SUPPORTING INFORMATION

Stereoselective Intermolecular Carboazidation of Chiral Allylsilanes

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REPRESENTATIVE PROCEDURE FOR PREPARATION OF β -HYDROXYALLYLSILANE.

4-[Dimethyl(phenyl)silyl]-2-methyl-hex-5-en-3-ol 4: To a solution of allyl(dimethyl)phenyl-

silane (1.00 g, 5.68 mmol) in dry THF (10 mL) was added a 2.5 M solution of *n*-butyllithium in hexane (2.5 mL, 6.25 mmol) followed by TMEDA (1.41 mL, 9.37 mmol) at 0 °C. The resulting pale-yellow solution was stirred at 0°C for 2 h, turning reddish brown, then cooled to -78°C. Titanium tetraisopropoxide (1.68 mL, 5.68 mmol) was added at -78°C and the mixture was stirred for 1h at this temperature. Finally, a solution of isobutyraldehyde (0.46 mL, 5.11 mmol) was added at -78°C, and the reaction mixture was then stirred for 2h. The reaction was hydrolyzed with an aqueous solution of NH_4Cl at -78°C. The organic layer was decanted and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O , dried over MgSO_4 and the solvents were removed under reduced pressure. The residue was purified by chromatography (petroleum ether/EtOAc 98:2) to afford a colorless oil (971 mg, 77%). IR (neat) 3582-3490 (OH), 3070-2872 (CH), 1623 (C=C), 1247 (SiMe), 1112 (SiPh) cm^{-1} . ^1H NMR (CDCl_3) δ 7.60-7.30 (m, 5H, aromatic H), 5.86 (ddd, J = 17.0, 10.7, 10.0 Hz, 1H, $\text{CH}=\text{CH}_2$), 5.03 (dd, J = 10.0, 2.1 Hz, 1H, $\text{CH}=\text{CH}_2$, *cis*), 4.88 (dd, J = 17.0, 2.1 Hz, 1H, $\text{CH}=\text{CH}_2$, *trans*), 3.30 (m, 1H, CHOH), 2.09 (dd, J = 10.7, 3.7 Hz, 1H, CHSi), 1.65 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.42 (d, J = 4.9 Hz, 1H, OH), 0.87 (d, J = 6.4 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.79 (d, J = 6.7 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.36 (s, 3H, SiCH_3), 0.33 (s, 3H, SiCH_3). ^{13}C NMR (CDCl_3) δ 138.0 (aromatic C_q), 134.8 ($\text{CH}=\text{CH}_2$), 134.1 (aromatic CH), 129.0 (aromatic CH), 127.7 (aromatic CH), 114.9 ($\text{CH}_2=\text{CH}$), 77.2 (CHOH), 39.6 (CH), 32.9 (CH), 18.9 ($\text{CH}(\text{CH}_3)_2$), 18.5 ($\text{CH}(\text{CH}_3)_2$), -3.6 (SiCH_3), -3.9 (SiCH_3). MS; m/z (%) : 271 ($[\text{M}+\text{Na}]^+$), 205 (18) (M^+-iPr), 135 (100) (Me_2PhSi^+). HRMS : exp. 271.1499, calc. 271.1494. PPM Error : 1.8.

REPRESENTATIVE PROCEDURE FOR PREPARATION OF γ -HYDROXYALLYLSILANE.

3-[Dimethyl(phenyl)silyl]-1-phenylpent-4-en-1-ol 6: To a solution of allyl(dimethyl)phenyl-

silane (0.60 g, 3.4 mmol) in dry THF (8.5 mL) was added a 2.5 M solution of *n*-butyllithium in hexane (1.5 mL, 3.74 mmol) at 0°C, followed by TMEDA (0.85 mL, 5.61 mmol). The resulting pale-yellow solution was stirred at 0°C for 2 h, turning reddish brown, then cooled to -78 °C. Styrene oxide (0.41 mL, 3.57 mmol) was added, and the mixture was stirred for 2h at -40°C. The reaction was hydrolyzed with an aqueous solution of NH_4Cl at -78°C. The organic layer was decanted and the aqueous layer extracted with ether. The combined organic layers were then washed with H_2O , dried over MgSO_4 and the solvents were removed under reduced pressure. The residue was purified by chromatography (petroleum ether/EtOAc 92:8) to afford the less polar diastereomer as a yellow oil (152 mg, 15%) and an inseparable mixture of the other diastereomers contaminated by the γ -isomer. (less polar) IR (neat) 3424 (OH), 3069-2906 (CH), 1624 ($\text{CH}_2=\text{CH}$), 1248 (SiMe), 1114 (SiPh) cm^{-1} . ^1H NMR (CDCl_3) δ 7.49-7.24 (m, 10H, aromatic H), 5.69 (ddd, J = 17.0, 10.4, 9.7 Hz, 1H, $\text{CH}=\text{CH}_2$), 5.02 (dd, J = 10.4, 1.8 Hz, 1H, $\text{CH}=\text{CH}_2$, *cis*), 4.95 (dd, J = 17.0, 1.8 Hz, 1H, $\text{CH}=\text{CH}_2$, *trans*), 4.71 (dt, J = 9.1, 4.0 Hz, 1H, CHOH), 2.23 (m, 1H, CHSi), 1.83 (d, J = 4.0 Hz, 1H, OH), 1.80-1.67 (m, 2H, CH_2), 0.29 (s, 3H, CH_3Si), 0.28 (s, 3H, CH_3Si). ^{13}C NMR (CDCl_3) δ 145.7 (aromatic C_q), 139.3 (aromatic CH), 137.5 (aromatic C_q), 134.5 (aromatic CH), 129.5 (aromatic CH), 128.8 (aromatic CH), 128.1 (aromatic CH), 127.6 (aromatic CH), 125.9 ($\text{CH}=\text{CH}_2$), 114.1 ($\text{CH}=\text{CH}_2$), 72.6 (CHOH), 38.6 (CH_2), 31.0 (CHSi), -

4.2 (CH₃Si), -4.8 (CH₃Si). MS (LSIMS); m/z (%) : 279 (6) (M⁺ – OH), 145 (6), 135 (100) (Me₂PhSi⁺). HRMS : exp. 279.157556, calc. 279.156904. PPM Error : -2.3.

REPRESENTATIVE PROCEDURE FOR PREPARATION OF α -SUBSTITUTED ALLYLSILANE.

Dimethyl(1-methylpropenyl)phenylsilane 1: To a suspension of CuCN (955 mg, 10.67

mmol) in dry THF (79 mL) was added at -30°C under a nitrogen atmosphere, a 0.61 M solution of dimethyl(phenyl)silyl lithium in THF (35 mL, 21.35 mmol). The mixture was stirred for 1h at -30°C, and freshly distilled crotylchloride (0.94 mL, 9.6 mmol) was added at -78°C. The resulting mixture was then stirred for 1h at -78°C. The reaction mixture was quenched with a saturated solution of NH₄Cl

at -78°C, and the aqueous layer was extracted with ether. The combined extracts were washed with brine, dried over MgSO₄ and the solvent were evaporated in vacuo. The residue was purified by chromatography over silica gel with petroleum ether affording an inseparable 93:7 mixture of dimethyl(1-methylpropenyl)phenylsilane and but-2-en-1-yl(dimethyl)phenylsilane (1.271 g, 70%). All spectroscopic data (NMR, IR, MS) were in good agreement with those reported in the literature.¹

RADICAL CARBOAZIDATION

Caution: Sulfonyl azides are capable of exploding, it is strongly recommended to apply standard safety rules and to use a safety shield.

General procedure A. A solution of [(ethoxycarbonothioyl)thio]acetate (0.39 mmol), allylsilane (0.39 mmol), benzenesulfonylazide (192 mg, 1.05 mmol), (Bu₃Sn)₂ (0.27 mL, 0.52 mmol) and di-*tert*-butylhyponitrite (= DTBHN, 2.5 mg, 0.015mmol) was heated under reflux in dry benzene (1.5 mL). The reaction was monitored by TLC and further portions di-*tert*-butylhyponitrite (2.5 mg, 0.015 mmol) were added every 1.5 h. Upon completion, the solvent was removed under reduced pressure and the crude product was filtered through silica gel (petroleum ether, then petroleum ether/EtOAc 9:1), and the combined fractions were concentrated in vacuo. The residue was purified by chromatography (petroleum ether/EtOAc).

Ethyl 4-azido-5-[dimethyl(phenyl)silyl]-6-hydroxy-6-phenylhexanoate *syn*-10: Prepared

according to general procedure A from [(ethoxycarbonothioyl)thio]acetate (49.2 mg, 0.24 mmol), allylsilane **3** (164 mg, 0.52 mmol), benzenesulfonylazide (100 mg, 0.78 mmol), (Bu₃Sn)₂ (0.20 mL, 0.39 mmol) and DTBHN (5.3 mg, 0.03 mmol) added by 3% portion every 90 min, in dry benzene (0.52 mL). The two diastereoisomers (63:37) were separated by chromatography (Petroleum ether/EtOAc 95:5) to

afford yellow oil (70.7 mg, 71%). *syn*-**10**: IR (neat) 3426 (OH), 3068-2957, 2106 (CN₃), 1734 (CO₂Et), 1253 (SiMe), 1118 (SiPh) cm⁻¹. ¹H NMR (CDCl₃) δ 7.61-7.19 (m, 10H, aromatic H), 5.03 (m, J = 4.2 Hz, 1H, CHOH), 4.02 (q, J = 7.0 Hz, 2H, CH₂OOC), 3.69 (m, 1H, CHN₃), 2.43 (d, J = 4.2 Hz, 1H, OH), 2.09 (m, 2H, CH₂COO), 1.78 (m, 2H, CH₂CHN₃), 1.61 (m, 1H, CHSi), 1.19 (t, J = 7.0 Hz, 3H, CH₃CH₂O), 0.47 (s, 3H, CH₃Si), 0.38 (s, 3H, CH₃Si). ¹³C NMR (CDCl₃) δ 172.49 (C=O), 143.90 (aromatic C_q), 133.92 (aromatic CH), 133.01 (aromatic CH), 132.96 (aromatic CH), 129.63 (aromatic CH), 129.22 (aromatic CH), 128.37

(aromatic CH), 128.01 (aromatic CH), 127.89 (aromatic CH), 127.67 (aromatic CH), 127.29 (aromatic CH), 125.67 (aromatic CH), 72.94 (CHOH), 62.19 (CHN₃), 60.43 (CH₂O), 41.64 (CHSi), 31.44 (CH₂COOR), 30.57 (CH₂CHN₃), 14.12 (CH₃CH₂OOC), -1.80 (CH₃Si), -2.12 (CH₃Si). MS (LSIMS); m/z (%) : 435 (30) ([M+Na]⁺), 434 (100), 391 (10), 288 (20), 257 (7), 245 (12), 217 (30). HRMS : exp. 434.189919, calc. 434.187590. PPM Error : -5.4.

Ethyl 4-azido-5-[dimethyl(phenyl)silyl]-6-hydroxy-7-methyloctanoate *syn-11*: Prepared

according to general procedure A from [(ethoxycarbonothioyl)thio]acetate (79 mg, 0.38 mmol), allylsilane **4** (177.8 mg, 0.72 mmol), benzenesulfonylazide (203 mg, 1.11 mmol), (Bu₃Sn)₂ (0.27 mL, 0.54 mmol) and DTBHN (10 mg, 0.06 mmol) in dry benzene (1 mL). The crude was purified by chromatography (pentane/EtOAc 98:2)

to afford the two diastereomer (>90:10) as a colorless oil (major diastereomer *syn-11* : 42 mg, 40%). IR (neat) 3533 (OH), 2960 (CH), 2108 (CN₃), 1732 (CO₂Et), 1252 (SiMe), 1111 (SiPh) cm⁻¹. ¹H NMR (CDCl₃) δ 7.70-7.30 (m, 5H, aromatic H), 4.12 (q, J = 7.0 Hz, 2H, CH₂OOC), 3.91 (ddd, J = 9.8, 5.2, 1.5 Hz, 1H, CHN₃), 3.46 (m, 1H, CHOH), 2.33 (m, 2H, CH₂COO), 1.78 (m, 4H, CH₂CHN₃, CHSi, CH(CH₃)₂), 1.47 (m, 1H, OH), 1.25 (t, J = 7.0 Hz, 3H, CH₃CH₂O), 0.88 (d, J = 6.4 Hz, 3H, CH(CH₃)₂), 0.78 (d, J = 6.7 Hz, 3H, CH(CH₃)₂), 0.47 (s, 3H, CH₃Si), 0.44 (s, 3H, CH₃Si). ¹³C NMR (CDCl₃) δ 172.77 (C=O), 138.50 (aromatic C_q), 133.96 (aromatic CH), 129.69 (aromatic CH), 129.14 (aromatic CH), 127.98 (aromatic CH), 127.48 (aromatic CH), 76.19 (CHOH), 62.50 (CHN₃), 60.53 (CH₂OOC), 36.29 (CH), 32.41 (CH), 31.68 (CH₂), 31.19 (CH₂), 19.79 (CH(CH₃)₂), 18.26 (CH(CH₃)₂), 14.19 (CH₃CH₂O), -1.71 (CH₃Si), -2.33 (CH₃Si). MS (LSIMS); m/z (%) : 400 (100) ([M+Na]⁺), 360 (9), 329 (31), 288 (40), 248 (13). HRMS : exp. 400.205277, calc. 400.203240. PPM Error : -5.1.

Ethyl 4-azido-6-hydroxy-6-phenyl-5-triphenylsilylhexanoate *syn-12*: Prepared according

to general procedure A from [(ethoxycarbonothioyl)thio]acetate (80 mg, 0.38 mmol), allylsilane **5** (333 mg, 0.82 mmol), benzenesulfonylazide (208 mg, 1.14 mmol), (Bu₃Sn)₂ (0.29 mL, 0.57 mmol) and DTBHN (12 mg, 0.06 mmol) in dry benzene (2 mL). The crude was purified by chromatography (petroleum ether/EtOAc 95:5) to

afford a brown oil (major diastereomer *syn-12* : 60 mg, 29%). IR (neat) 3486 (OH), 3069-2871 (CH), 2106 (CN₃), 1732 (CO₂Et), 1106 (SiPh), 701 cm⁻¹. ¹H NMR (CDCl₃) δ 7.80-7.60 (m, 8H, aromatic H), 7.50-7.20 (m, 12H, aromatic H), 5.24 (m, 1H, CHOH), 3.92 (m, 3H, CH₂OOC, CHN₃), 2.29 (dd, J = 3.9, 1.8 Hz, 1H, CHSi), 2.08 (m, 1H, OH), 1.97 (t, J = 7.3 Hz, 2H, CH₂COO), 1.51 (m, 2H, CH₂CHN₃), 1.12 (t, J = 7.0 Hz, 3H, CH₃CH₂OOC). ¹³C NMR (CDCl₃) δ 172.44 (C=O), 144.35 (aromatic C_q), 136.56 (aromatic CH), 136.33 (aromatic CH), 136.22 (aromatic CH), 134.95 (aromatic CH), 134.52 (aromatic C_q), 130.01 (aromatic CH), 129.69 (aromatic CH), 129.51 (aromatic CH), 128.42 (aromatic CH), 127.91 (aromatic CH), 127.78 (aromatic CH), 127.14 (aromatic CH), 125.09 (aromatic CH), 71.61 (CH), 61.18 (CH), 60.29 (CH₂OOC), 41.96 (CHSi), 31.92 (CH₂), 31.21 (CH₂), 14.10 (CH₃CH₂O). MS; m/z (%) : 558 (100) ([M+Na]⁺), 518 (37) ([M⁺-OH]⁺), 493 (33) ([M⁺-N₃]⁺), 277 (34) ([M⁺-Ph₃Si]⁺), 259 (72) (Ph₃Si⁺). HRMS : exp. 558.2180, calc. 558.2188. PPM Error : -1.6.

Ethyl 4-azido-5-[dimethyl(phenyl)silyl]-7-hydroxy-7-phenyl-heptanoate *syn/anti*-13:

Prepared according to general procedure A from [(ethoxycarbonothioyl)thio]acetate (173.2 mg, 0.83 mmol), allylsilane **6** (474 mg, 1.60 mmol), benzenesulfonylazide (468.2 mg, 2.54 mmol), $(\text{Bu}_3\text{Sn})_2$ (0.61 mL, 1.20 mmol) and DTBHN (25 mg, 0.14 mmol) added by 3% portion every 1.5h. The residue was purified by chromatography (petroleum ether/EtOAc 95:5) to afford an inseparable 80:20 mixture of the two diastereomer as a colorless oil (255 mg, 70%). IR (neat) 3406 (OH), 2961-2872 (CH), 2099 (CHN_3), 1716 (CO_2Et), 1253 (SiMe), 1112 (SiPh), 702 cm^{-1} . ^1H NMR (CDCl_3) δ 7.55-7.20 (m, 10H, aromatic H), 4.77 (m, 1H, CHOH , *maj.*), 4.62 (m, 1H, CHOH , *min.*), 4.13 (q, $J = 7.0$ Hz, 2H, CH_2OOC , *maj.*), 3.70 (m, 1H, CHN_3 , *maj.*), 3.59 (m, 1H, CHN_3 , *min.*), 2.46-2.20 (m, 4H, *maj.* + *min.*), 2.10 (d, $J = 4.0$ Hz, 1H, OH), 1.90-1.64 (m, 10H, CH_2CHN_3 , CHSi , CH_2CHSi , *maj.* + *min.*), 1.25 (t, $J = 7.0$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{O}$, *maj.*), 1.24 (t, $J = 7.0$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{O}$, *min.*), 0.42 (s, 3H, CH_3Si , *min.*), 0.40 (s, 6H, CH_3Si , *maj.* + *min.*), 0.39 (s, 3H, CH_3Si , *maj.*). ^{13}C NMR (CDCl_3) δ 172.6 (C=O), 144.4 (aromatic C_q , *maj.*), 137.4 (aromatic C_q , *maj.*), 133.7 (aromatic CH, *maj.*), 129.0 (aromatic CH, *maj.*), 128.3 (aromatic CH, *maj.*), 127.7 (aromatic CH, *maj.*), 127.3 (aromatic CH, *maj.*), 125.5 (aromatic CH, *maj.*), 72.5 (CH, *maj.*), 64.9 (CH, *maj.*), 60.4 (CH_2OOC , *maj.*), 36.0 (CH_2 , *maj.*), 31.5 (CH_2 , *maj.*), 28.4 (CH_2 , *maj.*), 27.6 (CHSi , *maj.*), 14.2 ($\text{CH}_3\text{CH}_2\text{O}$, *maj.*), -3.03 (CH_3Si , *maj.*), -3.39 (CH_3Si , *maj.*). MS; m/z (%) : 448 (6) ($[\text{M}+\text{Na}]^+$), 383 (89) ($[\text{M}^+-\text{N}_3^-]$), 380 (100). HRMS : exp. 448.2043, calc. 448.2032. PPM Error : 2.4.

Ethyl 4-azido-7-hydroxy-7-phenyl-5-triphenylsilylheptanoate *syn*-14:

Prepared according to general procedure A from [(ethoxycarbonothioyl)thio]acetate (70 mg, 0.34 mmol), allylsilane **7** (286 mg, 0.68 mmol), benzenesulfonylazide (179 mg, 1.02 mmol), $(\text{Bu}_3\text{Sn})_2$ (0.26 mL, 0.51 mmol) and DTBHN (12 mg, 0.06 mmol) added by 3% portion every 90min. The crude was purified by chromatography (petroleum ether/EtOAc 95:5) to afford a brown oil (major diastereomer ***syn*-14** : 56 mg, 30%). IR (neat) 3498 (OH), 3069-2850 (CH), 2100 (CHN_3), 1732 (CO_2Et), 1107 (SiPh), 701 cm^{-1} . ^1H NMR (CDCl_3) δ 7.70-7.20 (m, 20H, aromatic H), 4.91 (m, 1H, CHOH), 4.05 (q, $J = 7.0$ Hz, 2H, CH_2OOC), 4.00 (m, 1H, CHN_3), 2.74 (dt, $J = 11.0, 2.4$ Hz, 2H, CHSi), 2.40-2.10 (m, 4H), 1.94 (m, 1H), 1.7-1.5 (m, 2H), 1.20 (t, $J = 7.0$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{O}$). ^{13}C NMR (CDCl_3) δ 172.7 (C=O), 144.9 (aromatic C_q), 136.0 (aromatic CH), 133.6 (aromatic C_q), 129.6 (aromatic CH), 128.5 (aromatic CH), 128 (aromatic CH), 127.4 (aromatic CH), 125.6 (aromatic CH), 72.8 (CH), 64.6 (CH), 60.4 (CH_2OOC), 36.5 (CH_2), 31.9 (CH_2), 28.4 (CH_2), 25.7 (CHSi), 14.1 ($\text{CH}_3\text{CH}_2\text{O}$). MS (LSIMS); m/z (%) : 572 (27) ($[\text{M}+\text{Na}]^+$), 530 (5), 507 (15) ($[\text{M}-\text{N}_3]^+$), 329 (66), 307 (43), 259 (100) (Ph_3Si^+). HRMS : exp. 572.231409, calc. 572.234540. PPM Error : 5.5.

Ethyl 4-azido-5-[dimethyl(phenyl)silyl]hexanoate *syn/anti*-8:

Prepared according to general procedure A from [(ethoxycarbonothioyl)thio]acetate (91.5 mg, 0.44 mmol), allylsilane **1** (334 mg, 0.88 mmol), benzenesulfonylazide (241 mg, 1.32 mmol), $(\text{Bu}_3\text{Sn})_2$ (0.33 mL, 0.65 mmol) and DTBHN (13 mg, 0.06 mmol) in dry benzene (1.5 mL). The crude was purified by chromatography

(petroleum ether/EtOAc 98:2) to afford the two diastereomer (73:27) as a colorless oil (90.3mg, 64%). IR (neat) 3069-2874 (CH), 2097 (CHN₃), 1734 (CO₂Et), 1251 (SiMe), 1112 (SiPh), 702 cm⁻¹. ¹H NMR (CDCl₃) δ 7.60-7.30 (m, 10H, aromatic H, *maj.* + *min.*), 4.11 (q, *J* = 7.0 Hz, 2H, CH₂OOC, *maj.*), 4.10 (q, *J* = 7.0 Hz, 2H, CH₂OOC, *min.*), 3.45 (m, 1H, CHN₃, *maj.*), 3.35 (m, 1H, CHN₃, *min.*), 2.41-2.26 (m, 4H, CH₂COO, *maj.* + *min.*), 1.80-1.60 (m, 4H, CH₂CHN₃, *maj.* + *min.*), 1.43-1.35 (m, 2H, CHSi, *maj.* + *min.*), 1.25 (t, *J* = 7.0 Hz, 3H, CH₃CH₂O, *maj.*), 1.23 (t, *J* = 7.0 Hz, 3H, CH₃CH₂O, *min.*), 1.02 (d, *J* = 7.3 Hz, 6H, CH₃CHSi, *maj.* + *min.*), 0.38 (s, 6H, CH₃Si, *maj.*), 0.34 (s, 6H, CH₃Si, *min.*). ¹³C NMR (CDCl₃) δ 172.9 (C=O, *maj.*), 137.4 (aromatic C_q, *maj.*), 133.8 (aromatic CH, *maj.*), 129.1 (aromatic CH, *maj.*), 127.8 (aromatic CH, *maj.*), 65.4 (CHN₃, *maj.*), 60.5 (CH₂OOC, *maj.*), 31.2 (CH₂, *maj.*), 28.6 (CH₂, *min.*), 27.4 (CH₂, *maj.*), 25.5 (CHSi, *maj.*), 25.2 (CHSi, *min.*), 14.1 (CH₃CH₂O, *maj.*), 10.4 (CH₃CHSi, *maj.*), 9.6 (CH₃CHSi, *min.*), -3.8 (CH₃Si, *maj.*), -3.9 (CH₃Si, *maj.*), -4.4 (CH₃Si, *min.*). MS; *m/z* (%) : 342 (100) ([M+Na]⁺), 277 (74) ([M-N₃]⁺), 135 (80) (PhMe₂Si⁺). HRMS : exp. 342.1613, calc. 342.1613. PPM Error : 0.1.

Ethyl 4-azido-5-[dimethyl(phenyl)silyl]-5-phenylpentanoate *syn/anti*-9: Prepared

according to general procedure A from [(ethoxycarbonothioyl)thio]acetate (70.2 mg, 0.34 mmol), allylsilane **2** (161 mg, 0.64 mmol), benzenesulfonylazide (199 mg, 1.09 mmol), (Bu₃Sn)₂ (0.25 mL, 0.49 mmol) and DTBHN (10 mg, 0.06 mmol) in dry benzene (0.6 mL). The crude product was purified by chromatography (petroleum

ether/EtOAc 95:5) to afford an inseparable mixture of the two diastereomer (80:20) as a colorless oil (74.4 mg, 55%). IR (neat) 3069-2958 (CH), 2099 (CN₃), 1733 (CO₂Et), 1250 (SiMe), 1112 (SiPh), 702 cm⁻¹. ¹H NMR (CDCl₃) δ 7.50-7.00 (m, 20H, aromatic H, *maj.* + *min.*), 4.08 (q, *J* = 7.0 Hz, 2H, CH₂OOC, *maj.*), 4.06 (q, *J* = 7.0 Hz, 2H, CH₂OOC, *min.*), 3.77 (ddd, *J* = 8.5, 7.3, 7.0 Hz, 1H, CHN₃, *maj.*), 3.61 (m, 1H, CHN₃, *min.*), 2.47 (d, *J* = 7.3 Hz, 1H, CHSi, *maj.*), 2.42 (d, *J* = 10.7 Hz, 1H, CHSi, *min.*), 2.30 (t, *J* = 7.6 Hz, 2H, CH₂COO, *maj.*), 2.29 (t, *J* = 7.0 Hz, 2H, CH₂COO, *min.*), 1.93-1.62 (m, 4H, CH₂CHN₃, *maj.* + *min.*), 1.21 (t, *J* = 7.0 Hz, 3H, CH₃CH₂O, *maj.*), 1.20 (t, *J* = 7.0 Hz, 3H, CH₃CH₂O, *min.*). ¹³C NMR (CDCl₃) δ 172.6 (C=O, *maj.*), 139.2 (aromatic C_q, *maj.*), 137.2 (aromatic C_q), 133.9 (aromatic CH, *maj.*), 129.3 (aromatic CH, *maj.*), 129.1 (aromatic CH, *maj.*), 128.3 (aromatic CH, *maj.*), 127.9 (aromatic CH, *maj.*), 126.7 (aromatic CH, *maj.*), 64.0 (CHN₃, *maj.*), 60.5 (CH₂OOC, *maj.*), 42.5 (CHSi, *min.*), 42.0 (CHSi, *maj.*), 30.9 (CH₂, *maj.*), 30.6 (CH₂, *min.*), 29.5 (CH₂, *maj.*), 29.1 (CH₂, *min.*), 14.1 (CH₃CH₂O, *maj.*), 13.7 (CH₃CH₂O, *min.*), -2.4 (CH₃Si, *min.*), -2.6 (CH₃Si, *maj.*), -3.9 (CH₃Si, *min.*), -3.9 (CH₃Si, *maj.*), -4.6 (CH₃Si, *maj.*). MS; *m/z* (%) : 404 (8) ([M+Na]⁺), 339 (100) ([M-N₃]⁺). HRMS : exp. 404.1748, calc. 404.1770. PPM Error : -5.5.

REPRESENTATIVE PROCEDURE FOR THE β-ANTI-STEROSPECIFIC ELIMINATION.

6-Hydroxy-hept-4-enoic acid ethyl ester **15:** To a solution of silylazide *syn*-**10** (62.3 mg,

0.151 mmol) was added 1M solution of TBAF in THF (0.16 mL, 0.16 mmol). The mixture was stirred at rt for 1 h under nitrogen atmosphere and the reaction concentrated under vacuum. The residue was purified by chromatography (petroleum ether/AcOEt 8:2) to afford a yellow oil (14.1 mg, 40%). IR (neat) 3430 (OH), 2959-2850, 1732 (CO₂Et), 700 cm⁻¹. ¹H NMR (C₆D₆) δ 7.50-7.00

(m, 5H, aromatic H), 5.68 (m, 1H, ethylenic H), 5.56 (m, $J = 9$ Hz, 1H, CHOH), 5.20 (m, 1H, ethylenic H), 3.86 (q, $J = 7.3$ Hz, 2H, CH₂OOC), 2.60-2.00 (m, 5H, CH₂CH₂, OH), 0.90 (t, $J = 7.3$ Hz, 3H, CH₃CH₂O). ¹³C NMR (C₆D₆) δ 172.72 (C=O), 144.27 (aromatic C_q), 134.79 (CH=CH), 128.99 (CH=CH), 128.34 (aromatic CH), 127.08 (aromatic CH), 126.13 (aromatic CH), 68.99 (CHOH), 60.21 (CH₂O), 33.45 (CH₂COO), 22.84 (CH₂CH=), 14.03 (CH₃CH₂O). MS; m/z (%) 257 (43) ([M+Na]⁺), 234 (10) ([M]⁺), 217 (100). HRMS : exp. 257.115036, calc. 257.115364. PPM Error : 1.3.

7-Methyl-oct-4-enoic acid ethyl ester 16: According to the precedent procedure from

silylazide **syn-11** (64.6 mg, 0.17 mmol), TBAF (0.19 mL, 0.19 mmol). The residue was purified by chromatography (petroleum ether/EtOAc 8:2) to afford an oil ($m = 28.2$ mg, 83%). IR (neat) 3416 (OH), 2959-2848 (CH), 1736 (CO₂Et) cm⁻¹. ¹H NMR (CDCl₃) δ 5.49-5.45 (m, 2H, ethylenic H), 4.17 (m, 1H, CHOH), 4.12 (q, $J = 7.3$ Hz, 2H, CH₂OOC), 2.62-2.48 (m, 1H), 2.45-2.36 (m, 2H, CH₂), 2.33-2.21 (m, 1H), 1.69 (m, 1H, CH(CH₃)₂), 1.25 (t, $J = 7.3$ Hz, 3H, CH₃CH₂O), 0.97 (d, $J = 6.7$ Hz, 3H, CH(CH₃)₂), 0.86 (d, $J = 6.7$ Hz, 3H, CH(CH₃)₂). ¹³C NMR (CDCl₃) δ 173.07 (C=O), 132.49 (CH=CH), 130.20 (CH=CH), 72.07 (CHOH), 60.46 (CH₂OOC), 33.76 (CH₂COO), 33.70 (CH(CH₃)₂), 22.98 (CH₂CH=), 18.29 (CH(CH₃)₂), 18.11 (CH(CH₃)₂), 14.17 (CH₃CH₂O). MS; 223.12 ([M+Na]⁺), 183.13 ([M⁺-OH]⁻). HRMS : exp. 223.1316 calc. 223.1310. PPM Error : 2.6.

¹ Fleming, I.; Waterson, D. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1809.