Two-Carbon Homologation of Aldehydes via Silyl Ketene Acetals. 2.[1] Study of the Stereochemical Control in the Formation of (*E*)-Alkenoic Acids

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The condensation of *C,O,O*-tris(trimethylsilyl)ketene acetal **1** with aldehydes **2** in the presence of catalytic amounts of mercuric iodide at room temperature affords *syn* and *anti* β-trimethylsiloxy α-trimethylsilyl alkanoic acid silyl esters **3** in good yields. These new compounds gave, under acidic or basic conditions, *E* and (or) *Z* enoic acids **4**. The paths for the formation of these alkenoic acids are discussed.

Introduction

Recently, we have developed a new and convenient method for the direct conversion of aldehydes into (*E*)-alkenoic acids **4** using *C,O,O*-tris(trimethylsilyl)ketene acetal **1** through a condensation−elimination reaction[1] (Scheme 1). We have noted, at the end of our article, that further detailed study on the correlation between the elimination mechanism and the product's stereochemistry was in progress. We report here an account of our investigations concerning this olefination process. We also provide full characterization data for a series of β-siloxy-α-silyl trimethylsilyl esters **3**, the reaction-sensitive intermediates.

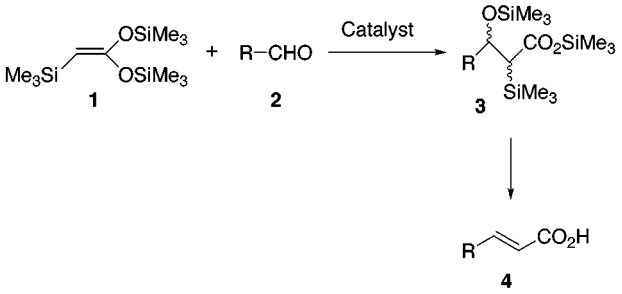
Results and Discussion

Our first investigations were focused on the reaction of **1** with benzaldehyde **2a** in the presence of catalytic amounts of mercuric iodide[2] at room temperature. The mildness of these aldol conditions permitted the isolation of the sensitive intermediates **3a**.[1] Typically, the silyl ketene acetal **1** and benzaldehyde **2a** were added to a stirring suspension of HgI_2 in toluene. TLC monitoring revealed the complete conversion of the aldehyde into **3a** after 6 h. Simple workup, which consists of removing the toluene under high vacuum, diluting the crude product with cyclohexane, filtering away the catalyst and stripping off the solvent, affords adducts **3a** (*anti* + *syn*) in 96% yield (Scheme 2).

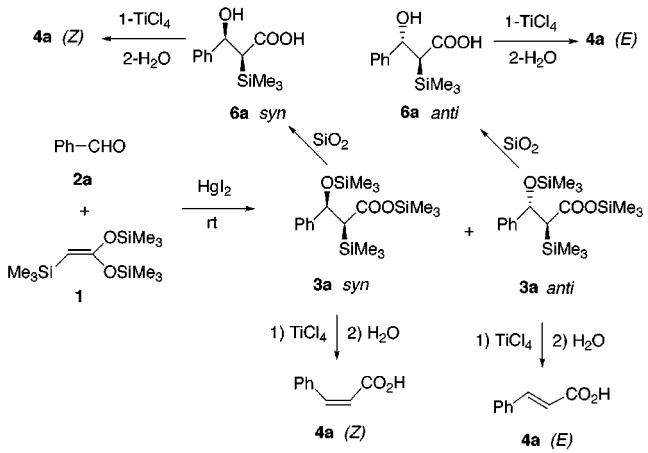
The diastereoselectivity of the reaction, as shown by ^{1}H NMR on the crude product, is in the range of 67:33. The vicinal coupling constant J_{ab} is less (10.35 Hz) for the major than for the minor isomer (10.91 Hz).

The major problem concerned the stereochemistry of the intermediates **3a**: which is *syn* and which is *anti*? Since suitable crystals were not obtained for rigorous assignment by X-ray spectroscopy, we sought another approach to determine the configuration of these diastereomers.

Scheme 1



Scheme 2



The mixture of the diastereomers (*syn* + *anti*) obtained previously was treated with 1 equiv of $TiCl_4$ in dichloromethane at room temperature. Quenching the reaction with water gave a mixture of (*E*) and (*Z*) **4a** alkenoic acids. Their *E*/*Z* ratio corresponded to the ratio (67/33) of the starting β-siloxytrimethylsilyl esters **3a**. Since elimination of hexamethyldisiloxane is highly regulated to the *anti* manner in acidic medium,[3,4] the major diastereomer is assigned to *anti* **3a** and the minor isomer to *syn* **3a**. For rigorous proof, the diastereomers **6a** were

(1) Part 1: Bellassoued, M.; Lensen, N.; Bakasse, M.; Mouelhi, S. *J. Org. Chem.* **1998**, *63*, 8785.
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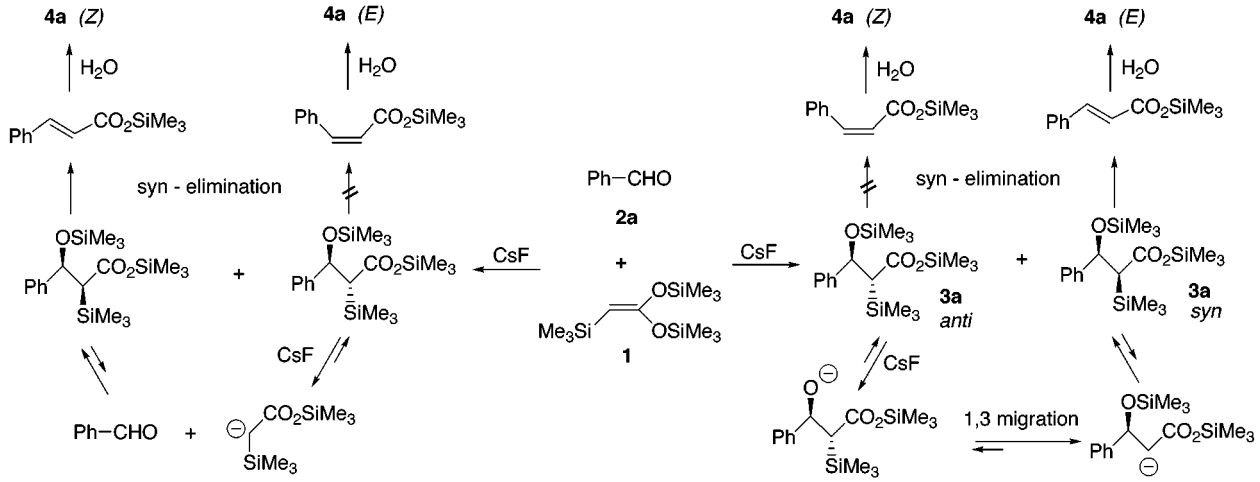
Scheme 3



obtained *from* a mixture of **3a** (*syn* + *anti*) by being passed through a silica gel column and separated at the same time. Each isomer was treated with $TiCl_4$ at room temperature for 1 h. After quenching of the reaction with H_2O, *anti* **6a** afforded (*E*) **4a** and *syn* **6a** gave (*Z*) **4a** (Scheme 2).

Pure *syn* **6a** could also be obtained when benzaldehyde and reagent **1** were treated at −78 °C with $TiCl_4$ in CH_2Cl_2 with quenching of the reaction at −78 °C. However, when the reaction was performed at −78 °C and then warmed to 25 °C for 1 h before quenching of the reaction at −78 °C, cinnamic acids **4a** were found with a diastereomeric ratio *E*/*Z* = 67/33. This result may be explained as follows: an equilibrium between *syn* and *anti* **3a** (or their corresponding titanium complex derivatives) could take place during the temperature rise. Subsequent elimination yields the mixture of (*E*) and (*Z*) cinnamic acids **4a**.

Interestingly, when the reaction of **1** with **2a** was carried out in the presence of catalytic amounts of $ZnBr_2$ (10%) in tetrahydrofuran at room temperature for 4 h, only (*E*) cinnamic acid **4a** was obtained (95% yield).[1] Several attemps to isolate the presumable intermediate *anti* **3a** (or its derivatives) failed. However, addition of zinc bromide (10%) at room temperature to a mixture of the preformed intermediates **3a** (*anti*/*syn* = 67/33) leads to the formation of (*E*) and (*Z*) **4a** in the ratio *E*/*Z* = 67/33. These results allowed us to speculate reasonably that *anti* **3a** is the only intermediate when the reaction of **1** with **2a** was catalyzed by $ZnBr_2$.

Next, we investigated the fluoride-promoted reaction of **1** with benzaldehyde **2a** (Scheme 3).[1] When the reaction was performed at −30 °C in the presence of cesium fluoride (10%) for 30 min and then quenched at the same temperature with water, β-siloxy-α-silyl acid *anti* **5a** was isolated (30%) with (*E*) cinnamic acid **4a** (70%). As the same reaction, carried out at room temperature, gave the (*E*) **4a** isomer exclusively, we assumed that formation of the (*E*) cinnamic acid **4a** occurred via the two diastereoisomers *anti* and *syn* **3a**. The latter undergoes, in the basic medium, spontaneous elimination even at low temperature (−30 °C). Elimination of hexamethyldisiloxane from the *syn* isomer **3a** might be expected to be preferred because of the configuration required for *syn*-elimination, affording the thermodynamically more stable *E* alkenoic acid. However, the difficulty of the *syn*-elimination in *anti* **3a** at −30 °C, leads, with the elevation of temperature, to the formation of *syn* **3a** isomer through a retro-aldol reaction or by 1,3-migration of the silyl group[5] (Scheme 3). In fact, when this reaction was tested at room temperature starting from a mixture of the β-siloxy-α-silyl esters **3a** (*anti*/*syn* = 67/33), synthesized using mercuric iodide, we obtained only the *E* isomer **4a** in almost quantitative yield. This result clearly supports the postulated elimination pathway since we have already verified that (*Z*) trimethylsilyl cinnamate did not isomerize to the more stable *E* isomer in the presence of CsF. Similar results were obtained using potassium *tert*-butoxide or KOH as catalyst.[6]

Last, a systematic study of the reaction reveals that the preparation of β-siloxy-α-silyltrimethylsilyl esters **3** can be performed cleanly by reaction of **1** with a variety of structurally different aldehydes **2**. As shown in Table 1, aromatic, vinylic, and aliphatic aldehydes afford the corresponding intermediates **3** in good yield. All these compounds are, to our knowledge, unknown and could be used as prodrugs for cinnamic acids analogues. The usefulness of these condensations lies also in the subsequent chemistry of the silyl moiety to obtain polyfunctionalized products.

Selected ^{1}H NMR spectral data for *anti* **3a**−**h** and *syn* **3a**−**h** are listed in the same table. We noticed that the chemical shifts of the α-hydrogens (Ha) are less for the major than for the minor isomer and conversely those of the β-hydrogens (Hb) are larger for the major than for the minor isomer. The vicinal coupling constant J_{ab} is less for the major than for the minor isomer. Moreover, mixtures of diastereoisomers **3b**−**h** were also treated with $TiCl_4$ to give mixtures of (*E*) and (*Z*) **4**. Their *E*/*Z* ratios corresponded with the ratios of major and minor **3**. Therefore the stereochemistry of the major isomer was assigned as *anti* and the minor isomer as *syn*. These data are in agreement with those of the β-hydroxy-α-silyl alkyl esters.[7,8]

Conclusion

The stereochemical outcome of this olefination reaction is intriguing. However, from the results reported here,

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(6) Lensen, N.; Mouelhi, S.; Bellassoued, M. *Synth. Commun.* In press.

(7) Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1981**, *22*, 1805.

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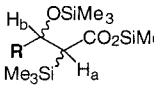
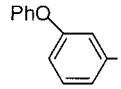
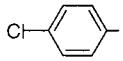
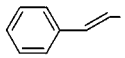
Table 1. Preparation of β-Siloxy-α-trimethylsilylalkanoic Acid Trimethylsilyl Esters 3 and Selected ^{1}H NMR Spectral Data

	R	Yield[a] (%)	anti/syn[b]	Chemical shift δ Ha anti	Chemical shift δ Ha syn	Chemical shift δ Hb anti	Chemical shift δ Hb syn	Coupling constant J_{ab} (Hz) anti	Coupling constant J_{ab} (Hz) syn
3a		95	67/33	2.59	2.62	5.08	5.07	10.35	10.91
3b		88	67/33	2.56	2.59	5.04	5.02	10.35	10.90
3c		82	73/27	2.49	2.57	5.00	4.99	10.34	10.86
3d		82	67/33	2.72	2.77	5.34	5.31	10.36	11.01
3e		88	53/47	2.17	2.21	4.52	4.49	9.80	10.00
3f		88	60/40	2.20	2.29	4.80	4.79	9.90	10.28
3g		67	57/43	2.33	2.41	4.26	4.04	8.48	10.86
3h	C_7H_{15}–	78	52/48	2.27	2.32	4.24	4.21	8.28	9.57

[a] Isolated yield. [b] The ratio of *anti* and *syn* of each compound was determined by the ^{1}H NMR spectrum of the crude product.

we can assume that the geometrical ratio of cinnamic acids **4a** reflects the diastereochemical ratio of the intermediates **3a** when the reactions are carried out in the presence of $TiCl_4$ or $ZnBr_2$. In the case of cesium fluoride-catalyzed reaction, formation of the (*E*) **4a** occurs via the two diastereomers *syn* and *anti* **3a**. Equilibration of the latter to the preferred *syn* isomer followed by synchronous elimination to the *E*-olefin seems very likely.

Experimental Section

General Information. All experiments were carried out under a nitrogen atmosphere using freshly distilled solvents under anhydrous conditions. Starting aldehydes and catalysts were purchased from commercial sources and used as received. *C*,*O*,*O*-Tris(trimethylsilyl)ketene acetal **1** was prepared using our previously reported procedure.[1] ^{1}H and ^{13}C NMR spectra were recorded at 250 MHz using $CDCl_3$ or acetone-d_6 as solvent. Chemical shifts were given in ppm (*J* in hertz) relative to chloroform or acetone. Melting points are uncorrected. Flash column chromatography was carried out on Merck grade 60 silica gel (230−400 mesh) with a mixture of cyclohexane/ethyl acetate as eluent.

Preparation of Trimethylsilyl 3-(Trimethylsiloxy)-2-(trimethylsilyl)propanoates (3). General Procedure. A toluene (10 mL) solution of aldehyde **2** (1.7 mmol) and **1** (0.552 g, 2 mmol) was added to HgI_2 (0.077 g, 0.17 mmol) at room temperature. The reaction was stirred for 5 h; then 10 mL of distilled cyclohexane was added. After decantation, the solution was removed by a syringe and the solvent was stripped off under high vacuum. The residual oil showed *anti* and *syn* compounds **3**. The ratio of these diastereoisomers was determined from integrated values of protons of ^{1}H NMR (yields and ratios are listed in Table 1). Since *syn* and *anti* isomers **3** are unseparable, some data (infrared, mass, and microanalyses) were collected from the mixture of diastereoisomers.

Trimethylsilyl 3-Phenyl-3-(trimethylsiloxy)-2-(trimethylsilyl)propanoate (3a). *Anti*: ^{1}H NMR (acetone-d_6) δ −0.12 (s, 9 H, $CSi(CH_3)_3$), 0.00 (s, 9 H, $OSi(CH_3)_3$), 0.14 (s, 9 H, $COOSi(CH_3)_3$), 2.55 (d, 1 H, *J* = 10.35 Hz, H-2), 5.08 (d, 1 H, *J* = 10.35 Hz, H-3), 7.22−7.48 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ −1.45, −0.42, 0.25, 51.12, 75.51, 126.84, 127.39, 127.93, 145.17, 173.52.

***Syn*:** ^{1}H NMR (acetone-d_6) δ −0.28 (s, 9 H, $CSi(CH_3)_3$), −0.15 (s, 9 H, $OSi(CH_3)_3$), 0.26 (s, 9 H, $COOSi(CH_3)_3$), 2.62 (d, 1 H, *J* = 10.91 Hz, H-2), 5.07 (d, 1 H, *J* = 10.91 Hz, H-3), 7.22−7.48 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ −2.44, −0.05, 0.01, 51.58, 75.41, 127.44, 128.01, 128.27, 143.38, 174.35.

IR ($CDCl_3$): 1695 (C═O). MS: $M^{\bullet+}$ = 382. Anal. Calcd for $C_{18}H_{34}O_3Si_3$: C, 56.49; H, 8.95. Found: C, 56.38; H, 8.91.

Trimethylsilyl 3-(3-Phenoxyphenyl)-3-(trimethylsiloxy)-2-(trimethylsilyl)propanoate (3b). *Anti*: ^{1}H NMR (acetone-d_6) δ 0.00 (s, 9 H, $CSi(CH_3)_3$), 0.16 (s, 9 H, $OSi(CH_3)_3$), 0.21 (s, 9 H, $COOSi(CH_3)_3$), 2.60 (d, 1 H, *J* = 10.35 Hz, H-2), 5.08 (d, 1 H, *J* = 10.35 Hz, H-3), 6.95−7.42 (m, 9 H, ArH); ^{13}C NMR ($CDCl_3$) δ −1.52, −0.43, 0.22, 50.93, 75.07, 118.31, 118.49, 121.92, 122.82, 128.09, 129.20, 129.53, 146.99, 156.67, 157.43, 172.86.

***Syn*:** ^{1}H NMR (acetone-d_6) δ −0.15 (s, 9 H, $CSi(CH_3)_3$), −0.02 (s, 9 H, $OSi(CH_3)_3$), 0.36 (s, 9 H, $COOSi(CH_3)_3$), 2.63 (d, 1 H, *J* = 10.90 Hz, H-2), 5.05 (d, 1 H, *J* = 10.90 Hz, H-3), 6.95−7.42 (m, 9 H, ArH); ^{13}C NMR ($CDCl_3$) δ −2.41, −0.16, 0.01, 51.37, 74.96, 118.26, 118.91, 122.24, 123.07, 125.18, 128.88, 129.60, 145.16, 157.20, 157.30, 173.58.

IR ($CDCl_3$): 1695 (C═O). MS: $M^{\bullet+}$ = 474. Anal. Calcd for $C_{24}H_{38}O_4Si_3$: C, 60.71; H, 8.07. Found: C, 60.67; H, 8.01.

Trimethylsilyl 3-(4-Chlorophenyl)-3-(trimethylsiloxy)-2-(trimethylsilyl)propanoate (3c). *Anti*: ^{1}H NMR ($CDCl_3$) δ −0.12 (s, 9 H, $CSi(CH_3)_3$), 0.04 (s, 9 H, $OSi(CH_3)_3$), 0.14 (s, 9 H, $COOSi(CH_3)_3$), 2.49 (d, 1 H, *J* = 10.34 Hz, H-2), 5.00 (d, 1 H, *J* = 10.34 Hz, H-3), 7.22 (m, 4 H, ArH); ^{13}C NMR ($CDCl_3$) δ −1.46, −0.39, 0.29, 51.23, 74.80, 128.11, 128.12, 133.05, 143.55, 172.95.

***Syn*:** ^{1}H NMR ($CDCl_3$) δ −0.26 (s, 9 H, $CSi(CH_3)_3$), −0.13 (s, 9 H, $OSi(CH_3)_3$), 0.28 (s, 9 H, $COOSi(CH_3)_3$), 2.57 (d, 1 H, *J* = 10.86 Hz, H-2), 4.99 (d, 1 H, *J* = 10.86 Hz, H-3), 7.22 (m,

4 H, ArH); ^{13}C NMR ($CDCl_3$) δ −2.33, −0.08, 0.03, 51.55, 74.63, 128.67, 128.50, 133.66, 141.74, 173.58.

IR (KBr): 1693 (C═O). MS: $M^{\bullet+}$ = 416; 418. Anal. Calcd for $C_{18}H_{33}ClO_3Si_3$: C, 51.82; H, 7.97. Found: C, 51.78; H, 7.92.

Trimethylsilyl 3-(3-Thienyl)-3-(trimethylsiloxy)-2-(trimethylsilyl)propanoate (3d). ***Anti*****:** ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H, $CSi(CH_3)_3$), 0.23 (s, 9 H, $OSi(CH_3)_3$), 0.30 (s, 9 H, $COOSi(CH_3)_3$), 2.72 (d, 1 H, J = 10.36 Hz, H-2), 5.31 (d, 1 H, J = 10.36 Hz, H-3), 7.27 (m, 3 H, ArH); ^{13}C NMR ($CDCl_3$) δ −1.48, −0.38, 0.11, 50.37, 70.99, 121.33, 125.41, 126.11, 146.11, 173.15.

Syn**:** ^{1}H NMR ($CDCl_3$) δ −0.06 (s, 9 H, $CSi(CH_3)_3$), 0.05 (s, 9 H, $OSi(CH_3)_3$), 0.45 (s, 9 H, $COOSi(CH_3)_3$), 2.77 (d, 1 H, J = 11.01 Hz, H-2), 5.31 (d, 1 H, J = 11.01 Hz, H-3), 7.27 (m, 3 H, ArH); ^{13}C NMR ($CDCl_3$) δ −2.59, −0.12, −0.06, 50.93, 70.55, 121.63, 126.11, 126.73, 144.34, 173.71.

IR (KBr): 1693 (C═O). MS: $M^{\bullet+}$ = 388. Anal. Calcd for $C_{16}H_{32}O_3SSi_3$: C, 49.43; H, 8.30. Found: C, 49.39; H, 8.25.

Trimethylsilyl 5-Phenyl-3-(trimethylsiloxy)-2-(trimethylsilyl)-4-pentenoate (3e). ***Anti*****:** ^{1}H NMR ($CDCl_3$) δ −0.13 (s, 9 H, $CSi(CH_3)_3$), −0.10 (s, 9 H, $OSi(CH_3)_3$), 0.09 (s, 9 H, $COOSi(CH_3)_3$), 2.17 (d, 1 H, J = 9.80 Hz, H-2), 4.52 (dd, 1 H, J = 9.80 Hz, 8.39 Hz, H-3), 5.89 (dd, 1 H, J = 15.90 Hz, 8.39 Hz, H-4), 6.32 (d, 1 H, J = 15.90 Hz, H-5), 7.23 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ −0.15, 0.41, 0.59, 49.68, 74.06, 126.29, 127.69, 128.57, 129.90, 130.77, 136.32, 173.47.

Syn**:** ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9 H, $CSi(CH_3)_3$), −0.05 (s, 9 H, $OSi(CH_3)_3$), 0.00 (s, 9 H, $COOSi(CH_3)_3$), 2.21 (d, 1 H, J = 10.00 Hz, H-2), 4.49 (dd, 1 H, J = 10.00 Hz, 8.22 Hz, H-3), 5.90 (dd, 1 H, J = 15.80 Hz, 8.22 Hz, H-4), 6.23 (d, 1 H, J = 15.80 Hz, H-5), 7.23 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ −1.78, −1.44, −0.29, 48.71, 74.59, 126.29, 127.44, 128.41, 131.25, 132.72, 136.56, 173.08.

IR (KBr): 1693 (C═O). MS: $M^{\bullet+}$ = 408. Anal. Calcd for $C_{20}H_{36}O_3Si_3$: C, 58.77; H, 8.88. Found: C, 58.71; H, 8.81.

Trimethylsilyl 5-Methyl-3-(trimethylsiloxy)-2-(trimethylsilyl)-4-hexenoate (3f). ***Anti*****:** ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $CSi(CH_3)_3$), 0.10 (s, 9 H, $OSi(CH_3)_3$), 0.20 (s, 9 H, $COOSi(CH_3)_3$), 1.65 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 2.20 (d, 1 H, J = 9.90 Hz, H-2), 4.80 (dd, 1 H, J = 9.90 Hz, 9.50 Hz, H-3), 5.07 (d, 1 H, J = 9.50 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ −1.48, −0.25, 0.55, 18.44, 25.61, 49.15, 69.44, 129.43, 131.94, 173.41.

Syn**:** ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H, $CSi(CH_3)_3$), 0.04 (s, 9 H, $OSi(CH_3)_3$), 0.27 (s, 9 H, $COOSi(CH_3)_3$), 1.67 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 2.29 (d, 1 H, J = 10.28 Hz, H-2), 4.79 (dd, 1 H, J = 10.28 Hz, 9.50 Hz, H-3), 5.07 (d, 1 H, J = 9.50 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ −1.87, −0.07, 0.38, 18.90, 25.68, 50.22, 69.22, 127.84, 132.54, 174.03.

IR (KBr): 1693 (C═O). MS: $M^{\bullet+}$ = 360. Anal. Calcd for $C_{16}H_{36}O_3Si_3$: C, 53.28; H, 10.06. Found: C, 53.20; H, 10.01.

Trimethylsilyl 4-Methyl-3-(trimethylsiloxy)-2-(trimethylsilyl)pentanoate (3g). ***Anti*****:** ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H, $CSi(CH_3)_3$), 0.08 (s, 9 H, $OSi(CH_3)_3$), 0.22 (s, 9 H, $COOSi(CH_3)_3$), 0.76 (d, 3H, CH_3, J = 7.0 Hz), 0.83 (d, 3H, CH_3, J = 6.80 Hz), 1.83 (m, 1H, H-4), 2.33 (d, 1 H, J = 8.48 Hz, H-2), 4.26 (dd, 1 H, J = 8.48 Hz, 4.25 Hz, H-3); ^{13}C NMR ($CDCl_3$) δ −1.16, −0.43, 0.55, 15.42, 18.09, 29.49, 35.16, 42.61, 174.71.

Syn**:** ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 9 H, $CSi(CH_3)_3$), 0.21 (s, 9 H, $OSi(CH_3)_3$), 0.24 (s, 9 H, $COOSi(CH_3)_3$), 0.92 (d, 3H, CH_3, J = 6.80 Hz), 1.0 (d, 3H, CH_3, J = 7.30 Hz), 1.83 (m, 1H, H-4), 2.41 (d, 1 H, J = 10.86 Hz, H-2), 4.04 (d, 1 H, J = 10.86 Hz, H-3); ^{13}C NMR ($CDCl_3$) δ −2.17, −0.94, 0.51, 15.16, 18.25, 29.49, 35.06, 41.26, 174.71.

IR (KBr): 1693 (C═O). MS: $M^{\bullet+}$ = 348. Anal. Calcd for $C_{15}H_{36}O_3Si_3$: C, 51.67; H, 10.41. Found: C, 51.60; H, 10.30.

Trimethylsilyl 3-(Trimethylsiloxy)-2-(trimethylsilyl)-decanoate (3h). ***Anti*****:** ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H, $CSi(CH_3)_3$), 0.09 (s, 9 H, $OSi(CH_3)_3$), 0.24 (s, 9 H, $COOSi(CH_3)_3$), 0.88 (t, 3H, CH_3), 1.27 (m, 10 H, H-5−9), 1.42 (m, 2 H, H-4), 2.27 (d, 1 H, J = 8.28 Hz, H-2), 4.24 (m, 1 H, H-3); ^{13}C NMR ($CDCl_3$) δ −1.35, −0.11, 0.73, 14.10, 22.68, 24.29, 28.99, 29.90, 31.84, 36.39, 47.64, 72.41, 174.30.

Syn**:** ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H, $CSi(CH_3)_3$), 0.22 (s, 9 H, $OSi(CH_3)_3$), 0.23 (s, 9 H, $COOSi(CH_3)_3$), 0.88 (t, 3H, CH_3), 1.27 (m, 10 H, H-5−9), 1.61 (m, 2 H, H-4), 2.32 (d, 1 H, J = 9.57 Hz, H-2), 4.24 (m, 1 H, J = 9.57 Hz, H-3); ^{13}C NMR ($CDCl_3$) δ −1.05, 0.16, 0.64, 14.10, 22.11, 23.75, 29.36, 29.78, 31.66, 38.00, 46.75, 72.68, 173.59.

IR (KBr): 1693 (C═O). MS: $M^{\bullet+}$ = 404. Anal. Calcd for $C_{19}H_{44}O_3Si_3$: C, 56.37; H, 10.96. Found: C, 56.29; H, 10.90.

Preparation of 3-(Trimethylsiloxy)-3-phenyl-2-(trimethylsilyl)propanoic Acid (5a). A toluene (10 mL) solution of benzaldehyde **2a** (0.172 mL, 1.7 mmol) and **1** (0.552 g, 2 mmol) was added to HgI_2 (0.077 g, 0.17 mmol) at room temperature. The reaction was stirred for 5 h, and 10 mL of distilled cyclohexane was added by a syringe to the mixture. After 1 h, the solution was filtered and placed under high vacuum to remove toluene and cyclohexane. The limpid residual oil was quenched by NH_4Cl (10 mL) for 1.5 h and extracted with ether (3 × 20 mL). The organic layers were washed with H_2O (30 mL) and dried over $MgSO_4$, and the solvent was evaporated under reduced pressure, affording a white powder (yield: 85%). The solid crude product, analyzed by ^{1}H NMR, showed a mixture of *anti* and *syn* isomers **(5a)** (*anti*/*syn* = 67/33). The ratio of the diastereoisomers was determined from integrated values of hydrogens at the C-3 carbon.

Anti**:** ^{1}H NMR (acetone-d_6) δ −0.07 (s, 9 H, $CSi(CH_3)_3$), 0.21 (s, 9 H, $OSi(CH_3)_3$), 2.63 (d, 1 H, J = 10.40 Hz, H-2), 5.15 (d, 1 H, J = 10.40 Hz, H-3), 7.28−7.47 (m, 5 H, ArH); ^{13}C NMR (acetone-d_6) δ −1.16, 0.40, 49.91, 76.30, 127.60, 128.31, 128.79, 145.76, 174.50.

Syn**:** ^{1}H NMR (acetone-d_6) δ −0.23 (s, 9 H, $CSi(CH_3)_3$), −0.09 (s, 9 H, $OSi(CH_3)_3$), 2.64 (d, 1 H, J = 10.75 Hz, H-2), 5.13 (d, 1 H, J = 10.75 Hz, H-3), 7.28−7.47 (m, 5 H, ArH); ^{13}C NMR (acetone-d_6) δ −2.24, −0.18, 50.37, 75.95, 127.60, 128.79, 129.07, 144.12, 175.85.

IR (KBr): 1700 (C═O). MS: $M^{\bullet+}$ = 310. Anal. Calcd for $C_{15}H_{26}O_3Si_2$: C, 58.02; H, 8.44. Found: C, 58.05; H, 8.37.

Preparation of 3-Hydroxy-3-phenyl-2-(trimethylsilyl)-propanoic Acid (6a). Procedure A. A mixture of propanoate **3a** was chromatographed (silica gel, cyclohexane/ethyl acetate 70/30); two fractions were isolated containing pure isomers *syn* **6a** (30%) and *anti* **6a** (60%).

Procedure B. To a cooled (−70 °C) dichloromethane (10 mL) solution of benzaldehyde **2a** (0.172 mL, 1.7 mmol) was added $TiCl_4$ (1.7 mmol) via a syringe. Reagent **1** (0.552 g, 2 mmol) was added dropwise, and the resulting mixture was stirred at −70 °C for 1 h. After quenching with a saturated NH_4Cl solution (10 mL) at the same temperature, the temperature of the solution was raised to room temperature. The aqueous layer was extracted with dichloromethane (2 × 20 mL) and ether (1 × 20 mL), and the combined organic phases were washed with water and dried over $MgSO_4$. The solvents were evaporated in vacuo. Purification by recrystallization in pentane gave pure *syn* 3-hydroxy-3-phenyl-2-(trimethylsilyl)-propanoic acid **6a** (yield: 95%).

Anti**:** recrystallized in cyclohexane; mp = 87−94 °C; ^{1}H NMR (acetone-d_6) δ −0.01 (s, 9 H, $CSi(CH_3)_3$), 2.68 (d, 1 H, J = 7.28 Hz, H-2), 2.95 (s, 1 H, OH), 5.01 (d, 1 H, J = 7.28 Hz, H-3), 7.24−7.44 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) −2.08, 46.23, 72.47, 126.04, 127.71, 128.43, 143.10, 180.53; IR (KBr) 3345 (OH), 1690 (C═O); MS $M^{\bullet+}$ = 238. Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.46; H, 7.61. Found: C, 60.44; H, 7.59.

Syn**:** recrystallized in pentane; mp = 135−137 °C; ^{1}H NMR (acetone-d_6) δ 0.20 (s, 9 H, $CSi(CH_3)_3$), 2.57 (d, 1 H, J = 10.32 Hz, H-2), 4.45 (s, 1 H, OH), 5.11 (d, 1 H, J = 10.32 Hz, H-3), 7.15−7.45 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ −1.18, 46.94, 72.97, 125.80, 127.66, 128.41, 143.68, 180.11; IR (KBr) 3394 (OH), 1672 (C═O); MS $M^{\bullet+}$ = 238. Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.46; H, 7.61. Found: C, 60.48; H, 7.58.

Supporting Information Available: NMR spectra of compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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