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Intermolecular Homocoupling of Alkenyltrimethylstannane Functions Mediated by CuCl: Preparation of Functionalized Conjugated Diene and Tetraene Systems

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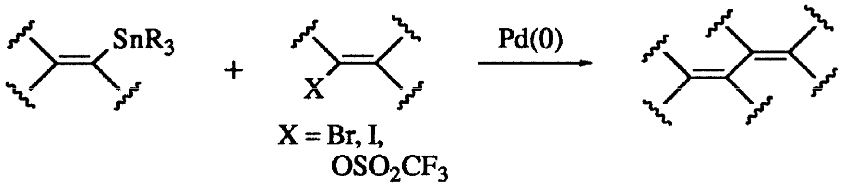
Abstract: Copper(I) chloride–mediated oxidative homocouplings of a variety of substrates containing an alkenyltrimethylstannane function are reported. Thus, treatment of each of the stannanes **1–15** with 2.5 equivalents of CuCl in *N,N*-dimethylformamide (DMF) provides the corresponding dienes or tetraenes **16-32**.

Introduction

The Stille coupling, formulated in general terms in eq. [1], involves the palladium(0)–catalyzed coupling of an aryl– or alkenylstannane with an aryl or alkenyl bromide, iodide, or triflate. This process unquestionably represents a powerful method for synthesizing conjugated diene systems in a stereospecific manner.[1-5] Both the intra– and intermolecular versions of this reaction are effective and the addition of a copper(I) salt as a co-catalyst[6,7] often results in the products being formed more quickly and in higher yield.



[1]

A recent paper from our laboratory disclosed that the *intra*molecular coupling of alkenylstannanes with vinylic iodides or bromides can be accomplished with 2 to 3 equivalents of CuCl in DMF, *in the absence of a palladium(0) catalyst.*[8] An example is shown in eq. [2]. An important extension to this type of process was reported by Allred and Liebeskind, who showed that *inter*molecular cross couplings of alkenyl– and aryltributylstannanes with vinylic and aryl iodides can be effected by treatment of a mixture of the reactants with copper(I) thiophene-2-carboxylate (CuTC) in *N*-methylpyrrolidone (NMP).[9] Several other related studies have been reported recently, four of which involve the copper(II) nitrate–mediated intermolecular coupling of alkenyltributylstannane groups.[10-13] There has also been a publication concerning the cross coupling of α-heteroatom–substituted alkyltributylstannanes with organic halides mediated by copper(I) salts,[14] as well as a report detailing the CuI–promoted allylation of alkenyltributylstannanes.[15]

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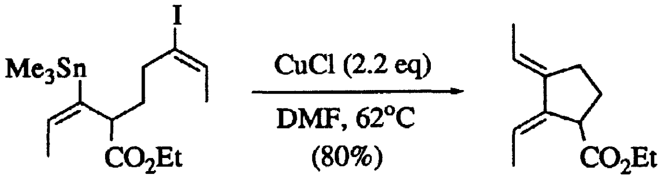
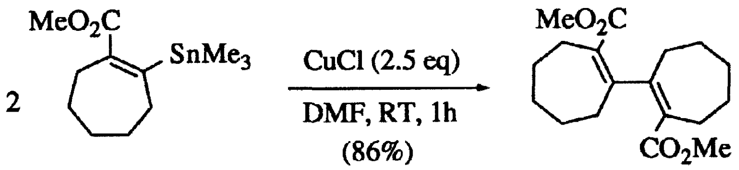


[2]

Further research into Cu(I)–mediated organic reactions conducted in our laboratory revealed that intra– and intermolecular coupling of two alkenyltrimethylstannane groups can be effected by CuCl in DMF.[16-18] A recent report has described the CuCl–mediated intermolecular homocoupling of alkyl 3-trialkylstannyl-2-alkenoates and alkyl 2-trimethylstannyl-1-cycloalkenecarboxylates.[18] A specific example is formulated in eq. [3]. It was of interest to determine whether or not this methodology could be extended to include as substrates a variety of other β-trimethylstannyl α,β-unsaturated carbonyl compounds, as well as some corresponding allylic alcohols and selected structurally related analogs. The results of this study are given in this report.

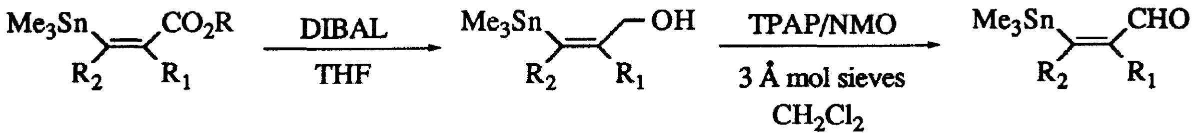


[3]

Results and Discussion

Of the various starting materials given in Table 1, compounds **1**,[19] **5–8**,[20] **14**,[21] and **15**[16] have been previously reported. The unsaturated aldehydes **2–4** were prepared from the corresponding esters **33-35**,[16,18] respectively, as shown in Scheme 1. Reduction of the esters with diisobutylaluminum hydride (DIBAL) in tetrahydrofuran (THF), followed by oxidation of the resultant allylic alcohols **37–39** with tetrapropylammonium peruthenate (TPAP)–*N*-methylmorpholine *N*-oxide (NMO),[22] provided the required aldehydes **2–4**. The aldehyde **41**, which proved to be a very poor substrate for the coupling process (*vide infra*), was similarly prepared from **36**[23] via the allylic alcohol **40**.

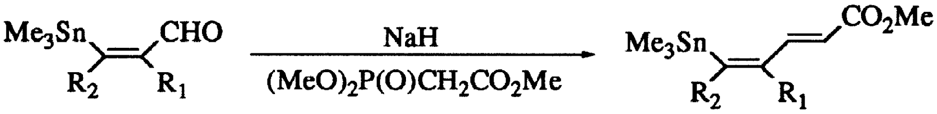
Scheme 1



33 R = Me, R_1,R_2 = $(CH_2)_3$	**37**	**2** (82%)
34 R = Et, R_1,R_2 = $(CH_2)_4$	**38**	**3** (75%)
35 R = Me, R_1,R_2 = $(CH_2)_5$	**39**	**4** (81%)
36 R = Me, R_1 = H, R_2 = $(CH_2)_3Cl$	**40**	**41** (75%)

The δ-trimethylstannyl dienoates **9-13** were synthesized from aldehydes **1**, **41**, and **2–4**, respectively, via Horner-Wadsworth-Emmons chemistry. Thus, reaction (THF) of each of the aldehydes with the phosphonate anion derived from treatment of trimethyl phosphonoacetate with sodium hydride afforded **9**–**13** in very good yields (Scheme 2).

Scheme 2



1 $R_1 = H$, $R_2 = (CH_2)_4OSi(t\text{-}Bu)Me_2$ — **9** (89%)
41 $R_1 = H$, $R_2 = (CH_2)_3Cl$ — **10** (96%)
2 $R_1,R_2 = (CH_2)_3$ — **11** (92%)
3 $R_1,R_2 = (CH_2)_4$ — **12** (97%)
4 $R_1,R_2 = (CH_2)_5$ — **13** (79%)

The coupling processes carried out during the course of this investigation are summarized in Table 1. In each case, 2.5 equivalents of CuCl were employed and the reactions were carried out in DMF, either at 0 °C (Table 1, entries 1, 9–13) or at room temperature (entries 2–8, 14, 15). For some of the processes (entries 1–4, 9–13), exclusion of light from the reaction mixtures by wrapping the reaction vessel with aluminum foil was found to be beneficial. When these reactions were carried out under "normal" lighting conditions, greater amounts of side products were produced and the yields of the expected coupling products were somewhat diminished.

Treatment of the β-trimethylstannyl α,β-unsaturated aldehydes **1**–**4** with CuCl in DMF gave variable yields of the coupled products **16**–**19**, respectively (entries 1–4). Thus, substrates **3** and **4** were transformed into the corresponding dienes **18** and **19** in good yields, while compounds **1** and **2** produced the dienes **16** and **17**, respectively, in rather poor yields. In general, the results derived from the coupling reactions of substrates possessing a formyl function were somewhat inconsistent, and, in fact, attempts to perform a CuCl–mediated coupling of aldehyde **41** led only to complex mixtures, from which none of the desired diene could be isolated. In contrast, the structurally unusual, crystalline bis-enones **20**–**23** were produced in excellent yields when the β-trimethylstannyl α,β-unsaturated ketones **5**–**8**, respectively, were allowed to react with CuCl in DMF at room temperature (entries 5–8).

The intermolecular homocouplings of the δ-trimethylstannyl α,β,γ,δ-bis-unsaturated esters **9**–**13** were quite efficient, although coupling of the acyclic substances **9** and **10** proceeded with only moderate stereospecificity. Thus, treatment of **9** and **10** with CuCl in DMF gave mixtures of products in which the "expected" substances (**25** and **27**, respectively) were accompanied by minor amounts of the corresponding diastereomers **24** and **26** (entries 9 and 10). It should also be noted that the allylic alcohol **14** and the allylic ether **15** provided only moderate yields of the corresponding dienes.

In the majority of the reactions summarized in Table 1 (entries 2–8 and 11–13), the alkenyltrimethylstannane function is part of a ring and, therefore, the stereospecificity of each of these coupling processes was not an issue. However, for the experiments related to entries 1, 9, 10, 14, and 15, the production of more than one product was theoretically possible. It was found that the allylic alcohol **14** and the corresponding ether **15** underwent stereospecific coupling to give dienes **31** and **32**, respectively, as the sole diene products (entries 14 and 15). In this connection, it may be noted that the diene **31** had been reported[24] prior to the work described herein. The coupling of aldehyde **1** (entry 1) was also stereoselective, affording **16** as the only diene product.

Table 1 Intermolecular Homocoupling of Alkenyltrimethylstannane Functions

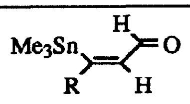
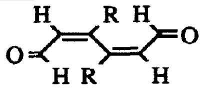
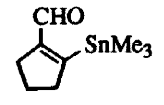
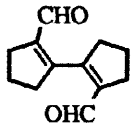
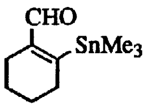
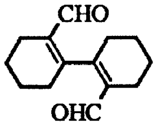
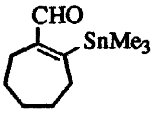
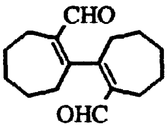
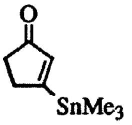
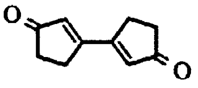
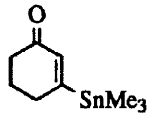
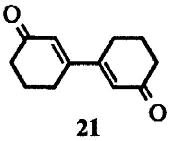
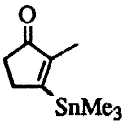
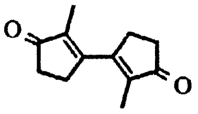
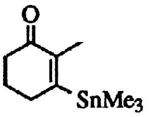
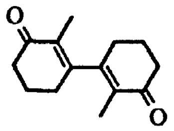
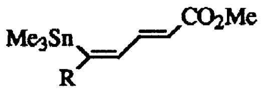
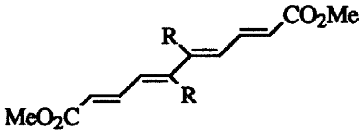
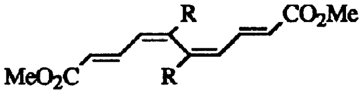
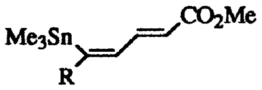
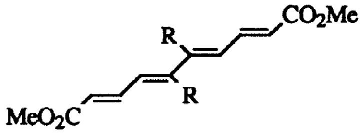
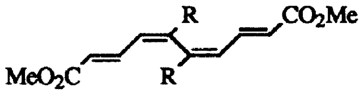
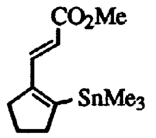
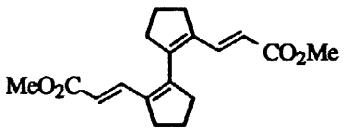
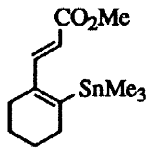
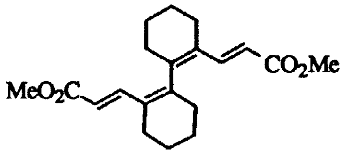
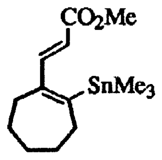
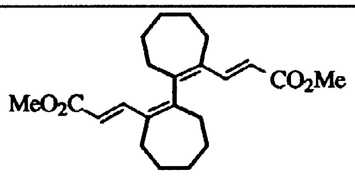
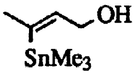
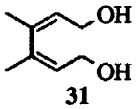
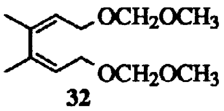
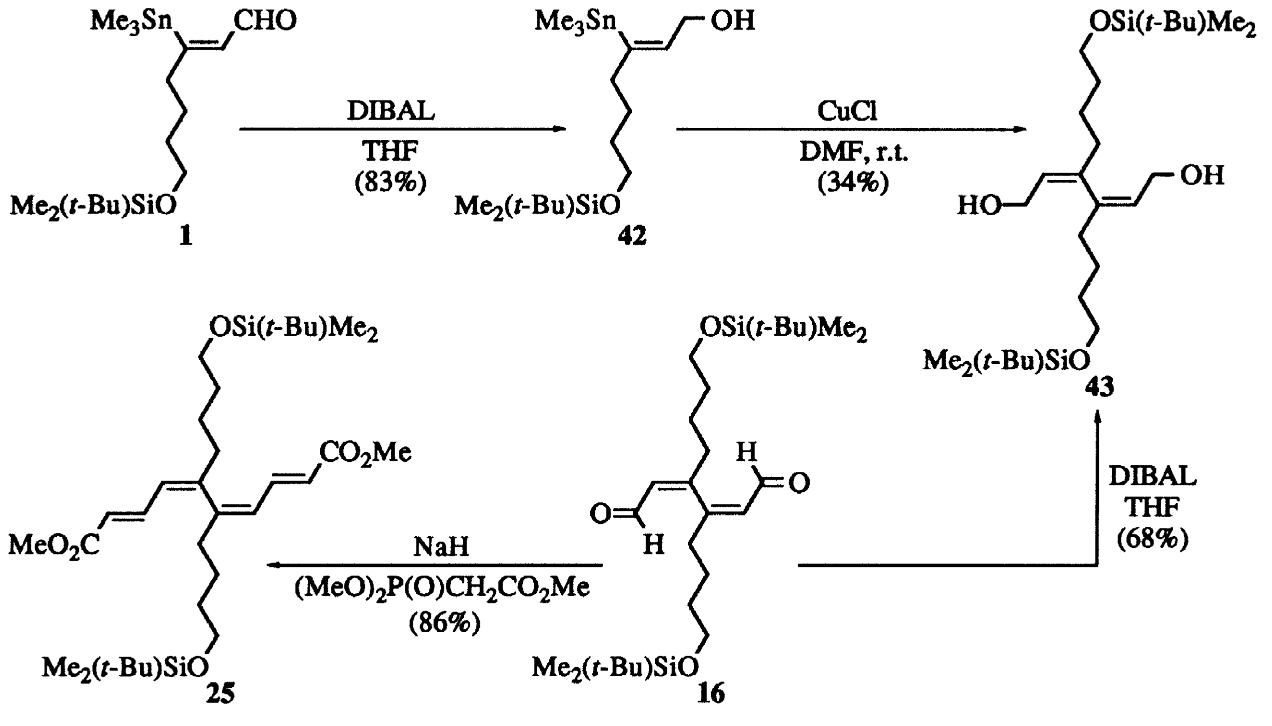
Entry	Starting Material	Reaction Conditions	Product(s)	Yield (%)
1	 R = $(CH_2)_4OSi(t\text{-}Bu)Me_2$ **1**	CuCl (2.5 eq) DMF, 0 °C, 1h dark	 R = $(CH_2)_4OSi(t\text{-}Bu)Me_2$ **16**	61
2	 **2**	CuCl (2.5 eq) DMF, r.t., 1h dark	 **17**	43
3	 **3**	CuCl (2.5 eq) DMF, r.t., 1h dark	 **18**	83
4	 **4**	CuCl (2.5 eq) DMF, r.t., 1h dark	 **19**	76
5	 **5**	CuCl (2.5 eq) DMF, r.t. 30 min	 **20**	81
6	 **6**	CuCl (2.5 eq) DMF, r.t. 30 min	 **21**	91
7	 **7**	CuCl (2.5 eq) DMF, r.t. 30 min	 **22**	94
8	 **8**	CuCl (2.5 eq) DMF, r.t. 30 min	 **23**	91

Table 1 (cont.)

Entry	Starting Material	Reaction Conditions	Product(s)	Yield (%)
9	 R = $(CH_2)_4OSi(t\text{-}Bu)Me_2$ **9**	CuCl (2.5 eq) DMF, 0 °C, 1h dark	 R = $(CH_2)_4OSi(t\text{-}Bu)Me_2$ **24**	18
			 R = $(CH_2)_4OSi(t\text{-}Bu)Me_2$ **25**	69
10	 R = $(CH_2)_3Cl$ **10**	CuCl (2.5 eq) DMF, 0 °C, 1h dark	 R = $(CH_2)_3Cl$ **26**	18
			 R = $(CH_2)_3Cl$ **27**	60
11	 **11**	CuCl (2.5 eq) DMF, 0 °C, 1h dark	 **28**	83
12	 **12**	CuCl (2.5 eq) DMF, 0 °C, 1h dark	 **29**	83
13	 **13**	CuCl (2.5 eq) DMF, 0 °C, 1h dark	 **30**	74
14	 **14**	CuCl (2.5 eq) DMF, r.t., 1h	 **31**	63
15	 **15**	CuCl (2.5 eq) DMF, r.t., 1h	 **32**	53

In the case of the methyl dienoate **9**, in which the Me_3Sn group is bonded to the δ-carbon and is thus more remote from the electron-withdrawing ester function, the coupling reaction proceeded to give two products, the tetraenes **24** and **25**, in isolated yields of 18% and 69%, respectively (Table 1, entry 9). Similar results were obtained from the coupling of substrate **10**, which provided the products **26** (18%) and **27** (60%) (entry 10). Spectral data (^1H and ^{13}C NMR) derived from **24** and **25** showed that both compounds possess an element of symmetry. For example, the ^1H NMR spectrum of **24** contains only three vinylic proton signals and one singlet for the six methyl ester protons, while the ^{13}C NMR spectrum contains resonances for only 13 magnetically distinct carbon atoms. Moreover, the α and β olefinic protons of **24** display a large coupling constant (J=15.5 Hz), indicating that they are in a *trans* relationship. Compound **25** gave similar spectral data. It was also clear from a comparison of the ^1H and ^{13}C NMR spectra that products **26** and **27**, derived from **10** (entry 10), are configurationally related to the tetraenes **24** and **25**, respectively. Thus, if the stereochemical assignments related to the products listed in entries 9 and 10 of Table 1 are correct, the major product from each of these couplings is that of retention of configuration of the two reacting centers, while the minor product is the result of inversion at these two carbons. Interestingly, none of the (*E,Z,E,E*)-tetraenes were isolated from the coupling of either **9** or **10**. A mechanistic rationale for the formation of the minor products **24** and **26** remains obscure.

Scheme 3



Conclusive evidence for the stereochemical assignments of compounds **24** and **25** was obtained by carrying out the correlation reactions summarized in Scheme 3. Reduction of the aldehyde **1**[19] with DIBAL in THF gave the alcohol **42**, which, upon treatment with CuCl in DMF at room temperature, gave a single diene product **43** (*cf.* **14** → **31**, Table 1, entry 14). Reduction of the dienedial **16**, the CuCl–mediated coupling product derived from **1** (Table 1, entry 1), also produced the diol **43**, thereby confirming the structure of **16**. On the other hand, treatment of **16** with the anion obtained from trimethyl phophonoacetate gave **25**, which displayed spectral data identical with the *major* product formed from the CuCl–mediated coupling of substrate **9** (Table 1, entry 9).

Mechanistic considerations regarding the homocoupling processes have been discussed previously.[18]

Conclusion

Oxidative dimerization of a variety of substrates containing alkenyltrimethylstannane functions can be effected with CuCl in DMF. The substrates employed in our study are readily prepared and the homocouplings are readily accomplished via experimentally simple procedures. Most of the products, which possess usefully functionalized conjugated diene or tetraene systems, are constitutionally novel and have the potential to be useful intermediates for the synthesis of structurally more complex organic substances. In a majority of the coupling reactions carried out (Table 1), the stereospecificity of the process is not an issue. However, for the aldehyde **1**, the allylic alcohol **14** and the allylic ether **15**, the reaction proceeds in a stereospecific manner with retention of configuration at the alkenyl centers that are being coupled. On the other hand, the dienoates **9** and **10** dimerize to afford two products in each case. The major products result from a coupling process in which the alkenyl centers involved retain their configuration, while the minor products are due to the coupling of two fragments that have undergone inversion at the alkenyl centres that bore the trimethylstannyl group.

Experimental Section

General Information

Melting points and distillation temperatures (short-path Kugelrohr distillations) are uncorrected. Infrared (IR) spectra were recorded using potassium bromide pellets or liquid films on sodium chloride discs. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded using $CDCl_3$ solutions. Signal positions in ^{1}H NMR spectra were measured relative to signals for Me_4Si (δ 0) (internal standard) or $CHCl_3$ (δ 7.24), while resonances in ^{13}C NMR spectra were recorded relative to the signal for $CDCl_3$ (δ 77.0). Tin-hydrogen coupling constants ($J_{Sn\text{-}H}$) are given as the average of the ^{117}Sn and ^{119}Sn values. Molecular mass determinations (high-resolution mass spectrometry) for substances containing Me_3Sn are based on ^{120}Sn. Flash chromatography[25] was carried out with 230-400 flash silica gel (E. Merck). Thin-layer chromatography (TLC) was accomplished with commercial aluminum backed plates (E. Merck, Type 5554). Gas-liquid chromatography (GLC) was performed on instruments equipped with flame ionization detectors and 25 m × 0.20 mm fused silica columns coated with HP-5 (cross-linked 5% phenyl methyl silicone).

Petroleum ether refers to a mixture of alkanes with bp 35-60 °C. Commercial copper(I) chloride (99.995%) was used without further purification.

Aqueous NH_4Cl–NH_4OH (pH 8) was prepared by the addition of ~50 mL of aqueous ammonia (58%) to ~950 mL of saturated aqueous NH_4Cl.

Note: Unless otherwise stated, all reactions were carried out under an inert atmosphere (dry argon) in oven-(110 °C) or flame-dried glassware.

General Procedure 1: Preparation of β-Trimethylstannyl α,β-Unsaturated Aldehydes 2–4 and 41

To a cold (-78 °C), stirred solution of the appropriate β-trimethylstannyl α,β-unsaturated ester (1 eq) in dry THF (~10 mL per mmol of substrate) was added a 1.0 M solution of DIBAL in hexanes (2.5 eq). After 30 minutes, the reaction mixture was warmed to room temperature and stirred for an additional hour. Saturated aqueous NH_4Cl (~1 mL per mmol of substrate) was added, and the mixture was stirred open to the atmosphere for 30 minutes. $MgSO_4$ (~250 mg per mmol of substrate) was added and the mixture was stirred for a further 30 minutes. The mixture was filtered through Florisil and the collected material was washed with diethyl ether (~50 mL per mmol of substrate). The filtrate was concentrated to yield the allylic alcohol, which was used without further purification.

To a cold (0 °C), stirred solution of the crude allylic alcohol (1 eq) in CH_2Cl_2 (~2.5 mL per mmol of substrate) was added sequentially 3 Å molecular sieves (~500 mg per mmol of substrate), NMO (1.5 eq), and TPAP (0.1 eq). The solution turned green-black immediately. After 30 minutes, the reaction mixture was warmed to room temperature for 1 hour. The mixture was filtered through silica gel (~7 g per mmol of substrate) and the cake was washed with diethyl ether (~50 mL per mmol of substrate). The filtrate was concentrated and the oil thus obtained was distilled to yield the β-trimethylstannyl α,β-unsaturated aldehyde.

The following compounds were prepared via this general procedure.

2-Trimethylstannyl-1-cyclopentenecarbaldehyde (2)

This compound was prepared from methyl 2-(trimethylstannyl)-1-cyclopentenecarboxylate (33)[18] (955 mg, 3.29 mmol). Distillation (90-94 °C, 0.3 Torr) afforded 727 mg (82%) of 2 as a colourless oil that exhibited IR (neat): 1727, 1673, 1125, 774 cm^{-1}; ^1H NMR (400 MHz) δ: 0.27 (s, 9H, $^2J_{Sn\text{-}H}$=56 Hz), 1.89 (quintet, 2H, J=7.5 Hz), 2.57 (t, 2H, J=7.5 Hz), 2.70 (t, 2H, J=7.5 Hz), 9.75 (s, 1H); ^{13}C NMR (75 MHz) δ: -8.5, 23.6, 30.6, 41.8, 155.0, 175.8, 190.8. Exact Mass calcd. for $C_8H_{13}O^{120}Sn$ (M^+-Me): 244.9988. Found: 244.9987. Anal. calcd. for $C_9H_{16}OSn$: C 41.70, H 6.23. Found: C 41.43, H 6.10.

2-Trimethylstannyl-1-cyclohexenecarbaldehyde (3)

Distillation (96-104 °C, 0.3 Torr) of the crude oil derived from ethyl 2-(trimethylstannyl)-1-cyclohexenecarboxylate (34)[18] (1.27 g, 4.00 mmol) provided 855 mg (75%) of 3 as a colourless oil that showed IR (neat): 1678, 1572, 1141, 867, 722 cm^{-1}; ^1H NMR (400 MHz) δ: 0.23 (s, 9H, $^2J_{Sn\text{-}H}$=54 Hz), 1.60-1.64 (m, 4H), 2.27-2.29 (m, 2H), 2.47-2.50 (m, 2H), 9.42 (s, 1H); ^{13}C NMR (125.8 MHz) δ: -7.8, 21.5, 23.3, 24.6, 34.6, 146.5, 172.4, 194.2. Exact Mass calcd. for $C_9H_{15}O^{120}Sn$ (M^+-Me): 259.0145. Found: 259.0146. Anal.

calcd. for $C_{10}H_{18}OSn$: C 44.06, H 6.65. Found: C 44.32, H 6.72.

2-Trimethylstannyl-1-cycloheptenecarbaldehyde (4)

Distillation (102-106°C, 0.3 Torr) of the crude material derived from methyl 2-(trimethylstannyl)-1-cycloheptenecarboxylate (**35**)[18] (852 mg, 2.68 mmol) gave 624 mg (81%) of **4** as a colourless oil that displayed IR (neat): 2720, 1680, 1562, 772 cm^{-1}; ^{1}H NMR (400 MHz) δ: 0.23 (s, 9H, $^2J_{Sn-H}$=53 Hz), 1.37-1.49 (m, 4H), 1.77-1.82 (m, 2H), 2.53-2.56 (m, 2H), 2.63-2.66 (m, 2H), 9.43 (s, 1H); ^{13}C NMR (75 MHz) δ: -7.2, 25.0, 26.0, 26.3, 32.5, 36.4, 153.4, 179.6, 193.8. Exact Mass calcd. for $C_{10}H_{17}O^{120}Sn$ (M^+-Me): 273.0302. Found: 273.0301. Anal. calcd. for $C_{11}H_{20}OSn$: C 46.04, H 7.02. Found: C 46.28, H 7.24.

(Z)-6-Chloro-3-trimethylstannyl-2-hexenal (41)

This material was synthesized from methyl (Z)-6-chloro-3-trimethylstannyl-2-hexenoate (**36**)[23] (2.02 g, 6.20 mmol). Distillation (120-132 °C, 0.1 Torr) of the crude product afforded 1.36 g (75%) of **41** as a colourless oil that exhibited IR (neat): 2746, 1679, 1563, 779, 532 cm^{-1}; ^{1}H NMR (400 MHz) δ: 0.25 (s, 9H, $^2J_{Sn-H}$=54 Hz), 1.84-1.91 (m, 2H), 2.63 (td, 2H, J=7.5, 1.5 Hz, $^3J_{Sn-H}$=44 Hz), 3.51 (t, 2H, J=7.5 Hz), 6.69 (dt, 1H, J=5.0, 1.5 Hz, $^3J_{Sn-H}$=116 Hz), 9.57 (d, 1H, J=5.0 Hz, $^4J_{Sn-H}$=5 Hz); ^{13}C NMR (75 MHz) δ: -7.4, 31.5, 37.8, 43.9, 139.2, 179.4, 192.3. Exact Mass calcd. for $C_8H_{14}O^{35}Cl^{120}Sn$ (M^+-Me): 280.9755. Found: 280.9757. Anal. calcd. for $C_9H_{17}OClSn$: C 36.60, H 5.80. Found: C 36.78, H 5.72.

General Procedure 2: Preparation of δ-Trimethylstannyl α,β,γ,δ-bis-Unsaturated Esters 9–13

To a stirred suspension of sodium hydride (1.7 eq) in dry THF (~7 mL per mmol of substrate) at 0 °C was added trimethyl phosphonoacetate (1.7 eq). The mixture was stirred for 5 minutes, warmed to room temperature for 20 minutes, and then recooled to 0 °C. A solution of the aldehyde (1 eq) in dry THF (~2 mL per mmol of substrate) was added and the reaction mixture was stirred for 2 hours. Diethyl ether (~10 mL per mmol of substrate) and water (~10 mL per mmol of substrate) were added, the layers separated, the aqueous layer was washed twice with diethyl ether (~10 mL per mmol of substrate), and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. The crude product was purified by flash chromatography on silica gel.

The following compounds were prepared via this general procedure.

Methyl (2E,4Z)-9-t-butyldimethylsilyloxy-5-trimethylstannyl-2,4-nonadienoate (9)

This compound was prepared from (Z)-7-*t*-butyldimethylsilyloxy-3-trimethylstannyl-2-heptenal (**1**) (858 mg, 2.11 mmol). Flash chromatography of the crude product (20 g of silica gel, 95:5 petroleum ether–Et_2O) provided 865 mg (89%) of **9** as a colourless oil that displayed IR (neat): 1723, 1625, 1266, 1199, 1141, 1104, 776 cm^{-1}; ^{1}H NMR (400 MHz) δ: 0.02 (s, 6H), 0.25 (s, 9H, $^2J_{Sn-H}$=53.3 Hz), 0.87 (s, 9H), 1.36-1.51 (m, 4H), 2.36 (t, 2H, J=7.1 Hz, $^3J_{Sn-H}$=51.5 Hz), 3.58 (t, 2H, J=6.1 Hz), 3.72 (s, 3H), 5.78 (d, 1H, J=15.0 Hz), 6.68 (d, 1H, J=11.3 Hz, $^3J_{Sn-H}$=121.0 Hz), 7.30 (dd, 1H, J=15.0, 11.3 Hz, $^4J_{Sn-H}$=7.7 Hz); ^{13}C NMR (50.3 MHz) δ: -8.0, -5.3, 18.3, 26.0, 26.1, 32.4, 41.2, 51.4, 62.9, 120.0, 137.5, 145.8, 166.3, 167.8. Exact Mass calcd. for

$C_{19}H_{38}O_3Si^{120}Sn$: 462.1612. Found: 462.1599. Anal. calcd. for $C_{19}H_{38}O_3SiSn$: C 49.47, H 8.30. Found: C 49.73, H 8.52.

Methyl (2E,4Z)-8-chloro-5-trimethylstannyl-2,4-octadienoate (10)

Flash chromatography (7 g of silica gel, 9:1 petroleum ether–Et_2O) of the crude oil obtained from (*Z*)-6-chloro-3-trimethylstannyl-2-hexenal (**41**) (303 mg, 1.03 mmol) afforded 346 mg (96%) of **10** as a white solid (m.p. 23-24 °C) that showed IR (CH_2Cl_2 cast): 1719, 1625, 1268, 1200, 1152, 1132, 976, 774 cm^{-1}; ^1H NMR (400 MHz) δ: 0.27 (s, 9H, $^2J_{Sn\text{-}H}$=53.5 Hz), 1.79-1.86 (m, 2H), 2.50 (t, 2H, *J*=7.5 Hz, $^3J_{Sn\text{-}H}$=49.7 Hz), 3.48 (t, 2H, *J*=6.5 Hz), 3.72 (s, 3H), 5.80 (d, 1H, *J*=15.0 Hz), 6.72 (d, 1H, *J*=11.3 Hz, $^3J_{Sn\text{-}H}$=120.3 Hz), 7.28 (dd, 1H, *J*=15.0, 11.3 Hz, $^4J_{Sn\text{-}H}$=7.5 Hz); ^{13}C NMR (50.3 MHz) δ: -8.0, 32.3, 38.1, 44.1, 51.5, 120.7, 138.6, 145.3, 163.7, 167.6. Exact Mass calcd. for $C_{11}H_{18}O_2{}^{35}Cl^{120}Sn$ (M^+-Me): 337.0017. Found: 337.0012. Anal. calcd. for $C_{12}H_{21}O_2ClSn$: C 41.01, H 6.02. Found: C 41.12, H 6.01.

Methyl (E)-3-(2-trimethylstannyl-1-cyclopenten-1-yl)propenoate (11)

Purification (flash chromatography, 5.5 g of silica gel, 9:1 petroleum ether–Et_2O) of the crude material obtained from 2-trimethylstannyl-1-cyclopentenecarbaldehyde (**2**) (210 mg, 0.809 mmol), followed by recrystallization from petroleum ether–Et_2O, gave 235 mg (92%) of **11** as colourless crystals (m.p. 35-36 °C) that exhibited IR (CH_2Cl_2 cast): 1719, 1620, 1306, 1273, 1164, 773 cm^{-1}; ^1H NMR (400 MHz) δ: 0.23 (s, 9H, $^2J_{Sn\text{-}H}$=54.5 Hz), 1.89 (quintet, 2H, *J*=7.5 Hz), 2.49 (t, 2H, *J*=7.5 Hz), 2.60 (t, 2H, *J*=7.5 Hz), 3.73 (s, 3H), 5.73 (d, 1H, *J*=15.5 Hz), 7.49 (d, 1H, *J*=15.5 Hz); ^{13}C NMR (50.3 MHz) δ: -9.1, 23.8, 32.8, 41.2, 51.4, 117.9, 142.7, 149.6, 160.9, 168.0. Exact Mass calcd. for $C_{12}H_{20}O_2{}^{120}Sn$: 316.1485. Found: 316.0480. Anal. calcd. for $C_{12}H_{20}O_2Sn$: C 45.76, H 6.40. Found: C 45.94, H 6.54.

Methyl (E)-3-(2-trimethylstannyl-1-cyclohexen-1-yl)propenoate (12)

This material was synthesized from 2-trimethylstannyl-1-cyclohexenecarbaldehyde (**3**) (284 mg, 1.04 mmol). Flash chromatography (5.5 g of silica gel, 9:1 petroleum ether–Et_2O) of the crude oil, followed by recrystallization from petroleum ether–Et_2O, provided 330 mg (97%) of **12** as colourless crystals (m.p. 53-54 °C) that displayed IR (CH_2Cl_2 cast): 1719, 1617, 1294, 1270, 1166, 771 cm^{-1}; ^1H NMR (400 MHz) δ: 0.23 (s, 9H, $^2J_{Sn\text{-}H}$=52.9 Hz), 1.55-1.61 (m, 2H), 1.63-1.69 (m, 2H), 2.19-2.22 (m, 2H), 2.38-2.40 (m, 2H), 3.73 (s, 3H), 5.76 (d, 1H, *J*=15.4 Hz), 7.36 (d, 1H, *J*=15.4 Hz, $^4J_{Sn\text{-}H}$=9.6 Hz); ^{13}C NMR (50.3 MHz) δ: -8.2, 22.2, 23.2, 26.4, 34.3, 51.4, 114.4, 141.9, 149.8, 159.9, 168.2. Exact Mass calcd. for $C_{13}H_{22}O_2{}^{120}Sn$: 330.0642. Found: 330.0637. Anal. calcd. for $C_{13}H_{22}O_2Sn$: C 47.46, H 6.74. Found: C 47.69, H 6.88.

Methyl (E)-3-(2-trimethylstannyl-1-cyclohepten-1-yl)propenoate (13)

Flash chromatography (6 g of silica gel, 9:1 petroleum ether–Et_2O) of the crude product derived from 2-trimethylstannyl-1-cycloheptenecarbaldehyde (**4**) (297 mg, 1.03 mmol) afforded 279 mg (79%) of **13** as a colourless oil that showed IR (neat): 1719, 1613, 1299, 1269, 1167, 772 cm^{-1}; ^1H NMR (400 MHz) δ: 0.23 (s, 9H, $^2J_{Sn\text{-}H}$=52.7 Hz), 1.39-1.44 (m, 4H), 1.73-1.79 (m, 2H), 2.41-2.53 (m, 4H), 3.73 (s, 3H), 5.80 (d, 1H, *J*=15.4 Hz), 7.41 (d, 1H, *J*=15.4 Hz, $^4J_{Sn\text{-}H}$=10.6 Hz); ^{13}C NMR (50.3 MHz) δ: -7.9, 25.6, 25.7, 28.3, 32.2, 35.7, 51.4, 114.7, 150.0, 150.3, 165.3, 168.3. Exact Mass calcd. for $C_{14}H_{24}O_2{}^{120}Sn$: 344.0798. Found:

344.0807. Anal. calcd. for $C_{14}H_{24}O_2Sn$: C 49.02, H 7.05. Found: C 49.19, H 7.13.

(Z)-1-Methoxymethoxy-3-trimethylstannyl-2-butene (15)

To a stirred solution of (Z)-3-trimethylstannyl-2-butenol (**14**)^{21} (500 mg, 2.13 mmol) in CH_2Cl_2 (30 mL) at room temperature was added diisopropylethylamine (0.56 mL, 3.20 mmol) and chloromethylmethyl ether (0.24 mL, 3.20 mmol). After 6 hours, aqueous NH_4Cl–NH_4OH (pH 8, 20 mL) was added to the pale yellow solution and the phases were separated. The aqueous layer was extracted with diethyl ether (3x20 mL), and the combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), and concentrated. Flash chromatography (50 g of silica gel, 10:1 pentane–Et_2O) of the crude oil afforded 494 mg (83%) of **15** as a colourless oil that displayed IR (neat): 1440, 1039, 924, 769, 526 cm^{-1}; ^{1}H NMR (400 MHz) δ: 0.14 (s, 9H, $^2J_{Sn\text{-}H}$=53 Hz), 1.91 (dt, 3H, J=2, 1 Hz, $^3J_{Sn\text{-}H}$=47 Hz), 3.32 (s, 3H), 3.96 (dq, 2H, J=6, 1 Hz), 4.58 (s, 2H), 6.14 (tq, 1H, J=6, 2 Hz, $^3J_{Sn\text{-}H}$=137 Hz); ^{13}C NMR (50.3 MHz) δ: 8.6, 26.5, 55.2, 68.7, 95.7, 135.8, 144.5. Exact Mass calcd. for $C_8H_{17}O_2{}^{120}Sn$ (M^+-Me): 265.0251. Found: 265.0245. Anal. calcd. for $C_9H_{20}O_2Sn$: C 38.75, H 7.23. Found: C 38.82, H 7.34.

General Procedure 3: Copper(I) Chloride–Mediated Coupling of Substrates 1–4 and 9–13. Preparation of Products 16–19 and 24–30

Throughout these experiments, the flask containing the reaction mixture was protected from light by being wrapped with aluminum foil. To a stirred suspension of CuCl (2.5 eq) in dry DMF (~4 mL per mmol of substrate) at room temperature or 0 °C was added a solution of the alkenyltrimethylstannane (1 eq) in dry DMF (~4 mL per mmol of substrate) and the resulting brown mixture was stirred for 1 hour. Saturated aqueous NH_4Cl (~the same volume as DMF) and water (~the same volume as DMF) were added and the mixture was stirred, open to the atmosphere, until the aqueous phase turned bright blue. The mixture was extracted three times with diethyl ether and the combined organic layers were washed with water and brine, dried ($MgSO_4$), and concentrated. The crude product was purified by flash chromatography on silica gel.

The following compounds were prepared via this general procedure.

*(Z,Z)-3,4-Bis-(4-*t*-butyldimethylsilyloxybutyl)-2,4-hexadienedial (16)*

This material was synthesized at 0 °C from (Z)-7-*t*-butyldimethylsilyloxy-3-trimethylstannyl-2-heptenal (**1**) (100 mg, 0.246 mmol). Flash chromatography of the crude oil on silica gel (5 g, 9:1 to 4:1 petroleum ether–Et_2O) afforded 36 mg (61%) of **16** as a colourless oil that displayed IR (neat): 1684, 1605, 1256, 1145, 838, 777 cm^{-1}; ^{1}H NMR (400 MHz) δ: 0.01 (s, 12H), 0.86 (s, 18H), 1.48-1.63 (m, 8H), 2.37-2.45 (m, 4H), 3.57-3.64 (m, 4H), 6.14 (d, 2H, J=8.1 Hz), 9.60 (d, 2H, J=8.1 Hz); ^{13}C NMR (50.3 MHz,) δ: -5.4, 18.3, 23.6, 25.9, 32.2, 37.0, 62.3, 130.1, 161.8, 191.2. Exact Mass calcd. for $C_{26}H_{50}O_4Si_2$: 482.3248. Found: 482.3242. Anal. calcd. for $C_{26}H_{50}O_4Si_2$: C 64.68, H 10.44. Found: C 64.33, H 10.60.

2-(2-Methanoyl-1-cyclopenten-1-yl)-1-cyclopentenecarbaldehyde (17)

This compound was prepared at room temperature from 2-trimethylstannyl-1-cyclopentenecarbaldehyde (**2**) (102 mg, 0.392 mmol). Flash chromatography of the crude product on silica gel (5 g, 4:1 to 1:1 petroleum ether–Et_2O), followed by recrystallization from petroleum ether–Et_2O, afforded 16 mg (43%) of **17** as colourless crystals (m.p. 74-75 °C) that showed IR (CH_2Cl_2 cast): 2817, 1670, 1651, 1592, 1221 cm^{-1}; ^1H NMR (400 MHz) δ: 2.00 (quintet, 4H, J=7.7 Hz), 2.69-2.80 (m, 8H), 9.68 (s, 2H); ^{13}C NMR (75 MHz) δ: 21.8, 30.8, 38.8, 144.3, 155.5, 188.1. Exact Mass calcd. for $C_{12}H_{14}O_2$: 190.0994. Found: 190.0995. Anal. calcd. for $C_{12}H_{14}O_2$: C 75.76, H 7.42. Found: C 76.06, H 7.48.

2-(2-Methanoyl-1-cyclohexen-1-yl)-1-cyclohexenecarbaldehyde (18)

Flash chromatography (5 g, 4:1 petroleum ether–Et_2O) of the crude oil obtained at room temperature from 2-trimethylstannyl-1-cyclohexenecarbaldehyde (**3**) (98 mg, 0.36 mmol), followed by recrystallization from petroleum ether–Et_2O, provided 32 mg (83%) of **18** as colourless crystals (m.p. 145-146 °C) that exhibited IR (KBr): 2867, 1671, 1628, 1606, 1278, 1220 cm^{-1}; ^1H NMR (400 MHz) δ: 1.60-1.80 (m, 8H), 2.15-2.35 (m, 6H), 2.50-2.61 (m, 2H), 9.69 (s, 2H); ^{13}C NMR (50.3 MHz) δ: 21.3, 21.6, 22.0, 32.8, 136.3, 157.2, 191.6. Exact Mass calcd. for $C_{14}H_{18}O_2$: 218.1307. Found: 218.1300. Anal. calcd. for $C_{14}H_{18}O_2$: C 77.03, H 8.31. Found: C 77.09, H 8.13.

2-(2-Methanoyl-1-cyclohepten-1-yl)-1-cycloheptenecarbaldehyde (19)

Purification (flash chromatography, 5 g of silica gel, 4:1 petroleum ether–Et_2O) of the crude product obtained at room temperature from 2-trimethylstannyl-1-cycloheptenecarbaldehyde (**4**) (105 mg, 0.367 mmol), followed by recrystallization from petroleum ether–Et_2O, gave 34 mg (76%) of **19** as colourless crystals (m.p. 125.5-127 °C) that displayed IR (KBr): 2852, 1657, 1250, 1206, 967 cm^{-1}; ^1H NMR (400 MHz) δ: 1.45-1.89 (m, 12 H), 2.43-2.69 (m, 8H), 9.57 (s, 2H). Exact Mass calcd. for $C_{16}H_{22}O_2$: 246.1620. Found: 246.1617. Anal. calcd. for $C_{16}H_{22}O_2$: C 78.01, H 9.00. Found: C 77.74, H 8.82.

Dimethyl (E,E,E,E)-5,6-Bis-(4-t-butyldimethylsilyloxybutyl)-2,4,6,8-nonatetraenedioate (24) and Dimethyl (E,Z,Z,E)-5,6-Bis-(4-t-butyldimethylsilyloxybutyl)-2,4,6,8-nonatetraenedioate (25)

These substances were prepared at 0 °C from methyl (*E,Z*)-9-*t*-butyldimethylsilyloxy-5-trimethylstannyl-2,4-nonadienoate (**9**) (95 mg, 0.21 mmol). Flash chromatography of the crude reaction mixture on silica gel (5g, 19:1 to 17:3 petroleum ether–Et_2O) provided 11 mg (18%) of **24** and 42 mg (69%) of **25**. Diester **24** is a colourless oil that displayed IR (neat): 1724, 1635, 1257, 1142, 1106, 836 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.02 (s, 12H), 0.87 (s, 18H), 1.46-1.53 (m, 4H), 1.62-1.69 (m, 4H), 2.45 (t, 4H, J=7.3 Hz), 3.60 (t, 4H, J=6.2 Hz), 3.74 (s, 6H), 5.89 (d, 2H, J=15.5 Hz), 6.20 (d, 2H, J=10.8 Hz), 7.61 (dd, 2H, J=15.5, 10.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -5.3, 18.3, 23.8, 25.9, 31.6, 39.9, 51.6, 62.7, 121.7, 123.1, 139.5, 144.9, 167.2. Exact Mass calcd. for $C_{32}H_{58}O_6Si_2$: 594.3772. Found: 594.3764. Anal. calcd. for $C_{32}H_{58}O_6Si_2$: C 64.60, H 9.83. Found: C 64.88, H 9.76.

Diester **25** is a colourless oil that exhibited IR (neat): 1723, 1631, 1269, 1143, 1106, 837, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.00 (s, 12H), 0.85 (s, 18H), 1.35-1.53 (m, 8H), 2.23 (br s, 4H), 3.58 (t, 4H, J=5.7 Hz), 3.67 (s, 6H), 5.82 (d, 2H, *J*=15.3 Hz), 6.17 (d, 2H, *J*=11.4 Hz), 7.10 (dd, 2H, *J*=15.3, 11.5 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: -5.3, 18.3, 24.1, 25.9, 32.5, 36.5, 51.4, 62.7, 121.0, 126.0, 141.3, 150.7, 167.5. Exact Mass calcd. for $C_{32}H_{58}O_6Si_2$: 594.3772. Found: 594.3768. Anal. calcd. for $C_{32}H_{58}O_6Si_2$: C 64.60, H 9.83. Found: C 64.44, H 9.72.

*Dimethyl (*E,E,E,E*)-5,6-Bis-(3-chloropropyl)-2,4,6,8-nonatetraenedioate (26) and Dimethyl (*E,Z,Z,E*)-5,6-Bis-(3-chloropropyl)-2,4,6,8-nonatetraenedioate (27)*

Flash chromatography (6 g of silica gel, 4:1 to 3:2 petroleum ether-Et_2O) of the crude product derived from methyl (*E,Z*)-8-chloro-5-trimethylstannyl-2,4-octadienoate (**10**) (106 mg, 0.301 mmol) at 0°C gave 10 mg (18%) of **26** and 34 mg (60%) of **27**. Diester **26** is a colourless oil that showed IR (neat): 1719, 1636, 1267, 1201, 1153, 984 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03-2.10 (m, 4H), 2.62 (t, 4H, *J*=7.1 Hz), 3.53 (t, 4H, *J*=6.2 Hz), 3.74 (s, 6H), 5.93 (d, 2H, *J*=15.5 Hz), 6.28 (dd, 2H, *J*=10.1, 0.7 Hz), 7.59 (dd, 2H, *J*=15.5, 10.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.8, 37.0, 43.4, 51.7, 122.5, 124.3, 139.0, 142.5, 167.1. Exact Mass calcd. for $C_{18}H_{24}O_4{}^{35}Cl_2$: 374.1052. Found: 374.1055. Anal. calcd. for $C_{18}H_{24}O_4Cl_2$: C 57.61, H 6.45. Found: C 57.83, H 6.52.

Diester **27** is a colourless oil that displayed IR (neat): 1713, 1631, 1269, 1157, 988, 913 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.82-1.89 (m, 4H), 2.41 (t, 4H, *J*=7.7 Hz), 3.52 (t, 4H, *J*=6.2 Hz), 3.67 (s, 6H), 5.87 (d, 2H, *J*=15.3 Hz), 6.25 (d, 2H, *J*=11.4 Hz), 7.06 (dd, 2H, *J*=15.3, 11.4 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 30.4, 33.6, 44.2, 51.5, 122.1, 127.3, 140.3, 148.0, 167.2. Exact Mass calcd. for $C_{18}H_{24}O_4{}^{35}Cl_2$: 374.1052. Found: 374.1058. Anal. calcd. for $C_{18}H_{24}O_4Cl_2$: C 57.61, H 6.45. Found: C 57.61, H 6.58.

*1-{2-[(*E*)-2-(Methoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}-2-[(*E*)-2-(methoxycarbonyl)ethenyl]cyclopentene (28)*

Purification (flash chromatography, 5 g of silica gel, 4:1 to 1:1 petroleum ether–Et_2O) of the crude product obtained from methyl (*E*)-3-(2-trimethylstannyl-1-cyclopenten-1-yl)propenoate (**11**) (97 mg, 0.31 mmol) at 0 °C, followed by recrystallization from petroleum ether–Et_2O, provided 39 mg (83%) of **28** as colourless crystals (m.p. 115-116 °C) that displayed IR (CH_2Cl_2 cast): 1718, 1619, 1308, 1270, 1165, 981 cm^{-1}; ^{1}H NMR (400 MHz) δ: 1.95 (quintet, 4H, *J*=7.5 Hz), 2.55-2.62 (m, 8H), 3.67 (s, 6H), 5.78 (d, 2H, *J*=15.6 Hz), 7.26 (d, 2H, *J*=15.6 Hz); ^{13}C NMR (50.3 MHz) δ: 21.9, 32.9, 37.7, 51.4, 118.7, 137.2, 139.1, 146.7, 167.8. Exact Mass calcd. for $C_{18}H_{22}O_4$: 302.1518. Found: 302.1514. Anal. calcd. for $C_{18}H_{22}O_4$: C 71.50, H 7.33. Found: C 71.45, H 7.28.

*1-{2-[(*E*)-2-(Methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}-2-[(*E*)-2-(methoxycarbonyl)ethenyl]cyclohexene (29)*

This material was synthesized from methyl (*E*)-3-(2-trimethylstannyl-1-cyclohexen-1-yl)propenoate (**12**) (111 mg, 0.336 mmol) at 0 °C. Flash chromatography of the crude oil on silica gel (5 g, 4:1 petroleum ether–Et_2O), followed by recrystallization from petroleum ether–Et_2O, afforded 46 mg (83%) of **29** as colourless crystals (m.p. 123-124.5°C) that exhibited IR (CH_2Cl_2 cast): 1719, 1620, 1298, 1274, 1166, 983 cm^{-1}; ^{1}H NMR (400 MHz) δ: 1.57-1.76 (m, 8H), 2.04-2.30 (m, 8H), 3.67 (s, 6H), 5.77 (d, 2H, *J*=15.8 Hz), 7.29 (d, 2H, *J*=15.8

Hz); ^{13}C NMR (50.3 MHz) δ: 22.2, 22.3, 24.5, 31.3, 51.4, 115.4, 129.1, 143.8, 148.0, 168.1. Exact Mass calcd. for $C_{20}H_{26}O_4$: 330.1831. Found: 330.1830. Anal. calcd. for $C_{20}H_{26}O_4$: C 72.70, H 7.93. Found: C 72.42, H 7.97.

1-{2-[(E)-2-(Methoxycarbonyl)ethenyl]-1-cyclohepten-1-yl}-2-[(E)-2-(methoxycarbonyl)ethenyl]cycloheptene (30)

This compound was prepared at 0 °C from methyl (*E*)-3-(2-trimethylstannyl-1-cyclohepten-1-yl)propenoate (**13**) (96 mg, 0.28 mmol). Flash chromatography of the resulting crude material (5 g of silica gel, 4:1 petroleum ether–Et$_2$O), followed by recrystallization from petroleum ether–Et$_2$O, gave 37 mg (74%) of **30** as colourless crystals (m.p. 91-93 °C) that displayed IR (CH$_2$Cl$_2$ cast): 1718, 1615, 1310, 1274, 1170, 987, 856 cm^{-1}; ^{1}H NMR (400 MHz) δ: 1.54-1.63 (m, 8H), 1.69-1.79 (m, 2H), 1.83-1.90 (m, 2H), 2.30-2.51 (m, 8H), 3.66 (s, 6H), 5.80 (d, 2H, *J*=15.7 Hz), 7.33 (d, 2H, *J*=15.7 Hz); ^{13}C NMR (50.3 MHz) δ: 25.6, 25.9, 28.0, 32.2, 34.0, 51.3, 115.4, 136.9, 145.2, 152.7, 168.3. Exact Mass calcd. for $C_{22}H_{30}O_4$: 358.2144. Found: 358.2137. Anal. calcd. for $C_{22}H_{30}O_4$: C 73.71, H 8.43. Found: C 73.61, H 8.57.

General Procedure 4: Copper(I) Chloride–Mediated Coupling of Substrates 5–8. Preparation of Products 20–23

To a stirred suspension of CuCl (2.5 eq) in dry DMF (~4 mL per mmol of substrate) at room temperature was added the alkenyltrimethylstannane (1 eq) in dry DMF (~4 mL per mmol of substrate), and the resulting brown mixture stirred for 30 minutes. Saturated aqueous NH$_4$Cl (~the same volume as DMF) and water (~the same volume as DMF) were added, and the mixture was stirred open to the atmosphere until the aqueous phase turned bright blue. The mixture was extracted three times with diethyl ether or CH$_2$Cl$_2$ and the combined organic layers were washed with water and brine, dried (MgSO$_4$), and concentrated. The crude product was purified by flash chromatography on silica gel.

The following compounds were prepared via this general procedure.

3-(3-Oxo-1-cyclopenten-1-yl)-2-cyclopenten-1-one (20)

This compound was synthesized from 3-trimethylstannyl-2-cyclopenten-1-one (**5**) (101 mg, 0.41 mmol) and was isolated by extraction with CH$_2$Cl$_2$. Flash chromatography of the crude product (12 g of silica gel, ethyl acetate) provided 27 mg (81%) of **20** as a colourless crystalline solid (m.p. 211-214 °C) that exhibited IR (KBr): 1698, 1675, 1561, 1243, 1184, 865, 848 cm^{-1}; ^{1}H NMR (400 MHz) δ: 2.52-2.57 (m, 4H), 2.85-2.90 (m, 4H), 6.43 (t, 2H, *J*=1.5 Hz); ^{13}C NMR (50.3 MHz) δ: 28.2, 35.1, 132.6, 166.9, 208.7. Exact Mass calcd. for $C_{10}H_{10}O_2$: 162.0681. Found: 162.0677. Anal. calcd. for $C_{10}H_{10}O_2$: C 74.06, H 6.21. Found: C 74.13, H 6.10.

3-(3-Oxo-1-cyclohexen-1-yl)-2-cyclohexen-1-one (21)

The crude product derived from 3-trimethylstannyl-2-cyclohexen-1-one (**6**) (121 mg, 0.47 mmol) was obtained by extraction with diethyl ether and, upon purification by flash chromatography (7 g of silica gel, diethyl ether), afforded 40 mg (91%) of **21** as a colourless crystalline solid (m.p. 107-108 °C) that showed IR (KBr): 1662, 1575, 1263, 1186, 1144, 901 cm^{-1}; ^{1}H NMR (400 MHz) δ: 2.00-2.15 (m, 4H), 2.42 (t, 4H, *J*=6.7 Hz), 2.50 (t, 4H, *J*=6.0 Hz), 6.27 (s, 2H); ^{13}C NMR (50.3 MHz) δ: 22.2, 25.8, 37.4, 128.0, 156.5, 199.7. Exact Mass calcd. for $C_{12}H_{14}O_2$: 190.0994. Found: 190.0993. Anal. calcd. for $C_{12}H_{14}O_2$: C 75.76, H 7.42. Found: C 75.54, H 7.42.

2-Methyl-3-(2-methyl-3-oxo-1-cyclopenten-1-yl)-2 cyclopenten-1-one (22)

The crude product derived from 2-methyl-3-trimethylstannyl-2-cyclopenten-1-one (**7**) (110 mg, 0.43 mmol) was obtained by extraction with CH_2Cl_2 and, upon purification (flash chromatography, 20 g of silica gel, ethyl acetate), gave 38 mg (94%) of **22** as a colourless crystalline solid (m.p. 94-94.5 °C) that showed IR (KBr): 1690, 1626, 1292, 995, 947, 781 cm^{-1}; ^{1}H NMR (400 MHz) δ: 1.67 (t, 6H, *J*=2.1 Hz), 2.48-2.53 (m, 4H), 2.65-2.72 (m, 4H); ^{13}C NMR (50.3 MHz) δ: 9.9, 28.5, 33.8, 138.7, 163.5, 208.6. Exact Mass calcd. for $C_{12}H_{14}O_2$: 190.0994. Found: 190.0993. Anal. calcd. for $C_{12}H_{14}O_2$: C 75.76, H 7.42. Found: C 75.72, H 7.68.

2-Methyl-3-(2-methyl-3-oxo-1-cyclohexen-1-yl)-2 cyclohexen-1-one (23)

This compound was prepared from 2-methyl-3-trimethylstannyl-2-cyclohexen-1-one (**8**) (114 mg, 0.42 mmol), and was isolated by extraction with CH_2Cl_2. Flash chromatography (21 g of silica gel, 1:1 petroleum ether–Et_2O) of the crude product provided 41 mg (91%) of **23**, a colourless crystalline solid (m.p. 121-122.5 °C) that displayed IR (KBr): 1657, 1606, 1299, 1195, 1113, 1035, 900 cm^{-1}; ^{1}H NMR (400 MHz) δ: 1.61 (t, 6H, *J*=1.9 Hz), 1.95-2.11 (m, 4H), 2.20-2.32 (m, 2H), 2.38-2.52 (m, 6H); ^{13}C NMR (50.3 MHz) δ: 11.9, 22.9, 28.9, 37.7, 129.8, 155.4, 198.9. Exact Mass calcd. for $C_{14}H_{18}O_2$: 218.1307. Found: 218.1309. Anal. calcd. for $C_{14}H_{18}O_2$: C 77.03, H 8.31. Found: C 77.11, H 8.46.

General Procedure 5: Copper(I) Chloride–Mediated Coupling of Substrates 14 and 15. Preparation of Products 31 and 32

To a solution of the alkenyltrimethylstannane in DMF (~0.5 mL per mmol of substrate) at room temperature was added solid copper(I) chloride (2.5 eq) and the resulting brown mixture was stirred for 1 hour. Aqueous NH_4Cl–NH_4OH (pH 8, ~the same volume as DMF) was added and the mixture was stirred open to the atmosphere until the aqueous layer was bright blue. The layers were separated and the aqueous layer was extracted three times with diethyl ether. The combined organic layers were washed once with water, once with brine, dried ($MgSO_4$), and concentrated. The crude product was purified by flash chromatography on silica gel.

The following compounds were prepared via this general procedure.

(Z,Z)-3,4-Dimethylhexa-2,4-diene-1,6-diol (31)[24]

This compound was prepared from (Z)-3-trimethylstannyl-2-buten-1-ol (**14**)[21] (250 mg, 1.06 mmol). Flash chromatography (5 g of silica gel, 1:1 pentane–Et_2O) of the crude oil afforded 47 mg (63%) of **31** as a colourless oil that exhibited IR (neat): 3328, 1650, 1445, 1239, 1086, 998 cm^{-1}; ^{1}H NMR (400 MHz) δ: 1.75 (m, 6H), 3.46 (br s, 2H), 3.84 (d, 4H, J=8 Hz), 5.52 (tq, 2H, J=8, 1 Hz); ^{13}C NMR (50.3 MHz) δ: 22.6, 58.8, 124.4, 141.1. Exact Mass calcd. for $C_8H_{14}O_2$: 142.0994. Found: 142.0993. Anal. calcd. for $C_8H_{14}O_2$: C 67.57, H 9.92. Found: C 67.73, H 10.03.

(Z,Z)-3,4-Dimethyl-1,6-bis-(methoxymethoxy)-2,4-hexadiene (32)

Purification (flash chromatography, 5g of silica gel, 4:1 pentane–Et_2O) of the crude material acquired from (Z)-1-methoxymethoxy-3-trimethylstannyl-2-butene (**15**)[16] (100 mg, 0.36 mmol) provided 22 mg (53%) of **32** as a colourless oil that displayed IR (neat): 1718, 1448, 1151, 1105, 1048, 924 cm^{-1}; ^{1}H NMR (400 MHz) δ: 1.80 (q, 6H, J=1 Hz), 3.32 (s, 6H), 3.87 (dq, 4H, J=7, 1 Hz), 4.57 (s, 4H), 5.42 (tq, 2H, J=7, 1 Hz); ^{13}C NMR (50.3 MHz) δ: 22.6, 55.1, 64.8, 95.8, 122.5, 140.2. Exact Mass calcd. for $C_{12}H_{23}O_4$ (M^++H): 231.1596. Found: 231.1596. Anal. calcd. for $C_{12}H_{22}O_4$: C 62.58, H 9.63. Found: C 62.69, H 9.79.

(Z)-7-*t*-Butyldimethylsilyloxy-3-trimethylstannyl-2-hepten-1-ol (42)

To a cold (-78 °C), stirred solution of (Z)-7-*t*-butyldimethylsilyloxy-3-trimethylstannyl-2-heptenal (**1**) (66.8 mg, 0.165 mmol) in 2 mL of dry THF was added a 1.0 M solution of DIBAL in hexanes (300 μL, 0.30 mmol). After 45 minutes, the reaction mixture was warmed to room temperature and stirred for an additional 45 minutes. Saturated aqueous NH_4Cl (1 mL) was added and the reaction mixture was stirred, open to the atmosphere, for 30 minutes. $MgSO_4$ (200 mg) was added and the mixture was stirred a further 30 minutes. The mixture was filtered through Florisil and the collected material was washed with Et_2O (20 mL). The filtrate was concentrated and the crude oil was purified by flash chromatography (4.5 g of silica gel, 4:1 petroleum ether-Et_2O) to afford 56.0 mg (83%) of **42** as a colourless oil that displayed IR (neat): 3359, 1472, 1256, 1104, 1006, 775, 526 cm^{-1}; ^{1}H NMR (400 MHz) δ: 0.02 (s, 6H), 0.16 (s, 9H, $^2J_{Sn-H}$=53.3 Hz), 0.87 (s, 9H), 1.22 (br s, 1H), 1.31-1.39 (m, 2H), 1.44-1.51 (m, 2H), 2.22 (t, 2H, J=7.5 Hz, $^3J_{Sn-H}$=53.6 Hz), 3.58 (t, 2H, J=6.3 Hz), 4.07 (t, 2H, J=5.3 Hz), 6.18 (t, 1H, J=6.3 Hz, $^3J_{Sn-H}$=139 Hz); ^{13}C NMR (50.3 MHz) δ -8.0, -5.3, 18.3, 26.0, 26.4, 32.4, 40.1, 63.0, 64.4, 138.2, 149.5. Exact mass calcd. for $C_{15}H_{33}O_2Si^{120}Sn$ (M^+-Me): 393.1272. Found: 393.1268. Anal. calcd. for $C_{16}H_{36}O_2SiSn$: C 47.19, H 8.91. Found: C 47.46, H 8.92.

(Z, Z)-3,4-Bis-(4-*t*-butyldimethylsilyloxybutyl)-2,4-hexadiene-1,6-diol (43)

(a) By CuCl–Mediated Coupling of Compound 42

To a solution of **42** (64.5 mg, 0.158 mmol) in dry DMF (2 mL) at room temperature was added CuCl (43.6 mg. 0.440 mmol) and the resulting brown mixture was stirred for 1 hour. Aqueous NH_4Cl–NH_4OH (pH 8, 2 mL) was added and the mixture was stirred, open to the atmosphere, until the aqueous layer was bright blue. The layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed twice with water, dried ($MgSO_4$), and concentrated. The crude product was purified (flash chromatography, 5 g of silica gel, 1:1 to 1:4 petroleum ether-Et_2O) to provide 13 mg (34%) of **43** as a colourless oil that displayed IR (neat): 3324, 1646, 1472, 1256, 1104, 838 cm^{-1}; ^{1}H NMR (400 MHz) δ: 0.02 (s, 12H), 0.86 (s, 18H), 1.34-1.43 (m, 4H), 1.44-1.52 (m, 4H), 2.01-2.16 (m, 4H), 2.32 (br s, 2H), 3.55-

3.58 (m, 4H), 3.90 (d, 4H, J=7.4 Hz), 5.60 (t, 2H, J=7.6 Hz). Exact mass calcd. for $C_{26}H_{52}O_3Si_2$ (M^+-H_2O): 468.3455. Found: 468.3462. Anal. calcd. for $C_{26}H_{54}O_4Si_2$: C 64.14, H 11.18. Found: C 63.86, H 11.35.

*(b) By DIBAL Reduction of Compound **16***

To a cold (-78 °C), stirred solution of **16** (36 mg, 0.075 mmol) in 2 mL of dry THF was added a 1.0 M solution of DIBAL in hexanes (250 µL, 0.250 mmol). After 45 minutes, the reaction mixture was warmed to room temperature and stirred for an additional 45 minutes. Saturated aqueous NH_4Cl (0.5 mL) was added and the reaction mixture was stirred, open to the atmosphere, for 30 minutes. $MgSO_4$ (100 mg) was added and the mixture was stirred a further 30 minutes. The mixture was filtered through Florisil and the collected material was washed with Et_2O (60 mL). The filtrate was concentrated and the crude oil was purified by flash chromatography (5 g of silica gel, 1:3 petroleum ether-Et_2O) to afford 25 mg (68%) of **43** as a colourless oil that displayed spectral data identical to that described above.

Dimethyl (*E,Z,Z,E*)-5,6-Bis-(4-*t*-butyldimethylsilyloxybutyl)-2,4,6,8-nonatetraenedioate (25) from the Dialdehyde 16

To a stirred suspension of sodium hydride (13.5 mg, 0.563 mmol) in dry THF (2 mL) at 0 °C was added trimethyl phosphonoacetate (0.10 mL, 0.62 mmol). The mixture was stirred for 5 minutes, warmed to room temperature for 20 minutes, and then was recooled to 0 °C. A solution of **16** (58.4 mg, 0.121 mmol) in dry THF (1 mL) was added and the reaction mixture was stirred for 2 hours. Et_2O (30 mL) and water (30 mL) were added, the layers were separated, the aqueous layer was washed twice with Et_2O, and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. The crude oil was purified by flash chromatography (5 g of silica gel, 4:1 petroleum ether-Et_2O) to give 31 mg (86%) of **25** as a colourless oil that displayed spectral data identical with those described above.

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