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P,N,N-Pincer nickel-catalyzed cross-coupling of aryl fluorides and chlorides†

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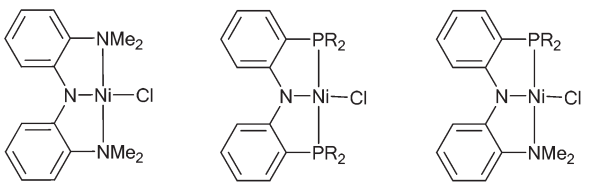
P,N,N-Pincer nickel complexes [Ni(Cl){N(2-$R_2PC_6H_4$)(2′-$Me_2NC_6H_4$)}] (R = Ph, **3a**; R = Pr^i, **3b**; R = Cy, **3c**) were synthesized and their catalysis toward the Kumada or Negishi cross-coupling reaction of aryl fluorides and chlorides was evaluated. Complex **3a** effectively catalyzes the cross-coupling of (hetero)aryl fluorides with aryl Grignard reagents at room temperature. Complex **3a** also catalyzes the cross-coupling of (hetero)aryl chlorides and arylzinc reagents at 80 °C with low catalyst loadings and good functional group compatibility.

Introduction

Transition-metal-catalyzed cross-coupling reactions are powerful tools to construct new C–C bonds. Nucleophiles used in these cross-couplings include various organometallic reagents such as organo-magnesium, -zinc, -tin, -boron, and -silicon compounds.[1,2] In the earlier stage of the study organoiodides and bromides were predominately employed as the electrophiles.[1–3] In the last 15 years organochlorides as the electrophiles were extensively explored because of their lower cost and the diversity of available compounds.[4] However, the use of chlorides as electrophiles has proven more difficult due to the low reactivity of the C–Cl bond. Hence developing highly active catalyst systems is an important research topic.[5] Cross-coupling using organofluorine compounds as electrophiles also attracted considerable attention in recent years. The C–F bond is known as the strongest single bond to carbon. It is very challenging to cut off such a bond and helpful for the fundamental understanding of the reactivity of very stable bonds.[6] On the other hand, it is one of the effective ways to prepare partially fluorinated compounds from poly- or perfluorinated species.[6d,7] Some catalysts for the activation of organochlorides or fluorides have been reported, including palladium, nickel, copper, cobalt, iron and other transition metal complexes. However, investigations of highly active and widely applicable catalysts are still attractive. Pincer nickel complexes have been proven to catalyze cross-couplings of organohalides including chlorides and fluorides with various nucleophiles.[5o–r,8] Among the pincer nickel complexes with catalytic activity, we noticed that *N,N,N*-pincer nickel complex **1** (Chart 1) can efficiently catalyze Kumada coupling of β-hydrogen-containing nucleophiles or electrophiles.[9] *P,N,P*-Pincer nickel complexes **2a–2c** (Chart 1) can catalyze Kumada coupling of phenyl iodide or bromide with aryl or alkyl Grignard reagents.[10] A *P,N,N*-pincer ligand with similar skeletal structure to those in **1** and **2** will provide a different coordination environment and its nickel complexes may exhibit different catalytic properties from **1** and **2**. Hence we synthesized *P,N,N*-pincer nickel complexes **3a–3c** (Chart 1) and examined their catalytic action. The study showed that complex **3a** effectively catalyzes cross-couplings of aryl fluorides with aryl Grignard reagents and aryl chlorides with arylzinc reagents. Herein we report the results.



1 | **2a** R = Ph, **2b** R = Pr^i, **2c** R = Cy | **3a** R = Ph, **3b** R = Pr^i, **3c** R = Cy

Chart 1 *N,N,N*-, *P,N,P*- and *P,N,N*-pincer nickel complexes.

Results and discussion

Synthesis of complexes **3a–3c** is summarized in Scheme 1 and the experimental details are provided in the ESI.†

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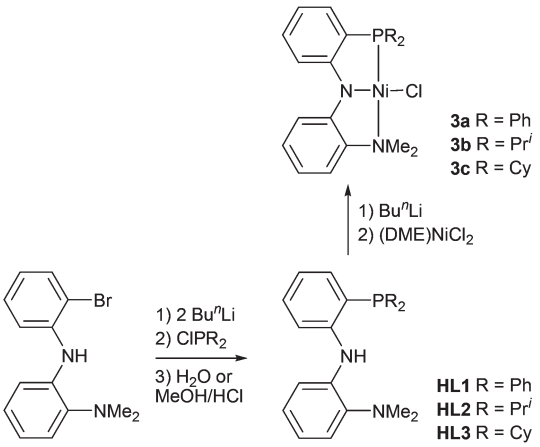
† Electronic supplementary information (ESI) available: Details of synthesis and characterization of complexes **3a–3c**; details of single crystal X-ray diffraction determination of complex **3c**. Copies of ^1H and ^{13}C NMR spectra of the cross-coupling products. CCDC 996222. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob01041h



Scheme 1 Synthesis of complexes **3a–3c**.

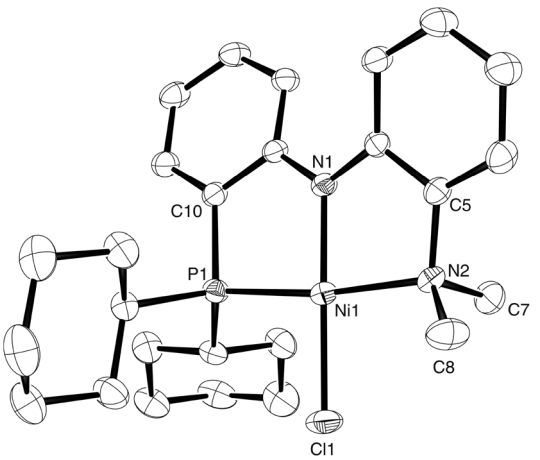
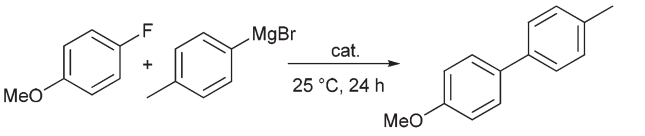


Fig. 1 Molecular structure of complex **3c**. Selected bond lengths (Å): Ni1–P1 2.1368(8), Ni1–N1 1.858(2), Ni1–N2 2.006(2), Ni1–Cl1 2.1636(10).

Each of the complexes is a diamagnetic crystalline solid and was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. Complex **3c** was also characterized by single crystal X-ray diffraction.[11] The result showed that the central nickel atom is coordinated by P1N1N2 and Cl1 atoms and has an approximate square planar geometry (Fig. 1). The Ni1–N1 distance of 1.858(2) Å is between the corresponding bond distances of complexes **1** and **2b** [1.835(2) Å and 1.9030(17) Å, respectively].[9b,10] The Ni1–N2 distance of 2.006(2) Å is longer than those in complex **1** [1.956(2) and 1.9598(19) Å].[9b] The Ni1–P1 distance of 2.1368(8) Å is shorter than those in complex **2b** [2.1884(6) and 2.1913(6) Å].[10]

Catalytic properties of complexes **3a–3c** were evaluated using reaction of *p*-$MeOC_6H_4F$ with *p*-MeC_6H_4MgBr in THF. The reaction was run at room temperature for 24 h in the presence of 1 mol% of **3a**, **3b** or **3c**. Complex **3a** resulted in the cross-coupling product in 46% yield, and **3b** and **3c** led to 24% and 34% yields, respectively (entries 1–3, Table 1). The reaction was found to proceed more effectively in either Et_2O or toluene, giving 82% and 90% product yields, respectively (entries 4 and 5, Table 1). The reaction using 0.5 mol% of **3a** afforded the corresponding product in 84% yield in Et_2O and 87% yield in toluene (entries 6 and 7, Table 1).

Table 1 Evaluation of catalytic activity of complexes **3a–3c** in the Kumuda reaction[a]



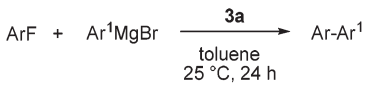
Entry	Cat. (mol%)	Solvent	Yield[b] (%)
1	**3a** (1)	THF	46
2	**3b** (1)	THF	24
3	**3c** (1)	THF	34
4	**3a** (1)	Et_2O	82
5	**3a** (1)	Toluene	90
6	**3a** (0.5)	Et_2O	84
7	**3a** (0.5)	Toluene	87

[a] The reaction was carried out according to the conditions indicated by above equation; 0.5 mmol *p*-FC_6H_4OMe and 0.75 mmol *p*-MeC_6H_4MgBr were employed. [b] Isolated yield.

It has been reported that catalyst-free nucleophilic aromatic substitution of aryl fluorides by nitrogen, oxygen, sulfur or carbon nucleophiles can occur under appropriate conditions, but usually apply to electron-deficient aryl fluorides.[6c] In order to rule out the possibility, we respectively ran the reaction of fluorobenzene and 2-fluoropyridine with *p*-MeC_6H_4MgBr in toluene at room temperature in the absence of a catalyst. The results showed that no substitution products were observed in 24 h and the starting materials remained.

The substrate scope of the catalytic reactions was examined using **3a** as the catalyst and toluene as the solvent. *m*-FC_6H_4OMe showed higher reactivity than *p*-FC_6H_4OMe. The former reacted with *p*-MeC_6H_4MgBr using 0.5 mol% **3a** in toluene at 25 °C to afford the cross-coupling product in 91% yield (entry 1, Table 2). However, this small reactivity difference between *meta*- and *para*-positions of fluorinated anisoles does not allow for selective defluorination in a polyfluoroanisole molecule. For example, reaction of 2,3,4,5,6-pentafluoroanisole with 1 equiv. of *p*-MeC_6H_4MgBr under the same conditions as above resulted in a complicated mixture of products. *p*-$FC_6H_4NMe_2$ exhibited lower reactivity than *p*-FC_6H_4OMe due to strong electron donating properties of the NMe_2 group. Its reaction with *p*-MeC_6H_4MgBr in the presence of 0.5 mol% **3a** afforded the cross-coupling product in 77% yield. However, the reaction using 2 mol% of **3a** gave quantitative amounts of the product (entry 2, Table 2). 4-Fluoro-1,2-dimethoxybenzene is a very inert electrophile. Its reaction with either *p*-MeC_6H_4MgBr or *p*-$Me_2NC_6H_4MgBr$ required higher reaction temperature (70 °C) and higher catalyst loadings (2 mol%), giving the corresponding cross-coupling products in moderate yields (entries 3 and 4, Table 2). Reaction of 3-(4-fluorophenyl)-1-isopropyl-1*H*-indole, (4-fluorophenyl)methanol and 1-fluoro-2-methylbenzene with *p*-MeC_6H_4MgBr or

Table 2 Cross-coupling of aryl fluorides with ArMgBr catalyzed by **3a**[a]



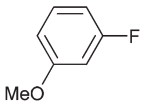
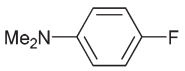
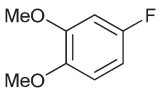
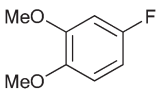
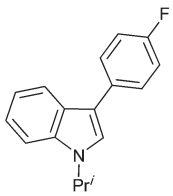
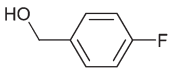
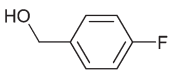
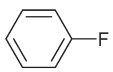
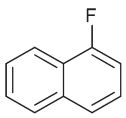
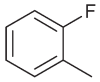
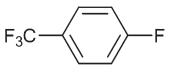
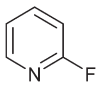
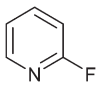
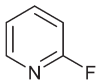
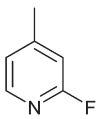
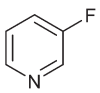
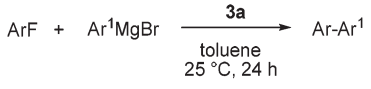
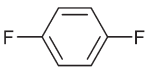
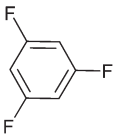
Entry	ArF	Ar^1	mol% **3a**	Yield[b] (%)
1		*p*-MeC_6H_4	0.5	91
2		*p*-MeC_6H_4	0.5	77(99[c])
3		*p*-MeC_6H_4	2	54[d]
4		*p*-$Me_2NC_6H_4$	2	66[d]
5		*p*-MeC_6H_4	0.5	91
6		*p*-MeC_6H_4	2	90[e]
7		*p*-$Me_2NC_6H_4$	2	81[e]
8		*p*-$Me_2NC_6H_4$	0.5	99
9		*p*-$Me_2NC_6H_4$	0.5	99
10		*p*-$Me_2NC_6H_4$	2	95
11		*p*-MeC_6H_4	2	63
12		*p*-MeC_6H_4	0.5	77(89[f])
13		*p*-$MeOC_6H_4$	0.5	81
14		*p*-$Me_2NC_6H_4$	0.5	86
15		*p*-MeC_6H_4	0.5	86
16		*p*-MeC_6H_4	2	81

Table 2 *(Contd.)*

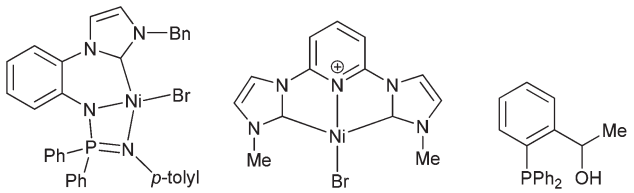


Entry	ArF	Ar^1	mol% **3a**	Yield[b] (%)
17		*p*-MeC_6H_4	1	74[g]
18		*p*-MeC_6H_4	3	76[h]

[a] Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation, 0.75 mmol ArMgBr were used. [b] Isolated yield. [c] 2 mol% catalyst loading. [d] The reaction was carried out at 70 °C. [e] 1.25 mmol ArMgBr were used. [f] The reaction was run in Et_2O. [g] 3 equiv. of ArMgBr were used. [h] 4.5 equiv. of ArMgBr were used.

p-$Me_2NC_6H_4MgBr$ gave good product yields although the reaction of (4-fluorophenyl)methanol and 1-fluoro-2-methylbenzene required 2 mol% of catalyst loadings (entries 5–7, Table 2). Reaction of (4-fluorophenyl)methanol also required more amount of Grignard reagents due to the presence of the hydroxy group in the molecule. Both fluorobenzene and 1-fluoronaphthalene showed good reactivity in the cross-coupling. Their reactions with *p*-$Me_2NC_6H_4MgBr$ in the presence of 0.5 mol% **3a** afforded desired products in quantitative yields. Cross-coupling of 1-fluoro-2-methylbenzene with *p*-$Me_2NC_6H_4MgBr$ in the presence of 2 mol% **3a** produced *N*,*N*,2′-trimethylbiphenyl-4-amine in 95% yield (entries 8–10, Table 2). As an electron-poor aryl fluoride, 1-fluoro-4-(trifluoromethyl)benzene was expected to be a reactive substrate in the cross-coupling. However, its reaction with *p*-MeC_6H_4MgBr required 2 mol% catalyst loading and gave only 63% product yield for unclear reasons (entry 11, Table 2). 2-Fluoropyridine, 2-fluoro-4-methylpyridine and 3-fluoropyridine showed good reactivity with Grignard reagents including *p*-MeC_6H_4MgBr, *p*-$MeOC_6H_4MgBr$ and *p*-$Me_2NC_6H_4MgBr$. Each reaction gave good product yield although reaction of 3-fluoropyridine required higher catalyst loading (2 mol%) than the others (entries 12–16, Table 2). Reactions of 1,4-difluorobenzene and 1,3,5-trifluorobenzene were also evaluated. The reaction of the former with 3 equiv. of *p*-MeC_6H_4MgBr in the presence of 1 mol% **3a** afforded 1,4-bis(*p*-tolyl)benzene in 74% yield, and the latter with 4.5 equiv. of *p*-MeC_6H_4MgBr in the presence of 3 mol% **3a** generated 1,3,5-tris(*p*-tolyl)benzene in 76% yield (entries 17 and 18, Table 2). Attempts to selectively prepare a monoarylated product using less amounts of Grignard reagents under the same conditions were unsuccessful. A mixture of mono- and multi-arylated products was formed.

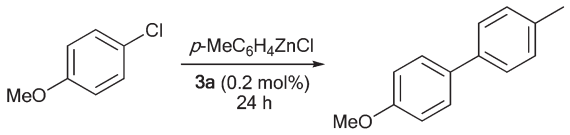
Nickel, palladium, manganese, titanium, and tantalum complexes including pincer nickel complexes (*e.g.* **4** and **5**,



4 5 6

Chart 2 Pincer nickel complexes and hydroxyphosphine ligand.

Table 3 Screening of reaction conditions of the cross-coupling catalyzed by **3a**[a]



Entry	Solvent	Temp. (°C)	Yield[b] (%)
1	THF–NMP (1 : 1)	80	68
2	THF–NMP (2 : 1)	80	94
3	THF–DMA (2 : 1)	80	87
4	THF–DMA (2 : 1)	40	40
5	THF–DMA (2 : 1)	60	59
6	THF–toluene (1 : 1)	80	Trace
7	THF	80	Trace
8	Toluene	80	Trace
9	NMP	80	68
10	THF–NMP (2 : 1)	80	32[c]
11	THF–NMP (2 : 1)	80	2[d]

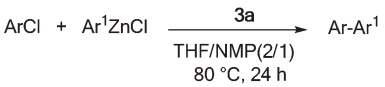
[a] Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation; 1.0 mmol *p*-MeC_6H_4ZnCl were employed. *p*-MeC_6H_4ZnCl was prepared from $ZnCl_2$ and an equiv. of *p*-MeC_6H_4MgBr in the presence of two equiv. of LiCl. [b] Isolated yield. [c] *p*-MeC_6H_4ZnCl was prepared from $ZnCl_2$ and an equiv. of *p*-MeC_6H_4Li. [d] *p*-MeC_6H_4ZnCl was prepared from $ZnCl_2$ and an equiv. of *p*-MeC_6H_4MgBr.

Chart 2) were demonstrated to catalyze cross-coupling of aryl fluorides with Grignard reagents.[5q,6c,12] However, most of them showed lower catalytic activity than complex **3a**. The combination of $Ni(acac)_2$ and hydroxyphosphine ligand **6** (Chart 2) exhibited high activity which was attributed to a Ni–Mg bimetallic cooperation.[5j] Activity of complex **3a** is comparable with that of $Ni(acac)_2$/**6** combination. Hence complex **3a** is one of the most active catalysts for the Kumada coupling of aryl fluorides.

Aryl C–Cl bonds are weaker than aryl C–F bonds. Complex **3a** was expected to effectively catalyze the activation of aryl C–Cl bonds. However, preliminary test showed that complex **3a** was not very effective in catalyzing the Kumada coupling of aryl chlorides under the same conditions as above. Further test proved that it was a very effective catalyst for the Negishi coupling of *p*-ClC_6H_4OMe with *p*-MeC_6H_4ZnCl in a mixed solvent of THF and NMP at 80 °C (entries 1 and 2, Table 3). A series of solvents or solvent combinations involving THF–NMP, THF–DMA, THF–toluene, THF, toluene and NMP were tried and a 2 : 1 mixture of THF and NMP was proven to be the best one (Table 3). Temperature lower than 80 °C resulted in a yield decrease (entries 4 and 5, Table 3). In addition, we also noticed that the zinc reagent, *p*-MeC_6H_4ZnCl, prepared from the corresponding Grignard reagent in the presence of 2 equiv. of LiCl gave better reaction results than those prepared from $ZnCl_2$ and *p*-MeC_6H_4Li or $ZnCl_2$ and *p*-MeC_6H_4MgBr in the absence of LiCl (entries 10 and 11, Table 3).

With the optimized reaction conditions in hand, we examined the scope of electrophiles and nucleophiles (Table 4). Deactivated *m*- and *o*-ClC_6H_4OMe can also react with *p*-MeC_6H_4ZnCl. However, the reaction of *o*-ClC_6H_4OMe was much more difficult than *p*- or *m*-ClC_6H_4OMe due to its steric hindrance, higher catalyst loading and higher reaction temperature being required (entries 1 and 2, Table 4). Reaction of 2,5-$Me_2C_6H_3Cl$ with *p*-$Me_2NC_6H_4MgBr$ also required relatively high catalyst loading and reaction temperature, giving the desired product in 95% yield. Reaction of unactivated C_6H_5Cl with *p*-$Me_2NC_6H_4ZnCl$ was very efficient, 0.01 mol% **3a** resulting in 99% yield of the product. *p*-$MeOC_6H_4MgBr$ seems to be less reactive than *p*-$Me_2NC_6H_4ZnCl$ in the reaction with C_6H_5Cl. The former required 0.1 mol% of catalyst loading and led to 81% product yield (entries 4 and 5, Table 4). A series of functionalized aryl chlorides were tested. Reaction of *p*-$ClC_6H_4CF_3$, *p*-$ClC_6H_4C(O)Ph$, *p*-ClC_6H_4COOEt and *p*-$ClC_6H_4C(O)NEt_2$ with *p*-MeC_6H_4ZnCl, *p*-$MeOC_6H_4ZnCl$ or *p*-$Me_2NC_6H_4ZnCl$ proceeded smoothly in the presence of 0.01 mol% **3a**, giving the corresponding cross-coupling products in excellent yields (entries 6–14, Table 4). Reaction of *p*-ClC_6H_4CN required a higher catalyst loading and gave a relatively low yield (entry 15, Table 4). This is ascribed to the coordination of the nitrile group with the catalyst species.[13] *o*-$ClC_6H_4C(O)Ph$ and *o*-ClC_6H_4CN showed lower reactivity compared with the corresponding *para*-substituted partners due to steric hindrance. However, reaction of *o*-MeC_6H_4ZnCl with either deactivated or activated aryl chlorides including *p*-ClC_6H_4OMe, *p*-$ClC_6H_4C(O)Ph$, *p*-ClC_6H_4COOEt and *p*-$ClC_6H_4C(O)NEt_2$ resulted in excellent product yields (entries 19–22, Table 4). Several heteroaryl chlorides including 2-chloronicotinonitrile, 2-chloro-6-methoxypyridine and 2-chloro-4-methylquinoline were also proven to be suitable electrophiles for the coupling. Reaction of each of them gave excellent yields (entries 23–26, Table 4). The electron-poor arylzinc reagent *p*-$CF_3C_6H_4ZnCl$ also exhibited good reactivity in the cross-coupling with *p*-$ClC_6H_4C(O)Ph$, *p*-ClC_6H_4COOEt, *p*-$ClC_6H_4C(O)NEt_2$ or *o*-$ClC_6H_4C(O)Ph$. But the reaction with *o*-$ClC_6H_4C(O)Ph$ required higher catalyst loading (0.5 mol%) than the others due to steric hindrance. A heteroarylzinc reagent, 2-furylzinc chloride, was also tested. It showed a relatively low reactivity although it is an electron-rich nucleophile. Its reaction with *p*-$ClC_6H_4CF_3$, *p*-$ClC_6H_4C(O)Ph$, *p*-ClC_6H_4COOEt or *p*-$ClC_6H_4C(O)NEt_2$ gave excellent yields, but much higher catalyst loadings are necessary compared with *p*-MeC_6H_4ZnCl (entries 31–34, Table 4). Reaction of 2-furylzinc chloride with *o*-ClC_6H_4CN was also carried out in the presence of 2 mol% **3a** at 90 °C, giving 71% product yield.

Table 4 Cross-coupling of arylzinc chlorides with aryl chlorides catalysed by **3a**[a]



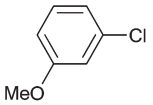
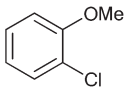
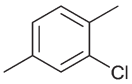
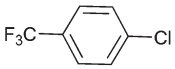
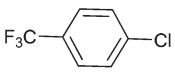
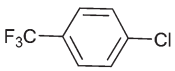
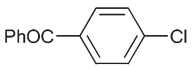
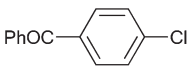
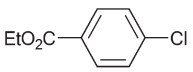
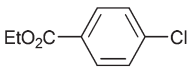
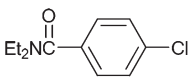
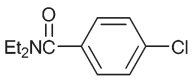
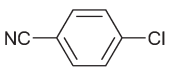
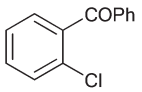
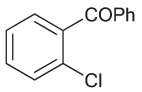
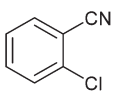
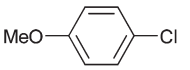
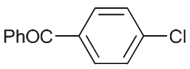
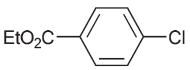
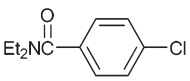
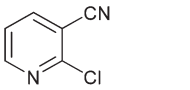
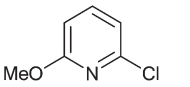
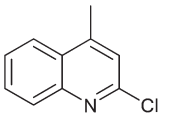
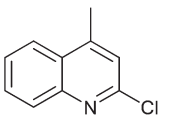
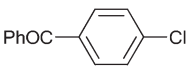
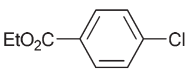
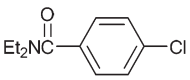
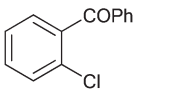
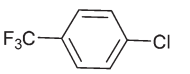
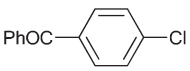
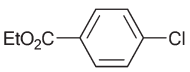
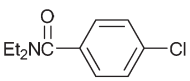
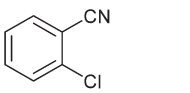
Entry	ArCl	Ar^1	mol% **3a**	Yield[b] (%)
1		*p*-MeC_6H_4	0.1	83
2		*p*-MeC_6H_4	4	68[c]
3		*p*-$Me_2NC_6H_4$	1	95[c]
4		*p*-$Me_2NC_6H_4$	0.01	99
5		*p*-$MeOC_6H_4$	0.1	81
6		*p*-MeC_6H_4	0.01	96
7		*p*-$MeOC_6H_4$	0.01	98
8		*p*-$Me_2NC_6H_4$	0.01	74
9		*p*-MeC_6H_4	0.01	99
10		*p*-$MeOC_6H_4$	0.01	91
11		*p*-MeC_6H_4	0.01	99
12		*p*-$MeOC_6H_4$	0.01	85
13		*p*-MeC_6H_4	0.01	96
14		*p*-$MeOC_6H_4$	0.01	97
15		*p*-MeC_6H_4	0.1	58
16		*p*-MeC_6H_4	0.2	99
17		*p*-$MeOC_6H_4$	0.5	73
18		*p*-MeC_6H_4	0.5	92

Table 4 *(Contd.)*

Entry	ArCl	Ar^1	mol% **3a**	Yield[b] (%)
19		*o*-MeC_6H_4	1	85
20		*o*-MeC_6H_4	0.05	96
21		*o*-MeC_6H_4	0.01	99
22		*o*-MeC_6H_4	0.01	91
23		*p*-MeC_6H_4	0.5	93
24		*p*-MeC_6H_4	0.01	99
25		*p*-MeC_6H_4	0.01	99
26		*p*-$MeOC_6H_4$	0.01	90
27		*p*-$CF_3C_6H_4$	0.01	88
28		*p*-$CF_3C_6H_4$	0.01	99
29		*p*-$CF_3C_6H_4$	0.01	89
30		*p*-$CF_3C_6H_4$	0.5	98
31		2-furyl	1	90
32		2-furyl	2	84[d]
33		2-furyl	2	92[d]
34		2-furyl	1	99
35		2-furyl	2	71[d]

[a] Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation, 2.0 equiv. of ArZnCl were employed. [b] Isolated yield. [c] The reaction was run at 100 °C. [d] The reaction was run at 90 °C.

Compared with the reported catalysts for the Negishi coupling of aryl chlorides, the current catalyst exhibited lower activity than Buchwald's ones, especially for the bulky substrates.[14] However, its activity is comparable to or higher than that of the reported nickel catalyst systems.[5p,8c–e,15] In comparison with complexes **1** and **2a–2c**, it can be seen that a small adjustment of the ligand structure results in marked changes in the catalytic properties. Complex **3a** exhibits much higher activity than complexes **2a–2c** in catalyzing aryl C–halide bond activation, but it is ineffective in catalyzing the alkyl C–Cl bond activation. We expect further improvement of catalytic properties through the modification of ligands.

Conclusions

We synthesized three *P*,*N*,*N*-pincer nickel complexes (**3a–3c**) and evaluated their catalysis in aryl C–F and C–Cl bond activation. Complex **3a** effectively catalyzes cross-coupling of activated, unactivated and deactivated aryl fluorides and 2- or 3-fluoropyridines with aryl Grignard reagents, forming biaryls in 54–99% yields. A series of aryl or heteroaryl chlorides were also catalytically coupled with arylzinc reagents by **3a**. The zinc reagents used in the reactions include electron-rich and electron-poor substituted phenylzinc chlorides and 2-furylzinc chloride. The reactions required low catalyst loadings in most cases and tolerated functional groups including PhC(O), COOEt, $C(O)NEt_2$, CN and CF_3 and nitrogen-containing heterocycles. Compared with the reported catalyst systems, complex **3a** is one of the most effective nickel catalysts for the Kumada cross-coupling of aryl fluorides and the Negishi cross-coupling of aryl chlorides.

Experimental section

The reactions were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. THF and Et_2O were distilled under nitrogen over sodium/benzophenone and degassed prior to use. Toluene was distilled under nitrogen over sodium and degassed prior to use. NMP and DMA were dried over 4 Å molecular sieves, fractionally distilled under reduced pressure and stored under a nitrogen atmosphere. Grignard reagents were prepared according to literature procedures.[16] Arylzinc chlorides were prepared from $ZnCl_2$ and an equiv. of ArMgBr in the presence of 2 equiv. of LiCl. All other solvents and reagents were used as received. NMR spectra were determined on a Bruker av300 or a Bruker Avance III 400 NMR spectrometer at room temperature. The chemical shifts of the ^1H NMR spectra were referenced to TMS or solvent residual signal; the chemical shifts of the ^{13}C NMR spectra were referenced to internal solvent resonances. HR-MS data were recorded on an Agilent 6890/Micromass LCT-MS spectrometer (EI).

General procedure for the Kumada cross-coupling of aryl fluorides

ArMgBr (1.5 cm^3, 0.5 M solution in THF, 0.75 mmol) was added into a Schlenk tube by syringe. The solvent was removed *in vacuo*. Toluene (2 cm^3), complex **3a** (1.2 mg, 0.0025 mmol) and aryl fluorides (0.5 mmol) were respectively added. The mixture was stirred at 25 °C for 24 h. Water (10 cm^3) and several drops of acetic acid were successively added. The mixture was extracted with Et_2O (3 × 10 cm^3). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

General procedure for the Negishi cross-coupling of aryl chlorides

A Schlenk tube was charged with aryl chloride (0.5 mmol), NMP (1.05 cm^3) and a solution of complex **3a** (0.1 cm^3, 0.0005 M solution in THF, 0.00005 mmol). To the stirred mixture ArZnCl solution (2.0 cm^3, 0.5 M solution in THF, 1.0 mmol) was added by syringe. The reaction mixture was stirred at 80 °C for 24 h. Water (10 mL) and several drops of hydrochloric acid were successively added. The mixture was extracted with Et_2O (3 × 10 cm^3). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

Product characterization

4-Methoxy-4′-methylbiphenyl.[17] ^1H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H, Me), 3.83 (s, 3H, OMe), 6.95 (d, J = 8.8 Hz, 2H, C_6H_4), 7.21 (d, J = 7.9 Hz, 2H, C_6H_4), 7.44 (d, J = 8.1 Hz, 2H, C_6H_4), 7.50 (d, J = 8.8 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.18, 55.45, 114.29, 126.71, 128.08, 129.57, 133.87, 136.47, 138.10, 159.07.

3-Methoxy-4′-methylbiphenyl.[18] ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H, Me), 3.79 (s, 3H, OMe), 6.83 (d, J = 7.9 Hz, 1H, C_6H_4), 7.10–7.32 (m, 5H, C_6H_4), 7.46 (d, J = 7.5 Hz, 2H, C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.18, 55.32, 112.49, 112.86, 119.60, 127.12, 129.56, 129.80, 137.27, 138.35, 142.81, 160.09.

4′-Methyl-*N*,*N*-dimethylbiphenyl-4-amine.[19] ^1H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, Me), 2.85 (s, 6H, NMe_2), 6.68 (d, J = 8.8 Hz, 2H, C_6H_4), 7.09 (d, J = 7.9 Hz, 2H, C_6H_4), 7.35 (d, J = 8.2 Hz, 2H, C_6H_4), 7.38 (d, J = 8.9 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.17, 40.77, 112.97, 126.31, 127.65, 129.47, 129.50, 135.74, 138.51, 149.95.

3,4-Dimethoxy-4′-methylbiphenyl.[5q] ^1H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H, Me), 3.91 (s, 3H, OMe), 3.93 (s, 3H, OMe), 6.92 (d, J = 8.2 Hz, 1H, C_6H_3), 7.09–7.13 (m, 2H, C_6H_3), 7.22 (d, J = 7.9 Hz, 2H, C_6H_4), 7.45 (d, J = 8.1 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.16, 56.02, 56.08, 110.46, 111.60, 119.27, 126.80, 129.54, 134.34, 136.67, 138.29, 148.51, 149.22.

3′,4′-Dimethoxy-*N*,*N*-dimethylbiphenyl-4-amine.[5q] ^1H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 6H, NMe), 3.90 (s, 3H, OMe), 3.94 (s, 3H, OMe), 6.80 (d, J = 8.8 Hz, 2H, C_6H_4), 6.91 (d, J = 8.1 Hz, 1H, C_6H_3), 7.06–7.11 (m, 2H, C_6H_3), 7.46 (d, J = 8.5 Hz, 2H,

C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 40.77, 55.99, 56.09, 109.99, 111.65, 112.96, 118.54, 127.55, 129.41, 134.59, 147.80, 149.17, 149.83.

1-Isopropyl-3-(4′-methylbiphenyl-4-yl)-1*H*-indole. ^1H NMR (400 MHz, $CDCl_3$): δ 1.58 (d, J = 6.7 Hz, 6H, Me), 2.40 (s, 3H, Me), 4.72 (sept, J = 6.7 Hz, 1H, CH), 7.19 (t, J = 7.4 Hz, 1H, Ar), 7.25–7.29 (m, 3H, Ar), 7.41–7.45 (m, 2H, Ar), 7.56 (d, J = 8.0 Hz, 2H, Ar), 7.66 (d, J = 8.2 Hz, 2H, Ar), 7.73 (d, J = 8.3 Hz, 2H, Ar), 7.99 (d, J = 7.9 Hz, 1H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.26, 22.98, 47.26, 109.91, 116.64, 120.07, 120.21, 121.65, 121.86, 126.40, 126.90, 127.38, 127.68, 129.63, 134.85, 136.55, 136.90, 138.36, 138.46. HR-MS (EI): m/z = 325.1823, calcd for $C_{24}H_{23}N$: 325.1830.

(4′-Methylbiphenyl-4-yl)methanol.[5q] ^1H NMR (400 MHz, $CDCl_3$): δ 1.66 (t, J = 5.9 Hz, 1H, OH), 2.40 (s, 3H, Me), 4.74 (d, J = 5.8 Hz, 2H, CH_2), 7.25 (d, J = 8.1 Hz, 2H, C_6H_4), 7.43 (d, J = 8.1 Hz, 2H, C_6H_4), 7.49 (d, J = 8.1 Hz, 2H, C_6H_4), 7.58 (d, J = 8.1 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.24, 65.31, 127.07, 127.28, 127.60, 129.65, 137.27, 138.07, 139.71, 140.74.

(4′-*N*,*N*-Dimethylaminobiphenyl-4-yl)methanol.[5q] ^1H NMR (400 MHz, $CDCl_3$): δ 1.63 (t, J = 6.0 Hz, 1H, OH), 3.00 (s, 6H, NMe), 4.72 (d, J = 5.9 Hz, 2H, CH_2), 6.81 (d, J = 8.8 Hz, 2H, C_6H_4), 7.40 (d, J = 8.2 Hz, 2H, C_6H_4), 7.51 (d, J = 8.9 Hz, 2H, C_6H_4), 7.56 (d, J = 8.2 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 40.72, 65.41, 112.92, 126.55, 127.65, 127.78, 128.92, 138.65, 140.84, 150.16.

2′-Methyl-*N*,*N*-dimethylbiphenyl-4-amine.[19] ^1H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, Me), 2.98 (s, 6H, NMe), 6.78 (d, J = 8.8 Hz, 2H, C_6H_4), 7.18–7.25 (m, 6H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.81, 40.74, 112.22, 125.85, 126.64, 130.07, 130.21, 130.40, 135.65, 142.14. 149.52.

***N*,*N*-Dimethylbiphenyl-4-amine.**[8c] ^1H NMR (400 MHz, $CDCl_3$): δ 2.99 (s, 6H, NMe), 6.80 (d, J = 8.8 Hz, 2H, C_6H_4), 7.23–7.27 (m, 1H, C_6H_5), 7.39 (t, J = 7.7 Hz, 2H, C_6H_5), 7.50 (d, J = 8.8 Hz, 2H, C_6H_4), 7.55 (d, J = 7.3 Hz, 2H, C_6H_5). ^{13}C NMR (101 MHz, $CDCl_3$): δ 40.73, 112.92, 126.12, 126.43, 127.84, 128.78, 129.41, 141.37, 150.12.

***N*,*N*-Dimethyl-(4-naphthalen-1-yl)aniline.**[20] ^1H NMR (400 MHz, $CDCl_3$): δ 2.90 (s, 6H, NMe), 6.74 (d, J = 8.6 Hz, 2H, C_6H_4), 7.30 (t, J = 8 Hz, Ar), 7.33–7.40 (m, 2H, Ar), 7.69 (d, J = 8.1 Hz, 1H, Ar), 7.77 (d, J = 7.9 Hz, 1H, Ar), 7.93 (d, J = 8.3 Hz, 1H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 40.72, 112.38, 125.61, 125.70, 125.82, 126.46, 126.87, 126.96, 128.33, 128.87, 130.93, 132.09, 134.06, 140.62, 149.91.

4′-Methyl-4-(trifluoromethyl)biphenyl.[8d] ^1H NMR (400 MHz, $CDCl_3$): 2.45 (s, 3H, Me), 7.31 (d, J = 8.0 Hz, 2H, C_6H_4), 7.53 (d, J = 8.1 Hz, 2H, C_6H_4), 7.70 (s, 4H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.26, 124.51 (q, J = 272.7 Hz), 125.80 (q, J = 4.0 Hz), 127.24, 127.30, 129.17 (q, J = 32.3 Hz), 129.85, 136.99, 138.30, 144.77.

2-*p*-Tolylpyridine.[17] ^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H, Me), 7.13–7.17 (m, 1H, Py), 7.26 (d, J = 7.8 Hz, 2H, C_6H_4), 7.66–7.67 (m, 2H, Py), 7.89 (d, J = 8.0 Hz, 2H, C_6H_4), 8.65–8.66 (m, 1H, Py). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.30, 120.25, 121.82, 126.83, 129.53, 136.68, 136.70, 138.96, 149.64, 157.52.

2-(4-Methoxyphenyl)pyridine.[3h] ^1H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H, OMe), 6.99 (d, J = 8.9 Hz, 2H, C_6H_4), 7.13–7.16 (m, 1H, Py), 7.63–7.70 (m, 2H, Py), 7.95 (d, J = 8.9 Hz, 2H, C_6H_4), 8.64 (d, J = 4.7 Hz, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.41, 114.20, 119.87, 121.48, 128.24, 132.11, 136.73, 149.61, 157.18, 160.54.

***N*,*N*-Dimethyl-(4-pyridin-2-yl)benzenamine.**[21] ^1H NMR (400 MHz, $CDCl_3$): δ 3.02 (s, 6H, NMe), 6.80 (d, J = 9.0 Hz, 2H, C_6H_4), 7.08–7.11 (m, 1H, Py), 7.62–7.69 (m, 2H, Py), 7.92 (d, J = 9.0 Hz, 2H, C_6H_4), 8.61–8.62 (m, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ 40.52, 112.38, 119.28, 120.72, 127.38, 127.84, 136.60, 149.53, 151.20, 157.73.

4-Methyl-2-*p*-tolylpyridine.[22] ^1H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H, Me), 2.39 (s, 3H, Me), 7.00 (d, J = 5.0 Hz, 1H, pyridine), 7.26 (d, J = 8.0 Hz, 2H, C_6H_4), 7.50 (s, 1H, pyridine), 7.87 (d, J = 8.2 Hz, 2H, C_6H_4), 8.52 (d, J = 5.0 Hz, 1H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.30, 21.34, 121.28, 122.93, 126.87, 129.50, 136.82, 138.84, 147.71, 149.43, 157.44.

3-*p*-Tolylpyridine.[23] ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 7.28 (b, 3H, Ar), 7.46 (b, 2H, Ar), 7.82 (b, 1H, Ar), 8.55 (b, 1H, Ar), 8.83 (b, 1H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.25, 123.63, 127.07, 129.91, 134.26, 135.00, 136.69, 138.14, 148.23, 148.25.

1,4-Di(*p*-methylphenyl)benzene.[8d] ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 6H, Me), 7.27 (d, J = 6.7 Hz, 4H, C_6H_4), 7.54 (d, J = 7.9 Hz, 4H, C_6H_4), 7.65 (s, 4H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.27, 127.01, 127.40, 129.67, 137.22, 138.03, 139.92.

1,3,5-Tris(*p*-methylphenyl)benzene.[5j] ^1H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 9H, Me), 7.32 (d, J = 7.9 Hz, 6H, C_6H_4), 7.63 (d, J = 8.1 Hz, 6H, C_6H_4), 7.77 (s, 3H, C_6H_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.27, 124.70, 127.32, 129.67, 137.39, 138.53, 142.30.

1-Methoxy-2-(*p*-toyl)benzoate.[8d] ^1H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H, Me), 3.79 (s, 3H, OMe), 6.96 (d, J = 8.4 Hz, 1H, C_6H_4), 6.98–7.04 (m, 1H, C_6H_4), 7.21 (d, J = 7.9 Hz, 2H, C_6H_4), 7.27–7.31 (m, 1H, C_6H_4), 7.42 (d, J = 8.1 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.34, 55.65, 111.30, 120.92, 128.49, 128.86, 129.53, 130.83, 130.92, 135.73, 136.72, 156.63.

***N*,*N*,2′,5′-Tetramethylbiphenyl-4-amine.**[24] ^1H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H, Me), 2.33 (s, 3H, Me), 2.99 (s, 6H, NMe_2), 6.78 (d, J = 8.8 Hz, 2H, C_6H_4), 7.00–7.07 (m, 2H, C_6H_3), 7.14 (d, J = 7.6 Hz, 1H, C_6H_3), 7.22 (d, J = 8.8 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.31, 21.08, 40.77, 112.23, 127.34, 130.04, 130.34, 130.82, 132.46, 135.21, 141.92, 149.46.

4-Methoxybiphenyl.[25] ^1H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H, OMe), 7.00 (d, J = 8.8 Hz, 2H, Ar), 7.30–7.35 (m, 1H, Ar), 7.42–7.46 (m, 2H, Ar), 7.54–7.59 (m, 4H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.47, 114.34, 126.79, 126.87, 128.29, 128.86, 133.92, 140.97, 159.29.

4′-Methoxy-4-(trifluoromethyl)biphenyl.[26] ^1H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H, OMe), 7.01 (d, J = 8.8 Hz, 2H, C_6H_4), 7.55 (d, J = 8.8 Hz, 2H, C_6H_4), 7.66 (s, 4H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.52, 114.58, 124.53 (q, J = 273 Hz),

125.82 (q, J = 4.0 Hz), 127.01, 128.50, 128.84 (q, J = 32.3 Hz), 132.33, 144.44, 160.00.

Dimethyl-(4′-trifluoromethylbiphenyl-4-yl)-amine.[27] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02 (s, 6H, NMe), 6.81 (d, J = 8.8 Hz, 2H, C_6H_4), 7.53 (d, J = 8.9 Hz, 2H, C_6H_4), 7.64 (s, 4H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.27, 124.52 (q, J = 272.9 Hz), 125.81(q, J = 3.8 Hz), 127.25, 127.31, 129.19 (q, J = 32.5 Hz), 129.85, 137.01, 138.30, 144.79.

(4′-Methylbiphenyl-4-yl)(phenyl)methanone.[28] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, Me), 7.29 (d, J = 7.9 Hz, 2H, C_6H_4), 7.50 (t, J = 7.5 Hz, 2H, Ph), 7.55 (d, J = 8.1 Hz, 2H, Ph), 7.59 (t, J = 7.4 Hz, 1H, Ph), 7.69 (d, J = 8.4 Hz, 2H, C_6H_4), 7.83 (d, J = 8.4 Hz, 2H, C_6H_4), 7.88 (d, J = 8.3 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.31, 126.84, 127.27, 128.43, 129.84, 130.12, 130.88, 132.45, 136.09, 137.21, 137.99, 138.32, 145.33, 196.49.

(4′-Methoxybiphenyl-4-yl)(phenyl)methanone.[29] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H, OMe), 7.02 (d, J = 8.8 Hz, 2H, C_6H_4), 7.50 (t, J = 7.6 Hz, 2H, C_6H_5), 7.58–7.62 (m, 3H, C_6H_5 + C_6H_4), 7.67 (d, J = 8.3 Hz, 2H, C_6H_4), 7.82–7.84 (m, 2H, C_6H_5), 7.88 (d, J = 8.3 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.52, 114.55, 126.51, 128.42, 128.53, 130.11, 130.94, 132.42, 132.47, 135.71, 138.00, 144.98, 160.01, 196.48.

Ethyl 4′-methylbiphenyl-4-carboxylate.[30] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, J = 7.1 Hz, 3H, Et), 2.41 (s, 3H, Me), 4.40 (q, J = 7.1 Hz, 2H, Et), 7.28 (d, J = 7.9 Hz, 2H, C_6H_4), 7.53 (d, J = 8.1 Hz, 2H, C_6H_4), 7.65 (d, J = 8.5 Hz, 2H, C_6H_4), 8.10 (d, J = 8.6 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.51, 21.30, 61.06, 126.88, 127.24, 129.06, 129.77, 130.17, 137.27, 138.20, 145.59, 166.71.

Ethyl 4′-methoxybiphenyl-4-carboxylate.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, J = 7.1 Hz, 3H, Et), 3.86 (s, 3H, OMe), 4.40 (q, J = 7.1 Hz, 2H, Et), 7.00 (d, J = 8.8 Hz, 2H, C_6H_4), 7.57 (d, J = 8.8 Hz, 2H, C_6H_4), 7.62 (d, J = 8.5 Hz, 2H, C_6H_4), 8.09 (d, J = 8.5 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.47, 55.45, 61.00, 114.45, 126.51, 128.44, 128.67, 130.16, 132.51, 145.17, 159.90, 166.67.

***N*,*N*-Diethyl-4′-methylbiphenyl-4-carboxamide.**[8c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (b, 6H, Et), 2.40 (s, 3H, Me), 3.32 (b, 2H, Et), 3.57 (b, 2H, Et), 7.26 (d, J = 7.9 Hz, 2H, C_6H_4), 7.44 (d, J = 8.5 Hz, 2H, C_6H_4), 7.50 (d, J = 8.1 Hz, 2H, C_6H_4), 7.60 (d, J = 8.5 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.06, 14.38, 39.45, 43.49, 55.47, 114.42, 126.71, 126.98, 128.26, 132.99, 135.55, 141.72, 159.57, 171.34.

***N*,*N*-Diethyl-4′-Methoxybiphenyl-4-carboxamide.**[32] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (b, 6H, Et), 3.33 (b, 2H, Et), 3.55 (b, 2H, Et), 3.85 (s, 3H, OMe), 6.98 (d, J = 8.8 Hz, 2H, C_6H_4), 7.42 (d, J = 8.0 Hz, 2H, C_6H_4), 7.53 (d, J = 8.9 Hz, 2H, C_6H_4), 7.57 (d, J = 8.1 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.08, 14.33, 21.21, 39.34, 43.40, 126.93, 126.97, 127.04, 129.67, 135.88, 137.60, 142.03, 171.29.

4′-Methylbiphenyl-4-carbonitrile.[33] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H, Me), 7.29 (d, J = 8 Hz, 2H, C_6H_4), 7.49 (d, J = 8 Hz, 2H, C_6H_4), 7.67 (d, J = 8.6 Hz, 2H, C_6H_4), 7.71 (d, J = 8.6 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.33, 110.66, 119.19, 127.19, 127.60, 129.97, 132.71, 136.40, 138.89, 145.74.

(4′-Methylbiphenyl-2-yl)(phenyl)methanone.[34] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3H, Me), 7.01 (d, J = 7.8 Hz, 2H, C_6H_4), 7.15 (d, J = 8.1 Hz, 2H, C_6H_4), 7.29 (t, J = 7.7 Hz, 2H, Ph), 7.39–7.50 (m, 4H, Ar), 7.54–7.59 (m, 1H, Ar), 7.66–7.69 (m, 2H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.28, 126.88, 128.22, 128.82, 128.97, 129.14, 130.11, 130.23, 130.41, 132.92, 137.17, 137.42, 137.56, 139.03, 141.30, 198.96.

(4′-Methoxybiphenyl-2-yl)(phenyl)methanone.[35] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69 (s, 3H, OMe), 6.72 (d, J = 8.8 Hz, 2H, C_6H_4), 7.17 (d, J = 8.8 Hz, 2H, C_6H_4), 7.26 (t, J = 7.6 Hz, 2H, C_6H_5), 7.36–7.49 (m, 4H, Ar), 7.50–7.56 (m, 1H, Ar), 7.63–7.65 (m, 2H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.23, 113.85, 126.71, 128.18, 128.74, 129.97, 130.04, 130.19, 130.37, 132.73, 132.91, 137.46, 138.93, 140.77, 159.03, 199.05.

4′-Methylbiphenyl-2-carbonitrile.[5q] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H, Me), 7.30 (d, J = 8.1 Hz, 2H, C_6H_4), 7.42 (td, J = 1.3, 7.6 Hz, 1H, C_6H_4), 7.46 (d, J = 8.1 Hz, 2H, C_6H_4), 7.49–7.52 (m, 1H, C_6H_4), 7.63 (td, J = 1.4, 7.7 Hz, 1H, C_6H_4), 7.74–7.76 (m, 1H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.38, 111.35, 119.00, 127.40, 128.75, 129.58, 130.11, 132.88, 133.85, 135.41, 138.83, 146.68.

4′-Methoxy-2-methylbiphenyl.[36] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, Me), 3.91 (s, 3H, OMe), 7.02 (d, J = 8.7 Hz, 2H, C_6H_4), 7.29–7.33 (m, 6H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.66, 55.35, 113.61, 125.87, 127.09, 130.02, 130.36, 130.41, 134.49, 135.57, 141.67, 158.64.

(2′-Methylbiphenyl-4-yl)(phenyl)methanone.[8c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, Me), 7.26–7.30 (m, 4H, Ar), 7.45 (d, J = 8.3 Hz, 2H, Ar), 7.51 (t, J = 7.5 Hz, 2H, Ar), 7.61 (t, J = 7.4 Hz, 1H, Ar), 7.85–7.88 (m, 4H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.59, 126.09, 128.02, 128.46, 129.33, 129.73, 130.17, 130.18, 130.69, 132.52, 135.38, 136.12, 137.89, 140.99, 146.52, 196.63.

Ethyl 2′-methylbiphenyl-4-carboxylate.[17] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (t, J = 7.1 Hz, 3H, Et), 2.26 (s, 3H, Me), 4.41 (q, J = 7.1 Hz, 2H, Et), 7.20–7.29 (m, 4H, C_6H_4), 7.39 (d, J = 8.5 Hz, 2H, C_6H_4), 8.09 (d, J = 8.5 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.51, 20.51, 61.09, 126.03, 127.94, 129.06, 129.35, 129.50, 129.66, 130.61, 135.30, 141.03, 146.76, 166.70.

***N*,*N*-Diethyl-2′-methylbiphenyl-4-carboxamide.**[8c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (b, 3H, Et), 1.27 (b, 3H, Et), 2.27 (s, 3H, Me), 3.35 (b, 2H, Et), 3.58 (b, 2H, Et), 7.21–7.28 (m, 4H, C_6H_4), 7.35 (d, J = 8.2 Hz, 2H, C_6H_4), 7.43 (d, J = 8.2 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.04, 14.40, 20.55, 39.34, 43.46, 125.93, 126.28, 127.63, 127.93, 128.78, 129.31, 129.79, 130.52, 135.40, 135.74, 141.23, 142.94, 171.34.

2-*p*-Tolyl-nicotinonitrile.[37] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, Me), 7.33–7.36 (m, 3H, C_6H_4 + Py), 7.84 (d, J = 8.2 Hz, 2H, C_6H_4), 8.05 (dd, J = 1.7, 7.9 Hz, 1H, Py), 8.85 (dd, J = 1.7, 4.8 Hz, 1H, Py). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.54, 107.35, 117.96, 121.36, 128.92, 129.55, 134.51, 140.67, 141.95, 152.73, 161.19.

2-Methoxy-6-*p*-tolylpyridine.[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, Me), 4.03 (s, 3H, OMe), 6.66 (d, J = 8.2 Hz, 1H, Py), 7.26 (d, J = 7.3 Hz, 2H, C_6H_4), 7.31 (d, J = 7.4 Hz, 1H, Py), 7.60 (dd, J = 7.5, 8.1 Hz, 1H, Py), 7.94 (d, J = 8.2 Hz, 2H, C_6H_4).

^{13}C NMR (101 MHz, $CDCl_3$): δ 21.42, 53.31, 108.93, 112.55, 126.71, 129.45, 136.45, 138.93, 139.23, 154.85, 163.80.

2-(4-Methylphenyl)-4-methylquinoline.[39] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, Me), 2.76 (s, 3H, Me), 7.33 (d, J = 7.9 Hz, 2H, C_6H_4), 7.51–7.55 (m, 1H, quinolyl), 7.69–7.73 (m, 2H, quinolyl), 7.98–8.00 (m, 1H, quinolyl), 8.06 (d, J = 8.2 Hz, 2H, C_6H_4), 8.21–8.13 (m, 1H, quinolyl). ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.16, 21.48, 119.74, 123.73, 125.96, 127.33, 127.54, 129.38, 129.65, 130.36, 137.15, 139.37, 144.76, 148.30, 157.18.

2-(4-Methoxyphenyl)-4-methylquinoline.[40] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (s, 3H, Me), 3.89 (s, 3H, OMe), 7.04 (d, J = 8.8 Hz, 2H, C_6H_4), 7.50–7.54 (m, 1H, quinolyl), 7.68–7.72 (m, 2H, quinolyl), 7.97 (d, J = 8.3 Hz, 1H, quinolyl), 8.12–8.15 (m, 3H, C_6H_4 + quinolyl). ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.17, 55.52, 114.28, 119.42, 123.72, 125.79, 127.13, 128.96, 129.37, 130.19, 132.51, 144.70, 148.27, 156.75, 160.82.

(4′-(Trifluoromethyl)biphenyl-4-yl)(phenyl)methanone.[41] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (t, J = 7.6 Hz, 2H, Ph), 7.62 (t, J = 7.4 Hz, 1H, Ph), 7.72 (d, J = 8.4 Hz, 2H, C_6H_4), 7.75 (s, 4H, C_6H_4), 7.83–7.86 (m, 2H, Ph), 7.92 (d, J = 8.4 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 124.29 (q, J = 273.7 Hz), 126.06 (q, J = 4.0 Hz), 127.32, 127.77, 128.52, 130.16, 130.33 (q, J = 32.3 Hz), 130.93, 132.71, 137.27, 137.65 143.66, 143.72, 196.27.

Ethyl 4′-(trifluoromethyl)biphenyl-4-carboxylate.[42] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, J = 7.1 Hz, 3H, Et), 4.42 (q, J = 7.1 Hz, 2H, Et), 7.66 (d, J = 8.5 Hz, 2H, C_6H_4), 7.72 (s, 4H, C_6H_4), 8.14 (d, J = 8.5 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.45, 61.26, 124.28 (q, J = 272.7 Hz), 125.98 (q, J = 4.0 Hz), 127.32, 127.73, 130.23 (q, J = 32.3 Hz), 130.28, 130.35, 143.68, 144.05, 166.38.

***N*,*N*-Diethyl-4′-(trifluoromethyl)biphenyl-4-carboxamide.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (b, 3H, Et), 1.26 (b, 3H, Et), 3.32 (b, 2H, Et), 3.57 (b, 2H, Et), 7.48 (d, J = 8.3 Hz, 2H, C_6H_4), 7.62 (d, J = 8.3 Hz, 2H, C_6H_4), 7.70 (s, 4H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.06, 14.47, 39.48, 43.46, 124.35 (q, J = 272.7 Hz), 125.95 (q, J = 4.0 Hz), 127.19, 127.46, 127.57, 129.88 (q, J = 32.3 Hz), 137.21, 140.63, 144.04, 170.93. HR-MS (EI): m/z = 321.1335, calcd for $C_{18}H_{18}F_3NO$: 321.1340.

(4′-(Trifluoromethyl)biphenyl-2-yl)(phenyl)methanone.[43] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.8 Hz, 2H, Ar), 7.38 (d, J = 8.0 Hz, 2H, C_6H_4), 7.44–7.55 (m, 6H, Ar), 7.59–7.63 (m, 1H, Ar), 7.66–7.68 (m, 2H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ 124.19 (q, J = 272.7 Hz), 125.32 (q, J = 4.0 Hz), 127.86, 128.43, 129.14, 129.41, 129.53 (q, J = 32.3 Hz), 130.07, 130.28, 130.71, 133.31, 137.41, 139.08, 140.03, 144.02, 198.25.

2-(4-(Trifluoromethyl)phenyl)furan.[8c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 6.77 (d, J = 3.4 Hz, 1H, furyl), 7.52 (d, J = 1.3 Hz, 1H, furyl), 7.63 (d, J = 8.1 Hz, 2H, C_6H_4), 7.76 (d, J = 8.1 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 107.10, 112.10, 123.88, 124.32 (q, J = 272.7 Hz), 125.83 (q, J = 4.0 Hz), 129.05 (q, J = 32.3 Hz), 134.08, 143.22, 152.63.

(4-(Furan-2-yl)phenyl)(phenyl)methanone.[8c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.53 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 6.82 (d, J = 3.4 Hz, 1H, furyl), 7.50 (t, J = 7.5 Hz, 2H, Ph), 7.54 (d, J = 1.2 Hz, 1H, furyl), 7.60 (t, J = 7.4 Hz, 1H, Ph), 7.77 (d, J = 8.6 Hz, 2H, C_6H_4), 7.78–7.82 (m, 2H, Ph), 7.85 (d, J = 8.6 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 107.51, 112.23, 123.46, 128.44, 130.07, 130.98, 132.46, 134.56, 136.01, 137.91, 143.39, 153.02, 196.18.

Ethyl 4-(furan-2-yl)benzoate.[8c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (t, J = 7.1 Hz, 3H, Et), 4.38 (q, J = 7.1 Hz, 2H, Et), 6.51 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 6.79 (d, J = 3.4 Hz, 1H, furyl), 7.52 (d, J = 1.7 Hz, 1H, furyl), 7.72 (d, J = 8.6 Hz, 2H, C_6H_4), 8.06 (d, J = 8.6 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.50, 61.10, 107.30, 112.15, 123.50, 129.03, 130.21, 134.80, 143.23, 153.11, 166.49.

***N*,*N*-Diethyl-4-(furan-2-yl)carboxamide.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (b, 3H, Et), 1.24 (b, 3H, Et), 3.28 (b, 2H, Et), 3.54 (b, 2H, Et), 6.47 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 6.69 (d, J = 3.4 Hz, 1H, furyl), 7.39 (d, J = 8.4 Hz, 2H, C_6H_4), 7.47 (d, J = 1.2 Hz, 1H, furyl), 7.68 (d, J = 8.4 Hz, 2H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.02, 14.32, 39.41, 43.43, 105.95, 111.90, 123.72, 126.98, 131.65, 135.97, 142.60, 153.30, 171.06. HR-MS (EI): m/z = 243.1252, calcd for $C_{15}H_{17}NO_2$: 243.1259.

2-Furan-2-yl-benzonitrile. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (dd, J = 1.8, 3.5 Hz, 1H, furyl), 7.31 (d, J = 3.1 Hz, 1H, furyl), 7.34 (dd, J = 1.1, 7.7 Hz, 1H, C_6H_4), 7.56 (d, J = 1.7 Hz, 1H, furyl), 7.62 (td, J = 1.3, 8.1 Hz, 1H, C_6H_4), 7.70 (dd, J = 1.0, 7.8 Hz, 1H, C_6H_4), 7.89 (d, J = 8.1 Hz, 1H, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 106.96, 110.58, 112.40, 119.16, 126.05, 127.24, 133.08, 133.35, 134.28, 143.46, 149.88. HR-MS (EI): m/z = 169.0520, calcd for $C_{11}H_7NO$: 169.0528.

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