Supplementary Materials

The unusual course of the reaction of allyl phosphine oxides with the Grundmann ketone

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General Methods and Materials:

Optical rotations were measured in chloroform using a Perkin-Elmer 241 polarimeter at 24 °C. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrum 2000 spectrophotometer in KBr or CHCl₃. Ultraviolet spectra were obtained on a Perkin-Elmer Lambda 3B UV-VIS spectrophotometer in 100% ethanol (EtOH). The ¹H and ¹³C nuclear magnetic resonance spectra were taken on a Varian Unity plus 200 MHz, Bruker DMX 500, and Varian 700 Active Shield spectrometers in deuteriochloroform. Chemical shifts are reported downfield to Me₄Si (δ 0.00) as an internal standard. COSY, HMQC spectra and spin decoupling experiments NOE, DEPT 90 and DEPT 135 were used to assign particular signals in ¹H NMR and ¹³C NMR spectra. To describe the signals in ¹H NMR spectra, the following abbreviations were used: s - singlet, d - doublet, t - triplet, q - quartet, b - broad, narr. – narrow, w/2 = half-width. High resolution mass spectra were recorded on LCT (TOF) or Mass Quattro LC spectrometers. Flash column chromatography was performed using Merck Silica Gel 60 (230-400 mesh). High-performance liquid chromatography (HPLC) was performed on a Waters Associates liquid chromatograph equipped with a Model 486 tunable absorbance detector or Shimadzu UFLS liquid chromatograph equipped with SPD-20A tunable absorbance detector.

All reactions involving oxygen- or moisture-sensitive compounds were carried out under dry argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon, whereas diethyl ether (Et₂O), dichloromethane (CH₂Cl₂) and toluene were distilled from P₂O₅.

Experimental Procedure and Product Characterization:

2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexylidene]-propionaldehyde (13). [α]²⁴_D +22° (*c* 1.52, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 0.049 and 0.063 (6H and 6H, each s, 4 × SiCH₃), 0.847 and 0.868 (9H and 9H, each s, 2 × Si-*t*-Bu), 1.72 – 1.94 (2H, m, 4'-H₂), 1.80 (3H, s, CH₃) 2.40 (1H, dd, *J* = 13.2, 7.4 Hz, 6'β-H), 2.58 (1H, dd, *J* = 13.2, 3.6 Hz, 6'α-H), 2.73 (1H, dd, *J* = 13.4, 7.0 Hz, 2'α-H), 2.83 (1H, dd, *J* = 13.4, 3.4 Hz, 2'β-H) 4.17 (2H, m, 3'β- and 5'α-H), 10.15 (1H, s, CHO); ¹³C NMR (50 MHz) δ -4.79, -4.76, -4.70 and -4.68 (4 × SiCH₃), 11.04 (CH₃) 18.17 and 18.22 [SiC(CH₃)₃], 25.89 and 25.91 [SiC(CH₃)₃], 37.32 (C-6'), 41.66 (C-2'), 43.64 (C-4'), 68.17 and 68.25 (C-3' and C-5'), 133.60 (=CCHO), 155.88 (C-1'), 190.75 (=CCHO); HRMS (ESI) exact mass calculated for C₂₁H₄₂O₃Si₂Na (M + Na)⁺ 421.2570, measured 421.2549.

2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexylidene]propan-1-ol

(14). [α]²⁴_D +8.5° (*c* 1.37, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 0.057 and 0.071 (3H and 9H, each s, 4 $\times$ SiCH₃), 0.884 (9H and 9H, each s, 2 $\times$ Si-*t*-Bu), 1.56 – 1.70 (2H, br m, 4'-H₂), 1.83 (3H, s, CH₃), 1.98 (1H, dd, *J* = 12.7, 9.2 Hz, 6' β -H), 2.19 (1H, br d, *J* ~ 13.5 Hz, 2' β -H), 2.43 (1H, dd, *J* = 13.6, 5.4 Hz, 2' α -H), 2.29 (1H, dd, *J* = 12.7, 3.6 Hz, 6' α -H), 3.89 (1H, d, *J* = 11.4 Hz, one of CH₂OH), 3.93 (1H, tt, *J* ~ 9, 4 Hz, 5' α -H), 4.14 (1H, tt, *J* = 6.4, 3.2 Hz, 3' β -H), 4.21 (1H, d, *J* = 11.4 Hz, one of CH₂OH); ¹³C NMR (50 MHz) δ -4.65, -4.64, -4.61 and -4.54 (4 $\times$ SiCH₃), 17.48 (CH₃), 18.30 and 18.32 [SiC(CH₃)₃], 26.03 and 26.10 [SiC(CH₃)₃], 38.03 and 40.10 (C-2' and C-6'), 43.57 (C-4'), 63.68 (CH₂OH), 68.18 and 68.54 (C-3' and C-5'), 130.53 (C-1'), 131.17 (=CCH₂OH); HRMS (ESI) exact mass calculated for C₂₁H₄₄O₃Si₂Na (M + Na)⁺ 423.2727, measured 423.2721.

[2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexylidene]propyl]-

diphenyl-phosphine oxide (7). [α]²⁴_D +2.5° (*c* 1.39, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 0.002 and 0.015 (9H and 9H, each s, 4 $\times$ SiCH₃), 0.845 (18H, s, Si-*t*-Bu), 1.59 (2H, m), 1.68 (1H, m), 1.75 (3H, d, *J* = 3.2 Hz, 3-H₃), 1.80 (1H, m), 2.14 (1H, m), 2.26 (1H, m), 3.11 and 3.27 (1H and 1H, each t, *J* = 14.4 Hz, CH₂P), 3.86 and 3.95 (1H and 1H, each m, 3'- and 5'-H), 7.47 (6H, m, Ar-H), 7.72 (4H, m, Ar-H); ¹³C NMR (50 MHz; selected signals) δ -4.73, -4.71 and -4.57 (SiCH₃), 18.24 and 18.29 [SiC(CH₃)₃], 20.70 (d, *J* = 6.4 Hz, CH₃), 25.97 and 25.99 [SiC(CH₃)₃], 36.45, 38.89, 39.05 (d, *J* ~ 17 Hz, CH₂P), 43.55 (C-4'), 68.00 and 67.99 (C-3' and C-5'), 119.62 (d, *J* = 10.3 Hz, =CCH₂P), 128.61 and 128.63 (2 $\times$ d, *J* = 11.1 Hz, Ar-C_{ortho}), 131.18 and 131.28 (2 $\times$ d, *J* = 9.0 Hz, Ar-C_{meta}), 131.83 (d, *J* ~ 4.5 Hz, Ar-C_{para}), 131.94 (d, *J* ~ 10 Hz, C-1'); HRMS (ESI) exact mass calculated for C₃₃H₅₃O₃PSi₂Na (M + Na)⁺ 607.3169, measured 607.3192.

(1R,4R,7aR)-4-[(*E*)-2''-[(3'''R,5'''R)-3''',5'''-Bis[(*tert*-butyldimethylsilyl)oxy]-cyclo-hexyl]-3''-(diphenyl-phosphinoyl)-allyl]-1-[(*R*)-1',5'-dimethyl-5'-[(triethylsilyl)oxy]-hexyl]-7a-methyl-octahydro-inden-4-ol (15). [α]²⁴_D -43.7° (*c* 1.31, CHCl₃); IR (CHCl₃) 3476, 3313 cm⁻¹; ¹H NMR (700 MHz, CDCl₃) δ 0.032, 0.074, 0.079 and 0.082 (each 3H, each s, 4 $\times$ SiCH₃), 0.558 (6H, q, *J* = 8.0 Hz, 3 $\times$ SiCH₂CH₃), 0.867 (9H, s, one of Si-*t*-Bu), 0.889 (3H, d, *J* = 6.3 Hz, 1'-CH₃), 0.900 (9H, s, one of Si-*t*-Bu), 0.924 (3H, s, 7a-CH₃), 0.940 (9H, t, *J* = 8.0 Hz, 3 $\times$ SiCH₂CH₃), 1.176 and 1.178 (3H and 3H, each s, 5'-CH₃ and 6'-H₃), 1.95 (1H, d, *J* ~ 12 Hz, 1'' β -H), 2.74 (1H, t, *J* = 12.0 Hz, 1'''-H), 3.31 (1H, d, *J* = 12.0 Hz, 1'' α -H), 4.03 (1H, tt, *J* = 10.5, 4.2 Hz, 5''' α -H), 4.21 (1H, br s, 3''' β -H), 5.66

(1H, d, $J = 2.1$ Hz, OH; disappears after D₂O), 5.93 (1H, d, $J = 25.9$ Hz, 3''-H), 7.44 (3H, m, Ar-H), 7.67 (3H, m, Ar-H); ¹³C NMR (125 MHz) δ -5.133, -4.102, -4.617 and -4.559 (4 $\times$ Si-CH₃), 6.82 (SiCH₂CH₃), 7.12 (SiCH₂CH₃), 13.01 [C(7a)-CH₃], 17.85 and 18.22 [SiC(CH₃)₃], 18.51 [C(1')-CH₃], 19.42 (CH₂), 20.37 (CH₂), 20.79 (CH₂), 25.63 and 25.93 [SiC(CH₃)₃], 27.26 (CH₂), 29.81 and 29.98 [C(5')-CH₃ and C-6'], 35.20 (C-1'), 36.35(C-2'), 36.70 (C-2''), 39.29 (CH₂), 40.72 (CH₂), 40.81(d, $J = 15$ Hz, C-1''), 43.06 (C-4''), 43.50 (C-7a), 44.03 (C-6''), 45.59 (CH₂), 46.55 (d, $J = 7.3$ Hz, C-1'), 57.17 (CH), 57.64 (C-3a), 67.42 (C-3''), 67.59 (C-5''), 73.27 (d, $J = 2.0$ Hz, C-4), 73.50 (C-5'), 116.42 (d, $J = 125.3$ Hz, C-3'), 128.50 (2 $\times$ d, $J = 12.2$ Hz, Ar-C_{ortho}), 128.57 (2 $\times$ d, $J = 11.7$ Hz, Ar-C_{ortho}), 130.81 (d, $J = 9.6$ Hz, Ar-C_{meta}), 131.13 (d, $J = 9.6$ Hz, Ar-C_{meta}), 131.38 (d, $J = 3.0$ Hz, Ar-C_{para}), 131.61 (d, $J = 3.0$ Hz, Ar-C_{para}), 133.89 (d, $J = 14.1$ Hz, Ar-C_{ipso}), 134.73 (d, $J = 12.6$ Hz, Ar-C_{ipso}), 168.99 (C-2''); HRMS (ESI) exact mass calculated for C₅₇H₉₉O₅PSi₃Na (M + Na)⁺ 1001.6436, measured 1001.6423.

2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexylidene]acetic acid methyl ester (17). $[\alpha]^{24}_D +26.1^\circ$ (c 1.07, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 0.020 (12H, s, 4 $\times$ SiCH₃), 0.823 and 0.840 (9H and 9H, each s, 2 $\times$ Si-*t*-Bu), 1.71 (2H, m, 4' α - and 4' β -H), 2.12 (1H, dd, $J = 13.2, 7.6$ Hz, 6' β -H), 2.36 (1H, dd, $J = 13.2, 4.2$ Hz, 6' α -H), 2.80 (1H, dd, $J = 13.4, 3.6$ Hz, 2' β -H), 2.97 (1H, dd, $J = 13.4, 6.4$ Hz, 2' α -H), 3.64 (3H, s, COOCH₃), 4.12 (2H, m, 3' β - and 5' α -H), 5.67 (1H, s, 2-H); ¹³C NMR (50 MHz) δ -4.89, -4.84, -4.64 and -4.60 (4 $\times$ SiCH₃), 18.26 [SiC(CH₃)₃], 25.90 and 26.00 [SiC(CH₃)₃], 37.77 (C-6'), 43.37 (C-2'), 46.24 (C-4'), 51.06 (COOCH₃), 68.10 and 68.22 (C-3' and C-5'), 117.09 (=CCOOCH₃), 157.21 (C-1'), 167.01 (COOCH₃); HRMS (ESI) exact mass calculated for C₂₁H₄₂O₄Si₂Na (M + Na)⁺ 437.2519, measured 437.2523.

[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexyl]-acetic acid methyl ester (18). $[\alpha]^{24}_D -3.3^\circ$ (c 1.06, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 0.021, 0.030 and 0.044 (3H, 3H and 6H, each s, 4 $\times$ SiCH₃), 0.878 (18H, s, 2 $\times$ Si-*t*-Bu), 1.04 (2H, m, 2'- and 6'-H), 1.29 (1H, ddd, $J = 13.2, 10.8, 2.4$ Hz, 4'-H), 1.62 (1H, br d, $J = 13.0$ Hz, 4'-H), 1.87 (2H, m, 2'- and 6'-H), 2.12 – 2.37 (3H, m, CH₂COOCH₃ and 1'-H), 3.66 (3H, s, COOCH₃), 4.04 (1H, tt, $J = 10.8, 4.4$ Hz, 3' β -H), 4.14 (1H, br s, 5' α -H); ¹³C NMR (50 MHz) δ -4.87, -4.81, -4.53 and -4.51 (4 $\times$ SiCH₃), 18.13 and 18.37 [SiC(CH₃)₃], 25.88 and 26.10 [SiC(CH₃)₃], 28.16 (C-1'), 39.15 (CH₂COOCH₃), 41.40 (CH₂), 42.34 (CH₂), 43.09 (CH₂), 51.50 (COOCH₃), 67.03

and 67.66 (C-3' and C-5'), 173.23 (COOCH_3); HRMS (ESI) exact mass calculated for $\text{C}_{21}\text{H}_{44}\text{O}_4\text{Si}_2\text{Na}$ ($\text{M} + \text{Na}$)⁺ 439.2676, measured 439.2673.

2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexyl]-propionic acid methyl ester (19). ¹H NMR (200 MHz, selected signals; CDCl_3) δ 1.09 and 1.13 (2.4H and 0.6H, each d, $J = 7.0$ Hz, CH_3), 3.65 and 3.66 (2.4H and 0.6H, each s, COOCH_3), 4.04 (1H, tt, $J = 10.6, 4.4$ Hz, 3' β -H), 4.16 (1H, br d, $J = 2.8$ Hz, 5' α -H); HRMS (ESI) exact mass calculated for $\text{C}_{22}\text{H}_{46}\text{O}_4\text{Si}_2\text{Na}$ ($\text{M} + \text{Na}$)⁺ 453.2832, measured 453.2817.

2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexyl]-2-phenylselenenyl-propionic acid methyl ester (20). ¹H NMR (200 MHz, selected signals; CDCl_3) δ 1.47 (3H, s, CH_3), 3.63 (3H, s, COOCH_3), 4.08 (1H, tt, $J = 11.0, 4.4$ Hz, 3' β -H), 4.16 (1H, br t, $J = 2.6$ Hz, 5' α -H), 7.37 and 7.63 (3H and 2H, each m, Ar-H); HRMS (ESI) exact mass calculated for $\text{C}_{28}\text{H}_{50}\text{O}_4\text{SeSi}_2\text{Na}$ ($\text{M} + \text{Na}$)⁺ 609.2311, measured 609.2330.

2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexyl]acrylic acid methyl ester (21). $[\alpha]_{\text{D}}^{24} -19^\circ$ (c 1.59, CHCl_3); ¹H NMR (200 MHz, CDCl_3) δ 0.062 and 0.062 (6H and 6H, each s, $4 \times \text{SiCH}_3$), 0.889 and 0.891 (9H and 9H, each s, $2 \times \text{Si-}t\text{-Bu}$), 1.75 (2H, m), 1.94 (3H, m), 2.29 (1H, m), 3.03 (1H, br t, $J = 12.6$ Hz, 1'-H), 3.75 (3H, s, COOCH_3), 4.08 (1H, tt, $J = 10.8, 4.2$ Hz, 3' β -H), 4.19 (1H, narr m, 5' α -H), 5.51 and 6.17 (2H, each s, $=\text{CH}_2$); ¹³C NMR (50 MHz) δ -4.84 and -4.49 ($4 \times \text{SiCH}_3$), 18.17 and 18.44 [$\text{SiC}(\text{CH}_3)_3$], 25.90 and 26.14 [$\text{SiC}(\underline{\text{CH}}_3)_3$], 33.02 (C-1'), 39.02, 41.33 and 43.23 (C-2', C-4' and C-6'), 51.88 (COOCH_3), 67.48 and 67.90 (C-3' and C-5'), 123.23 ($=\text{CH}_2$), 145.29 ($\text{C}=\text{CH}_2$), 167.84 (COOCH_3); HRMS (ESI) exact mass calculated for $\text{C}_{22}\text{H}_{44}\text{O}_4\text{Si}_2\text{Na}$ ($\text{M} + \text{Na}$)⁺ 451.2676, measured 451.2693.

2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexyl]prop-2-en-1-ol (22). $[\alpha]_{\text{D}}^{24} -18^\circ$ (c 1.41, CHCl_3); ¹H NMR (200 MHz, CDCl_3) δ 0.029, 0.045 and 0.059 (3H, 3H, and 6H, each s, $4 \times \text{SiCH}_3$), 0.886 (18H, s, $2 \times \text{Si-}t\text{-Bu}$), 1.15 – 1.40 (3H, br m), 1.68 (1H, br d, $J = 13.4$ Hz), 1.92 (2H, m), 2.52 (1H, br t, $J = 12.6$ Hz, 1'-H), 4.05 (1H, tt, $J = 11.0, 4.4$ Hz, 3' β -H), 4.12 (2H, m, $\underline{\text{CH}}_2\text{OH}$), 4.19 (1H, br s, 5' α -H), 4.91 (1H, t, $J = 1.0$ Hz, one of $=\text{CH}_2$), 5.06 (1H, d, $J = 1.2$ Hz, one of $=\text{CH}_2$); ¹³C NMR (50 MHz) δ -4.83, -4.78, -4.48 and -4.45 (SiCH_3), 18.15 and 18.43 [$\text{SiC}(\text{CH}_3)_3$], 25.90 and 26.13 [$\text{SiC}(\underline{\text{CH}}_3)_3$], 33.81 (C-1'), 38.93, 41.50 and 43.19 (C-2', C-4' and C-6'), 65.17 (CH_2OH), 67.99 and 67.57 (C-3' and C-5'), 108.20 ($=\text{CH}_2$), 153.29 ($\text{C}=\text{CH}_2$); HRMS (ESI) exact mass calculated for $\text{C}_{21}\text{H}_{44}\text{O}_3\text{Si}_2\text{Na}$ ($\text{M} + \text{Na}$)⁺ 423.2727, measured 423.2713.

[2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]cyclohexyl]prop-2-en]diphenyl-phosphine oxide (23). $[\alpha]_D^{24} +9.6^\circ$ (*c* 1.42, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 0.019, 0.024 and 0.034 (3H, 6H, and 3H, each s, 4 $\times$ SiCH₃), 0.877 and 0.878 (9H and 9H, each s, 2 $\times$ Si-*t*-Bu), 1.10 (2H, m), 1.23 (1H, m), 1.60 (1H, br d, *J* = 13.5 Hz), 1.70 (1H, br d, *J* = 12.1 Hz), 1.84 (1H, br d, *J* = 12.5 Hz), 2.20 (1H, br t, *J* = 11.5 Hz, 1'-H), 2.97 and 3.14 (1H and 1H, each t, *J* ~ 15 Hz, CH₂P), 3.82 (1H, tt, *J* = 11.0, 4.5 Hz, 3'β-H), 4.12 (1H, narr. m, 5'α-H), 4.97 and 5.13 (1H and 1H, each d, *J* = 3.7 Hz, =CH₂), 7.47 and 7.75 (6H and 4H, each m, Ar-H); ¹³C NMR (125 MHz) δ -4.65, -4.59, -4.30 and -4.26 (4 $\times$ SiCH₃), 18.31 and 18.53 [SiC(CH₃)₃], 26.11 and 26.29 [SiC(CH₃)₃], 36.14 (d, *J* = 67.4 Hz, CH₂P), 38.36, 38.78, 40.98 (C-1'), 43.27, 67.49 and 67.96 (C-3' and C-5'), 114.55 (d, *J* ~ 8 Hz, =CH₂), 128.75 and 128.86 (2 $\times$ d, *J* = 11.8 Hz, Ar-C_{ortho}), 131.45 (d, *J* = 8.7 Hz, Ar-C_{meta}), 131.99 (d, *J* ~ 3 Hz, Ar-C_{para}), 134.12 (d, *J* ~ 13 Hz, Ar-C_{ipso}), 143.68 (d, *J* ~ 9 Hz, C=CH₂); HRMS (ESI) exact mass calculated for C₃₃H₅₃O₃PSi₂Na (M + Na)⁺ 607.3169, measured 607.3179.

[2-[(3'R,5'R)-3',5'-Bis[(*tert*-butyldimethylsilyl)oxy]-cyclohexyl]prop-1-en]diphenyl-phosphine oxide (24). $[\alpha]_D^{24} -11.0^\circ$ (*c* 1.75, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 0.024, 0.042, 0.054 and 0.059 (each 3H, each s, 4 $\times$ SiCH₃), 0.874 and 0.883 (9H and 9H, each s, 2 $\times$ Si-*t*-Bu), 1.33 (2H, m), 1.72 (2H, m), 1.94 (2H, m), 2.04 (3H, dd, *J* = 2.4, 0.8 Hz, 3-H₃), 2.62 (1H, br t, *J* = 12.2 Hz, 1'-H), 4.09 (1H, br m, 3'β-H), 4.21 (1H, narr m, 5'α-H), 5.89 (1H, d, *J* = 62.0 Hz, =CH), 7.44 and 7.72 (6H and 4H, each m, Ar-H); ¹³C NMR (50 MHz) δ -4.81, -4.86, -4.46 and -4.41 (4 $\times$ SiCH₃), 18.16 and 18.45 [SiC(CH₃)₃], 25.92 and 26.79 [SiC(CH₃)₃], 38.24, 40.75, 41.69 (d, *J* = 15 Hz, C-1'), 43.15, 67.33 and 67.96 (C-3' and C-5'), 115.19 (d, *J* = 104.2 Hz, =CH), 128.75 (d, *J* = 11.9 Hz, Ar-C_{ortho}), 131.12 and 131.56 (2 $\times$ d, *J* = 9.5 Hz, Ar-C_{meta}), 131.57 (d, *J* = 2.6 Hz, Ar-C_{para}), 167.78 (C=CH); HRMS (ESI) exact mass calculated for C₃₃H₅₃O₃PSi₂Na (M + Na)⁺ 607.3169, measured 607.3170.

(1R,4R,7aR)-4-[(*E*)-2''-[(3'''R,5'''R)-3''',5'''-Bis[(*tert*-butyldimethylsilyl)oxy]-cyclo-hexyl]-3''-[(*R*)-(butyl-phenyl-phosphinoyl)]-allyl]- and (1R,4R,7aR)-4-[(*E*)-2''-[(3'''R,5'''R)-3''',5'''-bis[(*tert*-butyldimethylsilyl)oxy]-cyclo-hexyl]-3''-[(*S*)-(butyl-phenyl-phos-phinoyl)]-allyl]-1-[(*R*)-1',5'-dimethyl-5'-[(triethylsilyl)oxy]-hexyl]-7a-methyl-octahydro-inden-4-ol (25a and 25b). **25a:** $[\alpha]_D^{24} +9.6^\circ$ (*c* 0.52, CHCl₃); IR (CHCl₃) 3434 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ -0.004, 0.020, 0.077 and 0.088 (each 3H, each s, 4 $\times$ SiCH₃), 0.566 (6H, q, *J* = 8.0 Hz, 3 $\times$ SiCH₂CH₃), 0.856 and 0.903 (9H and 9H, each s, 2 $\times$

Si-*t*-Bu), 0.877 (3H, d, $J = 7.0$ Hz, 1'-CH₃), 0.949 (9H, t, $J = 8.0$ Hz, $3 \times \text{SiCH}_2\text{CH}_3$), 0.979 (3H, s, 7a-CH₃), 1.187 (6H, s, 5'-CH₃ and 6'-H₃), 1.99 (1H, d, $J = 13.0$ Hz, 1''β-H), 2.65 (1H, t, $J \sim 13$ Hz, 1'''-H), 3.51 (1H, d, $J = 13.0$ Hz, 1''α-H), 4.02 (1H, ddd, $J = 14.5, 10.0, 3.5$ Hz, 5'''α-H), 4.19 (1H, br s, 3'''β-H), 5.58 (1H, d, $J = 25.5$ Hz, 3''-H), 7.46 and 7.70 (3H and 2H, each m, Ar-H); HRMS (ESI) exact mass calculated for C₅₅H₁₀₃O₅PSi₃Na (M + Na)⁺ 981.6749, measured 981.6758. **25b**: $[\alpha]^{24}_{\text{D}} +1.2^\circ$ (*c* 0.58, CHCl₃); IR (CHCl₃) 3431 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ -0.001, 0.010, 0.042 and 0.045 (each 3H, each s, $4 \times \text{SiCH}_3$), 0.558 (6H, q, $J = 8.0$ Hz, $3 \times \text{SiCH}_2\text{CH}_3$), 0.872 (18H, s, $2 \times \text{Si-}t\text{-Bu}$), 0.883 (3H, d, $J = 8.0$ Hz, 1'-CH₃), 0.941 (9H, t, $J = 8.0$ Hz, $3 \times \text{SiCH}_2\text{CH}_3$), 0.988 (3H, s, 7a-CH₃), 1.178 (6H, s, 5'-CH₃ and 6'-H₃), 1.79 (1H, d, $J \sim 13.0$ Hz, 1'β-H), 2.66 (1H, t, $J = 11.5, 11.5$ Hz, 1'''-H), 3.05 (1H, d, $J = 12.0$ Hz, 1''α-H), 3.99 (1H, ddd, $J = 14.5, 10.0, 3.5$ Hz, 5'''α-H), 4.11 (1H, br s, 3'''β-H), 5.80 (1H, d, $J = 26.5$ Hz, 3''-H), 7.47 and 7.66 (3H and 2H, each m, Ar-H); HRMS (ESI) exact mass calculated for C₅₅H₁₀₃O₅PSi₃Na (M + Na)⁺ 981.6749, measured 981.6764.

Spectra:

¹H NMR spectrum of **13**

¹³C NMR spectrum of **13**

¹H NMR spectrum of **14**

¹³C NMR spectrum of **14**

¹H NMR spectrum of **7**

¹³C NMR spectrum of **7**

^1H NMR spectrum of **15**

Fragment of ^1H NMR spectrum of **15**; insert **A** shows part of the COSY spectrum of **15**

Fragment of ^1H NMR spectrum of **15**; insert **B** shows part of the ^1H NMR spectrum of **15** after spin decoupling experiment.

COSY spectrum of **15**

HMBC NMR spectrum of **15**

HSQC NMR spectrum of **15**

Fragment of HSQC NMR spectrum of **15**

^{13}C NMR spectrum of **15**

Fragment of ^{13}C NMR spectrum of **15**

HPLC profile of **15**

¹H NMR spectrum of **17**

¹³C NMR spectrum of **17**

^1H NMR spectrum of **18**

^1H NMR spectrum of **19**

^1H NMR spectrum of **20**

^1H NMR spectrum of **21**

^{13}C NMR spectrum of **21**

^1H NMR spectrum of **22**

^{13}C NMR spectrum of **22**

^1H NMR spectrum of **23**

^{13}C NMR spectrum of **23**

^1H NMR spectrum of **24**

^{13}C NMR spectrum of **24**

^1H NMR spectrum of **25a**

GCOSY NMR spectrum of **25a**

^1H NMR spectrum of **25b**

GCOSY NMR spectrum of **25b**