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Optically Active Acylsilanes. Synthesis of Selected 2,3-O-Isopropylidene-1-(Trialkyl/arylsilyl)glyceraldehyde Derivatives

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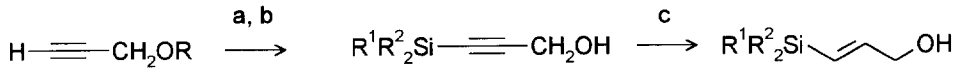
Abstract: Syntheses of 1-trimethylsilyl-, 1-*tert*-butyldimethylsilyl, 1-dimethylphenylsilyl- and 1-triphenylsilyl-2,3-O-isopropylideneglyceraldehyde derivatives, **6a**, **6b**, **6c**, and **6d**, respectively, is described.

Until recently only a few chiral acylsilanes[1] have been prepared and examined with respect to their application in stereocontrolled synthesis. Even with such a narrow group of examples it has been clearly shown that acylsilanes with a stereogenic centre α to the carbonyl group in reactions with nucleophiles afford the corresponding products with high diastereoselectivity, both in non-chelation-[2] and chelation - controlled[3] processes. Encouraging diastereoselectivities have also been observed in reactions of the acylsilanes bearing a stereogenic silicon atom[4]. Recently[5], we have reported an efficient approach to the optically active acylsilane derivatives with an alkoxy group in the α-position, including 1-(trimethylsilyl)-2,3-isopropylideneglyceraldehyde **6a** (Scheme 2); this approach is based upon Korblum-type oxidation of α,β-epoxysilanes. Almost simultaneously with our publication, Cirillo and Panek[6,7] have described an alternative method for the enantioselective synthesis of acylsilanes bearing in the α-position an alkoxy group, that involves reduction of the carbonyl group in unsaturated acylsilanes. These authors have also demonstrated that the stereochemistry of acylsilane reactions depends a great deal upon the nature of substituents on the silicon atom. The products of nucleophilic addition to acylsilanes may be utilized in many ways[1,8]. On the other hand, it has been shown that some acylsilanes may be conveniently transformed into aldehydes[6], and consequently one may expect that α-alkoxyacylsilanes may serve as surrogates of the corresponding α-alkoxyaldehydes, which may be less stable or difficult to obtain by another route.

In continuation of our studies on the synthesis of acylsilanes we prepared 2,3-O-isopropylideneglyceraldehyde derivatives bearing different silyl groups at the position 1. Herewith we present the details of preparation of compound **6a** and describe the synthesis of its derivatives substituted with a *tert*-butyldimethylsilyl, dimethylphenylsilyl, and triphenylsilyl group, **6b**, **6c**, and **6d**, respectively.

Allylic alcohols **3a - 3d** were prepared following the standard procedures. The reagents used and the results obtained are presented in Scheme 1.

Scheme 1



1a, R=H
1b, R=CH(OEt)Me
1c, R=$CMe_2(OMe)$

2a, $R^1=R^2=Me$
2b, $R^1={}^tBu$, $R^2=Me$
2c, $R^1=Ph$. $R^2=Me$
2d, $R^1=R^2=Ph$

3a, $R^1=R^2=Me$
3b, $R^1={}^tBu$, $R^2=Me$
3c, $R^1=Ph$. $R^2=Me$
3d, $R^1=R^2=Ph$

Reagents: a, BuLi/THF-hexane; b. $R^1R^2{}_2SiCl$; c. $[(CH_3OCH_2CH_2O)_2AlH_2]Na$/toluene-ether

Starting material	$R^1R^2{}_2SiCl$	**Intermediate**, yield (%)	**Product**, yield (%)
1a	Me_3SiCl	**2a**	**3a**, 65[a] (from **1a**)
1b	$^tBuMe_2SiCl$	**2b**, 76	**3b**, 89
1b	$PhMe_2SiCl$	**2c**, 87	**3c**, 78
1c	Ph_3SiCl	**2d**[b,c]	**3d**, 89 (from **1c**)

[a] Ref. 9c; [b]intermediate was not purified, [c]$LiAlH_4$ was used for reduction

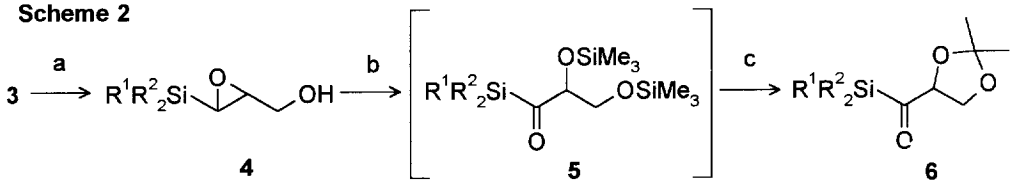
Catalytic asymmetric epoxidation[9] of alcohols **3a - 3d** using D-(-)-diisopropyl tartrate (DIPT) or L-(+)-DIPT afforded products **4a - 4d**. Their yields and enantiomeric purities determined by Moshers method[10] are given in Scheme 2.

Glycidol **4a** dissolved in methylene chloride was treated with dimethylsulfoxide (DMSO), allyltrimethylsilane and trimethylsilyl triflate at O to 15 °C. After an appropriate period of time (see Experimental) the mixture was cooled to -78 °C and hexamethyldisilazane was added; after 30 min acylsilane **5a** was isolated. This product, without purification, was reacted with 2,2-dimethoxypropane and a catalytic amount of $TsOH \cdot H_2O$ to give **6a** which was purified by distillation (72% yield). Similar oxidation of glycidols **4b - 4d**, with subsequent transformation of the bis(trimethylsilyl) derivatives into acetonides, afforded acylsilanes **6b - 6d**, respectively. Yields and specific rotations of the products are given in Scheme 2. It is noteworthy that the use of hexamethyldisilazane as the base in the oxidation procedure was advantageous, since in parallel experiments where hexamethyldisilazane was replaced by triethylamine markedly lower yields of the acylsilanes were obtained

(see Experimental).

To determine the enantiomeric excess of acylsilane **6a**, its ^{1}H NMR spectrum was measured in the presence of tris-[3-heptafluoropropylhydroxymethylene)-d-camphorato]europium(III) [Eu(hfc)$_3$] and compared with the respective spectrum of racemic **6a**. No signals corresponding to the other enantiomer could be seen. This suggests that during the transformation of trimethylsilylglicidol **4a** into acylsilane **6a** there is an only small, if any, loss

Scheme 2



a, R^1=R^2=Me
b, R^1=^{t}Bu, R^2=Me
c, R^1=Ph, R^2=Me
d, R^1=R^2=Ph

Reagents: a. D-(-)-DIPT or L-(+)-DIPT, Ti(O^iPr)$_4$, ^{t}BuO$_2$H; b. (CH_2=$CHCH_2$)Me_3Si, DMSO, Me_3SiOTf, hexamethyldisilazane or Et_3N; c. 2,2-dimethoxypropane, TsOH

Starting material	DIPT	Epoxide, configuration yield (%), ee (%) specific rotation	Acylsilane, configuration yield (%), specific rotation
3a	L-(+)-	**4a** (2*S*,3*S*) 84 94 $[\alpha]_D^{14}$ -26.5	**6a** (2*S*) 72 $[\alpha]_D^{22}$ -94.7
3b	L-(+)-	**4b** (2*S*,3*S*) 94 94 $[\alpha]_D^{28}$ -26	**6b** (2*S*) 75 $[\alpha]_D^{25}$ -77.1
3c	L-(+)-	**4c** (2*S*,3*S*) 87 97 $[\alpha]_D^{25}$ -12.2	**6c** (2*S*) 77 $[\alpha]_D^{25}$ -40.6
3d	D-(-)-	**4d** (2*R*,3*R*) 85 >97 $[\alpha]_D^{25}$ +22.5	**6d** (2*R*) 50 $[\alpha]_D^{22}$ +47.3

of the enantiomeric purity. It should be noted that we failed to prepare a Mosher ester of the diol corresponding to di-O-trimethylsilyl ether **5a** or of the other α-hydroxy silanes[11].

In conclusion, optically active acylsilanes **6a - 6d** were prepared from propargyl alcohol using as the key steps asymmetric epoxidation of 3-(trialkyl/arylsilyl)allylic alcohols **3a - 3d** and Kornblum-type oxidation of glycidols **4a - 4d**.

Experimental Section

Melting points were determined on a hot - stage apparatus. ^{1}H and ^{13}C NMR spectra were recorded using Bruker AM 500 (500 and 125 MHz) or Varian GEM (200 and 50 MHz) spectrometers, for $CDCl_3$ solutions with

Me_4Si as internal standard. MS were obtained with an AMD 604 unit at 70 eV ionizing potential. All reactions involving organometallic reagents were carried out under argon with stirring. Organic solutions were dried over anhyd. Na_2SO_4 and solvents were evaporated on a rotary evaporator. Column chromatography was performed on Merck silica gel 60, 230-400 mesh, and TLC - on Merck silica gel G. Optical rotations were measured using a 8 mL capacity cell (10 cm path length), in $CHCl_3$, unless otherwise stated. 3-(Trimethylsilyl)allylalcohol **3a** was prepared from **1a** according to the published procedure[12].

3-(*tert*-Butyldimethylsilyl)prop-2-yne-1-ol (2b). To a stirred solution of **1b** (5 g, 39 mmol) in THF (60 mL) BuLi (1.3 M in hexane, 30 mL, 39 mmol) was added at -78 °C. The mixture was allowed to warm up to -20 °C, was stirred at this temperature for 0.5 h and then was cooled to -78 °C. A solution of *tert*-butyldimethylsilyl chloride (6 g, 39 mmol) in THF (30 mL) was added dropwise during 15 min. The mixture was set aside for 20 h whereupon it was poured into saturated aqueous NH_4Cl. The aqueous layer was separated and extracted with ether (3x30 mL). The combined organic layers were dried, filtered and concentrated. The residue was dissolved in MeOH (20 mL) containing a trace of $HClO_4$ (MeOH : 70% $HClO_4$ = 100:0.1) and after 0.5 h it was diluted with ether (200 mL), and washed with saturated aqueous $NaHCO_3$ and brine. The solvent was removed and the residue was distilled under reduced pressure to give **2b** as a colourless oil (5.06 g, 76%); bp 80-82 °C/3 mm Hg; IR (KBr) 3332 (OH), 2175 (C≡C) cm^{-1} ; ^1H NMR δ 0.11 (s, 6, $SiCH_3$), 1.58 (br s, 1, OH), 0.93 (s, 9, $SiCCH_3$), 4.27 (s, 2, C_1 H); ^{13}C NMR δ -4.7 ($SiCH_3$), 16.4 ($SiCCH_3$), 27.0 ($SiCCH_3$), 51.5 (C_1), 88.7 (C_3), 105.5 (C_2); Anal. Calcd for $C_9H_{18}OSi$ (170.32): C, 63.46; H, 10.65. Found: C, 63.25; H, 10.92.

3-(Dimethylphenylsilyl)prop-2-yne-1-ol (2c) was prepared in an analogous way. The reagents were used as follows: **1b** (4.8 g, 37.5 mmol), THF (50 mL), BuLi (2.1 M in hexane, 17 mL), and then dimethylphenylsilyl chloride (5.13 g, 30 mmol) in THF (10 mL). Product **2c** was obtained (5 g, 87% yield), bp 116-120 °C/3 mm Hg; IR (KBr) 3344 (OH), 2177 (C≡C) cm^{-1} ; ^1H NMR δ 0.43 (s, 6, $SiCH_3$), 1.62 (t, 1, J = 6.2 Hz, OH), 4.31 (d, 2, J = 6.2 Hz, C_1 H), 7.35-7.43 (m, 3H), 7.55-7.65 (m, 2H); ^{13}C NMR δ -1.1 ($SiCH_3$), 51.6 (C_1), 88.7 (C_3), 105.5 (C_2), 127.9 (C_m), 129.5 (C_p), 133.6 (C_o), 136.5 (C_{ipso}); EIMS m/z (rel intensity, %) 175 (M^+-CH_3, 35), 75 (100); HRMS calcd for $C_{10}H_{11}OSi$ (M^+-CH_3) 175.0579218, found 175.05772.

3-(Triphenylsilyl)prop-2-yne-1-ol (2d). To a stirred solution of **1c** (11.1 g, 86.7 mmol) in THF (60 mL), BuLi (2.25 M in hexane, 38 mL) and triphenylsilyl chloride (23 g, 78 mmol) in THF (60 mL) were added successively, with the temperature maintained below O °C. After 2 h the mixture was warmed up to rt and poured into water. The aqueous layer was separated and extracted with ether (2X50 mL). Combined organic extracts were evaporated. The residue was filtered through silica gel (30 g, hexane-acetone), whereupon it was treated with

methanol (20 mL) containing a trace of $HClO_4$. After 30 min the mixture was diluted with ether (200 mL), washed with aqueous $NaHCO_3$ and then with brine, and the solvent was removed. So obtained crude **2d** was used for the next step without purification. A sample purified by chromatography showed mp 128.5-129.5 ^{o}C; IR (KBr) 3210 (OH), 2150 (C≡C) cm^{-1}; ^{1}H NMR δ 1.78 (t, 1, *J* = 6.3 Hz, OH), 4.39 (d, 2, *J* = 6.3 Hz, C_1 H), 7.3-7.5 (m, 9), 7.55-7.70 (m, 6); ^{13}C NMR δ 51.9 (C_1), 85.9 (C_3), 108.4 (C_2), 128.0 (C_m), 130.0 (C_p), 133.0 (C_{ipso}), 135.5 (C_o); EIMS m/z (rel intensity, %) 314 (M^+, 0.6), 199 (100), 77 (15).
Described[13]: mp 125-126 ^{o}C

(*E*)-3-(*tert*-Butyldimethylsilyl)-2-propene-1-ol (3b). To a stirred mixture of Red-Al (3.4 M in toluene, 16 mL, 54.4 mmol) and ether (20 mL) a solution of acetylene **2b** (5 g, 29.4 mmol) in ether (25 mL) was added at 0-5 ^{o}C. The mixture was stirred at rt for 1.5 h whereupon it was cooled to 0 ^{o}C and the reaction was quenched with 2 M H_2SO_4. The aqueous layer was separated and extracted with ether (3x30 mL). The combined organic layers were dried, filtered and concentrated. The residue was distilled to give **3b** as a colourless oil (4.46 g, 89%); bp. 70-74 ^{o}C/2 mm Hg; IR (film) 3317 (OH), 1620 (C=C) cm^{-1}; ^{1}H NMR δ 0.03 (s, 6, $SiCH_3$), 0.87 (s, 9, $SiCCH_3$), 1.44 (t, 1, *J* = 6.0 Hz, OH), 4.20 (ddd, 2, *J* = 1.6, 4.4, 6.0 Hz, C_1 H), 5.90 (dt, 1, *J* = 1.6, 18.8 C_3 H), 6.20 (dt, 1, *J* = 4.3, 18.8 C_3 H); ^{13}C NMR δ -6.2 ($Si\underline{C}H_3$), 16.4 ($Si\underline{C}CH_3$), 26.4 ($SiC\underline{C}H_3$), 65.6 (C_1), 126.6 (C_3), 146.2 (C_2); EIMS m/z (rel intensity) 172 (M^+, 2), 115 (100), 75 (47); HRMS calcd for $C_9H_{20}OSi$ 172.128344, found 172.12829. *(E/Z* = 96:4 by GC)

(*E*)-3-(Dimethylphenylsilyl)-2-propene-1-ol (3c) was prepared from **2c** in an analogous way. The reagents were used as follows: **2c** (5 g, 26.3 mmol) in ether (25 mL), Red-Al (18 mL) in ether (20 mL). Product **3c** was obtained (3.7 g, 73%); bp 116-120 ^{o}C/3 mm Hg; IR (KBr) 3318 (OH), 1622 (C=C) cm^{-1}; ^{1}H NMR δ 0.36 (s, 6, $SiCH_3$), 1.49 (br t, 1, *J* = 5.4 Hz, OH), 4.21 (m, 2, C_1 H), 6.05 (dt, 1, *J* = 1.5, 18.7 Hz, C_2 H), 6.26 (dt, 1, *J* = 4.0, 18.7 Hz, C_3 H), 7.3-7.4 (m, 3) and 7.48-7.56 (m, 2, aromatic H); ^{13}C NMR δ -2.7 ($Si\underline{C}H_3$), 65.4 (C_1), 127.15 (C_3), 127.8 (C_m), 129.0 (C_p), 133.7 (C_o), 138.4 (C_{ipso}), 146.6 (C_2). EIMS m/z (rel intensity, %) 193 (M^++H, 2) 177 (M^+-CH_3, 24), 137 (59),75 (100); HRMS calcd for $C_{10}H_{13}OSi$ (M^+-CH_3) 177.073569, found 177.07358.

(*E*)-3-(Triphenylsilyl)-2-propene-1-ol (3d). To a mixture of $LiAlH_4$ (5 g) and THF (160 mL) stirred at 0-5 ^{o}C a solution of crude compound **2d** (25 g) in THF (100 mL) was added dropwise. The mixture was stirred for 1 h whereupon it was cooled to 0 ^{o}C and the excess of the reagent was decomposed by careful addition of diluted H_2SO_4 (16 mL conc. H_2SO_4 in 200 ml of water). The water layer was separated and extracted with ether (3x50 mL). Combined organic extracts were evaporated and the residue was crystallized from a mixture of ether and hexane. Product **3d** (22 g, 89% yield from **1c**) was obtained; mp 149-150 ^{o}C; IR (KBr) 3290 (OH), 1625 (C=C)

cm^{-1}; ^1H NMR δ 1.51 (t, 1, J = 6.2 Hz, OH), 4.29 (ddd, 2, J = 1.6, 3.7, 6.0 Hz, C_1 H), 6.29 (dt, 1, J = 3.7, 18.7 Hz, C_2 H), 6.50 (dt, 1, J = 1.6, 18.7 Hz, C_3 H), 7.3-7.45 (m, 9) and 7.50-7.60 (m, 6, aromatic H); ^{13}C NMR δ 65.3 (C_1), 122.9 (C_3), 127.9 (C_m), 129.6 (C_p), 134.4 (C_{ipso}), 135.9 (C_o), 150.7 (C_2).

Glycidol **4a** was obtained from **3a** essentially as described earlier[10c], yield 84%, 94% ee.

(2*S*,3*S*)-3-(*tert*-butyldimethylsilyl)-2,3-epoxypropane-1-ol (4b). To a suspension of powdered and freshly activated molecular sieves 4A (3 g) in anhydrous CH_2Cl_2 (40 mL), stirred under argon at -20 °C, addition was made of: L-(+)-DIPT (0.4 mL, 1.92 mmol), (E)-3-(*tert*-butyldimethylsilyl)prop-2-ene-1-ol **3b** (4.35, 25.2 mmol), $Ti(O^iPr)_4$ (0.48 mL, 1.64 mmol) and (after 15 min) TBHP (3.5 M in toluene, 14.5 mL, 50.8 mmol). Stirring at -20 °C was continued for 5 h and then the mixture was set aside in a freezer (-22 °C) for 16 h. The reaction mixture was transferred to an ice-cooled mixture of $FeSO_4 \cdot 7H_2O$ (8.25 g), tartaric acid (1 g), water (60 mL) and ether (60 mL), and was stirred at 0 °C for 1 h. Solid material was removed by filtration through Celite. The filtrate was washed with brine (200 mL). The aqueous layer was separated and extracted with ether. The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was chromatographed on silica gel (50 g, hexane-acetone) to afford the epoxide **4b** (4.46 g, 94%); 94% ee, $[\alpha]_D^{28}$ - 26.0 (c 1.4); IR (film) 3417 (OH) cm^{-1}; ^1H NMR δ -0.05 and 0.01 (s, 3, $SiCH_3$), 0.95 (s, 9, $SiCCH_3$), 1.97 (m, 1H, OH), 2.32 (d, 1, J = 3.7 Hz, C_3 H), 3.01 (ddd, 1, J = 2.4, 3.7, 4.6 Hz, C_2 H), 3.57 (ddd, 1, J = 4.6, 7.0, 12.5 Hz, C_1 Ha), 3.98 (ddd, 1, J = 2.3, 6.0, 12.5 Hz, C_1 Hb); ^{13}C NMR δ -8.45 and -8.32 ($SiCH_3$), 16.6 ($SiCCH_3$ 26.5 ($SiCCH_3$), 46.3 (C_3), 55.5 (C_2), 63.4 (C_1); Anal. Calcd for $C_9H_{20}O_2Si$ (188.34): C, 57.39; H, 10.70. Found: C, 57.24; H, 10.90.

The Moshers ester of **4b**, prepared from (*R*)-(+) acid: ^1H NMR δ -0.07 and -0.01 (s, 3, $SiCH_3$), 0.94 (s, 9, $SiCCH_3$), 2.17 (d, 1, J = 3.5 Hz, C_3 H), 3.07 (ddd, 1, J = 3.3, 6.3, 6.8 Hz, C_2 H), 3.58 (q, 3, J = 1.2, OMe), 4.24 (dd, 1, J = 6.3, 12. Hz, C_1 Ha), 4.56 (dd, 1, J = 3.2, 12.0 Hz, C_1 Hb), 7.40-7.45 (m, 3), 7.5-7.6 (m, 2); ^{13}C NMR δ -8.5 and -8.4 ($SiCH_3$), 16.6 ($SiCCH_3$ 26.4 ($SiCCH_3$), 47.1 (C_3), 51.8 (OMe), 55.5 (C_2), 68.2 (C_1), 120.3 (CF_3), 127.3 (C_p), 128.4 (C_m), 129.6 (C_o), 132.1 (C_{ipso}), 166.3 (C=O).

Moshers esters prepared from racemic material showed additionally diagnostic signals at 2.17 (d, 1, J = 3.6 Hz) and 2.20 (d, 1, J = 3.5 Hz).

(2*S*,3*S*)-3-(Phenyldimethylsilyl)-2,3-epoxypropane-1-ol (4c) was prepared in an analogous way. The reagents were used as follows: molecular sieves (3 g), CH_2Cl_2 (35 mL), L-(+)-DIPT (0.29 mL), $Ti(O^iPr)_4$ (0.35 mL), allylic alcohol **3c** (3.44 g, 17.9 mmol), TBHP (10.5 mL, 3.5 M in toluene, 36.75 mmol). The crude product was chromatographed on silica gel (30 g, hexane:acetone). Product **4c** was obtained (3.24 g, 87%, 97% ee); $[\alpha]_D^{25}$ - 12.2 (c 1.11); IR (film) 3415 (OH) cm^{-1}; ^1H NMR δ 0.33 and 0.37 (2s, 3, $SiCH_3$), 1.71 (br t, 1, J = 7 Hz, OH), 2.46 (d, 1, J = 3.6 Hz, C_3 H), 3.02 (ddd, 1, J = 2.4, 3.6, 4.4 Hz, C_2 H), 3.59 (ddd, 1, J = 4.4, 7.0, 12.4 Hz, C_1 Ha), 3.97 (ddd, 1, J = 2.4, 5.7, 12.4 Hz, C_1 Hb), 7.35-7.43 (m, 3), 7.5-7.6 (m, 2); ^{13}C NMR δ -5.4 and -5.1

($SiCH_3$), 47.6 (C_3), 56.1 (C_2), 63.2 (C_1), 127.9 (C_m), 129.6 (C_p), 133.8 (C_o), 135.6 (C_{ipso}); Anal. Calcd for $C_{11}H_{16}O_2Si$ (208.33): C, 63.42; H, 7.74. Found: C, 63.17; H, 8.00.

Moshers ester of **4c**, prepared from (*R*)-(+)-acid: ^{1}H NMR δ 0.31 and 0.35 (2s, 3, $SiCH_3$), 2.29 (d, 1, *J* = 3.4 Hz, C_3 H), 3.07 (ddd, 1, *J* = 3.3, 3.4, 6.7 Hz, C_2 H), 3.54 (q, 3, *J* = 1.2 Hz, OCH_3), 4.22 (dd, 1, *J* = 6.3, -12.0 Hz, C_1 Ha), 4.55 (dd, 1, *J* = 3.3, 12.o Hz, C_1 Hb), 7.35-7.45 (m, 6), 7.48-7.55 (m, 4);

Moshers esters prepared from racemic material showed additionally diagnostic signals at 2.29 (d, 1, *J* = 3.4 Hz) and 2.31 (d, 1, *J* = 3.4 Hz).

(2*R*,3*R*)-3-(Triphenylsilyl)-2,3-epoxypropane-1-ol (4d) was prepared in an analogous way. The reagents were used as follows: molecular sieves (8 g), CH_2Cl_2 (100 mL), D-(-)-DIPT (1.2 mL), $Ti(O^iPr)_4$ (1.4 mL), allylic alcohol **3d** (22 g, 69.6 mmol), TBHP (40 mL, 3.5 M in toluene, 140 mmol). The crude product was crystallized from a mixture of ether and hexane. Product **4d** was obtained (21.5 g, 92% yield, 95% ee). After one recrystallization from the same solvent 19.5 g of the product were obtained (85% yield, >97% ee); $[\alpha]_D^{25}$ +22.5 (c 1.78); mp 129.5-130.5 °C; IR (KBr) 3420 (OH) cm^{-1}; ^{1}H NMR δ 3.0 (m, 2, C_2 H, C_3 H), 3.60-3.75 (m, 1, C_1 Ha), 3.90-4.05 (m, 1, C_1 Hb), 7.3-7.7 (m, 15, aromat. H); ^{13}C NMR δ 46.2 (C_3), 56.2 (C_2), 62.8 (C_1), 128.2 (C_m), 130.2 (C_p), 132.1 (C_{ipso}), 136.0 (C_o); EIMS m/z (rel intensity, %) 331 (M^+-H, 0.8), 276 (33), 259 (100), 199 (47), 181 (35), 77 (8); Anal. Calcd for $C_{21}H_{20}O_2Si$ (332.46): C, 75.86; H, 6.06. Found: C, 75.78; H, 5.98.

Moshers ester of **4d**, prepared from (*R*)-(+)-acid: ^{1}H NMR δ 2.86 (d, 1, *J* = 3.4 Hz, C_3 H), 3.05 (dt, 1, *J* = 3.8, 5.2 Hz, C_2 H), 3.50 (q, 3, *J* = 1.2 Hz, OMe), 4.38 (dd, 1, *J* = 5.2, 12.0 Hz, C_1 Ha), 4.61 (dd, 1, *J* = 3.8, 12.0 Hz, C_1 Hb), 7.3-7.6 (m, 20H, aromat. H).

Moshers esters prepared from racemic material showed additionally diagnostic signals at δ 2.84 (d, *J* = 3.3 Hz, C_3 H) and 3.52 (q, *J* = 1.2 Hz, OCH_3).

(*S*)-2,3-O-Isopropylidene-1-oxo-1-(trimethylsilyl)propan-2,3-diol (6a). To a stirred mixture of trimethylsilylglycidol **4a** (2.03 g, 13.9 mmol), (allyl)trimethylsilane (2.23 mL, 14 mmol), DMSO (6 mL), and CH_2Cl_2 (25 mL), Me_3SiOTf (3.16 mL, 17.4 mmol) was added at O °C. The mixture was stirred at 15 °C for 5 h and then it was cooled to -78 °C whereupon triethylamine (5.85 mL, 42 mmol) was added dropwise. The mixture was allowed to warm up to rt within 30 min and then it was diluted with CH_2Cl_2 (70 mL) and washed successively with saturated aqueous $NaHCO_3$, water (3 times) and brine. The organic solution was dried (Na_2SO_4) and the solvent was evaporated to give crude acylsilane **5a**.

This product was dissolved in CH_2Cl_2 (20 mL) and treated with 2,2-methoxypropane (2.6 mL, 21 mmol) and TsOH monohydrate (125 mg, 0.66 mmol). The mixture was stirred at rt for 3 h and then anhydrous K_2CO_3 (300 mg) was added, followed after a few min by ether (50 mL). The mixture was washed successively with saturated

aqueous $NaHCO_3$, water and brine. The organic solution was dried (Na_2SO_4) and the solvent was evaporated. The residue was distilled under reduced pressure. The fraction distilling at 80-84 °C/15 mm Hg was collected to give acylsilane **6a** (2.01 g, 72% yield) as a pale yellow liquid: $[\alpha]_D^{22}$ -94.7 (c 1.01) (a sample was immediately before this measurement redistilled at 60-61 °C/4 mm Hg); ν (film) 1649 (Me_3SiC=O) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) 0.24 (s, 9H, $SiMe_3$), 1.36 (br s, 3H, CH_3C), 1.47 (br s, 3H, CH_3C), 3.87 (dd, 1H, $J_{3a\text{-}3b}$= 6.4, $J_{3a\text{-}2}$= 8.4 Hz, C_3 Ha), 4.07 (t, 1H, $J_{2\text{-}3}$= 8.3 Hz, C_2 H), 4.36 (dd, 1H, $J_{3b\text{-}3a}$= 6.4, $J_{3b\text{-}2}$= 7.9 Hz, C_3 Hb); ^{13}C NMR ($CDCl_3$, 50 MHz) -2.6 ($SiMe_3$), 24.06, 26.0, 65.0 (C_3), 85.1 (C_2), 110.3 (Me_2C), 246.1 (Me_3SiC=O). Anal. Calcd for $C_9H_{18}O_3Si$ (202.32) C, 53.43; H, 8.97. Found: C, 53.55; H, 9.20.

To determine the optical purity of compound **6a**, its ^1H NMR spectrum was measured in the presence of [Eu(hfc)$_3$]. Protons of the acetonide methyl groups appeared as two singlets. In the spectrum of racemic **6a**, in the presence of [Eu(hfc)$_3$], under similar conditions two well-resolved pairs of singlets (four signals) of the equal integration occurred.

(*S*)-2,3-O-Isopropylidene-1-oxo-1-(*tert*-butyldimethylsilyl)propan-2,3-diol (6b). a. To a mixture of epoxysilane **4b** (436 mg, 2.3 mmol), allyl(trimethyl)silane (0.37 mL, 2.33 mmol), DMSO (1 mL) and CH_2Cl_2 (5 mL), stirred at rt, Me_3SiOTf (0.49 mL, 2.7 mmol) was added. After 16 h hexamethyldisilazane (1 mL) was added and stirring was continued for 1 h. The mixture was diluted with hexane (40 mL) and washed successively with aqueous $NaHCO_3$ and twice with water. The solvent was removed to give crude acylsilane **5b** (759 mg, 86%). The latter was dissolved in CH_2Cl_2 (5 mL) and then was treated with 2,2-dimethoxypropane (1.2 mL), TsOH (20 mg) and methanol (0.07 mL). After stirring for 1.5 h the mixture was diluted with hexane (40 mL) and washed with aqueous $NaHCO_3$, water and brine, and the solvent was removed. The residue was chromatographed on silica gel (3 g, hexane:acetone) to give acylsilane **6b** (420 mg, 75%, 91% ee); bp 82-83 °C/3 mm Hg; $[\alpha]_D^{25}$ - 77.1 (c 1.58); IR (film) 1643 (C=O) cm^{-1}; ^1H NMR δ 0.21 and 0.26 (s, 3, $SiCH_3$), 0.94 (s, 9, $SiCCH_3$), 1.37 (br q, 3, J = 0.6 Hz, Me_2C), 1.46 (br q, 3, J = 0.6 Hz, Me_2C), 3.89 (dd, 1, J = 6.5, 8.3 Hz, C_3 Ha), 4.07 (dd, 1, J = 7.8, 8.4 Hz, C_3 Hb), 4.38 (dd, 1, J = 6.5, 7.8 Hz, C_2 H); ^{13}C NMR δ -6.4 and -6.1 ($Si\underline{C}H_3$), 16.7 ($Si\underline{C}CH_3$), 24.6 and 25.8 ($C\underline{C}H_3$), 26.5 ($SiC\underline{C}H_3$), 64.6 (C_3), 85.3 (C_2), 110.2 ($\underline{C}CH_3$), 244.5 (C=O); EIMS m/z (rel intensity, %) 244 (M^+, 0.3), 229 (M^+-CH_3, 2), 115 (65), 101 (40), 75 (100); HRMS calcd for $C_{11}H_{21}O_3Si$ (M^+-CH_3) 229.125998, found 229.12598.

b. To a stirred mixture of epoxysilane **4b** (219 mg, 1.16 mmol), allyl(trimethyl)silane (0.19 mL, 1.19 mmol), DMSO (0.6 mL) and CH_2Cl_2 (3 mL), Me_3SiOTf (0.49 mL, 2.7 mmol) was added. After 16 h triethylamine (0.8 mL) was added and stirring was continued for additional 40 min. The mixture was diluted with CH_2Cl_2 (40 mL) and washed successively with aqueous $NaHCO_3$ and water. The solvent was removed to give acylsilane **5b** which was dissolved in CH_2Cl_2 (3 mL) and then was treated with 2,2-dimethoxypropane (0.28 mL) and TsOH (13 mg).

After stirring for 1 h the mixture was diluted with hexane (30 mL) and washed with aqueous $NaHCO_3$, water and brine, and the solvent was removed. The residue was chromatographed on silica gel (2 g, hexane:acetone) to give acylsilane **6b** (170 mg, 60%, 91% ee) identical in all respects with the product described above.

(*S*)-2,3-O-Isopropylidene-1-oxo-1-(dimethylphenylsilyl)propan-2,3-diol (6c). To a stirred mixture of epoxysilane **4c** (259 mg, 1.24 mmol), allyl(trimethyl)silane (0.2 mL, 1.26 mmol), DMSO (0.5 mL) and CH_2Cl_2 (3 mL), Me_3SiOTf (0.27 mL, 1.49 mmol) was added. After 16 h hexamethyldisilazane (0.9 mL) was added and stirring was continued for 1 h. The mixture was diluted with hexane (40 mL), washed with aqueous $NaHCO_3$ and twice with water. The solvent was removed to give acylsilane **5c** (446 mg, 98%). The latter was dissolved in CH_2Cl_2 (5 mL), 2,2-dimethoxypropane (0.4 mL), TsOH (10 mg) and methanol (0.05 mL) were added and the mixture was stirred for 1 h. The mixture was diluted with hexane (40 mL) and washed successively with aqueous $NaHCO_3$, water and brine. The solvent was removed and the residue was chromatographed on SiO_2 (1 g, hexane:acetone) to give acylsilane **6c** (252 mg, 77%) $[\alpha]_D^{25}$ - 40.6 (c 2.01, benzene); IR (film) 1649 (C=O) cm^{-1}; ^1H NMR δ 0.53 and 0.58 (s, 3, $SiCH_3$), 1.25 (br q, 3, J = 0.6 Hz, Me_2C), 1.32 (b q, 3, J = 0.6 Hz, Me_2C), 3.81 (dd, 1, J = 6.4, 8.4 Hz, C_3 Ha), 3.97 (dd, 1, J = 7.7, 8.4 Hz, C_3 Hb), 4.38 (dd, 1, J = 6.4, 7.7 Hz, C_2 H); 7.3-7.45 (m, 3), 7.5-7.6 (m, 2); ^{13}C NMR δ -4.4 and -3.8 ($Si\underline{C}H_3$), 24.8 and 25.6 ($[\underline{C}H_3]_2C$), 64.9 (C_3), 85.1 (C_2), 110.3 ($[CH_3]_2\underline{C}$), 128.0 (C_m), 129.8 (C_p), 134.2 (C_o), 243.6 (C=O); EIMS m/z (rel intensity, %) 249 (M^+-CH_3, 0.7), 135 (100); HRMS calcd for $C_{13}H_{17}O_3Si$ (M^+-CH_3) 249.094698, found 249.09453.

b) In an analogous experiment with the use of triethylamine instead of hexamethyldisilazane acylsilane **6c** was obtained in 61% yield.

(*R*)-2,3-O-Isopropylidene-1-oxo-1-(triphenylsilyl)propan-2,3-diol (6d). To a stirred mixture of epoxysilane **4d** (215 mg, 0.65 mmol), allyl(trimethyl)silane (0.11 mL, 0.69 mmol), DMSO (0.5 mL) and CH_2Cl_2 (3 mL), Me_3SiOTf (0.3 mL, 1.65 mmol) was added. After 44 h hexamethyldisilazane (0.7 mL) was added and stirring was continued for 30 min. The mixture was diluted with hexane (40 mL) and washed with aqueous $NaHCO_3$ and water. The solvent was evaporated. The residue was dissolved in CH_2Cl_2 (5 mL), and 2,2-dimethoxypropane (0.55 mL) and TsOH (20 mg) were added. After 1 h the mixture was diluted with hexane (30 mL) and washed successively with aqueous $NaHCO_3$, water and brine. The solvent was removed and the residue was chromatographed on SiO_2 (2 g, hexane:acetone) to give acylsilane **6d** (125 mg, 50%); $[\alpha]_D^{22}$ +47.3 (c 2.35); IR (film) 1650 (C=O) cm^{-1}; ^1H NMR δ 1.10 (2, 3, Me_2C), 1.29 (s, 3, Me_2C), 3.81-3.95 (m, 2, C_3 H), 4.69 (dd, 1, J = 6.3, 7.7 Hz, C_2 H); 7.3-7.7 (m, 15, aromat. H); ^{13}C NMR δ 25.0 and 25.2 ($[\underline{C}H_3]_2C$), 64.8 (C_3), 85.3 (C_2), 110.7 ($[CH_3]_2\underline{C}$), 128.1 (C_m), 130.3 (C_p), 130.8 (C_{ipso}), 136.3 (C_o), 239.3 (C=O); Anal. Calcd for $C_{24}H_{24}O_3Si$ (388.52): C, 74.20; H, 6.23. Found: C, 74.29; H, 6.19.

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