Chiral [2.2.2] Dienes as Ligands for Rh(I) in Conjugate Additions of Boronic Acids to a Wide Range of Acceptors

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The following includes general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the new compounds prepared. All reactions were performed in oven dried glass ware under argon. For the reactions, solvents were purified by distillation and dried by passage over activated alumina under an argon atmosphere (H₂O content < 30 ppm, Karl-Fischer titration). 2-Cyclohexenone and 2-cyclopentenone were distilled before used. Other commercially available chemicals were used as received unless noted otherwise. ¹H and ¹³C NMR spectra were recorded on a VARIAN Mercury 300 MHz or a Gemini 300 MHz. Infrared spectra were recorded on a Perkin-Elmer spectrum RX-I FT-IR or a Perkin Elmer spectrometer. High resolution mass spectra were obtained on a VG-TRIBRID for electron impact ionization (EI) or on a TSQ 7000 for electron-spray ionization (ESI). Combustion analyses were performed on a
Perkin Elmer AAnalyst 800 or on a Varian SpectraAA 400 Zeemann. Enantiomeric excesses were determined by chiral HPLC analysis with Merck-Hitachi D-7000 system. Optical rotation $[\alpha]_D$ were measured on a Jasco DID-1000 Polarimeter. The absolute configurations were assigned by comparison of the $[\alpha]_D$ values of known compounds. For the new adducts, it was assigned based on the established stereochemical outcome of the reaction.

**Ligand Synthesis**

The following includes the experimental details for the synthesis of the ligands as exemplified for ligand 1.

\[
\begin{align*}
\text{L-(-)-carvone (8)} & \xrightarrow{1. \text{ i-BuBr, Li, } \text{THF}} \text{L-(-)-carvone (8)} \\
& \xrightarrow{2. \text{ PCC, silica gel CH}_2\text{Cl}_2} 52\% \rightarrow \text{(5R)-3-isobutyl-5-isopropenyl-2-methyl-2-cyclohexen-1-one (9a).}
\end{align*}
\]

A solution of L-(-)-carvone (3.13 mL, 19.9 mmol), Li (693 mg, 99.8 mmol), iso-butylbromide (8.69 mL, 79.9 mmol) in THF (150 mL) was sonicated for 1.5 h. The reaction
mixture was cooled to 0 °C and quenched slowly with a saturated aqueous NH₄Cl solution followed by cold water. The THF was removed and the residual aqueous layer was extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over Na₂SO₄, and the solvent was evaporated. The crude alcohol was used for the next step without further purification. To a suspension/solution of PCC (8.40 g, 38.9 mmol) and silica gel (8.40 g) in CH₂Cl₂ (35 mL) was added a solution the crude alcohol in CH₂Cl₂ (35 mL). After stirring for 3 h, the reaction mixture was filtered through a pad of silica gel using CH₂Cl₂ as eluent to give the crude product. The latter was purified by flash chromatography using EtOAc/hexane (10:1) to give 9a (2.15 g, 52% from L-(-)-carvone) as a colorless oil. [α]D²⁷ 59.7 (c 0.95, CHCl₃); IR (neat) ν = 2956, 2869, 1667, 1627, 1463, 1381, 1165, 1129, 1081, 891 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.76-4.72 (m, 2H), 2.57-2.50 (m, 2H), 2.33-2.24 (m, 2H), 2.17-2.14 (m, 1H), 1.94-1.81 (m, 1H), 1.74 (s, 3H), 1.71 (s, 3H), 0.91 (d, 3H, J = 6.6 Hz), 0.88 (d, 3H, J = 6.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 199.1, 157.1, 146.7, 131.1, 110.1, 44.3, 42.7, 41.5, 36.5, 27.5, 23.0, 22.5, 20.6, 11.2; Anal. Calcd for C₁₄H₂₂O: C, 81.50; H, 10.75. Found: C,
81.24; H, 10.67. HRMS-EI calcd for C_{14}H_{22}O [M]^+ 206.1671, found 206.1666.

(1S,4S,8R)-6-isobutyl-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one (11a)

To a solution of 9a (2.11 g, 10.2 mmol) in CH_{2}Cl_{2} (11 mL) and MeOH (7 mL) at -10 °C was added NBS (2.18 g, 12.3 mmol) in small portions over 1 h and the reaction was allowed to warm to room temperature overnight. The reaction was diluted with CH_{2}Cl_{2} and washed with 1M aqueous NaOH. The aqueous layer was extracted with CH_{2}Cl_{2} (3×), the combined organic layers washed with brine, dried over Na_{2}SO_{4}, and the solvent evaporated. The crude product was purified by flash chromatography using EtOAc/hexane (85:15) to give the intermediate bromo compound (2.17 g, 68%) as a colorless oil. IR (neat) ν = 2955, 2688, 1663, 1629, 1459 cm^{-1}; ^1H NMR
(300 MHz, CDCl$_3$) δ 3.48-3.37 (m, 2H), 3.21 (m, 3H), 2.58-2.08 (m, 7H), 2.00-1.83 (m, 1H), 1.74 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 199.2, 199.0, 158.0, 156.9, 131.3, 131.1, 75.9, 75.7, 49.5, 49.4, 44.4, 44.3, 40.0, 39.9, 38.7, 37.9, 36.7, 36.5, 32.1, 31.2, 27.4 (2), 22.9 (2), 22.3, 18.1, 17.8, 11.0. To a solution of t-BuOK (1.18 g, 10.5 mmol) in t-BuOH (10.5 mL) at 0 °C was added a solution of the bromo compound in THF (11 mL). The reaction mixture was warmed to room temperature and stirred 28 h. Et$_2$O (75 mL) was added and the solution was washed with 0.5 M aqueous HCl (3×), brine, dried over Na$_2$SO$_4$, and the solvent was evaporated. Purification of the crude by flash chromatography using EtOAc/hexane (5:1) gave 11a (336 mg), dia-11a (133 mg) along with mixed fraction (845 mg), as colorless oils (1.31 g, 79%). [α]$_D^{28}$ 320.76 (c 1.37, CHCl$_3$); IR (neat) ν = 2954, 2869, 2826, 1722, 1464, 1368, 1144, 1083, 1068 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 6.04 (d, 1H, $J = 6.9$ Hz), 3.14 (s, 3H), 2.84-2.80 (m, 1H), 2.50 (dd, 1H, $J = 18.1$, 2.0 Hz), 1.93-1.76 (m, 3H), 1.70 (d, 1H, $J = 13.8$ Hz), 1.65-1.54 (m, 1H), 1.43 (d, 1H, $J = 13.8$ Hz), 1.23 (s, 3H), 1.10 (s, 3H), 0.88 (d, 3H, $J = 6.5$ Hz), 0.79 (d, 3H, $J = 6.5$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 213.1, 142.5, 129.8, 78.1, 52.7, 49.5, 46.7, 40.6, 40.2, 34.8, 26.7, 24.8, 22.6, 22.3, 14.8; Anal. Calcd
for C\textsubscript{15}H\textsubscript{24}O\textsubscript{2}: C, 76.23; H, 10.23. Found: C, 76.04; H, 10.12. HRMS-EI calcd for C\textsubscript{15}H\textsubscript{24}O\textsubscript{2} [M]\textsuperscript{+} 236.1776, found 236.1772.

\[
\text{LDA} \quad \text{allyl bromide} \quad \text{THF/DMPU (10:1)} \quad -78 \degree C \text{ to rt}
\]

\[
\begin{align*}
10a \quad 11a (87%)
\end{align*}
\]

\((1S,3S,4R,5R)-3\text{-allyl}-7\text{-isobutyl}-5\text{-methoxy-1,5-dimethylbicyclo[2.2.2]oct-7-en-2-one (11a)}\)

To a solution of \(i\)-Pr\textsubscript{2}NH (210 \mu L, 1.58 mmol) in THF (5 mL) and DMPU (500 \mu L) at 0 \degree C was added \(n\)-BuLi (1.44 mL, 1.58 mmol, 1.6 M/hexane) dropwise and the reaction was stirred 10 min at 0 \degree C. The solution was cooled to -78 \degree C and 10a (250 mg, 1.06 mmol) was added. After 1 h at -78 \degree C, freshly distilled allyl bromide (140 \mu L, 1.58 mmol) was added. The reaction was stirred for 1 h at -78 \degree C and warmed to rt and stirred another 5 h. The reaction was diluted with Et\textsubscript{2}O and a saturated aqueous solution of NH\textsubscript{4}Cl was added. The aqueous layer was extracted with Et\textsubscript{2}O (3\times), the combined organic layer washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, and the solvent evaporated. Purification of the crude by flash chromatography using EtOAc/hexane (10:1) gave 11a (254 mg, 87%) as a colorless oil. \([\alpha]\)\textsubscript{D}\textsuperscript{29} 189.0 (c 0.93,
CHCl₃); IR (neat) ν = 2954, 2862, 2812, 1717, 1639, 1460, 1368, 1072, 912 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.96 (d, 1H, J = 6.8 Hz), 5.83-5.70 (m, 1H), 5.04-4.98 (m, 2H), 3.12 (s, 3H), 2.78 (dd, 1H, J = 6.8, 1.7 Hz), 2.64-2.48 (m, 2H), 1.87-1.60 (m, 5H), 1.46 (d, 1H, J = 13.8 Hz), 1.22 (s, 3H), 1.12 (s, 3H), 0.86 (d, 3H, J = 6.8 Hz), 0.84 (d, 3H, J = 6.8 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 212.5, 141.1, 136.6, 128.4, 116.1, 78.3, 52.9, 49.4, 46.7, 43.5, 42.4, 39.9, 36.1, 26.9, 24.9, 22.8, 22.6, 15.0; Anal. Calcd for C₁₈H₂₈O₂: C, 78.21; H, 10.21. Found: C, 78.26; H, 10.43. HRMS-EI calcd for C₁₈H₂₈O₂ [M⁺] 276.2089, found 276.2084.

\[
\begin{align*}
1. \text{Et₂NLi, PhNTf₂} & \\
\text{THF/DMPU (10:1)} & -78 \degree \text{C to rt} \\
2. \text{Pd(OAc)₂, PPh₃} & \\
\text{HCO₂H, n-Bu₃N} & \\
\text{DMF, 60 °C} & 62% \\
\end{align*}
\]

(1R,4R,8R)-5-allyl-2-isobutyl-8-methoxy-1,8-dimethylbicyclo[2.2.2]octa-2,5-diene (1)

To a solution of Et₂NH (364 µL, 3.5 mmol) in THF (3.5 mL) and DMPU (350 µL) at 0 °C was added n-BuLi (2.55 mL, 3.5 mmol, 1.4 M/hexane) dropwise and the reaction was stirred
10 min at 0 °C. The solution was cooled to -78 °C and 11a (243 mg, 0.88 mmol) was added. After 1 h at -78 °C, a solution of PhNTf$_2$ (1.25 g, 3.5 mmol) in THF (1 mL) was added. The reaction was stirred for 1 h at -78 °C and warmed to rt and stirred overnight. The reaction was diluted with Et$_2$O and a saturated aqueous solution of NH$_4$Cl was added. The aqueous layer was extracted with Et$_2$O (3×), the combined organic layer washed with brine, dried over Na$_2$SO$_4$, and the solvent evaporated. The crude product was purified by flash chromatography using Et$_2$O/pentane (10:1) to give the triflate contaminated with PhNTf$_2$ side-products (348 mg). The crude was used in the next step without further purification. However, an analytically pure sample could be obtained as a colorless oil by additional flash chromatography. [α]$_D^{34}$ = -46.2 (c 0.50, CHCl$_3$); IR (neat) ν = 2957, 1445, 1402, 1245, 1210, 1140, 1093, 1063, 1027, 862 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 5.83 (d, 1H, $J = 6.3$ Hz), 5.78-5.63 (m, 1H), 5.09-4.99 (m, 2H), 3.35 (d, 1H, $J = 6.3$ Hz), 3.31-3.22 (m, 1H), 3.15 (s, 3H), 2.72 (dd, 1H, $J = 15.7$, 7.6 Hz), 2.01-1.84 (m, 2H), 1.79-1.68 (m, 2H), 1.41 (s, 3H), 1.25 (s, 3H), 0.88 (d, 3H, $J = 6.6$ Hz), 0.86 (d, 3H, $J = 6.6$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.3, 148.4, 134.3, 133.9, 126.9, 118.5 (q, $J = 320$ Hz), 117.0, 50.7,
50.3, 49.7, 46.9, 39.1, 33.9, 26.2, 24.7, 22.8, 22.6, 15.5.
To a solution of Pd(OAc)$_2$ (19 mg, 0.085 mmol), Ph$_3$P (45 mg, 0.17 mmol), and n-Bu$_3$N (610 µL, 2.56 mmol) in DMF (4 mL) was added the crude triflate (348 mg). The solution was stirred 5 min at room temperature, HCO$_2$H (64 µL, 1.70 mmol) was added, and the resulting solution was heated to 60 °C for 2 h. The reaction mixture was diluted with Et$_2$O, washed with 2M aqueous HCl (3×), the combined organic layers washed with brine, dried over Na$_2$SO$_4$, and the solvent evaporated. Purification of the crude by flash chromatography using Et$_2$O/pentane (20:1) gave the ligand **1** (142 mg, 62% from **11a**) as a colorless liquid). [α]$^{33}_{D}$ -83.2 (c 0.93, CHCl$_3$); IR (neat) ν = 3037, 2955, 2823, 1638, 1461, 1366, 1120, 1072, 910 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 5.87-5.74 (m, 2H), 5.67 (d, 1H, $J$ = 1.4 Hz), 5.04-4.98 (m, 2H), 3.27 (dd, 1H, $J$ = 6.4, 1.9 Hz), 3.18 (s, 3H), 3.19-2.96 (m, 1H), 2.89-2.81 (m, 1H), 1.91 (dd, 2H, $J$ = 6.8, 1.4 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.8, 145.8, 136.1, 132.1, 126.8, 115.6, 83.5, 50.7, 50.2, 50.1, 44.9, 39.6, 39.0, 26.6, 25.0, 22.9, 22.8, 20.3; Anal. Calcd for C$_{18}$H$_{28}$O: C, 83.02; H, 10.84. Found: C, 83.27; H, 11.00. HRMS-EI calcd for C$_{18}$H$_{28}$O [M]$^+$ 260.2140, found 260.2138.
1,4-addition of Boronic Acids

(3S)-3-phenylcyclohexanone. General procedure at 25 °C.

To [Rh(C₂H₄)₂Cl] (2.1 mg, 5.4 μmol) and 1 (3.1 mg, 11.9 μmol) in a Schlenk was added dioxane (1 mL). The resulting solution was stirred for 15 min, and KOH (1.5 M/H₂O, 120 μL, 0.18 mmol) was added. After stirring 15 min, PhB(OH)₂ (88 mg, 0.72 mmol) was added followed by 2-cyclohexenone (35 μL, 0.36 mmol) and the reaction was stirred until completion by TLC. Saturated aqueous NH₄Cl was added, and the aqueous layer was extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, and the solvent was evaporated to give the crude. The desired product was obtained (55 mg, 87%) as a colorless liquid after purification by flash chromatography using 20% Et₂O/hexane. The enantioselectivity was 95% ee (AD-H, 254 nm, hexane:2-propanol = 98:2, flow rate 0.5 ml/min). [α]ᵇ₂⁰⁻¹₈.₆ (c 1.045, CHCl₃) {lit.¹ [α]ᵇ₂⁰⁻₂².₀ (c 1.01, CHCl₃)}. 
All other spectroscopic data was in agreement with the literature.\textsuperscript{1}

(3S)-3-phenylcyclohexanone.

Following the general procedure at 25 °C on a 0.33 mmol scale using 2-cyclohexenone and 2-phenyl-1,3,2-dioxaboriane, the desired product (48 mg, 83%) was isolated by flash chromatography using 20% Et\textsubscript{2}O/hexane. The enantioselectivity was 96% ee.

(3R)-3-(4-methoxyphenyl)cyclohexanone. General procedure at 50 °C.

To [Rh(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}Cl] (1.9 mg, 4.9 µmol) and ent-1 (2.8 mg, 10.7 µmol) in a Schlenk was added dioxane (1 mL). The
resulting solution was stirred for 15 min, and KOH (1.5 M/H₂O, 113 µL, 0.17 mmol) was added. After stirring 15 min, 4-MeOPhB(OH)₂ (100 mg, 0.66 mmol) was added followed by 2-cyclohexenone (32 µL, 0.33 mmol) and the reaction was heated at 50 °C stirred until completion by TLC. Saturated aqueous NH₄Cl was added, and the aqueous layer was extracted with Et₂O (3×). The combined organic layers were washed with brine, dried over MgSO₄, and the solvent was evaporated to give the crude. The desired product was obtained (57 mg, 85%) was a colorless liquid after purification by flash chromatography using 25% Et₂O/hexane. The enantioselectivity was 96% ee (AD-H, 254 nm, hexane:2-propanol = 98:2, flow rate 0.5 ml/min). [α]D³³ 13.6 (c 1.15, CHCl₃) {lit.² [[α]D²⁰ 17.2 (c 0.96, CHCl₃)}. All other spectroscopic data was in agreement with the literature.²

![Chemical Reaction Diagram](image)

(3S)-3-(2-methoxyphenyl)cyclohexanone

Following the general procedure at 50 °C on a 0.34 mmol scale using 2-cyclohexenone and 2-methoxylphenylboronic
acid, the desired product (69 mg, 93%) was isolated by flash chromatography using 20% Et$_2$O/hexane. The enantioselectivity was 94% ee (OD, 254 nm, hexane:2-propanol = 95:5, flow rate 1.0 ml/min). [α]$_D^{32}$ -36.3 (c 1.02, CHCl$_3$). All other spectroscopic data was in agreement with the literature.$^3$

![Chemical Reaction Diagram]

(3S)-3-(4-acetylphenyl)cyclohexanone

Following the general procedure at 50 ºC on a 0.38 mmol scale using 2-cyclohexenone and 4-acetylphenylboronic acid, the desired product (79 mg, 96%) was isolated by flash chromatography using 30% EtOAc/hexane. The enantioselectivity was 97% ee (AD-H, 254 nm, hexane:2-propanol = 90:10, flow rate 0.5 ml/min). [α]$_D^{32}$ -7.8 (c 1.02, CHCl$_3$); IR (neat) ν = 2940, 1737, 1717, 1667, 1365, 1268, 1226, 1217, 960, 827 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.87 (m, 2H), 7.26 (m, 2H), 3.02 (m, 1H), 2.59-2.28 (m, 7H), 2.15-2.01 (m, 2H), 1.86-1.70 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ
Following the general procedure at 50 °C on a 0.36 mmol scale using 2-cyclohexenone and 2-fluorophenylboronic acid, the desired product (69 mg, 93%) was isolated by flash chromatography using 20% Et₂O/hexane. The enantioselectivity was 97% ee (OD, 254 nm, hexane:2-propanol = 99.5:0.5, flow rate 1.0 ml/min). [α]₀⁺D⁻³²⁻¹2.2 (c 1.40, CHCl₃). All other spectroscopic data was in agreement with the literature.³

Following the general procedure at 25 °C on a 0.30 mmol scale using 2-cyclopentenone and phenylboronic acid, the desired product (44 mg, 91%) was isolated by flash...
chromatography using EtOAc/hexane (5:1). The enantioselectivity was 94% ee (OBH, 254 nm, hexane:2-propanol = 99:1, flow rate 1.0 ml/min). $[\alpha]_D^{23} 24.2$ (c 0.49, CHCl$_3$). \cite{lit.4} $[[\alpha]_D^{20} 42.0$ (c 1.07, CHCl$_3$)}. All other spectroscopic data was in agreement with the literature.\cite{4}

\begin{center}
\begin{align*}
\text{[Rh(C$_2$H$_4$)$_2$Cl] (1.5 mol\%)} & \quad \text{ent-1 (3.3 mol\%)} \\
& \quad \text{KOH (0.5 equiv)} \\
& \quad \text{dioxane/H$_2$O} \\
& \quad 25 \, ^\circ\!\!C \\
\rightarrow & \quad \text{95\%, 97\% ee}
\end{align*}
\end{center}

\textbf{(3S)-3-phenylcyclopentanone}

Following the general procedure at 25 °C on a 0.30 mmol scale using 2-cyclopentenone and phenylboric anhydride, the desired product (46 mg, 95%) was isolated by flash chromatography using EtOAc/hexane (5:1). The enantioselectivity was 97% ee.

\begin{center}
\begin{align*}
\text{[Rh(C$_2$H$_4$)$_2$Cl] (1.5 mol\%)} & \quad \text{ent-1 (3.3 mol\%)} \\
& \quad \text{KOH (0.5 equiv)} \\
& \quad \text{dioxane/H$_2$O} \\
& \quad 50 \, ^\circ\!\!C \\
\rightarrow & \quad \text{98\%, 95\% ee}
\end{align*}
\end{center}

\textbf{(3R)-3-(3-chlorophenyl)cyclopentanone}

Following the general procedure at 50 °C on a 0.34 mmol scale using 2-cyclopentenone and 3-chlorophenylboronic
acid, the desired product (65 mg, 98%) was isolated by flash chromatography using 20% Et$_2$O/hexane. The enantioselectivity was 95% ee (OB-H, 254 nm, hexane:2-propanol = 98:2, flow rate 1.0 ml/min). [$\alpha$]$_D^{33}$ 57.9 (c 0.95, CHCl$_3$). [lit.$^2$] [[$\alpha$]$_D^{20}$ 75.3 (c 0.96, CHCl$_3$)]. All other spectroscopic data was in agreement with the literature.$^2$

\[
\begin{align*}
\text{cis-1} & \quad \text{KOH (0.5 equiv)} \\
\text{dioxane/H$_2$O} & \quad 25 ^\circ \text{C} \\
\text{EtOAc/hexane (4:1)} & \quad \text{97%, 90% ee}
\end{align*}
\]

\textbf{(3R)-3-[(\textit{E})-2-phenylvinyl]cyclopentanone}

Following the general procedure at 25 °C on a 0.30 mmol scale using 2-cyclopentenone and trans-2-phenylvinylphenylboronic acid, the desired product (53 mg, 97%) was isolated by flash chromatography using EtOAc/hexane (4:1). The enantioselectivity was 90% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 1.0 ml/min). [$\alpha$]$_D^{33}$ 70.7 (c 0.49, CHCl$_3$). All other spectroscopic data was in agreement with the literature.$^5$
(3R)-3-phenylcycloheptanone

Following the general procedure at 25 °C on a 0.30 mmol scale using 2-cycloheptenone and phenylboronic acid, the desired product (49 mg, 81%) was isolated by flash chromatography using EtOAc/hexane (5:1). The enantioselectivity was 95% ee (AD-H, 254 nm, hexane:2-propanol = 98:2, flow rate 0.5 ml/min). \([\alpha]_D^{25} 116.8 (c 0.35, CHCl_3)\). All other spectroscopic data was in agreement with the literature.\(^6\)

(4S)-4-phenyldihydro-2(3H)-furanone

Following the general procedure at 25 °C on a 0.36 mmol scale using 2-(5H)-furanone and phenylboronic acid, the desired product (39 mg, 80%) was isolated by flash chromatography using EtOAc/hexane (4:1). The enantioselectivity was 90% ee (AD-H, 254 nm, hexane:2-propanol = 98:2, flow rate 1.0 ml/min). \([\alpha]_D^{25} 45.8 (c 0.76, \ldots\)
(4S)-4-phenyl-2-chromanone

Following the general procedure at 50 °C on a 0.30 mmol scale using coumarin and phenylboronic acid, the desired product (29 mg, 43%) was isolated by flash chromatography using EtOAc/hexane (7:1). The enantioslectivity was 98% ee (OJ-H, 254 nm, hexane:2-propanol = 97:3, flow rate 1.0 ml/min). \([\alpha]_d^{33} 37.4 (c 0.74, \text{CHCl}_3)\) \{lit.\} \([\alpha]_d^{20} 43.7 (c 5.58, \text{C}_6\text{H}_6)\}. All other spectroscopic data was in agreement with the literature.\(^7\)

(4S)-4-(4-methoxyphenyl)-4-phenyl-2-butanone

Following the general procedure at 25 °C on a 0.30 mmol scale using trans-4-phenyl-3-buten-2-one and 4-
methoxyphenylboronic acid, the desired product (52 mg, 68%) was isolated by flash chromatography using EtOAc/hexane (5:1). The enantioselectivity was 90% ee (OD-H, 254 nm, hexane:2-propanol = 98:2, flow rate 1.0 ml/min). \([\alpha]_D^{33} -0.6 (c 0.72, \text{CHCl}_3)\). All other spectroscopic data was in agreement with the literature.\(^{10}\)

\[
\begin{align*}
\text{O} & \quad + \quad (\text{HO})_2\text{B} & \quad \text{Ph} \\
\text{2 equiv} & & \\
\text{[Rh}(\text{C}_2\text{H}_4)\text{Cl]}(1.5 \text{ mol\%}) & \quad \text{1 (3.3 mol\%)} & \quad \text{KOH (0.5 equiv)} \\
\text{dioxane/H}_2\text{O} & \quad 25 ^\circ\text{C} & \quad \text{78\%, 89\% ee}
\end{align*}
\]

\((4R,5E)-4\text{-methyl}-6\text{-phenyl}-5\text{-hexen}-2\text{-one}\)

Following the general procedure at 25 °C on a 0.26 mmol scale using 3-penten-2-one and trans-2-phenylvinylboronic acid, the desired product (37 mg, 78%) was isolated by flash chromatography using EtOAc/hexane (5:1). The enantioselectivity was 89% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min). \([\alpha]_D^{24} -58.4 (c 0.85, \text{CHCl}_3)\). {lit.\(^{11}\) \([\alpha]_D^{20} -57.3 (c 0.78, \text{CHCl}_3)\). All other spectroscopic data was in agreement with the literature.\(^{11}\)
(3R)-\(N, N, 3\)-triphenylbutanamide

Following the general procedure at 50 °C on a 0.30 mmol scale using (2E)-\(N, N\)-diphenyl-2-butenamide and phenylboronic acid, the desired product (93 mg, 93%) was isolated by flash chromatography using EtOAc/hexane (7:1). The enantioselectivity was 93% ee (OD-H, 254 nm, hexane:2-propanol = 98:2, flow rate 1.0 ml/min). \([\alpha]_D^{32} -71.4 (c 0.64, CHCl_3)\); IR (neat) \(\nu = 3060, 3027, 2962, 1666, 1591, 1489, 1451, 1363, 1292 \text{ cm}^{-1}\); \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta 7.31-7.01 \text{ (m, 15H)}, 3.40-3.18 \text{ (m, 1H)}, 2.44-2.61 \text{ (m, 2H)}, 1.29 \text{ (d, 3H, } J = 7.2 \text{ Hz)}\); \(^13C\) NMR (75 MHz, CDCl\(_3\)) \(\delta 171.7, 145.7, 142.7, 128.3, 127.1, 126.2, 43.6, 37.3, 21.6\).

(3R)-Methyl 3-phenylbutanoate

Following the general procedure at 25 °C on a 0.30 mmol scale using methyl crotonate and phenylboronic acid, the desired product (50 mg, 93%) was isolated by flash
chromatography using EtOAc/hexane (10:1). The enantioselectivity was 88% ee (OB-H, 254 nm, hexane:2-propanol = 99:1, flow rate 1.0 ml/min). $[\alpha]_D^{33} -18.9$ (c 0.72, CHCl$_3$). {lit.$^{12}$ $[\alpha]_D^{22} -29.4$ (c 1.02, CHCl$_3$)}. All other spectroscopic data was in agreement with the literature.

**Characterization data for the other ligands prepared**

![Molecule](image)

$(1S,3S,4R,5R)$-3-benzyl-5-methoxy-1,5-dimethyl-7-phenylbicyclo[2.2.2]oct-7-en-2-one

$[\alpha]_D^{29} -2.7$ (c 0.53, CHCl$_3$); IR (neat) $\nu = 3026, 2970, 2933, 2826, 1715, 1452, 1085, 1071, 1055, 762, 744$ cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.19-7.32 (m, 8H), 7.03-7.06 (m, 2H), 6.23 (d, 1H, $J = 6.9$ Hz), 3.34-3.38 (m, 1H), 2.91 (s, 3H), 2.87 (m, 1H), 2.81 (dd, 1H, $J = 6.9$ Hz, $J = 1.9$ Hz), 2.30-2.39 (m, 1H), 1.90 (d, 1H, $J = 14.0$ Hz), 1.70 (d, 1H, $J = 13.7$ Hz), 1.27 (s, 3H), 1.08 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 211.7, 144.2, 139.9, 138.1, 131.8, 128.7, 128.4, 128.2, 127.9, 127.3, 126.2, 78.7, 53.0, 49.2, 47.7, 44.8,
43.2, 37.6, 25.1, 16.7; HRMS-EI calcd for C$_{24}$H$_{26}$O$_2$ [M]$^+$ 346.1933, found 346.1927.

(1S,4R,8R)-3-benzyl-8-methoxy-1,8-dimethyl-6-phenylbicyclo[2.2.2]octa-2,5-dien-2-yltrifluromethanesulfonate

$[\alpha]_D^{34}$ -174.5 (c 0.69, CHCl$_3$); IR (neat) $\nu$ = 2968, 2938, 2824, 1686, 1599, 1400, 1207, 1136, 1086, 1063, 1046, 865, 764 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.21-7.34 (m, 6H), 7.12-7.15 (m, 4H), 6.00 (d, 1H, $J$ = 6.5 Hz), 4.12 (d, 1H, $J$ = 15.6 Hz), 3.32 (d, 1H, $J$ = 16.5 Hz), 3.31 (d, 1H, $J$ = 6.2 Hz), 3.20 (s, 3H), 1.95 (d, 1H, $J$ = 12.5 Hz), 1.48 (d, 1H, $J$ = 12.1 Hz), 1.36 (s, 3H), 1.31 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 185.2, 150.9, 140.6, 137.5, 135.2, 130.9, 129.0, 128.4, 128.3, 127.9, 127.2, 126.3, 83.3, 51.0, 50.7, 50.5, 47.3, 35.8, 24.8, 17.7; Anal. Calcd for C$_{25}$H$_{25}$F$_3$O$_4$S: C, 62.75; H, 5.27. Found: C, 63.02; H, 5.27.
(1R,4R,8R)-5-benzyl-8-methoxy-1,8-dimethyl-2-phenylbicyclo[2.2.2]octa-2,5-diene (2)

$[\alpha]_D^{33} = -150.4 \ (c \ 0.73, \ CHCl_3)$; IR (neat) $\nu = 3020, 2961, 2823, 1601, 1493, 1452, 1366, 1213, 1117, 1071, 751 \ \text{cm}^{-1}$; $^1H$ NMR (300 MHz, CDCl$_3$) $\delta 7.06-7.33 \ (m, \ 10H)$, 6.01 (d, 1H, $J = 6.2 \ \text{Hz}$), 5.79 (s, 1H), 3.72 (d, 1H, $J = 15.9 \ \text{Hz}$), 3.47 (d, 1H, $J = 15.9 \ \text{Hz}$), 3.35 (dd, 1H, $J = 6.5 \ \text{Hz}$, $J = 1.9 \ \text{Hz}$), 3.24 (s, 3H), 1.55 (d, 1H, $J = 11.8 \ \text{Hz}$), 1.44 (d, 1H, $J = 11.8 \ \text{Hz}$), 1.31 (s, 3H), 1.29 (s, 3H); $^{13}C$ NMR (75 MHz, CDCl$_3$) $\delta 151.7, 146.8, 139.4, 133.2, 131.4, 129.1, 128.1, 127.9, 127.6, 126.5, 125.8, 84.0, 51.1, 50.8, 50.3, 45.1, 41.0, 25.1, 22.0; HRMS-ESI calcd for C$_{24}$H$_{26}$NaO [MNa]$^+$ 353.1876, found 353.1881.
(1S,3S,4R,5R)-3-allyl-5-methoxy-1,5-dimethyl-7-phenylbicyclo[2.2.2]oct-7-en-2-one

[α]D31 115.3 (c 1.74, CHCl3); IR (neat) ν = 3016, 2970, 2943, 2933, 1737, 1442, 1366, 1228, 1216, 1075, 912, 699 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 7.46-7.54 (m, 3H), 7.23-7.26 (m, 2H), 6.44 (d, 1H, J = 6.9 Hz), 5.95-6.08 (m, 1H), 5.23-5.29 (m, 2H), 3.41 (s, 3H), 3.17 (d, 1H, J = 6.9 Hz), 2.86-2.92 (m, 2H), 2.07-2.18 (m, 1H), 2.12 (d, 1H, J = 14.0 Hz), 1.89 (d, 1H, J = 14.0 Hz), 1.56 (s, 3H), 1.25 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 212.0, 143.9, 138.1, 136.4, 132.0, 128.1, 127.8, 127.2, 116.5, 78.6, 53.0, 49.6, 47.2, 44.1, 42.5, 36.2, 25.2, 16.7; Anal. Calcd for C20H24O2: C, 81.04; H, 8.16. Found: C, 81.15; H, 8.30; HRMS-EI calcd for C20H24O2 [M]+ 296.1776, found 296.1772.
(1S,4R,8R)-3-allyl-8-methoxy-1,8-dimethyl-6-phenylbicyclo[2.2.2]octa-2,5-dien-2-yltrifluromethanesulfonate

$[\alpha]_D^{34} -126.3$ (c 1.42, CHCl$_3$); IR (neat) $\nu = 2976, 2828, 1686, 1639, 1400, 1206, 1137, 1088, 1046, 860$ cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.25-7.35 (m, 3H), 7.10-7.13 (m, 2H), 6.12 (d, 1H, $J = 6.5$ Hz), 5.71-5.85 (m, 1H), 5.06-5.13 (m, 2H), 3.53 (d, 1H, $J = 6.2$ Hz), 3.32-3.48 (m, 1H), 3.22 (s, 3H), 2.78-2.85 (m, 1H), 1.90 (d, 1H, $J = 12.4$ Hz), 1.47 (d, 1H, $J = 12.1$ Hz), 1.39 (s, 3H), 1.31 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 151.3, 148.1, 137.5, 134.6, 133.7, 130.6, 128.2, 127.8, 127.1, 117.1, 83.3, 51.2, 50.5, 50.4, 47.3, 34.2, 24.9, 17.4; Anal. Calcd for C$_{21}$H$_{23}$F$_3$O$_4$S: C, 58.87; H, 5.41. Found: C, 58.68; H, 5.63. HRMS-ESI calcd for C$_{21}$H$_{23}$F$_3$NaO$_4$S [MNa]$^+$ 451.1161, found 451.1163.
(1R,4R,8R)-5-allyl-8-methoxy-1,8-dimethyl-2-
phenylbicyclo[2.2.2]octa-2,5-diene (3)

$[\alpha]_D^{33} -150.3$ (c 0.84, CHCl$_3$); IR (neat) $\nu = 3040, 2961,$
2822, 1637, 1597, 1454, 1366, 1119, 1071, 910, 756 cm$^{-1}$; $^1$H
NMR (300 MHz, CDCl$_3$) $\delta$ 7.21-7.32 (m, 3H), 7.06-7.09 (m, 2H),
6.09 (d, 1H, $J = 6.5$ Hz), 5.79-5.93 (m, 2H), 5.03-5.10 (m, 2H),
3.43 (dd, 1H, $J = 6.5$ Hz, $J = 1.9$ Hz), 3.23 (s, 3H),
2.88-3.23 (m, 2H), 1.53 (d, 1H, $J = 12.1$ Hz), 1.43 (d, 1H, $J = 11.8$ Hz),
1.34 (s, 3H), 1.29 (s, 3H); $^{13}$C NMR (75 MHz,
CDCl$_3$) $\delta$ 152.0, 146.1, 139.4, 135.9, 132.3, 131.1, 127.8,
127.6, 126.4, 115.9, 83.9, 51.2, 50.7, 50.3, 45.1, 39.1,
25.1, 22.0; Anal. Calcd for C$_{20}$H$_{24}$O: C, 85.67; H, 8.63.
Found: C, 85.41; H, 8.76. HRMS-ESI calcd for C$_{20}$H$_{24}$NaO
[MNa]$^+$ 303.1719, found 303.1716.
(1S,3S,4R,5R)-5-methoxy-1,5-dimethyl-7-phenyl-3-propylbicyclo[2.2.2]oct-7-en-2-one

$[\alpha]_D^{31}$ 157.6 (c 1.70, CHCl$_3$); IR (neat) $\nu$ = 2957, 2932, 2871, 2826, 1714, 1451, 1144, 1069, 853, 764 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.24-7.30 (m, 3H), 7.01-7.04 (m, 2H), 6.22 (d, 1H, $J$ = 7.2 Hz), 3.21 (s, 3H), 2.95 (dd, 1H, $J$ = 6.9 Hz, $J$ = 1.9 Hz), 2.55-2.60 (m, 1H), 1.87 (d, 1H, $J$ = 13.7 Hz), 1.77-1.84 (m, 1H), 1.66 (d, 1H, $J$ = 13.7 Hz), 1.33-1.49 (m, 2H), 1.35 (s, 3H), 1.17-1.24 (m, 1H), 1.03 (s, 3H), 0.91 (t, 3H, $J$ = 7.2 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 213.5, 144.0, 138.1, 132.1, 128.2, 127.9, 127.2, 78.7, 52.8, 49.5, 47.1, 44.8, 42.6, 34.0, 25.2, 21.0, 16.6, 14.1; Anal. Calcd for C$_{20}$H$_{26}$O$_2$: C, 80.50; H, 8.78. Found: C, 80.38; H, 9.05; HRMS-EI calcd for C$_{20}$H$_{24}$O$_2$ [M]$^+$ 298.1933, found 298.1931.
(1S,4R,8R)-8-methoxy-1,8-dimethyl-6-phenyl-3-propylbicyclo[2.2.2]octa-2,5-dien-2-yl trifluoromethanesulfonate

$[\alpha]_D^{34} -55.0$ (c 1.26, CHCl$_3$); IR (neat) $\nu = 2969$, 1443, 1399, 1385, 1206, 1137, 1091, 1062, 1045, 862 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.26-7.34 (m, 3H), 7.08-7.11 (m, 2H), 6.12 (d, 1H, $J = 6.5$ Hz), 3.52 (d, 1H, $J = 6.2$ Hz), 3.21 (s, 3H), 2.44-2.54 (m, 1H), 2.02-2.12 (m, 1H), 1.90 (d, 1H, $J = 12.1$ Hz), 1.41-1.60 (m, 2H), 1.42 (d, 1H, $J = 12.1$ Hz), 1.39 (s, 3H), 1.29 (s, 3H), 0.92 (t, 3H, $J = 7.2$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 151.5, 147.5, 137.6, 137.2, 130.6, 129.8, 128.2, 127.8, 127.1, 83.2, 51.5, 50.4, 49.7, 47.1, 42.7, 31.7, 25.0, 20.4, 17.5, 14.0; HRMS-EI calcd for C$_{17}$H$_{17}$F$_3$O$_3$S [M-C$_4$H$_9$O]$^+$ 358.0850, found 358.0847 (Retro-Diels-Alder product).
(1R,4R,8R)-8-methoxy-1,8-diemthyl-2-phenyl-5-propylbicyclo[2.2.2]octa-2,5-diene (4)

$\alpha_D^{33} -71.5$ (c 0.65, CHCl$_3$); IR (neat) $\nu = 3039, 2956, 2928, 2870, 2823, 1596, 1454, 1366, 1196, 1158, 1120, 1071, 865, 847$ cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.23-7.32 (m, 3H), 7.05-7.08 (m, 2H), 6.08 (d, 1H, $J = 6.5$ Hz), 5.76 (s, 1H), 3.42 (dd, 1H, $J = 6.5$ Hz, $J = 1.9$ Hz), 3.23 (s, 3H), 2.17-2.23 (m, 2H), 1.41-1.55 (m, 2H), 1.52 (d, 1H, $J = 11.8$ Hz), 1.43 (d, 1H, $J = 12.1$ Hz), 1.34 (s, 3H), 1.28 (s, 3H), 0.88 (t, 3H, $J = 7.5$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 152.1, 148.1, 139.5, 131.2, 131.0, 127.8, 127.6, 126.4, 83.8, 51.5, 50.3, 44.9, 36.7, 25.1, 22.0, 20.5, 14.0; HRMS-ESI calcd for C$_{20}$H$_{26}$NaO $[\text{MNa}]^+$ 305.1876, found 305.1873.
(1S,3S,4R,5R)-3-(but-3-enyl)-5-methoxy-1,5-dimethyl-7-phenylbicyclo[2.2.2]oct-7-en-2-one

\([\alpha]_D^{31}\) 147.5 (c 1.74, CHCl\(_3\)); IR (neat) \(\nu = 3016, 2970, 2942, 1737, 1441, 1366, 1228, 1216, 1068, 910, 760\) cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.26-7.32\) (m, 3H), \(7.02-7.06\) (m, 2H), 6.25 (d, 1H, \(J = 6.9\) Hz), 5.77-5.86 (m, 1H), 5.00-5.09 (m, 2H), 3.22 (s, 3H), 2.97 (dd, 1H, \(J = 6.9, J = 1.9\) Hz), 2.58-2.63 (m, 1H), 2.14-2.22 (m, 2H), 1.92-1.96 (m, 1H), 1.88 (d, 1H, \(J = 14.0\) Hz), 1.67 (d, 1H, \(J = 13.7\) Hz), 1.37 (s, 3H), 1.18-1.40 (m, 1H), 1.04 (s, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 213.6, 152.9, 144.4, 138.4, 132.2, 128.4, 128.1, 127.5, 115.3, 78.9, 53.0, 49.8, 47.4, 45.0, 42.4, 32.2, 31.3, 25.4, 16.8; Anal. Calcd for C\(_{21}\)H\(_{26}\)O\(_2\): C, 81.25; H, 8.44. Found: C, 81.18; H, 8.35; HRMS-EI calcd for C\(_{21}\)H\(_{26}\)O\(_2\) [M]\(^+\) 310.1933, found 310.1929.
(1S,4R,8R)-3-(but-3-enyl)-8-methoxy-1,8-dimethyl-6-phenylbicyclo[2.2.2]octa-2,5-dien-2-yl trifluoromethanesulfonate

$[\alpha]_{D}^{34} -70.9$ (c 1.44, CHCl$_3$); IR (neat) $\nu = 2976, 2827, 1684, 1641, 1399, 1205, 1138, 1087, 1046, 861$ cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.26-7.35 (m, 3H), 7.07-7.11 (m, 2H), 6.11 (d, 1H, $J = 6.2$ Hz), 5.78-5.83 (m, 1H), 4.96-5.07 (m, 2H), 3.53 (d, 1H, $J = 6.2$ Hz), 3.21 (s, 3H), 2.58-2.64 (m, 1H), 2.16-2.30 (m, 3H), 1.90 (d, 1H, $J = 12.1$ Hz), 1.42 (d, 1H, $J = 12.1$ Hz), 1.39 (s, 3H), 1.29 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 151.4, 147.6, 137.6, 137.5, 136.6, 130.6, 128.2, 127.8, 127.1, 115.1, 83.2, 51.8, 50.4, 49.6, 47.1, 31.3, 29.3, 25.0, 17.4; Anal. Calcd for C$_{22}$H$_{25}$F$_3$O$_4$S: C, 59.72; H, 5.69. Found: C, 59.83; H, 5.83. HRMS-ESI calcd for C$_{22}$H$_{25}$F$_3$NaO$_4$S $[\text{MNa}]^+$ 465.1318, found 465.1325.
(1R,4R,8R)-5-(but-3-enyl)-8-methoxy-1,8-dimethyl-2-
phenylbicyclo[2.2.2]-octa-2,5-diene (5)

\[ \alpha \] \text{D}_{30} -53.4 (c 0.19, CHCl\textsubscript{3}); IR (neat) \nu = 2927, 1457, 1213, 1073, 864 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta 7.23-7.31 (m, 3H), 7.04-7.11 (m, 2H), 6.08 (d, 1H, \textit{J} = 6.3 Hz), 5.78-5.90 (m, 2H), 4.93-5.05 (m, 2H), 3.44 (dd, 1H, \textit{J} = 6.7 Hz, \textit{J} = 1.9 Hz), 3.22 (s, 3H), 2.22-2.34 (m, 3H), 1.38-1.50 (m, 3H), 1.33 (s, 3H), 1.28 (s, 3H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \delta 147.6, 139.5, 138.5, 131.2, 131.1, 128.2, 127.8, 127.6, 126.4, 114.4, 83.8, 51.8, 50.6, 50.3, 45.0, 34.1, 31.7, 25.2, 22.1; HRMS-ESI calcd for C\textsubscript{21}H\textsubscript{26}NaO \textit{[MNa]}\textsuperscript{+} 317.1876, found 317.1871.

(1R,4R,5R)-5-methoxy-1,5-dimethylbicyclo[2.2.2]octan-2-one

\[ \alpha \] \text{D}_{30} 1.5 (c 1.02, CHCl\textsubscript{3}); IR (film) \nu = 2927, 2826, 1721, 1454, 1375, 1220, 1174, 1085, 772 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta 3.13 (s, 3H), 2.62 (dt, 1H, \textit{J} = 18.6 Hz, \textit{J} = 2.9 Hz).
Hz), 2.18 (t, 1H, $J = 2.9$ Hz), 1.98 (dd, 1H, $J = 18.6$ Hz, $J = 2.8$ Hz), 1.50-1.86 (m, 6H), 1.33 (s, 3H), 0.91 (s, 3H);

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 216.4, 75.2, 48.9, 47.1, 44.0, 39.7, 36.6, 29.9, 23.2, 22.3, 19.9; HRMS-EI calcd for C$_{11}$H$_{18}$O$_2$ [M]$^+$ 182.1307, found 182.1302.

(1R,3S,4R,5R)-3-allyl-5-methoxy-1,5-dimethylbicyclo[2.2.2]octan-2-one

$[\alpha]_D^{24}$ 5.3 (c 0.57, CHCl$_3$); IR (film) $\nu = 2927$, 1718, 1640, 1457, 1375, 1067 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.69-5.82 (m, 1H), 5.00-5.13 (m, 2H), 3.10 (s, 3H), 2.64-2.72 (m, 2H), 1.86-2.09 (m, 2H), 1.40-1.79 (m, 6H), 1.36 (s, 3H), 0.90 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 218.0, 136.7, 116.4, 75.3, 48.7, 46.7, 45.4, 44.5, 38.0, 31.5, 30.6, 23.7, 19.9, 17.2; HRMS-ESI calcd for C$_{14}$H$_{22}$NaO$_2$ [MNa]$^+$ 245.1512, found 245.1509.
(1R,4R,5R)-3-allyl-5-methoxy-1,5-dimethylbicyclo[2.2.2]oct-2-en-2-yltrifluoromethanesulfonate

$[\alpha]_D^{26} \ 64.7$ (c 0.78, CHCl$_3$); IR (film) $\nu = 2943, 2823, 1401, 1209, 1140, 881$ cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.63-5.79 (m, 1H), 5.07-5.18 (m, 2H), 3.28-3.35 (m, 1H), 3.24 (dt, 1H, $J = 5.7$ Hz, $J = 1.5$ Hz), 3.09 (s, 3H), 2.79 (m, 1H), 2.71 (t, 1H, $J = 2.8$ Hz), 1.64-1.73 (m, 2H), 1.42-1.53 (m, 1H), 1.28 (s, 3H), 1.19 (s, 3H), 1.17-1.34 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 143.7, 133.9, 133.2, 117.4, 78.7, 50.8, 49.0, 45.0, 42.7, 34.5, 32.8, 23.2, 22.7, 20.2; Anal. Calcd for C$_{15}$H$_{21}$F$_3$O$_4$S: C, 50.84; H, 5.97. Found: C, 50.62; H, 5.98; HRMS-ESI calcd for C$_{15}$H$_{21}$F$_3$O$_4$NaS $[MNa]^+$ 377.1005, found 377.1000.

(1R,4R,5R)-3-allyl-5-methoxy-1,5-dimethylbicyclo[2.2.2]oct-2-ene (12)

$[\alpha]_D^{28} \ 95.4$ (c 0.67, CHCl$_3$); IR (film) $\nu = 2947, 1637, 1456, 1369, 1120, 1075, 994$ cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.78-
5.89 (m, 1H), 5.58 (s, 1H), 5.00-5.12 (m, 2H), 3.14 (s, 3H), 1.84-2.09 (m, 2H), 1.57-1.68 (m, 1H), 1.29 (s, 3H), 1.09-1.35 (m, 5H), 1.08 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.6, 136.1, 129.1, 115.7, 79.1, 50.9, 49.2, 42.6, 40.1, 35.6, 32.3, 25.2, 23.8, 23.6; Anal. Calcd for C$_{14}$H$_{22}$O: C, 81.50; H, 10.75. Found: C, 81.23; H, 10.72; HRMS-ESI calcd for C$_{14}$H$_{22}$NaO [MNa]$^+$ 229.1563, found 245.1559.

(1S,3S,4R,5R)-3-allyl-5-methoxy-1,5-dimethylbicyclo[2.2.2]oct-7-en-2-one

[α]$^D$$^25$ -275.5 (c 0.78, CHCl$_3$); IR (film) ν = 2972, 2930, 1720, 1640, 1449, 1080 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 6.34 (t, 1H, J = 6.8 Hz), 5.70-5.84 (m, 2H), 5.00-5.06 (m, 2H), 3.16 (s, 3H), 2.86 (d, 1, J = 6.8 Hz), 2.53-2.62 (m, 2H), 1.78 (d, 1H, J = 13.7 Hz), 1.75-1.81 (m, 1H), 1.47 (d, 1H, J = 13.7), 1.25 (s, 3H), 1.17 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 212.5, 136.5, 134.6, 133.2, 116.3, 78.9, 50.5, 49.5, 45.9, 44.4, 42.4, 36.0, 25.0, 17.4; HRMS-EI calcd for C$_{14}$H$_{20}$O [M]$^+$ 220.1463, found 220.1460.
(1S,4R,5R)-3-allyl-5-methoxy-1,5-
dimethylbicyclo[2.2.2]octa-2,7-dien-2-
yl trifluoromethanesulfonate

[α]_D^{27} 44.4 (c 0.65, CHCl₃); IR (film) ν = 2928, 2931, 2825, 1403, 1210, 1141, 869 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 6.27 (t, 1H, J = 6.2 Hz), 6.10 (dd, 1H, J = 7.2 Hz, J = 1.6 Hz), 5.64-5.77 (m, 1H), 5.00-5.10 (m, 2H), 3.42 (dd, 1H, J = 6.2 Hz, J = 1.6 Hz), 3.23-3.31 (m, 1H), 3.16 (s, 3H), 2.71-2.78 (m, 1H), 1.84 (d, 1H, J = 11.8 Hz), 1.47 (s, 3H), 1.25 (s, 3H), 1.23 (d, 1H, J = 11.8 Hz); ^1C NMR (75 MHz, CDCl₃) δ 147.8, 140.7, 133.9, 133.7, 133.3, 120.5, 117.1, 83.5, 51.7, 50.3, 48.6, 44.7, 34.1, 24.7, 17.9; Anal. Calcd for C₁₅H₁₉F₃O₄S: C, 51.13; H, 5.43. Found: C, 51.34; H, 5.58; HRMS-ESI calcd for C₁₅H₁₉F₃O₄NaS [MNa]^+ 375.0848, found 375.0842.
(1S,4R,5R)-3-allyl-5-methoxy-1,5-
dimethylbicyclo[2.2.2]octa-2,7-diene (13)

[$\alpha$]$_D^{33}$ 64.3 (c 0.45, CHCl$_3$); IR (film) $\nu$ = 2954, 2926, 2823,
1456, 1365, 1331, 1101, 1072 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$
6.26 (t, 1H, $J = 6.9$ Hz), 6.07 (d, 1H, $J = 7.2$ Hz), 5.72-
5.87 (m, 2H), 5.00-5.06 (m, H), 3.36 (dd, 1H, $J = 6.2$ Hz, $J$
= 1.5 Hz), 3.18 (s, 3H), 2.81-3.17 (m, 2H), 1.40 (s, 3H),
1.40 (d, 1H, $J = 11.8$ Hz), 1.22 (s, 3H), 1.19 (d, 1H, $J$
= 11.8 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 145.9, 141.7, 136.0,
133.4, 131.7, 115.9, 84.0, 51.2, 50.2, 49.5, 42.6, 39.1,
24.7, 22.2; Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87.
Found: C, 82.37; H, 9.81.

References


