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Palladium-Catalyzed Hydrostannylation of α-Heteroalkynes and Alkynyl Esters in Ionic Liquids

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Palladium-catalyzed hydrostannylation reactions of α-heteroalkynes and alkynyl esters were achieved with high regio- and stereoselectively in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) at 60 °C in high yields. Our system not only avoids the use of highly toxic benzene or volatile THF as solvent but also solves the basic problem of palladium catalyst reuse.

Introduction

The development of environmentally friendly synthetic procedures has become a major concern throughout the chemical industry due to the continuing depletion of natural resources and growing environmental awareness.[1] One of the prime concerns of industry and academia is the search for replacements to the environmentally damaging organic solvents used on a large scale, especially those that are volatile and difficult to contain. Room-temperature ionic liquids, especially those based upon the 1,3-dialkylimidazolium cation, have attracted growing interest in the last few years.[2] They offer an alternative and ecologically sound medium in comparison to conventional organic solvents, as they are nonvolatile, recyclable, thermally robust, and excellent solvents for a wide range of organic and inorganic materials. Furthermore, their high compatibility with transition-metal catalysts and limited miscibility with common solvents enables easy product and catalyst separation with the retention of the stabilized catalyst in the ionic phase.[3] These and related ionic liquids have been successfully applied to hydrogenations,[4] alkene dimerizations,[5] Friedel–Crafts reactions,[6] Diels–Alder reactions,[7] Heck reactions,[8] Bechmann condensations,[9] Suzuki reactions,[10] Baylis–Hillman reactions,[11] Stille reactions,[12] and Sonogashira reactions.[13]

Vinylstannanes are proven synthons and building blocks for organic synthesis.[14] As a result of their synthetic utility, considerable effort has been expended toward their synthesis, particularly in the case of trisubstituted vinylstannanes.[15] Although a number of methods have been developed for their preparation, including those involving carbonyl addition chemistry,[16] transmetalation of vinylmetallic species,[17] and metallometalation of alkynes,[18] the addition of tributyltin hydride to unsymmetrical alkynes is a simple and most straightforward route to these vinylstannane intermediates.[19] The main difficulty with this transformation is control of the stereo- and regiochemistry of the vinylstannane products. Under radical conditions, the addition of the tin hydride to alkynes suffers generally from its low selectivity and mixtures of both stereo- and regioisomers are obtained.[20] In contrast, palladium-catalyzed hydrostannylation of disubstituted alkynes proceeds in a stereoselective manner (*cis* addition).[21] However, the regiochemistry of this reaction appears to be highly dependent on the nature of the alkyne substituents. Alami et al.[22] reported that the regioselectivity of palladium-catalyzed hydrostannylation of enynols can be controlled by the geometry of the double bond (*Z*- or *syn*-directing effect) and *ortho* substituents can control regioselective addition of tributyltin hydride to unsymmetrical diaryl alkynes. The palladium-catalyzed hydrostannylation reaction of α-heteroalkynes such as alkynyl sulfides, alkynyl selenides, alkynyl sulfones, and alkynyl esters has been reported to occur regio- and stereoselectively.[23] The hydrostannylation reactions of α-heteroalkynes and alkynyl esters are catalyzed by homogeneous palladium catalysts such as $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ by using benzene or THF as the solvent; however, the homogeneous palladium catalysts cannot be recovered and reused and benzene is highly toxic. These disadvantages have so far precluded its practical applications. Recently, Imperato et al.[24] reported Stille reactions with tetraalkylstannanes and phenyltrialkylstannanes in low-melting sugar–urea–salt mixtures. Vitz et al.[25] described ionic-liquid-supported tin reagents for Stille cross-coupling reactions. In this paper, we describe the palladium-catalyzed hydrostannylation of alkynyl sulfides, alkynyl selenides, alk-

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ynyl esters, and alkynyl sulfones in room-temperature ionic liquids. The developed methodology has important practical advantages deserving special note.

Results and Discussion

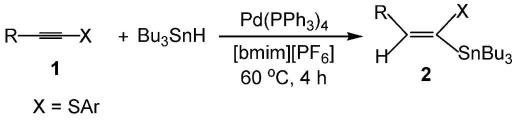
As a suitable solvent for the hydrostannylation of alkynes, moisture-stable and readily available 1-butyl-3-methylimidiazolium hexafluorophosphate ([bmim][PF$_6$]) was chosen. Initially, to determine the optimum conditions, the hydrostannylation of 1-phenylthio-1-hexyne with Bu$_3$SnH was examined, and the results are summarized in Table 1. It was found that among the palladium catalysts tested, Pd(PPh$_3$)$_4$ proved to be the most efficient. For the temperatures evaluated (25, 40, 60, and 80 °C), 60 °C gave the best results. Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of (*E*)-1-phenylthio-1-tributylstannyl-1-hexene (Table 1, Entry 8). The low palladium concentration usually led to a long reaction time, which was consistent with our experimental results (Table 1, Entries 9, 10). Taken together, excellent results were obtained when the coupling reaction was carried out with 2 mol-% of Pd(PPh$_3$)$_4$ in [bmim][PF$_6$] at 60 °C (Table 1, Entry 3).

Table 1. Palladium-catalyzed hydrostannylation of 1-phenylthio-1-hexyne with Bu$_3$SnH under various conditions.[a]

Entry	Catalyst (mol-%)	Temp. [°C]	Time [h]	Yield[b] [%]
1	Pd(PPh$_3$)$_4$ (2)	25	24	0
2	Pd(PPh$_3$)$_4$ (2)	40	24	0
3	Pd(PPh$_3$)$_4$ (2)	60	4	88
4	Pd(PPh$_3$)$_4$ (2)	80	4	79
5	PdCl$_2$(PPh$_3$)$_2$ (2)	40	24	0
6	PdCl$_2$(PPh$_3$)$_2$ (2)	60	5	63
7	PdCl$_2$(PPh$_3$)$_2$ (2)	80	5	61
8	Pd(PPh$_3$)$_4$ (5)	60	2	86
9	Pd(PPh$_3$)$_4$ (1)	60	10	87
10	Pd(PPh$_3$)$_4$ (0.5)	60	24	82
11	PdCl$_2$(PhCN)$_2$ (2)	60	24	0

[a] Reactions were conducted with 1-phenylthio-1-hexyne (1.0 mmol) and Bu$_3$SnH (1.05 mmol) in [bmim][PF$_6$] (2.0 mL) under an atmosphere of argon. [b] Isolated yield based on the amount of 1-phenylthio-1-hexyne used.

The hydrostannylation of a variety of alkynyl sulfides with Bu$_3$SnH in the presence of Pd(PPh$_3$)$_4$ (2 mol-%) was investigated (Scheme 1), and the experimental results are showed in Table 2. The hydrostannylation reactions of a variety of alkynyl sulfides with Bu$_3$SnH in [bmim][PF$_6$] at 60 °C proceeded very smoothly to give highly regio- and stereoselectively the corresponding (*E*)-α-stannylvinyl sulfides **2a**–**i** in high yields after 4 h. The ionic liquid [bmim][PF$_6$] has the advantages of providing increased yields and higher regioselectivities than benzene as the solvent. For example, in [bmim][PF$_6$] at 60 °C after 4 h, **2d** was successfully prepared in 86% yield and with 100% regioselectivity (Table 2, Entry 4), but the same reaction run in benzene at 23 °C gave a 75% yield with 95% regioselectivity when stopped after 1 h.[23a] Investigations of crude products **2** by ^{1}H NMR spectroscopy (400 MHz) showed their isomeric purities to be more than 99%. One olefinic proton signal of compounds **2a**–**c** and **2g**–**i** splits characteristically into one triplet at δ = 5.98–6.17 ppm with a coupling constant J = 5.2–6.8 Hz, which indicated that the hydrostannylation to the alkynyl sulfides had taken place with strong preference for the addition of the tin atom at the carbon atom adjacent to the arylthio groups. The regiochemistry of compounds **2d**–**f** was easily established by their ^{1}H NMR spectra, as the chemical shift of one olefinic proton was located at δ = 6.88–6.93 ppm, which indicated that the hydrostannylation to the arylacetylenic sulfides had also taken place with strong preference for the addition of the tin atom at the carbon atom adjacent to the arylthio groups. In addition, compound **2d** is known and its ^{1}H NMR spectrum is consistent with that reported in the literature.[23a] The stereochemistry of the addition was readily apparent from the ^{1}H NMR spectra of compounds **2a**–**i**, which showed a $^3J_{\mathrm{Sn,H}}$ coupling constant of 48 Hz; this value is in full accord with an *E* geometry and overall *cis* addition of tin hydride.[26]



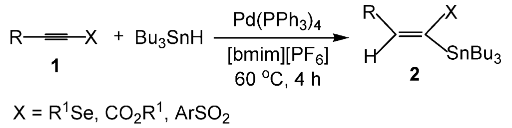
Scheme 1.

Table 2. Synthesis of (*E*)-α-stannylvinyl sulfides **2a**–**i** (X = SAr).[a]

Entry	R	Ar	Product	Yield[b] [%]	α/β[c]
1	*n*-C$_4$H$_9$	Ph	**2a**	88	100:0
2	*n*-C$_4$H$_9$	4-CH$_3$C$_6$H$_4$	**2b**	85	100:0
3	*n*-C$_4$H$_9$	4-ClC$_6$H$_4$	**2c**	87	100:0
4	Ph	Ph	**2d**	86	100:0
5	Ph	4-CH$_3$C$_6$H$_4$	**2e**	84	99:1
6	Ph	4-ClC$_6$H$_4$	**2f**	85	99:1
7	CH$_3$OCH$_2$	Ph	**2g**	86	100:0
8	CH$_3$OCH$_2$	4-CH$_3$C$_6$H$_4$	**2h**	83	99:1
9	CH$_3$OCH$_2$	4-ClC$_6$H$_4$	**2i**	85	100:0

[a] Reactions were conducted with alkynyl sulfide **1** (1.0 mmol), Bu$_3$SnH (1.05 mmol), and Pd(PPh$_3$)$_4$ (0.02 mmol) in [bmim][PF$_6$] (2.0 mL) at 60 °C for 4 h under an atmosphere of argon. [b] Isolated yield based on the amount of alkynyl sulfide **1** used. [c] Determined by ^{1}H NMR spectroscopy.

The developed methodology was also applicable for hydrostannylation reactions of alkynyl selenides, alkynyl esters, and alkynyl sulfones with Bu$_3$SnH (Scheme 2), and the palladium(0)-catalyzed experimental results are summarized in Table 3. We found that the palladium(0)-catalyzed hydrostannylation reactions of alkynyl selenides, alkynyl esters, and alkynyl sulfones with Bu$_3$SnH in [bmim][PF$_6$] did not occur at room temperature and a higher temperature (60 °C) was required, as in the above hydrostannylation reactions of alkynyl sulfides in [bmim][PF$_6$]. From Table 3, we can see that the hydrostannylation reactions of a variety of alkynyl selenides with Bu$_3$SnH in the presence of Pd(PPh$_3$)$_4$ catalyst at 60 °C proceeded smoothly to afford highly regio- and stereoselectively the corresponding (*E*)-α-stannylvinyl selenides **2j**–**m** in high yields after 4 h. The hydrostannylation reaction run in [bmim][PF_6] also has the advantages of increased yield and higher regioselectivity relative to the reaction run in benzene. For example, the hydrostannylation reaction of 1-phenylseleno-3-methoxy-1-propyne with Bu_3SnH in [bmim][PF_6] at 60 °C gave **2k** in 87% yield with 100% regioselectivity after 4 h (Table 3, Entry 2), but the same reaction run in benzene at 25 °C gave **2k** in 73% yield with 95% regioselectivity after 2 h.[23b] The hydrostannylation reactions of a variety of alkynyl esters and alkynyl sulfones with Bu_3SnH in the presence of $Pd(PPh_3)_4$ (2 mol-%) in [bmim][PF_6] at 60 °C also proceeded smoothly to afford highly regio- and stereoselectively the corresponding (*E*)-α-stannyl-α,β-unsaturated esters and (*E*)-α-stannylvinyl sulfones in good-to-high yields (Table 3, Entries 5–12). Increased yields and higher regioselectivities in the hydrostannylation reactions of alkynyl esters run in [bmim][PF_6] were also observed relative to those obtained when the reaction was run in THF. For example, the reaction of 1-phenyl-2-ethoxycarbonylethyne with Bu_3SnH under the original conditions afforded **2o** in 71% yield with 90% regioselectivity,[23d] whereas the same reaction run in [bmim][PF_6] at 60 °C gave **2o** in 80% yield and with 98% regioselectivity (Table 3, Entry 6).



Scheme 2.

Table 3. Synthesis of (*E*)-α-stannylvinyl selenides **2j–m**, (*E*)-α-stannyl-α,β-unsaturated esters **2n–p**, and (*E*)-α-stannylvinyl sulfones **2q–u**.[a]

Entry	R	X	Product	Yield[b] [%]	α/β[c]
1	*n*-C_4H_9	PhSe	**2j**	89	100:0
2	CH_3OCH_2	PhSe	**2k**	87	100:0
3	CH_3OCH_2	CH_3Se	**2l**	85	100:0
4	*n*-C_6H_{13}	PhSe	**2m**	88	100:0
5	*n*-C_4H_9	CO_2Et	**2n**	83	99:1
6	Ph	CO_2Et	**2o**	80	98:2
7	*n*-C_6H_{13}	CO_2Et	**2p**	81	99:1
8	*n*-C_4H_9	$PhSO_2$	**2q**	89	100:0
9	*n*-C_4H_9	4-$MeC_6H_4SO_2$	**2r**	87	100:0
10	Ph	$PhSO_2$	**2s**	84	100:0
11	CH_3OCH_2	$PhSO_2$	**2t**	85	100:0
12	CH_3OCH_2	4-$MeC_6H_4SO_2$	**2u**	86	100:0

[a] Reactions were conducted with **1** (1.0 mmol), Bu_3SnH (1.05 mmol), and $Pd(PPh_3)_4$ (0.02 mmol) in [bmim][PF_6] (2.0 mL) at 60 °C for 4 h under an atmosphere of argon. [b] Isolated yield based on the amount of **1** used. [c] Determined by ^1H NMR spectroscopy.

Investigations of crude products **2j–u** by ^1H NMR spectroscopy (400 MHz) showed their isomeric purities of more than 98%. One olefinic proton signal of compounds **2j–u**, except for **2o** and **2s**, splits characteristically into one triplet at $\delta = 6.04–6.42$ ppm with $J = 4.8–7.2$ Hz, which indicated that the hydrostannylation reactions of alkynyl selenides, alkynyl esters, and alkynyl sulfones had taken place with strong preference for the addition of the tin atom to the carbon atom adjacent to the electron-withdrawing groups. Compounds **2o** and **2s** are known, and their ^1H NMR spectra are consistent with those reported in the literature.[23d,23e] The stereochemistry of the addition was also apparent from the ^1H NMR spectra of compounds **2j–u**, which showed a $^3J_{Sn,H}$ coupling constant of 48–64 Hz; this value is in full accord with an *E* geometry and overall *cis* addition of tin hydride.

Isolation of products **2** from the [bmim][PF_6] reaction mixtures can be conveniently achieved by extraction with light petroleum ether (3×). To evaluate the possibility of recycling the ionic liquid and the palladium catalyst used in the reaction, 1-phenylsulfonyl-1-hexyne, Bu_3SnH, and $Pd(PPh_3)_4$ were allowed to react in [bmim][PF_6] at 60 °C for 4 h, and the product was then extracted with light petroleum ether (3×) to afford the clean ionic liquid catalytic solution. After the recovered ionic liquid containing the palladium catalyst was concentrated in vacuo (5.0 Torr/room temp. for 1 h), a second amount of reactants was added and the process was repeated up to six times. It seems that there is no effect on the rate and yield of the reaction during 1–4 cycles (Table 4); this result is important from a practical point of view. However, the yield of **2q** decreased by 17% in the sixth cycle as a result of the extraction of the palladium catalyst into light petroleum ether. The palladium content in the crude products was determined to be 3.2 ppm by ICP analysis after the first cycle.

Table 4. Ionic liquid and catalyst recycling in the hydrostannylation of 1-phenylsulfonyl-1-hexyne.[a]

Cycle	Yield[b] [%]	Cycle	Yield[b] [%]
1	89	4	86
2	87	5	80
3	88	6	72

[a] Reaction was conducted with 1-phenylsulfonyl-1-hexyne (1.0 mmol) and Bu_3SnH (1.05 mmol) in the presence of $Pd(PPh_3)_4$ (2 mol-%) in [bmim][PF_6] (2.0 mL) at 60 °C for 4 h. [b] Isolated yield based on the amount of 1-phenylsulfonyl-1-hexyne used.

Conclusions

The present article describes the palladium-catalyzed hydrostannylation reactions of alkynyl sulfides, alkynyl selenides, alkynyl esters, and alkynyl sulfones with tributyltin hydride in ionic liquid. The high yields and high regioselectivities were observed for a variety of alkynyl sulfides, alkynyl selenides, alkynyl esters, and alkynyl sulfones. Important advantages of the developed methodology include easy product isolation, ionic liquid and catalyst recycling, and the use of highly toxic benzene or volatile THF as solvent is avoided.

Experimental Section

General: Chemicals were obtained from Aldrich and Merck and were used as received. ^1H NMR spectra were recorded with a Bruker AC-P400 spectrometer with TMS as an internal standard by using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded with a Bruker AC-P400 spectrometer by using $CDCl_3$ as the solvent. IR spectra were determined with an FTS-185 instrument as neat films. Mass spectra were determined with a Finnigan 8230 mass spectrometer. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer.

General Procedure for the Hydrostannylation of Alkynes in Ionic Liquid: Into a two-necked flask equipped with a magnetic stirring bar were placed $Pd(PPh_3)_4$ (0.02 mmol), alkyne (1.0 mmol), Bu_3SnH (1.05 mmol), and $[bmim][PF_6]$ (2.0 mL) under an argon atmosphere. The mixture was stirred at 60 °C for 4 h, then cooled to 30 °C and extracted with light petroleum ether (3×10 mL). The recovered ionic liquid containing palladium catalyst was concentrated in vacuo (5.0 Torr/room temp. for 1 h) and reused in the next run. The combined organic layer was concentrated under reduced pressure to give an oil, which was purified by SiO_2 column chromatography.

(*E*)-1-Phenylthio-1-tributylstannyl-1-hexene (2a):[23a] Yield: 0.423 g, 88%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.16 (m, 5 H), 6.05 (t, J = 6.8 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 2.43–2.39 (m, 2 H), 1.43–1.19 (m, 16 H), 0.92 (t, J = 7.2 Hz, 3 H), 0.84 (t, J = 7.2 Hz, 9 H), 0.72–0.69 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0 (CH), 138.2 (C), 136.1 (CH), 129.8 ($CH\times2$), 128.7 ($CH\times2$), 125.8 (C), 31.5 (CH_2), 30.8 (CH_2), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 22.4 (CH_2), 14.0 (CH_3), 13.7 ($CH_3\times3$), 11.0 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3182, 3085, 2957, 2928, 1584, 1460, 1446, 689 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 482 (2.7) $[M]^+$, 425 (51), 343 (83), 291 (32), 229 (100), 177 (69). $C_{24}H_{42}SSn$ (481.36): calcd. C 59.88, H 8.79; found C 59.56, H 8.65.

(*E*)-1-[(4-Methylphenyl)thio]-1-tributylstannyl-1-hexene (2b): Yield: 0.421 g, 85%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, J = 8.0 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 5.98 (t, J = 6.8 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 2.42–2.36 (m, 2 H), 2.31 (s, 3 H), 1.43–1.19 (m, 16 H), 0.92 (t, J = 7.2 Hz, 3 H), 0.85 (t, J = 7.2 Hz, 9 H), 0.71–0.68 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6 (CH), 136.9 (C), 135.9 (C), 134.4 (C), 130.4 ($CH\times2$), 129.4 ($CH\times2$), 31.5 (CH_2), 30.8 (CH_2), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 22.3 (CH_2), 21.0 (CH_3), 14.0 (CH_3), 13.6 ($CH_3\times3$), 11.0 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3176, 3058, 2957, 2926, 1586, 1470, 812, 670 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 496 (2.7) $[M]^+$, 439 (57), 357 (85), 243 (100), 177 (50), 91 (24). $C_{25}H_{44}SSn$ (495.39): calcd. C 60.61, H 8.95; found C 60.39, H 8.71.

(*E*)-1-[(4-Chlorophenyl)thio]-1-tributylstannyl-1-hexene (2c): Yield: 0.449 g, 87%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.8 Hz, 2 H), 7.18 (d, J = 8.8 Hz, 2 H), 6.11 (t, J = 6.8 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 2.41–2.37 (m, 2 H), 1.42–1.20 (m, 16 H), 0.91 (t, J = 7.2 Hz, 3 H), 0.85 (t, J = 7.2 Hz, 9 H), 0.75–0.71 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3 (CH), 137.0 (C), 135.4 (C), 131.6 (C), 130.6 ($CH\times2$), 128.7 ($CH\times2$), 31.4 (CH_2), 30.9 (CH_2), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 22.3 (CH_2), 14.0 (CH_3), 13.7 ($CH_3\times3$), 11.1 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3146, 3088, 2957, 2857, 1566, 1450, 814, 743 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 516 (1.4) $[M]^+$, 459 (41), 377 (87), 291 (30), 263 (100), 177 (79). $C_{24}H_{41}ClSSn$ (515.81): calcd. C 55.88, H 8.01; found C 55.63, H 8.09.

(*E*)-2-Phenyl-1-phenylthio-1-tributylstannylethene (2d):[23a] Yield: 0.431 g, 86%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.56 (m, 2 H), 7.38–7.22 (m, 8 H), 6.88 (s, $^3J_{Sn,H}$ = 48 Hz, 1 H), 1.43–1.35 (m, 6 H), 1.30–1.22 (m, 6 H), 0.86 (t, J = 7.2 Hz, 9 H), 0.77–0.74 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5 (CH), 137.6 (C), 131.1 ($CH\times2$), 130.1 (C), 129.2 ($CH\times2$), 128.8 ($CH\times2$), 128.3 (C), 128.0 ($CH\times2$), 127.1 (CH), 126.8 (CH), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 13.7 ($CH_3\times3$), 11.8 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3046, 2956, 2925, 1566, 1490, 803, 691 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 445 (65) $[M - Bu]^+$, 343 (74), 291 (23), 229 (100), 177 (58). $C_{26}H_{38}SSn$ (501.35): calcd. C 62.28, H 7.64; found C 62.39, H 7.49.

(*E*)-1-[(4-Methylphenyl)thio]-2-phenyl-1-tributylstannylethene (2e): Yield: 0.433 g, 84%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 2 H), 7.36–7.20 (m, 7 H), 6.93 (s, $^3J_{Sn,H}$ = 48 Hz, 1 H), 2.35 (s, 3 H), 1.44–1.35 (m, 6 H), 1.30–1.25 (m, 6 H), 0.86 (t, J = 7.2 Hz, 9 H), 0.76–0.71 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4 (CH), 140.2 (C), 137.7 (C), 137.1 (C), 133.9 (C), 131.8 ($CH\times2$), 129.6 ($CH\times2$), 129.2 ($CH\times2$), 128.0 ($CH\times2$), 126.9 (CH), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 21.1 (CH_3), 13.6 ($CH_3\times3$), 11.8 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3056, 3018, 2958, 2927, 1566, 1480, 809, 740 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 516 (2.5) $[M]^+$, 459 (68), 357 (87), 291 (31), 243 (100), 91 (27). $C_{27}H_{40}SSn$ (515.38): calcd. C 62.92, H 7.82; found C 62.60, H 7.63.

(*E*)-1-[(4-Chlorphenyl)thio]-2-phenyl-1-tributylstannylethene (2f): Yield: 0.455 g, 85%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.53 (m, 2 H), 7.38–7.23 (m, 7 H), 6.92 (s, $^3J_{Sn,H}$ = 48 Hz, 1 H), 1.42–1.36 (m, 6 H), 1.29–1.23 (m, 6 H), 0.87 (t, J = 7.2 Hz, 9 H), 0.80–0.75 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8 (CH), 140.4 (C), 137.3 (C), 136.4 (C), 132.7 (C), 132.0 ($CH\times2$), 129.1 ($CH\times2$), 128.9 ($CH\times2$), 128.0 ($CH\times2$), 127.3 (CH), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 13.7 ($CH_3\times3$), 11.8 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3076, 3028, 2957, 2926, 1586, 1480, 813, 760, 695 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 536 (1.4) $[M]^+$, 479 (91), 377 (87), 291 (25), 263 (100), 177 (86). $C_{26}H_{37}ClSSn$ (535.80): calcd. C 58.28, H 6.96; found C 58.49, H 6.79.

(*E*)-3-Methoxy-1-phenylthio-1-tributylstannyl-1-propene (2g): Yield: 0.403 g, 86%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.20 (m, 5 H), 6.13 (t, J = 5.2 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 4.26 (d, J = 5.2 Hz, 2 H), 3.39 (s, 3 H), 1.39–1.19 (m, 12 H), 0.86 (t, J = 7.2 Hz, 9 H), 0.73–0.69 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9 (CH), 140.6 (C), 137.2 (C), 130.6 ($CH\times2$), 128.8 ($CH\times2$), 126.6 (CH), 70.7 (CH_2), 58.1 (CH_3), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 13.6 ($CH_3\times3$), 11.2 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3176, 3088, 2957, 2926, 1545, 1120, 768, 739, 691 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 470 (4.8) $[M]^+$, 413 (59), 343 (86), 291 (32), 229 (100), 179 (86), 177 (97). $C_{22}H_{38}OSSn$ (469.31): calcd. C 56.30, H 8.16; found C 56.44, H 8.31.

(*E*)-3-Methoxy-1-[(4-methylphenyl)thio]-1-tributylstannyl-1-propene (2h): Yield: 0.401 g, 83%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, J = 8.0 Hz, 2 H), 7.08 (d, J = 8.0 Hz, 2 H), 6.04 (t, J = 5.6 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 4.25 (d, J = 5.6 Hz, 2 H), 3.39 (s, 3 H), 2.32 (s, 3 H), 1.36–1.30 (m, 6 H), 1.26–1.19 (m, 6 H), 0.84 (t, J = 7.2 Hz, 9 H), 0.72–0.68 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4 (CH), 136.8 (C), 133.4 (C), 131.2 ($CH\times2$), 129.6 ($CH\times2$), 127.3 (C), 70.6 (CH_2), 58.1 (CH_3), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 21.1 (CH_3), 13.6 ($CH_3\times3$), 11.2 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3166, 3078, 2955, 2927, 1535, 1110, 760 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 484 (5.8) $[M]^+$, 427 (93), 357 (100), 243 (94), 193 (58), 91 (24). $C_{23}H_{40}OSSn$ (483.33): calcd. C 57.15, H 8.34; found C 56.84, H 8.19.

(*E*)-1-[(4-Chlorophenyl)thio]-3-methoxy-1-tributylstannyl-1-propene (2i): Yield: 0.428 g, 85%. Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.4 Hz, 2 H), 7.21 (d, J = 8.4 Hz, 2 H), 6.17 (t, J = 5.2 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 4.24 (d, J = 5.2 Hz, 2 H), 3.38 (s, 3 H), 1.39–1.20 (m, 12 H), 0.87 (t, J = 7.2 Hz, 9 H), 0.76–0.72 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0 (CH), 139.9 (C), 135.9 (C), 133.5 (C), 131.5 ($CH\times2$), 128.9 ($CH\times2$), 70.6 (CH_2), 58.2 (CH_3), 28.8 ($CH_2\times3$), 27.3 ($CH_2\times3$), 13.6 ($CH_3\times3$), 11.3 ($CH_2\times3$) ppm. IR (neat): $\tilde{\nu}$ = 3172, 3085, 2956, 2927, 1545, 1110, 769 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 504 (4.9) [M]$^+$, 463 (100), 447 (61), 377 (57), 263 (67), 177 (90). $C_{22}H_{37}ClOSSn$ (503.75): calcd. C 52.45, H 7.40; found C 52.20, H 7.19.

(*E*)-1-Phenylseleno-1-tributylstannyl-1-hexene (2j):[23b] Yield: 0.470 g, 89%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2 H), 7.22–7.20 (m, 3 H), 6.25 (t, *J* = 6.8 Hz, $^3J_{Sn,H}$ = 52 Hz, 1 H), 2.40–2.35 (m, 2 H), 1.45–1.32 (m, 10 H), 1.26–1.19 (m, 6 H), 0.92 (t, *J* = 7.2 Hz, 3 H), 0.84 (t, *J* = 7.2 Hz, 9 H), 0.70 (t, *J* = 8.0 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0 (CH), 133.6 (C), 132.8 (C), 132.4 (CH × 2), 128.8 (CH × 2), 126.4 (CH), 33.4 (CH_2), 31.4 (CH_2), 28.8 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 22.3 (CH_2), 14.0 (CH_3), 13.7 ($CH_3 \times 3$), 11.0 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 3071, 2958, 1579, 1475, 1464, 1377, 1072, 1023, 734, 690 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 528 (1.6) [M]$^+$, 471 (26), 389 (100), 291 (27), 275 (70), 177 (57). $C_{24}H_{42}SeSn$ (528.30): calcd. C 54.56, H 8.01; found C 54.69, H 8.20.

(*E*)-3-Methoxy-1-phenylseleno-1-tributylstannyl-1-propene (2k):[23b] Yield: 0.449 g, 87%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.43 (m, 2 H), 7.25–7.23 (m, 3 H), 6.39 (t, *J* = 5.2 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 4.19 (d, *J* = 5.2 Hz, 2 H), 3.38 (s, 3 H), 1.38–1.31 (m, 6 H), 1.27–1.19 (m, 6 H), 0.84 (t, *J* = 7.2 Hz, 9 H), 0.72 (t, *J* = 8.0 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5 (CH), 137.9 (C), 133.0 (CH × 2), 132.1 (C), 129.0 (CH × 2), 127.0 (CH), 72.8 (CH_2), 58.1 (CH_3), 28.8 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 13.7 ($CH_3 \times 3$), 11.1 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 3059, 2927, 1578, 1476, 1464, 1116, 735, 690 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 516 (4.9) [M]$^+$, 459 (43), 389 (100), 275 (86), 177 (87). $C_{22}H_{38}OSeSn$ (516.25): calcd. C 51.18, H 7.42; found C 51.42, H 7.65.

(*E*)-3-Methoxy-1-methylseleno-1-tributylstannyl-1-propene (2l):[23b] Yield: 0.386 g, 85%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.34 (t, *J* = 5.2 Hz, $^3J_{Sn,H}$ = 48 Hz, 1 H), 4.18 (d, *J* = 5.2 Hz, 2 H), 3.35 (s, 3 H), 2.17 (s, 3 H), 1.36–1.29 (m, 6 H), 1.25–1.17 (m, 6 H), 0.82 (t, *J* = 7.2 Hz, 9 H), 0.70 (t, *J* = 8.0 Hz, 6 H) ppm. IR (neat): $\tilde{\nu}$ = 3012, 2958, 1456, 1117, 1032, 670 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 454 (4.5) [M]$^+$, 397 (56), 327 (100), 271 (49). $C_{17}H_{36}OSeSn$ (454.18): calcd. C 44.95, H 7.98; found C 44.67, H 7.85.

(*E*)-1-Phenylseleno-1-tributylstannyl-1-octene (2m):[23b] Yield: 0.489 g, 88%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2 H), 7.23–7.20 (m, 3 H), 6.25 (t, *J* = 6.8 Hz, $^3J_{Sn,H}$ = 52 Hz, 1 H), 2.38–2.34 (m, 2 H), 1.46–1.17 (m, 20 H), 0.92–0.81 (m, 12 H), 0.71 (t, *J* = 8.0 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1 (CH), 133.6 (C), 132.8 (C), 132.4 (CH × 2), 128.8 (CH × 2), 126.4 (CH), 33.6 (CH_2), 31.7 (CH_2), 29.2 (CH_2), 28.9 ($CH_2 \times 3$), 28.8 (CH_2), 27.3 ($CH_2 \times 3$), 22.7 (CH_2), 14.1 (CH_3), 13.7 ($CH_3 \times 3$), 11.0 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 3071, 2924, 2853, 1579, 1475, 1464, 1376, 1072, 1023, 734, 691 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 556 (2.3) [M]$^+$, 499 (23), 389 (100), 291 (34), 275 (73), 177 (57). $C_{26}H_{46}SeSn$ (556.35): calcd. C 56.13, H 8.33; found C 56.31, H 8.46.

(*E*)-1-Ethoxycarbonyl-1-tributylstannyl-1-hexene (2n): Yield: 0.369 g, 83%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.04 (t, *J* = 6.8 Hz, $^3J_{Sn,H}$ = 64 Hz, 1 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 2.44–2.40 (m, 2 H), 1.58–1.26 (m, 19 H), 0.95–0.84 (m, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3 (CO), 153.6 (CH), 135.6 (C), 59.9 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.9 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 22.3 (CH_2), 14.4 (CH_3), 13.9 (CH_3), 13.7 ($CH_3 \times 3$), 10.3 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 2958, 2929, 1709, 1603, 1464, 1182, 1038 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 446 (2.3) [M]$^+$, 389 (69), 205 (50), 105 (100), 73 (75). $C_{21}H_{42}O_2Sn$ (445.27): calcd. C 56.64, H 9.50; found C 56.34, H 9.25.

(*E*)-1-Ethoxycarbonyl-1-tributylstannyl-2-phenylethene (2o):[23d] Yield: 0.372 g, 80%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.29 (m, 5 H), 6.70 (s, $^3J_{Sn,H}$ = 64 Hz, 1 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 1.58–1.52 (m, 6 H), 1.37–1.32 (m, 6 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.07 (t, *J* = 8.0 Hz, 6 H), 0.91 (t, *J* = 7.2 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2 (CO), 142.1 (CH), 139.8 (C), 137.0 (CH × 2), 128.3 (C), 128.1 (CH × 2), 128.0 (C), 60.3 (CH_2), 28.9 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 14.2 (CH_3), 13.7 ($CH_3 \times 3$), 10.6 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 3059, 2958, 2923, 1700, 1596, 1463, 1183, 1034, 788, 695 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 466 (1.5) [M]$^+$, 409 (100), 407 (87), 179 (54), 177 (46). $C_{23}H_{38}O_2Sn$ (465.26): calcd. C 59.37, H 8.23; found C 59.57, H 8.35.

(*E*)-1-Ethoxycarbonyl-1-tributylstannyl-1-octene (2p): Yield: 0.383 g, 81%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.04 (t, *J* = 7.2 Hz, $^3J_{Sn,H}$ = 64 Hz, 1 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 2.45–2.39 (m, 2 H), 1.53–1.26 (m, 23 H), 0.96–0.84 (m, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3 (CO), 153.7 (CH), 135.5 (C), 59.9 (CH_2), 32.1 (CH_2), 31.7 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.9 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 22.6 (CH_2), 14.4 (CH_3), 14.1 (CH_3), 13.7 ($CH_3 \times 3$), 10.3 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 2957, 2927, 1709, 1603, 1464, 1377, 1180 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 473 (3.9) [M – 1]$^+$, 417 (100) [M – Bu]$^+$, 371 (21), 291 (19), 235 (28), 177 (36). $C_{23}H_{46}O_2Sn$ (473.32): calcd. C 58.36, H 9.79; found C 58.08, H 9.62.

(*E*)-1-Phenylsulfonyl-1-tributylstannyl-1-hexene (2q):[23e] Yield: 0.457 g, 89%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.84 (m, 2 H), 7.56–7.48 (m, 3 H), 6.28 (t, *J* = 7.2 Hz, $^3J_{Sn,H}$ = 52 Hz, 1 H), 2.40–2.36 (m, 2 H), 1.56–1.48 (m, 6 H), 1.38–1.29 (m, 6 H), 1.22–1.15 (m, 4 H), 1.11–1.06 (m, 6 H), 0.90 (t, *J* = 7.2 Hz, 9 H), 0.80 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4 (CH), 149.0 (C), 143.5 (C), 132.5 (CH), 128.8 (CH × 2), 127.1 (CH × 2), 31.0 (CH_2), 30.6 (CH_2), 28.8 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 22.3 (CH_2), 13.8 (CH_3), 13.7 ($CH_3 \times 3$), 11.4 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 3066, 2958, 2927, 1713, 1587, 1446, 1285, 1138, 1082, 822, 689 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 514 (9.1) [M]$^+$, 457 (100), 291 (56). $C_{24}H_{42}O_2SSn$ (513.36): calcd. C 56.15, H 8.24; found C 55.89, H 8.02.

(*E*)-1-[(4-Methylphenyl)sulfonyl]-1-tributylstannyl-1-hexene (2r): Yield: 0.458 g, 87%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 6.25 (t, *J* = 7.2 Hz, $^3J_{Sn,H}$ = 52 Hz, 1 H), 2.42 (s, 3 H), 2.41–2.34 (m, 2 H), 1.57–1.49 (m, 6 H), 1.36–1.30 (m, 6 H), 1.22–1.16 (m, 4 H), 1.10–1.05 (m, 6 H), 0.91 (t, *J* = 7.2 Hz, 9 H), 0.81 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9 (CH), 149.3 (C), 143.2 (C), 140.6 (C), 129.4 (CH × 2), 127.2 (CH × 2), 30.9 (CH_2), 30.7 (CH_2), 28.8 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 22.3 (CH_2), 21.5 (CH_3), 13.8 (CH_3), 13.7 ($CH_3 \times 3$), 11.4 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 2957, 2926, 1588, 1456, 1285, 1138, 1082, 812, 665 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 528 (1.6) [M]$^+$, 471 (100), 469 (71), 211 (39), 91 (18). $C_{25}H_{44}O_2SSn$ (527.39): calcd. C 56.94, H 8.40; found C 56.75, H 8.09.

(*E*)-1-Phenylsulfonyl-2-phenyl-1-tributylstannylethene (2s):[23e] Yield: 0.448 g, 84%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.0 Hz, 2 H), 7.27–7.09 (m, 9 H), 1.67–1.61 (m, 6 H), 1.43–1.37 (m, 6 H), 1.27–1.22 (m, 6 H), 0.95 (t, *J* = 7.2 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (CH), 149.7 (C), 141.4 (C), 135.3 (C), 131.9 (CH), 128.9 (CH × 2), 128.2 (CH), 127.9 (CH × 2), 127.7 (CH × 2), 127.4 (CH × 2), 29.0 ($CH_2 \times 3$), 27.3 ($CH_2 \times 3$), 13.7 ($CH_3 \times 3$), 11.9 ($CH_2 \times 3$) ppm. IR (neat): $\tilde{\nu}$ = 3063, 2957, 2921, 1585, 1446, 1286, 1136, 1081, 878, 745 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 477 (100) [M – Bu]$^+$, 475 (71), 197 (35). $C_{26}H_{38}O_2SSn$ (533.35): calcd. C 58.55, H 7.18; found C 58.32, H 6.94.

(*E*)-3-Methoxy-1-Phenylsulfonyl-1-tributylstannyl-1-propene (2t): Yield: 0.426 g, 85%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.83 (m, 2 H), 7.60–7.53 (m, 3 H), 6.42 (t, J = 4.8 Hz, $^3J_{\mathrm{Sn,H}}$ = 48 Hz, 1 H), 4.39 (d, J = 4.8 Hz, 2 H), 3.30 (s, 3 H), 1.48–1.41 (m, 6 H), 1.32–1.26 (m, 6 H), 1.05–1.00 (m, 6 H), 0.88 (t, J = 7.2 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8 (CH), 148.4 (C), 142.3 (C), 133.0 (CH), 129.0 (CH × 2), 127.0 (CH × 2), 70.7 (CH_2), 58.5 (CH_3), 28.7 (CH_2 × 3), 27.2 (CH_2 × 3), 13.7 (CH_3 × 3), 11.3 (CH_2 × 3) ppm. IR (neat): $\tilde{\nu}$ = 2958, 2926, 1712, 1597, 1455, 1285, 1138, 1083, 830, 667 cm^{-1}. MS (EI, 70 eV): m/z (%) = 502 (1.4) [M]$^+$, 445 (100), 443 (72), 441 (34), 197 (27). $C_{22}H_{38}O_3SSn$ (501.31): calcd. C 52.71, H 7.64; found C 52.48, H 7.41.

(*E*)-3-Methoxy-1-[(4-methylphenyl)sulfonyl]-1-tributylstannyl-1-propene (2u): Yield: 0.443 g, 86%. Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 6.39 (t, J = 4.8 Hz, $^3J_{\mathrm{Sn,H}}$ = 48 Hz, 1 H), 4.39 (d, J = 4.8 Hz, 2 H), 3.30 (s, 3 H), 2.43 (s, 3 H), 1.47–1.42 (m, 6 H), 1.32–1.26 (m, 6 H), 1.04–1.00 (m, 6 H), 0.88 (t, J = 7.2 Hz, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3 (CH), 148.7 (C), 143.8 (C), 139.4 (C), 129.6 (CH × 2), 127.1 (CH × 2), 70.7 (CH_2), 58.5 (CH_3), 28.7 (CH_2 × 3), 27.2 (CH_2 × 3), 21.6 (CH_3), 13.6 (CH_3 × 3), 11.3 (CH_2 × 3) ppm. IR (neat): $\tilde{\nu}$ = 2959, 2925, 1713, 1598, 1456, 1285, 1138, 1085, 831, 809 cm^{-1}. MS (EI, 70 eV): m/z (%) = 459 (100) [M – Bu]$^+$, 457 (86), 455 (44), 211 (25). $C_{23}H_{40}O_3SSn$ (515.33): calcd. C 53.61, H 7.82; found C 53.43, H 7.52.

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