



# Alkoxylation reactions of aryl halides catalyzed by magnetic copper ferrite



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## ABSTRACT

Copper ferrite ( $\text{CuFe}_2\text{O}_4$ ), which is easy-made, air-stable, low cost, easy separable, and regenerable, was applied as catalyst in an efficient method for C–O coupling reactions between various kinds of unactivated alkyl alcohols and aryl halides. This method only adopts 2.5% mol  $\text{CuFe}_2\text{O}_4$  catalyst and selectively proceeds to C–O bond formation even sensitive substituents exist in the system.

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## 1. Introduction

The formation of C–O bond is very useful in organic synthesis because it occurs in the synthesis of numerous natural products, biological compounds and pharmaceuticals.<sup>1</sup> In recent years, methods using palladium<sup>1a,2,3</sup> have been extensively improved and high catalytic efficiency has been achieved. However, the drawbacks, such as high cost, toxicity, and the utilization of environmental unfriendly phosphine ligands often limit their applications inorganic synthesis. Meanwhile, copper<sup>4,5</sup> systems are cheaper but the recycle of the catalyst is still a challenge. Thus, there is still requirement for the development of less expensive and recyclable catalysts with high efficiency. Herein, we report the magnetic  $\text{CuFe}_2\text{O}_4$  as the catalyst, which couples the inactive alcohols with both aryl and heteroaryl halides successfully and can be easily recycled.

## 2. Results and discussion

The magnetic  $\text{CuFe}_2\text{O}_4$  powder was prepared according to the previous report.<sup>6</sup> The X-ray diffraction (XRD) pattern of this

$\text{CuFe}_2\text{O}_4$  was in good agreement with the standard one (JCPDS34-0425) (Fig. 1). From the TEM and SEM images, it was found that the morphology of the prepared  $\text{CuFe}_2\text{O}_4$  was blocky with many mac-

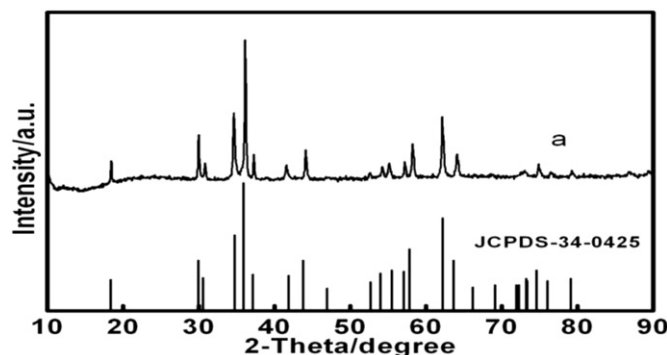


Fig. 1. XRD spectrum of the prepared  $\text{CuFe}_2\text{O}_4$ .

ropores on the surface (Figs. S1–S4, ESI). The magnetization-field plots showed that  $\text{CuFe}_2\text{O}_4$  exhibited ferrimagnetic behavior with a coercivity about 296 Oe and a saturation magnetization about 26 emu/g at 300 K (Fig. S5, ESI).

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Various solvents were examined by choosing iodobenzene (**1a**) and *n*-butyl alcohol (**1b**) as the model substrates and 1,10-phenanthroline as the ligand. The other commonly used polar and non-polar solvents did not supply any products under the experimental conditions. Surprisingly, an 88% yield was reached by using *n*-butyl alcohol (**1b**) as both solvent and substrate (Table 1).

**Table 1**  
Solvent exploration<sup>a</sup>

Entry	Solvent	GC yield [%]
1	NMP	0
2	DMSO	0
3	DMF	0
4	DMAc	0
5	Toluene	0
6	THF	0
7	Dioxane	0
8	—	88 <sup>b</sup>

<sup>a</sup> Reaction conditions were: iodobenzene (0.5 mmol), *n*-butyl alcohol (1.0 mmol), CuFe<sub>2</sub>O<sub>4</sub> (2.5 mol %), 1,10-phenanthroline (5.0 mol %), Cs<sub>2</sub>CO<sub>3</sub> (1.0 mmol, 2.0 equiv), solvent (1.0 mL), 110 °C, under argon atmosphere, 12 h.

<sup>b</sup> 1.0 mL *n*-butyl alcohol was used as both reactant and solvent.

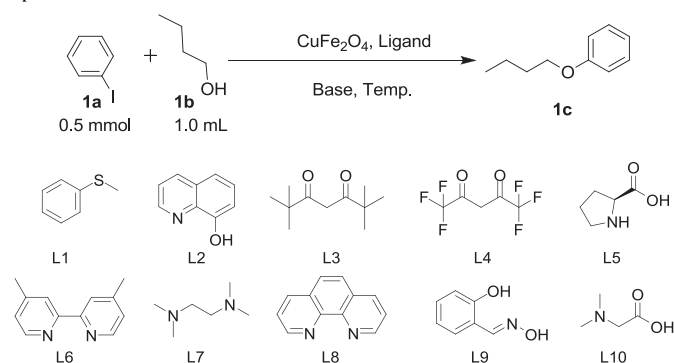
Next, a series of ligands were examined using iodobenzene (**1a**, 0.5 mmol), 10 mol % CuFe<sub>2</sub>O<sub>4</sub>, 20 mol % ligand, 2.0 equiv Cs<sub>2</sub>CO<sub>3</sub>, 110 °C, 12 h and *n*-butyl alcohol (**1b**) as both solvent and substrate (Table 2). Among them, 1,10-phenanthroline (**L8**) gave the highest yield (Table 2, entry 14). In addition, the molar ratio of metal and ligand, temperature, base, and reaction time were also tested. Under the optimized conditions (2.5 mol % CuFe<sub>2</sub>O<sub>4</sub>, 5.0 mol % 1,10-phenanthroline, 2.0 equiv of Cs<sub>2</sub>CO<sub>3</sub>, 110 °C, 12 h reaction time, and under argon atmosphere), an 88% GC yield of butyl phenyl ether (**1c**) was obtained (Table 2, entry 23).

With the optimized conditions, the substrate scope was subsequently investigated (Table 3). Aryl iodides with either electron-donating or electron-neutral groups at the para position reacted with *n*-butyl alcohol smoothly and the corresponding aryl alkyl ethers were obtained with good yields (Table 3, entries 1–3). *Ortho*-substituted iodobenzene was slightly inert and only afforded a yield of 58% (Table 3, entry 4). Interesting, the existence of free amino group was well tolerated, producing the desired product with a 72% yield. No C–N self-coupling product was detected by GC–MS analysis (Table 3, entry 5). Additionally, the system was chemoselective toward iodides, providing a complete replacement of the iodo-group in the presence of a bromo substituent on the aryl ring (Table 3, entry 6). The left C–Br bond was very useful for late-stage modifications.

In order to extend the scope of the proposed catalytic system, the thioetherification had also been studied. As shown in Scheme 1, both alkyl- and aryl thiols<sup>7</sup> afforded good yields also.

The recycle experiment was also carried out adopting iodobenzene and *n*-butyl alcohol as the model substrates and the results were shown in Fig. 2. After the third run, when this catalyst was simply grinded by an agate mortar, the yield raised to 82% dramatically with 2.5 mol % of the used catalyst. In addition, even in the seventh run, 86% yield could also be obtained with 2.5 mol % previous used CuFe<sub>2</sub>O<sub>4</sub>, which indicated that the as-prepared catalyst was highly stable in the reaction system. The XRD

**Table 2**  
Optimization



Entry	Catalyst (mol %)	Ligand (mol %)	Base	T/[°C]	Yield [%] <sup>a</sup>
1	—	—	—	110	n.r.
2	CuFe <sub>2</sub> O <sub>4</sub> (10)	—	—	110	n.r.
3	—	L8 (20)	—	110	n.r.
4	—	L8 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	2%
5	CuFe <sub>2</sub> O <sub>4</sub> (10)	L8 (20)	—	110	n.r.
6	—	—	Cs <sub>2</sub> CO <sub>3</sub>	110	4%
7	CuFe <sub>2</sub> O <sub>4</sub> (10)	L1 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	71%
8	CuFe <sub>2</sub> O <sub>4</sub> (10)	L2 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	48%
9	CuFe <sub>2</sub> O <sub>4</sub> (10)	L3 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	69%
10	CuFe <sub>2</sub> O <sub>4</sub> (10)	L4 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	70%
11	CuFe <sub>2</sub> O <sub>4</sub> (10)	L5 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	73%
12	CuFe <sub>2</sub> O <sub>4</sub> (10)	L6 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	78%
13	CuFe <sub>2</sub> O <sub>4</sub> (10)	L7 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	74%
14	CuFe <sub>2</sub> O <sub>4</sub> (10)	L8 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	87%
15	CuFe <sub>2</sub> O <sub>4</sub> (10)	L9 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	72%
16	CuFe <sub>2</sub> O <sub>4</sub> (10)	L10 (20)	Cs <sub>2</sub> CO <sub>3</sub>	110	79%
17	CuFe <sub>2</sub> O <sub>4</sub> (10)	L8 (20)	K <sub>2</sub> CO <sub>3</sub>	110	<1%
18	CuFe <sub>2</sub> O <sub>4</sub> (10)	L8 (20)	K <sub>3</sub> PO <sub>4</sub>	110	25%
19	CuFe <sub>2</sub> O <sub>4</sub> (10)	L8 (20)	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O	110	23%
20	CuFe <sub>2</sub> O <sub>4</sub> (10)	L8 (20)	Net <sub>3</sub>	110	n.r.
21	CuFe <sub>2</sub> O <sub>4</sub> (10)	L8 (20)	CsOAc	110	n.r.
22	CuFe <sub>2</sub> O <sub>4</sub> (5)	L8 (10)	Cs <sub>2</sub> CO <sub>3</sub>	110	89%
23	<b>CuFe<sub>2</sub>O<sub>4</sub> (2.5)</b>	<b>L8 (5)</b>	Cs <sub>2</sub> CO <sub>3</sub>	<b>110</b>	<b>88%</b>
24	CuFe <sub>2</sub> O <sub>4</sub> (1)	L8 (2)	Cs <sub>2</sub> CO <sub>3</sub>	110	70%
25	CuFe <sub>2</sub> O <sub>4</sub> (2.5)	L8 (5)	Cs <sub>2</sub> CO <sub>3</sub>	100	84%
26	CuFe <sub>2</sub> O <sub>4</sub> (2.5)	L8 (2.5)	Cs <sub>2</sub> CO <sub>3</sub>	110	81%
27	CuFe <sub>2</sub> O <sub>4</sub> (2.5)	L8 (5)	Cs <sub>2</sub> CO <sub>3</sub>	110	82% <sup>b</sup>
28	CuFe <sub>2</sub> O <sub>4</sub> (2.5)	L8 (5)	Cs <sub>2</sub> CO <sub>3</sub>	110	88% <sup>c</sup>
29	CuFe <sub>2</sub> O <sub>4</sub> (2.5)	L8 (5)	Cs <sub>2</sub> CO <sub>3</sub>	110	35% <sup>d</sup>
30	Fe <sub>3</sub> O <sub>4</sub> (2.5)	L8 (5)	Cs <sub>2</sub> CO <sub>3</sub>	110	n.r.

<sup>a</sup> Ar–I (0.5 mmol), CuFe<sub>2</sub>O<sub>4</sub> (10 mol %), ligand (20 mol %), base (2.0 equiv), *n*-BuOH (1.0 mL), 110 °C, 12 h. GC yields.

<sup>b</sup> Cs<sub>2</sub>CO<sub>3</sub> was 1.5 equiv.

<sup>c</sup> Reaction time was 24 h.

<sup>d</sup> 150 mg 4A molecular sieves were added.

patterns indicated that the crystal structure of the CuFe<sub>2</sub>O<sub>4</sub> remained intact after third run (Fig. S7, ESI). This suggested that the loss of the activity mainly came from the aggregation of the CuFe<sub>2</sub>O<sub>4</sub>, which could be observed even by naked eyes. The grinding re-dispersed the catalyst, which resulted in the dramatic yield increase.

Only 4% GC yield was obtained when CuFe<sub>2</sub>O<sub>4</sub> was absent, which implied that the RO<sup>−</sup> nucleophilic attack of Ar–X was not the main mechanism. Aryl radical mechanism could also be excluded because very strong bases, such as *t*-BuOK or *t*-BuONa, were often required to produce the aryl radical in the previous reports about C–H activation of Ar–X.<sup>8</sup> In addition, during our previous report,<sup>9</sup> we found that Cs<sub>2</sub>CO<sub>3</sub> was not strong enough to remove an *ortho*-hydrogen from the Ar–X to produce arylene, which told us that the arylene mechanism was not included. According to the above discuss and the reactivity information of Table 3, we thought that the reaction should proceed through oxidative addition followed by a reductive elimination process. Firstly, Ar–X reacted with CuFe<sub>2</sub>O<sub>4</sub>,

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