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# Synthesis of novel stereodefined vinylgermanes bearing an allyl group or an allenyl group: (*E*)-2-aryl-1-germylalka-1,4-dienes and (*E*)-4-aryl-5-germylpenta-1,2,4-trienes[†]

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**Stereodefined synthesis of an unprecedented family of vinylgermanes bearing an allyl group, (*E*)-2-aryl-1-germylalka-1,4-dienes, or an allenyl group, (*E*)-4-aryl-5-germylpenta-1,2,4-trienes, via a cross-coupling reaction of (*Z*)-germyl(stannyl)ethenes with the respective allyl halide (Br, Cl) and propargyl bromide is described. In the reaction with allyl halides, either a $Pd(dba)_2$–CuI combination (dba: dibenzylideneacetone) or CuI alone readily catalyzes or mediates the coupling reaction of (*Z*)-germyl(stannyl)ethenes, producing the novel vinylgermanes bearing an allyl group. The thienyl group or hydroxy group of the (*Z*)-germyl(stannyl)ethene survives the reaction. Copper(I) iodide alone readily mediates the reaction with allyl chloride or methallyl chloride upon addition of sodium bromide to produce the respective cross-coupled product in good yield. In contrast, crotyl halides (Br, Cl) or prenyl chloride couple with/without allylic transposition in the bromide or the chloride. In the reaction with propargyl bromide, a $Pd(dba)_2$ and CuI combination efficiently drives the coupling reaction of (*Z*)-germyl(stannyl)ethenes in NMP (*N*-methylpyrrolidone), providing the stereochemically defined allenyl vinylgermanes, (*E*)-4-aryl-5-germylpenta-1,2,4-trienes, in good yields. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** vinylgermanes; vinylstannanes; cross-coupling; 1,4-dienes; allenes; germylvinyl allenes; palladium-catalyzed reaction; copper-mediated reaction

## INTRODUCTION

Alka-1,4-dienes are very interesting compounds, because the diene framework is an important part of the structure of a number of naturally occurring compounds possessing biological activity.[1,2] Penta-1,4-diene, which could also be called allylated ethylene, is itself a key substance in the synthesis of transition metal 1,4-diene complexes,[3] or can undergo a coupling reaction with substituted aryl iodides such as 2-iodophenol or 2-iodoaniline to produce an interesting annulation product.[4] In addition, the 1,4-diene undergoes deprotonation with the use of butyl lithium to produce penta-2,4-dienyl lithium reagents, which can react with various electrophiles, producing carbon–carbon bond formation products.[5] The cross-coupling of vinylstannanes with allylic halides is one of the more effective methods of synthesizing such penta-1,4,-dienes. Stille *et al.* first reported the reaction of simple vinylstannanes with allyl halides.[6] Since then, many workers have demonstrated the coupling

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[†] Dedicated to the memory of Professor Desmond Cunningham who made numerous important contributions to the chemistry of Group 14 derivatives.

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of vinylstannanes with various types of allylic halides, which proceeds with retention of configuration.[6–19,21,24]

Recent advances in the synthesis of (*Z*)-germyl(stannyl) ethenes[19–23] were the stimulus for an examination of the cross-coupling reaction of (*Z*)-germyl(stannyl)ethenes with allyl halides leading to 1-germylpenta-1,4-dienes or allylated vinylgermanes, as the (*Z*)-silyl(stannyl)ethenes couple with allyl halides with retention of configuration.[24] To date, no report has been published for such a reaction except for our previous communication.[21]

Despite a limitation associated with steric hindrance[25] for the reaction of (*Z*)-germyl(stannyl)ethenes **1** in that the tri-*n*-butylstannyl group is sterically congested by the presence of a neighboring triethylgermyl group, an examination of the synthesis of a family of (*E*)-2-aryl-1-silylalka-1,4-dienes was attempted.

Closely related to the synthesis of allylated vinylgermanes, the reaction with propargyl bromide is also of great interest because of the possibility of producing allenyl vinylgermanes or germylvinyl allenes, (*E*)-4-aryl-5-germyl-1,2,4-trienes, which may be important in allene chemistry,[26] particularly in cycloaddition reactions.[27–30] Allenes also undergo hydrosilylation,[31] hydrogermylation,[31] hydrostannylation,[31] bisstannylation,[31] silastannylation,[31–33] germastannylation,[1,34] bisboration[31,35,36] and silaboration.[31,37–39] Reported herein are the stereodefined syntheses of novel (*E*)-vinylgermanes bearing an allyl group or an allenyl group $\beta$ to germanium with *cis*-disposition via the cross-coupling of (*Z*)-germyl(stannyl)ethenes with the respective allyl halides or propargyl bromide (Scheme 1).

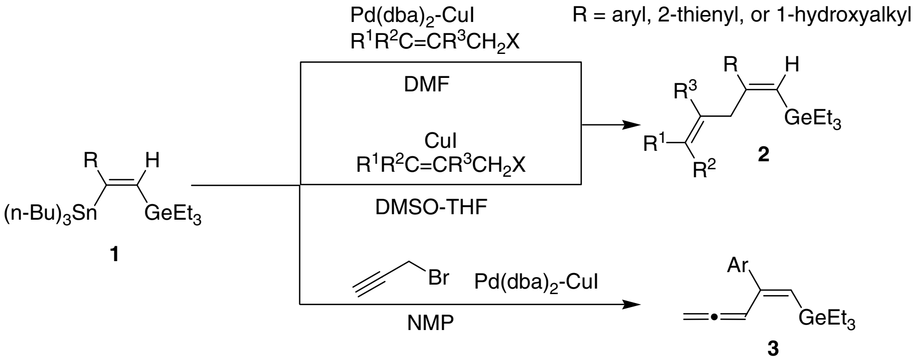
# RESULTS AND DISCUSSION

## Synthesis of vinylgermanes bearing an allyl group: (*E*)-2-aryl-1-germylalka-1,4-dienes

### *Optimization of reaction conditions*

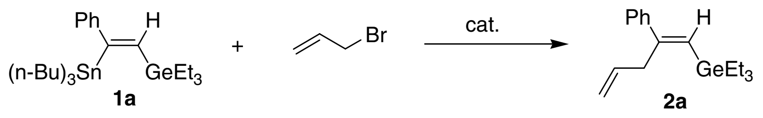
(*Z*)-1-Germyl-2-stannyl-2-substituted ethenes **1** in Scheme 1 were prepared according to the literature procedure,[21–23] for which arylacetylenes and 2-thienylacetylene were prepared via the Sonogashira–Hagihara method.[40–44] To determine the optimum conditions (catalyst, temperature, solvent, time) the reaction of **1a** with allyl bromide according to Scheme 2 was first explored.

The reaction using Pd(dba)$_2$–PPh$_3$ or Pd(dba)$_2$ alone as a catalyst at 60–80 °C without solvent produced the cross-coupled product, (*E*)-1-(triethylgermyl)-2-phenylpenta-1,4-diene **2a**, in 65 and 85% glc yields, respectively. NMR analysis of the product disclosed that the vinyl proton $\alpha$ to the germyl group appeared at 6.02 ppm, which is at somewhat higher field than that of the starting (*Z*)-germyl(stannyl)ethene **1a** ($\delta = 6.63$ ppm).[21,22] However, the chemical shift of the vinylic proton of **2a** ($\delta = 6.02$ ppm) was very close to that of its silicon analog, (*E*)-1-(trimethyl*silyl*)-2-phenylpenta-1,4-diene **(*E*)-2a-Si** ($\delta = 5.97$ ppm).[24,45] On the other hand, the vinyl proton $\alpha$ to Si in **(*Z*)-2a-Si** has been reported to appear at 5.59 ppm.[46,47] These results indicate that the deshielding effect by the neighboring aromatic ring distinctly affects only the *cis* vinyl proton $\alpha$ to the silyl group, not the *trans* one. It also means that the disposition between the phenyl group and the vinyl proton in **2a** is *cis*. On the other hand, the silyl methyl protons of **(*E*)-2a-Si** are observed at 0.19 ppm,[24,45] while those in **(*Z*)-2a-Si** are at −0.2 ppm.[46,47] The methyl protons of the (*E*)-isomer



allyl-X: allyl bromide, allyl chloride, crotyl bromide, crotyl chloride, methallyl chloride,
or prenyl chloride
dba: dibenzylideneacetone

**Scheme 1.** Reaction of (*Z*)-germyl(stannyl)ethenes with allyl halides or propargyl bromide.



**Scheme 2.** Reaction of **1a** with allyl bromide.

appear at lower field than TMS, but those of the (*Z*)-isomer appear at higher field than TMS. The chemical shift of the former is normal, while the latter is unusual. The higher field shift of the (Z)-isomer seems to be caused by the shielding effect of the neighboring aromatic ring, which distinctly affects only the methyl protons of the trimethylsilyl group. This means that the silyl group may face the plane of the ring and locate its methyl proton in the middle of the ring current of the aromatic ring. For the germyl derivative **2a**, the methyl and methylene protons of the ethyl group were observed at lower field ($\delta = 1.07$ and 0.91 ppm, respectively) than those of TMS. This data guarantees that the phenyl and triethylgermyl group are disposed *trans* to each other. Consequently, the present destannylative allylation is consistent with the many examples previously reported,[6–19,21,24] wherein Migita–Kosugi–Stille-type coupling proceeds with well-known retention of configuration, without exception. Continuing the comparison of the catalysts in Table 1, $BnPdCl(PPh_3)_2$ was also active as a catalyst in the reaction; however, yields were somewhat low. $Pd(dba)_2$–$PPh_3$ was not effective in *N*,*N*-dimethylformamide(DMF) at 40 °C. Addition of copper iodide (1.6 mol% based on **1a**) as a co-catalyst[25,48–50] drove the reaction, producing **2a** in 54% yield. A $Pd(dba)_2$—CuI combination catalyst, without a phosphine ligand, positively affected the reaction to produce **2a** in 86% yield. This catalyst, interestingly enough, effected the coupling reaction even at room temperature to produce **2a** in high isolated yield, though it required a longer reaction time. $Pd(dba)_2$ alone was ineffective at 40 °C for 40 h. Other palladium catalyst combination such as $BnPdCl(PPh_3)_2$–CuI and $[(\pi\text{-allyl})PdCl]_2$–CuI were also effective, but yields were somewhat low. Consequently, it was found that the $Pd(dba)_2$–CuI combination was the best catalyst choice for the allylation reaction.

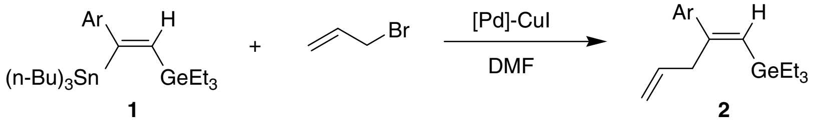
## $Pd(dba)_2$–CuI catalyzed allylation of (*Z*)-germyl(stannyl)ethenes 1 with allyl bromides

A family of (*Z*)-2-aryl-2-(tri-*n*-butylstannyl)-1-(triethylgermyl)ethenes were treated with allyl bromide under conditions similar to run 7 in Table 1. The reaction is outlined in Scheme 3. Table 2 summarizes the results for the synthesis of (*E*)-2-aryl-1-(triethylgermyl)penta-1,4-dienes **2** along with the chemical shifts of the vinyl protons $\alpha$ to germanium. In all cases except for two (runs 2 and 5 in Table 2), the reaction readily took place at 40 °C and went to completion quickly, producing the expected 1,4-dienes **2** in good to high isolated yields. An exceptionally longer reaction time and somewhat higher reaction temperature was needed for **1d**, which bears a chlorine atom at the *ortho* position on the aromatic ring. The reason for the slow rate is not clear at present, but it may

**Table 1.** Optimization of the cross-coupling of **1a** with allyl bromide

| Run[a] | GSPE[b] (mmol) | Allyl Br (mmol) | Cat.(mol%)[c] | Solvent | Conditions (°C/h) | Yield[d] (%) |
|---|---|---|---|---|---|---|
| 1[e] | 1.0 | 1.0 | $Pd(dba)_2$ (1), $PPh_3$ (2) | neat | 80/45 | (65) |
| 2[e] | 1.0 | 1.0 | $Pd(dba)_2$ (1) | neat | 60/45 | (85) |
| 3[e] | 1.0 | 1.0 | BnPdCl $(PPh_3)_2$ (1)[f] | neat | 80/45 | (32) |
| 4[e] | 1.0 | 1.0 | BnPdCl $(PPh_3)_2$ (1) | PhH[g] | 80/45 | (30) |
| 5 | 0.2 | 1.0 | $Pd(dba)_2$ (1), $PPh_3$ (2) | DMF[h] | 40/40 | 0 |
| 6 | 0.2 | 1.0 | $Pd(dba)_2$ (1), $PPh_3$ (2), CuI (1.6) | DMF | 40/25 | 54 |
| 7 | 1.0 | 5.5 | $Pd(dba)_2$ (1), CuI (1.6) | DMF | 40/5 | 86 |
| 8 | 1.0 | 5.5 | $Pd(dba)_2$ (1), CuI (1.6) | DMF | r.t./45 | 84 |
| 9 | 0.25 | 1.5 | $Pd(dba)_2$ (1), CuBr (1.6) | DMF | r.t./20 | 55 |
| 10 | 1.0 | 5.5 | $Pd(dba)_2$ (1) | DMF | 40/40 | 0 |
| 11 | 0.2 | 1.0 | BnPdCl $(PPh_3)_2$ (1), CuI (1.6) | DMF | 40/9 | 65 |
| 12 | 0.2 | 1.0 | $[(\pi\text{-allyl})PdCl]_2$ (1), CuI (1.6) | DMF | 40/25 | 70 |
| 13 | 0.25 | 1.5 | CuI (1.6) | DMF | 40/20 | 53 |

[a] The reaction was carried out using a small round-bottom flask under nitrogen. [b] (*Z*)-2-(tri-*n*-Butylstannyl)-1-(triethylgermyl)-2-phenylethene **2a**. [c] Based on the amount of (*Z*)-germyl(stannyl)ethene used. [d] Isolated yields by column chromatography [silica gel(neutral), hexane or 20% ethyl acetate in hexane]; in parentheses are shown glc yields. [e] The reaction was carried out in a degassed sealed glass-tube, unless otherwise stated. [f] Bn, benzyl. [g] Benzene. [h] *N*,*N*-dimethylformamide.



**Scheme 3.** $Pd(dba)_2$–CuI-catalyzed cross-coupling of (*Z*)-germyl(stannyl)ethenes **1** with allyl bromide in DMF.

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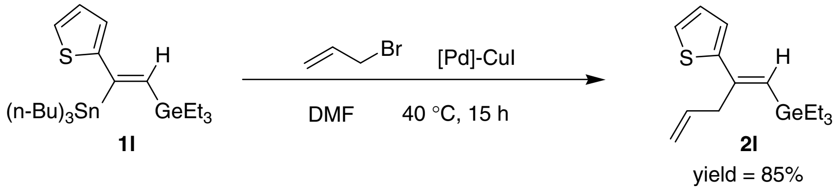
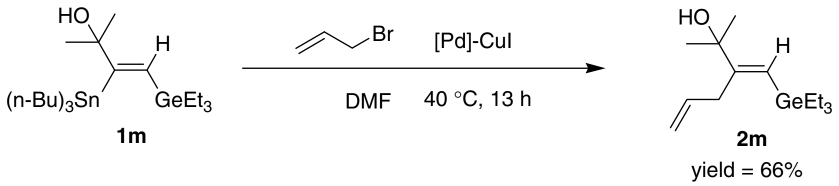
**Table 2.** Reaction conditions, yields, and selected NMR data for $CH_2{=}CHCH_2CAr{=}CHGeEt_3$

| Run[a] | X in Ar (mmol) | Allyl Br mmol | Conditions (°C/h) | Product no. | Yield[b] (%) | =C**H**(Ge) δ (ppm) |
|---|---|---|---|---|---|---|
| 1 | H (1.0) **1a** | 5.5 | 40/5 | **2a** | 86 | 6.02 |
| 2 | 3-F (0.24) **1b** | 1.25 | 40/9 | **2b** | 77 | 6.06 |
| 3 | 4-F (0.24) **1c** | 1.25 | 40/12 | **2c** | 83 | 5.96 |
| 4 | 2-Cl (0.5) **1d** | 2.5 | 60/30 | **2d** | 79 | 5.58 |
| 5 | 3-Cl (1.0) **1e** | 5.5 | 40/7 | **2e** | 96 | 6.04 |
| 6 | 4-Cl (1.0) **1f** | 5.5 | 40/15 | **2f** | 80 | 6.01 |
| 7 | 3-$CF_3$ (1.0) **1g** | 5.5 | 40/7 | **2g** | 86 | 6.08 |
| 8 | 3-$NO_2$ (0.25) **1h** | 1.25 | 40/7 | **2h** | 73 | 6.17 |
| 9 | 4-$NO_2$ (0.5) **1i** | 2.5 | 40/7 | **2i** | 91 | 6.22 |
| 10 | 4-CN(0.5) **1j** | 2.5 | 40/7 | **2j** | 98 | 6.16 |
| 11 | 3-$CH_3$ (0.5) **1k** | 2.5 | 40/5 | **2k** | 75 | 5.99 |

[a] 1 mol% of $Pd(dba)_2$ and 1.6 mol% of CuI were employed based on **1**. [b] Isolated yield by column chromatography [silica gel(neutral), hexane or ethyl acetate–hexane(1 : 4)].



**Scheme 4.** Cross-coupling of (*Z*)-germyl(stannyl)ethene bearing 2-thienyl group **1l** with allyl bromide in DMF.



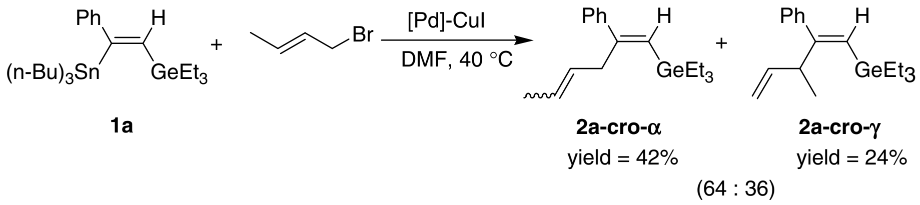
**Scheme 5.** Cross-coupling of (*Z*)-germyl(stannyl)ethene bearing a 1-hydroxyalkyl group **1m** with allyl bromide in DMF.

be associated with coordination of the halogen atom lone pair electrons to a metal (copper or palladium) in a putative intermediate (Scheme 8) or with steric hindrance caused by the chlorine atom. In fact, once produced, the chemical shift of the vinylic proton α to the germyl group in **2d** was observed at higher field (5.58 ppm) than those of the others (Table 2).

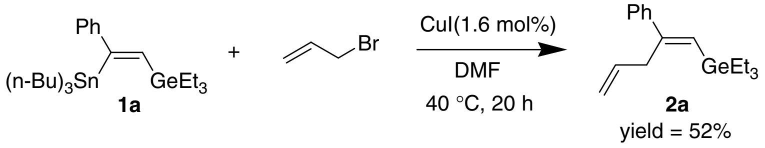
The chemical shift of the vinyl proton α to the germyl group in all products appeared in the range 6.22–5.58 ppm (Table 2). Other germyl(stannyl)ethenes such as (*Z*)-2-(tri-*n*-butylstannyl)-1-(triethylgermyl)-2-(2-thienyl)ethene **1l**[22] and (*Z*)-3-(tri-*n*-butylstannyl)-4-(triethylgermyl)-2-methylbut-3-en-2-ol **1m**[22] were also subjected to the destannylative allylation under similar conditions producing the respective (*E*)-1-germyl-2-substituted penta-1,4-dienes **2l** and **2m** exclusively with good isolated yields (Schemes 4 and 5). In the latter case, it should be emphasized that the hydroxy group tolerated the coupling reaction.

Next, **1a** was allowed to react with crotyl bromide under similar conditions. The reaction produced cross-coupled products with/without allylic transposition in the bromide (Scheme 6). Both isomers could be separately isolated by column chromatography. Similar competition between $S_N2$ and $S_N2'$ type reactions has been reported to take place in the $BnPdCl(PPh_3)_2$-catalyzed reaction of (*Z*)-2-(tri-*n*-butylstannyl)-1-(trimethylsilyl)-2-phenylethene with *trans*-cinnamyl bromide.[24]

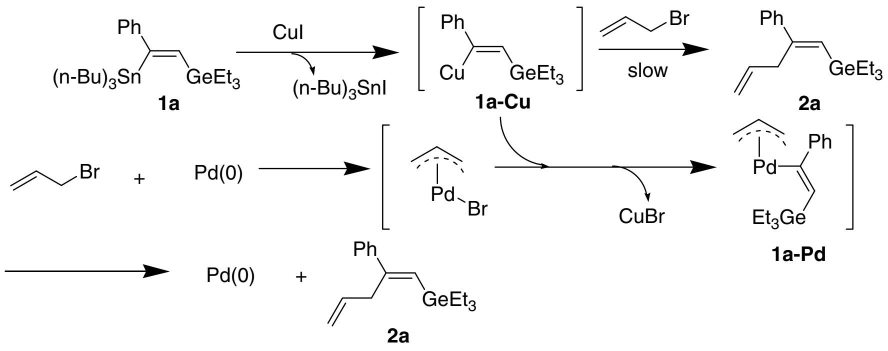
To evaluate the role of copper iodide in the coupling reaction, the copper iodide-catalyzed reaction of **1a** with allyl bromide was examined at room temperature in DMF (Scheme 7). The reaction proceeded with retention of configuration, producing cross-coupled product **2a** in 52% yield, but the reaction required a longer reaction time than that for $Pd(dba)_2$–CuI catalysis. Yet, it suggests that the 1,4-diene-forming reaction might pass through a putative



**Scheme 6.** Product yields in the cross-coupling of **1a** with crotyl bromide in DMF.



**Scheme 7.** CuI-catalyzed cross-coupling of **1a** with allyl bromide in DMF.



**Scheme 8.** Plausible mechanism for cross-coupling in the presence of a Pd(dba)$_2$–CuI combination.

vinyl copper species,[25,48–50] presumably generated from the reaction of vinylstannane **1a** with copper(I) iodide in DMF, and the putative vinyl copper species may attack the bromide in an $S_N2$ or $S_N2'$-type fashion.

Consequently, a mechanism is proposed in Scheme 8 for the palladium-catalyzed cross-coupling reaction in the presence of copper(I) iodide that can accommodate the results above. Copper(I) iodide reacts with the (*Z*)-germyl(stannyl)ethene **1a** to form a vinyl copper species **1a-Cu**, which spontaneously reacts with $\pi$-allyl palladium bromide[51] to form copper(I) bromide and a putative $\beta$-germylvinyl($\pi$-allyl)palladium intermediate **1a-Pd**, from which the expected 1,4-diene **2a** reductively eliminates to liberate the Pd(0) catalyst.

The reaction of a putative **1a-Cu** with allyl bromide proceeds slowly under these conditions; consequently, this reaction may take another possible course primarily via **1a-Pd**. The copper(I) bromide produced on the way to **1a-Pd** probably enters into the catalysis as copper(I) iodide. Thus, problems with a sluggish Migita–Kosugi–Stille-type reaction using a palladium–phosphine complex catalyst of sterically congested (*Z*)-2-(tri-*n*-butylstannyl)-1-(triethylgermyl)-2-substituted ethenes with allyl bromide were overcome by the use of catalytic amounts of a Pd(dba)$_2$ and CuI combination catalyst.

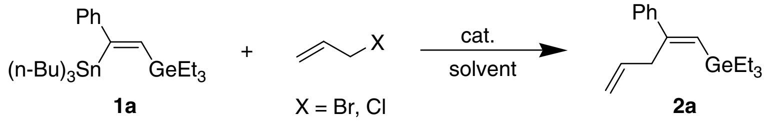
## CuI-mediated cross-coupling of (*Z*)-germyl(stannyl)ethenes with allyl halides

Scheme 7 stimulated an examination of the coupling reaction using copper(I) iodide alone or without palladium catalyst. No precedent was found for the copper(I) iodide-mediated cross-coupling of (*Z*)-$(R'_3Sn)CR{=}CH(GeR''_3)$ with allylic halides, while copper (I) iodide[52] has been reported to mediate the coupling reaction of a simple vinylstannane, 1-(tri-*n*-butylstannyl)-1-phenylethene, with an allyl halide. (*Z*)-Germyl(stannyl)ethenes **1** are much more congested compared with 1-(tri-*n*-butylstannyl)-1-phenylethene. To determine the optimum conditions (catalyst, temperature, solvent, time) the reaction of **1a** with an allyl halide was first examined. The results are summarized in Table 3. Table 3 shows that only 5 mol% of CuI in DMF brought about the coupling reaction at 40 °C, producing **2a** in 82% yield, while the use of 100 mol% of CuI led to a lower yield of the product. It seems that use of 5–10 mol% of copper iodide in DMF is better to obtain the expected product in higher yield.

**Table 3.** Optimization for CuI-mediated allylation of (*Z*)-(n-Bu)$_3$SnCPh=CHGeEt$_3$ with CH$_2$=CHCH$_2$X

| Run | X in allyl-X (equiv.) | CuI[a] (mol%) | Additive (equiv.) | Solvent | Conditions (°C/h) | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1 | Br (5.0) | 1.6 | — | DMF | 40/20 | 53 |
| 2 | Br (5.0) | 5.0 | — | DMF | 40/10.5 | 82 |
| 3 | Br (5.0) | 100 | — | DMF | 40/9 | 60 |
| 4 | Br (2.0) | 50 | — | DMSO–THF | r.t./3 | 79 |
| 5 | Br (2.0) | 100 | — | DMSO–THF | r.t./2 | 85 |
| 6 | Cl (2.0) | 100 | — | DMSO–THF | r.t./4 | 29 |
| 7 | Cl (2.0) | 100 | NaBr (3.0) | DMSO–THF | r.t./7 | 78 |

[a] Based on the amount of (Z)-germyl(stannyl)ethene used. [b] Isolated yields by column chromatography [silica gel (neutral), hexane].



**Scheme 9.** Cross-coupling of **1a** with allyl halides.

However, DMSO-THF is also attractive as a mixed solvent in the reaction, because, as mentioned above, Takeda *et al.* have reported that CuI in DMSO–THF is effective in the cross-coupling of 1-(tri-*n*-butylstannyl)-1-phenylethene with allyl bromide.[52] Therefore, the reaction of **1a** with allyl bromide was examined in DMSO–THF solvent. The reaction readily took place at room temperature, providing **2a** in 85% yield. Allyl chloride was also found to enter into the reaction with **1a** upon adding sodium bromide (3 equiv.), producing **2a** in 78% yield. The reaction without sodium bromide produced **2a** only in 29% yield.

The reaction conditions and yields for the cross-coupling of **1a** with an allyl halide outlined in Scheme 9 are compiled in Table 4, of which the CuI-mediated reaction in DMSO-THF is recommended for the synthesis of 1,4-dienes, because it takes place at room temperature.

These optimized conditions (CuI/DMSO–THF) were applied to the reaction of (Z)-germyl(stannyl)ethene **1k** with allyl bromide. Surprisingly, the reaction completed in 30 min, producing **2k** in 87% isolated yield (Scheme 10), which is higher than that from the Pd(dba)$_2$–CuI catalyzed reaction (75% yield, run 11 in Table 2).

**Table 4.** Comparison of yields and conditions in allylation reaction outlined in Scheme 9

| X | Cat. (mol%) | Solvent | Conditions | Yield (%)[a] |
|---|---|---|---|---|
| Br | Pd(dba)$_2$ (1.0)–CuI (1.6) | DMF | 40 °C, 5 h | 86 |
| Br | CuI (5) | DMF | 40 °C, 10.5 h | 82 |
| Br | CuI (100) | DMSO-THF | r.t., 2 h | 85 |
| Cl | CuI (100) | DMSO-THF | r.t., 4 h | 29 |
| Cl | CuI (100)–NaBr (300) | DMSO-THF | r.t., 7 h | 78 |

[a] Isolated yield.

The reaction of **1a** with crotyl, methallyl, and prenyl halide in a DMSO–THF mixed solvent was carried out under similar conditions (Scheme 11). The reaction with crotyl bromide completed at room temperature in 40 min, providing **2a-cro-*α*** and **2a-cro-*γ*** in 68.4% and 21.6% yield, respectively (combined yield = 90%, isolated product ratio: **2a-cro-*α***: **2a-cro-*γ*** = 76 : 24) (Table 5). Regioselectivity and yield for the formation of **2a-cro-*α*** were higher than in the Pd(dba)$_2$–CuI catalysis. In contrast, the reaction with the chloride in the presence of sodium bromide was not selective; isolated yields of **2a-cro-*α*** and **2a-cro-*γ*** were each only 43%, while combined yield was rather high (86%) (Table 5).

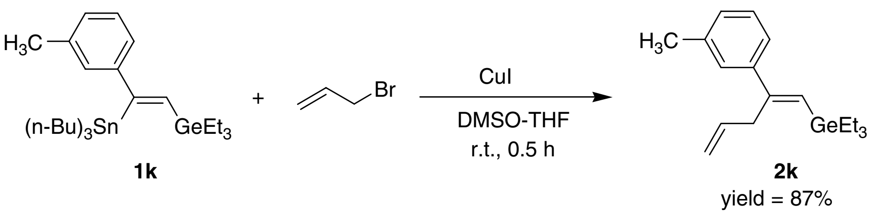
Methallyl chloride afforded (*E*)-1-germyl-4-methyl-2-phenylpenta-1,4-diene as the sole product in good isolated yield (Scheme 12).

The reaction with prenyl bromide unfortunately gave a complex mixture including small amounts of destannylation product (Scheme 13). Addition of potassium carbonate led

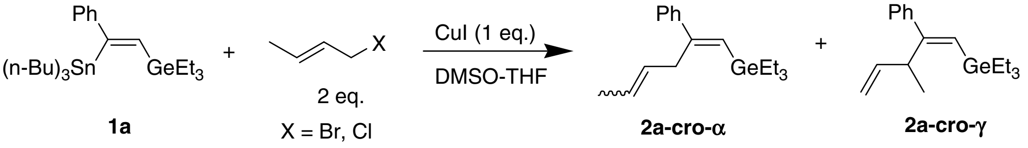
**Table 5.** Product yields and isomer ratio in the reaction outlined in Scheme 11

| X | Additive | Conditions | Yield (%)[a] 2a-cro-$\alpha$ | Yield (%)[a] 2a-cro-$\gamma$ | Combined yield (%)[a] |
|---|---|---|---|---|---|
| Br | None | r.t., 40 min | 68.4 | 21.6 | 90 |
| Cl | NaBr (3 eq.) | r.t., 4 h | 43 | 43 | 86 |

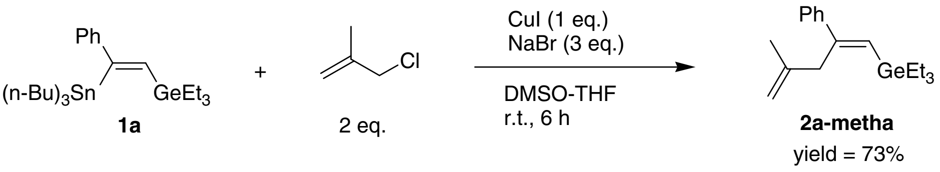
[a] Isolated yield.



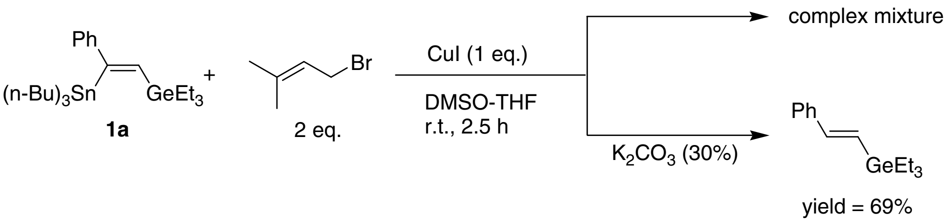
**Scheme 10.** Cross-coupling of (*Z*)-germyl(stannyl)ethene bearing *m*-tolyl group **1k** with allyl bromide in DMSO–THF.



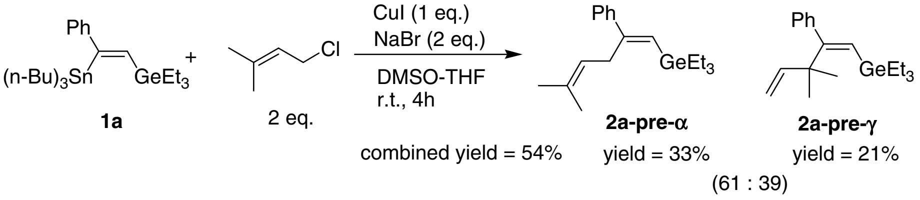
**Scheme 11.** CuI-mediated cross-coupling of **1a** with crotyl halides in DMSO–THF.



**Scheme 12.** CuI-mediated cross-coupling of **1a** with methallyl chloride in the presence of a CuI–NaBr combination in DMSO–THF.



**Scheme 13.** Profile for the CuI-mediated reaction of **1a** with prenyl bromide in DMSO–THF.



**Scheme 14.** CuI-mediated cross-coupling of **1a** with prenyl chloride in the presence of NaBr in DMSO–THF.

to the exclusive formation of undesired (*E*)-styryltriethylgermane.[23] Since the cross-coupling did not occur in a similar reaction in the absence of copper iodide, it is suggested that (*E*)-styryltriethylgermane may be formed by the decomposition of a putative vinyl copper species such as **1a-Cu** in Scheme 8 produced from the transmetallation of **1a** with copper iodide.

In contrast, from the reaction of prenyl chloride in the presence of sodium bromide (3 equiv.), 1-germyl-2-phenyl-5-methylhexa-1,4-diene, **2a-pre-*α*** and 1-germyl-2-phenyl-3,3-dimethylpenta-1,4-diene, **2a-pre-*γ***, were isolated in 33 and 21% yields, respectively. The formation of **2a-pre-*α*** prevailed compared with that of the *γ*-type product (Scheme 14).

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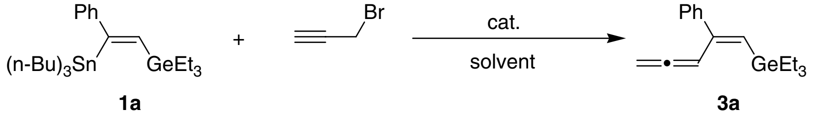
## Synthesis of vinylgermanes bearing an allenyl group: (*E*)-4-aryl-5-germylpenta-1,2,4-trienes

The reaction of a simple vinylstannane[16] or a (*Z*)-tri-*n*-butylstannyl(trimethylsilyl)ethene[17] with propargyl bromide in the presence of a palladium catalyst has been reported to proceed with retention of configuration, producing stereochemically defined silylvinyl allenes. However, there is no report of the cross-coupling of a (*Z*)-germyl(stannyl)ethene with propargyl bromide. To determine the optimum conditions (catalyst, temperature, solvent, time), the reaction of **1a** with propargyl bromide according to Scheme 15 was first examined.

The results are summarized in Table 6. In the reaction outlined in Scheme 15, a combination of Pd(dba)$_2$ and CuI in DMF was not particularly effective. The CuI-mediated reaction in DMSO–THF solvent produced 5-(triethylgermyl)-4-phenylpenta-1,2,4-triene **3a** in 40% yield. The vinylic proton $\alpha$ to the germyl group of **3a** appeared at 5.79 ppm with a coupling constant of $J = 0.4$ Hz. The chemical shift is very close to that of **2a** ($\delta = 6.02$ ppm), and the chemical shift of the ethyl proton on **3a** was observed at lower field than that of TMS. The Pd(dba)$_2$–CuI combination-catalyzed reaction in NMP produced **3a** in much higher yield (67%).

Consequently, as the conditions in run 4 in Table 6 were appropriate to the purpose, several (*Z*)-germy(stannyl) ethenes (**1c, 1j** and **1k**) were allowed to react with propargyl bromide under similar conditions. Each reaction completed within a short reaction time and produced the respective allenylated vinylgermanes, (*E*)-4-aryl-5-(triethylgermyl)penta-1,2,4-trienes (**3c, 3j** and **3k**), in good isolated yields (Table 7). All of these products, including **3a**, showed the characteristic stretching absorption band of an allenyl group near 1940 cm$^{-1}$ in IR analyses. In addition, the vinyl protons $\alpha$ to the germyl group were observed near 5.85–5.75 ppm in NMR analysis. In $^{13}$C-NMR analysis, the central carbons of the allenyl groups were observed near 211 ppm.

In closing, novel vinylgermanes bearing an allyl group and an allenyl group with *cis*-disposition have been successfully synthesized in good isolated yields by the use of Pd(dba)$_2$–CuI in DMF or Pd(dba)$_2$–CuI in NMP. Copper iodide was also found to be effective as a mediator in the destannylative allylation of (*Z*)-germyl(stannyl)ethenes. All new compounds were spectroscopically analyzed.



**Scheme 15.** Cross-coupling of **1a** with propargyl bromide.

**Table 6.** Optimization of the cross-coupling of **1a** with propargyl bromide

| Run | **1a**[a] (mmol) | Prop. Br (mmol) | Catalyst (mol%)[b] | Solvent | Conditions (°C/h) | Yield[c] (%) |
|---|---|---|---|---|---|---|
| 1 | 0.25 | 1.5 | Pd(dba)$_2$ (1.0), CuI (1.6) | DMF | r.t./72 | 5 |
| 2 | 0.25 | 1.5 | Pd(dba)$_2$ (3.0), CuI (4.8) | DMF | r.t./72 | 37 |
| 3 | 0.3 | 0.6 | CuI (100) | DMSO-THF | r.t./1 | 40 |
| 4 | 0.5 | 3.0 | Pd(dba)$_2$ (3.0), CuI (4.8) | NMP | r.t./24 | 67 |
| 5 | 0.5 | 2.5 | Pd(dba)$_2$ (10), CuI (16) | NMP | r.t./3.5 | 69 |

[a] (Z)-PhC[Sn(n-Bu)$_3$]=CHGeEt$_3$. [b] Based on the amount of (Z)-germyl(stannyl)ethene used. [c] Isolated yield by column chromatography [silica gel (neutral), hexane].

**Table 7.** Reaction conditions, yields, and selected spectral data of (*E*)-CH$_2$=C=CHCAr=CHGeEt$_3$

| Run | X in Ar (mmol) | Prop. Br[a] (mmol) | Conditions (°C/h) | Product no. | Yield[b] (%) | CH$_2$=C=CHR- | =C**H**(Ge) |
|---|---|---|---|---|---|---|---|
| | | | | | | IR ($\nu$) (cm$^{-1}$) | $\delta$ (ppm) |
| 1 | H(0.5) **1a** | 2.5 | r.t./3.5 | **3a** | 67 | 1930 | 5.79 |
| 2 | 4-F (2.0) **1c** | 10.0 | r.t./2.5 | **3c** | 65 | 1940 | 5.75 |
| 3 | 4-CN (1.6) **1j** | 7.5 | r.t./2.0 | **3j** | 64 | 1940 | 5.85 |
| 4 | 3-CH$_3$ (1.6) **1k** | 7.5 | r.t./5.0 | **3k** | 54 | 1940 | 5.77 |

[a] Prop.Br : propargyl bromide. [b] Isolated yield by column chromatography [silica gel (neutral), hexane].

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# EXPERIMENTAL

## Method and measurements

The cross-coupling reaction was carried out in a small round-bottom flask under nitrogen or argon. Gas chromatography was performed using an Ohkura Model 730 gas chromatograph equipped with a thermal conductivity detector connected to a stainless column packed with 10% Silicone KF-96/Celite 545 AW (60–80 mesh, 2 m × 3 mm). The IR spectra were recorded on a Jasco Report 100 spectrophotometer. Absorbance frequencies are reported in reciprocal centimeters ($cm^{-1}$). Bands are characterized as follows: s = strong, m = medium or w = weak. $^1$H-NMR spectra were recorded at 400 MHz on a Varian Unity-400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. $^{13}$C-NMR spectra were measured at 100 MHz on the Varian Unity-400 spectrometer in $CDCl_3$, and chemical shifts are shown in ppm from that of chloroform-d$_1$ ($\delta = 77.00$ ppm). Chemical shifts are expressed as part per million (ppm) with respect to TMS. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets of doublets), ddt (doublet of doublets of triplets) and m (multiplet). Coupling constants are given in Hz. The assignments of aromatic carbons in the (*E*)-1-germylalka-1,4-dienes are based on intensity information, coupling constants (e.g. $J_{F,C}$ etc.) and additivity of $^{13}$C chemical shifts for the aromatic ring[53] as well as by reference to the $^{13}$C-NMR data of (*E*)-1-silylpenta-1,4-dienes.[24,45] Mass spectra were obtained at 70 eV using a Jeol JMS-AX-500 with a DA 7000 data system.

## Materials

(Z)-Germyl(stannyl)ethenes were prepared by the germastannation of the respective arylacetylenes,[40–44] 2-thienylacetylene and 2-methyl-3-butyn-2-ol with tri-*n*-butyl(triethylgermyl)tin in THF using catalytic amounts of $Pd(dba)_2$-2 $P(OCH_2)_3CEt$.[21–23] Bis(dibenzylideneacetone) palladium was prepared by the literature method.[54] Benzyl(chloro)bis(triphenylphosphine)palladium and chloro($\pi$-allyl)palladium dimer were purchased from Aldrich Chemical Co. Copper(I) iodide, allyl bromide, allyl chloride, methallyl chloride, crotyl bromide, crotyl chloride, prenyl bromide and prenyl chloride were commercially available and used as received. DMF and DMSO were distilled from calcium hydride and stored over molecular sieves. THF was distilled from lithium aluminum hydride and stored over molecular sieves.

## Synthesis

### *Typical procedure for the synthesis of 2-aryl-1-germylpenta-1,4-dienes via the $Pd(dba)_2$–CuI-catalyzed reaction of (Z)-germyl(stannyl)ethenes with allyl halides*

To a mixture of $Pd(dba)_2$ (0.0062 g, 0.011 mmol) and CuI (0.0033 g, 0.017 mmol) in dry DMF (5 ml) were successively added allyl bromide (0.666 g, 5.51 mmol), and (*Z*)-2-(tri-*n*-butylstannyl)-1-(triethylgermyl)-2-phenylethene **1a** (0.555 g, 1.0 mmol) with a micro syringe under nitrogen. The mixture was stirred at 40 °C. The reaction was monitored by TLC. After 5 h, the (*Z*)-**1a** was completely consumed. The resulting mixture was passed through a short silica gel column to remove the catalyst with hexane as the eluent. The eluent was collected and concentrated. An ether solution of the concentrate was stirred with saturated aqueous potassium fluoride solution at room temperature for 24 h. Filtration of the liberated white solid (tri-*n*-butyltin fluoride) and column chromatography [silica gel(neutral), hexane] gave a spectroscopically pure sample of (*E*)-1-(triethylgermyl)-2-phenylpenta-1,4-diene **2a** (0.263 g, 86%). IR (neat): 3065 (m), 3050 (m), 3000 (m), 2950 (s), 2920 (s), 2900 (s), 2860 (s), 1635 (m), 1590 (s), 1563 (m), 1490 (m), 1460 (m), 1450 (m), 1440 (m), 1420 (m), 1375 (m), 1220 (w), 1070 (w), 1020 (s), 1000 (s), 985 (s), 965 (m), 908 (s), 840 (m), 770 (s), 750 (s), 700 (s), 695 (s) $cm^{-1}$. $^1$H-NMR($CDCl_3$): $\delta$ 7.43 (t, 1H, $J = 1.6$ Hz), 7.41 (t, 1H, $J = 1.2$ Hz), 7.3 (m, 2H), 7.23 (m, 1H), 6.02 (s, 1H), 5.77 (ddt, 1H, $J = 17.2, 10.0, 6.0$ Hz), 5.04 (ddt, 1H, $J = 17.2, 2.0, 2.0$ Hz), 4.97 (ddt, 1H, $J = 10.2, 2.0, 2.0$ Hz), 3.33 (ddd, 2H, $J = 6.0, 2.0, 2.0$ Hz), 1.07 (t, 9H, $J = 7.2$ Hz), 0.91 (q, 6H, $J = 7.2$ Hz) ppm. $^{13}$C-NMR ($CDCl_3$): $\delta$ 153.2 (C2 of 1-germylpenta-1,4-diene), 143.2 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 136.6 (C4 of the penta-1,4-diene), 128.2 (aromatic carbon *meta* to C2 of the penta-1,4-diene), 128.1 (C1 of the penta-1,4-diene), 127.1 (aromatic carbon *para* to C2 of the penta-1,4-diene), 126.3 (aromatic carbon *ortho* to C2 of the penta-1,4-diene), 116.0 (C5 of the penta-1,4-diene), 39.7 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 304 ($M^+$), 276 ($M^+ - 28$). HRMS (EI, 70 eV): calcd for $C_{17}H_{26}Ge$, 304.1229; found, 304.1246.

By a procedure similar to that for **2a**, other allylated vinylgermanes **2b-2a-cro-$\gamma$** were obtained from the (*Z*)-germyl(stannyl)ethenes **1**. Analytical data for the **2b-2a-cro-$\gamma$** isolated by column chromatography are shown below.

### *(E)-1-(Triethylgermyl)-2-(3-fluorophenyl)penta-1,4-diene **2b***

A reaction similar to that for the synthesis of **2a** was carried out using **1b** (0.138 g, 0.24 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2b** as a colorless oil (0.059 g, 77%). IR (neat): 3075 (w), 2950 (s), 2920 (s), 2900 (s), 2860 (s), 1640 (w), 1610 (s), 1575 (s), 1480 (s), 1425 (s), 1263 (m), 1240 (m), 1150 (m), 1020 (m), 915 (m), 835 (m), 780 (s), 705 (s) $cm^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 7.23 (m, 2H), 7.11 (m, 1H), 6.92 (m, 1H), 6.06 (s, 1H), 5.76 (ddt, 1H, $J = 17.2, 10.4, 6.4$ Hz), 5.02 (m, 2H), 3.3 (ddd, 2H, $J = 6.4, 1.6, 1.6$ Hz), 1.07 (t, 9H, $J = 7.2$ Hz), 0.91 (q, 6H, $J = 7.2$ Hz) ppm. $^{13}$C-NMR ($CDCl_3$): $\delta$ 162.8 (d, $^1J_{F,C} = 243.5$ Hz, aromatic carbon bearing fluorine), 151.9 (C2 of 1-germylpenta-1,4-diene), 145.5 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 136.2 (C4 of the penta-1,4-diene), 129.5 (d, $^3J_{F,C} = 7$ Hz, aromatic carbon *meta* to

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fluorine and to C2 of the penta-1,4-diene), 129.4 (C1 of the penta-1,4-diene), 122.0 (aromatic carbon *ortho* to C2 of the penta-1,4-diene and *para* to fluorine), 116.3 (C5 of the penta-1,4-diene), 113.8 (d, $^2J_{F,C} = 21.3$ Hz, aromatic carbon *ortho* to fluorine and *para* to C2 of the penta-1,4-diene), 113.3 (d, $^2J_{F,C} = 22.0$ Hz, aromatic carbon *ortho* to fluorine and C2 of the penta-1,4-diene), 39.6 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 322 ($M^+$, weak), 293 ($M^+ - 29$). Anal. calcd for $C_{17}H_{25}FGe$, C, 63.61; H, 7.85; found, C, 63.58; H, 7.64%.

### *(E)-1-(Triethylgermyl)-2-(4-fluorophenyl)penta-1,4-diene* 2c

A reaction similar to that for the synthesis of **2a** was carried out using **1c** (0.137 g, 0.24 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2c** as a colorless oil (0.064 g. 83%). IR (neat): 3075 (w), 2950 (s), 2905 (s), 2879 (s), 1720 (w), 1680 (m), 1600 (s), 1505 (s), 1460 (w), 1235 (s), 1160 (m), 1015 (m), 915 (w), 820 (s), 700 (s) $cm^{-1}$. $^1H$-NMR ($CDCl_3$): $\delta$ 7.37 (dd, 2H, $J = 8.8$, 5.2 Hz), 6.97 (dd, 2H, $J = 8.8$, 8.8 Hz), 5.96 (s, 1H), 5.75 (ddt, 1H, $J = 17.2$, 10.4, 6 Hz), 5.01 (m, 2H), 3.3 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 1.07 (t, 9H, $J = 7.2$ Hz), 0.9 (q, 6H, $J = 7.2$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 164.1 (C2 of 1-germylpenta-1,4-diene), 162.1 (d, $^1J_{F,C} = 244.3$ Hz, aromatic carbon bearing fluorine), 152.1 (quart. aromatic carbon *para* to fluorine), 136.4 (C4 of the penta-1,4-diene), 128.2 (C1 of the penta-1,4-diene), 127.9 (d, $^3J_{F,C} = 7.6$ Hz, aromatic carbon *meta* to fluorine), 116.2 (C5 of the penta-1,4-diene), 114.8 (d, $^2J_{F,C} = 21.3$ Hz, aromatic carbon *ortho* to fluorine), 39.8 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 322 ($M^+$, weak), 293 ($M^+ - 29$). Anal. calcd for $C_{17}H_{25}FGe$, C, 63.61; H, 7.85; found, C, 63.35; H, 7.86%.

### *(E)-1-(Triethylgermyl)-2-(2-chlorophenyl)penta-1,4-diene* 2d

A reaction similar to that for the synthesis of **2a** was carried out using **1d** (0.293 g, 0.50 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2d** as a colorless oil (0.134 g, 79%). IR (neat): 3075 (m), 3050 (w), 2950 (s), 2910 (s), 2875 (s), 1640 (m), 1605 (m), 1585 (m), 1465 (s), 1430 (s), 1380 (m), 1230 (w), 1060 (s), 1020 (s), 915 (s), 840 (m), 740 (s), 700 (s), 680 (m) $cm^{-1}$. $^1H$-NMR ($CDCl_3$): $\delta$ 7.33 (m, 1H), 7.15 (m, 3H), 5.64 (ddt, 1H, $J = 16.8$, 10.0, 6.8 Hz), 5.58 (s, 1H), 4.92 (m, 2H), 3.27 (ddd, 2H, $J = 6.8$, 1.6, 1.6 Hz), 1.09 (t, 9H, $J = 7.6$ Hz), 0.92 (q, 6H, $J = 7.6$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 153.3 (C2 of 1-germylpenta-1,4-diene), 143.8 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 135.7 (C4 of the penta-1,4-diene), 131.5 (aromatic carbon bearing chlorine), 130.6 (aromatic carbon *meta* to chlorine and *para* to C2 of the penta-1,4-diene), 130.3 (aromatic carbon *ortho* to chlorine and *meta* to C2 of the penta-1,4-diene), 129.3 (aromatic carbon *meta* to chlorine and *ortho* to C2 of the penta-1,4-diene), 127.7 (C1 of the penta-1,4-diene), 126.2 (aromatic carbon *para* to chlorine and *meta* to C2 of the penta-1,4-diene), 116.1 (C5 of the penta-1,4-diene), 41.3 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 310 ($M^+ - 28$). Anal. calcd for $C_{17}H_{25}ClGe$, C, 60.51; H, 7.47; found, C, 60.31; H, 7.62%.

### *(E)-1-(Triethylgermyl)-2-(3-chlorophenyl)penta-1,4-diene* 2e

A reaction similar to that for the synthesis of **2a** was carried out using **1e** (0.587 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2e** as a colorless oil (0.324 g, 96%). IR (neat): 3080 (w), 2950 (s), 2925 (s), 2900 (s), 2870 (m), 1725 (m), 1590 (s), 1560 (s), 1470 (s), 1460 (s), 1430 (s), 1385 (w), 1280 (m), 1020 (s), 915 (s), 780 (s), 730 (s), 700 (m) $cm^{-1}$. $^1H$-NMR ($CDCl_3$): $\delta$ 7.38 (m, 1H), 7.27 (m, 1H), 7.21 (m, 2H), 6.04 (s, 1H), 5.75 (ddt, 1H, $J = 17.0$, 10.4, 6.0 Hz), 5.03 (ddt, 1H, $J = 17.0$, 1.6, 1.6 Hz), 4.99 (ddt, 1H, $J = 10.4$, 1.6, 1.6 Hz), 3.29 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 1.07 (t, 9H, $J = 7.2$ Hz), 0.91(q, 6H, $J = 7.2$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 151.9 (C2 of 1-germylpenta-1,4-diene), 145.1 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 136.1 (C4 of the penta-1,4-diene), 134.0 (aromatic carbon bearing chlorine), 129.9 (aromatic carbon *meta* to chlorine and C2 of the penta-1,4-diene), 129.3 (aromatic carbon *ortho* to chlorine and *para* to C2 of the penta-1,4-diene), 127.0 (C1 of the penta-1,4-diene), 126.6 (aromatic carbon *ortho* to chlorine and C2 of the penta-1,4-diene), 124.5 (aromatic carbon *ortho* to C2 of the penta-1,4-diene and *para* to chlorine), 116.4 (C5 of the penta-1,4-diene), 39.5 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 310 ($M^+ - 28$), 282 ($M^+ - 56$). Anal. calcd for $C_{17}H_{25}ClGe$, C, 60.51; H, 7.47; found, C, 60.52; H, 7.68%.

### *(E)-1-(Triethylgermyl)-2-(4-chlorophenyl)penta-1,4-diene* 2f

A reaction similar to that for the synthesis of **2a** was carried out using **1f** (0.586 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2f** as a colorless oil (0.270 g, 80%). IR (neat): 3080 (w), 2950 (s), 2925 (s), 2900 (s), 2870 (s), 1730 (m), 1590 (m), 1490 (s), 1460 (m), 1430 (m), 1380 (w), 1280 (m), 1100 (m), 1020 (s), 915 (m), 820 (s), 703 (m) $cm^{-1}$. $^1H$-NMR($CDCl_3$): $\delta$ 7.34 (d, 2H, $J = 8.4$ Hz), 7.25 (d, 2H, $J = 8.4$ Hz), 6.01 (s, 1H), 5.74 (ddt, 1H, $J = 17.0$, 10.4, 6.0 Hz), 5.02 (ddt, 1H, $J = 17.2$, 1.6, 1.6 Hz), 4.98 (ddt, 1H, $J = 10.4$, 1.6, 1.6 Hz), 3.29 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 1.07 (t, 9H, $J = 7.2$ Hz), 0.90 (q, 6H, $J = 7.2$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 151.9 (C2 of 1-germylpenta-1,4-diene), 145.1 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 136.3 (C4 of the penta-1,4-diene), 132.8 (aromatic carbon bearing chlorine), 129.1 (aromatic carbon *ortho* to chlorine), 128.2 (aromatic carbon *meta* to chlorine), 127.7 (C1 of the penta-1,4-diene), 116.3 (C5 of the penta-1,4-diene), 39.6 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI,

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70 eV): 309 ($M^+ - 29$). Anal. calcd for $C_{17}H_{25}ClGe$, C, 60.51; H, 7.47; found, C, 60.28; H, 7.68%.

### *(E)-1-(Triethylgermyl)-2-[3-(trifluoromethyl)phenyl]penta-1,4-diene* **2g**

A reaction similar to that for the synthesis of **2a** was carried out using **1g** (0.620 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2g** as a colorless oil (0.319 g, 86%). IR (neat): 3065 (w), 3000 (w), 2950 (s), 2900 (s), 2865 (s), 1640 (w), 1595 (w), 1580 (m), 1430 (s), 1335 (s), 1275 (m), 1160 (s), 1135 (s), 1095 (m), 1080 (s), 1020 (m), 910 (m), 800 (m), 720 (m), 700 (m) $cm^{-1}$. $^1H$-NMR ($CDCl_3$): $\delta$ 7.64 (m, 1H), 7.57 (a set of two multiplets, 1H), 7.48 (a set of two multiplets, 1H), 7.40 (a set of three multiplets, 1H), 6.08 (s, 1H), 5.74 (ddt, 1H, $J = 17.2$, 10.4, 6.0 Hz), 5.04 (ddt, 1H, $J = 17.2$, 1.6, 1.6 Hz), 4.99 (ddt, 1H, $J = 10.4$, 1.6, 1.6 Hz), 3.34 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 1.08 (t, 9H, $J = 7.2$ Hz), 0.92 (q, 6H, $J = 7.2$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 151.9 (C2 of 1-germylpenta-1,4-diene), 143.9 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 136.0 (C4 of the penta-1,4-diene), 130.5 (aromatic carbon *para* to $CF_3$ and *ortho* to C2 of the penta-1,4-diene), 130.3 (q, $^2J_{F,C} = 37$ Hz, aromatic carbon bearing $CF_3$), 129.6 (aromatic carbon *meta* to C2 of the penta-1,4-diene and to $CF_3$), 128.5 (C1 of the penta-1,4-diene), 124.3 (q, $^1J_{F,C} = 270$ Hz, carbon of $CF_3$), 123.7 (q, $^3J_{F,C} = 4$ Hz, aromatic carbon *ortho* to $CF_3$ group and *para* to C2 of the penta-1,4-diene), 123.1 (q, $^3J_{F,C} = 3$ Hz, aromatic carbon *ortho* to $CF_3$ group and C2 of the penta-1,4-diene), 116.6 (C5 of the penta-1,4-diene), 39.6 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 343 ($M^+ - 29$), 315 ($M^+ - 57$). Anal. calcd for $C_{18}H_{25}F_3Ge$, C, 58.27; H, 6.79; found, C, 58.54; H, 7.16%.

### *(E)-1-(Triethylgermyl)-2-(3-nitrophenyl)penta-1,4-diene* **2h**

A reaction similar to that for the synthesis of **2a** was carried out using **1h** (0.150 g, 0.25 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2h** as a colorless oil (0.064 g, 73%). IR (neat) 3080 (w), 2955 (s), 2940 (s), 2905 (s), 2870 (s), 1735 (m), 1600 (m), 1530 (s), 1460 (m), 1425 (m), 1350 (s), 1280 (w), 1020 (m), 920 (m), 720 (s) $cm^{-1}$. $^1H$-NMR ($CDCl_3$): $\delta$ 8.26 (m, 1H), 8.07 (a set of three multiplets, 1H), 7.72 (a set of two multiplets, 1H), 7.45 (t, 1H, $J = 8.0$ Hz), 6.17 (s, 1H), 5.74 (ddt, 1H, $J = 17.2$, 10.0, 6.0 Hz), 5.04 (d, 1H, $J = 17.2$ Hz), 3.36 (d, 2H, $J = 6.0$ Hz), 1.08 (t, 9H, $J = 7.2$ Hz), 0.93(q, 6H, $J = 7.2$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 150.8 (C2 of 1-germylpenta-1,4-diene), 148.3 (aromatic carbon bearing nitro group), 144.7 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 135.7 (C4 of the penta-1,4-diene), 132.3 (aromatic carbon *ortho* to C2 of the penta-1,4-diene and *para* to nitro group), 132.0 (aromatic carbon *meta* to C2 of the penta-1,4-diene and to nitro group), 129.0 (C1 of the penta-1,4-diene), 121.8 (aromatic carbon *ortho* to C2 of the penta-1,4-diene and nitro group), 121.2 (aromatic carbon *ortho* to nitro group and *para* to C2 of the penta-1,4-diene), 117.0 (C5 of the penta-1,4-diene), 39.4 (C3 of the penta-1,4-diene), 8.9 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 320 ($M^+ - 29$), 290 ($M^+ - 59$). Anal. calcd for $C_{17}H_{25}NO_2Ge$, C, 58.67; H, 7.24; N, 4.02 found; C, 58.88; H, 7.54; N, 3.99%.

### *(E)-1-(Triethylgermyl)-2-(4-nitrophenyl)penta-1,4-diene* **2i**

A reaction similar to that for the synthesis of **2a** was carried out using **1i** (0.299 g, 0.50 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2i** as a colorless oil (0.158 g, 91%). IR (neat): 3080 (w), 3000 (w), 2950 (s), 2925 (s), 2900 (s), 2870 (s), 1735 (w), 1595 (s), 1520 (s), 1460 (m), 1430 (m), 1345 (s), 1110 (m), 1020 (m), 920 (m), 860 (m), 835 (m), 720 (m) $cm^{-1}$. $^1H$-NMR($CDCl_3$): $\delta$ 8.15 (d, 2H, $J = 8.8$ Hz), 7.54 (d, 2H, $J = 8.8$ Hz), 6.22 (s, 1H), 5.74 (m, 1H), 5.52 (m, 2H), 3.35 (d, 2H, $J = 5.6$ Hz), 1.08 (t, 9H, $J = 7.6$ Hz), 0.94 (q, 6H, $J = 7.6$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 151.2 (C2 of 1-germylpenta-1,4-diene), 149.5 (aromatic carbon bearing nitro group), 146.7 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 135.7 (C4 of the penta-1,4-diene), 133.6 (aromatic carbon *ortho* to C2 of the penta-1,4-diene), 127.1 (C1 of the penta-1,4-diene), 123.5 (aromatic carbon *ortho* to nitro group), 116.9 (C5 of the penta-1,4-diene), 39.4 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 320 ($M^+ - 29$), 292 ($M^+ - 57$). Anal. calcd for $C_{17}H_{25}NO_2Ge$, C, 58.67; H, 7.24; N, 4.02; found, C, 58.70; H, 7.66; N, 3.84%.

### *(E)-1-(Triethylgermyl)-2-(4-cyanophenyl)penta-1,4-diene* **2j**

A reaction similar to that for the synthesis of **2a** was carried out using **1j** (0.289 g, 0.50 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2j** as a colorless oil (0.161 g, 98%). IR (neat): 3080 (w), 2950 (s), 2925 (s), 2900 (s), 2870 (s), 2210 (s), 1725 (m), 1635 (m), 1600 (s), 1500 (m), 1460 (m), 1430 (m), 1400 (m), 1380 (m), 1280 (m), 1020 (m), 915 (m), 820 (s), 705 (s) $cm^{-1}$. $^1H$-NMR($CDCl_3$): $\delta$ 7.58 (d, 2H, $J = 8.8$ Hz), 7.49 (d, 2H, $J = 8.8$ Hz), 6.16 (s, 1H), 5.73 (ddt, 1H, $J = 17.2$, 10.0, 6.0 Hz), 5.02 (ddt, 1H, $J = 17.2$, 1.6, 1.6 Hz), 5.0 (ddt, 1H, $J = 10.0$, 1.6, 1.6 Hz), 3.32 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 1.07 (t, 9H, $J = 7.6$ Hz), 0.92 (q, 6H, $J = 7.6$ Hz) ppm. $^{13}C$-NMR($CDCl_3$): $\delta$ 151.5 (C2 of 1-germylpenta-1,4-diene), 147.5 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 135.8 (C4 of the penta-1,4-diene), 132.6 (aromatic carbon *ortho* to cyano group), 131.9 (aromatic carbon *meta* to cyano group), 127.0 (C1 of the penta-1,4-diene), 119.0 (carbon of cyano group), 116.7 (C5 of the penta-1,4-diene), 110.4 (aromatic carbon bearing cyano group), 39.2 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 301 ($M^+ - 28$), 273 ($M^+ - 56$). Anal. calcd for $C_{18}H_{25}NGe$, C, 65.91; H, 7.68; N, 4.27; found, C, 65.92; H, 7.83; N, 3.97%.

### *(E)-1-(Triethylgermyl)-2-(3-tolyl)penta-1,4-diene* **2k**

A reaction similar to that for the synthesis of **2a** was carried out using **1k** (0.283 g, 0.50 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2k** as a colorless oil (0.119 g, 75%). IR (neat): 3075 (m), 3050 (m), 3000 (m), 2950 (s), 2900 (s), 2875 (s), 2825 (m), 1640 (m), 1600 (s), 1580 (s), 1480 (m), 1460 (s), 1430 (s), 1380 (m), 1280 (w), 1240 (w), 1160 (w), 1100 (w), 1020 (s), 1000 (m), 970 (m), 910 (s), 880 (w), 870 (w), 840 (s), 790 (s), 730 (s), 700 (s), 630 (w) $\mathrm{cm^{-1}}$. $^1$H-NMR($\mathrm{CDCl_3}$): $\delta$ 7.23 (m, 1H), 7.2 (m, 1H), 7.17 (dd, 1H, $J = 7.4$, 0.8 Hz), 7.04 (a set of two multiplets, 1H), 5.99 (s, 1H), 5.77 (ddt, 1H, $J = 17.2$, 10.0, 6.0 Hz), 5.04 (ddt, 1H, $J = 17.2$, 1.6, 1.,6 Hz), 4.96 (ddt, 1H, $J = 10.0$, 1.6, 1.6 Hz), 3.33 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 2.34 (s, 3H), 1.07 (t, 9H, $J = 7.6$ Hz), 0.90 (q, 6H, $J = 7.6$ Hz) ppm. $^{13}$C-NMR ($\mathrm{CDCl_3}$): Only 13 signals were observed. $\delta$ 153.4 (C2 of 1-germylpenta-1,4-diene), 143.2 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 137.6 (aromatic carbon bearing methyl group), 136.7 (C4 of the penta-1,4-diene), 127.9 (C1 of the penta-1,4-diene), 127.8 (aromatic carbon *ortho* to methyl and *para* to C2 of the penta-1,4-diene, aromatic carbon *meta* to methyl and to C2 of the penta-1,4-diene), 127.1 (aromatic carbon *ortho* to methyl group and to C2 of the penta-1,4-diene), 123.4 (aromatic carbon *ortho* to C2 of the penta-1,4-diene and *para* to methyl group), 115.9 (C5 of the penta-1,4-diene), 39.7 (C3 of the penta-1,4-diene), 21.5 (methyl carbon on aromatic ring), 9.2 (C1 of ethyl), 5.7 (C2 of ethyl) ppm. LRMS (EI, 70 eV): 318 ($\mathrm{M^+}$), 289 ($\mathrm{M^+} - 29$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{18}H_{28}Ge}$, 318.1403; found, 318.1367.

### *(E)-1-(Triethylgermyl)-2-(2-thienyl)penta-1,4-diene* **2l**

A reaction similar to that for the synthesis of **2a** was carried out using **1l** (0.558 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2l** as a colorless oil (0.263 g, 85%). IR (neat): 3070 (w), 2950 (s), 2925 (s), 2900 (s), 2860 (s), 1635 (m), 1580 (s), 1460 (m), 1425 (m), 1235 (m), 1020 (m), 910 (m), 850 (m), 810 (s), 750 (m), 720 (m), 695 (s) $\mathrm{cm^{-1}}$. $^1$H-NMR($\mathrm{CDCl_3}$): $\delta$ 7.13(dd, 1H, $J = 5.2$, 1.2 Hz), 7.0 (dd, 1H, $J = 3.6$, 1.2 Hz), 6.94(dd, 1H, $J = 5.2$, 3.6 Hz), 6.16(s, 1H), 5.87(ddt, 1H, $J = 17.2$, 10.0, 6.0 Hz), 5.14(ddt, 1H, $J = 17.2$, 1.6, 1.6 Hz), 5.05 (ddt, 1H, $J = 10.0$, 1.6, 1.6 Hz), 3.28 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 1.06 (t, 9H, $J = 7.6$ Hz), 0.9 (q, 6H, $J = 7.6$ Hz) ppm. $^{13}$C-NMR($\mathrm{CDCl_3}$): $\delta$ 147.5 (C2 of 1-germylpenta-1,4-diene), 145.9 (C2 of thienyl ring bearing C2 of the penta-1,4-diene), 136.6 (C4 of the penta-1,4-diene), 127.3 (C5 of thienyl ring), 127.1 (C1 of the penta-1,4-diene), 124.2 (C4 of thienyl ring), 123.4 (C3 of thienyl ring), 116.2 (C5 of the penta-1,4-diene), 39.9 (C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 310 ($\mathrm{M^+}$), 281 ($\mathrm{M^+} - 29$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{15}H_{24}SGe}$, 310.0811; found, 310.0833.

### *(E)-1-(Triethylgermyl)-2-(1-methyl-1-hydroxyethyl) penta-1,4-diene* **2m**

A reaction similar to that for the synthesis of **2a** was carried out using **1m** (0.267 g, 0.50 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2m** as a colorless oil (0.086 g, 66%). IR (neat): 3400 (s), 3080 (w), 2950 (s), 2910 (s), 2870 (s), 1730 (m), 1605 (m), 1460 (m), 1130 (m), 1020 (m), 915 (m), 810 (s), 710 (m) $\mathrm{cm^{-1}}$. $^1$H-NMR($\mathrm{CDCl_3}$): $\delta$ 5.85 (ddt, 1H, $J = 17.3$, 10.2, 6.0 Hz), 5.75 (s, 1H), 5.10 (ddt, 1H, $J = 17.3$, 1.8, 1.8 Hz), 5.04 (ddt, 1H, $J = 10.2$, 1.8, 1.8 Hz), 3.0 (ddd, 2H, $J = 6.0$, 1.8, 1.8 Hz), 1.68 (s, 1H), 1.36 (s, 6H), 1.02 (t, 9H, $J = 7.4$ Hz), 0.83 (q, 6H, $J = 7.4$ Hz) ppm. $^{13}$C-NMR ($\mathrm{CDCl_3}$): $\delta$ 160.8 (C2 of 1-germylpenta-1,4-diene), 139.3 (C4 of the penta-1,4-diene), 121.6 (C1 of the penta-1,4-diene), 115.5 (C5 of the penta-1,4-diene), 75.4 (tertiary carbon of 1-methyl-1-(hydroxy)ethyl group), 37.6 (C3 of the penta-1,4-diene), 30.5 (methyl carbon of 1-methyl-1-(hydroxy)ethyl group), 9.0 (C1 of ethyl group), 5.5 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 286 ($\mathrm{M^+}$, very weak), 257 ($\mathrm{M^+} - 29$). LRMS (CI, methane): 287 ($\mathrm{M^+} + 1$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{12}H_{23}OGe}$ ($\mathrm{M^+}$ − Et), 257.0983; found, 257.0953.

### *(E)-1-(Triethylgermyl)-2-phenylhexa-1,4-diene* **2a-cro-$\alpha$**

A reaction similar to that for the synthesis of **2a** was carried out using **1a** (0.552 g, 1.0 mmol) and crotyl bromide (0.7425 g, 2 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2a-cro-$\alpha$** as a colorless oil (0.119 g, 42%). IR (neat): 3050 (m), 3020 (m), 2950 (s), 2900 (s), 2870 (s), 1733 (m), 1688 (m), 1595 (s), 1570 (m), 1495 (s), 1460 (s), 1440 (s), 1430 (s), 1380 (m), 1275 (m), 1220 (m), 1080 (m), 1020 (s), 970 (s), 840 (s), 760 (s), 705 (s) $\mathrm{cm^{-1}}$. $^1$H-NMR ($\mathrm{CDCl_3}$): $\delta$ 7.43 (a set of three multiplets, 2H), 7.26 (m, 3H), 5.97 (s, 1H), 5.41 (m, 2H), 3.25 (a set of two multiplets, 2H), 1.57 (a set of two multiplets, 3H), 1.07 (t, 9H, $J = 7.6$ Hz), 0.9 (q, 6H, $J = 7.6$ Hz) ppm. $^{13}$C-NMR ($\mathrm{CDCl_3}$): $\delta$ 154 (C2 of 1-germylhexa-1,4-diene), 143.3 (quart. aromatic carbon bearing C2 of the hexa-1,4-diene), 129.0 (C4 of the hexa-1,4-diene), 128.0 (aromatic carbon *meta* to C2 of the hexa-1,4-diene), 127.4 (C1 of the hexa-1,4-diene), 127 (aromatic carbon *para* to C2 of the hexa-1,4-diene), 126.4 (C5 of the hexa-1,4-diene), 126.4 (aromatic carbon *ortho* to C2 of the hexa-1,4-diene), 38.6 (C3 of the hexa-1,4-diene), 18.0 (C6 of the hexa-1,4-diene), 9.2 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 318 ($\mathrm{M^+}$), 289 ($\mathrm{M^+} - 29$). HRMS (EI, 70 eV): calcd for $\mathrm{C_{18}H_{28}Ge}$, 318.1403; found, 318.1385.

### *(E)-1-(Triethylgermyl)-3-methyl-2-phenylpenta-1,4-diene* **2a-cro-$\gamma$**

From the reaction mixture of the synthesis of **2a-cro-$\alpha$**, **2a-cro-$\gamma$** was isolated by column chromatography as a spectroscopically pure oil (0.0674 g, 24%). IR (neat): 3075 (m), 3050 (m), 2950 (s), 2875 (s), 1630 (m), 1590 (s), 1570 (m), 1490 (m), 1460 (s), 1440 (m), 1420 (m), 1380 (m), 1080 (w), 1020 (s), 970 (m), 910 (s), 840 (s), 770 (s), 740 (s) $\mathrm{cm^{-1}}$. $^1$H-NMR ($\mathrm{CDCl_3}$): $\delta$ 7.23 (m, 5H), 5.97 (ddd, 1H, $J = 17.6$, 10.0, 5.2 Hz), 5.60 (s, 1H), 5.06 (ddd, 1H, $J = 17.6$, 1.6, 1.6 Hz), 5.06 (ddd, 1H, $J = 10.0$, 1.6, 1.6 Hz), 3.37 (m, 1H), 1.13 (d, 3H, $J = 6.8$ Hz), 1.08 (t, 9H, $J = 8.0$ Hz), 0.90 (q, 6H, $J = 8$ Hz) ppm. $^{13}$C-NMR

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($CDCl_3$): $\delta$ 160.3 (C2 of 1-germylpenta-1,4-diene), 142.6 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 128.5 (C4 of the penta-1,4-diene), 128.2 (aromatic carbon *meta* to C2 of the penta-1,4-diene), 128.1 (aromatic carbon *para* to C2 of the penta-1,4-diene), 127.4 (C1 of the penta-1,4-diene), 126.5 (aromatic carbon *ortho* to C2 of the penta-1,4-diene), 113.6 (C5 of the penta-1,4-diene), 44.7 (C3 of the penta-1,4-diene), 18.3 (methyl carbon connecting to C3 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.8 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 318 ($M^+$). HRMS (EI, 70 eV): calcd for $C_{18}H_{28}Ge$, 318.1403; found, 318.1451.

## Typical procedure for the CuI-mediated reaction[52] of (*Z*)-germyl(stannyl)ethenes with allyl halides

### *(E)-1-(Triethylgermyl)-4-methyl-2-phenylpenta-1,4-diene* ***2a-metha***

A mixture of methallyl chloride (0.1449 g, 1.6 mmol), sodium bromide (0.2469 g, 2.4 mmol) and DMSO (3.5 ml) was stirred at room temperature under nitrogen for 5 min. To the mixture, copper iodide (0.1524 g, 0.8 mmol) and then a THF (1.2 ml) solution of (*Z*)-**1a** (0.4416 g, 0.8 mmol) was successively added. The reaction was monitored by TLC. After 6 h, the (*Z*)-**1a** was completely consumed. The resulting mixture was diluted with ether and washed with aqueous $NH_3$ solution (3.5%). The organic layer was separated and dried with anhydrous sodium sulfate, and column chromatography eluted with hexane gave spectroscopically pure **2a-metha** as a colorless oil (0.1861 g, 73%). IR (neat): 3075 (m), 3010 (m), 2940 (s), 2860 (s), 1650 (m), 1590 (s), 1570 (s), 1490 (s), 1440 (s), 1380 (m), 1230 (m), 1080 (w), 1020 (s), 970 (m), 890 (s), 850 (m),780 (m), 750 (s), 700 (s) $cm^{-1}$. $^1H$-NMR ($CDCl_3$): $\delta$ 7.39 (dm, 2H, $J = 8.0$ Hz), 7.27 (tm, 2H, $J = 8.0$ Hz), 7.20 (tm, 1H, $J = 8.0$ Hz), 6.12 (s, 1H), 4.74 (m, 1H), 4.68 (m, 1H), 3.25 (s, 2H), 1.69 (m, 3H), 1.07 (t, 9H, $J = 8.0$ Hz), 0.90 (q, 6H, $J = 8.0$ Hz) ppm. $^{13}C$-NMR ($CDCl_3$): $\delta$ 152.9 (C2 of 1-germylpenta-1,4-diene), 143.5 (C4 of the penta-1,4-diene), 143.4 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 129.5 (aromatic carbon *meta* to C2 of the penta-1,4-diene), 127.9 (aromatic carbon *para* to C2 of the penta-1,4-diene), 127 (C1 of the penta-1,4-diene), 126.2 (aromatic carbon *ortho* to C2 of the penta-1,4-diene), 112.2 (C5 of the penta-1,4-diene), 43.3 (C3 of the penta-1,4-diene), 23 (methyl carbon connecting to C4 of the penta-1,4-diene), 9.1 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 289 ($M^+ - 29$). LRMS (CI, methane): 319 ($M^+ + 1$). HRMS (EI, 70 eV): calcd for $C_{16}H_{23}Ge$ ($M^+ - Et$), 289.1012; found, 289.1003.

By a procedure similar to that for **2a-metha**, other allylated vinylgermanes **2a-pre-$\alpha$** and **2a-pre-$\gamma$** were obtained from the (*Z*)-germyl(stannyl)ethenes **1a**. The analytical data of the **2a-pre-$\alpha$** and **2a-pre-$\gamma$** isolated by column chromatography are shown below.

### *(E)-1-(Triethylgermyl)-5-methyl-2-phenylhexa-1,4-diene* ***2a-pre-$\alpha$***

A reaction similar to that for the synthesis of **2a-metha** was carried out using **1a** (0.2760 g, 0.50 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2a-pre-$\alpha$** as a colorless oil (0.0532 g, 32%). IR (neat): 3050 (w), 3025 (w), 2950 (m), 2875 (m), 1590 (w), 1570 (w), 1495 (w), 1480 (w), 1380 (w), 1100 (w), 1120 (w), 840 (w), 760 (w), 700 (s) $cm^{-1}$. $^1H$-NMR ($CDCl_3$) $\delta$ 7.39 (m, 2H), 7.26 (m, 3H), 5.94 (s, 1H), 4.98 (m, 1H), 3.25 (d, 2H, $J = 6.4$ Hz), 1.67 (s, 3H), 1.61 (s, 3H), 1.07 (t, 9H, $J = 7.6$ Hz), 0.9 (q, 6H, $J = 7.6$ Hz) ppm. $^{13}C$-NMR($CDCl_3$) $\delta$ 154.9 (C2 of 1-germylhexa-1,4-diene), 143.4 (quart. aromatic carbon bearing C2 of the hexa-1,4-diene), 131.8 (C5 of the hexa-1,4-diene), 128 (aromatic carbon *meta* to C2 of 1-germylhexa-1,4-diene), 126.9 (aromatic carbon *para* to C2 of the hexa-1,4-diene), 126.7 (C1 of the hexa-1,4-diene), 126.3 (aromatic carbon *ortho* to C2 of the hexa-1,4-diene), 123.2 (C4 of the hexa-1,4-diene), 34.7 (C3 of the hexa-1,4-diene), 25.6 (C6 of the hexa-1,4-diene, *trans*-carbon), 18.1 (C6 of the hexa-1,4-diene, *cis*-carbon), 9.2 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 332 ($M^+$), 303 ($M^+ - 29$). HRMS (EI, 70 eV): calcd for $C_{19}H_{30}Ge$, 332.1638; found, 332.1618.

### *(E)-1-(Triethylgermyl)-3,3-dimethyl-2-phenylpenta-1,4-diene* ***2a-pre-$\gamma$***

From the reaction mixture of the synthesis of **2a-pre-$\alpha$** **2a-pre-$\gamma$** was isolated by column chromatography as a spectroscopically pure oil (0.0341 g, 21%). IR (neat): 3075 (m), 3050 (m), 2950 (s), 2875 (s), 1600 (w), 1580 (m), 1480 (m), 1460 (s), 1440 (m), 1430 (m), 1380 (m), 1360 (w), 1230 (w), 1200 (w), 1190 (w), 1080 (m), 1020 (s), 970 (m), 910 (m), 840 (m), 810 (w), 790 (m), 760 (m), 700 (s), 620 (w) $cm^{-1}$. $^1H$-NMR ($CDCl_3$) $\delta$ 7.20 (m, 5H), 6.05 (dd, 3H, $J = 17.6$, 10.8 Hz), 5.37 (s, 1H), 5.07 (dd, 1H, $J = 17.6$, 1.2 Hz), 5.01 (dd, 1H, $J = 10.8$, 1.2 Hz), 1.16(s, 6H), 1.04 (m, 9H), 0.88 (m, 6H) ppm. $^{13}C$-NMR ($CDCl_3$) $\delta$ 165.4 (C2 of 1-germylpenta-1,4-diene), 147.7 (C4 of the penta-1,4-diene), 142.1 (quart. aromatic carbon bearing C2 of the penta-1,4-diene), 128.3 (aromatic carbon *meta* to C2 of the penta-1,4-diene), 128 (aromatic carbon *para* to C2 of the penta-1,4-diene), 127.2 (C1 of the penta-1,4-diene), 125.8 (aromatic carbon *ortho* to C2 of the penta-1,4-diene), 111.4 (C5 of the penta-1,4-diene), 43.4 (C3 of the penta-1,4-diene), 28.2 (methyl carbons connecting to C3 of the penta-1,4-diene), 9.2 (C1 of ethyl group), 7.4 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 332 ($M^+$, weak), 303 ($M^+ - 29$). HRMS (EI, 70 eV): calcd for $C_{11}H_{25}Ge$ ($M^+ - Et$), 303.1168; found, 303.1129.

## Typical procedure for the synthesis of (*E*)-4-aryl-5-germylpenta-1,2,4-trienes via the Pd $(dba)_2$–CuI catalyzed reaction of (*Z*)-germyl (stannyl)ethenes with propargyl bromide

### *(E)-5-(Triethylgermyl)-4-phenylpenta-1,2,4-triene* ***3a***

A mixture of $Pd(dba)_2$ (0.0086 g, 0.015 mmol) and CuI (0.0046 g, 0.024 mmol) in dry NMP (1 ml) was stirred for 5 min. To the mixture were successively added (*Z*)-2-(tri-*n*-butylstannyl)-1-(triethylgermyl)-2-phenylethene **1a** (0.2760 g, 0.50 mmol) in NMP (1.5 ml) and propargyl bromide (0.3569 g, 3.0 mmol) in NMP (1.5 ml) with a micro syringe under argon or nitrogen. The mixture was stirred at room temperature under nitrogen. The reaction was monitored by TLC. After 24 h, the (*Z*)-**1a** was completely consumed. To remove the catalyst, the resulting mixture was passed through a short silica gel column with hexane. The eluent was collected and concentrated. An ether solution of the concentrate was stirred with saturated aqueous potassium fluoride solution at room temperature for 24 h. Filtration of the liberated white solid (tri-*n*-butyltin fluoride), drying with anhydrous sodium sulfate, and silica gel (neutral) column chromatography (chromatography was carried out by wrapping the column with an aluminum foil) gave a spectroscopically pure sample of (*E*)-5-(triethylgermyl)-4-phenylpenta-1,2,4-triene **3a** (0.1003 g, 67%). IR (neat): 3050 (w), 3025 (w), 2950 (m), 2875 (m), 1930(s), 1680 (m), 1580 (s), 1490 (s), 1460 (s), 1020 (s), 970 (m), 840 (s), 780 (s), 700 (s) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 7.34 (a set of two multiplets, 2H), 7.27 (m, 3H), 6.19 (dt, 1H, $J = 6.8, 0.4$ Hz), 5.79 (d, 1H, $J = 0.4$ Hz), 4.83 (dd, 2H, $J = 6.8, 1.6$ Hz), 1.09 (t, 9H, $J = 8.0$ Hz), 0.93 (q, 6H, $J = 8.0$ Hz) ppm. $^{13}$C-NMR ($CDCl_3$): $\delta$ 211.6 (C2 of 5-germylpenta-1,2,4-triene), 150.1 (C4 of the penta-1,2,4-triene), 142.8 (quart. aromatic carbon bearing C4 of the penta-1,2,4-triene), 131.2 (C5 of the penta-1,2,4-triene), 127.9 (aromatic carbon *meta* to C4 of the penta-1,2,4-triene), 127.6 (aromatic carbon *para* to C4 of the penta-1,2,4-triene), 127.2 (aromatic carbon *ortho* to C4 of the penta-1,2,4-triene), 95.1 (C3 of the penta-1,2,4-triene), 77.8 (C1 of the penta-1,2,4-triene), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 302 ($M^+$). HRMS (EI, 70 eV): calcd for $C_{17}H_{24}Ge$, 302.1090; found, 302.1094.

By a procedure similar to that for **3a**, other allenylated vinylgermanes **3c**,**3j** and **3k** were obtained from (*Z*)-germyl(stannyl)ethenes **1**. Analytical data of the **3c**,**3j** and **3k** isolated by column chromatography are shown below.

### *(E)-5-(Triethylgermyl)-4-(4-fluorophenyl)penta-1,2,4-triene 3c*

A reaction similar to that for the synthesis of **3a** was carried out using **1c** (1.1400 g, 2.0 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **3c** as a colorless oil (0.4169 g, 65%). IR (neat): 3050 (w), 2950 (s), 2900 (s), 2875 (s), 2825 (w), 1940 (s), 1890 (w), 1600 (s), 1570 (m), 1510 (s), 1460 (m), 1430 (m), 1380 (m), 1300 (m), 1220 (s), 1160 (s), 1100 (m), 1020 (m), 970 (m), 870 (m), 850 (m), 820 (s), 740 (m), 710 (s) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 7.3 (ddd, 2H, $^4J_{F,H} = 6.8$ Hz, $J = 6.8, 2.4$ Hz), 6.96 (ddd, 2H, $^3J_{F,H} = 9.2$ Hz, $J = 6.8, 2.4$ Hz), 6.18 (t, 1H, $J = 6.4$ Hz), 5.75 (s, 1H), 4.83 (dd, 2H, $J = 6.4, 1.2$ Hz), 1.09 (t, 9H, $J = 8.0$ Hz), 0.93 (q, 6H, $J = 8.0$ Hz) ppm. $^{13}$C-NMR ($CDCl_3$): $\delta$ 211.6 (C2 of 5-germylpenta-1,2,4-triene), 163.3 (d, $^1J_{F,C} = 244$ Hz, aromatic carbon bearing fluorine), 149.0 (C4 of the penta-1,2,4-triene), 138.8(aromatic carbon bearing C4 of the penta-1,2,4-triene), 131.4 (C5 of the penta-1,2,4-triene), 129.5 (d, $^3J_{F,C} = 7.6$ Hz, aromatic carbon *meta* to fluorine), 114.4 (d, $^2J_{F,C} = 20.7$ Hz, aromatic carbon *ortho* to fluorine), 95.2 (C3 of the penta-1,2,4-triene), 77.9 (C1 of the penta-1,2,4-triene), 9.1 (C1 of ethyl group), 5.4 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 320 ($M^+$). HRMS (EI, 70 eV): calcd for $C_{17}H_{23}FGe$, 320.0996; found, 320.0973.

### *(E)-4-(4-Cyanophenyl)-5-(triethylgermyl)penta-1,2,4-triene 3j*

A reaction similar to that for the synthesis of **3a** was carried out using **1j** (0.8835 g, 1.6 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **3j** as a colorless oil (0.3364 g, 64%). IR (neat): 3050 (w), 2950 (s), 2900 (s), 2875 (s), 2225 (s), 1940 (s), 1600 (m), 1580 (m), 1500 (m), 1430 (m), 1400 (m), 1380 (m), 1290 (w), 1230 (w), 1180 (w), 1110 (w), 1020 (m), 970 (w), 910 (w), 860 (m), 820 (m), 740 (m), 710 (m) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 7.58 (dt, 2H, $J = 6.4, 1.6$ Hz), 7.41 (dt, 2H, $J = 6.4, 1.6$ Hz), 6.18 (t, 1H, $J = 6.8$ Hz), 5.85 (s, 1H), 4.85 (dd, 2H, $J = 6.8, 1.6$ Hz), 1.09 (t, 9H, $J = 8.0$ Hz), 0.95 (q, 6H, $J = 8.0$ Hz) ppm. $^{13}$C-NMR ($CDCl_3$): $\delta$ 211.4 (C2 of 5-germylpenta-1,2,4-triene), 148.6 (C4 of the penta-1,2,4-triene), 147.3 (quart. aromatic carbon bearing C4 of the penta-1,2,4-triene), 134.0 (C5 of the penta-1,2,4-triene), 131.6 (aromatic carbon *ortho* to cyano group), 128.7 (aromatic carbon *meta* to cyano group), 119.0 (carbon of cyano group), 110.7 (aromatic carbon bearing cyano group), 94.5 (C3 of the penta-1,2,4-triene), 78.4 (C1 of the penta-1,2,4-triene), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 327($M^+$). HRMS (EI, 70 eV): calcd for $C_{18}H_{23}NGe$, 327.1042; found, 327.1001.

### *(E)-5-(Triethylgermyl)-4-(3-tolyl)penta-1,2,4-triene 3k*

A reaction similar to that for the synthesis of **3a** was carried out using **1k** (0.8670 g, 1.6 mmol). Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **3k** as a colorless oil (0.2746 g, 54%). IR (neat): 3010 (m), 2950 (s), 2925 (s), 2875 (s), 1940 (s), 1680 (m), 1600 (m), 1560 (m), 1480 (m), 1460 (m), 1420 (m), 1380 (m), 1290 (m), 1230 (m), 1180 (m), 1090 (m), 1020 (s), 970 (m), 910 (m), 870 (m), 850 (s), 830 (s), 790 (s), 730 (s), 710 (s), 610 (s) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 7.16 (m, 3H), 7.07 (a set of two multiplets, 1H), 6.18 (t, 1H, $J = 6.4$ Hz), 5.77 (s, 1H), 4.83 (dd, 2H, $J = 6.4, 1.6$ Hz), 2.34 (s, 3H), 1.09 (t, 9H, $J = 8.0$ Hz), 0.93 (q, 6H, $J = 8.0$ Hz) ppm. $^{13}$C-NMR ($CDCl_3$): $\delta$ 211.6 (C2 of 5-germylpenta-1,2,4-triene), 150.1 (C4 of the penta-1,2,4-triene), 142.7 (quart. aromatic carbon bearing C4 of the penta-1,2,4-triene), 137.2 (aromatic carbon bearing methyl group), 130.9 (C5 of the penta-1,2,4-triene), 128.6 (aromatic carbon *meta* to methyl group and C4 of the penta-1,2,4-triene), 128 (aromatic carbon *para* to C4 of the penta-1,2,4-triene), 127.4 (aromatic carbon *ortho* to C4 of the penta-1,2,4-triene and to methyl group), 125 (aromatic carbon *para* to methyl group), 95.2 (C3 of the penta-1,2,4-triene), 77.7 (C1 of the penta-1,2,4-triene), 21.5 (methyl carbon on aromatic ring), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. LRMS (EI, 70 eV): 320 ($M^+$). HRMS (EI, 70 eV): calcd for $C_{18}H_{30}Ge$, 320.1559; found, 320.1538.

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