296 K. One octant of data was collected[20] to a 2θ limit of 145° for 6268 measured reflections with 2708 observed with $I \geq 3\sigma(I)$. The structure was solved using SHELXS-86[21] and refined[22] using full-matrix least-squares on F with a weighting scheme of $1/\sigma^2(F)$. The final agreement statistics are as follows: $R = 0.065$, $wR = 0.065$, $S = 2.88$, $(\Delta/\sigma)_{max} = 0.07$ for 550 parameters. The maximum peak height in a final difference Fourier is 0.25(6) e Å^{-3}. The refined structure model has all non-H atoms refined with anisotropic thermal parameters and the H atoms included at their calculated positions and constrained to ride with their attached atom. The trimethylsilyl groups possibly suffer from rotational disorder, as indicated by the large thermal parameters for these atoms. However, examination of difference Fourier maps does not reveal obvious alternate positions, and it was decided to limit the model to anisotropic refinement without disorder positions.

Refinement of the enantiomeric structure, under identical conditions, gave R-factors which were not significantly different from the original model. Thus, the anomalous dispersion effects of the Si atoms do not, in this case, permit assignment of the absolute configuration based solely on the crystallography.

Tables of crystallographic coordinates, thermal parameters, and geometrical quantities have been included in the supplementary material.

Acknowledgment. We thank Dr. Frank VanMiddlesworth and Dr. Guy Harris for a generous supply of zaragozic acid A. We also thank Dr. Lawrence Colwell, Dr. E. Tracy Jones and Debrah Zink for obtaining mass spectrometric data and Dr. Gautam Sanyal for determining the CD spectra.

Supplementary Material Available: Proton NMR spectra of 4–6 and 8–15 and the ORTEP diagram of 17 (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(20) The diffractometer control programs are those supplied by Rigaku and Molecular Structure Corporation for operating the AFC5R diffractometer.

(21) Sheldrick, G. M. SHELXS-86. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Oxford University Press: New York, 1985; pp 175–189.

(22) *Structure Determination Package Version 3*; Enraf-Nonius: Delft, The Netherlands, 1985.

(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

(Z)- and (E)-γ-Silyloxy Allylic Stannanes. Highly Syn Selective Reagents for S_E' Additions to Aldehydes

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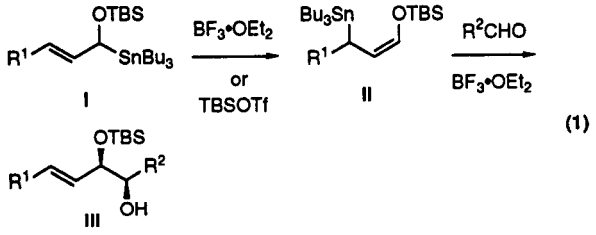
The (E)-γ-silyloxy allylic stannane **2E**, available in one step through addition of $Bu(Bu_3Sn)Cu(CN)Li_2$ to crotonaldehyde and subsequent in situ quenching of the enolate with t-$BuMe_2SiCl$, undergoes BF_3-promoted addition to representative aldehydes **3a–e**, affording syn adducts **4a–e** with >99:1 diastereoselectivity. The (Z)-γ-silyloxy allylic stannane **2Z** can be prepared by treatment of the adduct from Bu_3SnLi and crotonaldehyde with TBSOTf in the presence of i-Pr_2NEt. Stannane **2Z** also affords syn adducts upon BF_3-promoted addition to aldehydes **3a–e** but with somewhat lower diastereoselectivity (93:7–99:1).

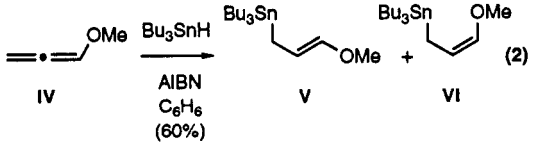
We recently described the synthesis of (Z)-γ-silyloxy allylic stannanes through 1,3-isomerization of the (E)-α-silyloxy isomers (eq 1).[1] At the time we noted that the



(1)

crotyl reagent (**II**, $R^1 = CH_3$) added to heptanal to give the adduct **III** ($R^1 = CH_3$, $R^2 = n$-C_6H_{13}) with 97:3 syn:anti selectivity. We subsequently employed the tridecenyl analogue of **II** ($R^1 = n$-$C_{10}H_{21}$) in a synthesis of the cytotoxic acetogenins (+)- and (−)-muricatacin.[2] In that application addition of **II** ($R^1 = n$-$C_{10}H_{21}$) to a conjugated aldehyde also proceeded with high syn stereoselectivity (95:5). The present report discloses a general route to (E)-γ-silyloxy allylic stannanes and summarizes our findings on additions of both Z and E isomers to representative aldehydes leading to syn 1,2-diol derivatives with >99:1 diastereoselectivity in the case of the latter reagents.

Prior to these studies (E)-γ-alkoxy allylic stannanes were not generally available. Koreeda prepared the (E)-(γ-methoxyallyl)stannane **V** as a 1:1 mixture with the Z isomer **VI**, through hydrostannation of methoxyallene (eq 2).[3]



(2)

We find that the higher order cyanocuprate $Bu(Bu_3Sn)Cu(CN)Li_2$[4] smoothly adds 1,4 to enals, and the resulting (E)-enolate can be trapped with TBSCl (eq 3).[5] In contrast, the 1,2-adduct of enal 1, secured through addition of Bu_3SnLi undergoes O-silylation and in situ isomerization

(1) Marshall, J. A.; Welmaker, G. S. *Tetrahedron Lett.* **1991**, *32*, 2101.

(2) Marshall, J. A.; Welmaker, G. S. *Synlett* **1992**, 537.

(3) Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143.

(4) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065.

(5) These enolates can also be trapped with reactive halides such as MOMCl and BOMCl. Additional studies to examine the scope of this method are in progress.

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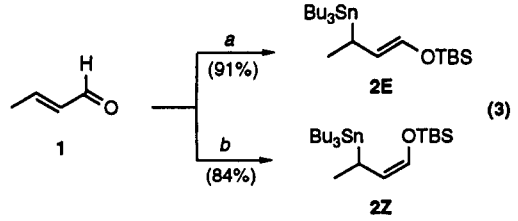
to the (Z)-γ-silyloxy isomer **2Z**.



(3)

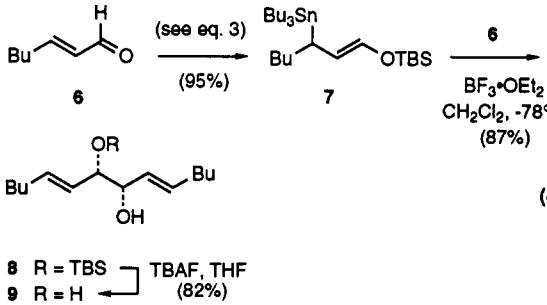
[a] $Bu(Bu_3Sn)Cu(CN)Li_2$, THF, -78°C then TBSCl, -78°C

[b] Bu_3SnLi, THF, -78°C; TBSOTf, *i*-Pr_2NEt, CH_2Cl_2, 0°C

Table I summarizes results for $BF_3{\cdot}OEt_2$-promoted additions of the allylstannanes **2** to representative aldehydes **3a–e**.[6] Our previously published findings with the MOM counterpart of **2Z** are included for comparison.[7]

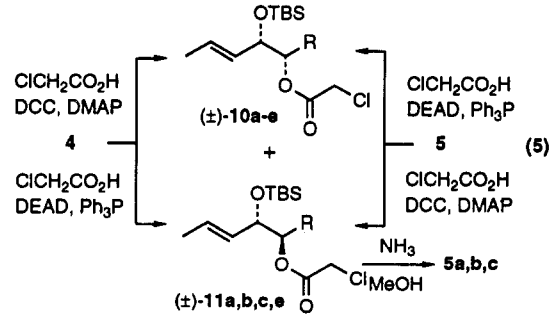
Especially noteworthy are the uniformly high syn:anti ratios obtained with the (E)-(silyloxy)stannane **2E** (entries 3, 6, 9, 12, and 15), even in the case of the sterically undemanding propargylic aldehyde **3c** (entry 9). In contrast, the (Z)-(silyloxy)stannane **2Z** shows only modest improvement over the OMOM analogue (93:7 vs 90:10, entry 8 vs 7).

The relative stereochemistry of adducts **4a–e** and **5a–e** can be assigned by analogy to additions involving the (Z)-OMOM reagents[7] and from our synthesis of muricatacin.[2] As an added check we prepared the known syn diol **9**[7] through addition of the (γ-(silyloxy)allyl)stannane **7** to (E)-2-heptenal (eq 4).



(4)

The stereomeric ratios **4:5** were calculated from integrated ^1H NMR spectra of the crude products. Assignments of the minor peaks as the trans isomers **5** were confirmed by comparison of the ^1H NMR spectra of the chloroacetate derivatives **10** and **11**, prepared by treatment of the mixtures of **4** and **5** with $ClCH_2CO_2H$ and DCC, DMAP, with those of the inverted mixtures of **11** and **10** secured through Mitsunobu inversion of the alcohols with $ClCH_2CO_2H$ and DEAD, Ph_3P (eq 5).[8] The cyclohexyl

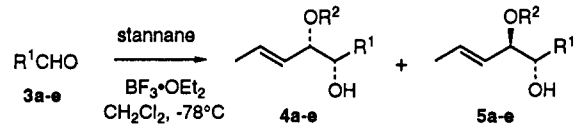


(5)

(6) Ratios were initially determined by integration of the CHOH or OH signals in the regions 3.5–4.2 and 2.1–3.2 ppm and subsequently confirmed by integration of the $CHOCOCH_2Cl$ signals at 4.0–5.5 ppm in the ^1H NMR spectra of the chloroacetate derivatives **10** and **11**.

(7) Marshall, J. A.; Welmaker, G. S.; Gung, W. Y. *J. Am. Chem. Soc.* **1991**, *113*, 647.

Table I. Addition of γ-Oxygenated Allylic Stannanes to Representative Aldehydes



entry	stannane	R^1	series	yield, %	4:5[a]
1	(Z)-MOM[b]	n-C_6H_{13}	a	75	96:4[c]
2	**2Z**	n-C_6H_{13}	a	86	97:3
3	**2E**	n-C_6H_{13}	a	89	>99:1
4	(Z)-MOM[b]	(E)-BuCH=CH	b	84	94:6[c]
5	**2Z**	(E)-BuCH=CH	b	81	>99:1
6	**2E**	(E)-BuCH=CH	b	84	>99:1
7	(Z)-MOM[b]	BuC≡C	c	70	90:10[c]
8	**2Z**	BuC≡C	c	84	93:7
9	**2E**	BuC≡C	c	84	>99:1
10	(Z)-MOM[b]	c-C_6H_{11}	d	74	95:5[c]
11	**2Z**	c-C_6H_{11}	d	85	94:6
12	**2E**	c-C_6H_{11}	d	79	>99:1
13	(Z)-MOM[b]	Ph	e	89	95:5[c]
14	**2Z**	Ph	e	88	96:4
15	**2E**	Ph	e	89	>99:1

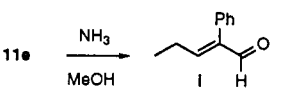
[a] The products are racemic. Ratios were determined from the integrated ^1H NMR spectra of crude adducts. [b] (Z)-CH_3CH-$(SnBu_3)CH$=CHOMOM. [c] From ref 7.

adducts **4d/5d** failed to undergo the Mitsunobu inversion. The anti alcohols **5a,b** and **c** could be prepared in high yield by ammonolysis of the corresponding chloroacetates **11**.[8] Thus, both diastereomeric alcohols **4** and **5** (except for **5d** and **5e**[9]) and the derived diols (cf. **8** → **9**) are readily available in high purity through this methodology.

Lewis acid promoted additions of allylic trialkylstannanes proceed via nonchelated acyclic transition states. Both antiperiplanar and synclinal orientations have been proposed.[10,11] According to Yamamoto, the antiperiplanar arrangement, in which the aldehyde substituent (R) and the γ-vinylic substituent (OTBS) are anti as in **A** and **D**, represents the lowest energy transition state for (Z)- and (E)-allylic stannane additions.[10a,12] Interactions between the aldehyde substituent (R) and the Sn-bearing allylic center, as in **D**, are thought to be relatively unimportant.[10a] The steric role of the Lewis acid is negligible in Denmark's synclinal transition states.[10b] In light of these considerations, **A** and **D** offer the best arrangements for additions involving **2Z** and **2E**, respectively, leading to the syn adducts **4**.

(8) Saïah, M.; Bessodes, M.; Antonakis, K. *Tetrahedron Lett.* **1992**, *33*, 4317.

(9) Unexpectedly the chloroacetate **11e** underwent pinacol rearrangement to aldehyde **i** upon treatment with NH_4OH in MeOH.



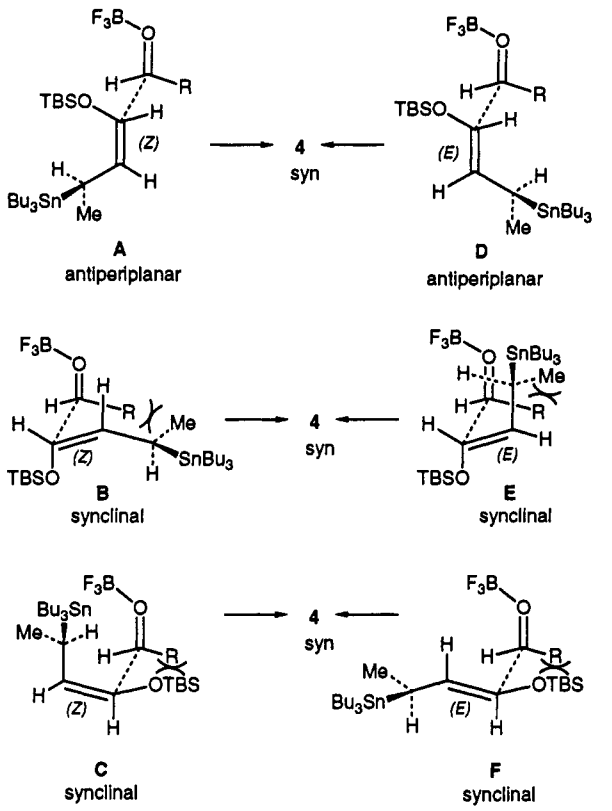
(10) (a) Yamamoto, Y.; Yatagi, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107. (b) A preferred synclinal arrangement has been suggested for an intramolecular addition leading to a bicyclo [2.2.2] homoallylic alcohol. Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970.

(11) For a discussion of this point, see: Fleming, I. *Chemtracts - Org. Chem.* **1991**, 21. Marshall, J. A. *Chemtracts - Org. Chem.* **1992**, *75*.

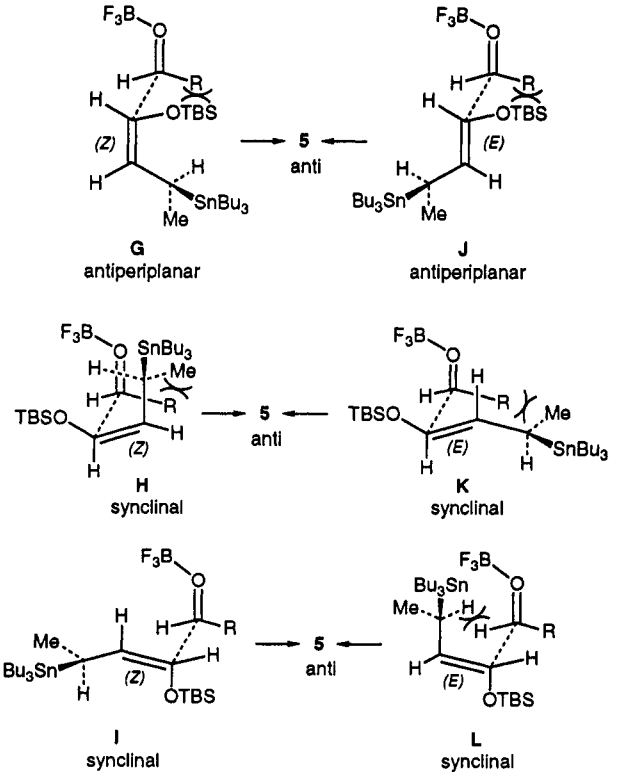
(12) These transition state arrangements are traditionally depicted as Newman projections along the axis of the forming C–C bond.[7,10] We feel that the chairlike representations **A–L** more accurately reflect the Dunitz–Bergi attack angle (~105°)[13] and the Felkin–Ahn bias[14] of these additions.

(13) Bergi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563.

(14) For an excellent discussion of this point as applied to aldol additions, see: Roush, W. R. *J. Org. Chem.* **1991**, *56*, 4151.



Possible transition state arrangements for the anti adducts **5** are depicted as **G–L**. Of these the synclinal (*Z*) **I** appears least encumbered by steric interactions. Accordingly, the higher syn:anti ratios obtained with stannane **2E** may result from the higher energy of transition state leading to the anti adducts for such stannanes. Of course, stereoelectronic, dipolar and orbital symmetry may also play a role in the reaction outcome. These issues await detailed analysis.



Whatever the explanation, the unprecedented levels of syn selectivity displayed by the (*E*)-silyloxy allylic stannanes, their ready availability from enals, and the high yields of S_E' adducts from structurally diverse aldehydes should be of great value for the synthesis of syn 1,2-diols.

Experimental Section[15]

(*Z*)-1-((*tert*-Butyldimethylsilyl)oxy)-3-(tri-*n*-butylstannyl)-1-butene (2Z). To a stirred, cooled (0 °C) solution of 1.2 mL (8.6 mmol) of $HN(i\text{-}Pr)_2$ in 20 mL of THF was added 3.4 mL (8.5 mmol) of 2.5 M *n*-BuLi in hexanes. The solution was stirred for 10 min at 0 °C, and then 2.3 mL (8.6 mmol) of Bu_3SnH was introduced. The resulting solution was stirred for 20 min at 0 °C and then cooled to −78 °C. To this stirred, cooled (−78 °C) reaction mixture was added 0.50 g (7.1 mmol) of crotonaldehyde in 4 mL of THF. The reaction mixture was stirred for 10 min at −78 °C and then quenched with saturated aqueous NH_4Cl and diluted with ether. The phases were separated, and the aqueous phase was extracted with ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was dissolved in 20 mL of CH_2Cl_2 and cooled to 0 °C. To this stirred solution was added 3.6 mL (20 mmol) of $EtN(i\text{-}Pr)_2$ and 1.8 mL (7.7 mmol) of TBSOTf, sequentially. The reaction mixture was stirred for 3 h while warming to ambient temperature and then quenched with water and diluted with ether. The phases were separated, and the aqueous phase was extracted with ether. The combined organic extracts were dried over $MgSO_4$, concentrated under reduced pressure, and purified by chromatography through silica gel (elution with hexanes) to afford 2.8 g (84%) of γ-silyloxystannane: IR (neat) 3019, 2953 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95 (dd, 1 H, J = 5.7, 1.0 Hz, H1), 4.45 (dt, 1 H, J = 10.9, 5.7 Hz, H2), 2.50 (dq, 1 H, J = 10.8, 7.5 Hz, H3), 1.75–1.11 (m, 18 H, CH_2's), 0.90 (s, 9 H, $SiC(CH_3)_3$), 0.87 (t, 9 H, J = 7.4 Hz, CH_3's), 0.09 (d, 6 H, J = 2.6 Hz, $Si(CH_3)_2$); HRMS calcd for $C_{25}H_{54}OSi^{120}Sn$ (M^+) 476.2487, found 476.2492. Anal. Calcd for $C_{22}H_{48}OSiSn$: C, 55.58; H, 10.18. Found: C, 55.70; H, 10.21.

(*E*)-1-((*tert*-Butyldimethylsilyl)oxy)-3-(tri-*n*-butylstannyl)-1-butene (2E). To a stirred, cooled (−78 °C) suspension of 0.12 g (1.3 mmol) of CuCN in 10 mL of THF was added 1.1 mL (2.8 mmol) of *n*-BuLi (2.5 M in hexanes). The reaction mixture was warmed slightly until a light yellow solution persisted, and then it was recooled to −78 °C. To this stirred solution was added 0.71 mL (2.6 mmol) of Bu_3SnH. The resulting, bright yellow solution was stirred at −78 °C for 10 min, and then 0.10 mL (1.2 mmol) of crotonaldehyde was introduced. The red solution was stirred at −78 °C for 15 min, and then 0.45 g (3.0 mmol) of TBSCl was added. The reaction mixture was stirred at −78 °C for 30 min, quenched with saturated aqueous $NaHCO_3$, diluted with ether, and allowed to warm to ambient temperature. The phases were separated, and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by chromatography through silica gel (elution with hexanes) to give 0.52 g (91%) of the (*E*)-γ-(silyloxy)stannane: IR (neat) 2956, 1648 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.07 (dd, J = 11.8, 1.2 Hz, H1), 5.22 (dd, J = 11.8, 11.0 Hz, H2), 1.96 (p, J = 7.5 Hz, H3), 1.56–1.25 (m, CH_2's), 1.24 (d, J = 7.4 Hz, H4), 0.90 (s, $SiC(CH_3)_3$), 0.88 (t, J = 7.2 Hz, CH_3's), 0.10 (s, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 118.3, 29.3, 27.5, 25.8, 18.5, 18.4, 18.2, 13.7, 8.5, −5.2, −5.2; HRMS (EI^+) calcd for $C_{22}H_{48}OSi^{116}Sn$ (M^+) 472.2492, found 472.2492. Anal. Calcd for $C_{22}H_{48}OSiSn$: C, 55.58; H, 10.18. Found: C, 55.65; H, 10.13.

(*E*)-(*rel*-4*R*,5*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-2-undecen-5-ol (4a). From (*E*)-γ-Stannane 2E. To a stirred, cooled (−78 °C) solution of 0.30 g (0.63 mmol) of (*E*)-γ-stannane **2E** in 5 mL of CH_2Cl_2 was added 0.12 mL (0.98 mmol) of $BF_3{\cdot}Et_2O$, followed by a solution of 86 mg (0.75 mmol) of heptaldehyde in 1 mL of CH_2Cl_2. The reaction mixture was stirred at −78 °C for 20 min, quenched with saturated aqueous $NaHCO_3$, diluted with ether, and allowed to warm to ambient temperature. The phases were separated, and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude

(15) For typical experimental protocols, see ref 7.

product was purified by chromatography through silica gel (elution with 5% ethyl acetate–hexanes), affording 0.17 g (89%) of the alcohol, which was shown by ^{1}H NMR analysis to be >99:1 syn:anti.

From (Z)-γ-Stannane 2Z. The procedure described above was employed with 0.20 g (0.42 mmol) of (Z)-γ-stannane **2Z**, 78 μL (0.63 mmol) of BF_3·Et_2O, and 58 mg (0.51 mmol) of heptaldehyde affording 99 mg (79%) of the alcohol, which was shown by ^{1}H NMR analysis to be 97:3 syn:anti: IR (neat) 3575, 3490, 2930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (dq, J = 15.4, 6.5 Hz, H2), 5.37 (ddd, J = 15.4, 7.8, 1.6 Hz, H3), 3.79 (t, J = 7.2 Hz, H5), 3.32 (m, H4), 2.46 (bs, OH), 1.68 (dd, J = 6.3, 1.5 Hz, H1), 1.42–1.27 (m, CH_2's), 0.87 (s, $SiC(CH_3)_3$), 0.86 (t, J = 8.0 Hz, H11), 0.02 (d, J = 11.0 Hz, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.9, 128.9, 78.3, 75.2, 33.1, 32.2, 29.8, 26.3, 23.0, 18.5, 18.2, 14.5, –3.4, –4.4; HRMS (EI$^+$) calcd for $C_{13}H_{27}O_2Si$ (M – t-Bu) 243.1786, found 243.1780. Anal. Calcd for $C_{17}H_{36}O_2Si$: C, 67.94; H, 12.07. Found: C, 68.17; H, 12.04.

(E,E)-(*rel*-4*R*,5*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-2,6-undecadien-5-ol (4b). From (E)-γ-Stannane 2E. The procedure described for **4a** was employed with 0.30 g (0.63 mmol) of (E)-γ-stannane **2E**, 0.12 mL (0.98 mmol) of BF_3·Et_2O, and 85 mg (0.76 mmol) of *trans*-2-heptenal affording 0.16 g (84%) of the alcohol, which was shown by ^{1}H NMR analysis to be >99:1 syn:anti.

From (Z)-γ-Stannane 2Z. The procedure described for **4a** was employed with 0.15 g (0.32 mmol) of (Z)-γ-stannane **2Z**, 0.58 μL (0.47 mmol) of BF_3·Et_2O, and 42 mg (0.38 mmol) of *trans*-2-heptenal affording 76 mg (81%) of the alcohol, which was shown by ^{1}H NMR analysis to be >99:1 syn:anti: IR (neat) 3564, 3466 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62 (m, H2 and H7), 5.40 (m, H3 and H6), 3.82 (p, H4 and H5), 2.44 (bs, OH), 1.66 (dd, J = 6.2, 1.2 Hz, H1), 1.37–1.23 (m, CH_2's), 0.88 (s, $SiC(CH_3)_3$), 0.86 (t, J = 7.2 Hz, H11), 0.03 (d, J = 9.8 Hz, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.1, 131.4, 129.0, 128.8, 78.1, 76.3, 32.4, 31.6, 26.3, 22.5, 18.5, 18.1, 14.3, –3.6, –4.4; HRMS (EI$^+$) calcd for $C_{13}H_{25}O_2Si$ (M – t-Bu) 241.1624, found 241.1626. Anal. Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48; found: C, 68.48; H, 11.46.

(E)-(*rel*-4*R*,5*R*)-((*tert*-Butyldimethylsilyl)oxy)-2-undecen-6-yn-5-ol (4c). From (E)-γ-Stannane 2E. The procedure described for **4a** was employed with 0.30 g (0.63 mmol) of (E)-γ-stannane **2E**, 0.12 mL (0.98 mmol) of BF_3·Et_2O, and 85 mg (0.76 mmol) of 2-heptynal affording 0.16 g (84%) of the alcohol, which was shown by ^{1}H NMR analysis to be >99:1 syn:anti.

From (Z)-γ-Stannane 2Z. The procedure described for **4a** was employed with 0.15 g (0.32 mmol) of (Z)-γ-stannane **2Z**, 0.58 μL (0.47 mmol) of BF_3·Et_2O, and 42 mg (0.38 mmol) of 2-heptynal affording 79 mg (84%) of the alcohol, which was shown by ^{1}H NMR analysis to be 93:7 syn:anti: IR (neat) 3580, 3500, 2930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (dq, J = 15.3, 6.5 Hz, H2), 5.46 (ddd, J = 15.4, 7.0, 1.6 Hz, H3), 4.07 (dt, J = 6.0, 2.0 Hz, H5), 4.02 (t, J = 6.7 Hz, H4), 2.18 (dt, J = 6.9, 2.0 Hz, H8), 1.68 (dd, J = 6.3, 1.0 Hz, H1), 1.48–1.33 (m, CH_2's), 0.88 (s, $SiC(CH_3)_3$), 0.88 (t, J = 7.3 Hz, H11), 0.05 (d, J = 12.9 Hz, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.3, 128.8, 86.3, 78.6, 77.4, 66.7, 30.5, 25.8, 21.8, 18.4, 18.1, 17.7, 13.6, –4.1, –4.8; HRMS (EI$^+$) calcd for $C_{13}H_{23}O_2Si$ (M – t-Bu) 239.1467, found 239.1463. Anal. Calcd for $C_{17}H_{32}C_{17}HO_2Si$: C, 68.86; H, 10.88. Found: C, 68.99; H, 10.94.

(E)-(*rel*-1*R*,2*R*)-2-((*tert*-Butyldimethylsilyl)oxy)-1-cyclohexyl-3-penten-1-ol (4d). From (E)-γ-Stannane 2E. The procedure described for **4a** was employed with 0.30 g (0.63 mmol) of (E)-γ-stannane **2E**, 0.12 mL (0.98 mmol) of BF_3·Et_2O, and 85 mg (0.76 mmol) of cyclohexanecarboxaldehyde affording 0.15 g (79%) of the alcohol, which was shown by ^{1}H NMR analysis to be >99:1 syn:anti.

From (Z)-γ-Stannane 2Z. The procedure described for **4a** was employed with 0.15 g (0.32 mmol) of (Z)-γ-stannane **2Z**, 0.58 μL (0.47 mmol) of BF_3·Et_2O, and 42 mg (0.38 mmol) of cyclohexanecarboxaldehyde affording 76 mg (81%) of the alcohol, which was shown by ^{1}H NMR analysis to be 94:6 syn:anti: IR (neat) 3575, 2900 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (dq, J = 15.4, 6.4 Hz, H4), 5.43 (dd, J = 15.4, 7.8 Hz, H3), 4.04 (dd, J = 7.7, 5.6 Hz, H1), 3.08 (t, J = 5.3 Hz, H2), 2.38 (bs, OH), 1.71–1.04 (m, CH_2's), 1.68 (dd, J = 6.2, 1.4 Hz, H5), 0.87 (s, $SiC(CH_3)_3$), 0.20 (d, J = 10.8 Hz, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.3, 128.3, 79.4, 75.1, 39.9, 30.7, 27.5, 26.9, 26.8, 26.6, 26.3, 18.5, 18.1, –3.4, –4.4; HRMS (EI$^+$) calcd for $C_{13}H_{25}O_2Si$ (M – t-Bu) 241.1624, found 241.1629. Anal. Calcd for $C_{17}H_{36}O_2Si$: C, 68.39; H, 11.48. Found: C, 68.59; H, 11.49.

(E)-(*rel*-1*R*,2*R*)-2-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-3-penten-1-ol (4e). From (E)-γ-Stannane 2E. The procedure described for **4a** was employed with 0.30 g (0.63 mmol) of (E)-γ-stannane **2E**, 0.12 mL (0.98 mmol) of BF_3·Et_2O, and 80 mg (0.75 mmol) of benzaldehyde affording 0.18 g (89%) of the alcohol, which was shown by ^{1}H NMR analysis to be >99:1 syn:anti.

From (Z)-γ-Stannane 2Z. The procedure described for **4a** was employed with 0.15 g (0.32 mmol) of (Z)-γ-stannane **2Z**, 0.58 μL (0.47 mmol) of BF_3·Et_2O, and 40 mg (0.38 mmol) of benzaldehyde affording 81 mg (88%) of the alcohol, which was shown by ^{1}H NMR analysis to be 96:4 syn:anti: IR (neat) 3570, 3500, 3100, 2930, 1500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, aryl H's), 5.41 (m, H3 and H4), 4.43 (d, J = 6.0 Hz, H1), 4.04 (t, J = 6.1 Hz, H2), 1.60 (dd, J = 4.9, 0.7 Hz, H5), 0.87 (s, $SiC(CH_3)_3$), –0.06 (d, J = 14.6 Hz, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.6, 129.8, 128.4, 127.9, 127.5, 127.0, 78.9, 77.6, 25.9, 18.2, 17.7, –4.1, –5.1; HRMS (EI$^+$) calcd for $C_{13}H_{19}O_2Si$ (M = t-Bu) 235.1154, found 235.1156. Anal. Calcd for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.65. Found: C, 69.90; H, 9.70.

(*rel*-4*R*,5*S*)-(E)-4-((*tert*-Butyldimethylsilyl)oxy)-2-undecen-5-ol (5a). To a stirred solution of 20 mg (0.053 mmol) of chloroacetate **11a** in 5 mL of methanol was added 1 mL of concentrated ammonium hydroxide. The reaction mixture was stirred at ambient temperature for 2 h and diluted with ether. The phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by chromatography through silica gel (elution with 5% ethyl acetate–hexanes), affording 12 mg (75%) of the alcohol: IR (neat) 3580, 3477 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.60 (dq, J = 15.4, 6.4 Hz, H2), 5.43 (dd, J = 15.4, 7.4 Hz, H3), 3.93 (dd, J = 6.2, 1.2 Hz, H5), 3.50 (m, H4), 2.19 (bs, OH), 1.69 (dd, J = 6.2, 1.2 Hz, H1), 1.46–1.23 (m, CH_2's), 0.87 (s, $SiC(CH_3)_3$), 0.86 (t, J = 6.9 Hz, H11), 0.02 (d, J = 7.8 Hz, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.8, 128.5, 77.0, 76.6, 74.9, 32.0, 31.8, 29.4, 25.8, 25.8, 22.6, 18.2, 17.8, 14.1, –4.1, –4.9; HRMS (EI$^+$) calcd for $C_{16}H_{33}O_2Si$ (M – CH_3): 285.2250, found 285.2247.

(E,E)-(*rel*-4*R*,5*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-2,6-undecadien-5-ol (5b). The procedure described for **5a** was employed with 0.10 g (0.27 mmol) of chloroacetate **11b** in 5 mL of methanol and 1 mL of concentrated NH_4OH affording 65 mg (81%) of alcohol **5b**: IR (neat) 3466 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64 (m, H2 and H7), 5.39 (m, H3 and H6), 3.95 (m, H4 and H5), 2.24 (d, J = 3.9 Hz, OH), 2.02 (q, J = 6.7 Hz, H8), 1.68 (dd, J = 6.5, 1.5 Hz, H1), 1.37–1.23 (m, CH_2's), 0.87 (s, $SiC(CH_3)_3$), 0.86 (t, J = 5.7 Hz, H11), 0.02 (d, J = 7.8 Hz, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.9, 130.1, 128.5, 128.3, 77.2, 76.1, 32.1, 31.9, 25.8, 22.1, 18.2, 17.9, 13.9, –4.2, –4.8; HRMS (EI$^+$) calcd for $C_{16}H_{31}O_2Si$ (M – CH_3) 283.2093, found 283.2092. Anal. Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48. Found: C, 68.47; H, 11.42.

(E)-(*rel*-4*R*,5*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-2-undecen-6-yn-5-ol (5c). The procedure described for **5a** was employed with 0.10 g (0.27 mmol) of chloroacetate **11c** in 5 mL of methanol and 1 mL of concentrated NH_4OH affording 61 mg (77%) of alcohol **5c**: IR (neat) 3455, 2230 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (dq, J = 15.3, 6.4 Hz, H2), 5.54 (dd, J = 15.3, 6.7 Hz, H3), 4.21 (m, H5), 4.11 (m, H4), 2.32 (d, J = 6.0 Hz, OH), 2.19 (dt, J = 6.8, 2.0 Hz, H8), 1.70 (dd, J = 7.3, 1.2 Hz, H1), 1.52–1.33 (m, CH_2's), 0.88 (s, $SiC(CH_3)_3$), 0.88 (t, J = 7.3 Hz, H11), 0.04 (d, J = 6.3 Hz, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.5, 129.0, 86.8, 78.1, 76.5, 66.7, 30.6, 25.8, 21.8, 18.4, 18.1, 17.8, 13.6, –4.2, –4.8; HRMS (EI$^+$) calcd for $C_{17}H_{32}O_2Si$ (M$^+$) 296.2172, found 296.2167. Anal. Calcd for $C_{17}H_{32}C_{17}HO_2Si$: C, 68.86; H, 10.88. Found: C, 69.01; H, 10.85.

(E)-1-((*tert*-Butyldimethylsilyl)oxy)-3-(tri-*n*-butylstannyl)-1-heptene (7). The adduct was prepared as described for **2E** from 75 mg (0.84 mmol) of CuCN in 10 mL of THF, 0.67 mL (1.7 mmol) of *n*-BuLi (2.5 M in hexanes), 0.45 mL (1.7 mmol) of Bu_3SnH, 0.10 mL (0.76 mmol) of *trans*-2-heptenal, and 0.29 g (1.9 mmol) of TBSCl. The crude product was purified by chromatography through silica gel (elution with hexanes) to give 0.37 g (95%) of the (E)-γ-(silyloxy)stannane **7**: IR (neat) 2927,

1646 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.09 (dd, J = 11.8, 0.8 Hz, H1), 5.05 (dd, J = 11.8, 10.8 Hz, H2), 1.91 (m, H3), 1.56–1.21 (m, CH_2's), 0.91 (s, $SiC(CH_3)_3$), 0.88 (t, J = 7.3 Hz, CH_3's), 0.10 (s, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 116.4, 33.0, 32.3, 29.3, 27.6, 25.8, 25.2, 22.4, 18.4, 14.1, 13.7, 8.8, –5.2, –5.2; HRMS (EI$^+$) calcd for $C_{25}H_{54}OSi^{116}Sn$ (M^+) 514.2961, found 514.2968. Anal. Calcd for $C_{25}H_{54}OSiSn$: C, 58.03; H, 10.52. Found: C, 57.88; H, 10.53.

(*E*,*E*)-(*rel*-7*R*,8*R*)-8-((*tert*-Butyldimethylsilyl)oxy)-5,9-tetradecadien-7-ol (8). The addition was carried out as described for **4a** with 0.35 g (0.67 mmol) of (*E*)-γ-stannane in 5 mL of CH_2Cl_2, 0.12 mL (0.98 mmol) of $BF_3{\cdot}Et_2O$, and 91 mg (0.81 mmol) of *trans*-2-heptenal (**6**) in 1 mL of CH_2Cl_2. The crude product was purified by chromatography through silica gel (elution with 5% ethyl acetate–hexanes), affording 0.19 g (84%) of the alcohol, which was shown by ^{1}H NMR analysis to be >99:1 syn:anti. IR (neat) 3564, 3477 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64 (m, H5 and H10), 5.37 (m, H6 and H9), 3.83 (m, H4 and H5), 2.62 (d, J = 3.5 Hz, OH), 2.00 (q, J = 5.8 Hz, H4 and H11), 1.34–1.26 (m, CH_2's), 0.88 (s, $SiC(CH_3)_3$), 0.86 (m, H1 and H14), 0.03 (d, J = 9.7 Hz, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.9, 133.7, 129.7, 128.9, 77.9, 76.0, 32.1, 31.9, 31.2, 25.9, 22.2, 18.2, 13.9, 13.9, –3.9, –4.8; HRMS (EI$^+$) calcd for $C_{19}H_{37}O_2Si$ ($M - CH_3$) 325.2563, found 325.2558. Anal. Calcd for $C_{20}H_{40}O_2Si$: C, 70.52; H, 11.84. Found: C, 70.52; H, 11.81.

(*E*,*E*)-(*rel*-7*R*,8*R*)-5,9-Tetradecadiene-7,8-diol (9). To a stirred solution of 50 mg (0.15 mmol) of TBS ether **8** in 1 mL of THF was added 0.73 mL (0.73 mmol) of tetra-*n*-butylammonium fluoride (1.0 M in THF). The reaction mixture was stirred at ambient temperature for 3 h, diluted with ether, and quenched with water. The phases were separated, and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by chromatography through silica gel (elution with 25% ethyl acetate–hexanes) affording 27 mg (82%) of the diol: IR (neat) 3368 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (dt, J = 15.6, 6.8 Hz, H5 and H10), 5.40 (dd, J = 15.5, 6.7 Hz, H6 and H9), 3.86, 3.85 (AB q, J = 0.5 Hz, H7 and H8), 2.74 (bs, OH), 2.00 (q, J = 6.7 Hz, H4 and H11), 1.34–1.20 (m, CH_2's), 0.85 (t, J = 7.0 Hz, H1 and H14); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.6, 128.5, 76.1, 32.0, 31.2, 22.2, 13.9. The spectra were identical to those of an authentic sample.[8]

(*E*)-(*rel*-4*R*,5*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-5-(chloroacetoxy)-2-undecene (10a). To a stirred solution of 35 mg (0.12 mmol) of alcohol **4a** (97:3 **4a**:**5a**) in 2 mL of CH_2Cl_2 was added 36 mg (0.17 mmol) of dicyclohexylcarbodiimide, 17 mg (0.18 mmol) of chloroacetic acid, and 7 mg (0.06 mmol) of DMAP, sequentially. The reaction mixture was stirred at ambient temperature for 1.5 h and then concentrated under reduced pressure. The crude product was purified by flash chromatography through silica gel (elution with 5% ethyl acetate–hexanes) affording 39 mg (89%) of ester **10a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62 (dq, J = 15.3, 6.5 Hz, H2), 5.37 (dd, J = 15.3, 7.0 Hz, H3), 4.84 (m, H5), 4.07 (t, J = 6.1 Hz, H4), 4.04 (s, CH_2Cl), 1.68 (d, J = 6.5 Hz, H1), 1.54–1.23 (m, CH_2's), 0.87 (t, J = 7.2 Hz, H11), 0.85 (s, $SiC(CH_3)_3$), 0.01 (d, J = 10.0 Hz, $Si(CH_3)_2$; HRMS (EI$^+$) calcd for $C_{15}H_{28}{}^{35}ClO_3Si$ ($M - t$-Bu) 319.1496, found 319.1496.

(*E*,*E*)-(*rel*-4*R*,5*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-5-(chloroacetoxy)-2,6-undecadiene (10b). The procedure described for **10a** was employed with 30 mg (0.10 mmol) of alcohol **4b**, 31 mg (0.15 mmol) of DCC, 14 mg (0.15 mmol) of chloroacetic acid, and 6 mg (0.05 mmol) of DMAP affording 35 mg (92%) of ester **10b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76–5.56 (m, H2 and H7), 5.37–5.28 (m, H3 and H6), 5.16 (t, J = 7.2 Hz, H5), 4.09 (t, J = 6.8 Hz, H4), 4.03 (s, CH_2Cl), 2.00 (q, J = 6.9 Hz, H8), 1.65 (d, J = 6.5 Hz, H1), 1.33–1.24 (m, CH_2's), 0.86 (t, J = 7.0 Hz, H11), 0.85 (s, $SiC(CH_3)_3$), 0.01 (d, J = 9.9 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{26}{}^{35}ClO_3Si$ ($M - t$-Bu) 317.1340, found 317.1336.

(*E*)-(*rel*-4*R*,5*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-5-(chloroacetoxy)-2-undecen-6-yne (10c). The procedure described for **10a** was employed with 30 mg (0.10 mmol) of alcohol **4c** (93:7 **4c**:**5c**), 31 mg (0.15 mmol) of DCC, 14 mg (0.15 mmol) of chloroacetic acid, and 6 mg (0.05 mmol) of DMAP affording 34 mg (89%) of ester **10c** (96:4 **10c**:**10c**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (dq, J = 15.3, 6.5 Hz, H2), 5.47 (dd, J = 15.3, 6.7 Hz, H3), 5.27 (dt, J = 7.4, 2.1 Hz, H5), 4.15 (dd, J = 7.5, 7.3 Hz, H4), 4.05 (d, J = 3.6 Hz, CH_2Cl), 2.18 (dt, J = 6.8, 2.1 Hz, H8), 1.70 (dd, J = 6.4, 1.6 Hz, H1), 1.46–1.30 (m, CH_2's), 0.88 (t, J = 7.1 Hz, H11), 0.85 (s, $SiC(CH_3)_3$), 0.02 (d, J = 8.5 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{24}{}^{35}ClO_3Si$ ($M - t$-Bu) 315.1183, found 315.1184.

(*E*)-(*rel*-1*R*,2*R*)-2-((*tert*-Butyldimethylsilyl)oxy)-1-(chloroacetoxy)-1-cyclohexyl-3-pentene (10d). The procedure described for **10a** was employed with 30 mg (0.10 mmol) of alcohol **4d** (94:6 **4d**:**5d**), 31 mg (0.15 mmol) of DCC, 14 mg (0.15 mmol) of chloroacetic acid, and 6 mg (0.05 mmol) of DMAP affording 33 mg (87%) of ester **10d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64 (dq, J = 15.3, 6.5 Hz, H4), 5.35 (dd, J = 15.3, 7.5 Hz, H3), 4.73 (dd, J = 6.3, 4.8 Hz, H1), 4.16 (dd, J = 7.1, 6.7 Hz, H2), 4.05 (d, J = 1.4 Hz, CH_2Cl); 1.68 (dd, J = 6.4, 1.6 Hz, H5), 1.54–1.10 (m, CH_2's), 0.83 (s, $SiC(CH_3)_3$), –0.01 (d, J = 8.7 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{26}{}^{35}ClO_3Si$ ($M - t$-Bu) 317.1340, found 317.1340.

(*E*)-(*rel*-1*R*,2*R*)-2-((*tert*-Butyldimethylsilyl)oxy)-1-(chloroacetoxy)-1-phenyl-3-pentene (10e). The procedure described for **10a** was employed with 40 mg (0.14 mmol) of alcohol **4e**, 42 mg (0.20 mmol) of DCC, 19 mg (0.20 mmol) of chloroacetic acid, and 8 mg (0.07 mmol) of DMAP affording 44 mg (88%) of ester **10e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.24 (m, aryl H's), 5.67 (d, J = 6.9 Hz, H1), 5.47 (dq, J = 15.3, 6.6 Hz, H4), 5.18 (dd, J = 15.3, 6.6 Hz, H3), 4.31 (t, J = 7.8 Hz, H2), 4.07 (s, CH_2Cl), 1.55 (d, J = 5.6 Hz, H5), 0.86 (s, $SiC(CH_3)_3$), –0.01 (d, J = 6.3 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{20}{}^{35}ClO_3Si$ ($M - t$-Bu) 311.0870, found 311.0876.

(*E*)-(*rel*-4*R*,5*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-5-(chloroacetoxy)-2-undecene (11a). To a stirred solution of 60 mg (0.20 mmol) of alcohol **4a** in 2 mL of toluene was added 105 mg (0.40 mmol) of triphenylphosphine, 38 mg (0.40 mmol) of chloroacetic acid, and 63 μL (0.40 mmol) of diethyl azodicarboxylate (DEAD), sequentially. The reaction mixture was stirred at ambient temperature for 12 h and then concentrated under reduced pressure. The crude product was purified by flash chromatography through silica gel (elution with 5% ethyl acetate–hexanes) affording 63 mg (84%) of ester **11a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (dq, J = 15.3, 6.5 Hz, H2), 5.36 (dd, J = 15.3, 7.1 Hz, H3), 4.85 (m, H5), 4.06 (t, J = 7.3 Hz, H4), 4.00 (d, J = 2.6 Hz, CH_2Cl), 1.68 (d, J = 6.5 Hz, H1), 1.56–1.24 (m, CH_2's), 0.87 (t, J = 7.1 Hz, H11), 0.85 (s, $SiC(CH_3)_3$), –0.01 (d, J = 8.7 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{28}{}^{35}ClO_3Si$ ($M - t$-Bu) 319.1498, found 319.1496.

(*E*,*E*)-(*rel*-4*R*,5*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-5-(chloroacetoxy)-2,6-undecadiene (11b). The procedure described for **11a** was employed with 40 mg (0.13 mmol) of alcohol **4b**, 70 mg (0.27 mmol) of Ph_3P, 25 mg (0.26 mmol) of chloroacetic acid, and 42 μL (0.27 mmol) of DEAD affording 23 mg (46%) of ester **11b** and 18 mg (36%) of S_N2' ester: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75–5.57 (m, H2 and H7), 5.47–5.34 (m, H3 and H6), 5.15 (dd, J = 7.9, 4.3 Hz, H5), 4.11 (dd, J = 7.4, 6.6 Hz, H4), 4.01 (s, CH_2Cl), 2.02 (q, J = 6.6 Hz, H8), 1.66 (d, J = 5.9 Hz, H1), 1.32–1.23 (m, CH_2's), 0.86 (t, J = 7.2 Hz, H11), 0.85 (s, $SiC(CH_3)_3$), 0.00 (d, J = 8.8 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{26}{}^{35}ClO_3Si$ ($M - t$-Bu) 317.1340, found 317.1341.

(*E*)-(*rel*-4*R*,5*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-5-(chloroacetoxy)-2-undecen-6-yne (11c). The procedure described for **11a** was employed with 50 mg (0.17 mmol) of alcohol **4c**, 88 mg (0.34 mmol) of Ph_3P, 32 mg (0.34 mmol) of chloroacetic acid, and 53 μL (0.34 mmol) of DEAD affording 54 mg (86%) of ester **11c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (dq, J = 15.3, 7.4 Hz, H2), 5.45 (dd, J = 15.3, 7.0 Hz, H3), 5.39 (dt, J = 4.6, 2.1 Hz, H5), 4.18 (dd, J = 7.0, 4.6 Hz, H4), 4.05 (d, J = 3.8 Hz, CH_2Cl), 2.19 (dt, J = 6.9, 2.0 Hz, H8), 1.69 (dd, J = 6.5, 1.0 Hz, H1), 1.46–1.34 (m, CH_2's), 0.88 (t, J = 7.1 Hz, H11), 0.86 (s, $SiC(CH_3)_3$), 0.02 (d, J = 9.5 Hz, $Si(CH_3)_2$; HRMS (EI$^+$) calcd for $C_{15}H_{24}{}^{35}ClO_3Si$ ($M - t$-Bu) 315.1183, found 315.1178.

Attempted Preparation of (*E*)-(*rel*-1*R*,2*S*)-2-((*tert*-Butyldimethylsilyl)oxy)-1-(chloroacetoxy)-1-cyclohexyl-3-pentene (11d). The procedure described for **11a** was employed with 45 mg (0.15 mmol) of alcohol **4d**, 79 mg (0.30 mmol) of Ph_3P, 28 mg (0.30 mmol) of chloroacetic acid, and 47 μL (0.30 mmol) of DEAD. After reaction times up to 48 h, only starting material was recovered.

(*E*)-(*rel*-1*R*,2*S*)-2-((*tert*-Butyldimethylsilyl)oxy)-1-(chloroacetoxy)-1-phenyl-3-pentene (11e). The procedure

described for 11a was employed with 50 mg (0.17 mmol) of alcohol 4e, 90 mg (0.34 mmol) of Ph_3P, 32 mg (0.34 mmol) of chloroacetic acid, and 54 μL (0.34 mmol) of DEAD affording 54 mg (86%) of ester 11e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.18 (m, aryl H's), 6.23 (d, J = 6.2 Hz, H1), 5.75-5.51 (m, H3 and H4), 3.97 (d, J = 2.2 Hz, CH_2Cl), 3.55 (dd, J = 14.6, 8.3 Hz, H2), 1.65 (d, J = 7.2 Hz, H5), 0.73 (s, $SiC(CH_3)_3$), -0.06 (d, J = 29.0 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{20}{}^{35}ClO_3Si$ (M - t-Bu) 311.0870, found 311.0874.

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Supplementary Material Available: Representative ^{1}H NMR spectra (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Free-Radical Ring Expansion of Fused Cyclobutanones: Stereospecific Construction of 5,7-, 6,7-, 7,7-, 8,7-, and 5,8-Cis-Fused Bicyclic Systems[1]

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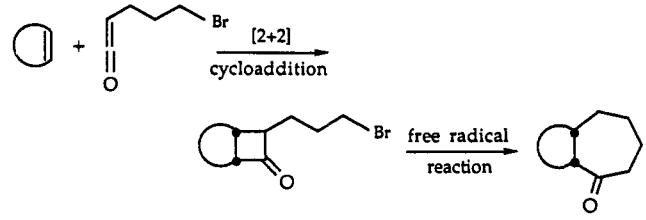
A new method of appending seven- and eight-membered rings to cycloalkenes is described. Treatment of selected alkene precursors with an ω-bromoalkyl ketene or a keteniminium salt leads to haloalkyl cyclobutanone formation. Tri-*n*-butyltin hydride promoted ring expansion then yields the annulated product. Since the initial cyclobutanone is cis fused, the final product is also produced stereospecifically with a cis ring fusion.

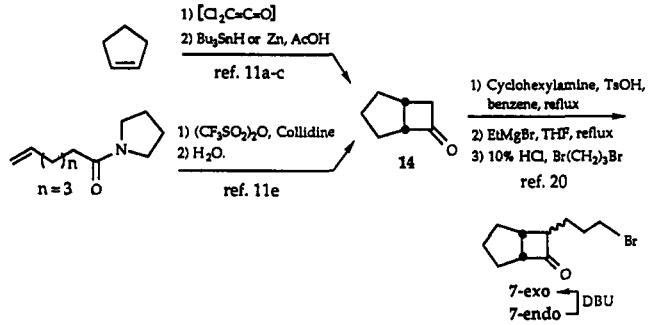
Introduction

Development of methods for the synthesis of carbocyclic molecules containing fused seven- and eight-membered rings[2,3] is currently an area of active investigation. Such carbon skeletons form the basic structures of many biologically active natural products.[4] During a study of the free-radical reactions of cyclobutanones,[5] we discovered a free-radical-based[6] ring expansion[7,8] reaction which

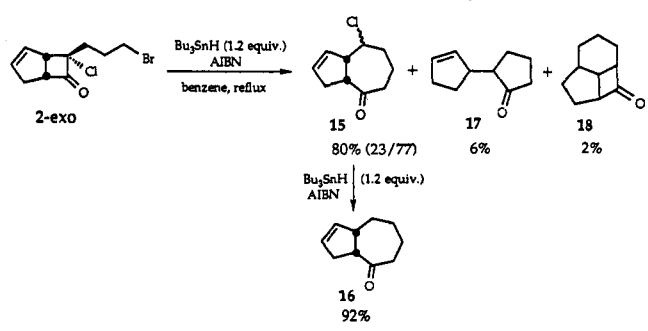
Scheme I. [2 + 2] Cycloaddition and Subsequent Ring Expansion



Scheme II. Preparation and Subsequent Alkylation of 17



Scheme III. Free-Radical Reaction of Cyclobutanone



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