Highly Stereocontrolled Cyclopropanation by the 1,3-Elimination of a Bis(tributylstannyl)propanol Derivative

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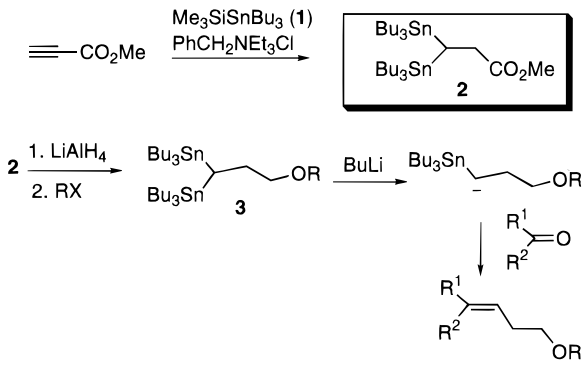
The highly stereoselective ring closure of γ-hydroxystannyl derivative was realized. The aldol reaction of methyl bis(tributylstannyl)propionate (**2**) with aldehyde **5** proceeds stereoselectively to give (γ-hydroxypropyl)stannane **6**, and the cyclopropanation reaction of aldol product **6** proceeds smoothly in a highly stereoselective manner presumably *via* a *W*-shape transition state. The stannyl group on the cyclopropane ring can be converted into various electrophiles with a retention of configuration. As a result, various stereocontrolled 1,2,3-trisubstituted cyclopropanes can be obtained in high yields.

The cyclopropane unit is very important and useful for synthetic organic chemistry. There are many methods for the highly stereoselective synthesis of disubstituted cyclopropanes including an asymmetric synthesis.[1] However, only a few reports are described for the synthesis of 1,2,3-trisubstituted cyclopropyl derivatives with high control of relative stereochemistry.[2] We have already reported that the reaction of methyl propiolate with $Me_3SiSnBu_3$[3] (**1**) and $BnEt_3NCl$ in DMF to give methyl 3,3-bis(tributylstannyl)propionate (**2**) in high yield, which is useful for synthetic organic chemistry. For example, we have previously shown that 3,3-bis(tributylstannyl)-propanol derivative **3** derived from **2** is a useful C-3 elongation reagent because the stannyl group can convert into a carbanion by treatment with BuLi.[4]

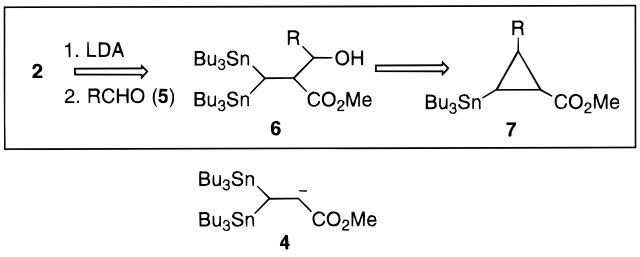
On the other hand, compound **2** was treated with LDA to give anion **4**, which can react with various electrophiles. In this paper, we report a novel highly stereocontrolled synthesis of 1,2,3-trisubstituted cyclopropanes **7** by 1,3-elimination of (γ-hydroxypropyl)stannanes **6** derived from anion **4** and aldehydes **5**, as shown in Scheme 2.

The aldol reaction between anion **4** and aldehyde **5** would give (γ-hydroxylpropyl)stannanes **6a** and **6b**. In this reaction, the major product is expected to be **6a** because the reaction would proceed *via* a-six membered transition state, and the bulky bis(tributylstannylmethyl) group should occupy the equatorial position, as shown in Figure 1.

Scheme 1



Scheme 2



It is generally accepted that the cyclopropanation proceeds *via* a *W*-shape transition state.[5] Thus, the γ-elimination of **6a** should proceed from conformer **6a-A**, and not conformer **6a-B**, to give cyclopropane **7a** as a main product. It is expected that steric repulsion between the alkyl group and the large tributylstannyl group might disfavor cyclization from this conformer **6a-B** (Figure 2). Thus, treatment of (γ-hydroxypropyl)stan-

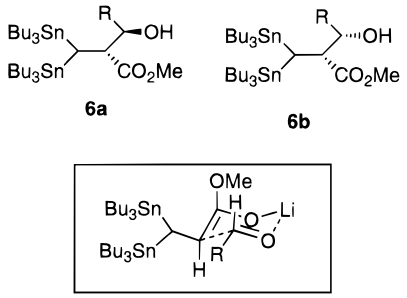


Figure 1.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) Lautens, M.; Patrick, H. M. D. *J. Org. Chem.* **1995**, *60*, 2474 and references therein.

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(3) (a) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354. Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schnieder, U. *J. Org. Chem.* **1987**, *52*, 4868. (b) Chenard, B. L.; Laganis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3666. Chenard, B. L.; Van Zyl, C. M.; Sanderson, D. R. *Tetrahedron Lett.* **1986**, *27*, 2801. Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561.

(4) Isono, N.; Mori, M. *Tetrahedron Lett.* **1995**, *36*, 9345. Isono, N.; Mori, M. *Main Group Metal Chem.* **1996**, *19*, 277.

(5) (a) Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3914. (b) Mori, M.; Kanda, N.; Ban, Y.; Aoe, K. *J. Chem. Soc., Chem. Commun.* **1988**, 12. (c) Mori, M.; Kanda, N.; Ban, Y. *Ibid.* **1986**, 1375.

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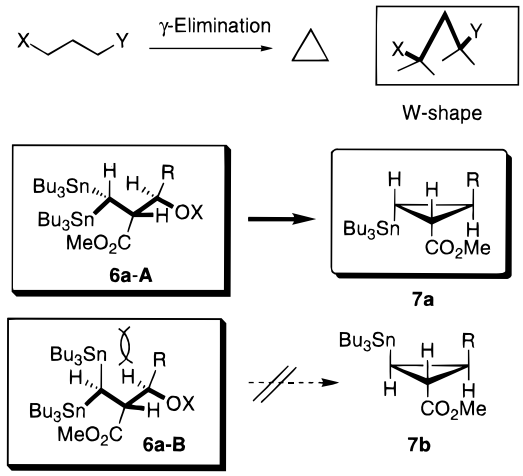


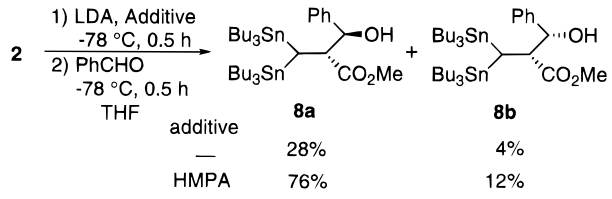
Figure 2.

Table 1. Reaction of 2 with Various Aldehydes[a]

run	RCHO		product	yield (**a** : **b**)
1	PhCHO	(**5a**)	**8** (R=Ph)	88% (6.3 : 1)
2	*t*-BuCHO	(**5b**)	**9** (R=^{t}Bu)	84% (17 : 1)
3	CHO	(**5c**)	**10** (R=CH_2CH)	66% (15 : 1)
4	Ph CHO	(**5d**)	**11** (R=(*E*)-PhCH=CH-)	78% (3.2 : 1)

a) HMPA (1 eq.) was added

Scheme 3

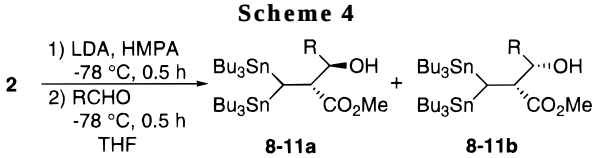


nane derivative **6a** with $BF_3{\cdot}Et_2O$,[6] PCl_3, or $SOCl_2$ in pyridine[7] should afford cyclopropane derivative **7a** in a highly stereoselective fashion.

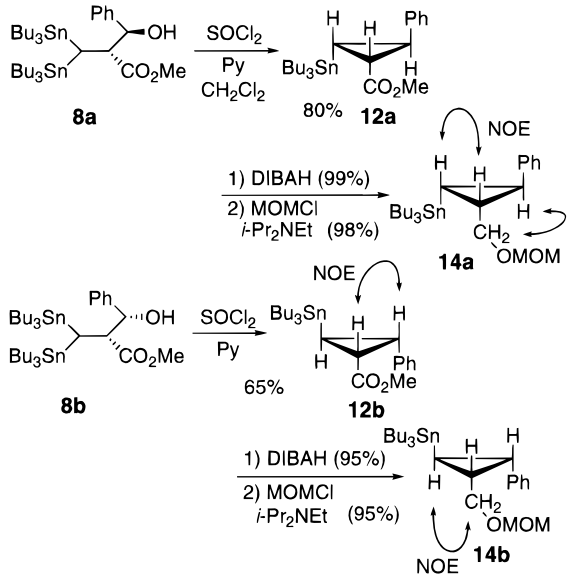
Aldol Reaction of Bis(tributylstannyl)propionate with Aldehyde. When methyl bis(tributylstannyl)-propionate (**2**) was treated with LDA in THF at −78 °C and then benzaldehyde **5a** was added at the same temperature, the aldol products **8a** and **8b** were obtained in 32% yield in a 7:1 ratio (Scheme 3). These compounds were easily separated by column chromatography on silica gel. The yield was improved when HMPA (1 equiv) was added to the reaction mixture (88% yield) and the ratio of **8a** to **8b** is almost the same (6.3:1).

Various aldehydes **5** were reacted with **2** in a similar manner, and the results are shown in Table 1. The aldol product of **2** with pivalaldehyde **5b** was obtained stereoselectively (**9a:9b** = 17:1) in good yield (run 2). Unsaturated aldehydes, such as acrolein (**5c**) and cinnamaldehyde (**5d**), gave the desired products **10** and **11** in good yields (runs 3 and 4). These results indicated that the aldol reaction of **2** with aldehydes **5** stereoselectively proceeded in good yields. However, the stereochemistry of these compounds are not determined at this stage.

Scheme 4



Scheme 5



Stereocontrolled Cyclopropanation of (γ-Hydroxypropyl)stannanes. We next attempted the cyclopropanation of (γ-hydroxypropyl)stannanes. Treatment of **8a** with $SOCl_2$ in the presence of pyridine[7d] gave the three-membered product **12a** in 80% yield and as a single isomer. To determine the stereochemistry of this compound, **12a** was converted into the methoxymethyl ether **14a**. The stereochemistry of this compound was determined to be that shown in Scheme 5 by NOE experiments. In a similar manner, the minor aldol product **8b** was also converted into cyclopropane **12b** in 65% yield and as a single isomer. The stereochemistry of this compound was established by NOE experiments on cyclopropanes **12b** and **14b**. Based on this and assuming that the reaction proceeds *via* a *W*-shape transition state,[5] the stereochemistry of the major aldol reaction product must be that shown for **8a** and that of the minor product is to be **8b**. For further confirmation of the stereochemistry of cyclopropanes **12a** and **12b**, Sn NMR chemical shifts of **12a**, **12b** and related compounds were compared to those reported by Lautens[8a] (Table 2). As the results, the chemical shifts of the stannyl group when it is on the same side of the oxygen substituent appeared at the higher field than those observed when the stannyl group is on the opposite site of the oxygen substituent.

The major aldol products **9a**, **10a**, and **11a** were treated with $SOCl_2$ in the presence of pyridine to give cyclopropanes **16a**, **17a**, and **18a** in yields of 95%, 78%, and 76% and as single isomers.[9] The vinylcyclopropanes

(6) Murayama, E.; Kikuchi, T.; Sasaki, K.; Saotome, N.; Sato, T. *Chem. Lett.* **1984**, 1897. Fujiwara, J.; Tokuyasu, J.; Sato, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 289.

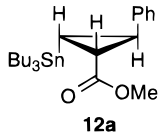
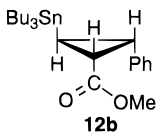
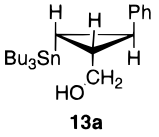
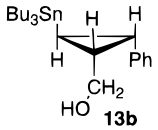
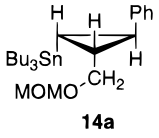
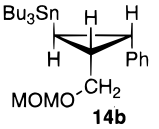
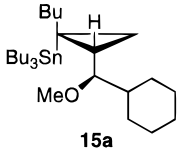
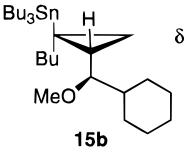
(7) (a) Kuivila, H. G.; Scarpa, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 6990. (b) Davis, D. D.; Chambers, R. L.; Johnson, H. T. *J. Organomet. Chem.* **1970**, *25*, C13. (c) Fleming, I.; Urch, C. *J. Organomet. Chem.* **1985**, *285*, 173. (d) Kadow, J. F.; Johnson, C. R. *Tetrahedron Lett.* **1984**, *25*, 5255. (e) Sato, T.; Nagatsuka, S. *Synlett* **1995**, 653.

(8) (a) Lautens, M.; Patrick, H. M. D.; Goh, J. B.; Zhang, C. H. *J. Org. Chem.* **1995**, *60*, 4213. (b) Seyferth, D.; Cohen, H. M. *Inorg. Chem.* **1963**, *2*, 625. (c) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1984**, *25*, 2415.

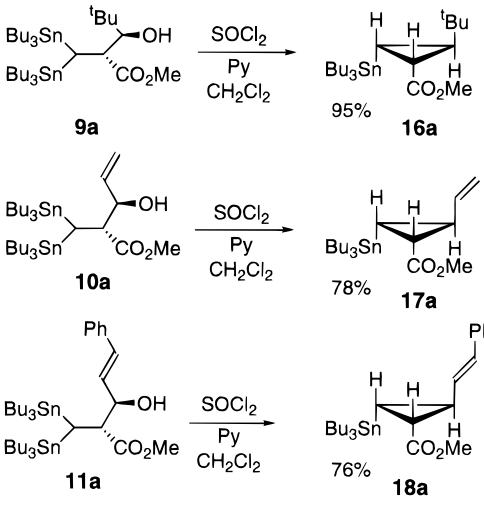
(9) In the case of **11a**, a trace amount (0.5%) of β-isomer in regard to the tributylstannyl group of **18a** was obtained.

(10) Hudlicky, T.; Reed, J. W. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, pp 899.

Table 2. Chemical Shifts of ^{119}Sn NMR

cyclopropane	chemical shift	cyclopropane	chemical shift
 **12a**	δ -15.8 ppm	 **12b**	δ -7.4 ppm
 **13a**	δ -11.6 ppm	 **13b**	δ -6.0 ppm
 **14a**	δ -11.4 ppm	 **14b**	δ -5.7 ppm
 **15a**	δ -9.6 ppm [9a]	 **15b**	δ -2.4 ppm [9a]

Scheme 6



9a → (SOCl$_2$, Py, CH$_2$Cl$_2$) → **16a** 95%

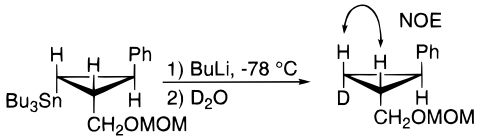
10a → (SOCl$_2$, Py, CH$_2$Cl$_2$) → **17a** 78%

11a → (SOCl$_2$, Py, CH$_2$Cl$_2$) → **18a** 76%

17a and **18a** are very interesting, since vinylcyclopropane rearrangement could occur easily.[10]

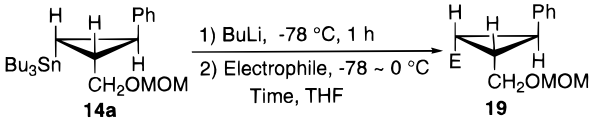
Synthesis of 1,2,3-Trisubstituted Cyclopropanes. Recently, Lautens studied the transmetalation of cyclopropyl stannanes.[8a] Diastereomerically pure cyclopropyl stannanes have been converted to the corresponding organolithium species and trapped with a variety of electrophiles.[8] The stereochemistry of the products was retained throughout the transmetalation-trapping sequences. Thus, the stannyl group on the cyclopropane ring could be converted into the corresponding organolithium species by transmetalation with retention of configuration and should react with various electrophiles. To confirm it, deuterated product **19a** was obtained in 99% yield (D content, 90%) when cyclopropylstannane **14a** was treated with BuLi at −78 °C followed by deuterium oxide (Scheme 7). From the NOE experiment on **19a**, the reaction proceeded with retention of configuration under these reaction conditions. The stannyl group of **14a** could be converted by various electrophiles, such as alkyl halides and aldehydes (Scheme 8), with a retention of configuration, and the results are shown in Table 3. In each case, a trisubstituted cyclopropane derivative was obtained in a highly stereocontrolled

Scheme 7



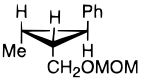
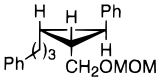
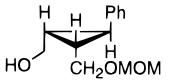
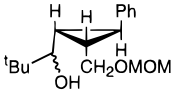
14a → (1) BuLi, -78 °C; (2) D$_2$O; NOE → 99% (90% D content) **19a**

Scheme 8



14a → (1) BuLi, -78 °C, 1 h; (2) Electrophile, -78 ~ 0 °C; Time, THF → **19**

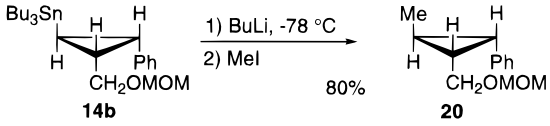
Table 3. Reaction of Cyclopropyl Lithium with Various Electrophiles

Entry	Electrophile	Time	Product		Yield
1	MeI	1 h		**19b**	96%
2 [a]	PhCH$_2$CH$_2$CH$_2$Br	2 h		**19c**	51%
3 [a]	(CH$_2$O)$_n$	1.5 h		**19d**	54%
4 [a]	^{t}BuCHO	2 h		**19e**	75% [b]

a) HMPA was added to the reaction mixture.

b) major : minor = 1.5 : 1

Scheme 9



14b → (1) BuLi, -78 °C; (2) MeI; 80% → **20**

fashion and in good to moderate yield. On the other hand, it was very interesting that the diastereoisomer **14b** could be converted into the corresponding methylated product **20** in 80% yield with a retention of configuration (Scheme 9). These results indicate that the various electrophiles could be introduced on the cyclopropyl ring by transmetalation of the stannyl group. Recently, Romo reported the palladium-catalyzed coupling reaction between a cyclopropylstannane and an aryl halide.[11] These facts indicate that the cyclopropane with a stannyl group is very useful for the synthesis of various cyclopropane derivatives.

In conclusion, we have shown that highly stereoselective ring closure of (γ-hydroxypropyl)stannanes is possible. The aldol reaction of methyl bis(tributylstannyl)-propionate (**2**) with aldehyde **5** proceeds stereoselectively, and the ring closure of the aldol product proceeds smoothly in a highly stereoselective manner *via* a *W*-shape transition state. The stannyl group on the cyclopropane ring can be converted into various electrophiles with a retention of configuration. As a result, various stereocontrolled 1,2,3-trisubstituted cyclopropanes can be obtained in high yields.

Experimental Section

Solvents were distilled under an argon atmosphere from sodium benzophenone (THF), CaH_2 (DMF, Et_3N), or P_2O_5 (CH_2Cl_2). All other reagents and solvents were purified when

(11) Schmitz, W. D.; Romo, D. *Tetrahedron Lett.* **1996**, *37*, 4857.

necessary by standard procedures. ^{1}H-NMR spectra were recorded at 270 MHz and 500 MHz. ^{13}C-NMR spectra were recorded at 67.5 MHz and 125 MHz. ^{119}Sn-NMR spectra were recorded at 100 MHz. ^{119}Sn NMR shifts (ppm) were reported relative to external tetramethyltin (Me_4Sn). Kieselgel 60 (Merck, 70−230 mesh) and Kieselgel 60 (Merck, 230−400 mesh) were used for column chromatography and flash column chromatography, respectively.

Methyl 3,3-Bis(tributylstannyl)propionate (2). To a solution of benzyltriethylammonium chloride (138 mg, 0.607 mmol) and methyl propiolate (27 μL, 0.303 mmol) in DMF (2.0 mL) was added $Me_3SiSnBu_3$ (210 μL, 0.601 mmol) at 0 °C, and the solution was stirred at room temperature for 6 h. Aqueous 10% NH_4OH solution was added, and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (hexane:ethyl acetate = 100:1 to 20:1) to give a colorless oil of **2** (184 mg, 91%). IR (neat) 1736, 1196 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.76−0.95 (m, 31 H), 1.22−1.57 (m, 24 H), 2.78 (d, J = 7.4 Hz, 2 H, $^3J(^{119}Sn-^1H)$ = 30.5, 30.5 Hz), 3.65 (s, 3 H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ −2.0, 10.1, 13.6, 27.6, 29.3, 35.3, 51.6, 176.1, ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ 11.4. MS m/z 665 (M^+ − 1), 609, 552, 319. EI-HRMS m/z calcd for $C_{24}H_{51}O_2{}^{120}Sn_2$ (M^+ − Bu) 611.1934, found 611.1923. Anal. Calcd for $C_{28}H_{60}O_2Sn_2$: C, 50.48; H, 9.08. Found: C, 50.50; H, 9.08.

General Procedure for the Preparation of Aldol Product. To a solution of LDA prepared from BuLi (1.6 equiv) and diisopropylamine (2.2 equiv) in THF (0.4 M solution of LDA) was added HMPA (1.0 equiv) and **2** (1.0 equiv) in THF (0.17 M solution of **2**) at −78 °C, and the solution was stirred at −78 °C for 1 h. Then aldehyde (2.0 equiv) was added to the solution at −78 °C, and the solution was stirred at −78 °C for 1.5 h. Saturated NH_4Cl solution was added, and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to give **8**−**11**.

(2*R,1′*S**)-Methyl 3,3-Bis(tributylstannyl)-2-(hydroxybenzyl)propionate (8a) and (2*R**,1′*R**)-Methyl 3,3-Bis(tributylstannyl)-2-(hydroxybenzyl)propionate (8b).** A crude product which was prepared from **2** (1.39 g, 2.09 mmol) and benzaldehyde (0.43 mL, 4.23 mmol) was purified by flash chromatography on silica gel [hexane−ethyl acetate (50:1−5:1)] to give a colorless oil of **8a** (1.22 g, 76%) and **8b** (0.25 g, 12%). **8a**: IR (neat) 3448, 1728, 1458, 1164 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.46 (d, J = 2.6 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 34.9, 34.8 Hz), 0.70−0.94 (m, 30 H), 1.20−1.53 (m, 24 H), 2.75 (brs, 1 H), 3.27 (dd, J = 8.6, 2.6 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 83.3, 31.7 Hz), 3.71 (s, 3 H), 4.61 (d, J = 8.6 Hz, 1 H), 7.27−7.36 (m, 5 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 4.8, 10.2, 11.9, 13.6, 13.7, 27.5, 27.7, 29.0, 29.4, 52.0, 54.2, 78.2, 127.0, 128.2, 128.5, 141.8, 177.3; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −2.6, 12.6; MS m/z 715 (M^+ − Bu), 607, 551, 483, 425, 409, 369, 319, 177, 91, 77; EI-HRMS m/z calcd for $C_{31}H_{57}O_3{}^{120}Sn_2$ (M^+ − Bu) 717.2351, found 717.2370. Anal. Calcd for $C_{35}H_{66}O_3Sn_2$: C, 54.43; H, 8.61. Found: C, 54.22; H, 8.88. **8b**: IR (neat) 3568, 1726, 1458, 1160 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82−0.94 (m, 30 H), 1.25 (d, J = 2.6 Hz, 1 H), 1.27−1.54 (m, 24 H), 2.03 (d, J = 2.8 Hz, 1 H), 3.26 (dd, J = 8.4, 2.6 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 82.3, 18.1 Hz), 3.40 (s, 3 H), 4.72 (dd, J = 8.4, 2.8 Hz, 1 H), 7.23−7.33 (m, 5 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 4.7, 10.5, 12.0, 13.7, 13.7, 27.6, 27.7, 29.2, 29.4, 51.4, 55.3, 76.8, 127.9, 126.4, 128.3, 142.6, 176.0; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −0.2, 8.8; MS m/z 715 (M^+ − Bu), 609, 551, 425, 409, 319, 265, 179, 77, 59, 41; EI-HRMS m/z calcd for $C_{31}H_{57}O_3{}^{120}Sn_2$ (M^+ − Bu) 717.2351, found 717.2311. Anal. Calcd for $C_{35}H_{66}O_3Sn_2$: C, 54.43; H, 8.61. Found: C, 54.41; H, 8.56.

(2*R,1′*S**)-Methyl 3,3-Bis(tributylstannyl)-2-(2,2-dimethyl-1-hydroxypropyl)propionate (9a) and (2*R**,1′*R**)-Methyl 3,3-Bis(tributylstannyl)-2-(2,2-dimethyl-1-hydroxypropyl)propionate (9b).** A crude product which was prepared from **2** (155 mg, 0.23 mmol) and pivaladehyde (60 μL, 0.55 mmol) was purified by chromatography on silica gel [hexane−ether (100:1−50:1)] to give a colorless oil of **9a** (139 mg, 80 %) and **9b** (8 mg, 4%). **9a**: IR (neat) 3462, 1726, 1162 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73−0.92 (m, 30 H), 0.88 (s, 9 H), 1.03 (d, J = 4.8 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 35.7, 31.6 Hz), 1.28−1.37 (m, 12 H), 1.40−1.51 (m, 12 H), 3.08 (dd, J = 9.5, 2.4 Hz, 1 H), 3.14 (dd, J = 4.8, 2.4 Hz, 1 H), 3.39 (d, J = 9.5 Hz, 1 H), 3.66 (s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 9.9, 11.1, 11.2, 13.7, 26.4, 27.6, 27.7, 29.3, 29.4, 36.2, 45.2, 51.8, 84.6, 178.3; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ 2.0, 7.1; MS m/z 751 (M^+ − 1), 695, 637, 607, 579, 551, 319, 291, 179, 57; HRMS m/z calcd for $C_{29}H_{61}O_3{}^{120}Sn_2$ (M^+ − Bu) 697.2664, found 697.2679. **9b**: IR (neat) 3566, 1730, 1152 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80−0.92 (m, 30 H), 0.88 (s, 9 H), 1.14 (d, J = 2.2 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 31.4, 30.8 Hz), 1.29−1.36 (m, 12 H), 1.40−1.51 (m, 13 H), 3.08 (dd, J = 9.0, 2.2 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 84.5, 18.3 Hz), 3.47 (d, J = 9.0, 5.5 Hz, 1 H), 3.62 (s, 3 H); MS m/z 695 (M^+ − Bu), 637, 607, 579, 551, 389, 319, 291, 179, 57; HRMS m/z calcd for $C_{29}H_{61}O_3{}^{120}Sn_2$ (M^+ − Bu) 697.2664, found 697.2653.

(2*R,1′*S**)-Methyl 3,3-Bis(tributylstannyl)-2-(1-hydroxy-2-propenyl)propionate (10a) and (2*R**,1′*R**)-Methyl 3,3-Bis(tributylstannyl)-2-(1-hydroxy-2-propenyl)propionate (10b).** A crude product which was prepared from **2** (667 mg, 1.00 mmol) and acrolein (130 μL, 1.95 mmol) was purified by chromatography on silica gel [hexane−ethyl acetate (50:1−5:1)] to give a colorless oil of **10a** (448 mg, 62 %) and **10b** (30 mg, 4%). **10a**: IR (neat) 3450, 1728, 1462, 1168 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77−0.94 (m, 31 H), 1.26−1.52 (m, 25 H), 2.95 (dd, J = 7.7, 3.6 Hz, 1 H), 3.69 (s, 3 H), 4.04 (dd, J = 7.7, 6.9 Hz), 5.24 (d, J = 10.4 Hz, 1 H), 5.31 (d, J = 17.1 Hz, 1 H), 5.80 (ddd, J = 17.1, 10.4, 6.9 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 4.8, 10.5, 11.6, 13.7, 13.7, 27.6, 27.7, 29.2, 29.3, 51.9, 52.5, 76.8, 117.6, 138.7, 177.0; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −1.7, 11.3; MS m/z 721 (M^+ − 1), 607, 665, 609, 551, 319, 291, 235, 177, 121, 41; HRMS m/z calcd for $C_{27}H_{55}O_3{}^{119}Sn{}^{120}Sn$ (M^+ − Bu) 665.2189, found 665.2174. Anal. Calcd for $C_{31}H_{64}O_3Sn_2$: C, 51.55; H, 8.93. Found: C, 51.51; H, 8.93. **10b**: IR (neat) 3510, 1732, 1464, 1198, 1164 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.79−0.96 (m, 30 H), 1.14 (d, J = 3.3 Hz, 1 H), 1.19−1.53 (m, 24 H), 1.84 (d, J = 4.4 Hz, 1 H), 3.01 (dd, J = 7.6, 3.3 Hz, 1 H), 3.63 (s, 3 H), 4.18 (ddd, J = 7.6, 6.2, 4.4 Hz), 5.13 (d, J = 10.4 Hz, 1 H), 5.25 (d, J = 17.2 Hz, 1 H), 5.82 (ddd, J = 17.2, 10.4, 6.2 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 3.8, 10.7, 12.0, 13.7, 13.7, 27.6, 27.7, 29.3, 29.3, 51.6, 53.3, 75.5, 116.3, 138.7, 176.1; MS m/z 691 (M^+ − OMe), 607, 665, 607, 551, 319, 291, 235, 179, 121, 41; HRMS m/z calcd for $C_{27}H_{55}O_3{}^{119}Sn{}^{120}Sn$ (M^+ − Bu) 665.2189, found 665.2151.

(2*R,1′*S**)-Methyl 3,3-Bis(tributylstannyl)-2-(1-hydroxy-3-phenyl-2-propenyl)propionate (11a) and (2*R**,1′*R**)-Methyl 3,3-Bis(tributylstannyl)-2-(1-hydroxy-3-phenyl-2-propenyl)propionate (11b).** A crude product which was prepared from **2** (201 mg, 0.30 mmol) and cinnamaldehyde (40 μL, 0.32 mmol) was purified by chromatography on silica gel [hexane−ethyl acetate (100:1−10:1)] to give a colorless oil of **11a** (144 mg, 60 %) and **11b** (45 mg, 19%). **11a**: IR (neat) 3440, 1728, 1464, 1206 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77−0.92 (m, 31 H), 1.26−1.37 (m, 12 H), 1.38−1.51 (m, 12 H), 2.63 (d, J = 4.9 Hz, 1 H), 3.05 (dd, J = 7.9, 3.1 Hz, 1 H), 3.70 (s, 3 H), 4.24 (ddd, J = 7.9, 7.4, 4.9 Hz), 6.13 (dd, J = 15.9, 7.4 Hz, 1 H), 6.62 (d, J = 15.9 Hz, 1 H), 7.24 (t, J = 7.4 Hz, 1 H), 7.31 (dd, J = 7.6, 7.5 Hz, 2 H), 7.37 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 4.9, 10.5, 11.8, 13.7, 13.7, 27.6, 27.7, 29.3, 29.4, 51.9, 53.0, 76.8, 126.6, 127.9, 128.6, 129.8, 133.2, 136.4, 177.1; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ 0.7, 12.3; MS m/z 741 (M^+ − Bu), 723, 665, 609, 577, 319, 235, 177, 131, 103, 41; HRMS m/z calcd for $C_{33}H_{59}O_3{}^{119}Sn{}^{120}Sn$ (M^+ − Bu) 741.2503, found 741.2549. Anal. Calcd for $C_{37}H_{68}O_3Sn_2$: C, 55.66; H, 8.59. Found: C, 55.68; H, 8.62. **11b**: IR (neat) 3510, 1730, 1458, 1158 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76−0.91 (m, 30 H), 1.28 (d, J = 3.2 Hz, 1 H), 1.28−1.36 (m, 12 H), 1.39−1.53 (m, 12 H), 2.00 (d, J = 4.0 Hz, 1 H), 3.12 (dd, J = 7.5, 3.2 Hz, 1 H), 3.60 (s, 3 H), 4.35 (ddd, J = 7.5, 6.8, 4.0 Hz), 6.16 (dd, J = 15.8, 6.8 Hz, 1 H), 6.57 (d, J = 15.8 Hz, 1 H), 7.23 (t, J = 7.2 Hz, 1 H), 7.30 (dd, J = 7.4, 7.2 Hz, 2 H), 7.35 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 3.7, 10.7, 11.9, 13.7, 13.7, 27.6, 27.7, 29.3, 29.4, 51.8, 53.3, 75.5, 126.6, 127.8, 128.6, 129.8, 131.7, 136.5, 176.1; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ 0.9, 9.9; MS m/z 741 (M^+ − Bu), 723,

665, 577, 435, 319, 235, 179, 131, 103, 41; HRMS *m/z* calcd for $C_{33}H_{59}O_3{}^{119}Sn^{120}Sn$ (M^+ − Bu) 741.2503, found 741.2521. Anal. Calcd for $C_{37}H_{68}O_3Sn_2$: C, 55.66; H, 8.59. Found: C, 55.75; H, 8.73.

General Procedure for the Cyclopropanation. To the solution of (γ-hydroxypropyl)stannane (1.0 equiv) in CH_2Cl_2 (0.1 M solution) was added pyridine (4.0 equiv) and $SOCl_2$ (2.0 equiv) at −30 °C. After the solution was stirred at the same temperature for 2 h, saturated $NaHCO_3$ was added and the aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel to give cyclopropane derivative.

(1*R,2*R**,3*R**)-Methyl 3-Phenyl-2-(tributylstannyl)cyclopropane-1-carboxylate (12a).** A crude product which was prepared from **8a** (92 mg, 0.12 mmol) was purified by chromatography on silica gel [hexane−ethyl acetate (50:1−20:1)] to give a colorless oil of **12a** (44 mg, 80%). IR (neat) 1722, 1437, 1198, 1176 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.83 (dd, *J* = 9.3, 8.3, Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 75.6 Hz), 0.85−0.94 (m, 15 H), 1.28−1.58 (m, 12 H), 2.11 (dd, *J* = 9.3, 3.7 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 32.8 Hz), 2.38 (dd, *J* = 8.3, 3.7 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 48.2 Hz), 3.69 (s, 3 H), 7.09 (d, *J* = 7.5 Hz, 2 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 7.27 (dd, *J* = 7.5, 7.2 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 10.3, 13.7, 17.3, 27.4, 27.7, 29.1, 31.0, 51.9, 125.8, 126.1, 128.4, 142.1, 175.5; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −15.8; MS *m/z* 465 (M^+), 409, 295, 265, 235, 177, 151, 91, 57; HRMS *m/z* calcd for $C_{19}H_{29}O_2{}^{120}Sn$ (M^+ − Bu) 409.1189, found 409.1193. Anal. Calcd for $C_{23}H_{38}O_2Sn$: C, 59.38; H, 8.23. Found: C, 59.33; H, 8.35.

(1*S,2*S**,3*R**)-Methyl 3-Phenyl-2-(tributylstannyl)cyclopropane-1-carboxylate (12b).** A crude product which was prepared from **8b** (79 mg, 0.10 mmol) was purified by chromatography on silica gel [hexane−ethyl acetate (100:1−10:1)] to give a colorless oil of **12b** (31 mg, 65%). IR (neat) 1734, 1436, 1194, 1168 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.85−0.93 (m, 15 H), 1.28−1.36 (m, 6 H), 1.31 (dd, *J* = 8.7, 7.5 Hz, 1 H), 1.45−1.60 (m, 6 H), 2.02 (dd, *J* = 8.2, 7.5 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 40.5 Hz), 2.52 (dd, *J* = 8.7, 8.2 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 47.0 Hz), 3.44 (s, 3 H), 7.17−7.28 (m, 5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.9, 9.0, 13.7, 25.7, 27.3, 29.1, 30.4, 51.4, 126.5, 127.8, 129.1, 138.1, 172.5; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −7.4; MS *m/z* 466 (M^+), 409, 291, 265, 235, 179, 151, 91, 57; HRMS *m/z* calcd for $C_{19}H_{29}O_2{}^{120}Sn$ (M^+ − Bu) 409.1190, found 409.1180. Anal. Calcd for $C_{23}H_{38}O_2Sn$: C, 59.38; H, 8.23. Found: C, 59.27; H, 8.36.

(1*R,2*R**,3*R**)-Methyl 3-*tert*-Butyl-2-(tributylstannyl)-cyclopropane-1-carboxylate (16a).** A crude product which was prepared from **9a** (49 mg, 0.065 mmol) was purified by chromatography on silica gel [hexane−ethyl acetate (100:1−20:1)] to give a colorless oil of **16a** (27 mg, 95%). IR (neat) 1720, 1176 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.37 (dd, *J* = 9.2, 9.0 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 18.8 Hz), 0.83−0.91 (m, 15 H), 0.86 (s, 9 H), 1.27 (dd, *J* = 9.0, 4.3 Hz, 1 H), 1.28−1.35 (m, 6 H), 1.44−1.53 (m, 6 H), 1.63 (dd, *J* = 9.2, 4.3 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 10.6 Hz), 3.64 (s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 9.9, 10.1, 13.8, 19.6, 27.4, 28.2, 29.2, 30.6, 39.4, 51.7, 177.0; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −16.07; MS *m/z* 389 (M^+ − Bu + 1, bp), 265, 235, 177, 151, 121, 57; HRMS *m/z* calcd for $C_{17}H_{33}O_2{}^{120}Sn$ (M^+ − Bu) 389.1502, found 389.1473. Anal. Calcd for $C_{21}H_{42}O_2Sn$: C, 56.65; H, 9.51. Found: C, 56.76; H, 9.52.

(1*R,2*R**,3*R**)-Methyl 2-(Tributylstannyl)-3-vinylcyclopropane-1-carboxylate (17a).** A crude product which was prepared from **10a** (38 mg, 0.052 mmol) was purified by chromatography on silica gel [hexane−ethyl acetate (100:1−50:1)] to give a colorless oil of **17a** (17 mg, 78%). IR (neat) 1728, 1168 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.40 (dd, *J* = 9.2, 8.4 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 16.2 Hz), 0.74−0.88 (m, 15 H), 1.21−1.28 (m, 6 H), 1.34−1.47 (m, 6 H), 1.77 (dd, *J* = 9.2, 3.5 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 23.2 Hz), 1.84 (ddd, *J* = 8.7, 8.4, 3.5 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 46.2 Hz), 3.59 (s, 3 H), 4.86 (dd, *J* = 9.9, 0.6 Hz, 1 H), 5.07 (dd, *J* = 17.1, 0.6 Hz, 1 H), 5.28 (ddd, *J* = 17.1, 9.9, 8.7 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 10.3, 13.8, 14.6, 25.3, 27.4, 29.1, 30.6, 51.9, 113.5, 140.8, 175.6; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −14.5; MS *m/z* 415 (M^+), 359, 265, 235, 179, 121; HRMS *m/z* calcd for $C_{19}H_{35}O_2{}^{120}Sn$ (M^+ − 1) 415.1659, found 415.1650. Anal. Calcd for $C_{19}H_{36}O_2Sn$: C, 54.96; H, 8.74. Found: C, 54.70; H, 8.69.

(1*R,2*R**,3*R**)-Methyl 3-((*E*)-2-Phenylethenyl)-2-(tributylstannyl)cyclopropane-1-carboxylate (18a).** A crude product which was prepared from **11a** (129 mg, 0.16 mmol) was purified by chromatography on silica gel [hexane−ethyl acetate (100:1−10:1)] to give a colorless oil of **18a** (60 mg, 76%) and (1*R**,2*S**,3*R**)-methyl 3-((*E*)-2-phenylethenyl)-2-(tributylstannyl)cyclopropane-1-carboxylate (**18b**) (0.3 mg, 0.5%). **18a**: IR (neat) 1720, 1438, 1198, 1164 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.59 (dd, *J* = 9.2, 8.4 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 16.0 Hz), 0.84−0.98 (m, 15 H), 1.28−1.36 (m, 6 H), 1.43−1.59 (m, 6 H), 1.95 (dd, *J* = 9.2, 3.4 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 23.6 Hz), 2.06 (ddd, *J* = 8.8, 8.4, 3.4 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 46.0 Hz), 3.68 (s, 3 H), 5.72 (dd, *J* = 15.7, 8.8 Hz, 1 H), 6.50 (d, *J* = 15.7 Hz, 1 H), 7.16−7.31 (m, 5 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 10.4, 13.8, 15.1, 25.8, 27.4, 29.1, 30.5, 51.9, 125.8, 127.0, 128.6, 129.2, 133.0, 137.3, 175.5; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −14.1; MS *m/z* 492 (M^+ + 1), 435, 403, 289, 265, 235, 179, 121; HRMS *m/z* calcd for $C_{21}H_{31}O_2{}^{120}Sn$ (M^+ − Bu) 435.1346, found 435.1340. Anal. Calcd for $C_{25}H_{40}O_2Sn$: C, 61.12; H, 8.21. Found: C, 61.05; H, 8.19. **18b**: IR (neat) 1728, 1456, 1212, 1170 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.82−0.95 (m, 15 H), 1.04 (dd, *J* = 10.0, 7.1 Hz, 1 H), 1.23−1.56 (m, 12 H), 1.78 (dd, *J* = 7.1, 3.5 Hz, 1 H), 2.45 (ddd, *J* = 10.0, 9.0, 3.5 Hz, 1 H), 3.72 (s, 3 H), 5.66 (dd, *J* = 15.7, 9.0 Hz, 1 H), 6.56 (d, *J* = 15.7 Hz, 1 H), 7.20−7.30 (m, 5 H); MS *m/z* 492 (M^+ + 1), 435, 403, 291, 265, 235, 179 (bp), 151, 121; HRMS *m/z* calcd for $C_{21}H_{31}O_2{}^{120}Sn$ (M^+ − Bu) 435.1346, found 435.1360.

(1*R,2*R**,3*R**)-2-(Methoxymethyloxymethyl)-3-phenyl-1-(tributylstannyl)cyclopropane (14a).** To the solution of **12a** (614 mg, 1.32 mmol) in toluene (13 mL) was added DIBAH in toluene solution (1.02 M, 3.9 mL, 4.0 mmol) at −78 °C. After the solution was stirred at the same temperature for 2 h, methanol (0.5 mL) and then brine were added and the aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane−ether (10:1−5:1)] to give a colorless oil of (1*R**,2*R**,3*R**)-2-(Hydroxymethyl)-3-phenyl-1-(tributylstannyl)cyclopropane (**13a**) (571 mg, 99%). IR (neat) 3356, 1498, 1456 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.44 (dd, *J* = 9.5, 7.0 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 6.0 Hz), 0.86−0.91 (m, 15 H), 1.28−1.56 (m, 13 H), 1.72 (dddd, *J* = 9.5, 7.5, 5.9, 4.0 Hz, 1 H), 1.77 (dd, *J* = 7.0, 4.0 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 49.6 Hz), 3.45 (dd, *J* = 10.9, 7.5 Hz, 1 H), 3.66 (dd, *J* = 10.9, 5.9 Hz, 1 H), 7.06 (d, *J* = 7.6 Hz, 2 H), 7.12 (t, *J* = 7.4 Hz, 1 H), 7.24 (dd, *J* = 7.6, 7.4 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 10.1, 12.8, 13.7, 26.1, 27.4, 29.1, 29.6, 67.5, 125.3, 125.5, 128.3, 144.2; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −11.6; MS *m/z* 381 (M^+ − Bu + 1), 251 (bp), 235, 177, 91, 57; HRMS *m/z* calcd for $C_{18}H_{29}O^{120}Sn$ (M^+ − Bu) 381.1241, found 381.1240. Anal. Calcd for $C_{22}H_{38}OSn$: C, 60.43; H, 8.76. Found: C, 60.31; H, 8.78. To the solution of **13a** (571 mg, 1.31 mmol) in CH_2Cl_2 (13 mL) were added *i*-Pr_2-NEt (0.25 mL, 3.29 mmol) and MOMCl (chloromethyl methyl ether, 1.1 mL, 6.31 mmol) at 0 °C. After the solution was stirred at room temperature for 24 h, saturated $NaHCO_3$ was added and the aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane−ether (50:1−25:1)] to give a colorless oil of **14a** (618 mg, 98%). IR (neat) 1498, 1456, 1150, 1106, 1048 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.44 (dd, *J* = 9.5, 7.0 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 6.0 Hz), 0.86−0.90 (m, 15 H), 1.28−1.60 (m, 12 H), 1.71 (dddd, *J* = 9.5, 7.4, 5.8, 4.1 Hz, 1 H), 1.79 (dd, *J* = 7.0, 4.1 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 49.8 Hz), 3.35 (s, 3 H), 3.41 (dd, *J* = 10.4, 7.4 Hz, 1 H), 3.61 (dd, *J* = 10.4, 5.8 Hz, 1 H), 4.61 (d, *J* = 6.6 Hz, 1 H), 4.67 (d, *J* = 6.6 Hz, 1 H), 7.07 (d, *J* = 7.6 Hz, 2 H), 7.11 (t, *J* = 7.3 Hz, 1 H), 7.23 (dd, *J* = 7.6, 7.3 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 10.1, 12.6, 13.7, 26.4, 26.7, 27.4, 29.1, 55.2, 71.7, 96.0, 125.2, 125.5, 128.2, 144.4; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −11.4; MS *m/z* 424 (M^+ − Bu), 265, 235, 177, 151, 91, 57, 45; HRMS *m/z* calcd for

$C_{20}H_{33}O_2{}^{120}Sn$ (M^+ − Bu) 425.1502, found 425.1502. Anal. Calcd for $C_{24}H_{42}O_2Sn$: C, 59.89; H, 8.80. Found: C, 59.79; H, 8.87.

(1*S,2*S**,3*R**)-2-(Methoxymethyloxymethyl)-3-phenyl-1-(tributylstannyl)cyclopropane (14b).** In a similar treatment of **12b** (66 mg, 0.14 mmol) with DIBAH (1.02 M, 0.34 mL, 0.35 mmol) at −78 °C gave (1*S**,2*S**,3*R**)-2-(hydroxymethyl)-3-phenyl-1-(tributylstannyl)cyclopropane (**13b**) (59 mg, 95%). IR (neat) 3346, 1464 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.39 (dd, J = 7.3, 7.2 Hz, 1 H), 0.86−0.90 (m, 15 H), 1.28−1.36 (m, 6 H), 1.43−1.60 (m, 8 H), 2.27 (dd, J = 7.7, 7.3 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 47.3 Hz), 3.18 (dd, J = 11.5, 9.0 Hz, 1 H), 3.57 (dd, J = 11.5, 5.3 Hz, 1 H), 7.18−7.30 (m, 5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 2.6, 8.9, 13.7, 25.3, 25.7, 27.4, 29.2, 64.3, 126.1, 128.2, 128.7, 139.6; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −6.0; MS m/z 381 (M^+ − Bu), 291; 251, 235, 177, 130. **14b**: 95%, IR (neat) 1496, 1464, 1150, 1108, 1052 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.34 (dd, J = 7.4, 7.3 Hz, 1 H, $^2J(^{119}Sn-^1H)$ = 16.3 Hz), 0.87−0.90 (m, 15 H), 1.27−1.61 (m, 12 H), 1.45 (dddd, J = 9.2, 7.7, 7.3, 5.5 Hz, 1 H), 2.26 (dd, J = 7.7, 7.4 Hz, 1 H, $^3J(^{119}Sn-^1H)$ = 48.0 Hz), 3.05 (s, 3 H), 3.13 (dd, J = 10.5, 9.2 Hz, 1 H), 3.38 (dd, J = 10.5, 5.5 Hz, 1 H), 4.33 (d, J = 6.3 Hz, 1 H), 4.47 (d, J = 6.3 Hz, 1 H), 7.14−7.27 (m, 5H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 2.9, 8.9, 13.7, 22.9, 25.5, 27.4, 29.2, 54.7, 68.8, 96.1, 125.8, 127.8, 129.1, 139.8; ^{119}Sn NMR (100.55 MHz, $CDCl_3$) δ −5.7; MS m/z 425 (M^+ − Bu + 1), 395, 265, 235, 179, 151, 130, 91, 45; HRMS m/z calcd for $C_{20}H_{33}O_2{}^{120}Sn$ (M^+ − Bu) 425.1503, found 425.1531.

General Procedure for the Transmetalation Reaction. To a solution of **14a** (1.0 equiv) in THF (0.1 M solution) were added BuLi (2.0 equiv) and HMPA (2.0 equiv) at −78 °C. After the solution was stirred at the same temperature for 0.5 h, an electrophile (3.0 equiv) was added and the solution was stirred at 0 °C for 2 h. Saturated NH_4Cl was added, and the aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel to give **19**.

(1*R,2*R**,3*R**)-3-Deuterio-1-(methoxymethyloxymethyl)-2-phenylcyclopropane (19a).** To a solution of **14a** (48 mg, 0.10 mmol) in THF (1.0 mL) was added BuLi (1.66 *N* hexane solution, 0.12 mL, 0.20 mmol) at −78 °C. After the solution was stirred at the same temperature for 0.5 h, and D_2O (0.2 mL) was added. After the usual workup, the residue was purified by chromatography on silica gel [hexane−ethyl acetate (50:1−10:1)] to give a colorless oil of **19a** (19 mg, 99%, D content, 90%). IR (neat) 1498, 1142, 1106, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.97 (dd, J = 8.5, 5.3 Hz, 1 H), 1.43 (dddd, J = 8.5, 6.8, 6.7, 4.6 Hz, 1 H), 1.82 (dd, J = 5.3, 4.6 Hz, 1 H), 3.36 (s, 3 H), 3.52 (dd, J = 10.6, 6.7 Hz, 1 H), 3.57 (dd, J = 10.6, 6.8 Hz, 1 H), 4.65 (d, J = 6.7 Hz, 1 H), 4.67 (d, J = 6.7 Hz, 1 H), 7.07 (d, J = 7.6 Hz, 2 H), 7.14 (t, J = 7.4 Hz, 1 H), 7.25 (dd, J = 7.6, 7.4 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 13.7, 21.4, 22.4, 55.2, 71.0, 96.0, 125.6, 125.8, 128.3, 142.5; MS m/z 193 (M^+), 178, 161, 148, 132, 118, 91, 44; HRMS m/z calcd for $C_{12}H_{15}O_2D$ (M^+) 193.1213, found 193.1198.

(1*R,2*R**,3*R**)-1-(Methoxymethyloxymethyl)-3-methyl-2-phenylcyclopropane (19b).** A crude produce which was prepared from **14a** (31 mg, 0.065 mmol) and MeI (12 μL, 0.78 mmol) was purified by chromatography on silica gel [hexane−ether (50:1−10:1)] to give a colorless oil of **19b** (13 mg, 95%). IR (neat) 1500, 1148, 1106, 1048 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, J = 7.8 Hz, 3 H), 1.31 (ddd, J = 11.7, 7.8, 5.7 Hz, 1 H), 1.47−1.53 (m, 2 H), 3.37 (s, 3 H), 3.58 (dd, J = 10.6, 7.8 Hz, 1 H), 3.79 (dd, J = 10.6, 5.7 Hz, 1 H), 4.65 (d, J = 6.5 Hz, 1 H), 4.68 (d, J = 6.5 Hz, 1 H), 7.03−7.25 (m, 5 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.0, 21.7, 27.0, 29.5, 55.2, 66.9, 96.2, 125.4, 125.7, 128.3, 142.9; MS m/z 174 (M^+ − MeOH), 161, 145, 131, 129, 91, 45; HRMS m/z calcd for $C_{13}H_{18}O_2$ (M^+) 206.1307, found 206.1308.

(1*R,2*R**,3*R**)-1-(Methoxymethyloxymethyl)-3-(3-phenylpropyl)-2-phenylcyclopropane (19c).** A crude product which was prepared from **14a** (43 mg, 0.09 mmol) and 1-bromo-3-phenylpropane (40 μL, 0.27 mmol) was purified by chromatography on silica gel [hexane−ether (50:1−10:1)] to give a colorless oil of **19c** (14 mg, 51%). IR (neat) 1498, 1452, 1150, 1106, 1046 cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 1.09 (dddd, J = 8.8, 7.7, 6.4, 5.3 Hz, 1 H), 1.30 (dddd, J = 14.1, 9.3, 7.2, 6.4 Hz, 1 H), 1.40 (dd, J = 5.3, 5.1 Hz, 1 H), 1.47 (dddd, J = 7.9, 7.7, 6.6, 5.1 Hz, 1 H), 1.45−1.55 (m, 1 H), 1.64−1.76 (m, 2 H), 2.49 (ddd, J = 10.8, 7.9, 7.5 Hz, 1 H), 2.54 (ddd, J = 10.8, 7.8, 7.3 Hz, 1 H), 3.19 (s, 3 H), 3.45 (dd, J = 10.7, 7.9 Hz, 1 H), 3.58 (dd, J = 10.7, 6.6 Hz, 1 H), 4.49 (d, J = 6.5 Hz, 1 H), 4.54 (d, J = 6.5 Hz, 1 H), 6.95−7.20 (m, 10 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.7, 27.7, 28.1, 28.5, 31.6, 35.8, 55.2, 67.1, 96.2, 125.5, 125.7, 125.8, 128.3, 128.3, 128.4, 142.4, 142.8; MS m/z 278 (M^+ − CH_3OH), 265, 247, 235, 144, 131, 117, 104, 91, 45; HRMS m/z calcd for $C_{21}H_{26}O_2$ (M^+), 310.1933, found 310.1912.

(1*S,2*R**,3*R**)-2-(Hydroxymethyl)-1-(methoxymethyloxymethyl)-3-phenylcyclopropane (19d).** A crude product which was prepared from **14a** (49 mg, 0.10 mmol) and paraformaldehyde (14 mg) was purified by chromatography on silica gel [hexane−ether (50:1−1:1)] to give a colorless oil of **19d** (12 mg, 54%). IR (neat) 3422, 1500, 1152, 1102, 1040 cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 1.41 (dd, J = 7.1, 4.1 Hz, 1 H), 1.44−1.50 (m, 1 H), 1.58−1.68 (m, 1 H), 2.64 (brs, 1 H), 3.12 (s, 2 H), 3.17 (dd, J = 11.2, 10.1 Hz, 1 H), 3.27 (dd, J = 12.1, 10.1 Hz, 1 H), 3.68 (dd, J = 11.9, 5.5 Hz, 1 H), 3.93 (dd, J = 11.9, 5.1 Hz, 1 H), 4.35 (s, 2 H), 6.82−6.86 (m, 2 H), 6.99−7.13 (m, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 25.9, 26.9, 29.4, 55.6, 62.1, 67.2, 96.3, 126.0, 126.0, 128.4, 141.0; MS m/z 190 (M^+ − CH_3OH), 172, 160, 130, 115, 91, 45; HRMS m/z calcd for $C_{13}H_{18}O_3$ (M^+) 222.1256, found 222.1251.

(1*R,2*S**,3*S**)-1-(2,2-Dimethyl-1-hydroxypropyl)-2-(methoxymethyloxymethyl)-3-phenylcyclopropane (19e).** A crude product which was prepared from **14a** (49 mg, 0.10 mmol) and pivalaldehyde (35 μL, 0.32 mmol) was purified by chromatography on silica gel [hexane−ether (50:1−3:1)] to give a colorless oil of **19e** (21 mg, 75% major:minor = 1.5:1). **19e** (major isomer): IR (neat) 3482, 1498, 1464, 1154, 1104, 1046 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.97 (s, 9 H), 1.44 (ddd, J = 9.1, 7.1, 5.5 Hz, 1 H), 1.56 (brs, 1 H), 1.63 (dddd, J = 9.1, 7.7, 6.4, 5.5 Hz, 1 H), 2.00 (dd, J = 5.5, 5.5 Hz, 1 H), 3.30 (d, J = 7.1 Hz, 1 H), 3.36 (s, 3 H), 3.71 (dd, J = 10.6, 7.7 Hz, 1 H), 3.83 (dd, J = 10.6, 6.4 Hz, 1 H), 4.64 (d, J = 6.6 Hz, 1 H), 4.67 (d, J = 6.6 Hz, 1 H), 7.11 (d, J = 7.2 Hz, 2 H), 7.15 (t, J = 7.4 Hz, 1 H), 7.26 (dd, J = 7.4, 7.2 Hz, 2 H); MS m/z 260 (M^+ − H_2O), 246, 233, 221, 159, 91, 57, 45; HRMS m/z calcd for $C_{17}H_{26}O_3$ (M^+) 278.1882, found 278.1888. **19e** (minor isomer): IR (neat) 3504, 1502, 1464, 1154, 1102, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.97 (s, 9 H), 1.54 (ddd, J = 10.1, 9.2, 5.2 Hz, 1 H), 1.66 (dddd, J = 10.7, 9.2, 5.5, 5.1 Hz, 1 H), 1.75 (dd, J = 5.2, 5.1 Hz, 1 H), 3.12 (d, J = 10.1 Hz, 1 H), 3.41 (s, 3 H), 3.46 (brs, 1 H), 3.50 (dd, J = 10.9, 10.7 Hz, 1 H), 4.12 (dd, J = 10.9, 5.5 Hz, 1 H), 4.68 (d, J = 6.6 Hz, 1 H), 4.71 (d, J = 6.6 Hz, 1 H), 7.02 (d, J = 7.4 Hz, 2 H), 7.17 (t, J = 7.3 Hz, 1 H), 7.26 (dd, J = 7.4, 7.3 Hz, 2 H); MS m/z 260 (M^+ − H_2O), 246, 233, 221, 159, 91, 57, 45.

(1*R,2*S**,3*S**)-1-(Methoxymethyloxymethyl)-3-methyl-2-phenylcyclopropane (20).** A crude product which was prepared from **14b** (24 mg, 0.05 mmol) and MeI (10 μL, 0.16 mmol) was purified by chromatography on silica gel [hexane−ether (50:1−10:1)] to give a colorless oil of **20** (9.2 mg, 80%). IR (neat) 1498, 1148, 1108, 1044 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.19−1.22 (m, 2 H), 1.25 (s, 3 H), 1.97 (dd, J = 10.4, 3.3 Hz, 1 H), 3.11 (s, 3 H), 3.27 (d, J = 7.2 Hz, 2 H), 4.39 (d, J = 6.5 Hz, 1 H), 4.49 (d, J = 6.5 Hz, 1 H), 7.15 (t, J = 7.2 Hz, 1 H), 7.19 (d, J = 7.4 Hz, 2 H), 7.24 (dd, J = 7.4, 7.2 Hz, 2 H); MS m/z 206 (M^+), 176, 145, 131, 115, 91, 45; HRMS m/z calcd for $C_{13}H_{18}O_2$ (M^+) 206.1306, found 206.1312.

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