

Review

Development of Dinuclear Vanadium Catalysts for Enantioselective Coupling of 2-Naphthols via a Dual Activation Mechanism

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This review describes our recent efforts in the development of chiral dinuclear vanadium complexes which work as dual activation catalysts for oxidative coupling of 2-naphthols. A chiral dinuclear vanadium(IV) complex ($R_{a,S,S}$)-1a possessing (*S*)-*tert*-leucine moieties at the 3,3'-positions of the (*R*)-binaphthyl skeleton was developed, and found to promote oxidative coupling of 2-naphthol to afford (*S*)-1,1'-bi-2-naphthol (BINOL) with 91% ee. To verify the dual activation mechanism, mononuclear vanadium(IV) complex (*S*)-10 was also prepared. Kinetic analysis revealed that the reaction rate of oxidative coupling of 2-naphthol promoted by ($R_{a,S,S}$)-1a is 48.3 times faster than that of (*S*)-10. In the coupling reaction, the two vanadium metals in the chiral complex activate two molecules of 2-naphthol simultaneously achieving a high reaction rate with high enantiocontrol. Since the dinuclear vanadium(IV) complex was found to be readily oxidized to afford a corresponding vanadium(V) species during preparation in air, a new synthetic procedure using VOCl_3 and a convenient one-pot procedure using VOSO_4 under O_2 have been applied towards dinuclear vanadium(V) complexes ($R_{a,S,S}$)-2. The coupling of 2-naphthol was catalyzed by ($R_{a,S,S}$)-2 with reaction rates enhanced 2.3 times faster than that of ($R_{a,S,S}$)-1a, which is likely a precatalyst. To the best of our knowledge, ($R_{a,S,S}$)-1a, 2, and 3 show considerably higher catalytic activity than previously reported vanadium complexes for oxidative coupling of 2-naphthols.

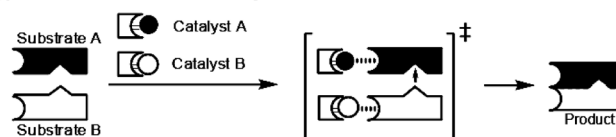
Key words dual activation; enantioselective oxidative coupling; dinuclear vanadium complex; 1,1'-bi-2-naphthol; chiral catalyst

Catalytic asymmetric reactions are among the most powerful synthetic methods to obtain optically active compounds.^{1,2)} Recent challenges focus on the development of asymmetric catalysts for carbon-carbon bond-forming reactions with high activity and broad substrate generality, which lead to practical, efficient, and environmentally benign chemical syntheses. Dual activation systems for substrates such as nucleophiles and electrophiles lead to enhanced reaction rates and more specific control of the transition structure with respect to the catalyst's asymmetric environment.^{3–41)} Dual activation catalyses can be classified into three categories (Fig. 1): Type 1) dual activation using two different kinds of catalysts^{3–12)}; Type 2) conjugated-type dual activation with a functional group such as a phosphate which has both acidic and basic sites in one functionality^{13–15)}; and Type 3) dual activation by two catalytic sites in a single catalyst.^{16–41)} For efficient dual activation of the substrates, a balance between these two functionalities in the catalyst is required. For example, in an acid-base type catalyst the self-quenching reaction of acidic and basic moieties on the catalyst can lead to its inactivation.

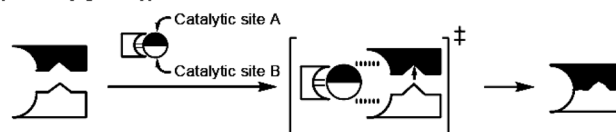
We postulated that a chiral complex possessing two identical metal centers in a single molecule, which could activate two substrates simultaneously in a homolytic coupling reaction of 2-naphthol molecules, would enhance the reaction

rate with high enantioselectivity. To achieve the new dual activation catalysis in an oxidative coupling reaction, we designed the catalyst ($R_{a,S,S}$)-1⁴²⁾ bearing two active sites attached to a binaphthyl skeleton, taking advantage of the activation entropy (Fig. 2). Activation entropy strongly con-

Type 1: two different kinds of catalysts



Type 2: conjugated-type functionalities



Type 3: two catalytic sites in a single catalyst

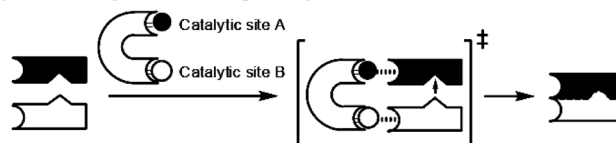


Fig. 1. Dual Activation Systems in Catalytic Enantioselective Reactions

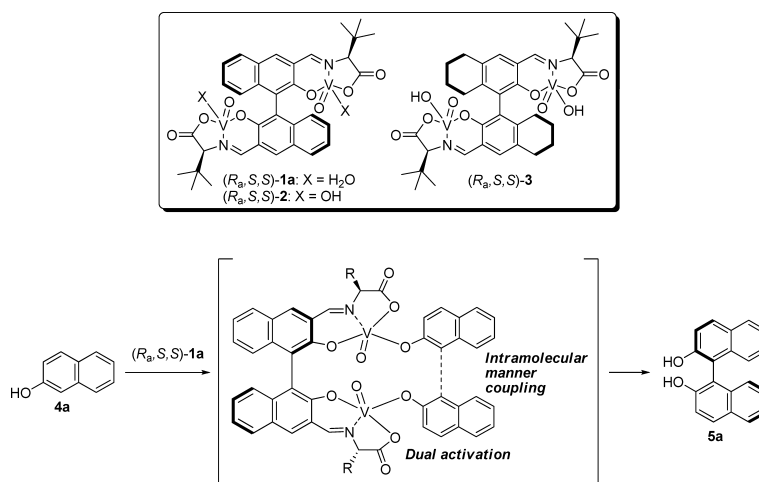


Fig. 2. Dinuclear Vanadium Complex with Dual Activation System in Oxidative Coupling of 2-Naphthol

tributes to intramolecular manner coupling after two molecules of 2-naphthol are complexed with the dinuclear vanadium catalyst.⁴³ This review presents our recent research on development of chiral dinuclear vanadium complexes which work as dual activation catalysts for oxidative coupling of 2-naphthols.^{44–48}

The synthesis of optically pure 1,1'-bi-2-naphthol (BINOL) derivatives is of importance because these moieties are used as chiral ligands and auxiliaries for a wide range of organic functional transformations.^{49,50} Catalytic asymmetric preparation of BINOL systems has continued to attract the attention of many researchers.^{51–61} The asymmetric oxidative coupling of 2-naphthol molecules is one of the most useful methods for synthesis of optically pure BINOL derivatives. Vanadium-mediated couplings, which occur *via* a favorable one-electron phenolic oxidation, proceed under mild reaction conditions and tolerate many functional groups, with the further advantage that only water is formed as side product.^{62–71} In 2001, Chen and colleagues⁶² and Uang and colleagues⁶⁴ independently reported the first efficient asymmetric vanadium(IV) catalysts for oxidative coupling of 2-naphthol molecules prepared from vanadium(IV) oxide sulfate (VOSO₄), aldehyde derivatives, and (*S*)-amino acids. Gong and colleagues^{66–68} reported dinuclear vanadium catalysts which possess a V–O–V linkage with a maximum enantioselectivity of 98%. These vanadium catalysts showed good enantioselectivity for the coupling of 2-naphthol derivatives,

although the catalytic activity was moderate. Chu and Uang found that catalytic activity could be improved by the addition of Lewis⁶⁴ or Brønsted acids,⁶⁵ resulting in the production of BINOL with moderate to good enantioselectivity. Barhate and Chen⁶³ also developed the vanadium(IV) catalysts derived from VOSO₄, (+)-ketopinic acid, and α -amino acids. To improve the coupling yields, the effect of oxygen pressure was examined. Although the coupling rate of 2-naphthol was greatly enhanced by more than six times under an oxygen pressure of 8.8 atm, a significant drop in ee for BINOL was observed. Development of active vanadium complexes with high enantiocontrol remains a challenge.

1. Preparation of Dinuclear Vanadium(IV) Complexes

To create a dual activation system in an oxidative coupling reaction, dinuclear vanadium(IV) complexes **1** were prepared from VOSO₄, (*R*)- or (*S*)-3,3'-diformyl-2,2'-dihydroxy-1,1'-binaphthyl (**6**) and amino acids (Chart 1). Since NMR spectroscopy is not suitable for paramagnetic vanadium(IV) species, FAB-HR-MS, ESR spectroscopy, and FT-IR analyses were used to characterize **1**. ESR of (*R_a,S,S*)-**1a** showed eight peaks which can be assigned to a vanadium(IV) species (Fig. 3).

The oxidative coupling reactions of 2-naphthol by the catalysts were carried out in CH₂Cl₂ at 30 °C in 24 h under oxygen (Table 1). Among the catalysts we studied, (*R_a,S,S*)-**1a** possessing *tert*-butyl groups exhibited extremely high cat-

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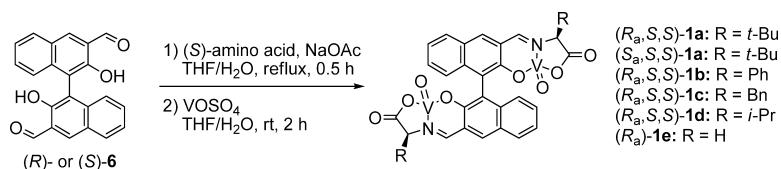
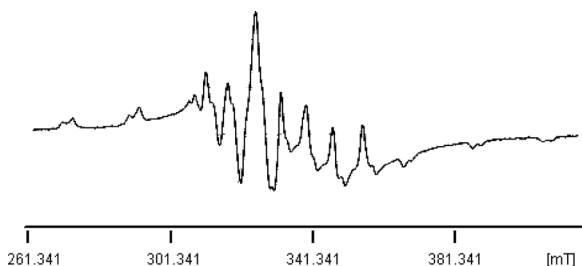
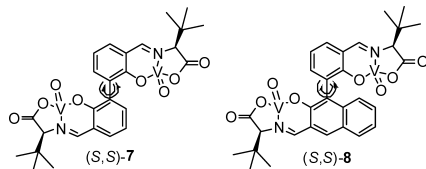
Chart 1. Preparation of Dinuclear Vanadium(IV) Complexes **1**Fig. 3. ESR Spectrum of (R_a,S,S) -**1a** in CH_2Cl_2 at $-120\text{ }^\circ\text{C}$

Table 1. Enantioselective Coupling of 2-Naphthol Catalyzed by Chiral Dinuclear Vanadium(IV) Catalysts

Entry	Catalyst	Yield (%)	Ee (%)
1	(R_a,S,S) - 1a	83	83 (<i>S</i>)
2	(S_a,S,S) - 1a	9	2 (<i>R</i>)
3	(R_a,S,S) - 1b	21	<i>Rac</i>
4	(R_a,S,S) - 1c	30	8 (<i>R</i>)
5	(R_a,S,S) - 1d	52	66 (<i>S</i>)
6	(R_a) - 1e	6	<i>Rac</i>
7	(S,S) - 7	57	81 (<i>S</i>)
8	(S,S) - 8	63	81 (<i>S</i>)



alytic activity in the oxidative coupling of 2-naphthol (entry 1). No byproduct was observed in any reaction. Since the diastereomeric catalyst (S_a,S,S) -**1a** was less active (entry 2), (R_a,S,S) -**1a** constitutes a *matched pair* and (S_a,S,S) -**1a** would be a *mismatched pair* for oxidative coupling of 2-naphthol. The tropos-type⁷² complexes (S,S) -**7** and **8**, with free rotation of either phenyl–phenyl or phenyl–naphthyl units, were also prepared, though their reaction rates were decreased compared to (R_a,S,S) -**1a** (entries 7, 8). In the case of the complexes (S,S) -**7** and **8**, the equilibrium between matched and mismatched conformations diminished the reaction rate. These results revealed that two *tert*-leucine derived moieties in the catalyst affect the enantiocontrol of the coupling and the binaphthyl backbone assists to align the two molecules of 2-naphthol with each other for oxidative coupling.

An insufficient amount of VOSO_4 leads to the formation of vanadium(IV) complex **9**, which bears only one vanadium metal in the catalyst molecule. An attempt deliberately to prepare complex **9** for comparison of its catalytic activity with (R_a,S,S) -**1a** resulted in a switch of the major product

enantiomer to (R) -BINOL with 13% ee (Table 2, entry 1). To avoid the formation of a mononuclear vanadium catalyst, 4 eq of VOSO_4 was used (entry 3). The excess VOSO_4 can be filtered off after complex formation. Although the reaction rate promoted by (R_a,S,S) -**1a** was slightly decreased under air, (S) -BINOL was obtained with higher enantioselectivity (91% ee) than that produced under oxygen (entry 4). In either CCl_4 or CHCl_3 , the reaction mixture was heterogeneous and (S) -BINOL was obtained in low yields with moderate enantioselectivity (entries 6, 7). In $(\text{CH}_2\text{Cl}_2)_2$, the coupling reaction proceeded smoothly to afford (S) -BINOL with similar enantiocontrol to that mediated in CH_2Cl_2 (entry 8).

2. Confirmation of the Oxidative State of Vanadium in the Catalyst

During further characterization, single crystals suitable for X-ray analysis were obtained by recrystallization of (R_a,S,S) -**1a** from $\text{MeOH}/\text{Et}_2\text{O}/\text{H}_2\text{O}$ in the presence of NaOAc as an interdiffusion form in the complexation as shown in Chart 1.^{73,74} The binding energy of $\text{V } 2p_{3/2}$ for the crystals was 516.9 eV by X-ray photoelectron spectroscopy (XPS), which is attributed to V(V) not V(IV) .⁷⁵ The complex was oxidized to a distorted octahedral vanadium(V) species with one extra hydroxide to each vanadium center [V1-O3 , 1.747(5) Å] (Fig. 4).⁷⁶ The hydroxyl group is anti to the imine nitrogen. The V=O [V1-O2 , 1.602(8) Å] bond is syn to the *tert*-butyl groups in the template. The sodium cation is coordinated by the oxygen atoms of two carboxylic groups [Na1-O4 , 2.393(5) Å] on the (S) -*tert*-leucine regions.

To determine the oxidative state of vanadium after complex formation to give (R_a,S,S) -**1a**, superconducting quantum interference device (SQUID) analyses were performed on the dinuclear vanadium complexes using VOSO_4 and V_2O_5 as standards for the vanadium(IV) and vanadium(V) samples, respectively (Fig. 5).⁷⁷ The magnetic susceptibility of (R_a,S,S) -**1a** prepared under air was 5 emu/mol at 5 K in 5 T (curve c). In contrast, the vanadium complex prepared under argon gave a value of 28 emu/mol (curve b). The magnetic susceptibility of the single crystals obtained by recrystallization, as shown in Fig. 4, exhibited 0 emu/mol, clearly indicating a vanadium(V) species (curve d). These results suggest the dinuclear vanadium(IV) complex is readily oxidized to afford a vanadium(V) species during preparation in air.

When single crystals (Fig. 4) were used as catalyst for oxidative coupling of 2-naphthol, no catalytic activity was observed. This may be attributed to the low solubility in CH_2Cl_2 . However, addition of 1 eq of 5 N HCl aq. to the sodium in the crystal gave a homogeneous solution.⁷⁸ To the homogeneous solution containing 5 mol% of dinuclear vanadium(V) complex was added 2-naphthol under air, providing (S) -BINOL in 90% yield with 83% ee after 24 h.

Table 2. Activity of the Catalyst Derived from Various Amounts of VOSO₄, (*R*)-**6** and (*S*)-*tert*-Leucine

Entry	VOSO ₄ ^{a)} (mol eq)	Atmosphere	Solvent	Catalyst (mol%)	Time (h)	Yield (%)	Ee (%)
1	1	O ₂	CH ₂ Cl ₂	5	24	15	13 (<i>R</i>)
2	2	O ₂	CH ₂ Cl ₂	5	24	65	78 (<i>S</i>)
3	4	O ₂	CH ₂ Cl ₂	5	24	83	83 (<i>S</i>)
4	4	Air	CH ₂ Cl ₂	5	24	76	91 (<i>S</i>)
5	4	Air	CH ₂ Cl ₂	1	168	99	90 (<i>S</i>)
6	4	Air	CCl ₄	5	24	42	36 (<i>S</i>)
7	4	Air	CHCl ₃	5	24	40	63 (<i>S</i>)
8	4	Air	(CH ₂ Cl) ₂	5	24	99	89 (<i>S</i>)

a) Numbers show molar equivalent to the diformyl compounds.

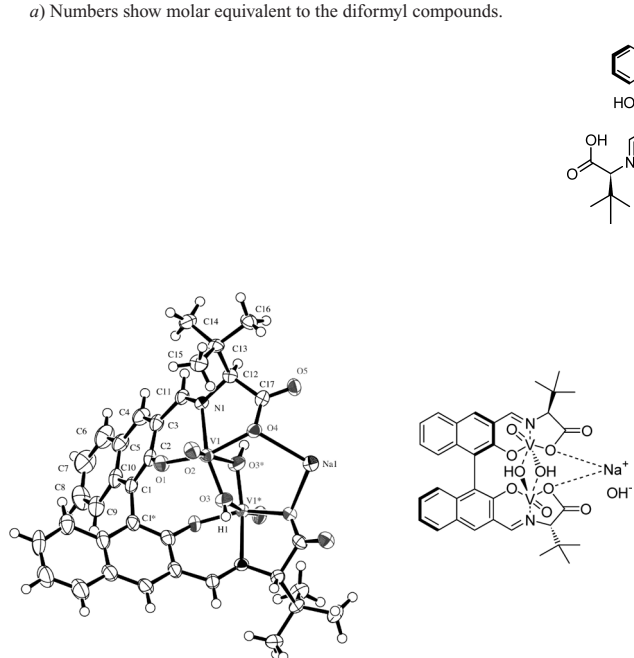


Fig. 4. Structure of the Dinuclear Vanadium(V) Complex (*R*_a,*S*,*S*,*S*)-**2** · 2 NaOH

A counter anion OH⁻, the hydrogen atom of which has not been determined, is omitted for clarity.

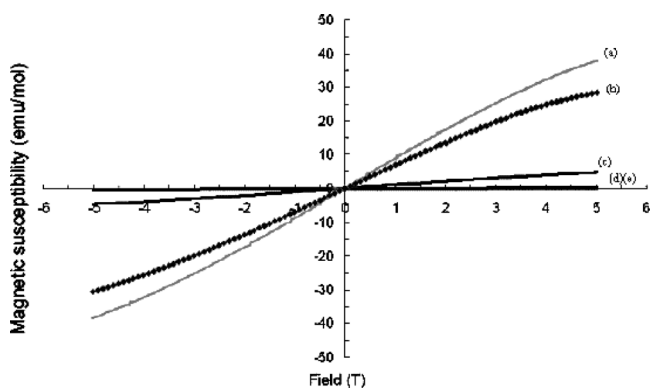
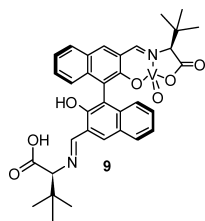


Fig. 5. SQUID Magnetometer Plot of Magnetic Susceptibility for Vanadium under a Magnetic Field at 5 K for (a) VOSO₄, (b) (*R*_a,*S*,*S*,*S*)-**1a** (Prepared under Ar), (c) (*R*_a,*S*,*S*,*S*)-**1a** (Prepared under Air), (d) Single Crystals Obtained by Recrystallization of (*R*_a,*S*,*S*,*S*)-**1a** from MeOH/Et₂O/H₂O Containing NaOAc, and (e) V₂O₅

3. Kinetic Analysis of Dinuclear and Mononuclear Vanadium Complexes in the Coupling of 2-Naphthol

To clarify the *dual activation* mechanism in the dinuclear vanadium catalyst (*R*_a,*S*,*S*,*S*)-**1a**, mononuclear vanadium(IV)



complex (*S*)-**10** was prepared. In kinetic analysis (Fig. 6), the amount of (*S*)-**10** used was twice that of (*R*_a,*S*,*S*,*S*)-**1a** because (*S*)-**10** has only one active center. The catalysis by (*R*_a,*S*,*S*,*S*)-**1a** and (*S*)-**10** obeyed second-order kinetics up to about 15 h. The mononuclear complex (*S*)-**10** had quite low activity and gave almost racemic BINOL. The calculated rate constants for the coupling reactions were $k_{(R_a,S,S,S)-1a} = 0.1738 \text{ M}^{-1} \text{ h}^{-1}$ and $k_{(S)-10} = 0.0036 \text{ M}^{-1} \text{ h}^{-1}$. The coupling rate in the presence of 5 mol% of dinuclear complex (*R*_a,*S*,*S*,*S*)-**1a** was shown to be up to 48.3 times faster than that using 10 mol% of mononuclear complex (*S*)-**10**. Calculations based on Arrhenius and Eyring plots indicated the activation energies of catalysts (*R*_a,*S*,*S*,*S*)-**1a** and (*S*)-**10** were $\Delta E_{(R_a,S,S,S)-1a} = 0.74 \text{ kcal/mol}$ and $\Delta E_{(S)-10} = 23 \text{ kcal/mol}$. The activation entropy and enthalpy of catalyst (*R*_a,*S*,*S*,*S*)-**1a** were $\Delta S_{(R_a,S,S,S)-1a}^\ddagger = -7.8 \times 10^{-2} \text{ kcal/mol} \cdot \text{K}$ and $\Delta H_{(R_a,S,S,S)-1a}^\ddagger = 0.16 \text{ kcal/mol}$, and those of (*S*)-**10** were $\Delta S_{(S)-10}^\ddagger = -1.5 \times 10^{-2} \text{ kcal/mol} \cdot \text{K}$, and $\Delta H_{(S)-10}^\ddagger = 21 \text{ kcal/mol}$, respectively. The *lower activation entropy* using (*R*_a,*S*,*S*,*S*)-**1a** compared to (*S*)-**10** is attributed to the dual activation of two 2-naphthol molecules in one chiral complex to produce BINOL. The *higher activation enthalpy* using (*S*)-**10** compared to (*R*_a,*S*,*S*,*S*)-**1a** is due to the intermolecular radical-radical coupling of reaction intermediates after complexation of (*S*)-**10** with 2-naphthol. To realize the most powerful dual activation catalyst in the oxidative coupling, dinuclear vanadium(V) complex (*R*_a,*S*,*S*,*S*)-**2** and mononuclear vanadium(V) complex (*S*)-**11** were also prepared by the use of vanadium(V) oxytrichloride (VOCl₃) as vanadium(V) source. The coupling of 2-naphthol was catalyzed by (*R*_a,*S*,*S*,*S*)-**2** with reaction rates enhanced 2.3 times faster than that of (*R*_a,*S*,*S*,*S*)-**1a**. The dinuclear vanadium(IV) complex is likely a precatalyst. Interestingly, not only the reaction rate but also the enantioselectivity of mononuclear vanadium(V) complex (*S*)-**11** was significantly higher than that of mononuclear vanadium(IV) complex (*S*)-**10**. (*S*)-**11** produced (*S*)-BINOL with 37% yield and 81% ee at 30 °C in 24 h under air.

4. One-Pot Preparation of Chiral Dinuclear Vanadium(V) Complex

Preparation of (*R*_a,*S*,*S*,*S*)-**2** involves extraction of a Schiff base formed by condensation of (*R*)-**6** with (*S*)-*tert*-leucine

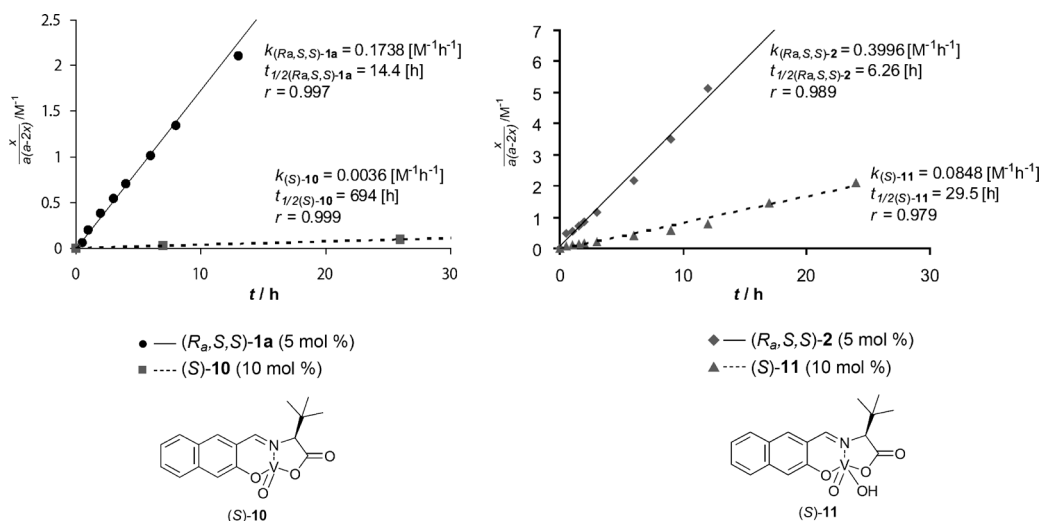


Fig. 6. Kinetic Analysis of Either Mononuclear or Dinuclear Vanadium Catalyst-Mediated Oxidative Coupling Reactions of 2-Naphthol
 a =initial concentration of 2-naphthol (0.2 M), x =concentration of BINOL.

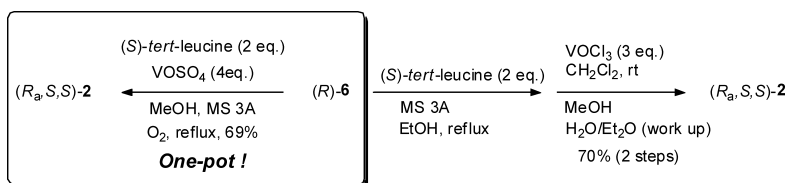


Chart 2. One-Pot Synthesis of (R_a,S,S) -2

followed by complexation with $VOCl_3$. Finally, addition of MeOH/ H_2O to the reaction mixture results in halogen exchange, giving the dinuclear vanadium(V) catalyst. Although this two-step process provided highly active and pure (R_a,S,S) -2, hours must be spent removing $VOCl_3$ -derived residue, and additional care is required to avoid decomposition of the Schiff base due to hydrogen chloride generation during complexation. We developed an expedient one-pot procedure for production of chiral dinuclear vanadium complex (R_a,S,S) -2 by mixing (R) -6, (S) -tert-leucine, and $VOSO_4$. When a mixture of (R) -6, (S) -tert-leucine, and $VOSO_4$ was refluxed, condensation of (R) -6 with (S) -tert-leucine afforded the corresponding Schiff base, which subsequently reacted with $VOSO_4$. Under O_2 , simultaneous auto-oxidation of vanadium(IV) to (V) took place, and (R_a,S,S) -2 was produced in 69% overall yield. This procedure gave highly active **2**, which was identical to the catalyst prepared by the previous method using $VOCl_3$ for complexation.⁴⁵⁾ The use of **2** prepared by the one-pot procedure was found to promote coupling, affording (S) -BINOL in 91% yield and 82% ee at 30 °C in 24 h under air.⁷⁹⁾

5. Dinuclear Vanadium Complexes Catalyzed Oxidative Coupling Reaction of 2-Naphthols

To elucidate the generality of the dual activation of the dinuclear vanadium complexes in the oxidative coupling, the C3, C4, C6, or C7 substituted 2-naphthol derivatives were explored (Table 3). 2-Naphthol possessing electron donating or withdrawing groups at the C4 (R^2), C6 (R^3), or C7 (R^4) positions resulted in coupling products with high enantioselectivities (entries 6–28). However, appending a substituent at the C3 position ($R^1=CO_2Me$, OMe) led to the correspond-

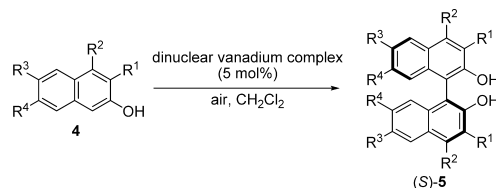
ing product with diminished yield and ee (entries 4, 5, 29, 30). These C3 substituted 2-naphthols barely approach vanadium on the catalyst due to steric hindrance. In terms of enantioselectivity, the best outcome was achieved using the H8-BINOL-based⁶⁸⁾ dinuclear vanadium(V) complex (R_a,S,S) -3. (S) -BINOLs were obtained in 97% ee when using (R_a,S,S) -3 (entries 3, 18).

Optically pure 10,10'-dihydroxy-9,9'-biphenanthryl (**5o**) is used as asymmetric ligand^{80–83)}; however, there have been few catalytic processes for **5o**.^{51,80,84,85)} Oxidative coupling of 9-phenanthrol (**4o**) using catalyst (R_a,S,S) -2 was investigated; the results are summarized in Table 4. Among the reaction solvents studied, CH_2Cl_2 provided the highest reaction rate with high enantioselectivity, giving biphenanthrol **5o** in 94% yield with 88% ee (entry 4). Although the reaction also proceeded under air, the ee of **5o** decreased slightly to 76% (entry 6). Finally, we found that decreasing the reaction temperature to -10 °C gave the coupling product **5o** in quantitative yield with 93% ee (entry 7). To examine the practicality of (R_a,S,S) -2-mediated coupling, enantioselective coupling of **4o** was carried out on a gram scale (6.0 g, entry 8). As expected, **5o** was obtained in 79% yield (>99% ee) after a single recrystallization.

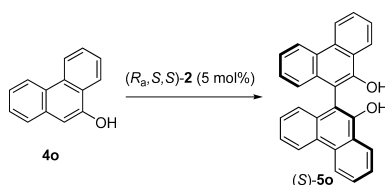
6. Reaction Mechanism for Dinuclear Vanadium Complex Catalyzed Oxidative Coupling

An induction period was observed when dinuclear vanadium(IV) complex (R_a,S,S) -1a was used for the coupling of 2-naphthol. The % ee of the product increased during the course of the reaction when using (R_a,S,S) -1a, from 38% ee at 4% conversion to 86% ee at 14% conversion, while that of the product remained nearly constant (83–85% ee) when

Table 3. Coupling Reaction of 2-Naphthols Catalyzed by Dinuclear Vanadium Complexes



Entry	Catalyst	Substrate	Temp. (°C)	Time (h)	Yield (%)	Ee (%)
1	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ³ =R ⁴ =H, 4a	30	24	5a , 76	91
2	(<i>R_a,S,S</i>)- 2	4a	0	72	5a , 100	90
3	(<i>R_a,S,S</i>)- 3	4a	0	72	5a , 56	97
4	(<i>R_a,S,S</i>)- 1a	R ¹ =CO ₂ Me, R ² =R ³ =R ⁴ =H, 4b	30	240	5b , trace	—
5	(<i>R_a,S,S</i>)- 2	4b	30	240	5b , 10	4
6	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ⁴ =H, R ³ =OMe, 4c	30	24	5c , 100	86
7	(<i>R_a,S,S</i>)- 2	4c	30	24	5c , 98	89
8	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ⁴ =H, R ³ =Br, 4d	30	48	5d , 43	68
9	(<i>R_a,S,S</i>)- 2	4d	30	48	5d , 83	81
10	(<i>R_a,S,S</i>)- 3	4d	30	48	5d , 31	78
11	(<i>R_a,S,S</i>)- 1a	R ¹ =R ³ =R ⁴ =H, R ² =Br, 4e	30	48	5e , 35	86
12	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ⁴ =H, R ³ =Me, 4f	0	72	5f , 62	92
13	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ⁴ =H, R ³ =OMOM, 4g	0	72	5g , 83	89
14	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ⁴ =H, R ³ =OBn, 4h	30	24	5h , 94	89
15	(<i>R_a,S,S</i>)- 2	4h	0	72	5h , 94	80
16	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ⁴ =H, R ³ =Bn, 4i	0	72	5i , 91	93
17	(<i>R_a,S,S</i>)- 2	4i	0	72	5i , 91	90
18	(<i>R_a,S,S</i>)- 3	4i	0	72	5i , 69	97
19	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ⁴ =H, R ³ =Ph, 4j	30	24	5j , 82	88
20	(<i>R_a,S,S</i>)- 2	4j	30	36	5j , 100	86
21	(<i>R_a,S,S</i>)- 3	4j	30	72	5j , 100	93
22	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ³ =H, R ⁴ =OMe, 4k	30	24	5k , 55	86
23	(<i>R_a,S,S</i>)- 2	4k	30	24	5k , 98	86
24	(<i>R_a,S,S</i>)- 3	4k	0	72	5k , 67	93
25	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ³ =H, R ⁴ =OMOM, 4l	0	72	5l , 51	92
26	(<i>R_a,S,S</i>)- 1a	R ¹ =R ² =R ³ =H, R ⁴ =Oallyl, 4m	30	24	5m , 71	87
27	(<i>R_a,S,S</i>)- 2	4m	30	24	5m , 100	87
28	(<i>R_a,S,S</i>)- 3	4m	0	72	5m , 45	87
29	(<i>R_a,S,S</i>)- 1a	R ¹ =OMe, R ² =R ³ =R ⁴ =H, 4n	30	240	5n , 35	45
30	(<i>R_a,S,S</i>)- 2	4n	30	240	5n , 35	48

Table 4. Oxidative Coupling of 9-Phenanthrol Using (*R_a,S,S*)-**2**

Entry	Solvent	Atmosphere	Temp. (°C)	Time (h)	Yield (%)	Ee (%) ^{b)}
1	CH ₃ CN	O ₂	-5	70	92	89
2	Toluene	O ₂	-5	72	80	86
3	CHCl ₃	O ₂	-5	60	90	54
4	CH ₂ Cl ₂	O ₂	-5	36	94	88
5	CH ₂ Cl ₂	O ₂	0	24	92	84
6	CH ₂ Cl ₂	Air	-5	74	80	76
7	CH ₂ Cl ₂	O ₂	-10	48	100 (80) ^{a)}	93 (>99) ^{a)}
8 ^{b)}	CH ₂ Cl ₂	O ₂	-10	48	100 (79) ^{a)}	90 (>99) ^{a)}

a) After recrystallization. b) 6.0 g scale reaction.

using dinuclear vanadium(V) complex (*R_a,S,S*)-**2**. In the coupling of 2-naphthol using 5 mol% of (*R_a,S,S*)-**2** under Ar, BINOL was formed with only 9% yield after 48 h due to no re-oxidation of the vanadium(IV) complex in the absence of air. After introducing air to the reaction vessel, the catalytic

cycle sufficiently resumed to produce BINOL in 99% yield (Fig. 7).

An attempt at promoting cross-couplings of **4a** with **4b** and **4c** with **4d** catalyzed by (*R_a,S,S*)-**2** afforded only homolytic coupling products **5** and no cross-coupling product

was observed in any case (Chart 3). The (R_a,S,S) -**2**-mediated coupling includes neither a radical-anion nor a radical-radical coupling, in contrast to Gong's dinuclear vanadium(V) catalyzed coupling for which radical-radical coupling is observed.⁶⁸⁾

All these results are in agreement with an intramolecular manner of coupling as shown in Chart 4. Dinuclear vanadium(V) complex (R_a,S,S) -**2** reacts with two molecules of 2-naphthol resulting in **1a**. The C1 positions of the 2-naphthol molecules approach each other by rotation of the binaphthyl axis yielding **1b**, which is then intramolecularly coupled after

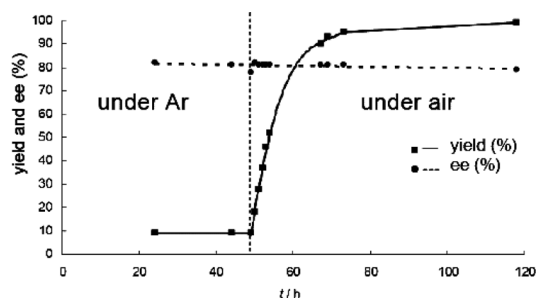


Fig. 7. Time Course in Homolytic Coupling Reaction of 2-Naphthol Catalyzed by 5 mol% of (R_a,S,S) -**2** at 30 °C under Ar and Air

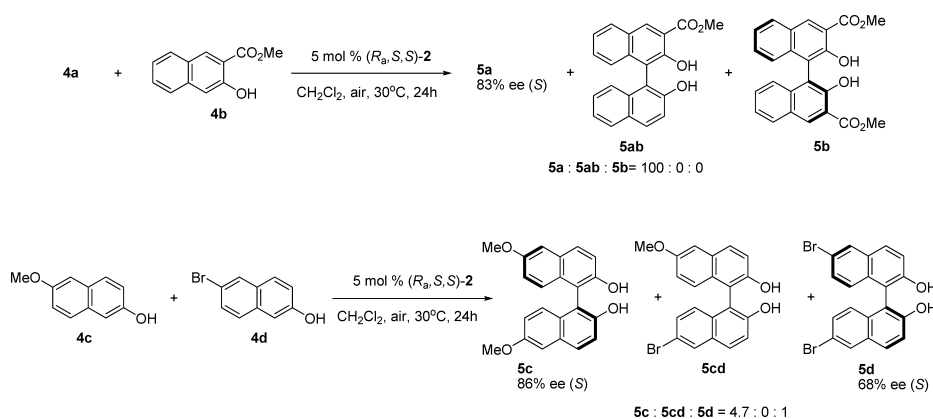


Chart 3. Cross-Coupling of **4a** with **4b** and **4c** with **4d** Promoted by (R_a,S,S) -**2**

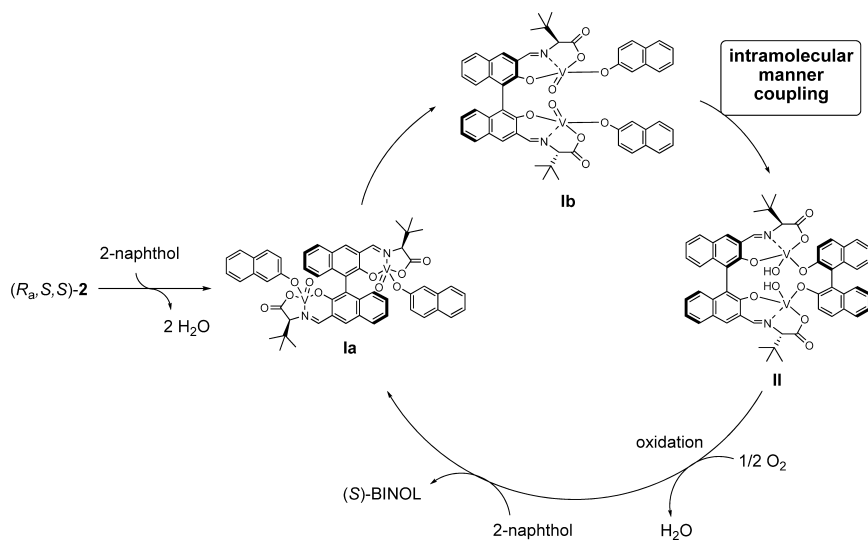


Chart 4. Plausible Mechanism for (R_a,S,S) -**2** Catalyzed Oxidative Coupling Reaction

a single electron transfer to a vanadium(V) species. After enolization of the coupling product and oxidation of the vanadium(IV) species **11**, the vanadium(V) species was regenerated⁸⁶⁾ and (S) -BINOL was released. Since the coupling of 2-naphthol was catalyzed by (R_a,S,S) -**2** with reaction rates enhanced 4.7 times faster than that of mononuclear vanadium(V) complex (S) -**11** (Fig. 6), intermolecular manner couplings proceeded as a minor pathway.

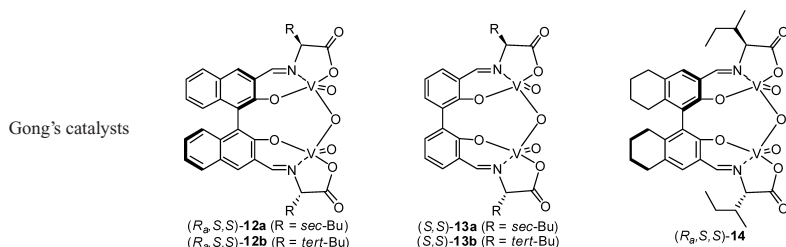
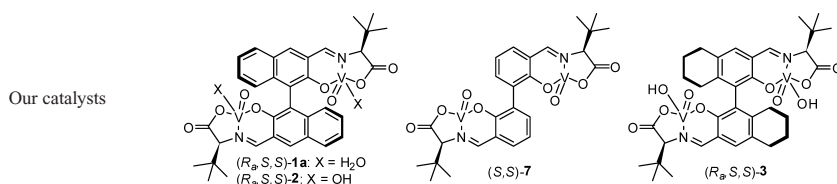
7. Comparison of Our Dinuclear Vanadium(IV) and (V) Catalysts with Gong's Catalysts

Although we independently developed dinuclear vanadium(IV) catalysts and dinuclear vanadium(V) catalysts for enantioselective oxidative coupling of 2-naphthols,^{44–48)} the preparation procedure for dinuclear vanadium(IV) catalysts is similar to that of Gong's catalysts^{66–68)} except for the use of 2.0–2.2 eq of vanadyl sulfate in EtOH–tetrahydrofuran (THF)–H₂O for the complexation. Even though the absolute configurations of the components of the catalysts are the same, the absolute configurations of the major products were opposite to each other (Table 5).

Since Gong carried out the coupling reaction in CCl₄ at 0 °C under oxygen, we examined the (R_a,S,S) -**1a**-catalyzed reaction under the same conditions to compare the new character of our catalysts (Table 6). A large difference was ob-

Table 5. Preparation and Catalytic Activity of Dinuclear Vanadium(IV) Catalysts (R_a,S,S)-**1a**, (S,S)-**7**, Dinuclear Vanadium(V) Catalysts (R_a,S,S)-**2**, (R_a,S,S)-**3**, and Gong's Catalysts **12**—**14**

Catalyst	Preparation of complex			Catalytic activity	
	Vanadium source (mol eq) ^{a)}	Solvent for complexation	Characterization	Optimized reaction conditions	Coupling of 5a
(R_a,S,S)- 1a	$\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, $x=3-5$ (4.0) ^{b)}	THF/H ₂ O	IR, HR-MS (FAB), ESR	Cat. 5 mol%, 30 °C, air, CH ₂ Cl ₂ , 24 h	76% yield, 91% ee (<i>S</i>)
(R_a,S,S)- 2	VOCl_3 (4.0)	CH ₂ Cl ₂	¹ H-, ¹³ C-, ⁵¹ V-NMR, IR, HR-MS (ESI), X-ray crystallography and elemental analysis, SQUID, XANES, XPS	Cat. 5 mol%, 0 °C, air, CH ₂ Cl ₂ , 72 h	100%, 90% ee (<i>S</i>)
(S,S)- 7	$\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, $x=3-5$ (4.0) ^{b)}	THF/H ₂ O	IR, HR-MS (FAB), ESR	Cat. 2.5 mol%, 30 °C, air, CH ₂ Cl ₂ , 72 h	84% yield, 92% ee (<i>S</i>)
(R_a,S,S)- 3	VOCl_3 (4.0)	CH ₂ Cl ₂	¹ H-, ¹³ C-NMR, IR, HR-MS (ESI)	Cat. 5 mol%, 0 °C, air, CH ₂ Cl ₂ , 72 h	56% yield, 97% ee (<i>S</i>)
(R_a,S,S)- 12a ⁶⁸⁾	$\text{VO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (2.0)	EtOH/THF/H ₂ O	⁵¹ V-NMR, IR, HR-MS (ESI)	Cat. 10 mol%, 0 °C, O ₂ , CCl ₄ , 144 h	93% yield, 83% ee (<i>R</i>)
(R_a,S,S)- 12b ⁶⁸⁾	$\text{VO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (2.0)	EtOH/THF/H ₂ O	IR, HR-MS (ESI)	Cat. 10 mol%, 0 °C, O ₂ , CCl ₄ , 192 h	63% yield, 71% ee (<i>R</i>)
(S,S)- 13a ⁶⁸⁾	$\text{VO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (2.2)	EtOH/THF/H ₂ O	¹ H-, ¹³ C-, ⁵¹ V-NMR, IR, HR-MS (ESI), elemental analysis	Cat. 10 mol%, 0 °C, O ₂ , CCl ₄ , 168 h	89% yield, 89% ee (<i>R</i>)
(S,S)- 13b ⁶⁸⁾	$\text{VO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (2.2)	EtOH/THF/H ₂ O	IR, HR-MS (ESI)	Cat. 10 mol%, 0 °C, O ₂ , CCl ₄ , 168 h	56% yield, 79% ee (<i>R</i>) ⁸⁷⁾
(R_a,S,S)- 14 ⁶⁸⁾	$\text{VO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (2.2)	EtOH/THF/H ₂ O	IR, HR-MS (ESI)	Cat. 5 mol%, 0 °C, air, CCl ₄ , 96 h	58% yield, 60% ee (<i>R</i>)



a) Numbers show molar equivalent to the diformyl compounds. b) 99.99% $\text{VO}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, $x=3-5$ (Aldrich, product No. 204862) was used.

served between our catalysts and Gong's catalysts: (R_a,S,S)-**1a** and 2-naphthol had limited solubility in CCl₄ at 0 °C, and the coupling product was obtained in quite low yield and low enantioselectivity (entry 1). The use of Gong's catalyst **12b**, which we prepared according to his procedure,^{66,68)} provided poorly reproducible outcomes (entry 2). Finally we realized the absolute configuration of the major products was switched by choosing CCl₄ when using the dinuclear vanadium(V) catalyst. However, (R_a,S,S)-**2** showed much higher activity than that of Gong's catalyst **12b** (entries 3, 4). The reason for a switch of enantioselectivity in the (R_a,S,S)-**2**-mediated coupling by the choice of solvent is not clearly understood at the moment, but may involve generation of oligomeric dinuclear complexes with different asymmetric

Table 6. Catalyst Activities in Oxidative Coupling of 2-Naphthol under Gong's Optimized Conditions⁶⁶⁻⁶⁸⁾

4a		Catalyst (10 mol %)			(<i>R</i>)- 5a
		O ₂ , CCl ₄ , 0 °C			
Entry	Chiral catalyst	Time (h)	Yield (%)	Ee (%)	
1 ^{a)}	(R_a,S,S)- 1a	192	16	8	
2 ^{a)}	Gong's catalyst 12b (according to Gong's procedure) ^{b)}	192	7-42	39-60	
3 ^{a)}	(R_a,S,S)- 2	72	70	76	
4	Gong's result using 12b (refs. 66, 68)	192	63	71	

a) Heterogeneous. b) Gong's catalyst **12b** was prepared from (*R*)-**6** (1 mol eq), (*S*)-*tert*-leucine (2.0 mol eq) and VO_2SO_4 (2.0 mol eq).^{66,68)}

Table 7. Coupling Reaction of 2-Naphthols Catalyzed by Dinuclear Vanadium(V) Complexes

Entry	Catalyst	Atmosphere	4		5		Ee (%)
			dinuclear vanadium(V) complex (10 mol%)		solvent, 0 °C		
Entry	Catalyst	Atmosphere	Solvent	Substrate	Time (h)	Yield (%)	Ee (%)
1	(<i>R_a,S,S</i>)- 2	O ₂	CH ₂ Cl ₂	4a	72	5a , quant	90 (<i>S</i>)
2	(<i>R_a,S,S</i>)- 2	O ₂	CH ₂ Cl ₂	4a	72	5a , 49	67 (<i>S</i>)
3 ^{a)}	(<i>R_a,S,S</i>)- 2	O ₂	Toluene	4a	72	5a , 33	64 (<i>R</i>)
4 ^{a)}	(<i>R_a,S,S</i>)- 2	O ₂	CCl ₄	4a	72	5a , 70	76 (<i>R</i>)
5 ^{a)}	(<i>R_a,S,S</i>)- 2	O ₂	CCl ₄	4b	240	5b , Trace	—
6 ^{a)}	(<i>R_a,S,S</i>)- 2	O ₂	CCl ₄	4b	219	5d , 52	91 (<i>R</i>)
7 ^{a)}	(<i>R_a,S,S</i>)- 2	O ₂	CCl ₄	4j	195	5j , 23	73 (<i>R</i>)
8 ^{a)}	(<i>R_a,S,S</i>)- 2	O ₂	CCl ₄	4k	144	5k , 48	95 (<i>R</i>)
9 ^{a)}	(<i>R_a,S,S</i>)- 2	O ₂	CCl ₄	4n	240	4n , Trace	—
10 ^{a)}	(<i>R_a,S,S</i>)- 3	O ₂	CCl ₄	4a	76	5a , 85	78 (<i>R</i>)
11	(<i>R_a,S,S</i>)- 14 ^{b)}	Air	CCl ₄	4a	96	5a , 58	60 (<i>R</i>)
12 ^{a)}	(<i>R_a,S,S</i>)- 3	O ₂	CCl ₄	4d	168	5d , 84	83 (<i>R</i>)
13	(<i>R_a,S,S</i>)- 14 ^{b)}	Air	CCl ₄	4d	48	5d , 82	86 (<i>R</i>)
14 ^{a)}	(<i>R_a,S,S</i>)- 3	O ₂	CCl ₄	4k	167	5k , 98	90 (<i>R</i>)
15	(<i>R_a,S,S</i>)- 14 ^{b)}	Air	CCl ₄	4k	48	5k , 94	92 (<i>R</i>)

a) Heterogeneous. b) Reported by Gong and colleagues using 5 mol% of the catalyst. See ref. 68.

induction ability from that of monomeric dinuclear complex (*R_a,S,S*)-**2**.^{88,89} As a result, reactions run in CH₂Cl₂ or (CH₂Cl)₂ provided (*S*)-configuration of BINOLs (Table 7, entries 1, 2), and for all reactions run in CCl₄ or toluene gave (*R*)-BINOLs (entries 3—10, 12, 14).

8. Conclusion

We developed dual activation catalysts for homolytic coupling of 2-naphthol promoted by dinuclear vanadium complexes. Chiral dinuclear vanadium(IV) complex (*R_a,S,S*)-**1a**, vanadium(V) complex (*R_a,S,S*)-**2**, and **3** possessing (*S*)-tert-leucine moieties at the 3,3'-positions of (*R*)-binaphthyl skeletons smoothly promoted oxidative coupling of 2-naphthol with high reaction rates to afford (*S*)-BINOL products in high yield and high enantioselectivity. Structural and kinetic analyses of the mononuclear vanadium complexes and dinuclear vanadium complexes revealed that two vanadium metals in one chiral complex activate two molecules of 2-naphthol simultaneously in a homolytic coupling reaction, achieving a high reaction rate with high enantiocontrol. Extensions of the dinuclear vanadium complexes to other enantioselective reactions and further studies to explore the utility of the coupling products in asymmetric catalysis are underway.

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