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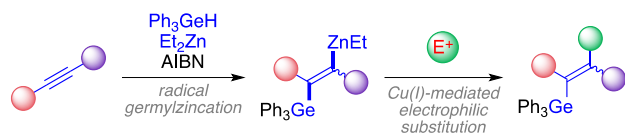
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# Radical Germylzincation of Aryl- and Alkyl-Substituted Internal Alkynes

Karen de la Vega-Hernández, Fabrice Chemla, Franck Ferreira, Olivier Jackowski, and Alejandro Perez-Luna\*

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Supporting Information Placeholder



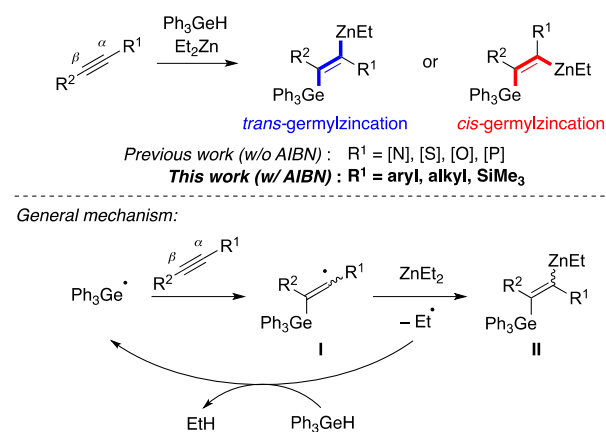
**ABSTRACT:** The stereoselective germylzincation of internal alkynes delivering trisubstituted vinylgermanes is achieved via a radical chain process involving  $\text{Ph}_3\text{GeH}$  and  $\text{Et}_2\text{Zn}$  with AIBN as initiator. Excellent levels of regiocontrol are observed for non-symmetric (aryl, alkyl)-substituted alkynes, as well as for propargylic alcohols with aryl-, alkyl-, or silyl-substituted alkynes. The germylzincation reaction can be combined in one pot with the Cu(I)-mediated electrophilic substitution of the  $\text{C}(\text{sp}^2)\text{-Zn}$  bond to obtain synthetically challenging tetrasubstituted vinylgermanes.

The increasing demand in germanium-containing compounds also raises considerable interest in the regio- and stereocontrolled preparation of vinylgermanes.<sup>1</sup> For this, carbon–germanium bond-forming addition reactions to alkynes using hydrogermanes as germanium source are most popular. The regio- and stereoselective hydrogermylation of alkynes was disclosed under several conditions, including thermal, sonochemical or microwave activation,<sup>2</sup> transition-metal catalysis,<sup>3</sup> main-group Lewis-acid catalysis,<sup>4</sup> as well as in the presence of radical initiators.<sup>2,3c,5</sup> These methods share however the common intrinsic limitation that they cannot give access to tetrasubstituted or 1,2,2-substituted vinylgermanes which have two substituents distal to the germyl group.<sup>6</sup> Alkyne germylmetalation is attractive in this context, as the newly formed  $\text{C}(\text{sp}^2)\text{-metal}$  bond can serve as linchpin for further functionalization, but remains virtually unexplored: reports on alkyne germylcupration are scarce,<sup>7,8</sup> and limited to terminal alkynes.<sup>9</sup> Moreover, subsequent  $\text{C}(\text{sp}^2)\text{-Cu}$  bond-functionalization is poorly effective or impeded by the reversible character of the addition step. Alkyne germylstannylation was also considered for the same purpose,<sup>10</sup> but again only on terminal alkynes and  $\text{C}(\text{sp}^2)\text{-Sn}$  bond-functionalization required an additional synthetic step.

To overcome these shortcomings, we recently disclosed the germylzincation reaction of  $\alpha$ -heteroatom-substituted alkynes relying on their reaction with a hydrogermane and  $\text{Et}_2\text{Zn}$  in a radical chain process<sup>11</sup> (Scheme 1). The decisive feature of this new germylmetalation reaction is the possibility to combine it readily in one-pot with a subsequent stereoretentive electrophilic substitution reaction of the created  $\text{C}(\text{sp}^2)\text{-Zn}$  bond. In continuation of this work and given that organogermyl radicals

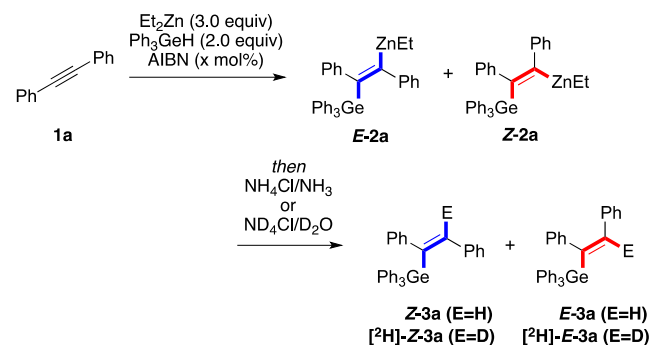
add across various types of C–C triple bonds, we became interested in applying the method with other alkynes.<sup>12</sup> In this Letter, we report the radical germylzincation of internal alkynes, including symmetrical diaryl- and dialkylacetylenes, non-symmetrical (aryl, alkyl)-substituted alkynes, as well as aryl-, alkyl-, or trimethylsilyl-substituted propargylic alcohols. High levels of regio- (where appropriate) and stereocontrol can be achieved through modulation of the operating conditions for germylzincation reactions that can be either *trans*- or *cis*-selective depending on the substrate type.

## Scheme 1. Radical Germylzincation of Internal Alkynes



We commenced our study by investigating the reaction of diphenylacetylene **1a** with a combination of Ph<sub>3</sub>GeH and Et<sub>2</sub>Zn (Table 1).

**Table 1. Gernylzincation of Diphenylacetylene (1a)**



entry	solvent	conditions	AIBN (mol%)	E	d.r. <b>3a</b> (Z/E) <sup>a</sup>	yield <b>3a</b> (%) <sup>b</sup>
1	THF	40 °C, 16 h	–	H	88:12	49 <sup>c,d</sup>
2	THF	80 °C, 1 h	25	H	92:8	67 <sup>d</sup>
3	THF	80 °C, 1 h	25	D	92:8	71 <sup>d</sup>
4	THF	80 °C, 1 h	–	H	>98:2	<10 <sup>e</sup>
5	THF	80 °C, <sup>f</sup> 1 h	25	H	84:16	74
6	THF	80 °C, 1 h	50	H	80:20	85 <sup>e</sup>
7	benzene	100 °C, 16 h	10	H	23:77	88 <sup>e</sup>
8	benzene	100 °C, <sup>f</sup> 1 h	10	H	26:74	78 <sup>e</sup>
9	heptane	120 °C, 16 h	100	H	30:70	83 <sup>e</sup>

<sup>a</sup>Determined by <sup>1</sup>H NMR prior to purification. <sup>b</sup>Isolated yield of both diastereomers. <sup>c</sup>Ph<sub>3</sub>GeH (1.3 equiv). <sup>d</sup>Reference 11. <sup>e</sup>Yield estimated by <sup>1</sup>H NMR analysis of the crude reaction mixture using butadiene sulfone as internal standard. <sup>f</sup>Microwave heating.

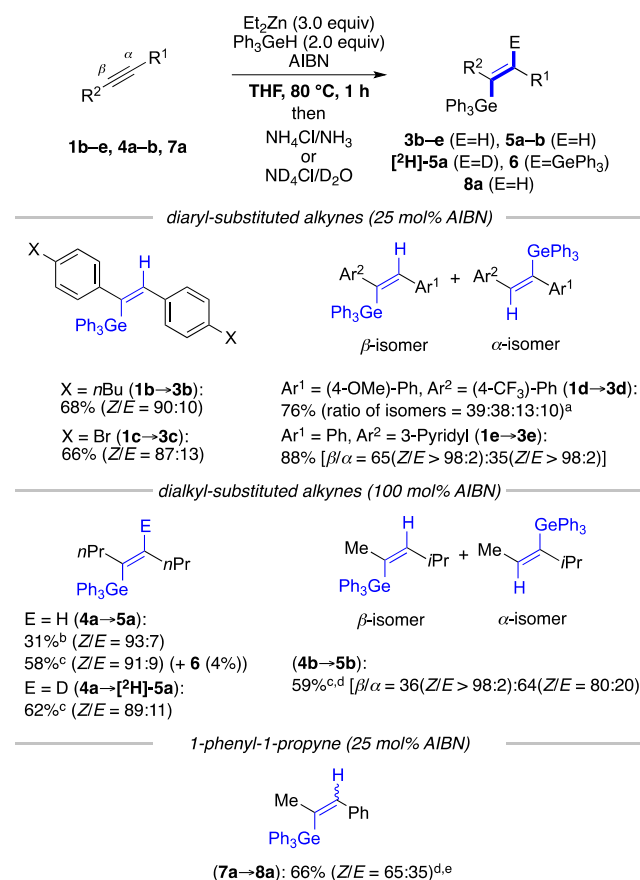
Under the operating conditions previously applied for the gernylzincation of internal ynamides, i.e. Ph<sub>3</sub>GeH (1.3 equiv) and Et<sub>2</sub>Zn (3.0 equiv) in THF at 40 °C (entry 1), after 16 h and following work-up, vinylgermane **3a** was obtained with high *Z*-stereoselectivity (*Z/E* = 88:12), albeit in moderate 49% yield because conversion was not complete (~35–40% unreacted **1a** were recovered). Using higher amounts of Ph<sub>3</sub>GeH (2.0 equiv), adding AIBN (25 mol%) as radical initiator, and operating at 80 °C to ensure decomposition of the latter, made possible to reduce the amount of unreacted **1a** to ~20% and allowed for improved results: 67% yield was observed within a much shorter reaction time (1 h), along with a significant enhancement of the stereoselectivity (*Z/E* = 92:8) (entry 2). Under these conditions, D-labeling confirmed the formation of a vinylzinc intermediate as [<sup>2</sup>H]-**3a** was obtained (98% D incorporation) on quenching with ND<sub>4</sub>Cl (entry 3). Importantly, the critical role played by AIBN here was established through a control experiment: in the same conditions but in the absence of the radical initiator, **3a** was detected in amounts lower than 10% (entry 4). Conversely, heating through microwave irradiation instead of an oil-bath (entry 5) or increasing to 50 mol% the amount of AIBN (entry 6) led to full or close-to-full conversion. However, this was not beneficial overall, since the stereoselectivity dropped. In benzene at 100 °C (entries 7 and 8), 88% and 78% yield was achieved with only 10 mol% AIBN, but reversal of stereoselectivity was observed and vinylgermane **3a** was delivered in a *E/Z*

~ 75:25 ratio both upon heating in an oil-bath (for 16 h) or through microwave irradiation (1 h). A similar outcome was observed operating in heptane at 120 °C in the presence of 100 mol% AIBN (entry 9).

These results point towards the coexistence of two regimes: a non-equilibrating one which is *trans*-stereoselective,<sup>15</sup> and an equilibrating one which is (moderately) *cis*-stereoselective. In line with analogous observations for radical hydrogermylation reactions of terminal alkynes, we surmise that the triphenylgermyl radical is responsible for the isomerization of the β-triphenylgermyl vinylzinc intermediates **2a**.<sup>5b</sup> Accordingly, kinetic selectivity is prevalent for short reaction times and in THF wherein radical chains are short, while thermodynamic selectivity is observed for long reaction times and in benzene or heptane wherein the triphenylgermyl radical-promoted isomerization is facilitated by the existence of longer radical chains.

Having identified these two possibilities, we focused on assessing their scope. In THF at 80 °C (Scheme 2), other diaryl-substituted acetylenes also underwent readily *trans*-selective gernylzincation.

**Scheme 2. Radical Gernylzincation of Aryl- and Alkyl-Substituted Alkynes in THF**



<sup>a</sup>The configuration of each isomer could not be determined unequivocally. The two major isomers had a *Z* configuration. <sup>b</sup>AIBN (25 mol%). <sup>c</sup>Microwave heating. <sup>d</sup>Yield calculated by <sup>1</sup>H NMR analysis of the crude reaction mixture using butadiene sulfone as internal standard. <sup>e</sup>Only *β*-regioisomers were detected.

Symmetrical diphenylacetylenes **1b–c** afforded the corresponding vinylgermanes **3b–c** in good yields (66–68%) and high *Z*-selectivity (*Z/E* ≥ 87:13). In the case of non-symmetrical diarylacetylenes however, the regioselectivity of the process could

not be controlled. Illustratively, the gerymlyzincation of diphenylacetylene **1d** having both an electron-rich *para*-OMe-phenyl substituent and an electron-deficient *para*-CF<sub>3</sub>-phenyl substituent delivered **3d** (in 76% yield) as an  $\alpha/\beta = 50:50$  mixture of regioisomers, thus evidencing that an electronic bias of the carbon-carbon triple bond has no influence on the regioselectivity of the addition. The poor regioselectivity observed in the gerymlyzincation of **1e**, substituted by a 3-pyridyl group and a phenyl group further confirmed this fact. Here however, the major ( $\beta$ ) regioisomer of **3e**, formed as a single *Z* diastereomer, was isolated in a decent 57% yield.

Dialkyl-substituted acetylenes were also amenable to *trans*-germylzincation in THF at 80 °C (Scheme 2).<sup>14</sup> In the presence of 25 mol% AIBN, the reaction of 4-octyne **4a** delivered vinylgermane **5a** in 31% yield with *Z/E* = 93:7. A more satisfactory 58% yield was obtained with 100 mol% AIBN using microwave heating. Here also, fully D-labeled [<sup>2</sup>H]-**5a** was recovered on quenching the reaction with ND<sub>4</sub>Cl, thus confirming the formation of vinylzinc intermediates. Note that the formation of bisgermylated byproduct **6**, the structure of which was determined by X-Ray crystallographic analysis,<sup>15</sup> was also detected under these harsher conditions (4% yield).<sup>16</sup> The same protocol was also applied to alkyne **4b** having two different alkyl substituents, but louse regiocontrol was observed in spite of the recognizable steric bias, and product **5b** was obtained as a mixture of regio- and stereoisomers.

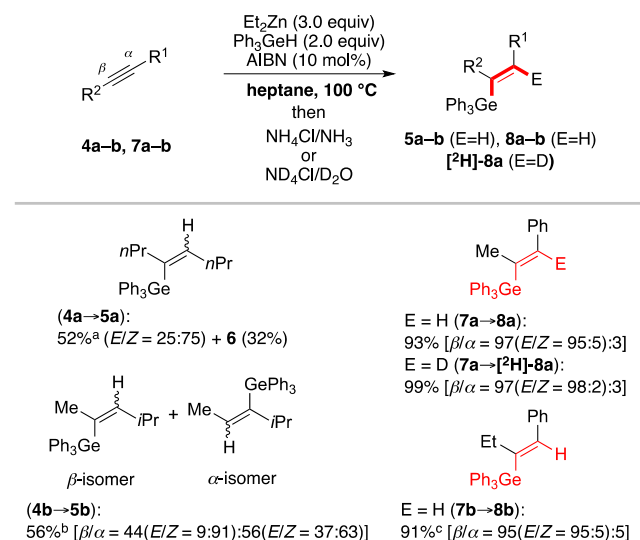
Conversely, regiocontrol was not a problem in the case of 1-phenyl-1-propyne **7a** having substituents different in nature. As for the diaryl-substituted alkynes, 25 mol% AIBN sufficed to achieve a good 66% gerymlyzincation yield. Only the  $\beta$ -regioisomers were detected, what can be ascribed to stabilization by the adjacent phenyl group of the vinyl radical intermediate (**1** (R<sup>1</sup>=Ph), Scheme 1) arising from the triphenylgermyl radical addition. Nevertheless, the isomerization of the *E*-vinylzinc adduct is more facile and observable to some extent even if full conversion only requires 1 h reaction time. Hence, vinylgermane **8a** was obtained as a *Z/E* = 65:35 mixture of stereoisomers. The structure of *E*-**8a** was confirmed by X-ray crystallography.<sup>15</sup>

We next surveyed the possibilities offered by operating in heptane at 100 °C (Scheme 3). The reaction of 4-octyne **4a** in the presence of 50 mol% AIBN and under microwave irradiation delivered vinylgermane **5a** in 52% yield as a *Z/E* = 75:25 mixture of isomers. Hence, while some isomerization was observed, the process did not seem suitable to steer the reaction towards *E*-stereoselectivity for this substrate class. In addition, bisgermylated product **6** was formed in 32% yield. As previously observed in THF, non-symmetrical dialkyl-substituted alkyne **4b** led to a mixture of regio and stereoisomers.

By contrast, with 1-phenyl-1-propyne **7a** for which the isomerization occurs more readily,<sup>17</sup> performing the reaction in the presence of 10 mol% AIBN delivered the desired product **8a** in excellent 93% yield, with perfect regioselectivity, and remarkable *E*-stereoselectivity (*E/Z* = 95:5). No difference was observed using conventional heating (2 h) or microwave irradiation (1 h). Again, D-labeling experiments ascertained that gerymlyzincation was also in these conditions the exclusive reaction pathway accounting for vinylgermane formation. The protocol appears to be general for (alkyl, aryl)-substituted alkynes as, similarly, 1-phenyl-1-butyne **7b** afforded vinylgermane **8b** in 91% yield and *E/Z* = 95:5 ratio, with complete

control of the regioselectivity. Importantly, no appreciable difference of outcome was noted on running the reaction on a 1 mmol scale.

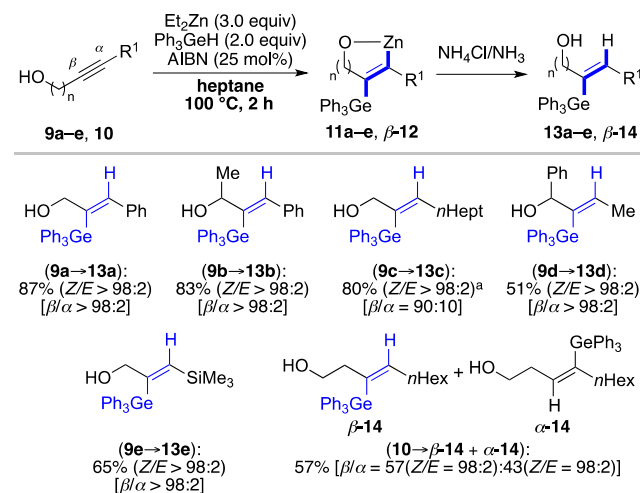
### Scheme 3. Radical Gerymlyzincation of Dialkyl- and (Alkyl, Aryl)-substituted Alkynes in Heptane



<sup>a</sup>AIBN (50 mol%), microwave heating (1 h). <sup>b</sup>Microwave heating (1 h). <sup>c</sup>94% yield was obtained on a 1 mmol scale (25 mol% AIBN).

We then considered propargylic alcohols (Scheme 4), a synthetically important family of substrates for which we awaited to achieve high levels of regio- and stereocontrol. An *O*-directing effect allowing for exquisite vicinal-regiocontrol in the addition of triorganostannyl radicals is well documented for radical hydrostannation reactions of propargyloxy dialkylacetylenes with tin hydrides,<sup>18</sup> and we observed similar levels of regioselectivity in a preliminary survey of AIBN-initiated radical hydrogermylation reactions with  $\text{Ph}_3\text{GeH}$ .<sup>19</sup> Stereocontrol could be secured through chelate formation (**11**).

### Scheme 4. Radical Gerymlyzincation of Propargylic Alcohols

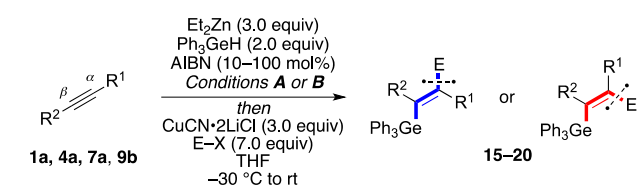


<sup>a</sup>For the major  $\beta$ -isomer.

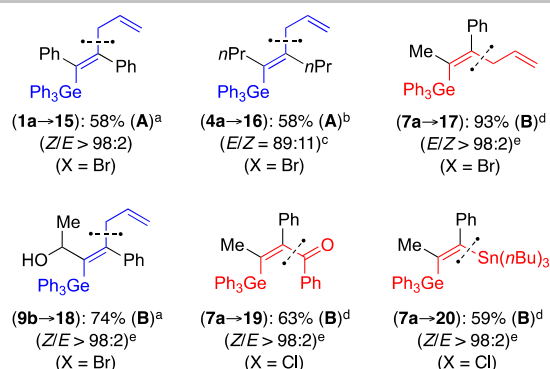
Aryl- or alkyl substituted primary (**9a**, **9c**) and secondary (**9b**, **9d**) propargylic alcohols performed well, and germylated alcohols **13a–d** were obtained in good-to-high yields, with excellent  $\beta$ -regio- and *Z*-stereoselectivity. The methodology was also amenable to the utilization of trimethylsilyl-substituted propargylic alcohol **9e** which afforded  $\beta$ -trimethylsilyl vinylgermane **13e** in 65% yield. Lastly, homopropargylic alcohol **10** was investigated. Here, given that the hydroxy unit is too far away from the alkyne and no regiocontrol is induced in the germyl radical addition,<sup>19,20</sup> a mixture of regioisomers was obtained in  $\beta$ -**14**/ $\alpha$ -**14** = 57:43 ratio and 57% combined yield. Nevertheless, chelate formation remains possible for both regioisomers of the germylzinc adducts  $\beta$ -**12** and  $\alpha$ -**12** (not shown in the scheme) and allows for almost complete stereocontrol in favor of the *Z*-isomers of  $\beta$ -**14** and  $\alpha$ -**14**.

In the final part of our study, we established the potential of our new germylzincation procedures to prepare tetrasubstituted vinylgermanes through functionalization *in one pot* of the C(sp<sup>2</sup>)–Zn bond of the vinylzinc adducts formed. Cu(I)-mediated allylation was performed for each substrate class: tetrasubstituted vinylgermanes **15–18** were obtained from **1a**, **4a**, **7a** and **9b** in good-to-excellent yields (58–93%) and with exquisite retention of the geometry of the vinylzinc intermediates (Scheme 5). The configuration of products *Z*-**15** and *E*-**17** was established by X-ray crystallography.<sup>15</sup>

### Scheme 5. Preparation of Tetrasubstituted Vinylgermanes through Alkyne Germylzincation/Cu(I)-Mediated Electrophilic Substitution



A: THF, 80 °C, 1 h  
B: heptane, 100 °C, 2 h



<sup>a</sup>AIBN (25 mol%). <sup>b</sup>AIBN (100 mol%), microwave heating. <sup>c</sup>5% of **6** was detected. <sup>d</sup>AIBN (10 mol%). <sup>e</sup>Only  $\beta$ -regioisomers were detected.

Benzoyl chloride and tributyltin chloride were also competent electrophiles, leading to benzoylated vinylgermane **19** and  $\beta$ -stannyl vinylgermane **20** as single regio- and stereoisomers. The domino alkyne germylzincation/Cu(I)-mediated stannylation reaction giving **20** is remarkable as it allows for the direct synthesis of these tetrasubstituted 1,2-dimetallated alkenes not accessible through the oxidative addition chemistry of Ge–Sn compounds.<sup>21</sup>

In summary, we describe here the germylzincation of internal alkynes by reaction with Ph<sub>3</sub>GeH and Et<sub>2</sub>Zn in the presence of AIBN as radical initiator. Upon tuning of the reaction conditions, an array of substrate-types is amenable to germylzincation with high levels of stereoselectivity, including symmetrical diaryl- or dialkylsubstituted acetylenes, non-symmetrical (alkyl, aryl)-substituted acetylenes and propargylic alcohols. Superb regiocontrol is obtained for alkyl-substituted arylacetylenes and propargylic alcohols. As part of this work, we demonstrate the possibility to engage the C(sp<sup>2</sup>)–Zn bond formed in subsequent stereoretentive Cu(I)-mediated electrophilic substitution reactions. This two-step one-pot protocol offers a versatile and modular route to access valuable tetrasubstituted vinylgermanes with substitution patterns that have so far remained synthetically challenging.

## ASSOCIATED CONTENT

### Supporting Information.

Additional data and discussion, experimental details, NMR spectra for new compounds, and X-ray crystal structures for compounds **6**, *E*-**8a**, *Z*-**15** and *E*-**17** (PDF)

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### Author Contributions

All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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- (12) Terminal alkynes were found to be unsuitable substrates because direct radical hydrogermylation (with Ph<sub>3</sub>GeH) overrides germylzincation. The feasibility of the approach for conventional internal alkynes was demonstrated in reference 11.
- (13) Here, the intermediate vinylradical **I** (sp<sup>2</sup>-hybridized) is linear and the approach of Et<sub>2</sub>Zn favored from the less hindered side opposite to the bulky Ph<sub>3</sub>Ge group. For a similar situation in the case of radical silylzincation reactions, see: Romain, E.; de la Vega-Hernández, K.; Guégan, F.; Sanz García, J.; Fopp, C.; Chemla, F.; Ferreira, F.; Gerard, H.; Jackowski, O.; Halbert, S.; Oestreich, M.; Perez-Luna, A. Radical Silylzincation of (Het)Aryl-Substituted Alkynes and Computational Insights into the Origin of the trans-Stereoselectivity. *Adv. Synth. Catal.* **2021**, in press (DOI: [10.1002/adsc.202001566](https://doi.org/10.1002/adsc.202001566)).
- (14) Here, the intermediate vinylradical **I** (sp<sup>2</sup>-hybridized) is bent and exists as a rapidly interconverting mixture of *Z* and *E* isomers. The reaction of Et<sub>2</sub>Zn with the *Z*-isomer, leading to an *E*-vinylzinc intermediate, is more favorable because the interaction with the bulky Ph<sub>3</sub>Ge group is avoided. The same stereoselective outcome is observed in radical hydrogermylation reactions of internal alkynes with Ph<sub>3</sub>GeH, see references 3c and 5a.
- (15) Crystal structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 2077757 (**6**), 2077610 (*E*-**8a**), 2077611 (*Z*-**15**) and 2077612 (*E*-**17**) and can be obtained free of charge via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).
- (16) Product **6** is likely formed following reductive elimination from intermediate vinylzinc derivatives upon exchange of the ethyl ligand on zinc by a triphenylgermyl ligand. Formation of elementary zinc in the reaction media supports this proposal that is reminiscent of an analogous bisilylation pathway reported in the context of alkyne silylzincation reactions, see: Auer, G.; Oestreich, M. Silylzincation of carbon-carbon multiple bonds revisited. *Chem. Commun.* **2006**, *49*, 311–313.
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- (19) See Table S1 in the *Supporting Information*.
- (20) The same lack of regiocontrol is observed for homopropargyloxy functionalities in radical hydrostannation reactions, see: Nativi, C.; Taddei, M. Some Observations on the Stereochemical and Regiochemical Outcome of Hydrostannylation of Substituted Propargylic Alcohols. *J. Org. Chem.* **1988**, *53*, 820–826.
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