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Chiral oxovanadium complex catalyzed enantioselective oxidative coupling of 2-naphthols†

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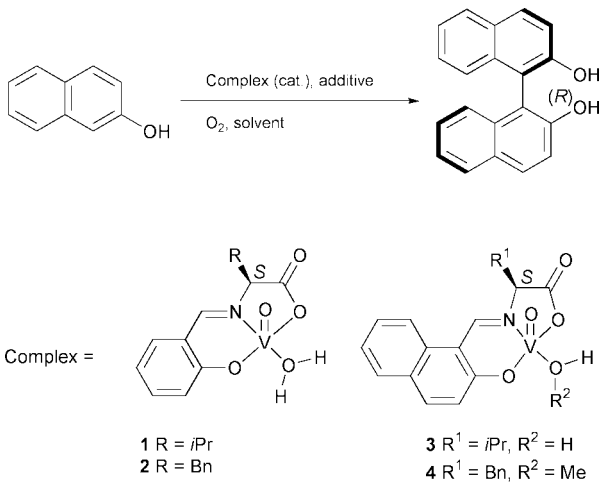
The enantioselective oxidative coupling of 2-naphthols using 2 mol% chiral oxovanadium complex under mild conditions afforded chiral BINOLs in moderate enantioselectivity.

Vanadium plays a vital role in biological systems with its participation in redox processes catalyzed by enzymes such as bromoperoxidase[1] and nitrogenase.[2] The utility of vanadium complexes in oxidation, reduction and Lewis acid promoted reactions is well documented.[3] Except for oxidation of sulfides[4] and epoxidation of allylic alcohols,[5] there are very few vanadium complex catalyzed enantioselective reactions. Recently we reported the aerobic oxidative coupling of 2-naphthols and phenols catalyzed by $VO(acac)_2$.[6] Replacement of acac in this complex by chiral bidentate ligands, such as 3-formylcamphor and 3-heptafluorobutyrylcamphor, did not lead to any enantioselectivity in coupling products. Earlier, Fujita had utilized some chiral tridentate Schiff base ligands containing vanadium complexes in asymmetric oxidation of sulfides with moderate enantioselectivity.[4a]

In the light of these observations, we have studied the oxidative coupling of 2-naphthols using chiral tridentate oxovanadium complexes as a method for the enantioselective synthesis of chiral BINOLs; although enantioselective coupling of naphthols has been earlier reported, Katsuki used a ruthenium complex and Nakajima employed a copper complex as the catalyst in their reactions.[7] Herein, we report chiral oxovanadium complex catalyzed C–C bond formation in aryl compounds with 51% ee and 50–91% isolated yield (Scheme 1).‡

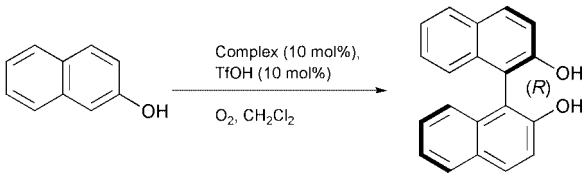
Following the literature procedure,[8] we have synthesized chiral oxovanadium complexes from aldehyde, (*S*)-valine or (*S*)-phenylalanine and vanadyl sulfate, and applied them in our reactions. At first, we examined oxidative coupling of 2-naphthol by using 10 mol% complex **1** as catalyst, molecular oxygen as oxidant and dichloromethane as solvent, but the product could only be isolated in trace amounts (Table 1, entry 1). Earlier Carrano and Tsuchida reported that vanadium(IV) undergoes disproportion to vanadium(III) and vanadium(V) in strong acidic condition.[9] When we added a catalytic amount of trifluoromethanesulfonic acid to the reaction mixture, it led to improved chemical yield but with only 27% ee (Table 1, entry 2). Catalysts **2** to **4** gave similar enantioselectivity in these reactions (Table 1, entries 3–5). Complexes containing bulkier amino acids, such as (*S*)-*tert*-leucine and (*S*)-phenylglycine as ligands, did not produce appreciable enantioselectivity. We



Scheme 1

† Electronic supplementary information available: HPLC analyses. See http://www.rsc.org/suppdata/cc/b1/b101670i/

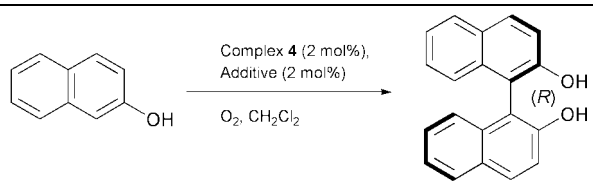
Table 1 Enantioselective oxidative coupling of 2-naphthol



Entry	Complex	Time/h	Yield (%)	Ee (%)[a]
1[b]	**1**	6	trace	—
2	**1**	24	79	27
3	**2**	24	70	23
4	**3**	12	42	26
5	**4**	12	56	27
6[c]	**4**	12	94	23
7[cd]	**4**	12	87	31
8[cde]	**4**	24	80	42

[a] Determined by HPLC with Kromasil 100-5CHI-DMB column (*i*PrOH–hexane = 5:95, 1 mL min^{-1}). [b] TfOH was not added. [c] TMSOTf replaced TfOH. [d] Concentration was 0.5 M. [e] Catalyzed by 2 mol% complex.

Table 2 Promoter effect for enantioselective oxidative coupling of 2-naphthol



Entry	Additive	Yield (%)	Ee (%)[a]
1	TMSOTf	80	42
2	TFAA	50	43
3	$HClO_4$	64	29
4	TMSCl	73	48
5	TESCl	45	48
6	TBDPSCl	48	49
7	TMSBr	60	48
8	TMSCl + $AgClO_4$	68	31

[a] Determined by HPLC with Kromasil 100-5CHI-DMB column (iPrOH–hexane = 5:95, 1 mL min^{-1}).

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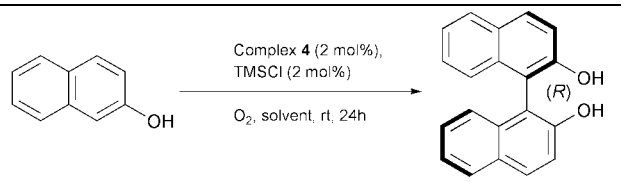
Table 3 Solvent effect for enantioselective oxidative coupling of 2-naphthol



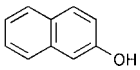
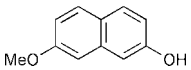
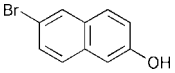
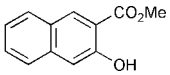
Entry	Solvent	Yield (%)	Ee (%)[a]
1	CH_2Cl_2	73	48
2	$CHCl_3$	82	51
3	$(CH_2Cl)_2$	38	46
4	CCl_4	12	13
5	CH_3CN	46	8
6	THF	24	0

[a] Determined by HPLC with Kromasil 100-5CHI-DMB column (iPrOH–hexane = 5:95, 1 mL min^{-1}).

presumed that the electronic effect of substituents in the aromatic ring could influence catalyzing oxidative coupling, and investigated complexes containing 3,5-di-*tert*-butyl, 3-*tert*-butyl, 5-methoxy and 5-nitro substituents, but no significant enantioselectivity was observed with these complexes. However, we observed a marginal increase in enantioselectivity when the concentration of the substrate was increased from 0.1 to 0.5 M (Table 1, entry 7). An interesting feature was that enantioselectivity increased with decrease in concentration of complexes from 10 to 2 mol%, more so, in the case of complex **4** (Table 1, entry 8), and (*R*)-binaphthol was obtained in 42% ee.

To study the promoter effect, we used various additives. The enantioselectivity was better in TMSCl than in TMSOTf, and the chemical yield was a little lower (Table 2, entry 4). There was no change in enantioselectivity with variation of silyl groups in the additives, but it affected the reaction rate (Table 2, entries 4–6). Polar chlorosolvents such as dichloromethane, chloroform and 1,2-dichloroethane merely improved the enantioselectivity (Table 3).

Table 4 Enantioselective oxidative coupling of 2-naphthol derivatives

Entry	Naphthol	Time/h	Yield (%)	Ee (%)[a]
1		24	82	51
2		24	91	51
3		24	50	51
4		69	trace	—

[a] Determined by HPLC with Kromasil 100-5CHI-DMB column (*i*PrOH–hexane = 5:95, 1 mL min^{-1}).

The results obtained from the enantioselective oxidation of other substituted 2-naphthols catalyzed by complex **4** are summarized in Table 4. No variation in enantioselectivities was observed, but reaction rate was increased with electron donating capacity of the substituent.

In conclusion, oxovanadium complex has been used for the first time[10] in the enantioselective coupling of 2-naphthols. A low concentration requirement of catalyst, mild reaction conditions and high chemical yields render our method attractive.

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Notes and references

‡ *Representative procedure for enantioselective oxidative coupling of 2-naphthols*: to a stirred solution of complex (0.1 mmol) and TMSCl (13 μL, 0.1 mmol) in chloroform (10 mL) exposed to molecular oxygen at room temperature was added 2-naphthol (5 mmol). After 24 h, the reaction mixture was treated with 6 M HCl (10 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic extracts were dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography eluting with ethyl acetate–hexane (1:5) to furnish the coupling product.

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