A Stereoselective Carbocyclization of Bis(allenes) with Germylstannane Catalyzed by Palladium Complexes

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Diastereoselective germastannylation of bis(allenes) with germylstannanes, catalyzed by palladium complexes, for the construction of *cis* or *trans* five-membered cyclic systems has been investigated. We observed that the relative stereochemical arrangements of the reaction products depends on the substituents in the reagents containing Ge–Sn σ-bonds. When the reagent $Ph_3GeSnBu_3$ was employed in the Pd^0-catalyzed carbocyclization of bis(allenes), *trans*-cyclized products and/or *cis*-fused bicyclic dienes were produced. In contrast, *cis* cyclic compounds were obtained, again along with *cis*-fused bicyclic dienes, from the reaction with $Bu_3GeSnBu_3$. NMR experiments to establish the stereochemical relationships and a mechanistic speculation for this transformation as a possible explanation for the different stereochemical outcomes are also described.

Introduction

The availability of efficient synthetic methods in the construction of cyclic systems with the aid of organotransition metal catalysts or reagents is of considerable current interest in organic chemistry. As a consequence, many advances in transition metal mediated cyclizations in a variety of ways have been made.[1] Of particular interest is a cyclization strategy between unsaturated carbon−carbon bonds for the preparation of carbo- and heterocycles, mainly because the chemical process could provide a unique and useful structure in simple trial. In this regard, transition metal catalyzed addition reactions of reagents containing interheteroatom bonds (X−Y = group 14 elements Si, Sn, Ge, etc.) to unsaturated carbon−carbon bonds, generating two heteroatom−carbon bonds in a one-step fashion, have recently been extensively studied.[2] As a result, the palladium-catalyzed addition of heteroatom bonds to alkynes, dienes, and allenes has been well documented.[3−5] Little attention, however, has been paid to palladium-catalyzed intramolecular addition/cyclization between unsaturated carbon bonds. The palladium-catalyzed intramolecular addition/carbocyclization of tethered acyclic diynes,[6] enynes,[7] or bis(dienes)[8] with reagents containing X−Y σ-bonds (X, Y = Si, Sn, B) as a stereo- and regioselective route to functionalized carbocyclic and heterocyclic ring systems is a synthetically useful chemical transformation involving the formation of new C−C bonds along with C−X and C−Y bonds. As part of our ongoing efforts to prepare and utilize allenyl functionalities,[9] we disclosed our findings on the first palladium-catalyzed cyclization of bis(allenes) with organostannanes as shown in Scheme 1.[10] The efficiency of this approach in terms of catalytic ability and the characteristic structures of the products has encouraged us to apply the extension of cyclization of bis(allenes) to more versatile systems that should expand the scope and utility of transition metal catalyzed cyclizations.[11] To the best of our knowledge, the utilization of organogermylstannanes as reagents for transition metal promoted reactions with an allene functionality has not previously been investigated. Here we describe an extension of allene−allene cyclization aimed at finding new reagents and achieving useful routes to cyclization, reporting our studies of the germastannylation of bis(allenes) with $Ph_3GeSnBu_3$ and $Bu_3GeSnBu_3$ with catalysis by palladium complexes to form five-membered carbo- and heterocyclic ring systems. We found that the stereoselectivity of the cyclization is highly dependent on the reagents and reaction conditions. NMR experiments were also conducted for stereochemical assignments of the different stereochemical outcomes.

Results and Discussion

The first investigations for preliminary experiments focused on the feasibility of the use of germylstannane with bis(allenes) for the cyclization to **4** or **5** with appropriate palladium complexes. To investigate the sequence outlined in Scheme 1, we began with **1a** as a starting material; this compound was readily prepared in quantity from *N*,*N*-dipropargyl-*p*-toluenesulfonamide by a Crabbé reaction.[12] Initially attempted carbocyclization of **1a** with $Me_3GeSnBu_3$

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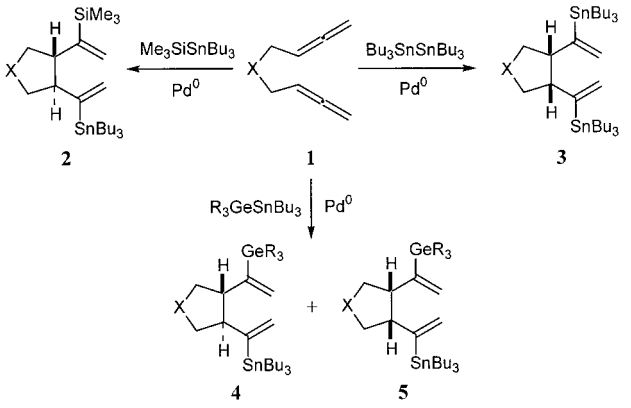
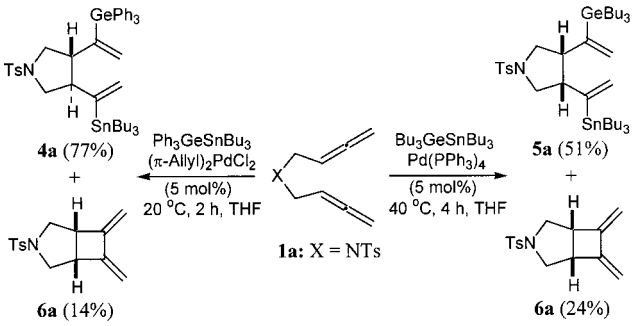


Scheme 1. General reaction routes for the carbocyclization of bis(allene) **1** catalyzed by Pd complexes

indicated that conversion into the corresponding **4** or **5** could not be achieved with a variety of palladium complexes under various reaction conditions, mainly due to a lack of reactivity. Fortunately, though, we found that $Ph_3GeSnBu_3$ and $Bu_3GeSnBu_3$ were capable of acting as effective reagents for this purpose. Initial experiments on the catalytic carbocyclization of **1a** with $Ph_3GeSnBu_3$ in the presence of $[Pd(PPh_3)_4]$ (5 mol %) at 20 °C for 20 h in THF afforded encouraging but marginal results. Although products were produced (as a mixture) during the reaction, a long reaction time and a low chemical yield (34% combined yield) remained problems to be solved. We subsequently speculated that the nature of the catalyst might be a control factor governing the process. After numerous conditions for orientation experiments had been surveyed, several key findings emerged: 1) when the bis(allene) **1a** was treated with $Ph_3GeSnBu_3$ in the presence of $(\pi\text{-allyl})_2Pd_2Cl_2$ (5 mol %) in THF at 20 °C for 2 h, the *trans*-cyclized product **4a** (77%) and the *cis*-fused bicyclic diene **6a** (14%) were produced in a total isolated yield of 91%, as shown in Scheme 2, 2) $(\pi\text{-allyl})_2Pd_2Cl_2$ was superior over other palladium complexes for the cyclization of **1a** with $Ph_3GeSnBu_3$, 3) on the other hand, treatment of **1a** with $Bu_3GeSnBu_3$ and $[Pd(PPh_3)_4]$ (5 mol %) at 40 °C for 5 h in THF resulted in the formation of the *cis*-cyclized product **5a** (51%), once more together with the *cis*-fused diene **6a** (24%), 4) $[Pd(PPh_3)_4]$ proved to be the most effective catalyst for **1a** with $Bu_3GeSnBu_3$, 5) the reaction provided the best chemical yields when performed in THF, in comparison with other solvents such as CH_2Cl_2, toluene, CH_3CN, and DMF, 6) group 14 atom species such as $Et_3GeSnBu_3$, Me_3SiPPh_2, Bu_3SnPPh_2, and $PhMe_2SiB(pin)$ (pin = pinacol, 2,3-dimethylbutane-2,3-diol) as reagents did not provide the cyclized product,[13] and 7) the use of palladium complexes such as $[PdCl_2(dppf)]$ [dppf = (diphenylphosphanyl)ferrocene], $[PdCl_2(PPh_3)_2]$, and $[Pd_2(dba)_3]\cdot CHCl_3$ proved unsuccessful, only the starting material being recovered. Under the optimal conditions, the reaction was conducted by dropwise addition of $Ph_3GeSnBu_3$ (1.1 equiv.) in THF at 20 °C to a solution of **1a** (1.0 equiv.) in the presence of $(\pi\text{-allyl})_2Pd_2Cl_2$ (0.05 equiv.) in THF. The reaction was cleanly complete within 2 h, and workup and chromatography gave separable **4a** along with **6a** in 91% yield as shown in Scheme 2.



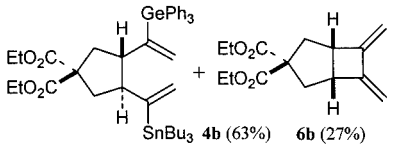
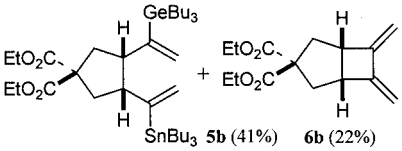
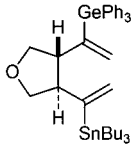
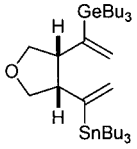
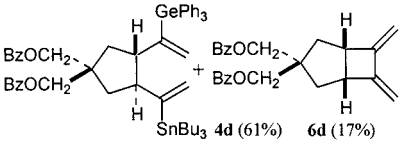
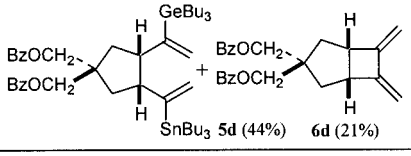
1b: X = $C(CO_2Et)_2$; **1c:** X = O; **1d:** X = $(PhCO_2CH_2)_2C$

Scheme 2. Preliminary investigations into the carbocyclization of **1a** catalyzed by Pd complexes

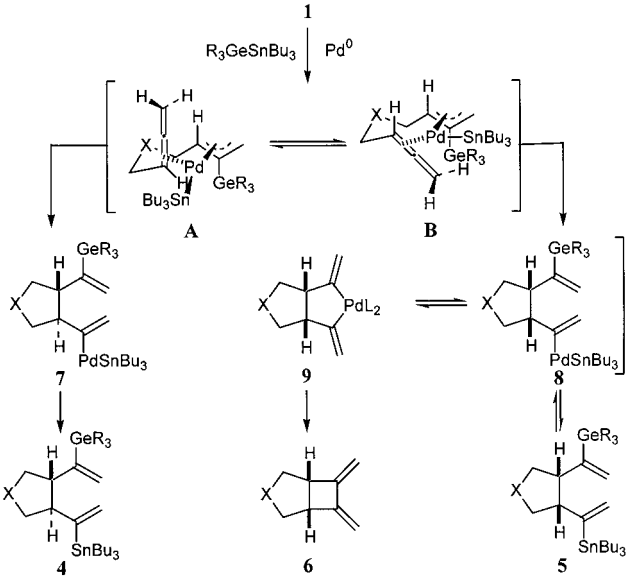
In the hope that this approach might provide a general method for the synthesis of substituted compounds **4** and **5**, we set out to determine the substituent effects with **1b**, **1c**, and **1d** to produce structurally varied products. Indeed, the method was successful in terms of reactivity, but these reactions also produced the *cis*-fused dienes **6**, as can be seen in Table 1. When **1b** was employed as a substrate, treatment of **1b** with $Ph_3GeSnBu_3$ afforded the *trans* adduct **4b** (63%) along with the *cis* bicyclic diene **6b** (27%) (Entry 1). In contrast, treatment of **1b** with $Bu_3GeSnBu_3$ gave the *cis* adduct **5b** (41%), again together with the *cis* bicyclic diene **6b** (22%) (Entry 2). In particular, it is notable that the *trans*-cyclized product **4c** was produced by treatment of bis(allenyl)ether **1c** with $Ph_3GeSnBu_3$ as a sole product in 74% yield, and the *cis*-cyclized product **5c** was obtained on treatment with $Bu_3GeSnBu_3$ as a single adduct in 47% yield (Entries 3 and 4). We observed that the cyclization was very sensitive to the substrates and the palladium complexes. For example, use of the catalyst $(\pi\text{-allyl})_2Pd_2Cl_2$ with the substrates **1b** and **1c** and $Bu_3GeSnBu_3$ did not promote the cyclization. In the case of **1c** (Entry 4), $Pd_2(dba)_3$ proved to be the only effective catalyst with $Bu_3GeSnBu_3$, other palladium complexes such as $(\pi\text{-allyl})_2Pd_2Cl_2$ and $[Pd(PPh_3)_4]$ proving unsatisfactory.

During our investigations, we observed an equilibrium between **5a** and the reaction intermediate **8**, which could also be a precursor for **6a** as shown in Scheme 3. Treatment of **1a** with $Bu_3GeSnBu_3$ in the presence of $[Pd(PPh_3)_4]$ at 40 °C for 4 h (conditions identical to those in Table 1) and subsequent warming to 60 °C for 3 h resulted in decreased formation of **5a** (22%) and increased formation of **6** (37%) in a somewhat lower (59%) combined yield. On the other hand, treatment of **1a** with $Ph_3GeSnBu_3$ in the presence of $(\pi\text{-allyl})_2Pd_2Cl_2$ at 20 °C for 2 h and then at 60 °C for 3 h gave a result almost identical to that in Table 1. These observations might reflect the stereochemical relationships of products **4** and **5** and offer mechanistic insights into this chemical transformation.

Table 3. Germastannylative carbocyclization of bis(allenes) **1** catalyzed by Pd complexes

Entry	1	$R_3GeSnBu_3$	Conditions[a]	t [h]	Products	Yield (%)[b]
1	**b**	Ph	A	5	 **4b** (63%) **6b** (27%)	90
2	**b**	Bu	B	6	 **5b** (41%) **6b** (22%)	63
3	**c**	Ph	A	4	 **4c** (74%)	74
4	**c**	Bu	C	5	 **5c** (47%)	47
5	**d**	Ph	A	2	 **4d** (61%) **6d** (17%)	78
6	**d**	Bu	B	2	 **5d** (44%) **6d** (21%)	65

[a] Method A: $(\pi\text{-allyl})_2Pd_2Cl_2$ (5 mol %), 20 °C, THF; Method B: $[Pd(PPh_3)_4]$ (5 mol %), 40 °C, THF; Method C: $Pd_2(dba)_3$ (5 mol %), 60 °C, THF. [b] Yields refer to purified and combined yields.



Scheme 3. Plausible reaction pathways

Even though the chemical behavior hinted strongly at the relative stereochemical arrangements of *trans*-**4** and *cis*-**5**, it was necessary to verify this by spectroscopic evidence. In the case of **4a**, the coupling constant of the two protons at the ring juncture was determined to be 13.8 Hz, which could suggest a *trans* configuration. To clarify this, NOESY experiments were carried out. Since only weak NOE crosspeaks between the two olefinic protons were observed in the NOESY spectrum of **4a**, the *trans* configuration was indeed assumed. The NOESY crosspeaks were also investigated in the NOESY spectrum of **5a**, which was considered to have the *cis* configuration. Unfortunately, unlike in **4a**, the ring protons of **5a** could not be clearly assigned. To clarify the ambiguity, compounds **10** and **11** were prepared from **4a** and **5a** by the Stille coupling reaction {PhCOCl, $[PdCl_2(PPh_3)_2]$ (4 mol %), CuCN (8 mol %), 90 °C, 3 h, toluene} in 44% and 31% yields, respectively. Fortunately, the stereochemical arrangements assigned to the cyclized products *trans*-**4a** and *cis*-**5a** were supported by NOE experiments performed with **10** and **11**, as shown in Figure 1. Specifically, irradiation of the ring junction proton

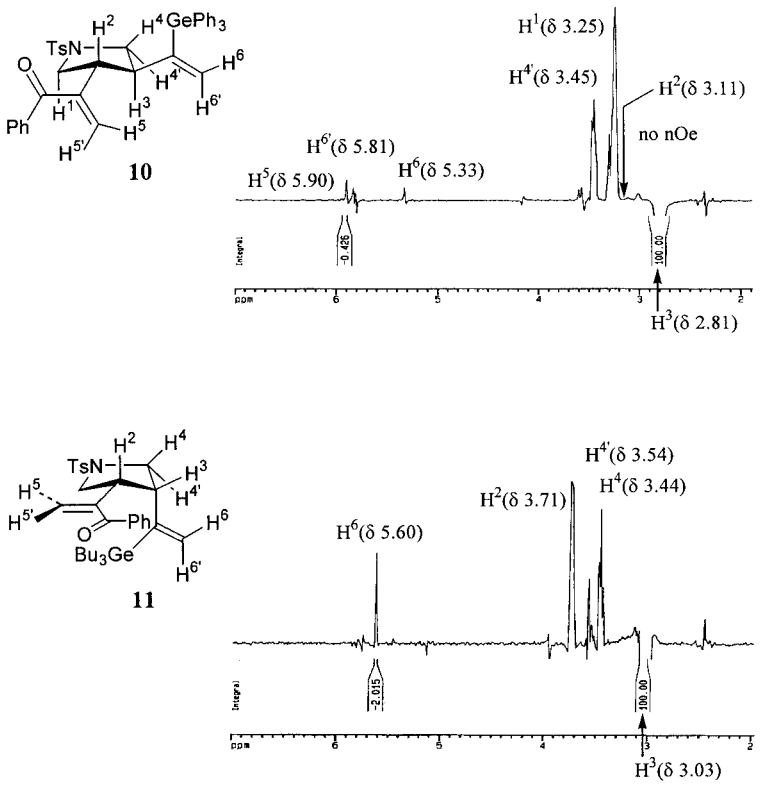


Figure 1. NOE experiments of **10** and **11**

H^3 at δ = 2.81 ppm in **10** strongly enhanced the signals of protons H^1 (9%) and $H^{4'}$ (4%) and weakly enhanced the signals of vinylic protons H^6 (0.3%), $H^{6'}$ (1%), and H^5 (0.5%), presumably due to rotation of vinyl groups during the measurements. More crucial evidence of the stereochemistry was the lack of any NOE effect between H^2 and H^3. Similarly, irradiation of the ring junction proton H^3 at δ = 3.03 ppm in **11** produced a relatively small enhancement in the signal of vinylic proton H^6 (2%) and strong enhancements in the signals of protons H^4 (6%) and $H^{4'}$ (2%), and especially in that of the ring junction proton H^2. These observations clearly support the stereochemical relationships of **4a** and **5a**.

Although the exact mechanistic aspects of this transformation have not been rigorously elucidated, the following pathway seems a probable stereochemical route on the basis of product formation and our observations as illustrated in Scheme 3. It is presumed that $R_3GePdSnBu_3$ is produced through the oxidative addition of germylstannane to the allenyl moiety, catalyzed by the palladium complex. The germyl group could be attached irreversibly to the central carbon atom of the allene to form π-allylpalladium complexes **A** and/or **B**.[10] Since migratory insertion would lead to the particular product **7** or **8** via stereochemical models **A** or **B**, the major reaction pathway, including orientations and steric factors, could be dependent on the stability of the transition state under kinetic control. Thus, we believe that the origin of the *trans* and *cis* stereochemical outcomes for this transformation might be subtle geometrical preferences for orientation in the appropriate transition states governed by substituents, reagents, and ligands. The stereochemical course of this catalytic process is likely to be due to a geometrical preference for **A** with a Ph_3Ge substituent and for **B** with a Bu_3Ge substituent for a minimum strain with existing components, as depicted in Scheme 3. Reductive elimination of **7** and **8** would afford the products **4** and **5** along with the regeneration of palladium catalyst. However, the intermediate **8** might also undergo transmetallation to form **9**, which could be transformed into **6** by a reductive elimination. However, an intermediate **7** would not allow transmetallation to *trans*-**9**, mainly because of the longer distance between the vinylic palladium complex and the germyl group in the *trans* geometry of **7**. Therefore, the formation of **6** could be explained if the reaction produced products from the equilibrium of **3** to **8** and **9** under the reaction conditions.

Conclusion

We have described the palladium-catalyzed regioselective and stereoselective carbocyclization of bis(allenes) with germylstannanes such as $Ph_3GeSnBu_3$ and $Bu_3GeSnBu_3$ to form the substituted five-membered cyclic compounds **4** or **5**, along with the *cis*-fused dienes **6**. In each case, the observed products indicate that the stereochemical outcome of this carbocyclization depends on the reagents. The relative stereochemistry of products was unambiguously established

by NMR experiments. Further studies including the extension of this method to more versatile systems are currently underway.

Experimental Section

General Remarks: All reactions were run in flame-dried glassware under nitrogen. Tetrahydrofuran (THF) and diethyl ether was dried by heating at reflux in the presence of sodium/benzophenone ketyl until a permanent purple coloration was present, and were distilled prior to use. All liquid reagents purchased from Aldrich were distilled appropriately prior to use, unless otherwise indicated. Purification was conducted by flash column chromatography on silica gel (230−400 mesh), by elution with a mixture of hexane and ethyl acetate, unless otherwise stated. All reactions were monitored by thin layer chromatography carried out on Merck silica gel plates (60 F_{254}) with use of UV light as visualizing agent and ethanolic anisaldehyde solution and heat as developing agent. FT-IR spectra were recorded with a Nicolet 205 instrument. ^{1}H NMR spectra were recorded with a Varian Unity Inova spectrometer at 500 MHz in $CDCl_3$ as a solvent with TMS or residual chloroform as the internal standard. Coupling constants (*J*) are reported in Hz. ^{13}C NMR spectra were measured with a Varian Unity Inova machine at 125 MHz in $CDCl_3$ as solvent. Germylstannanes $Ph_3GeSnBu_3$ [14] and $Bu_3GeSnBu_3$ [15] were prepared by modifiied literature procedures. The reported yields are for chromatographically pure isolated products.

Tributyl(triphenylgermyl)stannane: A solution of Ph_3GeH (0.30 g, 0.1 mmol) in THF (10 mL) was cooled to −23 °C, and butyllithium (0.09 mL, 0.1 mmol) was added slowly with rapid stirring. The resulting pale green solution was stirred for 0.5 h. After lithiation was complete, the reaction mixture was quenched with tributyltin chloride (0.27 mL, 0.1 mmol) and stirred at room temperature for 20 min. The reaction mixture was extracted with diethyl ether (3 × 10 mL) and washed with water (10 mL). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 column chromatography to afford tributyl(triphenylgermyl)stannane (0.52 g, 87%). TLC (SiO_2, hexanes): R_f = 0.45. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (m, 9 H, CH_3), 1.14 (m, 6 H, CH_2), 1.28 (m, 6 H, CH_2), 1.49 (m, 6 H, CH_2), 7.39 (m, 9 H, Ph), 7.50 (m, 6 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.5, 135.9, 129.0, 128.9, 30.6, 28.1, 14.3, 10.5 ppm. HRMS (EI): calcd. for $C_{30}H_{42}GeSn$ 594.1520, found 594.1527.

Tributyl(tributylgermyl)stannane: A solution of tributyltin chloride (0.27 mL, 0.1 mmol) in THF (3 mL) was added slowly to a mixture of Li (0.07 g, 1 mmol) and THF (3 mL) with stirring at 0 °C. After completion of the addition, stirring was continued at 50 °C for 3 h. The reaction mixture changed to a green solution. After removal of Li metal by filtration, a THF (3 mL) solution of tributylgermyl chloride (0.27 g, 0.1 mmol) was slowly added to the THF solution of tributylstannyllithium at 0 °C with stirring under Ar. After completion of the addition, the mixture was stirred at room temperate overnight. After evaporation of THF, dry ether was added. The mixture was carefully poured into water to decompose unchanged tributylstannyllithium, and the organic layer was extracted with diethyl ether (2 ×), dried with anhydrous $CaCl_2$, filtered, and concentrated under reduced pressure. The crude product was separated by SiO_2 column chromatography to afford tributyl(tributylgermyl)-stannane (0.31 g, 58%). TLC (SiO_2, hexanes): R_f = 0.81. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (m, 24 H, CH_2CH_3), 1.32 (m, 18 H, CH_2), 1.48 (m, 12 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.3, 29.9, 28.2, 27.4, 16.4, 14.4, 10.7, 9.4 ppm. HRMS (EI): calcd. for $C_{24}H_{54}GeSn$ 534.2459, found 534.2486.

***trans*-1-(4-Tolylsulfonyl)-3-(1-tributylstannylvinyl)-4-(1-triphenylgermylvinyl)pyrrolidine (4a) and 6,7-Dimethylene-3-(4-tolylsulfonyl)-3-azabicyclo[3.2.0]heptane (6a), Method A:** Tributyl(triphenylgermyl)stannane (178 mg, 0.30 mmol) in THF (2 mL) was added at 20 °C to a stirred solution of bis(allene) **1a** (75 mg, 0.27 mmol) and $(\pi\text{-allyl})_2Pd_2Cl_2$ (5.0 mg, 5 mol %) in THF (4 mL). The reaction mixture was stirred at 20 °C for 2 h, and the THF was then evaporated in vacuo. The crude product was purified by column chromatography (SiO_2, deactivated with 1% Et_3N, EtOAc/hexanes, 1:30) to afford the cyclized product **4a** (180.8 mg, 0.21 mmol, 77%) along with **6a** (10.4 mg, 0.037 mmol, 14%) as colorless oils.

Compound 4a: TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.35. IR (neat): $\tilde{\nu}$ = 2923, 1597, 1431, 1350, 1163, 1090, 928, 816 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (m, 15 H, $SnCH_2CH_2CH_2CH_3$), 1.26 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 1.38 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 2.38 (s, 3 H, *Me* Ts), 2.68 (ddd, *J* = 5.4, 7.2, 13.8 Hz, 1 H, $TsNCH_2CH$), 2.87 (ddd, *J* = 6.9, 7.6, 13.8 Hz, 1 H, $TsNCH_2CH$), 3.28 (dd, *J* = 6.9, 10.3 Hz, 1 H, TsNCHHCH), 3.32 (dd, *J* = 7.2, 9.8 Hz, 1 H, TsNCHHCH), 3.39 (dd, *J* = 5.4, 9.8 Hz, 1 H, TsNCHHCH), 3.47 (dd, *J* = 7.6, 10.3 Hz, 1 H, $TsNCH_2CH$ TsNCHHCH), 5.23 (s, 1 H, GeC=CHH), 5.46 (s, 1 H, SnC= CHH), 5.54 (s, 1 H, Sn=CHH), 5.88 (s, 1 H, GeC= CHH), 7.17 (d, *J* = 8.2 Hz, 2 H, Ph), 7.37 (m, 15 H, Ph), 7.60 (d, *J* = 8.2 Hz, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3, 144.8, 143.9, 136.0, 135.9, 134.8, 130.9, 130.3, 129.9, 129.0, 128.9, 128.2, 54.2, 53.2, 51.3, 47.1, 29.7, 28.1, 22.2, 14.4, 11.0 ppm. HRMS (EI): calcd. for $C_{45}H_{59}GeNO_2SSn$ 869.2500, found 869.2531. $C_{45}H_{59}GeNO_2SSn$ (869.25): calcd. C 62.17, H 6.84, Ge 8.35, N 1.61, S 3.69, Sn 13.66; found C 62.05, H 6.91, Ge 8.11, N 1.55, S 3.71, Sn 13.58.

Compound 6a: TLC (SiO_2, EtOAc/hexanes, 1:4): R_f = 0.30. IR (neat): $\tilde{\nu}$ = 2997, 1673, 1492, 1432, 1330, 1076 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, *Me* Ts), 2.75 (dd, *J* = 6.5, 9.5 Hz, 2 H, $TsNCH_2CH$), 3.30 (d, *J* = 6.5 Hz, 2 H, TsN CH_2CH), 3.62 (d, *J* = 9.5 Hz, 2 H, $TsNCH_2CH$), 4.80 (s, 2 H, C=CHH), 5.22 (s, 2 H, C= CHH), 7.31 (d, *J* = 8.0 Hz, 2 H, Ph), 7.73 (d, *J* = 8.0 Hz, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.7, 144.2, 132.8, 130.2, 128.8, 106.2, 54.0, 45.4, 22.2 ppm. HRMS (EI): calcd. for $C_{15}H_{17}NO_2S$ 275.0980, found 275.0979.

***cis*-1-(4-Tolylsulfonyl)-3-(1-tributylgermylvinyl)-4-(1-tributylstannylvinyl)pyrrolidine (5a), Method B:** Tributyl(tributylgermyl)stannane (160 mg, 0.30 mmol) in THF (2 mL) was added at 20 °C to a stirred solution of bis(allene) **1a** (70 mg, 0.27 mmol) and $[Pd(PPh_3)_4]$ (15 mg, 5 mol %) in THF (4 mL). The reaction mixture was stirred at 40 °C for 4 h, and the THF was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, deactivated with 1% Et_3N, EtOAc/hexanes, 1:30) to afford the cyclized product **5a** (120 mg, 0.14 mmol, 51%) along with **6a** (17.8 mg, 0.065 mmol, 24%). TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.49. IR (neat): $\tilde{\nu}$ = 2925, 1598, 1464, 1351, 1163, 1042, 920, 815 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (m, 30 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.29 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.42 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 2.43 (s, 3 H, *Me* Ts), 2.93 [m, 2 H, $TsN(CH_2CH)_2$], 3.38 (dd, *J* = 5.87, 9.68 Hz, 2 H, TsNCHHCH), 3.43 (dd, *J* = 6.89, 9.68 Hz, 2 H, $TsNCH_2CH$), 5.19 (s, 2 H, SnC=CHH and GeC=CHH), 5.59 (s, 2 H, SnC= CHH and GeC=CHH), 7.31 (d, *J* = 8.2 Hz, 2 H, Ph), 7.73 (d, *J* =

8.2 Hz, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.4, 143.2, 134.5, 129.6, 127.4, 127.3, 52.7, 50.5, 29.1, 27.4, 21.5, 13.7, 10.3 ppm. HRMS (EI): calcd. for $C_{39}H_{71}GeNO_2SSn$ 811.3439, found 811.3433. $C_{39}H_{71}GeNO_2SSn$ (811.34): calcd. C 57.87, H 8.84, Ge 8.97, N 1.73, S 3.96, Sn 14.67; found C 57.55, H 8.90, Ge 8.89, N 1.77, Sn 14.65.

Diethyl *trans*-3-(1-Tributylstannylvinyl)-4-(1-triphenylgermylvinyl)-cyclopentane-1,1-dicarboxylate (4b) and Diethyl 6,7-(Dimethylene)bicyclo[3.2.0]heptane-3,3-dicarboxylate (6b): Compound **4b** was obtained in 63% yield along with **6b** (27% yield) by the above procedure for **4a** (Method A).

Compound 4b: TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.46. IR (neat): ' = 2956, 1732, 1431, 1256, 1090, 917, 861 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82 (m, 15 H, $SnCH_2CH_2CH_2CH_3$), 1.17 (m, 6 H, $CO_2CH_2CH_3$), 1.25 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 1.38 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 2.43 [m, 4 H, $(EtO_2C)_2CCH_2CH$), 2.85 [m, 1 H, $(EtO_2C)_2CCH_2CH$), 3.16 [m, 1 H, $(EtO_2C)_2CCH_2CH$), 4.13 (m, 4 H, $CO_2CH_2CH_3$), 5.19 (d, J = 2 Hz, 1 H, GeC=CH_2), 5.50 (d, J = 2 Hz, 1 H, SnC=CHH), 5.60 (d, J = 2 Hz, 1 H, SnC=CHH), 6.02 (d, J = 2 Hz, 1 H, GeC=CH_2), 7.36 (m, 9 H, Ph), 7.47 (m, 6 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.6, 172.6, 156.2, 148.2, 137.1, 136.1, 129.5, 128.8, 126.6, 126.5, 62.2, 62.0, 59.1, 51.9, 47.4, 39.9, 39.8, 29.8, 28.1, 14.8, 14.7, 14.4, 10.9 ppm. HRMS (EI): calcd. for $C_{45}H_{62}GeO_4Sn$ 858.2882, found 858.2886.

Compound 6b: TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.38. IR (neat): ṽ = 2988, 1730, 1673, 1427, 1379 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (m, 6 H, $CO_2CH_2CH_3$), 2.29 {dd, J = 6.5, 13.5 Hz, 2 H, $(EtO_2C)_2CCH_2CH$}, 2.63 (d, J = 13.5 Hz, 2 H, $(EtO_2C)_2CCH_2CH$), 3.38 {d, J = 6.5 Hz, 2 H, $(EtO_2C)_2C(CH_2CH)_2$}, 4.16 {m, 4 H, $(CO_2CH_2CH_3)_2$}, 4.74 {d, J = 2.0 Hz, 2 H, $(C=CH_2)_2$}, 5.13 {d, J = 2.0 Hz, 2 H, $(C=CH_2)_2$} ppm. ^{13}C NMR (125M Hz, $CDCl_3$): δ = 171.8, 151.7, 105.4, 62.0, 46.6, 40.1, 30.4, 14.8 ppm. HRMS (EI): calcd. for $C_{15}H_{20}O_4$ 264.1361, found 264.1360.

Diethyl *cis*-3-(1-Tributylgermylvinyl)-4-(1-tributylstannylvinyl)cyclopentane-1,1-dicarboxylate (5b): This compound was obtained in 41% yield along with **6b** (22% yield) as described in the above procedure for **5a** (Method B). TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.53. IR (neat): ṽ = 2945, 1731, 1433, 1274, 1083, 913, 811 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 30 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.25 (m, 6 H, $CO_2CH_2CH_3$), 1.32 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.46 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 2.41 (dd, J = 7.5, 13.5 Hz, 2 H, $(EtO_2C)_2CCH_2CH$), 2.52 (dd, J = 7.5, 13.5 Hz, 2 H, $(EtO_2C)_2CCH_2CH$), 3.03 {m, 2 H, $(EtO_2C)_2C(CH_2CH)_2$}, 4.16 {m, 4 H, $(CO_2CH_2CH_3)_2$}, 5.15 (s, 2 H, SnC=CHH and GeC=CHH), 5.70 (s, 2 H, SnC=CHH and GeC=CHH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.7, 172.8, 156.5, 126.1, 62.1, 59.5, 51.5, 39.8, 29.8, 28.0, 14.8, 14.4, 10.8 ppm. HRMS (EI): calcd. for $C_{39}H_{74}GeO_4Sn$ 798.3821, found 798.3814.

***trans*-Triphenyl-{1-[4-(1-tributylstannylvinyl)tetrahydrofuran-3-yl]-vinyl}germane (4c):** This compound was obtained in 74% yield as described in the above procedure for **4a** (Method A). TLC (SiO_2, EtOAc/hexanes, 1:15): R_f = 0.53. IR (neat): ṽ = 2926, 1484, 1375, 1089, 901 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 0.88 (m, 9 H, $SnCH_2CH_2CH_2CH_3$), 1.25 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 1.37 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 3.17 (m, 1 H, OCH_2CH), 3.22 (m, 1 H, 2-H), 3.58 (m, 4 H, OCH_2CH), 5.17 (d, J = 1.5 Hz, 2 H, SnC=CHH and GeC=CHH), 5.50 (d, J = 1.5 Hz, 1 H, SnC=CHH), 5.56 (d, J = 1.5 Hz, 1 H, GeC=CHH), 7.35 (m, 9 H, Ph), 7.47 (m, 6 H, Ph) ppm. ^{13}C NMR (125 MHz) δ 155.2, 155.1, 137.1, 136.5, 129.4, 128.6, 127.3, 127.2, 73.0, 72.9, 41.7, 41.4, 29.9, 28.1, 14.5, 10.8 ppm. HRMS (EI): calcd. for $C_{38}H_{52}GeOSn$ 716.2252, found 716.2275. $C_{38}H_{52}GeOSn$ (716.22): calcd. C 63.73, H 7.32, Ge 10.14, Sn 16.58; found C 63.71, H 7.22, Ge 10.41, Sn 16.39.

***cis*-Tributyl-{1-[4-(1-tributylstannylvinyl)tetrahydrofuran-3-yl]vinyl}-germane (5c), Method C:** Tributyl(tributylgermyl)stannane (360 mg, 0.67 mmol) in THF (2 mL) was added at 20 °C to a stirred solution of bis(allene) **1c** (75 mg, 0.61 mmol) and $Pd_2(dba)_3$ (28 mg, 5 mol %) in THF (4 mL). The reaction mixture was stirred at 60 °C for 5 h, and the THF was evaporated in vacuo. The crude product was purified by column chromatography (1% Et_3N, EtOAc/hexanes, 1:30) to afford the cyclized product **5c** (188mg, 0.29 mmol, 47%). TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.53. IR (neat): ṽ = 2925, 1464, 1376, 1072, 916 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (m, 30 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.32 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2$ CH_2CH_3), 1.47 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 3.19 (m, 2 H, OCH_2CH), 3.83 (dd, J = 5.9, 8.2 Hz, 2 H, OCH_2CH), 3.97 (dd, J = 6.6, 8.2 Hz, 2 H, OCH_2CH), 5.25 (d, J = 1.5 Hz, 2 H, SnC=CHH and GeC=CHH), 5.68 (d, J = 1.5 Hz, 2 H, SnC=CHH and GeC=CHH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 127.8, 73.4, 53.2, 29.8, 28.2, 14.4, 11.0 ppm. HRMS (EI): calcd. for $C_{32}H_{64}GeOSn$ 656.3191, found 656.3188.

***trans*-1,1-(Dibenzoylmethyl)-3-(1-tributylstannylvinyl)-4-(1-triphenylgermylvinyl)cyclopentane (4d) and 3,3-Dibenzoylmethyl-6,7-(dimethylene)bicyclo[3,2,0]heptane (6d):** Compound **4d** was obtained in 61% yield along with **6d** (17% yield) as described in the above procedure for **4a** (Method A).

Compound 4d: TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.53. IR (neat): ṽ = 2955, 1721, 1602, 1451, 1267, 1110, 1026, 711 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79 (m, 15 H, $SnCH_2CH_2CH_2CH_3$), 1.22 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 1.37 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 1.98 (m, 4 H, $PhCH_2CO$), 2.99 [m, 1 H, $(BzOCH_2)_2CCH_2CH$), 3.23 [m, 1 H, $(BzOCH_2)_2CCH_2CH$), 4.18 [m, 2 H, $(BzOCH_2)_2CCH_2CH$), 4.33 {m, 1 H, $(BzOCH_2)_2CCHCH$}, 4.37 (m, 1 H, {m, 1 H, $(BzOCH_2)_2CCHCH$}, 5.27 (s, 1 H, GeC=CHH), 5.56 (s, 1 H, SnC=CHH), 5.80 (s, 1 H, SnC=CHH), 6.09 (s, 1 H, GeC=CHH), 7.30 (m, 9 H, Ph), 7.40 (m, 4 H, $PhCH_2CO$), 7.48 (m, 6 H, Ph), 7.53 (m, 2 H, $PhCH_2CO$), 7.91 (m, 3 H, $PhCH_2CO$), 8.02 (m, 1 H, $PhCH_2CO$) ppm. ^{13}C NMR (125 MHz): δ = 166.9, 166.8, 156.3, 149.4, 136.6, 135.7, 133.4, 130.0, 129.4, 128.8, 128.7, 128.6, 68.9, 67.9, 51.8, 47.6, 44.9, 38.1, 37.2, 29.5, 27.7, 14.1, 10.5. $C_{55}H_{66}GeO_2Sn$ (954.46): calcd. C 67.24, H 6.77, Ge 7.39, Sn 12.08; found C 67.05, H 6.62, Ge 7.41, Sn 12.21.

Compound 6d: TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.31. IR (neat): ṽ = 2918, 1719, 1601, 1450, 1269, 1110 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.01 {m, 4 H, $(BzOCH_2)_2C(CH_2CH)_2$}, 3.44 {m, 2 H, $(BzOCH_2)_2C(CH_2CH)_2$}, 4.31 (s, 2 H, $PhCH_2CO$), 4.49 (s, 2 H, $PhCH_2CO$), 4.80 {s, 2 H, $(C=CH_2)_2$}, 5.20 {s, 2 H, $(C=CH_2)_2$}, 7.42 (m, 4 H, Ph), 7.55 (m, 2 H, Ph), 8.01 (m, 4 H, Ph) ppm. HRMS (EI): calcd. for $C_{25}H_{24}O_2$ 388.1675, found 388.1662.

***cis*-1,1-(Dibenzoylmethyl)-3-(1-tributylgermylvinyl)-4-(1-tributylstannylvinyl)cyclopentane (5d):** This compound was obtained in

44% yield along with **6d** (21% yield) as described in the above procedure for **5a** (Method B). TLC (SiO_2, EtOAc/hexanes, 1:10): R_f = 0.55. IR (neat): $\tilde{\nu}$ = 2955, 1725, 1606, 1456, 1267, 1113, 1070, 710 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 [(m, 30 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.28 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.47 (m, 12 H, $SnCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 1.95 (dd, J = 6.5, 13.2 Hz, 2 H, $(BzOCH_2)_2CCH_2CH$), 2.03 (dd, J = 7.4, 13.2 Hz, 2 H, $(BzOCH_2)_2CCH_2CH$), 3.11 {m, 2 H, $(BzOCH_2)_2C(CH_2CH)_2$}, 4.32 (s, 2 H, $PhCH_2CO$), 4.38 (s, 2 H, $PhCH_2CO$), 5.21 (s, 2 H, SnC=CH*H* and GeC=CH*H*), 5.80 (s, 2 H, SnC=C*H*H and GeC=C*H*H), 7.42 (m, 4 H, Ph), 7.55 (m, 2 H, Ph), 8.01 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz): δ = 167.3, 167.1, 157.2, 133.7, 130.8, 130.3, 129.1, 129.0, 125.8, 69.6, 69.3, 51.6, 45.4, 38.0, 29.8, 27.1, 14.4, 10.8. $C_{49}H_{78}GeO_2Sn$ (924.41): calcd. C 63.80, H 8.52, Ge 7.87, Sn 12.87: found C 63.79, H 8.62, Ge 7.97, Sn 12.66.

***trans*-1-Phenyl-2-[1-(4-tolylsulfonyl)-4-(1-triphenylgermylvinyl)-pyrrolidin-3-yl]propenone (10):** Compound **4a** (190 mg, 0.22 mmol) was added at 22 °C to a stirred suspension of $[PdCl_2(PPh_3)_2]$ (6.1 mg, 4 mol %), CuCN (1.6 mg, 8 mol %), and benzoyl chloride (33.9 mg, 0.24 mmol) in toluene (3 mL). The reaction mixture was then warmed to 90 °C. After stirring at 90 °C for 3 h, the resulting mixture was allowed to cool to room temperature, and the concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, EtOAc/hexanes, 1:5) to afford **10** (66.3 mg, 0.097 mmol, 44%) as a yellow oil. TLC (SiO_2, EtOAc/hexanes, 1:5): R_f = 0.20. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, *Me* Ts), 2.81 {ddd, J = 6.7, 6.8, 9.4 Hz, 1 H, $TsNCH_2CHC(GePh_3)=CH_2$}, 3.11 {ddd, J = 3.1, 6.7, 7.1 Hz, 1 H, $TsNCH_2CHC(COPh)=CH_2$}, 3.25 {dd, J = 7.1, 10.0 Hz, 1 H, $TsNCHHCHC(COPh)=CH_2$}, 3.45 {dd, J = 6.8, 10.7 Hz, 1 H, $TsNCHHCHC(GePh_3)=CH_2$}, 3.49 {dd, J = 3.1, 10.0 Hz, 1 H, $TsNCHHCHC(COPh)=CH_2$}, 3.58 {dd, J = 9.4, 10.7 Hz, 1 H, $TsNCHHCHC(GePh_3) =CH_2$}, 5.33 (d, J = 1.5 Hz, 1 H, GeC=CH*H*), 5.81 (d, J = 1.5 Hz, 1 H, GeC=C*H*H), 5.84 (d, J = 1.4 Hz, 1 H, PhCOCC= CH*H*), 5.90 (d, J = 1.4 Hz, 1 H, GeC=C*H*H), 7.18−8.13 (m, 24 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.3, 172.8, 172.8, 146.6, 144.8, 144.0, 137.6, 135.7, 134.3, 132.6, 130.7, 130.3, 130.1, 129.8, 129.6, 128.9, 128.7, 128.5, 127.8, 53.4, 50.9, 46.0, 42.1, 21.9 ppm. HRMS (EI): calcd. for $C_{40}H_{37}GeNO_3S$ 685.1706, found 685.1732.

***cis*-1-Phenyl-2-[1-(4-tolylsulfonyl)-4-(1-tributylgermylvinyl)-pyrrolidin-3-yl]-1-propenone (11):** This compound was obtained in 31% yield as described in the above procedure for **10**. TLC (SiO_2, EtOAc/hexanes, 1:5): R_f = 0.49. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.72−0.82 (m, 15 H, $GeCH_2CH_2CH_2CH_3$), 1.21 (m, 6 H, $GeCH_2CH_2CH_2CH_3$), 1.25 (m, 6 H, $GeCH_2CH_2CH_2CH_3$), 2.45 (s, 3 H, *Me* Ts), 3.03 {ddd, J = 6.9, 8.2, 10.8 Hz, 1 H, $TsNCH_2CHC(GeBu_3)=CH_2$}, 3.44 {dd, J = 6.9, 9.9 Hz, 1 H, $TsNCHHCHC(GeBu_3)=CH_2$}, 3.54 {dd, J = 8.2, 9.9 Hz, 1 H, $TsNCHHCHC(GeBu_3)$}, 3.57 {dd, J = 5.0, 10.2 Hz, 1 H, $TsNCHHCHC(COPh)=CH_2$}, 3.59 {dd, J = 7.0, 10.2 Hz, 1 H, $TsNCHHCHC(COPh)=CH_2$}, 3.71 {ddd, J = 5.0, 7.0, 10.8 Hz, 1 H, $TsNCH_2CHC(COPh)=CH_2$}, 5.11 (d, J = 2.0 Hz, 1 H, GeC=CH*H*), 5.60 (d, J = 2.0 Hz, 1 H, GeC=C*H*H), 5. 73 (d, J = 0.9 Hz, 1 H, PhCOCC=CH*H*), 5.79 (d, J = 0.9 Hz, 1 H, PhCOCC=C*H*H), 7.37 (m, 4 H, Ph), 7.50 (m, 1 H, Ph), 7.63 (m, 2 H, Ph), 7.77 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.7, 151.5, 146.4, 143.5, 137.2, 134.2, 132.1, 129.9, 129.8, 128.0, 127.5, 127.4, 127.4, 52.3, 52.2, 49.7, 41.6, 27.9, 26.9, 21.5, 13.6, 10.1 ppm. HRMS (EI): calcd. for $C_{34}H_{49}GeNO_3S$ 625.2645, found 625.2639.

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