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Dual activation in oxidative coupling of 2-naphthols catalyzed by chiral dinuclear vanadium complexes

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Abstract

An efficient enantioselective oxidative coupling of 2-naphthol derivatives based on a concept of *dual activation catalysis* is realized. A chiral dinuclear vanadium(IV) complex (R_a,*S*,*S*)-**1e** possessing (*S*)-*tert*-leucine moieties at the 3,3′-positions of the (*R*)-binaphthyl skeleton was developed, which was found to promote the oxidative coupling of 2-naphthol to afford (*S*)-BINOL with 91% ee. To verify the dual activation mechanism, mononuclear vanadium(IV) complex (*S*)-**8** was also prepared. Kinetic analysis revealed that the reaction rate of oxidative coupling of 2-naphthol promoted by (R_a,*S*,*S*)-**1e** is 48.3 times faster than that of (*S*)-**8**. The two vanadium metals in the chiral complex activate two molecules of 2-naphthol simultaneously in an intramolecular manner coupling reaction, achieving a high reaction rate with high enantiocontrol. Reaction mechanisms of the oxidative coupling reaction promoted by either vanadium(IV) or vanadium(V) complexes are also described.

1. Introduction

Catalytic asymmetric reactions are among the most powerful synthetic methods to obtain optically active compounds.[1] 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.[2–4] Dual activation catalyses can be classified into three categories (Fig. 1): (1) dual activation using two different kinds of catalysts;[2] (2) conjugated-type dual activation with a functional group such as a phosphate, which has both acidic and basic sites in one functionality;[3] and (3) dual activation by two catalytic sites in a single catalyst.[4] 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*)-**1**[5] bearing two active sites attached to a binaphthyl skeleton, taking advantage of the activation entropy (Fig. 2). Activation entropy strongly contributes to intramolecular manner coupling after two molecules of 2-naphthol are complexed with the dinuclear vanadium catalyst. In 2003 Gao reported promising results on oxidative coupling reaction of 2-naphthol promoted by dinuclear copper catalysts, though

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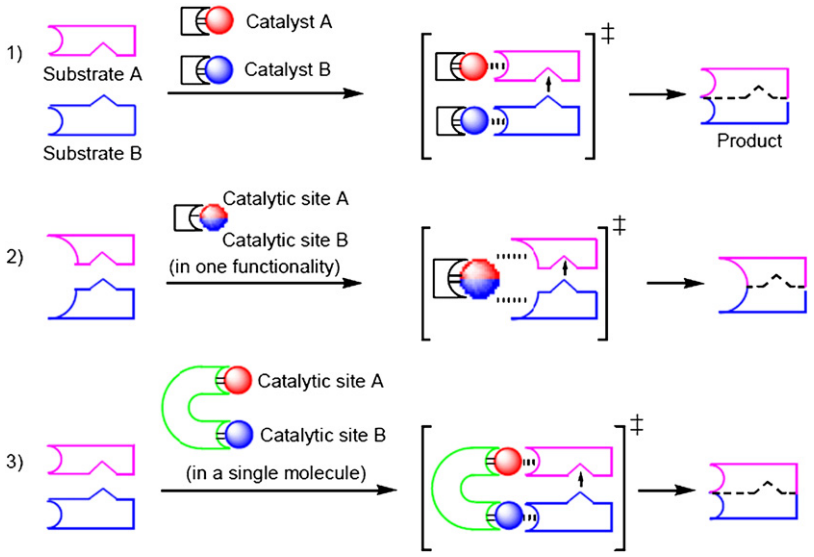


Figure 1. Schematic drawing of dual activation systems in catalytic asymmetric reactions.

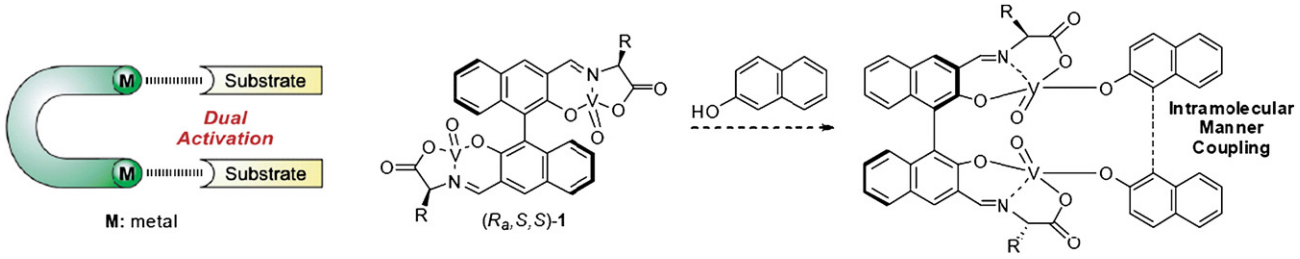


Figure 2. Design of dinuclear vanadim complex (R_a,*S*,*S*)-**1** for the oxidative coupling.

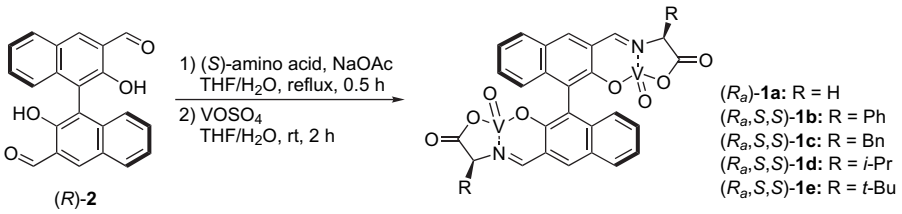
seven days are required for the complete attainment (85% yield, 88% ee).[6a] In this manuscript, the design and synthesis of dinuclear vanadium complexes that promote enantioselective oxidative coupling of 2-naphthol derivatives through an intramolecular dual activation mechanism[6] are described.

The synthesis of optically pure BINOL derivatives are of importance because they are used as chiral ligands and auxiliaries for a wide range of organic functional transformations.[7] Catalytic asymmetric preparation of BINOL systems has continued to attract the attention of many researchers.[8] The asymmetric oxidative coupling of 2-naphthol molecules is one of the most useful methods for the 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 a side product.[9–13] In 2001, Chen et al.[9a] and Uang et al.[10a] independently reported the first efficient asymmetric vanadium(IV) catalysts for oxidative coupling of 2-naphthol molecules prepared from vanadyl sulfate, aldehyde derivatives, and (*S*)-amino acids. Gong et al. reported dinuclear vanadium catalysts, which possess a V–O–V linkage with a maximum enantioselectivity of 98%.[12] These vanadium catalysts showed good enantioselectivity for the coupling of 2-naphthol derivatives, although the catalytic activity was moderate. Uang et al. found that catalytic activity could be improved by the addition of Lewis[10a] or Brønsted acids,[10b] resulting in the production of BINOL with moderate to good enantioselectivity. Chen et al. also developed the vanadium(IV) catalysts[9b] derived from vanadyl sulfate, (+)-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.

2. Results and discussion

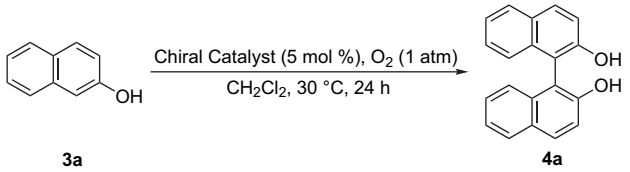
2.1. Preparation of dinuclear vanadium(IV) complexes

Scheme 1 shows the synthetic procedure for preparing catalysts **1a**–**e**.[14] Since NMR spectroscopy is not applicable for paramagnetic vanadium(IV) species,[15] FAB-HRMS and FTIR analyses were used to characterize the complex **1**. The oxidative coupling reactions of 2-naphthol by catalysts **1** were carried out in CH_2Cl_2 at 30 °C for 24 h under oxygen. The catalytic activities of (R_a)-**1a** and (R_a,*S*,*S*)-**1b** were low and racemic BINOL was obtained (Table 1, entries 1 and 2). (R_a,*S*,*S*)-**1c**, possessing benzyl groups, promoted the coupling reaction in 30% yield with low enantioselectivity (8% ee) (entry 3). However, (R_a,*S*,*S*)-**1d** bearing *iso*-propyl groups promoted the oxidative coupling reaction to afford (*S*)-BINOL in 52% yield with 66% ee (entry 4). (R_a,*S*,*S*)-**1e**, possessing



Scheme 1. Preparation of dinuclear vanadium(IV) complexes **1**.

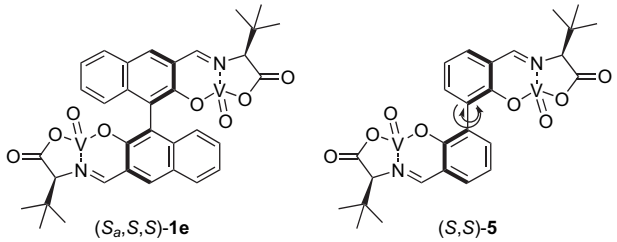
Table 1
Enantioselective coupling of 2-naphthol catalyzed by chiral dinuclear vanadium-(IV) catalysts



Entry	Catalyst	Yield[a] (%)	ee[b] (%)
1	(R_a)-**1a**	6	*rac*
2	(R_a,*S*,*S*)-**1b**	21	*rac*
3	(R_a,*S*,*S*)-**1c**	30	8 (*R*)
4	(R_a,*S*,*S*)-**1d**	52	66 (*S*)
5	(R_a,*S*,*S*)-**1e**	83	83 (*S*)
6	(S_a,*S*,*S*)-**1e**	9	2 (*R*)
7	(*S*,*S*)-**5**	57	81 (*S*)

[a] Isolated yields.
[b] Determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH=9:1).

tert-butyl groups, made the reaction proceed faster than the other complexes, maintaining the highest enantioselectivity (83% ee) (entry 5). The diastereomeric complex (S_a,*S*,*S*)-**1e** and the tropos[16] complex (*S*,*S*)-**5** were also prepared. The diastereomeric complex (S_a,*S*,*S*)-**1e** was less active than (R_a,*S*,*S*)-**1e**, giving (*R*)-BINOL in only 9% yield with 2% ee (entry 6). The complex (*S*,*S*)-**5** also showed a decreased reaction rate (entry 7). (R_a,*S*,*S*)-**1e** would constitute a *matched pair* and (S_a,*S*,*S*)-**1e** would be a *mismatched pair*,[17] for the intramolecular manner coupling of 2-naphthol as shown in Figure 2. In the case of complex (*S*,*S*)-**5** with free rotation of the biphenyl unit, the equilibrium between matched and mismatched conformations diminishes the reaction rate. These results revealed that two amino derived active sites affect the enantiocontrol of the coupling and the binaphthyl backbone assists to align the two molecules of 2-naphthol with each other for the oxidative coupling reaction.



An insufficient amount of vanadyl sulfate leads to the formation of vanadium(IV) complex **6**, which bears only one vanadium metal in the catalyst molecule. An attempt to

Table 2
Activity of the catalyst derived from various amounts of $VOSO_4$, (*R*)-**2** and (*S*)-*tert*-leucine

Entry	$VOSO_4$[a]	Atmosphere	Catalyst (mol %)	Time (h)	Yield[b] (%)	ee[c] (%)
1	1	O_2	5	24	15	13 (*R*)
2	2	O_2	5	24	64	78 (*S*)
3	4	O_2	5	24	83	83 (*S*)
4	4	Air	5	24	76	91 (*S*)
5	4	Air	1	168	99	90 (*S*)

[a] Numbers show molar equivalents to diformyl compounds.
[b] Isolated yields.
[c] Determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH=9:1).

Table 3
Effects of solvent on (R_a,*S*,*S*)-**1e** catalyzed coupling reaction of 2-naphthol[a]

Entry	Solvent	Yield[b] (%)	ee[c] (%)
1	THF	Trace	—
2	MeCN	Trace	—
3	CCl_4	42	36 (*S*)
4	$CHCl_3$	40	63 (*S*)
5	CH_2Cl_2	76	91 (*S*)
6	$(CH_2Cl)_2$	99	89 (*S*)

[a] At 30 °C for 24 h under air.
[b] Isolated yields.
[c] Determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH=9:1).

deliberately prepare complex **6** for comparison of its catalytic activity with (R_a,*S*,*S*)-**1e** resulted in a switch of the major product enantiomer to (*R*)-BINOL with 13% ee (Table 2, entry 1). In order to avoid the formation of a mononuclear vanadium catalyst, 4 equiv of vanadyl sulfate was used (entry 3). The excess vanadyl sulfate can be filtered off after complex formation. Although the reaction rate promoted by (R_a,*S*,*S*)-**1e** was slightly decreased under air, (*S*)-BINOL was obtained with higher enantioselectivity (91% ee) than that produced under oxygen (entry 4). The effects of reaction solvents are shown in Table 3. In polar solvents such as THF and MeCN, the coupling reaction did not proceed (Table 3, entries 1 and 2). In either CCl_4 or $CHCl_3$, the reaction mixture was heterogeneous

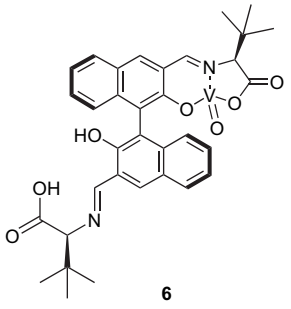


Table 4
Effects of temperature on (R_a,*S*,*S*)-**1e** catalyzed coupling reaction of 2-naphthol[a]

Entry	Solvent	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)
1	CH_2Cl_2	−20	168	Trace	—
2	CH_2Cl_2	−10	144	67	76 (*S*)
3	CH_2Cl_2	0	72	Quant	87 (*S*)
4	CH_2Cl_2	20	24	59	90 (*S*)
5	CH_2Cl_2	30	24	76	91 (*S*)
6	CH_2Cl_2	Reflux	24	50	90 (*S*)
7	$(CH_2Cl)_2$	0	24	45	92 (*S*)
8	$(CH_2Cl)_2$	30	24	76	87 (*S*)
9	$(CH_2Cl)_2$	60	24	Quant	71 (*S*)
10	$(CH_2Cl)_2$	Reflux	24	31	79 (*S*)

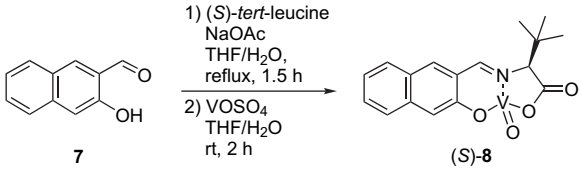
[a] Under air.
[b] Isolated yields.
[c] Determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH=9:1).

and (*S*)-BINOL was obtained in low yields with moderate enantioselectivity (entries 3 and 4). In $(CH_2Cl)_2$, the coupling reaction proceeded smoothly to afford (*S*)-BINOL with similar enantiocontrol to that mediated in CH_2Cl_2 (entries 5 and 6).

The effects of reaction temperature were then examined in CH_2Cl_2 or $(CH_2Cl)_2$ (Table 4). Although higher reaction temperatures resulted in higher catalytic activity in this system, the catalytic activity was diminished at the reflux condition due to decomposition of the complex (entries 6 and 10). The reaction did not proceed below −20 °C due to the low solubility of (R_a,*S*,*S*)-**1e** (entry 1).

2.2. Kinetic analysis of dinuclear and mononuclear vanadium(IV) complexes in coupling of 2-naphthol

To confirm the *dual activation* in this reaction, mononuclear vanadium(IV) complex (*S*)-**8** was prepared from 3-formyl-2-naphthol (**7**), (*S*)-*tert*-leucine, and vanadyl sulfate (Scheme 2), and was characterized by FAB-HRMS, FTIR, and ESR spectroscopy.



Scheme 2. Preparation of mononuclear vanadium(IV) complex (*S*)-**8**.

In the kinetic analysis, the amount of the mononuclear catalyst (*S*)-**8** used was twice to that of (R_a,*S*,*S*)-**1e** since (*S*)-**8** has only one active center (Fig. 3). The catalysis by (R_a,*S*,*S*)-**1e** and (*S*)-**8** obeyed second-order kinetics up to about 15 h. Catalyst (*S*)-**8** gave almost racemic BINOL. The calculated rate constants for the coupling reactions at 20 °C were $k_{(R_a,S,S)\text{-}\mathbf{1e}} = 0.1738\ M^{-1}\ h^{-1}$ and $k_{(S)\text{-}\mathbf{8}} = 0.0036\ M^{-1}\ h^{-1}$.[18] The coupling reaction in the presence of 5 mol % of (R_a,*S*,*S*)-**1e** was thus shown to be 48.3 times faster than that using 10 mol % of (*S*)-**8** (Fig. 3). The calculations based on Arrhenius and Eyring plots between 20 and 30 °C indicated activation energies

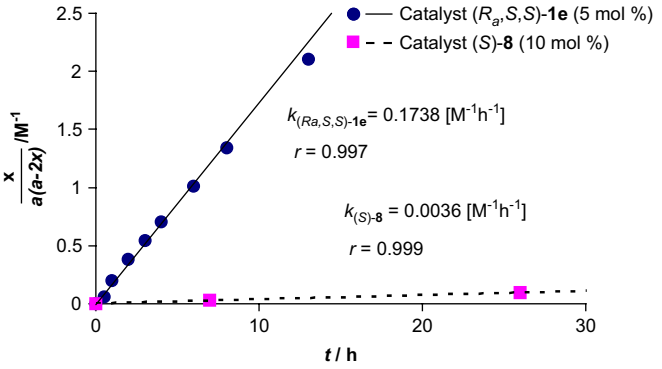


Figure 3. Kinetic analysis of (R_a,*S*,*S*)-**1e** and (*S*)-**8** catalyzed oxidative coupling reactions of 2-naphthol; *a*=initial concentration of 2-naphthol (0.2 M), *x*=concentration of BINOL.

of catalyst (R_a,*S*,*S*)-**1e** and (*S*)-**8** were $\Delta E_{(R_a,S,S)\text{-}\mathbf{1e}} = 0.74\ kcal\ mol^{-1}$ and $\Delta E_{(S)\text{-}\mathbf{8}}$=23 kcal mol^{-1}, and activation entropy and enthalpy of catalyst (R_a,*S*,*S*)-**1e** were $\Delta S^{\ddagger}_{(R_a,S,S)\text{-}\mathbf{1e}} = -7.8 \times 10^{-2}$ kcal mol K and $\Delta H^{\ddagger}_{(R_a,S,S)\text{-}\mathbf{1e}} = 0.16$ kcal mol, and those of (*S*)-**8** were $\Delta S^{\ddagger}_{(S)\text{-}\mathbf{8}} = -1.5 \times 10^{-2}$ kcal mol K, and $\Delta H^{\ddagger}_{(S)\text{-}\mathbf{8}} = 21$ kcal mol, respectively. The *lower activation entropy* using (R_a,*S*,*S*)-**1e** than those of (*S*)-**8** catalyzed reaction are attributed to the dual activation of two 2-naphthol molecules in one chiral complex to produce BINOL. The *lower activation enthalpy* using (*S*)-**8** than those of (R_a,*S*,*S*)-**1e** mediated reaction contributes to the intermolecular radical–radical coupling of reaction intermediates after complexation of (*S*)-**8** with 2-naphthol. A difference of activation enthalpy between (R_a,*S*,*S*)-**1e** and (*S*)-**8** suggests that (R_a,*S*,*S*)-**1e** mediated coupling excludes a simple radical–radical coupling mechanism.

2.3. Development of dinuclear vanadium(V) complex (R_a,*S*,*S*)-**9**

Single crystals suitable for X-ray analysis were obtained by recrystallization of (R_a,*S*,*S*)-**1e** from MeOH/Et_2O/H_2O in the presence of NaOAc.[19,20] The binding energy of V $2p_{3/2}$ for the crystals is 516.9 eV by X-ray photoelectron spectroscopy (XPS), which is attributed to V(V).[21] 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. 4a).[22] The hydroxide 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 the two carboxylic groups [Na1–O4, 2.393(5) Å] on the (*S*)-*tert*-leucine regions. The coordination of oxygen to several sodium cations results in a helical molecular aggregation within the crystal (Fig. 4b).

To determine the oxidative state of vanadium after complex formation to give (R_a,*S*,*S*)-**1e**, 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).[23] The magnetic susceptibility of (R_a,*S*,*S*)-**1e** prepared under air was 5 emu mol^{-1} at 5 K in 5 T (curve c). In contrast, the vanadium complex prepared under argon

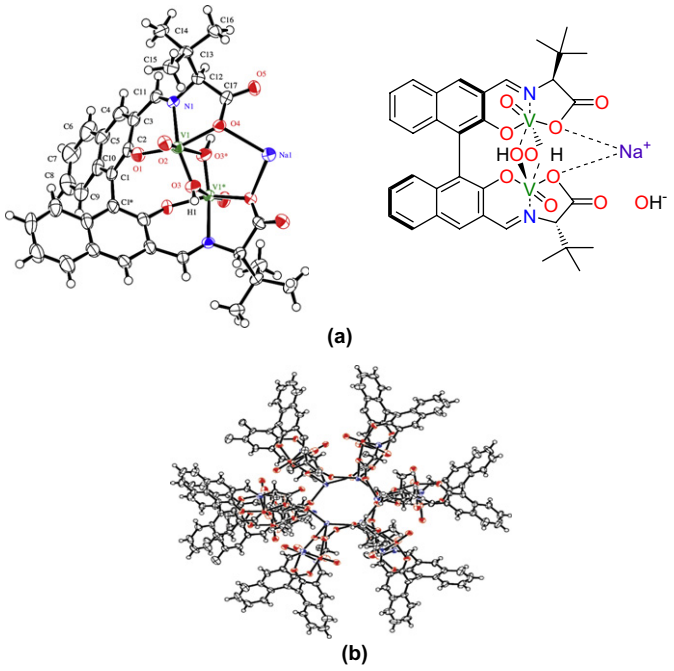


Figure 4. (a) Structure of dinuclear vanadium(V) complex (*Ra*,*S*,*S*)-**9**·NaOH. A counter anion OH^-, the hydrogen atom of which has not been determined, is omitted for clarity and (b) a perspective view of molecular aggregation of the vanadium (V) complex.

gave a value of 28 emu mol^{-1} (curve b). The magnetic susceptibility of the single crystals obtained by the recrystallization, as shown in Figure 4, exhibited 0 emu mol^{-1}, clearly indicating a vanadium(V) species (curve d). These results suggest that 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 the catalyst for the oxidative coupling of 2-naphthol, no catalytic activity was observed. This may be attributed to the low solubility in CH_2Cl_2. However, the addition of 1 equiv of 5 N HCl (aq) to the sodium in the crystal gave a homogeneous solution. To the homogeneous solution containing 5 mol % of the dinuclear vanadium(V) complex was added 2-naphthol under air,

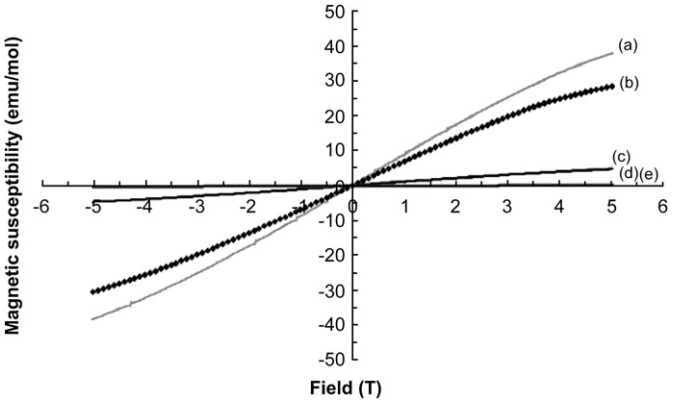
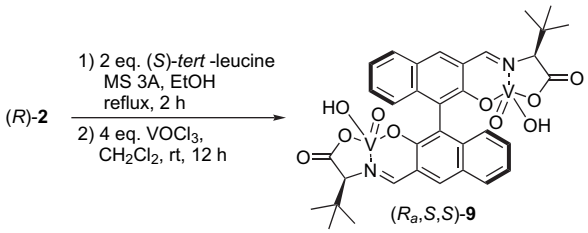


Figure 5. SQUID magnetometer plot of magnetic susceptibility for vanadium under a magnetic field at 5 K for (a) $VOSO_4$; (b) (R_a,*S*,*S*)-**1e** (prepared under Ar); (c) (R_a,*S*,*S*)-**1e** (prepared under air); (d) single crystals (*Ra*,*S*,*S*)-**9**·NaOH obtained by recrystallization of (*Ra*,*S*,*S*)-1e from MeOH–Et_2O–H_2O containing NaOAc and (e) V_2O_5.



Scheme 3. Preparation of dinuclear vanadium(V) complex (R_a,*S*,*S*)-**9**.

providing (*S*)-BINOL in 90% yield with 83% ee after 24 h.[24] To compare the catalytic activity of the dinuclear vanadium(V) complex, (R_a,*S*,*S*)-**9** was prepared from $VOCl_3$, (*R*)-**2**, and (*S*)-*tert*-leucine as shown in Scheme 3. The complex (R_a,*S*,*S*)-**9** was characterized by ^1H, ^{13}C, ^{51}V NMR, FTIR, and MS. The coupling of 2-naphthol was catalyzed by (R_a,*S*,*S*)-**9** with reaction rates enhanced 2.3 times faster than that of (R_a,*S*,*S*)-**1e**.[25] Gong also reported dinuclear vanadium(V) catalysts for oxidative coupling of 2-naphthol bearing a V–O–V linkage. In contrast to our catalysts, Gong's catalyst affords the (*R*)-configuration of BINOL as a major product (8 days, 63%, 71% ee (*R*)) although the absolute configurations of the components of the catalysts are the same.[12]

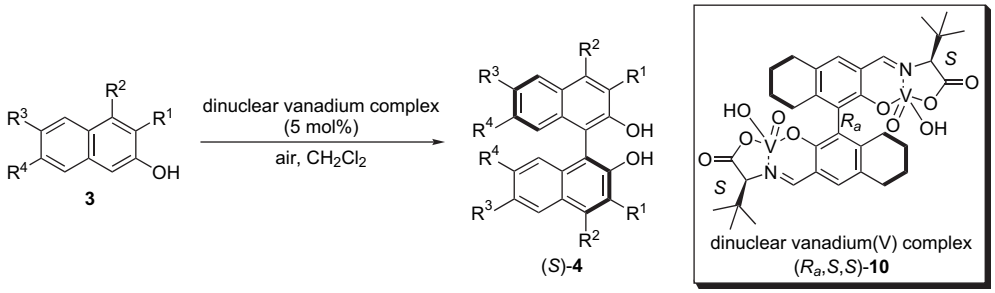
2.4. Dinuclear vanadium complex catalyzed oxidative coupling reaction of 2-naphthol

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 derivative was explored (Table 5). 2-Naphthol possessing electron donating or withdrawing groups at the C4 (R^2), C6 (R^3), and C7 (R^4) positions resulted in coupling products with high enantioselectivities (entries 6–28). 9-Phenanthrol was found to be an adequate substrate (entries 29–31), although appending a substituent at the C3 position (R^1=CO_2Me, OMe) led to the corresponding product with diminished yield and ee (entries 4, 5, 32, and 33). These C3 substituted 2-naphthols barely approach vanadium on the catalyst due to the steric hindrance. The dinuclear vanadium-mediated coupling of 5,6,7,8-tetrahydro-2-naphthol afforded H8-BINOL[26] for the first time but with low chemical yields and low enantioselectivities (entries 34 and 35). In terms of enantioselectivity, the best outcome was achieved by using dinuclear vanadium(V) complex (R_a,*S*,*S*)-**10**, which was prepared from $VOCl_3$, (*R*)-3,3′-diformyl-H8-BINOL, and (*S*)-*tert*-leucine. (*S*)-BINOL products were obtained in 97% ee when using (R_a,*S*,*S*)-**10** (entries 3 and 18). Gong also has reported the H8-BINOL-based dinuclear vanadium(V) complex with high enantiocontrol.[12c]

2.5. Reaction mechanism for dinuclear complex catalyzed oxidative coupling

An induction period was observed when (R_a,*S*,*S*)-**1e** was used for the coupling of 2-naphthol. The %ee of the product increased during the course of the reaction when using

Table 5
Coupling reaction of 2-naphthol derivatives catalyzed by dinuclear vanadium complexes



Entry	Vanadium complex	Substrate	Temp (°C)	Time (h)	Yield[a] (%)	ee[b] (%)
1	(R_a,*S*,*S*)-**1e**	R^1=R^2=R^3=R^4=H, **3a**	30	24	**4a**, 76	91
2	(R_a,*S*,*S*)-**9**	**3a**	0	72	**4a**, Quant	90
3	(R_a,*S*,*S*)-**10**	**3a**	0	72	**4a,** 56	97
4	(R_a,*S*,*S*)-**1e**	R^1=CO_2Me, R^2=R^3=R^4=H, **3b**	30	240	**4b**, Trace	—
5	(R_a,*S*,*S*)-**9**	**3b**	30	240	**4b**, 10	4
6	(R_a,*S*,*S*)-**1e**	R^1=R^2=H, R^3=OMe, R^4=H, **3c**	30	24	**4c**, Quant	86
7	(R_a,*S*,*S*)-**9**	**3c**	30	24	**4c**, 98	89
8	(R_a,*S*,*S*)-**1e**	R^1=R^2=H, R^3=Br, R^4=H, **3d**	30	48	**4d**, 43	68
9	(R_a,*S*,*S*)-**9**	**3d**	30	48	**4d**, 83	81
10	(R_a,*S*,*S*)-**10**	**3d**	30	48	**4d**, 31	78
11	(R_a,*S*,*S*)-**1e**	R^1=H, R^2=Br, R^3=R^4=H, **3e**	30	48	**4e**, 35	86
12	(R_a,*S*,*S*)-**1e**	R^1=R^2=H, R^3=Me, R^4=H, **3f**	0	72	**4f**, 62	92
13	(R_a,*S*,*S*)-**1e**	R^1=R^2=H, R^3=OMOM, R^4=H, **3g**	0	72	**4g**, 83	89
14	(R_a,*S*,*S*)-**1e**	R^1=R^2=H, R^3=OBn, R^4=H, **3h**	30	24	**4h**, 94	89
15	(R_a,*S*,*S*)-**9**	**3h**	0	72	**4h**, 94	80
16	(R_a,*S*,*S*)-**1e**	R^1=R^2=H, R^3=Bn, R^4=H, **3i**	0	72	**4i**, 91	93
17	(R_a,*S*,*S*)-**9**	**3i**	0	72	**4i**, 91	90
18	(R_a,*S*,*S*)-**10**	**3i**	0	72	**4i**, 69	97
19	(R_a,*S*,*S*)-**1e**	R^1=R^2=H, R^3=Ph, R^4=H, **3j**	30	24	**4j**, 82	88
20	(R_a,*S*,*S*)-**9**	**3j**	30	36	**4j,** Quant	86
21	(R_a,*S*,*S*)-**10**	**3j**	30	72	**4j**, Quant	93
22	(R_a,*S*,*S*)-**1e**	R^1=R^2=R^3=H, R^4=OMe, **3k**	30	24	**4k**, 55	86
23	(R_a,*S*,*S*)-**9**	**3k**	30	24	**4k**, 98	86
24	(R_a,*S*,*S*)-**10**	**3k**	0	72	**4k**, 67	93
25	(R_a,*S*,*S*)-**1e**	R^1=R^2=R^3=H, R^4=OMOM, **3l**	0	72	**4l**, 51	92
26	(R_a,*S*,*S*)-**1e**	R^1=R^2=R^3=H, R^4=OCH_2CHCH_2, **3m**	30	24	**4m**, 71	87
27	(R_a,*S*,*S*)-**9**	**3m**	30	24	**4m**, Quant	87
28	(R_a,*S*,*S*)-**10**	**3m**	0	72	**4m**, 45	87
29	(R_a,*S*,*S*)-**1e**	9-Phenanthrol, **3n**	0	24	**4n**, 84	77
30	(R_a,*S*,*S*)-**9**	**3n**	0	24	**4n**, 94	84
31	(R_a,*S*,*S*)-**10**	**3n**	0	24	**4n**, 84	77
32	(R_a,*S*,*S*)-**1e**	R^1=OMe, R^2=R^3=R^4=H, **3o**	30	240	**4o**, 35	45
33	(R_a,*S*,*S*)-**9**	**3o**	30	240	**4o**, 35	48
34	(R_a,*S*,*S*)-**1e**	5,6,7,8-Tetrahydro-2-naphthol, **3p**	30	120	**4p**, 12	13
35	(R_a,*S*,*S*)-**9**	**3p**	30	120	**4p**, 26	14

[a] Isolated yields.
[b] Determined by HPLC (**4a**, **4f**, **4g**, **4k**, **4l**, Chiralpak AS-H, hexane/*i*-PrOH=9:1; **4b**, **4e**, **4o**, Chiralpak AS, hexane/*i*-PrOH=1:1; **4c**, Chiralpak AS, hexane/*i*-PrOH=4:1; **4d**, Chiralpak AD, hexane/*i*-PrOH=9:1; **4h**, **4j**, Chiralpak IA, hexane/*i*-PrOH=17:3; **4i**, Chiralcel OD, hexane/*i*-PrOH=17:3; **4m**, Chiralpak IA, hexane/*i*-PrOH=19:1; **4n**, Chiralpak AD-H, hexane/*i*-PrOH=17:3; **4p**, Chiralpak AS, hexane/*i*-PrOH=19:1).

(R_a,*S*,*S*)-**1e**, from 38% ee at 4% conversion to 86% ee at 14% conversion, while the %ee of the product remained nearly constant (83–85% ee) when using (R_a,*S*,*S*)-**9**. In the coupling of 2-naphthol using 5 mol % of (R_a,*S*,*S*)-**9** 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. 6).

An attempt at promoting cross-couplings of **3a** with **3b** and **3c** with **3d** catalyzed by (R_a,*S*,*S*)-**9** afforded only homolytic coupling products **4** and no cross-coupling product was observed in any case (Scheme 4). The (R_a,*S*,*S*)-**9** 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.[12c] Dinuclear vanadium complex-mediated reaction mechanisms have been controversial, although all of these results are in agreement with an

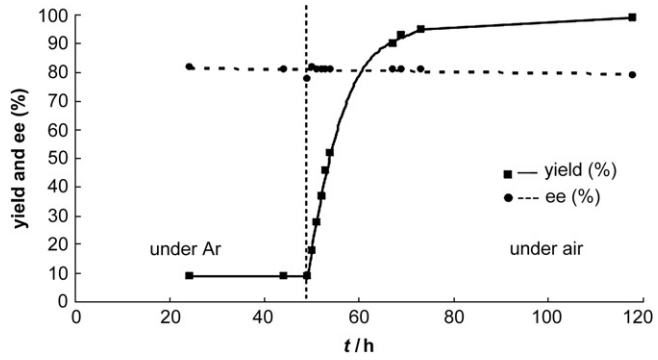


Figure 6. Time course in homolytic coupling reaction of 2-naphthol catalyzed by 5 mol % of (R_a,*S*,*S*)-**9** at 30 °C under Ar and air.

intramolecular manner coupling as shown in Scheme 5. In this mechanism, the dinuclear vanadium(V) complex reacts with two molecules of 2-naphthol resulting in **Ia**. The C1 positions of 2-naphthol molecules approach each other by the rotation of the binaphthyl axis yielding **Ib**, and **Ib** is then intramolecularly coupled after a single electron transfer to a vanadium(V) species. (*S*)-BINOL was released from **II** and vanadium(V) species was regenerated after isomerization of the coupling product and oxidation of the vanadium(IV) species.[27]

Table 6 shows the results of 2-naphthol coupling by vanadium(V) complexes under various reaction conditions. No by-product was observed in any reaction. Both mononuclear and dinuclear vanadium(V) complexes promote couplings under air[6b] with higher enantioselectivity than that under oxygen (entries 1, 2, 4, and 5). Recently, Gong also reported that higher enantioselectivity was seen by a dinuclear vanadium(V) complex bearing a V–O–V linkage under air.[12c] Lowering the temperature to 0 °C led to an increase in the enantioselectivity (entries 3 and 6). Since the coupling of 2-naphthol was catalyzed by (R_a,*S*,*S*)-**9** with reaction rates enhanced 4.7 times faster than that of mononuclear vanadium(V) complex (*S*)-**11**,[28] intermolecular manner couplings proceeded as a minor pathway. Interestingly, not only the reaction rate but also the enantioselectivity of (*S*)-**11** were significantly higher than that of the mononuclear vanadium(IV) complex (*S*)-**8** (Scheme 2). These results suggest that intermolecular manner coupling would not proceed readily when using the dinuclear vanadium(IV) complex in comparison to the dinuclear vanadium(V) complex.

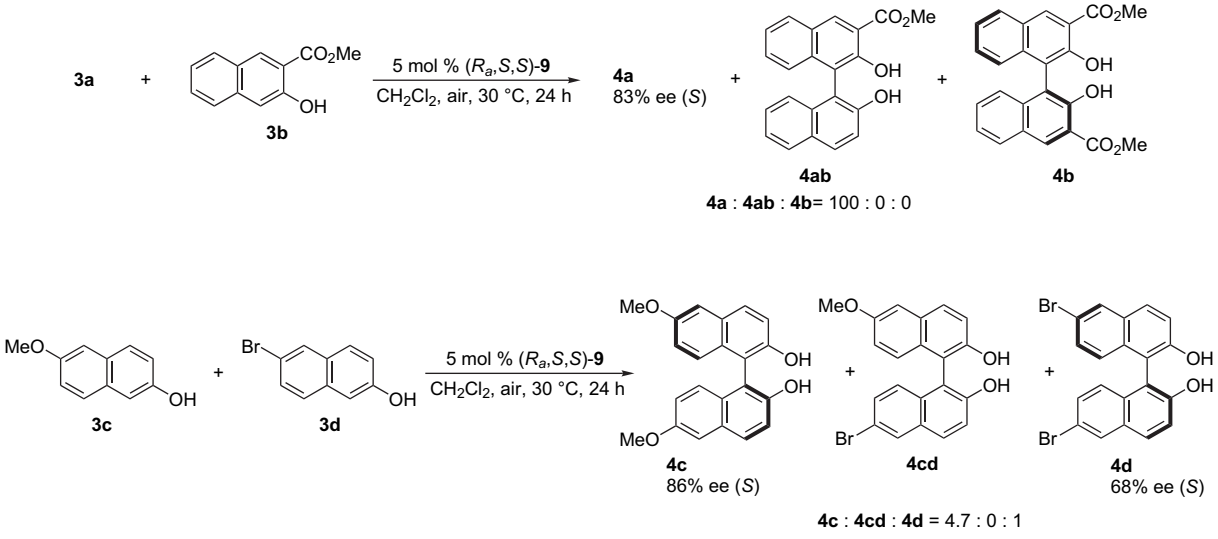
3. Conclusion

We have developed dual activation catalysts for the homolytic coupling of 2-naphthol promoted by dinuclear vanadium complexes. Chiral dinuclear vanadium(IV) complex (R_a,*S*,*S*)-**1e** and vanadium(V) complex (R_a,*S*,*S*)-**9** possessing (*S*)-*tert*-leucine moieties at the 3,3′-positions of a (*R*)-binaphthyl skeleton smoothly promoted the oxidative coupling of 2-naphthol with high reaction rates to afford (*S*)-BINOL products in high yield and high enantioselectivity. The 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. Applications of the dinuclear vanadium complexes on a large scale as well as their extension to other asymmetric reactions are in progress.

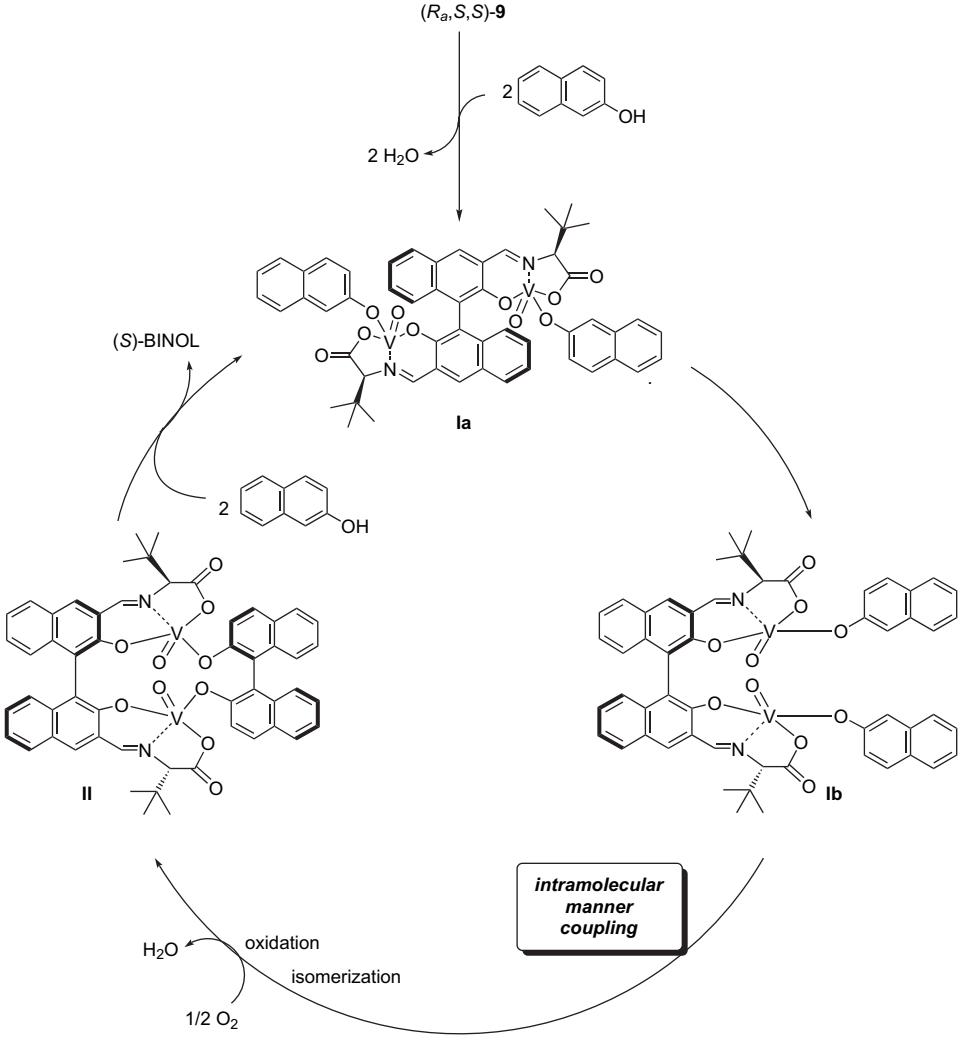
4. Experimental section

4.1. General remarks

^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-EX270 FT NMR spectrometer (^{1}H NMR 270 MHz, ^{13}C NMR 67.7 MHz). All signals are expressed as parts per million downfield from tetramethylsilane used as an internal standard. ^{51}V NMR spectra were recorded on a JEOL JNM-LA600 (158 MHz) spectrometer in CD_3OD or CD_2Cl_2 with $VOCl_3$ as an external standard (0 ppm). FTIR spectra were recorded



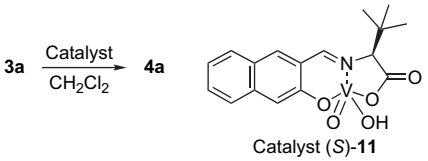
Scheme 4. Cross-coupling of **3a** with **3b** and **3c** with **3d** in the presence of (R_a,*S*,*S*)-**9**.



Scheme 5. Proposed reaction mechanism for (R_a,*S*,*S*)-**9** catalyzed oxidative coupling reaction.

on a Perkin–Elmer system 2000 FT-IR. Optical rotations were measured with a JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU-980 pump and UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH as an eluent. X-ray crystallographic analyses were carried out with a RIGAKU AFC-7R, and all calculations were performed using the crystal structure determination package of Molecular Structure Corporation. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL JMS-600H. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-D 300. ESI-TOF mass spectra were recorded on a JEOL JMS-T100LC. Elemental analysis was performed on a Perkin–Elmer 2400. Analytical TLC was performed on Merck silica gel plates with 60 F_{254} indicator. Visualization was accomplished with UV light and phosphomolybdic acid. Column chromatography on SiO_2 was performed with Kanto Silica Gel 60 (40–100 μm). Commercially available organic and inorganic compounds were used without further purification, except for the solvent, which was distilled by a known method before use.

Table 6
Coupling reaction of 2-naphthol catalyzed by vanadium(V) complexes



Entry	Catalyst (mol %)	Atmosphere (1 atm)	Temp (°C)	Time (h)	Yield[a] (%)	ee[b] (%)
1	(R_a,*S*,*S*)-**9** (5)	O_2	30	24	Quant	71
2	(R_a,*S*,*S*)-**9** (5)	Air	30	24	96	85
3	(R_a,*S*,*S*)-**9** (5)	Air	0	72	Quant	90
4	(*S*)-**11** (10)	O_2	30	24	46	61
5	(*S*)-**11** (10)	Air	30	24	37	81
6	(*S*)-**11** (10)	Air	0	24	20	85

[a] Isolated yields.
[b] Determined by HPLC (Chiralpak AS-H, hexane/i-PrOH=9:1).

4.2. Chiral dinuclear vanadium complexes *1*

A round-bottomed flask (100 mL) was charged with the corresponding amino acid (3.3 mmol), anhydrous NaOAc

(500 mg, 6.0 mmol), and water (6 mL). After stirring at 70 °C for 10 min to generate a clear solution, a solution of (*R*)-**2**,[14] (1.5 mmol) in THF (22 mL) was added to the reaction mixture. The reaction mixture was refluxed for 1.5 h to generate a clear red solution, and the consumption of (*R*)-**2** was monitored by TLC (acetone/hexane=1:3). The resulting solution was gradually cooled to room temperature for 2 h. A solution of vanadyl sulfate hydrate (978 mg, 6.0 mmol) in H_2O (5 mL) was added to the reaction mixture and the solution was stirred for 2 h under Ar. THF was evaporated and the corresponding vanadium complex was collected by filtration, washed sequentially with water (ca. 60 mL) and ether (ca. 60 mL) under air, and dried under vacuum to give **1** as a dark green powder (71–85%). (R_a)-**1a**: IR (cm^{-1}): 1647 (C=N), 1625 (C=O), 931 (V=O); FAB-HRMS: found: *m/z* 586.9864; calcd for $C_{26}H_{17}N_2O_8V_2$: $[M+H]^+$, 586.9822. (R_a,*S*,*S*)-**1b**: IR (cm^{-1}): 1650 (C=N), 1610 (C=O), 981 (V=O); FAB-HRMS: found: *m/z* 739.0490; calcd for $C_{38}H_{25}N_2O_8V_2$: $[M+H]^+$, 739.0498. (R_a,*S*,*S*)-**1c**: IR (cm^{-1}): 1654 (C=N), 1614 (C=O), 975 (V=O); FAB-HRMS: found: *m/z* 767.0807; calcd for $C_{40}H_{29}N_2O_8V_2$: $[M+H]^+$, 767.0803. (R_a,*S*,*S*)-**1d**: IR (cm^{-1}): 1652 (C=N), 1612 (C=O), 977 (V=O); FAB-HRMS: found: *m/z* 671.0778; calcd for $C_{32}H_{29}N_2O_8V_2$: $[M+H]^+$, 671.0803. (R_a,*S*,*S*)-**1e**: IR (cm^{-1}): 1661 (C=N), 1614 (C=O), 987 (V=O); FAB-HRMS: found: *m/z* 699.1111; calcd for $C_{34}H_{33}N_2O_8V_2$: $[M+H]^+$, 699.1116; ESI-TOF-LRMS (MeOH): found: *m/z* 783 $[M+2MeO+Na]^+$. (S_a,*S*,*S*)-**1e**: IR (cm^{-1}): 1655 (C=N), 1600 (C=O), 989 (V=O); FAB-HRMS: found: *m/z* 699.1074; calcd for $C_{34}H_{33}N_2O_8V_2$: $[M+H]^+$, 699.1116.

4.3. (*S*,*S*)-**5**

A round-bottomed flask (50 mL) was charged with (*S*)-*tert*-leucine (1.0 mmol), anhydrous NaOAc (167 mg, 2.0 mmol), and water (10 mL). After stirring at 70 °C for 10 min to generate a clear homogeneous solution, the reaction mixture was treated with a solution of 3,3′-diformyl-2,2′-dihydroxy-1,1′-biphenyl[14] (0.5 mmol) in THF (5 mL). The reaction mixture was refluxed for 30 min to generate a red homogeneous solution, and then was gradually cooled to 30 °C for 2 h. To the Schiff base solution was added a solution of vanadyl sulfate (4 mmol) in water (4 mL). The reaction mixture was stirred for 2 h under Ar and then evaporated to remove the residual THF. The vanadium complex was collected by filtration and washed sequentially with water (3×10 mL) and CCl_4 (3×10 mL) under air, and then dried under vacuum to provide (*S*,*S*)-**5** as a dark blue powder (226 mg, 76%). IR (cm^{-1}): 1651 (C=N), 1614 (C=O), 976 (V=O); FAB-HRMS: found: *m/z* 599.0805; calcd for $C_{26}H_{29}N_2O_8V_2$: $(M+H)^+$, 599.0803.

4.4. (*S*)-**8**

A round-bottomed flask (100 mL) was charged with (*S*)-*tert*-leucine (144 mg, 1.1 mmol), anhydrous NaOAc (164 mg, 2.0 mmol), and water (4 mL). After stirring at 70 °C for 10 min to generate a clear solution, a solution of 3-formyl-2-naphthol (**7**) (173 mg, 1.0 mmol) in THF (6 mL) was added. The reaction mixture was refluxed for 2 h to generate a clear red solution, and the consumption of **7** was monitored by TLC (acetone/hexane=1:3). The resulting solution was gradually cooled to 30 °C for 2 h. A solution of vanadyl sulfate hydrate (277 mg, 1.7 mmol) in water (0.5 mL) was added to the reaction mixture and the solution was stirred for 2 h under Ar. THF was evaporated and the vanadium complex was collected by filtration, washed sequentially with water and ether under air, and dried under vacuum to give (*S*)-**8** as a dark green powder (248 mg, 71%). FABMS: found: *m/z* 351 $(M+H)^+$. IR (cm^{-1}): 1661 (C=N), 1621 (C=O), 985 (V=O); FAB-HRMS: found: *m/z* 351.0670; calcd for $C_{17}H_{18}NO_4V$: $[M+H]^+$, 351.0675.

4.5. (*R*$_a$,*S*,*S*)-**9**

A round-bottomed flask (100 mL) was charged with (*R*)-**2** (342 mg, 1.0 mmol), (*S*)-*tert*-leucine (289 mg, 2.2 mmol), MS 3 Å (1.0 g), and EtOH (30 mL). The reaction mixture was refluxed at 80 °C for 2 h to generate a red-orange suspension and the consumption of (*R*)-**2** was monitored by TLC (acetone/hexane=1:3). After evaporation of EtOH, the residue was suspended in CH_2Cl_2 (20 mL) and then $VOCl_3$ (0.38 mL, 4.0 mmol) was added under Ar. The reaction mixture was stirred for 12 h, and filtered by Celite to remove MS 3 Å. The filtrate was evaporated and the resulting black solid was dissolved in MeOH (ca. 20 mL) and the solvent was evaporated again. The residue was dissolved in CH_2Cl_2 (ca. 50 mL) and washed with H_2O (4×ca. 40 mL), and the aqueous layer was extracted with CH_2Cl_2 (4×ca. 40 mL). The combined extract was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give (R_a,*S*,*S*)-**9** (461 mg, 63%) as a black powder. Complex (R_a,*S*,*S*)-**9** (952 mg, 1.3 mmol) and NaOH (57 mg, 1.4 mmol) were dissolved in MeOH (44 mL) and the resulting dark-brown solution was filtered through a membrane filter. Ether (ca. 350 mL) was added to the filtrate, and the solution was allowed to stand at room temperature for 3–7 days. Dark-brown needles (266 mg, 27%) were obtained as (R_a,*S*,*S*)-**9**·NaOH salt. The needles (296 mg, 0.38 mmol) were suspended in CH_2Cl_2 and neutralized with 5 N HCl (aq) (77 μL, 0.38 mmol). The reaction mixture was diluted with water and extracted with CH_2Cl_2 two times. The extract was dried over Na_2SO_4 and then filtered. The organic solvent was removed by evaporation. After drying under vacuum, an extra pure (R_a,*S*,*S*)-**9** (194 mg, 69%) resulted as a black powder. (R_a,*S*,*S*)-**9**: ^{1}H NMR (270 MHz, CD_3OD): δ 8.96 (s, 2H, CH=N), 8.48 (s, 2H, Ar–H), 8.06 (t, J=4.7 Hz, 2H, Ar–H), 7.70 (t, J=4.9 Hz, 2H, Ar–H), 7.44–7.38 (m, 4H, Ar–H), 4.23 (s, 2H, CH–*t*-Bu), 1.25 (s, 18H, *t*-Bu); ^{13}C NMR (67.7 MHz, CD_3OD): δ 167.9, 138.7, 137.6, 130.6, 130.5, 129.6, 127.4, 125.3, 124.1, 83.8, 38.8, 28.2; ^{51}V NMR (CD_3OD): δ −557.2; IR (cm^{-1}): 3436 (O–H), 1683 (C=N), 1608 (C=O), 996 (V=O); ESI-TOF-LRMS (MeOH): found: *m/z* 783 $[M-2(OH)+2(OMe)+Na]^+$; CSI-TOF-LRMS (CH_2Cl_2): found: *m/z* 1511 $[2(M+Na+H)]^+$. Anal. Calcd for $C_{34}H_{36}N_2O_{11}V_2$: C, 54.41; H, 4.83; N, 3.73. Found: C, 53.98; H, 4.60; N, 3.56.

4.6. (R_a,S,S)-**10**

A round-bottomed flask (50 mL) was charged with (*R*)-5,5′,6,6′,7,7′8,8′-octahydro-3,3′-diformyl-BINOL[26] (70 mg, 0.2 mmol), (*S*)-*tert*-leucine (58 mg, 0.44 mmol), MS 3 Å (ca. 500 mg), and EtOH (7 mL). The reaction mixture was refluxed at 80 °C for 30 min to generate a yellow suspension and the consumption of (*R*)-5,5′,6,6′,7,7′8,8′-octahydro-3,3′-diformyl-BINOL was monitored by TLC (acetone/hexane=1:3). After evaporation of EtOH, the residue was suspended in CH_2Cl_2 (10 mL), and then $VOCl_3$ (75 μL, 0.8 mmol) was added to give a dark green solution. The reaction mixture was stirred for 6 h under Ar, and filtered with Celite to remove MS 3 Å. The filtrate was evaporated to afford a dark green solid. The resulting solid was dissolved in MeOH (15 mL) and the solvent was evaporated again. The residue was washed with water (ca. 50 mL) and Et_2O (ca. 50 mL). Drying under vacuum gave (R_a,*S*,*S*)-**10** (84 mg, 56%) as a dark green powder. ^{1}H NMR (270 MHz, CD_3OD): δ 8.59 (s, 2H, CH=N), 7.41 (s, 2H, Ar−H[3]), 4.12 (s, 2H, CH−*t*-Bu), 2.89 (br, 4H, CH_2), 2.34 (br, 4H, CH_2), 1.82 (br, 8H, CH_2), 1.19 (s, 18H, *t*-Bu); ^{13}C NMR (67.7 MHz, CD_3OD): δ 168.1×2, 148.3, 135.6, 134.8×2, 131.9, 102.0, 84.8, 39.4, 31.6, 31.2, 29.1, 29.0, 25.1; IR (cm^{-1}): 3449 (O-H), 1686 (C=N), 1611 (C=O), 1001 (V=O); ESI-TOF HRMS: found: *m*/*z* 791.1929 $[M-2(OH)+2(OMe)+Na]^+$; calcd for $C_{36}H_{46}N_2NaO_{10}V_2$: 791.1929.

4.7. (S)-**11**

A round-bottomed flask (50 mL) was charged with **7** (86 mg, 0.5 mmol), (*S*)-*tert*-leucine (58 mg, 0.5 mmol), MS 3 Å, and EtOH (7 mL). The reaction mixture was refluxed at 80 °C for 4 h to generate a red suspension and the consumption of **7** was monitored by TLC (acetone/hexane=1:3). After evaporation of EtOH, the residue was suspended in CH_2Cl_2 (ca. 8 mL) and then $VOCl_3$ (0.09 mL, 1 mmol) was added. The reaction mixture was stirred for 15 h under Ar and filtered by Celite to remove MS 3 Å. The filtrate was evaporated to afford a dark green solid. The resulting solid was dissolved in MeOH and the solvent was evaporated again. The residue was washed sequentially with water and ether. Drying under vacuum gave (*S*)-**11** as a dark green powder (69 mg, 38%). FAB-LRMS: found: *m*/*z* 368 $(M+H)^+$; IR (cm^{-1}): 3439 (O−H), 1661 (C=N), 1615 (C=O), 992 (V=O); ^{1}H NMR (269.6 MHz, CD_3OD): δ 8.95 (br, 2H, CH=N), 4.24 (br, 2H, CH−*t*-Bu), 1.25 (s, 9H, *t*-Bu); ESI-TOF HRMS: Found: *m*/*z* 404.0679 $[M-OH+OMe+Na]^+$; calcd for $C_{18}H_{20}NNaO_5V$: 404.0679.

4.8. Representative procedure for oxidative coupling of 2-naphthol

A round-bottomed flask (20 mL) was charged with a CH_2Cl_2 solution (1 mL) of 2-naphthol (0.2 mmol). The vanadium catalyst (0.01 mmol) was added to the solution as a powder, and the reaction mixture was stirred. The consumption of 2-naphthol was monitored by TLC (acetone/hexane=1:3). The reaction mixture was purified by silica gel column chromatography (acetone/hexane=1:4) to give the coupled product.

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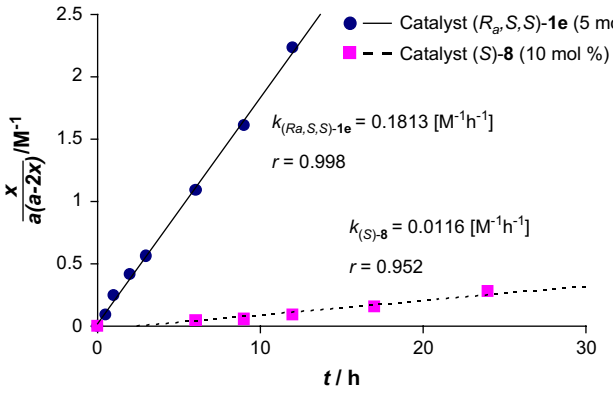

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24. The ^1H NMR chart of the vanadium(V) species causing form the addition of 1 equiv of 5 N HCl aq to the sodium cation on the crystal was same as that of (R_a,*S*,*S*)-**9**.
25. The calculated rate constant for (R_a,*S*,*S*)-**9** catalyzed coupling reaction at 20 °C was $k_{(R_a,S,S)\text{-}\mathbf{9}} = 0.4000\ M^{-1}\ h^{-1}$
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