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Functionalization of BINOL and application in the homo- and heterogeneous enantioselective epoxidation of α,β-unsaturated ketones

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ABSTRACT

The selective functionalization of BINOL derivatives with 3-(dimethylamino)prop-1-yn-1-yl is described. The corresponding La and Yb complexes were evaluated toward the epoxidation of α,β-unsaturated ketones. The Yb-complexes display the highest catalytic activity and selectivity, affording the expected chiral epoxides in quantitative yields and up to 90% ee in homogeneous conditions, and 93% ee when supported on silica gel.

The asymmetric epoxidation of olefins is one of the most versatile but challenging reactions in modern organic chemistry. Indeed, it is very valuable for affording chiral intermediates commonly used for the synthesis of a large variety of natural products and pharmaceuticals.[1] In 1980, Sharpless et al. reported the stoichiometric asymmetric epoxidation of allylic alcohols,[2] further optimized to a catalytic version thanks to the addition of molecular sieves (MS).[3] About ten years later, the groups of Jacobsen,[4] Katsuki,[5] and Mukaiyama[6] developed the asymmetric epoxidation of unfunctionalized olefins using salen ligands. Ultimately, the more challenging asymmetric epoxidation of electron-deficient olefins was investigated. The first results in this field appeared at the end of the 90s in the literature. During the course of our studies on epoxidation,[7] we and others[8] have been interested in the chiral metal peroxide catalytic system pioneered by Weitz and Scheffer.[9] Considering the moderate yields and enantioselectivities obtained when using the chiral platinum/diphosphine/peroxide complex,[10] a number of metals, including zinc associated to (1*R*,2*R*)-*N*-methylpseudoephedrine[11] and magnesium combined with (+)-diethyl tartrate,[12] were proposed, affording excellent results.

By the same period of time, Shibasaki et al.[13] disclosed an alternative based on lanthanides. The catalytic system involved lanthanum or ytterbium, (*R*)- or (*S*)-2,2′-dihydroxy-1,1′-binaphthalene (BINOL), *tert*-butyl hydroperoxide (TBHP) or cumene hydroperoxide (CMHP), and 4 Å MS in THF. Using the latter system, the enantioselective epoxidation of unsaturated ketones was greatly improved, affording up to 98% ee, with the addition of a small amount of phosphine- or arsine oxide (15 mol %) as additive.[14] When ytterbium was used, the activity was further improved by the addition of water (4.5 equiv relative to Yb).[15] Consequently, these lanthanide/BINOL catalysts appeared as very efficient catalysts both in terms of reactivity and enantioselectivity for the epoxidation of α,β-unsaturated *N*-acylimidazoles,[16] amides,[17] and *N*-acylpyrroles as carboxylic acid derivatives,[18] and moderately selective for ester derivatives.[19]

BINOL is a robust and versatile chiral reagent, easily functionalized.[20] However, it is worth reminding that the introduction of substituents on the BINOL skeleton might have a profound impact on the activity and enantioselectivity of the catalyst due to the modified electronic and steric properties. As far as we know, few reports have discussed this problem in the asymmetric epoxidation of α,β-unsaturated ketones. Noticeably, de Vries et al. have reported on the advantages of the 6,6′-dibromo- or 6,6′-diphenyl-BINOL on the epoxidation of α,β-enones.[21] Correlatively, several groups have proposed to functionalize BINOL with ammonium salts in order to use the catalysts in asymmetric phase-transfer reactions.[22] However, to the best of our knowledge, only one example of ammonium salt derived from BINOL has been reported in the case of asymmetric phase-transfer epoxidation of chalcone with alkaline hydrogen peroxide.[23] In addition, the phase-transfer nucleophilic epoxidation of α,β-enones is based mainly on the use of ammonium salts derived from cinchonine or quinidine derivatives,[24] even if two examples of ammonium salts derived from binaphthyl were also reported.[25]

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Based on the limited number of precedents described in the literature and on our experience in BINOL modification[26] and catalyst recycling,[27] we decided to undertake the synthesis of the two new ligands **1** and **2** (Fig. 1), designed for allowing an easy, non-covalent grafting on a polar silica-gel support. **1** and **2** derive from BINOL and display one or two *N,N*-dimethyl-2-propynylamine functions on the 6, or 6,6′ positions of BINOL. The catalytic performances of the two new ligands were evaluated toward the catalytic asymmetric epoxidation of two α,β-unsaturated ketones (chalcone and benzalacetone) under homo- and heterogeneous conditions, including phase-transfer catalysis.

The 6- and 6′-positions of BINOL are equally activated toward electrophilic aromatic substitution.[28] However, it has been reported that the introduction of a bulky pivaloyl group on the 2-position alters the electronic character of the naphthalene units allowing a desymmetrization of the 6- and 6′-positions.[29] Thus, we decided to use this strategy to prepare the (*R*)-6-[3-(dimethylamino)prop-1-yn-1yl]-2,2′-dihydroxy-1,1′-binaphthalene ligand **1** (Scheme 1). Compound **3** was prepared according to literature protocols,[29,30] and was reacted with *N,N*-dimethyl-2-propynylamine under classical Pd-catalyzed Sonogashira coupling conditions, to give, after deprotection under basic condition, the expected ligand **1** in 85% yield after purification.

In parallel, we investigated the synthesis of (*R*)-6,6′-bis[3-(dimethylamino)prop-1-yn-1yl]-2,2′-dihydroxy-1,1′-binaphthalene ligand **2** (Scheme 2). Firstly, we tried the direct Pd-catalyzed Sonogashira coupling between the dibromo-BINOL derivative **4**,[31] and *N,N*-dimethyl-2-propynylamine. If the ^{1}H NMR spectra of the crude material confirmed that the expected coupling compound **2** had been formed as the major product, its isolation by column chromatography remained unsuccessful, because of the strong interaction between **2** and silica-gel. To prevent this issue, we protected the hydroxyl groups as methoxy function after bromination of the 6,6′-positions of the BINOL. Thus, a direct methylation of compound **4** with NaH and methyliodide afforded the corresponding protected derivative **5a** in quantitative yield.[32] Following, the Sonogashira-coupling was performed, affording product **6a** in 50% yield after purification on silica gel. Unfortunately, the deprotection of the methoxy groups using the classical BBr_3 method,[33] remained elusive because of the presence of the dimethylamines. For this reason, we decided to protect the hydroxyl groups as –OMOM functions that can be cleaved under mild acidic conditions. Thus, the protected derivative **5b** was isolated in quantitative yield.[34] Interestingly, in comparison with the corresponding methoxy derivative **5a**, compound **5b** displayed a higher reactivity toward the Sonogashira coupling as the bis-dimethylamino derivative **6b** was isolated after purification on silica gel in 85% yield. An acidic treatment followed by a careful adjustment of the pH using a saturated aqueous solution of $NaHCO_3$, afforded ligand **2** in quantitative yield.

In an attempt to evaluate the catalytic performance of ligands **1** and **2**, we examined the asymmetric epoxidation of α,β-unsaturated ketones such as chalcone and benzalacetone. Using the epoxidation conditions pioneered by Shibasaki et al.,[14b] the asymmetric epoxidation of the afore-mentioned olefins was performed in THF

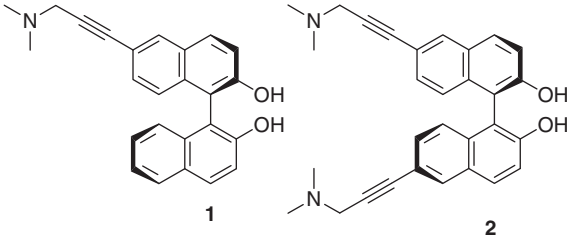
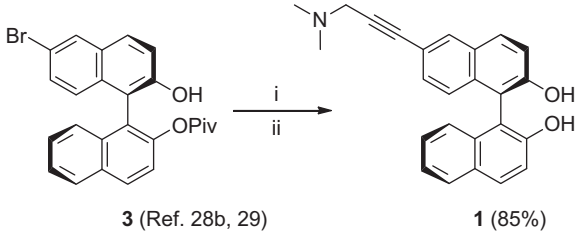
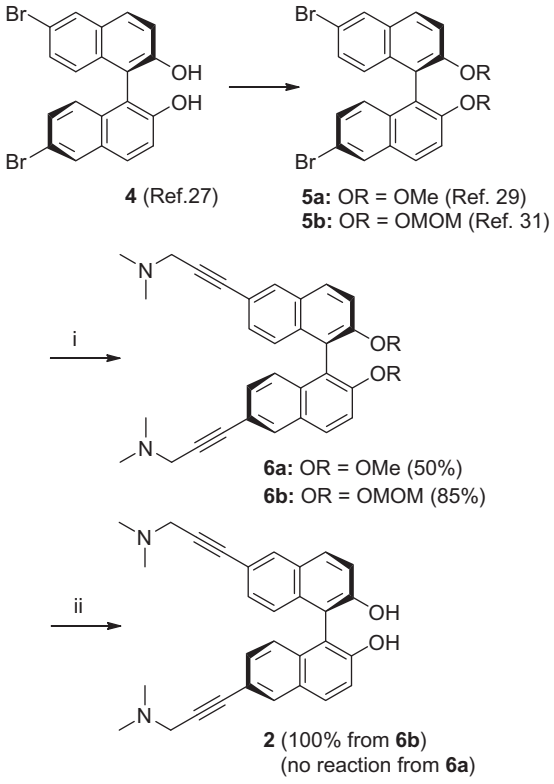


Figure 1. Target BINOL-based ligands.



i: $Me_2NCH_2C{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 75°C, 5 days
ii: KOH, MeOH - THF, r.t., 15 h

Scheme 1. Synthesis of the (*R*)-6-monosubstituted-BINOL ligand **1**.



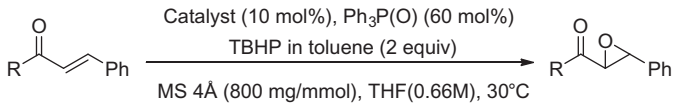
i: $Me_2NCH_2C{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 75°C; 5 days
ii for **6a** BBr_3, r.t.
for **6b** HCl (37%), MeOH, r.t.; 15h, pH-neutralization with $NaHCO_3$

Scheme 2. Synthesis of the (*R*)-6,6′-disubstituted-BINOL ligand **2**.

(0.66 M), using 10 mol % of catalyst prepared in situ from La(O*i*Pr)$_3$ or Yb(O*i*Pr)$_3$ and ligand **1** or **2** in a 1:1 ratio and by adding 60 mol % of triphenylphosphine oxide as additive, 2 equiv of *tert*-butyl hydroperoxide (TBHP) and dried 4 Å MS (800 mg per mmole of enone). The reactions were performed at 30 °C. The results obtained are gathered in Table 1.

In order to test our catalytic reactions and compare our results with Shibasaki's,[14b] we decided to run a reference reaction using La/(*R*)-BINOL and chalcone (R = Ph) as a substrate. After 2 days, a full conversion was obtained, and a medium enantiomeric excess of 57% was measured (Table 1, entry 3). The difference with results reported in the literature (Y = 99%, ee = 96%) may be attributed to the source of lanthanide salt or the water content (amount of MS) that is known to be critical for this type of reactions. A reference reaction with the Yb/(*R*)-BINOL catalyst was also performed (Table 1, entry 4). In the latter case, the enantiomeric excess reached 81%. Replacing (*R*)-BINOL with ligand **1** or **2** also afforded the best enantioselectivities when Yb was used at the expense of

Table 1
Representative results for the catalytic asymmetric epoxidation of α,β-unsaturated ketones[36]



N°	R	Catalyst[a]	Time (d)	Yield[b] (%)	ee[c] (%)
1	Ph	La(O*i*Pr)$_3$	2	100	0
2		Yb(O*i*Pr)$_3$	2	65	0
3		La/(*R*)-BINOL	2	100	57
4		Yb/(*R*)-BINOL	2	100	81
5		La/**1**	2	41	0
6		La/**2**	2	84	0
7		La/**2**$^{++}$[d]	2	80	0
8		Yb/**1**	2	75	49
9		Yb/**2**	2	100	57
10		Yb/**2**$^{++}$[d]	2	10	0
11	Me	La/(*R*)-BINOL[e]	4	29	50
12		Yb/(*R*)-BINOL[e]	7	26	73
13		La/**1**	5	100	0
14		La/**2**	5	38	0
15		Yb/**1**	5	100	90
16		Yb/**2**	5	100	90
17		Yb/**2**/SiO$_2$[f]	7	10	86
18		Yb/**2**/SiO$_2$[g]	10	40	93

[a] Catalytic system.
[b] Determined by HPLC.
[c] Determined by HPLC by comparison with the corresponding racemate.
[d] Dicationic ammonium salts after quaternization with MeI.
[e] 5 mol % of catalyst.
[f] Heterogeneous catalysis with Yb complex immobilized on silica.
[g] Second run without any addition of Yb complex.

La. Indeed, in the case of La complexes prepared from ligand **1** or **2**, the yields reached 41 and 84% respectively, but no enantiomeric excess was measured (Table 1, entries 5 and 6). The rationale for this observation relies on the presence of the remote dimethylamines that offer a pincer-type system able to coordinate the metal.[35] Interestingly, even if **1** can not bind La as tightly as **2**, the presence of a single dimethylamino-group is sufficient for preventing the required O-alkylation (Table 1, entry 5). To prevent this coordination, we decided to quaternarize the amino-functions by reacting methyliodide with compound **2**. Under these conditions, the corresponding dicationic ligand, noted **2**$^{++}$ was isolated in quantitative yield. Using the catalyst prepared from La(O*i*Pr)$_3$ and dicationic ligand **2**$^{++}$ in Shibasaki's conditions (Table 1, entry 7), a similar yield (80%) was obtained but the enantiomeric excess remained insignificant. This result was ascribed to the poor solubility of ligand **2**$^{++}$ and the corresponding La complex in THF, the conversion resulting from the presence of a small amount of uncoordinated La(O*i*Pr)$_3$ in solution. To confirm this hypothesis, a ligand-free reaction was done (Table 1, entry 1), and after the same reaction time, full conversion in epoxide was obtained. Interestingly, as Yb is more oxophilic than La, the amine functions do not compete with the O-coordination. Hence, using Yb complexes prepared with ligands **1** or **2**, asymmetric epoxidations of chalcone proceeded with medium enantiomeric excesses of 49% and 57%, respectively (Table 1, entries 8 and 9). Noticeably, the Yb complex based on the dicationic ligand **2**$^{++}$ only gave a low conversion in epoxide with no enantiomeric excess (Table 1, entry 10) because of the insolubility reasons mentioned above.

In the epoxidation of benzalacetone case, using the catalyst prepared from La(O*i*Pr)$_3$ and ligands **1** or **2** (Table 1, entries 13 and 14), no enantiomeric excess was measured. A full conversion was obtained with ligand **1**, whereas the benzalacetone epoxide was isolated in 38% yield with ligand **2**. A comparison of the results obtained with (*R*)-BINOL (Table 1, entry 11) and our ligand revealed a higher reactivity with our ligand at the expense of the enantioselectivity. Indeed, La (*R*)-BINOL complex gave a 29% conversion and 50% ee after 4 days of reaction. The best results were obtained with complexes prepared from Yb(O*i*Pr)$_3$ and ligand **1** or **2** (Table 1, entries 15 and 16). With the two Yb complexes, the conversions of the benzalacetone to the corresponding epoxides were complete after 5 days, with enantiomeric excesses reaching 90%. When Yb (*R*)-BINOL complex was used as catalyst, after 7 days of reaction a yield of 26% with an enantiomeric excess of 73% was obtained (Table 1, entry 12).

Finally, we decided to take advantage of the high polarity of the amino-groups for supporting **2** on silica gel. Indeed, not only grafting on SiO2 would prevent the deleterious coordination of the lanthanides by the amine, but release of the ligand could be achieved by simple addition of NEt$_3$. Accordingly, we immobilized the Yb/ligand **2** complex on silica and evaluated the resulting heterogeneous catalyst in the epoxidation of benzalacetone (Table 1, entry 17). Using the optimized conditions determined for the homogeneous catalysis, after 7 days of reaction, a low conversion of ca 10%. was measured. Despite the poor conversion possibly attributable to diffusion limitations, we did not observe any noticeable loss of enantioselectivity, as an ee of 86% was measured. After filtration, the supported Yb catalyst was reused in second epoxidation without any addition of ligand and Yb metal (Table 1, entry 18). Interestingly, after 10 days, a conversion of 40% and a similar enantioselectivity of 93% were measured (difference in the experimental error range), confirming the absence of leaching of the catalyst during the reaction and the treatment.

In this Letter, we have demonstrated that the selective introduction of one or two 3-(dimethylamino)prop-1-yn-1yl functions on the BINOL skeleton constitutes a promising approach for the development of a recyclable version of the catalytic system pioneered by Shibasaki et al. In particular, we have demonstrated that, in solution, the presence of the amino-function(s) does not hamper noticeably the catalytic performances of BINOL for the enantioselective epoxidation of electron poor olefins. Interestingly, we have proven that the amino-functionalized BINOL displays a higher catalytic activity when Yb was used at the expense of La. At last, we have taken advantage of the basicity of the BINOL-derived catalyst for immobilizing the Yb-complex on silica gel without post-functionalization. The latter complex could be recycled without loss of (enantio)selectivity, highlighting the potentiality of the approach. Work is underway in our Laboratory for improving the catalytic efficacy (conversion) of the supported catalyst using a silica gel with a larger surface area.

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Supplementary data

Supplementary data (experimental details and complete spectroscopic characterizations of new products) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.09.004.

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36. For the details of the experimental conditions, see Supplementary data.