

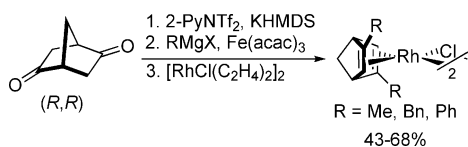
Expanding the C_2 -Symmetric Bicyclo[2.2.1]hepta-2,5-diene Ligand Family: Concise Synthesis and Catalytic Activity in Rhodium-Catalyzed Asymmetric Addition

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New C_2 -symmetric bicyclo[2.2.1]hepta-2,5-dienes bearing methyl and phenyl substituents at the 2 and 5 positions were prepared enantiomerically pure through a two-step sequence starting from the readily available bicyclo[2.2.1]hepta-2,5-dione. Due to the instability or volatility of these dienes, their isolation was achieved through the formation of the corresponding stable $[RhCl(diene)]_2$ complexes. These chiral rhodium complexes displayed high activity and enantioselectivity (up to 99% ee) in the rhodium-catalyzed 1,4-addition and 1,2-addition of phenylboronic acid to cyclic enones and N -sulfonylimines, respectively.

The recent introduction of chiral diene ligands is a major landmark in the field of asymmetric catalysis.¹ Chiral diene ligands have displayed higher activity and enantioselectivities than chiral diphosphine ligands in a number of rhodium- and iridium-catalyzed reactions.²⁻⁴ Of the several of chiral diene backbones explored by our group² and others,³⁻⁵ 2,5-disubstituted

[2.2.1] and [2.2.2] bicyclic olefins have emerged as privileged structures, forming stable rhodium complexes and displaying consistently high levels of enantiocontrol and activity. Chiral 2,5-disubstituted bicyclo[2.2.1]heptadienes (nbd*) are ideal scaffolds as they can be efficiently generated through the palladium-catalyzed asymmetric hydrosilylation of norbornadiene.⁶ However, attempts to expand the nbd* substitution pattern to aromatic groups were foiled by the instability of the resulting 2,5-aryl bicyclo[2.2.1]heptadienes (Ar-nbd*).^{2a} These downfalls with the nbd* backbone led us to investigate the structurally similar 2,5-disubstituted bicyclo[2.2.2]octadiene (bod*) ligands of which we have recently reported the preparation.^{2e} The major drawbacks from the synthesis of the chiral bod* ligands are the low yielding resolution of the key intermediate, bicyclo[2.2.2]octa-2,5-dione, or the need to separate the racemic ligand by chiral HPLC in the final step. Prompted by the spectacular results obtained with the 2,5-diphenyl bicyclo[2.2.2]octadiene (Ph-bod*) ligand and the very similar levels of enantiocontrol between Bn-nbd* and Bn-bod*, we set out to reinvestigate the synthesis of 2,5-disubstituted bicyclo[2.2.1]heptadienes. We present herein a highly efficient two-step synthesis of the chiral methyl, benzyl, and phenyl disubstituted bicyclo[2.2.1]heptadienes, from the easily accessible chiral bicyclo[2.2.2]hepta-2,5-dione.^{7,8} This novel route allows a rapid access to previously unattainable Me and Ph substituted bicyclo[2.2.1]hepta-2,5-dienes. The catalytic activity of the $[RhCl(nbd*)]_2$ complexes in the 1,4-addition of phenylboronic acid to cyclic enones and the 1,2-addition to N -sulfonylimines is presented.

Our previously disclosed synthetic route for Bn-nbd* involved the circuitous mono acetal protection of chiral diketone (R,R)-1. This route was chosen because the corresponding bistriflate 2 proved difficult to isolate.⁷ Very recently, Van der Eycken et al. reported the synthesis of the racemic bistriflate 2 directly from the corresponding racemic diketone 1, where the combination of a mild triflating agent (PhNTf₂), KHMDS, and low reaction temperature proved instrumental for the isolation of bistriflate 2 in good yield.⁹ We were able to further refine these reaction conditions to obtain chiral bistriflate (R,R)-2 reproducibly in over 85% isolated yield on a 10 mmol scale. Thus, a clean conversion of diketone (R,R)-1 was obtained by slow addition of a toluene solution of KHMDS onto a mixture of (R,R)-1 and 2-PyNTf₂ in THF (Scheme 1).¹⁰ Bistriflate 2 was unstable and prone to rapid decomposition (formation of a black tar) if traces of acid were present, but this could be avoided by storing 2 over a small amount of anhydrous K₂CO₃.¹¹

With convenient access to bistriflate (R,R)-2, we set forth to find optimal cross-coupling conditions with Grignard reagents. From literature precedents, we selected NiCl₂(dppe),¹² PdCl₂(dppf),¹³ Co(acac)₃,¹⁴ and Fe(acac)₃¹⁵ as potential catalysts for

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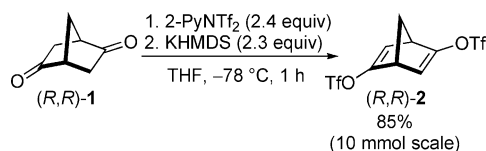
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(11) When stored over K₂CO₃, bistriflate (R,R)-2 showed no sign of decomposition at R.T. for several weeks.

SCHEME 1. Optimized Synthesis of Bistriflate (*R,R*)-2TABLE 1. Screening of Catalyst Systems for the Grignard Cross-Coupling of Bistriflate (*R,R*)-2 with *BnMgCl*^a

entry	cat. (mol %)	<i>T</i> (°C)	<i>t</i> (h) ^b	3a/4 ^c	yield (%) ^d
1	NiCl ₂ (dppf), 1	40	1	0.7	44
2	PdCl ₂ (dppf), 1	40	1	0.6	45
3	Co(acac) ₃ , 5 ^e	0	0.25	0.6	28
4	Fe(acac) ₃ , 5 ^e	0	0.25	13	98

^a To a mixture of bistriflate (*R,R*)-2 (0.25 mmol, 1 equiv) and catalyst in THF (2.5 mL, 0.1 M) was added *BnMgCl* (1.0 mmol, 1 M in Et₂O, 4 equiv) at 0 °C, and the mixture was stirred at the indicated temperature.

^b Time for complete conversion of (*R,R*)-2 (GC/MS). ^c Ratio of products determined by ¹H NMR. ^d Yield calculated from the mixture of (*R,R*)-3a and 4. ^e NMP (1 equiv relative to *BnMgCl*) used as cosolvent. dppf: 1,2-bis(diphenylphosphino)ethane; dppf: 1,1'-bis(diphenylphosphino)ferrocene; NMP: *N*-methylpyrrolidinone.

the Grignard cross-coupling. As a model reaction, we chose the reaction of bistriflate (*R,R*)-2 with four equivalents *BnMgCl*, which yields the stable and isolable (*R,R*)-*Bn-nbd** diene. The results are depicted in Table 1.

The palladium- and nickel-catalyzed cross-coupling reactions (Table 1, entries 1 and 2) displayed very similar product profiles and proceeded swiftly to lead to complete conversion of the starting bistriflate (*R,R*)-2 in less than 1 h (GC/MS analysis). These reactions were hampered by a significant amount of homocoupling product, 1,2-diphenylethane (4), which consumed the excess *BnMgCl* employed.¹⁶ Use of a larger excess of *BnMgCl* (6 equiv) leads to a higher yield of diene (*R,R*)-3a, but the product is contaminated with several equivalents 4.¹⁷ Gratifyingly, the iron-catalyzed reaction provided an almost quantitative yield of (*R,R*)-3a in less than 5 min with the end product being contaminated with only a minute amount of 4 (7 mol %) (Table 1, entry 4).

With efficient cross-coupling conditions in hand, we next turned our attention to the synthesis of Me-*nbd** and Ph-*nbd** ligands. Bistriflate (*R,R*)-2 reacted smoothly with MeMgBr to yield (*R,R*)-2,5-dimethylbicyclo[2.2.1]heptadiene ((*R,R*)-Me-*nbd**, 3b) as a volatile compound which rendered its isolation in an analytically pure form exceedingly difficult.¹⁸ In the case

TABLE 2. Iron-Catalyzed Cross-Coupling and Rhodium-Complexation Sequence^a

entry	RMgX	product	yield (%) ^b
1	<i>BnMgCl</i> ^c	[RhCl((<i>R,R</i>)- <i>Bn-nbd*</i>)] ₂ (5a)	80
2	MeMgBr ^d	[RhCl((<i>R,R</i>)-Me- <i>nbd*</i>)] ₂ (5b)	50
3	PhMgBr ^e	[RhCl((<i>R,R</i>)-Ph- <i>nbd*</i>)] ₂ (5c)	55

^a Reagent and conditions: (a) (*R,R*)-2 (1 equiv), RMgX (4 equiv), Fe(acac)₃ (5 mol %), THF/NMP (*N*-methylpyrrolidinone, 20/1, 0.1 M), 0 °C, 5 min; (b) [RhCl(C₂H₄)₂]₂ (0.5 equiv), toluene, 25 °C, 2 h. ^b Isolated yield over 2 steps. ^c 2 M in THF. ^d 1 M in Et₂O. ^e 3 M in Et₂O.

of the cross-coupling with PhMgBr, the reaction yielded the desired (*R,R*)-Ph-*nbd** (3c) along with a significant amount of biphenyl due to the homocoupling of the Grignard reagent. Although GC/MS analysis of the crude reaction mixture was very clean, all attempts to obtain a pure sample of (*R,R*)-Ph-*nbd** (3c) were frustrated by its decomposition in solution and its contamination by biphenyl. To circumvent the problem associated with the isolation of (*R,R*)-Me-*nbd** (3b) and (*R,R*)-Ph-*nbd** (3c), the crude dienes were reacted directly with 0.5 equivalents of [RhCl(C₂H₄)₂]₂ in toluene (Table 2). This led to the formation of the corresponding [RhCl(*nbd**)]₂ (5a–c) complexes which could be isolated in analytically pure form by chromatography on silica gel.

To assess whether the Ph-*nbd** decomposes when subjected to light or acid or both, a fresh sample of Ph-*nbd** in C₆D₆ was shielded from light while another sample was stored over K₂CO₃. Two control samples were prepared; one was left in C₆D₆ under ambient conditions while the other was kept at –30 °C. The decomposition rates of the Ph-*nbd** samples were monitored by ¹H NMR. The decomposition of the Ph-*nbd** C₆D₆ solutions displayed roughly zero-order kinetics, 5.7 × 10^{–3} h^{–1} (*t*_{1/2} ≈ 75 h) and 6.6 × 10^{–3} h^{–1} (*t*_{1/2} ≈ 62 h) for the sample stored over K₂CO₃ and the sample shielded from light, respectively. The control sample under ambient conditions decomposed only slightly faster (8.0 × 10^{–3} h^{–1}, *t*_{1/2} ≈ 54 h), although complete decomposition of Ph-*nbd** in CDCl₃ occurred in less than 24 h. The sample at –30 °C showed only a small amount of decomposition after 5 days. The origin of the instability of the Ph-*nbd** is presumably due to the presence of a styrene moiety in a strained bicyclo[2.2.1] core, and this effectively lowers π* of the alkene rendering it highly reactive and prone to radical and acid-catalyzed decomposition. Although it leads to inherent instability of the ligand, this property is key for increasing the stability of the corresponding [RhCl(Ph-*nbd**)]₂ complex.

The rhodium dimer [RhCl(Ph-*nbd**)]₂ (5c) proved to be remarkably stable and showed no sign of decomposition when its toluene solution was exposed to air for several weeks. Moreover, the melting point of 5c was over 300 °C (in an air atmosphere) and the complex remained stable at this elevated temperature. This is in contrast with the [RhCl(*Bn-nbd**)]₂ complex which slowly decomposed at its melting point (163–165 °C). The X-ray crystal structure of [RhCl((*R,R*)-Ph-*nbd**)]₂ (5c) is depicted in Figure 1. Analysis of the key structural parameters of 5c reveals a very close resemblance with the parent [RhCl((*S,S*)-Ph-*bod**)]₂ dimer.^{2e,f} Hence, the Rh–Cl bond distance 2.4001(6) (vs 2.405(3) Å for [RhCl(Ph-*bod**)]₂), the alkene bond distance (C(1)–C(2)) 1.407(3) Å (vs. 1.42(1) Å for [RhCl(Ph-*bod**)]₂), and the bite angle (C(2)–Rh(1)–C(4)) 67.64(9)° (vs. 67.8(3)° for [RhCl(Ph-*bod**)]₂) are in close

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(16) In the GC/MS analysis of the reaction mixture, a significant amount of monocoupled product in which the triflate function has been reduced is observed.

(17) The separation of 4 from 3a is difficult due to the low polarity of these compounds (*R*_f > 0.6 in pentane). Thus, minimizing the amount of 4 is necessary for obtaining *Bn-nbd** with acceptable purity.

(18) The low molecular weight, 120 g/mol, and its branched structure contribute to making (*R,R*)-Me-*nbd** a highly volatile compound.

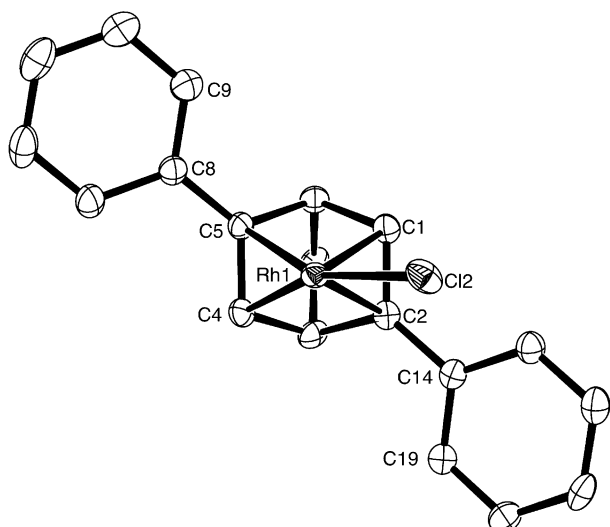
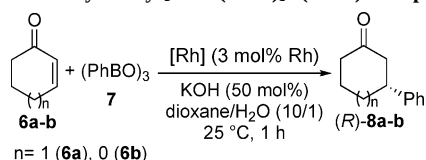


FIGURE 1. ORTEP illustration of [RhCl(*(R,R)*-Ph-nbd*)₂] (**5c**) with thermal ellipsoids at the 50% probability level (shown as a monomer for clarity). Selected bond distances (Å) and angles (°): Rh(1)–Cl(2), 2.4001(6); Rh(1)–C(1), 2.080(2); Rh(1)–C(2), 2.127(2); C(1)–C(2), 1.407(3); C(4)–C(5), 1.414(3); C(2)–Rh(1)–C(5), 81.94(8); C(1)–Rh(1)–C(4), 81.19(9); C(2)–Rh(1)–C(4), 67.64(9); C(1)–C(2)–C(4)–C(5), 1.1(2); C(1)–C(2)–C(14)–C(19), –179.7(2); C(4)–C(5)–C(8)–C(9), 166.4(2).

TABLE 3. Asymmetric 1,4-Addition of Phenylboronic Acid to Cyclic Enones Catalyzed by [RhCl(nbd*)]₂ (5a–c) Complexes^a



entry	6	[RhCl(nbd*)] ₂	yield (%) ^b	% ee ^c
1	6a	[RhCl(Me-nbd*)] ₂ (5b)	90 (8a)	95
2	6a	[RhCl(Bn-nbd*)] ₂ (5a)	87 (8a)	96
3	6a	[RhCl(Ph-nbd*)] ₂ (5c)	89 (8a)	97
4	6b	[RhCl(Me-nbd*)] ₂ (5b)	86 (8b)	85
5	6b	[RhCl(Ph-nbd*)] ₂ (5c)	92 (8b)	96

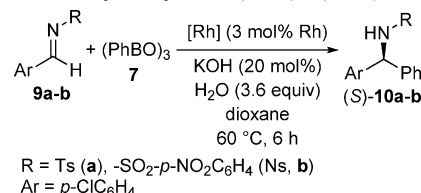
^a The reaction was carried out with **6** (0.5 mmol, 1 equiv), **7** (0.2 mmol, 1.2 equiv B), [RhCl(nbd*)]₂ (**5**) (3 mol % Rh), and 1.5 M aq KOH (0.25 mmol, 0.17 mL, 0.5 equiv) in 1,4-dioxane (1.7 mL) at 25 °C for 1 h.

^b Isolated yield after silica gel chromatography. ^c Determined by HPLC analysis with a chiral stationary phase column (Chiracel OD-H for **8a** and Chiracel OB-H for **8b**).

agreement. The elongated alkene bond in **5c** reveals predominant back-bonding of the rhodium center onto the alkene. The small dihedral angle between the double bond and the plane of the phenyl group ($-179.7(2)^\circ$ and $166.4(2)^\circ$ for C(1)–C(2)–C(14)–C(19) and C(4)–C(5)–C(8)–C(9), respectively) indicates conjugation of the π system; this effect further reinforces the back-bonding through delocalization and probably accounts for the higher stability of [RhCl(Ph-nbd*)]₂ (**5c**) over [RhCl(Bn-nbd*)]₂ (**5a**). The similarities between the solid-state structures of [RhCl(Ph-nbd*)]₂ (**5c**) and [RhCl(Ph-bod*)]₂ is somewhat surprising when one considers the large difference in stability between the free Ph-nbd* and Ph-bod* dienes.¹⁹

The catalytic activity of these new complexes in the 1,4-addition of phenylboronic acid to cyclic enones was evaluated (Table 3). The high level of enantiocontrol achieved by [RhCl-((*R,R*)-Me-nbd*)₂] (**5b**), 95% ee, (Table 3, entry 1) is truly impressive, given the small size of the Me-nbd* ligand with a molecular weight of only 120 g/mol and only two methyl groups effecting the enantiocontrol of the reaction. The increase of steric

TABLE 4. Asymmetric 1,2-Addition of Phenylboronic Acid to *N*-Sulfonylimine Catalyzed by [RhCl(nbd*)]₂ (5a–c)^a



entry	9	[RhCl(nbd*)] ₂	yield (%) ^b	% ee ^c
1	9a	[RhCl(Me-nbd*)] ₂ (5b)	96 (10a)	89
2	9a	[RhCl(Bn-nbd*)] ₂ (5a)	98 (10a)	92 ^d
3	9a	[RhCl(Ph-nbd*)] ₂ (5c)	96 (10a)	99
4	9b	[RhCl(Me-nbd*)] ₂ (5b)	93 (10b)	82
5	9b	[RhCl(Bn-nbd*)] ₂ (5a)	88 (10b)	81 ^e
6	9b	[RhCl(Ph-nbd*)] ₂ (5c)	92 (10b)	98

^a The reaction was carried out with **9** (0.10 mmol, 1 equiv), **7** (0.12 mmol, 3.6 equiv **B**), [RhCl(*o*-nbd*)₂] (5.3 mol % Rh), and 3.1 M aq KOH (0.02 mmol, 6.5 μ L, 2.0 equiv) in 1,4-dioxane (0.4 mL) at 60 °C for 6 h. ^b Isolated yield after silica gel chromatography. ^c Determined by HPLC analysis with a chiral stationary phase column (Chiracel OD-H). ^d Reported in ref 2c. ^e Reported in ref 2d.

bulk of the substituents on the nbd* ligand (Table 3, entries 2 and 3) leads to incremental but marginal increase in enantioselectivity. The 1,4-addition to 2-cyclopentenone (**6b**), a much more demanding substrate, proved more telling of the difference of steric effects between (*R,R*)-Me-nbd* (85% ee) and (*R,R*)-Ph-nbd* (96% ee) (Table 3, entries 4 and 5); the latter is close to the enantioselectivity previously reported with the (*R,R*)-Phbod* ligand (99% ee).^{2e}

To gain further insight into the reaction scope offered by the Me-nbd* and Ph-nbd* ligands, we investigated the rhodium-catalyzed 1,2-addition of phenylboronic acid to *N*-sulfonyl-imines. This reaction is much more sensitive to the size of the substituents on the diene and on the backbone-type.^{2c,d} Both the 1,2-addition to *N*-tosyl and *N*-nosyl imines was investigated, the latter being more synthetically useful though more challenging.

The enantioselectivities observed with (*R,R*)-Me-nbd* and (*R,R*)-Bn-nbd* were quite similar for both imines **9a** and **9b** (Table 4, entries 1 vs 2 and 4 vs 5). It is remarkable that the (*R,R*)-Ph-nbd* ligand showed high enantiocontrol in the phenylation of the imines **9a** and **9b** (Table 4, entries 3 and 6). Particularly, the enantioselectivity of 98% ee observed for *N*-nosyl imine **9b** is striking because the closely related (*R,R*)-Ph-bod* ligand only gave 89% ee under the same reactions conditions.^{2d} Thus, subtle steric and electronic differences in these ligands that are not revealed by comparison of structural features in the X-ray analysis bring about a significant effect on the enantioselection process.

In summary, two new rhodium complexes bearing chiral methyl and phenyl 2,5-disubstituted bicyclo[2.2.1]heptadiene ligands were synthesized and fully characterized. The synthesis is highly efficient, and the corresponding rhodium complexes ($[\text{RhCl}(\text{nbd}^*)]_2$) can be isolated in 42–68% yield over three steps starting from the readily available (*R,R*)-2,5-norbornanedi-one. These new rhodium complexes displayed high levels of activity and enantioselectivities in the 1,4-addition and 1,2-addition of phenylboronic acid to cyclic enones and to aryl *N*-sulfonyl imines, respectively. The $[\text{RhCl}(\text{Ph-nbd}^*)]_2$ complex performs exceptionally well in both reactions and leads to enantioselectivities that are similar or better than the parent $[\text{RhCl}(\text{Ph-bod}^*)]_2$ complex.

Experimental Section

Preparation of Bistriflate (*R,R*)-2. To a solution diketone (*R,R*)-1⁸ (1.24 g, 10 mmol, 1 equiv) and 2-PyNTf₂¹⁰ (8.60 g, 24 mmol, 2.4 equiv) in dry THF (30 mL, 0.30 M) at –78 °C was slowly added KHMDS (44 mL, 0.50 M in toluene, 23 mmol, 2.3 equiv) affording a clear, light-red solution. Stirring was further continued for 1 h at –78 °C at which point the reaction turned light brown and turbid. The reaction was quenched with a sat. NaHCO₃ solution at this temperature. After warming to room temperature, the layers were separated and the aqueous layer was extracted twice with hexane. The combined organic layers were sequentially washed with 5% NaOH solution (until the aqueous layer remained colorless), water, and brine. The organic layer was dried over K₂CO₃. The crude product was purified by flash chromatography over silica gel (hexane/ethyl acetate 95/5) affording 3.30 g (8.5 mmol, 85%) of bistriflate (*R,R*)-2 as a colorless oil. To avoid decomposition, the product was stored over K₂CO₃. Racemic bistriflate 2 has been reported in ref 9. ¹H NMR (CDCl₃): δ 2.60 (t, *J* = 1.8 Hz, 2H), 3.51 (m, 2H), 6.49 (dd (app. t), *J* = 2.4, 2.4 Hz, 2H) ppm; ¹³C{¹H} NMR (CDCl₃): 50.3 (CH), 73.1 (CH₂), 118.5 (q, *J*_{C–F} = 321 Hz, CF₃), 123.7 (CH), 168.2 (C) ppm; [α]_D²⁵ +24 (c 0.35, CHCl₃).

Procedure for the Catalyst Screening for Cross-Coupling of Bistriflate (*R,R*)-2 with Benzylmagnesium Chloride (Table 1). To a solution of bistriflate (*R,R*)-2 (97 mg, 0.25 mmol, 1 equiv), NMP (120 μL, Table 1, entries 3 and 4), and a catalyst (amount indicated in Table 1) in THF (2.5 mL, 0.1 M) at 0 °C was added the BnMgCl (1 mL, 1 mmol, 1.0 M in Et₂O, 4 equiv) under nitrogen. The reaction was stirred for the indicated time and temperature before being quenched by sat. NH₄Cl at 0 °C. The aqueous layer was extracted three times with hexane. The combined organic extracts were washed three times with water followed by a wash with brine and dried over MgSO₄. The crude product was passed through a plug of silica gel, eluted with hexane, and concentrated in vacuo. The crude product, consisting of (*R,R*)-Bn-nbd* (**3b**) and 1,2-diphenylethane (**4**), was analyzed by ¹H NMR and compared to the spectral data previously reported in ref 2a.

A Typical Procedure for the Preparation of [RhCl(nbd*)]₂ Complexes. Preparation of [RhCl((*R,R*)-Bn-nbd*)]₂ (5a**) (Table 2, entry 1).** A solution of BnMgCl (2 mL, 2 mmol, 1.0 M in Et₂O, 4 equiv) was added dropwise to a solution of bistriflate (*R,R*)-2 (194 mg, 0.50 mmol), Fe(acac)₃ (8.8 mg, 5 mol %), and NMP (250 μL) in THF (5 mL, 0.1 M) at 0 °C under nitrogen. The initial clear, orange solution became pale yellow before turning dark brown toward the end of the addition. The reaction mixture was further stirred for 5 min at that temperature before being quenched by sat. NH₄Cl. The aqueous layer was extracted three times with hexane. The combined organic extracts were washed three times with water followed by a wash with brine and dried over K₂CO₃. The crude product was passed through a plug of silica gel and eluted with hexane. Crude (*R,R*)-Bn-nbd* (**3a**) was characterized by comparison of the spectral and analytical data with those reported in the literature.^{2a} The crude product was dissolved in toluene (5 mL, 0.1 M), and [RhCl(C₂H₄)₂]₂ (97 mg, 0.25 mmol, 1 equiv) was added. The mixture was stirred under nitrogen for 2 h and the solvents were removed in vacuo. The product was purified by flash chromatography over silica gel (hexane/CH₂Cl₂, 1/1) to yield a 164 mg (0.20 mmol, 80%) of complex **5a** as a light-yellow crystalline solid. ¹H NMR (CDCl₃): δ 0.77 (s, 4H), 3.08 (d, *J* = 14.4 Hz, 4H), 3.51 (s, 4H), 3.76 (d, *J* = 14.4 Hz, 4H), 3.80 (s, 4H), 7.26 (d, *J* = 7.0 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 8H), 7.26 (d, *J* = 7.5 Hz, 8H). ¹³C{¹H} NMR (CDCl₃): 40.6 (CH₂), 47.7 (d, *J*_{C–Rh} = 10.8 Hz, CH), 53.3 (d, *J*_{C–Rh} = 3.0 Hz, CH₂), 60.1 (d, *J*_{C–Rh} = 7.1 Hz, CH), 70.1 (d, *J*_{C–Rh} = 11.4 Hz, C), 126.4 (CH), 128.5 (CH), 129.1 (CH), 138.7 (C) ppm; [α]_D²⁵ +56 (c 0.60, CHCl₃); mp = 163–165 °C (dec).

Preparation of [RhCl((*R,R*)-Me-nbd*)]₂ (5b**).** The reaction was run on 0.50 mmol of (*R,R*)-2 using a MeMgCl (3 M in Et₂O) solution. Hexane was substituted for pentane. The residual solvent was carefully evaporated on a rotary evaporator to yield crude (*R,R*)-Me-nbd* (**3b**). ¹H NMR (CDCl₃): δ 1.76 (d, *J* = 1.8 Hz, 6H), 1.87 (t, *J* = 1.7 Hz, 2H), 3.02 (m, 2H), 6.06 (dd (app. t), *J* = 1.9, 2.0 Hz, 2H) ppm; ¹³C{¹H} NMR (CDCl₃): 16.9 (CH₃), 54.9 (CH), 71.7 (CH₂), 132.5 (CH), 154.9 (C) ppm. Complex **5b** was isolated as an orange solid after flash chromatography (hexane/CH₂Cl₂, 60/40), 65 mg (0.13 mmol, 50%). ¹H NMR (CDCl₃): δ 1.22 (s, 2H), 1.73 (d, *J* = 11.0 Hz, 6H), 3.47 (d, *J* = 1.9 Hz, 2H), 3.55 (d, *J* = 1.5 Hz, 2H) ppm; ¹³C{¹H} NMR (CDCl₃): 20.3 (d, *J*_{C–Rh} = 2 Hz, CH₃), 46.9 (d, *J*_{C–Rh} = 10.9 Hz, CH), 55.6 (d, *J*_{C–Rh} = 3.6 Hz, CH₂), 58.6 (d, *J*_{C–Rh} = 7.8 Hz, CH), 66.5 (d, *J*_{C–Rh} = 11.3 Hz, C) ppm; [α]_D²⁵ –285 (c 0.6, CHCl₃); mp 137–139 °C; anal. calcd for C₁₈H₂₄Cl₂Rh₂: C, 41.81, H, 4.68; found C, 42.08, H, 4.55.

Preparation of [RhCl((*R,R*)-Ph-nbd*)]₂ (5c**).** The reaction was run on 0.50 mmol of (*R,R*)-2 using a solution of PhMgBr (2.5 M in Et₂O) to yield crude Ph-nbd* (**3c**). ¹H NMR (CDCl₃): δ 2.31 (t, *J* = 1.4 Hz, 2H), 4.10 (t, *J* = 2.0 Hz, 2H), 7.06 (dd (app. t), *J* = 2.2, 2.1 Hz, 2H), 7.49–7.46 (m, 6H), 7.63–7.65 (m, 4H) ppm; ¹³C{¹H} NMR (CDCl₃): 52.3 (CH), 69.7 (CH₂), 124.9 (CH), 127.3 (CH), 128.5 (CH), 134.6 (CH), 141.3 (C), 156.9 (C) ppm. Complex **5c** was isolated as a bright-red crystalline solid after flash chromatography (hexane/CH₂Cl₂, 60/40), 105 mg (0.14 mmol, 55%). ¹H NMR (CDCl₃): δ 1.28 (s, 2H), 3.67 (d, *J* = 2.4 Hz, 2H), 4.21 (dd, *J* = 1.4, 1.7 Hz, 2H), 7.36–7.37 (m, 6H), 7.50–7.53 (m, 4H) ppm; ¹³C{¹H} NMR (CDCl₃): 41.3 (d, *J*_{C–Rh} = 10.8 Hz, CH), 52.9 (d, *J*_{C–Rh} = 2.6 Hz, CH₂), 57.9 (d, *J*_{C–Rh} = 6.8 Hz, CH), 65.1 (d, *J*_{C–Rh} = 10.9 Hz, C), 127.2 (CH), 127.8 (CH), 128.2 (CH), 138.5 (C) ppm; [α]_D²⁵ –52 (c 1.05, CHCl₃); mp > 300 °C; anal. calcd for C₃₈H₃₂Cl₂Rh₂·H₂O: C, 58.26, H, 4.37; found C, 58.63, H, 4.24.

General Procedure for the Asymmetric 1,4-Addition of Phenylboronic Acid to Cyclic Enones (6**).** To a solution of [RhCl(nbd*)]₂ (**5**) (3 mol % Rh) and phenylboroxine (**7**, 62 mg, 0.20 mmol, 1.2 equiv of boron) in 1.7 mL of 1,4-dioxane was added the cyclic enone **6** (0.50 mmol, 1 equiv) and KOH aq. (1.5 M, 0.17 mL, 0.25 mmol, 0.5 equiv). The solution was stirred at 25 °C for 1 h. The resulting mixture was passed through a short silica gel pad and eluted with Et₂O. Evaporation of the solvent followed by chromatography over silica gel (hexane/ethyl acetate = 95/5) gave (*R*)-3-phenylcycloalkanone **8** as a colorless oil. Compounds **8a–b** were fully characterized by comparison of the spectral and analytical data with those reported in the literature.²⁰

General Procedure for the Asymmetric 1,2-Addition of Phenylboronic Acid to *N*-Sulfonyl Imines. To a solution of [RhCl(nbd*)]₂ (**5**) (3 mol % Rh), phenylboroxine (**7**) (0.12 mmol, 1.2 equiv), and imine **9** (0.10 mmol, 1 equiv) in 1,4-dioxane (0.4 mL) was added KOH aq. (6.5 μL, 3.1 M, 0.2 equiv, H₂O: 1 equiv to boron) at room temperature. The resulting homogeneous solution was stirred for 6 h at 60 °C. The mixture was passed through a short silica gel pad and eluted with Et₂O. Evaporation of the solvent followed by chromatography over silica gel (hexane/ethyl acetate = 4/1) gave the arylated product **10**. Compounds **10a** and **10b** were fully characterized by comparison of their spectral and analytical data with those reported in the literature.^{2c,d}

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Supporting Information Available: Experimental details for the acquisition and structure refinement for rhodium complex (*R,R*)-**5c**, the corresponding CIF file, and spectroscopic data for all new compounds are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>. JO061385S

(19) Ph-bod* can be easily handled and stored indefinitely at room temperature.

(20) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579.