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Cross-Coupling of ArX with ArMgBr Catalyzed by N-Heterocyclic Carbene-Based Nickel Complexes

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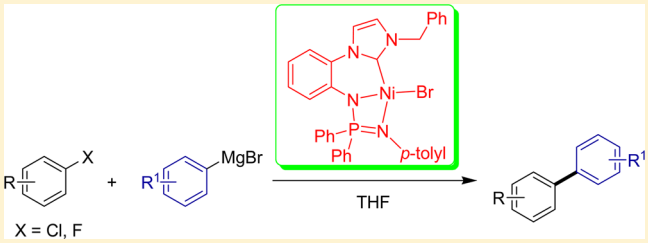
Supporting Information

ABSTRACT: N-Heterocyclic carbene-based pincer nickel complexes were synthesized and characterized. These complexes efficiently catalyze cross-coupling of aryl Grignard reagents with aryl chlorides or fluorides under mild conditions.



INTRODUCTION

The Kumada cross-coupling reaction has been extensively investigated and widely applied in organic synthesis to construct carbon−carbon bonds since its discovery in the 1970s.[1,2] Catalysts for the Kumada coupling reaction derived from transition metals such as nickel, palladium, copper, iron, and cobalt were developed.[3] In the past decades, organic bromides and iodides were widely used as the electrophiles in the Kumada reaction.[2,4−10] In recent decades, organic chlorides received much more attention due to their low cost in industrial processes and the diversity of available compounds.[11,12] For example, Herrmann et al. carried out cross-coupling of aryl chlorides with aryl Grignard reagents using $Ni(acac)_2$−NHC as the catalyst.[13] Kambe et al. reported that in the presence of 1,3-butadiene $NiCl_2$ efficiently catalyzes cross-coupling of primary alkyl chlorides and alkyl Grignard reagents.[14] We and other groups found that pincer nickel complexes have good catalytic activity for the Kumada reactions of aryl, heteroaryl, or vinyl chlorides.[15] Hu and co-workers showed that N,N,N-pincer nickel complex is effective for the coupling of alkyl halides and alkylmagnesium reagents.[16] Some palladium, iron, cobalt, and copper complexes were also proven to be active for the Kumada coupling of chloroarenes.[17]

Compared with C−Cl bond, the C−F bond is more difficult to transform because of its thermal and chemical stability. In recent years, transition-metal-catalyzed activation and conversion of organic fluorides attracted considerable attention. The conversion of organic fluorides is important for the fundamental understanding of the reactivity of very stable bonds, selective defluorination of aliphatic fluorides, cross-coupling with aryl fluorides, and transformation of poly- or perfluorinated compounds to partially fluorinated compounds.[18,19] Some stoichiometric and catalytic C−F bond activation reactions have been reported, including several transition-metal-catalyzed cross-coupling reactions of aryl fluorides.[18,20,21]

In our studies on search for new catalyst systems for the activation of inert C-heteroatom bonds, we found that N-heterocyclic carbene-based pincer nickel complexes can activate not only aryl C−Cl bonds but also aryl C−F bonds and lead to cross-couplings with aryl Grignard reagents efficiently. Herein we report the results.

RESULTS AND DISCUSSION

Our studies on catalysis of P,N,P- and P,N,N-pincer nickel complexes showed that the complexes containing small chelate nickel rings, e.g., 4,5- and 4,6-fused metal rings, exhibited good catalytic activity for the Kumada coupling of aryl chlorides.[15a,b] In 2009, we reported synthesis of N-heterocyclic carbene-based pincer nickel complexes containing 5,6- and 6,6-fused nickel rings and their catalysis in the cross-coupling of aryl chlorides with arylmagnesium or zinc reagents.[15c] In these studies, iminophosphoranyl groups were also proven to be excellent coordination groups for the stabilization and catalytic properties of the complexes. In order to examine the effect of small chelate ring in the NHC-based pincer nickel catalyst systems and try to improve the catalytic properties of NHC-based pincer nickel complexes, we designed and synthesized new C,N,N-pincer nickel complexes **3a−g** (Scheme 1) that involve 4,6-fused nickel ring structures and iminophosphoranyl coordination groups.

The new N-heterocyclic carbene-based nickel complexes were constructed by a two-step process as shown in Scheme 1. The ligand precursors **2a−g** were prepared by reaction of **1**[15c] with R^1NHPPh_2[22] in CH_2Cl_2. Treatment of **2a−g** with *n*-BuLi and subsequent $(DME)NiCl_2$ generated nickel complexes **3a−g**. Compounds **2a−g** and **3a−e,g** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analyses. Complex **3f** is paramagnetic and was characterized by elemental analysis

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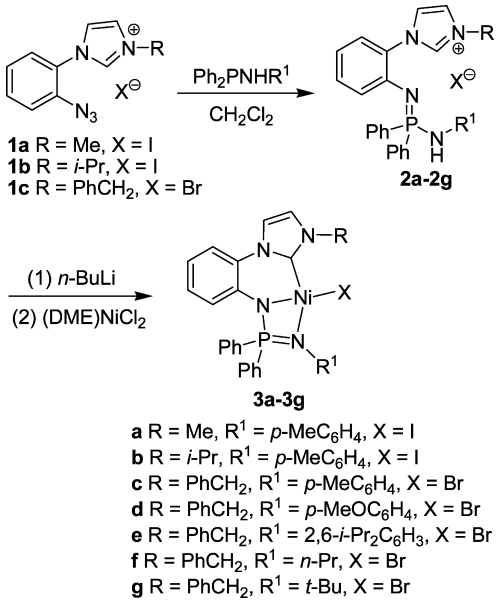
Scheme 1. Synthesis of Complexes 3a−g



and IR spectroscopy. The single-crystal X-ray diffraction of complex **3e** confirmed a pincer coordination mode (Figure 1).

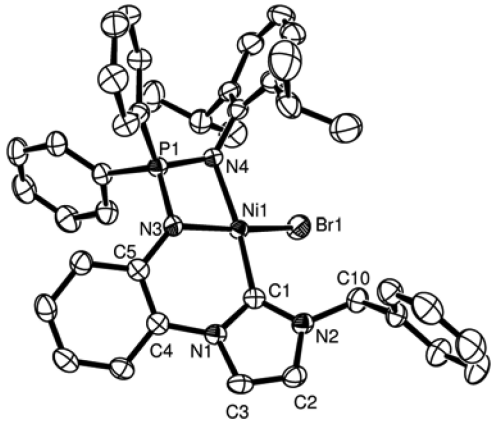
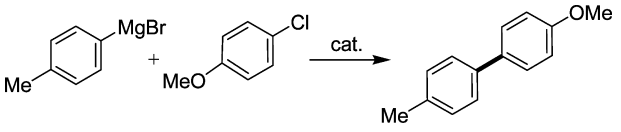


Figure 1. ORTEP drawing of complex **3e** (30% probability thermal ellipsoids).

First, the catalysis of complexes **3a−g** was evaluated using the cross-coupling of *p*-chloroanisole and *p*-tolylmagnesium bromide in THF at room temperature as the model reaction (Table 1). Compounds **3b−d** showed the highest catalytic activity, and **3e** exhibited the lowest activity (entries 1−3 and 9−12, Table 1). The activity order is approximately **3b** ≈ **3c** ≈ **3d** > **3a** ≈ **3f** > **3g** > **3e**. It seems that very bulky R^1 groups hinder catalysis of the complexes, whereas influence of electronic effect of R^1 groups on the catalytic property of the complexes is negligible. Except for **3e**, each of these complexes shows higher catalytic activity than the NHC-based pincer nickel complexes containing 5,6- and 6,6-fused metal rings we reported previously.[15c] Activity of complexes **3b**, **3c**, and **3d** is also higher than most reported nickel-based catalysts for the Kumada coupling of deactivated chloroarenes and comparable to those of P,N,O-pincer nickels **4** and **5** (Scheme 2)[15d] and bimetallic nickel complex **6** (Scheme 2).[23] We also tested the reaction in other solvents using **3c**. The results showed that

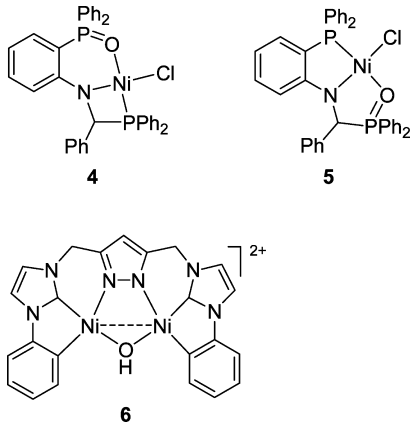
Table 1. Evaluation of Catalytic Activity of Complexes 3a−g[a]



entry	complex	solvent	yield[b] (%)
1	**3a**	THF	75
2	**3b**	THF	86
3	**3c**	THF	87
4	**3c**	toluene	67
5	**3c**	Et_2O	31
6	**3c**	1,4-dioxane	30
7	**3c**	THF/toluene (1:1)	80
8	**3c**	DME	
9	**3d**	THF	86
10	**3e**	THF	31
11	**3f**	THF	75
12	**3g**	THF	70

[a]The reactions were carried out at 25 °C for 24 h in the presence of 1 mol % of catalyst, 0.5 mmol of *p*-ClC_6H_4OMe, and 0.75 mmol of *p*-MeC_6H_4MgBr were employed. [b]Isolated product yields.

Scheme 2



toluene, Et_2O, 1,4-dioxane, and a 1:1 mixture of THF and toluene were less effective in comparison with THF (entries 4−7, Table 1). The catalytic reaction run in DME did not give cross-coupling product (entry 8, Table 1).

Next we examined substrate scope using **3c** as the catalyst (Table 2). The reaction between C_6H_5Cl and *p*-MeC_6H_4MgBr afforded cross-coupling product in nearly quantitative yield at room temperature for 12 h using 1 mol % of **3c** (entry 1, Table 2). The deactivated aryl chlorides including *o*-$MeOC_6H_4Cl$ and 2,4-$Me_2C_6H_3Cl$ also reacted with *p*-MeC_6H_4MgBr at room temperature (entries 2 and 3, Table 2). However, higher catalyst loadings were required due to steric hindrance of the chlorides, 5 mol % of **3c** for *o*-$MeOC_6H_4Cl$, and 2 mol % of **3c** for 2,4-$Me_2C_6H_3Cl$. When the temperature of the reaction between *o*-$MeOC_6H_4Cl$ and *p*-MeC_6H_4MgBr was raised to 70 °C, the catalyst loading could be decreased to 2 mol % and the product yield increased to 82%. Reaction of activated aryl chlorides including *p*-NCC_6H_4Cl, *o*-NCC_6H_4Cl and *p*-$Et_2NC(O)C_6H_4Cl$ with *p*-MeC_6H_4MgBr proceeded smoothly and gave excellent yields (entries 4−6, Table 2). The functional groups CN and $Et_2NC(O)$ were tolerated. Reaction of 2-chloropyridine with *p*-MeC_6H_4MgBr in THF in the presence of **3c** gave only moderate yield. However, the reaction in Et_2O led to excellent

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Table 2. Cross-Coupling of Arylmagnesium Bromides with Aryl Chlorides Catalyzed by 3c[a]

$$ArMgBr + Ar^1Cl \xrightarrow[THF]{\mathbf{3c}} Ar\text{-}Ar$$

entry	Ar	Ar^1Cl	amt of cat. (mol %)	time (h)	yield[b] (%)
1	*p*-MeC_6H_4	C_6H_5Cl	1	12	98
2	*p*-MeC_6H_4	*o*-$MeOC_6H_4Cl$	5	24	73 (82[c,d])
3	*p*-MeC_6H_4	2,4-$Me_2C_6H_3Cl$	2	24	90
4	*p*-MeC_6H_4	*p*-NCC_6H_4Cl	1	14.5	97
5	*p*-MeC_6H_4	*o*-NCC_6H_4Cl	1	17	98
6	*p*-MeC_6H_4	*p*-$Et_2NC(O)C_6H_4Cl$	3	13	92
7	*p*-MeC_6H_4	2-ClC_5H_4N	0.5	12	64 (91[e])
8	*o*-MeC_6H_4	C_6H_5Cl	1	24	63 (94[c,f])
9	*o*-MeC_6H_4	*p*-$MeOC_6H_4Cl$	1	24	81
10	*o*-MeC_6H_4	*p*-NCC_6H_4Cl	1	14	93
11	*o*-MeC_6H_4	*o*-NCC_6H_4Cl	2	24	91
12	*o*-MeC_6H_4	2-ClC_5H_4N	1	12	89[e]
13	*p*-$MeOC_6H_4$	C_6H_5Cl	1	12	86
14	*p*-$MeOC_6H_4$	*p*-MeC_6H_4Cl	1	24	93[c]
15	*p*-$MeOC_6H_4$	*o*-MeC_6H_4Cl	1	17	99[c]
16	*p*-$MeOC_6H_4$	2-ClC_5H_4N	1	12	93
17	*p*-$MeOC_6H_4$	2,4-$Me_2C_6H_3Cl$	2	24	97
18	*p*-$MeOC_6H_4$	*p*-$Et_2NC(O)C_6H_4Cl$	5	24	78
19	*p*-$Me_2NC_6H_4$	C_6H_5Cl	1	12	91
20	*p*-$Me_2NC_6H_4$	*o*-MeC_6H_4Cl	1	12	97[c]
21	*p*-$Me_2NC_6H_4$	*p*-MeC_6H_4Cl	1	12	85[c]
22	*p*-$Me_2NC_6H_4$	*o*-$MeOC_6H_4Cl$	2	24	72[c]
23	*p*-$Me_2NC_6H_4$	*p*-$MeOC_6H_4Cl$	1	24	96[c]
24	*p*-$Me_2NC_6H_4$	2-ClC_5H_4N	1	12	97
25	*p*-$Me_2NC_6H_4$	2,4-$Me_2C_6H_3Cl$	1	19	92

[a]Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale and run at 25 °C; 1.5 equiv of ArMgBr were used. [b]Isolated product yields. [c]The reaction was run at 70 °C. [d]The reaction was run for 22 h with 2 mol % of catalyst. [e]The reaction was run in diethyl ether. [f]The reaction time was 12 h.

result. Sterically hindered Grignard reagent, *o*-MeC_6H_4MgBr, showed lower reactivity than *p*-MeC_6H_4MgBr. Reaction of *o*-MeC_6H_4MgBr with aryl chlorides including *p*-$MeOC_6H_4Cl$, *p*-NCC_6H_4Cl, *o*-NCC_6H_4Cl, and 2-ClC_5H_4N gave lower product yields compared with those using *p*-MeC_6H_4MgBr as the nucleophilic species. Catalyst loadings of 2 mol % were also necessary to complete the reaction between *o*-MeC_6H_4MgBr and *o*-NCC_6H_4Cl. Electron-rich Grignard reagents *p*-$MeOC_6H_4MgBr$ and *p*-$Me_2NC_6H_4MgBr$ exhibited good reactivity with aryl chlorides in the presence of **3c**. However, their reactions with deactivated or sterically hindered aryl chlorides required elevated temperature. For example, reaction of *p*-$MeOC_6H_4MgBr$ with *o*-MeC_6H_4Cl was carried out at 70 °C in the presence of 1 mol % **3c**, leading to cross-coupling product in 99% yield (entry 15, Table 2). Reaction of *p*-$Me_2NC_6H_4MgBr$ with *o*-$MeOC_6H_4Cl$ at 70 °C in the presence of 2 mol % of **3c** gave a 72% yield of *p*-(*o*-$MeOC_6H_4$)$C_6H_4NMe_2$ (entry 22, Table 2). In addition, both *p*-$MeOC_6H_4MgBr$ and *p*-$Me_2NC_6H_4MgBr$ were incompatible with *p*-NCC_6H_4Cl or *o*-NCC_6H_4Cl. Reaction between them in the presence of **3c** resulted in addition products, whereas reaction of 2-ClC_5H_4N with either *p*-$MeOC_6H_4MgBr$ or *p*-$Me_2NC_6H_4MgBr$ using 1 mol % of **3c** as catalyst formed cross-coupling products in excellent yields (entries 16 and 24, Table 2).

Complex **3c** also exhibited good catalytic activity for the activation of aryl C−F bonds as shown in Table 3. Activated,

Table 3. Reaction of Aryl Fluorides with Aryl Grignard Reagents Catalyzed by 3c[a]

$$ArMgBr + Ar^1F \xrightarrow[THF]{\mathbf{3c}} Ar\text{-}Ar$$

entry	Ar	Ar^1F	amt of cat. (mol %)	time (h)	yield[b] (%)
1	*p*-MeC_6H_4	C_6H_5F	2	24	99
2	*p*-MeC_6H_4	*p*-$MeOC_6H_4F$	2	24	91
3	*p*-MeC_6H_4	*p*-$MeOC_6H_4F$	3	24	99
4	*p*-MeC_6H_4	1-$FC_{10}H_7$	4	12	95
5	*p*-MeC_6H_4	*p*-$Et_2NC(O)C_6H_4F$	8	24	92
6	*p*-MeC_6H_4	2-FC_5H_4N	2	12	91
7	*p*-MeC_6H_4	3,4-$(MeO)_2C_6H_3F$	4	24	74[c]
8	*p*-MeC_6H_4	*p*-$FC_6H_4CH_2OH$	4	12	96[d]
9	*p*-$MeOC_6H_4$	C_6H_5F	2	17	99
10	*p*-$MeOC_6H_4$	1-$FC_{10}H_7$		4	12
11	*p*-$MeOC_6H_4$	2-FC_5H_4N	2	11	95
12	*p*-$MeOC_6H_4$	*p*-$Et_2NC(O)C_6H_4F$	10	24	74
13	*p*-$MeOC_6H_4$	3,4-$(MeO)_2C_6H_3F$	4	24	72[c]
14	*p*-$MeOC_6H_4$	*p*-$FC_6H_4CH_2OH$	4	12	88[c,d]
15	*p*-$Me_2NC_6H_4$	C_6H_5F	2	12	92
16	*p*-$Me_2NC_6H_4$	1-$FC_{10}H_7$	4	12	95
17	*p*-$Me_2NC_6H_4$	*p*-$MeOC_6H_4F$	2	24	94
18	*p*-$Me_2NC_6H_4$	2-FC_5H_4N	2	12	92
19	*p*-$Me_2NC_6H_4$	3,4-$(MeO)_2C_6H_3F$	4	24	66[c]
20	*p*-$Me_2NC_6H_4$	4-$FC_6H_4CH_2OH$	4	12	86[c,d]
21	*o*-MeC_6H_4	C_6H_5F	3	12	92[c]
22	*o*-MeC_6H_4	*p*-$MeOC_6H_4F$	3	24	76[c]
23	*o*-MeC_6H_4	2-FC_5H_4N	4	12	69[c]

[a]Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale and run at 25 °C; 1.5 equiv of ArMgBr were used. [b]Isolated product yields. [c]The reaction was run at 70 °C. [d]3 equiv of ArMgBr was used.

unactivated, and deactivated aryl fluorides including PhF, 1-$FC_{10}H_7$, *p*-$MeOC_6H_4F$, *p*-$Et_2NC(O)C_6H_4F$, and 2-FC_5H_4N reacted efficiently with *p*-MeC_6H_4MgBr, *p*-$MeOC_6H_4MgBr$, or *p*-$Me_2NC_6H_4MgBr$ at room temperature in the presence of **3c**. For example, reaction of deactivated aryl fluoride, *p*-$MeOC_6H_4F$, with *p*-MeC_6H_4MgBr proceeded smoothly. Loadings of **3c** (2 mol %) led to 91% product yield. This reaction could be further improved by using higher catalyst loadings. A 3 mol % loading of **3c** resulted in 99% product yield (entries 2 and 3, Table 3). However, **3c**-catalyzed reaction of 3,4-$(MeO)_2C_6H_3F$ with Grignard reagents required elevated temperature and gave only moderate product yields (entries 7, 13, and 19, Table 3). *p*-$FC_6H_4CH_2OH$ also reacted efficiently with the Grignard reagents mentioned above when excess Grignard reagents were employed. *p*-$Et_2NC(O)C_6H_4F$ could couple with *p*-MeC_6H_4MgBr and *p*-$MeOC_6H_4MgBr$, respectively, when 8−10 mol % of **3c** was used as catalyst (entries 5 and 12, Table 3), whereas reaction of *p*-$Me_2NC_6H_4MgBr$ with *p*-$Et_2NC(O)C_6H_4F$ resulted in addition product. Reaction of *p*-FC_6H_4CN and *o*-FC_6H_4CN with various Grignard reagents also afforded addition products. *o*-MeC_6H_4MgBr also reacted with aryl fluorides using **3c** as the catalyst but showed lower reactivity in comparison with *p*-MeC_6H_4MgBr. Reactions of *o*-MeC_6H_4MgBr with activated, unactivated, and deactivated aryl fluorides required elevated temperature, giving mederate to excellent product yields (entries 21−23, Table 3). Compared with the known

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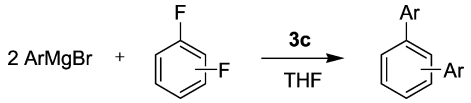
nickel catalysts for the coupling of aryl fluorides and Grignard reagents, **3c** shows higher activity than the Ni(II)/phosphine, Ni(II)/IPr, and Ni(II)/phosphine oxide systems[21e−h] but lower activity than Ni(acac)$_2$/2-(Ph$_2$P)C$_6$H$_4$CH(OH)Me system.[21d] The high activity of the latter is ascribed to a cooperative push−pull action of the nucleophilic nickel and Lewis acidic magnesium centers based on experimental and computational studies.[21d]

Reactions of difluorobenzenes with Grignard reagents at room temperature catalyzed by complex **3c** were also carried out (Table 4). Treatment of 1,4-difluorobenzene with 3 equiv

Table 4. Reaction of Arylmagnesium Reagents with Difluorobenzene Catalyzed by 3c[a]



entry	Ar	ArF$_2$	amt of cat. (mol %)	time (h)	yield[b] (%)
1	*p*-MeC$_6$H$_4$	1,4-F$_2$C$_6$H$_4$	4	13	97
2	*p*-MeC$_6$H$_4$	1,2-F$_2$C$_6$H$_4$	5	12	82[c]
3	*o*-MeC$_6$H$_4$	1,4-F$_2$C$_6$H$_4$	5	22	85[c]
4	*p*-MeOC$_6$H$_4$	1,4-F$_2$C$_6$H$_4$	4	12	99
5	*p*-Me$_2$NC$_6$H$_4$	1,4-F$_2$C$_6$H$_4$	4	12	99
6	*p*-Me$_2$NC$_6$H$_4$	1,2-F$_2$C$_6$H$_4$	5	12	95[c]

[a]Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale and run at 25 °C; 3 equiv of ArMgBr were used. [b]Isolated product yields. [c]The reaction was run at 70 °C.

of *p*-MeC$_6$H$_4$MgBr, *p*-MeOC$_6$H$_4$MgBr, or *p*-Me$_2$NC$_6$H$_4$MgBr in the presence of 4 mol % **3c** at room temperature gave 1,4-bis(*p*-tolyl)benzene, 1,4-di(*p*-methoxyphenyl)benzene and 1,4-bis(p-dimethylaminophenyl)benzene, respectively, in nearly quantitative yields (entries 1, 4, and 5, Table 4). A similar reaction using *o*-MeC$_6$H$_4$MgBr required 5 mol % of **3c** and elevated temperature (70 °C) and gave the cross-coupling product in 82% yield (entry 3, Table 4). Reaction of 1,2-difluorobenzene with 3 equiv of *p*-MeC$_6$H$_4$MgBr or *p*-Me$_2$NC$_6$H$_4$MgBr in the presence of 5 mol % of **3c** at 70 °C generated the cross-coupling products in 82% and 95% yields, respectively (entries 2 and 6, Table 3). It seems that the steric hindrance of 1,2-difluorobenzene hinders the reaction to some extent, and hence, the reactions required elevated temperature and higher catalyst loadings.

CONCLUSION

In summary, we have developed new NHC-based nickel complex catalysts for the Kumada reaction of aryl chlorides and fluorides. Complex **3c** displayed high activity and is able to catalyze cross-coupling of activated, unactivated, and deactivated chloroaromatics and fluoroaromatics efficiently with aryl Grignard reagents under mild conditions.

EXPERIMENTAL SECTION

The reactions were performed under nitrogen atmosphere. Solvents were distilled under nitrogen over sodium (toluene and 1,4-dioxane), sodium/benzophenone (THF, Et$_2$O and DME), or CaH$_2$ (CH$_2$Cl$_2$) and degassed prior to use. *n*-BuLi, CDCl$_3$, aryl chlorides, and fluorides were purchased from commercial venders and used as received. Compounds **1a−c**,[15c] R^{1}NHPPh$_2$,[22] (DME)NiCl$_2$,[24] and aryl Grignard reagents[25] were prepared according to the reported methods. NMR spectra were determined on a 300 MHz NMR spectrometer at room temperature using CDCl$_3$ as solvent. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to TMS or internal solvent resonances, and the ^{31}P NMR spectra were referenced to external 85% H$_3$PO$_4$. Infrared (IR) spectra were recorded in the range 4000−600 cm^{-1} as KBr pellets. High-resolution mass spectra (HRMS) were acquired in the electron-impact mode (EI) using a TOF mass analyzer. Elemental analyses were performed by the Analytical Center of University of Science and Technology of China.

Synthesis of [*o*-(4-MeC$_6$H$_4$NHP(Ph$_2$)=N)C$_6$H$_4$N(CH)$_2$N(Me)CH]$^+$I$^-$ (2a). *p*-MeC$_6$H$_4$NHPPh$_2$ (0.91 g, 3.11 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and then cooled to 0 °C. To the solution was added a solution of **1a** (0.95 g, 2.90 mmol) in CH$_2$Cl$_2$ (10 mL). The mixture was warmed to room temperature and stirred overnight. The solution was filtered and then about half volume of CH$_2$Cl$_2$ was removed from the filtrate. Diethyl ether (30 mL) was added. Yellowish precipitates were formed from the mixture. The precipitates were collected by filtration, washed with diethyl ether (15 mL × 2), and dried in vacuo to give a yellowish powder of **2a**·0.17CH$_2$Cl$_2$·0.35Et$_2$O (1.47 g, 80%). Mp: 123−124 °C. ^{1}H NMR: δ 1.20 (t, J = 6.9 Hz, Et$_2$O), 2.17 (s, 3H), 3.48 (q, J = 6.9 Hz, Et$_2$O), 4.00 (s, 3H), 5.29 (s, 0.35H, CH$_2$Cl$_2$), 6.26 (b, 1H), 6.74 (t, J = 7.5 Hz, 1H), 6.87−7.09 (m, 6H), 7.33−7.37 (m, 1H), 7.42−7.53 (m, 7H), 7.63 (s, 1H), 7.74−7.81 (m, 4H), 9.59 (s, 1H). ^{13}C NMR: δ 15.3, 20.7, 37.2, 65.9, 119.2, 119.3, 122.5, 123.6, 124.5, 125.2, 129.3 (d, J = 13.1 Hz), 129.8, 131.0, 131.8, 131.9, 132.1, 132.7, 136.9, 137.3. ^{31}P NMR: δ −0.20. Anal. Calcd for C$_{29}$H$_{28}$IN$_4$P: C, 58.99; H, 4.80; N, 9.49. Found: C, 58.49; H, 5.19; N, 9.32. (The sample for elemental analysis was recrystallized from CH$_2$Cl$_2$.)

Synthesis of [*o*-(4-MeC$_6$H$_4$NHP(Ph$_2$)=N)C$_6$H$_4$N(CH)$_2$N(*i*-Pr)CH]$^+$I$^-$ (2b). *p*-MeC$_6$H$_4$NHPPh$_2$ (0.71 g, 2.44 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and then cooled to 0 °C. To the solution was added a solution of **1b** (0.72 g, 2.03 mmol) in CH$_2$Cl$_2$ (10 mL). The resulting mixture was warmed to room temperature and stirred overnight. The solution was filtered, and the filtrate was concentrated to about half of the original volume. Diethyl ether (30 mL) was added. Yellowish precipitates were formed. The precipitates were collected by filtration, washed with diethyl ether (15 mL × 2), and dried in vacuo to give a yellowish powder of **2b**·0.16CH$_2$Cl$_2$·0.5Et$_2$O (1.20 g, 84%). Mp: 123−124 °C. ^{1}H NMR: δ 1.20 (t, J = 7.2 Hz, 3H, Et$_2$O), 1.56 (d, J = 6.6 Hz, 6H), 2.16 (d, 3H), 3.48 (q, J = 7.2 Hz, 2H, Et$_2$O), 5.04−5.18 (m, 1H), 5.29 (s, 0.31H, CH$_2$Cl$_2$), 6.39 (b, 1H), 6.71−6.82 (m, 1H), 6.89 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 3.9 Hz, 2H), 7.35−7.55 (m, 8H), 7.75−7.81 (m, 4H), 7.86 (s, 1H), 9.48 (s, 1H). ^{13}C NMR: δ 15.3, 20.6, 23.2, 53.3, 65.9, 119.1, 119.5, 119.6, 123.8, 124.1, 125.2, 128.7, 128.9, 129.2 (d, J = 13.1 Hz), 129.8, 130.9, 131.9 (d, J = 10 Hz), 132.7, 134.8, 137.3. ^{31}P NMR: δ 0.26. Anal. Calcd for C$_{31}$H$_{32}$IN$_4$P: C, 60.20; H, 5.22; N, 9.06. Found: C, 60.40; H, 5.49; N, 8.91. (The sample for elemental analysis was recrystallized from CH$_2$Cl$_2$.)

Synthesis of [*o*-(4-MeC$_6$H$_4$NHP(Ph$_2$)=N)C$_6$H$_4$N(CH)$_2$N(Bn)CH]$^+$Br$^-$ (2c). *p*-MeC$_6$H$_4$NHPPh$_2$ (1.70 g, 5.85 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and cooled to 0 °C. To the solution was added a solution of **1c** (1.95 g, 5.47 mmol) in CH$_2$Cl$_2$ (10 mL). The mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered, and the filtrate was concentrated to afford a pale yellow powder of **2c**·0.33CH$_2$Cl$_2$ (3.05 g, 88%). Mp: 132−133 °C. ^{1}H NMR: δ 2.16 (s, 3H), 5.29 (s, 0.67H, CH$_2$Cl$_2$), 5.63 (s, 2H), 6.41 (d, J = 9 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), 6.83−6.93 (m, 5H), 7.00−7.05 (m, 1H), 7.25−7.33 (m, 4H), 7.36−7.51 (m, 10H), 7.71−7.78 (m, 4H), 10.14 (s, 1H). ^{13}C NMR: δ 20.7, 53.4, 118.5, 119.3 (d, J = 6 Hz), 120.8, 123.6, 124.1 (d, J = 9.7 Hz), 125.2, 129.1, 129.2, 129.3, 129.4, 129.8, 130.9, 131.5, 131.9, 132.4 (d, J = 2.3 Hz), 133.5, 136.9, 137.7. ^{31}P NMR: δ −0.97. Anal. Calcd for C$_{35}$H$_{32}$BrN$_4$P·0.5CH$_2$Cl$_2$: C, 64.41; H, 5.02; N, 8.46. Found: C, 64.73; H, 5.22; N, 8.77. (The sample for elemental analysis was recrystallized from CH$_2$Cl$_2$.)

Synthesis of [*o*-(4-MeOC$_6$H$_4$NHP(Ph$_2$)=N)C$_6$H$_4$N(CH)$_2$N(Bn)CH]$^+$Br$^-$ (2d). *p*-MeOC$_6$H$_4$NHPPh$_2$ (0.76 g, 2.47 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and cooled to 0 °C. To the solution was added a solution of **1c** (0.74 g, 2.08 mmol) in CH$_2$Cl$_2$ (10 mL). The mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered, and the filtrate was concentrated to

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about half of the volume. Diethyl ether (30 mL) was added. Yellowish precipitates were formed. The precipitates were collected by filtration, washed with diethyl ether (15 mL × 2), and dried in vacuo to give a yellowish powder of **2d**·0.16CH_2Cl_2·0.46Et_2O (1.30 g, 91%). Mp: 119−120 °C. ^{1}H NMR: δ 1.20 (t, J = 6.9 Hz, 2.82H, Et_2O), 3.47 (q, J = 6.9 Hz, 1.84H, Et_2O), 3.63 (s, 3H), 5.29 (s, 0.32H, CH_2Cl_2), 5.64 (s, 2H), 6.58 (d, J = 9 Hz, 3H), 6.69 (t, J = 7.2 Hz, 1H), 6.91−7.03 (m, 4H), 7.27−7.31 (m, 4H), 7.34−7.48 (m, 9H), 7.73−7.80 (m, 4H), 10.12 (s, 1H). ^{13}C NMR: δ 15.4, 53.3, 55.5, 65.9, 114.5, 118.3, 120.8, 121.6 (d, J = 5.7 Hz), 123.6, 123.9, 124.0, 125.1, 129.0, 129.2, 129.3, 129.4, 130.9, 132.0, 132.2, 132.3 (d, J = 2.3 Hz), 133.2, 133.5, 136.9, 155.2. ^{31}P NMR: δ 0.50. Anal. Calcd for $C_{35}H_{32}BrN_4PO$·0.2Et_2O: C, 66.11; H, 5.27; N, 8.61. Found: C, 66.56; H, 5.57; N, 8.64. (The sample for elemental analysis was further purified. Thus, the crude product was dissolved in CH_2Cl_2. The solution was added Et_2O to form precipitate of **2d**.)

Synthesis of [*o*-(2,6-*i*-$Pr_2C_6H_3NHP(Ph_2)$=N)C_6H_4N(CH$_2$N(Bn)CH]$^+Br^-$ (2e). 2,6-*i*-$Pr_2C_6H_3NHPPh_2$ (1.58 g, 4.37 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. To the solution was added a solution of **1c** (1.45 g, 4.07 mmol) in CH_2Cl_2 (10 mL). The mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered, and the filtrate was concentrated to about half of the volume. Diethyl ether (30 mL) was added. Yellowish precipitates were formed. The precipitates were collected by filtration, washed with diethyl ether (15 mL × 2), and dried in vacuo to give a yellowish powder of **2e** (2.58 g, 92%). Mp: 237−238 °C. ^{1}H NMR: δ 0.81 (d, J = 6.6 Hz, 12H), 3.15−3.34 (m, 2H), 5.81 (s, 2H), 6.33−6.39 (m, 2H), 6.65 (t, J = 7.5 Hz, 1H), 6.84−6.91 (m, 3H), 7.07 (t, J = 7.6 Hz, 1H), 7.22−7.51 (m, 13H), 7.63−7.70 (m, 4H), 10.52 (s, 1H). ^{13}C NMR: δ 23.6, 28.8, 53.4, 117.3, 120.2, 122.7, 123.4, 124.0, 127.3, 128.5, 128.7, 129.3 (d, J = 7.8 Hz), 130.0, 132.0, 132.3, 132.4, 132.7, 137.4, 148.4. ^{31}P NMR: δ 6.91. Anal. Calcd for $C_{40}H_{42}BrN_4P$·0.7CH_2Cl_2: C, 65.26; H, 5.84; N, 7.48. Found: C, 65.28; H, 5.99; N, 7.68. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [*o*-(*n*-PrNHP(Ph$_2$)N)C_6H_4N(CH)$_2$N(Bn)-CH]$^+Br^-$(2f). *n*-PrNHPPh_2 (0.50 g, 2.06 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. To the solution was added a solution of **1c** (0.68 g, 1.91 mmol) in CH_2Cl_2 (10 mL). The mixture was warmed to room temperature and stirred overnight. The resulting solution was filtered, and the filtrate was concentrated to about half of the volume. Diethyl ether (30 mL) was added. Yellowish precipitates were formed. The precipitates were collected by filtration, washed with diethyl ether (15 mL × 2), and dried in vacuo to give a yellowish powder of **2f**·0.14CH_2Cl_2·0.83Et_2O (1.04 g, 84%). Mp: 96−97 °C. ^{1}H NMR: δ 0.83 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 5.2H, Et_2O), 1.48−1.60 (m, 2H), 2.78−2.88 (m, 2H), 3.48 (q, J = 7.2 Hz, 3.3H, Et_2O), 3.84 (b, 1H), 5.29 (s, 0.28H, CH_2Cl_2), 5.89 (s, 2H), 6.72 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 7.01−7.07 (m, 1H), 7.29−7.36 (m, 4H), 7.37−7.44 (m, 4H), 7.46−7.51 (m, 4H), 7.54−7.56 (m, 2H), 7.71−7.78 (m, 4H), 10.36 (s, 1H). ^{13}C NMR: δ 11.5, 15.4, 25.0 (d, J = 7.4 Hz), 43.2, 53.5, 65.9, 120.7, 123.1, 123.3, 123.6, 125.0, 128.9, 129.1, 129.3, 129.4, 130.6, 132.0, 132.1, 133.7, 137.4. ^{31}P NMR: δ 7.96. Anal. Calcd for $C_{31}H_{32}BrN_4P$: C, 65.15; H, 5.64; N, 9.80. Found: C, 65.26; H, 5.84; N, 9.73. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [*o*-(*t*-BuNHP(Ph$_2$)N)C_6H_4N(CH)$_2$N(Bn)CH]$^+Br^-$ (2g). *t*-BuNHPPh_2 (1.80 g, 7.00 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. To the solution was added a solution of **1c** (2.30 g, 6.46 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was warmed to room temperature and stirred overnight. The solution was filtered, and the filtrate was concentrated to about half of the volume. Diethyl ether (30 mL) was added. Yellowish precipitates were formed. The precipitates were collected by filtration, washed with diethyl ether (15 mL × 2), and dried in vacuo to give a yellowish powder of **2g**·0.13CH_2Cl_2·0.2Et_2O (3.70 g, 93%). Mp: 217−218 °C. ^{1}H NMR: δ 1.13 (s, 9H), 1.20 (t, J = 6.9 Hz, 1.26H, Et_2O), 3.14 (d, J = 8.4 Hz, 1H), 3.48 (q, J = 6.9 Hz, 0.81H, Et_2O), 5.29 (s, 0.25H, CH_2Cl_2), 5.96 (s, 2H), 6.72−6.77 (m, 1H), 6.83 (d, J = 8.4 Hz, 1H), 7.05−7.10 (m, 1H), 7.30−7.48 (m, 10H), 7.51−7.55 (m, 2H), 7.65 (t, J = 1.8 Hz, 1H), 7.69−7.77 (m, 4H), 7.80 (s, 1H), 10.07 (s, 1H). ^{13}C NMR: δ 32.0, 53.6, 65.9, 117.7, 121.1, 123.5 (d, J = 14 Hz), 124.4, 125.7, 128.9, 129.1, 129.3, 129.4, 130.6, 131.6, 131.7, 131.9 (d, J = 2 Hz), 133.7, 136.7. ^{31}P NMR: δ −1.19. Anal. Calcd for $C_{32}H_{34}BrN_4P$·0.1CH_2Cl_2: C, 64.91; H, 5.80; N, 9.43. Found: C, 64.66; H, 5.93; N, 9.57. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [Ni(I){*o*-(4-MeC$_6$H$_4$NP(Ph$_2$)=N)C$_6$H$_4$N(CH)$_2$N(Me)C}] (3a). To a stirred suspension of **2a** (0.51 g, 0.86 mmol) in THF (15 mL) was added dropwise *n*-BuLi (0.70 mL, a 2.5 M of solution in hexanes, 1.75 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred for 3 h. The resultant solution was transferred to a stirred suspension of (DME)$NiCl_2$ (0.19 g, 0.86 mmol) in THF (10 mL) at about −80 °C. The mixture was stirred for 20 h at room temperature. Solvent was removed in vacuo. The residual solid was dissolved in CH_2Cl_2 and then filtered. The filtrate was concentrated to form pink crystals of **3a**·0.09CH_2Cl_2 (0.39 g, 69%). Mp: 227−228 °C. ^{1}H NMR: δ 2.13 (s, 3H), 4.20 (s, 3H), 5.30 (s, 0.17H, CH_2Cl_2), 6.35 (d, J = 7.8 Hz, 1H), 6.60−6.78 (m, 6H), 6.99 (s, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.31 (s, 1H), 7.48−7.62 (m, 6H), 8.04 (dd, J = 8.1, 11.7 Hz, 4H). ^{13}C NMR: δ 20.9, 43.8, 118.2, 119.2, 119.6, 119.8, 120.0, 125.5, 126.6, 126.8, 128.7, 129.0, 129.2, 130.1, 132.3, 132.5, 132.9 (d, J = 2.8 Hz), 153.2. ^{31}P NMR: δ 46.77. Anal. Calcd for $C_{29}H_{26}IN_4PNi$·0.4CH_2Cl_2: C, 51.85; H, 3.97; N, 8.23. Found: C, 51.82; H, 4.05; N, 8.43. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [Ni(I){*o*-(4-MeC$_6$H$_4$NP(Ph$_2$)N)C$_6$H$_4$N(CH$_2$)N(*i*-Pr)C}] (3b). To a stirred suspension of **2b** (0.46 g, 0.74 mmol) in THF (10 mL) was added *n*-BuLi (0.60 mL, a 2.5 M of solution in hexanes, 1.5 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred for 4 h. The resultant solution was transferred to a stirred suspension of (DME)$NiCl_2$ (0.16 g, 0.74 mmol) in THF (10 mL) at about −80 °C. The mixture was allowed to warm to room temperature and stirred overnight. The precipitates were collected by filtration and then dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to generate purple crystals of **3b**·0.09CH_2Cl_2 (0.41 g, 81%). Mp: 196−198 °C. ^{1}H NMR: δ 1.61 (d, J = 6.6 Hz, 6H), 2.12 (s, 3H), 5.30 (s, 0.19H, CH_2Cl_2), 5.91−6.04 (m, 1H), 6.32 (d, J = 7.8 Hz, 1H), 6.57−6.78 (m, 6H), 7.09 (s, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.35 (s, 1H), 7.46−7.62 (m, 6H), 8.03−8.10 (m, 4H). ^{13}C NMR: δ 20.9, 23.7, 54.6, 118.2, 119.2, 120.1 (d, J = 10 Hz), 120.2 (d, J = 4.1 Hz), 125.4, 126.5, 126.7, 128.7, 129.0, 129.1, 129.9, 130.1, 131.3, 132.3, 132.5, 132.8 (d, J = 2.6 Hz), 136.0, 141.8, 152.3. ^{31}P NMR: δ 46.14. Anal. Calcd for $C_{31}H_{30}IN_4PNi$·0.3CH_2Cl_2: C, 53.66; H, 4.40; N, 8.00. Found: C, 53.79; H, 4.58; N, 8.05. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [Ni(Br){*o*-(4-MeC$_6$H$_4$NP(Ph$_2$)=N)C$_6$H$_4$N(CH)$_2$N(Bn)C}] (3c). To a stirred suspension of **2c**·0.33CH_2Cl_2 (0.662 g, 1.00 mmol) in THF (10 mL) was added *n*-BuLi (0.80 mL, a 2.5 M solution in hexanes, 2.00 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred for 4 h. The resultant solution was added dropwise to a stirred suspension of (DME)$NiCl_2$ (0.22 g, 1.00 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. The filtrate was concentrated to give brown crystals of **3c**·0.21CH_2Cl_2 (0.56 g, 80%). Mp: 235−236 °C. ^{1}H NMR: δ 2.10 (s, 3H), 5.29 (s, 0.42H, CH_2Cl_2), 5.95 (s, 2H), 6.32 (d, J = 7.5 Hz, 1H), 6.58−6.80 (m, 6H), 6.82−6.85 (m, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.27−7.76 (m, 12H), 8.03−8.14 (m, 4H). ^{13}C NMR: δ 20.8, 55.1, 56.2, 118.1, 118.2, 118.7, 118.9, 119.0, 119.2, 119.8 (d, J = 9.7 Hz), 124.1, 124.2, 125.2, 125.4, 125.5, 125.9 (d, J = 11.5 Hz), 128.2, 128.8, 128.87, 128.9, 129.0, 129.2, 129.8 (d, J = 9.9 Hz), 131.1, 132.4, 132.6, 132.9 (d, J = 2.3 Hz), 135.8, 137.1, 140.4, 148.8, 150.8. ^{31}P NMR: δ 46.26. Anal. Calcd for $C_{35}H_{30}BrN_4PNi$·0.25CH_2Cl_2: C, 60.70; H, 4.41; N, 8.03. Found: C, 60.46; H, 4.46; N, 8.05.

Synthesis of [Ni(Br{*o*-(4-MeOC$_6$H$_4$NP(Ph$_2$)=N)C$_6$H$_4$N(CH)$_2$N-(Bn)C})] (3d). To a stirred suspension of **2d**·0.2Et_2O (0.62 g, 0.95 mmol) in THF (15 mL) was added *n*-BuLi (0.76 mL, a 2.5 M solution in hexanes, 1.90 mmol) at about −80 °C. The mixture was warmed to

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room temperature and stirred for 3 h. The resultant solution was added dropwise to a stirred suspension of (DME)$NiCl_2$ (0.21g, 0.95 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 yellow crystals of **3d**·0.12CH_2Cl_2 (0.52 g, 78%). Mp: 174−176 °C. ^{1}H NMR: δ 3.63 (s, 3H), 5.30 (s, 0.23H, CH_2Cl_2), 5.94 (s, 2H), 6.31 (d, J = 7.8 Hz, 1H), 6.45−6.77 (m, 6H), 6.83 (s, 1H), 7.16−7.45 (m, 5H), 7.47−7.74 (m, 8H), 7.99−8.13 (m, 4H). ^{13}C NMR: δ 55.4, 56.1, 113.7, 113.8, 118.2, 118.7, 118.9, 119.1, 119.3, 119.7, 119.9, 124.2, 125.6, 127.2, 127.4, 128.2, 128.8, 128.9, 129.00, 129.2, 132.4, 132.5, 132.9. ^{31}P NMR: δ 46.75. Anal. Calcd for $C_{35}H_{30}BrN_4PONi$·0.4CH_2Cl_2: C, 58.55; H, 4.28; N, 7.72. Found: C, 58.61; H, 4.32; N, 7.75. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [Ni(Br{*o*-(2,6-*i*-$Pr_2C_6H_3NP(Ph_2)$═N)C_6H_4-$\overline{N(CH)_2N(Bn)C}$})] (3e). To a stirred suspension of **2e**·0.7CH_2Cl_2 (0.69 g, 0.92 mmol) in THF (15 mL) was added *n*-BuLi (0.74 mL, a 2.5 M solution in hexanes, 1.85 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)$NiCl_2$ (0.20 g, 0.92 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 brown crystals of **3e** (0.52 g, 76%). Mp: 264−266 °C. ^{1}H NMR: δ 0.32−0.37 (m, 6H), 1.39−1.42 (m, 6H), 4.11−4.32 (m, 2H), 5.88 (s, 2H), 6.08 (d, J = 8.1 Hz, 1H), 6.47−6.52 (m, 1H), 6.64−6.70 (m, 1H), 6.77−6.79 (m, 1H), 6.83−6.96 (m, 3H), 7.24−7.46 (m, 11H), 7.81−7.89 (m, 4H). ^{13}C NMR: δ 22.9, 25.4, 29.1, 54.6, 55.9, 118.3, 118.8, 118.9, 119.5, 121.4 (d, J = 10.7 Hz), 122.9, 123.7, 123.9, 124.0, 125.2, 128.1, 128.5, 128.6, 128.8, 131.6, 131.7, 132.2, 147.9. ^{31}P NMR: δ 47.94. Anal. Calcd for $C_{40}H_{40}BrN_4PNi$·0.4CH_2Cl_2: C, 62.18; H, 5.27; N, 7.18. Found: C, 62.16; H, 5.25; N, 7.37. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [Ni(Br){*o*-(*n*-PrNP(Ph$_2$)═N)$C_6H_4$$\overline{N(CH)_2N(Bn)C}$}] (3f). To a stirred suspension of **2f** (0.69 g, 1.20 mmol) in THF (15 mL) was added *n*-BuLi (0.96 mL, a 2.5 M solution in hexanes, 2.40 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred for 3 h. The resultant solution was added dropwise to a stirred suspension of (DME)$NiCl_2$ (0.27 g, 1.20 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 a green powder of **3f**·1.45CH_2Cl_2 (0.65 g, 72%). Mp: 251−252 °C. This complex is paramagnetic. IR: ν (cm^{-1}) 3270vs, 2960s, 2930m, 2870m, 1620w, 1610w, 1590w, 1490s, 1460m, 1440s, 1260s, 1230m, 1100vs, 1030s, 995s, 819s, 743s, 723s, 691s, 629m. Anal. Calcd for $C_{31}H_{30}BrN_4PNi$·1.45CH_2Cl_2: C, 51.88; H, 4.41; N, 7.46. Found: C, 51.79; H, 4.67; N, 7.54. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

Synthesis of [Ni(Br){*o*-(*t*-BuNP(Ph$_2$)═N)$C_6H_4$$\overline{N(CH)_2N(Bn)C}$}] (3g). To a stirred suspension of **2g**·0.1CH_2Cl_2 (0.58 g, 0.98 mmol) in THF (15 mL) was added *n*-BuLi (0.80 mL, a 2.5 M solution in hexanes, 2 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred for 3 h. The resultant solution was added dropwise to a stirred suspension of (DME)$NiCl_2$ (0.22 g, 1.00 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 **3g** (0.35 g, 56%). Mp: 235−237 °C. ^{1}H NMR: δ 1.03 (d, J = 3.3 Hz, 9H), 5.89 (s, 1H), 5.92 (s, 1H), 6.09−6.14 (m, 1H), 6.52−6.62 (m, 2H), 6.86 (d, J = 9.6 Hz, 1H), 7.09−7.19 (m, 2H), 7.37−7.65 (m, 9H), 7.93 (d, J = 7.2 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 8.21−8.31 (m, 4H). ^{13}C NMR: δ 33.1 (d, J = 8.7 Hz), 33.4 (d, J = 8.7 Hz), 51.3, 51.6, 54.9, 55.9, 117.0 (d, J = 4 Hz), 118.4, 118.7, 118.8, 119.0, 119.4, 119.5, 119.6, 124.2, 124.5, 125.3, 125.5, 128.1 (d, J = 5.7 Hz), 128.7, 128.9, 129.0, 132.1, 132.6, 132.8, 149.0. ^{31}P NMR: δ 42.44. Anal. Calcd for $C_{32}H_{32}BrN_4PNi$·0.1CH_2Cl_2: C, 59.25; H, 4.99; N, 8.61. Found: C, 59.19; H, 5.28; N, 8.79. (The sample for elemental analysis was recrystallized from CH_2Cl_2.)

General Procedures for the Cross-Coupling Reactions. A Schlenk tube was charged with nickel complex (the amount needed), aryl halide (0.5 mmol), and THF (1.5 mL). To the solution was added dropwise a solution of ArMgBr (1.5 mL, 0.5 M in THF, 0.75 mmol) at 25 °C and the resulting solution stirred for 24 h. The reaction was quenched with water, and the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic phases were dried over Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography on silica gel (eluent: a mixture of petroleum ether and ethyl acetate).

Spectral Data of the Cross-Coupling Products. *4-(N,N-Dimethylamino)-2′,5′-dimethylbiphenyl.*[26] ^{1}H NMR: δ 2.26 (s, 3H), 2.32 (s, 3H), 2.96 (s, 6H), 6.76 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 7.5 Hz, 1H), 7.05 (s, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.21 (d, J = 8.7 Hz, 2H). ^{13}C NMR: δ 20.3, 21.1, 29.8, 40.7, 112.2, 127.3, 130.0, 130.3, 130.8, 132.4, 135.2, 141.9, 149.5.

4′-Methoxy-2,5-dimethylbiphenyl.[27] ^{1}H NMR: δ 2.22 (s, 3H), 2.32 (s, 3H), 3.81 (s, 3H), 6.92 (d, J = 8.7 Hz, 2H), 7.04 (s, 2H), 7.12−7.16 (m, 1H), 7.23 (d, J = 8.7 Hz, 2H). ^{13}C NMR: δ 20.1, 21.0, 29.8, 55.3, 113.6, 127.8, 130.3, 130.8, 132.4, 134.6, 135.2, 141.5, 158.6.

4′-Methy-2,5-dimethylbiphenyl.[28] ^{1}H NMR: δ 2.22 (s, 3H), 2.32 (s, 3H), 2.38 (s, 3H), 7.04 (s, 2H), 7.12−7.14 (m, 1H), 7.17−7.22 (m, 4H). ^{13}C NMR: δ 20.1, 21.0, 21.3, 126.9, 127.9, 128.9, 129.2, 129.6, 130.4, 130.7, 132.3, 135.2, 136.4, 139.3, 141.9.

3,4-Dimethoxy-4′-methylbiphenyl.[29] ^{1}H NMR: δ 2.37 (s, 3H), 3.89 (s, 3H), 3.92 (s, 3H), 6.89 (d, J = 8.1 Hz, 1H), 7.06−7.13 (m, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 21.3, 56.0, 56.1,110.5, 111.6, 119.3, 126.8, 129.6, 134.4, 136.7, 138.3, 148.5, 149.2.

3,4-Dimethoxy-4′-methoxybiphenyl.[29] ^{1}H NMR: δ 3.85 (s, 3H), 3.92 (s, 3H), 3.94 (s, 3H), 6.91−6.97 (m, 3H), 7.06−7.11 (m, 2H), 7.46−7.50 (m, 2H). ^{13}C NMR: δ 29.8, 55.5, 56.0, 56.1, 110.4, 111.7, 114.3, 119.1, 128.0, 133.8, 134.1, 148.3, 149.3, 159.0.

3,4-Dimethoxy-4′-N,N-dimethylaminobiphenyl. Yellowish crystalline solid. Mp: 138−140 °C. ^{1}H NMR: δ 2.98 (s, 6H), 3.90 (s, 3H), 3.94 (s, 3H), 6.80 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.1 Hz, 1H), 7.07−7.11 (m, 2H), 7.46 (d, J = 9 Hz, 2H). ^{13}C NMR: δ 40.7, 56.0, 56.1, 110.1, 111.8, 113.0, 118.6, 127.5, 129.5, 133.3, 134.6, 147.9, 149.3, 149.8. HR-MS (EI): m/z 257.1413 $[M]^+$, calcd for $C_{16}H_{19}NO_2$ 257.1416.

4-(4-Methoxyphenyl)benzyl Alcohol.[30] ^{1}H NMR: δ 1.75 (s, 1H), 3.85 (s, 3H), 4.72 (s, 2H), 6.98 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.51−7.55 (m, 4H). ^{13}C NMR: δ 55.5, 65.3, 114.4, 127.0, 127.6, 128.2, 133.5, 139.4, 140.4, 159.4.

4-(4-Methylphenyl)benzyl Alcohol.[31] ^{1}H NMR: δ 1.74 (s, 1H), 2.39 (s, 3H), 4.73 (d, J = 3.6 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 21.2, 65.3, 127.1, 127.2, 127.6, 129.6, 137.2, 138.1, 139.7, 140.7.

[4-(4-Dimethylaminophenyl)phenyl]methanol. Pale yellow microcrystals. Mp: 142−144 °C. ^{1}H NMR: δ 1.70 (s, 1H), 2.99 (s, 6H), 4.70 (s, 2H), 6.80 (d, J = 9 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 40.7, 65.4, 112.9, 126.6, 127.7, 127.8, 128.9, 138.7, 140.8, 150.2. HR-MS (EI): m/z 227.1308 $[M]^+$, calcd for $C_{15}H_{17}NO$ 227.1310.

1-(4-Methylphenyl)naphthalene.[32] ^{1}H NMR: δ 2.44 (s, 3H), 7.29 (d, J = 8.1 Hz, 2H), 7.37−7.52 (m, 6H), 7.81−7.93 (m, 3H). ^{13}C NMR: δ 21.4, 125.5, 125.8, 126.1, 126.2, 127.0, 127.6, 128.4, 129.1, 130.1, 131.9, 134.0, 137.0, 138.0, 140.4.

1-(4-Methoxyphenyl)naphthalene.[33] ^{1}H NMR: δ 3.88 (s, 3H), 7.02 (d, J = 8.4 Hz, 2H), 7.39−7.53 (m, 6H), 7.81−7.94 (m, 3H). ^{13}C NMR: δ 55.5, 113.9, 125.5, 125.8, 126.1, 126.2, 127.0, 127.5, 128.4, 131.3, 132.0, 133.3, 134.0, 140.1, 159.1.

1-(4-N,N-Dimethylaminophenyl)naphthalene.[34] ^{1}H NMR: δ 3.02 (s, 6H), 6.86 (d, J = 9 Hz, 2H), 7.38−7.52 (m, 6H), 7.80 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H). ^{13}C NMR:

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δ 40.8, 112.4, 125.6, 125.7, 125.8, 126.5, 126.9, 127.0, 128.4, 131.0, 132.1, 134.1, 140.6, 149.9.

4-Methylbiphenyl.[35] ^{1}H NMR: δ 2.36 (s, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR: δ 21.2, 126.9, 127.1, 128.8, 129.6, 137.1, 138.5, 141.3.

4-Methoxy-4′-methylbiphenyl.[35] ^{1}H NMR: δ 2.38 (s, 3H), 3.86 (s, 3H), 6.96 (d, *J* = 8.7 Hz, 2H), 7.22 (D, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR: δ 21.1, 55.4, 114.3, 126.7, 128.0, 129.6, 133.8, 136.4, 138.1, 159.1.

1-Methoxy-2-p-tolylbenzene.[35] ^{1}H NMR: δ 2.38 (s, 3H), 3.79 (s, 3H), 6.95−7.03 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR: δ21.3, 55.7, 111.4, 120.9, 128.5, 128.9, 129.5, 130.9, 135.8, 136.7, 156.7.

2-p-Tolylpyridine.[35] ^{1}H NMR: δ 2.39 (s, 3H), 7.14−7.20 (m, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.65−7.69 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 8.66 (dt, *J* = 1.2, 4.8 Hz, 1H). ^{13}C NMR: δ 21.3, 115.5, 120.3, 121.9, 126.9, 129.6, 130.0, 136.8, 139.0, 149.7, 157.6.

N,N-Diethyl-4′-methylbiphenyl-4-carboxamide.[35] ^{1}H NMR: δ 1.13 (b, 3H), 1.24 (b, 3H), 2.38 (s, 3H), 3.30 (b, 2H), 3.54 (b, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR: δ 12.9, 14.1, 21.0, 39.3, 43.3, 126.8, 126.9, 129.5, 135.8, 137.4, 141.9, 171.1.

4′-Methylbiphenyl-4-carbonitrile.[35] ^{1}H NMR: δ 2.44 (s, 3H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR: δ 21.8, 128.7, 129.2, 130.3, 131.5, 133.5, 134.7, 136.4, 138.7, 143.7, 195.4.

4′-Methylbiphenyl-2-carbonitrile.[17c] ^{1}H NMR: δ 2.36 (s, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.29−7.37 (m, 3H), 7.39−7.43 (m, 1H), 7.53 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR: δ 21.5, 126.9, 127.9, 129.2, 129.4, 129.9, 130.1, 130.3, 134.9, 139.8, 141.4, 175.6.

2′-Methylbiphenyl-4-carbonitrile.[36] ^{1}H NMR: δ 2.12 (s, 3H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.22−7.27 (m, 2H), 7.31−7.35 (m, 3H), 7.62 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR: δ 19.8, 126.1, 127.5, 128.7, 129.1, 129.5, 130.6, 134.5, 136.8, 137.2, 140.4, 177.7.

2′-Methylbiphenyl-2-carbonitrile.[37] ^{1}H NMR: δ 2.31 (s, 3H), 7.15−7.41 (m, 8H). ^{13}C NMR: δ 20.6, 125.8, 127.0, 129.0, 129.6, 130.3, 130.5, 130.6, 131.2, 139.9, 177.7.

4′-Methoxy-2-methylbiphenyl.[35] ^{1}H NMR: δ 2.27 (s, 3H), 3.84 (s, 3H), 6.94 (d, *J* = 8.7 Hz, 2H), 7.16−7.26 (m, 6H). ^{13}C NMR: δ 20.7, 55.4, 113.6, 125.9, 127.1, 130.0, 130.4, 134.5, 135.6, 141.7, 158.7.

2-o-Tolylpyridine.[38] ^{1}H NMR: δ 2.35 (s, 3H), 7.10−7.18 (m, 1H), 7.21−7.27 (m, 3H), 7.32−7.39 (m, 2H), 7.61−7.68 (m, 1H), 8.66 (d, *J* = 3.9 Hz, 1H). ^{13}C NMR: δ 20.2, 121.5, 123.9, 125.7, 128.1, 129.5, 130.6, 135.6, 136.0, 140.3, 149.0, 159.9.

4-Methoxybiphenyl.[39] ^{1}H NMR: δ 3.85 (s, 3H), 6.98 (d, *J* = 9 Hz, 2H), 7.27−7.33 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.51−7.57 (m, 4H). ^{13}C NMR: δδ 55.4, 114.3, 126.8, 126.8, 128.2, 128.8, 133.8, 140.9, 159.2.

2-(p-Methoxyphenyl)pyridine.[40] ^{1}H NMR: δ 3.86 (s, 3H), 7.00 (d, *J* = 9 Hz, 2H), 7.14−7.19 (m, 1H), 7.64−7.73 (m, 2H), 7.95 (d, *J* = 9 Hz, 2H), 8.65 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR: δ 55.5, 114.2, 119.9, 121.5, 128.3, 132.2, 136.8, 149.7, 157.3, 160.6.

N,N-Diethyl-4′-methoxybiphenyl-4-carboxamide.[41] ^{1}H NMR: δ 1.21 (b, 6H), 3.35 (b, 2H), 3.54 (b, 2H), 3.85 (s, 3H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.51−7.58 (m, 4H). ^{13}C NMR: δ 13.0, 14.3, 39.3, 43.4, 55.4, 114.4, 126.6, 126.9, 128.2, 132.9, 135.5, 141.7, 159.5, 171.3.

4-(Dimethylamino)biphenyl.[35] ^{1}H NMR: δ 2.99 (s, 6H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.24−7.27 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.49−7.57 (m, 4H). ^{13}C NMR: δ 40.9, 113.1, 113.9, 114.0, 126.2, 126.46, 126.54, 127.8, 127.9, 128.8.

2′-Methyl-N,N-dimethylbiphenyl-4-amine.[42] ^{1}H NMR: δ 2.30 (s, 3H), 2.95 (s, 6H), 6.76 (d, *J* = 8.4 Hz, 2H), 7.17−7.24 (m, 6H). ^{13}C NMR: δ 20.8, 40.7, 112.2, 125.8, 126.6, 130.0, 130.4, 135.6, 142.2, 149.5.

4′-Methyl-N,N-dimethylbiphenyl-4-amine.[43] ^{1}H NMR: δ 2.37 (s, 3H), 2.98 (s, 6H), 6.78 (d, *J* = 8.7 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 8.4 Hz, 4H). ^{13}C NMR: δ 21.1, 40.7, 113.0, 126.3, 127.6, 129.5, 135.7, 138.5, 149.9.

2′-Methoxy-N,N-dimethylbiphenyl-4-amine.[44] ^{1}H NMR: δ 2.96 (s, 6H), 3.78 (s, 3H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.92−7.01 (m, 2H), 7.19−7.32 (m, 2H), 7.44 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR: δ 40.7, 55.7, 111.4, 112.3, 120.9, 126.7, 127.7, 130.3, 130.6, 131.0, 149.7, 156.7.

4′-Methoxy-N,N-dimethylbiphenyl-4-amine.[35] ^{1}H NMR: δ 2.98 (s, 6H), 3.83 (s, 3H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 7.43−7.49 (m, 4H). ^{13}C NMR: δ 40.9, 55.5, 113.2, 114.3, 127.5, 134.1, 149.7, 158.4.

2-(p-N,N-Dimethylaminophenyl)pyridine.[45] ^{1}H NMR: δ 3.01 (s, 6H), 6.79 (d, *J* = 8.7 Hz, 2H), 7.05−7.13 (m, 1H), 7.61−7.69 (m, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 8.61 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR: δ 40.5, 112.4, 119.3, 120.7, 127.8, 136.6, 149.5, 151.2, 157.7.

1,4-Di(p-methylphenyl)benzene.[15f] ^{1}H NMR: δ 2.40 (s, 6H), 7.26 (d, *J* = 7.2 Hz, 4H), 7.54 (d, *J* = 8.1 Hz, 4H), 7.64 (s, 4H). ^{13}C NMR: δ 21.3, 127.0, 127.4, 129.7, 137.2, 138.1, 139.9.

1,4-Di(p-methoxyphenyl)benzene.[46] ^{1}H NMR: δ 3.86 (s, 6H), 6.99 (d, *J* = 8.7 Hz, 4H), 7.57 (d, *J* = 8.7 Hz, 4H), 7.61 (s, 4H). ^{13}C NMR: δ 55.5, 114.4, 127.2, 128.2, 133.5, 139.3, 159.3.

1,4-Di(N,N-dimethylaminophenyl)benzene.[47] ^{1}H NMR: δ 3.00 (s, 12H), 6.82 (d, *J* = 8.7 Hz, 4H), 7.54 (d, *J* = 9 Hz, 4H), 7.59 (s, 4H). ^{13}C NMR: δ 40.8, 113.1, 126.7, 127.7, 139.0, 150.0.

1,4-Di(o-methylphenyl)benzene.[48] ^{1}H NMR: δ 2.33 (s, 6H), 7.21−7.31 (m, 8H), 7.36 (s, 4H). ^{13}C NMR: δ 20.7, 125.9, 127.4, 129.0, 130.0, 130.5, 135.6, 140.5, 141.8.

1,2-Di(p-methylphenyl)benzene.[49] ^{1}H NMR: δ 2.31 (s, 6H), 7.03 (s, 8H), 7.38 (s, 4H). ^{13}C NMR: δ 21.3, 127.4, 128.8, 129.8, 130.8, 136.1, 138.9, 140.6.

1,2-Di(N,N-dimethylaminophenyl)benzene.[47] ^{1}H NMR: δ 2.91 (s, 12H), 6.62 (d, *J* = 8.7 Hz, 4H), 7.07 (d, *J* = 7.8 Hz, 4H), 7.26−7.41 (m, 4H). ^{13}C NMR: δ 40.7, 112.3, 126.7, 130.4, 130.7, 140.5, 149.1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic routes of the ligand precursors and nickel complexes. Crystal structure determination details and crystal data of complex **3e**. Copies of ^{1}H and ^{13}C NMR spectra of the cross-coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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