STEREOSELECTIVE SYNTHESIS OF DI- and TRISUBSTITUTED ALKENYLSTANNANES AND 2-(TRIMETHYLSTANNYL)-1,3-BUTADIENES. CONVERSION OF THE TRISUBSTITUTED ALKENYLSTANNANES TO THE TETRASUBSTITUTED ALKENES

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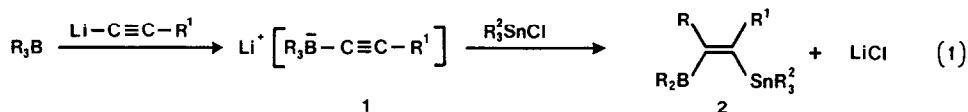
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Summary

Di- and trisubstituted alkenylstannanes were synthesized by selective conversion of the dialkylboryl moiety of $\underline{3}$ to the alkenylcopper followed by treatment with methanol or alkyl halides. By starting from conjugated terminal enynes to produce $\underline{3}$, 2-(trimethylstannyl)-1,3-butadienes were similarly synthesized. The readily available trisubstituted alkenylstannanes are useful precursors for the synthesis of stereochemically defined tetrasubstituted alkenes.

INTRODUCTION

Alkenylstannanes have been utilized for a variety of synthetic applications.[1] The palladium-catalyzed coupling reaction of vinyl triflates and vinyl halides with alkenylstannanes and related reactions have been intensively investigated.[2] The facile transmetalation reaction between alkenylstannane and alkyllithium remains as one of the most direct routes to certain alkenyllithium reagents.[3] Treatment with iodine affords the corresponding vinyl iodide with retention of configuration of the vinyl group.[4] The versatility of these reactions has stimulated an intense interest in the development of new synthetic methodologies for alkenylstannanes.

Although the hydrostannation reaction of alkynes provides a simple route to alkenylstannanes, it is generally not stereoselective.[5] The addition reaction of (trialkylstannyl)copper and related reagents to 1-alkynes and α,β-acetylenic esters and amides has become the focus of attention in recent years.[6] This interest is due in part to the fact that the reaction exhibits high regio- and stereoselectivity. Vinyl triflates and vinyl iodides have also been converted to alkenylstannanes by the reaction with Me₃SnMgMe in the presence of CuCN catalyst.[6b]

Another approach to alkenylstannanes involves the use of organoborate chemistry. It has been reported that the intramolecular transfer reaction of lithium 1-alkynyltrialkylborate $\underline{1}$ induced by trimethyltin chloride is highly stereoselective with the resultant dialkylboryl-substituted alkenylstannane $\underline{2}$ having the migrating alkyl group <u>trans</u> to the trialkyltin group (eq 1).[7] The synthetic potential of the alkenyl intermediate $\underline{2}$ constructed

$$R_3B \xrightarrow{\text{Li}-C\equiv C-R^1} \text{Li}^+\left[R_3\bar{B}-C\equiv C-R^1\right] \xrightarrow{R_3^2\text{SnCl}} \underset{2}{\overset{R}{\underset{R_2B}{>}}\!\!=\!\!\overset{R^1}{\underset{SnR_3^2}{<}}} + \text{LiCl} \qquad (1)$$

with both boron and tin appendages has been recognized and several interesting applications have been discovered.[8] The possibility of independently applying a variety of reactions of alkenylborane and alkenylstannane to this bifunctional adduct provides many opportunities for subsequent synthetic elaborations. We recently reported the use of $\underline{2}$ for the regio- and stereoselective synthesis of trisubstituted alkenylstannanes;[9] we now disclose the full account of that effort.

RESULTS AND DISCUSSION

Di- and Trisubstituted Alkenylstannanes

It has been shown that both alkenylboranes and alkenylstannanes can be converted to
alkenylcopper derivatives by first treating with an alkyllithium reagent followed by adding
the resultant solution to a coper(I) species.[10,11] We found that the dialkylboryl moiety of $\underline{3}$
could be selectively reacted with n-butyllithium without interference from the adjacent
trimethylstannyl group. Apparently the empty p-orbital of the boron atom makes it the
preferred target. The resultant alkenylcopper derivative was then treated with allyl bromide,
methyl iodide, or 2,3-dibromopropene to form the trisubstituted alkenylstannane $\underline{4}$ or was
protonated with methanol to form the corresponding disubstituted alkenylstannane (Scheme I).
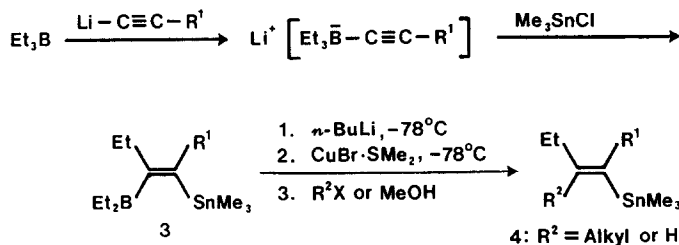
Scheme I

Table I. Synthesis of Di- and Trisubstituted Alkenylstannanes

alkenylstannane	R^1	$R^{2\underline{a}}$	isolated yield,$^{\underline{b}}$ %
$\underline{4a}$	$\underline{n}\text{-}C_6H_{13}$	$H_2C=CHCH_2$	80
$\underline{4b}$	$\underline{n}\text{-}C_6H_{13}$	CH_3	70
$\underline{4c}$	$\underline{n}\text{-}C_6H_{13}$	$H_2C=CBrCH_2$	80
$\underline{4d}$	$CH_2CH_2CH_2Cl$	$H_2C=CHCH_2$	75
$\underline{4e}$	C_6H_5	$H_2C=CHCH_2$	58
$\underline{4f}$	CH_2SiMe_3	$H_2C=CHCH_2$	61
$\underline{4g}$	$\underline{n}\text{-}C_6H_{13}$	H	76(85:15)
$\underline{4h}$	$CH_2CH_2CH_2Cl$	H	64(88:12)
$\underline{4i}$	CH_2SiMe_3	H	53(95:5)

$\underline{a}$ R^2X = allyl bromide, methyl iodide, or 2,3-dibromopropene. $\underline{b}$ The number in parentheses is
the ratio of 4:5.

The trisubstituted alkenylstannanes summarized in Table I were found to contain only one
stereoisomer (>98%) as indicated by the ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra.
Protonolysis of $\underline{4b}$ with 4 N hydrochloric acid produced ($\underline{Z}$)-3-methyl-3-decene. We have also
synthesized ($\underline{E}$)-3-methyl-3-decene by Normant's procedure[12] and have compared the ^1H and ^{13}C NMR
spectra of these two isomers. The $\underline{Z}$ isomer was free from contamination of the $\underline{E}$ isomer. The
reaction sequence outlined in Scheme I thus provides a highly regio- and stereoselective
pathway to the trisubstituted alkenylstannanes. Although the disubstituted species can be
synthesized by a variety of methods, a general route to the trisubstituted adducts from simple
nonconjugated alkynes has not been reported previously.[13]

Attempts to selectively protonate the dialkylboryl moiety of $\underline{3}$ to form the corresponding
disubstituted alkenylstannane with methanol, acetic acid, or 2,4-pentanedione were
unsuccessful. However, it was reported that an alkenylcopper is susceptible to attack by

methanol and could be selectively protonated in the presence of an alkenylstannane moiety.[6d] Indeed, when the dialkylboryl moiety of **3** was first converted to alkenylcopper followed by treatment with methanol, the corresponding disubstituted alkenylstannane was obtained (Table I). Surprisingly, unlike the trisubstituted cases, a substantial amount of the regioisomer **5** was also produced. The assignments of the geometry to the major and the minor isomers were

5
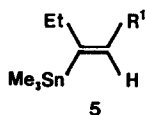
based on the fact that the coupling constants between the vinyl protons and $^{117}Sn/^{119}Sn$ are about 80 Hz, indicating a _cis_ H-Sn relationship,[4] and the formation of (_Z_)-3-decene exclusively when the mixture of **4g** and **5g** was treated with acetic acid.

The isomerization does not appear to occur because of heating during distillation, since treatment of the crude products without distillation with iodine produced alkenyl iodides also containing an equal amount of the minor isomers. One possible explanation is that alkenylcopper **6** derived from **3** is in equilibrium with **7** through the elimination of (trimethylstannyl)copper followed by addition (eq 2).[6d,14] We observed that when **6a** was generated at higher reaction
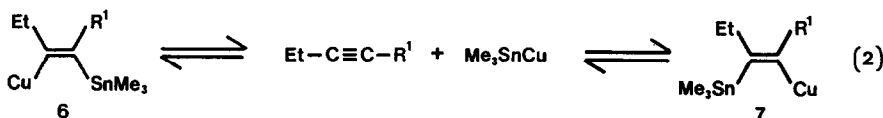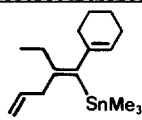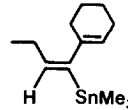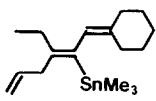

temperatures before allyl bromide was introduced, a significant amount of 3-decyne was produced. Presumably in the trisubstituted cases, the equilibration process was repressed because of fast coupling reactions with alkyl halides and/or (trimethylstannyl)copper was destroyed by the presence of alkyl halides. It is known that (trimethylstannyl)coper is stable to methanol[6d] and therefore the equilibration process could occur. We are currently investigating the cause of this isomerization and developing new reaction conditions to avoid this problem.
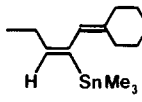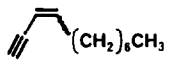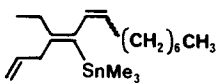
2-(Trimethylstannyl)-1,3-butadienes

It has been reported that 2-(tributylstannyl)-1,3-butadiene could be easily converted to 2-lithio-1,3-butadiene by the transmetalation reaciton with _n_-butyllithium.[15] Subsequent reactions with carbonyl compounds afforded a variety of 2-sutstituted 1,3-butadienes. The Diels-Alder reaction with activated dienophiles has also been investigated.[16] The alkenylstannane functionality in the resultant cyclohexene adducts provides a useful handle for subsequent chemical transformations. However, only a few synthetic methodologies for the substituted 2-(trialkylstannyl)-1,3-butadienes have been reported.[17] We envisioned that Scheme I could be easily adopted for the synthesis of 2-(trimethylstannyl)-1,3-butadienes by starting from conjugated terminal enynes.

Indeed, the reaction sequence outlined in Scheme I was found to be equally applicable to several conjugated terminal enynes (Table II). Only one isomer of the resulting dienes **8a-8d** could be detected by ^1H(270 MHz) and ^{13}C(67.9 MHz) NMR spectra even in the cases of **8b** and **8d**. Triene **8e** is a 4:1 mixture of the (**4Z, 6Z**) and the (**4Z, 6E**) isomers simply because the starting enyne is a 4:1 mixture of the _Z_ and the _E_ isomers. The coupling constant between the vinyl

Table II. Synthesis of 2-(Trimethylstannyl)-1,3-butadienes.

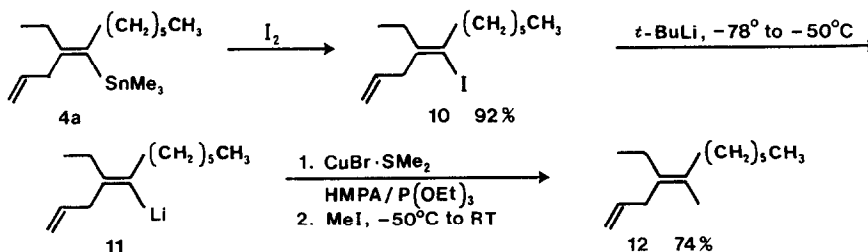| enyne	R²X	alkenylstannane		isolated yield, %
	Br		8a	68
	MeOH		8b	62
	Br		8c	65
	MeOH		8d	63
	Br		8e	65

proton and $^{117}Sn/^{119}Sn$ on the same double bond is around 78 Hz for both 8b and 8d, again indicating a cis H-Sn relationship. Protonolysis of the dialkylboryl-substituted alkenylstannane intermediates derived from tri-n-butylborane with formic acid afforded dienes 9. Typical cis coupling constants between the vinyl protons of the newly formed double bond were observed.

9a: J = 11.7 Hz ; 69%   9b: J = 11 Hz ; 62%   9c: 5Z,7Z J = 9 Hz
                                                      5Z,7E J = 11 Hz   62%
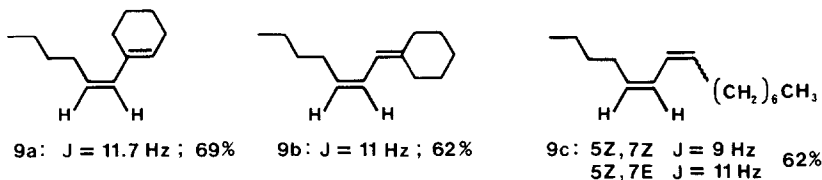
Tetrasubstituted Alkenes

Stereoselective synthesis of tetrasubstituted alkenes has been a challenging synthetic task.[13,18] With the trisubstituted alkenylstannanes now readily available, several stereochemically defined tetrasubstituted alkenes have been easily synthesized. Alkenylstannane 4a was converted to alkene 12 by the procedure outlined in Scheme II.

Scheme II

4a $\xrightarrow{I_2}$ 10   92% $\xrightarrow{t\text{-BuLi, }-78° \text{ to }-50°C}$

11    $\xrightarrow[\substack{\text{HMPA/P(OEt)}_3 \\ 2. \text{ MeI, }-50°C \text{ to RT}}]{\text{1. CuBr·SMe}_2}$ 12   74%

Vinyllithium 11 was obtained by treatment of 4a with iodine followed by treating the isolated vinyl iodide 10 with 2.5 equiv of tert-butyllithium. Attempts to convert 4a to 11 directly by

transmetalation with n-butyllithium failed. This failure is perhaps not surprising, because other cis-alkenylstannanes have been found to be very unreactive toward n-butyllithium even at room temperature.[19] Apparently, the tin-lithium exchange reaction with highly substituted alkenylstannanes is thermodynamically unfavorable.[3a] Direct treatment of 11 with methyl iodide resulted in the foramtion of 10 again, presumably through a "reverse" lithium-iodine exchange. This problem was circumvented by first converting 11 to the corresponding alkenylcopper followed by coupling with methyl iodide to afford 12. The structural isomer, (E)-3-methyl-4-(2-propenyl)-3-decene (14), was also obtained by first converting 4b to the corresponding vinyl iodide 13 (79%) followed by coupling with allyl bromide through alkenylcopper (61% yield). The ^{13}C NMR (67.9 MHz) spectra showed that 12 and 14 were free from the presence of each other.

Compounds similar to 4d have been utilized as donor-acceptor conjunctive reagents for the construction of carbocyclic structures.[11] We simply adopted the same strategy by first converting 4d to the corresponding alkenylcopper followed by treatment with 2-cyclohexenone. The conjugate addition reaction using a sterically hindered trisubstituted alkenylcopper proceeded smoothly to give 16 without difficulty. Subsequent treatment of 16 with KH led to intramolecular alkylation which produced a 1-decalone derivative 17 having a tetrasubstituted exocyclic double bond (Scheme III).

Scheme III
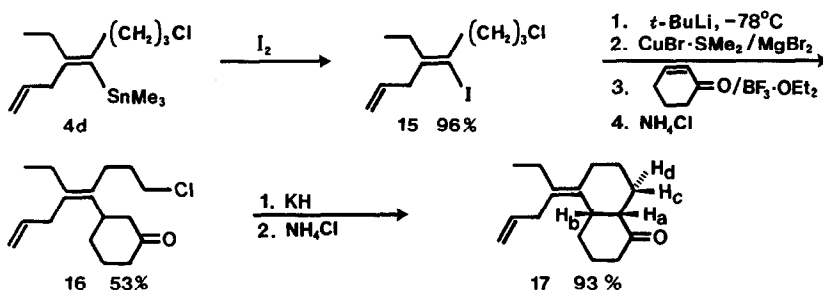
Unlike the previous cases,[11] 17 contains only one isomer. The assignment of the cis-fused structure to 17 is based on the fact that the signal at δ 2.92 of the ^{1}H NMR (270 MHz) spectrum attributed to H_a is a triplet of doublet with J = 4.4 Hz and 12.3 Hz, respectively. Similarly, the signal at δ 2.37 attributed to H_b is also a triplet of doublet with J = 4.7 Hz and 12.8 Hz, respectively. These results indicate that H_a is in a gauche relationship with both H_b and H_c and an anti relationship with H_d, suggesting a cis-fused structure for 17. The trans-fused isomer 18 would have an anti relationship with both H_b and H_c and a gauche relationship with H_d.

Attempts to convert 17 to 18 by prolonged heating (48 h) at the reflux temperature of a NaOMe/MeOH solution resulted only in slow decomposition of 17 without detecting the trans-fused isomer 18 (eq 3).


(3)
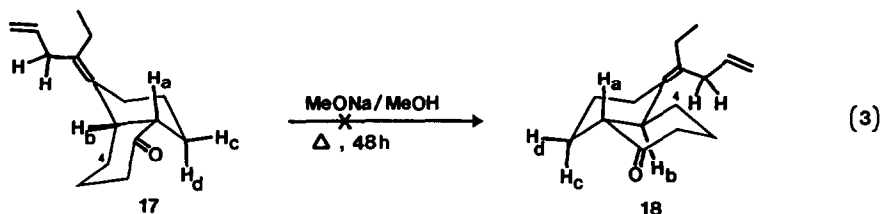
This lack of isomerization is in sharp contrast with 1-decalone derivative 19 which can be converted completely to the trans isomer 20 (eq 4).[11] Examination of

(4)
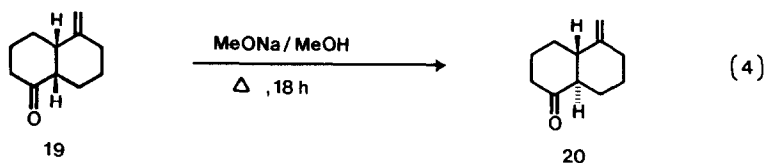
molecular models shows that 18 suffers from a large nonbonded $A^{(1,3)}$ steric interaction[20] between the allylic side chain and C(4). Apparently, this repulsion is severe enough to shift the equilibrium in favor of 17 which can avoid this $A^{(1,3)}$ strain.

Functionalized terminal alkyne 23 has also been utilized for the synthesis of bicyclic compound 27 having a stereochemically defined tetrasubstituted exocyclic double bond (Scheme IV).

Scheme IV
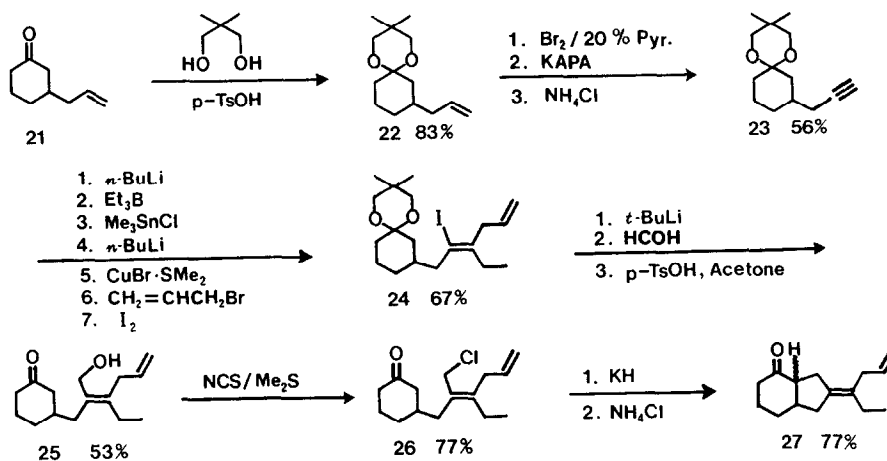
Treatment of 22 with bromine in the presence of 20% pyridine followed by dehydrobromination of the resultant dibromide with potassium 3-aminopropylamide (KAPA)[21] produced 23. In a what is essentially a single operation, 23 was converted to 24 in 67% yield. Transformation of 24 to 25 was accomplished by treating the vinyllithium derived from 24 with formaldehyde followed by deketalization. Reaction of 25 with a mixture of dimethyl sulfide and N-chlorosuccinimide in methylene chloride[22] afforded allyl chloride 26. Cyclization of 26 by treatment with KH gave 27 as a mixture of the cis- and trans-fused isomers (isomer ratio = 3:2).

In summary, we have demonstrated that dialkylboryl-substituted alkenylstannane 3 is a synthon of dianion 28 and the different reactivities of boron and tin functionalities can be independently exploited. This synthetic flexibility creates ways to pull various
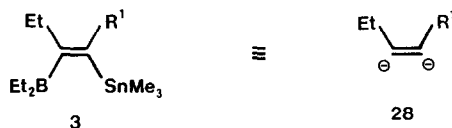
functionalized fragments together and making it possible to transform them into a complex chemical structure.

EXPERIMENTAL

General procedures described in Chapter 9 of ref. 23 for the manipulation of organoborane and other organometallic reagnets were employed. All glassware, syringes, and needles were oven dried at 140°C for several hours. The glassware were assembled while hot and cooled under a stream of dry nitrogen. The ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded on a JEOL GX-270 NMR spectrometer with CDCl$_3$ as solvent and Me$_4$Si or CHCl$_3$ (^{1}H δ 7.26; ^{13}C δ 77.02) as internal standard. The IR spectra were taken on a Beckman IR8 or a Perkin-Elmer 1310 spectrometer. Mass spectra were obtained on a Finnigan 4500 GC/MS instrument, and the fragments containing ^{118}Sn are indicated with an asterisk. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN.

Materials. Tetrahydrofuran and diethyl ether were distilled from LiAlH$_4$ and stored under nitrogen. Triethylborane, Trimethyltin chloride, CuBr·SMe$_2$, 2,3-dibromopropene, 1,3-diaminopropane, KH (35% in oil), and N-chlorosuccinimide were obtained from Aldrich Chemical Inc. and used directly without further purification. n-Butyllithium in hexane and tert-butyllithium in pentane were purchased from Alfa and used after the concentration was standardized. 5-Chloro-1-pentyne was obtained from Farchan Laboratories. 3-(Trimethylsilyl)propyne,[24] conjugated terminal enynes,[25] and 3-(2-propenyl)cyclohexanone[26] were synthesized according to the reported procedures.

Alkenylstannanes. The following procedure for the preparation of (Z)-4-ethyl-5-(trimethylstannyl)-1,4-undecadiene (4a) is representative. The intermediate 3a (10 mmol) was prepared as described previously.[7] The reaction flask was cooled to -78°C and charged with 4.10 mL of n-butyllithium (2.44 M in hexane, 10 mmol). After 15 min, the reaction mixture was transferred via cannula to a separate reaction flask containing 2.06 g (10 mmol) of CuBr·SMe$_2$ in 20 ml of THF maintained at -78°C. After an additional 1 h of stirring at -78°C, 2.60 mL of allyl bromide (3.63 g, 30 mmol) was introduced.[27] The reaction mixture was then allowed to warm to room temperature. After an oxidative workup with 4 mL of 3 N NaOH and 4 mL of 30% H$_2$O$_2$, the organic layer was then washed with water, dried over MgSO$_4$, and concentrated. The residue was filtered through a short aluminum oxide (acid washed from Merck) column. Distillation on a short-path distilling head afforded 2.74 g (80% yield) of 4a as a colorless liquid: bp 66°C (0.01 torr); IR (neat) 1640, 1605, 1455, 1375, 1190, 990, 910, 760, 710 cm^{-1}; ^{1}H NMR δ 5.72 (1H, ddt, J = 17.0, 10.1 and 6.4 Hz), 5.02 (1H, dm, J = 17 Hz), 4.99 (1H, dm, J = 10 Hz), 2.79 (2H, br d, J = 6.4 Hz), 2.22 (2H, t), 2.12 (2H, q), 1.28 (8H, br), 0.96 (3H, t), 0.89 (3H, t), 0.14 (9H, s); ^{13}C NMR δ 148.00, 139.45, 137.75, 115.51, 43.79, 34.24, 31.98, 30.97, 29.47, 23.39, 22.75, 14.10, 13.86, -7.63; MS, m/e 327* (M$^+$-CH$_3$), 189*, 163*, 149*, 133*, 109, 95. Anal. Calcd for C$_{16}$H$_{32}$Sn: C, 56.01; H, 9.40. Found: C, 56.15; H, 9.40.

(E)-3-Methyl-4-(trimethylstannyl)-3-decene (4b): bp 64°C (0.01 torr); IR (neat) 1615, 1460, 1375, 1190, 760, 705 cm^{-1}; ^{1}H NMR δ 2.14 (4H, m), 1.76 (3H, s), 1.27 (8H, br), 0.98 (3H, t), 0.88 (3H, t), 0.13 (9H, s); ^{13}C NMR δ 145.83, 136.79, 34.02, 31.97, 30.99, 29.42, 26.18, 25.04, 22.74, 14.10, 13.54, -7.98; MS, m/e 301* (M$^+$-CH$_3$), 163*, 153, 152, 149*, 97, 83. Anal. Calcd for C$_{14}$H$_{30}$Sn: C, 53.03; H, 9.54. Found: C, 53.13, H, 9.33.

(Z)-2-Bromo-4-ethyl-5-(trimethylstannyl)-1,4-undecadiene (4c): bp 92°C (0.02 torr); IR (neat) 1630, 1610, 1455, 1430, 1375, 1190, 1085, 880, 765, 705 cm^{-1}; ^{1}H NMR δ 5.61 (1H, dt, J = 1.5 and 1.7 Hz), 5.47 (1H, d, J = 1.5 Hz), 3.16 (2H, br s), 2.24 (2H, br), 2.14 (2H, q, J = 7.5 Hz), 1.29 (8H, br), 0.97 (3H, t, J = 7.51 Hz), 0.89 (3H, t, J = 7.0 Hz), 0.16 (9H, s); ^{13}C NMR δ 145.64, 143.48, 133.45, 117.22, 50.53, 34.33, 31.89, 30.56, 29.43, 23.58, 22.71, 14.09, 13.85, -7.66; MS, m/e 405* (M$^+$-CH$_3$), 227*, 197*, 177, 163*, 149, 133*, 121, 107, 93, 79.

(Z)-8-Chloro-4-ethyl-5-(trimethylstannyl)-1,4-octadiene (4d). To a 100-mL flask containing a solution of 1.03 g of 5-chloro-1-pentyne (10 mmol) in 20 mL of THF maintained at -78°C was

introduced 4.10 mL of a 2.44 M n-butyllithium (10 mmol) in hexane. After stirring for 15 min,
10 mL of a 1.0 M solution of Et_3B in THF was added and the reaction mixture was allowed to warm
to room temperature. The remaining procedure was carried out as described for **4a** to afford
2.51 g (75%) of **4d** as a colorless liquid: bp 62°C (0.01 torr); IR (neat) 1640, 1605, 1435,
1305, 1190, 990, 910, 765, 650 cm^{-1}; ^1H NMR δ 5.71 (1H, ddt, J = 16.9, 10.3, and 6.4 Hz), 5.03
(1H, dm, J = 17 Hz), 5.01 (1H, dm, J = 10 Hz), 3.51 (2H, t, J = 6.6 Hz), 2.80 (2H, dt, J = 6.4
and 1 Hz), 2.38 (2H, t, J = 7.7 Hz), 2.14 (2H, q, J = 7.5 Hz), 1.72 (2H, m), 0.97 (3H, t, J =
7.5 Hz), 0.16 (9H, s); ^{13}C NMR δ 149.85, 137.38, 137.27, 115.76, 44.63, 43.67, 33.67, 31.36,
23.45, 13.76, -7.61; MS, m/e 319* (M^+-CH_3), 283*, 255*, 183*, 163*, 149*, 135, 107, 93, 79.
Anal. Calcd for $C_{13}H_{25}ClSn$: C, 46.54; H, 7.51. Found: C, 46.73; H, 7.70.

(Z)-2-Ethyl-1-(trimethylstannyl)-1-phenyl-1,4-pentadiene (**4e**): bp 50°C (0.01 torr); IR (neat)
1640, 1610, 1485, 1465, 1430, 1370, 1185, 1060, 1030, 990, 910, 765, 700 cm^{-1}; ^1H NMR δ 7.25
(2H, t, J = 7.4 Hz), 7.08 (1H, tt, J = 7.4 and 1.3 Hz), 6.86 (2H, dd, J = 7.1 and 1.3 Hz), 5.84
(1H, ddt, J = 17.0, 10.1, and 6.2 Hz), 5.13 (1H, dm, J = 17 Hz), 5.07 (1H, dm, J = 10 Hz), 2.95
(2H, dt, J = 6.4 and 1.5 Hz), 1.96 (2H, q, J = 7.5 Hz), 0.87 (3H, t, J = 7.5 Hz), 0.04 (9H, s);
^{13}C NMR δ 150.08, 146.06, 142.16, 137.24, 128.02, 127.13, 124.54, 115.84, 41.97, 25.40, 13.66,
-7.75; MS, m/e 319* (M^+-CH_3), 189*, 171, 163*, 149*, 143, 129, 91. Anal. Calcd for $C_{16}H_{24}Sn$:
C, 57.36; H, 7.22. Found: C, 57.14; H, 7.31.

(Z)-4-Ethyl-6-(trimethylsilyl)-5-(trimethylstannyl)-1,4-hexadiene (**4f**): bp 50°C (0.01 torr); IR
(neat) 1640, 1595, 1410, 1245, 1185, 1155, 990, 910, 850, 760, 700 cm^{-1}; ^1H NMR δ 5.70 (1H,
ddt, J = 17.0, 9.9, and 6.6 Hz), 5.04 (1H, dm, J = 17 Hz), 4.99 (1H, dm, J = 10 Hz), 2.79 (2H,
d, J = 6.4 Hz), 2.06 (2H, q, J = 7.5 Hz), 1.82 (2H, s), 0.94 (3H, t, J = 7.5 Hz), 0.15 (9H, s,
$^2J_{SnH}$ = 51.8 Hz), -0.004 (9H, s); ^{13}C NMR δ 145.29, 138.15, 134.19, 115.30, 43,47, 24.56,
23.40, 12.70, -0.67, -7.08; MS, m/e 329* (M^+-CH_3), 163*, 107, 73. Anal. Calcd for $C_{14}H_{30}SiSn$:
C, 48.72; H, 8.76. Found: C, 48.51; H, 8.83.

(E)-4-(Trimethylstannyl)-3-decene (**4g**): bp 46°C (0.01 torr); IR (neat) 1610, 1460, 1375, 1185,
760, 705 cm^{-1}; ^1H NMR δ 5.53 (1H, tt, J = 6.8 and 1.3 Hz, $^3J_{SnH}$ = 83 Hz), 2.27 (2H, t, J = 6.8
Hz), 2.12 (2H, quintet, J = 7 Hz), 1.28 (8H, br), 0.97 (3H, t, J = 6.3 Hz), 0.89 (3H, t, J =
6.6 Hz), 0.09 (9H, s); ^{13}C NMR δ 143.59, 142.07, 32.63, 31.86, 30.36, 29.21, 22.71, 21.61,
14.39, 14.12, -9.27; MS, m/e = 287* (M^+-CH_3), 163*, 149*, 138, 97. The ^{13}C NMR and GC-MS
spectra of **4g** and the ^1H and ^{13}C NMR spectra of the corresponding alkenyl iodide indicate the
presence of about 15% **5g**.

(E)-7-Chloro-4-(trimethylstannyl)-3-heptene (**4h**): bp 46°C (0.01 torr); IR (neat) 1610, 1455,
1305, 1185, 765, 650 cm^{-1}; ^1H NMR δ 5.60 (1H, t, J = 6.8 Hz, $^3J_{SnH}$ = 78.4 Hz), 3.49 (2H, t, J =
6.6 Hz), 2.42 (2H, t, J = 7.5 Hz), 2.14 (2H, quintet, J = 7.2 Hz), 1.79 (2H, quintet, J = 7
Hz), 0.98 (3H, t, J = 7.5 Hz), 0.11 (9H, s); ^{13}C NMR δ 143.84, 141.30, 44.54, 33.07, 29.74,
21.71, 14.32, -9.33; MS, m/e 279* (M^+-CH_3), 243*, 183*, 163*, 149*, 95, 81. The ^1H, ^{13}C, and
GC-MS spectra of **4h** and the corresponding alkenyl iodide indicate the presence of about 12% **5h**.

(E)-1-(Trimethylsilyl)-2-(trimethylstannyl)-2-pentene (**4i**): bp 36°C (0.04 torr); IR (neat)
1600, 1410, 1300, 1250, 850, 755, 700 cm^{-1}; ^1H NMR δ 5.37 (1H, tt, J = 6.4 and 1.3 Hz, $^3J_{SnH}$ =
80.1 Hz), 2.05 (2H, quintet, J = 7.2 Hz), 1.81 (3H, s), 0.97 (3H, t, J = 7.5 Hz), 0.10 (9H, s,
Me_3Sn), 0.01 (9H, s, Me_3Si); ^{13}C NMR δ 140.36, 139.24, 24.22, 22.08, 14.11, -0.81, -8.81; MS,
m/e 304* (M^+), 289*, 163*, 149*, 141, 133*, 125, 73. Anal. Calcd for $C_{11}H_{26}SiSn$: C, 43.31; H,
8.59. Found: C, 43.77; H, 8.74. The ^1H and ^{13}C NMR spectra of **4i** and the corresponding
alkenyl iodide indicate the presence of about 5% **5i**.

(Z)-1-(1-Cyclohexenyl)-2-ethyl-1-(trimethylstannyl)-1,4-pentadiene (**8a**): bp 64°C (0.01 torr);
IR (neat) 1640, 1600, 1430, 990, 910, 760 cm^{-1}; ^1H NMR δ 5.75 (1H, ddt, J = 16.8, 10.0 and 6.5

Hz), 5.11 (1H, br), 5.05 (1H, dd, J = 17 and 1.6 Hz), 5.00 (1H, dd, J = 10 and 1.6 Hz), 2.79 (2H, d, J = 6.4 Hz), 2.08 (2H, q, J = 7.5 Hz), 2.04 (2H, br), 1.82 (2H, br), 1.58 (4H, m), 0.94 (3H, t, J = 7.5 Hz), 0.12 (9H, s); ^{13}C NMR δ 147.60, 143.90 141.47, 137.60, 119.57, 115.45, 41.64, 30.07, 25.17, 24.09, 23.05, 22.53, 14.29, -7.71; MS, m/e 338* (M+), 323*, 189*, 175, 174, 165*, 133*, 91. Anal. Calcd for $C_{16}H_{28}Sn$: C, 56.67; H, 8.32. Found: C, 56.52; H, 8.30.

(E)-1-(1-Cyclohexenyl)-1-(trimethylstannyl)-1-butene (8b): bp 48⁰C (0.01 torr); IR (neat) 1600, 1440, 1185, 915, 760, 705 cm^{-1}; ^{1}H NMR δ 5.45 (1H, t, J = 6.9 Hz, $^3J_{Sn-H}$ = 78 Hz), 5.15 (1H, m), 2.10 (2H, quintet, J = 7.3 Hz), 2.05 (2H, m), 1.87 (2H, br), 1.59 (4H, br), 0.95 (3H, t, J = 7.5 Hz), 0.08 (9H, s); ^{13}C NMR δ 146.73, 140.90, 140.13, 119.70, 29.83, 25.24, 23.31, 23.13, 22.55, 14.80, -9.29; MS, m/e 298* (M+), 283*, 163*, 149*, 135, 133*, 107, 93.

(Z)-4-Ethyl-1,1-pentamethylene-3-(trimethylstannyl)-1,3,6-heptatriene (8c): bp 80⁰C (0.01 torr); IR 1640, 1600, 1440, 1230, 1180, 990, 910, 850, 760 cm^{-1}; ^{1}H NMR δ 5.76 (1H, ddt, J = 16.9, 10.1, and 6.4 Hz), 5.65 (1H, br s), 5.06 (1H, d, J = 16 Hz), 5.01 (1H, d, J = 10 Hz), 2.83 (2H, d, J = 6.4 Hz), 2.12 (2H, br), 2.08 (2H, q, J = 7.6 Hz), 1.97 (2H, t, J = 6 Hz), 1.53 (6H, br), 0.90 (3H, t, J = 7.7 Hz). 0.13 (9H, s); ^{13}C NMR δ 149.36, 137.49, 137.28, 137.04, 124.28, 115.58, 42.43, 36.34, 29.58, 28.86, 27.33, 26.85, 25.32, 12.55, -7.60; MS, m/e 337* (M+-CH₃), 189, 188, 163*, 133*, 107, 91, 79.

(E)-1,1-Pentamethylene-3-(trimethylstannyl)-1,3-hexadiene (8d): bp 52⁰C (0.01 torr); IR (neat) 1630, 1600, 1440, 1370, 1340, 1230, 1180, 1060, 1020, 840, 760, 700 cm^{-1}; ^{1}H NMR δ 5.63 (1H, br), 5.54 (1H, t, J = 6.7 Hz, $^3J_{Sn-H}$ = 78 Hz), 2.12 (2H, br), 2.08-1.95 (4H, m), 1.54 (6H, br), 0.94 (3H, t, J = 7.5 Hz), 0.09 (9H, s); ^{13}C NMR δ 142.60, 140.39, 137.90, 122.36, 36.64, 29.67, 28.99, 27.56, 26.86, 23.62, 13.68, -9.47; MS, m/e 312* (M+), 297*, 163*, 149, 133*, 107, 93.

(4Z, 6Z)- and (4Z, 6E)-4-Ethyl-5-(trimethylstannyl)-1,4,6-tetradecatriene (8e): bp 82⁰C (0.01 torr); IR (neat) 1630, 1595, 1450, 1370, 1185, 990, 960, 910, 760 cm^{-1}; ^{1}H NMR (4Z, 6Z) δ 5.93 (1H, d, J = 11.0 Hz), 5.75 (1H, ddt, J = 17.0, 10.1, and 6.4 Hz), 5.25 (1H, dt, J = 11.0 Hz), 5.07 (1H, dm, J = 17 Hz), 5.03 (1H, dm, J = 10 Hz), 2.84 (2H, dm, J = 6.4 Hz), 2.09 (2H, q, J = 7.4 Hz), 1.88 (2H, q, J = 5.9 Hz), 1.26 (10 H, br), 0.91 (3H, t), 0.88 (3H, t), 0.14 (9H, s); ^{13}C NMR (4Z, 6Z) δ 149.21, 137.35, 131.84, 127.71, 115.73, 42.41, 31.88, 29.56, 29.48, 29.26, 28.58, 25.41, 22.69, 14.10, 12.53, -7.58; MS, m/e 367* (M+-CH₃), 219, 218, 189*, 163*, 133*, 121, 107. The ^{1}H and ^{13}C NMR spectra showed the presence of the (4Z, 6E) isomer.

(Z)-1-(1-Cyclohexenyl)-1-hexene (9a): bp 40⁰C (0.1 torr); IR (neat) 1640, 1445, 910, 840, 790, 720 cm^{-1}; ^{1}H NMR δ 5.73 (1H, d, J = 11.7 Hz), 5.61 (1H, br s), 5.26 (1H, dt, J = 11.7 and 7.3 Hz), 2.23 (2H, q, J = 7 Hz), 2.13 (4H, br m), 1.6 (4H, br m), 1.35 (4H, br m), 0.90 (3H, t); ^{13}C NMR δ 135.56, 131.65, 129.75, 127.03, 32.64, 29.13, 28.69, 25.66, 23.01, 22.43, 22.23, 14.00; MS, m/e 164 (M+), 149, 135, 121, 107, 93, 79, 67, 55.

(Z)-1,1-Pentamethylene-1,3-octadiene (9b): bp 50⁰C (0.05 torr); IR (neat) 1650, 1605, 1445, 1375, 1345, 1230, 980, 850, 735 cm^{-1}; ^{1}H NMR δ 6.22 (1H, t, J = 11 Hz), 6.02 (1H, d, J = 11.5 Hz), 5.33 (1H, dt, J = 11 and 7.5 Hz), 2.27 (2H, br), 2.16 (4H, br), 1.56 (6H, br), 1.36 (4H, br), 0.91 (3H, t); ^{13}C NMR δ 143.00, 130.02, 123.80, 117.20, 37.66, 31.99, 28.98, 28.64, 27.72, 27.21, 26.89, 22.44, 14.00; MS, m/e 178 (M+), 163, 149, 135, 121, 107, 93, 79, 67, 55.

(5Z, 7Z)- and (5Z, 7E)-Pentadecadiene (9c): bp 64⁰C (0.02 torr); IR (neat) 1600, 1450, 1375, 975, 945, 715 cm^{-1}; ^{1}H NMR δ 6.25 (2H, d, J = 8.6 Hz), 5.45 (2H, q, J = 8.2 Hz), 2.17 (4H, br m), 1.28 (14 H, br), 0.89 (6H, m); ^{13}C NMR δ 132.10, 132.03, 123.68, 123.64, 31.89, 29.71, 29.31, 29.23, 27.54, 27.22, 22.70, 22.38, 14.10, 13.96; MS, m/e 208 (M+), 165, 152, 123, 110, 95, 81, 67. The ^{1}H and ^{13}C NMR spectra showed the presence of the (5Z, 7E) isomer.

(Z)-4-Ethyl-5-iodo-1,4-undecadiene (10). To a 50-mL round-bottomed flask containing 3.43 g (10 mmol) of 4a and 20 mL of diethyl ether was added dropwise 16.4 mL of an iodine solution (0.61 M in diethyl ether, 10 mmol). After 1 h, an aqueous solution of 0.42 g NaF was introduced and the reaction mixture was stirred vigorously for 10 min and then allowed to stand for 30 min. The organic layer was then separated, washed with water, dired over MgSO$_4$, and concentrated. Distillation on a short-path distilling heat afforded 2.82 g (92%) of 10 as a colorless liquid: bp 60^{0}C (0.01 torr); IR (neat) 1640, 1625, 1450, 1430, 1375, 1185, 990, 910 cm^{-1}; ^{1}H NMR δ 5.75 (1H, ddt, J = 17.0, 10.1, and 6.4 Hz), 5.09 (1H, dm, J = 17 Hz), 5.06 (1H, dm, J = 10 Hz), 3.02 (2H, d, J = 6.4 Hz), 2.53 (2H, t, J = 7.6 Hz), 2.20 (2H, q, J = 7.5 Hz), 1.53 (2H, m), 1.30 (6H, br), 0.99 (3H, t), 0.89 (3H, t); ^{13}C NMR δ 142.85, 134.74, 115.95, 106.08, 46.61, 41.31, 31.74, 29.86, 28.28, 24.66, 22.62, 14.06, 13.25; MS, m/e 306 (M$^+$), 179, 137, 123, 109, 95, 81.

(E)-4-Ethyl-5-methyl-1,4-undecadiene (12). To a 100-mL flask containing 0.61 g of 10 (2 mmol) in 20 mL of THF maintained at -78^{0}C was introduced 2.65 mL of a 1.89 M tert-butyllithium in pentane. After stirring for 15 min, the reaction mixture was transferred via cannula to a separate flask containing 0.412 g (2 mmol) of CuBr·SMe$_2$ in 20 mL of THF maintained at -50^{0}C. After an additional hour of stirring at -50^{0}C, 0.696 mL of HMPA (0.717 g, 4 mmol), 1.03 mL of triethyl phosphite (0.997 g, 6 mmol) and 0.38 mL of methyl iodide (0.85 g, 6 mmol) were introduced successively. The reaction mixture was then allowed to warm to room temperature and stirred overnight. After the addition of a saturated aqueous solution of NH$_4$Cl, the organic layer was separated, washed with water, dried over MgSO$_4$, and concentrated. Distillation on a short-path distilling head afforded 0.286 g (74%) of 12 as a colorless liquid: bp 34^{0}C (0.01 torr); IR (neat) 1635, 1465, 1375, 1150, 990, 910, 790, 720 cm^{-1}; ^{1}H NMR δ 5.75 (1H, ddt, J = 17.0, 9.9 and 6.4 Hz), 4.97 (1H, dm, J = 17 Hz), 4.94 (1H, dm, J = 10 Hz), 2.76 (2H, d, J = 6.2 Hz), 2.01 (4H, m), 1.62 (3H, s), 1.29 (8H, br), 0.93 (3H, t), 0.89 (3H, t); ^{13}C NMR δ 136.86, 131.52, 130.10, 114.17, 36.35, 34.24, 31.93, 29.54, 28.77, 24.99, 22.71, 18.03, 14.11, 13.52; MS, m/e 194 (M$^+$), 179, 165, 151, 137, 123, 109, 95, 81.

(E)-4-Iodo-3-methyl-3-decene (13): bp 74^{0}C (0.45 torr); IR (neat) 1635, 1445, 1380, 1310, 1260, 1210, 985, 800, 765, 725 cm^{-1}; ^{1}H NMR δ 2.52 (2H, t, J = 7.5 Hz), 2.21 (2H, q, J = 7.5 Hz), 1.91 (3H, s), 1.51 (2H, m), 1.29 (6H, br), 1.00 (3H, t), 0.89 (3H, t); ^{13}C NMR δ 141.34, 104.35, 41.22, 31.75, 29.81, 29.29, 28.28, 26.76, 22.63, 14.07, 13.04; MS, m/e 280 (M$^+$), 111, 97, 83.

(E)-3-Methyl-4-(2-propenyl)-3-decene (14): bp 62^{0}C (0.8 torr); IR (neat) 1635, 1460, 1375, 1065, 990, 910 cm^{-1}; ^{1}H NMR δ 5.74 (1H, ddt, J = 17.0, 10.1, and 6.2 Hz), 4.96 (1H, dm, J = 17 Hz), 4.94 (1H, dm, J = 10 Hz), 2.75 (2H, d, J = 6.2 Hz), 2.04 (2H, q, J = 7.9 Hz), 1.62, (3H, s), 1.28 (8H, br), 0.96 (3H, t), 0.88 (3H, t); ^{13}C NMR δ 136.86, 131.80, 129.83, 114.16, 36.86, 32.15, 31.92, 29.70, 29.12, 27.21, 22.73, 17.48, 14.11, 13.24; MS, m/e 194 (M$^+$), 179, 165, 151, 137, 123, 109, 95, 81.

(Z)-8-Chloro-4-ethyl-5-iodo-1,4-octadiene (15): bp 92^{0}C (0.09 torr); IR (neat) 1640, 1620, 1435, 1375, 1310, 1290, 1270, 1190, 1180, 1035, 990, 910, 800, 780, 730, 650 cm^{-1}; ^{1}H NMR δ 5.74 (1H, ddt, J = 17.0, 10.4, and 6.4 Hz), 5.10 (1H, dm, J = 17 Hz), 5.07 (1H, dm, J = 10 Hz), 3.54 (2H, t, J = 6.3 Hz), 3.03 (2H, d, J = 6.4 Hz), 2.72 (2H, t, J = 7.2 Hz), 2.25 (2H, q, J = 7.5 Hz), 2.03 (2H, quintet), 1.01 (3H, t); ^{13}C NMR δ 144.87, 134.39, 116.26, 103.17, 46.59, 43.58, 38.10, 32.62, 24.80, 13.25; MS, m/e 298 (M$^+$), 268, 247, 171, 129, 119, 107, 92, 81.

3-[(Z)-1-(3-Chloropropyl)-2-ethyl-1,4-pentadienyl]cyclohexanone (16). To a 100-mL flask containing 1.50 g of 15 (5.0 mmol) in 40 mL of THF maintained at -78^{0}C was introduced 4.28 mL of a 2.34 M tert-butyllithium (10.0 mmol) in pentane. After 15 min, the reaction mixture was transferred via cannula to a separate 100-mL flask containing 1.11 g of anhydrous

MgBr$_2$ (6.0 mmol) and 3.09 g of CuBr·SMe$_2$ (15 mmol) in 10 mL of THF maintained at -78^0C. After stirring for 15 min, 0.576 g of 2-cyclohexenone (6 mmol) and 0.85 g of BF$_3$·OEt$_2$ (6.0 mmol) was successively introduced. After an additional 2 h of stirring at -78^0C, the reaction mixture was allowed to warm to 0^0C and then treated with a saturated aqueous solution of NH$_4$Cl. The organic layer was then separated, washed with water, dried over MgSO$_4$, and concentrated. Column chromatogrphy (silica gel/19:1 hexane-ether) afforded 0.706 g (53%) of 16 as a colorless liquid: IR (neat) 1710, 1635, 1445, 1340, 1310, 1265, 1220, 1180, 1050, 1030, 990, 940, 910, 860, 765, 715, 640 cm^{-1}; ^{1}H NMR δ 5.71 (1H, ddt, J = 17.8, 9.7, and 5.9 Hz), 4.97 (2H, m), 3.57 (2H, t, J = 6.4 Hz), 2.84 (1H, m), 2.77 (2H, t), 2.35-1.55 (12H, m), 0.98 (3H, t); ^{13}C NMR δ 210.37, 135.63, 133.97, 133.24, 113.76, 45.69, 44.41, 40.93, 40.18, 34.04, 32.73, 29.10, 24.72, 24.50, 24.19, 12.09.

Compound 17. To a 250-mL flask was introduced a suspension of KH (~0.09 g, ~0.75 mmol) in mineral oil. The mineral oil was then removed by washing with hexane followed by the addition of 10 mL of THF and 0.081 g of 16 (0.30 mmol). The solution was stirred overnight and then treated with a saturated aqueous solution of NH$_4$Cl. The organic layer was separated, washed with water, dried over MgSO$_4$, and concentrated. Column chromatography (silica gel/19:1 hexane-ether) afforded 0.065 g (93%) of 17 as a colorless liquid: IR (neat) 1705, 1635, 1445, 1255, 1220, 1185, 1030, 990, 910, 800 cm^{-1}; ^{1}H NMR δ 5.72 (1H, ddt, J = 17.0, 10.1, and 6.2 Hz), 4.98 (1H, dm, J = 17 Hz), 4.95 (1H, dm, J = 10 Hz), 2.92 (Ha, dt, J = 12.3 and 4.4 Hz), 2.76 (2H, d, J = 6.1 Hz), 2.57-1.21 (15H, m), 0.92 (3H, t); ^{13}C NMR δ 214.87, 136.87, 133.74, 131.07, 114.66, 54.21, 40.61, 37.84, 36.14, 26.99, 25.71, 25.57, 25.49, 25.32, 24.94, 13.63; MS, m/e 232 (M$^+$), 203, 191, 173, 161, 150, 131, 119, 105, 91, 79.

3-(2-Propenyl)cyclohexanone 2,2-Dimethyltrimethylene Ketal (22). To a 250-mL flask containing 6.51 g of 21 (47.2 mmol) and 15.59 g of 2,2-dimethyl-1,3-propanediol (150 mmol) were added 150 mL of benzene and 0.2 g of p-toluenesulfonic acid monohydrate. The reaction mixture was heated to reflux for 14 h with azeotropic removal of water. After cooling to room temperature, benzene was evaporated and the residue was dissolved in 150 mL of diethyl ether. The solution was then washed with water, dried over MgSO$_4$, and concentrated. Distillation on a short-path distilling head afforded 8.80 g of 22 (83%) as a colorless liquid: bp 58^{0}C (0.03 torr); IR (neat) 1630, 1460, 1440, 1390, 1365, 1280, 1270, 1245, 1205, 1185, 1155, 1110, 1080, 1030, 1010, 990, 960, 910, 835, 805, 790, 730, 650 cm^{-1}; ^{1}H NMR δ 5.73 (1H, ddt, J = 17.8, 10, and 7.2 Hz), 4.95 (1H, dm, J = 17 Hz), 4.94 (1H, dm, J = 10 Hz), 3.48 (2H, s), 3.43 (2H, s), 2.22 (2H, t, J = 10 Hz), 1.94 (2H, t, J = 6.5 Hz), 1.75-1.5 (3H, m), 1.39 (1H, tq, J = 3.5 and 13 Hz), 1.14 (1H, dt, J = 4 and 13 Hz), 0.94 (3H, s), 0.92 (2H, m), 0.90 (3H, s); ^{13}C NMR δ 136.84, 115.73, 98.10, 69.85, 69.79, 41.22, 39.04, 33.73, 32.07, 31.89, 30.11, 22.76, 22.68, 21.87.

3-(2-Propynyl)cyclohexanone 2,2-Dimethyltrimethylene Ketal (23). To a solution of 6.272 g of 22 (28 mmol), 0.468 g of pyridine (6 mmol) and 80 mL of CCl$_4$ in a 250-ml flask was added dropwise a solution of 4.808 g of bromine (30.1 mmol) in 30 mL of CCl$_4$. The mixture was then washed with a saturated solution of sodium bicarbonate and water, dried over MgSO$_4$, and concentrated. The crude dibromide (10.8 g) was obtained in quantitative yield and was used immediately for dehydrobromination without further purification. In a separate 500-mL flask was placed 8.930 g of KH (233 mmol) in mineral oil. The mineral oil was removed by washing with hexane. The flask was then kept under a nitrogen atmosphere at 0^{0}C and 150 mL of 1,3-diaminopropane was introduced dropwise via cannula. The reaction flask was flushed periodically with nitrogen until the evolution of hydrogen subsided in about 2 h. The crude dibromide in 40 mL of 1,3-diaminopropane was introduced to the 500-mL flask and the reaction mixture was allowed to warm to room temperature. After stirring for 4 h, the mixture was transferred via cannula to a 500-mL Erlenmeyer flask containing 100 mL of a saturated aqueous

solution of NH$_4$Cl and 100 mL of diethyl ether maintained at 0^{0}C. The organic layer was then separated, washed with water, dried over MgSO$_4$, and concentrated. Column chromatography (silica gel, 5% ether in hexane) of the residue afforded 3.516 g (56%) of 23 as a colorless liquid: IR (neat) 2110, 1460, 1440, 1390, 1360, 1310, 1280, 1240, 1205, 1175, 1140, 1095, 1035, 1010, 995, 960, 920, 895, 835, 810, 790, 730, 620 cm^{-1}; ^{1}H NMR δ 3.54 (1H, d AB), 3.53 (1H, d AB), 3.46 (2H, s), 2.36 (1H, dm, J = 13 Hz), 2.24 (1H, dm, J = 13 Hz), 2.13 (2H, dd, J = 2.6 and 6.2 Hz), 1.98 (1H, t, J = 2.6 Hz), 1.85-1.58 (3H, br m), 1.48 (1H, tq, J = 3 and 13 Hz), 1.25-1.0 (3H, m), 0.96 (6H, s); ^{13}C NMR δ 97.91, 82.61, 69.85, 69.77, 69.42, 37.89, 33.25, 32.18, 31.51, 30.07, 25.46, 22.70, 22.68, 21.61; MS, m/e 222 (M$^+$), 207, 183, 137, 128, 97, 69.

3-[(Z)-3-Ethyl-2-iodo-2,5-hexadienyl]cyclohexanone 2,2-Dimethyltrimethylene Ketal (24). Terminal alkyne 23 (2.130 g, 9.6 mmol) was converted to the corresponding trisubstituted alkenylstannane by utilizing the procedure outlined for 4a. The crude alkenylstannane was treated with 2.651 g of iodine (10.3 mmol) in 20 mL of diethyl ether. The organic solvent was evaporated and the residue was purified by column chromatography (silica gel, 5% ether in hexane) to afford 2.708 g (67%) of 24 as a colorless liquid: R$_f$ = 0.5; IR (neat) 1630, 1460, 1440, 1385, 1355, 1310, 1280, 1250, 1200, 1180, 1165, 1140, 1090, 1030, 1010, 985, 955, 940, 910, 835, 810, 785, 730 cm^{-1}; ^{1}H NMR δ 5.77 (1H, ddt, J = 17.0, 10.1, and 6.4 Hz), 5.12 (1H, dm, J = 17 Hz), 5.07 (1H, dm, J = 10 Hz), 3.58 (1H, d, J = 11.4 Hz), 3.56 (1H, d, J = 11.5 Hz), 3.44 (1H, d, J = 11 Hz), 3.41 (1H, d, J = 10 Hz), 3.06 (2H, t, J = 6 Hz), 2.5-1.0 (13 H, m), 1.03 (3H, s), 0.99 (3H, t), 0.89 (3H, s); ^{13}C NMR δ 144.19, 134.70, 115.95, 104.21, 97.94, 69.95, 69.86, 47.17, 46.57, 36.11, 34.46, 34.06, 31.73, 30.13, 25.16, 22.99, 22.63, 21.96, 13.04; MS, m/e 291 (M$^+$-I), 183, 97, 79, 69.

3-[(Z)-3-Ethyl-2-hydroxymethyl-2,5-hexadienyl]cyclohexanone (25). To a 50-mL, three-necked flask equipped with a low temperature thermometer, a magnetic stirring bar, and a gas inlet were successively added by syringes 0.882 g of 24 (2.1 mmol) and 20 mL of THF. The reaction flask was cooled to -78^{0}C and 2.0 mL of a 2.65 M tert-butyllithium (5.3 mmol) in pentane was introduced. After 30 min of stirring, the reactin mixture was allowed to warm to -40^{0}C and then treated with formaldehyde. The monomeric formaldehyde was generated in a separate flask by thermal depolymerization (180^{0}C, bath temperature) of 1.439 g (48 mmol) of anhydrous paraformaldehyde and was swept into the reaction vessel in a stream of dry nitrogen nitrogen. The reaction mixture was then treated with 10 mL of a saturated aqueous solution of NH$_4$Cl. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2x20 mL). The combined organic layers were washed with water, dried over MgSO$_4$, and concentrated. The residue and 0.026 g of p-toluenesulfonic acid were then dissolved in 30 mL of acetone and the resulting mixture was stirred for 12 h. After the introduction of 60 mL of diethyl ether, the solution was washed with water (3x20 mL), dried over MgSO$_4$, and concentrated. The residue was purified by column chromatogrophy (silica gel, 20% diethyl ether in hexane) to afford 0.261 g (53%) of 25 as a colorless liquid: IR (neat) 3400, 1695, 1630, 1440, 1410, 1370, 1340, 1305, 1220, 1005, 990, 905, 865, 790, 750 cm^{-1}; ^{1}H NMR δ 5.80 (1H, ddt, J = 17.0, 10.2, and 6.2 Hz), 5.02 (1H, dm, J = 17 Hz), 5.00 (1H, dm, J = 10 Hz), 4.10 (1H, d AB, J = 12.1 Hz), 4.05 (1H, d AB, J = 12.1 Hz), 2.89 (2H, d, J = 6.1 Hz), 2.45-1.25 (13H, m), 0.97 (3H, t); ^{13}C NMR δ 211.74, 139.01, 137.29, 131.64, 115.11, 61.85, 48.22, 41.41, 38.51, 37.06, 35.67, 31.59, 25.43, 25.41, 12.92; MS, m/e 218 (M$^+$-H$_2$O), 195, 175, 161, 121, 107, 97. In addition to 25, 0.124 g of the hydrolyzed adduct, 3-[(E)-3-ethyl-2,5-hexadienyl]cyclohexanone (29%), was also isolated.

3-[(Z)-2-Chloromethyl-3-ethyl-2,5-hexadienyl]cyclohexanone (26). To a 50-mL flask containing 0.361 g of N-chlorosuccinimide (2.7 mmol) in 10 mL of anhydrous methylene chloride maintained at 0^{0}C was introduced 2.36 mL of a 1.16 M solution of dimethyl sulfide (2.67 mmol) in methylene chloride. The reaction mixture was then cooled to -20^{0}C, and 0.18 g of 25 (0.76 mmol) in 5 mL of methylene chloride was added. The resulting solution was then allowed to warm to room

temperature. After an addition 8 h of stirring, the mixture was poured into 20 mL of cold brine solution. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2x20 mL). The combined organic layers were washed with cold brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel, 10% diethyl ether in hexane) to afford 0.149 g (77%) of 26 as a colorless liquid: IR (neat) 1700, 1625, 1440, 1340, 1310, 1250, 1220, 1180, 1090, 1050, 990, 950, 910, 865, 790, 750, 700, 650 cm^{-1}; ^{1}H NMR δ 5.78 (1H, ddt, J = 17.6, 9.7, and 6.2 Hz), 5.03 (1H, dm, J = 17 Hz), 5.02 (1H, dm, J = 10 Hz), 4.10 (1H, d AB, J = 11.3 Hz), 4.03 (1H, d AB, J = 11.3 Hz), 2.92 (2H, d, J = 6.1 Hz), 2.45–1.3 (13 H, m), 0.97 (3H, t); ^{13}C NMR δ 211.01, 142.49, 135.86, 128.23, 115.71, 48.13, 44.49, 41.36, 38.15, 37.18, 35.88, 31.54, 25.51, 25.34, 12.63; MS, m/e 218 (M$^+$–HCl), 175, 121, 107, 97, 93, 79.

Compound 27. To a 50-mL flask containing 0.195 g of KH (4.86 mmol) was introduced a solution of 0.145 g of 26 (0.57 mmol) in 2 mL of THF. The reaction mixture was stirred for 6 h before the usual workup. The residue was purified by column chromatography (silica gel, 10% diethyl ether in hexane) to afford a mixture of the cis- and trans-fused isomers (isomer ratio = 3:2) of 27 (0.098 g, 77%) as a colorless liquid: IR (neat) 1700, 1630, 1445, 1395, 1365, 1335, 1310, 1225, 1180, 1110, 1040, 990, 960, 910, 860, 790 cm^{-1}; ^{1}H NMR δ 5.73 (1H, m), 4.98 (2H, m), 2.8–1.5 (16H, m), 0.95 (3H, m); ^{13}C NMR (R_f = 0.43, major isomer) δ 213.25, 136.05, 133.58, 131.49, 114.78, 52.98, 42.55, 39.10, 37.22, 35.35, 31.35, 26.84, 26.31, 24.25, 12.44; ^{13}C NMR (R_f = 0.33, minor isomer) δ 215.92, 136.30, 135.63, 128.64, 114.85, 46.65, 44.28, 37.70, 36.82, 34.71, 28.65, 25.87, 24.61, 23.74, 13.20; MS, m/e 218 (M$^+$), 203, 177, 147, 131, 119, 105, 91, 79.

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27. (a) In the case of methyl iodide, 2 equiv of HMPA and 3 equiv of triethyl phosphite were
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         and stirred for 18 h.

    (b) In the case of **4c**, 1.1 equiv of 2,3-dibromopropene was utilized.

    (c) In the cases of disubstituted alkenylstannanes, 5 mL of methanol was introduced.
         After an additional 3 h of stirring at -78^0C, the reaction mixture was then allowed
         to warm to 0^0C before oxidative workup.