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The coupling reactions of aryl halides and phenols catalyzed by palladium and MOP-type ligands

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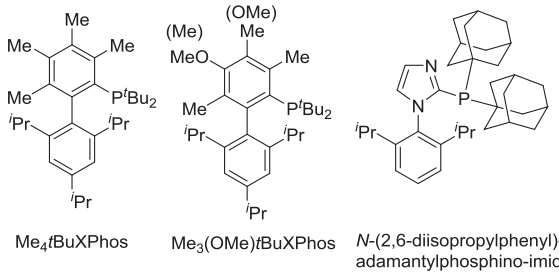
ABSTRACT

Palladium-catalyzed coupling reactions of aryl halides and phenols are described employing the bulky and electron-rich MOP-type ligands. When K_3PO_4 was used as base and toluene as solvent, the catalyst system exhibited high efficiency for the coupling reaction of the activated aryl halides. When NaH was used as base and *o*-xylene as solvent, unactivated aryl halides can be used as substrates.

1. Introduction

Diaryl ethers are common structural motifs in numerous natural products and biologically active compounds.[1] Traditionally, these ethers are prepared by the reaction of aryl halides with sodium or potassium aryl oxides promoted by copper reagents.[2] However, this protocol is often inhibited by high temperatures, stoichiometric amounts of copper, limited substrate scope, and poor functional group tolerance. The transition metal (Cu, Pd and Fe) catalyzed coupling reactions of aryl halides and phenols provide effective access to diaryl ethers.[3] In general, compared to copper catalysts, palladium catalysts are tuned more easily for activating aryl C–X bonds especially for aryl chlorides, and conduct the synthesis of diaryl ethers under relatively mild reaction conditions.[4] Hence, a lot of effort has been devoted to developing efficient palladium catalysts for the transformation.[5]

Using electron-rich, sterically bulky phosphines[6] or *N*-heterocyclic carbene ligands[7] is crucial to realize the palladium catalyzed the cross coupling of electron-deficient, electron-neutral, and electron-rich aryl halides with a variety of phenols. Despite these advances, poor conversions are observed for the coupling reactions of unactivated aryl halides and phenols without an *ortho*-substituent, and electron-deficient phenols were poor substrates.[8] To overcome these limitations, the more sterically hindered aryl dialkyl phosphines (Fig. 1) were synthesized and utilized in the formation of aryl C–O bonds.[9] Although these ligands succeeded in some difficult substrates, the high cost and difficult synthesis of these ligands would potentially prevent the utilization of these catalysts.[9c] In the coupling reaction, base and solvent are requisite components in the catalyst system and influence the catalytic activity.[10] Tuning of the base and solvent in the catalyst system may therefore, provide a readily accessible protocol for the difficult substrates.



Me$_4$*t*BuXPhos Me$_3$(OMe)*t*BuXPhos *N*-(2,6-diisopropylphenyl)-2-di-1-adamantylphosphino-imidazole

Fig. 1. Structures of sterically hindered phosphine ligands utilized in the palladium catalyzed formation of aryl C–O bonds.

The MOP-type ligands (2-(dialkyl-phosphino)-2′-alkoxy-1,1′-binaphthyls) that are bulky monodentate phosphines with a binaphthyl skeleton and a tunable alkoxy group at the adjacent position of phosphorus atom, have showed high effectiveness for

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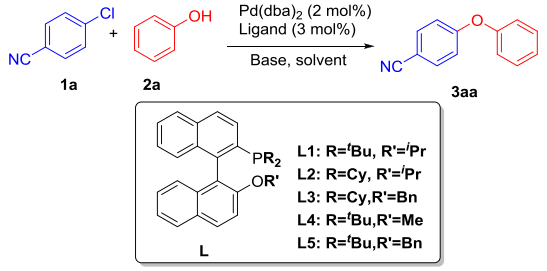
the palladium catalyzed formation of aryl C–N bonds.[11] Herein, we report the efficiency of the MOP-type ligands in the palladium-catalyzed coupling reaction of aryl halides and phenols and the effect of solvents and base in the catalyst system.

2. Results and discussion

We initially chose the coupling reaction of *p*-chlorobenzonitrile (**1a**), an activated aryl chloride, and phenol as the model reaction to examine the use of the MOP-type ligands in the palladium catalyzed formation of aryl C–O bonds. When di-*tert*-butyl(2′-isopropoxy-[1,1′-binaphthalen]-2-yl) phosphane (**L1**) was used as ligand with NaH as base and toluene as solvent, the desired product, 4-phenoxybenzonitrile (**3aa**), was obtained in only 38% yield, and 4,4′-di-CN-biphenyl was formed as the main byproduct (Table 1, entry 1). Replacing NaH with Cs_2CO_3 or K_2CO_3 increased the yield of the diaryl ether (**3aa**) to 95% (entries 2 and 3). When Na_2CO_3 was used as base, a decreased conversion of *p*-chlorobenzonitrile was observed (entry 4). To our surprise, nearly exclusive formation of the diaryl ether (**3aa**) was observed when K_3PO_4 was used as base (entry 5). Using an ethereal solvent such as, THF and DME (dimethoxyethane), resulted in a slightly decreased yield of **3aa**. When $PdCl_2(CH_3CN)_2$ was used as precatalyst, the high activity of the catalyst system remained (entry 9).

Table 1
Optimization of reaction conditions for coupling reaction of *p*-chlorobenzonitrile (**1a**) with phenol (**2a**)[a]



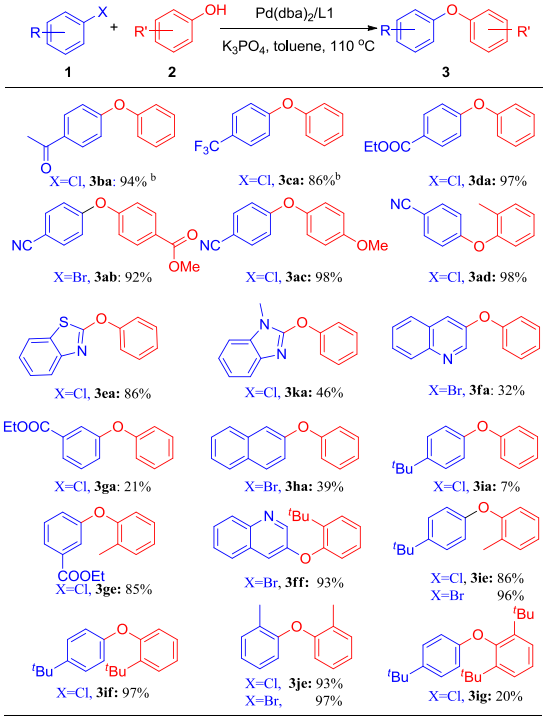
Entry	Ligand	Base	Solvent	Conv. (%)	Yield[b] (%)
1	L1	NaH	Toluene	>99	38
2	L1	Cs_2CO_3	Toluene	>99	95
3	L1	K_2CO_3	Toluene	>99	96
4	L1	Na_2CO_3	Toluene	85	69
5	L1	K_3PO_4	Toluene	>99	>99
6	L1	K_3PO_4	THF[c]	92	84
7	L1	K_3PO_4	Dioxane[d]	>99	72
8	L1	K_3PO_4	DME[e]	>99	82
9[f]	L1	K_3PO_4	Toluene	>99	>99
10	L2	K_3PO_4	Toluene	44	29
11	L3	K_3PO_4	Toluene	<1	<1
12	L4	K_3PO_4	Toluene	>99	>99
13	L5	K_3PO_4	Toluene	>99	>99

[a] *p*-Chlorobenzonitrile (**1a**) (1.0 mmol), phenol (**2a**) (1.2 mmol), $Pd(dba)_2$ (2 mol %), ligand (3 mol %), base (2.0 mmol), solvent (2.5 mL), 110 °C, 18 h.
[b] Yields determined by GC analysis.
[c] Reaction temperature: 65 °C.
[d] Reaction temperature: 101 °C.
[e] Reaction temperature: 85 °C.
[f] $PdCl_2(CH_3CN)_2$ (2 mol %).

Next, the structural influence of ligands on the catalytic activity was explored. The substituents on the phosphorus atom of the ligands significantly influenced the activity of the catalyst. When the ligand with a dicyclohexylphosphino group (**L2** or **L3**) was used, the catalytic activity decreased greatly (Table 1, entries 10 and 11), while the ligands with bulky di *tert*-butylphosphino group were highly efficient for the formation of aryl C–O bonds (entries 5 and 12, 13). The sterics of the alkyl substituents on the oxygen atom did not appear to affect the catalytic activity. When the alkyl group was isopropyl (**L1**), methyl (**L4**), or benzyl (**L5**), high conversions and yields of the diaryl ether were obtained. This result is in contrast to palladium-catalyzed formation of aryl C–N and C–C bonds in which increasing the steric profile of the dialkylphosphino group or alkoxy group led to an increase in catalyst activity.[11] This difference may be attributed to the absence of hemilabile coordination of the oxygen to the palladium center in the rate-determining step of the coupling of aryl halides and phenols.

Under the optimized conditions in which $Pd(dba)_2$ and **L1** were used as the catalyst, K_3PO_4 as the base, and toluene as the solvent, the scope and limitations of the catalytic system were explored. As shown in Table 2, the activated aryl halides including the chlorides and the bromides were coupled with phenols to generate the desired diaryl ether (**3**) in excellent yield. Even the coupling of the electron-deficient methyl 4-hydroxybenzoate (**2b**) with *p*-bromobenzonitrile occurred in 92% yield. The bulky *o*-methyl phenol was coupled with chlorobenzonitrile (**1a**) to generate the corresponding diaryl ether (**3ad**) in 98% yield. Moreover, the catalytic system showed the good tolerance for functional groups such as ketones, esters, and heterocycles. Reaction of 2-chlorobenzo[*d*]thiazole (**1e**) proceeded smoothly to give the desired product (**3ea**) in 86% yield. However, the coupling reaction provided low yields for electron-neutral aryl halides or aryl halides with electron-withdrawing groups at the *meta*-position. Coupling of ethyl 3-chlorobenzoate (**1g**) with phenol gave the diaryl ether (**3ga**) in 21% yield, while the diaryl ether (**3da**) was obtained in 97% yield when ethyl 4-chlorobenzoate (**1d**) was coupled. The results are similar with that obtained from the reported palladium catalyzed the formation of aryl C–O bonds.[6,8] But the existence of *ortho*-substituent in the substrates, either aryl halides or phenols, increased the yield of diaryl ether significantly regardless of the electronic nature of the aryl halide. Ethyl 3-(*o*-tolyloxy)benzoate (**3ge**) was obtained in 85% yield in the reaction of ethyl 3-chlorobenzoate (**1g**) with *o*-methyl

Table 2
Coupling reactions of aryl halides (**1**) with phenols (**2**) catalyzed by $Pd(dba)_2$/**L1** using K_3PO_4 as base and toluene as solvent[a]

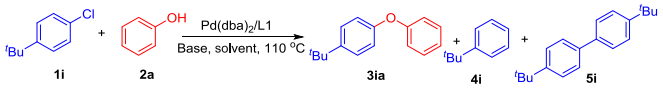


[a] Aryl halide (**1**) (1.0 mmol), phenol (**2**) (1.2 mmol), $Pd(dba)_2$ (2 mol%), **L1** (3 mol%), K_3PO_4 (2.0 mmol), toluene (2.5 mL), 18 h, and isolated yield was gave.
[b] $Pd(dba)_2$ (1.0 mol%), Ligand (1.5 mol%).

phenol. The coupling of *p*-*tert*-butyl chlorobenzene (**1i**) with *o*-*tert*-butyl phenol afforded the diaryl ether (**3if**) in 97% yield. These results may be attributed to the larger steric profile of the substrate, which promotes the reductive elimination step of the C–O bonds formation.[6b] However, the coupling yield was decreased in the case of highly hindered substrate (**3ig**).

The unactivated aryl halides without *ortho*-substituents were always limited in the palladium catalyzed coupling reactions with phenols, which do not possess *ortho*-substituents, even though electron-rich, sterically bulky phosphines were used as ligands. Increasing the steric hindrance of ligands has been used to solve the problem, but the high cost and difficulty in the synthesis of these ligands would potentially prevent the utilization of these catalysts.[9] We focused on studying the effect of solvent and base to improve the catalytic activity in some of more difficult coupling reactions (Table 3). The coupling reaction of *p*-*tert*-butyl chlorobenzene (**1i**) with phenol was chosen as the model reaction. When K_3PO_4 was used as base and toluene as solvent, 29% of *p*-*tert*-butyl chlorobenzene (**1i**) was consumed, but the desired diaryl ether (**3ia**) was obtained in 7% yield (entry 1). Most of the aryl chloride was reduced to *tert*-butyl benzene (**4i**). This indicated that electron-neutral aryl group decreased the electrophilicity of the aryl palladium complex to inhibit the formation the important intermediate, aryl (aryloxy) palladium complex. Using the stronger base, Cs_2CO_3, increased the yield of the diaryl ether (**3ia**) to 21%, but the byproduct (**4i**) was also formed in 30% yield (entry 2). When NaH was used as base, the yield of **3ia** was increased to 77%, and 4,4′-di-*tert*-butyl-biphenyl (**5i**) was generated as the main byproduct (entry 3). *t*-BuONa was inferior for the coupling reaction (entry 4). Therefore, NaH was used as base for the further screening of solvent. Gratifyingly, the desired product (**3ia**) was obtained in 90% yield when *o*-xylene was used as solvent and the reaction temperature kept at 110 °C (entry 5). However, replacing *o*-xylene with *p*-xylene or *m*-xylene decreased the yield of **3ia**, and the byproduct, 4,4′-di-*tert*-butyl-biphenyl (**5i**) was formed in about 40% yield. These results indicate that the structure of aromatic solvents significantly affect the activity of the catalyst system. In addition, a remarkable decrease of yield was observed when *o*-ethyltoluene was used as solvent. Therefore, the optimized condition for the electron neutral aryl chloride was identified as: Pd(dba)$_2$/**L1** as catalyst, NaH as base and *o*-xylene as solvent at 110 °C.

Table 3
Optimization of reaction conditions for coupling reaction of *p*-*tert*-butyl chlorobenzene (**1i**) with phenol (**2a**)[a]

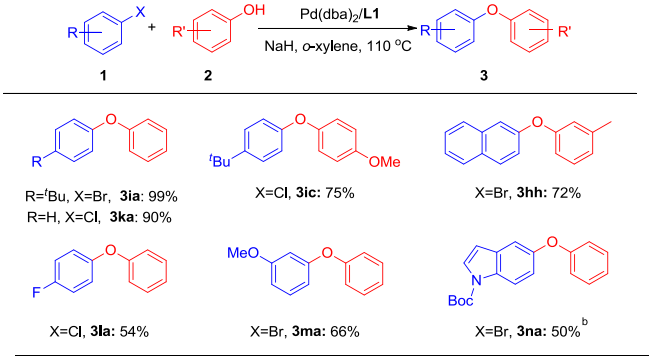


Entry	Solvent	Base	Conv. (%)	Yield[b] (%)		
				3ia	**4i**	**5i**
1	Toluene	K_3PO_4[c]	29	7	21	<1
2	Toluene	Cs_2CO_3[c]	55	21	30	<1
3	Toluene	NaH[d]	>99	77	6	12
4	Toluene	*t*-BuONa[d]	22	18	<1	2
5	*o*-Xylene	NaH[d]	>99	90	1	6
6	*p*-Xylene	NaH[d]	>99	50	8	41
7	*m*-Xylene	NaH[d]	>99	52	7	43
8	*o*-Ethyltoluene	NaH[d]	84	8	64	8

[a] *p*-*tert*-Butyl chlorobenzene (**1i**) (1.0 mmol), phenol (**2a**) (1.2 mmol), Pd(dba)$_2$ (2 mol %), **L1** (3 mol %), solvent (2.5 mL), 18 h 110 °C.
[b] Yields determined by GC analysis.
[c] Base (2.0 mmol).
[d] Base (1.2 mmol).

The scope and limitations of the catalyst system with NaH as base and *o*-xylene as solvent were then explored. The new catalyst system showed good activity for the coupling reaction of difficult substrates, such as electron neutral aryl halides without substituents at *ortho*-position. Coupling reaction of *p*-*tert*-butyl bromobenzene with phenol occurred in quantitative yield. 2-(*m*-Tolyloxy)naphthalene (**3hh**) was generated in 72% from the coupling reaction of 2-bromonaphthalene (**1h**) with phenol. Aryl bromide with *meta*-electron donating group was coupled with phenol to give the corresponding ether (**3ma**) in moderate yield. In addition, the electron-rich heterocyclic substrate was tolerated in the catalytic system. *N*-Boc-5-bromo-indol (**1n**) was coupled with phenol in 50% yield. Regretably, in the new catalyst system, the reaction of 4-bromo-*N*,*N*-dimethylaniline with phenol afford the corresponding ether in only 13% yield, and N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[1,1′-biphenyl]-4,4′-diamine was formed as the main byproduct (Table 4).

Table 4
Coupling reactions of aryl halides (**1**) with phenols (**2**) catalyzed Pd(dba)$_2$/**L1** using NaH as base and *o*-xylene as solvent[a]



[a] Aryl halide (**1**) (1.0 mmol), phenol (**2**) (1.2 mmol), Pd(dba)$_2$ (2 mol%), **L1** (3 mol%), NaH (1.2 mmol), *o*-xylene (2.5 mL), 110°C, 18 h and isolated yield was gave.
[b] Pd(dba)$_2$ (4.0 mol%), **L1** (6.0 mol%).

3. Conclusion

In summary, the bulky MOP-type ligands were found to be efficient ligands for the Pd-catalyzed coupling reaction of aryl halide and various phenols. Using K_3PO_4 as base and toluene as solvent, the catalyst, Pd(dba)$_2$/**L1**, exhibited high efficiency for the coupling reaction of the activated aryl halides and the substrates (aryl halides and/or phenols) with the *ortho*-substituents. This mild catalytic protocol showed good functional group tolerance. The unactivated aryl halides without substituents at *ortho*-position were effectively coupled when NaH was used as base and *o*-xylene as solvent.

4. Experimental

4.1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. The MOP-type ligands were prepared according to methods described in the literature.[11a] Solvent was freshly distilled from sodium and benzophenone under nitrogen atmosphere. Flash column chromatography was performed on silica gel (300–400 mesh). ^{1}H NMR spectra were recorded on 400 MHz spectrometer. Chemical shifts were reported on the δ (δ) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Coupling constants (J) were reported in hertz (Hz) and refer to apparent peak multiplications. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrometer ($CDCl_3$: 77.16 ppm).

4.2. Typical procedure for the palladium-catalyzed the coupling reactions of aryl halides and phenols with K_3PO_4 as base and toluene as solvent

An oven-dried Schlenk tube was evacuated and backfilled with nitrogen. The Schlenk tube was charged with $Pd(bda)_2$ (11.5 mg, 0.02 mmol), L1 (13.7 mg, 0.03 mmol), K_3PO_4 (424.5 mg, 2 mmol), and toluene (1.0 mL). After stirring for 15 min, the solution of aryl halide (1.0 mmol) and phenol (1.2 mmol) in toluene (1.5 mL) was added. The septum was replaced with an inside reflux condenser, and then the reaction mixture was stirred for 18 h at 110 °C. Then, the reaction mixture was cooled to room temperature and quenched with water (5 mL). After separating the organic phase, the aqueous phase was extracted with ethyl acetate (3 mL×3), and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was concentrated under reduced pressure, and then the crude material was purified by column chromatography on silica gel.

*4.2.1. 4-Phenoxybenzonitrile (**3aa**).*[12] Yellow solid (195.1 mg, yield: 99%), mp: 42–46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99–7.02 (m, 2H), 7.06–7.08 (m, 2H), 7.23 (t, J=7.2 Hz, 1H), 7.40–7.44 (m, 2H), 7.58–7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 105.7, 117.9, 118.9, 120.4, 125.2, 130.2, 134.1, 154.8, 161.6.

*4.2.2. 4-Phenoxyacetophenone (**3ba**).*[13] Yellow solid (202.1 mg, yield: 94%), mp: 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.57 (s, 3H), 6.99–7.01 (m, 2H), 7.06–7.08 (m, 2H), 7.18–7.22 (m, 1H), 7.38–7.42 (m, 2H), 7.93–7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.7, 117.4, 120.3, 124.7, 129.7, 130.8, 132.0, 155.6, 162.1, 196.9.

*4.2.3. 1-Phenoxy-4-(trifluoromethyl)benzene (**3ca**).*[14] Colorless oil (203.1 mg, yield: 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04–7.07 (m, 4H), 7.18–7.22 (m, 1H), 7.38–7.42 (m, 2H), 7.57 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.0, 120.1, 124.6, 124.8, 125.7, 127.2, 130.2, 155.9, 160.7.

*4.2.4. Ethyl 4-phenoxybenzoate (**3da**).*[3d] Pale yellow oil (234.3 mg, yield: 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, J=7.2 Hz, 3H), 4.36 (q, J=7.2 Hz, 2H), 6.97–7.00 (m, 2H), 7.04–7.08 (m, 2H), 7.16–7.21 (m, 1H), 7.37–7.41 (m, 2H), 7.99–8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 61.0, 117.4, 120.1, 124.5, 125.0, 130.1, 131.7, 155.8, 161.8, 166.2.

*4.2.5. Methyl 4-(4-cyanophenoxy)benzoate (**3ab**).*[15] Colorless oil (228.8 mg, yield: 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.07–7.10 (m, 4H), 7.64–7.67 (m, 2H), 8.06–8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.4, 107.2, 118.6, 119.2, 119.3, 126.6, 132.1, 134.5, 159.3, 160.3, 166.3.

*4.2.6. 4-(4-Methoxyphenoxy)benzonitrile (**3ac**).*[9d] Pale yellow oil (221.9 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.94–6.99 (m, 4H), 7.01–7.05 (m, 2H), 7.58–7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8, 105.4, 115.4, 117.3, 119.1, 122.0, 134.2, 148.0, 157.1, 162.6.

*4.2.7. 4-(o-Tolyloxy)benzonitrile (**3ad**).*[9d] Colorless oil (206.4 mg, yield: 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H), 6.90–6.92 (m, 2H), 6.98 (dd, J=1.2, 7.6 Hz, 1H), 7.17 (td, J=1.2 Hz, 7.6 Hz, 1H), 7.23 (dd, J=1.6, 7.6 Hz, 1H), 7.29 (dd, J=1.6, 7.6 Hz, 1H), 7.56–7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1, 105.3, 116.8, 119.0, 121.1, 125.8, 127.7, 130.6, 132.0, 134.2, 152.4, 161.8.

*4.2.8. 2-Phenoxybenzo[d]thiazole (**3ea**).*[13] Colorless oil (199.1 mg, yield: 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.33 (m, 2H), 7.36–7.41 (m, 3H), 7.44–7.48 (m, 2H), 7.67 (dd, J=0.8, 8.0 Hz, 1H), 7.74 (dd, J=0.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.8, 121.4, 121.9, 124.2, 126.38, 126.4, 130.1, 132.4, 149.2, 154.9, 172.1.

*4.2.9. 3-Phenoxyquinoline (**3fa**).*[9a] Yellow solid (71.3 mg, yield: 32%), mp: 62–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.12 (m, 2H), 7.19–7.23 (m, 1H), 7.39–7.44 (m, 2H), 7.52–7.54 (m, 2H), 7.61–7.65 (m, 1H), 7.68 (dd, J=1.2, 8.0 Hz, 1H), 8.10 (d, J=8.4 Hz, 1H), 8.82 (d, J=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.3, 120.1. 124.3, 127.0, 127.3, 127.9, 128.6, 129.3, 130.1, 144.7, 145.2, 151.1, 156.2.

*4.2.10. Ethyl 3-phenoxybenzoate (**3ga**).*[16] Colorless oil (49.3 mg, yield: 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, J=7.2, 3H), 4.36 (q, J=7.2 Hz, 2H), 7.00–7.23 (m, 2H), 7.13 (t, J=7.2 Hz, 1H), 7.20–7.21 (m, 1H), 7.33–7.42 (m, 3H), 7.68–7.69 (m, 1H), 7.78 (td, J=1.2, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 61.3, 119.1, 119.8, 123.3, 123.8, 124.4, 129.8, 130.0, 132.4, 156.9, 157.4, 166.1.

*4.2.11. 2-Phenoxynaphthalene (**3ha**).*[3d] Pale red solid (85.8 mg, yield: 39%), mp: 47–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05–7.09 (m, 2H), 7.14–7.18 (m, 1H), 7.28 (dd, J=2.4, 8.8 Hz, 1H), 7.30–7.49 (m, 5H), 7.69 (d, J=8.4 Hz, 1H), 7.80–7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.2, 119.3, 120.1, 123.6, 124.8, 126.6, 127.9, 129.96, 130.00, 130.3, 134.4, 155.2, 157.3.

*4.2.12. Bis(2-methylphenyl)ether (**3je**).*[17] When 2-methyl bromobenzene was used, the product was obtained as pale yellow oil (194.6 mg, yield: 97%). When 2-methyl chlorobenzene was used, the product was obtained (180.7 mg, yield: 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 6H), 6.74 (dd, J=0.8, 8.0 Hz, 2H), 7.02 (td, J=0.8, 7.2 Hz, 2H), 7.11–7.13 (m, 2H), 7.25–7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 117.8, 123.1, 127.1, 128.9, 131.4, 155.3.

*4.2.13. 4-tert-Butyl-2′-methyldiphenyl ether (**3ie**).*[6a] When 2-methyl bromobenzene was used, the product was obtained as colorless oil (231.2 mg, yield: 96%). When 2-methyl chlorobenzene was used, the product was obtained (205.0 mg, yield: 86%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.32 (s, 9H), 2.27 (s, 3H), 6.84–6.87 (m, 2H), 6.90 (d, J=8.0 Hz, 1H), 7.05 (dt, J=0.8, 7.6 Hz, 1H), 7.14 (td, J=1.6, 7.6 Hz, 1H), 7.24–7.29 (m, 1H), 7.30–7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.4, 31.7, 34.4, 117.1, 119.5, 123.8, 126.6, 127.2, 139.9, 131.5, 145.3, 155.0, 155.6.

*4.2.14. 1-(tert-Butyl)-2-(4-(tert-butyl)phenoxy)benzene (**3if**).* Colorless oil (273.9 mg, yield: 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 1.42 (s, 9H), 6.82 (d, J=8.0 Hz, 1H), 6.91 (d, J=8.8 Hz, 2H), 7.02 (t, J=7.6 Hz, 1H), 7.11 (t, J=7.6 Hz, 1H), 7.33 (d, J=8.8 Hz, 2H), 7.38 (d, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.2, 31.7, 34.4, 34.9, 118.6, 119.8, 122.9, 126.6, 127.1, 127.2, 140.7, 145.6, 155.3, 156.5. IR (cm^{-1}): 3073, 2960, 2868, 1596, 1575, 1510, 1483, 1439, 1363, 1234, 1198, 1129, 1108, 1088, 1051, 881, 853, 746. HRMS m/z calcd for $C_{20}H_{26}ONa$ $[M+Na]^+$: 305.1881, found: 305.1881.

*4.2.15. Ethyl 3-(o-tolyloxy)benzoate (**3ge**).* Colorless oil (214.3 mg, yield: 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, J=7.2 Hz, 3H), 2.23 (s, 3H), 4.35 (q, J=7.2 Hz, 2H), 6.90 (d, J=8.0 Hz, 1H), 7.06–7.11 (m, 2H), 7.16–7.21 (m, 1H), 7.25–7.28 (m, 1H), 7.35 (t, J=8.0 Hz, 1H), 7.58 (dd, J=1.6, 2.4 Hz, 1H), 7.72–7.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 16.3, 61.2, 118.3, 119.9, 121.7, 123.6, 124.5, 127.4, 129.7, 130.1, 131.7, 132.3, 154.1, 158.0, 166.3. IR (cm^{-1}): 3068, 3027, 2981, 1721, 1580, 1484, 1442, 1272, 1234, 1202, 1180, 1112, 1098, 1075, 1023, 943, 754. HRMS m/z calcd for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1178, found: 257.5195.

*4.2.16. 3-(2-(tert-Butyl)phenoxy)quinoline (**3ff**).* Yellow solid (262.9 mg, yield: 93%), mp 87–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 9H), 6.91 (dd, J=1.6, 7.6 Hz, 1H), 7.13–7.23 (m, 2H),

7.47–7.53 (m, 3H), 7.60–7.64 (m, 1H), 7.67 (dd, *J*=0.8, 8.0 Hz, 1H), 8.10 (d, *J*=7.6 Hz, 1H), 8.81 (d, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.3, 34.9, 119.7, 120.6, 124.5, 127.1, 127.3, 127.6, 127.77, 127.79, 128.8, 129.3, 141.5, 144.5, 145.2, 151.7, 154.9. IR (cm^{-1}): 3061, 2957, 2868, 1606, 1597, 1485, 1441, 1422, 1340, 1270, 1213, 1087, 855, 750. HRMS *m*/*z* calcd for $C_{19}H_{19}NO$ $[M+H]^+$: 278.1545, found: 278.1533.

*4.2.17. 1,3-Di-tert-butyl-2-(4-(tert-butyl)phenoxy)benzene (**3ig**).* Colorless solid (67.7 mg, yield: 20%), mp 117–120 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.30 (s, 9H), 1.43 (s, 18H), 7.02 (s, 1H), 7.28 (s, 2H), 7.41–7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.5, 31.6, 34.6, 124.2, 125.7, 126.9, 132.7, 136.2, 139.6, 149.4, 153.4. IR (cm^{-1}): 3030, 2956, 2866, 1518, 1466, 1431, 1390, 1361, 1225, 1137, 1116, 885, 840, 830. HRMS *m*/*z* calcd for $C_{24}H_{34}O$ $M^{\bullet+}$: 338.2610, found: 338.2603.

*4.2.18. 1-Methyl-2-phenoxy-1H-benzo[d]imidazole (**3ka**).* Yellow oil (mg, yield: 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H), 7.17–7.28 (m, 4H), 7.35–7.38 (m, 2H), 7.42–7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.5, 108.3, 118.6, 120.1, 121.5, 121.9, 125.5, 129.9, 134.0, 139.7, 153.7, 155.8. IR (cm^{-1}): 3055, 2935, 1622, 1589, 1520, 1484, 1448, 1402, 1324, 1284, 1220, 1157, 1125, 1023, 1007, 774, 740, 688. HRMS *m*/*z* calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$: 225.0950, found: 225.1027.

4.3. Typical procedure for the palladium catalyzed the coupling reactions of aryl halides and phenols with NaH as base and *o*-xylene as solvent

An oven-dried Schlenk tube was evacuated and backfilled with nitrogen. The Schlenk tube was charged with NaH (60.0 mg, 60%, 1.2 mmol) and *o*-xylene (1 mL), and then phenol (1.2 mmol) was added. After stirring for 15 min, aryl halide (1.0 mmol) and the solution of $Pd(dba)_2$ (11.5 mg, 0.02 mmol) and **L1** (13.7 mg, 0.03 mmol) in *o*-xylene (1.5 mL) were added sequentially. The septum was replaced with an inside reflux condenser, and then the reaction mixture was stirred for 18 h at 110 °C. Then, reaction mixture was cooled to room temperature and quenched with saturated NH_4Cl (5 mL). After separating the organic phase, the aqueous phase was extracted with diethyl ether (3 mL×3), and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was concentrated under reduced pressure, and then the crude material was purified by column chromatography on silica gel.

*4.3.1. 1-(tert-Butyl)-4-phenoxybenzene (**3ia**).*[3d] When 4-*tert*-butyl bromobenzene was used, the product was obtained as colorless oil (225.4 mg, yield: 99%). When 4-*tert*-butyl chlorobenzene was used, the product was obtained (199.4 mg, yield: 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 6.92–6.95 (m, 2H), 7.00–7.02 (m, 2H), 7.08 (t, *J*=7.2 Hz, 1H), 7.30–7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.6, 34.4, 118.6, 118.7, 123.0, 126.7, 129.8, 146.2, 154.8, 157.7.

*4.3.2. 1-(tert-Butyl)-4-(4-methoxyphenoxy)benzene (**3ic**).*[3c] Colorless oil (197.7 mg, yield: 75%). H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 3.82 (s, 3H), 6.86–6.90 (m, 4H), 6.90–7.00 (m, 2H), 7.30–7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.6, 34.3, 55.7, 114.9, 117.3, 120.7, 126.5, 145.4, 150.6, 155.8, 156.2.

*4.3.3. Diphenyl ether (**3ka**).*[12] Colorless oil (163.4 mg, yield: 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00–7.04 (m, 4H), 7.09–7.13 (m, 2H), 7.32–7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.2, 123.5, 130.1, 157.6.

*4.3.4. 2-(m-Tolyloxy)naphthalene (**3hh**).*[18] Colorless oil (168.6 mg, yield: 72%). ^{1}H NMR (100 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.91–6.93 (m, 2H), 6.99 (d, *J*=7.6, 1H), 7.26–7.35 (m, 3H), 7.42–7.54 (m, 2H), 7.74 (d, *J*=8.0, 1H), 7.85–7.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 114.1, 116.3, 119.9, 120.1, 124.7, 126.6, 127.2, 127.8, 129.6, 129.9, 134.5, 140.1, 155.3, 157.3.

*4.3.5. 4-Phenoxy fluorobenzene (**3la**).*[3d] Colorless oil (99.9 mg, yield: 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92–7.05 (m, 6H), 7.06–7.11 (m, 1H), 7.30–7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.3, 118.4, 120.7, 123.2, 129.9, 153.0, 157.7, 160.1.

*4.3.6. 3-Phenoxy methoxybenzene (**3ma**).*[3d] Colorless oil (136.3 mg, yield: 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 6.57–6.60 (m, 2H), 6.64–6.66 (m, 1H), 7.01–7.04 (m, 2H), 7.08–7.12 (m, 1H), 7.20–7.24 (m, 1H), 7.31–7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 104.9, 108.9, 111.0, 119.1, 123.4, 129.8, 130.2, 157.1, 158.6, 161.1.

*4.3.7. tert-Butyl 5-phenoxy-1H-indole-1-carboxylate (**3na**).* While solid (152.8 mg, yield: 50%), mp 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67 (s, 9H), 6.50 (d, *J*=3.6 Hz, 1H), 6.97–6.99 (m, 2H), 7.03–7.08 (m, 2H), 7.19 (d, *J*=2.4 Hz, 1H), 7.29–7.33 (m, 2H), 7.61 (d, *J*=3.6 Hz, 1H), 8.09 (d, *J*=8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.3, 83.9, 107.3, 111.3, 116.3, 117.1, 118.1, 122.7, 127.1, 129.8, 131.7, 149.8, 152.6, 158.7. IR (cm^{-1}): 3152, 3119, 2978, 2932, 2360, 1734, 1592, 1463, 1371, 1330, 1257, 1159, 1116, 1081, 1023, 848, 765, 750. HRMS *m*/*z* calcd for $C_{19}H_{20}NO_3$ $[M+H]^+$: 310.1443, found: 310.3599.

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Supplementary data

These data include ^{1}H NMR and ^{13}C NMR spectra for all products (**3aa**–**3na**) described in this article. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.05.104.

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