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Catalytic enantioselective coupling of 2-naphthols by new chiral oxovanadium complexes bearing a self accelerating functional group

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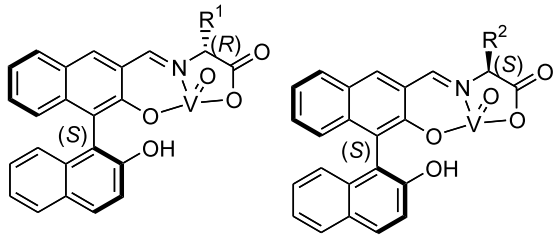
Abstract—New chiral oxovanadium complexes containing an extra phenolic hydroxyl group were found to enhance the catalytic enantioselective coupling of 2-naphthols in moderate to good enantioselectivity. © 2003 Published by Elsevier Science Ltd.

Optically active 1,1′-bi-2-naphthol (BINOL) and its derivatives have been extensively utilized as chiral auxiliaries and ligands in asymmetric synthesis.[1] The enantiomerically pure BINOLs could be obtained from their racemates by a number of methods such as kinetic resolution, enzymatic hydrolysis of the corresponding ester, and enantiomeric separation on chiral stationary phases.[2] However, the stoichiometric use of these resolving agents hinders their practical application. Therefore, it is of synthetic value to search for a convenient catalytic method for the enantioselective coupling of 2-naphthols. Research toward the catalytic asymmetric synthesis of BINOLs has produced encouraging results. The use of CuCl in the presence of optically active diamines was able to achieve the coupling of 3-carboalkoxy-2-naphthols with high enantioselectivity (ee = 93%), whereas the coupling of 2-naphthol gave lower enantiomeric excesses (13-38%).[3a] A photo-activated chiral Ru(II) complex has been used for the aerobic oxidative coupling of 2-naphthol derivatives with 33–71% ee.[4] We reported the first aerobic oxidative coupling of 2-naphthols and phenols catalyzed by $VO(acac)_2$,[5a] and chiral Schiff base ligands derived vanadium complexes in the asymmetric catalytic coupling of 2-naphthols, which occurred with moderate enantioselectivity.[5b] Chen conducted a similar work independently at the same time, achieving ees of 10–68%.[6a] Recently, Chen also reported the use of chiral vanadyl dicarbonylates for the asymmetric coupling of 2-naphthols with 42–87% ee at 44°C after 7–10 days,[6b] and Gong utilized dioxovanadium complexes for the asymmetric coupling of 2-naphthols to achieve 81–98% ee at 0°C after 5–8 days.[6c] To the best of our knowledge, there is no reported chiral oxovanadium species that could catalyze the asymmetric coupling of naphthols at a reasonable reaction rate with high enantioselectivity in the absence of a promoter.[5b] As an extension of our ongoing interest in this area, we now report new oxovanadium complexes which are able to accelerate the catalytic asymmetric coupling of 2-naphthols in the absence of any promoter with moderate to good enantioselectivity (Fig. 1).

At the outset, we synthesized chiral oxovanadium complexes **1a–d** and **2** by the condensation of (*S*)-3-formyl-1,1′-bi-2-naphthol with chiral amino acids and vanadyl sulfate.[7] Mass analyses by FAB technique indicated



$_1$**a** R^1 = Bn
$_1$**b** R^1 = *t*Bu
$_1$**c** R^1 = *i*Pr
$_1$**d** R^1 = Ph

$_2$ R^2 = Bn

Figure 1.

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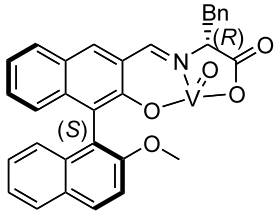
that these complexes were mainly composed of tetradentate monomer and pentadentate dimers.[8]

We then investigated the oxidative coupling of 2-naphthol by using 10 mol% complex **1a** as catalyst, molecular oxygen as oxidant and chloroform as solvent. It was surprising to note that the *R*-configured product could be isolated in good yield with moderate enantioselectivity within 12 h (Table 1, entry 1). This is contrary to previous reports, where the catalytic oxidative coupling of 2-naphthol required longer reaction times in the absence of a promoter.[6] Under similar conditions, complex **2**, derived from (*S*)-3-formyl-1,1′-bi-2-naphthol and the (*S*)-α-amino acid, induced inferior enantioselectivity (Table 1, entry 2). These results indicate that the combination of the (*S*)-BINOL-derived aldehyde and the (*R*)-α-amino acid represents a matched pair for the asymmetric oxidative coupling of 2-naphthol, whereas the complex derived from (*S*)-BINOL and the (*S*)-α-amino acid is mismatched.[6c] No considerable difference in terms of enantioselectivity was observed upon increasing the concentration of 2-naphthol or reducing the concentration of the catalyst (Table 1, entries 3–7). Complex **1b**, bearing a *tert*-butyl substituent, led to the formation of BINOL with similar enantioselectivity to complex **1a**, but a significant drop in reactivity was observed (Table 1, entry 8). Complexes **1c** and **1d** were inferior catalysts when compared with **1a** in terms of reaction rate and enantioselectivity (Table 1, entries 9 and 10).

We surmised that the phenolic hydroxyl group on complex **1** or **2** played an important role in the catalytic reaction and served as a promoter.[5b] To clarify our hypothesis, complex **3**—bearing a methoxy group instead of a hydroxyl group—was studied under the same conditions. As expected, the *R*-BINOL was isolated after 24 h in only 26% yield and 38% ee. It is apparent that the phenolic hydroxyl group activated the oxovanadium complex to accelerate the oxidative coupling of 2-naphthol. From FT-IR spectroscopic measurements, the V=O stretching frequency of complex **1a** was found at 967 cm^{-1}, whereas that of complex **3** shifted to 997 cm^{-1}. The data seems to suggest that hydrogen bonding between the hydroxyl group and the oxovanadium moiety occurs, which should affect the redox potentials of the vanadium species involved in the catalytic cycle and, in turn, the turnover rate. It would be very interesting to understand the difference between these two catalysts. Unfortunately, we are unable to obtain the crystal structure of complexes **1a** and **3** at this moment.



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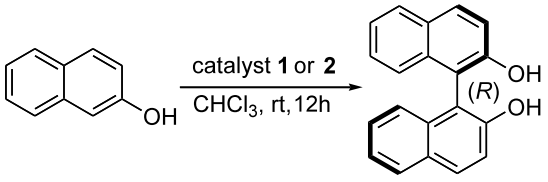
To study the scope of the reaction, a number of substrates were tested using catalyst **1a** at a loading of 5 mol%. The results are summarized in Table 2. Lower enantioselectivities were observed in the asymmetric coupling with substrates bearing C-6-substituents, however, the C-7-substituted substrates gave the corresponding binaphthols in high yields with good enantioselectivities (entries 4–8). The enantioselectivity of the asymmetric coupling remained the same over a range of reaction temperatures, although the yields were different (entries 4–6). Substitution at C-3 led to suppressed the rate of the oxidative coupling (entries 9 and 10).

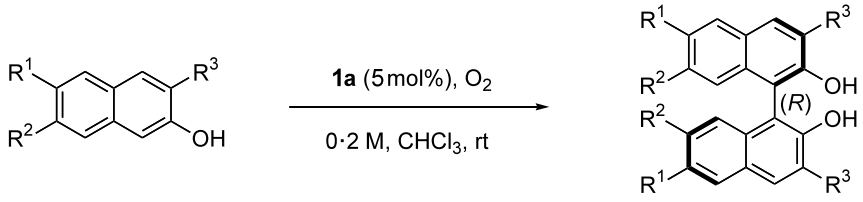
Table 1. Oxidative coupling of 2-naphthol using catalysts **1** and **2**



Entry	Conc.[a]	Catalyst	Loading (mol%)	Yield (%)	E.e. (%)[b]
1	0.1	**1a** (R^1 = Bn)	10	78	52
2	0.1	**2** (R^2 = Bn)	10	78	8
3	0.2	**1a**	5	80	54
4	0.3	**1a**	3.3	83	48
5	0.5	**1a**	2	78	46
6	0.1	**1a**	5	55	51
7	0.1	**1a**	2	44	53
8	0.2	**1b** (R^1 = *t*Bu)	5	60	55
9	0.2	**1c** (R^1 = *i*Pr)	5	63	45
10	0.2	**1d** (R^1 = Ph)	5	48	25

[a] Substrate concentration (M).
[b] Determined by HPLC with Kromasil 100-5CHI-DMB column (*i*PrOH/hexane = 5/95, 1 mL/min).

Table 2. Enantioselective oxidative coupling of 2-naphthol derivatives catalyzed by chiral oxovanadium complex **1a**



(*R*)-**4a** R^1 = H, R^2 = H, R^3 = H
(*R*)-**4b** R^1 = Br, R^2 = H, R^3 = H
(*R*)-**4c** R^1 = OMe, R^2 = H, R^3 = H
(*R*)-**4d** R^1 = H, R^2 = OMe, R^3 = H
(*R*)-**4e** R^1 = H, R^2 = OEt, R^3 = H
(*R*)-**4f** R^1 = H, R^2 = OBn, R^3 = H
(*R*)-**4g** R^1 = H, R^2 = H, R^3 = CO_2Me
(*R*)-**4h** R^1 = H, R^2 = H, R^3 = OMe

Entry	Time (h)	Product	Yield (%)	E.e. (%)[a]
1	16	**4a**	93	54
2	36	**4b**	80	18
3	11	**4c**	96	25
4	11	**4d**	96	72
5[b]	8	**4d**	90	73
6[c]	18	**4d**	40	73
7	9	**4e**	93	72
8	18	**4f**	74	68
9	48	**4g**	Trace	ND
10	60	**4h**	Trace	ND

[a] Determined by HPLC with Kromasil 100-5CHI-DMB column (*i*PrOH/hexane = 5/95, 1 mL/min).
[b] Reaction temp: 44°C.
[c] Reaction temp: 0°C.

In conclusion, enantiomerically enriched BINOLs can be prepared using chiral vanadium complexes derived from (*S*)-3-formyl-1,1′-bi-2-naphthol and (*R*)-α-amino acids. The function of the phenolic hydroxyl group in the catalyst and the mechanism of the asymmetric coupling are currently under investigation.

Acknowledgements

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8. LRMS (FAB) analysis for **1a** ($C_{30}H_{21}NO_5V$, 526): 1051 (M_2-H^+, 17), 527 ($M+H^+$, 42), 526 (M, 45), 239 (78), 154 (94), 136 (100); LRMS (FAB) analysis for **3** ($C_{31}H_{23}NO_5V$, 540): 1081 (M_2+H^+, 25), 541 ($M+H^+$, 60), 496 (100), 334 (29), 239 (49), 136 (36).