Highly regio- and stereoselective synthesis of (1*Z*,3*E*)-2-sulfonyl-3-stannyl-1,3-dienes by hydrostannylation of (*Z*)-2-sulfonyl-1,3-enynes

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The Stille coupling of (*E*)-α-stannylvinyl sulfones with alkynyl bromides in DMF in the presence of $Pd(PPh_3)_4$ and CuI gave (*Z*)-2-sulfonyl-1,3-enynes in good yields. (*Z*)-2-Sulfonyl-1,3-enynes underwent palladium-catalysed hydrostannylation with tributyltin hydride to afford highly regio- and stereoselectively (1*Z*,3*E*)-2-sulfonyl-3-stannyl-1,3-dienes.

Keywords: difunctionalised 1,3-diene, hydrostannylation, (*E*)-α-stannylvinyl sulfone, stereoselective synthesis

The stereocontrolled synthesis of 1,3-dienes containing metal or heteroatom functional groups has received much attention in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. The stereoselective synthesis of 1,3-dienyl sulfides,[1–3] 1,3-dienyl selenides,[4–6] 1,3-dienylsilanes[7–9] and 1,3-dienylstannanes[10–12] has already been described in the literature. Recently, the synthesis of difunctionalised 1,3-dienes has also attracted great interest in organic synthesis since such dienes may find use as synthetic building blocks.[13–18] In addition, difunctionalised 1,3-dienes containing a heteroatom can control reactions both regio- and stereoselectivity and play a very important role in cycloadditions.[19–22] Jin and co-workers reported the stereoselective synthesis of 2-alkoxy-3-alkyl(aryl) thiobuta-1,3-dienes by a Negishi coupling reaction between an α-alkyl(aryl)thio vinyl zinc chloride and α-bromo vinyl ether.[23] Coleman and Walczak reported the stereoselective synthesis of (*E,E*)-1-tributylstannyl-4-borylbuta-1,3-diene and its use as an orthogonal Stille and Suzuki–Miyaura coupling partner.[24] Recently, we have described the stereoselective synthesis of (*Z,Z*)-2-silyl-3-stannyl-substituted 1,3-dienes by the hydromagnesiation of alkynylsilanes, followed by the cross-coupling reaction with (*E*)-α-iodovinylstannanes in the presence of $Pd(PPh_3)_4$ catalyst.[25] However, to the best of our knowledge, no well-established method is used to prepare stereoselectively (1*Z,*3*E*)-2-sulfonyl-3-stannyl-1,3-dienes. Here we report that (1*Z,*3*E*)-2-sulfonyl-3-stannyl-1,3-dienes can be conveniently obtained by Stille coupling of (*E*)-α-stannylvinyl sulfones with alkynyl bromides, followed by hydrostannylation with tributyltin hydride in the presence of $Pd(PPh_3)_4$.

The starting (*E*)-α-stannylvinyl sulfones were easily prepared by the palladium-catalysed hydrostannylation of alkynyl sulfones according to the procedure reported by us previously.[26] (*E*)-α-Stannylvinyl sulfones **1** are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl sulfones. With a convenient route to the (*E*)-α-stannylvinyl sulfones **1**, we decided to establish the feasibility of using **1** in cross-coupling reactions with alkynyl bromides **2**. Gratifyingly, when the cross-coupling reactions of **1** with a variety of alkynyl bromides **2** were conducted in DMF at room temperature using $Pd(PPh_3)_4$ and CuI as co-catalyst (Scheme 1), fairly rapid reactions occurred affording stereoselectively the desired (*Z*)-2-sulfonyl-1,3-enynes **3** in good yields. The experimental results are summarised in Table 1.

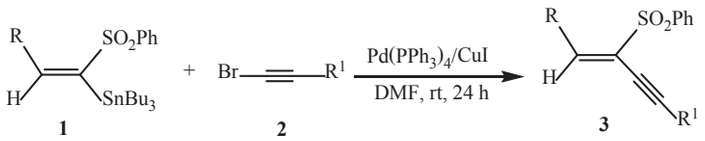
Table 1 Synthesis of (*Z*)-2-sulfonyl-substituted 1,3-enynes **3a–h**[a]

Entry	R	R^1	Product	Yield/%[b]
1	*n*-C_4H_9	*n*-C_6H_{13}	**3a**	81
2	*n*-C_4H_9	Ph	**3b**	78
3	*n*-C_4H_9	$CH_3OCH_2CH_2$	**3c**	80
4	*n*-C_4H_9	Cyclopropyl	**3d**	67
5	Ph	*n*-C_6H_{13}	**3e**	78
6	$CH_3OCH_2CH_2$	*n*-C_6H_{13}	**3f**	71
7	$CH_3OCH_2CH_2$	Ph	**3g**	76
8	$CH_3OCH_2CH_2$	$CH_3OCH_2CH_2$	**3h**	74

[a]Reaction was performed with (E)-α-stannylvinyl sulfone **1** (1 mmol), alkynyl bromide **2** (1.1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), CuI (0.75 mmol) in DMF (8 mL) at room temperature under Ar.
[b]Isolated yield based on the (E)-α-stannylvinyl sulfone **1** used.

It is well documented that the cross-coupling reaction (Stille coupling) of vinyl-stannanes with organic halides in the presence of a palladium catalyst occurs with retention of configuration.[27,28] In addition, the *Z*-configuration of the compound **3c** was confirmed by the NOESY in the ^1H NMR spectrum. An enhancement of the allylic protons was observed as the vinylic proton (δ=6.49) of **3c** was irradiated. A correlation between the allylic protons (δ=2.81–2.76) and aromatic protons (δ=7.96) was observed. The NOE results indicate that **3c** has the expected *Z*-configuration and the cross-coupling reaction of (*E*)-α-stannylvinyl sulfones **1** with alkynyl bromides **2** occurs with the retention of the configuration of the starting compounds **1**.

Palladium-catalysed hydrostannylation of alkynes provides a simple, general route for the synthesis of vinylstannanes.[29] The palladium-catalysed hydrostannylation of substituted enynes generally leads to the α-addition product, providing a convenient route for the synthesis of 1,3-dienylstannanes. The Pd-catalysed hydrostannylation of 1-methoxycarbonyl-substituted enynes,[30] chloroenynes and alkyl-substituted enynes,[31] enediynes,[32] eneynols[33] has been reported. In order to prepare highly regio- and stereoselectively (1*Z*,3*E*)-2-sulfonyl-3-stannyl-substituted 1,3-dienes, we investigated



Scheme 1

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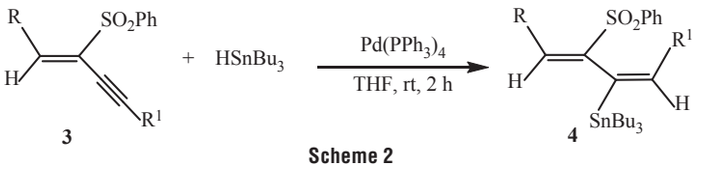

Scheme 2

the palladium-catalysed hydrostannylation of (*Z*)-2-sulfonyl-substituted 1,3-enynes **3** with tributyltin hydride (Scheme 2).

Our initial efforts were devoted to the selection of an efficient catalyst and a suitable solvent for an efficient hydrostannylation reaction of (*Z*)-2-sulfonyl-substituted 1,3-enynes **3** with Bu_3SnH. The reaction of (*Z*)-6-phenylsulfonyltetradec-5-en-7-yne **3a**(1 mmol) and Bu_3SnH (1.1 mmol) was chosen as the model reaction. The influences of the catalysts and solvents on the reaction were examined, and the results are listed in Table 2. This shows that for the palladium catalysts evaluated [$Pd(OAc)_2$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $PdCl_2$], $Pd(OAc)_2$ and $PdCl_2$ were inefficient, and $Pd(PPh_3)_4$ proved to be the most efficient. Both THF and benzene could be used as solvent, but THF was the best choice. Increasing the amount of $Pd(PPh_3)_4$ could shorten the reaction time, but did not increase the yield of (5*Z*,7*E*)-6-phenylsulfonyl-7-tributylstannyltetradeca-5,7-diene (**4a**). Taken together, a good result was obtained when the hydrostannylation reaction was carried out with 2 mol% $Pd(PPh_3)_4$ in THF at room temperature for 4 h under an argon atmosphere (entry 5).

To examine the scope for this hydrostannylation reaction, the hydrostannylation reactions of a variety of (*Z*)-2-sulfonyl-substituted 1,3-enynes **3** with Bu_3SnH were investigated under the optimum conditions and the experimental results are listed in Table 3. As shown in Table 3, the palladium-catalysed hydrostannylation reactions of a variety of (*Z*)-2-sulfonyl-substituted 1,3-enynes **3** with Bu_3SnH proceeded smoothly in the presence of 2 mol% $Pd(PPh_3)_4$ in THF at room temperature to afford regio- and stereoselectively the desired (1*Z*,3*E*)-2-sulfonyl-3-stannyl-substituted 1,3-dienes **4** in good yields. In all cases, a single regio- and geometric isomer was formed according to Scheme 2 and the isolation of products only involved direct flash chromatography.

Table 2 Influences of catalysts and solvents in the hydrostannylation reaction[a]

Entry	Catalyst (mol%)	Solvent	Time/h	Yield/%[b] of **4a**
1	$Pd(OAc)_2$ (2)	THF	24	0
2	$Pd(OAc)_2$ (2)	Benzene	24	0
3	$PdCl_2(PPh_3)_2$ (2)	THF	8	57
4	$PdCl_2(PPh_3)_2$ (2)	Benzene	8	49
5	$Pd(PPh_3)_4$ (2)	THF	4	85
6	$Pd(PPh_3)_4$ (2)	Benzene	8	69
7	$Pd(PPh_3)_4$ (5)	THF	2	84
8	$PdCl_2$ (2)	THF	24	0
9	$PdCl_2$ (2)	Benzene	24	0

[a]Reaction was performed with **3a** (1 mmol), Bu_3SnH (1.1 mmol), solvent (2 mL) at room temperature under Ar.
[b]Isolated yield.

Table 3 Synthesis of (1*Z*,3*E*)-2-sulfonyl-3-stannyl-substituted 1,3-dienes **4**[a]

Entry	R	R^1	Product	Yield/%[b]
1	*n*-C_4H_9	*n*-C_6H_{13}	**4a**	80
2	*n*-C_4H_9	Ph	**4b**	82
3	*n*-C_4H_9	$CH_3OCH_2CH_2$	**4c**	78
4	*n*-C_4H_9	Cyclopropyl	**4d**	74
5	Ph	*n*-C_6H_{13}	**4e**	77
6	$CH_3OCH_2CH_2$	*n*-C_6H_{13}	**4f**	79
7	$CH_3OCH_2CH_2$	Ph	**4g**	81
8	$CH_3OCH_2CH_2$	$CH_3OCH_2CH_2$	**4h**	76

[a]Reaction was performed with **3** (1 mmol), Bu_3SnH (1.1 mmol), $Pd(PPh_3)_4$ (0.02 mmol), THF (2 mL) at room temperature under Ar for 4 h.
[b]Isolated yield.

The regioselectivity is easily assessed by the appropriate coupling patterns of the vinylic proton. One olefinic proton signal of compounds **4a**, **4c**, **4e**, **4f** and **4h** splits characteristically into one triplet at $\delta = 5.60–5.77$ with coupling constant $J = 6.8–7.6$ Hz, which indicated that the hydrostannylation to the compounds **3** had taken place with strong preference for the addition of the hydride at the more electron-deficient terminus of the acetylene. A reasonable explanation lies in the electronic polarisation of the acetylene due to the electron-withdrawing nature of the sulfone moiety. The stereochemistry of the addition was readily apparent from the ^1H NMR spectra of compounds **4** which showed a ($^3J_{Sn117\text{-}H}$) coupling constant of 56–64 Hz, fully in accord with an *E* geometry and overall *cis* addition of tin hydride.[34]

In conclusion, we have developed a highly efficient method for the stereoselective synthesis of (1*Z*,3*E*)-2-sulfonyl-3-stannyl-substituted 1,3-dienes by Stille coupling of (*E*)-α-stannylvinyl sulfones with alkynyl bromides, followed by the palladium-catalysed hydrostannylation reaction with tributyltin hydride. The present method has some attractive advantages of readily available starting materials, mild reaction conditions, high regio- and stereoselectivity and good yields.

Experimental

THF was distilled from sodium prior to use; all other reagents were used as received without further purification. All reactions were carried out under an atmosphere of Ar in oven-dried glassware with magnetic stirring. ^1H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer using $CDCl_3$ as the solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyser.

Synthesis of (Z)-2-sulfonyl-substituted 1,3-enynes **3a–h***; general procedure*

(*E*)-α-Stannylvinyl sulfone **1** (1.0 mmol) and alkynyl bromide **2** (1.1 mmol) were dissolved in DMF (8 mL) under Ar at room temperature. $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.75 mmol) were then added. The mixture was stirred for 20–24 h at room temperature and monitored by TLC (SiO_2) for the disappearance of the starting (*E*)-α-stannylvinyl sulfone **1**. The reaction mixture was diluted with diethyl ether (30 mL), filtered and then treated with 20% aqueous KF (10 mL) for 30 min before being dried and concentrated. The residue was purified by column chromatography on silica gel (eluent: light petroleum ether/Et_2O, 5:1).

(Z)-6-Phenylsulfonyltetradec-5-en-7-yne (**3a**): Colourless oil. IR (film): ν (cm^{-1}) 2957, 2933, 2873, 2238, 1712, 1448, 1330, 1155, 721, 688; ^1H NMR ($CDCl_3$): δ 7.96–7.94 (m, 2H), 7.63–7.51 (m, 3H), 6.45 (t, $J = 7.6$ Hz, 1H), 2.83–2.78 (m, 2H), 2.22 (t, $J = 7.6$ Hz, 2H), 1.44–1.22 (m, 12H), 0.93–0.85 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 150.5, 140.2, 133.6, 128.7, 128.3, 127.1, 95.5, 74.6, 31.2, 30.5, 29.2, 28.7, 28.3, 22.6, 22.4, 19.7, 13.9, 13.8; Anal. Calcd for $C_{20}H_{28}SO_2$: C, 72.29; H, 8.43. Found: C, 72.05; H, 8.22%.

(Z)-6-Phenylsulfonyl-8-phenyloct-5-en-7-yne (**3b**): Colourless oil. IR (film): ν (cm^{-1}) 2957, 2929, 2874, 2206, 1720, 1593, 1447, 1323, 1158,

756, 688; ^{1}H NMR ($CDCl_3$): δ 8.06–8.03 (m, 2H), 7.69–7.56 (m, 3H), 7.36–7.28 (m, 5H), 6.66 (t, *J*=7.6 Hz, 1H), 2.93–2.87 (m, 2H), 1.54–1.32 (m, 4H), 0.98 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 151.5, 140.2, 133.6, 131.5, 128.9, 128.6, 128.4, 128.3, 127.4, 122.0, 93.5, 83.4, 31.1, 28.5, 22.4, 13.9; Anal. Calcd for $C_{20}H_{20}SO_2$: C, 74.08; H, 6.17. Found: C, 73.90; H, 5.93%.

(Z)-6-Phenylsulfonyl-10-methoxydec-5-en-7-yne (**3c**): Colourless oil. IR (film): ν (cm^{-1}) 2952, 2922, 2875, 2219, 1586, 1447, 1315, 1149, 1119, 1083, 730, 688; ^{1}H NMR ($CDCl_3$): δ 7.96 (d, *J*=8.4 Hz, 2H), 7.63–7.52 (m, 3H), 6.49 (t, *J*=7.4 Hz, 1H), 3.40 (t, *J*=6.8 Hz, 2H), 3.33 (s, 3H), 2.81–2.76 (m, 2H), 2.52 (t, *J*=6.8 Hz, 2H), 1.45–1.32 (m, 4H), 0.91 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 150.4, 140.3, 133.6, 128.8, 128.2, 127.1, 95.8, 75.1, 70.4, 58.6, 31.2, 30.5, 28.6, 22.4, 13.9; Anal. Calcd for $C_{17}H_{22}SO_3$: C, 66.63; H, 7.24. Found: C, 66.35; H, 6.97%.

(Z)-6-Phenylsulfonyl-8-cyclopropyloct-5-en-7-yne (**3d**): Colourless oil. IR (film): ν (cm^{-1}) 2952, 2931, 2876, 2215, 1595, 1448, 1324, 1157, 757, 689; ^{1}H NMR ($CDCl_3$): δ 7.95–7.93 (m, 2H), 7.63–7.53 (m, 3H), 6.28 (t, *J*=7.4 Hz, 1H), 2.68–2.64 (m, 2H), 1.67–1.60 (m, 1H), 1.53–1.28 (m, 4H), 0.96–0.88 (m, 7H); ^{13}C NMR ($CDCl_3$): δ 151.0, 140.3, 133.7, 128.7, 128.3, 127.1, 94.6, 76.8, 31.1, 28.4, 22.5, 14.0, 9.8, 0.1; Anal. Calcd for $C_{17}H_{20}SO_2$: C, 70.80; H, 6.99. Found: C, 70.55; H, 6.72%.

(Z)-1-Phenyl-2-phenylsulfonyldec-1-en-3-yne (**3e**): Colourless oil. IR (film): ν (cm^{-1}) 3065, 2958, 2927, 2878, 2216, 1589, 1446, 1322, 1149, 752, 689; ^{1}H NMR ($CDCl_3$): δ 7.97–7.92 (m, 4H), 7.86 (s, 1H), 7.63–7.34 (m, 6H), 2.21 (t, *J*=7.2 Hz, 2H), 1.66–1.54 (m, 2H), 1.38–1.24 (m, 6H), 0.92 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 140.7, 139.2, 133.5, 133.1, 131.1, 130.1, 128.9, 128.8, 128.6, 124.8, 105.2, 73.2, 30.8, 29.5, 28.4, 22.7, 19.8, 14.0; Anal. Calcd for $C_{22}H_{24}SO_2$: C, 74.96; H, 6.81. Found: C, 74.68; H, 6.67%.

(Z)-1-Methoxy-4-phenylsulfonyldodec-3-en-5-yne (**3f**): Colourless oil. IR (film): ν (cm^{-1}) 3056, 2959, 2930, 2875, 2211, 1584, 1449, 1320, 1149, 1089, 751, 687; ^{1}H NMR ($CDCl_3$): δ 7.97–7.94 (m, 2H), 7.65–7.51 (m, 3H), 6.56 (t, *J*=7.6 Hz, 1H), 3.50 (t, *J*=6.0 Hz, 2H), 3.34 (s, 3H), 3.11–3.06 (m, 2H), 2.22 (t, *J*=7.2 Hz, 2H), 1.42–1.20 (m, 8H), 0.91 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 150.7, 140.1, 133.8, 128.6, 128.3, 127.2, 96.3, 74.4, 70.8, 58.7, 32.1, 31.5, 29.1, 28.4, 22.6, 19.6, 14.0; Anal. Calcd for $C_{19}H_{26}SO_3$: C, 68.23; H, 7.84. Found: C, 67.96; H, 7.62%.

(Z)-1-Methoxy-4-phenylsulfonyl-6-phenylhex-3-en-5-yne (**3g**): Colourless oil. IR (film): ν (cm^{-1}) 3053, 2955, 2928, 2876, 2208, 1586, 1446, 1324, 1147, 1085, 756, 689; ^{1}H NMR ($CDCl_3$): δ 8.03 (d, *J*=7.2 Hz, 2H), 7.66–7.55 (m, 3H), 7.30–7.24 (m, 5H), 6.75 (t, *J*=7.6 Hz, 1H), 3.56 (t, *J*=6.0 Hz, 2H), 3.37 (s, 3H), 3.23–3.15 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 151.7, 140.3, 133.8, 131.4, 129.0, 128.7, 128.5, 128.4, 127.6, 122.2, 93.3, 83.7, 70.6, 58.5, 31.9; Anal. Calcd for $C_{19}H_{18}SO_3$: C, 69.91; H, 5.56. Found: C, 69.67; H, 5.73%.

(Z)-1,8-Dimethoxy-4-phenylsulfonyloct-3-en-5-yne (**3h**): Colourless oil. IR (film): ν (cm^{-1}) 3058, 2954, 2929, 2873, 2178, 1594, 1449, 1327, 1145, 1088, 752, 685; ^{1}H NMR ($CDCl_3$): δ 7.96 (d, *J*=7.2 Hz, 2H), 7.64–7.52 (m, 3H), 6.60 (t, *J*=7.6 Hz, 1H), 3.49 (t, *J*=6.0 Hz, 2H), 3.40 (t, *J*=7.0 Hz, 2H), 3.34 (s, 3H), 3.32 (s, 3H), 3.14–3.10 (m, 2H), 2.51 (t, *J*=7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 150.2, 140.1, 133.7, 128.9, 128.2, 127.3, 95.2, 74.9, 71.8, 70.6, 58.8, 58.4, 30.5, 29.6; Anal. Calcd for $C_{16}H_{20}SO_4$: C, 62.31; H, 6.54. Found: C, 62.52; H, 6.31%.

Synthesis of (1Z,3E)-2-sulfonyl-3-stannyl-substituted 1,3-dienes **4a–h***; general procedure*

(*Z*)-2-Sulfonyl-substituted 1,3-enyne **3** (1.0 mmol) was added dropwise to a solution prepared by adding tributylstannane (1.1 mmol) to $Pd(PPh_3)_4$ (0.02 mmol) in THF (2 mL) at room temperature under an argon atmosphere. After 4 h, the reaction mixture was evaporated under reduced pressure and the residue was purified by column chromatography (light petroleum ether/ethyl ether, 4:1) on silica gel.

(5Z,7E)-6-Phenylsulfonyl-7-tributylstannyltetradeca-5,7-diene (**4a**): Colourless oil. IR (film): ν (cm^{-1}) 3067, 2957, 2922, 2878, 1587, 1464, 1447, 1304, 1151, 1084, 727, 688; ^{1}H NMR ($CDCl_3$): δ 7.80 (d, *J*=7.2 Hz, 2H), 7.56–7.44 (m, 3H), 5.63 (t, *J*=7.2 Hz, 1H), 5.60 (t, *J*=7.6 Hz, $^3J_{Sn-H}$=56 Hz, 1H), 2.82–2.76 (m, 2H), 1.64–0.84 (m, 47H); ^{13}C NMR ($CDCl_3$): δ 148.0, 142.1, 140.9, 140.3, 140.2, 132.9, 128.6, 128.1, 31.9, 31.6, 29.4, 29.3, 29.0, 28.9, 27.8, 27.4, 22.5, 22.4, 14.0, 13.9, 13.7, 11.2; Anal. Calcd for $C_{32}H_{56}SO_2Sn$: C, 61.64; H, 9.05. Found: C, 61.38; H, 8.87%.

(1E,3Z)-1-Phenyl-2-tributylstannyl-3-phenylsulfonylocta-1,3-diene (**4b**): Colourless oil. IR (film): ν (cm^{-1}) 3060, 2956, 2925, 2871, 1585, 1464, 1447, 1304, 1152, 1084, 727, 688; ^{1}H NMR ($CDCl_3$): δ 7.75 (d, *J*=8.0 Hz, 2H), 7.46–7.32 (m, 3H), 7.02–6.73 (m, 5H), 6.58 (s, $^3J_{Sn-H}$=64 Hz, 1H), 5.79 (t, *J*=7.2 Hz, 1H), 2.74–2.69 (m, 2H), 1.62–1.28 (m, 16H), 1.20–1.15 (m, 6H), 0.96–0.84 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 144.5, 143.5, 142.3, 141.3, 140.4, 136.6, 133.2, 128.7, 128.2, 128.1, 127.8, 127.1, 31.3, 29.0, 28.1, 27.5, 22.4, 13.9, 13.8, 11.6; Anal. Calcd for $C_{32}H_{48}SO_2Sn$: C, 62.44; H, 7.86. Found: C, 62.17; H, 7.59%.

(3E,5Z)-1-Methoxy-4-tributylstannyl-5-phenylsulfonyldeca-3,5-diene (**4c**): Colourless oil. IR (film): ν (cm^{-1}) 3067, 2956, 2924, 2871, 1587, 1464, 1447, 1305, 1153, 1119, 1085, 728, 688; ^{1}H NMR ($CDCl_3$): δ 7.81 (d, *J*=7.2 Hz, 2H), 7.57–7.46 (m, 3H), 5.66 (t, *J*=6.8 Hz, $^3J_{Sn-H}$=56 Hz, 1H), 5.64 (t, *J*=7.6 Hz, 1H), 3.18 (s, 3H), 2.95 (t, *J*=6.8 Hz, 2H), 2.81–2.76 (m, 2H), 1.78–1.71 (m, 2H), 1.57–1.25 (m, 16H), 1.01–0.88 (m, 18H); ^{13}C NMR ($CDCl_3$): δ 143.2, 142.9, 141.7, 140.7, 140.5, 133.0, 128.8, 128.1, 71.8, 58.5, 31.9, 29.8, 29.0, 27.8, 27.4, 22.5, 13.9, 13.8, 11.2; Anal. Calcd for $C_{29}H_{50}SO_3Sn$: C, 58.30; H, 8.44. Found: C, 58.07; H, 8.21%.

(1E,3Z)-1-Cyclopropyl-2-tributylstannyl-3-phenylsulfonylocta-1,3-diene (**4d**): Colourless oil. IR (film): ν (cm^{-1}) 2957, 2924, 2872, 1587, 1464, 1447, 1304, 1152, 1083, 728, 688; ^{1}H NMR ($CDCl_3$): δ 7.86 (d, *J*=7.2 Hz, 2H), 7.55–7.44 (m, 3H), 5.78 (t, *J*=7.2 Hz, 1H), 4.88 (d, *J*=9.6 Hz, $^3J_{Sn-H}$=56 Hz, 1H), 2.81–2.75 (m, 2H), 1.65–1.23 (m, 23H), 1.03–0.86 (m, 16H); ^{13}C NMR ($CDCl_3$): δ 151.5, 142.7, 141.2, 140.5, 137.6, 132.8, 128.6, 128.3, 31.9, 29.0, 27.9, 26.9, 22.5, 17.5, 13.8, 13.6, 11.1, 7.2; Anal. Calcd for $C_{29}H_{48}SO_2Sn$: C, 60.11; H, 8.35. Found: C, 59.87; H, 8.09%.

(1Z,3E)-1-Phenyl-2-phenylsulfonyl-3-tributylstannyldeca-1,3-diene (**4e**): Colourless oil. IR (film): ν (cm^{-1}) 3063, 2955, 2923, 2854, 1586, 1464, 1447, 1306, 1148, 1086, 750, 689; ^{1}H NMR ($CDCl_3$): δ 7.87 (d, *J*=7.6 Hz, 2H), 7.56–7.28 (m, 8H), 6.64 (s, 1H), 5.77 (t, *J*=7.0 Hz, $^3J_{Sn-H}$=56 Hz, 1H), 1.84–1.74 (m, 2H), 1.65–0.85 (m, 38H); ^{13}C NMR ($CDCl_3$): δ 150.2, 148.4, 145.2, 135.1, 134.5, 133.0, 132.8, 130.0, 129.1, 128.6, 128.4, 127.7, 31.7, 29.7, 29.3, 29.1, 29.0, 27.5, 22.6, 14.0, 13.7, 11.3; Anal. Calcd for $C_{34}H_{52}SO_2Sn$: C, 63.46; H, 8.15. Found: C, 63.21; H, 7.87%.

(3Z,5E)-1-Methoxy-4-phenylsulfonyl-5-tributylstannyldodeca-3,5-diene (**4f**): Colourless oil. IR (film): ν (cm^{-1}) 3067, 2956, 2923, 2852, 1587, 1464, 1447, 1316, 1150, 1119, 1082, 730, 688; ^{1}H NMR ($CDCl_3$): δ 7.82 (d, *J*=8.0 Hz, 2H), 7.56–7.44 (m, 3H), 5.71 (t, *J*=7.6 Hz, 1H), 5.63 (t, *J*=7.2 Hz, $^3J_{Sn-H}$=56 Hz, 1H), 3.51 (t, *J*=6.4 Hz, 2H), 3.34 (s, 3H), 3.11–3.06 (m, 2H), 1.64–1.58 (m, 2H), 1.56–0.83 (m, 38H); ^{13}C NMR ($CDCl_3$): δ 148.5, 143.2, 140.4, 139.8, 136.5, 133.0, 128.7, 128.3, 71.9, 58.5, 31.6, 29.4, 29.3, 29.1, 29.0, 28.5, 27.4, 22.6, 14.1, 13.8, 11.2; Anal. Calcd for $C_{31}H_{54}SO_3Sn$: C, 59.52; H, 8.70. Found: C, 59.26; H, 8.55%.

(1E,3Z)-1-Phenyl-2-tributylstannyl-3-phenylsulfonyl-6-methoxyhexa-1,3-diene (**4g**): Colourless oil. IR (film): ν (cm^{-1}) 3060, 2956, 2924, 2871, 1585, 1464, 1447, 1316, 1305, 1149, 1118, 1082, 729, 687; ^{1}H NMR ($CDCl_3$): δ 7.72 (d, *J*=7.6 Hz, 2H), 7.41–7.28 (m, 3H), 7.02–6.79 (m, 5H), 6.56 (s, $^3J_{Sn-H}$=64 Hz, 1H), 5.91 (t, *J*=7.2 Hz, 1H), 3.44 (t, *J*=6.4 Hz, 2H), 3.30 (s, 3H), 3.08–3.00 (m, 2H), 1.62–1.54 (m, 6H), 1.42–1.25 (m, 6H), 1.13–1.05 (m, 6H), 0.93 (t, *J*=7.2 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 144.2, 143.7, 143.4, 139.9, 137.5, 136.6, 133.2, 128.6, 128.4, 128.3, 127.7, 127.1, 71.5, 58.5, 29.0, 28.7, 27.5, 13.8, 11.6; Anal. Calcd for $C_{31}H_{46}SO_3Sn$: C, 60.30; H, 7.51. Found: C, 60.48; H, 7.32%.

(3Z,5E)-1,8-Dimethoxy-4-phenylsulfonyl-5-tributylstannylocta-3,5-diene (**4h**): Colourless oil. IR (film): ν (cm^{-1}) 3066, 2922, 2873, 1586, 1463, 1447, 1316, 1188, 1149, 1118, 1083, 730, 688; ^{1}H NMR ($CDCl_3$): δ 7.82 (d, *J*=7.6 Hz, 2H), 7.58–7.46 (m, 3H), 5.74 (t, *J*=7.2 Hz, 1H), 5.68 (t, *J*=7.2 Hz, $^3J_{Sn-H}$=56 Hz, 1H), 3.51 (t, *J*=6.2 Hz, 2H), 3.34 (s, 3H), 3.17 (s, 3H), 3.12–3.06 (m, 2H), 2.93 (t, *J*=7.0 Hz, 2H), 1.68–1.60 (m, 2H), 1.57–1.48 (m, 6H), 1.38–1.27 (m, 6H), 0.99 (t, *J*=8.0 Hz, 6H), 0.89 (t, *J*=7.2 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 143.6, 143.0, 142.6, 140.3, 136.7, 133.1, 128.7, 128.3, 71.9, 71.8, 58.5, 58.4, 29.7, 29.0, 28.5, 27.4, 13.8, 11.2; Anal. Calcd for $C_{28}H_{48}SO_4Sn$: C, 56.10; H, 8.07. Found: C, 55.84; H, 7.79%.

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