Highly Enantioenriched Homoenolate Reagents by Asymmetric γ -Deprotonation of Achiral 1-Silyl-Substituted 1-Alkenyl Carbamates

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Supporting Information

General Methods

All organometallic reactions were performed under anhydrous conditions in an inert atmosphere of Argon in dried glassware. Solutions were transferred by means of syringes. Toluene and diethyl ether were dried with Na before use. Electrophiles were distilled prior to use. Analytical thin-layer chromatography was performed on Merck silica gel plates (Silica gel 60 F₂₅₄). Visualization was accomplished with UV light and KMnO₄- or vanillin-solution. Column chromatography was carried out at 1.5 bar on silica gel 40-63 μ m (Merck, Darmstadt). Only distilled solvents were used as eluents. ¹H NMR spectra and ¹³C NMR spectra were recorded on a Bruker AM 300 (300 MHz and 75.5 MHz for ¹H and ¹³C NMR, respectively). CDCl₃ was used as solvent; chemical shifts are reported in ppm (δ); ¹H-shifts are related to TMS or CDCl₃ and ¹³C-shifts to $\delta_C = 77.0$ ppm; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and bs (broad singlet); * refers to signals which are interchangeable; brackets refer to signals which arise from frozen rotations of the amide bond. The numbering of the compounds can differ from the IUPAC name. Mass spectroscopy and elemental analysis were performed at the Institute of Organic Chemistry, University of Münster. IR absorption spectra were recorded using a Perkin-Elmer 298. The optical rotations were measured using a Perkin-Elmer polarimeter 241. Analytical capillary gas chromatography (GC) was performed using the following gas chromatograph, fitted with a flame detector: Hewlett Packard Series 5890 Series II, column HP5 and the following temperature programme: 50°C, 10°C/min, 300°C, 10 min. Chiral stationary phase HPLC was performed on a set with the following components: Waters 717 plus autosampler, Waters 600 Controller, Waters 996 Photodiode Array Detector and Waters In-Line Degasser (GROM Analytic + HPLC GmbH, Herrenberg, Germany).

Detailed Reaction Procedures and Analytical Data of Representative Examples

1. Isomerization of Allyl Carbamates

A solution of *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 36 mmol, 4.184 g.) in diethyl ether (70 ml) was cooled to -78°C and *n*butyllithium (1.6 M in hexane, 36 mmol, 22.5 ml) was added, followed after 10 min by a solution of the (*E*)-2-alkenyl *N,N*-diisopropylcarbamate (**15**) (30 mmol) in diethyl ether (10 ml). The solution was stirred for 1 hour at -78°C , then a solution of titanium tetrakisopropoxide (39 mmol, 11.086 g) in diethyl ether (15 ml) was added dropwise. Stirring was continued for 1 hour before methanol (25 ml) was added at -78°C followed by 2N aq. HCl (30 ml). After warming to r.t. and separation of the phases, the aqueous solution was extracted with diethyl ether (3 $\times$ 50 ml). The organic layers were combined and dried with MgSO₄. After evaporation of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (pentane/diethyl ether) which afforded the (*Z*)-1-alkenyl *N,N*-diisopropylcarbamate (**14**).

1.1 (Z)-1-Butenyl *N,N*-Diisopropylcarbamate (**14a**)

Isomerization of (*E*)-2-butenyl *N,N*-diisopropylcarbamate (**15a**)^[1] (30 mmol, 5.979 g) and purification (pentane/diethyl ether 20:1) yielded (*Z*)-1-butenyl *N,N*-diisopropylcarbamate (**14a**) as a colourless oil (5.441 g, 91%).

t_R = 9.30 min; R_f = 0.40 (pentane/diethyl ether 4:1).

^1H NMR (300 MHz, CDCl_3): δ/ppm = 1.01 (t, 3H, 4-H); 1.26 (m, 12H, $\text{CH}_3(\text{Cb})$); 2.17 (ddq, 2H, 3-H); 3.78 [4.14] (bs, 2H, $\text{CH}(\text{Cb})$); 4.75 (dt, 1H, 2-H); 6.98 (dt, 1H, 1-H).

$^3J_{1,2}$ = 6.4 Hz; $^4J_{1,3}$ = 1.6 Hz; $^3J_{2,3}$ = 7.3 Hz; $^3J_{3,4}$ = 7.5 Hz.

^{13}C NMR (75 MHz, CDCl_3): δ/ppm = 14.1 (C-4); 18.3 (C-3); 20.4 [21.1] ($\text{CH}_3(\text{Cb})$); 45.6 [46.8] ($\text{CH}(\text{Cb})$); 112.7 (C-2); 134.4 (C-1); 153.5 (OCON).

IR (neat): $\tilde{\nu}/\text{cm}^{-1}$ = 2968, 2931, 2871, 1699, 1470, 1438, 1314, 1291, 1244, 1148, 1139, 1090, 1072, 1049.

MS (ESI) (m/z): $[\text{M}+\text{Na}]^+ = 222.3$.

Elemental analysis:	calcd.: C 66.29	H 10.62	N 7.03
$\text{C}_{11}\text{H}_{21}\text{NO}_2$	found: C 66.14	H 10.91	N 7.00.

1.2 (Z)-3-Phenyl-1-propenyl *N,N*-Diisopropylcarbamate (**14b**)

Isomerization of (*E*)-3-phenyl-2-propenyl *N,N*-diisopropylcarbamate (**15b**)^[2] (30 mmol, 7.841 g) and purification (pentane/diethyl ether 6:1 → 4:1) afforded (*Z*)-3-phenyl-1-propenyl *N,N*-diisopropylcarbamate (**14b**) as a yellow oil (6.273 g, 80%).

t_R = 15.69 min; R_f = 0.25 (pentane/diethyl ether = 6:1).

^1H NMR (300 MHz, CDCl_3): δ/ppm = 1.26 (m, 12H, $\text{CH}_3(\text{Cb})$); 3.52 (d, 2H, 3-H); 3.84 [4.07] (bs, 2H, $\text{CH}(\text{Cb})$); 4.94 (dt, 1H, 2-H); 7.14-7.28 (m, 6H, aryl-H/1-H).

$^3J_{1,2}$ = 7.5 Hz; $^3J_{2,3}$ = 6.4 Hz.

¹ Hoppe, D.; Hanko, R.; Brönneke, A.; Lichtenberg, F.; van Hülsen, E. *Chem. Ber.* **1985**, *118*, 2822.

² Hoppe, D.; Behrens, K.; Fröhlich, R.; Meyer, O. *Eur. J. Org. Chem.* **1998**, 2397.

^{13}C NMR (75 MHz, CDCl_3): δ/ppm = 20.5 [21.4] ($\text{CH}_3(\text{Cb})$); 31.2 (C-3); 45.7 [46.6] ($\text{CH}(\text{Cb})$); 109.2 (C-2); 126.0/128.2/128.3 (C-aryl); 135.7 (C-1); 140.5 (Cq-aryl); 152.8 (OCON).

IR (neat): $\tilde{\nu}/\text{cm}^{-1}$ = 2972, 2933, 2873, 1709, 1470, 1437, 1373, 1313, 1286, 1244, 1216, 1160, 1134, 1091, 1072, 1049, 750, 699.

MS (ESI) (m/z): $[\text{M}+\text{Na}]^+ = 284.5$.

Elemental analysis:	calcd.: C 73.53	H 8.87	N 5.36
$\text{C}_{16}\text{H}_{23}\text{NO}_2$	found: C 73.55	H 8.90	N 5.25.

2 Deprotonation of 1-Alkenyl carbamates **14**^[3] and Addition of Trimethylsilyl Chloride

To a solution of TMEDA (22 mmol, 2.557 g) in diethyl ether (60 ml) *n*butyllithium (1.6 M in hexane, 22 mmol, 13.8 ml) was added at -78°C , followed after 10 min by a solution of the (*Z*)-1-alkenyl *N,N*-diisopropylcarbamate (**14**) (20 mmol) in diethyl ether (10 ml). The solution was stirred for 1 hour at -78°C . A solution of trimethylsilyl chloride (24 mmol, 2.609 g) in diethyl ether (8 ml) was added slowly within 15 min. Stirring was continued for 1 hour before the reaction was stopped by addition of sat. ammonium chloride solution (25 ml) at -78°C . After warming to room temperature and separation of the phases, the aqueous solution was extracted with diethyl ether (3×50 ml) and dried with MgSO_4 . After evaporation of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (pentane/diethyl ether 20:1) which afforded the (*E*)-1-trimethylsilyl-1-alkenyl *N,N*-diisopropylcarbamate (**1**).

2.1 (*E*)-1-Trimethylsilyl-1-butenyl *N,N*-Diisopropylcarbamate (**1a**)

Deprotonation of (*Z*)-1-butenyl *N,N*-diisopropylcarbamate (**14a**) (20 mmol, 3.986 g) and substitution with trimethylsilyl chloride yielded (*E*)-1-trimethylsilyl-1-butenyl *N,N*-diisopropylcarbamate (**1a**) as a colourless oil (3.746 g, 69%).

$t_R = 10.47$ min; $R_f = 0.40$ (pentane/diethyl ether = 4:1).

^1H NMR (300 MHz, CDCl_3): δ/ppm = 0.10 (s, 9H, CH_3Si); 0.94 (t, 3H, 4-H); 1.21 (m, 12H, $\text{CH}_3(\text{Cb})$); 2.07 (dq, 2H, 3-H); 3.78 [4.04] (bs, 2H, $\text{CH}(\text{Cb})$); 5.32 (t, 1H, 2-H).

$^3J_{2,3} = 7.0$ Hz; $^3J_{3,4} = 7.6$ Hz.

^{13}C NMR (75 MHz, CDCl_3): δ/ppm = -0.8 (CH_3Si); 13.6 (C-4); 19.3 (C-3); 20.0 [21.5] ($\text{CH}_3(\text{Cb})$); 45.7 [46.7] ($\text{CH}(\text{Cb})$); 131.5 (C-2); 154.1 (C-1)*; 154.3 (OCON)*.

IR (neat): $\tilde{\nu}/\text{cm}^{-1}$ = 2968, 2935, 2899, 1701, 1435, 1334, 1246, 1137, 1068, 841, 767.

ESI-MS (m/z): $[\text{M}+\text{H}]^+ = 272.2$; $[\text{M}+\text{Na}]^+ = 294.2$; $[\text{M}+\text{K}]^+ = 310.2$.

³ Snieckus, V.; Sengupta, S. *J. Org. Chem.* **1990**, 55, 5680.

HRMS:
C₁₄H₂₉NO₂Si

calcd.: [M+H]⁺ = 272.2046; [M+Na]⁺ = 294.1865
found: [M+H]⁺ = 272.2026; [M+Na]⁺ = 294.1906.

2.2 (*E*)-3-Phenyl-1-trimethylsilyl-1-propenyl *N,N*-Diisopropylcarbamate (**1b**)

Deprotonation of (*Z*)-3-phenyl-1-propenyl *N,N*-diisopropylcarbamate (**14b**) (20 mmol, 5.230 g) and substitution with trimethylsilyl chloride yielded (*E*)-3-Phenyl-1-trimethylsilyl-1-propenyl *N,N*-diisopropylcarbamate (**1b**) as a colourless oil (5.537 g, 83%).

t_R = 15.95 min; R_f = 0.37 (pentane/diethyl ether = 6:1).

¹H NMR (300 MHz, CDCl₃): δ /ppm = 0.00 (s, 9H, CH₃Si); 0.90 (d, 12H, CH₃(Cb)); 3.30 (d, 2H, 3-H); 3.68 [3.88] (bs, 2H, CH(Cb)); 5.37 (t, 1H, 2-H); 7.01-7.13 (m, 5H, aryl-H).

³ J_{Cb} = 6.9 Hz; ³ $J_{2,3}$ = 7.0 Hz.

¹³C NMR (75 MHz, CDCl₃): δ /ppm = -0.8 (CH₃Si); 20.5 [21.5] (CH₃(Cb)); 32.2 (C-3); 45.8 [46.4] (CH(Cb)); 125.9 (C-2); 127.9/128.4/128.5 (CH-aryl); 141.2 (Cq-aryl); 154.0 (OCON)*; 155.6 (C-1)*.

IR (neat): $\tilde{\nu}$ /cm⁻¹ = 3025, 2972, 2904, 1699, 1437, 1368, 1328, 1293, 1248, 1213, 1161, 1135, 1095, 1074, 1150, 842, 764, 748, 703.

MS (ESI) (m/z): [M+H]⁺ = 334.7; [M+Na]⁺ = 356.6.

Elemental analysis:	calcd.: C 68.42	H 9.37	N 4.20
C ₁₉ H ₃₁ NO ₂ Si	found: C 68.39	H 9.25	N 4.15.

3 Lithiation and Electrophilic Substitution of **1a**

3.1 (+)-(1*E*, 3*S*)-1,3-Bis(trimethylsilyl)-1-butenyl *N,N*-Diisopropylcarbamate (**4a**)

A solution of (–)-sparteine (1.5 mmol, 352 mg) in toluene (2 ml) was cooled to -78°C. *n*-butyllithium (1.6 M in hexane, 1.5 mmol, 0.94 ml) was added followed by a solution of (*E*)-1-trimethylsilyl-1-butenyl *N,N*-diisopropylcarbamate (**1a**) (0.5 mmol, 136 mg) in toluene (1.0 ml) after 10 min and the clear yellow solution was stirred for 12 hours. A solution of

trimethylsilyl chloride (4.5 mmol, 489 mg) in toluene (1.0 ml) was added slowly within 10 min. The solution was stirred additional 2 h and then the reaction was quenched by addition of a mixture of glacial acid (0.05 ml) and methanol (0.3 ml) at -78°C . After warming to r.t. and dilution of the organic phase with diethyl ether (10 ml) it was dried with MgSO_4 and the solvent was removed in vacuo. Purification by column chromatography (pentane/diethyl ether 20:1) furnished (1*E*, 3*S*)-1,3-bis(trimethylsilyl)-1-butenyl *N,N*-diisopropylcarbamate (**4a**) (146 mg, 85%).

$t_{\text{R}} = 13.16$ min; $R_{\text{f}} = 0.60$ (pentane/diethyl ether = 6:1).

$[\alpha]_{\text{D}}^{20} = +32$ ($c = 1.31$ in CHCl_3 ; $\geq 95\%$ *ee*).

^1H NMR shift-experiment: 39 mol% $\text{Eu}(\text{hfc})_3$ in CDCl_3 , $\Delta\delta(\text{CH}_3\text{Si}) = 0.01$ ppm (major enantiomer: $\delta = 0.17$ ppm, minor enantiomer: $\delta = 0.18$ ppm).

^1H NMR (300 MHz, CDCl_3): $\delta/\text{ppm} = -0.05$ (s, 9H, CH_3Si); 0.12 (s, 9H, CH_3Si); 1.03 (d, 3H, 4-H); 1.23 (d, 12H, $\text{CH}_3(\text{Cb})$); 2.07 (dq, 1H, 3-H); 3.92 (bs, 2H, $\text{CH}(\text{Cb})$); 5.10 (d, 1H, 2-H); $^3J_{\text{Cb}} = 6.6$ Hz; $^3J_{2,3} = 10.7$ Hz; $^3J_{3,4} = 7.2$ Hz.

^{13}C NMR (75 MHz, CDCl_3): $\delta/\text{ppm} = 0.4$ (CH_3Si); 14.6 (C-4); 21.0 (C-3); 21.4 [20.6] ($\text{CH}_3(\text{Cb})$); 46.0 ($\text{CH}(\text{Cb})$); 132.7 (C-2); 151.6 (C-1); 154.1 (OCON).

IR (neat): $\tilde{\nu}/\text{cm}^{-1} = 2960, 2900, 2870, 1702, 1433, 1333, 1291, 1247, 1131, 1070, 1048, 839, 767, 751$.

MS (ESI) (m/z): $[\text{M}+\text{H}]^+ = 344.3$; $[\text{M}+\text{Na}]^+ = 366.2$; $[\text{M}+\text{K}]^+ = 382.2$.

Elemental analysis:	calcd.: C 59.42	H 10.85	N 4.08
$\text{C}_{17}\text{H}_{37}\text{NO}_2\text{Si}_2$	found: C 59.20	H 11.03	N 3.78.

3.2 (–)-(1*E*,3*S*,4*R*)-4-Hydroxy-3,5-dimethyl-1-trimethylsilyl-1-hexenyl *N,N*-Diisopropylcarbamate (*anti*-**6b**)

(*E*)-1-Trimethylsilyl-1-butenyl *N,N*-diisopropylcarbamate (**1a**) (0.5 mmol, 136 mg) was lithiated as described above (3.1). After titanation with a solution of $\text{ClTi}(\text{NEt}_2)_3$ (1.75 mmol, 525 mg) in toluene (1 ml) for 6 h, the red-brown intermediate was trapped with a solution of 2-methylpropanal (3.5 mmol, 252 mg) in toluene (0.5 ml). The solution was then allowed to warm to -25°C and stirred additional 2 h. During this time period the solution became orange. The reaction was stopped by the addition of a mixture of methanol (0.5 ml) and glacial acid (0.1 ml) at -78°C . The mixture was warmed to r.t., poured into 2N aq. HCl (10 ml), extracted with diethyl ether (3×10 ml), and dried with MgSO_4 . Evaporation of the solvent and chromatography of the crude product (cyclohexane/ethyl acetate 10:1) afforded (–)-(1*E*,3*S*,4*R*)-4-hydroxy-3,5-dimethyl-1-trimethylsilyl-1-hexenyl *N,N*-diisopropylcarbamate (*anti*-**6b**) as a colourless oil (120 mg, 70%).

$t_{\text{R}} = 14.90$ min; $R_{\text{f}} = 0.13$ (pentane/diethyl ether 5:1).

$[\alpha]_D^{20} = -27$ ($c = 0.97$ in CHCl_3 ; $\geq 95\%$ *ee*).

^1H NMR shift-experiment: 27 mol% $\text{Eu}(\text{hfc})_3$ in CDCl_3 , $\Delta\delta$ (CH_3Si) = 0.04 ppm (major enantiomer: $\delta = 0.33$ ppm, minor enantiomer: $\delta = 0.29$ ppm).

^1H NMR (300 MHz, CDCl_3): $\delta/\text{ppm} = 0.12$ (s, 9H, CH_3Si); 0.81 (d, 3H, 7-H); 0.92/0.98 (d, 6H, 6-H); 1.16-1.23 (m, 12H, $\text{CH}_3(\text{Cb})$); 1.67-1.77 (m, 1H, 5-H); 2.61-2.72 (m, 1H, 3-H); 2.84-2.85 (m, 1H, OH); 3.07-3.12 (m, 1H, 4-H); 3.93 (m, 2H, $\text{CH}(\text{Cb})$); 5.37 (d, 1H, 2-H). $^3J_{2,3} = 6.7$ Hz; $^3J_{6,5} = 6.6$ Hz.

^{13}C NMR (75 MHz, CDCl_3): $\delta/\text{ppm} = -0.8$ (CH_3Si); 15.3/17.9/20.8 (C-6/C-7); 21.0 [21.8] ($\text{CH}_3(\text{Cb})$); 30.6 (C-5)*; 34.9 (C-3)*; 46.5 [47.2] ($\text{CH}(\text{Cb})$); 79.8 (C-4); 134.7 (C-2); 155.0 (OCN)*; 156.1 (C-1)*.

IR (neat): $\tilde{\nu}/\text{cm}^{-1} = 3444, 2969, 2935, 2903, 2875, 1683, 1436, 1335, 1305, 1248, 1214, 1153, 1051, 1002, 843, 764$.

MS (ESI) (m/z): $[\text{M}+\text{H}]^+ = 344$; $[\text{M}+\text{Na}]^+ = 366$; $[\text{M}+\text{K}]^+ = 368$.

Elemental analysis:	calcd.: C 62.92	H 10.85	N 4.08
$\text{C}_{18}\text{H}_{37}\text{NO}_3\text{Si}$	found: C 62.80	H 10.88	N 3.99.

4 Lithiation and Electrophilic Substitution of **1b**

4.1 (+)-(1*E*,3*S*)-3-Methoxycarbonyl-3-phenyl-1-trimethylsilyl-1-propenyl *N,N*-Diisopropylcarbamate (*ent*-**9d**)

To a stirred solution of (–)-sparteine (1.5 mmol, 352 mg) in toluene (2 ml) was added *n*-butyllithium (1.6 M in hexane, 1.5 mmol, 0.94 ml) at -78°C . After 10 min (*E*)-3-phenyl-1-trimethylsilyl-1-propenyl *N,N*-diisopropylcarbamate (**1b**) (0.5 mmol, 167 mg) was added dropwise and the clear yellow solution was stirred for 1 hour. A solution of methyl chloroformate (1.5 mmol, 142 mg) in toluene (0.5 ml) was added dropwise over 10 min. The mixture became colourless within 2 h and was quenched with a mixture of glacial acid (0.05 ml) and methanol (0.3 ml). After warming to r.t. and dilution of the organic phase with diethyl ether it was dried with MgSO_4 and the solvent was removed in vacuo. Purification by column chromatography (pentane/diethyl ether 6:1) furnished (+)-(1*E*, 3*S*)-3-methoxycarbonyl-3-phenyl-1-trimethylsilyl-1-propenyl *N,N*-diisopropylcarbamate (*ent*-**9d**) (141 mg, 72%).

$t_R = 17.57$ min; $R_f = 0.27$ (pentane/diethyl ether = 4:1).

$[\alpha]_D^{20} = +76$ ($c = 0.77$ in CHCl_3 ; $\geq 95\%$ *ee*).

^1H NMR shift-experiment: 20 mol% $\text{Eu}(\text{hfc})_3$ in CDCl_3 , $\Delta\delta$ (CH_3Si) = 0.01 ppm (major enantiomer: $\delta = 0.23$ ppm, minor enantiomer: $\delta = 0.24$ ppm); $\Delta\delta$ (5-H) = 0.02 ppm (major enantiomer: $\delta = 3.82$ ppm, minor enantiomer: $\delta = 3.84$ ppm).

^1H NMR (300 MHz, CDCl_3): δ/ppm = -0.01 (s, 9H, CH_3Si); 1.01-1.05 (m, 12H, $\text{CH}_3(\text{Cb})$); 3.50 (s, 3H, 5-H); 3.70 (bs, 2H, $\text{CH}(\text{Cb})$); 4.58 (d, 1H, 3-H); 5.66 (d, 1H, 2-H); 7.05-7.13 (m, 5H, aryl-H).

$^3J_{2,3}$ = 8.8 Hz.

^{13}C NMR (75 MHz, CDCl_3): δ/ppm = -0.6 (CH_3Si); 20.4 [21.4] ($\text{CH}_3(\text{Cb})$); 46.3 ($\text{CH}(\text{Cb})$); 48.2 (C-3); 52.1 (C-5); 125.0 (C-2); 127.1/127.8/128.6 (CH-aryl); 138.6 (Cq-aryl); 153.2 (OCON^*); 157.1(C-1)*; 172.7 (C-4).

IR (neat): $\tilde{\nu}/\text{cm}^{-1}$ = 2971, 2899, 1744, 1698, 1471, 1457, 1438, 1370, 1245, 1214, 1193, 1161, 1134, 1073, 1060, 1044, 839, 773, 730, 701.

MS (ESI) (m/z): $[\text{M}+\text{Na}]^+ = 414.3$.

Elemental analysis:	calcd.: C 64.41	H 8.49	N 3.58
$\text{C}_{21}\text{H}_{33}\text{NO}_4\text{Si}$	found: C 64.54	H 8.68	N 3.49.

4.2 (–)-(1*E*,3*R*,4*R*)-4-Hydroxy-5-methyl-3-phenyl-1-trimethylsilyl-1-hexenyl *N,N*-Diisopropylcarbamate (*anti*-11*b*)

(*E*)-3-Phenyl-1-trimethylsilyl-1-propenyl *N,N*-diisopropylcarbamate (**1b**) (0.5 mmol, 167 mg) was lithiated as described above (4.1). After titration with a solution of $\text{ClTi}(\text{NEt}_2)_3$ (0.75 mmol, 225 mg) in toluene (0.5 ml) for 30 min, the red-brown coloured intermediate was trapped with a solution of 2-methylpropanal (2.0 mmol, 144 mg) in toluene (0.5 ml). Within 2 h the solution became orange. The reaction was stopped by the addition of methanol (0.5 ml) and glacial acid (0.1 ml) at -78°C . The mixture was warmed to r.t. and was poured into 2N aq. HCl (10 ml). The aqueous phase was extracted with diethyl ether (3×10 ml) and the ethereal extracts were dried with MgSO_4 and the solvent was removed in vacuo. Purification of the crude product by chromatography (cyclohexane/ethyl acetate 10:1) afforded (–)-(1*E*,3*R*,4*R*)-4-hydroxy-5-methyl-3-phenyl-1-trimethylsilyl-1-hexenyl *N,N*-diisopropylcarbamate (*anti*-**11b**) as a colourless oil (193 mg, 95%).

t_R = 18.12 min; R_f = 0.45 (ether/pentane = 1:1).

$[\alpha]_D^{20} = -162$ ($c = 0.78$ in CHCl_3 ; 94% *ee*).

Chiral HPLC (chiral stationary phase: CHIRA-Grom-2, GROM Analytic + HPLC GmbH, Herrenberg, Germany): isopropanol/hexane = 1:1000; 0.3 ml/min; major enantiomer: t_{R1} = 10.13 min and minor enantiomer: t_{R2} = 9.01 min.

^1H NMR (300 MHz, CDCl_3): δ/ppm = 0.00 (s, 9H, CH_3Si); 0.69/0.78 (d, 6H, 6-H); 1.11-1.20 (m, 12H, $\text{CH}_3(\text{Cb})$); 1.31 (m_c , 1H, 5-H); 3.17 (m, 1H, OH); 3.47-3.53 (m, 1H, 3-H); 3.68 (dd, 1H, 4-H); 3.78 [3.94] (m, 2H, $\text{CH}(\text{Cb})$); 5.69 (d, 1H, 2-H); 7.04-7.19 (m, 5H, aryl-H).

$^3J_{2,3} = 10.5$ Hz; $^3J_{3,4} = 9.6$ Hz; $^3J_{4,5} = 9.6$ Hz; $^3J_{5,6} = 6.7$ Hz.

^{13}C NMR (75 MHz, CDCl_3): δ/ppm = -1.5 (CH_3Si); 14.7/20.4 (C-6); 20.3[21.6] ($\text{CH}_3(\text{Cb})$); 29.7 (C-5); 46.3 (C-3); 45.9[46.7] ($\text{CH}(\text{Cb})$); 78.8 (C-4); 126.5/127.9/128.7 (CH-aryl); 131.8 (C-2); 141.7 (Cq-aryl); 154.4 (OCON^*); 156.2 (C-1)*.

IR (neat): $\tilde{\nu} / \text{cm}^{-1} = 3273, 2826, 1620, 1385, 1324, 1272, 1236, 1201, 1170, 1102, 1014, 969, 813, 728, 675, 643.$

MS (ESI) (m/z): $[\text{M}+\text{H}]^+ = 406.4; [\text{M}+\text{Na}]^+ = 428.4.$

Elemental analysis:	calcd.: C 68.10	H 9.69	N 3.45
$\text{C}_{23}\text{H}_{39}\text{NO}_3\text{Si}$	found: C 67.81	H 9.40	N 3.33.

5 ^1H NMR spectra for important compounds

5.1 (+)-(1*E*, 3*S*)-1,3-Bis(trimethylsilyl)-1-butenyl *N,N*-Diisopropylcarbamate (**4a**)

5.2 (-)-(1*E*, 3*S*, 4*R*)-4-Hydroxy-3,5-dimethyl-1-trimethylsilyl-1-hexenyl *N,N*-Diisopropylcarbamate (*anti*-**6b**)

5.3 (+)-(1*E*,3*S*)-3-Methoxycarbonyl-3-phenyl-1-trimethylsilyl-1-propenyl *N,N*-Diisopropylcarbamate (*ent*-9d)

5.4 (–)-(1*E*,3*R*,4*R*)-4-Hydroxy-5-methyl-3-phenyl-1-trimethylsilyl-1-hexenyl *N,N*-Diisopropylcarbamate (*anti*-11b)