Direct Preparation of Allylstannanes from Allyl Alcohols: Convenient Synthesis of β-Substituted Allylstannanes and of Stereodefined γ-Substituted Allylstannanes

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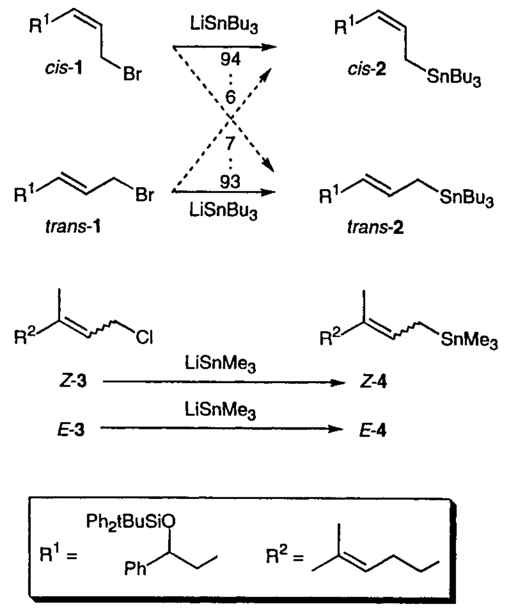
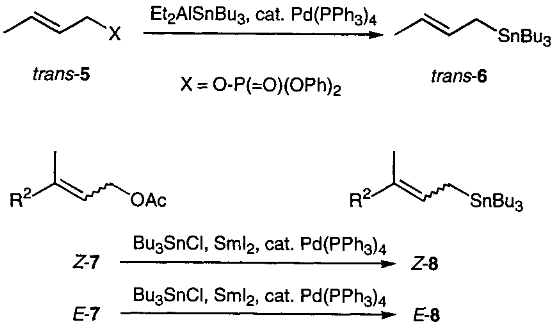
Primary allyl alcohols are converted into allyltributylstannanes in a one-pot operation. It entails (i) deprotonation with BuLi, (ii) sulfonylation with mesyl chloride, and (iii) nucleophilic substitution by $LiSnBu_3$. Conversions are quantitative with isolated yields ranging from 70% to 100%. If the starting allyl alcohol contains a stereogenic double bond its configuration is retained.

Allylstannanes and their derivatives are important reagents in organic synthesis.[1] Accordingly, various methods for their preparation are known. Many of them are based on an "R_3Sn" + "C–C=C" strategy as summarized in Schemes 1–5.



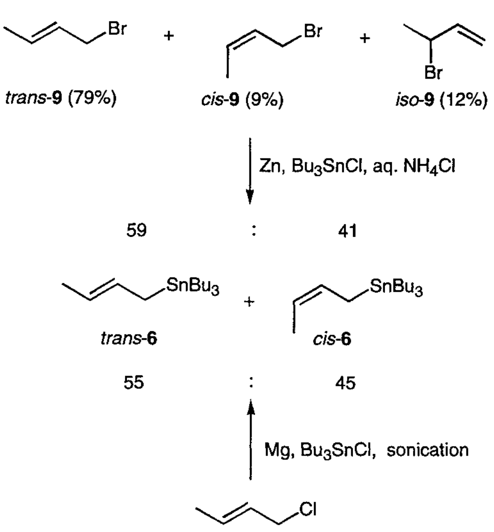
Scheme 1

$LiSnBu_3$ or $LiSnMe_3$[2] react with allyl bromides (e.g. **1** → **2**,[3] Scheme 1) or allyl chlorides (e.g. **3** → **4**[4]) to give γ-monosubstituted or γ,γ-disubstituted allylstannanes. Starting from bromides the configuration of the allyl moiety is essentially preserved,[3] starting from chlorides the configuration of the allyl moiety is completely preserved.[4,5] γ-Substituted allyl phenyl sulfides[6] or allyl phenyl selenides[7] react with $LiSnBu_3$ or $LiSnMe_3$ similarly; little is known about the extent of stereocontrol, with respect to the configuration of the resulting C=C bond, that can be exerted.



Scheme 2

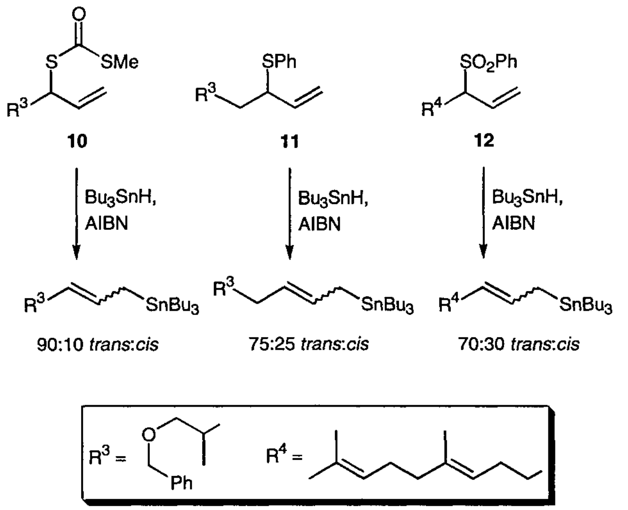
Allyl acetates[8,9] and allyl phosphates[10] are converted into allylstannanes in the presence of Pd(0) (Scheme 2). Appropriate tin nucleophiles are $Et_2Al-SnBu_3$[8,10] or a species which is obtained in situ from $Cl-SnBu_3$ and SmI_2.[9] In at least one instance a crotyl acetate reacted completely nonstereoselectively under these conditions,[9] while the corresponding phosphate *trans*-**5** exhibited rigorous stereocontrol.[10]



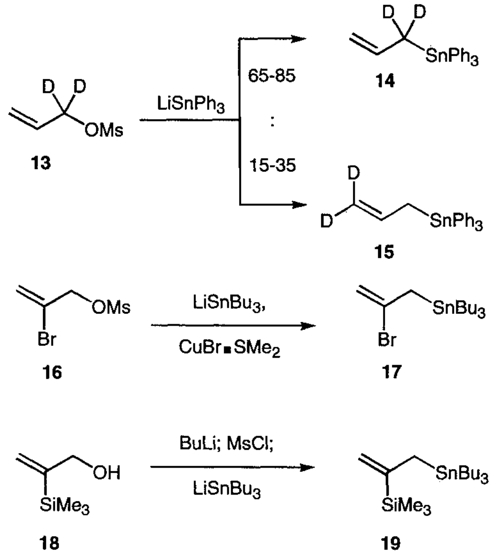
Scheme 3

An "R_3Sn" + "C–C=C" approach to allylstannanes with opposite polarities of the reactants is equally well-known: the stannylation of allyl metals. Success was met in stannylations of allyllithium[11] or allyl Grignard reagents[12] with R_3Sn-Cl or of allyl silicates by $Bu_3Sn-O-SnBu_3$.[13] However, the application of this strategy to the synthesis of stereodefined allylstannanes is unknown. The co-reduction of allyl halides and Bu_3SnCl with Zn[14] or Mg[15] constitutes another "R_3Sn" + "$C-C=C$" route to allylstannanes (Scheme 3), but starting from crotyl halides one obtains only *cis/trans* mixtures.[16]

S_R' Reactions between allyl dithiocarbonates (e.g. compound **10**,[17] Scheme 4), allyl dithioiminocarbonates,[18] allyl sulfides (e.g. compound **11**[19]) or allyl sulfones (e.g. compound **12**[20]) and $Bu_3Sn^{\bullet}$ radicals also lead to allylstannanes. Due to the elevated temperatures, none of these reactions reveals more than a modest *trans* selectivity; *trans/cis* ratios vary between 90:10 and 70:30.

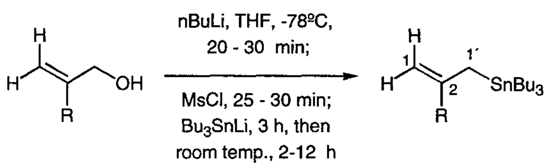


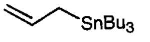
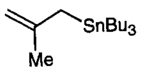
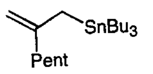
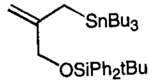
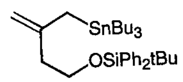
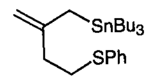
Scheme 4



Scheme 5

Table 1. One-Pot Syntheses of β-Substituted Allylstannanes



				^{1}H NMR		
Entry	Alcohol	Yield (%)	Stannane	δ(1-H$_2$)	δ(1'-H$_2$)	$^{2}J_{1'-\mathrm{H,Sn}}$ (Hz)
1	–[a]	100	**20** 	4.64 4.78	1.77	60.5
2	–[a]	84	**21** 	4.43 4.47	1.78	–
3	**30**[b]	85	**22** 	4.44 4.49	1.78	59.4
4	**34**[b]	81	**23** 	4.65 4.97	1.70	58.8
5	**38**[b]	70	**24** 	4.42 4.52	1.73	60.5
6	**41**[b]	99	**25** 	4.51 4.59	1.78	59.1

[a] Commercially available.

[b] Prepared as described.

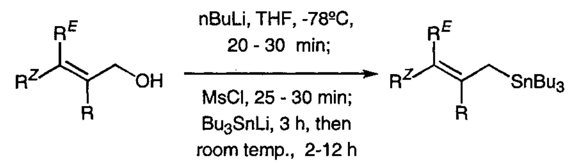
In connection with a synthesis project,[21] we required access to allylstannanes devoid of α-substituents which would allow the introduction of a variety of β- or γ-substituents; in addition, the γ-substituted allylstannanes had to be isomerically pure. We have found that such allylstannanes are advantageously prepared from allyl alcohols via allyl mesylates, rather than via the previously used derivatives thereof, which are almost always utilized (cf. Schemes 1–4). Allyl mesylates have been utilized only once by Matarasso–Tchiroukhine/Cadiot,[22] once by Corey's group,[23] and once by Overman's[24] for synthesizing allylstannanes; mesylate **13**, mesylate **16**, and the mesylate obtained in situ from alcohol **18** were thereby converted into the allylstannanes **14**/**15**,[22] **17**,[23] and **19**,[24] respectively.[25] The present paper reports an extension of this approach and its application to:

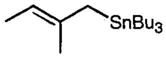
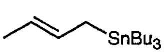
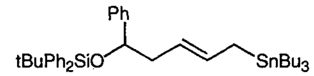
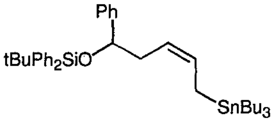
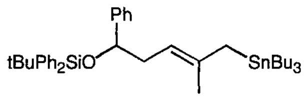
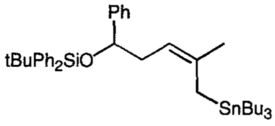
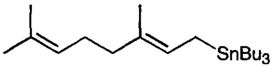
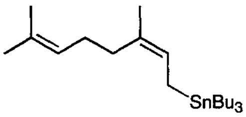
- the preparation of β-substituted allylstannanes (Table 1), which may contain an additional functional group in the side chain (entries 4–6); and to
- the synthesis of γ-substituted allylstannanes (Table 2) as pure *cis*, *trans*, *E* or *Z* isomers, respectively (entries 1–5, 7, 8).

These allylstannane syntheses are easily performed. At – 78 °C in THF, an alcoholate is prepared from an allyl alcohol and BuLi. When treated with MsCl at the same temperature it gives a mesylate. Then, 1.0 equivalent of a THF solution of $LiSnBu_3$[26] is added. Subsequently, the reaction mixture is gradually warmed to room temperature. After aqueous workup, the product is flash chromatographed using silica gel[27] and petroleum ether. Just filtering the crude product through a pad of such silica gel is usually a sufficiently good purification. When the stannane is volatile enough, it can alternatively be purified by Kugelrohr or by bulb-to-bulb distillation. The isolated yields were 70–100% (Tables 1, 2). Only stannane *Z*-**27** was inaccessible by this method (Table 2, entry 6).

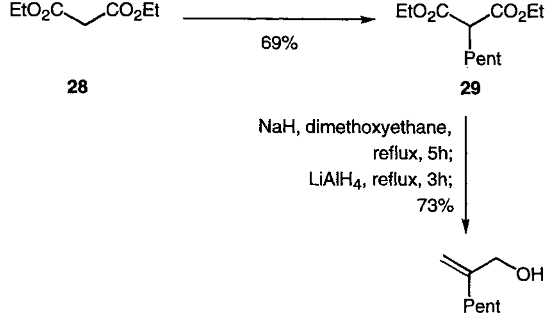
The allylstannane syntheses from Table 2 are stereoselective. This was concluded from the absence of excess resonances in their 300 MHz ^{1}H NMR spectra. In this respect, the novel access to allylstannanes is superior to some of the reported syntheses which exhibit less stereocontrol in the preparation of *trans*-**6** (cf. Scheme 3) or *cis*- and *trans*-**2** (cf. Scheme 1). The stereochemistry of stannanes **2** and **6** follows from the magnitude of the olefinic coupling constants. The stereochemical assignments of the other stannanes of Tables 1 and 2 are founded upon the following assumptions. Since essentially complete stereoselectivities were observed in all syntheses and complementary stereoselectivities were observed when two isomers of a given stannane (**2**, **8**) were prepared (^{1}H NMR evidence supporting this statement with respect to allylstannanes *E*- and *Z*-**8** see Figure), the configurations of the C=C double bonds in each stannane and its alcohol precursor are the same.

Table 2. One-Pot Syntheses of Stereodefined γ-Substituted Allylstannanes



Entry	Alcohol	Yield (%)	Stannane	
1	–[a]	100	*E*-**26**	
2	–[a]	81	*trans*-**6**	
3	–[b]	79	*trans*-**2**	
4	–[b]	71	*cis*-**2**	
5	**45**[c]	71	*E*-**27**	
6	–[d]	0	*Z*-**27**	
7	geraniol[a]	100	*E*-**8**	
8	nerol[a]	100	*Z*-**8**	

[a] Commercially available.
[b] Ref 3.
[c] Prepared as described.
[d] Ref 28.



Scheme 6

Aside from the ease of stereocontrol, the novel allylstannane syntheses are attractive because of the ease of preparation of the requisite alcohol precursors (Schemes 6–10). Scheme 6 shows a two-step preparation of the β-pentylated allyl alcohol **30** from diethyl malonate.[29]

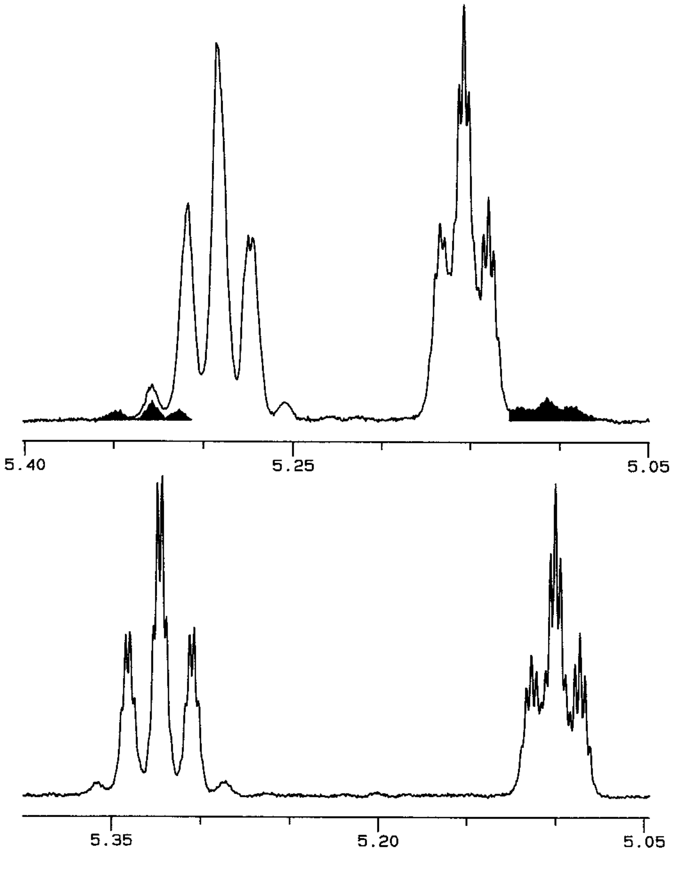
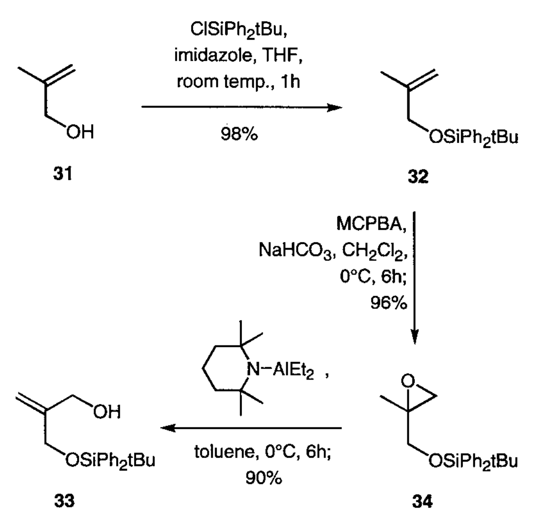
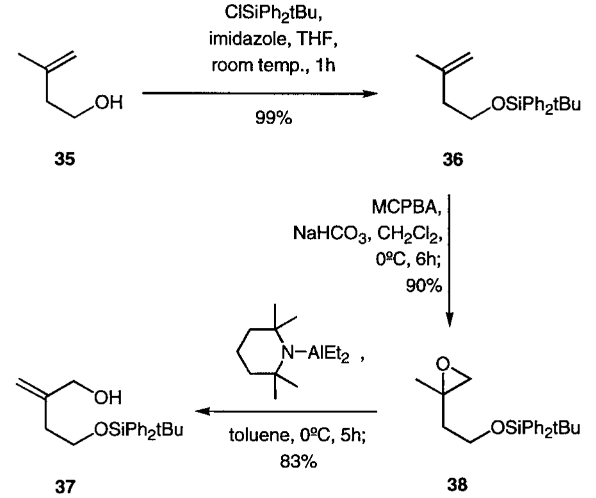


Figure. Olefinic resonances from the 500 MHz ^1H NMR spectra of the isomeric allylstannanes *Z*-**8** (top) and *E*-**8** (bottom) which visualize the extent of mutual contamination as blackened areas (*Z*/*E* 93:7 and *E*/*Z* 100:0, respectively)

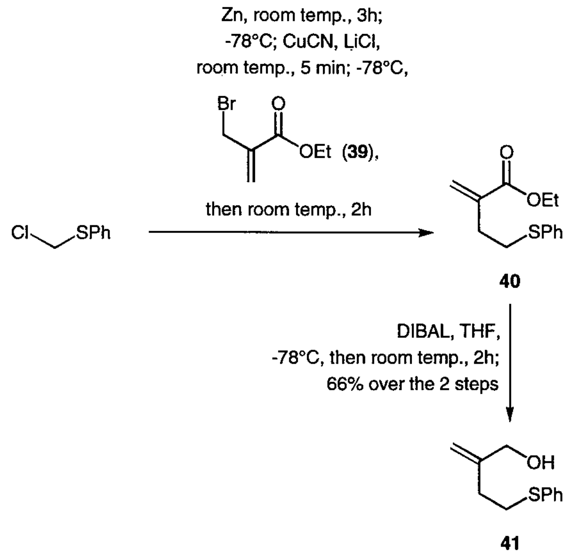
Schemes 7 and 8 show three-step syntheses of allyl alcohols which contain *t*-$BuPh_2SiO$ groups in C_1 or C_2 side chains at C-β. The key step is a regioselective β-elimination from the *gem*-disubstituted epoxides **34** and **38**, respectively. It is effected by exposure to a sterically severely hindered aluminum amide.[30] Scheme 9 shows how an organozinc compound[31] and methyl β-(bromomethyl)acrylate (**39**)[32] can be converted into a PhS containing allyl alcohol within two steps. Finally, Scheme 10 shows the stereoselective synthesis of an allyl alcohol which contains a trisubstituted C=C bond by an allyl sulfoxide → allyl sulfenate rearrangement.[33]



Scheme 7

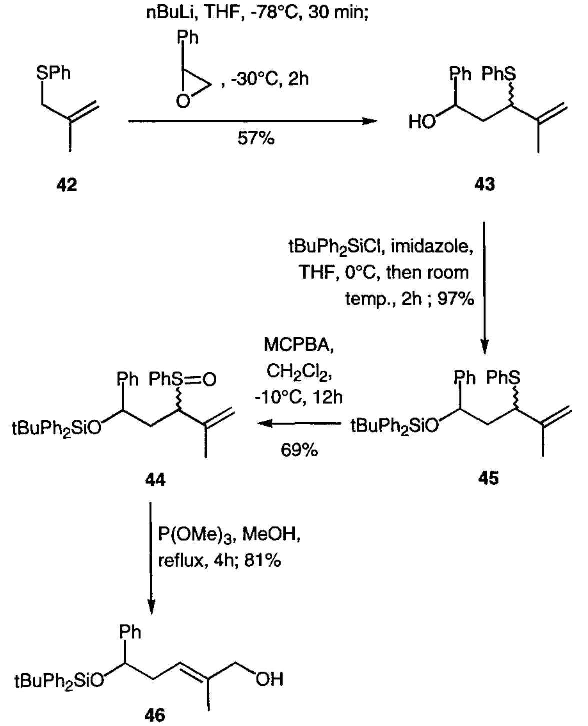


Scheme 8



Scheme 9

All reactions were performed in oven-dried (100 °C) glassware under dry N_2. THF was freshly distilled from K, CH_2Cl_2 from CaH_2. Products were purified by flash chromatography[27] on Merck silica gel 60 (particle size 0.040–0.063 mm, 230–240 mesh ASTM; eluents given in brackets). Yields refer to analytically pure samples. Combustion analyses for compounds *cis*-**2**, *trans*-**2**, **23**, *E*-**27**, **29**, **30**, **32**, **33**, **34**, **36**–**38**, **41**, **43**, **45**, **46** C ± 0.29, H ± 0.19; no correct combustion analyses was obtained for **24**, **25** and **44**. HRMS were obtained on a Finnigan MAT 95 spectrometer for compounds *E*-**8**, *Z*-**8** and *E*-**26**; they confirmed their molecular masses with respect to the ^{119}Sn isotope with a precision of ± 2 mDa. ^1H NMR spectra (TMS or $CHCl_3$ internal standard in $CDCl_3$): Varian VXL-200 (200 MHz) and Bruker AMX 300 (300 MHz); integrals in accord with assignments; coupling constants in Hz; AB spectra: H_A refers to high- and H_B to lowfield resonance. IR spectra (film): Perkin Elmer FT-IR 1600.



Scheme 10

2-[(Tributylstannyl)methyl]hept-1-ene (22); Typical Procedure:

1.78 M BuLi in cyclohexane (2.81 mL, 5.0 mmol) was added at – 78°C to a solution of alcohol (0.6411 g, 5.001 mmol, 1.0 equiv) in THF (4 mL). After 20 min MsCl (0.39 mL, 0.57 g, 5.0 mmol) was added. After 35 min a solution of Bu_3SnLi^{26} [prepared from i-Pr_2NH (0.77 mL, 0.56 g, 5.5 mmol, 1.1 equiv.), 1.78 M BuLi in cyclohexane (2.95 mL, 5.25 mmol, 1.05 equiv), and Bu_3SnH (1.32 mL, 1.46 g, 5.0 mmol)] in THF (4 mL) was added dropwise via cannula. After 2 h at – 78 °C the solution was allowed to warm to r. t. and quenched after 12 h with H_2O (20 mL). Extraction with t-BuOMe (3 × 20 mL), evaporation of the solvent, and filtration over a pad of flash silica gel (deactivated with NEt_3) with petroleum ether (100 mL) gave the title compound; yield: 1.705 g (85 %).

^{1}H NMR (300 MHz): $\delta = 0.89$ (t, $J_{4',3'} = 7.2$ Hz, 3 × 4″-H_3), 0.81–0.99 (m, 3 × 1″-H_2, 7-H_3), 1.24–1.54 (m, 4-H_2, 5-H_2, 6-H_2, 3 × 2″-H_2, 3 × 3″-H_2), 1.78 (s flanked by Sn satellites, $^2J_{H,Sn} \approx 59.4$ Hz, 1′-H_2), 1.92 (br t, $J_{3,4} = 7.6$ Hz, 3-H_2), 4.44 and 4.49 (2 m_c, Sn satellites visible as $^4J_{H,Sn} \approx 19$ and $^4J_{H,Sn} \approx 14$ Hz, 1-H_2).

IR: $\nu = 2955, 2925, 1625, 1460, 1375, 1070, 860$ cm^{-1}.

Similarly were prepared (for yields see Tables 1 and 2):

*(Z)-5-(tert-Butyldiphenylsilyloxy)-5-phenyl-1-(tributylstannyl)-pent-2-ene (cis-**2**):*

^{1}H NMR (300 MHz): $\delta = 0.75$ (m_c, 3 × 1′-H_2), 0.86 (t, $J_{4',3'} = 7.2$ Hz, 3 × 4′-H_3), 1.03 (s, t-Bu), 1.16–1.57 (m, 3 × 2′-H_2, 3 × 3′-H_2, 1-H_2), AB signal ($\delta_A = 2.31$, $\delta_B = 2.45$, $J_{AB} = 14.1$ Hz, in addition split by $J_{A,3} = J_{A,5} = 7.1$, $J_{B,3} = J_{B,5} = 6.8$ Hz, 4-H_2), 4.65 (dd, $J_{5,4\text{-}H(A)} = 7.2$, $J_{5,4\text{-}H(B)} = 5.7$ Hz, 5-H), 4.81 (ddd, $J_{cis} = 10.6$, $J_{3,4\text{-}H(A)} = J_{3,4-H(B)} = 7.2$ Hz, 3-H), 5.44 (td, $J_{2,1} = J_{cis} = 9.5$ Hz, 2-H), 7.14–7.48 and 7.68–7.73 (2 m, ca. 13 and 2 H, respectively, 3 × C_6H_5).

IR: $\nu = 2955, 2925, 2855, 1590, 1460, 1425, 1365, 1110, 1070, 960, 825$ cm^{-1}.

*(E)-5-(tert-Butyldiphenylsilyloxy)-5-phenyl-1-(tributylstannyl)-pent-2-ene (trans-**2**):*

^{1}H NMR [300 MHz; impurities at $\delta = 0.89$ (t) and 4.75]: $\delta = 0.73$ (m_c, 3 × 1′-H_2), 0.86 (t, $J_{4',3'} = 7.2$ Hz, 3 × 4′-H_3), 1.03 (s, t-Bu), 1.21–1.51 (m, 3 × 2′-H_2, 3 × 3′-H_2), superimposes 1.53 (d, $J_{1,2} = 7.9$ Hz, 1-H_2), 2.35 (m_c, 4-H_2), 4.58 (dd, $J_{5,4\text{-}H(1)} = 6.8$, $J_{5,4\text{-}H(2)} = 5.7$ Hz, 5-H), 4.86 (dt, $J_{trans} = 14.8$, $J_{3,4} = 7.4$ Hz, 3-H), 5.29 (dt, $J_{trans} = 16.0$, $J_{2,1} = 8.3$ Hz, 2-H), 7.14–7.27, 7.29–7.47 and 7.67–7.73 (3 × m, 3 × C_6H_5).

IR: $\nu = 2925, 2860, 1650, 1590, 1460, 1425, 1370, 1105, 1065, 960, 740, 700$ cm^{-1}.

*(E)-2,6-Dimethyl-8-(tributylstannyl)octa-2,6-diene (E-**8**):*

^{1}H NMR (300 MHz): $\delta = 0.83$ (m_c, 3 × 1′-H_2), 0.89 (t, $J_{4',3'}$) = 7.3 Hz, 3 × 4′-H_3), 1.30 (tq, $J_{3',2'} = J_{3',4'} = 7.3$ Hz, 3 × 3′-H_2), 1.42–1.55 (m, 3 × 2′-H_2), 1.57, 1.61 and 1.68 (3 × s, 1-H_3, 2-CH_3, 6-CH_3), superimposes 1.66 (d, $J_{8,7} \approx 11$ Hz, 8-H_2), 1.90–2.11 (m, 4-H_2, 5-H_2), 5.10 (m_c, 7-H), 5.32 (tm_c, $J_{3,4} = 9.1$ Hz, 3-H).

IR: $\nu = 2955, 2920, 1455, 1375, 1115, 1070, 865$ cm^{-1}.

*(Z)-2,6-Dimethyl-8-(tributylstannyl)octa-2,6-diene (Z-**8**):*

^{1}H NMR (300 MHz): $\delta = 0.83$ (m_c, 3 × 1′-H_2), 0.89 (t, $J_{4',3'} = 7.2$ Hz, 3 × 4′-H_3), 1.29 (m_c, presumably interpretable as tq, $J_{3',2'} = J_{3',4'} = 7.2$ Hz, 3 × 3′-H_2), 1.41–1.59 (m, 3 × 2′-H_2), 1.63, 1.67 and 1.70 (3 × s, 1-H_3, 2-CH_3, 6-CH_3), superimposes 1.66 (d, $J_{8,7} \approx 7$ Hz, 8-H_2), 2.01 (m_c, 4-H_2, 5-H_2), 5.15 (m_c, 7-H), 5.29 (tm_c, $J_{3,4} = 8.5$ Hz, 3-H).

IR: $\nu = 2955, 2920, 1455, 1375, 1075, 865$ cm^{-1}.

*(E)-4-(Tributylstannyl)but-2-ene(trans-**6**):*

^{1}H NMR [300 MHz; impurity at $\delta = 1.11$ (m)]: $\delta = 0.89$ (t, $J_{4',3'} = 7.2$ Hz, 3 × 4′-H_3), superimposes 0.80–0.94 (m, 3 × 1′-H_2), 1.23–1.40 (m, 3 × 3′-H_2), 1.42–1.72 (m, 3 × 2′-H_2), superimposes 1.62 (dm_c, $J_{4,3} = 6.4$ Hz, 4-H_3*) and 1.67 (dm_c, $J_{1,2} = 8.3$ Hz, 1-H_2*), 5.21 (dqm_c, $J_{trans} = 14.9$, $J_{3,4} = 6.8$ Hz, 3-H), 5.53 (dtq, $J_{trans} = 15.8$, $J_{2,1} = 8.1$, $J_{allyl} = 1.5$ Hz, 2-H); *assignments interchangeable.

IR: $\nu = 2920, 1810, 1655, 1460, 1375, 1070, 960, 870$ cm^{-1}.

3-(Tributylstannyl)propene **(20)**:

^{1}H NMR (300 MHz): $\delta = 0.89$ (t, $J_{4',3'} = 7.4$ Hz, 3 × 4′-H_3), superimposes 0.83–0.99 (m, 3 × 1′-H_2), 1.24–1.37 (m, 3 × 3′-H_2), 1.43–1.53 (m, 3 × 2′-H_2), 1.77 (d flanked by Sn satellites, $J_{3,2} = 8.7$, $^2J_{H,Sn} = 60.5$ Hz, 3-H_2), 4.64 (dd with transition to higher order spectrum, $J_{cis} = 9.8$, $J_{gem} = 2.3$ Hz, 1-H^E), 4.78 (ddt, $J_{trans} = 16.9$, $J_{gem} = 2.3$, $J_{allyl} = 1.1$ Hz, 1-H^Z), 5.94 (ddt, $J_{trans} = 16.9$, $J_{cis} = 9.8$, $J_{2,3} = 8.5$ Hz, 2-H).

IR: $\nu = 2920, 1620, 1460, 875$ cm^{-1}.

2-Methyl-3-(tributylstannyl)propene **(21)**:

^{1}H NMR (300 MHz; impurities in the alkyl region): $\delta = 0.82$–0.99 (m, 3 × 3′-H_2), 0.89 (t, $J_{4',3'} = 7.4$ Hz, 4′-H_3), 1.23–1.37 and 1.42–1.55 (2 × m, 1′-H_2, 2′-H_2), 1.70 (s flanked by Sn satellites, $^4J_{H,Sn} = 10.9$ Hz, 2-Me), 1.78 (d, $J_{allyl} = 1.1$ Hz, 3-H_2), 4.43 and 4.47 (2 m_c, 1-H_2).

IR: $\nu = 2955, 2920, 1810, 1630, 1460, 1375, 1275, 1070, 860, 660$ cm^{-1}.

2-[(tert-Butyldiphenylsilyloxy)methyl]-3-(tributylstannyl)propene **(23)**:

^{1}H NMR (300 MHz): $\delta = 0.73$–0.99 (m, 3 × 1″-H_2, 3 × 4″-H_3), 1.07 (s, t-Bu), 1.17–1.52 (m, 3 × 2″-H_2, 3 × 3″-H_2), 1.70 (s flanked by Sn satellites, $^2J_{H,Sn} = 58.8$ Hz, 3-H_2), 3.99 (s flanked by Sn satellites, $^4J_{H,Sn} \approx 10$ Hz, 1′-H_2), 4.65 and 4.97 (m_c flanked by Sn satellites, $^4J_{H,Sn} = 16.6$ Hz and dt flanked by Sn satellites, $J_{gem} = J_{allyl} = 1.9$, $^4J_{H,Sn} = 17.6$ Hz, 1-H_2), 7.34–7.45 and 7.66–7.71 (2 × m, 6 and 4 H, respectively, 2 × C_6H_5).

IR: $\nu = 3070, 2955, 2925, 2855, 1635, 1460, 1425, 1380, 1110, 1075, 870, 825, 740, 700$ cm^{-1}.

4-(tert-Butyldiphenylsilyloxy)-2-[(tributylstannyl)methyl]but-1-ene **(24)**:

^{1}H NMR (300 MHz): $\delta = 0.88$ (t, $J_{4'',3''} = 7.2$ Hz, 3 × 4″-H_3), superimposes 0.79–0.95 (m, 3 × 1″-H_2), 1.05 (s, t-Bu), 1.18–1.38 (m, 3 × 3″-H_2), 1.40–1.53 (m, 3 × 2″-H_2), 1.73 (s flanked by Sn satellites, $^2J_{H,Sn} = 60.5$ Hz, 1′-H_2), 2.21 (m_c which is essentially a t modified by Sn satellites, $J_{3,4} = 7.0$ Hz, 3-H_2), 3.77 (t, $J_{4,3} = 7.2$ Hz, 4-H_2), 4.42 and 4.52 (2 × m_c, Sn satellites visible as $^4J_{H,Sn} \approx 19$ and $^4J_{H,Sn} \approx 18$ Hz, 1-H_2), 7.31–7.45 and 7.65–7.72 (2 × m, 6 and 4 H, respectively, 2 × C_6H_5).

IR: ν = 3070, 2925, 1625, 1460, 1425, 1110, 865, 735, 700 cm^{-1}.

4-(Phenylthio)-2-[(tributylstannyl)methyl]but-1-ene (**25**):

^1H NMR (300 MHz): δ = 0.71–1.01 (m, 3 × 1″-H_2), superimposes 0.88 (t, $J_{4'',3''} = 7.5$ Hz, 3 × 4″-H_3), 1.21–1.59 (m, 3 × 2″-H_2, 3 × 3″-H_2), 1.78 (s flanked by Sn satellites, $^2J_{H,Sn} = 59.1$ Hz, 1′-H_2), 2.25 (t, $J_{3,4} = 7.9$ Hz, 3-H_2), 3.04 (m_c, presumably interpretable as t, $J_{4,3} = 7.9$ Hz, 4-H_2), 4.51 and 4.59 (d flanked by Sn satellites, $J_{gem} = 1.1$, $^4J_{H,Sn} = 17.0$ Hz, and br s flanked by Sn satellites, $^4J_{H,Sn} = 18.9$ Hz, 1-H_2), 7.13–7.21 and 7.24–7.37 (2 m, 1 and 4 H, respectively, C_6H_5).

IR: ν = 3070, 2920, 1625, 1580, 1460, 1375, 1255, 1075, 1020, 865, 735, 690 cm^{-1}.

*(E)-2-Methyl-1-(tributylstannyl)but-2-ene (E-***26***):*

^1H NMR (300 MHz): δ = 0.83 (m_c, 3 × 1′-H_2), 0.89 (t, $J_{4',3'} = 7.2$ Hz, 3 × 4′-H_3), 1.30 (m_c, interpretable as tq, $J_{3',2'} = J_{3',4'} = 7.2$ Hz, 3 × 3′-H_2), 1.39–1.61 (m, 3 × 2′-H_2), superimposed by 1.57 (s, 4-H_3, 3-CH_3), 1.73 (s flanked by Sn satellites, $^2J_{H,Sn} = 58.8$ Hz, 1-H_2), 5.03 (qm_c, $J_{3,4} = 6.3$ Hz, 3-H).

IR: ν = 2955, 2920, 1660, 1460, 1375, 1210, 1075, 870, 815 cm^{-1}.

*(E)-5-(tert-Butyldiphenylsilyloxy)-2-methyl-5-phenyl-1-(tributylstannyl)pent-2-ene (E-***27***):*

^1H NMR [300 MHz, impurity at δ = 0.89 (t)]: δ = 0.72 (m_c, 3 × 1′-H_2), 0.88 (t, $J_{4',3'} = 7.2$ Hz, 3 × 4′-H_3), 1.03 (s, *t*-Bu), 1.16–1.59 (m, 2-CH_3, 3 × 2′-H_2, 3 × 3′-H_2), superimposes 1.56 (s, presumably with a Sn satellite on the free lowfield side, $^2J_{H,Sn} \approx 60$ Hz, 1-H_2), AB signal ($\delta_A = 2.30$, $\delta_B = 2.44$, $J_{AB} = 14.1$, in addition split by $J_{A,3} = J_{A,5} = 7.2$, $J_{B,3} = 8.0$, $J_{B,5} = 5.7$ Hz, 4-H_2), 4.56 (dd, $J_{5,4\text{-}H(A)} = 7.9$, $J_{5,4\text{-}H(B)} = 5.3$ Hz, 5-H), 4.86 (br t with shoulders indicating partially superimposed Sn satellites, $J_{3,4\text{-}H(A)} = J_{3,4\text{-}H(B)} = 7.5$ Hz, 3-H), 7.16–7.26 and 7.29–7.48 and 7.67–7.74 (3 × m, 3 × C_6H_5).

IR: ν = 2925, 1460, 1375, 1110, 1070, 940, 865, 825, 740, 700 cm^{-1}.

Diethyl Hexane-1,1-dicarboxylate (29):

Diethyl malonate (**28**; 4.74 mL, 5.04 g, 31.2 mmol) was added dropwise to a hot solution of NaOEt (Na: 0.7178 g, 31.22 mmol, 1.0 equiv) in EtOH (25 mL) followed 5 min later by 1-bromopentane (4.07 mL, 4.95 g, 32.8 mmol, 1.05 equiv). The solution was refluxed until the pH was neutral (3 h) and then concentrated to half of its volume. The resulting precipitate was dissolved in ice-cold H_2O (12 mL), and the phases were separated. Extraction with *t*-BuOMe (3 × 15 mL), drying ($MgSO_4$), and a fractionating distillation (125 °C/20 mbar) gave **29**; yield: 4.961 g (69 %).

^1H NMR (200 MHz): δ = 0.88 (t, $J_{6,5} = 6.5$ Hz, 6-H_3), 1.27 (t, $J_{2',1'} = 7.2$ Hz, 2 × 2′-H_3), superimposes in part 1.20–1.40 (m, 3-H_2, 4-H_2, 5-H_2), 1.80–1.97 (m, 2-H_2), 3.31 (t, $J_{1,2} = 7.6$ Hz, 1-H), 4.19 (q, $J_{1',2'} = 7.1$ Hz, 2 × 1′-H_2).

IR: ν = 2960, 2865, 1735, 1460, 1370, 1220, 1155, 1120, 1035 cm^{-1}.

2-Methyleneheptan-1-ol (30):[29]

A solution of **29** (10.14 g, 44.03 mmol) in dry dimethoxyethane (15 mL) was added dropwise to a suspension of NaH (1.268 g, 52.83 mmol, 1.2 equiv) in the same solvent (90 mL). After refluxing for 5 h, $LiAlH_4$ (4.394 g, 0.1158 mmol, 2.64 equiv) was added at 0 °C. The solution was heated at reflux for another 3 h. Ethyl formate (3 mL) was added at 0 °C and subsequently H_2O (4.4 mL), 15 % NaOH (4.4 mL), and more H_2O (14 mL). Filtration, extraction of the liquid phases with *t*-BuOMe (3 × 30 mL), drying ($MgSO_4$), evaporation of the solvent, and distillation (bp 40 °C at ca. 10^{-2} mbar) gave **30**; yield: 4.143 g (73 %).

^1H NMR [200 MHz; impurity at δ = 3.34–3.60 (m)]: δ = 0.89 (t, $J_{7,6} = 7.2$ Hz, 7-H_3), 1.17–1.55 (m, OH, 4-H_2, 5-H_2, 6-H_2), 2.06 (t, $J_{3,4} = 7.5$ Hz, 3-H_2), 4.08 (d, $J_{1,OH} = 5.7$ Hz, 1-H_2), 4.87 and 5.01 (2 m_c, 2=CH_2); the assignment of the OH resonance was verified by H/D exchange.

IR: ν = 3330, 3085, 2955, 2930, 2860, 1650, 1455, 1380, 1235, 1100, 1030, 895, 725 cm^{-1}.

3-(*tert*-Butyldiphenylsilyloxy)-2-methylprop-1-ene (32):

A solution of *tert*-butyldiphenylsilyl chloride (17.5 mL, 15.9 g, 58.0 mmol, 1.05 equiv) in THF (10 mL) was added dropwise to a solution of methallyl alcohol (**31**; 4.70 mL, 4.00 g, 55.5 mmol) and imidazole (4.15 g, 61.0 mmol, 1.1 equiv) in THF (60 mL). After 1 h, Et_2O (70 mL) and sat. aq NH_4Cl (50 mL) were added. Phase separation, extraction of the aqueous phase with Et_2O (3 × 30 mL), drying ($MgSO_4$), and flash chromatography (petroleum ether/Et_2O 100:1 → 25:1) gave **32**; yield: 16.87 g (98 %).

^1H NMR (200 MHz): δ = 1.06 [s, $C(CH_3)_3$], 1.69 (br s, 2-CH_3), 4.07 (br s, 3-H_2), 4.86 and 5.13 (2 m_c, 1-H_2), 7.33–7.49 and 7.63–7.80 (2 m, 6 and 4 H, respectively, 2 × C_6H_5).

IR: ν = 3370, 2930, 2895, 2855, 1655, 1465, 1430, 1415, 1390, 1360, 1260, 1110, 1005, 895, 825, 740, 700, 615, 505 cm^{-1}.

2-[(*tert*-Butyldiphenylsilyloxy)methyl]prop-2-en-1-ol (33):

2.47 M BuLi in cyclohexane (2.94 mL, 7.26 mmol, 2.3 equiv) was added at 0 °C to a stirred solution of 2,2,6,6-tetramethylpiperidine (1.26 mL, 1.05 g, 7.42 mmol, 2.3 equiv) in toluene (20 mL). After 30 min, 1.0 M Et_2AlCl in hexane (7.26 mL, 7.26 mmol, 2.2 equiv) was added.[30] After another 30 min, **34** (1.077 g, 3.299 mmol) in toluene (5 mL) was added via cannula so slowly that the added solution entered the reaction mixture precooled because it descended the inside wall of the reaction flask. After 3 h more at 0 °C, HCl/H_2O (1:5; 20 mL), H_2O (100 mL), and *t*-BuOMe (200 mL) were added. Extraction with *t*-BuOMe (5 × 120 mL), drying (Na_2SO_4), and flash chromatography (petroleum ether/*t*-BuOMe 10:1 → 5:1) gave **33**; yield: 0.9027 g (84 %).

^1H NMR [200 MHz; singlet resonances of contaminant(s) at δ = 1.12 and 3.84)]: δ = 1.07 [s, $C(CH_3)_3$], 1.81 (t, $J_{OH,1} = 6.1$ Hz, OH), 4.18 (d, $J_{1,OH} = 5.4$ Hz, 1-H_2), 4.26 (s, 1′-H_2), 5.12 and 5.15 (2 m_c, 3-H_2), 7.30–7.48 and 7.62–7.81 (2 m, 6 and 4 H, respectively, 2 × C_6H_5).

IR: ν = 3375, 3070, 3050, 2960, 2930, 2855, 1590, 1470, 1425, 1390, 1360, 1190, 1110, 940, 910, 825 cm^{-1}.

1-(*tert*-Butyldiphenylsilyloxy)-2,3-epoxy-2-methylpropane (34):

Compound **32** (0.5552 g, 1.787 mmol) was added at 0 °C to a suspension of $NaHCO_3$ (0.3007 g, 3.575 mmol, 2.0 equiv) and 70 % MCPBA (0.8813 g, 3.575 mmol, 2.0 equiv) in CH_2Cl_2 (5 mL). Stirring was continued for 3 h at 0 °C and for another 3 h at r.t., excess peracid was reduced with sat. aq Na_2SO_3, and CH_2Cl_2 (30 mL) and sat. aq $NaHCO_3$ (13 mL) were added. Phase separation, extraction of the aqueous phase with CH_2Cl_2 (3 × 10 mL), drying ($MgSO_4$), and flash chromatography (petroleum ether/Et_2O 10:1) yielded the title compound; yield: 0.5573 g (96 %).

^1H NMR (200 MHz): δ = 1.06 [s, $C(CH_3)_3$], 1.38 (s, 2-CH_3), 2.59 (d, $J_{gem} = 5.2$ Hz, 3-H^1), 2.71 (d, $J_{gem} = 5.1$ Hz, 3-H^2), 3.66 (s, 1-H_2), 7.31–7.48 and 7.60–7.80 (2 m, 6 and 4 H, respectively, 2 × C_6H_5).

IR: ν = 3050, 2960, 2930, 2855, 1650, 1560, 1470, 1430, 1360, 1190, 1115, 1010, 935, 895, 825, 805 cm^{-1}.

4-(*tert*-Butyldiphenylsilyloxy)-2-methylbut-1-ene (36):

According to the procedure described for **32**, 3-methylbut-2-en-1-ol (4.69 mL, 4.00 g, 46.3 mmol), imidazole (3.47 g, 50.9 mmol, 1.1 equiv), and *tert*-butyldiphenylsilyl chloride (14.63 mL, 13.36 g, 48.61 mmol, 1.05 equiv) gave **36**; yield: 16.87 g (99 %).

^1H NMR (200 MHz): δ = 1.05 [s, $C(CH_3)_3$], 1.68 (s, 2-CH_3), 2.28 (t, $J_{3,4} = 6.7$ Hz, 3-H_2), 3.76 (t, $J_{4,3} = 6.9$ Hz, 4-H_2), 4.69 and 4.75 (2 m_c, 1-H_2), 7.32–7.48 and 7.60–7.75 (2 m, 6 and 4 H, respectively, 2 × C_6H_5).

IR: ν = 3050, 2930, 2855, 1660, 1590, 1470, 1430, 1390, 1360, 1110, 1070, 1005, 890, 825, 740, 700, 615, 505 cm^{-1}.

4-(*tert*-Butyldiphenylsilyloxy)-2-methylenebutan-1-ol (37):

According to the procedure in ref 30 described for **33**, 2.47 M BuLi in cyclohexane (1.39 mL, 3.42 mmol, 2.2 equiv), 2,2,6,6-tetramethylpiperidine (0.59 mL, 0.50 g, 3.5 mmol, 2.3 equiv), 1.0 M Et_2AlCl in hexane (3.42 mL, 3.42 mmol, 2.2 equiv) and epoxide **38** (0.5297 g, 1.556 mmol) gave **37**; yield: 0.4369 g (83 %).

^{1}H NMR (200 MHz): $\delta = 1.05$ [s, $C(CH_3)_3$], 2.25 (t, $J_{OH,1} = 5.6$ Hz, OH), 2.35 (t, $J_{3,4} = 6.1$ Hz, 3-H_2), 3.77 (t, $J_{4,3} = 6.3$ Hz, 4-H_2), 4.08 (d, $J_{1,OH} = 5.6$ Hz, 1-H_2), 4.89 and 5.07 (2 m_c, 2=CH_2), 7.33–7.50 and 7.58–7.73 (2 m, 6 and 4 H, respectively, 2 × C_6H_5).

IR: ν = 3360, 3050, 2930, 2855, 1650, 1590, 1470, 1425, 1390, 1360, 1255, 1190, 1110, 1030, 900, 820, 740, 700, 615 cm^{-1}.

4-(*tert*-Butyldiphenylsilyloxy)-1,2-epoxy-2-methylbutane (38):
According to the procedure described for **34**, the olefin **36** (0.5982 g, 1.843 mmol), $NaHCO_3$ (0.3106 g, 3.686 mmol, 2.0 equiv), and 70 % MCPBA (0.9089 g, 3.686 mmol, 2.0 equiv) gave **38**; yield: 0.5618 g (90 %).

^{1}H NMR [(200 MHz; impurity at $\delta = 1.53$ (m_c)]: $\delta = 1.05$ [s, $C(CH_3)_3$], 1.31 (s, 2-CH_3), AB signal ($\delta_A = 1.69$, $\delta_B = 1.91$, $J_{AB} = 14.1$ Hz, in addition split by $J_{A,4} = 7.0$, $J_{B,4} = 5.8$, $^4J_{B,1\text{-}H(1)} = 0.7$ Hz, 3-H_2), 2.59 (dd, $J_{gem} = 5.0$, $^4J_{1\text{-}H(1),3\text{-}H(B)} = 0.7$ Hz, 1-H^1), 2.70 (d, $J_{gem} = 5.1$ Hz, 1-H^2), 3.77 (dd, $J_{4,3\text{-}H(A)} = 6.8$, $J_{4,3\text{-}H(B)} = 5.9$ Hz, 4-H_2), 7.32–7.44 and 7.60–7.71 (2 m, 6 and 4 H, respectively, 2 × C_6H_5).

IR ($CDCl_3$): ν = 3070, 2935, 2860, 1770, 1470, 1430, 1390, 1215, 1105 cm^{-1}.

2-[2-(Phenylthio)ethyl]prop-2-en-1-ol (41):
Chloro(phenylthio)methane[31] (2.54 g, 16.0 mmol, 1.3 equiv) was added at r.t. to a suspension of activated Zn powder[31] (3.14 g, 48.0 mmol, 4.0 equiv) in THF (5 mL). After 3 h the residual Zn was allowed to settle down. The supernatant solution was transferred via cannula to a – 78 °C suspension of LiCl (1.36 g, 32.0 mmol, 2.7 equiv) and CuCN (1.43 g, 16.0 mmol, 1.3 equiv) in THF (12 mL). The mixture was warmed to 0 °C for 5 min and cooled again to – 78 °C. Ethyl 2-(bromomethyl)prop-2-enoate[32] (2.82 g, 12.0 mmol, 1.0 equiv) in THF (5 mL) was added.The solution was warmed to r.t. After 2 h, H_2O (40 mL) was added. Extraction with *t*-BuOMe (3 × 20 mL) yielded a crude sample of ester **40** (2.5965 g), which was directly reduced with 1.0 M DIBAL in hexane (24.2 mL, 24.2 mmol, 2.2 equiv) in THF (40 mL) at – 78 °C. After 1 h the mixture was warmed to r.t. and quenched after a further 4 h with sat. aq Na/K tartrate soln (30 mL). Extraction with *t*-BuOMe (3 × 20 mL) and flash chromatography (petroleum ether/*t*-BuOMe 10 : 1 → 5 : 1) gave the title compound; yield: 1.5389 g (66 %).

^{1}H NMR (300 MHz; slightly impure: $\delta = 1.54$ (br s, OH), 2.42 (br t, $J_{1',2'} = 7.6$ Hz, 1'-H_2), 3.07 (t, $J_{2',1'} = 7.8$ Hz, 2'-H_2), 4.10 (br s, 1-H_2), 4.95 and 5.12 (2 dm_c, 3-H_2), 7.14–7.39 (m, C_6H_5).

IR: ν = 3465, 3070, 2930, 1755, 1680, 1640, 1585, 1465, 1375, 1195, 1110, 910, 825, 735 cm^{-1}.

4-Methyl-1-phenyl-3-(phenylthio)pent-4-en-1-ol (43):
At – 78 °C a solution of methallyl phenyl sulfide (1.134 g, 6.904 mmol) in THF (6.5 mL) was added dropwise to a solution of 1.78 M BuLi in hexane (4.3 mL, 7.7 mmol, 1.1 equiv) in THF (4 mL). After 15 min the mixture was warmed to – 30 °C and stirred for 40 min. Styrene oxide (0.78 mL, 0.83 g, 6.9 mmol, 1.1 equiv) was added over 5 min after recooling to – 78 °C. After 45 min the mixture was warmed to – 30 °C and stirred for 2 h. The reaction was quenched with sat. aq NH_4Cl (20 mL). Extraction with *t*-BuOMe (3 × 20 mL), drying ($MgSO_4$), and flash chromatography (petroleum ether/t-BuOMe 20 : 1 → 15 : 1) gave the title compound; yield: 1.092 g (57 %); 82 : 18 mixture of unassigned diastereomers.

^{1}H NMR (300 MHz, contains *t*-BuOMe): $\delta = 1.83$ (br s, lowfield side presumably superimposed by 4-CH_3 [minor diastereomer], 4-CH_3 [major diastereomer]), AB signal which towers over multiplet of minor diastereomer ($\delta_A = 2.00$, $\delta_B = 2.18$, $J_{AB} = 13.8$ Hz, in addition split by $J_{A,3} = 9.4$, $J_{A,1} = 4.2$, $J_{B,1} = 9.2$, $J_{B,3} = 6.0$ Hz, 2-H_2 [major diastereomer]), 2.07 (d, $J_{OH,1} = 3.8$ Hz, OH [major diastereomer]), both signals presumably superimpose the signals of 2-H_2 [minor diastereomer] and OH [minor diastereomer], 3.78 (dd, $J_{3,2\text{-}H(1)} = 8.7$, $J_{3,2\text{-}H(2)} = 6.4$ Hz, 3-H [minor diastereomer]), 3.88 (dd, $J_{3,2\text{-}H(A)} = 9.0$, $J_{3,2\text{-}H(B)} = 6.0$ Hz, 3-H [major diastereomer]), 4.62 (br s, 5-H^1 [minor diastereomer]), 4.68 (br s, 5-H^1 [major diastereomer]), 4.75–4.81 (m, 5-H^2 [major diastereomer] and [minor diastereomer], 1-H [major diastereomer]), 4.99 (incompletely resolved ddd, $J_{1,2\text{-}H(1)} = 8.4^*$, $J_{1,2\text{-}H(2)} = 4.7^*$, $J_{1,OH} = 3.9^*$ Hz, 1-H [minor diastereomer]), 7.22–7.40 (m , 2 × C_6H_5); *assignments interchangeable.

IR: ν = 3400, 3065, 2940, 1640, 1580, 1480, 1440, 1375, 1025, 895, 745, 695 cm^{-1}.

5-(*tert*-Butyldiphenylsilyloxy)-2-methyl-5-phenyl-3-(phenylsulfinyl)-pent-1-ene (44):
Sulfide **45** (0.6262 g, 1.1979 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added at – 10 °C to a solution of 70 % (MCPBA, 0.3084 g, 1.251 mmol, 1.05 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred for 3 h, filtered from precipitated solids, extracted with sat. aq Na_2CO_3 (2 × 30 mL), and dried ($MgSO_4$). Flash chromatography (petroleum ether/*t*-BuOMe 10 : 1 → 4: 1) gave the title compound; yield: 0.4455 g (69 %); mixture of 4 diastereomers.

^{1}H NMR (300 MHz; contains *t*-BuOMe): $\delta = 0.91$, 0.94, and 0.97 (3 × s, 3 × *t*-Bu), 1.23, 1.30, and 1.38 (fourth signal superimposed; 3 × s, 2-CH_3), 1.81–2.07 and 2.09–2.57 (2 × m, 4-H_2), [2.73 (dd, $J^*_{3,4} = 11.1$, $J^*_{3,5} = 4.0$ Hz), 3.28 (dd, $J^*_{3,4} = 10.7$, $J^*_{3,5} = 3.6$ Hz), and 3.37 (dd, $J^*_{3,4} = 10.0$, $J^*_{3,5} = 3.9$ Hz), 3-H], [4.08 and 4.30 (2 × s), 4.30 (!) and 4.42 (2 × s), 4.75 and 4.78 (2 × s with finesplitting), 4.82 and 4.85 (2 × s with finesplitting), 1-H_2], [4.48 (dd, $J^*_{5,3} = 9.8$, $J^*_{5,4} = 4.5$ Hz), 4.54 (dd, $J^*_{5,3} = 9.4$, $J^*_{5,4} = 5.3$ Hz), 4.63 (dd, $J^*_{5,3} = J^*_{5,4} = 4.2$ Hz), superimposes in part 4.66 (dd, $J^*_{5,3} = J^*_{5,4} = 3.4$ Hz), 5-H], 6.96–7.50 and 7.56–7.71 (2 × m, 3 and 17 H, respectively, 4 × C_6H_5); *assignments interchangeable.

IR: ν = 3065, 2935, 2860, 1590, 1430, 1365, 1200, 1080, 850, 745, 700 cm^{-1}.

5-(*tert*-Butyldiphenylsilyloxy)-2-methyl-5-phenyl-3-(phenylthio)pent-1-ene (45):
tert-Butyldiphenylsilyl chloride (0.54 mL, 0.58 g, 2.1 mmol, 1.05 equiv) was added dropwise at 0 °C to a solution of the diastereomeric sulfides **43** (0.5721 g, 2.0112 mmol) and imidazole (0.2739 g, 4.023 mmol, 2.0 equiv) in CH_2Cl_2 (5 mL). After stirring at r.t. for 2 h, $MgSO_4$ (0.5 g) and petroleum ether (30 mL) were added, and the solid was removed by filtration. Purification by flash chromatography (petroleum ether/*t*-BuOMe 25 : 1) gave the title compound; yield: 0.9637 g (97 %); 81 : 19 mixture of unassigned diastereomers.

^{1}H NMR (300 MHz, sample contains *t*-BuOMe): $\delta = 0.99$ (br s, *t*-Bu), 1.47 (br s, 2-CH_3 [minor diastereomer]), 1.60 (br s, 2-CH_3 [major diastereomer]), AB signal ($\delta_A = 1.98$, $\delta_B = 2.23$, $J_{AB} = 14.0$ Hz, in addition split by $J_{A,3} = J_{A,5} = 6.9$, $J_{B,3} = J_{B,5} = 7.0$ Hz, 4-H_2 [major diastereomer]), superimposes partially 1.92–2.07 and 2.13–2.27 (2 × m, 4-H_2 [minor diastereomer]), 3.31 (dd, $J_{3,4\text{-}H(1)} = 9.3^*$, $J_{3,4\text{-}H(2)} = 5.8^*$ Hz, 3-H [major diastereomer]), 3.40 (dd, $J_{3,4\text{-}H(A)} = J_{3,4\text{-}H(B)} = 7.3$ Hz, 3-H [major diastereomer]), 4.20 (br s, J_{gem} not resolved, 1-H^1 [major diastereomer]), 4.28 (br s, J_{gem} not resolved, 1-H^1 [minor diastereomer]), 4.51 (dd, $J_{gem} = J_{1\text{-}H(2),3} = 1.5$ Hz, 1-H^2 [major diastereomer]), 4.56 (dd, $J_{gem} = J_{1\text{-}H(2),3} = 1.5$ Hz, 1-H^2 [minor diastereomer]), 4.64 (dd, $J_{5,4\text{-}H(1)} = 8.1^{**}$, $J_{5,4\text{-}H(2)} = 5.3^{**}$ Hz, 5-H [minor diastereomer]), 4.84 (dd, $J_{5,4\text{-}H(A)} = J_{5,4\text{-}H(B)} = 6.6$ Hz, 5-H [major diastereomer]), 7.12–7.44 and 7.66–7.70 (m, 4 × C_6H_5); *, **assignments interchangeable.

IR: ν = 3065, 2930, 2855, 1585, 1430, 1370, 1105, 1070, 825, 740, 700 cm^{-1}.

(*E*)-5-(*tert*-Butyldiphenylsilyloxy)-2-methyl-5-phenylpent-2-en-1-ol (46):
A solution of the diastereomeric sulfides **44** (0.4000 g, 0.7424 mmol, 1.0 equiv) in MeOH (4 mL) was added to a stirred solution of $(MeO)_3P$ (0.44 mL, 0.46 g, 3.7 mmol, 5.0 equiv) in MeOH (10 mL). After 3 h at r.t. and 4 h of refluxing, the solvent was evaporated in vacuo and H_2O (10 mL) and *t*-BuOMe (20 mL) were added. Extraction with *t*-BuOMe (3 × 10 mL), drying (Na_2SO_4), and flash chromatography (petroleum ether/*t*-BuOMe 6 : 1) gave **46**; yield: 0.2604 g (81 %).

^{1}H NMR (300 MHz): $\delta = 0.90$ (t, $J_{OH,1} = 6.5$ Hz, OH), 1.02 [s, $C(CH_3)_3$], 1.35 (br s, 2-CH_3), AB signal ($\delta_A = 2.31$, $\delta_B = 2.47$, $J_{A,B} = 14.1$ Hz, in addition split by $J_{A,3} = J_{A,5} = 6.8$, $J_{B,3} = J_{B,5} = 7.1$ Hz, 4-H_2), 3.78 (br d, $J_{1,OH} = 6.0$ Hz, 1-H_2), 4.70 (t, $J_{5,4} = 6.0$ Hz, 5-H), 5.14 (tm_c, $J_{3,4} = 7.4$ Hz, 3-H), 7.17–7.48 and 7.68–7.74 (2 × m, 13 and 2 H, respectively, 3 × C_6H_5).

IR: ν = 3380, 3065, 2930, 2860, 1590, 1430, 1365, 1200, 1110, 1070, 940, 825, 740, 700 cm^{-1}.

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(1) (a) Yamamoto, Y. *Chem. Rev.* **1993**, *93*, 2207.
(b) *Tetrahedron*, Tetrahedron Symposium-in-Print No. 36 (Guest Editor: Yamamoto, Y.) **1989**, *45*, 909.
(c) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.
(2) The chemistry of these reagents was reviewed: Sato, T. *Synthesis* **1990**, 259.
(3) Winter, E.; Brückner, R. *Synlett* **1994**, 1049.
(4) Naruta, G.; Maruyama, K. *Chem. Lett.* **1979**, 881.
(5) Keck, G.E.; Tonnies, S.D. *Tetrahedron Lett.* **1993**, *34*, 4607.
(6) Takeda, T.; Ogawa, S.; Ohta, N.; Fujiwara, T. *Chem. Lett.* **1987**, 1967. The presence of HMPA and CuBr was essential for the success of this reaction.
(7) Reich, H.J.; Ringer, J.W. *J. Org. Chem.* **1988**, *53*, 455.
(8) Trost, B.M.; Herndon, J.W. *J. Am. Chem. Soc.* **1984**, *106*, 6835.
(9) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1987**, *28*, 215.
(10) Matsubara, S.; Wakamatsu, K.; Marizawa, J.; Tsuboniwa, N.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1196.
(11) For example: Cabral, J.A.; Cohen, T.; Doubleday, W.W.; Duchelle, E.F.; Fraenkel, G.; Guo, B.S.; Yü, S.H. *J. Org. Chem.* **1992**, *57*, 3680.
(12) (a) Matarasso-Tchiroukhine, E.; Cadiot, P. *C.R. Acad. Sci. Paris Sér. C* **1972**, *274*, 2118.
(b) Abel, E.W.; Rowley, R.J. *J. Organomet. Chem.* **1975**, *84*, 199.
(13) Warner, B.P.; Buchwald, S.L. *J. Org. Chem.* **1994**, *59*, 5822.
(14) Carofiglio, T.; Marton, D.; Tagliarini, G. *Organometallics* **1992**, *11*, 2961.
(15) Naruta, Y.; Nishigaishi, Y.; Maruyama, K. *Chem. Lett.* **1986**, 1857.
(16) For related stereoselective reactions with *trans*-cinnamyl chloride cf. Tanigawa, Y.; Moritani, I.; Nishida, S. *J. Organomet. Chem.* **1971**, *28*, 73 or Tanaka, H.; Abdul Hai, A.K.M.; Ogawa, H.; Torii, S. *Synlett* **1993**, 835.
(17) Mortlock, S.V.; Thomas, E.J. *Tetrahedron Lett.* **1988**, *29*, 2479.
(18) Ueno, Y.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 1893.
(19) Keck, G.E.; Palani, A.; McHardy, S.F. *J. Org. Chem.* **1994**, *59*, 3113.
(20) Ueno, Y.; Aoki, S.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 5414.
(21) Weigand, S. Diplomarbeit, Universität Göttingen, 1994.
(22) Matarasso-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976**, *121*, 155.
(23) Corey, E.J.; Yu, C.-M.; Kim, S.S. *J. Am. Chem. Soc.* **1989**, *111*, 5495.
(24) Overman, L.E.; Renhowe, P.A. *J. Org. Chem.* **1994**, *59*, 4138.
(25) For the preparation of an allylstannane from an allyl tosylate and Me_3SnLi see also Quintard, J.-P.; Degeil-Castaing, M.; Dumartin, G.; Rahm, A.; Pereyre, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1004. In this case, the C=C bond could only be *cis* because it was part of a cyclohexene.
(26) Still, W.C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.
(27) Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(28) Goeppel, D.; Brückner, R. unpublished results.
(29) The second step of this sequence was performed following a procedure by Noda, G.; Kikuchi, M. *Synth. Commun.* **1985**, *15*, 1243.
(30) Method: Yasuda, A.; Tanaka, S.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 6513.
(31) Preparation of the zinc reagent: Rao, S.A.; Chou, T.-S.; Schipor, J.; Knochel, P. *Tetrahedron* **1992**, *48*, 2025.
(32) Villieras, J.; Rambaud, M. *Synthesis* **1982**, 924.
(33) Review of applications of this method: Hoffmann, R.W. *Angew. Chem.* **1979**, *91*, 625; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.