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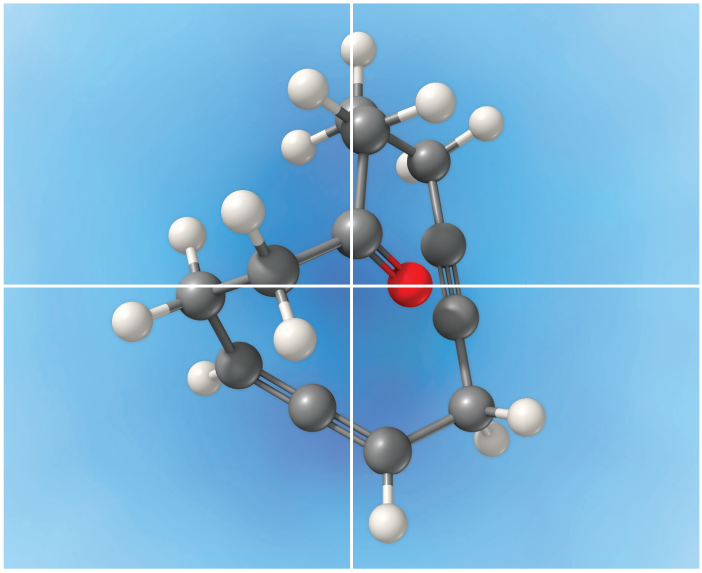

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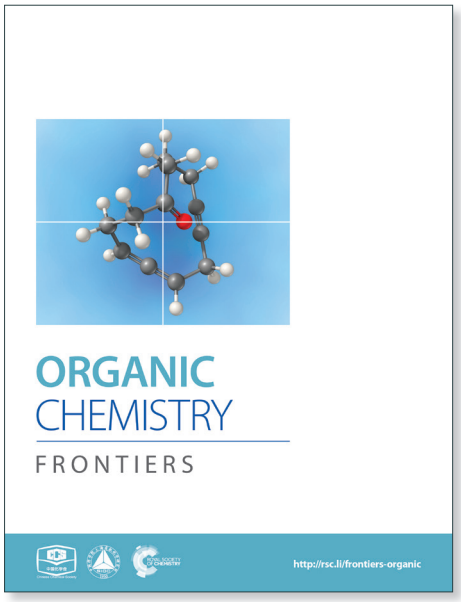

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ARTICLE

A mechanistic study on S_Hi reaction at tin atoms in a radical cascade reaction

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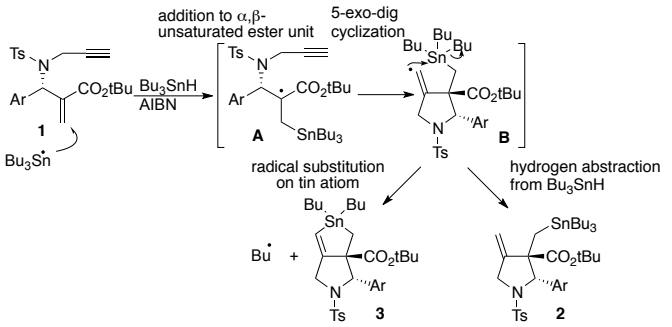
A kinetic study on radical cascade reactions of 1,6-enyne compounds was undertaken. The efficiency of the reaction depended on the presence of an ester group at the alkene unit, which clearly suggests that the addition of tin radical was accelerated by the α,β-unsaturated system. Stannolane formation progressed very quickly after a short induction period and finished within 12 min in the presence of Bu_3SnH at 10^{-2} M concentration conditions at 110 °C. Product ratios between stannolane and exo-methylene compound depended on the concentration of Bu_3SnH; a linear relationship was observed between the ratios of the two and the concentration of Bu_3SnH. These results clearly indicate that the S_Hi process is irreversible. The slope of the graph allowed us to estimate k_s value, S_Hi reaction rate at the tin atom, as 4.23 × 10^8 s^{-1} at 303 K. Use of Bu_2PhSnH for the reaction suggests that the S_Hi process partially progresses by the front side attack of the vinyl radical, which generates a methylene radical that undergoes neophyl rearrangement to give methylene piperidine in a *cis*-selective manner.

Introduction

Radical reactions are regarded as a useful method in organic synthesis.[1] A carbon-centered radical usually undergoes radical cyclisation,[2] rearrangement,[3] and fragmentation[4] reactions that give new carbon frameworks. The intramolecular substitution reaction of radicals, S_Hi reaction, occurs on heteroatoms such as sulfur, silicon and tin, which release a heteroatom-centered radical as a leaving group in the substitution reaction.[5] For example, Studer reported that the acyl radical attacks tin atoms in an S_Hi manner and generates a silyl radical as a leaving radical.[6] Through *ab initio* and DFT calculations Schiesser reported that S_Hi and S_H2 processes can take place at tin, germanium and silicon atoms resulting in the formation of alkyl radicals.[7] Although an alkyl radical serves as a leaving group in S_Hi reaction on a sulfur atom,[8] a similar reaction on a tin atom is rather rare.[5e-g] Recently, we found that 1,6-enyne compounds undergo a new type of radical cascade reaction, in which tin radicals progressed addition, cyclization and S_Hi substitution reaction on tin atom in one step to give bicyclic stannolane in high yields.[9] The reaction progressed in a stereoselective manner, forming only one diastereomer. Note that an alkyl radical is released as a leaving group from trialkyltin atom in a highly efficient manner. The products, stannolanes, serve as a good precursor for the double Stille coupling reaction, giving benzodihydroisoindoles and pyrrolidinoindanes in short steps.[10]

We assume that the stannolane formation reaction progresses through the following mechanism (Scheme 1). The reaction starts by the addition reaction of a tin radical to the α,β-unsaturated ester part of compound **1** to generate α-carbonyl radical **A**. Then the α-carbonyl radical **A** attacks the terminal alkyne unit in a 5-dig-exo manner to generate vinyl radical **B**. Vinyl radicals are usually regarded as a highly reactive radical. Therefore the vinylic radical in intermediate **B** attacks the tin atom in an intramolecular manner to give stannolane **3** in good yields. However, when the reaction is performed without solvent, i.e., with very high concentration of Bu_3SnH, a 1:1 mixture of compound **3** and exo-methylene pyrrolidine **2** is obtained. These results clearly support the reaction mechanism shown in Scheme 1. The rate determining step of the cascade reaction should be the addition process (i.e., **1** to **A**) or substitution process (i.e., **B** to **3**). The cyclization step must be faster than these two processes, because we could not have detected any products of the simple addition of Bu_3SnH to the α,β-unsaturated ester unit of **1**.



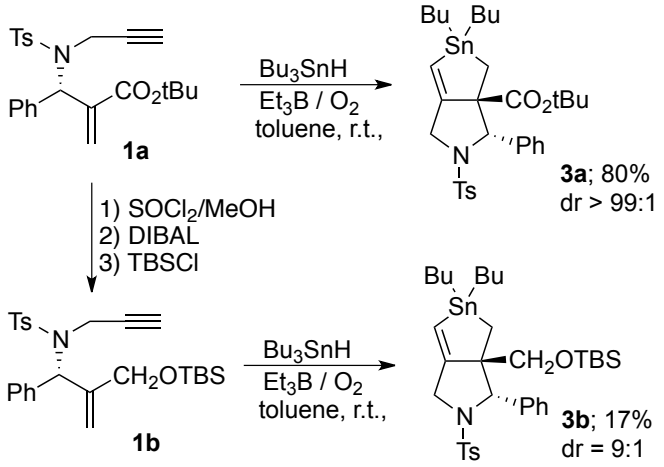
Scheme 1

During our investigation of this chemistry, we were interested in the rate constant of the radical substitution reaction from intermediate **B** to compound **3**. Although some kinetic studies on S_Hi reaction have been reported, to the best of our

knowledge, these reports are related only to heteroatom-centered radicals as leaving groups, and there seems to be no mechanistic study on S_Hi processes using an alkyl radical as a leaving group. In this paper we report the kinetic estimation of the radical substitution reaction on tin atoms. We also found that the presence of an ester group in the α,β-unsaturated system is crucial to efficient progress of the cascade reaction. Use of $PhBu_2SnH$ provides another reaction pathway and clearly suggests that the S_Hi process partially occurs via a front-side attack of the tin radical to give a methylene radical. This radical undergoes neophyl rearrangement, giving piperidine derivatives as a minor product.

Results and discussion

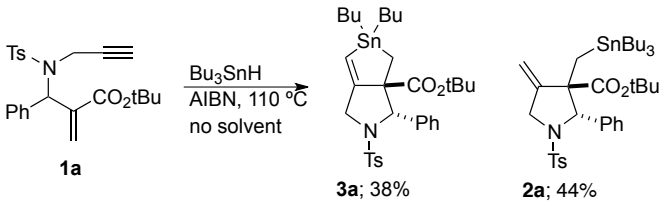
Compound **1a** was prepared using a previously reported method.[11] We checked the role of the ester group in the cascade reaction. We examined the reaction of compound **1b**, which was prepared by the reduction of ester **1a**, under the same conditions. Treatment of **1b** with Bu_3SnH at a concentration of 10^{-2} M in toluene at room temperature resulted in a sluggish reaction; all of the starting material was consumed, and compound **3b** was formed in only 17% as an approximately 9:1 mixture of two diastereoisomers (Scheme 2).



Scheme 2

The structure of compound **3b** was confirmed by chemical conversion from compound **3a**. This is in sharp contrast to the reaction of **1a**, in which a single isomer of stannolane **3a** was produced in 80% yield in a highly selective manner.[10] These results suggest that the α,β-unsaturated ester unit in **1** is important in promoting the radical addition, the first step of the cascade process. Thus, the reaction rate of the addition of the Bu_3Sn radical becomes slow in the absence of the ester group.

We next examined the reaction kinetics based on the product ratio. Before performing the investigation, we prepared compound **2a** under solvent-free conditions (Scheme 3). Compound **2a** was obtained in 44% yield along with **3a** in 38% yield. Thus, the direct radical substitution at the tin atom by the vinyl radical became competitive with hydrogen abstraction from external Bu_3SnH when its concentration was very high.



Scheme 3

The time course of the reaction between **1a** and Bu_3SnH (10^{-2} M) at 110 °C was examined (Figure 1). The reaction started after short induction period (approximately 4 min). The yields of the products increased in proportion to the reaction time and the reaction was complete in 12 min.

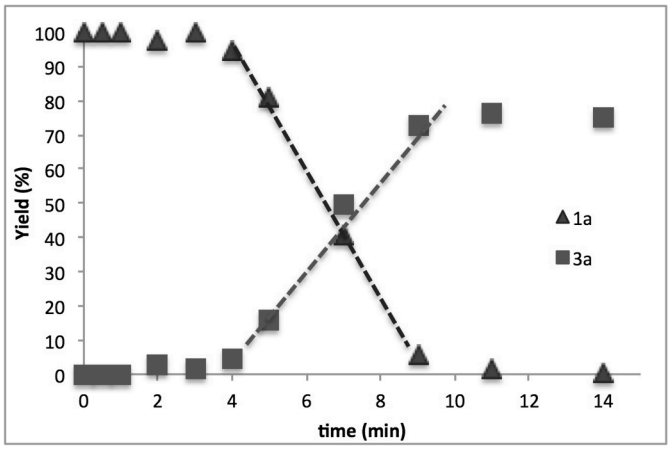
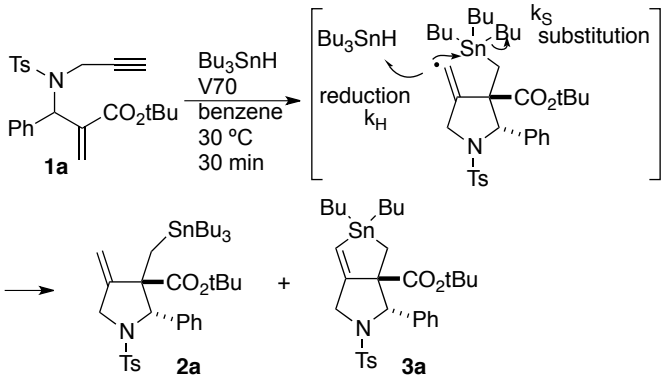


Figure 1. Time course of the reaction of **1a** at 110 °C

To obtain the kinetic parameter of the S_Hi process in the cascade reaction, we examined the reaction of **1** in the presence of various concentrations of Bu_3SnH (Scheme 4). We performed the reaction at 30 °C using approximately 5 equiv. of Bu_3SnH. V70 was employed as a radical initiator. The yields of compound **2a** and **3a** after 30 min were estimated by NMR proton integration using anisole as an internal standard. The yields of **2a** and **3a** are summarized in Table 1.



Scheme 4

Table 1. The yields of compounds **2a** and **3a** in the reaction of **1a** at 30 °C with a variety of Bu_3SnH concentrations.

entry	Bu_3SnH (M)	**2a**; yield (%)[a]	**3a**; Yield (%)[a]	**2a**/**3a** ratio
1	0.50	20.7 ± 1.3	54.3 ± 2.7	0.38
2	1.00	32.3 ±1.3	40.3 ± 1.7	0.80
3	1.44	37.3 ± 0.7	30.7 ± 0.7	1.22

a. Yields were determined by ^{1}H NMR ratios using anisole as an internal standard.

The product ratio of compound **2a**/**3a** depended on the concentration of Bu_3SnH. As the Bu_3SnH concentration increased, the yield of compound **2a** increased. This contrasts with the reaction performed with a 10^{-2} M concentration of Bu_3SnH, in which the formation of compound **2a** was almost non-detectable, i.e., the yield of **2a** was almost zero under such conditions. Figure 2 shows the relationship between the ratios of compound **2a**/**3a** and the concentration of Bu_3SnH.

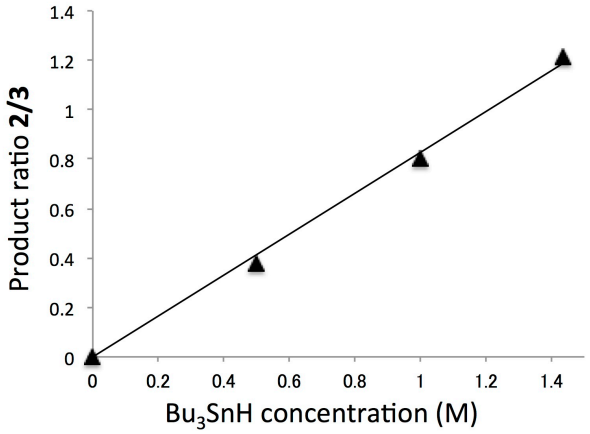


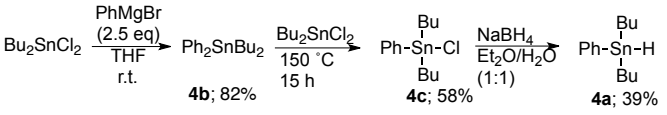
Figure 2. Relationship between the ratio of compound **2a/3a** and Bu_3SnH concentration for the reaction at 30 ºC.

The plot shows a strong linear relationship between the ratios and the concentration of Bu_3SnH. The line passed through the origin, indicating that the radical substitution reaction is irreversible.[12] The slope was calculated to be 0.828, where correlation coefficient, R^2, was 0.994. The absolute rate constant of hydrogen abstraction from Bu_3SnH by the vinyl radical at 30 °C was estimated by Ingold and co-workers to be $k_H = 3.5 \times 10^8$ $M^{-1}sec^{-1}$.[13] This value allows us to estimate the rate constant of the direct substitution reaction at the tin atom, k_s, at 30 °C as follows:

$$k_s = k_H/\text{slope} = 3.5 \times 10^8/0.828 = 4.23 \times 10^8\ \text{sec}^{-1}$$

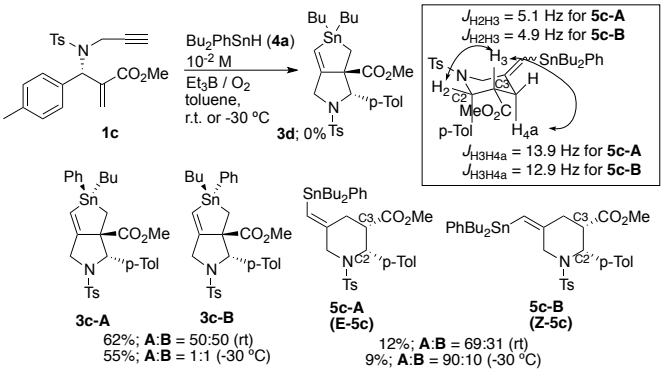
These results suggest that the S_Hi process in this cascade reaction is relatively fast. This is probably due to the configuration of the vinyl radical intermediate **B**, which places the vinylic radical center close to the position of the tin atom that undergoes S_Hi reaction smoothly. Thus, we estimate the rate constant for the tin atom S_Hi reaction that forms bicyclic stannolane to release an alkyl radical.

To further explore the reaction mechanism, we employed differently substituted tin hydride. Phenyldibutyltin hydride **4a** was prepared from dibutyltindichloride by treatment with Grignard reagent, and subsequent disproponation reaction and reduction (Scheme 5).[14] Dibutyltindichloride underwent diphenylation by exposure to 2.5 equiv. of phenyl Grignard reagent to give dibutyldiphenyltin **4b** in 82% yield. Compound **4b** was converted to dibutylphenyltin chloride **4c** in 58% yield by heating of a 1:1 mixture of **4b** and dibutyltin dichloride. Reduction of **4c** was performed by treatment with $NaBH_4$ and desired dibutylphenyltin hydride **4a** was obtained in 39% yield.



Scheme 5

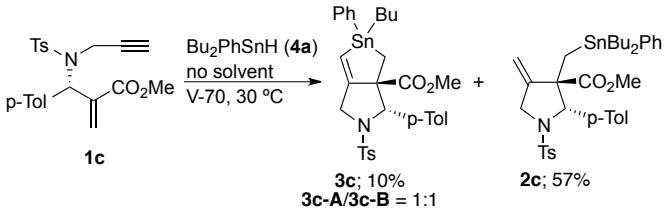
The reaction of **1c**, prepared from the corresponding *tert*-butyl ester,[11] and **4a** was examined under the same conditions as the radical cascade process. Thus, a mixture of **1c** and **4a** in toluene at a concentration of 10^{-2} M was stirred at room temperature. Compound **1c** was smoothly consumed after 30 min. Then a typical workup provided compound **3c** in 62% yield. Note that we could not observe any trace of **3d** in the reaction mixture. This is reasonable because the phenyl radical is highly reactive and should not be generated in this substitution. Compound **3c** contained two diastereomers whose ratio was approximately 1:1. Thus, no stereoselectivity on the radical substitution reaction at the tin atom was observed. The diastereomers were separated by careful chromatography, and one of the isomers, **3c-A**, afforded a good crystal for which X-ray crystallographic analysis unambiguously showed the expected structure.[15] Comparison of ^{1}H NMR spectra revealed that the other isomer, **3c-B**, showed a downfield shift at the CO_2Me signal, indicating that the difference in structure between **3c-A** and **3c-B** was the difference on the configuration at the tin atom.



Scheme 6

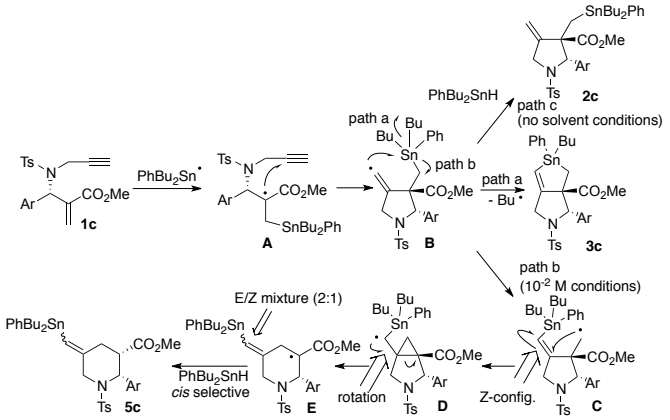
We attempted to identify minor products of this reaction. We isolated minor product **5c** in 12% yield. Compound **5c** contained the two diastereomers, **5c-A** and **5c-B**, and their ratio was 69:31. Careful chromatographic separation of **5c-A** and **5c-B** allowed us to determine their structures. NMR spectra of these compounds revealed a methylenepiperidine structure. Interestingly, the difference in stereochemistry between these two isomers was the geometry of the alkene unit, and both isomers contained *cis*-configuration between C2 and C3. This was clearly supported by the observation of large coupling constants (12.9 and 13.9 Hz) between H4a and H3. Note that the H2 proton shows a relatively small coupling constant in *cis*- and *trans*-2,3-substituted-*N*-tosyl-2-arylpiperidines.[16] NOESY spectra for **5c-A** and **5c-B** showed a cross peak between H6 and

=CHSnPhBu$_2$ in **5c-A**, and a cross peak between H3 and =CHSnPhBu$_2$ in **5c-B**. Thus, we concluded that **5c-A** had E-configuration and **5c-B** had Z-configuration, and the E/Z ratio of **5c** was approximately 2:1. This E/Z ratio was improved to approximately 10:1 when the reaction was performed at –30 °C.



Scheme 7

We next examined the radical cascade reaction with high concentration of Bu$_2$PhSnH (Scheme 7). Treatment of compound **1c** with Bu$_2$PhSnH under solvent-free conditions at 30 °C resulted in the quick consumption of **1c**. The reaction was initiated by catalytic amounts of V70. We observed two products in the reaction mixture: one was stannolane **3c** in 10% yield, and the other was exo-methylene pyrrolidine **2c**, which was unambiguously determined by NMR analysis. Compound **2c** was the major product of the reaction and its yield reached 57%. Note that neither **3d** nor **5c** were observed in the reaction mixture under these conditions.



Scheme 8

With the results of our experiments using Bu$_2$PhSnH, we assumed the reaction pathway shown in Scheme 8. Thus, the PhBu$_2$Sn radical attacks the terminal carbon-carbon double bond to give radical **A**. This is supported by the fact that the presence of the ester group attracts the addition of the tin radical to the alkene terminal. Then, cyclization yields vinyl radical **B**, which mainly releases the butyl radical through path a as a major process to give **3c**. However, in this case there is a phenyl substituent present on the tin atom that never serves as a leaving group during the substitution reaction. Alternatively, methylene radical **C** was released, which undergoes neophyl rearrangement through cyclopropylradical **D**, to give 3-piperidino radical **E**. Due to the steric bias introduced by the phenyl group at the C2 position, *cis*-selective hydrogen abstraction from **E** occurs to give *cis*-**5c**. Note that radical **E** should be a mixture of geometrical isomers of the vinyltin unit because a rotation around the carbon-carbon single bond is possible in radical **D**. This rotation should be slow and suppressed under low temperature conditions. When the reaction was performed under solvent-free conditions, intermediate radical **B** should be trapped by PhBu$_2$SnH due to its high concentration. This result also indicates that the radical addition was initiated by the attack of the tin radical to the α,β-unsaturated ester unit, not to the terminal alkyne unit.

In conclusion, we have explored the reaction mechanism for the radical cascade reaction, including direct radical substitution on tin atom. To progress the cascade reaction efficiently, the presence of an ester group is crucial for promoting the radical addition of the tin radical, the initial process of the cascade. The reaction profile was examined and the cascade reaction is a very fast reaction that is complete within 12 min after an approximately 4 min induction period. The kinetic parameter for the direct radical substitution reaction on the tin atom, the S_Hi reaction, was estimated. The rate constant was determined to be 4.23×10^8 sec^{-1}, which is regarded as a relatively fast process when compared with the hydrogen abstraction reaction for tin hydride by an alkyl radical. Use of dibutylphenyltin hydride revealed a side reaction for the cascade process, which showed no diastereoselectivity on the substitution at the tin atom. Note that there is a possibility of neophyl rearrangement of the reaction intermediate to give small amounts of methylene piperidine **5a**. We are now investigating the reaction mechanism using the MO calculation method and will be published in due course.

Experimental

General: All ^{1}H and ^{13}C NMR spectra were recorded on JEOL Delta-500 or Lambda-500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) spectrometer. High-resolution mass spectra (HRMS) were measured on JEOL JMS-T100 LP spectrometer. Compound **1a** and (*S*)-*tert*-butyl 2-((4-methyl-*N*-(prop-2-yn-1-yl)phenyl-sulfonamido)(*p*-tolyl)methyl)acrylate **1d** were prepared by the reported methods.[9,12] All reactions in this paper were performed under a nitrogen atmosphere unless otherwise mentioned. Other compounds were purchased from Aldrich Co. Ltd. and were used without further purification.

Preparation of (*S*)-3-(*N*-*p*-tosyl-*N*-propargyl)amino-3-phenyl-2-methylene-1-(*tert*-butyldimethylsilyl)oxypropane 1b: Compound **1a** (986.3 mg, 2.32 mmol) was solved in MeOH (30 mL) and $SOCl_2$ (0.3 mL, 4.64 mmol) was added to the solution at 0 °C. The reaction mixture was heated to refluxing temperature for 13 h. The reaction mixture was concentrated in vacuo and the residue was subjected to flash chromatography (silica gel, hexane-EtOAc 10:1 then 7:1 v/v) to give methyl ester in 88% yield (781.3 mg, 2.04 mmol). White solid, mp 82.5 - 83.5 ºC, $[\alpha]_D$ +146.3 (c 1.07, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.06 – 7.00 (m, 2H), 6.49 (d, J = 1.3 Hz, 1H), 6.12 (s, 1H), 5.98 (d, J = 1.8 Hz, 1H), 4.09 (dd, J = 18.4, 2.5 Hz, 1H), 3.81 (dd, J = 18.4, 2.5 Hz, 1H), 3.59 (s, 3H), 2.43 (s, 3H), 1.99 (t, J = 2.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 143.6, 138.9, 137.4, 136.3, 129.5 (2C), 128.7 (2C), 128.7 (2C), 128.3, 127.8 (2C), 79.2, 72.5, 61.9, 52.1, 35.2, 21.7; HRMS (ESI-TOF): calcd for $C_{21}H_{21}NNaO_4S$ 406.1079 [M + Na$^+$], found 406.1089.

Methyl ester (715.0 mg, 1.87 mmol) was dissolved in dry toluene (40 mL) and DIBAL-H (1.0 M in toluene, 5.0 mL, 5 mmol) was added to the resulting solution at -78 ºC. The reaction mixture was stirred at the same temperature for 2.5 h, then warmed to 0 ºC. The reaction was quenched by adding saturated aqueous solution of Rochelle salt (15 mL). The

reaction mixture was then extracted with ether (4 × 20 mL). The organic phase was combined, washed with brine (20 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash chromatography (silica gel, hexane-EtOAc 10:1 then 2:1 v/v) to give corresponding alcohol in 57% yield (376.2 mg, 1.06 mmol). Colorless oil, $[\alpha]_D$ +55.9 (c 1.03, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.18 (m, 5H), 7.04 (dd, *J* = 6.3, 3.2 Hz, 2H), 5.73 (s, 1H), 5.42 (s, 1H), 5.05 (s, 1H), 4.13 (dd, *J* = 18.3, 2.5 Hz, 1H), 4.07 (d, *J* = 13.8 Hz, 1H), 4.02 – 3.94 (m, 2H), 2.47 (s, 1H), 2.37 (s, 3H), 2.03 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 143.7, 137.2, 136.1, 129.5 (2C), 128.8 (2C), 128.5 (2C), 128.0, 127.7 (2C), 116.8, 79.3, 72.4, 64.5, 62.4, 34.7, 21.6; HRMS (ESI-TOF): calcd for $C_{20}H_{21}NNaO_3S$ 378.1140 [M + Na^+], found 378.1148.

Alcohol (148.3 mg, 0.42 mmol) was dissolved in dry CH_2Cl_2 (20 mL), and imidazole (72.1 mg, 1.04 mmol) and TBSCl (83.1 mg, 0.55 mmol) in CH_2Cl_2 (5 mL) were added to the solution. The reaction mixture was stirred at room temperature for 2 days. Saturated $NaHCO_3$ aq (10 mL) and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was combined, washed with brine (20 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash chromatography (silica gel, hexane-EtOAc 15:1 then 10:1 v/v) to give **1b** in 89% yield (174.7 mg, 0.37 mmol). Colorless oil, $[\alpha]_D$ +48.5 (c 1.04, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.22 (m, 5H), 7.15 (dd, *J* = 12.6, 3.3 Hz, 2H), 5.74 (s, 1H), 5.44 (t, *J* = 1.2 Hz, 1H), 5.06 (t, *J* = 1.3 Hz, 1H), 4.21 (dd, *J* = 18.3, 2.5 Hz, 1H), 4.01 (dd, *J* = 18.3, 2.5 Hz, 1H), 3.99 – 3.97 (m, 2H), 2.43 (s, 3H), 2.02 (t, *J* = 2.4 Hz, 1H), 0.90 (s, 9H), 0.01 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 143.4, 137.6, 136.6, 129.3 (2C), 129.0 (2C), 128.4 (2C), 127.9, 127.8 (2C), 115.4, 79.3, 72.2, 64.7, 62.5, 34.7, 25.9, 21.6 (3C), 18.3, -5.4, -5.4; HRMS (ESI-TOF): calcd for $C_{26}H_{35}NNaO_3SSi$ 492.2005 [M + Na^+], found 492.2016.

Preparation of methyl (*S*)-3-(*N*-*p*-tosyl-*N*-propargyl)amino-3-phenyl-2-methylenepropionate 1c: Compound **1d** (413.3 mg, 0.94 mmol) was solved in MeOH (30 mL) and $SOCl_2$ (0.14 mL, 1.88 mmol) was added to the solution at 0 °C. The reaction mixture was heated to refluxing temperature overnight. The reaction mixture was concentrated in vacuo and the residue was subjected to flash chromatography (silica gel, hexane-EtOAc 20:1, 10:1 then 8:1 v/v) to give methyl ester in 82% yield (307.1 mg, 0.77 mmol).

Pale yellow oil, $[\alpha]_D$ +128.2 (c 1.03, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.48 (d, *J* = 1.1 Hz, 1H), 6.08 (s, 1H), 6.03 (d, *J* = 1.7 Hz, 1H), 4.09 (dd, *J* = 18.3, 2.5 Hz, 1H), 3.75 (dd, *J* = 18.3, 2.5 Hz, 1H), 3.60 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H), 2.02 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 143.6, 139.0, 138.1, 137.4, 133.1, 129.5, 129.4, 128.6, 128.3, 127.7, 79.4, 72.6, 61.8, 52.1, 35.1, 21.6, 21.2; HRMS (ESI-TOF): calcd for $C_{22}H_{23}NNaO_3S$ 420.1239 [M + Na^+], found 420.1246.

Radical cascade reaction of compound 1b: Compound **1b** (215.6 mg, 0.46 mmol) was dissolved toluene (60 mL) and Et_3B (1.0 M in toluene, 0.70 mL, 0.70 mmol) was added. The solution was stirred under air atmosphere for 1 h. Additional Et_3B (0.46 mL) was added since starting material **1b** was detected in TLC analysis, and the reaction solution was stirred additional 3 h. The reaction mixture was concentrated in vacul and the residue was subjected to flash chromatography (silica gel, hexane-EtOAc 50:1) to give **3b** in 17% yield (54.3 mg, 0.07 mmol). Identification of the compounds was confirmed by comparison of spectra of the compound **3b** prepared from corresponding alcohol.

(3*S*,3a*S*)-*tert*-butyl 5,5-dibutyl-3-phenyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-*c*]- pyrrole-3a-carboxylate (301.2 mg, 0.51 mmol), which was prepared in the reported method,[11] was dissolved in CH_2Cl_2 (20 mL) and TBSOTf (202.7 mg, 0.77 mmol) and 2,6-lutidine (0.09 mL, 0.77 mmol) were added to the solution. The reaction mixture was stirred for 24 h at room temperature. Water (10 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was combined, washed with brine (10 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash chromatography (silica gel, hexane-EtOAc 15:1 then 5:1 v/v) to give **3b** in 100% yield (360.3 mg, 0.51 mmol). Colorless oil, $[\alpha]_D$ –7.0 (c 1.00, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.12 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.83 (m, 2H), 6.40 (s, 1H, $J^{119}Sn–^1H$ = 109.2 Hz), 5.09 (s, 1H), 4.16 (dd, *J* = 14.0, 2.2 Hz, 1H), 4.08 (dd, *J* = 13.9, 1.5 Hz, 1H), 3.22 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.86 (d, *J* = 9.5 Hz, 1H), 2.34 (s, 3H), 1.52 – 1.43 (m, 2H), 1.30 – 1.06 (m, 8H), 1.04 – 0.97 (m, 2H), 0.95 (s, 9H), 0.85 (t, *J* = 7.3 Hz, 3H), 0.81 – 0.84 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.03 (s, 3H), 0.02 (s, 3H), -0.02 (dd, *J* = 13.0, 2.5 Hz, 1H, $J^{119}Sn–^1H$ = 57.4 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7 ($J^{119}Sn–^{13}C$ = 61.0 Hz), 142.7, 141.4, 136.2, 129.3 (2C), 128.1 (br, 3C), 127.2 (2C), 127.0 (2C), 126.1 ($J^{117}Sn–^{13}C$ = 328.9 Hz, $J^{119}Sn–^{13}C$ = 343.8 Hz), 68.6, 67.6 ($J^{119}Sn–^{13}C$ = 38.2 Hz), 65.9 ($J^{119}Sn–^{13}C$ = 17.7 Hz), 50.6 ($J^{119}Sn–^{13}C$ = 61.8 Hz), 29.3 ($J^{119}Sn–^{13}C$ = 21.9 Hz), 28.8 ($J^{119}Sn–^{13}C$ = 22.5 Hz), 27.2 ($J^{119}Sn–^{13}C$ = 55.8 Hz), 27.0 ($J^{119}Sn–^{13}C$ = 55.4 Hz), 26.1 (3C), 21.6, 18.4 ($J^{119}Sn–^{13}C$ = 65.6 Hz), 13.7 (2C), 13.4 ($J^{117}Sn–^{13}C$ = 315.3 Hz, $J^{119}Sn–^{13}C$ = 331.4 Hz), 12.1, 11.9 ($J^{117}Sn–^{13}C$ = 325.4 Hz, $J^{119}Sn–^{13}C$ = 339.3 Hz), -5.2, -5.3; HRMS (ESI-TOF): calcd for $C_{34}H_{53}NNaO_3SSi^{120}Sn$ 726.2435 [M + Na^+], found 726.2439.

Preparation of (3*S,3a*S**)-*tert*-butyl 5,5-dibutyl-3-phenyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-*c*]pyrrole-3a-carboxylate 3a and (2*S**,3*S**)-*tert*-butyl 4-methylene-2-phenyl-1-tosyl-3-((tributylstannyl)methyl)pyrrolidine-3-carboxylate 2a:** Compound **1a** (racemic, 851.0 mg, 2.0 mmol) was added to Bu_3SnH (0.65 mL, 2.4 mmol), and AIBN (33 mg, 0.2 mmol) was added. The reaction mixture was heated at 110 ºC for 2.5 h. Then the mixture was subjected to flash chromatography (silica gel, hexane then hexane-EtOAc 30:1 v/v) to give **2a** in 44% yield (633.2 mg, 0.88 mmol) and **3a** in 38% yield (497.4 mg, 0.75 mmol).

Compound **2a**: Colorless oil, ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.07 (m, 5H), 6.98 – 6.90 (m, 4H), 5.22 (s, 1H), 5.19 (t, *J* = 1.8 Hz, 1H), 5.12 (dd, *J* = 2.6, 1.5 Hz, 1H), 4.42 (dt, *J* = 12.9, 2.4 Hz, 1H), 3.96 (dt, *J* = 13.1, 1.5 Hz, 1H), 2.29 (s, 3H), 1.40 – 1.13 (m, 12H), 0.98 (d, *J* = 12.8 Hz, 1H), 0.82 (t, *J* = 7.1 Hz, 9H), 0.75 – 0.59 (m, 6H), 0.35 (d, *J* = 12.8 Hz, 1H, $J^{119}Sn–^1H$ = 44.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 149.8, 142.4, 138.5, 136.8, 129.0 (2C), 128.6 (br, 2C), 128.2 (2C), 127.8, 126.9 (2C), 109.4, 82.2, 70.4, 61.4, 52.1, 29.1 (3C), 27.9 (3C), 27.5 (3C), 21.5, 13.9, 13.8 (3C), 11.0 (3C, $J^{119}Sn–^{13}C$ = 330.1 Hz); HRMS (ESI-TOF): calcd for $C_{36}H_{55}NNaO_4S^{120}Sn$ 740.2772 [M + Na^+], found 740.2761.

Compound **3a**: Colorless oil, ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 3H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.94 (s, 2H), 6.56 (s, 1H, $J^{119}Sn–^1H$ = 115.3 Hz), 5.44 (s, 1H), 4.15 (d, *J* = 12.9 Hz, 1H), 4.01 (d, *J* = 12.9 Hz,

1H), 2.32 (s, 3H), 1.53 – 1.43 (m, 2H), 1.37 (s, 9H), 1.29 – 1.18 (m, 4H), 1.29 – 1.18 (m, 6H), 0.90 (d, J = 13.4 Hz, 1H), 0.84 (t, J = 7.4 Hz, 3H), 0.73 (t, J = 6.8 Hz, 3H), 0.22 (d, J = 13.2 Hz, 1H, J^{119}Sn–^{1}H = 53.4 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 158.3, 142.6, 139.6, 136.5, 129.1 (2C), 128.1 (br, 3C), 128.0 (2C), 127.5, 127.3 (2C), 81.6, 69.7, 68.6, 50.6, 29.0, 28.7, 27.8 (4C), 27.1, 27.0, 21.5, 13.7, 13.7, 13.1, 12.9, 12.3; HRMS (ESI-TOF): calcd for $C_{32}H_{45}NNaO_4S^{120}Sn$ 682.1989 [M + Na^+], found 682.1996.

General procedure for kinetic estimation: typical procedure: Compound **1a** (425.1 mg, 1 mmol) and Bu_3SnH (1.4552 g, 5.0 mmol) was dissolved in benzene using a measuring flask (10 mL) to prepare a reaction solution at 0.5 M concentration of Bu_3SnH. A 2 mL of the solution was transferred to a 10 mL of flask using a measuring pipette, and V70 (6.3 mg, 0.02 mmol) was added to the mixture. The reaction mixture was heated at 30 ºC for 1 h. After the reaction finished, anisole (7.2 mg, 0.067 mmol) was added and compound 2a and 3a were quantified using integrations of 0.54 ppm (1 H for **3a**), 5.12 ppm (1H for **2a**), and 3.74 ppm (3 H for anisole) in 1H NMR spectra.

Preparation of dibutyldiphenyltin 4b: Bromobenzene (8 mL,66 mmol) was added to a suspension of magnesium metal (1.96 g, 80 mmol) in THF (100 mL) over 1 h. Dibutyltin dichloride (9.10 g, 19 mmol) in THF (30 mL) was added to the solution of PhMgBr at 0 °C and the reaction mixture was stirred for 1 h. Saturated NH_4Cl aq (30 mL) was added to the reaction mixture and the resulting solution was extracted with ether (3 × 30 mL). Organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator. Obtained crude product was purified through flash chromatography (silica gel, hexane) to give dibutyldiphenyltin **4b** in 82% yield (8.76 g, 24 mmol). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 4H), 7.30 – 7.23 (m, 6H), 1.59 – 1.50 (m, 4H), 1.33 – 1.24 (m, 4H), 1.24 – 1.17 (m, 4H), 0.80 (t, J = 7.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7 (2C, J^{119}Sn–^{13}C = 175.7 Hz), 137.0 (4C, J^{119}Sn–^{13}C = 37.4 Hz), 128.6 (2C, J^{119}Sn–^{13}C = 446.9 Hz), 128.4 (4C, J^{119}Sn–^{13}C = 40.6 Hz), 29.0 (2C, J^{119}Sn–^{13}C = 21.4 Hz), 27.4 (2C, J^{119}Sn–^{13}C = 61.1 Hz), 13.7 (2C), 10.3 (2C, J^{119}Sn–^{13}C = 368.0 Hz); HRMS (ESI-TOF): calcd for $C_{20}H_{28}Na^{120}Sn$ 411.1112 [M + Na^+], found 411.1110.

Preparation of dibutylphenyltin chloride 4c: Dibutyldiphenyl tin (**4b**, 8.511 g, 22.0 mmol) and dibutyltin dichloride (13.35 g, 43.9 mmol) was mixted and heated at 150 °Cfor 12 h. The mixture was distilled under reduced pressure by kugelrohr (280 °C/0.1 mmHg) to give dibutylphenyltin chloride **4c** in 58% yield 813.19 g, 28.2 mmol). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.54 (m, 2H), 7.54 – 7.35 (m, 3H), 2.06 – 1.66 (m, 4H), 1.66 – 1.22 (m, 8H), 0.97 (t, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8 (2C, J^{119}Sn–^{13}C = 466.1 Hz), 135.6 (2C, J^{119}Sn–^{13}C = 41.2 Hz), 129.8 (2C, J^{119}Sn–^{13}C = 11.7 Hz), 128.9 (2C, J^{119}Sn–^{13}C = 53.9 Hz), 27.9 (2C, J^{119}Sn–^{13}C = 27.8 Hz), 26.8 (2C, J^{119}Sn–^{13}C = 67.4 Hz), 17.7 (2C, J^{117}Sn–^{13}C = 361.8 Hz, J^{119}Sn–^{13}C = 377.4 Hz), 13.6 (2C); HRMS (ESI-TOF): calcd for $C_{14}H_{24}Cl^{120}Sn$ 347. 0589 [M + H^+], found 347. 0580.

Preparation of dibutylphenyltin hydride 4a: Dibutylphenyltin chloride (**4c**, 12.4 g, 35.9 mmol) was added to a mixture of $NaBH_4$ (6.81 g, 180 mmol) in THF-water (100mL-30 mL) and the reaction mixture was stirred for 3 h at room temperature. Water (30 mL) was added to the reaction mixture and the resulting solution was extracted with ether (3 × 30 mL). Organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by roary evaporator. Obtained crude product was distilled by kugelrohr (230 °C/0.1 mmHg) to give dibutylphenyltin hydride **4a** in 39% yield (4.36 g, 14.0 mmol). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.6, 2.2 Hz, J^{119}Sn–^{1}H = 51.3 Hz, 2H), 7.46 – 7.37 (m, 3H), 5.29 (s, J^{119}Sn–^{1}H = 177.8 Hz, 1H), 1.76 – 1.66 (m, J^{119}Sn–^{1}H = 78.6 Hz , 4H), 1.52 (t, J = 6.9 Hz, J^{119}Sn–^{1}H = 50.4 Hz 4H), 1.39 (h, J = 6.9 Hz, J^{119}Sn–^{1}H = 83.2 Hz, 4H), 0.92 (t, J = 7.3 Hz, 6H);^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9 (J^{117}Sn–^{13}C = 447.9 Hz, J^{119}Sn–^{13}C = 473.2 Hz), 135.6 (2C, J^{119}Sn–^{13}C = 46.9 Hz), 129.8 (J^{119}Sn–^{13}C = 12.4 Hz), 128.9 (2C, J^{119}Sn–^{13}C = 53.3 Hz), 27.9 (2C, J^{119}Sn–^{13}C = 25.0 Hz), 27.0 (2C, J^{119}Sn–^{13}C = 68.1 Hz), 17.9 (2C, J^{117}Sn–^{13}C = 359.4 Hz, J^{119}Sn–^{13}C = 381.2 Hz), 13.8 (2C); HRMS (ESI-TOF): calcd for $C_{14}H_{25}{}^{120}Sn$ 313.0978 [M + H^+], found 313.0974.

The reaction of compound 1c with Bu_2PhSnH (4a) under 10^{-2} M concentration: A solution of Et_3B (1 M in toluene, 0.24 mL) was added to a solution of compound **1c** (79.7 mg, 0.201 mmol) and $PhBu_2SnH$ (**4a**, 76.5 mg, 0.246 mmol) in toluene (20 mL), and the reaction mixture was stirred at 30 °C for 30 min. The reaction mixture was concentrated by rotary evaporator, and residue was subjected to flash chromatography (siloca gel, hexane, then hexane-EtOAc 25:2 to 10:1 v/v) to give **5c** in 12% yield (16.7 mg, 0.024 mmol) and **3c** in 68% yield (89.2 mg, 0.137 mmol). Diastereomeric ratios for **3c** and **5c** were determined to be 50:50 and 69:31 by HPLC analyses, respectively. The diastereomeric mixture of these compounds were separated by further carful flash chromatography.

(*3S,3aS,5S*)-methyl 5-butyl-5-phenyl-3-(*p*-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (3c-A): white solid; mp 102.0 – 103.0 °C; $[\alpha]_D$ – 36.8 (*c* 0.37, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.31 – 7.27 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 6.69 (s, J^{119}Sn–^{1}H = 120.2 Hz, 1H), 5.43 (s, 1H), 4.21 (dd, J = 13.4, 1.9 Hz, 1H), 4.17 (dd, J = 13.3, 1.2 Hz, 1H), 3.34 (s, 3H), 2.37 (s, 3H), 2.30 (s, 3H), 1.31 – 1.11 (m, 4H), 1.08 (d, J = 13.6 Hz, 1H), 1.06 – 0.97 (m, 2H), 0.76 (t, J = 7.1 Hz, 3H), 0.45 (d, J = 13.5 Hz, J^{119}Sn–^{1}H = 48.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 159.6, 142.8, 140.3, 137.4, 136.5, 136.4, 136.2 (2C), 129.2 (2C), 129.0 (2C), 128.9, 128.4 (2C), 127.9(2C), 127.6, 127.5 (2C), 68.8, 68.6, 52.6, 50.8, 28.5, 27.0, 21.5, 21.2, 14.0, 13.6, 12.3; HRMS (ESI-TOF): calcd for $C_{32}H_{37}NNaO_4S^{120}Sn$ 674.1363 [M + Na^+], found 674.1375.

(*3S,3aS,5R*)-methyl 5-butyl-5-phenyl-3-(*p*-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (3c-B): Colorless oil; $[\alpha]_D$ +70.7 (*c* 0.36, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.20 (t, J = 7.1 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H),

7.07 (d, J = 7.1 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.94 (d, J = 7.5 Hz, 2H), 6.65 (s, J^{119}Sn–^{1}H = 116.8 Hz, 1H), 5.49 (s, 1H), 4.19 (d, J = 13.7 Hz, 1H), 4.16 (d, J = 13.6 Hz, 1H), 3.50 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 1.66 – 1.53 (m, 2H), 1.43 – 1.23 (m, 4H), 1.12 (d, J = 13.3 Hz, 1H), 0.87 (t, J = 7.3 Hz, 3H), 0.49 (d, J = 13.3 Hz, J^{119}Sn–^{1}H = 60.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 159.0, 142.8, 140.8, 137.4, 136.7, 136.3, 136.1 (2C), 129.2 (2C), 129.0 (2C), 128.9, 128.4, 128.2 (2C), 128.0 (2C), 127.5 (2C), 68.6, 68.3, 52.9, 50.6, 28.9, 27.1, 21.5, 21.2, 15.6, 13.7, 12.3; HRMS (ESI-TOF): calcd for $C_{32}H_{38}NO_4S^{120}Sn$ 652.1544 [M + H^+], found 652.1542.

(*2R*,*3S*,*E*)-methyl 5-((dibutyl(phenyl)stannyl)methylene)-2-(*p*-tolyl)-1-tosylpiperidine-3-carboxylate *E*-5c: Colorless oil; $[\alpha]_D$ +30.3 (*c* 0.34, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.19 (d, J = 7.4 Hz, 4H), 7.07 (d, J = 8.0 Hz, 2H), 5.80 (s, J^{119}Sn–^{1}H = 65.9 Hz, 1H), 5.62 (d, J = 5.1 Hz, 1H), 4.27 (d, J = 15.1 Hz, 1H), 3.66 (d, J = 15.1 Hz, 1H), 3.55 (s, 3H), 2.67 (t, J = 13.9 Hz, 1H), 2.51 (dt, J = 13.2, 4.4 Hz, 1H), 2.36 (s, 3H), 2.33 – 2.38 (m, 1 H), 2.30 (s, 3H), 1.51 – 1.39 (m, 4H), 1.33 – 1.23 (m, 6H), 1.12 – 0.98 (m, 2H), 0.94 – 0.80 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0 (J^{119}Sn–^{1}H = 371.0 Hz,), 148.7, 143.3, 140.8, 137.6, 137.5, 136.3 (2C), 133.6, 129.7 (2C), 129.3 (2C), 128.4, 128.3 (2C), 127.9 (2C), 127.5 (2C), 125.7, 55.9, 52.1, 50.9, 44.1, 32.1, 31.1, 29.0, 27.4, 27.3, 21.7, 21.1, 13.7, 13.6, 11.0, 10.9; HRMS (ESI-TOF): calcd for $C_{36}H_{47}NNaO_4S^{120}Sn$ 732.2146 [M + Na^+], found 732.2152.

(*2R*,*3S*,*Z*)-methyl 5-((dibutyl(phenyl)stannyl)methylene)-2-(*p*-tolyl)-1-tosylpiperidine-3-carboxylate *Z*-5c: Colorless oil; $[\alpha]_D$ –4.5 (*c* 0.27, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 2H), 7.37 – 7.30 (m, 5H), 7.05 (d, J = 8.1 Hz, 2H), 7.02 – 6.97 (m, 4H), 5.80 (s, J^{119}Sn–^{1}H = 60.8 Hz, 1H), 5.51 (d, J = 4.9 Hz, 1H), 4.17 (d, J = 14.8 Hz, 1H), 3.57 (d, J = 16.1 Hz, 1H), 3.55 (s, 3H), 2.85 (t, J = 14.5 Hz, 1H), 2.80 (dt, J = 12.9, 3.9 Hz, 1H), 2.59 (dd, J = 13.1, 3.4 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 1.66 – 1.15 (m, 12H), 0.93 – 0.85 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 148.7, 143.0, 141.0, 136.7 (2C), 135.5, 133.7, 129.4 (2C), 129.1 (2C), 128.9, 128.4, 128.4 (2C), 128.2 (2C), 127.4 (2C), 125.4, 56.1, 52.0, 49.1, 44.6, 33.5, 30.4, 29.8, 29.1, 27.4, 21.6, 21.1, 13.8, 13.8, 10.9, 10.8; HRMS (ESI-TOF): calcd for $C_{36}H_{47}NNaO_4S^{120}Sn$ 732.2146 [M + Na^+], found 732.2140.

The reaction of compound 1c with Bu_2PhSnH (4a) under no solvent conditions: A mixture of compound **1c** (75.0 mg, 18.9 mmol), $PhBu_2SnH$ (**4a**, 189.8 mg, 61.0 mmol), and V70 (6.9 mg, 0.022 mmol) was stirred at 30 °C for 1 h. The reaction mixture was subjected to flash chromatography (silica gel, hexane then hexane-EtOAc 30:1 to 5:1 v/v) to give **3c** in 10% yield (12.0 mg, 0.018 mmol) and **2c** in 57% yield (76.8 mg, 0.108 mmol). Diastereomeric ratio for **3c** was determined to be 50:50 by HPLC analyses.

(2S,3S)-methyl 3-((dibutyl(phenyl)stannyl)methyl)-4-methylene-2-(p-tolyl)-1-tosylpyrrolidine-3-carboxylate 2c: Colorless oil; $[\alpha]_D$ –8.9 (*c* 1.07, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.1 Hz, 2H), 7.25 (s, 5H), 7.11 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.9 Hz, 2H), 6.92 (d, J = 7.8 Hz, 2H), 5.27 (s, 1H), 5.16 (s, 1H), 5.10 (s, 1H), 4.33 (d, J = 13.1 Hz, 1H), 4.12 (d, J = 13.2 Hz, 1H), 3.37 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H), 1.48 – 1.19 (m, 8H), 1.16 (d, J = 13.1 Hz, 1H), 1.09 – 0.87 (m, 4H), 0.84 (t, J = 7.3 Hz, 3H), 0.82 (t, J = 6.8 Hz, 3H), 0.73 (d, J = 13.0 Hz, J^{119}Sn–^{1}H = 45.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 148.4, 142.8, 142.0, 137.8, 136.4 (2C), 136.0, 135.5, 129.2 (2C), 129.0 (2C), 128.4 (2C), 128.1, 127.9 (2C), 127.4 (2C), 110.4, 70.4, 60.5, 52.8, 52.2, 28.9, 28.9, 27.4 (2C), 21.6, 21.2, 15.2, 13.7, 13.7, 11.8, 11.4; HRMS (ESI-TOF): calcd for $C_{36}H_{47}NNaO_4S^{120}Sn$ 732.2146 [M + Na^+], found 732.2147.

Notes and references

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