Synthesis and Radical Induced Ring Opening Reaction of 1-Trialkylsilyl-2-vinylcyclopropanes

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A variety of trialkylsilylvinylcyclopropanes were prepared by two different routes: (a) Cyclopropanation of 1-alkenylsilanes and (b) the reactions of 1-bromocyclopropyllithium with trimethylsilyl chloride. Radical induced ring opening reaction of these cyclopropanes were examined. 1-Dimethylphenylsilyl-2-vinylcyclopropane or 3-methyl-1-trialkylsilyl-2-vinylcyclopropane provided the corresponding homoallylic silane exclusively upon treatment with PhSH, Ph_3SnH, n-Bu_3SnH, or n-$C_6F_{13}I$. On the other hand, 2-phenyl-1-trimethylsilyl-3-vinylcyclopropane or 2-acetyl-1-trimethylsilyl-3-vinylcyclopropane gave allylic silane selectively.

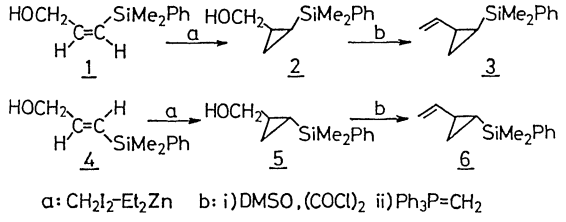
Trimethylsilyl substituent behaves in a dichotomous manner, showing the properties of both electron donor and acceptor groups. α-Trimethylsilyl carbanions are stabilized by $(\sigma^*\text{-p})\pi$ overlap between the antibonding σ^* level of the C-Si bond with the adjacent filled p-orbital of the carbanion, or highly polarized carbon-metal bond, whereas reactions which involve carbonium ion formation or development β to silicon are positively encouraged. Organosilicon chemistry based on these ionic effects has been extensively studied.[1] In contrast, there has been little investigation of the stabilizing effect of trimethylsilyl group on carbon radicals.[2] By using 3-substituted 1-trimethylsilyl-2-vinylcyclopropanes as models of free radical substituent effects we found that α-trimethylsilyl stabilization was substantial.[3]

(1) Synthesis of 1-Trialkylsilyl-2-vinylcyclopropanes. In recent years, increasing interest has been devoted to the chemistry of silicon containing molecules and much effort has been made to introduce the silyl moiety into organic compounds. Several methods are known for the synthesis of trimethylsilylcyclopropanes.[4-8] Here we want to describe two different routes to the title 1-trialkylsilyl-2-vinylcyclopropanes: (a) Cyclopropanation of 1-alkenylsilanes and (b) the reaction of 1-bromocyclopropyllithium with trimethylsilyl chloride.

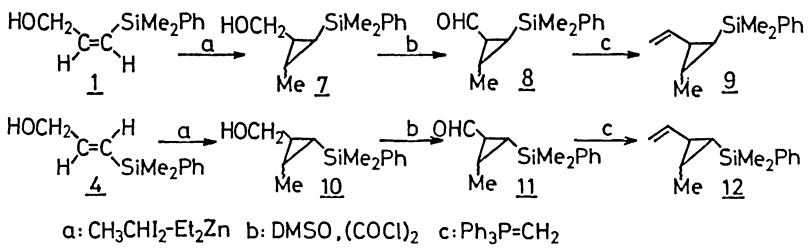
Treatment of (*Z*)-3-dimethylphenylsilyl-2-propen-1-ol (**1**) with CH_2I_2-Et_2Zn[9] in diisopropyl ether gave *cis* cyclopropane **2** in 60% yield. Swern oxidation[10] followed by Wittig methylenation afforded *cis*-1-dimethylphenylsilyl-2-vinylcyclopropane (**3**). Trans isomer **6** was prepared starting from (*E*)-3-dimethylphenylsilyl-2-propen-1-ol (**4**) following the same procedure (Scheme 1).

Synthesis of methyl-substituted cyclopropanes were performed by the reaction of olefins **1** and **4** with CH_3CHI_2-Et_2Zn.[11] The reaction yielded predominantly trans isomer. Thus, (*Z*)-alcohol **1** gave a 25 : 1 mixture **7** of *r*-1-dimethylphenylsilyl-*c*-2-hydroxymethyl-*t*-3-methylcyclopropane and *r*-1-dimethylphenylsilyl-*c*-2-hydroxymethyl-*c*-3-methylcyclopropane. In the meantime, (*E*)-alcohol **4** gave a 7 : 4 mixture **10** of *r*-1-dimethylphenylsilyl-*t*-2-hydroxymethyl-*t*-3-methylcyclopropane and *c*-3-methylcyclopropane. Oxidation and successive methylenation afforded the corresponding vinylcyclopropanes **9** and **12** (Scheme 2).

Alternatively, trimethylsilylcyclopropanes were prepared from 1,1-dibromocyclopropanes. An Addition of butyllithium to a mixture of 1,1-dibromocyclopropane **13** and large excess of trimethylsilyl chloride at −107 °C in tetrahydrofuran provided 1-bromocyclopropyltrimethylsilane.[5] Treatment of crude product



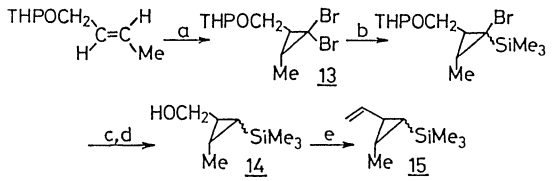
Scheme 1.



Scheme 2.

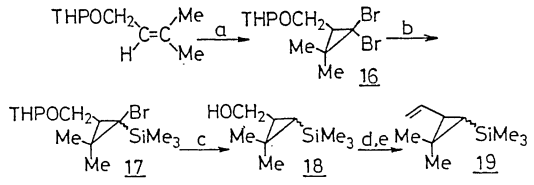
with *n*-Bu_3SnH-Et_3B[12] followed by deprotection of tetrahydropyranyl ether gave a 1.8:1 mixture of **14** in 71% yield from **13**. Oxidation followed by Wittig methylenation provided the desired 1-trimethylsilyl-2-vinyl-3-methylcyclopropane **15** (Scheme 3).

In similar fashion, dimethyl-substituted cyclopropane **19** or phenyl-substituted cyclopropane **22** was prepared starting from tetrahydropyranyl ether of pre-



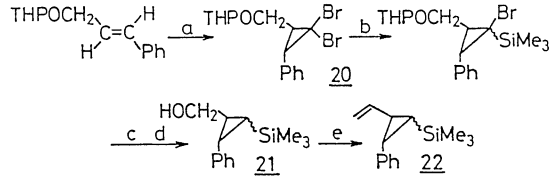
a: $CHBr_3$, t-BuOK b: n-BuLi, TMSCl c: n-Bu_3SnH-Et_3B
d: TsOH, MeOH e: i) DMSO, $(COCl)_2$ ii) $Ph_3P{=}CH_2$

Scheme 3.



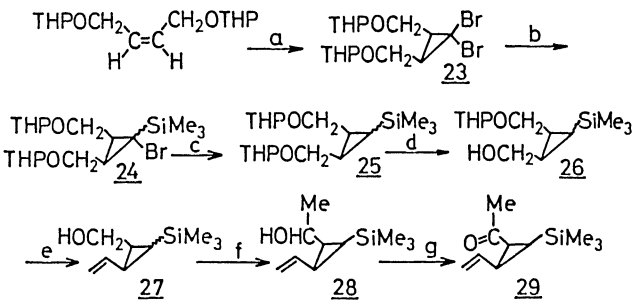
a: $CHBr_3$, t-BuOK b: n-BuLi, TMSCl
c: n-BuLi, AcOH or n-Bu_3SnH, Et_3B
d: TsOH, MeOH e: i) DMSO, $(COCl)_2$ ii) $Ph_3P{=}CH_2$

Scheme 4.



a: $CHBr_3$, t-BuOK b: n-BuLi, TMSCl c: n-Bu_3SnH-Et_3B
d: TsOH, MeOH e: i) DMSO, $(COCl)_2$ ii) $Ph_3P{=}CH_2$

Scheme 5.



a: $CHBr_3$, t-BuOK b: n-BuLi, TMSCl c: n-Bu_3SnH, Et_3B
d: TsOH, MeOH e: i) DMSO, $(COCl)_2$ ii) $Ph_3P{=}CH_2$
iii) TsOH, MeOH f: i) DMSO, $(COCl)_2$ ii) MeMgI
g: PCC, CH_2Cl_2

Scheme 6.

nyl alcohol or cinnamyl alcohol, respectively (Scheme 4, 5).

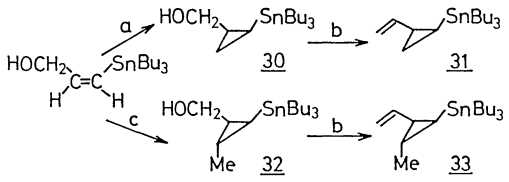
Acetylcyclopropane **29** was prepared from bis(2-tetrahydropyranyl) ether of *cis*-2-butene-1,4-diol as shown in Scheme 6.

Tributylstannylvinylcyclopropanes were also prepared by the following sequences (Scheme 7).

(2) Radical Induced Ring Opening Reaction of 1-Trialkylsilyl-2-vinylcyclopropanes. A priori, it is predictable that two isomers, homoallylic silane (**37**, $PhSCH_2CH{=}CHCR^1(R^2)CH_2SiMe_2R^3$) and allylic silane (**38**, $PhSCH_2CH{=}CHCH(SiMe_2R^3)CHR^1R^2$) will be generated under cyclopropane ring cleavage in the reaction of vinylcyclopropane (**34**)[13,14] with PhSH and the ratio of two products will reflect the stabilizing effect of R^3Me_2Si group on the intermediary carbon radicals (α to silicon (**35**) and β to silicon (**36**)) (Scheme 8).

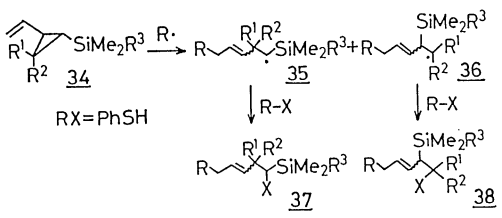
Treatment of *cis*-1-dimethylphenylsilyl-2-vinylcyclopropane (**3**) with PhSH at 60 °C in benzene provided homoallylic silane (**39a**, *E*/*Z*=9/1) in 88% yield. Other reagents such as Ph_3SnH, *n*-Bu_3SnH, and *n*-$C_6F_{13}I$ also afforded the corresponding homoallylic silanes in the triethylborane-induced radical reaction,[12,15] and no trace of allylic silanes were observed in the reaction mixture. The results are summarized in Table 1. The cis, trans stereochemistry of the cyclopropane did not affect the selectivity of the C–C bond fission. *Cis* isomer **3** as well as *trans* isomer **6** provided the same homoallylic silane **39** as a single regioisomer, although the *E*, *Z* ratios of the products **39** derived from **3** were slightly different from those generated from **6**. For instance, *cis* isomer **3** provided a mixture of (*E*)- and (*Z*)-5-dimethylphenylsilyl-1-phenylthio-2-pentene in a 9:1 ratio upon treatment with benzenethiol, whereas *trans* isomer **6** gave a mixture of (*E*)/(*Z*)=5/1.

Methyl-substituted cyclopropane **9**, **12**, or **15** gave homoallylic silane **40** or **41** exclusively upon treat-



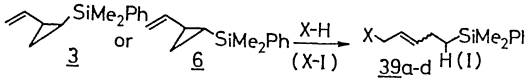
a: CH_2I_2, Et_2Zn b: i) DMSO, $(COCl)_2$ ii) $Ph_3P{=}CH_2$
c: $MeCHI_2$, Et_2Zn

Scheme 7.



Scheme 8.

Table 1. Radical-Induced Ring Opening Reaction of 1-Dimethylphenylsilyl-2-vinylcyclopropane



3 6 39a-d

Substrate	X-H (X-I)	Reaction Conditions[a]				Products 39	
		Solvent	Initiator	Temp/°C	Time/h	Y/%	E/Z[b]
3	PhSH	benzene	—	60	3	88	9/1
6	PhSH	benzene	—	60	5	88	5/1
3	Ph_3SnH	benzene	Et_3B	25	1	96	7/2
6	Ph_3SnH	benzene	Et_3B	25	1	95	5/3
3	n-Bu_3SnH	benzene	Et_3B	25	1	86	10/3
6	n-Bu_3SnH	benzene	Et_3B	25	1	92	4/3
3	n-$C_6F_{13}I$	hexane	Et_3B	25	3	91	50/1
6	n-$C_6F_{13}I$	hexane	Et_3B	25	3	93	8/1

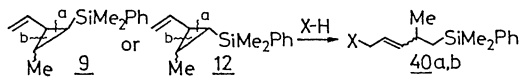
a) Silylcyclopropane (**3** or **6**, 1.0 mmol) and X-H (1.1 mmol) were employed in the absence or in the presence of Et_3B (0.2 mmol). b) Determined by ^1H NMR.

ment with PhSH or Ph_3SnH. Again, one (bond a) of two carbon-carbon bonds was broken selectively independent of the stereochemistry of the substrate. Thus, both *cis* isomer **9** and *trans* isomer **12** afforded the same homoallylic silane **40** (Scheme 9).

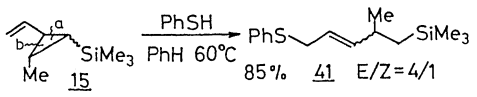
Exposure of dimethyl-substituted trimethylsilylcyclopropane **19** to PhSH provided a mixture of homoallylic silane **42a** and allylic silane **43a** (**42a**/**43a**=ca. 2/1) in 94% combined yield. In the case of n-$C_6F_{13}I$ as a reagent, 5-methyl-1-tridecafluorohexyl-2,4-hexadiene (**45**) was obtained instead of 5-iodo-5-methyl-1-tridecafluorohexyl-4-trimethylsilyl-2-hexene because (β-iodoalkyl)trimethylsilane was extremely unstable with respect to β-elimination. The stereochemistry of the cyclopropane **19** did not affect the ratios of the product **42**/**43** (or **44**/**45**) so much. *E* isomers were obtained exclusively in the reactions of **19** with PhSH, Ph_3SnH, and n-$C_6F_{13}I$ as shown in Scheme 10.

Two other vinylcyclopropanes (**22** and **29**) were treated with PhSH or Ph_3SnH-Et_3B. The results showed that phenyl group or acetyl group stabilized the radical on adjacent carbon[16] more strongly than trimethylsilyl group (Scheme 11 and 12).

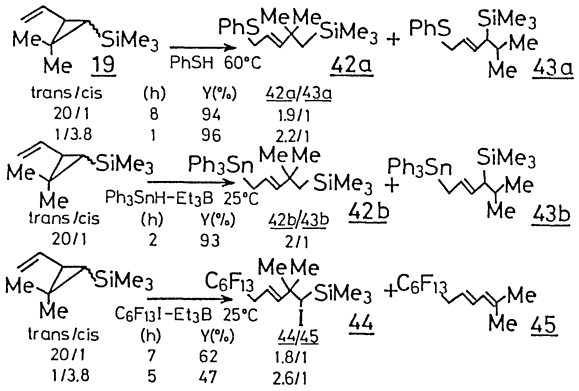
Treatment of stannylcyclopropanes **31** and **33** with benzenethiol also provided homoallylic stannanes exclusively (Scheme 13).



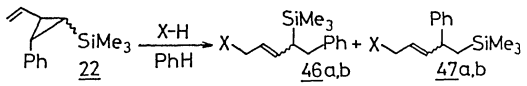
9	PhSH	60 °C	1 h	90%	*E*/*Z*=18/1
12	PhSH	60 °C	3 h	90%	*E*/*Z*=8/1
9	Ph_3SnH-Et_3B	25 °C	0.5 h	79%	*E*/*Z*=8/1
12	Ph_3SnH-Et_3B	25 °C	2 h	88%	*E*/*Z*=7/2



Scheme 9.

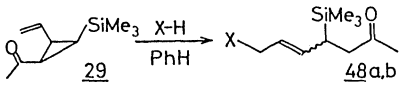


Scheme 10.



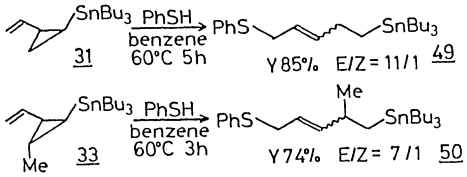
PhSH 60 °C 1.5 h, 88%
46a(*E*/*Z*) : **47a**(*E*/*Z*)=20(15/1) : 1(5/2)
Ph_3SnH-Et_3B 25 °C 0.5 h, 74%
46b(*E*/*Z*) : **47b**(*E*/*Z*)=16(15/1) : 1(2/1)

Scheme 11.



PhSH 60 °C 3 h, 45% **48a**
Ph_3SnH-Et_3B 25 °C 0.5 h, 65% **48b**

Scheme 12.



Scheme 13.

Experimental

Distillations of the products were performed by use of Kugelrohr (Böchi), and boiling points are indicated by air-bath temperature without correction. Analytical TLC (thin layer chromatography) was performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel PF254. Preparative TLC (PLC) plates were prepared as follows: a free-flowing slurry of Merck silica gel PF254 (25 g) in water (60 ml) was spread on a clean glass plate (20×20 cm) to an even depth of 1.5 mm and the plate was air-dried at room temperature for at least two days before use. The TLC mobility of a given component is described by its R_f value, the ratio of the distance moved by that component to the distance moved by the solvent front. Analytical and preparative GLPC were performed with a Shimadzu Gas Chromatograph, Model GC-8A using thermal conductivity detector and helium as carrier gas. Product percentages were calculated from peak area ratios without correction for detector response. Two columns (OV-1 2%, 2 m on Chromosorb W 60—80 mesh AW DMCS (Column A) and SE-30 1.5%, 2 m on Chromosorb W 60—80 mesh AW DMCS (Column B)) were used. The GLPC retention time (t_r) of a component denotes the time (in minutes) at which the maximum concentration of that component reached the detector. Liquid chromatography (LC) was performed with Japan Analytical Industry Co., Ltd. LC-908 (Column: JAIGEL 1-H and 2-H) using chloroform at a flow rate of 4 ml min^{-1}.

^1H NMR and ^{13}C NMR spectra were taken on a Varian XL-200 spectrometer, $CDCl_3$ was used as solvent, chemical shifts being given in δ with tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded on JEOL JNM-FX 90Q spectrometer and the chemical shifts are given in δ with $CFCl_3$ as an external standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl.

(*Z*)-3-Dimethylphenylsilyl-2-propen-1-ol (1). Diisobutylaluminium hydride (6.6 ml, 37 mmol) was added dropwise to a solution of tetrahydropyranyl ether of 3-dimethylphenylsilyl-2-propyn-1-ol (8.6 g, 31 mmol) in hexane (30 ml) at 0 °C. After stirring for 10 h at 25 °C, the reaction mixture was poured into 1 M (1 M=1 mol dm^{-3}) aqueous HCl (70 ml). The product was extracted with hexane (50 ml×2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was dissolved in MeOH (50 ml) and *p*-TsOH (100 mg) was added. The resulting mixture was stirred for 2 h at 25 °C. Et_3N (1 ml) was added and stirring of the mixture was continued for another 5 min. The mixture was concentrated in vacuo and crude product was purified by silica-gel column chromatography (hexane/ethyl acetate=5/1) to give the title alcohol in 86% yield (5.1 g).

***cis*-1-Dimethylphenylsilyl-2-hydroxymethylcyclopropane (2).** According to the reported procedure,[9] diiodomethane (2.2 ml, 7.3 g, 27 mmol) was added dropwise over 20 min to a mixture of allylic alcohol **1** (2.5 g, 13 mmol), diethylzinc (2 ml, 20 mmol), and diisopropyl ether (15 ml) under argon atmosphere at 25 °C. Exothermic reaction occurred. Stirring was continued for 30 min after completion of the addition. The resulting mixture was poured slowly into 1 M HCl solution and the product was extracted with ethyl acetate. The organic layer was washed with 10% aqueous $Na_2S_2O_3$ and dried over anhydrous sodium sulfate. Purification by silica-gel column chromatography (hexane/ethyl acetate=5/1) gave the title compound in 60% yield (1.57 g): Bp 74 °C (1 Torr, 1 Torr=133.322 Pa, bath temp); IR (neat) 3322, 3064, 2994, 2952, 1427. 1412, 1292, 1248, 1112, 1036, 1015, 939, 889, 864, 832, 814, 771, 730, 699, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.00 (ddd, *J*=9.9, 9.3, 7.6 Hz, 1H), 0.27—0.35 (m, 1H), 0.32 (s, 6H), 0.95 (ddd, *J*=9.9, 7.9, 3.8 Hz, 1H), 1.15 (bs, 1H), 1.40 (ddtd, *J*=9.3, 7.9, 7.6, 5.0 Hz, 1H), 3.40 (bs, 2H), 7.35—7.40 (m, 3H) , 7.55—7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.88, −1.19, 1.77, 7.72, 19.51, 65.23, 127.9, 129.1, 133.6, 139.6. Found: C, 69.80; H, 9.09%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

***cis*-1-Dimethylphenylsilyl-2-vinylcyclopropane (3).** DMSO (1.38 ml, 19.5 mmol) in CH_2Cl_2 (3 ml) was added dropwise over 5 min at −78 °C to a mixture of $(COCl)_2$ (0.85 ml, 9.8 mmol) and CH_2Cl_2 (10 ml). After stirring for 15 min, a solution of **2** (1.34 g, 6.5 mmol) in CH_2Cl_2 (10 ml) was added over 10 min. The reaction mixture was stirred for 30 min and then Et_3N (5.4 ml, 39 mmol) was added. After 5 min, dry ice-MeOH cooling bath was removed and H_2O (50 ml) was added to the resulting white suspension. Instantly the solid dissolved and clear solution was obtained. The mixture was extracted with CH_2Cl_2 (50 ml×2) and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. A THF solution of crude aldehyde (1.3 g) was added to a suspension of triphenylphosphonium methylide prepared from triphenylphosphonium iodide (3.5 g, 8.5 mmol) and potassium *t*-butoxide (0.95 g, 8.5 mmol) in THF (25 ml) at 0 °C and the resultant mixture was stirred for 1 h at 25 °C. The mixture was poured into saturated aqueous ammonium chloride (50 ml) and extracted with hexane (50 ml×2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to 20 ml to afford triphenylphosphine oxide as white precipitate. The white solid was filtered off and the filtrate was concentrated again. Purification of the residual crude product by silica-gel column chromatography gave vinylcyclopropane **3** in 89% yield (1.17 g) from **2**: Bp 52 °C (1 Torr, bath temp); IR (neat) 3066, 2994, 2952, 1637, 1428, 1286, 1248, 1112, 1040, 989, 961, 937, 895, 847, 830, 812, 772, 728, 699, 668, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.14 (ddd, *J*=10.1, 9.7, 8.0 Hz, 1H), 0.29 (s, 6H), 0.54 (ddd, *J*=8.0, 4.9, 3.9 Hz, 1H), 1.10 (ddd, *J*=10.1, 7.7, 3.9 Hz, 1H), 1.79 (dddd, *J*=9.7, 9.0, 7.7, 4.9 Hz, 1H), 4.88 (dd, *J*=9.9, 2.2 Hz, 1H), 5.12 (dd, *J*=16.9, 2.2 Hz, 1H), 5.41 (ddd, *J*=16.9, 9.7, 9.0 Hz, 1H), 7.33—7.42 (m, 3H), 7.55—7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.75, −1.69, 5.26, 10.75, 20.58, 113.5, 127.7, 128.8, 133.8, 139.7, 140.8. Found: C, 77.22; H, 8.91%. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97%.

(*E*)-3-Dimethylphenylsilyl-2-propen-1-ol (4). The title compound (9.4 g, 87% yield) was prepared by the reduction of 3-dimethylphenylsilyl-2-propyn-1-ol (10.7 g, 56.2 mmol) with sodium bis(2-methoxyethoxy)aluminum hydride (70% toluene solution, 26.7 ml) following the procedure for the synthesis of (*E*)-3-trimethylsilyl-2-propen-1-ol.[17]

***trans*-1-Dimethylphenylsilyl-2-hydroxymethylcyclopropane (5).** In similar fashion to the synthesis of **2**, treatment of alcohol **4** (3.13 g, 16.3 mmol) with CH_2I_2 (2.7 ml, 9.0 g, 33.5 mmol) and Et_2Zn (2.5 ml, 25 mmol) in diisopropyl ether (18 ml) gave cyclopropane **5** in 76% yield (2.56 g): Bp 79 °C (1 Torr, bath temp); IR (neat) 3316, 3064, 2994, 2952, 2864,

1428, 1411, 1302, 1249, 1114, 1054, 1020, 942, 865, 831, 813, 771, 728, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.28 (ddd, J=9.9, 7.0, 6.4 Hz, 1H), 0.21 (s, 3H), 0.22 (s, 3H), 0.48—0.60 (m, 2H), 0.99—1.15 (m, 1H), 1.39 (bs, 1H), 3.46 (dd, J=14.4, 6.6 Hz, 1H), 3.52 (dd, J=14.4, 6.9 Hz, 1H), 7.34—7.39 (m, 3H) , 7.53—7.60 (m, 2H); ^{13}C NMR ($CDCL_3$) δ=−3.90, 1.37, 7.22, 18.11, 68.46, 127.7, 129.0, 133.7, 138.6. Found: C, 69.58; H, 8.85%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

***trans*-1-Dimethylphenylsilyl-2-vinylcyclopropane (6).** The compound (2.04 g, 81% yield) was prepared from **5** (2.56 g) following the procedure described for the synthesis of **3**: Bp 54 °C (1 Torr, bath temp); IR (neat) 3066, 2994, 2954, 1636, 1428,1249, 1115, 1087, 1062, 985, 969, 947, 892, 831, 817, 772, 728, 698, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.06 (ddd, J=10.0, 7.6, 6.1 Hz, 1H), 0.20 (s, 3H), 0.21 (s, 3H), 0.65—0.78 (m, 2H), 1.39 (dddd, J=8.5, 7.2, 6.1, 4.9 Hz, 1H), 4.85 (dd, J=10.0, 2.0 Hz, 1H), 5.09 (dd, J=17.0, 2.0 Hz, 1H), 5.36 (ddd, J=17.0, 10.0, 8.5 Hz, 1H), 7.33—7.38 (m, 3H), 7.52—7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.83, −3.77, 5.62, 10.73, 19.37, 111.4, 127.7, 128.9, 133.8, 138.7, 143.1. Found: C, 77.10; H, 9.22% Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97%.

***r*-1-Dimethylphenylsilyl-*c*-2-hydroxymethyl-*t*-3-methylcyclopropane (*trans*-7) and *r*-1-Dimethylphenylsilyl-*c*-2-hydroxymethyl-*c*-3-methylcyclopropane (*cis*-7).** A solution of ethylidene iodide (2.8 ml, 28 mmol) in diisopropyl ether (5 ml) was added dropwise over 1 h to a mixture of allylic alcohol **1** (1.90 g, 9.4 mmol), diethylzinc (2.8 ml, 28 mmol) , and diisopropyl ether (13 ml) under argon atmosphere at 25 °. Exothermic reaction proceeded gradually. After stirring at 25 °C for 12 h, the reaction mixture was poured into 1 M HCl (50 ml) and the product was extracted with ethyl acetate (50 ml×2). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by silica-gel column chromatography gave the title compounds (1.22 g, 59% yield) which was contaminated by the starting allylic alcohols **1**. ^1H NMR spectrum showed that the ratio between products (two isomers) and **1** was 4.6 : 1. The analytical pure samples of both isomers were prepared by preparative GLPC (Column B, 150 °C, t_r=4.67 min (*t*-isomer) t_r=6.35 min (*c*-isomer), *t*-isomer/*c*-isomer=25 : 1). *trans*-**7**: Bp 77 °C (1 Torr, bath temp); IR (neat) 3318, 3064, 2990, 2948, 2862, 1458, 1448, 1428, 1380, 1249, 1113, 1077, 1018, 991, 941, 924, 832, 817, 773, 728, 699, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.25 (dd, J=9.2, 6.9 Hz, 1H), 0.30 (s, 3H), 0.31 (s, 3H), 0.69—0.83 (m, 1H), 1.0—1.15 (m, 2H), 1.18 (d, 3H), 3.34 (dd J=11.4, 7.5 Hz, 1H), 3.48 (dd, J=11.4, 7.5 Hz, 1H), 7.34—7.39 (m, 3H), 7.54—7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.67, −0.91, 11.29, 16.70, 20.46, 28.46, 65.07, 127.9, 129.0, 133.6, 139.8. Found: C, 70.69; H, 9.38%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%. **cis-7**: Bp 79 ° (1 Torr, bath temp), IR (neat) 3316, 3064, 3046, 2996, 2950, 1459, 1450, 1427, 1407, 1389, 1288, 1249, 1111, 1074, 1057, 1018, 939, 914, 834, 816, 773, 728, 699, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08 (t, J=9.6 Hz, 1H), 0.37 (s, 6H), 1.14 (d, J=6.3 Hz, 3H), 1.17—1.54 (m, 3H), 3.61 (dd, J=11.3, 8.1 Hz, 1H), 3.70 (dd, J=11.3, 6.9 Hz, 1H), 7.33—7.38 (m, 3H), 7.56—7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=0.23, 7.72, 11.82, 14.80, 23.12, 61.48, 127.8, 128.9, 133.5, 140.3. Found: C, 70.62; H, 9.37%. Calcd for ,$C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

***r*-1-Dimethylphenylsilyl-*c*-2-formyl-*t*-3-methylcyclopropane (*trans*-8) and *r*-1-Dimethylphenylsilyl-*c*-2-formyl-*c*-3-methylcyclopropane (*cis*-8).** The mixture of **7** (1.22 g, 5.54 mmol) and **1** (0.26 g, 1.35 mmol) was oxidized with $(COCl)_2$ (0.90 ml, 10.3 mmol), DMSO (1.46 ml, 20.6 mmol), and Et_3N (5.72 ml, 41.7 mmol) (Swern oxidation) following the procedure described for the synthesis of **3**. Purification of crude product by silica-gel column chromatography gave pure aldehyde **8** (*t*/*c*=20/1) in 81% yield (0.98 g). Careful separation by preparative thin layer chromatography (PLC) (R_f=0.48 (*t*-isomer) R_f=0.43 (*c*-isomer), hexane/ethyl acetate=10/1) gave the analytical pure samples. *trans*-**8**: Bp 68 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 2996, 2952, 2924, 2864, 2820, 2730, 1707, 1459, 1428, 1412, 1252, 1179, 1111, 1076, 952, 923, 863, 833, 818, 781, 731, 701, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.36 (s, 3H), 0.37 (s, 3H), 0.45 (dd, J=9.4, 8.8 Hz, 1H), 1.25 (d, J=5.8 Hz, 3H), 1.60 (dqd, J=8.8, 5.8, 4.1 Hz, 1H), 1.77 (ddd, J=9.4, 6.8, 4.1 Hz, 1H), 7.35—7.42 (m, 3H), 7.51—7.57 (m, 2H), 8.88 (d, J=6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.68, 18.96, 19.54, 21 47, 37.79, 128.0, 129.3, 133.6, 138.2, 201.2. Found: C, 71.45; H, 8.52%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%. *cis*-**8:** Bp 70 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 3006, 2952, 2846, 2758, 2724, 1701, 1648, 1458, 1452, 1428, 1389, 1375, 1289, 1251, 1173, 1112, 1068, 998, 942, 895, 869, 834, 816, 778, 732, 699, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.44 (s, 3H), 0.47 (s, 3H), 0.73 (t, J=9.6 Hz, 1H), 1.33 (d, J=6.5 Hz, 3H), 1.92 (ddq, J=9.6, 8.1, 6.5 Hz, 1H), 2.08 (ddd, J=9.6, 8.1, 6.4 Hz, 1H), 7.35—7.40 (m, 3H), 7.54—7.60 (m, 2H), 9.36 (d, J=6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.33, 0.07, 12.51, 16.53, 22.84, 32.62, 127.9, 129.2, 133.6, 139.2, 202.7. Found: C, 71.51; H, 8.34%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%.

***r*-1-Dimethylphenylsilyl-*t*-3-methyl-*c*-2-vinylcyclopropane (*trans*-9) and *r*-1-Dimethylphenylsilyl-*c*-3-methyl-*c*-2-vinylcyclopropane (*cis*-9).** Wittig reaction (Ph_3PCH_3I (2.1 g, 5.2 mmol) and *t*-BuOK (0.58 g, 5.2 mmol)) of **8** (*t*/*c*=20/1, 0.87 g, 4.0 mmol) followed by purification by silica-gel column chromatography gave the title compound **9** in 90% yield (0.78 g, *t*/*c*=17/1). Analytical samples were prepared by preparative GLPC (Column A, 150 °, t_r=3.55 min (*t*-isomer), t_r=4.28 min (*c*-isomer)). *trans*-**9:** Bp 53 °C (1 Torr, bath temp); IR (neat) 3066, 3048, 2992, 2948, 2922, 2896, 2862, 1635, 1459, 1428, 1376, 1249, 1113, 1073, 981, 950, 925, 893, 832, 811, 770, 728, 700, 676, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.09 (dd, J=9.6, 7.4 Hz, 1H), 0.27 (s, 6H), 0.93 (dqd, J=7.4, 5.7, 4.4 Hz, 1H), 1.18 (d, J=5.7 Hz, 3H), 1.47 (td, J=9.6, 4.4 Hz, 1H), 4.85 (dd, J=9.9, 2.2 Hz, 1H), 5.09 (dd, J=17.0, 2.2 Hz, 1H), 5.41 (ddd, J=17.0, 9.9, 9.6 Hz, 1H), 7.34—7.40 (m, 3H), 7.54—7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.57, −1.46, 14.96, 19.50, 20.30, 29.74, 112.9, 127.7, 128.7, 133.8, 140.0, 140.7. Found: C, 77.76; H, 9.49%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%. *cis*-**9:** Bp 51 °C (1 Torr, bath temp); IR (neat) 3066, 3048, 2996, 2952, 2924, 2872, 2852, 1631, 1428, 1286, 1259, 1249, 1112, 1070, 1017, 992, 920, 895, 833, 818, 775, 728, 698, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.24 (t, J=9.7 Hz, 1H), 0.34 (s, 3H), 0.37 (s, 3H), 1.14 (d, J=6.5 Hz, 3H), 1.47 (ddq, J=9.7, 8.3, 6.5 Hz, 1H), 1.90 (ddd, J=9.9, 9.7, 8.3 Hz, 1H), 5.00 (ddd, J=10.2, 2.2, 0.6 Hz, 1H), 5.22 (ddd, J=16.8, 2.2, 0.6 Hz, 1H), 5.68 (ddd, J=16.8, 10.2, 9.9 Hz, 1H), 7.32—7.37 (m, 3H), 7.54—7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=0.12, 0.19, 11.67, 12.61, 17.50, 25.12, 114.5, 127.7, 128.7, 133.7, 137.6, 140.6. Found: C, 77.59; H, 9.29%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

***r*-1-Dimethylphenylsilyl-*t*-2-hydroxymethyl-*c*,*t*-3-methylcyclopropane (10).** Cyclopropanation of **4** (2.0 g, 10.4 mmol) with ethylidene iodide (2 ml, 20 mmol) and diethylzinc (2 ml, 20 mmol) gave the cyclopropane **10** (0.53

g, 23% yield) which was contaminated by **4** (0.90 g, 46% recovery). **10** (*c*/*t*=36/64) was separated from **4** by preparative GLPC: Bp 75 °C (1 Torr, bath temp); IR (neat) 3316, 3064, 3046, 2992, 2950, 2870, 1458, 1449,1428, 1382, 1248, 1113, 1072, 1021, 949, 924, 817, 773, 728, 698, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.54 (t, *J*=6.7 Hz, 0.64H), −0.26 (t, *J*=8.0 Hz, 0.36H), 0.20 (s, 3.84H), 0.30 (s, 1 .08H), 0.32 (s,1.08H), 0.89—1.40 (m, 6H), 3.45—3.61 (m, 1.36H), 3.77 (dd, *J*=11.2, 6.1 Hz, 0.64H), 7.34—7.40 (m, 3H), 7.51—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.68, −1.19, −1.15, 8.66, 10.20, 14.11, 14.46, 16.47, 17.17, 22.69, 27.14, 63.63, 68.56, 127.8, 128.8, 128.9, 133.6, 139.0, 139.9. Found: C, 71.12; H, 9.39%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

***r*-1-Dimethylphenylsilyl-*t*-2-formyl-*t*-3-methylcyclopropane (*trans*-11) and *r*-1-Dimethylphenylsilyl-*t*-2-formyl-*c*-3-methylcyclopropane (*cis*-11).** The mixture of **4** (4.8 mmol) and **10** (2.4 mmol) was treated with $(COCl)_2$ (0.94 ml, 10.8 mmol), DMSO (1.53 ml, 21.6 mmol) and Et_3N (6.0 ml, 43.2 mmol) to give the title compound in 50% yield (0.26 g, 1.2 mmol, *t*/*c*=2/1). PLC separation of isomers (R_f=0.41 (*t*-isomer) and R_f=0.34 (*c*-isomer), hexane/ethyl acetate=10/1) provided the analytical samples. ***trans*-11:** Bp 67 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 2996, 2952, 2874, 2822, 2746, 2718, 1701, 1655, 1647,1459, 1428, 1396, 1379, 1251, 1171, 1115, 1073, 1017, 997, 954, 928, 881, 834, 780, 731, 700, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.24 (s, 3H), 0.27 (s, 3H), 0.80 (dd, *J*=7.7, 6.4 Hz, 1H), 1 32—1.53 (m, 4H), 1.75 (dt, *J*=7.7, 5.9 Hz, 1H), 7.34—7.41 (m, 3H), 7.47—7.53 (m, 2H), 9.28 (d, *J*=5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−4.07, −3.77, 14.51, 16.40, 21.98, 32.00, 127.9, 129.4, 133.6, 137.0, 201 4. Found: C, 71.28; H, 8.45%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%. ***cis*-11:** Bp 67 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 2994, 2954, 2816, 2718, 1709, 1459, 1428, 1412, 1251, 1206, 1173, 1115, 1085, 1068, 1022, 1005, 935, 874, 834, 815, 777, 731, 701, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.36 (s, 3H), 0.37 (s, 3H), 0.77 (dd, *J*=10.4, 6.3 Hz, 1H), 1.12 (d, *J*=6.2 Hz, 3H), 1.65 (ddd, *J*=6.3, 6.1, 3.9 Hz, 1H), 1.75 (ddq, *J*=10.4, 6.2, 3.9 Hz, 1H), 7.35—7.41 (m, 3H), 7.50—7.57 (m, 2H), 8.77 (d, *J*=6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.78, −1.53, 13.75, 15.34, 20.74, 35.77, 127.9, 129.3, 133.6, 138.0, 201.0. Found: C, 71.51; H, 8.34%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; N, 8.31%.

***r*-1-Dimethylphenylsilyl-*t*-3-methyl-*t*-2-vinylcyclopropane (*trans*-12) and *r*-1-Dimethylphenylsilyl-*c*-3-methyl-*t*-2-vinylcyclopropane (*cis*-12).** Wittig reaction (Ph_3PCH_3I (0.67 g, 1.67 mmol) and *t*-BuOK (0.19 g, 1.67 mmol)) of **11** (0.26 g, 1.2 mmol) gave **12** in 74% yield (0.19 g, *t*/*c*=2/1). Each pure sample was prepared by PLC (R_f=0.62 (*trans*-isomer) R_f=0.60 (*cis*-isomer), hexane). ***trans*-12:** Bp 57 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 2994, 2952, 2926, 2900, 2868, 1633, 1459, 1428, 1249, 1115, 1090, 1071, 990, 961, 929, 894, 835, 780, 729, 698, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.27 (t, *J*=6.7 Hz, 1H), 0.20 (s, 6H), 1.02 (ddq, *J*=8,7, 6.7, 5.8 Hz, 1H), 1.14 (d, *J*=5.8 Hz, 3H), 1.47 (td, *J*=8.7, 6.7 Hz, 1H), 4.98 (dd, *J*=10.1 , 2.0 Hz, 1H), 5.12 (dd, *J*=17.0, 2.0 Hz, 1H), 5.63 (ddd, *J*=17.0, 10.1, 8.7 Hz, 1H), 7.32—7.39 (m, 3H), 7.50—7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.54, 13.69, 14.85, 17.00, 24.67, 113.7, 127.7, 128.9, 133.8, 138.7, 139.1. Found: C, 77.76; H, 9.38%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32% ***cis*-12:** Bp 57 °C (1 Torr, bath temp); IR (neat) 3066, 3048, 2994, 2950, 2868, 1635, 1459, 1450, 1428, 1410, 1249, 1113, 1069, 1015, 980, 927, 891, 835, 811, 795, 783, 768, 728, 699, 650cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.00 (dd, *J*=9.6, 6.6 Hz, 1H), 0.28 (s, 3H), 0.31 (s, 3H), 1.02—1.29 (m, 5H), 4.82 (dd, *J*=10.0, 1.7 Hz, 1H), 5.05 (dd, *J*=17.1, 1.7 Hz, 1H), 5.39 (ddd, *J*=17.1, 10.0, 8.5 Hz, 1H), 7.31—7.38 (m, 3H), 7.50—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.37, −0.91, 13.09, 16.37, 20.53, 28.61, 111.0, 127.7, 128.8, 133.7, 140.0, 143.4. Found: C, 78.01; H, 9.49%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

(2,2-Dibromo-*trans*-3-methylcyclopropyl)methyl 2-Tetrahydropyranyl Ether (13). Tetrahydropyranyl ether of 2-buten-1-ol (15.7 g, 100 mmol) was added to a mixture of hexane (150 ml) and potassium *t*-butoxide (22.5 g, 200 mmol) at −20 °C under argon atmosphere. Then bromoform (17.5 ml, 200 mmol) was added dropwise to the solution over 1.5 h from dropping funnel. After stirring at −20 °C for 2 h and at 25 °C for 10 h, reaction mixture was poured into saturated aqueous NaCl (200 ml). The organic layer was removed and the aqueous layer was extracted with hexane (200 ml). The combined organic layer was dried over anhydrous sodium sulfate. Concentration and successive purification by silica-gel column chromatography (hexane/ethyl acetate=20/1) gave **13** in 70% yield (diastereomeric mixture, 23.0 g): Bp 80 °C (decomp, 1 Torr, bath temp); IR (neat) 2938,2868, 1466, 1453, 1382, 1350, 1262, 1202, 1184, 1158, 1133, 1121, 1059, 1033, 991, 965, 943, 905, 869, 814, 743, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.15—1.89 (m, 11H), 3.49—3.64 (m, 2H), 3.78—3.96 (m, 2H), 4.69 (bs, 1H) ^{13}C NMR ($CDCl_3$) δ=16.90, 19.13, 19.41, 25.38, 29.89, 30.46, 30.62, 36.26, 36.70, 61.99, 62.28, 68.95, 69.38, 98.37, 98.94. Found: C, 36.82; H, 4.98%. Calcd for $C_{10}H_{16}O_2Br_2$: C, 36.61; H, 4.92%.

***t*-2-Hydroxymethyl-*c*-3-methyl-*r*-1-trimethylsilylcyclopropane (*trans*-14) and *c*-2-Hydroxymethyl-*t*-3-methyl-*r*-1-trimethylsilylcyclopropane (*cis*-14).** A hexane solution of butyllithium (1.6 M, 34 ml, 54 mmol) was added dropwise over 20 min from dropping funnel to a THF (100 ml) solution of **13** (17 g, 52 mmol) and trimethylsilyl chloride (33 ml, 260 mmol) at −107 °C (isooctane-liq. N_2) under argon atmosphere. After stirring for 2 h, cooling bath was removed and the mixture was stirred for another 20 min. The mixture was slowly poured into saturated aqueous sodium hydrogencarbonate (200 ml). The product was extracted with ethyl acetate (150 ml×2) and the extracts were dried and concentrated in vacuo. The residual oil was dissolved in benzene (100 ml) and tributyltin hydride (17.5 g, 60 mmol) was added to the solution under argon atmosphere. A hexane solution of triethylborane (1.0 M, 3.0 ml, 3.0 mmol) was added to the mixture at 25 °C and exothermic reaction occurred instantly. After stirring for 1 h, dichloromethane (200 ml), potassium fluoride (35 g), and water (11 ml) were added and the resulting mixture was stirred for 12 h. The precipitate was filtered by glass filter and the filtrate was concentrated in vacuo. The crude product was dissolved into methanol (150 ml) and *p*-toluenesulfonic acid mono hydrate (1.0 g) was added. After stirring for 2 h, triethylamine (3 ml) was added and the reaction mixture was concentrated. Purification of the product by silica-gel column chromatography (hexane/ethyl acetate=10/1) gave **14** in 71% yield (5.73 g, *t*-isomer/*c*-isomer=64/36). The isomers were separated each other by PLC. ***trans*-14:** Bp 95 °C (27 Torr, bath temp); IR (neat) 3322, 2988, 2950, 2868, 1458, 1406, 1249, 1086, 1020, 990, 948, 926, 854, 835, 755, 687, 664 cm^{-1}; ^1H NMR (CDC_3) δ=−0.49 (dd, *J*=9.5, 6.8 Hz, 1H), 0.04 (s, 9H), 0.80—1.00 (m, 2H), 1.10 (d, *J*=5.8 Hz, 3H), 1.54 (bs, 1H), 3.46 (d, *J*=6.4 Hz, 2H); ^{13}H NMR ($CDCl_3$) δ=−0.10, 9.21, 16.44, 16.95, 26.89, 68.64. Found: C, 60.88; H, 11.64%.

Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46%. *cis*-**14:** Bp 100 °C (27 Torr, bath temp); IR (neat) 3328, 2990, 2950, 2898, 2866, 1462, 1448, 1380, 1249, 1076, 1021, 992, 944, 924, 837, 757, 688, 662 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.50 (dd, J=9.4, 7.0 Hz, 1H), 0.03 (s, 9H), 0.67 (dqd, J=7.0, 5.8, 4.2 Hz, 1H), 1.07 (dddd, J=9.4, 7.9, 7.3, 4.2 Hz, 1H), 1.14 (d, J=5.8 Hz, 3H), 1.44 (bs, 1H), 3.47 (dd, J=11.0, 7.9 Hz, 1H), 3.56 (dd, J=11.0, 7.3 Hz, 1H); ^{13}H NMR ($CDCl_3$) δ=−0.05, 11 99, 16.50, 20.58, 28.34, 65.28. Found: C, 60.68; H, 11.68%. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46%.

***c*-3-Methyl-*r*-1-trimethylsilyl-*t*-2-vinylcyclopropane and *t*-3-Methyl-*r*-1-trimethylsilyl-*c*-2-vinylcyclopropane (74 : 26) (15).** Swern oxidation and successive Wittig reaction provided vinylcyclopropane **15** in 53% overall yield from **14:** Bp 70—72 °C (55 Torr); IR (neat) 3078, 2994, 2950, 2896, 2868, 1635, 1459, 1375, 1289, 1249, 1090, 1069, 980, 950, 927, 891, 837, 793, 748, 688, 657, 636 cm^{-1}; ^1H NMR (CDC_3) δ=−0.31 (dd, J=9.5, 7.2 Hz, 0.26H), −0.22 (dd, J=9.3, 6.8 Hz, 0.74H), 0.02 (s, 2.34H), 0.06 (s, 6.66H), 0.78—0.99 (m, 0.26H), 1.00—1.27 (m, 4.48H), 1.41 (td, J=10.0, 4.5 Hz, 0.26H), 4.79 (dd, J=10.0, 1.9 Hz, 0.74H), 4.87 (dd, J=10.0, 2.2 Hz, 0.26H), 5.02 (dd, J=17.2, 1.9 Hz, 0.74H), 5.09 (dd, J=16.8, 2.2 Hz, 0.26H), 5.37 (ddd, J=17.2, 10.0, 8.3 Hz, 0.74H), 5.46 (dt, J=16.8, 10.0 Hz, 0.26H); ^{13}C NMR ($CDCl_3$) δ=−0.29, 0.00, 14.08, 15.93, 16.36, 19.36, 20.44, 28.39, 29.65, 110.4, 112.4, 141.1, 143.9. Found: C, 69.80; H, 11.92%. Calcd for $C_9H_{18}Si$: C, 70.05; N, 11.76%.

2,2-Dibromo-3,3-dimethylcyclopropylmethyl 2-Tetrahydropyranyl Ether (16). An addition of dibromocarbene ($CHBr_3$, *t*-BuOK) to prenyl alcohol tetrahydropyranyl ether gave cyclopropane **16** (diastereomeric mixture) in 81% yield: Bp 85 °C (dec, 1 Torr, bath temp); IR (neat) 2938, 2868, 1455, 1441, 1374, 1353, 1342, 1322, 1284, 1274, 1262, 1201, 1183, 1158, 1134, 1121, 1079, 1059, 1031, 979, 906, 869, 815, 755, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (s, 3H), 1.43 (s, 3H), 1.50—1.98 (m, 7H), 3.44—4.01 (m, 4H), 4.64—4.71 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=19.14, 19.34, 19.47, 25.35, 27.16, 28.38, 30.51, 30.57, 38.24, 38.43, 44.63, 44.81, 61.94, 62.16, 66.08, 66.21, 98.45, 98.85. Found: C, 38.53; H, 5.26%. Calcd for $C_{11}H_{18}O_2Br_2$: C, 38.62; H, 5.30%.

2-Bromo-3,3-dimethyl-2-trimethylsilylcyclopropylmethyl Tetrahydropyranyl Ether (17, *cis* trans Mixture). According to the description for the synthesis of **14**, the title compound was obtained in 65% yield (8.5 g) starting from **16** (13.3 g, 39 mmol): Bp 82 °C (decomp, 1 Torr, bath temp); IR (neat) 2942, 2868, 1456, 1442, 1408, 1384, 1373, 1342, 1322, 1284, 1249, 1201, 1184, 1160, 1134, 1119, 1078, 1056, 1029, 997, 974, 951, 929, 904, 841, 815, 763, 735, 682, 628 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19—0.27 (m, 9H), 0.90—1.28 (m, 4H), 1.43—1.95 (m, 9H), 3.40—3.65 (m, 2H), 3.72—4.03 (m, 2H), 4.64 (bs, 1H). Found: C, 50.23; H, 8.39%. Calcd for $C_{14}H_{27}O_2SiBr$: C, 50.14; H, 8.12%.

***trans*-2-Hydroxymethyl-3,3-dimethyl-1-trimethylsilylcyclopropane (*trans*-18) and *cis*-2-Hydroxymethyl-3,3-dimethyl-1-trimethylsilylcyclopropane (*cis*-18).** Hydrodebromination of **17** was performed by two methods. Procedure A: Reduction with tributyltin hydride (3.33 g, 11.4 mmol)-triethylborane (1.0 M hexane solution, 1 ml) system as described for the synthesis of **14** followed by deprotection of tetrahydropyranyl ether (*p*-TsOH-MeOH) gave **18** in 90% yield (1.61 g, *cis*-**18**/*trans*-**18**=3.8/1) starting from **17** (3.49 g, 10.4 mmol). Procedure B: Butyllithium (1.54 M hexane solution, 7.9 ml, 12.2 mmol) was added over 5 min to a solution of **17** (3.73 g, 11.1 mmol) in THF (22 ml) at −78 °C. After stirring for 1 h, acetic acid (1.4 ml, 24 mmol) was added to the reaction mixture and then cooling bath was removed. After stirring for additional 15 min at 25 °C, the resulting mixture was poured into saturated sodium hydrogencarbonate aqueous solution (50 ml) and the product was extracted with ethyl acetate (50 ml×2). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Deprotection of tetrahydropyranyl ether followed by purification by silica-gel column chromatography (hexane/ethyl acetate=10/1) gave **18** in 62% yield (1.19 g, t/c=11/1). Analytical pure samples were prepared by preparative GLPC (Column B, 130 °C, t_r=8.37 min (*trans*-isomer) and 9.46 min (*cis*-isomer)). *trans*-**18:** Bp 52 °C (1 Torr, bath temp); IR (neat) 3314, 2948, 2870, 1454, 1412, 1376, 1300, 1248, 1120, 1083, 1049, 1016, 964, 953, 926, 865, 835, 760, 687, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.67 (d, J=7.2 Hz, 1H), 0.02 Is, 9H), 0.96 (ddd, J=8.3, 7.2, 6.3 Hz, 1H), 1.12 (s, 3H), 1.16 (s, 3H), 1.28 (bs, 1H), 3.53 (dd, J=11.4, 8.3 Hz, 1H), 3.72 (dd, J=11.4, 6.3 Hz, 1N); ^{13}C NMR ($CDCl_3$) δ=−0.17, 17.86, 21.90, 22.77, 25.14, 31.78, 64.98. Found: C, 62.83; H, 11.91%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%. *cis*-**18:** Bp 50 °C (1 Torr, bath temp); IR (neat) 3308, 2948, 2890, 1453, 1412, 1375, 1290, 1248, 1120, 1045, 1018, 966, 938, 835, 757, 685, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.36 (d, J=9.9 Hz, 1H), 0.07 (s, 9H), 1.12—1.26 (m, 8H), 3.61 (dd, J=11.2, 8.7 Hz, 1H), 3.72 (dd, J=11.2, 6.7 Hz, 1N); ^{13}C NMR ($CDCl_3$) δ=1.13, 17.55, 18.17, 21.09, 30.81, 32.07, 62.39. Found: C, 62.45; H, 11.97%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

***trans*-3,3-Dimethyl-1-trimethylsilyl-2-vinylcyclopropane (*trans*-19) and cis-3,3-Dimethyl-1-trimethylsilyl-2-vinylcyclopropane (*cis*-19).** According to the synthesis of **3**, Swern oxidation and Wittig reaction of **18** (*cis* rich) or **18** (*trans* rich) gave **19** (*cis* rich) or **19** (*trans* rich) in 57% or 51% yield, respectively. Analytical samples were obtained by preparative GLPC (Column B, 50 °C, t_r=6.78 min (*t*-isomer) t_r=8.09 min (*c*-isomer)). *trans*-**19:** Bp 63 °C (40 Torr, bath temp); IR (neat) 3078, 2948, 2868, 1634, 1458, 1375, 1248, 1133, 1117, 982, 909, 892, 860, 836, 768, 752, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.38 (d, J=7.0 Hz, 1H), 0.03 (s, 9H), 1.11 (s, 6H), 1.31 (dd, J=8.7, 7.0 Hz, 1H), 4.92 (dd, J=10.0, 2.1 Hz, 1H), 5.06 (dd, J=17.0, 2.1 Hz, 1H), 5.62 (ddd, J=17.0, 10.0, 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.14, 21.69, 23.60, 24.24, 24.82, 33.86, 112.8, 140.4. Found: C, 71.23; H, 12.20%. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97%. *cis*-**19:** Bp 58 °C (40 Torr, bath temp); IR (neat) 3078, 2950, 1632, 1457, 1375, 1248, 1118, 984, 920, 894, 836, 765, 754, 722, 686, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.17 (d, J=9.9 Hz, 1H), 0.07 (s, 9H), 1.13 (s, 3H), 1.15 (s, 3H), 1.58 (t, J=9.9 Hz, 1H), 4.94 (dd, J=10.2, 2.2 Hz, 1H), 5.14 (dd, J=16.9, 2.2 Hz, 1H), 5.66 (ddd, J=16.9, 10.2, 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.00, 19.06, 21.62, 23.59, 30.58, 34.20, 113.5, 138.6. Found: C, 71.12; H, 12.20%. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97%.

(*trans*-3,3-Dibromo-2-phenylcyclopropyl)methyl 2-Tetrahydropyranyl Ether (20). Treatment of tetrahydropyranyl ether of *E*-cinnamyl alcohol (21.8 g, 100 mmol) with $CHBr_3$ (17.5 ml, 200 mmol) and *t*-BuOK (22.5 g, 200 mmol) as described for the synthesis of **13** gave the compound **20** in 57% yield (22.2 g, 57/43 diastereomeric mixture): Bp 110 °C (decomp, 1 Torr, bath temp); IR (neat) 3056, 3028, 2938, 2866, 1654, 1602, 1498, 1465, 1452, 1387, 1364, 1351, 1323, 1261, 1201, 1183, 1120, 1077, 1063, 1034, 1001, 971, 950, 905, 869, 812, 753, 733, 694, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.45—

2.06 (m, 6H), 2.27 (ddd, J=7.5, 5.5, 3.2 Hz, 0.43H), 2.31 (ddd, J=7.7, 5.6, 3.5 Hz, 0.57H), 2.66 (d, J=7.7 Hz, 0.57H), 2.70 (d, J=7.5 Hz, 0.43H), 3.49—3.61 (m, 1H), 3.72—4.07 (m, 3H), 4.78 (bs, 1H), 7.25—7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=19.14, 19.35, 25.39, 30.52, 30.63, 34.35, 34.78, 39.62, 62.13, 62.27, 68.90, 69.13, 98.64, 98.97, 127.6, 128.3, 128.8, 135.6. Found: C, 46.30; H, 4.64%. Calcd for $C_{15}H_{18}O_2Br_2$: C, 46.18; H, 4.65%.

***c*-2-Hydroxymethyl-*t*-3-phenyl-*r*-1-trimethylsilylcyclopropane (*cis*-21) and *t*-2-Hydroxymethyl-*c*-3-phenyl-*r*-1-trimethylsilylcyclopropane (*trans*-21).** Following the procedure for the synthesis of **14**, an addition of butyllithium to a mixture of **20** (12.1 g, 31 mmol) and trimethylsilyl chloride (19 ml, 150 mmol) in THF to give a silylated cyclopropane which was treated with n-Bu_3SnH-Et_3B followed by deprotection with p-TsOH gave **21** in 59% yield (4.0 g, *cis*-**21**/*trans*-**21**=2/1). Separation by PLC gave analytical samples (R_f=0.46 (*t*-isomer) and R_f=0.51 (*c*-isomer), hexane/ethyl acetate=3/1). *cis*-**21:** Bp 96 °C (1 Torr, bath temp); IR (neat) 3316, 3058, 3026, 2996, 2948, 2892, 1604, 1499, 1458, 1249, 1032, 920, 838, 751, 694, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.11 (s, 9H), 0.25 (dd, J=10.0, 7.2 Hz, 1H), 1.46 (bs, 1H), 1.70 (dddd, J=10.0, 7.5, 7.0, 4.6 Hz, 1H), 1.82 (dd, J= 7.2, 4.6 Hz, 1H), 3.63 (dd, J=11.2, 7.5 Hz, 1H), 3.70 (dd, J= 11.2, 7.0 Hz, 1H), 7.08—7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−0.14, 15.77, 26.51, 30.65, 64.91, 125.6, 125.8, 128.3, 143.4. Found: C, 71.13; H, 9.36%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%. *trans*-**21:** Bp 98 °C (1 Torr, bath temp); IR (neat) 3310, 3080, 3058, 3026, 2948, 2860, 1603, 1497, 1448, 1420, 1247, 1116, 1031, 905, 836, 791, 753 697, 661 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.25 (s, 9H), 0.02 (dd, J=10.5, 7.0 Hz, 1H), 1.57 (bs, 1H), 1.70 (dtd, J= 7.0, 6.6, 4.8 Hz, 1H), 2.25 (dd, J=10.5, 4.8 Hz, 1H), 3.66 (d, J=6.6 Hz, 2H), 7.10—7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−1.10, 12.60, 23.51, 27.00, 68.21, 126.1, 127.9, 129.3, 140.0. Found: C, 70.58; H, 9.37%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

***t*-2-Phenyl-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (*cis*-22) and *c*-2-Phenyl-*r*-1-trimethylsilyl-*t*-3-vinylcyclopropane (*trans*-22).** Swern oxidation followed by Wittig reaction of **21** (3.13 g, 14.2 mmol) provided **22** in 82% yield (2.53 g, *cis*/*trans*=2/1). *cis*-**22** (R_f=0.58, hexane): Bp 60 °C (1 Torr, bath temp); IR (neat) 3078, 3026, 2998, 2950, 1634, 1603, 1499, 1449, 1249, 1072, 984, 893, 839, 750, 694, 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.10 (s, 9H), 0.47 (dd, J=9.7, 7.9 Hz, 1H), 1.92—2.04 (m, 2H), 4.97 (dd, J=9.9, 1.9 Hz, 1H), 5.16 (dd, J=16.8, 1.9 Hz, 1H), 5.48—5.68 (m, 1H), 7.06—7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−0.37, 18.19, 29.12, 32.65, 113.9, 125.5, 125.7, 128.3, 139.6, 143.3. Found: C, 77.70; H, 9.47%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%. *trans*-**22** (R_f=0.65, hexane): Bp 55 °C (1 Torr, bath temp); IR (neat) 3078, 3058, 3024, 2996, 2950, 2894, 1636, 1603, 1497, 1448, 1248, 983, 959, 894, 856, 839, 752, 740, 697, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.25 (s, 9H), 0.23 (dd, J=10.5, 6.9 Hz, 1H), 1.98 (ddd, J=8.2, 6.9, 4.7 Hz, 1H), 2.37 (dd, J=10.5, 4.7 Hz, 1H), 4.92 (dd, J=10.0, 1.7 Hz, 1H), 5.19 (dd, J=17.1, 1.7 Hz, 1H), 5.57 (ddd, J=17.1, 10.0, 8.2 Hz, 1H), 7.10—7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−1.01, 16.70, 24.87, 30.14, 111.7, 126.1, 127.9, 129.2, 140.2, 142.7. Found: C, 77.70; H, 9.52%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

1,2-Bis[(2-tetrahydropyranyloxy)methyl]-3,3-dibromocyclopropane (23). An addition of dibromocarbene ($CHBr_3$ (27.2 ml, 312 mmol) and *t*-BuOK (35 g, 312 mmol)) to tetrahydropyranyl ether of *cis*-2-buten-1,4-diol (20.3 g, 79.3 mmol) afforded the compound **23** (21.4 g) in 63% yield: Bp 158 °C (decomp, 0.13 Torr, bath temp); IR (neat) 2938, 2868, 1466, 1453, 1440, 1386, 1366, 1353, 1263, 1201, 1183, 1135, 1121, 1077, 1060, 1032, 968, 905, 869, 815, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.54—1.93 (m, 12H), 2.03—2.17 (m, 2H), 3.44—3.63 (m, 4H), 3.75—4.00 (m, 4H) 4.65—4.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=19.06, 19.29, 25.35, 30.46, 30.54, 32.57, 32.77, 61.95, 62.00, 62.18, 65.25, 65.33, 98.62, 98.70, 98.83. Found: C, 42.05; H, 5.72%. Calcd for $C_{15}H_{24}O_4Br_2$: C, 42.08; H, 5.65%.

1,2-Bis[(2-tetrahydropyranyloxy)methyl]-3-bromo-3-trimethylsilylcyclopropane (24). Treatment of **23** (16 g, 37 mmol) with butyllithium (1.6 M, 25 ml, 40 mmol) in THF (100 ml) in the presence of trimethylsilyl chloride (24 ml, 190 mmol) gave **24** in 64% yield (10.0 g, a mixture of two stereoisomers, 1/1). An isomer (R_f=0.55, hexane/ethyl acetate=5/1): Bp 147 (dec. 0.13 Torr, bath temp); IR (neat) 2940, 2868, 1466, 1454, 1441, 1385, 1366, 1354, 1249, 1201, 1183, 1159, 1120, 1079, 1057, 1029, 976, 905, 868, 843, 815, 758, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.27 (s, 9H), 1.55—1.95 (m, 12H), 2.05—2.21 (m, 2H), 3.34—3.60 (m, 4H), 3.72—3.93 (m, 4H), 4.61—4.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=0.47, 19.12, 19.44, 25.38, 30.53, 30.65, 31.13, 32.46, 32.59, 61.82, 62.30, 63.42, 63.50, 63.88, 64.00, 98.33, 98.44. Found: C, 51.28; H, 8.09%. Calcd for $C_{18}H_{33}O_4SiBr$: C, 51.30; H, 7.89%. Another isomer (R_f=0.59, hexane/ethyl acetate=5/1): Bp 140 °C (decomp, 0,12 Torr, bath temp); IR (neat) 2940, 2868, 1466, 1454, 1441, 1385, 1366, 1354, 1283, 1250, 1201, 1184, 1161, 1137, 1120, 1078, 1057, 1029, 975, 905, 888, 868, 841, 816, 745, 620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.10 (s, 9H), 1.20—1.32 (m, 2H), 1.48—1.88 (m, 12H), 3.47—3.71 (m, 4H), 3.83—4.03 (m, 4H), 4.65—4.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.41, 19.27, 19.55, 21.78, 22.16, 25.43, 30.70, 34.63, 35.20, 62.00, 62.24, 62.30, 65.71, 65.85, 65.92, 98.40, 98.70. Found: C, 51.18; H, 8.16%. Calcd for $C_{18}H_{33}O_4SiBr$: C, 51.30; H, 7.89%.

2,3-Bis[(2-tetrahydropyranyloxy)methyl]-1-trimethylsilylcyclopropane (25). Reduction of **24** with n-Bu_3SnH-Et_3B afforded the compound **25** in 92% yield as a stereoisomeric mixture (*cis*/*trans*=17/1, GLPC Column A, 220 °C, t_r=3.57 min (*t*-isomer) t_r=4.63 min (*c*-isomer)): Bp 160 °C (1 Torr, bath temp); IR (neat) 2940, 2870, 1466, 1454, 1442, 1385, 1369, 1343, 1320, 1285, 1247, 1201, 1184, 1159, 1136, 1119, 1079, 1056, 1026, 973, 905, 886, 836, 815, 756, 686, 645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.09-0.14 (m, 10H), 1.45—1.92 (m, 14H), 3.34—3.53 (m, 4H), 3.80—3.95 (m, 4H), 4.61—4.65 (m, 2H); ^{13}C NMR ($CDCl_3$) for cis isomer δ=1.03, 7.67, 19.43, 19.61, 19.66, 20.06, 20.17, 25.49, 30.70, 30.82, 61.96, 62.04, 62.31, 62.36, 65.83, 65.93, 66.07, 98.53, 98.70. Found: C, 62.95; H, 10.25%. Calcd for $C_{18}H_{34}O_4Si$: C, 63.11; H, 10.00%.

3-Hydroxymethyl-2-(2-tetrahydropyranyloxy)methyl-1-trimethylsilylcyclopropane (26). Half deprotection of tetrahydropyranyl ether **25** (including two isomers) with p-TsOH in methanol provided the title compound (*cis* major) in 57% yield: Bp 143 °C (1 Torr, bath temp); IR (neat) 3432, 2944, 2892, 2872, 1442, 1413, 1383, 1285, 1248, 1202, 1160, 1133, 1119, 1078, 1053, 1025, 977, 903, 837, 758, 688, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.07—0.08 (m, 10H), 1.10—1.90 (m, 8H), 2.91—3.65 (m, 4H), 3.79—3.93 (m, 2.5H), 4.11—4.19 (m, 0.5H), 4.68 (bs, 1H); ^{13}C NMR ($CDCl_3$) for *cis* isomer δ=1.31, 7.64, 7.73, 19.13, 19.47, 19.59, 19.77, 23.21, 23.29, 25.15, 25.26, 30.42, 30.54, 60.92, 61.11, 62.10, 62.45, 65.80, 66.20, 98.04, 98.80. Found: C, 60.13; H, 10.38%. Calcd for

$C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14%.

***c*-2-Hydroxymethyl-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (27).** Starting from **26**, the compound **27** (*cis*/*trans*=14/1, GLPC Column A, 110 °C, t_r=3.49 min (*c*-isomer) and t_r=2.51 min (*t*-isomer)) was obtained in 80% yield by the following sequence, Swern oxidation, Wittig reaction, and deprotection: Bp 81 °C (1 Torr, bath temp); IR (neat) 3326, 3076, 2996, 2952, 2892, 1633, 1411, 1286, 1249, 1024, 988, 945, 922, 897, 837, 757, 690, 665, 645 cm^{-1}; ^1H NMR ($CDCl_3$) for *cis* isomer δ=0.10 (s, 9H), 0.17 (t, J=9.8 Hz, 1H), 1.44 (bs, 1H), 1.66 (dddd, J=9.8, 9.4, 8.0, 6.7 Hz, 1H), 1.96 (ddd, J=10.2, 9.8, 8.0 Hz, 1H), 3.65 (dd, J= 11.3, 9.4 Hz, 1H), 3.82 (dd, J=11.3, 6.7 Hz, 1H), 5.05 (dd, J=10.2, 1.9 Hz, 1H), 5.27 (dd, J=16.8, 1.9 Hz, 1H), 5.69 (dt, J=16.8, 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) for *cis* isomer δ=0.97, 11.50, 24.42, 25.75, 61.59, 115.5, 136.4. Found: C, 63.17; H, 10.67%. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65%.

***c*-2-(1-Hydroxyethyl)-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (28).** Swern oxidation of **27** and successive treatment of the crude product with methylmagnesium iodide gave **28** in 82% yield (threo/erythro=1/1) by purification by silica-gel column chromatography. Diastereomers were seperated by PLC. Fast moving band (R_f=0.50, hexane/ethyl acetate=3/1): Bp 75 °C (1 Torr, bath temp); IR (neat) 3314, 2966, 2952, 1633, 1367, 1286, 1261, 1247, 1186, 1108, 1099, 995, 982, 896, 833, 751, 689, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.13 (t, J=9.5 Hz, 1H), 0.15 (s, 9H), 1.25 (d, J=6.1 Hz, 3H), 1.38 (ddd, J=10.3, 9.5, 8.3 Hz, 1H), 1.41 ((bs, 1H), 1.92 (ddd, J=10.1, 9.5, 8.3 Hz, 1H), 3.58 (dq, J=10.3, 6.1 Hz, 1H), 5.00 (dd, J=10.1, 2.2 Hz, 1H), 5.20 (dd, J=16.8, 2.2 Hz, 1H), 5.57 (dt, J=16.8, 10.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.87, 12.10, 23.21, 24.82, 31.84, 67.31, 115.3, 136.6. Found: C, 65.10; H, 11.10%. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93%. Slow moving band (R_f=0.44): Bp 76 °C (1 Torr, bath temp); IR (neat) 3368, 2952, 2896, 1634, 1283, 1251, 1105, 1063, 980, 967, 937, 895, 836, 757, 687, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.10 (s, 9H), 0.17 (t, J=9.6 Hz, 1H), 1.34 (d, J=6.1 Hz, 3H), 1.45 (ddd, J=10.3, 9.6, 7.9 Hz, 1H), 1.71 (bs, 1H), 1.90 (ddd, J= 10.1, 9.6, 7.9 Hz, 1H), 3.70 (dq, J=10.3, 6.1 Hz, 1H), 5.08 (dd, J=10.1, 1.9 Hz, 1H), 5.29 (dd, J=16.9, 1.9 Hz, 1H), 5.73 (dt, J=16.9, 10.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.00, 12.35, 22.99, 24.38, 32.49, 67.03, 116.0, 136.5. Found: C, 65.15; H, 11.07%. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93%.

***c*-2-Acetyl-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (29).** PCC (6.2 g, 28.9 mmol) oxidation of **28** (1.33 g, 7.2 mmol) provided the compound **29** in 65% yield (0.85 g, 4.7 mmol): Bp 58 °C (1 Torr, bath temp); IR (neat) 3080, 2996, 2948, 2896, 1699, 1634, 1425, 1388, 1351, 1284, 1246, 1172, 1136, 1031, 999, 977, 902, 872, 841, 765, 686, 643, 626, 604 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.11 (s, 9H), 0.49 (dd, J=10.1, 9.1 Hz, 1H), 2.24 (s, 3H), 2.32 (td, J=10.1, 8.3 Hz, 1H), 2.47 (dd, J=9.1, 8.3 Hz, 1H), 4.98 (dd, J=10.1, 2.2 Hz, 1H), 5.20 (dd, J=17.0, 2.2 Hz, 1H), 5.82 (dt, J=17.0, 10.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.79, 17.87, 31.81, 32.63, 115.2, 135.3, 207.3. Found: C, 65.71; H, 10.25% Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95%.

***cis*-2-Hydroxymethyl-1-tributylstannylcyclopropane (30).** Diiodomethane (2 ml, 24 mmol) was added dropwise over 30 min to a mixture of 3-tributylstannyl-2-propen-1-ol[18] (4.3 g, 12.4 mmol), diethylzinc (2.4 ml, 24 mmol) and diisopropyl ether (25 ml). After stirring for 1.5 h, workup and purification by silica-gel column chromatography (hexane/ethyl acetate=5/1) gave **30** in 39% yield (1.72 g): Bp 123 °C (1 Torr, bath temp); IR (neat) 3336, 3048, 2952, 2920, 2868, 2850, 1458, 1419, 1376, 1071, 1028, 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.02 (ddd, J=9.7, 8.8, 7.5 Hz, 1H), 0.21 (ddd, J=7.5, 4.6, 3.8 Hz, 1H), 0.68—1.05 (m, 16H), 1.16—1.70 (m, 14H), 3.25 (dd, J=10.9, 7.8 Hz, 1H), 3.57 (dd, J=10.9, 6.2 Hz 1H); ^{13}C NMR ($CDCl_3$) δ=−1.40, 7.24, 9.76, 13.68, 17.46, 27.36, 29.09, 68.57. Found: C, 53.26; H, 9.76%. Calcd for $C_{16}H_{34}OSn$: C, 53.21; H, 9.49%.

***cis*-1-Tributylstannyl-2-vinylcyclopropane (31).** By means of Swern oxidation and Wittig reaction, the title compound **31** was obtained in 91% yield from **30:** Bp 70 °C (1 Torr, bath temp); IR (neat) 3078, 3048, 2954, 2922, 2868, 2848, 1635, 1458, 1419, 1376, 1340, 1289, 1072, 1033, 984, 960, 925, 893, 878, 834 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.21 (ddd, J=9.8, 9.3, 7.9 Hz, 1H), 0.44 (ddd, J=7.9, 4.1, 3.8 Hz, 1H), 0.67—0.99 (m, 15H), 1.07 (ddd, J= 9.3, 7.9, 3.8 Hz, 1H), 1.22—1.57 (m, 12H), 1.71 (dddd, J=9.8, 8.8, 7.9, 4.1 Hz, 1H), 4.87 (dd, J=9.9, 2.0 Hz, 1H), 5.10 (dd, J=17.0, 2.0 Hz, 1H), 5.30 (ddd, J=17.0, 9.9, 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=3.63, 9.71, 10.60, 13.73, 18.61, 27.36, 29.08, 112.2, 143.9. Found: C, 56.98; H, 9.87%. Calcd for $C_{17}H_{34}Sn$: C, 57.17; H, 9.59%.

***c*-2-Hydroxymethyl-*t*-3-methyl-*r*-1-tributylstannylcyclopropane (32).** Ethylidene iodide (2.0 ml, 21 mmol) was added to a solution of 3-tributylstannyl-2-propen-1-ol (3.7 g, 11 mmol) and diethylzinc (2.1 ml, 21 mmol) in diisopropyl ether (25 ml). Extractive workup followed by silica-gel column chromatography gave the compound **32** in 28% yield (1.11 g): Bp 120 °C (1 Torr, bath temp); IR (neat) 3312, 2950, 2920, 2852, 1459, 1419, 1377, 1357, 1341, 1291, 1249, 1073, 1019, 982, 961, 912, 873, 864, 685, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.27 (dd, J=9.1, 6.9 Hz, 1H), 0.60—1.68 (m, 33H, including 1.15 (d, J=5.7 Hz, 3H)), 3.23—3.37 (m, 1H), 3.46—3.59 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=8.33, 9.83, 13.71. 16.17, 20.78, 26.56, 27.35, 29.13, 68.10. Found: C, 54.39; H, 9.91%. Calcd for $C_{17}H_{36}OSn$: C, 54.42; H, 9.67%.

***t*-3-Methyl-*r*-1-tributylstannyl-*c*-2-vinylcyclopropane (33).** Swern oxidation ($(COCl)_2$ (0.30 ml, 3.5 mmol), DMSO (0.49 ml, 7.0 mmol), and Et_3N (1.9 ml, 14 mmol)) followed by Wittig reaction (Ph_3PCH_3I (1.22 g, 3.0 mmol) and *t*-BuOK (0.34 g, 3.0 mmol)) afforded **33** in 88% yield (0.76 g) from **32** (0.87 g, 2.3 mmol): Bp 75 °C (1 Torr, bath temp); IR (neat) 3078, 2952, 2920, 2866, 2852, 2332, 1634, 1458, 1419, 1375, 1070, 975, 891, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.01 (dd, J=9.2, 7.2 Hz, 1H), 0.65—1.65 (m, 32H including 1.15 (d, J=5.7 Hz, 3H)), 4.83 (dd, J=9.6, 2.3 Hz, 1H), 5.06 (dd, J=16.9, 2.3 Hz, 1H), 5.31 (ddd, J=16.9, 9.6, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=9.72, 13.50, 13.73, 19.26, 20.63, 27.31, 28.01, 29.09, 111.7, 143.7. Found: C, 58.40; H, 10.06%. Calcd for $C_{18}H_{36}Sn$: C, 58.24; H, 9.78%.

General Procedure for the Radical Induced Ring Opening Reaction of Vinylcyclopropane. Procedure A: Benzenethiol (1.1 mmol) was added to a solution of vinylcyclopropane (1.0 mmol) in benzene (2 ml) under argon atmosphere and the mixture was heated at 60 °C for several hours under stirring. The reaction mixture was concentrated in vacuo and the residue was purified by silica-gel column chromatography. Procedure B: Triethylborane (1.0 M hexane solution, 0.2 ml) was added to a solution of vinylcyclopropane (1.0 mmol) and triphenyltin or tributyltin hydride (1.1 mmol) in benzene (3.0 ml) under argon atmosphere at 25 °C. After stirring for several hours, the reaction mixture was concentrated in vacuo and the residual oil was purified by

silica-gel column chromatography. Procedure C: In the case of the reaction between vinylcyclopropane and tridecafluorohexyl iodide (1.2 mmol), hexane (2 ml) was used as a solvent instead of benzene in the Procedure B.

(*E*)-5-Dimethylphenylsilyl-1-phenylthio-2-pentene ((*E*)-39a) and (*Z*)-5-Dimethylphenylsilyl-1-phenylthio-2-pentene ((*Z*)-39a): Procedure A; Glpc Column A, 180 °C (initial) 220 °C (final) 2 °C min^{-1}, t_r=17.09 min (*E*-isomer) and t_r=15.34 min (*Z*-isomer). *E*-isomer: Bp 118 °C (1 Torr, bath temp); IR (neat) 3064, 3016, 2950, 2912, 2846, 1584, 1480, 1438, 1427, 1248, 1223, 1113, 1091, 1025, 965, 835, 819, 774, 735, 699, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.24 (s, 6H), 0.72—0.81 (m, 2H), 1.94—2.06 (m, 2H), 3.49 (d, *J*= 6.0 Hz, 2H), 5.45 (dt, *J*=15.1, 6.6 Hz, 1H), 5.60 (dt, *J*= 15.1, 6.0 Hz, 1H), 7.13—7.39 (m, 8H), 7.48—7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.05, 15.18, 26.51, 36.33, 123.5, 126.0, 127.7, 128.7, 128.8, 129.6, 133.5, 136.4, 136.9, 139.1. Found: C, 73.29; H, 7.85%. Calcd for $C_{19}H_{24}SiS$: C, 73.01; H, 7.74%. *Z*-isomer: Bp 123 °C (1 Torr, bath temp); IR (neat) 3064, 3012, 2952, 2918, 1584, 1481, 1459, 1439, 1427, 1248, 1224, 1113, 1090, 1025, 909, 835, 816, 775, 734, 699, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.25 (s, 6H), 0.67—0.76 (m, 2H), 1.90—2.02 (m, 2H), 3.48 (d, *J*=7.0 Hz, 2H), 5.41 (dt, *J*=11.0, 7.6 Hz, 1H), 5.52 (dt, *J*=11.0, 7.0 Hz, 1H), 7.13—7.37 (m, 8H), 7.45—7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.04, 15.85, 21.41, 31.33, 123.1, 126.3, 127.8, 128.8, 128.9, 130.3, 133.5, 136.2, 139.0, 139.5. Found: C, 73.26; H, 7.86%. Calcd for $C_{19}H_{24}SiS$: C, 73.01; H, 7.74%.

(*E*)-5-Dimethylphenylsilyl-1-triphenylstannyl-2-pentene ((*E*)-39b) and (*Z*)-5-Dimethylphenylsilyl-1-triphenylstannyl-2-pentene ((*Z*)-39b): Procedure B; Lc t_r=42 min (*E*-isomer) and t_r=45 min (*Z*-isomer). *E*-isomer: Bp 210 °C (0.13 Torr, bath temp); IR (neat) 3060, 3044, 3010, 2950, 2902, 1654, 1480, 1428, 1248, 1113, 1074, 1022, 997, 959, 835, 772, 726, 697, 669, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.21 (s, 6H), 0.65—0.73 (m, 2H), 1.89—2.00 (m, 2H), 2.36 (d, *J*=7.8 Hz, 2H), 5.42 (dt, *J*=15.0, 6.3 Hz, 1H), 5.63 (dt, *J*=15.0, 7.8 Hz, 1H), 7.33—7.73 (m, 20H); ^{13}C NMR ($CDCl_3$) δ=−3.04, 15.78, 15.87, 26.71, 125.3, 127.7, 128.4, 128.8, 128.9, 131.4, 133.5, 137.1, 138.7, 139.4. Found: C, 67.00; H, 6.18%. Calcd for $C_{31}H_{34}SiSn$: C, 67.28; H, 6.19%. *Z*-isomer: Bp 205 °C (0.13 Torr, bath temp); IR (neat) 3060, 3044, 3006, 2950, 2918, 1655, 1637, 1480, 1428, 1248, 1113, 1074, 1022, 997, 835, 818, 776, 725, 697, 656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 6H), 0.56—0.65 (m, 2H), 1.83—1.96 (m, 2H), 2.33 (d, *J*=8.9 Hz, 2H), 5.19 (dt, *J*=10.5, 6.9 Hz, 1H), 5.62 (dt, *J*=10.5, 8.9 Hz, 1H), 7.33—7.73 (m, 20H); ^{13}C NMR ($CDCl_3$) δ=−3.12, 12.20, 15.62, 21.25, 124.5, 127.7, 128.4, 128.7, 128.9, 130.1, 133.5, 137.0, 138.6, 139.3. Found: C, 67.34; H, 6.17%. Calcd for $C_{31}H_{34}SiSn$: C, 67.28; H, 6.19%.

(*E*)-5-Dimethylphenylsilyl-1-tributylstannyl-2-pentene ((*E*)-39c) and (*Z*)-5-Dimethylphenylsilyl-1-tributylstannyl-2-pentene ((*Z*)-39c): Procedure B; Lc t_r=42 min (*E*-isomer) t_r=44 min (*Z*-isomer). *E*-isomer: Bp 150 °C (0.15 Torr, bath temp); IR (neat) 3066, 3006, 2952, 2920, 2868, 2850, 1654, 1648, 1459, 1427, 1376, 1248, 1114, 1069, 957, 836, 771, 726, 697, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.26 (s, 6H), 0.68-1.02 (m, 17H), 1.23—1.63 (m, 12H), 1.66 (d, *J*=8.2 Hz, 2H), 1.92—2.04 (m, 2H), 5.25 (dt, *J*= 15.0, 6.3 Hz, 1H), 5.50 (dt, *J*=15.0, 8.2 Hz, 1H), 7.33—7.38 (m, 3H), 7.49—7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−2.99, 9.13, 13.74, 13.98, 16.21, 26.82, 27.35, 29.15, 127.6, 127.7, 128.4, 128.7, 133.6, 139.6. Found: C, 60.60; H, 9.58%. Calcd for $C_{25}H_{46}SiSn$: C, 60.85; H, 9.40%. *Z*-isomer: Bp 119 °C (0.13 Torr, bath temp); IR (neat) 3066, 3046, 3002, 2952, 2920, 2868, 2848, 1637, 1459, 1388, 1376, 1248, 1114, 1071, 998, 900, 836, 817, 775, 727, 697, 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.28 (s, 6H), 0.68—1.02 (m, 17H), 1.23—1.63 (m, 12H), 1.66 (d, *J*=9.1 Hz, 2H), 1.96—2.07 (m, 2H), 5.07 (dt, *J*=10.6, 6.8 Hz, 1H), 5.46 (dt, *J*=10.6, 9.1 Hz, 1H), 7.34—7.39 (m, 3H), 7.50—7.57 (m, 2); ^{13}C NMR ($CDCl_3$) δ=−2.99, 9.30, 10.30, 13.73, 16.05, 21.03, 27.37, 29.16, 127.1, 127.2, 127.7, 128.8, 133.6, 139.5. Found: C, 60.97; H, 9.62%. Calcd for $C_{25}H_{46}SiSn$: C, 60.85; H, 9.40%.

(*E*)-5-Dimethylphenylsilyl-5-iodo-1-tridecafluorohexyl-2-pentene ((*E*)-39d) and (*Z*)-5-Dimethylphenylsilyl-5-iodo-1-tridecafluorohexyl-2-pentene ((*Z*)-39d): Procedure C; GLPC Column A, 190 °C; t_r=6.24 min (*E*-isomer) t_r=4.90 min (*Z*-isomer). *E*-isomer: Bp 105 °C (1 Torr, bath temp); IR (neat) 3068, 2998, 2956, 2922, 1654, 1428, 1362, 1334, 1240, 1205, 1145, 1115, 1071, 1028, 968, 836, 815, 779, 734, 698, 651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.48 (s, 6H), 2.39 (ddd, *J*=15.6, 10.6, 7.2 Hz, 1H), 2.54 (ddd, *J*=15.6, 6.2, 4.1 Hz, 1H), 2.78 (td, *J*=18.6, 6.9 Hz, 2H), 3.24 (dd, *J*=10.6, 4.1 Hz, 1H), 5.40 (dt, *J*=15.2, 6.9 Hz, 1H), 5.68 (ddd, *J*=15.2, 7.2, 6.2 Hz, 1H), 7.37—7.42 (m, 3H), 7.53—7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−4.39, −2.59, 19.68, 34.60 (t, *J*=22.5 Hz), 36.92, 118.6 (t, *J*=4.1 Hz), 128.0, 129.7, 134.1, 135.8, 138.4; ^{19}F NMR ($CDCl_3$) δ=81.34 (bs, 3F), 113.4—113.8 (m, 2F), 122.4 (bs, 2F), 123.5 (bs, 4F), 126.4—126.8 (m, 2F). Found: C, 35.23; H, 2.75%. Calcd for $C_{19}H_{18}F_{13}SiI$: C, 35.20; H, 2.80%. *Z*-isomer: Bp 89 °C (1 Torr, bath temp); IR (neat) 2954, 2920, 2850, 1654, 1429, 1364, 1346, 1315, 1239, 1204, 1144, 1115, 1067, 837, 814, 782, 733 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.48 (s, 3H), 0.50 (s, 3H), 2.39 (ddd, *J*=15.7, 10.4, 7.9 Hz, 1H), 2.53 (ddd, *J*=15.7, 6.6, 4.1 Hz, 1H), 2.68 (td, *J*= 19.0, 7.0 Hz, 2H), 3.22 (dd, *J*=10.4, 4.1 Hz, 1H), 5.52 (dt, *J*= 10.5, 7.0 Hz, 1H), 5.80 (ddd, *J*=10.5, 7.9, 6.6 Hz, 1H), 7.35—7.43 (m, 3H), 7.53—7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−4.57, −2.62, 19.25, 29.55 (t, *J*=22.3 Hz), 31.62, 117.1 (t, *J*=4.0 Hz), 128.0, 129.7, 133.9, 135.6, 136.8. Found: C, 35.14; H, 2.82%. Calcd for $C_{19}H_{18}F_{13}SiI$: C, 35.20; H, 2.80%.

(*E*)-5-Dimethylphenylsilyl-4-methyl-1-phenylthio-2-pentene ((*E*)-40a): Procedure A; GLPC Column B, 210 °C, t_r=8.82 min; Bp 143 °C (1 Torr, bath temp); IR (neat) 3064, 3004, 2952, 2918, 2896, 2864, 1584, 1480, 1450, 1438, 1427, 1248, 1219, 1112, 1090, 1025, 967, 832, 792, 735, 698, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.25 (s, 6H), 0.74 (dd, *J*=14.6, 7.1 Hz, 1H), 0.83 (dd, *J*=14.6, 7.1 Hz, 1H), 0.90 (d, *J*=6.7 Hz, 3H), 2.15—2.36 (m, 1H), 3.43 (d, *J*=5.6 Hz, 2H), 5.33 (dt, *J*=15.0, 5.6 Hz, 1H), 5.42 (dd, *J*=15.0, 6.0 Hz, 1H), 7.12—7.37 (m, 8H), 7.45—7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−2.13, −2.01, 24.12, 32.98, 36.42, 121.7, 126.0, 127.6, 128.6, 128.7, 129.9, 133.5, 136.2, 139.7, 142.3. Found: C, 73.44; H, 8.10%. Calcd for $C_{20}H_{26}SiS$: C, 73.56; H, 8.02%.

(*Z*)-5-Dimethylphenylsilyl-4-methyl-1-phenylthio-2-pentene ((*Z*)-40a): Procedure A; GLPC Column B, 210 °C t_r=7.60 min; Bp 139 °C (1 Torr, bath temp); IR (neat) 3066, 3006, 2952, 2920, 2864, 1726, 1480, 1438, 1427, 1248, 1113, 827, 793, 734, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.26 (s, 3H), 0.28 (s, 3H), 0.76 (dd, *J*= 14.7, 7.3 Hz, 1H), 0.85 (d, *J*=6.4 Hz, 3H), 0.86 (dd, *J*=14.7, 8.2 Hz, 1H), 2.43—2.66 (m, 1H), 3.33 (dd, *J*=13.4, 6.3 Hz, 1H), 3.45 (dd, *J*=13.4, 7.1 Hz, 1H), 5.27 (ddd, *J*=10.6, 7.1, 6.3 Hz, 1H), 5.34 (dd, *J*=10.6, 7.4 Hz, 1H), 7.14—7.38 (m, 8H), 7.46—7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−2.18, −1.86, 24.61, 24.83, 28.17, 31.33, 121.0, 126.1, 127.7, 128.7, 128.8, 129.8, 133.6, 136.4, 139.5, 141.8. Found: C, 73.57; H, 8.16%. Calcd for $C_{20}H_{26}SiS$: C, 73.56;

H, 8.02%.

(*E*)-5-Dimethylphenylsilyl-4-methyl-1-triphenylstannyl-2-pentene ((*E*)-40b): Procedure B; Lc t_r=41 min; Bp 230 °C (0.17 Torr, bath temp); IR (neat) 3060, 3044, 3010, 2952, 2894, 1480, 1429, 1247, 1113, 1074, 1022, 997, 962, 833, 792, 726, 697, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.21 (s, 3H), 0.22 (s, 3H), 0.69 (dd, J=14.7, 7.3 Hz, 1H), 0.78 (dd, J=14.7, 7.1 Hz, 1H), 0.84 (d, J=6.7 Hz, 3H), 2.10—2.31 (m, 1H), 2.31 (d, J=7.9 Hz, 2H), 5.27 (dd, J=15.1, 7.6 Hz, 1H), 5.54 (dt, J=15.1, 8.5 Hz, 1H), 7.31—7.50 (m, 20H); ^{13}C NMR ($CDCl_3$) δ=−2.15, =−2.01, 15.73, 24.37, 24.51, 33.17, 123.4, 127.6, 128.4, 128.6, 128.9, 133.5, 137.1, 137.2, 138.7, 140.1. Found: C, 67.93; H, 6.44%. Calcd for $C_{32}H_{36}SiSn$: C, 67.74; H, 6.39%.

(*E*),(*Z*)-5-Dimethylphenylsilyl-4-methyl-1-triphenylstannyl-2-pentene ((*E*)-40b: (*Z*)-40b=73 : 27): Procedure B; Lc t_r=43 min for *Z*-isomer; Bp 190 °C (0.07 Torr, bath temp); IR (neat) 3060, 3044, 3010, 2952, 2918, 2896, 1481, 1459, 1450, 1428, 1300, 1247, 1189, 1113, 1075, 1022, 997, 963, 833, 795, 725, 696, 656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.21 (s, 3H), 0.22 (s, 3H), 0.63 (d, J=6.6 Hz, 0.81H), 0.70—0.76 (m, 2H), 0.84 (d, J=6.7 Hz, 2.19H), 2.11—2.35 (m, 2.73H), 2.45—2.61 (m, 0.27H), 5.03 (dd, J=10.5, 9.6 Hz, 0.27H), 5.27 (dd, J=15.1, 7.6 Hz, 0.73H), 5.38—5.63 (m, 1H including 5.54 (dt, J=15.1, 8.5 Hz)), 7.30—7.69 (m, 20H). Found: C, 67.62; H, 6.47%. Calcd for $C_{32}H_{36}SiSn$: C, 67.74; H, 6.39%.

(*E*),(*Z*)-4-Methyl-1-phenylthio-5-trimethylsilyl-2-pentene ((*E*)-41: (*Z*)-41=88 : 12): Procedure A; Bp 115 °C (1 Torr, bath temp); IR (neat) 2950, 2920, 2892, 1585, 1480, 1452, 1439, 1415, 1294, 1248, 1219, 1120, 1090, 1068, 1025, 967, 855, 837, 783, 757, 736, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.00 (s, 7.92H), 0.02 (s, 1.08H), 0.47—0.67 (m, 2H), 0.93 (d, J=7.0 Hz, 0.36H), 0.97 (d, J=6.7 Hz, 2.64H), 2.19—2.39 (m, 0.88H), 2.54—2.66 (m, 0.12H), 3.52 (d, J=5.8 Hz, 1.76H), 3.55 (dd, J=13.0, 6.2 Hz, 0.12H), 3.66 (dd, J=13.0, 6.6 Hz, 0.12H), 5.34—5.55 (m, 2H), 7.15—7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) for (*E*)-isomer δ=−0.65, 24.04, 25.05, 33.09, 36.53, 121.4, 126.0, 128.6, 129.9, 136.3, 142.7. Found: C, 67.92; H, 9.10%. Calcd for $C_{15}H_{24}SSi$: C, 68.11; H, 9.15%.

(*E*)-4,4-Dimethyl-1-phenylthio-5-trimethylsilyl-2-pentene (42a): Procedure A; GLPC Column B, 170 °C, t_r=6.29 min; Bp 105 °C (1 Torr, bath temp); IR (neat) 3056, 2950, 2876, 1584, 1480, 1458, 1438, 1418, 1379, 1361, 1247, 1092, 1025, 969, 856, 838, 761, 736, 688, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.02 (s, 9H), 0.69 (s, 2H), 0.99 (s, 6H), 3.52 (d, J=6.8 Hz, 2H), 5.35 (dt, J=15.4, 6.8 Hz, 1H), 5.56 (d, J=15.4 Hz, 1H), 7.14—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=0.80, 30.37, 32.66, 35.77, 36.96, 119.1, 126.1, 128.7, 130.1, 136.3, 146.4. Found: C, 68.74; H, 9.66%. Calcd for $C_{16}H_{26}SiS$: C, 69.00; H, 9.41%.

(*E*)-5-Methyl-1-phenylthio-4-trimethylsilyl-2-hexene (43a): Procedure B; GLPC Column B, 170 °C, t_r=6.76 min; Bp 100 °C (1 Torr, bath temp); IR (neat) 3056, 3014, 2952, 2890, 1585, 1480, 1465, 1438, 1419, 1383, 1364, 1248, 1220, 1149, 1091, 1072, 1025, 970, 859, 837, 761, 736, 688, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.08 (s, 9H), 0.82 (d, J=6.8 Hz, 6H), 1.36 (dd, J=10.3, 4.9 Hz, 1H), 1.75—1.92 (m, 1H), 3.58 (d, J=6.7 Hz, 2H), 5.31 (dt, J=15.0, 6.7 Hz, 1H), 5.48 (dd, J=15.0, 10.3 Hz, 1H), 7.11—7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−1.81, 20.63, 23.72, 28.34, 36.69, 41.25, 124.1, 125.8, 128.7, 129.5, 133.1, 140.2. Found: C, 69.01; H, 9.37%. Calcd for $C_{16}H_{26}SiS$: C, 69.00; H, 9.41%.

(*E*)-4,4-Dimethyl-5-trimethylsilyl-1-triphenylstannyl-2-pentene (42b): Procedure B; PLC R_f=0.47 (hexane/ethyl acetate=20/1); Bp 160 °C (0.10 Torr, bath temp); IR (neat) 3060, 3046, 3010, 2950, 1481, 1466, 1460, 1429, 1247, 1075, 1022, 997, 966, 858, 840, 761, 725, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.05 (s, 9H), 0.63 (s, 2H), 0.93 (s, 6H), 2.37 (d, J=7.0 Hz, 2H), 5.42 (d, J=15.4 Hz, 1H), 5.53 (dt, J=15.4, 7.0 Hz, 1H), 7.33—7.48 (m, 9H), 7.52—7.73 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=0.77, 15.96, 30.59, 33.10, 35.68, 120.6, 128.4, 128.9, 137.1, 138.8, 141.1. Found: C, 64.83; H, 7.14%. Calcd for $C_{28}H_{36}SiSn$: C, 64.75; H, 6.99%.

(*E*)-5-Methyl-4-trimethylsilyl-1-triphenylstannyl-2-hexene (43b): Procedure B; PLC R_f=0.42 (hexane/ethyl acetate=20/1); Bp 165 °C (0.10 Torr, bath temp); IR (neat) 3060, 3044, 3008, 2950, 2894, 1481, 1460, 1428, 1300, 1258, 1247, 1075, 1023, 997, 962, 860, 837, 761, 726, 697, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.14 (s, 9H), 0.75 (d, J=6.7 Hz, 6H), 1.26 (dd, J=10.3, 4.5 Hz, 1H), 1.69-1.85 (m, 1H), 2.45 (d, J=7.6 Hz, 2H), 5.31 (dd, J= 15.2, 10.3 Hz, 1H), 5.50 (dt, J=15.2, 7.6 Hz, 1H), 7.33—7.48 (m, 9H), 7.52—7.73 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=−1.73, 16.27, 20.47, 23.70, 28.57, 41.13, 126.1, 127.0, 128.4, 128.9, 137.1, 138.7. Found: C, 64.52; H, 7.04%. Calcd for $C_{28}H_{36}SiSn$: C, 64.75; H, 6.99%.

(*E*)-5-Iodo-4,4-dimethyl-1-tridecafluorohexyl-5-trimethylsilyl-2-pentene (44): Procedure C; Bp 98 °C (1 Torr, bath temp); IR (neat) 2966, 1465, 1458, 1430, 1387, 1364, 1240, 1206, 1144, 1121, 1096, 1070, 1026, 974, 840, 808, 765, 746, 729, 698, 653 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.22 (s, 9H), 1.26 (s, 3H), 1.27 (s, 3H), 2.83 (td, J=18.3, 6.8 Hz, 2H), 3.33 (s, 1H), 5.37 (dt, J=15.6, 6.8 Hz, 1H), 5.80 (d, J=15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.71, 28.17, 29.38, 34.80 (t, J=22.5 Hz), 40.49, 40.58, 113.7, 146.4. Found: C, 31.54; H, 3.29%. Calcd for $C_{16}H_{20}F_{13}SiI$: C, 31.28; H, 3.28%.

(*E*)-5-Methyl-1-tridecafluorohexyl-2,4-hexadiene (45): Procedure C; Bp 86 °C (20 Torr, bath temp); IR (neat) 3030, 2968, 2918, 2858, 1663, 1648, 1431, 1381, 1364, 1345, 1240, 1199, 1145, 1121, 1069, 1044, 986, 959, 894, 866, 845, 808, 778, 744, 728, 706, 697, 652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.77 (s, 3H), 1.79 (s, 3H), 2.88 (td, J=18.3, 7.6 Hz, 2H), 5.47 (dt, J=14.9, 7.6 Hz, 1H), 5.86 (d, J=11.0 Hz, 1H), 6.46 (dd, J=14.9, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=18.33, 25.97, 34.97 (t, J=22.4 Hz), 116.0, 124.0, 133.9, 136.9. Found: C, 37.88; H, 2.69%. Calcd for $C_{13}H_{11}F_{13}$: C, 37.70; H, 2.68%.

(*E*),(*Z*)-5-Phenyl-1-phenylthio-4-trimethylsilyl-2-pentene ((*E*)-46a: (*Z*)-46a=93 : 7): Procedure A; PLC R_f=0.42 (hexane/ethyl acetate=20/1); Bp 155 °C (1 Torr, bath temp); IR (neat) 3056, 3022, 2950, 2918, 2850, 1584, 1495, 1480, 1453, 1438, 1248, 1121, 1088, 1069, 1025, 966, 839, 737, 690, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.08 (s, 8:37H), 0.04 (s, 0.63H), 1.83 (ddd, J=10.8, 9.1, 4.0 Hz, 0.93H), 2.16 (ddd, J=11.0, 7.0, 3.5 Hz, 0.07H), 2.49 (dd, J=13.8, 11.0 Hz, 0.07H), 2.58 (dd, J=14.3, 10.8 Hz, 0.93H), 2.80 (dd, J=14.3, 4.0 Hz, 0.93H), 2.89 (dd, J=13.8, 3.5 Hz, 0.07H), 3.27—3.30 (m, 0.14H), 3.48 (d, J=6.8 Hz, 1.86H), 5.22 (dt, J=15.2, 6.8 Hz, 0.93H), 5.30—5.47 (m, 0.14H), 5.47 (dd, J=15.2, 9.1 Hz, 0.93H), 7.08—7.32 (m, 10H); ^{13}C NMR ($CDCl_3$) for (*E*)-isomer δ=−3.23, 34.78, 34.98, 36.42, 123.1, 125.6, 125.7, 128.0, 128.5, 128.7, 129.2, 135.0, 136.5, 142.2. Found: C, 73.36; H, 8.09%. Calcd for $C_{20}H_{26}SiS$: C, 73.56; H, 8.02%.

(*E*),(*Z*)-4-Phenyl-1-phenylthio-5-trimethylsilyl-2-pentene ((*E*)-47a: (*Z*)-47a=66 : 34): Procedure A; PLC R_f=0.47 (hexane/ethyl acetate=20/1); Bp 149 °C (1 Torr, bath temp); IR (neat) 3056, 3022, 2948, 2898, 1584, 1491, 1480, 1453, 1438, 1413, 1247, 1090, 1026, 967, 860, 837, 738, 698, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.16 (s, 5.94H), −0.12 (s, 3.06H), 0.86

(dd, J=14.6, 7.3 Hz, 0.34H), 0.97 (d, J=7.8 Hz, 1.32H), 1.06 (dd, J=14.6, 7.9 Hz, 0.34H), 3.37 (td, J=7.8, 7.3 Hz, 0.66H), 3.49 (d, J=6.7 Hz, 1.32H), 3.53—3.76 (m, 1.02H), 5.40 (dt, J=10.7, 7.5 Hz, 0.34H), 5.48 (dt, J=15.1, 6.7 Hz, 0.66H), 5.68 (dd, J= 15.1, 7.3 Hz, 0.66H), 5.70 (dd, J=10.7, 9.0 Hz, 0.34H), 7.07—7.35 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=−1.02, 1.01, 23.92, 25.67, 31.47, 36.53, 39.55, 44.52, 122.4, 123.2, 126.0, 126.1, 127.1, 127.2, 127.3, 128.3, 128.5, 128.7, 128.8, 129.8, 130.1, 136.0, 139.7, 140.4, 146.0; for (*E*)-isomer δ=−1.02, 23.92, 36.53, 44.52, 123.2, 126.0, 126.1, 127.1, 127.3, 128.3, 128.7, 130.1, 140.4, 146.0. Found: C, 73.65; H, 8.10%. Calcd for $C_{20}H_{26}SiS$: C, 73.56; H, 8.02%.

(*E*),(*Z*)-5-Phenyl-4-trimethylsilyl-1-triphenylstannyl-2-pentene and (*E*),(*Z*)-4-phenyl-5-trimethylsilyl-1-triphenylstannyl-2-pentene ((*E*)-46b: (*Z*)-46b: (*E*)-47b: (*Z*)-47b=80.4: 11.3:5.3:3.0): Procedure B; Bp 190 °C (0.11 Torr, bath temp); IR (neat) 3060, 3044, 3014, 2948, 2900, 2850, 1494, 1481, 1453, 1429, 1247, 1108, 1075, 1022, 997, 960, 859, 838, 748, 726, 697, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.23 (s, 0.270H), −0.19 (s, 0.477H), −0.13 (s, 7.236H), −0.08 (s, 1.017H), 0.78 (dd, J=14.5, 6.8 Hz, 0.030H), 0.87 (dd, J=14.5, 7.3 Hz, 0.053H), 0.96 (dd, J=14.5, 8.2 Hz, 0.053H), 0.97 (dd, J=14.5, 8.6 Hz, 0.030H), 1.72 (ddd, J=10.9, 7.9, 3.8 Hz, 0.804H), 2.13—2.54 (m, 3.030H), 2.74 (dd, J=14.0, 3.8 Hz, 0.917H), 3.25—3.36 (m, 0.053H), 3.60—3.72 (m, 0.030H), 5.10 (t, J=10.8 Hz, 0.113H), 5.22—5.70 (m, 1.887H), 6.95—7.17 (m, 5H), 7.23—7.65 (m, 15H); ^{1}H NMR ($CDCl_3$) for (*E*)-**46b** δ=−0.13 (s, 9H), 1.72 (ddd, J=10.9, 7.9, 3.8 Hz, 1H), 2.35 (d, J=6.9 Hz, 2H), 2.48 (dd, J=14.0, 10.9 Hz, 1H), 2.74 (dd, J=14.0, 3.8 Hz, 1H), 5.28 (dd, J=15.0, 7.9 Hz, 1H), 5.37 (dt, J=15.0, 6.9 Hz, 1H), 6.95—7.17 (m, 5H), 7.23—7.65 (m, 15H); ^{13}C NMR ($CDCl_3$) for (*E*)-**46b** δ=−3.12, 16.03, 35.03, 35.52, 125.1, 125.3, 128.0, 128.4, 128.6, 128.8, 129.2, 137.1, 138.7, 142.6. Found: C, 67.45; H, 6.51%. Calcd for $C_{32}H_{36}SiSn$: C, 67.74; H, 6.39%.

(*E*)-7-Phenylthio-4-trimethylsilyl-5-hepten-2-one (48a): Procedure A; Bp 102 °C (1 Torr, bath temp); IR (neat) 3056, 3016, 2950, 1709, 1654, 1648, 1584, 1480, 1438, 1419, 1356, 1249, 1171, 1118, 1090, 1025, 967, 841, 739, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.13 (s, 9H), 1.99 (ddd, J=9.5, 8.0, 5.0 Hz, 1H), 2.03 (s, 3H), 2.33 (dd, J=16.0, 5.0 Hz, 1H), 2.43 (dd, J=16.0, 9.5 Hz, 1H), 3.50 (d, J=6.5 Hz, 2H), 5.28 (dt, J=15.4, 6.5 Hz, 1H), 5.43 (dd, J=15.4, 8.0 Hz, 1H), 7.09—7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−3.44, 28.47, 29.73, 36.38, 43.02, 123.1, 125.9, 128.8, 129.5, 133.9, 136.0, 208.7. Found: C, 65.90; H, 8.43%. Calcd for $C_{16}H_{24}OSiS$: C, 65.70; H, 8.27%.

(*E*)-4-Trimethylsilyl-7-triphenylstannyl-5-hepten-2-one (48b): Procedure B; Bp 195 °C (0.15 Torr, bath temp); IR (neat) 3060, 3044, 3008, 2950, 1710, 1481, 1429, 1356, 1248, 1075, 997, 961, 909, 864, 838, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.18 (s, 9H), 1.93 (ddd, J=8.8, 8.4, 6.6 Hz, 1H), 1.94 (s, 3H), 2.27 (dd, J=16.2, 6.6 Hz, 1H), 2.37 (dd, J=16.2, 8.4 Hz, 1H), 2.39 (d, J= 7.7 Hz, 2H), 5.26 (dd, J=15.1, 8.8 Hz, 1H), 5.51 (dd, J=15.1, 7.7 Hz, 1H), 7.33—7.78 (m, 15); ^{13}C NMR ($CDCl_3$) δ=−3.40, 16.14, 28.54, 29.59, 43.47, 125.3, 128.0, 128.4, 128.9, 137.0, 138.5, 209.3. Found: C, 62.90; H, 6.49%. Calcd for $C_{28}H_{34}OSiSn$: C, 63.05; H, 6.43%.

(*E*),(*Z*)-1-Phenylthio-5-tributylstannyl-2-pentene ((*E*)-49: (*Z*)-49=92:8): Procedure A; Bp 150 °C (1 Torr, bath temp); IR (neat) 3056, 3016, 2952, 2920, 2868, 2048, 1585, 1480, 1458, 1438, 1418, 1375, 1070, 1025, 962, 735, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.63—0.96 (m, 17H), 1.20—1.58 (m, 12H), 2.00—2.11 (m, 0.16H), 2.12—2.23 (m, 1.84H), 3.52 (d, J=6.0 Hz, 1.84H), 3.56 (d, J=7.1 Hz, 0.16H), 5.40—5.70 (m, 2H including 5.48 (dt, J=15.2, 6.5 Hz), 5.62 (dt, J=15.2, 6.0 Hz)), 7.13-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) for (*E*)-isomer δ=8.20, 8.84, 13.74, 27.39, 29.22, 29.54, 36.41, 123.3, 125.9, 128.7, 129.6, 136.4, 137.8. Found: C, 59.10; H, 8.55%. Calcd for $C_{23}H_{40}SSn$: C, 59.11; H, 8.63%.

(*E*),(*Z*)-4-Methyl-1-phenylthio-5-tributylstannyl-2-pentene ((*E*)-50, (*Z*)-50=92.5:7.5): Procedure A; Bp 158 °C (1 Torr, bath temp); IR (neat) 3056, 2952, 2920, 2868, 2850, 1585, 1479, 1458, 1438, 1419, 1375, 1341, 1292, 1220, 1113, 1089, 1070, 1025, 1001, 964, 873, 735, 688, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.62-0.98 (m, 20H), 1.20—1.58 (m, 12H), 2.26—2.48 (m, 1H), 3.49 (d, J=5.7 Hz, 1.85H), 3.51 (dd, J=13.0, 6.2 Hz, 0.075H), 3.62 (dd, J=13.0, 6.5 Hz, 0.075H), 5.31—5.37 (m, 0.15H), 5.39 (dt, J=15.1, 5.7 Hz, 0.925H), 5.48 (dt, J=15.1, 6.0 Hz, 0.925H), 7.13—7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) for (*E*)-isomer δ=9.40, 13.74, 18.22, 24.40, 27.45, 29.23, 34.96, 36.60, 121.4, 126.0, 128.7, 130.0, 136.3, 142.9. Found: C, 59.68; H, 8.66%. Calcd for $C_{24}H_{42}SSn$: C, 59.88; H, 8.79%.

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