Supporting Information

Catalytic Enantioselective Hydrostannation of Cyclopropenes

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NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz) instrument. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. ^{29}Si and ^{119}Sn NMR spectra were recorded using inverse-gated decoupling technique and chemical shifts were assigned relative to Me_4Si (δ 0.0) and Me_3SnPh (δ -30.0), correspondingly. Values of selected X-Sn coupling constants are given for ^{117}Sn and ^{119}Sn nuclei, respectively. If only one value is listed, it represents an averaged constant observed in cases where the difference between constant values for these isotopes was smaller than digital resolution of the recorded spectrum. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Chiral GC analysis was performed on a Hewlett Packard Model 5890 Series II GC equipped with J&W Scientific capillary columns Cyclodex B and Cyclosil B (both 30 m x 0.25 mm x 0.25 m). Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 63-200 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. HRMS (EI) analysis was performed on a JEOL GCmate II instrument, optical rotations were measured on Autopol III Rudolph Research Analytical polarimeter.

All manipulations with cyclopropenes and cyclopropylstannanes were conducted under argon atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous dichloromethane, DMSO, diethyl ether, and THF were purchased from Aldrich and stored over calcium hydride. Trimethyltin hydride,¹ ligands **C**, **D**,² and cyclopropenes **1a**,^{3,4} **1b**,⁵ were prepared according to the known procedures. Procedures for preparation of other cyclopropenes are provided below. All other reagents and solvents used were commercially available and purchased from Aldrich, Strem Chemicals Inc. or Acros Organics.

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  3. (a) Kudrevich, S. V.; Rubin, M. A.; Tarabaeva, O. G.; Surmina, L. S.; Baird, M. S.; Bolesov, I. G. *Russ. J. Org. Chem. (Engl. Transl.)* **1994**, 30, 1008; *Zh. Org. Khim.* **1994**, 30, 945.
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  5. (a) See Supporting Information: Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2002**, 124, 11566. (b) Rubin, M.; Gevorgyan, V. *Synthesis* **2004**, in press.

Cyclopropenes.

(1-Phenylcycloprop-2-en-1-yl)methanol MOM ether (1c). To a stirred at -78°C solution of ester **3**^{4,5b} (25 mmol, 4.35 g) in dry ether, DIBAL-H (1.0M solution in hexane, 2.0 equiv., 50 mmol, 50 mL) was added dropwise. The mixture was stirred for 1 hr at -78°C , then additionally for 1 hr at room temperature. Then, the mixture was quenched (saturated NH_4Cl), acidified (aqueous HCl), and extracted (ether). Combined organic phases were washed (NaHCO_3 , brine), dried (MgSO_4), filtered, and concentrated. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc, 3:1 to give alcohol **4**. Yield 3.323 g (22.7 mmol, 91%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.35 (s, 2H), 7.33 (t, 2H), 7.25 (d, 2H), 7.21 (t, 1H), 4.09 (s, 2H), 1.53 (br. s, 1H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 145.7, 128.2 (+, 2C), 126.3 (+, 2C), 125.9 (+, 113.1 (+, 2C), 67.9 (-), 29.1.

Cyclopropenylmethanol **4** (893 mg, 6.11 mmol) and $i\text{-Pr}_2\text{NEt}$ (1.5 equiv., 9.17 mmol, 1.57 mL) were stirred in dry dichloromethane (10 mL) at 0°C , and MOMCl (1.5 equiv., 9.17 mmol, 0.71 mL) was added. The mixture was stirred at room temperature overnight. When GC/MS analysis had shown the completion of the reaction, the mixture was quenched (2% aqueous HCl) and extracted (CH_2Cl_2). The combined organic phases were washed (water, brine), dried (MgSO_4), filtered, and concentrated. The residue was purified by preparative column chromatography on Silica gel, eluent – hexane:EtOAc 10:1 (R_f = 0.26) to give **1c**. Yield 925 mg (4.86 mmol, 80%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.32 (s, 2H), 7.33-7.26 (m, 4H), 7.19 (t, 1H), 4.70 (s, 2H), 4.03 (s, 2H), 3.37 (s, 3H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 146.3, 128.0 (+, 2C), 126.3 (+, 2C), 125.6 (+, 112.8 (+, 2C), 96.3 (-), 74.9 (-), 55.3 (+), 26.5; GC/MS m/z 190 (M^+ , 2%), 145 ($\text{M}^+ - \text{CH}_2\text{OMe}$, 10%), 128 ($\text{M}^+ - \text{HOCH}_2\text{OMe}$, 100%), 115 ($\text{M}^+ - \text{CH}_2\text{OCH}_2\text{OMe}$, 75%).

[1-Phenylcycloprop-2-en-1-yl]methyl acetate (1e). To a stirred solution of alcohol **4** (1.00 g, 6.84 mmol) and dry pyridine (1.2 mL) in anhydrous CH_2Cl_2 (10 mL) was added acetic anhydride (1.0 mL). The mixture was stirred overnight at room temperature, then quenched (water) and extracted (CH_2Cl_2). Combined organic phases were washed (diluted aqueous HCl , 10% NaHCO_3 , brine), dried (MgSO_4), filtered, and concentrated in vacuum. The residue was purified by preparative column chromatography on silica gel, eluent hexane-ether 5:1. Yield: 1.043 g (5.54 mmol, 81%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.34-7.31 (m, 2H), 7.25 (s, 2H), 7.24-7.20 (m, 3H), 4.55 (s, 2H), 2.07 (s, 3H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 171.2, 145.5, 128.2 (+, 2C), 126.2 (+, 2C), 125.8 (+, 112.0 (+, 2C), 71.2 (-), 25.9, 21.1 (+); GC/MS m/z 188 (M^+ , 1%), 145 ($\text{M}^+ - \text{CH}_3\text{CO}$, 7%), 128 ($\text{M}^+ - \text{AcOH}$, 100%), 115 ($\text{M}^+ - \text{CH}_2\text{OAc}$, 45%).

[1-(4-Chlorophenyl)cycloprop-2-en-1-yl]methyl acetate (1f). To a suspension of $\text{Rh}_2(\text{OAc})_4$ (29 mg) in TMS-acetylene (60 mL) stirred at reflux a solution of methyl diazo(4-chlorophenyl)acetate **5**⁶ (2.11 g, 10 mmol) in TMS-acetylene (7 mL) was added *via* syringe pump over 16 hrs. After the addition was complete, the mixture was refluxed for additional 2 hrs, when GC/MS analysis showed completion of the reaction. Then, the reflux condenser was changed for distillation unit and the most of TMS-acetylene was distilled off under ambient pressure. The residue was filtered through a short column of Silica gel, (eluent – EtOAc) and the eluate was concentrated and dissolved in THF (50 mL). To the obtained solution 10% aqueous K_2CO_3 (20 mL) was added dropwise at 0°C. The mixture was warmed to room temperature and stirred for 1 hr, when GC/MS analysis showed completion of the reaction. Two layers were separated; an organic layer was concentrated and combined back with aqueous phase. Ice-cold water was added, and the mixture was extracted with ether. Combined organic phases were washed (brine), dried (MgSO_4), filtered, and concentrated in vacuum. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc 5:1 to obtain ester **6**. Yield 1.785 g (8.56 mmol, 86%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.27-7.26 (m, 2H), 7.22-7.19 (m, 2H), 7.20 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 175.1, 140.0, 132.4, 129.6 (+, 2C), 128.2 (+, 2C), 107.4 (+, 2C), 52.4 (+), 30.0;

To a stirred solution of ester **6** (1.785 g 8.56 mmol) in dry ether (20 mL), DIBAL-H (1.0 M solution in hexanes, 17.5 mL, 2.0 equiv.) was added dropwise at -78°C. The mixture was stirred for 1 hr at -78°C, then warmed to room temperature and stirred for additional 1 hr, and then quenched with saturated NH_4Cl . Formed gel was dissolved in 2 N aqueous HCl, and extracted with ether. Combined ethereal layers were washed with NaHCO_3 and brine, dried MgSO_4 , filtered, and evaporated. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc 3:1 to obtain alcohol **7**. Yield 1.108 g (6.13 mmol, 72%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.31 (s, 2H), 7.30-7.28 (m, 2H), 7.20-7.18 (m, 2H), 4.03 (s, 2H), 2.33 (br. s 1H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 144.6, 131.5, 128.2 (+, 2C), 127.9 (+, 2C), 112.9 (+, 2C), 68.2 (-), 28.6.

To a stirred solution of cyclopropenyl methanol **7** (1.108 g, 6.13 mmol) and dry pyridine (1.5 mL) in dry CH_2Cl_2 (10 mL), acetyl chloride (1.0 mL) was added dropwise. The mixture was stirred at room temperature for 1 hr, when GC/MS analysis showed completion of the reaction. The reaction mixture was quenched with water and extracted

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with CH_2Cl_2 . Combined organic phases were washed (dilute aqueous HCl , NaHCO_3 , brine), dried (MgSO_4), filtered, and concentrated. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-ether 7:1 to afford **1f**. Yield 1.201 g (5.39 mmol, 88%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.26-7.24 (m, 2H), 7.23 (s, 2H), 7.13-7.11 (m, 2H), 4.47 (s, 2H), 2.05 (s, 3H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 171.1, 144.1, 131.6, 128.2 (+, 2C), 127.6 (+, 2C), 112.0 (+, 2C), 71.0 (-), 25.6, 21.0 (+).

3-[1-(methoxymethoxy)-1-methylethyl]-3-methylcyclopropene (1g). Methyl 1-methyl-2-bromocyclopropylcarboxylate **8** (10.0 g, 51.8 mmol) in dry ether (20 mL) was added dropwise to a solution of methylmagnesium bromide (109 mmol, 36 mL of 3N solution, Aldrich) in dry ether (100 mL) stirred at -20°C . The reaction mixture was warmed up to room temperature, stirred for additional 30 min, then cooled down to 0°C and quenched (saturated NH_4Cl). The ethereal phase was separated, and the aqueous phase was extracted with ether. Combined organic phases were washed (brine), dried (K_2CO_3), filtered, and concentrated in vacuum. 2-(2-bromo-1-methylcyclopropyl)propan-2-ol (**9**), obtained as a colorless oil with strong menthol smell, was identical to the material previously described in literature.⁷ Yield 9.607 g (49.76 mmol, 96%). This material was pure enough to use for the following transformations without an additional purification.

To a stirred solution of monobromocyclopropane **9** (4.5 g, 23.3 mmol) in dry dichloromethane (10 mL), was added $i\text{-Pr}_2\text{NEt}$ (1.5 equiv. 35 mmol, 4.5 g, 6.02 mL); the mixture was cooled to 0°C and MOMCl (1.5 equiv., 35 mmol, 2.8 g, 2.7 mL) was added. The reaction mixture was stirred at room temperature overnight. GC/MS analysis shown completion of the reaction and the mixture was quenched (ice-cold water), extracted (CH_2Cl_2), washed (3% aqueous HCl , brine), dried (MgSO_4), filtered, and concentrated. Crude MOM ether **10**, obtained as an orange oil, was used for dehydrobromination without further purification. Yield 4.466 g (18.8 mmol, 81%).

$t\text{-BuOK}$ (1.2 eq. 22.6 mmol, 2.52 g) was stirred in dry DMSO (10 mL) at 50°C until the mixture became homogenous, and 4.466 g (18.8 mmol) of MOM-protected monobromide **10** in dry DMSO (10 mL) was added dropwise to this mixture, maintaining the temperature below 60°C . The reaction mixture was stirred for 2 hrs at 50°C , when GC/MS analysis shown completion of the reaction. The reaction mixture was poured into ice-cold water and extracted with ether. Combined ethereal phases were washed (water,

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brine), dried (MgSO₄), filtered, and evaporated. The residue was distilled in vacuum to obtain cyclopropene **1g** as a colorless oil, bp 65°C (10 mm Hg). Yield 1.774 g (11.35 mmol, 60.4%). ¹H NMR (500.13 MHz, CDCl₃) δ 7.20 (s, 2H), 4.76 (s, 2H), 3.36 (s, 3H), 1.15 (s, 3H), 1.04 (s, 6H); ¹³C NMR (125.76 MHz, CDCl₃) δ 118.4 (+, 2C), 91.8 (-), 81.0, 55.6 (+), 26.9 (+, 2C), 26.5, 22.4 (+); GC/MS *m/z* 156 (M⁺, 5%), 111 (M⁺-CH₂OMe, 60%), 53 (M⁺-CMe₂OCH₂OMe, 100%).

1'-(methoxymethoxy)-1-methyl-1,1'-bi(cyclopropan)-2-ene (1h). 2'-Bromo-1'-methyl-1,1'-bi(cyclopropyl)-1-ol **11**⁸ (1.250 g, 6.54 mmol) was stirred in dry CH₂Cl₂ (10 mL) with *i*-Pr₂NEt (1.5 equiv., 9.81 mmol, 1.68 mL) at 0°C, and MOMCl (1.5 equiv., 9.81 mmol, 0.76 mL) was added. The reaction mixture was stirred overnight at room temperature, when GC/MS analysis shown completion of the reaction. The mixture was quenched (ice-cold water), extracted (CH₂Cl₂), washed (3% aqueous HCl, brine), dried (MgSO₄), filtered, and concentrated. Crude MOM ether **12** obtained as an orange oil was used for dehydrobromination without further purification. Yield 1.357 g (5.77 mmol, 88%).

MOM-protected monobromocyclopropane **12** (1.357 g, 5.77 mmol) was added to a stirred at 50°C solution of *t*-BuOK (1.2 equiv., 6.92 mmol, 775 mg) in dry DMSO (5 mL). The mixture was stirred for 2 hrs at 50°C, when GC/MS analysis shown completion of the reaction. The mixture was quenched with ice-cold water and extracted with ether. Combined organic phases were washed (water, brine), dried (Na₂SO₄), filtered, and concentrated. The residue was distilled in high vacuum (1 mm Hg, bath temperature 30-35°C, receiver at -78°C). Yield 630 mg (4.09 mmol, 71%). ¹H NMR (500.13 MHz, CDCl₃) δ 7.13 (s, 2H), 4.70 (s, 2H), 3.38 (s, 3H), 1.31 (s, 3H), 0.75-0.72 (m, 2H), 0.32-0.30 (m, 2H); ¹³C NMR (125.76 MHz, CDCl₃) δ 118.5 (+, 2C), 95.8 (-), 69.1, 56.2 (+), 24.0 (+), 23.1, 12.5 (+, 2C);

[1-(trimethylsilyl)cycloprop-2-en-1-yl]methyl acetate (1i). To a stirred solution of 3.886 g (21.1 mmol) of cyclopropene ester **13**^{4,9} in a 1:1 mixture of hexane-ether (40 mL), a 1M solution of DIBAL-H in hexane (2 equiv., 42.2 mL) was added dropwise at -78°C. The mixture was stirred for 30 min at -78°C, and then warmed up to room temperature and stirred for additional 1 hr. The mixture was quenched with saturated NH₄Cl, and the formed gel was dissolved by slow addition of 5% aqueous HCl (a little of gel particles was left to ensure neutral media). The mixture was extracted (diethyl ether), and combined ethereal phases were washed (brine), dried (Na₂SO₄), filtered, and concentrated in vacuum at room temperature to obtain 3.366 g of crude material. Preparative column chromatography on silica gel (eluent hexane-ether 4:1) gave pure alcohol **14**. Yield 2.550 g (17.9 mmol, 85%). ¹H NMR (500.13 MHz, CDCl₃) δ 7.23 (s,

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2H), 3.55 (s, 2H), 1.16 (br. s 1H), -0.06 (s, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 113.3 (+, 2C), 68.6 (-), 16.1, -2.5 (+, 3C); ^{29}Si NMR (99.36 MHz, CDCl_3) δ 0.71.

To a stirred solution of 1.080 g (7.59 mmol) of cyclopropenyl methanol **14** and dry pyridine (1.2 mL) in anhydrous CH_2Cl_2 (20 mL) was added acetic anhydride (1.0 mL). The mixture was stirred overnight at room temperature, then quenched with water and extracted with CH_2Cl_2 . Combined organic phases were washed (diluted aqueous HCl, 10% NaHCO_3 , brine), dried (MgSO_4), filtered, and concentrated in vacuum. The residue was purified by preparative column chromatography on silica gel, eluent hexane-ether 15:1 to afford acetate **1i**. Yield: 1.082 g (5.87 mmol, 77%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.14 (s, 2H), 3.96 (s, 2H), 2.01 (s, 2H), -0.07 (s, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 171.0, 112.7 (+, 2C), 73.5 (-), 21.0 (+), 12.6, -2.4 (+, 3C); ^{29}Si NMR (99.36 MHz, CDCl_3) δ 1.34;

[1-(trimethylsilyl)cycloprop-2-en-1-yl]methyl 3,3-dimethylacrylate (1j). To a stirred solution of 1.000 g (7.03 mmol) of cyclopropenyl methanol **14** and dry pyridine (1.2 mL) in anhydrous CH_2Cl_2 (20 mL) was added 3,3-dimethylacryloyl chloride (835 μL , 7.40 mmol). The mixture was stirred at room temperature for 2 hrs, then quenched with water, and extracted with CH_2Cl_2 . Combined organic phases were washed (5% aqueous HCl, brine), dried (MgSO_4), filtered, and concentrated. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-ether 15:1 to give **1j**. Yield 1.171 g (5.22 mmol, 74%). ^1H NMR (500.13 MHz, CDCl_3) δ 7.15 (s, 2H), 5.65 (septet, $J = 1.3$ Hz, 1H), 3.99 (s, 2H), 2.14 (d, $J = 1.3$ Hz, 3H), 1.87 (d, $J = 1.3$ Hz, 3H), -0.06 (s, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 166.7, 156.0, 116.2 (+), 112.8 (+, 2C), 72.4 (-), 27.3 (+), 20.1 (+), 12.7, -2.4 (+, 3C); ^{29}Si NMR (99.36 MHz, CDCl_3) δ 1.35; GC/MS m/z 224 (M^+ , <1%), 209 ($\text{M}^+ - \text{Me}$, 3%), 111 ($\text{Me}_3\text{SiC}_3\text{H}_2^+$, 45%), 83 ($\text{Me}_2\text{C}=\text{CHCO}^+$, 100%), 73 (Me_3Si^+ , 30%).

Typical Procedure for Asymmetric Hydrostannylation of Cyclopropenes

An oven dried 3 mL Wheaton microreactor was charged with $[\text{Rh}(\text{COD})\text{Cl}]_2$ (15 mg, 3 mol %) and ligand **D** (50 mg, 6 mol %) in nitrogen-filled glovebox. Anhydrous THF (1 mL) was added followed by cyclopropene **1c** (188 mg, 1 mmol). The mixture was cooled down to -30°C in actone/dry ice bath. Me_3SnH (150 μL , 1.1 mmol) was added, and the mixture was stirred at -30°C for 45 min. Then the mixture was warmed up to room temperature and filtered through a short column of Silica gel. The eluate was concentrated and the residue was purified by preparative column chromatography on

Silica gel (eluent hexane-ether 15:1) to obtain cyclopropyl stannane **2c** as colorless oil. Yield 311 mg (0.88 mmol, 88%).

2c: ^1H NMR (500.13 MHz, CDCl_3) δ 7.39 (d, $J = 7.7$ Hz, 2H), 7.32 (t, $J = 7.7$ Hz, 2H), 7.22 (t, $J = 7.3$ Hz, 1H), 4.62 (d, $J = 6.6$ Hz, 1H), 4.56 (d, $J = 6.6$ Hz, 1H), 3.85 (d, $J = 9.9$ Hz, 1H), 3.60 (d, $J = 9.9$ Hz, 1H), 3.27 (s, 3H), 1.35 (dd, $J = 10.1$ Hz, 3.9 Hz, $^3J_{\text{Sn-H}} = 34$ Hz, 1H), 1.00 (dd, $J = 7.8$ Hz, 3.9 Hz, $^3J_{\text{Sn-H}} = 66.0$ Hz, 64.9 Hz, 1H), 0.39 (dd, $J = 10.1$ Hz, 7.8 Hz, 1H), 0.21 (s, $^2J_{\text{Sn-H}} = 53$ Hz, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 145.2, 128.1 (+, 4C), 126.0 (+), 96.1 (-), 74.1 (-), 55.3 (+), 28.9, 15.8 (-), 10.9 (+, $^1J_{\text{Sn-C}} = 466$ Hz, 443 Hz), -8.6 (+, $^1J_{\text{Sn-C}} = 346$ Hz, 333 Hz, 3C); ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 1.33; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{21}\text{O}_2^{120}\text{Sn}$ ($\text{M}^+ - \text{Me}$) 341.0564. Found 341.0535.

2d: ^1H NMR (500.13 MHz, CDCl_3) δ 5.91 (ddt, $J = 17.3$ Hz, 10.2 Hz, 5.5 Hz, 1H), 5.29 (dq, $J = 17.3$ Hz, 1.5 Hz, 1H), 5.21 (dq, $J = 10.2$ Hz, 1.5 Hz, 1H), 4.55 (dt, $J = 5.5$ Hz, 1.5 Hz, 2H), 1.56 (dd, $J = 11.0$ Hz, 3.2 Hz, $^3J_{\text{Sn-H}} = 39.9$ Hz, 1H), 1.29 (s, 3H), 0.82 (dd, $J = 11.0$ Hz, 8.5 Hz, 1H), 0.66 (dd, $J = 8.5$ Hz, 3.2 Hz, $^3J_{\text{Sn-H}} = 61.8$ Hz, 59.2 Hz, 1H), 0.13 (s, $^2J_{\text{Sn-H}} = 54.5$ Hz, 52.2 Hz, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 176.6, 132.6 (+), 117.5 (-), 65.2 (-), 22.0, 21.5 (-), 20.3 (+), 15.6 (+, $^1J_{\text{Sn-C}} = 446$ Hz, 426 Hz), -9.1 (+, $^1J_{\text{Sn-C}} = 353$ Hz, 332 Hz, 3C); ^1H - ^{13}C HMQC NMR (500.13 MHz, 125.76 MHz, CDCl_3) $\delta_{\text{H}}/\delta_{\text{C}}$ 5.91/132.6, (5.29/117.5 & 5.21/117.5), 4.55/65.2, (1.56/21.5 & 0.66/21.5), 1.29/20.3, 0.82/15.6, 0.13/-9.1; ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 1.85; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{17}\text{O}_2^{120}\text{Sn}$ ($\text{M}^+ - \text{Me}$) 289.0251. Found 289.0261.

2e: ^1H NMR (500.13 MHz, CDCl_3) δ 7.33-7.28 (m, 4H), 7.21 (m, 1H), 4.28 (d, $J = 11.4$ Hz, 1H), 4.02 (d, $J = 11.4$ Hz, 1H), 2.02 (s, 3H), 1.34 (dd, $J = 10.1$ Hz, 4.2 Hz, $^3J_{\text{Sn-H}} = 33.7$ Hz, 1H), 0.94 (dd, $J = 7.9$ Hz, 4.2 Hz, $^3J_{\text{Sn-H}} = 64.9$ Hz, 62.0 Hz, 1H), 0.46 (dd, $J = 10.1$ Hz, 7.9 Hz, 1H), 0.19 (s, $^2J_{\text{Sn-H}} = 53.9$ Hz, 51.7 Hz, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 171.0, 144.5, 128.20 (+, 2C), 128.16 (+, 2C), 126.3 (+), 72.2 (-), 28.2, 21.0 (+), 16.8 (-), 11.2 (+, $^1J_{\text{Sn-C}} = 439$ Hz, 420 Hz), -9.1 (+, $^1J_{\text{Sn-C}} = 346$ Hz, 331 Hz, 3C); ^1H - ^{13}C HMQC NMR (500.13 MHz, 125.76 MHz, CDCl_3) $\delta_{\text{H}}/\delta_{\text{C}}$ (7.33-7.28)/128.2, 7.21/126.3, (4.28/72.2 & 4.02/72.2), 2.02/21.0, (1.34/16.8 & 0.94/16.8), 0.46/11.2, 0.19/-9.1; ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 3.73; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2^{120}\text{Sn}$ ($\text{M}^+ - \text{Me}$) 339.0407. Found 339.0413.

2f: ^1H NMR (500.13 MHz, CDCl_3) δ 7.26-7.21 (m, 4H), 4.22 (d, $J = 11.7$ Hz, 1H), 3.96 (d, $J = 11.7$ Hz, 1H), 2.01 (s, 3H), 1.28 (dd, $J = 10.3$ Hz, 4.4 Hz, $^3J_{\text{Sn-H}} = 33.7$ Hz, 1H), 0.92 (dd, $J = 8.1$ Hz, 4.4 Hz, $^3J_{\text{Sn-H}} = 63.8$ Hz, 61.3 Hz, 1H), 0.39 (dd, $J = 10.3$ Hz, 8.1 Hz, 1H), 0.18 (s, $^2J_{\text{Sn-H}} = 54.3$ Hz, 52.1 Hz, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 170.9, 143.0, 132.0, 129.7 (+, 2C), 128.2 (+, 2C), 72.0 (-), 27.9, 21.0 (+), 16.7 (-), 11.1 (+, $^1J_{\text{Sn-C}} = 433$ Hz, 414 Hz), -9.1 (+, $^1J_{\text{Sn-C}} = 348$ Hz, 333 Hz, 3C); ^1H - ^{13}C HMQC NMR (500.13 MHz, 125.76 MHz, CDCl_3) $\delta_{\text{H}}/\delta_{\text{C}}$ (7.26-7.21)/(129.7 & 128.2), (4.22/72.0 & 3.96/72.0), 2.01/21.0, (1.28/16.7 & 0.92/16.7), 0.39/11.1, 0.18/-9.1; ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 4.10; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2^{120}\text{SnCl}$ ($\text{M}^+ - \text{Me}$) 373.0017. Found 373.0010.

2g: ^1H NMR (500.13 MHz, CDCl_3) δ 4.77 (d, $J = 7.0$ Hz, 1H), 4.76 (d, $J = 7.0$ Hz, 1H), 3.36 (s, 3H), 1.20 (s, 3H), 1.17 (s, 3H), 1.06 (s, 3H), 0.93 (dd, $J = 10.3$ Hz, 3.7 Hz, $^3J_{\text{Sn-H}} = 35.2$ Hz, 1H), 0.24 (dd, $J = 7.0$ Hz, 3.7 Hz, $^3J_{\text{Sn-H}} = 67.3$ Hz, 64.7 Hz, 1H), 0.15 (dd, $J = 10.3$ Hz, 7.0 Hz, 1H), 0.09 (s, $^2J_{\text{Sn-H}} = 53.2$ Hz, 51.0 Hz, 9H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 91.2 (-), 78.6, 55.2 (+), 25.8, 24.4 (+), 23.9 (+), 21.8 (+, $^3J_{\text{Sn-C}} = 35$ Hz), 15.0 (-), 7.2 (+, $^1J_{\text{Sn-C}} = 488$ Hz, 466 Hz), -9.1 (+, $^1J_{\text{Sn-C}} = 333$ Hz, 3C); ^1H - ^{13}C HMQC NMR (500.13 MHz, 125.76 MHz, CDCl_3) $\delta_{\text{H}}/\delta_{\text{C}}$ (4.77/91.2 & 4.76/91.2), 3.36/55.2, 1.20/24.4, 1.17/23.9, 1.06/21.8, (0.93/15.0 & 0.24/15.0), 0.15/7.2, 0.09/-9.1; ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 2.20; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{23}\text{O}_2^{120}\text{Sn}$ (M^+ -Me) 307.0720. Found 307.0717.

2h: ^1H NMR (500.13 MHz, CDCl_3) δ 4.79 (d, $J = 5.9$ Hz, 1H), 4.75 (d, $J = 5.9$ Hz, 1H), 3.35 (s, 3H), 1.24 (s, 3H), 0.80 (ddd, $J = 11.0$ Hz, 6.2 Hz, 4.8 Hz, 1H), 0.71 (ddd, $J = 11.0$ Hz, 6.6 Hz, 5.5 Hz, 1H), 0.51 (ddd, $J = 10.3$ Hz, 6.4 Hz, 4.9 Hz, 1H), 0.45 (dd, $J = 10.6$ Hz, 4.0 Hz, $^3J_{\text{Sn-H}} = 42.9$ Hz, 1H), 0.32 (ddd, $J = 10.3$ Hz, 6.2 Hz, 5.1 Hz, 1H), 0.22 (dd, $J = 7.3$ Hz, 4.0 Hz, 1H), 0.09 (s, $^2J_{\text{Sn-H}} = 53.9$ Hz, 51.4 Hz, 9H), -0.04 (dd, $J = 10.6$ Hz, 7.3 Hz, 1H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 95.0 (-), 66.4, 56.0 (+), 22.5 (+), 21.6, 15.0 (-), 11.3 (-), 9.8 (-), 9.3 (+), -9.2 (+, 3C); ^1H - ^{13}C HMQC NMR (500.13 MHz, 125.76 MHz, CDCl_3) $\delta_{\text{H}}/\delta_{\text{C}}$ (4.79/95.0 & 4.75/95.0), 3.35/56.0, 1.24/22.5, (0.80/11.3 & 0.51/11.3), (0.71/9.8 & 0.32/9.8), (0.45/15.0 & 0.22/15.0), 0.09/-9.2, -0.04/9.3; ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 1.33; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{21}\text{O}_2^{120}\text{Sn}$ (M^+ -Me) 305.0564. Found 305.0622.

2i: ^1H NMR (500.13 MHz, CDCl_3) δ 4.10 (d, $J = 11.4$ Hz, 1H), 3.60 (d, $J = 11.4$ Hz, 1H), 2.03 (s, 3H), 0.83 (dd, $J = 9.2$ Hz, 3.7 Hz, $^3J_{\text{Sn-H}} = 29$ Hz, 1H), 0.43 (dd, $J = 7.0$ Hz, 3.7 Hz, $^3J_{\text{Sn-H}} = 60.6$ Hz, 57.9 Hz, 1H), 0.10 (s, $^2J_{\text{Sn-H}} = 53.6$ Hz, 51.7 Hz, 9H), -0.02 (s, 9H), -0.07 (dd, $J = 9.2$ Hz, 7.0 Hz, 1H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 171.0, 72.5 (-), 21.1 (+), 12.2 (-), 9.6, 5.1 (+, $^1J_{\text{Sn-C}} = 459$ Hz, 449 Hz), -2.8 (+, 3C), -8.9 (+, $^1J_{\text{Sn-C}} = 341$ Hz, 327 Hz, 3C); ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 6.07; ^{29}Si NMR (99.36 MHz, CDCl_3) δ 5.02; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{23}\text{O}_2^{28}\text{Si}^{120}\text{Sn}$ (M^+ -Me) 335.0489. Found 335.0521.

2j: ^1H NMR (500.13 MHz, CDCl_3) δ 5.65 (septet, $J = 1.3$ Hz, 1H), 4.07 (d, $J = 11.4$ Hz, 1H), 3.64 (d, $J = 11.4$ Hz, 1H), 2.17 (d, $J = 1.5$ Hz, 3H), 1.90 (d, $J = 1.1$ Hz, 3H), 0.83 (dd, $J = 9.2$ Hz, 3.7 Hz, $^3J_{\text{Sn-H}} = 29.0$ Hz, 1H), 0.44 (dd, $J = 7.0$ Hz, 3.7 Hz, $^3J_{\text{Sn-H}} = 60.2$ Hz, 58.0 Hz, 1H), 0.09 (s, $^2J_{\text{Sn-H}} = 53.9$ Hz, 51.7 Hz, 9H), -0.02 (s, 9H), -0.07 (dd, $J = 9.2$ Hz, 7.0 Hz, 1H); ^{13}C NMR (125.76 MHz, CDCl_3) δ 166.7, 156.8, 115.9 (+), 71.5 (-), 27.4 (+), 20.1 (+), 12.3 (-), 9.7, 5.1 (+, $^1J_{\text{Sn-C}} = 461$ Hz, 443 Hz), -2.7 (+, 3C), -8.8 (+, $^1J_{\text{Sn-C}} = 341$ Hz, 326 Hz, 3C); ^1H - ^{13}C HMQC NMR (500.13 MHz, 125.76 MHz, CDCl_3) $\delta_{\text{H}}/\delta_{\text{C}}$ 5.65/115.9, (4.07/71.5 & 3.64/71.5), 2.17/20.1, 1.90/27.4, (0.83/12.3 & 0.44/12.3), 0.09/-8.8, -0.02/-2.7, -0.07/5.1; ^{119}Sn NMR (186.50 MHz, CDCl_3) δ 6.08; ^{29}Si NMR (99.36 MHz, CDCl_3) δ 5.01; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{27}\text{O}_2\text{Si}^{120}\text{Sn}$ (M^+ -Me) 375.0802. Found 375.0770.

Assignment of configuration

Relative configurations of cyclopropylstannanes **2a** and **2b** were confirmed by comparison with racemic compounds, characterized previously.^{4a} Relative and absolute configurations of cyclopropylstannanes **2e** and absolute configuration of **2a** were assigned by derivatization of these compounds into products with known configuration. Compounds **2g** and **2h** then were independently synthesized from **2a**, and compound **2c** was derived from **2e**. Independently synthesized compounds were identical by GC/MS and chiral GC properties to those obtained *via* asymmetric hydrostannation. Since all these compounds showed the same absolute configuration (*1R,2S*), we presumed this to be the general rule for the described asymmetric hydrostannation reaction, employing ligand **D**, thus configuration (*1R,2S*) was attributed for compounds **2d,f,i,j** as well.

(+)-(1*R,2S*)-1-Methyl-2-bromocyclopropanecarboxylic acid (17). Cyclopropylstannane **2a** (490 mg) was stirred with bromine (600 mg, 3equiv.) in CCl₄ (15 mL) overnight at room temperature. Then, solvent was removed in vacuum, and the residue was purified by preparative column chromatography on Silica gel (eluent hexane-ether 10:1) to obtain *trans*-isomer of bromocyclopropane **16** with 92% *ee*. This material was stirred in methanol with excess KOH at room temperature overnight. The mixture was concentrated in vacuum, the residue was dissolved in 10% aqueous HCl and extracted with EtOAc. Combined organic phases were washed (water, brine), dried (CaCl₂), filtered, and concentrated. ¹H and ¹³C NMR spectra of the residue were identical to those for the sample of (-)-(1*S,2R*)-acid, previously reported in literature,¹⁰ however demonstrated opposite sign of optical rotation, α_D²⁰ = +81.1 (c 1.00, CHCl₃). Based on this fact the (*1R,2S*) configuration was assigned for (+)-**17** and consecutively for **2a**.

Preparation of 2g from 2a. 352 mg (1.27 mmol) of chiral ester **2a** was stirred in dry ether (10 mL) at 0°C, and MeMgBr 3.0 M in ether (3 equiv., 3.81 mmol, 1.27 mL) was added dropwise. The mixture was warmed up to room temperature, stirred for 2 hrs, and then quenched with saturated aqueous NH₄Cl. The ethereal phase was separated and the aqueous layer was extracted with ether. Combined organic phases were washed (brine),

10. Baird, M. S.; Licence, P.; Tverezovsky, V. V.; Bolesov, I. G.; Clegg, W. *Tetrahedron* **1999**, *55*, 2733.

dried (MgSO_4), filtered, and concentrated. The residue was dissolved in dry CH_2Cl_2 (5 mL), and $(i\text{-Pr})_2\text{NEt}$ (500 μL) and MOMCl (150 μL , 1.89 mmol) were added. The mixture was stirred for 3 hrs, then quenched by addition of saturated aqueous NH_4Cl , and extracted with ether. The ethereal phase was filtered through a short column of Silica gel, and concentrated. Compound **2g**, obtained as described, was identical by GC/MS and chiral GC properties to one obtained *via* asymmetric hydrostannation of cyclopropene **1g**. Thus the absolute configuration (1*R*,2*S*) was assigned for **2g**, as for its precursor **2a**.

Preparation of 2h from 2a. 372 mg (1.34 mmol) of chiral ester **2a** and $\text{Ti}(\text{OPr-}i)_4$ (89 μL , 0.30 mmol, 22 mol%) were stirred in dry ether (10 mL), and EtMgBr 3.0 M in ether (1.5 equiv., 2.00 mmol, 0.67 mL) was added dropwise at room temperature. The mixture was stirred for 2 hrs, then quenched with saturated aqueous NH_4Cl . Formed precipitate was dissolved in diluted H_2SO_4 , and the mixture was extracted with ether. Combined ethereal phases were washed (saturated aqueous NaHCO_3 , brine), dried (MgSO_4), filtered and concentrated. The residue was dissolved in dry CH_2Cl_2 (5 mL), and $(i\text{-Pr})_2\text{NEt}$ (500 μL) and MOMCl (150 μL , 1.89 mmol) were added. The mixture was stirred for 5 hrs, then quenched by addition of saturated aqueous NH_4Cl , and extracted with ether. The ethereal phase was filtered through a short column of Silica gel, and concentrated. Compound **2h**, obtained as described, was identical by GC/MS and chiral GC properties to one obtained *via* asymmetric hydrostannation of cyclopropene **1h**. Thus the absolute configuration (1*R*,2*S*) was assigned for **2h**, as for its precursor **2a**.

(+)-(1*R*,2*S*)-(2-Hydroxymethyl-1-phenyl-cyclopropyl)-methanol (19). To a stirred solution of cyclopropyl stannane **2e** (912 mg, 2.6 mmol) in anhydrous ether (10 mL) was added LiAlH_4 (3 equiv., 3.9 mmol, 145 mg) by small portions at 0°C . The mixture was stirred at room temperature for 2 hrs, then quenched by addition of saturated aqueous NH_4Cl and extracted (EtOAc). The extract was filtered through a short column of Silica gel and concentrated to give crude alcohol **18** in nearly quantitative yield. This material was dissolved in anhydrous THF (10 mL) at 0°C , and 1.5 N MeLi in ether (3 equiv., 7.8 mmol, 5.2 mL) was added dropwise. The mixture was stirred at 0°C for 2 hrs, then transferred *via* cannula into the stirred suspension of paraformaldehyde (10 equiv., 26 mmol, 832 mg). The mixture was stirred at room temperature overnight, then quenched (saturated aqueous NH_4Cl), extracted (EtOAc), and concentrated. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc, 1:1

to obtain diol **19**, which had ^1H and ^{13}C spectra identical to those for (-)-enantiomer compound previously described in literature,¹¹ and an opposite sign of optical rotation, $[\alpha]_{\text{D}}^{20} = +53.1$ (c 1.00, CHCl_3). Yield 126 mg (0.7 mmol, 27%). Based on these facts the configuration (1*R*,2*S*) was assigned for (+)-**19**, and consecutively for compound **2e**.

Preparation of 2c from 2e. To a stirred solution of (1*R*,2*S*)-**18**, obtained as described above (93 mg, 0.3 mmol), and *i*-Pr₂NEt (200 μL) in anhydrous CH_2Cl_2 (5 mL) was added MOMCl (75 μL , 1.0 mmol) was added dropwise. The mixture was stirred for 5 hrs, then quenched by addition of saturated aqueous NH_4Cl , and extracted with ether. The ethereal phase was filtered through a short column of Silica gel, and concentrated. Compound **2c**, obtained as described, was identical by GC/MS and chiral GC properties to one obtained *via* asymmetric hydrostannation of cyclopropene **1c**, thus the absolute configuration (1*R*,2*S*) was assigned for **2c**, as for its precursor, compound **2e**.

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11. Yamaguchi, K.; Kazuta, Y.; Abe, H.; Matsuda, A.; Shuto, S. *J. Org. Chem.* **2003**, 68, 9255.

¹H spectrum of **1g** ¹³C spectrum of **1g**

¹H spectrum of **1h** ¹³C spectrum of **1h**

¹H spectrum of **2g** ¹³C spectrum of **2g**

¹H spectrum of **2h** ¹³C spectrum of **2h**

¹H spectrum of **2i** ¹³C spectrum of **2i**