Xphos ligand and platinum catalysts: A versatile catalyst for the synthesis of functionalized β-(E)-vinylsilanes from terminal alkynes

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ABSTRACT

Hydrosilylation of functionalized terminal arylalkynes with a variety of silanes catalyzed by $PtCl_2$ or PtO_2 in the presence of the air-stable and bulky Xphos ligand was investigated. Regardless of the electronic nature (electron withdrawing or donating group) and the position (o, m, p) of the substituents on the aromatic ring, a single β-(E)-styrylsilanes was obtained in good to excellent yields. The regioselectivity of the H-Si bond addition was found to be governed by steric effects induced by the bulky Xphos ligand. A dramatic regioselectivity was also observed when functionalized terminal aliphatic alkynes were employed as a substrate and in these cases regioisomeric β-(E)-vinylsilanes were generated with excellent selectivity.

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1. Introduction

The hydrosilylation of terminal alkynes with transition-metal catalysts remains an area of intense research interest [1] as it provides a simple and straightforward, atom-economical method for the synthesis of vinylsilanes [2]. Their low cost, high chemical stabilities associated to a lack of toxicity make them ideal candidates for palladium-catalyzed cross-coupling reactions [3]. Vinylsilanes also constitute versatile starting materials for natural products [4] and polymers [5]. The main difficulty with the hydrosilylation reaction is control of the stereo- and regiochemistry of the alkenylsilanes products. For example, hydrosilylation of terminal alkynes may give a primary mixture of three isomeric vinylsilanes including the β-(Z)- and β-(E)-linear vinylsilanes as well as the branched α-isomer (Scheme 1).

Although metal-catalyzed hydrosilylation of terminal aliphatic alkynes is well documented [1], however the reaction with terminal arylalkynes, particularly those bearing functionalized groups on the aromatic ring, has received scant attention probably because of the difficulty in controlling the regioselectivity of the H–Si bond addition. The regio- and stereochemical outcome of this reaction depends on several factors including the nature of the

silane, the metal species and the ligand. With $(EtO)_2MeSiH$, the branched α-isomer is best obtained in the presence of a cationic Ru complex $[Cp^*Ru(MeCN)_3]PF_6$ [6]. Using ruthenium carbene complexes [7] or $[RuCl_2(p\text{-}cymene)]_2$ [8] as well as $[Cp^*IrCl_2]_2$ [9] catalysts, selective formation of stereoisomeric β-(Z)-vinylsilanes, is generally achieved. The formation of the third β-(E)-isomer is best accomplished by using Rh-[10] Ir-[11] and Pd-based [12] catalysts. With platinum catalyst which holds certain supremacy in the *cis*-hydrosilylation of alkynes, low to moderate regioselectivities were generally observed with terminal arylalkynes when using industrial catalysts such as Speier's (H_2PtCl_6) and Karstedt's catalysts ($Pt_2(dvtms)_3$; dvtms = divinyltetramethyldisiloxane) [13]. The importance of bulky ligands effect for achieving β-(E) selectivities was reported. The use of Pt catalysts associated with $P(cC_6H_{11})_3$ [14] or $P(t\text{-}Bu)_3$[15] as the catalysts systems was shown to display moderate to high β-(E)-selectivities depending on the silane employed. Changing the air-sensitive and pyrophoric $P(t\text{-}Bu)_3$ to the sterically aminomonophosphine ligand $P(i\text{-}BuN\text{-}CH_2CH_2)_3N$ [16] also led to β-(E) selectivity when using Ph_3SiH or Et_3SiH. To our knowledge, however, such hydrosilylation reactions were only studied with the simple substrate phenylacetylene (**1a**). The remaining challenge is to obtain high β-(E)-selectivity from functionalized arylalkynes without compromising reagent stability and practicality. Therefore, considering the potential utility of β-(E)-styrylsilanes **2** in synthetic organic chemistry [17], the search of an efficient and versatile catalytic system for the highly selective formation of **2** with various silanes is strongly desirable and presents an interesting challenge.

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Scheme 1.
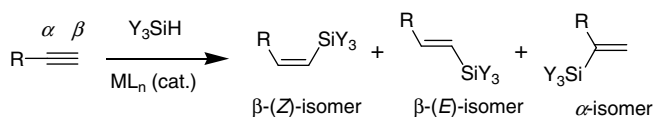
Previously, we reported that heterogeneous commercially available platinum oxide (PtO_2) proved to be a versatile catalyst for the hydrosilylation of internal arylalkynes [18]. Unfortunately, in the case of terminal alkynes, the regioselectivity of the H–Si bond addition with triethysilane was found to be weak providing a mixture of the branched α-isomer and β-(E)-vinylsilane isomer. To ensure the synthetic utility of terminal arylalkynes hydrosilylation, both the regio- and stereoselectivity of this process must be addressed. Therefore, we anticipated that the tuning of platinum complex catalysts (platinum species and ligands) would affect the regioselectivity of H–Si bond addition. Herein, our detailed study is reported [19]. We found that the use of 2-dicyclohexyl-phosphino-2′,4′,6′-triisopropylbiphenyl (Xphos) (Scheme 3) associated with PtO_2 or $PtCl_2$ proved to be efficient and versatile catalytic systems for the highly selective formation of β-(E)-styrylsilanes **2**. The selectivity issues of this reaction mediated by platinum have been studied extensively and contributions of steric, electronic and coordinative factors controlling this regioselectivity are discussed.

2. Results and discussion

For optimization of our reaction conditions, the hydrosilylation of commercially available phenylacetylene with triethylsilane was chosen as a model substrate to evaluate the effects of various solvents, platinum catalysts and ligands. The results are summarized in Table 1.
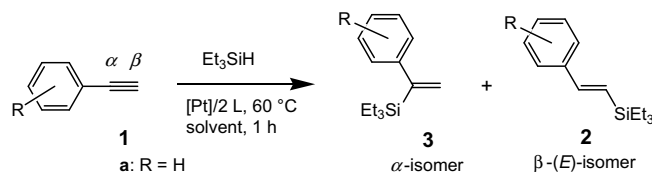
2.1. Optimization of the platinum-catalyzed hydrosilylation of phenylacetylene

To begin our study, phenylacetylene **1a** was reacted with Et_3SiH (1.5 equiv.) in the presence of PtO_2 (5 mol%). Without solvent at 60 °C, the reaction proceeded in 1 h and gave a 15:85 mixture of vinylsilanes **2a** and **3a** and no β-(Z)-isomer was detected (Table 1, entry 1). Performing the reaction at room temperature resulted in a similar selectivity but with a prolonged reaction time (16 h). We next investigated the hydrosilylation in various solvents and found that similar selectivities were obtained when C_6H_6 and THF were employed (entries 2 and 3). Use of other non-protic polar solvents such as DMF or NMP provided a slightly lower β-(E)-selectivity (entries 4 and 5). Employment of both EtOH, HFIP or H_2O can replace THF to achieve same level of selectivity (entries 6–8).

As the ligand nature has been previously shown to affect the hydrosilylation selectivity [14,16], we examined the process in the presence of a range of phosphine ligands. With PtO_2/PPh_3 as the catalytic system, no reaction took place (entry 9). Changing the monodentate ligand triphenylphosphine to electron rich and bulky ligand PCy_3 gave an excellent β-(E)-selectivity (entry 10) whereas P(t-Bu)₃ induced a dramatic lowering of the conversion rate (entry 11). We were delighted to find that the catalytic activity of the heterogeneous PtO_2/Xphos system proved to be superior to the catalyst couple PtO_2/PCy_3 leading, with an excellent yield, to a total control of the β-(E)-selectivity (entry 12). The use of bidentate phosphine ligands (dppp, dppb, dppf or BINAP) however, induced a dramatic lowering of the conversion rate associated with a significant change on the α:β ratio (entries 13–16).

Table 1
Screening of solvents and phosphines ligands for platinum-catalyzed hydrosilylation of phenylacetylene (**1a**) with triethylsilane

Entry [Pt]	L	Solvent	α/β^a ratio	Conv.^{a} (%)	Yield^b (%)
1 PtO₂	–	–	15:85	100	86^c
2 PtO₂	–	C₆H₆	10:90	100	88
3 PtO₂	–	THF	9:91	100	95
4 PtO₂	–	DMF	20:80	100	62
5 PtO₂	–	NMP	24:76	100	68
6 PtO₂	–	H₂O	10:90	100	71
7 PtO₂	–	EtOH	8:92	100	67
8 PtO₂	–	HFIP^d	12:88	100	45
9 PtO₂	PPh₃	THF	–	0	–
10 PtO₂	PCy₃	THF	4:96	100	92
11 PtO₂	P t-Bu₃	THF	0:100	15	nd
12 PtO₂	**Xphos^e**	**THF**	**0:100**	**100**	**96**
13 PtO₂	dppp	THF	–	0	–
14 PtO₂	dppb	THF	19:81	13	nd^f
15 PtO₂	dppf	THF	15:85	14	nd
16 PtO₂	BINAP	THF	10:90	12	nd
17 Pt/C	Xphos	THF	0:100	10	nd
18 H₂PtCl₆	Xphos	THF	3:97	100	56
19 PtCl₄	Xphos	THF	0:100	100	75
20 PtCl₂	**Xphos**	**THF**	**0:100**	**100**	**98**

^{a} Determined by GC analysis and ^1H NMR in the crude reaction mixture.
^{b} Isolated yield of the mixture of vinylsilanes **2** and **3** after column chromatography.
^{c} At room temperature, the reaction required 16 h for completion and led to a 10:90 α/β ratio in a 76% yield.
^{d} Hexafluoroisopropanol.
^{e} By using a 1:1 ratio of Pt:L (5 mol%), **3a** was exclusively formed (α:β = 0:100) in 82% yield.
^{f} nd: not determined.

Considering its high catalytic activity, ligand Xphos was evaluated with other platinum sources. With heterogeneous Pt/C, although a total β-(E)-selectivity was obtained the conversion rate was mediocre (entry 17). Next, homogeneous platinum catalysts were examined. Speier's (H_2PtCl_6) catalyst associated with Xphos afforded a high β-regiocontrol (α:β = 3:97) within a moderate isolated yield (entry 18). More interestingly, a total control of the β-(E)-selectivity was observed when using the catalyst systems $PtCl_4$/Xphos or $PtCl_2$/Xphos with good to excellent isolated yield respectively (entries 19 and 20). Finally, the increase of the amount of catalyst, ligand or silane, had no significant improvement in the yield of the hydrosilylation reaction.

2.2. Hydrosilylation of phenylacetylene with various hydrosilanes

As the silane source is well-known to influence the α:β distribution [13a], we examined the effect of other hydrosilanes under our optimized conditions and the results of this screening are presented in Table 2.

Contrary to our expectation, all the hydrosilanes examined including $PhMe_2SiH$, Ph_2MeSiH, $EtOMe_2SiH$ or $(EtO)_3SiH$ showed an exclusive β-regiocontrol. Therefore, Xphos associated with either PtO_2 or $PtCl_2$ proved to be a versatile and efficient ligand for the hydrosilylation of phenylacetylene with various hydrosilanes.

Table 2
PtO$_2$/Xphos and PtCl$_2$/Xphos complexes-catalyzed hydrosilylation of phenylacetylene (**1a**) with various hydrosilanes
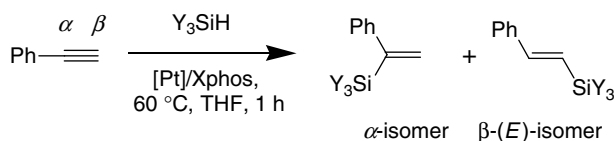
Entry [Pt]	Y$_3$SiH	α/β ratio[a]	β-(E)-vinylsilane **2**	Yield[b] (%)
1 PtO$_2$	PhMe$_2$SiH	0:100	SiMe$_2$Ph **2b**	96
2 PtCl$_2$	PhMe$_2$SiH	0:100		94
3 PtO$_2$	Ph$_2$MeSiH	0:100	SiPh$_2$Me **2c**	95
4 PtCl$_2$	Ph$_2$MeSiH	0:100		97
5 PtO$_2$	EtOMe$_2$SiH	0:100	SiMe$_2$OEt **2d**	61[c]
6 PtCl$_2$	EtOMe$_2$SiH	0:100		64[c]
7 PtO$_2$	(EtO)$_3$SiH	0:100	Si(OEt)$_3$ **2e**	72
8 PtCl$_2$	(EtO)$_3$SiH	0:100		68

[a] Determined by GC analysis and ^{1}H NMR in the crude reaction mixture.
[b] Isolated yield.
[c] Reaction was performed at room temperature within 12 h. At 60 °C, less than 2% of α-isomer was detected.

2.3. Scope and limitations

We next selected the PtO$_2$/Xphos catalyst system for evaluating the scope of this hydrosilylation with a range variety of functionalized terminal arylalkynes. As seen in Table 3, functionalized arylalkynes were converted in 1 h at 60 °C with Et$_3$SiH to the corresponding vinylsilanes in good to excellent yields. Analysis of the crude reaction mixtures by ^{1}H NMR spectroscopy revealed no trace of the β-(Z)-vinylsilanes demonstrating that the H–Si bond addition proceeded exclusively in a *syn* fashion. Additionally, the reaction exhibited a remarkable selectivity for β-(E)-vinylsilanes.

Arylalkynes with a *para*- or a *meta*-electron donating group (*e.g.* EDG = OMe, Me) were cleanly hydrosilylated in the presence of PtO$_2$/Xphos couple to their corresponding β-(E)-adducts with excellent yields (entries 1, 2 and 4). One can note that in the absence of any ligand, hydrosilylation of *para*-methoxyphenylacetylene (**1b**) produced a 18:82 mixture of α:β adducts. Next, we evaluated the influence of ortho substituents on the reaction selectivity [20]. By switching the substituent group from the para or meta to the ortho position, again a total β-regiocontrol was observed (entries 3 and 5). This result clearly demonstrated that the regioselectivity of the H–Si bond addition is governed by steric effects induced by Xphos ligand rather than ortho-directing effect (ODE) as we previously reported [18]. To support this explanation, the hydrosilylation of ortho methoxyphenylacetylene was conducted without Xphos and produced a 38:62 ratio of α:β regioisomers.

Encouraged by these findings, we examined the reaction with terminal arylalkynes having an electron withdrawing group. Surprisingly under the above optimized conditions (PtO$_2$/Xphos), no reaction took place with *para*-methoxycarbonyl phenylacetylene (entry 6). We were pleased to observe however, that using the alternative PtCl$_2$/Xphos catalytic system the hydrosilylation proceeded cleanly leading to a single β-(E)-vinylsilane in excellent yield (entry 7). Similarly, a total β-(E)-selectivity was also observed with *p*-CN and *p*-Br-substituted phenylacetylene (entries 8 and 9) indicating clearly that steric effects totally supplant electronic

effects of substituents. However, with *ortho*-methoxycarbonyl phenylacetylene (**1j**), the PtCl$_2$-catalyzed hydrosilylation was less selective and led to a regioisomeric mixture with a preference for the β-isomer (α:β = 19:81, entry 10). This result clearly shows that ODE, which is opposed to steric effects, [18a] rebalance the isomeric distribution, thus increasing the amounts of α-adduct. To show the versatility of the PtCl$_2$/Xphos couple, we examined its catalytic activity with alkynes having an electron donating group. Thus, the hydrosilylation of both *para*- and *ortho*-methoxyphenylacetylene exclusively produced the desired β-(E) vinylsilanes **2** with excellent yields (entries 11 and 12). In the following example (entry 13), it is interesting to note that 2-pyridylacetylene was regioselectively hydrosilylated with Et$_3$SiH and PtCl$_2$/Xphos couple without any difficulties. After completing cursory investigation of functionalized terminal arylalkynes, further examination revealed that the PtCl$_2$/Xphos system efficiently catalyzes the hydrosilylation of terminal aliphatic alkynes. With triethylsilane, reactions gave complete conversion of the substrate alkynes **1l** and **1m** at 60 °C within 1 h to afford exclusively their corresponding β-(E)-vinylsilanes **2p** and **2q**, respectively (entries 14 and 15).

We were also pleased to observe that the PtCl$_2$/Xphos couple was still efficient with aliphatic alkynes bearing a primary or secondary alcohol function (entries 16 and 17). Inspired by the success of the versatile and easy to handle PtCl$_2$/Xphos catalyst system, we turned our attention to the preparation of a variety of functionalized vinylalkoxysilanes. The results of this study are reported in Table 4 and clearly indicated the efficiency of the present methodology.

Performing the reaction with various alkoxysilanes resulted in the formation of vinylalkoxysilanes **2t-z** in good yields. Electron-donating and electron-withdrawing substituents on the aromatic ring did not interfere with the outcome of the present reaction and similar yields and selectivities were obtained (entries 1–5). Further examination revealed that the PtCl$_2$/Xphos system efficiently catalyzed the hydrosilylation of aliphatic alkynes. Complete conversion of the starting alkynes was observed within 1 h affording exclusively their corresponding β-(E)-vinyldimethylethoxysilanes in good yields (entries 6 and 7) showing in this manner the general character of the present process.
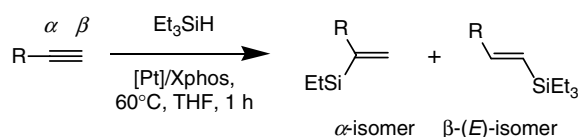
The synthetic utility of β-(E)-styrylalkoxysilanes was successfully demonstrated in the Hiyama coupling reaction [3]. Thus, selective palladium-catalyzed cross-coupling of styryldimethylethoxysilane **2u** with iodobenzene according to Trost's conditions [21] resulted in the formation of the coupling product in good yield 85% (Scheme 2).
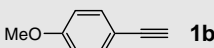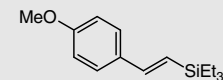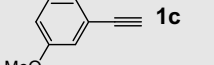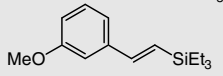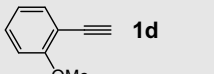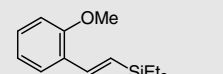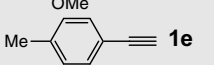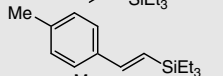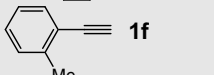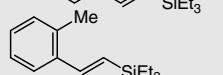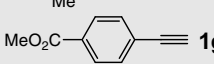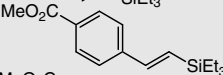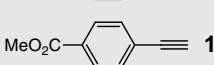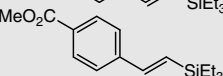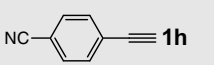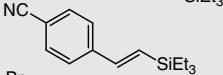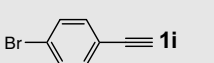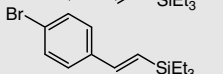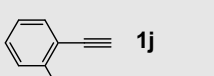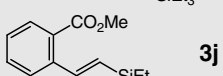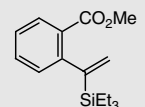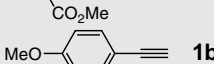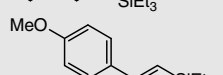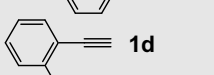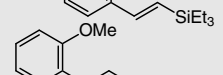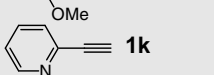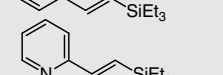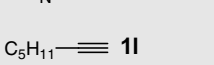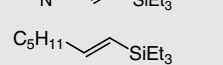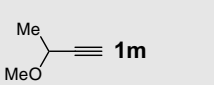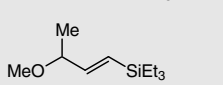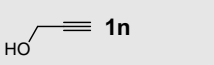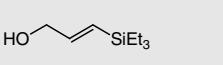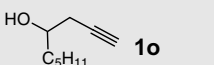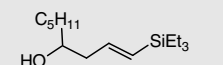
3. Mechanistic considerations

Although there is no clear experimental evidence, it is interesting to speculate on the mechanism of the hydrosilylation reaction that rationalizes the observed β-(E)-selectivity. Initially, the PtCl$_2$L$_2$ complex is formed from PtCl$_2$ and Xphos ligand [22] which is then reduced with the silane to metal platinum(0) catalyst, associated with one or two ligands. The next step involves oxidative addition of the silane to the platinum species to generate the platinum complex **I** or **II** and a further coordination with the alkyne would afford species **III** (Scheme 3).

Then the alkyne would insert into the Pt–H bond (Chalk–Harrod mechanism) rather than Pt–Si bond as was suggested by ab initio molecular orbital and Møller–Plesset perturbation theory calculations [23]. In the presence of Xphos ligand, the total selectivity for the β-(E)-isomers **2** can be rationalized by the formation of the species **A** as it would be sterically less demanding and constitutes the unique pathway to furnish vinyl organometallic **IV**, while species **B**, is more congested due to steric repulsion between the R substituent and the hindered Xphos ligand. This argument is

Table 3
PtO$_2$/Xphos and PtCl$_2$/Xphos complexes-catalyzed hydrosilylation of various functionalized terminal alkynes with triethylsilane

Entry	Alkyne **1**	[Pt]	α/β[a] ratio	Vinylsilanes[b] **2**		Yield[c] (%)
1	**1b** (MeO–C$_6$H$_4$–C≡CH)	PtO$_2$	0:100[d]	**2f**		91
2	**1c** (m-MeO–C$_6$H$_4$–C≡CH)	PtO$_2$	0:100	**2g**		92
3	**1d** (o-OMe–C$_6$H$_4$–C≡CH)	PtO$_2$	0:100[e]	**2h**		98
4	**1e** (Me–C$_6$H$_4$–C≡CH)	PtO$_2$	0:100	**2i**		88
5	**1f** (o-Me–C$_6$H$_4$–C≡CH)	PtO$_2$	0:100	**2j**		93
6	**1g** (MeO$_2$C–C$_6$H$_4$–C≡CH)	PtO$_2$	–	**2k**		0[f]
7	**1g**	PtCl$_2$	0:100	**2k**		86
8	**1h** (NC–C$_6$H$_4$–C≡CH)	PtCl$_2$	0:100	**2l**		80
9	**1i** (Br–C$_6$H$_4$–C≡CH)	PtCl$_2$	0:100	**2m**		94
10	**1j** (o-CO$_2$Me–C$_6$H$_4$–C≡CH)	PtCl$_2$	19:81	**2n**	**3j**	83[g]
11	**1b**	PtCl$_2$	0:100	**2f**		88
12	**1d**	PtCl$_2$	0:100	**2h**		92
13	**1k** (pyridin-2-yl–C≡CH)	PtCl$_2$	0:100	**2o**		98[h]
14	**1l** (C$_5$H$_{11}$–C≡CH)	PtCl$_2$	0:100	**2p** (C$_5$H$_{11}$–CH=CH–SiEt$_3$)		93
15	**1m** (Me, MeO)	PtCl$_2$	0:100	**2q**		96
16	**1n** (HO–CH$_2$–C≡CH)	PtCl$_2$	0:100	**2r** (HO–CH$_2$–CH=CH–SiEt$_3$)		96[i]
17	**1o** (HO, C$_5$H$_{11}$)	PtCl$_2$	0:100	**2s**		96

[a] Determined by ^{1}H NMR in the crude reaction mixture.
[b] All of the reported compounds exhibited spectral data in agreement with the assigned structures.
[c] Isolated yield.
[d] A 18:82 α:β mixture was obtained in the absence of Xphos ligand.
[e] A 38:62 α:β mixture was obtained in the absence of Xphos ligand.
[f] Reproducible result after three runs and starting alkyne was recovered unchanged.
[g] Isolated yield of the vinylsilane α:β mixture after column chromatography.
[h] 10 mol% of PtCl$_2$ and 20 mol% of Xphos were used.
[i] Reaction was performed at r.t.
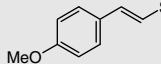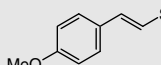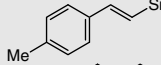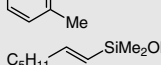
consistent with the fact that in the absence of ligand, the hydrosilylation exhibited a poor regioselectivity (see footnotes d and e, Table 3) probably due to the diminished steric requirements around the platinum center in both species **C** and **D**.

Table 4
Preparation of functionalized β-(E)-vinylalkoxysilanes **2** using the PtCl₂/Xphos complex
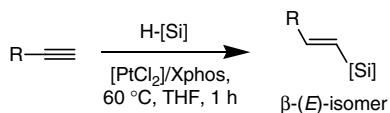
Entry	Vinylalkoxysilanes **2**[a]	α/β ratio[b]	Yield[c](%)
1	2t	2:98	65
2	2u	0:100	83[d]
3	2v	2:98	83
4	2w	3:97	68
5	2x	0:100	75
6	2y	0:100	94
7	2z	0:100	72[d]

[a] All of the reported compounds exhibited spectral data in agreement with the assigned structures.

[b] Determined by GC analysis and ¹H NMR in the crude reaction mixture.

[c] Isolated yield.
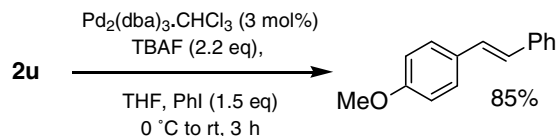
Scheme 2.

4. Conclusion

In conclusion, we have demonstrated that the use of the commercially available PtO₂ or PtCl₂ catalysts in conjunction with the air-stable and bulky Xphos ligand constitutes a versatile combination for the selective hydrosilylation of a series of functionalized terminal arylalkynes as well as aliphatic alkynes. Results from these studies indicated that various silanes including alkoxysilanes could be used successfully to provide β-(E)-vinylsilanes with high or even total selectivity. This catalytic hydrosilylation protocol is characterized by its excellent chemo, regio-, and stereoselectivity, functional group compatibility and mild reaction conditions. It represents a very attractive procedure for the univocal synthesis of β-(E)-vinylsilanes from terminal alkynes and should find many applications in organic synthesis. Future developments will focus on several synthetic applications of these vinylsilanes.

5. Experimental

5.1. General

All glasswares were oven-dried at 140 °C and all reactions were conducted under a nitrogen atmosphere. Solvents for chromato-
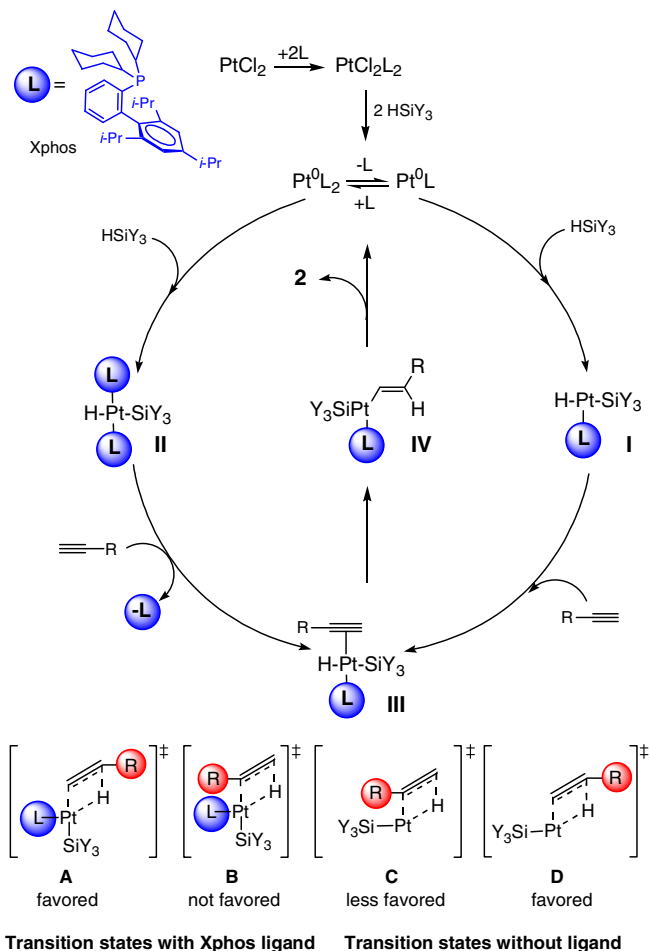
Scheme 3. Proposed Chalk–Harrod mechanism for the platinum-catalyzed hydrosilylation of terminal alkynes.

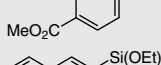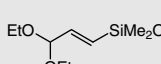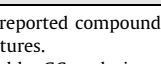graphy: cyclohexane, ethyl acetate (EtOAc), were technical grade. Tetrahydrofuran (THF) was distilled under argon from sodium-benzophenone ketyl.

The compounds were all identified by usual physical methods, i.e. ¹H NMR, ¹³C NMR, IR, elemental analysis. ¹H and ¹³C NMR spectra were measured in CDCl₃ or DMSO-d_6 with a Bruker ARX 400 or Bruker Avance 300 and chemical shifts are reported in ppm. The following abbreviation are used: m (multiplet), s (singlet), br s (broad singlet), d (doublet), t (triplet) dd (doublet of doublet), td (triplet of doublet), q (quadruplet). IR spectra were measured on a Bruker Vector 22 spectrophotometer (neat, cm⁻¹). Elemental analyses were performed with a Perkin–Elmer 240 analyser. Analytical TLC was performed on Merck precoated silica gel 60F plates. Merck silica gel 60 (230–400 mesh) was used for column chromatography.

5.2. Experimental procedure for the PtCl₂ or PtO₂-catalyzed hydrosilylation of terminal alkynes

Under a nitrogen atmosphere, PtCl₂ (13 mg; 0.05 mmol) or PtO₂ (11 mg; 0.05 mmol) and Xphos (48 mg; 0.1 mmol) in THF (0.5 mL) were heated at 60 °C for 15 min. Then, terminal alkyne (1 mmol) and hydrosilane (1.5 mmol) were successively added via syringe and the mixture was stirred at 60 °C for 1 h. After evaporation of the solvent, the residue was purified by column chromatography to yield the (E)-vinylsilane **2**.

5.2.1. (E)-1-triethylsilyl-2-phenylethene (2a) [16]

Yield: colorless oil, 98%.

TLC: R_f 0.61 (cyclohexane, SiO_2).

IR (neat, cm^{-1}): 3023, 2952, 2909, 2874, 1603, 1574, 1494, 1458, 1416, 1236, 1198, 1072, 1012, 988, 827, 784, 734.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.55 (q, 6H, J = 7.6 Hz), 0.87 (t, 9H, J = 7.6 Hz), 6.31 (d, 1H, J = 19.3 Hz), 6.78 (d, 1H, J = 19.3 Hz), 7.12 (t, 1H, J = 7.3 Hz), 7.21 (d, 2H, J = 7.3 Hz), 7.33 (d, 2H, J = 7.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 3.5 (3 CH_2), 7.4 (3 CH_3), 126.0 (CH), 126.3 (2 CH), 127.9 (CH), 128.5 (2 CH), 138.5 (C), 144.8 (CH).

MS(EI): 218 (M$^+$).

Anal. Calc. for $C_{14}H_{22}Si$ (218.41): C, 76.99; H, 10.15. Found: C, 77.12; H, 10.05%.

5.2.2. (E)-1-dimethylphenylsilyl-2-phenylethene (2b) [11]

Yield: colorless oil, 94%.

TLC: R_f 0.40 (cyclohexane, SiO_2).

IR (neat, cm^{-1}): 3067, 3023, 2956, 1605, 1573, 1494, 1447, 1427, 1334, 1248, 1215, 1196, 1114, 1068, 1028, 989, 844, 828, 808, 774, 726, 697, 689.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.46 (s, 6H), 6.61 (d, 1H, J = 19.1 Hz), 7.00 (d, 1H, J = 19.1 Hz), 7.20–7.42 (m, 6H), 7.46 (d, 2H, J = 7.3 Hz), 7.53–7.65 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ −2.5 (2 CH_3), 126.5 (2 CH), 127.1 (CH), 127.8 (2 CH), 128.1 (CH), 128.5 (2 CH), 129.0 (CH), 133.0 (CH), 133.9 (CH), 138.1 (C), 138.5 (C), 145.3 (CH).

MS(EI): 238 (M$^+$).

Anal. Calc. for $C_{16}H_{18}Si$ (238.40): C, 80.61; H, 7.61. Found: C, 80.47; H, 7.56%.

5.2.3. (E)-1-methyldiphenylsilyl-2-phenylethene (2c) [24]

Yield: colorless oil, 97%.

TLC: R_f 0.21 (cyclohexane, 100%, SiO_2).

IR (neat, cm^{-1}): 3067, 3021, 2958, 1602, 1573, 1494, 1446, 1427, 1333, 1251, 1215, 1104, 1111, 834, 801, 785, 730.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76 (s, 3H), 6.80 (d, 1H, J = 19.1 Hz), 7.02 (d, 1H, J = 19.1 Hz), 7.26–7.47 (m, 9H), 7.51–7.68 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ −3.6 (CH$_3$), 125.0 (CH), 126.7 (2 CH), 128.0 (4 CH), 128.4 (CH), 128.6 (2 CH), 129.4 (2 CH), 135.0 (4 CH), 136.5 (2 C), 138.0 (C), 147.2 (CH).

MS(EI): 300 (M$^+$).

Anal. Calc. for $C_{21}H_{20}Si$ (300.47): C, 83.94; H, 6.71. Found: C, 83.90; H, 6.82%.

5.2.4. (E)-1-ethoxydimethylsilyl-2-phenylethene (2d) [25]

Yield: yellow oil, 64%.

TLC: R_f 0.43 (Et$_2$O/cyclohexane, 5/95, SiO_2).

IR (neat, cm^{-1}): 3024, 2964, 2925, 1605, 1574, 1495, 1447, 1390, 1250, 1104, 1074, 1029, 991, 832, 813, 780, 758.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 6H), 1.10 (t, 3H, J = 7.0 Hz), 3.60 (q, 2H, J = 7.0 Hz), 6.30 (d, 1H, J = 19.3 Hz), 6.90 (d, 1H, J = 19.3 Hz), 7.09–7.25 (m, 3H), 7.33 (d, 2H, J = 6.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ −1.6 (2 CH_3), 18.6 (CH$_3$), 58.6 (CH$_2$), 126.5 (CH), 126.7 (2 CH), 128.4 (CH), 128.6 (2 CH), 138.0 (C), 145.6 (CH).

MS(ESI): 207 (M+H)$^+$, 229 (M+Na)$^+$.

Anal. Calc. for $C_{12}H_{18}OSi$ (206.36): C, 69.84; H, 8.79. Found: C, 69.85; H, 8.70%.

5.2.5. (E)-1-triethoxysilyl-2-phenylethene (2e) [24]

Yield: colorless oil, 70%.

TLC: R_f 0.23 (Et$_2$O/cyclohexane, 5/95, SiO_2).

IR (neat, cm^{-1}): 2974, 2885, 1603, 1574, 1495, 1447, 1390, 1293, 1219, 1197, 1166, 1099, 1071, 995, 956, 838, 775, 733.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (t, 9H, J = 7.0 Hz), 3.91 (q, 6H, J = 7.0 Hz), 6.20 (d, 1H, J = 19.3 Hz), 7.24 (d, 1H, J = 19.3 Hz), 7.28–7.39 (m, 3H), 7.50 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3 (3 CH_3), 58.6 (3 CH_2), 117.7 (CH), 126.8 (2 CH), 128.6 (2 CH), 128.8 (CH), 137.6 (C), 149.2 (CH).

MS(ESI): 267 (M+H)$^+$, 289 (M+Na)$^+$.

Anal. Calc. for $C_{14}H_{22}O_3Si$ (266.41): C, 63.12; H, 8.32. Found: C, 62.97; H, 8.31%.

5.2.6. (E)-1-triethylsilyl-2-(4-methoxyphenyl)ethene (2f) [18b]

Yield: colorless oil, 91%.

TLC: R_f 0.5 (Et$_2$O/cyclohexane, 5/95, SiO_2).

IR (neat, cm^{-1}): 2952, 2909, 2874, 2835, 1606, 1570, 1508, 1463, 1441, 1416, 1378, 1332, 1303, 1294, 1250, 1171, 1106, 1037, 1014, 986, 843, 789, 749, 717.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.57 (q, 6H, J = 7.8 Hz), 0.90 (t, 9H, J = 7.8 Hz), 3.72 (s, 3H), 6.17 (d, 1H, J = 19.3 Hz), 6.70–6.82 (m, 3H), 7.30 (d, 2H, J = 8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 3.7 (3 CH_2), 7.6 (3 CH_3), 55.4 (OCH$_3$), 114.0 (2 CH), 123.1 (CH), 127.6 (2 CH), 131.7 (C), 144.3 (CH), 159.6 (C).

MS(ESI): 248 (M$^+$).

Anal. Calc. for $C_{15}H_{24}OSi$ (248.44): C, 72.52; H, 9.74. Found: C, 72.48; H, 9.82%.

5.2.7. (E)-1-triethylsilyl-2-(3-methoxyphenyl)ethene (2g)

Yield: colorless oil, 92%.

TLC: R_f 0.54 (Et$_2$O/cyclohexane, 5/95, SiO_2).

IR (neat, cm^{-1}): 2952, 2909, 2874, 2834, 1598, 1575, 1485, 1456, 1431, 1416, 1378, 1317, 1286, 1263, 1237, 1202, 1152, 1080, 1049, 1013, 986, 923, 906, 859, 794, 766.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.58 (q, 6H, J = 7.8 Hz), 0.91 (t, 9H, J = 7.8 Hz), 3.75 (s, 3H), 6.33 (d, 1H, J = 19.3 Hz), 6.70–6.74 (m, 1H), 6.78 (d, 1H, J = 19.3 Hz), 6.88–7.00 (m, 2H), 7.17 (t, 1H, J = 7.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 3.6 (3 CH_2), 7.5 (3 CH_3), 55.4 (OCH$_3$), 111.3 (CH), 113.8 (CH), 119.2 (CH), 126.4 (CH), 129.6 (CH), 140.12 (C), 144.8 (CH), 160.0 (C).

MS(ESI): 248 (M$^+$).

Anal. Calc. for $C_{15}H_{24}OSi$ (248.44): C, 72.52; H, 9.74. Found: C, 72.87; H, 9.54%.

5.2.8. (E)-1-triethylsilyl-2-(2-methoxyphenyl)ethene (2h) [18b]

Yield: colorless oil, 98%.

TLC: R_f 0.70 (Et$_2$O/cyclohexane, 30/70, SiO_2).

IR (neat, cm^{-1}): 2952, 2909, 2874, 2835, 1596, 1485, 1462, 1437, 1416, 1327, 1288, 1241, 1211, 1176, 1161, 1104, 1050, 1030, 1015, 994, 973, 852, 833, 802, 747, 720.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.59 (q, 6H, J = 7.8 Hz), 0.91 (t, 9H, J = 7.8 Hz), 3.77 (s, 3H), 6.31 (d, 1H, J = 19.5 Hz), 6.75-6.92 (m, 2H), 7.10-7.30 (m, 2H), 7.47 (dd, 1H, J = 7.7 Hz, J = 1.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 3.7 (3 CH_2), 7.6 (3 CH_3), 55.7 (OCH$_3$), 111.1 (CH), 120.7 (CH), 126.2 (CH), 126.3 (CH), 127.9 (C), 129.0 (CH), 139.2 (CH), 156.7 (C).

MS(ESI): 248 (M$^+$).

Anal. Calc. for $C_{15}H_{24}OSi$ (248.44): C, 72.52; H, 9.74. Found: C, 72.64; H, 9.80%.

5.2.9. (E)-1-triethylsilyl-2-(4-methylphenyl)ethene (2i) [26]

Yield: colorless oil, 88%.

TLC: R_f 0.60 (cyclohexane, SiO_2).

IR (neat, cm^{-1}): 2952, 2909, 2874, 1608, 1566, 1510, 1458, 1415, 1377, 1236, 1197, 1178, 1115, 1014, 986, 842, 790, 778, 753, 715.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81 (q, 6H, J = 7.9 Hz), 1.13 (t, 9H, J = 7.9 Hz), 2.45 (s, 3H), 6.50 (d, 1H, J = 19.3 Hz), 7.02 (d, 1H, J = 19.3 Hz), 7.26 (d, 2H, J = 8.0 Hz), 7.47 (d, 2H, J = 8.0 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.7 (3 CH$_2$), 7.5 (3 CH$_3$), 21.3 (CH$_3$), 124.5 (CH), 126.4 (2 CH), 129.3 (2 CH), 136.0 (C), 137.8 (C), 144.9 (CH).

MS(EI): 232 (M$^+$).

Anal. Calc. for C$_{15}$H$_{24}$Si (232.44): C, 77.51; H, 10.41. Found: C, 77.48; H, 9.95%.

5.2.10. (E)-1-triethylsilyl-2-(2-methylphenyl)ethene (2j) [26]

Yield: yellow oil, 93%.

TLC: R_f 0.67 (cyclohexane, 100%, SiO$_2$).

IR (neat, cm^{-1}): 2952, 2909, 2874, 1596, 1569, 1479, 1458, 1415, 1379, 1288, 1236, 1208, 1011, 989, 973, 805, 741, 717.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.58 (q, 6H, J = 7.9 Hz), 0.92 (t, 9H, J = 7.9 Hz), 2.30 (s, 3H), 6.22 (d, 1H, J = 19.2 Hz), 6.96–7.17 (m, 4H), 7.38-7.48 (m, 1H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.8 (3 CH$_2$), 6.9 (3 CH$_3$), 19.8 (CH$_3$), 125.4 (CH), 126.2 (CH), 127.8 (CH), 127.9 (CH), 130.4 (CH), 135.3 (C), 138.1 (C), 142.9 (CH).

MS(EI): 232 (M$^+$).

Anal. Calc. for C$_{15}$H$_{24}$Si (232.44): C, 77.51; H, 10.41. Found: C, 77.37; H, 10.30%.

5.2.11. (E)-1-triethylsilyl-2-(4-methoxycarbonyl phenyl) -ethene (2k)

Yield: brown oil, 86%.

TLC: R_f 0.32 (Et$_2$O/cyclohexane, 5/95, SiO$_2$).

IR (neat, cm^{-1}): 2952, 2910, 2874, 1721, 1605, 1564, 1458, 1435, 1409, 1308, 1274, 1242, 1215, 1194, 1174, 1106, 1016, 988, 969, 867, 843, 806, 782, 752, 690.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.58 (q, 6H, J = 7.9 Hz), 0.89 (t, 9H, J = 7.9 Hz), 3.81 (s, 3H), 6.49 (d, 1H, J = 19.3 Hz), 6.83 (d, 1H, J = 19.3 Hz), 7.39 (d, 2H, J = 8.3 Hz), 7.90 (d, 2H, J = 8.3 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.3 (3 CH$_2$), 7.5 (3 CH$_3$), 52.1 (CH$_3$), 126.3 (2 CH), 129.1 (C), 129.8 (CH), 130.0 (2 CH), 142.7 (C), 143.8 (CH), 167.0 (C).

MS(ESI): 277 (M+H)$^+$, 299 (M+Na)$^+$.

Anal. Calc. for C$_{16}$H$_{24}$O$_2$Si (276.45): C, 69.51; H, 8.75. Found: C, 69.64; H, 8.53%.

5.2.12. (E)-1-triethylsilyl-2-(4-cyanophenyl)ethene (2l) [26]

Yield: yellow oil, 80%.

TLC: R_f 0.62 (AcOEt/cyclohexane, 10/90, SiO$_2$).

IR (neat, cm^{-1}): 2953, 2910, 2874, 2227, 1604, 1555, 1501, 1458, 1410, 1379, 1283, 1236, 1197, 1174, 1011, 988, 858, 839, 784, 723, 678, 579.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.44 (q, 6H, J = 7.8 Hz), 0.75 (t, 9H, J = 7.8 Hz), 6.38 (d, 1H, J = 19.3 Hz), 6.66 (d, 1H, J = 19.3 Hz), 7.28 (d, 2H, J = 8.3 Hz), 7.39 (d, 2H, J = 8.3 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.5 (3 CH$_2$), 7.5 (3 CH$_3$), 111.1 (C), 119.1 (CN), 126.9 (2 CH), 131.7 (CH), 132.5 (2 CH), 142.7 (C), 143.0 (CH).

MS(ESI): 266 (M+Na)$^+$, 509 (2M+Na)$^+$.

Anal. Calc. for C$_{15}$H$_{21}$NSi (243.42): C, 74.01; H, 8.70; N, 5.75. Found: C, 73.97; H, 8.71; N, 5.63%.

5.2.13. (E)-1-triethylsilyl-2-(4-bromophenyl)ethene (2m)

Yield: yellow oil, 94%.

TLC: R_f 0.68 (cyclohexane, SiO$_2$).

IR (neat, cm^{-1}): 2952, 2908, 2873, 1603, 1587, 1560, 1485, 1458, 1415, 1396, 1379, 1327, 1236, 1212, 1197, 1072, 1008, 986, 846, 828, 806, 780, 717, 633, 581.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.58 (q, 6H, J = 7.7 Hz), 0.91 (t, 9H, J = 7.7 Hz), 6.33 (d, 1H, J = 19.3 Hz), 6.74 (d, 1H, J = 19.3 Hz), 7.22 (d, 2H, J = 8.5 Hz), 7.37 (d, 2H, J = 8.5 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 7.5 (3 CH$_2$), 7.5 (3 CH$_3$), 121.8 (C), 127.3 (CH), 127.9 (2 CH), 131.7 (2 CH), 137.5 (C), 143.6 (CH).

MS(EI): 296, 298 (M$^+$).

Anal. Calc. for C$_{14}$H$_{21}$BrSi (297.31): C, 56.56; H, 7.12. Found: C, 56.45; H, 7.20%.

5.2.14. (E)-1-triethylsilyl-2-(2-methoxycarbonyl phenyl)-ethene (2n)

Yield: colorless oil, 83% α/β (ca. 19/81) mixture of isomers.

TLC: R_f 0.42 (Et$_2$O/cyclohexane, 5/95, SiO$_2$).

IR (neat, cm^{-1}): 2951, 2909, 2874, 1721, 1598, 1563, 1475, 1458, 1433, 1416, 1289, 1256, 1200, 1126, 1076, 1047, 1011, 988, 819, 783, 740, 720, 666, 604, 571.

^{1}H NMR (300 MHz, CDCl$_3$): major β-isomer: δ 0.62 (q, 6H, J = 7.6 Hz), 0.94 (t, 9H, J = 7.6 Hz), 3.80 (s, 3H), 6.24 (d, 1H, J = 19.2 Hz), 7.19 (td, 1H, J = 7.6 Hz, J = 1.2 Hz), 7.36 (td, 1H, J = 7.6 Hz, J = 1.2 Hz), 7.48–7.61 (m, 2H), 7.76 (dd, 1H, J = 7.6 Hz, J = 1.2 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): major β-isomer: δ 3.6 (3 CH$_2$), 7.4 (3 CH$_3$), 51.8 (OCH$_3$), 127.2 (CH), 127.3 (CH), 128.5 (C), 129.2 (CH), 130.0 (CH), 132.0 (CH), 140.6 (C), 143.9 (CH), 168.0 (C).

^{1}H NMR (300 MHz, CDCl$_3$): minor α-isomer: δ 3.70 (s, 3H), 5.48 (d, 1H, J = 3.0 Hz), 5.53 (d, 1H, J = 3.0 Hz). (Only the most significant resonances are listed).

MS(EI): 276 (M$^+$).

Anal. Calc. for C$_{16}$H$_{24}$O$_2$Si (276.45): C 69.51, H 8.75 Found: C 69.29, H 8.70%.

5.2.15. (E)-1-triethylsilyl-2-(4-pyridyl)ethene (2o)

Yield: yellow oil, 98%.

TLC: R_f 0.51 (Et$_2$O/cyclohexane, 30/70, SiO$_2$).

IR (neat, cm^{-1}): 3002, 2952, 2909, 2874, 1583, 1562, 1462, 1427, 1378, 1322, 1297, 1237, 1192, 1148, 1049, 993, 843, 785, 750, 719, 629, 565.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.60 (q, 6H, J = 7.7 Hz), 0.92 (t, 9H, J = 7.7 Hz), 6.85 (d, 1H, J = 19.2 Hz), 6.94 (d, 1H, J = 19.2 Hz), 7.00–7.10 (m, 1H), 7.29 (d, 1H, J = 7.9 Hz), 7.55 (td, 1H, J = 5.9 Hz, J = 1.7 Hz), 8.49 (d, 1H, J = 4.8 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.4 (3 CH$_2$), 7.4 (3 CH$_3$), 121.3 (CH), 122.4 (CH), 131.4 (CH), 136.5 (CH), 144.6 (CH), 149.5 (CH), 156.0 (C).

MS(EI): 219 (M$^+$).

Anal. Calc. for C$_{13}$H$_{21}$NSi (219.40): C, 71.17; H, 9.65; N, 6.38. Found: C, 71.23; H, 9.54; N, 6.23%.

5.2.16. (E)-1-triethylsilylhept-1-ene (2p) [18b]

Yield: colorless oil, 93%.

TLC: R_f 0.86 (cyclohexane, SiO$_2$).

IR (neat, cm^{-1}): 2954, 2927, 2874, 1616, 1459, 1416, 1378, 1014, 991, 781, 717, 590.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.56 (q, 6H, J = 7.8 Hz), 0.83–1.01 (m, 12 H), 1.21–1.59 (m, 6H), 2.14 (m, 2H), 5.56 (d, 1H, J = 18.7 Hz), 6.06 (dt, 1H, J = 18.7 Hz, J = 6.2 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.7 (3 CH$_2$), 7.5 (3 CH$_3$), 14.2 (CH$_3$), 22.7 (CH$_2$), 28.6 (CH$_2$), 31.5 (CH$_2$), 37.2 (CH$_2$), 125.6 (CH), 148.8 (CH).

MS(EI): 212 (M$^+$). Anal. Calc. for C$_{13}$H$_{28}$Si (212.45): C, 73.50; H, 13.28. Found: C, 73.38; H, 13.05%.

5.2.17. (E)-1-trietylsilyl-3-methoxy-but-1-ene (2q) [18b]

Yield: colorless oil, 96%.

TLC: R_f 0.43 (Et$_2$O/cyclohexane, 5/95, SiO$_2$).

IR (neat, cm^{-1}): 2953, 2911, 2875, 2818, 1619, 1459, 1416, 1370, 1329, 1236, 1199, 1109, 1080, 1043, 992, 910, 849, 777, 717, 682.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.50 (q, 6H, J = 7.9 Hz), 0.88 (t, 9H, J = 7.9 Hz), 1.16 (d, 3H, J = 7.1 Hz), 3.20 (s, 3H), 3.56-3.68 (m, 1H), 5.66 (d, 1H, J = 18.9 Hz), 5.82 (dd, 1H, J = 18.9 Hz, J = 6.5 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.5 (3 CH$_2$), 7.4 (3 CH$_3$), 21.2 (CH$_3$), 56.1 (CH$_3$), 80.8 (CH), 127.8 (CH), 149.1 (CH).

MS(EI): 200 (M$^+$).

Anal. Calc. for C$_{11}$H$_{24}$OSi (200.39): C, 65.93; H, 12.07. Found: C, 65.89; H, 12.03%.

5.2.18. (E)-3-Triethylsilylprop-2-en-1-ol (2r) [16]

Yield: colorless oil, 80%.

TLC: R_f 0.31 (Et$_2$O/cyclohexane, 30/70, SiO$_2$).

IR (neat, cm^{-1}): 3318, 2953, 2910, 2875, 1624, 1458, 1416, 1236, 1071, 1003, 785, 717.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.60 (q, 6H, J = 7.9 Hz), 0.97 (t, 9H, J = 7.9 Hz), 1.50 (brs, 1H), 4.21 (m, 2H), 5.87 (d, 1H, J = 19.0 Hz), 6.22 (dt, 1H, J = 19.0 Hz, J = 4.4 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.5 (3 CH$_2$), 7.4 (3 CH$_3$), 65.9 (OCH$_2$), 125.9 (CH), 146.2 (CH).

MS(ESI): 173, (M+H)$^+$, 195 (M+Na)$^+$.

Anal. Calc. for C$_9$H$_{20}$OSi (172.34): C, 62.72; H, 11.70. Found: C, 62.68; H, 11.54%.

5.2.19. (E)-1-triethylsilylnon-1-en-4-ol (2s)

Yield: colorless oil, 78%.

TLC: R_f 0.43 (Et$_2$O/cyclohexane, 30/70, SiO$_2$).

IR (neat, cm^{-1}): 3354, 2953, 2931, 2874, 1615, 1459, 1416, 1378, 1237, 1125, 994, 761, 717, 579 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.45 (q, 6H, J = 7.9 Hz), 0.76–0.94 (m, 12H), 1.11–1.54 (m, 8H), 2.06–2.20 (m, 1H), 2.26-2.37 (m, 1H), 3.54–3.64 (m, 1H), 5.62 (d, 1H, J = 18.8 Hz), 5.97 (ddd, 1H, J = 18.8 Hz, J = 7.4 Hz, J = 6.0 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 3.6 (3 CH$_2$), 7.5 (3 CH$_3$), 14.2 (CH$_3$), 22.7 (CH$_2$), 25.4 (CH$_2$), 32.0 (CH$_2$), 36.9 (CH$_2$), 45.4 (CH$_2$), 70.7 (CH), 130.9 (CH), 144.3 (CH).

MS(EI): 256 (M$^+$).

Anal. Calc. for C$_{15}$H$_{32}$OSi (256.50): C, 70.24; H, 12.57. Found: C, 70.35; H, 12.45%.

5.2.20. (E)-1-triethoxysilyl-2-(4-methoxyphenyl) ethene (2t) [24]

Yield: yellow oil, 65%; ratio α/β (2/98 of isomers).

TLC: R_f 0.50 (Et$_2$O/cyclohexane, 30/70, SiO$_2$).

IR (neat, cm^{-1}): 3288, 2974, 2891, 2883, 1606, 1572, 1508, 1465, 1442, 1418, 1390, 1293, 1250, 1169, 1099, 1071, 1032, 994, 956, 832, 797, 776, 748, 709, 685, 640.

^{1}H NMR (300 MHz, CDCl$_3$): δ 1.20 (t, 9H, J = 7.0 Hz), 3.72 (s, 3H), 3.80 (q, 6H, J = 7.0 Hz), 5.92 (d, 1H, J = 19.5 Hz), 6.80 (d, 2H, J = 8.3 Hz), 7.08 (d, 1H, J = 19.5 Hz), 7.34 (d, 2H, J = 8.3 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 18.3 (3 CH$_3$), 55.3 (3 CH$_2$), 58.7 (OCH$_3$), 113.9 (2 CH), 114.7 (CH), 128.3 (2 CH), 130.6 (C), 133.7 (CH), 160.3 (C).

MS(ESI): 319 (M+Na)$^+$.

Anal. Calc. for C$_{15}$H$_{24}$O$_4$Si (219.40): C, 60.78; H, 8.16. Found: C, 60.65; H, 8.15%.

5.2.21. (E)-1-dimethylethoxysilyl-2-(4-methoxyphenyl) ethene (2u)

Yield: yellow oil, 83%.

TLC: R_f 0.34 (AcOEt/cyclohexane, 5/95, SiO$_2$).

IR (neat, cm^{-1}): 2959, 1605, 1572, 1509, 1464, 1418, 1390, 1295, 1248, 1170, 1104, 1075, 1034, 988, 945, 828, 794, 758, 740, 633.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.15 (s, 6H), 1.11 (t, 3H, J = 7.0 Hz), 3.62 (q, 2H, J = 7.0 Hz), 3.70 (s, 3H), 6.15 (d, 1H, J = 19.3 Hz), 6.75-6.82 (m, 3H), 7.29 (d, 2H, J = 8.6 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ −1.5 (2 CH$_3$), 18.7 (CH$_3$), 55.4 (CH$_3$), 58.6 (CH$_2$), 114.0 (2 CH), 123.7 (CH), 128.0 (2 CH), 131.0 (C), 145.1 (CH), 159.9 (C).

MS(ESI): 237, (M+H)$^+$.

Anal. Calc. for C$_{13}$H$_{20}$O$_2$Si (236.38): C, 66.05; H, 8.53. Found: C, 65.98; H, 8.46%.

5.2.22. (E)-1-triethoxysilyl-2-(4-methylphenyl)ethene (2v) [27]

Yield: yellow oil, 83% ratio of isomers α/β (ca. 2/98).

TLC: R_f 0.21 (Et$_2$O/cyclohexane, 5/95, SiO$_2$).

IR (neat, cm^{-1}): 2974, 2926, 2885, 1610, 1568, 1511, 1442, 1390, 1293, 1197, 1166, 1099, 1072, 994, 956, 848, 824, 786.

^{1}H NMR (300 MHz, CDCl$_3$): δ 1.10–1.26 (m, 9H), 2.28 (s, 3H), 3.70–3.90 (m, 6H), 6.04 (d, 1H, J = 19.4 Hz), 7.01–7.20 (m, 3H), 7.30 (d, 2H, J = 8.1 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ 18.3 (3 CH$_3$), 21.0 (CH$_3$), 58.6 (3 CH$_2$), 116.3 (CH), 126.7 (2 CH), 129.3 (2 CH), 135.0 (C), 138.9 (C), 149.1 (CH).

MS(ESI): 303 (M+Na)$^+$.

Anal. Calc. for C$_{15}$H$_{24}$O$_3$Si (280.43): C, 64.24; H, 8.63. Found: C, 64.14; H, 8.47%.

5.2.23. (E)-1-ethoxydimethylsilyl-2-(4-methoxy-carbonylphenyl)ethene (2w)

Yield: colorless oil, 68%. ratio of isomers α/β (ca. 3/97).

TLC: R_f 0.60 (Et$_2$O/cyclohexane, 10/90, SiO$_2$).

IR (neat, cm^{-1}): 2955, 1720, 1606, 1565, 1435, 1409, 1276, 1251, 1216, 1196, 1176, 1104, 1075, 1017, 990, 946, 834, 780, 752.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.16 (s, 6H), 1.11 (t, 3H, J = 7.0 Hz), 3.60 (q, 2H, J = 7.0 Hz,), 3.80 (s, 3H), 6.44 (d, 1H, J = 19.3 Hz), 6.89 (d, 1H, J = 19.3 Hz), 7.38 (d, 2H, J = 8.3 Hz), 7.88 (d, 2H, J = 8.3 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ −1.6 (2 CH$_3$), 18.7 (CH$_3$), 52.2 (OCH$_3$), 58.7 (CH$_2$), 126.6 (2 CH), 129.7 (C), 130.0 (2 CH), 130.2 (CH), 142.3 (C), 144.4 (CH), 167.0 (CO).

MS(ESI): 265, (M+H)$^+$.

Anal. Calc. for C$_{14}$H$_{20}$O$_3$Si (264.39): C, 63.60; H, 7.62. Found: C, 63.48; H, 7.50%.

5.2.24. (E)-1-triethoxysilyl-2-(2-methylphenyl)ethene (2x)

Yield: yellow oil, 75%.

TLC: R_f 0.28 (Et$_2$O/cyclohexane, 5/95, SiO$_2$). ratio α/β (ca. 3/97) of isomers α and β.

IR (neat, cm^{-1}): 2974, 2926, 2885, 1602, 1569, 1481, 1442, 1390, 1292, 1210, 1166, 1099, 1072, 995, 956, 831, 776, 742.

^{1}H NMR (300 MHz, CDCl$_3$): δ 1.35–1.50 (m, 9 H), 2.47 (s, 3 H), 3.93–4.10 (m, 6H), 6.23 (d, 1H, J = 19.2 Hz), 7.20-7.38 (m, 3H), 7.56–7.75 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 18.1 (3 CH$_3$), 19.6 (CH$_3$), 58.6 (3 CH$_2$), 120.1 (CH), 125.4 (CH), 126.3 (CH), 128.5 (CH), 130.4 (CH), 135.8 (C), 137.0 (C), 146.9 (CH).

MS(ESI): 303 (M+Na)$^+$.

Anal. Calc. for C$_{15}$H$_{24}$O$_3$Si (280.43): C, 64.24; H, 8.63. Found: C, 63.97; H, 8.55%.

5.2.25. (E)-1-ethoxydimethylsilylhept-1-ene (2y)

Yield: yellow oil, 94%.

TLC: R_f 0.66 (Et$_2$O/cyclohexane, 10/90, SiO$_2$).

IR (neat, cm^{-1}): 2958, 2926, 1618, 1460, 1390, 1250, 1166, 1107, 1078, 992, 945, 831, 789.

^{1}H NMR (300 MHz, CDCl$_3$): δ 0.00 (s, 6H), 0.67–0.77 (t, 3H, J = 7.0 Hz), 0.90–1.35 (m, 9H), 1.96 (q, 2H, J = 7.0 Hz), 3.49 (qd, 2H, J = 7.0 Hz, J = 1.3 Hz), 5.45 (dd, 1H, J = 18.7 Hz, J = 1.4 Hz), 6.02 (dt, 1H, J = 18.7 Hz, J = 6.2 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ −1.6 (2 CH$_3$), 14.2 (CH$_3$), 18.6 (CH$_3$), 22.7 (CH$_2$), 28.3 (CH$_2$), 31.5 (CH$_2$), 36.7 (CH$_2$), 58.4 (OCH$_2$), 127.2 (CH), 150.1 (CH).

MS(ESI): 201, (M+H)$^+$.

Anal. Calc. for C$_{11}$H$_{24}$OSi (200.39): C, 65.93; H, 12.07. Found: C, 65.85; H, 11.91%.

5.2.26. (E)-1-ethoxydimethylsilyl-3, 3-diethoxyprop-1-ene (2z)

Yield: colorless oil, 72%.

TLC: R_f 0.33 (AcOEt/cyclohexane, 10/90, SiO_2).

IR (neat, cm^{-1}): 2974, 2876, 1391, 1335, 1252, 1206, 1106, 1049, 998, 947, 835, 796.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 6H), 1.12-1.30 (m, 9H), 3.38–3.84 (m, 6H), 4.87 (d, 1H, $J = 3.8$ Hz), 6.02 (d, 1H, $J = 19.1$ Hz), 6.12 (dd, 1H, $J = 19.1$ Hz, $J = 3.8$ Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ −1.7 (CH_3), 15.4 (CH_3), 18.6 (CH_3), 58.6 (OCH_2), 61.2 (2 OCH_2), 102.5 (CH), 131.3 (CH), 144.5 (CH).

MS(ESI): 233, (M+H)$^+$.

Anal. Calc. for $C_{11}H_{24}O_3Si$ (232.39): C, 56.85; H, 10.41. Found: C, 56.58; H, 10.30%.

Acknowledgement

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