Stereo- and Regioselective Pt(DVDS)/P(^{i}BuNCH$_2$CH$_2$)$_3$N-Catalyzed Hydrosilylation of Terminal Alkynes

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The catalyst system Pt(DVDS)/P(^{i}BuNCH$_2$CH$_2$)$_3$N (DVDS = [(H$_2$C═CH)Me$_2$Si]$_2$O), containing a bulky aminophosphine ligand, catalyzes the hydrosilylation of terminal alkynes possessing a variety of functional groups using Ph$_3$SiH or Et$_3$SiH. These reactions occur stereo- and regioselectively to give β-(*E*)-vinylsilanes with 97−99% selectivity in 76−98% yield. Using Pt$_2$(DVDS)$_3$, this selectivity ranged from 63 to 93%, except in one case, where the selectivities were the same for both catalyst systems.

The hydrosilylation of alkynes is one of the most convenient, straightforward, and atom-economical methods of synthesizing vinylsilanes,[1] a class of compounds that has attracted considerable attention in recent years as important building blocks in organic synthesis.[2−6] One of the most significant uses of vinylsilanes is as nucleophilic partners in Pd-catalyzed Hiyama-type cross-coupling reactions.[7] Their ease of handling and compatibility with a range of organic transformations, along with their low cost and low toxicity, have added to their growing importance. However, the use of vinylsilanes has been inhibited because of difficulties in accessing stereo- and regiodefined isomers in hydrosilylations of terminal alkynes, owing to the possibility of forming a mixture of three isomeric vinylsilanes (viz. α- and β-(*E*) and β-(*Z*)).

Recently, significant progress has been made in this area and a myriad of catalyst systems have been developed in efforts to generate stereo- and regiodefined isomers.[8] In most cases the stereo- and regioselectivity appears to be capriciously affected by various factors such as the metal species, the ligand, the type of alkyne and silane, and reaction parameters such as solvent and temperature.[8] Among the various catalysts employed, the cationic rhodium complex [Rh(COD)$_2$]BF$_4$ has achieved high regio- and stereoselectivity for β-(*E*)-vinylsilane formation,[8a−c] although the use of propargylic amines[8a] and arylalkynes[8b] as substrates resulted in complete or partial polymerization. Neutral rhodium complexes usually provided (*Z*)-alkenylsilanes with moderate to high selectivities.[8d,e] However, a stereodivergent synthesis of (*Z*)- and (*E*)-alkenylsilanes was recently reported using a neutral rhodium(I) iodide complex.[8f] Employing ruthenium catalysts, others have obtained regioisomeric α-vinylsilanes with good selectivity.[8g−i] Although platinum complexes such as H$_2$PtCl$_6$ (Speier's catalyst)[8d] and Pt$_2$(DVDS)$_3$ (DVDS = [(H$_2$C═CH)Me$_2$Si]$_2$O; Karstedt's catalyst)[8j] are generally known as the most active and widely used hydrosilylation catalysts, recent reports describe the use of Pt(DVDS)/P(^{t}Bu)$_3$ for achieving β-(*E*) selectivities in the 90−99% range for a variety of terminal alkynes[7b,8k] employing tetramethyldisiloxane[7b] or 2-pyridyldimethylsilane.[8k] In the former work, the products were generated in solution and were used in a further reaction.[7b]

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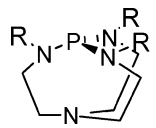
Chart 1



R	Me	^{i}Pr	^{i}Bu	Bn
L	**1a**	**1b**	**1c**	**1d**

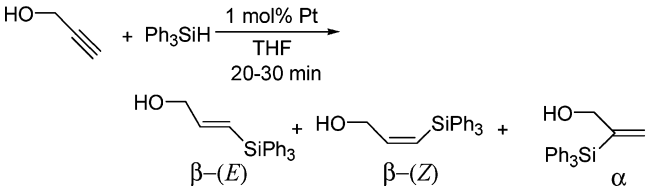
In the second report, product yields ranged from 63 to 93% when reactions were carried out at 100 °C for 15 h.[8k]

We have had a strong interest in the salutary properties of bicyclic aminophosphines of the proazaphosphatrane type (Chart 1) as nonionic bases and ligands ever since the first examples were synthesized in our laboratories (of which **1a**−**c** are now commercially available).[9] The electronic and steric properties of these rigid but relatively strain-free bicyclic structures can be easily tuned by introducing suitable organic groups at the PN_3 nitrogen centers. Because of their tunable electronic and steric properties, these aminophosphines have proven to be exceedingly efficient as catalysts or promoters and as strong nonionic phosphorus bases for a variety of organic transformations.[10] More recently, they have been shown to function as effective ligands in several palladium-catalyzed cross-coupling reactions.[11] We envisioned that these aminophosphines might also act as good ligands in platinum-catalyzed hydrosilylation reactions.

We report herein a rapid and efficient room-temperature method for the highly stereo- and regioselective hydrosilylation of terminal alkynes using the Pt(DVDS)/**1c** catalyst system and compare it with results obtained with $Pt_2(DVDS)_3$.[12] For optimization of our reaction conditions, the hydrosilylation of propargyl alcohol with triphenylsilane was chosen as a model reaction. As shown in Table 1, the $Pt_2(DVDS)_3$ complex did not facilitate good selectivity (entry 1) and 30−40% of the triphenylsilane remained unreacted. With the Pt(DVDS)/**1a** system, only 10−20% of the silane was consumed. In contrast, the catalyst systems Pt(DVDS)/**1b**, Pt(DVDS)/**1c**, and Pt(DVDS)/**1d** containing a proazaphosphatrane ligand with bulky substituents on the PN_3 nitrogen atoms gave rise to excellent stereo- and regioselective hydrosilylation in 20 min.[13]

Similar stereo- and regioselectivities were observed when THF or dioxane was used as a solvent. We selected the Pt(DVDS)/**1c** catalyst system for evaluating the scope of our protocol.[9] The complexes [Pt(DVDS)(L)], where L = **1a**−**d**, were synthesized (see the Experimental Section) and characterized by ^{31}P NMR spectroscopy (Table 2).

Table 1. Screening of Catalysts[a]



		product distribn[b]		
entry no.	catalyst	*β*-(*E*)	*β*-(*Z*)	α
1[c]	$[Pt_2(DVDS)_3]$	69	trace	31
2[d]	Pt(DVDS)/(**1a**)	76	trace	24
3	Pt(DVDS)/(**1b**)	98		2
4[e]	Pt(DVDS)/(**1c**)	98		2
5[e]	Pt(DVDS)/(**1d**)	98		2

[a] A mixture of propargyl alcohol (1 mmol), triphenylsilane (1.1 equiv), and catalyst (1 mol % Pt) was stirred in THF for 20 min. [b] The ratio of regioisomers was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] 30−40% of the silane remained unreacted. [d] Less than 20% of the silane was consumed. [e] Similar stereo- and regioselectivity was observed when dioxane was used as a solvent.

Table 2. ^{31}P NMR Chemical Shifts and ^{31}P−^{195}Pt Coupling Constants for the [Pt(DVDS)(L)] Complexes (L = 1a−d)[a]

complex	*δ* (ppm)	J_{P-Pt} (Hz)
[Pt(DVDS)(**1a**)]	118.47	5389
[Pt(DVDS)(**1b**)]	121.09	5201
[Pt(DVDS)(**1c**)]	124.21	5478
[Pt(DVDS)(**1d**)]	128.26	5511

[a] The spectra were recorded in a xylenes−benzene-d_6 solvent mixture at 20 °C.

Using the aforementioned optimized conditions, a variety of alkynes bearing various functional groups were selected to evaluate the scope of our catalyst system. As seen in Table 3, alkynes were smoothly converted in 20−30 min at ambient temperature to the corresponding *β*-(*E*)-vinylsilanes in good to excellent yields. Analysis of the crude reaction mixtures by ^{1}H NMR spectroscopy revealed in general a maximum of 2% of α-isomeric products and only traces of the *β*-(*Z*) adducts in some cases.

Employment of either triethylsilane or triphenylsilane as a hydrosilylation reagent resulted in similar regio- and stereoselectivities. Although $Pt_2(DVDS)_3$ exhibited considerable selectivity for *β*-(*E*)-vinylsilanes in the case of hydrocarbon alkynes (especially with triphenylsilane, entries 2 and 4), a distinct improvement in these selectivities was observed in the presence of **1c.** The effect of the bulky and electron-rich aminophosphine ligand **1c** was clearly seen in the case of alkynes bearing functional groups. The influence of **1c** was particularly striking in the case of substrates where the functional group is closer to the triple bond and is sterically unhindered (Table 3, entries 5, 6, 19−22, 27, and 28). In the absence of the ligand **1c**, the reactions were either incomplete or gave a mixture of isomers.

A variety of alkynes were amenable to our protocol. Thus, primary, secondary, and tertiary propynylic alcohols were cleanly hydrosilylated to their corresponding *β*-(*E*) adducts (entries 5−16) and no dehydrogenative silylation of alcohols was observed. When the hydroxyl

(9) Ligands **1a**−**c** are commercially available from either Aldrich or Strem.

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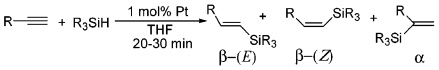
(12) Whereas the Pt(DVDS) complex is probably the catalytically active species, the precursor is probably the Pt(0) complex $[Pt_2(DVDS)_3]$, which is preponderant in such solutions and has been characterized by an X-ray structural determination. Hitchcock, P. B.; Lappert, M. F.; Warhurst, N. J. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 438.

(13) The catalyst solutions were prepared by adding 1 equiv of the aminophosphine ligand to $Pt_2(DVDS)_3$ solution (see the Experimental Section for details).

Table 3. Hydrosilylation[a] of Terminal Alkynes Catalyzed by Pt(DVDS)/(1c) and by [Pt_2(DVDS)$_3$][b]



Entry	Alkyne	R_3SiH	Product distribution[c]			Isolated yield[d] (%)	Entry	Alkyne	R_3SiH	Product distribution[c]			Isolated yield[d] (%)
		R	-(*E*)	-(*Z*)					R	-(*E*)	-(*Z*)		
1	C_4H_9—≡	Et	99		1	90	17	HO	Et	97		3	90[e]
			(85)	tr	(15)					(78)	tr	(22)	
2		Ph	99		1	94	18		Ph	97		3	92
			(93)		(7)					(90)		(10)	
3		Et	99		1	92	19	MeO	Et	99		1	84
			(83)		(17)					(63)		(37)	
4		Ph	98		2	93	20		Ph	99		1	98
			(93)		(7)					(63)		(37)	
5	HO	Et	98		2	92[e]	21	$PhCH_2O$	Et	99		1	87
			(71)	tr	(29)					(63)		(37)	
6[f]		Ph	98		2	96	22		Ph	98		2	92
			(69)		(31)					(65)		(35)	
7	HO	Et	99		1	92	23	Cl	Et	99		1	82
			(85)	tr	(15)					(76)	(6)	(18)	
8		Ph	99		1	95	24		Ph	98		2	88
			(85)		(15)					(88)		(12)	
9	Ph, HO	Et	98		2	91	25	NC	Et	99		1	85
			(80)		(20)					(74)	(10)	(16)	
10		Ph	98		2	96	26		Ph	99		1	94
			(80)		(20)					(91)		(9)	
11	HO	Et	99		1	81	27	O	Et	97		3	83
			(88)		(12)					(64)		(36)	
12		Ph	99		1	95	28[g]		Ph	97		3	95
			(91)		(9)		29[h]	EtOOC, EtOOC	Et	90		10	87[e]
13	OH	Et	98		2	84	30[h]		Ph	97		3	91
			(85)		(15)								
14		Ph	99		1	93	31[h]	H_2N	Et	99		1	79
			(92)		(8)		32[i]		Ph	99		1	89
15	OH	Et	97		3	76							
			(84)		(16)								
16		Ph	98		2	91							
			(98)		(2)								

[a] All reactions were carried out on a 1 mmol scale in 1 mL of THF employing 1.1 equiv of silane and 1 mol % of Pt (2 mol % for entries 29 and 30). Reactions were generally complete in 20−30 min, except for entries 29 and 30, where reactions were complete in 3 h. [b] Where comparison was possible, the product distributions of reactions catalyzed by [Pt_2(DVDS)$_3$] are shown in parentheses. [c] The ratio of regioisomers was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d] Yield refers to isolated pure β-(*E*) isomers. [e] The product contained 1−2% α-isomer. [f] With [Pt_2(DVDS)$_3$], 30−40% of the silane remained unreacted. [g] With [Pt_2(DVDS)$_3$], the ^{1}H NMR spectrum exhibited broad features. [h] With [Pt_2(DVDS)$_3$], the ^{1}H NMR spectrum showed overlapping peaks that precluded proper integration. [i] With [Pt_2(DVDS)$_3$], less than 5% of the silane was consumed.

Table 4. Crystal Data and Structure Refinement Details for (*E*)-1-(Triphenylsilyl)-3,4,4-trimethyl-1-penten-3-ol (Entry 16, Table 3)

empirical formula	$C_{26}H_{30}OSi$
formula wt	386.59
temp	298(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a	9.692(2) Å
b	11.462(3) Å
c	11.968(3) Å
α	99.307(4)°
β	113.666(4)°
γ	99.323(4)°
V	1163.2(5) Å^3
Z	2
density (calcd)	1.104 Mg/m^3
abs coeff	0.114 mm^{-1}
F(000)	416
cryst size	0.40 × 0.40 × 0.30 mm^3
θ range for data collecn	1.86−26.37°
index ranges	$-12 \le h \le 12$
	$-14 \le k \le 14$
	$-14 \le l \le 14$
no. of rflns collected	9702
no. of indep rflns	4696 (R(int) = 0.0174)
completeness to $\theta = 26.37°$	98.9%
abs cor	semiempirical from equivalents
max and min transmissn	1 and 0.91
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	4696/0/258
goodness of fit on F^2	1.020
final *R* indices ($I > 2\sigma(I)$)[a]	R1 = 0.0531, wR2 = 0.1435
R indices (all data)[a]	R1 = 0.0661, wR2 = 0.1560
largest diff peak and hole	0.717 and −0.203 e Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

group on an alkyne was sterically protected by an adjacent bulky *tert*-butyl group (entry 16), both the $Pt_2(DVDS)_3$ and the Pt(DVDS)/**1c** catalyst systems exhibited similar selectivities in the case of triphenylsilane. In the ^{1}H NMR spectrum of the product, a single olefinic resonance (doublet with J = 1−2 Hz) was observed instead of a pair of doublets. A single-crystal X-ray molecular structure determination (Table 4 and Figure 1) confirmed the expected structure of this compound, however. The reaction was also tolerant of other functionalities, including an ether (entries 19−22), halide (entries 23 and 24), cyano (entries 25 and 26), and ester (entries 31 and 32) substituents. Enynes (entries 27−30) were also chemoselectively converted to their *β*-(*E*) adducts in good yields, although the reaction of the enyne containing two electron-withdrawing ester groups (entries 29 and 30) was sluggish, requiring a longer reaction time (3 h) and higher catalyst loading (2 mol % Pt). An alkyne with a free amino group (entries 31 and 32) was also cleanly converted to its corresponding *β*-(*E*) adduct, which was isolated in good yield, unlike the case with the $[Rh(COD)_2]BF_4$ catalyst, wherein protection of the amino group was required to prevent alkyne polymerization.[8a] However, the reaction with triphenylsilane involving $Pt_2(DVDS)_3$ as a catalyst was incomplete, exhibiting less than 5% consumption of the silane. In the absence of ligand **1c**, it is reasonable to suggest that the free amino group coordinates to the metal, thus deactivating the catalyst in that reaction.

The high selectivities for *β*-(*E*)-vinylsilanes shown by the present catalyst system can be rationalized on the

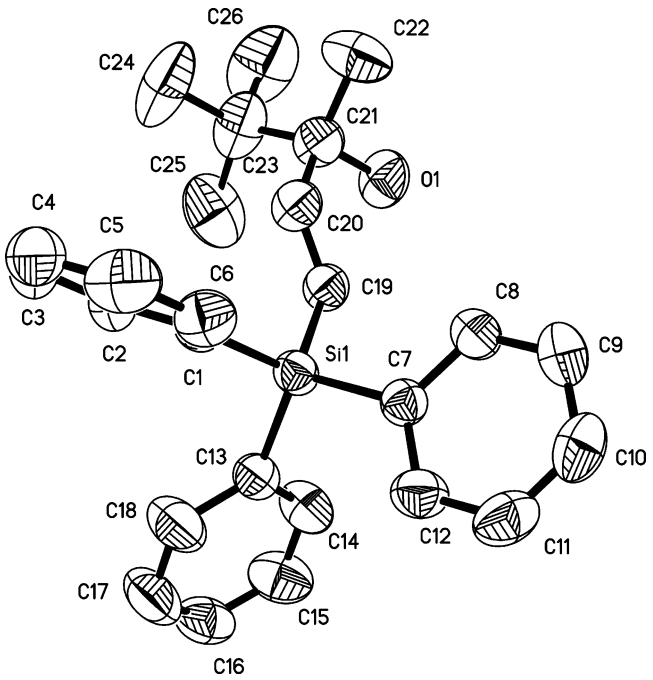
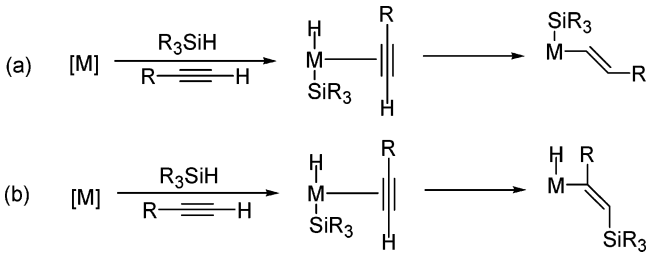


Figure 1. ORTEP diagram of the molecular structure of (*E*)-1-(triphenylsilyl)-3,4,4-trimethyl-1-penten-3-ol (entry 16, Table 3) at the 50% probability level. H atoms are omitted for clarity.

Scheme 1



basis of the Chalk−Harrod[14] or the modified Chalk−Harrod[8t,15,16] mechanisms for transition-metal-catalyzed hydrosilylations. In both mechanisms, the first step involves oxidative addition of the silane to the metal, but the olefin inserts into the Pt−H bond in the first pathway, while it inserts into the M−Si bond in the second (paths a and b in Scheme 1, respectively). Recently ab initio molecular orbital and Møller−Plesset perturbation theory calculations showed that acetylene insertion into a Pt−H bond required an activation energy of 12.8 kcal/mol compared to 20.9 kcal/mol for insertion into an Pt−Si bond.[17] Moreover, the reaction energy of the acetylene insertion into a Pt−H bond was 9.7 kcal/mol lower than for insertion into a Pt−Si

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bond.[17] The very high selectivity for the β-(*E*) isomers shown in Table 3 can be rationalized by insertion of an alkyne into a Pt−H bond of the oxidative addition product followed by reductive elimination. Insertion into the Pt−H bond may be favored because of decreased hindrance in the vinyl intermediate in path a of Scheme 1 (the metal and bulky aminophosphine ligand are represented as [M] in Scheme 1) compared with that in the analogous intermediate in path b of this scheme.

In conclusion, an efficient stereo- and regioselective method of hydrosilylation has been developed using Pt(DVDS)/**1c** as the catalyst system. Our results demonstrate that ligand **1c** possesses a propitious balance of stereochemical properties that enable it to facilitate highly stereo- and regioselective hydrosilylations. Our screening experiments also showed that other proazaphosphatranes (ligands **1b** and **1d**), possessing bulky groups other than isobutyl on the PN_3 nitrogen atoms, can also catalyze these reactions efficiently. The short reaction times, mild reaction conditions, and tolerance for a variety of functional groups makes the Pt(DVDS)/**1c** catalyst system attractive to use.

Experimental Section

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. All solvents were dried and distilled following standard procedures. The alkynes and the silanes were obtained from Aldrich and were used without purification. A xylenes solution of Pt(DVDS) containing 2% Pt was obtained from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 300 MHz or Varian Unity 400 MHz spectrometer. ^{1}H NMR spectra are referenced to the residual $CHCl_3$ peak (δ 7.27 ppm) in $CDCl_3$, and ^{13}C NMR spectra are referenced to $CDCl_3$ (δ 77.23 ppm). The ^{31}P spectra were recorded in a xylenes−benzene-d_6 solvent mixture (1/0.25 v/v) at 20 °C on a Varian Unity 400 MHz spectrometer (161.89 MHz for ^{31}P). The peaks are referenced to 85% H_3PO_4. Combustion analyses were performed by Instrumentation Services, Iowa State University, or Desert Analytics.

In Situ Synthesis of Metal Complexes. To a xylenes solution of Pt(DVDS) (1 mL containing 2% Pt) was added **1c** (1.0 equiv per Pt) in benzene-d_6 (0.25 mL). The mixture was stirred at 65 °C for 10 min, and cooled to room temperature. The ^{31}P NMR spectrum of the reaction mixture showed a peak at δ 124.2 ppm (J_{P-Pt} = 5478 Hz) indicating probable formation of [Pt(DVDS)(**1c**)], and this solution was stored under argon and used within 1 month.[18] (We were unable to isolate the complexes from the oils which persisted upon repeated crystallization attempts.) The platinum complexes of other proazaphosphatrane ligands (**1a**,**b**,**d**) were synthesized analogously. We were also unable to isolate these complexes, but ^{31}P NMR spectra of the reaction mixtures they formed indicated formation of an analogous Pt(DVDS)(L) species (Table 2).

Hydrosilylation Reactions. A general procedure for hydrosilylation reactions using a commercially available xylenes solution of Pt(DVDS) or a xylenes−benzene (1/0.25 v/v) solution of the Pt(DVDS)/**1c** catalyst system is now described. To an alkyne (1 mmol) solution of THF (1 mL) was added silane (1.1 equiv) under argon. A benzene−xylenes (0.25/1) solution of Pt(DVDS)/**1c** or a xylenes solution of [Pt_2(DVDS)$_3$] was added (each containing 1 mol % of Pt), and the reaction mixture was stirred at 20 °C for 20−30 min (except for entries 29 and 30 in Table 3, in which cases 2 mol % of Pt and 3 h were employed). The crude reaction mixture was concentrated in vacuo and was purified by column chromatography on silica gel (or on neutral alumina for the reactions in entries 23 and 24 in Table 3) to afford analytically pure samples upon elution. The eluent was hexanes for entries 1−4, 20% ether in hexanes for entries 5−18, 29, and 30, 5% ether in hexanes for entries 19−24, 27, and 28, 10% ether in hexanes for entries 25 and 26, and 80% ether in hexanes for entries 31 and 32 in this table.

The ^{1}H and ^{13}C NMR data of the pure compounds compare well with the literature values (see below).

^{1}H and ^{13}C NMR Spectral Data for Products in Entries 1−32 of Table 3. (*E*)-1-(Triethylsilyl)-1-hexene[8b,c,m−o,19] (Entry 1, Table 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.54 (q, J = 7.9 Hz, 6H), 0.86−0.94 (m, 12H), 1.24−1.43 (m, 4H), 2.09−2.16 (m, 2H), 5.55 (dt, 1H, J = 18.7, 1.5 Hz), 6.05 (dt, J = 18.7 Hz, 6.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 3.6, 7.4, 14.0, 22.2, 31.1, 36.8, 125.5, 148.8.

(*E*)-1-(Triphenylsilyl)-1-hexene[8n,20] (Entry 2, Table 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.93 (t, J = 7.2 Hz, 2H), 1.28−1.51 (m, 5H), 2.23−2.31 (m, 2H), 6.21 (m, 2H), 7.35−7.47 (m, 9H), 7.52−7.58 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 14.2, 22.5, 30.9, 37.0, 123.3, 128.0, 129.6, 135.3, 136.2, 153.9.

(*E*)-1-(Triethylsilyl)-2-phenylethene[8m,n,p,19,21,22] (Entry 3, Table 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.67 (q, J = 7.9 Hz, 6H), 0.99 (t, J = 7.9 Hz, 9H), 6.42 (d, J = 19.5 Hz, 1H), 6.89 (d, J = 19.5 Hz, 1H), 7.22−7.28 (m, 1H), 7.30−7.37 (m, 2H), 7.42−7.47 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 3.7, 7.6, 126.1, 126.5, 128.0, 128.7, 138.7, 145.0.

(*E*)-1-(Triphenylsilyl)-2-phenylethene[8n,p,23] (Entry 4, Table 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.1 (d, J = 2.7 Hz, 2H), 7.28−7.56 (m, 14H), 7.61−7.67 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 123.1, 127.0, 128.1, 128.7, 128.8, 129.8, 134.7, 136.2, 138.2, 149.1.

(*E*)-1-(Triethylsilyl)-1-propen-3-ol[8b,c,m] (Entry 5, Table 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.54 (q, J = 7.9 Hz, 6H), 0.9 (t, J = 7.9 Hz, 9H), 2.17 (br, 1H), 4.14 (dd, J = 4.1, 1.7 Hz, 2H), 5.81 (dt, J = 18.9 Hz, 1.7 Hz, 1H), 6.16 (dt, J = 18.9 Hz, 4.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 3.5, 7.4, 65.7, 125.7, 146.3.

(*E*)-1-(Triphenylsilyl)-1-propen-3-ol[24−28] (Entry 6, Table 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.51 (br, 1H), 4.29 (dd, J = 3.9, 1.7 Hz, 2H), 6.30 (dt, J = 18.8 Hz, 3.9 Hz, 1H), 6.50 (dt, J = 18.8 Hz, 1.7 Hz., 1H), 7.33−7.45 (m, 9H), 7.50−7.55 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 65.5, 122.9, 128.1, 129.8, 134.5, 136.1, 150.9.

(*E*)-1-(Triethylsilyl)-1-buten-3-ol[29−33] (Entry 7, Table 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.55 (q, J = 7.9 Hz, 6H), 0.91 (t, J = 7.9 Hz, 9H), 1.24 (d, J = 6.7 Hz, 3H), 1.88 (br, 1H), 4.26 (m, 1H), 5.73 (dd, J = 18.9 Hz, 1.5 Hz, 1H), 6.08 (dd, J =

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18.9, 5.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.5, 7.5, 23.2, 70.8, 124.3, 151.3.

(*E*)-1-(Triphenylsilyl)-1-buten-3-ol[27,34] (Entry 8, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.31 (d, J = 6.6 Hz, 3H), 1.62 (d, br, J = 4.6 Hz), 4.42 (m, 1H), 6.25 (dd, J = 18.7, 4.5 Hz, 1H), 6.42 (dd, J = 18.7, 1.4 Hz, 1H), 7.34−7.46 (m, 9H), 7.51−7.55 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 23.2, 70.6, 121.9, 128.1, 129.8, 134.5, 136.1, 155.6.

(*E*)-1-(Triethylsilyl)-3-phenyl-1-propen-3-ol[8b,c,35] (Entry 9, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.61 (q, J = 7.9 Hz, 6H), 0.96 (t, J = 7.9 Hz, 9H), 2.23 (b, 1H), 5.19 (m, 1H), 5.97 (dd, J = 18.7, 1.5 Hz, 1H), 6.24 (dd, J = 18.7, 5.0 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.5, 7.5, 76.8, 126.1, 126.7, 127.8, 128.7, 142.8, 148.7.

(*E*)-1-(Triphenylsilyl)-3-phenyl-1-propene-3-ol[36] (Entry 10, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.64 (br, 1H), 5.39 (d, J = 4.1 Hz, 1H), 6.55 (dd, J = 18.5, 4.5 Hz, 1H), 6.77 (dd, J = 18.5, 1.4 Hz, 1H), 7.38−7.58 (m, 14H), 7.69−7.75 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 76.6, 123.2, 126.8, 127.9, 128.0, 128.7, 129.7, 134.4, 136.1, 142.3, 152.8.

(*E*)-1-(Triethylsilyl)-3-methyl-1-buten-3-ol[8b,c,34] (Entry 11, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.55 (q, J = 7.9 Hz, 6H), 0.91 (t, J = 7.9 Hz, 9H), 1.27 (s, 6H), 1.67 (br, 1H), 5.71 (d, J = 19.2 Hz, 1H), 6.15 (d, J = 19.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.6, 7.5, 29.6, 72.3, 120.6, 155.0.

(*E*)-1-(Triphenylsilyl)-3-methyl-1-buten-3-ol[34] (Entry 12, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.35 (s, 6H), 1.55 (br, 1H), 6.41 (d, J = 18.8 Hz, 1H), 6.31 (d, J = 18.8 Hz, 1H), 7.34−7.46 (m, 9H), 7.50−7.55 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 29.6, 72.6, 118.8, 128.1, 129.7, 134.7, 138.1, 159.3.

(*E*)-2-Cyclohexanol-1-(triethylsilyl)ethene[8b−d,m,37] (Entry 13, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.55 (q, J = 7.9 Hz, 6H), 0.91 (t, J = 7.9 Hz, 9H), 1.38 (br 1H), 1.18−1.28 (m, 2H), 1.51−1.72 (m, 8H), 5.77 (d, J = 19.2 Hz, 1H), 6.13 (d, J = 19.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.6, 7.5, 22.3, 25.7, 37.7, 72.9, 121.3, 155.0.

(*E*)-2-Cyclohexanol-1-(triphenylsilyl)ethene (Entry 14, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.41 (br, 1H), 1.17−1.32 (m, 2H), 1.44−1.73 (m, 8H), 6.43 (d, J = 18.8 Hz, 1H), 6.28 (d, J = 18.8 Hz, 1H), 7.32−7.44 (m, 9H), 7.48−7.53 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 22.1, 25.7, 37.6, 73.3, 119.3, 128.1, 129.7, 134.8, 136.2, 159.5. Anal. Calcd for $C_{26}H_{28}OSi$: C, 81.20; H, 7.34. Found: C, 80.72; H, 7.53.

(*E*)-1-(Triethylsilyl)-3,4,4-trimethyl-1-penten-3-ol[38] (Entry 15, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.58 (q, J = 7.9 Hz, 6H), 0.94 (t, J = 7.9 Hz, 9H), 0.94, (s, 9H), 1.23 (s, 3H), 1.45 (br, 1H), 5.74 (d, J = 19.2 Hz, 1H), 6.26 (d, J = 19.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.7, 7.6, 23.5, 25.6, 37.4, 78.3, 122.3, 152.3.

(*E*)-1-(Triphenylsilyl)-3,4,4-trimethyl-1-penten-3-ol (Entry 16, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.99 (s, 9H), 1.3 (s, 3H), 1.6 (br 1H), 6.49 (d, J = 1.0 Hz, 2H), 7.38−7.50 (m, 9H), 7.58−7.63 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 23.4, 25.7, 37.6, 78.7, 120.3, 128.0, 129.7, 134.9, 136.1, 157.2.

(*E*)-1-(Triethylsilyl)-1-buten-4-ol[8b,c,m] (Entry 17, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.54 (q, J = 7.9 Hz, 6H), 0.91 (t, J = 7.9 Hz, 9H), 1.63 (br, 1H), 2.39 (qd, 2H, J = 6.4, 1.4 Hz), 3.66 (t, J = 6.4 Hz, 2H), 5.68 (dt, J = 18.7, 1.4 Hz, 1H), 6.01 (dt, J = 18.7, 6.4 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 3.6, 7.5, 40.5, 61.7, 130.3, 144.1.

(*E*)-1-(Triphenylsilyl)-1-buten-4-ol (Entry 18, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.39 (br, 1H), 2.53 (qd, J = 6.4, 1.2 Hz, 2H), 3.73 (t, J = 6.4 Hz, 2H), 6.15 (dt, J = 18.6, 6.4 Hz, 1H), 6.34 (dt, J = 18.6, 1.2 Hz, 1H), 7.33−7.46 (m, 9H), 7.49−7.54 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 40.6, 61.7, 127.7, 128.2, 129.8, 134.8, 136.2, 149.0. Anal. Calcd for $C_{22}H_{22}OSi$: C, 79.95; H, 6.71. Found: C, 80.07; H, 6.78.

(*E*)-3-Methoxy-1-(triethylsilyl)-1-propene (Entry 19, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.57 (q, J = 7.9 Hz, 6H), 0.93 (t, J = 7.9 Hz, 9H), 3.33 (s, 3H), 3.95 (dd, J = 4.9, 1.5 Hz, 1H), 5.84 (dt, J = 18.9 Hz, 1.5 Hz, 1H), 6.09 (dt, J = 18.9 Hz, 4.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.6, 7.5, 58.2, 75.8, 128.6, 143.7.

(*E*)-3-Methoxy-1-(triphenylsilyl)-1-propene[28] (Entry 20, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.39 (s, 3H), 4.07 (dd, J = 4.6 Hz, 1.7 Hz), 6.21 (dt, J = 18.6 Hz, 4.6 Hz, 1H), 6.51 (dt J = 18.6 Hz, 1.7 Hz, 1H), 7.33−7.46 (m, 9H), 7.51−7.57 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 58.5, 75.2, 125.2, 128.1, 129.7, 134.6, 136.1, 148.3.

(*E*)-3-(Benzyloxy)-1-(triethylsilyl)-1-propene[8m] (Entry 21, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.62 (q, J = 7.9 Hz, 6H), 0.98 (t, J = 7.9 Hz, 9H), 4.10 (dd, J = 4.9, 1.5 Hz, 2H), 4.55 (s, 2H), 5.91 (dt, J = 19.0, 1.5 Hz, 1H), 6.18 (dt, J = 19.0, 4.9 Hz, 1H), 7.27−7.35 (m, 1H), 7.36−7.41 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.6, 7.5, 72.3, 73.5, 127.8, 128.0, 128.6, 128.7, 138.5, 143.8.

(*E*)-3-(Benzyloxy)-1-(triphenylsilyl)-1-propene (Entry 22, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.26 (dd, J = 4.6, 1.5 Hz, 2H), 4.67 (s, 2H), 6.37 (dt, J = 18.7, 4.5 Hz, 1H), 6.67 (dt, J = 18.7, 1.5 Hz, 1H), 7.35−7.55 (m, 14H), 7.63−7.69 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 72.6, 72.9, 125.3, 127.8, 128.0, 128.1, 128.6, 129.7, 134.5, 136.1, 138.4, 148.4. Anal. Calcd for $C_{28}H_{26}OSi$: C, 82.71; H, 6.45. Found: C, 82.09; H, 6.52.

(*E*)-5-Chloro-1-(triethylsilyl)-1-pentene[8b,c,39,40] (Entry 23, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.55 (q, J = 7.9 Hz, 2H), 0.92 (t, J = 7.9 Hz, 2H), 1.88 (m, J = 6.7 Hz, 2H), 2.28 (q, J = 6.7 Hz, 2H), 3.53 (t, J = 6.7 Hz, 2H), 5.62 (dt, J = 18.7, 1.5 Hz, 1H), 5.99 (dt, J = 18.7, 6.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.7, 7.5, 31.8, 34.2, 44.5, 127.8, 146.4.

(*E*)-5-Chloro-1-(triphenylsilyl)-1-pentene (Entry 24, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.99 (m, J = 6.7 Hz, 2H), 2.47 (q, J = 6.7 Hz, 2H), 3.61 (t, J = 6.7 Hz, 2H), 6.21 (dt, J = 18.6, 6.0 Hz, 1H), 6.36 (dt, J = 18.6, 1.3 Hz, 1H), 7.40−7.52 (m, 9H), 7.57−7.63 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 31.5, 34.1, 44.6, 125.4, 128.0, 129.7, 134.9, 136.1, 151.1. Anal. Calcd for $C_{23}H_{23}ClSi$: C, 76.11; H, 6.39. Found: C, 76.31; H, 6.17.

(*E*)-5-Cyano-1-(triethylsilyl)-1-pentene (Entry 25, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.55 (q, J = 7.9 Hz, 6H), 0.91, (t, J = 7.9 Hz, 9H), 1.77 (m, J = 7.3 Hz, 2H), 2.28 (m, J = 7.3 Hz, 2H), 2.32 (t, J = 7.3 Hz, 2H), 5.65 (dt, J = 18.7, 1.4 Hz, 1H), 5.94 (dt, J = 18.7, 6.3 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.7, 7.6, 16.6, 24.6, 35.7, 119.9, 129.1, 145.3. Anal. Calcd for $C_{12}H_{23}NSi$: C, 68.83; H, 11.07. Found: C, 68.57; H, 11.23.

(*E*)-5-Cyano-1-(triphenylsilyl)-1-pentene (Entry 26, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.85 (m, J = 7.3 Hz, 2H), 2.37 (t, J = 7.3 Hz, 2H), 2.46 (m, J = 7.3 Hz, 2H), 6.17 (dt, J = 18.5, 6.0 Hz, 1H), 6.39 (dt, J = 18.5, 1.5 Hz, 1H), 7.40−7.52 (m, 9H), 7.58−7.62 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 16.6, 24.3, 35.5, 119.6, 126.5, 128.0, 129.7, 134.6, 136.0, 150.0. Anal. Calcd for $C_{24}H_{23}NSi$: C, 81.54; H, 6.56. Found: C, 81.64; H, 6.46.

(*E*)-3-(Propenyloxy)-1-(triethylsilyl)-1-propene[8m] (Entry 27, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.57 (q, J = 7.9 Hz, 6H), 0.93 (t, J = 7.9 Hz, 9H), 3.98 (dt, J = 5.6, 1.4 Hz, 2H), 4.02 (dd, J = 4.9, 1.4 Hz, 2H), 5.17 (m, 1H), 5.27 (m, 1H), 5.84 (dt, J = 18.9, 1.4 Hz, 1H), 5.92 (ddt, J = 17.2, 10.5, 5.6

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Hz, 1H), 6.11 (dt, J = 18.9, 4.9 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.6, 7.5, 71.3, 73.4, 117.2, 128.5, 135.0, 143.8.

(*E*)-3-(Propenyloxy)-1-(triphenylsilyl)-1-propene (Entry 28, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.04 (dt, J = 4.5, 1.5 Hz, 2H), 4.14 (dd, J = 4.5, 1.8 Hz, 2H), 5.21 (m, 1H), 5.31 (m, 1H), 5.95 (ddt, J = 17.3, 10.7, 5.6 Hz, 1H), 6.23 (dt, J = 18.6, 4.4 Hz, 1H), 6.52 (dt, J = 18.6, 1.7, 1H), 7.34−7.46 (m, 9H), 7.51−7.57 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 71.6, 72.9, 117.4, 125.1, 128.1, 129.8, 134.6, 134.9, 136.2, 148.4. Anal. Calcd for $C_{24}H_{24}OSi$: C, 80.85; H, 6.78. Found: C, 80.82; H, 6.91.

(*E*)-4,4-Bis(ethoxycarbonyl)-1-(triethylsilyl)-1,6-heptadiene[8b,c] (Entry 29, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.53 (q, J = 7.9 Hz, 6H), 0.90 (t, J = 7.9 Hz, 9H), 1.24 (t, J = 7.1 Hz, 6H), 2.62 (d, J = 7.6 Hz, 2H), 2.70 (d, J = 7.6 Hz, 2H), 4.16 (q, J = 7.1 Hz, 4H), 5.08 (m, 2H), 5.66 (m, 1H), 5.67 (dt, J = 18.6, 1.1 Hz, 1H), 5.84 (dt, J = 18.6, 6.6 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 3.6, 7.5, 14.3, 37.1, 40.1, 57.5, 61.4, 119.2, 132.2, 132.7, 141.5, 171.0.

(*E*)-4,4-Bis(ethoxycarbonyl)-1-(triphenylsilyl)-1,6-heptadiene (Entry 30, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.22 (t, J = 7.1 Hz, 6H), 2.73 (br, d, J = 7.5 Hz, 2H), 2.94 (br, d, J = 7.5 Hz, 2H), 4.17 (q, J = 7.1 Hz, 4H), 5.12 (m, 2H), 5.74 (m, 1H), 6.09 (dt, J = 18.3, 7.1 Hz, 1H), 6.41 (dt, J = 18.3, 1.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 14.2, 37.2, 40.0, 57.5, 61.4, 119.3, 127.9, 129.65, 129.7, 132.5, 134.4, 136.0, 146.4, 170.7. Anal. Calcd for $C_{31}H_{34}O_4Si$: C, 74.66; H, 6.87. Found: C, 74.90; H, 6.71.

(*E*)-3-Amino-1-(triethylsilyl)-1-propene (Entry 31, Table 3). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.55 (q, J = 7.9 Hz, 6H), 0.92 (t, J = 7.9 Hz, 9H), 1.30 (br, 2H), 3.34 (dd, J = 4.7, 1.7 Hz, 2H), 5.70 (dt, J = 18.8 Hz, 1.7 Hz, 1H), 6.17 (dt, J = 18.8, 4.7 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 3.6, 7.5, 47.1, 124.2, 149.0. Anal. Calcd for $C_9H_{21}NSi$: C, 63.08; H, 12.35. Found: C, 62.75; H, 12.36.

(*E*)-3-Amino-1-(triphenylsilyl)-1-propene (Entry 32, Table 3). ^1H NMR ($CDCl_3$, 300 MHz)**:** δ 1.30 (br, 2H), 3.48 (br, d, 2H), 6.37 (m, 2H), 7.35−7.47 (m, 9H), 7.54−7.58 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 46.9, 121.7, 128.0, 129.7, 134.8, 136.1, 153.7. Anal. Calcd for $C_{21}H_{21}NSi$: C, 79.95; H, 6.71. Found: C, 79.98; H, 6.95.

X-ray Crystal Structure of (*E*)-1-(Triphenylsilyl)-3,4,4-trimethyl-1-penten-3-ol (Entry 16, Table 3). Data Collection, Structure Solution, and Refinement. The crystals of (*E*)-1-(triphenylsilyl)-3,4,4-trimethyl-1-penten-3-ol were grown by diffusion of pentane into a dichloromethane solution of the compound. A colorless crystal with approximate dimensions 0.4 × 0.4 × 0.3 mm^3 was selected under ambient conditions. Crystal evaluation and data collection were performed at 298 K on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.710 73 Å) radiation and a detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω with an exposure time of 5 s per frame. A total of 86 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built into the SMART program. The final cell constants were calculated from a set of 865 strong reflections from the actual data collection. The data were collected using the full sphere routine. A total of 9702 data were harvested by collecting four sets of frames with 0.3° scans in ω with an exposure time of 10 s per frame. This data set was corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface, as sampled by multiple equivalent measurements[41] using SADABS software.[42] The systematic absences in the diffraction data were consistent for the space groups $P1$ and $P\bar{1}$.[42] The E statistics strongly suggested the centrosymmetric space group $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The position of the heavy atom was found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in the full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Final least-squares refinement of 258 parameters against 4696 independent reflections converged to R (based on F^2 for $I \geq 2\sigma$) and R_w (based on F^2 for $I \geq 2\sigma$) values of 0.053 and 0.144, respectively. The resulting CIF file has been tested with PLATON[43] software.

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Supporting Information Available: Tables giving atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles and hydrogen coordinates of (*E*)-1-(triphenylsilyl)-3,4,4-trimethyl-1-penten-3-ol (entry 16, Table 3); crystallographic data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).
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