Stereoselective Synthesis of 1,4-Dienes. Application to the Preparation of Insect Pheromones (3Z,6Z)-Dodeca-3,6-dien-1-ol and (4E,7Z)-Trideca-4,7-dienyl Acetate

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Stereoselective synthesis of *Z,E*- and *Z,Z*-1,4-dienes has been achieved by the cross-coupling of allylic substrates with vinyl organometallic reagents. Key to this strategy was the development of a method for regiospecific incorporation of a tri-*n*-butylstannyl group in the γ-position of the allylic cross-coupling partner. The steric bulk of this moiety ensures the stereochemical integrity of the allylic double bond throughout the coupling sequence and is easily replaced by hydrogen in the coupled product. This strategy has been applied to the synthesis of the termite trail marker pheromone **22** and the leafminer moth sex pheromone **28**.

Introduction

Since the first pheromone was identified from the silk worm moth *Bombyx mori* by Butenandt *et al.* in 1961,[1] a vast array of these semiochemicals have been identified.[2] The availability of high purity synthetic pheromones has allowed use of these behavior modifying chemicals in pest management. Most Lepidopteran pheromones are linear alcohols, aldehydes, or acetates containing one or more double bonds. It is the strict maintenance of double bond geometry which often conveys biological activity and presents the greatest difficulty in preparation. Increasing demand for pheromones of high isomeric purity has spurred development of improved syntheses of these behavior modifying chemicals.[3]

In connection with ongoing projects in our laboratory dealing with characterization and synthesis of insect pheromones, new methods have been developed which would allow stereoselective assembly of 1,5-disubstituted 1,4-dienes which are structural units commonly found in a multitude of biologically active molecules including pheromones.

Common methods to stereoselectively assemble 1,4-dienes are (a) reduction of 1,4-diynes or 1,4-enynes by catalytic hydrogenation[4a] or reduction with sodium in liquid ammonia;[4b,c] (b) coupling of carbonyl compounds with ylides in Wittig and related reactions[5] and (c) organometallic mediated reactions.[6]

Palladium(0) catalyzed cross-coupling of vinyl organometallics as well as direct coupling of vinyl cuprates with allylic substrates are well established stereoselective routes to 1,4-dienes.[7] Stereochemistry of the vinyl partner is maintained in these reactions, but regio- and stereochemistry of the allylic partner is often lost (Scheme 1). While cross-coupling of γ,γ-disubstituted allylic compounds generally proceeds with high stereo- and regioselectivity, similar reactions with γ-monosubstituted analogs give rise to mixtures of isomers (**i**–**iii**). Superior selectivity in palladium-catalyzed reactions involving γ,γ-disubstituted allylic compounds is likely due to steric effects in the resultant π-allylpalladium complex. In the currently accepted mechanism of isomerization, π-allylpalladium species are postulated to exist in equilibrium with σ-bonded counterparts. Rotation about the C_2–C_3 bond in the σ-bonded complex followed by formation of a π-allylpalladium intermediate results in isomerization of the allylic double bond.[8,9b] Presumably, greater steric repulsion at C_3 disfavors formation of a σ-bonded palladium-C_3 intermediate, essential for *E* to *Z* interconversion (Scheme 2).

In the case of direct coupling of vinyl cuprates with allylic chlorides the main problem is one of regioselectivity. In cases where the allylic substrate is either unsubstituted or monosubstituted both α- and γ-attack occur (Scheme 1).

Recently, a new palladium(0) cross-coupling strategy was developed which showed promise as a stereoselective route to 1,4-dienes.[9] It was demonstrated that isomerization in γ-monosubstituted allylic substrates during palladium-catalyzed cross-coupling with *E*-vinyl organometallic reagents could effectively be eliminated by substitution of the γ-hydrogen in the allylic coupling

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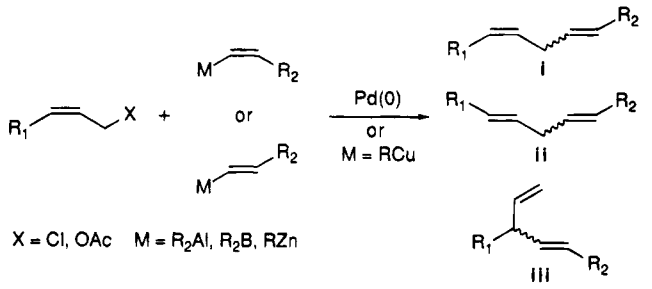
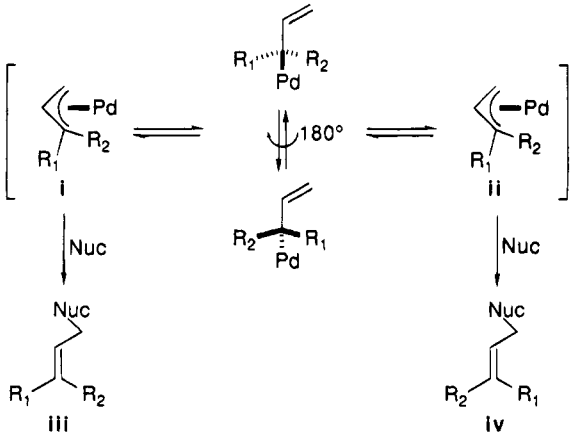
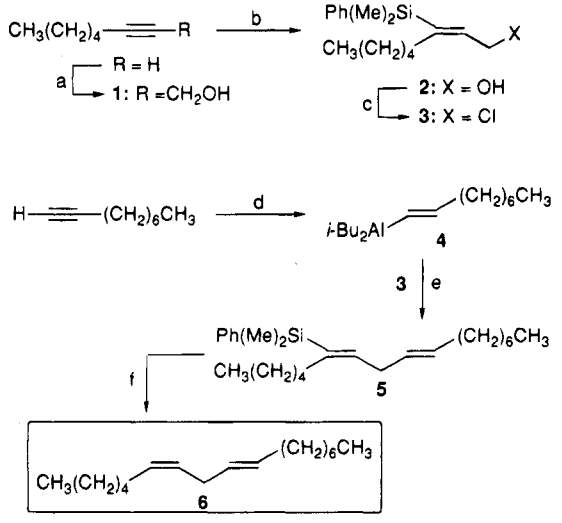
Scheme 1. Palladium-Catalyzed Cross-Coupling of γ-Monosubstituted Allylic Substrates with Vinyl Organometallic Reagents



Scheme 2. Double Bond Isomerization in π-Allylpalladium Complexes



Scheme 3. γ-Substitution in Allylic Substrates with a Ph(Me)2Si Group as a Strategy to the Stereospecific Synthesis of 1,4-Dienes[a]

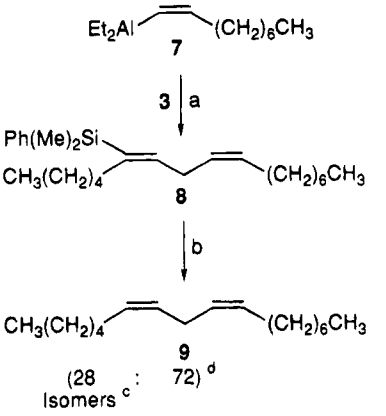


[a] n-BuLi, THF, −78 °C/30 min, $(CH_2O)_n$ (1.3 equiv), −78 °C → rt, 12 h, 85%; (b) $Ph(Me)_2SiZnEt_2Li$ (3 equiv), CuCN (2%), THF, −78 °C → rt, 12 h, 83%; (c) PPh_3, CCl_4/CH_3CN (1:1), rt/45 min, 81%; (d) DIBAL-H, hexane, 50 °C/2 h; (e) **4** (5 equiv), $Pd(PPh_3)_4$, THF, rt/30 min, 88%; (f) n-Bu_4NF, DMF, reflux/4 h, 85% (by GC).

partner with a $Ph(Me)_2Si$ group (Scheme 3). The stereochemical integrity of the allylic double bond was maintained throughout the coupling sequence yielding 1,4-diene, **5**, containing a vinyl $Ph(Me)_2Si$ functionality. Replacement of the trialkylsilyl moiety by hydrogen afforded the desired *Z,E*-1,4-diene **6**.

Desilylation occurred under conditions that tolerated alcohols, aldehydes, and acetates, commonly found in

Scheme 4. Trial Synthesis of (6Z,9Z)-Heptadeca-6,9-diene (9)[a]



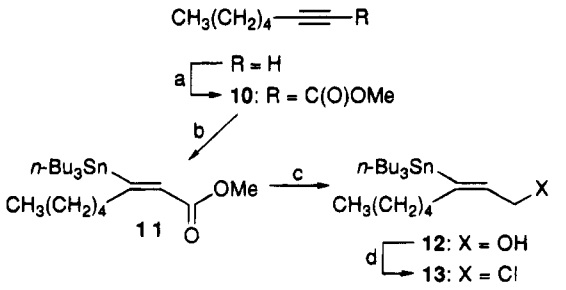
[a] $Pd(PPh_3)_4$ (10%), THF, 60 °C/2 h, 73%; (b) n-Bu_4NF (excess), DMF, 60 °C/1.5 h; (c) determined by GC/MS; (d) GC ratio.

pheromones. Thus, assembly of 1,4-dienic pheromones could, in principle, be accomplished *via* routes in which the final step from precursors already contained unprotected functionalities. Both $Ph(Me)_2Si$ and Bu_3Sn can act as bulky hydrogen surrogates. In the present work we show that for stereoselective synthesis of 1,4-dienes the tributylstannyl group is preferred. If Bu_3Sn is substituted in the γ-position of an allylic chloride the regio- and stereoselectivity of palladium(0) catalyzed cross-coupling of vinylalanes and direct coupling of vinyl cuprates is increased to the point that these couplings become useful reactions The strategy is applied to the synthesis of two 1,4-dienic pheromones.

Syntheses of Model *Z,Z*-1,4-Dienes. While cross-coupling reactions of γ-silyl substituted allylic chlorides with *E* vinyl organoalanes proceeded smoothly at room temperature, more forcing reaction conditions were generally required in cross-coupling reactions involving more sterically congested *Z*-vinyl organometallic reagents. Thus, cross-coupling of **3** with (*Z*)-nonenyldiethylalane, **7**, yielded 1,4-diene **8** in 73% yield upon heating for 2 h at 60 °C (Scheme 4). Although stereospecific assembly of the desired silylated 1,4-diene **8** could be achieved by this method, subsequent desilylation afforded a mixture of isomers in addition to the desired 1,4-diene **9**. In light of this difficulty, attention was focussed on cross-coupling reactions of allylic substrates in which the γ-silane was substituted by a trialkyltin moiety. It was hoped that replacement of tin with hydrogen in the coupled product could be achieved under more mild reaction conditions that would leave the geometry of the double bonds intact.

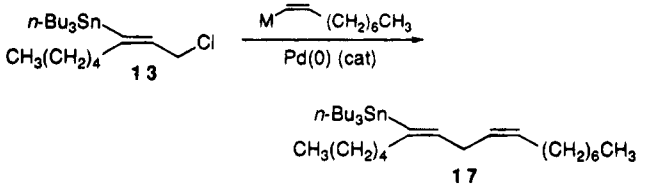
To examine this possibility we required a γ-trialkylstannyl substituted allylic chloride such as **13**. Synthesis of **13** was initially carried out by a procedure similar to that used in the preparation of **3**. Stannylzincation of propargylic alcohol **1** yielded **12** in good yield and high isomeric purity. Formation of appreciable amounts of tin byproducts which complicated workup and purification made this method unsuitable for multigram synthesis. It was found that **12** could be prepared more conveniently via **10** by reduction of **11** with DIBAL-H (Scheme 5). Ester **11** was obtained in excellent yield, high stereoselectivity, and relatively free of tin byproducts by stannylcupration of **10**. Subjecting **12** to usual chlorination conditions (PPh_3, CCl_4/CH_3CN)[21] did not give the corresponding allylic chloride **13** but yielded the destannylated product 1-chloro-2(*Z*)-octene. It was speculated that

Scheme 5. Synthesis of Allylic Chloride **13**[a]



[a] *n*-BuLi, THF, −78 °C/30 min, methyl chloroformate, −78 °C → rt, 15 min, 97%; (b) *n*-Bu_3SnLi (1.3 equiv), CuBr·DMS (1.3 equiv), THF, −78 °C/30 min, **10**, −78 °C/1 h, MeOH (excess), −78 °C → rt, 12 h, 91%; (c) DIBAL-H (2.4 equiv), THF, −78 °C/1 h, 93%; (d) *N*-chlorosuccinimide (1.2 equiv), DMS (1.4 equiv), CH_2Cl_2, 0 °C/10 min, **12**, 0 °C/1 h, 84%.

Table 1. Palladium-Catalyzed Cross-Coupling of Allylic Chloride 13 with *Z* Vinyl Organometallic Reagents[a]



entry	reagent (M)		reaction conditions	yield, (%)[b]
1	Li[9-OMe-9BBN]	(**14**)	A	5
2	Cp_2ClZr	(**15**)	A	4
3	Et_2Al	(**7**)	B	42
4	BrZn	(**16**)	C	80[c]

[a] Reactions conducted in THF/ether (1:1): A = 60 °C/3 h; B = 50 °C/2 h; C = rt/30 min. [b] GC yield. [c] 16% of another isomer also formed.

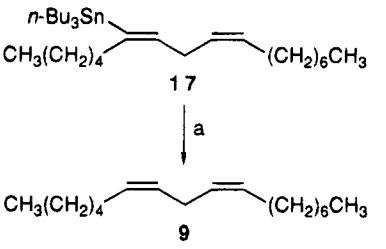
destannylation was due to the formation of traces of acid since **13** did form when this reaction was repeated under anhydrous conditions. Allylic alcohol **12** was readily converted to **13** in good yield under Corey halogenation conditions.[10]

Cross-coupling of **13** with vinylboron **14**, and vinylzirconium **15** reagents gave only traces of 1,4-diene **17** (Table 1, entries 1 and 2). Conducting these reactions at higher temperatures did not improve yields. Reaction of allylic chloride **13** with *Z*-vinylalane **7** in the presence of a catalytic amount of $Pd(PPh_3)_4$ afforded 1,4-diene **17** in moderate yield (Table 1, entry 3) while reaction with vinylzinc reagent **16** afforded **17** in 80% yield (Table 1, entry 4). Unfortunately, when produced by reaction with **16** formation of **17** was accompanied by 16% of another isomer, rendering this process unsuitable in synthetic applications requiring stringent control of stereochemistry.

Stereospecific replacement of the trialkyltin moiety by hydrogen in **17** could be achieved under mild acidic conditions. Thus, treatment of **17** with excess *p*-toluenesulfonic acid in THF/MeOH gave the unisomerized diene **9** in excellent yield (Scheme 6).

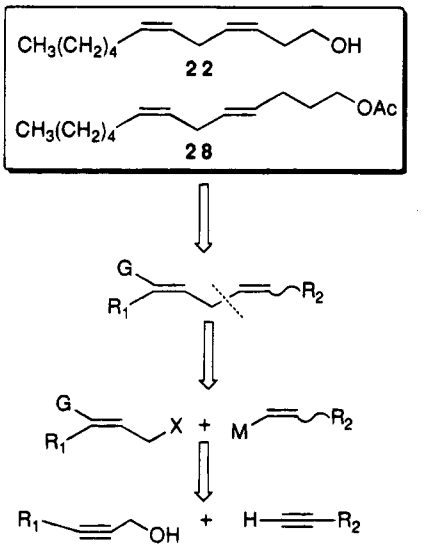
Synthesis of the Termite Trail Marker Pheromone 22 and the Leafminer Moth Sex Attractant 28. Retrosynthetic analysis of the termite trail marker pheromone **22**[11] and the leafminer moth sex attractant

Scheme 6. Destannylation of (6*E*,9*Z*)-6-(Tri-*n*-butylstannyl)heptadeca-6,9-diene (17)[a]



[a] *p*-Toluenesulfonic acid (excess), THF, rt/30 min, 90% (by GC).

Scheme 7. Retrosynthetic Analysis of the Termite Trail Marker Pheromone 22 and the Leafminer Moth Sex Attractant 28



28 via disconnection of an allyl−vinyl bond connecting the diene leads to a synthesis requiring the chemistry outlined above. Incorporation of a trialkylstannyl group at the γ-carbon in the allylic coupling partner **13** was expected to ensure stereospecific coupling (Scheme 7).

Preparation of the *Z*-vinyl organometallic fragment required in the synthesis of the termite trail marker pheromone **22** proceeded from the tetrahydropyranyl ether of 1-butynol **18**, which was initially converted to **19**. Hydroboration of alkynyl iodide **19** with disiamylborane,[12,13] followed by treatment with glacial acetic acid at rt, furnished **20** in respectable yield (Scheme 8). Cross-coupling of **13** with the *Z*-vinylalane derived from **20** afforded diene **21** in 51% yield. Tri-*n*-butyltin and THP groups were readily removed in a single step by stirring **21** in an acidified (*p*-toluenesulfonic acid) solution of THF/MeOH (1:1), affording pheromone **22** in 27% overall yield. The *Z,Z*-geometry was confirmed by ^1H decoupling which revealed vicinal vinyl hydrogen cou-

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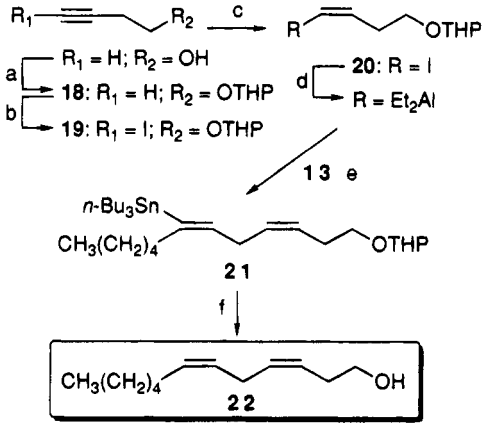
Scheme 8. Synthesis of the Termite Trail Marker Pheromone, (3Z,6Z)-Dodeca-3,6-dien-1-ol (22)[a]



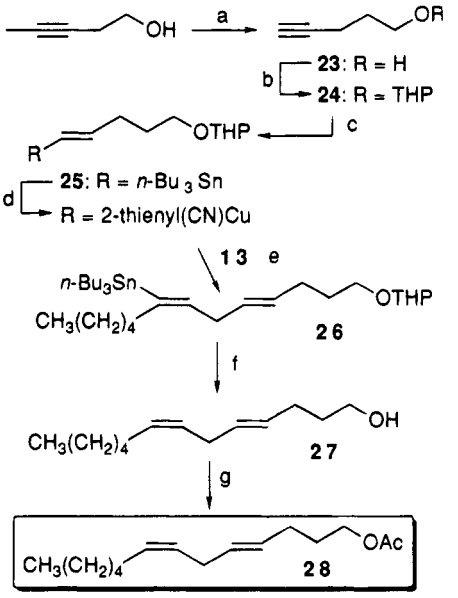
[a] Dihydropyran (excess), CH_2Cl_2, *p*-toluenesulfonic acid (cat.), 0 °C/10 min and then rt/1 h, 92%; (b) *n*-BuLi, THF, −78 °C/10 min, I_2, −78 °C/10 min and then rt/10 min, 92%; (c) 2-methyl-2-butene, BH_3·DMS, neat, 0 °C/2 h, **19**, THF, rt/2 h, glacial acetic acid, rt/2 h, 56%; (d) *t*-BuLi (2 equiv), ether, −70 °C/30 min and then −30 °C/30 min, Et_2AlCl, THF/ether (1:1), −30 °C/15 min; (e) **13**, $Pd(PPh_3)_4$ (10%), THF/ether (1:1), 50 °C/2 h, 51%; (f) *p*-toluenesulfonic acid (excess), THF/MeOH (1:1), rt/30 min, 77%.

pling for both double bonds was 10.5 Hz, characteristic of *Z* double bonds.[14]

The synthesis of **28**[15] was envisioned as proceeding by direct coupling of an *E*-vinyl cuprate and an allylic chloride such as **13** or its destannylated analog. Such couplings are attended by the same regio- and stereochemical problems in the allylic coupling partner as the palladium catalyzed cross-couplings illustrated above. Access to the required *E*-vinyl cuprate commenced with conversion of 3-pentyn-1-ol to 4-pentyn-1-ol, **23**, *via* a zipper reaction in 78% yield.[27] The latter was protected as the THP derivative **24** and reacted with *n*-Bu_3Sn-$(PhC{\equiv}C)_2CuLi_2$·LiI to give **25** in 78% yield and 96% isomeric purity. Recent work in this laboratory has shown that copper reagents of this composition react with 1-alkynes to yield 1(*E*)-(trialkylstannyl)alkenes (>95%) (Scheme 9).[9a,16] Transmetalation of **25** to a vinylcuprate followed by reaction with allylic chloride **13** gave 1,4-diene **26** in moderate yield and high isomeric purity. Cross-coupling of this vinylcuprate with 1-chloro-2(*Z*)-octene gave an isomeric mixture of coupled products.[9a] As in the case of the synthesis of **22**, removal of tri-*n*-butyltin and THP groups was accomplished in a single step by stirring **26** in a solution of MeOH and THF containing excess *p*-toluenesulfonic acid. Acetylation of alcohol **27**, under standard conditions, afforded the desired pheromone **28**, in 31% overall yield. The ^1H NMR spectrum of **28** exhibited resonances attributable to vinyl hydrogens on two different double bonds. ^1H Decoupling experiments revealed the presence of a trans coupling of 16 Hz.[14] Although the complexity of the second vinyl resonance did not allow measurement of a coupling constant, its width (12.5 Hz) suggested the presence of a *Z*-double bond.[14]

The use of dimethylphenylsilyl and tributylstannyl groups as γ-hydrogen surrogates in allylic partners of

Scheme 9. Synthesis of the Leafminer Moth Sex Attractant, (4*E*,7*Z*)-Trideca-4,7-dienyl Acetate (28)[a]



[a] Li (6.5 equiv), diaminopropane, rt/5 h, *t*-BuOK (4 equiv), rt/30 min, 3-pentyn-1-ol, rt/2 h, 78%; (b) dihydropyran (2 equiv), CH_2Cl_2, rt/45 min, 94%; (c) *n*-$Bu_3Sn(PhC{\equiv}C)_2CuLi_2$·LiI (2 equiv), THF, **24**, −30 °C → 0 °C, 1 h, 78%; (d) lithium 2-thienylcyanocuprate, MeLi, THF, −10 °C/10 min, **25**, 0 °C/1.5 h; (e) **13**, −78 → rt, 12 h, 55%; (f) *p*-toluenesulfonic acid (excess), MeOH/THF (1:1), rt/30 min, 89%; (g) pyridine, acetic anhydride, rt/45 min, 92%.

allyl-vinyl cross-coupling reactions significantly improves stereoselectivity.

Experimental Section

General Methods.[9b,17] GC yields were determined by using hexadecane as an internal standard and calculated according to the formula: $g_1 = A_1/A_2 \times RRF \times g_2$ (g_1 = grams of product; g_2 = grams of ISTD.; A_1 = area under product (g_1) peak; A_2 = area under ISTD. (g_2) peak; RRF = relative response factor, R_{f_1}/R_{f_2}). R_f (g_x/A_x) values were determined for solutions containing a known mixture of g_1 and g_2. An average value for solutions of varying concentration was used. Calculations and analyses were performed on the same gas chromatograph under identical operating conditions.

2-Octyn-1-ol (1). This compound was prepared in 85% yield from 1-hepytne according to a literature procedure.[18] Distillation under reduced pressure afforded **1** as a clear liquid: bp 51 °C/0.25 mmHg (lit.[19] 91 °C/12 mmHg).

3-[Dimethyl(phenyl)silyl]-2(*E*)-octen-1-ol (2). This compound was prepared in 83% yield from propargylic alcohol **1**, according to a literature procedure.[20] The product was purified by flash chromatography (SiO_2, 10% EtOAc in hexanes) to afford **2** as a colorless liquid. IR (vapor) 3061(m), 2937(s), 2868(m), 2361(m), 2336(w), 1425(w), 1375(w), 1256(m), 1195(w), 1109(m), 1026(m) cm^{-1}; ^1H NMR δ 7.46−7.34 (5 H, m), 6.09 (1 H, t, J = 6 Hz), 3.96 (2 H, q, J = 6 Hz); 2.12 (2 H, t, J = 7 Hz), 1.27−1.09 (6 H, m), 0.93 (3 H, t, J = 7 Hz), 0.24 (6 H, s); mass spectrum (EI) 262 (M^+, < 0.5), 247(3), 229(1), 205(1), 185(2), 173(2), 152(3), 137(100), 136(11), 121(11), 105(10),

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91(6), 75(33). Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.27; H, 9.91. Found: C, 73.60; H, 10.19.

1-Chloro-3-(dimethylphenylsilyl)-2(*E*)-octene (3). This compound was prepared in 81% yield from allylic alcohol **2**, according to a literature procedure.[21] The product was purified by flash chromatography (SiO_2, hexanes) to afford **3** as a colorless liquid: IR (vapor) 3200(w), 3065(m), 2964(s), 2937(s), 2887(m), 2361(w), 1256(s), 1105(m), 818(s) cm^{-1}; ^1H NMR δ 7.48–7.38 (5 H, m); 5.97 (1 H, tt, J = 7.5 Hz; 1 Hz); 4.13 (2 H, dt, J = 7.5 Hz; 0.5 Hz); 2.15 (2 H, t, J = 7 Hz); 1.38–1.22 (4 H, m); 1.21–1.14 (2 H, m); 0.90 (3 H, t, J = 7 Hz); 0.26 (6 H, s); mass spectrum (EI) 280(M^+, < 0.5), 265(5), 224(3), 209(2), 196(4), 187(3), 173(4), 155(62), 145(5), 135(100), 121(18), 105-(17), 93(29), 67(26), 54(12). Anal. Calcd for $C_{16}H_{25}ClSi$: C, 68.57; H, 8.93. Found: C, 68.82; H, 8.90.

(6*E*,9*E*)-6-(Dimethylphenylsilyl)heptadeca-6,9-diene (5). To a stirred solution of $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol) in THF (30 mL) was added at rt, *via* syringe, a solution of allylic chloride **3** (0.5 g, 1.8 mmol, 2 mL THF) followed by a solution of vinyl alane **4** [prepared according to a literature procedure][22] (9 mmol in hexanes). The reaction was quenched after 30 min by slow addition of HCl (3 N, 20 mL). The aqueous layer was extracted with hexanes (2 × 50 mL) and the combined organic extract filtered through Celite, dried ($MgSO_4$), and concentrated *in vacuo* to give a crude oil which was purified by flash chromatography (SiO_2, hexanes) to afford **5** (0.58 g, 88%) as a colorless oil: IR (vapor) 2964(m), 2934(s), 2864(m), 1460(w), 1355(w), 966(w), cm^{-1}; ^1H NMR δ 7.57–7.30 (5 H, m); 5.82 (1H, t, J = 7 Hz); 5.47 (1 H, dt, J = 15 Hz; 6 Hz); 5.38 (1 H, dt, J = 15 Hz; 6 Hz); 2.84 (2 H, dd, J = 7 Hz; 5 Hz); 2.15–2.03 (2 H, m); 2.03–1.97 (2 H, m); 1.28–1.12 (16 H, m); 0.90 (3 H, t, J = 7 Hz); 0.85 (3 H, t, J = 7 Hz); 0.37 (6 H, s); mass spectrum (EI) 370(M^+, 1), 292(1), 271(2), 234(12), 208(1), 194-(1), 173(1), 159(1), 152(2), 145(2), 135(100), 121(16), 107(6), 91(3), 79(3), 59(3), 43(6). Anal. Calcd for $C_{25}H_{42}Si$: C, 81.08; H, 11.35. Found: C, 80.83; H, 11.60.

(6*Z*,9*E*)-Heptadeca-6,9-diene (6). To a solution of **5** (0.02 g, 0.05 mmol) in DMF (10 mL) was added n-Bu_4NF (0.1 mL, 1 M/THF, 0.1 mmol). The mixture was refluxed 4 h, cooled to rt, and diluted with hexanes (5 mL). Gas chromatographic analysis revealed that diene **6** had formed in 85% yield. The solution was washed with brine (3 × 50 mL), dried ($MgSO_4$), and concentrated *in vacuo* to give a yellow oil. An analytically pure sample of **6** was obtained by preparative TLC (SiO_2/$AgNO_3$ (20%), hexanes): IR (vapor) 3018(w), 2966(s), 2866-(m), 1460(w), 1385(w), 1350(w), 966(w), 714(w) cm^{-1}; ^1H NMR δ 5.47–5.31 (4 H, m); 2.72 (2 H, t, J = 6 Hz); 2.01 (4 H, q, J = 7 Hz); 1.39–1.16 (16 H, m); 0.87 (6 H, t, J = 7 Hz); ^{13}C NMR δ 130.9, 130.6, 128.4, 127.9, 32.5, 31.8, 31.5, 30.8, 30.4, 29.6, 29.5, 29.3, 29.1, 27.0, 22.5, 22.3, 13.9; mass spectrum (EI) 236-(M^+, 15), 152(4), 151(3), 138(10), 124(21), 110(40), 96(57), 95-(67), 83(21), 81(95), 79(39), 67(100), 55(34), 42(34). Anal. Calcd for $C_{17}H_{32}$: C, 86.36; H, 13.64. Found: C, 86.22; H, 13.76.

(6*E*,9*Z*)-6-[Dimethyl(phenyl)silyl]heptadeca-6,9-diene (8). To a solution of vinylalane **7** (1.1 mmol) in Et_2O/THF (1:1, 4 mL) were added allylic chloride **3** (0.174 g, 1 mmol) and $Pd(PPh_3)_4$ (0.1 g, 0.1 mmol) at rt, and the yellow solution was heated to 60 °C for 2 h. The solution was diluted with aqueous NH_4Cl (100 mL) and this mixture extracted with hexanes (2 × 30 mL). The combined organic extract was dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude oil was purified by preparative TLC (SiO_2/$AgNO_3$ (20%), hexanes) to yield **8** (0.22 g, 73%) as a colorless oil: ^1H NMR δ 7.55–7.43 (2 H, m), 7.38–7.28 (3 H, m), 5.77 (1 H, t, J = 7Hz), 5.45–5.32 (2 H, m), 2.85 (2 H, t, J = 6.5 Hz), 2.13–2.00 (4 H, m), 1.34–1.06 (16 H, m), 0.83 (3 H, t, J = 7 Hz), 0.76 (3 H, t, J = 7 Hz), 0.28–0.25 (6 H, m); ^{13}C NMR δ 139.4, 134.0, 130.5, 128.7, 127.7, 127.6, 32.2, 31.9, 29.9, 29.7, 29.3, 29.2, 27.3, 27.1, 22.7, 22.4, 14.1, 14.0, −2.6; mass spectrum (EI) 370(M^+, <1), 234(4), 152(1), 137(5), 136(14), 135-(100), 123(1), 122(2), 121(11), 119(2), 109(2), 107(4), 105(3), 91(2). Anal. Calcd for $C_{25}H_{42}Si$: C, 81.08; H, 11.35. Found: C, 80.97; H, 11.48.

(6*Z*,9*Z*)-Heptadeca-6,9-diene (9). (a) To a solution of diene **8** (0.19 g, 0.5 mmol) in DMF (5 mL) was added n-Bu_4NF (1.0 mL, 1.0 M/THF, 1.0 mmol) and the mixture heated to 60 °C. Desilylation was monitored by GC and was complete after 1.5 h. Diene, **9**, was accompanied (72:28) by products of similar GC elution characteristics. The latter were identified by GC/MS to have the same molecular weight as **9** and therefore are presumed to be isomers of **9**. (b) To a solution of diene **17** (0.06 g, 0.1 mmol) in THF (5 mL) at rt were added several crystals of *p*-toluenesulfonic acid, and the solution was stirred for 30 min. Gas chromatographic analysis of an aliquot withdrawn after this time revealed that destannylation was complete and that **8** (90%) was formed. An analytically pure sample was obtained by preparative TLC (SiO_2/$AgNO_3$ (20%), hexanes): ^1H NMR δ 5.43–5.28 (4 H, m), 2.78 (2 H, t, J = 6.5 Hz), 2.05 (4 H, q, J = 7 Hz), 1.41–1.20 (18 H, m), 0.94–0.84 (6 H, m); ^{13}C NMR δ 130.21, 127.98, 31.86, 31.53, 29.35, 29.28, 29.21, 27.24, 27.21, 25.64, 22.65, 22.56, 14.06; mass spectrum (EI) 236(M^+, 4), 138(2), 110(9), 96(15), 95(18), 81(39), 79(24), 67(69), 55(47), 54(39), 43(45), 41(100). Anal. Calcd for $C_{17}H_{32}$: C, 86.36; H, 13.64. Found: C, 86.15; H, 13.41.

Methyl 2-Octynoate (10). To a solution of 1-heptyne (8.73 mL, 65 mmol) in THF (100 mL) was added at −78 °C n-BuLi (26 mL, 2.5 M, 65 mmol) followed, after 30 min by methyl chloroformate (5.0 mL, 65 mmol). The solution was warmed to rt, quenched with brine (10 mL), and diluted with Et_2O (50 mL). The mixture was washed with brine (3 × 50 mL), and the combined aqueous layers were back-extracted with hexanes (10 mL). Concentration of the organic extract yielded, after distillation, **10** (9.76 g, 97%) as a colorless liquid: bp: 37 °C/0.01 mmHg; IR (neat) 2956(s), 2863(s), 2238(s), 1718-(s), 1459(m), 1435(s), 1254(s), 1077(s) cm^{-1}; ^1H NMR δ 3.75 (3 H, s), 2.32 (2 H, t, J = 7.1 Hz), 1.62–1.53 (2 H, m), 1.42–1.26 (4 H, m), 0.89 (3 H, t, J = 7.1 Hz); mass spectrum (EI) 139 (M^+ − Me, 7), 123(46), 95(91), 93(39), 81(28), 79(81), 69(28), 67(74), 66(100), 59(37), 55(76), 53(50). Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 69.99; H, 9.05.

Methyl 3-(Tri-*n*-butylstannyl)-2(*E*)-octenoate (11). This compound was prepared following a literature procedure.[23] To a solution of n-Bu_3SnLi[24] (70 mmol) in THF (200 mL) was added at −78 °C CuBr·DMS (14.4 g, 70 mmol). The solution turned black immediately; the solution was stirred at −78 °C for 30 min. A solution of alkynynoate **10** (8.3 g, 54 mmol) in THF (10 mL) was then added to the mixture. After 1 h anhydrous MeOH (excess) was introduced and the solution warmed to rt overnight. The mixture was subsequently poured into brine (300 mL) and extracted with Et_2O (3 × 50 mL). Concentration of the combined organic layers under reduced pressure yielded a crude liquid which was purified by flash chromatography (SiO_2, 3% EtOAc in hexanes) to afford **11** (28.4 g, 91%) as a colorless liquid: IR (neat) 2956(s), 2854-(s), 1721(s), 1592(m), 1464(m), 1432(w), 1377(w), 1351(m), 1254(w), 1191(s), 1167(s), 1128(w) cm^{-1}; ^1H NMR (C_6D_6) δ 6.36 (1 H, t, J = 1.2 Hz; $^3J^{119}_{Sn-H}$ = 67 Hz; $^3J^{117}_{Sn-H}$ = 65 Hz), 3.46 (3 H, s), 3.27 (2 H, dt, J = 7 Hz; 1.2 Hz; $^3J_{Sn-H}$ = 59 Hz), 1.70–1.55 (8 H, m), 1.53–1.33 (10 H, m), 1.12–0.92 (18 H, m); mass spectrum (EI) 389(M^+ − Bu, 100), 387(70), 333(51), 277(43), 177(27), 151(32). Anal. Calcd for $C_{21}H_{42}O_2Sn$: C, 56.50; H, 9.42. Found: C, 56.88; H, 9.27.

3-(Tri-*n*-butylstannyl)-2(*E*)-octen-1-ol (12). To a solution of alkenoate **11** (7.72 g, 17.4 mmol) in THF (150 mL) was added dropwise, at −78 °C, neat diisobutylaluminum hydride (7.5 mL, 42 mmol), and the solution was stirred for 1 h. The solution was warmed to −30 °C and carefully quenched (exothermic!) after 1 h by dropwise addition of MeOH. The mixture was diluted at rt with brine (200 mL), acidified (2 M HCl), and extracted with Et_2O (3 × 50 mL). The combined organic extract was concentrated *in vacuo* and the resultant crude oil purified by flash chromatography (SiO_2, 10% EtOAc in hexanes) to afford **12** (6.71 g, 93%) as a colorless oil: IR

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(neat) 3330(s), 2954(s), 2853(s), 2360(w), 1464(s), 1418(w), 1376(m), 1340(w), 1292(w), 1060(m), 1004(s) cm^{-1}; ^1H NMR δ 5.37 (1 H, tt, J = 6 Hz; 1.2 Hz; $^3J_{^{119}Sn-H}$ = 70 Hz; $^3J_{^{117}Sn-H}$ = 67 Hz), 4.23 (2 H, d, J = 2 Hz), 2.26 (2 H, t, J = 7 Hz; $^3J_{Sn-H}$ = 56 Hz), 1.52–1.44 (6 H, m), 1.35–1.28 (12 H, m), 0.96–0.86 (18 H, m); mass spectrum (EI) 361(M^+ – Bu, 100), 359(72), 305(75), 249(95), 247(68), 177(60), 137(78), 121(39). Anal. Calcd for $C_{20}H_{42}OSn$: C, 57.55; H, 10.07. Found: C, 57.26; H, 10.10.

1-Chloro-3-(tri-*n*-butylstannyl)-2(*E*)-octene (13). This compound was prepared by reaction of allylic alcohol **12** (6.71 g, 1.61 mmol) with *N*-chlorosuccinimide (0.23 g, 1.7 mmol) and DMS (0.15 mL, 2 mmol) in CH_2Cl_2 (5 mL) at 0 °C for 1 h according to a literature procedure.[10] Workup and purification by flash chromatography (SiO_2, hexanes) yielded **13** (5.9 g, 84%) as a colorless liquid: d = 1.072; ^1H NMR (C_6D_6) δ 5.92 (1 H, tt, J = 7 Hz; 1.1 Hz; $^3J_{^{119}Sn-H}$ = 66 Hz; $^3J_{^{117}Sn-H}$ = 64 Hz), 3.94 (2 H, d, J = 7 Hz), 2.31 (2 H, dt, J = 7 Hz; 1.1 Hz; $^3J_{Sn-H}$ = 57 Hz), 1.72–1.52 (6 H, m), 1.46–1.35 (8 H, m), 1.34–1.21 (4 H, m), 1.10–0.92 (18 H, m); mass spectrum (EI) 381-(22), 379(M^+ – Bu, 54), 377(44), 343(14), 323(44), 291(14), 269(100), 213(27), 177(47), 173(19), 155(35), 121(21), 67(19). Anal. Calcd for $C_{20}H_{41}ClSn$: C, 55.05; H, 9.40. Found: C, 54.88; H, 9.22.

(6*E*,9*Z*)-6-(Tri-*n*-butylstannyl)heptadeca-6,9-diene (17). An analytically pure sample was obtained by flash chromatography (SiO_2, hexanes): ^1H NMR δ 5.48 (1 H, t, J = 7 Hz; $^3J_{^{119}Sn-H}$ = 105 Hz; $^3J_{^{117}Sn-H}$ = 101 Hz), 5.45–5.33 (2 H, m), 2.80 (2 H, t, J = 5 Hz), 2.26–2.18 (2 H, m, $^3J_{Sn-H}$ = 60 Hz), 1.98 (6 H, q, J = 7 Hz), 1.52–1.22 (22 H, m), 0,92–0.80 (21 H, m); ^{13}H NMR δ 144.7, 138.1, 130.3, 128.0, 31.9, 30.8, 30.0, 29.4, 29.3, 29.2, 27.3, 27.0, 25.7, 22.7, 22.6, 14.1, 14.0, 13.6, 9.7; mass spectrum (EI) 469(M^+ – Bu, 100), 467(74), 465(43), 413(40), 357(39), 235(16), 177(80), 121(40). Anal. Calcd for $C_{29}H_{58}Sn$: C, 66.28; H, 11.12. Found: C, 66.03; H, 11.09.

Palladium Catalyzed Cross-Coupling of 13 with *Z*-Vinyl Organometallic Reagents: [a] Cross-Coupling with 1(*Z*)-Nonenyl-9-methoxy-9-BBN (14). To a solution of 1(*Z*)-nonenyllithium (1.5 mmol) [prepared by adding *t*-BuLi (2 equiv) to a solution (Et_2O) of 1-iodo1(*Z*)-nonene at −70 °C followed by warming to −30 °C over 1 h] in THF (5 mL) was added at −30 °C a solution of 9-methoxy-9-BBN[25] (0.23 g, 1.5 mmol) in THF (1 mL). After 5 min NaOMe (0.25 g, 5 mmol) was added followed by allylic chloride **13** (0.2 mL, 0.5 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol). The solution was heated to 60 °C for 3 h. Gas chromatographic analysis of a quenched aliquot revealed that diene **17** had formed in 5% yield.

[b] Cross-Coupling with 1(*Z*)-Nonenylcyclopentadienylzirconocene Chloride (15). To a solution of 1(*Z*)-nonenyllithium (0.5 mmol) [prepared as above] in Et_2O/THF (1:1, 4 mL) was added Cp_2ZrCl_2 (0.15 g, 0.5 mmol) at −30 °C. The suspension was stirred at 0 °C for 15 min to yield a faint yellow solution. Allylic chloride **10** (0.2 g, 0.5 mmol) was added followed by $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol). The mixture was heated to 60 °C for 3 h. Gas chromatographic analysis of a quenched aliquot revealed that diene **16** had formed in 4% yield.

[c] Cross-Coupling with 1(*Z*)-Nonenyldiisobutylalane (7). To a solution of 1(*Z*)-nonenyllithium (0.5 mmol) [prepared as above] in Et_2O/THF (1:1, 4 mL) was added Et_2AlCl (0.06 mL, 0.5 mmol) at −30 °C, giving rise to a white suspension (LiCl) within seconds. After 15 min allylic chloride **13** (0.2 mL, 0.5 mmol) was added followed by $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) and the mixture heated to 50 °C for 2 h. Gas chromatographic analysis of a quenched aliquot revealed that diene **17** had formed in 42% yield.

(d) 1(*Z*)-Nonenylzinc Bromide (16). To a solution of 1(*Z*)-nonenyllithium (0.5 mmol) [prepared as above] in Et_2O/THF (1:1, 4 mL) at −30 °C was added $ZnBr_2$ (0.113 g, 0.5 mmol). The suspension was stirred at 0 °C for 15 min during which time the precipitate dissolved. Allylic chloride **13** (0.2 mL, 0.5 mmol) was then added followed by $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) and the solution stirred at rt for 30 min. Gas chromatographic analysis of a quenched aliquot revealed that diene **17** had formed in 80% yield. In addition, a compound presumed to be an isomer of **17** (close GC retention time) was formed (16%).

4-(Tetrahydropyranyloxy)-1-butyne (18). This compound was prepared from 3-butyn-1-ol in 92% yield following a literature procedure.[26] Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.18; H, 9.24.

1-Iodo-4-(tetrahydropyranyloxy)-1-butyne (19). To a solution of alkyne **18** (5.0 mL, 32 mmol) in THF (50 mL) was added at −78 °C *n*-BuLi (14 mL, 2.5 M, 35 mmol). After 30 min a solution of I_2 (10 g, 39 mmol) in THF (15 mL) was slowly added until a red color persisted for 10 min. The mixture was warmed to rt and diluted with brine (150 mL) and a saturated solution of $Na_2S_2O_3$ (15 mL). The solution was extracted with hexanes (3 × 75 mL) and the combined organic extract dried ($MgSO_4$) and concentrated *in vacuo* to give a green oil. Purification by flash chromatography (SiO_2, 5% EtOAc in hexanes) yielded **19** (8.2 g, 92%) as a colorless oil: d = 1.543; IR (neat) 2939(s), 2872(s), 2189(w), 1440(m), 1352(m), 1201-(m), 1121(m), 1070(m), 1032(m) cm^{-1}; ^1H NMR δ 4.62–4.59 (1 H, m), 3.90–3.75 (2 H, m), 3.59–3.46 (2 H, m), 2.66 (2 H, t, J = 7 Hz), 1.88–1.38 (6 H, m); mass spectrum (EI) 279 (M^+ – H, < 1), 225(9), 224(21), 179(30), 178(50), 115(13), 85(100), 67-(12), 52(10). Anal. Calcd for $C_9H_{13}O_2I$: C, 38.57; H, 4.64. Found: C, 38.68; H, 4.67.

1-Iodo-4-(tetrahydropyranyloxy)-1(*Z*)-butene (20). To disiamylborane (5 mmol) [prepared by adding BH_3·DMS (0.47 mL, 5 mmol) to 2-methyl-2-butene (1.1 mL, 10 mmol) at 0 °C/2 h][12,13] was added THF (4 mL) followed by alkynyl iodide **19** (0.91 mL, 5.0 mmol) and the homogeneous solution stirred at rt for 2 h. The mixture was then treated with glacial acetic acid (1 mL) and poured into a solution of NaOH (2 M, 50 mL) after 2 h. The solution was extracted with hexanes (3 × 10 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (SiO_2, 5% EtOAc in hexanes) to afford **20** (0.80 g, 56%) as a colorless liquid: IR (neat) 3067(w), 2940(s), 2869(s), 1610(w), 1440(m), 1352(m), 1284(m), 1258(m), 1201(m), 1135(m) cm^{-1}; ^1H NMR δ 6.33–6.26 (2 H, m), 4.63–4.58 (1 H, m), 3.89–3.76 (2 H, m), 3.54–3.45 (2 H, m), 2.51–2.39 (2 H, m), 1.88–1.77 (1 H, m), 1.75–1.66 (1 H, m), 1.63–1.43 (4 H, m); mass spectrum (EI) 281 (M^+ – H, <1), 198(100), 183(61), 182(24), 181(90), 180(80), 168-(78), 167(40), 127(28), 115(12), 85(76), 84(16), 71(21). Anal. Calcd for $C_9H_{15}O_2I$: C, 38.30; H, 5.32. Found: C, 38.61; H, 5.36.

(6*E*,9*Z*)-12-(Tetrahydopyranyloxy)-6-(tri-*n*-butylstannyl)dodeca-6,9-diene (21). To a solution of vinyl iodide **20** (0.28 g, 1 mmol) in Et_2O (2 mL) was added *t*-BuLi (1.18 mL, 1 mmol) at −70 °C. The solution was stirred at −70 °C for 30 min and then at −30 °C for an additional 30 min. To this solution was added at −30 °C Et_2AlCl (0.13 mL, 1 mmol) which resulted in the formation of a white precipitate (LiCl) within several minutes. After 15 min allylic chloride **13** (0.4 mL, 1 mmol) was added followed by $Pd(PPh_3)_4$ (0.1 g, 0.1 mmol) and the mixture warmed to 50 °C for 2 h. The yellow solution was quenched with aqueous NH_4Cl (100 mL) and extracted with hexanes (3 × 10 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (SiO_2, 3% EtOAc in hexanes) to afford **21** in >95% isomeric purity (0.28 g, 51%) as a faint yellow oil: IR (neat) 3011(w), 2955(s), 2922(s), 2871(s), 2853(s), 1600(w), 1464(m), 1377(w), 1352(w), 1138(m), 1121(m) cm^{-1}; ^1H NMR δ 5.49–5.37 (3 H, m, $^3J_{Sn-H}$ = 70 Hz), 4.63–4.58 (1 H, m), 3.92–3.83 (1 H, m), 3.75 (1 H, dt, J = 9.5 Hz; 7 Hz), 3.54–3.47 (1 H, m), 3.42 (1 H, dt, J = 9.5 Hz; 7 Hz), 2.89 (2 H, dt, J = 6.5 Hz), 2.38 (2 H, q, J = 6.7 Hz), 2.24 (2 H, t, J = 7 Hz; $^3J_{Sn-H}$ = 60 Hz), 1.88–1.78 (1 H, m), 1.75–1.67 (1 H, m), 1.63–1.38 (10 H, m), 1.34–1.23 (12 H, m), 0.94–0.81 (18 H, m); ^{13}C NMR δ 144.7, 138.0, 130.4, 125.7, 98.8, 67.1, 62.2, 33.2, 31.9, 30.8, 30.0, 29.1, 28.1, 27.4, 27.0, 25.5, 22.6, 19.6, 14.0, 13.6, 9.7; mass spectrum (EI) 499-

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(M^+ − Bu, 42), 497(33), 413(30), 235(5), 177(17), 119(10), 85-(100), 67(30), 57(36). Anal. Calcd for $C_{29}H_{56}O_2Sn$: C, 62.59; H, 10.07. Found: C, 62.87; H, 10.11.

(3Z,6Z)-Dodeca-3,6-dien-1-ol (22). To a solution of diene **21** (0.2 g, 0.36 mmol) in THF/MeOH (1:1, 4 mL) was added at rt an excess of *p*-toluenesulfonic acid (ca. 0.1 g). The mixture was stirred at rt for 30 min and then concentrated to ca.1 mL under slightly reduced pressure [product is volatile]. The suspension was flash chromatographed (SiO_2, 15% EtOAc in hexanes) and yielded **22** (0.05 g, 77%) as a colorless liquid: IR (neat) 3328(s), 3011(w), 2957(s), 2927(s) 2872(s), 1654(w), 1458(m), 1048(m) cm^{-1}; ^1H NMR δ 5.58−5.49 (1 H, m), 5.44−5.28 (3 H, m), 3.65 (2 H, t, J = 6.5 Hz), 2.82 (2 H, t, J = 7 Hz), 2.36 (2 H, q, J = 7 Hz), 2.05 (2 H, q, J = 7 Hz), 1.50 (1 H, s), 1.40−1.22(6 H, m), 0.88 (3 H, t, J = 7 Hz); ^{13}C NMR δ 131.5, 130.6, 127.4, 125.3, 62.3, 31.5, 30.9, 29.3, 27.2, 25.8, 22.5, 14.0; mass spectrum (EI) 182(M^+, 1), 135(5), 121(11), 107(15), 93-(45), 91(26), 81(46), 79(100), 77(26), 67(65), 55(30). Anal. Calcd for $C_{12}H_{22}O$: C, 79.05; H, 12.16. Found: C, 78.77; H, 12.02.

5-(Tetrahydropyranyloxy)-1-pentyne (24). This compound was prepared in the same manner as described for the synthesis of alkyne **18** starting with alcohol **23** (0.75 g, 8.9 mmol). Workup and purification yielded **24** (1.4 g, 94%) as a colorless liquid: IR (neat) 3295(m), 2942(s), 2871(s), 2118(w), 1441(m), 1354(m), 1200(m), 1137(m), 1120(m), 1076(m), 1035-(m) cm^{-1}; ^1H NMR δ 4.61−4.58 (1 H, m), 3.91−3.78 (2 H, m), 3.54−3.44 (2 H, m), 2.31 (2 H, dt, J = 7 Hz; 2.5 Hz), 1.94 (1 H, t, J = 2.5 Hz), 1.86−1.76 (3 H, m), 1.75−1.65 (1 H, m), 1.62−1.46 (4 H, m); mass spectrum (EI) 167(M^+ − H, 5), 125(6), 111-(8), 101(8), 85(100), 84(16), 79(13), 67(45), 65(23), 55(23). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.47; H, 9.37.

5-(Tetrahydropyranyloxy)-1-(tri-*n*-butylstannyl)-1(*E*)-pentene (25). To a stirred solution of phenylacetylene (2.64 mL, 24 mmol) in THF (10 mL) at -30 °C was added *n*-BuLi *via* syringe. After 15 min CuI (2.29 g, 12 mmol) was added and the mixture stirred at 0 °C for 30 min. The resulting colorless solution was transferred to a solution of *n*-Bu_3SnLi (12 mmol) in THF (5 mL) [prepared in the reaction of *n*-Bu_3-SnH with lithium diisopropylamide][24] at −30 °C. The yellow solution was stirred for 30 min, a THF (2 mL) solution of alkyne **24** (1.0 g, 6 mmol) added, and the mixture warmed to 0 °C over 1 h. The solution was quenched with methanol, diluted with brine (200 mL), and extracted with hexanes (3 × 50 mL). The combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to afford an oil which, after purification by flash chromatography (SiO_2, 5% EtOAc in hexanes), yielded **25** (2.15 g, 78%) in 96% isomeric purity: IR (neat) 2923(s), 2870(s), 2852(s), 1599(m), 1484(m), 1376(w), 1136(m), 1120-(m), 1077(m), 1035(m), 1022(m) cm^{-1}; ^1H NMR δ 5.97 (1 H, dt, J = 19 Hz; 5.5 Hz), 5.89 (1 H, d, J = 19 Hz), 4.59−4.54 (1 H, m), 3.91−3.82 (1 H, m), 3.74 (1 H, dt, J = 9.6 Hz; 6.6 Hz), 3.53−3.45 (1 H, m), 3.39 (1 H, dt, J = 9.6 Hz; 6.7 Hz), 2.25−2.17 (2 H, m), 1.88−1.78 (1 H, m), 1.75−1.65 (3 H, m), 1.62−1.37 (10 H, m), 1.29 (6 H, sext, J = 7.6 Hz), 0.95−0.82 (15 H, m); ^{13}C NMR δ 149.3, 127.4, 99.8, 67.5, 62.3, 37.6, 30.8, 29.4, 29.1, 27.3, 27.0, 25.6, 25.5, 19.7, 13.7, 9.4; mass spectrum (EI) 403(M^+ − Bu, 13), 401(10), 319(3), 317(3), 261(3), 233(4), 205-(5), 177(29), 135(15), 119(20), 85(100), 67(25). Anal. Calcd for $C_{22}H_{44}O_2Sn$: C, 57.39; H, 9.56. Found: C, 58.13; H, 9.32.

(6E,9E)-13-(Tetrahydropyranyloxy)-6-(tri-*n*-butylstannyl)trideca-6,9-diene (26). To a solution of lithium 2-thienylcyanocuprate (2.8 mL, 0.25 M, 0.7 mmol) in THF (5 mL) at −10 °C was added MeLi (0.5 mL, 1.4 M, 0.7 mmol) followed, after 10 min, by a solution of vinylstannane **25** (0.32 g, 0.7 mmol) in THF (2 mL). The solution was stirred at 0 °C for 1.5 h and cooled to −78 °C, and then allylic chloride **13** was (0.2 mL, 0.5 mmol) added. The solution was slowly warmed to rt and allowed to stand overnight. The solution was quenched with aqueous NH_4Cl (100 mL) and extracted with hexanes (3 × 10 mL), and the combined organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to give an oil. Flash chromatography (SiO_2, 3% EtOAc in hexanes) yielded **26** in >95% isomeric purity (0.16 g, 55%) as a colorless oil: IR (neat) 2955(s), 2923(s), 2853(s), 1600(w), 1464(m), 1376(w), 1352(w), 1200(w), 1138(m), 1121(m), 1078(m), 1035(m) cm^{-1}; ^1H NMR δ 5.52−5.34 (3 H, m), 4.61−4.55 (1 H, m), 3.92−3.82 (1 H, m), 3.73 (1 H, dt, J = 9.5 Hz; 6.7 Hz), 3.54−3.45 (1 H, m), 3.38 (1 H, dt, J = 9.6 Hz; 6.6 Hz), 2.84−2.76 (2 H, m), 2.26−2.18 (2 H, m, $^3J_{Sn-H}$ = 61 Hz), 2.16−1.99 (2 H, m), 1.88−1.41 (14 H, m), 1.37−1.22 (12 H, m), 0.95−1.21 (18 H, m); ^{13}C NMR δ 144.7 , 138.1, 129.9, 129.2, 98.8, 67.0, 62.2, 33.1, 31.9, 31.6, 30.8, 30.0, 29.7, 29.2, 27.4, 25.5, 22.6, 19.6, 14.0, 13.6, 9.7; mass spectrum (EI) 513(M^+ − Bu, 23), 511(14), 509(8), 427(5), 319-(18), 293(33), 279(30), 277(25), 275(15), 233(18), 179(26), 177-(36), 121(22), 119(16), 85(100), 67(20). Anal. Calcd for $C_{30}H_{58}$-O_2Sn: C, 63.16; H, 10.17. Found: C, 63.45; H, 10.19.

(4E,7Z)-Trideca-4,7-dien-1-ol (27). To a solution of diene **26** (0.36 g, 0.61 mmol) in THF/MeOH (1:1, 5 mL) was added *p*-toluenesulfonic acid (excess) and the mixture stirred for 30 min at rt. The solution was concentrated *in vacuo* to approximately 1 mL and subjected to flash chromatography (SiO_2, 10% EtOAc in hexanes) to yield **27** (0.11 g, 89%) as a colorless liquid: IR (neat) 3342(m) 3010(w), 2957(s), 2927(s), 2857(s), 1780(w), 1457(m), 1158(w), 1058(m) cm^{-1}; ^1H NMR δ 5.50−5.32 (4 H, m), 3.65 (2 H, t, J = 6.5 Hz), 2.79−2.67 (2 H, m), 2.12−2.05 (2 H, m), 2.02 (2 H, q, J = 7 Hz), 1.63 (2 H, quint, J = 7.5 Hz), 1.56 (1 H, s), 1.39−1.21 (6 H, m), 0.88 (3 H, J = 7 Hz); ^{13}C NMR δ 131.5, 130.6, 127.4, 125.3, 62.3, 31.5, 30.9, 29.3, 27.2, 27.2, 25.8, 22.5, 14.0; mass spectrum (EI) 196-(M^+, 2), 178(3), 150(2), 149(3), 135(6),121(14), 107(14), 98(14), 93(38), 81(54), 79(100), 67(59), 55(29); HRMS calcd for $C_{13}H_{24}O$: 196.1817, found 196.1822.

(4E,7Z)-Trideca-4,7-dienyl Acetate (28). To a solution of diene **27** (0.10 g, 0.50 mmol) in pyridine (1 mL) at rt was added acetic anhydride (0.5 mL). After 45 min the mixture was diluted with hexanes (10 mL) and washed with brine (3 × 50 mL) and the combined aqueous fraction back-extracted with hexanes (2 × 10 mL). The combined organic extract was concentrated *in vacuo* and the resulting oil purified by flash chromatography (SiO_2, 10%, EtOAc in hexanes) to afford **28** (0.11 g, 92%) as a colorless liquid: IR (neat) 3010(w), 2958(s), 2929(s), 2857(s), 1743(s), 1458(w), 1366(m), 1240(m), 1041(m) cm^{-1}; ^1H NMR δ 5.46−5.32 (4 H, m), 4.05 (2 H, t, J = 7 Hz), 2.76−2.70 (2 H, m), 2.16 (3 H, s), 2.10−1.98 (4 H, m), 1.68 (2 H, quint, J = 7 Hz), 1.38−1.21 (6 H, m), 0.88 (3 H, t, J = 7 Hz); ^{13}C NMR δ 171.0, 130.7, 129.5, 129.0, 127.3, 63.9, 31.5, 30.3, 29.3, 28.8, 28.4, 27.1, 22.6, 22.5, 14.0; mass spectrum (EI) 238(M^+, <1), 178(20), 150(9), 135(12), 121(24), 107(20), 93-(53), 79(100), 67(37), 55(14); HRMS calcd for $C_{15}H_{26}O_2$ 238.1932, found 238.1933.

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