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Full Paper

Nickel Pincer Complexes

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

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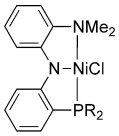
Abstract: The nickel pincer complexes [Ni(Cl){N(2-$R_2PC_6H_4$)(2′-$Me_2NC_6H_4$)}] (R = Ph, **1a**; R = *i*Pr, **1b**; R = Cy, **1c**) were demonstrated to catalyze cross-coupling of aryl or heteroaryl chlorides with aryllithium compounds under mild reaction conditions. The catalytic activity of **1a** was highest 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-chlorothiophene, 2-chlorobenzofuran, 2-chlorobenzo[*d*]oxazole, and 2-chlorobenzo[*d*]thiazole, were used in this coupling reaction.

Introduction

Transition-metal-catalyzed cross-coupling reactions, such as the Kumada, Negishi, Stille, Suzuki, and Hiyama reactions, are powerful tools for constructing C–C bonds in organic synthesis.[1–3] Nucleophiles used in these cross-couplings are various organometallic reagents including organomagnesium, organozinc, organotin, organoboron, and organosilicon compounds. Organolithium compounds have rarely been used as a nucleophilic reagent in cross-coupling reactions due to their high reactivity, which often results in side reactions and a lack of selectivity. However, the direct use of organolithium compounds as nucleophiles in cross-coupling reactions is highly desirable because it offers a more direct approach to the desired products because organozinc, organotin, organoboron, and organosilicon reagents are frequently prepared from the corresponding organolithium compounds, and 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 was reported in the following decades.[6] Recently, Feringa and coworkers carried out Pd-catalyzed cross-coupling of organic halides/triflates with aryl, alkenyl, or alkyllithium reagents.[7] In the reported examples palladium was almost the sole catalyst in combination with appropriate ligands. It was indicated that 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 of using nickel as a catalyst for the cross-coupling.

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



1a R = Ph
1b R = *i*Pr
1c R = Cy

Results and Discussion

The reaction of *p*-$MeOC_6H_4Cl$ with *p*-MeC_6H_4Li was used to evaluate the catalytic activity of complexes **1a**–**1c** and optimize the reaction conditions. In the presence of 5 mol% of **1a**, **1b**, or **1c** the reaction of *p*-$MeOC_6H_4Cl$ with two equivalents of *p*-MeC_6H_4Li in THF at room temperature resulted in the desired product in 45%, 42%, and 35% yields, respectively (Table 1, entries 1–3). Slow, dropwise addition of *p*-MeC_6H_4Li to a mixture of *p*-$MeOC_6H_4Cl$ and the catalyst was necessary to suppress side reactions. Lower reaction temperatures than room temperature resulted in lower product yields (Table 1, entries 4–7). Raising the reaction temperature to 40 °C led to a slight increase in yield (Table 1, entry 8). A solvent screen at room tem-

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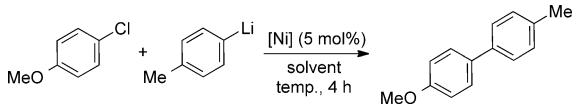
Table 1. Catalyst evaluation and optimization of reaction conditions.[a]



Entry	Catalyst	Solvent	T [°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_2O	25	78
11[c]	**1a**	Et_2O	25	83
12[c,d]	**1a**	Et_2O	25	82
13[c,e]	**1a**	Et_2O	25	65
14[c,d]	$[NiCl_2(PCy_3)_2]$	Et_2O	25	56
15[c,d]	$[NiCl_2(PPh_3)_2]$	Et_2O	25	37
16[c]	none	Et_2O	25	trace

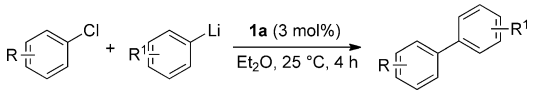
[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation. *p*-MeC_6H_4Li (0.6 mmol, diluted with appropriate solvent to reach the concentration of 0.3 M) was added to a stirred solution of *p*-$MeOC_6H_4Cl$ (0.3 mmol) in corresponding solvent (1 mL) by syringe over 1 h. [b] Isolated yield. [c] 2.5 equiv of *p*-MeC_6H_4Li were used. [d] 3 mol% of catalyst was used. [e] 1 mol% of catalyst was used.

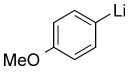
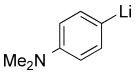
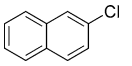
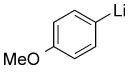
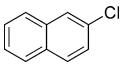
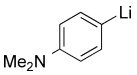
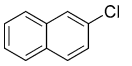
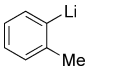
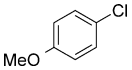
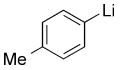
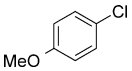
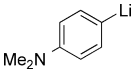
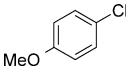
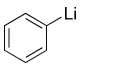
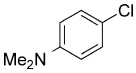
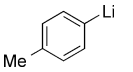
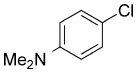
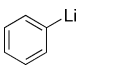
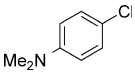
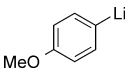
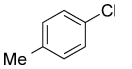
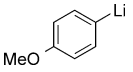
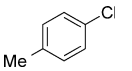
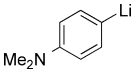
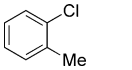
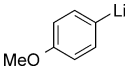
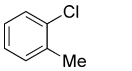
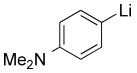
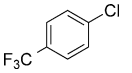
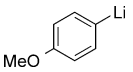
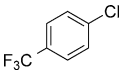
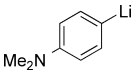
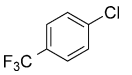
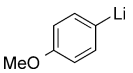
perature showed that Et_2O was a better solvent than toluene and THF in this transformation (Table 1, entries 9 and 10). Further tests showed that use of 2.5 equivalents of *p*-MeC_6H_4Li led to a better result, with 83% yield being achieved in Et_2O at room temperature (Table 1, entry 11). The demand for excess *p*-MeC_6H_4Li is due to the homocoupling side reaction, which consumed part of *p*-MeC_6H_4Li reagent.

We also tested the reaction with lower catalyst loadings. 3 mol% of **1a** led to almost the same yield as that with 5 mol% of **1a**, whereas 1 mol% of **1a** resulted in a marked decrease in yield (Table 1, entries 12 and 13). For comparison, $[NiCl_2(PCy_3)_2]$ and $[NiCl_2(PPh_3)_2]$ were 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, 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 $[NiCl_2(PCy_3)_2]$ or $[NiCl_2(PPh_3)_2]$ under the reaction conditions. We also examined the reaction in the absence of a catalyst. Only a trace amount of cross coupling product was obtained (Table 1, entry 16).

We next examined the substrate scope with **1a** as the catalyst under the optimized reaction conditions. The reactivity of 1- and 2-chloronaphthalenes was good in the reaction with *p*-$MeOC_6H_4Li$ or *p*-$Me_2NC_6H_4Li$, each reaction giving excellent product yield (Table 2, entries 1–4). However, reaction of 2-chloronaphthalene with *o*-MeC_6H_4Li led to a much lower yield (Table 2, entry 5). This is ascribed to steric hindrance from *o*-MeC_6H_4Li. Deactivated aryl chlorides, including *p*-$MeOC_6H_4Cl$, *p*-$Me_2NC_6H_4Cl$, and *p*-MeC_6H_4Cl, were also demonstrated to

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



Entry	Aryl chloride	Aryllithium	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 Et_2O 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 Et_2O (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 at 40 °C and stirred for 4 h. [d] 5 mol% of complex **1a** was used. [e] No catalyst was used.

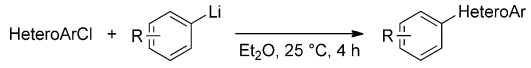
couple smoothly with aryllithium compounds such as PhLi, *p*-MeC_6H_4Li, *p*-$MeOC_6H_4Li$, and *p*-$Me_2NC_6H_4Li$, giving the desired products in 81–87% yields (Table 2, entries 6–13). However, except for the reaction of *p*-$MeOC_6H_4Cl$ with *p*-MeC_6H_4Li, the reactions of deactivated aryl chlorides required a higher reaction temperature (40 °C, bath temperature). *o*-MeC_6H_4Cl was less reactive due to steric hindrance. Its reaction with *p*-$MeOC_6H_4Li$ or *p*-$Me_2NC_6H_4Li$ required 5 mol% catalyst loading and 40 °C, resulting in the corresponding products in 65% and 67% yields, respectively (Table 2, entries 14 and 15). The reaction of electron-deficient *p*-$CF_3C_6H_4Cl$ with either *p*-$MeOC_6H_4Li$ or *p*-$Me_2NC_6H_4Li$ gave the corresponding cross-coupling products in low yields of 32% and 35%, respectively, due to side reactions. We detected a range of side products by TLC. In the absence of a catalyst, the reaction of *p*-$CF_3C_6H_4Cl$ with *p*-$MeOC_6H_4Li$ resulted in only trace amount of desired product and a range of unidentified species, as indicated by TLC (Table 2, entry 18). The reaction of functionalized aryl chlorides such as *p*-ClC_6H_4CN, *p*-$ClC_6H_4C(O)NEt_2$, and *p*-$ClC_6H_4CO_2Et$ with aryllithium reagents cannot lead to normal cross-coupling products under these conditions. The addition of the aryllithium to the reactive functional groups of aryl chlorides occurred in each case.

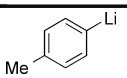
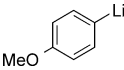
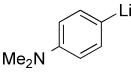
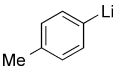
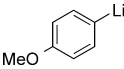
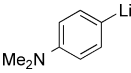
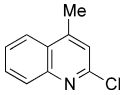
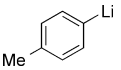
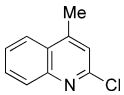
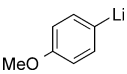
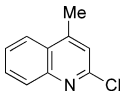
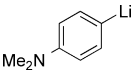
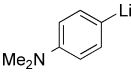
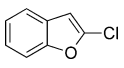
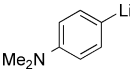
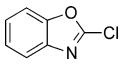
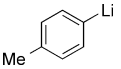
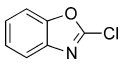
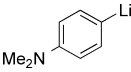
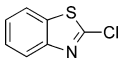
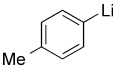
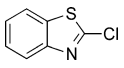
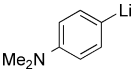
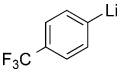
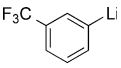
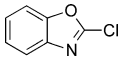
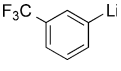
In addition, we also tested the reaction of *p*-ClC_6H_4OMe with *n*BuLi or PhCH=CHLi under the same conditions as shown in Table 2. However, no desired product was obtained in either case. A complicated mixture was formed in each reaction.

This method is also suitable for the cross-coupling of heteroaryl chlorides, and 1.8–2 equivalents of aryllithium reagents were used in these transformations. Both 2- and 3-chloropyridines reacted smoothly with 2 equivalents of *p*-MeC_6H_4Li, *p*-$MeOC_6H_4Li$, or *p*-$Me_2NC_6H_4Li$ at room temperature to afford the desired cross-coupling products in excellent yields (Table 3, entries 1–6). No addition or lithiation products were obtained in the reactions, although excess aryllithium was used. 2-Chloro-4-methylquinoline is also a suitable coupling partner. Its reaction with *p*-MeC_6H_4Li, *p*-$MeOC_6H_4Li$, or *p*-$Me_2NC_6H_4Li$ proceeded smoothly at room temperature to give the corresponding 2-aryl-4-methylquinolines in 90–91% yields. No lithiation products were obtained, although a reactive methyl group was present 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*-$Me_2NC_6H_4Li$ required loadings of 5 mol% of **1a** and gave corresponding cross-coupling products in 38% and 52% yields, respectively (Table 3, entries 10 and 11).

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*-MeC_6H_4Li and *p*-$Me_2NC_6H_4Li$, respectively, in the presence of 5 mol% of **1a** afforded the 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-

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



Entry	Heteroaryl chloride	Aryllithium	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 Et_2O 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 Et_2O (1.5 mL) by syringe over 1 h. [b] Isolated yield. [c] 1.8 equiv of aryllithium and 1.7 mL of Et_2O were used. [d] 5 mol% of **1a** was used. [e] 2-Chloropyridine (0.3 mmol) and complex **1a** were added to a stirred solution of *p*-$CF_3C_6H_4Li$ (0.6 mmol) in Et_2O (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.

coupling. However, none of the reactions gave desired product at room temperature or 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*-$CF_3C_6H_4Li$ and *m*-$CF_3C_6H_4Li$ were less reactive compared with the electron-rich ones (Table 3, entries 16–18). For example, reaction of *m*-$CF_3C_6H_4Li$ with 2-chloropyridine at room temperature in the presence of 5 mol% of **1a** gave 2-(3-(trifluoromethyl)phenyl)-pyridine in 56% yield, which is much lower than that from the reaction of 2-chloropyridine with *p*-MeC_6H_4Li (Table 3, entry 1). Two heteroaryllithium 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 one equivalent of LiBr was added into the stirred solution of aryl chloride (2-chloropyridine or 2-chloronaphthalene) and complex **1a** in Et_2O, 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 heteroaryllithium were obtained. This is ascribed to decomposition of the catalyst due to addition of the heteroaryllithium. Heterocyclic halides, especially electron-poor ones, may undergo 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 obtained under catalytic conditions.

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 a 1,1-diphenylethene additive.[9] When 10 mol% of 1,1-diphenylethene was added into a reaction system composed of *p*-$MeOC_6H_4Cl$, *p*-MeC_6H_4Li and 3 mol% of **1a**, no desired cross-coupling product was obtained. In our previous study we found that a **1a**-catalyzed reaction of cinnamyl methyl ether with *p*-$Me_2NC_6H_4ZnCl$ was not affected by 1,1-diphenylethene.[8j] This rules out the possibility that diphenylethene inhibits the reaction through its reaction with nickel catalyst. Hence, it seems that the current reaction involves a radical intermediate. On the other hand the catalytic activity of a combination of bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$) and a lithiated (2-$Ph_2PC_6H_4$)NH(2′-$Me_2NC_6H_4$), supposing [Li{N(2-$Ph_2PC_6H_4$)(2′-$Me_2NC_6H_4$)}] (**2**) was similar to complex **1a**; 3 mol% $Ni(cod)_2$/**2** loading resulted in 78% product yield for the cross-coupling of *p*-$MeOC_6H_4Cl$ with *p*-MeC_6H_4Li 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 nickel pincer complexes can effectively catalyze the cross-coupling of aryllithium 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*-$CF_3C_6H_4Cl$, *p*-$CF_3C_6H_4Li$, and *m*-$CF_3C_6H_4Li$ can also be used 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 by using standard Schlenk techniques. Toluene was distilled under nitrogen over sodium. THF and Et_2O were distilled under nitrogen over sodium/benzophenone. Substituted phenyllithium compounds were prepared from the 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 tetramethylsilane (TMS) and the ^{13}C 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 anhydrous Et_2O (1.0 mL). To the stirred mixture was added ArLi solution (0.75 mmol, diluted with Et_2O to reach the concentration of 0.3 M) 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 Et_2O (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel)

^1H and ^{13}C 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 (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H, Me), 3.80 (s, 3H, OMe), 6.94 (d, J = 8.6 Hz, 2H, C_6H_4), 7.20 (d, J = 8.1 Hz, 2H, C_6H_4), 7.43 (d, J = 8.1 Hz, 2H, C_6H_4), 7.49 ppm (d, J = 8.6 Hz, 2H, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 55.4, 114.3, 126.7, 128.1, 129. 6, 133.9, 136.4, 138.1, 159.1 ppm.

1-(4-Methoxyphenyl)naphthalene.[13] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 63.1 mg (90%). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3H, OMe), 7.00 (d, J = 8.6 Hz, 2H, C_6H_4), 7.36–7.50 (m, 6H, Ph + naphthyl), 7.79–7.94 ppm (m, 3H, naphthyl). ^{13}C NMR (75 MHz, $CDCl_3$): 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 ppm.

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, $CDCl_3$): δ = 3.03 (s, 6H, Me), 6.86 (d, J = 8.8 Hz, 2H, C_6H_4), 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 ppm (m, 1H, naphthyl). ^{13}C NMR

(101 MHz, $CDCl_3$): 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 ppm.

2-(4-Methoxyphenyl)naphthalene.[8a] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 65.5 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.88 (s, 3H, OMe), 7.03 (d, J = 8.8 Hz, 2H, C_6H_4), 7.42–7.53 (m, 2H, naphthyl), 7.67 (d, J = 8.8 Hz, 2H, C_6H_4), 7.72 (dd, J = 1.8, 8.6 Hz, 1H, naphthyl), 7.81–7.92 (m, 3H, naphthyl), 7.99 ppm (s, 1H, naphthyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5, 114.5, 125.2, 125.6, 125.8, 126.4, 127.8, 128.2, 128.5, 128.6, 132.5, 133.8, 133.9, 138.3, 159.4 ppm.

***N,N*-Dimethyl-4-(naphthalen-2-yl)aniline**.[8a] Eluent: petroleum ether/EtOAc (60:1 v/v), yield 70.2 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.01 (s, 6H, Me), 6.85 (d, J = 8.9 Hz, 2H, C_6H_4), 7.39–7.49 (m, 2H, naphthyl), 7.64 (d, J = 9.0 Hz, 2H, C_6H_4), 7.72–7.75 (m, 1H, naphthyl), 7.80–7.89 (m, 3H, naphthyl), 7.98 ppm (s, 1H, naphthyl). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

2-*o*-Tolylnaphthalene.[14] Eluent: petroleum ether, yield 31.9 mg (49%). ^{1}H NMR (400 MHz, $CDCl_3$): 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 ppm (m, 3H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

4′-Methoxy-*N,N*-dimethylbiphenyl-4-amine.[8a] Eluent: petroleum ether/EtOAc (50:1 v/v), yield 56.7 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.96 (s, 6H, NMe), 3.82 (s, 3H, OMe), 6.79 (d, J = 8.8 Hz, 2H, C_6H_4), 6.92 (d, J = 8.7 Hz, 2H, C_6H_4), 7.42–7.48 ppm (m, 4H, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.9, 55.5, 113.2, 114.3, 127.45, 127.47, 129.5, 134.1, 149.7, 158.4 ppm.

4-Methoxybiphenyl.[8a] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 44.8 mg (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OMe), 6.98 (d, J = 8.8 Hz, 2H, C_6H_4), 7.26–7.33 (m, 1H, Ph), 7.42 (t, J = 7.6 Hz, 2H, Ph), 7.50–7.58 ppm (m, 4H, Ph + C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 55.5, 114.4, 126.8, 126.9, 128.3, 128.9, 133.9, 141.0, 159.3 ppm.

***N,N*,4′-Trimethylbiphenyl-4-amine**.[14] Eluent: petroleum ether/EtOAc (60:1 v/v), yield 53.0 mg (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3H, Me), 2.88 (s, 6H, NMe), 6.70 (d, J = 8.6 Hz, 2H, C_6H_4), 7.11 (d, J = 7.7 Hz, 2H, C_6H_4), 7.34–7.41 ppm (m, 4H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.2, 40.7, 113.0, 126.3, 127.6, 129.45, 129.49, 135.7, 138.5, 149.9 ppm.

***N,N*-Dimethylbiphenyl-4-amine**.[8b] Eluent: petroleum ether/EtOAc (60:1 v/v), yield 49.3 mg (83%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00 (s, 6H, NMe), 6.82 (d, J = 8.8 Hz, 2H, C_6H_4), 7.22–7.30 (m, 1H, Ph), 7.40 (t, J = 7.6 Hz, 2H, Ph), 7.52 (d, J = 8.8 Hz, 2H, C_6H_4), 7.57 ppm (d, J = 7.2 Hz, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.8, 113.0, 126.1, 126.4, 127.9, 128.8, 129.4, 141.4, 150.1 ppm.

4′-Methoxy-2-methylbiphenyl.[8a] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 38.4 mg (65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3H, Me), 3.84 (s, 3H, OMe), 6.94 (d, J = 8.7 Hz, 2H, C_6H_4), 7.21–7.26 ppm (m, 6H, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): 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 ppm.

***N,N*,2′-Trimethylbiphenyl-4-amine**.[8a] Eluent: petroleum ether/EtOAc (60:1 v/v), yield 42.7 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3H, Me), 2.99 (s, 6H, NMe), 6.77–6.81 (m, 2H, C_6H_4), 7.18–7.27 ppm (m, 6H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 20.8, 40.8, 112.2, 125.9, 126.7, 130.1, 130.2, 130.4, 135.7, 142.2, 149.5 ppm.

4-Methoxy-4′-(trifluoromethyl)biphenyl.[8a] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 24.1 mg (32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OMe), 6.99 (d, J = 8.7 Hz, 2H, C_6H_4), 7.53 (d, J = 8.6 Hz, 2H, C_6H_4), 7.64 ppm (s, 4H, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): 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 ppm.

***N,N*-Dimethyl-4′-(trifluoromethyl)biphenyl-4-amine**.[8a] Eluent: petroleum ether/EtOAc (60:1 v/v), yield 27.9 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.01 (s, 6H, NMe), 6.80 (d, J = 8.9 Hz, 2H, C_6H_4), 7.52 (d, J = 8.9 Hz, 2H, C_6H_4), 7.60–7.67 ppm (m, 4H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

2-*p*-Tolylpyridine.[8a] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 48.1 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, Me), 7.18–7.21 (m, 1H, Py), 7.28 (d, J = 7.9 Hz, 2H, C_6H_4), 7.68–7.74 (m, 2H, Py), 7.89 (d, J = 8.2 Hz, 2H, C_6H_4), 8.66–8.69 ppm (m, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.4, 120.4, 121.9, 126.9, 129.6, 136.76, 136.79, 139.1, 149.7, 157.6 ppm.

2-(4-Methoxyphenyl)pyridine.[8b] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 52.0 mg (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H, OMe), 7.00 (d, J = 8.9 Hz, 2H, C_6H_4), 7.13–7.20 (m, 1H, Py), 7.65–7.73 (m, 2H, Py), 7.95 (d, J = 8.9 Hz, 2H, C_6H_4), 8.65 ppm (d, J = 4.4 Hz, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 55.5, 114.2, 119.9, 121.5, 128.3, 132.2, 136.8, 149.7, 157.2, 160.6 ppm.

***N,N*-Dimethyl-4-(pyridin-2-yl)aniline**.[8b] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 56.1 mg (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.01 (s, 6H, NMe), 6.79 (d, J = 8.9 Hz, 2H, C_6H_4), 7.05–7.13 (m, 1H, Py), 7.60–7.72 (m, 2H, Py), 7.92 (d, J = 9.0 Hz, 2H, C_6H_4), 8.61 ppm (d, J = 4.7 Hz, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 40.5, 112.3, 119.3, 120.7, 127.3, 127.8, 136.6, 149.5, 151.2, 157.7 ppm.

3-(*p*-Tolyl)pyridine.[13] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 47.1 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, Me), 7.28 (d, J = 7.9 Hz, 2H, C_6H_4), 7.33 (dd, J = 4.8, 7.9 Hz, 1H, Py), 7.48 (d, J = 8.1 Hz, 2H, C_6H_4), 7.84 (dt, J = 2.0, 7.6 Hz, 1H, Py), 8.56 (dd, J = 1.6, 4.8 Hz, 1H, Py), 8.83 ppm (d, J = 2.0 Hz, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.2, 123.6, 127.1, 129.9, 134.2, 135.0, 136.6, 138.1, 148.2, 148.3 ppm.

3-(4-Methoxyphenyl)pyridine.[15] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 52.6 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H, OMe), 7.01 (d, J = 8.7 Hz, 2H, C_6H_4), 7.32–7.35 (m, 1H, Py), 7.52 (d, J = 8.7 Hz, 2H, C_6H_4), 7.83 (d, J = 7.9 Hz, 1H, Py), 8.54 (d, J = 3.8 Hz, 1H, Py), 8.82 ppm (s, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 55.5, 114.6, 123.6, 128.3, 130.3, 134.0, 136.4, 147.9, 148.0, 159.9 ppm.

***N,N*-Dimethyl-4-(pyridin-3-yl)aniline**.[16] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 57.1 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.01 (s, 6H, NMe), 6.82 (d, J = 8.8 Hz, 2H, C_6H_4), 7.30 (dd, J = 4.8, 8.0 Hz, 1H, Py), 7.49 (d, J = 8.8 Hz, 2H, C_6H_4), 7.82 (dt, J = 2.0, 8.0 Hz, 1H, Py), 8.48 (dd, J = 1.6, 4.8 Hz, 1H, Py), 8.82 ppm (d, J = 2.0 Hz, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 40.6, 112.9, 123.6, 125.5, 127.8, 133.4, 136.7, 147.2, 147.7, 150.5 ppm.

4-Methyl-2-(*p*-tolyl)quinoline.[8b] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 63.1 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H, Me), 2.73 (s, 3H, Me), 7.31 (d, J = 7.9 Hz, 2H, C_6H_4), 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, C_6H_4), 8.15 ppm (d, J = 8.4 Hz, 1H, quinolyl). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

2-(4-Methoxyphenyl)-4-methylquinoline.[8b] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 67.8 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 3H, Me), 3.86 (s, 3H, OMe), 7.03 (d, J = 8.9 Hz, 2H, C_6H_4), 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 ppm (m, 3H, C_6H_4 + quinolyl). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

***N*,*N*-Dimethyl-4-(4-methylquinolin-2-yl)aniline**.[8c] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 71.1 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 3H, Me), 3.03 (s, 6H, NMe), 6.82 (d, J = 8.9 Hz, 2H, C_6H_4), 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 ppm (m, 3H, C_6H_4 + quinolyl). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

***N*,*N*-Dimethyl-4-(thiophen-2-yl)aniline**.[17] Eluent: petroleum ether/EtOAc (60:1 v/v), yield 23.3 mg (38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, 6H, NMe), 6.73 (d, J = 8.8 Hz, 2H, C_6H_4), 7.02–7.04 (m, 1H, thienyl), 7.14–7.16 (m, 2H, thienyl), 7.49 ppm (d, J = 8.8 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 40.7, 112.7, 121.0, 122.9, 123.1, 125.3, 127.0, 127.9, 145.4, 150.1 ppm.

4-(Benzofuran-2-yl)-*N*,*N*-dimethylaniline.[18] Eluent: petroleum ether/EtOAc (60:1 v/v), yield 37.1 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (s, 6H, NMe), 6.77 (d, J = 8.8 Hz, 2H, C_6H_4), 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 ppm (d, J = 8.8 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

2-(*p*-Tolyl)benzo[d]oxazole.[8e] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 53.3 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): 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 ppm (d, J = 8.4 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

4-(Benzo[*d*]oxazol-2-yl)-*N*,*N*-dimethylaniline.[19] Eluent: petroleum ether/EtOAc (50:1 v/v), yield 61.6 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.05 (s, 6H, NMe), 6.76 (d, J = 8.8 Hz, 2H, C_6H_4), 7.24–7.32 (m, 2H, Ar), 7.50–7.52 (m, 1H, Ar), 7.68–7.71 (m, 1H, Ar), 8.10 ppm (d, J = 8.8 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

2-(*p*-Tolyl)benzo[*d*]thiazole.[8e] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 37.3 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H, Me), 7.29 (d, J = 8.0 Hz, 2H, C_6H_4), 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, C_6H_4), 8.04–8.07 ppm (m, 1H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

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^4,N^4,$N^{4'}$,$N^{4'}$-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 ^{1}H NMR integral). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.05 (s, 6H, NMe), 6.74 (d, J = 8.8 Hz, 2H, C_6H_4), 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 ppm (m, 3H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 40.3, 111.8, 121.5, 122.4, 124.3, 126.1, 129.0, 134.7, 152.3, 154.5, 168.9 ppm.

2-(4-(Trifluoromethyl)phenyl)pyridine.[21] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 15.4 mg (23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.30 (m, 1H, Py), 7.72 (d, J = 8.4 Hz, 2H, C_6H_4), 7.75–7.80 (m, 2H, Py), 8.10 (d, J = 8.4 Hz, 2H, C_6H_4), 8.71–8.73 ppm (m, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

2-(3-(Trifluoromethyl)phenyl)pyridine.[22] Eluent: petroleum ether/EtOAc (30:1 v/v), yield 37.6 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.28 (m, 1H, Py), 7.57 (t, J = 7.8 Hz, 1H, C_6H_4), 7.66 (d, J = 7.8 Hz, 1H, C_6H_4), 7.72–7.79 (m, 2H, Py), 8.16 (d, J = 8.0 Hz, 1H, C_6H_4), 8.29 (s, 1H, C_6H_4), 8.71 ppm (d, J = 4.8 Hz, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

2-(3-(Trifluoromethyl)phenyl)benzo[*d*]oxazole.[23] Eluent: petroleum ether/EtOAc (100:1 v/v), yield 36.9 mg (47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.43 (m, 2H, Ar), 7.59–7.65 (m, 1H, Ar), 7.67 (t, J = 7.8 Hz, 1H, C_6H_4), 7.78–7.83 (m, 2H, Ar), 8.45 (d, J = 7.8 Hz, 1H, C_6H_4), 8.54 ppm (s, 1H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): 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 ppm.

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