Aerobic oxidative coupling of 2-naphthols by simple copper salts: a highly efficient catalytic system in the absence of ligand or carrier

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A ligand-free or carrier-free copper salt system that catalysed aerobic oxidative coupling of 2-naphthols has been established. 1,1'-Bi-2-naphthols were afforded in excellent yields in methanol in the presence of 5 mol % copper (I or II) salts. The coupling reaction could also be performed very well in aqueous solvents.

Keywords: oxidative coupling, copper salt, 2-naphthol, binaphthol

1,1'-Bi-2-naphthol and its derivatives have received intense attention due to wide applications of their enantiomers as chiral inducers in synthetic chemistry.[1] Oxidative coupling of 2-naphthols represents a well-established method for preparation of binaphthols. For example, stoichiometric reagents, such as $FeCl_3$,[2] $Mn(acac)_3$[3] and Cu(II)-amine complex,[4] have been used for the coupling of 2-naphthols. However, these routes suffer from stoichiometric amounts of waste, which must be disposed with special care. A great development of this coupling was made by Pac.[5] Using 0.2 equiv supported catalyst ($CuSO_4/Al_2O_3$), binaphthol was obtained in up to 97% yield in chlorobenzene at 140°C. This is the highest yield reported to date. Unfortunately, 3-(methoxycarbonyl)-2-naphthol was very unreactive. Many ligands have also been employed for the coupling reaction. For instance, Nakajima and coworkers used a catalytic amount of [Cu(OH)Cl·(TMEDA)] as catalyst and afforded binaphthol in 92% yield.[6] Uang et al obtained good results using [$VO(acac)_2$] (92% for binaphthol).[7] Cu(II)-Schiff base as catalyst has also been documented.[8] However, most of these methods require the complex preparations of catalysts. Recently, our group developed the coupling reaction catalysed by Cu(I or II) and commercially available N-methylimidazole, and obtained binaphthol in 91% yield.[9]

As continuation of our research on simple copper salt systems,[10] here we report a more simple and efficient aerobic oxidative coupling of 2-naphthols. Using only 5 mol % copper (I or II) salts, without any other ligands or carriers, the coupling reaction was performed in methanol to give corresponding 1,1'-bi-2-naphthols in excellent yields (Scheme 1).

In view of successful application of protic solvents in C–N coupling in our laboratory,[10] CH_3OH was first chosen as reaction solvent. Not surprisingly, binaphthol (**2a**) was obtained in good yield. Then five other solvents, CH_2Cl_2, C_2H_5OH, CH_3COCH_3, THF and CH_3CN, were examined. The results showed CH_3OH was the best solvent. Temperature is another important factor. Although the coupling reaction could run either under ice water, at room temperature or refluxing, it took longer time and gave lower yields below 50°C. When this reaction was carried out in methanol and refluxed for 10 h, excellent yields were obtained.

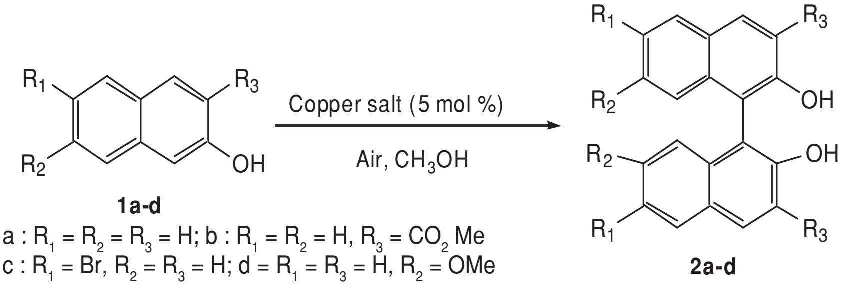
Table 1 Effect of copper salts on the coupling of 2-naphthol[a]

Entry	Copper salt	Yield/%[b]
1	CuCl	93
2[c]	CuCl	93
3	CuBr	57
4	CuI	trace
5	$CuCl_2$	53
6	$CuCl_2·2H_2O$	55
7	$Cu(NO_3)_2·3H_2O$	91
8	$Cu(OAc)_2·H_2O$	85
9	$CuSO_4$	31
10	$CuSO_4·5H_2O$	34

[a]2-Naphthol (1 mmol), copper salt (5 mol %) in methanol (10 ml) were refluxed 10 h under air. [b]isolated yield. [c]10 mol % CuCl was used and refluxed 8.5 h.

The effects of different copper salts on the coupling reaction have also been investigated. As shown in Table 1, when CuCl was used, binaphthol was obtained in 93% yield (Table 1, entry 1). However, if CuBr or CuI were used, the yields were quite low, which indicated that the anion played an important role in the coupling reaction. Copper(II) salts, $Cu(NO_3)_2·3H_2O$ and $Cu(OAc)_2·H_2O$, also demonstrated excellent catalytic activity (Entries 7 and 8). On the other hand, we can see that the presence of crystal water in the copper salts had no notable influence on the coupling (Entries 5, 6, 9 and 10). Moreover, no improvement of the yield was observed with increase of copper salt (Entry 2). It turned out that 5 mol % of copper salts was sufficient.

Several 2-naphthols have been employed for this catalytic coupling. 2-Naphthol afforded up to 93% yield (Table 2, entry 1). When 3-(methoxycarbonyl)-2-naphthol was introduced, the corresponding product **2b** was gained in almost quantitative yield (Entry 2). It is implied that the electron-withdrawing group at the 3-postion of the naphthol ring restrained the formation of byproducts. At the same time, we carried out



1a-d

a : $R_1 = R_2 = R_3 = H$; b : $R_1 = R_2 = H$, $R_3 = CO_2Me$
c : $R_1 = Br$, $R_2 = R_3 = H$; d = $R_1 = R_3 = H$, $R_2 = OMe$

2a-d

Scheme 1

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Table 2 Simple copper salt catalysed the coupling of 2-naphthols[a]

Entry	Naphthol	Time/h	Product	Yield/%[b]
1	**1a**	10	**2a**	93
2	**1b**	8	**2b**	99
3	**1c**	12	**2c**	74
4	**1d**	7	**2d**	86

[a]2-Naphthols (1 mmol), CuCl (5 mol %) in methanol (10 ml) were refluxed under air. [b]isolated yield.

Table 3 Coupling reaction in different aqueous solvent[a]

Entry	Solvent/(v:v)	Product	Yield/%[b]
1	H_2O	**2a**	24
2	CH_3OH-H_2O (0.2:1)	**2a**	83
3	CH_3OH-H_2O (1:1)	**2a**	87(93)[c]
4	CH_3OH-H_2O (5:1)	**2a**	90
5	C_2H_5OH-H_2O (1:1)	**2a**	85
6	THF-H_2O (1:1)	**2a**	67(0)[d]
7	CH_3OH-H_2O (1:1)	**2b**	99
8	C_2H_5OH-H_2O (1:1)	**2b**	92

[a]2-Naphthols (1 mmol), CuCl (5 mol %) in aqueous solvent were refluxed 24 h under air. [b]isolated yield. [c]Data in parentheses are the yield in methanol. [d]Data in parentheses are the yield in THF.

a preliminary exploration of other two 2-naphthols and also obtained good results (Entries 3, 4).

Water as a reaction medium is very important for organic synthesis. To date, few examples of the coupling of 2-naphthols were carried out in aqueous media.[2b,11] We tried our coupling reaction in aqueous solvent. When water was used solely, the yield was poor (Table 3, entry 1). This may be attributed to the poor solubility of reactants in water. CH_3OH was hence added into water. As shown in Table 3, only a small quantity of CH_3OH was employed, but the result was improved significantly (Entry 2), and the yields improved with increase of CH_3OH in mixed solvents (Entries 3, 4). Subsequently, we examined the coupling reaction in other mixed solvents, such as C_2H_5OH-H_2O and THF-H_2O in 1:1 ratio, and the corresponding products were also generated in moderate to excellent yields (Entries 5-8).

In summary, we have developed a very simple and efficient aerobic oxidative coupling of 2-naphthols by simple copper salts in methanol. The coupling reaction could also be performed very well in aqueous solvents. This method, involving no ligand or carrier, should have wide applicability for the preparation of binaphthols.

Experimental

Melting points were determined on a micro-melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker AV-300 spectrometer. Mass spectra were measured on a Finnigan-LCQ^{DECA} instrument.

General experimental procedure: A 25 ml two-necked round-bottom flask was charged with 2-naphthols (1 mmol), copper salt (5 mol %) and methanol (10 ml), then the mixture was refluxed under an atmosphere of air. Progress of the reaction was monitored by TLC. After completion of the reaction the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc–petroleum ether) to give the corresponding binaphthols.

1,1'-Binaphthalene-2,2'-diol **2a:** m.p. 215–217°C (lit.[5] 216–218°C); ^1H NMR ($CDCl_3$, ppm) δ: 5.04 (s, 2H), 7.15 (d, 2H, *J* = 8.25 Hz), 7.28–7.47 (m, 6H), 7.90 (d, 2H, *J* = 7.77 Hz), 7.98 (d, 2H, *J* = 8.94 Hz); ESI-MS (*m/z*, RA%): 285 (M-H^+, 100).

3,3'-Bismethoxycarbonyl-1,1'-binaphthyl-2,2'-diol **2b:** m.p. 275–277°C (lit.[5] 276–278°C); ^1H NMR ($CDCl_3$, ppm) δ: 4.06 (s, 6H), 7.14–7.18 (m, 2H), 7.33–7.36 (m, 4H), 7.91–7.94 (m, 2H), 8.69 (s, 2H), 10.72 (s, 2H); ESI-MS (*m/z*, RA%): 401 (M-H^+, 100).

6,6'-Dibromo-1,1'-binaphthyl-2,2'-diol **2c:** m.p. 194–196°C (lit.[5] 197–198°C); ^1H NMR ($CDCl_3$, ppm) δ: 5.02 (s, 2H), 6.97 (d, 2H, *J* = 8.94 Hz), 7.36 (d, 2H, *J* = 2.04 Hz), 7.41 (d, 2H, *J* = 9.06 Hz), 7.90 (d, 2H, *J* = 9.00 Hz), 8.06 (d, 2H, *J* = 1.95 Hz); ESI-MS (*m/z*, RA%): 443 (M-H^+, 100).

7,7'-Dimethoxy-1,1'-binaphthyl-2,2'-diol **2d**: m.p. 150–152°C (lit.[5] 151–152°C); ^1H NMR ($CDCl_3$, ppm) δ: 3.58 (s, 6H), 5.05 (s, 2H), 6.48 (d, 2H, *J* = 2.40 Hz), 7.03 (2d, 2H, *J* = 2.49 and 2.52 Hz), 7.23 (d, 2H, *J* = 8.88 Hz), 7.79 (d, 2H, *J* = 8.88 Hz), 7.88 (d, 2H, *J* = 8.82 Hz); ESI-MS (*m/z*, RA%): 345 (M-H^+, 100).

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