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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 O_2 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 C_1 symmetrical BINOL derivative.

Keywords: Binaphthol; Cross-coupling; Oxidative coupling; Lewis acid

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 C_1 skeleton from the homo-coupling, which affords a C_2 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 trifluoromethansulfonate [$Yb(OTf)_3$] 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

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☆ See Ref. 1.

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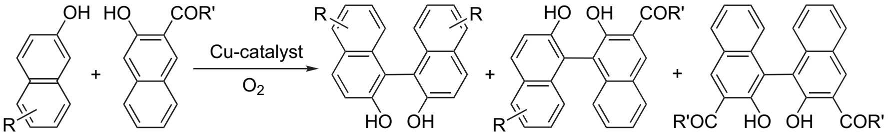


Scheme 1.

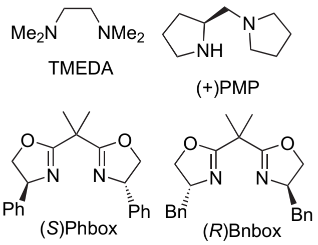


Figure 1. Structure of ligands.

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]

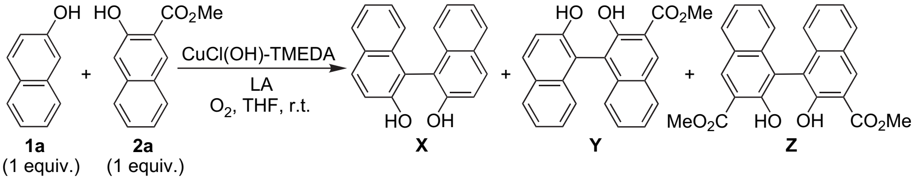
2. Results and discussion

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)−TMEDA[11] (Fig. 1) catalyst at room temperature under an O_2 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 $Sc(OTf)_3$, $Zn(OTf)_2$, $Ti(O^iPr)_4$, 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 O_2 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	$Ti(O^iPr)_4$ (0.1)	48	>99	38
11[e]	0.1	$Ti(O^iPr)_4$ (0.1)	72	>99	65

[a] Determined from isolated yields.

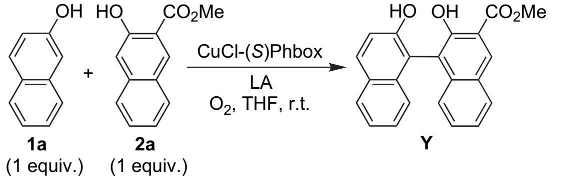
[b] Isolated yield of cross-coupling product **Y**.

[c] **X/Y/Z**=12:88:0.

[d] **X/Y/Z**=2:98:0.

[e] Solvent=CH_2Cl_2.

Table 2
Asymmetric oxidative cross-coupling of **1a** and **2a** with CuCl–(*S*)Phbox (0.2 equiv) in THF at rt under an O_2 atmosphere

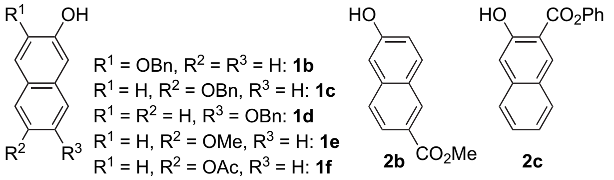


Entry	LA (equiv)	Time (h)	Cross-coupling selectivity[a] (%)	Yield[b] (%)	ee[c] (%)
1	—	6	97[d]	82	8 (*S*)
2	$Yb(OTf)_3$ (0.2)	48	>99	98	0
3	$Sc(OTf)_3$ (0.2)	48	>99	21	12 (*S*)
4	$Y(OTf)_3$ (0.2)	48	>99	93	5 (*S*)
5[e]	$Zn(OTf)_2$ (0.1)	72	>99	88	5 (*R*)
6[e,f]	$Ti(O^iPr)_4$ (0.1)	48	>99	95	4 (*R*)

[a] Determined from isolated yields.
[b] Isolated yield of cross-coupling product **Y**.
[c] Determined by HPLC (Chiralpak AD-H).
[d] **X**/**Y**/**Z**=0:97:3.
[e] (*R*)Phbox was used.
[f] Cu-catalyst: 0.1 equiv.

The asymmetric oxidative cross-coupling reaction of various 2-naphthol derivatives in the presence of $Yb(OTf)_3$ at room temperature under an O_2 atmosphere was conducted (Table 3). The reaction between **1a** and methyl 6-hydroxy-2-naphthoate **2b** in the absence of the Lewis acid gave a cross-coupling product in a 57% yield with a selectivity of 67% (entry 1), while the $Yb(OTf)_3$ catalyst system showed a much lower **Y**-selectivity that mainly afforded a homo-coupling product **X** (entry 2). These results indicate that the substitution position of the ester group on the substrate plays an important role in the oxidative cross-coupling. The coupling reaction of the 2-naphthol having a phenyl ester **2c** proceeded in a highly cross-coupling-selective or cross-coupling-specific manner (entries 3–9) with a much higher stereoselectivity than that observed for the reaction of the methyl ester **2a**, as well as the reaction in the absence of the Lewis acid.[6] These results again support the fact that the ester group significantly affects the coupling process, and the effect of the Lewis acid catalyst on the stereocontrol was also demonstrated. The stereoselectivity reached 86% ee when 3-benzyloxy-2-naphthol **1b** was used as the other substrate (entry 5).

Table 3
Asymmetric oxidative cross-coupling of various 2-naphthol derivatives with CuCl–(*R*)Phbox (0.2 equiv) in THF at rt under an O_2 atmosphere



R^1 = OBn, R^2 = R^3 = H: **1b**
R^1 = H, R^2 = OBn, R^3 = H: **1c**
R^1 = R^2 = H, R^3 = OBn: **1d**
R^1 = H, R^2 = OMe, R^3 = H: **1e**
R^1 = H, R^2 = OAc, R^3 = H: **1f**

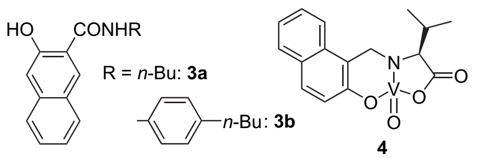
Entry	Substrates 1	Substrates 2	$Yb(OTf)_3$ (equiv)	Time (h)	Selectivity[a] **X**/**Y**/**Z**	Yield[b] (%)	ee[c] (%)
1	**1a**	**2b**	—	48	20:67:13	57	9 (*R*)
2	**1a**	**2b**	0.2	72	52:35:13	13	27 (*R*)
3[d]	**1a**	**2c**	0.1	48	0:>99:0	98	59 (*R*)
4	**1a**	**2c**	0.1	12	0:>99:0	36	59 (*S*)
5[d]	**1b**	**2c**	0.1	48	3:97:0	93	86 (*R*)
6	**1c**	**2c**	0.1	48	0:>99:0	97	9 (*R*)
7	**1d**	**2c**	0.1	48	0:96:4	74	67 (*S*)
8	**1e**	**2c**	0.1	48	0:>99:0	99	45 (*S*)
9[d]	**1f**	**2c**	0.1	48	0:>99:0	85	55 (*R*)

[a] Determined from isolated yields.
[b] Isolated yield of cross-coupling product **Y**.
[c] Determined by HPLC (Chiralpak AD-H or AS-H).
[d] (*S*)Phbox was used.

The 12-h reaction of **1a** and **2c** in the presence of $Yb(OTf)_3$ was also performed and resulted in a 36% yield with a cross-coupling selectivity of >99% and a stereoselectivity of 59% ee (entry 4), which are the same as those for the cross-coupling product obtained during the coupling reaction for 48 h (entry 3). Therefore, the racemization or deracemization[12] should hardly occur during the reaction with this binary catalyst system.

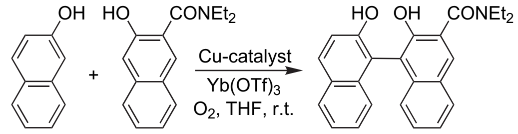
A plausible mechanism for the Lewis acid-assisted catalytic oxidative coupling has been proposed in a previous report,[1] in which the 2-naphthol bearing ester group serves as an acceptor for the radical species generated by the one-electron oxidation of the other 2-naphthol derivative, and the Lewis acid activates the former substrate to effectively promote the cross-coupling. The oxidative homo-coupling reaction of **2a** with CuCl(OH)–TMEDA (0.2 equiv) and $Yb(OTf)_3$ (0.1 equiv) catalyst system under an O_2 atmosphere (conditions: rt, 48 h, THF) was carried out and resulted in a 12% yield, whereas the reaction in the absence of the Lewis acid under the same conditions gave a homo-coupling product of **2a** in a 54% yield. Therefore, this should be due to the fact that the generation of the radical species of **2a** is restrained by the Lewis acid. Thus the hydroxynaphthoate more effectively acts as an acceptor molecule during the cross-coupling reaction in the presence of Lewis acid. In addition, the bidentate-type coordination of the Lewis acid to the ester and hydroxyl groups must be important as previously mentioned for the reaction results of the substrate **2b**. These facts well supported the proposed coupling mechanism.

Recently, we reported that the oxidative coupling of 2-naphthol and 3-hydroxy-2-naphthamide having a secondary amide group, such as **3a** and **3b**, proceeds in a cross-coupling specific manner regardless of the ligand structure of the copper catalyst.[7] The reaction of **1a** and **3a** with the typical chiral vanadium catalyst **4**[4b] (0.4 equiv) in THF took 168 h under an O_2 atmosphere, however, a cross-coupling product was produced in a 35% yield with a selectivity of **X**/**Y**/**Z**=47:53:0. Accordingly, the copper catalyst is necessary for this cross-coupling specific reaction.



On the other hand, the reactions of 3-hydroxy-2-naphthamide with a tertiary amide group with copper catalysts

Table 4
Oxidative cross-coupling of **1a** and **3c** in THF at rt under an O_2 atmosphere



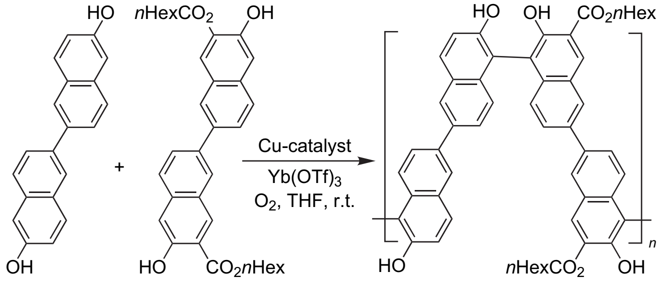
1a (1 equiv.) **3c** (1 equiv.)

Entry	Catalyst (equiv)	$Yb(OTf)_3$ (equiv)	Time (h)	Cross-coupling selectivity[a] (%)	Yield[b] (%)	ee[c] (%)
1[d]	CuCl(OH)−TMEDA (0.1)	—	72	78	50	—
2	CuCl(OH)−TMEDA (0.1)	0.2	72	92	19	—
3[d]	CuCl−(*S*)Phbox (0.1)	—	24	77	53	27 (*S*)
4[d,e]	CuCl−(*S*)Phbox (0.1)	—	9	95	91	0
5	CuCl−(*S*)Phbox (0.1)	0.1	48	86	58	41 (*S*)
6[e]	CuCl−(*R*)Phbox (0.1)	0.2	30	>99	83	13 (*S*)
7[f]	CuCl−(*R*)Phbox (0.1)	0.2	72	76	15	41 (*R*)

[a] Determined from isolated yields (homo-coupling product **Z** was obtained as a by-product).
[b] Isolated yield of cross-coupling product **Y**.
[c] Determined by HPLC (Chiralpak AD-H).
[d] See Ref. 7.
[e] Solvent=CH_2Cl_2.
[f] Solvent=THF/MeOH=9:1 (v/v).

resulted in a mixture of homo- and cross-coupling products.[7] For instance, the coupling between **1a** and *N*,*N*-diethyl-3-hydroxy-2-naphthamide **3c** with CuCl(OH)−TMEDA in THF gave a cross-coupling product[13] in 50% yield with a selectivity of 78% (Table 4, entry 1). The amide structure, probably due to its steric, electronic, and hydrogen-bonding effects is also an important factor for the cross-coupling process. The effect of the $Yb(OTf)_3$ co-catalyst on the reaction of **1a** and **3c** with copper catalysts was then investigated (Table 4).

Table 5
Oxidative cross-coupling copolymerization of **5** and **6**[a]



5 **6** poly-**5/6**

Entry	Catalyst	$Yb(OTf)_3$ (equiv)	Time (h)	Yield[b] (%)	$M_n \times 10^{-3}$ (M_w/M_n)[c]	Unit ratio		$[\alpha]_D^{25}$[f]
						X/Y/Z[d]	**5/6**[e]	
1[g]	CuCl(OH)−TMEDA	—	24	40	6.9 (1.6)	23:75:2	56:44	—
2	CuCl(OH)−TMEDA	0.2	48	10	9.5 (1.4)	1:96:3	48:52	—
3[g]	CuCl−(+)PMP	—	24	23	2.8 (1.8)	87:13:0	84:16	+6
4	CuCl−(+)PMP	0.2	120	31	4.2 (1.4)	2:90:8	50:50	−30
5[g]	CuCl−(*S*)Phbox	—	24	80	11 (1.9)	3:93:4	50:50	+56
6	CuCl−(*S*)Phbox	0.2	48	59	8.9 (1.3)	0:99:1	50:50	+130
7[g]	CuCl−(*R*)Bnbox	—	24	51	7.4 (1.4)	4:89:7	51:49	−71
8	CuCl−(*R*)Bnbox	0.2	72	94	3.3 (1.5)	1:93:6	51:49	−100

[a] Conditions: [**5**]/[**6**]/[Cu]/[Yb]=0.5:0.5:0.2:0.2, solvent=THF, temp=rt, O_2 atmosphere.
[b] Methanol−ethyl acetate−1 N HCl (1:3:0.2, v/v/v) insoluble part.
[c] Determined by SEC.
[d] Estimated by ^1H NMR analysis.[10]
[e] Determined by ^1H NMR analysis of the acetylated polymer.
[f] In THF.
[g] See Ref. 10.

The reaction with CuCl(OH)−TMEDA in the presence of Yb(OTf)$_3$ (0.2 equiv) in THF showed a much higher cross-coupling selectivity, although the product was obtained in a much lower yield than that of the reaction in the absence of the Lewis acid (entry 2). A significant effect of the Lewis acid was observed for the reaction with CuCl−Phbox in THF, in which both the cross-coupling and stereoselectivities were improved to some extent (entry 5). Furthermore, the cross-coupling specific reaction was attained in CH$_2$Cl$_2$, although the stereoselectivity was still quite low (entry 6).

The cross-coupling specific oxidative coupling reaction between 2-naphthol and 3-hydroxy-2-naphthoate derivatives was accomplished. This method was then used for the polymerization producing poly(BINOL)[7,14] with an alternating copolymer structure. There is no report on the alternating sequence control during the oxidative coupling copolymerization to the best of our knowledge, except for our previous study.[10] The copolymerization of 6,6′-dihydroxy-2,2′-binaphthalene **5** and dihexyl 6,6′-dihydroxy-2,2′-binaphthalene-7,7′-dicarboxylate **6** (1:1) with various copper catalysts in the presence of Yb(OTf)$_3$ in THF under an O$_2$ atmosphere was performed and the results are listed in Table 5.

The copolymerization without the Lewis acid was significantly affected by the copper catalyst. For example, CuCl−(+)PMP (Fig. 1) gave an oligomer in a low yield, which mainly consists of the homo-coupling unit of **5** (**X**=87%) (entry 3), whereas the CuCl−Phbox catalyst showed a good catalyst activity that produced a cross-coupling unit with a selectivity of **Y**=93% and a monomer unit ratio of **5**/**6**=50:50 (entry 5). Every copolymerization in the presence of Yb(OTf)$_3$ showed a significant increase of the cross-coupling unit ratio, and the highly cross-coupling selective copolymerization took place. The copolymerization with the Phbox catalyst afforded a polymer with a cross-coupling selectivity of 99% and a monomer unit ratio of 50:50 (entry 6), indicating that poly(BINOL) with an almost complete alternating copolymer structure was successfully constructed.

Figure 2 shows the CD spectra of the copolymers obtained using the chiral catalysts. The spectral patterns of the polymer obtained with (+)PMP without a Lewis acid was quite different from those of the copolymers prepared using the bisoxazolines, as well as the (+)PMP and Yb(OTf)$_3$ system, due to the fact that the polymers have quite different unit ratios from one another. The spectral patterns demonstrated that the copolymers obtained with the Phbox catalyst preferentially have a *S*-configuration, while polymers obtained with the Bnbox (Fig. 1) and (+)PMP-Yb(OTf)$_3$ catalysts are rich in the *R*-structure.[10,14] The absorption intensity showed a good relation to the [α]$_D$ value of the copolymers, and these results indicated that the stereoselectivity of the polymer obtained in the presence of the Lewis acid is much higher than that of the polymer prepared in the absence of the Lewis acid, although details are not clear. Therefore, the Lewis acid catalyst significantly affected the stereocontrol, as well as the cross-coupling one, during the asymmetric oxidative cross-coupling copolymerization of **5** and **6**.

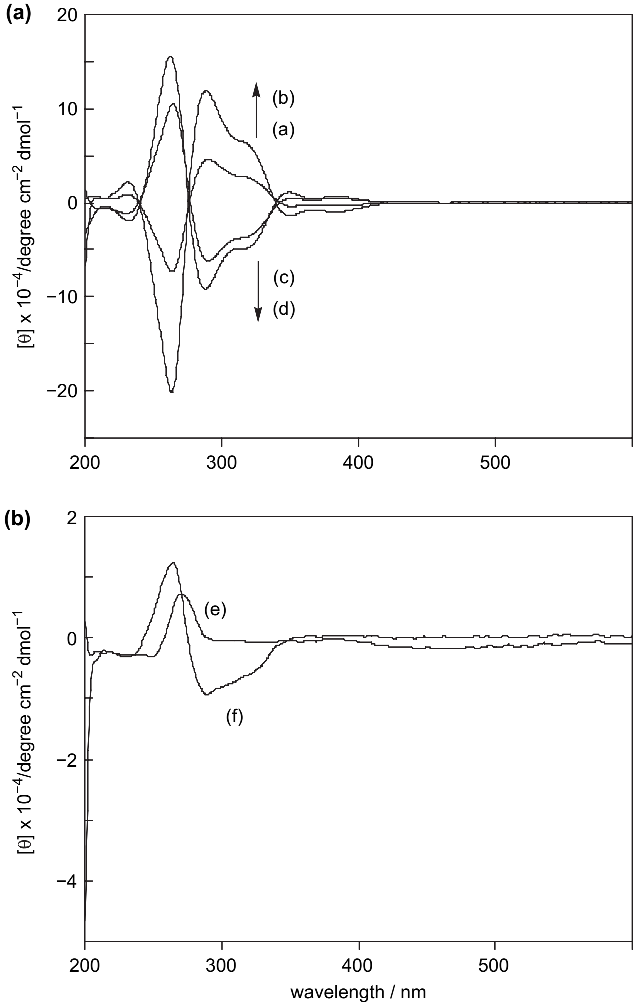


Figure 2. CD spectra of poly-**5**/**6** obtained with (a) CuCl−(*S*)Phbox without Lewis acid (Table 5, entry 5), (b) CuCl−(*S*)Phbox in the presence of Yb(OTf)$_3$ (entry 6), (c) CuCl−(*R*)Bnbox without Lewis acid (Table 5, entry 7), (d) CuCl−(*R*)Bnbox in the presence of Yb(OTf)$_3$ (entry 8), (e) CuCl−(+)PMP without Lewis acid (Table 5, entry 3), and (f) CuCl−(+)PMP in the presence of Yb(OTf)$_3$ (entry 4) (THF).

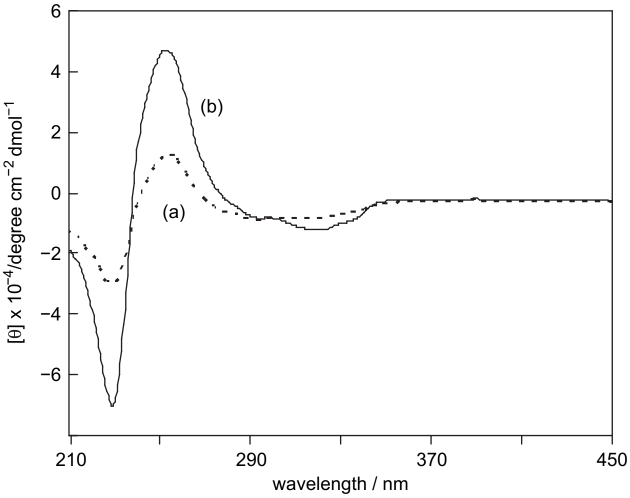


Figure 3. CD spectra of the cross-coupling product obtained with **1a** and **2b** (a) Table 3, entry 1 and (b) entry 2 (THF).

3. Conclusion

In conclusion, a catalytic amount of the Lewis acid, such as $Yb(OTf)_3$, can control the oxidative cross-coupling reaction between 2-naphthol and 3-hydroxy-2-naphthoic acid derivatives with the copper catalyst to selectively produce a C_1 symmetrical BINOL, that is, the radical coupling reaction is effectively controlled by the Lewis acid catalyst. This novel binary catalyst system also produces poly(BINOL) with an alternating copolymer structure. The yields of the cross-coupling products, cross-coupling, and stereoselectivities were significantly affected by the structures of both the copper catalyst and Lewis acid.

4. Experimental

4.1. General

The ^{1}H and ^{13}C NMR spectra were measured by a Varian Unity Inova (500 MHz for ^{1}H) or Mercury 200 (200 MHz for ^{1}H) spectrometer. The infrared (IR) spectra were recorded by a Horiba FT-720 spectrometer. The optical rotation was measured using a Jasco P-1010 polarimeter at 25 °C. The circular dichroism (CD) spectra were obtained with a Jasco J-720WI apparatus. The high-performance liquid chromatography (HPLC) analyses were performed by a Jasco 986-PU chromatograph equipped with a UV (Jasco 970-UV) detector at room temperature. The size exclusion chromatography (SEC) analyses were conducted by a Jasco PU-2080-Plus equipped with a Jasco UV-2075-Plus UV detector with KF-806L and KF-803L columns connected in series (eluent=THF, flow rate=1.0 mL/min, calibration: polystyrene standard).

4.2. General procedure for oxidative cross-coupling in the presence of Lewis acid[1]

To a solution of 2-naphthols **1**, 3-hydroxy-2-naphthoates **2**, and $Yb(OTf)_3$, a mixture of CuCl and a diamine in THF ($[\mathbf{1}]_0=0.17$ M) was added. After room temperature stirring under an O_2 atmosphere, the reaction mixture was diluted with $CHCl_3$ and then washed with 1 N HCl and brine. The organic layer was dried over $MgSO_4$. Subsequent filtration and concentration afforded the crude products. Purification was accomplished by silica gel column chromatography that produced the BINOL derivatives.[6,7]

4.3. Procedure for oxidative cross-coupling copolymerization in the presence of Lewis acid

A mixture of CuCl and ligand in THF ([CuCl]/[diamine]=0.1:0.12) was stirred for 30 min under an O_2 atmosphere. To this mixture, monomers and a Lewis acid were added ([**5**]=[**6**]=0.065 M). After stirring at room temperature, a polymer was isolated as the methanol–ethyl acetate–1 N HCl (1:3:0.2, v/v/v) insoluble fraction by centrifugation and drying in vacuo. The cross-coupling selectivity (**X/Y/Z**) of the obtained polymer was estimated from the ^{1}H NMR analysis of the hydroxyl protons. The unit ratio (**5/6**) was determined by the ^{1}H NMR analysis of the polymer after acetylation of the hydroxyl groups with an excess amount of acetyl chloride and pyridine in CH_2Cl_2.[10]

4.4. Materials

Dry solvents, such as THF and CH_2Cl_2 (Kanto) were used for the oxidative coupling reactions. The optically active liagnds, (+)PMP (TCI), (−)Sp (Sigma), Phbox (Aldrich), and (*R*)Bnbox (Aldrich) were used as received. The achiral copper complex, CuCl(OH)–TMEDA, was purchased from TCI. Monomers, **5** and **6**, were synthesized according to a previously reported procedure.[10]

Cross-coupling product was obtained from **1a** and **2b** (Fig. 3). Mp 113.0–114.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 8.73 (d, 1H, J=1.8 Hz, aromatic), 8.08–7.82 (m, 4H, aromatic), 7.46–7.07 (m, 6H, aromatic), 5.31 (s, 1H, –OH), 5.22 (s, 1H, –OH), 3.93 (s, 3H, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) 167.12, 154.73, 152.93, 136.02, 133.29, 132.74, 131.69, 131.43, 129.42, 128.46, 128.38, 127.59, 126.77, 125.39, 124.45, 124.11, 123.94, 118.57, 117.98, 111.53, 110.13, 52.21; IR (KBr, cm^{-1}) 3379, 2949, 1709, 1620, 1597, 1508, 1475, 1387, 1284, 1205, 1146; $[\alpha]_D^{25}$ −2 (*c* 0.8, THF) for 27% ee (*R*). Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.73; H, 4.63.

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