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tert-Butyldimethylsilyldihalomethyllithium as a Dihalomethylene Dianion Synthon. 1,3-Rearrangement and 1,4-Rearrangement of Silyl Group from Carbon to Oxide

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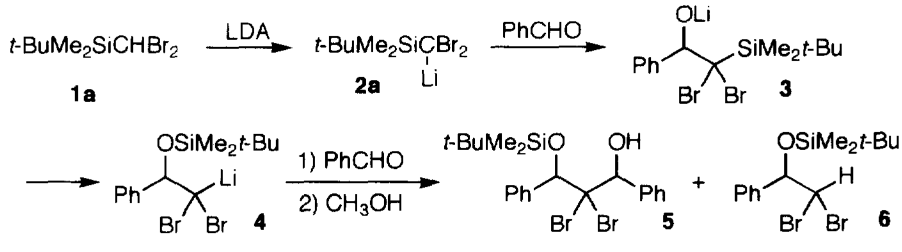
Abstract: One-pot synthesis of $R^1CH(OSiMe_2\text{-}t\text{-}Bu)CX_2CH(OH)R^2$ (X=Cl, Br) by successive addition of two different aldehydes (R^1CHO and R^2CHO) has been achieved starting from *tert*-butyldimethylsilyldihalomethyllithium. Treatment of a THF solution of the title carbanion (X=Cl) with $p\text{-}MeOC_6H_4CHO$ or $n\text{-}BuCHO$ followed by an addition of HMPA and benzaldehyde gave the corresponding 1,3-diol monosilyl ether in 83% or 45% yield, respectively. The use of oxirane in place of aldehyde as the first electrophile followed by addition of benzaldehyde provided 1,4-diol monosilyl ether.

(1) *Reaction of* tert-*butyldimethylsilyldihalomethyllithium with aldehydes followed by 1,3-rearrangement of silyl group from carbon to oxide.*

Intramolecular 1,2-rearrangement of silicon from carbon to negatively charged oxygen is well known as Brook rearrangement[1] and many examples have been reported[2] for the construction of organic molecules. In contrast, 1,3-rearrangement of silicon from carbon to β-oxyanion is rare since olefin formation via 1,2-elimination of β-oxidosilanes is rapid. We wish to report a synthetic method for formation of two carbon-carbon bonds in one-pot based on organosilicon chemistry which involves an unprecedented 1,3-rearrangement of silicon.[3, 4, 5]

tert-Butyl(dibromomethyl)dimethylsilane (**1a**)[6] was deprotonated by treatment with lithium diisopropylamide in DME-THF (2:1) at −78 °C to give *tert*-butyldimethylsilyldibromomethyllithium (**2a**). Treatment of **2a** with benzaldehyde (2.4 eq) lead to 1,3-diol monosilyl ether **5** (1:2 adduct, 72% yield) via the intermediacy of lithium carbenoid **4** along with 1:1 adduct ($PhCH(OSiMe_2\text{-}t\text{-}Bu)CHBr_2$, **6**, 22%). This was

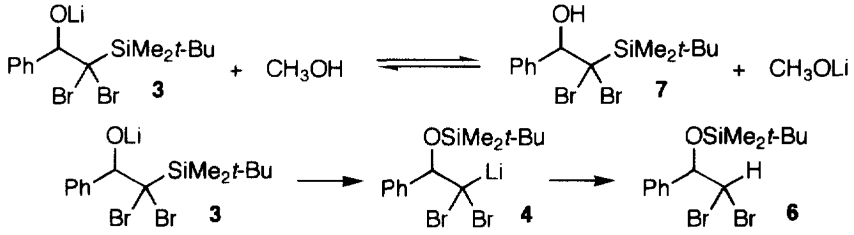
Scheme 1



a surprising result since the intermediate β-oxidosilane **3**, by analogy with the examples of $Me_3SiCH(Li)Cl$[7] and $Me_3SiC(Li)(SR)_2$,[8] would have been expected to eliminate lithium bromide or lithium *tert*-butyldimethylsilanoxide to give α,β-epoxy silane or alkene rather than 1,3-diol monosilyl ether **5** (Scheme 1).

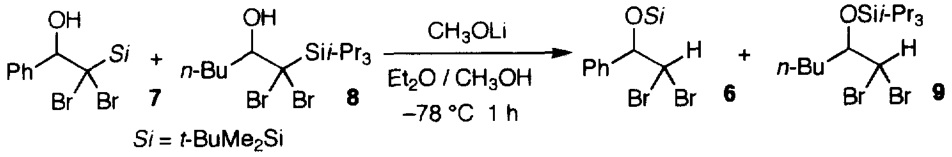
The distribution of the products (1:1 adduct to 1:2 adduct) depends heavily on the nature of the substituent on the silicon. The respective dibromomethylsilane and the yields[9] of the corresponding products (1:1 adduct and 1:2 adduct) in the reaction of $R_3SiCLiBr_2$ (1.2 mmol) with PhCHO (1.0 mmol) in THF were as follows: $Me_3SiCHBr_2$,[10] 29%, 0%; *t*-$BuMe_2SiCHBr_2$, 68%, 22%;[11] *i*-$Pr_3SiCHBr_2$, 18%, 25%; $Ph_2MeSiCHBr_2$, 36%, 49%; $Ph_3SiCHBr_2$, 18%, 74%. Thus, $Ph_3SiCLiBr_2$ was the best reagent for the preparation of 1,3-diol monosilyl ether ($PhCH(OSiR_3)CBr_2CH(OH)Ph$).[12] The rate of rearrangement was also sensitive to the reaction solvent . In ether, instead of DME-THF, rearrangement of silicon (**3** → **4**) did not proceed and the reaction of *tert*-butyldimethylsilyldibromomethyllithium (**2a**) with benzaldehyde gave an adduct $PhCH(OH)CBr_2(SiMe_2$-*t*-Bu), **7** in 77% yield after work up (1 N HCl-ether). Addition of methanol (10 eq) before workup to the reaction mixture provided the rearranged product **6** in 87% yield. In the same way, the reaction between **2a** and heptanal, cinnamaldehyde, or acetophenone provided the corresponding rearranged silyl ether $R^1R^2C(OSiMe_2$-*t*-$Bu)CHBr_2$ in 71%, 75% or 65% yield, respectively, by the addition of methanol before workup. Rearrangement by an addition of methanol might proceed as follows: (1) Protonation of **3** by methanol gives **7** and lithium methoxide, (2) lithium methoxide can deprotonate **7** to regenerate **3** and an equilibrium mixture of **3** and lithium methoxide is obtained, (3) equilibration shifts via C→O rearrangement of silyl group to form dibromoalkyllithium **4**, and (4) finally protonation of **4** by methanol affords the rearranged product **6** (Scheme 2). This assumption was supported by the following two facts. The use of MeOD gave $PhCH(OSiMe_2$-*t*-$Bu)CDBr_2$. When the carbinol **7** (0.5 mmol) was treated with a catalytic amount of CH_3OLi (0.1 mmol) in ether (3 ml)-methanol (5.0 mmol), the carbinol was transformed rapidly to the alkoxysilane **6** in 90% yield .

Scheme 2



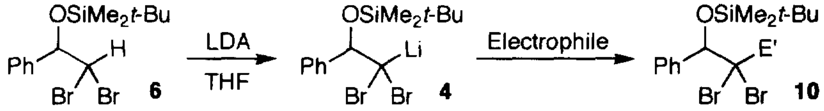
A crossover experiment was conducted to demonstrate the intramolecularity of the migration process. Upon treatment of a mixture of **7** and **8** with a catalytic amount of CH_3OLi in Et_2O-MeOH at −78 °C for 1 h, only two products (**6** and **9**) were isolated. No crossover products could be observed (Scheme 3).

Scheme 3



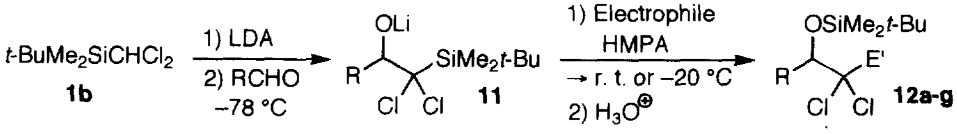
Treatment of **6** with lithium diisopropylamide in THF provided carbanion **4** which reacted with electrophile such as methyl iodide, allyl bromide, benzaldehyde, pentanal, or cyclohexanone to give the corresponding adduct in 97% (**10a**), 97% (**10b**), 95% (**5**), 85% (**10c**), or 70% (**10d**) yield, respectively (Scheme 4).

Scheme 4



Then we turned out our attention toward one-pot synthesis of **10** by successive addition of two different electrophiles to *tert*-butyldimethylsilyldibromomethyllithium (**2a**). It was anticipated that an addition of DME and second electrophile to the reaction mixture of **2a** and benzaldehyde in ether would provide **10** in one-pot. However, an addition of DME and methyl iodide or 4-methoxybenzaldehyde as a second electrophile gave no desired product and only **6** was isolated in 50–55% yield. An addition of HMPA instead of DME afforded an adduct **10** (E'=Me) in 53% yield upon successive treatment with MeI as the second electrophile. Fortunately, *tert*-butyldimethylsilyldichloromethyllithium (**2b**), generated from *tert*-butyl(dichloromethyl)dimethylsilane (**1b**) and LDA, proved to be more effective than dibromo analogue **2a** for the purpose. In this case, the migration of silicon in the adduct **11**, derived from **2b** and aldehyde such as PhCHO, PhCH=CHCHO, or *n*-BuCHO, did not proceed in THF. An addition of HMPA to the reaction mixture, however, caused the rearrangement providing carbon anion which reacted with various second electrophiles effectively (Table 1).

Table 1. One-pot synthesis of $RCH(OSiMe_2\text{-}t\text{-}Bu)CCl_2E'$ from *tert*-butyl(dichloromethyl)dimethylsilane (**1b**)

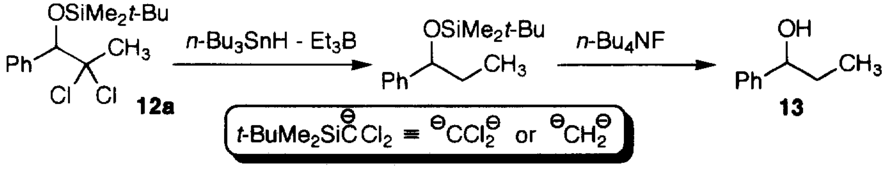


	R	Electrophile	E'	Yield of **12** (%)
a	Ph	MeI	Me	71
b	Ph	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$	70
c	PhCH=CH	MeI	Me	74
d	*n*-Pr	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$	40
e	4-MeO-C_6H_4	PhCHO	PhCH(OH)	83[a]
f	PhCH=CH	PhCHO	PhCH(OH)	73[a]
g	*n*-Bu	PhCHO	PhCH(OH)	45[a]

a) The products consist of two monosilyl ethers such as $PhCH(OH)CCl_2CH(OSiMe_2\text{-}t\text{-}Bu)C_6H_4\text{-}p\text{-}OMe$ and $PhCH(OSiMe_2\text{-}t\text{-}Bu)CCl_2CH(OH)C_6H_4\text{-}p\text{-}OMe$. Each isomer was a mixture of two diastereomers ((1*R**,3*R**):(1*R**,3*S**) = 4:6 or 1:1).

Dichlorides were easily reduced by *n*-Bu_3SnH-Et_3B[13] to give the corresponding methylene compounds. For instance, treatment of **12a** (0.6 mmol) with *n*-Bu_3SnH (1.75 mmol) in the presence of Et_3B (0.7 mmol) in hexane at 80 °C afforded $PhCH(OSiMe_2$-*t*-$Bu)CH_2CH_3$ in 97% yield which was converted into 1-phenyl-1-propanol (**13**) by treatment with *n*-Bu_4NF. Thus, *tert*-butyldimethylsilyldichloromethyllithium can be regarded as a synthon of dichloromethylene dianion (CCl_2^{2-}) or methylene dianion (CH_2^{2-}) (Scheme 5).[14]

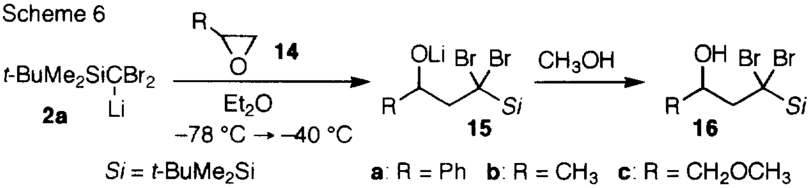
Scheme 5



(2) *Reaction of* tert*-butyldimethylsilyldihalomethyllithium with oxiranes followed by 1,4-rearrangement of silyl group from carbon to oxide.*

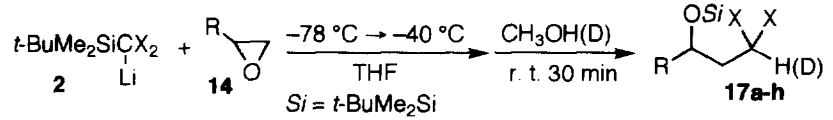
The new method described in section (1) was applied to the reaction with oxiranes. Treatment of 2-phenyloxirane (**14a**) with *tert*-butyldimethylsilyldibromomethyllithium (**2a**) in ether at –40 °C[15] provided 3,3-dibromo-3-*tert*-butyldimethylsilyl-1-phenyl-1-propanol (**16a**) in 32% yield. Other oxiranes such as **14b** or **14c** also gave the corresponding alcohol **16b** or **16c** in 51% or 80% yield, respectively (Scheme 6). The reaction did not proceed at –78 °C in contrast to the reaction with aldehyde which took place easily at that temperature. Di-substituted oxiranes such as 1,2-epoxycyclopentane and 2-methoxymethyl-3-phenyloxirane did not react with **2a** and oxiranes were recovered unchanged even after prolonged reaction period. 2-Phenyloxetane and 2-methoxymethyloxolane were also recovered upon treatment with **2a**.

Scheme 6



Then we studied the 1,4-rearrangement[16] of silyl group from carbon to oxide in the adduct **15** and found that the rate of the rearrangement depended heavily on the reaction solvent as in the case of the adduct **3** generated from **2a** and aldehyde. In ether, migration did not take place. However, change of the solvent from ether to THF facilitated the 1,4-rearrangement of silyl group.[17] For instance, treatment of 1,2-epoxypropane with **2a** in THF at –40 °C gave 1,1-dibromo-1-deuterio-3-*tert*-butyldimethylsiloxybutane in 83% yield (81% D) after quenching with MeOD. Various oxiranes provided the corresponding products as shown in Table 2. Among them, ethylene oxide gave the best results and the reaction with **2a** afforded 3,3-dibromo-1-siloxypropane almost quantitatively. *t*-Butyldimethylsilyldichloromethyllithium (**2b**) reacted with oxiranes equally effectively as **2a**.

Table 2. Reaction of *tert*-butyldimethylsilyldihalomethyllithium **2** with oxiranes in THF

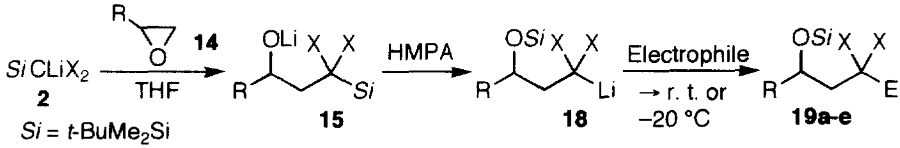


	X	R	Yield (%)		X	R	Yield (%)
a	Br	CH_3	83 (81%D)[a]	**e**	Cl	CH_3	80
b	Br	H	98	**f**	Cl	H	96
c	Br	Ph	65	**g**	Cl	Ph	62 (83%D)[a]
d	Br	CH_2=CH	63	**h**	Cl	$ClCH_2$	78

a) MeOD was used instead of MeOH

Dihaloalkyllithium **18**, regenerated by 1,4-rearrangement of silyl group in THF in the presence of HMPA smoothly reacted with second electrophiles to give the corresponding adducts in good yields. The representative results are summarized in Table 3. The use of isopropyl formate afforded 2,2-dichloro-4-siloxybutanal.

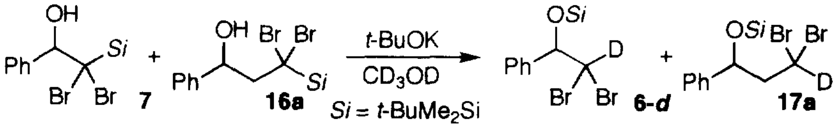
Table 3. One-pot synthesis of RCH(OSiMe$_2$-t-Bu)CH$_2$CX$_2$E' from **2**



	X	R	Electrophile	E'	Yield of **19** (%)
a	Br	CH_3	CH_3I	CH_3	60
b	Cl	CH_3	CH_3I	CH_3	68
c	Cl	CH_3	PhCHO	PhCH(OH)	65
d	Cl	H	CH_3I	CH_3	80
e	Cl	H	HCOO*i*Pr	CHO	56

Finally, we examined the relative reaction rate between 1,3-rearrangement and 1,4-rearrangement. A catalytic amount of *tert*-BuOK was added to a mixture of **7** and **16a** (**7**:**16a** = 1:1) in CD_3OD. The reaction mixture was monitored by ^1H NMR (PhC$\underline{H}$ vs PhC$\underline{H}$(OSi)). Whereas 1,3-rearrangement completed within 5 min, 1,4-rearrangement was slow and took 30 min to complete (Scheme 7).

Scheme 7



Experimental

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Melting points were obtained on a Yanako MP-50929 melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were taken on a Varian GEMINI 300 spectrometer, $CDCl_3$ was used as a solvent, and chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Toluene, hexane, and diethyl ether were dried over a slice of sodium. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use.

***tert*-Butyl(dibromomethyl)dimethylsilane (1a)**: Bp 60 °C (1 Torr); IR (neat) 2926, 2856, 1464, 1364, 1252, 839, 824, 779 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 6H), 1.02 (s, 9H), 5.27 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -6.84, 17.94, 27.30, 34.11. Found: C, 29.22; H, 5.76%. Calcd for $C_7H_{16}Br_2Si$: C, 29.18; H, 5.60%.

***tert*-Butyl(dichloromethyl)dimethylsilane (1b)**: Bp 70 °C (20 Torr); IR (CH_2Cl_2) 2930, 2856, 1465, 1365, 1264, 832, 785, 740, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 6H), 1.00 (s, 9H), 5.41 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -7.95, 17.42, 26.97, 62.27. Analytically pure sample could not be obtained because of its sublimation character.

General Procedure for the Reaction of *tert*-Butyldimethylsilyldibromomethyllithium (2a) with aldehydes. An ethereal solution (2 ml) of *tert*-butyl(dibromomethyl)dimethylsilane (0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in Et_2O (3 ml) at –78 °C under argon atmosphere. After being stirred for 1 h at –78 °C benzaldehyde (0.13 g, 1.2 mmol) in Et_2O (1 ml) was added and the reaction mixture was stirred for 20 min at –78 °C. The mixture was quenched with methanol (1 ml). Extractive workup (1*M* HCl and hexane) followed by purification by silica-gel column chromatography gave 1,1-dibromo-2-(*tert*-butyldimethylsiloxy)-2-phenylethane (**6**) in 87% yield: Bp 90 °C (1.0 Torr); IR (neat) 2926, 2852, 1455, 1362, 1255, 1135, 1094, 857, 836, 778, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.13 (s, 3H), 0.15 (s, 3H), 0.91 (s, 9H), 4.94 (d, J = 5.3 Hz, 1H), 5.63 (d, J = 5.3 Hz, 1H), 7.30–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -4.94, -4.68, 18.25, 25.69, 51.56, 79.90, 127.48, 128.07, 128.61, 139.75. Found: C, 42.78; H, 5.79%. Calcd for $C_{14}H_{22}Br_2OSi$: C, 42.65; H, 5.62%.

2,2-Dibromo-2-(*tert*-butyldimethylsilyl)-1-phenylethanol (7): Bp 110 °C (0.5 Torr); IR (neat) 3546, 3448, 2956, 2854, 1464, 1365, 1250, 1027, 821, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (s, 3H), 0.37 (s, 3H), 1.15 (s, 9H), 2.65 (d, J = 6.4 Hz, 1H), 5.06 (d, J = 6.4 Hz, 1H), 7.35–7.65 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -3.73, -3.67, 19.91, 28.69, 72.18, 80.10, 127.32, 128.74, 129.26, 138.84. Found: C, 42.77; H, 5.49%. Calcd for $C_{14}H_{22}Br_2OSi$: C, 42.65; H, 5.62%.

2,2-Dibromo-1-(*tert*-butyldimethylsiloxy)-1-phenylpropane (10a): A THF (2 ml) solution of 2,2-dibromo-1-(*tert*-butyldimethylsiloxy)-1-phenylethane (**6**, 0.39 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in THF (3 ml) at –78 °C. After being stirred for 15 min at –78 °C, methyl iodide (0.09 ml, 1.5 mmol) in THF (1 ml) was added and the reaction mixture was stirred for 1 h at –78 °C. Extractive workup followed by purification by silica-gel column chromatography gave a title compound **10a** (0.40 g) in 97% yield: Bp 90 °C (1.0 torr); IR (neat) 2926, 2854, 1454, 1373, 1255, 1099, 1071, 858, 777, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.26 (s, 3H), 0.15 (s, 3H), 0.91 (s, 9H), 2.40 (s, 3H), 4.92 (s, 1H), 7.30–7.55 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -5.12, -4.65, 18.20, 25.73, 35.60, 72.78, 83.80, 127.40, 128.48, 129.23, 138.64. Found: C, 43.90; H, 6.02%. Calcd for $C_{15}H_{24}Br_2OSi$: C, 44.13; H, 5.93%.

4,4-Dibromo-5-(*tert*-butyldimethylsiloxy)-5-phenyl-1-pentene (10b): Bp 105 °C (1.0 Torr); IR (neat) 3078, 3028, 2926, 2854, 1643, 1455, 1361, 1257, 1098, 923, 855, 777, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.29 (s, 3H), 0.14 (s, 3H), 0.92 (s, 9H), 3.00 (ddt, J = 15.0, 6.6, 1.3 Hz, 1H), 3.08 (ddt, J = 15.0, 6.6, 1.3 Hz, 1H), 4.98 (s, 1H), 5.20 (ddt, J = 16.8, 1.7, 1.3 Hz, 1H), 5.29 (ddt, J = 10.2, 1.7, 1.3 Hz, 1H), 6.08 (ddt, J

= 16.8, 10.2, 6.6 Hz, 1H), 7.30-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -5.06, -4.57, 18.20, 25.75, 48.50, 79.13, 83.29, 119.65, 127.39, 128.55, 129.58, 133.93, 138.59. Found: C, 46.73; H, 6.01%. Calcd for $C_{17}H_{26}Br_2OSi$: C, 47.02; H, 6.03.

(*1R,*3R**)-2,2-Dibromo-1,3-diphenyl-3-(*tert*-butyldimethylsiloxy)propanol (5):** Mp 92.0–93.0 °C; IR (CH_2Cl_2) 3550, 3432, 3028, 2926, 2852, 1471, 1454, 1389, 1264, 1199, 1099, 1070, 837, 737, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.24 (s, 3H), 0.21 (s, 3H), 0.95 (s, 9H), 4.55 (bd, *J* = 2.8 Hz, 1H), 5.08 (d, *J* = 2.8 Hz, 1H), 5.40 (s, 1H), 7.30–7.70 (m, 10H); ^{13}C NMR ($CDCl_3$) δ -5.34, -4.82, 18.11, 25.69, 77.32, 80.93, 84.01, 127.11, 127.63, 128.60, 128.90, 129.80, 137.78, 138.70. Found: C, 50.63; H, 5.63%. Calcd for $C_{21}H_{28}Br_2O_2Si$: C, 50.41; H, 5.64%.

(*1R,*3S**)-2,2-Dibromo-1,3-diphenyl-3-(*tert*-butyldimethylsiloxy)propanol (5'):** Mp 120–121 °C; IR (CH_2Cl_2) 3542, 3050, 2926, 2854, 1454, 1265, 1113, 863, 838, 732, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.29 (s, 3H), 0.17 (s, 3H), 0.96 (s, 9H), 3.10 (d, *J* = 5.4 Hz, 1H), 4.53 (d, *J* = 5.4 Hz, 1H), 5.27 (s, 1H), 7.30–7.75 (m, 10H); ^{13}C NMR ($CDCl_3$) δ -4.91, -4.28, 18.27, 25.83, 78.65, 81.35, 85.94, 127.33, 127.59, 128.74, 129.43, 138.61, 138.85. Found: C, 50.24; H, 5.64%. Calcd for $C_{21}H_{28}Br_2O_2Si$: C, 50.41; H, 5.64%. The physical and spectra data of **5** and **5'** were identical with those of authentic sample.[18]

(*1R,*3R**)-2,2-Dibromo-1-phenyl-1-(*tert*-butyldimethylsiloxy)-3-heptanol (10c):** Bp 115 °C (0.5 Torr); IR (neat) 3464, 2952, 2854, 1459, 1379, 1255, 1200, 1098, 1072, 867, 838, 778, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.28 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 0.92 (t, J = 7.3 Hz, 3H), 1.10–2.20 (m, 6H), 3.36 (bs, 1H), 3.81 (bs, 1H), 5.23 (s, 1H), 7.30–7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -5.34, -4.80, 14.04, 18.07, 22.52, 25.65, 28.09, 34.92, 75.70, 82.07, 84.95, 127.37, 128.67, 129.79, 138.19. Found: C, 47.75; H, 6.74%. Calcd for $C_{19}H_{32}Br_2O_2Si$: C, 47.51; H, 6.71%.

(*1R,*3S**)-2,2-Dibromo-1-phenyl-1-(*tert*-butyldimethylsiloxy)-3-heptanol (10c'):** Bp 115 °C (0.5 Torr); IR (neat) 3546, 3446, 3030, 2926, 2859, 1459, 1362, 1253, 1120, 838, 777, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.31 (s, 3H), 0.13 (s, 3H), 0.89 (t, J = 7.0 Hz, 3H), 0.95 (s, 9H), 1.20–2.20 (m, 7H), 3.23 (t, *J* = 10.0 Hz, 1H), 5.19 (s, 1H), 7.30–7.65 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -5.04, -4.39, 14.03, 18.22, 22.58, 25.78, 28.10, 34.65, 76.79, 80.19, 90.42, 127.48, 128.46, 129.26, 138.56. Found: C, 47.68; H, 6.72%. Calcd for $C_{19}H_{32}Br_2O_2Si$: C, 47.51; H, 6.71%. The assignment of the stereochemistry of **10c** and **10c'** were performed by NOE experiment.

1-(*tert*-Butyldimethylsiloxy)-2,2-dibromo-2-(1-hydroxycyclohexyl)-1-phenylpropane (10d): Mp 100–101 °C; IR (CH_2Cl_2) 3474, 2930, 2856, 1452, 1265, 1051, 858, 837, 738, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.46 (s, 3H), 0.09 (s, 3H), 0.92 (s, 9H), 1.10–2.30 (m, 10H), 3.97 (bs, 1H), 5.28 (s, 1H), 7.30–7.80 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -4.74, -4.05, 18.04, 21.76, 22.24, 25.55, 25.81, 31.50, 35.50, 79.56, 80.98, 126.90, 128.88, 131.07, 138.96. Found: C, 48.84; H, 6.81%. Calcd for $C_{20}H_{32}Br_2O_2Si$: C, 48.79; H, 6.55%.

General Procedure for One-pot Synthesis of 12 ($RCH(OSiMe_2$-*t*-$Bu)CCl_2E'$) from 1b. A THF (2 ml) solution of *tert*-butyl(dichloromethyl)dimethylsilane (**1b**, 0.24 g, 1.2 mmol) was added to a solution of lithium diisopropylamide (1.4 mmol) in THF (3 ml) at -78 °C under argon atmosphere. After being stirred for 1 h at -78 °C, benzaldehyde (0.11 g, 1.0 mmol) in THF (1 ml) was added and the reaction mixture was stirred for 20 min at -78 °C. Methyl iodide (1.5 mmol) in THF (1 ml) and HMPA (0.24 ml, 1.4 mmol) in THF (1 ml) were added successively to the reaction mixture and the resulting mixture was allowed to warm to room temperature over 5 h. Extractive workup (1*M* HCl and hexane) followed by purification by silica-gel column chromatography gave 1-(*tert*-butyldimethylsiloxy)-2,2-dichloro-1-phenylpropane **12a** (0.23 g) in 71% yield. When aldehydes were used as second electrophiles, the reaction mixture was allowed to warm to -20 °C and kept there for 1 h before workup. **12a**: Bp 90 °C (1.0 Torr); IR (neat) 2928, 2884, 2854, 1455, 1375, 1254, 1105, 1076, 861, 836, 777, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.21 (s, 3H), 0.12 (s, 3H), 0.90 (s, 9H), 2.04 (s, 3H), 4.92 (s, 1H), 7.30–7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -5.21, -4.75, 18.16, 25.67, 31.96, 82.83, 92.10, 127.44, 128.42, 129.01, 138.58. Found: C, 56.32; H, 7.65%. Calcd for $C_{15}H_{24}Cl_2OSi$: C, 56.42; H, 7.58%.

5-(*tert*-Butyldimethylsiloxy)-4,4-dichloro-5-phenyl-1-pentene (12b): Bp 95 °C (1.0 Torr); IR (neat) 3080, 2950, 2854, 1644, 1455, 1254, 1105, 930, 858, 837, 777, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ –0.24 (s, 3H), 0.11 (s, 3H), 0.90 (s, 9H), 2.83 (dd, *J* = 14.7, 6.7 Hz, 1H), 2.97 (dd, *J* = 14.7, 6.7 Hz, 1H), 4.96 (s, 1H), 5.19 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.27 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.05 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 7.30–7.40 (m, 3H), 7.45–7.55 (m, 2H); ^{13}C NMR (CDCl$_3$) δ –5.15, –4.66, 18.16, 25.69, 46.31, 82.49, 95.04, 120.03, 127.44, 128.49, 129.32, 131.80, 138.32. Found: C, 59.32; H, 7.60%. Calcd for $C_{17}H_{26}Cl_2OSi$: C, 59.12; H, 7.59%.

(*E*)-3-(*tert*-Butyldimethylsiloxy)-4,4-dichloro-1-phenyl-1-pentene (12c): Bp 100 °C (1.0 Torr); IR (neat) 3010, 2928, 2854, 1650, 1460, 1253, 1130, 1073, 968, 873, 836, 777, 748, 691 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.08 (s, 3H), 0.16 (s, 3H), 0.94 (s, 9H), 2.08 (s, 3H), 4.49 (d, *J* = 6.8 Hz, 1H), 6.31 (dd, *J* = 15.9, 6.8 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 7.27–7.45 (m, 5H); ^{13}C NMR (CDCl$_3$) δ –4.84, –3.99, 18.22, 25.77, 32.19, 81.64, 91.88, 126.70, 128.09, 128.65, 134.42, 136.23. Found: C, 59.36; H, 7.88%. Calcd for $C_{17}H_{26}Cl_2OSi$: C, 59.12; H, 7.59%.

5-(*tert*-Butyldimethylsiloxy)-4,4-dichloro-1-octene (12d): Bp 65 °C (1.0 Torr); IR (neat) 2956, 2856, 1464, 1362, 1257, 1146, 1104, 924, 835, 775 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.12 (s, 3H), 0.15 (s, 3H), 0.92 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H), 1.20–2.05 (m, 4H), 2.80–3.00 (m, 2H), 3.90 (dd, *J* = 7.0, 2.6 Hz, 1H), 5.22 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.27 (dq, *J* = 10.2, 1.7 Hz, 1H), 6.03 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ –3.98, –3.60, 14.17, 18.43, 26.02, 35.95, 46.75, 80.81, 96.27, 119.86, 131.92. Found: C, 53.83; H, 9.29%. Calcd for $C_{14}H_{28}Cl_2OSi$: C, 54.01; H, 9.06%.

(*1R*,3R)-2,2-Dichloro-1-(4-methoxyphenyl)-3-phenyl-1,3-propanediol:** 1,3-Diol monosilyl ether **12e** was converted into diol with saturated aqueous KF in the presence of a catalytic amount of *n*-Bu$_4$NF in THF and two diastereomers of diol were separated by silica-gel column chromatography. IR (neat) 3382, 2954, 2930, 1710, 1611, 1513, 1250, 1177, 1066, 1032, 832, 731, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.04 (bs, 1H), 3.12 (bs, 1H), 3.82 (s, 3H), 5.05 (s, 1H), 5.07 (s, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.35–7.60 (m, 7H); ^{13}C NMR (CDCl$_3$) δ 55.22, 78.92, 79.23, 98.49, 113.20, 127.71, 127.80, 128.80, 128.90, 129.20, 129.93, 130.15, 137.15, 154.97. Found: C, 58.87; H, 4.94%. Calcd for $C_{16}H_{16}O_3Cl_2$: C, 58.73; H, 4.93%.

(*1R*,3S)-2,2-Dichloro-1-(4-methoxyphenyl)-3-phenyl-1,3-propanediol:** Bp 110 °C (0.5 Torr); IR (neat) 3388, 2954, 2930, 1707, 1611, 1514, 1252, 1178, 1035, 860, 829, 730, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.57 (bs, 1H), 3.69 (bs, 1H), 3.82 (s, 3H), 5.27 (s, 1H), 5.30 (s, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.35–7.60 (m, 7H); ^{13}C NMR (CDCl$_3$) δ 55.21, 78.87, 79.17, 95.02, 113.10, 127.68, 127.78, 128.80, 128.87, 129.08, 130.04, 130.23, 137.02, 159.85. Found: C, 58.50; H, 4.96%. Calcd for $C_{16}H_{16}O_3Cl_2$: C, 58.73; H, 4.93%.

(*1R*,3R)-2,2-Dichloro-1-phenyl-1,3-heptanediol:** Bp 90 °C (0.2 Torr); IR (neat) 3838, 3820, 2956, 2860, 1492, 1455, 1379, 1191, 1089, 1063, 859, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, *J* = 7.3 Hz, 3H), 1.20–2.15 (m, 6H), 2.26 (d, *J* = 9.3 Hz, 1H), 3.38 (d, *J* = 3.5 Hz, 1H), 3.66 (dt, *J* = 9.3, 1.9 Hz, 1H), 5.31 (d, *J* = 3.5 Hz, 1H), 7.35–7.65 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 13.94, 22.46, 27.82, 32.15, 77.52, 79.50, 100.33, 127.74, 127.84, 128.70, 136.91. Found: C, 56.05; H, 6.58%. Calcd for $C_{13}H_{18}Cl_2O_2$: C, 56.33; H,6.55%.

(*1R*,3S)-2,2-Dichloro-1-phenyl-1,3-heptanediol:** IR (neat) 3364, 2954, 2858, 1495, 1455, 1380, 1201, 1123, 1089, 1054, 971, 857, 756, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.20–2.20 (m, 6H), 2.58 (bs, 1H), 3.37 (bs, 1H), 4.12 (m, 1H), 5.30 (s, 1H), 7.35–7.60 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 13.96, 22.47, 28.29, 31.77, 77.30, 78.74, 97.29, 127.55, 127.70, 127.86, 128.87, 129.15, 137.17. Found: C, 56.54; H, 6.55%. Calcd for $C_{13}H_{18}Cl_2O_2$: C, 56.33; H, 6.55%.

(*E*)-(*1R*,3R)-2,2-Dichloro-1,5-diphenyl-4-pentene-1,3-diol:** IR (nujol) 3458, 1455, 1198, 1118, 1064, 1046, 966, 906, 835, 737, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.57 (d, *J* = 6.5 Hz, 1H), 3.07 (d, *J* = 4.3 Hz, 1H), 4.47 (t, *J* = 6.5 Hz, 1H), 5.34 (d, *J* = 4.3 Hz, 1H), 6.50 (dd, *J* = 16.0, 6.5 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 7.25–7.65 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 78.01, 79.10, 98.83, 124.98, 126.69, 126.86, 126.95, 127.86, 128.06, 128.28, 128.55, 128.73, 129.04, 135.47, 135.81, 136.76. Found: C, 62.93; H, 5.06%. Calcd for $C_{17}H_{16}Cl_2O_2$: C, 63.17; H,4.99%.

(E)-(1R*,3S*)-2,2-Dichloro-1,5-diphenyl-4-pentene-1,3-diol: IR (neat) 3306, 3028, 2920, 1719, 1638, 1493, 1452, 1201, 1123, 1044, 966, 909, 866, 746, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.97 (bs, 1H), 3.27 (bs, 1H), 4.88 (bd, J = 6.0 Hz, 1H), 5.33 (s, 1H), 6.53 (dd, J = 15.9, 6.0 Hz, 1H), 6.83 (d, J = 15.9 Hz, 1H), 7.25–7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 77.63, 78.65, 95.85, 124.69, 126.76, 126.86, 127.70, 127.84, 128.26, 128.34, 128.59, 128.70, 128.81, 129.03, 135.32, 135.95, 136.93. Found: C, 62.88; H, 4.98%. Calcd for $C_{17}H_{16}Cl_2O_2$: C, 63.17; H, 4.99%.

Reduction of Dichloride 12a with *n*-Bu_3SnH-Et_3B. A hexane solution of Et_3B (0.96 M, 0.73 ml, 0.7 mmol) was added to a solution of **12a** (186 mg, 0.6 mmol) and *n*-Bu_3SnH (0.47 ml, 1.75 mmol) in hexane (5 ml). The mixture was heated at 80 °C for 24 h. The resulting mixture was concentrated *in vacuo* and the residual oil was diluted with dichloromethane (20 ml). Potassium fluoride (1.0 g) and saturated aqueous potassium fluoride (1.0 ml) were added and the resulting mixture was stirred at 25 °C for 15 h. The reaction mixture was filtered and filtrate was concentrated. Purification of the residual oil by silica-gel column chromatography gave 1-phenyl-1-*tert*-butyldimethylsiloxypropane (0.15 g) in 97% yield.

3,3-Dibromo-3-(*tert*-butyldimethylsilyl)-1-phenyl-1-propanol (16a): IR (neat) 3562, 3426, 2958, 2928, 2884, 2856, 1465, 1253, 1039, 835, 820, 776, 761, 698, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 3H), 0.32 (s, 3H), 1.06 (s, 9H), 2.80 (dd, J = 15.3, 2.7 Hz, 1H), 2.87 (dd, J = 15.3, 6.3 Hz, 1H), 2.98 (d, J = 2.4 Hz, 1H), 5.54 (ddd, J = 6.3, 2.7, 2.4 Hz, 1H), 7.25–7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ –5.87, 19.59, 28.46, 55.05, 67.89, 73.70, 125.80, 127.55, 128.68, 144.30. Found: C, 44.13; H, 5.93%. Calcd for $C_{15}H_{24}OBr_2Si$: C, 44.29; H, 5.95%.

4,4-Dibromo-4-(*tert*-butyldimethylsilyl)-2-butanol (16b): Bp 100 °C (1 Torr); IR (neat) 3390, 2960, 2930, 2896, 2858, 1465, 1366, 1253, 1073, 930, 836, 776, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.307 (s, 3H), 0.314 (s, 3H), 1.081 (s, 9H), 1.31 (d, J = 6.3 Hz, 3H), 2.53 (dd, J = 15.3, 2.7 Hz, 1H), 2.60 (dd, J = 15.3, 5.7 Hz, 1H), 2.64 (d, J = 2.7 Hz, 1H), 4.59 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –5.95, 19.54, 24.06, 28.43, 53.90, 68.11, 68.59. Found: C, 34.67; H, 6.53%. Calcd for $C_{10}H_{22}Br_2OSi$: C, 34.70; H, 6.41%.

4,4-Dibromo-4-(*tert*-butyldimethylsilyl)-1-methoxy-2-butanol (16c): Bp 95 °C (0.5 Torr); IR (neat) 3426, 2928, 2884, 2856, 1465, 1253, 1195, 1126, 1086, 934, 835, 775, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 6H), 1.08 (s, 9H), 2.59 (dd, J = 15.5, 4.8 Hz, 1H), 2.65 (dd, J = 15.5, 3.6 Hz, 1H), 2.74 (d, J = 3.3 Hz, 1H), 3.438 (s, 3H), 3.442 (dd, J = 9.6, 7.2 Hz, 1H), 3.57 (dd, J = 9.6, 3.9 Hz, 1H), 4.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –5.93, –5.83, 19.53, 28.44, 49.35, 59.09, 67.60, 70.40, 76.55. Found: C, 35.36; H, 6.58%. Calcd for $C_{11}H_{24}Br_2O_2Si$: C, 35.12; H, 6.43%.

General Procedure for the Reaction of Silyldihalomethyllithium 2 with Oxirane. A reaction of *tert*-butyldimethylsilyldibromomethyllithium (**2a**) with styrene oxide is representative. A THF (2 ml) solution of *tert*-butyl(dibromomethyl)dimethylsilane (**1a**, 0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in THF (3 ml) at –78 °C. After being stirred for 1 h at –78 °C, styrene oxide (0.14 g, 1.2 mmol) in THF (1 ml) was added and the mixture was warmed to –40 °C over 1 h. The resulting mixture was quenched with methanol and stirred another 10 min at room temperature. Extractive workup (1*M* HCl and hexane) followed by purification by silica-gel column chromatography gave 1,1-dibromo-3-(*tert*-butyldimethylsiloxy)-3-phenylpropane (**17c**, 0.27 g) in 65 % yield: Bp 135 °C (1.0 Torr); IR (neat) 2948, 2928, 2884, 2854, 1471, 1456, 1362, 1255, 1156, 1089, 1002, 929, 837, 777, 699, 615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.24 (s, 3H), 0.05 (s, 3H), 0.86 (s, 9H), 2.55 (ddd, J = 14.5, 9.2, 4.0 Hz, 1H), 2.79 (ddd, J = 14.5, 9.2, 4.0 Hz, 1H), 4.87 (dd, J = 9.2, 3.5 Hz, 1H), 5.69 (dd, J = 9.8, 4.0 Hz, 1H), 7.20–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ –4.96, –4.47, 18.08, 25.79, 42.91, 56.18, 73.62, 126.07, 127.83, 128.44, 143.14. Found: C, 44.00; H, 5.94%. Calcd for $C_{15}H_{24}Br_2OSi$: C, 44.13; H, 5.93%.

1,1-Dibromo-3-(*tert*-butyldimethylsiloxy)butane (17a): Bp 90 °C (1.0 Torr); IR (neat) 2952, 2926, 2886, 2854, 1463, 1375, 1256, 1135, 1046, 967, 836, 775, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 3H), 0.11 (s, 3H), 0.89 (s, 9H), 1.18 (d, J = 6.0 Hz, 3H), 2.41 (ddd, J = 14.4, 10.2, 3.0 Hz, 1H), 2.54 (ddd, J = 14.4, 9.0, 3.6 Hz, 1H), 4.00 (ddq, J = 3.0, 9.0, 6.0 Hz, 1H), 5.72 (dd, J =10.2, 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.90, –4.27, 17.84, 23.33, 25.73, 43.38, 55.06, 67.04. Found: C, 34.99; H, 6.56%. Calcd for $C_{10}H_{22}Br_2OSi$: C, 34.70; H, 6.41%.

1,1-Dibromo-3-(*tert*-butyldimethylsiloxy)propane (17b): Bp 80 °C (1 Torr); IR (neat) 2952, 2926, 2856, 1471, 1387, 1256, 1161, 1104, 932, 836, 777, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 6H), 0.90 (s, 9H), 2.58 (dt, J = 6.6, 5.7 Hz, 2H), 3.72 (t, J = 5.7 Hz, 2H), 5.84 (t, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –5.60, 18.14, 25.76, 43.16, 48.13, 60.70. Found: C, 32.82; H, 6.01%. Calcd for $C_9H_{20}Br_2OSi$: C, 32.55; H, 6.07%.

5,5-Dibromo-3-(*tert*-butyldimethylsiloxy)-1-pentene (17d): Bp 90 °C (1 Torr); IR (neat) 3078, 3008, 2952, 2928, 2884, 2856, 1645, 1463, 1419, 1362, 1253, 1086, 923, 836, 776, 680, 562 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 3H), 0.10 (s, 3H), 0.90 (s, 9H), 2.46 (ddd, J = 14.4, 9.3, 3.9 Hz, 1H), 2.61 (ddd, J = 14.4, 9.0, 4.5 Hz, 1H), 4.25 (m, 1H), 5.13 (d, J = 10.2 Hz, 1H), 5.24 (d, J = 17.1 Hz, 1H), 5.69 (dd, J = 9.3,4.5 Hz, 1H), 5.78 (ddd, J = 17.1, 10.2, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.96, –4.20, 17.98, 25.74, 42.42, 63.42, 72.68, 115.94, 139.83. Found: C, 36.91; H, 6.21%. Calcd for $C_{11}H_{22}Br_2OSi$: C, 36.89; H, 6.19%.

3-(*tert*-butyldimethylsiloxy)-1,1-dichlorobutane (17e): Bp 110 °C (8 Torr); IR (neat) 2954, 2928, 2888, 2856, 1472, 1363, 1257, 1139, 1050, 973, 836, 775, 754, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.89 (s, 9H), 1.18 (d, J = 6.0 Hz, 3H), 2.21 (ddd, J = 14.0, 9.6, 3.0 Hz, 1H), 2.32 (ddd, J = 14.0, 9.3, 3.6 Hz, 1H), 4.03 (ddq, J = 9.3, 3.0, 6.0 Hz, 1H), 5.81 (dd, J = 9.6, 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –5.09, –4.33, 17.82, 23.57, 25.69, 53.25, 65.61, 71.29. Found: C, 46.58; H, 8.84%. Calcd for $C_{10}H_{22}Cl_2OSi$: C, 46.69; H, 8.62%.

3-(*tert*-butyldimethylsiloxy)-1,1-dichloropropane (17f): Bp 100 °C (9 Torr); IR (neat) 2952, 2928, 2880, 2856, 1472, 1387, 1257, 1108, 938, 835, 777, 756, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 6H), 0.89 (s, 9H), 2.38 (dt, J = 6.3, 5.4 Hz, 2H), 3.78 (t, J = 5.4 Hz, 2H), 5.92 (t, J = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –5.66, 18.13, 25.74, 46.40, 59.19, 71.07. Found: C, 44.53; H, 8.54%. Calcd for $C_9H_{20}Cl_2OSi$: C, 44.44; H, 8.29%.

1-(*tert*-Butyldimethylsiloxy)-3,3-dichloro-1-phenylpropane (17g): Bp 100 °C (1.0 Torr); IR (neat) 2952, 2928, 2886, 2854, 1464, 1363, 1254, 1093, 1005, 937, 836, 777, 745, 698, 671, 611 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.22 (s, 3H), 0.05 (s, 3H), 0.88 (s, 9H), 2.37 (ddd, J = 14.1, 9.3, 3.3 Hz, 1H), 2.60 (ddd, J = 14.1, 9.6, 3.9 Hz, 1H), 4.84 (dd, J = 9.3, 3.3 Hz, 1H), 5.82 (dd, J = 9.6, 3.6 Hz, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ –5.29, –4.68, 17.67, 25.68, 54.41, 70.91, 72.33, 126.09, 127.91, 128.54, 143.46. Found: C, 56.19; H, 7.71%. Calcd for $C_{15}H_{24}Cl_2OSi$: C, 56.42; H, 7.57%.

2-(*tert*-Butyldimethylsiloxy)-1,4,4-trichlorobutane (17h): Bp 70 °C (0.5 Torr); IR (neat) 2952, 2928, 2886, 2856, 1465, 1390, 1363, 1257, 1153, 1092, 935, 836, 776, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6H), 0.91 (s, 9H), 2.44 (ddd, J = 14.4, 8.1, 4.2 Hz, 1H), 2.52 (ddd, J = 14.4, 9.3, 3.3 Hz, 1H), 3.44 (dd, J = 11.4, 6.3 Hz, 1H), 3.51 (dd, J = 11.4, 3.9 Hz, 1H), 4.10 (m, 1H), 5.81 (dd, J = 9.3, 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.97, –4.57, 17.87, 25.60, 47.72, 48.82, 69.36, 70.55. Found: C, 41.38; H, 7.39%. Calcd for $C_{10}H_{21}Cl_3OSi$: C, 41.17; H, 7.26%.

General Procedure for One-pot synthesis of 19 ($RCH(OSiMe_2$-*t*-$Bu)CH_2CX_2E'$) from 1. A THF (2 ml) solution of *tert*-butyl(dichloromethyl)dimethylsilane (0.20 g, 1.0 mmol) was added to a solution of lithium diisopropyl amide (1.2 mmol) in THF (3 ml) at –78 °C. After being stirred for 1 h at –78 °C, propylene oxide (0.07 g, 1.2 mmol) in THF (1 ml) was added and the mixture was warmed to –40 °C over 1 h. The resulting mixture was cooled to –78 °C and iodomethane (0.21 g, 1.5 mmol) and HMPA (0.24 ml, 1.4 mmol) in THF (1 ml) were added successively. The whole mixture was allowed to warm to room temperature over 5 h. Extractive workup (1*M* HCl and hexane) followed by purification by silica-gel column chromatography gave 2-(*tert*-butyldimethylsiloxy)-4,4-dichloropentane (**19b**, 0.16 g) in 68% yield. When aldehydes were used as second electrophiles, the reaction mixture was allowed to warm to –20 °C and kept there for 1 h before workup. **19b**: Bp 105 °C (9 Torr); IR (neat) 2954, 2928, 2894, 2856, 1464, 1377, 1257, 1138, 1037, 976, 938, 836, 775, 698, 655, 599 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 6H), 0.89 (s, 9H), 1.26 (d, *J* = 6.0 Hz, 3H), 2.20 (s, 3H), 2.38 (dd, *J* = 14.7, 3.9 Hz, 1H), 2.46 (dd, *J* = 14.7, 6.3 Hz, 1H), 4.25 (ddq, *J* = 6.3, 3.9, 6.0 Hz 1H); ^{13}C NMR ($CDCl_3$) δ –4.61, –4.05, 17.81, 25.05, 25.79, 38.05, 58.72, 66.66, 89.43. Found: C, 48.44; H, 9.10%. Calcd for $C_{11}H_{24}Cl_2OSi$: C, 48.70; H, 8.92%.

2,2-Dibromo-4-(*tert*-butyldimethylsiloxy)pentane (19a): Bp 95 °C (1 Torr); IR (neat) 2954, 2928, 2892, 2854, 1463, 1376, 1257, 1136, 1098, 1033, 972, 836, 774, 652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 3H), 0.11 (s, 3H), 0.89 (s, 9H), 1.27 (d, *J* = 6.0 Hz, 3H), 2.59 (s, 3H), 2.62 (d, *J* = 5.1 Hz, 2H), 4.23 (dq, *J* = 5.1, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.43, –3.92, 17.80, 24.91, 25.82, 41.82, 61.78, 66.70, 68.50. Found: C, 36.85; H, 6.81%. Calcd for $C_{11}H_{24}Br_2OSi$: C, 36.68; H, 6.72%.

4-(*tert*-butyldimethylsiloxy)-2,2-dichloro-1-phenyl-1-pentanol (19c, 53:47 diastereomeric mixture): Bp 125 °C (0.3 Torr); IR (neat) 3424, 2952, 2926, 2892, 2854, 1456, 1377, 1256, 1128, 1052, 1004, 966, 833, 774, 700, 604 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 1.59H), 0.18 (s, 1.41H), 0.90 (s, 4.77H), 0.91 (s, 4.23H), 1.29 (d, *J* = 6.3 Hz, 1.59H), 1.31 (d, *J* = 6.3 Hz, 1.41H), 2.34 (dd, *J* = 15.3, 4.2 Hz, 0.53H), 2.43 (dd, *J* = 15.3, 6.6 Hz, 0.53H), 2.44 (dd, *J* = 15.3, 5.4 Hz, 0.47H), 2.86 (dd, *J* = 15.3, 8.4 Hz, 0.47H), 3.50 (d, *J* = 3.6 Hz, 0.53H), 4.07 (d, *J* = 4.5 Hz, 0.47H), 4.41 (m, 1H), 5.12 (d, *J* = 4.5 Hz, 0.47H), 5.14 (d, *J* = 3.6 Hz, 0.53H), 7.30–7.40 (m, 3H), 7.50–7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.49, –4.36, –4.30, –4.02, 17.92, 24.69, 24.90, 25.83, 52.28, 54.22, 66.91, 66.97, 79.28, 81.16, 94.55, 96.12, 143.91, 144.18, 144.90, 145.16, 145.64, 145.68, 153.43, 153.55. Found: C, 56.10; H, 7.82%. Calcd for $C_{17}H_{28}Cl_2O_2Si$: C, 56.19; H, 7.77%.

1-(*tert*-Butyldimethylsiloxy)-3,3-dichlorobutane (19d): Bp 110 °C (8 Torr); IR (neat) 2952, 2928, 2882, 2856, 1472, 1382, 1257, 1110, 902, 838, 776, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 6H), 0.90 (s, 9H), 2.20 (s, 3H), 2.49 (t, *J* = 6.6 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.56, 18.07, 25.76, 37.98, 51.87, 60.05, 88.88. Found: C, 46.67; H, 8.57%. Calcd for $C_{10}H_{22}Cl_2OSi$; C, 46.69; H, 8.62%.

4-(*tert*-butyldimethylsiloxy)-2,2-dichlorobutanal (19e): Bp 95 °C (4 Torr); IR (neat) 2952, 2928, 2882, 2856, 1751, 1472, 1390, 1363, 1257, 1105, 977, 837, 777, 663, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6H), 0.86 (s, 9H), 2.64 (t, *J* = 5.7 Hz, 2H), 3.83 (t, *J* = 5.7 Hz, 2H), 9.15 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –5.69, 18.20, 25.77, 46.18, 58.93, 87.65, 184.43. Found: C, 44.32; H, 7.73%. Calcd for $C_{10}H_{20}Cl_2O_2Si$: C, 44.28; H, 7.43%.

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