An Alternative, Highly Stereocontrolled Synthesis of Trisubstituted Cyclopropane Derivatives from Methyl Bis(tributylstannyl)propionate

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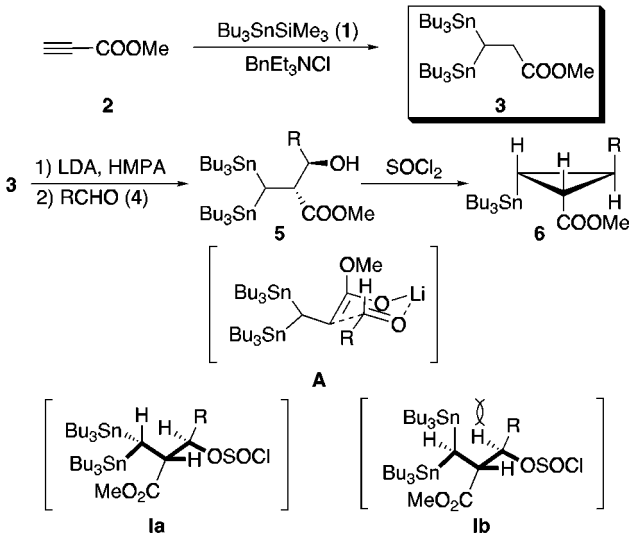
We previously reported the synthesis of highly stereocontrolled cyclopropane derivatives **6** from methyl bis(tributylstannyl)propionate (**3**),[1a,b] which was synthesized from methyl propiolate (**2**) and $Bu_3SnSiMe_3$ (**1**) in the presence of $BnEt_3NCl$.[1c] The aldol condensation of **3** and aldehyde **4** gave **5** via six-membered transition state **A** in good yield and in a highly stereocontrolled manner (Scheme 1). Cyclopropanation of **5** with $SOCl_2$ by 1,3-elimination gave **6** in good yield via W-shaped transition state[3] **Ia** not **Ib**, because of the steric hindrance between the bulky stannyl group and the alkyl group in **Ib**. Thus, we synthesized various 1,2,3-trisubstituted cyclopropane derivatives using this procedure in a highly stereoselective manner.

We now want to report the synthesis of the fragment **8** for the synthesis of the natural product, ambruticin (**7**), for the application of our method. The first total synthesis of **7** was reported by Kende.[2] The retrosynthetic analysis of amburuticin is shown in Scheme 2. The key intermediate **8** would be prepared from stannylated cyclopropane derivative **9**, which would be prepared from **3** and aldehyde **4a**.

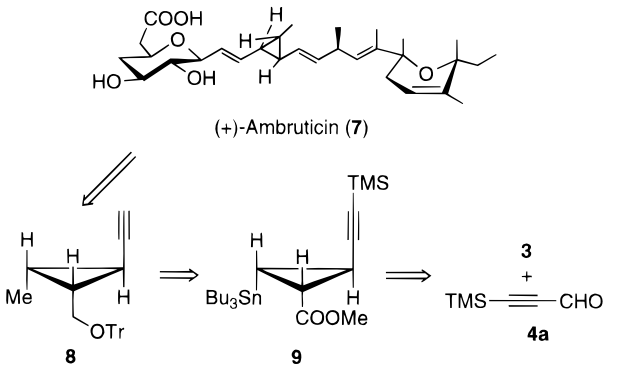
Aldol condensation of **3** and aldehyde **4a** smoothly proceeded to produce the alcohols, **10** and **11**, in 54% yield. The ratio of the major isomer **10** to the minor isomer **11** is 2.6 to 1. The stereochemistries of these products were not determined at this stage. Cyclopropanation of the major isomer **10** with $SOCl_2$ and pyridine afforded the desired cyclopropane **9** in 46% yield. The yield was improved to 89% when the reaction was carried out in a similar manner in the presence of KI. Treatment of **9** with DIBAL-H followed by tritylation gave cyclopropane **13** in 85% yield from **9**. The stereochemistry of compound **13** (and these for compounds **10** and **9**) was determined by NOESY spectra. These stereochemistries are as depicted in Scheme 3. In this reaction, undesired cyclopropane **12** was not obtained because of the steric hindrance. The stannyl group of **9** was stereoselectively converted into the methyl group by treatment with BuLi and then MeI at −78 °C in 73% yield. Desilylation smoothly proceeded to give a quantitative yield of the desired key intermediate **8**, whose spectral data agreed with those previously reported.[2]

In this synthesis, the ratio of the aldol products, **10** and **11**, was moderate. Thus, we tried to develop an alternative cyclopropanation for the synthesis of **8**. The procedure is shown in Scheme 4. Methylation of **3** gives compound **14** (R^1 = Me), which converts into the aldehyde **15** (R^1 = Me). If lithium (trimethylsilyl)acetylide **16a**

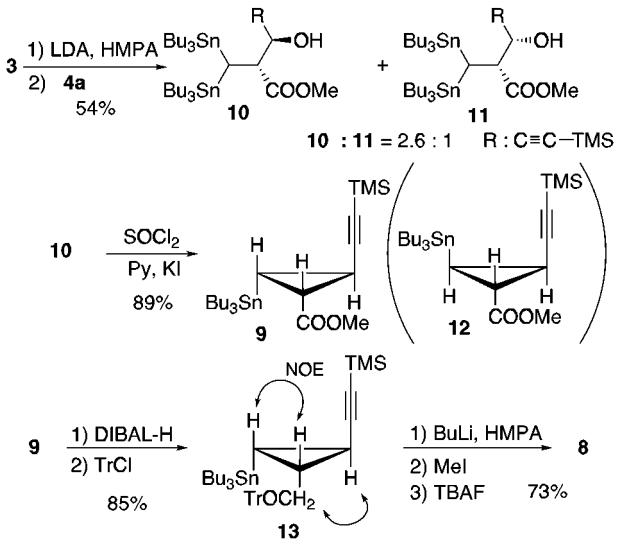
Scheme 1



Scheme 2



Scheme 3



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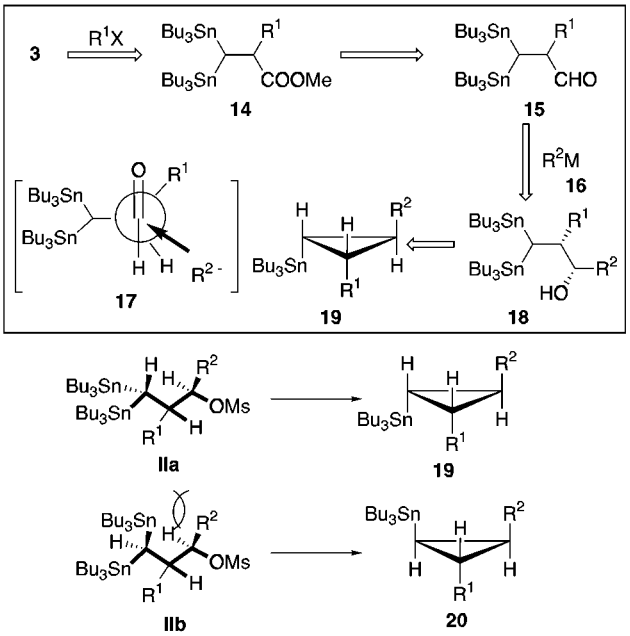
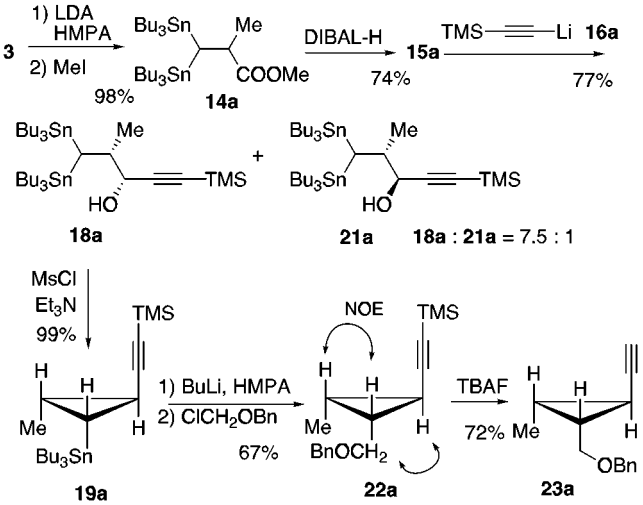
Scheme 4



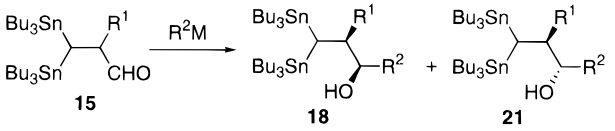
Scheme 5



attacks the carbonyl group of the aldehyde **15** according to the Felkin−Anh model **17**, the alcohol **18** (R^1 = Me, R^2 = CCTMS) would be obtained. Then, cyclopropanation of **18** would give **19** stereoselectively via 1,3-elimination. In this case, the cyclopropane **19** should be formed because of the steric hindrance of the stannyl group and R^2 in **IIb** as shown in Scheme 4. If the stannyl group on the cyclopropane ring can be converted into the hydroxymethyl group stereoselectively, we should obtain compound **8**.

Methylation of compound **3** gave compound **14a** in 98% yield, which was reduced with DIBAL-H to give **15a** in 74% yield (Scheme 5). Reaction of **15a** with lithium (trimethylsilyl)acetylide **16a** smoothly proceeded to give the alcohols **18a** and **21a** in 77% yield. As expected, the ratio of the major isomer **18a** to the minor isomer **21a** was 7.5 to 1 according to the Felkin−Anh model, although the stereochemistry was not determined at this stage. Treatment of **18a** with MsCl in the presence of Et_3N gave the cyclopropane **19a** via W-shaped transition state **IIa**, and the cyclopropane **20a** was not obtained. Successive treatment of **19a** with BuLi and chloromethyl benzyl ether at −78 °C in THF gave the cyclopropane

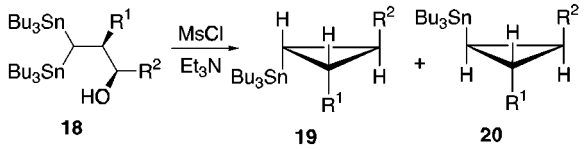
Table 1.[a] **Reaction of 15 with R^2M**



run	R^1		R^2M	total yield (%)	**18/21**
1[b]	CH_3	**15a**	Li≡TMS	77	7.5/1
2[b]	CH_2OBn	**15b**	Li≡TMS	91	5.7/1
3[b]	CH_2Ph	**15c**	Li≡TMS	93	13.1/1
4[b]	$CH_2CH{=}CH_2$	**15d**	Li≡TMS	92	5.0/1
5[b]	CH_2OTES	**15e**	Li≡TMS	80	2.5/1
6[c]	CH_2Ph	**15f**	BuMgCl	79	7.8/1
7[c]	CH_2Ph	**15g**	PhMgBr	100	6.5/1
8[c]	CH_2Ph	**15h**	*t*-BuMgCl	98	23.2/1
9[b]	$CH_2CH{=}CH_2$	**15i**	BuMgCl	97	5.3/1
10[b]	$CH_2CH{=}CH_2$	**15j**	PhMgBr	99	2.9/1

[a] All reactions were carried out in THF. [b] at −78 °C. [c] at −78 °C to 0 °C.

Table 2.[a] **Cyclopropanation of 18**



run	R^1		R^2	total yield (%)	**19/20**
1	CH_3	**18a**	≡TMS	99	100/0
2	CH_2OBn	**18b**	≡TMS	87	100/0
3	CH_2Ph	**18c**	≡TMS	94	36/64
4	$CH_2CH{=}CH_2$	**18d**	≡TMS	97	86/14
5	CH_2OTES	**18e**	≡TMS	87	100/0
6	CH_2Ph	**18f**	Bu	90	93/7
7	CH_2Ph	**18g**	Ph	97	93/7
8	CH_2Ph	**18h**	*t*-Bu	93	100/0
9	$CH_2CH{=}CH_2$	**18i**	Bu	93	100/0
10	$CH_2CH{=}CH_2$	**18j**	Ph	93	100/0

[a] All reactions were carried out at −30 °C in CH_2Cl_2.

22a. An NOE experiment performed on **22a** showed that the desired cyclopropane was obtained from **18a**. Deprotection of the silyl group of **22a** gave **23a**, which would be a fragment for the synthesis of ambruticin (**7**).

The procedure shown in Scheme 4 was considered to be an alternative general synthetic method for the 1,2,3-trisubstituted cyclopropane derivative. Thus, we tried to develop this alternative cyclopropanation reaction. At first, we examined the reaction of the aldehyde **15** with alkylmetal complex **16a**. The results are shown in Table 1. As expected, the alkylation products **18** and **21** are obtained in good yield according to the Felkin−Anh model, and the ratios of the major isomer **18** to the minor one **21** are high. The Grignard reagent can be used, and a higher yield and higher selectivity were obtained in each case.

Subsequently, cyclopropanation of the major isomer **18** was carried out by treatment with MsCl and Et_3N. The results are shown in Table 2. In these cases, the yields are high, and the expected cyclopropane derivatives **19** are obtained as the major product. In the case of cyclopropanation of **18c**, the ratio of **19c** to **20c** is 1 to 2. Presumably, the reason would be the steric hindrance between the bulky benzyl group (R^1) and the stannyl group compared with that between the (R^2) alkynyl group and the stannyl group in **IIb**.

These results indicate that an alternative cyclopropanation can be developed from methyl 3,3-bis(tributylstannyl)propionate. This means that various 1,2,3-

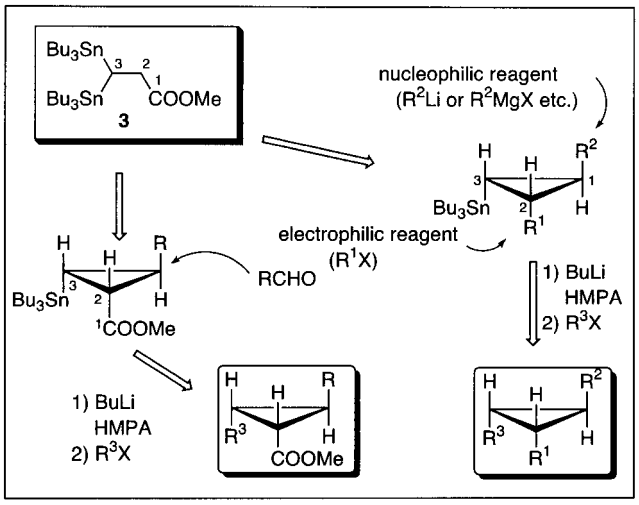


Figure 1.

trisubstituted cyclopropanes can be prepared stereoselectively using two methods (Figure 1). Namely, in the case of the first procedure[1c] that was reported by our group, the aldol condensation of **3** is followed by cyclopropanation.

In this case, the cyclopropane ring is constructed by two carbons (C-2 and C-3) of **3** and the carbonyl carbon of the aldehyde. Thus, the alkyl group on the cyclopropane ring is derived from the aldehyde. On the other hand, in the alternative cyclopropanation, the cyclopropane ring is formed by three carbons of **3**, and the nucleophilic reagent is introduced onto the C-1 carbon and the electrophilic reagent is introduced onto the C-2 carbon. In each case, the stannyl group on the cyclopropane ring can be converted into another alkyl group, stereoselectively.

Experimental Section

General. Solvents were distilled under an argon atmosphere from sodium benzophenone (THF, toluene) or CaH_2 (CH_2Cl_2). All other reagents were purified when necessary by standard procedure. All reactions were conducted under an argon atmosphere. ^{1}H NMR spectra were recorded at 500 MHz. ^{13}C NMR spectra were recorded at 125 MHz. ^{1}H NMR and ^{13}C NMR shifts (ppm) were reported relative to internal tetramethylsilane (Me_4Si). For ^{13}C NMR spectra, carbon type is defined as 3 (CH_3), 2 (CH_2), 1 (CH), or 0 (C) on the basis of DEPT experiments. ^{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.

(2*R,1′*S**)-Methyl 3,3-Bis(tributylstannyl)-2-(1′-hydroxy-3′-(trimethylsilyl)-2′-propynyl)propionate (10) and (2*R**,1′*R**)-Methyl 3,3-Bis(tributylstannyl)-2-(1′-hydroxy-3′-(trimethylsilyl)-2′-propynyl)propionate (11).** To a solution of LDA prepared from diisopropylamine (0.21 mL, 1.46 mmol) and BuLi (1.71 M in hexane solution) in THF (2.5 mL) was added HMPA (0.12 mL, 0.66 mmol) at −78 °C, and the solution was stirred for 20 min. To the solution was added **3** (433 mg, 0.65 mmol) in THF (4.0 mL), and the solution was stirred for 1 h at −78 °C. Then **4a** (165.4 mg, 1.31 mmol) in THF (1.5 mL) was added to the solution at −78 °C, and the solution was stirred for 3 h. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (50:1 hexane/AcOEt) to provide **10** (203 mg, 39%), **11** (77 mg, 15%), and recovered **3** (112 mg, 26%). **10**: IR (neat) 3494, 1730, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.78−0.92 (m, 30 H), 1.21 (d, J = 3.1 Hz, 1 H, ^2J (^{119}Sn−^{1}H) = 27.9 Hz), 1.29−1.51 (m, 24 H), 2.67 (d, J = 5.9 Hz, 1 H), 3.10 (dd, J = 3.1, 9.0 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 49.4, 25.4 Hz), 3.69 (s, 3 H), 4.39 (dd, J = 5.9, 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -0.2 (3), 4.6 (1), 10.4 (2), 11.4 (2), 13.6 (3), 27.6 (2), 27.6 (2), 29.1 (2), 29.2 (2), 52.0 (3), 53.8 (1), 67.5 (1), 91.5 (0), 104.6 (0), 176.1 (0); MS m/z 735 (M^+ − Bu), 677, 579, 551, 429, 318, 179, 72, 59, 43; HRMS m/z calcd for $C_{30}H_{61}O_3Si^{120}Sn_2$ (M^+ − Bu) 737.2435, found 737.2407. **11**: IR (neat) 3504, 1734, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 0.79−0.91 (m, 30 H), 1.24 (d, J = 3.9 Hz, 1 H, ^2J (^{119}Sn−^{1}H) = 27.3 Hz), 1.28−1.49 (m, 24 H), 2.19 (d, J = 5.8 Hz, 1 H), 3.18 (dd, J = 3.9, 6.4 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 54.6, 28.2 Hz), 3.68 (s, 3 H), 4.50 (t, J = 6.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3), 2.8 (1), 10.8 (2), 11.8 (2), 13.6 (3), 27.6 (2), 27.6 (2), 29.2 (2), 29.3 (2), 51.9 (3), 53.8 (1), 65.8 (1), 91.1 (0), 104.7 (0), 175.2 (0); MS m/z 735 (M^+ − Bu), 677, 579, 551, 429, 319, 177, 72, 59, 41; HRMS m/z calcd for $C_{30}H_{61}O_3Si^{120}Sn_2$ (M^+ − Bu) 737.2435, found 737.2439.

(1*R,2*R**,3*R**)-Methyl 2-(Tributylstannyl)-3-((trimethylsilyl)ethynyl)cyclopropane-1-carboxylate (9).** A solution of **10** (66 mg, 0.08 mmol) in CH_2Cl_2 (1.0 mL) was cooled to −30 °C. To the solution were added KI (23 mg, 0.14 mmol), pyridine (23 μL, 0.28 mmol), and $SOCl_2$ (10 μL, 0.14 mmol). The solution was stirred for 4 h at the same temperature. Saturated $NaHCO_3$ solution was added, and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (100:1 hexane/Et_2O) to provide **9** (36.0 mg, 89%). IR (neat) 2164, 1724, 1440, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 0.69 (t, J = 9.0 Hz, 1 H), 0.81−0.95 (m, 15 H), 1.25−1.34 (m, 6 H), 1.40−1.55 (m, 6 H), 1.72 (dd, J = 3.5, 8.5 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 19.7 Hz), 2.15 (dd, J = 3.5, 9.5 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 11.7 Hz), 3.66 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3), 10.3 (2), 13.7 (3), 15.2 (1), 16.8 (1), 26.5 (1), 27.3 (2), 29.0 (2), 52.1 (3), 81.4 (0), 108.2 (0), 174.5 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −14.0; MS m/z 429 (M^+ − Bu), 314, 265, 177, 149, 121, 89, 73, 57, 41; HRMS m/z calcd for $C_{18}H_{33}O_2Si^{120}Sn$ (M^+ − Bu) 429.1272, found 429.1279.

(1*R,2*R**,3*R**)-2-(Tributylstannyl)-3-((trimethylsilyl)ethynyl)cyclopropylmethyl Triphenylmethyl Ether (13).** DIBAL-H in toluene solution (1.02 M, 0.56 mL, 0.57 mmol) was added to the solution of **9** (92 mg, 0.19 mmol) in toluene (2.0 mL) at −78 °C. After the solution was stirred at the same temperature for 2 h, MeOH (0.1 mL) and then brine were added, and the aqueous phase was extracted with Et_2O. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (30:1 hexane/AcOEt) to provide alcohol (74.0 mg, 85%). IR (neat) 3358, 2148, 1464, 1248 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 0.40 (dd, J = 7.0, 9.6 Hz, 1 H), 0.79−0.96 (m, 15 H), 1.13 (dd, J = 4.0, 7.0 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 22.0 Hz), 1.25−1.58 (m, 12 H), 1.38 (br, 1H), 1.69−1.76 (m, 1 H), 3.31 (t, J = 9.0 Hz, 1 H), 3.53 (dd, J = 5.2, 10.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2 (3), 10.0 (1), 10.1 (2), 11.4 (1), 13.7 (3), 27.3 (2), 28.8 (1), 29.0 (2), 66.4 (2), 80.3 (0), 110.5 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −10.0; MS m/z 401 (M^+ − Bu), 311, 251, 193, 177, 135, 119, 73, 57, 41; HRMS m/z calcd for $C_{17}H_{33}OSi^{120}Sn$ (M^+ − Bu) 401.1323, found 401.1294. A solution of triphenylmethyl chloride (117 mg, 0.42 mmol), DMAP (6.0 mg, 0.053 mmol), and alcohol (48.0 mg, 0.105 mmol) in pyridine (1.0 mL) was heated at 50 °C for 50 h. The solution was diluted with Et_2O, washed with 10% HCl, saturated $NaHCO_3$ solution, and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (30:1∼20:1 hexane/AcOEt) to provide **13** (73 mg, 100%). IR (neat) 2150, 1448, 1248 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 0.37 (dd, J = 7.1, 9.6 Hz, 1 H), 0.56−0.61 (m, 6 H), 0.83 (t, J = 7.3 Hz, 9 H), 0.98 (dd, J = 4.0, 7.1 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 21.6 Hz), 1.16−1.23 (m, 6 H), 1.24−1.35 (m, 6 H), 1.81−1.84 (m, 1 H), 2.70 (dd, J = 7.9, 9.7 Hz, 1 H), 2.86 (dd, J = 6.1, 9.7 Hz, 1 H), 7.22−7.46 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.3 (3), 9.8 (2), 10.5 (1), 11.7 (1), 13.7 (3), 26.3 (1), 27.2 (2), 28.9 (2), 68.6 (2), 80.0 (0), 86.6 (0), 111.1 (0), 126.9 (1), 127.8 (1), 128.7 (1), 144.1 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −10.4.

(1*R,2*R**,3*R**)-(2-Ethynyl-3-methylcyclopropyl)methyl Triphenylmethyl Ether (8).** A solution of **13** (42 mg, 0.06

mmol) in THF (0.6 mL) was cooled to −78 °C, and BuLi (1.54 M Hexane solution, 43 μL, 0.066 mmol) was added. The solution was stirred for 30 min at the same temperature, and then MeI (37 μL, 0.600 mmol) was added. The solution was stirred for 2 h. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (50:1 hexane/AcOEt) to provide (1*R**,2*R**,3*R**)-(3-methyl-2-((trimethylsilyl)ethynyl)cyclopropyl)methyl triphenylmethyl ether (16.4 mg, 64%) and recovered **13** (7.8 mg, 19%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 0.71 (t, J = 4.9 Hz, 1 H), 0.96 (d, J = 6.4 Hz, 3 H), 1.27−1.33 (m, 1 H), 1.50−1.56 (m, 1 H), 2.70 (t, J = 9.4 Hz, 1 H), 3.39 (dd, J = 5.5, 9.9 Hz, 1 H), 7.21−7.46 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2 (3), 12.3 (3), 13.1 (1), 21.4 (1), 26.8 (1), 62.1 (2), 80.4 (0), 86.4 (0), 109.3 (0), 126.9 (1), 127.7 (1), 128.7 (1), 144.2 (0); MS *m*/*z* 424 (M^+), 409, 347, 243, 165, 105, 73; HRMS *m*/*z* calcd for $C_{29}H_{32}OSi$ (M^+) 424.2224, found 424.2218. A solution of TBAF (1.0 M THF solution, 0.14 mL, 0.141 mmol) and (1*R**,2*R**,3*R**)-(3-methyl-2-((trimethylsilyl)-ethynyl)cyclopropyl)methyl triphenylmethyl ether (16.4 mg, 0.039 mmol) in THF (1.0 mL) was stirred for 20 min at rt. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (30:1 hexane/AcOEt) to provide **8** (13.4 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69 (dt, J = 2.0 and 4.9 Hz, 1 H), 0.96 (d, J = 6.4 Hz, 3 H), 1.26−1.31 (m, 1 H), 1.49−1.55 (m, 1 H), 1.83 (d, J = 2.0 Hz, 1 H), 2.77 (dd, J = 8.9, 9.8 Hz, 1 H), 3.34 (dd, J = 5.9, 9.8 Hz, 1 H), 7.21−7.46 (m, 15 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (1), 12.3 (3), 20.8 (1), 26.3 (1), 62.1 (2), 64.3 (0), 86.4 (0), 86.8 (1), 126.9 (1), 127.7 (1), 128.6 (1), 144.1 (0); MS *m*/*z* 352 (M^+), 275, 243, 183, 165, 105, 77; HRMS *m*/*z* calcd for $C_{26}H_{24}O$ (M^+) 352.1828, found 352.1846.

General Procedure for the Synthesis of 14. To a solution of LDA prepared from BuLi (1.6 equiv) and diisopropylamine (2.2 equiv) in THF (0.1 M solution) were added HMPA (1.4 equiv) and **3** (1.0 equiv) in THF (0.1 M solution) at −78 °C, and the solution was stirred at −78 °C for 1 h. The electrophile (3.0 equiv) was then added to the solution at −78 °C, and the solution was stirred at −78 °C until **3** was consumed. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to provide **14**.

Methyl 3,3-Bis(tributylstannyl)-2-methylpropionate (14a). A reaction mixture which was prepared from LDA, **3** (2.8418 g, 4.266 mmol), and MeI was stirred for 2 h, and the crude product was purified by column chromatography on silica gel (6:1 hexane/benzene) to provide **14a** (2.8412 g, 98%). IR (neat) 1732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75−0.95 (m, 30 H), 1.07 (d, J = 3.9 Hz, 1 H, ^2J (^{119}Sn−^{1}H) = 31.3 Hz), 1.18 (d, J = 6.9 Hz, 3 H), 1.25−1.52 (m, 24 H), 3.07 (dq, J = 3.9, 6.9 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 38.7 Hz), 3.64 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.1 (1), 10.8 (2), 11.0 (2), 13.6 (3), 22.2 (3), 27.6 (2), 29.3 (2), 41.0 (1), 51.7 (3), 178.2 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ 3.8, 6.5; MS *m*/*z* 623 (M^+ − Bu), 333, 303, 219, 179, 149, 71, 57, 43; HRMS *m*/*z* calcd for $C_{25}H_{53}O_2{}^{120}Sn_2$ (M^+ − Bu) 625.2091, found 625.2071.

General Procedure for the Synthesis of 15. A solution of **14** (1.0 equiv) in toluene (0.1 M) was cooled to −78 °C, and DIBAL-H (1.02 M toluene solution, 1.1∼3.0 equiv) was added. The solution was stirred at the same temperature until **14** was consumed. Methanol and then 1 N HCl solution were added, and the aqueous phase was extracted AcOEt. The combined organic phase was washed with 1 N HCl solution and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to provide **15** and alcohol derivatives. Alcohol derivatives were converted to **15** by Swern oxidation: DMSO (2.2 equiv) was added to a solution of oxalyl chloride (1.1 equiv) in CH_2Cl_2 (0.1 M solution) at −78 °C. After 5 min, alcohol (1.0 equiv) in CH_2Cl_2 (0.1 M solution) was added. This solution was stirred at −78 °C for 10 min, and Et_3N (5.0 equiv) was added. The thick slurry was stirred at −78 °C for 5 min and at rt for 20 min, diluted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to provide **15**.

3,3-Bis(tributylstannyl)-2-methylpropanal (15a). A reaction mixture which was prepared from **14a** (2.8412 g, 4.177 mmol) and DIBAL-H (1.02 M toluene solution, 4.5 mL, 4.595 mmol) was stirred for 2 h, and the crude product was purified by column chromatography on silica gel (5:1∼0:1 hexane/AcOEt) to provide a mixture of **15a** (1.6084 g, 59%) and **14a** (478.3 mg, 17%), and alcohol (480.4 mg, 18%). The yields of **15a** and **14a** were calculated by ^{1}H NMR. **15a**: IR (neat) 1722 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72−0.91 (m, 30 H), 1.01 (d, J = 3.8 Hz, 1 H, ^2J (^{119}Sn−^{1}H) = 31.2 Hz), 1.15 (d, J = 6.9 Hz, 3 H), 1.26−1.51 (m, 24 H), 2.88 (ddq, J = 0.8, 3.8, 6.9 Hz, 1 H, ^3J (^{119}Sn−^{1}H) = 37.0 Hz), 9.57 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.2 (1), 11.1 (2), 11.3 (2), 13.6 (3), 18.3 (3), 27.6 (2), 29.3 (2), 48.4 (1), 205.0 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ 6.0, 12.5; MS *m*/*z* 593 (M^+ − Bu), 303, 235, 179, 149, 70, 61, 43. 3,3-Bis(tributylstannyl)-2-methylpropanol: IR (neat) 3344 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76−0.91 (m, 30 H), 0.95 (d, J = 6.7 Hz, 3 H), 1.00 (d, J = 3.2 Hz, 1 H), 1.29−1.36 (m, 12 H), 1.39−1.52 (m, 13 H), 2.16−2.43 (m, 1 H), 3.29−3.35 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1 (2), 11.3 (1), 11.6 (2), 13.6 (3), 21.6 (3), 27.6 (2), 27.6 (2), 29.3 (2), 38.8 (1), 71.5 (2); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ 1.8, 7.8; MS *m*/*z* 595 (M^+ − Bu), 303, 233, 177, 149, 72, 59, 43.

General Procedure for Alkylation by Lithium (Trimethylsilyl)acetylide. A solution of (trimethylsilyl)acetylene (1.6 equiv) in THF (0.1∼0.2 M solution) was cooled to −78 °C, and BuLi (hexane solution, 1.3 equiv) was added. This solution was stirred for 30 min at −78 °C. To the solution was added aldehyde **15** (1.0 equiv) in THF (0.1∼0.2 M solution). The solution was stirred at −78 °C until aldehyde was consumed. Saturated NH_4Cl solution added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to provide alcohol derivatives.

(3*S,4*S**)-5,5-Bis(tributylstannyl)-4-methyl-1-(trimethylsilyl)-1-pentyn-3-ol (18a) and (3*R**,4*S**)-5,5-Bis(tributylstannyl)-4-methyl-1-(trimethylsilyl)-1-pentyn-3-ol (21a).** A reaction mixture which was prepared from **15a** (1.6084 g, 2.474 mmol) was stirred for 2.5 h, and crude product was purified by column chromatography on silica gel (5:1 hexane/benzene) to provide **18a** (1.2514 g, 68%) and **21a** (0.1669 g, 9%). **18a**: IR (neat) 3440, 2170, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.76−0.95 (m, 30 H), 1.02 (d, J = 6.4 Hz, 3 H), 1.29−1.55 (m, 25 H), 1.75 (br, 1 H), 2.24−2.30 (m, 1 H), 3.86 (d, J = 7.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -0.1 (3), 10.7 (2), 11.8 (2), 12.0 (1), 13.6 (3), 13.6 (3), 20.3 (3), 27.6 (2), 27.7 (2), 29.3 (2), 29.3 (2), 43.1 (1), 70.8 (1), 90.2 (0), 107.2 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −0.0, 11.0; MS *m*/*z* 691 (M^+ − Bu), 385, 329, 303, 291, 271, 235, 179, 161, 121, 73, 59, 41; HRMS *m*/*z* calcd for $C_{29}H_{61}OSi^{120}Sn_2$ (M^+ − Bu) 693.2537, found 693.2547. **21a**: IR (neat) 3452, 2170, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.77−0.91 (m, 30 H), 1.02 (d, J = 6.7 Hz, 3 H), 1.28−1.50 (m, 25 H), 1.70 (d, J = 5.0 Hz, 1 H), 2.26−2.30 (m, 1 H), 3.86 (dd, J = 5.0, 7.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3), 10.9 (2), 11.0 (1), 11.9 (2), 13.6 (3), 21.6 (3), 27.6 (2), 27.7 (2), 29.3 (2), 29.3 (2), 42.9 (1), 70.1 (1), 90.2 (0), 106.5 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −1.8, 8.0; MS *m*/*z* 691 (M^+ − Bu), 385, 329, 303, 291, 271, 235, 179, 163, 121, 73, 59, 41; HRMS *m*/*z* calcd for $C_{29}H_{61}OSi^{120}Sn_2$ (M^+ − Bu) 693.2537, found 693.2533.

(3*S,4*S**)-4-((Benzyloxy)methyl)-5,5-bis(tributylstannyl)-1-(trimethylsilyl)-1-pentyn-3-ol (18b) and (3*R**,4*S**)-4-((Benzyloxy)methyl)-5,5-bis(tributylstannyl)-1-(trimethylsilyl)-1-pentyn-3-ol (21b).** A reaction mixture which was prepared from **15b** (431.7 mg, 0.571 mmol) was stirred for 2 h, and the crude product was purified by flash column chromatography on silica gel (2:1 hexane/benzene) to provide **18b** (379.1 mg, 78%) and **21b** (66.8 mg, 14%). **18b**: IR (neat) 3450, 2172, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 0.72−0.91 (m, 30 H), 1.25−1.47 (m, 25 H), 2.46−2.56 (m, 1 H), 3.37 (dd, J = 8.0, 9.2 Hz, 1 H), 3.49 (dd, J = 3.7, 9.2 Hz, 1 H), 3.59 (d, J = 3.0 Hz, 1 H), 4.18−4.20 (m, 1 H), 4.47 (d, J = 11.9 Hz, 1 H), 4.52 (d, J = 11.9 Hz, 1 H), 7.28−7.36 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3), 5.3 (1), 10.6 (2), 11.9 (2), 13.6 (3), 27.6 (2), 29.2 (2), 47.4 (1), 70.4 (1), 73.7 (2), 75.7 (2), 90.1 (0), 106.4 (0), 128.0 (1), 128.1 (1), 128.5 (1), 137.2 (0); ^{119}Sn NMR

(100 MHz, $CDCl_3$) δ 1.3, 13.0; MS *m/z* 797 ($M^+ - Bu$), 491, 381, 291, 235, 179, 91, 73. HRMS *m/z* calcd for $C_{36}H_{67}O_2Si^{120}Sn_2$ ($M^+ - Bu$) 799.2956, found 799.2936.

(3*S,4*S**)-4-Benzyl-5,5-bis(tributylstannyl)-1-(trimethylsilyl)-1-pentyn-3-ol (18c) and (3*R**,4*S**)-4-Benzyl-5,5-bis(tributylstannyl)-1-(trimethylsilyl)-1-pentyn-3-ol (21c).** A reaction mixture which was prepared from **15c** (89.6 mg, 0.123 mmol) was stirred for 6 h, and the crude product was purified by flash column chromatography on silica gel (3:1 hexane/benzene) to provide **18c** (72.3 mg, 71%), **21c** (5.5 mg, 5%) and recovered **15c** (as alcohol derivative, 15.9 mg, 18%). **18c**: IR (neat) 3510, 2170, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 0.73−0.92 (m, 30 H), 1.00 (d, J = 2.1 Hz, 1 H, ^2J ($^{119}Sn-^1H$) = 30.0 Hz), 1.21−1.49 (m, 24 H), 1.60 (d, J = 5.3 Hz, 1 H), 2.39 (dd, J = 9.0, 13.2 Hz, 1 H), 2.45−2.68 (m, 1 H), 3.07 (dd, J = 4.5, 13.2 Hz, 1 H), 4.25 (dd, J = 3.8, 5.3 Hz, 1 H), 7.16−7.29 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3), 8.2 (1), 10.7 (2), 12.4 (2), 13.6 (3), 13.7 (3), 27.6 (2), 27.7 (2), 29.1 (2), 29.5 (2), 40.0 (2), 50.0 (1), 68.2 (1), 90.8 (0), 106.6 (0), 126.0 (1), 128.3 (1), 129.1 (1), 141.5 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −0.7, 6.6; MS *m/z* 766 ($M^+ - Bu - 1$), 461, 347, 291, 235, 179, 73; HRMS *m/z* calcd for $C_{35}H_{65}OSi^{120}Sn_2$ ($M^+ - Bu$) 769.2850, found 769.2847.

(3*S,4*S**)-4-Allyl-5,5-bis(tributylstannyl)-1-(trimethylsilyl)-1-pentyn-3-ol (18d) and (3*R**,4*S**)-4-Allyl-5,5-bis(tributylstannyl)-1-(trimethylsilyl)-1-pentyn-3-ol (21d).** A reaction mixture which was prepared from **15d** (303.9 mg, 0.449 mmol) was stirred for 3 h, and the crude product was purified by flash column chromatography on silica gel (5:1 hexane/benzene) to provide **18d** (265.8 mg, 76%) and **21d** (52.9 mg, 15%). **18d**: IR (neat) 3516, 2170, 1638, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.77−0.94 (m, 30 H), 1.19 (d, J = 2.2 Hz, 1 H, ^2J ($^{119}Sn-^1H$) = 34.1 Hz), 1.26−1.52 (m, 24 H), 1.78 (d, J = 5.4 Hz, 1 H), 1.98 (ddd, J = 6.9, 7.1, 13.9 Hz, 1 H), 2.16−2.43 (m, 2 H), 4.14 (dd, J = 5.4, 5.5 Hz, 1 H), 5.00−5.08 (m, 2 H), 5.84−5.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.2 (3), 9.7 (1), 11.3 (2), 11.8 (2), 13.6 (3), 13.6 (3), 27.6 (2), 27.7 (2), 29.3 (2), 29.4 (2), 39.5 (2), 47.8 (1), 69.5 (1), 90.6 (0), 106.7 (0), 115.9 (2), 138.6 (1); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ 4.3, 4.5; MS *m/z* 717 ($M^+ - Bu$), 411, 355, 329, 297, 235, 179, 73; HRMS *m/z* calcd for $C_{31}H_{63}OSi^{120}Sn_2$ ($M^+ - Bu$) 719.2694, found 719.2714.

(3*S,4*S**)-5,5-Bis(tributylstannyl)-4-(((triethylsilyl)oxy)methyl)-1-(trimethylsilyl)-1-pentyn-3-ol (18e) and (3*R**,4*S**)-5,5-Bis(tributylstannyl)-4-(((triethylsilyl)oxy)methyl)-1-(trimethylsilyl)-1-pentyn-3-ol (21e).** A reaction mixture which was prepared from **15e** (154.9 mg, 0.198 mmol) was stirred for 2 h, and the crude product was purified by flash column chromatography on silica gel (3:1 hexane/benzene) to provide **18e** (100.2 mg, 58%) and **21e** (39.8 mg, 23%). **18e**: IR (neat) 3462, 2172, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.62 (q, J = 8.0 Hz, 6 H), 0.80−0.94 (m, 31 H), 0.97 (t, J = 8.0 Hz, 9 H), 1.29−1.53 (m, 24 H), 2.34−2.59 (m, 1 H), 3.52 (dd, J = 9.8, 10.0 Hz, 1 H), 3.73 (dd, J = 3.7, 10.0 Hz, 1 H), 4.26 (dd, J = 1.0, 8.8 Hz, 1 H), 4.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1 (3), 4.1 (2), 4.4 (1), 6.6 (3), 10.6 (2), 12.0 (2), 13.6 (3), 27.6 (2), 27.7 (2), 29.2 (2), 29.3 (2), 48.4 (1), 70.6 (2), 71.9 (1), 89.9 (0), 106.3 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ 3.0, 14.6; MS *m/z* 821 ($M^+ - Bu$), 763, 707, 515, 291, 235, 179, 115, 73; HRMS *m/z* calcd for $C_{35}H_{75}O_2Si_2{}^{120}Sn_2$ ($M^+ - Bu$) 823.3351, found 823.3344.

General Procedure for Alkylation by Grignard Reagents. A solution of aldehyde **15** (1.0 equiv) in THF (0.1 M solution) was cooled to −78 °C, and Grignard reagent (1.5∼3.0 equiv) in THF was added. The solution was stirred at −78 °C to 0 °C until aldehyde **15** was consumed. Saturated NH_4Cl solution added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to provide alcohol derivatives.

(2*S,3*R**)-2-Benzyl-1,1-bis(tributylstannyl)-3-heptanol (18f) and (2*S**,3*S**)-2-Benzyl-1,1-bis(tributylstannyl)-3-heptanol (21f).** A reaction mixture which was prepared from **15c** (52.7 mg, 0.073 mmol) and BuMgCl (1.89 M, 0.06 mL, 0.109 mmol) was stirred at −78 °C for 2 h and at 0 °C for 1 h. A crude product was purified by flash column chromatography on silica gel (5:1 hexane/benzene) to provide **18f** (39.9 mg, 70%) and **21f** (5.1 mg, 9%). **18f**: IR (neat) 3464 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.67−1.01 (m, 34 H), 1.10 (d, J = 5.6 Hz, 1 H), 1.18−1.56 (m, 31 H), 2.24−2.47 (m, 2 H), 2.85 (dd, J = 3.2, 12.8 Hz, 1 H), 3.48 (d, J = 4.5 Hz, 1 H), 7.13−7.27 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.1 (1), 10.6 (2), 12.5 (2), 13.6 (3), 13.7 (3), 14.1 (3), 22.8 (2), 27.6 (2), 27.8 (2), 28.7 (2), 29.2 (2), 29.6 (2), 36.1 (2), 38.7 (2), 48.3 (1), 76.9 (1), 125.8 (1), 128.3 (1), 129.1 (1), 141.9 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −3.9, 8.2; MS *m/z* 727 ($M^+ - Bu$), 421, 365, 335, 307, 291, 235, 177, 121, 91; HRMS *m/z* calcd for $C_{34}H_{65}O^{120}Sn_2$ ($M^+ - Bu$) 729.3081, found 729.3077. **21f**: IR (neat) 3462 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.74−1.00 (m, 35 H), 1.18−1.55 (m, 31 H), 2.36−2.44 (m, 2 H), 2.74 (dd, J = 7.9, 12.4 Hz, 1 H), 3.29 (brs, 1 H), 7.14−7.29 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.7 (1), 11.5 (2), 12.1 (2), 13.7 (3), 14.0 (3), 22.8 (2), 27.7 (2), 27.7 (2), 28.2 (2), 29.3 (2), 29.4 (2), 35.2 (2), 42.3 (2), 47.3 (1), 74.3 (1), 125.9 (1), 128.3 (1), 129.1 (1), 141.2 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ 3.2, 8.7; MS *m/z* 727 ($M^+ - Bu$), 421, 365, 335, 307, 291, 235, 177, 121, 91; HRMS *m/z* calcd for $C_{34}H_{65}O^{120}Sn_2$ ($M^+ - Bu$) 729.3081, found 729.3094.

(1*S,2*S**)-2-Benzyl-3,3-bis(tributylstannyl)-1-phenylpropanol (18g) and (1*R**,2*S**)-2-Benzyl-3,3-bis(tributylstannyl)-1-phenylpropanol (21g).** A reaction mixture which was prepared from **15c** (172.2 mg, 0.237 mmol) and PhMgBr (0.91 M, 0.39 mL, 0.356 mmol) was stirred at −78 °C for 1 h and at 0 °C for 30 min. A crude product was purified by flash column chromatography on silica gel (3:1 hexane/benzene) to provide **18g** (164.8 mg, 86%) and **21g** (25.4 mg, 13%). **18g**: IR (neat) 3556 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.79−0.94 (m, 31 H), 1.23−1.49 (m, 24 H), 1.67 (d, J = 3.4 Hz, 1 H), 2.35 (dd, J = 9.6, 13.0 Hz, 1 H), 2.54−2.79 (m, 2 H), 4.76 (br, 1 H), 6.96−7.36 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.0 (1), 10.7 (2), 12.6 (2), 13.6 (3), 13.7 (3), 27.7 (2), 27.8 (2), 29.2 (2), 29.6 (2), 37.8 (2), 50.5 (1), 78.6 (1), 125.7 (1), 125.8 (1), 127.2 (1), 128.1 (1), 128.3 (1), 129.0 (1), 141.8 (0), 144.5 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −4.1, 7.6; MS *m/z* 747 ($M^+ - Bu$), 441, 385, 351, 327, 291, 235, 179, 91; HRMS *m/z* calcd for $C_{36}H_{61}O^{120}Sn_2$ ($M^+ - Bu$) 749.2768, found 749.2769.

(2*S,3*S**)-1,1-Bis(tributylstannyl)-4,4-dimethyl-2-benzyl-3-pentanol (18h) and (2*S**,3*R**)-1,1-Bis(tributylstannyl)-4,4-dimethyl-2-benzyl-3-pentanol (21h).** A reaction mixture which was prepared from **15c** (146.3 mg, 0.201 mmol) and *t*-BuMgCl (1.13 M, 0.53 mL, 0.604 mmol) was stirred at −78 °C for 1 h and at 0 °C for 30 min. A crude product was purified by flash column chromatography on silica gel (10:1 hexane/benzene) to provide **18h** (148.2 mg, 94%) and **21h** (6.4 mg, 4%). **18h**: IR (neat) 3630 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.70−0.92 (m, 31 H), 1.00 (s, 9 H), 1.12−1.51 (m, 25 H), 2.25 (dd, J = 10.2, 13.1 Hz, 1 H), 2.56−2.81 (m, 1 H), 3.02 (dd, J = 2.3, 13.1 Hz, 1 H), 6.43 (d, J = 6.8 Hz, 1 H), 7.14−7.26 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.5 (2), 12.5 (2), 13.2 (1), 13.6 (3), 13.7 (3), 27.3 (3), 27.6 (2), 27.8 (2), 29.2 (2), 29.7 (2), 36.1 (0), 39.2 (2), 43.6 (1), 84.4 (1), 125.7 (1), 128.2 (1), 129.1 (1), 142.1 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −5.6, 7.5; MS *m/z* 727 ($M^+ - Bu$), 421, 365, 307, 291, 235, 179, 121, 91; HRMS *m/z* calcd for $C_{34}H_{65}O^{120}Sn_2$ ($M^+ - Bu$) 729.3081, found 729.3046.

(2*S,3*R**)-2-Allyl-1,1-bis(tributylstannyl)-3-heptanol (18i) and (2*S**,3*S**)-2-Allyl-1,1-bis(tributylstannyl)-3-heptanol (21i).** A reaction mixture which was prepared from **15d** (101.4 mg, 0.150 mmol) and BuMgCl (1.89 M, 0.24 mL, 0.450 mmol) was stirred at −78 °C for 1.5 h, and the crude product was purified by flash column chromatography on silica gel (10:1 hexane/benzene) to provide **18i** (89.6 mg, 81%) and **21i** (16.9 mg, 15%). **18i**: IR (neat) 3472, 1638 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.76−1.03 (m, 34 H), 1.25−1.54 (m, 31 H), 1.86−1.92 (m, 1 H), 2.01−2.28 (m, 2 H), 3.39−3.41 (m, 1 H), 5.00−5.07 (m, 2 H), 5.79−5.87 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9 (1), 11.1 (2), 12.0 (2), 13.6 (3), 13.6 (3), 14.1 (3), 22.8 (2), 27.7 (2), 27.7 (2), 28.4 (2), 29.4 (2), 29.5 (2), 35.9 (2), 38.4 (2), 46.3 (1), 77.7 (1), 115.7 (2), 139.2 (1); $^{119}Sn-NMR$ (100 MHz, $CDCl_3$) δ 0.6, 6.4; MS *m/z* 677 ($M^+ - Bu$), 371, 315, 291, 235, 177, 121, 81; HRMS *m/z* calcd for $C_{30}H_{63}O^{120}Sn_2$ ($M^+ - Bu$) 679.2925, found 679.2910.

(1*S,2*S**)-2-Allyl-3,3-bis(tributylstannyl)-1-phenylpropanol (18j) and (1*S**,2*R**)-2-Allyl-3,3-bis(tributylstannyl)-1-phenylpropanol (21j).** A reaction mixture which was prepared from **15d** (141.9 mg, 0.210 mmol) and PhMgBr (0.91 M, 0.69 mL, 0.630 mmol) was stirred at −78 °C for 0.5 h, and the crude product was purified by flash column chromatography on silica gel (5:1 hexane/benzene) to provide **18j** (116.4 mg, 74%), **21j** (40.0 mg, 25%), and recovered **15d** (trace). **18j**: IR (neat)

3422, 1640 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.73−0.97 (m, 31 H), 1.27−1.53 (m, 24 H), 1.91 (d, J = 2.9 Hz, 1 H), 1.98−2.06 (m, 1 H), 2.16−2.21 (m, 1 H), 2.34−2.55 (m, 1 H), 4.56 (br, 1 H), 4.97−5.04 (m, 2 H), 5.74−5.82 (m, 1 H), 7.23−7.29 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.7 (1), 11.4 (2), 11.8 (2), 13.6 (3), 27.7 (2), 27.7 (2), 29.4 (2), 29.4 (2), 38.3 (2), 48.1 (1), 80.1 (1), 115.7 (2), 126.3 (1), 127.4 (1), 128.3 (1), 139.1 (1), 144.2 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ 2.8, 4.7; MS m/z 697 (M^+ − Bu), 391, 291, 235, 177, 157, 115, 91; HRMS m/z calcd for $C_{32}H_{59}O^{120}Sn_2$ (M^+ − Bu) 699.2611, found 699.2623.

General Procedure for Cyclopropanation. A solution of alcohol **18** (1.0 equiv) in CH_2Cl_2 (0.1 M solution) was cooled to −30 °C, and then Et_3N (10.0 equiv) and MsCl (5.0 equiv) was added. The solution was stirred at −30 °C until alcohol **18** was consumed. Saturated $NaHCO_3$ solution added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to provide cyclopropane derivatives. The ratio of the diastereomers are determined by ^1H NMR spectraum.

(1*S,2*R**,3*S**)-3-Methyl-1-(tributylstannyl)-2-((trimethylsilyl)ethynyl)cyclopropane (19a).** A reaction mixture which was prepared from **18a** (69.4 mg, 0.093 mmol) was stirred for 1.5 h, and the crude product was purified by column chromatography on silica gel (50:1 hexane/benzene) to provide **19a** (40.3 mg, 99%). IR (neat) 2172, 2142, 1458, 1248 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 0.37 (dd, J = 6.9 and 9.4 Hz, 1 H), 0.76−0.91 (m, 15 H), 1.03 (d, J = 6.1 Hz, 3 H), 1.29−1.57 (m, 14 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.3 (3), 10.0 (2), 12.6 (1), 13.7 (3), 15.3 (1), 19.6 (3), 21.4 (1), 27.3 (2), 29.1 (2), 79.5 (0), 112.0 (0); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −11.5; MS m/z 385 (M^+ − Bu + 1), 325, 313, 291, 271, 235, 179, 121; HRMS m/z calcd for $C_{17}H_{33}Si^{120}Sn$ (M^+ − Bu) 385.1374, found 385.1376.

(1*R,2*R**,3*R**)-(3-Methyl-2-((trimethylsilyl)ethynyl)cyclopropyl)methyl Benzyl Ether (22a).** A solution of **19a** (102.7 mg, 0.233 mmol) in THF (2.3 mL) was cooled to −78 °C, BuLi (1.72 M, 0.14 mL, 0.244 mmol) was added, and then HMPA (45 μL, 0.256 mmol) was added. The resulting solution was stirred for 30 min at the same temperature. To the solution was added $ClCH_2OCH_2Ph$ (0.16 mL, 1.163 mmol). The solution was stirred for 1 h at −78 °C, saturated NH_4Cl solution was added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (3:1 hexane/benzene) to provide **22a** (42.2 mg, 67%). IR (neat) 2154, 1454, 1248, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.14 (s, 9 H), 0.88 (t, J = 4.9 Hz, 1 H), 1.11 (d, J = 6.3 Hz, 3 H), 1.29−1.35 (m, 1 H), 1.49−1.54 (m, 1 H), 3.31 (dd, J = 8.6, 10.4 Hz, 1 H), 3.64 (dd, J = 6.0, 10.4 Hz, 1 H), 4.50 (d, J = 12.1 Hz, 1 H), 4.56 (d, J = 12.1 Hz, 1 H), 7.23−7.39 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2 (3), 12.3 (3), 13.5 (1), 21.4 (1), 26.5 (1), 68.3 (2), 72.7 (2), 80.7 (0), 108.9 (0), 127.6 (1), 127.7 (1), 128.4 (1), 138.3 (0); MS m/z 272 (M^+), 257, 243, 227, 199, 181, 167, 151, 135, 91, 73; HRMS m/z calcd for $C_{17}H_{24}OSi$ (M^+) 272.1597, found 272.1570.

(1*R,2*R**,3*R**)-(2-Ethynyl-3-methylcyclopropyl)methyl Benzyl Ether (23a).** A solution of **22a** (23.7 mg, 0.087 mmol) was cooled to 0 °C, and TBAF (1.0 M THF solution, 0.22 mL, 0.218 mmol) was added. The resulting solution was stirred for 1.5 h at rt, saturated NH_4Cl solution was added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (1:1 hexane/benzene) to provide **23a** (12.5 mg, 72%). IR (neat) 3292, 3028, 2118, 1454, 1096, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (dt, J = 2.1, 4.9 Hz, 1 H), 1.10 (d, J = 6.5 Hz, 3 H), 1.28−1.34 (m, 1 H), 1.47−1.53 (m, 1 H), 1.84 (d, J = 2.1 Hz, 1 H), 3.33 (dd, J = 8.5, 10.5 Hz, 1 H), 3.62 (dd, J = 6.1, 10.5 Hz, 1 H), 4.50 (d, J = 11.9 Hz, 1 H), 4.56 (d, J = 11.9 Hz, 1 H), 7.23−7.36 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.2 (1), 12.3 (3), 20.8 (1), 26.0 (1), 64.5 (0), 68.2 (2), 72.7 (2), 86.4 (1), 127.6 (1), 127.7 (1), 128.4 (1), 138.3 (0); MS m/z 199 (M^+ − 1), 185, 155, 141, 129, 91, 77; HRMS m/z calcd for $C_{14}H_{15}O$ (M^+ − 1) 199.1124, found 199.1148.

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Supporting Information Available: Experimental procedures for the synthesis of **14b**−**e**, **15b**−**e**, and **19b**−**j**, characterization data of **21b**−**e** and **21g**−**j**, and ^1H NMR spectra for almost all compounds (60 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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