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Synthetic Applications of Functionalized Silyl Anions: Aminosilyl Anions as Hydroxy Anion Equivalent

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Abstract: An (aminosilyl)lithium and the corresponding copper and magnesium reagents serve as a hydroxy anion equivalent through (1) allylic substitution, (2) addition to vinyloxirane, and (3) addition to acetylene, followed by oxidative cleavage of the silicon-carbon bonds. Highly regio- and stereoselective transformations have been achieved in all cases. Copyright © 1996 Elsevier Science Ltd

Introduction

Silyl anions are good nucleophiles, which undergo nucleophilic substitution with alkyl halides, allylic substitution, conjugate addition, and addition to alkynes.[1] The introduced silyl group can be converted into the hydroxy group by oxidative cleavage of the silicon-carbon bond.[2] Thus, silyl anions serve as a hydroxy anion equivalent.

The conventional Fleming's $PhMe_2Si$ anion chemistry[3] requires introduction of a heteroatom on silicon via cleavage of the Si-Ph bond by acid treatment before oxidative cleavage of the silicon-carbon bond. This method therefore cannot be applied to at least three types of silanes, that is, allylsilane, vinylsilane, and β-hydroxy-silane, because the acid treatment might cleave the silicon-allyl and -vinyl carbon bond much faster than the silicon-phenyl carbon bond[4] or might cause the Peterson olefination of the β-hydroxy-silane.[5] The aminosilyl anion chemistry which we developed recently[6] has afforded a solution to this problem: No acid treatment is required since the silyl group is already functionalized. Recently, Fleming et al. have found another solution to this problem by use of a well-designed (allylsilyl)lithium:[7] An allyl group, 2-methylbut-2-enyl group, on silicon can be removed selectively with very weak acids with other allyl-, vinyl-, and β-hydroxy-silane moieties intact. Taber et al. also reported quite recently that a phenyl group on silicon can be removed in two steps under basic conditions which involve reduction with lithium/ammonia to cyclohexadienyl group followed by treatment with tetrabutylammonium fluoride.[8]

Reported herein are some examples of synthetic applications of (aminosilyl)lithium **1**, the corresponding copper reagent **2**, and the corresponding magnesium reagent **3**: regio- and stereoselective synthesis of allylsilanes, β-hydroxy-silanes, and vinylsilanes and their conversion to the corresponding alcohols and aldehyde.

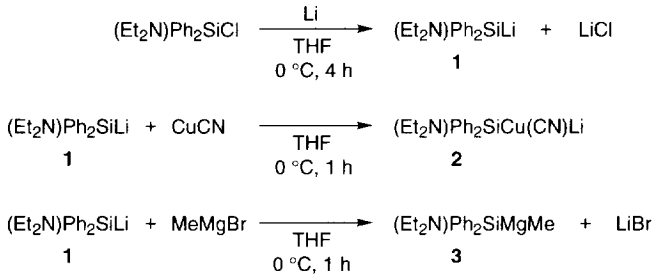
$(Et_2N)Ph_2SiLi$ **1** $(Et_2N)Ph_2SiCu(CN)Li$ **2** $(Et_2N)Ph_2SiMgMe$ **3**

$(Et_2N)Ph_2Si^- \equiv OH^-$

Results and Discussion

1. Preparation of the reagents

(Aminosilyl)lithium **1** was prepared from the corresponding (amino)chlorosilane with lithium metal in THF at 0 °C for 4 h in quantitative yield.[8] The copper reagent[3] **2** and the magnesium reagent[9] **3** were prepared from **1** with 1 equiv of copper cyanide and methylmagnesium bromide in THF, respectively (Scheme 1). The solutions were used without titration.

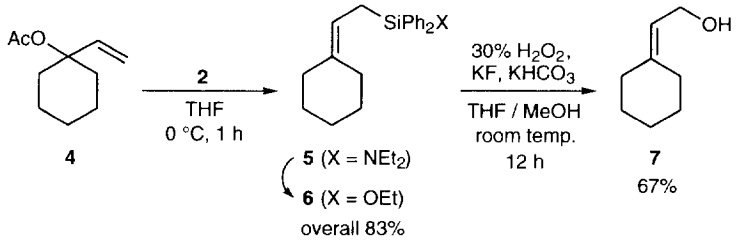


Scheme 1

2. Allylsilane via allylic substitution

The silyl cuprate reagent **2** underwent allylic substitution reaction with 1-vinylcyclohexyl acetate **4** to give amino-substituted [2-(cyclohexylidene)ethyl]silane **5** (Scheme 2).[10] Although the silicon-nitrogen bond of **5** could be tolerated with neutral aqueous workup, it decomposed on silica gel. For isolation, **5** was converted by ethanolysis into ethoxy derivative **6** (83% yield) which was stable on silica gel.

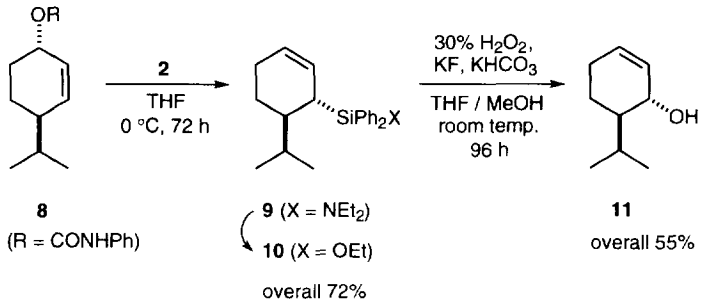
Conversion of the ethoxy derivative **6** into the corresponding allyl alcohol **7** was achieved by the H_2O_2 oxidation in 67% yield without cleavage of the silicon-allyl carbon bond. Direct H_2O_2 oxidation of amino derivative **5** without purification was also successful to afford **7** in 63% yield.



Scheme 2

Reaction of cyclohexyl carbamate[11] **8** (R = CONHPh) with **2** proceeded in an S_N2' manner and with *syn* selectivity to the leaving group (-OR) (Scheme 3).[10b] The selectivity may be explained in terms of the interaction between nitrogen of the carbamate and copper of the cuprate, as proposed for reactions with ordinary organocuprates.[12] Excess amounts of **2** (6 equiv) and longer reaction period were required as compared with the case of **4**. The attempted Goering's method[12b] (**8**/MeLi/CuI/$(Et_2N)Ph_2SiLi$ = 1/1/1/1) was unsuccessful. Ethanolysis of the resulting amino-substituted allylsilane **9** afforded ethoxy derivative **10** in 72% yield. The allylsilane **9** was converted into the corresponding allyl alcohol **11** by the H_2O_2 oxidation with retention of configuration in 55% yield. The stereochemistry was confirmed by ^1H NMR data, which are identical with

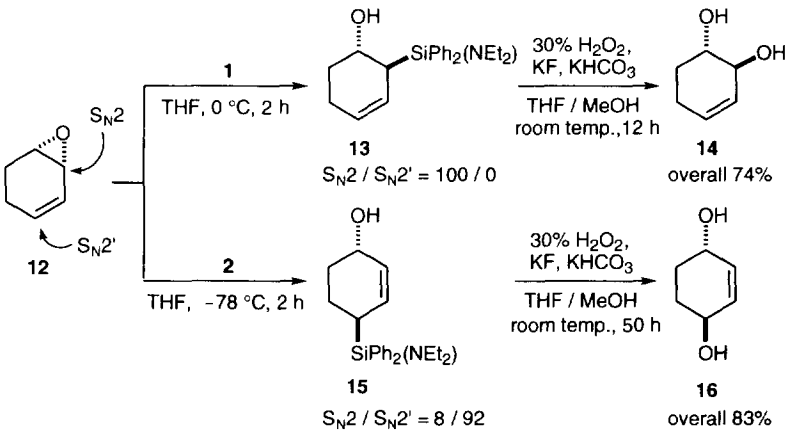
authentic data.[13] The reagent **2** underwent no substitution with an acetate[14a] (R = Ac in **8**) and a 2,4,6-trimethylbenzoate[14b] (R = 2,4,6-$Me_3C_6H_2CO$ in **8**). The choice of the leaving group is thus essential, but the S_N2' replacement reaction also affords a new access to regio- and stereo-defined sila-functionalized allylsilanes, which have potential utility for organic synthesis.



Scheme 3

3. (β-Hydroxy)silane via ring-opening of epoxides

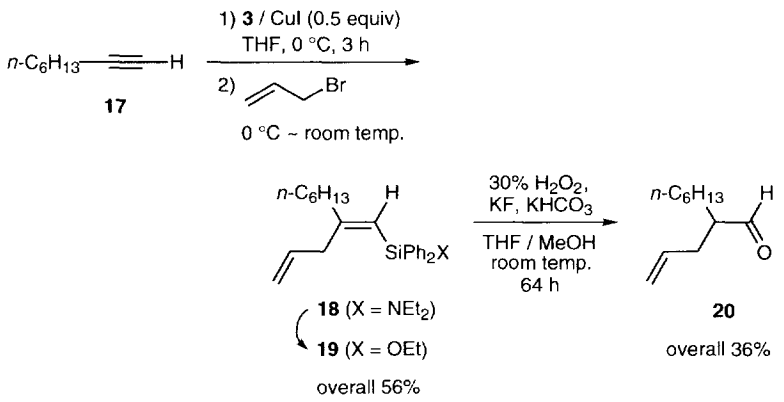
Monoepoxide of 1,3-cyclohexadiene[15] **12** can be converted into 1,2- and 1,4-diol by use of **1** and **2**, respectively, as summarized in Scheme 4. The lithium reagent **1** underwent an S_N2 type ring opening reaction with **12** in a completely regio- and stereoselective fashion to give the *trans*-(β-hydroxy)silane **13** which contains an allylsilane unit also.[16] Treatment of **13** with H_2O_2 afforded the corresponding alcohol **14** in 74% yield. The stereochemistry of **14** was confirmed by the ^1H NMR spectroscopic data, which are identical with the authentic data.[17] In contrast to this, the silyl cuprate **2** underwent an S_N2' allylic substitution reaction with **12** with high regioselectivity and complete stereoselectivity to give the *trans* product **15** which is regarded as a vinylogous (β-hydroxy)silane.[16] While no *cis* product was formed at all, the regioselectivity depended on the reaction temperature. Thus, the S_N2': S_N2 ratio was 92 : 8 at -78 °C, but roughly 50 : 50 at 0 °C. The corresponding 1,4-diol **16** was obtained in 83% yield by the H_2O_2 oxidation, which required larger amounts of H_2O_2 and longer reaction period than the oxidation of **13**. The stereochemistry of **16** was also confirmed by the ^1H NMR spectroscopic data, which are identical with the authentic data.[17]



Scheme 4

4. Vinylsilane by addition to alkyne

Addition of silyl anions to alkynes is one of the well-established routes to vinylsilanes. For example, silylcuprate $(Me_2PhSi)_2Cu(CN)Li_2$ has been reported to undergo addition to 1-alkynes in a highly regioselective fashion to carry the silyl group onto the terminal carbon.[18] It has also been reported that a silylmagnesium reagent prepared from $MePh_2SiLi$ and MeMgI underwent a similar regioselective addition to alkynes in the presence of a catalytic amount of CuI.[9] In the present cases, however, addition of the (aminosilyl)cuprate **2** to 1-alkyne **17** occurred with low regioselectivity, together with deprotonation. The observed deprotonation makes a sharp contrast to the fact that the Fleming's $(Me_2PhSi)_2Cu(CN)Li_2$ does not remove the proton from 1-alkyne.[18] Stereo- and regioselective addition to the 1-alkyne was achieved by the (aminosilyl)magnesium reagent **3** in the presence of 0.5 equiv of CuI to give vinylsilane **18** after trapping with allyl bromide (Scheme 5). The use of at least 0.5 equiv of CuI was essential to prevent the deprotonation. The amino derivative **18** was converted into **19** by ethanolysis for characterization. Direct treatment of **18** with H_2O_2 afforded the corresponding aldehyde[19] **20** in 36% overall yield.



Scheme 5

Experimental Section

General Remarks. ^1H (200 MHz), ^{13}C (50.29 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer. ^1H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^1H δ 7.200 ppm and ^{13}C δ 128.00 ppm) or $CDCl_3$ (^{13}C δ 77.00 ppm). Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. Melting points were measured with a Yanaco-MP-S3 apparatus. The elemental analyses were performed at the Microanalysis Center of Kyoto University: Analytical samples were purified by recrystallization, preparative GLC, or preparative MPLC. Column chromatography was performed by using Kieselgel 60 (70-230 mesh) (Merck). Thin layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck). Preparative medium pressure liquid chromatography (MPLC) was performed with a silica gel prepacked C.I.G. (Si-10) column (Kusano).

Lithium granular was purchased from Chemetall Gesellshaft. Spray-dried KF was purchased from Wako Pure Chemical Industries. THF was distilled under nitrogen from sodium/benzophenone. Hexane was distilled under nitrogen from sodium. Ethanol was dried with magnesium ethoxide and distilled. Copper(I) cyanide was

dried by azeotropic distillation with dry toluene (1 - 3 mL) two or three times. All reactions were carried out under a nitrogen atmosphere.

Preparation of [(Diethylamino)diphenylsilyl]lithium (1). To a mixture of lithium granular (397 mg, 57.2 mg-atom) and THF (7.0 mL) was added dropwise (diethylamino)diphenylchlorosilane (4.24 g, 14.6 mmol) with stirring at room temperature over 5 min. An exothermic reaction started in a few minutes and then THF (7.0 mL) was added. After about 20 min, the solution turned blue. The mixture was then cooled to 0 °C and stirred for 4 h, resulting in the formation of a dark green solution of **1** in quantitative yield. The solution was used without titration.

Typical Procedure for Preparation of Lithium [(Diethylamino)diphenylsilyl]-(cyano)cuprate (2) and Synthesis of [2-(Cyclohexylidene)ethyl](diethylamino)diphenylsilane (5). To a suspension of copper(I) cyanide (purity >90%, 1.47 g, 14.7 mmol) in THF (7.0 mL) was added the whole solution of **1**, prepared above, over a few minutes: The mixture was stirred at 0 °C for 1 h. The resulting black solution of **2** was cooled at -20 °C and 1-vinylcyclohexyl acetate **4** (1.70 g, 10.1 mmol) was added over 3 min. After being stirred at -20 °C for 5 min and at 0 °C for 1 h, the reaction was quenched by a 5% aq. solution of NH_4Cl (30 mL). The mixture was filtered and the filtrate was extracted with ether (30 mL x 3). The combined organic layer was washed several times with a 5% aq. solution of NH_4Cl (20 mL each) for the purpose of complete removal of copper salts from the organic layer until the aqueous layer became colorless, followed by washing with brine (20 mL) and drying over Na_2SO_4. Filtration and evaporation of solvent gave crude **5** as a yellow oil, which is used in the next oxidation step without purification. ^1H NMR (C_6D_6): δ 1.00 (t, J = 7.0 Hz, 6H), 1.25-1.60 (m, 6H), 2.00-2.13 (m, 4H), 2.19 (d, J = 8.4 Hz, 2H), 2.97 (q, J = 7.0 Hz, 4H), 5.42 (m, 1H), 7.26-7.31 (m, 6H), 7.72-7.77 (m, 4H).

Hydrogen Peroxide Oxidation of 5: Synthesis of 2-(Cyclohexylidene)ethyl alcohol (7). A flask was charged with the crude **5** obtained above, followed by successive addition of THF (15.0 mL), methanol (15.0 mL), KF (6.10 g, 105 mmol; 7.2 molar equiv to the aminochlorosilane), $KHCO_3$ (5.89 g, 58.5 mmol; 4 molar equiv to the aminochlorosilane). To the stirring mixture was added dropwise 30% H_2O_2 (7.4 mL, 65.5 mmol; 4.5 molar equiv to the aminochlorosilane) via pipet over 10 min at room temperature. A somewhat cloudy organic layer and a milky-white heavy inorganic layer resulted. An exothermic reaction started during the addtion to raise the temperature up to 40 °C and ceased in about 30 min. The mixture was stirred at room temperature for 6 h and at 35 - 40 °C for another 6 h. After being cooled to room temperature, the mixture was poured into water (50 mL) and the insoluble white precipitates were removed by decantation. The liquid phase was extracted with Et_2O (30 mL x 5). The combined organic layer was washed successively with a 10% aq. solution of $Na_2S_2O_3$ (50 mL), a 1 M aq. solution of NaOH (30 mL x 3), and water, and then dried over $MgSO_4$. After filtration and evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane/AcOEt (7/1) to give **7** (798 mg, 63% overall yield based on **4**) (R_f = 0.18) as a colorless oil. ^1H NMR ($CDCl_3$): δ 1.20-1.35 (broad, 1H), 1.42-1.65 (m, 6H), 2.02-2.25 (m, 4H), 4.13 (d, J = 7.1 Hz, 2H), 5.35 (tt, J = 7.1 and 1.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 26.66, 27.85, 28.37, 28.82, 37.02, 58.54, 120.21, 144.53. IR (neat): cm^{-1} 3340, 2930, 2860, 1670, 1450, 1060, 995. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.76; H, 11.16.

Typical Procedure for Conversion of Diethylamino Group into Ethoxy Group: [2-(Cyclohexylidene)ethyl](ethoxy)diphenylsilane (6). To an ethanol (5.0 mL) solution of the crude **5**, which was prepared from 3.8 mmol of **4**, was added NH_4Cl (103 mmg, 1.9 mmol) in one portion at room temperature and the mixture was stirred for 24 h. The volatile materials were removed at reduced pressure. The

residue was diluted with hexane (20 mL), filtered, and the solvent was evaporated. The remaining oil was subjected to column chromatography on silica gel (50 mL) eluted with hexane/AcOEt (100/1) to give **6** (1.07 g, R_f = 0.29) in 83% yield (based on **4**). ^{1}H NMR (C_6D_6): δ 1.17 (t, J = 7.0 Hz, 3H), 1.22-1.35 (m, 2H), 1.35-1.50 (m, 4H), 2.00-2.07 (m, 4H), 2.19 (d, J = 8.1 Hz, 2H), 3.74 (q, J = 7.0 Hz, 2H), 5.41 (q, J = 8.1 Hz, 1H), 7.22-7.27 (m, 6H), 7.72-7.77 (m, 4H). ^{13}C NMR ($CDCl_3$): 15.06, 18.40, 26.87, 27.05, 28.39 (2C), 37.29, 59.37, 114.21, 127.69, 129.72, 134.83, 135.04, 138.85. IR (neat): cm^{-1} 3080, 2940, 2860, 1960, 1890, 1820, 1590, 1430, 1390, 1115, 1080. Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.52; H, 8.39. Found: C, 78.62; H, 8.24.

Hydrogen Peroxide Oxidation of 6: To a solution of **6** (269 mg, 0.80 mmol) in THF (2.0 mL) and methanol (2.0 mL), was added successively KF (334 mg, 5.8 mmol), $KHCO_3$ (360 mg, 3.2 mmol), and 30% H_2O_2 (0.35 mL, 3.6 mmol) at room temperature. The reaction mixture was stirred at room temperarure for 12 h. The mixture was subjected to the same workup and purification as above to give **7** in 67% yield.

3-[(Ethoxy)diphenylsilyl]-4-isopropylcyclohexene (10). Overall 72 % yield based on **8**. R_f = 0.30 (hexane/AcOEt = 60/1). ^{1}H NMR ($CDCl_3$): δ 0.82 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H), 1.30-2.05 (m ,6H), 2.32-2.38 (m, 1H), 3.73 (q, J = 7.0 Hz, 2H), 5.57-5.80 (m, 2H), 7.35-7.40 (m, 6H), 7.58-7.68 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 18.33, 18.86, 21.87, 22.00, 22.33, 28.74, 29.10, 38.75, 59.52, 126.08, 126.21, 127.59, 127.71, 129.59, 129.64, 134.43, 134.79, 135.07, 135.23. IR (neat): cm^{-1} 3030, 2960, 2880, 1960, 1890, 1830, 1645, 1590, 1430, 1105, 1080, 950. Anal. Calcd for $C_{23}H_{30}OSi$: C, 78.80; H, 8.62. Found: C, 78.52; H, 8.68.

***trans*-6-Isopropyl-2-cyclohexen-1-ol (11).** (1) To a solution of **2** in THF (11.0 mL), which was prepared from **1** (7.58 mmol) and copper(I) cyanide (7.58 mmol), was added a solution of **8** (0.32 g, 1.22 mmol) in THF (2.5 mL) over 18 min at 0 °C and the solution was stirred at 0 °C for 72 h. The reaction was quenched by a 10% aq. solution of NH_4Cl and filtered to remove the resulting salts. The filtrate was extracted with Et_2O (12 mL x 3) and the combined organic layer was washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated to give crude **9** (1.90 g). (2) To a solution of **9** in THF (8.0 mL) and MeOH (8.0 mL) was added successively $KHCO_3$ (3.10 g, 30.9 mmol), KF (3.20 g, 55.0 mmol), and 30% H_2O_2 (7.71 mL, 68.2 mmol) and the mixture was stirred for 96 h. To the mixture was added anhydrous $Na_2S_2O_3$ to the amount that the excess H_2O_2 was consumed completely. The mixture was filtered and concentrated. The residue was diluted with Et_2O (15 mL), washed with a 1 M aq. solution of NaOH (10 mL x 3), water (10 mL), and dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (20 mL) eluted with hexane/AcOEt (15/1) to afford **11** (94 mg, overall 55% yield based on **8**) (R_f = 0.13). ^{1}H NMR ($CDCl_3$): δ 0.84 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.22-1.33 (m, 3H), 1.59-1.71 (m, 1H), 1.96-2.07 (m, 3H), 3.98-4.10 (m, 1H), 5.60-5.68 (m, 1H), 5.72-5.81 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 17.16, 20.69, 21.06, 25.31, 26.62, 48.01, 68.92, 129.58, 130.92. IR (neat): cm^{-1} 3332, 2968, 2880, 1658, 1468, 1388, 1192. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.11; H, 11.70.

***trans*-3-Cyclohexene-1,2-diol (14).** (1) To a solution of **1** (4.08 mol) in THF (3.0 mL) was added **12** (204 mg, 2.12 mmol) at 0 °C and the reaction mixture was stirred for 2 h. The reaction was quenched with a 10% aq. solution of NH_4Cl (10 mL) and extracted with Et_2O (10 mL x 3). The combined organic layer was washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated to give crude **13** (1.19 g). (2) To a solution of **13** in THF (3.0 mL) and MeOH (3.0 mL) was added successively $KHCO_3$ (860 mg, 8.61 mmol), KF (890 mg, 15.3 mmol), and 30% H_2O_2 (1.08mL, 9.56 mmol) and the mixture was stirred for 12 h. To the mixture was added anhydrous $Na_2S_2O_3$ to the amount that the excess H_2O_2 was consumed completely. The

mixture was dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (35 mL) eluted with hexane/AcOEt (1/2) to afford **14** (180 mg, overall 51% yield based on **12**) (R_f = 0.30) as colorless crystal. Recrystallization was performed from hexane-AcOEt. mp 75.9-76.7 °C. ^{1}H NMR (DMSO-d_6, δ 2.50 ppm):[17] δ 1.37-1.52 (m, 1H), 1.68-1.77 (m, 1H), 1.96-2.01 (m, 2H), 3.33-3.42 (m, 1H), 3.71-3.74 (m, 1H), 4.66 (d, J = 4.0 Hz, 1H), 4.76 (d, J = 5.3 Hz, 1H), 5.46 (dq, J = 10.2 and 2.2 Hz, 1H), 5.43-5.62 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 24.78, 28.46, 73.57 (2C), 128.07, 129.14. IR (KBr): cm^{-1} 3330, 3270, 3045, 2920, 1090, 1060. Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.86; H, 8.55.

***trans*-2-Cyclohexene-1,4-diol (16).** To a solution of **2** in THF (5.5 mL), which was prepared from **1** (2.18 mmol) and copper(I) cyanide (2.20 mmol) was added a solution of **12** (140 mg, 1.08 mmol) in THF (1.0 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 2 h and warmed to the ambient temperature. The reaction was quenched with a 10% aq. solution of NH_4Cl (16 mL) and filtered. The filtrate was extracted with Et_2O (10 mL x 3), washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (24 mL) eluted with hexane/AcOEt (1/2) to afford a mixture of **16** and **14** (102 mg, **16/14** = 92/8 determined by means of ^{1}H NMR) (R_f = 0.13) as colorless crystal in overall 83% yield based on **12**. Pure **16** was obtained by recrystallization from hexane-AcOEt. mp 85.9-86.9 °C. ^{1}H NMR (DMSO-d_6, δ 2.50 ppm):[17] δ 1.25-1.34 (m, 2H), 1.86-1.93 (m, 2H), 3.95-4.05 (m, 2H), 4.70 (d, J = 5.3 Hz, 2H), 5.57 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 30.40, 66.23, 132.66. IR (KBr): cm^{-1} 3325, 2950, 2875, 1450, 1390, 1300, 1060, 955. Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.78; H, 8.53.

1-[(Ethoxy)diphenylsilyl]-2-propenyl-1-octene (19). Overall 56% yield based on **17**. R_f = 0.18 (hexane/AcOEt = 40/1). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.7 Hz, 3H), 1.20 (t, J = 7.0 Hz, 3H), 1.22-1.38 (m, 6H), 1.40-1.55 (m, 2H), 2.16 (t, J = 7.2 Hz, 2H), 2.89 (dt, J = 6.9 and 1.3 Hz, 2H), 3.77 (q, J = 7.0 Hz, 2H), 4.78-4.89 (m, 2H), 5.41-5.62 (m, 1H), 5.65 (s, 1H), 7.34-7.39 (m, 6H), 7.61-7.65 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.09, 18.33, 22.65, 27.86, 29.03, 31.75, 38.69, 41.20, 59.18, 116.20, 117.83, 127.74, 129.57, 134.79, 136.00, 136.28, 163.24. IR (neat): cm^{-1} 3025, 2940, 2900, 2830, 1950, 1880, 1810, 1595, 1415, 1100, 1065. Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.41; H, 9.01.

Preparation of [(Diethylamino)diphenylsilyl](methyl)magnesium (3) and Synthesis of 2-Propenyl-octanal (20).[19] (1) To a solution of **1** (4.22 mmol) in THF (3.5 mL) was added methylmagnesium bromide in Et_2O (1.50 mL, 4.25 mmol) at 0 °C and the solution was stirred at 0 °C for 1 h to give a solution of **3**. To the solution was added copper(I) iodide (403 mg, 2.12 mmol) in one portion at 0 °C and the stirring was continued for 1 h. To the solution was added a solution of **17** (200 mg, 1.86 mmol) in THF (1.0 mL) over 2 min at 0 °C and the reaction mixture was stirred at 0 °C for 3 h. To the mixture was added allyl bromide (0.440 mL, 5.08 mmol) at 0 °C. The mixture was warmed to the ambient temperature slowly. The reaction mixture was decomposed with a 5% aq. solution of NH_4Cl (10 mL) and filtered. The filtrate was extracted with Et_2O (10 mL x 4), washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated to give crude **18**. (2) To a solution of **18** in THF (4.0 mL) and MeOH (4.0 mL) was added successively $KHCO_3$ (1.69 g, 16.9 mmol), KF (1.73 g, 30.9 mmol), and 30% H_2O_2 (6.45 mL, 57.1 mmol) and the reaction mixture was stirred at room temperature for 64 h. Water (12 mL) was poured into the mixture, which was extracted with Et_2O (12 mL x 4). The combined organic layer was washed with a 10% aq. solution of $Na_2S_2O_3$ (15 mL), a saturated aqueous solution of $NaHCO_3$ (15 mL), water (15 mL), dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (50 mL) eluted with hexane/AcOEt (30/1) (R_f =

0.33) and subsequent MPLC eluted with hexane/AcOEt (40/1) to give **20** (111 mg, overall 36% yield based on **17**) as colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.83-0.90 (m, 3H), 1.20-1.35 (m, 8H), 1.42-1.72 (m, 2H), 2.13-2.45 (m, 3H), 5.02-5.10 (m, 2H), 5.63-5.83 (m, 1H), 9.60 (d, J = 2.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.04, 22.56, 26.87, 28.39, 29.31, 31.60, 33.05, 51.28, 117.08, 135.02, 204.94. IR (neat): cm^{-1} 2936, 2864, 2724, 1732, 1646, 1468, 994, 916.

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