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Nickel(0)-catalyzed disilylative and silastannylative cyclizations of 1,3-diene and tethered aldehyde

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Abstract

Nickel(0)-catalyzed bismetallative cyclization of 1,3-diene and a tethered aldehyde in the presence of $PhF_2SiSiMe_3$ or $Me_3SiSnBu_3$ gave the corresponding cyclized product having an allylsilyl or an allylstannyl unit in the side chain in good yields. The cyclized product obtained from the reaction in the presence of $Me_3SiSnBu_3$ had reactivity as an allylstannane derivative, and the coupling reaction with benzaldehyde proceeded in a diastereoselective manner. When the silastannylative cyclization was carried out in the presence of a chiral monodentate phosphine ligand, the cyclized product was produced as an optically active form with modest enantiomeric excess.

Keywords: Nickel; Silylstannane; Disilane; Bismetallation; Bismetallative cyclization; 1,3-Diene; Aldehyde

1. Introduction

Transition metal-catalyzed addition of homo- or hetero-bimetallic compounds to multiple bonds is of interest because new metal–carbon bonds are formed in the product and these bonds can be utilized in further transformations as an active bimetal functional group [1]. A generally accepted mechanism of this reaction is shown in Scheme 1. Oxidative addition of a bimetallic compound to a low-valent metal complex initially occurs to produce X–M–Y complex **I**. Then insertion of a multiple bond in the substrate into the X–M or Y–M bond proceeds to give the intermediate **II** or **II′**, and the bismetallated product **III** is produced from these intermediates through reductive elimination.

Bismetallative cyclization between two multiple bonds in a tether might be useful in synthetic organic chemistry, by which cyclic compounds having an active metal–carbon bond is produced. Indeed, the cyclization of various substrates (e.g., bis-dienes, diynes, enynes, allene-yne, allene-aldehyde or -ketone, bis-allene, and dienal) with a bimetallic reagent (e.g., M–M′, M, M′ = B, Si, Ge, and Sn) has been reported [2]. Recently, we have reported a nickel-catalyzed stereoselective cyclization of 1,3-dienes and tethered carbonyl groups in the presence of silane [3]. We speculated that if a bimetallic reagent is used instead of silane in this cyclization, a cyclized product **2** having an allylmetal unit, which could be used for the further carbon–carbon bond-forming reaction, would be produced (Scheme 2).

Herein, we report a nickel(0)-catalyzed bismetallative cyclization of 1,3-diene and a tethered aldehyde in the presence of disilanes or $Me_3SiSnBu_3$ [4].

2. Results and discussion

2.1. Bismetallative cyclization of 1,3-diene and a tethered aldehyde in the presence of disilanes

Initially, bismetallative cyclizations of **3** in the presence of various disilanes were investigated under optimized conditions for the above-mentioned cyclization in the presence of silane. However, the reaction did not proceed and no desired bismetallated product was obtained (Scheme 3).

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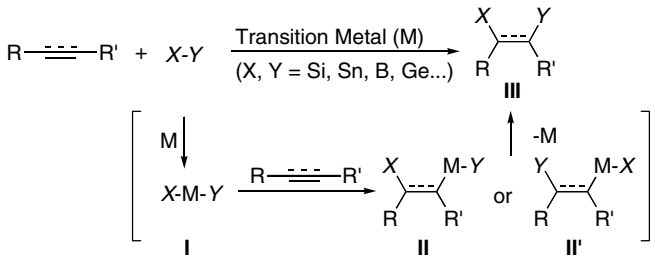
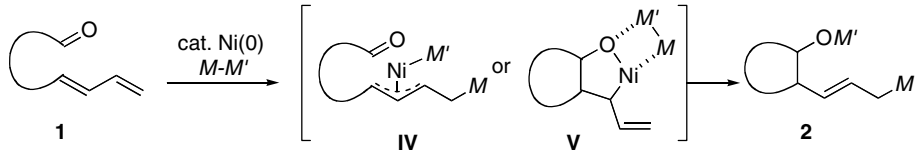


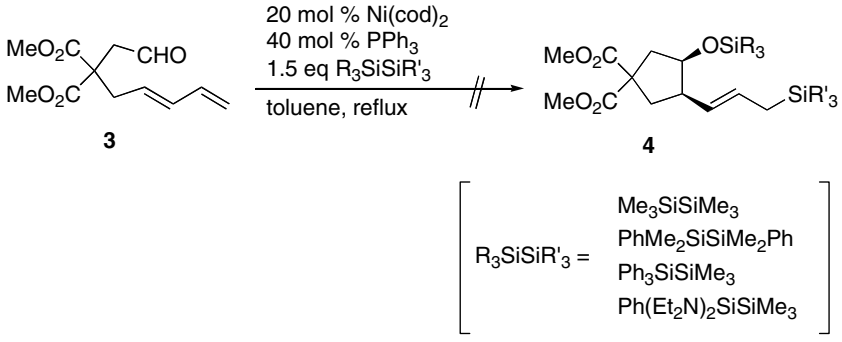
Scheme 1.

It is generally thought that oxidative addition of disilanes is the rate-determining step in bismetallation reactions, and these results indicate that the reactivity of disilanes used in the reaction toward the nickel(0) catalyst would be relatively low. It is known that disilanes such as $PhCl_2SiSiMe_3$ and $PhF_2SiSiMe_3$, in which two halogens are attached to one silicon atom, have higher reactivity in Pd(0)-catalyzed disilylation of enones [5] or alkynes [6]. Thus, we investigated the bismetallative cyclizations of **3** using these disilanes. The results of the bismetallative cyclization of **3** using $PhCl_2SiSiMe_3$ are summarized in Table 1.

The substrate **3** was treated with 20 mol% of $Ni(cod)_2$ and 40 mol% of PPh_3 in the presence of $PhCl_2SiSiMe_3$ (1.5 equiv.) and $^iPr_2NEt$ (4 equiv.) in toluene at 80 °C for 12 h. Then the reaction mixture was quenched with EtOH in the presence of Et_3N for substitution of chlorides on the silicon atom of the product for ethoxide (EtO), which was expected to facilitate the isolation of the products. After

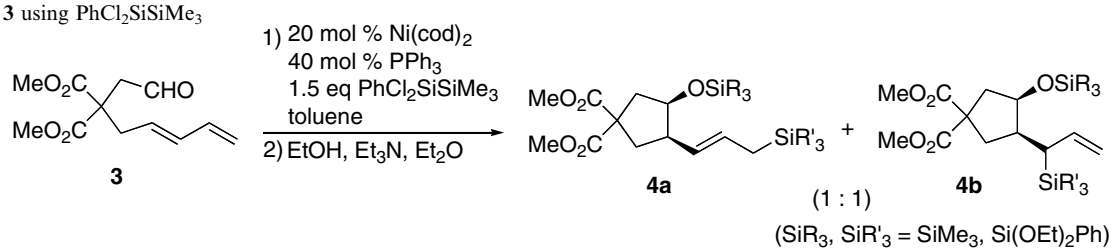


Scheme 2.



Scheme 3.

Table 1
Cyclization of **3** using $PhCl_2SiSiMe_3$



Run	Temp (°C)	Time (h)	Base (4 mol equiv.)	Yield (%)
1	80	12	$^iPr_2NEt$	38
2	80	10	Proton sponge	–
3	80	17	DABCO	–
4	80	18	$CaCO_3$	–

the usual work-up, products **4a** and **4b** (ratio of 1:1) having two silyl groups were obtained in a total yield of 38% as an inseparable mixture (Table 1, run 1). In order to confirm the structures of **4a** and **4b**, the mixture (**4a**:**4b** = 1:1) was treated with HF/CH_3CN, giving the known compounds **5** and **6** (ratio of 1:1) in total yield of 91% (Scheme 4).

It is well known that the cleavage of a Si–C bond in an allylsilane group under acidic conditions proceeds via the S_E2' pathway [7]. This means that **5** or **6** was produced from **4b** or **4a**, respectively, in a stereospecific manner, although the regiochemistry with respect to two silyl groups (i.e., Me_3Si– and $Ph(EtO)_2Si$–) in the products **4a** and **4b** could not be determined by this transformation. In the bismetallative cyclization of **3** using $PhCl_2SiSiMe_3$, both the presence and the choice of bases were very significant. Thus, the reaction under similar conditions in the absence of a base gave no desired products, and deposition of a nickel catalyst was observed. Among the various bases tested as shown in Table 1 (runs 2–4), only $^iPr_2NEt$ was effective in this reaction.

Next, the bismetallative cyclization of **3** using PhF_2Si-$SiMe_3$ was investigated (Scheme 5). The reaction of **3** with 20 mol% of $Ni(cod)_2$ and 40 mol% of PPh_3 in the presence of $PhF_2SiSiMe_3$ (1.5 equiv.) smoothly proceeded even at room temperature without any base and gave the cyclized product **4c** having only one silyl group (PhF_2Si–) at the allylic position in 45% yield. It is noteworthy that the bismetallative cyclization of **3** using $PhF_2SiSiMe_3$ proceeded in a completely regio- and stereoselective manner and the product **4c** was produced as the sole product, the stereochemistry of which was unequivocally determined by NOE experiments (Fig. 1).

Having obtained the product **4c** as the single isomer, we next investigated the reactivity of **4c** as an allylsilane derivative (Scheme 6). The cleavage of a Si–C bond in **4c** under acidic conditions [7] did not proceed and the expected product **6** was not produced, completely different from that of the above-mentioned **4a** or **4b** (see, Scheme 4). Similarly, it was found that the Si–C bond was also unreactive under the conditions of Tamao–Fleming oxidation [8]. These results indicate that the allylsilane unit in **4c** could not be utilized in further transformations.

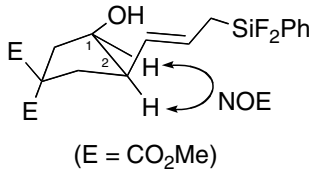
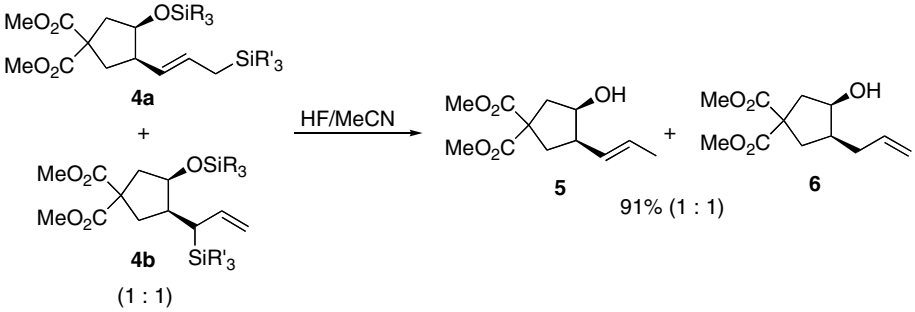


Fig. 1. Determination of stereochemistry of **4c**.

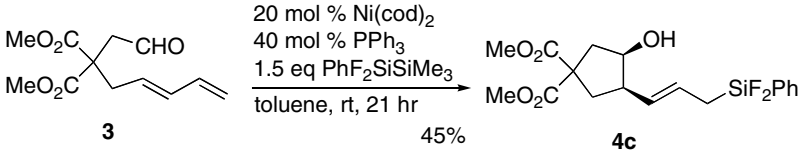
2.2. Bismetallative cyclization of 1,3-diene and a tethered aldehyde in the presence of $Me_3SiSnBu_3$

Next, we investigated bismetallative cyclization using $Me_3SiSnBu_3$ as a bimetallic reagent. Initially, the reaction of **3** was examined using 20 mol% of $Ni(cod)_2$ and 40 mol% of various phosphine ligands in the presence of $Me_3SiSnBu_3$ (1.5 equiv.) in toluene. The results are summarized in Table 2.

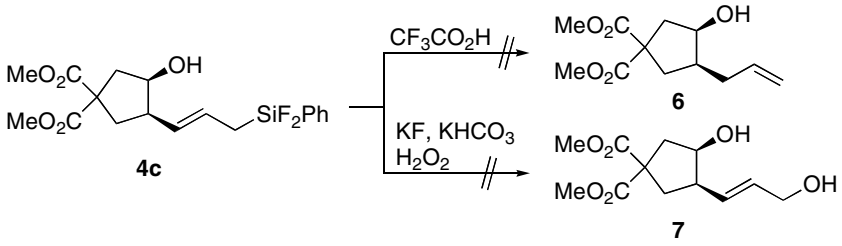
Although the use of PPh_3, $P(OEt)_3$, or PCy_3 as a ligand did not promote bismetallative cyclization (runs 1–3), the reaction using PMe_2Ph proceeded even at room temperature and gave the desilylated product (*E*)-**8b** instead of the expected product (*E*)-**8a** in 23% yield as a sole product along with the recovery of **3** in 30% yield (run 4). The stereochemistry of (*E*)-**8b** was determined by NOE experiments of **9**, which was derived from (*E*)-**8b** by a simple acetylation (Fig. 2).



Scheme 4.

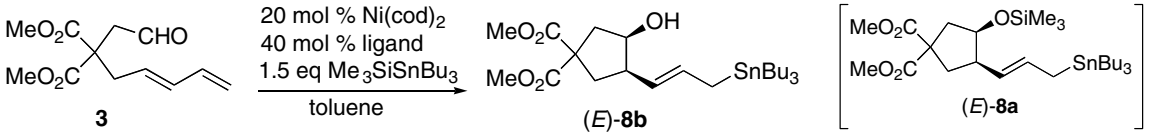


Scheme 5.



Scheme 6.

Table 2
Effect of ligand



Run	Ligand	Temp (°C)	Time (h)	Yield (%)
1	PPh_3	Reflux	18	–
2	$P(OEt)_3$	50	11	–
3	PCy_3	50	13	–
4	PMe_2Ph	rt	24	23[a]

[a] **3** was recovered in 30% yied.

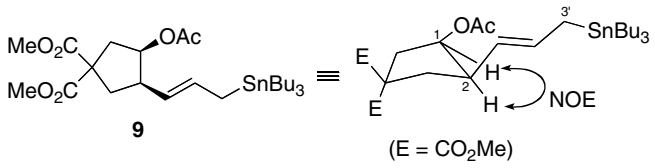


Fig. 2. Determination of stereochemistry of **9**.

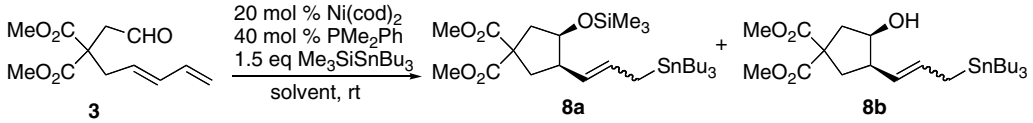
Encouraged by this result, we examined the effects of a solvent using PMe_2Ph as a ligand (Table 3).

The cyclization of **3** in THF provided a mixture of **8a** and **8b** in a ratio of 1:21 in 43% yield (Table 3, run 1). The reaction in a polar solvent gave a good result (runs 2 and 3), and the total yields of **8a** and **8b** reached 66% in the reaction in DMF. In all cases shown in Table 3, the products were obtained as isomers with respect to the olefinic geometry in the side chain, which differed from the above-mentioned reaction in toluene (see, Table 2, run 4). When the resulting crude product, which was obtained under the conditions shown in Table 3, run 3, was directly treated with CF_3CO_2H, a protodestannylation product **6** was obtained in 78% yield. This result suggests that the products **8a** and **8b** would be produced in a yield of over 78% in the reaction mixture and that the yield of **8a** and **8b** shown in Table 3, run 3 would be somewhat decreased due to a partial decomposition during purification and isolation.

Interestingly, the bismetallative cyclization in DMF proceeded even in the absence of a phosphine ligand, and only (*E*)-**8a** was obtained as the sole product (Scheme 7). On the other hand, the bismetallative cyclization in a non-polar solvent such as toluene did not proceed in the absence of a phosphine ligand, suggesting that the coordination of a polar solvent such as DMF would activate $Me_3SiSnBu_3$ and/or the catalyst.

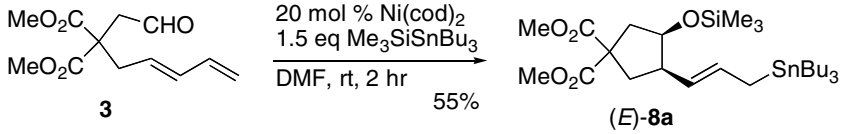
Next, cyclization of other substrates was examined. The cyclization of **10** using 20 mol% of $Ni(cod)_2$ and 40 mol%

Table 3
Nickel-catalyzed cyclization of **3** in the presence of $Me_3SiSnBu_3$



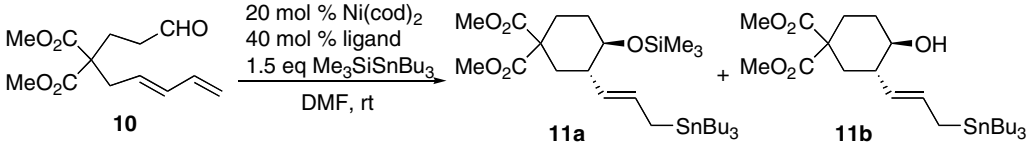
Run	Solvent	Time (h)	Yield (%) (**8a**+**8b**)	Ratio (**8a**/**8b**)	Ratio of *E*/*Z*	
					8a	**8b**
1	THF	18	43	1/21	–[a]	7.61
2	MECN	4	46	2.5/1	3.8/1	2.5/1
3	DMF	2	66	1.5/1	3.6/1	3.4/1

[a] Ratio of *E* to *Z* was not determined.



Scheme 7.

Table 4
Cyclization of **10** in the presence of $Me_3SiSnBu_3$



Run	Ligand	Time (h)	Yield (%) (**11a**+**11b**)	Ratio (**11a**/**11b**)
1	PMe_2Ph	5	51	1/7.5
2	–	6	31	1.8/1

of PMe_2Ph in the presence of $Me_3SiSnBu_3$ in DMF provided the cyclohexane derivatives **11a** and **11b** in a ratio of 1 to 7.5 in a total yield of 51% (Table 4, run 1).

The stereochemistry of **11a** or **11b** with respect to the side chains on the cyclohexane ring was determined to be an *anti*-orientation by the coupling constant between H_1 and H_2 protons in H^1 NMR, respectively (Fig. 3).

Interestingly, the absence of a ligand in the cyclization of **10** reversed the ratio of the products, and **11a** and **11b** were produced in a ratio of 1.8:1 in 31% yield (Table 4, run 2). It is also noteworthy that complete *E*-selectivity with respect to the olefinic geometry was observed in the reaction of the substrate **10**.

It was found that this bismetallative cyclization was applicable to construction of a pyrrolidine ring (Table 5). Thus, the reaction of **12** and $Me_3SiSnBu_3$ in the presence of $Ni(cod)_2$ and PMe_2Ph afforded pyrrolidine derivatives **13a** and **13b** in a ratio of 1:1.9 in 38% yield (run 1). On the other hand, the cyclization of **12** in the absence of PMe_2Ph gave (*E*)-**13a** in 18% yield as the sole product, the result of which is in accord with the results shown in Scheme 7 and Table 4.

In order to confirm the structure of the cyclized products, **13a** or **13b** was converted to **15** by treatment with CF_3CO_2H followed by catalytic hydrogenation with Pd/C. The spectral data of **15** derived from **13a** or **13b** was completely identical with that derived from the known compound **16** [3e], by which the stereochemistry of **13a** or **13b** with respect to the side chains on the pyrrolidine ring was determined to be a *syn*-orientation (Scheme 8).

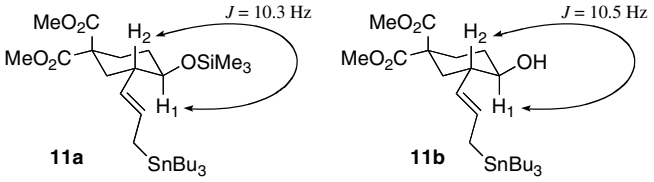
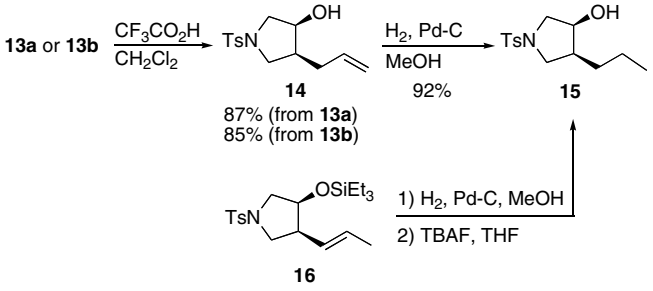
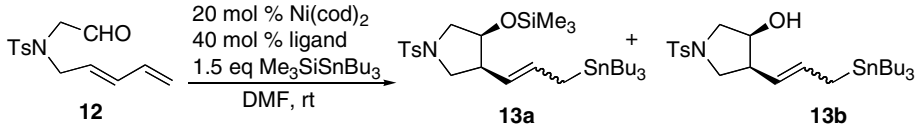


Fig. 3. Determination of stereochemistries of **11a** and **11b.**



Scheme 8.

Table 5
Cyclization of **12** in the presence of $Me_3SiSnBu_3$



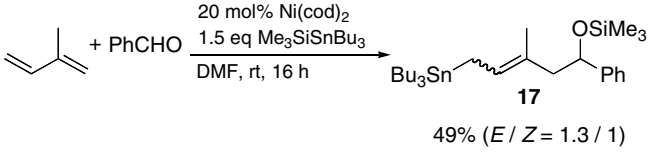
Run	Ligand	Time (h)	Yield (%) (**13a**+**13b**)	Ratio (**13a**/**13b**)	Ratio of *E*/*Z*	
					13a	**13b**
1	PMe_2Ph	2	38	1/1.9	3/1	2.4/1
2	–	2	18	>99/1	>99/1	–

Next, we tried an intermolecular nickel-catalyzed three-component coupling reaction (Scheme 9) [3m,3n,3o,3p,9]. When a DMF solution of isoprene, benzaldehyde (1 equiv.), $Me_3SiSnBu_3$ (1.5 equiv.), and $Ni(cod)_2$ (20 mol%) in the absence of a ligand was stirred at room temperature for 16 h, a coupling product **17** ($E/Z = 1.3/1$) was obtained in 49% yield. It is remarkable that the regioselective C–C bond-forming reaction between isoprene and benzaldehyde occurred to give a product **17** having an allylstannane unit, although the olefinic geometry could not be controlled.

2.3. Mechanistic consideration for bismetallative cyclization of 1,3-diene and a tethered aldehyde in the presence of $Me_3SiSnBu_3$

In the above-mentioned bismetallative cyclization of various substrates in the presence of $Me_3SiSnBu_3$, products having an allylstannane unit were always produced, and no products having an allylsilane unit were obtained. Thus, two plausible mechanisms consistent with these results are considered (Scheme 10).

One mechanism starts from oxidative addition of $Me_3SiSnBu_3$ to a zerovalent nickel catalyst (Scheme 10, path A). A silyl(stannyl)nickel complex **19** is initially formed by the oxidative addition. Then the insertion of the diene unit of **18** into a Ni–Sn bond of **19** would selectively occur to give π-allylnickel intermediate **20**, which reacts with the tethered aldehyde group to give **21**. The reductive elimination from **21** affords the cyclized product **22**, which has an allylstannane unit, accompanying regeneration of a zerovalent nickel complex. Alternatively, a mechanism involving a nickelacycle intermediate is also considered as shown in Scheme 10, path B. The nickelacycle intermediate **23** is formed by oxidative cycloaddition of 1,3-diene and aldehyde in **18** to a zerovalent nickel complex. Since silicon is harder than tin according to the HSAB principle [10], the σ-bond metathesis between the nickelacycle **23** and $Me_3SiSnBu_3$ would be expected to occur in such a direction as shown in **24**, giving the intermediate **25** [11]. Finally, the cyclized product **22** having an allylstannane unit would be produced via π-allylnickel intermediate **26**. Both mechanisms can account for the formation and distribution of the bismetallated products, but the real reaction pathway cannot be determined from the present experimental data.



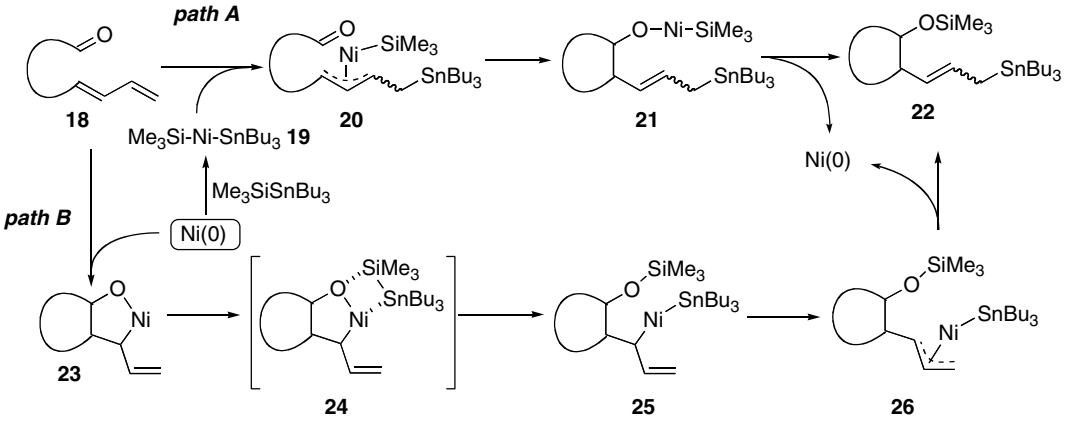
Scheme 9.

2.4. Catalytic asymmetric bismetallative cyclization in the presence of $Me_3SiSnBu_3$

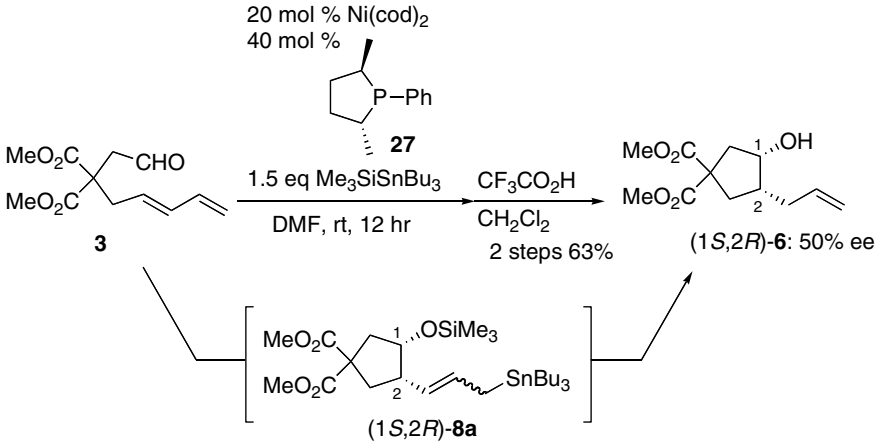
We have recently reported nickel-catalyzed asymmetric cyclization of 1,3-diene and tethered aldehyde in the presence of silane using chiral phosphorane **27** [3i,3k]. Thus, we tried the above-mentioned bismetallative cyclization of **3** in the presence of $Me_3SiSnBu_3$ using **27** (Scheme 11). The reaction of **3** using $Ni(cod)_2$ (20 mol%) and **27** [12] (40 mol%) in the presence of $Me_3SiSnBu_3$ (1.5 equiv.) in DMF at room temperature afforded the crude products **8a** as a mixture of isomers with respect to the olefin in the side chain. The mixture of the crude products was treated with CF_3CO_2H to give the corresponding protodestannylation product **6** in 63% (two steps). The enantiomeric excess and the absolute configuration of **6** were determined to be 50% ee and (1*S*,2*R*), respectively, according to the literature [3k]. This result indicates that (1*S*,2*R*)-**8a** having an allylstannane unit should be produced as an optically active form by the bismetallative cyclization.

2.5. Utilization of the bismetallative cyclized product as an allylstannane derivative

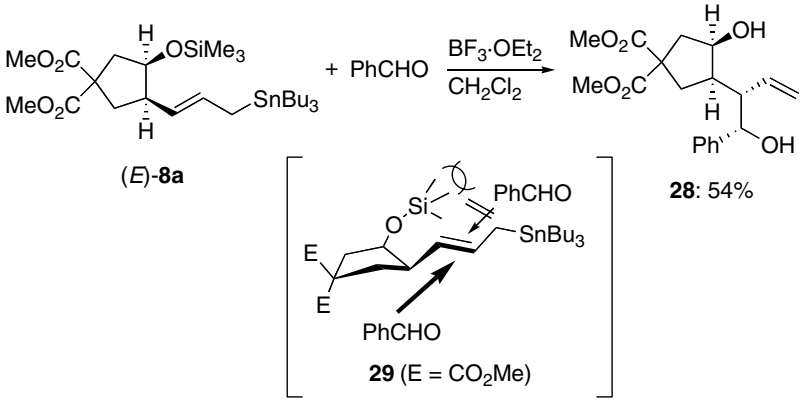
The products obtained by bismetallative cyclization in the presence of $Me_3SiSnBu_3$ have an allylstannyl group



Scheme 10.



Scheme 11.



Scheme 12.

that should be useful in further transformation [13]. Thus, the cyclized product (*E*)-**8a** was reacted with benzaldehyde to give the coupling product **28** as the sole product in 54% yield (Scheme 12).

The stereochemistry of **28** was tentatively assigned from analogy to the literature on reaction of allylstannane and aldehyde in the presence of Lewis acid [14]. It is thought that benzaldehyde attacks allylstannane from the opposite side with a trimethylsilyloxy group as in **29** due to steric repulsion, which might have controlled the stereochemistry of **28**.

2.6. Conclusion

Nickel(0)-catalyzed bismetallative cyclizations of 1,3-diene and a tethered aldehyde in the presence of disilanes or $Me_3SiSnBu_3$ were investigated. In the disilylative cyclization, the use of $PhCl_2SiSiMe_3$ or $PhF_2SiSiMe_3$, which has two halogens attached to one silicon atom, was effective to produce the cyclized product having an allylsilane unit. In the silastannylative cyclization, the reaction of various substrates proceeded in DMF at room temperature in the presence of PMe_2Ph as a ligand or without any ligand to give the corresponding cyclized product having an allylstannane unit in good yield. When the silastannylative cyclization was carried out in the presence of a chiral monodentate phosphine ligand, the cyclized product was produced as an optically active form with modest enantiomeric excess. The cyclized product obtained from the reaction in the presence of $Me_3SiSnBu_3$ had reactivity as an allylstannane derivative, and the coupling reaction with benzaldehyde proceeded in a diastereoselective manner.

3. Experimental

3.1. General

All manipulations were performed under an argon atmosphere unless otherwise mentioned. All solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh), and flash chromatography was performed silica gel 60 (Merck, 230–400 mesh) using the indicated solvent. ^1H (500 MHz) and ^{13}C (125 MHz) spectra were recorded on a Bruker ARX-500 spectrometers. ^1H and ^{13}C chemical shifts were referenced to internal Me_4Si or internal $CHCl_3$. Mass spectra were measured on a JEOL DX303, JEOL JMS-FAB mate, or JMS 700TZ mass spectrometer.

3.2. Disilylative cyclization of **3** in the presence of $PhCl_2SiSiMe_3$ using $^iPr_2NEt$ as a base (Table 1, run 1) and confirmation of the structure of the cyclized products (Scheme 4)

A solution of $Ni(cod)_2$ (15.4 mg, 0.056 mmol) and PPh_3 (29.4 mg, 0.112 mmol) in toluene (2.2 ml) was stirred at 0 °C for 20 min. To the mixture were added $^iPr_2NEt$ (0.2 ml, 1.15 mmol) and $PhCl_2SiSiMe_3$ (98 μl, 0422 mmol), and the mixture was stirred at 0 °C for 10 min. To the mixture was added a solution of **3** [3k] (67.4 mg, 0.28 mmol) in toluene (3.4 ml), and the mixture was stirred at 80 °C for 12 h. To the mixture were added Et_2O (2.8 ml), Et_3N (0.14 ml, 1.00 mmol), and EtOH (74 ml, 1.26 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1.5 h. The mixture was filtered through a pad of Celite®, and the filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt, 10:1) to give **4a** and **4b** (50.3 mg, 38%) as an inseparable mixture. To the mixture of **4a** and **4b** (13.0 mg, 25.5 mmol) in CH_3CN (1 ml) was added HF–CH_3CN solution (9:1, 1 ml) at 0 °C, and the mixture was stirred at room temperature for 1 h. To the mixture was added satd. $NaHCO_3$ aqueous solution, and the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/AcOEt, 3:1–2:1) to give **5** and **6** (5.6 mg, 91%, ratio of 1:1) as an inseparable mixture, whose spectral data were completely identical with those previously reported [3k].

3.3. (1R*,2R*)-2-[(E)-3-Difruorophenylsilylprop-1-enyl]-4,4-dimethoxycarbonyl-cyclopentan-1-ol (**4c**) (disilylative cyclization of **3** in the presence of PhF_2 $SiSiMe_3$ shown in Scheme 5)

A solution of $Ni(cod)_2$ (15.4 mg, 0.056 mmol) and PPh_3 (29.4 mg, 0.112 mmol) in toluene (2.2 ml) was stirred at 0 °C for 20 min. To the mixture was added $PhF_2SiSiMe_3$ (90 μl, 042 mmol), and the mixture was stirred for 10 min. To the mixture was added a solution of **3** (67.4 mg, 0.28 mmol) in toluene (3.4 ml), and the mixture was stirred at room temperature for 12 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt, 3:1–2:1) to give **4c** (48.1 mg, 45%) as a colorless oil. IR (neat) 3536, 1732, 1654, 1602, 1264 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.95 (br d, $J = 3.4$ Hz, 1H), 2.45 (dd, $J = 13.6$, 11.9 Hz, 1H), 2.48–2.54 (m, 2H), 2.57 (br d, $J = 14.5$ Hz, 1H), 2.74 (m, 1H), 3.46 (d, $J = 6.8$ Hz, 2H), 3.80 (s, 3H), 3.83 (s, 3H), 4.26 (br s, 1H), 5.76 (dd, $J = 15.6$, 7.0 Hz, 1H), 5.83 (dt, $J = 15.6$, 6.8 Hz, 1H), 7.23–7.30 (m, 3H), 7.34–7.39 (m, 2H); EI-LRMS m/z 241 (M^+-SiF_2Ph), 181, 174, 145, 113, 77, 59; EI-HRMS calcd for $C_{12}H_{17}O_5$ 241.1138 (M^+-SiF_2Ph), found 241.1159.

3.4. Typical procedure for bismetallative cyclization in the presence of $Me_3SiSnBu_3$ affording (1R*,2R*)-4,4-bismethoxycarbonyl-2-[(E)-3-tributylstannylprop-1-enyl]cyclopentan-1-ol ((E)-**8b**) (Table 2, run 4)

To a solution of $Ni(cod)_2$ (15.4 mg, 0.056 mmol) in toluene (2.2 ml) was added PMe_2Ph (16 μl, 0.11 mmol), and the mixture was stirred at 0 °C for 20 min. To the mixture was added $Me_3SiSnBu_3$ (0.15 ml, 0.43 mmol), and the mixture was stirred at the same temperature for 10 min. To the mixture was added a solution of **3** (67.4 mg, 0.28 mmol) in toluene (3.4 ml), and the mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (hexane/Et_2O, 10:1) to give (*E*)-**8b** (35.1 mg, 23%) as a colorless oil along with **3** (20.0 mg, 30%). IR (neat) 3854, 1736, 1654, 1264, 1170 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.80–0.92 (m, 15H), 1.25–1.33 (m, 6H), 1.38–1.55 (m, 6H), 1.73 (d, $J = 3.5$ Hz, 1H), 1.75 (ddd, $J = 8.6$ Hz, $^2J(^{119}Sn–H) = 29.4$ Hz, $^2J(^{117}Sn–H) = 29.4$ Hz, 2H), 2.29–2.39 (m, 2H), 2.40–2.48 (m, 2H), 2.60 (m, 1H), 3.71 (s, 3H), 3.74 (s, 3H), 4.09 (m, 1H), 5.25 (dd, $J = 15.3$, 7.3 Hz, 1H), 5.73 (dt, $J = 15.3$, 8.6 Hz, 1H); ^{13}C NMR (67.4 MHz, $CDCl_3$) δ 9.20, 13.5, 14.8, 27.3, 29.1 36.9, 42.3, 48.5, 52.8, 52.9, 58.4, 75.2, 221.4, 133.5, 173.1, 163.2; EI-LRMS m/z 532 (M^+), 475, 369, 291, 235, 177, 164, 105; EI-HRMS calcd for $C_{24}H_{44}O_5{}^{120}Sn$ 532.2210, found 532.2187.

3.5. (1R*,2R*)-1-Acetoxy-4,4-bismethoxycarbonyl-2-[(E)-3-tributylstannylprop-1-enyl]cyclopentane (**9**)

To a solution of (*E*)-**8b** (24.0 mg, 45 mmol) in pyridine (0.1 ml) was added Ac_2O (0.1 ml), and the mixture was stirred at room temperature for 11 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (hexane/Et_2O, 8:1, containing 1% Et_3N) to give **9** (23.3 mg, 90%) as a colorless oil. IR (neat) 1742, 1738, 1654, 1232 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.77–0.91 (m, 15H), 1.25-1.33 (m, 6H), 1.38–1.55 (m, 6H), 1.70 (ddd, $J = 8.6$ Hz, $^2J(^{119}Sn–H) = 29.5$ Hz, $^2J(^{117}Sn–H) = 29.5$ Hz, 2H), 2.00 (s, 3H), 2.31 (dd, $J = 13.4$, 12.2 Hz, 1 H), 2.38 (dd, $J = 13.4$, 7.5 Hz, 1H), 2.29–2.56 (m, 2H), 2.69 (m, 1H), 3.71 (s, 3H), 3.73 (s, 3H), 5.06 (m, 1H), 5.15 (dd, $J = 15.1$, 8.0 Hz, 1H), 5.77 (dt, $J = 15.1$, 8.6 Hz, 1H); EI-LRMS m/z 574 (M^+), 517, 291, 235, 179, 164, 105; EI-HRMS calcd for $C_{26}H_{46}O_6{}^{120}Sn$ 574.2316, found 574.2305.

3.6. (1R*,2R*)-4,4-Bismethoxycarbonyl-2-(3-tributylstannylprop-1-enyl)-1-trimethylsilyloxycyclopentane (**8a**) and (1R*,2R*)-4,4-bismethoxycarbonyl-2-(3-tributylstannylprop-1-enyl)cyclopentan-1-ol (**8b**) (Table 3, run 3)

Following the above-mentioned typical procedure for bismetallative cyclization in the presence of $Me_3SiSnBu_3$, a crude product, which was obtained from **3** (67.4 mg,

0.28 mmol), $Ni(cod)_2$ (15.4 mg, 0.056 mmol), PMe_2Ph (16 μl, 0.11 mmol), and $Me_3SiSnBu_3$ (0.15 ml, 0.43 mmol) in DMF (5.6 ml) at room temperature for 2 h, was purified by flash column chromatography on silica gel (hexane/Et_2O, 100:1–10:1, containing 1% Et_3N) to give an inseparable mixture of (*E*)-**8a** and (*Z*)-**8a** (67.6 mg, 40%, *E*:*Z*=3.6:1) along with (*E*)-**8b** (29.2 mg, 20%) and (*Z*)-**8b** (8.7 mg, 6%) as a colorless oil.

Compound (*E*)-**8a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.057 (s, 9H), 0.82–0.91 (m, 15H), 1.26–1.34 (m, 6H), 1.40–1.56 (m, 6H), 1.70 (ddd, $J = 8.5$ Hz, $^2J(^{119}Sn–H) = 29.6$ Hz, $^2J(^{117}Sn–H) = 29.6$ Hz, 2H), 2.15 (dd, $J = 12.3$, 6.7 Hz, 1H), 2.34 (dd, $J = 14.1$, 3.8 Hz, 1H), 2.39 (dd, $J = 14.1$, 1.4 Hz, 1H), 2.42 (m, 1H), 2.46 (m, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 4.05 (m, 1H), 5.23 (dd, $J = 15.2$, 7.9 Hz, 1H), 5.73 (dt, $J = 15.2$, 8.5 Hz, 1H).

Compound (*Z*)-**8a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.051 (s, 9H), 0.82–0.91 (m, 15H), 1.26–1.34 (m, 6H), 1.40–1.56 (m, 6H), 1.60–1.80 (m, 2H), 2.23 (dd, $J = 13.4$, 7.9 Hz, 1H), 2.32–2.51 (m, 3H), 2.77 (m, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 4.08 (m, 1H), 5.12 (dd, $J = 10.0$, 10.0 Hz, 1H), 5.57 (m, 1H).

Compound (*Z*)-**8b**: IR (neat) 3828, 1736, 1654, 1264 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84–0.91 (m, 15H), 1.25–1.34 (m, 6H), 1.40–1.54 (m, 6H), 1.74 (ddd, $J = 9.2$ Hz, $^2J(^{119}Sn–H) = 30.4$ Hz, $^2J(^{117}Sn–H) = 30.4$ Hz, 2H), 1.80 (br d, $J = 3.3$ Hz, 1H), 2.28 (dd, $J = 13.6$, 11.3 Hz, 1H), 2.43 (dd, $J = 13.6$, 8.1 Hz, 1H), 2.45–2.50 (m, 2 H), 2.86 (m, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 4.19 (m, 1H), 5.07 (dd, $J = 9.7$, 9.7 Hz, 1H), 5.76 (dt, $J = 9.7$, 9.2 Hz, 1H); EI-LRMS *m*/*z* 532 (M^+), 475, 291, 233, 177, 164, 105; EI-HRMS calcd for $C_{24}H_{44}O_5{}^{120}Sn$ 532.2210, found 532.2186.

3.7. Bismetallative cyclization of **3** in the presence of $Me_3SiSnBu_3$ without ligands (Scheme 7)

Following the above-mentioned typical procedure for bismetallative cyclization in the presence of $Me_3SiSnBu_3$, a crude product, which was obtained from **3** (67.4 mg, 0.28 mmol), $Ni(cod)_2$ (15.4 mg, 0.056 mmol), and $Me_3SiSnBu_3$ (0.15 ml, 0.43 mmol) in DMF (5.6 ml) at room temperature for 2 h, was purified by flash column chromatography on silica gel (hexane/Et_2O, 100:1–10:1, containing 1% Et_3N) to give (*E*)-**8a** (93.2 mg, 55%) as a colorless oil.

Spectral data of pure (*E*)-**8a**: IR (neat) 1738, 1654, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.057 (s, 9H), 0.82–0.91 (m, 15H), 1.26–1.34 (m, 6H), 1.40–1.56 (m, 6H), 1.70 (ddd, $J = 8.5$ Hz, $^2J(^{119}Sn–H) = 29.6$ Hz, $^2J(^{117}Sn–H) = 29.6$ Hz, 2H), 2.15 (dd, $J = 12.3$, 6.7 Hz, 1H), 2.34 (dd, $J = 14.1$, 3.8 Hz, 1H), 2.39 (dd, $J = 14.1$, 1.4 Hz, 1H), 2.42 (m, 1H), 2.46 (m, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 4.05 (m, 1H), 5.23 (dd, $J = 15.2$, 7.9 Hz, 1H), 5.73 (dt, $J = 15.2$, 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.01, 9.14, 13.7, 14.4, 27.3, 29.2, 38.2, 43.8, 49.2, 52.5, 52.7, 58.5, 76.1, 124.0, 130.7, 172.5, 173.8; EI-LRMS *m*/*z* 604 (M^+), 547, 483, 291, 235, 177, 164, 105; EI-HRMS calcd for $C_{27}H_{52}O_5Si^{120}Sn$ 604.2606, found 604.2628.

3.8. Bismetallative cyclization of **10** in the presence of $Me_3SiSnBu_3$ affording (1R*,2S*)-4,4-bismethoxycarbonyl-2-[(E)-3-tributylstannylprop-1-enyl]-2-trimethylsilyloxycyclohexane (**11a**) and (1R*,2S*)-4,4-bismethoxycarbonyl-2-[(E)-3-tributylstannylprop-1-enyl]cyclohexan-1-ol (**11b**) (Table 4, run 1)

Following the above-mentioned typical procedure for bismetallative cyclization in the presence of $Me_3SiSnBu_3$, a crude product, which was obtained from **10** (69.5 mg, 0.27 mmol), $Ni(cod)_2$ (15.2 mg, 0.055 mmol), PMe_2Ph (16 μl, 0.112 mmol), and $Me_3SiSnBu_3$ (0.145 ml, 0.42 mmol) in DMF (5.5 ml) at room temperature for 5 h, was purified by flash column chromatography on silica gel (hexane/Et_2O, 100:1–10:1, containing 1% Et_3N) to give **11a** (10.6 mg, 6%) and **11b** (67.0 mg, 45%) as a colorless oil, respectively.

Spectral data of **11a**: IR (neat) 1738, 1654, 1206, 1108 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.081 (s, 9H), 0.78–0.91 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H), 1.25–1.35 (m, 6H), 1.38–1.53 (m, 6H), 1.63–1.60 (m, 2H), 1.60–1.89 (m, 3H), 1.91 (br d, $J = 13.3$ Hz, 1H), 2.03 (m, 1H), 2.32–2.38 (m, 2H), 3.23 (ddd, $J = 10.3$, 10.3, 4.4 Hz, 1H), 3.68 (s, 3H), 3.73 (s, 3H), 5.08 (dd, $J = 15.7$, 7.4 Hz, 1H), 5.57 (dd, $J = 15.7$, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.42, 9.2, 13.7, 14.4, 27.5, 29.2, 30.0, 32.3, 36.4, 44.9, 52.4, 52.6, 54.7, 74.3, 127.2, 130.1; EI-LRMS *m*/*z* 618 (M^+), 547, 561, 327, 291, 178, 119; EI-HRMS calcd for $C_{28}H_{54}O_5Si^{120}Sn$ 618.2762, found 618.2791.

Spectral data of **11b**: IR (neat) 3566, 1736, 1654, 1206, 1104 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81–0.95 (m, 6H), 0.89 (t, $J = 7.1$ Hz, 9H), 1.25–1.36 (m, 6H), 1.40–1.61 (m, 8H), 1.65–1.83 (m, 3H), 1.94 (br s, 1H), 1.90–2.13 (m, 2H), 2.34 (br d, $J = 13.5$ Hz, 1H), 2.41 (br d, $J = 3.5$ Hz, 1H), 3.19 (ddd, $J = 10.5$, 10.5, 4.0 Hz, 1H), 3.69 (s, 3H), 3.75 (s, 3H), 4.97 (dd, $J = 15.2$, 9.0 Hz, 1H), 5.78 (dt, $J = 15.2$, 8.5 Hz, 1H); EI-LRMS *m*/*z* 546 (M^+), 489, 369, 291, 255, 238, 233, 177, 119; EI-HRMS calcd for $C_{25}H_{46}O_5{}^{120}Sn$ 546.2367, found 546.2387.

3.9. Bismetallative cyclization of **12** in the presence of $Me_3SiSnBu_3$ (Table 5, run 1)

Following the above-mentioned typical procedure for bismetallative cyclization in the presence of $Me_3SiSnBu_3$, a crude product, which was obtained from **12** (78.2 mg, 0.28 mmol), $Ni(cod)_2$ (15.4 mg, 0.056 mmol), PMe_2Ph (16 μl, 0.11 mmol), and $Me_3SiSnBu_3$ (0.15 ml, 0.43 mmol) in DMF (5.6 ml) at room temperature for 2 h, was purified by flash column chromatography on silica gel (hexane/Et_2O, 100:1–1:1, containing 1% Et_3N) to give an inseparable mixture of (*E*)- and (*Z*)-**13a** (27.6 mg, 6%) and an inseparable mixture of (*E*)- and (*Z*)-**13b** (40.0 mg, 13%).

^{1}H NMR peaks assignable to those of (*E*)-**13a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.063 (s, 9H), 0.76–0.91 (m, 6H), 0.89 (t, $J = 7.2$ Hz, 9H), 1.24–1.33 (m, 6H), 1.36–1.54 (m, 6H), 1.58–1.73 (m, 2H), 2.42 (s, 3H), 2.53 (m, 1H), 3.03 (dd, $J = 10.8$, 9.0 Hz, 1H), 3.18 (br d, $J = 11.1$ Hz, 1H), 3.40 (dd, $J = 10.8$, 8.3 Hz, 1H), 3.45 (dd, $J = 11.3$, 3.6 Hz, 1H), 3.99 (m, 1H), 5.02 (dd, $J = 15.3$, 8.4 Hz, 1H), 5.60 (dt, $J = 15.3$, 8.5 Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 2H).

^{1}H NMR peaks assignable to those of (*Z*)-**13a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.063 (s, 9H), 0.76–0.91 (m, 6H), 0.89 (t, $J = 7.2$ Hz, 9H), 1.24–1.33 (m, 6H), 1.36–1.54 (m, 6H), 1.58–1.73 (m, 2H), 2.44 (s, 3H), 2.95 (m, 1H), 3.03 (dd, $J = 11.0$, 1.6 Hz, 1H), 3.50–3.55 (m, 3H), 4.20 (m, 1H), 4.80 (dd, $J = 9.7$, 9.5 Hz, 1H), 5.81 (dt, $J = 9.7$, 9.6 Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 2H).

^{1}H NMR peaks assignable to those of (*E*)-**13b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80–0.92 (m, 6H), 0.89 (t, J =7.3 Hz, 9H), 1.23–1.33 (m, 6H), 1.35–1.52 (m, 6H), 1.60 (br s, 1H), 1.72 (ddd, $J = 8.6$ Hz, $^2J(^{119}\text{Sn–H}) = 29.4$, $^2J(^{117}\text{Sn–H}) = 29.4$ Hz, 2H), 2.43 (s, 3H), 2.67 (m, 1H), 3.10 (dd, $J = 9.9$, 9.9 Hz, 1H), 3.31 (br d, $J = 11.2$ Hz, 1H), 3.46 (dd, $J = 9.9$, 7.8 Hz, 1H), 3.51 (dd, $J = 11.2$, 4.3 Hz, 1H), 4.09 (m, 1H), 5.06 (dd, $J = 15.4$, 7.6 Hz, 1H), 5.71 (dt, $J = 15.4$, 8.6 Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 2H).

^{1}H NMR peaks assignable to those of (*Z*)-**13b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80–0.92 (m, 6H), 0.89 (t, J =7.3 Hz, 9H), 1.23–1.33 (m, 6H), 1.35–1.52 (m, 6H), 1.60 (br s, 1H), 1.69 (ddd, $J = 9.6$ Hz, $^2J(^{119}\text{Sn–H}) = 30.0$ Hz, $^2J(^{117}\text{Sn–H}) = 30.0$ Hz, 2H), 2.43 (s, 3H), 2.92 (m, 1H), 3.04 (dd, $J = 11.2$, 1.6 Hz, 1H), 3.30 (dd, $J = 11.3$, 1.6 Hz, 1H), 3.51 (m, 1H), 3.56 (dd, $J = 11.2$, 4.6 Hz, 1H), 4.18 (m, 1H), 4.87 (dd, $J = 9.7$, 9.7 Hz, 1H), 5.81 (dt, $J = 9.7$, 9.6 Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 2H).

*3.10. Bismetallative cyclization of **12** in the presence of $Me_3SiSnBu_3$ without ligands (Table 5, run 2) affording (3S*,4S*)-4-[(E)-3-tributylstannylprop-1-enyl]-2-trimethylsilyloxy-1-(p-toluenesulfonyl)pyrrolidine ((E)-**13a**)*

Following the above-mentioned typical procedure for bismetallative cyclization in the presence of $Me_3SiSnBu_3$, a crude product, which was obtained from **12** (78.2 mg, 0.28 mmol), $Ni(cod)_2$ (15.4 mg, 0.056 mmol), and $Me_3SiSnBu_3$ (0.15 ml, 0.43 mmol) in DMF (5.6 ml) at room temperature for 2 h, was purified by flash column chromatography on silica gel (hexane/Et_2O, 100:1–1:1, containing 1% Et_3N) to give an inseparable mixture of (*E*)-**13a** (32.0 mg, 18%) as a colorless oil. IR (neat) 1654, 1598, 1348, 1164, 1020 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.063 (s, 9H), 0.76–0.91 (m, 6H), 0.89 (t, $J = 7.2$ Hz, 9H), 1.24–1.33 (m, 6H), 1.36–1.54 (m, 6H), 1.58–1.73 (m, 2H), 2.42 (s, 3H), 2.53 (m, 1H), 3.03 (dd, $J = 10.8$, 9.0 Hz, 1H), 3.18 (br d, $J = 11.1$ Hz, 1H), 3.40 (dd, $J = 10.8$, 8.3 Hz, 1H), 3.45 (dd, $J = 11.3$, 3.6 Hz, 1H), 3.99 (m, 1H), 5.02 (dd, $J = 15.3$, 8.4 Hz, 1H). 5.60 (dt, $J = 15.3$, 8.5 Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.22, 9.18, 13.7, 14.6, 27.3, 29.0, 48.1, 51.0, 57.0, 74.6, 119.7, 126.5, 127.6, 129.5, 133.3, 143.0; EI-LRMS *m/z* 643 (M^+), 586, 291, 235, 209, 177, 108; EI-HRMS calcd for $C_{29}H_{53}NO_3SSi^{120}Sn$ 643.2537, found 643.2542.

*3.11. Confirmation of the structure of the cyclized products **13a** and **13b** (Scheme 8)*

*3.11.1. Conversion of **13a** to (3S*,4S*)-3-hydroxy-4-(prop-2-enyl)-1-(p-toluenesulfonyl)pyrrolidine (**14**)*

To a solution of **13a** (29.7 mg, 0.046 mmol) in CH_2Cl_2 (2 ml) was added CF_3CO_2H (37 μl, 0.048 mmol) at 0 °C, and the mixture was stirred at room temperature for 10 min. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt, 3:2) to give **14** (11.3 mg, 87%) as a colorless oil. IR (neat) 3510, 1654, 1598, 1338, 1160 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (br d, $J = 4.5$ Hz, 1H), 2.03–2.15 (m, 2H), 2.23 (ddd, $J = 14.0$, 6.6, 6.6 Hz, 1H), 2.43 (s, 3H), 2.98 (dd, $J = 10.0$, 10.0 Hz, 1H), 3.36 (br d, $J = 11.3$ Hz, 1H), 1.90 (dd, $J = 11.3$, 4.2 Hz, 1H), 3.48 (dd, $J = 10.0$, 7.5 Hz, 1H), 4.20 (m, 1H), 5.01 (d, $J = 10.1$ Hz, 1H), 5.05 (d, $J = 17.0$ Hz, 1H), 5.73 (dddd, $J = 17.3$, 10.1, 6.6, 6.6 Hz, 1H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 8.2$ Hz, 2H); EI-LRMS *m/z* 281 (M^+), 264, 239, 184, 155, 126, 108, 91, 68; EI-HRMS calcd for $C_{14}H_{19}NO_3S$ 281.1085, found 281.1075.

*3.11.2. Conversion of **13b** to **14***

According to the similar procedure for conversion of **13a** to **14**, a crude product, which was obtained from **13b** (20.1 mg, 0.031 mmol) and CF_3CO_2H (28 μl, 0.036 mmol) in CH_2Cl_2 (2 ml) at room temperature for 10 min, was purified by flash column chromatography on silica gel (hexane/AcOEt, 3:2) to give **14** (8.4 mg, 85%) as a colorless oil, whose spectral data was completely identical with the above-mentioned compound **14** obtained from **13a**.

*3.11.3. Conversion of **14** to **15***

A solution of **14** (8.4 mg, 0.030 mmol) and 10% Pd–C (1.6 mg, 1.5 μmol) in CH_3OH (1 ml) was stirred at room temperature for 12 h under an atmosphere of hydrogen. The reaction mixture was filtered through a pad of silica gel, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (Et_2O) to give **15** (7.8 mg, 98%) as a colorless oil, whose spectral data was identical with those previously reported [3e].

3.12. Intermolecular bismetallative coupling of isoprene and benzaldehyde (Scheme 9)

To a solution of $Ni(cod)_2$ (16.5 mg, 0.06 mmol) in DMF were added isoprene (30 μl, 0.3 mmol) and benzaldehyde (30 μl, 0.3 mmol) at 0 °C, and the mixture was stirred at room temperature for 16 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (hexane, containing 1% Et_3N) to give (*E*)-**17** (43.7 mg, 28%) and (*Z*)-**17** (33.7 mg, 21%) as a colorless oil, respectively.

Compound (*E*)-**17**: IR (neat) 1654, 1602, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.01 (s, 9H), 0.72–0.85 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H), 1.25–1.33 (m, 6H), 1.40–1.45 (m, 6H), 1.55 (s, 3H), 1.51–1.70 (m, 2H), 2.29 (dd, $J = 13.5$, 6.0 Hz, 1H), 2.41 (dd, $J = 13.5$, 7.2 Hz, 1H), 4.69 (dd, $J = 7.2$, 6.0 Hz, 1H), 5.28 (t, $J = 9.0$ Hz, 1H), 7.18–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.12, 9.3, 10.7, 13.7, 16.4, 27.4, 29.2, 51.1, 74.8, 125.7, 126.1, 126.3, 126.8, 127.9, 145.5; EI-LRMS *m/z* 470, 323, 291, 267, 235, 209, 179, 158; EI-HRMS calcd for $C_{27}H_{50}OSi^{120}Sn$ 538.2653, found 538.2669.

Compound (*Z*)-**17**: IR (neat) 1654, 1602, 1082 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 9H), 0.75–0.91 (m, 6H), 0.88 (t, $J = 7.3$ Hz, 9H), 1.24–1.32 (m, 6H), 1.38–1.50 (m, 6H), 1.50–1.68 (m, 2H), 1.61 (s, 3H), 2.26 (dd, $J = 13.3$, 5.9 Hz, 1H), 2.43 (dd, $J = 13.3$, 5.9 Hz, 1H), 4.74 (dd, $J = 13.3$, 7.5 Hz, 1H), 5.35 (t, $J = 9.2$ Hz, 1H), 7.20–7.34 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.09, 9.4, 10.6, 13.7, 24.4, 27.4, 29.2, 43.3, 74.1, 125.8, 125.9, 126.3, 126.8, 127.9, 145.6; EI-LRMS *m/z* 470, 323, 291, 267, 235, 209, 179, 158; EI-HRMS calcd for $C_{27}H_{50}OSi^{120}Sn$ 538.2653, found 538.2648.

3.13. Asymmetric bismetallative cyclization of **3** in the presence of $Me_3SiSnBu_3$ using **27** as a chiral ligand (Scheme 11)

To a solution of $Ni(cod)_2$ (15.4 mg, 0.056 mmol) in DMF (0.8 ml) was added a solution of **27** (21.5 mg, 0.112 mmol) in DMF (1.4 ml) at 0 °C, and the mixture was stirred at the same temperature for 20 min. To the solution were added $Me_3SiSnBu_3$ (0.15 ml, 0.43 mmol) and a solution of **3** (67.4 mg, 0.28 mmol) in DMF (3.4 ml), and the mixture was stirred at room temperature for 12 h. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (2.8 ml), and to the mixture was added CF_3COOH (0.11 ml, 1.43 mmol). The mixture was stirred at room temperature for 10 min. After removal of the solvent, the residue was dissolved in THF (2.8 ml), and CsF (213 mg, 1.4 mmol) was added to the mixture. Then the mixture was stirred at room temperature for 2 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt, 3:1) to give (1*S*,2*R*)-**6** (42.7 mg, two steps 63%) as a colorless oil, whose spectral data was identical with those previously reported [3k]. The enantiomeric excess and absolute configuration of **6** was determined according to the method previously reported [3k].

3.14. Reaction of the cyclized product (*E*)-***8a*** with benzaldehyde (Scheme 12)

To a solution of (*E*)-**8a** (77.9 mg, 0.129 mmol) in CH_2Cl_2 (1.5 ml) were added benzaldehyde (15.7 mg, 0.148 mmol) and $BF_3 \cdot OEt_2$ (57 μl, 0.450 mmol) at −78 °C, and the mixture was stirred at the same temperature for 1.5 h. The reaction temperature was slowly raised to 0 °C, and the mixture was stirred at 0 °C for 1.5 h. To the mixture was added satd. $NaHCO_3$ aqueous solution, and the solution was extracted with AcOEt. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was dissolved in THF (2 ml), and CsF (98.0 mg, 0.645 mmol) was added to the solution. The mixture was stirred at room temperature for 2 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/AcOEt, 2:1) to give **28** (24.5 mg, 54%) as a colorless oil. IR (neat) 3418, 1732, 1654, 1604, 1202, 1168 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.97 (m, 1H), 2.20 (dd, $J = 13.8$, 12.1 Hz, 1H), 2.29 (dd, $J = 13.8$, 7.8 Hz, 1H), 2.46–2.56 (m, 2H), 2.58 (br s, 1H), 2.65 (ddd, $J = 9.7$, 9.7, 8.3 Hz, 1H), 3.16 (br s, 1H), 3.70 (s, 3H), 3.74 (s, 3H), 4.54 (br s, 1H), 4.67 (br d, $J = 8.3$ Hz, 1H), 4.81 (d, $J = 9.7$ Hz, 1H), 4.82 (d, $J = 17.7$, Hz, 1H), 5.32 (ddd, $J = 17.7$, 9.7, 9.7 Hz, 1H), 7.23–7.27 (m, 3H), 7.28–7.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.0, 42.7, 48.8, 51.6, 52.8, 52.9, 57.6, 73.2, 77.8, 117.3, 127.0, 127.9, 128.3, 173.2, 173.3; EI-LRMS *m/z* 330 (M^+-H_2O), 242, 224, 210, 192, 164, 105, 77, 59; EI-HRMS calcd for $C_{19}H_{22}O_5$ (M^+-H_2O) 330.1467, found 330.1476.

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