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 (H_2O 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 ^{13}C 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**.

(5R)-3-isobutyl-5-isopropenyl-2-methyl-2-cyclohexen-1-one (9a).

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 NH_4Cl solution followed by cold water. The THF was removed and the residual aqueous layer was extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over Na_2SO_4 , 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 CH_2Cl_2 (35 mL) was added a solution the crude alcohol in CH_2Cl_2 (35 mL). After stirring for 3 h, the reaction mixture was filtered through a pad of silica gel using CH_2Cl_2 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. $[\alpha]_{\text{D}}^{27}$ 59.7 (c 0.95, CHCl_3); IR (neat) ν = 2956, 2869, 1667, 1627, 1463, 1381, 1165, 1129, 1081, 891 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) 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); ^{13}C NMR (75 MHz, CDCl_3) 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 $\text{C}_{14}\text{H}_{22}\text{O}$: 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.

(1*S*,4*S*,8*R*)-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 CH₂Cl₂ (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 CH₂Cl₂ and washed with 1M aqueous NaOH. The aqueous layer was extracted with CH₂Cl₂ (3×), the combined organic layers washed with brine, dried over Na₂SO₄, 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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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. Et₂O (75 mL) was added and the solution was washed with 0.5 M aqueous HCl (3×), brine, dried over Na₂SO₄, 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]_D²⁸ 320.76 (*c* 1.37, CHCl₃); IR (neat) ν = 2954, 2869, 2826, 1722, 1464, 1368, 1144, 1083, 1068 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₅H₂₄O₂: C, 76.23; H, 10.23. Found: C, 76.04; H, 10.12.

HRMS-EI calcd for C₁₅H₂₄O₂ [M]⁺ 236.1776, found 236.1772.

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

To a solution of *i*-Pr₂NH (210 μ L, 1.58 mmol) in THF (5 mL) and DMPU (500 μ L) at 0 $^\circ$ 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 $^\circ$ C. The solution was cooled to -78 $^\circ$ C and **10a** (250 mg, 1.06 mmol) was added. After 1 h at -78 $^\circ$ C, freshly distilled allyl bromide (140 μ L, 1.58 mmol) was added. The reaction was stirred for 1 h at -78 $^\circ$ C and warmed to rt and stirred another 5 h. The reaction was diluted with Et₂O and a saturated aqueous solution of NH₄Cl was added. The aqueous layer was extracted with Et₂O (3 $\times$), the combined organic layer washed with brine, dried over Na₂SO₄, 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. $[\alpha]_D^{29}$ 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.

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

To a solution of Et₂NH (364 μ L, 3.5 mmol) in THF (3.5 mL) and DMPU (350 μ L) 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 PhNTf₂ (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 Et₂O and a saturated aqueous solution of NH₄Cl was added. The aqueous layer was extracted with Et₂O (3×), the combined organic layer washed with brine, dried over Na₂SO₄, and the solvent evaporated. The crude product was purified by flash chromatography using Et₂O/pentane (10:1) to give the triflate contaminated with PhNTf₂ 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. $[\alpha]_D^{34}$ -46.2 (*c* 0.50, CHCl₃); IR (neat) ν = 2957, 1445, 1402, 1245, 1210, 1140, 1093, 1063, 1027, 862 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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), Ph₃P (45 mg, 0.17 mmol), and *n*-Bu₃N (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, HCO₂H (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 Et₂O, washed with 2M aqueous HCl (3×), the combined organic layers washed with brine, dried over Na₂SO₄, and the solvent evaporated. Purification of the crude by flash chromatography using Et₂O/pentane (20:1) gave the ligand **1** (142 mg, 62% from **11a**) as a colorless liquid). $[\alpha]_D^{33}$ -83.2 (*c* 0.93, CHCl₃); IR (neat) ν = 3037, 2955, 2823, 1638, 1461, 1366, 1120, 1072, 910 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₈H₂₈O: C, 83.02; H, 10.84. Found: C, 83.27; H, 11.00. HRMS-EI calcd for C₁₈H₂₈O [M]⁺ 260.2140, found 260.2138.

1,4-addition of Boronic Acids **(3S)-3-phenylcyclohexanone. General procedure at 25 °C.**

To $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]$ (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/ H_2O , 120 μL , 0.18 mmol) was added. After stirring 15 min, $\text{PhB}(\text{OH})_2$ (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 NH_4Cl was added, and the aqueous layer was extracted with Et_2O (3 $\times$). The combined organic layers were washed with brine, dried over MgSO_4 , 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% Et_2O /hexane. The enantioselectivity was 95% ee (AD-H, 254 nm, hexane:2-propanol = 98:2, flow rate 0.5 ml/min). $[\alpha]_{\text{D}}^{27}$ -18.6 (c 1.045, CHCl_3) {lit.¹ $[[\alpha]_{\text{D}}^{20}$ -22.0 (c 1.01, CHCl_3)}.

All other spectroscopic data was in agreement with the literature.¹

(3*S*)-3-phenylcyclohexanone.

Following the general procedure at 25 °C on a 0.33 mmol scale using 2-cyclohexenone and 2-phenyl-1,3,2-dioxaborinane, the desired product (48 mg, 83%) was isolated by flash chromatography using 20% Et_2O /hexane. The enantioselectivity was 96% ee.

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

To $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]$ (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 μ L, 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 μ L, 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 $\times$). 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). $[\alpha]_D^{33}$ 13.6 (*c* 1.15, CHCl₃) {lit.² $[\alpha]_D^{20}$ 17.2 (*c* 0.96, CHCl₃)}. All other spectroscopic data was in agreement with the literature.²

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

Following the general procedure at 50 °C on a 0.34 mmol scale using 2-cyclohexenone and 2-methoxyphenylboronic

acid, the desired product (69 mg, 93%) was isolated by flash chromatography using 20% Et₂O/hexane. The enantioselectivity was 94% ee (OD, 254 nm, hexane:2-propanol = 95:5, flow rate 1.0 ml/min). $[\alpha]_D^{32}$ -36.3 (*c* 1.02, CHCl₃). All other spectroscopic data was in agreement with the literature.³

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

Following the general procedure at 50 °C 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). $[\alpha]_D^{32}$ -7.8 (*c* 1.02, CHCl₃); IR (neat) ν = 2940, 1737, 1717, 1667, 1365, 1268, 1226, 1217, 960, 827 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) δ

210.0, 197.4, 149.5, 135.6, 128.7, 126.7, 48.4, 44.6, 41.1, 32.5, 26.6, 25.5; MS-ESI (m/z) 239 $[M + Na]^+$.

(3S)-3-(2-fluorophenyl)cyclohexanone

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). $[\alpha]_D^{32}$ -12.2 (c 1.40, CHCl₃). All other spectroscopic data was in agreement with the literature.³

(3R)-3-phenylcyclopentanone

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). $[\alpha]_D^{33}$ 24.2 (*c* 0.49, CHCl₃). {lit.⁴ $[[\alpha]_D^{20}$ 42.0 (*c* 1.07, CHCl₃)}. All other spectroscopic data was in agreement with the literature.⁴

(3*S*)-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.

(3*R*)-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% Et₂O/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, CHCl₃). {lit.² $[[\alpha]_D^{20}$ 75.3 (*c* 0.96, CHCl₃)}. All other spectroscopic data was in agreement with the literature.²

(3R)-3-[(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, CHCl₃). 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). $[\alpha]_{\text{D}}^{33}$ 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). $[\alpha]_{\text{D}}^{33}$ 45.8 (c 0.76,

CHCl₃). {lit.⁷ $[\alpha]_D^{20}$ 49.0 (c 3.1, CHCl₃)}. All other spectroscopic data was in agreement with the literature.⁷

(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 enantioselectivity 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, CHCl₃) {lit.⁸ $[\alpha]_D^{20}$ 43.7 (c 5.58, C₆H₆)}. All other spectroscopic data was in agreement with the literature.⁹

(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, CHCl_3). All other spectroscopic data was in agreement with the literature.¹⁰

(4*R*,5*E*)-4-methyl-6-phenyl-5-hexen-2-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, CHCl_3). {lit.¹¹ $[[\alpha]_D^{20} -57.3$ (c 0.78, 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). $[\alpha]_{\text{D}}^{32}$ -71.4 (c 0.64, CHCl_3); IR (neat) ν = 3060, 3027, 2962, 1666, 1591, 1489, 1451, 1363, 1292 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.31–7.01 (m, 15H), 3.40–3.18 (m, 1H), 2.44–2.61 (m, 2H), 1.29 (d, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 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, CHCl₃). {lit.¹² $[\alpha]_D^{22}$ -29.4 (c 1.02, CHCl₃)}. All other spectroscopic data was in agreement with the literature.

Characterization data for the other ligands prepared

(1*S*,3*S*,4*R*,5*R*)-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, CHCl₃); IR (neat) ν = 3026, 2970, 2933, 2826, 1715, 1452, 1085, 1071, 1055, 762, 744 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 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); ¹³C NMR (75 MHz, CDCl₃) δ 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.

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

$[\alpha]_D^{34}$ -174.5 (c 0.69, $CHCl_3$); IR (neat) ν = 2968, 2938, 2824, 1686, 1599, 1400, 1207, 1136, 1086, 1063, 1046, 865, 764 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{25}H_{25}F_3O_4S$: C, 62.75; H, 5.27. Found: C, 63.02; H, 5.27.

(1*R*,4*R*,8*R*)-5-benzyl-8-methoxy-1,8-dimethyl-2-phenylbicyclo[2.2.2]octa-2,5-diene (2)

$[\alpha]_{\text{D}}^{33}$ -150.4 (*c* 0.73, CHCl_3); IR (neat) ν = 3020, 2961, 2823, 1601, 1493, 1452, 1366, 1213, 1117, 1071, 751 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.06–7.33 (m, 10H), 6.01 (d, 1H, J = 6.2 Hz), 5.79 (s, 1H), 3.72 (d, 1H, J = 15.9 Hz), 3.47 (d, 1H, J = 15.9 Hz), 3.35 (dd, 1H, J = 6.5 Hz, J = 1.9 Hz), 3.24 (s, 3H), 1.55 (d, 1H, J = 11.8 Hz), 1.44 (d, 1H, J = 11.8 Hz), 1.31 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 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 $\text{C}_{24}\text{H}_{26}\text{NaO}$ $[\text{MNa}]^+$ 353.1876, found 353.1881.

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

$[\alpha]_D^{31}$ 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.

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

$[\alpha]_D^{34}$ -126.3 (*c* 1.42, CHCl_3); IR (neat) ν = 2976, 2828, 1686, 1639, 1400, 1206, 1137, 1088, 1046, 860 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{21}\text{H}_{23}\text{F}_3\text{O}_4\text{S}$: C, 58.87; H, 5.41. Found: C, 58.68; H, 5.63. HRMS-ESI calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{NaO}_4\text{S}$ $[\text{MNa}]^+$ 451.1161, found 451.1163.

(1*R*,4*R*,8*R*)-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) ν = 3040, 2961, 2822, 1637, 1597, 1454, 1366, 1119, 1071, 910, 756 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.41; H, 8.76. HRMS-ESI calcd for $\text{C}_{20}\text{H}_{24}\text{NaO}$ $[\text{MNa}]^+$ 303.1719, found 303.1716.

(1*S*,3*S*,4*R*,5*R*)-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, CHCl₃); IR (neat) ν = 2957, 2932, 2871, 2826, 1714, 1451, 1144, 1069, 853, 764 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 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); ¹³C NMR (75 MHz, CDCl₃) δ 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 C₂₀H₂₆O₂: C, 80.50; H, 8.78. Found: C, 80.38; H, 9.05; HRMS-EI calcd for C₂₀H₂₄O₂ [M]⁺ 298.1933, found 298.1931.

(1*S*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-6-phenyl-3-propylbicyclo[2.2.2]octa-2,5-dien-2-yltrifluoromethanesulfonate

$[\alpha]_{\text{D}}^{34}$ -55.0 (*c* 1.26, CHCl_3); IR (neat) ν = 2969, 1443, 1399, 1385, 1206, 1137, 1091, 1062, 1045, 862 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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, 1 H, 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) δ 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 $\text{C}_{17}\text{H}_{17}\text{F}_3\text{O}_3\text{S}$ $[\text{M}-\text{C}_4\text{H}_8\text{O}]^+$ 358.0850, found 358.0847 (Retro-Diels-Alder product).

(1*R*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-2-phenyl-5-propylbicyclo[2.2.2]octa-2,5-diene (4)

$[\alpha]_{\text{D}}^{33}$ -71.5 (*c* 0.65, CHCl_3); IR (neat) ν = 3039, 2956, 2928, 2870, 2823, 1596, 1454, 1366, 1196, 1158, 1120, 1071, 865, 847 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{20}\text{H}_{26}\text{NaO}$ $[\text{MNa}]^+$ 305.1876, found 305.1873.

(1*S*,3*S*,4*R*,5*R*)-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, CHCl₃); IR (neat) ν = 3016, 2970, 2942, 1737, 1441, 1366, 1228, 1216, 1068, 910, 760 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 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 Hz, *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); ¹³C NMR (75 MHz, CDCl₃) δ 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 C₂₁H₂₆O₂: C, 81.25; H, 8.44. Found: C, 81.18; H, 8.35; HRMS-EI calcd for C₂₁H₂₆O₂ [M]⁺ 310.1933, found 310.1929.

(1*S*,4*R*,8*R*)-3-(but-3-enyl)-8-methoxy-1,8-dimethyl-6-phenylbicyclo[2.2.2]octa-2,5-dien-2-yltrifluoromethanesulfonate

$[\alpha]_D^{34}$ -70.9 (*c* 1.44, CHCl_3); IR (neat) ν = 2976, 2827, 1684, 1641, 1399, 1205, 1138, 1087, 1046, 861 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{22}\text{H}_{25}\text{F}_3\text{O}_4\text{S}$: C, 59.72; H, 5.69. Found: C, 59.83; H, 5.83. HRMS-ESI calcd for $\text{C}_{22}\text{H}_{25}\text{F}_3\text{NaO}_4\text{S}$ $[\text{MNa}]^+$ 465.1318, found 465.1325.

(1*R*,4*R*,8*R*)-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_3); IR (neat) ν = 2927, 1457, 1213, 1073, 864 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.23–7.31 (m, 3H), 7.04–7.11 (m, 2H), 6.08 (d, 1H, J = 6.3 Hz), 5.78–5.90 (m, 2H), 4.93–5.05 (m, 2H), 3.44 (dd, 1H, J = 6.7 Hz, 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); ^{13}C NMR (75 MHz, CDCl_3) δ 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 $\text{C}_{21}\text{H}_{26}\text{NaO}$ $[\text{MNa}]^+$ 317.1876, found 317.1871.

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

$[\alpha]_{\text{D}}^{30}$ 1.5 (*c* 1.02, CHCl_3); IR (film) ν = 2927, 2826, 1721, 1454, 1375, 1220, 1174, 1085, 772 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.13 (s, 3H), 2.62 (dt, 1H, J = 18.6 Hz, J = 2.9

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) δ 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 $\text{C}_{11}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 182.1307, found 182.1302.

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

$[\alpha]_{\text{D}}^{24}$ 5.3 (c 0.57, CHCl_3); IR (film) ν = 2927, 1718, 1640, 1457, 1375, 1067 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{14}\text{H}_{22}\text{NaO}_2$ $[\text{MNa}]^+$ 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) ν = 2943, 2823, 1401, 1209, 1140, 881 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.63–5.79 (m, 1H), 5.07–5.18 (m, 2H), 3.28–3.50 (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) δ 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 $\text{C}_{15}\text{H}_{21}\text{F}_3\text{O}_4\text{S}$: C, 50.84; H, 5.97. Found: C, 50.62; H, 5.98; HRMS-ESI calcd for $\text{C}_{15}\text{H}_{21}\text{F}_3\text{O}_4\text{NaS}$ $[\text{MNa}]^+$ 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) ν = 2947, 1637, 1456, 1369, 1120, 1075, 994 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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 $\text{C}_{14}\text{H}_{22}\text{O}$: C, 81.50; H, 10.75. Found: C, 81.23; H, 10.72; HRMS-ESI calcd for $\text{C}_{14}\text{H}_{22}\text{NaO}$ $[\text{MNa}]^+$ 229.1563, found 245.1559.

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

$[\alpha]_{\text{D}}^{25}$ -275.5 (c 0.78, CHCl_3); IR (film) ν = 2972, 2930, 1720, 1640, 1449, 1080 cm^{-1} ; ^1H 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 $\text{C}_{14}\text{H}_{20}\text{O}$ $[\text{M}]^+$ 220.1463, found 220.1460.

(1*S*,4*R*,5*R*)-3-allyl-5-methoxy-1,5-dimethylbicyclo[2.2.2]octa-2,7-dien-2-yltrifluoromethanesulfonate

$[\alpha]_D^{27}$ 44.4 (c 0.65, CHCl_3); IR (film) ν = 2928, 2931, 2825, 1403, 1210, 1141, 869 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) 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); ^{13}C NMR (75 MHz, CDCl_3) 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 $\text{C}_{15}\text{H}_{19}\text{F}_3\text{O}_4\text{S}$: C, 51.13; H, 5.43. Found: C, 51.34; H, 5.58; HRMS-ESI calcd for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{O}_4\text{NaS}$ $[\text{MNa}]^+$ 375.0848, found 375.0842.

(1*S*,4*R*,5*R*)-3-allyl-5-methoxy-1,5-dimethylbicyclo[2.2.2]octa-2,7-diene (13)

$[\alpha]_{\text{D}}^{33}$ 64.3 (c 0.45, CHCl_3); IR (film) ν = 2954, 2926, 2823, 1456, 1365, 1331, 1101, 1072 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{14}\text{H}_{20}\text{O}$: C, 82.30; H, 9.87. Found: C, 82.37; H, 9.81.

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