

Ytterbium triflate-assisted catalytic oxidative cross-coupling of 2-naphthol derivatives

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Abstract—The oxidative coupling of 2-naphthol and 3-hydroxy-2-naphthoate derivatives with a copper catalyst under an O₂ atmosphere was carried out. The reaction in the presence of a catalytic amount of the Lewis acid, Yb(OTf)₃, proceeded in a cross-coupling specific manner.

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The precise control of radical reactions has been an attractive topic in the fields of synthetic organic and polymer chemistry over the past decade. A Lewis acid catalyst is often used as a powerful tool for controlling their selectivities, etc.^{1,2} For instance, during the radical polymerization of acrylamides and methacrylamides, a catalytic amount of the Lewis acid, such as the trifluoromethanesulfonate salts of ytterbium and yttrium [Yb(OTf)₃ and Y(OTf)₃], significantly increased the isotacticity of the obtained polymer, and this method was further combined with one of the living radical polymerization processes, the reversible addition–fragmentation chain transfer polymerization, to afford a polymer with the simultaneously controlled molecular weight and tacticity.³

The oxidative coupling of 2-naphthol derivatives is a facile and effective preparation route to the 1,1'-bi-2-naphthol (BINOL). We recently reported the oxidative cross-coupling between 2-naphthol and 3-hydroxy-2-naphthoate derivatives using the CuCl-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) [CuCl-Phbox] catalyst (Fig. 1), in which the unsymmetrical BINOL (Y) was selectively produced (Scheme 1).^{4–6} However, the cross-coupling and stereoselectivities were significantly

affected by the substrate structure, as well as the catalyst, and have not still been sufficiently controlled.

The oxidative coupling process involves a radical coupling step.^{7,8} Therefore, the reaction between the 2-naphthol and 3-hydroxy-2-naphthoate derivatives with copper catalysts in the presence of a Lewis acid was examined, and it was found that the cross-coupling specific reaction proceeds when a catalytic amount of Yb(OTf)₃ is used. The Lewis acid effect on the oxidative coupling of the 2-naphthol derivatives has been scarcely reported to the best of our knowledge.

The oxidative coupling reaction of a 1:1 mixture of 2-naphthol (**1a**) and methyl 3-hydroxy-2-naphthoate (**2a**) with the CuCl(OH)-TMEDA catalyst (Fig. 1) in THF at room temperature under an O₂ atmosphere in the absence and presence of Yb(OTf)₃ was carried out⁹ and the results are listed in Table 1. The reaction without the Lewis acid gave a cross-coupling product in a low yield with a cross-coupling selectivity (Y-selectivity) of 88% (entry 1). In contrast, a catalytic amount of

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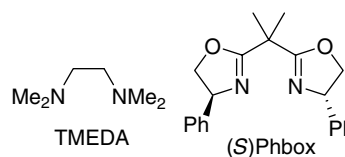
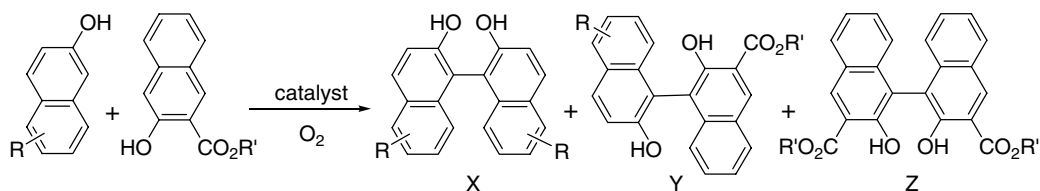
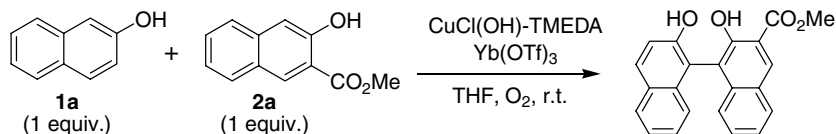


Figure 1. Ligands.



Scheme 1.

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

Entry	CuCl(OH)-TMEDA (equiv)	Yb(OTf) ₃ (equiv)	Time (h)	Y-selectivity ^a (%)	Yield ^b (%)
1	0.2	—	48	88 ^c	47
2	0.2	0.2	36	>99	91
3	0.1	0.2	48	>99	78
4	0.2	0.1	48	>99	91
5	0.1	0.1	24	98 ^d	81
6 ^e	0.1	0.1	62	79 ^f	22
7	—	0.2	48	—	0

^a Cross-coupling selectivity.

^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.

^f X:Y:Z = 21:79:0.

Yb(OTf)₃ in THF significantly increased both the yield and Y-selectivity, and the reaction proceeded in a cross-coupling specific manner (entries 2–5). The solvent also influenced on the yield and Y-selectivity (entry 6). The reaction without the copper catalyst did not give any coupling product (entry 7). Accordingly, the Lewis acid effectively promotes the oxidative cross-coupling reaction when using the copper catalyst.

The asymmetric oxidative cross-coupling reaction of various 2-naphthol derivatives with the CuCl-Phbox catalyst was examined (Table 2). The cross-coupling specific reaction again proceeded when a catalytic amount of Yb(OTf)₃ was used as the co-catalyst. The cross-coupling product obtained by the reaction between **1a** and **2a** hardly showed an ee value (entry 1), whereas the reaction of the substrate having a phenyl ester **2b** resulted in a higher stereoselectivity than that observed for the reaction in the absence of the Lewis acid. For example, the reaction between 3-benzyloxy-2-naphthol (**1b**) and **2b** at 0 °C afforded a product with a Y-selectivity of >99% and 88% ee (entry 6). The Lewis acid catalyst significantly improves the stereoselectivity, as well as the cross-coupling value. Y(OTf)₃ was also effective as an additive and showed a catalyst effect almost equal to that of Yb(OTf)₃ (entry 3). Although the reaction in the presence of Sc(OTf)₃ also proceeded

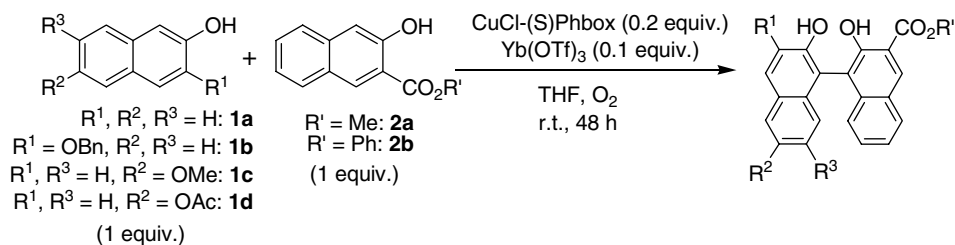
in a cross-coupling specific manner, the system did not work as a catalytic process (entry 2).

A plausible mechanism for the catalytic oxidative cross-coupling reaction has been suggested in previous reports.⁴ During the reaction, the β-naphthol with electron-withdrawing group works as an acceptor for the radical species generated by the one-electron oxidation of the other substrate, 2-naphthol. The Lewis acid catalyst, such as Yb(OTf)₃ and Y(OTf)₃, should effectively activate the former acceptor substrate as shown in Figure 2, in which the structure of the ester group can also significantly affect the coupling stereochemistry.

In conclusion, a novel catalyst system for the oxidative coupling reaction of 2-naphthol derivatives, the binary catalyst of the copper complex and lanthanide triflate, simultaneously controls both cross-coupling and stereoselectivities. Further investigation and extension of this system are now in progress.

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Table 2. Asymmetric oxidative cross-coupling of **1** and **2**

Entry	1	2	Y-selectivity ^a (%)	Yield ^b (%)	ee ^c (%)
1 ^d	1a	2a	>99 (97)	98	~0 (8)
2 ^e	1a	2a	>99	21	12, <i>S</i>
3 ^f	1a	2a	>99	93	5, <i>S</i>
4	1a	2b	>99 (86)	98	59, <i>R</i> (55)
5	1b	2b	97 ^g (85)	93	86, <i>R</i> (65)
6 ^h	1b	2b	>99 (87)	70	88, <i>S</i> (70)
7 ⁱ	1c	2b	>99 (97)	99	45, <i>S</i> (3)
8	1d	2b	>99 (97)	85	55, <i>R</i> (46)

^a Cross-coupling selectivity. In parentheses, values for the reaction without Lewis acid are given.^{4a,b}

^b Isolated yield of cross-coupling product.

^c Determined by HPLC (Chiralpak AD-H or AS-H). In parentheses, values for the reaction without Lewis acid are given.^{4a,b}

^d (*R*)Phbox and Yb(OTf)₃ (0.2 equiv) were used.

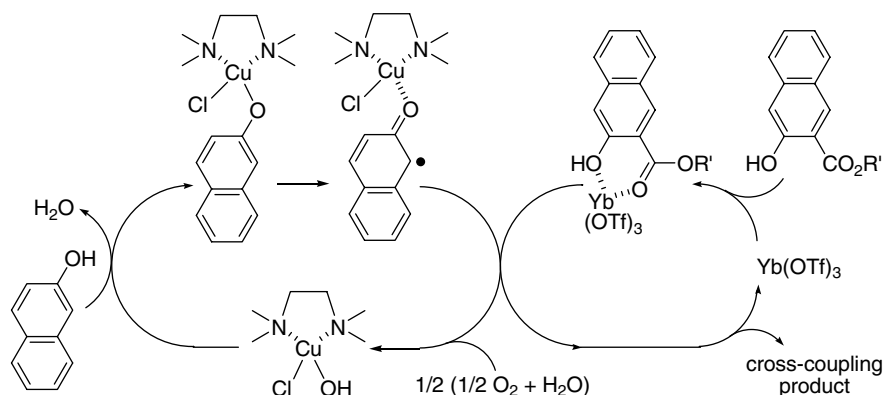
^e Sc(OTf)₃ (0.2 equiv) as a Lewis acid was used.

^f Y(OTf)₃ (0.2 equiv) was used.

^g X:Y:Z = 3:97:0.

^h (*R*)Phbox was used (temp. = 0 °C, time = 168 h).

ⁱ (*R*)Phbox was used.

**Figure 2.** Plausible mechanism.

References and notes

- Yamamoto, Y.; Onuki, S.; Yumoto, M.; Asao, N. *J. Am. Chem. Soc.* **1994**, *116*, 421–422.
- (a) Sibi, M. P.; Porter, N. A. *Acc. Chem. Res.* **1999**, *32*, 163–171; (b) Sibi, M. P.; Manyem, S.; Zimmerman, J. *Chem. Rev.* **2003**, *103*, 3263–3295; (c) Srikanth, G. S. C.; Castle, S. L. *Tetrahedron* **2005**, *61*, 10377–10441; (d) Zimmerman, J.; Sibi, M. P. *Top. Curr. Chem.* **2006**, *263*, 107–162.
- (a) Mero, C. L.; Porter, N. A. *J. Org. Chem.* **2000**, *65*, 775–781; (b) Baraki, H.; Habaue, S.; Okamoto, Y. *Macromolecules* **2001**, *34*, 4724–4729; (c) Isobe, Y.; Fujioka, D.; Habaue, S.; Okamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 7180–7181; (d) Ray, B.; Isobe, Y.; Morioka, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2003**, *36*, 543–545.
- (a) Temma, T.; Habaue, S. *Tetrahedron Lett.* **2005**, *46*, 5655–5657; (b) Temma, T.; Hatano, B.; Habaue, S. *Tetrahedron* **2006**, *62*, 8559–8563; (c) Habaue, S.; Takahashi, Y.; Temma, T. *Tetrahedron Lett.* **2007**, *48*, 7301–7304.
- The cross-coupling reaction with an excess amount of copper complex, see: (a) Hovorka, M.; Ščigel, R.; Gunterová, J.; Tichý, M.; Závada, J. *Tetrahedron* **1992**, *48*, 9503–9516; (b) Hovorka, M.; Závada, J. *Tetrahedron* **1992**, *48*, 9517–9530; (c) Smrčina, M.; Vyskočil, Š.; Máca, B.; Poláková, J.; Claxton, T. A.; Abbott, A. P.; Kočovský, P. *J. Org. Chem.* **1994**, *59*, 2156–2163.
- The preliminary data on the catalytic cross-coupling are available: (a) Smrčina, M.; Poláková, J.; Vyskočil, Š.; Kočovský, P. *J. Org. Chem.* **1993**, *58*, 4534–4538; (b) Hon, S.-W.; Li, C.-H.; Kuo, J.-H.; Barhate, N. B.; Liu, Y.-H.;

- Wang, Y.; Chen, C.-T. *Org. Lett.* **2001**, *3*, 869–872; (c) Caselli, A.; Giovenzana, G. B.; Palmisano, G.; Sisti, M.; Pilati, T. *Tetrahedron: Asymmetry* **2003**, *14*, 1451–1454.
7. Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–897.
8. (a) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, *64*, 2264–2271; (b) Li, X.; Yang, J.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 1137–1140; (c) Gao, J.; Reibenspies, J. H.; Martell, A. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 6008–6012.
9. Typical procedure for the catalytic cross-coupling reaction in the presence of Yb(OTf)₃: To a THF solution of **1**, **2**, and Yb(OTf)₃ (Aldrich), a mixture of CuCl(OH)-TMEDA (TCI) and THF was added. The reaction mixture ([**1**]₀ = 0.17 M) was then stirred at room temperature under an O₂ atmosphere, diluted with CHCl₃, and washed with 1 N HCl and brine. The organic layer was dried over MgSO₄. After filtration and concentration to obtain the crude products, the cross-coupling compound was isolated by silica gel column chromatography.