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Cross-Coupling of Aryltrimethylammonium Iodides with Arylzinc Reagents Catalyzed by Amido Pincer Nickel Complexes

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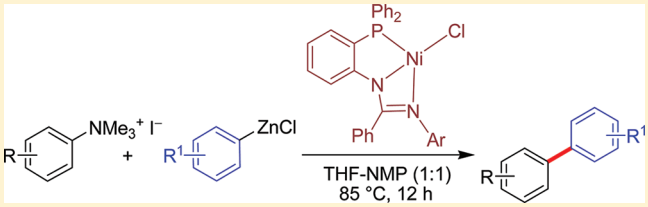
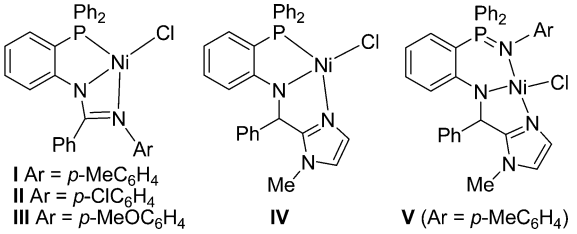
Supporting Information

ABSTRACT: The cross-coupling reaction of aryltrimethylammonium iodides with aryl- or heteroarylzinc chlorides catalyzed by amido pincer nickel complexes was performed. The reaction requires low catalyst loading and displays broad substrate scope.



Transition-metal-catalyzed cross-coupling reactions, including Kumada, Negishi, Suzuki, and Stille cross-couplings, are powerful tools to construct carbon−carbon bonds in organic synthesis.[1,2] The electrophiles exploited in these reactions are principally organic iodides, bromides, triflates,[1−3] and, more recently, chlorides[4] and other O-based substrates such as tosylates, mesylates, and carboxylates.[5] Reactions through C−N bond cleavage of the electrophilic substrates are scarce, although Wenkert and co-workers carried out the nickel-catalyzed reaction of aryltrimethylammonium iodides with Grignard reagents in the early stage of cross-coupling studies.[6] On the other hand, nitrogen-containing compounds such as aryl and alkylamines are very important and widely available in the natural world and in industry. The amino groups in arylamines are also important activating and directing groups, which can lead to selective functionalization of aromatic rings. Hence, the transformation of N-containing compounds through catalytic activation of C−N bonds is an attractive topic. Several related studies have been reported. In 2007, Kakiuchi and co-workers reported a ruthenium-catalyzed Suzuki coupling through C−N bond cleavage of anilines with the aid of a carbonyl group at the ortho position.[7] In 2003, MacMillan et al. carried out the Suzuki coupling of aryltrimethylammonium triflates with $Ni(cod)_2$/IMes as a catalyst.[8] Recently, Reeves et al. developed the coupling of aryltrimethylammonium triflates with Grignard reagents using palladium as the catalyst.[9] More recently, we reported the coupling of aryltrimethylammonium iodides with aryl or alkylzinc chlorides catalyzed by $Ni(PCy_3)_2Cl_2$.[10] After that, we intended to develop new catalyst systems to improve the coupling reaction. Amido pincer nickel complexes were found to be very effective to catalyze cross-coupling of aryl chlorides and arylzinc reagents.[11] The preliminary experiments showed that the pincer nickel complexes we reported previously can catalyze the reaction of aryltrimethylammonium salts with arylzinc reagents, although the activity is lower than $Ni(PCy_3)_2Cl_2$. However, the catalytic properties could be improved through modifying the ligands. For this purpose, we designed new amido pincer ligands and synthesized their complexes of nickel (**I**−**V**, Scheme 1). Catalytic properties of these complexes in the reaction of aryltrimethylammonium salts with arylzinc chlorides were evaluated, and a series of efficient cross-couplings were carried out. Here we report the results.

Scheme 1. Complexes I−V Used for Catalyzing the Cross-Coupling of an Arylammonium Salt with an Arylzinc Reagent



Synthetic routes of complexes **I**−**V** are summarized in the Supporting Information. The catalytic investigation began with an examination of the reaction of p-$MeOC_6H_4NMe_3^+I^-$ with p-MeC_6H_4ZnCl to evaluate the solvent effect and the catalytic activities of complexes **I**−**V**. The screening results are listed in Table 1. In the presence of 1 mol % **I**, the reaction can proceed in either THF or a 1:1 mixture of THF and toluene, and each gives the cross-coupling product in 40% yield, while in toluene, no desired product was obtained (entries 1−3, Table 1). NMP is often a good solvent or cosolvent in the catalyzed cross-coupling of organozinc reagents. Hence, NMP and a mixture of NMP and THF or toluene were examined as a solvent in the **I**-catalyzed reaction of p-$MeOC_6H_4NMe_3^+I^-$ with p-MeC_6H_4ZnCl. The results showed that the suitable solvent is a 1:1 mixture of NMP and THF, which leads to 90% yield of cross-coupling product (entries 4−8, Table 1). This solvent system was

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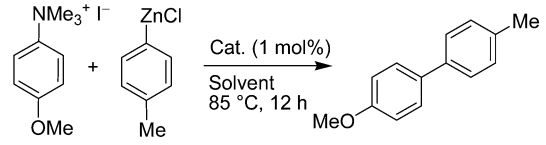
Table 1. Evaluation of the Catalytic Activity of Complexes I–V in the Reaction of *p*-MeOC$_6$H$_4$NMe$_3^+$ I$^-$ with *p*-MeC$_6$H$_4$ZnCl[a]

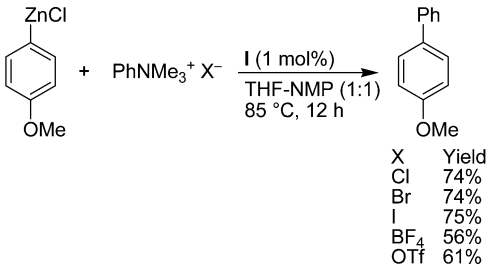


entry	complex	solvent	yield (%)[b]
1	**I**	THF	40
2	**I**	toluene	nr[c]
3	**I**	THF/toluene (1:1)	40
4	**I**	NMP	62
5	**I**	NMP/toluene (1:1)	62
6	**I**	THF/NMP (1:2)	56
7	**I**	THF/NMP (2:1)	67
8	**I**	THF/NMP (1:1)	90
9[d]	**I**	THF/NMP (1:1)	72
10	**II**	THF/NMP (1:1)	67
11	**III**	THF/NMP (1:1)	74
12	**IV**	THF/NMP (1:1)	52
13	**V**	THF/NMP (1:1)	45

[a]Unless otherwise stated, reactions were carried out according to the conditions indicated by the above equation. 1.5 equiv of PhZnCl was used. [b]Isolated product yields. [c]nr = no reaction. [d]Reaction time was 9 h.

applied in the following tests. Further studies using complexes **II**–**V** as the catalyst showed that each of them gives lower yield than **I** (entries 10–13, Table 1). The yields are **I** > **III** > **II** > **IV** > **V**. It was also noted that in the **I**-catalyzed reaction, shorter reaction time results in lower product yield (entry 9, Table 1).

Next, the counterion effect was examined using phenyltrimethylammonium salts as the electrophilic substrates and Cl$^-$, Br$^-$, I$^-$, BF$_4^-$, and OTf$^-$, respectively, as the counterion. The reaction of *p*-MeOC$_6$H$_4$ZnCl with PhNMe$_3^+$X$^-$ was carried out in the presence of 1 mol % **I** in a 1:1 mixture of NMP and THF at 85 °C (eq 1). The results showed that the

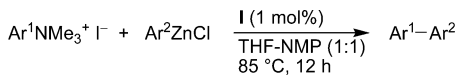


(1)

halide salts are the most reactive, while the tetrafluoroborate salt exhibits the lowest reactivity. The chloride, bromide, and iodide display similar reactivity.

With the optimized reaction conditions, we tested the scope of the cross-coupling reaction of aryltrimethylammonium iodides with arylzinc reagents (Table 2). Reaction of phenyltrimethylammonium iodide with a series of arylzinc chlorides gives good to excellent product yields (entries 1–4, Table 2). It was noted that both *p*-MeOC$_6$H$_4$ZnCl and *p*-Me$_2$NC$_6$H$_4$ZnCl are less reactive than *p*-MeC$_6$H$_4$ZnCl, although the former two nucleophiles are electron-rich ones. A supposed reason is that coordination of the OMe or NMe$_2$ group to a metal center (e.g., Zn^{2+}) decreases the nucleophilic activity of 4-methoxyphenyl or 4-dimethylaminophenyl anion. The electron-rich

Table 2. Reaction of Aryltrimethylammonium Iodides with Arylzinc Chlorides Catalyzed by Complex I[a]



entry	Ar^1	Ar^2	yield (%)[b]
1	Ph	*p*-MeC$_6$H$_4$	96
2	Ph	*o*-MeC$_6$H$_4$	80
3	Ph	*p*-MeOC$_6$H$_4$	75
4	Ph	*p*-Me$_2$NC$_6$H$_4$	80
5	*p*-MeOC$_6$H$_4$	*p*-MeC$_6$H$_4$	90
6	*m*-MeOC$_6$H$_4$	*p*-MeC$_6$H$_4$	87
7	*p*-MeOC$_6$H$_4$	*o*-MeC$_6$H$_4$	68
8[c]	*p*-MeOC$_6$H$_4$	*o*-MeC$_6$H$_4$	78
9[d]	*p*-MeOC$_6$H$_4$	*o*-MeC$_6$H$_4$	88
10[c]	*m*-MeOC$_6$H$_4$	*p*-Me$_2$NC$_6$H$_4$	87
11	*p*-EtOOCC$_6$H$_4$	*p*-MeC$_6$H$_4$	92
12	*p*-PhC(O)C$_6$H$_4$	*p*-MeC$_6$H$_4$	88
13	*p*-EtOOCC$_6$H$_4$	*o*-MeC$_6$H$_4$	91
14	*p*-PhC(O)C$_6$H$_4$	*o*-MeC$_6$H$_4$	94
15	*p*-EtOOCC$_6$H$_4$	*p*-MeOC$_6$H$_4$	89
16	*o*-MeC$_6$H$_4$	*p*-MeC$_6$H$_4$	97
17	*o*-MeC$_6$H$_4$	*p*-MeOC$_6$H$_4$	75
18	*o*-MeC$_6$H$_4$	*p*-Me$_2$NC$_6$H$_4$	86
19	*p*-EtOOCC$_6$H$_4$	*p*-CF$_3$C$_6$H$_4$	66
20[e]	*p*-EtOOCC$_6$H$_4$	*p*-CF$_3$C$_6$H$_4$	88
21	*p*-PhC(O)C$_6$H$_4$	*p*-CF$_3$C$_6$H$_4$	80
22	*p*-MeOC$_6$H$_4$	*p*-CF$_3$C$_6$H$_4$	42
23[f]	*p*-MeOC$_6$H$_4$	*p*-CF$_3$C$_6$H$_4$	56
24	*p*-EtOOCC$_6$H$_4$	2-furyl	99
25	*p*-PhC(O)C$_6$H$_4$	2-furyl	99
26	*m*-MeOC$_6$H$_4$	2-furyl	75
27[g]	*p*-EtOOCC$_6$H$_4$	2-thienyl	80
28[g]	*p*-PhC(O)C$_6$H$_4$	2-thienyl	78
29	2-Py	*p*-MeC$_6$H$_4$	97
30	2-Py	*o*-MeC$_6$H$_4$	93
31	2-Py	*p*-MeOC$_6$H$_4$	90
32	2-Py	*p*-Me$_2$NC$_6$H$_4$	97
33	2-Py	2-furyl	94
34	2-Py	*p*-CF$_3$C$_6$H$_4$	82

[a]Unless otherwise stated, reactions were performed with 0.5 mmol aryltrimethylammonium iodides and 0.75 mmol arylzinc chlorides according to the conditions indicated by the above equation. [b]Isolated product yields. [c]2 mol % **I** was employed as the catalyst. [d]1 mol % **III** was employed as the catalyst. [e]Bath temperature was 130 °C. [f]5 mol % **I** was employed as the catalyst. [g]2.5 equiv of 2-thienylzinc chloride was employed.

aryltrimethylammonium iodides *p*-MeOC$_6$H$_4$NMe$_3^+$I$^-$ and *m*-MeOC$_6$H$_4$NMe$_3^+$I$^-$ also react with *p*-MeC$_6$H$_4$ZnCl smoothly, giving cross-coupling products in excellent yields (entries 5 and 6, Table 2). However, reaction of *p*-MeOC$_6$H$_4$NMe$_3^+$I$^-$ with *o*-MeC$_6$H$_4$ZnCl seems to be more difficult because of the hindered effect of the *ortho*-methyl group in *o*-MeC$_6$H$_4$ZnCl. **I** (1 mol %) results in only 68% product yield. Higher catalyst loadings (2 mol %) lead to higher product yields (entries 7 and 8, Table 2). These results are consistent with the conversion of the ammonium salt determined by ^{1}H NMR spectra of the crude products, 1 mol % **I** giving 75% conversion and 2 mol % **I** leading to 86% conversion. We also estimated the TON of the reaction of *p*-MeOC$_6$H$_4$NMe$_3^+$I$^-$ with *o*-MeC$_6$H$_4$ZnCl catalyzed by **I**, which is about 120. These facts showed that **I** is not very efficient in catalyzing the cross-coupling of *p*-MeOC$_6$H$_4$NMe$_3^+$I$^-$

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and *o*-MeC_6H_4ZnCl. Further studies proved that complex **III** is a better catalyst for this reaction. It leads to 88% isolated yield under the same conditions as those using **I** as the catalyst (entry 9, Table 2). The reaction using **II** as the catalyst gave similar yield to that using **I**, whereas the reaction using **IV** or **V** as the catalysts led to low yields. Reaction of *m*-$MeOC_6H_4NMe_3^+I^-$ with *p*-$Me_2NC_6H_4ZnCl$ catalyzed by **I** also requires higher catalyst loadings, which results in excellent product yields (entry 10, Table 2). The electron-deficient aryltrimethylammonium iodides show good reactivity. Reactions of both *p*-$EtOOCC_6H_4NMe_3^+I^-$ and *p*-$PhC(O)C_6H_4NMe_3^+I^-$ with either *p*-MeC_6H_4ZnCl or *o*-MeC_6H_4ZnCl gave excellent results under the standard conditions (entries 11−14, Table 2). Reaction of *p*-$MeOC_6H_4ZnCl$ with *p*-$EtOOCC_6H_4NMe_3^+I^-$ also affords cross-coupling product in excellent yield (entry 15, Table 2). *o*-$MeC_6H_4NMe_3^+I^-$ displays similar reactivity to $PhNMe_3^+I^-$ (entries 16−18, Table 2). The hindered effect of its *ortho*-methyl group seems to be less than the corresponding one in *o*-MeC_6H_4ZnCl. The electron-deficient nucleophiles exhibit lower reactivity than electron-rich ones. Reactions of *p*-$EtOOCC_6H_4ZnBr$ with both unactivated and activated aryltrimethylammonium iodides give poor results. However, reaction of *p*-$CF_3C_6H_4ZnCl$ with activated aryltrimethylammonium iodides generates cross-coupling products in good yields, although reaction of *p*-$EtOOCC_6H_4NMe_3^+I^-$ requires a higher reaction temperature (entries 19−21, Table 2). Reaction of deactivated *p*-$MeOC_6H_4NMe_3^+I^-$ with *p*-$CF_3C_6H_4ZnCl$ gives a poor result, only 42% yield of cross-coupling product being isolated under the standard conditions. Catalyst loadings of 5 mol % for this reaction result in 56% product yield (entries 22 and 23, Table 2). In this reaction, the homocoupling of *p*-$CF_3C_6H_4ZnCl$ is a main side reaction. Higher reaction temperatures can not increase the yield of the cross-coupling product.

Heteroarylzinc reagents are also good nucleophilic substrates in the reactions. Reactions of 2-furylzinc chloride with activated aryltrimethylammonium iodides, *p*-$EtOOCC_6H_4NMe_3^+I^-$ and *p*-$PhC(O)C_6H_4NMe_3^+I^-$, afford cross-coupling products in almost quantitative yields (entries 24 and 25, Table 2). However, the reaction using deactivated aryltrimethylammonium salt, *m*-$MeOC_6H_4NMe_3^+I^-$, results in a relatively low yield (entry 26, Table 2). 2-Thienylzinc chloride displays lower reactivity than 2-furylzinc chloride. Reactions of 2-thienylzinc chloride with either *p*-$EtOOCC_6H_4NMe_3^+I^-$ or *p*-$PhC(O)C_6H_4NMe_3^+I^-$ require excess zinc reagents (2.5 equiv) and form corresponding cross-coupling products in 80 and 78% yields, respectively (entries 27 and 28, Table 2). 2-Pyridyltrimethylammonium iodide is a highly active electrophilic species in the reaction. Its reactions with a range of electron-rich zinc reagents proceed smoothly, giving corresponding cross-coupling products in excellent yields (entries 29−33, Table 2). 2-Pyridyltrimethylammonium iodide also reacts with *p*-$CF_3C_6H_4ZnCl$, but the reaction gives a little lower product yield (entry 34, Table 2).

In summary, we have synthesized several new amido pincer nickel complexes and found them to be able to catalyze cross-coupling of aryltrimethylammonium salts and arylzinc reagents. Complex **I**, [Ni(Cl){2-$P(Ph_2)C_6H_4NC(Ph)$=N(*p*-MeC_6H_4)}], exhibits the highest catalytic activity among **I**−**V** and also shows higher catalytic activity than $Ni(PCy_3)_2Cl_2$. It leads to cross-coupling of activated, unactivated, and deactivated aryltrimethylammonium iodides as well as 2-pyridyltrimethylammonium iodide with aryl- or heteroarylzinc reagents in moderate to excellent yields. The reactions require low catalyst loadings in most cases and tolerate functional groups such as ester, keto, and CF_3 groups. Moreover, this investigation proves the potential of amido pincer nickel catalyst system for the C−N bond activation of aryltrimethylammonium salts. Further modification and optimization of the structure of the ligands to improve their activity are underway.

■ EXPERIMENTAL SECTION

All air or moisture sensitive manipulations were performed under dry nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (benzene, toluene), sodium/benzophenone (*n*-hexane, THF, and diethyl ether) or CaH_2 (CH_2Cl_2) and degassed prior to use. NMP was dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under nitrogen atmosphere. *n*-BuLi was purchased from Acros Organics and used as received. $CDCl_3$ and DMSO-d_6 were purchased from Cambridge Isotope Laboratories, Inc., and stored over 4 Å molecular sieves. ArN=C(Cl)Ph,[12] *p*-$MeC_6H_4N_3$,[13] 2-diphenylphosphanylaniline,[14] *N*-benzylidene-2-(diphenylphosphino) benzeneamine,[15] (DME)$NiCl_2$,[16] and (1-methylimidazol-2-yl)lithium[17] were prepared according to literature methods. Aryltrimethylammonium salts were obtained either by preparation according to the procedures we used previously[10] or by purchasing from commercial vendors. ArZnCl were prepared in situ through reaction of $ZnCl_2$ with corresponding aryllithium (*p*-MeC_6H_4Li,[18] *o*-MeC_6H_4Li,[19] *p*-$Me_2NC_6H_4Li$,[20] *p*-$CF_3C_6H_4Li$,[21] *p*-$MeOC_6H_4Li$,[21] 2-furyllithium,[22] and 2-thienyllithium[23]). All other chemicals were obtained from commercial vendors and used as received. NMR spectra were recorded on a 300 MHz spectrometer at ambient temperature. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to TMS or internal solvent resonances; the ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Elemental analysis was performed by the Analytical Center of University of Science and Technology of China. Column chromatography was performed on silica gel (200−300 mesh).

Synthesis of 2-$P(Ph_2)C_6H_4NHC(Ph)$=N(*p*-MeC_6H_4) (1). A mixture of 2-diphenylphosphanylaniline (1.20 g, 4.33 mmol), *N*-(*p*-tolyl)benzimidoyl chloride (1.00 g, 4.35 mmol), and triethylamine (0.66 mL, 4.57 mmol) in toluene (30 mL) was refluxed for 48 h. $(C_2H_5)_3N{\cdot}HCl$ was removed by filtration, and the filtrate was concentrated to afford a yellow solid of **1** (0.915 g, 45%): mp 223−224 °C; ^1H NMR ($CDCl_3$) δ 2.06 (s), 2.15 (s), 2.23 (s), 2.35 (s), 5.69 (b), 6.20−6.37 (m), 6.53−6.79 (m), 6.89−7.05 (m), 7.15−7.56 (m), 7.87 (d, J = 3.3 Hz); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.1, 29.8, 120.6, 120.9, 122.5, 125.8, 127.8, 128.3, 128.4, 128.4, 128.8, 128.9, 129.3, 130.2, 130.4, 132.9, 134.0, 134.2, 134.3, 134.4, 138.2, 139.0, 156.6; ^{31}P NMR ($CDCl_3$) δ −23.96, −16.94, −15.60, 26.42. Anal. Calcd for $C_{32}H_{27}N_2P$: C 81.68, H 5.78, N 5.95. Found: C 81.66, H 5.77, N 6.08.

*Compounds **2** and **3** Were Synthesized Using the Same Method as for **1**.* **2**, (0.70 g, 33%), yellow solid: mp 203−205 °C; ^1H NMR ($CDCl_3$) δ 6.10−6.67 (m), 6.77−6.98 (m), 7.11−7.27 (m), 7.34 (s), 7.48−7.78 (m), 8.94 (s), 10.17 (s); ^{13}C NMR ($CDCl_3$) δ 121.7, 121.9, 122.3, 122.4, 123.5, 123.8, 128.4, 128.65, 128.74, 129.4, 129.6, 129.9, 132.2, 132.3, 133.1, 134.0, 134.3; ^{31}P NMR ($CDCl_3$) δ −20.68, −17.03, 25.53, 32.61. Anal. Calcd for $C_{31}H_{24}N_2ClP{\cdot}0.2H_2O$ (the sample for elemental analysis was purified by recrystallization in a mixture of ethanol and water): C 75.29, H 4.97, N 5.66. Found: C 75.17, H 4.83, N 5.58.

3, (1.41 g, 67%), yellow solid: mp 170−172 °C; ^1H NMR (DMSO-d_6) δ 3.42 (s), 3.50 (s), 3.57 (s), 3.67 (s), 6.23 (s), 6.41 (s), 6.53−6.73 (m), 6.84−6.96 (m), 7.12 (s), 7.29 (s), 7.40 (s), 7.54−7.75 (m), 7.99 (d, J = 6.6 Hz), 8.35 (s), 9.10 (s), 9.16 (s); ^{13}C NMR (DMSO-d_6) δ 55.0, 55.3, 79.2, 113.1, 113.2, 113.4, 113.6, 113.7, 120.2, 120.7, 121.1, 121.2, 121.7, 122.0, 122.5, 126.8, 127.7, 128.0, 128.5, 128.6, 128.9, 129.0, 129.4, 129.7, 129.8, 130.3, 131.3, 131.8, 131.9, 133.6, 133.9, 134.1, 134.9, 137.3, 137.4, 153.6, 153.9, 154.3; ^{31}P NMR (DMSO-d_6) δ −19.30, −18.53, −17.54, 23.70. Anal. Calcd for $C_{32}H_{27}N_2OP$: C 78.99, H 5.59, N 5.76. Found: C 78.95, H 5.78, N 5.69.

Synthesis of [Ni(Cl){2-$P(Ph_2)C_6H_4NC(Ph)$=N(*p*-MeC_6H_4)}] (I). To a stirred suspension of **1** (0.37 g, 0.79 mmol) in THF (10 mL) was

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added dropwise LDA [prepared from diisopropylamine (0.12 mL, 0.85 mmol) and *n*-BuLi (0.34 mL, a 2.5 M of solution in hexane, 0.85 mmol) in THF (10 mL)] at about −80 °C. The mixture was warmed to room temperature and stirred for 3 h. The resultant solution was added dropwise to a stirred suspension of (DME)$NiCl_2$ (0.17 g, 0.79 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed in vacuo. The residue was dissolved in toluene. The resultant solution was filtered, and the filtrate was concentrated to give brown crystals of **I** (0.24 g, 53%): mp 252−254 °C; ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3H), 6.17 (dd, J = 4.2, 8.4 Hz, 1H), 6.69 (d, J = 8.1 Hz, 2H), 6.72−6.82 (m, 3H), 6.90 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 8.4 Hz, 1H), 7.37−7.57 (m, 11H), 7.91−7.98 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.8, 115.2 (d, J = 9.4 Hz), 121.7 (d, J = 7.2 Hz), 123.6, 127.6, 128.7, 128.9, 129.1, 129.3, 130.7, 131.2 (d, J = 2.3 Hz), 132.4, 132.9, 133.2, 133.4, 133.5, 139.8, 151.7, 152.0, 169.4; ^{31}P NMR ($CDCl_3$) δ 25.23. Anal. Calcd for $C_{32}H_{26}N_2PClNi$: C 68.18, H 4.65, N 4.97. Found: C 67.81, H 4.59, N 4.76.

*Complexes **II** and **III** Were Synthesized from **2** and **3** Using the Same Procedure as for **I**.* **II**, (0.20 g, 43%), brown solid: mp 238−240 °C; ^{1}H NMR ($CDCl_3$) δ 6.20 (dd, J = 4.5, 8.4 Hz, 1H), 6.71 (d, J = 8.7 Hz, 2H), 6.79 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 8.7 Hz, 1H), 6.95 (d, J = 8.7 Hz, 2H), 7.17 (t, J = 8.4 Hz, 1H), 7.39 (d, J = 6.9 Hz, 2H), 7.44−7.59 (m, 9H), 7.94 (dd, J = 7.2, 12.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 115.6 (d, J = 9.2 Hz), 122.3 (d, J = 6.7 Hz), 122.8, 125.0, 127.7, 128.5, 128.6, 129.2 (d, J = 10.9 Hz), 129.6, 131.06, 131.5, 132.6, 132.8, 133.4 (d, J = 10.7 Hz), 133.7, 141.4, 151.5, 151.8, 169.9; ^{31}P NMR ($CDCl_3$) δ 25.82. Anal. Calcd for $C_{31}H_{23}N_2Cl_2PNi$: C 63.74, H 3.97, N 4.80. Found: C 63.42, H 3.88, N 4.87.

III·0.8C_7H_8, (0.186 g, 36%), brown solid: mp 221−222 °C; ^{1}H NMR ($CDCl_3$) δ 2.36 (s), 3.66 (s, 3H), 6.16 (dd, J = 4.2, 8.1 Hz, 1H), 6.56 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 6.91 (t, J = 8.1 Hz, 1H), 7.15 (t, J = 8.4 Hz, 1H), 7.34−7.57 (m, 11H), 7.95 (dd, J = 7.2, 12 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.4, 113.8, 115.3 (d, J = 9.7 Hz), 121.4, 121.6 (d, J = 7.2 Hz), 122.1, 124.9, 125.4, 127.8, 128.4, 128.9, 129.1, 129.2, 129.5, 130.8, 131.3 (d, J = 2 Hz), 132.5, 133.0, 133.4, 133.5, 133.7, 152.0, 152.2, 169.1; ^{31}P NMR ($CDCl_3$) δ 25.39. Anal. Calcd for $C_{32}H_{26}N_2ClPONi$·0.8C_7H_8: C 69.12, H 5.00, N 4.29. Found: C 69.11, H 5.06, N 4.36.

Synthesis of 2-(PPh_2)C_6H_4NHC(Ph)CN(CH)$_2$NMe (5). A solution of compound **4** (0.45 g, 1.23 mmol) in THF (15 mL) was cooled to about −80 °C. To the stirred solution was added dropwise a THF solution of $C_4H_5N_2Li$ [prepared from 1-methylimidazole (0.10 g, 1.21 mmol) and *n*-BuLi (0.50 mL, a 2.5 M of solution in hexane, 1.25 mmol) in THF (10 mL)]. The mixture was warmed to room temperature and stirred for 12 h. Water (15 mL) was added to the mixture. The organic phase was separated, and the water phase was extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and recrystallized in toluene to afford a white solid of **5** (0.40 g, 72%): mp 150−151 °C; ^{1}H NMR ($CDCl_3$) δ 3.26 (s, 3H), 5.74−5.80 (m, 2H), 6.61−6.70 (m, 3H), 6.79−6.83 (m, 1H), 6.96 (s, 1H), 7.12−7.16 (m, 3H), 7.20−7.25 (m, 3H), 7.32−7.35(m, 10H); ^{13}C NMR ($CDCl_3$) δ 33.0, 56.0, 111.4, 118.1, 120.2 (d, J = 8.3 Hz), 122.0, 126.9, 127.6 (d, J = 12.8 Hz), 128.6, 128.7, 128.8, 129.0, 130.7, 133.7, 133.9 (d, J = 3 Hz), 134.2, 134.3 (d, J = 2.3 Hz), 135.3 (d, J = 7.2 Hz), 139.4, 147.1, 149.0, 149.3; ^{31}P NMR ($CDCl_3$) δ −25.45. Anal. Calcd for $C_{29}H_{26}N_3P$: C 77.83, H 5.86, N 9.39. Found: C 77.48, H 5.84, N 9.29.

Synthesis of [Ni(Cl){2-(PPh_2)C_6H_4NC(Ph)CN(CH)$_2$NMe}] (IV). To a stirred suspension of **5** (0.31 g, 0.69 mmol) in THF (10 mL) was added dropwise *n*-BuLi (0.28 mL, a 2.5 M solution in hexanes, 0.70 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred for 3 h. The resultant solution was added dropwise to a stirred suspension of (DME)$NiCl_2$ (0.15 g, 0.69 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed in vacuo, and the residue was dissolved in toluene. The resultant solution was filtered, and the filtrate was concentrated to give green crystals of **IV** (0.24 g, 63%): mp 242−244 °C; ^{1}H NMR ($CDCl_3$) δ 3.38 (s, 3H), 5.15 (s, 1H), 6.15−6.29 (m, 2H), 6.63 (s, 1H), 6.80−6.98 (m, 2H), 7.06 (s, 1H), 7.12−7.33 (m, 4H), 7.35−7.55 (m, 5H), 7.74 (d, J = 6.9 Hz, 2H), 7.83−8.04 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 34.3, 63.0, 112.4, 113.2, 121.1, 123.9, 128.1 128.2, 128.6, 128.8, 128.9, 130.8 (d, J = 12.1 Hz), 132.8, 133.1, 133.2, 133.3, 133.8 (d, J = 10.3 Hz), 139.3; ^{31}P NMR ($CDCl_3$) δ 26.35. Anal. Calcd for $C_{29}H_{25}N_3PClNi$·0.15C_7H_8: C 65.09, H 4.76, N 7.58. Found: C 64.96, H 4.76, N 7.47.

Synthesis of 2-(*p*-MeC_6H_4N=PPh_2)C_6H_4NHC(Ph)CN(CH)$_2$NMe (6). To a stirred solution of **5** (0.31 g, 0.69 mmol) in CH_2Cl_2 (10 mL) was added dropwise *p*-$MeC_6H_4N_3$ (0.097 g, 0.73 mmol). The mixture was stirred at room temperature for 2 h. Solvent was removed in vacuo. The residue was washed with hexane to afford a yellow powder (0.30 g, 79%): mp 163−165 °C; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 3.12 (s, 3H), 5.94 (d, J = 4.8 Hz, 1H), 6.39 (d, J = 8.1 Hz, 2H), 6.57 (dt, J = 2.4, 7.5 Hz, 1H), 6.67 (s, 1H), 6.74 (d, J = 8.1 Hz, 2H), 6.79−6.93 (m, 2H), 6.96 (s, 1H), 7.15−7.32 (m, 7H), 7.38−7.61 (m, 6H), 7.63−7.77 (m, 4H), 9.47 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 20.6, 22.8, 29.8, 33.0, 56.2, 112.6 (d, J = 8.5 Hz), 116.0 (d, J = 14.3 Hz), 122.2, 122.3, 122.6, 126.8, 127.1, 127.5, 128.8, 128.9 (d, J = 5.1 Hz), 129.4, 132.0, 132.8, 132.9, 133.0, 133.3, 133.4, 133.6, 138.9, 147.1, 151.6 (d, J = 3.4 Hz); ^{31}P NMR ($CDCl_3$) δ 8.20. Anal. Calcd for $C_{36}H_{33}N_4P$: C 78.24, H 6.02, N 10.14. Found: C 78.08, H 6.03, N 9.81.

Synthesis of [Ni(Cl){2-(*p*-MeC_6H_4N=PPh_2)C_6H_4NC(Ph)-CN(CH)$_2$NMe] (V). To a stirred suspension of **6** (0.34 g, 0.62 mmol) in THF (15 mL) was added dropwise *n*-BuLi (0.25 mL, a 2.5 M solution in hexanes, 0.63 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred for 3 h. The resultant solution was added dropwise to a stirred suspension of (DME)$NiCl_2$ (0.14 g, 0.94 mmol) in THF(10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2. The resultant solution was filtered, and the filtrate was concentrated to give blue crystals of **V** (0.28 g, 70%): mp 275−278 °C; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 3.22 (s, 3H), 5.30 (s), 5.63 (s, 1H), 6.07 (dt, J = 2.4, 7.2 Hz, 1H), 6.55 (s, 1H), 6.61−6.69 (m, 2H), 6.86 (d, J = 7.8 Hz, 2H), 6.92 (s, 1H), 7.13−7.40 (m, 8H), 7.45−7.59 (m, 5H), 7.60−7.68 (m, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 8.09 (d, J = 7.2, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 34.3, 53.6 (CH_2Cl_2), 62.0, 111.8 (d, J = 13.4 Hz), 119.4, 123.0, 127.8, 128.1, 128.4, 128.6, 128.65, 128.72, 128.8, 132.2, 132.6, 132.8, 133.0, 133.1, 134.3 (d, J = 9.8 Hz), 134.8 (d, J = 9.9 Hz), 141.9, 144.6, 154.3, 157.7; ^{31}P NMR ($CDCl_3$) δ 17.01. Anal. Calcd for $C_{36}H_{32}N_4PClNi$·0.5CH_2Cl_2: C 63.70, H 4.83, N 8.14. Found: C 63.79, H 4.83, N 8.13.

General Procedure for Reaction of ArZnCl with Aryltrimethylammonium Iodides. A Schlenk tube was charged with aryltrimethylammonium iodides (0.5 mmol), catalyst (0.005 mmol), and NMP (or other solvent needed) (1.5 mL). To the stirred mixture was added ArZnCl solution (1.5 mL, 0.5 M solution in THF, 0.75 mmol) by syringe. The reaction mixture was stirred at 85 °C (bath temperature) for 12 h and then cooled to room temperature. Water (10 mL) and several drops of acetic acid were successively added. The resulting mixture was extracted with Et_2O (3 × 10 mL). The extract was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on sillca gel.

Spectral Data for the Cross-Coupling Products. *4-Methoxy-4′-methylbiphenyl.*[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H), 3.72 (s, 3H), 6.86 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 55.4, 114.2, 126.7, 128.0, 129.6, 133.8, 136.4, 138.0, 159.0.

4-Methoxybiphenyl.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H), 7.03 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.57−7.62 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.3, 126.8, 126.8, 128.2, 128.3, 133.8, 140.9, 159.3.

4-Methylbiphenyl.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 7.24 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H); ^{13}C NMR

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($CDCl_3$) δ 21.2, 126.9, 127.1, 127.1, 128.8, 129.6, 129.6, 137.1, 138.5, 141.3.

2-Methylbiphenyl.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3H), 7.20−7.26 (m, 4H), 7.28−7.33 (m, 3H), 7.37−7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.6, 125.9, 126.9, 127.4, 128.2, 129.3, 129.9, 130.4, 135.5, 142.1, 142.1.

N,N-Dimethylbiphenyl-4-amine.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.86 (s, 6H), 6.69 (d, J = 9 Hz, 2H), 7.11−7.17 (m, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.44−7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 40.7, 112.9, 126.1, 126.4, 127.8, 128.8, 129.4, 141.4, 150.1.

3-Methoxy-4′-methylbiphenyl.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 3.82 (s, 3H), 6.85 (dd, J = 2.1, 8.1 Hz, 1H), 7.10 (t, J = 2.1, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.32 (t, J = 8.1 Hz, 1H), 7.47 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 55.4, 112.5, 112.8, 119.6, 127.1, 129.6, 129.8, 137.3, 138.3, 142.8, 160.1.

1-(4-Methoxyphenyl)-2-methylbenzene.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ2.27 (s, 3H), 3.82 (s, 3H), 6.93 (d, J = 8.4 Hz, 2H), 7.18−7.25 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 20.6, 55.3, 113.6, 125.9, 127.1, 129.4, 130.0, 130.3, 130.4, 134.5, 135.6, 141.7, 158.6.

3′-Methoxy-N,N-dimethylbiphenyl-4-amine. Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.95 (s, 6H), 3.82 (d, 3H), 6.75−6.81 (m, 3H), 7.09 (t, J = 2.1 Hz, 1H), 7.12−7.16 (m, 1H), 7.29 (t, J = 8.1 Hz, 1H), 7.47−7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 40.8, 55.3, 111.5, 112.1, 113.0, 119.0, 127.9, 129.5, 129.7, 142.8, 150.0, 160.0; HR-MS (EI) m/z 228.1388 $[M + H]^+$, calcd for $C_{15}H_{18}NO$ 228.1382.

Ethyl 4′-Methylbiphenyl-4-carboxylate.[11a] Spectral data: ^{1}H NMR ($CDCl_3$)) δ 1.41 (t, J = 7.2 Hz, 3H), 2.41 (s, 3H), 4.40 (q, J = 7.2 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 21.2, 61.0,126.8, 127.2, 129.0, 129.7, 130.1, 137.2, 138.1, 145.5, 166.7.

Phenyl(p-tolyl)methanone.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 7.19 (d, J = 7.8 Hz, 2H), 7.37−7.53 (m, 5H), 7.59 (d, J = 8.7 Hz, 2H), 7.72−7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.3, 126.8, 127.2, 128.4, 129.8, 130.1, 130.8, 132.4, 136.1, 137.2, 138.0, 138.3, 145.3, 196.4.

Ethyl 2′-Methylbiphenyl-4-carboxylate.[11a] Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 3H), 2.16 (s, 3H), 4.30 (q, J = 7.2 Hz, 2H), 7.12−7.17 (m, 4H), 7.29 (d, J = 7.8 Hz, 2H), 8.00 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 20.4, 61.0, 126.0, 127.9, 129.1, 129.3, 129.5, 129.6, 130.6, 135.2, 141.0, 146.7, 166.6.

(2′-Methylbiphenyl-4-yl)(phenyl)methanone.[11a] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 7.11−7.16 (m, 4H), 7.28−7.38 (m, 4H), 7.43−7.48 (m, 1H), 7.71−7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.5, 126.0, 127.9, 128.4, 129.2, 129.6, 130.1, 130.6, 132.4, 135.2, 136.0, 137.8, 140.9, 146.4, 196.4.

Ethyl 4′-Methoxybiphenyl-4-carboxylate.[24] Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.41 (t, J = 7.2, 3H), 3.86 (s, 3H), 4.40 (q, J = 7.2, 2H), 7.00 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 8.08 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 55.5, 61.1, 114.5, 126.6, 128.5, 128.8, 130.2, 132.6, 145.3, 160.0, 166.8.

2,4′-Dimethylbiphenyl.[25] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3H), 2.37 (s, 3H), 7.16- 7.24 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 20.6, 21.3, 125.9, 126.9, 127.2, 128.9, 129.2, 129.6, 130.0, 130.4, 135.5, 136.4, 139.2, 142.0.

2′-Methyl-N,N-dimethylbiphenyl-4-amine.[24] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 2.89 (d, 6H), 6.69 (d, J = 8.7 Hz, 2H), 7.09−7.17 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 20.8, 40.8, 112.3, 125.9, 126.7, 130.1, 130.4, 135.6, 142.1, 149.4.

Ethyl 4-[4-(Trifluoromethyl)phenyl]benzoate.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.42 (t, J = 7.2 Hz, 3H), 4.41 (q, J = 7.2 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 7.71 (s, 4H), 8.14 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.4, 61.2, 125.9 (q, J = 3.7 Hz), 122.5, 127.3, 127.7, 128.5, 129.7, 130.2, 130.3, 143.6, 144.0, 166.3.

Phenyl-[4-[4-(trifluoromethyl)phenyl]phenyl]methanone.[26] Spectral data: ^{1}H NMR ($CDCl_3$) δ 7.48- 7.54 (m, 2H), 7.59−7.65 (m, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.75 (s, 4H), 7.83−7.87 (m, 2H), 7.92 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 122.5, 126.1 (q, J = 3.8 Hz), 127.3, 127.8, 128.5, 130.2, 130.9, 132.7, 137.3, 137.7, 143.67, 143.69, 143.73, 196.3.

4′-Methoxy-4-(trifluoromethyl)biphenyl.[27] Spectral data: ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3H), 6.98 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 9 Hz, 2H),7.64 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 55.5, 114.6, 122.8, 125.8 (q, J = 3.8 Hz), 126.4, 127.0, 128.5, 128.6, 129.0, 132.3, 144.4, 160.0.

Ethyl 4-(Furan-2-yl)benzoate.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.39 (t, J = 7.2 Hz, 3H), 4.37 (q, J = 7.2 Hz, 2H), 6.48 (dd, J = 1.8, 3.6 Hz, 1H), 6.76 (d, J = 3.3 Hz, 1H), 7.49 (d, J = 1.5 Hz, 1H), 7.70 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.4, 61.0, 107.2, 112.1, 123.4, 128.9, 130.1, 134.7, 143.1, 153.0 166.4.

(4-(Furan-2-yl)phenyl)(phenyl)methanone.[11a] Spectral data: ^{1}H NMR ($CDCl_3$) δ 6.53 (dd, J = 1.8, 3.6 Hz, 1H), 6.82 (dd, J = 0.6, 3.3 Hz, 1H), 7.46−7.63 (m, 4H), 7.75−7.87 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 107.5, 112.2, 123.4, 128.4, 130.0, 130.9, 132.4, 134.6, 136.0, 137.9, 143.4, 153.0, 196.1.

2-(3-Methoxyphenyl)furan.[28] Spectral data: ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3H), 6.40 (dd, J = 1.8, 3.3 Hz, 1H), 6.59 (d, J = 3.3, Hz, 1H), 6.72−6.79 (m, 1H), 7.16−7.23 (m, 3H), 7.40 (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.3, 105.4, 109.3, 111.8, 113.3, 116.5, 129.8, 132.3, 142.2, 153.9, 160.0.

2-(4-Ethoxycarbonylphenyl)thiophene.[29] Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.41 (t, J = 6.9 Hz, 3H), 4.39 (q, J = 6.9 Hz, 2H), 7.11 (dd, J = 4.2, 4.8 Hz, 1H), 7.35 (d, J = 4.8 Hz, 1H), 7.42 (d, J = 3.6 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 61.1, 124.6, 125.6, 126.3, 128.4, 129.3, 130.4, 138.7, 143.3, 166.4.

Phenyl(4-(thiophen-2-yl)phenyl)methanone.[30] Spectral data: ^{1}H NMR ($CDCl_3$) δ 7.13 (dd, J = 3.9, 5.1 Hz, 1H), 6.81 (dd, J = 0.9, 5.1 Hz, 1H), 7.45 (dd, J = 1.2, 3.6 Hz, 1H), 7.47−7.53 (m, 2H), 7.57−7.63 (m, 1H), 7.70−7.74 (m, 2H), 7.80−7.86 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 124.7, 125.6, 126.5, 128.4, 128.5, 130.1, 131.1, 132.5, 136.2, 137.8, 138.4, 143.1, 196.1.

p-Tolylpyridine.[11a] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H), 7.02−7.18 (m, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.55−7.59 (m, 2H), 7.79 (d, J = 8.4 Hz, 2H), 8.56 (dt, J = 1.5, 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 120.3, 121.8, 126.8, 129.5, 136.7, 139.0, 149.6, 157.5.

o-Tolylpyridine.[24] Spectral data: ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3H), 7.11−7.21 (m, 4H), 7.28−7.31 (m, 2H), 7.63 (dt, J = 1.8, 7.8 Hz Hz, 1H), 8.59 (d, J = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.3, 121.7, 124.2, 125.9, 128.3, 129.7, 130.8, 135.8, 136.2, 140.5, 149.2, 160.1.

2-(4′-Methoxyphenyl)pyridine.[24] Spectral data: ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H), 6.99 (d, J = 8.7 Hz, 2H), 7.12−7.16 (m, 1H), 7.62−7.70 (m, 2H), 7.95 (d, J = 8.7 Hz, 2H), 8.64 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.2, 119.9, 121.5, 128.2, 132.1, 136.7, 149.6, 157.2, 160.5.

N,N-Dimethyl-4-(pyridin-2-yl)benzenamine.[10] Spectral data: ^{1}H NMR ($CDCl_3$) δ 3.02 (s, 6H), 6.80 (d, J = 8.7 Hz, 2H), 7.07−7.12 (m, 1H), 7.63−7.70 (m, 2H), 7.92 (d, J = 9 Hz, 2H), 8.61 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 40.4, 112.3, 119.1, 120.6, 127.3, 127.7, 136.5, 149.4, 151.1, 157.6.

2-(Furan-2-yl)pyridine.[11a] Spectral data: ^{1}H NMR ($CDCl_3$) δ 6.52 (dd, J = 1.8, 3.6 Hz, 1H), 7.05 (dd, J = 0.6, 3.3 Hz, 1H), 7.09−7.18 (m, 1H), 7.52 (dd, J = 0.6, 1.8 Hz, 1H), 7.65−7.73 (m, 2H), 8.58 (dt, J = 1.2, 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 108.7, 112.2, 118.7, 122.0, 136.7, 143.4, 149.5, 149.7, 153.7.

2-(4-(Trifluoromethyl)phenyl)pyridine.[31] Spectral data: ^{1}H NMR ($CDCl_3$) δ 7.28−7.32 (m, 1H), 7.72−7.83 (m, 4H), 8.11 (d, J = 8.1 Hz, 2H), 8.73 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 120.9, 122.6, 123.1, 125.8 (J = 3.8 Hz), 126.2, 127.3, 130.7, 131.1, 137.1, 142.8, 150.1, 156.0.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic routes of the ligand precursors and nickel complexes. Crystal structure determination details, crystal data, and ORTEP drawings of complexes **I** and **V**. Copies of ^{1}H and ^{13}C NMR spectra of the cross-coupling products, ligand precursors, and nickel complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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