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Highly selective oxidative cross-coupling of 2-naphthol derivatives with chiral copper(I)–bisoxazoline catalysts

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Abstract—The asymmetric oxidative coupling reaction of 3-hydroxy-2-naphthoate and 2-naphthol derivatives with the CuCl–(*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) catalyst under an O_2 atmosphere was carried out. The reaction proceeded in a highly cross-coupling selective manner (⩽99.7%) with a moderate enantioselectivity of up to 65%.

Axially dissymmetric 1,1′-bi-2-naphthol derivatives are very important and versatile chiral auxiliaries, and have been extensively utilized in asymmetric syntheses, catalyzes, and resolutions.[1] From this point of view, there has been an intense interest in the preparation of the optically active binaphthols. The catalytic asymmetric oxidative coupling reaction of 2-naphthols with chiral metal catalysts, such as Cu(I), Ru(II), and V(IV), is one of the most facile methods for their synthesis,[2–4] and the homo- or self-coupling of various 2-naphthols affording a symmetrical binaphthol skeleton has been mainly studied. In contrast, there are few reports on the catalytic cross-coupling reaction leading to a binaphthol having an unsymmetrical structure, although several reactions using a stoichiometric amount of a metal complex were reported.[5] Only the report by Kozlowski and co-workers, on the catalytic asymmetric oxidative cross-coupling reaction between 2-naphthol **1a** and methyl 3-hydroxy-2-naphthoate **2a** with the $CuBF_4$–(*S*,*S*)-1,5-diaza-*cis*-decalin catalyst has recently appeared,[6] in which the cross-coupling product was obtained in a poor yield (8%) with an enantioselectivity of 72% ee (*R*).

We reported the first synthesis of the poly(1,1′-bi-2-naphthol) derivative, poly(2,3-dihydroxy-1,4-naphthylene), through the asymmetric oxidative coupling polymerization of the commercially available monomer, 2,3-dihydroxynaphthalene, with a novel copper(I) catalyst system, CuCl–(*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) [(*S*)Phbox], at room temperature under an O_2 atmosphere, although the diamines, such as (+)-1-(2-pyrrolidinylmethyl)pyrrolidine [(+)-PMP] and (−)-sparteine [(−)Sp] (Fig. 1), which are well known as the conventional ligand for the copper catalyst of the asymmetric oxidative coupling, hardly showed a polymer productivity.[7]

During the course of our study, we found that this catalyst system is also effective for the cross-coupling reaction between 2-naphthol derivatives (**1**) and 3-hydroxy-2-naphthoates (**2**) (Scheme 1).

The results of the reaction between **1a** and the methyl ester **2a** using various copper(I) catalysts are listed in Table 1. During the reaction with (+)-PMP, the homo-coupling product of **2a** (**Z**) was predominantly produced (entry 1), whereas CuCl–(−)Sp preferentially afforded a cross-coupling compound (**Y**) with a high

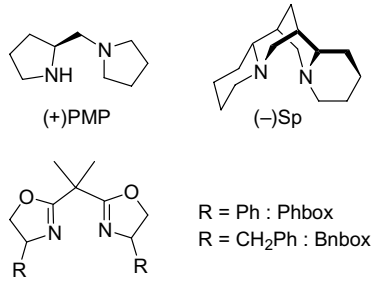

Figure 1. Chiral ligands.

Keywords: Binaphthol; Cross-coupling; Asymmetric oxidative coupling.
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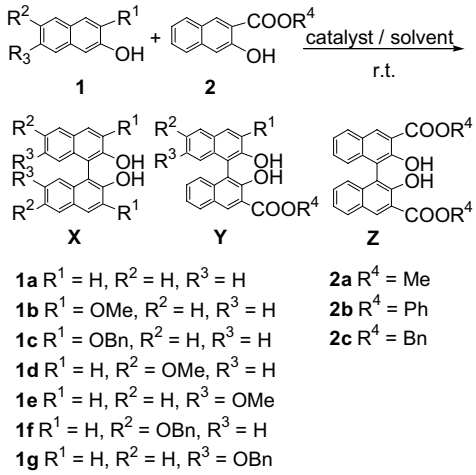

Scheme 1.

selectivity (93.8%) but in a poor yield (14%) (entry 2). These complexes did not show any catalyst activity. As is the case with the (*S*)Phbox ligand, in contrast, the cross-coupling product was obtained in a good yield with the high cross-coupling selectivity of 95.8% (entry 3), although the product showed a lower enantioselectivity, 10% ee (*S*), than that of the cross-coupling product obtained using the (−)Sp ligand (76% ee (*S*)). The reaction at the low temperature of −20 °C resulted in a lower cross-coupling yield with an opposite and poor enantioselectivity, while it showed the highest cross-coupling selectivity of 99.7% (entry 4). The solvent CH_2Cl_2 and the structure of the bisoxazoline ligand, such as (*R*)Bnbox, also significantly affected the catalyst activity and stereoselectivity, which were lower than those observed for the reaction with (*S*)Phbox in THF, although high cross-coupling ratios were again observed (entries 5 and 6).

Table 2 shows the results of the cross-coupling reaction between various 2-naphthol derivatives and 3-hydroxy-2-naphthoates using the CuCl–(*S*)Phbox catalyst at room temperature for 3 h. The absolute configuration of the cross-coupling compounds **4**–**12** was determined by CD measurement.[5b,c] Although the optical purity of the cross-coupling compound **3** was not able to be determined by a high performance liquid chromatographic (HPLC) analysis due to its mostly insoluble nature in EtOH and isopropanol, the small specific rotation value ($[\alpha]_D$ +1.0) and the CD intensity suggest that there is almost no enantioselectivity (entry 1). Both the cross-coupling selectivity and the enantioselectivity were significantly influenced by the structures of the substrates, **1** and **2**. The methyl and benzyl esters, **2a** and **2c**, afforded coupling products with a high **Y**-ratio, whereas the coupling reaction of the phenyl ester **2b** with **1a**,**b**, and **1c** showed lower cross-coupling selectivities (71.5–86.4%) (entries 3–5). The enantioselectivity during the latter cross-coupling reaction using **2b**, however, was much higher than that observed for the former reactions. For example, the coupling product **7** obtained from **1c** and **2b** exhibited a cross-coupling selectivity of 85.2% and an enantioselectivity of 65% ee (*R*).

Since the reaction of **2b** demonstrated a higher stereoselectivity for **Y**, the effect of the substituent position on the 2-naphthol was investigated (entries 7–10). The 6-substituted 2-naphthols, such as **1d** and **1f**, gave a cross-coupling product with the high selectivities of 97.3% and 98.7%, respectively, but with a poor ee value of 3% (*S*). The 2-naphthols having a substituent at the 7-position, **1e** and **1g**, in contrast, showed a much higher enantioselectivity (51% and 58% ee (*R*)), although they are still lower than that of the products obtained from the 3-substituted 2-naphthols, **1b** and **1c**. The position of the substituent on the 2-naphthol significantly affected the enantioselectivity, as well as the cross-coupling selectivity.

During the coupling reaction with CuCl–(*S*)Phbox, the catalytic cross-coupling reaction selectively proceeded. The following is one of the plausible mechanisms: the naphthols bearing the ester moiety may act as an acceptor molecule in the coupling reaction with the copper(I)–bisoxazoline catalyst due to its electron-deficient character, while the one-electron oxidation should be predominantly promoted on the other substrate, the 2-naphthols, to give a radical intermediate, and then the cross-coupling reaction between these two naphthyls may selectively occur.[5a,e]

Table 1. Asymmetric oxidative cross-coupling reaction between **1a** and **2a**[a]

Entry	Catalyst	Time (h)	Coupling ratio **X**:**Y**:**Z**[b]	Cross-coupling product **Y**	
				Yield[c] (%)	ee[d] (%)
1	CuCl–(+)-PMP	48	1.8:37.8:60.4	9	2 (*S*)
2	CuCl–(−)Sp	5	6.0:93.8:0.2	14	74 (*S*)
3	CuCl–(*S*)Phbox	3	0.3:95.8:3.9	87	10 (*S*)
4[e]	CuCl–(*S*)Phbox	5	0:99.7:0.3	45	3 (*R*)
5[f]	CuCl–(*S*)Phbox	3	0.4:94.4:5.2	54	2 (*R*)
6	CuCl–(*R*)Bnbox	5	0.6:95.3:4.1	68	5 (*R*)

[a] Conditions: [CuCl]/[ligand]/[**1a**]/[**2a**] = 0.20:0.25:0.5:0.5 [**1a**] = 0.065 M, temperature = rt, O_2 atmosphere.
[b] Determined by ^1H NMR analysis and isolated yields.
[c] Isolated yield.
[d] Determined by HPLC analysis (Chiralpak AD).
[e] Reaction temperature = −20 °C.
[f] Solvent = CH_2Cl_2.

Table 2. Asymmetric oxidative cross-coupling reaction with CuCl–(*S*)Phbox[a]

Entry	1	2	Coupling ratio **X**:**Y**:**Z**[b]	Cross-coupling product **Y**		
				Y	Yield[c] (%)	ee[d] (%)
1	**1b**	**2a**	6.8:93.2:0	**3**	75	ND
2	**1c**	**2a**	5.5:91.8:2.7	**4**	86	28 (*R*)[e]
3	**1a**	**2b**	5.0:86.4:8.6	**5**	72	55 (*R*)
4	**1b**	**2b**	26.6:71.5:1.9	**6**	55	64 (*R*)
5	**1c**	**2b**	12.9:85.2:1.9	**7**	73	65 (*R*)
6	**1a**	**2c**	0:96.4:3.6	**8**	84	9 (*S*)
7	**1d**	**2b**	0:97.3:2.7	**9**	81	3 (*S*)
8	**1e**	**2b**	3.9:90.4:5.7	**10**	71	51 (*R*)
9	**1f**	**2b**	0:98.7:1.3	**11**	76	3 (*S*)
10	**1g**	**2b**	1.3:93.0:5.7	**12**	63	58 (*R*)

[a] Conditions: [CuCl]/[(*S*)Phbox]/[**1**]/[**2**] = 0.20:0.25:0.5:0.5, [**1**] = 0.065 M, solvent = THF, O_2 atmosphere, temperature = rt, time = 3 h.
[b] Ratio of isolated yields.
[c] Isolated yield.
[d] Determined by HPLC analysis (Chiralpak AS or AD).
[e] Enantioselectivity of the homo-coupling products of **1c** and **2a** was 41% ee (*S*) and 37% ee (*R*), respectively.

In conclusion, the asymmetric oxidative cross-coupling reaction between two differently substituted 2-naphthol derivatives with the CuCl–(*S*)Phbox catalyst was accomplished. The cross-coupling and enantioselectivities were significantly affected by the structures of the 2-naphthol.

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Supplementary data

CD spectra of **4**–**12** are available. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.06.098.

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