Development of a Radical Silylzincation of (Het)Aryl-Substituted Alkynes and Computational Insights into the Origin of the trans-Stereoselectivity

Elise Romain, Karen de La Vega-Hernández, Frédéric Guégan, Juan Sanz García, Carolin Fopp, Fabrice Chemla, Franck Ferreira, Hélène Gerard, Olivier Jackowski, Stéphanie Halbert, et al.

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Development of a Radical Silylzincation of (Het)Aryl-Substituted Alkynes and Computational Insights into the Origin of the *Trans*-Stereoselectivity

Elise Romain,[a] Karen de la Vega-Hernández,[a] Frédéric Guégan,[b] Juan Sanz García,[b] Carolin Fopp,[c] Fabrice Chemla,[a] Franck Ferreira,[a] Hélène Gerard,[b] Olivier Jackowski,[a] Stéphanie Halbert,[b]* Martin Oestreich[c]* and Alejandro Perez-Luna[a]*

[a] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75005 Paris, France
Email: alejandro.perez_luna@sorbonne-universite.fr
[b] Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, LCT, F-75005 Paris, France
Email : stephanie.halbert@sorbonne-universite.fr
[c] Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 115, D-10623 Berlin, Germany
Email: martin.oestreich@tu-berlin.de

Received: ((will be filled in by the editorial staff))

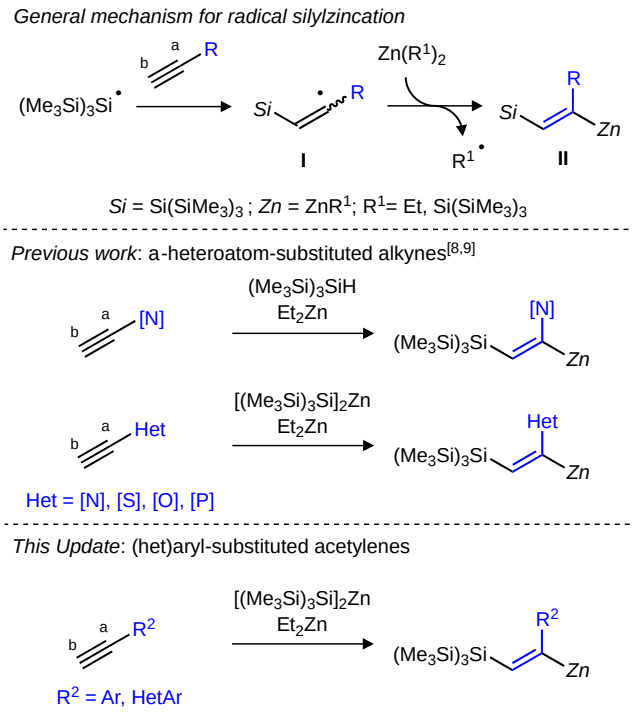
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. Aryl- and hetaryl-substituted acetylenes undergo regio- and stereoselective silylzincation by reaction with $[(Me_3Si)_3Si]_2Zn$ in the presence of Et_2Zn (10–110 mol%) as additive. The distinctive feature of this addition across the C–C triple bond is its *trans* stereoselectivity. The radical nature of the silylzincation process is supported by diagnostic experiments and DFT calculations, which also corroborate the role played by steric effects to obtain that stereoselectivity. The procedure can be combined in one-pot with the copper(I)-mediated electrophilic substitution of the $C(sp^2)$–Zn bond, with retention of the double bond geometry. This makes it valuable for the synthesis of stereodefined di- and trisubstituted vinylsilanes.

Keywords: Radical reactions; Silylmetalation; Silylzinc reagents; Vinylsilanes; Zinc

Vinylsilanes are popular synthetic building blocks, and their regio- and stereoselective preparation continues to attract significant attention.[1] The silylmetalation of alkynes, *i.e.*, the addition of a silicon–metal bond across a C–C triple bond, represents a reliable tool for this purpose, as it creates a $C(sp^2)$–Si bond and a $C(sp^2)$–metal bond in a single reaction, and the newly formed reactive bond can be used, in one pot, as linchpin for subsequent C−C bond formation upon electrophilic substitution. Sequenced silylmetalation–electrophilic substitution of aryl- and alkyl-substituted alkynes was reported with procedures involving silylcupration,[2] Pt(II)- or Cu(I)-catalyzed silylmagnesiation,[3] and also direct[4] and Cu(I)-catalyzed[5,6] silylzincation. Also, the silylcupration–arylation of internal alkynes was disclosed using a dual Cu(I)/Pd(0) catalytic system and silylboranes as silicon source.[7] These protocols rely on the transfer of anionic silicon, and involve *syn*-addition processes. Hence, the vinylsilanes accessible are restricted to those having the geometry resulting from *cis*-stereoselectivity.

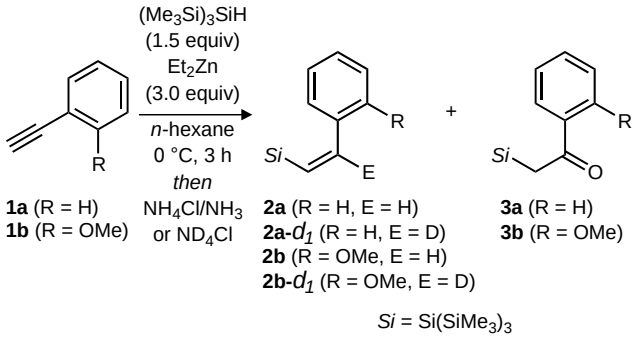
We recently addressed this limitation and developed synthetic methods to achieve the *β*-regio and *trans*-stereoselective silylzincation of *α*-heteroatom-substituted alkynes (Scheme 1, top). Reaction with a mixture of $(Me_3Si)_3SiH$ and Et_2Zn was suitable for terminal ynamides,[8] while reaction with a combination of $[(Me_3Si)_3Si]_2Zn$ and Et_2Zn proved more general, and was also applicable to sulfur-, oxygen- and phosphorus-substituted terminal alkynes (Scheme 1, middle).[9] Both the stereochemical outcome of the additions across the C–C triple bonds, and the radical-stabilizing effect of the trimethylsilyl groups on the silicon-center were consistent with a radical mechanism involving a Zn-transfer process. For both procedures, it was possible to associate, in one-pot, the *trans*-silylzincation with subsequent copper(I)-mediated electrophilic substitution of the intermediate $C(sp^2)$–Zn bond, with retention of the double bond geometry. Such reactions provide access to *β*,*β*'-substituted vinylsilanes that cannot be prepared using hydrosilylation chemistry. We have now found that the $[(Me_3Si)_3Si]_2Zn/Et_2Zn$ system is also applicable to terminal (het)aryl-substituted acetylenes (Scheme 1, bottom). In this Update, we report these new advances, including adjustments of the experimental conditions, as well as computational evaluation of energetics and geometrical features of the radical reaction mechanism giving insights into the origin of the stereoselectivity.



Scheme 1. *Trans*-stereoselective silylzincation of alkynes.

Given that the radical hydrosilylation of terminal aryl-substituted acetylenes can be achieved with excellent β-regioselectivity by reaction with $(Me_3Si)_3SiH$ under a variety of conditions and with diverse radical initiators,[10] we reasoned that this substrate class would also be suitable for our radical silylzincation procedures. Taking phenylacetylene (**1a**) and 2-ethynylanisole (**1b**) as model substrates, we first considered the protocol involving reaction with $(Me_3Si)_3SiH$ (1.5 equiv) and Et_2Zn (3.0 equiv) in *n*-hexane at 0 °C (Table 1). Following work-up, vinylsilanes **2a** and **2b** were obtained in, respectively, 61% and 91% yield, in excellent β-regio- and *Z*-stereoselectivity (entries 1 and 3).[11] However, when the reactions were quenched with ND_4Cl to evidence the putative formation of vinylzinc species (intermediate **II**, Scheme 1), **2a**-d_1 and **2b**-d_1 were recovered with only 22% and 15% deuterium incorporation (entries 2 and 4). Two plausible explanations could account for such low amounts of deuterium incorporation: 1) in-situ protonation of intermediate **II** by the starting alkyne leading to the loss of the C(sp^2)–Zn functionality, or 2) direct H-atom transfer from $(Me_3Si)_3SiH$ to vinyl radical **I**. The first process was reported to be only subsidiary in closely related radical carbozincation reactions,[12] and we also arrived to a similar conclusion for our system considering the reaction of **1b** having deuterium attached to the terminal alkyne C-atom.[13] Thus, in the reaction of terminal aryl-substituted acetylenes and $(Me_3Si)_3SiH/Et_2Zn$, hydrogen-atom transfer from the hydrosilane to vinyl radical **I** outcompetes ethylzinc-group transfer from Et_2Zn (leading to **II**) and thus hydrosilylation prevails over silylzincation. This procedure is to be regarded rather as a radical hydrosilylation wherein Et_2Zn acts chiefly as radical initiator. It is noteworthy, that these hydrosilylation reactions can also be conducted in the presence of deliberately added air (entries 5 and 6), with comparable yields and stereoselectivity. In this case however, aryl ketones (**3a** and **3b**) are also formed in ~ 10–15% yield. Similar side-products were described in reports on the radical hydrogermylation of alkynes, and their formation was attributed to the reaction of intermediate vinylic radicals (similar to **I**) with oxygen.[14]

Table 1. Reaction of Aryl-substituted Acetylenes **1a** and **1b** with $(Me_3Si)_3SiH/Et_2Zn$.



Entry	Substrate	Vinylsilane:[a] Yield (%)[b] [*Z*/*E*] [c]	Ketone: Yield (%) [b]
1	**1a**	**2a**: 61 [>98:2]	**3a**: <5[e]
2	**1a**	**2a**-d_1[d]: 58 [>98 (22% D):2]	**3a**: <5[e]
3	**1b**	**2b**: 91 [>98:2]	**3b**: <5[e]
4	**1b**	**2b**-d_1[d]: 82 [>98 (15% D):2]	**3b**: <5[e]
5[f]	**1a**	**2a**: 81 [>98:2]	**3a**: 9
6[f]	**1b**	**2b**: 72 [>98:2]	**3b**: 14

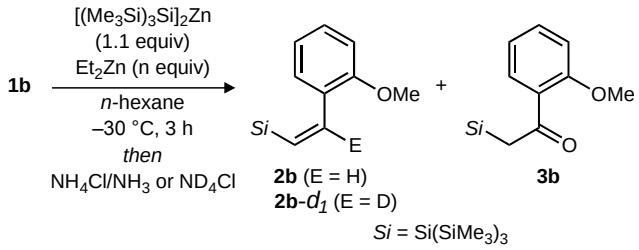
[a] Only β-silylated regioisomers were detected (β:α > 98:2).
[b] Determined by ^{1}H NMR spectroscopy using butadiene sulfone as internal standard.
[c] Determined by ^{1}H NMR analysis of the crude reaction mixture.
[d] The reaction was quenched with ND_4Cl/D_2O. The percentage of deuterium incorporation estimated by ^{1}H NMR spectroscopy is given in parenthesis.
[e] Not detected in the crude mixture (yield < 5%).
[f] Air (15 mL) was introduced in the reaction medium.

To prevent competitive hydrosilylation, we then turned our attention to the method relying on $[(Me_3Si)_3Si]_2Zn$ as source of silyl radicals, and focused on *ortho*-anisyl derivative **1b,** which seemed to afford better results (Table 2). The conditions previously developed for α-heteroatom-substituted

alkynes were applied first; **1b** was found to react with $[(Me_3Si)_3Si]_2Zn$[15, 16] in the presence of Et_2Zn (1.1 equiv), in *n*-hexane at –30 °C, with full *β*-regioselectivity and excellent control of the double bond geometry (entry 1). After reaction work-up, **2b** was isolated in an encouraging 58% yield, as a single *Z*-stereoisomer. Here also, ketone **3b** was recovered in 14% yield. It is however important to mention that this amount was variable (and often higher) if the reactions were conducted at small scale (0.25 mmol or less), likely because the relative amount of residual oxygen in the reaction media is higher in that case. To avoid this erratic behavior, we conducted routinely the reactions at 1 mmol scale.

It was possible to reduce the amount of Et_2Zn to 10 mol%: a slight improvement in the yield (69%) was obtained while keeping the same levels of regio- and stereoselectivity (entry 2). Notwithstanding, the presence of Et_2Zn as additive was necessary, because no reaction occurred in its absence (entry 4). We presumed that the critical role played by Et_2Zn was to allow for efficient radical chain initiation.[17] Close-to-complete D-incorporation was observed upon quenching the reaction with ND_4Cl (entry 3), thereby confirming that in this reaction system, silylzincation is the major pathway.

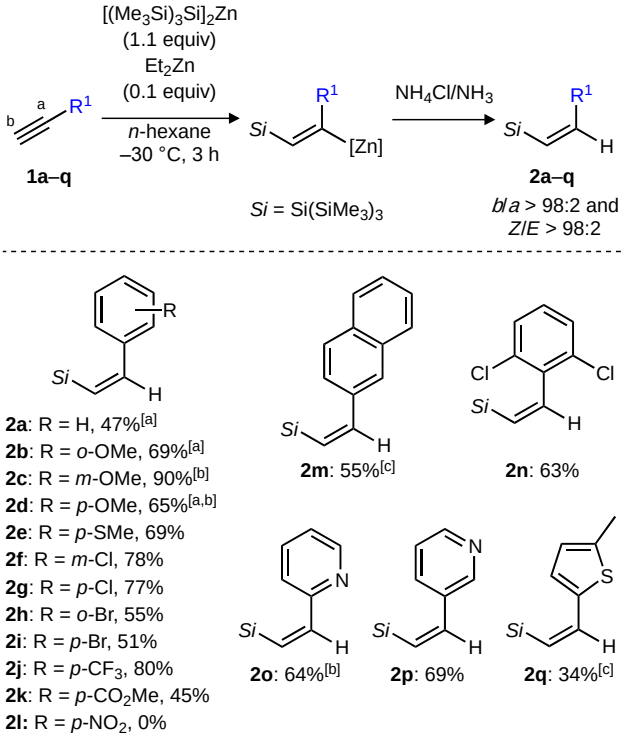
Table 2. Optimization of the *Trans*-Stereoselective Silylzincation of **1b**.



Entry	Et_2Zn (equiv)	Vinylsilane:[a] Yield (%) [*Z*/*E*][b]	**3b**: Yield (%)
1	1.1	**2b**: 58 [>98:2]	14
2	0.1	**2b**: 69 [>98:2]	12
3	0.1	**2b**-d_1[c]: 69 [>98 (84% D):2]	15
4	0	**2b**: <5 %	10

[a] Only *β*-silylated regioisomers were detected (*β*:*α* > 98:2).
[b] Determined by ^{1}H NMR analysis prior to purification.
[c] The reaction was quenched with ND_4Cl/D_2O. The percentage of deuterium incorporation estimated by ^{1}H NMR spectroscopy is given in parenthesis.

We then studied the scope of the conditions optimized for the silylzincation of **1b** with other aryl-substituted acetylenes (Scheme 2). A large variety of monosubstituted phenylacetylenes afforded the corresponding disubstituted *Z*-vinylsilanes in decent to good yields, with complete control of the stereoselectivity. Suitable substrates included **1b**–**1e** having electron-donating substituents such as OMe and SMe, as well as **1f**–**1k** having electron-withdrawing substituents such as Cl, Br, CF_3 and CO_2Me, but not NO_2-substituted **1l** for which only degradation was observed. With substrates **1c** and **1d**, the protocol involving 10 mol% Et_2Zn gave poorly-reproducible results, because conversion of the starting material was not always complete. Increasing the amount of Et_2Zn (1.1 equiv) was beneficial in these cases and *Z*-vinylsilanes **2c** and **2d** could be obtained with satisfactory yields.[18] Interestingly, no appreciable influence of the substituent's position (*para*-, *meta*- or *ortho*-) on the reaction outcome was noted, as it can be seen by comparing the yields in **2b** vs **2c** and **2d**, **2f** vs **2g,** and **2h** vs **2i**. 3-Naphtyl acetylene (**1m**), as well as di-*ortho*-chloro-substituted phenyl acetylene **1n** also afforded the desired *Z*-vinylsilanes in good yields and excellent stereoselectivity. In view of the large scope of the silylzincation reaction, the modest 47% yield in **2a** obtained from phenylacetylene (**1a**) is somewhat intriguing.[19]



[a] 10–15% of aryl ketone **3** was detected. [b] 1.1 equiv Et_2Zn was used.
[c] 20–25% of aryl ketone **3** was detected.

Scheme 2. *Trans*-stereoselective silylzincation of (het)aryl-substituted acetylenes.

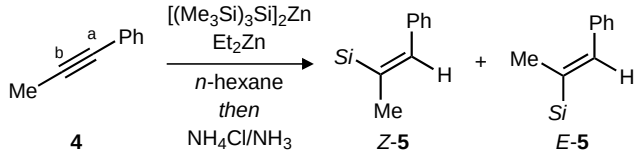
In most cases, the formation of aryl ketones **3** was not detected. However, along with **1b**, phenyl (**1a**), *para*-anisyl (**1d**), and naphtyl (**1m**) substituted alkynes were exceptions to this general trend. Small amounts (10–15%) of the corresponding ketones **3a**, **3b** and **3d** were recovered, as well as 20–25% of **3m**. Seemingly, this side reaction is less favorable for substrates having electron-poor aromatic rings.

Importantly, the silylzincation protocol was also suitable for hetaryl-substituted acetylenes. Thus, *Z*-

vinylsilanes with 2-pyridyl (**2o**), 3-pyridyl (**2p**) and 5-methyl-2-thienyl (**2q**) moieties β to the silicon atom were obtained with complete control of the regio- and the stereoselectivity. The yields were decent for **2o** (64%) and **2p** (69%), but only modest for **2q** (34%). The latter was hampered by the formation of significant amounts of oxidation product **3q**.

To finish our survey of substrates, we then considered the silylzincation of 1-phenyl-1-propyne (**4**) as model for internal aryl-substituted alkynes (Table 3). This substrate was much less reactive than terminal alkynes, but was nevertheless amenable to silylzincation. The reaction with $[(Me_3Si)_3Si]_2Zn$ at 40 °C for 16 h provided vinylsilane **5** with full β-regio- and very high *trans*-stereoselectivity, albeit in low 20% yield because large amounts of starting material remained unreacted (entry 1). As for terminal aryl-substituted acetylenes, adding 1.1 equiv Et_2Zn (entry 2) led to a considerably better yield (45%) keeping the same levels of regio- and stereoselectivity. An acceptable 62% yield (49% isolated) was obtained using a larger excess (2.0 equiv) of both $[(Me_3Si)_3Si]_2Zn$ and Et_2Zn (entry 3). Performing the reaction at 80 °C was also beneficial in terms of yield, but detrimental for stereocontrol. At this temperature, the reaction with $[(Me_3Si)_3Si]_2Zn$ for 16 h delivered vinylsilane **5** in 55% yield as a *Z*/*E* = 58:42 mixture (entry 4). Moreover, an excellent 88% yield was obtained in the presence of 1.1 equiv Et_2Zn and radical initiator AIBN, but again with no control of the double bond geometry (entry 6). In fact, as evidenced in entry 5, the stereoselectivity in favor of the *Z* diastereomer was found to be much better at early stages of the reaction, strongly suggesting that *trans*-stereoselectivity is favored kinetically but the alkenylzinc intermediate undergoes isomerization.[20]

Table 3. Silylzincation of 1-Phenyl-1-Propyne (**4**).

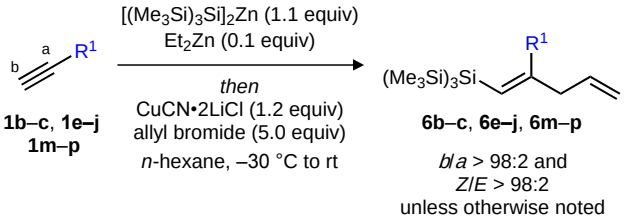


4

Entry	Si_2Zn/Et_2Zn (equiv)	Conditions	**5**:[a] Yield (%)[b] [*Z*/*E*][c]
1	1.1/0.0	40 °C, 16 h	20 [>98:2]
2	1.1/1.1	40 °C, 16 h	45 [92:8]
3	2.0/2.0	40 °C, 16 h	62[d] [91:9]
4	1.1/0.0	80 °C, 16 h	55 [58:42]
5	0.7/0.0	80 °C, 30 min	24[e] [79:21]
6	1.1/1.1	80 °C, 16 h AIBN (10 mol%)	88 [53:47]

[a] Only β-silylated regioisomers were detected (β:α > 98:2).
[b] Determined by ^{1}H NMR spectroscopy using butadiene sulfone as internal standard.
[c] Determined by ^{1}H NMR analysis of the crude reaction mixture.
[d] 49% isolated yield was obtained upon purification.
[e] Based on the disilylzinc reagent.

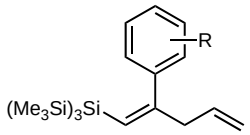
We then verified that the C(sp^2)–Zn bond created during silylzincation remains available for subsequent stereoretentive functionalization and thus, that the procedure developed for the *trans*-silylzincation of (het)aryl-substituted acetylenes is also suitable to access 1,2,2-trisubstituted vinylsilanes. Cu(I)-mediated electrophilic substitution with allyl bromide was taken as model reaction. Allylation of α-(het)aryl- substituted alkenylzinc intermediates **I** was readily achieved using the THF-soluble salt CuCN•2LiCl, as previously for α-heteroatom-substituted alkenylzinc species (Scheme 3). Importantly, introducing the copper-salt and the electrophile at –30 °C was critical to prevent the loss of the double bond geometry. Trisubstituted vinylsilanes **6b–c**, **6e–j** and **6m–p** were prepared fully stereoselectively as single *Z*-isomers[21] in comparable yields to those of the silylzincation reactions.



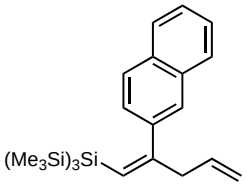
1b–c, **1e–j**
1m–p

6b–c, **6e–j**, **6m–p**

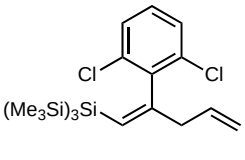
b/*a* > 98:2 and *Z*/*E* > 98:2 unless otherwise noted



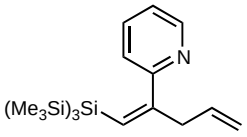
6b: R = *o*-OMe, 64%[a]
6c: R = *m*-OMe, 72%[b]
6e: R = *p*-SMe, 76%
6f: R = *m*-Cl, 72%
6g: R = *p*-Cl, 82%
6h: R = *o*-Br, 71%
6i: R = *p*-Br, 88%
6j: R = *p*-CF_3, 91%



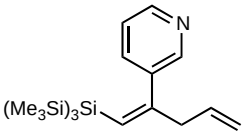
6m: 45%[c]



6n: 63%[d]



6o: 64%[b]



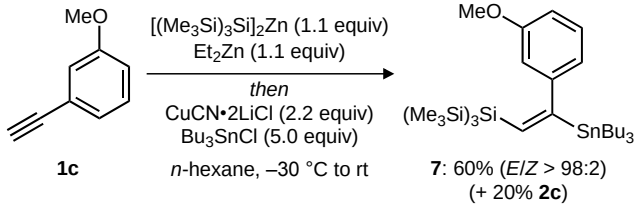
6p: 69%

[a] 13% of **3b** was detected. [b] 1.1 equiv Et_2Zn was used. [c] 20% of **3m** was detected. [d] Isolated product contained **2n** (**6n**/**2n** = 87:13).

Scheme 3. Tandem *trans*-stereoselective silylzincation–copper(I)-mediated allylation of (het)aryl-substituted acetylenes.

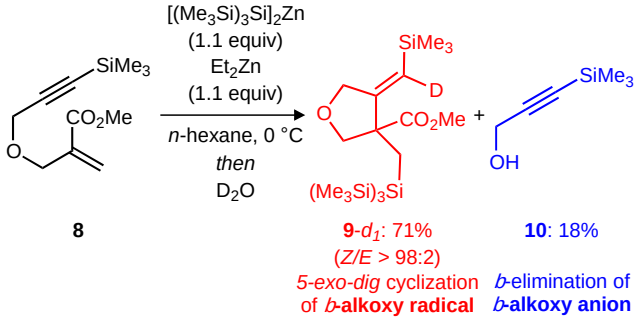
The preparation of silylstannyl alkene **7** through sequential *trans*-silylzincation–copper(I)-mediated stannylation demonstrates further that, similarly to α-

heteroatom-substituted alkynes, the electrophilic substitution step can be implemented with electrophiles other than allyl bromide (Scheme 4). Note also that this reaction represents a formal *trans*-selective alkyne silylstannylation reaction, which is virtually unknown.[22]



Scheme 4. Formal *trans*-stereoselective silylstannylation of **1c**.

The final stage of our update was focused on gaining further evidence to assess for the radical character of the silylzincation process. Towards this end, we considered first the reaction of $[(Me_3Si)_3Si]_2Zn$ and 1.1 equiv Et_2Zn with enoate **8** (Scheme 5), which we had previously used as probe to discriminate between radical and polar reaction pathways.[8,20] The (predominant) formation of cyclized product **9**-d_1 (71%) provided evidence for a silyl radical 1,4-addition (delivering an intermediate β-alkoxy radical that undergoes 5-*exo*-dig cyclisation).[23] Conversely, alcohol **10** arising from the fragmentation of an intermediate β-alkoxy anion[24] that could arise from a polar conjugate addition of $[(Me_3Si)_3Si]_2Zn$ was only formed in 18%[25] yield. These results lend clear evidence that $[(Me_3Si)_3Si]_2Zn$ has the potential to engage in radical reactions that override its anionic reactivity.



Scheme 5. Reaction of mechanistic probe **8** with $[(Me_3Si)_3Si]_2Zn$ /Et_2Zn.

Examination of the radical pathway was carried out using DFT calculations. The reaction of the $(Me_3Si)_3Si$ radical with 2-ethynylanisole **1b** leading to the β silylzincation isomers is depicted in Figure 1.[26]

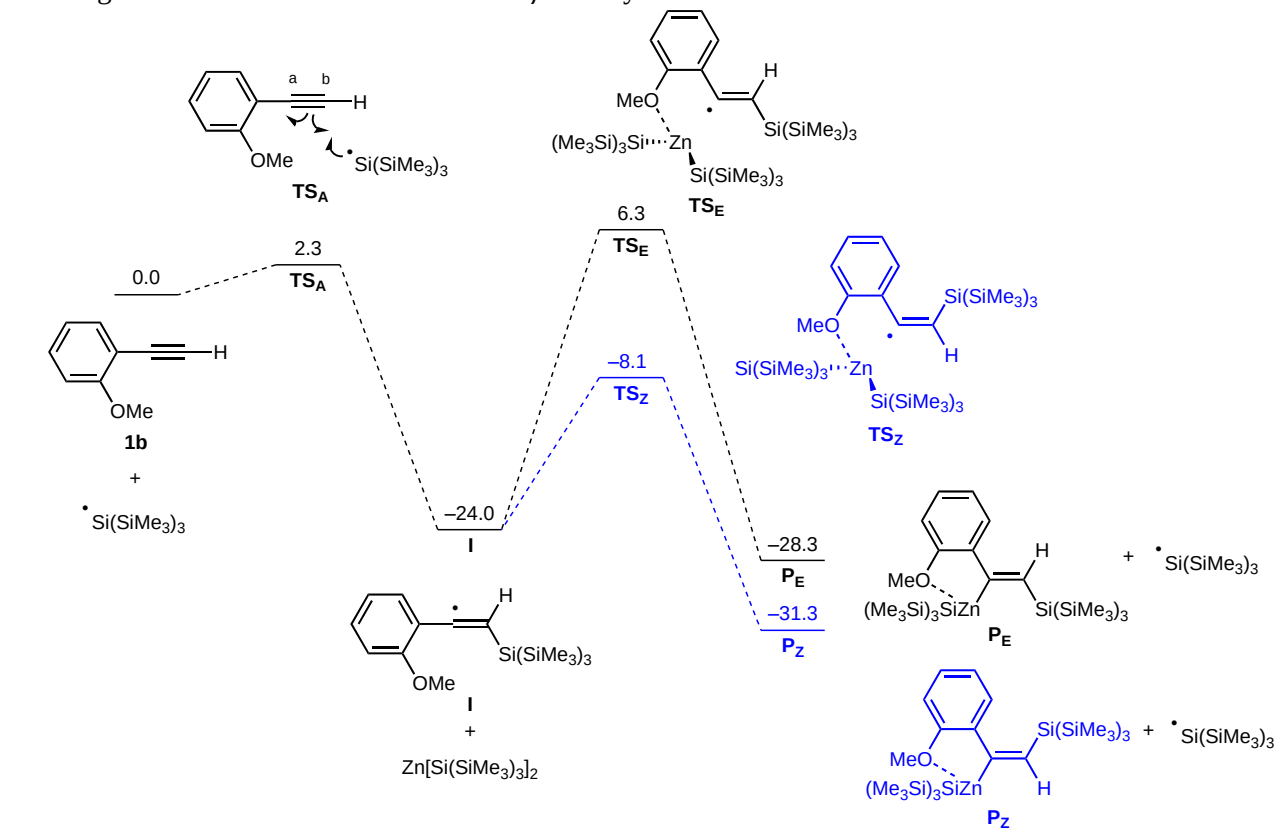
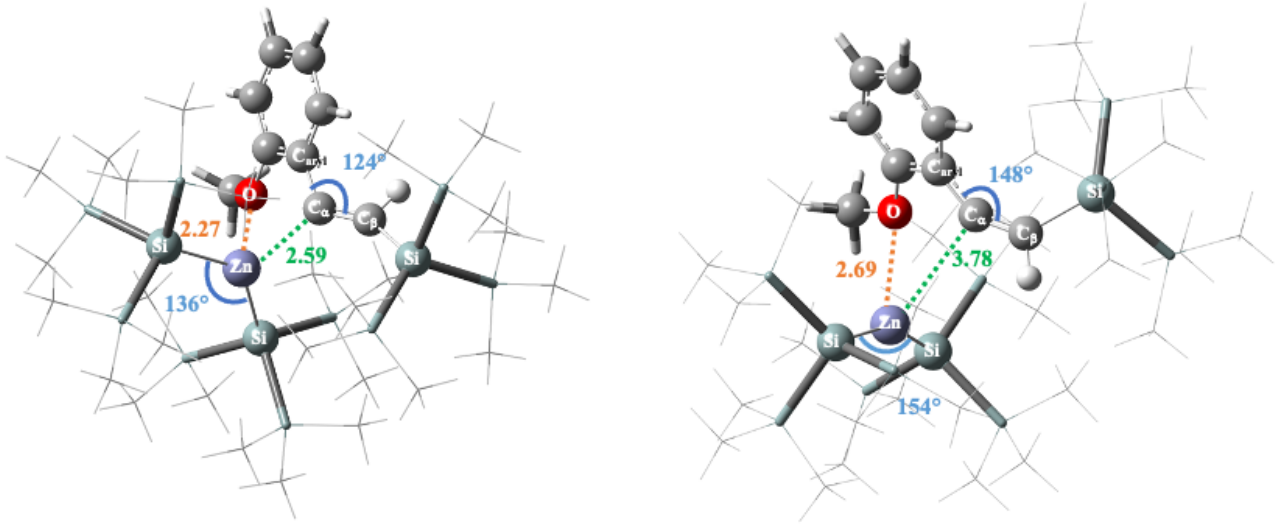


Figure 1. Energy profiles for the *cis*- and *trans*- radical silylzincation of 2-methoxyphenylacetylene (**1b**). Energies (in kcal mol^{-1}) are given relative to the separated reactants (see Table S1)

The activation energy for the addition of the $(Me_3Si)_3Si$ radical across the alkyne is only 2.3 kcal mol^{-1} (corresponding to 14.5 kcal mol^{-1} in Gibbs free energy due to the associative nature of this step).[27] The corresponding transition state $\mathbf{TS_A}$ is early, as demonstrated by the large Si–C_β distance of 2.889 Å (compared to 1.919 Å in **I**), and the quasi-linear geometry of the alkyne (H–C_β–C_α angle of 159° in $\mathbf{TS_A}$ compared to 178° in **1b**). The formed vinylic radical **I** is stable, with an energy of –24.0 kcal mol^{-1} below the free reactants (corresponding to ΔG = –10.5 kcal mol^{-1} with respect to the separated reactants), which suggests that the radical addition step is irreversible. The obtained vinyl radical is linear[28] (C_β–C_α–C_{aryl} angle equal to 178° in **I**), due to the delocalization of the radical over the aryl π system (the spin density is represented in Figure S1 of the *Supporting Information*).

The second part of the mechanism involves the reaction of radical **I** with $[(Me_3Si)_3Si]_2Zn$. It occurs in a single step through homolytic substitution (S_H2) at the zinc atom. Indeed, the coordination of the diorganosilylzinc reagent to vinyl radical **I** is associated in the same step with the concerted cleavage of one of the Zn–Si bonds, thus leading to the regeneration of the $(Me_3Si)_3Si$ radical, and the formation of the silylzincation products $\mathbf{P_Z}$ and $\mathbf{P_E}$. The *trans* product $\mathbf{P_Z}$ is kinetically favored by 14.4 kcal mol^{-1} and thermodynamically favored by 3 kcal mol^{-1} over the *cis* addition product $\mathbf{P_E}$.

Two transition states $\mathbf{TS_E}$ and $\mathbf{TS_Z}$ were identified (Figure 2) with significantly different geometrical features. In the structure of $\mathbf{TS_E}$, the zinc center is in a distorted tetrahedral geometry (see Table S1). The Zn–C_α bonding (2.585 Å) is well advanced (compared to 1.954 Å in $\mathbf{P_E}$) and the two Zn–Si bonds are equivalent (2.492 and 2.520 Å *vs.* 2.336 Å in free $[(Me_3Si)_3Si]_2Zn$). We note the presence of a secondary interaction between the oxygen atom of the methoxy group and the zinc center, as indicated by a Zn–O distance of 2.269 Å. In addition, the angle at C_α of the vinyl motif (C_β–C_α–C_{aryl} angle of 124° close to 118° in $\mathbf{P_E}$) and the Si–Zn–Si angle in the diorganosilylzinc unit (136° in comparison to 179° in free $[(Me_3Si)_3Si]_2Zn$) are clearly bent. By contrast, $\mathbf{TS_Z}$ is a more early-like TS, as indicated by the rather linear geometry of zinc unit (154°), the long Zn–C_α distance of 3.775 Å (compared to 1.945 Å in $\mathbf{P_Z}$) and the scantily bent configuration at the C_α center (148° *vs.* 125° in $\mathbf{P_Z}$). The arrangement around the zinc center is tricoordinated with similar Zn–Si distances (2.395 and 2.414 Å) and a longer Zn–O distance of 2.686 Å.



$\mathbf{TS_E}$ $\mathbf{TS_Z}$

Figure 2. Structures of the stereodivergent transition states $\mathbf{TS_E}$ (left, *cis*-silylzincation, 30.3 kcal mol^{-1} energy barrier) and $\mathbf{TS_Z}$ (right, *trans*-silylzincation, 15.8 kcal mol^{-1} energy barrier). Angles are given in degrees, distances in Å.; most methyl groups are omitted for clarity.

The energetic consequences of the geometrical differences between $\mathbf{TS_Z}$ and $\mathbf{TS_E}$ was then explored using the *activation strain* model.[29] In this approach, the transition state is described as two distorted reactants in weak interaction which allows to decompose the activation energy into distortion and interaction energies (Table 4).[30]

Table 4. Distortion and Interaction Energies (in kcal mol^{-1}) for $\mathbf{TS_Z}$ and $\mathbf{TS_E}$ transition states using the *activation strain model*.

	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}_{distortion}$	$\Delta E^{\ddagger}_{interaction}$
TS_Z	15.8	17.1	–1.3
TS_E	30.3	45.9	–15.6

The obtained results confirm the late nature of **TS_E**, for which the interaction term is much more stabilizing (–15.6 kcal mol^{-1}) than for **TS_Z** (–1.3 kcal mol^{-1}). Nevertheless, this difference is largely overridden by the larger distortion energy evaluated at 45.9 kcal mol^{-1} in **TS_E** (*vs.* 17.1 kcal mol^{-1} in **TS_Z**). In **TS_E**, this large distortion term is associated with about 12 kcal mol^{-1} for Si–Zn–Si bending and 8 kcal mol^{-1} for C_β–C_α–C_{aryl} bending (*vs.* 3 and 3 kcal mol^{-1}, respectively for **TS_Z**, Tables S2 and S3). In the case of **TS_Z**, distortion is the main contribution while interaction remains small. This transition state is thus well described as two fragments: a vinyl radical **I** and a diorganosilylzinc unit. In contrast, for **TS_E**, the interaction energy is much larger and cannot be considered as a weak interaction. This TS is thus viewed as a single metal complex in which Zn–O intramolecular interaction plays a role, probably by facilitating the addition of the vinylic radical to the Zn atom. Whereas the interaction energy is significantly higher in **TS_E**, a closer look at the geometrical data also highlights that the bulky $(Me_3Si)_3Si$ group significantly thwarts the approach of $[(Me_3Si)_3Si]_2Zn$ to **I**. In contrast, the major steric hinderance in **TS_Z** is localized within **I**, as the bulky $(Me_3Si)_3Si$ group tilts the o-methoxy aryl group from a planar geometry leading to an earlier **TS_Z**. Considering the relative energies of the two TS, we can assume that inter-fragment steric effects predominate over those within **I**, and disfavor the pathway leading to the E-isomer (**P_E**).

In conclusion, using $[(Me_3Si)_3Si]_2Zn$ as silicon donor in the presence of Et_2Zn, the silylzincation of terminal (het)aryl-substituted acetylenes was achieved with excellent *β*-regio and *trans*-stereoselectivity, which is unprecedented. Owing to the possibility to use the C(sp^2)–Zn bond to introduce, with retention of the double bond geometry, an additional substituent by copper(I)-mediated electrophilic substitution, the protocol offers a versatile access to stereodefined di- and trisubstituted vinylsilanes. In many cases, 10 mol% of Et_2Zn suffice to obtain optimal results for the silylzincation, strongly suggesting that its role is mainly to ensure radical initiation. DFT calculations provide support for the radical character of the mechanism and insight into the origin of the diastereoselection which is mostly related to steric effects associated with the large size of the $(Me_3Si)_3Si$ group. As part of this work, we have also demonstrated that this *trans*-silylzincation reaction is not fundamentally restricted to terminal alkynes. Even though further research is still necessary to obtain satisfactory procedures for synthetic purposes, this approach could offer a valuable solution for the stereodefined preparation of tetrasubstituted vinylsilanes, which remains an unsolved problem.[31]

Experimental Section

General procedure A for silylzincation of terminal (het)aryl-substituted acetylenes.

A Schlenk tube was charged with the appropriate (het)aryl-substituted acetylene (1.00 mmol) and a suspension of $[(Me_3Si)_3Si]_2Zn$ (620 mg, 1.11 mmol) in *n*-hexane (8 mL) was added at –30 °C, followed by Et_2Zn (1.0 M in hexane, 0.10 mL, 0.10 mmol). The turbid mixture was stirred at this temperature for 3 h. The mixture was then diluted with CH_2Cl_2 (60 mL) and quenched with aqueous NH_4Cl/NH_3 (2:1) (8 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (2 x 60 mL). The combined organics were washed with brine (20 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

General procedure B for tandem silylzincation / Cu(I)-mediated allylation.

A Schlenk tube was charged with the appropriate (het)aryl-substituted acetylene (0.25 mmol) and a suspension of $[(Me_3Si)_3Si]_2Zn$ (155 mg, 0.27 mmol) in hexane (2 mL) was added at –30 °C, followed by Et_2Zn (1.0 M in *n*-hexane, 0.025 mL, 0.025 mmol). The turbid mixture was stirred at this temperature for 3 h and then CuCN•2LiCl (1.0 M in THF, 0.30 mL, 0.30 mmol) was added, followed by allyl bromide (0.11 mL, 1.27 mmol). The mixture was stirred overnight at –30 °C and then diluted with CH_2Cl_2 (15 mL) and quenched with aqueous NH_4Cl/NH_3 (2:1) (2 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (2 x 15 mL). The combined organics were washed with brine (2 x 5 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-styryl-2-(trimethylsilyl)trisilane (2a)

Prepared according to the general procedure **A** from phenylacetylene (**1a**) (110 µL, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (cyclohexane) afforded analytically pure **2a** (165 mg, 47%, *Z*/*E* > 98:2) as a colorless oil. The spectral data was in good agreement with that previously reported.[10]

^{1}H NMR (C_6D_6, 400 MHz) δ 7.44 (d, *J* = 14.5 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.18–7.14 (m, 2H), 7.06–7.02 (m, 1H), 5.99 (dd, *J* = 14.5, 1.5 Hz, 1H), 0.22 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 147.4, 141.0, 128.7, 128.4, 127.7, 124.3, 1.5.

(*Z*)-2-(2-methoxystyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2b)

Prepared according to the general procedure **A** from 2-ethynylanisole (**1b**) (132 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2b** (262 mg, 69%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.81 (d, *J* = 14.4 Hz, 1H), 7.53–7.51 (m, 1H), 7.08 (ddd, *J* = 7.9, 7.8, 1.7 Hz, 1H), 6.90 (t, *J* =7.4 Hz, 1H), 6.52–6.50 (m, 1H), 6.03 (d, *J* = 14.4 Hz, 1H), 3.31 (s, 3H), 0.21 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 157.7, 143.9, 130.9, 129.5, 129.2, 123.5, 120.8, 110.5, 54.9, 1.5. IR (neat) ν 2948, 2893, 1590, 1483, 1241, 824, 747, 684, 622 cm^{-1}. **HRMS** (ESI) for $[C_{18}H_{36}OSi_4+Na]^+$ 403.1735 found 403.1753.

(*Z*)-2-(3-methoxystyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2c)

Prepared according to the general procedure **A** from 3-ethynylanisole (**1c**) (132 mg, 1.00 mmol) using a larger amount of Et_2Zn (1.0 M in hexane, 1.10 mL, 1.10 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O 100:0 then 98:2) afforded analytically pure **2c** (342 mg, 90%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.44 (d, *J* = 14.5 Hz, 1H), 7.12–7.04 (m, 2H), 6.97 (brs, 1H), 6.64–6.61 (m, 1H), 6.01 (d, *J* = 14.5 Hz, 1H), 3.32 (s, 3H), 0.24 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 160.3, 147.3, 142.6, 129.7, 124.8, 120.8, 115.1, 112.5, 54.8, 1.5. **IR** (neat) ν 2949, 2894, 1751, 1242, 1050, 825, 788, 685, 623 cm^{-1}. **HRMS** (ESI) calcd for $[C_{18}H_{36}OSi_4+Na]^+$ 403.1735 found 403.1746.

(*Z*)-2-(4-methoxystyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2d)

Prepared according to the general procedure **A** from 4-ethynylanisole (**1d**) (33 mg, 0.25 mmol) using a larger amount of Et_2Zn (0.27 mL, 1.0 M in hexane, 0.27 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O 100:0 then 98:2) afforded analytically pure **2d** (62 mg, 65%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.44 (d, *J* = 14.4 Hz, 1H), 7.37–7.34 (m, 2H), 6.84–6.81 (m, 2H), 5.92 (d, *J* = 14.4 Hz, 1H), 3.30 (s, 3H), 0.25 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 159.8, 147.0, 133.6, 129.8, 121.5, 114.2, 54.8, 1.6. **IR** (neat) ν 2948, 2893, 1608, 1506, 1243, 1036, 824, 684, 617 cm^{-1}. **HRMS** (ESI) calcd for $[C_{18}H_{36}OSi_4+Na]^+$ 403.1735 found 403.1742.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-[4-(methylthio)styryl]-2-(trimethylsilyl)trisilane (2e)

Prepared according to the general procedure **A** from 1-ethynyl-4-(methylthio)benzene (**1e**) (148 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2e** (273 mg, 69%, *Z*/*E* > 98:2) as a white gum.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.38 (d, *J* = 14.5 Hz, 1H), 7.32–7.27 (m, 2H), 7.19–7.16 (m, 2H), 5.99 (d, *J* = 14.5 Hz, 1H), 1.99 (s, 3H, 0.23 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 146.7, 138.7, 137.7, 129.0, 126.9, 123.7, 15.5, 1.5. **IR** (neat) ν 2948, 2892, 1595, 1491, 1398, 1241, 822, 684, 622 cm^{-1}. **HRMS** (ESI) calcd for $[C_{18}H_{36}SSi_4+H]^+$ 397.1688 found 397.1697.

(*Z*)-2-(3-chlorostyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2f)

Prepared according to the general procedure **A** from 1-chloro-3-ethynylbenzene (**1f**) (137 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2f** (300 mg, 78%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.38 (t, *J* = 1.8 Hz, 1H), 7.22 (d, *J* = 14.6 Hz, 1H), 7.09–7.06 (m, 1H), 7.01 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.01 (d, *J* = 14.6 Hz, 1H), 0.21 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 145.8, 143.0, 134.8, 129.9, 128.2, 127.8, 126.6, 126.5, 1.5. IR (neat) ν 2947, 2893, 1560, 1243, 862, 829, 789, 681, 623 cm^{-1}. **HRMS** (APCI) calcd for $[C_{17}H_{33}ClSi_4+H]^+$ 385.1421 found 385.1422.

(*Z*)-2-(4-chlorostyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2g)

Prepared according to the general procedure **A** from 1-chloro-4-ethynylbenzene (**1g**) (137 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2g** (295 mg, 77%, *Z*/*E* > 98:2) as a colorless oil. The spectral data was in good agreement with that previously reported.[10l]

^{1}H NMR (C_6D_6, 400 MHz) δ 7.24 (d, *J* = 14.5 Hz, 1H), 7.18–7.13 (m, 4H), 5.99 (d, *J* = 14.5 Hz, 1H), 0.19 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 145.8, 139.3, 133.6, 129.8, 128.9, 125.4, 1.5.

(*Z*)-2-(2-bromostyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2h)

Prepared according to the general procedure **A** from 1-bromo-2-ethynylbenzene (**1h**) (181 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2h** (236 mg, 55%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.48 (dd, *J* = 14.4, 0.4 Hz, 1H), 7.39–7.35 (m, 2H), 7.00–6.96 (m, 1H), 6.72–6.68 (m, 1H), 6.02 (d, *J* = 14.4 Hz, 1H), 0.17 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 146.7, 141.7, 132.9, 130.2, 129.2, 127.7, 126.6, 124.5, 1.4. **IR** (neat) ν 2946, 2893, 2360, 2341, 1461, 1433, 1243, 1026, 831 cm^{-1}. **HRMS** (ESI) calcd for $[C_{17}H_{33}BrSi_4+Na]^+$ 453.0715 found 453.0717.

(*Z*)-2-(4-bromostyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2i)

Prepared according to the general procedure **A** from 1-bromo-4-ethynylbenzene (**1i**) (181 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2i** (219 mg, 51%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.34–7.31 (m, 2H), 7.21 (d, *J* = 14.5 Hz, 1H), 7.08–7.05 (m, 2H), 6.00 (d, *J* = 14.5 Hz, 1H), 0.18 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 145.8, 139.7, 131.8, 130.1, 125.6, 121.7, 1.5. IR (neat) ν 2948, 2892, 1483, 1243, 826, 685, 622 cm^{-1}. **HRMS** (APCI) calcd for $[C_{17}H_{33}BrSi_4+H]^+$ 429.0915 found 429.0915.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-[4-(trifluoromethyl)styryl]-2-(trimethylsilyl)trisilane (2j)

Prepared according to the general procedure **A** from 1-ethynyl-4-(trifluoromethyl)benzene (**1j**) (170 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2j** (336 mg, 80%, *Z*/*E* > 98:2) as a colorless oil. The spectral data was in good agreement with that previously reported.[10 d]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58–7.56 (m, 2H), 7.46–7.41 (m, 3H), 6.07 (d, *J* = 14.7 Hz, 1H), 0.14 (s, 27H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 145.0, 144.2, 129.3 (q, *J* = 32.6 Hz), 128.4, 128.2, 125.4 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.4 Hz), 1.4. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –62.48.

(*Z*)-methyl 4-[2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl]benzoate (2k)

Prepared according to the general procedure **A** from methyl 4-ethynylbenzoate (**1k**) (160 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O 100:0 then 99:1) afforded analytically pure **2k** (184 mg, 45%, *Z*/*E* > 98:2) as a colorless oil. The spectral data was in good agreement with that previously reported.[10l]

^{1}H NMR (C_6D_6, 400 MHz) δ 8.21–8.19 (m, 2H), 7.38–7.36 (m, 2H), 7.32 (d, *J* = 14.6 Hz, 1H), 6.10 (d, *J* = 14.6 Hz, 1H), 3.48 (s, 3H), 0.19 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 166.4, 146.1, 145.1, 130.2, 129.8, 128.4, 127.5, 51.6, 1.5.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-[2-(naphtalen-2-yl)vinyl]-2-(trimethylsilyl)trisilane (2m)

Prepared according to general procedure **A** from 2-ethynylnaphtalene (**1m**) (152 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2m** (220 mg, 55%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.78−7.74 (m, 2H), 7.67–7.65 (m, 1H), 7.61–7.55 (m, 3H), 7.29–7.20 (m, 2H), 6.11 (d, *J* = 14.5 Hz, 1H), 0.23 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 147.5, 138.7, 134.0, 133.4, 128.3, 128.2, 127.3, 126.7, 126.6, 126.2, 124.6, 1.6 (*1 C signal is not visible*). IR (neat) ν 2947, 2892, 1242, 892, 826, 776, 746, 684 cm^{-1}. **HRMS** (APCI) calcd for $[C_{21}H_{36}Si_4+H]^+$ 401.1967 found 401.1965.

(*Z*)-2-(2,6-dichlorostyryl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2n)

Prepared according to the general procedure **A** from 1,3-dichloro-2-ethynylbenzene (**1n**) (171 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2n** (266 mg, 63%, *Z*/*E* > 98:2) as a white solid.

^{1}H NMR (C_6D_6, 400 MHz) δ 6.96 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 14.8 Hz, 1H), 6.56–6.51 (m, 1H), 6.22 (d, *J* = 14.8 Hz, 1H), 0.17 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 139.7, 139.4, 135.2, 132.6, 128.9, 128.2, 1.5. **IR** (neat) ν 2948, 2893, 1557, 1427, 1244, 824, 793, 773, 686, 622 cm^{-1}. **HRMS** (APCI) calcd for $[C_{17}H_{32}Cl_2Si_4+H]^+$ 419.1031 found 419.1031. **Mp:** 63 °C.

(*Z*)-2-[2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl]pyridine (2o)

Prepared according to the general procedure **A** from 2-ethynylpyridine (**1o**) (25 µL, 0.25 mmol) using a larger amount of Et_2Zn (1.0 M in hexane, 0.27 mL, 0.27 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O 100:0 then 99:1) afforded analytically pure **2o** (56 mg, 64%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 8.48–8.46 (m, 1H), 7.20 (d, *J* = 14.1 Hz, 1H), 6.99 (td, *J* = 7.6, 1.8 Hz, 1H), 6.69–6.67 (m, 1H), 6.54 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.35–6.31 (m, 1H), 0.32 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 157.3, 149.1, 144.4, 136.1, 131.2, 124.7, 121.7, 1.8. **IR** (neat) ν 2950, 2894, 1585, 1427, 1242, 826, 804, 743, 685, 625, 524 cm^{-1}. **HRMS** (ESI) calcd for $[C_{16}H_{33}NSi_4+H]^+$ 352.1763 found 352.1749.

(*Z*)-3-[2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl]pyridine (2p)

Prepared according to the general procedure **A** from 3-ethynylpyridine (**1p**) (103 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O 90:10) afforded analytically pure **2p** (244 mg, 69%, *Z*/*E* > 98:2) as a colorless oil. The spectral data was in good agreement with that previously reported.[10l]

^{1}H NMR (C_6D_6, 400 MHz) δ 8.84 (d, *J* = 2.2 Hz, 1H), 8.42 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.28–7.25 (m, 1H), 7,18 (d, *J* = 14.6 Hz, 1H), 6.73 (ddd, *J* = 7.8, 4.8, 0.7 Hz, 1H), 6.06 (d, *J* = 14.6 Hz, 1H), 0.20 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 149.4, 148.9, 143.4, 136.2, 134.9, 127.7, 123.2, 1.4.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-[2-(5-methylthiophen-2-yl)vinyl]-2-(trimethylsilyl)trisilane (2q)

Prepared according to the general procedure **A** from 5-methyl-2-ethynylthiophene (**1q**) (122 mg, 1.00 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **2q** (125 mg, 34%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.33 (d, *J* = 14.4 Hz, 1H), 6.90 (d, *J* = 3.4 Hz, 1H), 6.45–6.44 (m, 1H), 5.87 (d, *J* = 14.4 Hz, 1H), 2.12 (brs, 3H), 0.28 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 142.2, 140.1, 139.3, 126.2, 125.8, 123.8, 15.2, 1.8. **IR** (neat) ν 2947, 2892, 1242, 826, 800, 684, 622 cm^{-1}. **HRMS** (ESI) calcd for $[C_{16}H_{34}SSi_4+Na]^+$ 393.1350 found 393.1364.

2-[1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl]-1-phenylethenone (3a)

A fraction containing analytically pure **3a** was isolated during purification of the crude mixture of the reaction of phenylacetylene (**1a**) according to general procedure **A**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93–7.91 (m, 2H), 7.56–7.52 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 2.76 (s, 2H), 0.13 (s, 27 H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 201.1, 138.0, 132.8, 128.7, 128.6, 21.6, 1.0. **HRMS** (ESI) calcd for $[C_{17}H_{34}OSi_4+H]^+$ 367.1759 found 367.1760.

2-[1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl]-1-(2-methoxyphenyl)ethenone (3b)

A fraction containing analytically pure **3b** was isolated during purification of the crude mixture of the reaction of **1b** according to general procedure **A**.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.98 (dt, *J* = 7.6, 2.0 Hz, 1H), 7.04 (ddd, *J* = 8.3, 7.3, 2.0 Hz, 1H), 6.75 (td, *J* = 7.6, 1.0 Hz, 1H), 6.42 (d, *J* = 8.3 Hz, 1H), 3.25 (s, 3H), 3.10 (s, 2H), 0.25 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 200.8, 158.7, 133.0, 132.1, 129.8, 121.0, 111.8, 55.0, 26.4, 1.1. **HRMS** (ESI) calcd for $[C_{18}H_{36}O_2Si_4+H]^+$ 397.1865 found 397.1867.

2-[1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl]-1-(naphtalen-2-yl)ethenone (3m)

A fraction containing analytically pure **3m** was isolated during purification of the crude mixture of the reaction of **1m** according to general procedure **A**.

^{1}H NMR (C_6D_6, 400 MHz) δ 8.41–8.40 (m, 1H), 8.21 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.67–7.65 (m, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.53–7.50 (m, 1H), 7.24–7.18 (m, 2H), 2.80 (s, 2H), 0.21 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 199.4, 135.8, 135.7, 133.0, 130.2, 129.7, 128.8, 128.1, 126.9, 125.2, 21.3, 1.1. **HRMS** (ESI) calcd for $[C_{21}H_{36}OSi_4+H]^+$ 439.1735 found 439.1719.

2-[1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl]-1-(5-methylthiophen-2-yl)ethenone (3q)

A fraction containing analytically pure **3q** was isolated during purification of the crude mixture of the reaction of **1q** according to general procedure **A**.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.26 (d, *J* = 3.7 Hz, 1H), 6.35–6.34 (m, 1H), 2.52 (s, 2H), 1.94 (d, *J* = 0.7 Hz, 3H), 0.25 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 192.2, 149.1,

144.3, 131.8, 126.6, 21.8, 15.6, 1.1. **HRMS** (ESI) calcd for $[C_{16}H_{34O}SSi_4+Na]^+$ 409.1300 found 409.1293.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-(1-phenylprop-1-en-2-yl)-2-(trimethylsilyl)trisilane (5)

A Schlenk flask was charged with AIBN (9 mg, 0.05 mmol) and tris(trimethylsilyl)silane (0.31 mL, 1.0 mmol) and placed under Ar. Et_2Zn (0.53 mL, 1.0 M in hexanes, 0.53 mmol) was added and the mixture was heated at 80 °C for 20 min. The resulting pale-yellow turbid mixture was then cooled to 0 °C and diluted in *n*-hexane (0.36 mL). 1-Phenyl-1-propyne (32 μL, 0.25 mmol) and Et_2Zn (0.50 mL, 1.0 M in hexanes, 0.50 mmol) were added successively. The mixture was heated at 40 °C for 18 h. It was then cooled, diluted with CH_2Cl_2 (15 mL), and quenched with aq. NH_4Cl/NH_3 (2:1) (8 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (2 x 10 mL). The combined organics were washed with brine (10 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (cyclohexane) to afford analytically pure **5** (46 mg, 49%, *Z*/*E* = 91:9) as a colorless oil.

(*Z*-**5**): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36–7.32 (m, 3H), 7.30–7.25 (m, 3H), 2.18 (brs, 3H), 0.18 (s, 27H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.5, 141.2, 134.7, 129.0, 128.5, 126.8, 32.4, 2.6. The spectral data was in good agreement with that previously reported.[10l]

(*Z*)-2-[2-(2-methoxyphenyl)penta-1,4-dienyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6b)

Prepared according to the general procedure **B** from 2-ethynylanisole (**1b**) (132 mg, 1.00 mmol) and allyl bromide (0.44 mL, 5.0 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6b** (270 mg, 64%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.16–7.14 (m, 1H), 7.06 (ddd, *J* = 8.2, 7.5, 1.8 Hz, 1H), 6.88–6.84 (m, 1H), 6.53–6.51 (m, 1H), 5.94–5.85 (m, 2H), 5.00–4.95 (m, 2H), 3.31 (s, 3H), 3.29 (ddt, *J* = 6.9, 1.3, 1.2 Hz, 2H), 0.20 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 157.0, 155.8, 137.1, 134.2, 131.2, 128.8, 120.9, 120.3, 116.0, 110.9, 54.7, 46.7, 1.4. **IR** (neat) ν 2948, 2893, 1487, 1434, 1240, 826, 750, 686, 623 cm^{-1}. **HRMS** (ESI) calcd for $[C_{21}H_{40}OSi_4+Na]^+$ 443.2048 found 443.2049.

(*Z*)-2-[2-(3-methoxyphenyl)penta-1,4-dienyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6c)

Prepared according to the general procedure **B** from 3-ethynylanisole (**1c**) (33 mg, 0.25 mmol). A more important amount of Et_2Zn (1.0 M in hexane, 0.27 mL, 0.27 mmol, 1.1 equiv) was introduced in this case. Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6c** (76 mg, 72%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 300 MHz) δ 7.13–7.07 (m, 1H), 6.94 (brs, 1H), 6.89–6.87 (m, 1H), 6.67–6.63 (m, 1H), 5.90–5.76 (m, 2H), 5.00–4.96 (m, 2H), 3.37 (s, 3H), 3.15–3.12 (m, 2H), 0.22 (s, 27H). **^{13}C NMR** (C_6D_6, 75 MHz) δ 160.2, 157.0, 146.6, 136.7, 129.8, 121.0, 120.0, 116.4, 115.1, 112.3, 54.8, 48.1, 1.5. **IR** (neat) ν 2894, 2835, 2361, 2341, 1574, 1243, 833, 687 cm^{-1}. **HRMS** (ESI) calcd for $[C_{21}H_{40}OSi_4+Na]^+$ 443.2048 found 443.2041.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-[2-(4-(methylthio)phenyl)penta-1,4-dienyl]-2-(trimethylsilyl)trisilane (6e)

Prepared according to the general procedure **B** from 1-ethynyl-4-(methylthio)benzene (**1e**) (37 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6e** (82 mg, 76%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.16–7.11 (m, 4H), 5.81–5.77 (m, 2H), 5.01–4.96 (m, 2H), 3.11 (dq, *J* = 6.8, 1.3 Hz, 2H), 2.03 (s, 3H), 0.18 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 156.5, 141.8, 138.2, 136.7, 129.0, 127.4, 120.3, 116.5, 47.9, 15.8, 1.5. **IR** (neat) ν 2946, 2892, 1584, 1242, 1093, 830, 684 cm^{-1}. **HRMS** (ESI) calcd for $[C_{21}H_{40}SSi_4+Na]^+$ 459.1820 found 459.1833.

(*Z*)-2-[2-(3-chlorophenyl)penta-1,4-dienyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6f)

Prepared according to the general procedure **B** from 1-chloro-3-ethynylbenzene (**1f**) (34 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6f** (76 mg, 72%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 300 MHz) δ 7.31 (t, *J* = 1.8 Hz, 1H), 7.06–7.02 (m, 1H), 6.97–6.94 (m, 1H), 6.88–6.83 (m, 1H), 5.81 (t, *J* = 1.2 Hz, 1H), 5.71 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 4.98–4.88 (m, 2H), 2.98–2.95 (m, 2H), 0.17 (s, 27H). **^{13}C NMR** (C_6D_6, 75 MHz) δ 155.6, 147.1, 136.2, 134.7, 130.1, 128.7, 127.6, 126.7, 121.5, 116.8, 47.9, 1.4. **IR** (neat) ν 2948, 2893, 2361, 2341, 1243, 831, 686, 623 cm^{-1}. **HRMS** (APCI) calcd for $[C_{20}H_{37}ClSi_4+H]^+$ 425.1734 found 425.1733.

(*Z*)-2-[2-(4-chlorophenyl)penta-1,4-dienyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6g)

Prepared according to the general procedure **B** from 1-chloro-4-ethynylbenzene (**1g**) (34 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6g** (87 mg, 82%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.15–7.13 (m, 2H), 7.00–6.97 (m, 2H), 5.79 (t, *J* = 1.2 Hz, 1H), 5.73 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H), 4.99–4.91 (m, 2H), 3.00 (dq_{app}, *J* = 6.8, 1.2 Hz, 2H), 0.15 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 155.7, 143.3, 136.3, 133.5, 129.9, 128.9, 121.2, 116.7, 47.8, 1.4. IR (neat) ν 2947, 2893, 2360, 2341, 1487, 1393, 1091, 830, 784, 685, 623 cm^{-1}. **HRMS** (APCI) calcd for $[C_{20}H_{37}ClSi_4+H]^+$ 425.1734 found 425.1733.

(*Z*)-2-[2-(2-bromophenyl)penta-1,4-dienyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6h)

Prepared according to the general procedure **B** from 1-bromo-2-ethynylbenzene (**1h**) (45 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6h** (83 mg, 71%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.36 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.93 (ddd, *J* = 7.5, 7.4, 1.2 Hz, 1H), 6.70 (ddd, *J* = 7.9, 7.5, 1.8 Hz, 1H), 5.89 (t, *J* = 1.3 Hz, 1H), 5.81 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 4.98 (ddt, *J* = 10.1, 2.0, 1.0 Hz, 1H), 4.91–4.90 (m, 1H), 3.19–3.07 (m, 2H), 0.18 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 155.7, 145.7, 136.2, 133.3, 131.4, 128.9, 127.6, 123.3, 122.8, 116.9, 46.5, 1.5. **IR** (neat) ν 2946, 2892, 2360, 2341, 1463, 1431, 1242, 830 cm^{-1}. **HRMS** (ESI) calcd for $[C_{20}H_{37}BrSi_4+Na]^+$ 493.1028 found 493.0979.

(*Z*)-2-[2-(4-bromophenyl)penta-1,4-dienyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6i)

Prepared according to the general procedure **B** from 1-bromo-4-ethynylbenzene (**1i**) (45 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6i** (103 mg, 88%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.30–7.28 (m, 2H), 6.92–6.90 (m, 2H), 5.78–5.77 (m, 1H), 5.72 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H), 4.98–4.90 (m, 2H), 3.01–2.97 (m, 2H), 0.13 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 155.7, 143.8, 136.3, 131.9, 130.3, 121.5, 121.2, 116.7, 47.8, 1.4. **IR** (neat) ν 2947, 2892, 2360, 1483, 1242, 1071, 992, 830, 684, 622 cm^{-1}. **HRMS** (APCI) calcd for $[C_{20}H_{37}BrSi_4+H]^+$ 469.1228 found 469.1227.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-[2-(4-(trifluoromethyl)phenyl)penta-1,4-dienyl]-2-(trimethylsilyl)trisilane (6j)

Prepared according to the general procedure **B** from 1-ethynyl-4-(trifluoromethyl)benzene (**6j**) (43 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6j** (104 mg, 91%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58−7.56 (m, 2H), 7.33−7.31 (m, 2H), 5.76 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H), 5.73 (t, *J* = 1.2 Hz, 1H), 5.05−4.97 (m, 2H), 3.15 (dq_{app}, *J* = 6.8, 1.3 Hz, 2H), 0.04 (s, 27H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 154.8, 148.6, 136.1, 129.4 (q, *J* = 32.4 Hz), 128.7, 124.4 (q, *J* = 272.0 Hz), 125.5 (q, *J* = 3.7 Hz), 122.5, 116.8, 47.7, 1.2. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –62.6. **IR** (neat) ν 2949, 2895, 2360, 2341, 1324, 1244, 1167, 1129, 1067, 832 cm^{-1}. **HRMS** (APCI) calcd for $[C_{21}H_{37}F_3Si_4+H]^+$ 459.1997 found 459.1995.

(*Z*)-1,1,1,3,3,3-hexamethyl-2-[2-(naphtalen-2-yl)penta-1,4-dienyl]-2-(trimethylsilyl)trisilane (6m)

Prepared according to the general procedure **B** from 2-ethynyl-naphtalene (**1m**) (38 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded analytically pure **6m** (50 mg, 45%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.75−7.73 (m, 2H), 7.64−7.61 (m, 2H), 7.35−7.33 (m, 1H), 7.30−7.22 (m, 2H), 5.93 (t, *J* = 1.2 Hz, 1H), 5.86 (ddt, *J* = 16.1, 10.8, 6.8 Hz, 1H), 5.03−4.98 (m, 2H), 3.22−3.19 (m, 2H), 0.15 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 157.2, 142.7, 136.6, 134.0, 133.2, 128.5, 127.1, 126.9, 126.6, 126.1, 120.4, 116.5, 48.1, 1.5 (*2 C signals are not visible*). **IR** (neat) ν 2948, 2893, 2360, 2342, 1243, 832 cm^{-1}. **HRMS** (ESI) calcd for $[C_{24}H_{40}Si_4+Na]^+$ 463.2099 found 463.2120.

(*Z*)-2-[2-(2,6-dichlorophenyl)penta-1,4-dienyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (6n)

Prepared according to the general procedure **B** from 1,3-dichloro-2-ethynylbenzene (**1n**) (43 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane) afforded a mixture of **6n** (72 mg, 63%, *Z*/*E* > 98:2) and **2n** (10 mg, 10%, *Z*/*E* > 98:2) that could not be separated.

^{1}H NMR (C_6D_6, 400 MHz) δ 6.96 (d, *J* = 8.1 Hz, 2H), 6.50 (t, *J* = 8.1 Hz, 1H), 6.10 (t, *J* = 1.5 Hz, 1H), 5.96 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.05−5.02 (m, 1H), 5.00−4.95 (m, 1H), 3.06−3.03 (m, 2H), 0.22 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 149.7, 142.6, 135.6, 134.7, 128.9, 128.5, 125.8, 117.6, 44.9, 1.6. **HRMS** (APCI) calcd for $[C_{20}H_{36}Cl_2Si_4+H]^+$ 459.1344 found 459.1333.

(*Z*)-2-[1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)penta-1,4-dien-2-yl]pyridine (6o)

Prepared according to the general procedure **B** from 2-ethynylpyridine (**1o**) (25 µL, 0.25 mmol). A more important amount of Et_2Zn (1.0 M in hexane, 0.27 mL, 0.27 mmol, 1.1 equiv) was introduced in this case. Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O 100:0 then 99:1) afforded analytically pure **6o** (62 mg, 64%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 8.50 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.13−7.05 (m, 2H), 6.61 (ddd, *J* = 7.2, 4.8, 1.5 Hz, 1H), 6.14 (t, *J* = 1.1 Hz, 1H), 5.87 (ddt, *J* = 16.6, 10.1, 6.4 Hz, 1H), 5.06−4.98 (m, 2H), 3.29 (dq_{app}, *J* = 6.4, 1.3 Hz, 2H), 0.26 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 160.2, 153.6, 149.4, 137.1, 136.1, 125.8, 122.1, 121.8, 116.3, 44.6, 1.7. **IR** (neat) ν 2948, 2893, 2362, 1584, 1426, 1241, 823, 743, 684, 623 cm^{-1}. **HRMS** (ESI) calcd for $[C_{19}H_{37}NSi_4+H]^+$ 392.2076 found 392.2092.

(*Z*)-3-[1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)penta-1,4-dien-2-yl]pyridine (6p)

Prepared according to the general procedure **B** from 3-ethynylpyridine (**1p**) (26 mg, 0.25 mmol). Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O, 90:10) afforded analytically pure **6p** (68 mg, 69%, *Z*/*E* > 98:2) as a colorless oil.

^{1}H NMR (C_6D_6, 400 MHz) δ 8.75 (d, *J* = 1.4 Hz, 1H), 8.46 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.23−7.20 (m, 1H), 6.75 (dd, *J* = 7.8, 4.7 Hz, 1H), 5.88 (t, *J* = 1.2 Hz, 1H), 5.70 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H), 4.96−4.88 (m, 2H), 2.98−2.96 (m, 2H), 0.17 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 153.2, 149.7, 149.1, 140.1, 136.1, 134.9, 123.2, 122.9, 116.9, 47.6, 1.3. **IR** (neat) ν 2947, 2893, 2360, 1408, 1243, 830, 716, 685, 623 cm^{-1}. **HRMS** (ESI) calcd for $[C_{19}H_{37}NSi_4+H]^+$ 392.2076 found 392.2078.

(*E*)-2-[2-(3-methoxyphenyl)-2-(tributylstannyl)vinyl]-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (7)

A Schlenk tube was charged with 3-ethynylanisole (**1c**) (33 mg, 0.25 mmol) and a suspension of $[(Me_3Si)_3Si]_2Zn$ (155 mg, 0.27 mmol) in *n*-hexane (2 mL) was added at –30 °C, followed by Et_2Zn (1.0 M in *n*-hexane, 0.27 mL, 0.27 mmol). The turbid mixture was stirred at this temperature for 3 h, and then CuCN•2LiCl (1.0 M in THF, 0.30 mL, 0.30 mmol) was added, followed by tributyl(chloro)stannane (0.34 mL, 1.25 mmol). The mixture was stirred overnight at –30 °C and then diluted with CH_2Cl_2 (15 mL) and quenched with aqueous NH_4Cl/NH_3 (2:1) (2 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (2 x 15 mL). The combined organics were washed with brine (2 x 5 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure to afford the crude product (*E*/*Z* > 98:2). Purification by flash chromatography on silica gel (pentane) afforded analytically pure **7** (101 mg, 0.15 mmol, 60%, *E*/*Z* > 98:2) as a colorless oil and product **2c** (19 mg, 20%).

^{1}H NMR (C_6D_6, 400 MHz) δ 7.12–7.09 (m, 1H), 6.77–6.75 (m, 1H), 6.73–6.71 (m, 1H), 6.58 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.41 (s, 1H), 3.44 (s, 3H), 1.59–1.54 (m, 6H), 1.40–1.30 (m, 6H), 1.00–0.96 (m, 6H), 0.95–0.91 (m, 9H), 0.24 (s, 27H). **^{13}C NMR** (C_6D_6, 100 MHz) δ 168.5, 160.4, 150.8, 136.6, 129.9, 119.1, 112.9, 110.8, 54.8, 29.6, 27.9, 14.0, 11.0, 1.5. **IR** (neat) ν 2954, 2926, 1594, 1574, 1242,

828, 685, 622 cm^{-1}. **HRMS** (ESI) calcd for $[C_{30}H_{62}OSi_4Sn+Na]^+$ 693.2792 found 693.2770.

Computational Details. The calculations were carried out with the Gaussian09 package.[32] All geometries were calculated using Density Functional Theory (DFT) with the hybrid B3PW91 level of theory.[33] The 6-31-G(d,p) basis set[34] is used for all atoms. The geometry optimizations were performed without any constraint and the nature of the extrema (minima and transition states) were verified by analytical calculations of frequencies. In particular the connection between the transition state and minima was verified by carrying out a small displacement along the reaction coordinate in each direction and optimizing geometry starting from these structures.

Acknowledgements

This research was supported by the Deutsche Forschungsgemeinschaft (Oe 249/7-1) and by the Agence Nationale de la Recherche (SATRAZ Project, grant n° 2011-INTB-1015-01). LabEx MiChem (Investissement d'Avenir program under reference ANR-11-IDEX-0004-02) is also gratefully acknowledged for financial support.

References

[1] D. S. W. Lim, E. A. Anderson, *Synthesis* **2012**, *44*, 983.

[2] For an account, see: a) A. Barbero, F. J. Pulido, *Acc. Chem. Res.* **2004**, *37*, 817; for the original work, see: b) I. Fleming, T. W. Newton, F. Roessler, *J. Chem. Soc. Perkin Trans. 1* **1981**, 2527.

[3] a) H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, H. Nozaki, *J. Am. Chem. Soc.* **1983**, *105*, 4491. b) Y. Okuda, Y. Morizawa, K. Oshima, H. Nozaki, *Tetrahedron Lett.* **1984**, *25*, 2483. c) V. Liepins, A. S. E. Karlström, J.-E. Bäckvall, *J. Org. Chem.* **2002**, *67*, 2136.

[4] S. Nakamura, M. Uchiyama, T. Ohwada, *J. Am. Chem. Soc.* **2004**, *126*, 11146.

[5] Y. Okuda, K. Wakamatsu, W. Tückmantel, K. Oshima, H. Nozaki, *Tetrahedron Lett.* **1985**, *26*, 4629.

[6] The CuI catalyzed silylzincation using $(Me_2PhSi)_2Zn$ or $(t\text{-}BuPh_2Si)_2Zn$ as silicon donors was also reported, but the method was not exploited to prepare trisubstituted vinyl silanes, see: G. Auer, M. Oestreich, *Chem. Commun.* **2006**, 311–313.

[7] R. Shintani, H. Kurata, K. Nozaki, *J. Org. Chem.* **2016**, *81*, 3065.

[8] E. Romain, C. Fopp, F. Chemla, F. Ferreira, O. Jackowski, M. Oestreich, A. Perez-Luna, *Angew. Chem. Int. Ed.* **2014**, *53*, 11333.

[9] a) C. Fopp, E. Romain, K. Isaac, F. Chemla, F. Ferreira, O. Jackowski, M. Oestreich, A. Perez-Luna, *Org. Lett.* **2016**, *18*, 2054. b) C. Fopp, K. Isaac, E. Romain, F. Chemla, F. Ferreira, O. Jackowski, M. Oestreich, A. Perez-Luna, *Synthesis* **2017**, *49*, 724–735.

[10] For the most representative examples, see: a) B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, *J. Org. Chem.* **1992**, *57*, 3994–4000. b) K. Miura, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356–2364. c) Y. Liu, S. Yamazaki, S. Yamabe, *J. Org. Chem.* **2005**, *70*, 556–561. d) Y. Liu, S. Yamazaki, S. Yamabe, Y. Nakato, *J. Mat. Chem.* **2005**, *15*, 4906–4913. e) H. Yasuda, Y. Uenoyama, O. Nobuta, S. Kobayashi, I. Ryu, *Tetrahedron Lett.* **2008**, *49*, 367–370. f) Z. Wang, J. P. Pitteloud, L. Montes, M. Rapp, D. Derane, S. F. Wnuk, *Tetrahedron* **2008**, *64*, 5322–5327. g) J. Wang, Z. Zhu, W. Huang, M. Deng, X. Zhou, *J. Organomet. Chem.* **2008**, *693*, 2188–2192. h) A. Odedra, K. Geyer, T. Gustafsson, R. Gilmour, P. H. Seeberger, *Chem. Commun.* **2008**, *26*, 3025–3027. i) A. Postigo, S. Kopsov, S. S. Zlotsky, C. Ferreri, C. Chatgilialoglu, *Organometallics* **2009**, *28*, 3282–3287. j) S. Kobayashi, H. Kuroda, Y. Ohtsuka, T. Kashihara, A. Masuyama, K. Watanabe, *Tetrahedron* **2013**, *69*, 2251–2259. k) X. Yang, C. Wang, *Angew. Chem. Int. Ed.* **2018**, *57*, 923–928. l) J. Zhu, W.-C. Cui, S. Wang, Z.-J. Yao, *Org. Lett.* **2018**, *20*, 3174–3178.

[11] The *Z*-configuration of the vinylsilanes was unambiguously determined by ^1H NMR on the basis of the $^3J_{H-H}$ coupling constant of the vinylic protons (which were in the range [14.1 Hz, 14.8 Hz]).

[12] Z. Chen, Y.-X. Zhang, Y. An, X.-L. Song, Y.-H. Wang, L.-L. Zhu, L. Guo, *Eur. J. Org. Chem.* **2009**, 5146–5152.

[13] In the case of 2-ethynlanisole (**1b**), 8% of the product formed results from zinc/proton exchange between the vinylzinc intermediate and the starting alkyne (see Supporting Information for details).

[14] Y. Liang, J.-P. Pitteloud, S. F. Wnuk, *J. Org. Chem.* **2013**, *78*, 5761–5767.

[15] R. Dobrovetsky, Y. Kratish, B. Tumanskii, M. Botoshansky, D. Bravo-Zhivotovskii, Y. Apeloig, *Angew. Chem. Int. Ed.* **2012**, *51*, 4671–4675.

[16] $[(Me_3Si)_3Si]_2Zn$, prepared according to the procedure reported in ref 15, was either isolated (stored in glovebox) and used pure as a solid or alternatively, generated in-situ and used in solution immediately after its preparation (see Supporting Information for details).

[17] Initiation of radical chains by oxydation of Et_2Zn with residual oxygen is a well-established process. For the original work, see: a) I. Ryu, F. Araki, S. Minakata, M. Komatsu, *Tetrahedron Lett.* **1998**, *39*, 6335–6336. For most recent mechanistic considerations, see: b) J. Maury, L. Feray, S. Bazin, J.-L. Clement, S. R. A. Marque, D. Siri, M. P. Bertrand, *Chem. Eur. J.* **2011**, *17*, 1586–1595. c) M. Kubisiak, K. Zelga, W. Bury, I. Justyniak, K. Budny-Godlewski, Z. Ochal, J. Lewinski, *Chem. Sci.* **2015**, *6*, 3102–3108.

[18] It is documented that α-aryl-substituted vinylic radicals abstract hydrogen atoms α to the oxygen atom of ethers (ref 12). We speculate that for these substrates (**1c** and **1d**), termination reactions may occur through atom transfer from α-phenoxy H-atoms making radical chains shorter. Increasing the amount of radical initiator should compensate this effect and thus allow to drive the reaction to completion.

[19] In preliminary studies, the silylzincation of phenylacetylene with $[(Me_3Si)_3Si]_2Zn$ in the presence of Et_2Zn (1.7 equiv) was found to yield **2a** in a low 33% yield and with no control of the double bond geometry (ref 9a). A possible explanation, is that in the presence of larger amounts of Et_2Zn, competitive alkyne deprotonation interferes with the silylzincation reaction.

[20] A similar behavior at high temperature was observed for the related germylzincation reaction, see: K. de la Vega-Hernández, E. Romain, A. Coffinet, K. Bijouard, G. Gontard, F. Chemla, F. Ferreira, O. Jackowski, A. Perez-Luna, *J. Am. Chem. Soc.* **2018**, *140*, 17632–17642.

[21] The *Z*-configuration was determined for **6b** on the basis of NOESY experiments (see Supporting Information for details) and inferred for the other products by comparison of the NMR spectra.

[22] *Z*-to-*E* isomerization of β-stannyl vinylsilanes was achieved through selective energy transfer photocatalysis under irradiation at 364 nm. This approach, that can also be regarded as an entry to formal silylstannylation of alkynes, is not fully stereoselective (*E*/*Z* < 82:18), see : S. I. Faßbender, J. J. Molloy, C. Mück-Lichtenfeld, R. Gilmour, *Angew. Chem. Int. Ed.* **2019**, *58*, 18619–18626.

[23] Compound **9**-d_1 was also the major product formed in the reaction between **8** and $(Me_3Si)_3SiH/Et_2Zn$, see ref 8.

[24] For a related example of the fragmentation of a *β*-alkoxy zinc enolate, see: S. Giboulot, A. Perez-Luna, C. Botuha, F. Ferreira, F. Chemla, *Tetrahedron Lett.* **2008**, *49*, 3963–3966.

[25] Determined by ^{1}H NMR from the **9**-d_1/**10** = 80:20 ratio measured in the crude product. The companying product of *β*-fragmentation was not detected, likely because it reacts subsequently as 1,4-acceptor, see ref 8.

[26] The addition at the α-carbon was found to be less favorable. See Table S1 of the Supporting Information for details on the corresponding energetics and geometrical data.

[27] See Table S1 and Figure S1 of the Supporting Information.

[28] U. Wille, *Chem. Rev.* **2013**, *113*, 813–853.

[29] W.-J. van Zeist, F. M. Bickelhaupt, *Org. Biomol. Chem.* **2010**, *8*, 3118–3127.

[30] See Table S2 of the Supporting Information for the definition of the two terms.

[31] M. F. Wisthoff, S. B. Pawley, A. P. Cinderella, D. A. Watson, *J. Am. Chem. Soc.* **2020**, *142*, 12051–12055.

[32] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

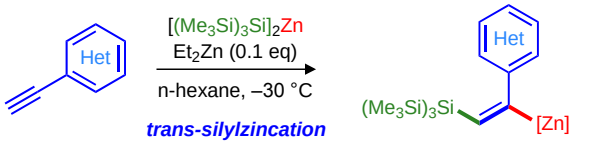
[33] a) J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244–13249. b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[34] a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261. b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665.

Development of a Radical Silylzincation of (Het)Aryl-Substituted Alkynes and Computational Insights into the Origin of the *Trans*-Stereoselectivity

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Elise Romain, Karen de la Vega-Hernández, Frédéric Guégan, Juan Sanz García, Carolin Fopp, Fabrice Chemla, Franck Ferreira, Hélène Gerard, Olivier Jackowski, Stéphanie Halbert*, Martin Oestreich*, Alejandro Perez-Luna*



up to *E*:*Z* > 98:2 and 80% yield

- high regio- and diastereoselectivity
- 16 examples
- functionalization of the C(sp2)–Zn bond possible
- radical mechanism supported by computational studies
- insights into the origin of the *trans*-stereoselectivity