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# 4,8-Disubstituted Bicyclo[3.3.1]nona-2,6-dienes as Chiral Ligands for Rh-Catalyzed Asymmetric 1,4-Addition Reactions

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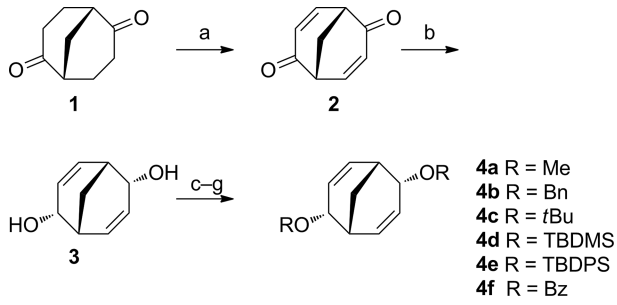
**Keywords:** Asymmetric catalysis / Diene ligands / Michael addition / Rhodium

$C_2$-symmetric chiral diene ligands based on 4,8-*endo*,*endo*-disubstituted bicyclo[3.3.1]nona-2,6-diene framework have been designed and synthesized. The rhodium complexes of the dienes, which were obtained in a few straightforward steps from enantiomerically pure bicyclo[3.3.1]nonane-2,6-dione, exhibited excellent catalytic activity and high enantioselectivity (up to 96 % *ee*) in the conjugate addition reaction of arylboronic acids to cyclic enones under mild reaction conditions with high atom efficiency.

## Introduction

The rhodium-catalyzed asymmetric conjugate addition of organoboron reagents to activated alkenes has emerged as one of the most functional-group-tolerant and reliable carbon–carbon bond-forming reactions.[1] The ability to impart high levels of enantioselectivity across a broad range of alkene acceptors, combined with the high stability and ready availability of many organoboron reagents, makes this methodology particularly attractive for the assembly of complex molecules and intermediates in drug discovery.[2] Recent developments in this research area included the utilization of bidentate diolefins as steering ligands for transition-metal-catalyzed asymmetric transformations. Since the first application of chiral dienes in asymmetric rhodium[3] and iridium[4] catalyzed reactions, the research efforts directed towards design, synthesis and study of novel ligands has burgeoned.[5] A variety of $C_2$- and $C_1$-symmetric chiral dienes based on rigid bicyclic and polycyclic skeletons, such as bicyclo[2.2.1]heptadienes,[3,6] bicyclo[2.2.2]octadienes,[7] bicyclo[3.3.0]octadienes,[8] bicyclo[3.3.1]nonadienes[9] and dicyclopentadienes,[10] as well as acyclic ligands,[11] have been developed. In terms of both catalytic activity and enantioselectivity chiral dienes often surpass other types of ligands, such as chiral bisphosphines, especially in the conjugate addition of boronic acids to α,β-unsaturated carbonyl compounds and arylation of imines,[6–11] as well as other synthetically useful asymmetric rhodium-catalyzed reactions.[12] Nevertheless, even though diene–Rh catalyzed arylation reactions are conducted under milder conditions, in order to achieve high yields an excess of aryl boronic acid is generally required as a result of competing protodeboronation[1b] and homocoupling[7g] side reactions. The multistep synthesis and, most notably, the necessity to use preparative chiral HPLC to access enantiomerically pure dienes or their synthetic precursors[7c,9] also remains a concern. Hence, the development of readily accessible chiral diene ligands with increased selectivity and catalytic activity is highly desirable. To this end, we have demonstrated the utility of (+)-(1*S*,5*S*)-bicyclo[3.3.1]nonane-2,6-dione (**1**) (Scheme 1), which can be easily obtained by kinetic resolution of the racemate with baker's yeast,[13] for the synthesis of related enantiomerically pure structures[14] and self-assembling supramolecular tectons.[15] We anticipated that the unsaturated diol **3** derived from diketone **1** would provide a convenient intermediate to access 4,8-*endo,endo*-disubstituted dienes **4**, where the steric bulk of the substituents and consequently the chiral environment around the diene-coordinated Rh atom could be tuned in a straightforward manner.




Scheme 1. Reagents and conditions: a) NaH, Ph(S=O)OMe, THF, then $Na_2CO_3$, Ph-$CH_3$, reflux (80–83 %); b) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH (72–78 %); c) MeI, NaH, DMF (82 %); d) BnCl, NaH, DMF (81–87 %); e) *t*BuO(C=NH)$CCl_3$, $BF_3 \cdot Et_2O$, $CH_2Cl_2$ (24 %); f) TBDMSCl or TBDPSCl, imidazole, DMF (99 %); g) PhCOCl, DMAP, Py (72 %). Bn = benzyl; TBDMS = *tert*-butyldimethylsilyl; TBDPS = *tert*-butyldiphenylsilyl; DMAP = 4-dimethylaminopyridine.

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Herein, we report the preparation of 4,8-disubstituted bicyclo[3.3.1]nona-2,6-diene ligands and their application in the Rh-catalyzed asymmetric 1,4-addition reaction of boronic acids to cyclic enones. Structural features of the active catalyst obtained from an X-ray crystallographic analysis are also presented.

## Results and Discussion

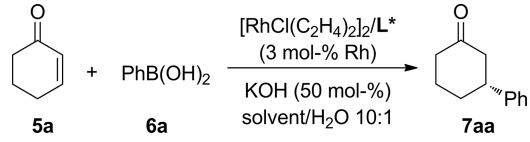
Synthesis of chiral dienes commenced with the preparation of (+)-(*1R*,*5R*)-bicyclo[3.3.1]nona-3,7-diene-2,6-dione (**2**)[16] by sulfinylation[17] of enantiomerically pure 2,6-dione **1** with methyl phenylsulfinate in the presence of sodium hydride, followed by thermal elimination (Scheme 1). Luche reduction[18] ($NaBH_4/CeCl_3$) of the obtained bis(enone) **2** in methanol afforded diol **3** as a mixture of *endo,endo*- and *endo,exo*-diastereomers in ca. 88:12 ratio. Subsequent purification by column chromatography and fractional crystallization furnished diastereomerically pure *endo,endo*-diol **3**[19] in 72–78% yield.

*O*-Alkyl derivatives **4a** and **4b** were prepared in good yields by alkylation of **3** with the corresponding alkyl halides in DMF, by using sodium hydride as a base. However, the methyl ether **4a** was found to be rather unstable at room temperature; the *O*-benzyl congener **4b** also partially decomposes on storage at room temperature apparently through a retro-ene reaction releasing benzaldehyde, but can be stored in the freezer for indefinite periods of time without appreciable signs of decomposition. Reaction of diol **3** with *tert*-butyl 2,2,2-trichloroacetimidate in the presence of a catalytic amount of boron trifluoride etherate[20] in dichloromethane afforded **4c** in rather low yield (24%), along with the monoprotected derivative 6-(*tert*-butoxy)-bicyclo[3.3.1]nona-3,7-dien-2-ol (24%) and recovered starting material. Imidazole-catalyzed silylation[21] of **3** with TBDMSCl or TBDPSCl in DMF proceeded uneventfully, providing the corresponding silylethers **4d** and **4e** in quantitative yields. Bis(benzoate) **4f** was obtained by standard benzoylation of diol **3** with benzoyl chloride in pyridine.

With bicyclic diene ligands **3** and **4a**–**4f** in hand, their efficiency in the Rh-catalyzed Michael addition reaction of phenylboronic acid (**6a**) to 2-cyclohexenone (**5a**) was evaluated (Table 1).

We were pleased to find that the catalyst prepared in situ from diene **3** and $[RhCl(C_2H_4)_2]_2$ (3 mol-% Rh) exhibited excellent activity under standard[3] conditions; complete conversions were attained in ca. 10–15 min at room temperature, by using 2 equiv. of phenylboronic acid (**6a**), aqueous potassium hydroxide as a base and dioxane as a solvent. (*1R*,*2R*,*5R*,*6R*)-Configured diol **3** favoured the formation of (*R*)-configured 3-phenylcyclohexanone (**7aa**) in 90% *ee* and 97% isolated yield (Table 1, entry 1). Ligand **3** exhibited the same sense of asymmetric induction, but notably outperformed the parent bicyclo[3.3.1]nona-2,6-diene (**8**)[22] (Figure 2, vide infra) both in terms of activity and enantioselectivity [1.25 h, 83% yield of **7aa** (86% *ee*)]. The beneficial effect of the *endo*-substituents on selectivity was further

Table 1. Ligand screening and optimization of reaction conditions.[a]




**5a** **6a** **7aa**

| Entry | Ligand | Solvent | Yield[b] [%] | *ee*[c] [%] |
|---|---|---|---|---|
| 1[d] | **3** | Dioxane | 97 | 90 |
| 2[d] | **4a** | Dioxane | 91 | 92 |
| 3 | **4b** | Dioxane | 97 | 94 |
| 4 | **4b** | MTBE[e] | 98 | 93 |
| 5 | **3** | THF | 92 | 92 |
| 6 | **4b** | THF | 98 | 95 |
| 7 | **4b** | Toluene | 96 | 86 |
| 8[f] | **3** | $H_2O$ | 96 | 88 |
| 9 | **4c** | THF | 96 | 94 |
| 10 | **4d** | THF | 91 | 92 |
| 11[g] | **4e** | THF | 90 | 78 |
| 12 | **4f** | THF | – | – |

[a] The reactions were carried out with enone **5a** (0.3 mmol), **6a** (0.36 mmol, 1.2 equiv.), $[Rh(C_2H_4)_2Cl]_2$ (3 mol-% Rh), ligand (3.3 mol-%) and 1.5 M aq. KOH (0.1 mL, 50 mol-%) in corresponding solvent (1 mL) at room temperature for 30 min, unless stated otherwise. [b] Isolated yield. [c] *ee* values determined by chiral HPLC; all products **7aa** were of (*R*)-configuration, as revealed by the comparison of their optical rotations with the literature data. [d] The reaction was carried out with 2 equiv. of **6a**. [e] MTBE = methyl *tert*-butyl ether. [f] The reaction was carried out for 1 h. [g] The reaction was carried out at 50 °C.

demonstrated with *O*-methyl and *O*-benzyl congeners **4a** and **4b**, which exhibited enhanced levels of asymmetric induction (92 and 94% *ee*, respectively; entries 2 and 3). Notably, the reaction could be performed with only 1.2 equiv. of phenylboronic acid (**6a**) without adverse effect on yield and enantioselectivity (entry 3; reaction in the presence of 2 equiv. of **6a** yielded **7aa** in 98% yield and 94% *ee*). Parallel screenings aimed at identifying an optimal combination of solvent and base by using ligand **4b** revealed virtually no effect on yield and enantioselectivity, when other bases, such as triethylamine, potassium carbonate or potassium phosphate, were used in aqueous dioxane. Comparable results were obtained when dioxane was replaced with methyl *tert*-butyl ether (93% *ee*, entry 4) and marginally improved enantioselectivities were attained in tetrahydrofuran with both **3** and **4b** (entries 5 and 6, compare with entries 1 and 3). By contrast, the use of toluene as a solvent had a detrimental effect on enantioselectivity (86% *ee*, entry 7). It is interesting to note that the high solubility of diol **3** in water allowed us to perform the reaction without any organic cosolvent, nevertheless, a decrease in enantioselectivity was observed (entry 8, compare with entries 1 and 5).

In light of the above observations, the efficiency of the remaining ligands **4c**–**4f** was evaluated in THF, by using 1.2 equiv. of $PhB(OH)_2$ (**6a**) and aqueous KOH as a base (Table 1, entries 9–12). Bis(*tert*-butyl) ether **4c** exhibited asymmetric induction comparable to that of **4b** (entry 9), whereas TBDMS-silylated ligand **4d** was found to offer slightly lower selectivity (92% *ee*, entry 10). Further in-

crease in the steric bulk of *endo*-substituents, as in *tert*-butyl diphenylsilyl congener **4e**, had a detrimental effect on catalytic activity. The Rh/**4e**-catalyzed reaction at room temperature was extremely sluggish, providing only trace amounts of **7aa**; nevertheless, at elevated temperature (50 °C) full conversion was achieved in 30 min at the substantial expense of enantioselectivity (78% *ee*, entry 11). In stark contrast to the behaviour of diol **3** and ethers **4a**–**4d**, bis(benzoate) **4f** was found to be totally ineffective in promoting the reaction under standard conditions at room temperature (entry 12).[23]

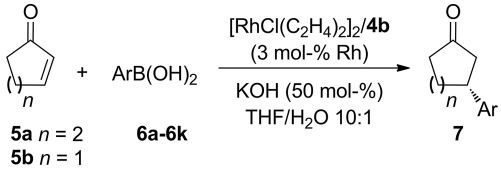
With the diene **4b** as the ligand of choice, the substrate scope was investigated under the optimal reaction conditions, by using 3 mol-% of Rh catalyst (Table 2). In the case of 2-cyclohexenone (**5a**), the expected addition products were produced smoothly at room temperature in excellent yields.[24]

The electron-donating or withdrawing groups on the phenyl ring of boronic acids did not seem to affect selectivity significantly; high enantioselectivities (94–96% *ee*) were maintained when sterically unhindered *p*- and *m*-substituted arylboronic acids **6a**–**6g** were employed (entries 1–7). On the other hand, a drop in asymmetric induction was observed when sterically encumbered *o*-substituted arylboronic acids **6h**–**6j** (entries 8–10) or (*E*)-styreneboronic acid **6k** were used (entry 11).

Conjugate addition reactions to 2-cyclopentenone (**5b**) also proceeded uneventfully, albeit with lower enantioselectivity (entries 12–13). By contrast, 2-cycloheptenone (**5c**) exhibited lower reactivity under standard conditions and 1.6 equiv. of the aryl boronic acids were required to achieve full conversions in 30 min. The stereochemistry followed the scenario observed for **5a**, i.e. high enantioselectivities (93–95% *ee*) were attained with a range of *p*- and *m*-substituted arylboronic acids **6a**–**6g** (entries 14–20). In diene-Rh catalyzed arylations excess of aryl boronic acid (typically two equivalents) is necessary in order to achieve high yields. This requirement for use of excess arylboronic acid was attributed to the competing protodeboronation[1b] and homocoupling[7g] side reactions. From this point of view, the high catalytic activity of the Rh/**4b** complex is noteworthy – in the presence of 0.5 mol-% of the catalyst, 3-phenylcyclohexanone (**7aa**) was obtained in 93% yield and 95% *ee* (Table 2, entry 21, compare with entry 1) with only 1.2 equiv. of **6a**.

Structural information on the active catalyst was obtained from an X-ray crystallographic analysis of the complex [RhCl(**4b**)]$_2$.[25] Treatment of the diene (*1R*,*2R*,*5R*,*6R*)-**4b** with [Rh($C_2H_4$)$_2$Cl]$_2$ in benzene at 50 °C afforded corresponding complex, which exhibited the same catalytic activity and asymmetric induction (Table 2, entry 22) as the catalyst formed in situ. The X-ray crystal structure of [RhCl(**4b**)]$_2$ is depicted in Figure 1.

Table 2. Rhodium/**4b**-catalyzed asymmetric 1,4-addition reactions.[a]




**5a** *n* = 2 **5b** *n* = 1 **5c** *n* = 3 **6a-6k** **7**

| Entry | 5 | Ar (6) | Product | Yield[b] [%] | *ee*[c] [%] |
|---|---|---|---|---|---|
| 1 | **5a** | $C_6H_5$ (**6a**) | **7aa** | 98 | 95 |
| 2 | **5a** | 4-F$C_6H_4$ (**6b**) | **7ab** | 97 | 96 |
| 3 | **5a** | 4-Br$C_6H_4$ (**6c**) | **7ac** | 97 | 96 |
| 4 | **5a** | 4-MeO$C_6H_4$ (**6d**) | **7ad** | 89 | 94 |
| 5 | **5a** | 3-Cl$C_6H_4$ (**6e**) | **7ae** | 96 | 95 |
| 6 | **5a** | 3-MeO$C_6H_4$ (**6f**) | **7af** | 90 | 94 |
| 7 | **5a** | 2-naphthyl (**6g**) | **7ag** | 94 | 94 |
| 8 | **5a** | 2-Cl$C_6H_4$ (**6h**) | **7ah** | 90 | 83 |
| 9 | **5a** | 2-MeO$C_6H_4$ (**6i**) | **7ai** | 97 | 76 |
| 10 | **5a** | 1-naphthyl (**6j**) | **7aj** | 89 | 72 |
| 11 | **5a** | (*E*)-$C_6H_5$CH=CH (**6k**) | **7ak** | 63 | 84 |
| 12 | **5b** | 4-Br$C_6H_4$ (**6c**) | **7bc** | 98 | 79 |
| 13 | **5b** | 4-MeO$C_6H_4$ (**6d**) | **7bd** | 97 | 73 |
| 14[d] | **5c** | $C_6H_5$ (**6a**) | **7ca** | 97 | 95 |
| 15[d] | **5c** | 4-F$C_6H_4$ (**6b**) | **7cb** | 97 | 95 |
| 16[d] | **5c** | 4-Br$C_6H_4$ (**6c**) | **7cc** | 97 | 95 |
| 17[d] | **5c** | 4-MeO$C_6H_4$ (**6d**) | **7cd** | 97 | 93 |
| 18[d] | **5c** | 3-Cl$C_6H_4$ (**6e**) | **7ce** | 95 | 95 |
| 19[d] | **5c** | 3-MeO$C_6H_4$ (**6f**) | **7cf** | 94 | 94 |
| 20[d] | **5c** | 2-naphthyl (**6g**) | **7cg** | 97 | 94 |
| 21[e] | **5a** | $C_6H_5$ (**6a**) | **7aa** | 93 | 95 |
| 22[f] | **5a** | $C_6H_5$ (**6a**) | **7aa** | 96 | 95 |

[a] The reactions were carried out with enone **5** (0.3 mmol), arylboronic acid **6** (0.36 mmol, 1.2 equiv.), [Rh($C_2H_4$)$_2$Cl]$_2$ (3 mol-% Rh), ligand **4b** (3.3 mol-%) and 1.5 M aq. KOH (0.1 mL, 50 mol-%) in THF (1 mL) at room temperature for 30 min, unless stated otherwise. [b] Isolated yield. [c] *ee* values determined by chiral HPLC; all products **7** were of (*R*)-configuration, as revealed by the comparison of their optical rotations with the literature data. [d] The reaction was conducted with 1.6 equiv. of **6**. [e] The reaction was carried out for 1.5 h on a 1.8 mmol scale with 1.2 equiv. of **6a** and 0.5 mol-% catalyst loading. [f] Preformed [RhCl(**4b**)]$_2$ complex (3 mol-% Rh) used as a catalyst.

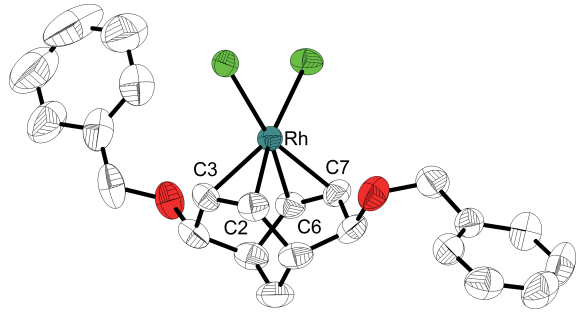
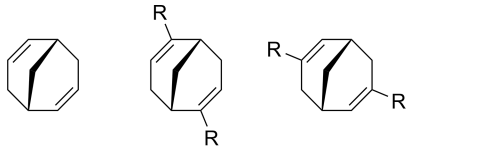



Figure 1. X-ray structure of [RhCl(**4b**)]$_2$ with thermal elipsoids drawn at the 50% probability (shown as a monomer; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh–C2 2.12, Rh–C3 2.09, ∠C2–Rh–C6 85, ∠C3–Rh–C7 102, ∠C2–C3/C7–C6 21.

Analysis of the key structural parameters of [RhCl(**4b**)]$_2$ reveals a very close resemblance to the Rh complexes of 2,6- and 3,7-disubstituted bicyclo[3.3.1]nona-2,6-diene ligands **9**[9b] and **10a**,[9c] reported by Hayashi (Figure 2). Thus, the core bicyclo[3.3.1]nona-2,6-diene scaffold in [RhCl(**4b**)]$_2$ complex shows similar structural data, i.e. the two double bonds (C2=C3 and C6=C7) coordinated to the rhodium centre are not parallel to each other but twisted

by 21°, resulting in very different C2–Rh–C6 and C3–Rh–C7 angles (85° and 102°, respectively). The bite angle of the diene coordination in [RhCl(**4b**)]$_2$ (87°) is almost identical to those reported for aryl-substituted bicyclo[3.3.1]nona-2,6-diene congeners **9** (89°) and **10a** (88°).




**8** **9** R = 4-MeC$_6$H$_4$ **10a** R = Ph **10b** R = 4-MeOC$_6$H$_4$CH$_2$

Figure 2. Other chiral bicyclo[3.3.1]nona-2,6-diene ligands.

Diene ligands **3**–**4** (Scheme 1) and **8**–**10** (Figure 2) belong to the same chiral series regardless of the actual chirality descriptors and all, with the exception of **9**, favour the formation of (*R*)-3-phenylcyclohexanone (**7aa**). Comparison of the results for bicyclo[3.3.1]nona-2,6-diene (**8**) (86 and 90% *ee* in dioxane and THF, respectively),[22] and ligands **3** (Table 1, entries 1 and 5), **4b** (Table 1, entries 3 and 6) clearly demonstrates the beneficial effect of the 4,8-*endo,endo*-substitution on asymmetric induction. In the [RhCl(**4b**)]$_2$ complex, the Rh–O distance was found to be 3.3 Å, whereas the distance between Rh and the methylene carbons of the benzyl groups ranged from 4.2 to 4.6 Å, depending on the conformation of the *O*-benzyl side chains. Inspection of the X-ray structure of [RhCl(**4b**)]$_2$, however, revealed no apparent steric distinction between the two diastereomeric reaction pathways that could rationalize the formation of (*R*)-configured 3-arylcycloalkanones **7** or diminished selectivity in the case of 2-cyclopentenone (**5b**) (Table 2, entries 12–13).[26,27] Similarly, in the case of the parent ligand **8**, which lacks bulky substituents but exhibits rather remarkable selectivity, no direct evidence of unfavourable steric hindrance to either diastereomeric transition state was found by theoretical calculations.[22] Apparently the stereochemical course of the reaction is determined by the cooperative effect of "crossed diene coordination" (expressed as the angle between the two Rh-coordinated C=C bonds) and by multiple, weak interactions between the spectator diene ligand and two substrate-derived, actor ligands arranged around the central Rh atom.[28] The enantioselectivity attained with **4b** in the reaction of cyclic enones with arylboronic acids matches the level reported for the most enantioselective ligand of bicyclo[3.3.1]nona-2,6-diene series, 3,7-bis(4-methoxybenzyl)bicyclo[3.3.1]-nona-2,6-diene (**10b**). The latter, however, is obtained from achiral bicyclo[3.3.1]nonan-3,7-dione, thus necessitating the preparative enantiomer resolution of diene **10b** by chiral HPLC.[9c]

## Conclusions

In conclusion, we have designed and synthesized 4,8-*endo,endo*-disubstituted bicyclo[3.3.1]nona-2,6-dienes as new $C_2$-symmetric chiral diene ligands for the Rh-catalyzed 1,4-addition of arylboronic acids to α,β-unsaturated ketones. Chiral dienes **4a**–**4f** were obtained in three straightforward synthetic steps from bicyclo[3.3.1]nonane-2,6-dione (**1**), easily available in an enantiomerically pure form by kinetic resolution of racemic **1** with baker's yeast. In comparison with the parent bicyclo[3.3.1]nona-2,6-diene (**8**), compounds **3** and **4a**–**4d** displayed enhanced levels of enantioselectivity, demonstrating the beneficial effect of 4,8-*endo,endo*-substitution on asymmetric induction. Rhodium catalyst with 4,8-bis(benzyloxy) diene **4b**, which emerged as a champion ligand, exhibited excellent activity under mild reaction conditions (30 min at room temperature) and high enantioselectivity (up to 96% *ee*) for cyclic enones with high atom efficiency (1.2–1.6 equiv. arylboronic acid). Further structural modification of chiral diene ligands based on 4,8-disubstituted bicyclo[3.3.1]nona-2,6-diene framework is currently under investigation.

## Experimental Section

**Typical Procedure for the 1,4-Addition of Boronic Acids to Cyclic Enones:** [Rh(C$_2$H$_4$)$_2$Cl]$_2$ (1.75 mg, 9.0 μmol Rh), ligand **4b** (3.3 mg, 9.9 μmol) and corresponding aryl boronic acid **6** (0.36 mmol, 1.2 equiv.) were combined in a flask equipped with a magnetic stir bar. The flask was flushed with argon, charged with deoxygenated THF (1 mL) and the resulting solution was stirred at 50 °C for 15 min to allow for ethylene–ligand exchange. The solution was cooled to room temperature and neat enone **5** (0.3 mmol, 1.0 equiv.) was added, followed by aqueous potassium hydroxide (100 μL, 1.5 M solution, 50 mol-%). The reaction mixture was allowed to stir for 30 min at room temperature, then diluted with ethyl acetate (10 mL), washed with a 10% aqueous solution of NaOH (2× 5 mL) and brine (2× 5 mL). The organic phase was dried (Na$_2$SO$_4$), evaporated and the obtained residue was purified by column chromatography on silica gel to afford corresponding 3-arylcycloalkanones **7** (for further details see the Supporting Information).

**Supporting Information** (see footnote on the first page of this article): Synthesis and characterization of the ligands, characterization of asymmetric 1,4-addition products, copies of $^1$H and $^{13}$C NMR spectra of new compounds, chiral HPLC traces and X-ray diffraction data.

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[23] It is unlikely that inactivity of bis(benzoate) **4f** is due to saponification under the reaction conditions. Control experiments revealed no signs of hydrolysis when **4f** (9.9 μmol) was stirred for 2 h at room temp. in a mixture of THF and 1.5 M aqueous KOH (10:1, 1.1 mL), whereas only partial hydrolysis occurred after 24 h at 50 °C.

[24] Typically, no starting enone in the reaction mixture could be detected by TLC after 10–15 min, but the reaction was carried out for 30 min to ensure full conversion.

[25] CCDC-1047973 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.

[26] Acyclic enones, such as 4-phenylbut-3-en-2-one (**5d**) and 1,3-diphenyl-2-propen-1-one (**5e**), exhibited diminished reactivity and rather modest enantioselectivity in Rh/**4b** catalyzed reaction with **6c** (40 and 17% *ee*, respectively) under standard conditions. In this case, the use of sterically encumbered boronic acids, such as **6j**, has beneficial effect on selectivity (89 and 81% *ee* with **5d** and **5e**, respectively).

[27] Rh/**4b** catalyzed arylation of unsaturated lactone furan-2(5*H*)-one with **6a** (1.2 equiv.) under standard conditions (30 min at room temp.) provided corresponding adduct in good yield (82%), but unsatisfactory enantioselectivity (30% *ee*).

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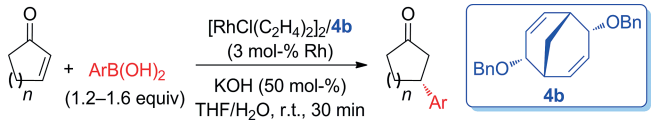
**Asymmetric Catalysis**




Chiral $C_2$-symmetric 4,8-*endo*,*endo*-disubstituted bicyclo[3.3.1]nona-2,6-diene ligands were synthesized from easily available bicyclo[3.3.1]nonane-2,6-dione and utilized in the asymmetric 1,4-addition reaction of arylboronic acids to cyclic enones. The catalyst prepared in situ from ligand **4b** and $[RhCl(C_2H_4)_2]_2$ exhibited excellent catalytic activity and high enantioselectivity (up to 96% *ee*) under mild reaction conditions with high atom efficiency.



**Keywords:** Asymmetric catalysis / Diene ligands / Michael addition / Rhodium