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Further studies on palladium-catalyzed bismetallative cyclization of enynes in the presence of $Bu_3SnSiMe_3$

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Dedicated to Professor J.P. Genêt on the occasion of his 60th birthday

Abstract

Bismetallative cyclization of enynes with $Bu_3SnSiMe_3$ catalyzed by Pd(0) complex was realized for the first time, which gives cyclized products containing a vinylsilane moiety and a homoallyltin moiety in good yield. In this cyclization, $Pd_2(dba)_3 \cdot CHCl_3$ or $Pd(OH)_2$ on charcoal is effective as a Pd(0) catalyst and the addition of a phosphine ligand increased the formation of alkyne bismetallation by-product. On the other hand, it was found that a nucleophilic *N*-heterocyclic carbene could be utilized as a ligand for this cyclization. The utility of the cyclized products obtained from this cyclization in synthetic organic chemistry have been proven by transformation into cyclopropanol derivatives.
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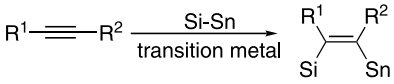
Keywords: Palladium; Silylstannane; Bismetallation; Enyne; Cyclization; N-heterocyclic carbene

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]. We have been interested in the nature and the reactivity of such a bimetallic reagent and/or a metal–carbon bond formed by the reaction of a bimetallic reagent with a substrate having multiple bonds, and our continuous interest have led to new findings for the reactivity of compounds having a Si–Sn bond [2a] or a Si–Zr bond [2b]. In this context, we turned our attention to transition metal-catalyzed bismetallative cyclization. Bismetallative cyclization between two multiple bonds might be particularly useful in synthetic organic chemistry because a cyclic compound having such 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 (M–M′, M, M′=B, Si, Ge, Sn, etc.) had been reported [3]. We had been interested in the bismetallative cyclization of enynes with a Si–Sn. It is well known that a Si–Sn reagent such as $Bu_3SnSiMe_3$ can react with alkynes in the presence of the Group 10 metals (i.e., Ni, Pd, Pt) producing the product having both a vinylsilane group and a vinylstannane group (1) [1,4].



(1)

We speculated that if an enyne **1** could react with a Si–Sn reagent in the presence of a Pd(0) catalyst, insertion of the alkyne part of **1** into the Si–Pd bond or the Sn–Pd bond of Si–Pd–Sn complex formed by

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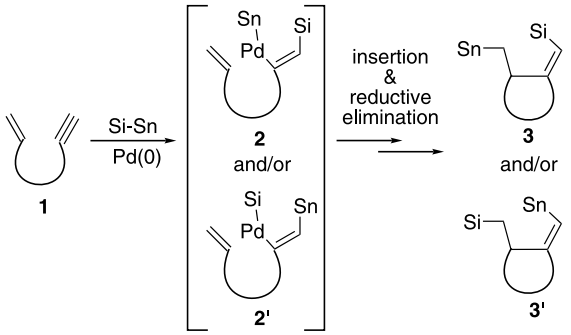


Scheme 1.

oxidative addition of a Si–Sn reagent to Pd(0) complex would occur producing the intermediate **2** or **2′** (Scheme 1). Next insertion of the tethered olefin into Pd–C bond in **2** or **2′** followed by reductive elimination would give a cyclized compound **3** or **3′**. The cyclized compounds **3** or **3′** should be converted to various compounds using the active Si–C and Sn–C bonds. Herein, we report a Pd(0)-catalyzed bismetallative cyclization of enynes in the presence of $Bu_3SnSiMe_3$ [5].

2. Results and discussions

2.1. Bismetallative cyclization of enynes using heterogeneous palladium catalysts [5a]

Initially, we investigated the bismetallative cyclization of **1a** using $Bu_3SnSiMe_3$ (**5**) in the presence of Pd(0) complex. When a THF solution containing equimolar quantities of enyne **1a** and $Bu_3SnSiMe_3$ was stirred at 50 °C in the presence of a catalytic amount of $Pd(PPh_3)_4$ for 4 h, a small amount of the cyclized product **3a** containing both a silyl group and a stannane group was obtained in 14% yield. In this reaction, a bismetallated product of the alkyne, **4a**, was obtained as a main product in 80% yield (Table 1, run 1). The ^{119}Sn-NMR spectrum of **4a** showed resonances at −53.2 ppm, which was unequivocally assigned as a ^{119}Sn peak of the vinylstannane moiety in **4a**. On the other hand, the ^{119}Sn-NMR spectrum of **3a** showed resonances at −15.7 ppm, which seemed to be a ^{119}Sn peak of the alkylstannane moiety. An NOE experiment indicated that the *Z*-olefin had been formed in the product **3a** or **4a** (Scheme 2). To confirm the structure of **3a**, destannylation was carried out by treating it with HI in the presence of $[Bu_4N]I$ at 0 °C [6] producing a three-membered ring compound **5a** in good yield (Scheme 3). Probably, protonation occurs at the α-position of vinylsilane in **3a**, and then the iodide anion attacks at a tin atom to close the three-membered ring [7]. This result indicates that the structure of the cyclized compound should be **3a** and not **3a′**.

The reaction of **1a** was investigated under various conditions to improve the yield of the desired cyclized product **3a** (Table 1).

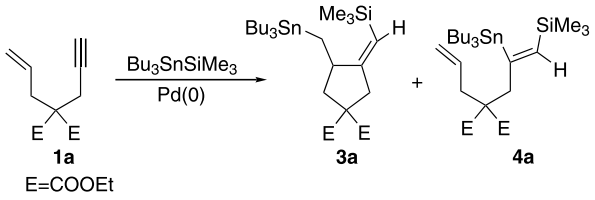
It was found that the formation of the alkyne bismetallation product **4a** could be suppressed by using a palladium catalyst in the absence of a phosphine ligand, and $Pd_2(dba)_3\cdot CHCl_3$ seemed to be the most effective catalyst (runs 1–6). THF was a suitable solvent and toluene also can be used (runs 6–8). It is noteworthy that heterogeneous Pd catalysts, Pd/C or $Pd(OH)_2$/C [8], also afforded the desired product **3a** in high yield, although the reaction time was longer than that in the reaction using $Pd_2(dba)_3\cdot CHCl_3$ in the absence of the phosphine ligand (runs 9–11).

Various enynes, **1b**–**1h**, were reacted with Bu_3Sn-$SiMe_3$ using $Pd_2dba_3\cdot CHCl_3$ (Method A) or $Pd(OH)_2$/C (Method B) and the results are summarized in Table 2.

In each case, the desired product **3** was obtained in moderate to good yield. The reaction of enyne **1e** which has an electron-withdrawing substituent on the C=C bond afforded the desired product **3e** in moderate yield [9], while the reaction of **1i** with a methyl substituent on the C=C bond (Fig. 1) under the similar conditions (Method A) gave **3i** in only 7% yield. It is noteworthy that bicyclic heterocycles **3g** or **3h** was produced stereospecifically from the corresponding enynes **1g** or **1h**, respectively. However, in the reaction of **1g**, the alkyne bismetallation product **4g** was also obtained, which resulted in a lower yield of desired product **3g**. The reaction rate of enyne **1j** (Fig. 1), which has a substituent on the alkyne, was relatively slow, and the cyclized product **3j** was obtained in only 5% yield, and the starting material **1j** was recovered in 76% yield after 46 h (Method A).

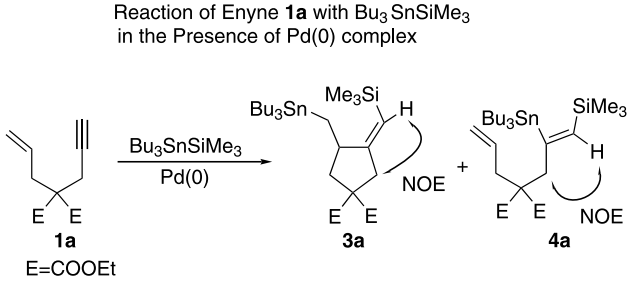
The possible mechanism of this cyclization is shown in Scheme 4. Initially, oxidative addition of $Bu_3SnSiMe_3$ to Pd(0) complex occurs to give Bu_3Sn–Pd–$SiMe_3$ complex (**I**) [10]. Insertion of the alkyne moiety in the substrate **1** into the Pd–silicon bond of **I** produces intermediate **II**. The alkyne bismetallation product **4** should be directly formed from the intermediate **II** through reductive elimination. On the other hand, for the formation of the cyclized product **3** from the intermediate **II**, two pathways can be considered. Intramolecular insertion of the C=C bond into the C–Pd bond of **II** then occurs (i.e., path a) to give complex **III**, and reductive elimination finally affords cyclized product **3**, and Pd(0) is regenerated. On the other hand, the possibility of the formation of IV [3c] cannot be excluded in this mechanism (path b). Thus, insertion of the C=C bond into the Sn–Pd bond in **II** could give complex **IV**. Reductive elimination from **IV** should afford the same cyclized product **3**. At present, it is not clear which pathway is followed in this reaction.

Table 1
Reaction of **1a** with $Bu_3SnSiMe_3$ in the presence of Pd(0) [a]

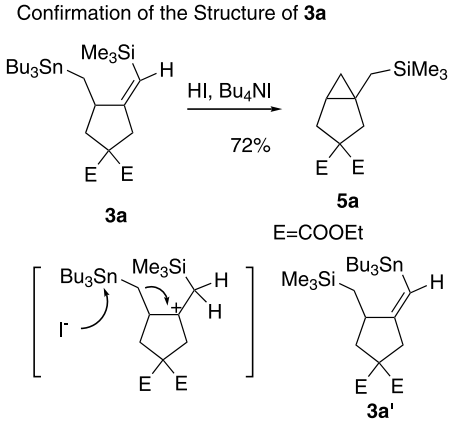


Run	Catalyst	Solvent	Time (h)	Temperature (°C)	Yield (%)		Recovery of **1a** (%)
					3a	**4a**	
1	$Pd(PPh_3)_4$	THF	4	50	14	80	–
2	$PdCl_2(PPh_3)_2$	THF	6	reflux	7	48	–
3	$Pd(OAc)_2$dppb	THF	5	reflux	20	34	–
4	$Pd(cod)Cl_2$	THF	16	rt	30	–	40
5	$PdCl_2$ [b]	THF	45	rt	42	–	–
6	$Pd_2(dba)_3$	THF	16	rt	63	–	–
7	$Pd_2(dba)_3$	DMF	16	rt	10	–	15
8	$Pd_2(dba)_3$	toluene	16	rt	53	–	–
9	Pd/C	THF	114	rt	86	–	10
10	$Pd(OH)_2/C$ [c]	THF	42	rt	88	–	5
11	$Pd(OH)_2/C$ [d]	THF	20	rt	90	–	2

[a] All reactions were carried out using 3 mol% of Pd catalyst and 1.1 equivalents of $Bu_3SnSiMe_3$.
[b] 6 mol% of $PdCl_2$ and 1.5 equivalents of $Bu_3SnSiMe_3$ were used.
[c] 6 mol% of $Pd(OH)_2$ on charcoal and 1.1 equivalents of $Bu_3SnSiMe_3$ were used.
[d] 10 mol% of $Pd(OH)_2$ on charcoal and 1.5 equivalents of $Bu_3SnSiMe_3$ were used.



Scheme 2.



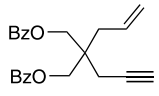
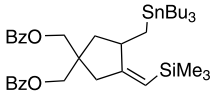
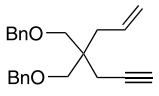
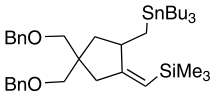
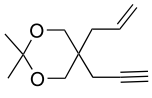
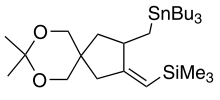
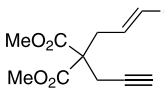
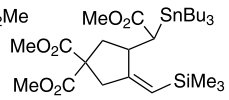
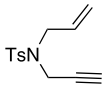
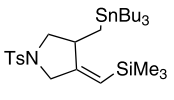
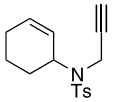
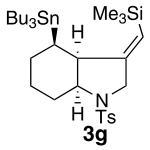
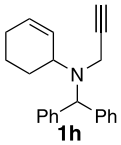
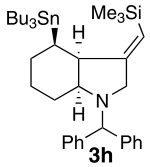
Scheme 3.

2.2. Pd(0)-catalyzed bismetallative cyclization of enynes using N-heterocyclic carbene as a ligand [5b]

As described in the previous section, we succeeded in developing a Pd(0)-catalyzed bismetallative cyclization of enynes in the presence of $Bu_3SnSiMe_3$, in which various cyclized products **3** having both a vinylsilane moiety and a homoallylstannane moiety were produced from enynes **1**. The potential of the cyclized product as a useful synthon prompted us to try to expand this cyclization to an asymmetric synthesis by virtue of the use of a chiral ligand in the reaction. Thus, the cyclization of **1a** using $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of a phosphine ligand was investigated (Table 3). However, the addition of any ligands (e.g., electron-rich or -poor phosphorus ligand, bulky phosphine, bidentate ligand, and so on) in this cyclization resulted in a decrease in the yield of the cyclized product **3a**, and the formation of a bismetallative product **4a** was increased. We therefore turned our attention to finding ligands that could be utilized in this bismetallative cyclization before the development of this reaction to an asymmetric version.

Recently, nucleophilic *N*-heterocyclic carbenes have attracted considerable attention not only as a stable isolable carbene species [11] but also as molecules to coordinate to various transition metals [12]. These transition metal complexes coordinated by *N*-hetero-

Table 2
Bismetallative cyclization of enynes

Substrate	Product	Method, Time (h)	Yield (%)
 **1b**	 **3b**	A 16 B 117	49 52
 **1c**	 **3c**	B 18	78
 **1d**	 **3d**	A 50 B 88	24 65
 **1e**	 **3e**	A 24 B 42	32 50
 **1f**	 **3f**	A 16 B 16	57 82
 **1g**	 **3g**	A 16 B 20	22 37
 **1h**	 **3h**	A 29 B 18	26 66

Method A: $Pd_2(dba)_3$ (3 mol%), $Bu_3SnSiMe_3$ (1.1 equivalents), THF, rt; Method B: $Pd(OH)_2/C$ (10 mol%), $Bu_3SnSiMe_3$ (1.5 equivalents), THF, rt.

cyclic carbenes were expected to have different reactivities compared with those coordinated by traditional ligands such as phosphines. In recent palladium chemistry, high catalytic efficiency has been found in a variety of reactions, including Suzuki–Miyaura coupling [13], Kumada–Tamao–Corriu-type coupling [14], Mizoroki–Heck reaction [15], amination of aryl halide [16], Sonogashira coupling [17], and Tsuji–Trost reaction [18] by virtue of using nucleophilic carbene as a ligand. However, there have been no reports on transition metal-catalyzed bismetallative cyclization using a nucleophilic carbene as a ligand [19]. So, we tried to use a nucleophilic carbene as a ligand in this bismetallative cyclization of enyne.

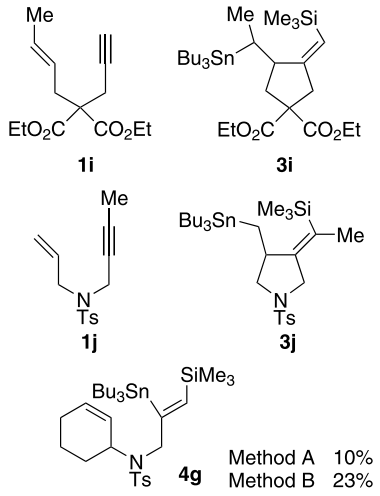
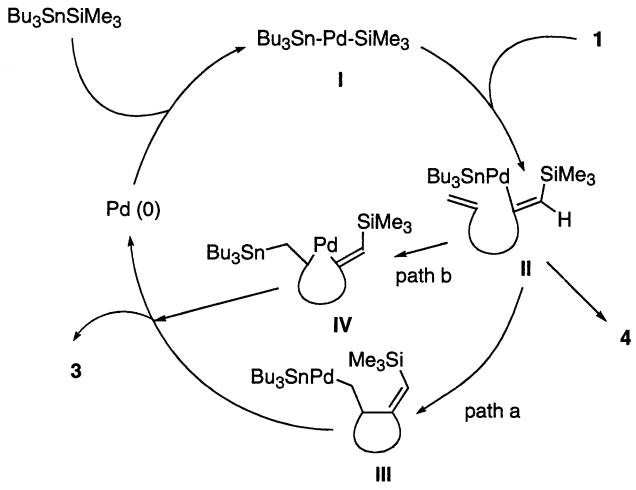


Fig. 1. Other saturates and products.

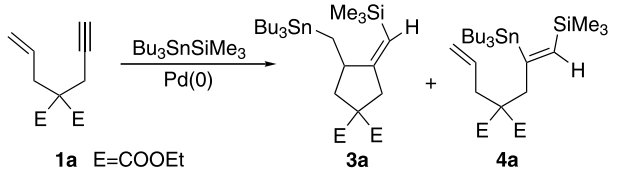


Scheme 4.

Initially, bismetallative cyclization of enyne **1f** in the presence of $Bu_3SnSiMe_3$ was investigated using a Pd–carbene catalyst formed from $Pd_2dba_3{\cdot}CHCl_3$ and various imidazolium salts **7** in the presence of Cs_2CO_3 (Table 4) [13c].

The bismetallative cyclization of **1f** in the presence of $Bu_3SnSiMe_3$ (1.1 equivalents) using a catalyst formed from $Pd_2dba_3{\cdot}CHCl_3$ (3 mol%), imidazolium salt **7a** (6 mol%), and Cs_2CO_3 (12 mol%) gave the desired product **3f** in only 5% yield along with many by-products, and the starting material **1f** was recovered in 11% yield (run 1). The reaction using **7b**, which has aromatic substituents on both nitrogen atoms in its imidazole skeleton, showed a tendency similar to that using **7a**, giving **3f** in a low yield (5%) (run 2). On the other hand, the use of **7c** having alkyl groups on the nitrogen atoms improved the yield of **3f** up to 21% yield (run 3). Solvent effects were carefully examined using **7c** as an imidazolium salt. Polar solvents (DMF, CH_3CN) retarded the reaction (runs 4 and 5) and non-polar solvent (runs 6 and 7) or

Table 3

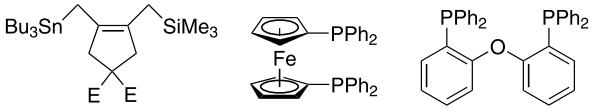


1a E=COOEt 3a 4a

Reaction of **1a** with $Pd_2(dba)_3$ in the presence of phosphine ligand[a)]

run	ligand	time	yield (%)		
			3a	4a	6a
1	PPh_3	21	9	44	16
2[b)]	$PMePh_2$	42	4	1	6
3	PMe_2Ph	52	-	6	-
4	PBu_3	8	10	15	3
5	$P(OEt)_3$	20	6	-	7
6	P(*o*-tolyl)$_3$	5	31	8	-
7	P(*p*-MeO-C_6H_4)$_3$	21	9	20	39
8	P(fulyl)$_3$	21	10	51	5
9	dppp	42	15	44	7
10	dppf	52	29	22	-
11[c)]	DPEPhos	48	37	29	-

a) All reactions were carried out using $Pd_2(dba)_3$ (3 mol %) and ligand (12 mol % for bidentate phosphine or 24 mol % for monodentate phosphine) in the presence of $Bu_3SnSiMe_3$ (1.1 eq.) in THF at reflux.
b) 1a was recovered in 74% yield.
c) 1a was recovered in 11% yield.



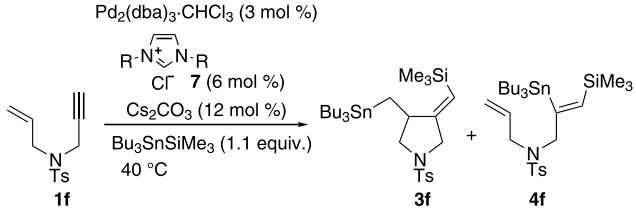
6a dppf DPEphos

chlorinated solvent (runs 8 and 9) were found to be more suitable for this reaction, giving **3f** in 36% yield (toluene at room temperature, run 7) or 47% yield ($ClCH_2CH_2Cl$ at 40 °C, run 8).

Encouraged by these results, we reinvestigated the effects of substituents on nitrogen atoms in the imidazole skeleton of imidazolium salts in the reaction of **1f** in $ClCH_2CH_2Cl$ at 40 °C (Table 5). The use of imidazolium salts **7d**–**7f** having alkyl groups on the nitrogen atoms gave good results, and the yield of **3f** reached 60% in the reaction using **7f** [20,21].

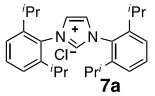
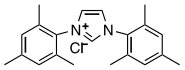
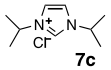
It was found that imidazolinium salts **8** [22], which are the saturated analogues of imidazolium salts **7**, have an equal or superior reactivity to that of **7** and that the use of **8** shortened the reaction time (Table 6). Namely, the bismetallative cyclization of **1f** using imidazolinium salt **8a** under similar conditions was completed in only 2.5 h to give cyclized product **3f** in 50% yield (run 1). Contrary to the imidazolium salt system, it is interesting that aromatic substituents on the nitrogen atoms in the

Table 4



1f 3f 4f

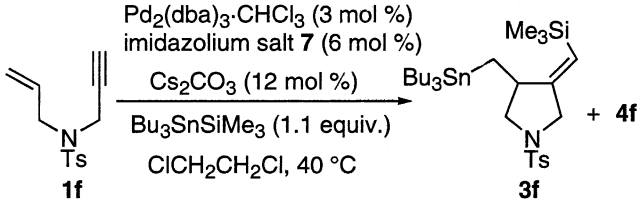
Bismetallative Cyclization of **1f** Using a Pd/Imidazolium Salt System

run	imidazolium salt **7** (R)	solvent	time (h)	yield (%)		SM (**1f**) recov. (%)
				3f	4f	
1	 **7a**	THF	17	5	-	11
2	 **7b**	THF	17	5	2	19
3	 **7c**	THF	20	21	2	10
4	**7c**	DMF	24	-	2	47
5	**7c**	CH_3CN	15	-	18	47
6	**7c**	toluene	6	33	6	-
7	**7c**	toluene[a)]	7.5	36	4	7
8	**7c**	$ClCH_2CH_2Cl$	10	47	5	9
9	**7c**	$ClCH_2CH_2Cl$[a)]	20	41	2	35

[a]The reaction was carried out at room temperature.

imidazoline skeleton were tolerated in this imidazolinium salt system, and the bismetallative cyclized product **3f** was obtained in 62% yield in the reaction using **8d** [23].

Table 5



1f 3f

Bismetallative Cyclization of **1f** Using Various Imidazolium Salts

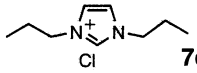
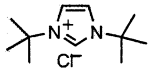
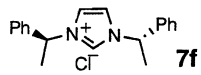
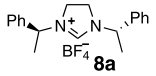
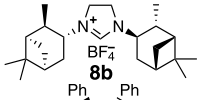
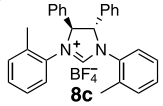
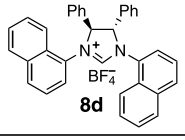
run	imidazolium salt **7**	time (h)	yield (%)		SM (**1f**) recov. (%)
			3f	4f	
1	 **7d**	15	43	2	17
2	 **7e**	9	55	—	—
3	 **7f**	11	60	3	—

Table 6
Bismetallative cyclization of **1f** using various imidazolinium salts **8** [a]

run	imidazolinium salt **8**	time (h)	yield (%) **3f**	yield (%) **4f**
1	 **8a**	2.5	50	2
2	 **8b**	4.5	46	—
3	 **8c**	1.5	54	2
4	 **8d**	1.5	62	—

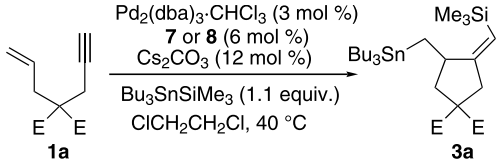
[a] All reactions were carried out using $Pd_2(dba)_3 \cdot CHCl_3$ (3 mol%), imidazolinium salt **8** (6 mol%), and Cs_2CO_3 (12 mol%) in the presence of $Bu_3SnSiMe_3$ (1.1 equivalents) in $ClCH_2CH_2Cl$ at 40 °C.

Next, the bismetallative cyclizations of **1a** were investigated under similar conditions using imidazolium salt **7f** and imidazolinium salts **8a**–**8d** (Table 7). In the case of substrate **1a**, the use of imidazolinium salts **8** (runs 2–5) was more efficient than was the use of **7f** (run 1), and the bismetallative cyclization using **8d** under conditions similar to those described above gave bismetallative cyclized product **3a** in 68% yield (run 5) [24].

2.3. Utilization of the bismetallative cyclized product as a synthon

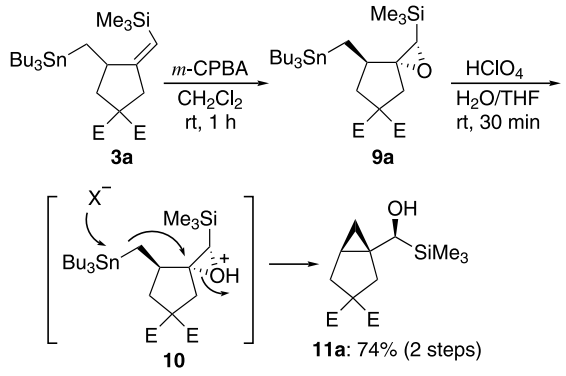
To evaluate the versatility of the cyclized product as a synthon, transformation using the metal–carbon bond of the product was investigated. Treatment of **3a** with *m*-CPBA produced epoxy-silane **9a** in good yield. In this reaction, epoxidation stereoselectively proceeded by

Table 7
Bismetallative cyclization of **1a**



Run	**7** or **8**	Time (h)	**3a** (%)
1	**7f**	36	25 [a]
2	**8a**	12	58
3	**8b**	11	50
4	**8c**	16	59
5	**8d**	11	68

[a] **1a** was recovered in 34% yield.



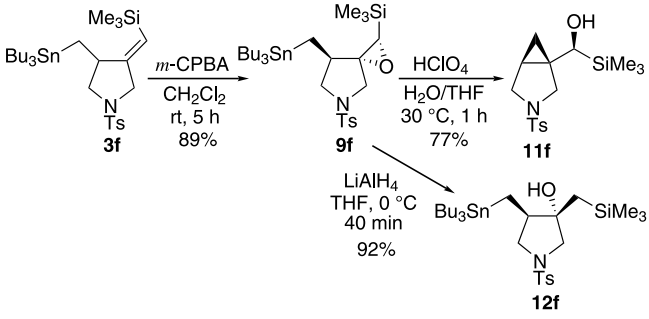
Scheme 5.

attack of the reagent to the less-hindered face of vinylsilane in **9a** (Scheme 5). When the epoxide **9a** was subjected to $HClO_4$ in H_2O–THF, a cyclopropanation reaction stereoselectively proceeded via intermediate **10** to give cyclopropanol derivative **11a** in 74% yield (2 steps from **3a**).

Similarly, the bismetallative cyclized product **3f** could be stereoselectively converted into epoxy-silane **9f**, which was also transformed into cyclopropanol **11f** (Scheme 6). On the other hand, reduction of **9f** with $LiAlH_4$ proceeded in a regio- and stereoselective manner, giving alcohol **12f** in 92% yield. These results prove the utility of the cyclized products obtained by this bismetallative cyclization.

2.4. Conclusion

Bismetallative cyclization of enynes with $Bu_3SnSiMe_3$ catalyzed by Pd(0) complex was realized for the first time, which gives cyclized products containing a vinylsilane moiety and a homoallyltin moiety in good yield. In this cyclization, $Pd_2(dba)_3 \cdot CHCl_3$ or $Pd(OH)_2$ on charcoal is effective as a Pd(0) catalyst, and the addition of a phosphine ligand increased the formation of alkyne bismetallation by-product. On the other hand, it was found that a nucleophilic *N*-heterocyclic carbene could be utilized as a ligand for this cyclization. It has been proven that an imidazolium salt having a bulky alkyl group attached to the nitrogen atoms in its imidazol-2-



Scheme 6.

ylidene skeleton or an imidazolinium salt is suitable as a ligand precursor. In addition, the utility of the cyclized products obtained from this cyclization in synthetic organic chemistry have been proven by transformation into cyclopropanol derivatives. Although the development of this bismetallative reaction to an asymmetric version has not been achieved yet, the present study is the first study in which a nucleophilic *N*-heterocyclic carbene was used as a ligand of a Pd(0) catalyst for this type of reaction.

3. Experimental

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 with silica gel 60 (Merck, 230–400 mesh) using the indicated solvent. ^{1}H- (270 MHz), ^{13}C- (125 MHz), and ^{119}Sn (100.6 MHz)-NMR spectra were recorded on a JEOL EX-270 (^{1}H and ^{119}Sn) and Bruker ARX-500 (^{13}C) spectrometers. ^{1}H and ^{13}C chemical shifts were referenced to internal Me_4Si or internal $CHCl_3$. ^{119}Sn chemical shift was referenced to external Me_4Sn. Mass spectra were measured on a JEOL JMS 700TZ mass spectrometer. Pd/C was purchased from N.E. Chemcat and $Pd(OH)_2$/C was prepared from $PdCl_2$ according to the literature (W.M. Pearlman, Tetrahedron Lett. (1967) 1663).

3.1. Typical procedure for bismetallative cyclization of enyne **1a** using $Pd(OH)_2$/C

A solution of ethyl 2-allyl-2-propargylmalonate **1a** (104.5 mg, 0.44 mmol) and $Me_3SiSnBu_3$ (0.23 ml, 0.658 mmol) in THF (2.2 ml) was stirred in the presence of 20% $Pd(OH)_2$/C (30.8 mg, 0.044 mmol) at room temperature for 20 h. Diethyl ether was added and the ether layer was washed with brine and dried over Na_2SO_4. The organic layer was evaporated, and the residue was purified by column chromatography on silica gel (hexane–diethyl ether, 10/1) to give **3a** as a colorless oil (236.1 mg, 90%).

3.2. Typical procedure for bismetallative cyclization of **1a** in the presence of $Bu_3SnSiMe_3$ using $Pd_2(dba)_3\cdot CHCl_3$/imidazolinium salt **8d**/Cs_2CO_3

A solution of $Pd_2(dba)_3\cdot CHCl_3$ (6 mg, 0.006 mmol), imidazolinium salt **8d** (7 mg, 0.012 mmol), and Cs_2CO_3 (8 mg, 0.024 mmol) in degassed $ClCH_2CH_2Cl$ (0.3 ml) was stirred at 50 °C for 10 min, and the solution was cooled to 0 °C. To the solution were added $Bu_3SnSiMe_3$ (80 μl, 0.23 mmol) and a solution of **1a** (48 mg, 0.20 mmol) in $ClCH_2CH_2Cl$ (0.7 ml) at 0 °C, and the solution was stirred at 40 °C for 11 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 100/1) to give **3a** as a colorless oil (81 mg, 68%).

3.3. Spectral data of cyclized products

3.3.1. 1,1-Bis(ethoxycarbonyl)-3-(tributylstannyl)methyl-4-(Z)-(trimethylsilyl)methylidene-cyclopentane (**3a**)

IR (neat) 1734, 1628, 1602, 1266, 1110 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 0.78–0.96 (m, 6H), 0.87 (t, J = 7.5 Hz, 9H), 0.96 (d, J = 12.7 Hz, 1H), 1.06 (dd, J = 12.7, 3.2 Hz, 1H), 1.20 (t, J = 6.7 Hz, 6H), 1.17–1.32 (m, 6H), 1.40–1.52 (m, 6H), 1.69 (dd, J = 13.3, 5.5 Hz, 1H), 2.68 (dd, J = 15.8, 13.3 Hz, 1H), 2.70 (d, J = 16.2 Hz, 1H), 2.75–2.88 (m, 1H), 3.28 (dt, J = 16.2, 2.0 Hz, 1H), 4.16 (q, J = 7.5 Hz, 4H), 5.25 (s, 1H) ppm; ^{13}C-NMR (68 MHz, $CDCl_3$) δ −0.3, 8.8, 13.2, 13.6, 26.9, 28.8, 39.8, 42.1, 43.9, 58.0, 60.8, 60.9, 119.3, 164.9, 171.2, 171.6 ppm. ^{119}Sn-NMR (C_6D_6) δ −15.7 ppm; EI-LRMS *m*/*z* 545 [M$^+$–Bu]; EI-HRMS Calcd. for $C_{24}H_{45}O_4SiSn$ 545.2109 [M$^+$–Bu]; Found: 545.2106.

3.3.2. 1,1-Bis(benzoyloxymethyl)-3-(tributylstannyl)methyl-4-(Z)-(trimethylsilyl)-methylidenecyclopentane (**3b**)

IR (neat) 1724, 1624, 1602, 1266, 1110 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.77–0.90 (m, 15H), 1.06 (dd, J = 12.9, 13.3 Hz, 1H), 1.19 (dd, J = 2.7, 12.9 Hz, 1H), 1.23–1.30 (m, 6H), 1.40 (dd, J = 5.9, 13.3 Hz, 1H), 1.42–1.52 (m, 6H), 2.13 (dd, J = 8.9, 13.3 Hz, 1H), 2.37 (d, J = 15.4 Hz, 1H), 2.83 (d, J = 15.4 Hz, 1H), 2.84–2.92 (m, 1H), 4.21 (d, J = 11.1 Hz, 1H), 4.28 (d, J = 11.1 Hz, 1H), 4.39 (d, J = 11.0 Hz, 1H), 4.42 (d, J = 11.0 Hz, 1H), 5.34 (s, 1H), 7.42 (dd, J = 7.3, 7.4 Hz, 4H), 7.56 (t, J = 7.4 Hz, 2H), 8.03 (d, J = 7.3 Hz, 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ 0.2 (CH_3), 9.3 (CH_2), 13.6 (CH_3), 20.3 (CH_2), 27.4 (CH_2), 29.2 (CH_2), 39.6 (CH), 41.0 (CH_2), 43.3 (CH_2), 44.5 (CH_2), 66.7 (CH_2), 68.9 (CH_2), 120.6 (CH), 128.4 (CH), 129.5 (CH), 129.9 (C), 130.0 (C), 133.0 (CH), 166.5 (C) ppm; ^{119}Sn-NMR ($CDCl_3$) δ −15.2 ppm; EI-MS *m*/*z* 669 [M$^+$–Bu+1], 355, 291, 241, 179, 105; EI-HRMS *m*/*z* Calcd. for $C_{37}H_{55}O_4Si^{120}Sn$ [M$^+$–Me+1] 711.2892; Found: 711.2903.

3.3.3. 1,1-Bis(benzyloxymethyl)-3-(tributylstannyl)methyl-4-(Z)-(trimethylsilyl)-methylidenecyclopentane (**3c**)

IR (neat) 1624, 1246, 1110 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.82 (t, J = 7.3 Hz, 9H), 0.74–0.84 (m, 6H), 0.95–1.00 (m, 2H), 1.10–1.30 (m, 7H), 1.35–1.46 (m, 6H), 1.84 (dd, J = 13.4, 8.7 Hz, 1H), 2.07 (d, J = 15.0 Hz, 2H), 2.54 (d, J = 15.0 Hz, 2H), 2.51–2.70 (m,

1H), 3.16 (d, $J = 9.9$ Hz, 1H), 3.19 (d, $J = 9.9$ Hz, 1H), 3.36 (d, $J = 10.7$ Hz, 1H), 3.40 (d, $J = 10.7$ Hz, 1H), 4.42 (s, 2H), 4.46 (s, 2H), 5.12 (s, 1H), 7.19–7.26 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) δ 0.3 (CH_3), 9.4 (CH_2), 11.7 (CH), 13.7 (CH_3), 27.5 (CH_2), 29.3 (CH_2), 39.8 (CH_2), 41.1 (C), 43.4 (CH_2), 46.0 (CH), 72.4 (CH), 73.1 (CH), 73.2 (CH), 75.1 (CH), 118.8 (CH), 127.3 (CH), 128.2 (CH), 1138.9 (CH), 139.0 (C), 169.0 (C) ppm; EI-MS *m/z* 641 [M^+–Bu], 91; EI-HRMS *m/z* Calcd. for $C_{34}H_{53}O_2Si^{120}Sn$ [M^+–Bu] 641.2848; Found: 641.2865.

3.3.4. 8,8-Dimethyl-2-(tributylstannyl)methyl-3-(Z)-(trimethylsilyl)methylidene-7, 9-dioxaspiro[4.5]decane (**3d**)

IR (neat) 1624, 1246, 1198 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.08 (s, 9H), 0.80–0.91 (m, 15H), 0.96 (dd, $J = 12.9$, 13.0 Hz, 1H), 1.00 (dd, $J = 5.4$, 13.3 Hz, 1H), 1.10 (dd, $J = 2.8$, 12.9 Hz, 1H), 1.25–1.34 (m, 6H), 1.40 (s, 3H), 1.42 (s, 3H), 1.44–1.52 (m, 6H), 1.86 (dd, $J = 8.5$, 13.3 Hz, 1H), 2.38 (d, $J = 15.3$ Hz, 1H), 2.50 (d, $J = 15.3$ Hz, 1H), 2.70–2.74 (m, 1H), 3.48 (d, $J = 11.4$ Hz, 1H), 3.51 (d, $J = 11.4$ Hz, 1H), 3.62 (d, $J = 11.2$ Hz, 1H), 3.73 (d, $J = 11.2$ Hz, 1H) 5.28 (s, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ 0.2 (CH_3), 9.3 (CH_2), 13.7 (CH_3), 20.3 (CH_2), 22.1 (CH_3), 25.5 (CH_3), 27.4 (CH_2), 29.3 (CH_2), 39.3 (CH), 39.8 (C), 41.9 (CH_2), 44.4 (CH_2), 67.7 (CH_2), 70.1 (CH_2), 97.7 (C), 120.0 (CH), 167.4 (C) ppm; ^{119}Sn-NMR ($CDCl_3$) δ −15.4 ppm; EI-MS *m/z* 543 [M^+–Me+1], 501, 443, 413, 291, 249, 235, 193, 177; EI-HRMS *m/z* Calcd. for $C_{26}H_{51}O_2Si^{120}Sn$ [M^+–Me] 543.2680; Found 543.2704. Anal. Calcd. for $C_{27}H_{54}O_2SiSn$: C, 58.17; H, 9.76. Found: C, 57.87; H, 9.67%.

3.3.5. 1,1-Bis(methoxycarbonyl)-3-{1-(tributylstannyl)-1-(methoxycarbonyl)methyl}-4-(Z)-(trimethylsilyl)methylidenecyclopentane (**3e**)

^{1}H-NMR ($CDCl_3$) δ 0.08 (s, 9H), 0.91 (t, $J = 7.3$ Hz, 9H), 1.01 (dd, $J = 7.9$, 8.6 Hz, 6H, $^2J(^{119}Sn–1H) = 25.1$ Hz), 1.23–1.40 (m, 6H), 1.44–1.72 (m, 6H), 2.51 (dd, $J = 8.6$, 10.6 Hz, 1H), 2.62–2.94 (m, 4H), 3.51 (d, $J =$ 15.8 Hz, 1H), 3.56 (s, 3H), 3.70 (s, 3H), 3.74 (s, 3H), 5.38 (s, 1H).

3.3.6. N-p-Toluenesulfonyl-4-(tributylstannyl)methyl-3-(E)-(trimethylsilyl)-methylidenepyrrolidine (**3f**)

^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.04 (s, 9H), 0.71–1.21 (m, 8H), 0.88 (t, $J = 7.1$ Hz, 9H), 1.24–1.36 (m, 6H), 1.39–1.59 (m, 6H), 2.40 (s, 3H), 2.79–2.86 (m, 1H), 3.02 (dd, $J = 9.3$, 1.8 Hz, 1H), 3.15 (dd, $J = 9.3$, 7.2 Hz, 1H), 3.54 (dd, $J = 14.1$, 1.6 Hz, 1H), 4.03 (d, $J = 14.1$ Hz, 1H), 5.18 (br s, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H) ppm; ^{119}Sn-NMR (100.55 MHz, C_6D_6) δ −15.8 ppm; IR (neat) 1630, 1376, 1166 cm^{-1}; MS *m/z* 598 [M^+–Me], 556 [M^+–Bu]; HRMS (M^+-Bu) Calcd. for $C_{24}H_{42}NO_2SSiSn$: 556.1727; Found: 556.1733. Anal. Calcd. for $C_{28}H_{51}NO_2SSiSn$: C, 54.90; H, 8.39; N, 2.29; S, 5.23. Found: C, 55.31; H, 8.39, N, 2.33; S, 5.20%.

3.3.7. (1S*,2R*,6S*)-N-p-Toluenesulfonyl-2-tributylstannyl-9-(E)-trimethylsilylmethylidene-7-azabicyclo[4.3.0]nonane (**3g**)

^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.03 (s, 9H), 0.88 (t, $J = 7.1$ Hz, 9H), 0.80–1.06 (m, 6H), 1.11–1.66 (m, 17H), 1.85–1.94 (m, 1H), 2.41 (s, 3H), 2.73–2.86 (m, 3H), 3.44 (d, $J = 15.4$ Hz, 1H), 4.12 (d, $J = 15.4$ Hz, 1H), 5.10 (s, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 1H) ppm; ^{119}Sn-NMR (100.55 MHz, C_6D_6) δ −14.2 ppm; IR (neat) 1636, 1350, 1162 cm^{-1}; MS *m/z* 653 [M^+], 596 [M^+–Bu]; HRMS Calcd. for $C_{31}H_{55}NO_2SSiSn$ 652.6354; Found: 653.2745.

3.3.8. (1S*,2R*,6S*)-N-p-Toluenesulfonyl-2-tributylstannyl-9-N-diphenylmethyl-2-tributylstannyl-9-(E)-(trimethylsilyl)methylidene-7-azabicyclo[4.3.0]nonane (**3h**)

^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.01 (s, 9H), 0.69–1.03 (m, 15H), 1.08–1.81 (m, 19H), 2.56–2.62 (m, 1H), 2.82 (dd, $J = 15.4$, 2.2 Hz, 1H) 2.81–2.87 (m, 1H), 3.58 (br d, $J = 15.4$ Hz, 1H), 4.62 (s, 1H), 4.99 (br s, 1H), 7.07–7.35 (m, 8H), 7.38 (d, $J = 6.7$ Hz, 2H) ppm; ^{119}Sn-NMR (100.55 MHz, C_6D_6) δ −26.0 ppm; IR (neat) 3026, 1636, 1492, 1454, 1352, 1166 cm^{-1}; MS *m/z* 650 [M^+–Me], 608 [M^+–Bu]; HRMS [M^+–Bu] Calcd. for $C_{33}H_{50}NSiSn$ 608.2735; Found: 608.2755. Anal. Calcd. for $C_{37}H_{59}NSiSn$: C, 66.86; H, 8.95; N, 2.11. Found: C, 67.11; H, 8.98; N, 2.09%.

3.4. Reaction of the cyclized products

3.4.1. Procedures for transformation of **3a** into **5a** (Scheme 2)

To a solution of **3a** (48 mg, 0.08 mmol) in toluene (0.5 ml) was added aqueous HI solution (57%, 0.10 ml, 0.80 mmol) at 0 °C and the solution was stirred at the same temperature for 1 h. To this solution was added saturated $NaHCO_3$ solution and the aqueous layer was extracted with diethyl ether. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane–ethyl acetate, 9/1) to give **5a** (18 mg, 72%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.02 (s, 9H), 0.17 (dd, $J = 5.5$, 4.4 Hz, 1H), 0.26 (dd, $J = 7.1$, 5.5 Hz, 1H), 0.58 (d, $J = 14.6$ Hz, 1H), 0.96 (d, $J = 14.6$ Hz, 1H), 0.94–1.01 (m, 1H), 1.22 (t, $J = 7.1$ Hz, 6H), 2.20 (dd, $J = 13.5$, 1.4 Hz, 1H), 2.44 (d, $J = 13.4$ Hz, 1H), 2.49 (d, $J = 13.4$ Hz, 1H), 2.57 (d, $J = 13.5$ Hz, 1H), 4.11–4.24 (m, 4H) ppm; IR (neat) 1732, 1446 cm^{-1}; MS *m/z* 312 [M^+], 297 [M^+–Me], 239 [M^+–$SiMe_3$]; HRMS Calcd. for $C_{16}H_{28}O_4Si$: 312.1757; Found: 312.1769.

*3.4.2. Procedures for transformation of **3a** into **11a** via **9a** (Scheme 5)*

To a solution of **3a** (20 mg, 0.03 mmol) in CH_2Cl_2 (0.7 ml) was added *m*-CPBA (9 mg, 0.05 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. To the mixture was added 10% $Na_2S_2O_3$ aqueous solution, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution, brined, and dried over $MgSO_4$. After removal of the solvent, the residual crude product **9a** was dissolved in THF (1 ml). To the solution was added 7% $HClO_4$ in THF–H_2O (9:1) solution (0.7 ml), and the mixture was stirred at room temperature for 30 min. To the mixture was added saturated $NaHCO_3$ aqueous solution at 0 °C, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane–EtOAc, 10/1) to give **11a** (8 mg, 74%, 2 steps) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.28 (dd, $J = 5.3$, 4.7 Hz, 1H), 0.50 (dd, $J = 6.5$, 5.3 Hz, 1H), 1.20 (t, $J = 7.3$ Hz, 3H), 1.23 (t, $J = 7.3$ Hz, 3H), 1.26–1.32 (m, 1H), 1.36 (bs, 1H), 2.38 (dd, $J = 13.8$, 5.0 Hz, 1H), 2.42 (d, $J = 13.5$ Hz, 1H), 2.59 (d, $J = 13.5$ Hz, 1H), 2.61 (d, $J = 13.8$ Hz, 1H), 3.04 (s, 1H), 4.14 (q, $J = 7.3$ Hz, 2H), 4.15 (q, $J = 7.3$ Hz, 2H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ −2.18, 14.4, 15.0, 22.7, 34.1, 36.2, 38.8, 60.6, 62.1, 71.4, 172.3, 172.9 ppm; IR (neat) 3528, 1732 cm^{-1}; EI-LRMS *m*/*z* 328 [M$^+$], 313, 254.

*3.4.3. Procedures for transformation of **3f** into **9f** (Scheme 6)*

To a solution of **3f** (101 mg, 0.16 mmol) in CH_2Cl_2 (3 ml) was added *m*-CPBA (53 mg, 0.24 mmol) at 0 °C and the mixture was stirred at room temperature for 5 h. To the mixture was added 10% $Na_2S_2O_3$ aqueous solution and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution, brined, and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane–EtOAc, 15/1–13/1) to give **9f** (90 mg, 89%) as a colorless oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.69 (dd, $J = 13.7$, 13.3 Hz, 1H), 0.85 (t, $J = 7.1$ Hz, 6H), 0.88 (t, $J = 7.1$ Hz, 9H), 0.99 (d, $J = 13.3$ Hz, 1H), 1.21–1.35 (m, 6H), 1.38–1.50 (m, 6H), 1.91 (dd, $J = 13.7$, 4.4 Hz, 1H), 2.25 (s, 1H), 2.39 (s, 3H), 2.85 (d, $J = 11.5$ Hz, 1H), 3.19 (d, $J = 9.1$ Hz, 1H), 3.32 (dd, $J = 9.1$, 4.4 Hz, 1H), 3.95 (d, $J = 11.5$ Hz, 1H), 7.25 (d, $J = 8.3$ Hz, 2H), 7.68 (d, $J = 8.3$ Hz, 2H) ppm; ^{13}C-NMR (68 MHz, $CDCl_3$) δ 9.27, 11.6, 13.6, 21.5, 27.4, 29.1, 40.9, 52.9, 53.1, 54.3, 73.3, 127.5, 129.7, 133.9, 143.4 ppm; IR (neat) 1350, 1250, 1164, 842 cm^{-1}; EI-LRMS *m*/*z* 628 [M$^+$], 572, 458, 416. EI-HRMS Calcd. for $C_{28}H_{51}NO_3SSiSn$: 628.2327; Found: 628.2366.

*3.4.4. Procedures for transformation of **9f** into **11f** (Scheme 6)*

To a solution of **9f** (16 mg, 0.03 mmol) in THF (1 ml) was added 7% $HClO_4$ in THF–H_2O (9:1) solution (0.5 ml), and the mixture was stirred at 30 °C for 1 h. To the mixture was added saturated $NaHCO_3$ aqueous solution at 0 °C, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane–Et_2O, 4/1–1/1) to give **11f** (7 mg, 77%) as a colorless oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ −0.07 (s, 9H), 0.61 (dd, $J = 7.1$, 5.1 Hz, 1H), 0.59–0.64 (m, 1H), 1.32 (ddd, $J = 7.1$, 4.0, 4.0 Hz, 1H), 1.43 (bs, 1H), 2.42 (s, 3H), 2.96 (d, $J = 9.5$ Hz, 1H), 3.51 (d, $J = 9.5$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 8.1$ Hz, 2H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ −2.74, 9.97, 13.4, 20.5, 21.6, 32.3, 49.8, 51.9, 68.7, 127.6, 129.5, 132.8, 143.5 ppm; IR (neat) 3518, 1341, 1164 cm^{-1}; EI-LRMS *m*/*z* 324 [M$^+$], 309, 279, 252.

*3.4.5. Procedures for transformation of **9f** into **12f** (Scheme 6)*

To a solution of **9f** (17 mg, 0.03 mmol) in THF (1.5 ml) was added $LiAlH_4$ (3 mg, 0.08 mmol) at 0 °C and the mixture was stirred at room temperature for 40 min. To the solution was added $Na_2SO_4 \cdot 10H_2O$ at 0 °C, and the mixture was stirred at room temperature for 3 h. The mixture was filtered through a pad of celite, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexane–Et_2O, 3/1) to give **12f** (15 mg, 92%) as a colorless oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.47 (dd, $J = 12.9$, 11.1 Hz, 1H), 0.81 (t, $J = 7.9$ Hz, 6H), 0.88 (t, $J = 7.9$ Hz, 9H), 0.91 (d, $J = 11.1$ Hz, 1H), 1.20–1.35 (m, 6H), 1.40–1.51 (m, 6H), 2.23 (dd, $J = 11.1$, 4.0 Hz, 1H), 2.41 (s, 3H), 2.96 (d, $J = 8.7$ Hz, 1H), 3.13 (d, $J = 8.5$ Hz, 1H), 3.17 (d, $J = 8.5$ Hz, 1H), 3.47 (dd, $J = 8.7$, 4.0 Hz, 1H), 3.59 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 0.7, 9.0, 9.6, 14.1, 21.9, 22.1, 27.8, 29.5, 49.5, 54.2, 59.0, 82.8, 127.7, 129.9, 134.2, 143.6 ppm; IR (neat) 3510, 1341, 1162 cm^{-1}; EI-LRMS *m*/*z* 630 [M$^+$], 614, 574, 558. EI-HRMS Calcd. for $C_{28}H_{52}NO_2SSiSn$ [M$^+$–OH]: 614.2487; Found: 614.2510.

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[24] The cyclized products **3a** in Table 7 were obtained with a low enantiomeric excess (e.g., **7f** → not determined, **8a** → 1% ee, **8b** → 2% ee, **8c** → 6% ee, **8d** → 8% ee), which was determined by the ^{1}H-NMR spectrum of MPTA ester of **11a** after derivation of **3a** by the procedure shown in Scheme 5.