. All aryl halides and arylboronic acids were purchased from Aldrich Chemical. Palladium chloride, chloromethyl ethyl ether, and *tert*-butyllithium (1.6 M, hexane) were purchased from Aldrich Chemical. Pyridine, 3-chloropyridine, and the solvents, were purchased from Guangzhou Chemical Reagent Factory and were used as received. The acenaphthenequinone, bases, and 2,6-diisopropylaniline were purchased from Darui Chemical Reagent Factory. The α-diimine compound of [2,6-(iPr)$_2$-C$_6$H$_3$)-N=C(An)C(An)=N-(2,6-(iPr)$_2$-C$_6$H$_3$)] (**1**) was prepared according to the previous report.[15a] Pd-PEPPSI-IPr and Pd-PEPPSI-IPr^{An} were synthesized according to literature methods.[12,15a]

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 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K for **C1**, **C2**. 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. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. CCDC 1501896 (**C1**) and 1501895 (**C2**) contain the supplementary crystallographic data for this paper.

Synthesis of {[2,6-(iPr)$_2$-C$_6$H$_3$)-N=C(DtBu-An)C(DtBu-An)=N-(2,6-(iPr)$_2$-C$_6$H$_3$)]} (2). According to a modified literature procedure, [2,6-(iPr)$_2$-C$_6$H$_3$)-N=C(An)C(An)=N-(2,6-(iPr)$_2$-C$_6$H$_3$)] (4 mmol) was diluted in hexane under a nitrogen atmosphere, and *tert*-butyllithium (5 mL, 1.6 M) was added using a syringe at ambient temperature. Then, the reaction was heated to 70 °C for 48 h. When having reached the determined time, the addition of water added to the dark purple solution resulted in the slow formation of a clear red colored solution. The latter hexane solution was extracted by means of a separatory funnel and dried over anhydrous magnesium sulfate. Concentration of the hexane solution afforded a mixture of products that was washed with hexane to remove impurities. The crude product was then extracted into a dichloromethane solution and recrystallized by slow vapor diffusion of hexane into the dichoromethane solution, which, in turn, resulted in the formation of a crop of red crystals (1.572 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 11.4 Hz, Ar-H, 5H), 7.15−7.09 (m, Ar-H, 1H), 7.03 (d, J = 7.4 Hz, Ar-H, 1H), 6.85 (m, Ar-H, 1H), 6.17 (d, J = 7.7 Hz, Ar-H, 1H), 5.35 (d, J = 5.2 Hz, Ar-H, 1H), 3.20−2.85 (m, CH(CH$_3$)$_2$, 4H), 2.59 (s, CH, 1H), 2.27 (d, J = 5.5 Hz, CH, 1H), 1.27 (d, J = 6.6 Hz, CH$_3$, 3H), 1.20 (m, CH$_3$, 9H), 1.17−1.13 (m, CH$_3$, 6H), 0.95 (d, J = 6.6 Hz, CH$_3$, 6H), 0.75 (s, CH$_3$, 9H), 0.64 (s, CH$_3$, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 159.4, 147.9, 147.6, 141.0, 135.6, 135.4, 135.3, 134.5, 133.7, 133.0, 132.0, 129.0, 127.5, 123.9, 123.7, 123.4, 123.3, 123.0, 122.9, 46.3, 45.6, 36.9, 35.7, 28.8, 28.6, 28.4, 28.2, 27.6, 27.1, 23.5, 23.4, 23.4, 23.3, 23.1, 23.0, 22.6, 22.5. Anal. Calcd for C$_{44}$H$_{58}$Cl$_2$N$_2$, C, 85.94; H, 9.51; N, 4.56. Found: C, 85.91; H, 9.57; N, 4.50.

Synthesis of Imidazolium Salts IPr$^{(DtBu-An)}$·HCl (3). α-Diimine compound of **2** (1 mmol) and chloromethyl ethyl ether (6 mL) were combined under a nitrogen atmosphere at room temperature, and then the reaction was heated to 100 °C for 24 h. When having reached the determined time, the solution was cooled to room temperature, and the reaction mixture was treated with Et$_2$O and stirred for 1 h, causing the formation of a great deal of precipitate. The solid was isolated by filtration and wash with Et$_2$O three times. The resulting crude was obtained as a yellowish white powder (0.451g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, NCHN, 1H), 7.60 (m, Ar-H, 2H), 7.39 (m, Ar-H, 4H), 7.16 (m, Ar-H, 1H), 7.11−7.05 (m, Ar-H, 1H), 6.60−6.35 (m, Ar-H, 1H), 6.03 (d, J = 5.6 Hz, Ar-H, 1H), 2.74−2.59 (m, CH(CH$_3$)$_2$, 4H), 2.33 (s, CH, 2H), 1.34 (m, CH$_3$, 9H), 1.25 (m, CH$_3$, 3H), 1.19 (m, CH$_3$, 3H), 1.16−1.10 (m, CH$_3$, 9H), 0.94 (s, CH$_3$, 3H), 0.77 (s, CH$_3$, 6H), 0.76 (s, CH$_3$, 6H), 0.68 (s, CH$_3$, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 145.0, 143.5, 140.7, 139.6, 136.0, 134.1, 133.4, 133.0, 132.0, 131.1, 130.4, 129.2, 128.1, 124.9, 124.8, 124.7, 123.6, 122.3, 116.4, 115.9, 47.8, 45.9, 37.8, 36.2, 36.0, 35.0, 31.1, 29.6, 29.4, 29.3, 28.7, 27.7, 27.5, 27.3, 24.5, 23.5, 23.3, 22.7. Anal. Calcd for C$_{45}$H$_{59}$ClN$_2$, C, 81.47; H, 8.96; N, 4.22. Found: C, 81.39; H, 9.03; N, 4.18.

General Procedures for the Synthesis of Pd-PEPPSI Compounds. A mixture of imidazolium salt (1 mmol), palladium dichloride (0.177 g, 1 mmol), and K_2CO_3 (0.690 g, 10 mmol) in pyridine or 3-chloropyridine (4 mL) was stirred at 80 °C for 24 h. When having reached the determined time, the solution was cooled to room temperature and 20 mL of dichloromethane was added, and then the reaction mixture was added into a short silica-gel column washing with substantial dichloromethane. Evaporation of the filtrate provided the yellow/brown solid. The solid was then washed and stirred with hexane (15 mL) for 1 h. The precipitate was isolated by filtration. The yellow solid was slowly treated with dichloromethane until it was dissolved completely; then, massive Et$_2$O was added, causing the formation of a white precipitate. The suspension was filtered through a sintered funnel. Drying the solid in vaccuo produced the desired palladium complexes as a yellowish powder.

Pd-PEPPSI-IPr$^{(DtBu-An)}$-Py (C1). **C1** was obtained as a yellowish powder (0.645 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 5.5 Hz, Ar-H, 2H), 7.66−7.51 (m, Ar-H, 3H), 7.47 (d, J = 7.7 Hz, Ar-H, 1H), 7.43 (d, J = 7.7 Hz, Ar-H, 2H), 7.35 (m, Ar-H, 1H), 7.11 (m, Ar-H, 2H), 6.94−6.72 (m, Ar-H, 2H), 6.11 (d, J = 7.1 Hz, Ar-H, 1H), 5.61 (d, J = 5.4 Hz, Ar-H, 1H), 3.86−3.59 (m, CH(CH$_3$)$_2$, 2H), 3.30 (m, 6.6 Hz, CH(CH$_3$)$_2$, 1H), 2.93 (m, CH(CH$_3$)$_2$, 1H), 2.67 (s, CH, 1H), 2.56 (d, J = 5.5 Hz, CH, 1H), 1.53 (d, J = 6.4 Hz, CH$_3$, 6H), 1.43 (m, CH$_3$, 6H), 1.13 (d, J = 6.7 Hz, CH$_3$, 3H), 1.07 (d, J = 6.8 Hz, CH$_3$, 3H), 0.98 (d, J = 6.7 Hz, CH$_3$, 3H), 0.94 (s, CH$_3$, 3H), 0.77 (s, CH$_3$, 9H), 0.69 (s, CH$_3$, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 151.5, 147.4, 147.2, 147.1, 146.8, 143.9, 137.3, 135.9, 135.0, 134.0, 133.8, 133.3, 130.3, 129.3, 128.4, 126.5, 125.6, 125.0, 124.9, 124.4, 124.1, 123.9, 115.9, 47.5, 45.8, 37.7, 35.7, 29.8, 29.0, 28.8, 28.7, 28.6, 28.1, 27.1, 26.1, 26.0, 25.4, 25.1, 24.8, 24.3, 23.4. Anal. Calcd for C$_{50}$H$_{63}$Cl$_2$N$_3$Pd, C, 67.98; H, 7.19; N, 4.76. Found: C, 67.76; H, 7.23; N, 4.72.

Pd-PEPPSI-IPr$^{(DtBu-An)}$-3ClPy (C2). **C2** was obtained as a yellowish powder (0.560, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, Ar-H, 1H), 8.57 (m, Ar-H, 1H), 7.57 (m, Ar-H, 3H), 7.46 (m, Ar-H, 3H), 7.38 (d, J = 7.7 Hz, Ar-H, 1H), 7.10−7.04 (m, Ar-H, 1H), 6.94−6.83 (m, Ar-H, 2H), 6.12 (d, J = 7.1 Hz, Ar-H, 1H), 5.62 (d, J = 5.5 Hz, Ar-H, 1H), 3.78−3.55 (m, CH(CH$_3$)$_2$, 2H), 3.30 (m, CH(CH$_3$)$_2$, 1H), 2.92 (m, CH(CH$_3$)$_2$, 1H), 2.68 (s, CH, 1H), 2.56 (m, CH, 1H), 1.53 (d, J = 6.4 Hz, CH$_3$, 3H), 1.43 (d, J = 5.4 Hz, CH$_3$, 9H), 1.13 (d, J = 6.5 Hz, CH$_3$, 3H), 1.07 (d, J = 6.6 Hz, CH$_3$, 3H), 0.99 (d, J = 6.3 Hz, CH$_3$, 3H), 0.79 (d, J = 8.6 Hz, CH$_3$, 12H), 0.70 (s, CH$_3$, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 151.2, 150.5, 149.5, 147.4, 147.2, 147.1, 146.8, 144.0, 137.4, 136.0, 135.0, 133.9, 133.7, 133.3, 131.8, 130.5, 130.4, 129.4, 128.4, 126.6, 125.6, 124.9, 124.5, 124.2, 116.0, 47.6, 45.8, 37.6, 35.7, 29.0, 28.8, 28.7, 28.6, 28.1, 27.1, 26.1, 26.0, 25.4, 25.1, 24.7, 24.4, 24.3, 23.4. Anal. Calcd for C$_{50}$H$_{62}$Cl$_3$N$_3$Pd, C, 65.43; H, 6.81; N, 4.58. Found: C, 65.12; H, 6.73; N, 4.47.

General Procedure for the Suzuki−Miyaura Reaction. Unless otherwise noted, the Suzuki−Miyaura reaction was carried out under aerobic conditions. All solvents were used as received, and no further purification was needed. A parallel reactor containing a stir bar was charged with Pd-PEPPSI complexes (0.05% mmol), aryl halides (1.0 mmol), boronic acid (1.2 mmol), base (1.5 mmol), and 3 mL of solvent. The reaction mixture was carried out at 80 °C for 4 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature and 20 mL of water was added. The mixture was diluted with dichloromethane (5 mL), followed by extraction three times (3 ×

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5 mL) with dichloromethane. The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The crude cross-coupling products were purified by silica-gel column chromatography using petroleum ether−dichloromethane (20/1) as eluent, and the isolated yield was then calculated based on the feeding of the aryl halides. The isolated cross-coupling products were characterized by ^{1}H NMR and ^{13}C NMR, and the spectra can be found in the Supporting Information.

General Information for NMR Data. The NMR data of compounds were obtained on a Varian Mercury-Plus 400 MHz spectrometer at ambient temperature, using $CDCl_3$ as solvent and referenced versus TMS as standard. Chemical shifts are reported in ppm, and coupling constants are reported in Hz.

2-Methyl-1,1′-biphenyl (**5aa**).[9j] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, Ar-H, 2H), 7.37 (m, Ar-H, 3H), 7.32−7.24 (m, Ar-H, 4H), 2.31 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 125.5, 20.5.

2-Methoxy-1,1′-biphenyl (**5ba**).[19a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, Ar-H, 2H), 7.48 (d, J = 5.2 Hz, Ar-H, 2H), 7.43−7.33 (m, Ar-H, 3H), 7.14−6.98 (m, Ar-H, 2H), 3.86 (s, Ar-OCH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 138.5, 130.8, 130.6, 129.5, 128.6, 127.9, 126.9, 120.8, 111.1, 55.5.

1-Phenylnaphthalene (**5ca**).[19a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.83 (m, Ar-H, 3H), 7.60−7.48 (m, Ar-H, 6H), 7.47−7.40 (m, Ar-H, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 140.2, 133.7, 131.6, 130.0, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4.

2,6-Dimethyl-1,1′-biphenyl (**5da**).[9q] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, Ar-H, 2H), 7.38 (m, Ar-H, 1H), 7.23−7.18 (m, Ar-H, 3H), 7.16 (d, J = 7.0 Hz, Ar-H, 2H), 2.09 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.1, 136.0, 129.0, 128.4, 127.3, 127.0, 126.6, 20.8.

4-Nitro-1,1′-biphenyl (**5ea**).[20b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.9 Hz, Ar-H, 2H), 7.74 (d, J = 8.9 Hz, Ar-H, 2H), 7.63 (d, J = 6.9 Hz, Ar-H, 2H), 7.49 (m, Ar-H, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 147.1, 138.7, 129.1, 128.9, 127.7, 127.3, 124.0.

[1,1′-Biphenyl]-4-carbonitrile (**5fa**).[9o] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, Ar-H, 4H), 7.59 (d, J = 7.3 Hz, Ar-H, 2H), 7.45 (m, Ar-H, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.1, 118.8, 110.9.

1-([1,1′-Biphenyl]-4-yl)ethanone (**5ga**).[9j] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, Ar-H, 2H), 7.69 (d, J = 8.5 Hz, Ar-H, 2H), 7.63 (d, J = 7.3 Hz, Ar-H, 2H), 7.48 (m, Ar-H, 2H), 7.41 (m, Ar-H, 1H), 2.64 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.8, 139.9, 135.9, 135.6, 128.9, 128.2, 127.9, 127.2, 26.6.

[1,1′-Biphenyl]-2-carbaldehyde (**5ha**).[24a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, CHO, 1H), 8.04 (m, Ar-H, 1H), 7.64 (m, Ar-H, 1H), 7.54−7.43 (m, Ar-H, 5H), 7.41−7.37 (m, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 146.0, 137.8, 133.7, 133.5, 130.7, 130.1, 128.5, 128.4, 128.1, 127.8, 127.6.

2-Nitro-1,1′-biphenyl (**5ia**).[24b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (m, Ar-H, 1H), 7.62 (m, Ar-H, 1H), 7.52−7.40 (m, Ar-H, 5H), 7.33 (m, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 137.4, 136.3, 132.2, 131.9, 128.6, 128.2, 128.1, 127.9, 124.0.

[1,1′-Biphenyl]-2-carbonitrile (**5ja**).[24c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, Ar-H, 1H), 7.65 (m, Ar-H, 1H), 7.60−7.55 (m, Ar-H, 2H), 7.54−7.50 (m, Ar-H, 2H), 7.49−7.42 (m, Ar-H, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 138.1, 133.7, 132.7, 130.0, 128.7, 128.7, 127.5, 118.6, 111.3.

2-Phenylpyridine (**5ka**).[9j] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.7 Hz, Ar-H, 1H), 8.11−7.92 (m, Ar-H, 2H), 7.79−7.66 (m, Ar-H, 2H), 7.48 (m, Ar-H, 2H), 7.45−7.39 (m, Ar-H, 1H), 7.24−7.19 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 149.6, 139.4, 136.7, 128.9, 128.7, 126.9, 122.0, 120.5.

3-Phenylpyridine (**5la**).[9q] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, Ar-H, 1H), 8.59 (d, J = 4.5 Hz, Ar-H, 1H), 7.88 (m, Ar-H, 1H), 7.59 (d, J = 7.5 Hz, Ar-H, 2H), 7.48 (m, Ar-H, 2H), 7.43−7.34 (m, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 148.3, 137.8, 136.7, 134.4, 129.1, 128.1, 127.1, 123.5.

2-Phenylthiophene (**5ma**).[21d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, Ar-H, 2H), 7.40 (m, Ar-H, 2H), 7.32 (m, Ar-H, 3H), 7.11 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 134.4, 128.9, 128.0, 127.4, 126.0, 124.8, 123.1.

2,2′-Dimethoxy-1,1′-biphenyl (**5bb**).[24d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, Ar-H, 2H), 7.23 (m, Ar-H, 2H), 7.07−6.89 (m, Ar-H, 4H), 3.76 (s, Ar-OCH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 131.4, 128.6, 127.9, 120.3, 111.1, 55.7.

2′-Methoxy-2,4-dimethyl-1,1′-biphenyl (**5bc**).[24e] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, Ar-H, 1H), 7.19 (d, J = 7.3 Hz, Ar-H, 1H), 7.13 (s, Ar-H, 2H), 7.11−6.98 (m, Ar-H, 3H), 3.80 (s, Ar-OCH_3, 3H), 2.41 (s, CH_3, 3H), 2.16 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 136.8, 136.6, 135.7, 131.1, 130.8, 130.4, 129.9, 128.4, 126.2, 120.4, 110.6, 55.3, 21.1, 19.8.

1-(2-Methoxyphenyl)naphthalene (**5cb**).[19a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, Ar-H, 2H), 7.60 (d, J = 6.1 Hz, Ar-H, 1H), 7.54 (m, Ar-H, 1H), 7.42 (m, Ar-H, 4H), 7.30 (d, J = 5.3 Hz, Ar-H, 1H), 7.08 (m, Ar-H, 2H), 3.71 (s, Ar-OCH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 137.0, 133.5, 132.1, 131.9, 129.5, 129.0, 128.1, 127.6, 127.3, 126.4, 125.6, 125.5, 125.3, 120.5, 111.0, 55.5.

1-(2,4-Dimethylphenyl)naphthalene (**5cc**).[24f] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, Ar-H, 2H), 7.63−7.50 (m, Ar-H, 3H), 7.48−7.34 (m, Ar-H, 2H), 7.21 (m, Ar-H, 3H), 2.50 (s, CH_3, 3H), 2.08 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.3, 137.1, 136.6, 133.5, 132.1, 130.6, 130.3, 128.1, 127.3, 126.7, 126.2, 126.1, 125.9, 125.6, 125.4, 21.2, 20.0.

1-(o-Tolyl)naphthalene (**5cd**).[21d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, Ar-H, 2H), 7.67−7.48 (m, Ar-H, 3H), 7.46−7.22 (m, Ar-H, 6H), 2.08 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.7, 136.8, 133.5, 132.0, 130.3, 129.8, 128.2, 127.5, 127.4, 126.6, 126.1, 125.9, 125.7, 125.5, 125.3, 20.0.

1-(4-Methoxyphenyl)naphthalene (**5ce**).[21d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, Ar-H, 2H), 7.87 (d, J = 7.9 Hz, Ar-H, 1H), 7.61−7.40 (m, Ar-H, 6H), 7.12−7.03 (m, Ar-H, 2H), 3.92 (s, Ar-OCH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 139.9, 133.8, 133.1, 131.8, 131.1, 128.2, 127.3, 126.9, 126.0, 125.9, 125.7, 125.4, 113.7, 55.3.

2′-Methoxy-2,6-dimethyl-1,1′-biphenyl (**5db**).[9o] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.32 (m, Ar-H, 1H), 7.20 (m, Ar-H, 1H), 7.14 (d, J = 7.4 Hz, Ar-H, 2H), 7.09−6.99 (m, Ar-H, 3H), 3.76 (s, Ar-OCH_3, 3H), 2.05 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 138.2, 136.6, 130.7, 129.6, 128.4, 127.0, 127.0, 120.7, 110.9, 55.4, 20.4.

2,2′,4,6′-Tetramethyl-1,1′-biphenyl (**5dc**).[24g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.07 (m, Ar-H, 5H), 6.93 (d, J = 7.6 Hz, Ar-H, 1H), 2.40 (s, CH_3, 3H), 1.98 (s, CH_3, 6H), 1.96 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 137.4, 136.4, 136.1, 135.3, 131.5, 130.7, 128.7, 127.1, 126.8, 21.1, 20.3, 19.3.

2,2′,6-Trimethyl-1,1′-biphenyl (**5dd**).[9q] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, Ar-H, 3H), 7.16 (m, Ar-H, 1H), 7.10 (d, J = 7.3 Hz, Ar-H, 2H), 7.04−6.97 (m, Ar-H, 1H), 1.96 (s, CH_3, 3H), 1.94 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 140.6, 135.9, 135.6, 130.0, 128.9, 127.2, 127.0, 126.9, 126.0, 20.3, 19.3.

2,4-Dimethyl-4′-nitro-1,1′-biphenyl (**5ec**).[24h] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, Ar-H, 2H), 7.48 (d, J = 8.8 Hz, Ar-H, 2H), 7.20−7.02 (m, Ar-H, 3H), 2.39 (s, CH_3, 3H), 2.26 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 138.3, 137.4, 136.8, 134.8, 131.5, 130.1, 129.4, 126.8, 123.3, 21.0, 20.2.

2′,4′-Dimethyl-[1,1′-biphenyl]-4-carbonitrile (**5fc**).[24i] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, Ar-H, 2H), 7.43 (d, J = 8.4 Hz, Ar-H, 2H), 7.11 (d, J = 12.4 Hz, Ar-H, 3H), 2.38 (s, CH_3, 3H), 2.24 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.82 (s), 138.1, 137.2, 134.8, 131.9, 131.4, 130.0, 129.3, 126.8, 118.9, 110.5, 21.0, 20.2.

1-(2′,4′-Dimethyl-[1,1′-biphenyl]-4-yl)ethanone (**5gc**).[24j] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, Ar-H, 2H), 7.43 (d, J = 8.2 Hz, Ar-H, 2H), 7.11 (m, Ar-H, 3H), 2.65 (s, CH_3, 3H), 2.39 (s, CH_3, 3H), 2.26 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 147.0, 146.2, 142.3, 137.6, 134.9, 131.3, 129.5, 128.2, 126.6, 126.0, 26.5, 21.0, 20.3.

4′-Chloro-2-nitro-1,1′-biphenyl (**5if**).[24k] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, Ar-H, 1H), 7.62 (m, Ar-H, 2H), 7.58−7.47 (m, Ar-H, 2H), 7.40 (d, J = 8.8 Hz, Ar-H, 3H). ^{13}C NMR

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(101 MHz, $CDCl_3$) δ 149.1, 139.9, 138.8, 136.7, 132.4, 131.8, 129.3, 129.0, 128.9, 124.2.

*4′-Methyl-[1,1′-biphenyl]-2-carbonitrile (**5jg**).*[24k] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, Ar-H, 1H), 7.63 (m, Ar-H, 1H), 7.51 (m, Ar-H, 1H), 7.47 (d, *J* = 8.1 Hz, Ar-H, 2H), 7.42 (m, Ar-H, 1H), 7.31 (d, *J* = 7.9 Hz, Ar-H, 2H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 138.6, 135.3, 133.7, 132.7, 129.9, 129.4, 128.6, 127.2, 118.8, 111.2, 21.2.

*2-(2,4-Dimethylphenyl)pyridine (**5kc**).*[24l] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.1 Hz, Ar-H, 1H), 7.72 (t, *J* = 7.2 Hz, Ar-H, 1H), 7.38 (d, *J* = 7.8 Hz, Ar-H, 1H), 7.31 (d, *J* = 7.5 Hz, Ar-H, 1H), 7.25−7.19 (m, Ar-H, 1H), 7.09 (d, *J* = 8.9 Hz, Ar-H, 2H), 2.37 (s, CH_3, 3H), 2.35 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 149.1, 137.9, 137.6, 135.9, 135.5, 131.4, 129.6, 126.5, 124.0, 121.3, 21.0, 20.1.

*2-(Naphthalen-1-yl)pyridine (**5kh**).*[9o] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.1 Hz, Ar-H, 1H), 8.11 (d, *J* = 7.4 Hz, Ar-H, 1H), 7.92 (d, *J* = 8.2 Hz, Ar-H, 2H), 7.81 (m, Ar-H, 1H), 7.60 (m, Ar-H, 3H), 7.50 (m, Ar-H, 2H), 7.33 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 149.4, 138.4, 136.3, 133.9, 131.1, 128.8, 128.3, 127.4, 126.4, 125.8, 125.5, 125.2, 125.0, 121.9.

*3-(2,4-Dimethylphenyl)pyridine (**5lc**).*[24m] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65−8.43 (m, Ar-H, 2H), 7.63 (d, *J* = 7.7 Hz, Ar-H, 1H), 7.38−7.29 (m, Ar-H, 1H), 7.10 (m, Ar-H, 3H), 2.37 (s, CH3, 3H), 2.25 (s, CH3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 147.8, 137.7, 137.3, 136.4, 135.2, 135.1, 131.2, 129.7, 126.7, 122.8, 21.0, 20.2.

*3-(Naphthalen-1-yl)pyridine (**5lh**).*[24k] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, Ar-H, 1H), 8.74−8.64 (m, Ar-H, 1H), 7.92 (m, Ar-H, 2H), 7.86−7.76 (m, Ar-H, 2H), 7.58−7.50 (m, Ar-H, 2H), 7.49−7.39 (m, Ar-H, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 148.5, 137.3, 136.4, 136.3, 133.8, 131.4, 128.5, 128.4, 127.3, 126.5, 126.0, 125.3, 125.2, 123.1.

*2-(2,4-Dimethylphenyl)thiophene (**5mc**).*[24n] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, Ar-H, 2H), 7.16 (m, Ar-H, 2H), 7.12 (m, Ar-H, 2H), 2.48 (s, CH_3, 3H), 2.43 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 137.5, 135.8, 131.5, 131.2, 130.3, 127.0, 126.6, 126.1, 124.7, 21.0, 19.8.

*2-(Naphthalen-1-yl)thiophene (**5mh**).*[21d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.5 Hz, Ar-H, 1H), 7.92 (m, Ar-H, 2H), 7.63 (m, Ar-H, 1H), 7.58−7.51 (m, Ar-H, 3H), 7.47 (m, Ar-H, 1H), 7.30 (m, Ar-H, 1H), 7.23 (m, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 133.9, 132.4, 131.9, 128.4, 128.3, 128.2, 127.4, 127.2, 126.4, 126.0, 125.7, 125.6, 125.2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00723.

Details of NMR spectra of all α-diimines, *N*-heterocarbene salts, Pd-PEPPSI complexes, and cross-coupling products (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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