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SYNTHESIS OF ENANTIOMERICALLY PURE TRIBUTYLSTANNYLCYCLOPROPANES THROUGH LIPASE-CATALYZED REACTION

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Abstract: Synthesis of optically active cyclopropylstannanes was accomplished through two synthetic pathways using lipase-catalyzed reaction. A direct resolution of racemic hydroxyl cyclopropylstannanes using PCL or LPL and a converting method from optically pure vinylstannanes. They were prepared via PCL-catalyzed reaction, and afforded five types of optically pure new tributylstannylcyclopropanes. Synthesis of an optically active biscyclopropane has also been demonstrated *via* palladium-catalyzed homocoupling reaction of tributylstannylcyclopropane. © 1998 Elsevier Science Ltd. All rights reserved.

The utility of cyclopropane derivatives in the construction of a variety of cyclic and acyclic organic compounds has been amply demonstrated.[1] Recent finding of structurally remarkable chiral cyclopropanes, i.e. U-106305 and FR-900848,[2] has particularly stimulated the chemistry of bis- and multicyclopropanes derivatives.[3,4,5] Development of efficient methods for the synthesis of highly functionalized cyclopropane derivatives is increasingly necessary.[6]

It has been well established that tin-lithium transmetallation of tributylstannylcyclopropane quickly took place chemoselectively to generate corresponding lithiocyclopropane with perfect retention, and was trapped with variety of electrophiles.[6,7] Studies of tin-lithium transmetallation of tributylstannylcyclopropane also revealed that presence of the α-alkoxy group greatly stabilizes lithiocyclopropane.[8] Therefore, chiral α-hydroxylcyclopropylstannanes **1** are viewed as useful building blocks for synthesizing chiral functionalized cyclopropyl compounds, **2** and **3** (Figure 1).[4,9]

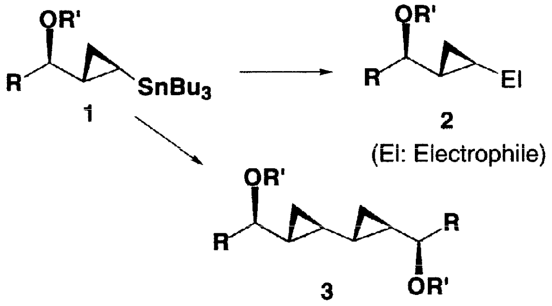

Figure 1. Chiral hydroxylcyclopropylstannanes as building blocks for organic synthesis

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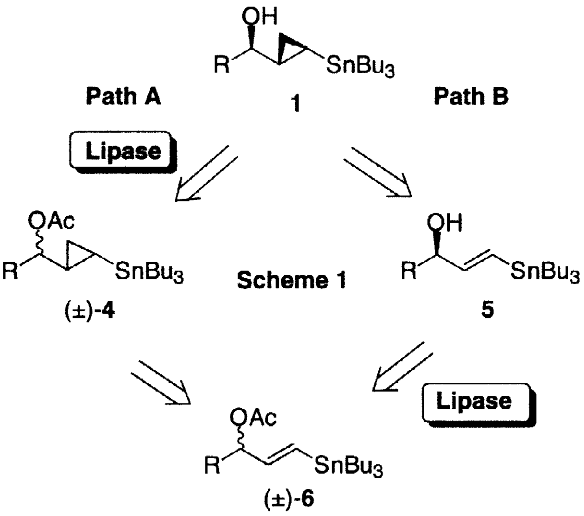
Although many methods have been developed to synthesize optically active cyclopropanes,[9] the Charette asymmetric cyclopropanation based on Simmons-Smith cyclopropanation is now most widely accepted.[10] However, the method requires an excess amount of chiral ligands to achieve a high level of stereocontrol.

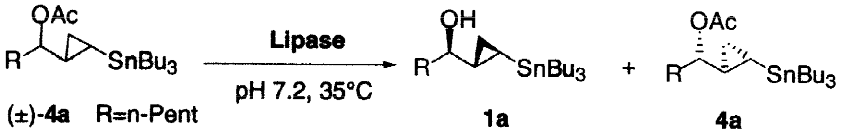
We have been studying the methodology of preparing optically active building blocks for organic synthesis using a natural enzymatic system,[12] and we reported that three types of hydroxylstannyl compounds were obtained with high optical purity *via* lipase-catalyzed reaction. [13-16] Lipases are the most frequently used enzymes in organic synthesis because of their stability, availability and their acceptance of a broad range of substrates.[17] We describe here the simple synthesis of cyclopropylstannanes through two synthetic pathways using a lipase-catalyzed reaction.

There are two pathways to access the target hydroxyltributylstannylcyclopropane **1** through lipase-catalyzed reaction (Scheme 1). Path B might be the sure route to obtain the target molecule 1 because we have already established the procedure for preparation of optically pure γ-hydroxylstannanes **5** *via* kinetic resolution of the corresponding racemic acetate (±)-**6** using *Pseudomonas cepacia* lipase (PCL).[15,16] Path A is interesting from a biological aspect because cyclopropane compounds sometimes act as serious inhibitors of an enzyme in microbes.[18] In addition, there has been no report concerning hydrolysis of this type of acetates of stannylcyclopropyl alcohol. Therefore, path A was initially examined.



Scheme 1

The hydrolysis of (±)-**4** was typically carried out as follows (Eq. 1). To a phosphate buffer solution (10 ml, 0.1 M at pH 7.2) was added an acetone (1.0 ml) solution of (±)-**4a** (1.0 mmol) and PCL (50 wt% towards the substrate) and the mixture was stirred at 35 ℃. The alcohol (*R*)-**1a** produced and remaining ester (*S*)-**2a** were extracted with ethyl acetate and separated by silica gel flash column chromatography (hexane / ethyl acetate = 20:1). The absolute configuration of product **1a** was assigned as (*R*) by comparing the value of optical rotation with the authentic sample which was derived from vinylstannane (*R*)-**5a**[15] using Simmons-Smith reaction.[19,20] The enantiomeric excess of product **1a** and remaining acetate (*S*)-**1a** were determined by ^{19}F NMR analysis of corresponding (+)-MTPA esters.[21] Because this reaction is a kinetic resolution of the racemic substrate, the optical purity of the producing alcohol and remaining acetate depends on the reaction conversion; hence the enzymatic reaction was evaluated by a comparison of E values, which were calculated by the equation



(1)

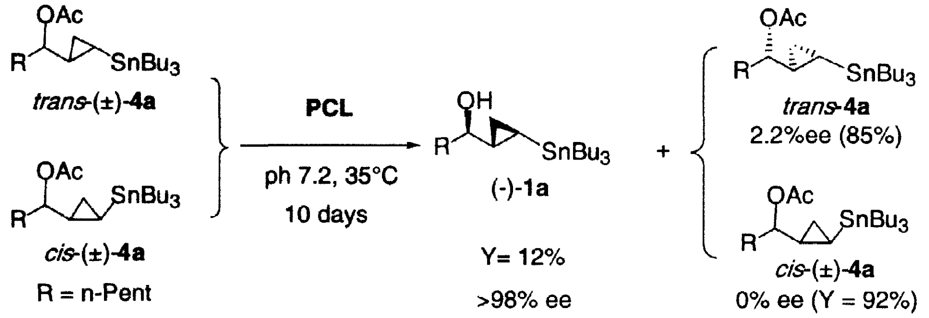
Table 1. Optical resolution of cyclopropyl alcohol through lipase-catalyzed hydrolysis of (±)-**4 a**

Entry	Lipase	Time (days)	%ee of **1 a** (Yield)	%ee of **4 a** (Yield)	E value
1	PCL	7 [a]	>98%ee (6%)	2%ee (94%)	203
2	PCL	7 [b]	91%ee (28%)	47%ee (49%)	34
3	LPL	7 [a]	91%ee (22%)	16%ee (77%)	26
4	AL	11 [a]	78%ee (8%)	15%ee (67%)	9
5	PL	7 [a]	72%ee (4%)	3%ee (93%)	6
6	QL	7 [a]	61%ee (10%)	8%ee (81%)	5

a) The reaction was carried out at pH 7.2 at 35°C and enantiomeric excess was determined by ^{19}F NMR analysis of corresponding (+)-MTPA ester. b) The reaction was performed at pH 8.5. c) PCL: *Pseudomonas cepacia*. AL: *Achromobacter* sp. LPL: *Pseudomonas aeruginosa*. PL: *Alcaligenes* sp. QL: *Alcaligenes* sp.

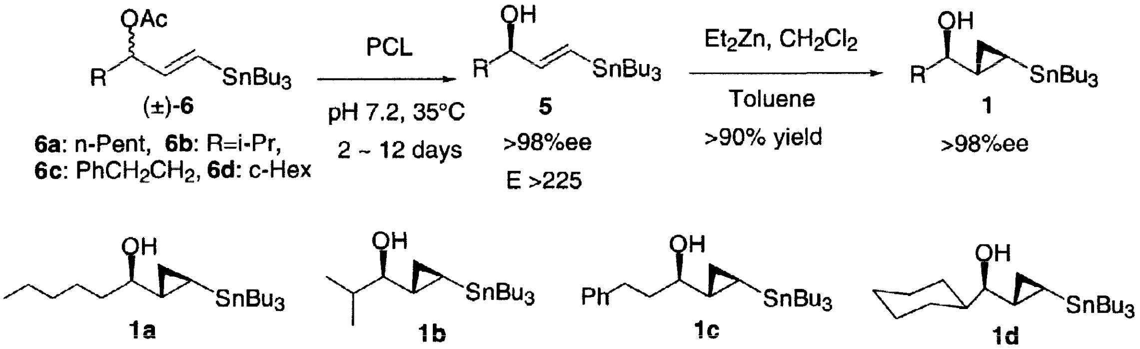
proposed by Sih et al.[22] Twenty-eight commercially available lipases were screened for their activity and only five lipases were found to have hydrolyzed the acetate and two enzymes, PCL and *Pseudomonas aeruginosa* lipase (LPL), provided the corresponding alcohol (*R*)-(-)-**1a** in high enantiomeric excess (Table 1, Entries 1, 2 and 3). PCL-catalyzed reaction of (±)-**4a** provided the corresponding alcohol (*R*)-**1a** with perfect enantioselectivity (>98% ee),[23] though the reaction stopped at low conversion (Entry 1). Although remarkable acceleration was observed when the reaction was performed at pH 8.5, enantiomeric excess of the product **1a** was significantly reduced (Entry 2). This would be due to the result of partial chemical hydrolysis of (±)-**4a** under higher pH conditions because the reaction proceeded very slowly. We assume that the enantioselectivity of PCL-catalyzed reaction is excellent, however, the reaction appears to be inhibited by the trace amount of by-product formed during a long reaction, because neither the addition of product **1a** nor substrate **4a** inhibited the hydrolytic reaction of 2-cyano-1-methylethyl acetate by PCL,[24] though we have not yet identified this by-product. We also attempted PCL-catalyzed trans-esterification of (±)-**1a** using vinyl acetate as an acyl donor in diisopropyl ether as solvent. Unfortunately, it was found that the acetate (+)-**4a** (89% ee) was produced only 10% yield after 14 days reaction at room temperature.

The most important aspect of this reaction is particularly high enantio- and substrate specificity. As shown in equation 2, only the *trans*-alcohol **1a** was obtained in 12 % yield with >98% ee when a 1:1 mixture of *trans*-(±)-**4a** and *cis*-(±)-**4a** was subjected to the reaction.



(2)

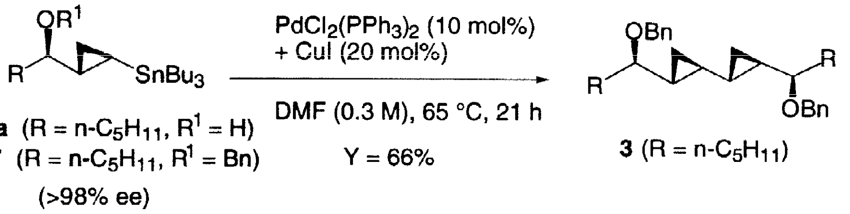
Path B might be the preferred route to access the target molecule because we have already established the procedure for preparation of γ-hydroxylvinylstannanes **5** in optically active form with extremely high enantiomeric excess (>98% ee).[15,16] The reaction was typically carried out as follows: a solution of acetate (±)-**6a** (10 mmol) in 20 ml of 0.1 M phosphate buffer (pH 7.2) and acetone (2 ml) was incubated with PCL (50wt%) at 35℃ for 7 days. The reaction mixture was extracted with ethyl acetate, then the extracts were evaporated to dryness. Purification by silica gel flash column chromatography gave the product **5a** and the unreacted ester **6a** in yield of 40% and 47%, respectively. The ee of alcohol **5a** was determined by ^{19}F NMR analysis of the corresponding (+)-MTPA ester. Optically active tributylstannylcyclopropanes **1a** were thus prepared using vinylstannanes **5a** [16]; to a toluene solution of optically pure **5a** was added Et_2Zn dropwise, this was stirred at room temperature for 10 min and a toluene solution of excess amounts of CH_2I_2 was added to this mixture at 60 ℃.[20] After being stirred for 3 h, the mixture was cooled to room temperature and was poured slowly into an ether solution of Et_3N. Silica gel flash column chromatography using hexane-ethyl acetate (50:1) afforded **1a** in 91% yield. Four types of new optically active tributylstannylcyclopropane derivatives **1a**-**1d** were thus prepared from the corresponding vinylstannanes **5a**-**5d** [16] using modified Simmons-Smith reaction [20] in more than 90% yield with more than 98% enantiomeric excess (Scheme 2).



Scheme 2. Synthesis of optical active cyclopropylstannanes

Suitably functionalized cyclopropane is particularly useful for homo-coupling reaction or cross-coupling reaction.[4,5,25] Homo-coupling of tributylstannylcyclopropane has been accomplished through copper-mediated oxidative coupling derived following lithiation.[27] We accomplished dimerization of tributylstannylcyclopropane **1a** simply using palladium(0) catalyst in the presence of a catalytic amount of copper(I) iodide (Eq. 3).[27] Hydroxylstannane **1a** was initially converted to benzyl ether **7** in quantitative yield. A mixture of **7**,

$PdCl_2(PPh_3)_2$ (5 mol%) and CuI (20 mol%) in DMF was stirred at 65 °C for 21 h, then an additional 5 mol% of $PdCl_2(PPh_3)_2$ was added to the reaction mixture. After further stirring for 4 h at the same temperature, the reaction was quenched by addition of water, extracted with Et_2O and evaporated. Silica gel flash column chromatography (hexane / ethyl acetate = 100:1) gave the coupling product **3** in 66% yield. Copper(I) catalyst was essential to complete this reaction, and none of the coupling product was obtained when the reaction was performed in the absence of this catalyst.



(-)-1a ($R = n\text{-}C_5H_{11}$, $R^1 = H$)
(-)-**7** ($R = n\text{-}C_5H_{11}$, $R^1 = Bn$)
(>98% ee)

3 ($R = n\text{-}C_5H_{11}$)

(3)

It should be emphasized that the key step of this synthesis is a pollution-free chemical reaction using a natural enzymatic system. Lipase-catalyzed reactions are particularly useful even for large-scale preparative organic synthesis. In particular, *Pseudomonas cepacia* lipase is commercially available and not very expensive; hence, the present protocol can undoubtedly allow us to evolve a smarter and convenient synthesis of chiral tributylstannylcyclopropane derivatives.

Experimental

Reagents and solvents were purchased from common commercial sources and were used as received or purified by distillation from appropriate drying agents. Reactions requiring anhydrous conditions were run under an atmosphere of dry argon. Silica gel (Wako gel C-300, 300E) was used for column chromatography and silica gel (Wako gel B-5F) for thin layer chromatography. ^1H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on a Varian VXR-200 (200 MHz) spectrometer, and chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in $CDCl_3$ or hexafluorobenzene (C_6F_6) as an internal reference. Lipases were provided by Amano Pharmaceutical Co., Ltd. and Meito Sangyo Co., Ltd. (Japan).

Path A (Direct optical resolution of (±)-4a by lipase-catalyzed reaction).

(1*R*,2*S*)-1-Tributylstannyl-2-[(*R*)-1-hydroxyhexyl]cyclopropane (1a). A mixture of acetate (±)-**4a** (110 mg, 0.23 mmol) and PCL (55 mg) was incubated at 35 °C in 0.1 M phosphate buffer (1.4 ml) and acetone (0.14 ml) for 7 days. The reaction was quenched with crushed ice and NaCl and the mixture was extracted with ether. The organic layer was dried over $MgSO_4$ and the crude product purified by silica gel flash column chromatography (hexane/ethyl acetate = 7:1) gave (-)-**1a** (6.5 mg, 0.015 mmol) and unreacted acetate **2a** (103 mg, 0.218 mmol) in 6% and 94% yield, respectively. (-)-**1a**: $[\alpha]^{21}_D$ -13.9° (c 0.65, $CHCl_3$); ^{19}F NMR (188 MHz, $CDCl_3$) analysis of (+)-MTPA ester of (-)-**1a** obtained showed a peak at 90.4 ppm.

Path B.

(3*R*)-(*E*)-1-tributylstannyl-1-octen-3-ol (5a).[15,16] Ester **6a** (1.17 g, 2.56 mmol), PCL (589 mg) in 13 mL of 0.1 M phosphate buffer (pH 7.2), and acetone (1.3 ml) were mixed and stirred at 35 °C for 47 h. The mixture was extracted with ether, dried over $MgSO_4$ and evaporated to dryness. Silica gel flash column chromatography gave (*R*)-**5a** ($[\alpha]^{21}_D$ -3.1°(c 1.00, $CHCl_3$); 464 mg, 1.11 mmol; 43%) and the unreacted (*S*)-**6a** ($[\alpha]^{21}_D$ -35.0°(c 1.00, $CHCl_3$); 580 mg, 1.26 mmol; 49%). The optical purity of the produced alcohol, **5a**, was measured by the ^{19}F NMR analysis of the corresponding (+)-MTPA ester. (+)-MTPA ester of **5a**: ^{19}F NMR (188 MHz, CDCl$_3$) δ 90.32, 90.47 ppm. Because only a single peak was detected at 90.32 ppm from the (+)-MTPA ester of **5a**, the % ee of the obtained (*R*)-**5a** was determined to be at least >98% ee. The % ee of unreacted (*S*)-**6a** was calculated as 75% from ^{19}F NMR analysis of the corresponding (+)-MTPA ester. Alkenyl stannanes, (*R*)-**5b**, (*R*)-**5c**, and (*R*)-**5d**, were prepared by the same procedure for the lipase-catalyzed reaction.[16] The absolute configurations of these three compounds were assigned by ^{19}F NMR analysis of the corresponding (+)-MTPA esters by the diastereomeric preferences compared with (*R*)-**5a**.

(1*R*,2*S*)-1-Tributylstannyl-2-[(*R*)-1-hydroxyhexyl]cyclopropane (1a). To a toluene (2.4 ml) solution of (*R*)-**5a** (2.00 g, 4.79 mmol) was added 9.6 ml of Et$_2$Zn (9.6 mmol, 1 M in hexane) dropwise and the mixture was stirred at rt for 10 min. To this solution was added a toluene solution of CH$_2$I$_2$ (2.60 g, 9.6 mmol) at 60 ℃ for 40 min. After being stirred for 3 h, the mixture was cooled to rt and was poured slowly into ether solution of triethylamine. The organic layer separated was washed with brine, dried (MgSO$_4$) and evaporated. SiO$_2$ flash column chromatography using hexane-ethyl acetate (50:1) afforded (-)-**1a** (1.88 g, 4.36 mmol) in 91% yield: [α]$^{23}_{D}$ -15.7° (c 1.37, CHCl$_3$); bp 130 ℃ / 5 mmHg (Kugelrohr); Rf 0.46 (hexane/ethyl acetate = 10:1); IR (neat) 3347, 2925, 1463, 1292, 1071, 1041, 945, 861 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ -0.31 (1H, dt, J = 10.2 Hz, J = 6.7 Hz) 0.4-0.6 (2H, m) 0.7-0.95 (2H, m) 0.78 (3H, t, J = 7.9 Hz) 0.88 (9H, t, J = 7.1 Hz) 1.2-1.6 (25H, m) 1.7 (1H, brs, OH) 2.78 (1H, dt, J = 8.4 Hz, J = 6.1 Hz) ; ^{13}C NMR (50 MHz, CDCl$_3$) -2.30, 7.13, 8.58, 13.64, 14.02, 22.39, 22.64, 25.43, 27.37, 29.05, 32.10, 37.30, 78.99 ppm; Anal. Calcd for C$_{21}$H$_{44}$OSn: C, 58.49; H, 10.28. Found: C, 58.47; H, 10.29.

(+)-MTPA ester of (±)-**1a**: ^{19}F NMR (188 MHz, CDCl$_3$) 90.4 ppm (*R*). Only a single signal at 90.4 ppm was detected while (+)-MTPA ester of (±)-**1a** showed two signals at 90.4 ppm and 90.3 ppm.

Using the same procedure, optically active stannylcyclopropanes **1b**-**1d** (>98% ee) were also prepared from the corresponding optically active vinylstannanes **5b**-**5d**.[16]

(1*R*,2*S*)-1-Tributylstannyl-2-[(*R*)-2-methyl-1-hydroxypropyl]cyclopropane (1b). [α]$^{23}_{D}$ -29.6° (c 1.3, CHCl$_3$); bp 120℃ /3 mmHg (Kugelrohr); Rf 0.25 (hexane/ethyl acetate = 10:1); IR (neat) 3350, 2900, 1460, 1380, 1180, 1080, 1020, 990, 690 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ -0.25 (1H, m) 0.3-0.6 (2H, m) 0.7-0.95 (16H, m) 0.9 (6H, d, J = 7.0 Hz) 1.2-1.4 (6H, m) 1.5-1.6 (6H, m) 1.61 (1H, brs, OH) 1.8 (1H, dd, J = 6.8 Hz, J = 12.1 Hz); ^{13}C NMR (50 MHz, CDCl$_3$) -1.21, 6.65, 8.56, 13.67, 17.86, 18.94, 19.89, 27.38, 29.09, 34.14, 83.86 ppm; ; Anal. Calcd for C$_{19}$H$_{40}$OSn: C, 56.60; H, 10.00. Found: C, 56.60; H, 9.97. (+)-MTPA ester of (±)-**1b**: ^{19}F NMR (188 MHz, CDCl$_3$) 90.6 ppm (*R*) and 90.2 ppm (*S*). (+)-MTPA ester of (-)-**1b**: ^{19}F NMR (188 MHz, CDCl$_3$) 90.6 ppm (*R*).

(1*R*,2*S*)-1-Tributylstannyl-2-[(*R*)-3-phenyl-1-hydroxypropyl]cyclopropane (1c). [α]$^{23}_{D}$ -18.8° (c 0.98, CHCl$_3$); bp 125℃ / 4 mmHg (Kugelrohr); Rf 0.29 (hexane/ethyl acetate = 10:1); IR (neat) 3350, 2960, 1375, 1075, 1050, 750, and 700 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ -0.33 (1H, dt, J = 10.2 Hz, J = 6.6 Hz) 0.4-0.6 (2H, m) 0.7-0.95 (15H, m) 0.85 (9H, t, J = 7.2 Hz) 1.20-1.35 (7H, m) 1.35-1.50 (6H, m) 1.7 (1H, brs, OH) 1.91 (2H, dt, J = 8.2 Hz, J = 8.0 Hz) 2.6-2.9 (3H, m) 7.1-7.3 (5H, m); ^{13}C NMR (50 MHz, CDCl$_3$) -2.36, 7.29, 8.62, 13.68, 22.43, 27.37, 29.10, 32.01, 38.74, 78.16, 125.67, 128.29, 142.24 ppm; Anal. Calcd for C$_{24}$H$_{42}$OSn: C, 61.95; H, 9.10. Found: C, 62.03; H, 9.42. (+)-MTPA ester of (±)-**1b**: ^{19}F NMR (188 MHz, CDCl$_3$) 90.6 ppm (*R*) and 90.3 ppm (*S*). (+)-MTPA ester of (-)-**1c**: ^{19}F NMR (188 MHz, CDCl$_3$) 90.6 ppm (*R*).

(1*R*,2*S*)-1-Tributylstannyl-2-[(*R*)-1-cyclohexylmethyl]cyclopropane (1d). $[\alpha]^{23}_D$ -27.7° (c 1.2, $CHCl_3$); bp 115℃ / 4 mmHg (Kugelrohr); Rf 0.33 (hexane/ethyl acetate = 10:1); IR (neat) 3350, 2925, 1450, 1380, 1180, 1070 cm^{-1} ;^{1}H NMR (200 MHz, $CDCl_3$) δ -0.25 (1H, m) 0.4-0.6 (2H, m) 0.87-0.98 (16H, m) 1.1-1.9 (29H, m) 1.61 (1H, brs, OH) 2.55 (1H, dd, J = 5.3 Hz, J = 8.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) -1.25, 6.66, 8.56, 13.67, 19.92, 26.26, 26.63, 27.40, 27.81, 28.53, 29.10, 83.38 ppm; Anal. Calcd for $C_{22}H_{44}OSn$: C, 59.61; H, 10.00. Found: C, 59.67; H, 10.03. (+)-MTPA ester of (±)-**1d**. ^{19}F NMR (188 MHz, $CDCl_3$) 90.6 ppm (*R*), 90.2 ppm (*S*). (+)-MTPA ester of (-)-**1d**: ^{19}F NMR (188 MHz, $CDCl_3$) 90.6 ppm (*R*).

(1*R*,2*S*)-1-Tributylstannyl-2-[(*R*)-1-benzyloxyhexyl]cyclopropane (7). To a solution of sodiumhydride (18 mg, oily, 0.44 mmol) in ether (2.0 ml) was added a THF (1.0 ml) solution of (-)-**1a** (172 mg, 0.40 mmol) at 0 ℃ dropwise and this was stirred for 0.5 h at the same temperature. To this solution was added a DMF (1.0 ml) solution of benzylbromide (75 mg, 0.44 mmol) dropwise at 0 ℃. After being stirred for 12 h at room temperature, the reaction was quenched by aq.NH_4Cl and extracted with ether. Silica gel flash column chromatography (hexane/ ethyl acetate = 50:1) gave (*R*)-**7** (203 mg, 0.39 mmol) as a colorless liquid in 97% yield: $[\alpha]^{23}_D$ -0.9° (c 1.01, $CHCl_3$); bp 220 ℃ / 4.5 mmHg (Kugelrohr); Rf 0.6 (hexane/ethyl acetate = 10:1); IR (neat) 2950, 1500, 1450, 1200, 1170, 1090, 1060, 940, 850, and 725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ -0.95 ~ -0.6 (1H, m) 0.6-0.9 (20H, m) 1.25-1.70 (21H, m) 2.55-2.68 (1H, m) 4.55 (1H, d, J = 12.0 Hz) 4.77 (1H, d, J = 12.0 Hz) 7.25-7.36 (5H, m); ^{13}C NMR (50 MHz, $CDCl_3$) 4.76, 8.62, 13.71, 14.12, 19.26, 22.71, 25.44, 27.42, 29.14, 32.10, 35.70, 70.37, 84.96, 127.21, 127.56, 128.21, 139.44 ppm; Anal. Calcd for $C_{28}H_{50}OSn$: C, 64.50; H, 9.67. Found: C, 64.56; H, 9.72.

(1*R*, 3*S*, 4*S*, 6*R*)-1,6-Bis[(*R*)-1-benzyloxyhexyl]bicyclopropane (3). A mixture of **7** (93 mg, 0.178 mmol), $PdCl_2(PPh_3)_2$ (6.0 mg) and CuI (7.0 mg) in DMF (0.6 ml) was stirred at 65 ℃ under atmosphere for 21 h, then 6.5 mg of $PdCl_2(PPh_3)_2$ was added to the reaction mixture. After being stirred for a further 4 h at the same temperature, the reaction was quenched by addition of water, extracted with ether, dried ($MgSO_4$) and evaporated. SiO_2 flash column chromatography (hexane-ethyl acetate = 100:1) gave **3** (27.4 mg, 0.059 mmol) in 66 % yield. No desired coupling product **3** was obtained when the reaction was carried out in the absence of Cu(I)I and the starting material was recovered in 81% yield. (1*R*,3*S*,4*S*,6*R*)-**3**: A single peak was detected at Rt. 4.9 min by HPLC analysis using Daicel OD column at 30 ℃ (ϕ4.6 x 75 mm, Hexane : *i*-PrOH = 10:1, 1.0 ml/min, 350 Kg/cm^2): $[\alpha]^{23}_D$ -2.9° (c 0.83, $CHCl_3$); bp 140 ℃ / 2.0 mmHg (Kugelrohr); Rf 0.5 (hexane/ethyl acetate = 10:1); IR (neat) 3050, 2950, 1740, 1600, 1580, 1450, 1430, 1370, 1340, 1310. 1270, 1170, 1100, 1060, 1020, 950, 850, 740, 710, 6900 cm^{-1};^{1}H NMR (200 MHz, $CDCl_3$) δ 0-0.15 (1H, m) 0.3-0.7 (3H, m) 0.89 (3H, m) 1.26-1.7 (8H, m) 2.63-2.74 (1H, m) 4.53 (1H, d, J = 12.0 Hz) 4.73 (1H, d, J = 12.0 Hz) 7.3 (5H, m); ^{13}C NMR (50 MHz, $CDCl_3$) 1.08, 4.58, 14.10, 14.91, 22.68, 25.36, 32.04, 35.33, 70.40, 83.20, 110.7, 127.26, 127.56, 128.25, 139.34 ppm; Anal. Calcd for $C_{32}H_{46}O_2$: C, 83.06; H, 10.02. Found: C, 83.11; H, 9.99.

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