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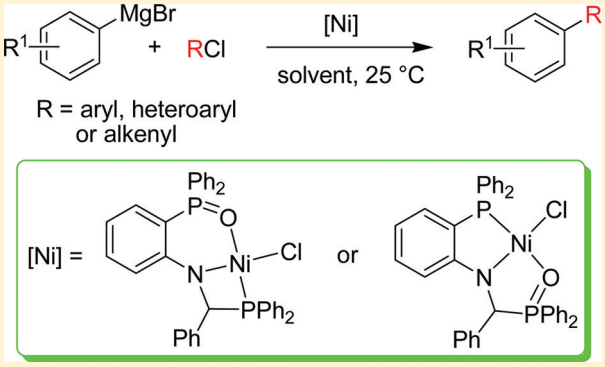
Kumada Coupling of Aryl, Heteroaryl, and Vinyl Chlorides Catalyzed by Amido Pincer Nickel Complexes

Ning Liu and Zhong-Xia Wang*

CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Supporting Information

ABSTRACT: A series of amido pincer complexes of nickel were examined for their catalysis in the Kumada cross-coupling reaction. The P,N,O-pincer nickel complexes tested are active catalysts for the cross-coupling of aryl, heteroaryl, and vinyl chlorides with aryl Grignard reagents. The reactions can proceed at room temperature and tolerate functional groups in aryl chlorides with the aid of LiCl and $ZnCl_2$ additives.



INTRODUCTION

The transition-metal-catalyzed Kumada cross-coupling reaction is one of the most important methods to construct new C−C bonds in organic synthesis.[1−3] Since the initial report of the nickel-catalyzed cross-coupling of a Grignard reagent with alkenyl or aryl halides by Kumada and Corriu independently,[4,5] the reaction has been extensively investigated and widely used in modern synthetic chemistry. Aryl, alkenyl, or alkyl bromides and iodides have been predominately used as the electrophilic partners in the last decades.[6−14] Organic chlorides, as the more useful substrates because of their lower cost in industrial processes and the diversity of available compounds,[15,16] have attracted considerable attention in recent years. Several types of catalysts have proven to be highly effective for the coupling of organic chlorides with Grignard reagents. For example, Herrmann and co-workers reported that a mixture of $Ni(acac)_2$ and imidazolium salts catalyzed cross-coupling of aryl chlorides with aryl Grignard reagents efficiently.[17] Nolan and Organ respectively carried out biaryl Kumada coupling using palladium−NHC catalysts.[18,19] Chen and co-workers described a series of Ni−NHC complexes that provide good results for Kumada coupling of aryl chlorides at room temperature.[20−22] Nickel and palladium with phosphine or phosphine oxide ligands are also effective catalysts for the Kumada coupling of aryl or alkyl chlorides.[23−27] We found that nickel complexes supported by pincer ligands exhibited good catalytic activity in the cross-coupling of aryl chlorides with aryl Grignard reagents.[28−30] Iron and cobalt complexes were also reported to catalyze the Kumada coupling of aryl or alkyl chlorides.[31,32] Although this progress has been achieved, investigations of widely applicable catalysts are still of interest. In addition, catalysts for the reactions using functionalized Grignard reagents or functionalized halides are very rare.[11,33−40] Exploration of the catalytic systems for the functionalized substrates is still challenging.

Recently, we reported the synthesis of several P,N,O- and P,N,S-pincer nickel complexes (Scheme 1) and their catalysis in the Negishi cross-couplings of aryl chlorides.[41] As a continuation, we investigated catalysis of the complexes in the Kumada coupling of aryl, heteroaryl, and alkenyl chlorides. For the substrates that tolerate the background reactivity of a Grignard reagent, Kumada cross-coupling offers a more direct access to the desired products and hence is a more atom-

Scheme 1. Amido-Pincer Nickel Complexes 1−4b

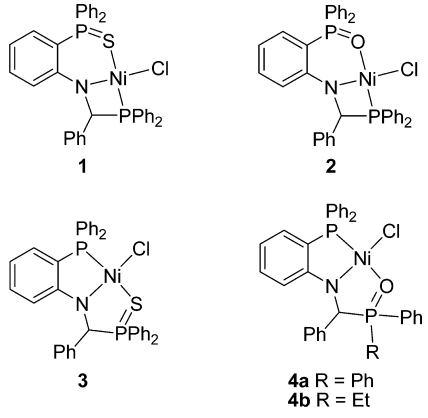


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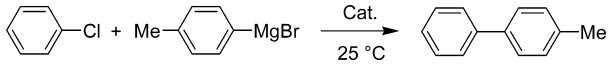
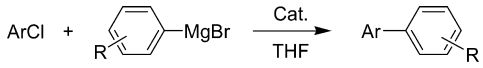
Table 1. Evaluation of Complexes 1−4b in the Reaction of PhCl with *p*-MeC_6H_4MgBr[a]



entry	catalyst (mol %)	solvent	time (h)	yield (%)[b]
1	**1** (1)	THF	24	51
2	**1** (1)	toluene	24	71
3	**2** (0.5)	THF	12	93
4	**2** (0.5)	THF	24	99
5	**2** (0.5)	toluene	12	39
6	**3** (1)	THF	24	69
7	**3** (1)	toluene	24	60
8	**4a** (0.5)	THF	12	85
9	**4a** (0.5)	THF	24	95
10	**4a** (0.5)	toluene	12	81
11	**4b** (0.5)	THF	12	88
12	**4b** (0.5)	THF	24	96
13	**4b** (0.5)	toluene	12	82

[a]Reactions were carried out with 0.5 mmol PhCl and 0.75 mmol *p*-MeC_6H_4MgBr in 2.5 mL of solvent at 25 °C. [b]Isolated product yields.

Table 2. Reaction of Aryl Chlorides with Aryl Grignard Reagents Catalyzed by 2, 4a, and 4b[a]



entry	ArCl	R	catalyst (mol %)	time (h)	yield (%)[b]
1	*p*-$MeOC_6H_4Cl$	*p*-Me	**2** (1)	24	97
2	*p*-$Me_2NC_6H_4Cl$	*p*-Me	**2** (4)	24	98
3	*p*-$MOMOC_6H_4Cl$	*p*-Me	**2** (2)	18	88
4	*p*-NCC_6H_4Cl	*p*-Me	**2** (1)	12	99
5	*p*-$MeOC_6H_4Cl$	*p*-Me	**4a** (2)	24	96
6	*p*-$MeOC_6H_4Cl$	*p*-Me	**4b** (2)	24	98
7	*p*-$Me_2NC_6H_4Cl$	*p*-Me	**4a** (4)	24	99
8	*p*-$Me_2NC_6H_4Cl$	*p*-Me	**4b** (4)	24	99
9	*o*-$MeOC_6H_4Cl$	*p*-Me	**4a** (2)	24	68
10	*o*-$MeOC_6H_4Cl$	*p*-Me	**4b** (2)	24	65
11	PhCl	*o*-Me	**2** (0.5)	24	96
12	*p*-$MeOC_6H_4Cl$	*o*-Me	**2** (1)	24	93
13	*p*-$Me_2NC_6H_4Cl$	*o*-Me	**2** (5)	18	83
14[c]	*p*-$Me_2NC_6H_4Cl$	*o*-Me	**2** (3)	12	98
15[c]	*p*-$MOMOC_6H_4Cl$	*o*-Me	**2** (2)	12	94
16	PhCl	*o*-Me	**4a** (1)	12	93
17	PhCl	*o*-Me	**4b** (1)	12	95
18	*p*-$MeOC_6H_4Cl$	*o*-Me	**4a** (2)	24	97
19	*p*-$MeOC_6H_4Cl$	*o*-Me	**4b** (2)	24	98
20	PhCl	*p*-OMe	**2** (1)	24	95
21	PhCl	*p*-OMe	**4a** (1)	24	97
22	*o*-MeC_6H_4Cl	*p*-OMe	**4a** (1.5)	24	92
23	2,5-$Me_2C_6H_3Cl$	*p*-OMe	**4a** (3)	24	82
24	*p*-$Me_2NC_6H_4Cl$	*p*-OMe	**4a** (5)	24	81
25[c]	*p*-$Me_2NC_6H_4Cl$	*p*-OMe	**4a** (3)	12	90
26	*p*-$MOMOC_6H_4Cl$	*p*-OMe	**4a** (3)	24	80

[a]Reactions were performed with 0.5 mmol aryl chlorides and 0.75 mmol Grignard reagents in 2.5 mL of THF at 25 °C unless otherwise stated. [b]Isolated product yields. [c]Reactions were carried out at 70 °C.

economical reaction. On the other hand, we found that in the presence of additives, this Ni-catalyzed Kumada cross-coupling is compatible with a series of functionalized aryl chlorides. Herein, we report the results.

RESULTS AND DISCUSSION

The investigation began with an examination of the reaction between PhCl and *p*-MeC_6H_4MgBr to evaluate the catalytic activities of complexes **1**−**4b**. The screening results are listed in Table 1. Among the complexes tested, the P,N,S-pincer nickel complexes (**1** and **3**, Scheme 1) exhibited relatively low catalytic activity. By contrast, the P,N,O-pincer nickel complexes (**2**, **4a**, and **4b**, Scheme 1) showed excellent catalytic activity. The desired biaryls were isolated in 93% yield by using 0.5 mol % of **2** in THF within 12 h (entry 3, Table 1). The lengthening of the reaction time to 24 h

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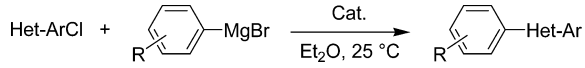
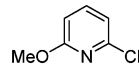
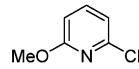
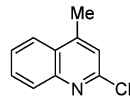
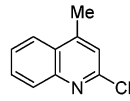
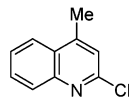
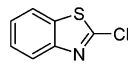
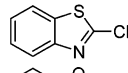
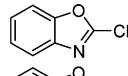
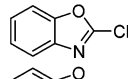
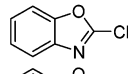
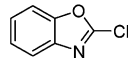
improved the yield of the coupling product to 99% (entry 4, Table 1). Complexes **4a** and **4b** displayed nearly same catalytic activity as **2** either in THF or in toluene (entries 8−13, Table 1). The higher activity of the P,N,O-pincer nickel complexes may be due to the ease of dissociation of the Ni−O bond to generate coordinatively unsaturated active species. The similar trend of catalytic activity was noted in the nickel-catalyzed Kuamda cross-coupling of aryl chlorides and fluorides when secondary phosphine sulfides and secondary phosphine oxides were employed as the ligands.[42−44] It was also proven that for this reaction, THF is a better solvent than toluene.

We next examined the reactions using different aryl chlorides and aryl Grignard reagents catalyzed by the P,N,O-pincer nickels (Table 2). As seen in Table 2, the deactivated aryl chlorides, such as *p*-$Me_2NC_6H_4Cl$, *p*-$MeOC_6H_4Cl$ and *p*-$MOMOC_6H_4Cl$, can react efficiently with *p*-MeC_6H_4MgBr at room temperature in the presence of complex **2** (entries 1−3, Table 2). The reaction of *p*-$Me_2NC_6H_4Cl$ required higher catalyst loading (entry 2, Table 2). Both **4a** and **4b** also catalyzed the reaction of *p*-$Me_2NC_6H_4Cl$ and *p*-$MeOC_6H_4Cl$ with *p*-MeC_6H_4MgBr efficiently, giving the products in nearly quantitative yield (entries 5−8, Table 2). However, *o*-$MeOC_6H_4Cl$ showed lower reactivity. Its reaction with *p*-MeC_6H_4MgBr catalyzed by either **4a** or **4b** gave relatively low product yields (entries 9 and 10, Table 2). This is ascribed to its steric hindrance. *o*-MeC_6H_4MgBr showed simlar reactivity to *p*-MeC_6H_4MgBr when PhCl and *p*-$MeOC_6H_4Cl$ were employed as the electrophiles. It was found that *p*-$Me_2NC_6H_4Cl$ and *p*-$MOMOC_6H_4Cl$ are more difficult to react with *o*-MeC_6H_4MgBr at room temperature. For example, reaction of *p*-$Me_2NC_6H_4Cl$ with *o*-MeC_6H_4MgBr at room temperature in the presence of **2** (5 mol %) afforded 83% yield of cross-coupling product. This can be improved by raising reaction temperature (entries 14 and 15, Table 2). The reaction of *p*-$Me_2NC_6H_4Cl$ with *o*-MeC_6H_4MgBr at 70 °C using 3 mol % **2** generated 98% yield of cross-coupling product. The electron-rich Grignard reagent *p*-$MeOC_6H_4MgBr$ also reacted efficiently with aryl chlorides in the presence of **2** or **4a**. However, the reactivity of *p*-$MeOC_6H_4MgBr$ seems to be lower than that of *p*-MeC_6H_4MgBr, although *p*-$MeOC_6H_4MgBr$ is a stronger nucleophilic species. Reaction of activated aryl chloride, *p*-NCC_6H_4Cl, with *p*-MeC_6H_4MgBr in the presence of **2** proceeded smoothly. The cross-coupling product was obtained in 99% yield (entry 4, Table 2). However, *p*-NCC_6H_4Cl is incompatible with other Grignard reagents. Each of the reactions of *p*-NCC_6H_4Cl with *o*-MeC_6H_4MgBr and 2,4,6-$Me_3C_6H_2MgBr$ catalyzed by **2** afforded an addition product of the Grignard reagent to the CN group in almost quantitative yield. *o*-NCC_6H_4Cl is incompatible with Grignard reagents. We tried reactions of *o*-NCC_6H_4Cl with *p*-MeC_6H_4MgBr, *o*-MeC_6H_4MgBr, and 2,4,6-$Me_3C_6H_2MgBr$ in the presence of **2** and found that each of the reactions afforded addition products.

Heteroarenes are important constituents of natural products, pharmaceuticals, and fine chemicals. Synthesis of heteroaryl derivatives through cross-coupling methodology has received much attention in recent years.[45−49] Development of effective catalysts are thus highly desired in this area.[50,51] We tested the catalysis of complexes **2** and **4a** in the reaction of heteroaryl chlorides with aryl Grignard reagents, and the results are listed in Table 3. For the catalytic reaction between a heteroaryl chloride and an aryl Grignard reagent, diethyl ether is a suitable solvent. This was revealed by the reaction of 2-chloropyridine with *p*-MeC_6H_4MgBr catalyzed by **2** or **4a**. The reaction in THF gave cross-coupling products in 74 and 64% yields, respectively (entries 1 and 2, Table 3), whereas reactions in Et_2O led to 90 and 99% product yields, respectively (entries 3 and 4, Table 3). Complex **4a** also showed higher catalytic activity than **2a** in Et_2O. Hence, further screening was carried out in Et_2O using **4a** as a catalyst. The reaction of *o*-MeC_6H_4MgBr with 2-chloropyridine required much higher catalyst loading compared with that of *p*-MeC_6H_4MgBr, giving

Table 3. Reaction of Heteroaryl Chlorides with Aryl Grignard Reagents Catalyzed by 2 and 4a[a]



Entry	Het-ArCl	R	Catalyst (mol %)	Time (h)	Yield (%)[b]
1[c]		*p*-Me	**2** (0.5)	12	74
2[c]		*p*-Me	**4a** (0.5)	12	64
3		*p*-Me	**2** (0.5)	12	90
4		*p*-Me	**4a** (0.5)	12	99
5		*o*-Me	**4a** (4)	24	87
6		*p*-OMe	**4a** (2)	12	98
7		*p*-NMe_2	**4a** (1)	12	96
8		*p*-Me	**4a** (1)	12	86
9		*p*-OMe	**4a** (2)	12	96
10		*p*-Me	**4a** (0.5)	12	99
11		*o*-Me	**4a** (4)	12	95
12		*p*-OMe	**4a** (2)	12	93
13		*p*-Me	**4a** (1)	12	98
14		*p*-OMe	**4a** (2)	12	74
15		*p*-Me	**4a** (0.5)	12	99
16		*o*-Me	**4a** (3)	24	99
17		*p*-OMe	**4a** (2)	12	94
18		2,4,6-Me_3	**4a** (5)	12	99

[a]Reactions were performed with 0.5 mmol heteroaryl chlorides and 0.75 mmol Grignard reagents in 2.5 mL of Et_2O at 25 °C unless otherwise stated. [b]Isolated product yields. [c]THF was used as a solvent.

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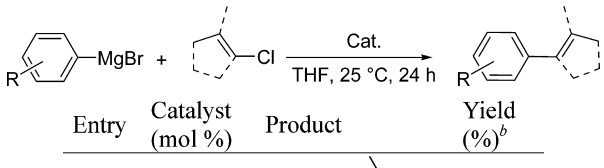
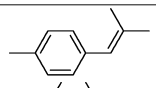
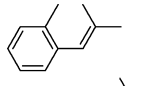
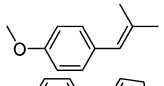
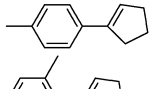
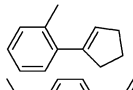
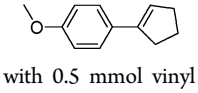
coupling product in 87% yield by using 4 mol % **4a** (entry 5, Table 3). This may be because the reaction is very sensitive to the steric hindrance of an ortho methyl group in *o*-MeC_6H_4MgBr. As expected, the reaction of electron-rich Grignard reagents, *p*-$MeOC_6H_4MgBr$ and *p*-$Me_2NC_6H_4MgBr$, with 2-chloropyridine in the presence of **4a** proceeded smoothly, forming corresponding cross-coupling products in 98 and 96% yields, respectively. 2-Chloro-6-methoxypyridine was expected to be less reactive than 2-chloropyridine in the cross-coupling. Its reaction with *p*-MeC_6H_4MgBr did require higher catalyst loading and gave a little lower yield than that of 2-chloropyridine. However, the reaction of 2-chloro-6-methoxypyridine with *p*-$MeOC_6H_4MgBr$ gave a comparable result to 2-chloropyridine under the same conditions. 2-Chloro-4-methylquinoline behaved similarly to 2-chloropyridine in the catalytic reactions. Its reaction with each of *p*-MeC_6H_4MgBr, *o*-MeC_6H_4MgBr, and *p*-$MeOC_6H_4MgBr$ gave excellent product yields. Both 2-chloro-1,3-benzothiazole and 2-chloro-1,3-benzoxazole were also tested in the catalyzed coupling reaction using **4a** as a catalyst. Reaction between 2-chloro-1,3-benzothiazole and *p*-$MeOC_6H_4MgBr$ afforded relatively low product yield (74%). However, each of the reactions of 2-chloro-1,3-benzothiazole and 2-chloro-1,3-benzoxazole with *p*-MeC_6H_4MgBr, *o*-MeC_6H_4MgBr, or *p*-$MeOC_6H_4MgBr$ in the presence of 0.5−3 mol % **4a** led to excellent product yields. A very bulky nucleophilic reagent, 2,4,6-$Me_3C_6H_2MgBr$, can react very well with 2-chloro-1,3-benzoxazole at room temperature in the presence of 5 mol % **4a**. The reaction gave cross-coupling product in 99% isolated yield (entry 18, Table 3).

Alkenyl chlorides were also used as coupling partners with aryl Grignard reagents. Both **2** and **4a** are efficient catalysts for the coupling of 1-chloro-2-methylprop-1-ene and 1-chlorocyclopent-1-ene with *p*-MeC_6H_4MgBr, *o*-MeC_6H_4MgBr, or *p*-$MeOC_6H_4MgBr$. The reactions were performed in THF at 25 °C in the presence of 1.5−2 mol % **2** or **4a** and gave 85−93% product yields (Table 4). The steric hindrance of the ortho methyl group in *o*-MeC_6H_4MgBr seems not to cause a decrease in the coupling product yields.

Table 4. Reaction of 1-Chloro-2-methyl-1-propene with Grignard Reagents Catalyzed by 2 and 4a[a]



Entry	Catalyst (mol %)	Product	Yield (%)[b]
1	**2** (1.5)		91
2	**2** (1.5)		93
3	**4a** (2)		88
4	**2** (1.5)		90
5	**2** (2)		88
6	**4a** (2)		85

[a]Reactions were performed with 0.5 mmol vinyl chlorides and 0.75 mmol Grignard reagents in 2.5 mL of THF at 25 °C. [b]Isolated product yields.

Because of the high reactivity of Grignard reagents relative to other organometallic species such as organozinc, organotin, and organoboron reagents, Kumada reaction is often incompatible with the functionalized substrates. However, organozinc reagents, organostannanes, and organoboronic acid and esters used in metal-catalyzed C−C coupling reactions are generally derived from the corresponding magnesium or lithium reagents. Therefore, direct use of Grignard reagents is an attractive alternative that eliminates an additional synthetic step. For this reason, we examined **2**- or **4a**-catalyzed reactions of functionalized aryl chlorides with aryl Grignard reagents. The initial test by reaction of *p*-ClC_6H_4COOEt with *p*-MeC_6H_4MgBr in THF using **4a** as a catalyst showed only trace cross-coupling product to be formed. In an earlier study, we found that suitable additives such as LiCl and $ZnCl_2$ can improve the compatibility of functional groups.[36] This strategy was used in the current reaction. When 1 equiv of LiCl was added and NMP was employed as a cosolvent, the reaction mentioned above gave cross-coupling product in 74% yield. More LiCl additives led to higher product yield. When 3 equiv of LiCl was employed, the reaction in a mixed solvent of THF and NMP gave 90% product yield. However, in the absence of a NMP cosolvent, the reaction gave a relatively low product yield (49%), although 3 equiv of LiCl were still employed. When DMA was used to replace NMP as a cosolvent, no cross-coupling product can be isolated (entry 6, Table 5). Further investigations showed that 1 equiv of LiCl and 2 mol % $ZnCl_2$ additives led to the same result as the 3 equiv of LiCl additives (entry 8, Table 5). Complex **2** exhibited a similar behavior to complex **4** in the reaction of *p*-ClC_6H_4COOEt with *p*-MeC_6H_4MgBr (entries 9 and 10, Table 5). It was also noted that excess Grignard reagents were required to improve the yields.

With the optimized conditions in hand, we surveyed the scope of functionalized substrates (Table 6). *p*-$ClC_6H_4COOBu^t$ displayed better results than *p*-ClC_6H_4COOEt in the reaction with *p*-MeC_6H_4MgBr catalyzed by **2** or **4a** (entries 1 and 2, Table 6). A similar phenomenon was observed in the **2**-catalyzed reaction of *p*-$ClC_6H_4COOBu^t$ and *p*-ClC_6H_4COOEt with *o*-MeC_6H_4MgBr (entries 7 and 8, Table 6). *p*-$ClC_6H_4C(O)NEt_2$ is also a suitable electrophilic substrate in the reaction with *p*-MeC_6H_4MgBr or *p*-$MeOC_6H_4MgBr$ (entries 3, 4, and 10, Table 6). In the reaction of *p*-$ClC_6H_4C(O)NEt_2$ with *p*-MeC_6H_4MgBr, complex **4a** showed a slightly higher catalytic activity than **2**. The reaction of *p*-ClC_6H_4COPh with *p*-MeC_6H_4MgBr also proceeded in moderate yields in the presence of **2** or **4a** but required higher catalyst loading and more $ZnCl_2$ additives (10 mol %) (entries 5 and 6, Table 6). This is probably because the ketone carbonyl group is more reactive than those of esters and carboxamide. The reaction of *p*-ClC_6H_4CHO with aryl Grignard reagents using **2** or **4a** as a catalyst can not generate cross-coupling products because of the high reactivity of CHO group. Surprisingly, 2-(4-chlorophenyl)-1,3-dioxolane can not catalytically couple with aryl Grignard reagents in the absence of additives. In the presence of LiCl (1 equiv) and $ZnCl_2$ (10 mol %), the **2**- or **4a**-catalyzed reaction of 2-(4-chlorophenyl)-1,3-dioxolane with *p*-MeC_6H_4MgBr in a mixture of THF and NMP afforded cross-coupling products in good yields (entries 11 and 12, Table 6). The cross-coupling of *p*-$ClC_6H_4CF_3$ with *p*-MeC_6H_4MgBr catalyzed by **4a** under the standard conditions gave excellent

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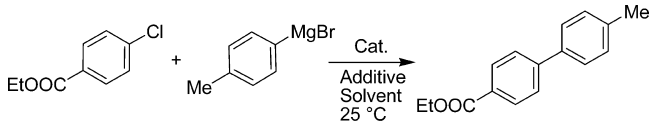
Table 5. Reaction of *p*-ClC_6H_4COOEt with *p*-MeC_6H_4MgBr Catalyzed by 2 and 4a[a]



entry	catalyst (mol %)	additive	solvent	yield (%)[b]
1	**4a** (2)		THF (3.7 mL)	trace
2	**4a** (2)	LiCl (1 equiv)	THF (2.2 mL) + NMP (1.5 mL)	74
3	**4a** (2)	LiCl (2 equiv)	THF (2.2 mL) + NMP (1.5 mL)	88
4	**4a** (2)	LiCl (3 equiv)	THF (2.2 mL) + NMP (1.5 mL)	90
5	**4a** (2)	LiCl (3 equiv)	THF (3.7 mL)	49
6	**4a** (2)	LiCl (3 equiv)	THF (2.2 mL) + DMA (1.5 mL)	0
7	**4a** (1)	LiCl (3 equiv)	THF (2.2 mL) + NMP (1.5 mL)	79
8	**4a** (2)	LiCl (1 equiv), ZnCl (2 mol %)	THF (2.2 mL) + NMP (1.5 mL)	90
9	**2** (2)	LiCl (3 equiv)	THF (2.2 mL) + NMP (1.5 mL)	76
10	**2** (2)	LiCl (1 equiv), ZnCl (2 mol %)	THF (2.2 mL) + NMP (1.5 mL)	85

[a]Reactions were performed with 0.5 mmol *p*-ClC_6H_4COOEt and 1.1 mmol *p*-MeC_6H_4MgBr at 25 °C. After the mixture of *p*-ClC_6H_4COOEt, additives, solvent, and 0.6 mmol *p*-MeC_6H_4MgBr in THF was stirred for 2 h, additional 0.5 mmol *p*-MeC_6H_4MgBr was injected, and stirring was continued for an additional 2 h. [b]Isolated product yields.

results. However, the reaction catalyzed by **2** under the same conditions led to a much lower yield (60%) (entries 13 and 14, Table 6). In fact, in most cases complex **4a** exhibited comparable catalytic activity to **2**, whereas complex **4a** showed higher catalytic activity than **2** in the reactions using *p*-$ClC_6H_4C(O)NEt_2$ and *p*-$ClC_6H_4CF_3$ as electrophilic substrates.

In summary, we have described a broadly applicable nickel-catalyzed Kumada reaction at room temperature. The P,N,O-chelate nickel complexes showed high catalytic activity for the coupling reactions of unactivated and deactivated aryl chlorides, heteroaryl chlorides, and vinyl chlorides with aryl Grignard reagents. In the presence of LiCl and $ZnCl_2$ additives, the reactions tolerate a few types of functional groups such as ester, ketone, carboxamide, and trifluoromethyl groups. In contrast, P,N,S-chelate complexes **1** and **3** revealed a relatively low catalytic activity. This work significantly expands the substrate scopes of Kumada cross-coupling reactions.

EXPERIMENTAL SECTION

All reactions were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene) or sodium/benzophenone (THF and Et_2O) and degassed prior to use. NMP and DMA were dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under nitrogen atmosphere. All catalysts were prepared according to the reported methods.[41] The Grignard reagents were prepared according to the procedure reported in literature.[52] All other chemicals and solvents 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.

General Procedure for the Cross-Coupling Reactions Catalyzed by 1−4b. *(1). Representative Procedure for the Kumada Coupling of Aryl Chlorides.* A Schlenk tube was charged with nickel complex **2** (0.05 mL, 0.05 M solution in THF, 0.0025 mmol), THF (1.5 mL), and PhCl (0.056 g, 0.5 mmol). To the solution was added dropwise a solution of *p*-MeC_6H_4MgBr (1.5 mL, 0.5 M in THF, 0.75 mmol) at 25 °C with stirring. After stirring at this temperature for 24 h, the reaction mixture was quenched with water and extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried over Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel, eluted using petroleum ether) to afford *p*-MeC_6H_4Ph (0.084 g, 99%).

The reactions in toluene or Et_2O followed the same procedure, only THF was replaced with the required solvent.

(2). Representative Procedure for the Kumada Coupling of Functionalized Aryl Chlorides. A Schlenk tube was charged with nickel complex **4a** (6.6 mg, 0.01 mmol), LiCl (21.2 mg, 0.5 mmol), $ZnCl_2$ (0.1 mL, a solution of 136 mg of $ZnCl_2$ in 10 mL of THF, 0.01 mmol), NMP (1.5 mL), and *p*-ClC_6H_4COOEt (0.092 g, 0.5 mmol). To the mixture was added slowly *p*-MeC_6H_4MgBr (1.2 mL, 0.5 M in THF, 0.6 mmol) at 25 °C with stirring. After the resulting solution was stirred at 25 °C for 2 h, a solution of *p*-MeC_6H_4MgBr (1 mL, 0.5 M in THF, 0.5 mmol) was slowly added again. After further stirring at 25 °C for 2 h, the reaction mixture was quenched with water and extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried over Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel, eluted using 3% CH_3COOEt−petroleum ether) to afford ethyl 4-(*p*-tolyl)benzoate (0.108 g, 90%).

Spectral Data of the Cross-Coupling Products. *4-Methylbiphenyl.*[36] ^1H NMR ($CDCl_3$): δ 2.35 (s, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.2, 126.9, 127.1, 127.3, 127.4, 128.8, 129.56, 129.61, 137.1, 138.5, 141.3.

4-Methoxy-4′-methylbiphenyl.[36] ^1H NMR ($CDCl_3$): δ 2.29 (s, 3H), 3.74 (s, 3H), 6.87 (d, *J* = 9 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.1, 55.4, 114.3, 126.7, 128.0, 129.6, 133.9, 136.4, 138.1, 159.1.

4′-Methyl-N,N-dimethylbiphenyl-4-amine.[53] ^1H NMR ($CDCl_3$): δ 2.27 (s, 3H), 2.86 (s, 6H), 6.69 (d, *J* = 9 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.2, 40.8, 113.0, 126.3, 127.6, 129.5, 135.7, 138.4, 149.8.

4-(Methoxymethoxy)-4′-methylbiphenyl.[54] ^1H NMR ($CDCl_3$): δ 2.28 (s, 3H), 3.39 (s, 3H), 5.10 (s, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.2, 56.1, 94.6, 116.6, 126.8, 128.1, 129.6, 135.1, 136.6, 138.0, 156.7.

4′-Methylbiphenyl-4-carbonitrile.[36] ^1H NMR ($CDCl_3$): δ 2.34 (s, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.3, 110.6, 119.1, 127.2, 127.6, 130.0, 132.7, 136.4, 138.9, 145.7, 157.2.

2-Methoxy-4′-methylbiphenyl.[36] ^1H NMR ($CDCl_3$): δ 2.30 (s, 3H), 3.71 (s, 3H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.3, 55.7, 111.4, 120.1, 120.9, 128.5, 128.9, 129.6, 130.9, 135.8, 136.7, 156.7.

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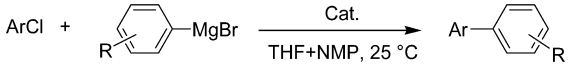
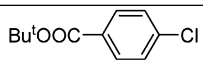
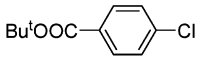
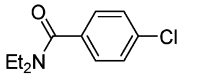
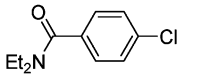
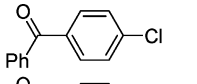
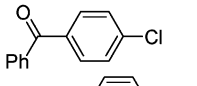
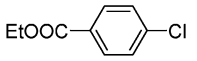
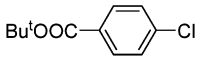
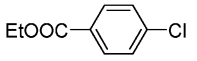
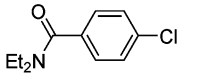
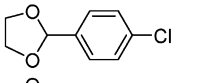
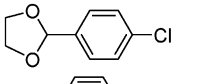
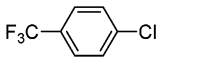
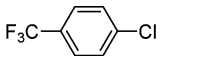
Table 6. Reaction of Functionalized Aryl Chlorides with Grignard Reagents Catalyzed by 2 and 4a[a]



Entry	ArCl	R	Catalyst (mol %)	Yield (%)[b]
1		*p*-Me	**2** (2)	97
2		*p*-Me	**4a** (2)	98
3		*p*-Me	**2** (2)	88
4		*p*-Me	**4a** (2)	99
5[c]		*p*-Me	**2** (5)	78
6[c]		*p*-Me	**4a** (5)	76
7		*o*-Me	**2** (5)	77
8		*o*-Me	**2** (5)	91
9[c]		*p*-OMe	**4a** (3)	81
10		*p*-OMe	**4a** (2)	86
11[c]		*p*-Me	**2** (4)	87
12[c]		*p*-Me	**4a** (4)	88
13		*p*-Me	**2** (3)	60
14		*p*-Me	**4a** (3)	90

[a]Unless otherwise stated, the reactions were carried out as the following procedure: a mixture of 0.5 mmol aryl chloride, 1 equiv of LiCl, 2 mol % $ZnCl_2$, 1.5 mL of NMP, required catalyst, and 0.6 mmol Grignard reagent in THF was stirred at 25 °C for 2 h. Then, additional 0.5 mmol Grignard reagent in THF was injected, and stirring was continued for an additional 2 h. [b]Isolated product yields. [c]10 mol % $ZnCl_2$ was used.

2-Methylbiphenyl.[55] ^{1}H NMR ($CDCl_3$): δ 2.26 (s, 3H), 7.20−7.26 (m, 4H), 7.28−7.34 (m, 3H), 7.36−7.42 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 20.6, 125.7, 125.9, 126.9, 127.3, 127.4, 128.29, 129.3, 129.9, 130.4, 135.5, 142.09, 142.13.

4′-Methoxy-2-methylbiphenyl.[41] ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H), 3.80 (s, 3H), 6.94 (d, J = 8.7 Hz, 2H), 7.17−7.22 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 20.7, 55.4, 113.6, 125.9, 127.1, 130.0, 130.37, 130.41, 134.5, 135.6, 141.7, 158.7.

2′-Methyl-N,N-dimethylbiphenyl-4-amine.[53] ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 3H), 2.86 (s, 6H), 6.67 (d, J = 8.4 Hz, 2H), 7.05−7.15 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 20.8, 40.7, 112.3, 125.8, 126.6, 130.1, 130.4, 135.5, 142.1, 149.5.

4-(Methoxymethoxy)-2′-methylbiphenyl. ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 3H), 3.40 (s, 3H), 5.10 (s, 2H), 6.97 (d, J = 8.6 Hz, 2H), 7.08−7.15 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 20.6, 56.1, 94.6, 115.9, 125.9, 127.2, 130.0, 130.4, 135.5, 135.7, 141.6, 156.3. HR-MS (EI): m/z 228.1152 $[M]^+$, calcd for $C_{15}H_{16}O_2$ 228.1150.

4-Methoxybiphenyl.[36] ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 3H), 6.96 (d, J = 8.7 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.49−7.55 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 55.4, 114.3, 126.8, 128.3, 128.8, 133.9, 140.9, 159.3.

4′-Methoxy-2,5-dimethylbiphenyl.[56] ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 3H), 2.33 (s, 3H), 3.84 (s, 3H), 6.94 (d, J = 8.7 Hz, 2H), 7.03−7.05 (m, 2H), 7.14 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.2, 21.0, 55.4, 113.6, 127.8, 130.4, 130.8, 132.4, 134.6, 135.3, 141.5, 158.6.

4′-Methoxy-N,N-dimethylbiphenyl-4-amine.[41] ^{1}H NMR ($CDCl_3$): δ 2.96 (s, 6H), 3.82 (s, 3H), 6.78 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 7.45 (t, J = 8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 40.8, 55.5, 113.1, 114.3, 127.5, 129.4, 134.1, 149.7, 158.4.

4-(Methoxymethoxy)-4′-methoxybiphenyl. ^{1}H NMR ($CDCl_3$): δ 3.49 (s, 3H), 3.81 (s, 3H), 5.19 (s, 3H), 6.94 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 55.4, 56.1, 94.6, 114.3, 116.7, 127.9, 127.9, 133.5, 134.8, 156.5, 158.9. HR-MS (EI): m/z 244.1102 $[M]^+$, calcd for $C_{15}H_{16}O_3$ 244.1099.

2-p-Tolylpyridine.[36] ^{1}H NMR ($CDCl_3$): δ 2.37 (s, 3H), 7.10−7.27 (m, 1H), 7.25 (d, J = 7.9 Hz, 2H), 7.65−7.67 (m, 2H), 7.88 (d, J = 8.1 Hz, 2H), 8.64−8.66 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 21.38, 120.2, 121.8, 126.8, 129.5, 136.7, 139.0, 149.6, 157.5.

2-o-Tolylpyridine.[14] ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H), 7.19−7.29 (m, 4H), 7.36−7.41 (m, 2H), 7.71 (dt, J = 1.8, 7.8 Hz, 1H), 8.68 (d, J = 4.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 20.3, 121.7, 124.1, 125.9, 128.3, 129.7, 130.8, 135.8, 136.2, 140.5, 149.2, 160.1.

2-(p-Methoxyphenyl)pyridine.[14] ^{1}H NMR ($CDCl_3$): δ 3.82 (s, $3H_3$), 6.98 (d, J = 8.7 Hz, 2H), 7.11−7.15 (m, 1H), 7.61−7.69 (m, 2H), 7.94 (d, J = 8.7 Hz, 2H), 8.63 (d, J = 4.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 55.3, 114.2, 119.8, 121.4, 128.2, 132.1, 136.7, 149.6, 157.1, 160.5.

2-(p-N,N-Dimethylaminophenyl)pyridine.[57] ^{1}H NMR ($CDCl_3$): δ 2.96 (s, 6H), 6.76 (d, J = 8.9 Hz, 2H), 7.05 (d, J = 4.5 Hz, 1H), 7.59−7.61 (m, 2H), 7.91 (d, J = 8.9 Hz, 2H), 8.60 (d, J = 4.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 40.3, 112.2, 119.1, 120.6, 127.7, 136.5, 149.4, 151.2, 157.6.

2-Methoxy-6-(4′-methylphenyl)pyridine.[58] ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H), 3.94 (s, 3H), 6.56 (d, J = 8.4 Hz, 1H), 7.15−7.22 (m, 3H), 7.50 (t, J = 7.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.4, 53.3, 108.9, 112.5, 118.1, 126.7, 127.0, 129.4, 136.5, 138.9, 139.2, 154.9, 163.8.

2-Methoxy-6-(4′-methoxyphenyl)pyridine.[59] ^{1}H NMR ($CDCl_3$): δ 3.72 (s, 3H), 3.91 (s, 3H), 6.51 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.89 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 53.2, 55.4, 108.4, 112.0, 114.0, 114.2, 127.8, 128.0, 131.8, 139.2, 154.5, 160.4, 163.7.

4-Methyl-2-(4′-methylphenyl)quinoline.[58] ^{1}H NMR ($CDCl_3$): δ 2.26 (s, 3H), 2.50 (s, 3H), 7.11−7.16 (m, 2H), 7.25−7.34 (m, 1H), 7.40−7.55 (m, 2H), 7.70−7.76 (m, 1H), 7.85−7.92 (m, 2H), 8.00−8.04 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 18.9, 21.3, 119.5, 123.6, 125.8, 127.1, 127.4, 129.2, 129.5, 130.2, 136.9, 139.2, 144.6, 148.1, 156.9.

4-Methyl-2-(2′-methylphenyl)quinoline.[60] ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 3H), 2.69 (s, 3H), 7.30 (s, 3H), 7.34 (s, 4H), 7.45−7.56 (m, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 18.9, 20.4, 123.1, 123.6, 126.0, 126.2, 126.8, 128.4, 129.3, 129.6, 130.2, 130.8, 136.0, 140.9, 144.2, 147.7, 160.1.

4-Methyl-2-(4′-methoxyphenyl)quinoline.[61] ^{1}H NMR ($CDCl_3$): δ 2.68 (s, 3H), 3.85 (s, 3H), 7.04 (d, J = 8.7 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.63 (s, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 8.10−8.19 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 19.0, 55.3, 114.1, 119.2, 123.6, 125.6, 127.0, 128.8, 129.2, 130.0, 132.3, 144.5, 148.1, 156.5, 160.7.

2-(4′-Methylphenyl)benzothiazole.[62] ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H), 7.11 (d, J = 7.8 Hz, 2H), 7.17−7.22 (m, 1H), 7.30−7.35 (m, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 121.6, 123.1, 125.0, 126.2, 127.5, 128.9, 129.7, 135.0, 141.4, 154.3, 168.2.

2-(4′-Methoxyphenyl)benzothiazole.[62] ^{1}H NMR ($CDCl_3$): δ 3.83 (s, 3H), 6.97 (d, J = 9 Hz, 2H), 7.31−7.36 (m, 1H), 7.44−7.49 (m,

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1H), 7.85 (d, J = 8.1 Hz, 1H), 8.03 (t, J = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 55.5, 114.4, 121.6, 122.9, 124.8, 126.2, 126.5, 129.1, 134.9, 154.3, 162.0, 167.9.

2-(4′-Methylphenyl)benzoxazole.[63] ^{1}H NMR ($CDCl_3$): δ 2.26 (s, 3H), 7.11−7.22 (m, 4H), 7.39−7.42 (m, 1H), 7.59−7.66 (m, 1H), 8.00 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.6, 110.5, 119.9, 124.5, 124.9, 127.6, 128.9, 129.6, 130.2, 142.0, 142.3, 150.7, 163.4.

2-(2′-Methylphenyl)benzoxazole.[63] ^{1}H NMR ($CDCl_3$): δ 2.68 (s, 3H), 7.13−7.9 (m, 5H), 7.40−7.46 (m, 1H), 7.66−7.69 (m, 1H), 8.03−8.06 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 22.3, 110.5, 120.2, 124.4, 125.1, 126.1, 130.0, 130.9, 131.8, 138.9, 142.3, 150.4, 163.4.

2-(4′-Methoxyphenyl)benzoxazole.[63] ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H), 6.97 (d, J = 8.7 Hz, 2H), 7.24−7.32 (m, 2H), 7.47−7.52 (m, 1H), 7.70−7.75 (m, 1H), 8.15 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 55.4, 110.4, 114.3, 119.6, 124.4, 124.6, 129.4, 142.3, 150.7, 162.3, 163.2.

2-(2′,4′,6′-Trimethylphenyl)benzoxazole.[64] ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 6H), 2.21 (s, 3H), 6.84 (s, 2H), 7.20−7.27 (m, 2H), 7.42−7.46 (m, 1H), 7.69−7.72 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 20.4, 21.3, 110.6, 120.2, 124.3, 124.9, 128.7, 138.5, 140.3, 141.7, 150.7, 163.3.

p-Methyl-β,β-dimethylstyrene.[65] ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 3H), 1.88 (s, 3H), 2.32 (s, 3H), 6.23 (s, 1H), 7.11 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 19.5, 21.2, 27.0, 125.2, 128.8, 128.9, 134.8, 135.4, 136.0.

o-Methyl-β,β-dimethylstyrene.[66] ^{1}H NMR ($CDCl_3$): δ 1.72 (s, 3H), 1.92 (s, 3H), 2.25 (s, 3H), 6.25 (s, 1H), 7.14 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 19.3, 20.0, 26.2, 124.3, 125.4, 127.4, 129.6, 129.8, 135.0, 136.4, 138.0.

p-Methoxy-β,β-dimethylstyrene.[67] ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 3H), 1.87 (s, 3H), 3.76 (s, 3H), 6.20 (s, 1H), 6.83 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 19.3, 26.8, 55.2, 113.5, 124.7, 129.9, 131.4, 133.9, 157.8.

1-Cyclopentenyl-4-methylbenzene.[68] ^{1}H NMR ($CDCl_3$): δ 1.95−2.05 (m, 2H), 2.33 (s, 3H), 2.48−2.55 (m, 2H), 2.65−2.72 (m, 2H), 6.11−6.14 (m, 1H), 7.11 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.3, 23.2, 33.37, 33.44, 125.2, 125.6, 129.1, 134.2, 136.6, 142.4.

1-Cyclopentenyl-2-methylbenzene.[16] ^{1}H NMR ($CDCl_3$): δ 1.94−2.05 (m, 2H), 2.35 (s, 3H), 2.49−2.56 (m, 2H), 2.62−2.70 (m, 2H), 5.75−5.78 (m, 1H), 7.12−7.21 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 21.3, 23.9, 33.7, 36.8, 125.7, 126.7, 128.1, 129.5, 130.6, 135.6, 138.4, 143.4.

1-Cyclopentenyl-4-methoxybenzene.[16] ^{1}H NMR ($CDCl_3$): δ 1.95−2.05 (m, 2H), 2.47−2.55 (m, 2H), 2.64−2.71 (m, 2H), 3.80 (s, 3H), 6.03−6.06 (m, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 23.5, 33.4, 55.4, 113.8, 124.1, 126.8, 129.9, 142.0, 158.7.

Ethyl 4′-Methylbiphenyl-4-carboxylate.[36] ^{1}H NMR ($CDCl_3$): δ 1.30 (t, J = 7.2 Hz, 3H), 2.29 (s, 3H), 4.29 (q, J = 7.1 Hz, 2H), 7.15 (d, J = 8 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.53 (d, 2H, J = 8.3 Hz), 7.99 (d, 2H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$): δ 14.5, 21.2, 61.0, 126.8, 127.2, 129.1, 129.7, 130.1, 137.2, 138.1, 145.6, 166.6.

tert-Butyl 4-(p-Tolyl)benzoate.[36] ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 9H), 2.27 (s, 3H), 7.12 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.2, 28.3, 80.9, 126.7, 127.2, 129.7, 130.0, 130.6, 137.4, 138.0, 145.2, 165.8.

N,N-Diethyl-4′-methylbiphenyl-4-carboxamide.[36] ^{1}H NMR ($CDCl_3$): δ 1.19 (b, 6H), 2.38 (s, 3H), 3.32 (b, 2H), 3.53 (b, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 13.0, 14.1, 21.0, 39.3, 43.3, 126.77, 126.80, 126.90, 129.5, 135.7, 137.4, 141.9, 171.1.

(4′-Methylbiphenyl-4-yl)(phenyl)methanone.[36] ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H), 7.17 (d, J = 8.1 Hz, 2H), 7.36−7.51 (m, 5H), 7.58 (d, J = 8.4 Hz, 2H), 7.71−7.79 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 21.3, 126.8, 127.2, 128.4, 129.8, 130.1, 130.8, 132.4, 136.0, 137.1, 137.9, 138.2, 145.2, 196.4.

Ethyl 2′-Methylbiphenyl-4-carboxylate.[36] ^{1}H NMR ($CDCl_3$): δ 1.30 (t, J = 7.1 Hz, 3H), 2.15 (s, 3H), 4.28 (q, J = 7.1 Hz, 2H), 7.08−7.16 (m, 4H), 7.27 (d, J = 8.7 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.4, 20.4, 61.0, 126.0, 127.9, 129.3, 129.5, 129.6, 130.6, 135.2, 141.0, 146.7, 166.6.

tert-Butyl 2-(o-Tolyl)benzoate. ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 9H), 2.14 (s, 3H), 7.09−7.15 (m, 4H), 7.26 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.5, 28.3, 81.0, 126.0, 127.8, 129.2, 129.4, 129.6, 130.5, 135.2, 141.1, 146.3, 165.8. HR-MS (EI): m/z 268.1459 $[M]^+$, calcd for $C_{18}H_{20}O_2$ 268.1463.

Ethyl 4′-Methoxybiphenyl-4-carboxylate.[36] ^{1}H NMR ($CDCl_3$): δ 1.39 (t, J = 7.2 Hz, 3H), 3.82 (s, 3H), 4.38 (q, J = 7.2 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.4, 55.4, 60.9, 114.5, 126.5, 128.4, 128.7, 130.1, 132.5, 145.2, 159.9, 166.6.

N,N-Diethyl-4′-methoxybiphenyl-4-carboxamide.[69] ^{1}H NMR ($CDCl_3$): δ 1.14 (b, 3H), 1.23 (b, 3H), 3.31 (b, 2H), 3.54 (b, 2H), 3.81 (s, 3H), 6.96 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 12.9, 14.2, 39.2, 43.3, 55.3, 114.2, 126.5, 126.8, 128.1, 132.7, 135.4, 141.5, 159.4, 171.1.

2-(4′-Methyl[1,1′-biphenyl]-4-yl)-1,3-dioxolane.[70] ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H), 3.88−4.08 (m, 4H), 5.75 (s, 1H), 7.14 (d, J = 7.9 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 21.2, 65.4, 103.7, 126.9, 127.0, 127.1, 129.6, 136.7, 137.3, 138.0, 142.1.

4-Methyl-4′-(trifluoromethyl)biphenyl.[41] ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H), 7.26 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.65 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 21.3, 125.8 (q, J = 3.5 Hz), 127.2, 127.3, 129.9, 137.0, 138.3, 144.8.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zxwang@ustc.edu.cn.

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