# Efficient Catalytic Activity of Copper/Aluminum Hydrotalcite in Diaryl Ether Synthesis

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**Abstract:** A simple copper/aluminum hydrotalcite (Cu/Al-HT) catalyzed arylation of phenols with aryl iodides afforded the corresponding diaryl ethers in moderate to excellent yields. This ligandfree Cu/Al-HT catalyzed coupling of aryl iodides with phenols resulted in high yields of diaryl ethers in the absence of an additive. The catalyst was quantitatively recovered from the reaction by simple filtration and reused for a number of cycles.

Key words: hydrotalcite, copper, coupling, phenol, reusable catalyst

Diaryl ethers constitute an important class of organic compounds that play a significant role in a number of polymer and life science industries.<sup>1</sup> A number of them have been shown to possess significant biological activity such as the antibiotic vancomycin<sup>2</sup> and the anti-HIV agents chloropeptins.<sup>3</sup> With this growing inventory of applications, developing efficient methods for the synthesis of diaryl ethers continues to be a challenging and active area of research. The usual synthetic methods for the synthesis of diaryl ethers are, Ullmann<sup>4</sup> palladium-catalyzed coupling of aryl halides,<sup>5</sup> C–O coupling reaction of aryl-boronic acids with phenols,<sup>6,7</sup> and, more recently, iron-catalyzed couplings.<sup>8</sup>

The major drawback of the above-mentioned procedures is that they proceed in a homogenous phase where expensive palladium, copper triflate, and ligands are used. It is thought that these ligands increase the efficiency of the Ullmann reaction by increasing the solubility of the copper salts by preventing their aggregation. However, whilst this advance in the field of Ullmann coupling is exceedingly beneficial, most of the reactions still require long reaction times of more than 24 hours, elevated reaction temperatures, and high catalyst loading. Moreover removing and recycling the catalyst is tedious, with loss of precious catalysts at the end of the reaction.

The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research recently, as the potential advantages of these materials (simplified recovery and reusability and the potential for incorporation in continuous reactors and microreactors) over homogeneous systems can make a major impact on the environmental performance of a synthesis.<sup>9</sup>

SYNTHESIS 2009, No. 3, pp 0483–0487 Advanced online publication: 09.01.2009 DOI: 10.1055/s-0028-1083304; Art ID: P09108SS © Georg Thieme Verlag Stuttgart · New York In recent years, layered double hydrotalcites (LDHs) of Mg and Al have received considerable attention due to the cation exchange capacity of the brucite layer, anion exchange by inter layer, and also as good support in heterogeneous catalysis; by exploiting these properties of LDHs, we earlier reported an effective N-arylation with chloroarenes using a layered double hydroxide supported copper catalyst.<sup>10</sup> In continuation of our studies on catalyst activity in organic transformations, we herein wish to report our investigations on Cu/Al-HT catalyzed C–O bond formation in the absence of ligands. This procedure is simple, mild, clean and works efficiently without additives (Scheme 1).



Scheme 1 Catalytic arylation of phenols with aryl halides

In our preliminary studies to find the best catalyst for the coupling reaction, we chose the coupling reaction of iodobenzene and phenol in N,N-dimethylformamide to give diphenyl ether (1a) as the model reaction; the results are summarized in Table 1. From Table 1, [Cu-(HAP), copper hydroxyapatite, Cu-(FAP) copper fluoroapatite, Cu/ Al-HT's (HT, hydrotalcite of Cu/Al in different ratios: Cu/Al-HTA, 3:1 (Cu/Al), Cu/Al-HTB, 2.5:1, Cu/Al-HTC, 2:1)] it can be seen that Cu/Al-HTB is the best catalyst amongst the catalysts screened; the catalyst can easily be separated by filtration. The copper content in the catalysts [Cu(HAP) copper hydroxyapatite, Cu(FAP) copper fluoroapatite, Cu/Al-HTA (Cu/Al 3:1), Cu/Al-HTB (Cu/Al 2.5:1), Cu/Al-HTC (Cu/Al 2:1)] was analyzed using atomic absorption spectroscopy (AAS) and found to be 5.24, 3.69, 35.64, 34.94, and 33.73 atm%, respectively. The recovered catalyst, after washing with acetone followed by drying at 65 °C, was used in the next six runs with consistent activity. Iodobenzene was fully consumed in 12 hours and the reaction afforded diphenyl ether (1a) in 97% yield (Table 1, entry 4).

Further, the same reaction was screened with several bases and solvents to increase the efficiency of the coupling reaction (Tables 2 and 3). To examine the effect of the base on the outcome of the reaction, different bases were employed in the coupling reaction of iodobenzene with phenol using Cu/Al-HTB as the catalyst and *N*,*N*-dimethylformamide as the solvent; it was observed that

**Table 1** Catalyst Screening for the Coupling of Iodobenzene with<br/>  $Phenol^{a,b}$ 

	+ CH catalyst, DMF, 110	К <sub>2</sub> CO <sub>3</sub> 0 °C, 12 h 1a
Entry	Catalyst <sup>b</sup> (20 wt%)	Isolated yield (%)
1	Cu(HAP)	58
2	Cu(FAP)	39
3	Cu/Al-HTA	79
4	Cu/Al-HTB	97
5	Cu/Al-HTC	65
6	Cu(NO <sub>3</sub> ) <sub>2</sub>	9
7	$Cu/\gamma Al_2O_3$	47

 $^a$  Reaction conditions: PhI (1 mmol), PhOH (1.5 mmol), K\_2CO\_3 (2.0 mmol), catalyst (100 mg), DMF (2 mL), 110 °C, 12 h.  $^b$  Entries 1–5, ref. 10.

**Table 2**Effect of the Base on the Coupling of Iodobenzene withPhenol Using Cu/Al-HTB Catalyst<sup>a</sup>

Entry	Base	Isolated yield (%)
1	t-BuOK	13
2	NaOMe	25
3	КОН	n.r.
4	NaOH	15
5	Na <sub>2</sub> CO <sub>3</sub>	45
6	K <sub>2</sub> CO <sub>3</sub>	97
7	Cs <sub>2</sub> CO <sub>3</sub>	76

<sup>a</sup> Reaction conditions: PhI (1 mmol), PhOH (1.5 mmol), base (2.0 mmol), Cu/Al-HTB (100 mg), DMF (2 mL), 110  $^{\circ}$ C, 12 h; n.r = no reaction.

potassium carbonate was the most effective base (Table 2). Therefore, potassium carbonate was used as the base in all further reactions.

Turning our attention to the effect of the solvent on the coupling reaction of iodobenzene with phenol with Cu/ Al-HTB catalyst and potassium carbonate as the base, we examined various solvents (Table 3). *N*,*N*-Dimethylformamide was the most effective solvent, furnishing diphenyl ether in 97% yield (Table 3, entry 7). Even at room temperature, Cu/Al-HTB afforded 45% of the desired product in 48 hours (Table 3, entry 7).

On the basis of the optimized reaction conditions, we explored the efficiency of the catalyst in the O-arylation of phenol with various functionalized iodobenzenes and the results are summarized in Table 4. Most of the substituted

 Table 3
 Effect of the Solvent on the Coupling of Iodobenzene with

 Phenol Using Cu/Al-HTB Catalyst<sup>a</sup>

Entry	Solvent (2 mL)	Isolated yield (%)	
1	МеОН	n.r.	
2	THF	21	
3	dioxane	40	
4	MeCN	43	
5	toluene	25	
6	xylene	59	
7	DMF	97, 45, <sup>b</sup> 91 <sup>c</sup>	
8	DMSO	72	

<sup>a</sup> Reaction conditions: PhI (1 mmol), PhOH (1.5 mmol),  $K_2CO_3$  (2.0 mmol), Cu/Al-HTB (100 mg), solvent (2 mL), 110 °C, 12 h; n.r = no reaction.

<sup>b</sup> Reaction at r.t.

<sup>c</sup> Isolated yield after fifth cycle.

iodobenzenes tested afforded the corresponding diaryl ethers 1 in very high yield (up to 97%, Table 4, entry 1). The catalyst is also active in activating bromobenzene and chlorobenzene albeit with moderate to low yields compared to iodobenzene (Table 4, entry 1). The reaction conditions were compatible with a variety of functionalized aryl iodides, including those bearing electron-donating and electron-withdrawing groups (Table 4, entries 2–12). The coupling reaction of sterically hindered aryl iodides was slightly disfavored. Hence, when employing 1-iodo-2-nitrobenzene, the reaction occurred to give 1c with a lower yield than with less hindered 1-iodo-4-nitrobenzene to give **1b** (Table 4, entries 2 and 3). It was observed that iodobenzene with chloro, bromo, and fluoro substituents in the *para* position yielded coupling products **1d-f** with decreasing yields (Table 4, entries 5-7). No product formation is seen with sterically hindered 1-bromo-2-nitrobenzene (Table 4, entry 9). Reduced yields were obtained for inactivated aryl iodides compared to activate aryl iodides (Table 4, entries 10–12).

Encouraged by the efficiency of the cross-coupling protocol described above, the scope of the substrate was investigated with various phenols. A variety of substituted phenols were tested under the optimized reaction conditions using iodobenzene as the arylating agent. Electrondeficient phenols provided the coupling products **1** in slightly lower yields (57–83%, Table 5, entries 2 and 3). A nitro group on the phenol yielded no product, which is in accordance with the literature<sup>11</sup> (Table 5, entry 4). On the other hand, several electron-rich phenols were suitable substrates for the O-arylation, affording the corresponding diaryl ethers **1g–l** in excellent yields (Table 5, entries 5–10).

To demonstrate the scope of Cu/Al-HTB catalyzed O-arylation reaction, benzyl alcohol (Table 6, entry 1), cyclohexanol (Table 6, entry 2 and 3), phenols (Table 6, entries

Table 4	O-Arylation	of Phenol	with Variou	s Aryl Iodides <sup>a</sup>
	/			

$R^{1} \xrightarrow{H} + HO \xrightarrow{DMF, 110 \circ C, 12 h} R^{1} \xrightarrow{H} HO \xrightarrow{DMF, 110 \circ C, 12 h} R^{1} \xrightarrow{H} HO \xrightarrow{H} H \oplus{H} HO \xrightarrow{H} HO \xrightarrow{H} H \to H HO \xrightarrow{H} H \to H \to$				
Entry	R <sup>1</sup> ArX	Х	Product	Isolated yield (%)
1	Н	Cl, Br, I	1a	47 (X = Cl) 65 (X = Br) 97, 91 <sup>b</sup> (X = I)
2	4-NO <sub>2</sub>	Ι	1b	96
3	2-NO <sub>2</sub>	Ι	1c	69
4	4-NO <sub>2</sub>	Cl	1b	82
5	4-C1	Ι	1d	89
6	4-Br	Ι	1e	85
7	4-F	Ι	1f	78
8	4-C1	Br	1d	97
9	2-NO <sub>2</sub>	Br	1c	n.r.
10	4-CO <sub>2</sub> Et	Ι	1g	92
11	4-OMe	Ι	1h	97
12	Me	Ι	1i	85

<sup>a</sup> Reaction conditions: ArI (1 mmol), PhOH (1.5 mmol),  $K_2CO_3$  (2.0 mmol), Cu/Al-HTB (100 mg), DMF (2 mL), 110 °C, 12 h; n.r = no reaction.

<sup>b</sup> Isolated yield after fifth cycle.

Table 5 O-Arylation of Phenols with Iodobenzene<sup>a</sup>

CH R <sup>1</sup> OH	+	Cu/AI-HTB, K <sub>2</sub> CO <sub>3</sub>	$\underset{R^{1}}{}^{0}$
Entry	$\mathbb{R}^1$	Product	Isolated yield (%)
1	Н	<b>1</b> a	97
2	4-Cl	1d	57
3	4-F	1f	83
4	4-NO <sub>2</sub>	1b	n.r.
5	4-Me	1i	97
6	4-OMe	1h	85
7	4-CO <sub>2</sub> Et	1g	78
8	4-Ph	1j	92
9	4-t-Bu	1k	97
10	3,4-Me <sub>2</sub>	11	85

<sup>a</sup> Reaction conditions: ArOH (1.0 mmol), PhI (2 mmol),  $K_2CO_3$  (2.0 mmol), Cu/Al-HTB (100 mg), DMF (2 mL), 110 °C, 12 h; n.r = no reaction.

4–6), biphenyl-4-ol (Table 6, entry 7) and 2-naphthol (Table 6, entry 8) were used as coupling partners with var-

ious substituted aryl iodides. The reaction of 1-iodo-4-nitrobenzene with benzylamine afforded 1-(benzyloxy)-4nitrobenzene (1m) in excellent yield (Table 6, entry 1). The same reaction with cyclohexanol gave a slightly lower yield of product 1m compared to benzyl alcohol (Table 6, entry 2), the decrease in the yield can be ascribed to enhanced steric hindrance at the reaction center. To test the versatility of this catalyst in the present coupling reaction, we chose the reaction between cyclohexanol and 1iodo-4-methoxybenezene since para-substituted electronrich aryl halides are difficult substrates for the corresponding transformations (Table 6, entry 3). We noticed that with 1-iodo-4-nitrobenzene the yield was slightly lower compared to 1-iodo-4-methoxybenzene (Table 6, entries 2 and 3). Electron-donating substituents on aryl iodides and electron-withdrawing substituents on phenols afforded the corresponding coupling products 1p-r in excellent yields (Table 6, entries 4-6) albeit in lower yields compared with electron-withdrawing substituents on aryl iodides. Iodobenzene gave lower yields with biphenyl-4ol compared to 2-naphthol (Table 6, entries 7 and 8). The results show that this catalytic system is relatively insensitive to electronic effects on the coupling partners.

R <sup>1</sup> OH	+ , , , , , , , , , , , , , , , , , , ,	Cu/Al-HTE DMF, 110	3, K₂CO₃ ) °C, 12 h	$R^2$ 1
Entry	$\mathbb{R}^1$	$\mathbb{R}^2$	Product	Isolated yield (%)
1	Bn	4-NO <sub>2</sub>	1m	93
2	Су	4-NO <sub>2</sub>	1n	86
3	Су	4-OMe	10	91
4	$4-BrC_6H_4$	4-Br	1p	85
5	4-MeOC <sub>6</sub> H <sub>4</sub>	4-NO <sub>2</sub>	1q	91
6	$4-BrC_6H_4$	4-OMe	1r	89
7	$4-PhC_6H_4$	Н	<b>1s</b>	99
8	2-naphthyl	Н	1t	94

 $^a$  Reaction conditions: alcohol (1.0 mmol), ArI (2 mmol), K\_2CO\_3 (2.0 mmol), Cu/Al-HTB (100 mg), DMF (2 mL), 110 °C, 12 h.

For any heterogeneous system, it is important to know its ease of separation and possible reuse. The Cu/Al-HTB catalyst can easily be separated by filtration. The recovered catalyst, after washing with acetone followed by drying at 65 °C, was used in the next run and consistent activity was observed (Table 3, entry 7, 1st cycle 97%; 5th cycle 91%). Next to see whether the reaction was occurring mainly due to leached metal or the supported catalyst, a reaction between iodobenzene and phenol was terminated after 20% conversion (50 min) and the catalyst was filtered off by hot filtration and the reaction was continued with the filtrate for 12 hours. Almost no change in the conversion of iodobenzene was observed. These studies and the inactivity of copper(II) nitrate in the O-arylation of phenols clearly proves that the reaction occurs hetero-geneously.

In conclusion, the described one-pot recyclable Cu/Al-HTB catalyzed C–O bond approach represents an efficient protocol for the synthesis of a wide variety of diaryl ethers. This method provides the products in good to excellent yields in short reaction times compared to the known procedures and in the absence of ligands and or a strong base. Solid-base catalyst, reaction times, and easy product isolation makes the process attractive for the synthesis of ethers. Moreover, the catalyst can be easily separated by simple filtration and reused for several cycles with consistent activity.

The catalyst was prepared according to the literature procedure.<sup>10</sup> All alcohols and amines were purchased from Aldrich or Fluka and were used without further purification. ACME silica gel (60–120 mesh) was used for product purification. All solvents and other chemicals were obtained from commercial sources and purified using standard methods. Melting points were recorded on a Barnstead Electrothermal 9200 instrument and are uncorrected. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer as KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini (200 MHz), a Bruker Avance (300 MHz) or a Varian Unity (400 MHz) spectrometer using TMS as an internal standard and CDCl<sub>3</sub> as solvent.

The spectroscopic data of all known compounds were identical to those reported in the literature;<sup>12–15</sup> the data of all novel compounds synthesized are given herein.

### **Diphenyl Ether (1a); Typical Procedure**

A mixture of PhI (1 mmol), PhOH (1.5 mmol), base (2.0 mmol) and Cu-Al/HTB (100 mg) in DMF (2 mL) was stirred in a 25-mL roundbottom flask in a pre-heated oil bath at 110 °C. After completion of the reaction (TLC) the catalyst was filtered through centrifugation and washed several times with EtOAc to make the catalyst free from organic matter. The organic solution was washed with brine (30 mL), dried (anhyd Na<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure using a rotavapor. The crude product was purified by column chromatography (silica gel, 60–120, hexane–EtOAc, 90:10) to afford the corresponding diaryl ether.

#### 1-(Benzyloxy)-4-nitrobenzene (1m)

Orange crystalline solid; yield: 93%; mp 185–186 °C.

IR (KBr): 2925, 1917, 1663, 1568, 1474, 1400, 1292, 1207, 1145, 1080, 1000, 843, 715, 647, 542  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79–7.81 (d, *J* = 7.6 Hz, 2 H), 7.49–7.31 (m, 7 H), 4.7 (s, 2 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 169.1, 141.7, 128.1, 121.9, 115.3, 70.7.

MS (EI, 70 eV): m/z (%) = 221 (4) [M<sup>+</sup>], 183 (5), 169 (4), 164 (9), 149 (8), 121 (7), 111 (15), 91 (18), 75 (21), 57 (24), 55 (100), 43 (52), 41 (46), 40 (16).

Anal Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>3</sub>: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.74; H, 4.79; N, 6.10.

**1-(Cyclohexyloxy)-4-nitrobenzene (1n)** Yellow oil; yield: 86%.

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IR (KBr): 2935, 2858, 1592, 1511, 1339, 1260, 1171, 1111, 1042, 1019, 961, 845, 753  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.25–8.10 (d, *J* = 8.30 Hz, 2 H), 7.55–7.41 (d, *J* = 8.30 Hz, 2 H), 3.75 (m, 1 H), 1.95–1.75 (m, 4 H), 1.49–1.41 (m, 6 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 158.9, 129.8, 124.5, 115.1, 35.2, 28.5, 23.

MS (EI, 70 eV): m/z (%) = 221 (2) [M<sup>+</sup>], 141 (8), 139 (3), 124 (8), 109 (7), 84 (5), 81 (28), 67 (45), 55 (100), 41 (92), 40 (6).

Anal Calcd for  $C_{12}H_{15}NO_3$ : C, 65.14; H, 6.83; N, 6.33. Found: C, 65.41; H, 6.88; N, 6.27.

## 1-(Cyclohexyloxy)-4-methoxybenzene (10)

Pale yellow liquid; yield: 91%.

FT-IR (neat): 2922, 2852, 1664, 1378, 1250, 1230, 1172, 1101, 1072, 961, 894, 723  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 6.65-6.70 (m, 4 H), 3.78 (s, 3 H), 3.65–3.61 (m, 1 H), 1.99–1.75 (m, 4 H), 1.50–1.41 (m, 6 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 151.9, 149.8, 114.5, 75.2, 52.5, 34.1, 29.1, 22.3.

MS (EI, 70 eV): *m/z* (%) = 206 (4) [M<sup>+</sup>], 191 (16), 167 (22), 149 (75), 124 (14), 111 (14), 97 (31), 81 (62), 69 (100), 47 (9), 44 (4).

Anal Calcd for  $C_{13}H_{18}O_2$ : C, 75.69; H, 8.80. Found: C, 76.02; H, 8.88.

## 1-Bromo-4-(4-bromophenoxy)benzene (1p)

Off-white solid; yield: 85%; mp 62 °C

IR (KBr): 3087, 2961, 2925, 2854, 1890, 1647, 1579, 1481, 1399, 1250, 1190, 1161, 1098, 1071, 1006, 868, 824, 645, 494 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.25–8.10 (d, *J* = 8.0 Hz, 4 H), 7.55–7.41 (d, *J* = 8.0 Hz, 4 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.9, 132.8, 120.5, 116.2.

MS (EI, 70 eV): m/z (%) = 330 (7) [M + 2], 328 (13) [M<sup>+</sup>], 326 (7) [M - 2], 221 (6), 219 (6), 183 (5), 168 (12), 139 (12), 122 (42), 105 (59), 85 (65), 83 (100), 43 (93), 41 (44), 40 (19).

Anal Calcd for  $C_{12}H_8Br_2O$ : C, 43.94; H, 2.46. Found: C, 44.74; H, 2.49.

#### 1-(4-Bromophenoxy)-4-methoxybenzene (1r)

Off-white solid; yield: 89%; mp 110-112 °C.

IR (KBr): 3108, 3004, 2978, 2843, 1609, 1586, 1447, 1341, 1297, 1237, 1189, 1160, 1105, 1029, 876, 843, 747  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.21–8.10 (d, *J* = 9.1 Hz, 2 H), 7.10–6.91 (m, 6 H), 3.81 (s, 3 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 158.5, 153.1, 149.8, 131.3, 118.3, 116.0, 114.7, 55.5.

MS (EI, 70 eV): *m/z* (%) = 279 (7) [M<sup>+</sup>], 256 (78), 241 (15), 226 (14), 220 (5), 193 (3), 165 (7), 149 (13), 97 (12), 71 (20), 57 (93), 45 (13), 43 (100).

Anal Calcd for C<sub>13</sub>H<sub>11</sub>BrO<sub>2</sub>: C, 55.94; H, 3.97. Found: C, 55.74; H, 3.99.

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