# Practical Cross-Coupling between O-Based Electrophiles and Aryl Bromides via Ni Catalysis

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Ⓢ *Supporting Information*

ABSTRACT: Cross-coupling of various O-based electrophiles with aryl bromides was developed through Ni-catalyzed C−O activation in the presence of magnesium. Beside carboxylates, carbamates, and ethers, phenols exhibited excellent reactivity under modified conditions. This chemistry was featured as a simple and environmentally benign process with low catalyst loading and easy manipulations. The method exhibited broad substrate scopes.
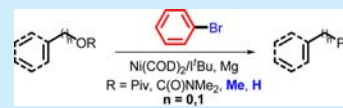
Transition-metal-catalyzed cross-coupling has become one of the most powerful tools to construct carbon−carbon bonds in organic synthesis since the 1970s.[1] Much attention has been paid to the preparation of the biaryl skeleton through cross-couplings due to its versatile application in pharmaceuticals, material chemistry, and total synthesis of natural products.[2] At the early stage of development, aryl halides and their equivalents were successfully employed as electrophiles to construct biaryl scaffolds.[3] Recently, O-based electrophiles have been used as alternatives to organic halides.[4] To date, carbamates,[5] carboxylates,[6] ethers,[6c,7] and so on have been successfully applied in various coupling reactions to construct C−C as well as C−heteroatom bonds. Sporadic cases employing phenols and alcohols as electrophiles have also been reported.[8]

A major disadvantage of the widespread application of the cross-coupling reactions is the employment of prepared organometallic reagents, for example, Grignard reagents, which are not only costly stepwise but also sensitive to moisture and air.[1] The cross-coupling between two electrophiles is an alternative method to circumvent this problem.[6j,k,9] Among recent advancements of cross-coupling between two electrophiles, an important pathway is to generate the active organometallic reagents in situ by avoiding the tedious preparations and complex manipulations of organometallic reagents. Recently, the elegant example of iron-catalyzed selective cross-coupling between aryl halides and alkyl halides was reported in the presence of magnesium.[9d] Cross-coupling of nonactivated alkyl tosylates and mesylates with alkyl and aryl bromides was also approached via Cu catalysis.[9i] In this paper, we demonstrated cross-coupling of arenol and their derivatives with aryl bromides to construct biaryl scaffolds through Ni-catalyzed C−O activation in the presence of magnesium under mild conditions. Under these conditions, vinyl and benzyl ethers also exhibited credible reactivity.

Our initial study was set to evaluate the cross-coupling between naphthyl methyl ether (**1a**) and aryl bromide (**2a**). Previous reports indicated that the combination of Ni(COD)2

and PCy3 was efficient to carry out the cross-coupling between **1a** and the prepared Grignard reagent **2a′** (eq 1).[7n,o,10] We first
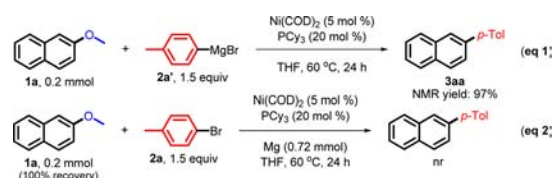
submitted the substrates **1a** and **2a** to the corresponding conditions in the presence of Mg. Unfortunately, the desired product **3aa** was not observed (eq 2) (see the SI for control experiments). This result indicated that a simple extension of the previously developed Kumada-type coupling of O-based electrophiles was not suitable for the development of targeted reductive coupling between aryl ethers and aryl halides.

After systematic investigations of reaction parameters (Table 1), we found that a cocktail containing Ni(COD)2, I[t]Bu, and Mg promoted the desired cross-coupling at 60 °C in THF for 24 h to give **3aa** in 88% yield (entry 1). Control experiments indicated the crucial roles of either Ni catalyst or Mg (entries 2−4). As expected, the ligand proved to be essential. When other N-heterocyclic carbene ligands, such as IMes, IPr, IAd, ICy(HCl), and SI[t]Bu(HCl), were used instead of I[t]Bu, IAd ICy(HCl), and SI[t]Bu(HCl), **3aa** was obtained in good yields (entries 5−9). When ICy(HCl) and SI[t]Bu(HCl) were used, MeMgBr was required as a deprotonating reagent (entries 8−9). Other reductants were also tested, and no desired product was observed (entries 10 and 11). Nonpolar solvent, such as toluene, was not suitable for the transformation (entry 12). 4-Chlorotoluene and 4-iodotoluene were used to take place the of **2a**, the desired product **3aa** was not observed at all, and the starting material **1a** was completely recovered (entries 13 and 14).

## Table 1. Investigation of Different Parameters in the Cross-Coupling of 1a and 2a[a]

entry	ligand (L)	reductant (M)	solvent	yield (%)
1	I^{t}Bu	Mg	THF	92 (88)
2[b]	I^{t}Bu	Mg	THF	0
3		Mg	THF	0
4	I^{t}Bu		THF	0
5	IAd	Mg	THF	65
6	IMes	Mg	THF	0
7	IPr	Mg	THF	0
8[c]	ICy(HCl)	Mg	THF	82
9[c]	SI^{t}Bu(HCl)	Mg	THF	87
10	I^{t}Bu	Zn	THF	0
11	I^{t}Bu	Mn	THF	0
12	I^{t}Bu	Mg	toluene	0
13[d]	I^{t}Bu	Mg	THF	0
14[e]	I^{t}Bu	Mg	THF	0

[a]1a (0.2 mmol), 2a (0.3 mmol), Ni(COD)$_2$ (5.0 mol %), ligand (20 mol %), Mg (3.6 equiv), THF (1.0 mL), 60 °C, 24 h. NMR yields were reported based on 1a, and benzo[d][1,3]dioxole was used as the inner standard; isolated yield is reported in the parentheses. [b]Ni(cod)$_2$ was omitted. [c]MeMgBr (0.04 mmol) was used to deprotonate the NHC(HCl). [d]4-Chlorotoluene was used to instead of 2a. [e]4-Iodotoluene was used to instead of 2a. Abbreviations: I^{t}Bu = 1,3-di-tert-butylimidazol-2-ylidene; IAd = 1,3-bis(1-adamantyl)imidazol-2-ylidene; IMes =1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; ICy(HCl) = 1,3-dicyclohexylimidazolium chloride; SI^{t}Bu(HCl) = 1,3-di-tert-butylimidazolinium chloride.

Under optimized conditions, we tested the reactivity of different 2-naphthol derivatives (Figure 1). Other ethers, such
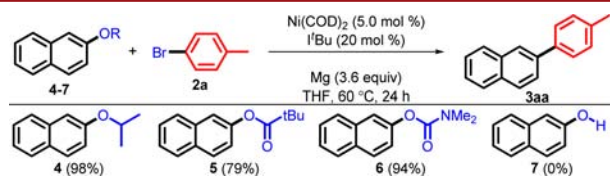
Figure 1. Nickel-catalyzed cross-coupling of 2a with various 2-naphthol derivatives. Conditions: 1, 4−8 (0.2 mmol), 2a (0.3 mmol), Ni(COD)$_2$ (5.0 mol %), I^{t}Bu (20 mol %), Mg (3.6 equiv), THF (1.0 mL), 60 °C, 24 h NMR yields are reported on the basis of 1a, and benzo[d][1,3]dioxole was used as the inner standard.

as isopropyl ether (4), proved to be suitable substrates and transformed into the desired product 3aa in quantitative yield. To our delight, the success of carboxylate (5) and carbamate (6) further indicated the power of this reaction. Unfortunately, unprotected 2-naphthol (7) was not suitable under the current conditions.

Various organo bromides were further examined carefully (Figure 2). The cross-coupling with aryl bromides 2 bearing different alkyl groups proceeded smoothly, and the corresponding products 3 were afforded in good to excellent yields (3aa−af). In comparison, the steric hindrance (3af) decreased the efficiency, while an excellent yield could also be reached with 3.0 equiv of 2f. To our delight, methoxy-substituted phenyl bromides (3ag and 3aj) were successfully applied as coupling partners, leaving the MeO− group in both starting materials
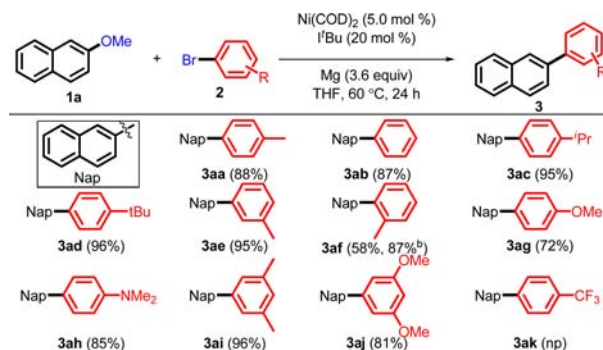
Figure 2. Nickel-catalyzed cross-coupling of naphthylmethyl ether 1a with different organo bromides 2. Conditions: aryl methyl ether (0.2 mmol), organo bromide (0.3 mmol), Ni(COD)$_2$ (5.0 mol %), I^{t}Bu (20 mol %), Mg (3.6 equiv), THF (1.0 mL), 60 °C, 24 h. Isolated yields are reported on the basis of aryl methyl ether. 0.6 mmol organo bromide was used.

and products untouched. This result indicated that different aryl C−O bonds could be discriminated under the reaction conditions, providing the opportunity for orthogonal cross-coupling to produce more complex molecules.[7n] Moreover, aryl bromide bearing an N,N-dimethylamino group was suitable to produce the desired product 3ah in an excellent yield. As expected, multisubstituted aryl bromides (3ai and 3aj) proved to be suitable in this catalytic system. It is important to note that the electronic property of aryl bromides played a vital role, and aryl bromides bearing a strong electron-withdrawing group, for example, trifluoromethyl (3ak), failed to facilitate this coupling. Analysis of the reaction mixture indicated the homocoupling of aryl bromides occurred.

Subsequently, different methyl naphthyl ethers were systematically investigated (Figure 3). Obviously, alkyl and aryl groups
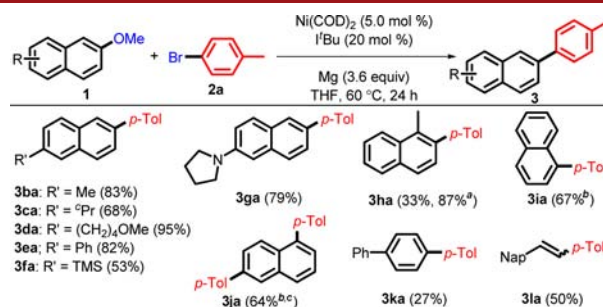

Figure 3. Nickel-catalyzed cross-coupling of 2a with aryl methyl ethers 1. Conditions: aryl methyl ether (0.2 mmol), organo bromide (0.3 mmol), Ni(COD)$_2$ (5.0 mol %), I^{t}Bu (20 mol %), Mg (3.6 equiv), THF (1.0 mL), 60 °C, 24 h. Isolated yields are reported on the basis of aryl methyl ether. (a) 0.6 mmol organo bromide was used. (b) NMR yield is reported. (c) Ni(cod)$_2$ (10 mol %), I^{t}Bu (40 mol %), p-TolBr (3.0 equiv).

at the 6-position did not affect the efficiency (3ba and 3ea), while a cyclopropyl substituent (3ca) led to a lower yield albeit the 3-membered ring was untouched. The aliphatic etheric group (3da) survived well. Similarly, the N,N-dialkylamino group was also compatible (3ga). Notably, the trimethylsilyl group survived under the reaction conditions (3fa). As for its coupling partner, the steric hindrance is critical for this coupling. For example, the efficiency of 1-naphthyl methyl ether (3ia) gave a lower efficacy. When methyl group was introduced at the ortho-position of 2-naphthyl ethers (3ha), the

coupling efficiency dramatically decreased while the same strategy (with 3.0 equiv of aryl bromides) could promote the efficiency. It is noteworthy that the methoxyl groups at both the α- and β-positions could be coupled with aryl bromide under the same conditions (**3ja**). Notably, the biphenyl substrate **1k** was also transformed to the corresponding product **3ka** although in a lower isolated yield. To our delight, the developed methodology was also suitable for the arylation of vinyl methyl ether, and desired product **3la** was obtained in an acceptable yield.

Inspired by the success of cross-coupling between aryl ethers and aryl bromides, sp³ O-based electrophiles were considered (Scheme 1). We tested primary benzyl methyl ether (**1m**), and

Scheme 1. Nickel-Catalyzed Cross-Coupling of Different Benzyl Methyl Ethers and Organobromide 2a
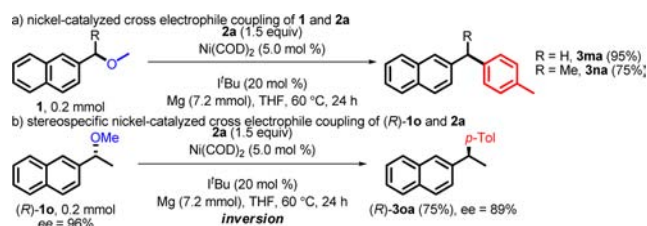
to our delight, the corresponding cross coupling took place smoothly and the desired product (**3ma**) was obtained in a quantative isolated yield (Scheme 1a). Besides primary 2-naphthyl methyl ether **1m**, the secondary carbon-centered ether (**1n**), which presents β-H, was also suitable, and the desired product (**3na**) was isolated. Notably, if the enantiopure substrate (**1o**) was submitted, the stereospecific cross-coupling occurred and the enantiopure product **3oa** was isolated in an excellent yield by keeping the ee value at the same level (Scheme 1b). The conversion of the absolute configuration of the stereogenic center implied that the oxidative addition of nickel catalyst to the C−O bond may proceed through the S_N2-type pathway; similar reactivity was also reported by the Jarvo group.[4g]

Compared to anisole derivatives, arenols are relatively cheap and easily available. However, because of its kinetic and thermodynamical stability, it is more challenging to directly apply arenols for the cross-coupling.[11] As mentioned above, cross-coupling of 2-naphthol **1a** with 4-toluyl bromide **2a** failed under the above conditions. Because of its potential application and fundamental challenges, we set out to evaluate direct cross-coupling between arenols and aryl halides (Figure 4). To our
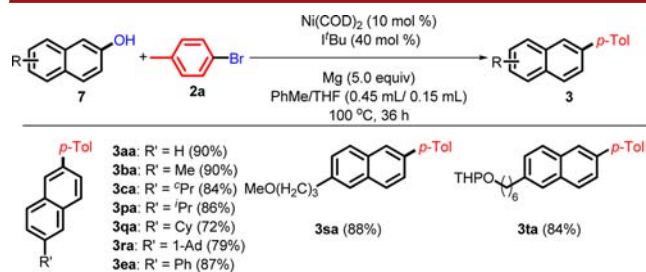
Figure 4. Nickel-catalyzed cross-coupling of organo bromide **2a** with various arenols. Conditions: phenol (0.2 mmol), organo bromide (0.6 mmol), Ni(COD)₂ (10.0 mol %), IʳBu (40 mol %), Mg (5.0 equiv), PhMe/THF (0.45 mL + 0.15 mL), 100 °C, 36 h. Isolated yields are reported on the basis of phenol.

delight, when we changed the conditions with the use of mixed toluene/THF (volume ratio: 3/1) to take the place of THF and increased the amount of both catalysts and magnesium, the desired product **3aa** was obtained directly from 2-naphthol **1a** in an excellent yield. Arenols bearing different alkyl substituents, including primary alkyl group (**3ba**), secondary alkyl groups (**3ca**, **3pa**, and **3qa**), and tertiary alkyl group (**3ra**), were transformed to the targeted corresponding products in high yields. Besides the alkyl group, arenol bearing an aryl substituent proved to be suitable (**3ea**). As anticipated, sp³ C−O survived well under the modified conditions (**3sa**). To our delight, when the substrate containing acetal was submitted to the system, the desired product **3ta** was furnished in high efficiency.

We set out to explore the mechanism of this cross-coupling reaction. A series of control experiments were conducted, and they revealed that this cross-coupling is not a simple combination of Kumada cross-coupling and Grignard reagent formation. Furthermore, a mercury poisoning test was performed, and the result indicated that a heterogeneous species may be involved in the catalytic cycle. Data collected from radical-capture experiments suggested that radical species may participate in the catalytic cycle (for detailed mechanistic information, see the Supporting Information).

In summary, we demonstrated the cross electrophile coupling between aryl ethers and aryl bromides via nickel catalysis in the presence of Mg as reductant. Aryl carboxylates and carbamates were suitable under standard conditions. Vinyl ethers and benzyl ether derivatives were efficient for the coupling. Under modified conditions, arenols were efficiently applied as coupling partners. This methodology is featured as a simple, robust process to forge carbon−carbon bonds efficiently. Continuous efforts to expand substrate scopes and to understand the detailed mechanism are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.6b02656.

Experimental procedures and characterization data of products (PDF)

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Notes

The authors declare no competing financial interest.

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