Catalytic Asymmetric Silane Alcoholysis: Practical Access to Chiral Silanes

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Supporting Information

General Information. All reactions were carried out under an atmosphere of nitrogen in flame- or oven-dried glassware with magnetic stirring unless otherwise indicated. High pressure reactions were carried out in a Parr stainless steel pressure vessel equipped with a pressure guage, gas inlet, and pressuer release valve. Degassed solvents were purified by passage through an activated alumina column. $((\text{PhO})_3\text{P})_2\text{Rh}(\text{CH}_3\text{COCH}_3)_2\cdot\text{BF}_4$ was synthesized following the procedure of Bosnich for closely related compounds.¹ ^1H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or a DPX-500 (500 MHz) spectrometer and are reported in ppm from CDCl_3 internal standard (7.26 ppm) or $(\text{CD}_3)_2\text{CO}$ internal standard (2.04 ppm). Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dt = doublet of triplets, dd = doublet of doublets, ddd = doublet of doublet of doublets; coupling constant(s) in Hz; integration; assignment). Proton decoupled ^{13}C NMR spectra were recorded on a Bruker DPX-300 (75 MHz) and are reported in ppm from CDCl_3 internal standard (77.0 ppm). ^{31}P NMR spectra were reported on a Bruker DPX-300 (121.6 MHz) and are reported in ppm from H_2PO_4 (85% in H_2O) external standard (0.0 ppm). ^{19}F NMR spectra were recorded on a Bruker DPX-300 (282 MHz) and are reported in ppm from CF_3Cl internal standard (0.0ppm). Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard 6890 Series Gas Chromatograph equipped with a capillary split-splitless inlet and flame ionization detector with electronic pneumatics control using an HP-5 capillary column (30 m x 0.32 mm). Optical rotations were recorded on a JASCO DIP-1000 digital polarimeter. Low resolution mass spectra were obtained on a JEOL HX110 mass spectrometer in the Columbia University Mass Spectrometry Laboratory.

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Preparation of allyl-*tert*-butyl-silane: A 3-neck 1L round bottom flask equipped with a mechanical stirrer, reflux condenser and a solid addition funnel was charged with *tert*-butyl-trichlorosilane (50 g, 261 mmol) and Et₂O (250 mL). The solution was heated to reflux and then allyl magnesium bromide (261 mL, 1.0 M in Et₂O) was added over 1 hour by cannula. Upon completion of the addition the reaction mixture was heated at reflux for an additional 3 hours, then cooled to room temperature. Lithium aluminum hydride (7.4 g, 196 mmol) was then added to the solid addition funnel, and was added in portions to the reaction mixture over the course of 20 min (CAUTION: exotherm). The reaction mixture was heated at reflux for 12 hours, then cooled to room temperature. The resultant heterogeneous mixture was poured slowly into a flask containing ice and water. The layers were separated and the aqueous layer was extracted with Et₂O (20 mL), and the combined organic layers were dried (MgSO₄) and filtered. The filtrate was concentrated by careful distillation and the residue was then distilled at ambient pressure to afford 14.0 g (41%) of allyl-*tert*-butyl-silane (bp $\approx$ 119 °C) as a clear, colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 5.88-5.77 (m, 1H, CH=CH₂), 4.98 (d, *J* = 16.9 Hz, 1H, one of CH=CH₂), 4.92 (d, *J* = 10.9 Hz, 1H, one of CH=CH₂), 3.54 (t, *J* = 3.7 Hz, 2H, SiH₂), 1.71-1.65 (m, 2H, CH₂CH=CH₂), 0.99 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.0, 113.8, 27.8, 16.2, 15.4 ; IR (thin film) 2930, 2859, 2131, 1633, 1470, 1160 cm⁻¹.

General procedure for the preparation of allyl-*tert*-butyl-silyl ethers: A 100 mL round bottom flask is charged with CuCl (20 mg, 0.20 mmol), NaO-*t*-Bu (19 mg, 0.20 mmol) and BDPP (88 mg, 0.20 mmol). Toluene (20 mL) is added and the mixture is stirred for 5-10 min. The reaction mixture is then cooled to the appropriate temperature (see note) and allyl-*tert*-butyl-silane (0.40 mL, 4.0 mmol) is added. After 10 min, the alcohol (2.0 mmol) is added. The reaction is typically complete in 10-20 h and may be monitored by following the disappearance of the alcohol by GC. The reaction mixture is concentrated and the residue is purified by chromatography on silica gel (hexanes) to yield the silyl ether as a clear oil.

Note: For benzylic alcohols, the reaction mixture is cooled to -20 °C prior to addition of the silane and maintained at that temperature throughout the procedure. For all other alcohols the reaction is performed at ambient temperature.

The tandem silylformylation-allylsilylation reactions described in Scheme 1 were carried out using our previously published procedure,² with the following modifications: $((\text{PhO})_3\text{P})_2\text{Rh}(\text{CH}_3\text{COCH}_3)_2 \cdot \text{BF}_4$ was employed as catalyst (10 mol %), and the reactions were carried out for 24 h.

Preparation of BDPP derivatives: A round bottom flask was charged with 1.9 mmol of the appropriate diarylphosphine (*bis*-3,5-difluorophenylphosphine) or phosphine borane salt (*bis*-*p*-fluorophenylphosphine-borane, *bis*-*p*-methoxyphenylphosphine-borane and *bis*-*p*-tolylphosphine-borane; prepared according to known procedures³) and THF (15 mL) and the solution was cooled to -78 °C. *n*-BuLi (0.77 mL, 2.5 M in Hexanes) was added, and after 5 min a solution of (2*S*,4*S*)-2,4-pentanediol di-*p*-toluenesulfonate^{3a,4} (397 mg, 0.96 mmol) in THF (5 mL) was then added. The reaction mixture was warmed to room temperature and stirred for 16 h. The reaction mixture was then concentrated and the residue was chromatographed (EtOAc/hexanes as eluant) to give the bis(diarylphosphino)pentane or bis(diarylphosphino)pentane-P:P'-hexahydrodiboron as a clear oil or white solid. The bis(diarylphosphino)pentane-P:P'-hexahydrodiboron substrates were decomplexed according to known procedures³.

Data for Chiral Silanes Described in Table 2.

Table 2, Entry 1: ¹H NMR (300 MHz, CDCl₃) δ 5.92-5.85 (m, 1H, CH=CH₂), 4.99-4.89 (m, 2H, CH=CH₂), 4.29 (t, *J* = 2.4 Hz, 1H, SiH), 3.89-3.84 (m, 1H, CH₂CH(OSi)), 2.42-2.30 (m, 2H, CH₂C≡CH), 1.97-1.96 (m, 1H, CH₂C≡CH), 1.77-1.67 (m, 2H, CH₂CH=CH₂), 1.64-1.53 (m, 2H, CH₂CH₃) 1.47-1.41 (m, 1H, one of CH₂CH₂CHOSi), 1.39-1.33 (m, 1H, one of CH₂CH₂CHOSi), 0.95 (s, 9H, C(CH₃)₃) 0.92 (t, *J* = 7.6 Hz, 3H, CH₃CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 133.9, 114.2, 81.4, 72.8, 69.9, 38.5, 27.0, 25.9, 20.2, 18.5, 18.4, 14.1, 18.5; IR (thin film) 3314, 3080, 2959, 2932, 2859, 2104, 1632, 1472, 1363, 1161, 1091, 1041 cm⁻¹; LRMS (EI+, M-C₃H₅) cal'd for C₁₁H₂₁OSi 197.14, found 197.17.

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(4) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc.* **1988**, *110*, 629-631.

Table 2, Entry 2: ^1H NMR (300 MHz, CDCl_3) δ 5.85-5.74 (m, 1H, $\text{CH}=\text{CH}_2$), 4.91-4.82 (m, 2H, $\text{CH}=\text{CH}_2$), 4.23 (t, $J = 2.4$ Hz, 1H, SiH), 3.83-3.78 (m, 1H, $\text{CH}_2\text{CH}(\text{OSi})$), 2.32-2.27 (m, 2H, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.88 (t, $J = 2.6$ Hz, 1H, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.65-1.61 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.56-1.48 (m, 2H, CH_2CH_3), 1.40-1.22 (m, 2H, $\text{CH}_2\text{CH}_2\text{CHOSi}$), 0.88 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.86 (t, $J = 5.9$ Hz, 3H, CH_3CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 133.8, 114.3, 81.3, 72.7, 70.0, 38.5, 26.7, 26.0, 20.1, 18.4, 18.3, 14.1; IR (thin film) 3314, 3080, 2959, 2932, 2859, 2106, 1632, 1472, 1390, 1363, 1161 cm^{-1} ; LRMS (EI+, $\text{M}-\text{C}_3\text{H}_5$) cal'd for $\text{C}_{11}\text{H}_{21}\text{OSi}$ 197.14, found 197.18.

Table 2, Entry 3: ^1H NMR (300 MHz, CDCl_3) δ 5.92-5.78 (m, 1H, $\text{CH}=\text{CH}_2$), 4.98-4.87 (m, 2H, $\text{CH}=\text{CH}_2$), 4.31 (t, $J = 2.3$ Hz, 1H, SiH), 3.73-3.66 (m, 1H, $\text{CH}_2\text{CH}(\text{OSi})$), 2.38-2.31 (m, 2H, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.99-1.88 (m, 2H, $\text{CH}_2\text{C}\equiv\text{CH}$ and $\text{CH}(\text{CH}_3)_2$), 1.72-1.54 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.92-0.86 (m, 6H, $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 133.9, 114.3, 81.7, 77.1, 69.9, 32.3, 26.0, 23.9, 20.0, 18.5, 16.4; IR (thin film) 3315, 2931, 2859, 2109, 1632, 1491, 1052 cm^{-1} ; LRMS (EI+, $\text{M}-\text{C}_3\text{H}_5$) cal'd for $\text{C}_{11}\text{H}_{21}\text{OSi}$ 197.14, found 197.10.

Table 2, Entry 4: ^1H NMR (300 MHz, CDCl_3) δ 5.95-5.78 (m, 1H, $\text{CH}=\text{CH}_2$), 4.98-4.87 (m, 2H, $\text{CH}=\text{CH}_2$), 4.29 (t, $J = 2.3$ Hz, 1H, SiH), 3.73-3.66 (m, 1H, $\text{CH}_2\text{CH}(\text{OSi})$), 2.38-2.31 (m, 2H, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.97-1.91 (m, 2H, $\text{CH}_2\text{C}\equiv\text{CH}$ and $\text{CH}(\text{CH}_3)_2$), 1.76-1.54 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.92-0.86 (m, 6H, $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 134.1, 114.2, 77.4, 77.3, 32.5, 26.0, 24.4, 18.7, 16.5, ; IR (thin film) 3315, 2931, 2859, 2109, 1632, 1491, 1052 cm^{-1} ; LRMS (EI+, $\text{M}-\text{C}_3\text{H}_5$) cal'd for $\text{C}_{11}\text{H}_{21}\text{OSi}$ 197.14, found 197.10.

Table 2, Entry 5: ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.24 (m, 5H, 5 x ArH), 5.94-5.86 (m, 1H, $\text{CH}=\text{CH}_2$), 5.02-4.86 (m, 3H, $\text{CH}=\text{CH}_2$ and PhCH), 4.23 (t, $J = 2.3$ Hz, 1H, SiH), 2.65 (ddd, $J = 2.6, 6.7, 11.5$ Hz, 1H, one of $\text{CH}_2\text{C}\equiv\text{CH}$), 2.53 (ddd, $J = 2.7, 6.1, 16.6$ Hz, 1H, one of $\text{CH}_2\text{C}\equiv\text{CH}$), 1.95 (t, $J = 2.6$ Hz, 1H, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.79-1.74 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.87 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 143.1, 134.3, 128.5, 128.1, 126.5, 114.8, 81.6, 76.2, 70.6, 30.9, 26.3, 20.3, 19.0; IR (thin film) 3310, 2930, 2858, 2111, 1631, 1471, 1364, 1093 cm^{-1} ; LRMS (EI+, $\text{M}-\text{C}_3\text{H}_5$) cal'd for $\text{C}_{14}\text{H}_{19}\text{OSi}$ 231.12, found 230.83.

Table 2, Entry 6: ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.24 (m, 5H, 5 x ArH), 5.65-5.54 (m, 1H, $\text{CH}=\text{CH}_2$), 4.80-4.73 (m, 3H, $\text{CH}=\text{CH}_2$ and PhCH), 4.30 (t, $J = 2.4$ Hz, 1H, SiH), 2.65 (ddd, $J = 2.6, 6.7, 12.8$ Hz, 1H, one of $\text{CH}_2\text{C}\equiv\text{CH}$), 2.53 (ddd, $J = 2.6, 6.1, 16.6$ Hz, 1H, one of $\text{CH}_2\text{C}\equiv\text{CH}$), 1.95 (t, $J = 2.1$ Hz, 1H, $\text{CH}_2\text{C}\equiv\text{CH}$),

1.57-1.53 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.98 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 142.9, 133.5, 129.1, 127.7, 126.0, 114.2, 81.1, 75.5, 70.2, 30.3, 26.0, 20.0, 19.6; IR (thin film) 3310, 2930, 2858, 2111, 1631, 1471, 1364, 1093 cm^{-1} ; LRMS (EI+, $\text{M}-\text{C}_3\text{H}_5$) cal'd for $\text{C}_{14}\text{H}_{19}\text{OSi}$ 231.12, found 230.82.

Table 2, Entry 7: ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.26 (m, 5H, 5 x ArH), 5.71-5.62 (m, 1H, $\text{CH}=\text{CH}_2$), 5.05-4.95 (m, 1H, PhCH), 4.85-4.75 (m, 2H, $\text{CH}=\text{CH}_2$), 4.32 (t, $J = 2.3$ Hz, 1H, SiH), 1.84-1.37 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2\text{CH}=\text{CH}_2$) 0.87 (s, 9H, $\text{C}(\text{CH}_3)_3$) 1.04-0.87 (m, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 144.9, 133.8, 128.0, 127.0, 126.1, 126.1, 113.9, 77.1, 42.6, 26.0, 20.2, 18.7, 14.0; IR (thin film) 2930, 2858, 2105, 1632, 1471, 1065 cm^{-1} ; LRMS (EI+) cal'd for $\text{C}_{17}\text{H}_{28}\text{OSi}$ 276.19, found 276.15.

Table 2, Entry 8: ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.25 (m, 5H, 5 x ArH), 5.96-5.84 (m, 1H, $\text{CH}=\text{CH}_2$), 5.05-4.93 (m, 1H, PhCH), 4.79-4.74 (m, 2H, $\text{CH}=\text{CH}_2$), 4.23 (t, $J = 2.3$ Hz, 1H, SiH), 1.82-1.31 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2\text{CH}=\text{CH}_2$) 1.02-0.92 (m, 3H, CH_2CH_3), 0.87 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 144.6, 134.1, 128.0, 127.0, 114.1, 77.1, 42.7, 25.9, 19.9, 18.6, 14.0; IR (thin film) 2930, 2858, 2105, 1632, 1471, 1065 cm^{-1} ; LRMS (EI+) cal'd for $\text{C}_{17}\text{H}_{28}\text{OSi}$ 276.19, found 276.17.

Data for Diols **3**, **4**, **7**, and **8**.

Diol 3: ^1H NMR (300 MHz, CDCl_3) δ 5.80-5.49 (m, 3H, $\text{CH}=\text{CH}$ and $\text{CH}=\text{CH}_2$), 5.09-5.03 (m, 2H, $\text{CH}=\text{CH}_2$), 4.07 (q, $J = 6.0$ Hz, 1H, $\text{CH}=\text{CHCHOH}$), 3.59-3.57 (m, 1H, $n\text{-PrCHOH}$), 3.10 (s, 2H, 2 x OH), 2.28-2.18 (m, 3H, one of $\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{CH}_2\text{CH}=\text{CH}$), 2.10-1.98 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.44-1.28 (m, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 0.88 (t, $J = 6.8$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 135.4, 134.4, 128.1, 117.85, 71.7, 70.5, 41.6, 40.2, 39.0, 18.7, 13.9; IR (thin film) 3350, 2959, 2932, 2873, 1642, 1434, 1079, 1023 cm^{-1} ; LRMS (FAB+, $\text{M}+\text{H}$) calc'd for $\text{C}_{11}\text{H}_{21}\text{O}_2$ 185.16, found 186.40.

Diol 4: ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.22 (m, 5H, ArH), 5.78-5.51 (m, 3H, $\text{CH}=\text{CH}$ and $\text{CH}=\text{CH}_2$), 5.11-5.06 (m, 2H, $\text{CH}=\text{CH}_2$), 4.66 (t, 1H, PhCH, $J = 6.7$ Hz), 4.09 (apparent q, 1H, $\text{CH}=\text{CHCHOH}$, $J = 12.9$ Hz), 2.46-2.42 (m, 2H, two of $\text{CH}_2\text{CH}=\text{CH}$ and $\text{CH}_2\text{CH}=\text{CH}_2$), 2.27-2.23 (m, 2H, two of $\text{CH}_2\text{CH}=\text{CH}$ and $\text{CH}_2\text{CH}=\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 143.9, 135.9, 134.3, 128.4, 127.5, 125.8, 117.9, 73.5, 71.6, 42.1, 41.6; IR (thin film) 3368, 3075, 3030, 2931, 1641, 1604, 1494, 1454, 1321, 1028 cm^{-1} ; LRMS (FAB+, $\text{M}+\text{H}$) calc'd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ 219.14, found 220.86.

Diol 7: ^1H NMR (300 MHz, CDCl_3) δ 5.80-5.49 (m, 3H, $\text{CH}=\text{CH}$ and $\text{CH}=\text{CH}_2$), 5.10-5.04 (m, 2H, $\text{CH}=\text{CH}_2$), 4.10 (q, $J = 6.0$ Hz, 1H, $\text{CH}=\text{CHCHOH}$), 3.60-3.56 (m, 1H, $n\text{-PrCHOH}$), 2.82 (s, 2H, 2 x OH), 2.29-2.18 (m, 3H, one of $\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{CH}_2\text{CH}=\text{CH}$), 2.13-2.01 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.45-1.30 (m, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 0.88 (t, $J = 7.0$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 135.5, 134.4, 127.6, 117.6, 71.6, 70.5, 41.7, 39.9, 38.7, 18.8, 14.0; IR (thin film) 3350, 2959, 2932, 2873, 1642, 1433, 1322, 1124, 1079, 1022 cm^{-1} ; LRMS (FAB+, M+H) calc'd for $\text{C}_{11}\text{H}_{21}\text{O}_2$ 185.16, found 186.40.

Diol 8: ^1H NMR (300 MHz, CDCl_3) δ 7.25-7.18 (m, 5H, ArH), 5.62-5.50 (m, 3H, $\text{CH}=\text{CH}$ and $\text{CH}=\text{CH}_2$), 5.03-4.99 (m, 2H, $\text{CH}=\text{CH}_2$), 4.61 (t, 1H, PhCH , $J = 6.3$ Hz), 4.02 (apparent q, 1H, $\text{CH}=\text{CHCHOH}$, $J = 6.4$ Hz), 2.40-2.37 (m, 2H, two of $\text{CH}_2\text{CH}=\text{CH}$ and $\text{CH}_2\text{CH}=\text{CH}_2$), 2.21-2.16 (m, 2H, two of $\text{CH}_2\text{CH}=\text{CH}$ and $\text{CH}_2\text{CH}=\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 143.8, 135.8, 134.3, 128.3, 127.4, 127.2, 125.7, 117.9, 73.4, 71.5, 41.9, 41.7; IR (thin film) 3368, 3075, 3030, 2932, 2360, 2012, 1641, 1604, 1494, 1453, 1322, 1028 cm^{-1} ; LRMS (FAB+, M+H) calc'd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ 219.14, found 220.84.

2R,4R-bis(di-4-methoxyphenylphosphino)pentane: $[\alpha]_{\text{D}}^{25} +56.1^\circ$ ($c = 1.53$, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.26 (m, 8H, 8 x ArH), 6.86-6.81 (m, 8H, 8 x ArH), 3.79 (s, 6H, 2 x OCH_3), 3.78 (s, 6H, 2 x OCH_3), 2.45-2.44 (m, 2H, 2 x CHP), 0.96 (dd, $J = 6.7$, 15.7 Hz, 6H, 2 x CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 160.2, 135.0, 134.8, 114.0, 55.1, 27.6, 15.7, 15.4; ^{31}P NMR (121.6 MHz, CDCl_3) δ -2.9; IR (thin film) 3001, 2958, 2836, 2360, 1594, 1568, 1498, 1463, 1283, 1248, 1177, 1095, 1030; HRMS (FAB+, M) calc'd for $\text{C}_{33}\text{H}_{38}\text{O}_4\text{P}_2$ 560.2245, found 560.2231.

2R,4R-bis(di-4-methylphenylphosphino)pentane: $[\alpha]_{\text{D}}^{25} +37.2^\circ$ ($c = 0.37$, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.27 (m, 8H, 8 x ArH), 7.10-7.06 (m, 8H, 8 x ArH), 2.55-2.45 (m, 2H, 2 x CHP), 2.30 (s, 6H, 2 x ArCH_3), 2.30 (s, 6H, 2 x ArCH_3), 1.36-1.25 (m, 2H, CH_2), 0.95 (dd, $J = 6.7$, 15.6 Hz, 6H, 2 x CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 134.5, 134.0, 29.7, 26.7, 21.9, 21.5; ^{31}P NMR (121.6 MHz, CDCl_3) δ -1.1; IR (thin film) 2924, 1725, 1601, 1454, 1276, 1173, 1116; LRMS (FAB+, M+H) calc'd for $\text{C}_{33}\text{H}_{39}\text{P}_2$ 497.25, found 497.40.

2R,4R-bis(di-4-fluorophenylphosphino)pentane: $[\alpha]_{\text{D}}^{25} +67.9^\circ$ ($c = 1.45$, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.39 (m, 8H, 8 x ArH), 7.05-6.99 (m, 8H, 8 x ArH), 2.40-2.20 (m, 2H, 2 x CHP), 1.33-1.25 (m, 2H, CH_2), 0.98 (dd, $J = 6.3$, 15.5 Hz, 6H, 2 x CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 165.3, 162.0, 135.4 (d, $J = 13.3$ Hz), 135.4 (d, $J = 20.8$ Hz), 35.7, 27.3; ^{31}P NMR (121.6 MHz, CDCl_3) δ -0.7; ^{19}F NMR (282 MHz, CDCl_3)

δ -111.3, -150.0; IR (thin film) 2924, 1588, 1495, 1230, 1159; LRMS (FAB+, M) calc'd for $C_{29}H_{26}F_4P_2$ 512.14, found 512.32.

2*R*,4*R*-bis(di-3,5-difluorophenylphosphino)pentane: $[a]_D^{25} +77.2^\circ$ ($c = 0.89$, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) 6.95-6.87 (m, 8H, 8 x ArH), 6.81-6.74 (m, 4H, 4 x ArH), 2.45-2.41 (m, 2H, 2 x CHP), 1.33-1.26 (m, 2H, CH_2), 1.03 (dd, $J = 6.8, 15.5$ Hz, 6H, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (dt, $J = 10.7, 252.7$ Hz), 140.0 (dd, $J = 6.3, 20.4$ Hz), 115.8 (t, $J = 22.0$ Hz), 105.0 (t, $J = 25.1$ Hz), 35.9 (t, $J = 23.5$ Hz); ^{31}P NMR (121.6 MHz, $CDCl_3$) δ -3.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -108.8, -108.9; IR (thin film) 2961, 2928, 1585, 1418, 1284, 1121; LRMS (FAB+, M+H) calc'd for $C_{29}H_{23}F_8P_2$ 585.11, found 585.27.

Stereochemical Proofs.

We have previously prepared diol **7**, and its stereochemistry was rigorously established.² We thus may conclude that diol **3** possesses the 1,5-*syn* stereochemistry. Working backwards, we may further derive the relative stereochemistry of silanes **1** and **5** based on the mechanism we have established for the conversion of **1** to **3** and **5** to **7**. Additional corroborating evidence was provided by an independent proof of the stereochemistry of silane **6** carried out as described below.

Silyl ether **6** was subjected to chloroplatinic acid hexahydrate-catalyzed hydrosilylation to provide oxasilacyclopentane **9** as shown in Figure 1. The illustrated nOe interactions established the relative stereochemistry at silicon. This establishes the stereochemistry of both **2** and **6**. The assignments for the products of entries 3, 4, 7, and 8, Table 2, were made based on analogy to silanes **1**, **2**, **5**, and **6**.

Figure 1. Conversion of silane **6** to oxasilacyclopentane **9**, and nOe interactions observed for **9**.

Data for silyl ether **9**: ^1H NMR (400 MHz, C_6D_6) δ 7.42-7.10 (m, 5H, ArH), 5.91-5.86 (m, 1H, $CHCH_2$), 5.72-5.71 (m, 1H, one of $SiCCH_2$), 5.36-5.35 (m, 1H, one of $SiCCH_2$), 5.05-4.95 (m, 3H, ArCH and $CHCH_2$), 2.66 (dd, $J = 4.9, 15.2$ Hz, 1H, one of $ArCHCH_2$), 2.41-2.33 (m, 1H, one of $ArCHCH_2$), 1.86 (dd, $J = 8.0, 13.9$ Hz, 1H, one of CH_2CHCH_2), 1.72 (dd, $J = 8.0, 18.5$ Hz, 1H, one of CH_2CHCH_2), 1.02 (s, 9H, $C(CH_3)_3$); ^{13}C NMR

(75 MHz, C_6D_6) δ 147.8, 144.9, 133.6, 127.3, 125.4, 123.5, 114.8, 48.2, 26.4, 20.3; IR (thin film) 2955, 2930, 2857, 1631, 1472, 1025 cm^{-1} ; LRMS (FAB+, M) calc'd for $C_{17}H_{24}OSi$ 272.16, found 272.10.

^1H NMR Spectra:

Assays for Diastereoselectivity. Table 2, entries 1 and 2 (^1H NMR assay):

Table 2, entries 3 and 4 (^1H NMR assay):

Table 2, entries 5 and 6 (GC assay):

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	51.104	BV	0.5899	3607.42334	72.66736	49.91345
2	52.764	VB	0.5259	3619.93335	81.82122	50.08655

Totals : 7227.35669 154.48858

Table 2, entry 5

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	50.502	MM	0.4847	78.88263	2.71266	10.03853
2	52.173	MM	0.5135	706.91626	22.94331	89.96147

Totals : 785.79889 25.65597

Table 2, entry 6

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	50.530	MM	0.5082	251.49921	8.24792	88.61131
2	51.867	MM	0.4187	32.32370	1.28680	11.38869

Totals : 283.82291 9.53472

Table 2, entries 7 and 8:

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	45.687	MM	1.0714	1.13829e4	177.07576	77.75546
2	46.708	MM	0.5098	3256.44824	106.45823	22.24454

Totals : 1.46393e4 283.53399

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.490	MM	0.7556	1363.41980	30.07513	12.13656
2	47.117	MM	0.9675	9870.57129	170.03558	87.86344

Totals : 1.12340e4 200.11071

¹H NMR spectrum