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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 O_2 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.

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.

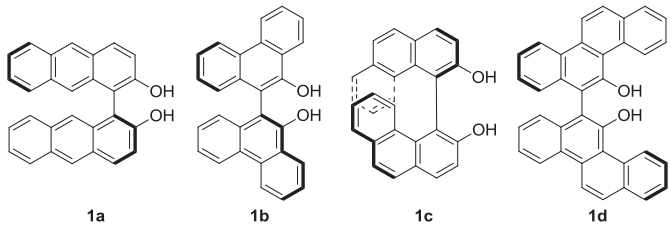

Fig. 1. Chiral polycyclic biphenol derivatives.

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].

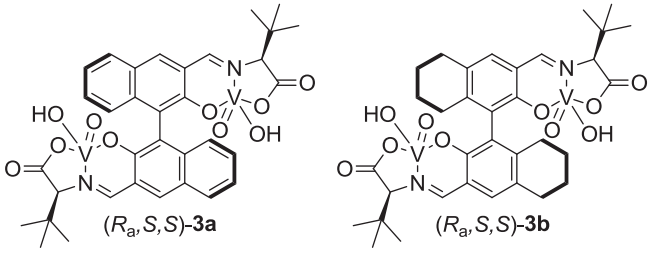

Fig. 2. Dinuclear vanadium(V) complexes, (R_a,*S*,*S*)-**3**.

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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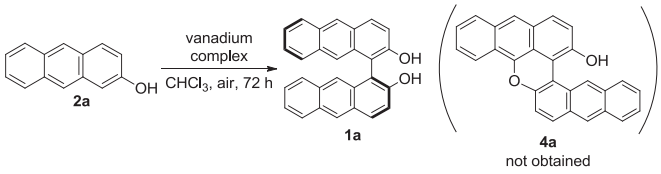
the efficient enantioselective catalytic coupling of 9-phenanthrol (**2b**)[3o] using chiral vanadium(V) complexes, in detail.

2. Results and discussion

2.1. Enantioselective coupling of anthracenol 2a

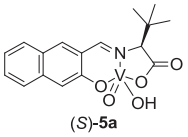
In 2013, Takahashi reported the first catalytic oxidative coupling of 2-anthracenol (**2a**) with 5 mol % of MnI_2, yielding bianthracenol **1a** in 74% yield.[4b] However, no catalytic asymmetric synthesis of **1a** has been achieved. Furthermore, **1a** is easily overoxidized to the ether derivative **4a**. To our delight, (R_a,*S*,*S*)-**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*,*S*)-**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*,*S*)-**3b** with H_8-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*,*S*)-**3a**, while using 10 mol % of the catalyst (*S*)-**5a** (entry 5). The higher reaction rate and enantioselectivity using dinuclear complex (R_a,*S*,*S*)-**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/CH_2Cl_2 (entry 1).

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



Entry	Vanadium complex (mol %)	Temp (°C)	Yield of isolated product %	ee %[a]
1	(R_a,*S*,*S*)-**3a** (5)	−10	80	85 (>99)[b]
2	(R_a,*S*,*S*)-**3b** (5)	−10	91	51
3	(R_a,*S*,*S*)-**3a** (5)	−20	60	74
4	(R_a,*S*,*S*)-**3b** (5)	−20	80	49
5	(*S*)-**5a** (10)	−10	47	29

[a] Determined using HPLC (Daicel Chiralpak AD-H).
[b] After a single recrystallization.



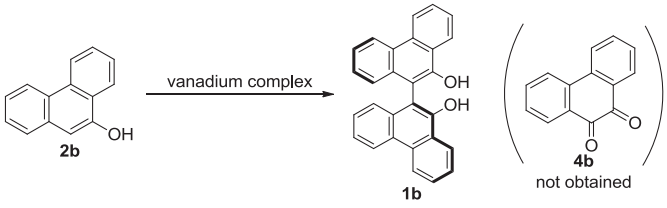
(*S*)-**5a**

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*,*S*)-**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, CH_2Cl_2 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 O_2, the reaction with 5 mol % of (R_a,*S*,*S*)-**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*,*S*)-**3b** in $(CH_2Cl)_2$ 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

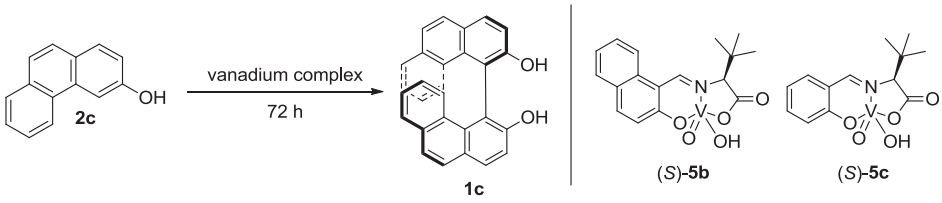
Table 2
Enantioselective coupling of 9-phenanthrol (**2b**)



Entry	Vanadium complex (mol %)	Solvent	Atmosphere	Temp (°C)	Time (h)	Yield of isolated product %	ee %[a]
1	(R_a,*S*,*S*)-**3a** (5)	MeCN	O_2	−5	70	92	89
2	(R_a,*S*,*S*)-**3a** (5)	Toluene	O_2	−5	72	80	86
3	(R_a,*S*,*S*)-**3a** (5)	$CHCl_3$	O_2	−5	60	90	54
4	(R_a,*S*,*S*)-**3a** (5)	CH_2Cl_2	O_2	−5	36	94	88
5	(R_a,*S*,*S*)-**3a** (5)	CH_2Cl_2	O_2	0	24	92	84
6	(R_a,*S*,*S*)-**3a** (5)	CH_2Cl_2	Air	−5	74	80	76
7	(*S*)-**5a** (10)	CH_2Cl_2	O_2	−10	48	29	10[b]
8	(R_a,*S*,*S*)-**3a** (5)	CH_2Cl_2	O_2	−10	48	100 (80)[c]	93 (>99)[c]
9[d]	(R_a,*S*,*S*)-**3a** (5)	CH_2Cl_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.

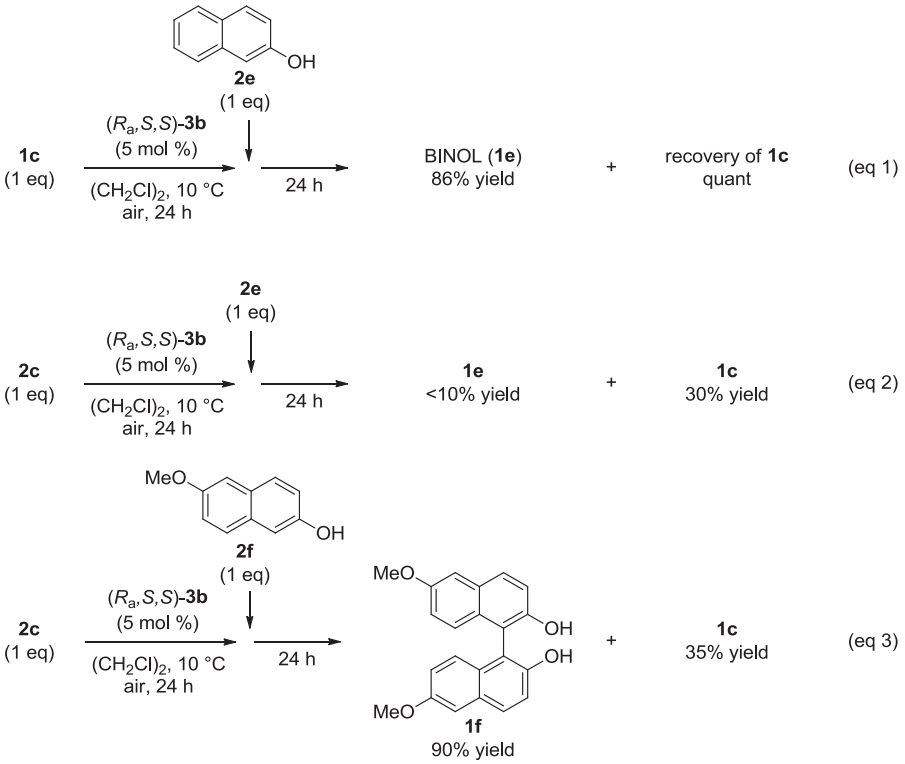
Table 3
Enantioselective coupling of 3-phenanthrol (**2c**)



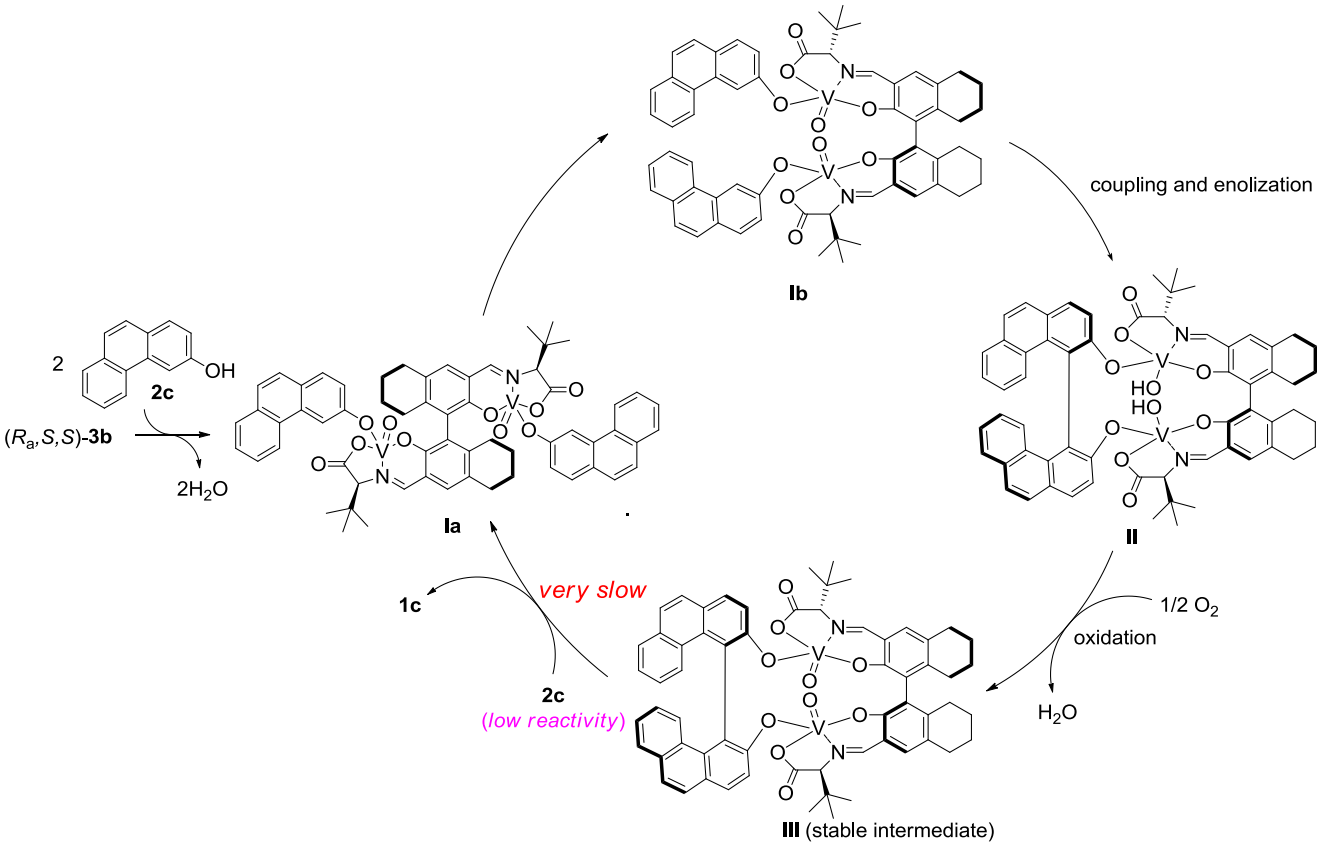
Entry	Vanadium complex (mol %)	Solvent	Atmosphere	Temp (°C)	Yield of isolated product %	ee %[a]
1	(R_a,*S*,*S*)-**3a** (5)	CH_2Cl_2	O_2	10	39	40
2	(R_a,*S*,*S*)-**3b** (5)	CH_2Cl_2	O_2	10	30	42
3	(R_a,*S*,*S*)-**3b** (5)	$(CH_2Cl)_2$	O_2	10	32	65
4	(R_a,*S*,*S*)-**3b** (5)	Toluene	O_2	10	15	20
5	(R_a,*S*,*S*)-**3b** (5)	$(CH_2Cl)_2$	O_2	−10	9	67
6	(R_a,*S*,*S*)-**3b** (5)	$(CH_2Cl)_2$	O_2	60	48	43
7	(R_a,*S*,*S*)-**3b** (5)	$CHCl_3$	Air	10	30	69
8	(R_a,*S*,*S*)-**3b** (5)	$CHCl_3$	O_2	10	32	68
9	(R_a,*S*,*S*)-**3b** (100)	$CHCl_3$	O_2	10	45	67
10	(*S*)-**5a** (10)	$(CH_2Cl)_2$	O_2	10	25	10
11	(*S*)-**5b** (10)	$(CH_2Cl)_2$	O_2	10	32	12
12	(*S*)-**5c** (10)	$(CH_2Cl)_2$	O_2	10	28	rac

[a] Determined using HPLC (Daicel Chiralpak OD-H).

might be responsible for the low conversion of the coupling of **2c**. To establish the reason for the low conversion of **2c**, the reactions of 2-naphthol (**2e**) or 6-methoxy-2-naphthol (**2f**) in the presence of **1c** or **2c** were investigated (Scheme 1). After mixing (R_a,*S*,*S*)-**3b** and biphenanthrol **1c** in $(CH_2Cl)_2$ under air for 24 h, 2-naphthol (**2e**) was added to the reaction mixture. The coupling reaction of **2e** proceeded smoothly to give BINOL **1e** in 86% yield, and biphenanthrol **1c** was recovered quantitatively (Eq. 1). Similarly, catalyst (R_a,*S*,*S*)-**3b** was mixed with phenanthrol **2c** for 24 h, followed by the addition of 2-naphthol (**2e**); however, almost no BINOL **1e** was formed, and biphenanthrol **1c** was obtained in 30% yield (Eq. 2). When 6-methoxy-2-naphthol (**2f**), a highly reactive substrate for the coupling, was added after mixing catalyst (R_a,*S*,*S*)-**3b** and phenanthrol **2c** for 24 h, the coupling products **1f** and **c** were obtained in 90% yield and 35% yield, respectively (Eq. 3). In all cases, no hetero-cross-coupling product was formed.[3n] The reason for the low conversion of **2c** remains unclear; however, given the results of the coupling reactions, our previously proposed reaction mechanism[3m–o] might be in agreement with an intramolecular coupling as shown in Scheme 2. The dinuclear vanadium(V) complex reacts with two molecules of **2c** resulting in **Ia**. The C-4 position of the substrates approaches each other by the rotation of the binaphthyl



Scheme 1. Coupling of 2-naphthols **2e** or **2f** in the presence of 1 equiv of biphenanthrol **1c** or phenanthrol **2c**.



Scheme 2. Enantioselective homo-coupling of **2c**.

axis yielding **Ib**, which is then intramolecularly coupled after a single electron transfer to a vanadium(V) species **III** via intermediate **II**. However, intermediate **III** would be very stable, resulting in the slow release of **1c** from **III**. As a result, low conversion was observed when **2c** was used as a substrate for the homo-coupling using catalyst (R_a,*S*,*S*)-**3b**.

2.3. Enantioselective coupling of chrysenol 2d

Bichrysenol **1d** is expected to create an effective asymmetric environment because of the additional aromatic ring adjacent to the hydroxy group.[1] The oxidative coupling of 5-chrysenol (**2d**) was also conducted using dinuclear vanadium(V) complexes (R_a,*S*,*S*)-**3** (Table 4). However, racemic **1d** was obtained when 5 mol % of (R_a,*S*,*S*)-**3a** or **3b** was used at −10 °C under O_2 (entry 1). These results may be attributed to the steric obstruction close to the reaction site of the dinuclear complex. Therefore, we tested mononuclear vanadium complexes **5**, which possess less steric hindrance. As expected, the mononuclear vanadium complexes could promote the coupling of **2d** enantioselectively. In this coupling reaction, the aromatic substitutions on catalysts **5** made a significant impact on the enantioselectivity of **1d**. As shown in Table 4, catalysts (*S*)-**5b** and **d**, bearing a 5- or 6-substituent on the aromatic ring of the catalyst, exhibited good asymmetric induction in **1d** (entries 3 and 5, 71% ee and 61% ee, respectively). In contrast, 3- and/or 4-mono- or disubstituted catalysts gave **1d** with <30% ee (entries 2 and 6–8). Among the reaction conditions we screened, mononuclear vanadium catalyst **5b** in CH_2Cl_2 led to coupling with the highest ee (75%). Finally, optically pure **1d** was readily obtained by a recrystallization from a hexane/CH_2Cl_2 mixed solvent system (entry 11).

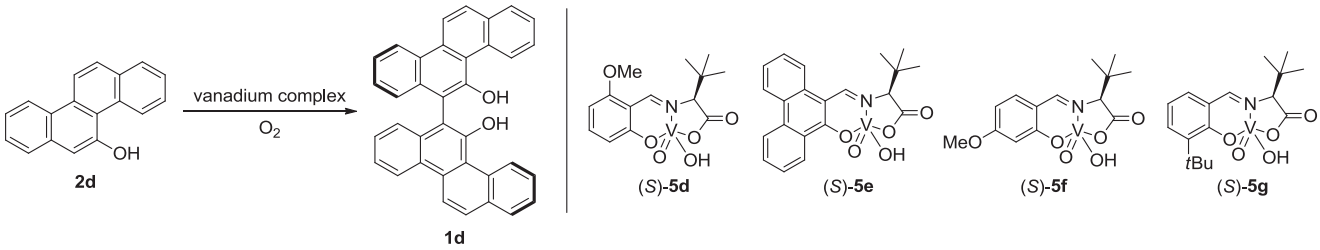
3. Application of coupling product 1 to enantioselective direct aza-hetero-Diels–Alder reaction

Chiral phosphoric acids have emerged as a class of powerful organocatalysts[7] for the activation of imine functional groups, resulting in a number of asymmetric additions of various nucleophiles to imines. In 2006, Gong[8a] and Rueping[8b] independently reported the direct aza-hetero-Diels–Alder reaction of 2-cyclohexenone (**7**) with aldimines **8** to produce isoquinuclidines. To confirm the ability of polycyclic biphenols **1** in asymmetric catalysis, the corresponding chiral phosphoric acids **6** were prepared from the coupling product **1** and then tested on the aza-hetero-Diels–Alder reaction (Table 5).[8a] Chiral phosphoric acids **6a**, **c**, and **e** could promote the reaction, but only afforded the racemic product **9a** (entries 1, 3, and 5). The 9,9′-bi(10-phenanthrol)- and bichrysenol-derived catalysts **6b** and **d** could provide better asymmetric environments than those of catalysts **6a**, **c**, and **e** because of the additional two or four aromatic rings near the phosphoric acid group, leading to the formation of product **9a** with up to 53% ee (entry 4). In comparison with the best result obtained using catalyst **6f**, reported by Rueping (Scheme 3),[8b] our catalyst **6d** would still need an increased bulk to create an efficient chiral environment for the aza-hetero-Diels–Alder reaction.

4. Transformation of polycyclic biphenol

In order to improve the chiral catalyst efficiency of the polycyclic biphenol, various transformations of **1b** were tested (Scheme 4). The reaction of **1b** using PtO_2 (1 equiv) in glacial acetic acid under H_2 (1 atm) at room temperature led to

Table 4
Enantioselective coupling of 5-chrysenol (**2d**)

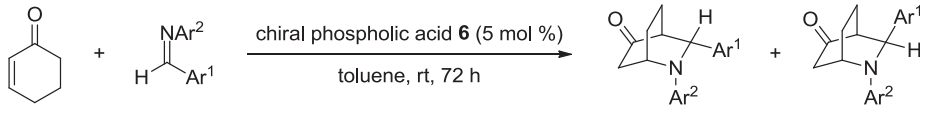


Entry	Vanadium complex (mol %)	Solvent	Temp (°C)	Time (h)	Yield of isolated product %	ee %[a]
1	(R_a,*S*,*S*)-**3a** (5) or **3b** (5)	CH_2Cl_2	−10	24	54 or 55	rac
2	(*S*)-**5a** (10)	CH_2Cl_2	−10	24	67	30
3	(*S*)-**5b** (10)	CH_2Cl_2	−10	24	55	71
4	(*S*)-**5c** (10)	CH_2Cl_2	−10	24	40	38
5	(*S*)-**5d** (10)	CH_2Cl_2	−10	24	32	61
6	(*S*)-**5e** (10)	CH_2Cl_2	−10	24	47	9[b]
7	(*S*)-**5f** (10)	CH_2Cl_2	−10	24	48	20[b]
8	(*S*)-**5g** (10)	CH_2Cl_2	−10	24	43	27[b]
9	(*S*)-**5b** (10)	CH_2Cl_2	−20	24	52	68
10	(*S*)-**5b** (10)	CH_2Cl_2	Rt	24	54	25
11	(*S*)-**5b** (10)	CH_2Cl_2	−10	36	83	75 (>99)[c]
12	(*S*)-**5b** (10)	$CHCl_3$	−10	36	36	63
13	(*S*)-**5b** (10)	CCl_4	−10	36	55	64
14	(*S*)-**5b** (10)	Toluene	−10	36	45	24

[a] Determined using HPLC (Daicel Chiralpak AD-H).
[b] The major product has (*R*)-configuration.
[c] After a single recrystallization.

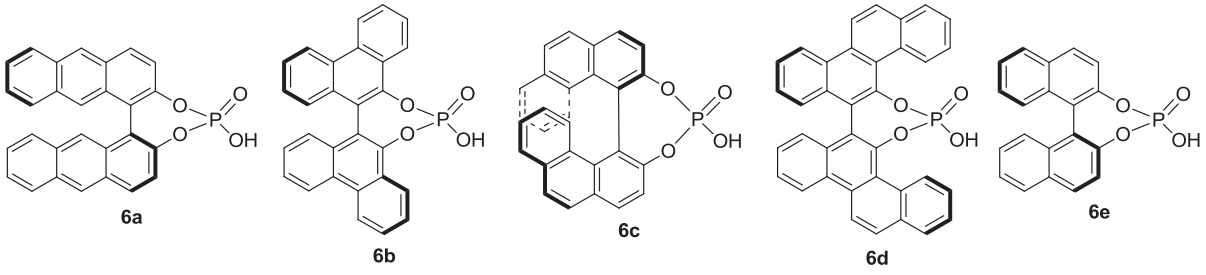
complete conversion to give H_{16}-biphenanthrol **10** in 80% yield.[9] The methyl capped biphenanthrol **11**[5a] underwent bromination by using *N*-bromosuccinimide (NBS), providing the 6,6′-dibrominated compound **12** quantitatively. The methyl capped dibromobiphenanthrol **12** could be a versatile intermediate for further derivatization. Thus, **12** was treated with $Pd(PPh_3)_4$, $PhB(OH)_2$, and Na_2CO_3 in 1,2-dimethoxyethane (DME) at reflux temperature providing **14**. The methoxy derivatives were easily deprotected in the presence of BBr_3, which provided diols **13** or **15** in good yields.

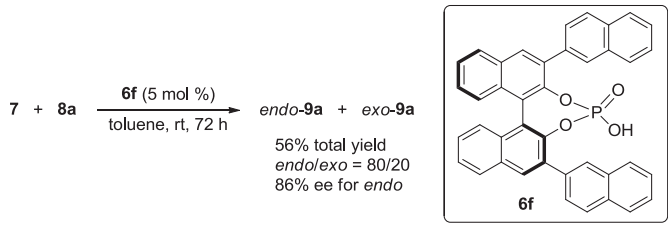
Table 5
Direct organocatalytic enantioselective Diels–Alder reaction of 2-cyclohexenone (**7**) and aldimines **8**



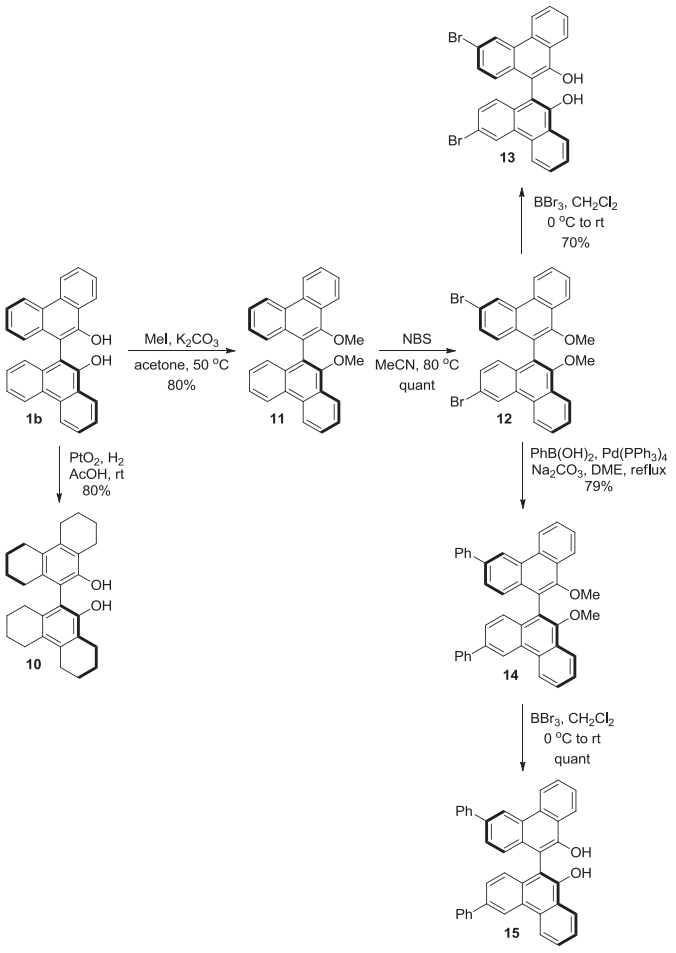
Entry	Phosphoric acids	Ar^1	Ar^2	8	Yield of isolated product % (ratio *endo*/*exo*)	ee % of *endo*[a]
1	**6a**	Ph	4-Br–C_6H_4	**8a**	80 (60/40), **9a**	rac
2	**6b**	Ph	4-Br–C_6H_4	**8a**	52 (67/32), **9a**	25
3	**6c**	Ph	4-Br–C_6H_4	**8a**	63 (60/40), **9a**	rac
4	**6d**	Ph	4-Br–C_6H_4	**8a**	54 (78/22), **9a**	53
5	**6e**	Ph	4-Br–C_6H_4	**8a**	50 (69/31), **9a**	rac
6	**6d**	Ph	4-MeO–C_6H_4	**8b**	74[b] (79/21), **9b**	36
7	**6d**	2-Naphthyl	4-MeO–C_6H_4	**8c**	92 (77/23), **9c**	34
8	**6d**	2-F–C_6H_4	4-Br–C_6H_4	**8d**	51 (75/25), **9d**	46

[a] Determined using HPLC (Daicel Chiralcel OD-H for **9a** and **9d**; Daicel Chiralpak AD for **9b**; Daicel Chiralpak AD-H for **9c**).
[b] 144 h.





Scheme 3. Enantioselective Diels–Alder reaction reported by Rueping.[8b]



Scheme 4. Transformation of **1b**.

5. Conclusions

We have developed a vanadium-mediated enantioselective catalytic oxidative-coupling of polycyclic phenols **2**; various phenols were successfully employed with 5 or 10 mol % of the catalyst to give the corresponding biphenols **1** in good to excellent yields with up to 93% ee. The conversion of **1** to the corresponding phosphoric acids was achieved and utilized them in the hetero-Diels–Alder reaction. Further transformations of **1** were carried out and their use in asymmetric catalysis is currently under investigation.

6. Experimental section

6.1. General information

^{1}H-, ^{13}C-, and ^{51}V NMR spectra were recorded with JEOL JMN ECS400 FT NMR, JNM ECA600 FT NMR or Bruker AVANCE II (^{1}H NMR 400, 600 or 700 MHz, ^{13}C NMR 100, 150 or 175 MHz, ^{51}V NMR 158 MHz). ^{1}H NMR spectra are reported as follows: chemical shift in parts per million relative to the chemical shift of $CHCl_3$ at 7.26 ppm, integration, multiplicities (s=singlet, d=doublet, q=quartet, t=triplet, m=multiplet), and coupling constants (Hertz). ^{13}C NMR spectra are reported in ppm relative to the central line of triplet for $CDCl_3$ at 77 ppm. ^{51}V NMR spectra were recorded with $VOCl_3$ as an external standard (0 ppm). FT-MS spectra were obtained with LTQ Orbitrap XL (Thermo Fisher Scientific). ESI-MS spectra were obtained with JMS-T100LC (JEOL). FAB-MS spectra were obtained with JMS-700 (JEOL). Optical rotations were measured with 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 2-propanol as eluents. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100). Mp was measured with SHIMADZU DSC-60. Column chromatography on SiO_2 was performed with Kishida Silica Gel (63–200 μm). Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled from sodium/benzophenone or CaH_2.

6.2. General procedure for coupling reactions using vanadium complexes

A test tube was charged with a halogenated solvent (1.0 mL) solution of coupling substrate (0.2 mmol) under air or O_2 atmosphere. Vanadium catalyst (0.01 or 0.02 mmol, 5 or 10 mol %) was added to the solution. The reaction mixture was stirred until the reaction had reached completion by monitoring with TLC analysis. Then the reaction mixture was directly purified by silica gel column chromatography eluting with ethyl acetate/*n*-hexane to give the coupling product.

(*S*)-**1a**[4]: 85% ee, $[\alpha]_D^{22}$ +513.3 (*c* 0.3, $CHCl_3$, for 97% ee); ^{1}H NMR ($CDCl_3$) δ 8.52 (s, 2H), 8.20 (d, *J*=9.6 Hz, 2H), 7.99 (d, *J*=8.4 Hz, 2H), 7.73 (s, 2H), 7.61 (d, *J*=8.4 Hz, 2H), 7.47 (d, *J*=9.6 Hz, 2H), 7.39 (t, *J*=8.4 Hz, 2H), 5.21 (br s, 2H); Daicel Chiralpak AD-H column, 2-propanol/*n*-hexane=3/17, flow rate 1.0 mL/min, 30.4 min (*R*-isomer) and 41.9 min (*S*-isomer).

(*S*)-**1b**[5a]: >99% ee, $[\alpha]_D^{23}$ −65.7 (*c* 1.2, $CHCl_3$, for >99% ee); ^{1}H NMR ($CDCl_3$) δ 8.81 (d, *J*=8.2 Hz, 2H), 8.75 (d, *J*=8.2 Hz, 2H), 8.46 (d, *J*=8.2 Hz, 2H), 7.84–7.80 (m, 2H), 7.74–7.71 (m, 2H), 7.55–7.52 (m, 2H), 7.37–7.33 (m, 2H), 7.28–7.24 (m, 2H), 5.55 (br s, 2H); Daicel Chiralpak AD-H column, 2-propanol/*n*-hexane=3/17, flow rate 1.0 mL/min, 21.0 min (*R*-isomer) and 23.0 min (*S*-isomer).

(*R*)-**1c**[5m]: 69% ee, $[\alpha]_D^{24}$ −59.1 (*c* 0.8, $CHCl_3$, for 95% ee); ^{1}H NMR ($CDCl_3$) δ 8.09 (d, *J*=8.7 Hz, 2H), 8.03 (d, *J*=8.7 Hz, 2H), 7.86–7.82 (m, 4H), 7.74 (d, *J*=8.7 Hz, 2H), 7.45 (d, *J*=8.7 Hz, 2H), 7.41–7.38 (m, 2H), 6.96–6.92 (m, 2H), 5.03 (br s, 2H); Daicel Chiralpak OD-H column, 2-propanol/*n*-hexane=3/7, flow rate 0.5 mL/min, 16.4 min (*S*-isomer) and 32.7 min (*R*-isomer).

(*S*)-**1d**: 75% ee, $[\alpha]_D^{22}$ +213.5 (*c* 0.1, $CHCl_3$, for 96% ee); ^{1}H NMR ($CDCl_3$) δ 9.80 (d, *J*=8.4 Hz, 2H), 8.92 (d, *J*=9.2 Hz, 2H), 8.90 (d, *J*=8.4 Hz, 2H), 8.19 (d, *J*=9.2 Hz, 2H), 8.07–8.05 (m, 2H), 7.69–7.59 (m, 6H), 7.39 (t, *J*=7.8 Hz, 2H), 7.29 (d, *J*=7.8 Hz, 2H), 6.32 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 152.6, 133.1, 132.2, 131.7, 130.7, 129.9, 129.1, 128.4,

127.9, 127.0, 126.5, 125.7, 124.9, 124.7, 123.8, 121.1, 120.3, 109.8; HRMS (ESI-TOF): calcd for $C_{36}H_{22}O_2Na$ $[M+Na]^+$ 509.1517, found: *m*/*z* 509.1511; IR (KBr): 3457, 2989, 1763, 1376, 1242, 1056 cm^{-1}; Daicel Chiralpak AD-H column, 2-propanol/*n*-hexane=3/17, flow rate 1.0 mL/min, 11.9 min (*S*-isomer) and 23.2 min (*R*-isomer).

6.3. Preparation of mononuclear vanadium complex (*S*)-5b

A round bottomed flask was charged with 2-hydroxy-1-naphthaldehyde (1.46 mmol), which were prepared according to the known method, (*S*)-*tert*-leucine (1.60 mmol), MS 3A (0.73 g) and EtOH (25 mL). The reaction mixture was refluxed at 80 °C and consumption of the aldehyde substrate was monitored by TLC. After evaporation of EtOH, the residue was suspended in CH_2Cl_2 (15 mL) and then $VOCl_3$ (3.21 mmol) was added. The reaction mixture was stirred for 12 h, and filtered by Celite to remove MS 3A. The filtrate was evaporated and the resulting black solid was dissolved in MeOH and the solvent was evaporated again. The residue was collected by filtration and washed sequentially with water and ether, and then dried in a vacuum to give (*S*)-**5b** in 58% yield as a black powder.

(*S*)-**5b**: ^1H NMR (CD_3OD): δ 9.48 (s, 1H), 8.29 (d, *J*=8.6 Hz, 1H), 8.09 (d, *J*=9.1 Hz, 1H), 7.87 (d, *J*=8.6 Hz, 1H), 7.63 (t, *J*=7.2 Hz, 1H), 7.43 (t, *J*=7.2 Hz, 1H), 7.14 (d, *J*=9.1 Hz, 1H), 4.37 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (CD_3OD); δ 180.3, 165.8, 163.3, 138.7, 134.9, 130.5, 130.04, 130.00, 125.4, 121.4, 120.9, 112.6, 85.4, 38.3, 28.2; ^{51}V NMR (CD_3OD): δ −558.3; HRMS (ESI-TOF): calcd for $C_{18}H_{20}NO_5VNa$ $[M-OH+OMe+Na]^+$ 404.0678, found: *m*/*z* 404.0674; IR (KBr): 3233, 2961, 1672, 1612, 1335, 971 cm^{-1}.

6.4. Preparation of organocatalyst (*S*)-6d

The organocatalyst (*S*)-**6d** was prepared according to the literature method.[8a]

(*S*)-**6d**: $[\alpha]_D^{22}$ +822.0 (*c* 0.2, $CHCl_3$, for 96% ee); ^1H NMR ($CDCl_3$) δ 9.71 (d, *J*=7.6 Hz, 2H), 8.75–8.63 (m, 4H), 7.90–7.19 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 146.68, 146.62, 143.2, 140.7, 133.0, 131.61, 131.25, 129.8, 129.2, 128.5, 128.2, 127.6, 127.3, 126.7, 126.4, 125.9, 125.0, 123.5, 123.0, 122.6, 120.7; ^{31}P NMR ($CDCl_3$) δ 1.62; HRMS (ESI-TOF): calcd for $C_{36}H_{21}O_4PNa$ $[M+Na]^+$ 571.1070, found: *m*/*z* 571.1072; IR (KBr): 3438, 2938, 1744, 1365, 1211, 1090 cm^{-1}.

6.5. General procedure for direct organocatalytic enantioselective Diels–Alder reaction of 2-cyclohexenone (7) and aldimines 8

2-Cyclohexenone (**7**) (0.07 mL, 0.73 mmol) was added to a vial containing aldimines **8** (0.073 mmol) and a catalytic amount of phosphoric acid **6** (5 mol %) in toluene (0.27 mL) at rt. After vigorously stirring the mixture for 72 h, the reaction mixture was directly purified by column chromatography on silica gel to afford **9**.

endo-**9c**: 34% ee, $[\alpha]_D^{20}$ +32.7 (*c* 0.6, $CHCl_3$, for 34% ee); ^1H NMR ($CDCl_3$) δ 7.83–7.74 (m, 4H), 7.45–7.39 (m, 3H), 6.75 (dd, *J*=6.6, 2.2 Hz, 2H), 6.66 (dd, *J*=6.6, 3.2 Hz, 2H), 4.72 (s, 1H), 4.50 (s, 1H), 3.70 (s, 3H), 2.88–2.83 (m, 2H), 2.49 (dd, *J*=18.8, 2.7 Hz, 1H), 2.37–2.29 (m, 1H), 2.25–2.15 (m, 1H), 2.11–2.03 (m, 1H), 1.81–1.74 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 211.8, 152.1, 142.5, 139.6, 133.6, 133.0, 128.9, 128.1, 127.7, 126.1, 125.8, 124.6, 123.8, 114.8, 114.6, 66.5, 55.6, 52.0, 49.3, 46.2, 22.8, 22.3; HRMS (ESI-TOF): calcd for $C_{24}H_{23}NO_2Na$ $[M+Na]^+$ 380.1621, found: *m*/*z* 380.1621; IR (KBr): 3422, 2948, 2372, 1721, 1510, 1248 cm^{-1}; Daicel Chiralpak AD-H column, 2-propanol/*n*-hexane=1/20, flow rate 1.0 mL/min, 28.8 min (minor isomer) and 39.8 min (major isomer).

6.6. Transformation of (*S*)-1b

*6.6.1. Preparation of (S)-**10**.* To a 5 mL round-bottomed flask at rt was added (*S*)-**1b** (50 mg, 0.13 mmol), and PtO_2 (31.7 mg, 0.12 mmol) in glacial acetic acid (1.5 mL). The flask was furnished with a stream of hydrogen (1 atm) at rt. After stirring for 5 days, the reaction mixture was filtered by Celite to remove PtO_2. The mother liquid was washed with H_2O, and then evaporated. The crude was purified by column chromatography to give (*S*)-**10** in 80% yield (42 mg, 0.10 mmol) as a pale brown solid.

(*S*)-**10**: Mp 177–179 °C; >99% ee, $[\alpha]_D^{21}$ −32.9 (*c* 0.5, $CHCl_3$, for >99% ee); ^1H NMR ($CDCl_3$): δ 4.60 (br, s, 2H), 2.78–2.43 (m, 12H), 2.35–2.08 (m, 4H), 1.94–1.54 (m, 16H); ^{13}C NMR ($CDCl_3$): δ 149.1, 137.3, 132.6, 127.7, 121.7, 115.6, 27.7, 26.7, 26.2, 23.7, 23.3, 23.1, 22.9, 22.2; HRMS (ESI-TOF): calcd for $C_{28}H_{34}O_2Na$ $[M+Na]^+$ 425.2451, found: *m*/*z* 425.2452; IR (KBr): 3517, 2928, 2860, 1438, 1301, 1212 cm^{-1}.

*6.6.2. Preparation of (S)-**11**.* To a solution of (*S*)-**1b** (1.0 g, 2.58 mmol) in anhydrous acetone (20 mL) was added to anhydrous K_2CO_3 (1.43 g, 10.4 mmol) and methyl iodide (1.83 g, 12.9 mmol). The reaction mixture was heated at 50 °C under Ar atmosphere for 4 h. After cooling to rt, the volatiles were removed in vacuum and the residues were washed with CH_2Cl_2. The organic layers were dried over anhydrous Na_2SO_4 and then evaporated. The crude was purified by column chromatography to give (*S*)-**11** in 80% yield (0.85 g, 2.06 mmol) as a white solid.

(*S*)-**11**[5a]: Mp 255–257 °C; >99% ee, $[\alpha]_D^{25}$ +35.8 (*c* 1.0, $CHCl_3$, for >99% ee); ^1H NMR ($CDCl_3$) δ 8.84 (d, *J*=8.1 Hz, 2H), 8.77 (d, *J*=8.3 Hz, 2H), 8.34 (d, *J*=9.5 Hz, 2H), 7.80–7.70 (m, 4H), 7.58–7.55 (m, 2H), 7.34–7.33 (m, 4H), 3.57 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 152.7, 132.9, 132.0, 128.2, 128.1, 127.2, 126.9×2, 126.8, 125.5, 123.6, 122.9, 122.7, 122.3, 61.2.

*6.6.3. Preparation of (S)-**12**.* To a solution of (*S*)-**11** (50 mg, 0.12 mmol) in MeCN (2 mL) was gradually added to NBS (107 mg, 0.6 mmol). The reaction mixture was stirred for 2 h under reflux conditions. The volatiles were removed in vacuum and the residues were washed with water, brine, and CH_2Cl_2. The organic layers were dried over anhydrous Na_2SO_4 and then evaporated. The crude was purified by column chromatography to give (*S*)-**12** in quantitative yield (68 mg, 0.12 mmol).

(*S*)-**12**: Mp 282–284 °C; >99% ee, $[\alpha]_D^{23}$ −17.4 (*c* 1.0, $CHCl_3$, for >99% ee); ^1H NMR ($CDCl_3$) δ 8.89 (d, *J*=2.0 Hz, 2H), 8.74–8.72 (m, 2H), 8.33–8.32 (m, 2H), 7.79–7.74 (m, 4H), 7.43–7.39 (m, 2H), 7.17–7.13 (m, 2H), 3.55 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 153.2, 131.4, 131.0, 130.2, 129.8, 128.3, 128.2, 127.7, 127.6, 125.6, 123.7, 123.0, 121.3, 120.1, 61.3; HRMS (ESI-TOF): calcd for $C_{30}H_{20}Br_2O_2Na$ $[M+Na]^+$ 594.9702, found: *m*/*z* 594.9702; IR (KBr): 3071, 2947, 1588, 1428, 1118, 1086 cm^{-1}.

*6.6.4. Preparation of (S)-**13**.* To a solution of (*S*)-**12** (200 mg, 0.36 mmol) in CH_2Cl_2 (4 mL) was slowly added to BBr_3 (1 M solution in CH_2Cl_2) (0.76 mL, 0.76 mmol) at 0 °C under Ar atmosphere. The reaction mixture was stirred for overnight. After addition of water (1 mL), the mixture was extracted with CH_2Cl_2. The organic layers were washed with water, brine, and dried over anhydrous Na_2SO_4. After the evaporation, (*S*)-**13** was obtained in 70% yield (130 mg, 0.25 mmol) as a white solid.

(*S*)-**13**: Mp 303–305 °C; >99% ee, $[\alpha]_D^{25}$ −49.6 (*c* 0.5, $CHCl_3$, for >99% ee); ^1H NMR ($CDCl_3$) δ 8.85 (d, *J*=2.0 Hz, 2H), 8.70 (d, *J*=8.3 Hz, 2H), 8.44 (d, *J*=8.3 Hz, 2H), 7.85–7.81 (m, 2H), 7.76–7.72 (m, 2H), 7.41 (dd, *J*=8.8, 2.0 Hz, 2H), 7.06 (d, *J*=8.8 Hz, 2H), 5.58 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 149.9, 131.0, 130.8, 130.2, 128.8, 128.7, 127.7, 126.7, 125.9, 125.1, 123.7, 122.8, 119.2, 106.3; HRMS (ESI-TOF): calcd for $C_{28}H_{14}Br_2O_2Na$ $[M-H_2+Na]^+$ 564.9233, found: *m*/*z* 564.9231; IR (KBr): 3488, 1591, 1491, 1423, 1207, 1002, 672 cm^{-1}.

*6.6.5. Preparation of (S)-**14**.* To a solution of (*S*)-**12** (50 mg, 0.09 mmol) in DME (1.5 mL) and 2 M aq Na_2CO_3 (0.25 mL) was added to $PhB(OH)_2$ (27 mg, 0.22 mmol) and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol) under Ar atmosphere. The reaction mixture was heated at 80 °C for 8 h. After filtration, the mixture was extracted with CH_2Cl_2. The organic layers were washed with water, brine, and dried over anhydrous Na_2SO_4 and then evaporated. The crude was purified by column chromatography to give (*S*)-**14** in 79% yield (39 mg, 0.07 mmol) as a white solid.

(*S*)-**14**: >99% ee, $[\alpha]_D^{22}$ −2.1 (*c* 0.5, $CHCl_3$, for >99% ee); ^{1}H NMR ($CDCl_3$) δ 9.00 (d, *J*=1.7 Hz, 2H), 8.96–8.93 (m, 2H), 8.39 (m, 2H), 7.83–7.74 (m, 8H), 7.61–7.58 (m, 2H), 7.52–7.34 (m, 8H), 3.63 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 152.8, 141.3, 138.3, 132.1, 128.9, 128.5, 128.4, 127.5, 127.3, 127.1, 126.4, 123.7, 123.0, 122.1, 121.2, 120.8, 115.3, 61.4 (One peak is merged with other peak.); HRMS (ESI-TOF): calcd for $C_{42}H_{30}O_2Na$ $[M+Na]^+$ 589.2138, found: *m*/*z* 589.2140; IR (KBr): 3416, 2841, 1593, 1227, 1080, 700 cm^{-1}.

*6.6.6. Preparation of (S)-**15**.* To a solution of (*S*)-**14** (40 mg, 0.071 mmol) in CH_2Cl_2 (4 mL) was slowly added to BBr_3 (1 M solution in CH_2Cl_2) (0.18 mL, 0.18 mmol) at 0 °C under Ar atmosphere. The reaction mixture was stirred for overnight. After addition of water (1 mL), the mixture was extracted with CH_2Cl_2. The organic layers were washed with water, brine, and dried over anhydrous Na_2SO_4. After the evaporation, (*S*)-**15** was obtained in quantitative yield (38 mg, 0.071 mmol) as a white solid.

(*S*)-**15**: Mp 184–186 °C; >99% ee, $[\alpha]_D^{25}$ −51.7 (*c* 0.5, $CHCl_3$, for >99% ee); ^{1}H NMR ($CDCl_3$) δ 8.96 (d, *J*=1.7 Hz, 2H), 8.92–8.90 (m, 2H), 8.49 (dd, *J*=4.0, 1.7 Hz, 2H), 7.87–7.83 (m, 2H), 7.77–7.72 (m, 6H), 7.63–7.59 (m, 2H), 7.50–7.48 (m, 4H), 7.40–7.36 (m, 4H), 5.61 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 149.6, 141.3, 137.7, 132.1, 130.9, 128.9, 128.3, 127.5, 127.3, 127.1, 125.6, 125.15, 125.13, 123.7, 122.8, 121.5, 107.0 (One peak is merged with other peak.); HRMS (ESI-TOF): calcd for $C_{40}H_{24}O_2Na$ $[M-H_2+Na]^+$ 559.1669, found: *m*/*z* 559.1667; IR (KBr): 3416, 2841, 1593, 1227, 1080, 700 cm^{-1}.

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