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Stereocomplementary Syntheses of 1,ω-Distannylated *E*,*Z*-Isomeric Conjugated Trienes, Tetraenes, and Pentaenes

Jochen Burghart,[a] Achim Sorg,[b] and Reinhard Brückner*[c]

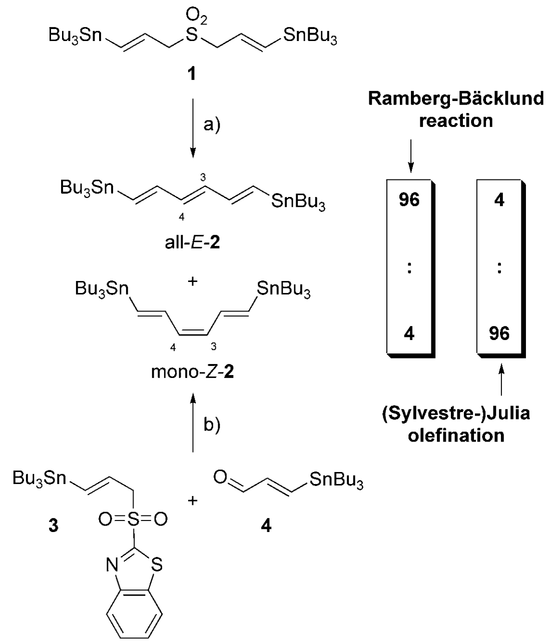
Abstract: Stereoselective syntheses of 1,6-bis(tributylstannyl)hexa-1,3,5-trienes, 1,8-bis(tributylstannyl)octa-1,3,5,7-tetraenes, and 1,10-bis(tributylstannyl)deca-1,3,5,7,9-pentaenes with various methylation patterns were achieved based on stereocomplementary C=C bond-forming reactions. All-*E* isomers resulted from Ramberg–Bäcklund rearrangements of distannylated diallyl-, allylpentadienyl-, or bis(pentadienyl)sulfones. Mono-*Z*-configured 1,ω-bis(tributylstannyl)-1,3,5-polyenes emerged from (Sylvestre–)Julia olefinations of Bu$_3$Sn-substituted enals or dienals with Bu$_3$Sn-substituted allyl or pentadienyl benzothiazolylsulfones. Related Ramberg–Bäcklund approaches provided all-*E*-1-bromo-6-(tributylstannyl)hexa-1,3,5-triene but not all-*E*-1-(tetramethyldioxaborolanyl)-6-(tributylstannyl)hexa-1,3,5-triene.

Keywords: olefination · polyenes · rearrangement · stannanes · stereoselectivity

Introduction

Transition-metal-catalyzed cross-coupling reactions have revolutionized the synthesis of styrenes, stilbenes, buta-1,3-dienes, and through-conjugated polyenes.[1] An important feature of such couplings is that they do not establish stereogenic C=C bonds but preserve them in the way that they were incorporated into the starting materials. This asset circumvents the need to exert stereocontrol during the C=C bond-forming step, which is a major advantage compared to the Wittig reaction and other C=C bond establishing strategies. Another virtue of transition-metal-catalyzed cross-coupling reactions is their tolerance toward a variety of functional groups, which is the more true the less nucleophilic the organometallic component. From the latter point of view, organotin compounds, which undergo Stille coupling,[2] are particularly worthwhile precursors of polyunsaturated structures.

The convergency of Stille coupling strategies increases when three components are involved and one is a 1,2-distannylated ethene, 1,4-distannylated buta-1,3-diene, or 1,ω-distannylated linear conjugated polyene. In spite of this conceptional advantage, such tandem Stille couplings have been reported only occasionally, that is, for *E*-1,2-bis(tributylstannyl)ethene a few times,[3,4] an isomeric mixture of 1,4-bis(trimethylstannyl)buta-1,3-dienes in two studies,[5] 1,6-bis(tributylstannyl)hexa-1,3,5-triene (all-*E*-**2**; Scheme 1) as an intermediate for syntheses of xerulinic acid[6–8] and xerulin,[8] 1,6-bis(tributylstannyl)hepta-1,3,5-triene (all-*E*-**9**; see Scheme 3)



Scheme 1. Stereoselective syntheses of 1,6-bis(tributylstannyl)-1,3,5-hexatriene isomers all-*E*- and mono-*Z*-**2**. a) CBr$_2$F$_2$ (4.0 equiv), KOH (30% on Al$_2$O$_3$, 20 equiv), THF, 0°C for 15 min to 25°C for 30 min (73%, all-*E*/mono-*Z*=96:4 mixture);[6,8] b) **3** (1.28 equiv), **4**, KHMDS (1.2 equiv), THF, −78°C→RT, overnight (66%, mono-*Z*/all-*E*=96:4 mixture).[7,8,19]

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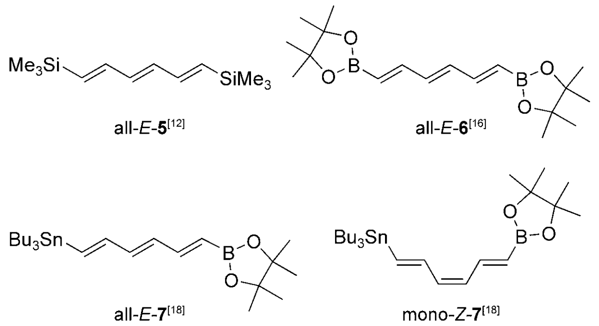
as an intermediate for pyrrhoxanthin,[9] and 1,10-bis(tributylstannyl)-1,3,5,7,9-decapentaene (mono-*Z*-**32**; see Scheme 11) as an intermediate for β-carotene.[10] The respective distannanes in the cited examples linked two different electrophiles either intramolecularly[3] or intermolecularly[4f,5a,6–9] or two equivalents of a single electrophile.[4a,b,d–f,5]

Of the 1,6-dimetalated-1,3,6-hexatrienes reported (Scheme 2),[11] the disilylated hexatriene all-*E*-**5**[12] was difunctionalized to give hexatrienes[13] or dodecahexaenes,[14] albeit not by cross-coupling.[15] The diboronylated hexatriene all-*E*-**6** did not react with 5-(bromomethylene)-(5*H*)-furan-2-one in the presence of [Pd(PPh$_3$)$_4$] in the only Suzuki coupling that we had tried.[16] In contrast, each of the Coleman tin- and boron-containing hexatrienes all-*E*-**7** and mono-*Z*-**7** underwent successive Stille and Suzuki coupling[17] cleanly.[18] We are unaware of the existence of vinylogues reagents, that is, any 1,8-dimetalo-1,3,5,7-tetraenes or 1,10-dimetalo-1,3,5,7,9-pentaenes.

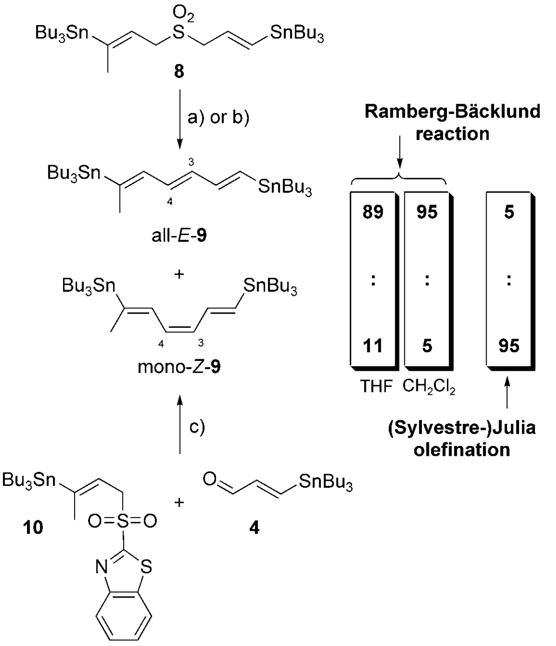


Scheme 2. 1,6-Dimetalo-1,3,5-hexatrienes other than **2**.

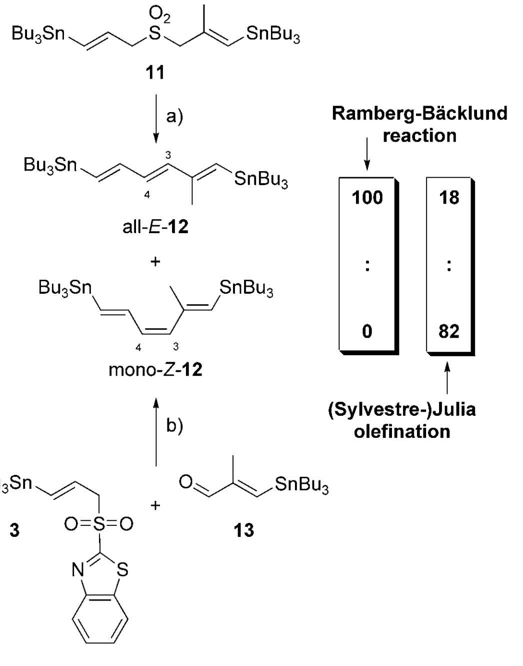
Results and Discussion

The scarcity of 1,ω-dimetalated polyenes in general and the success of previous syntheses[7,8,19] of 1,ω-distannylated polyenes specifically caused us to broaden our engagement in this area. As a result, we present a set of hitherto unknown all-*E*- or mono-*Z*-configured 1,6-bis(tributylstannyl)hexa-1,3,5-trienes, 1,6-bis(tributylstannyl)octa-1,3,5,7-tetraenes, and 1,10-bis(tributylstannyl)deca-1,3,5,7,9-pentaene. Our access routes are based on pertinent experience in this particular class of compound[6–8,19–21] with the stereocomplementarity of two key C=C bond-forming reactions: 1) the Ramberg–Bäcklund olefination[22] to *E*-selectively generate the C^3=C^4 bonds of trienes and tetraenes and the C^5=C^6 bond of pentaenes and 2) the (Sylvestre–)Julia olefination[23] to establish the same bonds with a *Z* configuration.

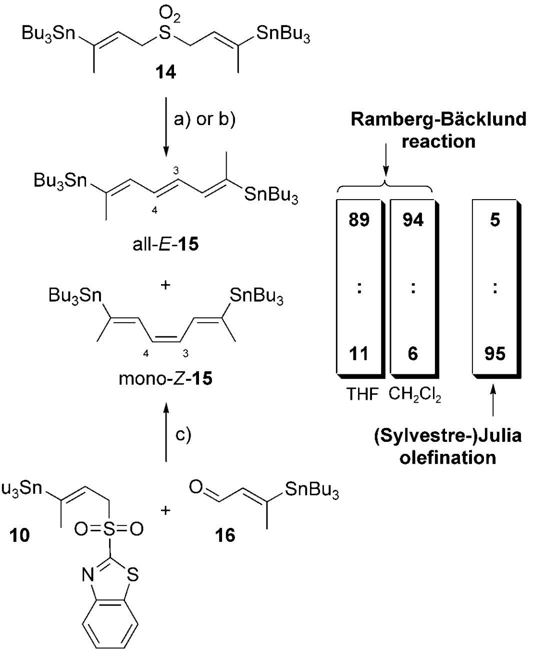
By applying a protocol to make tin-free conjugated trienes in one-pot sulfone bromination/Ramberg–Bäcklund reactions,[24] we treated the distannylated diallylsulfone **8**[9] (Scheme 3) and the similar compounds **11**, **14**, and **17** (Schemes 4–6, respectively) with CBr$_2$F$_2$ and KOH on Al$_2$O$_3$[25] between 0 °C and room temperature. Purification



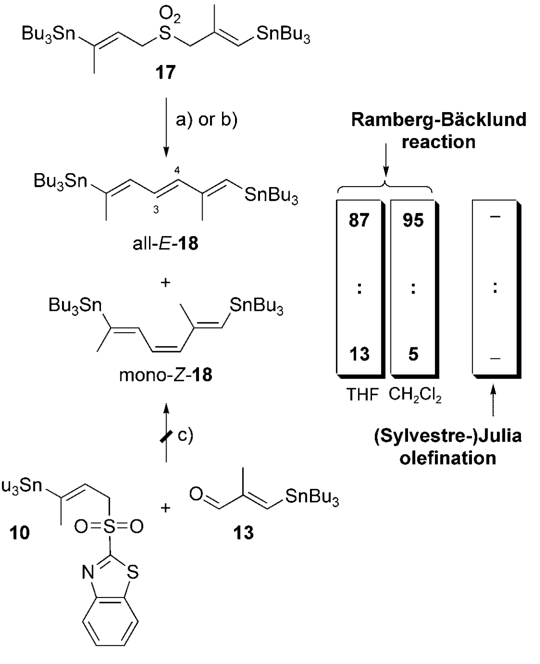
Scheme 3. Stereoselective syntheses of 1,6-bis(tributylstannyl)-1,3,5-heptatriene isomers all-*E*- and mono-*Z*-**9**. a) CBr$_2$F$_2$ (4.0 equiv), KOH (33 % on Al$_2$O$_3$, 10.0 equiv), THF, 0 °C for 15 min to 25 °C for 30 min (80 % of the all-*E*/mono-*Z* = 89:11 mixture). b) The conditions and reagents are the same as for (a), except the solvent is CH$_2$Cl$_2$; 82 % of a 95:5 mixture of **9** (78 %, all-*E*/mono-*Z* = 95:5 mixture) and 6-(tributylstannyl)hepta-1,3,5-triene (4 %, *E*,*E*/*E*,*Z* = 67:33 mixture). c) **10** (1.18 equiv), **4**, KHMDS (1.0 equiv), THF, −78 °C→RT, 12 h (56 %, mono-*Z*/all-*E* = 95:5 mixture).



Scheme 4. Stereoselective syntheses of 1,6-bis(tributylstannyl)-1,3,5-hexatriene isomers all-*E*- and mono-*Z*-**12**. a) CBr$_2$F$_2$ (4.0 equiv), KOH (33 % on Al$_2$O$_3$, 10.0 equiv), THF, 0 °C for 15 min, RT for 30 min (55 %, all-*E*/mono-*Z* = 100:0 mixture). b) **3** (1.2 equiv), **13**, KHMDS (1.2 equiv), THF, −78 °C→RT, 12 h (53 %, mono-*Z*/all-*E* = 82:18 mixture).



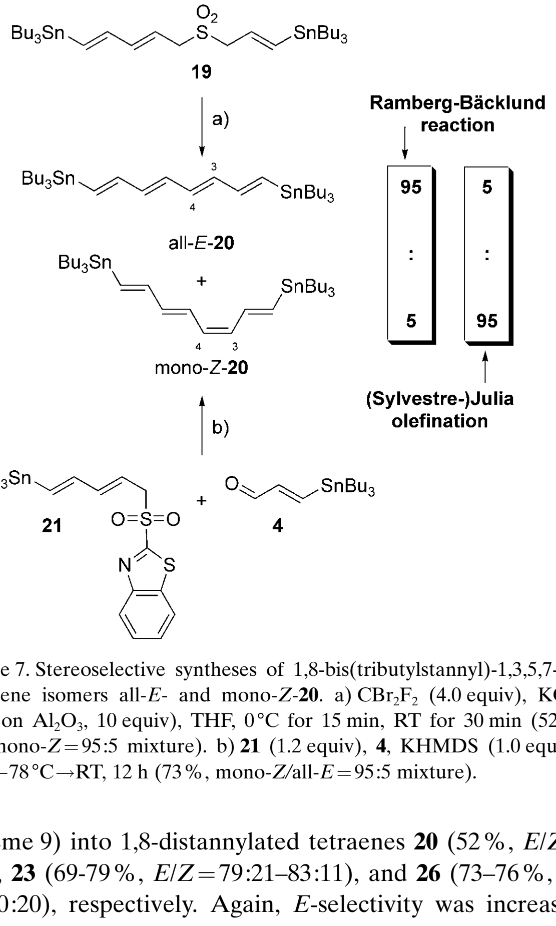
Scheme 5. Stereoselective syntheses of 2,7-bis(tributylstannyl)-2,4,6-octatriene isomers all-*E*- and mono-*Z*-**15**. a) CBr_2F_2 (4.0 equiv), KOH (30% on Al_2O_3, 4.0 equiv), THF, 0°C for 15 min, RT for 30 min (82%, all-*E*/mono-*Z* = 89:11 mixture). b) The same conditions and reagents as in (a) but with KOH (33% on Al_2O_3, 10.0 equiv) in CH_2Cl_2 (80%, all-*E*/mono-*Z* = 94:6 mixture). c) **10**, **16** (1.08 equiv), KHMDS (1.02 equiv), THF, −78°C→RT, 12 h (64%, mono-*Z*/all-*E* = 95:5 mixture).



Scheme 6. The approach toward 2,7-bis(tributylstannyl)-1,3,5-heptatrienes all-*E*- (successful) and mono-*Z*-**18** (failed). a) CBr_2F_2 (4.0 equiv), KOH (33% on Al_2O_3, 4.0 equiv), THF, 0°C for 15 min, RT for 30 min (75%, all-*E*/mono-*Z* = 87:13 mixture). b) The same conditions and reagents as (a) but with KOH (33% on Al_2O_3, 10.0 equiv) in CH_2Cl_2 [82%, 93.5:6.5 of **18** (77%, all-*E*/mono-*Z* = 95:5 mixture) and 2-methyl-6-(tributylstannyl)hepta-1,3,5-triene (5%; isomeric composition unknown)]. c) **10** (1.2 equiv), **13**, KHMDS (1.0 equiv), THF, −78°C→RT, 12 h (purification not possible as a result of decomposition on silica gel and on Al_2O_3).

by flash chromatography on silica gel[26] provided the distannylated trienes **9**[9] (80–82%), **12** (55%), **15** (80–82%), and **18** (75–77% yield; Schemes 3–6, respectively). These compounds were obtained as 87:13–100:0 mixtures of the all-*E* and mono-*Z* isomers. The preponderance of the former could be increased to 94:6–100:0 by conducting the Ramberg–Bäcklund reaction in CH_2Cl_2[24] rather than in THF. A drawback of employing CH_2Cl_2 was that up to 5% protodestannylation occurred at the less-hindered C−$SnBu_3$ bond of the desired product.

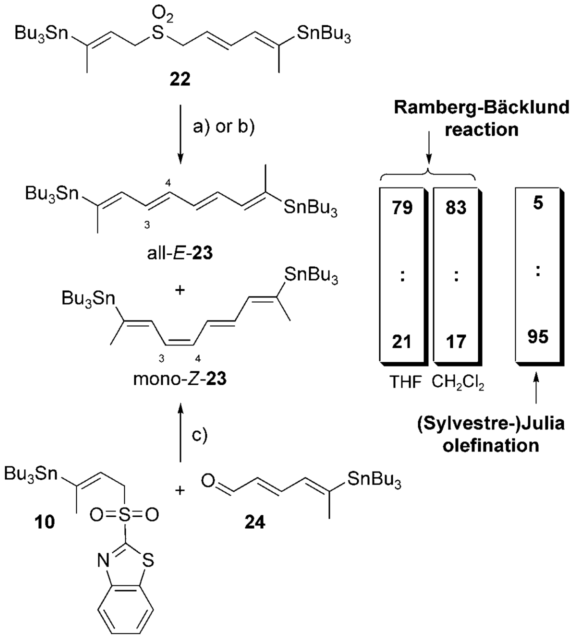
The same one-pot sulfone bromination/Ramberg–Bäcklund olefination procedure allowed the convertion of allyl pentadienylsulfones **19** (Scheme 7), **22** (Scheme 8), and **25** (Scheme 9) into 1,8-distannylated tetraenes **20** (52%, *E*/*Z* = 95:5), **23** (69-79%, *E*/*Z* = 79:21–83:11), and **26** (73–76%, *E*/*Z* = 80:20), respectively. Again, *E*-selectivity was increased by employing CH_2Cl_2 as the solvent rather than THF.



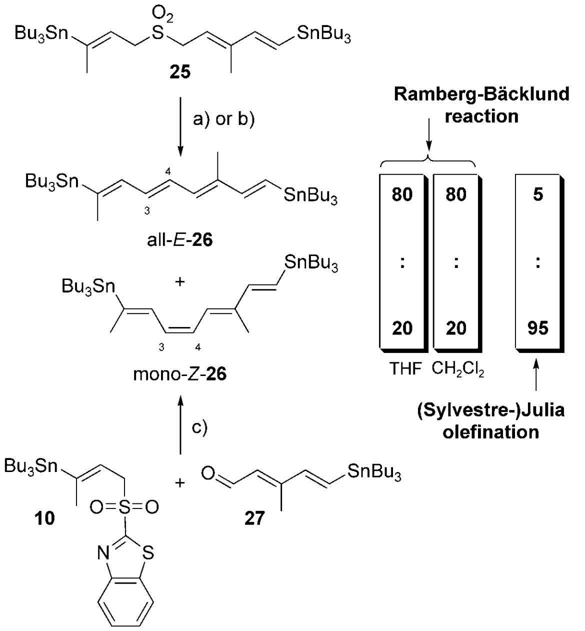
Scheme 7. Stereoselective syntheses of 1,8-bis(tributylstannyl)-1,3,5,7-octatetraene isomers all-*E*- and mono-*Z*-**20**. a) CBr_2F_2 (4.0 equiv), KOH (33% on Al_2O_3, 10 equiv), THF, 0°C for 15 min, RT for 30 min (52%, all-*E*/mono-*Z* = 95:5 mixture). b) **21** (1.2 equiv), **4**, KHMDS (1.0 equiv), THF, −78°C→RT, 12 h (73%, mono-*Z*/all-*E* = 95:5 mixture).

Before we became aware of the effect of CH_2Cl_2 increasing the selectivity, the previously used bromination/elimination procedure in THF proved suitable for transforming the distannylated bis(pentadienyl)sulfone **28** into an all-*E*/mono-*Z* mixture (92:8) of the linear distannylated pentaene **29** (45%; Scheme 10) and the analogous sulfone **31** into an all-*E*/mono-*Z* mixture (84:16) of the branched distannylated pentaene **32** (71%; Scheme 11).

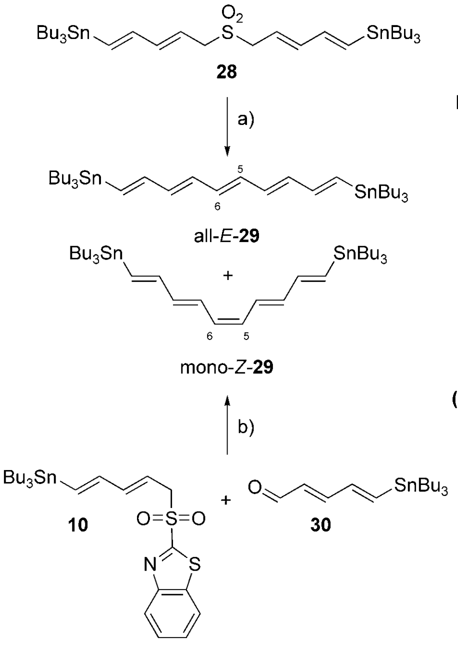
The newly prepared mono-*Z*-configured 1,6-distannylated triene **9** and its congeners **12** and **15** (Schemes 3–5, respectively) were obtained in the same manner as described[19] for core structure **2** (Scheme 1), that is, by using (Sylvestre–)



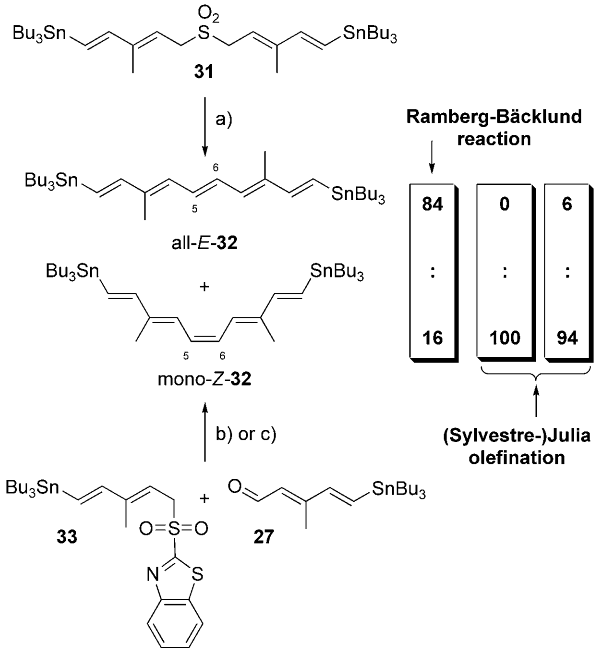
Scheme 8. Stereoselective syntheses of 2,9-bis(tributylstannyl)-2,4,6,8-decatetraene isomers all-*E*- and mono-*Z*-**23**. a) CBr$_2$F$_2$ (4.0 equiv), KOH (33 % on Al$_2$O$_3$, 10 equiv), THF, 0 °C for 15 min, RT for 30 min (69 %, all-*E*/mono-*Z* = 79:21 mixture). b) The same conditions and reagents as in (a) but in CH$_2$Cl$_2$ (79 %, mono-*Z*/all-*E* = 83:17 mixture). c) **10** (1.28 equiv), **24**, KHMDS (1.28 equiv), THF, −78 °C→RT, 12 h (64 %, mono-*Z*/all-*E* = 95:5 mixture).



Scheme 9. Stereoselective syntheses of 1,8-bis(tributylstannyl)-1,3,5,7-nonatetraene isomers all-*E*- and mono-*Z*-**26**. a) CBr$_2$F$_2$ (4.0 equiv), KOH (33 % on Al$_2$O$_3$, 10 equiv), THF, 0 °C for 15 min, RT for 30 min (73 %, all-*E*/mono-*Z* = 80:20 mixture). b) The same conditions and reagents as in (a) but with KOH (33 % on Al$_2$O$_3$, 10 equiv) in CH$_2$Cl$_2$ (76 %, all-*E*/mono-*Z* = 80:20 mixture). c) **10** (1.3 equiv), **27** (1.0 equiv), KHMDS (1.28 equiv), THF, −78 °C→RT, 12 h (73 %, mono-*Z*/all-*E* = 95:5 mixture).



Scheme 10. Stereoselective syntheses of 1,10-bis(tributylstannyl)-1,3,5,7,9-decapentaene isomers all-*E*- and mono-*Z*-**29**. a) CBr$_2$F$_2$ (4.0 equiv), KOH (33 % on Al$_2$O$_3$, 10 equiv), THF, 0 °C for 15 min, RT for 30 min (45 %, all-*E*/mono-*Z* = 92:8 mixture). b) **10** (1.2 equiv), **30**, KHMDS (1.05 equiv), THF, −78 °C→RT, 12 h (49 %, mono-*Z*/all-*E* = 95:5 mixture).



Scheme 11. Stereoselective syntheses of 1,10-bis(tributylstannyl)-1,3,5,7,9-decapentaene isomers all-*E*- and mono-*Z*-**32**. a) CBr$_2$F$_2$ (4.0 equiv), KOH (30 % on Al$_2$O$_3$, 10.0 equiv), THF, 0 °C for 15 min, 25 °C for 30 min (71 %, all-*E*/mono-*Z* = 84:16 mixture). b) **33** (1.3 equiv), NaHMDS (1.2 equiv), THF, −78 °C, 45 min;[10] **27**, THF, −78 °C→25 °C, 12 h (83 %, "high stereoselectivity" (assignment modified in accordance with refs [19 and 20]). c) **33** (1.12 equiv), **27**, KHMDS (1.12 equiv), THF, −78 °C→RT, 2 h [19] (63 %, mono-*Z*/all-*E* = 94:6 mixture).

Julia olefinations of appropriately stannylated/methylated α,β-unsaturated aldehydes with appropriately stannylated/methylated allyl(benzothiazolyl)sulfones and potassium hexamethyldisilazide (KHMDS) under Barbier conditions. Distannanes **9** (56 %, 95:5 mixture of the desired mono-*Z* and undesired all-*E* isomers), **12** (53 %; 82:18 mixture), and **15** [64 % (prone to decomposition on silica gel or Al_2O_3), 95:5 mixture] were obtained as expected.

The related 1,6-distannylated triene mono-*Z*-**18** was inaccessible by attempted (Sylvestre–)Julia syntheses either from aldehyde **13** and sulfone **10** (Scheme 6) or from aldehyde **16** and the matching sulfone **65** (formula in Table 5), at least as a pure compound. Nonetheless the ^{1}H NMR spectra of the respective crude products exhibited resonances that were surmised to belong to mono-*Z*-**18**; in this case, they would have accounted for about half of the material.

By contemplating (Sylvestre–)Julia syntheses of the 1,ω-distannylated tetraenes mono-*Z*-**20**, mono-*Z*-**23**, and mono-*Z*-**26** (Schemes 7–9, respectively), we had to join a reagent that contributes one C=C bond with a reagent that contributes two. For a given target molecule, this approach left us to decide which moiety should be incorporated into the benzothiazolylsulfone and which into the aldehyde. Nevertheless, we never studied both possibilities because our initial choices were satisfactory. In contrast, the C=C bonds, which had to be established *Z*-selectively in the teminating step of the (Sylvestre–)Julia syntheses of distannylated pentaenes mono-*Z*-**29** and mono-*Z*-**32** (Schemes 10 and 11, respectively) are symmetrically substituted. Thus, their benzothiazolylsulfone and the aldehyde precursors were chosen such that each of them contributes two C=C bonds to the target. The yields and corresponding *Z*/*E* ratios for the distannylated tetraenes were 73 % and *Z*/*E* = 95:5 for **20**, 64 % and *Z*/*E* = 95:5 for **23**, and 73 % and *Z*/*E* = 95:5 for **26** (Schemes 7–9, respectively). The yields and *Z*/*E* ratios for our access to distannylated pentaene **29** were 49 % and *Z*/*E* = 95:5 and to distannylated dimethylpentaene **32** were 63 % and *Z*/*E* = 94:6 (Scheme 10 and 11, respectively).

The configurations of the C^3=C^4 (or C^5=C^6) bonds, which were created in the syntheses of the distannylated trienes and tetraenes (or pentaenes) were deduced from the magnitude of the corresponding three-bond coupling constants $J_{3H,4H}$ and $J_{5H,6H}$, respectively (Table 1). For polyenes **9**, **12**, all-*E*-**18**, mono-*Z*-**20**, mono-*Z*-**23**, and **26**, which are unsymmetrical, these coupling constants emerged from first-order analyses of the hyperfine structure of the respective ^{1}H NMR peaks. For polyenes **2**,[8] **15**, and **32**, which are symmetrical, the $J_{3H,4H}$ and $J_{5H,6H}$ values were determined by the SELINCOR pulse sequence[27] and/or extracted from edited HSQC spectra ("^{1}H-coupled short-range H,C-COSY spectra").

In the unsymmetrical tetraenes all-*E*-**20** and all-*E*-**23**, at least one of the protons that couple across the newly formed C=C bond was part of a higher-order subspectrum, thus hindering us from extracting the $J_{3H,4H}$ values to prove the configuration from the SELINCOR or edited HSQC spectra. Furthermore, the standard ^{1}H NMR spectrum of pentaenes all-*E*-**29** and mono-*Z*-**29** did not reveal signal splitting due to the $J_{5H,6H}$ coupling because of their symmetry. Accordingly, the configurational assignment is solely based on analogy for these compounds.

Table 1. Vicinal H,H coupling constants across the newly formed C^3=C^4 or C^5=C^6 bonds of 1,ω-bis(tributylstannyl)polyenes (trienes and tetraene **23** in $CDCl_3$ and tetraenes **20** and **26** and pentaenes in [D_6]benzene).[a]

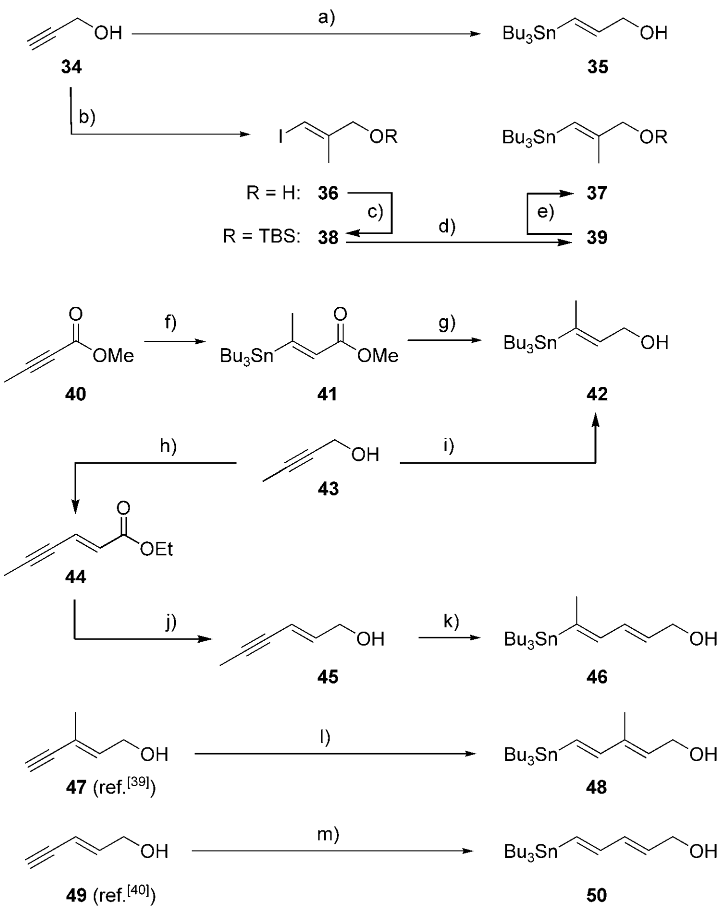
Polyene	all-*E* isomer	mono-*Z* isomer
	$J_{3\text{-H},4\text{-H}}$ [Hz]	
2	15.1[6,8]	10.1[8]
9	14.7	10.8
12	≈15	11.3
15	14.7	11.5
18	15.2	unknown due to signal overlap by the major isomer
20	unknown due to higher-order splitting	11.1
23	unknown due to higher-order splitting	10.9
26	14.3	11.3
	$J_{5\text{-H},6\text{-H}}$ [Hz]	
29	–	–
32	14.4[19]	11.2[19]

[a] The positional numbers of this compilation were chosen for ease of comparison; they may differ from the IUPAC numbering in the Experimental Section.

Synthesis of tin-containing alcohols: The building blocks for the Ramberg–Bäcklund rearrangements (i.e., allyl and pentadienyl thioacetates and bromides) and Sylvestre–Julia olefinations (i.e., conjugated aldehydes and allyl or pentadienylsulfones) were uniformly traced back to tributylstannylated allyl or pentadienyl alcohols (Scheme 12).[28–37] With the single exception of alcohol **37**, the latter originated from the *trans*-selective tributylstannylcupration[38] of alkynes with a terminal (i.e., **34**, **47**,[39] and **49**)[40] or an internal C≡C bond (i.e., **40**, **43**, and **45**). These stannylcuprations were efficient (71–86 % yield) and regioselective, except when starting from alkyne **43**, which delivered a separable 95:5 mixture of desired compound **42** and its regioisomer. No need for such a separation arose when **42** was prepared by the reduction of stannylated ester **41**, which stemmed from the regioselective stannylcupration of methyl tetrolate (**40**) and a subsequent reduction with diisobutylaluminum hydride (DIBAH).

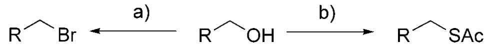
The attempted tributylstannylcupration of propargyl alcohol (**34**) followed by cuprate alkylation with MeI did not deliver stannylated alcohol **37** directly. Therefore, we gained **37** from **34** in a multistep sequence, that is, by using a [$ZrCp_2Cl_2$]-catalyzed (Cp = cyclopentadienyl) carboalumination followed by iodinolysis,[29] *tert*-butyldimethylsilylation,[30] iodine/lithium exchange with *t*BuLi followed by quenching with Bu_3SnCl,[30] and desilylation.[30]

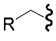
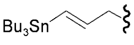
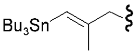
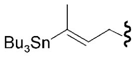
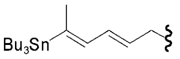
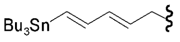
Synthesis of the Ramberg–Bäcklund sulfones: The stannylated alcohols **35**, **42**, and **50** were converted into the corresponding bromides **51**–**53** by Appel reactions with tetrabromomethane and triphenylphosphane (Table 2). After purification by flash chromatography on silica gel,[26] these com-



Scheme 12. Synthesis of Sn-containing allyl and pentadienyl alcohols. a) CuCN (1.2 equiv), *n*BuLi (2.4 equiv), THF, −78→25→−78 °C, $HSnBu_3$ (2.4 equiv), no addition of MeOH, **34**, −30 °C, 12 h [84 %;[9] ref. [28]: 52 % (as 65 % of a mixture isolated in 80 % yield)]. b) Me_3Al (3.0 equiv), $[ZrCp_2Cl_2]$ (0.25 equiv), **34**, CH_2Cl_2, 0→25 °C, 12 h; −30 °C, I_2 (1.5 equiv) in Et_2O (1.5 equiv), 30 min (53 %; ref. [29]: 60 %). c) TBSCl (1.1 equiv), NEt_3 (2.0 equiv), DMAP (2 mol %), CH_2Cl_2, 0→25 °C, 12 h (85 %; ref. [30]: 97 %). d) **38**, *t*BuLi (2.0 equiv), THF, −78 °C, 30 min; Bu_3SnCl (1.05 equiv), 25 °C, 30 min (67 %; (ref. [30]: 77 %). e) $Bu_4N^+F^-$ (1.0 equiv), THF, 0 °C, 1 h (75 %, (ref. [30]: 92 %). f) CuCN (1.3 equiv), *n*BuLi (2.6 equiv), THF, −78→25→−78 °C, $HSnBu_3$ (2.6 equiv), MeOH (1.5 equiv), **40**, 1 h (82 %;[9] ref. [31]: 100 %). g) DIBAH (2.3 equiv), CH_2Cl_2, −78 °C, 2 h (99 %;[9] ref. [32]: 98 %). h) MnO_2 (10.0 equiv), triethylphosphonoacetate (1.2 equiv), LiOH (2.0 equiv), THF, reflux, 2 days (53 %; ref. [33]: 72 %). i) CuCN (1.3 equiv), *n*BuLi (2.6 equiv), THF, −78→25→−78 °C, Bu_3SnH (2.6 equiv), MeOH (1.5 equiv), **43**, 1 h (79 % after separation from a 95:5 mixture with the regioisomer (ref. [28]: 71 %; ref. [34]: 82 %). j) DIBAH (2.3 equiv), CH_2Cl_2, −78 °C, 2 h (86 %).[35] k) CuCN (1.3 equiv), *n*BuLi (2.6 equiv), THF, −78→25→ −78 °C, $HSnBu_3$ (2.6 equiv), no addition of MeOH, **45**, −30 °C, 12 h (71 %; ref. [36]: 87 %). l) CuCN (1.5 equiv), *n*BuLi (3.0 equiv), THF, −78→25→ −78 °C, $HSnBu_3$ (3.0 equiv), no addition of MeOH, **47**, −30 °C, 12 h (86 %; ref. [28]: 92 %). m) CuCN (1.05 equiv), *n*BuLi (2.0 equiv), THF, −78→25→−78 °C, $HSnBu_3$ (2.0 equiv), no addition of MeOH, **49**, −30 °C, 12 h (77 %; ref. [37]: 78 %). Cp = cyclopentadienyl, DIBAH = diisobutylaluminium hydride, DMAP = 4-(dimethylamino)pyridine, TBSCl = *tert*-butyldimethylsilyl chloride.

Table 2. Syntheses[a] of the bromide and thioacetate precursors of the sulfides and sulfones shown in Tables 3 and 4.

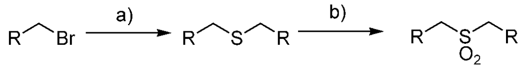


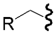
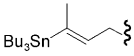
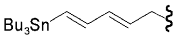
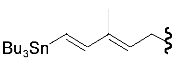
	Alcohol	Bromide	Yield [%]	Thioacetate	Yield [%]
	**35**	**51**	88;[9] refs [6,8]: 82	**54**[b]	89
	**37**	(not searched after)		**55**	82
	**42**	**52**	74	**56**[9]	85
	**46**	(not searched after)		**57**	74
	**50**	**53**[41]	70	**58**	73

[a] Reagents and conditions: a) CBr_4 (1.2 equiv), PPh_3 (1.2 equiv), CH_2Cl_2, 0 °C, 3 h; b) HSAc (1.5 equiv), PPh_3 (1.5 equiv), DIAD (1.5 equiv), THF, 25 °C, 12 h. [b] This compound is shown for coherence; it was needed for the synthesis shown in Scheme 13. DIAD = diisopropyl azodicarboxylate.

pounds were obtained in 70–88 % yield. Stannylated alcohols **37**, **46**, and **48** seemed to react analogously, as indicated by ^{1}H NMR spectroscopic analyses of the respective crude products. However, the respective bromides were prone to isomerization and protodestannylation during purification by flash chromatography, no matter whether silica gel or alumina was the adsorbent. Still, the bromide derived from alcohol **48** could be used without isolation to make sulfones **31** and **25** (Tables 3 and 4, respectively).

Table 3. Syntheses[a] of the symmetric Ramberg–Bäcklund sulfones.



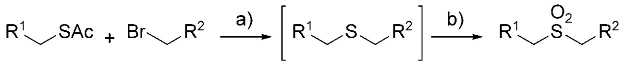
	Bromide	Sulfide	Yield [%]	Sulfone	Yield [%]
	**52**	**59**	91	**14**	87
	**53** (generated from alcohol **50** in situ)	[b]		**28**	19[c]
	(generated from alcohol **48** in situ)	[b]		**31**	16[d]

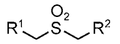
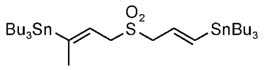
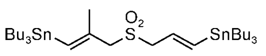
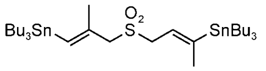
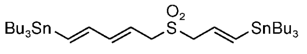
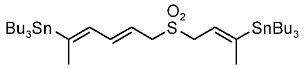
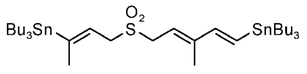
[a] Reagents and conditions: a) $Na_2S{\cdot}9H_2O$ (1.00 equiv), $NH_4^+HSO_4^-$ (1 mol %), THF, H_2O, 25 °C, 24 h; b) H_2O_2 (5–9 equiv), $[Mo_7(NH_4)_6O_{24}]$ (0.20 equiv), EtOH, 0 °C, 2 h. [b] Partial decomposition during column chromatography either on silica gel or Al_2O_3. [c] Yield over the three steps from alcohol **50**. [d] Yield over the three steps from alcohol **48**.

Under Mitsunobu conditions [i.e., diisopropyl azodicarboxylate (DIAD), triphenylphosphane, and thioacetic acid], stannylated alcohols **35**, **37**, **42**, **46**, and **50** furnished the corresponding thioacetates **54**–**58** in 73–89 % yield (Table 2). They could be purified without interfering isomerization reactions.

Bisstannylated symmetric sulfones **14**, **28**, and **31** were obtained after combining two equivalents of the respective

Table 4. Syntheses[a] of the unsymmetric Ramberg–Bäcklund sulfones.



Thioacetate	Bromide		Sulfone	Yield [%]
56	**51**		**8**[9]	62[b]
55	**51**		**11**	41
55	**52**		**17**[c]	48
58	**51**		**19**[c]	59
57	**52**		**22**[c]	57
56	(from alcohol **48** in situ)		**25**	36[d]

[a] Reagents and conditions: a) thioacetate (1.10 equiv), KOH (4.0 equiv), MeOH, 0 °C, 10 min; bromide (1.00 equiv), 2 h, 25 °C; isolation of crude product. b) H_2O_2 (5–9 equiv), $[Mo_7(NH_4)_6O_{24}]$ (0.20 equiv), EtOH, 0 °C, 2 h. [b] Yield of **56**+**51**→sulfide: 87 %;[9] yield of oxidation sulfide→sulfone: 71 %.[9] [c] Partial decomposition during column chromatography either on silica gel or Al_2O_3. [d] Yield over the three steps from alcohol **48**.

bromide with one equivalent of Na_2S in S_N2 reactions catalyzed by 1 mol % $Bu_4N^+HSO_4^-$ (Table 3).[42] The resulting sulfides were oxidized after isolation (i.e., **59**) or as crude products by employing hydrogen peroxide and peroxomolybdate catalysis,[43] thus providing the desired Ramberg–Bäcklund sulfones that were isomerically pure albeit in widely differing yields (16–88 %).

Table 4 shows that we made bisstannylated unsymmetric sulfones **8**,[9] **11**, **17**, **19**, and **25** accessible from thioacetates **55**–**58** in 36–62 % overall yields by KOH-mediated methanolysis, alkylation of the resulting thiolate in situ with the appropriate allyl or pentadienyl bromide, and Mo^{VI}-catalyzed oxidation with hydrogen peroxide.[43]

Synthesis of (Sylvestre–)Julia aldehydes and sulfones: The preparation of stannylated allyl or pentadienyl benzothiazolylsulfones for (Sylvestre–)Julia olefinations relied on a previously used methodology[19] (Table 5). Five of the alcohols were converted into stannylated allyl or pentadienyl benzothiazolyl sulfides **60**–**64** by using Mukaiyama redox condensation reactions with DIAD, triphenylphosphane, and benzothiazolthiol (84–98 % yield). Subsequent oxidation reactions with peroxomolybdate(VI)[43] regenerated in situ furnished the mentioned sulfones in 63–90 % yield.

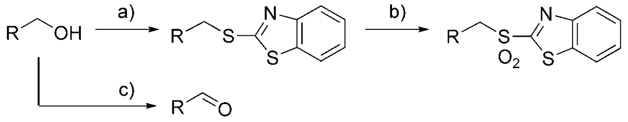
Finally, the alcohols shown in Table 5 were oxidized with MnO_2, thus providing the stannylated aldehydes depicted therein in 73–88 % yield.

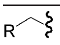
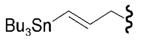
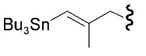
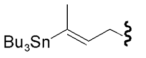
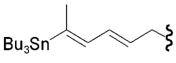
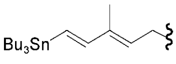
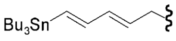
Conclusion and Perspectives

We have synthesized a family of 1,ω-bis(tributylstannylated) conjugated trienes, tetraenes, and pentaenes stereoselectively. Their central C=C bond was established by Ramberg–Bäcklund rearrangements in THF with moderate-to-good *E* selectivities or by (Sylvestre–)Julia olefinations with very good *Z* selectivities (usually $Z/E \geq 95{:}5$). The *E* selectivities were improved by up to 6 % in CH_2Cl_2 versus THF, albeit at the cost of up to 5 % protonolysis of the less-hindered $C(sp^2)-SnBu_3$ bond. Linear polyenes formed most selectively, for example, with $E/Z = 96{:}4$ in the case of hexatriene **32**.

The 1,6-distannylated trienes, 1,8-distannylated tetraenes, and 1,10-distannylated pentaenes, which became accessible through using the mentioned key reactions, merit interest as bifunctional reagents for three-component Stille coupling reactions. Such a usage had already been demonstrated for trienes all-*E*-**2**,[6,7,8] mono-*Z*-**2**,[46] and all-*E*-**9**[9] and for pentaene all-*E*-**32**.[10] By taking into account the variability of the methylation pattern with which we actually could endow or with which one should be able to endow this class of reagent, a manifold of applications in the stereoselective synthesis of extended polyenes is conceivable. In this regard, it is noteworthy that the side chains of hexatriene all-*E*-**18** on the one hand and hexatriene all-*E*-**15**, tetraene all-*E*-**26**, and

Table 5. Synthesis[a] of the (Sylvestre–)Julia olefination substrates.

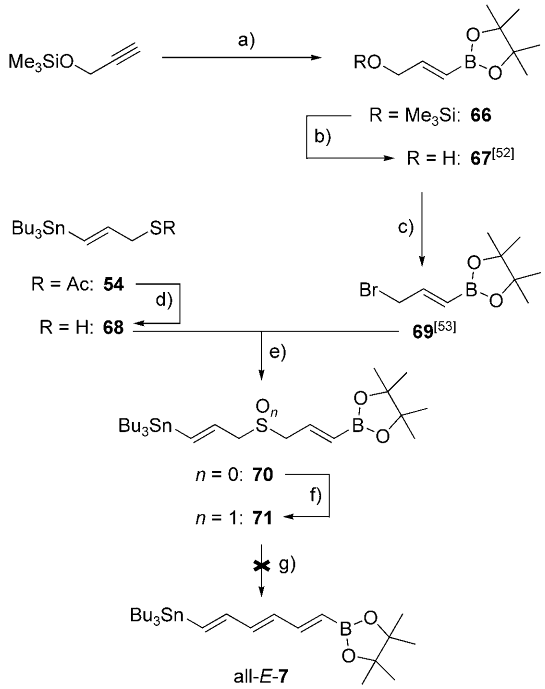


	Alcohol	Sulfide	Yield [%]	Sulfone	Yield [%]	Aldehyde	Yield [%]
	**35**	**60**	96[8]	**3**	83[8]	**4**	88; ref. [32]: 98
	**37**	**61**[b]	≤84	**65**[c]	65	**13**	84
	**42**	**62**	98[19]	**10**	90[19]	**16**	87; ref. [32]: 100
	**46**	not searched after		not searched after		**24**	73
	**48**	**63**	95;[19] ref. [10]: 93	**33**	68; ref. [19]: 48; ref. [10]: 61	**27**[44]	78; ref. [45]: 96
	**50**	**64**	95	**21**	63	**34**	86; ref. [45]: 70

[a] Reagents and conditions: a) benzo-1,3-thiazol-2-thiol (1.05 equiv), PPh_3 (1.10 equiv), DIAD (1.09 equiv), THF, 0 °C, 1–2 h. b) H_2O_2 (10.0 equiv), $[Mo_7(NH_4)_6O_{24}]$ (0.2 equiv), EtOH, 0 °C→RT, 2 h. c) MnO_2 (20.0 equiv), CH_2Cl_2, RT, 4–12 h. [b] This compound contained a contaminant, which was not identified. [c] This compound is mentioned in the discussion of Scheme 6, but is not depicted elsewhere.

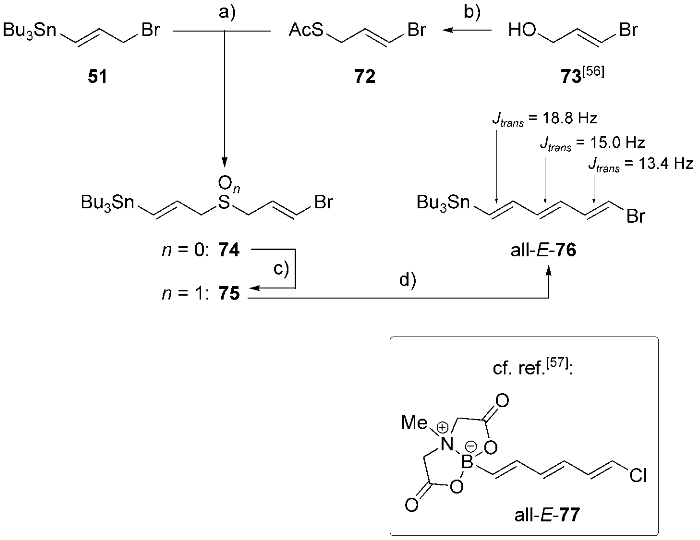
pentaene all-*E*-**32** on the other hand are interspersed exactly as widely as in head-to-tail and head-to-head linked isoprene units, respectively. This property makes compound **18** a potential building block for retinoids and compounds **18**, **15**, **26**, and **32** potential building blocks for carotenoids.[47] Moreover, distannylated tetraene all-*E*-**23** displays methyl substituents precisely at the unusual distance encountered in the core of the C_{37} carotenoids peridinin[48] and pyrrhoxanthin,[49] synthetic studies of which represent another focus of research in our group.[9,50]

Last but not least, we tested the scope and limitations of our Ramberg–Bäcklund route to all-*E*-configured 1,ω-dimetalopolyenes also with the goal of making the Coleman 1-(pinacolboryl)-6-(tributylstannyl)hexatriene all-*E*-**7**[18] and the hitherto unknown 1-bromo-6-(tributylstannyl)hexatriene all-*E*-**76** (Schemes 13 and 14, respectively). By relying on the stannylated allyl thioacetate **54** mentioned above and on an improved access via silylether **66**[52] (and its desilylation with $Bu_4N^+F^-$ rather than with citric acid as previously described)[52] to the known[53] borylated allyl bromide **69**,[54] we obtained the B/Sn-containing diallyl sulfide **70** (Scheme 13). Oxidation to the corresponding diallylsulfone **71** succeeded with Montmorillonite-supported oxone as an oxidant.[55] However, we failed to brominate and contract this material into the desired triene all-*E*-**7** under the previously established conditions and a few variations thereof.



Scheme 13. Attempted synthesis of the Coleman[18] tin- and boron-containing triene all-*E*-**7**. a) Prereaction between $[ZrCp_2Cl_2]$ (10 mol %) and $LiEt_3BH$ (10 mol %) in the absence of light;[51] THF, 0 °C, 2 h; addition to the silyl ether (1.0 equiv), pinacolborane (1.05 equiv), NEt_3 (10 mol %), 60 °C, 16 h (61 %). b) $Bu_4N^+F^-$ (1.0 equiv), THF, 0 °C→RT, 2 h (75 %). c) CBr_4 (1.2 equiv), PPh_3 (1.2 equiv), CH_2Cl_2, 0 °C, 3 h (50 %). d) KOH (5.0 equiv), MeOH, 0 °C, 2 h (89 %). e) **68**, THF, −78 °C, *t*BuLi (1.0 equiv), 30 min; **69** (1.0 equiv), −78 °C→RT (82 %). f) Oxone ($KHSO_5{\cdot}KHSO_4{\cdot}2K_2SO_4$; 2.5 equiv) on Montmorillonite,[55] CH_2Cl_2, RT, 2 h [91 % of crude product (spectroscopically essentially pure)]. g) CBr_2F_2 (4.0 equiv), KOH (30 % on Al_2O_3, 10.0 equiv), absence or presence of pinacol (3.0 equiv), THF, 0 °C→RT, 30 min.

Conversely, the stannylated allyl bromide **51** mentioned above and the unprecedented bromoallyl thioacetate **72** were linked by treatment with potassium methoxide to give Br/Sn-containing diallyl sulfide **74** (94 %; Scheme 14). Oxidation to the corresponding diallylsulfone **75** was effected by hydrogen peroxide with Mo^{VI} catalysis[43] (91 %). Under the previously established Ramberg–Bäcklund conditions, this compound rendered 61 % of 1-bromo-6-(tributylstannyl)hexatriene all-*E*-**76** as an 88:12 mixture of all-*E* and mono-*Z* isomers. Whether this compound undergoes a Stille coupling reaction with anything other than itself needs to be studied. Our “amphiphilic” triene all-*E*-**76** has an analogous design to triene all-*E*-**77**, which underwent a Suzuki cross-coupling reaction with a dienylboronic acid in instead of oligomerization through homo-coupling.[57]



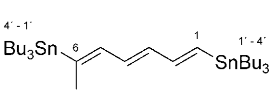
Scheme 14. Synthesis of a tin- and bromine-containing triene. a) KOH (5.0 equiv) in MeOH, **72** (1.1 equiv), 0 °C, 5 min; **51** (1.0 equiv), 1 h (91 %). b) AcSH (1.14 equiv), PPh_3 (1.2 equiv), diethyl azodicarboxylate (1.2 equiv), THF, 0 °C, 1 h (94 %). c) H_2O_2 (9.0 equiv), $[Mo_7(NH_4)_6O_{24}]$ (0.20 equiv), EtOH, 0 °C, 1 h (91 %). d) CBr_2F_2 (5.0 equiv), KOH (33 % on Al_2O_3, 10.0 equiv), THF, 0 °C→RT, 30 min (61 %, all-*E*-**76**/mono-*Z*-**76** = 88:12 mixture).

Experimental Section

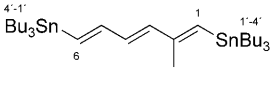
General: The reactions were performed under N_2 in glassware dried with a heatgun under vacuum. The products were purified by flash chromatography[26] on silica gel or deactivated alumina (filling height, column diameter, and eluent are given in parantheses; which fractions contained the isolated product are indicated as "fractions xx-yy") on Merck silica gel 60 (0.040–0.063 mm). The yields refer to analytically and/or spectroscopically pure samples. ^{1}H NMR spectra were obtained in $CDCl_3$ (δ_{CHCl_3} = 7.26 ppm) or in C_6D_6 ($\delta_{C_6D_5H}$ = 7.15 ppm) on Varian Mercury VX 300, Bruker AM 400, and Bruker DRX 500 spectrometers. The integrals agree with the given assignments. The coupling constants are given in Hertz (Hz). ^{13}C NMR spectra were obtained in $CDCl_3$ and C_6D_6 (δ = 77.10 and 128.62, respectively) on Bruker AM 400 and Bruker DRX 500 spectrometers. The assignments of ^{1}H and ^{13}C NMR spectroscopic resonances refer to the IUPAC nomenclature, except within substituents (where primed numbers are used). Heteronuclear couplings: the ratio between the coupling constants $^{n}J_{^{1}H,^{119}Sn}$ and $^{n}J_{^{1}H,^{117}Sn}$ across n interspersed bonds must equal the quotient of the gyromagnetic ratios of ^{119}Sn (-9.9708×10^{7} rad T^{-1} s^{-1})[58] and ^{117}Sn (-9.5301×10^{7} rad T^{-1} s^{-1}),[58] that is, 1.046. The same is true for the ratio between the coupling constants $^{n}J_{^{13}C,^{119}Sn}$ and $^{n}J_{^{13}C,^{117}Sn}$. In alkenylstannanes, the limits of the spectral resolution and occurrence of line splitting through H,H coupling allowed the determination of ^{1}H,Sn and ^{13}C,Sn coupling constants for ^{119}Sn and ^{117}Sn separately only for large J values; small J values are usually isotope-averaged.[59] The mass-spectrometric analysis was carried out by Dr. J. Wörth and C. Warth (Institut für Organische Chemie and Biochemie, Universität Freiburg). Combustion analyses were carried out by E. Hickl (Institut für Organische Chemie and Biochemie, Universität Freiburg). The IR spectra were obtained on a Perkin–Elmer Paragon 1000 spectrometer.

Syntheses of all-*E*-polyene distannanes:

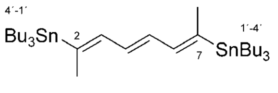
General procedure for Ramberg–Bäcklund polyene syntheses: CBr_2F_2 (4.0 equiv) was added to a solution (ca. 0.05 M) of the bisallylsulfone in THF or CH_2Cl_2 followed by KOH (33 % on Al_2O_3, 10.0 equiv) as one portion at 0 °C. After 15 min at 0 °C and 30 min at room temperature, the mixture was diluted with pentane. Filtration through a pad of celite and evaporation of the solvent under reduced pressure was followed by purification by chromatography on neutral alumina (deactivated by 3 % H_2O).



(1*E*,3*E*,5*E*)-1,6-Bis(tributylstannyl)hepta-1,3,5-triene (all-*E*-9): By following the general procedure, all-*E*-**9** was prepared in THF from bisallylsulfone **8** (368 mg, 0.498 mmol), CBr_2F_2 (184 µL, 418 mg, 2.0 mmol, 4.0 equiv), and KOH on Al_2O_3 (850 mg, 4.98 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 50:1 (v/v), fractions 3 and 4), all-*E*-**9** was obtained as a yellowish oil (263 mg, 80 %, all-*E*/mono-*Z* = 89:11). By following the general procedure, all-*E*-**9** was also prepared in CH_2Cl_2 from bisallylsulfone **8** (250 mg, 0.338 mmol), CBr_2F_2 (127 µL, 283.3 mg, 1.350 mmol), and KOH on Al_2O_3 (190 mg, 3.98 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 50:1 (v/v), fractions 3 and 4), the product was obtained in 82 % yield as an 95:5 mixture of all-*E*-**9** (177.2 mg, 78 %, 95:5 all-*E*/mono-*Z*) and 6-(tributylstannyl)hepta-1,3,5-triene (5.1 mg, 4 %; *E*,*E*/*E*,*Z* = 67:33) as a colorless oil. ^{1}H NMR (499.9 MHz, $CDCl_3$/TMS): δ = 0.88 (t, $J_{4',3'}$ = 7.1 Hz, 18 H; 6 × 4′-H_3), 0.89 (m$_c$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{1'\text{-}H,^{117}Sn} \approx {}^{2}J_{1'\text{-}H,^{119}Sn} \approx 50$ Hz, 12 H; 6 × 1′-H_2), 1.29 (qt, $J_{3',4'} = J_{3',2'}$ = 7.3 Hz, 12 H; 6 × 3′-H_2), 1.43–1.54 (m, 12 H; 6 × 2′-H_2), 2.02 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{7\text{-}H,^{117}Sn} \approx {}^{3}J_{7\text{-}H,^{119}Sn} \approx 46$ Hz, 3 H; 7-H^3), 6.16 (dd, $J_{3,4}$ = 14.5, $J_{3,2}$ = 10.4 Hz, 1 H; 3-H), 6.22 (d, $J_{5,4}$ = 10.7 Hz, 1 H; 5-H), 6.28 (d, $J_{1,2}$ = 18.6 Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^{2}J_{1\text{-}H,^{117}Sn}$ = 59.9, $^{2}J_{1\text{-}H,^{119}Sn}$ = 60.5 Hz, 1 H; 1-H), 6.55 (dd, $J_{4.3}$ = 14.8, $J_{4,5}$ = 11.0 Hz, 1 H; 4-H), 6.62 ppm (dd, $J_{2,1}$ = 18.6, $J_{2,3}$ = 10.1 Hz, 1 H; 2-H); ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 9.14 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{C\text{-}1',^{117}Sn}$ = 315.9, $^{1}J_{C\text{-}1',^{119}Sn}$ = 331.0 Hz; 3 × C-1′), 9.52 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{C\text{-}1',^{117}Sn}J$ = 328.8, $^{1}J_{C\text{-}1',^{119}Sn}$ = 343.9 Hz; 3 × C-1′), 13.89 (6 × C-4′), 20.17 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{C\text{-}7,^{117}Sn} \approx {}^{2}J_{C\text{-}7,^{119}Sn} \approx 38$ Hz; C-7), 27.18 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{C\text{-}3',^{117}Sn} \approx {}^{3}J_{C\text{-}3',^{119}Sn} \approx 55$ Hz; 3 × C-3′), 27.51 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{C\text{-}3',^{117}Sn} \approx {}^{3}J_{C\text{-}3',^{119}Sn} \approx 56$ Hz; 3 × C-3′), 29.18 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{C\text{-}2',^{117}Sn} \approx {}^{2}J_{C\text{-}2',^{119}Sn} \approx 20$ Hz; 3 × C-2′), 29.21 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{C\text{-}2',^{117}Sn} \approx {}^{2}J_{C\text{-}2',^{119}Sn} \approx 19$ Hz; 3 × C-2′), 126.19 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{C\text{-}4,^{117}Sn} \approx {}^{3}J_{C\text{-}4,^{119}Sn} \approx 62$ Hz; C-4), 134.62 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{C\text{-}3,^{117}Sn} \approx {}^{3}J_{C\text{-}3,^{119}Sn} \approx 74$ Hz; C-3), 134.76 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{C\text{-}1,^{117}Sn}$ = 364.3, $^{1}J_{C\text{-}1,^{119}Sn}$ = 381.5 Hz; C-1), 138.99 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{C\text{-}5,^{117}Sn} \approx {}^{2}J_{C\text{-}5,^{119}Sn} \approx 30$ Hz; C-5), 146.18 (C-6), 147.33 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{C\text{-}2,^{117}Sn} \approx {}^{2}J_{C\text{-}2,^{119}Sn} \approx 8$ Hz; C-2); IR (film): $\tilde{\nu}$ = 2955, 2925, 2875, 2855, 1465, 1420, 1375, 1340, 1290, 1250, 1180, 1150, 1070, 995, 960, 945, 875, 860, 750, 695, 660, 595 cm^{-1}; HRMS (CI, 120 eV): calcd for $C_{27}H_{53}Sn_2$: 617.21912 [$M-$Bu]; found: 617.22020 (+1.8 ppm).



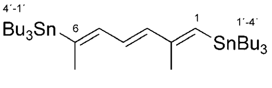
(1*E*,3*E*,5*E*)-2-Methyl-1,6-bis(tributylstannyl)hexa-1,3,5-triene (all-*E*-12): Following the general procedure, all-*E*-**12** was prepared in THF from bisallylsulfone **11** (188 mg, 0.255 mmol), CBr_2F_2 (96.0 µL, 214 mg, 1.02 mmol, 4.0 equiv), and KOH on Al_2O_3 (143 mg, 2.55 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 2 and 3), all-*E*-**12** was obtained as a colorless oil (94.2 mg, 55 %, all-*E*/mono-*Z* = 100:0). ^{1}H NMR (400.1 MHz, $CDCl_3$/$CHCl_3$): δ = 0.926 (t, $J_{4',3'}$ = 7.3 Hz, 9 H; 3 × 4′-H_3), 0.929 (t, $J_{4',3'}$ = 7.3 Hz, 9 H; 3 × 4′-H_3), 1.01 (m$_c$, 6 H; 3 × 1′-H_2), 1.02 (m$_c$, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^{2}J_{1'\text{-}H,^{117}Sn}$ = 49.3, $^{2}J_{1'\text{-}H,^{119}Sn}$ = 51.3 Hz, 6 H; 3 × 1′-H_2), 1.37 (qt, $J_{3',4'} = J_{3',2'}$ = 7.3 Hz, 6 H; 3 × 3′-H_2), 1.38 (qt, $J_{3',4'} = J_{3',2'}$ = 7.3 Hz, 6 H; 3 × 3′-H_2), 1.54–1.71 (m, 12 H; 6 × 2′-H_2), 1.96 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^{4}J_{2\text{-}Me,^{117}Sn} \approx {}^{4}J_{2\text{-}Me,^{119}Sn} \approx 9$ Hz, 3 H; 2-CH_3), 6.17 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{1\text{-}H,^{117}Sn} \approx {}^{2}J_{1\text{-}H,^{119}Sn} \approx 67$ Hz, 1 H; 1-H), 6.31 (dd, $J_{4,3}$ = 15.7, $J_{4,5}$ = 9.8 Hz, 1 H; 4-H), 6.46 (d, $J_{3,4}$ = 14.5 Hz, 1 H; 3-H), 6.46 (d, $J_{6.5}$ = 18.9 Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{6\text{-}H,^{117}Sn} \approx {}^{2}J_{6\text{-}H,^{119}Sn} \approx 72$ Hz, 1 H; 6-H), 6.86 ppm (dd, $J_{5.6}$ = 18.6, $J_{5.4}$ = 9.8 Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{5\text{-}H,^{117}Sn}$ = 59.1, $^{3}J_{5\text{-}H,^{119}Sn}$ = 62.8 Hz; 5-H); ^{13}C NMR (100.6 MHz, $CDCl_3$/$CDCl_3$): δ = 9.89 (3 × C-1′), 10.59 (3 × C-1′), 13.90 (3 × C-4′), 13.91 (3 × C-4′), 20.96 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{2\text{-}Me,^{117}Sn} \approx {}^{3}J_{2\text{-}Me,^{119}Sn} \approx 33$ Hz; 2-CH_3), 27.69 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{C\text{-}3',^{117}Sn} \approx {}^{3}J_{C\text{-}3',^{119}Sn} \approx 52$ Hz; 3 × C-3′), 27.70 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{C\text{-}3',^{117}Sn} \approx {}^{3}J_{C\text{-}3',^{119}Sn} \approx 55$ Hz; 3 × C-3′), 29.58 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{C\text{-}2',^{117}Sn} \approx {}^{2}J_{C\text{-}2',^{119}Sn} \approx 21$ Hz; 3 × C-2′), 29.66 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{C\text{-}2',^{117}Sn} \approx {}^{2}J_{C\text{-}2',^{119}Sn} \approx 20$ Hz; 3 × C-2′), 130.99 (C-4), 134.52 (C-6), 134.75 (C-1), 137.78 (C-3), 148.20 (C-5), 151.33 ppm (C-2); IR (film): $\tilde{\nu}$ = 2955, 2925, 2875, 2845, 1690, 1600, 1570, 1460, 1440, 1415, 1375, 1340, 1290, 1250, 1180, 1145, 1070, 1025, 1000, 960, 875, 810, 690, 675 cm^{-1}; no HRMS spectrum was obtained because the compound did not stand up to the ionization conditions.



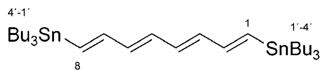
(2*E*,4*E*,6*E*)-2,7-Bis(tributylstannyl)octa-2,4,6-triene (all-*E*-15): Following the general procedure, all-*E*-**15** was prepared in THF from bisallylsulfone **14** (232.0 mg, 0.308 mmol), CBr_2F_2 (0.12 mL, 0.27 g, 1.3 mmol, 4.2 equiv), and KOH on Al_2O_3 (1080 mg, 6.66 mmol, 17.5 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2.5 cm, cyclohexane/NEt_3 100:1 (v/v), fractions 3 and 4), all-*E*-**15** was obtained as a yellowish oil (174.3 mg, 82 %, all-*E*/mono-*Z* = 89:11). This compound was also prepared in CH_2Cl_2 from bisallylsulfone **14** (300 mg, 0.399 mmol), CBr_2F_2 (150 µL, 336 mg, 1.60 mmol, 4.0 equiv), and KOH on Al_2O_3 (223 mg, 3.99 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 3 and 4), all-*E*-**15** was obtained as a yellowish oil (220 mg, 80 %, all-*E*/mono-*Z* = 94:6). ^{1}H NMR (499.9 MHz, C_6D_6/C_6D_5H): δ = 1.07 (t, $J_{4',3'}$ = 7.2 Hz, 18H; 6 × 4′-H_3), 1.14 (m$_c$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{1'\text{-}H,^{117}Sn} \approx {}^{2}J_{1'\text{-}H,^{119}Sn} \approx 52$ Hz, 12 H; 6 × 1′-H_2), 1.52 (qt,

$J_{3',4'} = J_{3',2'} = 7.4$ Hz, 12H; 6 × 3′-H$_2$), 1.70–1.82 (m, 12H; 6 × 2′-H$_2$), 2.08 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{1-H},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{8-H},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{1-H},{}^{119}\text{Sn}} \approx {}^{3}J_{\text{8-H},{}^{119}\text{Sn}} \approx 45$ Hz, 6H; 1-H$_3$ and 8-H$_3$), 6.30 (d, $J_{3,4} = J_{6,5} = 10.0$ Hz, 2H; 3-H and 6-H), 6.55 ppm (d, $J_{4,3} = J_{5,6} = 10.4$ Hz, 2H; 4-H and 5-H); ^{13}C NMR (125.7 MHz, CDCl$_3$/CDCl$_3$): $\delta = 9.20$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',{}^{119}\text{Sn}} = {}^{1}J_{\text{C-1}'',{}^{119}\text{Sn}} = 330.6$ Hz; $^{1}J_{\text{C-1}',{}^{117}\text{Sn}} = {}^{1}J_{\text{C-1}'',{}^{117}\text{Sn}} = 315.5$ Hz; 6 × C-1′), 13.70 (6 × C-4′), 20.02 (C-1, C-8), 27.38 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{C-3}',{}^{117}\text{Sn}} \approx {}^{3}J_{\text{C-3}'',{}^{117}\text{Sn}} \approx {}^{3}J_{\text{C-3}',{}^{119}\text{Sn}} \approx {}^{3}J_{\text{C-3}'',{}^{119}\text{Sn}} \approx 55$ Hz; 6 × C-3′), 29.17 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}'',{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',{}^{119}\text{Sn}} \approx {}^{2}J_{\text{C-2}'',{}^{119}\text{Sn}} \approx 21$ Hz; 6 × C-2′), 126.33 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{C-4},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{C-5},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{C-4},{}^{119}\text{Sn}} \approx {}^{3}J_{\text{C-5},{}^{119}\text{Sn}} \approx 66$ Hz; C-4, C-5), 139.58 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-3},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-6},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-3},{}^{119}\text{Sn}} \approx {}^{2}J_{\text{C-6},{}^{119}\text{Sn}} \approx 30$ Hz; C-3, C-6), 144.98 ppm (C-2, C-7; the *E* configuration of the $C^4{=}C^5$ double bond was shown by an edited HSQC spectrum (499.9/125.7 MHz, CDCl$_3$) in which the ^{13}C NMR resonance $\delta = 126.33$ ppm (C-4, C-5) was split by the coupling $^{1}J_{\text{C-4,4-H}} = {}^{1}J_{\text{C-5,5-H}} = 151.8$ Hz, such that both the low- and the highfield branch revealed splitting due to $J_{4,3} = J_{5,6} = 11.2$ and $J_{4,5} = 14.7$ Hz); IR (film): $\tilde{\nu} = 2955$, 2925, 2870, 2855, 1465, 1375, 1070, 960, 940, 875, 840, 770 cm^{-1}; HRMS (EI, 70 eV): calcd for $C_{28}H_{55}Sn_2$: 631.23477 [M^+−Bu]; found: 631.23169 (−4.9 ppm).

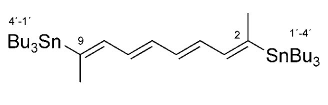
(1*E*,3*E*,5*E*)-2-Methyl-1,6-bis(tributylstannyl)hepta-1,3,5-triene (all-*E*-18): Following the general procedure, all-*E*-**18** was prepared in THF from bisallylsulfone **17** (217 mg, 0.288 mmol), CBr$_2$F$_2$ (110 µL, 250 mg, 1.15 mmol, 4.0 equiv), and KOH on Al$_2$O$_3$ (490 mg, 2.88 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al$_2$O$_3$ (5×2 cm, cyclohexane/NEt$_3$ 98:2 (v/v), fractions 3 and 4), all-*E*-**18** was obtained as a yellowish oil (148 mg, 75 %, all-*E*/mono-*Z* = 87:13). Following the general procedure, all-*E*-**18** was also prepared in CH$_2$Cl$_2$ from bisallylsulfone **17** (200 mg, 0.266 mmol), CBr$_2$F$_2$ (100 µL, 222 mg, 1.06 mmol, 4.0 equiv), and KOH on Al$_2$O$_3$ (150 mg, 2.66 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al$_2$O$_3$ (5×2 cm, cyclohexane/NEt$_3$ 98:2 (v/v), fractions 3 and 4), we obtained a 93.5:6.5 mixture of **18** (148 mg, 77 %, all-*E*/mono-*Z* = 95:5) and 2-methyl-6-(tributylstannyl)hepta-1,3,5-triene (5 %; isomeric composition unknown) as a colorless oil. ^{1}H NMR (400.1 MHz, C$_6$D$_6$/C$_6$D$_5$H): $\delta = 0.93$ (t, $J_{4',3'} = 7.3$ Hz, 18H; 6 × 4′-H$_3$), 1.02 (m$_c$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1}'\text{-H},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{1}'\text{-H},{}^{119}\text{Sn}} \approx 51$ Hz, 6H; 3 × 1′-H$_2$), superimposed by 1.02 (m$_c$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1}'\text{-H},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{1}'\text{-H},{}^{119}\text{Sn}} \approx 50$ Hz, 6H; 3 × 1′-H$_2$), 1.38 (qt, $J_{3',4'} = J_{3',2'} = 7.3$ Hz, 12H; 6 × 3′-H$_2$), 1.51–1.72 (m, 12H; 6 × 2′-H$_2$), 2.02 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^{4}J_{\text{2-Me},{}^{117}\text{Sn}} \approx {}^{4}J_{\text{2-Me},{}^{119}\text{Sn}} \approx 9$ Hz, 1H; 2-CH$_3$), 2.11 (incompletely resolved q, $^{4}J_{7,5} = 1.4$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{7-H},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{7-H},{}^{119}\text{Sn}} \approx 47$ Hz, 3H; 7-H$_3$), 6.17 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1-H},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{1-H},{}^{119}\text{Sn}} \approx 66$ Hz, 1H; 1-H), 6.51 (d, $J_{3,4} = 15.3$ Hz, 1H; 3-H), 6.58 (d, $J_{5,4} = 10.6$ Hz, 1H; 5-H), 6.73 ppm (dd, $J_{4.3} = 15.0$, $J_{4,5} = 10.6$ Hz, 1H; 4-H); ^{13}C NMR (100.6 MHz, C$_6$D$_6$/C$_6$D$_6$): $\delta = 9.55$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',{}^{117}\text{Sn}} = 314.6$, $^{1}J_{\text{C-1}',{}^{119}\text{Sn}} = 329.1$ Hz; 3 × C-1′), 10.61 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',{}^{117}\text{Sn}} = 325.7$, $^{1}J_{\text{C-1}',{}^{119}\text{Sn}} = 341.1$ Hz; 3 × C-1′), 13.91 (6 × C-4′), 20.21 (3 × C-1), 21.01 (3 × 2-CH$_3$), 27.71 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3}',{}^{117}\text{Sn}} = 53.6$, $^{3}J_{\text{C-3}',{}^{119}\text{Sn}} = 56.0$ Hz; 3 × C-3′), 27.78 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3}',{}^{117}\text{Sn}} = 52.6$, $^{3}J_{\text{C-3}',{}^{119}\text{Sn}} = 55.0$ Hz; 3 × C-3′), 29.62 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',{}^{119}\text{Sn}} \approx 20$ Hz; 3 × C-2′), 29.68 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',{}^{119}\text{Sn}} \approx 20$ Hz; 3 × C-2′), 122.38 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{C-4},{}^{117}\text{Sn}} \approx 63.3$, $^{3}J_{\text{C-4},{}^{119}\text{Sn}} \approx 67$ Hz; C-4), 134.06 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1},{}^{117}\text{Sn}} = 385.6$, $^{1}J_{\text{C-1},{}^{119}\text{Sn}} = 406.3$ Hz; C-1), 138.11 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3},{}^{117}\text{Sn}} = 69.3$, $^{3}J_{\text{C-3},{}^{119}\text{Sn}} = 72.9$ Hz; C-3), 140.58 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-5},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-5},{}^{119}\text{Sn}} \approx 31$ Hz; C-5), 144.28 (C-6), 151.72 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2},{}^{119}\text{Sn}} \approx 7$ Hz; C-2); IR (film): $\tilde{\nu} = 2960$, 2925, 2870, 2850, 1650, 1635, 1580, 1460, 1415, 1375, 1155, 1075, 1020, 960, 875, 860, 790, 685, 660, 590 cm^{-1}; HRMS (CI, 120 eV): calcd for $C_{28}H_{55}Sn_2$: 631.23477 [M^+−Bu]; found: 631.23340 (−2.2 ppm).



(1*E*,3*E*,5*E*,7*E*)-1,8-Bis(tributylstannyl)octa-1,3,5,7-tetraene (all-*E*-20): Following the general procedure, all-*E*-**20** was prepared in THF from bisallylsulfone **19** (199 mg, 0.265 mmol), CBr$_2$F$_2$ (132 µL, 287 mg, 1.33 mmol, 5.0 equiv), and KOH on Al$_2$O$_3$ (225 mg, 1.33 mmol, 5.0 equiv). After flash chromatography[26] on deactivated Al$_2$O$_3$ (5×2 cm, cyclohexane/NEt$_3$ 98:2 (v/v), fractions 3 and 4), all-*E*-**20** was obtained as a yellowish oil (95.1 mg, 52 %, all-*E*/mono-*Z* = 95:5). ^{1}H NMR (499.9 MHz, C$_6$D$_6$/C$_6$D$_5$H): $\delta = 0.93$ (t, $J_{4',3'} = 7.3$ Hz, 18H; 6 × 4′-H$_3$), 1.03 (m$_c$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1}'\text{-H},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{1}'\text{-H},{}^{119}\text{Sn}} \approx 53$ Hz, 12H; 6 × 1′-H$_2$), 1.37 (qt, $J_{3',4'} = J_{3',2'} = 7.4$ Hz, 12H; 6 × 3′-H$_2$), 1.52–1.69 (m, 12H; 6 × 2′-H$_2$), 6.19–6.25 (m$_c$, 2H, 4-H and 5-H), 6.26–6.36 (m$_c$, 2H, 3-H and 6-H), 6.43 (d, $J_{1,2} = J_{8,7} = 18.8$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1-H},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{8-H},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{1-H},{}^{119}\text{Sn}} \approx {}^{2}J_{\text{8-H},{}^{119}\text{Sn}} \approx 70$ Hz, 2H; 1-H and 8-H), 6.81 ppm (dd, $J_{2,1} = J_{7,8} = 18.7$, $J_{2,3} = J_{7,6} = 9.8$ Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{2-H},{}^{117}\text{Sn}} = {}^{3}J_{\text{7-H},{}^{117}\text{Sn}} = 57.8$, $^{3}J_{\text{2-H},{}^{119}\text{Sn}} = {}^{3}J_{\text{7-H},{}^{119}\text{Sn}} = 59.7$ Hz, 2H; 2-H and 7-H); ^{13}C NMR (125.7 MHz, C$_6$D$_6$/C$_6$D$_6$): $\delta = 9.88$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',{}^{117}\text{Sn}} = 328.2$, $^{1}J_{\text{C-1}',{}^{119}\text{Sn}} = 343.6$ Hz; 6 × C-1′), 13.90 (6 × C-4′), 27.69 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3}',{}^{117}\text{Sn}} = 53.0$, $^{3}J_{\text{C-3}',{}^{119}\text{Sn}} = 55.1$ Hz; 6 × C-3′), 29.56 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',{}^{119}\text{Sn}} \approx 20.6$ Hz; 6 × C-2′), 132.52 (C-4, C-5), 135.00 (C-1, C-8, flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1},{}^{117}\text{Sn}} = {}^{1}J_{\text{C-8},{}^{117}\text{Sn}} = 368.5$, $^{1}J_{\text{C-1},{}^{119}\text{Sn}} = {}^{1}J_{\text{C-8},{}^{119}\text{Sn}} = 385.7$ Hz), 136.75 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-7},{}^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2},{}^{119}\text{Sn}} \approx {}^{2}J_{\text{C-7},{}^{119}\text{Sn}} \approx 9$ Hz; C-2, C-7), 147.72 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{C-3},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{C-6},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{C-3},{}^{119}\text{Sn}} \approx {}^{3}J_{\text{C-6},{}^{119}\text{Sn}} \approx 59$ Hz; C-3, C-6); IR (film): $\tilde{\nu} = 2960$, 2925, 2850, 2880, 1605, 1530, 1465, 1415, 1380, 1340, 1295, 1245, 1180, 1155, 1075, 1045, 1005, 955, 870, 865, 670 cm^{-1}; HRMS (Cl, 120 eV): calcd for $C_{28}H_{53}Sn_2$: 629.21912 [M^+−Bu]; found: 629.22022 (+1.7 ppm).

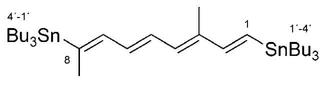


(2*E*,4*E*,6*E*,8*E*)-2,9-Bis(tributylstannyl)deca-2,4,6,8-tetraene (all-*E*-23): Following the general procedure, all-*E*-**23** was prepared in THF from bisallylsulfone **22** (250 mg, 0.321 mmol), CBr$_2$F$_2$ (123 µL, 270 mg, 1.29 mmol, 4.0 equiv), and KOH on Al$_2$O$_3$ (180 mg, 3.20 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al$_2$O$_3$ (5×2 cm, cyclohexane/NEt$_3$ 98:2 (v/v), fractions 3 and 4), all-*E*-**23** was obtained as a yellowish oil (157 mg, 69 %, all-*E*/mono-*Z* = 79:21). Following the general procedure, all-*E*-**23** was also prepared in CH$_2$Cl$_2$ from bisallylsulfone **22** (350 mg, 0.450 mmol), CBr$_2$F$_2$ (170 µL, 377 mg, 1.8 mmol, 4.0 equiv), and KOH on Al$_2$O$_3$ (252 mg, 4.50 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al$_2$O$_3$ (5×2 cm, cyclohexane/NEt$_3$ 98:2 (v/v), fractions 3 and 4), all-*E*-**23** was obtained as a colorless oil (254 mg, 79 %, all-*E*/mono-*Z* = 83:17). ^{1}H NMR (400.1 MHz, CDCl$_3$, TMS): $\delta = 0.89$ (t, $J_{4',3'} = 7.3$ Hz, 18H; 6 × 4′-H$_3$), 0.91 (m$_c$, 12H; 6 × 1′-H$_2$), 1.31 (qt, $J_{3',4'} = J_{3',2'} = 7.3$ Hz, 12H; 6 × 3′-H$_2$), 1.44–1.58 (m, 12H; 6 × 2′-H$_2$), 2.02 (d, $^{4}J_{1,3} = {}^{4}J_{10,8} = 1.5$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{1-H},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{10-H},{}^{117}\text{Sn}} \approx {}^{3}J_{\text{1-H},{}^{119}\text{Sn}} \approx {}^{3}J_{\text{10-H},{}^{119}\text{Sn}} \approx 47$ Hz, 6H; 1-H$_3$ and 10-H$_3$), 6.26 (m$_c$, 2H, 5-H and 6-H), 6.26 (d, $J_{3,4} = J_{8,7} = 12.0$ Hz, each peak flanked by Sn isotope satellites as 2 in-

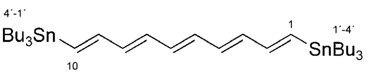


terwoven doublets, $^{3}J_{\text{3-H},^{117}\text{Sn}} = {}^{3}J_{\text{8-H},^{117}\text{Sn}} = 63.4$, $^{3}J_{\text{3-H},^{119}\text{Sn}} = {}^{3}J_{\text{8-H},^{119}\text{Sn}} = 66.7$ Hz, 2H; 3-H and 8-H), 6.60 ppm (m_c, 2H, 4-H and 7-H); ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS): $\delta = 9.32$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',^{117}\text{Sn}} = 316.3$, $^{1}J_{\text{C-1}',^{119}\text{Sn}} = 330.5$ Hz; 6 × C-1′), 13.80 (6 × C-4′), 20.16 (C-1, C-10), 27.49 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3}',^{117}\text{Sn}} = 53.1$, $^{3}J_{\text{C-3}',^{119}\text{Sn}} = 55.8$ Hz; 6 × C-3′), 29.26 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',^{119}\text{Sn}} \approx 20$ Hz; 6 × C-2′), 127.39 (C-4, C-7), 132.59 (C-5, C-6), 139.49 (C-3, C-8), 145.43 ppm (C-2, C-9); IR (film): $\tilde{\nu} = 3025$, 2955, 2925, 2875, 2850, 1460, 1415, 1375, 1340, 1295, 1180, 1070, 1000, 980, 955, 945, 875, 865, 680, 665, 595 cm^{-1}; HRMS (Cl, 120 eV): calcd for $C_{30}H_{57}Sn_2$: 714.32085 [$M^+ -$Bu]; found: 714.32120 (+0.5 ppm).

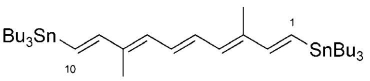
(1*E*,3*E*,5*E*,7*E*)-3-Methyl-1,8-bis(tributylstannyl)nona-1,3,5,7-tetraene (all-*E*-26): Following the general procedure, all-*E*-**26** was prepared in THF from bisallylsulfone **25** (276 mg, 0.354 mmol), CBr_2F_2 (131 µL, 297 mg, 1.41 mmol, 4.0 equiv), and KOH on Al_2O_3 (736 mg, 3.54 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 3–5), all-*E*-**26** was obtained as a yellowish oil (184 mg, 73 %, all-*E*/mono-*Z* = 80:20). Following the general procedure, all-*E*-**26** was also prepared in CH_2Cl_2 from bisallylsulfone **25** (200 mg, 0.257 mmol), CBr_2F_2 (97.0 µL, 216 mg, 1.03 mmol, 4.0 equiv), and KOH on Al_2O_3 (144 mg, 2.57 mmol, 10.0 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 3–5), all-*E*-**26** was obtained as a yellowish oil (159 mg, 76 %, all-*E*/mono-*Z* = 80:20). ^{1}H NMR (400.6 MHz, C_6D_6/C_6D_5H): $\delta = 1.05$ (t, $J_{4',3'} = 7.3$ Hz, 9H; 3 × 4′-H_3), 1.06 (t, $J_{4',3'} = 7.3$ Hz, 9H; 3 × 4′-H_3), 1.14 (m_c, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1}'\text{-H},^{117}\text{Sn}} \approx {}^{2}J_{\text{1}'\text{-H},^{119}\text{Sn}} \approx 50$ Hz, 6H; 3 × 1′-H_2), 1.17 (m_c, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1}'\text{-H},^{117}\text{Sn}} \approx {}^{2}J_{\text{1}'\text{-H},^{119}\text{Sn}} \approx 49$ Hz, 6H; 3 × 1′-H_2), 1.50 (qt, $J_{3',4'} = J_{3',2'} = 7.3$ Hz, 6H; 3 × 3′-H_2), 1.52 (qt, $J_{3',4'} = J_{3',2'} = 7.3$ Hz, 6H; 3 × 3′-H_2), 1.66–1.84 (m, 12H; 6 × 2′-H_2), 1.95 (s, 1H, 3-CH_3), 2.21 (incompletely resolved q, $^{4}J_{9,7} = 1.4$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{9-H},^{117}\text{Sn}} \approx {}^{3}J_{\text{9-H},^{119}\text{Sn}} \approx 47$ Hz, 3H; 9-H_3), 6.42 (d, $J_{4,5} = 10.9$ Hz, 1H; 4-H), 6.58 (d, $J_{1,2} = 19.2$ Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^{2}J_{\text{1-H},^{117}\text{Sn}} = 68.0$, $^{2}J_{\text{1-H},^{119}\text{Sn}} = 70.5$ Hz, 1H; 1-H), 6.76 (incompletely resolved qd, $J_{7,6} = 10.7$, $^{4}J_{7,9} = 1.6$ Hz, 1H; 7-H), 6.79 (dd, $J_{5,6}$, $J_{5,4} = 11.1$ Hz, 1H; 5-H), 6.90 (dd, $J_{6,5} = 14.1$, $J_{6,7} = 11.1$ Hz, 1H; 5-H), 7.05 ppm (d, $J_{2,1} = 19.2$ Hz, 1H; 2-H); ^{13}C NMR (100.6 MHz, C_6D_6/C_6D_6): $\delta = 9.60$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',^{117}\text{Sn}} = 314.8$, $^{1}J_{\text{C-1}',^{119}\text{Sn}} = 329.3$ Hz; 3 × C-1′), 9.96 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',^{117}\text{Sn}} = 326.4$, $^{1}J_{\text{C-1}',^{119}\text{Sn}} = 342.1$ Hz; 3 × C-1′), 12.26 (3-CH_3), 13.95 (3 × C-4′), 13.96 (3 × C-4′), 20.35 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-9},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-9},^{119}\text{Sn}} \approx 39$ Hz; C-9), 27.77 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3}',^{117}\text{Sn}} = 52.9$, $^{3}J_{\text{C-3}',^{119}\text{Sn}} = 55.0$ Hz; 3 × C-3′), 27.83 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3}',^{117}\text{Sn}} = 52.9$, $^{3}J_{\text{C-3}',^{119}\text{Sn}} = 55.3$ Hz; 3 × C-3′), 29.64 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',^{119}\text{Sn}} \approx 20.0$ Hz; 3 × C-2′), 29.66 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',^{119}\text{Sn}} \approx 20$ Hz; 3 × C-2′), 128.12 (C-1), 128.76 (C-6), 129.31 (flanked by Sn isotope satellites as an incompletely resolved d, $^{4}J_{\text{C-5},^{117}\text{Sn}} \approx {}^{4}J_{\text{C-5},^{119}\text{Sn}} \approx 7$ Hz; C-5), 132.57 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{4}J_{\text{C-4},^{117}\text{Sn}} = 6.0$, $^{4}J_{\text{C-4},^{119}\text{Sn}} = 8.0$ Hz; C-4), 137.20 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3},^{117}\text{Sn}} = 65.9$, $^{3}J_{\text{C-3},^{119}\text{Sn}} = 68.6$ Hz; C-3), 140.67 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-7},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-7},^{119}\text{Sn}} \approx 30$ Hz; C-7), 145.08 (C-8), 151.67 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2},^{119}\text{Sn}} \approx 11$ Hz; C-2); IR (film): $\tilde{\nu} = 2960$, 2925, 2885, 2850, 1460, 1415, 1380, 1075, 1045, 1020, 1005, 980, 965, 945, 875, 860, 765, 680, 66, 590 cm^{-1}; HRMS (Cl, 120 eV): calcd for $C_{30}H_{57}Sn_2$: 657.25042 [$M^+ -$Bu]; found: 657.25000 (−0.6 ppm).



(1*E*,3*E*,5*E*,7*E*,9*E*)-1,10-Bis(tributylstannyl)deca-1,3,5,7,9-pentaene (all-*E*-29): Following the general procedure, all-*E*-**29** was prepared in THF from bisallylsulfone **28** (400 mg, 0.515 mmol), CBr_2F_2 (238 µL, 540 mg, 2.58 mmol, 4.0 equiv), and KOH on Al_2O_3 (438 mg, 2.58 mmol, 4.0 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 3–5), all-*E*-**29** was obtained as a yellow oil (165.4 mg, 45 %, all-*E*/mono-*Z* = 92:8). ^{1}H NMR (499.9 MHz, C_6D_6/C_6D_5H): $\delta = 1.07$ (t, $J_{4',3'} = 7.2$ Hz, 18H; 6 × 4′-H_3), 1.14 (m_c, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1}'\text{-H},^{117}\text{Sn}} \approx {}^{2}J_{\text{1}'\text{-H},^{119}\text{Sn}} \approx 52$ Hz, 12H; 6 × 1′-H_2), 1.52 (qt, $J_{3',4'} = J_{3',2'} = 7.4$ Hz, 12H; 6 × 3′-H_2), 1.70–1.82 (m, 12H, 6 × 2′-H_2), 6.28–6.51 (m_c, 6H, 3-H/8-H, 4-H/7-H, 5-H/6-H), 6.59 (d, $J_{1,2} = J_{10,9} = 18.6$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1-H},^{117}\text{Sn}} \approx {}^{2}J_{\text{10-H},^{117}\text{Sn}} \approx {}^{2}J_{\text{1-H},^{119}\text{Sn}} \approx {}^{2}J_{\text{10-H},^{119}\text{Sn}} \approx 70$ Hz, 2H; 1-H, 10-H), 6.96 ppm (dd, $J_{2,1} = J_{9,10} = 18.6$, $J_{2,3} = J_{9,8} = 9.7$ Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{2-H},^{117}\text{Sn}} = {}^{3}J_{\text{9-H},^{117}\text{Sn}} = 57.2$, $^{3}J_{\text{2-H},^{119}\text{Sn}} = {}^{3}J_{\text{9-H},^{119}\text{Sn}} = 59.4$ Hz, 2H; 2-H, 9-H); ^{13}C NMR (125.7 MHz, C_6D_6/C_6D_6): $\delta = 9.89$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',^{117}\text{Sn}} = 327.7$, $^{1}J_{\text{C-1}',^{119}\text{Sn}} = 343.9$ Hz; 6 × C-1′), 13.92 (6 × C-4′), 27.70 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{C-3}',^{117}\text{Sn}} \approx {}^{3}J_{\text{C-3}',^{119}\text{Sn}} \approx 54$ Hz; 6 × C-3′), 29.57 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',^{119}\text{Sn}} \approx 20$ Hz; 6 × C-2′), 132.66 (C-4, C-7), 134.15 (C-5, C-6), 135.19 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1},^{117}\text{Sn}} = {}^{1}J_{\text{C-10},^{117}\text{Sn}} = 368.6$, $^{1}J_{\text{C-1},^{119}\text{Sn}} = {}^{1}J_{\text{C-10},^{119}\text{Sn}} = 385.8$ Hz; C-1/C-10), 136.26 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{C-3},^{117}\text{Sn}} \approx {}^{3}J_{\text{C-8},^{117}\text{Sn}} \approx {}^{3}J_{\text{C-3},^{119}\text{Sn}} \approx {}^{3}J_{\text{C-8},^{119}\text{Sn}} \approx 77$ Hz; C-3/C-8), 147.77 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-9},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2},^{119}\text{Sn}} \approx {}^{2}J_{\text{C-9},^{119}\text{Sn}} \approx 10$ Hz; C-2/C-6); IR (film): $\tilde{\nu} = 2955$, 2925, 2870, 2845, 2360, 2335, 1600, 1555, 1480, 1465, 1420, 1375, 1145, 1095, 1070, 1040, 1005, 875, 860, 760, 690, 670 cm^{-1}; HRMS (Cl, 120 eV): calcd for $C_{30}H_{55}Sn_2$: 655.23477 [$M^+ -$Bu]; found: 655.23550 (+1.1 ppm).



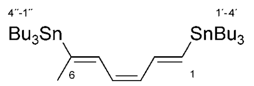
(1*E*,3*E*,5*E*,7*Z*,9*E*)-3,8-Dimethyl-1,10-bis(tributylstannyl)deca-1,3,5,7,9-pentaene (all-*E*-32): Following the general procedure, all-*E*-**32** was prepared in THF from bisallylsulfone **31** (90.0 mg, 0.112 mmol), CBr_2F_2 (0.12 µL, 90 mg, 0.4 mmol, 3.9 equiv), and KOH on Al_2O_3 (381 mg, 2.21 mmol, 19.7 equiv). After flash chromatography[26] on deactivated Al_2O_3 (5×2.5 cm, cyclohexane/NEt_3 100:1 (v/v), fractions 2 and 3), all-*E*-**32** was obtained as a yellow oil (59.2 mg, 71 %, all-*E*/mono-*Z* = 84:16). ^{1}H NMR (499.9 MHz, C_6D_6/C_6HD_5; sample not entirely pure): $\delta = \approx 0.90$–1.10 (m, 12H; 6 × 1′-H_2), superimposes 0.92 (t, $J_{\text{vic}} = 7.3$ Hz, 18H; 6 × 4′-H_3), 1.33–1.44 (m, approximately interpretable as 1.40, tq, both $J_{\text{vic}} = 7.3$ Hz, 12H; 6 × 3′-H_2), 1.52–1.70 (m, 12H; 6 × 2′-H_2), 1.87 (s, 2H; 3-CH_3 and 8-CH_3), 6.26 (br m_c, 2H; 4-H and 7-H), 6.50 (d, $J_{1,2} = 19.2$ Hz, Sn isotope satellites not unambiguously identified because of impurity, 2H; 1-H and 10-H), 6.62 (m_c, 2H; 5-H and 6-H), 6.93 ppm (d, $J_{2,1} = 19.1$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{^{117}\text{Sn,H}} \approx {}^{3}J_{^{119}\text{Sn,H}} \approx 65$ Hz, 2H; 2-H and 9-H); ^{13}C NMR (125.7 MHz, C_6D_6/C_6D_6): $\delta = 9.95$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{^{117}\text{Sn, C-1}'} = {}^{1}J_{^{117}\text{Sn, C-1}''} = 326.7$, $^{1}J_{^{119}\text{Sn, C-1}'} = {}^{1}J_{^{119}\text{Sn, C-1}''} = 342.1$ Hz, 6 × C-1′), 12.26 (3-CH_3, 8-CH_3), 13.92 (6 × C-4′), 27.73 (flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{^{117}\text{Sn, C-3}'} \approx {}^{3}J_{^{117}\text{Sn, C-3}''} \approx {}^{3}J_{^{119}\text{Sn, C-3}'} \approx {}^{3}J_{^{119}\text{Sn, C-3}''} \approx 54$ Hz, 6 × C-3′), 29.61 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{^{117}\text{Sn, C-2}'} \approx {}^{2}J_{^{117}\text{Sn, C-2}''} \approx {}^{2}J_{^{119}\text{Sn, C-2}'} \approx {}^{2}J_{^{119}\text{Sn,C-2}''}{}' \approx 21$ Hz, 6 × C-2′), 128.26 (seemingly flanked by Sn isotope satellites as an incompletely resolved d, $^{1}J_{^{117}\text{Sn,C-1}} \approx {}^{1}J_{^{117}\text{Sn,C-10}} \approx {}^{1}J_{^{119}\text{Sn,C-1}} \approx {}^{1}J_{^{119}\text{Sn,C-10}} \approx 324$ Hz; C-1, C-10), 130.94 (C-5, C-6), 132.62 (C-4, C-7), 137.06 (C-3, C-8), 151.58 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{^{117}\text{Sn,C-2}} \approx {}^{2}J_{^{117}\text{Sn,C-9}} \approx {}^{2}J_{^{119}\text{Sn,C-2}} \approx {}^{2}J_{^{119}\text{Sn,C-9}} \approx 11$ Hz; C-2, C-9); HRMS (EI, 70 eV): calcd for $C_{32}H_{59}Sn_2$: 683.26607[$M^+ -$Bu]; found: 683.26266



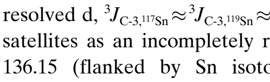
(−5.0 ppm). The *E* configuration of the $\mathrm{C^5{=}C^6}$ double bond was shown by an edited HSQC spectrum (499.9/125.7 MHz, $\mathrm{CDCl_3}$) in which the ^{13}C NMR resonance at $\delta = 130.84$ ppm (C-5, C-6) was split by $^1J_{\text{C-5,5-H}} = {}^1J_{\text{C-6,6-H}} = 152.4$ Hz, such that both the low- and the highfield branch revealed splittings due to $J_{4,3} = J_{5,6} = 11.9$ and $J_{4,5} = 14.4$ Hz.

Synthesis of mono-*Z*-polyene distannanes:

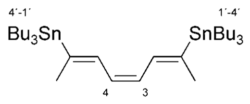
General procedure for (Sylvestre–)Julia polyene synthesis: KHMDS (1.0 M, 1.2 equiv) in THF was added dropwise to a solution of the aldehyde (~0.1 M) and benzothiazolylsulfone (1.28 equiv) in THF at −78 °C. After the reaction mixture was alowed to warm to room temperature overnight, *t*BuOMe and $\mathrm{H_2O}$ were added. The organic phase was separated and the aqueous phase extracted with *t*BuOMe (2×). The combined etheral phases were dried over $\mathrm{Na_2SO_4}$, the solvent was removed under reduced pressure, and the residue purified by chromatography on neutral alumina (deactivated by 3 % $\mathrm{H_2O}$).



(1*E*,3*Z*,5*E*)-1,6-Bis(tributylstannyl)hepta-1,3,5-triene (mono-*Z*-9): Following the general procedure, mono-*Z*-**9** was prepared from aldehyde **4** (69.1 mg, 0.200 mmol), benzothiazolylsulfone **10** (128.6 mg, 0.237 mmol, 1.18 equiv), and KHDMS (1.00 equiv). Flash chromatography[26] on deactivated $\mathrm{Al_2O_3}$ (5×2.5 cm, cyclohexane/$\mathrm{NEt_3}$ 50:1 (v/v), fractions 3 and 4), provided mono-*Z*-**9** as a yellow oil (74.9 mg, 56 %, mono-*Z*/all-*E* = 95:5). ^{1}H NMR (499.9 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 0.85$–0.95 (m, 12 H, 6 × 1′-$\mathrm{H_2}$), superimposes 0.89 and 0.90 (2× t, $J_{\text{vic}} = 7.3$ Hz, 18 H; 6 × 4′-$\mathrm{H_3}$), 1.316 and 1.325 (2× $\mathrm{m_c}$, approximately interpretable as 2× tq, each time both $J_{\text{vic}} = 7.3$ Hz, 12 H; 6 × 3′-$\mathrm{H_2}$), 1.44–1.57 (m, 12 H; 6 × 2′-$\mathrm{H_2}$), 2.02 (d, $^4J_{7,5} = 1.9$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{^{117}\mathrm{Sn,H}} \approx {}^3J_{^{119}\mathrm{Sn,H}} \approx 47$ Hz, 1 H; 7-$\mathrm{H^3}$), 5.95 (ddd, $J_{3,4} = J_{3,2} = 10.8$, $^4J_{3,1}$ or $^4J_{3,5} = 0.5$ Hz, 1 H; 3-H), 6.27 (dd$\mathrm{m_c}$, $J_{4,3} = J_{4,5} = 11.2$ Hz, 1 H; 4-H), 6.33 (d, $J_{1,2} = 18{,}6$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{^{117}\mathrm{Sn,H}} \approx {}^2J_{^{119}\mathrm{Sn,H}} \approx 72$ Hz, 1 H; 1-H), 6.75 (d$\mathrm{m_c}$, tentatively interpretable as dqd, $J_{5,4} = 11.3$, $^4J_{5,7} = 1.7$, $^4J_{5,3} = 1.1$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{^{117}\mathrm{Sn,H}} \approx {}^3J_{^{119}\mathrm{Sn,H}} \approx 67$ Hz, 1 H; 5-H), 7.08 ppm (ddd, $J_{2,1} = 18.5$, $J_{2,3} = 10.7$, $^4J_{2,4} = 1.0$ Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{^{117}\mathrm{Sn,H}} = 57.5$, $^3J_{^{119}\mathrm{Sn,H}} = 59.8$ Hz, 1 H; 2-H); ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3/CDCl_3}$): $\delta = 9.25$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-1}'',^{117}\mathrm{Sn}} = 315.8$, $^1J_{\text{C-1}'',^{119}\mathrm{Sn}} = 330.1$ Hz, 3 × C-1″)*, 9.57 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-1}',^{117}\mathrm{Sn}} = 329.1$, $^1J_{\text{C-1}',^{119}\mathrm{Sn}} = 344.5$ Hz, 3 × C-1′)*, 13.71 (3 × C-4′ + 3 ×C-4″), 19.68 (C-7), 27.29 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{\text{C-3}'',^{117}\mathrm{Sn}} \approx {}^3J_{\text{C-3}'',^{119}\mathrm{Sn}} \approx 55$ Hz, 3 × C-3″)*, 27.41 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{\text{C-3}',^{117}\mathrm{Sn}} \approx {}^3J_{\text{C-3}',^{119}\mathrm{Sn}} \approx 58$ Hz, 3 × C-3′)*, 29.12 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-2}'',^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-2}'',^{119}\mathrm{Sn}} \approx 21$ Hz, 3 × C-2″)**, 29.17 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-2}',^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-2}',^{119}\mathrm{Sn}} \approx 20$ Hz, 3 × C-2′)**, 122.16 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{\text{C-4},^{117}\mathrm{Sn}} \approx {}^3J_{\text{C-4},^{119}\mathrm{Sn}} \approx 63$ Hz; C-4), 130.76 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{\text{C-3},^{117}\mathrm{Sn}} \approx {}^3J_{\text{C-3},^{119}\mathrm{Sn}} \approx 74$ Hz; C-3), 134.04 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-5},^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-5},^{119}\mathrm{Sn}} \approx 31$ Hz; C-5), 136.15 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-1},^{117}\mathrm{Sn}} = 363.0$, $^1J_{\text{C-1},^{119}\mathrm{Sn}} = 380.0$ Hz; C-1), 141.87 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-2},^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-2},^{119}\mathrm{Sn}} \approx 10$ Hz; C-2), 146.56 ppm (C-6); *SnCH$_2$CH$_2$$CH_2CH_3$ resonances were distinguished based on the observation that this nucleus is shifted towards higher field in the α-$\mathrm{CH_3}$ group rather than α-H-substituted alkenylstannanes and that the corresponding $^1J_{\mathrm{C},^{118}\mathrm{Sn}}$ value is smaller; **assignments are interchangeable; IR (film): $\tilde{\nu} = 2955$, 2925, 2870, 2855, 1465, 1375, 1070, 990, 875, 865, 820, 690, 665, 595, 535 cm^{-1}; HRMS (EI, 70 eV): calcd for $\mathrm{C_{27}H_{53}Sn_2}$: 617.21912 $[M^+ - \mathrm{Bu}]$; found: 617.22040 (+2.1 ppm).

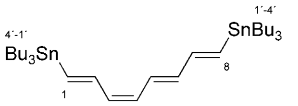


(1*E*,3*Z*,5*E*)-2-Methyl-1,6-bis(tributylstannyl)hexa-1,3,5-triene (mono-*Z*-12): Following the general procedure, mono-*Z*-**12** was prepared from aldehyde **13** (126 mg, 0.351 mmol), benzothiazolylsulfone **3** (222 mg, 0.421 mmol, 1.2 equiv), and KHMDS (1.2 equiv). Flash chromatography[26] on deactivated $\mathrm{Al_2O_3}$ (5×2 cm, cyclohexane/$\mathrm{NEt_3}$ 98:2 (v/v), fractions 2 and 3) provided mono-*Z*-**12** as a colorless oil (126 mg, 53 %, mono-*Z*/all-*E* = 82:18). ^{1}H NMR (400.1 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 0.93$ (t, $J_{4',3'} = 7.3$ Hz, 9 H; 3 × 4′-$\mathrm{H_3}$), 0.94 (t, $J_{4',3'} = 7.3$ Hz, 9 H; 3 × 4′-$\mathrm{H_3}$), 0.99 ($\mathrm{m_c}$, 6 H; 3 × 1′-$\mathrm{H_2}$), 1.02 ($\mathrm{m_c}$, 6 H; 3 × 1′-$\mathrm{H_2}$), 1.31–1.44 (m, 12 H; 6 × 3′-$\mathrm{H_2}$), 1.50–1.68 (m, 12 H; 6 × 2′-$\mathrm{H_2}$), 2.03 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^4J_{\text{2-Me},^{117}\mathrm{Sn}} \approx {}^4J_{\text{2-Me},^{119}\mathrm{Sn}} \approx 10$ Hz, 1 H; 2-$\mathrm{CH_3}$), 5.98 (d, $J_{3,4} = 11.6$ Hz, 1 H; 3-H), 6.10 (dd, $J_{4,3} = J_{4,5} = 11.0$ Hz, 1 H; 4-H), 6.20 (s, flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{1-H},^{117}\mathrm{Sn}} \approx {}^2J_{\text{1-H},^{119}\mathrm{Sn}} \approx 71$ Hz, 1 H; 1-H), 6.45 (d, $J_{6,5} = 18.6$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{6-H},^{117}\mathrm{Sn}} \approx {}^2J_{\text{6-H},^{119}\mathrm{Sn}} \approx 74$ Hz, 1 H; 6-H), 7.43 ppm (dd, $J_{5,6} = 18.8$, $J_{5,4} = 10.5$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{\text{5-H},^{117}\mathrm{Sn}} \approx {}^3J_{\text{5-H},^{119}\mathrm{Sn}} \approx 60$ Hz, 1 H; 5-H); ^{13}C NMR (100.6 MHz, $\mathrm{CDCl_3/CDCl_3}$): $\delta = 9.88$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-1}',^{117}\mathrm{Sn}} = 327.7$, $^1J_{\text{C-1}',^{119}\mathrm{Sn}} = 342.6$ Hz; 3 × C-1′), 10.50 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-1}',^{117}\mathrm{Sn}} = 324.7$, $^1J_{\text{C-1}',^{119}\mathrm{Sn}} = 339.7$ Hz; 3 × C-1′), 13.91 (6 × C-4′), 27.23 (2-Me), 27.70 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{\text{C-3}',^{117}\mathrm{Sn}} = 52.2$, $^3J_{\text{C-3}',^{119}\mathrm{Sn}} = 54.6$ Hz; 3 × C-3′), 27.74 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{\text{C-3}',^{117}\mathrm{Sn}} = 54.3$, $^3J_{\text{C-3}',^{119}\mathrm{Sn}} = 57.0$ Hz; 3 × C-3′), 29.59 (3 × C-2′,), 29.69 (3 × C-2′), 131.74 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{\text{C-4},^{117}\mathrm{Sn}} = 74.1$, $^3J_{\text{C-4},^{119}\mathrm{Sn}} = 77.0$ Hz; C-4), 132.81 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-1},^{117}\mathrm{Sn}} = 375.7$, $^1J_{\text{C-1},^{119}\mathrm{Sn}} = 393.5$ Hz; C-1), 133.94 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{\text{C-3},^{117}\mathrm{Sn}} = 62.8$, $^3J_{\text{C-3},^{119}\mathrm{Sn}} = 65.4$ Hz; C-3), 135.61 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-6},^{117}\mathrm{Sn}} = 372.3$, $^1J_{\text{C-6},^{119}\mathrm{Sn}} = 389.7$ Hz; C-6), 144.52 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-5},^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-5},^{119}\mathrm{Sn}} \approx 12$ Hz; C-5), 151.23 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-2},^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-2},^{119}\mathrm{Sn}} \approx 7$ Hz; C-2); no HRMS spectrum was obtained because the compound did not stand up to the ionization conditions.



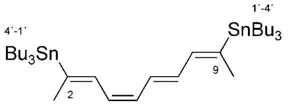
(2*E*,4*E*,6*E*)-2,7-Bis(tributylstannyl)octa-2,4,6-triene (mono-*Z*-15): Following the general procedure, mono-*Z*-**15** was prepared from aldehyde **16** (107.0 mg, 0.297 mmol, 1.08 equiv), benzothiazolylsulfone **10** (148.8 mg, 0.274 mmol), and KHMDS (1.02 equiv). Flash chromatography[26] on deactivated $\mathrm{Al_2O_3}$ (5×2.5 cm, cyclohexane/$\mathrm{NEt_3}$ 100:2 (v/v), fractions 4–6) provided mono-*Z*-**15** as a yellow oil (111.9 mg, 64 %, mono-*Z*/all-*E* = 95:5). ^{1}H NMR (499.9 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = \approx 0.86$–0.98 (m, 12 H; 6 × 1′-$\mathrm{H_2}$), superimposes 0.89 (t, $J_{\text{vic}} = 7.3$ Hz, 18 H; 6 × 4′-$\mathrm{H_3}$), 1.32 (tq, both $J_{\text{vic}} = 7.3$ Hz, 12 H; 6 × 3′-$\mathrm{H_2}$), 1.43–1.58 (m, 12 H; 6 × 2′-$\mathrm{H_2}$), 2.03 (d, $^4J_{1,3} = {}^4J_{8,6} = 1.7$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{^{117}\mathrm{Sn,H}} \approx {}^3J_{^{119}\mathrm{Sn,H}} \approx 45.1$ Hz, 6 H; 1-$\mathrm{H_3}$, 8-$\mathrm{H_3}$), 6.32 ($\mathrm{m_c}$, 2 H, 4-H and 5-H), 6.76 ppm ($\mathrm{m_c}$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{^{117}\mathrm{Sn,H}} \approx {}^3J_{^{119}\mathrm{Sn,H}} \approx 67$ Hz, 2 H; 3-H and 6-H); ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3/CDCl_3}$): $\delta = 9.26$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{\text{C-1}',^{117}\mathrm{Sn}} = 315.5$, $^1J_{\text{C-1}',^{119}\mathrm{Sn}} = 330.3$ Hz; 6 × C-1′), 13.70 (6 × C-4′), 19.69 (C-1, C-8), 27.40 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{\text{C-3}',^{117}\mathrm{Sn}} \approx {}^3J_{\text{C-3}',^{119}\mathrm{Sn}} \approx 55$ Hz; 6 × C-3′), 29.17 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-2}',^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-2}',^{119}\mathrm{Sn}} \approx 20$ Hz; 6 × C-2′), 121.89 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{\text{C-4},^{117}\mathrm{Sn}} \approx {}^3J_{\text{C-5},^{117}\mathrm{Sn}} \approx {}^3J_{\text{C-4},^{119}\mathrm{Sn}} \approx {}^3J_{\text{C-5},^{119}\mathrm{Sn}} \approx 64$ Hz; C-4, C-5), 134.05 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{\text{C-3},^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-6},^{117}\mathrm{Sn}} \approx {}^2J_{\text{C-3},^{119}\mathrm{Sn}} \approx {}^2J_{\text{C-6},^{119}\mathrm{Sn}} \approx 20$ Hz; C-3, C-6), 146.33 ppm (C-2, C-7). The *Z* configuration of the $\mathrm{C^4{=}C^5}$ double bond was shown by an edited HSQC spectrum (499.9/125.7 MHz, $\mathrm{CDCl_3}$) in which the ^{13}C NMR resonance $\delta = 121.89$ (C-4, C-5) was split by $^1J_{\text{C-4,4-H}} = {}^1J_{\text{C-5,5-H}} = 154.3$ Hz, such that both the low- and highfield branch revealed splittings due to $J_{4,5} \approx J_{4,3} \approx J_{5,4} \approx J_{5,6} \approx 11.5$ Hz; IR (film): $\tilde{\nu} = 2955$, 2925, 2870, 2855, 1465, 1375, 1070, 960, 875, 770, 690, 665 cm^{-1}; HRMS (EI, 70 eV): calcd for $\mathrm{C_{28}H_{55}Sn_2}$, 67 % intensity rather than 100 % intensity isotopomer): 631.23478 $[M^+ - \mathrm{Bu}]$; found: 631.23649 (+2.7 ppm).

(1*E*,3*Z*,5*E*,7*E*)-1,8-Bis(tributylstannyl)octa-1,3,5,7-tetraene (mono-*Z*-20): Following the general procedure, mono-*Z*-**20** was prepared from aldehyde **4** (100 mg, 0.265 mmol), benzothiazolylsulfone **21** (168 mg,

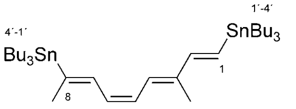


0.318 mmol, 1.2 equiv), and KHMDS (1.0 equiv). Flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 2 and 3) provided mono-*Z*-**20** as a colorless oil (132 mg, 73 %, mono-*Z*/all-*E* ≥ 96:4). ^{1}H NMR (400.1 MHz, C_6D_6/C_6D_5H): 0.92 (t, $J_{4',3'}=7.3$ Hz, 9H; 3 × 4′-H$_3$), 0.92 (t, $J_{4',3'}=7.3$ Hz, 9H; 3 × 4′-H$_3$), 0.97 (m$_c$, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^2J_{1'\text{-H},^{117}\text{Sn}}=50.0$, $^2J_{1'\text{-H},^{119}\text{Sn}}=52.5$ Hz, 6H; 3 × 1′-H$_2$), 0.97 (m$_c$, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^2J_{1'\text{-H},^{117}\text{Sn}}=49.0$, $^2J_{1'\text{-H},^{119}\text{Sn}}=51.8$ Hz, 6H; 3 × 1′-H$_2$), 1.35 (qt, $J_{3',4'}=J_{3',2'}=7.3$ Hz, 6H; 3 × 3′-H$_2$), 1.36 (qt, $J_{3',4'}=J_{3',2'}=7.3$ Hz, 6H; 3 × 3′-H$_2$), 1.47–1.68 (m, 12H; 6 × 2′-H$_2$), 6.00 (dd, $J_{5,6}=J_{5,4}=11.4$ Hz, 1H; 5-H), 6.12 (dd, $J_{6,7}=J_{6,5}=10.7$ Hz, 1H; 6-H), 6.29 (dd, $J_{3,4}=14.6$, $J_{3,2}=10.3$ Hz,1H; 3-H), 6.44 (d, $J_{1,2}=18.7$ Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^2J_{1\text{-H},^{117}\text{Sn}}=69.2$, $^2J_{1\text{-H},^{119}\text{Sn}}=72.5$ Hz, 1H; 1-H), 6.47 (d, $J_{8,7}=18.6$ Hz, 1H, 8-H), 6.82 (dd, $J_{2,1}=18.6$, $J_{2,3}=10.2$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{2\text{-H},^{117}\text{Sn}}\approx{}^3J_{2\text{-H},^{119}\text{Sn}}\approx59$ Hz, 1H; 2-H), 6.95 (dd, $J_{4,3}=14.7$, $J_{4,5}=11.7$ Hz, 1H; 4-H), 7.34 ppm (dd, $J_{7,8}=18.5$, $J_{7,6}=10.7$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{7\text{-H},^{117}\text{Sn}}\approx{}^3J_{7\text{-H},^{119}\text{Sn}}\approx59$ Hz, 1H; 7-H); ^{13}C NMR (100.6 MHz, C_6D_6/C_6D_6): $\delta=9.85$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{C\text{-}1',^{117}\text{Sn}}=332.9$, $^1J_{C\text{-}1',^{119}\text{Sn}}=339.2$ Hz; 3 × C-1′), 9.88 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{C\text{-}1',^{117}\text{Sn}}=332.7$, $^1J_{C\text{-}1',^{119}\text{Sn}}=339.2$ Hz; 3 × C-1′), 13.89 (6 × C-4′), 27.65 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{C\text{-}3',^{117}\text{Sn}}=52.9$, $^3J_{C\text{-}3',^{119}\text{Sn}}=54.8$ Hz; 6 × C-3′), 27.66 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{C\text{-}3',^{117}\text{Sn}}=52.6$, $^3J_{C\text{-}3',^{119}\text{Sn}}=55.0$ Hz; 6 × C-3′), 29.53 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}2',^{117}\text{Sn}}\approx{}^2J_{C\text{-}2',^{119}\text{Sn}}\approx21$ Hz; 3 × C-2′), 29.54 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}2',^{117}\text{Sn}}\approx{}^2J_{C\text{-}2',^{119}\text{Sn}}\approx21$ Hz; 3 × C-2′), 127.54 (C-4), 128.83 (C-5), 133.41 (flanked by Sn isotope satellites as 2 interwoven doublets, $^4J_{C\text{-}6,^{117}\text{Sn}}=72.4$, $^4J_{C\text{-}6,^{119}\text{Sn}}=75.3$ Hz; C-6), 135.96 (C-1), 136.50 (C-8), 137.23 (C-3), 142.61 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}7,^{117}\text{Sn}}\approx{}^2J_{C\text{-}7,^{119}\text{Sn}}\approx10$ Hz; C-7), 147.63 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}2,^{117}\text{Sn}}\approx{}^2J_{C\text{-}2,^{119}\text{Sn}}\approx9$ Hz; C-2); IR (film): $\tilde{\nu}=3020$, 2960, 2925, 2875, 2850, 1600, 1525, 1465, 1455, 1420, 1380, 1360, 1340, 1295, 1250, 1075, 1005, 990, 960, 875, 865, 820, 690, 665, 595, 570 cm^{-1}; HRMS (Cl, 120 eV): calcd for $C_{28}H_{53}Sn_2$: 627.21853 [M^+–Bu]; found: 627.21960 (+1.7 ppm).

(2*E*,4*Z*,6*E*,8*E*)-2,9-Bis(tributylstannyl)deca-2,4,6,8-tetraene (mono-*Z*-23): Following the general procedure, mono-*Z*-**23** was prepared from aldehyde **24** (234 mg, 0.608 mmol), benzothiazolylsulfone **10** (421 mg, 0.776 mmol, 1.28 equiv), and KHMDS (1.28 equiv). Flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 2–4) provided mono-*Z*-**23** as a colorless oil (276 mg, 64 %, mono-*Z*/all-*E* ≥ 96:4). ^{1}H NMR (400.1 MHz, $CDCl_3$, TMS): $\delta=0.95$ (t, $J_{4',3'}=7.3$ Hz, 9H; 3 × 4′-H$_3$), 0.96 (t, $J_{4',3'}=7.3$ Hz, 9H; 3 × 4′-H$_3$), 0.97 (m$_c$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{1'\text{-H},^{117}\text{Sn}}\approx{}^2J_{1'\text{-H},^{119}\text{Sn}}\approx51$ Hz, 6H; 3 × 1′-H$_2$), 0.99 (m$_c$, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{1'\text{-H},^{117}\text{Sn}}\approx{}^2J_{1'\text{-H},^{119}\text{Sn}}\approx51$ Hz, 6H; 3 × 1′-H$_2$), 1.37 (qt, $J_{3',4'}=J_{3',2'}=7.2$ Hz, 6H; 3 × 3′-H$_2$), 1.39 (qt, $J_{3',4'}=J_{3',2'}=7.2$ Hz, 6H; 3 × 3′-H$_2$), 1.45–1.66 (m, 12H; 6 × 2′-H$_2$), 2.07 (d, $^4J_{10,8}=1.3$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{10\text{-H},^{117}\text{Sn}}\approx{}^3J_{10\text{-H},^{119}\text{Sn}}\approx47$ Hz, 3H; 10-H$_3$), 2.09 (d, $^4J_{11,3}=1.5$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{1\text{-H},^{117}\text{Sn}}\approx{}^3J_{1\text{-H},^{119}\text{Sn}}\approx47$ Hz, 3H; 1-H$_3$), 6.11 (dd, $J_{6,7}=J_{6,5}=10.5$ Hz, 1H; 6-H), 6.37 (dd, $J_{3,4}=9.9$ Hz, $^4J_{3,1}=1.8$, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{3\text{-H},^{117}\text{Sn}}=63.4$, $^3J_{3\text{-H},^{119}\text{Sn}}=66.4$ Hz, 1H; 3-H), 6.37 (dd, $J_{7,8}=J_{7,6}=11.2$ Hz, 1H; 7-H), 6.66 (dd, $J_{4,5}=14.8$, $J_{4,3}=10.5$ Hz, 1H; 4-H), 6.72 (dd, $J_{5,4}=14.7$, $J_{5,6}=10.6$ Hz, 1H; 5-H), 6.72 (dd, $J_{5,4}=14.7$, $J_{5,6}=10.6$ Hz, 1H; 5-H), 6.79 ppm (d, $J_{8,7}=11.4$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{8\text{-H},^{117}\text{Sn}}\approx{}^3J_{8\text{-H},^{119}\text{Sn}}\approx66$ Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS): $\delta=9.31$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{C\text{-}1',^{117}\text{Sn}}=316.0$, $^1J_{C\text{-}1',^{119}\text{Sn}}=331.0$ Hz; 3 × C-1′), 9.41 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{C\text{-}1',^{117}\text{Sn}}=315.3$, $^1J_{C\text{-}1',^{119}\text{Sn}}=329.8$ Hz; 3 × C-1′), 13.78 (3 × C-4′), 13.80 (3 × C-4′), 19.82 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}1,^{117}\text{Sn}}\approx{}^2J_{C\text{-}1,^{119}\text{Sn}}\approx38$ Hz; C-10), 20.19 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}1,^{117}\text{Sn}}\approx{}^2J_{C\text{-}1,^{119}\text{Sn}}\approx36$ Hz; C-1), 27.48 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{C\text{-}3',^{117}\text{Sn}}=52.9$, $^3J_{C\text{-}3',^{119}\text{Sn}}=55.3$ Hz; 3 × C-3′), 27.51 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{C\text{-}3',^{117}\text{Sn}}=53.1$, $^3J_{C\text{-}3',^{119}\text{Sn}}=55.3$ Hz; 3 × C-3′), 29.26 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}2',^{117}\text{Sn}}\approx{}^2J_{C\text{-}2',^{119}\text{Sn}}\approx20$ Hz; 3 × C-2′), 29.31 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}2',^{117}\text{Sn}}\approx{}^2J_{C\text{-}2',^{119}\text{Sn}}\approx20$ Hz; 3 × C-2′), 123.62 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{C\text{-}7,^{117}\text{Sn}}\approx{}^3J_{C\text{-}7,^{119}\text{Sn}}\approx65$ Hz; C-7), 127.21 (C-5), 128.10 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{C\text{-}4,^{117}\text{Sn}}=62.8$, $^3J_{C\text{-}4,^{119}\text{Sn}}=66.2$ Hz; C-4), 128.59 (C-6), 134.41 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}8,^{117}\text{Sn}}\approx{}^2J_{C\text{-}8,^{119}\text{Sn}}\approx31$ Hz; C-8), 139.53 (flanked by Sn isotope satellites as an incompletely resolved d, $^2J_{C\text{-}3,^{117}\text{Sn}}\approx{}^2J_{C\text{-}3,^{119}\text{Sn}}\approx30$ Hz; C-3), 146.25 ppm (flanked by Sn isotope satellites as 4 interwoven doublets, $^1J_{C\text{-}2,^{117}\text{Sn}}=385.8^*$, $^1J_{C\text{-}9,^{117}\text{Sn}}=387.7^{**}$, $^1J_{C\text{-}2,^{119}\text{Sn}}=403.7^*$, $^1J_{C\text{-}9,^{119}\text{Sn}}=405.1$ Hz**; C-2, C-9); *,**assignments interchangeable; IR (film): $\tilde{\nu}=3025$, 2960, 2925, 2870, 2855, 1685, 1455, 1415, 1375, 1360, 1340, 1295, 1245, 1185, 1150, 1075, 1045, 1015, 1005, 955, 940, 875, 840, 770, 690, 665, 595 cm^{-1}; HRMS (Cl, 120 eV): calcd for $C_{34}H_{66}Sn_2$: 712.32026 [M^+]; found: 712.31970 (–0.8 ppm).

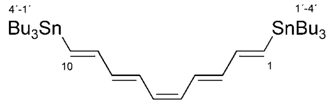


(1*E*,3*E*,5*Z*,7*E*)-3-Methyl-1,8-bis(tributylstannyl)nona-1,3,5,7-tetraene (mono-*Z*-26): Following the general procedure, mono-*Z*-**26** was prepared from aldehyde **27** (219 mg, 0.567 mmol), benzothiazolylsulfone **10** (400 mg, 0.737 mmol, 1.3 equiv), and KHMDS (1.28 equiv). Flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 2–4) povided mono-*Z*-**26** as a colorless oil (294 mg, 73 %, mono-*Z*/all-*E* ≥ 96:4). ^{1}H NMR (400.1 MHz, $CDCl_3$, TMS): $\delta=0.83$ (t, $J_{4',3'}=7.3$ Hz, 9H; 3 × 4′-H$_3$), 0.84 (t, $J_{4',3'}=7.3$ Hz, 9H; 3 × 4′-H$_3$), superimposes 0.85 (m$_c$, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^2J_{1'\text{-H},^{117}\text{Sn}}=50.4$, $^2J_{1'\text{-H},^{119}\text{Sn}}=52.0$ Hz, 6H; 3 × 1′-H$_2$), 0.87 (m$_c$, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^2J_{1'\text{-H},^{117}\text{Sn}}=49.0$, $^2J_{1'\text{-H},^{119}\text{Sn}}=50.8$ Hz, 6H; 3 × 1′-H$_2$), 1.25 (qt, $J_{3',4'}=J_{3',2'}=7.0$ Hz, 6H; 3 × 3′-H$_2$), 1.27 (qt, $J_{3',4'}=J_{3',2'}=7.0$ Hz, 6H; 3 × 3′-H$_2$), 1.40–1.52 (m, 12H; 6 × 2′-H$_2$), 1.82 (s, 1H; 3-CH$_3$), 1.96 (d, $^4J_{9,7}=1.4$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{9\text{-H},^{117}\text{Sn}}\approx{}^3J_{9\text{-H},^{119}\text{Sn}}\approx47$ Hz, 3H; 9-H$_3$), 6.24 (dd, $J_{5,4}=J_{5,6}=11.3$ Hz, 1H; 5-H), superimposes 6.24 (d, $J_{1,2}=18.9$ Hz, each peak flanked by Sn isotope satellites as 2 interwoven doublets, $^2J_{1\text{-H},^{117}\text{Sn}}=65.7$, $^2J_{1\text{-H},^{119}\text{Sn}}=67.7$ Hz, 1H; 1-H), 6.32 (dd, $J_{6,7}=J_{6,5}=11.2$ Hz, 1H; 6-H), 6.48 (d, $J_{4,5}=11.7$ Hz, 1H; 4-H), 6.58 (d, $J_{2,1}=19.2$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{2\text{-H},^{117}\text{Sn}}\approx{}^3J_{2\text{-H},^{119}\text{Sn}}\approx63$ Hz, 1H; 2-H), 6.71 ppm (dd, $J_{7,6}=11.1$, $^4J_{7,9}=1.6$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{7\text{-H},^{117}\text{Sn}}\approx{}^3J_{7\text{-H},^{119}\text{Sn}}\approx64.4$ Hz, 1H; 7-H); ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS): $\delta=8.31$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{C\text{-}1',^{117}\text{Sn}}=315.6$, $^1J_{C\text{-}1',^{119}\text{Sn}}=330.4$ Hz; 3 × C-1′), 8.55 (flanked by Sn isotope satellites as 2 interwoven doublets, $^1J_{C\text{-}1',^{117}\text{Sn}}=328.1$, $^1J_{C\text{-}1',^{119}\text{Sn}}=343.3$ Hz; 3 × C-1′), 10.76 (C-10), 12.67 (3 × C-4′), 12.70 (3 × C-4′), 18.78 (flanked by Sn isotope satellites as an incompletely resolved d, $^3J_{C\text{-}9,^{117}\text{Sn}}\approx{}^3J_{C\text{-}9,^{119}\text{Sn}}\approx39$ Hz; C-9), 26.28 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{C\text{-}3',^{117}\text{Sn}}=52.9$, $^3J_{C\text{-}3',^{119}\text{Sn}}=55.3$ Hz; 3 × C-3′), 26.99 (flanked by Sn isotope satellites as 2 interwoven doublets, $^3J_{C\text{-}3',^{117}\text{Sn}}=53.1$, $^3J_{C\text{-}3',^{119}\text{Sn}}=55.5$ Hz; 3 × C-3′), 28.10

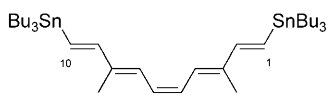


(flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',^{119}\text{Sn}} \approx 21$ Hz; 3 × C-2′), 28.18 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',^{119}\text{Sn}} \approx 20$ Hz; 3 × C-2′), 122.81 (C-6), 123.01 (C-5), 124.88 (C-4), 127.84 (C-1), 133.19 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-7},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-7},^{119}\text{Sn}} \approx 31$ Hz; C-7), 136.36 (C-3), 146.05 (C-8), 149.90 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2},^{119}\text{Sn}} \approx 11$ Hz; C-2); IR (film): $\tilde{\nu} = 3025$, 2955, 2925, 2870, 2850, 1560, 1465, 1420, 1375, 1340, 1295, 1075, 995, 940, 870, 735, 710, 690, 665, 610, 595 cm^{-1}; HRMS (Cl, 120 eV): calcd for $C_{34}H_{66}Sn_2$: 712.32026 [M^+]; found: 712.32260 (+3.3 ppm).

(1*E*,3*E*,5*Z*,7*E*,9*E*)-1,10-Bis(tributylstannyl)deca-1,3,5,7,9-pentaene (mono-*Z*-29): Following the general procedure, mono-*Z*-**29** was prepared from aldehyde **30** (100 mg, 0.265 mmol), benzothiazolylsulfone **10** (196 mg, 0.353 mmol, 1.2 equiv), and KHMDS (1.05 equiv). Flash chromatography[26] on deactivated Al_2O_3 (5×2 cm, cyclohexane/NEt_3 98:2 (v/v), fractions 2 and 3) provided mono-*Z*-**29** as a colorless oil (92.3 mg, 49 %, mono-*Z*/all-*E* ≥ 96:4). ^{1}H NMR (400.1 MHz, C_6D_6/C_6D_5H): $\delta = 0.92$ (t, $J_{4',3'} = 7.3$, 18 H; 6 × 4′-H_3), 1.01 (m_c, 12 H; 6 × 1′-H_2), 1.38 (qt, $J_{3',4'} = J_{3',2'} = 7.3$ Hz, 12 H; 6 × 3′-H_2), 1.51–1.72 (m, 12 H; 6 × 2′-H_2), 6.02 (m_c, d, 2 H; 5-H and 6-H), 6.26 (dd, $J_{3,4} = J_{8,7} = 14.5$, $J_{3,2} = J_{8,9} = 10.1$ Hz, 2 H; 3-H and 8-H), 6.45 (d, $J_{1,2} = J_{10,9} = 18.7$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{1-H},^{117}\text{Sn}} \approx {}^{2}J_{\text{1-H},^{119}\text{Sn}} \approx {}^{2}J_{\text{10-H},^{117}\text{Sn}} \approx {}^{2}J_{\text{10-H},^{119}\text{Sn}} \approx 69$ Hz, 2 H; 1-H, 10-H), 6.68 (m_c, 2 H; 4-H, 5-H), 6.84 ppm (dd, $J_{2,1} = J_{9,10} = 18.6$, $J_{2,3} = J_{9,8} = 10.2$ Hz, each peak flanked by Sn isotope satellites as an incompletely resolved d, $^{3}J_{\text{2-H},^{117}\text{Sn}} \approx {}^{3}J_{\text{2-H},^{119}\text{Sn}} \approx {}^{3}J_{\text{9-H},^{117}\text{Sn}} \approx {}^{3}J_{\text{9-H},^{119}\text{Sn}} \approx 58$ Hz, 2 H; 2-H, 9-H); ^{13}C NMR (100.6 MHz, C_6D_6/C_6D_6): $\delta = 9.90$ (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1}',^{117}\text{Sn}} = 328.4$, $^{1}J_{\text{C-1}',^{119}\text{Sn}} = 343.8$ Hz; 6 × C-1′), 13.91 (6 × C-4′), 27.70 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3}',^{117}\text{Sn}} = 52.9$, $^{3}J_{\text{C-3}',^{119}\text{Sn}} = 54.8$ Hz; 6 × C-3′), 29.57 (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2}',^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2}',^{119}\text{Sn}} \approx 21$ Hz; 6 × C-2′), 127.81 (C-4, C-7), 130.67 (C-5, C-6), 135.83 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{1}J_{\text{C-1},^{117}\text{Sn}} = {}^{1}J_{\text{C-10},^{117}\text{Sn}} = 367.2$, $^{1}J_{\text{C-1},^{119}\text{Sn}} = {}^{1}J_{\text{C-10},^{119}\text{Sn}} = 382.4$ Hz; C-1, C-10), 137.00 (flanked by Sn isotope satellites as 2 interwoven doublets, $^{3}J_{\text{C-3},^{117}\text{Sn}} = {}^{3}J_{\text{C-8},^{117}\text{Sn}} = 69.5$, $^{3}J_{\text{C-3},^{119}\text{Sn}} = {}^{3}J_{\text{C-8},^{119}\text{Sn}} = 75.3$ Hz; C-3, C-8), 147.73 ppm (flanked by Sn isotope satellites as an incompletely resolved d, $^{2}J_{\text{C-2},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-9},^{117}\text{Sn}} \approx {}^{2}J_{\text{C-2},^{119}\text{Sn}} \approx {}^{2}J_{\text{C-9},^{119}\text{Sn}} \approx 9$ Hz; C-2, C-6); HRMS (CI, 120 eV): calcd for $C_{34}H_{64}Sn_2$: 710.30461 [M^+]; found: 710.30590 (+1.8 ppm).



(1*E*,3*E*,5*Z*,7*E*,9*E*)-3,8-Dimethyl-1,10-bis(tributylstannyl)deca-1,3,5,7,9-pentaene (mono-*Z*-32): Following the general procedure, mono-*Z*-**32** was prepared from aldehyde **27** (89.0 mg, 0.231 mmol), benzothiazolylsulfone **33** (147.3 mg, 0.259 mmol, 1.12 equiv), and KHDMS (1.12 equiv). Flash chromatography[26] on deactivated Al_2O_3 (5×2.5 cm, cyclohexane/NEt_3 100:1 (v/v), fractions 3 and 4), provided mono-*Z*-**32** as a yellow oil (142.2 mg, 63 % (83 %),[10] mono-*Z*/all-*E* = 94:6; see refs [10] and [20] for the definitive stereochemical assignment and ref. [10] for analytical data.



Acknowledgements

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[1] a) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; b) Various authors in: *Handbook of Organopalladium Chemistry for Organic Synthesis* (Eds.: E. Negishi, A. de Meijere), Wiley-VCH, Weinheim, **2002**, pp. 215–994.

[2] a) J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524; b) V. Farina, G. P. Roth in *Advances in Metal-Organic Chemistry, Vol. 5* (Ed.: L. S. Liebeskind), JAI Press, Greenwich, **1996**, pp. 1–53; c) V. Farina, V. Krishnamurthy, W. J. Scott, *Org. React.* **1997**, *50*, 1–652; d) M. Kosugi, K. Fugami in *Handbook of Organopalladium Chemistry for Organic Synthesis* (Eds.: E. Negishi, A. de Meijere), Wiley-VCH, Weinheim, **2002**, pp. 263–284; e) P. Espinet, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 4808–4839; *Angew. Chem. Int. Ed.* **2004**, *43*, 4704–4734; f) T. N. Mitchell in *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 125–162; g) M. V. N. De Souza, *Curr. Org. Synth.* **2006**, *3*, 313–326.

[3] a) K. C. Nicolaou, T. K. Chakraborty, A. D. Piscopio, N. Minowa, P. Bertinato, *J. Am. Chem. Soc.* **1993**, *115*, 4419–4420; b) K. C. Nicolaou, A. D. Piscopio, P. Bertinato, T. K. Chakraborty, N. Minowa, K. Koide, *Chem. Eur. J.* **1995**, *1*, 318–333; c) C. E. Masse, M. Yang, J. Solomon, J. S. Panek, *J. Am. Chem. Soc.* **1998**, *120*, 4123–4134; for a conceptionally equivalent ring-closing biscoupling of *Z*-1,2-bis(trimethylstannyl)ethene, see: d) M. D. Shair, T. Y. Yoon, S. J. Danishefsky, *J. Org. Chem.* **1992**, *57*, 3755–3757; e) M. D. Shair, T. Y. Yoon, K. K. Mosny, T. C. Chou, S. J. Danishefsky, *J. Am. Chem. Soc.* **1996**, *118*, 9509–9525.

[4] a) D. A. Siesel, S. W. Staley, *Tetrahedron Lett.* **1993**, *34*, 3679–3682; b) D. A. Siesel, S. W. Staley, *J. Org. Chem.* **1993**, *58*, 7870–7875; c) A. M. Echavarren, M. Pérez, A. M. Castaño, J. M. Cuerva, *J. Org. Chem.* **1994**, *59*, 4179–4185; d) G. Macdonald, L. Alcaraz, X. Wei, N. J. Lewis, R. J. K. Taylor, *Tetrahedron* **1998**, *54*, 9823–9836; e) D. L. Andersen, T. G. Back, L. Janzen, K. Michalak, R. P. Pharis, G. C. J. Sung, *J. Org. Chem.* **2001**, *66*, 7129–7141; f) M. J. Frampton, H. Akdas, A. R. Cowley, J. E. Rogers, J. E. Slagle, P. A. Fleitz, M. Drobizhev, A. Rebane, H. L. Anderson, *Org. Lett.* **2005**, *7*, 5365–5368; g) a related mono-coupling was described by: P. M. Pihko, A. M. P. Koskinen, *Synlett* **1999**, 1966–1968.

[5] a) A. Kiehl, A. Eberhardt, K. Müllen, *Liebigs Ann.* **1995**, 223–230; b) D. Nozawa, H. Takikawa, K. Mori, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2043–2046; by refining this kind of approach, *E*,*E*-BnMe$_2$Si−CH=CH−CH=CH−SiMe$_2$(OH) and *E*,*E*-(thienyl)Me$_2$Si−CH=CH−CH=CH−SiMe$_2$(OH) were prepared (S. E. Denmark, S. A. Tymonko, *J. Am. Chem. Soc.* **2005**, *127*, 8004–8005) and the former compound was subjected to sequential Hiyama couplings (S. E. Denmark, S. Fujimori, *J. Am. Chem. Soc.* **2005**, *127*, 8971–8973).

[6] A. Sorg, R. Brückner, *Angew. Chem.* **2004**, *116*, 4623–4626; *Angew. Chem. Int. Ed.* **2004**, *43*, 4523–4526.

[7] R. Brückner, K. Siegel, A. Sorg in *Strategies and Tactics in Organic Synthesis, Vol. 5* (Ed.: M. Harmata), Elsevier, Amsterdam, **2004**, pp. 437–473.

[8] A. Sorg, K. Siegel, R. Brückner, *Chem. Eur. J.* **2005**, *11*, 1610–1624.

[9] J. Burghart, R. Brückner, *Angew. Chem.* **2008**, *120*, 7777–7782; *Angew. Chem. Int. Ed.* **2008**, *47*, 7664–7668.

[10] B. Vaz, R. Alvarez, A. R. de Lera, *J. Org. Chem.* **2002**, *67*, 5040–5043.

[11] a) Use of *E*,*E*-1-(tributylstannyl)-6-(trimethylsilyl)hexa-1,3-dien-5-yne as a synthetic equivalent of *E*,*E*,*E*-1-[chlorobis(cyclopentadienyl)zirconio]-6-(tributylstannyl)hexa-1,3,5-triene or *E*,*E*,*E*-1-[chlorobis(cyclopentadienyl)zirconio]-2-methyl-6-(tributylstannyl)hexa-1,3,5-triene: B. H. Lipshutz, C. Lindsley, *J. Am. Chem. Soc.* **1997**, *119*, 4555–4556; b) use of *E*,*E*- or *Z*,*E*-2-(tributylstannyl)-7-(trimethylsilyl)hepta-2,4-dien-6-yne as synthetic equivalents of *E*,*E*,*E*- and *E*,*E*,*Z*-1-(dialkylalumino)-2,6-dimethyl-6-(tributylstannyl)hepta-1,3,5-triene: B. H. Lipshutz, G. C. Closowski, W. Chrisman, D. W. Chung, D. B. Ball, J. Howell, *Org. Lett.* **2005**, *7*, 4561–4564.

[12] a) E. Angeletti, F. Montanari, A. Negrini, *Gazz. Chim. Ital.* **1956**, *86*, 406–414; b) V. Fiandanese, *Pure Appl. Chem.* **1990**, *62*, 1987–1992.

[13] E. g; a) F. Babudri, V. Fiandanese, F. Naso, *J. Org. Chem.* **1991**, *56*, 6245–6248; b) F. Babudri, G. M. Farinola, V. Fiandanese, L. Mazzone, F. Naso, *Tetrahedron* **1998**, *54*, 1085–1094.

[14] F. Babudri, A. R. Cicciomessere, G. M. Farinola, V. Fiandanese, G. Marchese, R. Musio, F. Naso, O. Sciacovelli, *J. Org. Chem.* **1997**, *62*, 3291–3298.

[15] S. E. Denmark, R. F. Sweis in *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 163–216.

[16] A. Sorg, Dissertation, Universität Freiburg (Germany), **2004**, p. 52; A. Sorg, Dissertation, Universität Freiburg (Germany), **2004**, pp. 192–193.

[17] a) N. Miyaura in *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 41–124; b) F. Bellina, A. Carpita, R. Rossi, *Synthesis* **2004**, 2419–2440.

[18] R. S. Coleman, X. Lu, I. Modolo, *J. Am. Chem. Soc.* **2007**, *129*, 3826–3827.

[19] A. Sorg, R. Brückner, *Synlett* **2005**, 289–293.

[20] B. Vaz, R. Alvarez, J. A. Souto, A. R. de Lera, *Synlett* **2005**, 294–298.

[21] The *Z*-selective olefination of aldehydes with lithioallyl and potassioallyl benzothiazolylsulfones, initially a side observation (Scheme 7 in R. Bellingham, K. Jarowicki, P. Kocienski, V. Martin, *Synthesis* **1996**, 285–296), was also exploited for the synthesis of a 1-stannylated 1*E*,3*Z*-1,3-diene W. Felzmann, V. B. Arion, J.-L. Mieusset, J. Mulzer, *Org. Lett.* **2006**, *8*, 3849–3851; J. Mulzer, D. Castagnolo, W. Felzmann, S. Marchart, C. Pilger, V. S. Enev, *Chem. Eur. J.* **2006**, *12*, 5992–6001 and of triene mono-*Z*-**7** (ref. [18]).

[22] First report: a) L. Ramberg, B. Bäcklund, *Arkiv Kemi Mineral Geol.* **1940**, *13A*, 1–50; L. Ramberg, B. Bäcklund, *Chem. Abstr.* **1940**, *34*, 4725. Reviews: b) L. A. Paquette, *Org. React.* **1977**, *25*, 1–71; c) R. J. K. Taylor, G. Casy, *Org. React.* **2003**, *62*, 357–475; d) X.-L. Wang, X.-P. Cao, Z.-L. Zhou, *Chin. J. Org. Chem.* **2003**, *23*, 120–128.

[23] a) First report: J. B. Baudin, G. Hareau, S. A. Julia, O. Ruel, *Tetrahedron Lett.* **1991**, *32*, 1175–1178. Reviews: b) P. R. Blakemore, *J. Chem. Soc. Perkin Trans. 1* **2002**, 2563–2585; c) R. Dumeunier, I. E. Markó in *Modern Carbonyl Olefination* (Ed.: T. Takeda), Wiley-VCH, Weinheim, **2004**, pp. 104–150; C. Aïssa, *Eur. J. Org. Chem.* **2009**, 1831–1844.

[24] X.-P. Cao, T.-L. Chan, H.-F. Chow, J. Tu, *J. Chem. Soc. Chem. Commun.* **1995**, 1297–1299.

[25] Method: T.-L. Chan, S. Fong, Y. Li, T.-O. Man, C.-D. Poon, *J. Chem. Soc. Chem. Commun.* **1994**, 1771–1772.

[26] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.

[27] S. Berger, *J. Magn. Reson.* **1989**, *81*, 561–564.

[28] J.-F. Betzer, F. Delaloge, B. Muller, A. Pancrazi, J. Prunet, *J. Org. Chem.* **1997**, *62*, 7768–7780.

[29] J. D. White, P. R. Blakemore, N. J. Green, E. B. Hauser, M. A. Holoboski, L. E. Keown, C. S. Nylund Kolz, B. W. Phillips, *J. Org. Chem.* **2002**, *67*, 7750–7760.

[30] G. R. Scarlato, J. A. DeMattei, L. S. Chong, A. K. Ogawa, M. R. Lin, R. W. Armstrong, *J. Org. Chem.* **1996**, *61*, 6139–6152.

[31] J. Schmidt-Leithoff, R. Brückner, *Helv. Chim. Acta* **2005**, *88*, 1943–1959.

[32] C. T. Brain, A. Chen, A. Nelson, N. Tanikkul, E. J. Thomas, *Tetrahedron Lett.* **2001**, *42*, 1247–1250 (oxidation with MnO_2).

[33] L. Blackburn, C. Pei, R. Taylor, *Synlett* **2002**, 0215–0218.

[34] J.-F. Betzer, A. Pancrazi, *Synlett* **1998**, 1129–1131.

[35] Compound **45** was prepared previously from **44** and $LiAlH_4$: U. Koop, G. Handke, N. Krause, *Liebigs Ann.* **1996**, 1487–1499.

[36] J. Schmidt-Leithoff, Dissertation, Universität Freiburg (Germany), **2006**, p. 119; J. Schmidt-Leithoff, Dissertation, Universität Freiburg (Germany), **2006**, pp. 269–271.

[37] K. Siegel, R. Brückner, *Chem. Eur. J.* **1998**, *4*, 1116–1122, and footnote [22] therein.

[38] A. Barbero, F. J. Pulido, *Chem. Soc. Rev.* **2005**, *34*, 913–920.

[39] A sample of this compound was kindly provided by Dr. Thomas Netscher (DSM, Kaiseraugst, Germany).

[40] This compound was prepared as described: R. Brückner, S. Braukmüller, H.-D. Beckhaus, J. Dirksen, D. Goeppel, M. Oestreich in *Praktikum Präparative Organische Chemie—Organisch-Chemisches Fortgeschrittenenpraktikum*, Spektrum, Heidelberg, **2008**, p. 195.

[41] Bromide **53** was previously prepared, but further reacted to give a dimethylphosphonate rather than isolated; L. A. Paquette, D. Pissarnitski, L. Barriault, *J. Org. Chem.* **1998**, *63*, 7389–7398.

[42] Method: F. Reimnitz, Dissertation, Universität Freiburg (Germany), **2000**, pp. 71–72; F. Reimnitz, Dissertation, Universität Freiburg (Germany), **2000**, pp. 147–148.

[43] Method: a) H_2O_2 oxidation/Mo^{VI} catalysis: H. S. Schultz, H. B. Freyermuth, S. R. Buc, *J. Org. Chem.* **1963**, *28*, 1140–1142; b) H_2O_2 oxidation/$(NH_4)_6Mo_7O_{24}$ catalysis: J. B. Baudin, G. Hareau, S. A. Julia, O. Ruel, *Bull. Soc. Chim. Fr.* **1993**, *130*, 336–357.

[44] For a conceptionally different approach to aldehyde **27**, see: T. D. Michels, J. U. Rhee, C. D. Vanderwal, *Org. Lett.* **2008**, *10*, 4787–4790.

[45] B. Domínguez, B. Iglesias, A. R. de Lera, *Tetrahedron* **1999**, *55*, 15071–15098 (oxidations with SO_3<M.>pyridine).

[46] I. Paterson, A. D. Findlay, C. Noti, *J. Chem. Soc. Chem. Commun.* **2008**, 6408–6410.

[47] For the generation of tin-free hexatriene substructures of carotenoids by Ramberg–Bäcklund rearrangements, see: a) M. Julia, D. Lavé, M. Mulhauser, M. Ramirez-Muñoz, D. Uguen, *Tetrahedron Lett.* **1983**, *24*, 1783–1786; b) H. Choi, M. Ji, M. Park, I.-K. Yun, S.-S. Oh, W. Baik, S. Koo, *J. Org. Chem.* **1999**, *64*, 8051–8053; c) M. Ji, H. Choi, J. C. Jeong, J. Jin, W. Baik, S. Lee. J. S. Kim, M. Park, S. Koo, *Helv. Chim. Acta* **2003**, *86*, 2620–2628.

[48] a) H. H. Strain, W. A. Svec, P. Wegfahrt, H. Rapoport, F. T. Haxo, S. Norgård, H. Kjøsen, S. Liaaen-Jensen, *Acta Chem. Scand.* **1976**, *30*, 109–120; b) J. E. Johansen, G. Borch, S. Liaaen-Jensen, *Phytochemistry* **1980**, *19*, 441–444.

[49] a) A. R. Loeblich III, V. E. Smith, *Lipids* **1968**, *3*, 5–13; b) W. A. Svec, S. Liaaen-Jensen, F. T. Haxo, *Phytochemistry* **1974**, *13*, 2261–2271; c) T. Skjenstad, F. T. Haxo, S. Liaaen-Jensen, *Biochem. Syst. Ecol.* **1984**, *12*, 149–153; d) T. Bjørnland, *Biochem. Syst. Ecol.* **1990**, *18*, 307–316; e) T. Aakermann, S. Liaaen-Jensen, *Phytochemistry* **1992**, *31*, 1779–1782.

[50] T. Olpp, R. Brückner *Angew. Chem.* **2006**, *118, 4128–4132; Angew. Chem. Int. Ed.* **2006**, 45, 4023–4027; *Angew. Chem. Int. Ed.* **2006**, *45*, 4023–4027.

[51] Generation of $[ZrCp_2ClH]$ from $[ZrCp_2Cl_2]$ and $LiEt_3BH$ in situ: B. H. Lipshutz, R. Keil, E. L. Ellsworth, *Tetrahedron Lett.* **1990**, *31*, 7257–7260.

[52] For a different conversion of **65** into **67**, see: B. Jin, Q. Liu, A. Sulikowski, *Tetrahedron* **2005**, *61*, 401–408.

[53] For a different synthesis of **69**, see: I. Pergament, R. Reich, M. Srebnik, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1215–1218.

[54] The $[ZrCp_2HCl]$-mediated hydroboration described in Y. D. Wang, G. Kimball, A. S. Prashad, Y. Wang, *Tetrahedron Lett.* **2005**, *46*, 8777–8780.

[55] Method: M. Hirano, J.-i. Tomaru, T. Morimoto, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3752–3754.

[56] Prepared as described in R. Polt, D. Sames, J. Chruma, *J. Org. Chem.* **1999**, *64*, 6147–6158.

[57] S. J. Lee, K. C. Gray, J. S. Peak, M. D. Burke, *J. Am. Chem. Soc.* **2008**, *130*, 466–468.

[58] H.-O. Kalinowski, S. Berger, S. Braun, *Carbon-13 NMR Spectroscopy*, Wiley, New York, **1984**, p. 4.

[59] J.-F. Betzer, P. Le Ménez, J. Prunet, J.-D. Brion, J. Ardisson, A. Pancrazi, *Synlett* **2002**, 1–15, and footnote [7] therein.

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