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A highly efficient synthesis of (*Z*)-1-aryl-2-silyl-1-stannylethenes and their conversion to (*E*)-2-arylethenyl-, (*Z*)-2-(2-pyridyl)ethenyl- and allenyl-silanes

Takanori Endo, Fumio Sasaki, Hisashi Hara, Jyunko Suzuki, Shizuka Tamura, Yoshikazu Nagata,Tetsuro Iyoshi, Atsuhiro Saigusa and Taichi Nakano*

Department of Materials Chemistry, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan

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A $Pd(dba)_2–P(OEt)_3$ combination allowed the silastannation of arylacetylenes, 1-hexyne or propargyl alcohols with tributyl(trimethylsilyl)stannane to take place at room temperature, producing (*Z*)-2-silyl-1-stannyl-1-substituted ethenes in high yields. Novel silyl(stannyl)ethenes were fully characterized by ^{1}H-, ^{13}C-, ^{29}Si- and ^{119}Sn-NMR as well as infrared and mass analyses. Treatment of a series of (*Z*)-1-aryl-2-silyl-1-stannylethenes and (*Z*)-1-(3-pyridyl)-2-silyl-1-stannylethene with hydrochloric acid or hydroiodic acid in the presence of tetraethylammonium chloride (TEACl) or tetrabutylammonium iodide (TBAI) led to the exclusive formation of (*E*)-trimethyl(2-arylethenyl)silanes with high stereoselectivity. A similar reaction of (*Z*)-1-(2-anisyl)-2-silyl-1-stannylethene also produced *E*-type trimethyl[2-(2-anisyl)ethenyl]silane, while (*Z*)-trimethyl [2-(2-pyridyl)ethenyl]silane was produced exclusively from (Z)-1-(2-pyridyl)-2-silyl-1-stannylethene. Protodestannylation of (*Z*)-1-[hydroxy(phenyl)methyl]-2-silyl-1-stannylethene with trifluoroacetic acid took place via the β-elimination of hydroxystannane, providing trimethyl(3-phenylpropa-1,2-dienyl)silane quite easily. The destannylation products were also fully characterized. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: palladium catalysis; copper iodide; protodestannylation; vinylstannanes; vinylsilanes; allenylsilanes

INTRODUCTION

vic-Silyl(stannyl)ethenes are very interesting compounds, because they have two different metal functionalities β from each other. Stepwise substitution reactions of the metal functionalities in silyl(stannyl)ethenes make the conversion of the ethenes to many other characteristic organic molecules possible via organic transformations involving a Migita–Kosugi–Stille-type reaction.[1–4] Therefore, much effort has been directed towards the synthesis of *vic*-silyl(stannyl)ethenes.[5–17] The silastannation of acetylenes is one of the most useful methods in the synthesis of *vic*-silyl(stannyl)ethenes, due to the simplicity of the single-step procedure. The addition has been reported to occur regio- and stereoselectively in the presence of tetrakis(triphenylphosphine)palladium(0), producing (Z)-silyl(stannyl)ethenes. For example, Mitchell *et al.* reported the reaction of several typical terminal acetylenes with trimethyl(trimethylsilyl)stannane, producing (Z)-silyl(stannyl)ethenes. The reaction was conducted at 60–70 °C without solvent.[5,6] Chenard *et al.* also reported the reaction of acetylenes including phenylacetylene with (*t*-butyldimethylsilyl)trimethylstannane at 65 °C in THF (tetrahydrofuran). The reaction was completed within 4–8 h to give the (Z)-silyl(stannyl)ethenes in 10–90% yields.[7–9] Ritter applied silastannation to the synthesis of stereodefined stannylethenes.[10] Mori and Shibasaki *et al.* applied the reaction to the preparation of vinylsilanes using hydroiodic

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*Correspondence to: Taichi Nakano, Department of Materials Chemistry, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan.
E-mail: naka1214@wing.ncc.u-tokai.ac.jp

acid.[11,12] Recently, the silastannation of acetylene alcohols under reflux in THF using Pd(PPh$_3$)$_4$ was reported.[17] All of these silastannations require elevated temperature reaction conditions. On the other hand, Murakami *et al.* showed that a Pd(OAc)$_2$-*t*-octyl isonitrile combination is an effective catalyst in the silastannation of acetylenes using (*t*-butyldimethylsilyl)trimethylstannane at room temperature,[13] which provides a valuable procedure. However, for large-scale synthesis, the catalysis requires a large amount of expensive *t*-octyl isonitrile ligand. We recently reported as a communication[18] that readily available and inexpensive phosphite ligands are the best alternative for the palladium-catalyzed silastannation.

Reported herein are the full results for the silastannation of acetylenes **1** with tributyl(trimethylsilyl)stannane in the presence of the combination catalyst, and the protodestannylation of the resulting (*Z*)-silyl(stannyl)ethenes **2** into (*E*)-styrylsilanes, (*Z*)-vinylsilane, and allenylsilane, depending on the substrate structure (Scheme 1).

RESULTS AND DISCUSSION

Comparison of reaction conditions in the palladium-catalyzed silastannation of phenylacetylene

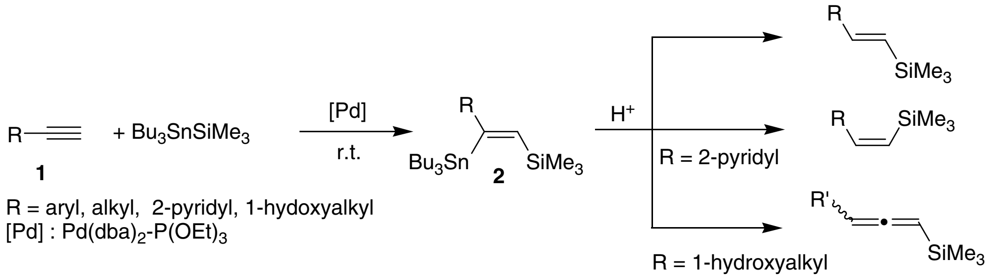
An investigation to determine the optimum conditions (ligand, solvent, temperature, time) for the silastannation of phenylacetylene with tributyl(trimethylsilyl)stannane was undertaken according to Scheme 2. A Pd(dba)$_2$–PPh$_3$-catalyzed reaction of phenylacetylene with tributyl(trimethylsilyl)stannane in THF at 60 °C completed in 3 h, producing (*Z*)-1-tributylsutannyl-2-trimethylsilyl-1-phenylethene **2a** in 64% glc yield. The configuration of **2a** was determined to be *Z* by comparing the NMR coupling constants, $^3J_{119\text{SnH}} = 166.0$ Hz and $^3J_{117\text{SnH}} = 158.8$ Hz, with those reported in the literature.[6,9,10,19,20]

Table 1 shows the outcome of the reaction conducted under various conditions. A similar reaction in THF at reflux was complete in 2 h, producing **2a** in 95% glc yield. Column chromatography gave **2a** in 85% yield. The

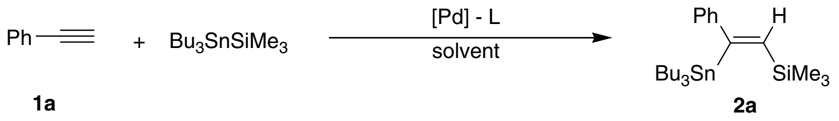
Table 1. Effect of ligand and solvent on the reaction shown in Scheme 2

Run[a]	[Pd]	Ligand	Solvent	Conditions (°C, h)	Yield[b] (%)
1	Pd(dba)$_2$	PPh$_3$	Benzene	60, 3	64
2	Pd(dba)$_2$	PPh$_3$	THF	Reflux, 2	95
3	Pd(dba)$_2$	PPh$_3$	THF	Reflux, 4	85[c]
4	Pd(dba)$_2$	PPh$_3$	THF	r.t., 3	43[d]
5	Pd(dba)$_2$	—	THF	Reflux, 5	0[e]
6	Pd(dba)$_2$	P(OCH$_2$)$_3$CEt	THF	r.t., 3	92[f]
7	Pd(dba)$_2$	P(OEt)$_3$	THF	r.t., 1.5	91
8	Pd(dba)$_2$	P(OEt)$_3$	dioxane	r.t., 1	90
9	Pd(dba)$_2$	P(OEt)$_3$	DMF	r.t., 1	32
10	Pd(dba)$_2$	P(OEt)$_3$	Benzene	r.t., 3	66[f]
11	Pd(dba)$_2$	P(OMe)$_3$	THF	r.t., 1	82
12	Pd(dba)$_2$	P(O^{i}Pr)$_3$	THF	r.t., 2	92
13	Pd(dba)$_2$	P(OPh)$_3$	THF	r.t., 3	92
14	PdCl$_2$	P(OEt)$_3$	THF	r.t., 2	87
15	Pd(OAc)$_2$	P(OEt)$_3$	THF	r.t., 3	54

[a] Phenylacetylene:Me$_3$SiSnBu$_3$: [Pd] : ligand : dry solvent = 1 mmol : 0.5 mmol : 0.01 mmol : 0.02 mmol : 1 mL. [b] Yields were determined by gas chromatography (glc) unless otherwise stated and are uncorrected. [c] Isolated yield by column chromatography (silica gel, hexane). [d] Small amounts of unknown byproducts were formed. [e] No reaction took place. [f] The reaction was accompanied by the formation of small amounts of two unknown byproducts.



Scheme 1.



Scheme 2.

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reaction in THF proceeded even at room temperature to produce **2a**; however, yield decreased to 43%. Catalysis by Pd(dba)$_2$ alone gave no product even at reflux. Pd(dba)$_2$–P(OCH$_2$)$_3$CEt (ligand = EPBO: 4-ethyl-1-phospha-2,6,7-bicyclo[2.2.2]octane), which is the best choice of catalyst for the germastannation of acetylenes,[21–23] effected the silastannation at room temperature and drove the reaction to completion quickly, forming **2a** in high yield; however, the reaction was accompanied by the formation of unknown byproducts. Accordingly, several non-caged phosphite ligands such as P(OEt)$_3$, P(OMe)$_3$, P(O^{i}Pr)$_3$ and P(OPh)$_3$ were examined in the palladium catalysis. The Pd(dba)$_2$–P(OEt)$_3$-catalyzed reaction in ether solvents such as THF or 1,4-dioxane gave good results, while in DMF (*N*,*N*-dimethylformamide) or benzene solvents, lower yields of **2a** were obtained. Pd(dba)$_2$–P(O^{i}Pr)$_3$ and Pd(dba)$_2$–P(OPh)$_3$ were also effective. A combination of PdCl$_2$ and P(OEt)$_3$ was effective, while the catalytic effect of a Pd(OAc)$_2$-P(OEt)$_3$ combination was inferior to that of Pd(dba)$_2$-P(OEt)$_3$. Consequently, readily accessible Pd(dba)$_2$ and a non-caged phosphite ligand were found to constitute an effective combination catalyst.

Synthesis of (*Z*)-silyl(stannyl)ethenes via the Pd(dba)$_2$–P(OEt)$_3$-catalyzed silastannation of acetylenes

A variety of arylacetylenes was allowed to react with tributyl(trimethylsilyl)stannane under conditions similar to run 7 in Table 1. Catalysis took place at room temperature and the reactions went to completion quickly, affording (*Z*)-silyl(stannyl)ethenes **2**, save for one example, in satisfactory yields (Scheme 3). Results are summarized in Table 2 together with $^3J_{\mathrm{SnH}}$ coupling constants for ^{119}Sn and ^{117}Sn with the vinyl proton α to the silyl group. The stereochemistry of the adducts was assigned by looking at $^3J_{\mathrm{SnH}}$ for the vinylic proton at 148–170 Hz, typical for a *trans*-H–Sn relationship.[6,7,9,10,19,20]

As shown above, each reaction produced Z-adducts, while the silastannation of *p*-nitrophenylacetylene **1j** (run 10, Table 2) was accompanied by the formation of (*E*)-1-tributylstannyl-2-trimethylsilyl-1-(*p*-nitrophenyl)ethene as well as the (*Z*)-isomer (combined yield: 84%, $Z:E = 90:10$). ^{1}H-NMR analysis of the product mixture disclosed proton signals arising from a small quantity of the (*E*)-isomer. In addition, the vinyl proton α to silicon of the (*E*)-isomer appeared at 6.23 ppm, and coupling constants with the Sn atom were 90.8 Hz for ^{119}Sn and 87.2 Hz for ^{117}Sn, which are typical for a *cis*-vinyl-H-Sn coupling.[6,7,9,10,19,20] Other proton signals were close to those of the (*Z*)-isomer. Interestingly, the (*E*)-isomer seems to be susceptible to isomerization to the (*Z*)-isomer when exposed to natural light. It isomerized to the (*Z*)-isomer while the mixture was being stored neat under natural light at room temperature within one month.

Table 3 compiles selected NMR data for ^{119}Sn- and ^{29}Si-NMR chemical shifts as well as coupling constants $^1J_{\mathrm{SnC(sp3)}}$, $^1J_{\mathrm{SnC(sp2)}}$, $^1J_{\mathrm{SiC(sp3)}}$, $^1J_{\mathrm{SiC(sp2)}}$ and $^3J_{\mathrm{SnSi}}$. The NMR signals of silicon-29 and tin-119 for **2b–s** were observed at −8.85 to −10.99 ppm and at −52.2 to −63.6 ppm, respectively. Among the compounds, the pyridyl nitrogen for **2n** seemed to be in closest proximity to the tin atom. The structure seems to suggest the coordination of pyridyl nitrogen to tin. However, in the ^{119}Sn-NMR spectrum, there was no evidence suggesting

Table 2. Synthesis and $^3J_{(\mathrm{SnH})}$ for compounds of the type (*Z*)-RC(SnBu$_3$)=CHSiMe$_3$

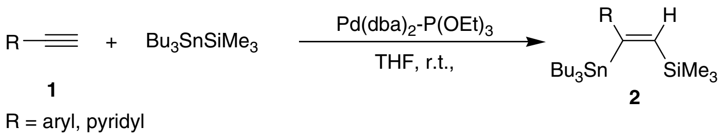
Run[a]	R in acetylene	Time (h)	Product no.	Yield (%)[b]	$^3J_{119\mathrm{SnH}}$(Hz)	$^3J_{117\mathrm{SnH}}$(Hz)
1[c]	C$_6$H$_5$ (**1a**)	2	**2a**	80	166	159
2	2-FC$_6$H$_4$ (**1b**)	1	**2b**	87	160	153
3	3-FC$_6$H$_4$ (**1c**)	5	**2c**	88	162	154
4	4-FC$_6$H$_4$ (**1d**)	3	**2d**	83	164	159
5.	2-ClC$_6$H$_4$ (**1e**)	1	**2e**	74	160	153
6	4-ClC$_6$H$_4$ (**1f**)	3	**2f** [d]	80	163	155
7	3-(CF$_3$)C$_6$H$_4$ (**1g**)	1	**2g**	90	160	153
8	4-COOEtC$_6$H$_4$ (**1h**)	1	**2h**	96	166	159
9	3-NO$_2$C$_6$H$_4$ (**1i**)	4	**2i**	72	156	148
10	4-NO$_2$C$_6$H$_4$ (**1j**)	5	**2j**	84[e]	154	148
11	4-CNC$_6$H$_4$ (**1k**)	3	**2k**	92	156	149
12	3,4-(MeO)$_2$C$_6$H$_3$ (**1l**)	3	**2l**	84	168	160
13	3-pyridyl (**1m**)	5	**2m**	99	159	157
14	2-pyridyl (**1n**)	13	**2n**	67	166	158
15	2-MeOC$_6$H$_4$ (**1o**)	4	**2o**	86	170	162

[a] The reaction was carried out at room temperature. Acetylene : silylstannane : Pd(dba)$_2$: P(OEt)$_3$: THF = 5 mmol : 2.5 mmol : 0.05 mmol : 0.1 mmol : 5 mL. [b] Isolated yields by column chromatography (silica gel, hexane). [c] Acetylene : silylstannane : Pd(dba)$_2$: P(OEt)$_3$: THF = 10 mmol : 4.3 mmol : 0.1 mmol : 0.2 mmol : 10 mL. [d] See Nakano *et al.*[18] [e] Isomeric purity 90%. The residual 10% is probably accounted for by the *E*-isomer. However, the two components transformed into solely the *Z*-isomer within one month under natural light.

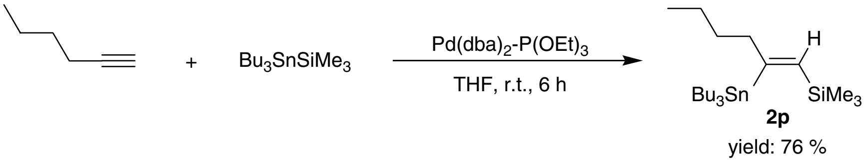
Table 3. Selected NMR data for compounds of the type (*Z*)-RC($SnBu_3$)=$CHSiMe_3$

Run	Product(R)	$\delta(^{119}Sn)^a$	$\delta(^{29}Si)^a$	$^1J(SnC)^{a,b}$	$^2J(SnC)^{a,c}$	$^1J(SiC)^{a,c}$	$^3J(SnSi)^a$
1	**2a**(Ph)	−55.7	−9.73	371.3	57.3	68.5	32.1
2	**2b**(2-FC_6H_4)	−54.9	−9.31	368.3	53.1	68.5	30.6
3	**2c**(3-FC_6H_4)	−54.6	−9.44	362.1	55.3	67.6	30.6
4	**2d**(4-FC_6H_4)	−55.1	−9.68	369.0	57.7	67.5	31.1
5	**2e**(2-ClC_6H_4)	−58.2	−9.13	366.6	52.3	67.7	30.2
6	**2f**(4-ClC_6H_4)	−55.0	−9.54	363.6	56.8	67.7	30.2
7	**2g**(3-$CF_3C_6H_4$)	−53.7	−9.28	356.0	53.7	68.5	30.2
8	**2h**(4-$CO_2EtC_6H_4$)	−54.6	−9.32	355.2	53.8	68.0	30.6
9	**2i**(3-$NO_2C_6H_4$)	−52.2	−8.96	347.6	53.0	66.5	28.7
10	**2j**(4-$NO_2C_6H_4$)	−52.8	−8.85	339.8	50.8	66.2	28.7
11	**2k**(4-CNC_6H_4)	−53.2	−8.97	342.7	51.6	67.0	28.7
12	**2l**(3,4-$(OMe)_2C_6H_3$)	−55.7	−9.90	377.4	60.7	68.4	32.1
13	**2m**(3-py)	−52.6	−9.28	353.7	53.1	66.5	29.7
14	**2n**(2-py)	−55.0	−9.23	392.1	52.3	68.5	31.6
15	**2o**(2-$OMeC_6H_4$)	−61.8	−9.76	401.3	57.6	68.5	32.6
16	**2p**(n-Bu)[d]	−57.8	−10.99	398.2	e	66.9	37.5
17	**2q**($HOCH_2$)[f]	−58.2	−9.46	373.6	52.3	69.2	34.0
18	**2r**($HOMe_2C$)[g]	−63.6	−9.80	406.6	59.9	70.7	38.4
19	**2s**[HO(Ph)CH][h]	−58.6	−9.47	374.3	53.8	68.4	32.6

[a] Chemical shifts referenced to TMS or TMT (tetramethyltin) in ppm, *J* in Hz. [b] ^{119}Sn-vinyl carbon. [c] ^{29}Si-vinyl carbon. [d] See Mitchell *et al.*[9] [e] $^2J_{SnC}$ was not observed. [f] See Mitchell *et al.*[9] and Nielsen *et al.*[17]. [g] See Mitchell *et al.*[26]. [h] See Nielsen *et al.*[17]



Scheme 3.



Scheme 4.

the coordination of 2-pyridyl nitrogen to tin.[24,25] The ^3J(SiSn) of **2a–s** were observed to lie within the range 28.7–38.4 Hz (Table 3).

$Pd(dba)_2$–$P(OEt)_3$ also catalyzed the silastannation of other acetylenes at room temperature. 1-Hexyne underwent silastannation under similar conditions to produce (*Z*)-1-butyl-1-tributylstannyl-2-trimethylsilylethene **2p** in 76% yield (Scheme 4). Adduct **2p** has been fully characterized by Mitchell *et al.*[9]

Propargyl alcohol produced (*Z*)-1-tributylstannyl-1-(hydroxymethyl)-2-trimethylsilylethene **2q** in 68% yield, even without protection of the hydroxyl group (Scheme 5). Adduct **2q** has been fully characterized by Mitchell *et al.*[9] and by Nielsen *et al.*[17]

3-Methyl-1-butyn-3-ol also reacted with the tributyl(trimethylsilyl)stannane to produce (*Z*)-1-tributylstannyl-1-(1-hydroxy-1-methylethyl)-2-trimethylsilylethene **2r**[26] in 77% yield (Scheme 6).

Similarly, (*Z*)-silyl(stannyl)ethene **2s**[17] could be prepared from 1-phenyl-2-propyn-1-ol and the silylstannane in 74% yield (Scheme 7), although the reaction required heat.

Protodestannylation of (*Z*)-1-aryl-1-tributylstannyl-2-trimethylsilylethenes leading to (*E*)-styrylsilanes

Vinylsilanes are precursors to silylisoxazolines, which possess antithrombotic activity.[27] Therefore, synthesis of stereochemically defined vinylsilanes by protodemetallation

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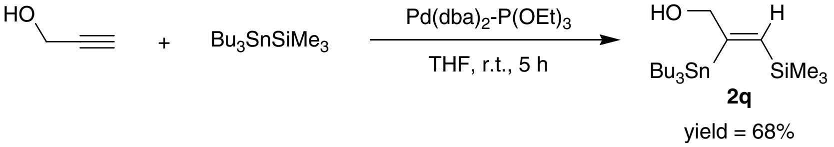
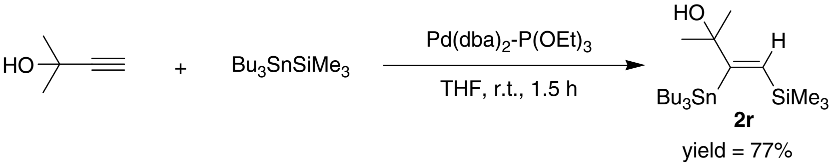
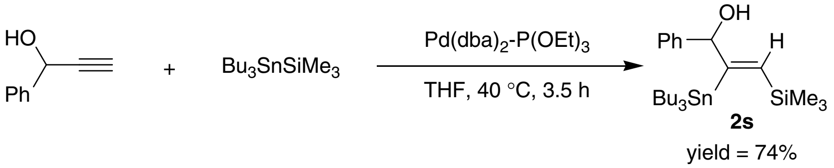


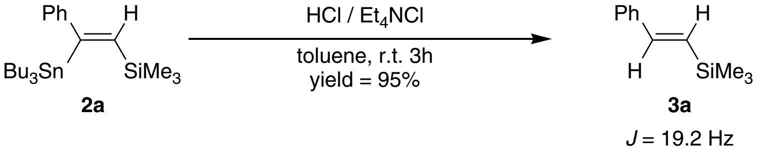
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

of (*Z*)-silyl(stannyl)ethenes **2** is of great value. The treatment of (*Z*)-1-alkyl-2-silyl-1-stannylethene with HI/TBAI has been reported to produce (*E*)-vinylsilanes.[11] The destannylation[11] has mechanistically been elucidated by the HSAB principle.[28] Therefore, if the HSAB principle plays an important role in the reaction, the use of inexpensive HCl–R_4NCl, which releases a hard chloride ion, may cause nonselective demetallation of the (*Z*)-1-aryl-2-silyl-1-stannylethenes **2**. An examination of the protodemetallation of (*Z*)-2-silyl-1-stannyl-1-phenylethene **2a** with HCl–TEACl (tetraethylammonium chloride) was undertaken. Contrary to what was predicted, the slow addition of HCl (20–30%) solution to **2a** with stirring at room temperature in the presence of tetraethylammonium chloride brought about the selective formation of (*E*)-1-phenyl-2-silylethene **3a** (Scheme 8), the structure of which was confirmed by the ^{1}H-NMR coupling constant ($J =$ 19.2 Hz) between the vinyl protons. Neither 1-phenyl-1-stannylethene[10] nor 1-phenyl-1-silylethene[29] was produced.

Under similar conditions, from the (*Z*)-1-aryl-2-silyl-1-stannylethenes **2a–l** the (*E*)-trimethyl(2-phenylethenyl) silanes **3a–l** were readily obtained exclusively in good to high yields as shown in Table 4, except for the 3-nitrophenyl derivative **2i**, which afforded an 88 : 12 mixture of (*E*)-**3i** and (*Z*)-**3i** trimethyl[2-(3-nitrophenyl)ethenyl]silanes. Reasons for the formation of (*Z*)-**3i** are unclear. However, to account for the results, intramolecular coordination of the negative oxygen in the nitro group to a vacant silicon d orbital in a protodestannylation reaction transition state (as in Scheme 12) may be considered, although it seems unlikely.

In these experiments, when yields of styrylsilanes are somewhat low, the use of HI/TBAI is recommended (e.g. runs 2, 8, 10 and 15 in Table 4). This simple, mild and economical procedure can provide a variety of stereochemically defined (*E*)-2-arylethenylsilanes, precursors to bioactive 4-silylisoxazolines.[27]

Table 4 also includes the outcome of the destannylation of (*Z*)-1-(3-pyridyl)-2-silyl-1-stannylethene **2m**, its 2-pyridyl isomer **2n** (runs 18 and 19), and (*Z*)-1-(2-methoxyphenyl)-2-silyl-1-stannylethene **2o**. In the destannylation of **2m**, the *E*-type product **3m** was given in high yield (Scheme 9). Although the protodesilylation of vinylsilane bearing a pyridyl group has been reported to need microwave

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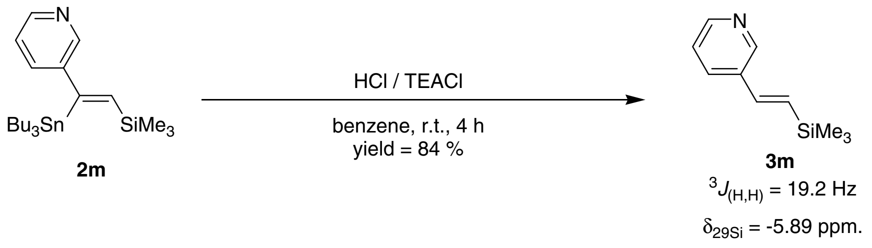
Table 4. Yields and selected NMR data for compounds of the type $RHC{=}CHSiMe_3$

Run[a]	X in $XC_6H_4(Sn)$ C=CHSi	Conditions (temperature, h)	Product no.	Yield [b] %	^3J(H,H) (Hz)	$\delta(^{29}Si)$ (ppm)	Geometry (ppm)
1	**2a**(H)	r.t., 3	**3a**	96	19.2	−6.26	*E*
2[c]	**2a**	0, 1	**3a**	86	19.2	−6.26	*E*
3	**2b**(2-F)	r.t., 7	**3b**	67	19.2	−5.89	*E*
4[d]	**2b**	r.t., 0.5	**3b**	90	19.2	−5.89	*E*
5	**2c**(3-F)	r.t., 3	**3c**	86	19.2	−6.06	*E*
6	**2d**(4-F)	r.t., 3	**3d**	97	19.2	−6.21	*E*
7[d]	**2e**(2-Cl)	r.t., 1.5	**3e**	92	19.1	−5.78	*E*
8[c]	**2e**	0, 4	**3e**	81	19.1	−5.78	*E*
9	**2f**(4-Cl)	r.t., 2	**3f** [e]	99	19.2	−6.10	*E*
10[c]	**2f**	0, 4	**3f**	86	19.2	−6.10	*E*
11	**2g**(3-CF_3)	r.t., 3	**3g**	98	19.0	−5.89	*E*
12	**2h**(4-COOEt)	r.t., 3	**3h**	95	19.0	−5.90	*E*
13	**2i**(3-NO_2)	r.t., 11	**3i**	87[f]	19.2	−5.66	*E*
14	**2j**(4-NO_2)	r.t., 8	**3j**	93	19.2	−5.53	*E*
15[c]	**2j**	0, 3	**3j**	86	19.2	−5.53	*E*
16	**2k**(4-CN)	r.t., 3	**3k**	98	19.2	−5.65	*E*
17	**2l**(3,4-$(OMe)_2$)	r.t., 3	**3l**	75	18.8	−6.36	*E*
18	**2m**(3-py)	r.t., 4	**3m**	84	19.2	−5.89	*E*
19[d]	**2n**(2-py)	r.t., 1.5	**3n**	50	14.4	−11.19	*Z*
20	**2o**(2-OMe)	r.t., 3	**3o**	39	19.2	−6.26	*E*

[a] Silyl(stannyl)ethene:Et_4NCl:benzene:HCl (20%) = 1.0 mmol : 1.0 mmol : 3.8 mL : 0.94 mL. [b] Isolated yields by column chromatography (silica gel, hexane). [c] Silyl(stannyl)ethene:Bu_4NI:benzene:HI (57%) = 1.0 mmol : 1.1 mmol : 4.0 mL : 1.0 mL. [d] Silyl(stannyl)ethene:Et_4NCl:benzene:HCl (30%) = 1.0 mmol : 1.1 mmol : 2.3 mL : 1.0 mL. [e] Characterization: see Nakano *et al.*[18] [f] Combined yield of *Z*- and *E*-isomers. The ratio was determined by ^{1}H-NMR to be 12 : 88 (*Z* : *E*).



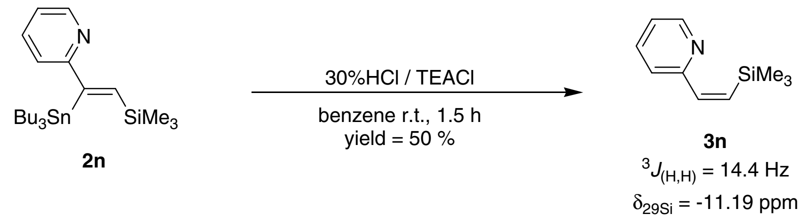
Scheme 9.

irradiation,[30] the reaction took place without difficulty, producing **3m** as depicted in Scheme 9.

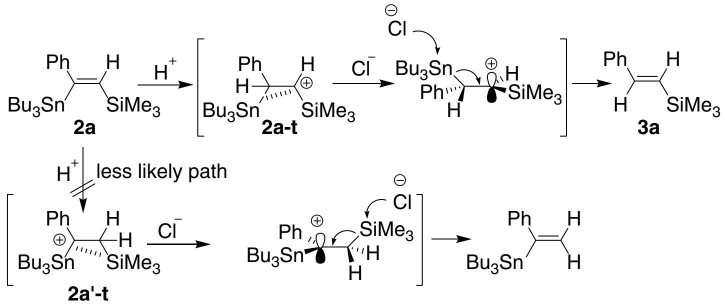
On the other hand, treatment of the 2-pyridyl derivative **2n** using HCl–TEACl produced (*Z*)-1-(2-pyridyl)-2-trimethylsilylethene **3n** predominately (Scheme 10). The geometry was confirmed primarily by ^{1}H- and ^{29}Si-NMR analyses. The coupling constant between neighboring vinyl protons in **3n** is 14.4 Hz (Table 4), which is typical for a *cis* configuration, and quite similar to that of (*Z*)-styryltrimethylsilane, 15.0 Hz.[31]

In addition, the ^{1}H- and ^{29}Si-NMR spectra of (*Z*)-1-(2-pyridyl)-2-trimethylsilylethene, prepared separately by DIBAL-H reduction[31] of trimethyl[(2-pyridyl)ethynyl]silane in *N*-methylpyrrolidine–pentane, were in good agreement with those of **3n**. Again, protodestannylation of the 2-anisyl derivative **2o** produced (*E*)-trimethyl[2-(2-anisyl)ethenyl]silane exclusively (run 20, Table 4).

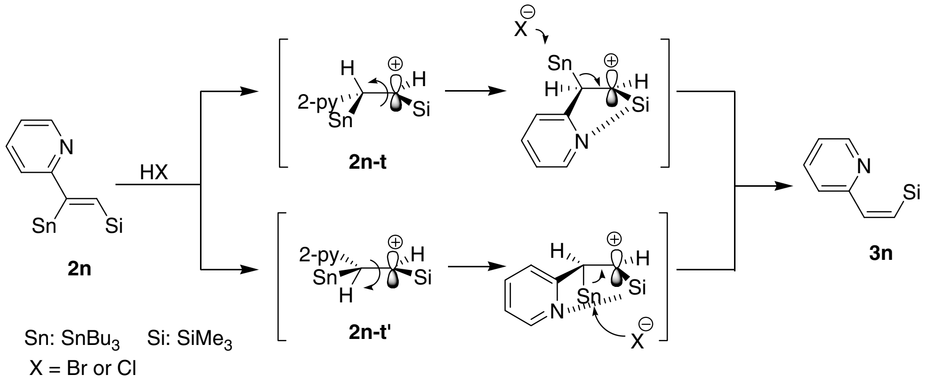
The protodestannylation of (*Z*)-silyl(stannyl)ethenes leading to (*E*)-vinylsilanes may be interpreted as shown in Scheme 11. The protodestannylation of (*Z*)-1-aryl-2-silyl-1-stannylethenes demonstrates the fact that the σ–π stabilization effect[32–35] of the stannyl group in the carbonium ion **2a–t** depicted in Scheme 11 is greater than that of the silyl group in another carbonium ion **2a′–t** and the conjugation effect of an aryl group. In other words, Markownikoff-type protonation of the adduct **2a** followed by attack of the chloride



Scheme 10.



Scheme 11.



Scheme 12. A plausible mechanism in the formation of (*Z*)-trimethyl[2-(2-pyridyl)ethenyl]silane.

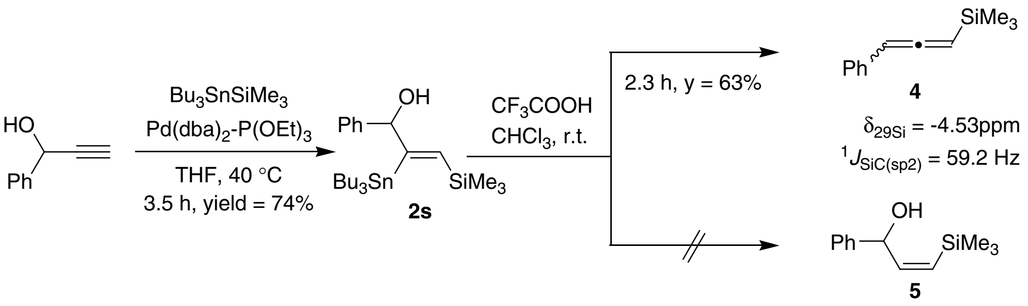
ion as a hard base on the silicon as a hard acid is an insignificant pathway.

This also means that the stability of the carbonium ion being dependent upon the $\sigma-\pi$ stabilization effect is much more important than the HSAB principle, providing further evidence for the validity of the pathway proposed in Scheme 11.

A plausible mechanism for the exclusive formation of vinylsilanes of *Z*-type from (*Z*)-silyl(stannyl)ethenes is proposed in Scheme 12. The 2-pyridyl substituent probably plays an important role in the formation of the (*Z*)-vinylsilane, i.e. the holding of a specific conformation via coordination of the pyridyl nitrogen to silicon is of importance. First, protonation of **2n** occurs at the vinyl carbon bearing tin (the β-effect of tin may be larger than that of silicon,[33,34] in addition to the conjugative effect of the 2-pyridyl group). Rotation around the single bond of **2n–t** or **2n–t′** in Scheme 12 may occur so that the pyridyl nitrogen coordinates to a vacant d orbital on a nearby silicon. The β-effect of tin is also collaterally important when assuming such a conformation. Attack of a halide ion at the tin followed by double bond formation seems to be the most favorable course of production of *Z*-vinylsilanes.

Protodestannylation of 2-stannyl-3-silyl-2-propen-1-ol

The acid-catalyzed reaction of a (*Z*)-silyl(stannyl)ethene bearing a hydroxymethyl functionality on the vinyl carbon α to tin was also eventually examined. (*Z*)-2-Tributylstannyl-3-trimethylsilyl-1-phenylprop-2-en-1-ol **2s**[9,18] was treated with trifluoroacetic acid in chloroform at room temperature. The reaction readily took place, producing the allenylsilane **4**.[36–39] Another possible destannylation product **5**, which potentially



Scheme 13.

could have been produced via a similar reaction course to Scheme 10, was not observed (Scheme 13).

For the formation of an allenylsilane like **4**, Mitchell *et al.* have reported an attractive method through a recombination reaction of a (*Z*)-1-(1-hydroxyalkyl)-2-silyl-1-stannylethene with dibromostannane followed by thermal decomposition.[9] However, the present method has no need for the additional recombination step. Scheme 13 is the first example of the direct synthesis of allenylsilane from a β-hydroxy vinylstannane like **2s,** and should be noted as an important, alternative route to allenylsilane synthesis, although a protocol for the formation of the C–C double bond by acid-catalyzed β-elimination of a hydroxystannane has been reported in the synthesis of 1-trimethylsilyl-2,3-dienes from β-stannylallyl alcohols.[40,41] Different methods of preparing the allenyl framework are also known, one of which is the hydrostannylation of propargylic alcohols producing β-stannylated allyl alcohols, followed by the methanesulfonylation of the hydroxy functionality and subsequent deoxystannylation.[42] Studies of the formation[43] and reaction[43,44] of allenes have been published in books by Krause and Hashmi[43] and well reviewed by Zimmer and Dinesh.[44]

EXPERIMENT

Methods and measurements

Silastannation was carried out using a small, round bottom flask under nitrogen and monitored by thin layer chromatography (TLC). GLC (gas–liquid chromatography) analysis of the reaction mixture or isolated products was performed using an Ohkura Model 103 gas chromatograph equipped with a thermal conductivity detector connected to a stainless steel column packed with 10% Silicone KF-96–Celite 545 AW (60–80 mesh, 2 m × 3 mm). ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100.7 MHz) spectra were recorded on a Varian Unity-400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed as parts per million (ppm) with respect to TMS (for ^{1}H) and chloroform-d$_1$ ($\delta = 77.00$ ppm) (for ^{13}C). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), sext (sextet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets of doublets), brs (broad singlet) and m (multiplet). Coupling constants are given in Hz. The assignments of aromatic carbons in the ^{13}C-NMR of (*Z*)-silyl(stannyl)ethenes **2** and vinylsilane derivatives **3** are based on the intensity information, coupling constants (e.g. J_{C-F} etc.) and additivity for the ^{13}C chemical shifts of the aromatic ring.[45] ^{29}Si- and ^{119}Sn-NMR spectra were recorded at 79.6 and 149.3 MHz, respectively, on a Varian Mercury plus 400 in $CDCl_3$ using TMS (for ^{29}Si) and tetramethyltin (TMT, for ^{119}Sn) as the internal standard. Mass spectra were recorded on a Jeol JMS-AX-500 with a DA 7000 data system.

Materials

Benzene, toluene, dioxane and tetrahydrofuran (THF) were kept over 4 Å molecular sieves and distilled over lithium aluminum hydride just before use. DMF was distilled from calcium hydride. Tributyl(trimethylsilyl)stannane was prepared as reported.[45,46] Arylacetylenes and pyridylacetylenes were prepared by the Sonogashira-Hagihara reaction.[47–49] 1-Hexyne, 2-propyn-1-ol and 2-methyl-3-butyn-2-ol were purified by distillation before use. The following compounds were used as received: triphenylphosphine, phosphites, 1-phenyl-2-propyn-1-ol, 2-anisylacetylene, dichloropalladium, palladium acetate, hydrochloric acid, hydroiodic acid, tetraethylammonium chloride, tetrabutylammonium iodide and trifluoroacetic acid. DIBAL-H (di-iso-butylaluminum hydride) was purchased from Aldrich Chemical Co. Silica gel was purchased from Wako Chemical Co. (Wako gel, C-300) or Kanto Co. (60N, spherical, neutral). Bis(dibenzylideneacetone)palladium was prepared according to the literature.[50]

General procedure for the reaction of an arylacetylene with tributyl(trimethylsilyl) stannane

A THF (6 ml) solution of $Pd(dba)_2$ (0.0587 g, 0.102 mmol) and triethylphosphite (0.0322 g, 0.194 mmol) was stirred at room temperature under nitrogen for 5 min. To the mixture was added the silylstannane **1** (1.577 g, 4.34 mmol) in THF (2 ml). After 5 min of stirring, phenylacetylene (1.027 g, 10.05 mmol) in THF (2 ml) was added. The resulting mixture was stirred at room temperature. After 2 h, TLC analysis revealed that the silylstannane **1** was completely consumed, and indicated formation of a new product. The mixture was passed through a short silica gel column with hexane to remove the catalyst and polymer materials. Column chromatography (silica gel, hexane) of the eluent gave 1.6216 g (80%) of (Z)-1-(tributylstannyl)-2-(trimethylsilyl)-1-phenylethene **2a**. Spectral data of **2a** are in good agreement with those reported.[7]

The silastannation of other acetylenes was conducted by a procedure similar to the above. Characteristic data for new compounds are shown below. For known compounds, heretofore unpublished spectra are shown.

(Z)-1-Tributylstannyl-1-(2-fluorophenyl)-2-trimethylsilylethene 2b

IR (neat): 2950, 2910, 1475, 1450, 1243, 1220, 860, 835, 750 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.12 (m, 1H), 7.05 (dt, 1H, $J = 7.6, 1.6$ Hz), 6.95 (m, 2H), 6.58 (s, 1H, $^{3}J_{119\text{Sn H}} = 160$ Hz, $^{3}J_{117\text{Sn,H}} = 153$ Hz), 1.38 (m, 6H), 1.23 (sext, 6H, $J = 7.2$ Hz), 0.89 (m, 6H), 0.98 (t, 9H, $J = 7.2$ Hz), 0.18 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 159.5 (d, $^{3}J_{\text{FC}} = 3.8$ Hz, $^{1}J_{119\text{SnC}} = 368.3$ Hz, $^{1}J_{117\text{SnC}} = 351.4$ Hz, vinyl carbon bearing tin), 158.0 (d, $^{1}J_{\text{FC}} = 242.2$ Hz, aromatic carbon bearing fluorine atom), 150.0 ($^{2}J_{\text{SnC}} = 53.1$ Hz, $^{1}J_{\text{SiC}} = 68.5$ Hz, vinyl carbon bearing silicon), 139.6 (d, $^{2}J_{\text{FC}} = 15.3$ Hz, $^{2}J_{\text{SnC}} = 40.1$ Hz, quart. aromatic carbon bearing vinyl group), 128.2 (d, $^{3}J_{\text{FC}} = 3.8$ Hz, aromatic carbon *meta* to fluorine atom and para to vinyl group), 127.2 (d, $^{3}J_{\text{FC}} = 8.4$ Hz, aromatic carbon *meta* to fluorine atom and *ortho* to vinyl group), 124.2 (d, $^{4}J_{\text{FC}} = 3.8$ Hz, aromatic carbon para to fluorine atom), 114.5 (d, $^{2}J_{\text{FC}} = 21.4$ Hz, aromatic carbon bearing hydrogen and *ortho* to fluorine atom), 28.9 ($^{3}J_{\text{SnC}} = 19.2$ Hz, C3 of butyl), 27.4 ($^{2}J_{\text{SnC}} = 61.4$ Hz, C2 of butyl), 13.6 (C4 of butyl), 11.8 ($^{5}J_{\text{FC}} = 1.5$ Hz, $^{1}J_{119\text{SnC}} = 333.3$ Hz, $^{1}J_{117\text{SnC}} = 318.3$ Hz, C1 of butyl), −0.01 ($^{1}J_{\text{SiC}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −9.31 ($^{3}J_{\text{SnSi}} = 30.6$ Hz) ppm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −54.9 ($^{4}J_{\text{FSn}} = 11.8$ Hz) ppm. LRMS (EI, 70 eV): 484 (M$^+$), 469 (M$^+$ − 15), 427 (M$^+$ − 57). HRMS (EI, 70 eV): calcd for C$_{23}$H$_{41}$FSiSn, 484.1987; found, 484.1985.

(Z)-1-Tributylstannyl-1-(3-fluorophenyl)-2-trimethylsilylethene 2c

IR (neat): 3070, 2950, 2920, 2870, 2850, 1605, 1580, 1480, 1460, 1420, 1375, 1260, 1245, 1135, 1070, 960, 945, 890, 880, 855, 840, 780, 690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.20 (dt, 1H, $J = 8.0, 6.0$ Hz), 6.83 (m, 1H), 6.74 (dt, 1H, $J = 8.0, 1.2$ Hz), 6.68 (m, 1H), 6.55 (s, 1H, $^{3}J_{119\text{SnH}} = 162$ Hz, $^{3}J_{117\text{SnH}} = 154$ Hz), 1.40 (m, 6H), 1.26 (sext, 6H, $J = 7.2$ Hz), 0.90 (m, 6H), 0.85 (t, 9H, $J = 7.2$ Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 164.9 ($^{1}J_{119\text{SnC}} = 362.1$ Hz, $^{1}J_{117\text{SnC}} = 345.2$ Hz, vinyl carbon bearing tin), 162.6 (d, $^{1}J_{\text{FC}} = 246.0$ Hz, aromatic carbon bearing fluorine atom), 154.3 (d, $^{3}J_{\text{FC}} = 6.9$ Hz, $^{2}J_{119\text{SnC}} = 51.6$ Hz, $^{2}J_{117\text{SnC}} = 39.2$ Hz, quart. aromatic carbon bearing vinyl group), 149.1 ($^{2}J_{\text{SnC}} = 55.3$ Hz, $^{1}J_{\text{SiC}} = 67.6$ Hz, vinyl carbon bearing silicon), 129.2 (d, $^{3}J_{\text{FC}} = 8.5$ Hz, aromatic carbon *meta* to fluorine atom and bearing hydrogen), 121.6 (d, $^{4}J_{\text{FC}} = 2.3$ Hz, aromatic carbon para to fluorine atom), 112.7 (d, $^{2}J_{\text{FC}} = 6.9$ Hz, $^{3}J_{\text{SnC}} = 20.7$ Hz, aromatic carbon *ortho* to fluorine atom and to vinyl group), 112.1 (d, $^{2}J_{\text{FC}} = 21.5$ Hz, aromatic carbon *ortho* to fluorine atom and para to vinyl group), 29.0 ($^{3}J_{\text{SnC}} = 19.2$ Hz, C3 of butyl), 27.3 ($^{2}J_{\text{SnC}} = 60.4$ Hz, C2 of butyl), 13.6, 12.0 ($^{1}J_{119\text{SnC}} = 330.7$ Hz, $^{1}J_{117\text{SnC}} = 315.2$ Hz, C1 of butyl), 0.08 ($^{1}J_{\text{SiC}} = 52.4$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ − 9.44 ($^{3}J_{\text{SnSi}} = 30.6$ Hz) ppm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −54.6 (satellite bands arising from coupling between Sn and F were not observed, $^{5}J_{\text{FSn}} \approx 0$) ppm. LRMS (EI, 70 eV): 484 (M$^+$), 469 (M$^+$ − 15), 427 (M$^+$ − 57). HRMS (EI, 70 eV): calcd for C$_{23}$H$_{41}$FSiSn, 484.1987; found, 484.1959.

(Z)-1-Tributylstannyl-1-(4-fluorophenyl)-2-trimethylsilylethene 2d

IR (neat): 3050, 2950, 2920, 2870, 2800, 1600, 1500, 1460, 1245, 1225, 1155, 880, 860, 835 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 6.95 (a set of multiplets, 2H), 6.94 (m, 2H), 6.53 (s, 1H, $^{3}J_{119\text{SnH}} = 164$ Hz, $^{3}J_{117\text{SnH}} = 157$ Hz), 1.4 (m, 6H), 1.25 (sext, 6H, $J = 7.2$ Hz), 0.9 (m, 6H), 0.85 (t, 9H, $J = 7.2$ Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 164.9 ($^{1}J_{119\text{SnC}} = 369.0$ Hz, $^{1}J_{117\text{SnC}} = 353.1$ Hz, vinyl carbon bearing tin), 161.1 (d, $^{1}J_{\text{FC}} = 243.7$ Hz, aromatic carbon bearing fluorine atom), 148.9 ($^{2}J_{\text{SnC}} = 57.7$ Hz, $^{1}J_{\text{SiC}} = 67.5$ Hz, vinyl carbon bearing silicon), 147.9 (d, $^{4}J_{\text{FC}} = 3$ Hz, $^{2}J_{\text{SnC}} = 45.4$ Hz, quart. aromatic carbon bearing vinyl group), 127.3 (d, $^{3}J_{\text{FC}} = 7.8$ Hz, $^{3}J_{\text{SnC}} = 14.5$ Hz, aromatic carbon *meta* to fluorine atom), 114.6 (d, $^{2}J_{\text{FC}} = 21.5$ Hz, aromatic carbon *ortho* to fluorine atom), 29.0 ($^{3}J_{\text{SnC}} = 19.2$ Hz, C3 of butyl), 27.3 ($^{2}J_{\text{SnC}} = 60.7$ Hz, C2 of butyl), 13.6 (C4 of butyl), 11.9 ($^{1}J_{119\text{SnC}} = 330.6$ Hz, $^{1}J_{117\text{SnC}} = 314.4$ Hz, C1 of butyl), 0.15 ($^{1}J_{\text{SiC}} = 51.5$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −9.68 ($^{3}J_{\text{SnSi}} = 31.1$ Hz) ppm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −55.1 ($^{6}J_{\text{FSn}} = 7.3$ Hz) ppm. LRMS (EI, 70 eV): 484 (M$^+$), 469 (M$^+$ − 15), 427 (M$^+$ − 57). HRMS (EI): calcd for C$_{23}$H$_{41}$FSiSn, 484.1987; found, 484.1982.

(Z)-1-Tributylstannyl-1-(2-chlorophenyl)-2-trimethylsilylethene 2e

IR (neat): 3050, 2950, 2920, 2870, 2850, 1460, 1435, 1245, 1050, 880, 860, 850, 755, 685 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.27 (dd, 1H, $J = 8.0, 1.2$ Hz), 7.17 (dt, 1H, $J = 7.6, 1.2$ Hz), 7.06 (dt, 1H, $J = 7.6, 1.6$ Hz), 6.92 (dd, 1H, $J = 7.6, 1.6$ Hz), 6.43 (s, 1H, $^{3}J_{119\text{SnH}} = 160$ Hz, $^{3}J_{117\text{SnH}} = 153$ Hz), 1.37 (m, 6H), 1.23 (sext, 6H, $J = 7.2$ Hz), 0.87 (m, 6H), 0.83 (t, 9H, $J = 7.2$ Hz) ppm. ^{13}C-NMR (CDCl$_3$): δ 165.7 ($^{1}J_{119\text{SnC}} = 366.6$ Hz, $^{1}J_{117\text{SnC}} = 349.7$ Hz, vinyl carbon bearing tin), 150.5 ($^{2}J_{\text{SnC}} = 36.2$ Hz, quart. aromatic carbon bearing vinyl group), 148.0 ($^{2}J_{\text{SnC}} = 52.3$ Hz, $^{1}J_{\text{SiC}} = 67.7$ Hz, vinyl carbon bearing silicon), 130.5 ($^{3}J_{\text{SnC}} = 11.5$ Hz, aromatic carbon bearing chlorine atom), 128.6 (aromatic carbon *meta* to chlorine atom and para to vinyl group), 127.8 ($^{3}J_{\text{SnC}} = 13.0$ Hz, aromatic carbon bearing hydrogen and *ortho* to vinyl group), 126.8 (aromatic carbon *ortho* to chlorine atom), 126.6 (aromatic carbon para to chlorine atom), 29.0 ($^{3}J_{\text{SnC}} = 19.2$ Hz, C3 of butyl), 27.4 ($^{2}J_{\text{SnC}} = 61.5$ Hz, C2 of butyl), 13.6(C4 of butyl), 12.3 ($^{1}J_{119\text{SnC}} = 332.1$ Hz, $^{1}J_{117\text{SnC}} = 317.5$ Hz, C1 of butyl), −0.07 ($^{1}J_{\text{SiC}} = 52.3$ Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −9.13 ($^3J_{SnSi} = 30.2$ Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −58.3 ppm. LRMS (EI, 70 eV): 500 (M^+), 485 ($M^+ - 15$), 443 ($M^+ - 57$). HRMS (EI, 70 eV): calcd for $C_{23}H_{41}ClSiSn$, 500.1688; found, 500.1667.

(Z)-1-Tributylstannyl-1-(4-chlorophenyl)-2-trimethylsilylethene **2f**[18]

^{13}C-NMR ($CDCl_3$) δ 164.8 ($^1J_{119SnC} = 363.6$ Hz, $^1J_{117SnC} = 347.4$ Hz, vinyl carbon-bearing tin), 150.4 ($^2J_{SnC} = 44.6$ Hz, quart. aromatic carbon bearing vinyl group), 149.2 ($^2J_{SnC} = 56.8$ Hz, $^1J_{SiC} = 67.7$ Hz, vinyl carbon bearing silicon), 131.2 (aromatic carbon bearing chlorine atom), 127.9 (aromatic carbon *ortho* to chlorine atom), 127.3 ($^3J_{SnC} = 14.6$ Hz, aromatic carbon *meta* to chlorine atom), 29.0 ($^3J_{SnC} = 19.2$ Hz, C3 of butyl), 27.3 ($^2J_{SnC} = 61.5$ Hz, C2 of butyl), 13.6 (C4 of butyl), 12.0 ($^1J_{119SnC} = 329.8$ Hz, $^1J_{117SnC} = 314.4$ Hz, C1 of butyl), 0.1 ($^1J_{SiC} = 51.5$ Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −9.54 ($^3J_{SnSi} = 30.2$ Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −55.0 ppm.

(Z)-1-Tributylstannyl-1-(3-trifluoromethylphenyl)-2-trimethylsilylethene **2g**

IR (neat): 2950, 2920, 2870, 2850, 1460, 1420, 1325, 1245, 1164, 1130, 1075, 860, 835, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.38 (m, 2H), 7.22 (s, 1H), 7.15 (m, 1H), 6.57 (s, 1H, $^3J_{119SnH} = 160$ Hz, $^3J_{117SnH} = 153$ Hz), 1.39 (m, 6H), 1.24 (sext, 6H, $J = 7.2$ Hz), 0.91 (m, 6H), 0.84 (t, 9H, $J = 7.2$ Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 164.7 ($^1J_{119SnC} = 356.0$ Hz, $^1J_{117SnC} = 348.3$ Hz, vinyl carbon bearing tin), 152.5 ($^2J_{SnC} = 44.5$ Hz, quart. aromatic carbon bearing vinyl group), 150.1 ($^2J_{SnC} = 53.7$ Hz, $^1J_{SiC} = 68.5$ Hz, vinyl carbon bearing silicon), 130.2(q, $^2J_{FC} = 31.8$ Hz, aromatic carbon bearing CF_3 group), 129.2 (aromatic carbon *para* to CF_3 group), 128.3 (aromatic carbon *meta* to CF_3 group and bearing hydrogen), 124.3 (q, $^1J_{FC} = 272.0$ Hz, carbon of CF_3 group), 122.7 (q, $^3J_{FC} = 3.6$ Hz, aromatic carbon *ortho* to CF_3 group and *para* to vinyl group), 122.0 (q, $^3J_{FC} = 3.8$ Hz, aromatic carbon *ortho* to CF_3 group and to vinyl group), 29 ($^3J_{SnC} = 19.9$ Hz, C3 of butyl), 27.3 ($^2J_{SnC} = 57.7$ Hz, C2 of butyl), 13.6 (C4 of butyl), 12.0 ($^1J_{119SnC} = 328.2$ Hz, $^1J_{117SnC} = 316.0$ Hz, C1 of butyl), 0.05 ($^1J_{SiC} = 52.2$ Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −9.28 ($^3J_{SnSi} = 30.2$ Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −53.7 ppm. LRMS (EI, 70 eV): 534 (M^+), 519 ($M^+ - 15$). HRMS (EI, 70 eV): calcd for $C_{24}H_{41}F_3SiSn$, 534.1952; found, 534.1942.

(Z)-1-Tributylstannyl-1-(4-ethoxycarbonylphenyl)-2-trimethylsilylethene **2h**[30]

IR (neat): 3025, 2950, 2925, 2875, 2850, 1720, 1600, 1460, 1400, 1360, 1270, 1245, 1180, 1100, 1020, 860, 760, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.94 (d, 2H, $J = 8.4$ Hz), 7.02 (d, 2H, $J = 8.4$ Hz), 6.56 (s, 1H, $^3J_{119SnH} = 166$ Hz, $^3J_{117SnH} = 159$ Hz), 4.37 (q, 6H, $J = 7.2$ Hz), 1.40 (m, 6H), 1.39 (t, 3H, $J = 7.2$ Hz), 1.25 (sext, 6H, $J = 7.2$ Hz), 0.90 (m, 6H), 0.84 (t, 9H, $J = 7.2$ Hz), 0.18 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 166.6 (carbonyl carbon of ethoxycarbonyl group), 165.4 ($^1J_{119SnC} = 355.2$ Hz, $^1J_{117SnC} = 339.0$ Hz, vinyl carbon bearing tin), 156.7 ($^2J_{SnC} = 43.8$ Hz, quart. aromatic carbon bearing vinyl group), 149.4 ($^2J_{SnC} = 53.8$ Hz, $^1J_{Si,C} = 68.0$ Hz, vinyl carbon bearing silicon), 129.3 (aromatic carbon *ortho* to ethoxycarbonyl group), 127.4 (aromatic carbon bearing ethoxycarbonyl group), 125.8 ($^3J_{SnC} = 13.8$ Hz, aromatic carbon *meta* to ethoxycarbonyl group), 60.7 (methylene carbon of ethyl group), 29.0 ($^3J_{SnC} = 19.1$ Hz, C3 of butyl), 27.3 ($^2J_{SnC} = 60.7$ Hz, C2 of butyl), 14.3 (methyl carbon of ethyl group), 13.6 (C4 of butyl), 12.0 ($^1J_{119SnC} = 330.5$ Hz, $^1J_{117SnC} = 316.8$ Hz, C1 of butyl), 0.06 ($^1J_{SiC} = 51.6$ Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −9.32 ($^3J_{SnSi} = 30.6$ Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −54.6 ppm. LRMS (EI, 70 eV): 538 (M^+), 481 ($M^+ - 57$).

(Z)-1-Tributylstannyl-2-trimethylsilyl-1-(3-nitrophenyl)ethene **2i**

IR (neat): 3050, 2950, 2910, 2870, 2850, 1525, 1460, 1345, 1245, 1075, 860, 835, 800, 740, 680 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.01 (ddd, 1H, $J = 8.0$, 2.4, 1.2 Hz), 7.85 (t, 1H, $J = 1.6$ Hz), 7.42 (t, 1H, $J = 8.0$ Hz), 7.29 (ddd, 1H, $J = 8.0$, 2.4, 1.6 Hz), 6.61 (s, 1H, $^3J_{119SnH} = 156$ Hz, $^3J_{117SnH} = 148$ Hz), 1.41 (m, 6H), 1.25 (sext, 6H, $J = 7.2$ Hz), 0.92 (m, 6H), 0.85 (t, 9H, $J = 7.2$ Hz), 0.2 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 163.7 ($^1J_{119SnC} = 347.6$ Hz, $^1J_{117SnC} = 335.1$ Hz, vinyl carbon bearing tin), 153.5 ($^2J_{SnC} = 45.4$ Hz, quart. aromatic carbon bearing vinyl group), 151.3 ($^2J_{SnC} = 53.0$ Hz, $^1J_{SiC} = 66.5$ Hz, vinyl carbon bearing silicon), 147.9 (aromatic carbon bearing nitro group), 132.1 (aromatic carbon *para* to nitro group), 128.7 (aromatic carbon *meta* to vinyl group), 120.7 (aromatic carbon *para* to vinyl group), 120.3 (aromatic carbon *ortho* to nitro and to vinyl group), 29 ($^3J_{SnC} = 19.2$ Hz, C3 of butyl), 27.3 ($^2J_{SnC} = 62.3$ Hz, C2 of butyl), 13.5 (C4 of butyl), 12.0 ($^1J_{119SnC} = 332.0$ Hz, $^1J_{117SnC} = 316.6$ Hz, C1 of butyl), 0.001 ($^1J_{SiC} = 52.3$ Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ−8.96 ($^3J_{SnSi} = 28.7$ Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −52.2 ppm. LRMS (EI, 70 eV): 511 (M^+), 481 ($M^+ - 30$), 454 ($M^+ - 57$). HRMS (EI, 70 eV): calcd for $C_{23}H_{41}NO_2SiSn$, 511.1932; found, 511.1945.

(Z)-1-Tributylstannyl-2-trimethylsilyl-1-(4-nitrophenyl)ethene **2j**

IR (neat): 3040, 2950, 2920, 2860, 2850, 1580, 1510, 1340, 1243, 1105, 855, 840, 755, 690, 660 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.13 (d, 2H, $J = 8.8$ Hz), 7.09 (d, 2H, $J = 8.8$ Hz), 6.58 (s, 1H, $^3J_{119SnH} = 154$ Hz, $^3J_{117SnH} = 148$ Hz), 1.40 (m, 6H), 1.26 (sext, 6H, $J = 7.2$ Hz), 0.92 (m, 6H), 0.85 (t, 9H, $J = 7.2$ Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 164.3 ($^1J_{119SnC} = 339.8$ Hz, $^1J_{117SnC} = 324.5$ Hz, vinyl carbon bearing tin), 159.0 ($^2J_{SnC} = 43.1$ Hz, quart. aromatic carbon bearing vinyl group), 151.0 ($^2J_{SnC} = 50.8$ Hz, $^1J_{SiC} = 66.2$ Hz, vinyl carbon bearing silicon), 145.6 (aromatic carbon bearing nitro group), 126.5 ($^3J_{SnC} = 13.0$ Hz, aromatic carbon *meta* to nitro group), 123.4 (aromatic carbon *ortho* to nitro group), 28.9 ($^3J_{SnC} = 20.0$ Hz, C3 of butyl), 27.2 ($^2J_{SnC} = 61.5$ Hz, C2 of butyl), 13.5 (C4 of butyl), 12.0 ($^1J_{119SnC} = 332.1$ Hz, $^1J_{117SnC} = 316.8$ Hz, C1 of butyl), −0.04 ($^1J_{SiC}$ = 49.9 Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −8.85 ($^3J_{SnSi}$ = 28.7 Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −52.8 ppm. LRMS (EI, 70 eV): 511 (M^+), 454 ($M^+ - 57$). HRMS (EI, 70 eV): calcd for $C_{23}H_{41}NO_2SiSn$, 511.1929; found, 511.1929.

(Z)-1-Tributylstannyl-1-(4-cyanophenyl)-2-tri-methylsilylethene **2k**

IR (neat): 3050, 2950, 2920, 2870, 2850, 2220, 1595, 1490, 1460, 1450, 1245, 880, 850, 835 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.55 (d, 2H, J = 8.0 Hz), 7.04 (d, 2H, J = 8.0 Hz), 6.54 (s, 1H, $^3J_{119SnH}$ = 156 Hz, $^3J_{117SnH}$ = 149 Hz), 1.40 (m, 6H), 1.25 (sext, 6H, J = 7.2 Hz), 0.90 (m, 6H), 0.85 (t, 9H, J = 7.2 Hz), 0.18 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 164.5 ($^1J_{119SnC}$ = 342.7 Hz, $^1J_{117SnC}$ = 328.6 Hz, vinyl carbon bearing tin), 156.8 ($^2J_{SnC}$ = 43.9 Hz, quart. aromatic carbon bearing vinyl group), 150.6 ($^2J_{SnC}$ = 51.6 Hz, $^1J_{SiC}$ = 67.0 Hz, vinyl carbon bearing silicon), 131.8 (aromatic carbon *ortho* to cyano group), 126.6 ($^3J_{SnC}$ = 1.3 Hz, aromatic carbon *meta* to cyano group), 119.3 (carbon of cyano group), 108.8 (aromatic carbon bearing cyano group), 28.9 ($^3J_{SnC}$ = 19.2 Hz, C3 of butyl), 27.3 ($^2J_{SnC}$ = 61.5 Hz, C2 of butyl), 13.5 (C4 of butyl), 12.0 ($^1J_{119SnC}$ = 332.1 Hz, $^1J_{117SnC}$ = 315.2 Hz, C1 of butyl), −0.02 ($^1J_{SiC}$ = 50.8 Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −8.97 ($^3J_{SnSi}$ = 28.7 Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −53.2 ppm. LRMS (EI, 70 eV): 511 (M^+), 454 ($M^+ - 57$). HRMS (EI, 70 eV): calcd for $C_{24}H_{41}NSiSn$, 491.2034; found, 491.2039.

(Z)-1-Tributylstannyl-1-(3,4-dimethoxyphenyl)-2-trimethylsilylethene **2l**

IR (neat): 3050, 2950, 2930, 2875, 2850, 1730, 1590, 1580, 1505, 1460, 1440, 1400, 1315, 1260, 1250, 1235, 1155, 1140, 1030, 875, 860, 850, 840 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 6.78 (d, 1H, J = 8.8 Hz), 6.55 [m, 3H(aromatic protons and vinyl proton), $^3J_{119SnH}$ = 168 Hz, $^3J_{117SnH}$ = 160 Hz], 3.88 (s, 3H), 3.87 (s, 3H), 1.43 (m, 6H), 1.26 (sext, 6H, J = 7.2 Hz), 0.91 (m, 6H), 0.85(t, 9H, J = 7.2 Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 165.6 ($^1J_{119SnC}$ = 377.4 Hz, $^1J_{117SnC}$ = 360.5 Hz, vinyl carbon bearing tin), 148.2 (aromatic carbon *meta* to vinyl and bearing OCH_3 group), 147.5 ($^2J_{SnC}$ = 60.7 Hz, $^1J_{SiC}$ = 68.4 Hz, vinyl carbon bearing silicon), 147.1(aromatic carbon *para* to vinyl and bearing OCH_3 group), 144.9 ($^2J_{SnC}$ = 45.4 Hz, quart. aromatic carbon bearing vinyl group), 117.9 ($^3J_{SnC}$ = 15.4 Hz, aromatic carbon *ortho* to vinyl and *para* to OCH_3 group), 110.8(aromatic carbon bearing hydrogen and *meta* to vinyl group), 109.5 ($^3J_{SnC}$ = 14.6 Hz, aromatic carbon *ortho* to OCH_3 and to vinyl group), 55.9 (carbon of OCH_3 group), 55.6 (carbon of OCH_3 group), 29.1 ($^3J_{SnC}$ = 19.2 Hz, C3 of butyl), 27.4 ($^2J_{SnC}$ = 60.7 Hz, C2 of butyl), 13.6 (C4 of butyl), 12.0 ($^1J_{119SnC}$ = 333.9 Hz, $^1J_{117SnC}$ = 315 Hz, C1 of butyl), 0.2 ($^1J_{SiC}$ = 52.3 Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −9.90 ($^3J_{SnSi}$ = 32.1 Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −55.7 ppm. LRMS (EI, 70 eV): 467 (M^+), 410 ($M^+ - 57$). HRMS (EI, 70 eV): calcd for $C_{25}H_{46}O_2SiSn$, 526.2289; found, 526.2313.

(Z)-1-Tributylstannyl-2-trimethylsilyl-1-(3-pyridyl)ethene **2m**

IR (neat): 3050, 2950, 2930, 2875, 2850, 1470,1405, 1380, 1250, 875, 860, 855, 835, 715 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 8.39 (dd, 1H, J = 4.8, 1.8 Hz), 8.27 (ddd, 1H, J = 7.9, 2.4, 1.8 Hz), 8.27 (dd, 1H, J = 2.4, 0.8 Hz), 7.17 (ddd, 1H, J = 7.8, 4.8, 0.8 Hz), 6.6 (s, 1H, $^3J_{119SnH}$ = 159 Hz, $^3J_{117SnH}$ = 152 Hz), 1.41 (m, 6H), 1.26 (sext, 6H, J = 7.2 Hz), 0.93 (m, 6H), 0.85(t, 9H, J = 7.2 Hz), 0.2 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 161.9 ($^1J_{119SnC}$ = 353.7 Hz, $^1J_{117SnC}$ = 336.7 Hz, vinyl carbon bearing tin), 151.4 ($^2J_{SnC}$ = 53.1 Hz, $^1J_{SiC}$ = 66.5 Hz, vinyl carbon bearing silicon), 147.13 (pyridyl carbon *ortho* to vinyl group and to nitrogen atom), 147.05 ($^2J_{SnC}$ = 33.8 Hz, pyridyl carbon bearing vinyl group), 146.7 (pyridyl carbon *ortho* to nitrogen and *para* to vinyl group), 133.0 ($^3J_{SnC}$ = 13.1 Hz, pyridyl carbon *ortho* to vinyl group and *para* to nitrogen), 122.6 (pyridyl carbon *meta* to vinyl group and to nitrogen), 29.0 ($^3J_{SnC}$ = 20.0 Hz, C3 of butyl), 27.3 ($^2J_{SnC}$ = 61.4 Hz, C2 of butyl, 13.5 (C4 of butyl), 11.9 ($^1J_{119SnC}$ = 329.8 Hz, $^1J_{117SnC}$ = 316.7 Hz, C1 of butyl), 0.02 ($^1J_{SiC}$ = 51.5 Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −9.28 ($^3J_{SnSi}$ = 29.7 Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −52.6 ppm. LRMS (EI, 70 eV): 467 (M^+), 410 ($M^+ - 57$). HRMS (EI, 70 eV): calcd for $C_{22}H_{41}NSiSn$, 467.2030; found, 467.2032.

(Z)-1-Tributylstannyl-2-trimethylsilyl-1-(2-pyridyl)ethene **2n**

IR (neat): 3075, 3060, 3045, 2950, 2925, 2875, 2850, 1580, 1560, 1460, 1430, 1255, 865, 840, 765 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.44 (ddd, 1H, J = 5.0, 1.8, 0.8 Hz), 7.59 (dt, 1H, J = 7.6, 1.8 Hz), 7.26 (m, 1H), 7.03 (ddd, 1H, J = 7.6, 5.0, 1.0 Hz), 6.94 (s, 1H, $^3J_{119SnH}$ = 166 Hz, $^3J_{117SnH}$ = 158 Hz), 1.42 (m, 6H), 1.26 (sext, 6H, J = 7.2 Hz), 0.93 (m, 6H), 0.84 (t, 9H, J = 7.2 Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$): δ 167.6 ($^1J_{119SnC}$ = 392.1 Hz, $^1J_{117SnC}$ = 372.6 Hz, vinyl carbon bearing tin), 167.0 ($^2J_{SnC}$ = 38.5 Hz, quart. pyridyl carbon bearing vinyl group), 149.0 ($^2J_{SnC}$ = 52.3 Hz, $^1J_{SiC}$ = 68.5 Hz, vinyl carbon bearing silyl group), 147.8 (pyridyl carbon *ortho* to nitrogen), 136.3 (pyridyl carbon *para* to nitrogen), 120.7 (pyridyl carbon *para* to vinyl group), 118.8 ($^3J_{SnC}$ = 15.3 Hz, pyridyl carbon *ortho* to vinyl group), 29.1 ($^3J_{SnC}$ = 19.2 Hz, C3 of butyl), 27.4 ($^2J_{SnC}$ = 63.0 Hz, C2 of butyl), 13.7 (C4 of butyl), 12.6 ($^1J_{119SnC}$ = 339.0 Hz, $^1J_{117SnC}$ = 323.6 Hz, C1 of butyl), 0.3 ($^1J_{SiC}$ = 53.1 Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, TMS): δ −9.23 ($^3J_{SnSi}$ = 31.6 Hz) ppm. ^{119}Sn-NMR ($CDCl_3$, TMT): δ −55.0 ppm. LRMS (EI, 70 eV): 467 (M^+), 410 ($M^+ - 57$). HRMS (EI, 70 eV): calcd for $C_{22}H_{41}NSiSn$, 467.2030; found, 467.2027.

(Z)-1-Tributylstannyl-2-trimethylsilyl-1-(2-methoxyphenyl)ethene **2o**

IR(neat): 3075(w), 2950(s), 2925(s), 2875(s), 2850(s), 1600(w), 1580(w), 1480(s), 1460(s), 1435(m), 1330(w), 1240(s), 1130(w), 1110(m), 1075(w), 10558m), 1030(m),880(s), 860(s), 835(s), 750(s), 695(m), 670(m) cm^{-1}. ^{1}H-NMR(CDCl$_3$): δ 7.14 (dd, $J = 8.0$ and 2.0 Hz, 1H), 6.92 (m, 2H), 6.74 (d, $J = 7.2$ Hz, 1H), 6.51 (s, $^{3}J_{119\mathrm{SnH}} = 170$ Hz, $^{3}J_{117\mathrm{SnH}} = 162$ Hz, 1H), 3.76 (s, 3H), 1.37 (m, 6H), 1,23 (sext, $J = 7.2$ Hz, 6H), 0.83 (m, 6H), 0.83 (t, $J = 7.2$ Hz, 9H), 0.17 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 163.3 ($^{1}J_{119\mathrm{SnC}} = 401.3$ Hz, $^{1}J_{117\mathrm{SnC}} = 383.7$ Hz, vinyl carbon bearing tin), 154.5 (aromatic carbon bearing methoxy group), 146.6 ($^{2}J_{\mathrm{SnC}} = 57.6$ Hz, $^{1}J_{\mathrm{SiC}} = 68.5$ Hz, vinyl carbon bearing silicon), 141.0 (aromatic carbon bearing vinyl group), 127.2 (aromatic carbon *para* to vinyl and *meta* to methoxy group), 127.1 (aromatic carbon *meta* to methoxy and *ortho* to vinyl group), 121.1 (aromatic carbon *para* to methoxy and *meta* to vinyl group), 109.1(aromatic carbon *ortho* to methoxy and *meta* to vinyl group), 55.0 (carbon in methoxy group), 29.0 ($^{3}J_{\mathrm{SnC}} = 18.4$ Hz, C3 of butyl), 27.5 ($^{2}J_{\mathrm{SnC}} = 60.7$ Hz, C2 of butyl), 13.7 (C4 of butyl), 11.9 ($^{1}J_{119\mathrm{SnC}} = 333.6$ Hz, $^{1}J_{117\mathrm{SnC}} = 318.2$ Hz, C1 of butyl), 0.1 ($^{1}J_{\mathrm{SiC}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −9.76 ($^{3}J_{\mathrm{SnSi}} = 32.6$ Hz) ppm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −61.8 ppm. LRMS (EI, 70 eV): 496 (M^{+}), 481 (M^{+} − 15), 439 (M^{+} − 57). HRMS (EI, 70 eV): calcd for $C_{24}H_{44}OSiSn$, 496.2183; found, 496.2165.

(Z)-1-Butyl-1-tributylstannyl-2-trimethylsilaneethene ***2p***[9]

^{13}C-NMR (CDCl$_3$): δ 165.8 ($^{1}J_{119\mathrm{SnC}} = 398.2$ Hz, $^{1}J_{117\mathrm{SnC}} = 379.8$ Hz, vinyl carbon bearing tin), 143.2 [only a set of satellite band (66.9 Hz) was observed. $^{1}J_{\mathrm{SiC}} = 66.9$ Hz, vinyl carbon bearing silicon], 47.4 ($^{2}J_{\mathrm{SnC}} = 56.9$ Hz, C3 of 1-hexene framework), 32.3 ($^{3}J_{\mathrm{SnC}} = 10.0$ Hz, C4 of 1-hexene framework), 29.3 ($^{3}J_{\mathrm{SnC}} = 18.4$ Hz, C3 of butyl in SnBu$_3$), 27.6 ($^{2}J_{\mathrm{SnC}} = 59.2$ Hz, C2 of butyl in SnBu$_3$), 22.3 (C5 of 1-hexene framework), 14.0 (C6 of 1-hexene framework), 13.7 (C4 of butyl in SnBu$_3$), 11.2 ($^{1}J_{119\mathrm{SnC}} = 321.3$ Hz, $^{1}J_{117\mathrm{SnC}} = 306.7$ Hz, C1 of butyl in SnBu$_3$), 0.3 ($^{1}J_{\mathrm{SiC}} = 51.6$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −10.99 ($^{3}J_{\mathrm{SnSi}} = 37.5$ Hz) ppm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −57.8 ppm.

(Z)-1-Tributylstannyl-1-(hydroxymethyl)-2-trimethylsilylethene ***2q***[9,17]

^{13}C-NMR (CDCl$_3$): δ 163.6 ($^{1}J_{119\mathrm{SnC}} = 373.6$ Hz, $^{1}J_{117\mathrm{SnC}} = 357.5$ Hz, vinyl carbon bearing tin), 140.4 ($^{2}J_{\mathrm{SnC}} = 52.3$ Hz, $^{1}J_{\mathrm{SiC}} = 69.2$ Hz, vinyl carbon bearing silicon), 73.5 ($^{2}J_{\mathrm{SnC}} = 67.6$ Hz, hydroxymethyl carbon), 29.2 ($^{3}J_{\mathrm{SnC}} = 19.2$ Hz, C3 of butyl), 27.4 ($^{2}J_{\mathrm{SnC}} = 62.3$ Hz, C2 of butyl), 13.6 (C4 of butyl), 10.9 ($^{1}J_{119\mathrm{SnC}} = 330.6$ Hz, $^{1}J_{117\mathrm{SnC}} = 315.2$ Hz, C1 of butyl), 0.05 ($^{1}J_{\mathrm{SiC}} = 51.5$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −9.46 ($^{3}J_{\mathrm{SnSi}} = 34.0$ Hz) ppm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −58.2 ppm.

(Z)-1-Tributylstannyl-2-trimethylsilyl-1-(1-hydroxy-1-methylethyl)ethene ***2r***[26]

IR (neat): 3800-3200 (br, m), 2950 (s), 2850 (s), 1550 (w), 1450 (s), 1370 (s), 1355 (m), 1240 (s), 1120 (m), 960 (w), 900 (m), 850 (s), 840 (s) 750 (m), 680 (m), 660 (m), 620 (w) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 6.39 (s, 1H, $^{3}J_{119\mathrm{SnH}} = 185.$ 2 Hz, $^{3}J_{117\mathrm{SnH}} = 176.8$ Hz), 1.55 (brs, 1H), 1.47 (m, 6H), 1.33 (sext, 6H, $J = 7.0$ Hz), 1.28 (s, 6H), 0.96 (m, 6H), 0.89 (t, 9H, $J = 7.2$ Hz), 0.12 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 175.6 ($^{1}J_{119\mathrm{SnC}} = 406.6$ Hz, $^{1}J_{117\mathrm{SnC}} = 388.3$ Hz, vinyl carbon bearing tin), 137.1 ($^{1}J_{\mathrm{SiC}} = 70.0$ Hz, $^{2}J_{\mathrm{SiC}} = 59.9$ Hz, vinyl carbon bearing silicon), 77.6 ($^{2}J_{\mathrm{SnC}} = 39.1$ Hz, tertiary methyl carbon), 30.2 ($^{3}J_{\mathrm{SnC}} = 7.7$ Hz, methyl carbon), 29.3 ($^{3}J_{\mathrm{SnC}} = 18.4$ Hz, C3 carbon of butyl), 27.5 ($^{2}J_{\mathrm{SnC}} = 60.7$ Hz, C2 of butyl), 13.7 (C4 of butyl), 13.0 ($^{1}J_{119\mathrm{SnC}} = 330.6$ Hz, $^{1}J_{117\mathrm{SnC}} = 316.7$ Hz, C1 of butyl), 0.7 ($^{1}J_{\mathrm{SiC}} = 51.5$ Hz, methyl carbon of SiMe$_3$) pm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −9.8 ($^{3}J_{\mathrm{SnSi}} = 38.4$ Hz) pm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −63.6 ppm. LRMS (EI, 70 eV): 430 (M^{+} − 18).

(Z)-1-Tributylstannyl-2-trimethylsilyl-1-[hydroxy(phenyl)methyl]ethene ***2s***[17]

^{13}C-NMR (CDCl$_3$): δ 166.5 ($^{1}J_{119\mathrm{SnC}} = 374.3$ Hz, $^{1}J_{117\mathrm{SnC}} = 358.2$ Hz, vinyl carbon bearing tin), 142.2 ($^{2}J_{\mathrm{SnC}} = 53.8$ Hz, $^{1}J_{\mathrm{SiC}} = 68.4$ Hz, vinyl carbon bearing silicon), 141.9 (quart. aromatic carbon attached to hydroxymethyl group), 128.2 (aromatic carbon *meta* to hydroxymethyl group), 127.4 (aromatic carbon *para* to hydroxymethyl group), 127.1 (aromatic carbon *ortho* to hydroxymethyl group), 83.8 ($^{2}J_{\mathrm{SnC}} = 57.6$ Hz, hydroxymethyl carbon), 29.0 ($^{3}J_{\mathrm{SnC}} = 18.4$ Hz, C3 of butyl), 27.4 ($^{2}J_{\mathrm{SnC}} = 63.8$ Hz, C2 of butyl), 13.6 (C4 of butyl), 11.6 ($^{1}J_{119\mathrm{SnC}} = 331.3$ Hz, $^{1}J_{117\mathrm{SnC}} = 316.8$ Hz, C2 of butyl), 0.3 ($^{1}J_{\mathrm{SiC}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −9.47 ($^{3}J_{\mathrm{SnSi}} = 32.6$ Hz) ppm. ^{119}Sn-NMR (CDCl$_3$, TMT): δ −58.6 ppm.

General procedure for the protodestannylation of (*Z*)-1-(tributylstannyl)-2-(trimethylsilyl)-1-phenyl ethene

To a toluene (2 ml) mixture of **2a** (0.184 g, 0.395 mmol) and tetraethylammonium chloride (0.088 g, 0.53 mmol), hydrochloric acid (20%, 0.5 ml) was added slowly with stirring using a syringe at room temperature. After the addition was complete, stirring was continued. After 3 h, TLC analysis of the resulting mixture disclosed that **2a** was completely consumed. Column chromatography (silica gel, hexane) gave 0.067 g (96%) of (*E*)-styryltrimethylsilane **3a**. The ^{1}H-NMR spectrum of the product was in good agreement with that from the literature.[9] ^{29}Si-NMR (CDCl$_3$, TMS): δ−6.26 ppm.

Other protodestannylations with hydrochloric acid (20 or 30%) or hydroiodic acid (57%) were carried out similarly, and analytical data for the products are shown below. For known compounds, heretofore unpublished spectra are shown.

(E)-Trimethyl[2-(2-fluorophenyl)ethenyl]silane ***3b***

IR (neat): 3075, 2950, 2920, 1610, 1480, 1455, 1250, 1225, 1210, 1095, 990, 870, 860, 850, 835, 750 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.55 (dt, 1H, $J = 7.6$, 2.0 Hz), 7.26 (m, 1H), 7.09 (d, 1H, $J = 19.2$ Hz), 7.08 (m, 1H), 7.02 (ddd, 1H, $J = 10.7$, 8.0, 1.2 Hz), 6.54 (d, 1H, $J = 19.2$ Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 160.2 (d,

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$^{1}J_{\mathrm{FC}} = 247.3$ Hz, aromatic carbon bearing fluorine atom), 135.2 (d, $^{3}J_{\mathrm{FC}} = 4.6$ Hz, vinyl carbon bearing aromatic ring), 132.4 (d, $^{4}J_{\mathrm{FC}} = 3.1$ Hz, $^{1}J_{\mathrm{SiC}} = 65.1$ Hz, vinyl carbon bearing silicon), 129.1 (d, $^{3}J_{\mathrm{FC}} = 8.5$ Hz, aromatic carbon *meta* to fluorine atom and *para* to vinyl group), 126.7 (d, $^{3}J_{\mathrm{FC}} = 3.9$ Hz, aromatic carbon *meta* to fluorine atom and *ortho* to vinyl group), 126.2 (d, $^{2}J_{\mathrm{FC}} = 11.5$ Hz, quart. aromatic carbon bearing vinyl), 124.0 (d, $^{4}J_{\mathrm{FC}} = 3.8$ Hz, aromatic carbon *para* to fluorine atom), 115.7 (d, $^{2}J_{\mathrm{FC}} = 22.4$ Hz, aromatic carbon *ortho* to fluorine atom and *meta* to vinyl group), −1.3 ($^{1}J_{\mathrm{SiC}} = 52.4$ Hz, methyl carbon of $\mathrm{SiMe_3}$) ppm. ^{29}Si-NMR ($\mathrm{CDCl_3}$, TMS): δ −5.89 ppm. LRMS (EI, 70 eV): 194 ($\mathrm{M^+}$), 179 ($\mathrm{M^+} - 15$), 153 ($\mathrm{M^+} - 41$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{11}H_{15}FSi}$, 194.0927; found, 194.0916.

(E)-Trimethyl[2-(3-fluorophenyl)ethenyl]silane ***3c***

IR (neat): 3060, 2950, 2900, 1605, 1580, 1485, 1480, 1440, 1260, 1245, 1200, 983, 935, 865, 840, 775 cm^{-1}. ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.27 (m, 1H), 7.15 (m, 2H), 6.93 (m, 1H), 6.82 (d, 1H, $J = 19.2$ Hz), 6.49 (d, 1H, $J = 19.2$ Hz), 0.16 (s, 9H) ppm. ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 163.2 (d, $^{1}J_{\mathrm{FC}} = 245.2$ Hz, aromatic carbon bearing fluorine atom), 142.3 ($^{4}J_{\mathrm{FC}} = 2.2$ Hz, vinyl carbon bearing aromatic ring), 140.8 ($^{3}J_{\mathrm{FC}} = 6.9$ Hz, quart. aromatic carbon bearing vinyl group), 131.3 ($^{1}J_{\mathrm{SiC}} = 64.5$ Hz, vinyl carbon bearing silicon), 129.9 ($^{3}J_{\mathrm{FC}} = 8.5$ Hz, aromatic carbon *meta* to fluorine atom and to vinyl group), 122.3 ($^{4}J_{\mathrm{FC}} = 2.3$ Hz, aromatic carbon *para* to fluorine atom and *ortho* to vinyl group), 114.7 (d, $^{2}J_{\mathrm{FC}} = 21.4$ Hz, aromatic carbon *ortho* to fluorine atom and *para* to vinyl group), 112.6 (d, $^{2}J_{\mathrm{FC}} = 21.5$ Hz, aromatic carbon *ortho* to fluorine atom and to vinyl group), −1.3 ($^{1}J_{\mathrm{SiC}} = 52.3$ Hz, methyl carbon of $\mathrm{SiMe_3}$) ppm. ^{29}Si-NMR ($\mathrm{CDCl_3}$, TMS): δ −6.06 ppm. LRMS (EI, 70 eV): 194 ($\mathrm{M^+}$), 179 ($\mathrm{M^+} - 15$), 163 ($\mathrm{M^+} - 31$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{11}H_{15}FSi}$, 194.0927; found, 194.0927.

(E)-Trimethyl[2-(4-fluorophenyl)ethenyl]silane ***3d***[51]

IR (neat): 3040, 2950, 1610, 1600, 1500, 1245, 1230, 1155, 980, 865, 835, 795, 740 cm^{-1}. ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.41 (m, 2H), 6.94 (m, 2H), 6.82 (d, 1H, $J = 19.2$ Hz), 6.36 (d, 1H, $J = 19.2$ Hz), 0.15 (s, 9H) ppm. ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 162.5 (d, $^{1}J_{\mathrm{FC}} = 245.9$ Hz, aromatic carbon bearing fluorine atom), 142.3 (vinyl carbon bearing aromatic ring), 134.6 (quart. aromatic carbon bearing vinyl group), 129.2 ($^{1}J_{\mathrm{SiC}} = 60.4$ Hz, vinyl carbon bearing silicon), 127.9 (d, $^{3}J_{\mathrm{FC}} = 7.8$ Hz, aromatic carbon *meta* to fluorine atom), 115.4 (d, $^{2}J_{\mathrm{FC}} = 21.5$ Hz, aromatic carbon *ortho* to fluorine atom), −1.3 ($^{1}J_{\mathrm{SiC}} = 50.8$ Hz, methyl carbon of $\mathrm{SiMe_3}$) ppm. ^{29}Si-NMR ($\mathrm{CDCl_3}$, TMS): δ −6.21 ppm. LRMS (EI, 70 eV): 194 ($\mathrm{M^+}$), 179 ($\mathrm{M^+} - 15$), 163 ($\mathrm{M^+} - 31$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{11}H_{15}FSi}$, 194.0927; found, 194.0924.

(E)-Trimethyl[2-(2-chlorophenyl)ethenyl]silane ***3e***[52,53]

IR (neat): 3070, 2950, 2900, 1600, 1465, 1440, 1260, 1245, 1120, 1050, 985, 970, 845, 755 cm^{-1}. ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 139.4 (vinyl carbon bearing aromatic ring), 136.3 (quart. aromatic carbon bearing vinyl group), 133.1 ($^{1}J_{\mathrm{SiC}} = 64.5$ Hz, vinyl carbon bearing silicon), 129.7 (aromatic proton *meta* to chlorine atom and *para* to vinyl group), Aromatic carbon bearing chlorine atom was not observed. 128.8 (aromatic carbon *ortho* to chlorine atom), 126.7 (aromatic carbon *meta* to chlorine atom and *ortho* to vinyl group), 126.6 (aromatic carbon *para* to chlorine atom), −1.3 ($^{1}J_{\mathrm{SiC}} = 53.1$ Hz, methyl carbon of $\mathrm{SiMe_3}$) ppm. ^{29}Si-NMR ($\mathrm{CDCl_3}$, TMS): δ −5.78 ppm. LRMS (EI, 70 eV): 210($\mathrm{M^+}$), 195 ($\mathrm{M^+} - 15$), 179 ($\mathrm{M^+} - 31$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{11}H_{15}ClSi}$, 210.0632; found, 210.0675.

(E)-Trimethyl[2-(4-chlorophenyl)ethenyl]silane ***3f***[18]

^{13}C-NMR ($\mathrm{CDCl_3}$) δ 142.2 (vinyl carbon bearing aromatic ring), 136.9 (aromatic carbon bearing chlorine atom), 133.5 (quart. aromatic carbon bearing vinyl group), 130.5 ($^{1}J_{\mathrm{SiC}} = 65.1$ Hz, vinyl carbon bearing silicon), 128.7 (aromatic carbon *meta* to vinyl group), 127.6 (aromatic carbon *ortho* to vinyl group), −1.3 ($^{1}J_{\mathrm{SiC}} = 53.0$ Hz, methyl carbon of $\mathrm{SiMe_3}$) ppm. ^{29}Si-NMR ($\mathrm{CDCl_3}$, TMS): δ −6.10 ppm.

(E)-Trimethyl[2-(3-trifluoromethylphenyl) ethenyl]silane ***3g***

IR (neat): 3040, 2950, 2900, 1610, 1325, 1245, 1160, 1120, 1075, 980, 870, 860, 840, 780 cm^{-1}. ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.68 (s, 1H), 7.59 (d, 1H, $J = 7.8$ Hz), 7.49 (d, 1H, $J = 7.8$ Hz), 7.43 (t, 1H, $J = 7.8$ Hz), 6.89 (d, 1H, $J = 19.0$ Hz), 6.57 (d, 1H, $J = 19.0$ Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 142.0 (vinyl carbon bearing aromatic ring), 139.1 (quart. aromatic carbon bearing vinyl group), 132.1 ($^{1}J_{\mathrm{SiC}} = 63.3$ Hz, vinyl carbon bearing silicon), 130.9 ($^{2}J_{\mathrm{FC}} = 32.3$ Hz, aromatic carbon bearing $\mathrm{CF_3}$ group), 129.5 (aromatic carbon *ortho* to vinyl and *para* to $\mathrm{CF_3}$ group), 128.9 (aromatic carbon *meta* to $\mathrm{CF_3}$ and to vinyl group), 124.4 (q, $^{3}J_{\mathrm{FC}} = 3.6$ Hz, aromatic carbon *ortho* to $\mathrm{CF_3}$ and *para* to vinyl group), 124.2 (q, $^{1}J_{\mathrm{FC}} = 272.4$ Hz, carbon of $\mathrm{CF_3}$ group), 123.0 (q, $^{3}J_{\mathrm{FC}} = 3.9$ Hz, aromatic carbon *ortho* to $\mathrm{CF_3}$ and to vinyl group), −1.4 ($^{1}J_{\mathrm{SiC}} = 52.3$ Hz, methyl carbon of $\mathrm{SiMe_3}$) ppm. ^{29}Si-NMR ($\mathrm{CDCl_3}$, TMS): δ −5.89 ppm. LRMS (EI, 70 eV): 244 ($\mathrm{M^+}$), 229 ($\mathrm{M^+} - 15$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{12}H_{15}F_3Si}$, 244.0895; found, 244.0892.

(E)-Trimethyl[2-(4-ethoxycarbonylphenyl) ethenyl]silane ***3h***[54]

IR (neat): 3040, 2980, 2950, 2900, 1715, 1602, 1560, 1440, 1405, 1363, 1300, 1270, 1250, 1220, 1178, 1090, 1020, 985, 855, 760, 725, 695, 642 cm^{-1}. ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 166.4 (carbonyl carbon of ethoxycarbonyl group), 142.5 (vinyl carbon bearing silicon), 142.4 (quart. aromatic carbon bearing vinyl group), 133.0 ($^{1}J_{\mathrm{SiC}} = 64.5$ Hz, vinyl carbon bearing silicon), 129.8 (aromatic carbon *ortho* to ethoxycarbonyl group), 129.6 (quart. aromatic carbon bearing ethoxycarbonyl group), 126.1 (aromatic carbon *ortho* to vinyl group), 60.8 (methylene carbon of ethoxycarbonyl group), 14.3 (methyl carbon of ethoxycarbonyl group), −1.4 ($^{1}J_{\mathrm{SiC}} = 52.3$ Hz, methyl carbon of $\mathrm{SiMe_3}$) ppm. ^{29}Si-NMR ($\mathrm{CDCl_3}$, TMS): δ −5.90 ppm. LRMS (EI, 70 eV): 248 ($\mathrm{M^+}$), 233 ($\mathrm{M^+} - 15$), 203 ($\mathrm{M^+} - 31$).

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(E)-Trimethyl[2-(3-nitrophenyl)ethenyl]silane ***(E)-3i***[55]

IR (neat): 3080, 2950, 2925, 2900, 1605, 1530, 1350, 1250, 985, 865, 840, 820, 750, 725 cm^{-1}. ^{13}C-NMR (CDCl$_3$): δ 148.6 (quart. aromatic carbon bearing nitro group), 140.9 (vinyl carbon bearing aromatic ring), 140.0 (quart. aromatic carbon bearing vinyl group), 133.8 ($^1J_{\mathrm{SiC}} = 60.0$ Hz, vinyl carbon bearing silicon). 132.2 (aromatic carbon *para* to nitro group), 129.3 (aromatic carbon *meta* to nitro and to vinyl group), 122.3 (aromatic carbon *ortho* to nitro and *para* to vinyl group), 120.8 (aromatic carbon *ortho* to nitro and to vinyl group), −1.5($^1J_{\mathrm{SiC}} = 53.2$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −5.66 ppm. LRMS (EI, 70 eV): 221 (M$^+$), 206 (M$^+$ − 15), 190 (M$^+$ − 31). HRMS (EI, 70 eV): calcd for C$_{11}$H$_{15}$NO$_2$Si, 221.0872; found, 221.0863.

(E)-Trimethyl[2-(4-nitrophenyl)ethenyl]silane ***3j***[52,54–57]

^{13}C-NMR (CDCl$_3$): δ 147.1 (aromatic carbon bearing nitro group), 144.4 (quart. aromatic carbon bearing vinyl group), 141.2 (vinyl carbon bearing aromatic ring), 136.2 ($^1J_{\mathrm{SiC}} = 65.8$ Hz, vinyl carbon bearing silicon), 126.9 (aromatic carbon *ortho* to vinyl group), 123.9(aromatic carbon *ortho* to nitro group), −1.5 ($^1J_{\mathrm{SiC}} = 51.5$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −5.53 ppm. LRMS (EI, 70 eV): 221 (M$^+$), 206 (M$^+$ − 15), 190 (M$^+$ − 31).

(E)-Trimethyl[2-(4-cyanophenyl)ethenyl]silane ***3k***

IR (neat): 3065, 2950, 2900, 2850, 2220, 1600, 1245, 985, 865, 840, 795 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.61 (dt, 2H, $J = 8.4$, 1.6 Hz), 7.50 (dt, 2H, $J = 8.4$, 1.6 Hz), 6.87 (d, 1H, $J = 19.2$ Hz), 6.65 (d, 1H, $J = 19.2$ Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 142.5 (aromatic carbon bearing vinyl group), 141.6 (vinyl carbon bearing aromatic ring), 134.9 (aromatic carbon *ortho* to cyano group), 132.4 ($^1J_{\mathrm{SiC}} = 60.4$ Hz, vinyl carbon bearing silicon), 126.8 (aromatic carbon *ortho* to vinyl group) 119.0 (cyano carbon), 111.0 (aromatic carbon bearing cyano group), −1.5 ($^1J_{\mathrm{SiC}} = 53.0$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −5.65 ppm. LRMS (EI, 70 eV): 201 (M$^+$), 186 (M$^+$ − 15), 170 (M$^+$ − 31). HRMS (EI, 70 eV): calcd for C$_{11}$H$_{15}$NSi, 201.0974; found, 201.0971.

(E)-Trimethyl[2-(3,4-dimethoxyphenyl)ethenyl]silane ***3l***

IR (neat): 3075(w), 2950(s), 2850(m), 1730(m), 1638(w), 1600(m), 1580(m), 1515(s), 1460(s), 1420(m), 1395(w), 1385(w), 1330(m), 1260(s), 1240(s), 1200(w), 1160(s), 1140(s), 1078(m), 1030(s), 990(m), 900(w), 670(m), 840(m), 810(w), 770(m), 695(w) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.02 (d, $J = 2$ Hz, 1H), 6.97 (dd, $J = 8.4$ and 2.0 Hz, 1H), 6.83 (d, $J = 8.4$ Hz, 1H), 6.76 (d, $J = 18.8$ Hz, 1H), 6.26 (d, $J = 18.8$ Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 0.15 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 149.1 (aromatic carbon bearing methoxy and *meta* to vinyl group), 149.0 (aromatic carbon bearing methoxy and *para* to vinyl group), 143.2 (vinyl carbon bearing aromatic ring), 131.6 (quart. aromatic carbon bearing vinyl group), 126.9 ($^1J_{\mathrm{SiC}} = 66.2$ Hz, vinyl carbon bearing silicon), 119.7 (aromatic carbon *ortho* to vinyl and *para* to methoxy group), 110.9 (aromatic carbon bearing hydrogen and *meta* to vinyl group), 108.3 (aromatic carbon *ortho* to vinyl and to methoxy group), 55.9 (methyl carbon in methoxy on aromatic carbon at *meta* to vinyl group), 55.8 (methyl carbon in methoxy on aromatic carbon at *para* to vinyl group), −1.2 ($^1J_{\mathrm{SiC}} = 53.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −6.36 ppm. LRMS (EI, 70 eV): 236 (M$^+$), 221 (M$^+$ − 15). HRMS (EI, 70 eV): calcd for C$_{13}$H$_{20}$O$_2$Si, 236.1233; found, 236.1273.

(E)-Trimethyl[2-(3-pyridyl)ethenyl]silane ***3m***

The reaction was conducted by a method similar to the synthesis of **3a**. Workup was as follows: after stirring for 4 h, the resulting mixture was neutralized by adding aqueous sodium bicarbonate. Extraction of the organic phase with ether, stirring with aqueous KF, extraction with ether, drying with sodium sulfate and then column chromatography (benzene) gave analytically pure **3m**.

IR (neat): 3070, 3020, 2980, 2950, 1720, 1600, 1560, 1480, 1470, 1405, 1250, 1203, 1020, 985, 860, 780, 725, 703 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 8.61 (m, 1H), 8.48 (d, 1H, $J = 4.4$ Hz), 7.76 (m, 1H), 7.73 (dt, 1H, $J = 7.6$, 1.6 Hz), 6.86 (d, 1H, $J = 19.2$ Hz), 6.58 (d, 1H, $J = 19.2$ Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 148.7 (pyridyl carbon *ortho* to vinyl group and to nitrogen), 148.4 (pyridyl carbon *para* to vinyl group), 139.9 (vinyl carbon bearing aromatic ring), 133.7 (pyridyl carbon bearing vinyl group), 132.8 ($^1J_{\mathrm{SiC}} = 63.8$ Hz, vinyl carbon bearing silicon), 132.7 (pyridyl carbon *ortho* to vinyl group and *para* to nitrogen), 123.4 (pyridyl carbon *meta* to vinyl group), −1.4 ($^1J_{\mathrm{SiC}} = 53.0$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −5.89 ppm. LRMS (EI, 70 eV): 177 (M$^+$), 162 (M$^+$ − 15), 147 (M$^+$ − 30). HRMS (EI, 70 eV): calcd for C$_{10}$H$_{15}$NSi, 177.0974; found, 177.0969.

(Z)-Trimethyl[2-(2-pyridyl)ethenyl]silane ***3n***

Workup was conducted similarly to the synthesis of **3m**. Column chromatography (benzene) followed by chromatography with 5% ethyl acetate in hexane gave analytically pure **3n**. IR (neat): 3050, 3000, 2970, 2950, 2880, 1720, 1580, 1555, 1255, 1240, 1145, 1095, 995, 8445, 805, 760, 742, 655 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 8.55 (m, 1H), 7.61 (dt, 1H, $J = 7.6$, 2.0 Hz), 7.22 (d, 1H, $J = 14.4$ Hz), 7.17 (d, 1H, $J = 7.6$ Hz), 7.12 (ddd, 1H, $J = 7.6$, 4.8, 1.2 Hz), 6.05 (d, 1H, $J = 14.4$ Hz), 0.17 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$): δ 156.2 (pyridyl carbon bearing vinyl group), 148.4 (pyridyl carbon *ortho* to nitrogen and *meta* to vinyl group), 143.8 (vinyl carbon bearing aromatic ring), 138.0 ($^1J_{\mathrm{SiC}} = 64.5$ Hz, vinyl carbon bearing silicon), 136.1 (pyridyl carbon *meta* to vinyl group and *para* to nitrogen), 123.4 (pyridyl carbon *para* to vinyl group), 121.9 (pyridyl carbon *ortho* to vinyl group), 0.58 ($^1J_{\mathrm{SiC}} = 53.8$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −11.19 ppm. LRMS (EI, 70 eV): 177 (M$^+$), 176 (M$^+$ − 1), 162 (M$^+$ − 15). HRMS (EI, 70 eV): calcd for C$_{10}$H$_{15}$NSi, 177.0974; found, 177.0938.

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(E)-Trimethyl[2-(2-methoxyphenyl)ethenyl]silane 3o[54]

IR (neat): 3075(w), 2950(s), 2850(m), 1600(s), 1485(s), 1460(s), 1420(m), 1325(m), 1290(m), 1245(s), 1210(m), 1180(w), 1160(w), 1105(m), 1055(m), 1035(s), 1000(s), 885(s), 840(s), 750(s), 730(m), 695(w), 620(w) cm^{-1}. ^{13}C-NMR (CDCl$_3$): δ 156.6 (aromatic carbon-bearing methoxy group), 137.7 (vinyl carbon bearing aromatic ring), 129.9 ($^1J_{\mathrm{SiC}} = 66.1$ Hz, vinyl carbon bearing silicon), 128.9 (aromatic carbon *meta* to methoxy and *para* to vinyl group), 127.4 (quart. aromatic carbon bearing vinyl group), 126.2 (aromatic carbon *ortho* to vinyl and *meta* to methoxy group), 120.6 (aromatic carbon *meta* to vinyl and *para* to methoxy group), 110.9 (aromatic carbon *ortho* to methoxy and *meta* to vinyl group), 55.4 (methyl carbon in methoxy group), −1.1 ($^1J_{\mathrm{SiC}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −6.26 ppm. LRMS (EI, 70 eV): 206 (M$^+$).

Trimethyl(3-phenylpropa-1,2-dienyl)silane 4[36–39]

^{13}C-NMR (CDCl$_3$): δ 210.2 (middle carbon of allene moiety), 135.1 (quart. aromatic carbon bearing allenyl group), 128.6 (aromatic carbon *meta* to allenyl group), 128.5 (aromatic carbon *para* to allenyl group), 125.9 (aromatic carbon *ortho* to allenyl group), 87.9 (allenyl carbon bearing phenyl group), 87.0 ($^1J_{\mathrm{SiC}} = 59.2$ Hz, allenyl carbon bearing silicon), −0.8 ($^1J_{\mathrm{SiC}} = 53.8$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, TMS): δ −4.53 ppm.

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