



Enantioselective oxidative-coupling of polycyclic phenols



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ABSTRACT

Enantioselective oxidative-coupling of polycyclic phenols, such as 2-anthracenol, 9- or 3-phenanthrol, and 5-chrysenol was established by using vanadium(V/IV) catalysis under air or O₂ as a co-oxidant. In the vanadium catalyzed reaction, the corresponding coupling products were obtained in good to excellent yields with up to 93% enantiomeric excess.

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1. Introduction

The preparation of optically pure 1,1'-bi-2-naphthol (BINOL) and its derivatives is of great importance because of their wide utility in asymmetric synthesis.¹ Among the synthetic methods to access enantiomerically pure BINOLs, the asymmetric and catalytic oxidative coupling of 2-naphthols is one of the most straightforward processes.^{2,3} Polycyclic biphenols, such as bianthracenol **1a**, biphenanthrols **1b**, **c**, and bichrysenol **1d** are also useful as chiral BINOL derivatives (Fig. 1).^{4–6} Despite their potential applications, no efficient enantioselective catalytic oxidative-coupling of the polycyclic phenols **2** to yield **1** has been achieved due to the facile over-oxidation of the product and/or side-reaction of the substrate.

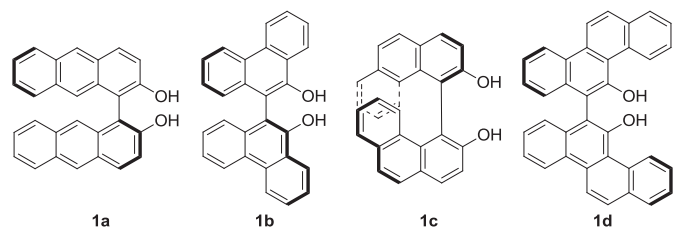


Fig. 1. Chiral polycyclic biphenol derivatives.

Enantioselective vanadium-mediated oxidative couplings, which occur via a favorable one-electron phenolic oxidation, proceed under mild reaction conditions and tolerate several functional groups; this has a further advantage that only water is formed as a side product.³ Previously, we reported a dinuclear vanadium(V) complex (R_a,S,S)-**3** possessing two active sites in a single molecule, which promotes the enantioselective oxidative coupling of 2-naphthols under air as a co-oxidant through a dual activation mechanism (Fig. 2)^{3m–o}.

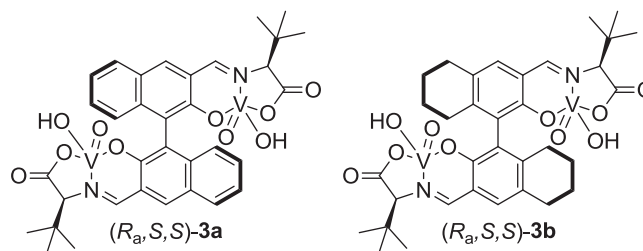


Fig. 2. Dinuclear vanadium(V) complexes, (R_a,S,S)-**3**.

We envisioned that, under the mild reaction conditions, the dinuclear vanadium(V) complex could work as a chiral catalyst for the oxidative-coupling of these easily oxidized polycyclic phenols **2** without the formation of any side-products. In this manuscript, we describe the first enantioselective catalytic coupling of 2-anthracenol (**2a**), 3-phenanthrol (**2c**), and 5-chrysenol (**2d**), and

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the efficient enantioselective catalytic coupling of 9-phenanthrol (**2b**)³⁰ using chiral vanadium(V) complexes, in detail.

2. Results and discussion

2.1. Enantioselective coupling of anthracenol **2a**

In 2013, Takahashi reported the first catalytic oxidative coupling of 2-anthracenol (**2a**) with 5 mol % of MnI₂, yielding bianthracenol **1a** in 74% yield.^{4b} However, no catalytic asymmetric synthesis of **1a** has been achieved. Furthermore, **1a** is easily over-oxidized to the ether derivative **4a**. To our delight, (*R*_a,*S*₁,*S*₂)-**3a** was found to promote the oxidative coupling reaction of **2a** to yield **1a** without the formation of **4a** (Table 1). The reaction with 5 mol % of (*R*_a,*S*₁,*S*₂)-**3a** at −10 °C under air produced **1a** in 80% yield with 85% ee (entry 1). The lowering of the reaction temperature to −20 °C or the use of the complex (*R*_a,*S*₁,*S*₂)-**3b** with H₈-BINOL backbone led

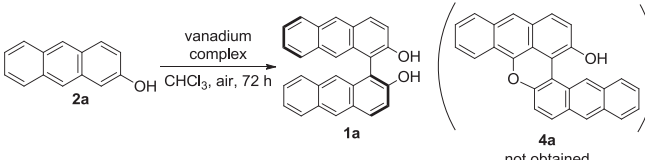
to reduction in the enantioselectivity of the product (entries 2–4). The reaction rate of mononuclear vanadium complex (*S*)-**5a**, which has only one catalytically active center, was quite low in comparison with that of (*R*_a,*S*₁,*S*₂)-**3a**, while using 10 mol % of the catalyst (*S*)-**5a** (entry 5). The higher reaction rate and enantioselectivity using dinuclear complex (*R*_a,*S*₁,*S*₂)-**3a** than those obtained using a mononuclear (*S*)-**5a** catalyzed reaction are attributable to the simultaneous activation^{3m-o} of two molecules of **2a**. Optically pure **1a** could be obtained after a recrystallization from hexane/CH₂Cl₂ (entry 1).

2.2. Enantioselective coupling of phenanthrols **2b** and **c**

An effective and enantioselective synthesis of 9,9'-bi(10-phenanthrol) (**1b**) via the oxidative coupling of 9-phenanthrol (**2b**) has also been a challenge in the oxidative-coupling reactions because **2b** is easily oxidized to the corresponding quinone derivative, phenanthrene-9,10-dione (**4b**).⁵ The results of coupling **2b** using vanadium complexes are shown in Table 2. The dinuclear vanadium catalyst (*R*_a,*S*₁,*S*₂)-**3a** was found to promote the oxidative coupling reaction of **2b** to give **1b** in high yields without the formation of **4b**. Among the reaction solvents studied, CH₂Cl₂ provided the highest reaction rate with high enantioselectivity, producing biphenanthrol **1b** in 94% yield with 88% ee (entry 4). Although the reaction proceeded under air, the ee of **1b** decreased slightly to 76% (entry 6). At −10 °C under O₂, the reaction with 5 mol % of (*R*_a,*S*₁,*S*₂)-**3a** produced **1b** in quantitative yield and with 93% ee (entry 8). The enantioselective coupling of **2b** on a gram scale (6.0 g, entry 9) led to **1b** in 90% yield with 90% ee. Optically pure **1b** could be obtained after a single recrystallization from hexane/acetone (entries 8 and 9).

Next, we focused on the coupling reaction of 3-phenanthrol (**2c**) to give 4,4'-bi(3-phenanthrol) (**1c**), which could be readily applied to construct hetero[7]helicenes.^{5m} During our screening of conditions (Table 3), the dinuclear vanadium complex (*R*_a,*S*₁,*S*₂)-**3b** in (CH₂Cl₂)₂ was found to exhibit moderate asymmetric induction to produce **1c** in 32% yield with 65% ee (entry 3). The yield of **1c** was increased to 48% at 60 °C; however, the enantioselectivity decreased to 43% ee (entry 6). Insufficient improvement in chemical yield was observed even when a quantitative amount of the vanadium complex was employed (entry 9). A product inhibition

Table 1
Enantioselective coupling of 2-anthracenol (**2a**)



Entry	Vanadium complex (mol %)	Temp (°C)	Yield of isolated product %	ee % ^a
1	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	−10	80	85 (>99) ^b
2	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3b (5)	−10	91	51
3	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	−20	60	74
4	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3b (5)	−20	80	49
5	(<i>S</i>)- 5a (10)	−10	47	29

^a Determined using HPLC (Daicel Chiralpak AD-H).

^b After a single recrystallization.

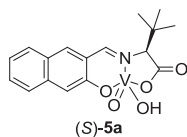
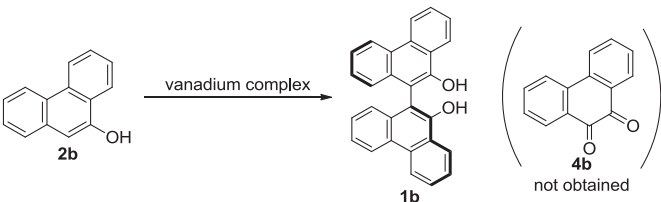


Table 2
Enantioselective coupling of 9-phenanthrol (**2b**)



Entry	Vanadium complex (mol %)	Solvent	Atmosphere	Temp (°C)	Time (h)	Yield of isolated product %	ee % ^a
1	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	MeCN	O ₂	−5	70	92	89
2	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	Toluene	O ₂	−5	72	80	86
3	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	CHCl ₃	O ₂	−5	60	90	54
4	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	CH ₂ Cl ₂	O ₂	−5	36	94	88
5	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	CH ₂ Cl ₂	O ₂	0	24	92	84
6	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	CH ₂ Cl ₂	Air	−5	74	80	76
7	(<i>S</i>)- 5a (10)	CH ₂ Cl ₂	O ₂	−10	48	29	10 ^b
8	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	CH ₂ Cl ₂	O ₂	−10	48	100 (80) ^c	93 (>99) ^c
9 ^d	(<i>R</i> _a , <i>S</i> ₁ , <i>S</i> ₂)- 3a (5)	CH ₂ Cl ₂	O ₂	−10	48	90 (79) ^c	90 (>99) ^c

^a Determined using HPLC (Daicel Chiralpak AD-H).

^b The major product has (*R*)-configuration.

^c After a single recrystallization.

^d 6.0 g scale.

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