

Lewis acid-assisted oxidative cross-coupling of 2-naphthol derivatives with copper catalysts[☆]

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Abstract

The oxidative coupling reactions between 2-naphthol and 3-hydroxy-2-naphthoic acid derivatives using a copper catalyst under an O₂ atmosphere in the presence of a catalytic amount of the Lewis acid, such as Yb(OTf)₃, were carried out. A highly cross-coupling selective or specific reaction effectively proceeded to give a C₁ symmetrical BINOL derivative.

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1. Introduction

The oxidative coupling of 2-naphthol derivatives using a metal catalyst, such as copper or vanadium complex, is a simple and effective synthetic method for the chiral 1,1'-bi-2-naphthol (BINOL) derivatives.² The oxidative cross-coupling reaction is attractive and distinguished by directly producing a BINOL with a C₁ skeleton from the homo-coupling, which affords a C₂ symmetrical BINOL. However, the reaction of a 1:1 mixture of two differently substituted 2-naphthol derivatives generally produces a mixture of three coupling products, that is, two homo-coupling and one cross-coupling (Scheme 1), and there have been few studies about the catalytic and selective cross-coupling processes.^{3,4}

Recently, we reported that the oxidative coupling between 2-naphthol and 3-hydroxy-2-naphthoate derivatives using CuCl-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) [CuCl-Phbox] catalyst (Fig. 1)⁵ proceeds in a highly cross-coupling selective manner.⁶ In addition, it was found that the specific

cross-coupling reaction takes place regardless of the ligand structure of the copper catalyst when 3-hydroxy-2-naphthamide bearing a secondary amide group is used as the substrate.⁷ However, during these reactions, the cross-coupling and stereoselectivities were significantly affected by the substrate structure, and still have not been sufficiently controlled.

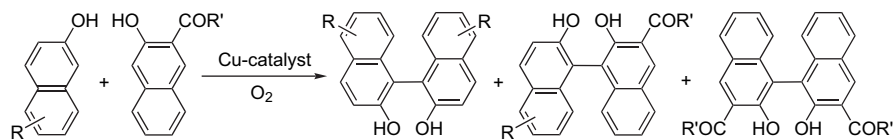
The oxidative coupling reaction involves a radical coupling step, in which the radical species generated by the one-electron oxidation of the substrate mediates the coupling process. On the other hand, a Lewis acid catalyst is often used as a powerful tool for controlling the selectivity during the radical reaction, most of which are related to the radical addition reaction.⁸ Thereupon, the coupling reaction between 2-naphthol and 3-hydroxy-2-naphthoate derivatives with the copper catalysts in the presence of a catalytic amount of the Lewis acid was initially examined, and the significant effect of ytterbium trifluoromethanesulfonate [Yb(OTf)₃] on the cross-coupling selectivity, as well as the stereoselectivity was observed.^{1,9}

In this study, further investigations on the oxidative cross-coupling reaction with the binary catalyst system of the copper complex and the Lewis acid were carried out. The effects of various Lewis acids and substrates, such as 2-naphthol and

[☆] See Ref. 1.

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Scheme 1.

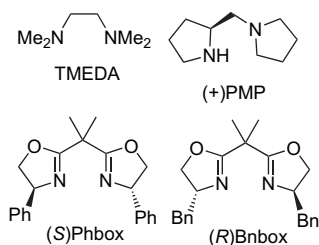


Figure 1. Structure of ligands.

3-hydroxy-2-naphthoic acid derivatives, on the cross-coupling and stereoselectivities were examined. The cross-coupling specific process was then extended to the copolymerization of 6,6'-dihydroxy-2,2'-binaphthalene and dihexyl 6,6'-dihydroxy-2,2'-binaphthalene-7,7'-dicarboxylate affording a poly-(BINOL) with an alternative copolymer structure.¹⁰

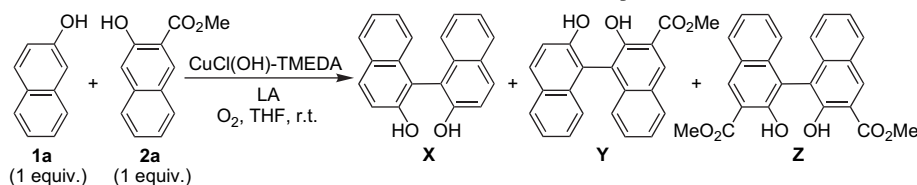
2. Results and discussion

The effect of the Lewis acid as an additive on the oxidative coupling between 2-naphthol **1a** and methyl 3-hydroxy-2-naphthoate **2a** (1:1) with the CuCl(OH)–TMEDA¹¹ (Fig. 1) catalyst at room temperature under an O₂ atmosphere was examined (Table 1). The reaction with 0.2 equiv of the copper catalyst in the absence of Lewis acid for 48 h resulted in

a low yield with the cross-coupling selectivity of 88% (entry 1). A catalytic amount of the Lewis acid showed a marked effect on the cross-coupling selectivity during the oxidative coupling reaction. Especially, Yb(OTf)₃ and Y(OTf)₃ gave a cross-coupling product in a good yield (entries 2–4 and 6). Although the reaction with the other Lewis acids, such as Sc(OTf)₃, Zn(OTf)₂, Ti(O^{*i*}Pr)₄, etc. also proceeded in a cross-coupling specific manner, the product was obtained in a much lower yield (entries 5 and 7–11). The catalyst ratio of the copper and Lewis acid also affected the coupling yield (entries 2–4). The Lewis acid catalyst significantly controls the cross-coupling selectivity during the radical coupling reaction, and some rare earth metal triflates successfully promoted it.

The asymmetric oxidative coupling reaction of **1a** and **2a** using the CuCl–Phbox catalyst in the presence of various Lewis acids was then carried out (Table 2). The cross-coupling specific reaction again proceeded when Lewis acid was used as the co-catalyst. Although the reaction with Sc(OTf)₃ resulted in a poor yield (entry 3), the salts of zinc and titanium, in addition to Yb(OTf)₃ and Y(OTf)₃, also afforded a cross-coupling product in a high yield (entries 2, 3, 5, and 6). However, the observed stereoselectivity for the reactions with these catalyst systems was lower than that for the reaction without the Lewis acid (entry 1).

Table 1
Oxidative cross-coupling of **1a** and **2a** with CuCl(OH)–TMEDA in THF at rt under an O₂ atmosphere



Entry	CuCl(OH)–TMEDA (equiv)	LA (equiv)	Time (h)	Cross-coupling selectivity ^a (%)	Yield ^b (%)
1	0.2	—	48	88 ^c	47
2	0.1	Yb(OTf) ₃ (0.2)	48	>99	78
3	0.2	Yb(OTf) ₃ (0.1)	48	>99	91
4	0.1	Yb(OTf) ₃ (0.1)	24	98 ^d	81
5	0.1	Sc(OTf) ₃ (0.1)	48	>99	50
6	0.1	Y(OTf) ₃ (0.1)	48	>99	77
7	0.1	Mg(OTf) ₂ (0.1)	48	>99	68
8	0.1	Cu(OTf) ₂ (0.1)	48	>99	68
9	0.1	Zn(OTf) ₂ (0.1)	72	>99	29
10	0.1	Ti(O ^{<i>i</i>} Pr) ₄ (0.1)	48	>99	38
11 ^e	0.1	Ti(O ^{<i>i</i>} Pr) ₄ (0.1)	72	>99	65

^a Determined from isolated yields.

^b Isolated yield of cross-coupling product Y.

^c X/Y/Z=12:88:0.

^d X/Y/Z=2:98:0.

^e Solvent=CH₂Cl₂.

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