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Reduction of α-Trialkylsiloxy Nitriles with Diisobutylaluminium Hydride (DIBAH): A Facile Preparation of α-Trialkylsiloxy Aldehydes and their Derivatives

Masahiko Hayashi, Tomoko Yoshiga, Kanako Nakatani, Kazuyuki Ono, and Nobuki Oguni*

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi City, Yamaguchi 753, Japan

Abstracts: The stepwise synthesis of α-trimethylsiloxy aldehydes and α-hydroxy aldehydes could be achieved *via* the reduction of α-trimethylsiloxy nitriles with diisobutylaluminium hydride (DIBAH) starting from a variety of ketones. The facile synthesis of optically active α-*tert*-butyldimethylsiloxy aldehydes was attained by combination of asymmetric silylcyanation of aldehydes and DIBAH reduction of optically active α-siloxy nitriles. Furthermore, in the reduction of some α-*tert*-butyldimethylsiloxy-β,γ-unsaturated nitriles, migration of the double bond took place to form more stable α-siloxy-α,β-unsaturated aldehydes under some reaction conditions.

Introduction

α-Hydroxy aldehydes and their *O*-protected derivatives are important compounds in organic synthesis. Especially, recent intensive studies for controlling diastereofacial selectivity in the addition of various nucleophiles to chiral carbonyl compounds[1,2] have required the convenient synthetic method of α-*O*-protected aldehydes.

One of the conventional methods for the synthesis of α-*O*-protected aldehydes involves the reduction of the corresponding α-*O*-protected carboxylic acid esters with DIBAH. However, the reaction at low reaction temperature such as less than -78 °C was required to avoid overreduction leading to alcohols.[1b]

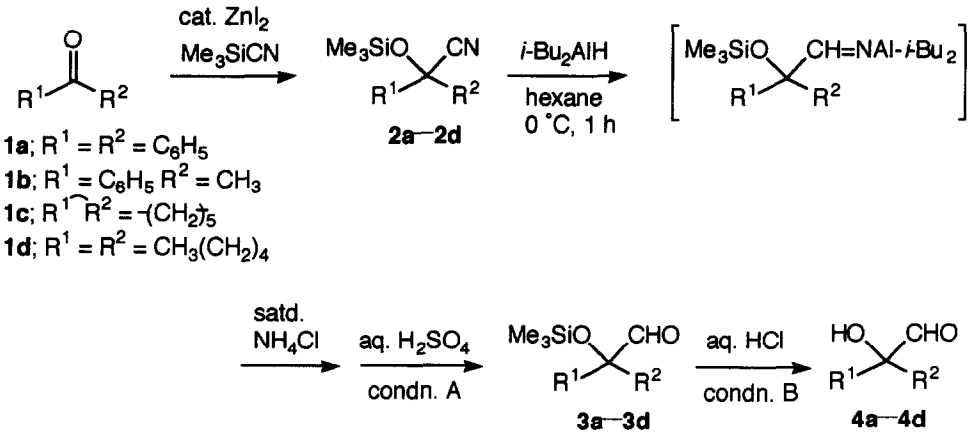
On the other hand, α-*O*-trialkylsiloxy nitriles can be easily prepared by the reaction of trialkylsilyl cyanide with carbonyl compounds in the presence of ZnI_2,[3,4] and the reduction of nitriles with DIBAH proceeds under mild conditions.[5] Actually, several examples for conversion of α-trimethylsiloxy nitriles derived from ketones to α-trimethylsiloxy aldehydes using DIBAH have been reported so far.[6] However, none of them involved the following hydrolysis step of α-trimethylsiloxy aldehydes to α-hydroxy aldehyde.

In this article, we at first want to report the stepwise preparation of α-trimethylsiloxy aldehydes and α-hydroxy aldehydes starting from ketones.[7] Next, we also describe the reduction of optically active α-*tert*-

butyldimethylsiloxy nitriles with DIBAH, which provides chiral α-siloxy aldehydes. The migration of the double bond in the reaction of some α-*tert*-butyldimethylsiloxy-β,γ-unsaturated nitriles to the corresponding aldehydes will also be disclosed.

Results and Discussion

Stepwise Synthesis of α-Trimethylsiloxy Aldehydes and α-Hydroxy Aldehydes from Ketones. The conversion process from α-trimethylsiloxy nitriles to α-trimethylsiloxy aldehydes consists of two steps. The first step is the reduction of α-trimethylsiloxy nitriles to the corresponding imines by DIBAH, and the second step is the intermediate hydrolysis of formed α-siloxy imines to α-siloxy aldehydes by treatment with aqueous acid solution. DIBAH (1.5—2 equiv. per substrate) was added to a hexane solution of α-trimethylsiloxy nitriles (**2a**—**2d**) at -45 °C and the starting materials were consumed completely after stirring at 0 °C for 1 h in all cases. Then the reaction mixture was poured into a mixture of ether and saturated aqueous ammonium chloride solution. Treating with sulfuric acid solution under stirring vigorously at room tempera-



Scheme 1

ture gave the α-trimethylsiloxy aldehydes (**3a**—**3d**) in good yields (61—86% isolated yield). The concentration of aqueous sulfuric acid solution in the hydrolysis was found to be very important for the aim of obtaining only α-trimethylsiloxy aldehydes without the production of α-hydroxy aldehydes and other by-products. The optimized results are summarized in Table 1.

There have been several reports concerning the synthesis of α-hydroxy aldehydes, but most of them are not satisfactory with respect to chemical yield and operational simplicity.[9] We found the facile method of conversion of α-trimethylsiloxy aldehydes (**3a**—**3d**) to α-hydroxy aldehydes (**4a**—**4d**) which was accomplished by treatment with dilute hydrochloric acid solution. In this reaction, also, the concentration of

Table 1. Preparation of α-trimethylsiloxy aldehydes (**3a—3d**) from α-trimethylsiloxy nitriles (**2a—2d**)[a]

	conditions A			
α-siloxy nitrile	H_2SO_4/N	time/h	product	% yield[b]
2a[c]	1.6	18	**3a**	86
2b	1.3	19	**3b**	63
2c	1.0	19	**3c**	61
2d	1.6	19	**3d**	79

[a] Reduction of α-trimethylsiloxy nitriles with DIBAH was carried out in hexane at 0 °C for 1 h unless otherwise noted, and hydrolysis with aqueous sulfuric acid solution (conditions A) was run at 15 °C. [b] Isolated yield. [c] Toluene was used as a solvent.

hydrochloric acid was important to obtain the desired product in high yield (Table 2). The completion of the reaction was confirmed by IR and ^1H NMR spectra (see experimental section).

Table 2. Conversion of α-trimethylsiloxy aldehydes (**3a—3d**) to α-hydroxy aldehydes (**4a—4d**)[a]

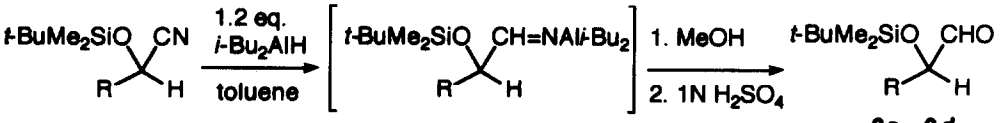
	condition B			
α-siloxy aldehyde	HCl/N	time/h	product	% yield[b]
3a	9	15	**4a**	80
3b	3	14	**4b**	65
3c	1	5	**4c**	75
3d	6	14	**4d**	72

[a] Reactions were carried out at 15 °C. [b] Isolated yield of α-hydroxy aldehydes.

It should be noted that we could obtain α-hydroxy aldehydes in a monomeric form, however, 1-hydroxycyclohexanecarboxaldehyde was unstable and easily dimerized.[8a] The present method is much advantageous in comparison with the reported procedure[8] from the standing points of the mildness of the reaction conditions, high yield, and operational simplicity.

Reduction of α-*tert*-Butyldimethylsiloxy Nitriles with DIBAH. We then examined the DIBAH reduction of α-*tert*-butyldimethylsiloxy nitriles starting from aromatic and aliphatic *aldehydes* (Scheme 2). DIBAH (1.2 eq. per substrate) was added to the toluene solution of **5a—5d** at -40 or -78 °C, and the mixture was stirred at this temperature for 2—5 h. Treatment of the intermediately formed *N*-organoaluminium

imines with methanol, followed by addition of 1N H_2SO_4 solution under vigorous stirring at room temperature afforded the corresponding α-*tert*-butyldimethylsiloxy aldehydes in high yields (Table 3).



5a; R = Ph
5b; R = $CH_3(CH_2)_7$
5c; R = *c*-C_6H_{11}
5d; R = $(CH_3)_3C$

Scheme 2

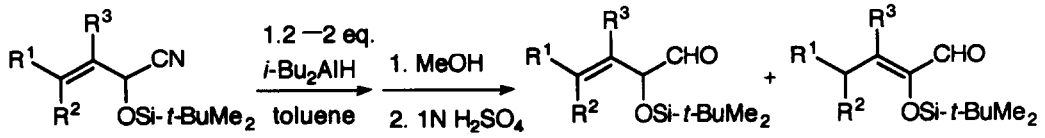
Table 3. Reduction of α-*tert*-butyldimethylsiloxy nitriles (**5a**—**5d**) with DIBAH[a]

α-*tert*-butyldimethylsiloxy nitrile	conditions		product (% yield)[b]
	temp/°C	time/h	
5a	-78	5	**6a** (67)
5b	-78	2	**6b** (86)
5c	-40	2	**6c** (89)
5d	-40	2.5	**6d** (80)

[a] Reduction of α-*tert*-butyldimethylsiloxy nitriles with DIBAH was carried out in toluene, and hydrolysis with aqueous sulfuric acid solution was run at 18 °C for 3 h unless otherwise noted. [b] Isolated yield of α-*tert*-butyldimethylsiloxy aldehyde after silica-gel column chromatography.

When optically active α-*tert*-butyldimethylsiloxy nitriles were used as substrates, no racemization was observed under the above reaction conditions. For example, the reaction of optically active phenyl-*tert*-butyldimethylsiloxyacetonitrile (**5a**) (*R*-enantiomer; 88% e.e.) with DIBAH followed by hydrolysis gave phenyl-*tert*-butyldimethylsiloxyacetaldehyde (**6a**) without any loss of optical purity.[9] Optically active cyanohydrins are easily available by enzymatic[10] and chemical methods,[11] this method by DIBAH reduction will be the general and convenient one for the synthesis of optically active α-*O*-protected aldehydes.

Migration of the Double Bond. During the investigation of the DIBAH reduction, we found very interesting phenomena, that is, migration of the double bond was observed in the reaction of α-*tert*-butyldimethylsiloxy-β,γ-unsaturated nitriles (**7a**—**7c**) prepared from α,β-unsaturated aldehydes (Scheme 3). Under certain reaction conditions, more stable α-siloxy-α,β-unsaturated aldehydes (**9a**—**9c**) were produced



7a; $R^1 = R^2 = R^3 = H$
7b; $R^1 = R^2 = H$, $R^3 = Me$
7c; $R^1 = Me$, $R^2 = R^3 = H$
7d; $R^1 = R^3 = Me$, $R^2 = H$
7e; $R^1 = Ph$, $R^2 = R^3 = H$

8a—8e **9a—9e**

Scheme 3

overwhelmingly than less stable α-siloxy-β,γ-unsaturated aldehydes (**8a—8e**).[12] Migratory aptitude was dependent on the kind of substrate structures and on the condition of the hydrolysis. Generally, the substrates giving highly substituted olefinic aldehydes after migration had a tendency to migrate. Treating of the imines at high concentration of sulfuric acid solution or for prolonged reaction time preferred the migration of double bond. The results obtained under a variety of reaction conditions of hydrolysis are summarized in Table 4.

Table 4. Reduction of α-*tert*-Butyldimethylsiloxy-β,γ-unsaturated Nitriles (**7a—7e**) with DIBAH[a]

		conditions[b]		
entry	substrate	temp/°C	time/h	% yield of product
1	**7a**	0	1	70 (**8a**:**9a** = 10:1)
2	**7a**	18	2	52 (**9a**)
3	**7b**	0	1	43 (**9b**)
4[c]	**7b**	18	2	79 (**8b**:**9b** = 10:1)
5	**7c**	0	2.5	50 (**8c**)
6	**7d**	18	1.5	77 (**8d**)
7[d]	**7d**	18	16	50 (**9c**)[e]
8	**7e**	18	4	46 (**8e**)

[a] Reduction of α-*tert*-butyldimethylsiloxy-β,γ-unsaturated aldehydes with DIBAH was carried out in toluene at -78 °C for 2 h. [b] Conditions of hydrolysis step. [c] Isolated imine was treated with 1N H_2SO_4. [d] 2N H_2SO_4 was used. [e] *E*/*Z* (1:1) mixture.

It should be noted that migration of the double bond was not observed in the intermediately formed imine, which was confirmed by ^1H NMR analysis. Therefore, migration of the double bond would occurr in the course of hydrolysis of imines with aqueous sulfuric acid solution.

Further study on the migration mechanism and synthetic utility of the migration product is now in progress.

Conclusion

The stepwise synthesis of α-trimethylsiloxy aldehydes and α-hydroxy aldehydes could be achieved by DIBAH reduction of α-trimethylsiloxy nitriles starting from ketones. The facile synthesis of optically active α-*tert*-butyldimethylsiloxy aldehydes was attained by combination of asymmetric silylcyanation of aldehydes and DIBAH reduction of obtained chiral α-siloxy nitriles. Furthermore, migration of the double bond was found to take place under some conditions, in the DIBAH reduction of α-*tert*-butyldimethylsiloxy-β,γ-unsaturated nitriles which afford α-siloxy-α,β-unsaturated aldehydes.

Experimental

General. Melting points were uncorrected. ^{1}H NMR (250 MHz) spectra were measured on a Hitachi R-250 Fourier Transfer NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts were reported as δ values in parts per milion relative to internal tetramethylsilane (δ = 0). *J* values are given in Hz. A high resolution mass spectra (HRMS) were recorded on a Hitachi M-2500 (EI, 4 kV). Optical rotations were measured on a JASCO DIP-4 digital polarimeter for solution in a 5 dm cell. All experiments were carried out under an argon atomosphere. Dichloromethane was distilled from P_4O_{10}. Toluene, hexane and diethyl ether were distilled from sodium benzophenone ketyl under argon.

General Procedure for the Synthesis of α-Trimethylsiloxy Nitriles from Ketones. α-Trimethysiloxy nitriles (**2a—2d**) were prepared by the reaction of ketones with trimethylsilyl cyanide in the presence of catalytic amount of ZnI_2.[3]

General Procedure for Stepwise Synthesis of α-Trimethylsiloxy Aldehydes and α-Hydroxy Aldehydes via DIBAH Reduction. α-Trimethylsiloxy nitrile (10 mmol) was stirred in 15 mL of toluene under argon atomosphere. To this solution was added DIBAH (14 mmol) dropwisely at -45 °C, and the mixture was warmed up to 0 °C. After stirring for 1 h at this temperature, the reaction mixture was poured into a mixture of ether (20 mL) and saturated aqueous ammonium chloride solution (20 mL) and then treated with sulfuric acid solution (50 mL) under stirring vigorously at 15 °C for 18 h. The hydrolysis was traced by infrared spectrum until the absorption of the imine at 1775 cm^{-1} disappeared completely. Extraction with ether (20 mL x 2) followed by evaporation, then purification by silica-gel column chromatography (eluent, hexane—ethyl acetate 10:1) gave α-trimethylsiloxy aldehyde. This was dissolved in ether (10 mL) and hydrochloric acid (10 mL) was added, and the mixture was stirred vigorously at 14 °C for 15 h. α-Hydroxy aldehyde was obtained by recrystallization or flash column chromatography.

Trimethylsiloxydiphenylacetaldehyde (3a). IR (neat) 2956, 1736, 1490, 1446, 1250, 1198, 1140, 1074, 928, 892, 836 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 7.2—7.5 (m, 10H), 9.92 (s, 1H).

Hydroxydiphenylacetaldehyde (4a). IR (KBr) 3448, 2920, 2856, 1716, 1446, 1338, 1172 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.39 (s, 1H), 7.2—7.4 (m, 10H), 9.99 (s, 1H).

2-Phenyl-2-trimethylsiloxypropanal (3b). IR (neat) 2960, 1734, 1448, 1378, 1252, 1230, 1150, 1074, 1008, 888, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9H), 1.71 (s, 3H), 7.3—7.5 (m, 5H), 9.46 (s, 1H).

2-Hydroxy-2-phenylpropanal (4b). IR (neat) 3456, 2984, 2932, 1732, 1496, 1448, 1070, 858 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3H), 3.86 (s, 1H), 7.3—7.6 (m, 5H), 9.56 (s, 1H).

1-Trimethylsiloxycyclohexanecarbaldehyde (3c). IR (neat) 2940, 2860, 1738, 1450, 1252, 1088, 1060, 1024, 902, 872, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 1.4—1.7 (m, 10H), 9.48 (s, 1H).

1-Hydroxycyclohexanecarbaldehyde (4c). IR (neat) 3400, 2950, 2880, 1735, 1445, 1250, 1095, 1058, 1040, 1020, 908, 840 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.3—1.7 (m, 10H), 2.8 (br s, 1H), 9.50 (s, 1H).

2-Pentyl-2-trimethylsiloxyheptanal (3d). IR (neat) 2956, 2868, 1740, 1468, 1382, 1252, 1160, 102, 1064, 990, 842 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 0.87 (t, J = 5.8 Hz, 6H), 1.0—1.4 (m, 12H), 1.4—1.6 (m, 4H), 9.52 (s, 1H).

2-Hydroxy-2-pentylheptanal (4d). IR (neat) 3452, 2928, 2860, 1728, 1468, 1382, 1354, 1138, 1082, 810 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 5.8 Hz, 6H), 1.1—1.4 (m, 12H), 1.5—1.7 (m, 4H), 3.0 (br s, 1H), 9.50 (s, 1H).

General Procedure for the Synthesis of α-*tert*-Butyldimethylsiloxy Nitriles from Aldehydes. α-*tert*-Butyldimethysiloxy nitriles (**5a—5d** and **7a—7e**) were prepared by the reaction of aldehydes with *tert*-butyldimethylsilyl cyanide according to the reported procedure[4], or by the reaction of aldehydes with trimethylsilyl cyanide, followed by hydrolysis with 1N HCl solution, and then *tert*-butyldimethylsilylation of α-hydroxy nitriles.

***tert*-Butyldimethylsiloxyphenylacetonitrile (5a).** IR (neat) 2956, 2932, 2860, 1098, 1072, 846 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.15 (s, 3H), 0.23 (s, 3H), 0.94 (s, 9H), 5.52 (s, 1H) 7.3—7.4 (m, 5H). HRMS *m/z* Calcd for $C_{14}H_{21}NOSi$: 247.1394. Found: 247.1440.

2-*tert*-Butyldimethylsiloxydecanenitrile (5b). IR (neat) 2928, 2860, 1466, 1256, 1128, 1106, 842 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.14 (s, 3H), 0.19 (s, 3H), 0.92 (s, 9H), 1.2—1.5 (m, 15H), 1.8 (dt, J = 6.4 Hz, 8.6 Hz, 2H), 4.41 (t, J = 6.4 Hz, 1H). HRMS *m/z* Calcd for $C_{16}H_{33}NOSi$: 283.2333. Found: 283.2336.

***tert*-Butyldimethylsiloxycyclohexylacetonitrile (5c).** IR (neat) 2932, 2860, 1256, 114, 1096, 1072, 848 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.18 (s, 3H), 0.91 (s, 9H), 1.0—1.3 (m, 5H), 1.6—1.9 (m, 6H), 4.17 (d, J = 6.1 Hz, 1H).HRMS *m/z* Calcd for $C_{14}H_{27}NOSi$: 253.1863. Found: 253.1894.

2-*tert*-Butyldimethylsiloxy-3,3-dimethylbutanenitrile (5d). IR (neat) 2960, 2936, 2860, 1474, 1258, 1110, 838 cm^{-1}.^1H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.21 (s, 3H), 0.93 (s, 9H), 1.0 (s, 9H), 4.0 (s, 1H). HRMS *m/z* Calcd for $C_{12}H_{25}NOSi$: 228.2982. Found: 228.2994.

2-*tert*-Butyldimethylsiloxy-3-butenenitrile (7a). IR (neat) 2956, 2932, 2888, 2860, 1474, 1466, 1258, 1148, 1094, 1036, 842 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.16 (s, 3H), 0.20 (s, 3H), 0.93 (s, 9H), 4.97 (ddd, J = 4.8 Hz, 1.8 Hz, 1.2 Hz, 1H), 5.38 (dd, J = 10.4 Hz, 1.8 Hz, 1H), 5.56 (dd, J = 16.5 Hz, 1.2 Hz, 1H), 5.90 (ddd, J = 10.4 Hz, 16.5 Hz, 4.9 Hz, 1H). HRMS *m/z* Calcd for $C_{10}H_{19}NOSi$: 197.1237. Found: 197.1241.

2-*tert*-Butyldimethylsiloxy-3-methyl-3-butenenitrile (7b). IR (neat) 2956, 2932, 2888, 2860, 1474, 1468, 1258, 1096, 916, 838 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.13 (s, 3H), 0.19 (s, 3H), 0.93 (s, 9H), 1.85 (s, 1H), 4.80 (s, 1H), 5.04 (s, 1H), 5.22 (s, 1H). HRMS *m/z* Calcd for $C_{11}H_{21}NOSi$: 211.1394. Found: 211.1387.

(*E*)-2-*tert*-Butyldimethylsiloxy-3-pentenenitrile (7c). IR (neat) 2932, 2888, 2860, 1474, 1466, 1256, 1142, 1100, 1096, 964, 840 cm^{-1}.^1H NMR ($CDCl_3$) δ 0.15 (s, 3H), 0.17 (s, 3H), 0.92 (s, 9H), 1.76 (dd, J = 6.7 Hz, 1.2 Hz, 3H), 4.89 (dd, J = 6.7 Hz, 1.2 Hz, 1H), 5.54 (ddd, J = 15.9 Hz, 6.1 Hz, 1.8 Hz, 1H), 5.96 (ddd, J = 15.9 Hz, 6.7 Hz, 1.2 Hz, 1H). HRMS *m/z* Calcd for $C_{11}H_{21}NOSi$: 211.1394. Found: 211.1395.

(*E*)-2-*tert*-Butyldimethylsiloxy-3-methyl-3-pentenenitrile (7d). ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 1.67 (d, *J* = 6.7 Hz, 3H), 1.74 (s, 3H), 4.77 (s, 1H), 5.70 (ddq, *J* = 6.7 Hz, 1.2 Hz, 1.2 Hz, 1H). HRMS *m/z* Calcd for $C_{11}H_{21}NOSi$-C_4H_9: 168.0845. Found: 168.0837.

(*E*)-2-*tert*-Butyldimethylsiloxy-4-Phenyl--3-butenenitrile (7e). IR (neat) 2956, 2932, 2888, 2860, 1472, 1256, 1110, 1082, 968, 866, 832 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3H), 0.22 (s, 3H), 0.95 (s, 9H), 5.14 (dd, *J* = 6.1 Hz, 1.2 Hz, 1H), 6.19 (dd, *J* = 15.9 Hz, 6.1 Hz, 1H), 6.81 (dd, *J* = 15.9 Hz, 1.2 Hz, 1H), 7.2—7.4 (m, 5H). HRMS *m/z* Calcd for $C_{16}H_{23}NOSi$: 273.1550. Found: 273.1523.

General Procedure for Conversion of α-*tert*-Butyldimethylsiloxy Nitriles to α-*tert*-Butyldimethylsiloxy Aldehydes. α-*tert*-Butyldimethylsiloxy nitrile (5.1 mmol) was stirred in 10 mL of toluene under argon atomosphere. To this solution was added DIBAH (10 mmol) dropwisely at -78 °C. After stirring for 2 h at this temperature, methanol (5 mL) was added to the reaction mixture and the mixture was warmed up at 0 °C and stirred for 2 h, then 1N H_2SO_4 solution (5 mL) was added and the mixture was stirred vigorously at 0 °C for 1 h. Usual extractive workup and evaporation of the volatiles gave α-*tert*-butyldimethylsiloxy aldehyde. The crude product was purified by silica-gel column chromatography.

***tert*-Butyldimethylsiloxyphenylacetaldehyde (6a).** 67% yield. IR (neat) 2956, 2932, 2860, 1738, 1258, 1100, 838 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 3H), 0.12 (s, 3H), 0.95 (s, 9H), 5.01 (d, *J* = 2.1 Hz, 1H), 7.3—7.4 (m, 5H), 9.51 (d, *J* = 2.1 Hz, 1H). HRMS *m/z* Calcd for $C_{14}H_{22}O_2Si$-CH_3: 235.1155. Found: 235.1161.

2-*tert*-Butyldimethylsiloxydecanal (6b). 86% yield. IR (neat) 2928, 2860, 1738, 1468, 1256, 1108, 838 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.92 (s, 9H), 1.2—1.3 (m, 15H), 1.6 (dt, *J* = 2.1 Hz, 9.5 Hz, 2H), 3.95 (dt, *J* = 1.8 Hz, 6.4Hz, 1H), 9.58 (d, *J* = 1.8 Hz, 1H). HRMS *m/z* Calcd for $C_{16}H_{34}O_2Si$-C_4H_9: 229.1625. Found: 229.1632.

***tert*-Butyldimethylsiloxycyclohexylacetaldehyde (6c).** 89% yield. IR (neat) 2932, 2856, 1738, 1472, 1464, 1452, 1256, 842 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6H), 0.92 (s, 9H), 1.1—1.2 (m, 5H), 1.6—1.8 (m, 6H), 3.70 (dd, *J* = 4.9 Hz, 2.4 Hz, 1H), 10.01 (d, *J* = 1.8 Hz, 1H). HRMS *m/z* Calcd for $C_{14}H_{28}O_2Si$-CH_3: 241.1625. Found: 241.1626.

2-*tert*-Butyldimethylsiloxy-3,3-dimethylbutanal (6d). 80% yield. IR (neat) 2956, 2860, 1738, 1474, 1364, 1254, 1102, 838 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 3H), 0.04 (s, 3H), 0.93 (s, 9H), 0.95 (s, 9H), 3.46 (d, *J* = 3.7 Hz, 1H), 9.60 (d, *J* = 3.7 Hz, 1H). HRMS *m/z* Calcd for $C_{12}H_{26}O_2Si$-C_4H_9: 229.625. Found: 229.1637.

The optical purity of **6a** was determined by comparison of the optical rotation value with that of the authentic sample prepared from (*R*)-(-)-ethyl mandelate *via* hydroxy protection, followed by reduction. Authentic sample derived from (*R*)-(-)-ethyl mandelate (100% e.e.), $[\alpha]_D^{24}$ -40.6° (*c* 1.9, C_2H_5OH); synthetic sample *via* DIBAH reduction of (*R*)-(-)-**5a** (88% e.e.), $[\alpha]_D^{24}$ -35.8° (*c* 1.0, C_2H_5OH).

2-*tert*-Butyldimethylsiloxy-3-butenal (8a). 70% yield. IR (neat) 2956, 2932, 2888, 2860, 1744, 1474, 1466, 1256, 1148, 1074, 1036, 838 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.93 (s, 9H), 4.51 (dd, *J* = 4.3 Hz, 1.8 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 5.47 (d, *J* = 17.7 Hz, 1H), 5.82 (dq, *J* = 17.9 Hz, 5.1 Hz, 1H), 9.45 (d, *J* = 1.2 Hz, 1H). HRMS *m/z* Calcd for $C_{10}H_{20}O_2Si$-C_4H_9: 143.0529. Found: 143.0537.

(*E*)-2-*tert*-Butyldimethylsiloxy-2-butenal (9a). 52% yield. IR (neat) 2956, 2932, 2888, 2860, 1700, 1640, 1352, 1254 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.18 (s, 6H), 0.97 (s, 9H), 1.9 (d, J = 7.3 Hz, 3H), 5.8 (q, J = 7.3 Hz, 1H), 9.1 (s, 1H). HRMS *m/z* Calcd for $C_{10}H_{20}O_2Si$-C_4H_9: 143.0529. Found: 143.0520.

2-*tert*-Butyldimethylsiloxy-3-methyl-3-butenal (8b). 79% yield (**8b**:**8c** = 10:1). IR (neat) 2932, 2888, 2860, 1738, 1680, 1472, 1256, 1114, 1006, 940, 838 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.92 (s, 9H), 1.70 (s, 3H), 4.31 (s, 1H), 5.06 (d, J = 1.8 Hz, 1H), 5.18 (s, 1H), 9.35 (d, J = 1.8 Hz, 1H). HRMS *m/z* Calcd for $C_{11}H_{22}O_2Si$-C_4H_9: 157.0686. Found: 157.0671.

2-*tert*-Butyldimethylsiloxy-3-methyl-2-butenal (9b). 43% yield. IR (neat) 2932, 2860, 1680, 1628, 1472, 1464, 1376, 1306, 1252, 1222, 974, 870, 840 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.15 (s, 6H), 0.95 (s, 9H), 1.93 (s, 3H), 2.12 (s, 3H), 9.88 (s, 1H). HRMS *m/z* Calcd for $C_{11}H_{22}O_2Si$-C_4H_9: 157.0686. Found: 157.0677.

(*E*)-2-*tert*-Butyldimethylsiloxy-3-pentenal (8c). 50% yield. IR (neat) 2956, 2888, 2868, 1740, 1472, 1466, 1256, 1140, 1102, 842 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.08 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 1.75 (dd, J = 6.7 Hz, 1.2 Hz, 3H), 4.43 (ddd, J = 6.1 Hz, 1.2 Hz, 1.8 Hz, 3H), 5.42 (ddd, J = 15.6 Hz, 5.5 Hz, 1.8 Hz, 1H), 5.87 (ddd, J = 15.6 Hz, 6.1 Hz, 1.2 Hz, 1H), 9.45 (d, J = 1.8 Hz, 1H). HRMS *m/z* Calcd for $C_{11}H_{22}O_2Si$-C_4H_9: 157.0686. Found: 157.0675.

(*E*)-2-*tert*-Butyldimethylsiloxy-3-methyl-3-pentenal (8d). 77% yield. ^1H NMR ($CDCl_3$) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.91 (s, 9H), 1.57 (d, J = 1.2 Hz, 3H), 1.67 (dd, J = 6.7 Hz, 1.2 Hz, 1H), 4.27 (s, 1H), 5.69 (dd, J = 6.7 Hz, 1.2 Hz, 1H), 9.37 (d, J = 1.8 Hz, 1H). HRMS *m/z* Calcd for $C_{12}H_{24}O_2Si$-C_4H_9: 171.0842. Found: 171.0807.

(*Z*)-2-*tert*-Butyldimethylsiloxy-3-methyl-2-pentenal (9d). 30% yield (*E*/*Z* 1:1 mixture). IR (neat) 2932, 2860, 1682, 1622, 1460, 1390, 1362, 1334, 1294, 1252, 1206, 936, 842 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.15 (s, 6H), 0.94, 0.95 (each s, 9H), 1.05, 1.14 (each t, J = 7.9 Hz, 3H), 1.93, 2.09 (each s, 3H), 2.34, 2.51 (each q, J = 7.9 Hz, 2H), 9.84, 9.86 (each s, 1H). HRMS *m/z* Calcd for $C_{12}H_{24}O_2Si$-C_4H_9: 171.0842. Found: 171.0840.

(*E*)-2-*tert*-Butyldimethylsiloxy-4-phenyl-3-butenal (8e). IR (neat) 2956, 2932, 1738, 256, 1130, 838 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.13 (s, 3H), 0.14 (s, 3H), 0.97 (s, 9H), 4.68 (ddd, J = 4.9 Hz, 1.8 Hz, 1.2 Hz, 1H), 6.14 (dd, J = 15.9 Hz, 4.9 Hz, 1H), 6.77 (dd, J = 15.9 Hz, 1.8 Hz, 1H), 7.2—7.4 (m, 5H), 9.51 (d, J = 1.2 Hz, 1H). HRMS *m/z* Calcd for $C_{16}H_{24}O_2Si$: 276.1547. Found: 276.1531.

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