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Nickel/N-Heterocyclic Carbene-Catalyzed Suzuki–Miyaura Type Cross-Coupling of Aryl Carbamates

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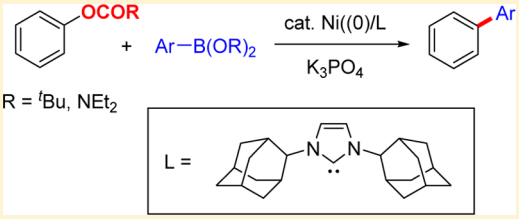
Supporting Information

ABSTRACT: The utility of N-heterocyclic carbene ligands in nickel-catalyzed Suzuki–Miyaura cross-coupling of aryl esters and carbamates is investigated. Imidazol-2-ylidene bearing 2-adamantyl groups at its nitrogen atoms generates the most active nickel species among the ligands examined, allowing cross-coupling of a range of aryl carbamates and pivalates. Unlike the previously reported system using tricyclohexylphosphine, this protocol is suitable for the cross-coupling using arylboronic esters in addition to arylboronic acids.



The Suzuki–Miyaura reaction has been recognized as a powerful carbon–carbon bond formation method because of the favorable features of organoboron reagents, such as high functional group compatibility and ease of handling.[1] The Suzuki–Miyaura reaction is particularly useful for the synthesis of (hetero)biaryls, in which various aryl halides and their equivalents are coupled with arylboronic acid derivatives. Recent efforts have been directed toward the use of inert phenol derivatives,[2] such as aryl ethers, esters, and carbamates, as aryl halide surrogates for Suzuki–Miyaura reactions. These efforts will not only provide cost-effective, halogen-free processes but also lead to diverse synthetic strategies such as orthogonal cross-coupling and late-stage functionalization. In this context, we have reported nickel-catalyzed Suzuki–Miyaura coupling of methoxyarenes via the cleavage of C(aryl)–O bonds.[3] Although we initially used tricyclohexylphosphine (PCy_3) as a suitable ligand for this cross-coupling,[3a] a subsequent study led us to identify 1,3-dicyclohexylimidazol-2-ylidene (ICy) as a superior ligand with broadened scope of methoxyarenes.[3c] The outstanding activity of the Ni/ICy system[4] for C(aryl)–O bond activation of methoxyarenes naturally encouraged us to consider whether this system is able to promote the C–O bond activation of other inert phenol derivatives. Aryl esters and carbamates have attracted substantial attention as a class of inert phenol derivatives for use in nickel-catalyzed cross-coupling reactions.[2] Although several groups have already revealed that the Ni/PCy_3 system is able to catalyze Suzuki–Miyaura type reactions of aryl esters[5] and carbamates,[6] the utility of an NHC ligand in these processes has not been verified.[7,8] Herein, we report Ni/NHC-catalyzed cross-coupling of aryl esters and carbamates with arylboron reagents.

Reliable catalytic conditions used for the cross-coupling of aryl esters and carbamates with arylboron reagents are summarized in Table 1. Close inspection of the reported boron sources employed indicates that these reactions apparently need precise control of the amount of water present in the reaction mixture. For example, Garg used arylboronic acid $ArB(OH)_2$,[5a,6a] which generates water by the reversible formation of arylboroxine $(ArBO)_3$ at elevated temperature. Shi used a mixture of $(ArBO)_3$ and 0.88 equiv of H_2O,[5b,6c] while Snieckus employed a 10:1 mixture of $ArB(OH)_2$ and $(ArBO)_3$.[6b] Although an excess amount of water is thought to be detrimental to Ni(0) catalysis,[6e] a suitable amount of water is essential, presumably to generate active Ni(0) species by the reaction of $NiCl_2(PCy_3)_2$ with $ArB(OR)_2$. To avoid the potential complexity associated with the effect of water during ligand screening experiments, we decided to use anhydrous conditions with $Ni(cod)_2$ as a catalyst and an arylboronic ester as a nucleophile. Thus, 2-naphthyl carbamate (**1a**) was reacted with phenylboronic ester **2a** in the presence of $Ni(cod)_2$ and a ligand using K_3PO_4 as a base at 120 °C (Table 2). When PCy_3 was used as the ligand under these conditions, cross-coupling product **3aa** was formed in only 9% yield (entry 1).[9] A series of NHC ligands were then examined. *N*-Aryl substituted carbenes such as **L1** (entry 2) and **L2** (entry 3) were found to be ineffective for this coupling. In contrast to our expectation, the use of **L3**, which represents the most effective ligand for nickel-catalyzed Suzuki–Miyaura reaction of methoxyarenes, afforded

Table 1. Reported Conditions for Nickel-Catalyzed Suzuki-Miyaura Cross–Coupling of Aryl Esters and Carbamates

	catalyst	boron sources	reference
Garg	$NiCl_2(PCy_3)_2$	$ArB(OH)_2$	5a, 6a
Shi	$NiCl_2(PCy_3)_2$	$(ArBO)_3$ + 0.88 H_2O	5b, 6c
Snieckus	$NiCl_2(PCy_3)_2$	$ArB(OH)_2$ + 0.1 $(ArBO)_3$	6b

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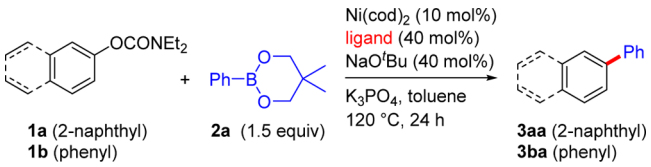
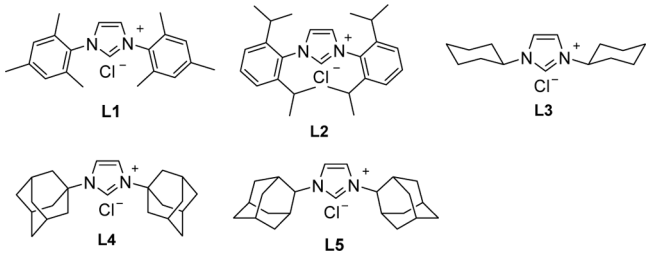
Table 2. Nickel/NHC-Catalyzed Cross-Coupling of Carbamate 1 with Phenylboronic Ester 2a[a]



entry	substrate	ligand	GC yield of **3aa** or **3ba** (%)
1[b]	**1a**	PCy_3	9
2	**1a**	**L1**	0
3	**1a**	**L2**	3
4	**1a**	**L3**	11
5	**1a**	**L4**	27
6	**1a**	**L5**	88
7	**1b**	**L5**	40
8[c]	**1b**	**L5**	71

[a]Reaction conditions: **1** (0.30 mmol), **2a** (0.45 mmol), $Ni(cod)_2$ (0.030 mmol), NHC·HCl (0.12 mmol), NaO^tBu (0.12 mmol), and K_3PO_4 (1.4 mmol) in toluene (1.0 mL) at 120 °C for 24 h. [b]Conducted in the absence of NaO^tBu. [c]Performed using $Ni(cod)_2$ (0.015 mmol), **L5** (0.045 mmol) and NaO^tBu (0.045 mmol) at 150 °C for 20 h.

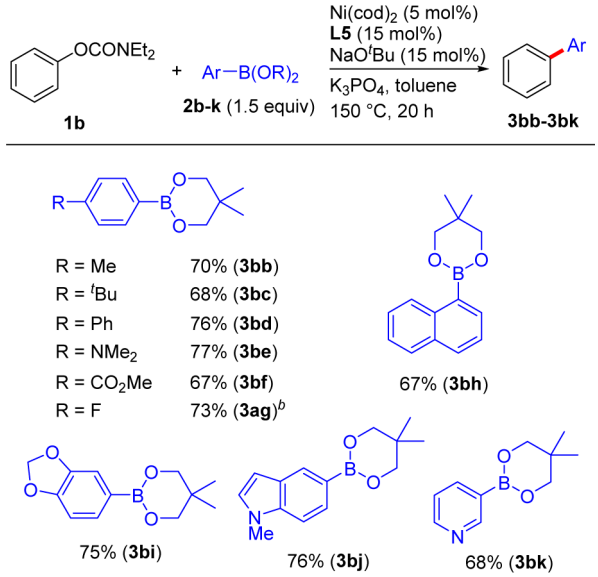


3aa in only 11% yield (entry 4). NHC ligands bearing adamantyl groups led to better results. Whereas 1-adamantyl derivative **L4** provided a slight increase in the yield of **3aa** to 27% (entry 5), isomeric 2-adamantyl ligand **L5**[4c,10] delivered **3aa** in 88% yield (entry 6). Having optimized ligand **L5** in hand, we next examined a less reactive substrate **1b**[11] using these conditions, which resulted in a lower yield of the coupling product (entry 7). Further optimization revealed that conducting the reaction at 150 °C with a lower catalyst loading (5 mol %) increased the yield of **3ba** to 71% (entry 8). These conditions were used to explore the scope of this reaction.

The scope of the reaction with respect to the boronic ester component was examined using **1b** as the substrate (Scheme 1). Both electron-rich and -deficient aryl groups can be introduced with comparable efficiency. Similar to the standard Suzuki–Miyaura reaction, functional groups such as amines (**3be**), esters (**3bf**), fluorides (**3bg**), and acetals (**3bi**) were well tolerated. In addition, heteroarylboronic esters including **2j** and **2k** successfully underwent the cross-coupling with **1b**.

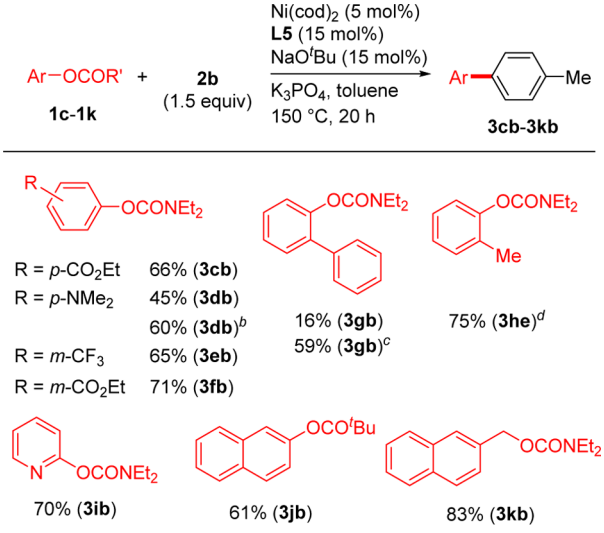
The scope of aryl carbamates was next investigated using **2b** as a coupling partner (Scheme 2). Although the Ni/**L5** system can catalyze the reactions of an electronically diverse set of aryl carbamates, electron-rich substrates such as **1d** required a higher catalyst loading to obtain satisfactory yields of the products. When ortho substituted derivative **1g** was used as the substrate, the yield was decreased markedly because of the formation of an undesired reduced product (i.e., biphenyl with ca. 75% yield). The yield of **3gb** was improved by switching the ligand to **L3** and increasing the amount of boronic ester **2b**. Carbamate is known as a versatile directing group for ortho C–H functionalization reactions.[12] Therefore, the compatibility of the ortho substituent allows sequential carbamate-directed ortho functionalization/arylation of the carbamate directing group.[13] Heteroaryl carbamates (i.e., **1i**) and aryl pivalates (i.e., **1j**) also underwent cross-coupling with **2b** under these conditions. Phenyl *p*-toluenesulfonate and *p*-*tert*-butylanisole were found to be much less reactive under these conditions

Scheme 1. Scope of Arylboron Reagents[a]



[a]Reaction conditions: **1b** (0.30 mmol), arylboron reagent (0.45 mmol), $Ni(cod)_2$ (0.015 mmol), **L5** (0.045 mmol), NaOtBu (0.045 mmol), and K_3PO_4 (1.4 mmol) in toluene (1.0 mL) at 150 °C for 20 h. [b]**1a** was used as the substrate. [c]Conducted using $Ni(cod)_2$ (0.030 mmol), **L5** (0.090 mmol), and NaOtBu (0.090 mmol) at 160 °C.

Scheme 2. Scope of Aryl Carbamates[a]



[a]Reaction conditions: substrate (0.30 mmol), **2b** (0.45 mmol), $Ni(cod)_2$ (0.015 mmol), **L5** (0.045 mmol), NaO^tBu (0.045 mmol), and K_3PO_4 (1.4 mmol) in toluene (1.0 mL) at 150 °C for 20 h. [b]Conducted using $Ni(cod)_2$ (0.030 mmol), **L5** (0.090 mmol), and NaO^tBu (0.090 mmol) at 160 °C. [c]Performed using **2b** (1.8 mmol), $Ni(cod)_2$ (0.030 mmol), **L3** (0.090 mmol), and NaO^tBu (0.090 mmol) at 160 °C. [d]Performed using **2e** (1.8 mmol), $Ni(cod)_2$ (0.030 mmol), **L3** (0.090 mmol), and NaO^tBu (0.090 mmol) at 160 °C.

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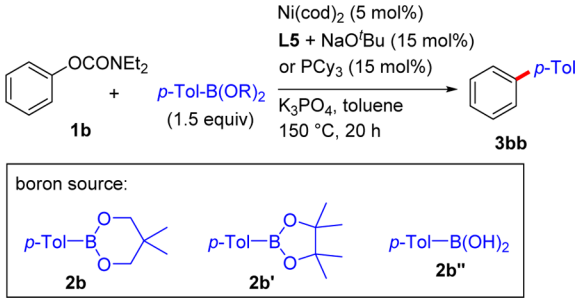
(34% and 0% yield, respectively, for the reaction with **2b**). Moreover, arylation at the benzylic position is also possible, as demonstrated by the reaction of **1k**.

One advantage of using an NHC ligand over PCy_3 in the nickel-catalyzed Suzuki–Miyaura reaction is its tolerance of a protecting group of the boronic acid component (Table 3).

Table 3. Effect of Ligands on the Reactivity of Boron Reagents[a]



entry	boron reagent	ligand	yield of **2b** (%)
1	**2b**	**L5**	70
2	**2b**	PCy_3	trace
3	**2b′**	**L5**	39 (61)[b]
4	**2b′**	PCy_3	trace
5	**2b″**	**L5**	81
6	**2b″**	PCy_3	75

[a]Reaction conditions: **1b** (0.30 mmol), organoboron reagent (0.45 mmol), $Ni(cod)_2$ (0.015 mmol), **L5** (0.045 mmol), NaO^tBu (0.045 mmol), and K_3PO_4 (1.4 mmol) in toluene (1.0 mL) at 150 °C for 20 h. [b]Conducted using $Ni(cod)_2$ (0.030 mmol), **L5** (0.090 mmol), and NaO^tBu (0.045 mmol) at 160 °C.

When the Ni/**L5** system was used, neopentylglycolate **2b**, pinacolate **2b′**, and free boronic acid **2b″** were all successfully coupled with aryl carbamate **1b** (entries 1,3 and 5, respectively). In stark contrast, boronic esters **2b′** and **2b″** did not form an appreciable amount of **3bb** under the conditions using PCy_3 (entries 2 and 4, respectively). The use of boronic esters is preferred over the parent boronic acids when boronic acids are unstable[14] or the boron compounds are prepared by C–H borylation.[15] In such a situation, our catalytic system should offer a useful protocol for the arylation of aryl esters and carbamates.[16] $ArBF_3K$ was unreactive under theses nickel/**L5**-catalyzed conditions.

In conclusion, we revealed that 2-adamantyl-substituted NHC ligand **L5** serves as an active ligand for nickel-catalyzed Suzuki–Miyaura cross-coupling of aryl esters and carbamates. Use of **L5** as the ligand allows boronic esters to participate in the cross-coupling reaction, which is in sharp contrast to the previously reported catalytic system using PCy_3, in which boronic acids are essential. Although the Ni/PCy_3 system dominates in catalytic transformations involving the activation of inert phenol derivatives,[2] we anticipate that this work will stimulate the application of NHC ligands to such reactions.

EXPERIMENTAL SECTION

General Information. ^1H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, in $CDCl_3$ with tetramethylsilane as an internal reference standard. High resolution mass spectra (HRMS) were recorded by EI using a double-focusing mass spectrometer. Column chromatography was performed with SiO_2 (230–400 mesh). Unless otherwise noted, all of the reagents used in this study were obtained from commercial suppliers and used as received without further purification. Aryl carbamates used in this study are all known compounds and were prepared by the reaction of the corresponding phenols with $ClCONEt_2$. Arylboronic esters used in this study are also known compounds and were prepared by the reaction of the corresponding arylboronic acids with 2,2-dimethylpropane-1,3-diol. $Ni(cod)_2$, NaO^tBu, K_3PO_4, **L1**, and **L2** were purchased from the commercial suppliers and used as received. **L3**,[17] **L4**,[18] and **L5**[4c] were prepared according to the literature procedure.

*4-(Dimethylamino)phenyl Diethylcarbamate (**1d**).* In a dried round-bottom flask, NaH (60% dispersion in mineral oil, 230 mg, 5.8 mmol) was dissolved in DME (20 mL) and then the mixture was cooled to 0 °C. 4-(Dimethylamino)phenol (660 mg, 4.8 mmol) was added portionwise. After the mixture was stirred at 0 °C for 10 min, diethylcarbamoyl chloride (781 mg, 5.8 mmol) was added dropwise. The mixture was warmed to rt and then stirred for another 1.5 h. The resulting mixture was quenched with H_2O, and an aqueous solution of NaOH (1.0 M) was added. The resulting mixture was extracted with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude mixture was purified by flash column chromatography over silica gel (eluted with hexane/AcOEt = 3/1) to give the target product as a white solid (916 mg, 81%); R_f 0.20 (hexane/AcOEt = 5/1); Mp: 37.5–38.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15–1.25 (m, 6H), 2.91 (s, 6H), 3.45–3.55 (m, 4H), 6.72 (dt, J = 8.8, 2.2 Hz, 2H), 6.98(dt, J = 8.8, 2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.4, 41.4, 41.9, 42.3, 113.6, 122.3, 142.8, 148.5, 155.1; IR(ATR): 3431 m, 2968 m, 2940 w, 2889 w, 2254 m, 1650 m, 1460 m, 1416 s, 1303 m, 1224 m, 1088 s, 1048 s, 907 s, 857 m, 805 w. HRMS (EI+) m/z $[M]^+$ calcd for $C_{13}H_{20}N_2O_2^+$ 236.1525, found 236.1527.

*Ethyl 3-((Diethylcarbamoyl)oxy)benzoate (**1f**).* In a dried round-bottom flask, NaH (60% dispersion in mineral oil, 480 mg, 12 mmol) was dissolved in DME (25 mL) and then the mixture was cooled to 0 °C. Ethyl 3-hydroxybenzoate (1.66 g, 10 mmol) was added portionwise. After the mixture was stirred at 0 °C for 10 min, diethylcarbamoyl chloride (1.63 g, 12 mmol) was added dropwise. The mixture was warmed to rt and then stirred for another 1.5 h. The resulting mixture was quenched with H_2O, and an aqueous solution of NaOH (1.0 M) was added. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude mixture was purified by flash column chromatography over silica gel (eluted with hexane/AcOEt = 3/1) to give the target product as a clear oil (2.61 g, 98%); R_f 0.54 (hexane/AcOEt = 1/1). ^1H NMR (400 MHz, $CDCl_3$) δ 1.18–1.28 (m, 6H), 1.39 (t, J = 7.2 Hz, 3H), 3.38–3.47 (m, 4H), 4.37 (q, J = 7.2 Hz, 2 H), 7.33–7.35 (m, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.73 (t, J = 1.8 Hz, 1H), 7.88 (dt, J = 8.0 Hz, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.38, 14.44, 42.1, 42.5, 61.3, 123.0, 126.4, 126.6, 129.2, 131.9, 151.6, 154.0, 166.0; IR(ATR): 2978 w, 2936 w, 2904 w, 2874 w, 1713 s, 1589 w, 1473 w, 1455 w, 1445 w, 1415 m, 1381 w, 1367 w, 1283 m, 1254 s, 1223 m, 1120 s, 1150 s, 1097 s, 1075 m, 1042 m, 1021 m, 965 m, 912 w, 866 w, 826 w, 784 w, 750 s, 684 m. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{19}NO_4$ 265.1314, found 265.1312.

Typical Procedure. $Ni(cod)_2$ (4.2 mg, 0.015 mmol, 5 mol %), **L5** (17 mg,0.045 mmol), NaO^tBu (4.3 mg, 0.045 mmol), and toluene (0.4 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox with a N_2 atomosphere. The resulting mixture was stirred at room temperature for 5 min. K_3PO_4 (287 mg, 1.35 mmol), **1b** (58 mg, 0.30 mmol), **2b** (92 mg, 0.45 mmol), and toluene (0.6 mL) were added to the vial, and the cap was closed. The contents of the vial were stirred at 150 °C for 20 h. The reaction mixture was cooled to room temperature, and then the crude mixture was filtered through a pad of silica gel and analyzed by GC. The filtrate was concentrated *in vacuo* to give a residue, which was purified by column chromatography over silica gel (eluent: hexane/EtOAc = 9/1) to give **3bb** as a white solid (35 mg, 70% yield).

*2-Phenylnaphthalene (**3aa**).*[19] The general procedure was used, except that the reaction was conducted at 120 °C for 24 h. The yield was only determined by GC since this is a model compound used for optimization studies (88% GC yield); ^1H NMR (400 MHz, $CDCl_3$) δ

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7.39−7.41 (m, 1H), 7.47−7.52 (m, 4H), 7.72−7.77 (m, 3H), 7.86−7.94 (m, 3H), 8.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.7, 125.9, 126.1, 126.4, 127.5, 127.6, 127.8, 128.3, 128.6, 129.0, 132.8, 133.8, 138.7, 141.3. HRMS (EI+) m/z $[M]^+$ calcd for $C_{16}H_{12}$ 204.0939, found 204.0937.

*Biphenyl (**3ba**).*[20] The general procedure was used, except that the reaction was conducted at 120 °C for 24 h. The yield was only determined by GC since this is a model compound used for optimization studies (71% GC yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.39 (m, 2H), 7.44−7.48 (m, 4H), 7.61−7.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.3, 127.4, 128.9, 141.4. HRMS (EI+) m/z $[M]^+$ calcd for $C_{12}H_{10}$ 154.0783, found 154.0780.

*4-Methyl-1,1′-biphenyl (**3bb**).*[21] The general procedure was used; white solid (35 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.24−7.28 (m, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.49 (dd, J = 6.4, 2.0 Hz, 2H), 7.58 (dd, J = 8.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 127.1, 128.9, 129.6, 137.2, 138.5, 141.3. HRMS (EI+) m/z $[M]^+$ calcd for $C_{13}H_{12}$ 168.0939, found 168.0935.

*4-(1,1-Dimethylethyl)-1,1′-biphenyl (**3bc**).*[22] The general procedure was used; white solid (43 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9H), 7.33 (t, J = 7.4 Hz, 1H), 7.41−7.49 (m, 4H), 7.54 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 34.7, 125.9, 126.9, 127.1, 127.2, 128.8, 138.5, 141.2, 150.4. HRMS (EI+) m/z $[M]^+$ calcd for $C_{16}H_{18}$ 210.1409, found 210.1405.

*1,1′:4′,1″-Terphenyl (**3bd**).*[23] The general procedure was used; white solid (53 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dt, J = 7.6, 1.2 Hz, 2H), 7.49 (t, J = 7.8 Hz, 4H), 7.64−7.67 (m, 4H), 7.69 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 127.5, 127.6, 129.0, 140.3, 140.9. HRMS (EI+) m/z $[M]^+$ calcd for $C_{18}H_{14}$ 230.1096, found 230.1095.

*N,N-Dimethyl-[1,1′-biphenyl]-4-amine (**3be**).*[24] The general procedure was used; white solid (46 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (s, 6H), 6.84 (d, J = 8.8 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.54 (dd, J = 6.8, 2.4 Hz, 2H), 7.59 (dd, J = 7.2, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.7, 112.9, 126.1, 126.4, 127.8, 128.8, 129.4, 141.4, 150.1. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{15}N$ 197.1204, found 197.1200.

*Methyl [1,1′-Biphenyl]-4-carboxylate (**3bf**).*[25] The general procedure was used; white solid (43 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3H), 7.40 (tt, J = 7.4, 1.6 Hz, 1H), 7.48 (tt, J = 7.4, 1.6 Hz, 2H), 7.63 (dt, J = 8.4, 1.2 Hz, 2H), 7.67 (dt, J = 8.2, 1.8 Hz, 2H), 8.11 (dt, J = 8.2, 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 127.2, 127.4, 128.3, 129.1, 130.2, 140.2, 145.8, 167.2. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0839.

*2-(4-Fluorophenyl)-naphthalene (**3ag**).*[26] The general procedure was used except that **1a** was used as the substrate; white solid (36 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.21 (m, 2H), 7.51−7.56 (m, 2H), 7.67−7.72 (m, 3H), 7.89−7.93 (m, 3H), 8.00−8.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.8 (d, J = 22.0 Hz), 125.5, 125.8, 126.1, 126.5, 127.8, 128.3, 128.7, 129.1 (d, J = 7.67 Hz), 132.7, 133.8, 137.4 (d, J = 2.88 Hz), 137.7, 162.7 (d, J = 246.3 Hz). HRMS (EI+) m/z $[M]^+$ calcd for $C_{16}H_{11}F$ 222.0845, found 222.0844.

*1-Phenylnaphthalene (**3bh**).*[27] The general procedure was followed used; white solid (41 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.44 (m, 9H), 7.86−7.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.5, 125.9, 126.2, 127.1, 127.4, 127.8, 128.4, 130.2, 131.7, 133.9, 140.4, 140.9. HRMS (EI+) m/z $[M]^+$ calcd for $C_{16}H_{12}$ 204.0939, found 204.0938.

*5-Phenylbenzo[d][1,3]dioxole (**3bi**).*[28] The general procedure was used; white solid (45 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 2H), 6.89 (dd, J = 8.0, 0.8 Hz, 1H), 7.08−7.05 (m, 2H), 7.32 (tt, J = 7.2, 1.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.52 (dd, J = 7.6, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.3, 107.8, 108.7, 120.8, 127.0, 127.1, 128.9, 135.8, 141.1, 147.2, 148.3. HRMS (EI+) m/z $[M]^+$ calcd for $C_{13}H_{10}O_2$ 198.0681, found 198.0682.

*1-Methyl-5-phenyl-1H-indole (**3bj**).*[29] The general procedure was used; pale yellow solid (47 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.55 (d, J = 2.4 Hz, 1H), 7.09 (d, J = 3.2 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.36−7.53 (m, 4H), 7.66 (dd, J = 8.0, 0.8 Hz, 2H), 7.85 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.1, 101.5, 109.5, 119.6, 121.5, 126.4, 127.5, 128.8, 129.1, 129.6, 133.0, 136.4, 142.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{15}H_{13}N$ 207.1048, found 207.1048.

*3-Phenylpyridine (**3bk**).*[30] The general procedure was used; white solid (32 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 7.6, 4.8 Hz, 1H), 7.29−7.31 (m, 1H), 7.33−7.38 (m, 2H), 7.44−7.47 (m, 2H), 7.71(dt, J = 8.0, 1.6 Hz, 1 H), 8.50 (dd, J = 4.8, 1.6 Hz, 1H), 8.78 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.2, 126.8, 127.8, 128.8, 133.9, 136.2, 137.4, 148.0, 148.2. HRMS (EI+) m/z $[M + H]^+$ calcd for $C_{11}H_{10}N^+$ 156.0808, found 156.0814.

*Ethyl 4′-Methyl-[1,1′-biphenyl]-4-carboxylate (**3cb**).*[31] The general procedure was used; white solid (43 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (t, J = 7.4 Hz, 3H), 2.42 (s, 3H), 4.41 (q, J = 7.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 21.3, 61.1, 126.9, 127.2, 129.1, 129.8, 130.2, 137.3, 138.2, 145.6, 166.7. HRMS (EI+) m/z $[M]^+$ calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1148.

*N,N,4′-Trimethyl-[1,1′-biphenyl]-4-amine (**3db**).*[32] The general procedure was used, except that the reaction was conducted at 160 °C using 10 mol % of $Ni(cod)_2$, 30 mol % of **L5** and NaO^{t}Bu; white solid (38 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.00 (s, 6H), 6.81 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 40.8, 113.0, 126.3, 127.0, 127.7, 129.5, 135.8, 138.5, 149.9. HRMS (EI+) m/z $[M]^+$ calcd for $C_{15}H_{17}N$ 211.1361, found 211.1360.

*4′-Methyl-3-(trifluoromethyl)-1,1′-biphenyl (**3eb**).*[33] The general procedure was used; white solid (46 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.29 (d, J = 8.4 Hz, 2H), 7.49−7.59 (m, 4H), 7.76 (d, J = 7.2 Hz, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 123.8 (q, J = 3.9 Hz), 124.4 (q, J = 271 Hz), 127.2, 129.3, 129.9, 130.3, 131.2 (q, J = 31.87 Hz), 137.0, 138.1, 142.1. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{11}F_3$ 236.0813, found 236.0809.

*Ethyl 4′-Methyl-[1,1′-biphenyl]-3-carboxylate (**3fb**).*[34] The general procedure was used; white solid (51 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J = 7.4 Hz, 3H), 2.34 (s, 3H), 4.34 (q, J = 7.2 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.68 (dt, J = 7.8, 1.6 Hz, 1H), 7.92 (dt, J = 7.8, 1.4 Hz, 1H), 8.19 (t, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 21.3, 61.2, 127.2, 128.2, 128.9, 129.7, 131.1, 131.4, 137.5, 137.7, 141.5, 166.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1153.

*4-Methyl-1,1′:2′,1″-terphenyl (**3gb**).*[35] The general procedure was used, except that the reaction was conducted at 160 °C using $Ni(cod)_2$ (10 mol %), **L3** (30 mol %), NaO^{t}Bu (30 mol %) and **2b** (6.0 equiv); colorless oil (43 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 6.94−7.05 (m, 4H), 7.18−7.15 (m, 2H), 7.26−7.22 (m, 3H), 7.41−7.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 126.5, 127.4, 127.6, 128.0, 128.7, 129.9, 130.0, 130.8, 136.2, 138.7, 140.7, 141.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{19}H_{16}$ 244.1252, found 244.1251.

*N,N,2′-Trimethyl[1,1′-biphenyl]-4-amine (**3he**).*[36] The general procedure was used, except that the reaction was conducted at 160 °C using $Ni(cod)_2$ (10 mol %), **L3** (30 mol %), NaO^{t}Bu (30 mol %) and **2e** (6.0 equiv); colorless oil (47 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.00 (S, 6H), 6.79−6.81 (m, 2H), 7.21−7.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 40.8, 112.3, 125.9, 126.7, 130.06, 130.08, 130.4, 135.6, 142.1, 149.4. HRMS (EI+) m/z $[M]^+$ calcd for $C_{15}H_{17}N^+$ 211.1361, found 211.1357.

*2-(p-Tolyl)pyridine (**3ib**).*[37] The general procedure was used; white solid (36 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.20 (ddd, J = 6.4, 4.8, 1.8 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.68−7.78 (m, 2H), 7.90 (d, J = 8.4 Hz, 2H), 8.68 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 120.4, 121.9, 126.9, 129.6, 136.8, 139.1, 149.7, 157.6. HRMS (EI+) m/z $[M]^+$ calcd for $C_{12}H_{11}N$ 169.0891, found 169.0880.

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*2-(p-Tolyl)naphthalene (**3jb**).*[38] The general procedure was used; white solid (40 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.30 (d, J = 7.8 Hz, 2H), 7.56−7.42 (m, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.74 (dd, J = 8.7, 1.8 Hz, 1H), 7.79−7.97 (m, 3H), 8.02 (d, J = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 125.5, 125.6, 125.8, 126.3, 127.3, 127.7, 128.2, 128.4, 129.7, 132.6, 133.8, 137.2, 138.3, 138.6. HRMS (EI+) m/z $[M]^+$ calcd for $C_{17}H_{14}$ 218.1096, found 218.1097.

*2-(4-Methylbenzyl)naphthalene (**3kb**).*[39] The general procedure was used; pale-yellow oil (58 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.14 (s, 2H), 7.07−7.25 (m, 4H), 7.35 (dd, J = 8.5, 1.6 Hz, 1H), 7.40−7.58 (m, 2H), 7.67 (s, 1H), 7.73−7.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 41.8, 125.4, 126.1, 127.1, 127.68, 127.75, 127.77, 128.2, 129.0, 129.3, 132.2, 133.8, 135.8, 138.1, 139.0. HRMS (EI+) m/z $[M]^+$ calcd for $C_{18}H_{16}$ 232.1252, found 232.1250.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01627.

^{1}H and ^{13}C NMR spectra for **1d**, **1f**, and all the cross-coupling products (PDF)

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Notes

The authors declare no competing financial interest.

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