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Highly Enantiomerically Enriched Planar Chiral Cyclopentadienyl(indenyl)ruthenium Complexes

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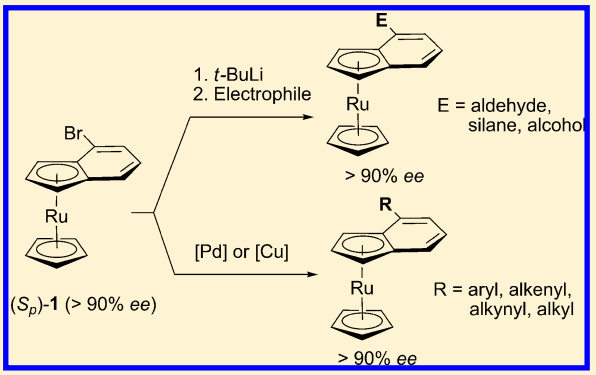
Supporting Information

ABSTRACT: The functionalization of highly enantiomerically enriched planar chiral cyclopentadienyl(4-bromoindenyl)ruthenium complexes is detailed. Lithium/bromine exchange followed by an electrophilic quench using *N*,*N*-dimethylformamide (DMF), trimethylsilyl chloride, benzaldehyde, acetone, or 1,2-diiodoethane afforded the corresponding enantiomerically enriched planar chiral complexes. Suzuki−Miyaura cross-coupling led to cyclopentadienyl(indenyl)ruthenium complexes bearing aryl and alkenyl groups in high yields. Similarly, in situ generation of the boronate intermediate using 9-MeO-9-BBN and a metalated species in the Suzuki−Miyaura reaction gave heteroaryl, alkynyl, and alkyl cyclopentadienyl(indenyl) ruthenium complexes with retention of configuration and enantiomeric excess.



INTRODUCTION

Planar chirality arising from the π coordination of a metal fragment on an enantiotopic face of an unsymmetrically substituted arene has found numerous applications in organic synthesis and catalysis.[1] The use of the planar chiral phosphine xyliphos in the key iridium-catalyzed hydrogenation step of the synthesis of metolachlor[2] and the kinetic resolution of secondary alcohols using Fu's planar chiral analogue of DMAP[3] are premier examples. The predominant routes of access to highly enantiomerically enriched planar chiral compounds rely on racemate resolution[4] or diastereoselective[5] or enantioselective[6] methods. In all of these methods, the use of a stoichiometric amount of a chiral auxiliary is required. Several research groups have focused on asymmetric catalysis to overcome this drawback.[7] A particularly attractive method was developed in our group for the desymmetrization of [Cr(CO)$_3$(η^6-5,8-dibromonaphthalene)] by means of a palladium/chiral phosphoramidite-catalyzed hydrogenolysis to access [Cr(CO)$_3$(η^6-5-bromonaphthalene)] in good yield and high enantiomeric purity.[8]

Replacement of the hydride source by various boronic acids led to the corresponding enantiomerically enriched naphthalenechromium complexes with an additional bromine atom for further functionalization[9] (Scheme 1, left). More recently, palladium-catalyzed hydrogenolysis was also applied to the isoelectronic cationic[10] [Ru(η^6-5,8-dibromonaphthalene)(η^5-C$_5$R$_5$)][PF$_6$] (R = H, Me) and neutral [Ru(η^5-4,7-dibromoindene)(η^5-C$_5$R$_5$)] (R = H, Me), affording the corresponding planar chiral complexes in high yield and enantiomeric excess (Scheme 1, middle and right).[11] These planar chiral scaffolds may find applications in synthesis and catalysis and material science because of their higher resistance to thermal or oxidative cleavage of the arene−metal bond in comparison to their chromium analogues.

With this efficient asymmetric synthesis of enantioenriched planar chiral metal−arene complexes in hand, the next step was to develop suitable procedures to construct valuable scaffolds of potential use in asymmetric catalysis or in the chemistry of new materials. Indeed, one can take advantage of the remaining bromide in the desymmetrized planar chiral complexes for further functionalization by metalation/electrophilic quench sequences or transition-metal-catalyzed coupling reactions. Functionalization of sensitive planar chiral naphthalene tricarbonylchromium complexes using these strategies has been previously reported,[12] and monodentate phosphine ligands derived from the neutral [Ru(η^5-Cp)(η^5-indene)] complexes were recently investigated.[13]

Herein, we report our efforts toward the functionalization of [Ru(η^5-4-bromoindene)(η^5-Cp)]complexes using lithiation/electrophile trapping reactions as well as palladium- and copper-catalyzed reactions. All experiments were first carried out and optimized with *rac*-**1**. Reactions were then repeated with enantioenriched (S_p)-**1**[14] with consistent yields and without erosion of enantiomeric excess.

RESULTS AND DISCUSSION

Metalation/Electrophilic Quench Procedure. Lithium/bromine exchange followed by an electrophilic quench was previously investigated for the synthesis of monodentate phosphines derived from compound (S_p)-**1**[13] with retention

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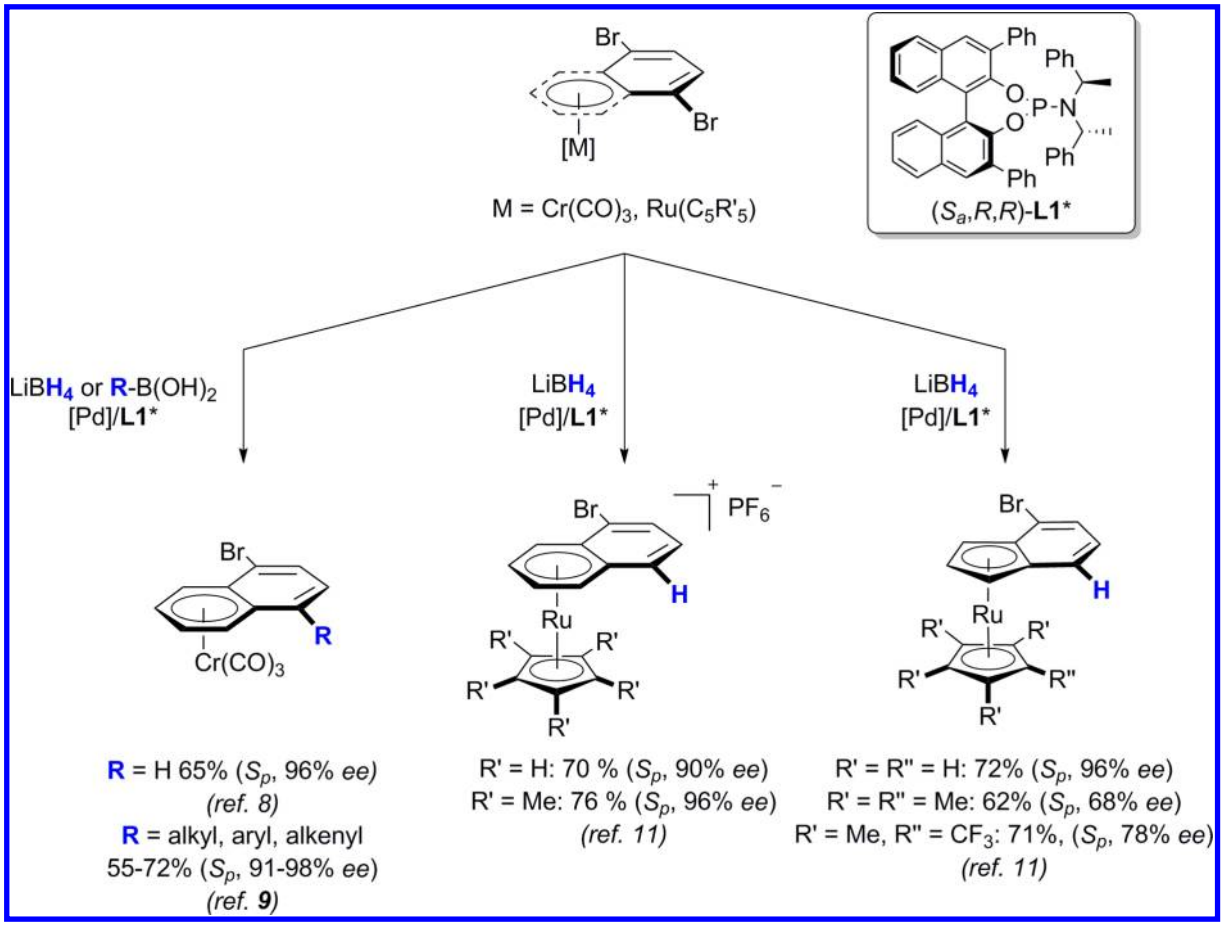
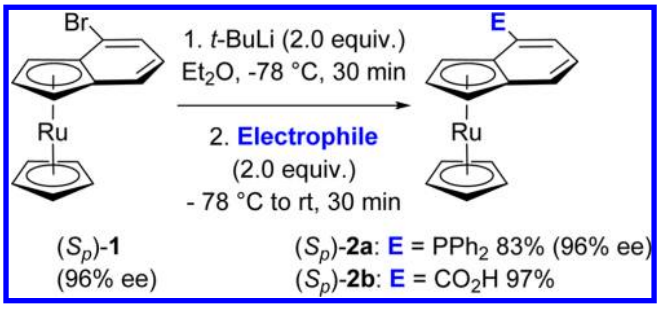
Scheme 1. Desymmetrization Strategy To Access Enantiomerically Enriched Planar Chiral Complexes



of stereochemistry and enantimeric purity and later applied to the synthesis of carboxylic acid (S_p)-**2b** (Scheme 2).[15]

Scheme 2. Initial Results of Lithiation/Electrophile Trapping Sequence



However, when different electrophiles such as DMF, benzaldehyde, and trimethylsilyl chloride were tested under these conditions, the results were disappointing and difficult to reproduce. Hence, a more robust protocol was sought and we turned our attention toward a noncoordinating solvent such as toluene in the presence of a diamine and an organolithium reagent. After optimization with DMF as the electrophile, it was found that complete conversion could be achieved along with a 91% product yield using 3 equiv of *t*-BuLi in toluene in the presence of a stoichiometric amount of TMEDA at −78 °C (Table 1, entry 1). This procedure proved to be also efficient for trimethylsilyl chloride and benzaldehyde, affording the desired products in high yields (Table 1, entries 2 and 3). In the latter case, the planar chiral complex (S_p)-**2e** was obtained as a 2.5:1 mixture of diastereomers. The tertiary alcohol (S_p)-**2f** and iodo derivative (S_p)-**2g** were also obtained with this procedure, albeit in moderate yields (Table 1, entries 4 and 5). In all cases, the air-stable planar chiral complexes (S_p)-**2c−g** were obtained with conservation of stereochemistry and enantiomeric excess.

The poor result obtained for (S_p)-**2g** prompted us to investigate an alternative strategy for the synthesis of this iodinated planar chiral complex (Scheme 3). A copper-catalyzed aromatic Finkelstein reaction procedure reported by Buchwald et al.[16] was successfully applied to substrate (S_p)-**1** that exhibits remarkable stability even under these relatively harsh conditions.

Palladium-Catalyzed Reactions. Suzuki−Miyaura cross-coupling conditions were previously developed for sensitive $Cr(CO)_3$ complexes[12] and cationic Ru(η^5-Cp) complexes.[13] Initial studies with phenylboronic acid revealed that the conditions previously developed for the chromium complexes ($Pd(dba)_2$, *t*-Bu_3P) were efficient at 100 °C, leading to complex (S_p)-**3a** in 92% yield. For practical reason, Organ's one-component catalyst[17] was subsequently chosen for probing the scope of this cross-coupling reaction. This set of conditions delivered high yields for phenyl-, 2-toluyl-, naphthyl-, and styrylboronic acids (Table 2, entries 1−3 and 5). The hindered substrate (S_p)-**3d** was obtained in moderate yield only (Table 2, entry 4). Here again, the transformations proceeded without erosion of the enantiomeric excess.

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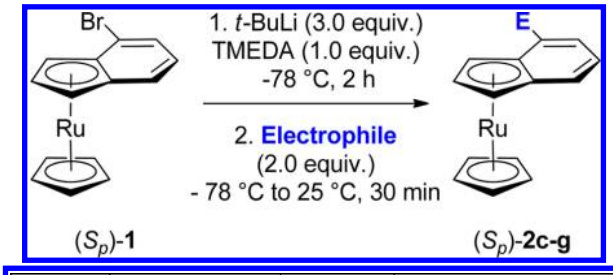
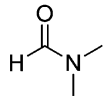
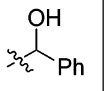
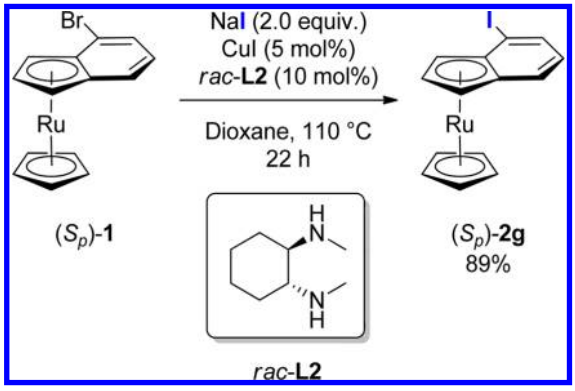
Table 1. Lithiation/Electrophile Trapping



Entry	Electrophile	E	Product (Yield)
1			*(Sp)*-**2c** (91%, 90% ee)[a]
2	TMS−Cl		*(Sp)*-**2d** (83%)
3			*(Sp)*-**2e**[b] (83%)
4			*(Sp)*-**2f** (55%)
5			*(Sp)*-**2g** (45%)

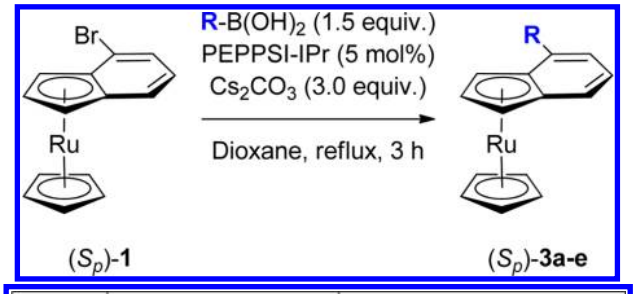
[a](Sp)-**1** (90% ee) afforded (Sp)-**2c** (90% ee). [b]Isolated as a 2.5:1 ratio of diastereomers.

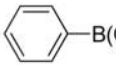
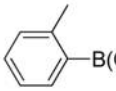
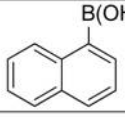
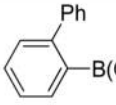
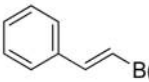
Scheme 3. Copper-Catalyzed Halogen Exchange



When the complex (Sp)-**1** was subjected to Sonogashira reaction conditions, the formation of a complex mixture was observed along with a difficult separation between (Sp)-**4a** and phenylacetylene dimer resulting from the Glaser oxidative coupling. We then turned our attention to the "9-MeO-9-BBN variant" of the Suzuki−Miyaura cross-coupling,[18] which had proved very useful for sensitive chromium complexes.[12] This modification allows broader substrate scope and particularly $S_p^2-S_p$ and $S_p^2-S_p^3$ C−C bond formation. The previously optimized conditions afforded a clean formation of alkyne (Sp)-**4a** in a 90% yield with retention of the enantiomeric excess

Table 2. Suzuki−Miyaura Cross-Coupling



Entry	R-B(OH)$_2$	Product (Yield)
1		*(Sp)*-**3a** (91%, 95% ee)[a]
2		*(Sp)*-**3b** (94%)
3		*(Sp)*-**3c** (93%)
4		*(Sp)*-**3d** (65%)
5		*(Sp)*-**3e** (97%)

[a](Sp)-**1** (95% ee) afforded (Sp)-**3a** (95% ee).

(Table 3, entry 1). Analogously, alkynes (Sp)-**4b−d** bearing silane, alkene, or ketals were isolated with the same efficiency (Table 3, entries 2−4). The versatility of this method permits coupling with simple methyllithium (Table 3, entry 5) as well as a wide range of lithiated species generated via heterocycle deprotonation (Table 3, entry 6) or lithium/bromine exchange (Table 3, entry 7). Finally, this procedure was compatible with sodium propynide (Table 3, entry 8). The silylethynylindenyl complex (Sp)-**4b** was readily desilylated to give the cyclopentadienyl(4-ethynylindenyl)ruthenium complex ((Sp)-**4i**).

As already observed in the [Cr(CO)$_3$] complexes,[12] all enantioenriched cyclopentadienyl(indenyl)ruthenium complexes products feature large optical rotation values. In particular, the carboxaldehyde complex (Sp)-**2c** had an $[\alpha]^{20}_D$ value of 3610° (*c* 0.1, $CHCl_3$).

CONCLUSION

The highly enantioenriched ruthenium complex (Sp)-**1** was recently synthesized via asymmetric palladium-catalyzed hydrogenolysis of the corresponding *meso*-dibromo complex. In this report, we demonstrate that this substrate constitutes a valuable building block to rapidly access a wide range of planar chiral complexes with retained enantiomeric excess through metalation/electrophile-trapping sequences and palladium-catalyzed cross-coupling reactions. These cyclopentadienyl(indenyl)ruthenium complexes are more robust toward temperature,

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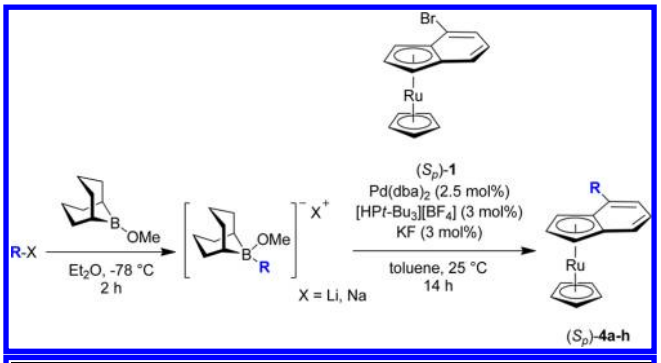
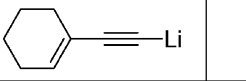
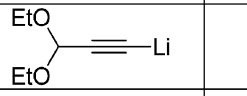
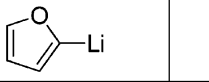
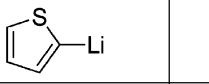
Table 3. "9-MeO-9-BBN Variant" of the Suzuki–Miyaura Cross-Coupling



Entry	R-X	Product (Yield)
1	Ph—≡—Li	(S_p)-**4a** (90%, 93% ee)[a]
2	TMS—≡—Li	(S_p)-**4b** (87%)
3		(S_p)-**4c** (71%)
4		(S_p)-**4d** (61%)
5	Me—Li	(S_p)-**4e** (71%)
6		(S_p)-**4f** (76%)
7		(S_p)-**4g** (58%)
8	—≡—Na	(S_p)-**4h** (85%)

(S_p)-**1** (93% ee) afforded (S_p)-**4b** (93% ee).

base, and air than their chromium analogues and thus represent a very attractive scaffold for the development of new chiral ligands or the chemistry of new materials.

EXPERIMENTAL SECTION

General Remarks. All reactions and manipulations were carried out under an inert atmosphere of nitrogen using an inert gas/vacuum double-manifold line and standard Schlenk techniques unless otherwise stated. Solvents were dried by passing through activated Al_2O_3 using a Solvtek purification system or by following standard procedures.[19] When required, the solvents were degassed by three successive freeze–thaw–pump cycles. Commercially available chemicals were used as received unless otherwise stated. [Pd_2(dba)$_3$][20] and [Ru(η^5-Cp)(η^5-4-bromoindene)] ((S_p)-**1**) were synthesized according to literature procedures.[11]

Flash column chromatography was performed using silica gel 60 (32–63 mesh) or neutral alumina (50–200 μm). Analytical thin-layer chromatography (TLC) was performed on precoated aluminum plates (silica gel 60 F_{254}). ^{1}H and ^{13}C NMR spectra were recorded on 500, 400, and 300 MHz Bruker Avance spectrometers in the solvent indicated. ^{1}H and ^{13}C NMR chemical shifts (δ) are quoted in ppm relative to $SiMe_4$ (residual $CHCl_3$, δ_H 7.26 ppm; $CDCl_3$, δ_C 77.05 ppm; residual $CHDCl_2$, δ_H 5.32 ppm; CD_2Cl_2, δ_C 53.9 ppm; residual C_6HD_5, δ_H 7.15 ppm; C_6D_6, δ_C 128.0 ppm). Coupling constants J are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer 1650 FT-IR spectrometer using diamond ATR Golden Gate sampling. Electron impact (EI) HRMS mass spectra were obtained using a Finnigan MAT 95 instrument operating at 70 eV. Electrospray ionization (ESI) HRMS analyses were measured on a VG Analytical 7070E instrument. Optical rotations were measured at 20 °C on a PerkinElmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (λ 589 nm). Melting points were measured in open capillary tubes on a Büchi 540 apparatus and are uncorrected.

Representative Procedure for the Lithiation/Electrophile Trapping Procedure. A solution of t-BuLi (166 μL, C = 1.6 M in pentane, 0.6 mmol, 3.0 equiv) was added to a 0.05 M solution of distilled tetramethylethylenediamine (30 μL,0.2 mmol, 1.0 equiv) in toluene at −78 °C. After 15 min, a 0.1 M solution of (S_p)-**1** (72 mg, 0.2 mmol, 1.0 equiv, 90% ee) in toluene was added and the resulting yellow mixture was stirred for 2 h at −78 °C. After addition of DMF (21 μL, 0.6 mmol, 3.0 equiv), the reaction mixture was stirred for 15 min more before being warmed to room temperature and quenched with aqueous HCl (1 M). The aqueous layer was separated and extracted with ether. The combined organic phases were dried with sodium sulfate and filtered, and the volatile materials were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel.

*[Ru(η^5-Cp)(η^5-4-(carboxaldehyde)indene)] ((S_p)-**2c**).* Purification by flash column chromatography (95/5 pentane/diethyl ether) on silica gel afforded (S_p)-**2c** as a yellow oil (56 mg, 91%, 90% ee). R_f = 0.3 (95/5 pentane/diethyl ether). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.98 (s, 1H), 7.82 (d, J = 8.6 Hz, 1H), 7.41 (d, J = 6.6 Hz, 1H), 6.93 (dd, J = 8.6, 6.6 Hz, 1H), 6.23–6.12 (m, 1H), 5.26 (dd, J = 2.5 Hz, J = 0.9 Hz, 1H), 4.76 (t, J = 2.5 Hz, 1H), 4.21 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 192.0, 136.9, 135.3, 134.7, 120.8, 91.0, 86.8, 75.0, 70.4, 67.2, 66.3. IR (thin film) 3097, 2924, 2803, 2720, 1668, 1600, 1521, 1453, 1391, 1334, 1309, 1099, 1061, 996, 808 cm^{-1}. $[\alpha]^{20}_D$ = +3610° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 19.6 min, t_{R2} = 22.2 min. HRMS (ESI): calcd for $C_{15}H_{13}ORu$ $[M + H]^+$ 311.0004, found 311.0005.

*[Ru(η^5-Cp)(η^5-4-(trimethylsilyl)indene)] ((S_p)-**2d**).* This compound was prepared according to the general procedure from (S_p)-**1** (32 mg, 0.09 mmol), TMEDA (13 μL, 0.09 mmol), t-BuLi (1.6 M, 167 μL, 0.27 mmol), and trimethylsilyl chloride (23 μL, 0.18 mmol). Purification by flash chromatography (pentane/diethyl ether, 90/10) gave (S_p)-**2d** as a yellow solid (26 mg, 83%). R_f = 0.3 (pentane). Mp: 79–80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, J = 8.7 Hz, 1H), 6.97 (dd, J = 6.3, 1.0 Hz, 1H), 6.77 (dd, J = 8.7, 6.3 Hz, 1H), 5.25 (d, J = 2.5 Hz, 1H), 5.21 (dd, J = 2.5, 1.0 Hz, 1H), 4.62 (t, J = 2.5 Hz, 1H), 4.18 (s, 5H), 0.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 138.2, 129.8, 128.2, 122.3, 95.1, 91.1, 72.8, 70.3, 67.1, 65.6. IR (thin film): 2956, 2924, 1405, 1330, 1145, 1099, 1043, 1028, 998, 919, 832, 801 cm^{-1}. $[\alpha]^{20}_D$ = +659° (c 0.1, $CHCl_3$). HRMS (EI): calcd for $C_{17}H_{20}RuSi$ $[M]^+$ 354.0372, found 354.0372.

*[Ru(η^5-Cp)(η^5-4-(phenylmethanol)indene)] ((S_p)-**2e**).* This compound was prepared according to the general procedure from (S_p)-**1** (72 mg, 0.2 mmol), TMEDA (30 μL, 0.2 mmol), t-BuLi (1.6 M, 177 μL, 0.6 mmol), and benzaldehyde (15 μL, 0.3 mmol). Purification by flash chromatography (pentane/diethyl ether, 95/5) gave (S_p)-**2e** as a yellow oil (64 mg, 83%). (S_p)-**2e** was isolated as a 2.5/1 mixture of unseparable diastereomers. R_f = 0.3 (major) and 0.25 (minor) (90/10 pentane/diethyl ether). Data for the major diastereomer are as follows. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, J = 6.9 Hz, 2H), 7.42–7.29 (m, 4H), 6.76 (dd, J = 8.6, 6.6 Hz, 1H), 6.66 (d, J = 6.6 Hz, 1H), 6.06 (d, J = 2.7 Hz, 1H), 5.35 (d, J = 2.5 Hz, 1H), 5.25 (dd, J = 2.5, 1.0 Hz, 1H), 4.61 (t, J = 2.5 Hz, 1H), 4.13 (s, 5H), 2.84 (d, J = 2.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 142.1, 140.7, 128.4, 127.7, 127.0, 126.7, 122.8, 120.2, 92.4, 89.4, 73.1, 70.3, 66.8, 64.8. Data for the minor diastereomer are as follows. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 7.4 Hz, 2H), 7.41–7.27 (m, 4H), 7.07 (d, J = 6.6 Hz, 1H),

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6.85 (dd, J = 8.6, 6.6 Hz, 1H), 5.92 (d, J = 3.9 Hz, 1H), 5.22 (dd, J = 2.5, 1.0 Hz, 1H), 5.13 (d, J = 2.5 Hz, 1H), 4.54 (t, J = 2.5 Hz, 1H), 4.02 (s, 5H), 2.80 (d, J = 3.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 143.3, 140.4, 128.4, 127.7, 126.7, 126.7, 122.9, 119.8, 92.5, 89.1, 73.1, 70.1, 66.3, 64.7. IR (thin film): 3342, 2922, 2851, 1718, 1648, 1603, 1492, 1452, 1334, 1187, 1098, 1063, 1026, 997, 953 cm^{-1}. $[\alpha]^{20}_D$ = +512° (c 0.1, $CHCl_3$). HRMS (EI): calcd for $C_{21}H_{18}O^{104}Ru$ $[M]^+$ 390.0405, found 390.0406.

*[Ru(η^5-Cp)(η^5-4-(2-propan-2-ol)indene)] ((S_p)-**2f**).* This compound was prepared according to the general procedure from (S_p)-**1** (32 mg, 0.09 mmol), TMEDA (13 μL, 0.09 mmol), *t*-BuLi (1.6 M, 167 μL, 0.27 mmol), and acetone (23 μL, 0.18 mmol). Purification by flash chromatography (pentane/diethyl ether, 90/10) gave (S_p)-**2f** as a yellow oil (26 mg, 55%). R_f = 0.3 (pentane). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.30 (d, J = 8.6 Hz, 1H), 6.86 (dd, J = 6.8, 0.9 Hz, 1H), 6.79 (dd, J = 8.5, 6.8 Hz, 1H), 5.49 (dd, J = 2.5, 1.0 Hz, 1H), 5.27 (dd, J = 2.5, 1.0 Hz, 1H), 4.67 (t, J = 2.5 Hz, 1H), 4.21 (s, 5H), 2.62 (s, 1H), 1.72 (d, J = 3.1 Hz, 6H). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 145.9, 126.1, 123.1, 117.9, 93.3, 89.2, 73.8, 73.4, 70.6, 67.6, 66.3, 60.7, 30.6, 30.6. IR (thin film): 3402, 2970, 2929, 1460, 1363, 1260, 1099, 807 cm^{-1}. $[\alpha]^{20}_D$ = +430° (c 0.1, $CHCl_3$). HRMS (EI): calcd for $C_{17}H_{18}ORu$ $[M]^+$ 340.0398, found 340.0396.

[Ru(η^5-Cp)(η^5-4-iodoindene)] ((S_p)-2g): Copper-Catalyzed Aromatic Finkelstein Reaction Procedure. A Schlenk tube was charged with (S_p)-**1** (100 mg, 0.28 mmol), CuI (3 mg, 0.014 mmol, 5.0 mol %), and NaI (100 mg, 0.56 mmol, 2.0 equiv), briefly evacuated and back-filled with nitrogen. Racemic *trans-N,N′*-dimethyl-1,2-cyclohexanediamine (5 μL, 0.03 mmol, 10 mol %) and dioxane (1 mL) were added under nitrogen. The Schlenk tube was sealed with a Teflon valve, and the reaction mixture was stirred at 110 °C for 24 h. The resulting suspension was warmed to reach room temperature, diluted with 30% aqueous ammonia (2 mL), poured into water (8 mL), and extracted with dichloromethane (3 × 5 mL). The combined organic phases were dried with sodium sulfate, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (pentane) to provide (S_p)-**2g** as a yellow solid (100 mg, 89%). R_f = 0.3 (pentane). Mp: 59−60 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, J = 8.6 Hz, 1H), 7.23 (d, J = 6.8 Hz, 1H), 6.47 (dd, J = 8.6, 6.8 Hz, 1H), 5.42 (dd, J = 2.5, 1.0 Hz, 1H), 5.25 (d, J = 2.5 Hz, 1H), 4.63 (t, J = 2.5 Hz, 1H), 4.27 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 132.0, 127.0, 123.2, 96.3, 95.7, 92.7, 72.9, 70.4, 70.0, 67.5. IR (thin film): 3087, 2923, 2852, 1771, 1494, 1464, 1434, 1404, 1376, 1327, 1298, 1121, 1098, 1030, 997, 886, 845, 809 cm^{-1}. $[\alpha]^{20}_D$ = +874° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralcel OD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 12.6 min, t_{R2} = 13.5 min. HRMS (EI): calcd for $C_{14}H_{11}IRu$ $[M]^+$ 407.8951, found 407.8944.

Representative Procedure for the Suzuki−Miyaura Cross-Coupling Procedure. (S_p)-**1** (36 mg, 0.1 mmol, 1.0 equiv, 95% ee), phenylboronic acid (18 mg, 0.15 mmol, 1.5 equiv), cesium carbonate (98 mg, 0.3 mmol, 3.0 equiv), and PEPPSI-IPr catalyst (4 mg, 0.005 mmol, 5 mol %) were placed in a Schlenk and evacuated three times before adding dioxane (0.5 mL). The resulting mixture was then stirred and refluxed for 3 h. The crude mixture was then passed through a short pad of silica, flushed with diethyl ether, and concentrated. The residue was purified by flash column chromatography on silica gel.

*[Ru(η^5-Cp)(η^5-4-phenylindene)] ((S_p)-**3a**).* Purification by flash chromatography on silica gel (pentane) afforded (S_p)-**3a** as a yellow oil (56 mg, 91%, 95% ee). The enantiomeric purity of the product was confirmed by HPLC analysis on a chiral stationary phase. R_f = 0.1 (pentane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82−7.78 (m, 2H), 7.49−7.43 (m, 2H), 7.41−7.35 (m, 2H), 6.91−6.86 (m, 2H), 5.32−5.29 (m, 2H), 4.66 (t, J = 2.5 Hz, 1H), 4.27 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 141.1, 139.7, 128.6, 128.2, 127.5, 126.0, 123.4, 122.1, 92.8, 90.5, 73.4, 70.3, 66.6, 66.2. IR (thin film): 3055, 2924, 1599, 1475, 1450, 1407, 1332, 1262, 1098, 1036, 996, 807, 729, 699 cm^{-1}. $[\alpha]^{20}_D$ = +1038° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 9.6 min, t_{R2} = 10.5 min. HRMS (EI): calcd for $C_{20}H_{16}Ru$ $[M]^+$ 358.0293, found 358.0290.

*[Ru(η^5-Cp)(η^5-4-(2-toluyl)indene)] ((S_p)-**3b**).* This compound was prepared according to the general procedure from (S_p)-**1** (36 mg, 0.1 mmol), *o*-tolylboronic acid (20 mg, 0.15 mmol), Cs_2CO_3 (98 mg, 0.3 mmol), and PEPPSI-IPr catalyst (4 mg, 0.005 mmol). Purification by flash chromatography (pentane) gave (S_p)-**3b** as a yellow oil (35 mg, 94%). R_f = 0.1 (pentane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50−7.40 (m, 1H), 7.38 (d, J = 8.6 Hz, 1H), 7.35−7.24 (m, 3H), 6.86 (dd, J = 8.6, 6.6 Hz, 1H), 6.68 (d, J = 6.6 Hz, 1H), 5.30 (dd, J = 2.5, 1.0 Hz, 1H), 4.92−4.84 (br s, 1H), 4.59 (t, J = 2.5 Hz, 1H), 4.23 (s, 5H), 2.31−2.21 (br s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 141.1, 136.2, 130.4, 129.8, 127.4, 125.7, 125.5, 122.8, 122.7, 92.3, 72.9, 70.1, 66.1, 66.0, 20.2. IR (thin film): 3054, 2922, 1600, 1475, 1334, 1262, 1098, 1034, 996, 804, 754, 730 cm^{-1}. $[\alpha]^{20}_D$ = +443° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralcel OD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1}, 10.3 min, t_{R2} = 12.2 min. HRMS (EI): calcd for $C_{21}H_{18}Ru$ $[M]^+$ 372.0446, found 372.0447.

*[Ru(η^5-Cp)(η^5-4-(1-naphthyl)indene)] ((S_p)-**3c**).* This compound was prepared according to the general procedure from (S_p)-**1** (72 mg, 0.2 mmol), 2-naphthylboronic acid (52 mg, 0.3 mmol), Cs_2CO_3 (196 mg, 0.6 mmol), and PEPPSI-IPr catalyst (8 mg, 0.01 mmol). Purification by flash chromatography (pentane) gave (S_p)-**3c** as a yellow solid (76 mg, 93%). (S_p)-**3c** was isolated as a mixture of two rotamers in a 1.4/1 ratio at 20 °C. R_f = 0.1 (pentane). Mp: 133−134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, J = 8.3 Hz, 1H), 7.97−7.86 (m, 4.8H), 7.80 (d, J = 8.5 Hz, 1.4H), 7.74 (d, J = 7.0 Hz, 1H), 7.62−7.44 (m, 9.6H), 7.41−7.34 (m, 1.4H), 6.98−6.91 (m, 2.4H), 6.89 (d, J = 6.3 Hz, 2.4H), 5.36−5.32 (m, 2.4H), 4.95 (d, J = 2.5 Hz, 1H), 4.80 (d, J = 2.5 Hz, 1.4H), 4.60 (t, J = 2.5 Hz, 1H), 4.56 (t, J = 2.5 Hz, 1.4H), 4.26 (s, 7H), 4.19 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 138.7, 138.4, 134.1, 133.9, 132.2, 132.0, 128.3, 128.3, 127.9, 127.5, 127.2, 126.6, 126.6, 126.3, 126.2, 126.0, 125.9, 125.8, 125.7, 125.5, 125.3, 124.0, 123.9, 123.0, 122.4, 94.7, 93.3, 92.6, 92.4, 73.0, 72.8, 70.2, 70.1, 66.4, 66.2, 66.0, 65.9. IR (thin film): 3045, 2925, 1590, 1505, 1335, 1262, 1099, 1023, 997, 801, 777 cm^{-1}. $[\alpha]^{20}_D$ = +465° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralcel OD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 10.3 min, t_{R2} = 12.2 min. HRMS (EI): calcd for $C_{24}H_{18}Ru$ $[M]^+$ 408.0447, found 408.0447.

*[Ru(η^5-Cp)(η^5-4-(2-biphenyl)indene)] ((S_p)-**3d**).* This compound was prepared according to the general procedure from (S_p)-**1** (36 mg, 0.1 mmol), 2-biphenylboronic acid (20 mg, 0.15 mmol), Cs_2CO_3 (98 mg, 0.3 mmol), and PEPPSI-IPr catalyst (4 mg, 0.005 mmol). Purification by flash chromatography (pentane) gave (S_p)-**3d** as a yellow solid (28 mg, 65%). R_f = 0.1 (pentane). Mp: 110−111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83−7.74 (br s), 7.53−7.44 (m, 3H), 7.26 (d, J = 8.6 Hz, 1H), 7.26−7.08 (m, 5H), 6.66 (dd, J = 8.6, 6.6 Hz, 1H), 6.48 (d, J = 6.6 Hz, 1H), 5.23−5.18 (br s, 1H), 5.00−4.88 (br s, 1H), 4.55−4.47 (br s, 1H), 4.23 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 141.7, 141.0, 139.1, 130.8, 130.5, 129.4, 127.9, 127.8, 127.5, 126.6, 125.5, 124.6,122.8, 92.2, 72.8, 70.1, 66.2, 65.9. IR (thin film): 3054, 2929, 1471, 1335, 1099, 1035, 997, 909, 756, 730 cm^{-1}. $[\alpha]^{20}_D$ = +1052° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralcel OD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 11.4 min, t_{R2} = 12.6 min. HRMS (EI): calcd for $C_{26}H_{20}Ru$ $[M]^+$ 434.0603, found 434.0603.

*[Ru(η^5-Cp)(η^5-4-(2-styryl)indene)] ((S_p)-**3e**).* This compound was prepared according to the general procedure from (S_p)-**1** (72 mg, 0.2 mmol), *trans*-2-phenylvinylboronic acid (45 mg, 0.3 mmol), Cs_2CO_3 (196 mg, 0.6 mmol), and PEPPSI-IPr catalyst (8 mg, 0.01 mmol). Purification by flash chromatography (pentane) gave (S_p)-**3e** as a yellow solid (76 mg, 93%). R_f = 0.1 (pentane). Mp: 98−99 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60−7.55 (d, J = 7.3 Hz, 2H), 7.43−7.37 (m, 2H), 7.35−7.25 (m, 4H), 7.01 (d, J = 6.8 Hz, 1H), 6.83 (dd, J = 8.6, 6.8 Hz, 1H), 5.52 (d, J = 2.5 Hz, 1H), 5.28 (dd, J = 2.5, 1.0 Hz, 1H), 4.68 (t, J = 2.5 Hz, 1H), 4.24 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 141.7, 141.0, 139.1, 130.8, 130.5, 129.4, 127.9, 127.8, 127.5, 126.6, 125.5, 124.6, 122.8, 92.2, 72.8, 70.1, 66.2, 65.9. IR (thin film): 3045, 2925, 1590, 1505, 1335, 1262, 1099, 1023, 997, 801, 777 cm^{-1}.

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$[\alpha]^{20}_D$ = +932° (*c* 0.025, $CHCl_3$). HRMS (EI): calcd for $C_{22}H_{18}Ru$ $[M]^+$ 384.0444, found 384.0447.

Representative Procedure for the "9-MeO-9-BBN Variant" of the Suzuki–Miyaura Cross-Coupling Procedure. A 0.4 M solution of phenylacetylene (44 μL, 0.4 mmol, 2.0 equiv) in diethyl ether was treated with *n*-BuLi (250 μL, *C* = 1.6 M in hexanes, 0.4 mmol, 2.0 equiv) at −78 °C for 30 min. 9-MeO-9-BBN (0.4 mL, *C* = 1.0 M in hexanes, 0.4 mmol, 2.0 equiv) was added dropwise at −78 °C, and the resulting solution was stirred at −78 °C for 2 h. In a separate Schlenk tube, (S_p)-**1** (72 mg, 0.2 mmol, 1.0 equiv, 93% ee) was added to a solution of $Pd(dba)_2$ (3 mg, 0.005 mmol, 2.5 mol %), [HP-*t*-Bu_3][BF_4] (2 mg, 0.006 mmol, 3 mol %), and KF (0.3 mg, 0.006 mmol, 3 mol %) in toluene (0.1 M). The boronate solution was then added by cannula to the latter solution, and the resulting mixture was stirred for 14 h at room temperature. The crude mixture was then passed through a short pad of silica, flushed with diethyl ether, and concentrated. The residue was purified by flash column chromatography on silica gel.

*[Ru(η⁵-Cp)(η⁵-4-(2-phenylethynyl)indene)] ((S_p)-**4a**).* Purification by flash chromatography on silica gel (pentane) afforded (S_p)-**4a** as a yellow oil (68 mg, 90%, 93% ee). R_f = 0.2 (pentane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.41−7.31 (m, 3H), 7.06 (d, *J* = 6.7 Hz, 1H), 6.78 (dd, *J* = 8.7, 6.7 Hz, 1H), 5.51 (d, *J* = 2.5 Hz, 1H), 5.26 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.66 (t, *J* = 2.5 Hz, 1H), 4.26 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 131.8, 128.5, 128.3, 128.2, 127.1, 123.8, 122.3, 120.8, 93.2, 92.9, 91.6, 88.0, 73.0, 70.3, 66.6, 65.8. IR (thin film): 3079, 3054, 2957, 2920, 2851, 2202, 1597, 1489, 1334, 1098, 1024, 998, 753, 719, 688 cm^{-1}. $[\alpha]^{20}_D$ = +1736° (*c* 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 11.9 min, t_{R2} = 13.0 min. HRMS (EI): calcd for $C_{22}H_{16}Ru$ $[M]^+$ 382.0295, found 382.0300.

*[Ru(η⁵-Cp)(η⁵-4-(2-trimethylsilylethynyl)indene)] ((S_p)-**4b**).* This compound was prepared according to the general procedure from (S_p)-**1** (72 mg, 0.2 mmol), *n*-BuLi (250 μL, 0.4 mmol), trimethylsilylacetylene (57 μL, 0.4 mmol), 9-MeO-9-BBN (1.0 M, 0.4 mL, 0.4 mmol), $Pd(dba)_2$ (3 mg, 0.005 mmol), [HP-*t*-Bu_3][BF_4] (2 mg, 0.006 mmol), and KF (0.3 mg, 0.006 mmol). Purification by flash chromatography (pentane) gave (S_p)-**4b** as a yellow oil (66 mg, 87%). R_f = 0.2 (pentane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 6.7 Hz, 1H), 6.72 (dd, *J* = 8.7, 6.7 Hz, 1H), 5.42 (d, *J* = 2.5 Hz, 1H), 5.23 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.63 (t, *J* = 2.5 Hz, 1H), 4.24 (s, 5H), 0.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 128.5, 127.5, 122.2, 120.8, 103.5, 98.3, 93.0, 91.5, 73.1, 70.3, 66.7, 65.9. IR (thin film): 3096, 2958, 2920, 2143, 1594, 1478, 1336, 1098, 1023, 986, 839, 801, 720, 699 cm^{-1}. $[\alpha]^{20}_D$ = +1711° (*c* 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 19.6 min, t_{R2} = 22.2 min. HRMS (EI): calcd for $C_{19}H_{20}RuSi$ $[M]^+$ 378.0376, found 378.0372.

*[Ru(η⁵-Cp)(η⁵-4-(2-cyclohexen-1-ylethynyl)indene)] ((S_p)-**4c**).* This compound was prepared according to the general procedure from (S_p)-**1** (72 mg, 0.2 mmol), *n*-BuLi (250 μL, 0.4 mmol), 1-ethynylcyclohexene (47 μL, 0.4 mmol), 9-MeO-9-BBN (*C* = 1.0 M, 0.4 mL, 0.4 mmol), $Pd(dba)_2$ (3 mg, 0.005 mmol), [HP-*t*-Bu_3][BF_4] (2 mg, 0.006 mmol), and KF (0.3 mg, 0.006 mmol). Purification by flash chromatography (pentane) gave (S_p)-**4c** as a yellow solid (55 mg, 71%). R_f = 0.1 (pentane). Mp: 96−97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (d, *J* = 8.6 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 1H), 6.73 (dd, *J* = 8.6, 6.6 Hz, 1H), 6.29−6.25 (m, 1H), 5.41 (d, *J* = 2.5 Hz, 1H), 5.22 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.62 (t, *J* = 2.5 Hz, 1H), 4.24 (s, 5H), 2.34−2.28 (m, 2H), 2.22−2.16 (m, 2H), 1.76−1.69 (m, 2H), 1.69−1.62 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 135.1, 127.4, 126.4, 122.4, 121.4, 121.2, 95.3, 93.0, 91.6, 85.3, 72.8, 70.2, 66.5, 65.8. IR (thin film): 3092, 2931, 2858, 2184, 1657, 1521, 1434, 1337, 1238, 1099, 1034, 998,805, 721 cm^{-1}. $[\alpha]^{20}_D$ = + 1231 (*c* 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 10.4 min, t_{R2} = 10.7 min. HRMS (EI): calcd for $C_{22}H_{20}Ru$ $[M]^+$ 386.0607, found 386.0603.

*[Ru(η⁵-Cp)(η⁵-4-(3,3-diethoxypropyn-1-yl)indene)] ((S_p)-**4d**).* This compound was prepared according to the general procedure from (S_p)-**1** (72 mg, 0.2 mmol), *n*-BuLi (250 μL, 0.4 mmol), 1-propiolaldehyde diethyl acetal (57 μL, 0.4 mmol), 9-MeO-9-BBN (*C* = 1.0 M, 0.4 mL, 0.4 mmol), $Pd(dba)_2$ (3 mg, 0.005 mmol), [HP-*t*-Bu_3][BF_4] (2 mg, 0.006 mmol), and KF (0.3 mg, 0.006 mmol). Purification by flash chromatography (pentane/diethyl ether, 96/4) gave (S_p)-**4d** as a yellow oil (55 mg, 61%). R_f = 0.3 (pentane/diethyl ether, 96/4). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 6.8 Hz, 1H), 6.78 (dd, *J* = 8.6, 6.8 Hz, 1H), 5.58 (s, 1H), 5.42 (d, *J* = 2.5 Hz, 1H), 5.23 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.63 (t, *J* = 2.5 Hz, 1H), 4.23 (s, 5H), 3.90 (qdd, *J* = 9.6, 7.0, 1.3 Hz, 2H), 3.72 (qdd, *J* = 9.4, 7.0, 1.3 Hz, 2H), 1.32 (t, *J* = 7.0 Hz, 3H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 128.8, 128.0, 122.0, 119.4, 92.7, 92.2, 91.4, 87.9, 83.8, 73.1, 70.2, 66.6, 65.7, 61.1, 61.0, 15.4. IR (thin film): 3096, 2974, 2929, 2880, 2222, 1353, 1330, 1233, 1099, 1048, 998,803, 773, 720 cm^{-1}. $[\alpha]^{20}_D$ = +2256° (*c* 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 13.7 min, t_{R2} = 17.6 min. HRMS (EI): calcd for $C_{21}H_{22}O_2Ru$ $[M]^+$ 408.0662, found 408.0658.

*[Ru(η⁵-Cp)(η⁵-4-methylindene)] ((S_p)-**4e**).* To a 0.4 M solution of methyllithium (*C* = 1.6 M in diethyl ether, 250 μL, 0.4 mmol) in diethyl ether was added dropwise at −78 °C 9-MeO-9-BBN (*C* = 1.0 M in hexanes, 0.4 mL, 0.4 mmol), and the resulting solution was stirred at −78 °C for 2 h. In a separate Schlenk tube, (S_p)-**1** (72 mg, 0.2 mmol) was added to a solution of $Pd(dba)_2$ (3 mg, 0.005 mmol), [HP-*t*-Bu_3][BF_4] (2 mg, 0.006 mmol), and KF (0.3 mg, 0.006 mmol) in toluene (0.1 M). The boronate solution was then added by cannula to the latter solution, and the resulting mixture was stirred overnight at room temperature. The crude mixture was then passed through a short pad of silica and flushed with diethyl ether. Flash chromatography on silica gel (pentane) afforded (S_p)-**4e** as a yellow oil (42 mg, 71%). R_f = 0.1 (pentane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 6.4 Hz, 1H), 6.57 (dt, *J* = 6.4, 1.0 Hz, 1H), 5.24 (dd, *J* = 2.5, 1.0 Hz, 1H), 5.26 (d, *J* = 2.5 Hz, 1H), 4.58 (t, *J* = 2.5 Hz, 1H), 4.19 (s, 5H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 136.3, 123.7, 123.3, 120.9, 93.0, 92.8, 72.3, 69.8, 66.3, 64.1, 18.9. IR (thin film): 3084, 2962, 2850, 2233, 1611, 1538, 1458, 1406, 1376, 1340, 1259, 1098, 1025, 996, 758, 723 cm^{-1}. $[\alpha]^{20}_D$ = +417° (*c* 0.1, $CHCl_3$). HPLC (Daicel Chiralcel OD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 13.7 min, t_{R2} = 15.9 min. HRMS (EI): calcd for $C_{15}H_{14}Ru$ $[M]^+$ 296.0137, found 296.0134.

*[Ru(η⁵-Cp)(η⁵-4-(2-furyl)indene)] ((S_p)-**4f**).* A 0.4 M solution of furan (38 μL, 0.4 mmol) in diethyl ether was treated with *t*-BuLi (*C* = 1.6 M in pentane, 230 μL, 0.4 mmol) at −78 °C for 90 min. 9-MeO-9-BBN (*C* = 1.0 M in hexanes, 0.4 mL, 0.4 mmol) was added dropwise at −78 °C, and the resulting solution was stirred at −78 °C for 2 h. In a separate Schlenk tube, (S_p)-**1** (72 mg, 0.2 mmol) was added to a solution of $Pd(dba)_2$ (3 mg, 0.005 mmol), [HP-*t*-Bu_3][BF_4] (2 mg, 0.006 mmol), and KF (0.3 mg, 0.006 mmol) in toluene (0.1 M). The boronate solution was then added by cannula to the latter solution, and the resulting mixture was stirred overnight at room temperature. The crude mixture was then passed through a short pad of silica and flushed with diethyl ether. Flash chromatography on silica gel (pentane) afforded (S_p)-**4f** as a yellow oil (53 mg, 76%). R_f = 0.1 (pentane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 6.86 (dd, *J* = 8.5, 7.0 Hz, 1H), 6.79 (d, *J* = 3.1 Hz, 1H), 6.55 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.62 (d, *J* = 2.5 Hz, 1H), 5.28 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.68 (t, *J* = 2.5 Hz, 1H), 4.21 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 153.5, 141.9, 128.6, 126.4, 122.7, 119.0, 111.7, 107.0, 92.9, 87.9, 73.3, 70.2, 66.4, 66.1. IR (thin film): 3096, 2925, 1527, 1494, 1472, 1407, 1261, 1214, 1099, 1016, 936, 884, 770, 722 cm^{-1}. $[\alpha]^{20}_D$ = +1370° (*c* 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 12.0 min, t_{R2} = 12.3 min. HRMS (EI): calcd for $C_{18}H_{14}RuO$ $[M]^+$ 348.0090, found 348.0083.

*[Ru(η⁵-Cp)(η⁵-4-(2-thiophenyl)indene)] ((S_p)-**4g**).* A 0.4 M solution of 2-bromothiophene (38 μL, 0.4 mmol) in diethyl ether was treated with *n*-BuLi (*C* = 1.6 M in hexanes, 250 μL, 0.4 mmol) at 0 °C for 90 min. 9-MeO-9-BBN (*C* = 1.0 M in hexanes, 0.4 mL, 0.4 mmol) was added dropwise at −78 °C, and the resulting solution was stirred at −78 °C for 2 h. In a separate Schlenk tube, (S_p)-**1** (72 mg, 0.2 mmol)

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was added to a solution of $Pd(dba)_2$ (3 mg, 0.005 mmol), [HP-*t*-Bu_3][BF_4] (2 mg, 0.006 mmol), and KF (0.3 mg, 0.006 mmol) in toluene (0.1 M). The boronate solution was then added by cannula to the latter solution, and the resulting mixture was stirred overnight at room temperature. The crude mixture was then passed through a short pad of silica and flushed with diethyl ether. Flash chromatography on silica gel (pentane) afforded (S_p)-**4g** as a yellow solid (42 mg, 58%). R_f = 0.2 (pentane). Mp: 73−74 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (dd, J = 3.6, 1.2 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.34 (dd, J = 5.1, 1.2 Hz, 1H), 7.15 (dd, J = 5.1, 3.6 Hz, 1H), 7.01 (d, J = 6.8 Hz, 1H), 6.84 (dd, J = 8.6, 6.8 Hz, 1H), 5.57 (d, J = 2.5 Hz, 1H), 5.30 (dd, J = 2.5, 1.0 Hz, 1H), 4.67 (t, J = 2.5 Hz, 1H), 4.27 (s, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 143.1, 132.8, 127.5, 126.3, 124.7, 124.6, 123.0, 121.8, 93.0, 89.5, 73.4, 70.3, 66.8, 66.3. IR (thin film): 3097, 2921, 2851, 2880, 1599, 1427, 1406, 1330, 1098, 1027, 997,805, 770, 722, 694 cm^{-1}. $[\alpha]^{20}_D$ = +1065° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 12.6 min, t_{R2} = 13.2 min. HRMS (EI): calcd for $C_{18}H_{14}RuS$ [M]$^+$ 363.9857, found 363.9854.

*[Ru(η^5-Cp)(η^5-4-(propyn-1-yl)indene)] ((S_p)-**4h**).* A 0.4 M solution of sodium propynide (26 mg, 0.4 mmol) in diethyl ether was treated with 9-MeO-9-BBN (C = 1.0 M in hexanes, 0.4 mL, 0.4 mmol) dropwise at −78 °C, and the resulting solution was stirred at −78 °C for 2 h. In a separate Schlenk tube, (S_p)-**1** (36 mg, 0.1 mmol), was added to a solution of $Pd(dba)_2$ (1.5 mg, 0.0025 mmol), [HP-*t*-Bu_3][BF_4] (1 mg, 0.003 mmol), and KF (0.15 mg, 0.003 mmol) in toluene (0.1 M). The boronate solution was then added by cannula to the latter solution, and the resulting mixture was stirred overnight at room temperature. The crude mixture was then passed through a short pad of silica and flushed with diethyl ether. Flash chromatography on silica gel (pentane) afforded (S_p)-**4h** as a yellow solid (27 mg, 85%). A 75% yield was obtained with 2.0 equiv of propynylsodium and 9-MeO-9-BBN. R_f = 0.1 (pentane). Mp: 136−137 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, J = 8.7 Hz, 1H), 6.90 (d, J = 6.7 Hz, 1H), 6.71 (dd, J = 8.7, 6.7 Hz, 1H), 5.40 (d, J = 2.5 Hz, 1H), 5.22 (dd, J = 2.5, 1.0 Hz, 1H), 4.61 (t, J = 2.5 Hz, 1H), 4.24 (s, 5H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 127.1, 127.0, 122.4, 121.7, 93.3, 91.6, 89.5, 78.0, 72.8, 70.2, 66.4, 65.8, 5.0. IR (thin film): 2921, 2852, 1726, 1460, 1409, 1336, 1260, 1098, 1075, 1017, 801, 767 cm^{-1}. $[\alpha]^{20}_D$ = +1543° (c 0.1, $CHCl_3$). HPLC (Daicel Chiralpak AD-H, hexane/isopropyl alcohol 99/1, 0.5 mL min^{-1}, λ 254 nm): t_{R1} = 8.8 min, t_{R2} = 9.0 min. HRMS (EI): calcd for $C_{17}H_{14}Ru$ [M] 320.0134, found 320.0133.

*[Ru(η^5-Cp)(η^5-4-ethynylindene)] ((S_p)-**4i**).* To a 0.05 M solution of (S_p)-**4b** (180 mg, 0.48 mmol) in methanol (10 mL) was added K_2CO_3 (20 mg, 0.14 mmol, 30 mol %), and the resulting mixture was stirred at room temperature overnight. Dichloromethane and water were added to the reaction mixture. The separated aqueous phase was extracted twice with dichloromethane. The combined organic layers were washed with water and brine and dried over sodium sulfate. Removal of the volatile materials afforded pure (S_p)-**4i** (144 mg, 99%) as a yellow oil. R_f = 0.2 (pentane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, J = 8.7 Hz, 1H), 7.05 (d, J = 6.6 Hz, 1H), 6.74 (dd, J = 8.7, 6.6 Hz, 1H), 5.44 (d, J = 2.5 Hz, 1H), 5.24 (dd, J = 2.5, 1.0 Hz, 1H), 4.64 (t, J = 2.5 Hz, 1H), 4.25 (s, 5H), 3.34 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 128.8, 128.2, 122.0, 119.6, 92.8, 91.4, 82.2, 80.6, 73.1, 70.2, 66.6, 65.7. IR (thin film): 3284, 3092, 2961, 2962, 2922, 2852, 1715, 1653, 1407, 1336, 1260, 1098, 1023, 803, 778, 723 cm^{-1}. $[\alpha]^{20}_D$ = +1205° (c 0.1, $CHCl_3$). HRMS (EI): calcd for $C_{16}H_{12}Ru$ [M]$^+$ 305.9979, found 305.9978.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra for all new compounds and HPLC traces for three representative examples (**2c**, **3a**, **4a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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