A New Chiral Rh(II) Catalyst for Enantioselective [2+1]-Cycloaddition. Mechanistic Implications and Applications

Yan Lou, Manabu Horikawa, Robin A. Kloster, Natalie A. Hawryluk and E. J. Corey^{*}

Department of Chemistry and Chemical Biology

Harvard University, Cambridge, Massachusetts, 02138, USA

Supplementary Material

Part 1. Preparation of Catalysts 1 , 2 and 10	S 2
Part 2. Cyclopropanation Reactions with Ethyl Diazoacetate Catalyzed by 1	S 7
Part 3. Cyclopropanation and Other Reactions Catalyzed by 1	S 11
Part 4. Transformations of Ethyl (1 <i>S</i>)-2- <i>n</i> -Pentyl-2-cyclopropene-carboxylate	S 15
Part 5. Synthesis of (9 <i>R</i> ,10 <i>S</i>)-Dihydrosterculic Acid (12)	S 20
Part 6. ORTEP Presentations of Catalysts 1 , 2 and 10	S 25

Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvent. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium/benzophenone before use. Dichloromethane was freshly distilled from CaH₂ before use. Toluene was distilled from sodium. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F₂₅₄ pre-coated plates (0.25 mm). Merck CN F₂₅₄ plates were used in the preparation of catalyst **1**. Preparative thin-layer chromatography separations were carried out on 0.50 mm E. Merck silica gel plates (60F-254). Column

chromatography was performed using Bakerbond silica gel (40 μm particle size). Bakerbond Cyano 40 μm Prep LC Packing silica gel was used in the large-scale purification of catalyst **1**. NMR spectra were recorded on Varian Innova-500, or Mercury-400 instruments using residual undeuterated solvent as an internal standard. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. Optical rotation was measured using a Perkin-Elmer 241 Polarimeter. High-resolution mass spectral analyses were performed at Harvard University Mass Spectrometry Center. Analytical high performance liquid chromatography (HPLC) was performed on an Isco 2350 Series or a Waters 626 HPLC using the indicated chiral columns. Gas chromatography (GC) analyses were performed on a Hewlett-Packard 6850 Series GC System equipped with flame ionization detector using a J & W Scientific Cyclosil-B column (30 x 0.25 mm) or an Alltech Chiraldex γ -TA column (30 x 0.25 mm). Commercial grade reagents and solvents were used without further purification unless otherwise stated. All isolated compounds described herein were judged to be of $\geq 95\%$ purity as determined by ^1H and ^{13}C NMR spectroscopy.

Part 1. Preparation of Catalysts **1**, **2** and **10**

(4*R*,5*R*)-Diphenyl-imidazolidin-2-one¹

(1*R*,2*R*)-Diphenylethanediamine (0.537 g, 2.53 mmol) and DMAP (0.309 g, 2.78 mmol) were dissolved in CH_3CN (40 mL). Boc_2O (0.607 g, 2.78 mmol) was added in one portion and the reaction mixture was stirred at room temperature overnight. After

removal of solvent by rotary evaporation, the residue was purified by column chromatography (1:1 CH₂Cl₂-EtOAc) to provide 0.53 g (87%) of the known cyclic urea ¹ as white solid: $[\alpha]^{23}_{\text{D}} = +96^{\circ}$ (*c* 1.40, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.37 (m, 6H), 7.27 (d, *J* = 7.5 Hz, 4H), 4.90 (s, 2H), 4.60 (s, 2H) ppm.

(4*R*,5*R*)-Diphenyl-1-trifluoromethanesulfonyl-imidazolidin-2-one

A solution of (4*R*,5*R*)-diphenyl-imidazolidin-2-one (0.522 g, 2.19 mmol) and Et₃N (1.22 mL, 8.76 mmol) in CH₂Cl₂ (10 mL) was cooled to -78 °C. Triflic anhydride (0.85 mL, 5.0 mmol) was added dropwise via syringe. The resulting solution was stirred at -78 °C for 45 min and 1:1 H₂O-MeOH (5 mL) was added. The reaction mixture was warmed to room temperature, maintained for 30 minutes, and then diluted with Et₂O (300 mL). The organic layer was washed with 1N HCl (50 mL), brine (50 mL), dried, filtered and then concentrated *in vacuo*. Purification of this residue by flash chromatography (SiO₂, 100% CH₂Cl₂) gave the mono triflamide (0.62 g, 92%) as a white solid, mp 132 °C; $[\alpha]^{23}_{\text{D}} = +86^{\circ}$ (*c* 3.5, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.49-7.36 (m, 8H), 7.25 (dd, *J* = 2.0 Hz, 8.0 Hz, 2H), 5.89 (br s, 1H), 5.01 (d, *J* = 3.5 Hz, 1H), 4.77 ppm (d, *J* = 3.5 Hz, 1H); ¹³C NMR (CDCl₃, 400 MHz): δ 153.5, 139.3, 138.8, 129.7, 129.6, 129.6, 129.4, 126.4, 125.5, 119.0 (q, *J* = 321 Hz), 69.9, 62.4 ppm; FTIR (film): 3314, 1758, 1457, 1408, 1378, 1221, 1208, 1148, 1102, 1079, 1058, 1029 cm⁻¹; HRMS (ESI⁺) calcd for C₁₆H₁₃N₂O₃F₃S (M + H)⁺ 371.0677, found 371.0692.

Procedure for the preparation of (R,R)-Rh₂(OAc)(DPTI)₃ (1)

A flame-dried 5 mL round bottom flask was fitted with a Dean-Stark apparatus that was charged with a 5:1 mixture of anhydrous Na_2CO_3 and 4Å molecular sieves (powder) covered by a layer of cotton to prevent the solid mixture from entering the reaction flask. A mixture of $\text{Rh}_2(\text{OAc})_4$ (44 mg, 0.099 mmol) and (4*R*,5*R*)-diphenyl-1-(trifluoromethanesulfonyl)imidazolidin-2-one (115 mg, 0.310 mmol) in chlorobenzene (3 mL)^a was transferred into the 5 mL flask and heated at reflux with vigorous stirring under nitrogen in the Dean-Stark setup. Reflux was continued until all insoluble $\text{Rh}_2(\text{OAc})_4$ was consumed and TLC analysis (10:1 $\text{C}_6\text{H}_6\text{-CH}_3\text{CN}$) of the deep blue solution indicated that **1** had formed as the predominant product (*ca.* 20 h).^b After cooling, the reaction mixture was purified by silica gel chromatography (100% $\text{PhCH}_3 \rightarrow 5\% \text{CH}_3\text{CN}$ in PhCH_3) to give a purple solid, which contained a small impurity having a slightly higher R_f than **1**.^c This slightly impure product was further purified by preparative thin-layer chromatography with CH_2Cl_2 to afford pure **1** as purple solid (97 mg, 71%): TLC (10:1 $\text{C}_6\text{H}_6\text{-CH}_3\text{CN}$, 0.25 mm E. Merck silica gel 60 F₂₅₄ precoated plate), $R_f = 0.4$; (20:1 EtOAc-MeOH , Merck CN F₂₅₄ plate)^d, $R_f = 0.3$; mp >250 °C; $[\alpha]_D^{23} = +185^\circ$ (*c* 0.043, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 7.62 (t, $J = 7.5$ Hz, 2H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.41-7.16 (m, 17H), 6.99 (m, 2H), 6.92 (dd, $J = 7.5\text{Hz}$, 15Hz, 4H), 6.74 (t, $J = 7.5$ Hz, 2H), 4.99 (d, $J = 2.5$ Hz, 1H), 4.92 (d, $J = 2.5$ Hz, 1H), 4.79 (d, $J = 2.5$ Hz, 1H), 4.56 (d, $J = 2.5$ Hz, 1H), 4.08 (d, $J = 2.5$ Hz, 1H), 3.86 (d, $J = 2.5$ Hz, 1H) ppm; ^{19}F NMR (CDCl_3 , 400 MHz): Φ -74.7 (s, 1F), -75.0 (s, 1F), -75.1 (s, 1F) ppm; FTIR (film): 1667, 1402, 1227, 1198, 1065, 802 cm^{-1} ; MS (FAB) calcd for

$\text{C}_{50}\text{H}_{39}\text{F}_9\text{N}_6\text{O}_{11}\text{Rh}_2\text{S}_3 (\text{M})^+$ 1372, found 1372. The structure of **1** was determined by X-ray diffraction method.

Note:

- Using more dilute conditions resulted in slower reaction and a lower yield of the desired product **1**.
- A significant amount of a purple dirhodium compound that has slightly higher R_f was formed more rapidly than **1**, and is possibly a kinetically formed isomer of **1**. Upon longer refluxing in chlorobenzene, this product was gradually converted into **1**.
- This minor impurity is the more rapidly formed “kinetic” isomer of $\text{Rh}_2(\text{OAc})(\text{DPTI})_3$.
- Alternatively, for large-scale purification, the higher R_f impurity can be removed by reverse phase column chromatography (Bakerbond Cyano 40 μm Prep LC Packing silica gel) with EtOAc as the eluent.

Procedure for the preparation of $(R,R)\text{-Rh}_2(\text{DPTI})_4$ (2**)**

A mixture of $\text{Rh}_2(\text{OAc})_4$ (60 mg, 0.14 mmol) and $(4R,5R)$ -diphenyl-1-trifluoromethanesulfonyl-imidazolidin-2-one (527 mg, 1.72 mmol) in *m*-xylene (5 mL) was heated at reflux in a 10 mL round-bottom flask. The flask was equipped with a 10 mL pressure equalizing addition funnel, which contained 3 g of 5:1 mixture of CaH_2 /Celite 545. The entire apparatus was wrapped in glass wool and aluminum foil to ensure a reflux rate of about 1 drop/min at the condenser. The deep blue mixture was heated for a total of 48 h, ensuring that the solvent volume in the 10 mL flask was kept at 2-3 mL. After TLC (2% CH_3CN in C_6H_6) indicated that the product formed was

predominant, the mixture was cooled and concentrated *in vacuo*. Purification by silica gel chromatography (20:1 C₆H₆-CH₃CN) gave 115 mg (49%) of Rh₂(DPTI)₄ (**2**) as a purple solid: TLC (20:1 C₆H₆-CH₃CN), R_f = 0.5; [α]_D²³ = +275° (*c* 0.04, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.45-6.90 (m, 30H), 6.8 (m, 4H), 6.62 (t, *J* = 7.2 Hz, 2H), 6.54 (t, *J* = 7.2 Hz, 2H), 6.45 (d, *J* = 7.2 Hz, 2H), 5.41 (d, *J* = 8.5 Hz, 1H), 5.17 (d, *J* = 1.5 Hz, 1H), 5.11 (d, *J* = 8.0 Hz, 1H), 4.97 (d, *J* = 5.0 Hz, 1H), 4.91 (d, *J* = 8.5 Hz, 1H), 4.87 (d, *J* = 8.0 Hz, 1H), 3.27 (d, *J* = 4.5 Hz, 1H), 3.00 (br s, 1H) ppm; MS (FAB) calcd for C₆₄H₄₈F₁₂N₆O₁₂Rh₂S₄ (M)⁺ 1681, found 1681. The structure of **2** was determined by X-ray diffraction method.

Procedure for the preparation of (*M*)-(*R,R*)-*cis*-(*N,O*)-Rh₂(Piv)₂(DPTI)₂ (10**)**

A mixture of dirhodium(II) tetrapivalate (51 mg, 0.084 mmol) and (4*R*,5*R*)-diphenyl-1-trifluoromethanesulfonyl-imidazolidin-2-one (124 mg, 0.334 mmol) in toluene (1 mL) was heated at reflux for approximately 36h. After cooling and concentration, the reaction mixture was purified with preparative thin-layer chromatography (20:1 C₆H₆-CH₃CN) to afford **10** as blue solid (14 mg, 14%). The yield of this preparation of **10** has not been optimized. TLC (20:1 C₆H₆-CH₃CN), R_f = 0.4; ¹H NMR (CDCl₃, 400 MHz): δ 7.6-7.1 (m, 20H), 4.92 (d, *J* = 5.0 Hz, 2H), 4.59 (d, *J* = 5.0 Hz, 2H), and 1.08 (s, 18H) ppm; ¹⁹F NMR (CDCl₃, 400 MHz): Φ -74.6 (s) ppm. The structure of **10** was determined by X-ray diffraction method.

Part 2. Cyclopropenation Reactions with Ethyl Diazoacetate Catalyzed by 1

General procedure for the cyclopropenation reactions.

To a solution of alkyne (1.9 mmol, 10 eq) and $(R,R)\text{-Rh}_2(\text{OAc})(\text{DPTI})_3$ (**1**) (0.00095 mmol, 0.005 eq) in CH_2Cl_2 (1.8 mL), was added ethyl diazoacetate (0.19 mmol, 1 eq) in CH_2Cl_2 (1.2 mL) at room temperature through a syringe pump at a rate of 0.5 mL/h. After the addition was complete, the reaction mixture was filtered through a pipette column of neutral alumina, and flushed with CH_2Cl_2 to ensure complete elution of product. After removal of volatiles by rotary evaporation, the crude residue was purified by silica gel chromatography to provide the desired cyclopropene. Absolute configuration of the cyclopropene was determined by comparing the rotation sign with that previously reported. Enantiomeric excess was obtained either by gas chromatography or by HPLC on the specified chiral column.

(*S*)-Ethyl 2-pentylcycloprop-2-enecarboxylate (Table 1, entry 1) ²

Purification by column chromatography (20:1 hexanes-EtOAc) afforded the above cyclopropene (31 mg, 90%) as colorless liquid. The enantiomeric excess was determined to be 95% by GC (γ -TA column): 90 °C; 25 psi; t_R = 22.1 min (major), t_R = 23.9 min (minor); $[\alpha]_D^{23} = +76^\circ$ (c 0.6, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 6.32 (d, J = 1.6 Hz, 1H), 4.12 (m, 2H), 2.48 (dt, J = 1.6, 7.2 Hz, 2H), 2.12 (d, J = 1.6 Hz, 1H), 1.58 (quintet, J = 6.8 Hz, 2H), 1.33 (m, 4H), 1.25 (t, J = 6.8 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H)

ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 176.7, 115.6, 93.9, 60.1, 31.3, 26.3, 24.9, 22.3, 19.7, 14.4, 13.9 ppm; FTIR (film): 1712, 1180, 910, and 729 cm^{-1} ; HRMS (CI^+): calcd for $\text{C}_{11}\text{H}_{22}\text{NO}_2$ ($\text{M} + \text{NH}_4$) $^+$ 200.1651, found 200.1650.

(S)-Ethyl 2-hexylcycloprop-2-enecarboxylate (Table 1, entry 2)

Purification by column chromatography (20:1 hexanes-EtOAc) afforded the above cyclopropene (34 mg, 90%) as colorless liquid. The enantiomeric excess was determined to be 93% by GC (Cyclosil B column): $90\text{ }^\circ\text{C}$; 25 psi; $t_R = 91.9\text{ min}$ (major), $t_R = 89.9\text{ min}$ (minor); $[\alpha]_D^{23} = +67^\circ$ (c 0.08, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 6.29 (d, $J = 1.2\text{ Hz}$, 1H), 4.08 (m, 2H), 2.45 (dt, $J = 1.2, 7.6\text{ Hz}$, 2H), 2.08 (d, $J = 1.2\text{ Hz}$, 1H), 1.54 (quintet, $J = 7.6\text{ Hz}$, 2H), 1.26 (m, 9H), 0.85 ppm (t, $J = 7.2\text{ Hz}$, 3H); ^{13}C NMR (CDCl_3 , 400 MHz): δ 176.8, 115.8, 94.1, 60.3, 31.7, 30.0, 26.8, 25.2, 22.7, 19.9, 14.6, 14.2 ppm; FTIR (film): 2929, 1717, 1177, 1030, 731 cm^{-1} ; HRMS (ESI^+): calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 197.1541, found 197.1543.

(S)-Ethyl 2-(*t*-butyl)cycloprop-2-ene-1-carboxylate (Table 1, entry 3)²

Purification by column chromatography (20:1 hexanes-EtOAc) afforded the above cyclopropene (26 mg, 81%) as colorless liquid. The enantiomeric excess was determined to be 92% by GC (Cyclosil B column): $70\text{ }^\circ\text{C}$; 25 psi; $t_R = 16.3\text{ min}$ (major), $t_R = 17.7\text{ min}$ (minor); $[\alpha]_D^{23} = +74^\circ$ (c 0.8, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 6.17 (d, $J = 1.6\text{ Hz}$, 1H), 4.09 (m, 2H), 2.12 (d, $J = 1.6\text{ Hz}$, 1H), 1.20 (t, $J = 7.6\text{ Hz}$, 3H), 1.14 (s, 9H)

ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 176.5, 123.2, 91.0, 59.9, 31.1, 27.7, 19.7, 14.3 ppm.

(*S*)-Ethyl 2-(diethoxymethyl)cycloprop-2-ene-1-carboxylate (Table 1, entry 4)²

Purification by column chromatography (silica gel pretreated with 1% Et_3N) with 10:1 hexanes-EtOAc afforded the above cyclopropene (26 mg, 64%) as colorless liquid. The enantiomeric excess was determined to be 92% by GC (Cyclosil B column): 100 °C; 25 psi; t_{R} = 30.7 min (major), t_{R} = 29.4 min (minor); $[\alpha]_{\text{D}}^{23} = +47^\circ$ (c 0.12, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 6.78 (d, J = 0.8 Hz, 1H), 5.49 (d, J = 0.8 Hz, 1H), 4.12 (m, 2H), 3.59 (m, 4H), 2.34 (d, J = 0.8 Hz, 1H), 1.22 (m, 9H) ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 175.3, 112.9, 100.7, 95.9, 61.8, 61.5, 21.1, 15.4, 14.5 ppm; FTIR (film): 1721, 1186, 1053 cm^{-1} ; HRMS (CI^+): calcd for $\text{C}_{11}\text{H}_{22}\text{NO}_4$ ($\text{M} + \text{NH}_4$)⁺ 232.1549, found 232.1550.

(*S*)-Ethyl 2-(benzyloxymethyl)cycloprop-2-ene-1-carboxylate (Table 1, entry 5)

Purification by column chromatography (10:1 hexanes-EtOAc) afforded the above cyclopropene (38 mg, 86%) as colorless liquid. The enantiomeric excess was determined to be 92% by GC (Cyclosil B column): 155 °C; 25 psi; t_{R} = 30.4 min (major), t_{R} = 30.1 min (minor); $[\alpha]_{\text{D}}^{23} = +11^\circ$ (c 0.6, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.35 (m, 5H), 6.67 (d, J = 1.2 Hz, 1H), 4.61 (d, J = 1.2 Hz, 2H), 4.54 (s, 2H), 4.14 (m, 2H), 2.31 (d, J = 1.2 Hz, 1H), 1.25 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 175.8, 137.7,

128.7, 128.2, 128.1, 112.6, 97.9, 72.8, 63.8, 60.7, 20.4, 14.6 ppm; FTIR (film): 1712, 1182, 1091, 1026, 730, 697 cm^{-1} ; HRMS (ESI⁺): calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3$ ($\text{M} + \text{H}$)⁺ 233.1177, found 233.1174.

(S)-Ethyl 2-(methoxymethyl)cycloprop-2-ene-1-carboxylate (Table 1, entry 6)²

Purification by column chromatography (20:1 hexanes-EtOAc) afforded the above cyclopropene (23 mg, 78%) as colorless liquid. The enantiomeric excess was determined to be 92% by GC (γ -TA column): 80 °C; 25 psi; t_R = 28.2 min (major), t_R = 29.5 min (minor); $[\alpha]_D^{23} = +57^\circ$ (c 0.3, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 6.64 (dd, J = 1.6, 3.2 Hz, 1H), 4.42 (d, J = 1.6 Hz, 2H), 4.11 (m, 2H), 3.39 (s, 3H), 2.26 (d, J = 1.6 Hz, 1H), 1.22 (t, J = 7.20 Hz, 3H) ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 175.5, 112.2, 97.4, 65.90, 60.3, 58.5, 19.9, 14.2 ppm.

(S)-Ethyl 2-bromomethyl-cycloprop-2-enecarboxylate (Table 1, entry 7)³

Purification by column chromatography (20:1 hexanes-EtOAc) afforded the above cyclopropene (24 mg, 62%) as colorless liquid. The enantiomeric excess was determined to be 95% by GC (γ -TA column): 80 °C, 25 psi; t_R = 67.6 min (major), t_R = 64.8 min (minor); $[\alpha]_D^{23} = +70^\circ$ (c 1.15, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 6.66 (d, J = 1.2 Hz, 1H), 4.30 (dd, J = 1.2, 12.8 Hz, 1H), 4.22 (dd, J = 1.2, 12.8 Hz, 1H), 4.11 (m, 2H), 2.35 (d, J = 1.2 Hz), 1.22 (t, J = 8.0 Hz, 3H) ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 174.6, 111.7, 99.6, 60.5, 22.4, 21.0, 14.2 ppm.

(S)-Ethyl 2-(3-phenyl-allyloxymethyl)-cycloprop-2-ene-1-carboxylate (Table 1, entry 8)

This reaction was performed in pentane as solvent because the yield was only around 20% when the reaction was done in dichloromethane. Purification by column chromatography (20:1 hexanes-EtOAc) afforded the above cyclopropene (24 mg, 76%) as colorless liquid. The enantiomeric excess was determined to be 95% by HPLC (Chiralcel OJ column): 5% isopropanol in hexanes as eluent; flow rate = 0.9 mL/min; λ = 254 nm; t_R = 71.9 min (major), t_R = 86.0 min (minor); $[\alpha]_D^{25} = +25^\circ$ (c 1.65, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.39 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.25 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 1.6 Hz, 1H), 6.63 (d, J = 16 Hz, 1H), 6.29 (td, J = 6.4, 16 Hz), 4.56 (d, J = 1.6 Hz, 2H), 4.25 (td, J = 1.2, 6.4 Hz, 2H), 4.14 (m, 2H), 2.32 (d, J = 1.6 Hz, 1H), 1.25 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 175.6, 136.4, 133.2, 128.6, 127.8, 126.5, 125.1, 112.4, 97.6, 71.1, 63.4, 60.4, 20.2, 14.3 ppm; FTIR (film): 1716, 1187, 736, 694 cm^{-1} ; HRMS (CI^+): calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3$ 276.1600, found 276.1605.

Part 3. Cyclopropanation and Other Reactions Catalyzed by 1

Cyclopropanation of styrene with ethyl diazoacetate

The procedure is identical to the cyclopropenation described in Part 2. The crude mixture was purified with preparative thin-layer chromatography (10:1 hexanes-EtOAc) to give 9.5 mg (56%) of the *cis*-cyclopropane (**3**) and 4.5 mg (28%) of the *trans*-cyclopropane (**4**).^{4, 5} Diagnostic data for the *cis*-cyclopropane **3**: ¹H NMR (CDCl₃, 400 MHz): δ 7.27 (m, 4H), 7.20 (m, 1H), 3.87 (q, *J* = 6.8 Hz, 2H), 2.58 (q, *J* = 8.0 Hz, 2H), 2.08 (m, 1H), 1.72 (m, 1H), 1.33 (m, 1H), 0.97 (t, *J* = 6.8 Hz, 3H) ppm; [α]_D²³ = +48° (*c* 1.84, CHCl₃). Diagnostic data for the *trans*-cyclopropane **4**: ¹H NMR (CDCl₃, 400 MHz): δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.52 (m, 1H), 1.90 (m, 1H), 1.60 (m, 1H), 1.31 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm; [α]_D²³ = +14° (*c* 2.33, CHCl₃). The absolute configuration of compounds **3** and **4** was determined by comparison of the sign of their optical rotations with that reported.⁴ The enantiomeric excess was determined to be 99% for the *cis*-cyclopropane and 94% for the *trans*-cyclopropane by GC (Cyclosil B column): 130 °C; 25 psi; *t*_R = 30.3 min (major isomer of **3**), *t*_R = 32.5 min (minor isomer of **3**), *t*_R = 40.8 min (major isomer of **4**), *t*_R = 40.1 min (minor isomer of **4**).

Cyclopropanation of ethyl diazoacetate and 1,1-diphenylethylene

The procedure is identical to the cyclopropenation described in Part 2. The crude mixture was purified by preparative thin-layer chromatography (10:1 hexanes-EtOAc) to give cyclopropane **5**⁵ (52 mg, 74%) as colorless liquid. ¹H NMR (CDCl₃, 500 MHz): δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.5

Hz, 2H), 7.3 – 7.1 (m, 3H), 3.91 (m, 2H), 2.54 (dd, $J = 6.0, 8.5$ Hz, 1H), 2.18 (dd, $J = 5.0, 6.0$ Hz, 1H), 1.59 (dd, $J = 5.0, 8.5$ Hz, 1H), 1.01 (t, $J = 7.0$ Hz, 3H) ppm; The enantiomeric excess was determined to be 92% by HPLC ((*S,S*) Whelk-O1 column): 1% isopropanol in hexanes as eluent; flow rate = 1.0 mL/min; $t_R = 15.6$ min (major), $t_R = 14.9$ min (minor); The ester **5** was reduced to 1*S*-(2,2-diphenyl-cyclopropyl)-methanol ⁴ ($[\alpha]_D^{23} = +181^\circ$ (c 0.33, CH₂Cl₂)) with LAH in Et₂O at room temperature in order to determine the absolute configuration.

Competition experiments with a mixture of 4-methoxystyrene and 4-nitrostyrene

To a solution of 4-methoxystyrene (0.78 mmol, 10 eq), 4-nitrostyrene (0.78 mmol, 10 eq) and (*R,R*)-Rh₂(OAc)(DPTI)₃ (**1**) (0.00039 mmol, 0.005 eq) in CH₂Cl₂ (1 mL), ethyl diazoacetate (0.078 mmol, 1 eq) in CH₂Cl₂ (1 mL) was added at room temperature through a syringe pump at the rate of 0.1 mL/h. After the addition was complete, the reaction mixture was filtered through a pipette column of neutral alumina, which was flushed with CH₂Cl₂ to ensure complete transfer of product. This crude mixture was analyzed by GC (Cyclosil B column): 110 °C for 8 min then 2 °C/min to 180 °C then 180 °C for 30 min; 25 psi; $t_R = 35.36$ min (major *cis*-cyclopropane from 4-methoxystyrene), $t_R = 35.74$ min (minor *cis*-cyclopropane from 4-methoxystyrene), $t_R = 39.10$ min (*trans*-cyclopropanes from 4-methoxystyrene), $t_R = 51.77$ min (major *cis*-cyclopropane from 4-

nitrostyrene), $t_R = 52.11$ min (minor *cis*-cyclopropane from 4-nitrostyrene), $t_R = 58.86$ min (*trans*-cyclopropanes from 4-nitrostyrene). The ratio of cyclopropanes from 4-methoxystyrene versus cyclopropanes from 4-nitrostyrene was determined to be $\sim 1.7:1$. The *cis/trans* ratio of diastereoisomeric cyclopropanes from 4-methoxystyrene and 4-nitrostyrene was found to be 2.3 and 2.2 respectively. The enantiomeric excess for both of the *cis*-cyclopropyl esters was 97%. The ratios of cyclopropanes were determined solely on the relative GC areas without correction of relative response factors.

(2*S*,3*R*)-2,3-*cis*-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (7) ⁶

To a solution of (*R,R*)- $\text{Rh}_2(\text{OAc})(\text{DPTI})_3$ (**1**) (1.5 mg, 0.0011 mmol) in CH_2Cl_2 (1 mL), a solution of diazo ester **6** ⁶ (30 mg, 0.11 mmol) in CH_2Cl_2 (0.5 mL) was added at room temperature through a syringe pump at the rate of 0.1 mL/h. After addition, the reaction mixture was allowed to stir at room temperature for another 6 h before being concentrated *in vacuo*. The *cis/trans* ratio of **7** was determined to be 5:1 by ^1H NMR of the crude product. Purification by column chromatography (10:1 hexanes-EtOAc) gave *cis*-**7** (14 mg, 51%) as a colorless solid. The ^1H NMR is in accordance with that reported in literature.⁶ The absolute configuration was determined to be opposite to that reported ⁶ by comparison of the order of elution of the major isomer. The enantiomeric excess of **7** was determined to be 96% by HPLC (Daicel Chiralcel OD-H column): 10% isopropanol in hexanes as eluent; flow rate = 1.0 mL/min; $t_R = 19.0$ min (major), $t_R = 9.5$ min (minor).

Part 4. Transformations of Ethyl (1*S*)-2-*n*-Pentyl-2-cyclopropene-carboxylate

Cycloaddition reaction with cyclopentadiene ⁷

A solution of ethyl (1*S*)-2-*n*-pentyl-2-cyclopropene-carboxylate (40 mg, 0.22 mmol) and cyclopentadiene (145 mg, 2.20 mmol) in benzene (2 mL) was stirred at room temperature for 12 h. The residue after rotary evaporation was purified by column chromatography (20:1 hexanes-EtOAc) to afford the desired cycloadduct (51 mg, 94%) as colorless liquid: $[\alpha]^{23}_{\text{D}} = +66^{\circ}$ (*c* 0.35, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 5.92 (dd, *J* = 3.5, 4.5 Hz, 1H), 5.84 (dd, *J* = 3.5, 4.5 Hz, 1H), 4.07 (m, 2H), 2.91 (m, 1H), 2.77 (m, 1H), 1.91 (m, 1H), 1.87 (m, 2H), 1.65 (m, 1H), 1.59 (d, *J* = 7.0 Hz, 1H), 1.48 (d, *J* = 3.5 Hz, 1H), 1.43 (m, 1H), 1.32 – 1.14 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (CDCl₃, 500 MHz): δ 171.4, 132.8, 132.8, 62.0, 60.3, 48.9, 43.6, 35.2, 34.2, 32.2, 29.2, 28.7, 26.7, 22.9, 14.5, and 14.3 ppm; FTIR (film): 1720, 1454, 1401, 1315, 1193, 1168 1046 cm⁻¹; HRMS (ES⁺) calcd for C₁₆H₂₅O₂ (*M* + *H*)⁺ 249.1854, found 249.1852.

Cycloaddition reaction with 2,3-dimethylbutadiene

A solution of ethyl (1*S*)-2-*n*-pentyl-2-cyclopropene-carboxylate (17 mg, 0.093 mmol) in 2,3-dimethylbutadiene (0.2 mL) was heated at 80 °C in a sealed tube for 28 h. After being cooled to room temperature, the mixture was concentrated and purified with

column chromatography (30:1 hexanes-EtOAc) to provide the desired adduct (22 mg, 89%) as colorless liquid: $[\alpha]_D^{23} = +52^\circ$ (c 1.1, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 4.10 (q, $J = 7.5$ Hz, 2H), 2.36 (d, $J = 17.5$ Hz, 1H), 2.26 (d, $J = 17.5$ Hz, 1H), 2.16 (d, $J = 17.5$ Hz, 2H), 1.7-1.5 (m, 10H), 1.41 (m, 1H), 1.3-1.1 (m, 8H), 0.86 (t, $J = 7.5$ Hz, 3H) ppm; ^{13}C NMR (CDCl_3 , 500 MHz): δ 173.8, 122.1, 121.8, 60.3, 36.0, 33.1, 32.3, 32.1, 30.9, 28.0, 27.0, 26.6, 22.9, 19.4, 19.2, 14.6, 14.3 ppm; FTIR (film): 2857, 1720, 1451, 1369, 1348, 1295, 1244, 1224, 1153 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{17}\text{H}_{28}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 265.2163, found 265.2163.

((1*S*,2*S*)-2-Pentylcyclopropyl)methanol⁸

Lithium aluminum hydride (13 mg, 0.34 mmol) was added in one portion at 0 °C to a solution of ethyl (1*S*)-2-*n*-pentyl-2-cyclopropene-carboxylate (40mg, 0.22 mmol) in ether (2 mL). The suspension was warmed up to room temperature and stirred for 2 h before the sequential treatment with ethyl acetate and water. The resulting mixture was extracted with ether (20 mL x 2), washed with brine (20 mL), and dried with MgSO_4 . After removal of volatiles by rotary evaporation, the residue was purified by column chromatography (6:1 hexanes-EtOAc) to give the desired alcohol (25 mg, 80%) as colorless liquid: $[\alpha]_D^{23} = +40^\circ$ (c 0.20, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 3.43 (m, 2H), 1.29 (m, 8H), 0.88 (t, $J = 7.2$ Hz, 3H), 0.83 (m, 1H), 0.59 (m, 1H), 0.36 (dt, $J = 4.8$, 8.4 Hz, 1H), 0.30 (dt, $J = 4.8$, 8.4 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 67.3,

33.5, 31.6, 29.3, 22.6, 21.2, 17.2, 14.1, 9.90 ppm; FTIR (film): 2924, 1163, 1029 cm^{-1} ; HRMS (CI^+) calcd for $\text{C}_9\text{H}_{22}\text{NO}$ ($\text{M} + \text{NH}_4$) $^+$ 160.1701, found 160.1699.

((1*S*,2*S*,3*R*)-2-Iodo-3-pentylcyclopropyl)methanol

Lithium aluminum hydride (62 mg, 1.63 mmol) was added in one portion at 0 °C to a solution of ethyl (1*S*)-2-*n*-pentyl-2-cyclopropene-carboxylate (148 mg, 0.813 mmol) in ether (2 mL). The suspension was warmed up to room temperature and stirred for 2h. The reaction mixture was treated first with ethyl acetate (0.1 mL, freshly distilled from CaH_2) then cooled to 0 °C. A solution of iodine (0.83 g, 3.3 mmol) in ether (2 mL) was added dropwise via syringe. The resulting mixture was warmed up to room temperature and stirred for another hour. The brown reaction mixture was diluted with ether (20 mL), and washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL x 2) and brine (20 mL). The organic layer was dried with anhydrous MgSO_4 . After removal of volatiles by rotary evaporation, the residue was purified by column chromatography (6:1 hexanes-EtOAc) to give the desired iodide (155 mg, 71%) as pale yellow liquid: $[\alpha]_D^{23} = -5.8^\circ$ (c 2.8, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 3.91 (m, 1H), 3.49 (m, 1H), 2.38 (dd, $J = 4.5, 7.5\text{Hz}$, 1H), 1.75 (dd, $J = 4.5, 7.5\text{Hz}$, 1H), 1.42-1.22 (m, 8H), 0.98 (quintet, $J = 6.5\text{Hz}$, 1H), 0.89 (t, $J = 6.5\text{Hz}$, 1H), 0.70 (quintet, $J = 4.5\text{Hz}$, 1H) ppm; ^{13}C NMR (CDCl_3 , 400 MHz): δ 68.0, 32.2, 31.7, 28.5, 28.1, 24.9, 22.8, 14.3, -4.01 ppm; FTIR (film): 3339 (br), 2919, 2852, 1461, 1453, 1414, 1378, 1233, 11.81, 1037 cm^{-1} ; HRMS (CI^+) calcd for $\text{C}_9\text{H}_{21}\text{NIO}$ ($\text{M} + \text{NH}_4$) $^+$ 286.0668, found 286.0667.

((*S*)-2-Pentylcycloallyl)methanol⁹

Di-isobutyl aluminum hydride (1M in toluene, 0.266 mL) was added at -78 °C to the solution of ethyl (1*S*)-2-*n*-pentyl-2-cyclopropene-carboxylate (23 mg, 0.13 mmol) in toluene (1 mL). The resulting solution was stirred at -78 °C for 1 h then at room temperature for 1 h. The reaction mixture was treated with 1N HCl solution (20 mL) and extracted with ether (20ml x 2). The ether extraction was washed with brine (20 mL), dried with anhydrous MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (6:1 hexanes-EtOAc) to give the desired product (15 mg, 83%) as a colorless liquid: $[\alpha]_D^{23} = +40^\circ$ (*c* 0.20, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 6.63 (d, *J* = 0.8 Hz, 1H), 3.58 (dd, *J* = 4.0, 10.4Hz, 1H), 3.46 (dd, *J* = 4.0, 10.4Hz, 1H), 2.48 (t, *J* = 7.2 Hz, 1H), 1.69 (dd, *J* = 1.6, 7.2Hz, 1H), 1.58 (m, 2H), 1.34 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (CDCl₃, 400 MHz): δ 125.8, 101.6, 68.7, 31.4, 26.9, 26.3, 22.4, 20.4, 14.0 ppm; FTIR (film): 2922, 2856, 1457, 1379, 1164, 1013 cm⁻¹; HRMS (CI⁺) calcd for C₉H₂₀NO (M + NH₄)⁺ 158.1545, found 158.1548.

(1*S*,2*R*)-Ethyl 2-pentylcyclopropanecarboxylate¹⁰

5% Pd on CaCO₃ (14 mg, 0.0058 mmol) was added to a solution of ethyl (1*S*)-2-*n*-pentyl-2-cyclopropene-carboxylate (105 mg, 0.577 mmol) in ethyl acetate (1.5 mL) after being purged with hydrogen. The suspension was stirred vigorously under hydrogen atmosphere for 2 h when TLC indicated the complete consumption of the starting

material. The reaction mixture was then filtered through a short plug of celite, and concentrated *in vacuo*. The residue was purified with column chromatography (40:1 hexanes-EtOAc) to give the desired cyclopropane (97 mg, 92%) as colorless liquid: $[\alpha]_D^{23} = +32^\circ$ (*c* 0.40, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 4.12 (q, *J* = 7.5 Hz, 1H), 1.65 (m, 1H), 1.52 (m, 1H), 1.46 (m, 1H), 1.34 (m, 1H), 1.24 (m, 9H), 0.97 (m, 1H), 0.90 (m, 1H), 0.86 (m, 3H) ppm; ¹³C NMR (CDCl₃, 400 MHz): δ 173.3, 60.4, 31.8, 29.5, 27.2, 22.8, 22.2, 18.4, 14.6, 14.2, 13.5 ppm; FTIR (film): 2922, 2856, 1724, 1438, 1398, 1380, 1170, 1000 cm⁻¹; HRMS (CI⁺) calcd for C₁₁H₂₄NO₂ (M + NH₄)⁺ 202.1807, found 202.1810.

(1*S*,2*R*,3*S*)-Ethyl 2-(tri-*n*-butylstannyl)-3-pentylcyclopropanecarboxylate¹¹

Palladium *tetrakis*-(triphenylphosphine) (1 mg, 0.0008 mmol) and tri-*n*-butyltin hydride (0.025 mL, 0.093 mmol) were dissolved in THF (1 mL) and the solution was cooled to -78°C . After 5 min, a solution of ethyl (1*S*)-2-*n*-pentyl-2-cyclopropene-1-carboxylate (15 mg, 0.082 mmol) in THF (1 mL) was added at -78°C . The reaction mixture was warmed up to room temperature after 1 h and concentrated *in vacuo*. The residue was purified by column chromatography (20:1 hexanes-EtOAc) to give the desired product (32 mg, 82%) as colorless liquid: $[\alpha]_D^{23} = +109^\circ$ (*c* 1.1, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 4.12 (m, 2H), 1.7-1.4 (m, 9H), 1.35-1.15 (m, 17H), 1.12 (t, *J* = 4.5 Hz, 1H), 0.98 (dd, *J* = 4.5, 6.5 Hz, 1H), 0.94-0.76 (m, 16H) ppm; ¹³C NMR (CDCl₃, 500 MHz): δ 173.4, 60.3, 33.4, 32.2, 30.7, 29.3, 27.7, 22.9, 22.5, 21.3, 18.8, 14.6, 14.3, 13.9,

9.41 ppm; FTIR (film): 1723, 1457, 1377, 1155 cm^{-1} ; HRMS (Cl^+) calcd for $\text{C}_{23}\text{H}_{50}\text{NO}_2\text{Sn}$ ($\text{M} + \text{NH}_4$) $^+$ 492.2863, found 492.2875.

Part 5. Synthesis of (9*R*,10*S*)-Dihydrosterculic acid (**12**)

(*R*)-Ethyl 2-octylcycloprop-2-enecarboxylate (**13**)

A solution of ethyl diazoacetate (0.25 mL, 2.4 mmol) in dichloromethane (2 mL) was added slowly at room temperature to a mixture of (*S,S*)- $\text{Rh}_2(\text{OAc})(\text{DPTI})_3$ (17 mg, 0.012 mmol) and 1-decyne (1.0 mL, 5.7 mmol) in dichloromethane (10 mL) over 5 h. After removal of volatiles, the residue was purified by column chromatography (40:1 hexanes-EtOAc) to give the desired cyclopropene (**13**) (0.52 g, 98%) as colorless oil. The enantiomeric excess was determined to be 87% by GC (γ -TA column): 100 $^\circ\text{C}$; 25 psi; t_{R} = 80.8 min (major), t_{R} = 75.9 min (minor); $[\alpha]_{\text{D}}^{23} = -30^\circ$ (c 1.55, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 6.29 (d, J = 1.5 Hz, 1H), 4.09 (m, 2H), 2.47 (t, J = 7.5 Hz, 2H), 2.09 (d, J = 1.5 Hz, 1H), 1.54 (quintet, J = 7.5 Hz, 2H), 1.4 – 1.1 (m, 15H), 0.84 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (CDCl_3 , 500 MHz): δ 176.8, 115.8, 94.1, 60.3, 32.0, 29.4, 29.4, 29.3, 26.8, 25.2, 22.8, 19.9, 14.6, 14.3 ppm; FTIR (film): 2921, 2856, 1720, 1458, 1364, 1336, 1246, 1176, 1029 cm^{-1} ; HRMS (ES^+): calcd for $\text{C}_{14}\text{H}_{25}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 225.1854 found 225.1851.

Recovery of the catalyst (*S,S*)-1: after the complete elution of cyclopropene **13**, the blue band of **1** was eluted down with CH_2Cl_2 and concentrated in vacuo. The residue was

purified with preparative thin-layer chromatography (20:1 C₆H₆-CH₃CN) to afford pure **1** as purple solid (11 mg, 65% recovery). The recovered catalyst has the same ¹H NMR spectrum to that of the freshly prepared catalyst **1** and gave almost identical ee% for this cyclopropanation reaction as the fresh catalyst **1**.

(1*R*,2*S*)-Ethyl 2-octylcyclopropanecarboxylate

A suspension of cyclopropene **13** (0.50 g, 2.2 mmol) and 5% Pd on CaCO₃ (70 mg, 0.022 mmol) in ethyl acetate (20 mL) was vigorously stirred under hydrogen atmosphere. The reaction progress was monitored by TLC analysis until the complete consumption of starting material. The reaction mixture was filtered through a short plug of Celite, and concentrated *in vacuo*. The residue was purified by column chromatography (40:1 hexanes-EtOAc) to give the desired cyclopropane (450 mg, 90%) as colorless liquid: $[\alpha]_D^{23} = -28^\circ$ (*c* 5.0, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 4.20 (q, *J* = 7.5 Hz, 2H), 1.65 (m, 1H), 1.52 (m, 1H), 1.45 (m, 1H), 1.33 (m, 1H), 1.24 (m, 15H), 0.98 (m, 1H), 0.89 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (CDCl₃, 500 MHz): δ 173.2, 60.4, 32.1, 29.9, 29.8, 29.5, 29.5, 27.2, 22.9, 22.2, 18.4, 14.6, 14.3, 13.5 ppm; FTIR (film): 2925, 2859, 1724, 1438, 1399, 1382, 1170, 1096 cm⁻¹; HRMS (CI⁺) calcd for C₁₄H₃₀NO₂ (M + NH₄)⁺ 244.2277, found 244.2276.

((1*R*, 2*S*)-2-Octylcyclopropyl)methanol

Lithium aluminum hydride (27 mg, 0.71 mmol) was added in one portion at 0 °C to a solution of cyclopropyl ester (80 mg, 0.35 mmol) in ether (2 mL). The suspension was warmed to room temperature and stirred for 1 h. The reaction mixture was treated with saturated Na₂SO₄ solution (20 mL) and extracted with ether (20 mL x 2). The extracted organic solution was washed with brine (20 mL) and concentrated *in vacuo*. The residue was purified by column chromatography (6:1 hexanes-EtOAc) to give the desired alcohol (51 mg, 78%): $[\alpha]_D^{23} = +19^\circ$ (*c* 3.25, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 3.65 (dd, *J* = 7.5, 11Hz, 1H), 3.56 (dd, *J* = 7.5, 11Hz, 1H), 1.51 (br s, 1H), 1.50–1.15 (m, 14H), 1.10 (m, 1H), 0.88 (m, 4H), 0.69 (dt, *J* = 5.0, 8.0Hz, 1H), –0.04 (q, *J* = 5.0 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 400 MHz): δ 63.6, 32.2, 30.4, 29.9, 29.8, 29.6, 28.8, 22.9, 18.4, 16.4, 14.4, 9.7 ppm; FTIR (film): 3323 (br), 2921, 2850, 1467, 1030 cm^{–1}; HRMS (Cl⁺) calcd for C₁₂H₂₈NO (M + NH₄)⁺ 202.2171, found 202.2176.

(1*R*, 2*S*)-2-Octylcyclopropanecarboxaldehyde (14)

A solution of DMSO (0.118 mL, 1.66mmol) in dichloromethane (1 mL) was added dropwise at –78 °C to a solution of oxalyl chloride (0.072 mL, 0.83 mmol) in dichloromethane (1.5 mL). After 10 min, a solution of alcohol (51 mg, 0.28 mmol) in dichloromethane (1 mL) was added and the resulted mixture was stirred for 30 min before Et₃N (0.347 mL, 2.49 mmol) was slowly added at –78 °C. The reaction mixture was warmed to room temperature 15 min later and treated with saturated NH₄Cl solution (10 mL). The resulting mixture was then extracted with ether (15 mL x 2), washed with brine (15 mL), dried over MgSO₄ and concentrated *in vacuo*. The residue was purified

with column chromatography (20:1 hexanes-EtOAc) to give aldehyde **14** (48 mg, 95%) as colorless liquid: $[\alpha]_D^{23} = +12^\circ$ (c 1.0, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 9.34 (d, $J = 5.5$ Hz, 1H), 1.85 (m, 1H), 1.59 (m, 1H), 1.48 (m, 2H), 1.38 (m, 1H), 1.34–1.12 (m, 13H), 0.87 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (CDCl_3 , 500 MHz): δ 202.1, 32.1, 30.2, 29.7, 29.5, 28.5, 28.0, 25.0, 22.9, 15.0, 14.3 ppm; FTIR (film): 2920, 2853, 1704, 1462, 1452, 1366, 1177 cm^{-1} ; HRMS (CI^+) calcd for $\text{C}_{12}\text{H}_{26}\text{NO}$ ($\text{M} + \text{NH}_4$) $^+$ 200.2114, found 202.2114.

9-((1*R*, 2*S*)-2-Octylcyclopropyl)non-8-enoic acid (15**)**

$^n\text{BuLi}$ (2.87M, 0.276 mL) was added to a solution of $i\text{-Pr}_2\text{NH}$ (0.112 mL, 0.791 mmol) in THF (2 mL) at -78°C and stirred at this temperature for 0.5 h. Then $\text{BrPh}_3\text{P}(\text{CH}_2)_6\text{CO}_2\text{H}^{12}$ (186 mg, 0.396 mmol) was added in one portion at -78°C . The mixture was allowed to warm to room temperature and stirred for 2 h when the color of the reaction mixture turned orange red. A solution of aldehyde **14** (48 mg, 0.26 mmol) in THF (1 mL) was introduced dropwise via syringe at room temperature. The reaction mixture was stirred overnight before the treatment with 1N HCl solution (15 mL). The resulting mixture was extracted with ether (15 mL x 2), washed with brine (15 mL), dried with MgSO_4 , and concentrated *in vacuo*. The residue was purified by column chromatography (5:1 hexanes-EtOAc) to provide **15** (58 mg, 72%, *cis:trans* = $\sim 4:1$ by ^1H NMR integration) as colorless liquid: $[\alpha]_D^{23} = +40^\circ$ (c 1.2, CHCl_3). ^1H NMR for the *cis* isomer (CDCl_3 , 400 MHz): δ 9.49 (br s), 5.38 (dt, $J = 10.8, 6.8$ Hz, 1H), 5.04 (dd, $J = 9.2, 10.8$ Hz, 1H), 2.32 (m, 3H), 2.15 (q, $J = 6.4$ Hz, 2H), 1.64 (m, 2H), 1.54 (m, 1H),

1.43–1.20 (m, 18H), 0.89 (m, 4H), 0.09 (m, 1H) ppm; ^{13}C NMR for the *cis* isomer (CDCl_3 , 400 MHz): δ 179.7, 129.8, 129.7, 31.9, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 28.7, 27.3, 24.7, 22.7, 18.5, 14.2, 14.1, 13.9 ppm; FTIR (film): 2921, 2853, 1707, 1462, 1452, 1413, 1278, 1225, 1027 cm^{-1} ; HRMS (CI^+) calcd for $\text{C}_{19}\text{H}_{38}\text{NO}_2$ ($\text{M} + \text{NH}_4$) $^+$ 312.2903, found 312.2893.

(9*R*, 10*S*)-Dihydrosterculic acid (12**)**

An isomeric mixture of **15** (0.70 g, 2.3 mmol) was dissolved in 95% ethanol (40 mL) and anhydrous hydrazine (10 mL). A saturated aqueous CuSO_4 solution (1 mL) was added in five equal portions once every day. The mixture was vigorously stirred at room temperature for 5 days when ^1H NMR analysis of an aliquot showed the complete consumption of the starting material **15**. The reaction mixture was acidified with concentrated HCl solution and extracted with ether (15 mL $\times$ 4) and the combined organic layer was washed with 2N HCl solution (30 mL) and brine (30 mL), dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (5:1 hexanes-EtOAc) to afford an almost colorless solid, which was crystallized from petroleum ether at $-50\text{ }^\circ\text{C}$ to give dihydrosterculic acid (**12**) (0.60 g, 85%) as colorless solid, mp 29–30 $^\circ\text{C}$ 13 ; $[\alpha]_D^{23} = +0.92^\circ$ (c 14, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 9.8 (br s, 1H), 2.35 (t, $J = 7.5$ Hz, 2H), 1.64 (quintet, $J = 2.0$ Hz, 2H), 1.43–1.20 (m, 22H), 1.14 (m, 2H), 0.89 (t, $J = 8.0$ Hz, 3H), 0.65 (br s, 2H), 0.56 (dt, $J = 4.0, 8.0$ Hz, 1H), -0.33 (q, $J = 4.0$ Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 500 MHz): δ 180.0, 31.9, 31.6, 30.2, 30.1, 29.7, 29.4, 29.4, 29.3, 29.1, 28.7, 28.6, 24.7, 22.7, 22.6, 15.8, 15.7, 14.1, 10.9 ppm; FTIR

(film): 2917, 2850, 1708, 1216, 934 cm^{-1} ; HRMS (CI^+) calcd for $\text{C}_{19}\text{H}_{40}\text{NO}_2$ ($\text{M} + \text{NH}_4$) $^+$ 314.3059, found 314.3051.

Part 6. ORTEP Presentations of Catalysts 1, 2 and 10^{14, 15}

Figure 1. ORTEP presentation of (*R,R*)- $\text{Rh}_2(\text{OAc})(\text{DPTI})_3$ (**1**)

Figure 2. ORTEP presentation of $(R,R)\text{-Rh}_2(\text{DPTI})_4$ (**2**)

Figure 3. ORTEP presentation of $(M)\text{-(}R,R\text{)-cis-(N,O)-Rh}_2(\text{Piv})_2(\text{DPTI})_2$ (**10**)

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15. The axially coordinated molecules and solvent molecules were removed from the ORTEP presentations of catalysts **1**, **2** and **10** for better viewing.