indicating an ee of 15.0% for the dibromo adduct of the major isomer derived from 3 and 5.4% for the dibromo adduct derived from 4.

Attempted Cycloaddition of Enantioenriched (*S*)-(+)-13DMA with 1,1-Diphenylethene (DPE). In a 9-in. × 5-mm NMR tube were placed 179.7 mg (1.03 mmol) of DPE, 140 mg (2.06 mmol) of (*S*)-(+)-13DMA (α = 0.261 ± 0.001°, c = 1.25 in diethyl ether, 25.8% ee), 300 μL of toluene-d_8, and 5 mg of hydroquinone. The contents of the tube were triply freeze–degassed, and the tube was sealed under reduced pressure. The tube was heated at 160 °C in the sand bath for 5 days, at which time the NMR spectrum of the sample showed only the resonances of 13DMA and DPE. The tube was opened, and the volatiles were removed on a vacuum line. The unreacted 13DMA was isolated from the volatiles by preparative GLC on a 8 ft × $^1/_4$ in. 20% Apiazon L on Chromosorb P column at 110 °C. The optical rotation of the recovered 13DMA was recorded (α = 0.000 ± 0.001°, c = 2.295 in diethyl ether, 0.0% ee). The ^{1}H NMR spectrum of the nonvolatile residue showed no characteristic resonances expected of cycloadducts derived from 13DMA and DPE or cyclodimers of either reactant.

Acknowledgment. We wish to achnowledge support of this research by the National Science Foundation, Grant No. CHE8709725.

Registry No. 3, 137396-55-5; 4, 137396-56-6; 5, 137396-57-7; 6, 137491-79-3; 7, 137396-58-8; 8, 137491-80-6; i, 137396-59-9; ii, 137491-81-7; (*S*)-(+)-13DMA, 23190-25-2; DPE, 530-48-3; 1122, 79-35-6.

Supplementary Material Available: 300-MHz ^{1}H NMR spectra for 5, 7, and 8 and 500-MHz NMR spectra for crude 6 (7 pages). Ordering information is given on any current masthead page.

β-Trichlorostannyl Ketones and Aldehydes. Preparation and Facile Amine-Induced Dehydrostannation Leading to α-Methylene Ketones and Aldehydes[1]

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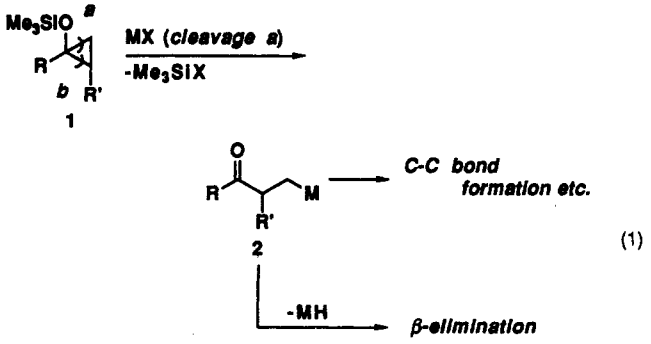
Received June 10, 1991

Ring-opening reactions of siloxycyclopropanes 1 with $SnCl_4$ take place under mild reaction conditions and site-selectively to give β-trichlorostannyl ketones and aldehydes 3 in high yields. The β-trichlorostannyl ketones and aldehydes thus obtained readily undergo base-induced dehydrotrichlorostannation at room temperature to give the corresponding α-methylene ketones and aldehydes 4. The reactions are quite general for amines, such as pyridine, triethylamine, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and 1,4-diazabicyclo[2.2.2]octane (DABCO), and the yields are good to high. *One-pot* conversion from siloxycyclopropanes 1 to α-methylene ketones or aldehydes 4 by consecutive treatment of 1 with $SnCl_4$ and TMEDA is also successful. The ^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR, and IR spectral properties of β-stannyl ketones and aldehydes are also reported.

In contrast to the extensive applications of metal enolates and α-metallo ketones in organic synthesis, the synthetic potential of β-metallo ketones has long been unexplored. The main limiting factor has been the lack of a convenient and general method for generating these compounds. We have reported a desilylative ring opening of siloxycyclopropanes 1 by metal salts (eq 1) which provides



(1)

a promising method for the generation of β-metallo ketones 2, enabling the development of useful synthetic transformations via 2.[2,3] In general, the ring opening of 2-substituted siloxycyclopropanes 1 occurred site-selectively at the methylene carbon (cleavage *a* in 1), and β-metallo ketones having a methylene group next to the metal were generated selectively by this method.

β-Metal hydride elimination to give alkenes is one of the fundamental and typical reactions of transition-metal alkyls. Accordingly, we thought that the conversion of

(1) A portion of this work has previously appeared; see: Ryu, I.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 2389.

(2) A similar approach for β-metallo *esters* from 1-ethoxy-1-siloxycyclopropane has been concurrently developed by Nakamura and Kuwajima at TIT, where they use the term "metal homoenolate". For reviews on the β-metallo ketones and esters, see: (a) Ryu, I.; Sonoda, N. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 112. (b) Nakamura, E. *J. Synth. Org. Chem. Jpn.* **1989**, *47*, 931. (c) Kuwajima, I.; Nakamura, E. In *Small Ring Compounds in Organic Synthesis IV*; de Meijere, A., Ed.; Springer: Berlin, 1990; pp 1–39.

(3) (a) Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283. (b) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192. (c) Ryu, I.; Ryang, M.; Rhee, I.; Omura, H.; Murai, S.; Sonoda, N. *Synth. Commun.* **1984**, *14*, 1175. (d) Ryu, I.; Ogawa, A.; Sonoda, N. *Nippon Kagaku Kaishi* **1985**, 442; *Chem. Abstr.* **1985**, *103*, 214888q. (e) Rubottom, G. M.; Beedle, E. C.; Kim, C.-W.; Mott, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4230. (f) Ryu, I.; Suzuki, H.; Ogawa, A.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1988**, *29*, 6137. (g) Aoki, S.; Fujiwara, T.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1989**, *30*, 6541. (h) Nakahira, H.; Ryu, I.; Han, L.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1991**, *32*, 229. (i) Ikura, K.; Ryu, I.; Ogawa, A.; Sonoda, N.; Harada, S.; Kasai, N. *Organometallics* **1991**, *10*, 528. (j) Giese, B.; Horler, H.; Zwick, W. *Tetrahedron Lett.* **1982**, *23*, 931. (k) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296. (l) Ito, Y.; Inoue, M.; Suginome, M.; Murakami, M. *J. Organomet. Chem.* **1988**, *342*, C41.

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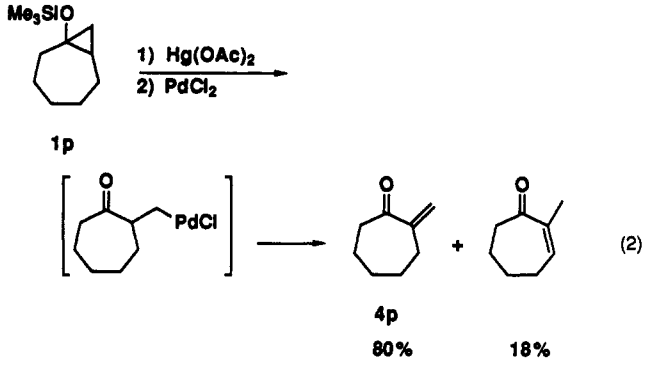
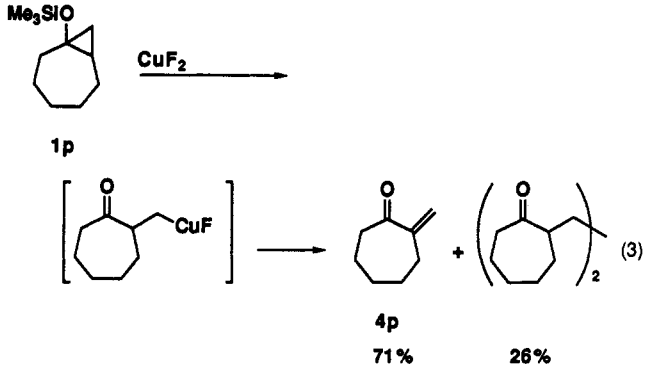
β-metallo ketones 2 into α-methylene ketones 4 via β-elimination should be feasible. Indeed, although β-Pd(II) ketones[3a] and β-Cu(II) ketones[3d] undergo this type of transformation, these reactions often suffered from side reactions, i.e., double bond isomerization and homocoupling, respectively (eqs 2 and 3). Unlike these transition

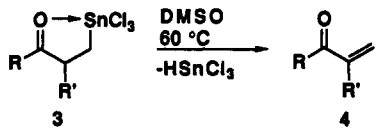


(2)



(3)

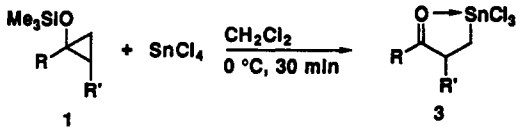
metal species, β-trichlorostannyl ketones 3 are isolable organometallics which can be derived from ring opening of siloxycyclopropanes 1 with $SnCl_4$. We found that 3 undergoes clean dehydrostannation leading to α-methylene ketones 4 on heating with dimethyl sulfoxide (DMSO)/$CHCl_3$ (eq 4).[1] Further study has revealed that the dehydrostannation occurs at room temperature in the presence of bases such as pyridine, triethylamine, TMEDA, DABCO, etc. In this paper, we describe (i) the full details of the ring-opening reactions of siloxycyclopropanes 1 to afford β-trichlorostannyl ketones and aldehydes, (ii) the synthetic scope of their base-promoted β-tin hydride elimination reactions, which give α-methylene ketones and aldehydes, and (iii) some mechanistic aspects of the reactions.



(4)

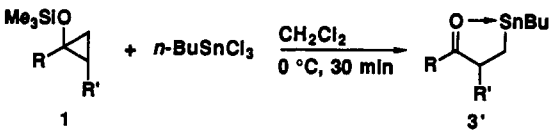
Results and Discussion

Synthesis of β-Trichlorostannyl Ketones and Aldehydes 3 from Siloxycyclopropanes 1 and $SnCl_4$. A series of siloxycyclopropanes 1 were prepared from the corresponding enol silyl ethers and zinc carbenoid reagents according to the reaction conditions established in our previous work.[4] The reaction of 1-alkyl- and 1-phenyl-substituted siloxycyclopropanes **1a-g** with $SnCl_4$ in dichloromethane took place readily at 0 °C to give β-trichlorostannyl ketones **3a-g** in high yields (Table I). These β-stannyl ketones were obtained as solids and were usually purified by recrystallization from chloroform/pentane. The IR spectra of 3 show lower frequency shifts (1617-1661 cm^{-1}) relative to normal ketone carbonyl groups, indicating that the carbonyl group coordinates to the internal tin atom which is highly polarized by the electronegative chlorine atoms.[5,6] The reaction of 2-methyl-substituted siloxycyclopropane **1i** with $SnCl_4$ gave **3i**, which resulted from site-selective ring cleavage at the methylene carbon. No signals, characteristic of the other isomers, were present in the NMR spectrum of the reaction mixture, indicating the complete regioselectivity of the ring cleavage. Similar site-selectivity was also observed for the bicyclic siloxycyclopropanes **1j-r**, from which the corresponding β-trichlorostannyl ketones **3j-r** were obtained in good yields (entries 18-27).



(5)

Analogous ring-opening reactions of 1 occurred with butyltin trichloride to yield β-dichlorobutylstannyl ketones (eq 6). Thus, treatment of **1a**, **1b**, **1d**, **1e**, and **1h** with 1



(6)

equiv of butyltin trichloride in dichloromethane at 0 °C gave β-dichlorobutylstannyl ketones **3a'**, **3b'**, **3d'**, **3e'**, and **3h'**, respectively (entries 2, 4, 8, 12, 16). In contrast, β-trichlorostannyl ketone **3e** did not react with **1e** even under more forcing conditions (60 °C, 12 h). The reduced Lewis acidity of the $SnCl_3$ group by intramolecular complexation in **3e** may account for this decreased reactivity.

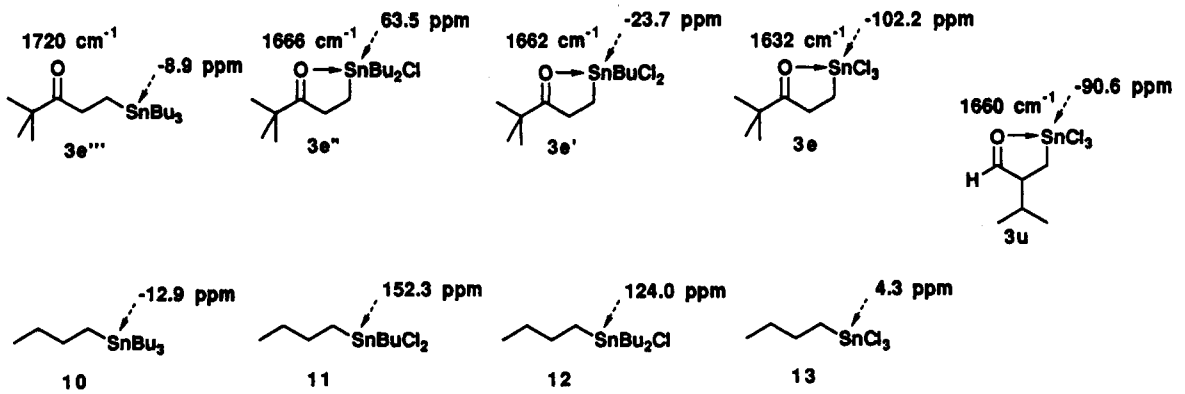
The reaction of siloxycyclopropanes **1s-w** with $SnCl_4$ also proceeded smoothly to give the corresponding β-trichlorostannyl aldehydes **3s-w**, respectively, which were usually obtained as semisolids (entries 28-32). Recrystallization of these aldehydes was very difficult, and purification by column chromatography on silica gel also failed owing to dehydrostannation during the attempted purification. The ring cleavage was again regioselective for the methylene carbon, according to NMR spectra of the crude products. We confirmed the high degree of regiochemical purity of **3s** by conversion to the corresponding β-triethylstannyl aldehyde **9**, which was conveniently effected by treatment with $ZnEt_2$ in 1,4-dioxane (eq 7). The siloxycyclopropane cleavage/alkylation se-

(4) (a) Ryu, I.; Aya, T.; Otani, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1987**, *321*, 279. (b) Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 4611; **1978**, 856. (c) Murai, S.; Aya, T.; Sonoda, N. *J. Org. Chem.* **1973**, *38*, 4354.

(5) Hydrotrichlorostannation of enones is an alternative approach for the preparation of β-trichlorostannyl ketones, and we have recently reported the modified hydrotrichlorostannation of enones: (a) Nakahira, H.; Ryu, I.; Ogawa, A.; Kambe, N.; Sonoda, N. *Organometallics* **1990**, *9*, 227. Also see: (b) Burley, J. W.; Hutton, R. E.; Oakes, V. *J. Chem. Soc., Chem. Commun.* **1976**, 803. (c) Hutton, R. E.; Burley, J. W. *J. Organomet. Chem.* **1978**, *156*, 369. (d) Burley, J. W.; Hope, P.; Hutton, R. E. *J. Organomet. Chem.* **1979**, *170*, 21. (e) Haigh, R. M.; Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* **1979**, *174*, 163. (f) Burley, J. W.; Hope, P.; Mack, A. G. *J. Organomet. Chem.* **1984**, *277*, 37.

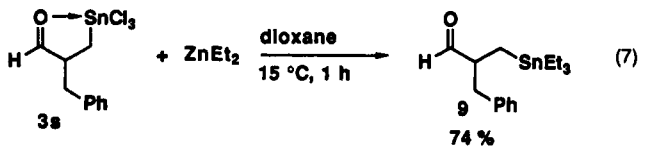
(6) For β-trichlorostannyl esters and other related β-halostannyl carbonyl compounds, see: (a) Bulten, E. J.; Hurk, J. W. G. *J. Organomet. Chem.* **1978**, *162*, 161. (b) Burley, J. W.; Hutton, R. E.; Jolley, M. R. J. *J. Organomet. Chem.* **1983**, *251*, 189. (c) Howie, R. A.; Paterson, E. S.; Wardell, J. L.; Burley, J. W. *J. Organomet. Chem.* **1983**, *259*, 71. (d) Devaud, M. *J. Chem. Research* **1977**, 50. (e) Matsuda, S.; Nomura, M. *J. Organomet. Chem.* **1970**, *25*, 101. (f) Matsuda, S.; Kikkawa, S.; Kashiwa, N. *Kogyo Kagaku Zasshi* **1966**, *69*, 1036. (g) Nakamura, E.; Shimada, J.-i.; Kuwajima, I. *Organometallics* **1985**, *4*, 641.

Scheme I[a]



[a] Chemical shift (δ(^{119}Sn), ppm, vs. external Me_4Sn) in ^{119}Sn NMR spectra (100 MHz, 25 °C, $CDCl_3$) and stretching frequency (cm^{-1}) in IR spectra.

quence offers a convenient route to β-trialkylstannyl aldehydes.[7]



(7)

Spectroscopic properties of β-stannyl ketones **3e** (Cl_3Sn), **3e′** (Cl_2BuSn), **3e″** ($ClBu_2Sn$), and **3e‴** (Bu_3Sn) are summarized in Scheme I.[8] β-Tributylstannyl ketone **3e‴** was prepared by the chemoselective alkylation of **3e** on the tin atom with 3 equiv of *n*-BuMgBr in THF at −78 °C according to our previously reported procedure.[5a,9] The C=O stretching frequency of **3e‴** appears at 1720 cm^{-1} which is a normal value for ketones. On the other hand, the C=O stretching frequency of β-trichlorostannyl ketone **3e** is lowered by 88 cm^{-1} compared with **3e‴**. Usually, ^{119}Sn NMR spectroscopy is a powerful tool for the determination of the coordination number of the tin atoms in organotin compounds.[10] Chemical shifts of β-stannyl ketone **3e‴** and tetrabutyltin **10** in ^{119}Sn NMR spectra showed nearly the same values. On the other hand, large upfield shifts (Δ89–Δ148 ppm) were observed in **3e″**, **3e′**, and **3e** as compared with the corresponding organotin halides **11**, **12**, and **13**, respectively. Similarly, high-field shift (Δ90.6 ppm) relative to **13** was also observed in β-trichlorostannyl aldehyde **3u**. These upfields shifts are attributed to increases in the electron density at the tin atom by coordination of the carbonyl oxygen.[11] Thus, the pentacoordination at the Sn of **3e″**, **3e′**, **3e**, and **3u** was supported by chemical shifts in ^{119}Sn NMR spectra.[12]

Dehydrostannation of β-Trichlorostannyl Ketones and Aldehydes 3 Leading to α-Methylene Ketones and Aldehydes 4. As reported in our preliminary communication, DMSO promotes the dehydrostannation of β-trichlorostannyl ketones to give α-methylene ketones, while the process requires heating to 60 °C.[1] In search for milder reaction conditions for this dehydrostannation, a series of experiments were conducted in which the reagents, their molar ratios to the β-trichlorostannyl ketone, the reaction period, and the reaction temperature were varied. The conditions were examined for **3e** in $CDCl_3$ under ultrasonic irradiation of a solution in an NMR tube. The results are summarized in Table II. When 3 molar equiv of DMSO was treated with **3e**, the characteristic signal pattern of enone **4e** emerged in the ^{1}H NMR spectra. The reaction, however, required 6 h for 48% yield of **4e** (entry 1). The use of 10 molar equiv of DMSO (60 °C, 5 h) was necessary for completion of the dehydrostannation (entry 3). After all, we have observed that amines are remarkably effective agents for the dehydrostannation. In general, the reactions with amines completed within 10 min even at 20 °C (entries 9–14). Although the reaction of **3e** with pyridine proceeded smoothly at 20 °C, a side reaction occurred giving 1-chloro-4,4-dimethyl-3-pentanone (entries 7 and 8).[13] Among the amines tried, TMEDA and DABCO exhibited notable efficiency (entries 12–14). Taking experimental convenience into account, we felt that TMEDA is the reagent of choice in view of the formation of an easily separable precipitate as well as the high efficiency.

We next sought to define the generality of this transformation by subjecting a variety of β-trichlorostannyl ketones **3a–g** and α-substituted β-trichlorostannyl ketones **3i–r** to the optimized TMEDA conditions. As illustrated in Table I, in each case addition of 1 molar equiv of TMEDA to a dichloromethane solution containing β-trichlorostannyl ketone led to rapid α-methylene ketone formation at 0 °C. Typically, when 1 molar equiv of TMEDA was added to a solution of β-trichlorostannyl ketone **3a** in dichloromethane, a white precipitate, supposed to be '$HSnCl_3$·TMEDA' complex, quickly appeared. After filtration of the precipitate, the filtrate was subjected to aqueous workup with pentane/aq. sat. NaCl. Purification of the crude product by short-column chromatography on silica gel gave 92% yield of α-methylene ketone **4a** (Table I, entry 1). Various α-methylene ketones **4** were conveniently prepared from **3** according to this general

(7) (a) Ueno, Y.; Ohta, M.; Okawara, M. *Tetrahedron Lett.* **1982**, *23*, 2577. (b) Fleming, I.; Rowley, M. *Tetrahedron Lett.* **1985**, *26*, 3857. (c) Piers, E.; Tillyer, R. D. *J. Org. Chem.* **1988**, *53*, 5366.

(8) For pertinent reviews of investigating tin compounds using spectroscopy, see: (a) Davies, A. G. In *Comprehensive Organometallic Chemistry, Vol. 2*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; pp 523–529. (b) Harrison, P. J. In *Chemistry of Tin*; Harrison, P. J., Ed.; Blackie: Glasgow, 1989; pp 60–117.

(9) Recently, we have reported that β-trialkylstannyl ketones can be used for the generation of β-lithio ketone enolates, which can behave as α,β-dianion of ketones; see: Nakahira, H.; Ryu, I.; Ikebe, M.; Kambe, N.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 177.

(10) Otera, J. *J. Organomet. Chem.* **1981**, *221*, 57 and references cited therein.

(11) For recent papers which reported intramolecular coordination of organostannanes, see: Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606 and references cited therein.

(12) In the X-ray structure of β-trichlorostannyl ester, the tin atom has a trigonal-bipyramidal configuration with the oxygen and chlorine atom in apical position. See: Harrison, P. G.; King, T. J.; Healy, M. A. *J. Organomet. Chem.* **1979**, *182*, 17.

(13) At 60 °C, the formation of β-chloroketone became predominant (entry 8 in Table II). We suspected that thermal decomposition of $HSnCl_3$·Py to give HCl·Py and $SnCl_2$ would take place so that the former would cause this further HCl addition.

Table I. Synthesis of β-Trichlorostannyl Ketones and Aldehydes 3 and Their Conversion to α-Methylene Ketones and Aldehydes 4

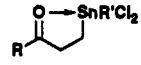
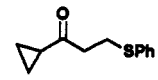
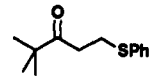
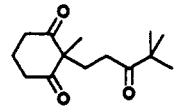
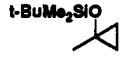
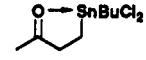
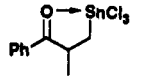
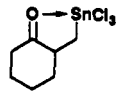
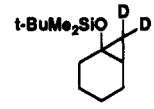
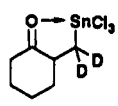
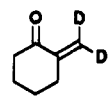
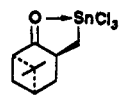
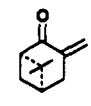
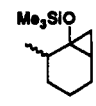
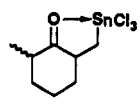
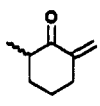
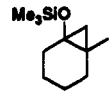
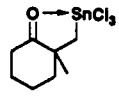
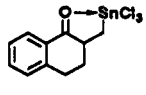
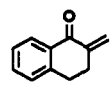
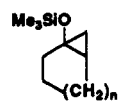
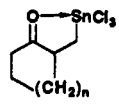
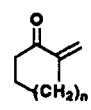
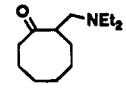
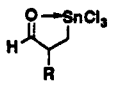
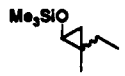
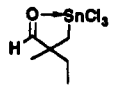
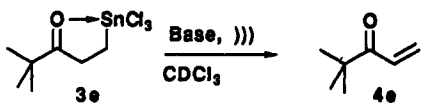
entry	substrate	no.	β-Sn ketone and aldehyde	no.	yield[a] (%)	product	no.	yield[b,c] (%)
								
1	R=*n*-C_6H_{13}	1a	R'=Cl	3a	98[d]		4a	92
2			R'=*n*-Bu	3a'	91[e,f]			NR[g]
3	R=*s*-Bu	1b	R'=Cl	3b	98		4b	86
4			R'=*n*-Bu	3b'	84[e,f]			
5	R=*c*-C_3H_5	1c	R'=Cl	3c	92		4c	79
6							5	72[h]
7	R=*i*-Pr	1d	R'=Cl	3d	96		4d	83
8			R'=*n*-Bu	3d'	92[e,f]			
9	R=*t*-Bu	1e	R'=Cl	3e	96		4e	81
10							6	81[h]
11							7	63[i,j]
12			R'=*n*-Bu	3e'	97[e,f]			
13	R=Ph	1f	R'=Cl	3f	90		4f	81
14								80[k]
15	R=1-cyclohexenyl	1g	R'=Cl	3g	82		4g	84
16		1h		3h'	90[e,f]			
17		1i		3i	81		4i	72
18		1j		3j	99		4j	76
19		1k		3k	99		4k	82
20		1l		3l	83		4l	90
21		1m[l]		3m	83[m]		4m	84
22		1n		3n	66			
23		1o		3o	80		4o	78
								
24	n=3	1p	n=3	3p	83	n=3	4p	80
25	n=4	1q	n=4	3q	84	n=4	4q	70
26							8	72[n]

Table I (Continued)

entry	substrate	no.	β-Sn ketone and aldehyde	no.	yield[a] (%)	product	no.	yield[b,c] (%)
27	n=8	1r	n=8	3r	86	n=8	4r	86
								
28	R=benzyl	1s	R=benzyl	3s[e]	.[p]	R=benzyl	4s	70
29	R=*n*-pentyl	1t	R=*n*-pentyl	3t[e]	.[p]	R=*n*-pentyl	4t	83
30	R=*i*-Pr	1u	R=*i*-Pr	3u[e]	.[p]	R=*i*-Pr	4u	71
31	R=8-nonenyl	1v	R=8-nonenyl	3v[e]	.[p]	R=8-nonenyl	4v	72[q]
32		1w		3w[e]	.[p]			

[a] Isolated yields of purified (recrystallization) products are given, except where otherwise indicated. [b] The reaction conditions were as follows: 1.0 equiv of TMEDA, 20 °C, 15 min, except where otherwise indicated. [c] Isolated yields of purified (column chromatography (SiO_2)) products are given. [d] Crude yield. [e] The reaction was conducted with *n*-$BuSnCl_3$. [f] Yields of distilled product. [g] The reaction conditions: TMEDA (1.0 equiv), 60 °C, 2 h. [h] The reaction conditions: (1) TMEDA (2.0 equiv) 20 °C, 15 min, (2) PhSH (1.2 equiv), 20 °C, 60 min. [i] The reaction conditions: (1) TMEDA (2.0 equiv), 20 °C, 15 min; (2) 2-Methyl-1,3-cyclohexanedione (1.0 equiv), 40 °C, 14 h. [j] See ref 16. [k] Overall yield of α-methylene ketone from the siloxycyclopropane without purification of β-trichlorostannyl ketone (one-pot procedure). [l] *E*/*Z* = 38/62 from 270-MHz ^1H NMR. [m] *E*/*Z* = 33/67 for the sample obtained by recrystallization from pentane/chloroform (determined by 270-MHz ^1H NMR spectroscopy). [n] The reaction conditions: Et_2NH (3.0 equiv), 20 °C, 60 min. [o] Obtained as semisolids and used for the next step without further purification. [p] ^1H NMR (270 MHz) indicated clean conversion of siloxycyclopropane to β-trichlorostannyl aldehyde. [q] The reaction conditions: DMSO, 15 °C, 1 h.

Table II. Base-Induced Dehydrostannation of β-Trichlorostannyl Ketone 3e Leading to 4e[a]



3e 4e

entry	base	equiv	temp (°C)	time (h)	yield[b] (%)
1	DMSO	3	60	6	48
2		3	60	10	62
3		10	60	5	97
4	DMF	3	60	8	28
5		10	60	5	37
6	HMPA	10	70	5	91
7	pyridine	1	20	2.5	86[c]
8		3	60	1	9[d]
9	Et_3N	1	20	0.1	90
10	Et_2NH	1	20	0.1	86
11	*i*-Pr_2NH	1	20	0.1	93
12	TMEDA	1	20	0.1	100
13		0.5	20	0.3	100
14	DABCO	1	20	0.1	100

[a] Reactions were carried out using an NMR tube with **3e** (0.03 g, 0.089 mmol) in $CDCl_3$ (0.5 mL) under ultrasonic irradiation. [b] Yield of **4e** was determined by ^1H NMR (270 MHz, $CDCl_3$). [c] 1-Chloro-4,4-dimethyl-3-pentanone was also obtained (8%). [d] 1-Chloro-4,4-dimethyl-3-pentanone was obtained as major product (91%).

procedure. *One-pot* conversion from siloxycyclopropane **1f** to α-methylene ketone **4f** by consecutive treating with $SnCl_4$ and TMEDA was also successful (entry 14). α-Methylene ketone **4g**, a key compound for Nazarov cyclization,[14] could be also obtained in good yield. α-Methylene ketones **4**, prepared in situ from **3**, are eligible for further derivation by *one-pot* procedures. The dehydrostannation of **3c** and **3e** with 2 equiv of TMEDA in dichloromethane and the subsequent treatment with PhSH gave β-phenylthio ketones **5** and **6**, respectively (entries 6 and 10).[15] Furthermore, treatment of in situ generated α-methylene ketone **4e** with 2-methyl-1,3-cyclohexanedione at 40 °C gave triketone **7** in 63% (entry 11).[16] In these reactions, excess amounts of TMEDA promoted the second reaction. Treatment of β-trichlorostannyl ketone **3q** with 3 equiv of Et_2NH gave β-amino ketone **8** via α-methylene ketone **4q** (entry 26).[17]

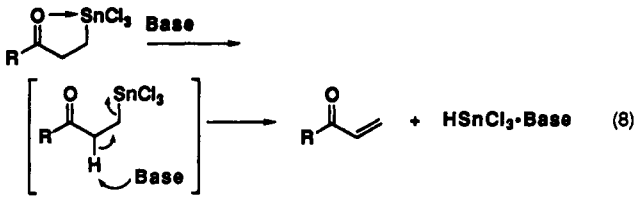
The dehydrostannation sequence was successfully extended to β-trichlorostannyl aldehydes, and the results of the *one-pot* procedure starting with siloxycyclopropanes to give α-methylene aldehydes are also given in Table I. Interestingly, the dehydrostannation of β-trichlorostannyl aldehydes is much more facile than β-trichlorostannyl ketones, and this is well demonstrated by the result with the use of DMSO, where the reaction occurred even at 15 °C within 1 h (entry 31). TMEDA also worked well for dehydrostannation of β-trichlorostannyl aldehydes (entries 28–30).

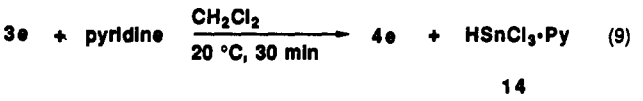
It should be noted that the reaction of β-dichlorobutylstannyl ketone **3a'** with TMEDA even under more forcing conditions (60 °C, 2 h) gave dehydrostannation product (entry 2). It seems probable that α-protons of β-trichlorostannyl ketones would be highly acidic, compared with the corresponding trialkyl, chlorodialkyl, and dichloroalkyl analogues, due to the highly negatively polarized tin atom caused by the three chlorine substituents. Similarly, the present dehydrostannation sequence failed for butyltin trichloride even under more forcing conditions (TMEDA, 60 °C, 2 h). Attempted dehydrostannation of β-trichlorostannyl *esters* was also unsuccessful.[18]

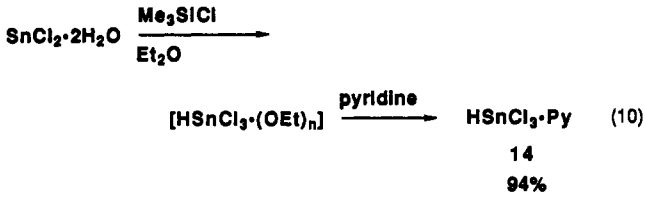
It may be reasonable to assume that added amines or DMSO cause the abstraction of acidic α-protons, which leads to the subsequent dehydrotrichlorostannation (eq 8). Although the precise mechanism of the dehydrostannation remains unclear, the composition of the Sn fragment after the dehydrostannation could be identified by analytical methods. Treatment of **3e** with 1 equiv of pyridine in dichloromethane (20 °C, 30 min) gave a white

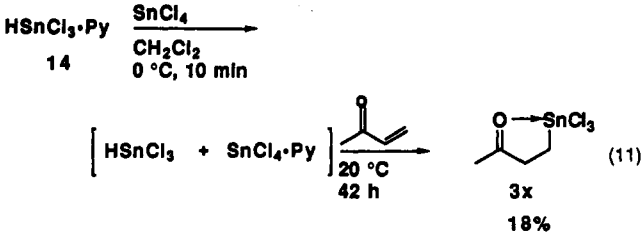
(14) For a review, see: Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429.
(15) Vidal, J.; Huet, F. *J. Org. Chem.* **1988**, *53*, 611.
(16) Harada, S.; Sugioka, T.; Uda, H.; Kuriki, T. *Synthesis* **1990**, 53.
(17) Fuhrhop, J.; Penzlin, G. *Organic Synthesis, concepts, methods, starting materials*; Verlag Chemie GmbH: Weinheim, 1983; p 54.
(18) The reaction of β-trichlorostannyl ester with 2 equiv of pyridine has been reported to give a stable pyridine complex of β-trichlorostannyl ester.[6c] Very slow β-elimination from β-phenoxy-substituted *ester* relative to the corresponding *ketone* has been known. See: Crosby, J.; Stirling, C. J. M. *J. Chem. Soc. B* **1970**, 671.

precipitate 14 together with 4e (eq 9). Its CH composition was characterized to be 1:1 hydrotrichlorostannane–pyridine complex ($HSnCl_3$·Py) 14 by elemental analysis, and the existence of coordinated pyridine was ascertained by ^1H NMR (270 MHz, acetone-d_6). This precipitate was further identified with a separately prepared sample by the reaction of pyridine with in situ generated $HSnCl_3$·$(OEt_2)_n$ (by treating $SnCl_2$·$2H_2O$ with 1 equiv of Me_3SiCl in ether at 20 °C for 15 min) (eq 10).[5a] Chemical support for 14 is also available: The serial treatment of 14 with 2 equiv of $SnCl_4$ and with methyl vinyl ketone resulted in the formation of β-trichlorostannyl ketone 3x in 18% yield, suggesting the generation of reactive hydrotrichlorostannane after removal of pyridine by $SnCl_4$ in this system (eq 11).

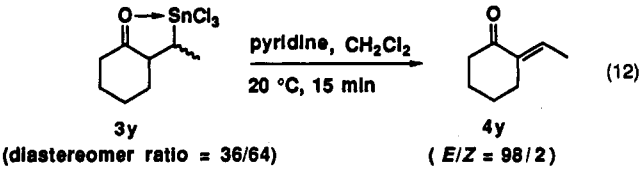






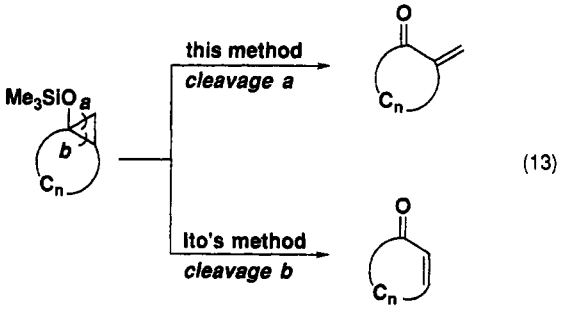


Stereochemistry of the dehydrostannation was examined by using a diastereomeric mixture of β-trichlorostannyl ketone 3y. Treatment of 3y with pyridine gave (*E*)-ethylidenecyclohexanone 4y as a predominant product (eq 12). This stereochemical outcome may exclude the possibility of the elimination with a concerted process like E2 elimination.[19]



Conclusion

We have demonstrated a convenient synthesis of β-trichlorostannyl ketones and aldehydes via the site-selective ring-opening reaction of siloxycyclopropanes with $SnCl_4$. This synthetic strategy for these unique organohalostannanes is complementary to the method based on hydrotrichlorostannation of enones.[5] β-Trichlorostannyl ketones and aldehydes undergo clean and smooth dehydrostannation at 20 °C on treatment with 1 equiv of an amine. The overall process starting with siloxycyclopropanes to give α-methylene ketones and aldehydes[20] can be conveniently carried out by a *one-pot* procedure. Conversion of bicyclic siloxycyclopropanes to ring-expanded enones was previously achieved by Ito et al.[21] based on the $FeCl_3$-induced chlorination/dechlorination sequence. Thus, now one can use both types of transformations to enones from the same siloxycyclopropanes (eq 13).



Experimental Section

General Comments. Melting points were determined on a hot-stage apparatus and are not corrected. For flash chromatography, silica gel 60 (230–400 mesh ASTM, E. Merck) was used. Columns were eluted with a positive nitrogen pressure. CH_2Cl_2, $SnCl_4$, and *n*-$BuSnCl_3$ were distilled from CaH_2. THF was distilled from sodium and benzophenone. All other solvents and reagents were of reagent grade or higher. Siloxycyclopropanes were prepared by the cyclopropanation of enol silyl ethers with zinc carbenoids according to the procedure established in our previous work.[4a] α-Methylene ketones **4c**,[22] **4d**,[23] **4f**,[24] **4g**,[25] **4j**,[20a] **4m**,[26] **4p**,[20h] and **4q**[20d] were isolated and characterized by previously reported data.

Reaction of Siloxycyclopropanes 1 with $SnCl_4$. Representative Procedure for the Synthesis of β-Trichlorostannyl

(19) We suspected the possibility of enolization to account for the loss of the initial stereochemistry, although attempted D/H exchange of α-proton in β-trichlorostannyl ketone by D_2O failed due to the unexpected dehydrostannation.

(20) For previous synthesis of α-methylene ketones and/or α,β-unsaturated ketones, see: Base-induced cleavage of diketo lactone: (a) Ksander, G. M.; McMurry, J. E.; Johnson, M. *J. Org. Chem.* **1977**, *42*, 1180. Sulfoxide elimination reaction: (b) Paterson, I. *Tetrahedron* **1988**, *44*, 4207. (c) Hannaby, M.; Warren, S. *Tetrahedron Lett.* **1985**, *26*, 3133. Selenoxide elimination reaction: (d) Reich, H. J.; Jasperse, C. P.; Renga, J. M. *J. Org. Chem.* **1986**, *51*, 2981. (e) Engman, L. *Tetrahedron Lett.* **1985**, *26*, 6385. (f) Toshimitsu, A.; Owada, H.; Terao, K.; Uemura, S.; Okano, M. *J. Org. Chem.* **1984**, *49*, 3796 and references cited therein. Wittig-Horner reaction of β-keto phosphonate with formaldehyde: (g) Amri, H.; Rambaud, M.; Villieras, J. *Tetrahedron Lett.* **1989**, *30*, 7381. Ramberg–Bäcklund reaction of 2-(bromomethyl)sulfonyl ketones: (h) Block, E.; Aslam, M.; Eswarakrishnan, V.; Gebreyes, K.; Hutchinson, J.; Iyer, R.; Laffitte, J.-A.; Wall, A. *J. Am. Chem. Soc.* **1986**, *108*, 4568. Palladium-catalyzed reaction of allyl β-keto carboxylates: (i) Tsuji, J.; Nisar, M.; Minami, I. *Tetrahedron Lett.* **1986**, *27*, 2483. Cp_2ZrH_2-catalyzed cross-aldol condensation: (j) Nakano, T.; Irifune, S.; Umano, S.; Inada, A.; Ishii, Y.; Ogawa, M. *J. Org. Chem.* **1987**, *52*, 2239. Denitration of α-nitro ketones: (k) Ono, N.; Miyake, H.; Fujii, M.; Kaji, A. *Tetrahedron Lett.* **1983**, *24*, 3477. Cuprate addition and deamination of 2-(pyrrolidinylmethyl)-2-cyclohexenone: (l) Tamura, R.; Watabe, K.-i.; Katayama, H.; Suzuki, H.; Yamamoto, Y. *J. Org. Chem.* **1990**, *55*, 408. Also see a review: (m) Shono, T.; Matsumura, Y. *J. Synth. Org. Chem. Jpn.* **1981**, *39*, 358.

(21) (a) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073. (b) Ito, Y.; Fujii, S.; Nakatsuka, M.; Kawamoto, F.; Saegusa, T. *Org. Synth.* **1980**, *59*, 113.

(22) Gras, J. L. *Tetrahedron Lett.* **1978**, 2955.

(23) (a) Fleming, I.; Goldhill, J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1493. (b) Naito, I.; Kinoshita, A.; Yonemitsu, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 339.

(24) (a) Ksander, G. M.; McMurry, J. E. *Tetrahedron Lett.* **1976**, 4691. (b) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

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Ketones 3. 4-Methyl-1-(trichlorostannyl)-3-hexanone (3b). The preparation of **3b** is described as a typical example. Under N_2, siloxycyclopropane **1b** (1.86 g, 10 mmol) was slowly added to a solution of $SnCl_4$ (2.60 g, 10 mmol) in CH_2Cl_2 (10 mL) at 0 °C with continuous stirring for 30 min. The solvent and produced Me_3SiCl were evaporated under reduced pressure. The crude product obtained was sufficiently pure. Recrystallization from CH_2Cl_2 and pentane afforded **3b** (3.31 g, 98%): mp 85 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, J = 7.5 Hz, 3 H, CH_3CH_2), 1.19 (d, J = 6.7 Hz, 3 H, CH_3CH), 1.50–1.63 (m, 1 H, CH_2CH_3), 1.69–1.82 (m, 1 H, CH_2CH_3), 1.89 (t, J = 7.2 Hz, 2 H, CH_2SnCl_3; average ^2J ($^{117,119}Sn$, ^1H) = 103.7 Hz), 2.71–2.78 (m, 1 H, CHC(O)), 3.09– 3.26 (m, 2 H, $CH_2CH_2SnCl_3$); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.23 (CH_3CH_2), 15.68 (CH_3CH), 18.65 (^1J (^{119}Sn, ^{13}C) = 817.8 Hz, ^1J (^{117}Sn, ^{13}C) = 781.2 Hz, CH_2SnCl_3), 26.12 (CH_3CH_2), 35.32 (average ^2J ($^{117,119}Sn$, ^{13}C) = 49.4 Hz, $CH_2CH_2SnCl_3$), 47.21 (CH_3CH), 221.57 (average ^3J ($^{117,119}Sn$, ^{13}C) = 102.5 Hz, C=O); IR (KBr) 1655 cm^{-1} (νC=O). Anal. Calcd for $C_7H_{13}OSnCl_3$: C, 24.85; H, 3.88. Found: C, 24.91; H, 3.78. All of the following trichlorostannyl ketones except **3a** were recrystallized from pentane/$CHCl_3$ and obtained as white solids unless specified otherwise.

1-(Trichlorostannyl)-3-nonanone (3a). The purity of the obtained crude product, a yellowish oil, was satisfactory according to NMR spectra: ^1H NMR (270 MHz, $CDCl_3$) δ 0.85–0.90 (m, 3 H), 1.19–1.38 (m, 6 H), 1.65–1.73 (m, 2 H), 1.87 (t, J = 7.3 Hz, 2 H, CH_2SnCl_3; ^2J (^{119}Sn, ^1H) = 104.5 Hz, ^2J (^{117}Sn, ^1H) = 100.6 Hz), 2.70 (t, J = 7.3 Hz, 2 H, $CH_2C(O)$), 3.13 (t, J = 7.3 Hz, 2 H, $CH_2CH_2SnCl_3$; ^3J (^{119}Sn, ^1H) = 183.5 Hz, ^3J (^{117}Sn, ^1H) = 175.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.78, 18.69 (^1J (^{119}Sn, ^{13}C) = 814.1 Hz, ^1J (^{117}Sn, ^{13}C) = 777.8 Hz, CH_2SnCl_3), 22.15, 23.64, 28.29, 31.08, 36.56 (average ^2J ($^{117,119}Sn$, ^{13}C) = 50.7 Hz, $CH_2CH_2SnCl_3$), 41.87, 218.33 (average ^3J ($^{117,119}Sn$, ^{13}C) = 117.9 Hz, C=O); IR (neat) 1661 cm^{-1} (νC=O). Anal. Calcd for $C_9H_{17}OSnCl_3$: C, 29.50; H, 4.68. Found: C, 29.68; H, 4.69.

1-Cyclopropyl-3-(trichlorostannyl)-1-propanone (3c): yield 92%; mp 127–128 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.33–1.48 (m, 4 H), 1.88 (t, J = 7.3 Hz, 2 H, CH_2SnCl_3; ^2J (^{119}Sn, ^1H) = 113.2 Hz, ^2J (^{117}Sn, ^1H) = 108.6 Hz), 2.14–2.23 (m, 1 H), 3.31 (t, J = 7.3 Hz, 2 H, $CH_2CH_2SnCl_3$; ^3J (^{119}Sn, ^1H) = 182.1 Hz, ^3J (^{117}Sn, ^1H) = 173.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.30, 18.56 (^1J (^{119}Sn, ^{13}C) = 822.7 Hz, ^1J (^{117}Sn, ^1H) = 786.1 Hz, CH_2SnCl_3), 21.70 (CH), 36.68 (average ^2J ($^{117,119}Sn$, ^{13}C) = 51.2 Hz, $CH_2CH_2SnCl_3$), 218.04 (average ^3J ($^{117,119}Sn$, ^{13}C) = 126.3 Hz, C=O); IR (KBr) 1630 cm^{-1} (νC=O). Anal. Calcd for $C_6H_9OSnCl_3$: C, 22.36; H, 2.82. Found: C, 22.10; H, 2.87.

4-Methyl-1-(trichlorostannyl)-3-pentanone (3d): yield 96%; mp 82–83 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.25 (d, J = 7.0 Hz, 6 H, $(CH_3)_2CH$), 1.90 (t, J = 7.0 Hz, 2 H, CH_2SnCl_3; average ^2J ($^{117,119}Sn$, ^1H) = 101.9 Hz), 2.83–2.93 (m, 1 H, $(CH_3)_2CH$), 3.18 (t, J = 7.0 Hz, 2 H, $CH_2CH_2SnCl_3$; average ^3J ($^{117,119}Sn$, ^1H) = 92.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.10 ($(CH_3)_2CH$), 18.80 (^1J (^{119}Sn, ^{13}C) = 819.7 Hz, ^1J (^{117}Sn, ^{13}C) = 783.1 Hz, CH_2SnCl_3), 34.46 (average ^2J ($^{117,119}Sn$, ^{13}C) = 49.4 Hz, $CH_2CH_2SnCl_3$), 40.56 ($CH(CH_3)_2$), 221.33 (average ^3J ($^{117,119}Sn$, ^{13}C) = 104.8 Hz, C=O); IR (KBr) 1640 cm^{-1} (νC=O). Anal. Calcd for $C_6H_{11}OSnCl_3$: C, 22.22; H, 3.42. Found: C, 21.87; H, 3.41.

4,4-Dimethyl-1-(trichlorostannyl)-3-pentanone (3e): yield 96%; mp 178–179 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.28 (s, 9 H, $(CH_3)_3C$), 1.88 (t, J = 7.3 Hz, 2 H, CH_2SnCl_3; average ^2J ($^{117,119}Sn$, ^1H) = 101.2 Hz), 3.17 (t, J = 7.3 Hz, 2 H, $CH_2CH_2SnCl_3$; average ^3J ($^{117,119}Sn$, ^1H) = 187.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 20.87 (^1J (^{119}Sn, ^{13}C) = 863.7 Hz, ^1J (^{117}Sn, ^{13}C) = 826.4 Hz, CH_2SnCl_3), 25.47 ($(CH_3)_3C$), 31.40 (average ^2J ($^{117,119}Sn$, ^{13}C) = 57.4 Hz, $CH_2CH_2SnCl_3$), 43.38 ($(CH_3)_3C$), 223.71 (average ^3J ($^{117,119}Sn$, ^{13}C) = 100.7 Hz, C=O); IR (KBr) 1632 cm^{-1} (νC=O). Anal. Calcd for $C_7H_{13}OSnCl_3$: C, 24.85; H, 3.88. Found: C, 25.02; H, 4.03.

3-(Trichlorostannyl)propiophenone (3f): yield 90%; a dark brown solid; mp 206–208 °C; ^1H NMR (270 MHz, acetone-d_6) δ 2.05 (t, J = 7.3 Hz, 2 H, CH_2SnCl_3; ^2J (^{119}Sn, ^1H) = 104.9 Hz, ^2J (^{117}Sn, ^1H) = 100.7 Hz), 3.66 (t, J = 7.3 Hz, 2 H, $CH_2CH_2SnCl_3$; ^3J (^{119}Sn, ^1H) = 183.7 Hz, ^3J (^{117}Sn, ^1H) = 175.1 Hz), 7.59 (t, J = 7.3 Hz, 2 H, m-Ph), 7.77 (t, J = 7.3 Hz, 1 H, p-Ph), 8.16 (d, J = 7.3 Hz, 2 H, o-Ph); ^{13}C NMR (68 MHz, acetone-d_6) δ 18.79 (^1J (^{119}Sn, ^{13}C) = 827.6 Hz, ^1J (^{117}Sn, ^{13}C) = 790.4 Hz, CH_2SnCl_3), 32.08 (average ^2J ($^{117,119}Sn$, ^{13}C) = 53.1 Hz, $CH_2CH_2SnCl_3$), 129.41, 129.88, 132.74, 136.80 (Ph), 203.15 (average ^3J ($^{117,119}Sn$, ^{13}C) = 139.1 Hz, C=O); IR (KBr) 1623 cm^{-1} (νC=O). Anal. Calcd for $C_9H_9OSnCl_3$: C, 30.17; H, 2.53. Found: C, 30.27; H, 2.58.

1-(1'-Cyclohexenyl)-3-(trichlorostannyl)propanone (3g): yield 82%; mp 182–183 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.53–1.79 (m, 4 H), 1.91 (t, J = 7.3 Hz, 2 H, CH_2SnCl_3; ^2J (^{119}Sn, ^1H) = 104.5 Hz, ^2J (^{117}Sn, ^1H) = 100.6 Hz), 2.26–2.56 (m, 4 H), 3.28 (t, J = 7.3 Hz, 2 H, $CH_2CH_2SnCl_3$; ^3J (^{119}Sn, ^1H) = 187.9 Hz, ^3J (^{117}Sn, ^1H) = 180.1 Hz), 7.43 (m, 1 H, vinyl); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.99 (^1J (^{119}Sn, ^{13}C) = 829.6 Hz, ^1J (^{117}Sn, ^{13}C) = 793.2 Hz, CH_2SnCl_3), 20.95, 21.30, 23.30, 27.14, 30.39 (average ^2J ($^{117,119}Sn$, ^{13}C) = 51.8 Hz, $CH_2CH_2SnCl_3$), 137.03, 150.32, 202.8 (average ^3J ($^{117,119}Sn$, ^{13}C) = 106.9 Hz, C=O); IR (KBr) 1626 cm^{-1} (νC=O). Anal. Calcd for $C_9H_{13}OSnCl_3$: C, 29.83; H, 3.62. Found: C, 29.70; H, 3.63.

2-Methyl-3-(trichlorostannyl)propiophenone (3i): yield 81%; a dark brown solid; mp 151–152 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.48 (d, J = 7.3 Hz, 3 H, CH_3), 2.00 (dd, J_{vic} = 0.9 Hz, J_{gem} = 13.1 Hz, 1 H, CH_2SnCl_3), 2.20 (dd, J_{vic} = 6.7 Hz, J_{gem} = 13.1 Hz, 1 H, CH_2SnCl_3), 4.30 (m, 1 H, CH; average ^3J ($^{117,119}Sn$, ^1H) = 364.1 Hz), 7.60 (t, J = 7.6 Hz, 2 H, m-Ph), 7.78 (t, J = 7.6 Hz, 1 H, p-Ph), 8.17 (d, J = 7.6 Hz, 2 H, o-Ph); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.91 (average ^3J ($^{117,119}Sn$, ^{13}C) = 10.4 Hz, CH_3), 30.37 (^1J (^{119}Sn, ^{13}C) = 810.6 Hz, ^1J (^{117}Sn, ^{13}C) = 775.2 Hz, CH_2SnCl_3), 37.11 (average ^2J ($^{117,119}Sn$, ^{13}C) = 55.6 Hz, $CHCH_2SnCl_3$), 129.52, 130.33, 131.33, 136.80 (aromatic), 207.30 (^3J (^{119}Sn, ^{13}C) = 97.1 Hz, ^3J (^{117}Sn, ^{13}C) = 93.4 Hz, C=O); IR (KBr) 1628 cm^{-1} (νC=O). Anal. Calcd for $C_{10}H_{11}OSnCl_3$: C, 32.26; H, 2.98. Found: C, 32.53; H, 3.13.

2-[(Trichlorostannyl)methyl]cyclohexanone (3j): yield 99%; a brown solid; mp 106–107 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.49 (dd, J_{vic} = 5.8 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2SnCl_3; ^2J (^{119}Sn, ^1H) = 101.3 Hz, ^2J (^{117}Sn, ^1H) = 93.9 Hz), 1.46–1.62 (m, 1 H), 1.71–2.05 (m, 3 H), 2.04 (dd, J_{vic} = 8.2 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2SnCl_3), 2.25–2.32 (m, 1 H), 2.42–2.59 (m, 2 H), 2.80–2.86 (m, 1 H), 3.02–3.14 (m, 1 H, $CHCH_2SnCl_3$; average ^3J ($^{117,119}Sn$, ^1H) = 143.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.77, 24.87 (^1J (^{119}Sn, ^{13}C) = 794.6 Hz, ^1J (^{117}Sn, ^{13}C) = 759.2 Hz, CH_2SnCl_3), 28.17, 37.22 (^3J (^{119}Sn, ^{13}C) = 86.6 Hz, ^3J (^{117}Sn, ^{13}C) = 83.0 Hz, $CH_2CHC(O)$), 39.82, 46.48 (average ^2J ($^{117,119}Sn$, ^{13}C) = 50.6 Hz, $CHCH_2SnCl_3$), 220.04 (average ^3J ($^{117,119}Sn$, ^{13}C) = 106.2 Hz, C=O); IR (KBr) 1651 cm^{-1} (νC=O). Anal. Calcd for $C_7H_{11}OSnCl_3$: C, 25.00; H, 3.30. Found: C, 25.08; H, 3.28.

2-[(Trichlorostannyl)dideuteriomethyl]cyclohexanone (3k): yield 99%; a brown solid; mp 105–106 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.43–2.63 (m, 7 H), 2.74–2.92 (m, 1 H), 3.05 (dd, J_{vic} = 6.3 and 12.6 Hz, 1 H, CHC(O); average ^3J ($^{117,119}Sn$, ^1H) = 145.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.71, 28.16, 37.12 (average ^3J ($^{117,119}Sn$, ^{13}C) = 84.8 Hz, $CH_2CHC(O)$), 39.79, 46.33 (average ^2J ($^{117,119}Sn$, ^{13}C) = 50.7 Hz, $CHC(O)$), 220.23 (average ^3J ($^{117,119}Sn$, ^{13}C) = 109.0 Hz, C=O); IR (KBr) 1651 cm^{-1} (νC=O).

2-[(Trichlorostannyl)methyl]nopinone (3l): yield 83%; a brown solid; decomposed >300 °C without melting; ^1H NMR (270 MHz, $CDCl_3$) δ 1.07 (s, 3 H, CH_3), 1.23 (d, J = 11.7 Hz, 1 H), 1.42 (s, 3 H, CH_3), 1.62–1.81 (m, 2 H), 2.33–2.51 (m, 2 H), 2.56–2.80 (m, 1 H), 2.85–3.13 (m, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.86, 25.89, 30.74, 32.20 (^1J (^{119}Sn, ^{13}C) = 818.6 Hz, ^1J (^{117}Sn, ^{13}C) = 781.1 Hz, CH_2SnCl_3), 33.66 (^2J (^{119}Sn, ^{13}C) = 176.3 Hz, ^2J (^{117}Sn, ^{13}C) = 168.6 Hz, $CHCH_2SnCl_3$), 39.27, 40.00 (average ^3J ($^{117,119}Sn$, ^{13}C) = 39.7 Hz, $CH_2CHCH_2SnCl_3$), 57.39, 220.86 (average ^3J ($^{117,119}Sn$, ^{13}C) = 63.9 Hz, C=O); IR (KBr) 1633 cm^{-1} (νC=O). Anal. Calcd for $C_{10}H_{15}OSnCl_3$: C, 31.91; H, 4.02. Found: C, 31.90; H, 4.01.

6-Methyl-2-[(trichlorostannyl)methyl]cyclohexanone (3m). Integration of the methyl group (C6) in a 270-MHz ^1H NMR spectrum of the crude reaction product showed that the ratios of (*E*)- to (*Z*)-β-trichlorostannyl ketones **3m** formed in the reaction was 37:63. Recrystallization of the crude product from pentane/chloroform gave **3m** (*E*/*Z* = 33/67, 83%) as a brown solid: mp 136–137.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.16 (d, J = 6.3 Hz, 3 H, $CH_3(Z)$), 1.32 (d, J = 7.3 Hz, 3 H, $CH_3(E)$), 1.40–3.35 (other protones (*E* and *Z* mixture)); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.09 ($CH_3(Z)$), 17.14 ($CH_3(E)$), 19.31 (*E*), 24.33 (*Z*), 25.11 (^1J (^{119}Sn, ^{13}C) = 788.8 Hz, ^1J (^{117}Sn, ^{13}C) = 753.6 Hz, $CH_2SnCl_3(Z)$), 25.20 (^1J (^{119}Sn, ^{13}C) = 795.2 Hz, ^1J (^{117}Sn, ^{13}C) = 759.8 Hz, $CH_2SnCl_3(E)$), 32.85 (*E*), 36.12 (average ^3J ($^{117,119}Sn$,

^{13}C) = 102.8 Hz, $CH_2CHC(O)(E)$), 37.70 (Z), 38.23 (average ^3J ($^{117,119}Sn$, ^{13}C) = 64.4 Hz, $CH_2CHC(O)(Z)$), 42.04 (E), 42.33 (average ^2J ($^{117,119}Sn$, ^{13}C) = 49.8 Hz, $CHCH_2SnCl_3(E)$), 44.98 (Z), 46.13 (average ^2J ($^{117,119}Sn$, ^{13}C) = 51.9 Hz, $CHCH_2SnCl_3(Z)$), 222.14 (average ^3J ($^{117,119}Sn$, ^{13}C) = 113.1 Hz, C=O(Z)), 224.54 (average ^3J ($^{117,119}Sn$, ^{13}C) = 100.6 Hz, C=O(E)); IR (KBr) 1651 cm^{-1} (νC=O). Anal. Calcd for $C_8H_{13}OSnCl_3$: C, 27.43; H, 3.74. Found: C, 27.25; H, 3.65.

2-Methyl-2-[(trichlorostannyl)methyl]cyclohexanone (3n): yield 66%; a brown solid; mp 148–151 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 1.30 (d, J = 11.0 Hz, 2 H, CH_2SnCl_3), 1.36 (s, 3 H, CH_3), 1.45–3.13 (m, 8 H); ^{13}C NMR (15 MHz, $CDCl_3$) δ 21.37 (average ^3J ($^{117,119}Sn$, ^{13}C) = 29.3 Hz, CH_3), 25.79 (average ^3J ($^{117,119}Sn$, ^{13}C) = 25.3 Hz, $CH_2CHC(O)$), 27.48, 36.32, 36.12, 42.36 (CH_2SnCl_3), 48.21 (CH_3C), 223.31 (C=O); IR (KBr) 1640 cm^{-1} (νC=O). Anal. Calcd for $C_8H_{13}OSnCl_3$: C, 27.43; H, 3.74. Found: C, 27.80; H, 3.93.

2-[(Trichlorostannyl)methyl]-α-tetralone (3o): yield 80%; a dark brown solid; mp 148–150 °C; ^1H NMR (270 MHz, THF-d_8) δ 1.17 (dd, J_{vic} = 10.2 Hz, J_{gem} = 11.2 Hz, 1 H, CH_2SnCl_3; ^2J (^{119}Sn, ^1H) = 132.7 Hz, ^2J (^{117}Sn, ^1H) = 123.9 Hz), 1.97–2.04 (m, 1 H), 2.01 (dd, J_{vic} = 8.1 Hz, J_{gem} = 11.2 Hz, 1 H, CH_2SnCl_3; ^2J(^{119}Sn, ^1H) = 106.2 Hz, ^2J (^{117}Sn, ^1H) = 97.3 Hz), 2.36–2.52 (m, 1 H), 2.82–3.34 (m, 3 H), 7.37 (d, J = 7.3 Hz, 1 H), 7.38 (m, 1 H), 7.65 (dd, J = 7.3 and 7.8 Hz, 1 H), 8.18 (d, J = 7.3 Hz, 1 H); ^{13}C NMR (68 MHz, THF-d_8) δ 27.90 (average ^3J ($^{117,119}Sn$, ^{13}C) = 33.3 Hz, $CH_2CHCH_2SnCl_3$), 30.93 (^1J (^{119}Sn, ^{13}C) = 184.8 Hz, ^1J (^{117}Sn, ^{13}C) = 176.5 Hz, CH_2SnCl_3), 33.31 ($CH_2CH_2CHC(O)$), 43.62 (average ^2J ($^{117,119}Sn$, ^{13}C) = 57.1 Hz, $CHCH_2SnCl_3$), 126.01, 127.79, 128.11, 128.53, 135.43, 146.43 (aromatic), 204.89 (^3J (^{119}Sn, ^{13}C) = 114.0 Hz, ^3J (^{117}Sn, ^{13}C) = 107.8 Hz, C=O); IR (KBr) 1617 cm^{-1} (νC=O). Anal. Calcd for $C_{11}H_{11}OSnCl_3$: C, 34.37; H, 2.89. Found: C, 34.43; H, 2.64.

2-[(Trichlorostannyl)methyl]cycloheptanone (3p): yield 83%; mp 130–134 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.28–1.37 (m, 1 H), 1.53–1.71 (m, 2 H), 1.69 (dd, J_{vic} = 4.8 Hz, J_{gem} = 13.1 Hz, 1 H, CH_2SnCl_3), 1.74–1.95 (m, 4 H), 1.96–2.09 (m, 1 H), 2.07 (dd, J_{vic} = 7.6 Hz, J_{gem} = 13.1 Hz, 1 H, CH_2SnCl_3), 2.68–2.88 (m, 2 H), 3.30–3.36 (m, 1 H, $CHCH_2SnCl_3$; average ^3J ($^{117,119}Sn$, ^1H) = 160.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.58, 28.16, 28.27, 29.46 (^1J (^{119}Sn, ^{13}C) = 805.5 Hz, ^1J (^{117}Sn, ^{13}C) = 770.2 Hz, CH_2SnCl_3), 33.59 (average ^3J ($^{117,119}Sn$, ^{13}C) = 66.4 Hz, $CH_2CHC(O)$), 41.79, 47.37 (average ^2J ($^{117,119}Sn$, ^{13}C) = 52.9 Hz, $CHCH_2SnCl_3$), 222.77 (average ^3J ($^{117,119}Sn$, ^{13}C) = 87.2 Hz, C=O); IR (KBr) 1630 cm^{-1} (νC=O). Anal. Calcd for $C_8H_{13}OSnCl_3$: C, 27.43; H, 3.74. Found: C, 27.51; H, 3.71.

2-[(Trichlorostannyl)methyl]cyclooctanone (3q): yield 84%; mp 154.5–156 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.59–0.72 (m, 1 H), 1.36–1.61 (m, 2 H), 1.69–2.01 (m, 5 H), 1.79 (dd, J_{vic} = 5.8 Hz, J_{gem} = 13.3 Hz, 1 H, CH_2SnCl_3), 1.97 (dd, J_{vic} = 7.8 Hz, J_{gem} = 13.3 Hz, 1 H, CH_2SnCl_3), 2.08–2.17 (m, 1 H), 2.48–2.69 (m, 2 H), 2.85–2.96 (m, 1 H), 3.18–3.27 (m, 1 H, $CHCH_2SnCl_3$; average ^3J ($^{117,119}Sn$, ^1H) = 167.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.56, 24.59, 25.09 (^1J (^{119}Sn, ^{13}C) = 820.0 Hz, ^1J (^{117}Sn, ^{13}C) = 782.7 Hz, CH_2SnCl_3), 26.34, 28.24, 31.16 (average ^3J ($^{117,119}Sn$, ^{13}C) = 800.0 Hz, $CH_2CHC(O)$), 39.39, 46.74 (average ^2J ($^{117,119}Sn$, ^{13}C) = 49.8 Hz, $CHCH_2SnCl_3$), 226.40 (average ^3J ($^{117,119}Sn$, ^{13}C) = 89.2 Hz, C=O); IR (KBr) 1625 cm^{-1} (νC=O). Anal. Calcd for $C_9H_{15}OSnCl_3$: C, 29.67; H, 4.15. Found: C, 29.45; H, 4.07.

2-[(Trichlorostannyl)methyl]cyclododecanone (3r): yield 86%; decomposed > 300 °C without melting; ^1H NMR (270 MHz, THF-d_8) δ 0.82–1.55 (m, 16 H), 1.62 (dd, J_{vic} = 4.4 Hz, J_{gem} = 12.2 Hz, 1 H, CH_2SnCl_3), 1.73–1.97 (m, 1 H), 1.83 (dd, J_{vic} = 9.0 Hz, J_{gem} = 12.2 Hz, 1 H, CH_2SnCl_3), 2.11–2.56 (m, 2 H), 3.30–3.53 (m, 2 H); ^{13}C NMR (68 MHz, THF-d_8) δ 23.46, 23.67, 24.30, 24.54, 24.63, 26.22, 27.77, 28.03, 29.52, 33.08 (average ^3J ($^{117,119}Sn$, ^{13}C) = 60.2 Hz, $CH_2CHC(O)$), 37.85, 48.87 (average ^2J ($^{117,119}Sn$, ^{13}C) = 60.2 Hz, $CHCH_2SnCl_3$), 224.45 (average ^3J ($^{117,119}Sn$, ^{13}C) = 123.50 Hz, C=O); IR (KBr) 1644 cm^{-1} (νC=O). Anal. Calcd for $C_{13}H_{23}OSnCl_3$: C, 37.13; H, 5.52. Found: C, 37.19; H, 5.56.

4-Methyl-1-(dichlorobutylstannyl)-3-pentanone (3d′). To a stirred solution of butyltin trichloride (0.555 g, 1.97 mmol) in CH_2Cl_2 (6 mL) was added siloxycyclopropane **1d** (0.339 g, 1.97 mmol) at 0 °C with continuous stirring for 30 min. The solvent and produced Me_3SiCl were evaporated under reduced pressure. Kugelrohr distillation at 140–145 °C (1.0 mmHg) gave **3d′** (0.625 g, 92%): mp 58.0–58.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3 H, $Sn((CH_2)_3CH_3)Cl_2$), 1.12 (d, J = 6.8 Hz, 6 H, $(CH_3)_2CH$), 1.32–1.46 (m, 2 H), 1.52 (t, J = 7.0 Hz, 2 H, $CH_2SnBuCl_2$; average ^2J ($^{117,119}Sn$, ^1H) = 76.1 Hz), 1.75–1.86 (m, 2 H), 1.91–1.99 (m, 2 H), 2.68–2.79 (m, 1 H), 3.09 (t, J = 7.0 Hz, 2 H, $CH_2CH_2SnBuCl_2$; ^3J (^{119}Sn, ^{13}C) = 122.0 Hz, ^3J (^{117}Sn, ^{13}C) = 116.7 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.40 ($Sn((CH_2)_3CH_3)Cl_2$), 17.28 (^1J (^{119}Sn, ^{13}C) = 558.4 Hz, ^1J (^{117}Sn, ^{13}C) = 533.6 Hz, $CH_2SnBuCl_2$), 17.98 ($(CH_3)_2CH$), 25.85 (^2J (^{119}Sn, ^{13}C) = 110.0 Hz, ^2J (^{117}Sn, ^{13}C) = 103.8 Hz, $Sn(CH_2CH_2CH_2CH_3)Cl_2$), 26.92 (average ^3J ($^{117,119}Sn$, ^{13}C) = 41.6 Hz, $Sn((CH_2)_2CH_2CH_3)Cl_2$), 28.53 (^1J (^{119}Sn, ^{13}C) = 607.2 Hz, ^1J (^{117}Sn, ^{13}C) = 580.2 Hz, $Sn(CH_2(CH_2)_2CH_3)Cl_2$), 35.65 (average ^2J ($^{117,119}Sn$, ^{13}C) = 40.5 Hz, $CH_2CH_2SnBuCl_2$), 40.28 (average ^4J ($^{117,119}Sn$, ^{13}C) = 8.3 Hz, $(CH_3)_2CH$), 222.86 (average ^3J ($^{117,119}Sn$, ^{13}C) = 44.6 Hz, C=O); IR (KBr) 1672 cm^{-1} (νC=O). Anal. Calcd for $C_{10}H_{20}OSnCl_2$: C, 34.72; H, 5.83. Found: C, 34.72; H, 5.70. Stannyl ketones **3a′**, **3b′**, **3e′**, and **3h′** were prepared as described above for **3d′**.

1-(Dichlorobutylstannyl)-3-nonanone (3a′): yield 91%; oil; Kugelrohr at 180–200 °C (1.0 mmHg); ^1H NMR (270 MHz, $CDCl_3$) δ 0.84–0.89 (m, 3 H), 0.94 (t, J = 7.0 Hz, 3 H, CH_3CH_2), 1.20–1.34 (m, 6 H), 1.36–1.70 (m, 4 H), 1.54 (t, J = 7.0 Hz, 2 H, $CH_2SnBuCl_2$), 1.80–2.13 (m, 4 H), 2.56 (t, J = 7.3 Hz, 2 H, $CH_2C(O)$), 3.06 (t, J = 7.3 Hz, 2 H, $CH_2CH_2SnBuCl_2$; ^3J (^{119}Sn, ^1H) = 120.1 Hz, ^3J (^{117}Sn, ^1H) = 115.2 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.37, 13.76, 17.09 (^1J (^{119}Sn, ^{13}C) = 555.3 Hz, ^1J (^{117}Sn, ^{13}C) = 531.0 Hz, $Sn(CH_2(CH_2)_2CH_3)Cl_2$), 22.16, 23.59, 25.86, 26.93 (average ^2J ($^{117,119}Sn$, ^{13}C) = 40.8 Hz, $Sn(CH_2CH_2CH_2CH_3)Cl_2$), 28.39, 28.57 (^1J (^{119}Sn, ^{13}C) = 608.1 Hz, ^1J (^{117}Sn, ^{13}C) = 581.7 Hz, $CH_2SnBuCl_2$), 31.16, 37.77 (average ^2J ($^{117,119}Sn$, ^{13}C) = 39.6 Hz, $CH_2CH_2SnBuCl_2$), 41.90, 219.35 (average ^3J ($^{117,119}Sn$, ^{13}C) = 48.5 Hz, C=O); IR (neat) 1674 cm^{-1} (νC=O). Anal. Calcd for $C_{13}H_{26}OSnCl_2$: C, 40.23; H, 6.76. Found: C, 40.46; H, 6.86.

4-Methyl-1-(dichlorobutylstannyl)-3-hexanone (3b′): yield 84%; semisolid; Kugelrohr at 150–155 °C (1.0 mmHg); ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.5 Hz, 3 H), 0.90–1.05 (m, 2 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.13 (d, J = 6.8 Hz, 3 H), 1.39–1.59 (m, 6 H), 1.62–1.93 (m, 2 H), 2.55–2.68 (m, 1 H), 3.10 (ddd, J = 5.6, 7.0, and 7.0 Hz, 2 H, $CH_2CH_2SnBuCl_2$; average ^3J ($^{117,119}Sn$, ^1H) = 122.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.18, 13.37, 15.56, 17.12 (^1J (^{119}Sn, ^{13}C) = 557.6 Hz, ^1J (^{117}Sn, ^{13}C) = 533.2 Hz, $CH_2SnBuCl_2$), 25.83 (average ^2J ($^{117,119}Sn$, ^{13}C) = 41.9 Hz, $Sn(CH_2CH_2CH_2CH_3)Cl_2$), 25.89, 26.93 (average ^3J ($^{117,119}Sn$, ^{13}C) = 37.5 Hz, $Sn((CH_2)_2CH_2CH_3)Cl_2$), 28.59 (^1J (^{119}Sn, ^{13}C) = 609.2 Hz, ^1J (^{117}Sn, ^{13}C) = 581.7 Hz, $Sn(CH_2(CH_2)_2CH_3)Cl_2$), 36.52 (average ^2J ($^{117,119}Sn$, ^{13}C) = 39.6 Hz, $CH_2CH_2SnBuCl_2$), 47.07, 222.95 (average ^3J ($^{117,119}Sn$, ^{13}C) = 44.1 Hz, C=O); IR (neat) 1670 cm^{-1} (νC=O). Anal. Calcd for $C_{11}H_{22}OSnCl_2$: C, 36.70; H, 6.17. Found: C, 36.65; H, 6.12.

4,4-Dimethyl-1-(dichlorobutylstannyl)-3-pentanone (3e′): yield 97%; mp 51.0–51.5 °C; Kugelrohr at 150–155 °C (1.0 mmHg); ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 3 H, $Sn((CH_2)_3CH_3)Cl_2$), 1.12 (s, 9 H, $(CH_3)_3C$), 1.29–1.47 (m, 2 H), 1.49 (t, J = 7.0 Hz, 2 H, $CH_2SnBuCl_2$; average ^2J ($^{117,119}Sn$, ^1H) = 75.2 Hz), 1.71–1.82 (m, 2 H), 1.86–1.95 (m, 2 H), 3.09 (t, J = 7.0 Hz, 2 H, $CH_2CH_2SnBuCl_2$; ^3J (^{119}Sn, ^1H) = 123.5 Hz, ^3J (^{117}Sn, ^1H) = 118.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.32 ($Sn((CH_2)_3CH_3)Cl_2$), 17.79 (^1J (^{119}Sn, ^{13}C) = 565.7 Hz, ^1J (^{117}Sn, ^{13}C) = 540.8 Hz, $CH_2SnBuCl_2$), 25.70 (^2J (^{119}Sn, ^{13}C) = 230.6 Hz, ^2J (^{117}Sn, ^{13}C) = 203.6 Hz, $Sn(CH_2CH_2CH_2CH_3)Cl_2$), 26.07 ($(CH_3)_3C$), 26.83 (average ^3J ($^{117,119}Sn$, ^{13}C) = 41.5 Hz, $Sn((CH_2)_2CH_2CH_3)Cl_2$), 28.50 (^1J (^{119}Sn, ^{13}C) = 609.4 Hz, ^1J (^{117}Sn, ^{13}C) = 582.4 Hz, $Sn(CH_2(CH_2)_2CH_3)Cl_2$), 32.58 (average ^2J ($^{117,119}Sn$, ^{13}C) = 41.5 Hz, $CH_2CH_2SnBuCl_2$), 43.69 (average ^4J ($^{117,119}Sn$, ^{13}C) = 8.3 Hz, $(CH_3)_3C$), 224.52 (average ^3J ($^{117,119}Sn$, ^{13}C) = 40.5 Hz, C=O); IR (KBr) 1662 cm^{-1} (νC=O). Anal. Calcd for $C_{11}H_{22}OSnCl_2$: C, 36.70; H, 6.17. Found: C, 36.71; H, 6.13.

4-(Dichlorobutylstannyl)-2-butanone (3h′): yield 90%; mp 51.5–52.0 °C; Kugelrohr at 150–155 °C (0.55 mmHg); ^1H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.1 Hz, 3 H, $Sn((CH_2)_3CH_3)Cl_2$), 1.37–1.50 (m, 2 H), 1.55 (t, J = 7.1 Hz, 2 H, $CH_2SnBuCl_2$; average ^2J ($^{117,119}Sn$, ^1H) = 75.2 Hz), 1.80–1.93 (m, 2 H), 1.94–2.02 (m, 2 H), 2.34 (s, 3 H, CH_3), 3.11 (t, J = 7.1 Hz, 2 H, $CH_2CH_2SnCl_2$; average ^3J ($^{117,119}Sn$, ^1H) = 119.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.50 ($Sn((CH_2)_3CH_3)Cl_2$), 16.97 (^1J (^{119}Sn, ^{13}C) = 545.3 Hz, ^1J (^{117}Sn, ^{13}C) = 521.1 Hz, $CH_2SnBuCl_2$), 26.04 (^2J (^{119}Sn, ^{13}C) = 109.1

Hz, ^2J (^{117}Sn, ^{13}C) = 104.7 Hz, Sn($CH_2CH_2CH_2CH_3$)Cl_2), 27.01 (average ^3J (^{117,119}Sn, ^{13}C) = 109.1 Hz, Sn($(CH_2)_2CH_2CH_3$)Cl_2), 28.46 (^1J (^{119}Sn, ^{13}C) = 603.7 Hz, ^1J (^{117}Sn, ^{13}C) = 577.2 Hz, Sn($CH_2(CH_2)_2CH_3$)Cl_2), 28.94 ($CH_3C(O)$), 38.85 (average ^2J (^{117,119}Sn, ^{13}C) = 39.7 Hz, $CH_2CH_2SnBuCl_2$), 216.53 (average ^3J (^{117,119}Sn, ^{13}C) = 49.6 Hz, C=O); IR (KBr) 1679 cm^{-1} (νC=O). Anal. Calcd for $C_8H_{16}OSnCl_2$: C, 30.23; H, 5.07. Found: 30.20; H, 5.12.

Representative Procedure for the Synthesis of β-Trichlorostannyl Aldehydes 3s–w. 2-Benzyl-3-(trichlorostannyl)propanal (3s). The preparation of **3s** from siloxycyclopropane **1s** and $SnCl_4$ is described as a typical example. Siloxycyclopropane **1s** (1.10 g, 5.0 mmol) was added to a solution of $SnCl_4$ (1.30 g, 5.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C with continuous stirring for 30 min. The solvent and produced Me_3SiCl were evaporated in vacuo to afford **3s** (1.90 g) as a semisolid, which could not be recrystallized. Chromatographic purification of **3s** on silica gel was also not successful due to the decomposition to the corresponding α-methylene aldehyde. Since the nearly quantitative formation of β-trichlorostannyl aldehydes was checked by ^{1}H NMR of the crude samples, they were subjected to the next dehydrostannation without further purification. Spectral data for **3s** are as follows: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.63 (dd, J_{vic} = 6.6 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2SnCl_3; average ^2J (^{117,119}Sn, ^{1}H) = 103.0 Hz), 1.95 (dd, J_{vic} = 7.5 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2SnCl_3; average ^2J (^{117,119}Sn, ^{1}H) = 103.0 Hz), 2.94 (dd, J_{vic} = 8.5 Hz, J_{gem} = 14.0 Hz, 1 H, CH_2Ph), 3.26 (dd, J_{vic} = 6.3 Hz, J_{gem} = 14.0 Hz, 1 H, CH_2Ph), 3.36–3.47 (m, 1 H, $CHCH_2Ph$), 7.19–7.38 (m, 5 H, Ph), 9.85 (s, 1 H, CHO; average ^4J (^{117,119}Sn, ^{1}H) = 24.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.10 (^1J (^{119}Sn, ^{13}C) = 788.5 Hz, ^1J (^{117}Sn, ^{13}C) = 753.7 Hz, CH_2SnCl_3), 37.37 (^3J (^{119}Sn, ^{13}C) = 90.3 Hz, ^3J (^{117}Sn, ^{13}C) = 86.6 Hz, CH_2Ph), 49.01 (average ^2J (^{117,119}Sn, ^{13}C) = 51.8 Hz, $CHCH_2SnCl_3$), 127.68, 128.83, 129.28, 135.17 (aromatic), 208.52 (average ^3J (^{117,119}Sn, ^{13}C) = 99.4 Hz, C=O); IR (neat) 1684 cm^{-1} (νC=O). For the reasons mentioned above, the elemental analysis of **3s** was not undertaken. However, conversion of **3s** to the stable triethylstannyl aldehyde **9** was carried out, which gave satisfactory spectral and analytical data. **2-Benzyl-3-(triethylstannyl)propanal (9).** Siloxycyclopropane **1s** (0.211 g, 0.957 mmol) was added to a stirred solution of $SnCl_4$ (0.266 g, 1.02 mmol) in $CHCl_3$ (5 mL) at 0 °C. After 15 min, the solvent and the resulting Me_3SiCl were removed by vacuum evaporation and the remaining reaction mixture was diluted with 1,4-dioxane (5 mL). To the solution containing β-trichlorostannyl aldehyde **3s**, $ZnEt_2$ (0.324 mL, 3.16 mmol) was added by a syringe at 15 °C. After 30 min the mixture was treated with saturated aqueous NH_4Cl and extracted with ether. The organic phases were collected, dried, and evaporated under reduced pressure. Crude **9** was purified by flash chromatography (SiO_2, pentane/ether = 40/1) to give **9** (0.251 g, 74%); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.75–1.26 (m, 17 H), 2.67 (dd, J_{vic} = 5.8 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2Ph), 2.70–2.86 (m, 1 H, CHCHO), 3.02 (dd, J_{vic} = 7.9 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2Ph), 7.14–7.29 (m, 5 H, Ph), 9.60 (d, J = 2.1 Hz, 1 H, CHO); ^{13}C NMR (68 MHz, $CDCl_3$) δ 0.99 (^1J (^{119}Sn, ^{13}C) = 332.64 Hz, ^1J (^{117}Sn, ^{13}C) = 318.0 Hz, Sn(CH_2CH_3)$_3$), 7.36 (average ^1J (^{117,119}Sn, ^{13}C) = 259.4 Hz, CH_2SnEt_3), 10.90 (average ^2J (^{117,119}Sn, ^{13}C) = 19.5 Hz, Sn-(CH_2CH_3)$_3$), 39.04 (average ^3J (^{117,119}Sn, ^{13}C) = 29.9 Hz, CH_2Ph), 51.58 (average ^2J (^{117,119}Sn, ^{13}C) = 16.5 Hz, $CHCH_2SnEt_3$), 126.40, 128.52, 128.90, 138.89 (aromatic), 204.13 (average ^3J (^{117,119}Sn, ^{13}C) = 32.3 Hz, C=O); IR (neat) 1720 cm^{-1} (νC=O); EIMS m/z (relative intensity) 325 (100, M^+ – Et), 267 (15, M^+ – 3Et), 207 (13, $SnEt_3$), 91 (30, CH_2Ph). Anal. Calcd for $C_{16}H_{26}OSn$: C, 54.42; H, 7.44. Found: C, 54.61; H, 7.64.

2-[(Trichlorostannyl)methyl]heptanal (3t): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 1.17–1.67 (m, 8 H), 2.00–2.12 (m, 2 H, CH_2SnCl_3), 3.12–3.19 (m, 1 H, $CHCH_2SnCl_3$; average ^3J (^{117,119}Sn, ^{1}H) = 140.0 Hz), 9.84 (s, 1 H, CHO; average ^4J (^{117,119}Sn, ^{1}H) = 28.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.8 (CH_3), 22.19, 23.70 (^1J (^{119}Sn, ^{13}C) = 783.6 Hz, ^1J (^{117}Sn, ^{13}C) = 749.5 Hz, CH_2SnCl_3), 26.57, 31.21 (average ^3J (^{117,119}Sn, ^{13}C) = 82.3 Hz, $CH_2(CH_2)_3CH_3$), 31.26, 47.43 (average ^2J (^{117,119}Sn, ^{13}C) = 54.3 Hz, $CHCH_2SnCl_3$), 209.13 (average ^3J (^{117,119}Sn, ^{13}C) = 110.4 Hz, C=O); IR (neat) 1680 cm^{-1} (νC=O).

3-Methyl-2-[(trichlorostannyl)methyl]butanal (3u): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (d, J = 7.0 Hz, 3 H, $(CH_3)_2CH$), 1.17 (d, J = 7.0 Hz, 3 H, $(CH_3)_2CH$), 1.64 (dd, J_{vic} = 7.0 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2SnCl_3; average ^2J (^{117,119}Sn, ^{1}H) = 81.6 Hz), 1.92 (dd, J_{vic} = 8.5 Hz, J_{gem} = 13.4 Hz, 1 H, CH_2SnCl_3; average ^2J (^{117,119}Sn, ^{1}H) = 81.6 Hz), 2.14–2.61 (m, 1 H, $(CH_3)_2CH$), 3.21–3.30 (m, 1 H, $CHCH_2SnCl_3$; average ^3J (^{117,119}Sn, ^{1}H) = 135.0 Hz), 9.87 (s, 1 H, CHO; average ^4J (^{117,119}Sn, ^{1}H) = 32.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.32 ($(CH_3)_2CH$), 19.81 (^1J (^{119}Sn, ^{13}C) = 794.0 Hz, ^1J (^{117}Sn, ^{13}C) = 759.2 Hz, CH_2SnCl_3), 20.49 ($(CH_3)_2CH$), 30.14 (^3J (^{119}Sn, ^{13}C) = 84.2 Hz, ^3J (^{117}Sn, ^{13}C) = 57.3 Hz, $CH(CH_3)_2$), 53.29 (average ^3J (^{117,119}Sn, ^{13}C) = 57.3 Hz, $CHCH_2SnCl_3$), 209.84 (average ^3J (^{117,119}Sn, ^{13}C) = 112.9 Hz, C=O); IR (neat) 1660 cm^{-1} (νC=O).

2-[(Trichlorostannyl)methyl]-10-undecenal (3v): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.10–1.85 (m, 12 H), 1.86–2.13 (m, 4 H), 3.13 (m, 1 H, $CHCH_2SnCl_3$; average ^3J (^{117,119}Sn, ^{1}H) = 166.2 Hz), 4.91 (dd, J_{vic} = 10.7 Hz, J_{gem} = 0.9 Hz, 1 H, CH=CH_2 (cis)), 4.96 (dd, J_{vic} = 16.8 Hz, J_{gem} = 0.9 Hz, 1 H, CH=CH_2 (trans)), 5.78 (ddt, J = 16.8, 10.2, and 6.7 Hz, 1 H, CH=CH_2), 9.81 (s, 1 H, CHO; average ^4J (^{117,119}Sn, ^{1}H) = 27.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.67 (^1J (^{119}Sn, ^{13}C) = 784.9 Hz, ^1J (^{117}Sn, ^{13}C) = 749.5 Hz, CH_2SnCl_3), 26.92, 28.68, 28.77, 28.97, 29.12, 31.27 (average ^3J (^{117,119}Sn, ^{13}C) = 81.7 Hz, $CH_2CHCH_2SnCl_3$), 33.58, 47.45 (average ^3J (^{117,119}Sn, ^{13}C) = 54.3 Hz, $CHCH_2SnCl_3$), 114.22, 138.85, 208.88 (average ^3J (^{117,119}Sn, ^{13}C) = 110.4 Hz, C=O); IR (neat) 1682 cm^{-1} (νC=O).

2-Methyl-2-[(trichlorostannyl)methyl]butanal (3w): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.33 (s, 3 H, CH_3C), 1.67–1.84 (m, 2 H, CH_3CH_2), 1.72 (d, J_{gem} = 13.1 Hz, 1 H, CH_2SnCl_3; ^2J (^{119}Sn, ^{1}H) = 100.5 Hz, ^2J (^{117}Sn, ^{1}H) = 96.6 Hz), 1.90 (d, J_{gem} = 13.1 Hz, 1 H, CH_2SnCl_3; ^2J (^{119}Sn, ^{1}H) = 107.4 Hz, ^2J (^{117}Sn, ^{1}H) = 102.5 Hz), 9.57 (s, 1 H, CHO; average ^4J (^{117,119}Sn, ^{1}H) = 32.7 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 8.40 (CH_3CH_2), 22.60 (average ^3J (^{117,119}Sn, ^{13}C) = 61.2 Hz, CH_3C), 30.42 (^1J (^{119}Sn, ^{13}C) = 772.2 Hz, ^1J (^{117}Sn, ^{13}C) = 737.0 Hz, CH_2SnCl_3), 30.90 (average ^3J (^{117,119}Sn, ^{13}C) = 42.6 Hz, CH_3CH_2), 49.42 (average ^2J (^{117,119}Sn, ^{13}C) = 55.2 Hz, CCH_2SnCl_3), 210.10 (^3J (^{119}Sn, ^{13}C) = 96.5 Hz, ^3J (^{117}Sn, ^{13}C) = 92.4 Hz, C=O); IR (neat) 1673 cm^{-1} (νC=O).

4,4-Dimethyl-1-(tributylstannyl)-3-pentanone (3e‴) and 4,4-Dimethyl-1-(chlorodibutylstannyl)-3-pentanone (3e″). To a solution of trichlorostannyl ketone (**3e**) (5.0 g, 14.8 mmol) in THF (100 mL) was added n-BuMgBr (20 mL of a 2.29 M solution in THF, 45.9 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h, quenched with a saturated aqueous NH_4Cl solution, and extracted with ether. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (SiO_2, hexane/ether = 40/1) to give **3e‴** (5.50 g, 92%) as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.68–0.97 (m, 15 H), 1.13 (s, 9 H, $(CH_3)_3C$), 1.17–1.55 (m, 14 H), 2.70 (t, J = 7.6 Hz, 2 H, $CH_2CH_2SnBu_3$; average ^3J (^{117,119}Sn, ^{1}H) = 51.2 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 2.29 (^1J (^{119}Sn, ^{13}C) = 305.8 Hz, ^1J (^{117}Sn, ^{13}C) = 292.4 Hz, CH_2SnBu_3), 9.06 (^1J (^{119}Sn, ^{13}C) = 322.1 Hz, ^1J (^{117}Sn, ^{13}C) = 308.8 Hz, Sn($CH_2(CH_2)_2CH_3$)$_3$), 13.71 (Sn($(CH_2)_3CH_3$)$_3$), 26.75 ($(CH_3)_3C$), 27.39 (average ^2J (^{117,119}Sn, ^{13}C) = 53.7 Hz, Sn($CH_2CH_2CH_2CH_3$)$_3$), 29.19 (average ^2J (^{117,119}Sn, ^{13}C) = 20.1 Hz, Sn($(CH_2)_2CH_2CH_3$)$_3$), 33.53 (average ^2J (^{117,119}Sn, ^{13}C) = 18.3 Hz, $CH_2CH_2SnBu_3$), 43.91 ($(CH_3)C$), 217.43 (average ^3J (^{117,119}Sn, ^{13}C) = 32.3 Hz, C=O); IR (neat) 1702 cm^{-1} (νC=O); EIMS m/z (relative intensity) 347 (100, M^+ – Bu), 291 (7, $SnBu_3$), 177 (17, SnBu). Anal. Calcd for $C_{19}H_{40}OSn$: C, 56.58; H, 10.02. Found: C, 56.56; H, 10.01. An NMR sample of 4,4-dimethyl-1-(chlorodibutylstannyl)-3-pentanone (**3e″**) was prepared by the reaction of dichlorostannane **3e′** with 1 equiv of n-BuMgBr in THF at –78 °C for 1 h. NMR data for **3e″** are as follows: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.77–0.94 (m, 5 H), 1.09–1.61 (m, 14 H), 1.14 (s, 9 H, *tert*-butyl), 2.98 (t, J = 7.1 Hz, 2 H, $CH_2CH_2SnBu_2Cl$); ^{13}C NMR (68 MHz, $CDCl_3$), δ 13.52 (Sn($(CH_2)_3CH_3$)$_2$Cl), 18.76 (^1J (^{119}Sn, ^{13}C) = 448.4 Hz, ^1J (^{117}Sn, ^{13}C) = 428.5 Hz, CH_2SnBu_2Cl), 26.25 (Sn($CH_2CH_2CH_2CH_3$)$_2$Cl), 26.32 ($(CH_3)_3C$), 26.53 (Sn($(CH_2)_2CH_2CH_3$)$_2$Cl), 27.90, (Sn($CH_2(CH_2)_2CH_3$)$_2$Cl), 33.79 (average ^2J (^{117,119}Sn, ^{13}C) = 27.5 Hz, $CH_2CH_2SnBu_2Cl$), 43.82 ($(CH_3)_3C$), 224.77 (C=O); IR (neat) 1666 cm^{-1} (νC=O).

Representative Procedure for Dehydrostannation of β-Trichlorostannyl Ketones 3a–r. 2-Methylene-α-tetralone (4o). The preparation of **4o** is described as a typical example.

TMEDA (0.472 g, 4.06 mmol) was added to a solution of β-trichlorostannyl ketone **3o** (1.56 g, 4.06 mmol) in CH_2Cl_2 (3 mL) at 20 °C with continuous stirring for 15 min. The resulting colorless precipitate was separated by filtration through Celite and washed with pentane. Saturated aqueous NaCl (60 mL) was added to the filtrate. The aqueous layer was extracted with pentane (20 mL × 3). The combined organic layers were dried with $MgSO_4$, filtered, and evaporated. Column chromatography (SiO_2, pentane/ether = 2/1) gave **4o** (0.501 g, 78%) as a white solid: mp 46–47 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.84 (t, J = 6.1 Hz, 2 H), 2.98 (t, J = 6.1 Hz, 2 H), 5.43 (s, 1 H, C=CH_2), 6.22 (s, 1 H, C=CH_2), 7.23 (d, J = 7.6 Hz, 1 H), 7.32 (t, J = 7.6 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 1 H), 8.11 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.55, 31.57, 121.52, 126.87, 128.01, 128.38, 133.00, 133.26, 143.28, 144.00, 187.36; IR (KBr) 1673 cm^{-1} (νC=O); EIMS m/z (relative intensity) 158 (M^+, 100), 129 (42), 118 (16), 115 (25), 90 (28); HRMS calcd for $C_{11}H_{10}O$ 158.0731, found 158.0727.

1-Nonen-3-one (4a): yield 92%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.78–0.98 (m, 3 H), 1.17–1.42 (m, 6 H), 1.45–1.73 (m, 2 H), 2.54 (t, J = 7.6 Hz, 2 H, CH_2C(O)), 5.57 (dd, J_{vic} = 10.2 Hz, J_{gem} = 1.5 Hz, 1 H, CH=CH_2), 6.17 (dd, J_{vic} = 17.5 Hz, J_{gem} = 1.5 Hz, 1 H, CH=CH_2), 6.32 (dd, J_{vic} = 10.2 and 17.5 Hz, 1 H, CH=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.91, 22.41, 23.90, 28.85, 31.52, 39.58, 127.68, 136.53, 200.96; IR (neat) 1681 cm^{-1} (νC=O); EIMS m/z (relative intensity) 140 (M^+, 1), 111 (12), 97 (10), 83 (14), 70 (100), 55 (70); HRMS calcd for $C_9H_{16}O$ 140.1201, found 140.1213.

4-Methyl-1-hexen-3-one (4b): yield 86%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.87 (t, J = 7.6 Hz, 3 H, CH_3CH_2), 1.08 (d, J = 6.8 Hz, 3 H, CH_3CH), 1.33–1.48 (m, 1 H, CH_3CH_2), 1.62–1.78 (m, 1 H, CH_3CH_2), 2.66–2.78 (m, 1 H, CH), 5.75 (dd, J_{vic} = 10.2 Hz, J_{gem} = 1.4 Hz, 1 H, CH=CH_2), 6.24 (dd, J_{vic} = 17.5 Hz, J_{gem} = 1.4 Hz, 1 H, CH=CH_2), 6.43 (dd, J_{vic} = 10.2 and 17.5 Hz, 1 H, CH=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.60, 15.89, 25.96, 44.92, 127.82, 135.26, 204.14; IR (neat) 1673 cm^{-1} (νC=O); EIMS m/z (relative intensity) 112 (M^+, 8), 97 (5), 84 (22), 55 (100), 41 (26); HRMS calcd for $C_7H_{12}O$ 112.0888, found 112.0891.

1-Cyclopropyl-1-propen-3-one (4c): yield 79%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90–0.97 (m, 2 H), 1.07–1.13 (m, 2 H), 2.15–2.24 (m, 1 H), 5.82 (dd, J_{vic} = 10.5 Hz, J_{gem} = 1.4 Hz, 1 H, CH=CH_2), 6.28 (dd, J_{vic} = 17.5 Hz, J_{gem} = 1.4 Hz, 1 H, CH=CH_2), 6.47 (dd, J_{vic} = 10.5 and 17.5 Hz, 1 H, CH=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.26, 18.31, 44.62, 127.56, 136.69, 200.72; IR (neat) 1666 cm^{-1} (νC=O); EIMS m/z (relative intensity) 96 (M^+, 8), 69 (34), 55 (100), 41 (30); HRMS calcd for C_6H_8O 96.0575, found 96.0569.

4-Methyl-1-penten-3-one (4d): yield 83%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.07 (d, J = 6.8 Hz, 6 H, $(CH_3)_2$CH), 2.79–2.89 (m, 1 H, $(CH_3)_2$CH), 5.72 (dd, J_{vic} = 10.2 Hz, J_{gem} = 1.9 Hz, 1 H, CH=CH_2), 6.21 (dd, J_{vic} = 17.5, J_{gem} = 1.9 Hz, 1 H, CH=CH_2), 6.40 (dd, J_{vic} = 10.2 and 17.5 Hz, 1 H, CH=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.17, 38.03, 127.85, 134.65, 204.06; IR (neat) 1695 cm^{-1} (νC=O); EIMS m/z (relative intensity) 98 (M^+, 10), 70 (13), 55 (100), 43 (18); HRMS calcd for $C_6H_{10}O$ 98.0731, found 98.0734.

4,4-Dimethyl-1-penten-3-one (4e): yield 81%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 9 H, $(CH_3)_3$C), 5.61 (dd, J_{vic} = 10.2 Hz, J_{gem} = 1.9 Hz, 1 H, CH=CH_2 (cis)), 6.29 (dd, J_{vic} = 17.0 Hz, J_{gem} = 1.9 Hz, 1 H, CH=CH_2 (trans)), 6.78 (dd, J_{vic} = 10.2 and 17.0 Hz, 1 H, CH=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.88, 42.88, 128.18, 130.67, 204.19; IR (neat) 1693 (νC=O), 1610 cm^{-1} (νC=C); EIMS m/z (relative intensity) 112 (M^+, 3), 84 (14), 70 (10), 57 (100), 55 (25), 41 (48); HRMS calcd for $C_7H_{12}O$ 112.0888, found 112.0889.

3-Phenyl-1-propen-3-one (4f): yield 81%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.93 (dd, J_{vic} = 11.2 Hz, J_{gem} = 1.9 Hz, 1 H, CH=CH_2), 6.43 (dd, J_{vic} = 17.1 Hz, J_{gem} = 1.9 Hz, 1 H, CH=CH_2), 7.16 (dd, J_{vic} = 11.2 and 17.1 Hz, 1 H, CH=CH_2), 7.48 (t, J = 7.3 Hz, 2 H, m-Ph), 7.58 (t, J = 7.3 Hz, 1 H, p-Ph), 7.95 (d, J = 7.3 Hz, 2 H, o-Ph); ^{13}C NMR (68 MHz, $CDCl_3$) δ 128.55, 128.62, 130.11, 132.33, 132.91, 137.21, 191.01; IR (neat) 1672 cm^{-1} (νC=O); EIMS m/z (relative intensity) 132 (M^+, 54), 105 (100), 77 (70), 55 (15), 51 (26); HRMS calcd for C_9H_8O 132.0575, found 132.0565.

3-Cyclohexenyl-1-propen-3-one (4g): yield 84%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.51–1.71 (m, 4 H), 2.20–2.34 (m, 4 H), 5.67 (dd, J_{vic} = 10.7 Hz, J_{gem} = 1.9 Hz, 1 H, CH=CH_2), 6.21 (dd, J_{vic} = 16.8 Hz, J_{gem} = 1.9 Hz, 1 H, CH=CH_2), 6.90 (dd, J_{vic} = 10.7 and 16.8 Hz, 1 H, CH=CH_2), 6.91 (m, 1 H, CH=C); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.48, 21.82, 23.19, 26.14, 127.53, 131.47, 139.58, 141.20, 191.43; IR (neat) 1654 (νC=O), 1636, 1604 cm^{-1} (νC=C); EIMS m/z (relative intensity) 136 (M^+, 68), 121 (19), 108 (32), 81 (100), 79 (55), 55 (68); HRMS calcd for $C_9H_{12}O$ 136.0888, found 136.0910.

3-Phenyl-2-methyl-1-propen-3-one (4i). For the isolation of this compound, evaporation was carefully undertaken with cooling (below −40 °C); yield 72%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.06 (s, 3 H, CH_3), 5.60 (d, J_{gem} = 1.8 Hz, 1 H, C=CH_2), 5.88 (d, J_{gem} = 1.8 Hz, 1 H, C=CH_2), 7.40 (t, J = 7.3 Hz, 2 H, o-Ph), 7.50 (t, J = 7.3 Hz, 1 H, p-Ph), 7.72 (d, J = 7.3 Hz, 2 H, m-Ph); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.46, 126.84, 127.98, 129.22, 131.83, 137.56, 143.60, 198.09; IR (neat) 1655 cm^{-1} (νC=O), EIMS m/z (relative intensity) 146 (M^+, 31); HRMS calcd for $C_{10}H_{10}O$ 146.0731, found 146.0736. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: 82.04; H, 6.84.

2-Methylenecyclohexanone (4j): yield 76%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.69–1.78 (m, 2 H), 1.82–1.91 (m, 2 H), 2.33–2.46 (m, 2 H), 2.52–2.57 (m, 2 H), 5.11 (d, J = 1.9 Hz, 1 H, C=CH_2), 5.80 (d, J = 1.9 Hz, 1 H, C=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.10, 24.33, 32.81, 40.71, 120.15, 145.30, 201.88; IR (neat) 1691 (νC=O), 1613 cm^{-1} (νC=C); EIMS m/z (relative intensity) 110 (M^+, 36), 82 (29), 67 (100), 54 (43), 41 (30); HRMS calcd for $C_7H_{10}O$ 110.0731, found 110.0748.

2-(Dideuteriomethylene)cyclohexanone (4k): yield 82%; EIMS m/z (relative intensity) 112 (M^+, 89), 84 (53), 69 (65), 67 (100), 56 (59), 41 (42). The product deuterium content was determined to be 95% by MS.

2-Methylenenopinone (4l):[27] yield 90%; EIMS m/z (relative intensity) 150 (M^+, 94), 135 (100), 107 (70), 83 (90), 55 (93); HRMS calcd for $C_{10}H_{14}O$ 150.1044, found 150.1037.

6-Methyl-2-methylenecyclohexanone (4m): yield 84%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.09 (d, J = 6.8 Hz, 3 H, CH_3), 1.43–2.10 (m, 4 H), 2.28–2.66 (m, 3 H), 5.04 (d, J_{gem} = 1.7 Hz, 1 H, C=CH_2), 5.66 (d, J_{gem} = 1.7 Hz, 1 H, C=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 15.42, 23.61, 32.68, 33.51, 44.75, 119.00, 146.00, 204.64; IR (neat) 1690 cm^{-1} (νC=O); EIMS m/z (relative intensity) 124 (M^+, 15), 109 (3), 96 (43), 81 (100), 67 (27), 55 (40), 41 (35); HRMS calcd for $C_8H_{12}O$ 124.0888, found 124.0866.

2-Methylenecycloheptanone (4p): yield 80%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.60–0.81 (m, 6 H), 2.46–2.49 (m, 2 H), 2.57–2.60 (m, 2 H), 5.23 (d, J_{gem} = 2.1 Hz, 1 H, CH_2=C), 5.94 (d, J_{gem} = 2.1 Hz, 1 H, CH_2=C); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.25, 30.47, 31.26, 33.79, 43.40, 122.44 (CH_2=C), 148.30 (CH_2=C), 203.66 (C=O); IR (neat) 1690 (νC=O), 1611 cm^{-1} (νC=C); EIMS m/z (relative intensity) 124 (M^+, 64), 96 (50), 81 (93), 67 (97), 54 (100); HRMS calcd for $C_8H_{12}O$ 124.0888, found 124.0903.

2-Methylenecyclooctanone (4q): yield 70%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.41–1.84 (m, 8 H), 2.57–2.63 (m, 4 H), 5.22 (d, J = 1.9 Hz, 1 H, C=CH_2), 5.86 (d, J = 1.9 Hz, 1 H, C=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.36, 26.17, 28.94, 30.65, 31.31, 39.39, 121.99, 148.67, 206.92; IR (neat) 1684 (νC=O), 1606 cm^{-1} (νC=C); EIMS m/z (relative intensity) 138 (M^+, 38), 110 (11), 95 (20), 82 (50), 67 (100), 54 (64), 41 (62); HRMS calcd for $C_9H_{14}O$ 138.1044, found 138.1044.

2-Methylenecyclododecanone (4r): yield 86%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.15–1.46 (m, 14 H), 1.61–1.77 (m, 2 H), 2.33–2.40 (m, 2 H), 2.65–2.73 (m, 2 H), 5.67 (s, 1 H, C=CH_2), 5.84 (s, 1 H, C=CH_2); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.60, 23.09, 23.58, 23.64, 24.34, 24.43, 26.31, 26.42, 31.87, 38.96, 124.39, 128.18, 204.83; IR (neat) 1673 cm^{-1} (νC=O); EIMS m/z (relative intensity) 194 (M^+, 43), 165 (8), 151 (17), 137 (27), 123 (40), 109 (60), 95 (69), 81 (63), 67 (73), 55 (90); HRMS calcd for $C_{13}H_{22}O$ 194.1670, found 194.1694.

***One-Pot* Conversion of Siloxycyclopropane 1f to α-Methylene Ketone 4f.** To a solution of $SnCl_4$ (1.53 g, 5.86 mmol) in CH_2Cl_2 (15 mL) was added siloxycyclopropane **1f** (1.21 g, 5.86 mmol) at 0 °C. After 30 min at 0 °C, TMEDA (0.817 g, 7.03 mmol) was added to the reaction mixture. The mixture was stirred for 15 min at 20 °C and filtered through Celite, and then saturated aqueous NaCl (60 mL) was added. The aqueous layer was extracted with pentane (20 mL × 3). The combined organic layer was dried with $MgSO_4$, filtered, and evaporated. Short-column

(27) Nishino, C.; Takayanagi, H. *Agric. Biol. Chem.* **1979**, *43*, 1967.

chromatography (SiO_2, pentane/ether = 10/1) gave **4f** (0.618 g, 80%).

1-Cyclopropyl-3-(phenylthio)-1-propanone (5). TMEDA (0.232 g, 2.0 mmol) was added to a solution of β-trichlorostannyl ketone **3c** (0.322 g, 1.0 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at 20 °C for 15 min. Thiophenol (0.132 g, 1.2 mmol) was added to the reaction mixture and stirred for 60 min. A saturated aqueous NaCl (60 mL) was added to the mixture. The aqueous layer was extracted with ether (20 mL × 2). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated. Flash chromatography (SiO_2, pentane/ether = 5/1) gave **5** (0.142 g, 72%): ^1H NMR (270 MHz, $CDCl_3$) δ 0.86–1.04 (m, 4 H), 1.83–1.90 (m, 1 H), 2.85–2.90 (m, 2 H), 3.12–3.17 (m, 2 H), 7.15–7.35 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.88, 20.61, 27.50, 42.75, 126.15, 128.92, 129.41, 135.78, 208.63; IR (neat) 1701 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 206 (M^+, 68), 178 (8), 165 (5), 150 (23), 137 (29), 123 (36), 109 (38), 97 (19), 69 (100), 41 (65); HRMS calcd for $C_{12}H_{14}OS$ 206.0765, found 206.0737.

2,2-Dimethyl-5-(phenylthio)-3-pentanone (6). Similar treatment of **3e** (0.338 g, 1 mmol), as described for **5**, **6** (0.188 g, 81%): ^1H NMR (270 MHz, $CDCl_3$) δ 1.10 (s, 9 H, $(CH_3)_3C$), 2.80 (t, *J* = 7.0 Hz, 2 H, CH_2SPh), 3.14 (t, *J* = 7.0 Hz, 2 H, CH_2CH_2SPh), 7.17–7.34 (m, 5 H, Ph); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.22, 27.84, 36.24, 44.08, 126.06, 128.95, 129.13, 136.06, 213.79; IR (neat) 1695 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 222 (M^+, 87), 165 (26), 137 (75), 123 (100), 110 (52), 57 (93). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.12; H, 8.17. Found: C, 70.10; H, 8.15.

2-Methyl-2-(4,4-dimethyl-3-oxopentyl)-1,3-cyclohexanedione (7). TMEDA (1.16 g, 10.0 mmol) was added to a solution of β-trichlorostannyl ketone **3e** (1.691 g, 5.0 mmol) in CH_2Cl_2 (1 mL). After 15 min of stirring at 20 °C, 2-methyl-1,3-cyclohexanedione (0.631 g, 5.0 mmol), hydroquinone (5.5 mg, 0.05 mmol), and distilled water (2 mL) were added to the reaction mixture. The mixture was stirred at 40 °C for 14 h.[15] Saturated aqueous NaCl (80 mL) was added to the mixture. The aqueous layer was extracted with ether (30 mL × 2). The combined organic layers were dried with $MgSO_4$, filtered, and evaporated. Column chromatography (SiO_2, hexane/ether = 2.1) gave **7** (0.763 g, 63%): ^1H NMR (270 MHz, $CDCl_3$) δ 1.10 (s, 9 H, $(CH_3)_3C$), 1.24 (s, 3 H, CH_3), 1.86–2.10 (m, 4 H), 2.37–2.42 (m, 2 H), 2.57–2.83 (m, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 17.57, 19.25, 26.22, 30.30, 31.05, 37.57, 44.05, 64.47, 209.87, 214.71; IR (neat) 1725 and 1696 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 238 (M^+, 7), 181 (77), 153 (12), 139 (100), 127 (21), 111 (41), 55 (42); HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1579. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.54; H, 9.32. Found: C, 70.20; H, 9.09.

2-[(Diethylamino)methyl]cyclooctanone (8). Diethylamine (0.662 g, 9.06 mmol) was added to a solution of β-trichlorostannyl ketone **3q** (1.10 g, 3.02 mmol) in CH_2Cl_2 (5 mL). After 30 min of stirring at 20 °C, saturated aqueous NaCl (50 mL) was added to the reaction mixture. The aqueous layer was extracted with pentane (20 mL × 2). The combined organic layers were dried with $MgSO_4$, filtered, and evaporated. Column chromatography (SiO_2, pentane/ether = 1/1) gave **8** (0.459 g, 72%): ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.0 Hz, 6 H, $N(CH_2CH_3)_2$), 1.11–2.08 (m, 10 H), 2.18–2.52 (m, 7 H), 2.66–2.93 (m, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.70, 24.63, 24.82, 25.47, 27.61, 31.42, 42.70, 47.30, 48.76, 55.98, 219.43; IR (neat) 1702 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 211 (M^+, 1), 196 (1), 86 (100), 72 (3), 58 (10); HRMS calcd for $C_{13}H_{25}ON$ 211.1936, found 211.1931. Anal. Calcd for $C_{13}H_{25}ON$: C, 73.88; H, 11.92; N, 6.63. Found: C, 73.88; H, 12.06; N, 6.34.

Dehydrostannation of β-Trichlorostannyl Aldehydes 3s, 3t, and 3u with TMEDA. 2-Methyleneheptanal (4t). The preparation of **4t** is described as a typical example. To a solution of $SnCl_4$ (1.16 g, 4.49 mmol) in CH_2Cl_2 (20 mL) was added siloxycyclopropane **1t** (0.900 g, 4.49 mmol) at 0 °C with continuous stirring for 30 min. TMEDA (0.572 g, 4.93 mmol) was added to the reaction mixture. After 15 min of stirring at 20 °C, the resulting colorless precipitate was separated by filtration through Celite and washed with pentane. Saturated aqueous NaCl (60 mL) was added to the filtrate. The aqueous layer was extracted with pentane (20 mL × 2). The combined organic layers were dried with $MgSO_4$, filtered, and evaporated. Column chromatography (SiO_2, pentane/ether = 1/1) gave 2-methyleneheptanal (**4t**) (0.470 g, 83%): ^1H NMR (270 MHz, $CDCl_3$) δ 0.83 (t, *J* = 6.5 Hz, 3 H, CH_3), 1.18–1.48 (m, 6 H), 2.18 (t, *J* = 7.5 Hz, 2 H, CH_2C), 5.93 (s, 1 H, C=CH_2), 6.19 (s, 1 H, C=CH_2), 9.48 (s, 1 H, CHO); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.83, 22.29, 27.32, 27.61, 31.34, 133.74, 150.38, 194.62; IR (neat) 1697 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 126 (M^+, 35), 83 (20), 70 (51), 55 (100), 41 (69); HRMS calcd for $C_8H_{14}O$ 126.1044, found 126.1061.

2-Methylene-3-phenylpropanal (4s): yield 70%; ^1H NMR (270 MHz, $CDCl_3$) δ 3.54 (s, 2 H, CH_2Ph), 6.02 (s, 1 H, C=CH_2), 6.07 (s, 1 H, C=CH_2), 7.14–7.30 (m, 5 H), 9.57 (s, 1 H, CHO); ^{13}C NMR (68 MHz, $CDCl_3$) δ 18.46, 126.84, 127.98, 129.22, 131.83, 137.56, 143.60, 198.09; IR (neat) 1655 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 146 (M^+, 92), 128 (19), 116 (100), 91 (63), 89 (12), 78 (30), 65 (28). Anal. Calcd for $C_{10}H_{10}O$: C, 82.14; H, 6.90. Found: C, 82.05; H, 7.04.

3-Methyl-2-methylenebutanal (4u): yield 71%; ^1H NMR (270 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.8 Hz, 6 H, $(CH_3)_2CH$), 2.69–2.78 (m, 1 H, $(CH_3)_2CH$), 5.89 (s, 1 H, C=CH_2), 6.18 (s, 1 H, C=CH_2), 9.46 (s, 1 H, CHO); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.17, 26.04, 132.02, 156.33, 194.48; IR (neat) 1697 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 98 (M^+, 80), 83 (30), 69 (73), 55 (48), 41 (100); HRMS calcd for $C_6H_{10}O$ 98.0731, found 98.0718.

2-Methylene-10-undecenal (4v). To a solution of $SnCl_4$ (1.04 g, 4.0 mmol) in CH_2Cl_2 (10 mL) was added siloxycyclopropane **1v** (1.02 g, 4.0 mmol) at 0 °C with continuous stirring for 30 min. The solvent and produced Me_3SiCl were evaporated under reduced pressure. The resulting crude was treated with DMSO (1.0 mL) in hexane (5 mL) at 15 °C for 1 h, followed by separation of a white precipitate and aqueous treatment (ether/aqueous NH_4Cl). The combined organic layers were dried with $MgSO_4$, filtered, and evaporated. Column chromatography (SiO_2, hexane/ether = 5/1) gave **4v** (0.519 g, 72%): ^1H NMR (270 MHz, $CDCl_3$) δ 1.16–1.50 (m, 10 H), 1.97–2.04 (m, 2 H), 2.18–2.23 (m, 2 H), 4.90 (dd, J_{vic} = 11.2 Hz, J_{gem} = 1.4 Hz, 1 H, CH=CH_2), 4.95 (dd, J_{vic} = 17.5 Hz, J_{gem} = 1.4 Hz, 1 H, CH=CH_2), 5.70–5.85 (m, 1 H, CH=CH_2), 5.95 (s, 1 H, C=CH_2), 6.21 (s, 1 H, C=CH_2), 9.51 (s, 1 H, CHO); ^{13}C NMR (68 MHz, $CDCl_3$) δ 27.69, 28.82, 28.96, 29.17, 29.20, 29.22, 33.71, 114.10, 133.78, 139.05, 150.42, 194.67; IR (neat) 1694 cm^{-1} (νC=O); EIMS *m/z* (relative intensity) 180 (M^+, 1), 165 (2), 151 (7), 137 (9), 123 (23), 109 (35), 95 (48), 81 (45), 67 (60), 55 (81), 41 (100); HRMS calcd for $C_{12}H_{20}O$ 180.1514, found 180.1510.

$HSnCl_3$·Py (14). Me_3SiCl (1.48 mL, 11.7 mmol) was added to a suspension of $SnCl_2·2H_2O$ (2.20 g, 9.75 mmol) in ether (20 mL) at 20 °C and stirred for 15 min. Then, pyridine (0.79 mL, 9.75 mmol) was added to this reaction mixture containing $HSnCl_3·(Et_2O)_n$[5a] at 20 °C. After stirring at 20 °C for 10 min, the precipitate was separated by filtration and washed with pentane. Recrystallization from pentane/acetone gave $HSnCl_3$·Py (**14**) (2.79 g, 94%): decomposed >300 °C without melting; ^1H NMR (270 MHz, acetone-d_6) δ 8.35 (bs, 2 H, aromatic), 8.87 (bs, 1 H, aromatic), 8.21 (bs, 2 H, aromatic). Significant peak belonging to Sn–H could not be identified. Anal. Calcd for $C_6H_6NSnCl_3$: C, 19.67; H, 1.98; N, 4.58. Found: C, 19.90; H, 2.00; N, 4.63.

Reaction of Methyl Vinyl Ketone with $HSnCl_3$·Py (14) in the Presence of $SnCl_4$. To a stirred solution of **14** (0.08 g, 0.262 mmol) and methyl vinyl ketone (0.018 g, 0.262 mmol) in $CDCl_3$ (1 mL) at 20 °C under N_2 was added $SnCl_4$ (0.136 g, 0.524 mmol). The mixture was stirred at 20 °C for 42 h. ^1H NMR analysis of the reaction mixture showed β-trichlorostannyl ketone **3x** (18%) and unreacted methyl vinyl ketone (77%). The assignment of structure is based on the ^1H NMR spectrum obtained by hydrotrichlorostannation of methyl vinyl ketone:[5a] δ 1.70 (t, *J* = 7.3 Hz, 2 H, CH_2SnCl_3), 2.50 (s, 3 H, CH_3), 3.17 (t, *J* = 7.3 Hz, 2 H, $CH_2CH_2SnCl_3$).

Dehydrostannation of 2-[1′-(Trichlorostannyl)ethyl]cyclohexanone (3y).[5a] To a stirred suspension of $SnCl_2·2H_2O$ (0.75 g, 3.3 mmol) in ether (7 mL) was added chlorotrimethylsilane (0.5 mL, 3.3 mmol) at 20 °C. After 10 min, (*E*)-ethylidenecyclohexanone (**4y**)[28] (0.414 g, 3.3 mmol) was added to the reaction mixture in one portion. The resulting mixture was stirred at 20 °C for 1 h. After removal of the solvent and the hexamethyl-

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siloxane formed as a byproduct, the residual oil was dried under reduced pressure to give **3y** (1.12 g, 97%) (a mixture of two isomers; 36:64): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.37 (d, J = 7.3 H, 3 H, CH_3(major); average ^3J (^{117,119}Sn, ^{1}H) = 220.7 Hz), 1.43 (d, J = 7.3 Hz, 3 H, CH_3(minor); average ^3J (^{117,119}Sn, ^{1}H) = 219.6 Hz), 1.56-1.90 (m, 3 H), 1.95-2.13 (m, 1 H), 2.20-2.61 (m, 4 H), 2.67-2.78 (m, 1 H, C*H*CH_3(minor)), 2.77-2.90 (m, 1 H), 3.03-3.20 (m, 1 H, C*H*CH_3(major); average ^2J (^{117,119}Sn, ^{1}H) = 254.2 Hz). Anal. Calcd for $C_8H_{13}OSnCl_3$: C, 27.43; H, 3.74. Found: C, 27.16; H, 3.65. To the solution of **3y** in $CDCl_3$ was added 1 equiv of pyridine at 20 °C. ^{1}H NMR analysis of the reaction mixture showed almost exclusive formation of (*E*)-ethylidenecylohexanone (>98%). We estimated the *E*/*Z* ratio of product to be 98/2 by integration of the vinyl protons; the chemical shift of *E* form is 6.92 and that of *Z* form is 5.49.

Acknowledgment. Support of this work by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan is gratefully acknowledged. Thanks are given to the Instrumental Analysis Center, Faculty of Engineering, Osaka University for assistance in obtaining MS, HRMS, 600-MHz NMR, and elemental analyses. We thank Shin-Etsu Chem. Co. Ltd. for a gift of trimethylchlorosilane.

Registry No. **1a**, 137518-38-8; **1b**, 137518-39-9; **1c**, 42161-97-7; **1d**, 101653-02-5; **1e**, 38858-75-2; **1f**, 38858-73-0; **1g**, 54781-38-3; **1h**, 137518-40-2; **1i**, 56011-29-1; **1j**, 38858-74-1; **1k**, 127375-76-2; **1l**, 99957-05-8; (*E*)-**1m**, 50629-63-5; (*Z*)-**1m**, 50629-49-7; **1n**, 50338-50-6; **1o**, 38858-76-3; **1p**, 50338-48-2; **1q**, 50338-49-3; **1r**, 59454-27-2; **1s**, 137518-41-3; **1t**, 137518-42-4; **1u**, 137518-43-5; **1v**, 101653-03-6; **1w**, 137518-44-6; **3a** (CC entry), 137518-67-3; **3a** (stannane entry), 137518-48-0; **3a'** (CC entry), 137518-68-4; **3a'** (stannane entry), 137518-49-1; **3b** (CC entry), 137518-69-5; **3b** (stannane entry), 137518-50-4; **3b'** (CC entry), 137518-70-8; **3b'** (stannane entry), 137518-51-5; **3c** (CC entry), 137518-71-9; **3c** (stannane entry), 137518-52-6; **3d** (CC entry), 101653-12-7; **3d** (stannane entry), 101653-05-8; **3d'** (CC entry), 137518-72-0; **3d'** (stannane entry), 137518-53-7; **3e** (CC entry), 101653-11-6; **3e** (stannane entry), 101653-04-7; **3e'** (CC entry), 137518-73-1; **3e'** (stannane entry), 137518-54-8; **3e''** (CC entry), 137518-85-5; **3e''** (stannane entry), 137518-47-9; **3e'''**, 97782-58-6; **3f** (CC entry, 137518-74-2; **3f** (stannane entry), 137518-55-9; **3g** (CC entry), 101653-13-8; **3g** (stannane entry), 101653-06-9; **3h'** (CC entry), 137518-75-3; **3h'** (stannane entry), 137518-56-0; **3i** (CC entry), 101653-14-9; **3i** (stannane entry), 101653-07-0; **3j** (CC entry), 137518-76-4; **3j** (stannane entry), 137518-57-1; **3k** (CC entry), 137518-77-5; **3k** (stannane entry), 137518-58-2; **3l** (CC entry), 137518-78-6; **3l** (stannane entry), 137518-59-3; **3m** (CC entry), 101653-15-0; **3m** (stannane entry), 101653-08-1; **3n** (CC entry), 101653-16-1; **3n** (stannane entry), 101653-09-2; **3o** (CC entry), 137518-79-7; **3o** (stannane entry), 137518-60-6; **3p** (CC entry), 101653-17-2; **3p** (stannane entry), 101653-10-5; **3** (CC entry), 101653-18-3; **3q** (stannane entry), 101670-94-4; **3r** (CC entry), 137518-80-0; **3r** (stannane entry), 137518-61-7; **3s** (CC entry), 137518-81-1; **3s** (stannane entry), 137518-62-8; **3t** (CC entry), 137518-82-2; **3t** (stannane entry), 137518-63-9; **3u** (CC entry), 137518-83-3; **3u** (stannane entry), 137518-64-0; **3v** (CC entry), 101653-19-4; **3v** (stannane entry), 137518-65-1; **3w** (CC entry), 137518-84-4; **3w** (stannane entry), 137518-66-2; **3x** (CC entry), 123992-97-2; **3x** (stannane entry), 59586-09-3; **3y** (CC entry), 137518-86-6; **3y** (stannane entry), 137518-46-8; **4a**, 24415-26-7; **4b**, 21509-95-5; **4c**, 59819-62-4; **4d**, 1606-47-9; **4e**, 2177-30-2; **4f**, 768-03-6; **4g**, 62672-77-9; **4i**, 769-60-8; **4j**, 3045-98-5; **4k**, 137518-37-7; **4l**, 57089-67-5; **4m**, 42858-50-4; **4o**, 13203-73-1; **4p**, 3045-99-6; **4q**, 3045-71-4; **4r**, 3045-76-9; **4s**, 30457-88-6; **4t**, 4125-23-9; **4u**, 4417-80-5; **4v**, 22414-69-3; (*E*)-**4y**, 7417-55-2; **5**, 137518-34-4; **6**, 137518-35-5; **7**, 137518-36-6; **8**, 100539-22-8; **9**, 137518-45-7; **14**, 137540-36-4; $SnCl_4$, 7646-78-8; *n*-$BuSnCl_3$, 1118-46-3; $HSnCl_3$, 20265-43-4; $CH_3COCH{=}CH_2$, 78-94-4.

Supplementary Material Available: ^{1}H or ^{13}C NMR spectra of new compounds for which elemental analyses were not obtained (14 pages). Ordering information is given on any current masthead page.

Pinacol Homocoupling of (*S*)-2-[*N*-(Benzyloxycarbonyl)amino] Aldehydes by $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$. Synthesis of C_2-Symmetric (1*S*,2*R*,3*R*,4*S*)-1,4-Diamino 2,3-Diols

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Received June 20, 1991

Six (*S*)-2-[*N*-(benzyloxycarbonyl)amino] aldehydes **3a-f** were homocoupled by $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (**1**) to give C_2-symmetric (1*S*,2*R*,3*R*,4*S*)-1,4-bis[*N*-(benzyloxycarbonyl)amino] 2,3-diols **4a-f** in good yield. High-yield conversions of the diols to bisoxazolidinones (sodium hydride, tetrahydrofuran) and to the deprotected (1*S*,2*R*,3*R*,4*S*)-1,4-diamino 2,3-diol dihydrochloride salts (10% Pd/C, formic acid, HCl in ether) were performed.

Multidentate, chiral, C_2-symmetric ligands are well-known for their ability to impart asymmetry to transition and main-group elements.[1] Among such molecules, C_2-symmetric diols,[2] diamines,[3] and diphosphines[4] have found the most frequent applications, especially in the area of asymmetric catalysis. Many of these ligands have been derived from naturally occurring C_2-symmetric molecules which are available in optically pure form (e.g., tartaric acid).[1] However, the small number of such chiral pre-

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