Regiochemical Aspects of the Platinum Oxide Catalyzed Hydrosilylation of Alkynes

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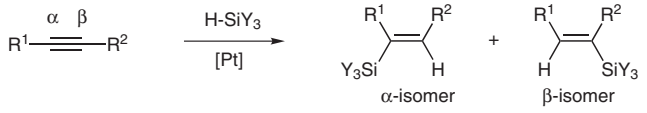
Abstract: The platinum-catalyzed hydrosilylation of unsymmetrical substituted arylalkynes with various hydrosilanes was investigated and the reaction selectivity of various *para*-substituted substrates was compared with that of their corresponding *ortho*-substituted derivatives. We showed that heterogeneous platinum oxide is a very efficient catalyst for such hydrosilylations and that H–Si bond addition proceeds in a stereoselective *cis*-fashion. The regioselectivity was found to be under the control of the *ortho*-substituent rather than due to the nature of the platinum catalyst. Arylalkynes with an *ortho*-substituent provided predominantly to exclusively α-selectivity, regardless of the electronic nature of the substituent. The precise contributions of steric, electronic, and coordinative factors controlling the regioselectivity of the H–Si bond addition are discussed.

Key words: hydrosilylation, platinum oxide, vinylsilane, alkyne

Alkenylsilanes are a class of organosilicon compounds commonly used in organic synthesis.[1] The lack of toxicity, high chemical stabilities, and low molecular weight of organosilanes make them ideal compounds for palladium-catalyzed cross-coupling reactions. Therefore, there has been a great impetus to assemble vinylsilanes in a rapid, selective, and atom-economical fashion.[2] The hydrosilylation of alkynes remains the simplest and most straightforward method for their preparation.[3] The main difficulty with this transformation concerns the control of both the stereo- and regiochemistry of the alkenylsilane products. Metal-mediated H–Si bond addition to alkynes is commonly employed for this purpose and it is well known to occur in a stereoselective manner.[4] A large number of transition metals have been used (e.g., Pd, Pt, Rh, Ru, etc.). Of these, platinum catalysts, which tolerated a wide range of functional substituents, hold certain supremacy and they are now routinely used for the *cis*-hydrosilylation of alkynes. Two regioisomers, α and β, can be formed (Scheme 1) and their ratio changes depending on the platinum catalyst, the alkyne, and the silane employed.



Scheme 1

With terminal alkynes (R^2 = H), industrial catalysts such as Speier's catalyst (H_2PtCl_6) and Karstedt's catalyst [Pt_2(dvtms)$_3$; dvtms = divinyltetramethyldisiloxane] have the advantages of excellent turnover numbers, however, the selectivity observed when using these catalysts is usually low.[5] The platinum–phosphine complexes [$PtCl_2(PPh_3)_2$] and [$Pt(PPh_3)_4$] also catalyze hydrosilylation but the reactivity decreases in the order H_2PtCl_6 > $PtCl_2(PPh_3)_2$ > $Pt(PPh_3)_4$. Platinum complexes with bulky phosphine ligands (e.g., [$Pt(PCy_3)$], [$Pt(P$*t*-$Bu_3)$]) show improved β-regioselectivity.[6] Recently, the use of N-heterocyclic carbene platinum(0) complexes has produced good β-selectivity allowing the synthesis of *E*-vinyldisiloxanes.[7] Excellent yields and β-selectivity can also be achieved by using ligand-free platinum catalysts (Pt/C, Pt/silica gel)[8,9] providing a significant cost advantages over homogeneous and elaborate platinum complexes. If solutions to the problems associated with the hydrosilylation of terminal alkynes mediated by platinum catalysts are satisfactory in favor of the β-isomers, the reaction with unsymmetrical internal alkynes, particularly those with one or two aromatic rings, has received scant attention,[8] probably because of the difficulty in controlling the regioselectivity of the H–Si bond addition. Therefore, the search for new selective procedures and more selective catalysts presents an interesting challenge.

It is well known that the regioselectivity of metalloid hydride addition to alkynes is governed by electronic and steric factors as well as chelating considerations.[3] Previously, we described the palladium-catalyzed hydrostannation of aryl-substituted alkynes.[10] We demonstrated that *ortho* substituents on one side of the two aromatic rings directed the regioselectivity of H-Sn bond addition whatever the electronic nature of the substituent. It occurred to us that this unprecedented *ortho*-directing effect could be extended to control the regiochemistry of the platinum-catalyzed hydrosilylation of internal aryl-substituted alkynes. Herein, we wish to detail our results[11] towards the platinum oxide catalyzed hydrosilylation of internal 1-arylalk-1-ynes as well as diarylacetylenes to provide trisubstituted vinylsilanes of defined stereochemistry. The selectivity issues of this reaction mediated by platinum oxide have been studied extensively and contributions of steric, electronic, and coordinative factors controlling this regioselectivity are discussed.

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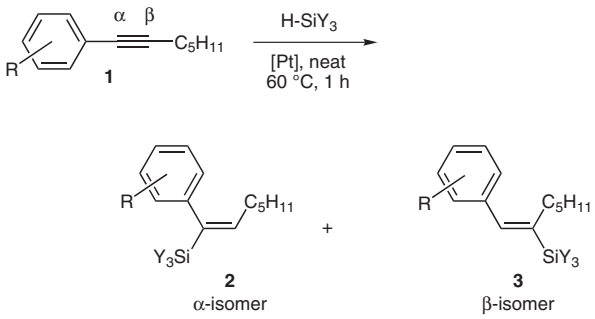
Hydrosilylation of 1-Arylalk-1-ynes

In our initial screening experiments, ethyl 4-hept-1-ynylbenzoate (**1a**) (Scheme 2) was used as a model substrate to evaluate the effects of various platinum catalysts and the results are summarized in Table 1. The addition of triethylsilane (1.5 equiv) to **1a** was examined in the presence of platinum complexes (5 mol%) at 60 °C without solvent. With the exception of tetrakis(triphenylphosphine)platinum(0) (entry 1), all the ligand-free platinum catalysts examined were found to be active in the *cis*-hydrosilylation of **1a**, providing α- and β-isomers with markedly similar selectivity and efficiency (entries 2–5). The triple bond polarization induced by a *para* π-electron-withdrawing group resulted mainly in α-selectivity as observed in the hydrostannation reaction.[10a] Performing the reaction in tetrahydrofuran had no significant change on the α-regioselectivity (α/β 82:18), but the yield of the reaction decreased significantly (65% cf. 92%, entry 5). Hydrosilylation of ethyl 2-hept-1-ynylbenzoate (**1b**) was next investigated to determine the impact of the *ortho* substituent on the regioselectivity. We were pleased to find that the reaction also occurred in a *syn*-fashion affording exclusively a single α-isomer (entries 7–10) still demonstrating the *ortho*-directing effect concept. In contrast to platinum oxide or platinum(II) chloride, the use of hexachloroplatinic acid or platinum on carbon catalysts (entries 7 and 8), however, furnished a notable amount of the reduced side product, which was formed from a competing platinum-catalyst-catalyzed direct semi-reduction of the alkyne bond.[12] Consequently, reaction in the presence of this heterogeneous catalyst proved to be high yielding (cf. entries 9 and 10). In addition, platinum oxide, which is less expensive than platinum(II) chloride, is easily removed from the reaction medium by simple filtration. Therefore, it was used as a catalyst of choice in the continuation of this study.



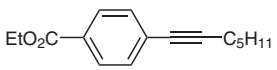
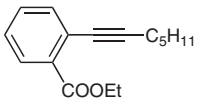
Scheme 2

To compare the catalytic activities of platinum oxide and platinum(II) chloride versus the metal-catalyzed hydrosilylation reaction, we tested a series of other catalysts, including $Pd_2(dba)_3$, Pd/C, $NiCl_2(PPh_3)_2$, $RhCl(PPh_3)_3$, Grubbs' I, and $RuHCl(CO)(PPh_3)_3$. With the exception of palladium on carbon, which gave a mixture of compounds resulting from the reduction of the triple bond, the use of other catalysts did not promote any transformation.

As the nature of the hydrosilane can impact the reaction selectivity,[8] we next examined the hydrosilylation of alkynes **1a**,**b** with a series of hydrosilanes. The results are summarized in Table 2.

Reactions of **1a** and **1b** carried out with silanes gave similar yields ranging from 82% [$(EtO)Me_2SiH$] to 96% ($PhMe_2SiH$) and 70% [$(EtO)_3SiH$] to 94% ($EtOMe_2SiH$), respectively. Moreover, all the hydrosilanes examined with **1a** showed comparable α-selectivity (entries 1–5). With alkyne **1b**, the *ortho*-substituent regiocontrol effect again provided significant α-isomer preference except in the case of $(EtO)_3SiH$ (entry 9). The most efficient silane is triethylsilane, leading to exclusive formation of the α-isomer. In contrast with the literature,[8] significantly it seems that the distribution of α/β-adducts in the platinum

Table 1 Hydrosilylation with Triethylsilane (Y = Et) of Substituted 1-Arylhept-1-ynes **1a**,**b** Using Various Platinum Catalysts

Entry	Alkyne	Platinum catalyst	Ratio[a] **2/3** (α/β)	Yield[b] (%)
1		$Pt(PPh_3)_4$	–	0
2		H_2PtCl_6	84:16	87[c]
3		Pt/C	80:20	91[c]
4	**1a**	$PtCl_2$	83:17	88[c]
5		PtO_2	83:17	92[c]
6		$Pt(PPh_3)_4$	–	0
7		H_2PtCl_6	100:0[d]	70[e]
8		Pt/C	100:0[d]	nd[f]
9		$PtCl_2$	100:0	72
10	**1b**	PtO_2	100:0	90

[a] The product distribution was determined by ^1H NMR on the crude reaction mixture.
[b] Isolated yield.
[c] Isolated yield of an inseparable mixture of α- and β-isomers.
[d] Contaminated with the corresponding alkene resulting from semi-reduction of the alkyne **1b**.
[e] Isolated yield of pure **2b** after flash column chromatography.
[f] Not determined.

Table 2 Platinum Oxide Catalyzed Hydrosilylation of Substituted 1-Arylhept-1-ynes **1a**,**b** Using Various Silanes

Entry	Alkyne	Hydrosilane H-SiY_3	Ratio[a] **2/3** (α/β)	Yield[b] (%)
1	**1a**	Et_3SiH	83:17	92
2		$PhMe_2SiH$	80:20	96
3		Ph_2MeSiH	77:23	88
4		$(EtO)_3SiH$	88:12	85
5		$(EtO)Me_2SiH$	67:33	82
6	**1b**	Et_3SiH	100:0	90[c]
7		$PhMe_2SiH$	95:5	85
8		Ph_2MeSiH	93:7	90
9		$(EtO)_3SiH$	75:25	70
10		$(EtO)Me_2SiH$	95:5	94

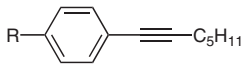
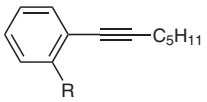
[a] The product distribution was determined by ^{1}H NMR on the crude reaction mixture.
[b] Isolated yield of an inseparable mixture of α- and β-isomers.
[c] Isolated yield of **2b**.

oxide catalyzed hydrosilylation of 1-arylalk-1-ynes does not depend on the silane employed.

Next we examined the hydrosilylation of various *para*-substituted 1-arylhept-1-ynes **1a**,**d–l** as well as their corresponding *ortho*-substituted derivatives **1b**,**m–u** and the selectivity issues were compared (Table 3).

In order to establish a baseline regioselectivity control, the reaction was first examined with the nonsubstituted alkyne **1c** and the H–Si bond addition occurred leading to a mixture of vinylsilanes **2c** and **3c** in a 65:35 ratio (entry 1). This trend in α-selectivity is more marked with *para*-substituted 1-arylhept-1-ynes bearing a π-electron-withdrawing group, which induces strong polarization of the C≡C bond (entries 2–6). Accordingly, less α-regioselectivity was observed when switching to substrates **1h–l** with a *para* σ-electron-donating group (entries 7–11). The results in Table 3 exhibit how changing the position of the substituent on the aromatic ring (from *para* to *ortho*) can affect the product distribution. Total α-regioselectivity is achieved with π-electron-withdrawing *ortho*-substituted 1-arylhept-1-ynes **1b**,**m–p**, producing the vinylsilanes **2b**,**m–p** and no observable β-isomers **3** (entries 12–16). Similarly, we were pleased to observe high to exclusive regioselectivity toward the formation of α-isomers **2q–u** from *ortho*-substituted 1-arylhept-1-ynes **1q–u** bearing an electron-donating group (entries 17–21). These results unambiguously demonstrate the *ortho*-substituent regiocontrol concept in the platinum oxide mediated hydrosilylation of 1-arylalk-1-ynes as was previously observed in the palladium-catalyzed hydrostannation reaction.[10]

Table 3 Hydrosilylation with Triethylsilane (Y = Et) of Various Substituted 1-Arylhept-1-ynes **1** Using Platinum Oxide Catalyst

Entry			Ratio[a] **2/3** (α/β)	Yield[b] (%)
	1	R		
1	**c**	H	65:35	71
2	**d**	NO_2	97:3	83
3	**e**	CHO	85:15	62
4	**f**	CF_3	84:16	95
5	**a**	CO_2Et	83:17	92
6	**g**	Br	82:18	90
7	**h**	Me	65:35	82
8	**i**	*i*-Pr	73:27	68
9	**j**	CH_2OAc	77:23	90
10	**k**	OMe	70:30	80
11	**l**	OAc	78:22	82
				
12	**m**	NO_2	100:0	90
13	**n**	CHO	100:0	71
14	**o**	CF_3	100:0	71
15	**b**	CO_2Et	100:0	90
16	**p**	Br	95:5	89
17	**q**	Me	85:15	63
18	**r**	*i*-Pr	81:19	83
19	**s**	CH_2OAc	100:0	74
20	**t**	OMe	91:9	92
21	**u**	OAc	95:5	76

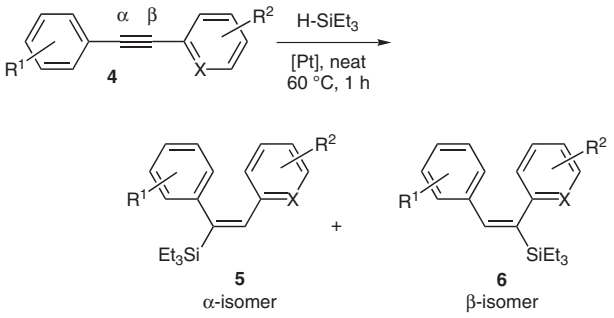
[a] The product distribution was determined by ^{1}H NMR on the crude reaction mixture.
[b] Isolated yields of the mixture of vinylsilanes after column chromatography.

Hydrosilylation of Diarylacetylenes

Having established the *ortho*-directing effect in the platinum oxide mediated hydrosilylation of 1-arylalk-1-ynes, we next examined the reaction in the cases of diarylacetylenes **4** that constitute a real challenge. To our best knowledge, the reaction with these substrates is not known, probably because of the difficulty in controlling the regioselectivity.

As can be seen in Table 4 (Scheme 3), the reaction proceeded with excellent regiocontrol and the corresponding vinylsilanes **5** were isolated with a high to exclusive α-selectivity. Diarylacetylenes with a *para* electron-donating group **4e**,**f** yielded an almost 1:1 mixture of the two regio-

isomeric adducts **5e**,**f** and **6e**,**f** (entries 5 and 6), whereas those with a *para* electron-withdrawing group **4a–d** favored predominant formation of α-vinylsilanes **5a–d** due to the polarization of the C≡C bond (entries 1–4). *ortho*-Substituted alkynes displayed much higher α-selectivity. With substrates **4k**,**l** bearing an electron-donating group the α-selectivity increased from ~1:1 to ~9:1 (entries 11, 12). More interestingly, as expected total α-regioselectivity was observed with substrates **4g–j** bearing an electron-withdrawing group (entries 7–10).



m: R^1 = 4-CN, R^2 = H, X = N 70%, α/β = 87:13

n: R^1 = 2-CN, R^2 = H, X = N 69%, α/β = 100:0

Scheme 3

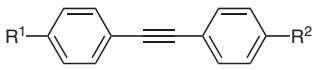
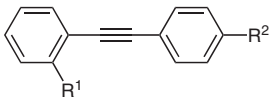
The efficiency of this platinum oxide-catalyzed hydrosilylation was investigated with *ortho*- and *para*-substituted substrates **4m**,**n** containing a pyridyl moiety. It should be noted that the presence of this heteroaromatic ring does not affect the hydrosilylation reaction and gives mainly α-adducts with a high levels of regiocontrol (cf. **4d** and **4m**). As shown in Scheme 3, again the presence of an *ortho*-substituent (e.g., CN) on one aromatic ring induced the exclusive formation of a single α-isomer **5n**.

Hydrosilylation of Terminal Alkynes

Although the platinum-on-carbon and hexachloroplatinic acid catalyzed hydrosilylation of terminal alkynes is well known, no results using platinum oxide have been described. To test its ability to catalyze the hydrosilylation of terminal alkynes, we next examined the reaction with terminal aryl- and alkyl-substituted alkynes (Tables 5 and 6).

Initial studies were carried out with terminal arylacetylenes **7** (Scheme 4, Table 5) and reactions proceed with high chemical yields. As baseline control, similar isomeric product distribution ratios were obtained for hydrosilylation of phenylacetylene with triethylsilane in the presence of platinum oxide, platinum-on-carbon, or Karstedt's catalysts.[8] The effect of aromatic ring substituents on the regioselectivity was examined for four representative systems **7b–e**. In these cases it was noted that where steric effects are dominant, β-selectivity occurred,

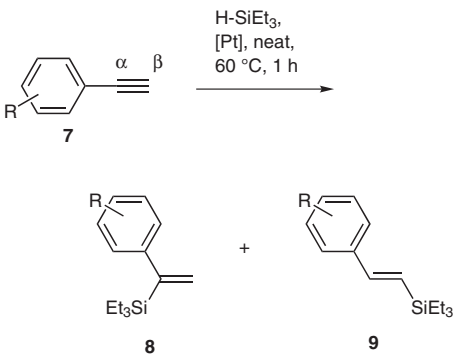
Table 4 Hydrosilylation with Triethylsilane of Various Substituted Diarylacetylenes **4** Using Platinum Oxide Catalyst

Entry				Ratio[a] **5/6** (α/β)	Yield[b] (%)
	4	R^1	R^2		
1	**a**	NO_2	H	80:20	80
2	**b**	CO_2Et	H	74:26	82
3	**c**	CO_2Et	OMe	77:23	95
4	**d**	CN	H	72:28	65
5	**e**	OMe	H	42:58	70
6	**f**	CH_2OAc	H	46:54	67
					
7	**g**	NO_2	H	100:0	92
8	**h**	CO_2Et	H	100:0	72
9	**i**	CO_2Et	OMe	100:0	74
10	**j**	CN	H	100:0	80
11	**k**	OMe	H	80:20	64
12	**l**	CH_2OAc	H	92:8	68

[a] The product distribution was determined by ^{1}H NMR on the crude reaction mixture.

[b] Isolated yield of the mixture of vinylsilanes after column chromatography; α- and β-isomers were unambiguously identified by NOE NMR spectroscopy except in entries 5 and 6; interchangeable ratio.

even with the arylacetylene **7b** bearing a 4-methoxycarbonyl group (entry 2). Switching the ester group to the *ortho*-position (entry 4) resulted in a ~1:1 mixture of the two regioisomeric adducts **8d** and **9d**. This result clearly shows that the *ortho*-directing effect, which is opposed to steric effects, rebalances the isomeric distribution, thus increasing the amount of α-products.



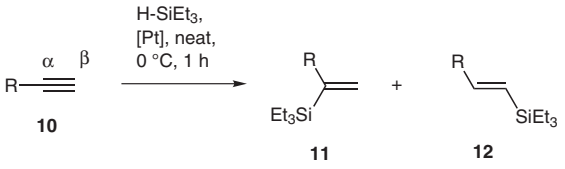
Scheme 4

Table 5 Hydrosilylation with Triethylsilane of Various Arylacetylenes **7** Using Platinum Oxide Catalyst

Entry	Arylacetylene **7**	R	Ratio[a] **8/9** (α/β)	Yield[b] (%)
1	**a**	H	15:85	86
2	**b**	4-CO_2Me	24:76	98
3	**c**	4-OMe	18:82	96
4	**d**	2-CO_2Me	52:48	84
5	**e**	2-OMe	38:62	97

[a] The product distribution was determined by ^{1}H NMR on the crude reaction mixture.
[b] Isolated yield of the mixture of vinylsilanes after column chromatography.

While the platinum oxide proved also to be an efficient catalyst for the hydrosilylation of terminal alk-1-ynes **10**, the difference in the reactions conditions is significant. Reaction with alkynes **7** required heating at 60 °C, whereas with alk-1-ynes **10**, 0 °C[13] was found to be the optimal reaction temperature (Scheme 5, Table 6). Under these conditions, as with arylacetylenes **7**, the hydrosilylation of alk-1-ynes **10** was not selective producing mainly β-isomers **12** even when coordinating oxygen atoms are at the secondary propargylic position. In these cases, the ester functionality impacts the regiochemistry of platinum oxide mediated hydrosilylation differently compared to the methyl ether group (cf. entries 2 and 3). In contrast, with the less bulky primary propargyl acetate **10d** (entry 4) the regiochemical preference is reversed, demonstrating the α-directing effect of the carbonyl-containing acetate.



Scheme 5

Table 6 Hydrosilylation with Triethylsilane of Various Terminal Alkynes **10** Using Platinum Oxide Catalyst

Entry	Alk-1-yne **10**		Ratio[a] **11/12** (α/β)	Yield[b] (%)
1	**a**	C_5H_{11}	10:90	98
2	**b**	CH(OMe)Me	12:88	78
3	**c**	CH(OAc)Me	29:71	60
4	**d**	CH_2OAc	82:18	90

[a] The product distribution was determined by ^{1}H NMR on the crude reaction mixture.
[b] Isolated yield of the mixture of vinylsilanes after column chromatography.

In summary, we have demonstrated that heterogeneous platinum oxide is a competent catalyst for the hydrosilylation of internal unsymmetrical arylalkynes as well as terminal alkynes. The H–Si bond addition to substituted 1-arylalk-1-ynes and diarylacetylenes occurred at the α-position leading preferentially to the α-silylated products when an *ortho*-substituent was present on the aryl group regardless of whether the *ortho*-substituent was an electron-donating or electron-withdrawing group. In comparison, *para*-substituents showed a weaker α-silylation directing effect. With terminal alkynes, the regioselectivity of the platinum-catalyzed hydrosilylation was found to be governed by both steric and electronic factors, affording mainly β-isomers.

IR spectra were recorded on a Perkin-Elmer 841 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker AC 200 and Bruker Avance 300. ^{1}H NMR chemical shifts are referenced to residual $CHCl_3$ (δ = 7.27). ^{13}C chemical shifts are referenced to the central peak of $CDCl_3$ (δ = 77.1). Elemental analyses were performed with a Perkin-Elmer 240 analyzer. Analytical TLC were performed on Merck precoated silica gel 60F plates. Merck silica gel 60 (230–400 mesh) was used for column chromatography. All solvents used in reactions were dried and purified according to standard procedures. Alkynes were prepared by Sonogashira couplings[14] of the corresponding halides and terminal alkynes under standard conditions.

1-Hept-1-ynyl-4-(trifluoromethyl)benzene (1f)
Yield: 83%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 3 H), 1.30–1.70 (m, 6 H), 2.45 (t, *J* = 7.0 Hz, 2 H), 7.50 (d, *J* = 8.3 Hz, 2 H), 7.55 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 19.4, 22.2, 28.6, 31.1, 79.5, 93.4, 124.0 (q, *J* = 272 Hz), 125.1 (2), 128.0, 129.2 (q, *J* = 33.7 Hz), 131.7 (2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –63.1.

Anal. Calcd for $C_{14}H_{15}F_3$: C, 69.99; H, 6.29. Found: C, 69.85; H, 6.20.

1-Hept-1-ynyl-2-(trifluoromethyl)benzene (1o)
Yield: 80%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3 H), 1.30–1.70 (m, 6 H), 2.45 (t, *J* = 7.0 Hz, 2 H), 7.30 (t, *J* = 7.7 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 1 H), 7.55 (d, *J* = 7.7 Hz, 1 H), 7.65 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 19.5, 22.2, 28.1, 30.9, 76.7, 96.8, 118.2, 125.7 (q, *J* = 5.1 Hz), 127.1, 127.2 (q, *J* = 273.2 Hz), 131.2, 131.4 (q, *J* = 29.8 Hz), 133.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –62.9.

Anal. Calcd for $C_{14}H_{15}F_3$: C, 69.99; H, 6.29. Found: C, 69.79; H, 6.15.

4-(Pyridin-2-ylethynyl)benzonitrile (4m)
Yield: 67%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (m, 1 H), 7.60 (d, *J* = 7.8 Hz, 1 H), 7.65–7.80 (m, 5 H), 8.70 (d, *J* = 4.8 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 87.0, 92.4, 112.3, 118.3, 123.5, 127.1, 127.5, 132.1 (2), 132.5 (2), 136.4, 142.5, 150.3.

Anal. Calcd for $C_{14}H_8N_2$: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.26; H, 3.74; N, 13.59.

Hydrosilylation of Alkynes; General Procedure

In a 20-mL flask, PtO_2 (11.35 mg, 0.05 mmol) and alkyne (1 mmol) were placed under N_2. Et_3SiH (0.24 mL, 1.5 mmol) was introduced via syringe and the mixture was stirred at 60 °C in an oil bath for 1 h. The residue was then purified by column chromatography (silica gel) to yield the title adducts either as a single α-isomer or as a mixture of inseparable α- and β-isomers.

Ethyl (*E*)-4-[1-(Triethylsilyl)hept-1-enyl]benzoate (2a)

Yield: 92%; ratio α/β ca. 83:17.

IR (neat): 2954, 2930, 2874, 1718, 1606, 1503, 1415, 1306, 1269, 1174, 1100, 1020, 973, 773, 731, 707 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2a**: δ = 0.40–0.60 (m, 6 H), 0.75–1.10 (m, 12 H), 1.10–1.35 (m, 6 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 1.85 (q, *J* = 7 Hz, 2 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 5.90 (t, *J* = 7.0 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3a**: δ = 2.15–2.35 (m, 2 H), 6.70 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2a**: δ = 2.7 (2), 3.1, 7.1 (2), 7.3, 13.8, 14.2, 22.3, 29.4, 30.9, 31.2, 60.5, 127.4, 127.5 (2), 129.2 (2), 140.7, 143.4, 148.5, 166.5.

Anal. Calcd for $C_{22}H_{36}O_2Si$ (360.61): C, 73.28; H, 10.06. Found: C, 73.10; H, 10.29.

Ethyl (*E*)-2-[1-(Triethylsilyl)hept-1-enyl]benzoate (2b)

Yield: 90%.

IR (neat): 3062, 2953, 2932, 2874, 1726, 1596, 1567, 1460, 1441, 1416, 1366, 1286, 1267, 1243, 1172, 1162, 1124, 1044, 760, 711, 685 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.40–0.60 (m, 6 H), 0.75–0.60 (m, 12 H), 1.10–1.35 (m, 6 H), 1.20 (t, *J* = 7.1 Hz, 3 H), 1.75 (q, *J* = 7.3 Hz, 2 H), 4.00–4.30 (m, 2 H), 5.80 (t, *J* = 6.8 Hz, 1 H), 6.80 (d, *J* = 7.6 Hz, 1 H), 7.10 (t, *J* = 7.6 Hz, 1 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 7.75 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 3.2 (3), 7.2 (3), 13.8, 14.2, 22.3, 28.7, 30.3, 31.4, 60.3, 125.1, 129.1, 129.6, 129.9, 130.9, 140.5, 141.4, 144.3, 167.4.

Anal. Calcd for $C_{22}H_{36}O_2Si$ (360.61): C, 73.28; H, 10.06. Found: C, 73.12; H, 10.25.

(*E*)-Triethyl(1-phenylhept-1-enyl)silane (2c)

Yield: 71%; ratio α/β ca. 65:35.

IR (neat): 2954, 2931, 2874, 1595, 1490, 1459, 1377, 1237, 1007, 718, 701 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2c**: δ = 0.60–0.80 (q, *J* = 7.8 Hz, 6 H), 1.00–1.80 (m, 18 H), 2.10 (q, *J* = 7.1 Hz, 2 H), 6.10 (t, *J* = 7.0 Hz, 1 H), 7.15 (d, *J* = 8.3 Hz, 2 H), 7.25–7.60 (m, 3 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3c**: δ = 2.45–2.60 (m, 2 H), 6.90 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): mixture α/β: δ = 2.8, 3.3, 7.2, 7.4, 13.9, 22.3, 22.4, 29.2, 29.5, 29.8, 30.8, 31.3, 32.2, 125.0, 126.3, 127.6 (2), 127.8, 128.0, 128.5, 138.6, 138.9 (β),141.1, 142.4, 143.1.

Anal. Calcd for $C_{19}H_{32}Si$ (288.54): C, 79.09; H, 11.18. Found: C, 78.90; H, 11.23.

(*E*)-Triethyl[1-(4-nitrophenyl)hept-1-enyl]silane (2d)

Yield: 83%; ratio α/β ca. 97:3.

IR (neat): 2954, 2931, 2874, 1592, 1517, 1489, 1459, 1416, 1378, 1342, 1281, 1107, 1006, 974, 914, 856, 758, 732, 719, 701 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2d**: δ = 0.40–0.60 (m, 6 H), 0.95–1.20 (m, 12 H), 1.25–1.65 (m, 6 H), 2.05 (q, *J* = 6.9 Hz, 2 H), 6.20 (t, *J* = 7.1 Hz, 1 H), 7.25 (d, *J* = 8.8 Hz, 2 H), 8.35 (d, *J* = 8.8 Hz, 2 H).

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3d**: δ = 2.15–2.35 (m, 2 H).6.90 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2d**: δ = 2.7 (3), 7.0 (3), 13.8, 22.3, 28.9, 30.1, 31.2, 123.3 (2), 128.3 (2), 140.0, 144.2, 145.8, 151.1.

Anal. Calcd for $C_{19}H_{31}NO_2Si$ (333.54): C, 68.42; H, 9.37; N, 4.20. Found: C, 68.23; H, 9.62; N, 4.23.

(*E*)-4-[1-(Triethylsilyl)hept-1-enyl]benzaldehyde (2e)

Yield: 62%; ratio α/β ca. 85:15.

IR (neat): 2953, 2931, 2874, 2727, 1703, 1600, 1563, 1459, 1415, 1302, 1237, 1208, 1164, 1103, 1005, 974, 912, 842, 820, 710 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2e**: δ = 0.40–0.60 (m, 6 H), 0.75–1.10 (m, 12 H), 1.20–1.55 (m, 6 H), 2.05 (q, *J* = 7.0 Hz, 2 H), 6.10 (t, *J* = 7.0 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 8.0 Hz, 2 H),10.1 (s, 1 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3e**: δ = 2.30–2.40 (m, 2 H), 6.90 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2e**: δ = 2.8 (2), 3.1, 7.1 (2), 7.3, 13.8, 22.2, 28.9, 30.0, 31.2, 128.2 (2), 129.5 (2), 133.8, 140.6, 143.6, 150.7, 191.8.

Anal. Calcd for $C_{20}H_{32}OSi$ (316.56): C, 75.88; H, 10.19. Found: C, 75.75; H, 10.12.

(*E*)-Triethyl{1-[4-(trifluoromethyl)phenyl]hept-1-enyl}silane (2f)

Yield: 95%; ratio α/β ca. 84:16.

IR (neat): 2955, 2876, 1614, 1459, 1404, 1322, 1237, 1163, 1124, 1105, 1067, 1018, 913, 835, 713 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2f**: δ = 0.55–0.65 (q, *J* = 6.6 Hz, 6 H), 0.80–1.00 (m, 12 H), 1.10–1.40 (m, 6 H), 1.90 (q, *J* = 7.2 Hz, 2 H), 6.00 (t, *J* = 7.2 Hz, 1 H), 7.05 (d, *J* = 7.9 Hz, 2 H), 7.55 (d, *J* = 7.9 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3f**: δ = 2.25–2.35 (m, 2 H), 6.75 (s, 1 H), 7.35 (d, *J* = 7.6 Hz, 2 H), 7.50 (d, *J* = 7.6 Hz, 2 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2f**: δ = 2.8 (3), 7.2 (3), 14.0, 22.4, 29.1, 30.0, 31.3, 122.7 (2), 124.5 (q, *J* = 271.6 Hz), 127.9 (2), 140.2, 144.0, 147.3 (C-CF_3 not seen).

^{19}F NMR (188 MHz, $CDCl_3$): major α-isomer **2f**: δ = –62.6.

^{19}F NMR (188 MHz, $CDCl_3$): minor β-isomer **3f**: δ = –62.8.

Anal. Calcd for $C_{20}H_{31}F_3Si$ (356.21): C, 67.37; H, 8.76. Found: C, 67.14; H, 8.55.

(*E*)-[1-(4-Bromophenyl)hept-1-enyl]triethylsilane (2g)

Yield: 90%; ratio α/β ca. 82:18.

IR (neat): 2953, 2932, 2874, 1712, 1586, 1483, 1458, 1415, 1378, 1236, 1181, 1071, 1009, 973, 910, 818, 714 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2g**: δ = 0.55–0.65 (q, *J* = 6.8 Hz, 6 H), 0.85–1.15 (m, 12 H), 1.00–1.30 (m, 6 H), 1.75 (q,

J = 7.2 Hz, 2 H), 5.80 (t, *J* = 7.1 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **3g**: δ = 0.55 (q, *J* = 7.6 Hz, 6 H), 2.00–2.20 (m, 2 H), 6.45 (s, 1 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2g**: δ = 2.8 (3), 7.1 (3), 13.8, 22.4, 29.1, 29.9, 31.3, 118.9, 129.3 (2), 131.0 (2), 137.5, 141.5, 143.7.

Anal. Calcd for $C_{19}H_{31}BrSi$ (366.14): C, 62.11; H, 8.50. Found: C, 62.04; H, 8.48.

(*E*)-Triethyl[1-(4-tolyl)hept-1-enyl]silane (2h)
Yield: 82%; ratio α/β ca. 65:35.

IR (neat): 2953, 2930, 2874, 1701, 1606, 1508, 1458, 1416, 1378, 1237, 1180, 1108, 1006, 973, 910, 810, 717 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **2h**: δ = 0.60–0.80 (q, *J* = 7.9 Hz, 6 H), 1.00–1.20 (m, 12 H), 1.30–1.50 (m, 6 H), 2.10 (q, *J* = 7.1 Hz, 2 H), 2.50 (s, 3 H), 6.30 (t, *J* = 7.0 Hz, 1 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **3h**: δ = 2.50 (s, 3 H), 6.85 (s, 1 H), 7.30 (m, 4 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2h**: δ = 2.8 (3), 7.2 (3), 13.9, 21.0, 22.4, 29.2, 29.8, 31.3, 127.5 (2), 128.5 (2), 134.2, 139.9, 140.9, 143.1.

Anal. Calcd for $C_{20}H_{34}Si$ (302.24): C, 79.39; H, 11.33. Found: C, 79.26; H, 11.20.

(*E*)-Triethyl[1-(4-isopropylphenyl)hept-1-enyl]silane (2i)
Yield: 68%; ratio α/β ca. 73:27.

IR (neat): 2955, 2930, 2874, 1707, 1603, 1507, 1459, 1415, 1379, 1237, 1099, 1054, 1006, 972, 912, 827, 717, 699, 675 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **2i**: δ = 0.60–0.80 (m, 6 H), 0.90–1.10 (m, 12 H), 1.00–1.50 (m, 12 H), 1.95–2.05 (q, *J* = 7.0 Hz, 2 H), 2.85–3.05 (m, 1 H), 6.00 (t, *J* = 7.0 Hz, 1 H), 6.95 (d, *J* = 8.5 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **3i**: δ = 2.40–2.50 (m, 2 H), 6.75 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2i**: δ = 2.8 (3), 7.2 (3), 13.8, 23.9, 26.8, 29.2, 29.8, 31.3, 33.5, 125.7 (2), 127.4 (2), 138.7, 140.1, 140.9, 143.0, 145.2.

Anal. Calcd for $C_{22}H_{38}Si$ (330.63): C, 79.92; H, 11.58. Found: C, 79.55; H, 11.62.

(*E*)-4-[1-(Triethylsilyl)hept-1-enyl]benzyl Acetate (2j)
Yield: 90%; ratio α/β ca. 77:23.

IR (neat): 2953, 2931, 2874, 1742, 1603, 1508, 1459, 1416, 1378, 1361, 1224, 1179, 1109, 1018, 965, 912, 820, 716, 675 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **2j**: δ = 0.40–0.60 (m, 6 H), 0.75–1.10 (m, 12 H), 1.35–1.85 (m, 6 H), 2.20 (q, *J* = 7.0 Hz, 2 H), 2.45 (s, 3 H), 5.40 (s, 2 H), 6.25 (t, *J* = 7.0 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 8.0 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **3j**: δ = 2.45 (s, 3 H), 2.50–2.65 (m, 2 H), 7.00 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2j**: δ = 2.7 (2), 3.2, 7.1 (2), 7.3, 13.8, 20.9, 22.3, 29.1, 29.8, 31.3, 66.2, 127.8 (2), 128.0 (2), 133.9, 140.6, 143.1, 143.4, 170.7.

Anal. Calcd for $C_{22}H_{36}O_2Si$ (360.61): C, 73.28; H, 10.06. Found: C, 73.21; H, 10.15.

(*E*)-Triethyl[1-(4-methoxyphenyl)hept-1-enyl]silane (2k)
Yield: 80%; ratio α/β ca. 70:30.

IR (neat): 2952, 2873, 1606, 1506, 1463, 1416, 1377, 1282, 1242, 1174, 1104, 1039, 1006, 902, 826, 716 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **2k**: δ = 0.70–0.90 (m, 6 H), 0.95–1.20 (m, 12 H), 1.20–1.60 (m, 6 H), 2.05 (q, *J* = 7.1 Hz, 2 H), 3.90 (s, 3 H), 6.05 (t, *J* = 7.1 Hz, 1 H), 6.95 (d, *J* = 8.5 Hz, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **3k**: δ = 2.45–2.55 (m, 2 H), 3.95 (s, 3 H), 6.80 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2k**: δ = 2.9 (3), 7.3 (3), 14.0, 22.4, 29.1, 30.0, 31.3, 55.1, 113.3 (2), 128.7 (2), 135.3, 140.4, 143.5, 157.2.

Anal. Calcd for $C_{20}H_{34}OSi$ (318.24): C, 75.40; H, 10.76. Found: C, 75.29; H, 10.65.

(*E*)-4-[1-(Triethylsilyl)hept-1-enyl]phenyl Acetate (2l)

Yield: 82%; ratio α/β ca. 78:22.

IR (neat): 2953, 2931, 2874, 1766, 1597, 1501, 1459, 1417, 1368, 1193, 1164, 1099, 1008, 916, 836, 716, 688 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **2l**: δ = 0.70–0.90 (m, 6 H), 0.95–1.20 (m, 12 H), 1.20–1.60 (m, 6 H), 2.10 (q, *J* = 7.0 Hz, 2 H), 2.60 (s, 3 H), 6.25 (t, *J* = 7.0 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **3l**: δ = 2.50–2.65 (m, 2 H), 2.60 (s, 3 H), 6.90 (s, 1 H), 7.60 (d, *J* = 8.5 Hz, 2 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2l**: δ = 2.7 (2), 3.2, 7.1 (2), 7.3, 13.8, 21.0, 22.3, 29.1, 29.8, 31.3, 120.7 (2), 128.4 (2), 140.2, 140.4, 143.7, 148.3, 169.2.

Anal. Calcd for $C_{21}H_{34}O_2Si$ (346.58): C, 72.77; H, 9.89. Found: C, 72.57; H, 10.08.

(*E*)-Triethyl[1-(2-nitrophenyl)hept-1-enyl]silane (2m)
Yield: 90%.

IR (neat): 2954, 2931, 2874, 1608, 1569, 1524, 1459, 1416, 1347, 1296, 1237, 1161, 1142, 1080, 1008, 974, 914, 868, 851, 785, 755, 705, 686 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.40–0.60 (m, 6 H), 0.60–0.95 (m, 12 H), 1.00–1.25 (m, 6 H), 1.75 (m, 2 H), 5.90 (t, *J* = 7.0 Hz, 1 H), 6.90 (dd, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 7.20 (td, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 7.40 (td, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 7.85 (dd, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 3.2 (3), 7.0 (3), 13.8, 22.3, 28.6, 30.7, 31.3, 124.1, 126.2, 130.4, 132.2, 137.3, 138.7, 143.3, 148.0.

Anal. Calcd for $C_{19}H_{31}NO_2Si$ (333.54): C, 68.42; H, 9.37; N, 4.20. Found: C, 68.40; H, 9.40; N, 4.17.

(*E*)-2-[1-(Triethylsilyl)hept-1-enyl]benzaldehyde (2n)
Yield: 71%.

IR (neat): 2955, 2932, 2875, 1780, 1693, 1595, 1465, 1415, 1379, 1285, 1266, 1239, 1196, 1180, 1095, 1006, 974, 926, 873, 825, 798, 717 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.40–0.60 (m, 6 H), 0.60–0.95 (m, 12 H), 1.00–1.35 (m, 6 H), 1.75 (q, *J* = 6.9 Hz, 2 H), 6.05 (t, *J* = 6.9 Hz, 1 H), 6.85 (d, *J* = 7.6 Hz, 1 H), 7.20 (t, *J* = 7.6 Hz, 1 H), 7.40 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.85 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 10.05 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 2.8 (3), 7.0 (3), 13.7, 22.2, 28.4, 30.5, 31.3, 126.0, 126.9, 128.9, 132.7, 133.7, 137.4, 145.4, 147.5, 192.6.

Anal. Calcd for $C_{20}H_{32}OSi$ (316.56): C, 75.88; H, 10.19. Found: C, 76.01; H, 10.30.

(*E*)-Triethyl{1-[2-(trifluoromethyl)phenyl]hept-1-enyl}silane (2o)
Yield: 71%.

IR (neat): 2955, 2876, 1603, 1574, 1459, 1313, 1257, 1164, 1125, 1058, 1034, 1014, 955, 913, 870, 766, 716, 681, 649 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.45–0.65 (m, 6 H), 0.80–1.00 (m, 12 H), 1.10–1.40 (m, 6 H), 1.65–1.90 (m, 2 H), 6.00 (dd, *J* = 7.9 Hz, *J* = 5.8 Hz, 1 H), 6.95 (d, *J* = 7.9 Hz, 1 H), 7.30 (t, *J* = 7.9 Hz, 1 H), 7.45 (t, *J* = 7.9 Hz, 1 H), 7.70 (d, *J* = 7.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.8 (3), 7.2 (3), 14.0, 22.4, 28.7, 30.9, 31.5, 124.9 (q, *J* = 177.8 Hz), 125.4, 126.1 (q, *J* = 4.9 Hz), 129.5, 131.1, 138.3, 142.5, 144.1 (q, *J* = 1.6 Hz) (one C missing).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –59.7.

Anal. Calcd for $C_{20}H_{31}F_3Si$ (356.21): C, 67.37; H, 8.76. Found: C, 67.27; H, 8.65.

(*E*)-[1-(2-Bromophenyl)hept-1-enyl]triethylsilane (2p)
Yield: 89%; ratio α/β ca. 95:5.

IR (neat): 2953, 2930, 2874, 1609, 1462, 1429, 1416, 1377, 1237, 1072, 1047, 1019, 973, 943, 911, 856, 754, 729, 714, 683 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2p**: δ = 0.55–0.65 (m, 6 H), 0.85–1.15 (m, 12 H), 1.20–1.60 (m, 6 H), 1.95 (m, 2 H), 6.05 (t, *J* = 6.3 Hz, 1 H), 6.90 (dd, *J* = 7.4 Hz, *J* = 1.8 Hz, 1 H), 7.05 (td, *J* = 7.4 Hz, *J* = 1.8 Hz, 1 H), 7.25 (td, *J* = 7.4 Hz, *J* = 1.4 Hz, 1 H), 7.60 (dd, *J* = 1.4 Hz, 1 H).

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3p**: δ = 2.15–2.25 (m, 2 H), 6.85 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2p**: δ = 3.3 (3), 7.3 (3), 14.0, 22.5, 28.5, 29.3, 31.5, 122.8, 126.8 (2), 128.3, 132.4, 140.0, 143.7, 144.3.

Anal. Calcd for $C_{19}H_{31}BrSi$ (366.14): C, 62.11; H, 8.50. Found: C, 61.89; H, 8.21.

(*E*)-Triethyl[1-(2-tolyl)hept-1-enyl]silane (2q)
Yield: 63%; ratio α/β ca. 88:12.

IR (neat): 2953, 2930, 2874, 1601, 1605, 1482, 1458, 1416, 1378, 1236, 1180, 1106, 1008, 973, 942, 909, 799, 754 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): major α-isomer **2q**: δ = 0.55–0.65 (q, *J* = 7.8 Hz, 6 H), 0.80–1.00 (m, 12 H), 1.15–1.45 (m, 6 H), 1.85 (q, *J* = 7.2 Hz, 2 H), 2.20 (s, 3 H), 6.00 (t, *J* = 7.2 Hz, 1 H), 6.80 (m, 1 H), 7.10–7.30 (m, 3 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3q**: δ = 2.30 (s, 3 H), 6.75 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (75 MHz, $CDCl_3$): major α-isomer **2q**: δ = 3.2 (3), 7.3 (3), 14.0, 19.9, 22.5, 28.8, 30.2, 31.5, 125.2, 125.3, 126.6, 129.6, 134.5, 139.1, 142.2, 143.1.

Anal. Calcd for $C_{20}H_{34}Si$ (302.24): C, 79.39; H, 11.33. Found: C, 79.21; H, 11.14.

(*E*)-Triethyl[1-(2-isopropylphenyl)hept-1-enyl]silane (2r)
Yield: 83%; ratio α/β ca. 81:19.

IR (neat): 3062, 2955, 2931, 2874, 1603, 1481, 1459, 1380, 1362, 1177, 1082, 1008, 972, 944, 912, 757, 746, 715 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2r**: δ = 0.60–0.80 (m, 6 H), 0.90–1.10 (m, 12 H), 1.00–1.30 (m, 12 H), 1.70–1.80 (m, 2 H), 2.85–2.95 (m, 1 H), 6.85 (t, *J* = 7.2 Hz, 1 H), 6.70 (dd, *J* = 8.5 Hz, *J* = 1.2 Hz, 1 H), 6.90–7.15 (m, 3 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3r**: δ = 1.95–2.05 (m, 2 H), 6.85 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2r**: δ = 3.4 (3), 7.2 (3), 13.9, 22.4, 23.4, 24.7, 29.0, 29.9, 31.4, 125.0 (2), 125.0, 127.9, 139.1, 140.2, 140.7, 143.5, 145.4.

Anal. Calcd for $C_{22}H_{38}Si$ (330.63): C, 79.92; H, 11.58. Found: C, 79.72; H, 11.58.

(*E*)-2-[1-(Triethylsilyl)hept-1-enyl]benzyl Acetate (2s)
Yield: 74%.

IR (neat): 2954, 2931, 2874, 1743, 1606, 1484, 1459, 1417, 1378, 1360, 1224, 1104, 1019, 965, 757, 714, 679 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.40–0.60 (m, 6 H), 0.75–1.10 (m, 12 H), 1.00–1.35 (m, 6 H), 1.65–1.80 (m, 2 H), 2.00 (s, 3 H), 4.90 (s, 2 H), 5.95 (t, *J* = 6.9 Hz, 1 H), 6.75 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1 H), 7.00–7.25 (m, 2 H), 7.30 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 3.0 (3), 7.1 (3), 13.8, 20.8, 22.3, 29.5, 30.3, 31.3, 64.1, 125.6, 127.6, 127.9, 128.3, 132.2, 138.8, 142.1, 144.4, 171.4.

Anal. Calcd for $C_{22}H_{36}O_2Si$ (360.61): C, 73.28; H, 10.06,. Found: C, 73.22; H, 10.00.

(*E*)-Triethyl[1-(2-methoxyphenyl)hept-1-enyl]silane (2t)
Yield: 92%; ratio α/β ca. 91:9.

IR (neat): 2952, 2873, 2833, 1593, 1577, 1487, 1433, 1377, 1240, 1160, 903, 844, 783 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2t**: δ = 0.60–0.90 (m, 6 H), 0.80–1.10 (m, 12 H), 1.20–1.55 (m, 6 H), 2.05 (q, *J* = 7.0 Hz, 2 H), 3.85 (s, 3 H), 6.10 (t, *J* = 7.1 Hz, 1 H), 6.90–7.05 (m, 3 H), 7.15–7.35 (m, 1 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^1H NMR (200 MHz, $CDCl_3$): minor β-isomer **3t**: δ = 2.25–2.35 (m, 2 H), 3.90 (s, 3 H), 6.90 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2t**: δ = 3.3 (3), 7.2 (3), 13.9, 22.2, 30.0 (2), 31.6, 54.7, 110.0, 120.1, 126.5, 129.2, 131.8, 137.4, 143.2, 156.0.

Anal. Calcd for $C_{20}H_{34}OSi$ (318.24): C, 75.40; H, 10.76. Found: C, 75.29; H, 10.65.

(*E*)-2-[1-(Triethylsilyl)hept-1-enyl]phenyl Acetate (2u)
Yield: 76%; ratio α/β ca. 95:5.

IR (neat): 2954, 2931, 2874, 1765, 1599, 1481, 1459, 1444, 1416, 1367, 1204, 1172, 1097, 1038, 1008, 974, 913, 816, 750, 713, 675 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): major α-isomer **2u**: δ = 0.70–0.90 (m, 6 H), 1.00–1.20 (m, 12 H), 1.30–1.60 (m, 6 H), 2.15 (q, *J* = 7.0 Hz, 2 H), 6.30 (t, *J* = 7.0 Hz, 1 H), 2.50 (s, 3 H), 7.15–7.25 (m, 1 H),

7.30–7.60 (m, 3 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **3u**: δ = 6.80 (s, 1 H). (Only the most significant resonance is listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **2u**: δ = 3.1 (3), 7.1 (3), 13.8, 20.7 (CH_3), 22.4, 28.9, 30.4, 31.3, 122.3, 125.9, 125.4, 129.5, 135.4, 135.8, 145.1, 147.2, 168.8.

Anal. Calcd for $C_{21}H_{34}O_2Si$ (346.58): C, 72.77; H, 9.89. Found: C, 73.00; H, 9.72.

(*E*)-Triethyl[1-(4-nitrophenyl)-2-phenylvinyl]silane (5a)
Yield: 80%; ratio α/β ca. 80:20.

IR (neat): 3069, 3024, 2956, 2910, 2891, 1807, 1595, 1515, 1494, 1379, 1341, 1279, 1080, 1000, 922, 857, 757, 735, 720, 694 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **5a**: δ = 0.55 (q, *J* = 8.1 Hz, 6 H), 0.85 (t, *J* = 8.1 Hz, 9 H), 6.80–6.95 (m, 4 H), 7.05 (d, *J* = 8.7 Hz, 2 H), 7.15 (s, 1 H), 7.20–7.30 (m, 1 H), 8.10 (d, *J* = 8.7 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **6a**: δ = 6.80 (s, 1 H), 7.85 (d, *J* = 8.9 Hz, 2 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **5a**: δ = 2.8 (3), 7.1 (3), 123.9 (2), 127.5, 128.0 (2), 128.3 (2), 129.3 (2), 136.5, 140.1, 142.2, 145.9, 151.3.

Anal. Calcd for $C_{20}H_{25}NO_2Si$ (339.51): C, 70.75; H, 7.42; N, 4.13. Found: C, 70.42; H, 7.55; N, 4.20.

Ethyl (*E*)-4-[2-Phenyl-1-(triethylsilyl)vinyl]benzoate (5b)
Yield: 82%; ratio α/β ca. 74:26.

IR (neat): 2953, 2906, 2874, 1716, 1605, 1561, 1493, 1366, 1207, 1100, 1006, 967, 771, 757, 730, 703, 692 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **5b**: δ = 0.70–0.90 (m, 6 H), 1.15 (t, *J* = 8.1 Hz, 9 H), 1.40–1.60 (t, *J* = 7.1 Hz, 3 H), 4.45–4.60 (q, *J* = 7.1 Hz, 2 H), 6.95 (s, 1 H), 6.90–7.20 (m, 6 H), 7.20–7.40 (m, 1 H), 8.10 (d, *J* = 8.3 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **6b**: δ = 7.90 (d, *J* = 8.4 Hz, 2 H). (Only the most significant resonance is listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **5b**: δ = 2.8 (3), 7.1 (3), 14.2, 60.7, 127.3, 127.7 (2), 127.9 (2), 128.6, 129.4 (2), 129.9 (2), 136.9, 139.2, 143.2, 148.7, 166.6.

Anal. Calcd for $C_{23}H_{30}O_2Si$ (366.57): C, 75.36; H, 8.25. Found: C, 75.11; H, 8.52.

Ethyl (*E*)-4-[2-(4-Methoxyphenyl)-1-(triethylsilyl)vinyl]benzoate (5c)
Yield: 95%; ratio α/β ca. 77:23.

IR (neat): 2953, 2906, 2874, 2836, 1716, 1604, 1508, 1462, 1366, 1270, 1248, 1174, 1100, 1019, 1005, 968, 945, 892, 856, 827, 775, 705 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): major α-isomer **5c**: δ = 0.50–0.70 (m, 6 H), 0.80–1.00 (m, 9 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 3.65 (s, 3 H), 4.30 (q, *J* = 7.1 Hz, 2 H), 6.55 (d, *J* = 8.9 Hz, 2 H), 6.65 (s, 1 H), 6.75 (d, *J* = 8.9 Hz, 2 H), 7.00 (d, *J* = 8.5 Hz, 2 H), 7.95 (d, *J* = 8.5 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **6c**: δ = 7.15 (s, 1 H). (Only the most significant resonance is listed.)

^{13}C NMR (75 MHz, $CDCl_3$): major α-isomer **5c**: δ = 3.1 (3), 7.3 (3), 14.4, 55.1, 60.8, 113.5 (2), 127.5 (2), 127.6, 129.8, 130.0 (2), 130.9 (2), 138.5, 140.6, 149.2, 158.7, 166.8.

Anal. Calcd for $C_{24}H_{32}O_3Si$ (396.21): C, 72.68; H, 8.13. Found: C, 72.31; H, 7.99.

(*E*)-4-[2-Phenyl-1-(triethylsilyl)vinyl]benzonitrile (5d)
Yield: 65%; ratio α/β ca. 72:28.

IR (neat): 2953, 2909, 2875, 2227, 1602, 1572, 1495, 1458, 1447, 1415, 1208, 1163, 1107, 1074, 1005, 966, 938, 838, 752, 736, 717, 693 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **5d**: δ = 0.50–0.70 (m, 6 H), 0.90 (t, *J* = 8.1 Hz, 9 H), 6.80 (s, 1 H), 6.70–7.05 (m, 6 H), 7.10–7.30 (m, 1 H), 7.50 (d, *J* = 8.3 Hz, 2 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor β-isomer **6d**: δ = 6.70 (s, 1 H). (Only the most significant resonance is listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **5d**: δ = 2.6 (3), 7.1 (3), 109.3, 119.0, 127.4, 128.3 (2), 128.7 (2), 129.7 (2), 136.5 (2), 136.8, 141.7, 142.4, 148.9.

Anal. Calcd for $C_{21}H_{25}NSi$ (319.52): C, 78.94; H, 7.89, N, 4.38. Found: C, 78.50; H, 8.11; N, 4.39.

(*E*)-Triethyl[1-(4-methoxyphenyl)-2-phenylvinyl]silane (5e) and (*E*)-Triethyl[2-(4-methoxyphenyl)-1-phenylvinyl]silane (6e)
Yield: 70%; ratio α/β ca. 42:58.

IR (neat): 2951, 2909, 2874, 2834, 1604, 1571, 1506, 1461, 1416, 1281, 1242, 1176, 1103, 1035, 1005, 965, 920, 896, 829, 769, 752, 716, 698 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major isomer: δ = 4.15 (s, 3 H). (The presence of an α/β mixture of isomers complicates the spectrum.) (Only the most significant resonance is listed.)

^{1}H NMR (200 MHz, $CDCl_3$): minor isomer: δ = 4.00 (s, 3 H). (Only the most significant resonance is listed.)

(*E*)-4-[2-Phenyl-1-(triethylsilyl)vinyl]benzyl Acetate (5f) and (*E*)-4-[2-Phenyl-2-(triethylsilyl)vinyl]benzyl Acetate (6f)
Yield: 67%; ratio α/β ca. 54:46.

IR (neat): 3024, 2953, 2910, 2874, 1741, 1599, 1572, 1508, 1492, 1416, 1378, 1224, 1018, 1006, 965, 818, 777, 756, 730, 700 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major isomer: δ = 0.50–0.70 (q, *J* = 8.1 Hz, 6 H), 0.90 (t, *J* = 8.1 Hz, 9 H), 2.00 (s, 3 H), 5.10 (s, 2 H), 6.75 (s, 1 H), 6.80–7.00 (m, 6 H), 7.05–7.20 (m, 3 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor isomer: δ = 2.95 (s, 3 H), 4.90 (s, 2 H), 6.70 (s, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): mixture **5f** and **6f**: δ = 2.7 (6), 7.2 (6), 20.8, 20.9, 65.8, 66.1, 125.5, 127.0, 127.1, 127.4, 127.7, 127.8, 128.4, 128.6, 129.4, 129.6, 133.1, 134.4, 137.2, 138.1, 139.0, 143.0, 143.1, 143.5, 144.7, 170.7.

(*E*)-Triethyl[1-(2-nitrophenyl)-2-phenylvinyl]silane (5g)
Yield: 92%.

IR (neat): 3062, 3023, 2954, 2909, 2875, 1607, 1568, 1520, 1342, 1302, 1238, 1006, 962, 939, 853, 786, 753, 691 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (m, 6 H), 1.10 (t, *J* = 8.0 Hz, 9 H), 6.95 (s, 1 H), 7.00–7.10 (m, 2 H), 7.15–7.35 (m, 4 H), 7.50 (td, *J* = 8.1 Hz, *J* = 1.5 Hz, 1 H), 7.65 (td, *J* = 7.4 Hz, *J* = 1.5 Hz, 1 H), 8.25 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 3.3 (3), 7.1 (3), 123.9, 124.7, 126.6, 127.2 (2), 128.8 (2), 130.3, 133.3, 137.0, 138.7, 139.5, 140.3, 147.6.

Anal. Calcd for $C_{20}H_{25}NO_2Si$ (339.51): C, 70.75; H, 7.42; N, 4.13. Found: C, 70.11; H, 7.70; N, 4.02.

Ethyl (*E*)-2-[2-Phenyl-1-(triethylsilyl)vinyl]benzoate (5h)
Yield: 72%.

IR (neat): 3059, 2953, 2908, 2875, 1709, 1596, 1566, 1494, 1286, 1266, 1244, 1171, 1131, 1044, 766, 754, 710, 691 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.50–0.70 (m, 6 H), 0.85 (t, *J* = 8.1 Hz, 9 H), 1.10 (t, *J* = 7.1 Hz, 3 H), 3.95–4.20 (m, 2 H), 6.70 (s, 1 H), 6.75–7.05 (m, 6 H), 7.15 (t, *J* = 7.5 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.85 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 3.2 (3), 7.2 (3), 14.0, 60.5, 125.5, 126.6, 127.8, 128.1, 128.8, 129.0, 129.3, 130.4, 131.3, 131.9, 137.0, 139.7, 143.8, 144.7, 167.0.

Anal. Calcd for $C_{23}H_{30}O_2Si$ (366.57): C, 75.44; H, 8.25. Found: C, 75.11; H, 8.41.

Ethyl (*E*)-2-[2-(4-Methoxyphenyl)-1-(triethylsilyl)vinyl]benzoate (5i)
Yield: 74%.

IR (neat): 2952, 2908, 2874, 2836, 1719, 1604, 1566, 1508, 1462, 1441, 1417, 1366, 1287, 1266, 1244, 1177, 1130, 1075, 1036, 1008, 964, 941, 889, 853, 824, 767, 750, 709 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.40–0.60 (m, 6 H), 0.75 (t, *J* = 7.7 Hz, 9 H), 1.10 (t, *J* = 7.1 Hz, 3 H), 3.50 (s, 3 H), 3.85–4.10 (m, 2 H), 6.40 (d, *J* = 8.8 Hz, 2 H), 6.45 (s, 1 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.75 (d, *J* = 7.7 Hz, 1 H), 6.95–7.10 (t, *J* = 7.7 Hz, 1 H), 7.15–7.25 (t, *J* = 7.7 Hz, 1 H), 7.70 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.3 (3), 7.4 (3), 14.2, 55.1, 60.6, 113.3 (2), 125.5, 129.0, 129.5, 130.5 (2), 130.6, 132.1, 136.6, 141.1, 145.1, 158.4, 167.3 (one C missing).

Anal. Calcd for $C_{24}H_{32}O_3Si$ (396.21): C, 72.68; H, 8.13. Found: C, 72.55; H, 8.01.

(*E*)-2-[2-Phenyl-1-(triethylsilyl)vinyl]benzonitrile (5j)
Yield: 80%.

IR (neat): 3061, 3023, 2953, 2910, 2875, 2224, 1597, 1572, 1494, 1459, 1416, 1379, 1208, 1076, 1006, 963, 938, 875, 795, 745, 717, 692 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.60–0.80 (m, 6 H), 1.00 (t, *J* = 8.0 Hz, 9 H), 6.85–7.00 (m, 2 H), 7.00 (s, 1 H), 7.05–7.40 (m, 5 H), 7.40–7.50 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 3.1 (3), 7.2 (3), 111.2, 118.1, 126.1, 127.5, 128.0 (2), 128.5, 129.0 (2), 132.5, 133.2, 136.7, 140.0, 141.9, 147.6.

Anal. Calcd for $C_{21}H_{25}NSi$ (319.52): C, 78.94; H, 7.89; N, 4.38. Found: C, 78.71; H, 8.20; N, 4.34.

(*E*)-Triethyl[1-(2-methoxyphenyl)-2-phenylvinyl]silane (5k)
Yield: 64%; ratio α/β ca. 80:20.

IR (neat): 3056, 2951, 2909, 2874, 2833, 1592, 1576, 1486, 1460, 1434, 1416, 1377, 1292, 1272, 1242, 1180, 1110, 1073, 1049, 1029, 1006, 966, 947, 919, 883, 846, 800, 749, 714, 691 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **5k**: δ = 0.50–0.70 (q, *J* = 8.1 Hz, 6 H), 0.90 (t, *J* = 8.1 Hz, 9 H), 3.65 (s, 3 H), 6.75–6.85 (m, 3 H), 6.90–7.20 (m, 7 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor α-isomer **6k**: δ = 3.85 (s, 3 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **5k**: δ = 3.2 (3), 7.2 (3), 54.9, 110.4, 120.8, 126.7, 126.9, 127.6, 127.8, 127.9, 128.4, 128.9, 132.0, 137.9, 138.5, 140.8, 156.0.

Anal. Calcd for $C_{21}H_{28}OSi$ (324.19): C, 77.72; H, 8.70. Found: C, 77.64; H, 8.64.

(*E*)-2-[2-Phenyl-1-(triethylsilyl)vinyl]benzyl Acetate (5l)
Yield: 68%; ratio α/β ca. 92:8.

IR (neat): 3062, 3022, 2953, 2910, 2875, 1799, 1739, 1601, 1571, 1494, 1459, 1443, 1416, 1379, 1360, 1224, 1073, 1018, 964, 839, 802, 754, 716, 691 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major α-isomer **5l**: δ = 0.55–0.75 (q, *J* = 8.1 Hz, 6 H), 0.90 (t, *J* = 8.1 Hz, 9 H), 1.70 (s, 3 H), 4.75 (d, *J* = 12.5 Hz, 1 H), 4.85 (d, *J* = 12.5 Hz, 1 H), 6.80 (s, 1 H), 6.80–6.90 (m, 2 H), 6.95–7.10 (m, 4 H), 7.15–7.35 (m, 3 H). (The presence of an α/β mixture of isomers complicates the spectrum.)

^{1}H NMR (200 MHz, $CDCl_3$): minor α-isomer **6l**: δ = 5.10 (s, 1 H). (Only the most significant resonance is listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major α-isomer **5l**: δ = 3.2 (3), 7.2 (3), 20.6, 64.3, 126.1, 127.4, 127.6, 128.0 (2), 128.5, 129.2 (2), 129.3, 131.7, 137.4, 140.1, 141.4, 142.3, 170.6.

Anal. Calcd for $C_{23}H_{30}O_2Si$ (366.57): C, 75.36; H, 8.25. Found: C, 75.21; H, 8.04.

(*E*)-4-(2-Pyridin-2-yl-1-(triethylsilyl)vinyl]benzonitrile (5m)
Yield: 61%.

IR (neat): 2957, 2910, 2890, 2228, 1605, 1582, 1565, 1496, 1459, 1435, 1414, 1379, 1265, 1233, 1163, 1109, 1050, 1002, 966, 932, 907, 891, 844, 775, 737, 718, 697 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.50–0.65 (q, *J* = 7.1 Hz, 6 H), 0.90 (t, *J* = 7.1 Hz, 9 H), 6.50 (d, *J* = 8.0 Hz, 1 H), 6.90–7.00 (m, 1 H), 6.95 (s, 1 H), 7.05 (d, *J* = 8.5 Hz, 2 H), 7.20–7.30 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 1 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 8.45 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.5 (3), 7.1 (3), 109.4, 118.9, 121.8, 123.6, 127.8 (2), 132.3 (2), 135.4, 140.3, 146.3, 148.4, 149.2, 155.0.

Anal. Calcd for $C_{20}H_{24}N_2Si$ (320.17): C, 74.95; H, 7.55; N, 8.74. Found: C, 74.77; H, 7.36; N, 8.58.

(*E*)-4-[2-Pyridin-2-yl-2-(triethylsilyl)vinyl]benzonitrile (6m)
Yield: 9%.

IR (neat): 2953, 2910, 2874, 2227, 1602, 1582, 1560, 1501, 1463, 1426, 1410, 1378, 1278, 1238, 1174, 1148, 1091, 1049, 1005, 974, 943, 887, 826, 788, 721 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.50–0.65 (q, *J* = 7.9 Hz, 6 H), 0.90 (t, *J* = 7.9 Hz, 9 H), 6.65 (m, 1 H), 6.70 s, 1 H), 6.80 (d, *J* = 8.6 Hz, 2 H), 7.00–7.10 (m, 1 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 7.50 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1 H), 8.55 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.0 (3), 7.3 (3), 110.4, 118.9, 121.0, 122.5, 129.7 (2), 131.7 (2), 136.3, 138.3, 141.7, 148.7, 149.9, 161.3.

Anal. Calcd for $C_{20}H_{24}N_2Si$ (320.17): C, 74.95; H, 7.55; N, 8.74. Found: C, 74.71; H, 7.28; N, 8.55.

(*E*)-2-[2-Pyridin-2-yl-1-(triethylsilyl)vinyl]benzonitrile (5n)
Yield: 69%.

IR (neat): 3061, 2954, 2910, 2876, 2224, 1582, 1566, 1458, 1435, 1425, 1379, 1265, 1237, 1192, 1175, 1151, 1096, 1006, 964, 934, 904, 876, 824, 794, 761, 742, 717, 705 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.50–0.65 (q, *J* = 8.1 Hz, 6 H), 0.90 (t, *J* = 8.1 Hz, 9 H), 6.60 (dt, *J* = 7.9 Hz, *J* = 0.9 Hz, 1 H), 6.90–6.95 (m, 1 H), 7.05 (s, 1 H), 7.00–7.10 (d, *J* = 9.2 Hz, 1 H), 7.20–7.30 (m, 2 H), 7.40–7.60 (m, 2 H), 8.40 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.0 (3), 7.2 (3), 110.8, 118.2, 122.0, 123.3, 126.2, 127.8, 132.8, 133.2, 135.8, 141.7, 144.1, 147.5, 149.4, 155.0.

Anal. Calcd for $C_{20}H_{24}N_2Si$ (320.17): C, 74.95; H, 7.55; N, 8.74. Found: C, 74.79; H, 7.35; N, 8.60.

(*E*)-Triethyl(styryl)silane (9a)
Yield: 86%; ratio α/β ca. 15:85.

IR (neat): 3300, 2953, 2910, 2875, 1603, 1494, 1457, 1415, 1378, 1238, 1014, 989, 974, 826, 785, 734 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major β-isomer **9a**: δ = 0.65 (q, *J* = 6.8 Hz, 6 H), 1.00 (t, *J* = 6.8 Hz, 9 H), 6.45 (d, *J* = 19.3 Hz, 1 H), 6.95 (d, *J* = 19.3 Hz, 1 H), 7.15–7.30 (m, 3 H), 7.30–7.40 (m, 2 H).

^{1}H NMR (200 MHz, $CDCl_3$): minor α-isomer **8a**: δ = 5.60 (d, *J* = 3.1 Hz, 1 H), 5.90 (d, *J* = 3.1 Hz, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major β-isomer **9a**: δ = 3.6 (3), 7.3 (3), 125.8, 126.3 (2), 128.0 (2), 128.7, 138.6, 145.0.

Anal. Calcd for $C_{14}H_{22}Si$ (218.15): C, 76.99; H, 10.15. Found: C, 76.77; H, 10.04.

Methyl (*E*)-4-[2-(Triethylsilyl)vinyl]benzoate (9b)
Yield: 98%; ratio α/β ca. 24:76.

IR (neat): 2952, 2874, 1721, 1605, 1458, 1435, 1409, 1274, 1243, 1193, 1176, 1106, 1016, 988, 969, 864, 842, 806, 782, 753 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major β-isomer **9b**: δ = 0.55–0.75 (q, *J* = 7.9 Hz, 6 H), 0.90 (t, *J* = 7.9 Hz, 9 H), 3.80 (s, 3 H), 6.50 (d, *J* = 19.2 Hz, 1 H), 6.85 (d, *J* = 19.2 Hz, 1 H), 7.40 (d, *J* = 8.3 Hz, 2 H), 7.90 (d, *J* = 8.3 Hz, 2 H).

^{1}H NMR (200 MHz, $CDCl_3$): minor α-isomer **8b**: δ = 0.55–0.75 (q, *J* = 7.8 Hz, 6 H), 0.85 (t, *J* = 7.8 Hz, 9 H), 3.78 (s, 3 H), 5.55 (d, *J* = 3.0 Hz, 1 H), 5.80 (d, *J* = 3.0 Hz, 1 H), 7.10 (d, *J* = 8.5 Hz, 2 H), 7.85 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): major β-isomer **9b**: δ = 3.4 (3), 7.2 (3), 52.0, 126.2 (2), 129.2, 129.7, 129.8 (2), 142.7, 143.7, 166.9.

Anal. Calcd for $C_{16}H_{24}O_2Si$ (276.15): C, 69.51; H, 8.75. Found: C, 69.48; H, 8.74.

(*E*)-Triethyl[2-(4-methoxyphenyl)vinyl]silane (9c)
Yield: 96%; ratio α/β ca. 18:82.

IR (neat): 2952, 2908, 2874, 2835, 1606, 1570, 1508, 1462, 1441, 1416, 1332, 1294, 1249, 1171, 1106, 1037, 1010, 986, 843, 789, 749, 717 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major β-isomer **9c**: δ = 0.55–0.75 (q, *J* = 7.9 Hz, 6 H), 0.85 (t, *J* = 7.9 Hz, 9 H), 3.70 (s, 3 H), 6.50 (d, *J* = 19.2 Hz, 1 H), 6.85 (d, *J* = 19.2 Hz, 1 H), 7.40 (d, *J* = 8.3 Hz, 2 H), 7.90 (d, *J* = 8.3 Hz, 2 H).

^{1}H NMR (200 MHz, $CDCl_3$): minor α-isomer **8c**: δ = 3.68 (s, 3 H),5.40 (d, *J* = 3.2 Hz, 1 H), 5.75 (d, *J* = 3.2 Hz, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (50 MHz, $CDCl_3$): major β-isomer **9c**: δ = 3.7 (3), 7.4 (3), 52.3, 113.9 (2), 123.4, 127.5 (2), 131.6, 144.3, 159.6.

Anal. Calcd for $C_{15}H_{24}OSi$ (248.16): C, 72.52; H, 9.74. Found: C, 72.38; H, 9.56.

Methyl (*E*)-2-[1-(Triethylsilyl)vinyl]benzoate (8d) and Methyl (*E*)-2-[2-(Triethylsilyl)vinyl]benzoate (9d)
Yield: 84%; ratio α/β ca. 52:48.

IR (neat): 2951, 2909, 2875, 1722, 1598, 1566, 1458, 1433, 1416, 1289, 1252, 1190, 1163, 1126, 1074, 1043, 1009, 967, 927, 840, 812, 783, 768 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): mixture **8d** and **9d**: δ = 0.30–0.50 (m, 12 H), 0.60–0.75 (t, *J* = 7.7 Hz, 9 H), 0.75–0.85 (t, *J* = 7.7 Hz, 9 H), 3.60 (s, 3 H), 3.65 (s, 3 H), 5.35 (d, *J* = 3.0 Hz, 1 H), 5.40 (d, *J* = 3.0 Hz, 1 H), 6.10 (d, *J* = 19.2 Hz, 1 H), 6.80 (d, *J* = 7.3 Hz, 1 H), 6.95–7.10 (m, 2 H), 7.15–7.30 (m, 2 H), 7.35–7.50 (m, 2 H), 7.55–7.70 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): mixture **8d** and **9d**: δ = 3.4 (3), 3.5 (3), 7.3 (3), 7.4 (3), 51.7, 52.0, 125.7, 126.8, 127.2, 127.3, 128.5, 128.8, 129.0, 129.6, 129.9, 130.2, 131.1, 131.9, 140.6, 143.8, 147.0, 151.8, 168.0, 168.4.

Anal. Calcd for $C_{16}H_{24}O_2Si$ (276.15): C, 69.51; H, 8.75. Found: C, 69.42; H, 8.67.

(*E*)-Triethyl[2-(2-methoxyphenyl)vinyl]silane (9e)
Yield: 97%; ratio α/β ca. 38:62.

IR (neat): 2952, 2909, 2874, 2834, 1596, 1486, 1462, 1436, 1415, 1327, 1288, 1242, 1178, 1161, 1105, 1092, 1049, 1030, 1006, 972, 929, 834, 802, 784, 747, 720 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): major β-isomer **9e**: δ = 0.30–0.50 (m, 6 H), 0.60–0.75 (m, 9 H), 3.70 (s, 3 H), 6.30 (d, *J* = 19.4 Hz, 1 H), 6.70–6.90 (m, 2 H), 7.00–7.15 (m, 1 H), 7.25 (d, *J* = 19.4 Hz, 1 H), 7.45 (dd, *J* = 7.7 Hz, *J* = 1.7 Hz, 1 H).

^{1}H NMR (300 MHz, $CDCl_3$): minor β-isomer **8e**: δ = 3.65 (s, 3 H), 5.50 (d, *J* = 3.4 Hz, 1 H), 5.75 (d, *J* = 3.4 Hz, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (75 MHz, $CDCl_3$): major β-isomer **9e**: δ = 53.1, 136.9. (Only the most significant resonances are listed.)

^{13}C NMR (75 MHz, $CDCl_3$): minor α-isomer **8e**: δ = 52.4, 126.1 (=CH_2). (Only the most significant resonances are listed.)

Anal. Calcd for $C_{15}H_{24}OSi$ (248.16): C, 72.52; H, 9.74. Found: C, 72.14; H, 9.48.

(*E*)-Triethyl(hept-1-enyl)silane (12a)
Yield: 98; ratio α/β ca. 10:90.

IR (neat): 2954, 2927, 2874, 1616, 1459, 1416, 1378, 1237, 1014, 991, 922, 781, 717 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): major β-isomer **12a**: δ = 0.40–0.50 (q, *J* = 7.3 Hz, 6 H), 0.80–0.95 (m, 12 H), 1.15–1.40 (m, 6 H), 1.95–2.10 (m, 2 H), 5.45 (dt, *J* = 18.7 Hz, *J* = 1.5 Hz, 1 H), 5.95 (dt, *J* = 18.7 Hz, *J* = 6.2 Hz, 1 H).

^{1}H NMR (300 MHz, $CDCl_3$): minor α-isomer **11a**: δ = 5.20 (td, *J* = 3.0 Hz, *J* = 0.9 Hz, 1 H), 5.50 (m, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (75 MHz, $CDCl_3$): major β-isomer **12a**: δ = 3.5 (3), 7.4 (3), 14.1, 22.5, 28.5, 31.4, 37.0, 125.4, 148.8.

Anal. Calcd for $C_{13}H_{28}Si$ (212.20): C, 73.50; H, 13.28. Found: C, 73.19; H, 13.07.

(*E*)-Triethyl(3-methoxybut-1-enyl)silane (12b)
Yield: 78%; ratio α/β ca. 12:88.

IR (neat): 2953, 2910, 2875, 2818, 1675, 1619, 1458, 1416, 1371, 1323, 1232, 1199, 1110, 1079, 1012, 992, 972, 910, 849, 778, 718 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major β-isomer **12b**: δ = 0.40–0.50 (m, 6 H), 0.80–0.95 (m, 9 H), 1.10 (d, *J* = 6.3 = Hz, 3 H), 3.20 (s, 3

H), 3.55–3.70 (q, *J* = 6.3 Hz, 1 H), 5.65 (d, *J* = 18.9 Hz, 1 H), 5.85 (dd, *J* = 18.9 Hz, *J* = 6.3 Hz, 1 H).

^{1}H NMR (300 MHz, $CDCl_3$): minor α-isomer **11d**: δ = 3.15 (s, 3 H), 5.35 (dd, *J* = 2.9 Hz, *J* = 0.7 Hz, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (75 MHz, $CDCl_3$): major β-isomer **12b**: δ = 3.3 (3), 7.3 (3), 21.1, 56.0, 80.6, 127.7, 148.9.

Anal. Calcd for $C_{11}H_{24}OSi$ (200.16): C, 65.93; H, 12.07. Found: C, 65.79; H, 11.99.

(*E*)-1-Methyl-3-(triethylsilyl)allyl Acetate (12c)
Yield: 60%; ratio α/β ca. 29:71.

IR (neat): 2954, 2911, 2876, 1740, 1623, 1458, 1417, 1369, 1235, 1135, 1043, 1009, 950, 849, 780, 718 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major β-isomer **12c**: δ = 0.40–0.55 (m, 6 H), 0.80–0.95 (m, 9 H), 1.30 (d, *J* = 6.6 = Hz, 3 H), 2.10 (s, 3 H), 3.30–5.50 (m, 1 H), 5.75 (dd, *J* = 19.0 Hz, *J* = 1.3 Hz, 1 H), 6.00 (dd, *J* = 19.0 Hz, *J* = 5.0 Hz, 1 H).

^{1}H NMR (300 MHz, $CDCl_3$): minor α-isomer **11c**: δ = 2.05 (s, 3 H), 5.90 (m, 1 H). (Only the most significant resonances are listed.)

^{13}C NMR (75 MHz, $CDCl_3$): major β-isomer **12c**: δ = 3.1 (3), 7.3 (3), 20.0, 21.1, 72.5, 126.7, 146.0, 170.3.

Anal. Calcd for $C_{12}H_{24}O_2Si$ (228.15): C, 63.10; H, 10.59. Found: C, 62.80; H, 10.40.

(*E*)-3-(Triethylsilyl)allyl Acetate (11d)
Yield: 90%; ratio α/β ca. 88:12.

IR (neat): 2954, 2912, 2876, 1742, 1624, 1459, 1417, 1374, 1226, 1005, 845, 779, 720 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): major β-isomer **11d**: δ = 0.40–0.55 (m, 6 H), 0.80–0.95 (m, 9 H), 2.00 (s, 3 H), 4.60 (t, *J* = 1.5 Hz, 2 H), 5.35 (m, 1 H), 5.80 (m, 1 H).

^{1}H NMR (300 MHz, $CDCl_3$): minor α-isomer **12d**: δ = 2.02 (s, 3 H), 4.55 (dd, *J* = 5.1 Hz, *J* = 1.5 Hz, 2 H). (Only the most significant resonances are listed.)

^{13}C NMR (75 MHz, $CDCl_3$): major β-isomer **11d**: δ = 3.3 (3), 7.3 (3), 20.9, 68.1, 126.6, 143.3, 170.6.

Anal. Calcd for $C_{11}H_{22}O_2Si$ (214.14): C, 61.63; H, 10.34. Found: C, 61.51; H, 10.10.

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References

(1) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, **1988**. (b) Oshima, K. In *Science of Synthesis*, Vol. 2; Fleming, I., Ed.; Georg Thieme Verlag: Stuttgart, **2002**, 685. (c) *The Chemistry of Organosilicon Compounds*; Patai, S.; Rappaport, Z., Eds.; Wiley: Chichester, **1998**, Chap. 3.

(2) Trost, B. M. *Science* **1991**, *254*, 1471.

(3) An excellent overview of the addition of metalloid hydrides to alkynes appeared recently, see: Trost, B. M.; Ball, Z. T. *Synthesis* **2005**, 853.

(4) For recent advances in the metal-catalyzed hydrosilylation of alkynes, see: (a) Arico, C. S.; Cox, L. R. *Org. Biomol. Chem.* **2004**, *2*, 2558. (b) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726. (c) Kawanami, Y.; Sonoda, Y.; Mori, T.; Yamamoto, K. *Org. Lett.* **2002**, *4*, 2825. (d) Maifeld, S. V.; Tran, M. N.; Lee, D. *Tetrahedron Lett.* **2005**, *46*, 105. (e) Faller, J. W.; D'Alliessi, D. G. *Organometallics* **2002**, *21*, 1743. (f) Kawanami, Y.; Yamamoto, K. *Synlett* **1995**, 1232. (g) Uno, T.; Wakayanagi, S.; Sonoda, Y.; Yamamoto, K. *Synlett* **2003**, 1997. (h) Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073. (i) Katayama, H.; Taniguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, *645*, 192.

(5) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Lewis, L. N.; Sy, K. G.; Bryant, G. L. Jr.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.

(6) (a) Green, M.; Spencer, J. L.; Stone, G. A. F.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1525. (b) Tsipis, C. A. *J. Organomet. Chem.* **1980**, *187*, 427. (c) Tsipis, C. A. *J. Organomet. Chem.* **1980**, *188*, 53. (d) Takahasi, K.; Minami, T.; Ohara, Y.; Hiyama, T. *Tetrahedron Lett.* **1993**, *34*, 8263. (e) Denmark, S. E.; Wang, Z. G. *Org. Lett.* **2001**, *3*, 1073. (f) Murphy, P. J.; Spencer, J. L.; Procter, G. *Tetrahedron Lett.* **1990**, *31*, 1051.

(7) De Bo, G.; Berthon-Gelloz, G.; Tinant, B.; Markó, I. E. *Organometallics* **2006**, *25*, 1881.

(8) Chauhan, M.; Hauck, B. J.; Keller, L. P.; Boudjouk, P. *J. Organomet. Chem.* **2002**, *645*, 1.

(9) Jiménez, R.; Martínez-Rosales, J. M.; Cervantes, J. *Can. J. Chem.* **2003**, *81*, 1370.

(10) (a) Liron, F.; Le Garrec, P.; Alami, M. *Synlett* **1999**, 246. (b) Alami, M.; Liron, F.; Gervais, M.; Peyrat, J. F.; Brion, J. D. *Angew. Chem. Int. Ed.* **2002**, *41*, 1578. (c) Liron, F.; Gervais, M.; Peyrat, J. F.; Alami, M.; Brion, J. D. *Tetrahedron Lett.* **2003**, *44*, 2789. For the hydrostannation of enynes and related compounds see: (d) Alami, M.; Ferri, F. *Synlett* **1996**, 755. (e) Ferri, F.; Alami, M. *Tetrahedron Lett.* **1996**, *37*, 7971. (f) Bujard, M.; Ferri, F.; Alami, M. *Tetrahedron Lett.* **1998**, *39*, 4243. (g) Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *J. Org. Chem.* **2007**, *72*, 3868.

(11) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2005**, *7*, 5625.

(12) Treatment of **2b** with Et_3SiH (1.5 equiv) in the presence of H_2PtCl_6 or Pt/C (5 mol%) at 60 °C for a prolonged time (3 h) did not promote any protodesilylation of **2b**, indicating that the reduced side product was formed from starting material **1b**.

(13) Performing the hydrosilylation of **10a** at 60 °C led to a mixture of α- (10%) and β-isomers (23%) together with the protodesilylated product (67%).

(14) Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.