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Nickel-Catalyzed Cross-Coupling of (Hetero)aryl Chlorides with Aryllithium Compounds

Jian-Long Tao,^[a] and Zhong-Xia Wang*^[a,b]

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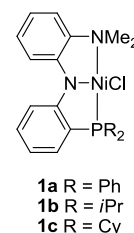
Abstract: The pincer nickel complexes [Ni(Cl){N(2-R₂PC₆H₄)(2'-Me₂NC₆H₄)}] (R = Ph, **1a**; R = *i*Pr, **1b**; R = Cy, **1c**) were demonstrated to catalyze cross-coupling of aryl or heteroaryl chlorides with aryl lithium compounds under mild reaction conditions. Complex **1a** showed higher catalytic activity and resulted in biaryl products in 23-96% yields. A series of aryl chlorides including deactivated ones such as 1-chloro-4-methoxybenzene, 4-chloro-N,N-dimethylaniline and 1-chloro-4-methylbenzene and heteroaryl chlorides including 2- and 3-chloropyridine, 2-chloro-4-methylquinoline, 2-chloro-thiophene, 2-chlorobenzofuran, 2-chlorobenzo[d]oxazole, and 2-chlorobenzo[d]thiazole were employed in this coupling reaction.

Introduction

Transition-metal-catalyzed cross-coupling reactions such as Kumada, Negishi, Stille, Suzuki and Hiyama reaction are powerful tools to construct C-C bond in organic synthesis.^[1-3] Nucleophiles used in these cross-couplings are various organometallic reagents including organomagnesium, -zinc, -tin, -boron, and -silicon compounds. Organolithium compounds were rarely used as a nucleophilic reagent in cross-coupling reactions due to their high reactivity which often results in side reactions and the lack of selectivity. However, the direct use of organolithium compounds as nucleophiles in cross-coupling reactions is highly desirable for (1) it offers a more direct approach to the desired products because organozinc, -tin, -boron, and -silicon reagents are frequently prepared from corresponding organolithium compounds, and (2) organolithium compounds are cheap, widely available or readily prepared. Murahashi et al. pioneered the use of organolithium reagents in cross-coupling in the 1970s.^[4,5] However, only sporadic work on this topic were reported in the following decades.^[6] Recently, Feringa and coworkers carried out Pd-catalyzed cross-coupling of organic halides/triflates with aryl, alkenyl or alkyl lithium reagents.^[7] In the reported examples palladium was almost sole catalyst in combination with appropriate ligands. It was indicated

that the nickel-catalyzed cross-coupling reaction with organolithium compounds did not work well.^[6b] However, nickel has a significant price advantage compared with palladium. Hence it is of significance to explore the possibility using nickel as a catalyst for the cross-coupling.

Our group demonstrated that pincer nickel complexes could catalyze cross-coupling of aryl chlorides with organomagnesium or -zinc reagents.^[8] Recently we found that N,N,P-pincer nickel complexes **1a-1c** could catalyze the cross-coupling of aryl fluorides with aryl Grignard reagents or aryl chlorides with aryl zinc reagents under mild conditions and complex **1a** exhibited excellent catalyst activity.^[8b] This success encouraged us to examine their catalysis in the cross-coupling of organolithium reagents.



Results and Discussion

Reaction of *p*-MeOC₆H₄Cl with *p*-MeC₆H₄Li was used to evaluate the catalytic efficiency of complexes **1a-1c** and optimize the reaction conditions. In the presence of 5 mol% **1a**, **1b** or **1c** the reaction of *p*-MeOC₆H₄Cl with 2 equiv. of *p*-MeC₆H₄Li in THF at room temperature resulted in desired product in 45%, 42% and 35% yields, respectively (Table 1, entries 1-3). Slow addition dropwise *p*-MeC₆H₄Li to a mixture of *p*-MeOC₆H₄Cl and the catalyst was necessary to suppress side reactions. Lower reaction temperature than room temperature resulted in decrease of product yields (Table 1, entries 4-7). Raising the reaction temperature to 40 °C led to slight yield increase (Table 1, entry 8). Solvent screen at room temperature showed that Et₂O was a better solvent than toluene and THF in this transformation (Table 1, entries 9 and 10). Further test showed that use of 2.5 equiv. of *p*-MeC₆H₄Li led to better result, 83% yield being achieved in Et₂O at room temperature (Table 1, entry 11). The demand of excess *p*-MeC₆H₄Li is due to the homocoupling side reaction which consumed part of *p*-MeC₆H₄Li reagent. We also tested the reaction with less catalyst loadings. 3 mol% of **1a** led to almost same yield as that using 5 mol% **1a**, whereas 1 mol% **1a** resulted in marked yield decrease (Table 1, entries 12 and 13). For comparison, NiCl₂(PCy₃)₂ and NiCl₂(PPh₃)₂ were respectively used to catalyze the reaction under the same conditions as shown in entry 12. The reactions gave the cross-coupling product in 56% and 37% yields,

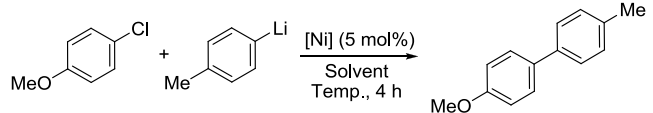
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respectively (Table 1, entries 14 and 15). This yield contrast may be due to higher stability of the catalytic active species formed from **1a** than that formed from $\text{NiCl}_2(\text{PCy}_3)_2$ or $\text{NiCl}_2(\text{PPh}_3)_2$ under the reaction conditions. We also examined the reaction in the absence of a catalyst. Only trace amount of cross coupling product was observed (Table 1, entry 16).

Table 1. Catalyst evaluation and optimization of reaction conditions^[a]



Entry	Catalyst	Solvent	Temp. (°C)	Yield (%) ^[b]
1	1a	THF	25	45
2	1b	THF	25	42
3	1c	THF	25	35
4	1a	THF	-30	13
5	1a	THF	-15	20
6	1a	THF	0	31
7	1a	THF	15	33
8	1a	THF	40	47
9	1a	Toluene	25	52
10	1a	Et ₂ O	25	78
11 ^[c]	1a	Et ₂ O	25	83
12 ^[c,d]	1a	Et ₂ O	25	82
13 ^[c,e]	1a	Et ₂ O	25	65
14 ^[c,d]	$\text{NiCl}_2(\text{PCy}_3)_2$	Et ₂ O	25	56
15 ^[c,d]	$\text{NiCl}_2(\text{PPh}_3)_2$	Et ₂ O	25	37
16 ^[f]	none	Et ₂ O	25	trace

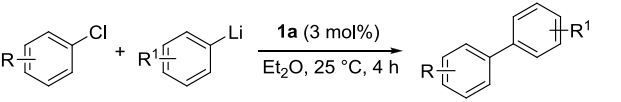
[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation. 0.6 mmol *p*-MeC₆H₄Li (diluted with appropriate solvent to reach the concentration of 0.3 M) were added to a stirred solution of *p*-MeOC₆H₄Cl (0.3 mmol) in corresponding solvent (1 mL) by syringe over 1 h. [b] Isolated yield. [c] 2.5 equiv. of *p*-MeC₆H₄Li were employed. [d] 3 mol% of catalyst were used. [e] 1 mol% of catalyst were used. [f] No catalyst was employed.

We next examined the substrate scope using **1a** as catalyst under the optimized reaction conditions. Both 1- and 2-chloronaphthalenes exhibited good reactivity in the reaction with *p*-MeOC₆H₄Li or *p*-Me₂NC₆H₄Li, each reaction giving excellent product yield (Table 2, entries 1-4). However, reaction of 2-chloronaphthalene with *o*-MeC₆H₄Li led to much lower yield (Table 2, entry 5). This is ascribed to steric hindrance of *o*-MeC₆H₄Li. Deactivated aryl chlorides including *p*-MeOC₆H₄Cl, *p*-Me₂NC₆H₄Cl and *p*-MeC₆H₄Cl were also demonstrated to couple smoothly with aryllithium compounds such as PhLi, *p*-MeC₆H₄Li,

p-MeOC₆H₄Li and *p*-Me₂NC₆H₄Li, giving desired products in 81-87% yields (Table 2, entries 6-13). However, except reaction of *p*-MeOC₆H₄Cl with *p*-MeC₆H₄Li, the reaction of deactivated aryl chlorides required a higher reaction temperature (40 °C, bath temperature). *o*-MeC₆H₄Cl showed lower reactivity due to the steric hindrance. Its reaction with *p*-MeOC₆H₄Li or *p*-Me₂NC₆H₄Li required 5 mol% catalyst loading and 40 °C, resulting in corresponding products in 65% and 67% yields, respectively (Table 2, entries 14 and 15). Reaction of electron-deficient *p*-CF₃C₆H₄Cl with either *p*-MeOC₆H₄Li or *p*-Me₂NC₆H₄Li gave corresponding cross-coupling products in low yields (32% and 35%, respectively) due to side reactions. We observed a range of side products from TLC. In the absence of a catalyst reaction of *p*-CF₃C₆H₄Cl with *p*-MeOC₆H₄Li resulted in only trace amount of desired product and a range of unidentified species indicated by TLC (Table 2, entry 18). Reaction of functionalized aryl chlorides such as *p*-ClC₆H₄CN, *p*-ClC₆H₄C(O)NEt₂ and *p*-ClC₆H₄CO₂Et with aryllithium reagents cannot lead to normal cross-coupling products under these conditions. The addition of aryllithium to the reactive functional groups of aryl chlorides occurred in each case.

In addition, we also tested reaction of *p*-ClC₆H₄OMe with *n*BuLi or PhCH=CHLi using the same conditions as shown in Table 2. However, no desired product was obtained in each case. A complicated mixture was formed in each reaction.

Table 2. Cross-coupling of aryl chlorides with aryllithium reagents catalyzed by **1a**^[a]



Entry	Aryl chloride	Aryl lithium	Yield (%) ^[b]
1			90
2			91
3			93
4			95
5			49
6 ^[c]			82
7 ^[c]			83
8 ^[c]			81

9 ^[c]			84
10 ^[c]			83
11 ^[c]			84
12 ^[c]			87
13 ^[c]			86
14 ^[c,d]			65
15 ^[c,d]			67
16			32
17			35
18 ^[e]			trace

[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation. ArLi (diluted with Et₂O to reach the concentration of 0.3 M, 0.75 mmol, 2.5 mL) was added to a stirred solution of ArCl (0.3 mmol) and complex **1a** (3 mol%) in Et₂O (1 mL) by syringe over 1 h. [b] Isolated yield. [c] After ArLi was completely added dropwise at 25 °C, the reaction mixture was moved to an oil bath of 40 °C and stirred for 4 h. [d] 5 mol% of complex **1a** was used. [e] No catalyst was employed.

This method is also suitable for the cross-coupling of heteroaryl chlorides and 1.8-2 equiv. of aryllithium reagents were employed in these transformations. Both 2- and 3-chloropyridines reacted smoothly with 2 equiv. of *p*-MeC₆H₄Li, *p*-MeOC₆H₄Li or *p*-Me₂NC₆H₄Li at room temperature to afford desired cross-coupling products in excellent yields (Table 3, entries 1-6). No addition or lithiation products were observed in the reactions although excess aryl lithium was employed. 2-Chloro-4-methylquinoline is also a suitable coupling partner. Its reaction with *p*-MeC₆H₄Li, *p*-MeOC₆H₄Li or *p*-Me₂NC₆H₄Li proceeded smoothly at room temperature, giving corresponding 2-aryl-4-methylquinolines in 90%-91% yields. No lithiation products were obtained although the presence of a reactive methyl group on the aromatic heterocycles (Table 3, entries 7-9). Two five-membered heteroaromatic chlorides, 2-chlorothiophene and 2-chlorobenzofuran, were also tested. Their reactions with *p*-Me₂NC₆H₄Li required 5 mol % of **1a** loadings and gave corresponding cross coupling products in 38% and 52% yields, respectively (Table 3, entries 10 and 11). The five-membered heteroaromatic chlorides with two heteroatoms, 2-chlorobenzo[*d*]oxazole and 2-chlorobenzo[*d*]thiazole, were also suitable coupling partners. Reaction of the former with *p*-

MeC₆H₄Li and *p*-Me₂NC₆H₄Li, respectively, in the presence of 5 mol% **1a** afforded corresponding coupling products in good yields, and reaction of the latter under the same conditions resulted in the desired products in moderate yields (Table 3, entries 12-15). Several six-membered heteroaromatic chlorides with two or three heteroatoms including 3,6-dichloropyridazine, 2-chloropyrimidine, 2-chloroquinoxaline and 2,4-dichloro-1,3,5-triazine were examined for the cross-coupling. However, none of them gave desired product at room temperature and at -20 °C. A complicated mixture was obtained in each case. This may be ascribed to the high reactivity of these heterocyclic aromatic chlorides. Electron-poor nucleophilic reagents *p*-CF₃C₆H₄Li and *m*-CF₃C₆H₄Li exhibited lower reactivity compared with the electron-rich ones (Table 3, entries 16-18). For example, reaction of *m*-CF₃C₆H₄Li with 2-chloropyridine at room temperature in the presence of 5 mol% **1a** gave 2-(3-(trifluoromethyl)phenyl)pyridine in 56% yield, which is much lower than that from the reaction of 2-chloropyridine with *p*-MeC₆H₄Li (Table 3, entry 1). Two heteroaryl lithium reagents, 2-furyllithium and 2-thienyllithium, were also tested as nucleophiles in the cross-coupling. When 2-furyllithium or 2-thienyllithium in the presence or absence of 1 equiv of LiBr was added into the stirred solution of a aryl chloride (2-chloropyridine or 2-chloronaphthalene) and complex **1a** in Et₂O, the color of the solution changed to black. After the mixture was stirred for 4 h at room temperature no cross-coupling products or homocoupling products of the heteroaryl lithium were obtained. This is ascribed to decomposition of the catalyst due to addition of the heteroaryl lithium. Heterocyclic halides, especially electron-poor ones, may occur nucleophilic substitution without any catalysts. Hence we examined the reactions in the absence of a catalyst (Table 3, entries 1-3 and 7-18). The results showed that some substrates can give corresponding nucleophilic substituted products, but the product yields were much lower than those under catalytic conditions.

Table 3. Reaction of heteroaryl chlorides with aryllithium reagents^[a]

Entry	Heteroaryl chloride	Aryl lithium	Yield (%) ^[b]	
			1a (3 mol%)	Cat. free
1			95	17
2			94	Trace
3			94	Trace
4			93	
5			95	

6			96	
7			90	50
8			91	13
9			90	Trace
10			38 ^[c]	Trace
11			52 ^[c]	Trace
12			85 ^[d]	41
13			86 ^[d]	13
14			55 ^[c,d]	24
15			61 ^[c,d]	28
16			23 ^[c,e]	Trace
17			56	Trace
18			47	23

[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation. ArLi (diluted with Et₂O to reach the concentration of 0.3 M, 2.0 mL, 0.6 mmol) was added dropwise to a stirred solution of heteroaryl chlorides (0.3 mmol) in the presence or absence of complex **1a** in Et₂O (1.5 mL) by syringe over 1 h. [b] Isolated yield. [c] 1.8 equiv. of aryllithium and 1.7 mL of Et₂O were employed. [d] 5 mol % of **1a** was employed. [e] 2-Chloropyridine (0.3 mmol) and complex **1a** were added to a stirred solution of *p*-CF₃C₆H₄Li (0.6 mmol) in Et₂O (2.75 mL) and pentane (0.75 mL) at -78 °C in one portion, then the solution was warmed to -20 °C slowly and stirred for 24 h.

The exact catalytic cycle is still unknown at the present time. However, some experimental facts related to the mechanism have been derived. The catalytic reaction is inhibited by 1,1-diphenylethene additive.^[9] When 10 mol % of 1,1-diphenylethene was added into the reaction system composed of *p*-MeOC₆H₄Cl, *p*-MeC₆H₄Li and 3 mol % **1a**, no desired cross-coupling product was observed. In our previous study we found **1a**-catalyzed reaction of cinnamyl methyl ether with *p*-Me₂NC₆H₄ZnCl was not affected by 1,1-diphenylethene.^[8] This rules out the possibility that diphenylethene inhibit the reaction through its reaction with nickel catalyst. Hence it seems that current reaction involves a

radical intermediate. On the other hand, a combination of Ni(COD)₂ and a lithiated (2-Ph₂PC₆H₄)NH(2'-Me₂NC₆H₄), supposing [Li{N(2-Ph₂PC₆H₄)(2'-Me₂NC₆H₄)}] (**2**), showed similar catalytic activity to complex **1a**; 3 mol % Ni(COD)₂/**2** loading resulted in 78% product yield for the cross-coupling of *p*-MeOC₆H₄Cl with *p*-MeC₆H₄Li under the standard conditions. This catalytic reaction is also inhibited by the 1,1-diphenylethene additive (10 mol %). Hence the active catalyst may be a Ni(0) species. But we cannot rule out the possibility of a Ni(I) active intermediate^[10] formed through an electron transfer from Ni(0) to ArCl^[11] or other routes.

Conclusions

We have demonstrated that pincer nickel can effectively catalyze the cross-coupling of aryl lithium reagents with aryl or heteroaryl chlorides. A series of aryl chlorides involving chloronaphthalenes, methyl-, methoxy-, and dimethylamino-substituted phenyl chlorides, as well as heteroaryl chlorides are suitable coupling partners. *p*-CF₃C₆H₄Cl, *p*-CF₃C₆H₄Li and *m*-CF₃C₆H₄Li can also be employed in the coupling reaction as electrophilic or nucleophilic substrates, but resulting in relatively low yields due to side reactions. The method requires relatively low catalyst loadings, short reaction times and mild reaction conditions, leading to good product yields in most cases.

Experimental Section

General information. All air or moisture sensitive manipulations were performed under nitrogen using standard Schlenk techniques. Toluene was distilled under nitrogen over sodium. THF and Et₂O were distilled under nitrogen over sodium/benzophenone. Substituted phenyllithium compounds were prepared from corresponding bromides and lithium and 2-furyllithium and 2-thienyllithium were prepared by lithiation of furan or thiophene with *n*BuLi according to reported procedures.^[12] Other chemicals and solvents were purchased from commercial vendors and used as received. NMR spectra were recorded on a Bruker avance III 400 NMR spectrometer or a Bruker av300 NMR spectrometer at ambient temperature. The chemical shifts of the ¹H NMR spectra were referenced to TMS and the ¹³C NMR spectra were referenced to internal solvent resonances.

General procedure for the cross-coupling of aryl chlorides with aryllithium reagents. A Schlenk tube was charged with aryl chloride (0.3 mmol), complex **1a** (4.4 mg, 0.009 mmol) and dry Et₂O (1.0 mL). To the stirred mixture ArLi solution (0.75 mmol, diluted with Et₂O to reach the concentration of 0.3 M) was added by syringe over 1 h. Then the reaction mixture was stirred at 25 °C for additional 3 h. Water (10 mL) and two drops of glacial acetic acid were successively added. The mixture was extracted with Et₂O (3 × 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

¹H and ¹³C NMR spectral data of the cross-coupling products:

4-Methoxy-4'-methylbiphenyl.^[8a] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 48.9 mg (82%). ¹H NMR (300MHz, CDCl₃): δ 2.36 (s, 3H, Me), 3.80 (s, 3H, OMe), 6.94 (d, *J* = 8.6 Hz, 2H, C₆H₄), 7.20 (d, *J* = 8.1 Hz, 2H,

C₆H₄), 7.43 (d, *J* = 8.1 Hz, 2H, C₆H₄), 7.49 (d, *J* = 8.6 Hz, 2H, C₆H₄). ¹³C NMR (75MHz, CDCl₃): δ 21.2, 55.4, 114.3, 126.7, 128.1, 129.6, 133.9, 136.4, 138.1, 159.1.

1-(4-Methoxyphenyl)naphthalene.^[13] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 63.1 mg (90%). ¹H NMR (300 MHz, CDCl₃): δ 3.84 (s, 3H, OMe), 7.00 (d, *J* = 8.6 Hz, 2H, C₆H₄), 7.36-7.50 (m, 6H, Ph+naphthyl), 7.79-7.94 (m, 3H, naphthyl). ¹³C NMR (75 MHz, CDCl₃): δ 55.4, 113.8, 125.5, 125.8, 126.0, 126.2, 127.0, 127.4, 128.4, 131.2, 131.9, 133.2, 134.0, 140.0, 159.1.

N,N-Dimethyl-4-(naphthalen-1-yl)aniline.^[13] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 67.5 mg (91%). ¹H NMR (400 MHz, CDCl₃): δ 3.03 (s, 6H, Me), 6.86 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.38-7.51 (m, 6H, Ph+naphthyl), 7.80 (d, *J* = 8.2 Hz, 1H, naphthyl), 7.87-7.90 (m, 1H, naphthyl), 8.00-8.03 (m, 1H, naphthyl). ¹³C NMR (101 MHz, CDCl₃): δ 40.8, 112.4, 125.6, 125.7, 125.8, 126.5, 126.9, 127.0, 128.3, 128.9, 131.0, 132.1, 134.1, 140.6, 150.0.

2-(4-Methoxyphenyl)naphthalene.^[6a] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 65.5 mg (93%). ¹H NMR (300 MHz, CDCl₃): δ 3.88 (s, 3H, OMe), 7.03 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.42-7.53 (m, 2H, naphthyl), 7.67 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.72 (dd, *J* = 1.8, 8.6 Hz, 1H, naphthyl), 7.81-7.92 (m, 3H, naphthyl), 7.99 (s, 1H, naphthyl). ¹³C NMR (75 MHz, CDCl₃): δ 55.5, 114.5, 125.2, 125.6, 126.4, 127.8, 128.2, 128.5, 128.6, 132.5, 133.8, 133.9, 138.3, 159.4.

N,N-Dimethyl-4-(naphthalen-2-yl)aniline.^[6a] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 70.2 mg (95%). ¹H NMR (400 MHz, CDCl₃): δ 3.01 (s, 6H, Me), 6.85 (d, *J* = 8.9 Hz, 2H, C₆H₄), 7.39-7.49 (m, 2H, naphthyl), 7.64 (d, *J* = 9.0 Hz, 2H, C₆H₄), 7.72-7.75 (m, 1H, naphthyl), 7.80-7.89 (m, 3H, naphthyl), 7.98 (s, 1H, naphthyl). ¹³C NMR (101 MHz, CDCl₃): δ 40.7, 113.0, 124.3, 125.4, 125.5, 126.2, 127.7, 128.08, 128.11, 128.3, 129.2, 132.2, 134.1, 138.7, 150.2.

2-o-Tolynaphthalene.^[14] Eluent: petroleum ether, yield 31.9 mg (49%). ¹H NMR (400 MHz, CDCl₃): δ 2.30 (s, 3H, Me), 7.24-7.35 (m, 4H, Ar), 7.44-7.54 (m, 3H, Ar), 7.76 (s, 1H, Ar), 7.83-7.90 (m, 3H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ 20.7, 125.97, 125.99, 126.3, 127.5, 127.6, 127.82, 127.88, 127.93, 128.1, 130.2, 130.5, 132.4, 133.5, 135.7, 139.7, 142.0

4'-Methoxy-N,N-dimethylbiphenyl-4-amine.^[6a] Eluent: petroleum ether/EtOAc (50 : 1 v/v), yield 56.7 mg (83%). ¹H NMR (300MHz, CDCl₃): δ 2.96 (s, 6H, NMe), 3.82 (s, 3H, OMe), 6.79 (d, *J* = 8.8 Hz, 2H, C₆H₄), 6.92 (d, *J* = 8.7 Hz, 2H, C₆H₄), 7.42-7.48 (m, 4H, C₆H₄). ¹³C NMR (75MHz, CDCl₃): δ 40.9, 55.5, 113.2, 114.3, 127.45, 127.47, 129.5, 134.1, 149.7, 158.4.

4-Methoxybiphenyl.^[6a] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 44.8 mg (81%). ¹H NMR (300 MHz, CDCl₃): δ 3.85 (s, 3H, OMe), 6.98 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.26-7.33 (m, 1H, Ph), 7.42 (t, *J* = 7.6 Hz, 2H, Ph), 7.50-7.58 (m, 4H, Ph+C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 55.5, 114.4, 126.8, 126.9, 128.3, 128.9, 133.9, 141.0, 159.3.

N,N,4'-Trimethylbiphenyl-4-amine.^[14] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 53.0 mg (84%). ¹H NMR (300MHz, CDCl₃): δ 2.28 (s, 3H, Me), 2.88 (s, 6H, NMe), 6.70 (d, *J* = 8.6 Hz, 2H, C₆H₄), 7.11 (d, *J* = 7.7 Hz, 2H, C₆H₄), 7.34-7.41 (m, 4H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 21.2, 40.7, 113.0, 126.3, 127.6, 129.45, 129.49, 135.7, 138.5, 149.9.

N,N-Dimethylbiphenyl-4-amine.^[6b] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 49.3 mg (83%). ¹H NMR (300 MHz, CDCl₃): δ 3.00 (s, 6H, NMe), 6.82 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.22-7.30 (m, 1H, Ph), 7.40 (t, *J* =

7.6 Hz, 2H, Ph), 7.52 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.57 (d, *J* = 7.2 Hz, 2H, Ph). ¹³C NMR (75 MHz, CDCl₃): δ 40.8, 113.0, 126.1, 126.4, 127.9, 128.8, 129.4, 141.4, 150.1.

4'-Methoxy-2-methylbiphenyl.^[6a] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 38.4 mg (65%). ¹H NMR (300MHz, CDCl₃): δ 2.27 (s, 3H, Me), 3.84 (s, 3H, OMe), 6.94 (d, *J* = 8.7 Hz, 2H, C₆H₄), 7.21-7.26 (m, 6H, C₆H₄). ¹³C NMR (75MHz, CDCl₃): δ 20.7, 55.4, 113.7, 125.9, 127.1, 130.0, 130.39, 130.43, 134.6, 135.6, 141.7, 158.7.

N,N,2'-Trimethylbiphenyl-4-amine.^[6a] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 42.7 mg (67%). ¹H NMR (400 MHz, CDCl₃): δ 2.31 (s, 3H, Me), 2.99 (s, 6H, NMe), 6.77-6.81 (m, 2H, C₆H₄), 7.18-7.27 (m, 6H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 20.8, 40.8, 112.2, 125.9, 126.7, 130.1, 130.2, 130.4, 135.7, 142.2, 149.5.

4-Methoxy-4'-(trifluoromethyl)biphenyl.^[6a] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 24.1 mg (32%). ¹H NMR (300 MHz, CDCl₃): δ 3.85 (s, 3H, OMe), 6.99 (d, *J* = 8.7 Hz, 2H, C₆H₄), 7.53 (d, *J* = 8.6 Hz, 2H, C₆H₄), 7.64 (s, 4H, C₆H₄). ¹³C NMR (75 MHz, CDCl₃): δ 55.5, 114.6, 124.6 (q, *J* = 271.8 Hz), 125.8 (q, *J* = 3.8 Hz), 127.0, 128.5, 128.8 (q, *J* = 32.4 Hz), 132.3, 144.3, 160.0.

N,N-Dimethyl-4'-(trifluoromethyl)biphenyl-4-amine.^[6a] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 27.9 mg (35%). ¹H NMR (400 MHz, CDCl₃): δ 3.01 (s, 6H, NMe), 6.80 (d, *J* = 8.9 Hz, 2H, C₆H₄), 7.52 (d, *J* = 8.9 Hz, 2H, C₆H₄), 7.60-7.67 (m, 4H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 40.6, 112.8, 124.7 (q, *J* = 272.6 Hz), 125.7 (q, *J* = 3.8 Hz), 126.4, 127.5, 127.99 (q, *J* = 32.4 Hz), 128.01, 144.8, 150.6.

2-p-Tolylpyridine.^[6a] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 48.1 mg (95%). ¹H NMR (400MHz, CDCl₃): δ 2.40 (s, 3H, Me), 7.18-7.21 (m, 1H, Py), 7.28 (d, *J* = 7.9 Hz, 2H, C₆H₄), 7.68-7.74 (m, 2H, Py), 7.89 (d, *J* = 8.2 Hz, 2H, C₆H₄), 8.66-8.69 (m, 1H, Py). ¹³C NMR (101MHz, CDCl₃): δ 21.4, 120.4, 121.9, 126.9, 129.6, 136.76, 136.79, 139.1, 149.7, 157.6.

2-(4-Methoxyphenyl)pyridine.^[6b] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 52.0 mg (94%). ¹H NMR (400 MHz, CDCl₃): δ 3.86 (s, 3H, OMe), 7.00 (d, *J* = 8.9 Hz, 2H, C₆H₄), 7.13-7.20 (m, 1H, Py), 7.65-7.73 (m, 2H, Py), 7.95 (d, *J* = 8.9 Hz, 2H, C₆H₄), 8.65 (d, *J* = 4.4 Hz, 1H, Py). ¹³C NMR (101 MHz, CDCl₃): δ 55.5, 114.2, 119.9, 121.5, 128.3, 132.2, 136.8, 149.7, 157.2, 160.6.

N,N-Dimethyl-4-(pyridin-2-yl)aniline.^[6b] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 56.1 mg (94%). ¹H NMR (400 MHz, CDCl₃): δ 3.01 (s, 6H, NMe), 6.79 (d, *J* = 8.9 Hz, 2H, C₆H₄), 7.05-7.13 (m, 1H, Py), 7.60-7.72 (m, 2H, Py), 7.92 (d, *J* = 9.0 Hz, 2H, C₆H₄), 8.61 (d, *J* = 4.7 Hz, 1H, Py). ¹³C NMR (101 MHz, CDCl₃): δ 40.5, 112.3, 119.3, 120.7, 127.3, 127.8, 136.6, 149.5, 151.2, 157.7.

3-(p-Tolyl)pyridine.^[13] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 47.1 mg (93%). ¹H NMR (400 MHz, CDCl₃): δ 2.40 (s, 3H, Me), 7.28 (d, *J* = 7.9 Hz, 2H, C₆H₄), 7.33 (dd, *J* = 4.8, 7.9 Hz, 1H, Py), 7.48 (d, *J* = 8.1 Hz, 2H, C₆H₄), 7.84 (dt, *J* = 2.0, 7.6 Hz, 1H, Py), 8.56 (dd, *J* = 1.6, 4.8 Hz, 1H, Py), 8.83 (d, *J* = 2.0 Hz, 1H, Py). ¹³C NMR (101 MHz, CDCl₃): δ 21.2, 123.6, 127.1, 129.9, 134.2, 135.0, 136.6, 138.1, 148.2, 148.3.

3-(4-Methoxyphenyl)pyridine.^[15] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 52.6 mg (95%). ¹H NMR (400 MHz, CDCl₃): δ 3.86 (s, 3H, OMe), 7.01 (d, *J* = 8.7 Hz, 2H, C₆H₄), 7.32-7.35 (m, 1H, Py), 7.52 (d, *J* = 8.7 Hz, 2H, C₆H₄), 7.83 (d, *J* = 7.9 Hz, 1H, Py), 8.54 (d, *J* = 3.8 Hz, 1H, Py), 8.82 (s, 1H, Py). ¹³C NMR (101 MHz, CDCl₃): δ 55.5, 114.6, 123.6, 128.3, 130.3, 134.0, 136.4, 147.9, 148.0, 159.9.

N,N-Dimethyl-4-(pyridin-3-yl)aniline.^[16] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 57.1 mg (96%). ¹H NMR (400 MHz, CDCl₃): δ 3.01 (s, 6H, NMe), 6.82 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.30 (dd, *J* = 4.8, 8.0 Hz, 1H, Py), 7.49 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.82 (dt, *J* = 2.0, 8.0 Hz, 1H, Py), 8.48 (dd, *J* = 1.6, 4.8 Hz, 1H, Py), 8.82 (d, *J* = 2.0 Hz, 1H, Py). ¹³C NMR (101 MHz, CDCl₃): δ 40.6, 112.9, 123.6, 125.5, 127.8, 133.4, 136.7, 147.2, 147.7, 150.5.

4-Methyl-2-(*p*-tolyl)quinoline.^[8b] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 63.1 mg (90%). ¹H NMR (400 MHz, CDCl₃): δ 2.42 (s, 3H, Me), 2.73 (s, 3H, Me), 7.31 (d, *J* = 7.9 Hz, 2H, C₆H₄), 7.49-7.53 (m, 1H, quinolyl), 7.66-7.72 (m, 2H, quinolyl), 7.96 (dd, *J* = 0.9, 8.3 Hz, 1H, quinolyl), 8.05 (d, *J* = 8.2 Hz, 2H, C₆H₄), 8.15 (d, *J* = 8.4 Hz, 1H, quinolyl). ¹³C NMR (101 MHz, CDCl₃): δ 19.1, 21.5, 119.7, 123.7, 125.9, 127.3, 127.5, 129.4, 129.6, 130.3, 137.1, 139.3, 144.7, 148.3, 157.1.

2-(4-Methoxyphenyl)-4-methylquinoline.^[8b] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 67.8 mg (91%). ¹H NMR (400 MHz, CDCl₃): δ 2.72 (s, 3H, Me), 3.86 (s, 3H, OMe), 7.03 (d, *J* = 8.9 Hz, 2H, C₆H₄), 7.48-7.52 (m, 1H, quinolyl), 7.63-7.72 (m, 2H, quinolyl), 7.95 (d, *J* = 8.3 Hz, 1H, quinolyl), 8.09-8.17 (m, 3H, C₆H₄+quinolyl). ¹³C NMR (101 MHz, CDCl₃): δ 19.1, 55.5, 114.3, 119.4, 123.7, 125.8, 127.1, 128.9, 129.4, 130.1, 132.5, 144.7, 148.2, 156.7, 160.8.

N,N-Dimethyl-4-(4-methylquinolin-2-yl)aniline.^[8c] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 71.1 mg (90%). ¹H NMR (400 MHz, CDCl₃): δ 2.71 (s, 3H, Me), 3.03 (s, 6H, NMe), 6.82 (d, *J* = 8.9 Hz, 2H, C₆H₄), 7.44-7.48 (m, 1H, quinolyl), 7.63-7.69 (m, 2H, quinolyl), 7.93 (d, *J* = 9.1 Hz, 1H, quinolyl), 8.07-8.12 (m, 3H, C₆H₄+quinolyl). ¹³C NMR (101 MHz, CDCl₃): δ 19.2, 40.5, 112.3, 119.1, 123.7, 125.2, 126.9, 127.6, 128.5, 129.2, 130.0, 144.2, 148.4, 151.4, 157.2.

N,N-Dimethyl-4-(thiophen-2-yl)aniline.^[17] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 23.3 mg (38%). ¹H NMR (400 MHz, CDCl₃): δ 2.98 (s, 6H, NMe), 6.73 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.02-7.04 (m, 1H, thienyl), 7.14-7.16 (m, 2H, thienyl), 7.49 (d, *J* = 8.8 Hz, 2H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 40.7, 112.7, 121.0, 122.9, 123.1, 125.3, 127.0, 127.9, 145.4, 150.1.

4-(Benzofuran-2-yl)-*N,N*-dimethylaniline.^[18] Eluent: petroleum ether/EtOAc (60 : 1 v/v), yield 37.1 mg (52%). ¹H NMR (400 MHz, CDCl₃): δ 3.02 (s, 6H, NMe), 6.77 (d, *J* = 8.8 Hz, 2H, C₆H₄), 6.80 (d, *J* = 0.8 Hz, 1H, benzofuryl), 7.46-7.53 (m, 2H, benzofuryl), 7.16-7.23 (m, 2H, benzofuryl), 7.74 (d, *J* = 8.8 Hz, 2H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 40.50, 98.2, 110.9, 112.3, 118.8, 120.3, 122.8, 123.2, 126.3, 130.0, 150.7, 154.7, 157.2.

2-(*p*-Tolyl)benzo[d]oxazole.^[8e] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 53.3 mg (85%). ¹H NMR (400 MHz, CDCl₃): δ 2.43 (s, 3H, Me), 7.31-7.36 (m, 4H, Ar), 7.54-7.59 (m, 1H, Ar), 7.73-7.78 (m, 1H, Ar), 8.14 (d, *J* = 8.4 Hz, 2H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 21.8, 110.6, 120.0, 124.6, 125.0, 127.7, 129.0, 129.8, 130.3, 142.2, 150.8, 163.4.

4-(Benzo[d]oxazol-2-yl)-*N,N*-dimethylaniline.^[19] Eluent: petroleum ether/EtOAc (50 : 1 v/v), yield 61.6 mg (86%). ¹H NMR (400 MHz, CDCl₃): δ 3.05 (s, 6H, NMe), 6.76 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.24-7.32 (m, 2H, Ar), 7.50-7.52 (m, 1H, Ar), 7.68-7.71 (m, 1H, Ar), 8.10 (d, *J* = 8.8 Hz, 2H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 40.2, 110.2, 111.7, 114.2, 119.2, 124.0, 124.3, 129.2, 142.7, 150.7, 152.5, 164.3.

2-(*p*-Tolyl)benzo[d]thiazole.^[8e] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 37.3 mg (55%). ¹H NMR (400 MHz, CDCl₃): δ 2.41 (s, 3H, Me), 7.29 (d, *J* = 8.0 Hz, 2H, C₆H₄), 7.34-7.38 (m, 1H, Ar), 7.45-7.50 (m, 1H,

Ar), 7.86-7.89 (m, 1H, Ar), 7.98 (d, *J* = 8.0 Hz, 2H, C₆H₄), 8.04-8.07 (m, 1H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ 21.7, 121.7, 123.2, 125.1, 126.4, 127.6, 129.9, 131.1, 135.1, 141.6, 154.3, 168.4.

4-(Benzo[d]thiazol-2-yl)-*N,N*-dimethylaniline.^[20] Eluent: petroleum ether/EtOAc (50 : 1 v/v), giving a mixture of 4-(benzo[d]thiazol-2-yl)-*N,N*-dimethylaniline and *N*¹,*N*²,*N*³,*N*⁴-tetramethylbiphenyl-4,4'-diamine, yield 48.7 mg. The yield of 4-(benzo[d]thiazol-2-yl)-*N,N*-dimethylaniline is 61% (based on the ¹H NMR integral). ¹H NMR (400 MHz, CDCl₃): δ 3.05 (s, 6H, NMe), 6.74 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.28-7.32 (m, 1H, Ar), 7.41-7.45 (m, 1H, Ar), 7.83-7.85 (m, 1H, Ar), 7.94-7.99 (m, 3H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ 40.3, 111.8, 121.5, 122.4, 124.3, 126.1, 129.0, 134.7, 152.3, 154.5, 168.9.

2-(4-(Trifluoromethyl)phenyl)pyridine.^[21] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 15.4 mg (23%). ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.30 (m, 1H, Py), 7.72 (d, *J* = 8.4 Hz, 2H, C₆H₄), 7.75-7.80 (m, 2H, Py), 8.10 (d, *J* = 8.4 Hz, 2H, C₆H₄), 8.71-8.73 (m, 1H, Py). ¹³C NMR (101 MHz, CDCl₃): δ 121.0, 123.1, 124.3 (q, *J* = 273.2 Hz), 125.8 (q, *J* = 3.8 Hz), 127.3, 130.9 (q, *J* = 32.5 Hz), 137.1, 142.8, 150.0, 156.0.

2-(3-(Trifluoromethyl)phenyl)pyridine.^[22] Eluent: petroleum ether/EtOAc (30 : 1 v/v), yield 37.6 mg (56%). ¹H NMR (400 MHz, CDCl₃): δ 7.25-7.28 (m, 1H, Py), 7.57 (t, *J* = 7.8 Hz, 1H, C₆H₄), 7.66 (d, *J* = 7.8 Hz, 1H, C₆H₄), 7.72-7.79 (m, 2H, Py), 8.16 (d, *J* = 8.0 Hz, 1H, C₆H₄), 8.29 (s, 1H, C₆H₄), 8.71 (d, *J* = 4.8 Hz, 1H, Py). ¹³C NMR (101 MHz, CDCl₃): δ 120.7, 122.9, 123.9 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 273.4 Hz), 125.6 (q, *J* = 3.9 Hz), 129.3, 130.1, 131.3 (q, *J* = 32.4 Hz), 137.1, 140.2, 150.0, 155.9.

2-(3-(Trifluoromethyl)phenyl)benzo[d]oxazole.^[23] Eluent: petroleum ether/EtOAc (100 : 1 v/v), yield 36.9 mg (47%). ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.43 (m, 2H, Ar), 7.59-7.65 (m, 1H, Ar), 7.67 (t, *J* = 7.8 Hz, 1H, C₆H₄), 7.78-7.83 (m, 2H, Ar), 8.45 (d, *J* = 7.8 Hz, 1H, C₆H₄), 8.54 (s, 1H, C₆H₄). ¹³C NMR (101 MHz, CDCl₃): δ 110.9, 120.5, 123.8 (q, *J* = 273.5 Hz), 124.6 (q, *J* = 3.8 Hz), 125.1, 125.9, 128.1 (q, *J* = 3.7 Hz), 128.2, 129.7, 130.8, 131.77 (q, *J* = 33.1 Hz), 142.0, 150.9, 161.7.

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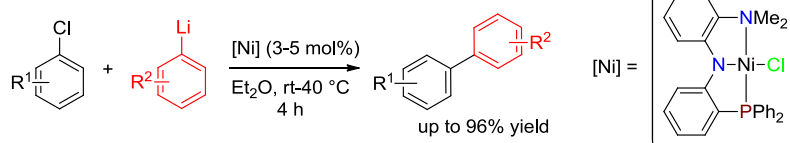
Keywords: pincer nickel • aryl chloride • aryl lithium • cross coupling • catalysis

- [1] a) J. R. Dunetz *Chem. Rev.* **2011**, *111*, 2177; b) J. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651.
- [2] a) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; b) *Cross-Coupling Reactions: A Practical Guide* (Ed.: N. Miyaoura), Springer, Berlin, **2002**.
- [3] a) S. P. Stanforth, *Tetrahedron* **1998**, *54*, 263; b) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359; c) C. Wolf, H. Xu, *J. Org. Chem.* **2008**, *73*, 162.
- [4] S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, K. Kondo, *J. Org. Chem.* **1979**, *44*, 2408.
- [5] M. Yamamura, I. Moritani, S.-I. Murahashi, *J. Organomet. Chem.* **1975**, *91*, C39.

- (6) a) V. Pace, R. Luisi, *ChemCatChem* **2014**, *6*, 1516; b) S.-I. Murahashi, *J. Organomet. Chem.* **2002**, *653*, 27; c) A. Nagaki, A. Kenmoku, Y. Moriwaki, A. Hayashi, J.-I. Yoshida, *Angew. Chem. Int. Ed.* **2010**, *49*, 7543; d) K. Fuji, S. Tamba, K. Shono, A. Sugie, A. Mori, *J. Am. Chem. Soc.* **2013**, *135*, 12208; e) H. Someya, H. Yorimitsu, K. Oshima, *Tetrahedron* **2010**, *66*, 5993; f) A. B. Smith III, A. T. Hoye, D. Martinez-Solorio, W.-S. Kim, R. Tong, *J. Am. Chem. Soc.* **2012**, *134*, 4533; g) M. H. Nguyen, A. B. Smith III, *Org. Lett.* **2013**, *15*, 4258; h) M. H. Nguyen, A. B. Smith III, *Org. Lett.* **2014**, *16*, 2070; i) H.-J. Cristau, C. Bouchitte, M. Taillefer, J.-F. Spindler, T. Schlama, World Patent WO2001058834, 2001.
- (7) a) M. Giannerini, M. Fañanás-Mastral, B. L. Feringa, *Nat. Chem.* **2013**, *5*, 667; b) V. Hornillos, M. Giannerini, C. Vila,; M. Fañanás-Mastral, B. L. Feringa, *Org. Lett.* **2013**, *15*, 5114; c) M. Giannerini, V. Hornillos, C. Vila, M. Fañanás-Mastral, B. L. Feringa, *Angew. Chem. Int. Ed.* **2013**, *52*, 13329; d) C. Vila, M. Giannerini, V. Hornillos, M. Fañanás-Mastral, B. L. Feringa, *Chem. Sci.* **2014**, *5*, 1361; e) C. Vila, V. Hornillos, M. Giannerini, M. Fañanás-Mastral, B. L. Feringa, *Chem. Eur. J.* **2014**, *20*, 13078; f) V. Hornillos, M. Giannerini, C. Vila, M. Fañanás-Mastral, B. L. Feringa, *Chem. Sci.* **2015**, *6*, 1394; g) L. M. Castelló, V. Hornillos, C. Vila, M. Giannerini, M. Fañanás-Mastral, B. L. Feringa, *Org. Lett.* **2015**, *17*, 62; h) D. Heijnen, V. Hornillos, B. P. Corbet, M. Giannerini, B. L. Feringa, *Org. Lett.* **2015**, *17*, 2262.
- (8) a) X. Yang, Z.-X. Wang, *Organometallics* **2014**, *33*, 5863; b) D. Wu, Z.-X. Wang, *Org. Biomol. Chem.* **2014**, *12*, 6414; c) X.-Q. Zhang, Z.-X. Wang, *Synlett* **2013**, *24*, 2081; d) W.-J. Guo, Z.-X. Wang, *J. Org. Chem.* **2013**, *78*, 1054; e) N. Liu, Z.-X. Wang, *J. Org. Chem.* **2011**, *76*, 10031; f) N. Liu, L. Wang, Z.-X. Wang, *Chem. Commun.* **2011**, *47*, 1598; g) C. Zhang, Z.-X. Wang, *Organometallics* **2009**, *28*, 6507; h) Z.-X. Wang, L. Wang, *Chem. Commun.* **2007**, 2423. i) D. Wu, J.-L. Tao, Z.-X. Wang, *Org. Chem. Front.* **2015**, *2*, 265; j) J.-L. Tao, B. Yang, Z.-X. Wang, *J. Org. Chem.* **2015**, *80*, 12627.
- (9) M. Ochiai, T. Shu, T. Nagaoka, Y. Kitagawa, *J. Org. Chem.* **1997**, *62*, 2130.
- (10) a) V. B. Phapale, D. J. Cárdenas, *Chem. Soc. Rev.* **2009**, *38*, 1598; b) S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature* **2014**, *509*, 299; c) A. N. Vedernikov, *ChemCatChem* **2014**, *6*, 2490.
- (11) T. T. Tsou, J. K. Kochi, *J. Am. Chem. Soc.* **1979**, *101*, 6319.
- (12) B. J. Wakefield, *Organolithium Methods*, Academic Press, London, **1988**.
- (13) F. Zhu, Z.-X. Wang, *J. Org. Chem.* **2014**, *79*, 4285.
- (14) E. Shirakawa, F. Tamakuni, E. Kusano, N. Uchiyama, W. Konagaya, R. Watabe, T. Hayashi, *Angew. Chem. Int. Ed.* **2014**, *53*, 521.
- (15) X. Chen, L. Zhou, Y. Li, T. Xie, S. Zhou, *J. Org. Chem.* **2014**, *79*, 230.
- (16) Vella, S. J.; Tiburcio, J.; Gauld, J. W.; Loeb, S. J. *Org. Lett.* **2006**, *8*, 3421.
- (17) A. F. Littke, C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 4020.
- (18) R. Cano, M. Yus, D. J. Ramon, *Tetrahedron.* **2012**, *68*, 1393.
- (19) A. Kumar, S. Sharma, R. A. Maurya, *Tetrahedron. Lett.* **2010**, *51*, 6224.
- (20) M. Bakthadoss, R. Selvakumar, J. Srinivasan, *Tetrahedron. Lett.* **2014**, *55*, 5808.
- (21) H. Kim, J. Park, J. G. Kim, S. Chang, *Org. Lett.* **2014**, *16*, 5466.
- (22) C. Gosmini, C. Bassene-Ernst, M. Durandetti, *Tetrahedron* **2009**, *65*, 6141.
- (23) L. Wang, X. Ren, J. Yu, Y. Jiang, J. Cheng, *J. Org. Chem.* **2013**, *78*, 12076.

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FULL PAPER



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**Nickel-Catalyzed Cross-Coupling of
(Hetero)aryl Chlorides with
Aryllithium Compounds**

The pincer-nickel-catalyzed cross-coupling of aryl or heteroaryl chlorides with aryl lithium compounds was performed under mild reaction conditions to afford biaryls in 23-96% yields.

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