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Acid-catalyzed intramolecular addition of a carboxy group to vinylsilanes

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Abstract

In the presence of a catalytic amount of $TsOH \cdot H_2O$ or $TiCl_4$, 5-silyl-4-pentenoic acids (**1**), namely vinylsilanes with a carboxy group, were smoothly cyclized to γ-lactones in good to high yields. The difference in the geometry of the carbon–carbon double-bond did not affect the reaction rate. The $TiCl_4$-catalyzed cyclization of the substrates bearing a phenyl or alkyl group at the homoallylic position showed moderate *cis*-selectivity, while introduction of a substituent into the allylic position led to high *trans*-selectivity.

Keywords: Acid Catalyst; Cyclization; Vinylsilane; γ-lactone

1. Introduction

The protonation of vinylsilanes is known to take place at the α-position to form β-silylcarbenium ions hyperconjugatively stabilized by the adjacent carbon–silicon bond [1]. The carbenium ions are thermodynamically stable; however, they are subject to desilylation leading to alkenes by nucleophilic attack of the counteranion or a solvent molecule to silicon. Previously, we have reported that the carbenium ions derived from vinylsilanes can be efficiently trapped with internal oxygen and nitrogen nucleophiles (Scheme 1) [2–4]. The acid-catalyzed cyclizations of vinylsilanes bearing a hydroxy or amino group are valuable for stereoselective construction of five- and six-membered cyclic ethers and amines.

Intramolecular addition of a carboxy group to alkenes under catalysis by a strong acid provides a straightforward route to γ- and δ-lactones [5,6]. However, the cyclization of alkenoic acids requires high concentration of the acid catalyst, which causes the formation of cyclic α-enones, skeletal rearrangements, and epimerization of the initially formed stereogenic center. Thus, this method is not necessarily suitable for efficient and stereoselective synthesis of lactones. On the basis of our previous studies, we expected a carboxy group to be reactive to an internal vinylsilane under milder conditions, and our efforts were directed toward the development of a highly efficient route to substituted lactones using vinylsilanes. We herein report the acid-catalyzed cyclization of 5-silyl-4-pentenoic acids (**1**) to γ-lactones and its stereochemical aspects.

2. Results and discussion

2.1. Cyclization of (*Z*)- and (*E*)-5-benzyldimethylsilyl-4-pentenoic acids (*1a*)

In the presence of $TsOH \cdot H_2O$ (5 mol%), (*Z*)-vinylsilane (**1a**) was slowly cyclized to γ-lactone (**2a**) at room temperature (entry 1 in Table 1). Increasing both the amount of the acid catalyst and the reaction tempera-

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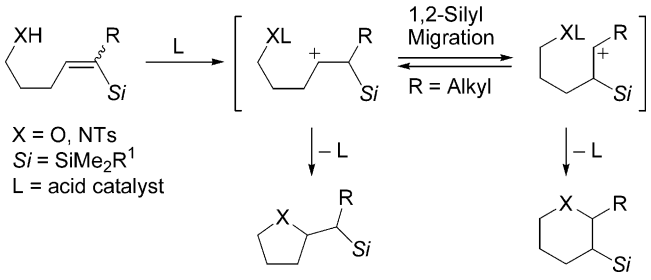
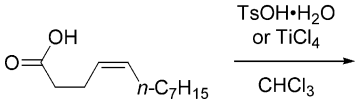


Scheme 1.

ture was fairly effective in promoting the cyclization. Thus, the reaction with 10 mol% of the catalyst at 60 °C was completed within 12 h to give **2a** in 92% yield (entry 3). $TiCl_4$ effectively promoted the cyclization even at room temperature, although a certain amount of desilylation product **3** was formed (entry 4). (*E*)-Vinylsilane (**1a**) also was efficiently converted into **2a** under these acidic conditions (entries 5 and 6). Unexpectedly, the reactivity of (*E*)-**1a** was similar to that of (*Z*)-**1a**. This result stands in sharp contrast with our previous observation that (*Z*)-vinylsilanes are more reactive than the corresponding *E*-isomers in acid-catalyzed intramolecular addition of a hydroxy group [2,4].

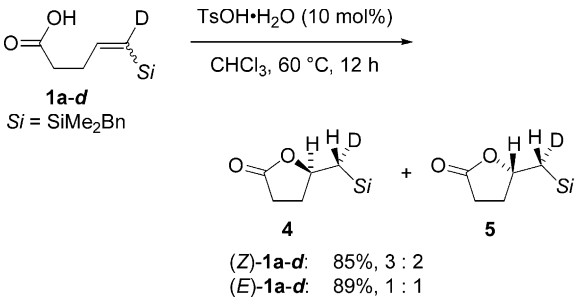
To make sure of the directing effect of the silyl group, we attempted the cyclization of (*Z*)-4-dodecenoic acid under similar conditions (Eq. (1)). As a result, no cyclized product was obtained and the substrate was intact. This result clearly shows that the silyl group of **1a** plays a crucial role in accelerating the acid-catalyzed cyclization.



(1)

2.2. Stereochemistry in intramolecular addition of a carboxy group

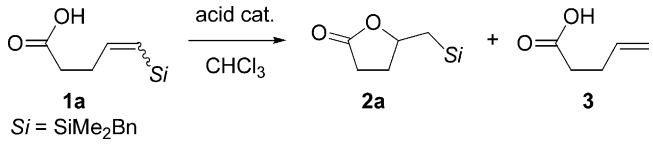
Our previous study disclosed that acid-catalyzed intramolecular addition of a hydroxy group to a vinylsilane proceeds in a stereospecific *syn* manner (3a). To gain stereochemical insight into the present reaction, α-deuterated (*Z*)- and (*E*)-vinylsilanes (**1a**–**1*d***) were used. In contrast with the previous result, the TsOH-catalyzed cyclization of **1a**–**1*d*** gave a diastereomeric mixture of **4** and **5** with low or no *syn*-addition selectivity.



(2)

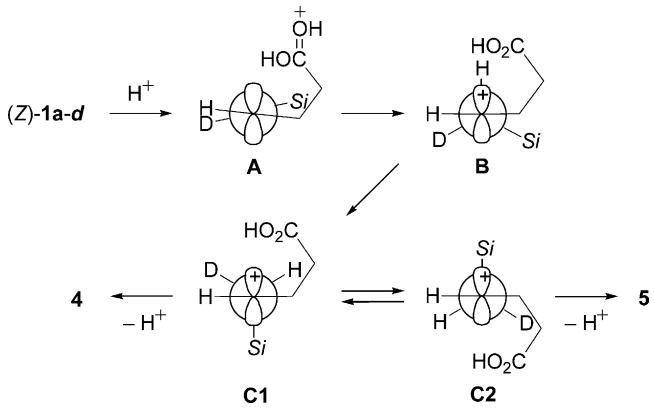
A plausible reaction mechanism for the cyclization of (*Z*)-**1a**–**1*d*** is as follows (Scheme 2): (1) a proton attaches to the carboxy group; (2) the proton on the oxygen atom shifts to the α-carbon; (3) the resultant β-silylcarbenium ion **B**, which may be a transition state, turns to its conformer **C1** stabilized by σ–π conjugation at the least motion [7]; (4) **C1** can be converted into conformer **C2** reversibly; (5) intramolecular attack of the carboxy oxygen from the side opposite to the silyl group gives *syn*-addition product **4** from **C1** or *anti*-addition product **5** from **C2**. Since (*Z*)-**1a** is similar in reactivity to (*E*)-**1a**, the rate-controlling step would be the last (cyclization) step rather than the intramolecular protonation step leading to **C1** and **C2** through **B**. On the other hand, in the case with vinylsilanes bearing a

Table 1
Optimization of reaction conditions for acid-catalyzed cyclization of vinylsilanes **1a** [a]



Entry	Substrate	Catalyst (mol%)	Temperature (°C)	Time (h)	Yield of **2a** (%)
1	(*Z*)-**1a**	$TsOH·H_2O$ (5)	rt	48	31 [b]
2	(*Z*)-**1a**	$TsOH·H_2O$ (5)	60	36	80
3	(*Z*)-**1a**	$TsOH·H_2O$ (10)	60	12	92
4	(*Z*)-**1a**	$TiCl_4$ (5)	rt	16	80
5	(*E*)-**1a**	$TsOH·H_2O$ (10)	60	12	92
6	(*E*)-**1a**	$TiCl_4$ (5)	rt	16	77

[a] All reactions were carried out with **1a** (0.50 mmol) in $CHCl_3$ (2.5 ml).
[b] The substrate (*Z*)-**1a** was recovered in 64% yield.



Scheme 2.

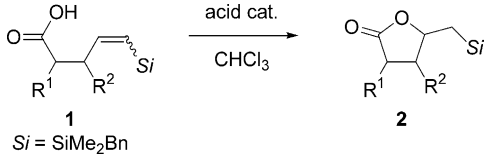
hydroxy group, a marked difference in reactivity between (*Z*)- and (*E*)-isomers suggests that the cyclization rate should be controlled by the protonation step 3a. The change of rate-controlling step is attributable to low nucleophilicity of the carboxy group, which may decelerate the last step. The low selectivity toward *syn*-addition of the carboxy group supports the relatively slow cyclization step because the deceleration would provide enough time for the rotation of **C1** to **C2**.

2.3. Stereoselective synthesis of disubstituted γ-lactones

The acid-catalyzed cyclization of 2-substituted 5-silyl-4-pentenoic acids (**1b**–**1d**) gave α,γ-disubstituted γ-lactones (**2b**–**2d**) in good yields with moderate selectivity with respect to the formation of the isomer with the side chains *cis* to each other (entries 1–8 in Table 2). The use of $TsOH \cdot H_2O$ at 60 °C led to higher yields of **2**, while the $TiCl_4$-catalyzed reaction at room temperature showed higher *cis*-diastereoselectivity. The presence of a phenyl substituent in the case of **1d** brought about a rapid cyclization (entry 7). Lowering the reaction temperature was ineffective in improving the stereoselectivity (entry 8). The geometry of the double-bond did not affect the sense of diastereoselectivity (entries 5 and 6).

We next examined the cyclization of 3-substituted (*Z*)-5-silyl-4-pentenoic acids (**1e** and **1f**) (entries 9–13 in Table 2). The substitution at the allylic position decreased the cyclization rate; however, high diastereoselectivity toward the formation of *trans*-β,γ-disubstituted γ-lactones (**2e** and **2f**) was observed in the $TiCl_4$-catalyzed system. The use of an increased amount of $TiCl_4$ achieved efficient and highly stereoselective transformation (entries 10 and 12). The cyclization of (*E*)-**1f** proceeded efficiently under the same conditions

Table 2
Stereoselective cyclization of vinylsilanes **1** [a]



1 *Si* = $SiMe_2Bn$ **2**

Entry	Substrate			Method	Temperature (°C)	Time (h)	Yield (%)	*cis*:*trans* [b]
	R^1	R^2						
1	Hex	H	(*Z*)-**1b**	$TsOH \cdot H_2O$ (10)	60	20	89	61:39
2			(*Z*)-**1b**	$TiCl_4$ (5)	rt	22	74	78:22
3	*i*-Pr	H	(*Z*)-**1c**	$TsOH \cdot H_2O$ (10)	60	12	92	60:40
4			(*Z*)-**1c**	$TiCl_4$ (5)	rt	16	85	83:17
5			(*E*)-**1c**	$TsOH \cdot H_2O$ (10)	60	12	95	77:23
6			(*E*)-**1c**	$TiCl_4$ (5)	rt	12	80	78:22
7	Ph	H	(*Z*)-**1d**	$TiCl_4$ (5)	rt	1	82	71:29
8			(*Z*)-**1d**	$TiCl_4$ (5)	0	12	81	69:31
9	H	Pen	(*Z*)-**1e**	$TsOH \cdot H_2O$ (10)	60	21	72	13:87
10			(*Z*)-**1e**	$TiCl_4$ (10)	rt	16	79	< 1:99
11	H	Ph	(*Z*)-**1f**	$TsOH \cdot H_2O$ (10)	60	48	63 [c]	7:93
12			(*Z*)-**1f**	$TiCl_4$ (10)	rt	16	83	< 1:99
13			(*E*)-**1f**	$TiCl_4$ (10)	rt	16	88	18:82

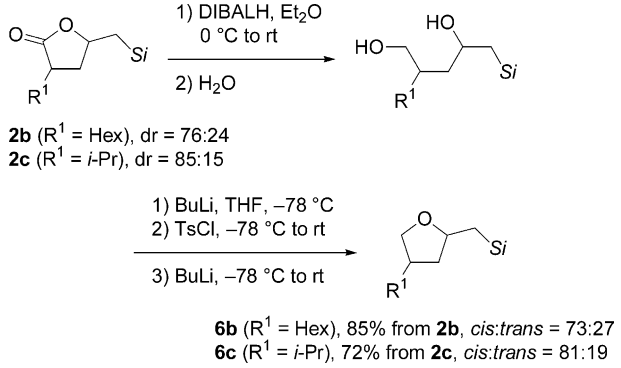
[a] All reactions were carried out with **1a** (0.50 mmol) in $CHCl_3$ (2.5 ml).
[b] Determined by ^{1}H-NMR analysis.
[c] The substrate was recovered in 17% yield.

although the *trans*-diastereoselectivity was diminished in some degree (entry 13).

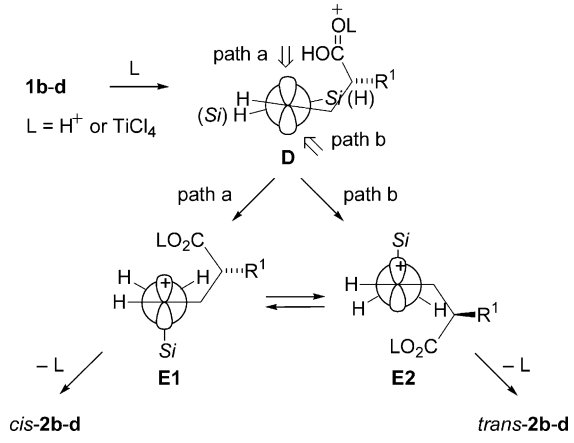
To determine the relative configurations of γ-lactones **2b** and **2c**, they were converted into the corresponding tetrahydrofurans **6b** and **6c** as shown in Scheme 3. Eliel et al. [8] reported that, in ^{13}C-NMR spectra of 2,4-disubstituted tetrahydrofurans, the signals of C-2, C-3 and C-4 of the *cis*-isomers appear at lower field than those of the *trans*-isomers. On the basis of this criterion, the major isomers of **6b** and **6c** were determined to possess the *cis*-configuration. The stereochemical assignment of **2d** was based on NOE experiments of the major isomer. Irradiation of one β-proton on the ring showed considerable enhancements (> 10%) of both α- and γ-protons. This observation agrees with the *cis*-configuration of the major isomer. The relative configurations of **2e** and **2f** were deduced from their ^{1}H-NMR data. In the *trans*-isomers, β- and γ-protons on the ring are shielded by the vicinal C–C bond, and their signals should be observed at higher field than those of the *cis*-isomers [9]. Judging from this consideration, the major isomers of **2e** and **2f** have the *trans*-configuration.

2.4. Origin of stereoselectivity

On the basis of Scheme 2, a plausible mechanism for the cyclization of **1b**–**1d** is shown in Scheme 4, in which the β-silylcarbenium ion intermediate corresponding to **B** is omitted for simplicity. The β-silylcarbenium ions **E1** and **E2** are generated by internal protonation from the top (path a) and bottom (path b) sides, respectively. When the rotation between **E1** and **E2** is much slower than their cyclizations, the diastereoselectivity is determined in the protonation step. In this situation, the selectivity would be strongly affected by the geometry of the C–C double bond as in the cyclization of vinylsilanes bearing a hydroxy group (3a). When the rotation is much faster, the diastereoselectivity depends on the relative cyclization rates of **E1** and **E2**, and the alkene geometry does not affect the stereochemical outcome. Judging from the low *syn*-addition selectivity with (*Z*)-**1a**–**1*d*** and a slight influence of the alkene geometry on



Scheme 3.

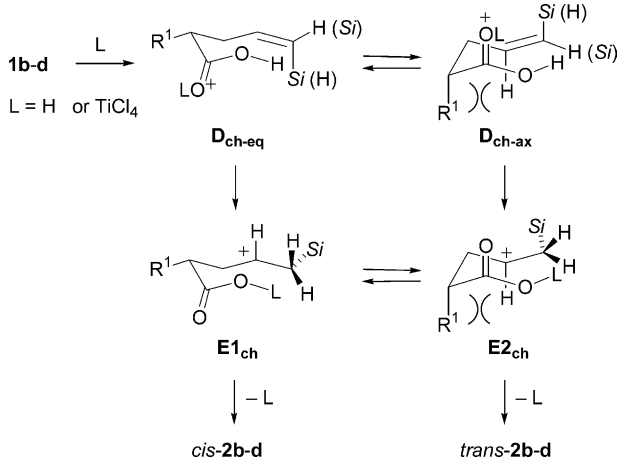


Scheme 4.

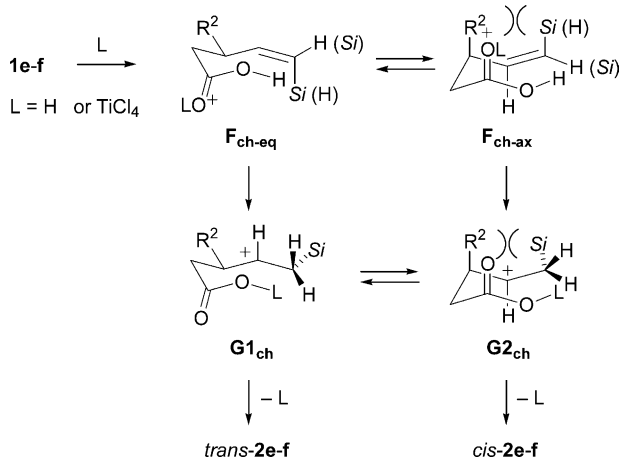
the diastereoselectivity, the present situation is in the middle of these two extremes, i.e., the rotation rates of **E1** and **E2** are comparable with their cyclization rates.

The intramolecular protonation of **D** would proceed mainly via energetically favorable conformation $\mathbf{D_{ch\text{-}eq}}$ to give β-silylcarbenium ion **E1** (Scheme 5). A part of **E1** is converted into **E2** reversibly. The intermediates **E1** and **E2** are cyclized to *cis*- and *trans*-**2b**–**2d**, respectively, probably via chair-like conformations $\mathbf{E1_{ch}}$ and $\mathbf{E2_{ch}}$. Since $\mathbf{E2_{ch}}$ is energetically less favored than $\mathbf{E1_{ch}}$ due to the presence of a pseudoaxial substituent, the cyclization of **E1** would be faster than that of **E2**. Accordingly, the *cis*-selective cyclization of **1b**–**1d** is attributable to the diastereoface-selective protonation and the fast cyclization of **E1**.

Similarly, the *trans*-selectivity with **1e** and **1f** can be rationalized by selective formation of β-silylcarbenium ion **G1** and its fast cyclization to *trans*-**2e** and **2f** (Scheme 6). The high diastereoselectivity would arise from 1,3-allylic strains by the pseudoaxial substituents (R^2) of $\mathbf{F_{ch\text{-}ax}}$ and $\mathbf{G2_{ch}}$, which severely destabilize these conformations [10].



Scheme 5.



Scheme 6.

3. Experimental

Unless otherwise noted, all reactions and distillations were carried out under N_2. Carboxylic acids **1** were synthesized from the corresponding alcohols by oxidation with PDC [11]. For the preparation of the starting alcohols, see the supporting information of Ref [3a]. A typical procedure for the synthesis of **1** is described below. Solvents were dried by distillation from sodium metal/benzophenone ketyl (THF, Et_2O), $CaCl_2$–$NaHCO_3$ (EtOH-free $CHCl_3$) and CaH_2 (DMF). $TiCl_4$ was simply distilled and stored as a CH_2Cl_2 solution (1.0 M). All other commercially obtained reagents were used as received.

Infrared spectra were measured on a JASCO FT/IR-230 spectrophotometer. ^{1}H-NMR spectra at 270 MHz and ^{13}C-NMR spectra at 67.7 MHz in $CHCl_3$ were recorded on a JEOL JNM-EX-270 spectrometer. The chemical shifts (δ) are reported with reference at 0.00 ppm (Me_4Si) or 7.26 ppm ($CHCl_3$) for the proton and at 77.00 ppm (centered on the signal of $CDCl_3$) for the carbon. The proton of the carboxy group of **1** was not detected due to broadening. Mass spectra were measured (by EI method) on a Shimadzu GCMS-QP5050 instrument. Elemental analyses were performed by the Analysis Center of the University of Tsukuba.

3.1. Typical procedure for synthesis of vinylsilanes *1*

A DMF (200 ml) solution of (*Z*)-5-benzyldimethylsilyl-4-penten-1-ol (7.00 g, 30.0 mmol) was dropwise added to a DMF (45 ml) solution of pyridinium dichromate (PDC, 39.0 g, 105 mmol) at room temperature [11]. After being stirred for 20 h, the resultant mixture was treated with water (100 ml) and extracted with *t*-BuOMe (100 ml). The extract was washed with water (3 × 50 ml). The aqueous layer was extracted with *t*-BuOMe (2 × 50 ml). The combined organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica gel column chromatography gave (*Z*)-5-benzyldimethylsilyl-4-pentenoic acid (**1a**, 4.70 g, 18.8 mmol) in 63% yield.

3.1.1. (*Z*)-5-Benzyldimethylsilyl-4-pentenoic acid ((*Z*)-*1a*)

b.p. 150 °C (bath temp., 0.4 Torr). IR (neat) 2920 (br), 1716 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.12 (s, 6H), 2.17 (s, 2H), 2.34–2.39 (m, 4H), 5.54 (d, $J = 14.0$ Hz, 1H), 6.29 (dm, $J = 14.0$ Hz, 1H), 7.00–7.09 (m, 3H), 7.18–7.27 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −1.81 ($CH_3 \times 2$), 26.47 (CH_2), 28.45 (CH_2), 33.87 (CH_2), 124.00 (CH), 128.06 (CH × 2), 128.11 (CH × 2), 128.89 (CH), 139.73 (C), 146.85 (CH), 179.26 (C) ppm; MS *m*/*z* (rel. intensity) 157 [M^+–$PhCH_2$, 17], 75 [100]. Anal. Calcd. for $C_{14}H_{20}O_2Si$: C, 67.69; H, 8.12. Found: C, 67.44; H, 8.28%.

3.1.2. (*E*)-5-Benzyldimethylsilyl-4-pentenoic acid ((*E*)-*1a*)

b.p. 160 °C (bath temp., 0.4 Torr). IR (neat) 2950 (br), 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.02 (s, 6H), 2.10 (s, 2H), 2.36–2.47 (m, 4H), 5.66 (d, $J = 18.6$ Hz, 1H), 5.99 (dm, $J = 18.6$ Hz, 1H), 6.96–7.08 (m, 3H), 7.17–7.24 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −3.44 ($CH_3 \times 2$), 26.04 (CH_2), 31.11 (CH_2), 32.98 (CH_2), 123.92 (CH), 128.03 (CH × 2), 128.19 (CH × 2), 129.18 (CH), 139.91 (C), 145.25 (CH), 179.65 (C) ppm. Anal. Calcd. for $C_{14}H_{20}O_2Si$: C, 67.69; H, 8.12. Found: C, 67.59; H, 8.06%.

3.1.3. (*Z*)-4-Dodecenoic acid

b.p. 150 °C (bath temp., 0.4 Torr). IR (neat) 2925 (br), 1712 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, $J = 6.7$ Hz, 3H), 1.27 (br s, 10H), 2.04 (q, $J = 6.6$ Hz, 2H), 2.32–2.44 (m, 4H), 5.31–5.49 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ 14.07 (CH_3), 22.49 (CH_2), 22.65 (CH_2), 27.19 (CH_2), 29.19 (CH_2), 29.24 (CH_2), 29.60 (CH_2), 31.84 (CH_2), 34.20 (CH_2), 126.87 (CH), 131.89 (CH), 179.89 (C) ppm. Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.66; H, 11.16%.

3.1.4. (*Z*)-5-Benzyldimethylsilyl-4-deuterio-4-pentenoic acid ((*Z*)-*1a*–*1d*)

^{1}H-NMR ($CDCl_3$) δ 0.12 (s, 6H), 2.17 (s, 2H), 2.34–2.39 (m, 4H), 6.28 (br s, 1H), 6.99–7.09 (m, 3H), 7.17–7.26 (m, 2H) ppm. Anal. Calcd. for $C_{14}H_{19}DO_2Si$: C, 67.42; H, 7.68; D, 0.81. Found: C, 67.67; H, 7.67; D, 0.80%.

3.1.5. (*E*)-5-Benzyldimethylsilyl-4-deuterio-4-pentenoic acid ((*E*)-*1a*–*1d*)

^{1}H-NMR ($CDCl_3$) δ 0.02 (s, 6H), 2.10 (s, 2H), 2.36–2.47 (m, 4H), 5.95–6.00 (m, 1H), 6.95–7.09 (m, 3H), 7.16–7.23 (m, 2H) ppm. Anal. Calcd. for $C_{14}H_{19}DO_2Si$:

C, 67.42; H, 7.68; D, 0.81. Found: C, 67.53; H, 7.75; D, 0.81%.

3.1.6. (*Z*)-5-Benzyldimethylsilyl-2-hexyl-4-pentenoic acid ((*Z*)-**1b**)

b.p. 160 °C (bath temp., 0.4 Torr). IR (neat) 2927 (br), 1704 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.10 (s, 6H), 0.88 (t, $J = 6.7$ Hz, 3H), 1.27 (br s, 8H), 1.37–1.68 (m, 2H), 2.15 (s, 2H), 2.16–2.43 (m, 3H), 5.55 (d, $J = 14.0$ Hz, 1H), 6.27 (ddd, $J = 14.0$, 7.4, 6.6 Hz, 1H), 6.99–7.09 (m, 3H), 7.17–7.23 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −1.74 ($CH_3 \times 2$), 14.04 (CH_3), 22.57 (CH_2), 26.58 (CH_2), 27.24 (CH_2), 29.14 (CH_2), 31.62 (CH_2), 31.71 (CH_2), 35.70 (CH_2), 45.63 (CH), 124.01 (CH), 128.10 (CH × 2), 128.20 (CH × 2), 129.45 (CH), 139.87 (C), 145.86 (CH), 182.44 (C) ppm. Anal. Calcd. for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70. Found: C, 72.27; H, 9.41%.

3.1.7. (*Z*)-5-Benzyldimethylsilyl-2-isopropyl-4-pentenoic acid ((*Z*)-**1c**)

b.p. 162 °C (bath temp., 0.4 Torr). IR (neat) 2962 (br), 1704 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.11 (s, 6H), 0.95 (d, $J = 6.8$ Hz, 6H), 1.81–1.95 (m, 1H), 2.11–2.38 (m, 5H) including 2.15 (s, 2H), 5.53 (d, $J = 14.2$ Hz, 1H), 6.27 (dt, $J = 14.2$, 7.2 Hz, 1H), 6.99–7.09 (m, 3H), 7.17–7.23 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −1.79 ($CH_3 \times 2$), 20.01 (CH_3), 20.28 (CH_3), 26.59 (CH_2), 30.22 (CH), 33.06 (CH_2), 52.58 (CH), 123.98 (CH), 128.09 (CH × 2), 128.20 (CH × 2), 129.15 (CH), 139.88 (C), 146.17 (CH), 181.67 (C) ppm; MS *m*/*z* (rel. intensity) 199 [M^+ – $PhCH_2$, 64], 75 [100]. Anal. Calcd. for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02. Found: C, 70.09; H, 8.99%.

3.1.8. (*E*)-5-Benzyldimethylsilyl-2-isopropyl-4-pentenoic acid ((*E*)-**1c**)

IR (neat) 2960 (br), 1707 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.967 (d, $J = 6.8$ Hz, 3H), 0.973 (d, $J = 6.9$ Hz, 3H), 1.84–1.97 (m, 1H), 2.09 (s, 2H), 2.22–2.42 (m, 3H), 5.68 (dt, $J = 18.6$, 1.3 Hz, 1H), 5.95 (dt, $J = 18.6$, 6.3 Hz, 1H), 6.96–7.08 (m, 3H), 7.16–7.22 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −3.43 (CH_3), −3.39 (CH_3), 20.07 (CH_3), 20.14 (CH_3), 26.04 (CH_2), 29.97 (CH), 36.33 (CH_2), 51.81 (CH), 123.89 (CH), 128.05 (CH × 2), 128.21 (CH × 2), 130.50 (CH), 139.98 (C), 144.76 (CH), 181.39 (C) ppm.

3.1.9. (*Z*)-5-Benzyldimethylsilyl-2-phenyl-4-pentenoic acid ((*Z*)-**1d**)

b.p. 190 °C (bath temp., 0.4 Torr). IR (neat) 2954 (br), 1707 cm^{-1}; ^{1}H-NMR (C_6D_6) δ 0.05 (s, 3H), 0.06 (s, 3H), 2.02 (s, 2H), 2.43–2.54 (m, 1H), 2.80–2.91 (m, 1H), 3.50 (t, $J = 7.6$ Hz, 1H), 5.50 (d, $J = 14.2$ Hz, 1H), 6.20 (dt, $J = 14.2$, 7.2 Hz, 1H), 6.91–7.21 (m, 10H) ppm; ^{13}C-NMR (C_6D_6) δ −1.69 ($CH_3 \times 2$), 26.66 (CH_2), 37.21 (CH_2), 52.05 (CH), 124.48 (CH), 127.76 (CH), 128.35 (CH × 2), 128.48 (CH × 2), 128.54 (CH × 2), 128.97 (CH × 2), 130.10 (CH), 138.17 (C), 140.00 (C), 145.68 (CH), 180.44 (C) ppm. Anal. Calcd. for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45. Found: C, 73.63; H, 7.65%.

3.1.10. (*Z*)-5-Benzyldimethylsilyl-3-pentyl-4-pentenoic acid ((*Z*)-**1e**)

b.p. 156 °C (bath temp., 0.4 Torr). IR (neat) 2927 (br), 1709 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.11 (s, 6H), 0.87 (t, $J = 6.7$ Hz, 3H), 1.20–1.45 (m, 8H), 2.15 (s, 2H), 2.21 (dd, $J = 14.8$, 7.2 Hz, 1H), 2.33 (dd, $J = 14.8$, 6.8 Hz, 1H), 2.59–2.73 (m, 1H), 5.50 (d, $J = 14.0$ Hz, 1H), 6.05 (dd, $J = 14.0$, 10.2 Hz, 1H), 6.99–7.09 (m, 3H), 7.17–7.23 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −1.68 ($CH_3 \times 2$), 14.01 (CH_3), 22.51 (CH_2), 26.68 (CH_2), 26.84 (CH_2), 31.90 (CH_2), 34.87 (CH_2), 39.89 (CH), 40.35 (CH_2), 123.98 (CH), 128.06 (CH × 2), 128.13 (CH), 128.19 (CH × 2), 139.90 (C), 151.51 (CH), 179.28 (C) ppm. Anal. Calcd. for $C_{19}H_{30}O_2Si$: C, 71.65; H, 9.49. Found: C, 71.78; H, 9.42%.

3.1.11. (*Z*)-5-Benzyldimethylsilyl-3-phenyl-4-pentenoic acid ((*Z*)-**1f**)

b.p. 152 °C (bath temp., 0.4 Torr). IR (neat) 2956 (br), 1709 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.15 (s, 3H), 0.16 (s, 3H), 2.17 (s, 2H), 2.58 (dd, $J = 15.3$, 7.4 Hz, 1H), 2.74 (dd, $J = 15.3$, 7.6 Hz, 1H), 3.97 (dt, $J = 10.4$, 7.4 Hz, 1H), 5.55 (d, $J = 14.0$ Hz, 1H), 6.43 (dd, $J = 14.0$, 10.4 Hz, 1H), 6.96–7.08 (m, 3H), 7.16–7.33 (m, 7H) ppm; ^{13}C-NMR ($CDCl_3$) δ −1.70 ($CH_3 \times 2$), 26.51 (CH_2), 41.32 (CH_2), 44.93 (CH), 124.03 (CH), 126.65 (CH), 126.99 (CH × 2), 128.11 (CH × 2), 128.19 (CH × 2), 128.35 (CH), 128.68 (CH × 2), 139.71 (C), 142.41 (C), 149.59 (CH), 178.08 (C) ppm. Anal. Calcd. for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45. Found: C, 73.88; H, 7.72%.

3.1.12. (*E*)-5-Benzyldimethylsilyl-3-phenyl-4-pentenoic acid ((*E*)-**1f**)

IR (KBr) 2954 (br), 1701 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.02 (s, 6H), 2.09 (s, 2H), 2.71 (dd, $J = 15.6$, 7.6 Hz, 1H), 2.77 (dd, $J = 15.6$, 7.7 Hz, 1H), 3.85 (td, $J = 7.7$, 6.2 Hz, 1H), 5.65 (dd, $J = 18.6$, 1.5 Hz, 1H), 6.08 (dd, $J = 18.6$, 6.3 Hz, 1H), 6.96–7.33 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) δ −3.46 ($CH_3 \times 2$), 26.01 (CH_2), 39.69 (CH_2), 47.33 (CH), 123.93 (CH), 126.72 (CH), 127.63 (CH × 2), 128.03 (CH × 3), 128.19 (CH × 2), 128.57 (CH × 2), 139.78 (C), 141.92 (C), 148.36 (CH), 178.39 (C) ppm.

3.2. Typical procedure for cyclization of vinylsilanes **1**

To a $CHCl_3$ (2.5 ml) solution of (*Z*)-**1a** (124 mg, 0.500 mmol) was added $TiCl_4$ (1 M in CH_2Cl_2, 25 μl, 25 μmol) at room temperature. The mixture was stirred for 16 h. The resultant mixture was treated with saturated aqueous $NaHCO_3$ (20 ml) and extracted with *t*-BuOMe

(3 × 10 ml). The extract was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica gel column chromatography gave 5-benzyldimethylsilyl-4-pentanolide (**2a**, 99.2 mg, 0.400 mmol) in 80% yield. When $TsOH \cdot H_2O$ was used as the catalyst, it was quickly added to a solution of (*Z*)-**1a** under the atmosphere and N_2 was passed through the flask to displace the air.

3.2.1. 5-Benzyldimethylsilyl-4-pentanolide (*2a*)

b.p. 142 °C (bath temp., 0.4 Torr). IR (neat) 1768, 1171 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.09 (s, 3H), 0.96 (dd, $J = 14.5$, 7.6 Hz, 1H), 1.22 (dd, $J = 14.5$, 7.2 Hz, 1H), 1.69–1.84 (m, 1H), 2.16 (s, 2H), 2.23–2.36 (m, 1H), 2.46–2.59 (m, 2H), 4.53–4.64 (m, 1H), 6.98–7.11 (m, 3H), 7.19–7.25 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −2.98 ($CH_3 \times 2$), 22.68 (CH_2), 25.69 (CH_2), 29.28 (CH_2), 31.20 (CH_2), 79.70 (CH), 124.11 (CH), 127.95 (CH × 2), 128.15 (CH × 2), 139.22 (C), 176.93 (C) ppm; MS *m*/*z* (rel. intensity) 157 [M^+–$PhCH_2$, 57], 75 [100]. Anal. Calcd. for $C_{14}H_{20}O_2Si$: C, 67.69; H, 8.12. Found: C, 67.69; H, 7.96%.

3.2.2. 5-Benzyldimethylsilyl-5-deuterio-4-pentanolide (*4* for the (*4R*, 5S**)-isomer and *5* for the (*4R*, 5R**)-isomer, *4*:*5* = 3:2)

^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.09 (s, 3H), 0.94 (dt, $J = 7.6$, 2.0 Hz, 0.6H), 1.20 (br d, $J = 7.1$ Hz, 0.4H), 1.69–1.84 (m, 1H), 2.15 (s, 2H), 2.23–2.36 (m, 1H), 2.45–2.59 (m, 2H), 4.54–4.62 (m, 1H), 6.98–7.11 (m, 3H), 7.19–7.25 (m, 2H) ppm. Anal. Calcd. for $C_{14}H_{19}DO_2Si$: C, 67.42; H, 7.68; D, 0.81. Found: C, 67.55; H, 7.69, D, 0.80%. The relative configurations of **4** and **5** were determined by stereo-defined desilylation with $BF_3 \cdot OEt_2$ [12] followed by ^{1}H-NMR analysis of the resultant deuterated alkene **3**.

3.2.3. 5-Benzyldimethylsilyl-2-hexyl-4-pentanolide (*2b*, *cis*:*trans* = 78:22)

b.p. 150 °C (bath temp., 0.09 Torr). IR (neat) 1768, 1165 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.86–0.99 (m, 4H), 1.12–1.47 (m, 11H), 1.74–2.07 (m, 1.22H), 2.15 (s, 2H), 2.38 (ddd, $J = 12.2$, 8.4, 5.1 Hz, 0.78H), 2.48–2.63 (m, 1H), 4.42 (dddd, $J = 10.2$, 7.7, 6.9, 5.3 Hz, 0.78H), 4.59 (qd, $J = 7.1$, 5.8 Hz, 0.22H), 6.98–7.11 (m, 3H), 7.18–7.25 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) for the major isomer δ −2.86 ($CH_3 \times 2$), 13.96 (CH_3), 22.47 (CH_2), 22.68 (CH_2), 25.81 (CH_2), 27.23 (CH_2), 28.93 (CH_2), 30.11 (CH_2), 31.51 (CH_2), 38.39 (CH_2), 41.58 (CH), 77.45 (CH), 124.16 (CH), 128.01 (CH × 2), 128.20 (CH × 2), 139.29 (C), 178.73 (C) ppm, for the minor isomer δ −2.94 ($CH_3 \times 2$), 22.80 (CH_2), 25.78 (CH_2), 28.90 (CH_2), 30.56 (CH_2), 36.52 (CH_2), 39.57 (CH), 77.28 (CH), 139.32 (C), 179.14 (C) ppm; MS *m*/*z* (rel. intensity) 317 [M^+–CH_3, 1.3], 241 [M^+–$PhCH_2$, 91], 75 [100]. Anal. Calcd. for $C_{20}H_{32}O_2Si$: C, 72.22; H, 9.70. Found: C, 72.33; H, 9.48%.

3.2.4. 5-Benzyldimethylsilyl-2-isopropyl-4-pentanolide (*2c*, *cis*:*trans* = 83:17)

b.p. 140 °C (bath temp., 0.4 Torr). IR (neat) 1766, 1171 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.09 (s, 3H), 0.88–1.03 (m, 7H) including 0.89 (d, $J = 6.8$ Hz) and 1.01 (d, $J = 6.8$ Hz), 1.16 (dd, $J = 14.5$, 7.6 Hz, 0.17H), 1.22 (dd, $J = 14.5$, 3.3 Hz, 0.83H), 1.52 (td, $J =$ 12.5, 10.2 Hz, 0.83H), 1.80 (ddd, $J = 13.0$, 9.7, 5.6 Hz, 0.17H), 2.09–2.23 (m, 4H) including 2.15 (s), 2.49–2.59 (m, 1H), 4.40 (dddd, $J = 10.4$, 7.6, 6.9, 5.4 Hz, 0.83H), 4.55 (qd, $J = 7.6$, 5.6 Hz, 0.17H), 6.98–7.11 (m, 3H), 7.19–7.25 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) for the major isomer δ −2.84 (CH_3), −2.81 (CH_3), 18.16 (CH_3), 20.65 (CH_3), 22.66 (CH_2), 25.85 (CH_2), 27.25 (CH), 33.59 (CH_2), 47.66 (CH), 77.08 (CH), 124.19 (CH), 128.06 (CH × 2), 128.23 (CH × 2), 139.34 (C), 177.81 (C) ppm, for the minor isomer δ −2.90 (CH_3), 18.67 (CH_3), 20.48 (CH_3), 23.27 (CH_2), 28.54 (CH), 32.62 (CH_2), 45.70 (CH), 77.41 (CH), 178.34 (C) ppm; MS *m*/*z* (rel. intensity) 275 [M^+–CH_3, 1.4], 199 [M^+–$PhCH_2$, 66], 75 [100]. Anal. Calcd. for $C_{17}H_{26}O_2Si$: C, 70.31; H, 9.02. Found: C, 70.18; H, 8.94%.

3.2.5. 5-Benzyldimethylsilyl-2-phenyl-4-pentanolide (*2d*, *cis*:*trans* = 71:29)

b.p. 180 °C (bath temp., 0.4 Torr). IR (neat) 1768, 1161 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.09 (s, 2.1H), 0.10 (s, 0.9H), 0.11 (s, 3H), 1.00 (dd, $J = 14.3$, 7.4 Hz, 0.29H), 1.05 (dd, $J = 14.3$, 7.7 Hz, 0.71H), 1.27 (dd, $J = 14.3$, 7.1 Hz, 0.71H), 1.32 (dd, $J = 14.3$, 6.9 Hz, 0.29H), 1.96 (td, $J = 12.7$, 10.4 Hz, 0.71H), 2.18 (s, 2H), 2.26 (ddd, $J =$ 13.0, 9.2, 6.1 Hz, 0.29H), 2.48 (dt, $J = 13.0$, 6.6 Hz, 0.29H), 2.71 (ddd, $J = 12.7$, 8.4, 5.1 Hz, 0.71H), 3.84 (dd, $J = 12.7$, 8.4 Hz, 0.71H), 3.89 (dd, $J = 9.2$, 6.4 Hz, 0.29H), 4.57 (dddd, $J = 10.4$, 7.6, 6.9, 5.1 Hz, 0.71H), 4.73 (quint, $J = 6.7$ Hz, 0.29H), 6.99–7.40 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) for the major isomer δ −2.75 ($CH_3 \times 2$), 22.63 (CH_2), 25.89 (CH_2), 41.46 (CH_2), 47.98 (CH), 77.47 (CH), 124.31 (CH), 127.54 (CH), 128.10 (CH × 4), 128.34 (CH × 2), 128.81 (CH × 2), 136.53 (C), 139.29 (C), 176.61 (C) ppm, for the minor isomer δ −2.81 (CH_3), 22.75 (CH_2), 39.43 (CH_2), 45.97 (CH), 77.68 (CH), 137.04 (C), 139.31 (C), 176.92 (C) ppm; MS *m*/*z* (rel. intensity) 233 [M^+–$PhCH_2$, 31], 73 [100]. Anal. Calcd. for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45. Found: C, 74.16; H, 7.51%.

3.2.6. trans-5-Benzyldimethylsilyl-3-pentyl-4-pentanolide (*2e*)

b.p. 150 °C (bath temp., 0.09 Torr). IR (neat) 1776, 1205 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.09 (s, 3H), 0.87–0.96 (m, 4H), 1.00 (dd, $J = 14.8$, 4.8 Hz, 1H), 1.27 (br s, 8H), 1.94–2.10 (m, 1H), 2.16 (dd, $J = 17.1$,

9.2 Hz, 1H), 2.17 (s, 2H), 2.65 (dd, $J = 17.1$, 8.1 Hz, 1H), 4.16 (ddd, $J = 9.7$, 6.9, 4.8 Hz, 1H), 6.99–7.10 (m, 3H), 7.19–7.24 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ −2.97 (CH_3), −2.73 (CH_3), 13.94 (CH_3), 21.24 (CH_2), 22.41 (CH_2), 25.86 (CH_2), 27.26 (CH_2), 31.68 (CH_2), 32.42 (CH_2), 35.17 (CH_2), 45.08 (CH), 84.45 (CH), 124.10 (CH), 128.10 (CH × 2), 128.20 (CH × 2), 139.61 (C), 176.44 (C) ppm; MS *m/z* (rel. intensity) 227 [M^+–$PhCH_2$, 38], 73 [100]. Anal. Calcd. for $C_{19}H_{30}O_2Si$: C, 71.65; H, 9.49. Found: C, 71.66; H, 9.38%.

3.2.7. 5-Benzyldimethylsilyl-3-pentyl-4-pentanolide (**2e**, *trans:cis* = 87:13)

^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.09 (s, 3H), 0.73 (dd, $J = 14.4$, 4.2 Hz, 0.13H), 0.87–0.96 (m, 4H), 1.00 (dd, $J = 14.8$, 4.8 Hz, 0.87H), 1.27 (br s, 8H), 1.94–2.10 (m, 0.87H), 2.16 (dd, $J = 17.1$, 9.2 Hz, 0.87H), 2.17 (s, 2H), 2.25 (dd, $J = 16.1$, 7.1 Hz, 0.13H), 2.32–2.46 (m, 0.13H), 2.53 (dd, $J = 16.1$, 7.4 Hz, 0.13H), 2.65 (dd, $J = 17.1$, 8.1 Hz, 0.87H), 4.16 (ddd, $J = 9.7$, 6.9, 4.8 Hz, 0.87H), 4.66 (ddd, $J = 11.4$, 6.1, 4.3 Hz, 0.13H), 6.99–7.10 (m, 3H), 7.19–7.24 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) for the minor isomer (see above for the signals of the major isomer) δ −3.07 (CH_3), −2.82 (CH_3), 15.56 (CH_2), 25.80 (CH_2), 27.13 (CH_2), 28.43 (CH_2), 31.76 (CH_2), 34.00 (CH_2), 39.98 (CH), 81.84 (CH), 176.60 (C) ppm.

3.2.8. trans-5-Benzyldimethylsilyl-3-phenyl-4-pentanolide (**2f**)

m.p. 86–88 °C (Et_2O). IR (KBr) 1774, 1223 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.03 (s, 3H), 0.04 (s, 3H), 1.01 (d, $J = 7.1$ Hz, 2H), 2.12 (s, 2H), 2.73 (dd, $J = 17.5$, 10.7 Hz, 1H), 2.93 (dd, $J = 17.5$, 8.4 Hz, 1H), 3.21 (dt, $J = 10.6$, 8.3 Hz, 1H), 4.53 (dt, $J = 7.9$, 7.1 Hz, 1H), 6.87–7.41 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) δ −2.97 (CH_3), −2.86 (CH_3), 20.74 (CH_2), 25.75 (CH_2), 37.40 (CH_2), 51.56 (CH), 85.54 (CH), 124.12 (CH), 127.26 (CH × 2), 127.78 (CH), 128.11 (CH × 2), 128.24 (CH × 2), 129.12 (CH × 2), 138.56 (C), 139.51 (C), 175.47 (C) ppm; MS *m/z* (rel. intensity) 233 [M^+–$PhCH_2$, 12], 73 [100]. Anal. Calcd. for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45. Found: C, 74.08; H, 7.47%.

3.2.9. 5-Benzyldimethylsilyl-3-phenyl-4-pentanolide (**2f**, *trans:cis* = 82:18)

^{1}H-NMR ($CDCl_3$) δ −0.01 (s, 0.54H), 0.03 (s, 2.46H), 0.04 (s, 2.46H), 0.15 (s, 0.54H), 0.40 (dd, $J = 14.8$, 3.6 Hz, 0.18H), 0.60 (dd, $J = 14.8$, 11.5 Hz, 0.18H), 1.01 (d, $J = 7.1$ Hz, 1.64H), 2.09 (s, 0.36), 2.12 (s, 1.64H), 2.73 (dd, $J = 17.5$, 10.7 Hz, 0.82H), 2.77 (dd, $J = 17.5$, 6.0 Hz, 0.18H), 2.93 (dd, $J = 17.5$, 8.4 Hz, 1H), 3.21 (dt, $J = 10.6$, 8.3 Hz, 0.82H), 3.68 (dt, $J = 8.1$, 6.1 Hz, 0.18H), 4.53 (dt, $J = 7.9$, 7.1 Hz, 0.82H), 4.87 (ddd, $J = 11.5$, 6.3, 3.6 Hz, 0.18H), 6.87–7.41 (m, 10H) ppm.

3.3. Typical procedure for synthesis of tetrahydrofurans **6**

To a solution of lactone **2b** (*cis:trans* = 76:24, 250 mg, 0.75 mmol) in Et_2O (2.5 ml) was added DIBALH (0.95 M in hexane, 2.0 ml, 1.9 mmol) at 0 °C. The mixture was warmed to room temperature over 3 h. The resultant mixture was cooled to 0 °C and aqueous potassium sodium tartrate (20%, 10 ml) was added slowly. The resultant precipitate was dissolved with a small amount of 2 M aqueous NaOH. The mixture was extracted with AcOEt (3 × 10 ml). The extract was washed with saturated aqueous NH_4Cl, dried over Na_2SO_4 and evaporated. The crude product was directly used for further transformation. To a solution of the crude product in THF (1.5 ml) was added BuLi (1.73 M in hexane, 0.48 ml, 0.83 mmol) at −78 °C. After 30 min, a THF (2.5 ml) solution of TsCl (160 mg, 0.84 mmol) was added. The mixture was warmed to room temperature over 3 h, and then cooled to −78 °C again. BuLi (1.73 M in hexane, 0.48 ml, 0.83 mmol) was added to the cooled mixture. The mixture was warmed to room temperature over 2 h, poured into saturated aqueous NH_4Cl and extracted with *t*-BuOMe (3 × 10 ml). The extract was dried over Na_2SO_4 and evaporated. Purification by silica gel column chromatography gave tetrahydrofuran **6b** (*cis:trans* = 73:27, 204 mg, 0.64 mmol) in 85% yield.

3.3.1. 2-Benzyldimethylsilylmethyl-4-hexyltetrahydrofuran (**6b**, *cis:trans* = 73:27)

^{1}H-NMR ($CDCl_3$) δ 0.00 (s, 3H), 0.01 (s, 2.2H), 0.02 (s, 0.8H), 0.76–1.15 (m, 6H), 1.27 (br s, 10H), 1.53–1.66 (m, 0.54H), 2.05–2.26 (m, 3.46H) including 2.11 (s), 3.23 (dd, $J = 8.4$, 7.6 Hz, 0.27H), 3.42 (dd, $J = 8.1$, 7.4 Hz, 0.73H), 3.82 (t, $J = 7.9$ Hz, 0.73H), 3.87–4.02 (m, 1.27H), 6.98–7.09 (m, 3H), 7.17–7.24 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) for the major isomer δ −2.95 (CH_3), −2.82 (CH_3), 14.03 (CH_3), 22.58 (CH_2), 22.74 (CH_2), 26.10 (CH_2), 28.48 (CH_2), 29.38 (CH_2), 31.75 (CH_2), 34.09 (CH_2), 40.45 (CH), 41.89 (CH_2), 72.49 (CH_2), 77.59 (CH), 123.88 (CH), 128.09 (CH × 4), 140.00 (C) ppm, for the minor isomer δ −2.91 (CH_3), 22.96 (CH_2), 28.37 (CH_2), 33.74 (CH_2), 39.14 (CH), 40.65 (CH_2), 73.01 (CH_2), 76.39 (CH), 140.06 (C) ppm.

3.3.2. 2-Benzyldimethylsilylmethyl-4-isopropyltetrahydrofuran (**6c**, *cis:trans* = 81:19)

^{1}H-NMR ($CDCl_3$) δ 0.01 (s, 3H), 0.02 (s, 3H), 0.76–0.92 (m, 7.19H), 0.99–1.14 (m, 1.81H), 1.39–1.72 (m, 1H), 1.86–2.13 (m, 4H) including 2.11 (s), 3.27 (t, $J = 8.7$ Hz, 0.19H), 3.50 (t, $J = 8.1$ Hz, 0.81H), 3.83 (t, $J = 8.1$ Hz, 0.81H), 3.89–4.01 (m, 1.19H), 6.98–7.09 (m, 3H), 7.17–7.23 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$) for the major isomer δ −2.94 (CH_3), −2.83 (CH_3), 21.35 (CH_3), 21.45 (CH_3), 22.55 (CH_2), 26.09 (CH_2), 32.25

(CH), 40.24 (CH_2), 48.06 (CH), 71.15 (CH_2), 77.83 (CH), 123.88 (CH), 128.06 (CH × 4), 139.97 (C) ppm, for the minor isomer δ 21.21 (CH_3), 21.54 (CH_3), 23.11 (CH_2), 31.70 (CH), 38.75 (CH_2), 46.58 (CH), 71.71 (CH_2), 76.90 (CH) ppm.

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