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Highly diastereoselective desymmetrizing intramolecular cyclization of allylstannane with a diketone promoted by Lewis acid or transition metal complex

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Dedicated to Professor Jean Normant on the occasion of his 65th birthday

Abstract

The Lewis acid mediated desymmetrizing intramolecular cyclization of prochiral allylstannyl diketone (**1**) gave a mixture of two diastereomers (**2** and **3**). Highly diastereoselective synthesis of each of the diastereomers was accomplished by appropriate choice of the Lewis acid. Compound **3** was also produced stereoselectively by using a palladium catalyst instead of Lewis acid. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Desymmetrizing cyclization; Allylstannane; Diketone; Lewis acid; Transition metal catalyst

1. Introduction

The condensation of allylstannane with ketones is one of the most important synthetic methods for C–C bond formation, and one of the most attractive reactions to construct a quaternary carbon stereocenters [1]. While a number of methods for intramolecular condensation with aldehydes have been studied during last decade [2], to the best of our knowledge, there are few reports on the intramolecular condensation of allylmetal reagents with ketones [3]. Wu and co-workers reported the intramolecular allylation of ketone by using an allylstannane prepared in situ from allyl bromide and tin metal in the presence of mercury chloride, and succeeded to synthesize the cyclic ether, which has two chiral centers containing a quaternary carbon stereocenter with moderate diastereoselectivity [3a]. The intramolecular cyclization of cyclic [3b] and acyclic [3c] β-diketones with allylsilane have been also accomplished. While these reactions can construct three contiguous chiral centers with desymmetric cyclization of the prochiral substrate, both chemical yields and diastereoselectivities were generally low.

Recently, we reported as a preliminary communication that the Lewis acid mediated intramolecular cyclization of prochiral allylstannyl diketone (**1**) gave a mixture of two diastereomers (**2** and **3**), and highly diastereoselective synthesis of each diastereoisomer was accomplished by proper choice of the Lewis acids (Scheme 1) [4]. Now we report the full details on the previous study along with the palladium catalyzed stereoselective cyclization of **1**.

2. Results and discussion

2.1. Preparation of the substrate *1*

The preparation of **1** is shown in Scheme 2. Reaction of 1,4-butanediol (**6**) with TBDMSCl/imidazole in DMF gave the monosilylated alcohol (**7**) in 86% yield. Swern oxidation of **7** followed by the treatment with methyl (triphenylphosphoranylidene)acetate gave the corresponding α,β-unsaturated ester (**8**) in 70% yield. The ester group of **8** was reduced by DIBAL-H, and

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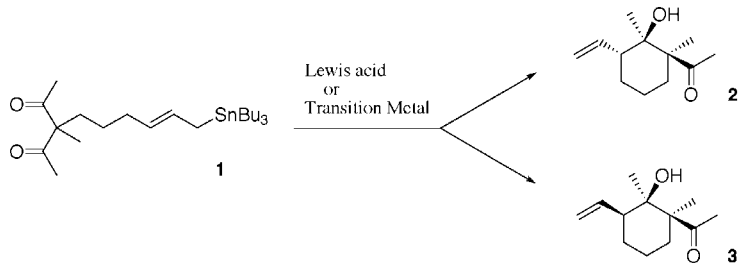
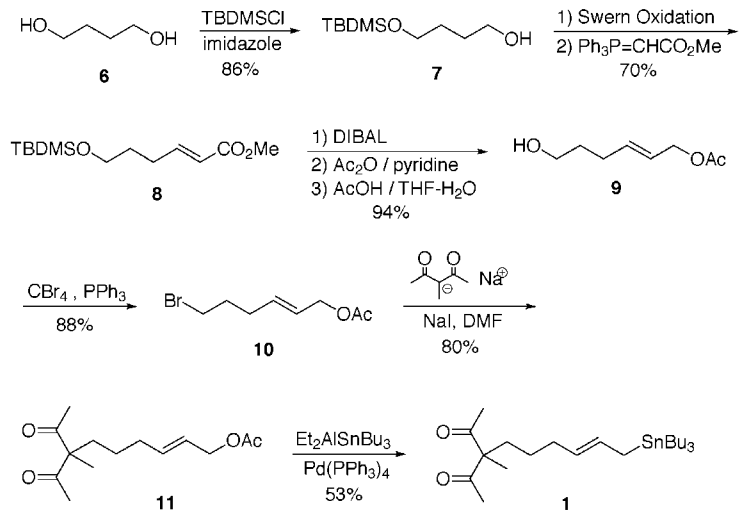


Scheme 1.

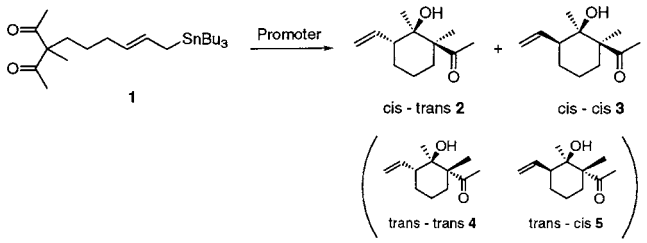


Scheme 2.

the resulting alcohol was acetylated with acetic anhydride in pyridine. Subsequent treatment with acetic acid in THF-H_2O gave **9** in 94% yield. Bromination of **9** was performed by CBr_4/PPh_3 to give **10** in 88% yield. Alkylation of **10** with 3-methyl-2,4-pentanedione with NaH in DMF produced **11** in 80% yield. The palladium-catalyzed reaction of **11** with $Et_2AlSnBu_3$ [5] gave **1** in 53% yield.

2.2. Lewis acid mediated intramolecular cyclization of allylstannane with diketone

The Lewis acid mediated cyclization of **1** was examined (Eq. (1)) and the results are summarized in Table 1. In all cases, only two diastereoisomers, *cis–trans* **2** and *cis–cis* **3**, were obtained among four possible stereoisomeric cyclization products (**2**–**5**). The reaction promoted by $TiCl_4$ (1.0 equivalents) gave a 92:8 mixture of *cis–trans* **2** and *cis–cis* **3** in 87% isolated yield (entry 1). The use of 0.5 equivalents of $TiCl_4$ gave two diastereomers in the yields just corresponding to the amount of $TiCl_4$ (entry 2). Although the diastereoselectivity of **2** increased up to 95:5 by using $TiCl_2(OiPr)_2$ instead of $TiCl_4$, the chemical yield decreased to 67% and the protodestannylated product **12** was obtained in 26% yield (entry 3) [6]. The reactions mediated by $AlCl_3$ and $EtAlCl_2$ also afforded *cis–trans* isomer **2** as a major product, but in both cases, the chemical yield and the diastereoselectivity were lower than those via the $TiCl_4$ mediated reaction (entries 4 and 5). The cyclization of **1** did not proceed in the presence of a weaker Lewis acid such as Et_2AlCl (entry 6). Interestingly, the reactions mediated by $BF_3{\cdot}OEt_2$ (entry 7), $ZnBr_2$ (entry 8), $InCl_3$ (entry 9), and $Yb(OiPr)_3$ (entry 10) afforded *cis–cis* **3** as a major product in moderate yields. The use of $SnCl_4$ gave only *cis–cis* isomer **3** in 66% isolated yield (entry 11). Surprisingly, the use of 0.5 equivalents of $SnCl_4$ afforded **3** in higher yield (entry 12). On the other hand, the use of protic acid such as camphorsulfonic acid (CSA) and CF_3CO_2H gave only the reduced product **12** in 85 and 89% yield, respectively (entries 13 and 14). HCl also afforded the reduced product **12** quantitatively. No thermal reaction took place even at elevated temperature (toluene, 110°C) in 2 days, and **1** was decomposed in 5 days.



(1)

2.3. Transition metal catalyzed intramolecular cyclization of allylstannane with diketone

The reactions catalyzed by several Pd(II) or Pt(II) complexes were examined and the results are summarized in Table 2. No reaction took place in the absence of any transition metal catalysts (entry 1). While neither $PdCl_2(PPh_3)_2$ nor $PtCl_2(PPh_3)_2$ catalyzed the cyclization reaction effectively (entries 2–4), the reaction catalyzed by $(\eta^3\text{-}C_3H_5PdCl)_2$ gave *cis–cis* isomer **3** as a major product in low yield (entry 5). The chemical yield was not improved either by using 30, 50 and 100 mol% amount of palladium or by using other solvents such as CH_2Cl_2, DMF, DMSO, toluene, and dioxane.

2.4. Determination of stereostructure

The configurations of the two products were assigned by ^{1}H-NMR decoupling and NOE experiments. The coupling constants between H_a and H_b of **2** and **3** were $J = 12.5$ Hz and $J = 12.0$ Hz, respectively, indicating that the stereochemical relation between H_a and H_b were axial–axial in both compounds. Therefore, the vinyl substituent of both isomers could be assigned to be equatorial. In *cis–trans* isomer **2**, NOE effects were observed between a hydroxyl proton and the neighboring methyl group, between H_b and the methyl group attached to the carbon of COH, and between these two methyl groups, indicating that the methyl group at COH was in the 1,3-diaxial position from H_b. It is clear that the stereochemical relation between the vinyl and

Table 1
Cyclization of **1** mediated by various Lewis acid and protic acid [a]

Entry	Promoter (equiv.)	Temp (°C)	Time (h)	Ratio (2:3) [b]	Yield (%) [c]
1	$TiCl_4$ (1.0)	−78	1	92:8	87 [e]
2	$TiCl_4$ (0.5)	−78	1	93:7	55
3	$TiCl_2(OiPr)_2$ (1.5)	−35	12	95:5	67 [d]
4	$AlCl_3$ (1.0)	−78	2	73:27	61
5	$EtAlCl_2$ (2.0)	−10	2	77:23	66
6	Et_2AlCl (2.0)	rt	50		0
7	$BF_3{\cdot}OEt_2$ (2.0)	−10	2	32:68	29 [d]
8	$ZnBr_2$ (1.0)	rt	96	21:79	60
9	$InCl_3$ (1.0)	−20	13	3:97	55
10	$Yb(OiPr)_3$ (1.0)	rt	1.3	8:92	76
11	$SnCl_4$ (1.0)	−78	1	2:>98	66 [d]
12	$SnCl_4$ (0.5)	−78 to 0	2	2:>98	88
13	CSA (2.0)	−40	16		0 [d]
14	CF_3CO_2H (2.0)	−78 to −20	1		0 [d]

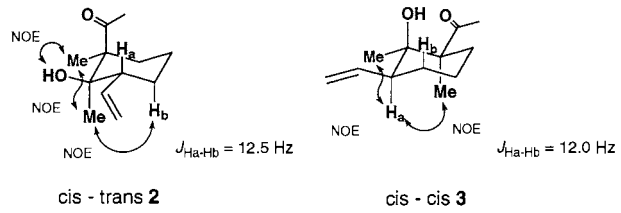
[a] The reactions were carried out with 0.1 M substrate (1 mmol) in CH_2Cl_2 under the conditions indicated in the table, and quenched with saturated aqueous $NaHCO_3$ at the reaction temperature.
[b] Determined by ^{1}H-NMR.
[c] Determined by ^{1}H-NMR (*p*-xylene was used as an internal standard).
[d] The reduced product **12** was obtained as a by-product (entry 3, 26%; entry 7, 10%; entry 13, 85%; entry 14, 89%); see Ref. [6].
[e] Isolated yield.

Table 2
Transition metal catalyzed cyclization of **1**

Entry	Catalyst (10 mol%)	Solvent	Temp (°C)	Time (h)	Ratio (2:3) [a]	Yield (%) [b]
1	none	THF	50	96		0
2	$PdCl_2(PPh_3)_2$	THF	50	11	2:>98	trace
3	$PtCl_2(PPh_3)_2$	THF	50	120		0
4	$PtCl_2(PPh_3)_2$	CH_3CN	50	72	13: 87	5
5	$(\eta^3\text{-}C_3H_5PdCl)_2$	CH_3CN	rt	19	8: 92	32

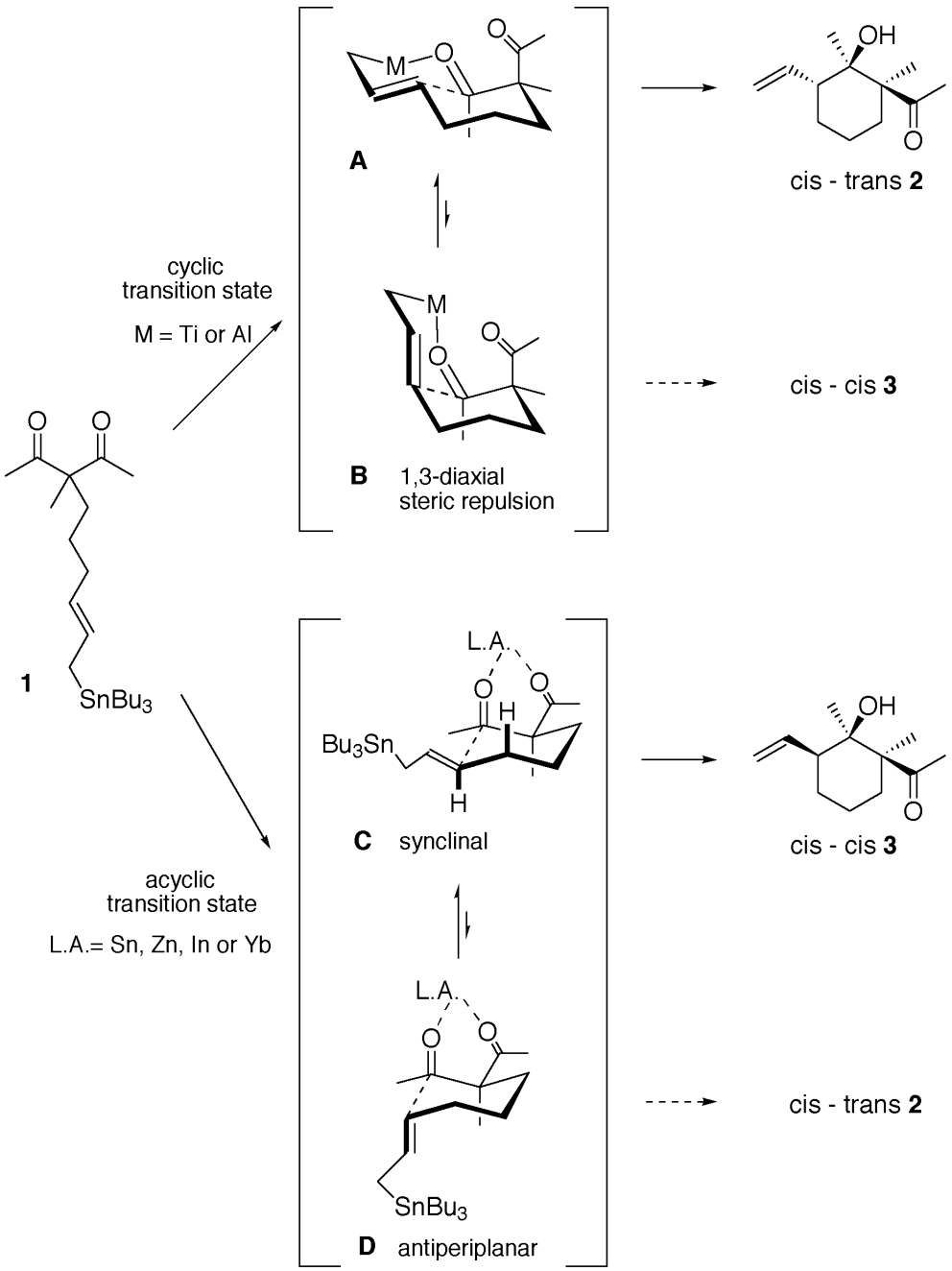
[a] Determined by ^{1}H-NMR.
[b] Determined by ^{1}H-NMR (*p*-xylene was used as an internal standard).

hydroxyl group is *trans*, and that of hydroxyl and acetyl group is *cis*. In *cis–cis* isomer **3**, NOE effects were observed between H_a and the neighboring methyl group, and between H_a and the methyl group attached to the carbon of $C(CO)CH_3$. It is clear that the stereochemical relation between the vinyl and hydroxyl group is *cis*, and that of hydroxyl and acetyl group is *cis*.

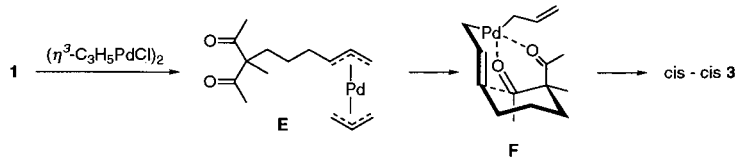


2.5. Mechanism

The mechanism for the diastereoselectivity difference between the $TiCl_4$ mediated and $SnCl_4$ (also $InCl_3$ and $Yb(OiPr)_3$) mediated reactions has not been unambiguously established. A plausible mechanism is shown in Scheme 3. When $TiCl_4$ is used as a Lewis acid, a transmetalation between stannane of **1** and $TiCl_4$ could



Scheme 3.



Scheme 4.

take place and the resulting allyltitanium compound could undergo cyclization via a cyclic transition state. Although there are two possibilities for the structure of cyclic transition state A and B, 1,3-diaxial steric repulsion between axial $C(O)CH_3$ and C=CH– destabilizes the transition state B. Therefore, the reaction would proceed via A. Perhaps the ethylaluminium dichloride mediated reaction would proceed also via A. On the other hand, the transmetalation reaction between stannane of **1** and $SnCl_4$ ($InCl_3$ and $Yb(OiPr)_3$) would be slower, and thus the cyclization would take place via an acyclic transition state. There are also two possibilities for the transition state structures; C (synclinal) and D (antiperiplanar). It was reported that the intramolecular cyclization of allylstannane with aldehydes would undergo synclinal transition state [2h–i]. Therefore, the reaction would proceed via C, in which the Lewis acid would coordinate to carbonyl oxygen and facilitate the cyclization.

On the other hand, the $(\eta^3\text{-}C_3H_5PdCl)_2$ catalyzed reaction would probably proceed via a bis-π-allylpalladium complex E in which the allyl group can add nucleophilically to one of the carbonyl groups (Scheme 4) [6]. The diastereoselective formation of *cis–cis* isomer **3** might be explained by the preferred formation of transition state F due to the chelation effect between palladium and two carbonyl groups. The hypothesis of the presence of the bis-π-allylpalladium intermediate E is supported by the fact that no reaction took place with $PdCl_2(PPh_3)_2$ and $PtCl_2(PPh_3)_2$, since those catalysts can not provide allyl unit to form bis-π-allylpalladium from **1**.

3. Conclusion

Highly diastereoselective desymmetric intramolecular cyclization of prochiral allylstannyl diketone (**1**) gives 6-membered carbocycles (**2** and **3**) with high stereoselectivities was accomplished. The cyclization of **1** produces only two diastereoisomers (**2** and **3**) among four possible stereoisomeric cyclization products. Moreover, highly diastereoselective synthesis of each diastereoisomer was accomplished by proper choice of the Lewis acid or Pd(II) catalyst.

4. Experimental

4.1. General

^1H- and ^{13}C-NMR spectra were recorded on JEOL JNM-GSX-270 (270 MHz and 67.9 MHz), JEOL JNM-AL 300 (300 and 75.5 MHz), or JEOL JNM-A500 (500 and 125.7 MHz) instrument. These spectra data are reported in the ppm downfield from tetramethylsilane. The IR spectra were recorded on a Shimadzu FT IR-8200A spectrometer. The high-resolution mass spectra were recorded on either Hitachi M-2500S or JEOL JMS-HX-110 spectrometer. Column chromatography was carried out by employing either Merck silica gel (Kiesegel 70-230 mesh) or Fuji Silysia Chemical basic silica gel (Chromatorex NH, 100–200 mesh), and the analytical thin layer chromatography (TLC) was performed on the 0.2 mm precoated silica gel plates (Kiesegel 60 F_{254}). All manipulations were conducted under an argon atmosphere by using the standard Schlenk techniques. Anhydrous solvents were purchased from Kanto Chemicals. All other compounds used were commercially available and purchased from Aldrich.

4.2. Preparation of starting material *1*

To a DMF (150 ml) solution of 1,4-butanediol (34 g, 378 mmol) at 0°C were added imidazole (5.8 g, 85 mmol) and TBDMSCl (10.6 g, 70 mmol), and the mixture was stirred for 2 h at room temperature (r.t.). Water (150 ml) was added, and the mixture was extracted with ether, washed with water and brine, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue **5** was used for further manipulation without purification. Oxalyl chloride (3.5 ml, 40 mmol) was added dropwise to the mixture of CH_2Cl_2 (100 ml) and DMSO (3.5 ml, 50 mmol) at -78°C under argon and stirred for 20 min. A CH_2Cl_2 (15 ml) solution of **5** (4.3 g, 21 mmol) was added dropwise and the mixture was stirred for 1 h at -78°C. Triethylamine (20 ml, 140 mmol) was added and the mixture was warmed gradually to r.t. and further stirred for 1 h at r.t. Addition of excess saturated aqueous NH_4Cl, extraction with ether, washing with water and brine, drying with anhydrous $MgSO_4$, concentration under reduced pressure, and purification

with column chromatography (silica gel; *n*-hexane/ethyl acetate, 10/1) gave the corresponding aldehyde (3.7 g, 87%). To a toluene (90 ml) solution of aldehyde obtained above (6.0 g, 30 mmol) at room temperature was added methyl (triphenylphosphpranyliden)acetate (11.7 g, 35 mmol) and the reaction mixture was stirred for 24 h at room temperature. Filtration, concentration under reduced pressure, purification with column chromatography (silica gel; *n*-hexane/ethyl acetate, 10/1) gave **6** (7.2 g, 93%). **6** dissolved in CH_2Cl_2 (65 ml), and 1.01 M CH_2Cl_2 solution of *i*-Bu_2AlH (DIBAL, 61 ml, 62 mmol) was added dropwise at −78°C in 20 min. The mixture was stirred for 1.5 h, and water (35 ml) was added slowly. The mixture was stirred overnight at r.t., dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in pyridine (20 ml), and Ac_2O (10 ml) was added and the mixture was stirred for 6 h at r.t. Water was added to the mixture, extracted with ether, washed with 1 N HCl, water, and brine, dried with anhydrous $MgSO_4$, concentrated under reduced pressure. The residue was dissolved in a mixture of THF (60 ml) and H_2O (20 ml), AcOH (20 ml) was added and the mixture was stirred overnight at r.t. Concentration under reduced pressure, and purification with column chromatography (silica gel; *n*-hexane/ethyl acetate, 1/1) gave **7** (4.1 g, 93%). To an ether solution of **7** (5.3 g, 34 mmol) were added PPh_3 (15.4 g, 59 mmol), CBr_4 (24.6 g, 74 mmol), and the reaction mixture was stirred for 24 h at room temperature. Filtration, concentration under reduced pressure, and purification with column chromatography (silica gel; *n*-hexane/ethyl acetate, 8/1) gave **8** (6.1 g, 88%). To a suspension of NaH (340 mg, 8.5 mmol, 60% in mineral oil) in DMF (8 ml) at 0°C under argon was added 3-methyl-2,4-pentanedione (1.0 ml, 8.6 mmol), and the mixture was stirred for 30 min. A DMF (5 ml) solution of **8** (1.4 g, 6.5 mmol) and NaI (240 mg, 1.6 mmol) were added and the resulting mixture was stirred for 6 h at 70–75°C. Addition of water at 0°C, extraction with ether, washing with water and brine, drying with anhydrous $MgSO_4$, and concentration under reduced pressure, and purification with column chromatography (silica gel; *n*-hexane/ethyl acetate, 3/1) gave **9** (1.3 g, 77%). To a THF (50 ml) solution of bis(tributyltin) (10.5 g, 18 mmol) was added a 1.63 M *n*-hexane solution of *n*-BuLi (11.0 ml, 18 mmol) at 0°C, and the mixture was stirred for 20 min. A 1.0 M *n*-hexane solution of Et_2AlCl (18 ml, 18 mmol) was added at −78°C and the mixture was stirred for 1 h. $Pd(PPh_3)_4$ (700 mg, 0.65 mmol) was added and the mixture was stirred for 30 min. A THF solution of **9** (3.3 g, 13 mmol) was added and the mixture was stirred for 26 h at r.t. Addition of aqueous NH_3, filtration extraction with ether, washing with water and brine, drying with anhydrous $MgSO_4$, and concentration under reduced pressure, and purification with column chromatography (silica gel; *n*-hexane/ethyl acetate, 8/1) gave **1** (2.4 g, 53%).

4.3. Procedure for Lewis acid mediated cyclization of **1**

The reaction mediated by $TiCl_4$ is representative. To a stirred solution of **1** (48.5 mg, 0.1 mmol) in 1 ml of dry CH_2Cl_2 under argon at −78°C was added $TiCl_4$ (1.0 M solution in CH_2Cl_2, 0.1 ml, 0.1 mmol), and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, extracted with ether, washed with brine, and dried over $MgSO_4$. The solvents were removed in vacuo, and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 8/1). The diastereomer ratio was determined by ^{1}H-NMR; a 92:8 mixture of **2** and **3** was obtained in 87% (17.1 mg).

4.4. Procedure for transition metal catalyzed cyclization of **1**

The reaction catalyzed by $(\eta^3\text{-}C_3H_5PdCl)_2$ in CH_3CN is representative. To a stirred solution of allyltributyltin (50 mg, 0.15 mmol) and **1** (48.5 mg, 0.1 mmol) in 1 ml of dry CH_3CN under argon at r.t. was added $(\eta^3\text{-}C_3H_5PdCl)_2$ (2 mg, 0.01 mmol), and the mixture was stirred for 5.5 h at 50°C. The reaction was quenched through short column (silica gel). Yield and ratios were determined by ^{1}H-NMR (*p*-xylene was used as an internal standard). 32% yield, 2:3 = 6:94.

4.5. Characterization of products

4.5.1. 7-Acetyl-7-methyl-8-oxo-1-tributylstannyl-2-nonene (**1**)

Colorless oil: ^{1}H-NMR ($CDCl_3$ 270 MHz) δ 5.54 (tt, J = 7.0, 7.0 Hz, 1H), 5.15 (tt, J = 7.0, 7.0 Hz, 1H), 2.08 (s, 6H), 1.99 (m, 2H), 1.82 (m, 2H), 1.52–0.80 (m, 31H), 1.30 (s, 3H). MS (EI) m/z 486 (M^+, 19), 429 ($M^+ - Bu$, 33), 291 (Bu_3Sn, 100). HRMS Calc. for $C_{24}H_{46}O_2Sn$ 486.2520, Found 486.2525.

4.5.2. (1R*, 2S*, 5R*)-2-Acetyl-1,2-dimethyl-5-vinylcyclohexanol (**2**)

Colorless oil: ^{1}H-NMR ($CDCl_3$ 500 MHz) δ 6.13 (ddd, J = 17.5, 10.5, 6.0 Hz, 1H), 5.09 (ddd, J = 10.0, 2.0, 2.0 Hz, 1H), 5.00 (ddd, J = 17.5, 2.0, 2.0 Hz, 1H), 4.55 (q, J = 1.2 Hz, 1H). 2.52 (ddd, J = 6.0, 6.0, 12.5 Hz, 1H), 2.23 (s, 3H), 2.07 (m, 1H), 1.77–1.70 (m, 2H), 1.57 (ddd, J = 3.8, 14.5, 14.5 Hz, 1H), 1.36 (dddd, J = 4.2, 12.0, 12.5, 12.5 Hz, 1H), 1.22 (s, 3H), 1.20 (m, 1H), 1.03 (d, J = 1.2 Hz, 3H). HRMS Calc. for $C_{12}H_{20}O_2$ 196.1463, Found 196.1473.

4.5.3. (1R*, 2S*, 5S*)-2-Acetyl-1,2-dimethyl-5-vinylcyclohexanol (**3**)

Colorless oil: ^{1}H-NMR ($CDCl_3$ 500 MHz) δ 5.92 (ddd, J = 17.0, 10.0, 8.5 Hz, 1H), 5.03 (ddd, J = 10.0, 2.2, 0.4 Hz, 1H), 4.99 (ddd, J = 17.0, 2.2, 0.8 Hz, 1H),

4.32 (s, 1H), 2.20 (s, 3H), 2.15 (ddd, $J = 4.0$, 8.5, 12.0 Hz, 1H), 2.05 (ddd $J = 13.0$, 13.0, 4.5 Hz, 1H), 1.75 (dddd, $J = 4.5$, 12.0, 12.5, 12.5 Hz, 1H), 1.65–1.58 (m, 2H), 1.45–1.38 (m, 2H), 1.30 (s, 3H), 1.13 (s, 3H). HRMS Calc. for $C_{12}H_{20}O_2$ 196.1463, Found 196.1460.

4.5.4. 3–Acetyl–3–methyl–2-oxo-8-nonene (**12**)

Colorless oil: ^{1}H-NMR ($CDCl_3$ 270 MHz) δ 5.77 (ddt, $J = 16.5$, 10.0, 6.5 Hz, 1H), 4.99 (ddt, $J = 16.5$, 1.7, 2.0 Hz, 1H), 4.94 (ddt, $J = 10.0$, 1.7, 2.0, 1H), 2.10 (s, 6H), 2.05 (dt, $J = 6.5$, 6.5 Hz, 2H), 1.83 (m, 2H), 1.41 (tt, $J = 7.5$, 7.5 Hz, 2H), 1.31 (s, 3H), 0.92 (t. $J = 7.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$ 75.45 MHz) δ 207.5, 138.4, 114.7, 66.7, 34.0, 33.3, 29.2, 26.5, 23.5, 17.9. MS (EI) m/z 196 (M^+, 1), 154 ($M^+ - CH_3CO$, 6), 43 (CH_3CO, 100). HRMS Calc. for $C_{24}H_{46}O_2Sn$ 196.1463, Found 196.1473.

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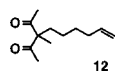
[6] Destannylated diketone **1 2** was obtained as a by-product.



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