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Supporting information

Intramolecular Coupling of Allyl Carboxylates with Allylstannanes and Allylsilanes: A New Type of Reductive Elimination Reaction?

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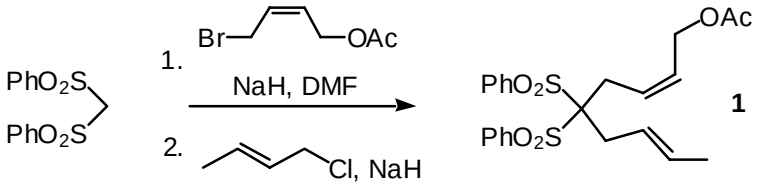
Methods: NMR spectra were recorded at 23 °C. Elemental analyses were performed at the UAM (SIdI). Solvents were purified and dried using standard procedures. Chromatography purifications were carried out using flash grade silica gel with distilled solvents. Extractive workup refers to partitioning of the crude reaction between an organic solvent and water, phase separation, drying (Na_2SO_4 or $MgSO_4$), and evaporation under reduced pressure. The saturated aqueous NH_4Cl solution was adjusted to pH 8 by addition of NH_4OH. All reactions were carried out under Ar.

In the Schemes the shorter notation "$Pd(dba)_2$" is used instead of $Pd_2(dba)_3 \cdot dba$.

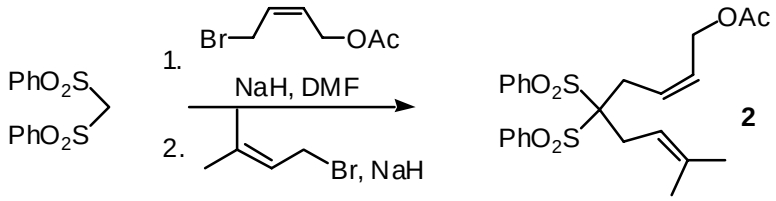
Substrates for the Oppolzer cyclizations of Scheme 2



5,5-Bis(phenylsulfonyl)-2,7-nonadien-1-ol Acetate (1). A mixture of bisphenylsulfonylmethane (1.300 g, 4.4 mmol) and NaH (175 mg, 4.4 mmol) in DMF (20 mL) was stirred at 23 °C for 30 min and (*Z*)-1-acetoxy-4-bromo-2-butene[1] (846 mg, 4.4 mmol) and the mixture was heated at 50 °C for 5 h. The resulting solution was transferred via cannula to a suspension of NaH (175 mg, 4.4 mmol) in DMF (5 mL). Crotyl chloride (399 mg, 4.4 mmol) was immediately added and the

[1] W. Reppe, *Justus Liebigs Ann. Chem.* **1955**, *596*, 80.

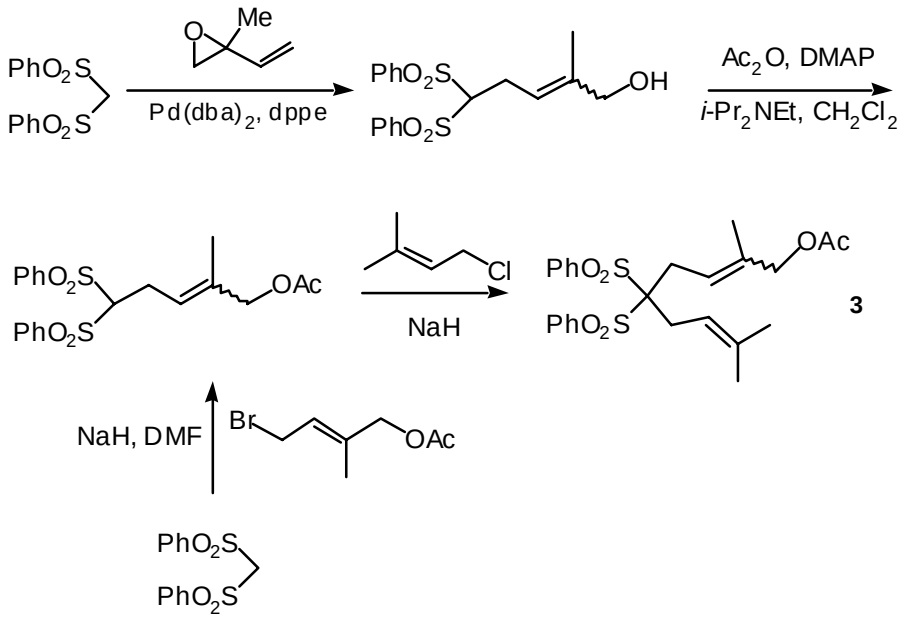
mixture was heated at 50 °C for 12 h. After being cooled to room temperature and extractive workup (Et_2O), the residue was chromatographed (4:1 hexane-EtOAc) to give **1** (1.476 g, 73%) as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.42 (m, 4H), 7.73- 7.60 (m, 2H), 7.59-7.54 (m, 4H), 5.92 (dtt, *J* = 10.9, 6.5, 1.6 Hz, 1H), 5.69 (dtt, *J* = 10.9, 6.8, 2.0 Hz, 1H), 5.63-5.53 (m, 2H), 4.53 (dd, *J* = 6.8, 1.6 Hz, 2H), 3.02-2.96 (m, 4H), 2.05 (s, 3H), 1.67 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.66, 136.67, 134.59, 132.25, 131.44, 128.51, 127.43, 125.45, 121.79, 90.08, 60.35, 60.07, 32.32, 31.54, 27.44, 22.62, 20.86, 18.07, 14.08. Anal. Calcd for $C_{23}H_{26}O_6S_2$: C, 59.72; H, 5.67; S, 13.86. Found, C, 59.33; H, 5.68; S, 13.90.



(*Z*)-1,1-Bis(phenylsulfonyl)-3-penten-5-ol Acetate . To a suspension of NaH (60 %, 697 mg, 10.5 mmol) in DMF (20 mL) at 0 °C was added a solution of 1,1-bis(phenylsulfonyl)methane (3.100 g, 10.5 mmol) and (*Z*)-1-acetoxy-4-bromo-2-butene (2.00 g, 10.5 mmol) and the mixture was stirred at 23 °C for 17 h. After the extractive workup (Et_2O), the residue was chromatographed (1:1 hexane-EtOAc) to give the acetate as a vitreous solid (5.03 g, quantitative): ^{1}H NMR (300 MHz, $CDCl_3$) δ 95-7.91 (m, 4H), 7.72-7.65 (m, 2H), 7.59-7.51 (m, 4H), 5.72-5.42 (m, 2H), 4.66 (t, *J* = 6.3 Hz, 1H), 4.47 (d, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 6.3 Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.65, 137.71, 134.65, 129.57, 129.12, 127.87, 127.39, 83.16, 59.73, 23.81, 20.86.

5,5-Bis(phenylsulfonyl)-7-methyl-2,7-nonadien-1-ol Acetate (2). To a suspension of NaH (161 mg, 4.03 mmol) in DMF, a solution of the above acetate (1.4 g, 3.35 mmol) was added followed by prenyl bromide (600 mg, 4.03 mmol). The mixture was stirred at 23 °C during 12 h, then quenched with H_2O. After extractive work-up and chromatography (4:1 hexanes:EtOAc) **2** was obtained as colorless oil (1.5 g, 93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.02 (m, 4H), 7.72-7.69 (m, 2H), 7.62-7.57 (m, 4H), 5.93-5.85 (m, 1H), 5.74-5.66 (m, 1H), 5.29-5.25 (m, 1H), 4.54 (dd, *J* = 6.6, 1.3 Hz, 2H), 3.04 (dd, *J* = 6.5, 1.8 Hz, 2H), 2.94 (d, *J* = 6.5 Hz, 2H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.52 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.59, 136.90, 136.54, 134.50, 131.35,

128.45, 127.45, 125.49, 114.90, 90.34, 60.02, 27.61, 27.00, 25.97, 20.84, 18.12.



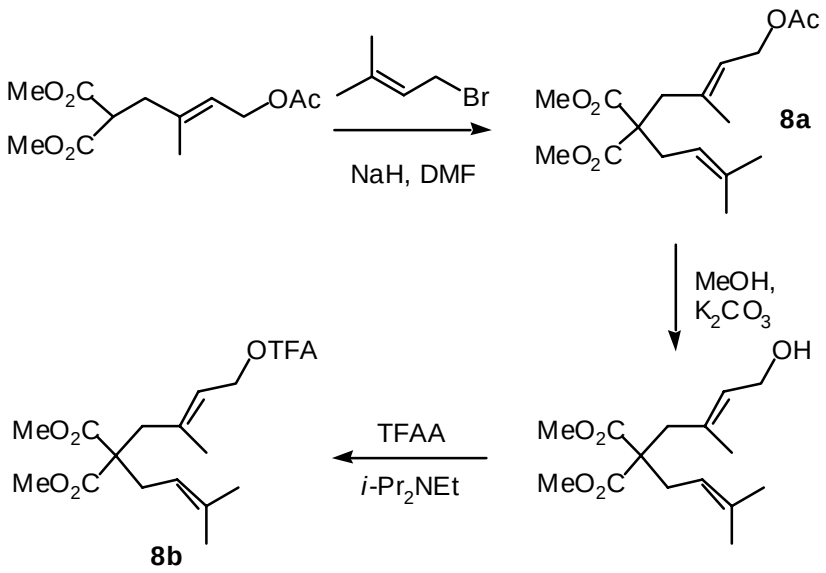
5,5-Bis(phenylsulfonyl)-2-methyl-2-penten-1-ol. To a solution of bis(phenylsulfonyl)methane (1.50 g, 5.06 mmol), $Pd_2(dba)_3 \cdot dba$ (290 mg, 0.25 mmol, 5 mol%), and dppe (200 mg, 0.51 mmol, 10 mol%) in THF (15 mL) at 23 °C was added 2-methyl-2-vinyloxirane (0.50 mL, 424 mg, 5.06 mmol). The resulting mixture was stirred at 23 °C for 16 h. The solvent was eliminated and the residue was chromatographed (1:1 hexane-EtOAc) to give the title compound (1.90 g, 98%) as a white solid (1:1 *E/Z* isomers mixture): mp 70-72 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.96-7.90 (m, 4H), 7.73-7.51 (m, 6H), 5.40 (t, *J* = 7.0 Hz, 1H, *E*), 5.16 (t, *J* = 7.5 Hz, 1H, *Z*), 4.56 (t, *J* = 5.9 Hz, 1H, *Z*), 4.50 (t, *J* = 6.1 Hz, 1H, *E*), 4.01 (d, *J* = 5.9 Hz, 2H, *E*), 3.92 (d, *J* = 6.0 Hz, 2H, *Z*), 2.99 (t, *J* = 6.3 Hz, 2H, *Z*), 2.93 (t, *J* = 6.3 Hz, 2H, *E*), 1.72 (s, 3H, *Z*), 1.50 (s, 3H, E); ^{13}C NMR (75 MHz, $CDCl_3$) δ (*Z*) 139.05, 137.92, 134.59, 129.40, 129.06, 121.12, 83.78, 61.14, 24.19, 21.65. Anal. Calcd for $C_{18}H_{20}O_5S_2$: C, 56.82; H, 5.30; S, 16.85. Found: C, 56.95; H, 5.31; S, 16.56.

5,5-Bis(phenylsulfonyl)-2-methyl-2-penten-1-ol Acetate. Method a: To a solution of above alcohol (2.10 g, 5.39 mmol), pyridine (0.48 mL, 5.9 mmol), and DMAP (30 mg, 0.25 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added Ac_2O (0.56 mL, 5.9 mmol) and the mixture was stirred at 23 °C for 3 h. After the extractive workup (CH_2Cl_2), the residue was chromatographed (2:3 hexane-EtOAc) to give the title compound (2.30 g, 99%) as a colorless oil (mixture of isomers). **Method b:** To a suspension of NaH (64 mg, 60% in

mineral oil, 1.60 mmol) in DMF (10 mL) at 23 °C was added bis(phenylsulfonyl)methane (469 mg, 1.60 mmol) dissolved in DMF (2 mL). After being stirred for 15 min, (*E*)-1-acetoxy-4-bromo-3-methyl-2-butene[2] (300 mg, 1.46 mmol) was added. After being stirred at 23 °C for 16 h, the mixture was diluted with Et_2O, washed with 10% aqueous HCl, dried ($MgSO_4$), and evaporated. The residue was chromatographed (7:3 hexane-EtOAc) to give the title compound (370 mg, 61%) as a vitreous solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ7.93 (d, *J* = 7.0 Hz, 4H), 7.75-7.65 (m, 2H), 7.60-7.50 (m, 4H), 5.45-5.30 (m, 1H), 4.70 (t, *J* = 5.9 Hz, 1H, *Z*), 4.47 (t, *J* = 5.9 Hz, 1H, *E*), 4.41 (s, 2H, *Z*), 4.32 (s, 2H, *E*), 3.05-2.90 (2H), 2.05 (s, 3H, *E*), 2.03 (s, 3H, *E*), 1.63 (s, 3H, *Z*), 1.50 (s, 3H, *E*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 70.53, 137.86, 137.75, 134.53, 134.43, 134.14, 129.40, 128.99, 123.20, 121.77, 83.31, 83.08, 68.59, 62.42, 24.18, 23.91, 21.15, 20.72, 13.76, (several signals were overlapping).

5,5-Bis(phenylsulfonyl)-2,8-dimethyl-2,7-nonadien-1-ol Acetate (3). A mixture of the above acetate (727 mg, 1.72 mmol) and NaH (60% in mineral oil, 76 mg, 1.89 mmol) was stirred for 30 min at 23 °C and prenyl bromide (282 mg, 1.89 mmol) was added. The mixture was stirred at 23 °C for 4 h. After extractive workup (Et_2O), the residue was chromatographed (7:3 hexane-EtOAc) to give **3** (650 mg, 77%) as a colorless oil and recovered starting material (130 mg, conversion: 82%). Yield corrected for conversion: 91%. ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) • 8.06 –8.01 (m, 4H), 7.72-7.66 (m, 2H), 7.59-7.54 (m, 4H), 5.67-5.65 (m, 1H, *Z*), 5.65-5.58 (m, 1H, *E*), 5.33-5.28 (m, 1H), 4.48 (bs, 2H, *E*), 4.45 (bs, 2H, *Z*), 3.03 (m, 4H, *E*), 2.97 (m, 4H, *Z*), 2.08 (s, 3H, *E*), 2.07 (s, 3H, *Z*), 1.76 (d, *J* = 1.4 Hz, 3H, *E*), 1.72 (d, *J* = 1.2 Hz, 3H, *Z*), 1.57 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.71, 136.93, 136.76, 134.42, 134.14, 131.44, 128.40, 121.12, 119.76, 115.18, 90.80, 69.19, 62.75, 27.92, 27.52, 27.16, 26.04, 20.89, 20.81, 18.10, 14.22.

[2] K. Hiroi, K. Hirasawa, *Chem. Pharm. Bull.* **1994**, *42*, 186.



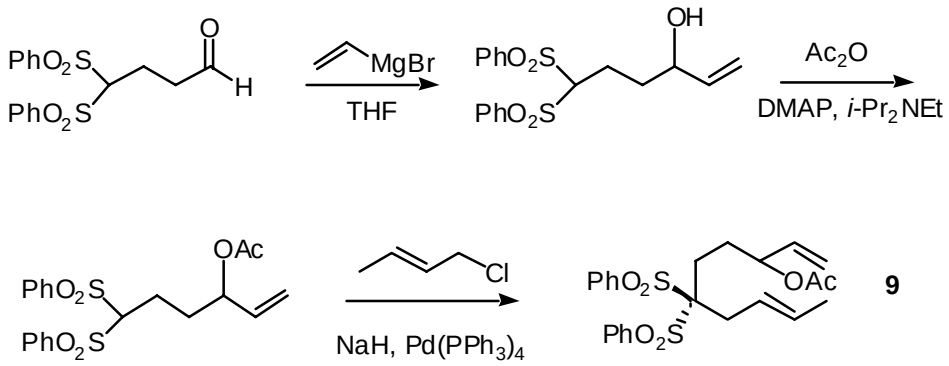
Dimethyl (*E*)-2-(4-Acetoxy-2-methyl-2-butenyl)-2-(2-propenyl)malonate (8a). To a suspension of NaH (60% in mineral oil, 330 mg, 8.47 mmol) in DMF (20 mL) was added dimethyl (*E*)-2-(4-acetoxy-2-methyl-2-butenyl)malonate[3] (1.90 g, 7.70 mmol) at 23 °C and the mixture was stirred for 15 min. To the resulting solution was added prenyl bromide (1.60 g, 10.8 mmol) and the mixture was stirred at 23 °C for 16 h. After extractive workup (EtOAc), the residue was chromatographed (9:1 hexane-EtOAc) to give **8a** (1.50 g, 62%) as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.35 (t, J = 6.9 Hz, 1H), 4.94 (tsept, J = 7.2, 1.3 Hz, 1H), 4.54 (d, J = 6.9 Hz, 2H), 3.69 (s, 6H), 2.69 (s, 2H), 2.59 (d, J = 7.3 Hz, 2H), 2.04 (s, 3H), 1.69 (d, J = 1.1 Hz, 3H), 1.61 (d, J = 0.7 Hz, 3H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.73, 170.89, 136.66, 135.50, 123.92, 117.51, 60.90, 57.43, 52.25, 41.85, 31.08, 25.95, 20.88, 17.85, 17.02; EI-MS *m/z* 294 (5), 198 (40), 166 (100), 138 (75).

Dimethyl (*E*)-2-(4-Hidroxy-2-methyl-2-butenyl)-2-(3-methyl-2-butenyl)malonate. A mixture of the **8a** (1.50 g, 4.77 mmol) and K_2CO_3 (1.98 g, 14.33 mmol) in MeOH (20 mL) at 23 °C was stirred for 18 h. The solvent was evaporated and, after extractive workup (Et_2O), the residue was chromatographed (7:3 hexane-EtOAc) to give the allylic alcohol (1.30 g, quantitative) as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.42 (t, J = 6.9 Hz, 1H), 4.97 (m, 1H), 4.14 (d, J = 6.9 Hz, 2H), 3.71 (s, 6H), 2.69 (s, 2H), 2.58 (d, J = 7.2 Hz, 2H), 1.69 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.82, 135.45, 128.78, 128.39, 117.42, 58.74, 57.56, 52.19, 41.77, 30.97, 25.83, 17.74, 16.88. Anal. Calcd

[3] M. Terakado, K. Murai, M. Miyazawa, K. Yamamoto, *Tetrahedron* **1994**, *50*, 5705.

for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.74; H, 8.17.

Dimethyl (*E*)-2-(2-methyl-4-trifluoroacetyloxy-2-butenyl)-2-(3-methyl-2-butenyl)malonate (8b). A solution of the above alcohol (380 mg, 1.33 mmol), *i*Pr_2NEt (258 mg, 1.99 mmol) and TFAA (418 mg, 1.99 mmol) in Cl_2Cl_2 (10 mL) was stirred at 23 °C for 30 min. After extractive workup (Et_2O), the residue was chromatographed (9:1 hexane-EtOAc) to give **8b** (480 mg, 95%) as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.40 (t, *J* = 7.8 Hz, 1H), 4.93 (tsept, *J* = 7.0, 1.4 Hz, 1H), 4.82 (d, *J* = 7.2 Hz, 2H), 3.70 (s, 6H), 2.72 (s, 2H), 2.59 (d, *J* = 7.2 Hz, 2H), 1.69 (s, 3H), 1.68 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.54, 140.44, 135.78, 121.08, 117.29, 64.19, 57.45, 52.30, 41.82, 31.31, 25.91, 17.84, 17.23, (the trifluoroacetate carbon signals were not observed).



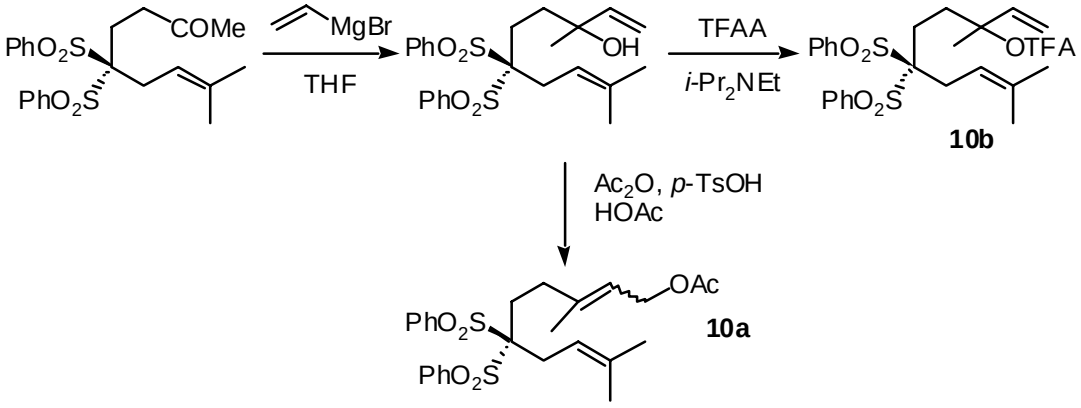
6,6-Bis(phenylsulfonyl)-1-hexen-3-ol. To a solution of 4,4-bis(phenylsulfonyl)butanal[4] (1.14 g, 3.23 mmol) in THF (30 mL) was slowly added vinylmagnesium bromide (81 mL, 1 M solution in THF, 8.10 mmol) at 0 °C and the resulting mixture was stirred at 23 °C for 2 h. Water was slowly added and, after extractive workup (Et_2O), the residue was chromatographed (1:1 hexane-EtOAc) to give the alcohol (1.20 g, 98%) as a white solid; mp: 82-84 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98-7.93 (m, 4H), 7.74-7.66 (m. 2H), 7.61-7.54 (m, 4H), 5.79 (ddd, *J* = 17.2, 10.2, 5.9 Hz, 1H), 5.20 (dm, *J* = 17.0 Hz, 1H), 5.10 (dm, *J* = 10.7 Hz), 4.76 (t, *J* = 5.4 Hz), 4.20-4.00 (m, 1H), 2.36-2.26 (m, 2H), 1.93-1.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.86, 137.80, 137.74, 134.45 (2C), 129.54, 129.48, 129.02 (2C), 115.21, 82.88, 72.29, 34.02, 21.09. Anal. Calcd for $C_{18}H_{20}O_5S_2$: C, 56.82; H, 5.30; S, 16.85. Found: C, 56.95; H, 5.35; S, 16.06.

6,6-Bis(phenylsulfonyl)-1-hexen-3-ol Acetate. To a solution of the above alcohol (940 mg, 2.5 mmol), *i*Pr_2NEt (0.52 mL, 2.7 mmol), and DMAP (30 mg, 0.25 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added Ac_2O (0.26 mL, 2.7 mmol) and the mixture was

[4] E. Gómez-Bengoa, J. M. Cuerva, C. Mateo, A. M. Echavarren, *J. Am. Chem. Soc.* **1996**, *118*, 8553.

stirred at 23 °C for 3 h. After the extractive workup (CH_2Cl_2), the allylic acetate (980 mg, 98 %) was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 4H), 7.72- 7.69 (m, 2H), 7.68-7.54 (m, 4H), 5.69 (ddd, J = 17.2, 10.5, 5.6 Hz, 1H), 5.21-5.18 (m, 1H), 5.17 (d, J = 10.5 Hz, 1H), 4.53 (t, J = 5.6 Hz, 1H), 2.27- 1.99 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.18, 137.88, 137.52, 135.17, 134.63, 134.54, 129.63, 129.48, 129.09, 117.47, 82.63, 72.98, 31.82, 21.19, 21.06. Anal. Calcd for $C_{20}H_{22}O_6S_2$: C, 56.86; H, 5.25. Found, C, 56.92; H, 5.27.

(*E*)-6,6-Bis(phenylsulfonyl)-1,8-decadien-3-ol Acetate (9). To a solution of crotyl chloride (0.15 mL, 1.5 mmol) and $Pd(PPh_3)_4$ (32 mg, 0.03 mmol) in DMF (9 mL) was added a solution of the above acetate (594 mg, 1.4 mmol) and NaH (60% in mineral oil, 59 mg, 1.5 mmol) in DMF (2 mL) and the mixture was stirred at 23 °C for 15 h. After the extractive workup (Et_2O), the residue was chromatographed (4:1 hexane-EtOAc) to give **9** (350 mg, 52%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.01 (m, 4H), 7.73- 7.70 (m, 2H), 7.61-7.55 (m, 4H), 5.70 (ddd, J = 17.2, 10.5, 6.1 Hz, 1H), 5.62-5.44 (m,1H), 5.22 (dt, J =17.2, 1.2 Hz, 1H), 5.19 (dt, J = 10.5, 1.2 Hz, 1H), 5.17- 5.10 (m, 1H),2.97- 2.94 (m, 4H), 2.26-2.06 (m, 2H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ169.93, 136.84, 135.28, 135.45, 131.97, 131.32, 128.45, 121.93, 117.43, 90.82, 74.23, 32.04, 27.91, 24.87, 21.03, 18.02. Anal. Calcd for $C_{24}H_{28}O_6S_2$: C, 60.48; H, 5.92; S, 13.45. Found, C, 60.20; H, 5.53; S, 12.89.



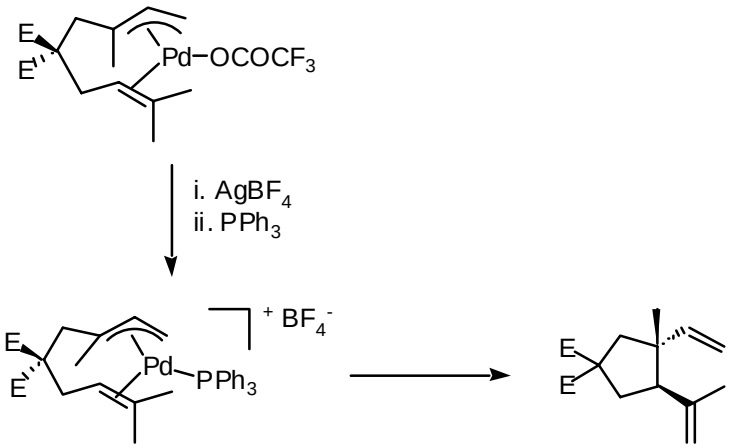
6,6-Bis(phenylsulfonyl)-3,9-dimethyl-1,8-decadien-3-ol. To a solution of 5,5-bis(phenylsulfonyl)-8-methyl-7-nonen-2-one**Fehler! Unbekanntes Schalterargument.** (2.23 g, 5.13 mmol) in THF (20 mL) at 0 °C was slowly added vinylmagnesium bromide (12.0 mL, 1M solution in THF, 12 mmol). After being stirred at this temperature for 2 h, the mixture was treated with aqueous NH_4Cl (pH 8) and extracted with Et_2O, and dried ($MgSO_4$). The mixture was evaporated and the residue was

chromatographed (1:1 hexane-EtOAc) to give the allylic alcohol (1.92 g, 81%) as a vitreous solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 4H), 7.70 (t, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 4H), 5.82 (dd, *J* = 17.0, 10.5 Hz, 1H), 5.21 (dd, *J* = 17.0, 1.3 Hz, 1H), 5.20 (m, 1H), 5.08 (dd, *J* = 10.5, 1.3 Hz, 1H), 3.00-2.90 (m, 2H), 2.35-2.25 (m, 2H), 2.00.1.85 (m, 2H), 1.72 (s, 3H), 1.53 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.88, 137.00, 136.38, 134.33, 131.31, 128.34, 115.32, 112.57, 91.45, 72.76, 35.27, 28.43, 27.46, 25.90, 23.47, 18.11.

1-Acetyloxy-6,6-bis(phenylsulfonyl)-3,9-dimethyl-2,8-decadiene (10a). A solution of the above alcohol (220 mg, 0.5 mmol) in HOAc (1 mL) was added at 0 °C over a solution of *p*-TsOH (40 mg, 0.23 mmol) in Ac_2O (1 mL) and HOAc (2 mL). The mixture was stirred at 0 °C for 1 h and at 25 °C for 1 h. After aqueous workup (5% aqueous $NaHCO_3$ and Et_2O) and drying (Na_2SO_4) the solvent was evaporated. The residue was chromatographed (10:1 hexane-EtOAc) to give **10a** (*E/Z* isomers mixture) (145 mg, 47%) as a vitreous solid. Major *E*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.12-7.97 (m, 4H), 7.71-7.54 (m, 6H), 5.34 (m, 2H), 4.57 (d, *J* = 7.0 Hz, 2H), 2.95 (d, *J* = 6.3 Hz, 2H), 2.41-2.27 (m, 4H), 2.07 (s, 3H), 1.76 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.00, 140.34, 136.61, 134.46, 131.26, 128.44, 119.61, 114.93, 91.33, 61.01, 32.77, 26.89, 26.45, 26.00, 20.99, 18.17, 16.41; EI-MS *m/z* 445 (M^+-59, 1), 302 (54), 161 (100).

6,6-Bis(phenylsulfonyl)-3,9-dimethyl-3-trifluoroacetyloxy-1,8-decadiene (10b). To a solution of the allylic alcohol (1.00 g, 2.10 mmol) and *i*Pr_2NEt (418 mg, 3.20 mmol) in CH_2Cl_2 was added $(TFA)_2O$ (672 mg, 3.20 mmol) and was stirred at 23 °C for 16 h. The mixture was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4) and evaporated. The residue was chromatographed (9:1 hexane-EtOAc) to give **10b** (950 mg, 78%) as a vitreous solid (decomposes on standing): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.04-7.90 (m, 4H), 4H), 7.70-7.45 (m, 6H), 5.83 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.22 (d, *J* = 10.4 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.00 (t, *J* = 6.0 Hz, 1H), 2.87 (d, *J* = 6.0 Hz, 2H), 2.32-2.10 (m, 4H), 1.54 (s, 6H), 1.50 (s, 3H).

Stoichiometric carbocyclization from a cationic palladium complex.

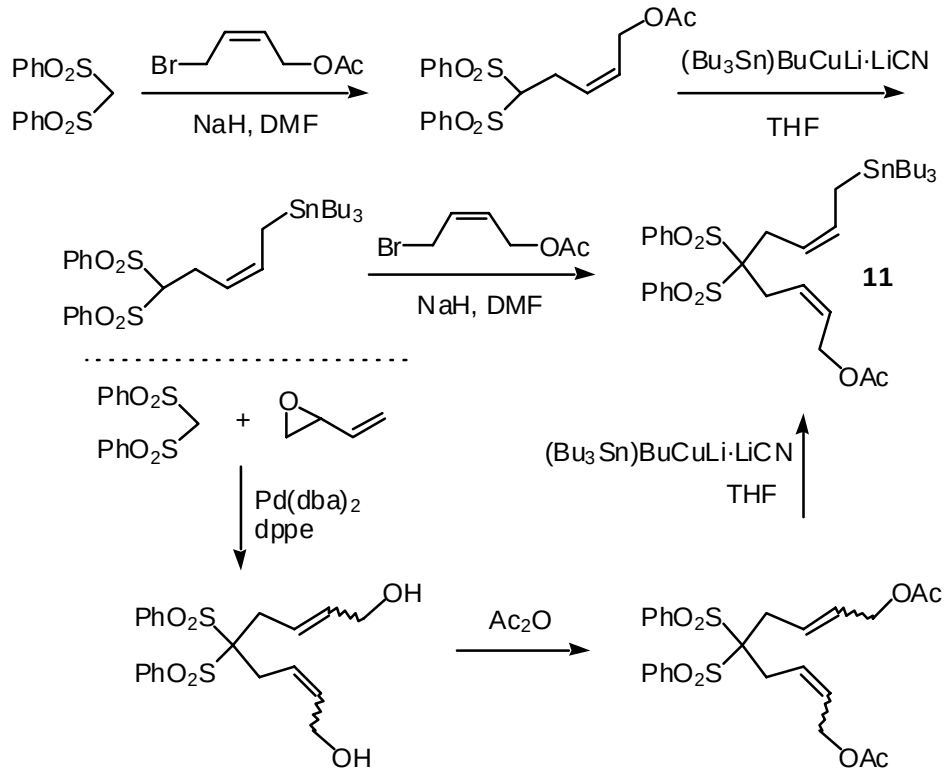


A solution of trifluoroacetate **8b** (160 mg, 0.42 mmol) and $Pd_2(dba)_3 \cdot dba$ (231 mg, 0.21 mmol) in 3:1 THF-MeCN (4 mL) at 23 °C was stirred for 30 min to give a violet solution. The solvent was evaporated and the residue was extracted with 10:1 H_2O-MeCN (10 mL). The extract was filtered through Celite and evaporated to give the palladium complex as a vitreous solid (165 mg, 75%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35-5.10 (bm, 1H), 4.93 (bs, 1H), 4.57 (bd, 1H), 4.23 (d, J = 14.1 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 2.72 (d, J = 14.5 Hz, 2H), 2.00-1.60 (m, 2H), 1.90 (bs, 3H), 1.72 (bs, 3H), 1.08 (bs, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.23, 171.09, 162.25 (q, ^2J(C,F) = 37.1 Hz), 125.51, 116.33 (q, ^1J(C,F) = 291.1 Hz), 114.43, 96.52, 86.60, 75.22, 60.15, 53.35, 52.89, 42.27, 31.17, 26.23, 20.06, 18.72. Anal. Calcd for $C_{17}H_{23}O_6F_3Pd$: C, 41.95; H, 4.76. Found: C, 41.75; H, 4.52.

The above trifluoroacetato complex was transformed into the cationic complex by treatment with $AgBF_4$ (1 equiv) in CH_2Cl_2 (5 mL) at 23 °C for 30 min. The resulting mixture was filtered through Celite and the filtrate was concentrated to give crude aquo complex, which was treated with PPh_3 in Et_2O at 23 °C to give the cationic triphenylphosphino complex. A solution of this cationic complex (62 mg, 0.12 mmol) was stirred at 23 °C for 48 h. The solvent was evaporated and the residue was chromatographed (9:1 hexane-EtOAc) to give the carbocycle as a colorless oil (10 mg, 29%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.90 (dd, J = 17.4, 10.6, Hz, 1H), 4.98 (dd, J = 17.4, 1.1 Hz, 1H), 4.96 (dd, J = 10.6, 1.1 Hz, 1H), 4.84 (bs, 1H), 4.75 (bs, 1H), 3.73 (s, 6H), 2.70-2.35 (m, 4H), 2.17 (d, J = 14.3 Hz, 1H), 1.67 (bs, 3H), 0.90 (s, 3H). The configuration was assigned as shown based on the known trans stereoselectivity for the Oppolzer cyclization.[5]

[5] Synthesis of a related compound (*cis* and *trans* isomers), but with a vinyl instead of the isopropenyl group, by a radical cyclization: C. P. Chang, S. S. Hau, T. H. Ngoi, J. *J. Chem. Res. (S)* **1991**, 216.

Synthesis of Allylstannanes



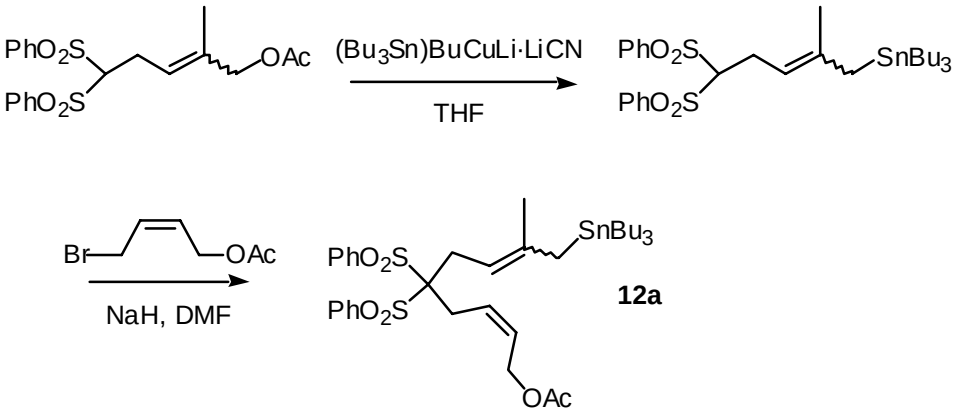
(*Z*)-5,5-Bis(phenylsulfonyl)-1-(tri-*n*-butylstannyl)-2-pentene. To a suspension of CuCN (734 mg, 8.2 mmol) in THF (30 mL) at -78 °C was added *n*BuLi (7 mL, 2.34 M solution in hexane, 16.4 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solid was cooled down to -78 °C and then nBu$_3$SnH (4.40 mL, 16.4 mmol) was slowly added to give a bright yellow solution. A solution of the above acetate (1.60 g, 3.9 mmol) in THF (40 mL) was added and the mixture was stirred at -40 °C for 12 h. The mixture was warmed up to 23 °C, and a saturated aqueous NH_4Cl solution was added. After extractive workup (Et_2O). the residue was chromatographed (9:1 hexane-EtOAc) to give the title compound as a vitreous solid (1.60 g, 64%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.97 (m, 4H), 7.93- 7.68 (m, 2H), 7.60-7.55 (m, 4H), 5.64 (dd, J = 15.0, 9.9 Hz,1H), 5.10-5.02 (m, 1H), 4.46 (t, J = 6.1 Hz, 1H), 2.86 (dd, J = 6.4, 6.1 Hz, 2H), 1.57 (d, J = 9.0 Hz, 2H),1.52-1.41 (m, 6H), 1.38-1.24 (m, 6H), 0.96-0.77 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ138.12, 134.48, 132.97, 129.68, 128.04, 116.91, 84.50, 29.12 (^3J(^{119}Sn-C) = 21 Hz), 27.34 (^2J(^{119}Sn-C) = 55 Hz), 23.50, 13.71, 10.85, 9.54 (^1J(^{119}Sn-C) = 320, ^1J(^{117}Sn-C) = 303 Hz). Anal. Calcd for $C_{29}H_{44}O_4S_2Sn$: C, 54.47; H, 6.94; S, 10.03. Found, C, 54.30; H, 6.95; S, 10.42.

5,5-Bis(phenylsulfonyl)-2,7-nonadien-1,9-diol. A mixture of bis(phenylsulfonyl)methane (550 mg, 1.86 mmol), butadiene epoxide (160 mg, 3.7 mmol), $Pd_2(dba)_3 \cdot dba$ (107 mg, 0.1 mmol), and dppe (74 mg, 0.19 mmol) in THF (5 mL) was stirred at 23 °C for 48 h. The solvent was evaporated and the residue was chromatographed (1:2 hexane-EtOAc) to give the diol (516 mg, 64%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.03 (m, 4H), 7.75-7.60 (m, 2H), 7.63-7.57 (m, 4H), 5.95-5.65 (m, 4H), 4.16-4.11 (m, 4H), 3.02-3.00 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 136.34 (C), 135.79 (CH), 134.73 (CH), 133.50 (CH), 131.41 (CH), 128.67 (CH), 122.87 (CH), 122.26 (CH), 90.11 (C), 63.14 (CH_2), 58.17 (CH_2), 31.57 (CH_2), 26.80 (CH_2). Anal. Calcd for $C_{21}H_{24}S_2O_6$: C, 57.68; H, 5.54; S, 14.69. Found: C, 57.30; H, 5.60; S, 14.20.

5,5-Bis(phenylsulfonyl)-2,7-nonadien-1,9-diol Diacetate. To a solution of the diol (487 mg, 1.1 mmol) and DMAP (30 mg, 0.25 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added *i*Pr_2NEt (0.40 mL, 2.2 mmol) and Ac_2O (0.24 mL, 2.5 mmol) and the mixture was stirred at 23 °C for 12 h. After the extractive workup (CH_2Cl_2) and the residue was chromatographed (1:1 hexane-EtOAc) to give the diacetate (547 mg, 95%) as a white solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.05- 8.02 (m, 4H), 7.72 (tt, *J* = 7.5, 1.2 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 4H), 5.94-5.85 (m, 2H), 5.74-5.63 (m, 2H), 4.54-4.50 (m, 4H), 3.02 (d, *J* = 6.9 Hz, 4H), 2.07 (s, 3H, *E*), 2.05 (s, 3H, *E*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.59, 136.40, 134.75, 131.44, 130.35, 130.21, 129.62, 129.12, 128.65, 128.12, 127.89, 126.08, 125.11, 125.02, 89.61, 64.14, 59.93, 32.74, 32.18, 27.69, 27.30, 20.86. Anal. Calcd for $C_{25}H_{28}O_8S_2$: C, 57.68; H, 5.42; S, 12.32. Found: C, 57.34; H, 5.45; S, 12.54.

9-Acetoxy-5,5-bis(phenylsulfonyl)-1-(tri-*n*-butylstannyl)-2,7-nonadiene (11). Method a: To a suspension of NaH (60 % in mineral oil, 65 mg, 1.63 mmol) in DMF (20 mL) at 0 °C was added a solution of stannane (1.00 g, 1.63 mmol) in DMF (10 mL) followed by (*Z*)-1-acetoxy-4-bromo-2-butene (3.16 mg, 1.63 mmol) and the mixture was stirred at 23 °C for 16 h. After the extractive workup (Et_2O) the residue was chromatographed (9:1 hexane EtOAc) to give **11** (1.150 g, 94%) as a colorless oil. **Method b:** To a suspension of CuCN (129 mg, 1.44 mmol) in THF (10 mL) at -78 °C was added *n*BuLi (2.38 mL, 2.5 M in hexane, 2.88 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solution was cooled down to -78 °C and *n*Bu_3SnH (0.53 mL, 2.88 mmol) was added to give a bright yellow solution. The diacetate (614 mg, 1.2 mmol) in THF (2 mL) was added and the mixture was stirred at -40 °C for 17 h. The mixture was warmed up to 23 °C, and an aqueous saturated solution of NH_4Cl was added. After extractive workup (Et_2O) the residue

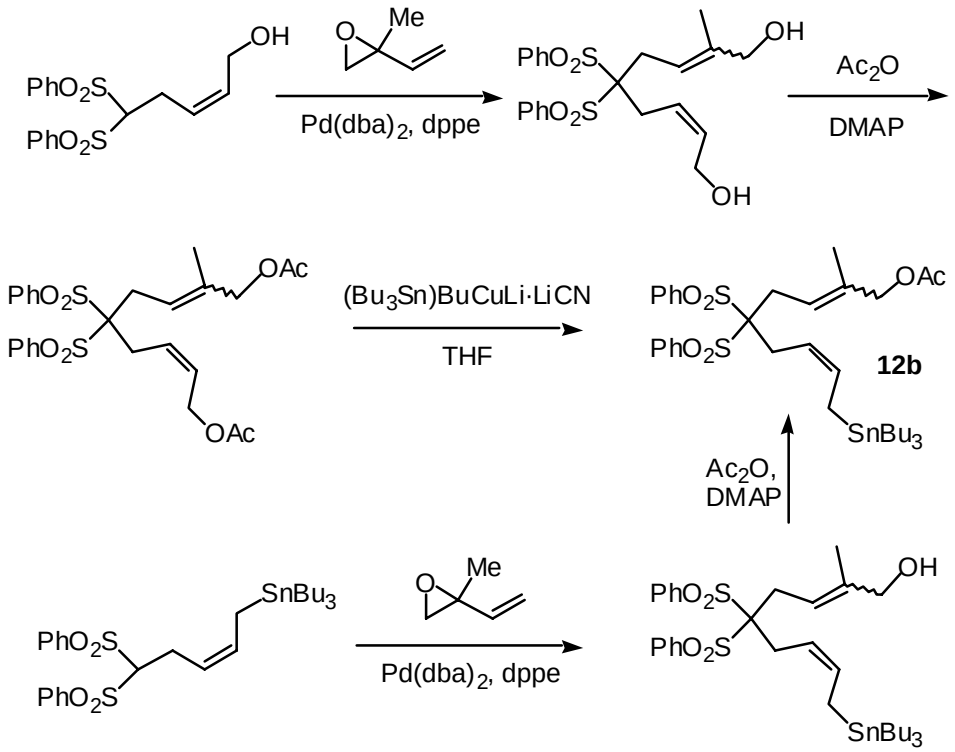
was chromatographed (9:1 hexane-EtOAc) to give **11** (560 mg, 62%) as a vitreous solid (3:2 mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 7.5, 2.1 Hz, 4H), 7.70 (tt, *J* = 7.5, 2.1 Hz, 2H), 7.56 (tt, J = 7.5, 2.1 Hz, 4H), 5.91-5.65 (m, 3H), 5.23 (m, 1H), 4.67 (d, *J* = 5.2 Hz, 2H, *E*), 4.55 (d, *J* = 6.5 Hz, *E*), 3.06 (d, *J* = 6.6 Hz, 2H), 2.91 (d, *J* = 6.5 Hz, 2H, *E*), 1.6 (d, *J* = 9.5 Hz, 2H), 1.53-1.40 (m, 6H), 1.33-1.21 (m, 6H), 0.93-0.79 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.65, 136.51, 134.48, 133.97, 131.41, 128.46, 128.00, 127.33, 125.58, 113.39, 90.39, 60.20, 59.19, 29.06 (^{3}J (^{119}Sn-C) = 21 Hz), 27.99 (^{2}J(^{117}Sn-C) = 55 Hz), 26.77, 26.26, 20.85, 13.64, 11.18, 9.56 (^{1}J(^{119}Sn-C) = 320, ^{1}J(^{117}Sn-C) = 303 Hz). Anal. Calcd for $C_{35}H_{52}O_6S_2Sn$: C, 55.93; H, 6.97; S, 8.53. Found: C, 55.77; H, 6.98; S, 8.31.



5,5-Bis(phenylsulfonyl)-2-methyl-1-(tri-*n*-butylstannyl)-2-pentene. To a suspension of CuCN (200 mg, 0.47 mmol) in THF (30 mL) at -78 °C was added *n*BuLi (8.06 mL, 2.35 M solution in hexane, 1.89 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solid was cooled down to -78 °C and then nBu$_3$SnH (0.7 mL, 1.89 mmol) was slowly added to give a bright yellow solution. A solution of the allyl acetate (1.60 g, 3.9 mmol) in THF (5 mL) was added and the mixture was stirred at -40 °C for 12 h. The mixture was warmed up to 23 °C, and a saturated aqueous NH_4Cl solution was added. After extractive workup (Et_2O), the residue was chromatographed (9:1 hexane-EtOAc) to give the allylstannane (270 mg, 87%) as a vitreous solid (1.1:1 *Z/E* mixture): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.94 (m, 4H), 7.74-7.52 (m, 6H), 4.91 (br t, *J* = 7.1 Hz, 1H, *Z*), 4.72 (br t, *J* = 7.2 Hz, 1H, *E*), 4.43 (t, *J* = 6.1 Hz, 1H, *Z*), 4.36 (t, *J* = 6.1 Hz, *E*), 2.90-2.70 (m, 2H), 1.63 (s, 3H, *Z*), 1.56 (s, 3H, *E*), 1.60-1.20 (m, 20H), 1.00-0.80 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.28, 138.21, 138.16, 134.36, 129.57, 128.98, 128.93, 113.25, 112.67, 84.61, 84.39, 29.00, 27.81, 27.33, 26.97, 26.80, 25.85, 24.79, 22.34, 18.38, 17.49, 15.53, 13.69, 9.79, 9.48. Anal. Calcd for $C_{30}H_{46}O_4S_2Sn$: C, 55.14; H, 7.09; S,

9.81. Found, C, 55.02; H, 7.09; S, 10.10.

9-Acetoxy-5,5-bis(phenylsulfonyl)-2-methyl-1-tri-*n*-butylstannyl-2,7-nonadiene (12a). To a suspension of NaH (60 % in mineral oil, 84 mg, 2.10 mmol) in DMF (20 mL) at 0 °C was added a solution of the above stannane (1.00 g, 2.10 mmol) in DMF (10 mL) followed by (*Z*)-1-acetoxy-4-bromo-2-butene (407 mg, 2.10 mmol) and the mixture was stirred at 23 °C for 16 h. After the extractive workup (Et_2O) the residue was chromatographed (9:1 hexane EtOAc) to give **12a** (1.50 g, 98%) as a colorless oil (1.1:1 mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.03 (m, 4H), 7.72- 7.66 (m, 2H), 7.60-7.53 (m, 4H), 5.96-5.81 (m, 1H), 5.73-5.65 (m, 1H), 5.12 (br t, *J* = 6.9 Hz, 1H, major isomer), 4.95 (br t, *J* = 5.7 Hz, 1H, minor isomer), 4.56 (d, *J* = 6.5 Hz, 2H, minor isomer), 4.54 (d, *J* = 5.6 Hz, 2H, major isomer), 3.06 (br d, *J* = 6.0 Hz, 2H, minor isomer), 3.02 (br d, *J* = 6.5 Hz, 2H, major isomer), 2.95 (d, *J* = 6.5 Hz. 2H, major isomer), 2.85 (d, *J* = 6.5 Hz, 2H, minor isomer), 2.06 (s, 3H), 1.76 (s, 2H, minor isomer), 1.67-1.38 (m, 8H), 1.37-1.28 (m, 6H), 0.95-0.72 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.72, 141.45, 141.14, 136.67, 136.62, 134.44, 134.40, 131.38, 128.98, 128.59, 128.40, 127.28, 127.20, 125.72, 125.59, 109.50, 109.18, 90.66, 90.58, 60.17, 29.20, 29.14, 29.06, 28.87, 27.75, 27.70, 27.58, 27.33, 26.97, 26.80, 26.66, 22.79, 20.86, 18.98, 17.49, 15.90, 13.56. 9.87, 9.56. Anal. Calcd for $C_{36}H_{54}O_6S_2Sn$: C, 56.48; H, 7.11; S, 8.37. Found, C, 56.12; H, 6.93; S, 8.28.



(*Z*)-1,1-Bis(phenylsulfonyl)-3-penten-5-ol. A solution of (*Z*)-1,1-Bis(phenylsulfonyl)-3-penten-5-ol acetate (2.20 g, 5.50 mmol) and K_2CO_3 (2.3 g, 16.30 mmol) in MeOH (20 mL) was stirred at 23 °C during 16 h. The mixture was diluted with Et_2O, washed with HCl (10%) and evaporated to give the title alcohol (1.98 g, 99%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.91 (m, 4H), 7.72-7-66 (m, 2H), 7.60- 7.53 (m, 4H), 5.58-5.69 (m, 1H), 5.58-5.49 (m, 1H), 4.54 (t, *J* = 5.8 Hz. 1H), 4.09 (t, *J* = 5.8 Hz, 2H), 3.00 (t, *J* =6.5 Hz, 2H), 1.90 (t, *J* = 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.77, 134.70, 132.21, 129.53, 129.15, 125.97, 83.68, 57.98, 23.93. Anal. Calcd for $C_{17}H_{18}O_5S_2$: C, 55.72; H, 4.95; S, 17.50. Found: C, 55.75; H 5.10; S, 17.64.

5,5-Bis(phenylsulfonyl)-2-methyl-2,7-nonadien-1,9-diol. To a solution of the above alcohol (640 mg, 2.09 mmol), $Pd_2(dba)_3$·dba (120 mg, 0.21 mmol) and dppe (83 mg. 0.21 mmol) in THF (20 mL) at 23 °C was added 2-methyl-2-vinyloxirane (0.22 mL, 2.3 mmol), and the resulting mixture was stirred at 23 °C for 17 h. The solvent was evaporated and the residue was chromatographed (1:2 hexane: EtOAc) to give the title diol (499 mg, 53 %) as a vitreous solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05-8.01 (m, 4H), 7.75-7.68 (m, 2H), 7.62-7.56 (m, 4H), 5.92-5.87 (m, 1H), 5.78-5.72 (m, 1H), 5.54-5.50 (m, 1H), 4.12-4.09 (m, 4H), 3.06-3.00 (m, 4H), 1.81 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.55, 136.62,

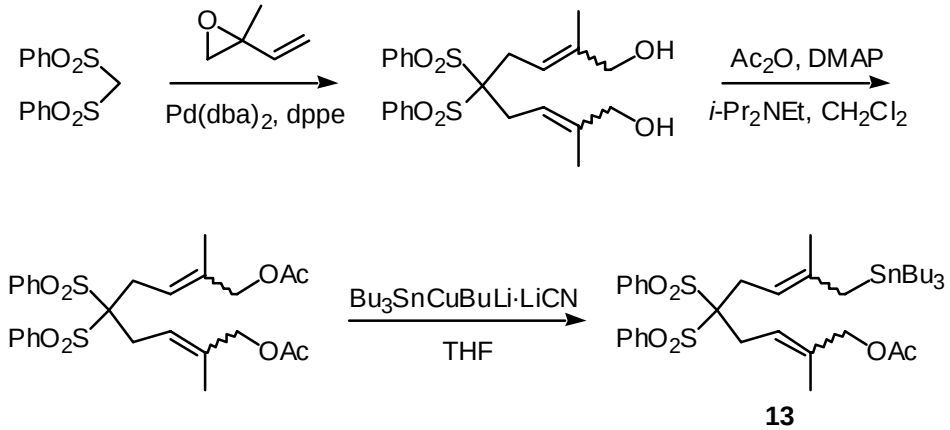
135.59, 134.64, 131.41, 128.62, 123.15, 120.06, 117.80, 90.61, 63.14, 61.16, 31.38.

5,5-Bis(phenylsulfonyl)-2-methyl-2,7-nonadien-1,9-diol Diacetate. To a solution of the above diol (600 mg, 1.58 mmol) and DMAP (5 mg) in CH_2Cl_2 (15 mL) at 23 °C was added Et_3N (0.5 mL, 1.16 mmol) and Ac_2O (0.33 mL, 1.16 mmol) and the mixture was stirred for 5 h at 23 °C. The mixture was evaporated and the residue was chromatographed (1:1 hexane-EtOAc) to give the title compound (625 mg, 74%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (dt, *J* = 8.5, 1.6 Hz, 4H), 7.69 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 4H), 5.87-5.54 (m. 3H), 4.53-4.51(m, 2H), 4.44-4.42 (m, 2H), 3.03 (d, *J* = 6.0 Hz, 2H), 2.95 (d, *J* = 6.0 Hz, 2H), 2.06 (s, 3H), 2.03 (s, 3H), 1.73 (s, 3H, *E*), 1.54 (s, 3H, *E*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.59, 170.51, 136.43, 136.29, 134.76, 134.62, 134.25, 131.25, 128.76, 128.54, 127.87, 127.82, 125.22, 125.11, 120.53, 118.85, 89.83, 89.66, 68.80, 62.55, 59.87, 27.67, 27.50, 27.63, 27.14, 21.70, 20.75, 20.67, 14.20. Anal. Calcd for $C_{26}H_{30}S_2O_8$: C, 58.41; H, 5.66; S, 12.02. Found: C, 58.71; H, 5.89; S, 12.02.

9-Hydroxy-5,5-bis(phenylsulfonyl)-1-(tri-*n*-butylstannyl)-8-methyl-2,7-nonadiene. To a solution of the allyl stannane (910 mg, 1.41 mmol), $Pd_2(dba)_3$·dba (81 mg, 0.14 mmol) and dppe (56 mg, 0.14 mmol) in THF (20 mL) at 23 °C was added 2-methyl-2-vinyloxirane (0.14 mL, 1.41 mmol), and the resulting mixture was stirred at 23 °C for 17 h. The solvent was evaporated and the residue was chromatographed (4:1 hexane: EtOAc) to give the allyl alcohol (909 mg, 85%). as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ8.10-8.00 (m, 4H), 7.70-7.65 (m, 2H), 7.57-7.51 (m, 4H), 5.81-5.71 (m, 1H), 5.64-5.49 (m, 1H, *Z*), 5.39 (bt, *J* = 6.9 Hz, 1H, *E*), 5.32-5.23 (m, 1H), 4.07 (d, *J* = 5.7 Hz, 2H, *E*), 3.97 (d, *J* = 4.9 Hz, *Z*), 3.07 (d, *J* = 7.3 Hz, 2H, *E*), 3.00 (d, *J* = 5.7 Hz, 2H, *Z*), 2.91-2.86 (m, 4H), 1.82 (d, *J* = 1.6 Hz, 3H), 1.63-1.58 (m, 5H), 1.50-1.39 (m, 6H), 1.31-1.20 (m, 6H), 0.90-0.70 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.05, 138.83, 137.01, 136.82, 134.36, 134.31, 133.78, 133.50, 131.35, 128.39, 128.34, 118.61, 116.69, 113.92, 113.84, 91.28, 90.89, 68.44, 61.30, 29.03 (^3J (^{119}Sn-C) = 21 Hz), 27.24, 27.05 (^2J(^{119}Sn-C) = 55 Hz), 26.50, 21.84, 14.03, 13.61, 11.07, 9.54 (^1J(^{119}Sn-C) = 320, ^1J(^{117}Sn-C) = 303 Hz). Anal. Calcd. for $C_{34}H_{52}O_5S_2Sn$: C, 56.43; H, 7.24; S, 8.86. Found: C, 56.77; H, 7.65; S, 8.71.

9-Acetoxy-5,5-bis(phenylsulfonyl)-1-(tri-*n*-butylstannyl)-8-methyl-2,7-nonadiene (12b). Method a: To a solution of the above alcohol (909 mg, 1.21 mmol), *i*Pr_2NEt (0.11 mL, 1.21 mmol), and DMAP (15 mg, 0.12 mmol) in CH_2Cl_2 (25 mL) at 0 °C

was added Ac_2O (0.15 mL, 1.21 mmol) and the mixture was stirred at 23 °C for 3 h. After the extractive workup (CH_2Cl_2) **12b** (890 mg, 96%) was obtained as a colorless oil. **Method b.** To a suspension of CuCN (76 mg, 0.85 mmol) in THF (10 mL) at -78 °C was added *n*BuLi (0.58 mL, 2.38 M in hexane, 1.40 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solution was cooled down to -78 °C and Bu_3SnH (0.37 mL, 1.40 mmol) was added to give a bright yellow solution. The corresponding diacetate (415 mg, 0.78 mmol) in THF (2 mL) was added and the mixture was stirred at -40 °C for 17 h. The mixture was warmed up to 23 °C, and an aqueous saturated solution of NH_4Cl was added. After the extractive workup (Et_2O) the residue was chromatographed (9:1 hexane-EtOAc) to give **12b** (224 mg, 42%) as a colorless oil (mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08-8.03 (m, 4H), 7.70 (t, J = 7.3 Hz, 2H), 7.57 (t, J = 7.8 Hz, 4H), 5.75-5.64 (m, 1H), 5.60-5.56 (m, 1H), 5.73-5.28 (m, 1H), 4.48 (s, 2H, *E*), 4.46 (s, 2H, *E*), 3.02-2.94 (m, 4H), 2.10 (s, 3H, *E*), 2.07 (s, 3H, *E*), 1.77-1.72 (m, 2H), 1.63(s, 3H, *E*), 1.62 (s, 3H, *E*), 1.56-0.98 (m, 27H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.72, 137.13, 137.03, 136.87, 134.39, 133.77, 131.49, 128.33, 121.12, 120.00, 115.20, 115.12, 90.80, 90.70, 69.30, 62.80, 32.49, 32.19, 30.90, 29.09 (^3J (^{119}Sn-C) = 21 Hz), 27.56, 27.30 (^2J(^{119}Sn-C) = 55 Hz), 21.76, 20.89, 14.87, 13.72, 9.23 (^1J(^{119}Sn-C) = 320, ^1J(^{117}Sn-C) = 303 Hz). Anal. Calcd. for $C_{36}H_{54}O_6S_2Sn$: C, 56.47; H, 7.11; S, 8.38. Found: C, 57.04; H, 6.80; S, 8.76.



13

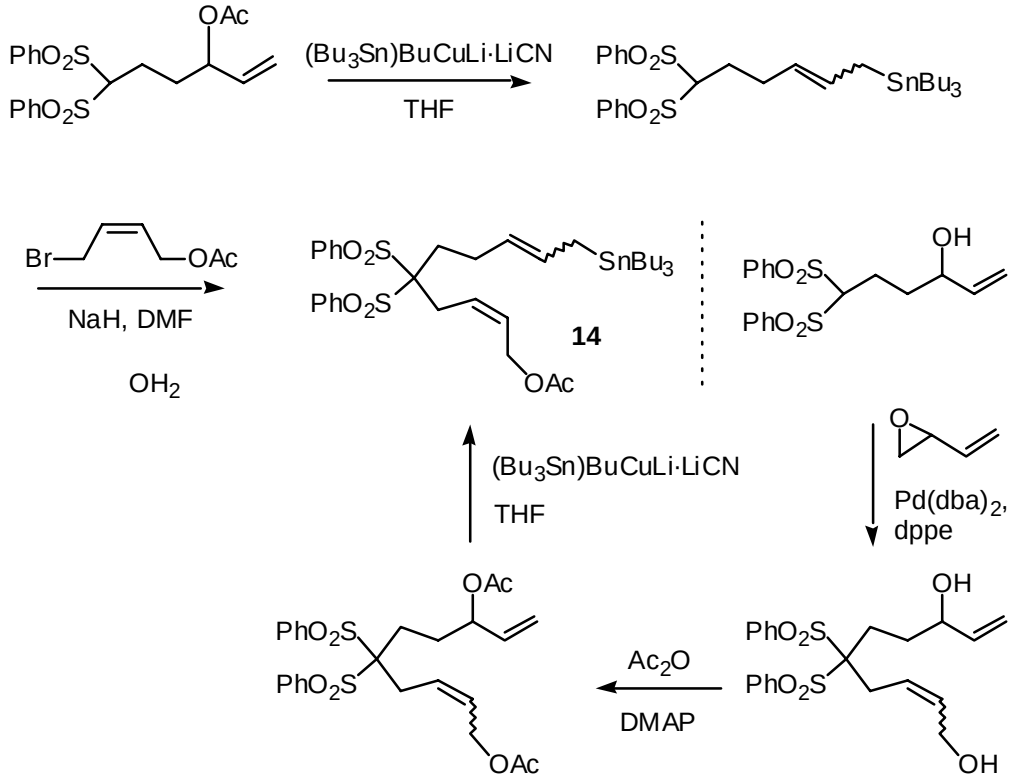
5,5-Bis(phenylsulfonyl)-2,8-dimethyl-2,7-nonadien-1,9-diol. To a solution of bis(phenylsulfonyl)methane (1.00 g, 3.80 mmol), $Pd_2(dba)_3$·dba (216 mg, 0.38 mmol) and dppe (151 mg, 0.38 mmol) in THF (30 mL) was added 2-methyl-2-vinyloxirane (0.7 mL, 7.6 mmol) and the resulting mixture was stirred at 23 °C for 17 h. The solvent was evaporated and the residue was chromatographed (1:4 hexane-EtOAc) to give the diol (1.480 g, 90%) as a vitreous solid (mixture of isomers): ^{1}H

NMR (300 MHz, $CDCl_3$) δ 8.16-7.92 (m, 4H), 7.75- 7.69 (m, 2H), 7.62-7.39 (m, 4H), 5.67 (t, *J* = 6.5 Hz, 1H, *E*), 5.55 (t, *J* = 7.5 Hz, 1H, *E*), 4.11 (br s, 2H, *E*), 4.01 (br s, 2H, *E*), 3.07 (d, *J* = 7.3 Hz, 2H, *E*), 2.99 (d, *J* = 6.5 Hz, 2H, *E*), 1.84 (s, 3H, *E*), 1.59 (s, 3H, *E*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.52, 136.51, 134.56, 131.40, 128.54, 117.71, 115.96, 90.89, 68.04, 61.01, 26.91, 26.50, 21.64, 14.03. Anal. Calcd for $C_{23}H_{28}S_2O_6$: C, 59.46; H, 6,07; S, 13.80. Found: C, 59.29; H, 5.80; S, 13.54.

5,5-Bis(phenylsulfonyl)-2,8-dimethyl-2,7-nonadien-1,9-diol Diacetate. To a solution of the above diol (340 mg, 0.73 mmol) and DMAP in CH_2Cl_2 (10 mL) at 0 °C was added *i*Pr_2NEt (0.21 mL, 1.48 mmol) and Ac_2O (0.14 mL, 1.48 mmol) and the mixture was stirred at 23 °C for 17 h. The solvent was evaporated and the residue was chromatographed (1:1 hexane-EtOAc) to give the diacetates (337 mg, 89%) as pale yellow oil (mixture of two isomers): ^1H NMR ($CDCl_3$, 200 MHz) δ 8.03 (m, 4H), 7.71 (m, 2H), 7.57 (m, 4H), 5.63 (t, *J* = 6.4 Hz, 2H, minor isomer), 5.59 (t, *J* = 7.0 Hz, 2H, major isomer), 4.48 (s, 4H, major isomer), 4.44 (s, 4H, minor isomer.), 3.05 (d, *J* = 7.0 Hz, major isomer), 2.97 (d, *J* = 6.4 Hz, minor isomer), 2.16 (s, 6H), 2.06 (s, 6H), 1.76 (s, 6H), 1.76 (s, 6H), 1.57 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.75, 136.48, 134.53, 131.35, 128.45, 120.76, 120.67, 119.28, 89.97, 68.94, 62.55, 27.81, 27.53, 27.47, 21.73, 20.81, 20.72, 14.14. Anal. Calcd for $C_{27}H_{32}S_2O_8$: C, 59.01; H, 5.88; S, 11.69. Found: C, 59.12; H; 5.96; S, 11.97.

9-Acetoxy-5,5-bis(phenylsulfonyl)-2,8-dimethyl-1-(tri-*n*-butylstannyl)2,7-nonadiene (13). To a suspension of CuCN (367 mg, 4.10 mmol) in THF (10 mL) at -78 °C was added *n*BuLi (2.5 mL, 2.38 M in hexane, 8.10 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solution was cooled down to -78 °C and *n*Bu_3SnH (2.36 g, 8.10 mmol) was added to give a bright yellow solution. The above diacetate (1.667 mg, 3.21 mmol) in THF (5 mL) was added and the mixture was stirred at -40 °C for 17 h. The mixture was warmed up to 23 °C, and an aqueous saturated solution of NH_4Cl was added. After the extractive workup (Et_2O) the residue was chromatographed (7:3 hexane-EtOAc) to give stannane **13** (580 mg, 39%; 64% conversion) as a colorless oil (mixture of isomers): ^1H NMR (300 MHz, $CDCl_3$) δ 8.17-7-92 (m, 4H), 7.79-7.42 (m, 6H), 5.77-5.38 (m, 1H), 5.25-4.89 (m, 1H), 4.65-4.31 (m, 2H), 3.15-2.70 (m, 4H), 2.09 (s, 3H, *E*), 2.08 (s, 3H, *E*), 1.84-0.53 (m, 29H); ^{13}C (75 MHz, $CDCl_3$) δ 170.56, 141.11, 140.84, 136.96, 136.82, 136.65, 134.20, 133.84, 133.64, 131.55, 131.30, 129.46, 128.84, 128.20, 121.17, 121.06, 120.03, 119.75, 109.94, 109.66, 109.32, 90.92, 90.80, 90.75, 69.22, 69.05, 62.69, 30.48, 29.09,

28.95, 28.89, 27.69, 27.61, 27.44, 27.30, 27.22, 27.08, 27.02, 26.85, 26.69, 22.67, 21.64, 20.75, 20.69, 18.77, 17.38, 15.70, 15.45, 14.14, 13.56, 13.44, 9.82, 9.76, 9.43.

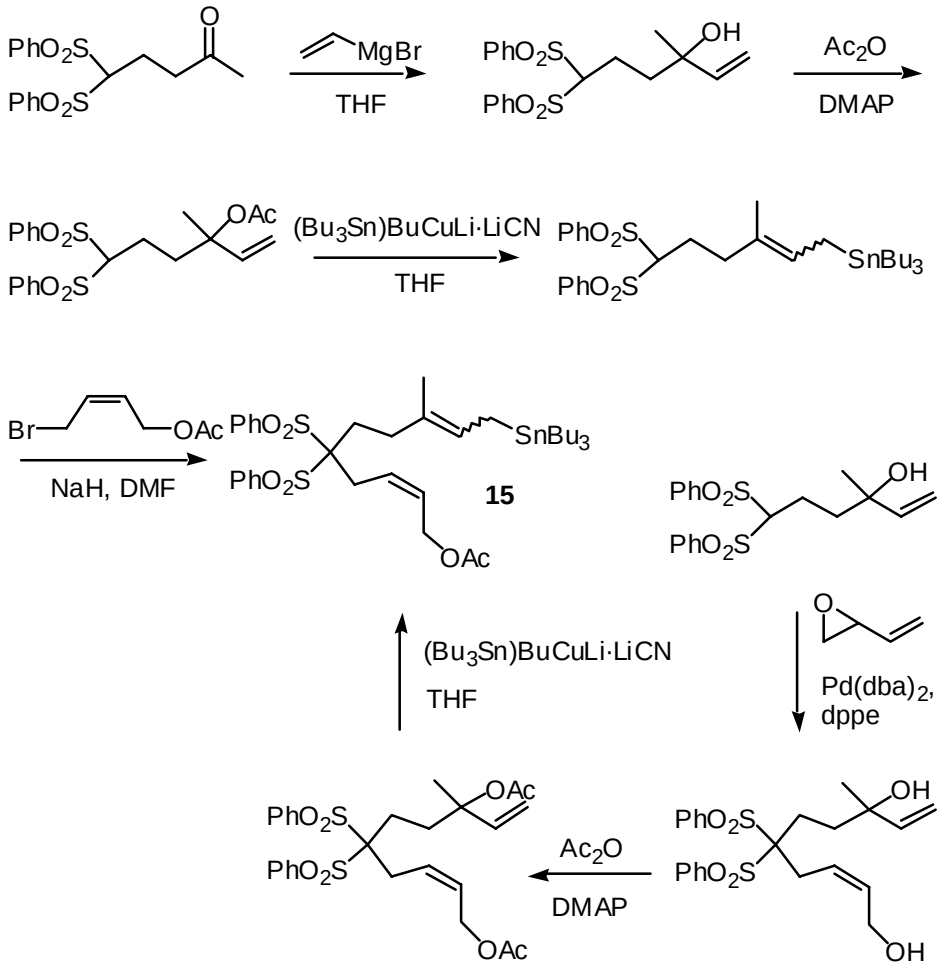


6,6-Bis(phenylsulfonyl)-1-(tri-*n*-butylstannyl)-2-hexene. To a suspension of CuCN (609 mg, 6.1 mmol) in THF (30 mL) at -78 °C was added *n*BuLi (7.2 mL, 1.90 M solution in hexane, 13.6 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solid was cooled down to -78 °C and then nBu$_3$SnH (1.40 g, 3.24 mmol) was slowly added to give a bright yellow solution. A solution of the 6,6-bis(phenylsulfonyl)-1-hexen-3-ol acetate (1.60 g, 3.9 mmol) in THF (5 mL) was added and the mixture was stirred at -40 °C for 12 h. The mixture was warmed up to 23 °C, and a saturated aqueous NH_4Cl solution (pH 8) was added. After extractive workup (Et_2O) the residue was chromatographed (9:1 hexane-EtOAc) to give the stannane (1.6 g, 80%) as a vitreous solid (1.1:1 mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.94 (m, 4H), 7.71- 7.68 (m, 2H), 7.66-7.54 (m, 4H), 5.68-5.49 (m, 2H), 4.88-4.81 (m,1H), 4.74-4.66 (m, 1H), 4.49 (t, J = 5.3 Hz, 1H, E), 4.47 (t, J = 5.4 Hz, 1H, E), 2.28-2.16 (m, 4H), 1.69 (d, J = 10.5 Hz, 2H, E), 1.63 (d, J = 8.5 Hz, 1H, E), 1.52-1.41 (m, 4H), 1.35-1.22 (m, 6H), 0.94-0.81 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.02, 134.37, 129.57, 128.96, 121.59, 82.13, 31.93, 29.05, 27.27, 27.23, 25.43, 14.34, 13.67, 9.35, 9.14.

5,5-Bis(phenylsulfonyl)-1,8-decadien-3,10-diol Diacetate. i. A mixture of 6,6-bis(phenylsulfonyl)-1-hexen-3-ol (1.508 g, 4.0 mmol), butadiene epoxide (280 mg, 4.0 mmol), $Pd_2(dba)_3 \cdot dba$ (228 mg, 0.20 mmol), and dppe (158 mg, 0.39 mmol) in THF (5 mL) was stirred at 23 °C for 12 h. The solvent was evaporated and the residue was chromatographed to give the diol (761 mg, 42%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) • 8.06-8.00 (m, 4H), 7.75-7.70 (m, 2H), 7.63-7.58 (m, 4H), 5.88-5.76 (m, 3H), 5.18 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 4.11-4.07 (m, 2H), 3.06-3.00 (m, 2H), 2.50-2.20 (m, 4H). **ii.** To a solution of 5,5-bis(phenylsulfonyl)-2,9-decadien-1,8-diol (761 mg, 1.4 mmol), Et_3N (0.44 mL, 3.1 mmol) and DMAP (5 mg) in CH_2Cl_2 (20 mL) was added Ac_2O (0.3 mL, 3.1mmol) and the mixture was stirred at 23 °C for 15 h. The solvent was evaporated and the residue was chromatographed(1:1 hexane-EtOAc) to give the title compound (600 mg, 80%) as a pale yellow solid (mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09-7.94 (m, 4H), 7.81-7.49 (m, 6H), 6.09-5.60 (m, 3H), 5.41-4.93 (m, 2H),4.80-4.43 (m, 1H), 4.27-3.64 (m, 1H), 3.28-2.70 (m, 2H), 2.35-1.82 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.51, 169.92, 136.62, 135,26, 134.64, 133.78, 132.78, 131.35, 130.32. 129.18, 129.04, 128.59, 128.45, 126.64, 126.25, 124.60, 120.00, 117.60, 90.33, 78.06, 74.18, 68.63, 66.09, 64.14, 59.49, 31.93, 27.97, 26.86, 25.18, 21.06, 20.83. Anal. Calcd for $C_{26}H_{30}O_8S_2$: C, 58.41; S, 11.99; H, 5.66. Found: C, 58.41; S, 9.53; H, 6.05.

10-Acetoxy-6,6-bis(phenylsulfonyl)-1-(tri-*n*-butylstannyl)-2,8-decadiene (14). Method a: To a suspension of NaH (60 % in mineral oil, 98 mg, 2.74 mmol) in DMF (20 mL) at 0 °C was added 6,6-bis(phenylsulfonyl)-1-(tri-*n*-butylstannyl)-2-hexene (1.60 g, 2.49 mmol) in DMF (10 mL) followed by (*Z*)-1-acetoxy-4-bromo-2-butene (500 mg, 2.74 mmol) and the mixture was stirred at 23 °C for 16 h. After extractive workup (Et_2O) the residue was chromatographed (9:1 hexane EtOAc) to give **14** (1.9 g, 94%) as a colorless oil. **Method b:** To a suspension of CuCN (138 mg, 1.54 mmol) in THF (10 mL) at -78 °C was added *n*BuLi (1.0 mL, 2.38 M in hexane, 3.08 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solution was cooled down to -78 °C and $n Bu_3SnH$ (0.8 mL, 3.08 mmol) was added to give bright yellow solution. The above acetate (600 mg, 1.12 mmol) in THF (2 mL) was added and the mixture was stirred at -40 °C for 17 h. The mixture was warmed up to 23 °C, and an aqueous saturated solution of NH_4Cl was added. After the extractive workup (Et_2O) the residue was chromatographed (9:1 hexane-EtOAc) to give **14** (290 mg, 34%) as a colorless oil (mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07- 8.02 (m, 4H), 7.72-7.60 (m, 2H), 7.57-7.55 (m, 4H), 5.99-5.88 (m, 1H),

5.79-5.67 (m, 1H), 5.63-5-52 (m, 1H), 4.97-4.86 (m, 1H), 4.57-4.52 (m, 2H), 3.09-3.06 (m, 2H), 2.31-3.03 (m, 4H), 1.69 (d, J = 8.9 Hz, 2H), 1.51-1.49 (m, 6H), 1.47-1.25 (m, 6H), 0.93-0.81 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.56, 136.99, 134.50, 131.38, 130.37, 129.74, 128.56, 126.95, 125.41, 122.88, 121.43, 119.28, 90.92, 90.86, 68.74, 66.21, 64.31, 31.96, 29.28, 29.14, 29.00, 27.69, 27.33, 26.99, 26.83, 21.08, 20.89, 14.20, 13.69, 11.49, 10.82, 9.40, 9.15. Anal. Calcd for $C_{36}H_{54}O_6S_2Sn$: C, 56.48; H, 7.11; S, 8.37. Found, C, 56.65; H, 6.89; S, 8.54.



6,6-Bis(phenylsulfonyl)-3-methyl-1-hexen-3-ol. To a solution of 5,5-bis(phenylsulfonyl)-pentan-2-one**Fehler! Unbekanntes Schalterargument.** (4.88 g, 13.5 mmol) in THF (20 mL) was slowly added at 0 °C vinylmagnesium bromide (29.8 mL, 1 M in THF, 29.8 mmol), and the mixture was stirred at 23 °C for 2 h. Water (5 mL) was slowly added and, after the extractive workup (Et_2O) the residue was chromatographed (3:7 hexane-EtOAc) to give the title allyl alcohol (4.45 g, 84%) as a white solid: mp 94-96 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ7.96-7.89 (m, 4H), 7.68 (t, J = 7.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 4H),

5.78 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 5.02 (d, *J* = 10.8 Hz, 1H) 4.76 (t, *J* = 5.9 Hz, 1H), 2.29-2.19 (m, 2H), 1.98-1.73 (m, 2H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.73, 137.97, 134.48, 129.57, 129.01, 112.71, 83.09, 73.16, 38.78, 28.42, 20.81. Anal. Calcd for $C_{19}H_{22}O_5S_2$: C, 57.84; H, 5.62; S, 16.22. Found: C, 57.93; H, 5.60; S, 16.22.

3-Acetoxy-6,6-bis(phenylsulfonyl)-3-methyl-1-hexene. To a solution of 6,6-bis(phenylsulfonyl)-3-methyl-1-hexen-3-ol (140 mg, 0.35 mmol), DMAP (48 mg, 0.39 mmol) in CH_2Cl_2 (5 mL) was added Ac_2O (0.04 mL; 0.39 mmol) and the mixture was stirred at 23 °C for 12 h. After extractive workup (Et_2O), the residue was chromatographed (7:3 hexane-EtOAc) to give the acetate (140 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ7.94-7.91 (m, 4H), 7.72-7.68 (m, 2H), 7.66-7.53 (m, 4H), 5.81 (dd, *J* = 16.6, 10.5 Hz, 1H), 5.09 (d, *J* = 10.5 Hz, 1H), 5.08 (d, *J* = 16.6 Hz, 1H), 4.37 (t, *J* = 5.7 Hz, 1H), 2.22-2.10 (m, 4H), 1.94 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 169.64 (C), 140.50 (CH), 137.71 (C), 134.62 (CH), 129.56 (CH), 129.09 (CH), 114.12 (CH_2), 83.58 (CH), 38.02 (CH_2), 23.67 (CH_3), 22.07 (CH_3), 20.30 (CH_2); EI-HRMS calcd for $C_{21}H_{24}6S_2$: 436.1014. Found: 436.1030 (M^+).

6,6-Bis(phenylsulfonyl)-3-methyl-1-(tri-*n*-butylstannyl)-2-hexene. To a suspension of CuCN (1.80 g, 20.11 mmol) in THF (40 mL) at -78 °C was added *n*BuLi (17.0 mL, 2.36 M in hexane, 40.22 mmol) and the mixture was stirred at -60 °C for 3 h. The resulting pale yellow solid was cooled down to -78 °C and then *n*Bu_3SnH (10.7 mL, 10.7 mmol) was slowly added to give a bright yellow solution. A solution of 3-acetoxy-6,6-bis(phenylsulfonyl)-3-methyl-1-hexene (4.20 g, 9.60 mmol) in THF (5 mL) was added and the mixture was stirred at -40 °C for 12 h. The mixture was warmed up to 23 °C, and a saturated aqueous NH4Cl solution (pH 8) was added. After extractive workup (Et_2O) the residue was chromatographed (9:1 hexane-EtOAc) to give the stannane (5.10 g, 84%) as a vitreous solid (3:1 mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.93 (m, 4H), 7.73-7.67 (m, 2H), 7.61-7.55 (m, 4H), 5.40 (t, *J* = 9.3 Hz, 1H, major isomer), 5.33 (br t, *J* = 8.9 Hz, 1H, minor isomer), 4.50-4.47 (m, 1H, minor isomer), 4.44 (t, *J* = 8.9 Hz, major isomer), 2.30-2.10 (m, 4H), 2.22 (br s, 3H), 1.69 (d, *J* = 9.3 Hz, 2H, major isomer), 1.62 (d, *J* = 8.9 Hz, 2H, minor isomer), 1.49-1.39 (m, 6H), 1.37-1.14 (m, 6H), 0.94-0.73 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.09, 138.02, 134.41, 129.60, 129.00 128.85, 127.15, 125.69, 125.55, 82.93, 81.94, 37.49, 29.48, 29.14, 27.95, 27.80, 27.67, 27.33, 26.97, 23.96, 23.48, 22.17, 14.75, 13.72, 13.64, 10.91, 9.46. Anal. Calcd for $C_{31}H_{43}O_4S_2Sn$: C, 55.78; H, 7.25; S, 9.61. Found, C,

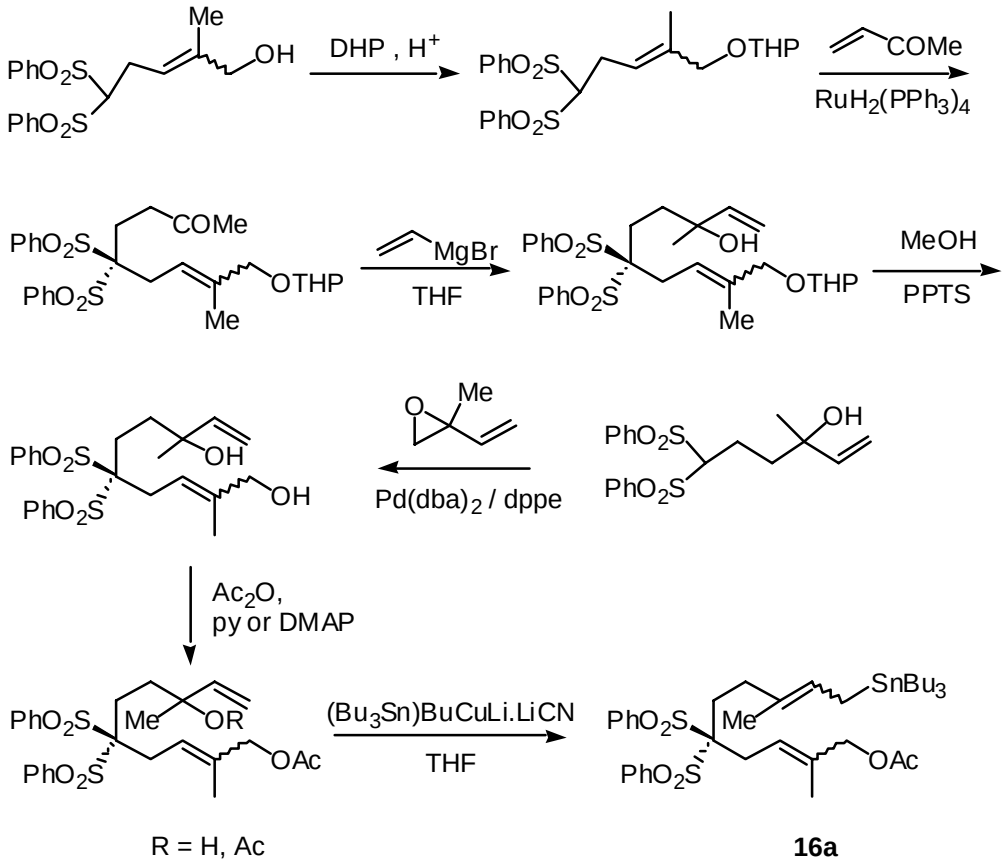
55.71; H, 6.92; S, 9.52.

5,5-Bis(phenylsulfonyl)-3-methyl-1,8-decadien-3,10-diol. To a solution of 6,6-bis(phenylsulfonyl)-3-methyl-1-hexen-3-ol (735 mg, 1.86 mmol), $Pd_2(dba)_3 \cdot dba$ (107 mg, 0.18 mmol) and dppe (74 mg, 0.18 mmol) in THF (20 mL) at 23 °C, was added butadiene epoxide (0.15 mL, 1.86 mmol) and the mixture was stirred at 23 °C for 16 h. The solvent was evaporated and the residue was chromatographed (1:2 hexane: EtOAc) to give the diol (800 mg, 96%) as a white solid (mixture of isomers): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.00 (ddd, *J* =7.0, 4.7, 1.6 Hz, 4H), 7.69 (br t, *J* = 7.0, 2H), 7.56 (br t, *J* =7.8, 4H), 5.84-5.70 (m, 3H), 5.14 (dd, *J* =18.8, 1.6 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.12-4.04 (m, 2H), 3.06-2.96 (m, 2H), 2.36-2.13 (m, 2H), 2.02-1.90 (m, 2H), 1.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.85, 143.74, 136.77, 135.35, 134.56, 132.98, 131.30, 124.50, 112.42, 91.00, 72.93, 63.03, 34.83, 31.90, 29.67, 28.64, 23.93, 1.00.

5,5-Bis(phenylsulfonyl)-3-methyl-1,8-decadien-3,10-diol Diacetate. To a solution of the above diol (800 mg, 1.7 mmol) and DMAP (5 mg) in CH_2Cl_2 (20 mL) was added Et_3N (0.53 mL, 3.8 mmol) and Ac_2O (0.36 mL. 3.8 mmol) and the mixture was stirred at 23 °C for 13 h. The solvent was evaporated and the residue was chromatographed (1:1 hexane-EtOAc) to give the title diacetate (566 mg, 61%) as a colorless oil (mixture of isomers): ^{1}H NMR (200 MHz, $CDCl_3$) (major *E*) δ 7.93 (d, *J* = 7.2 Hz, 4H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 4H), 5.76 (dd, *J* = 17.7, 11.3 Hz, 1H), 5.77-5.52 (m, 2H), 5.03 (d, *J* = 16.7, 1H), 5.02 (d, *J* = 11.8 Hz, 1H), 4.41 (d, *J* =4.8 Hz, 2H), 2.94 (d, *J* = 4.8 Hz, 2H), 2.23-2.02 (m, 4H), 1.95 (s, 3H), 1.83 (s, 3H), 1.44 (s, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 170.03, 169.06, 140.31, 136.32, 134.28, 129.79, 128.20, 125.64, 113.64, 90.22, 81.74, 63.75, 59.54, 33.16, 31.29, 28.61, 23.32, 22.20, 21.59, 20.44, 13.75, 13.33, 9.60. Anal. Calcd for $C_{27}H_{32}O_8S_2$: C, 59.11; H, 5.88; S, 11.69. Found: C, 59.24; H 6.02; S, 11. 62.

10-Acetoxy-6,6-bis(phenylsulfonyl)-3-methyl-1-(tri-*n*-butylstannyl)-2,8-decadiene (15). Method a: To a suspension of NaH (60 % in mineral oil, 23 mg, 0.35 mmol) in DMF (10 mL) at 0 °C was added 6,6-bis(phenylsulfonyl)-3-methyl-1-tri-*n*-butylstannyl-2-hexene (200 mg, 0.31 mmol) in DMF (10 mL) followed (*Z*)-1-acetoxy-4-bromo-2-butene (68 mg, 0.35 mmol) and the mixture was stirred at 23 °C for 16 h. After extractive workup (Et_2O) the residue was chromatographed (9:1 hexane EtOAc) to give **15** (230 mg, 95%) as a colorless oil. **Method b:** To a suspension of CuCN (40 mg, 0.45 mmol) in THF (10 mL) at -78 °C was added *n*BuLi (0.4 mL, 2.35 M in hexane, 0.91 mmol) and the mixture was stirred at -60 °C for

3 h. The resulting pale yellow solution was cooled down to -78 °C and *n*Bu_3SnH (2.4 mL, 0.91 mmol) was added to give bright yellow solution. A solution of the above acetate (180 mg, 0.30 mmol) in THF (2 mL) was added and the mixture was stirred at -40 °C for 17 h. The mixture was warmed up to 23 °C, and an aqueous saturated solution of NH_4Cl was added. After the extractive workup (Et_2O) the residue was chromatographed (9:1 hexane-EtOAc) to give stannane **15** (197 mg, 69%) as a colorless oil (mixture of isomers): ^1H NMR (300 MHz, $CDCl_3$) δ 8.08-8.04 (m, 4H), 7.71 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 8.1 Hz, 4H), 5.99-5.93 (m, 1H), 5.81-5.71 (m, 1H), 5.33 (t, J = 17 Hz, 1H), 4.54 (t, J = 7.3 Hz, 2H), 3.13-3.06 (m, 2H), 2.39-2.18 (m, 4H), 1.66- 0.32 (m, 30H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.56, 140.64, 137.10, 136.96, 134.48, 131.35, 129.85, 129.68, 127.00, 126.81, 125.75, 124.99, 91.08, 64.31, 64.23, 33.13, 31.99, 31.63, 29.28, 29.14, 29.00, 28.42, 27.81, 27.67, 27.30, 26.97, 26.80, 25.27, 22.70, 20.83, 17.49, 15.40, 13.69, 13.55, 11.46, 10.77, 9.40, 7.31. Anal. Calcd for $C_{37}H_{56}O_6S_2Sn$. C, 57.00; H, 7.24; S, 8.22. Found: C, 56.89; H, 7.52; S, 8.06.



R = H, Ac **16a**

5,5-Bis(phenylsulfonyl)-2-methyl-1-tetrahydropyranyloxy-2-pentene. A solution of 5,5-bis(phenylsulfonyl)-2-methyl-2-penten-1-ol (1.90 g, 5.0 mmol), DHP (840 mg, 10 mmol), and

p-TsOH (10 mg, 0.05 mmol) in CH_2Cl_2 (20 mL) was stirred at 23 °C for 24 h. After extractive workup (CH_2Cl_2), the residue was chromatographed (4:1 hexane-EtOAc) to give the title compound (2.07 g, 89%) as a vitreous solid (1:1 *E/Z* isomers mixture of isomers). The *E* was obtained as a white solid: mp 60-62 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.96-7.90 (m, 4H), 7.73-7.51 (m, 6H), 5.39 (t, *J* = 6.0 Hz, 1H, *E*), 5.34 (t, *J* = 5.9 Hz, 1H, *Z*), 4.65 (t, *J* = 6.0 Hz, 1H, *Z*), 4.54 (t, *J* = 3.5 Hz, 1H), 4.45 (t, *J* = 6.2 Hz, 1H, *E*), 3.99 (d, *J* = 12.3 Hz, 1H), 3.88-3.80 (m, 1H), 3.73 (d, *J* = 12.3 Hz, 1H), 3.54-3.46 (m, 1H), 2.91 (t, *J* = 6.5 Hz, 2H), 1.82-1.50 (m, 6H), 1.72 (s, 3H, *Z*) 1.50 (s, 3H, *E*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (*E*) 137.86, 136.23, 134.54, 129.52, 129.01, 120.38, 97.64, 83.68, 71.75, 62.11, 30.51, 25.32, 24.25, 19.35, 13.93. Anal. Calcd for $C_{23}H_{28}O_6S_2$: C, 59.46; H, 6.07; S, 13.80. Found: C, 59.41; H, 5.90; S, 13.53.

5,5-Bis(phenylsulfonyl)-8-methyl-9-tetrahydropyranyloxy-7-nonen-2-one. To a solution of 5,5-bis(phenylsulfonyl)-2-methyl-1-tetrahydropyranyloxy-2-pentene (2.60 g, 5.6 mmol), $RuH_2(PPh_3)_4$ (193 mg, 0.17 mmol, 3 mol%) in MeCN (15 mL) at 23 °C was added methyl vinyl ketone (4.78 g, 11.2 mmol) and the mixture was stirred at this temperature for 16 h. The solvent was evaporated and the residue was chromatographed (1:1 hexane-EtOAc) to give the title compound (3.00 g, 100%) as a colorless oil (1:1 *E/Z* isomers mixture of isomers): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.04-8.00 (m, 4H), 7.70-7.49 (m, 6H), 5.50 (t, *J* = 6.5 Hz, 1H, *E*), 5.31 (t, *J* = 6.5 Hz, 1H, *Z*), 4.60 (br s, 1H, *E*), 4.49 (br s, 1H, *Z*), 4.03 (d, *J* = 11.8 Hz, 1H), 3.83 (d, *J* = 11.8 Hz, 1H), 3.86-3.75 (m, 1H), 3.52-3.46 (m, 1H), 3.03-2.95 (m, 4H) 2.49 (t, *J* = 7.0 Hz, 2H), 2.14 (s, 3H), 2.01-1.50 (m, 6H), 1.72 (s, 3H, *Z*), 1.50 (s, 3H, *E*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (*Z*) 206.21, 137.14, 136.91, 134.52, 131.30, 128.59, 119.29, 97.85, 89.73, 65.30, 62.11, 37.86, 30.44, 29.96, 28.85, 25.34, 23.54, 22.22, 19.32. Anal. Calcd for $C_{27}H_{34}O_7S_2$: C, 60.65; H, 6.40; S, 11.99. Found: C, 61.05; H, 6.58; S, 11.41.

6,6-Bis(phenylsulfonyl)-3,9-dimethyl-10-tetrahydropyranyloxy-1,8-decadien-3-ol. To a solution of 5,5-bis(phenylsulfonyl)-8-methyl-9-tetrahydropyranyloxy-7-nonen-2-one (2.00 g, 3.7 mmol) in THF (30 mL) at 0 °C was added vinylmagnesium bromide (5.60 mL, 1M in THF, 5.6 mmol). The mixture was stirred at 23 °C for 2 h. An aqueous solution of NH_4Cl (pH 8; 1 mL) was added and the mixture was extracted with EtOAc, dried (Na_2SO_4), and evaporated. The residue was chromatographed (1:1 hexane-EtOAc) to give the title compound (1.55 g, 74%) as a vitreous solid (1:1 *E/Z* isomers mixture of isomers): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.04-8.00 (m, 4H), 7.70-7.49 (m, 6H), 5.91-5.70 (m, 1H), 5.70-

5.59 (m, 1H, *E*), 5.43-5.36 (m, 1H, *Z*), 5.21-4.96 (m, 2H), 4.62-4.49 (m, 1H), 4.09-4.03 (m, 1H), 3.93-3.76 (m, 2H), 3.56-3.43 (m, 1H), 3.00-2.83 (m, 2H), 2.51-2.20 (m, 2H), 2.01-1.50 (m, 8H), 1.73 (s, 3H, *Z*), 1.60 (s, 3H, *E*), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.23, 143.78, 143.45, 136.85, 136.59, 136.23, 136.11, 134.32, 131.21, 128.33, 119.53, 119.39, 119.19, 112.48, 112.14, 97.98, 97.59, 97.02, 96.85, 90.93, 72.54, 72.20, 65.38, 65.20, 62.10, 61.70, 35.58, 35.25, 30.25, 28.69, 28.31, 28.20, 27.69, 27.19, 26.73, 25.21, 23.72, 23.06, 22.01, 19.29, 19.12, 18.93. Anal. Calcd for $C_{29}H_{38}O_7S_2$: C, 61.89; H, 6.80; S, 11.39. Found: C, 61.68; H, 6.33; S, 11.52.

5,5-Bis(phenylsulfonyl)-2,8-dimethyl-2,9-decadiene-1,8-diol. Method a: A solution of 6,6-bis(phenylsulfonyl)-3,9-dimethyl-10-tetrahydropyranyloxy-1,8-decadien-3-ol (1.40 g, 2.49 mmol) and pyridinium *p*-toluenesulfonate (569 mg, 2.49 mmol) in MeOH (20 mL) was stirred at 23 °C for 16 h. The solvent was evaporated and the residue was chromatographed (1:2 hexane-EtOAc) to give the diol (910 mg, 76%) as a colorless oil (1:1 *E/Z* isomers mixture of isomers). **Method b:** To a solution of 6,6-bis(phenylsulfonyl)-3-methyl-1-hexen-3-ol (104 mg, 0.26 mmol), $Pd_2(dba)_3$·dba (15 mg, 0.01 mmol, 10 mol%) and dppe (11 mg, 0.03 mmol, 10 mol%) in THF (5 mL) at 23 °C was added methylvinyloxirane (39 mL, 33 mg, 0.39 mmol). The solution was stirred at this temperature for 16 h. The solvent was evaporated and the residue was chromatographed to give the diol (122 mg, 97%) as a colorless vitreous solid (1:1 *E/Z* isomers mixture): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.04-8.00 (m, 4H), 7.70-7.49 (m, 6H), 5.79 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.58-5.54 (m, 1H, *E*), 5.37-5.34 (m, 1H, *Z*), 5.17 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.02 (dd, *J* = 10.9, 1.2 Hz, 1H), 4.07 (s, 2H, *Z*), 3.96 (s, 2H, *E*), 3.10-2.90 (m, 2H), 2.55-2.20 (m, 2H), 2.00-1.85 (m, 2H), 1.79 (s, 3H, *Z*), 1.63 (s, 3H, *E*), 1.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.80, 143.73, 139.30, 137.15, 137.07, 136.80, 136.68, 134.46, 131.28, 129.52, 128.46, 118.45, 116.99, 112.59, 112.47, 91.72, 91.33, 72.78, 72.74, 68.15, 61.00, 35.36, 35.11, 28.46, 28.34, 27.49, 26.87, 24.48, 23.30, 21.71, 14.19 (1 carbon resonance was not observed). Anal. Calcd for $C_{24}H_{30}O_6S_2$: C, 60.22; H, 6.31; S, 13.40. Found: C, 60.07; H, 5.92; S, 13.03.

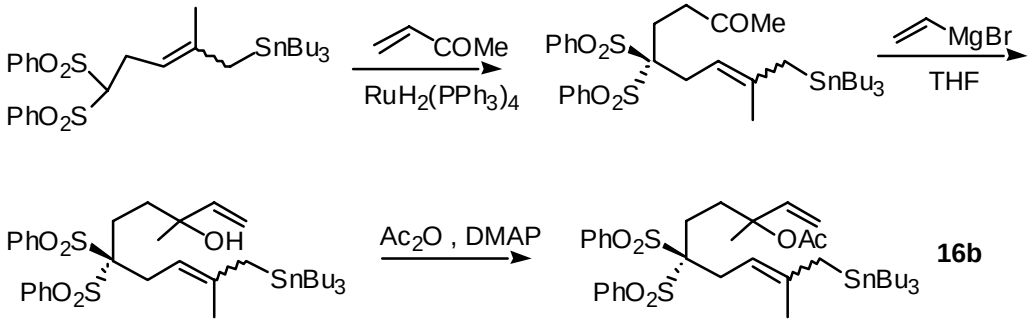
10-Acetyloxy-6,6-bis(phenylsulfonyl)-3,9-dimethyl-1,8-decadien-3-ol. A solution of 5,5-bis(phenylsulfonyl)-2,8-dimethyl-2,9-decadiene-1,8-diol (800 mg, 1.66 mmol), pyridine (397 mg, 5.03 mmol), and Ac_2O (513 mg, 5.03 mmol) in CH_2Cl_2 (10 mL) was stirred at 23 °C for 16 h. The mixture was diluted with CH_2Cl_2, washed with 10% aqueous HCl, dried (Na_2SO_4) and evaporated. The residue was chromatographed (7:3

hexane-EtOAc) to give the title compound (710 mg, 79%) as a vitreous solid (1:1 mixture of *E/Z* isomers): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 4H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 4H), 5.81 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.55 (t, *J* = 5.1 Hz, 1H, *E*), 5.45 (t, *J* = 5.0 Hz, 1H, *Z*), 5.20 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.01 (dd, *J* = 10.8, 1.7 Hz, 1H), 4.45 (s, 2H, *Z*), 4.40 (s, 2H, *E*), 3.00 (d, *J* = 5.0 Hz, 2H, *Z*), 2.93 (d, *J* = 5.3 Hz, 2H, *E*), 2.35-2.10 (m, 2H), 2.05 (s, 3H, *E*), 2.03 (s, 3H, *Z*), 1.97-1.89 (m, 2H), 1.70 (s, 3H, *Z*), 1.56 (s, 3H, *E*), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.81, 170.64, 143.73, 136.74, 136.52, 134.40, 134.26, 134.09, 131.21, 129..40, 128.99, 128.38, 120.77, 119.53, 112.52, 112.43, 90.81, 72.54, 72.31, 69.02, 62.55, 35.18, 28.31, 27.34, 26.84, 23.80, 23.18, 21.54, 20.76, 14.10 (some carbon resonances were not observed or overlapped). Anal. Calcd for $C_{26}H_{32}O_7S_2$: C, 59.97; H, 6.10; S, 12.29. Found: C, 59.78; H, 5.67; S, 12.11.

Bis(phenylsulfonyl)-3,10-diacetyloxy-3,9-dimethyl-1,8-decadiene. Method a: A solution of 5,5-bis(phenylsulfonyl)-2,8-dimethyl-2,9-decadiene-1,8-diol (3.50 g, 7.32 mmol), DMAP (1.96 g, 16.11 mmol), and Ac_2O (1.86 g, 18.3 mmol) in CH_2Cl_2 (20 mL) at 23 °C was stirred for 16 h. The mixture was evaporated and the residue was chromatographed (7:3 hexane-EtOAc) to give the diacetate (3.45 g, 80%) as at 1:1 mixture of *E/Z* isomers. **Method b:** A solution of 10-acetyloxy-6,6-bis(phenylsulfonyl)-3,9-dimethyl-1,8-decadien-3-ol (510 mg, 0.95 mmol), DMAP (174 mg, 1.42 mmol), and Ac_2O (200 mg, 1.90 mmol) in CH_2Cl_2 (10 mL) at 23 °C was stirred for 16 h. The mixture was evaporated and the residue was chromatographed (7:3 hexane-EtOAc) to give the diacetate (500 mg, 88%) as a vitreous solid (1:1 mixture of *E/Z* isomers): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.10-8.00 (m, 4H), 7.70 (t, *J* = 6.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 4H), 5.87 (dd, *J* = 17.7, 10.7 Hz, 1H), 5.54 (m, 1H, *E*), 5.48 (m, 1H, *Z*), 5.21-5.08 (m, 2H), 4.54 (d, *J* = 7.0 Hz, 2H, *Z*), 4.46 (d, *J* = 6.4 Hz, 2H, *E*), 3.11-3.03 (m, 2H, *Z*), 3.00-2.93 (m, 2H, *E*), 2.35-2.10 (m, 2H), 2.02 (s, 3H), 1.96 (s, 3H), 1.83-1.60 (m, 2H), 1.75 (s, 3H, *Z*), 1.57 (s, 3H, *E*), 1.55 (s, 3H). Anal. Calcd for $C_{28}H_{34}O_8S_2$: C, 59.76; H, 6.09. Found: C, 59.81; H, 5.84.

[10-Acetyloxy-6,6-bis(phenylsulfonyl)-3,9-dimethyl-2,8-decadienyl](tri-*n*-butyl)stannane (16a). To a suspension of CuCN (40 mg, 0.45 mmol) in THF (5 mL) at -78 °C was slowly added *n*BuLi (0.4 mL, 2.35 M in hexane, 0.91 mmol). The mixture was warmed up to -60 °C yielding a transparent solution. The mixture was cooled to -78 °C and nBu$_3$SnH (265 mg, 0.91 mmol) was slowly added yielding a pale yellow solution. To this solution was added the above diacetate (180 mg, 0.30 mmol) in THF (2 mL) and the mixture was warmed

up to -30 °C and was stirred at this temperature for 6 h. An aqueous solution of NH_4Cl was added and the mixture was extracted with Et_2O, dried ($MgSO_4$), and evaporated. The residue was chromatographed (4:1 hexane-EtOAc) to give the **16a** (197 mg, 79%) as a colorless oil (mixture of *E/Z* isomers): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.10-8.02 (m, 4H), 7.74-7.67 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 4H), 5.80-5.70 (m, 1H, two isomers), 5.65-5.55 (m, 1H, two isomers), 5.35-5.25 (m, 1H, four isomers), 4.49-4.47 (m, 2H), 3.15-3.00 (m, 2H), 2.40-2.20 (m, 2H), 2.10-2.06 (m, 3H), 1.70-1.20 (m, 28H), 1.00-0.80 (m, 9H). Anal. Calcd for $C_{38}H_{58}O_6S_2Sn$: C, 57.50; H, 7.36. Found: C, 57.16; H, 7.57.

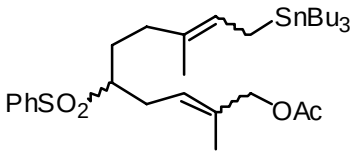


5,5-Bis(phenylsulfonyl)-8-methyl-9-(tri-*n*-butylstannyl)-7-nonen-2-one. A solution of 5,5-bis(phenylsulfonyl)-2-methyl-1-(tri-*n*-butylstannyl)-2-pentene (250 mg, 0.38 mmol), methyl vinyl ketone (53 mg, 0.77 mmol), and $RuH_2(PPh_3)_4$ (13 mg, 3 mol%) in MeCN (10 mL) was stirred at 23 °C for 16 h. The mixture was evaporated and the residue was chromatographed (9:1 hexane-EtOAc) to give the title compound (180 mg, 65%) as a colorless solid (1:1 mixture of *E/Z* isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.94 (m, 4H), 7.74-7.52 (m, 6H), 5.00-4.85 (m, 1H, *Z*), 4.85-4.70 (m, 1H, *E*), 3.10-2.98 (m, 2H), 2.85-2.70 (m, 2H), 2.60-2.45 (m, 2H), 2.14 (s, 3H), 2.13 (s, 3H), 1.68 (s, 3H, *Z*), 1.57 (s, 3H, *E*), 1.60-1.20 (m, 20H), 1.00-0.80 (m, 9H).

6,6-Bis(phenylsulfonyl)-3,9-dimethyl-10-(tri-*n*-butylstannyl)-1,8-decadien-3-ol. To a solution of 5,5-bis(phenylsulfonyl)-8-methyl-9-(tri-*n*-butylstannyl)-7-nonen-2-one (180 mg, 0.25 mmol) in THF (5 mL) at 0 °C was added vinylmagnesium bromide (0.3 mL, 1 M in THF, 0.30 mmol) and the resulting mixture was stirred for 2 h. An aqueous solution of NH_4Cl was added and the mixture was extracted with Et_2O, dried (MgSO4), and evaporated. The residue was chromatographed (4:1 hexane-EtOAc) to give the title compound (160 mg, 85%) as a vitreous solid (1:1 mixture of *E/Z* isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.94 (m, 4H), 7.74-7.52 (m, 6H), 5.81 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.19

(br d, *J* = 17.3 Hz, 1H), 5.06 (br d, *J* = 10.6 Hz, 1H), 5.10-5.00 (m, 1H, *E*), 4.92-4.80 (m, 1H, *E*), 3.00-2.80 (m, 2H), 2.35-2.25 (m, 2H), 2.05-1.85 (m, 2H), 1.73-1.20 (m, 23H), 1.28 (s, 3H), 1.00-0.80 (m, 9H). Anal. Calcd for $C_{36}H_{56}O_5S_2Sn$: C, 57.53; H, 7.51; S, 8.53. Found: C, 57.69; H, 7.52; S, 8.43.

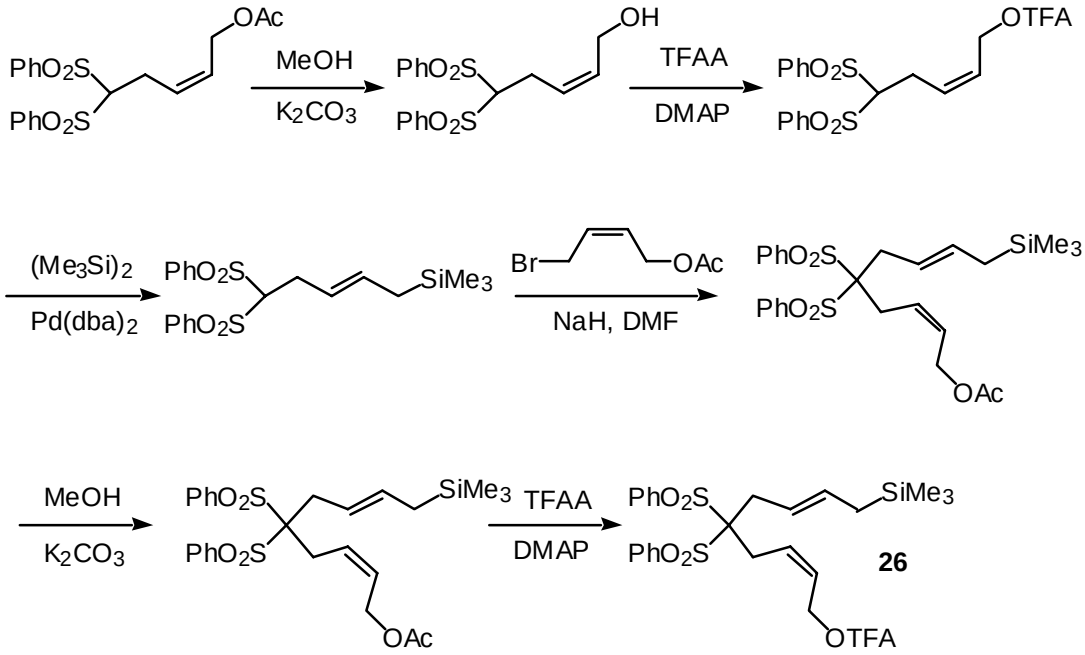
3-Acetyloxy-6,6-bis(phenylsulfonyl)-3,9-dimethyl-10-(tri-*n*-butylstannyl)-1,8-decadiene (16b). A solution of 6,6-bis(phenylsulfonyl)-3,9-dimethyl-10-(tri-*n*-butylstannyl)-1,8-decadien-3-ol (112 mg, 0.15 mmol), DMAP (55 mg, 0.45 mmol), and Ac_2O (32 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) was stirred at 23 °C for 16 h. The mixture was evaporated and the residue was chromatographed (4:1 hexane-EtOAc) to give the title compound (36 mg, 30%) as a colorless oil (1:1 mixture of *E/Z* isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.94 (m, 4H), 7.74-7.52 (m, 6H), 5.90 (dd, *J* = 11.4, 10.3 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 5.12 (d, *J* = 11.4 Hz, 1H), 4.95-4.85 (m, 1H), 2.95-2.85 (m, 2H), 2.35-2.20 (m, 2H), 1.96 (s, 3H), 1.70-1.20 (m, 28 H), 1.00-0.80 (m, 9H).



17

10-Acetoxy-3,9-dimethyl-1-(tri-*n*-butylstannyl)-6-phenyllsulfonyl-2,8-decadiene (17). A mixture of **16a** (180 mg, 0.22 mmol) and Na(Hg) 6% (167 mg, 0.44 mmol) was stirred in a mixture 1:2 MeCN-MeOH (15 mL) until metallic Hg appeared (ca. 30 min). The mixture was diluted with CH_2Cl_2, washed with H_2O, dried (Na_2SO_4) and concentrated. The residue was diluted with CH_2Cl_2 (10 mL) and DMAP (36 mg, 0.29 mmol) and Ac_2O (30 mg, 0.29 mmol) were added. The mixture was stirred at 23 °C during 1 h, concentrated and chromatographed (9:1 hexane-EtOAc) to give **17** (66 mg, 46%) as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.70-7.50 (m, 4H), 5.45-5.20 (m, 2H), 4.49 (s, 2H, *E*), 4.39 (s, 2H, *E*), 3.05-2.90 (m, 1H), 2.70-2.30 (m, 2H), 2.20-1.90 (m, 4H), 2.06-2.05 (m, 3H), 1.71 (s, 3H, *E*), 1.61 (s, 3H, *E*), 1.46 (s, 3H, *E*), 1.60-0.80 (m, 29H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.33, 133.56, 133.19, 129.07, 127.14, 125.25, 125.24, 125.05, 123.88, 110.13, 69.44, 63.78, 63.67, 63.42, 63.33, 62.69, 36.77, 29.70 (^3J (^{119}Sn-C) = 19 Hz), 27.36 (^2J(^{119}Sn-C) = 52 Hz), 26.49, 26.13, 26.02, 25.37, 22.59, 21.56, 20.89, 15.45, 13.69, 11.52, 9.45 (^1J(^{119}Sn-C) = 297 Hz), 9.39. FAB-HRMS calcd for $C_{32}H_{54}O_4SSn$: 654.2765. Found: 654.2768 (M^+).

Synthesis of Allylsilanes



(*Z*)-5,5-Bis(phenylsulfonyl)-2-penten-1-ol Trifluoroacetate. To solution of (*Z*)-5,5-bis(phenylsulfonyl)-2-penten-1-ol (1.50 g, 4.2 mmol) and DMAP (508 mg, 4.2 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added TFAA (0.6 mL, 4.2 mmol) and the resulting mixture was as stirred at 23 °C for 4 h. The solvent was evaporated and the residue was chromatographed (5:1 hexane-EtOAc) to give the title compound (1.50 g, 83 %) as a white solid: mp 70-72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.92 (m, 4H), 7.72 (tt, *J* = 7.5, 1.2 Hz, 2H), 7.61-7.54 (m, 4H), 5.87 (dtt, *J* = 10.9, 7.3, 1.2 Hz, 1H), 5.66 (dtt, *J* = 10.9, 6.9, 1.6 Hz, 1H), 4.78 (dd, *J* = 6.9, 0.8 Hz, 2H), 4.57 (t, *J* = 6.1 Hz, 1H), 3.05 (dd, *J* = 7.3, 5.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.59, 134.83, 130.79, 129.57, 129.23, 124.69, 82.99, 62.94, 23.96, (the signals of the trifluoroacetate group were not observed). Anal. Calcd for $C_{19}H_{17}O_6S_2F_3$: C, 49.35; H, 3.71; S, 13.87. Found, C, 49.41; H, 3.45; S, 14.15.

(*Z*)-5,5-Bis(phenylsulfonyl)1-trimethylsilyl-2-pentene. To solution of the above trifluoroacetate (1.20 g, 2.74 mmol) and $Pd_2(dba)_3$·dba (158 mg, 0.27 mmol) in THF (20 mL) was added $(Me_3Si)_2$ (0.56 mL, 2.74 mmol) and the mixture was stirred at 23 °C for 15 h. The solvent was evaporated and the residue was chromatographed (1:9 hexane-EtOAc) to give the title compound (984 mg, 85%) as a white solid: mp 102-104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.93 (m, 4H), 7.74-7.66 (m, 2H), 7.61-7.54 (m, 4H), 5.42 (dt, *J* = 14.9, 7.8 Hz, 1H), 5.20 (dt, *J* = 15.6, 6.3 Hz, 1H), 4.38 (t, *J* = 6.3 Hz,

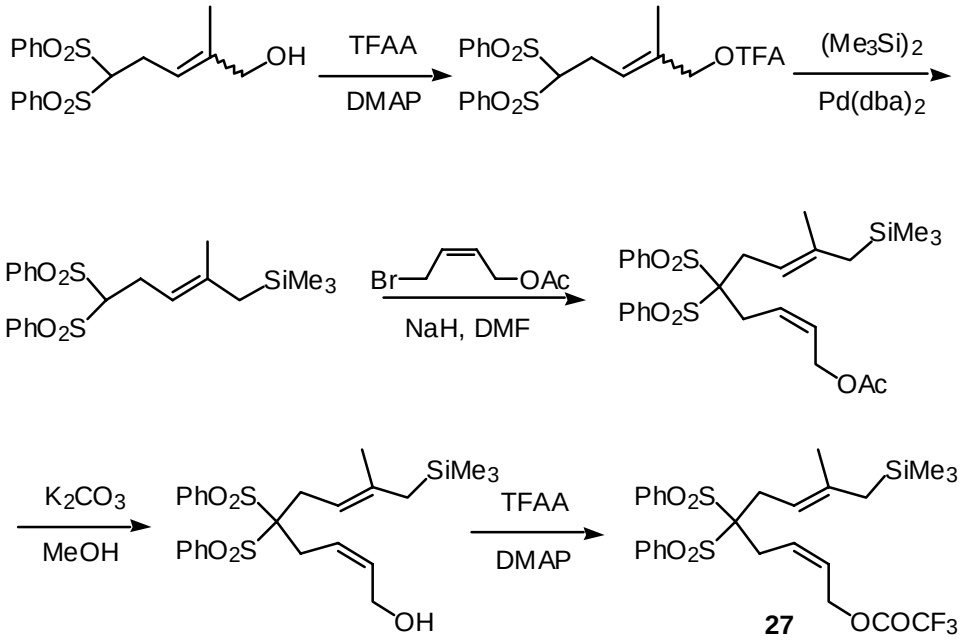
2H), 2.88 (dd, *J* = 6.5, 5.5 Hz, 2H), 1.35 (d, *J* =7.8 Hz, 2H), -0.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.99, 134.42, 131.80, 129.46, 128.95, 121.82, 84.22, 29.06, -2.04. Anal. Calcd for $C_{20}H_{26}O_4S_2Si$: C, 56.89; H, 6.20. Found, C, 56.80; H, 5.96.

9-Acetoxy-5,5-bis(phenylsulfonyl)-1-trimethylsilyl-2,7-nonadiene. To a solution of NaH (60 % in mineral oil, 70 mg, 1.74 mmol) in DMF (10 mL) at 0 °C was added a solution of (*Z*)-5,5-bis(phenylsulfonyl)1-trimethylsilyl-2-pentene (670 mg, 1.58 mmol) in DMF (10 mL) followed by (*Z*)-1-acetoxy-4-bromo-2-butene (336 mg, 1.74 mmol) and the mixture was stirred at 23 °C for 16 h. After extractive workup (Et_2O), the residue was chromatographed (4:1 hexane-EtOAc) to give the title compound (840 mg, quantitative) as a vitreous solid (1.1:1 mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.02 (m, 4H), 7.72- 7.66 (m, 2H), 7.59-7.54 (m, 4H), 5.91 (dtt, *J* = 11.2, 4.6, 1.5 Hz, 1H), 5.69 (dtt, *J* = 11.1, 6.6, 2.1 Hz, 1H), 5.88 (dtt, *J* = 15.0, 8.0 1.2 Hz, 1H), 5.36 (dtt, *J* = 15.0, 6.8, 1.5 Hz, 1H), 4.52 (dd, *J* = 6.6, 1.2 Hz, 1H, *E*), 2.28-2.16 (m, 4H), 1.69 (d, *J* = 10.5 Hz, 2H, *E*), 1.63 (d, *J* = 8.5 Hz, 2H), 3.00-2.98 (m, 4H), 1.47 (d, *J* = 8.0 Hz, 2H), -0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.54, 136.57,134.50, 134.12, 128.96, 128.45, 127.09, 125.53, 118.51, 90.19, 60.04, 32.26, 27.16, 23.28, 20.81, 0.32. Anal. Calcd for $C_{26}H_{34}O_{64}S_2Si$: C, 58.40; H, 6.41; Found, C, 58.62; H, 6.66.

5,5-Bis(phenylsulfonyl)-1-trimethylsilyl-2,7-nonadien-9-ol. A solution of the above acetate (840 mg, 1.57 mmol) and K_2CO_3 (326 mg, 2.35 mmol) in MeOH (20 mL) was stirred at 23 °C for 16 h. After extractive workup (Et_2O), the residue was chromatographed (1:1 hexane-EtOAc) to give the allyl alcohol (593 mg, 80%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.01 (m, 4H), 7.72- 7.66 (m, 2H), 7.60-7.54 (m, 4H), 5.85-5.68 (m, 2H), 5.63-5.50 (m, 1H), 5.41-5.27 (m, 1H), 4.16-4.07 (m, 2H), 3.01-2.98 (m, 2H), 1.46 (d, *J* = 7.9 Hz, 2H), -0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.79, 134.53, 134.11, 132.35, 131.35, 128.51, 123.15, 118.72, 90.86, 58.34, 32.83, 27.33, 23.29, -1.95. Anal. Calcd for $C_{24}H_{32}O_5S_2Si$: C, 58.50; H, 6.55; S, 13.01. Found, C, 58.43; H, 6.54: S, 12.64.

9-Trifluoroacetoxy-5,5-bis(phenylsulfonyl)-1-trimethylsilyl-2,7-nonadiene (26). To a solution of the above alcohol (593 mg, 1.2 mmol) and DMAP (147 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) at 23 °C was added TFAA (0.17 mL, 1.2 mmol) and the mixture was stirred for 30 min. The solvent was evaporated and the residue was chromatographed (4:1 hexane-EtOAc) to give **26** as a white solid (700 mg, 99%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-

8.02 (m, 4H), 7.76- 7.68 (m, 2H), 7.62-7.55 (m, 4H), 6.10-6.05 (m, 1H), 5.79-5.73 (m, 1H), 5.64-5.56 (m, 1H), 5.41-5.32 (m, 1H), 4.82 (d, *J* = 7.0 Hz, 2H), 3.07- 3.00 (m, 4H), 1.49 (d, *J* = 8.1 Hz, 2H), -0.23 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.68, 134.54, 131.42, 128.72, 128.61, 124.39, 118.58, 90.14, 63.24, 32.83, 30.92, 27.64, 23.37, 1.01, -1.92. Anal. Calcd for $C_{26}H_{31}O_6S_2SiF_3$: C, 53.04; H, 5.71; S, 10.89. Found, C, 53.40; H, 5.18; S, 11.17.



5,5-Bis(phenylsulfonyl)-2-methyl-2-penten-1-ol Trifluoroacetate. A solution of 5,5-bis(phenylsulfonyl)-2-methyl-2-penten-1-ol (1.10 g , 2.9 mmol), DMAP (353 mg, 2.9 mmol), and TFAA (0.4 mL, 2.9 mmol) in CH_2Cl_2 (10mL) was stirred at 0 °C for12 h. The solvent was evaporated to give the title trifluoroacetate (1.40 g, 98 %) as a vitreous solid (1.3:1 mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$)•• 7.96-7.89 (m, 4H), 7.73-7.66 (m, 2H), 7.59-7.53 (m, 4H), 5.56-5.49 (m, 1H), 4.73 (s, 2H, major isomer), 4.61 (s, 2H, minor isomer), 4.60 (t, *J* = 6.0 Hz, 1H, major isomer), 4.48 (t, *J* = 6.1 Hz, 1H, minor isomer), 3.01 (dd, *J* = 6,7, 6.4 Hz, 2H, major isomer), 2.96 (t, *J* = 6.6 Hz, 2H, minor isomer),1.69 (s, 3H, minor isomer), 1.56 (s, 3H, major isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.75, 134.65, 134.54, 129.46, 129.07, 125.91, 121.34, 83.09, 65.83, 61.15, 30.80, 24.14, 20.87, (the signals of the trifluoroacetate group were not observed). Anal. Calcd for $C_{20}H_{19}S_2O_6F_3$: C, 50.42; H, 4.02; S, 13.46. Found, C, 50.21; H, 4.52; S, 13.24.

[(*E*)-5,5-Bis(phenylsulfonyl)-2-pentenyl]trimethylsilane. To a solution of the above trifluoroacetate (780 mg, 1.63 mmol)

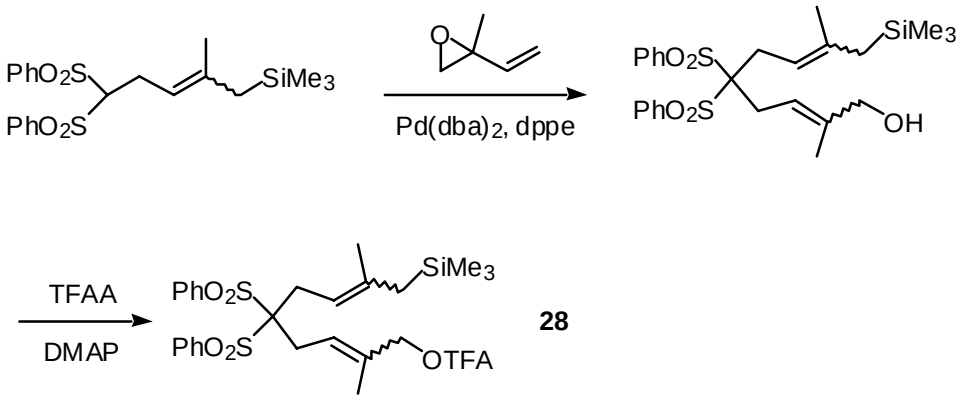
and $Pd_2(dba)_3 \cdot dba$ (94 mg, 0.16 mmol) in THF (20 mL) was added $(Me_3Si)_2$ (0.23 mL, 1.63 mmol) and the mixture was stirred at 23 °C for 15 h. The solvent was evaporated and the residue was chromatographed (1:9 hexane-EtOAc) to give the title silane (563 mg, 79%) as a white solid: mp 178-180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (m, 4H), 7.72 (m, 2H), 7.58 (m, 4H), 4.93 (t, *J* = 8.1 Hz, 1H), 4.39 (t, *J* = 6.1 Hz, 1H), 2.86 (t, *J* = 6.5 Hz, 2H), 1.47 (s, 3H), 1.42 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.13, 137.87, 134.44, 129.62, 129.01, 115.84, 84.55, 30.17, 24.87, 18.63, -1.22. Anal. Calcd for $C_{21}H_{28}O_4S_2Si$: C, 57.76; H, 6.46. Found: C, 58.03; H, 6.20.

9-Acetoxy-5,5-bis(phenylsulfonyl)-3-methyl-1-trimethylsilyl-2,7-nonadiene. To a suspension of NaH (60% in mineral oil, 65 mg, 1.62 mmol) in DMF (10 mL) at 0 °C a solution of the above silane (700 mg, 1.59 mmol)in DMF (5 mL) was added followed by 1-acetoxy-4-bromo-2-butene (313 mg, 1.62 mmol). The mixture was stirred for 13 h at 23 °C and then, after extractive work-up (Et_2O) and chromatography (4:1 hexane:EtOAc) the title compound was obtained (740 mg, 85%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8-07-8.03 (m, 4H), 7.73-7.67 (m, 2H), 7.60-7.54 (m, 4H), 5.91-5.80 (m, 1H), 5.75-5.66 (m, 1H), 5.13 (t, *J* = 6.5 Hz, 1H), 4.53 (dd, *J* = 6.5, 0.8 Hz, 2H), 3.03 (d, *J* = 4.9 Hz, 2H), 2.95 (d, *J* = 6.1 Hz, 2H), 2.07 (s, 3H), 1.55 (s, 3H). 1.54 (s, 2H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.65, 139.00, 136.46, 134.52, 131.38, 128.48, 127.26, 125.57, 112.08, 90.47, 60.16, 30.68, 27.50, 26.71, 20.89, 19.10, -1.23. Anal. Calcd. for $C_{27}H_{36}S_2O_6Si$: C, 59.01; H, 6.61. Found: C, 58.75; H, 6.30.

5,5-Bis(phenylsulfonyl)-8-methyl-9-trimethylsilyl-2,7-nonadien-1-ol. A solution of the above acetate (580 mg, 1.05 mmol) and K_2CO_3 (218 mg, 1.57 mmol) in MeOH (15 mL) was stirred at 23 °C for 12h. After extractive work-up (Et_2O) the title compound was obtained (531 mg, 100%) as a pale yellow oil ^{1}H NMR (300 MHz, $CDCl_3$) δ 8-05-8.01 (m, 4H), 7.72-7.66 (m, 2H), 7.59-7.53 (m, 4H), 5.80-5.68 (m, 2H), 5.11 (t, *J* = 5.3 Hz, 1H), 4.13 (D, *J* = 6.5 Hz, 2H), 3.02 (d, *J* = 6.6 Hz, 2H), 2.94 (d, *J* = 6.5 Hz, 2H), 1.85 (bs, 1H, OH), 1.54 (s, 3H). 1.42 (s, 2H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.97, 136.62, 134.51, 132. 44, 131.33, 128.48, 123.18, 112.28, 58.37, 30.65, 27.98, 26.78, 19.07, -1.22. EI-HRMS calcd for $C_{22}H_{25}O_5S_2$ (M^+-$SiMe_3$): 433.1143. Found: 433.1127.

[5,5-Bis(phenylsulfonyl)-1-trifluoroacetoxy-8-methyl-2,7-nonadienyl]trimethylsilane (27). A solution of the above alcohol (383mg, 0.75 mmol), DMAP (110 mg, 0.9 mmol) and TFAA (0.11 mL, 0.78 mmol) in CH_2Cl_2 (10 mL) was stirred for 45 min

at 23 °C. After extractive work-up (CH_2Cl_2), the solvent was concentrated to give **27** (430 mg, 95%) as a vitreous solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8-06-8.01 (m, 4H), 7.74-7.68 (m, 2H), 7.60-7.55 (m, 4H), 6.06-5.77 (m, 1H), 5.79-5.70 (m, 1H), 5.10 (t, *J* = 5.3 Hz, 1H), 4.81 (d, *J* = 6.9 Hz, 2H), 3.05 (dd, *J* = 6.9, 1.5 Hz, 2H), 2.95 (d, *J* = 6.5 Hz, 2H), 1.55 (s, 3H). 1.51 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.21 (m), 139.41, 136.31, 134.64, 131.30, 128.54, 124.46, 111.88, 90.16, 63.22, 30.62, 27.77, 26.91, 19.04, -1.31.

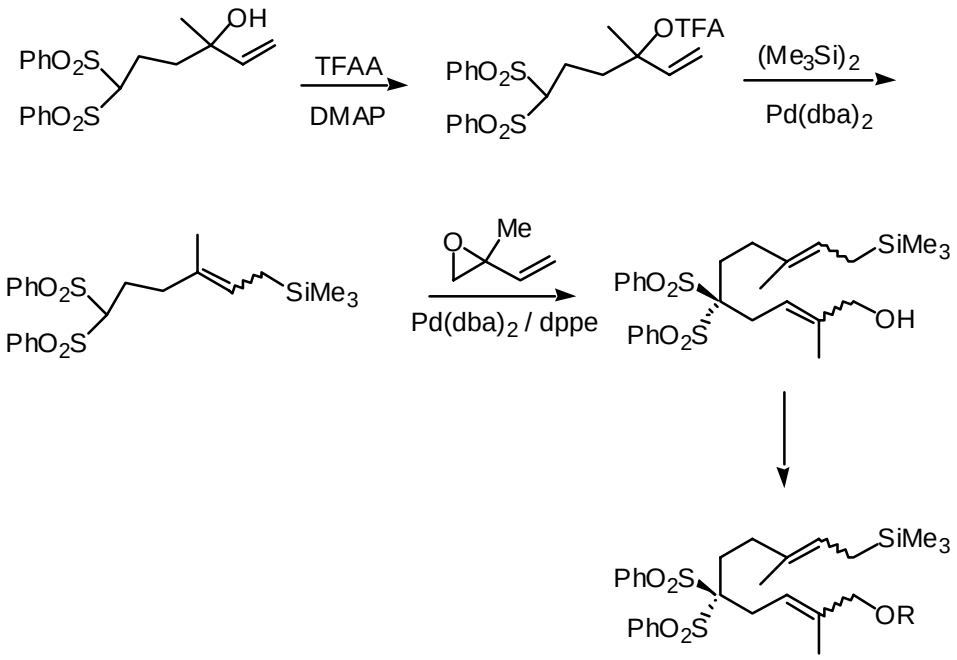


28

5,5-Bis(phenylsulfonyl)-9-trimethylsilyl-2,7-noandiene-1-ol. A solution of [(*E*)-5,5-bis(phenylsulfonyl)-2-pentenyl]trimethylsilane (807 mg, 1.84 mmol), 2-methyl-2-vinyloxirane (155 mg, 1.84 mmol), $Pd_2(dba)_3$·dba (106 mg, 0.09 mmol), dppe (73 mg, 0.18 mmol) in THF (20 mL) was stirred at 23 °C for 6 h. The solvent was evaporated and the residue was chromatographed (2:3 hexane-EtOAc) to give the alcohol (659 mg, 69%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.00 (m, 4H),7.72-7.66 (m, 2H), 7.60-7.53 (m, 4H), 5.62-5.57 (m, 1H), 5.15-5.11 (m, 1H), 3.99 (bs, 2H), 2.97 (m, 4H), 1.59 (d, *J* = 1.2 Hz, 3H), 1.54 (d, *J* = 1.2 Hz, 3H), 1.52 (d, *J* = 1.0 Hz, 2H), 0.00 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 138.72 (C), 138.52 (C), 136.74 (C), 134.36 (CH), 131.38 (CH), 128.37 (CH), 116.79 (CH), 112.44 (CH), 91.00 (C), 68.32 (CH_2), 30.68 (CH_2), 27.61 (CH_2), 26.86 (CH_2), 19.08 (CH_3), 14.03 (CH_3), -1.25 (CH_3). FAB-HMRS calcd for $C_{20}H_{31}O_3SSi$ (M-$PhSO_2$): 379.1763. Found: 379.1767.

[5,5-Bis(phenylsulfonyl)-1-trifluoroacetyloxy-2,7-noandienyl]trimethylsilane (28). A mixture of the above alcohol (121 mg, 0.23 mmol), DMAP (32 mg, 0.24 mmol), and TFAA (54 mg, 0.24 mmol) was stirred in CH_2Cl_2 (5 mL) at 23^{a}C for 30 min. After extractive workup (CH_2Cl_2), the crude **28** was obtained (100 mg, 70%) as an oil. This trifluoroacetate was used as such in the cyclization reaction. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-8.00 (m, 4H),7.79-7.66 (m, 2H), 7.58-7.52

(m, 4H), 5.79-5.75 (m, 1H), 5.15-5.11 (m, 1H), 4.70 (s, 2H), 3.00-2.97 (m, 4H), 1.60 (d, J = 1.2 Hz, 3H), 1.54 (s 2H), 1.53 (d, J = 1.2 Hz, 3H), -0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 157.71 (q, C), 139.11 (C), 136.48 (C), 134.56 (CH), 131.41 (CH), 128.45 (CH), 123.68 (CH), 112.11 (CH), 90.52 (C), 72.93 (CH_2), 30.71 (CH_2), 27.50 (CH_2), 27.02 (CH_2), 19.04 (CH_3), 14.14 (CH_3), -1.28 (CH_3).



25a: R = Ac
25b: R = TFA
25c: R = EtOCO

6,6-Bis(phenylsulfonyl)-3-methyl-1-hexen-3-ol Trifluoroacetate. A solution of 6.6-bis(phenylsulfonyl)-3-methyl-1-hexen-1-ol (254 mg, 0.64 mmol), DMAP (86 mg, 0.71 mmol) and TFAA (148 mg, 0.71 mmol) in CH_2Cl_2 (5 mL) was stirred at 23 °C for 1 h. The solvent was evaporated and the residue was chromatographed (4:1 hexane-EtOAc) to give the title compound (380 mg, 100%) as a vitreous solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03-7.90 (m, 4H), 7.75-7.50 (6H), 5.83 (dd, J = 17.2, 11.0 Hz, 1H), 5.22 (d, J = 17.2 Hz, 1H), 5.25 (d, J = 11.0 Hz, 1H), 4.40 (m, 1H), 2.40-2.18 (m, 4H), 1.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.51, 134.70, 129.16, 12910, 112.26, 87.82, 82.87, 37.56, , 22.99, 15.77, (three carbon signals were not observed due to overlapping).

6,6-Bis(phenylsulfonyl)-3-methyl-1-trimethylsilyl-2-hexene. To a solution of the above trifluoroacetate (4.50 g, 9.1 mmol) and $Pd_2(dba)_3$·dba (261mg, 0.45 mmol) in THF (50 mL) was added $(Me_3Si)_2$ (1.86 mL, 9.1 mmol) and the mixture was stirred at 23 °C for 15 h. The solvent was evaporated and

the residue was chromatographed (1:9 hexane-EtOAc) to give the title compound (3.00 g, 70%) as a vitreous solid (4.8:1 *E/Z* isomers mixture): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.93 (m, 4H), 7.72- 7.66 (m, 2H), 7.60-7.54 (m, 4H), 6.10-6.05 (m, 1H), 5.29-5.17 (m, 1H), 4.48 (t, *J* = 5.4 Hz,1H, *E*), 4.41 (t, *J* = 5.0 Hz,. 1H, *Z*), 2.28-2.23 (m, 4H), 1.50 (d, *J* = 2.8 Hz, 2H), 1.40 (d, *J* = 2.8 Hz, 3H, *Z*), 1.37 (d, *J* = 1.6 Hz, 3H, *E*), -0.01 (s, 9H, major isomer), -0.02 (s, 9H, minor isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.02, 137.96, 134.40, 129.51, 129.34, 129.23, 128.98, 124.30, 123.93, 82.46, 81.85, 37.45, 29.67, 23.77, 23.56, 22.45, 18.85, 18.55, 14.87, -1.70, -1.84. Anal. Calcd for $C_{22}H_{30}O_4S_2Si$: C, 58.63; H, 6.71; S, 14.23. Found, C, 58.75; H, 6.46; S, 13.81.

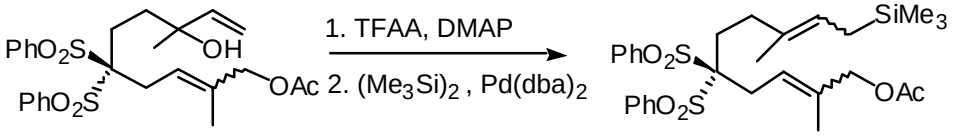
6,6-Bis(phenylsulfonyl)-3,9-dimethyl-1-(trimethylsilyl)-2,8-decadien-10-ol. A solution of the above silane (190 mg, 0.43 mmol),2-methyl-2-vinyloxirane (72 mg, 0.86 mmol), $Pd_2(dba)_3$·dba (24 mg, 0.043 mmol) and dppe (17 mg, 0.043 mmol) in THF (5 mL) at 23 °C was stirred for 16 h. The solvent was evaporated and the residue was chromatographed (3:2 hexane-EtOAc) to give the title alcohol (200 mg, 88%) as a colorless oil (mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05-8.00 (m, 4H), 7.70 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 6.8 Hz, 4H), 5.70-5.60 (m, 1H, *E*), 5.40-5.30 (m, 1H, *E*), 5.17 (t, *J* = 8.6 Hz, 1H), 4.10 (s, 2H, *E*), 4.01 (s, 2H, *E*), 3.15-2.95 (m, 2H), 2.40-2.20 (m, 4H), 1.83 (s, 3H, *E*), 1.51 (s, 3H, *E*), 1.51 (s, 3H, *E*), 1.40-1.22 (m, 2H), -0.9 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.16, 137.02, 134.37, 131.26, 130.53, 128.44, 122.69, 121.90, 118.18, 116.31, 91.32, 68.14, 61.31, 33.50, 33.28, 27.75, 26.90, 26.62, 23.07, 21.71, 18.61, 15.68, 13.98, -1.75, (some signals were not observed due to overlapping). Anal. Calcd for $C_{27}H_{38}O_5S_2Si$: C, 60.64; H, 7.16; S, 11.99. Found: C, 60.15; H, 7.24; S, 12.05.

10-Acetoxy- 6,6-bis(phenylsulfonyl)-3,9-dimethyl-1-(trimethylsilyl)-2,8-decadien-10-ol (25a). A solution of the above alcohol (85 mg, 0.16 mmol), DMAP (29 mg, 0.24 mmol), and Ac_2O (25mg, 0.24) in CH_2Cl_2 (10 mL) was stirred 23 °C for 30 min. The solvent was evaporated and the residue was chromatographed (3:2 hexane-EtOAc) to give **25a** (70 mg, 76%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.92 (m, 4H), 7.74-7.53 (m, 6H), 5.80-5.55 (m, 1H), 5.25-5.10 (m, 1H), 4.51-4.47 (m, 2H), 3.15-2.95 (m, 2H), 2.29 (m, 4H), 2.12-2.08 (m, 3H), 1.78 (s, 3H, *E*), 1.62 (s, 3H, *E*), 1.51 (s, 3H, *E*), 1.41-1.35 (m, 2H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.64, 136.82, 136.66, 134.44, 131.32, 130.51, 128.45, 122.04, 121.94, 120.84, 119.39, 91.15, 69.02, 62.66, 33.34, 28.05, 27.56, 26.87, 26.58, 21.75, 20.83, 20.73, 18.69, 18.45, 15.65, 14.31, -1.72, -1.78, (some carbon resonances

were not observed due to overlapping). Anal. Calcd for $C_{29}H_{40}S_2O_6Si$: C, 60.35; H, 6.35; S, 11.12. Found: C, 60.66; H, 6.87; S, 11.30.

6,6-Bis(phenylsulfonyl)-3,9-dimethyl-10-ethoxycarbonyloxy-1-(trimethylsilyl)-2,8-decadiene (25b). A solution of the allyl alcohol (350 mg, 0.66 mmol), DMAP (96 mg, 0.79 mmol), *i*Pr_2NEt (102 mg, 0.79 mmol), and ethyl chloroformiate (107 mg, 0.99 mmol) in CH_2Cl_2 (10 mL) at 23 °C was stirred for 3 days. The solvent was evaporated and the residue was chromatographed (9:1 hexane-EtOAc) to give **(25b)** (221 mg, 56%) as a vitreous solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.92 (m, 4H), 7.74-7.53 (m, 6H), 5.80-5.55 (m, 1H), 5.25-5.10 (m, 1H), 4.51-4.47 (m, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.15-2.95 (m, 2H), 2.29 (m, 4H), 1.82 (s, 3H, *E*), 1.64 (s, 3H, *E*), 1.51 (s, 3H, *E*), 1.41-1.35 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), -0.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.51, 136.73, 136.57, 134.49, 134.20, 133.91, 131.37, 130.48, 130.30, 128.50, 122.86, 122.07, 121.96, 121.34, 120.61, 91.06, 90.85, 72.53, 65.72, 64.08, 33.33, 27.46, 26.88, 26.57, 25.38, 23.13, 21.61, 18.72, 15.71, 14.27, -1.70, (some signals were not observed due to overlapping). Anal. Calcd for $C_{30}H_{42}S_2O_7Si$: C, 59.38; H, 6.98; S, 10.57. Found: C, 59.89; H, 7.09; S, 10.95.

[6,6-Bis(phenylsulfonyl)-3,9-dimethyl-10-trifluoroacetyloxy-2,8-decadienyl] trimethylsilane (25c). A solution of 6,6-bis(phenylsulfonyl)-3,9-dimethyl-1-(trimethylsilyl)-2,8-decadien-10-ol (190 mg, 0.36 mmol), DMAP (66 mg, 0.54 mmol), and trifluoroacetic anhydride (114 mg, 0.54 mmol) in CH_2Cl_2 (10 mL) was stirred at 23 °C for 1h. The mixture was evaporated and the residue was chromatographed (4:1 hexane-EtOAc) to give **25c** (97 mg, 30%) as a colorless oil (mixture of isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.92 (m, 4H), 7.74-7.53 (m, 6H), 5.95-5.70 (m, 1H), 5.25-5.10 (m, 1H), 4.81-4.74 (m, 2H), 3.15-2.95 (m, 2H), 2.29 (m, 4H), 2.12-2.08 (m, 3H), 1.82 (s, 3H), 1.66 (s, 3H), 1.62 (s, 3H), 1.51 (s, 3H), 1.41-1.35 (m, 2H), -0.04 (s, 9H). Anal. Calcd for $C_{29}H_{37}F_3O_6S_2Si$: C, 55.22; H, 5.91; S, 10.16. Found: C, 55.67; H, 5.94; S, 10.21.



25a

[6,6-Bis(phenylsulfonyl)-3,9-dimethyl-10-acetyloxy-2,8-decadienyl]trimethylsilane (25a). i. A solution of the allyl alcohol (160 mg, 0.30 mmol), DMAP (54 mg, 0.44 mmol), and

TFAA (94 mg, 0.44 mmol) in CH_2Cl_2 (10 mL) at 23 °C was stirred for 16 h. The mixture was evaporated and the residue was chromatographed (7:3 hexane-EtOAc) to give the trifluoroacetate (138 mg, 73%) as a vitreous solid (mixture of *E/Z* isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01-7.90 (m, 4H), 7.74-7.53 (m, 6H), 5.85 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.50-5.40 (m, 1H, *E*), 5.30-5.20 (m, 1H, *E*), 5.26 (d, *J* = 10.9 Hz, 1H), 5.24 (d, *J* = 17.5 Hz, 1H), 4.45-4.30 (m, 2H), 3.15-2.95 (m, 2H), 2.30-2.15 (m, 4H), 2.06-2.03 (m, 3H), 1.67 (s, 3H, *E*), 1.64 (s, 3H, *E*), 1.51 (s, 3H, *E*). ii. A solution of the trifluoroacetate (112 mg, 0.18 mmol), hexamethyldisilane (52 mg, 0.35 mmol), and $Pd_2(dba)_3$·dba (11 mg, 0.01 mmol) in THF (5 mL) was stirred at 23 °C. After 3 h the characteristic violet color of $Pd_2(dba)_3$·dba was recovered indicating the end of the reaction. The solvent was evaporated and the residue was chromatographed (4:1 hexane-EtOAc) to give the title compound (100 mg, 98%) as a colorless vitreous solid, identical to that described before.

Atomic coordinates for the model complexes of Figures 1-3

Complex VIII

Z	x	y	z
46	-0.000006	-0.000133	-0.000074
6	-2.152558	0.000162	-0.389880
6	-1.851026	1.235999	0.222240
6	-1.851567	-1.235783	0.222249
1	-1.883149	-1.336183	1.305267
1	-1.977969	-2.155448	-0.339731
1	-2.386131	0.000203	-1.454525
1	-1.977002	2.155692	-0.339794
1	-1.882716	1.336474	1.305249
6	2.152503	0.000166	0.390067
6	1.851060	1.235995	-0.222112
6	1.851617	-1.235773	-0.222120
1	1.883363	-1.336149	-1.305136
1	1.977925	-2.155448	0.339864
1	2.385903	0.000209	1.454749
1	1.976932	2.155697	0.339930
1	1.882929	1.336453	-1.305117

Complex IX

Z	x	y	z
46	-0.324651	-0.007179	-0.145641
6	1.653229	-0.074281	-0.933923
15	-0.371026	2.304310	0.143407
6	-1.556755	-1.715955	0.604879
6	-0.714516	-2.125800	-0.468083
6	-2.515277	-0.713321	0.462247
6	2.591623	0.028511	0.201974
6	3.301897	-0.972926	0.749408
1	1.734612	0.773670	-1.622954
1	1.771559	-1.007043	-1.489595
1	0.720177	3.104455	-0.276357
1	-0.510139	2.870547	1.434130
1	-1.389294	3.063185	-0.482505
1	-1.278915	-2.017381	1.614645
1	0.084642	-2.832810	-0.268746
1	-1.102493	-2.135285	-1.485601
1	-2.965614	-0.504416	-0.505463
1	-3.040006	-0.331596	1.332524
1	2.706733	1.024010	0.639662
1	3.245537	-1.988699	0.362061
1	3.961335	-0.810421	1.597570

Complex X

Z	x	y	z
15	0.000000	1.837699	1.932943
46	0.000000	0.000000	0.375849
6	-0.030196	-1.429178	-1.219189
15	0.000000	-1.837699	1.932943
6	0.030196	1.429178	-1.219189
1	0.899824	2.903104	1.686969

1	0.218581	1.761835	3.334261
1	-1.172351	2.630354	1.999295
1	-0.899824	-2.903104	1.686969
1	-0.218581	-1.761835	3.334261
1	1.172351	-2.630354	1.999295
1	-0.433451	2.339456	-0.817897
1	-0.611062	1.023097	-2.003531
6	1.418732	1.674453	-1.658919
1	0.611062	-1.023097	-2.003531
6	-1.418732	-1.674453	-1.658919
1	0.433451	-2.339456	-0.817897
6	-1.964562	-1.296261	-2.827198
1	-2.057300	-2.212690	-0.953699
1	-1.384115	-0.778293	-3.587717
1	-3.005268	-1.501206	-3.064510
6	1.964562	1.296261	-2.827198
1	2.057300	2.212690	-0.953699
1	1.384115	0.778293	-3.587717
1	3.005268	1.501206	-3.064510

Complex XII

Z	x	y	z
46	0.001895	-0.837771	-0.000550
6	-1.431868	0.723917	-0.463192
6	-0.765324	1.947475	0.147370
6	-2.190474	-0.224695	0.209059
1	-2.383278	-0.139244	1.276182
1	-2.840265	-0.898224	-0.343977
1	-1.488693	0.736450	-1.554214
1	-1.223075	2.864548	-0.253013
1	-0.926321	1.955935	1.232947
6	1.427695	0.729848	0.464247
6	0.756842	1.949978	-0.148395
6	2.192030	-0.215817	-0.205801
1	2.387138	-0.129914	-1.272474
1	2.843582	-0.886067	0.349139
1	1.482310	0.743318	1.555381
1	1.211483	2.869581	0.249777
1	0.916562	1.956822	-1.234168

Complex XIII

Z	x	y	z
46	-0.314991	-0.000184	-0.000626
15	-1.708064	-1.938906	-0.054051
15	-1.705169	1.940956	0.055141
6	1.591403	-0.533831	1.428826
6	2.787185	0.111024	0.760422
6	0.705680	0.131845	2.222391
6	1.590685	0.532529	-1.428365
6	2.786941	-0.111833	-0.760248
6	0.705131	-0.133748	-2.221860
1	-1.682192	-2.909341	0.990270
1	-1.698151	-2.916820	-1.091436
1	-3.127675	-1.826779	-0.044724

1	-3.124981	1.831270	0.047159
1	-1.678679	2.911739	-0.988840
1	-1.692573	2.918485	1.092885
1	1.557289	-1.622162	1.397085
1	3.714748	-0.295180	1.193384
1	2.785570	1.188384	0.972867
1	0.813612	1.196520	2.412184
1	-0.025453	-0.395329	2.827400
1	1.556658	1.620882	-1.397538
1	3.714233	0.294612	-1.193558
1	2.785596	-1.189215	-0.972604
1	0.813661	-1.198375	-2.411592
1	-0.025745	0.393085	-2.827485

Complex XIV

Z	x	y	z
46	1.350443	0.304948	-0.028764
6	-3.237288	0.369927	0.192858
15	3.005946	-1.287211	0.021902
6	-0.776624	0.897175	0.488152
6	-1.779563	-0.026844	-0.160897
6	-0.147549	1.941583	-0.154417
6	-4.251145	-0.533004	-0.454775
6	-5.114962	-1.312915	0.197084
1	-3.399867	1.407809	-0.132811
1	-3.369217	0.355748	1.282734
1	2.872621	-2.529080	-0.650702
1	3.472613	-1.834237	1.244570
1	4.291258	-0.981756	-0.497487
1	-0.762863	0.878647	1.578892
1	-1.650353	-0.012281	-1.250139
1	-1.609038	-1.059261	0.167012
1	-0.316090	2.128927	-1.213776
1	0.325822	2.743467	0.408212
1	-4.248563	-0.542311	-1.546502
1	-5.153169	-1.338584	1.284623
1	-5.819950	-1.952076	-0.328039

1,5-Hexadiene

Z	x	y	z
6	0.298677	0.440184	0.562416
6	-0.417934	0.269788	1.873931
6	0.134017	-0.182193	3.000555
1	-1.477541	0.533195	1.872350
1	1.185593	-0.458940	3.050467
1	-0.439365	-0.289902	3.917541
1	1.363763	0.204943	0.688106
1	0.243591	1.490738	0.242025
6	-0.298677	-0.440184	-0.562416
1	-0.243591	-1.490738	-0.242025
6	0.417934	-0.269788	-1.873931
1	-1.363763	-0.204943	-0.688106
6	-0.134017	0.182193	-3.000555
1	1.477541	-0.533195	-1.872350

1	-1.185593	0.458940	-3.050467
1	0.439365	0.289902	-3.917541

$Pd(PH_3)_2$ (XV)

Z	x	y	z
15	2.303398	0.003438	0.000000
46	0.000000	-0.003136	0.000001
15	-2.303398	0.003438	-0.000002
1	3.029036	1.222512	-0.000884
1	3.037835	-0.601735	-1.052222
1	3.037857	-0.600215	1.053078
1	-3.029035	1.222512	0.000469
1	-3.037835	-0.601379	1.052425
1	-3.037857	-0.600572	-1.052876

TS_1

Z	x	y	z
46	0.000002	-0.489512	-0.000068
6	1.869388	0.466697	0.436873
6	1.102490	1.595737	-0.093769
6	2.313712	-0.641640	-0.287530
1	2.349061	-0.636577	-1.373864
1	2.903854	-1.402937	0.210474
1	2.074561	0.485434	1.507560
1	1.109822	2.493156	0.518949
1	1.183148	1.794930	-1.159975
6	-1.869456	0.466668	-0.436724
6	-1.102455	1.595728	0.093733
6	-2.313699	-0.641607	0.287813
1	-2.348866	-0.636476	1.374152
1	-2.903933	-1.402927	-0.210048
1	-2.074803	0.485336	-1.507378
1	-1.109845	2.493097	-0.519059
1	-1.182987	1.795006	1.159932

TS_2

Z	x	y	z
46	-0.525860	0.107788	0.014293
6	1.608871	-0.739250	0.893081
15	-2.276241	-1.358905	-0.063153
6	0.498353	2.003848	-0.452637
6	1.357522	1.379172	0.546091
6	-0.782346	2.473358	-0.222477
6	2.321271	-1.312130	-0.255368
6	3.620953	-1.121296	-0.540350
1	0.858972	-1.405942	1.322184
1	2.258403	-0.380776	1.689654
1	-2.317148	-2.623390	0.590153
1	-2.665382	-1.853966	-1.334239
1	-3.576862	-0.962749	0.343090
1	0.863168	1.998803	-1.479625
1	2.405009	1.330485	0.264842
1	1.195990	1.679623	1.580343

1	-1.149839	2.658101	0.783845
1	-1.362688	2.897441	-1.035326
1	1.723311	-1.921178	-0.934414
1	4.266592	-0.527708	0.104938
1	4.085925	-1.565624	-1.415689

TS_3(syn)

Z	x	y	z
46	0.482738	-0.049701	-0.151520
15	2.631929	-1.196965	-0.173250
15	1.209085	2.146157	0.678475
6	-2.262866	1.318154	-0.487681
6	-3.429740	0.597151	-0.296984
6	-1.213715	0.918233	-1.337776
6	-1.573616	-1.537081	1.017899
6	-2.934432	-1.303560	0.867403
6	-0.683410	-1.926867	-0.020491
1	3.313069	-1.200210	-1.419154
1	2.746321	-2.597968	0.043881
1	3.783718	-0.855358	0.590880
1	2.550493	2.593691	0.837141
1	0.824281	2.439066	2.013159
1	0.733045	3.369448	0.132088
1	-2.078856	2.170548	0.169503
1	-4.206181	0.983364	0.357155
1	-3.778013	-0.049468	-1.094707
1	-0.540187	1.686603	-1.717794
1	-1.447266	0.146623	-2.071954
1	-1.134451	-1.355734	2.000547
1	-3.532933	-1.080641	1.745830
1	-3.462251	-1.811693	0.068438
1	-1.134658	-2.191512	-0.978427
1	0.129364	-2.594580	0.260727

TS_3(anti)

Z	x	y	z
46	0.482922	-0.000011	-0.000008
15	2.119459	1.761669	0.526690
15	2.119511	-1.761628	-0.526670
6	-2.178336	-1.207086	1.091773
6	-3.396264	-1.085669	0.475198
6	-0.975768	-1.620436	0.444806
6	-2.178348	1.207079	-1.091771
6	-3.396271	1.085663	-0.475188
6	-0.975764	1.620409	-0.444817
1	2.676764	1.720477	1.831164
1	1.700122	3.117168	0.589187
1	3.354841	2.034762	-0.126444
1	3.354824	-2.034762	0.126578
1	2.676968	-1.720310	-1.831074
1	1.700202	-3.117129	-0.589333
1	-2.097110	-0.894946	2.134241
1	-4.291398	-0.856943	1.045661
1	-3.555068	-1.513743	-0.510021

1	-1.113220	-2.151795	-0.499670
1	-0.272292	-2.128876	1.108978
1	-2.097138	0.894949	-2.134244
1	-4.291409	0.856943	-1.045649
1	-3.555072	1.513727	0.510036
1	-1.113199	2.151776	0.499657
1	-0.272291	2.128840	-1.109000

TS_4

Z	x	y	z
15	-1.976756	1.920627	0.197826
46	-0.576029	-0.000007	-0.000001
6	1.452837	-0.691016	0.828567
15	-1.976750	-1.920628	-0.197826
6	1.452836	0.691018	-0.828566
6	1.882074	2.011493	-0.342843
6	1.882106	-2.011473	0.342822
6	3.132109	-2.321503	-0.038106
6	3.132062	2.321546	0.038118
1	-2.441173	2.246317	1.499952
1	-3.261707	1.992811	-0.407006
1	-1.627074	3.259271	-0.140306
1	2.269590	-0.048224	1.150642
1	0.714861	-0.746980	1.646647
1	-2.441725	-2.245925	-1.499850
1	-3.261390	-1.993291	0.407612
1	-1.626644	-3.259326	0.139657
1	0.714868	0.746951	-1.646653
1	2.269606	0.048236	-1.150617
1	1.111068	2.778536	-0.277907
1	1.111107	-2.778521	0.277836
1	3.941140	-1.595153	0.010883
1	3.391108	-3.313586	-0.397381
1	3.941103	1.595205	-0.010824
1	3.391038	3.313643	0.397372

TS_5

Z	x	y	z
46	0.621879	-0.109695	-0.043303
15	2.938169	-0.021988	0.287689
15	-0.080045	-2.364097	-0.320390
6	-3.120051	-0.539166	-0.185263
6	-3.714332	-1.031161	0.923683
6	-1.968368	0.334304	-0.210412
6	-0.538936	2.720233	-0.481674
6	-1.872608	2.695047	-0.087345
6	0.555875	2.258186	0.274707
1	3.567067	0.929632	1.137362
1	3.763824	0.236662	-0.839083
1	3.687372	-1.137070	0.749628
1	-1.041544	-2.896165	0.575682
1	0.831003	-3.451354	-0.218689
1	-0.710143	-2.835688	-1.502832
1	-3.558224	-0.787642	-1.153504

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1        -4.603507       -1.651928       0.868436
1        -3.329510       -0.814825       1.918383
1        -1.480544       0.580343        0.720558
1        -1.525979       0.586274        -1.155961
1        -0.340102       2.957405        -1.528861
1        -2.645981       3.058314        -0.757394
1        -2.142794       2.668265        0.963936
1         0.453987       2.213502        1.360751
1         1.547305       2.556857        -0.058125
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