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Oxidative cross-coupling leading to 3-amido substituted 1,1′-bi-2-naphthol derivatives

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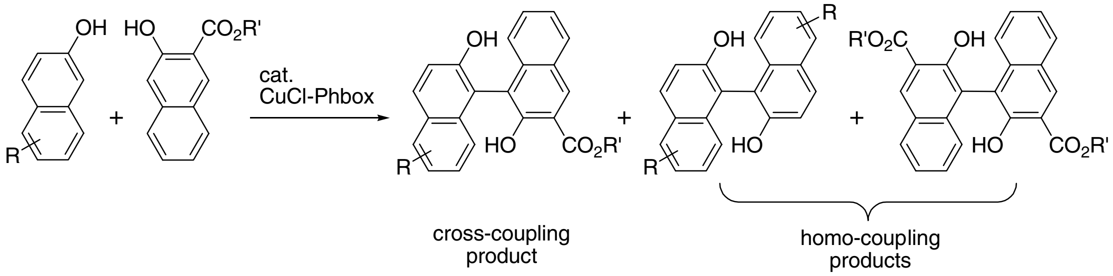
Abstract—The oxidative coupling of 2-naphthol and 3-hydroxy-2-naphthamide with various copper catalysts under an O_2 atmosphere was performed. The reaction proceeded in a cross-coupling specific manner when the substrate has a secondary amido group.

1,1′-Bi-2-naphthol (BINOL) is among the most important and versatile chiral auxiliaries in both catalytic and stoichiometric reactions. The oxidative coupling of the 2-naphthol derivatives is a facile and practical preparation method for the BINOL framework, and many metal catalysts have been developed.[1] However, most of these reported reactions involve the homo-coupling affording C_2 symmetrical BINOLs. The oxidative cross-coupling reaction directly produces a C_1 BINOL skeleton, which having a substituent at the 3-position, is interesting as a chiral ligand, because the *ortho*-site of the hydroxyl group is close to the reaction center.

For example, the oxidative coupling of a 1:1 mixture of 2-naphthol and 3-hydroxy-2-naphthoate derivatives gives three coupling products, that is, a cross-coupling and two homo-coupling ones (Scheme 1). Although several reports on the cross-coupling selective reactions with an excess amount of the copper complex are available,[2] little is known concerning the catalytic process. Recently, we attained the asymmetric oxidative cross-coupling reaction using the CuCl-2,2′-isopropylidenebis-(4-phenyl-2-oxazoline) [CuCl-Phbox] catalyst (Fig. 1).[3] On the other hand, the alternative and stepwise routes to a similar C_1-type BINOL, that is, the *ortho*-substitution of BINOL via the anionic Fries rearrangement,[4] have been reported.

In this study, the oxidative coupling reaction of 2-naphthol (**1**) and 3-hydroxy-2-naphthamide, **2a–e** (Fig. 2) with various copper catalysts was carried out, and it was found that the reaction of **2** with a secondary amide group proceeds in a cross-coupling specific manner to give a coupling product **3**. This cross-coupling specific



Scheme 1.

Keywords: Binaphthol; Cross-coupling; Oxidative coupling.

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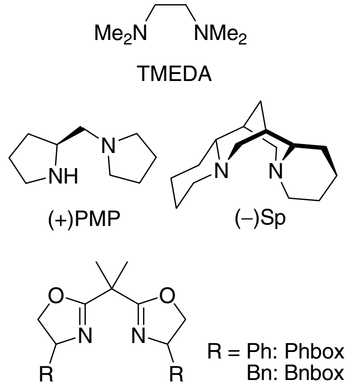


Figure 1. Ligands.

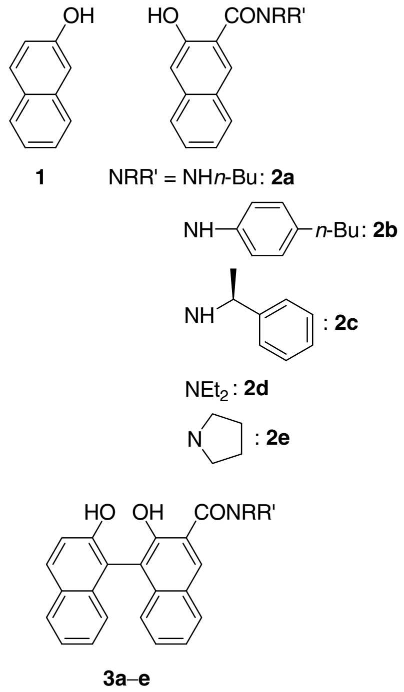


Figure 2. Substrates and cross-coupling products.

oxidative coupling was further used for the polymerization of a novel monomer, *N*-*n*-butyl-6,6′-dihydroxy-2,2′-binaphthalene-7-carboxamide (**4**), affording a poly(BINOL) with a head-to-tail main-chain structure.

Table 1. Oxidative cross-coupling of **1** and **2a** with various copper catalysts[a]

Run	Catalyst	Time (h)	Yield[b] (%)	ee[c] (%)
1	CuCl(OH)-TMEDA	72	60	—
2	CuCl-(+)PMP	72	42	22 (*S*)
3	CuCl-(−)Sp	72	78	60 (*S*)
4	CuCl-(*S*)Phbox	28	87	41 (*S*)
5	CuCl-(*R*)Bnbox	72	75	46 (*R*)

[a] Conditions: [**1**]/[**2a**]/[Cu] = 0.5/0.5/0.05, solvent = THF, temp = rt, O_2 atmosphere.

[b] Isolated yield of cross-coupling product **3a** (cross-coupling selectivity >99%).

[c] Determined by HPLC (Chiralpak AS-H).

The oxidative coupling reaction of **1** and **2a** (1:1) with various copper catalysts in THF at room temperature under an O_2 atmosphere was examined (Table 1). The catalytic cross-coupling reaction of **1** and methyl 3-hydroxy-2-naphthoate with the TMEDA-, PMP-, and Sp-complexes was unsuccessful as previously reported.[3] For example, the reaction with the CuCl-(+)PMP catalyst for 48 h afforded the homo-coupling compound of the latter substrate as the main product (selectivity: 60%) and the cross-coupling one was obtained in a 9% yield (selectivity: 38%).[3a] In marked contrast, these diamine complexes catalytically produced **3a** in moderate yields with a cross-coupling selectivity of >99% (entries 1–3). The reaction with the CuCl-bisoxazoline catalysts, such as (*S*)Phbox and (*R*)Bnbox, also resulted in a >99% selectivity (entries 4 and 5) to give **3a**. Accordingly, for the reaction of **1** and **2a**, the cross-coupling specific reaction takes place regardless of the ligand structure. The CuCl-Phbox catalyst shows the highest catalyst activity, whereas the (−)Sp ligand gave the coupling product with the highest ee value of 60% (*S*).

Table 2 lists the results of the oxidative coupling reaction between **1** and **2b–e** with CuCl(OH)-TMEDA and CuCl-Phbox. The coupling of **2b** bearing a secondary aromatic amide group again afforded **3b** in a cross-coupling specific manner with a moderate yield (entries 1 and 2). However, the reaction of 3-hydroxy-2-naphthamides with a tertiary amide group, such as **2d** and **2e**, in THF gave a mixture of two coupling products, the cross-coupling (major one)[4] and the homo-coupling of **2** (minor one) (entries 6, 7, 9, and 10). The solvent also influenced both the catalyst activity and selectivity. The reaction in dichloromethane produced **3** with a much higher cross-coupling selectivity and yield than those for the reaction in THF, while the stereoselectivity of obtained **3** was significantly reduced (entries 8 and 11). The amide structure, probably its steric and electronic effects as well as the hydrogen bonding effect, plays an important role in the coupling selectivity, and the secondary amide group as an *ortho*-substituent is quite effective.

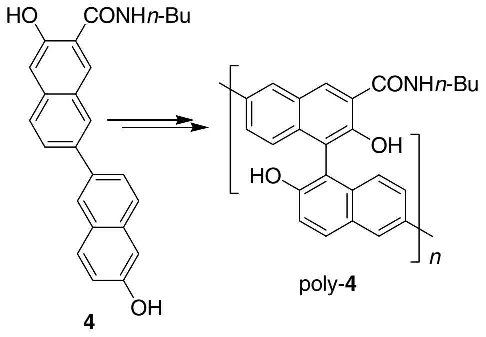
A plausible mechanism for the catalytic cross-coupling was suggested as follows: the β-naphthol with the electron-withdrawing group works as an acceptor, while the one-electron oxidation is promoted on the other substrate, 2-naphthol, by the copper(II) catalyst that generates a radical intermediate, which concertedly and selectively reacts with the acceptor molecule.[2a–c,3,5] The above coupling results for the 3-hydroxy-2-naphthamides adequately support this mechanism.

The cross-coupling specific oxidative coupling reaction between 2-naphthol and 3-hydroxy-2-naphthamide was developed. This method was then used for the polymerization to produce a novel poly(BINOL).[6] The polymerization of 6,6′-bi-2-naphthol with *N*-*n*-butylamide group, **4**, with various copper catalysts in THF at room temperature under an O_2 atmosphere was conducted (Scheme 2), and the results are summarized in Table 3. The polymerization with TMEDA and (−)Sp gave a methanol–ethyl acetate–1 N HCl (2.5/7.5/1, v/v/v)-insoluble

Table 2. Oxidative cross-coupling of **1** and **2**[a]

Run	2	Catalyst	Time (h)	Product	Cross-coupling selectivity[b] (%)	Yield[c] (%)	ee[d] (%)
1	**2b**	CuCl(OH)-TMEDA	72	**3b**	>99	49	—
2		CuCl-(*S*)Phbox	48		>99	54	53 (*R*)[e]
3	**2c**	CuCl(OH)-TMEDA	72	**3c**	>99	43	1 (*R*)[f]
4		CuCl-(*S*)Phbox	30		>99	65	16 (*S*)[f]
5		CuCl-(*R*)Phbox	48		>99	66	46 (*R*)[f]
6	**2d**	CuCl(OH)-TMEDA	72	**3d**	78[g]	50	—
7		CuCl-(*S*)Phbox	24		77[g]	53	27 (*S*)
8[h]		CuCl-(*S*)Phbox	9		95[g]	91	~0
9	**2e**	CuCl(OH)-TMEDA	72	**3e**	97[g]	30	—
10		CuCl-(*S*)Phbox	48		87[g]	61	38 (*S*)
11[h]		CuCl-(*S*)Phbox	24		98[g]	93	19 (*S*)

[a] Conditions: [**1**]/[**2**]/[Cu] = 0.5/0.5/0.05, solvent = THF, temp = rt, O_2 atmosphere.
[b] Ratio of isolated yields.
[c] Isolated yield of cross-coupling product **3**.
[d] Determined by HPLC (Chiralpak AD-H).
[e] Determined by HPLC (Chiralpak AS-H).
[f] de, %, Determined from isolated yields.
[g] Homo-coupling product of **2** was obtained as a by-product.
[h] Solvent = CH_2Cl_2.



Scheme 2.

polymer in no and low yields, respectively (entries 1 and 2). In contrast, the bisoxazoline catalyst systems produced poly-**4** in a 64% yield (entries 3 and 4).

The obtained polymers should be composed of the cross-coupling unit as demonstrated in the model coupling reaction of **1** and **2a** (Table 1). This is also supported by the ^1H NMR analysis, which shows a simple and sharp peak pattern assigned as the polymer with a regular head-to-tail configuration and without any homo-coupling units. The CD spectral patterns demonstrated that the poly-**4**'s obtained with (−)Sp and (*S*)Phbox preferentially have an *S*-configuration, whereas the polymer prepared by (*R*)Bnbox mainly consists of the *R*-structure.[6,7] These results are again quite comparable to those of the coupling reaction of **1** and **2a**. The stereocontrol effect for the (−)Sp catalyst system during the polymerization, however, is much lower than that of (*S*)Phbox, in contrast to the coupling reaction, based on the $[\alpha]_D$ value and the CD absorption intensity. This may be due to the fact that the 2,2′-binaphthyl monomer structure affects the coupling stereoselectivity.

In conclusion, the cross-coupling specific oxidative coupling of 2-naphthol and the 3-hydroxy-2-naphthamide derivatives with the copper catalyst was attained to give a C_1-symmetric BINOL with a 3-amido substituent. The cross-coupling and stereoselectivities were significantly affected by the amide structure as well as the copper catalyst.

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Supplementary data

The CD spectra of the obtained products and ^1H NMR spectrum of poly-**4** are available. Supplementary data

Table 3. Oxidative cross-coupling polymerization of **4**[a]

Run	Catalyst	Time (h)	Yield[b] (%)	$M_n \times 10^{-3}$ (M_w/M_n)[c]	$[\alpha]_D$[d]
1	CuCl(OH)-TMEDA	48	0	—	—
2	CuCl-(−)Sp	72	7	5.8 (2.1)	+23
3	CuCl-(*S*)Phbox	24	64 (52)[e]	7.1 (2.1)	+110
4	CuCl-(*R*)Bnbox	72	64	6.4 (1.8)	−67

[a] [**4**]/[catalyst] = 1/0.2, solvent = THF, temp = rt, O_2 atmosphere.
[b] MeOH–AcOEt–1 N HCl (2.5/7.5/1 v/v/v)-insoluble part.
[c] Determined by SEC.
[d] In $CHCl_3$.
[e] Yield of THF-soluble and MeOH–AcOEt–1 N HCl (2.5/7.5/1 v/v/v)-insoluble part.

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