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Easily Accessible C_2-Symmetric Chiral Bicyclo[3.3.0] Dienes as Ligands for Rhodium-Catalyzed Asymmetric 1,4-Addition

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The synthesis of a new type of C_2-symmetric chiral diene ligands with a nonbridged bicyclic [3.3.0] backbone was successfully introduced. Using highly efficient lipase-catalyzed transesterification and Suzuki-coupling strategies, a broad family of enantiopure 3,6-disubstituted bicyclo[3.3.0] dienes with different electronic and steric properties could be easily prepared. The application of these new diene ligands in the Rh-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds have been examined, and excellent enantioselectivities (up to 98% *ee*) as well as good yields are achieved under very mild reaction conditions at room temperature.

Keywords: 1,4-addition · asymmetric catalysis · boronic acids · diene ligands · rhodium

Introduction

Chiral dienes have recently been recognized as a new type of chiral ligand in asymmetric reactions since the pioneering work of Hayashi[1] and Carreira.[2] Considerable attention has been attracted by the sufficient stability and excellent catalytic activity of diene–metal complexes shown in asymmetric process,[3–5] with bridged bicyclic 1,4-cyclohexdiene and 1,5-cyclooctadiene structures identified as privileged frameworks. In catalysis, chiral dienes with these special frameworks can form stable complexes with a metal and exert a high catalytic activity as well as excellent stereocontrol. For example, the C_2-symmetric bicyclo-[2.2.1]heptadienes and C_1-symmetric bicyclo[2.2.2]octadienes are elegant ligands for Rh-catalyzed asymmetric 1,4-addition reactions;[1,4d,5] the C_2-symmetric bicyclo[2.2.2]octadienes have shown high performance in the Rh-catalyzed asymmetric arylation of *N*-tosylarylimines;[4b–c] and the C_1-symmetric bicyclo[2.2.2]octadiene–Ir^I complex is proved to be an efficient catalyst for kinetic resolution of allyl carbonates.[2] Despite this impressive progress, however, the design and use of easily accessible new chiral dienes with different frameworks and catalytic properties have been much less studied.[6] In early 2007, we reported our discovery of a new family of C_2-symmetric chiral diene ligands bearing a simple nonbridged bicyclo[3.3.0] backbone and their successful application in the Rh-catalyzed enantioselective arylation of *N*-tosylarylimines with arylboronic acids.[7] In this paper, we report a full description of the preparation of enantiopure 3,6-disubstituted bicyclo[3.3.0] dienes and their use in the Rh-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds.[8,9] Very recently, a similar work of 1,4-addition to enones using chiral bicyclo-[3.3.0] dienes has been published.[10]

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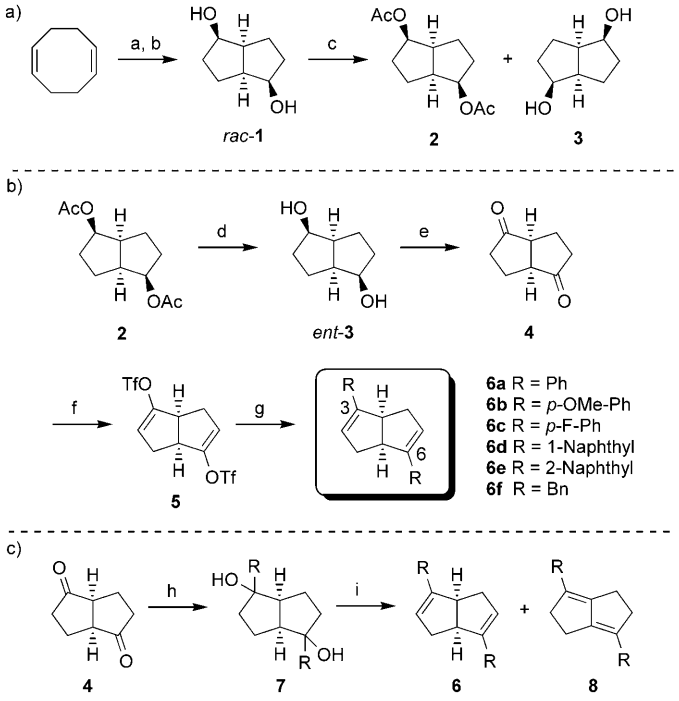
Results and Discussion

The synthetic pathway to the C_2-symmetric chiral bicyclo-[3.3.0] diene, (3a*S*,6a*S*)-3,6-disubstituted-1,3a,4,6a-tetrahydropentalene **6**, is shown in Scheme 1. The synthesis began with the palladium chloride-mediated transannular cycliza-



Scheme 1. Synthetic routes to C_2-symmetric chiral bicyclo[3.3.0] diene **6**. Reagents and conditions: a) $Pb(OAc)_4$, $PdCl_2$, AcOH, 60%; b) KOH, MeOH, 90%; c) PCL, vinyl acetate, TBME, 40% for **2** (99% *ee*), 40% for **3** (>99% *ee*); d) KOH, MeOH, 90%; e) PCC, CH_2Cl_2, 90%; f) Tf_2O, 2,6-lutidine, CH_2Cl_2, −78°C to room temperature, 72%; g) $ArB(OH)_2$, $[Pd(PPh_3)_4]$, 2N Na_2CO_3, toluene/EtOH, reflux, 90% for **6a**; 90% for **6b**; 90% for **6c**; 79% for **6d**; 86% for **6e**; $BnBF_3K$, $[Pd(PPh_3)_4]$, 2N Cs_2CO_3, THF/H_2O, reflux, 21% for **6f**; h) ArLi, Et_2O–benzene, −78°C; i) TsOH, CH_2Cl_2, room temperature or HCOOH, AcOH, reflux, 80% for **6a**, 70% for **6b**, 23% for **6c**, 62% for **6d**.

tion of the simple olefin compound 1,5-cyclooctadiene,[11] followed by a subsequent hydrolysis in basic conditions to give racemic octahydropentalene-1,4-diol **1**. The kinetic resolution of *rac*-**1** by transesterification with vinyl acetate catalyzed by lipase PCL is the key transformation to furnish optically active octahydropentalene derivatives (1*R*,3a*S*,4*R*,6a*S*)-1,4-diyl diacetate **2** and (1*S*,3a*R*,4*S*,6a*R*)-1,4-diol **3** (Scheme 1a).[12] Notably, both enantiomerically pure (>99% *ee*) **2** and **3** could be readily obtained after crystallization. For the preparation of the diene ligand (*S*,*S*)-**6**, (1*R*,3a*S*,4*R*,6a*S*)-diacetate **2** was used. Hydrolysis of **2** in KOH/MeOH gave the corresponding diol compound *ent*-**3**. This diol was then subjected to oxidation by PCC to afford diketone **4** in good yield. To construct the diene skeleton, diketone **4** was expected to convert into its tetrahydropentalene ditriflate form. Fortunately, when **4** was treated with Tf_2O in the presence of 2,6-lutidine, the ditriflate product **5** was successfully isolated as a white solid in 72% yield. In a similar reaction by Hayashi, more expensive *N*-(2-pyridyl)-triflimide (Tf_2NPy-2) and lithium diisopropylamide (LDA) were used.[1,4b] With ditriflate **5** as an electrophile, the designed chiral diene (*S*,*S*)-**6** could be readily prepared using the coupling strategy (Scheme 1b). Notably, enantiomerically pure dienes **6a–f** with the variation of the Ar substituents at C-3 and C-6 were easily produced by the Suzuki-coupling reaction of ditriflate **5** with different coupling reagents. This indicates that the electronic and steric properties of the diene ligands could be possibly tuned. An alternative way to prepare diene **6** from diketone **4** is the addition with organomagnesium or organolithium reagents followed by dehydration of diol **7**[13] in acidic conditions (Scheme 1c). However, the conjugated diene product **8** was also generated. The desired diene **6** is usually very difficult to be separated from **8** because of the similar polarity.

Treatment of the diene (*S*,*S*)-**6a** with $[RhCl(C_2H_4)_2]_2$ in dioxane at 50°C for 4 h gave the corresponding diene–rhodium complex $[RhCl(\mathbf{6a})]_2$. Suitable crystals of this complex were obtained by recrystallization from CH_2Cl_2/petroleum ether. For comparison, both of the structural properties of crystalline solids (*S*,*S*)-**6a** and $[RhCl((S,S)\text{-}\mathbf{6a})]_2$ were determined by X-ray diffraction (Figure 1). As depicted, the two *cis*-fused cyclopentene rings in the molecule **6a** effect a characteristic wedge structure, when the two double bonds coordinate to rhodium, the wedge structured tetrahydropentalene, together with two substitutions of a phenyl group at the C-3 and C-6 positions create a very good chiral environment around the metal. Similar to the case of Hayashi's complex [RhCl(bicyclo[3.3.1]nona-2,6-diene)]$_2$,[4e] the two double bonds of our rhodium complex $[RhCl(\mathbf{6a})]_2$ are also not parallel and twisted by 25° (23° in Hayashi's). A slightly larger angle 27° is found in the uncoordinated free diene ligand. The bite angle of the diene coordination in $[RhCl(\mathbf{6a})]_2$ is 83°.

To broaden the utility of these C_2-symmetric chiral bicyclo[3.3.0] dienes (**6**) as olefin ligands in catalysis, we examined them in the rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds. In our initial study, **6a** was used as the ligand, and the reaction of 2-cyclopentenone (**9a**) with phenylboronic acid (**10a**) was carried out under similar conditions to those reported by Hayashi.[1] The reaction proceeded smoothly at 50°C and went to completion in an hour. As shown in Table 1, entry 1, the 1,4-addition product **11aa** was isolated in 85% yield and with 96% *ee* using KOH (50 mol%) as a base additive. Being aware of the importance of the additive in Rh-catalyzed 1,4-additions,[14] we screened the reaction conditions by adding other inorganic bases such as K_3PO_4, $NaHCO_3$, Na_2CO_3, LiOH, and KF (Table 1, entries 2–6). In all cases, the enantioselectivities could be maintained to a very high degree (95~96%). Using 50 mol% of K_3PO_4 provided the best reaction with a 96% yield (Table 1, entry 2). Notably, it was also found that the reaction can be success-

Abstract in Chinese:

本文介绍了一类新型 C_2 对称的含有非桥联双环[3.3.0]骨架的手性双烯配体。利用高效的酯酶拆分和 Suzuki 偶联策略，可以方便地得到一系列拥有不同电子属性和立体位阻属性的光学纯 3,6-二取代双环[3.3.0]双烯配体。将这些新型的双烯配体用于铑催化的芳基硼酸对 α，β-不饱和羰基化合物的不对称加成反应中，取得了优良的对映选择性（最高 98% ee）。

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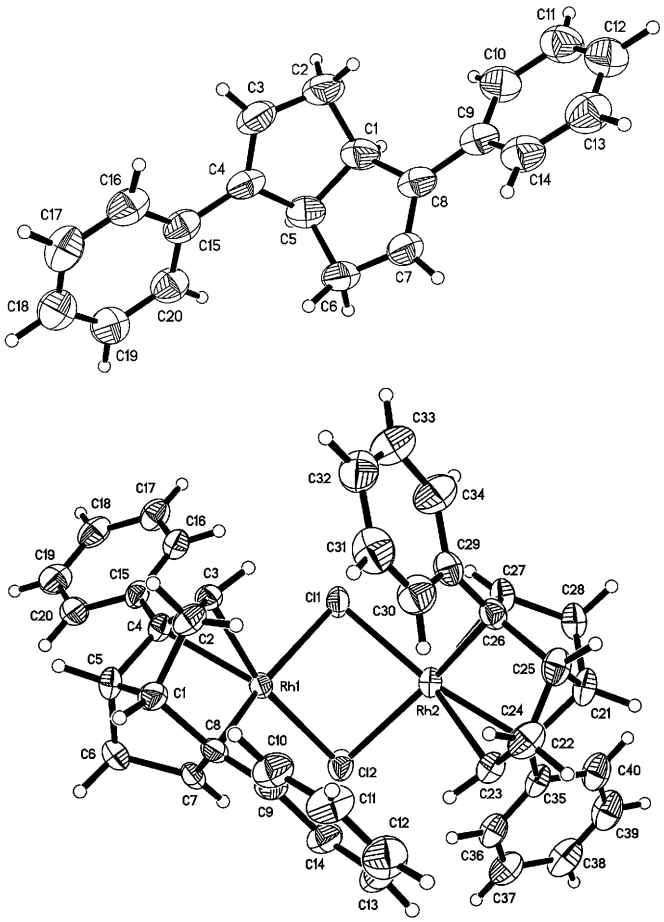
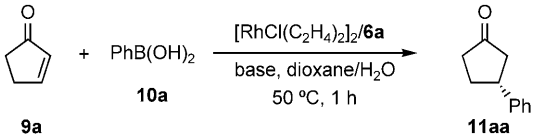


Figure 1. ORTEP illustration of **6a** (upper) and $[RhCl(\mathbf{6a})]_2$ (lower) with thermal ellipsoids drawn at the 50% probability level.

Table 1. Optimization of the reaction conditions.

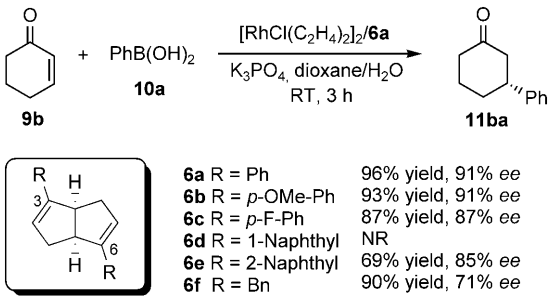


Entry[a]	Base	Yield [%][b]	*ee* [%][c,d]
1	KOH	85	96
2	K_3PO_4	96	96
3	$NaHCO_3$	77	96
4	Na_2CO_3	83	96
5	LiOH	88	95
6	KF	92	96
7[e]	K_3PO_4	96	96
8[f]	K_3PO_4	73	96

[a] The reaction was carried out with 0.5 mmol of 2-cyclopentenone, 2 equiv of phenylboronic acid in the presence of 2.5 mol% of $[RhCl(C_2H_4)_2]_2$, 5.5 mol% of chiral diene **6a**, and 1.5 M aq base (0.1 mL) in dioxane (1.0 mL) at 50°C, unless otherwise noted. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis. [d] The absolute configurations were determined by comparing the optical rotation $[\alpha]_D$ with known data. [e] The reaction was performed at room temperature for 3 h. [f] 1.5 mol% of $[RhCl(C_2H_4)_2]_2$ and 3.3 mol% of chiral diene **6a** were used.

fully run at room temperature, equally affording the addition product **11aa** in excellent yield (96%) and enantiomeric excess (96%; Table 1, entry 7). This result suggests that the catalytic efficiency of the diene–rhodium complex $[RhCl(\mathbf{6a})]_2$ is very high.

Having optimized the reaction conditions, we next focused on the evaluation of catalytic activities of other diene ligands (**6b–f**) in the reaction of phenylboronic acid to 2-cyclohexenone at room temperature. In most cases, the reaction was complete in 3 h. Among the ligands tested, **6a** performed best (Scheme 2). Using **6a**, the 1,4-addition product

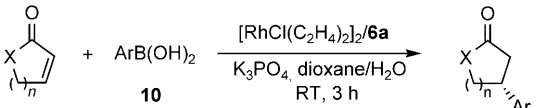


Scheme 2. Evaluation of catalytic activities of chiral diene ligands.

11ba was obtained in 96% yield and with 91% *ee*. Replacing both phenyl units in **6a** by two more electron-rich *p*-methoxylphenyl groups (**6b**) or two more electron-poor *p*-fluorophenyl groups (**6c**) did not significantly influence the enantioselectivity . When two more sterically bulky 1-naphthyl groups were introduced (**6d**), a significant loss of catalytic activity was observed and no reaction took place, probably owing to the coordination difficulty with rhodium. Using two 2-naphthyl substituents instead (**6e**), the reaction occurred with moderate yield (69%) and enantioselection (85%). A decrease in the size of the R group to a less hindered benzyl group (**6f**) led to an obvious drop in the enantioselectivity, though the high reaction yield was maintained. Therefore, the catalytic properties of diene ligands seem to be mainly affected by the steric nature of the R substituents at the C-3 and C-6 positions.

With these findings, we decided to pursue the reaction generality of this rhodium-catalyzed asymmetric 1,4-addition by using catalytic amounts of chiral diene ligand **6a**. A series of arylboronic acids **10** with different substituents on the phenyl ring were reacted with 2-cyclopentenone (**9a**) and 2-cyclohexenone (**9b**). In all cases, the expected addition products **11** were readily produced at room temperature with good to excellent enantioselectivities (Table 2, entries 1–17). The electron-donating or -withdrawing groups on the phenyl ring of boronic acids did not seem to affect the reaction significantly, either in the yield of the product or the enantioselectivity of the reaction. On the other hand, with the sterically more hindered 1-naphthylboronic acid or 2-tolylboronic acid, slightly better enantiomeric excesses of the adducts **11ai**, **11aj**, **11bi**, and **11bj** were achieved (Table 2, entries 9–10 and 16–17). When α,β-unsaturated

Table 2. Asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated cyclic carbonyl compounds catalyzed by $[RhCl(C_2H_4)_2]_2$/(*S*,*S*)-**6a**.



9a X = C, *n* = 1
9b X = C, *n* = 2
9c X = O, *n* = 2
9d X = O, *n* = 1

Entry[a]	9	Ar (10)	11	Yield [%][b]	*ee* [%][c]
1	**9a**	C_6H_5 (**10a**)	**11aa**	96	96
2	**9a**	4-FC_6H_4 (**10b**)	**11ab**	96	96
3	**9a**	4-ClC_6H_4 (**10c**)	**11ac**	97	97
4	**9a**	4-BrC_6H_4 (**10d**)	**11ad**	96	97
5	**9a**	4-MeC_6H_4 (**10e**)	**11ae**	94	96
6	**9a**	4-$MeOC_6H_4$ (**10f**)	**11af**	98	96
7	**9a**	3-ClC_6H_4 (**10g**)	**11ag**	81	94
8	**9a**	2-$MeOC_6H_4$ (**10h**)	**11ah**	93	97
9	**9a**	2-MeC_6H_4 (**10i**)	**11ai**	98	98
10	**9a**	1-Naphthyl (**10j**)	**11aj**	97	98
11	**9b**	C_6H_5 (**10a**)	**11ba**	96	91
12	**9b**	4-FC_6H_4 (**10b**)	**11bb**	91	86
13	**9b**	4-$CF_3C_6H_4$ (**10k**)	**11bk**	73	86
14	**9b**	3-ClC_6H_4 (**10g**)	**11bg**	79	91
15	**9b**	2-$MeOC_6H_4$ (**10h**)	**11bh**	89	90
16	**9b**	2-MeC_6H_4 (**10i**)	**11bi**	91	93
17	**9b**	1-Naphthyl (**10j**)	**11bj**	87	96
18	**9c**	C_6H_5 (**10a**)	**11ca**	87	93
19	**9c**	2-MeC_6H_4 (**10i**)	**11ci**	91	97
20	**9c**	4-MeC_6H_4 (**10e**)	**11ce**	93	89
21	**9c**	2-Naphthyl (**10l**)	**11cl**	94	94
22	**9d**	2-MeC_6H_4 (**10i**)	**11di**	55	95

[a] The reaction was carried out at room temperature with 0.3 mmol of enone, 2 equiv of phenylboronic acid in the presence of 2.5 mol% of $[RhCl(C_2H_4)_2]_2$, 5.5 mol% of chiral diene **6a**, and 1.5 M aq K_3PO_4 (0.1 mL) in dioxane (1.0 mL) for 3 h, unless otherwise noted. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis.

cyclic esters **9c** and **9d** were subjected to these reaction conditions, equally high levels of enantioselectivities were observed (Table 2, entries 18–22), indicating a very useful extension of the substrate scope. The attempts at the enantioselective 1,4-addition of linear enones (*E*)-3-heptenone and (*E*)-5-methyl-3-hexenone with phenylboronic acid, however, were unsuccessful under the optimized reaction conditions.[15] When the reaction temperature was elevated to 100 °C, the addition products were observed but with disappointing enantioselectivities, 20 and 32% *ee*, respectively.

Conclusions

In summary, a new type of C_2-symmetric chiral diene ligands with a nonbridged bicyclic [3.3.0] backbone has been successfully developed. Using mainly lipase-catalyzed transesterification and Suzuki-coupling strategies, a family of enantiopure 3,6-disubstituted bicyclo[3.3.0] dienes was easily prepared. The synthetic approach offers a highly flexible and convenient construction of diene ligands with different electronic and steric properties. With these bicyclo[3.3.0] dienes, we have demonstrated that they are new effective chiral ligands not only for the Rh-catalyzed enantioselective arylation of *N*-tosylarylimines but also for the Rh-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated cyclic carbonyl compounds. Under the optimized conditions, the reactions afforded the addition products smoothly at room temperature with very good to excellent enantioselectivities. Other applications of these readily available bicyclo[3.3.0] dienes in asymmetric synthesis are underway.

Experimental Section

General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. NMR spectra were recorded on a Varian or Bruker spectrometer (300 MHz for ^{1}H, and 75 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard for ^{1}H NMR and [D]chloroform (δ = 77.05 ppm) for ^{13}C NMR. Optical rotations were measured on a JASCO P-1030 polarimeter.

4: To a mixture of PCC (17.2 g) and CH_2Cl_2 (120 mL) was added dropwise a solution of diol **3** (2.84 g, 20 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred at RT for 4 h. When the reaction was completed, a large quantity of ether (about 500 mL) was added to the reaction system and vigorously stirred for 2 h. The dark mixture was then filtered over celite. The ether solution was combined and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford diketone **4** as a white solid (2.36 g, 86%). $[\alpha]_D^{20} = +467.2$ (*c* 1.02, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08–2.25 (m, 6H), 2.35–2.43 (m, 2H), 2.93–2.95 ppm (m, 2H).

5: To a mixture of 2,6-lutidine (1.6 mL, 13.6 mmol), triflic anhydride (2.7 mL, 16.3 mmol), and CH_2Cl_2 (35 mL) under nitrogen at −78 °C was dropped in slowly a solution of diketone **4** (500 mg, 3.6 mmol) in CH_2Cl_2 (8 mL). The mixture was allowed to warm to RT. After stirring at RT for 24 h, the solvent was removed. The residue was diluted with hexane and washed with 1 N HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford ditriflate **5** as a white solid (1.04 g, 72%). $[\alpha]_D^{20} = +35.9$ (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47–2.71 (m, 4H), 3.62–3.65 (m, 2H), 5.64 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.35, 44.14, 115.30, 116.95, 120.14, 149.02 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −73.84 ppm; FTIR (KBr): $\tilde{\nu}$ = 1661, 1426, 1251, 1211, 1141, 1116, 827, 614 cm^{-1}; MS (EI): *m*/*z* (%): 119 (5.11), 91 (14.55), 81 (5.49), 79 (5.10), 77 (9.65), 69 (28.23), 55 (100.00), 53 (11.44); elemental analysis calcd (%) for $C_{10}H_8F_6O_6S_2$: C 29.86, H 2.00; found: C 29.81, H 1.90.

General procedure for the synthesis of dienes **6a–e**: Under nitrogen, a mixture of arylboronic acid (1 mmol), $[Pd(PPh_3)_4]$ (29 mg, 5 mol%), ditriflate **7** (101 mg, 0.25 mmol), toluene (3 mL), EtOH (1 mL), and aqueous solution of Na_2CO_3 (2 M, 1.5 mL) was heated to reflux. After stirring at reflux for 4 h, the reaction was quenched with saturated NH_4Cl. The mixture was extracted with ethyl acetate and washed with brine. The organic layer was dried and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford chiral diene **6** as a white solid.

6a: Yield: 90%. $[\alpha]_D^{20} = +443.8$ (*c* 0.97, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (dd, 2H, J_1 = 17.4 Hz, J_2 = 2.4 Hz), 2.90–2.97 (m, 2H), 4.06–4.10 (m, 2H), 6.04 (s, 2H), 7.22–7.48 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.64, 48.36, 124.35, 126.24, 126.86, 128.35, 135.88, 145.16 ppm; FTIR (KBr): $\tilde{\nu}$ = 2904, 2835, 1494, 1444, 827, 771, 747, 694 cm^{-1}; MS (EI): *m*/*z* (%): 258 (49.78), 154 (18.83), 117 (100.00), 115 (59.51), 91 (39.05), 77 (15.79), 51 (15.67), 44 (29.08); elemental analysis calcd (%) for $C_{20}H_{18}$: C 92.98, H 7.02; found: C 92.81, H 6.99. Crystallographic data for (*S*,*S*)-**6a** ($C_{20}H_{18}$): *T* = 293 (2) K; wavelength: 0.71073 Å; crystal system: orthorhombic, space group: $P2_12_12_1$; unit cell dimensions: *a* = 5.3180 (6) Å, *b* = 13.1826 (14) Å, *c* = 20.997 (2) Å, α = 90°, β = 90°, γ =

90°; $V=1472.0$ (3) Å^3; $Z=4$; $\rho_{calcd}=1.166$ Mg m^{-3}; $F(000)=552$; final R indices [$I>2\sigma(I)$]: $R_1=0.0386$, $wR_2=0.0628$; R indices (all data), $R_1=0.0860$, $wR_2=0.0737$; 8689 reflections measured, 3146 were unique ($R_{(int)}=0.0607$). CCDC-682896 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

6b: Yield: 90%. $[\alpha]_D^{20}=+397.2$ (c 0.93, THF); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.39$ (dd, 2H, $J_1=17.4$ Hz, $J_2=2.7$ Hz), 2.86–2.94 (m, 2H), 3.86 (s, 6H), 4.00–4.01 (m, 2H), 5.88 (s, 2H), 6.87 (d, 4H, $J=8.7$ Hz), 7.39 ppm (d, 4H, $J=8.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=38.70$, 48.56, 55.26, 113.78, 122.12, 127.39, 128.73, 144.61, 158.64 ppm; FTIR (KBr): $\tilde{\nu}=2834$, 1608, 1512, 1284, 1251, 1179, 1032, 824 cm^{-1}; MS (EI): m/z (%): 318 (94.96), 184 (28.59), 147 (97.98), 121 (51.74), 91(38.06), 44 (100.00), 42 (41.54); HRMS (EI) calcd for $C_{22}H_{22}O_2$: 318.1622, found: 318.1620.

6c: Yield: 88%. $[\alpha]_D^{20}=+404.2$ (c 1.08, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.37$ (ddd, 2H, $J_1=17.7$ Hz, $J_2=5.7$ Hz, $J_3=2.7$ Hz), 2.86–2.96 (m, 2H), 4.00–4.05 (m, 2H), 5.93 (s, 2H), 6.99–7.05 (m, 4H), 7.38–7.43 ppm (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=38.50$, 48.57. 115.24 (d, $J=16.0$ Hz), 123.91 (d, $J=1.1$ Hz), 127.76 (d, $J=5.7$ Hz), 131.99 (d, $J=2.4$ Hz), 144.12, 161.95 ppm (d, $J=183.5$ Hz); FTIR (KBr): $\tilde{\nu}=2917$, 1507, 1220, 1154, 828, 807, 603, 500 cm^{-1}; MS (EI): m/z (%): 295 (22.06), 294 (100.00), 266 (16.49), 172 (24.19), 159 (13.72), 135 (69.54), 133 (26.65), 109 (16.96); HRMS (EI) calcd for $C_{20}H_{16}O_2$: 294.1220, found: 294.1220.

6d: Yield: 79%. $[\alpha]_D^{20}=+124.3$ (c 0.60, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.34$ (ddd, 2H, $J_1=17.4$ Hz, $J_2=4.8$ Hz, $J_3=2.4$ Hz), 2.64–2.74 (m, 2H), 4.15–4.18 (m, 2H), 5.75 (s, 2H), 7.39–7.42 (m, 2H), 7.47–7.53 (m, 6H), 7.79 (d, 2H, $J=8.1$ Hz), 7.87–7.90 (m, 2H), 8.20–8.23 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=36.96$, 51.87, 125.28, 125.67, 125.74, 125.93, 127.11, 128.35, 128.81, 132.44, 133.90, 136.29, 144.35 ppm; FTIR (KBr): $\tilde{\nu}=3041$, 2903, 2841, 1506, 1393, 843, 779, 651 cm^{-1}; MS (EI): m/z (%): 357 (40.80), 167 (54.10), 166 (42.44), 165 (54.15), 152 (21.92), 48 (14.38), 44 (100.00), 42 (25.53); elemental analysis calcd (%) for $C_{28}H_{22}$: C 93.81, H 6.19; found: C 93.96, H 6.09.

6e: Yield: 86%. $[\alpha]_D^{20}=+417.4$ (c 1.03, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.55$ (ddd, 2H, $J_1=17.7$ Hz, $J_2=5.7$ Hz, $J_3=2.7$ Hz), 3.03–3.14 (m, 2H), 4.23–4.26 (m, 2H), 6.18 (s, 2H), 7.42–7.50 (m, 4H), 7.69 (dd, 2H, $J_1=8.7$ Hz, $J_2=1.0$ Hz), 7.78–7.85 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=39.04$, 48.51, 124.77, 124.87, 125.29, 125.64, 126.12, 127.61, 127.89, 128.11, 132.60, 133.27, 133.61, 145.22; FTIR (KBr) 2834, 1503, 891, 857, 812, 751, 742, 472 cm^{-1}; MS (EI): m/z (%): 359 (24.69), 358 (100.00), 215 (16.18), 204 (23.86), 191 (15.45), 167 (65.30), 165 (28.23), 141 (17.61); elemental analysis calcd (%) for $C_{28}H_{22}$: C 93.81, H 6.19; found: C 94.02, H 6.03.

6f: Under nitrogen, a mixture of potassium benzyltrifluoroborates (106 mg, 0.5 mmol), [$PdCl_2$(dppf)] (18 mg, 9 mol%), ditriflate **7** (101 mg, 0.25 mmol), Cs_2CO_3 (489 mg, 1.5 mmol), THF (5 mL), and H_2O (0.5 mL) was heated to reflux. After stirring at reflux for 24 h, the reaction was quenched with saturated NH_4Cl. The mixture was extracted with ethyl ether, washed with brine. The organic layer was dried and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford chiral dienes **6f** as a colorless oil. Yield: 15%. $[\alpha]_D^{20}=+49.9$ (c 0.70, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=2.25$–2.31 (m, 2H), 2.43–2.48 (m, 2H), 3.19–3.29 (m, 4H), 3.47 (d, 2H, $J=15.3$ Hz), 5.15 (s, 2H), 7.16–7.30 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=35.93$, 36.01, 49.81, 123.33, 125.86, 128.23, 128.98, 140.00, 145.88 ppm; FTIR (KBr): $\tilde{\nu}=2918$, 2848, 1493, 1452, 838, 753, 701, 614 cm^{-1}; MS (EI): m/z (%): 286 (23.30), 195 (45.99), 167 (13.84), 129 (9.98), 117 (17.01), 115 (18.15), 91 (100.00), 65 (15.22); HRMS (EI) calcd for $C_{22}H_{22}$: 286.1722, found: 286.1735.

[RhCl((*S*,*S*)-**6a**)]$_2$: A mixture of [$RhCl(C_2H_4)_2$]$_2$ (23 mg, 0.059 mmol) and (*S*,*S*)-**6a** (20 mg, 0.078 mmol) in 5 mL of dioxane was stirred at 50°C for 4 h. The solvent was then evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered. Crystallization from CH_2Cl_2/petroleum ether gave the desired complex as red crystals (20 mg, 65%). m.p.: 110–113°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.80$–1.95 (m, 8H), 1.85 (d, $J=7.2$ Hz, 4H), 4.80 (s, 4H), 7.20–7.36 (m, 12H), 7.51–7.62 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=37.25$, 47.78, 93.81, 93.94, 126.78, 128.12, 128.30, 139.74 ppm. Crystallographic data for [RhCl((*S*,*S*)-**6a**)]$_2$ ($C_{40}H_{36}Cl_2Rh_2$): $T=293$ (2) K; wavelength: 0.71073 Å; crystal system: orthorhombic, space group: $P2_12_12_1$; unit cell dimensions: $a=9.9003$ (7) Å, $b=10.2094$ (7) Å, $c=35.051$ (3) Å, $\alpha=90°$, $\beta=90°$, $\gamma=90°$; $V=3542.8$ (4) Å^3; $Z=4$; $\rho_{calcd}=1.647$ Mg m^{-3}; F (000) $=1768$; final R indices [$I>2\sigma(I)$]: $R_1=0.0396$, $wR_2=0.0888$; R indices (all data), $R_1=0.0497$, $wR_2=0.0928$; 20970 reflections measured, 7603 were unique ($R_{(int)}=0.0614$). CCDC-682895 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The catalytic asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds: Under argon atmosphere, a solution of [$RhCl(C_2H_4)_2$]$_2$ (2.9 mg, 0.015 mmol of Rh), **6a** (4.3 mg, 0.0165 mmol), and arylboronic acid (0.60 mmol) in 1 mL of dioxane was stirred at room temperature for 15 min. To this mixture were added the α,β-unsaturated carbonyl compounds (0.30 mmol) and aqueous K_3PO_4 (0.1 mL, 1.5 M, 0.15 mmol). After being stirred at room temperature for 3 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product **11** (see the Supporting Information for characterization data).

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