

Synthesis of (-)-7-Epiaustraline and (-)-1-Epicastanospermine

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SUPPORTING INFORMATION

General

Bulb-to-bulb distillations were done on a Büchi GKR-50 Kugelrohr apparatus; boiling points (bp) refer to air bath temperatures and are uncorrected. Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are uncorrected. Analytical TLC was performed on Merck silica gel plates (10 cm) with QF-254 indicator. Plates were visualized using UV radiation (254 nm) in conjunction with the following reagents: potassium permanganate (alkenes, nitro compounds, alcohols), anisaldehyde and vanillin (nitroso acetals), 2,4-dinitrophenylhydrazine (aldehydes), and I₂ (alkenes, aromatics). Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments SFC with an internal spectrophotometric detector (wavelength = 210 nm) on a Diacel Chiralcel OD (250 x 4.5 mm) column. Solvents for HPLC use were spectrometric grade and filtered prior to use. Medium-pressure liquid chromatography (MPLC) was performed using a Perkin Elmer V series LC pump equipped with a Glenco 5480 UV detector and a 40 x 5 cm Merck Lobar silica gel (Kieselgel 60G) column.

All reactions were performed in oven (140 °C) or flame-dried glassware under an inert atmosphere of dry N₂. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: hexane (CaCl₂); dichloromethane (CaCl₂); *tert*-butyl methyl ether (TBME) (CaSO₄/FeSO₄); ethyl acetate (K₂CO₃). Diethyl ether (Et₂O) and chloroform (CHCl₃) were reagent grade and used as received. Reaction solvents were distilled from the indicated drying agents: benzene (CaH₂ or sodium-benzophenone ketyl), dichloromethane (P₂O₅), diethylether (sodium-benzophenone ketyl), methanol (magnesium), and tetrahydrofuran (THF) (sodium-benzophenone ketyl). Column chromatography was performed by the method of Still,¹ using 230-400 mesh silica gel, purchased from EM Science, or the support indicated. Ion exchange chromatography was performed on AG 50W-X8 resin (DOWEX, 100-200 mesh, H form) or AG 1-X8 (20-50 mesh, OH form) purchased from Bio-Rad. The AG 50W-X8 column was prepared by washing the resin successively with conc. NH₄OH, H₂O, 3 M H₂SO₄, and H₂O. The AG 1-X8 column was prepared by washing the resin successively with 2 M NH₄OH, and H₂O. Reverse phase chromatography was performed on Prep-20D-60 ODS

(Regis Chemical Company) obtained from Prof. William H. Pirkle. Raney Nickel was weighed by introducing a quantity of the solid, with as much of the water removed as possible, into the tared reaction vessel containing H₂O. Commercial Grignard reagents were titrated according to the method of Watson and Eastham.² Hydride reagents were titrated according to the method of Brown.³ Brine refers to a saturated aqueous solution of sodium chloride. A pH 4 methanol buffer was prepared by diluting sodium acetate (2.60 g) and acetic acid (10 mL) to a final volume of 50 mL with methanol. A pH 7 buffer was prepared by diluting Na₂HPO₄ (43.4 g) and KH₂PO₄ (26.5 g) to a final volume of 500 mL with water. Ozonolyses were performed with a Welsbach model T-816 ozonator employing typically an oxygen pressure of 8 psi and 70 watts producing an ozone flow rate of 1.5 mmol/min.

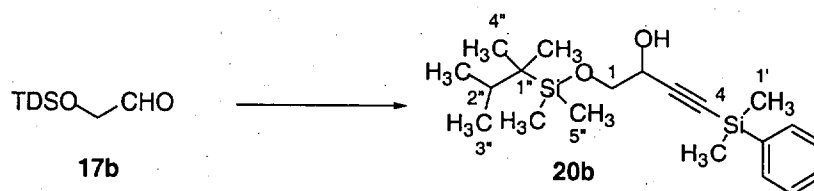
Optical rotations were obtained on a Jasco DIP-360 digital polarimeter and are reported as follows: $[\alpha]_{\text{wavelength}}^{\text{temperature}}$, concentration ($c = \text{g}/100 \text{ mL}$), and solvent. Eight measurements each at $\lambda = 589, 577, 546, 435, \text{ and } 405$ were averaged and plotted ($1/\alpha$ vs λ^2) to check for linearity. The value of $[\alpha]_{589}$ was quoted for non-linear plots and the value of $[\alpha]$ was generated by linear regression for linear plots. Infrared spectra (IR) were obtained on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67-100%), m (medium, 34-66%), w (weak, 0-33%). ¹H NMR and ¹³C NMR spectra were recorded on a Varian Inova 750 (750 MHz ¹H), Varian Inova 500 (500 MHz ¹H, 126 MHz ¹³C), a Varian Unity 500 (500 MHz ¹H, 126 MHz ¹³C), a Varian Unity 400 (400 MHz ¹H, 100 MHz ¹³C), a General Electric QE-300 (300 MHz ¹H, 75.5 MHz ¹³C), or a Varian XL-200 (200 MHz ¹H) spectrometer with CHCl₃ (δ 7.26 ppm for ¹H, 77.0 ppm for ¹³C) or tetramethylsilane (TMS) as an internal standard in CDCl₃. Spectra were also recorded in the following solvents: benzene [C₆D₆ (δ 7.15 ppm for ¹H, 128.0 ppm for ¹³C)], deuteriomethanol [CD₃OD (δ 3.30 ppm for ¹H, 49.0 ppm for ¹³C)], and deuterium oxide {D₂O [δ 4.67 ppm for ¹H, 128.0 ppm (benzene) for ¹³C]}. Chemical shifts are given in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or b (broadened). Coupling constants, J , are reported in Hertz. Mass spectra were obtained through the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. Low-resolution electron impact (EI) mass spectra were obtained on a Finnigan-MAT CH-5 spectrometer with a typical ionization voltage of 70 eV. Low-resolution chemical ionization (CI) mass spectra were obtained on a VG 70-VSE spectrometer using methane. Low-resolution fast atom bombardment (FAB) spectra were obtained on a VG ZAB-SE spectrometer in magic bullet (3/1, dithiothreitol/dithioerythritol) or 3-nitrobenzyl alcohol. Data are reported in the form m/z (intensity relative to base = 100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory and are the average of two combustions.

Literature Preparations

The following are known compounds prepared by standard methods: (t-hexyldimethylsilyl)oxyacetaldehyde (**17b**),⁴ (benzyloxy)acetaldehyde (**17a**),⁴ 1-(benzoyloxy)-2-nitroethene and nitronates ($\pm$)-**15** and (+)-**15**,⁵ phenyldimethylsilylethyne,⁴ 4-toluenesulfonic anhydride and methanesulfonic anhydride,⁶ and *trans*-phenylcyclohexyl vinyl ether.⁷

Experimental Procedures

1-[Dimethyl(1,1,2-trimethylpropyl)siloxy]-4-(dimethylphenylsilyl)-3-buten-2-ol (**20b**).



A solution of ethyl bromide (2.30 mL, 30.8 mmol, 1.25 equiv.) in Et₂O (12 mL) was added dropwise to a suspension of magnesium turnings (737 mg, 30.3 mmol, 1.23 equiv.) in Et₂O (13 mL) at a rate such as to maintain a gentle reflux. Upon complete addition, the reaction mixture was heated at reflux for 1.5 h then was allowed to cool to ambient temperature. A solution of alkyne **19** (4.95 g, 30.9 mmol, 1.25 equiv.) in THF (13 mL) was added dropwise over 15 min and the reaction mixture heated at reflux for 1 h. Upon cooling to RT, a solution of the aldehyde **17b** (5.00 g, 24.7 mmol) in THF (13 mL) was added dropwise over 15 min and the reaction mixture heated at reflux for 1 h, allowed to cool to ambient temperature, and quenched with sat. ammonium chloride. The contents of the reaction were poured onto water (300 mL) and extracted with pentane (3 x 100 mL). The organic phase was washed with water (100 mL) and brine (100 mL) and dried (Na₂SO₄). The crude material was purified by chromatography [hexane/EtOAc 15:1 (6 x 19 cm SiO₂)] and distilled (bulb to bulb) at high vacuum to provide the propargyl alcohol **20b** 7.71 g (86%) as a colorless liquid.

Analytical Data for **20b**:

bp: 175 °C (8.5 x 10⁻⁵ mm Hg)

¹H NMR: (500 MHz, CDCl₃)

7.63-7.61 and 7.39-7.35 (two m, 5 H, HC-Ph), 4.42 (ddd, 1 H, *J* = 6.2, 5.5, 3.8, HC-2), 3.77 (dd, 1 H, *J* = 10.1, 3.8, HC-1), 3.66 (dd, 1 H, *J* = 10.1, 6.4, HC-1), 2.60 (d, 1 H, *J* = 5.5, OH), 1.61 (sept., 1 H, *J* = 6.8, HC-2"), 0.88 (d, 6 H, *J*

= 6.8, HC-3"), 0.86 (s, 6 H, HC-4"), 0.42 (s, 6 H, HC-1'), 0.13 (two s, 3 H each, HC-5").

¹³C NMR: (126 MHz, CDCl₃)
136.5 (C-3'), 133.7 (C-Ph), 129.4 (C-Ph), 127.8 (C-Ph), 105.4 (C-3), 88.0 (C-4), 66.5 (C-1), 63.5 (C-2), 34.1 (C-2"), 25.1 (C-1"), 20.3 (C-3"), 18.5 (C-4"), -1.04 (C-1'), -3.50 (C-5").

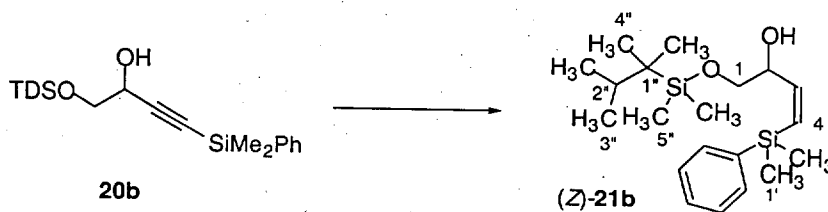
IR: (neat)
3568-3390 (b, w), 3070 (w), 2959 (s), 2868 (m), 2175 (w), 1466 (m), 1429 (m), 1408 (w), 1391 (w), 1379 (m), 1370 (w), 1366 (w), 1252 (s), 1117 (s), 1092 (s), 1065 (m), 1025 (m), 999 (w), 943 (w), 893 (m), 876 (m), 836 (s), 819 (s), 781 (s), 756 (m), 731 (s), 703 (m), 698 (s), 678 (w), 662 (w).

MS: (CI, CH₄)
364 ([M+H]⁺, 1.2), 363 (M⁺, 3.7), 346 (17), 345 (51), 262 (26), 261 (100), 149 (16), 73 (9).

Analysis: C₂₀H₃₄O₂Si₂ (362.66)
Calcd: C, 66.24%; H, 9.45%, Si, 15.49%.
Found: C, 66.07%; H, 9.41%; Si, 15.74%.

TLC: R_f 0.28 (hexane/EtOAc 9:1)

(Z)-1-[Dimethyl(1,1,2-trimethylpropyl)siloxy]-4-(dimethylphenylsilyl)-3-buten-2-ol ((Z)-21b).



Lindlar Hydrogenation Method

Palladium on calcium carbonate {201 mg [5 % (no lead content)]} was suspended in benzene (2 mL) and pre-hydrogenated for 20 min. Quinoline (130 μ L, 1.10 mmol, 0.2 equiv.) was added followed by a solution of alkyne **20b** (2.00 g, 5.51 mmol) in benzene (4 mL). The progress of the reaction was monitored by TLC and after 6 h 22 min, the starting material had been consumed. The catalyst was removed by filtration (Celite-Et₂O) and the eluent concentrated. [¹H NMR analysis indicated 91% conversion, 11.3:1 *cis:trans*) The crude material was purified by

chromatography [hexane/EtOAc 24:1 (1.6 L) then 19:1 (1L) (6 x 16 cm SiO₂)] to give 1.36 g of alcohol (Z)-**21b**. The alcohol was further purified by distillation (bulb to bulb) to provide 1.29 g (64%) of the *cis*-alkene as a colorless liquid.

Hydroboration Method (BH06.69)

Freshly distilled cyclohexene (3.4 mL, 34 mmol, 4 equiv.) was added dropwise over 5 min to a solution of BH₃·THF (1.0 M, 16.5 mL, 16.5 mmol, 2 equiv.) maintained at 0 °C. The reaction mixture was maintained for 1 h during which it gradually thickened. A solution of alkyne **20b** (3.00 g, 8.27 mmol) in THF (8 mL) was added dropwise to the white suspension over 15 min. The reaction mixture was maintained at 0 °C for 1 h (reaction mixture clarified) and then allowed to warm to ambient temperature. After 1 h, acetic acid (950 µL, 16.6 mmol, 2 equiv.) was added dropwise over 5 min and the reaction mixture maintained overnight (12 h). The contents of the reaction were diluted with Et₂O (100 mL) and washed with water (50 mL) and brine (50 mL). The combined aqueous layers were back-extracted with Et₂O (50 mL) and the organic layers dried (Na₂SO₄). The crude material was purified by chromatography [hexane/EtOAc 24:1 (6 x 19 cm SiO₂)] to give a colorless oil which was distilled (bulb to bulb) to provide 2.14 g (71%) of *cis*-alkene (Z)-**21b** as a colorless liquid (identical to the material prepared by Lindlar hydrogenation).

Analytical Data for (Z)-**21b**:

bp: 165 °C (7.0 x 10⁻⁵ mm Hg)

¹H NMR: (500 MHz, CDCl₃)

7.55-7.53 and 7.36-7.34 (two m, 5 H, HC-Ph), 6.32 (dd, 1 H, *J* = 14.5, 8.2, HC-3), 5.91 (d, 1 H, *J* = 14.3, HC-4), 4.19-4.16 (m, 1 H, HC-2), 3.43 (dd, 1 H, *J* = 10.1, 3.8, HC-1), 3.33 (dd, 1 H, *J* = 9.7, 7.9, HC-1), 2.48 (d, 1 H, *J* = 2.2, OH), 1.59 (sept., 1 H, *J* = 6.8, HC-2"), 0.85 (d, 6 H, *J* = 6.8, HC-3"), 0.82 (s, 6 H, HC-4"), 0.42 and 0.40 (two s, 3 H each, HC-5"), 0.05 and 0.03 (two s, 3 H each, HC-1').

¹³C NMR: (126 MHz, CDCl₃)

147.4 (C-3), 139.2 (C-Ph), 133.6 (C-Ph), 131.5 (C-4), 129.0 (C-Ph), 127.9 (C-Ph), 72.3 (C-1), 66.2 (C-2), 34.1 (C-2"), 25.1 (C-1"), 20.2 (C-3"), 18.5 (C-4"), -0.62 (C-1'), -0.94 (C-1'), -3.54 (C-5"), -3.59 (C-5").

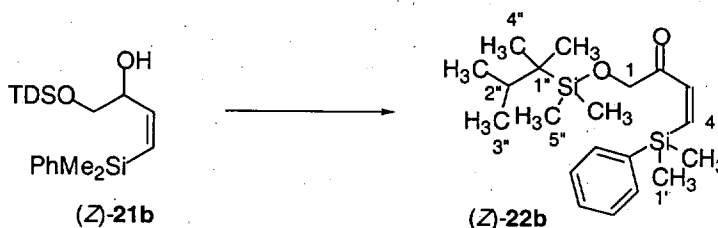
IR: (neat)

3570-3402 (b, w), 3069 (w), 3050 (w), 2958 (s), 2867 (m), 1613 (w), 1466 (m), 1428 (m), 1407 (w), 1391 (w), 1378 (m), 1313 (w), 1252 (s), 1190 (w), 1112 (s), 1064 (m), 1033 (m), 998 (w), 936 (w), 918 (w), 892 (m), 875 (m), 832 (s), 781 (s), 730 (s), 701 (s), 681 (m), 665 (w).

MS: (CI, CH₄)365 (M⁺, weak), 347 (18), 287 (80), 263 (61), 201 (16), 187 (25), 149 (59), 147 (100), 133 (36), 127 (48), 73 (34).**Analysis:** C₂₀H₃₆O₂Si₂ (364.68)

Calcd: C, 65.87%; H, 9.95%; Si, 15.40%.

Found: C, 65.90%; H, 10.28%; Si, 15.59%.

TLC: R_f 0.35 (hexane/EtOAc 9:1)**(Z)-1-[Dimethyl(1,1,2-trimethylpropyl)siloxy]-4-(dimethylphenylsilyl)-3-buten-2-one ((Z)-22b).**

A solution of dimethyl sulfoxide (1.55 mL, 21.5 mmol, 2.2 equiv.) in CH₂Cl₂ (80 mL) was cooled to -74 °C and treated with oxalyl chloride (955 μL, 10.9 mmol, 1.1 equiv.) in one portion. After 45 min, a solution of alcohol (Z)-21b (3.63 g, 9.95 mmol) in CH₂Cl₂ (18 mL) was added dropwise *via* cannula. The resultant cloudy mixture was maintained for 1 h before triethylamine (7.0 mL, 50 mmol, 5 equiv.) was introduced dropwise. The reaction mixture was maintained at -74 °C for 5 min and then allowed to warm over 15 min. The reaction mixture was diluted with pentane (300 mL) and washed with 0.1 M hydrochloric acid (100 mL), water (100 mL), and brine (100 mL). The combined aqueous layers were back-extracted with pentane (100 mL) and the organic layers dried (Na₂SO₄). The residue was purified by chromatography [pentane-Et₂O 1:0 (400 mL) then 39:1 (6 x 19 cm SiO₂)] and dried at 3.6 x 10⁻⁵ mm Hg to provide 3.51 g (97%) of ketone (Z)-22b as a light gold oil.

Analytical Data for (Z)-22b:**¹H NMR:** (500 MHz, CDCl₃)7.60-7.58 and 7.36-7.34 (two m, 5 H, HC-Ph), 7.22 (d, 1 H, *J* = 14.3, HC-3), 6.66 (d, 1 H, *J* = 14.3, HC-4), 4.24 (s, 2 H, HC-1), 1.66 (sept., 1 H, *J* = 6.8, HC-2"), 0.91 (d, 6 H, *J* = 7.0, HC-3"). 0.89 (s, 6 H, HC-4"), 0.47 (s, 6 H, HC-1'), 0.12 (s, 6 H, HC-5").

¹³C NMR: (126 MHz, CDCl₃)

199.5 (C-2), 150.2 (C-4), 139.5 (C-Ph), 138.3 (C-3), 133.7 (C-Ph), 128.7 (C-Ph), 127.6 (C-Ph), 69.3 (C-1), 34.1 (C-2"), 25.2 (C-1"), 20.2 (C-3"), 18.5 (C-4"), -2.55 (C-1'), -3.54 (C-5").

IR: (neat)

2958 (m), 2900 (w), 2867 (w), 1715 (w), 1694 (m), 1574 (w), 1466 (w), 1428 (w), 1377 (w), 1368 (m), 1253 (s), 1187 (w), 1172 (w), 1111 (s), 1061 (m), 872 (m), 833 (s), 822 (s), 781 (s), 734 (m), 700 (m), 669 (w).

MS: (CI, CH₄)

364 ([M+H]⁺, 3.6), 363 (M⁺, 11), 347 (30), 285 (22), 277 (46), 263 (14), 201 (100), 149 (50), 133 (83), 129 (66), 73 (41), 59 (55).

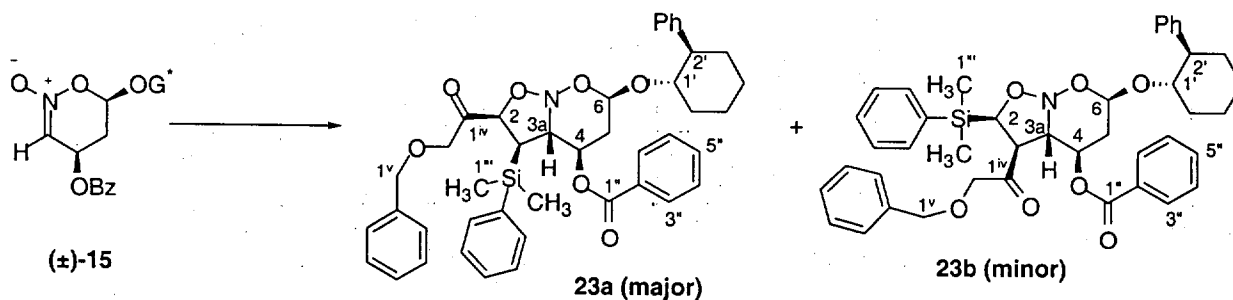
Analysis: C₂₀H₃₄O₂Si₂ (362.66)

Calcd: C, 66.24%; H, 9.45%; Si, 15.49%.

Found: C, 66.40%; H, 9.36%; Si, 15.32%.

TLC: R_f 0.57 (hexane/EtOAc 15:1)

rel-(2*S*,3*R*,3*aS*,4*R*,6*R*)-4-Benzoyloxy-2-(dimethylphenylsilyl)-6-[(1*S*,2*R*)-(2-phenylcyclohexyl)oxy]-3-[2-(phenylmethoxy)-1-oxoethyl]hexahydroisoxazolo-[1,7b][1,2]oxazine (23a) and *rel*-(2*S*,3*R*,3*aR*,4*R*,6*R*)-4-Benzoyloxy-3-(dimethylphenylsilyl)-6-[(1*S*,2*R*)-(2-phenylcyclohexyl)oxy]-2-[2-(phenylmethoxy)-1-oxoethyl]hexahydroisoxazolo-[1,7b][1,2]oxazine (23b).



Nitronate (±)-15 (469 mg, 1.19 mmol) was added to a solution of ketone (Z)-22b (443 mg, 1.43 mmol, 1.2 equiv.) in benzene (12 mL) and the reaction mixture was maintained at ambient temperature (23 °C) for 5 h. Upon concentration of the solution *in vacuo*, the residue was purified by chromatography [pentane/Et₂O 4:1 (5 x 15 cm SiO₂)]. The major nitroso acetal was dried by azeotropic removal of water (benzene) and further dried at high vacuum (10⁻⁵ mm Hg) to

provide **23a** 806 mg (96%) as a colorless foam. A sample of the sensitive minor nitroso acetal **23b** (14.5 mg, 1.7 %) was also obtained.

Data for 23b (minor):

¹H NMR: (500 MHz, CDCl₃)

7.90 (d, 2 H, $J = 8.3$, HC-3", 7"), 7.55 (t, 1 H, $J = 7.6$, HC-5"), 7.47 (d, 2 H, $J = 7.8$, HC-Ph), 7.40 (t, 2 H, $J = 8.1$, HC-4", 6"), 7.37-7.15 (m, 14 H, HC-Ph), 4.83 (dt, 1 H, $J_d = 10.5$, $J_t = 4.6$, HC-4), 4.70 (d, 1 H, $J = 10.7$, HC-2), 4.18 and 4.12 (two d, 1 H each, $J = 12.0$, HC-1^v), 4.16 (t, 1 H, $J = 6.6$, HC-6), 3.87 (dd, 1 H, $J = 8.3$, 4.6, HC-3a), 3.81 (dd, 1 H, $J = 10.7$, 8.5, HC-3), 3.60 (dt, 1 H, $J_d = 4.2$, $J_t = 10.3$, HC-1'), 3.44 and 3.40 (two d, 1 H each, $J = 17$, HC-2^{iv}), 2.52 (ddd, 1 H, $J = 12.9$, 10.3, 3.4, HC-2'), 2.37 (apparent dd, 1 H, $J = 12.7$, 3.4, HC-6'), 1.92-1.86 (m, 3 H, HC-5, 3', 5'), 1.77 (bd, 1 H, $J = 12.9$), 1.68-1.42 (m, 6 H), 1.37-1.28 (m, 1 H), 0.38 and 0.36 (two s, 3 H each, HC-1''').

¹³C NMR: (126 MHz, CDCl₃)

Select ¹³C resonances taken from HETCOR: 98.4 (C-6), 82.1 (C-1'), 78.8 (C-2), 78.6 (C-3a), 75.7 (C-2^{iv}), 72.4 (C-1^v), 69.5 (C-4), 52.8 (C-3), 51.1 (C-2').

Analytical Data for 23a (major):

¹H NMR: (500 MHz, CDCl₃)

8.03 (d, 2 H, $J = 7.6$, HC-3", 7"), 7.59 (t, 1 H, $J = 7.3$, HC-5"), 7.47 (t, 2 H, $J = 7.6$, HC-4", 6"), 7.39-7.13 (m, 15 H, HC-Ph), 5.06 (d, 1 H, $J = 9.8$, HC-2), 4.69 (ddd, 1 H, $J = 8.5$, 4.4, 4.2, HC-4), 4.40 (s, 2 H, HC-2^{iv}), 4.15 (t, 1 H, $J = 5.6$, HC-6), 3.94 and 3.89 (two d, 1 H each, $J = 18.6$, HC-1^v), 3.71 (dd, 1 H, $J = 12.7$, 3.9, HC-3a), 3.59 (dt, 1 H, $J_d = 4.4$, $J_t = 10.5$, HC-1'), 2.53-2.48 (m, 1 H, HC-2'), 2.39-2.36 (m, 1 H, HC-6'), 2.31 (dd, 1 H, $J = 12.7$, 9.8, HC-3), 1.87-1.84 (m, 2 H, HC-3', 5'), 1.76-1.73 (m, 1 H, HC-5), 1.66 (ddd, 1 H, $J = 13.9$, 5.6, 5.4, HC-5), 1.63-1.23 (m, 5 H, HC-3', 4', 5', 6'), 0.41 and 0.37 (two s, 3 H each, HC-1''').

¹³C NMR: (126 MHz, CDCl₃)

205.0 (C-1^{iv}), 165.0 (C-1"), 144.1 (C-Ph), 137.1 (C-Ph), 137.0 (C-Ph), 133.7 (C-Ph), 133.3 (C-5"), 129.8 (C-Ph), 129.7 (C-3", 7"), 129.4 (C-Ph), 128.42 (C-4", 6"), 128.39 (C-Ph), 128.1 (C-Ph), 128.01 (C-Ph), 127.97 (C-Ph), 127.92 (C-Ph), 127.7 (C-Ph), 126.3 (C-Ph), 99.2 (C-6), 88.6 (C-2), 82.5 (C-1'), 74.6 (C-3a), 73.8 (C-1^v), 73.1 (C-2^{iv}), 69.2 (C-4), 51.2 (C-2'), 34.7 (C-6'), 32.7 (C-3'), 32.1 (C-3), 29.6 (C-5), 25.8 (C-4'), 25.2 (C-5'), -2.7 (C-1'''), -3.2 (C-1''').

IR: (CCl₄)

3070 (w), 3031 (w), 2932 (m), 2903 (w), 2858 (w), 1725 (m), 1451 (w), 1316 (w), 1271 (s), 1253 (m), 1178 (w), 1140 (w), 1115 (s), 1106 (s), 1078 (w), 1070 (m), 1051 (m), 1027 (m), 908 (w), 799 (s), 795 (w), 782 (w), 774 (m), 768 (w), 765 (w), 762 (w), 755 (s), 746 (m), 737 (m), 711 (s), 700 (s).

MS: (FAB)

706 ([M+H]⁺, 5.6), 688 (10), 530 (12), 500 (3), 408 (3), 380 (4), 287 (8.8), 273 (9.1), 243 (13), 241 (17), 211 (11), 201 (8), 181 (16), 180 (12), 179 (57), 167 (11), 165 (15), 160 (38), 159 (84), 158 (12), 157 (15), 151 (10), 149 (11), 137 (29), 136 (34), 135 (89), 129 (17), 123 (20), 120 (13), 118 (25), 117 (50), 114 (16), 107 (16), 106 (33), 104 (100).

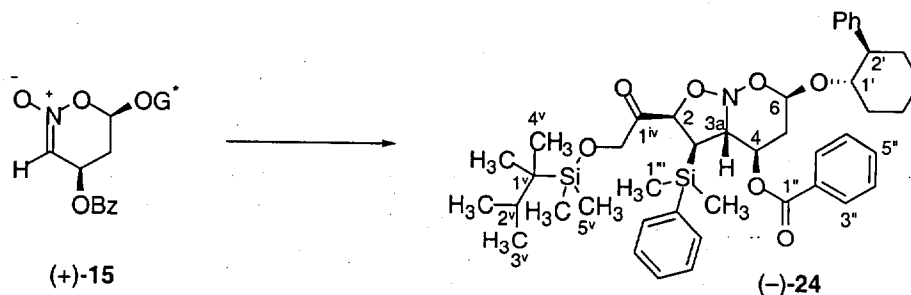
Analysis: C₄₂H₄₇NO₇Si (705.93)

Calcd: C, 71.46%; H, 6.71%; N, 1.98%; Si, 3.98%

Found: C, 71.19%; H, 6.70%; N, 1.93%; Si, 4.27%

TLC: R_f 0.30 (hexane/EtOAc 4:1)

(2*S*,3*R*,3*aR*,4*R*,6*R*)-4-Benzoyloxy-2-{2-[dimethyl(1,1,2-trimethylpropyl)]-1-oxoethyl}-3-(dimethylphenylsilyl)-6-[(1*S*,2*R*)-(2-phenylcyclohexyl)oxy]hexahydroisoxazolo-[1,7*b*][1,2]oxazine ((-)-24).



Nitronate (+)-15 (1.06 g, 2.68 mmol) was added to a solution of ketone (Z)-22b (1.17 g, 3.21 mmol, 1.2 equiv.) in benzene (25 mL) and the reaction mixture was maintained at ambient temperature (23 °C) for 12 h. Upon concentration of the solution *in vacuo*, the residue was purified by chromatography [pentane/Et₂O 9:1 (800 mL) then 7:3 (6 x 15 cm SiO₂)]. The nitroso acetal was dried under high vacuum (7.5 x 10⁻⁵ mm Hg) to provide (-)-24 1.96 g (97%) as a colorless foam.

Analytical Data for (-)-24:¹H NMR: (500 MHz, CDCl₃)

8.01 (dd, 2 H, $J = 8.4, 1.3$, HC-3", 7"), 7.59 (tt, 1 H, $J = 7.5, 1.3$, HC-5"), 7.47 (t, 2 H, $J = 7.9$, HC-4", 6"), 7.36 (dd, 2 H, $J = 8.1, 1.3$, HC-Ph), 7.30 (tt, 1 H, $J = 7.5, 1.3$, HC-Ph), 7.21 (t, 4 H, $J = 7.5$, HC-Ph), 7.15 (dt, 3 H, $J_d = 1.3, J_t = 7.9$, HC-Ph), 5.11 (d, 1 H, $J = 9.5$, HC-2), 4.62 (ddd, 1 H, $J = 8.8, 4.6, 4.2$, HC-4), 4.16 (t, 1 H, $J = 5.7$, HC-6), 4.13 and 4.08 (two d, 1 H each, $J = 18.8$, HC-2^{iv}), 3.73 (dd, 1 H, $J = 12.4, 4.0$, HC-3a), 3.59 (dt, 1 H, $J_d = 4.2, J_t = 10.4$, HC-1'), 2.51 (ddd, 1 H, $J = 13.0, 10.2, 3.5$, HC-2'), 2.42-2.38 (bm, 1 H, HC-6'), 2.30 (dd, 1 H, $J = 12.6, 9.9$, HC-3), 1.86 (bd, 2 H, $J = 12.4$, HC-3', 5'), 1.75 (bd, 1 H, $J = 13.0$, HC-4'), 1.68-1.40 (m, 6 H, HC-5, 3', 4', 6', 2^v), 1.31 (tt, 1 H, $J = 12.8, 3.5$, HC-5'), 0.88 (d, 6 H, $J = 6.8$, HC-3^v), 0.84 (s, 6 H, HC-4^v), 0.39 and 0.37 (two s, 3 H each, HC-1'''), 0.05 and 0.03 (two s, 3 H each, HC-5^v).

¹³C NMR: (126 MHz, CDCl₃)

205.9 (C-1^{iv}), 165.0 (C-1'''), 144.1 (C-Ph), 137.3 (C-Ph), 133.7 (C-Ph), 133.2 (C-5''), 129.8 (C-Ph), 129.7 (C-Ph), 129.37 (C-3", 7"), 129.36 (C-Ph), 128.1 (C-4", 6"), 128.0 (C-Ph), 127.7 (C-Ph), 126.3 (C-Ph), 99.2 (C-6), 88.2 (C-2), 82.5 (C-1'), 74.6 (C-3a), 69.3 (C-4), 68.2 (C-2^{iv}), 51.2 (C-2'), 34.7 (C-6'), 34.0 (C-2^v), 32.8 (C-3'), 32.0 (C-3), 29.7 (C-5), 25.8 (C-4'), 25.2 (C-5', 1^v), 20.21 (C-3^v), 20.18 (C-3^v), 18.47 (C-4^v), 18.44 (C-4^v), -2.53 (C-1'''), -3.40 (C-1'''), -3.51 (C-5^v), -3.56 (C-5^v).

IR: (CCl₄)

3072 (w), 2958 (m), 2931 (m), 1720 (m), 1451 (w), 1428 (w), 1316 (w), 1271 (s), 1253 (m), 1177 (m), 1139 (w), 1116 (s), 1107 (s), 1099 (m), 1078 (w), 1070 (m), 1051 (m), 1027 (w), 998 (w), 917 (w), 875 (w), 832 (s), 819 (w), 798 (w), 781 (w), 776 (s), 764 (w), 760 (w), 747 (w), 711 (s), 700 (s), 687 (w), 668 (w).

MS: (FAB)

759 ([M+H]⁺, 1.2), 758 (M⁺, 2.1), 740 (6), 606 (4), 582 (4), 460 (6), 431 (9), 345 (12), 288 (7), 269 (11), 253 (10), 211 (49), 179 (59), 159 (93), 135 (99), 117 (43), 105 (100).

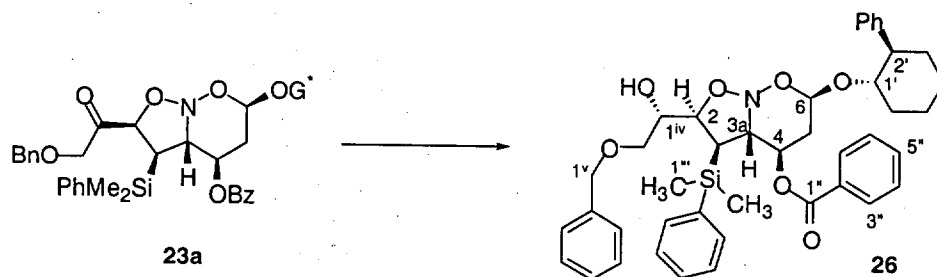
Rotation: [α]_D²³ -32.3 ° (c 1.07, CHCl₃)Analysis: C₄₃H₅₉NO₇Si₂ (758.12)

Calcd: C, 68.13%; H, 7.84%; N, 1.85%; Si, 7.41%

Found: C, 68.02%; H, 7.87%; N, 1.90%; Si, 7.27%

TLC: R_f 0.49 (hexane/EtOAc 4:1)

rel-(2*R*,3*R*,3*aR*,4*R*,6*R*)-4-Benzoyloxy-3-(dimethylphenylsilyl)-6-[(1*S*,2*R*)-(2-phenylcyclohexyl)oxy]-2-[(1*S*)-2-(phenylmethoxy)-1-(hydroxy)ethyl]hexahydroisoxazolo-[1,7*b*][1,2]oxazine (26).



L-Selectride (0.71 M, 1.6 mL, 1.1 mmol, 1.1 equiv.) was added dropwise over 5 min to a solution of nitroso acetal **23a** (710 mg, 1.01 mmol) in THF (17 mL) maintained at -74°C . After 3 h, the reaction was quenched with 1:1 glycerol/pH 7 (aq.) buffer (5 mL), diluted with CH_2Cl_2 (150 mL), and washed with water (2 x 50 mL) and brine (50 mL). The combined aqueous layers were back-extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried (Na_2SO_4). The residue was purified by chromatography [hexane/EtOAc 4:1 (5 x 10 cm SiO_2)] to give 667 mg (93%) of a foam. Crystallization from EtOAc/hexane provided 597 mg (83%) of nitroso acetal **26** as colorless needles.

Analytical Data for **26**:

mp: $165\text{--}166^{\circ}\text{C}$

$^1\text{H NMR}$: (500 MHz, CDCl_3)

8.03 (dd, 2 H, $J = 8.1, 0.9$, HC-3", 7"), 7.58 (t, 1 H, $J = 7.5$, HC-5"), 7.46 (t, 2 H, $J = 7.7$, HC-4", 6"), 7.44 (t, 1 H, $J = 7.3$, HC-Ph), 7.34-7.14 (m, 13 H, HC-Ph), 4.73 (d, 1 H, $J = 9.7$, HC-2), 4.66 (ddd, 1 H, $J = 8.8, 4.6, 4.4$, HC-4), 4.40 and 4.38 (two d, 1 H each, $J = 12.3$, HC-1^v), 4.14 (t, 1 H, $J = 5.7$, HC-6), 3.94 (dd, 1 H, $J = 12.8, 4.2$, HC-3a), 3.73 (dd, 1 H, $J = 13.2, 7.7$, HC-1^{iv}), 3.61 (dt, 1 H, $J_d = 4.4, J_t = 10.4$, HC-1ⁱ), 3.45 (dd, 1 H, $J = 9.5, 7.9$, HC-2^{iv}), 3.37 (dd, 1 H, $J = 9.7, 5.5$, HC-2^{iv}), 2.53-2.48 (m, 1 H, HC-2'), 2.42-2.40 (m, 1 H, HC-6'), 2.30 (dd, 1 H, $J = 12.6, 9.9$, HC-3), 1.93 (d, 1 H, $J = 7.5$, OH), 1.86 (bd, 2 H, $J = 12.3$, HC-3', 4'), 1.75 (bd, 1 H, $J = 12.6$, HC-5'), 1.69 (ddd, 1 H, $J = 13.7, 5.7, 4.9$, HC-5), 1.63-1.52 (m, 3 H, HC-5, 3', 6'), 1.49-1.41 (m, 1 H, HC-4'), 1.35-1.27 (m, 1 H, HC-5'), 0.44 and 0.36 (two s, 3 H each, HC-1ⁱⁱⁱ).

Et₂O (300 mL), and washed with water (100 mL) and brine (100 mL). The combined aqueous layers were back-extracted with Et₂O (100 mL) and dried (Na₂SO₄). The residue was purified by chromatography [hexane/EtOAc 6:1 (5 x 19 cm SiO₂)] to give 2.16 g (97%, 14:1 d.r.) of an oil which solidified upon standing. Recrystallization from hexane provided 1.93g (87%) of nitroso acetal (-)-**27** as colorless needles.

Analytical Data for (-)-**27**:

mp: 131-132 °C

¹H NMR: (500 MHz, CDCl₃)

8.07 (dd, 2 H, *J* = 8.1, 1.0, HC-3", 7"), 7.64 (t, 1 H, *J* = 7.3, HC-5"), 7.51 (t, 2 H, *J* = 7.8, HC-4", 6"), 7.38 (d, 2 H, *J* = 7.6, HC-Ph), 7.37 (t, 1 H, *J* = 7.6, HC-Ph), 7.31-7.20 (m, 7 H, HC-Ph), 4.82 (d, 1 H, *J* = 9.5, HC-2), 4.66 (ddd, 1 H, *J* = 9.3, 4.6, 4.4, HC-4), 4.21 (t, 1 H, *J* = 6.1, HC-6), 4.01 (dd, 1 H, *J* = 12.7, 4.2, HC-3a), 3.67 (dt, 1 H, *J*_d = 4.4, *J*_t = 10.5, HC-1'), 3.57 (dd, 2 H, *J* = 12.5, 7.1, HC-1^{iv}, 2^{iv}), 3.42 (dd, 1 H, *J* = 12.6, 9.3, HC-2^{iv}), 2.59-2.54 (m, 1 H, HC-2'), 2.50-2.47 (m, 1 H, HC-6'), 2.35 (dd, 1 H, *J* = 12.7, 9.8, HC-3), 2.00 (d, 1 H, *J* = 6.7, OH), 1.91 (bd, 2 H, *J* = 12.7, HC-3', 5'), 1.82-1.74 (m, 2 H, HC-5, 6'), 1.69-1.59 (m, 4 H, HC-5, 3', 4', 2^v), 1.54-1.46 (m, 1 H, HC-4'), 1.40-1.32 (m, 1 H, HC-5'), 0.89 (d, 6 H, *J* = 6.8, HC-3^v), 0.84 (s 6 H, HC-4^v), 0.48 and 0.42 (two s, 3 H each, HC-1'''), 0.073 and 0.066 (two s, 3 H each, HC-5^v).

¹³C NMR: (126 MHz, CDCl₃)

165.1 (C-1"), 144.2 (C-Ph), 137.4 (C-Ph), 133.4 (C-Ph), 133.1 (C-5"), 129.9 (C-3", 7"), 129.7 (C-Ph), 129.4 (C-4", 6"), 128.3 (C-Ph), 128.1 (C-Ph), 127.8 (C-Ph), 126.3 (C-Ph), 99.1 (C-6), 86.9 (C-2), 82.2 (C-1'), 74.7 (C-3a), 72.1 (C-1^{iv}), 70.0 (C-4), 64.2 (C-2^{iv}), 51.2 (C-2'), 34.7 (C-6'), 34.0 (C-2^v), 32.8 (C-3'), 31.3 (C-3), 29.8 (C-5), 25.8 (C-1^v), 25.2 (C-4'), 25.0 (C-5'), 20.24 (C-3^v), 20.18 (C-3^v), 18.5 (C-4^v), 18.4 (C-4^v), -2.86 (C-5^v), -3.16 (C-5^v), -3.60 (C-1'''), -3.63 (C-1''').

IR: (KBr)

3514 (m), 3069 (w), 3028 (w), 2955 (s), 2954 (s), 2931 (s), 2864 (s), 2858 (s), 1722 (s), 1703 (s), 1601 (w), 1585 (w), 1464 (m), 1451 (s), 1428 (m), 1391 (m), 1378 (m), 1348 (m), 1340 (m), 1318 (s), 1296 (s), 1271 (s), 1255 (s), 1179 (m), 1110 (s), 1071 (s), 1056 (s), 1036 (s), 1027 (s), 984 (m), 947 (m), 932 (s), 896 (s), 875 (m), 844 (s), 831 (s), 811 (s), 776 (s), 756 (s), 730 (s), 715 (s), 700 (s).

MS: (CI)

761 ([M+H]⁺, 2.3), 760 (M⁺, 4), 744 (1.7), 584 (6.6), 446 (12), 430 (6), 360 (6), 330 (5), 253 (5), 244 (8), 241 (5), 211 (5), 211 (5), 209 (8), 179 (21), 176 (15), 175 (19), 159 (100), 161 (6), 160 (20), 158 (12), 157 (15), 149 (12), 147 (10), 143 (11), 137 (31), 135 (40), 133 (11), 123 (96), 119 (30), 105 (60), 91 (57).

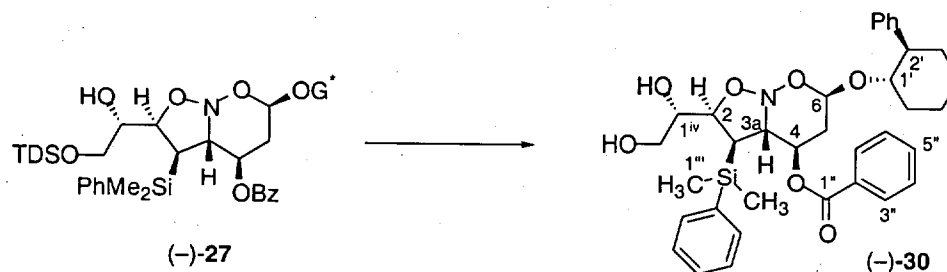
Rotation: $[\alpha]_D^{23}$ -31.3° (c 1.32, CHCl₃)**Analysis:** C₄₃H₆₁NO₇Si₂ (760.14)

Calcd: C, 67.95%; H, 8.09%; N, 1.84%; Si, 7.39%

Found: C, 68.11%; H, 8.22%; N, 1.94%; Si, 7.50%

TLC: R_f 0.33 (hexane/EtOAc 4:1)

(2R,3R,3aR,4R,6R)-4-Benzoyloxy-2-[(1S)-1,2-dihydroxyethyl]-3-(dimethylphenylsilyl)-6-[(1S,2R)-(2-phenylcyclohexyl)oxy]hexahydroisoxazolo-[1,7b][1,2]oxazine ((-)-30).



A solution of tetrabutylammonium fluoride (1.0 M, 3.2 mL, 3.2 mmol, 1.2 equiv.) was added dropwise over 3 min to a solution of nitroso acetal (-)-**27** (2.03 g, 2.67 mmol) in THF (26 mL) maintained at 0 °C. After 5 min, the yellow reaction mixture was allowed to warm to ambient temperature and maintained for 1 h. The orange-brown reaction mixture was poured onto water (150 mL) and extracted with Et₂O (200 mL). The organic layer was washed with water (150 mL) and brine (150 mL). The combined aqueous layers were back-extracted with Et₂O (2 x 75 mL) and the combined organic layers dried (Na₂SO₄). The residue was purified by chromatography [hexane/EtOAc 1:1 (6 x 12 cm SiO₂)] to give a light yellow oil which solidified upon standing. Recrystallization from CH₂Cl₂/pentane and drying at 10⁻⁵ mm Hg provided 1.17g (71%) of nitroso acetal (-)-**30** as colorless, spiny needles.

Analytical Data for (-)-30:

mp: 177-178 °C (dec.)

¹H NMR: (500 MHz, CDCl₃)

8.04 (d, 2 H, *J* = 7.6, HC-3", 7"), 7.59 (t, 1 H, *J* = 7.6, HC-5"), 7.46 (t, 2 H, *J* = 7.8, HC-4", 6"), 7.42 (d, 2 H, *J* = 6.8, HC-Ph), 7.33 (t, 1 H, *J* = 7.1, HC-Ph), 7.25 and 7.22 (two t, 4 H, *J* = 7.3, HC-Ph), 7.18-7.14 (m, 3 H, HC-Ph), 4.69 (d, 1 H, *J* = 9.8, HC-2), 4.62 (ddd, 1 H, *J* = 9.3, 4.6, 4.3, HC-4), 4.15 (t, 1 H, *J* = 5.9, HC-6), 3.96 (dd, 1 H, *J* = 12.7, 4.4, HC-3a), 3.66 (ddd, 1 H, *J* = 10.5, 6.6, 3.4, HC-2^{iv}), 3.62-3.53 (m, 2 H, HC-1', 1^{iv}), 3.45 (ddd, 1 H, *J* = 11.7, 8.5, 4.2, HC-2^{iv}), 2.57-2.49 (m, 2 H, HC-2', OH), 2.39-2.33 (m, 2 H, HC-6', OH), 2.28 (dd, 1 H, *J* = 12.7, 9.5, HC-3), 1.86 (bd, 1 H, *J* = 12.5, HC-3'), 1.80-1.69 (m, 2 H, HC-5, 5'), 1.63-1.53 (m, 2 H, HC-5, 3'), 1.48-1.40 (m, 1 H, HC-6'), 1.35-1.27 (m, 1 H, HC-5'), 0.44 and 0.36 (two s, 3 H each, HC-1''').

¹³C NMR: (126 MHz, CDCl₃)

165.1 (C-1"), 144.0 (C-Ph), 137.3 (C-Ph), 133.4 (C-Ph), 133.2 (C-5"), 129.7 (C-3", 7"), 129.5 (C-Ph), 128.4 (C-Ph), 128.14 (C-4", 6"), 128.09 (C-Ph), 127.8 (C-Ph), 126.3 (C-Ph), 99.3 (C-6), 89.4 (C-2), 82.6 (C-1'), 74.7 (C-3a), 71.4 (C-1^{iv}), 69.9 (C-4), 64.7 (C-2^{iv}), 51.2 (C-2'), 34.7 (C-6'), 32.7 (C-3'), 31.4 (C-3), 29.7 (C-5), 25.8 (C-4'), 25.2 (C-5'), -2.72 (C-1'''), -3.30 (C-1''').

IR: (KBr)

3522-3420 (b, m), 3068 (w), 3028 (w), 2930 (s), 2857 (m), 1721 (s), 1602 (w), 1493 (w), 1451 (s), 1428 (m), 1406 (w), 1384 (w), 1350 (m), 1340 (m), 1316 (m), 1273 (s), 1221 (w), 1178 (m), 1108 (s), 1100 (s), 1069 (s), 1052 (s), 1027 (s), 1003 (w), 983 (m), 947 (m), 928 (m), 885 (m), 849 (m), 816 (s), 772 (s), 758 (s), 736 (m), 713 (s), 702 (s), 656 (w), 626 (w).

MS: (FAB)

619 ([M+H]⁺, 1.7), 618 (M⁺, 4), 600 (15), 496 (3), 466 (4), 442 (11), 259 (4), 302 (3), 241 (3), 179 (34), 159 (69), 135 (58), 117 (26), 105 (100).

Rotation: [α]_D²³ -39.1 ° (c 0.93, CHCl₃)

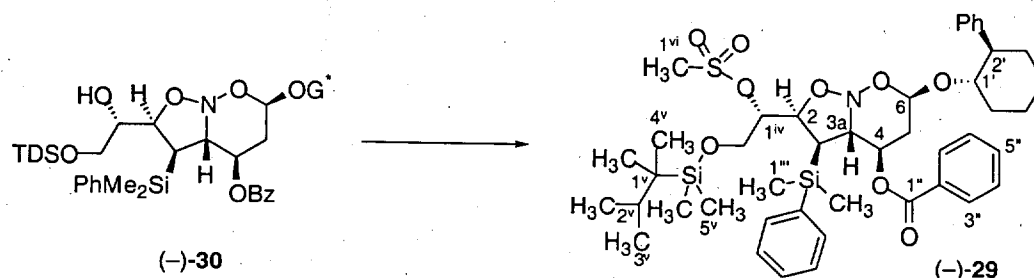
Analysis: C₃₅H₄₃NO₇Si (617.82)

Calcd: C, 68.04%; H, 7.02%; N, 2.27%; Si, 4.55%

Found: C, 68.01%; H, 7.11%; N, 2.22%; Si, 4.51%

TLC: R_f 0.26 (hexane/EtOAc 1:1)

(2*R*,3*R*,3*aR*,4*R*,6*R*)-4-Benzoyloxy-2-[(1*S*)-2-[dimethyl(1,1,2-trimethylpropyl)siloxy]-1-[(methanesulfonyl)oxy]ethyl]-3-(dimethylphenylsilyl)-6-[(1*S*,2*R*)-(2-phenylcyclohexyl)oxy]hexahydroisoxazolo-[1,7*b*][1,2]oxazine ((-)-29).



Methanesulfonic anhydride (1.12 g, 6.43 mmol, 6 equiv.) was added in one portion to a solution of nitroso acetal (-)-30 (815 mg, 1.07 mmol) in pyridine (3.6 mL) at room temperature. The reaction mixture became a thick, brown suspension. After 10 min, the reaction mixture was transferred to a SiO₂ column (6 x 16 cm) and purified by chromatography (hexane/EtOAc 4:1). The resultant foam was dried at 4 x 10⁻⁴ mm Hg to provide 863 mg (96%) of mesylate (-)-29.

Analytical Data for (-)-29:

¹H NMR: (500 MHz, C₆D₆)

8.18 (d, 2 H, *J* = 7.3, HC-3", 7"), 7.37-7.35 (m, 2 H, HC-Ph), 7.16-7.04 (m, 10 H, HC-Ph), 5.12 (d, 1 H, *J* = 9.3, HC-2), 5.08 (ddd, 1 H, *J* = 8.1, 7.3, 5.4, HC-4), 4.69 (t, 1 H, *J* = 5.4, HC-1^{iv}), 4.32 (t, 1 H, *J* = 5.1, HC-6), 4.23 (dd, 1 H, *J* = 12.0, 4.5, HC-3a), 4.00 (dd, 1 H, *J* = 10.5, 5.6, HC-2^{iv}), 3.82 (dd, 1 H, *J* = 10.5, 7.1, HC-2^{iv}), 3.78 (dt, 1 H, *J*_d = 4.2, *J*_t = 10.5, HC-1'), 2.78 (bd, 1 H, *J* = 12.2, HC-6'), 2.58-2.53 (m, 1 H, HC-2'), 2.47 (dd, 1 H, *J* = 12.0, 9.3, HC-3), 2.31 (s, 3 H, HC-1^{vi}), 1.87-1.82 (m, 2 H, HC-5), 1.73-1.63 (m, 3 H, HC-3', 5', 6'), 1.54-1.38 (m, 4 H, HC-3', 4', 6', 2'), 1.28-1.20 (m, 1 H, HC-4'), 1.29-1.05 (m, 1 H, HC-5'), 0.85 (d, 6 H, *J* = 6.8, HC-3^v), 0.77 (s, 6 H, HC-4^v), 0.62 and 0.35 (two s, 3 H each, HC-1ⁱⁱⁱ), -0.02 and -0.07 (two s, 3 H each, HC-5^v).

¹³C NMR: (126 MHz, C₆D₆)

165.5 (C-1"), 144.8 (C-Ph), 137.2 (C-Ph), 134.0 (C-Ph), 133.2 (C-5"), 130.4 (C-3", 7"), 130.1 (C-Ph), 129.8 (C-4", 6"), 128.6 (C-Ph), 128.5 (C-Ph), 128.4 (C-Ph), 127.8 (C-Ph), 126.6 (C-Ph), 98.9 (C-6), 84.7 (C-2), 81.6 (C-1^{iv}), 81.4 (C-1'), 74.8 (C-3a), 70.3 (C-4), 62.1 (C-2^{iv}), 51.8 (C-2'), 39.1 (C-1^{vi}), 35.2 (C-

6'), 34.3 (C-2^v), 33.0 (C-3'), 31.3 (C-3), 30.4 (C-5), 26.1 (C-1^v), 25.4 (C-4'), 25.3 (C-5'), 20.4 (C-3^v), 18.7 (C-4^v), -1.65 (C-5^v), -3.62 (C-1'''), -3.64 (C-1''').

IR: (CCl₄)

2959 (w), 2933 (w), 1725 (m), 1451 (w), 1365 (m), 1350 (m), 1332 (w), 1272 (s), 1255 (m), 1177 (s), 1106 (s), 1070 (w), 1060 (w), 1052 (m), 1027 (w), 955 (w), 924 (w), 897 (w), 884 (w), 836 (m), 712 (m), 700 (m).

MS: (FAB)

838 (M^+ , 1.7), 820 (3), 662 (9), 590 (3), 241 (4), 227 (5), 215 (5), 209 (4), 197 (5), 195 (10), 193 (4), 179 (36), 167 (7), 160 (9), 159 (67), 153 (32), 135 (74), 119 (17), 105 (100).

Rotation: $[\alpha]_D^{23} -21.4^\circ$ (*c* 1.31, CHCl₃)

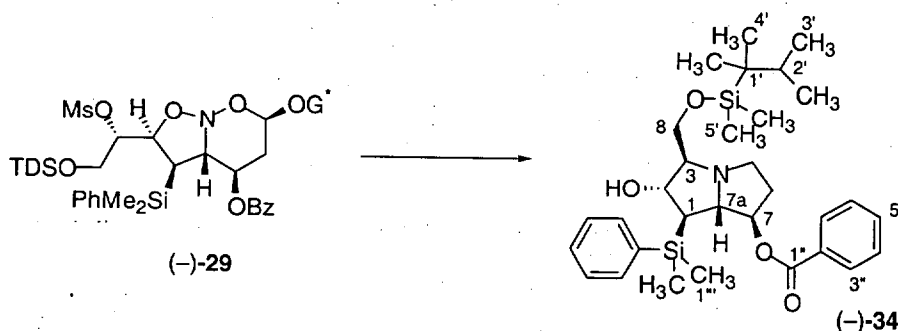
Analysis: C₄₄H₆₃NO₉SSi₂ (838.23)

Calcd: C, 63.05%; H, 7.58%; N, 1.67%

Found: C, 62.86%; H, 7.65%; N, 1.67%

TLC: R_f 0.26 (hexane/EtOAc 4:1)

(1*R*,2*R*,3*R*,7*R*,7*aR*)-7-(Benzoyloxy)-3-((dimethyl[1,1,2-trimethylpropyl]siloxymethyl)-1-(dimethylphenylsilyl)hexahydro-1*H*-pyrrolizin-2-ol ((-)-34).



To a suspension of Raney nickel (2.65 g) [washed with water (7 x 50 mL) and methanol (3 x 50 mL)] in methanol (254 mL) was added mesylate (–)-**29** (1.36 g, 1.62 mmol). The suspension was maintained under an atmosphere of H₂ (160 psi) with vigorous stirring for 36 h, filtered through Celite (methanol), and concentrated *in vacuo*. The crude material was diluted with CH₂Cl₂ (100 mL), treated with triethylamine (3.8 mL), and concentrated *in vacuo* with SiO₂ (2 g). Purification by flash chromatography [hexane/EtOAc 4:1 (6 x 18 cm SiO₂)] followed by

CHCl_3 /methanol 98:2 (3 x 18 cm SiO_2) provided 280 mg (98%) of the recovered chiral auxilliary and the amine. The amine (–)-**34** was dried at 3×10^{-5} mm Hg to a final yield of 732 mg (77%).

Analytical Data for (–)-**34**:

^1H NMR: (500 MHz, CDCl_3)

7.95 (d, 2 H, $J = 7.3$, HC-3", 7"), 7.56 (t, 1 H, $J = 7.3$, HC-5"), 7.52-7.50 (m, 2 H, HC-Ph), 7.42 (t, 2 H, $J = 7.6$, HC-4", 6"), 7.27-7.19 (m, 3 H, HC-Ph), 4.87 (d, 1 H, $J = 4.6$, HC-7), 3.89 (dd, 1 H, $J = 10.7$, 7.8, HC-2), 3.82 (dd, 1 H, $J = 9.5$, 5.1, HC-8), 3.59 (t, 1 H, $J = 9.3$, HC-8), 3.52 (d, 1 H, $J = 11.2$, HC-7a), 3.04 (dt, 1 H, $J_d = 5.1$, $J_t = 11.7$, HC-5), 2.83 (dd, 1 H, $J = 11.7$, 6.6, HC-5), 2.74 (s, 1 H, OH), 2.52 (dt, 1 H, $J_d = 5.1$, $J_t = 8.3$, HC-3), 2.21-2.13 (m, 1 H, HC-6), 1.81 (dd, 1 H, $J = 13.7$, 4.9, HC-6), 1.62 (sept, 1 H, $J = 6.8$, HC-2'), 1.23 (t, 1 H, $J = 11.2$, HC-1), 0.89 (d, 6 H, $J = 6.8$, HC-3'), 0.86 (s, 6 H, HC-4'), 0.44 (s, 6 H, HC-1"), 0.13 (s, 6 H, HC-5').

^{13}C NMR: (126 MHz, CDCl_3)

165.5 (C-1"), 136.6 (C-Ph), 133.8 (C-Ph), 132.8 (C-5"), 130.2 (C-Ph), 129.5 (C-Ph), 129.3 (C-3", 7"), 128.2 (C-Ph), 127.9 (C-4", 6"), 80.8 (C-7), 79.0 (C-2), 72.0 (C-3), 70.0 (C-7a), 67.9 (C-8), 51.8 (C-5), 38.0 (C-1), 34.0 (C-2'), 29.9 (C-6), 25.1 (C-1'), 20.3 (C-4'), 20.1 (C-4'), 18.5 (C-3'), 18.4 (C-3'), -3.62 (C-5'), -3.71 (C-5'), -4.04 (C-1"), -4.86 (C-1").

IR: (CHCl_3)

3683 (w), 3529 (w), 3070 (w), 3020 (w), 2961 (w), 2906 (w), 2868 (w), 2400 (w), 1714 (w), 1523 (w), 1492 (w), 1474 (w), 1452 (w), 1428 (w), 1393 (w), 1379 (w), 1367 (w), 1266 (m), 1254 (m), 1215 (s), 1116 (m), 1098 (w), 1070 (w), 1027 (w), 929 (w), 779-739 (b, s), 670 (s).

MS: (FAB)

555 ($[\text{M}+\text{H}]^+$, 46), 554 (M^+ , 100), 536 (3), 432 (5), 380 (16), 179 (4), 135 (20), 105 (10).

Rotation: $[\alpha]_D^{23} -53.85^\circ$ (c 1.40, CHCl_3)

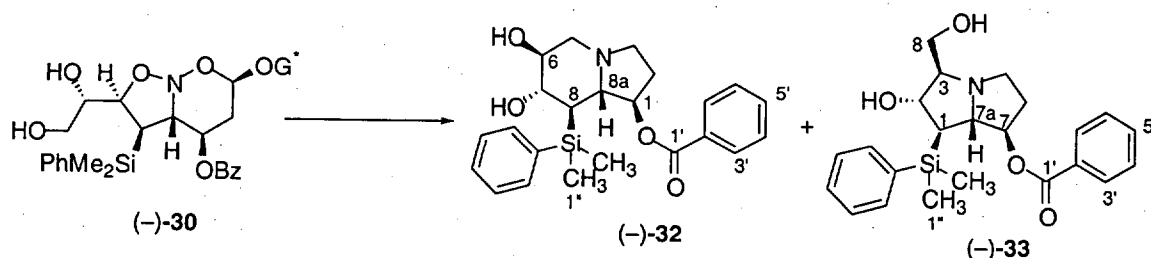
Analysis: $\text{C}_{31}\text{H}_{47}\text{NO}_4\text{Si}_2$ (553.90)

Calcd: C, 67.22%; H, 8.55%; N, 2.53%; Si, 10.14%.

Found: C, 66.99%; H, 8.48%; N, 2.62%; Si, 10.35%.

TLC: R_f 0.35 (hexanes/EtOAc 2:1)

(1*R*,6*S*,7*R*,8*R*,8*aR*)-1-(Benzoyloxy)-8-(dimethylphenylsilyl)octahydro-6,7-indolizindiol ((-)-**32**) and (1*R*,2*R*,3*R*,7*R*,7*aR*)-7-(Benzoyloxy)-1-(dimethylphenylsilyl)hexahydro-3-hydroxymethyl-1*H*-pyrrolizin-2-ol ((-)-**33**).



Part 1. Activation.

Toluenesulfonic anhydride (1.04 g, 3.19 mmol, 3 equiv.) was added in one portion to a solution of nitroso acetal (-)-**30** (655 mg, 1.06 mmol) in 2,6-lutidine (3.5 mL) at ambient temperature. The reaction mixture gradually darkened from yellow to a wine-red. After 10 min, the reaction mixture was transferred to a SiO₂ column (2 x 12 cm) and purified by chromatography (hexane/EtOAc 1:1). Fractions containing tosylate **35** and 2,6-lutidine were pooled and concentrated to a red liquid.

Part 2. Hydrogenolysis.

To a suspension of Raney nickel (4.30 g) [washed with water (6 x 40 mL), pH 7 buffer (2 x 40 mL), and methanol (3 x 40 mL)] in methanol (132 mL) was added the tosylate solution. The suspension was maintained under an atmosphere of H₂ (260 psi) with vigorous stirring for 36 h, treated with Et₃N (2 mL), filtered through Celite (methanol), and concentrated *in vacuo*. The residue was pre-purified by flash chromatography [CHCl₃/MeOH/NH₄OH 90:9:1 (3 x 16 cm SiO₂)] to provide 175 mg (94%) of the recovered chiral auxiliary and a mixture of amines (-)-**32** and (-)-**33** (8:1 by ¹H NMR). Purification of the amine mixture by radial chromatography [CHCl₃/MeOH/NH₄OH 90:9:1 (4 cm SiO₂ plate)] provided 16.0 mg (4%) of pyrrolizidine (-)-**33** as an oil and the indolizidine. Recrystallization from Et₂O/pentane gave 278 mg (64%) of amine (-)-**32** as colorless needles.

Data for tosylate **35**:

¹H NMR: (500 MHz, CDCl₃)

8.01 (dd, 2 H, *J* = 8.3, 1.2), 7.71 (d, 2 H, *J* = 8.5), 7.59 (tt, 1 H, *J* = 7.3, 1.2), 7.47 (q, 5 H, *J* = 7.3), 7.41 (dd, 4 H, *J* = 8.1, 1.5), 7.37-7.33 (m, 2 H), 7.28-7.13 (m, 8 H), 4.67-4.63 (m, 2 H), 3.89-3.88 (m, 2 H), 3.84 (dd, 1 H, *J* = 12.7, 4.2), 3.77-3.72 (m, 1 H), 3.58 (dt, 1 H, *J*_d = 4.4, *J*_t = 10.5), 2.58-2.44 (m), 2.46

(s, 3 H), 2.37-2.34 (m, 1 H), 2.27 (dd, 1 H, $J = 12.7, 9.8$), 1.87-1.85 (m, 2 H), 1.77-1.74 (m, 1 H), 1.70-1.29 (m, 7 H), 0.40 and 0.34 (two s, 3 H each).

¹³C NMR: (126 MHz, CDCl₃)

170.5, 143.7, 133.0, 132.7, 132.1, 129.5, 129.4, 129.3, 129.1, 127.9, 127.7, 127.6, 127.5, 127.4, 125.9, 112.0, 98.7, 86.7, 74.2, 70.9, 69.1, 50.9, 34.3, 32.3, 25.5, 24.8, 21.1, 20.5, -3.00, -3.47.

Analytical Data for (-)-32:

mp: 111-112 °C

¹H NMR: (500 MHz, CDCl₃)

7.99 (d, 2 H, $J = 7.8$, HC-3',7'), 7.59 (t, 1 H, $J = 7.3$, HC-5"), 7.48-7.44 (m, 4 H, HC-Ph), 7.33 (t, 1 H, $J = 7.1$, HC-Ph), 7.27-7.24 (m, 2 H, HC-Ph), 4.88 (apparent t, 1 H, $J = 5.9$, HC-1), 3.62 (ddd, 1 H, $J = 10.0, 8.5, 5.1$, HC-6), 3.45 (dd, 1 H, $J = 11.0, 8.5$, HC-7), 3.27 (dd, 1 H, $J = 10.7, 5.1$, HC-5), 2.92-2.90 (m, 1 H, HC-3), 2.55 (dd, 1 H, $J = 11.0, 5.6$, HC-8a), 2.46-2.38 (m, 2 H, HC-2,3), 2.20 (t, 1 H, $J = 10.3$, HC-5), 2.00-1.70 (two br s, 1 H each, OH), 1.69-1.61 (m, 1 H, HC-2), 1.42 (t, 1 H, $J = 11.0$, HC-8), 0.40 and 0.37 (two s, 3 H each, HC-1").

¹³C NMR: (126 MHz, CDCl₃)

165.8 (C-1'), 138.3 (C-Ph), 133.7 (C-Ph), 133.1 (C-Ph), 130.2 (C-Ph), 129.6 (C-Ph), 129.4 (C-Ph), 128.4 (C-Ph), 128.2 (C-Ph), 78.1 (C-1), 76.6 (C-7), 72.9 (C-6), 68.5 (C-8a), 55.5 (C-5), 51.5 (C-3), 35.0 (C-8), 32.9 (C-2), -2.05 (C-1"), -2.61 (C-1").

IR: (KBr)

3395-3121 (b,s), 3109 (m), 3045 (m), 2987 (m), 2979 (m), 2951 (m), 2823 (m), 2796 (m), 2782 (m), 1723 (s), 1697 (s), 1625 (w), 1602 (w), 1584 (w), 1451 (m), 1428 (m), 1402 (m), 1384 (w), 1370 (w), 1320 (m), 1304 (m), 1278 (s), 1260 (s), 1249 (s), 1177 (m), 1155 (m), 1144 (m), 1115 (s), 1087 (m), 1070 (s), 1063 (s), 1036 (m), 1026 (s), 994 (m), 983 (w), 969 (m), 931 (m), 843 (s), 820 (s), 778 (m), 739 (m), 735 (m), 716 (s), 704 (s).

MS: (FAB)

412 ([M+H]⁺, 100), 394 (12), 289 (11), 232 (4.4), 154 (4.3), 135 (37), 120 (19), 105 (26).

HRMS: Calcd. for (C₂₃H₃₀NO₄Si): 412.1944.

Found: 412.1947.

Rotation: [α]_D²³ -66.67 ° (c 1.14, CHCl₃)

Analysis: $C_{23}H_{29}NO_4Si \cdot 1/4 H_2O$ (411.58)

Calcd: C, 66.39%; H, 7.15%; N, 3.37%.

Found: C, 66.30%; H, 7.21%; N, 3.42%.

TLC: R_f 0.28 ($CHCl_3/MeOH/NH_4OH$ 90:9:1).

Data for (-)-33:

1H NMR: (500 MHz, $CDCl_3$)

7.99 (dd, 2 H, $J = 8.1, 1.5$, HC-3', 7'), 7.58 (tt, 1 H, $J = 7.3, 1.5$, HC-5'), 7.54-7.52 (m, 2 H, HC-Ph), 7.45 (t, 2 H, $J = 8.1$, HC-4', 6'), 7.30-7.26 (m, 3 H, HC-Ph), 5.03 (apparent d, 1 H, $J = 4.9$, HC-7), 4.04 (dd, 1 H, $J = 10.7, 8.1$, HC-2), 3.67 (dd, 1 H, $J = 11.0, 2.4$, HC-8), 3.60 (dd, 1 H, $J = 11.0, 4.4$, HC-8), 3.53 (d, 1 H, $J = 11.0$, HC-7a), 3.09 (dt, 1 H, $J_d = 5.4, J_t = 11.7$, HC-5), 2.87 (ddd, 1 H, $J = 11.7, 7.1, 1.5$, HC-5), 2.53 (ddd, 1 H, $J = 7.8, 4.2, 2.4$, HC-3), 2.24-2.17 (m, 1 H, HC-6), 1.91-1.87 (m, 1 H, HC-6), 1.24 (t, 1 H, $J = 11.0$, HC-1), 0.46 and 0.44 (two s, 3 H each, HC-1").

^{13}C NMR: (126 MHz, $CDCl_3$)

165.7 (C-1'), 136.5 (C-Ph), 133.7 (C-Ph), 133.0 (C-Ph), 130.1 (C-Ph), 129.6 (C-Ph), 128.3 (C-Ph), 128.2 (C-Ph), 80.9 (C-7), 74.5 (C-2), 72.9 (C-3), 70.1 (C-7a), 60.9 (C-8), 50.9 (C-5), 38.8 (C-1), 29.8 (C-6), -4.2 (C-1"), -4.9 (C-1").

IR: ($CHCl_3$)

3440-3107 (b, w), 3069 (w), 2955 (w), 2926 (w), 2900 (w), 2884 (w), 2858 (w), 1718 (s), 1602 (w), 1585 (w), 1491 (w), 1451 (m), 1439 (w), 1428 (m), 1408 (w), 1370 (w), 1315 (m), 1272 (s), 1218 (w), 1194 (w), 1176 (m), 1114 (s), 1070 (m), 1043 (m), 1026 (m), 999 (w), 963 (w), 940 (w), 893 (w), 844 (m), 815 (m), 780 (m), 757 (m), 713 (s), 702 (m).

MS: (FAB)

412 ($[M+H]^+$, 100), 396 (3.4), 380 (6.7), 290 (4.0), 135 (27), 105 (12).

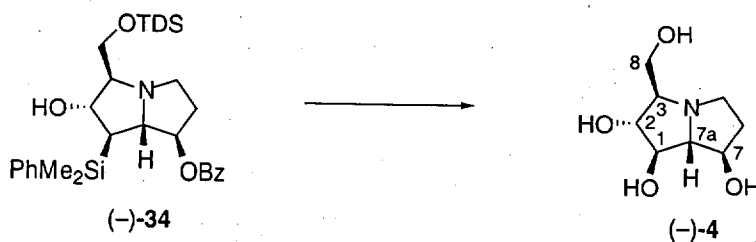
HRMS: Calcd. for ($C_{23}H_{30}NO_4Si$): 412.1944.

Found: 412.1943.

Rotation: $[\alpha]_D^{23}$ -56.67° (c 0.72, $CHCl_3$)

TLC: R_f 0.34 ($CHCl_3/MeOH/NH_4OH$ 90:9:1)

(1*R*,2*R*,3*R*,7*R*,7*aR*)-Hexahydro-3-(hydroxymethyl)-1*H*-pyrrolizine-1,2,7-triol
[(-)-7-Epiaustraline] ((-)-4).



To the viscous solution of silane (-)-**34** (142 mg, 0.256 mmol) in CHCl_3 (200 μL) at ambient temperature was added trifluoroacetic acid (800 μL), HOAc (400 μL), and mercuric trifluoroacetate (161 mg, 0.377 mmol, 1.5 equiv). The pinkish-tan solution was maintained for 1 h and was then cooled to 0 $^\circ\text{C}$. The reaction mixture was diluted with peracetic acid (37% in HOAc, 7 mL) and was heated at 50 $^\circ\text{C}$ for 24 h. The formation of a grey precipitate was noted after 12 h. The reaction mixture was cooled to 0 $^\circ\text{C}$ and slowly quenched with Me_2S (3 mL) so as to maintain the internal temperature ≤ 15 $^\circ\text{C}$. The contents of the reaction were transferred to a column of DOWEX resin (H-form, 10 g), washed with H_2O (200 mL), and the *N*-oxide was eluted with 7 M NH_4OH (100 mL) and conc. NH_4OH (5 x 100 mL). The fractions containing the *N*-oxide were pooled and concentrated to a tan solid (79.3 mg). 10% Palladium on carbon (150 mg) was added to the solid under N_2 and the contents diluted with MeOH (40 mL) and HOAc (10 drops) at 0 $^\circ\text{C}$. The reaction mixture was maintained under an atmosphere of H_2 (1 ATM) at ambient temperature for 16 h and the catalyst removed by filtration through Celite (MeOH). Upon concentration to ~ 2 mL, the solution of the amine was purified on a DOWEX resin (H-form, 10 g), washing with H_2O (100 mL) and eluting with 2 M NH_4OH (4 x 100 mL) to give 36.1 mg (74%) as an off-white solid. The free amine was recrystallized from MeOH- CHCl_3 to provide cubic crystals. The mother liquor was concentrated, chromatographed on reverse phase silica gel [$\text{CHCl}_3/\text{MeOH}/\text{NH}_4\text{OH}$ 1:0:0 (50 mL), 90:9:1 (150 mL), and 20:5:1 (2 x 10 cm C-18 SiO_2)], and recrystallized. That procedure was repeated twice yielding 29.5 mg (61%) of analytically pure (-)-**4**.

Analytical Data for (-)-4:

mp: 193-4 °C (dec)

¹H NMR: (750 MHz, D₂O, pH 8.37)

4.24 (dt, 1 H, $J_d = 4.8$, $J_t = 2.6$, HC-7), 3.66 (dd, 1 H, $J = 11.7$, 3.8, HC-8), 3.65 (t, 1 H, $J = 9.0$, HC-2), 3.60 (t, 1 H, $J = 8.0$, HC-1), 3.53 (dd, 1 H, $J = 11.9$, 6.4, HC-8), 2.97 (ddd, 1 H, $J = 11.1$, 10.6, 5.6, HC-5), 2.90 (dd, 1 H, $J =$

8.0, 1.3, *HC-7a*), 2.76 (ddd, 1 H, $J = 11.2, 7.2, 3.5$, *HC-5*), 2.56 (ddd, 1 H, $J = 9.9, 6.2, 4.0$, *HC-3*), 1.99-1.94 (m, 1 H, *HC-6*), 1.68-1.65 (m, 1 H, *HC-6*) (500 MHz, D₂O, pH 8.37)

4.18 (dt, 1 H, $J_d = 4.6, J_t = 2.7$, *HC-7*), 3.60 (dd, 1 H, $J = 11.7, 3.9$, *HC-8*), 3.58 (t, 1 H, $J = 8.5$, *HC-2*), 3.54 (t, 1 H, $J = 8.1$, *HC-1*), 3.46 (dd, 1 H, $J = 11.7, 6.3$, *HC-8*), 2.90 (ddd, 1 H, $J = 11.5, 10.3, 5.9$, *HC-5*), 2.84 (dd, 1 H, $J = 7.8, 2.0$, *HC-7a*), 2.70 (ddd, 1 H, $J = 11.0, 7.1, 3.4$, *HC-5*), 2.50 (ddd, 1 H, $J = 9.3, 6.3, 3.9$, *HC-3*), 1.90 (m, 1 H, *HC-6*), 1.60 (ddt, 1 H, $J_d = 12.7, 6.1, J_t = 3.4$, *HC-6*)

¹³C NMR: (126 MHz, D₂O, pH 8.37)

77.5 (C-1), 75.9 (C-2), 74.8 (C-7), 73.5 (C-7a), 67.9 (C-3), 62.3 (C-8), 51.4 (C-5), 33.2 (C-6).

IR: (KBr)

3414-3251 (b, s), 2974 (m), 2933 (m), 2919 (m), 2913 (m), 2888 (m), 2875 (m), 2849 (m), 1479 (m), 1468 (m), 1455 (m), 1444 (m), 1341 (w), 1317 (w), 1294 (w), 1289 (w), 1273 (w), 1265 (w), 1146 (s), 1128 (s), 1109 (s), 1084 (m), 1054 (w), 1029 (s), 981 (s), 949 (m), 899 (w), 734 (w), 672 (w), 643 (m), 539 (w).

MS: (FAB)

190 ([M+H]⁺, 58), 155 (52), 154 (15), 153 (21), 152 (31), 137 (12), 135 (46), 121 (17), 119 (100).

Analysis: C₈H₁₅NO₄ (189.21)

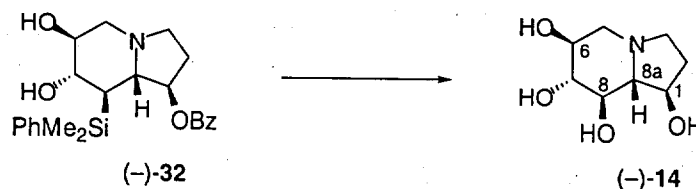
Calcd: C, 50.78%; H, 7.99%; N, 7.40%

Found: C, 50.65%; H, 7.91%; N, 7.21%

Rotation: $[\alpha]_D^{23} -13.04^\circ$ (c 0.55, H₂O, pH 8.37)

TLC: *R_f* 0.23 (CHCl₃/MeOH/NH₄OH 5:5:1)

(1*R*,6*S*,7*R*,8*R*,8*aR*)-Octahydro-1,6,7,8-indolizinetetrol
[(-)-1-Epicastanospermine] ((-)-14).



To the viscous solution of silane (-)-32 (102 mg, 0.248 mmol) in CHCl_3 (200 μL) at ambient temperature was added trifluoroacetic acid (800 μL), HOAc (400 μL), and mercuric trifluoroacetate (161 mg, 0.377 mmol, 1.5 equiv). The pinkish-tan solution was maintained for 1 h and was then cooled to 0 $^\circ\text{C}$. The reaction mixture was diluted with peracetic acid (37% in HOAc, 7 mL) and was heated at 50 $^\circ\text{C}$ for 17 h. The formation of a grey precipitate was noted after 12 h. The reaction mixture was cooled to 0 $^\circ\text{C}$ and slowly quenched with Me_2S (3 mL) so as to maintain the internal temperature ≤ 10 $^\circ\text{C}$. The contents of the reaction were transferred to a column of DOWEX resin (10 g H-form), washed with H_2O (110 mL), and the *N*-oxide was eluted with 7 M NH_4OH (2 x 50 mL) and conc. NH_4OH (6 x 50 mL). The fractions containing the *N*-oxide were pooled and concentrated to a tan solid (62.5 mg). 10% Palladium on carbon (150 mg) was added to the solid under N_2 and the contents diluted with MeOH (40 mL) and HOAc (10 drops) at 0 $^\circ\text{C}$. The reaction mixture was maintained under an atmosphere of H_2 (1 ATM) at ambient temperature for 18 h and the catalyst removed by filtration through Celite (MeOH). Upon concentration to ~ 2 mL, the solution of the amine was purified on a DOWEX resin (10 g H-form), washing with H_2O (100 mL) and eluting with 2 M NH_4OH (5 x 100 mL) to give 42.6 mg as a tan solid. The free amine was purified by chromatography on reverse phase silica gel [$\text{CHCl}_3/\text{MeOH}/\text{NH}_4\text{OH}$ 1:0:0 (50 mL), 90:9:1 (150 mL), 20:5:1 (2 x 10 cm C-18 SiO_2)] to provide 35.9 mg (77%) of amine (-)-14 as an oil which failed analysis. An analytical sample was obtained as follows: Concentrated HCl (2 mL) was added to the oil and the solution was concentrated to dryness. Toluene was added and residual H_2O was removed by evaporation. The resultant oily wax was crystallized from MeOH- Et_2O and then recrystallized from MeOH- CHCl_3 to provide the analytically pure HCl salt as fine needles. The free base was obtained by passage of a H_2O solution (500 μL) of the analytical sample through an AG 1-X8 column (1 x 4 cm, OH form) eluting with H_2O .

Analytical Data for (+)-14•HCl:

mp: 207-208 $^\circ\text{C}$

¹H NMR: (500 MHz, D₂O)4.47 (bs, 1 H, HC-1), 3.76 (bs, 1 H, HC-7), 3.48 (apparent dd, 2 H, *J* = 12.7, 4.9, HC-3,5), 3.40-3.37 (bm, 3 H, HC-3,6,8), 3.26 (bs, 1 H, HC-8a), 3.04 (t, 1 H, *J* = 11.5, HC-5), 2.47-2.39 (m, 1 H, HC-2), 1.95-1.89 (m, 1 H, HC-2).¹³C NMR: (126 MHz, D₂O)

75.2 (b), 70.8 (b), 70.3, 50.2 (b), 29.8 (b).

IR: (KBr)

3430-3057 (b,s), 1477 (w), 1459 (w), 1452 (w), 1428 (w), 1413 (w), 1385 (w), 1376 (w), 1359 (w), 1349 (w), 1337 (w), 1309 (w), 1277 (w), 1246 (w), 1139 (m), 1125 (m), 1099 (m), 1091 (m), 1077 (w), 1057 (m), 1045 (s), 1029 (m), 1015 (m), 998 (w), 986 (m), 881 (w), 874 (w).

MS: (FAB)190 ([M+H]⁺, 28), 154 (100), 136 (65), 120 (11), 107 (18).Analysis: C₈H₁₆ClNO₄ (225.67)

Calcd: C, 42.58%; H, 7.15%; N, 6.21%

Found: C, 42.38%; H, 7.04%; N, 6.01%

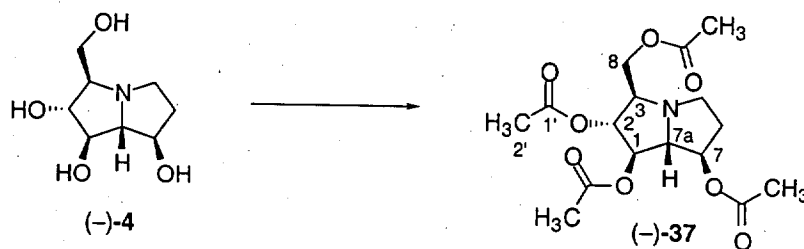
Rotation: $[\alpha]_D^{23}$ +18.25 ° (c 1.23, H₂O)Data for (-)-14 (free base):¹H NMR: (500 MHz, D₂O, pH 9.7)4.02 (ddd, 1 H, *J* = 9.8, 6.6, 3.7, HC-1), 3.40 (ddd, 1 H, *J* = 10.5, 8.8, 5.1, HC-6), 3.17 (t, 1 H, *J* = 9.0, HC-8), 3.12 (t, 1 H, *J* = 9.0, HC-7), 2.94 (dd, 1 H, *J* = 10.7, 5.1, HC-5), 2.73 (dt, 1 H, *J*_d = 2.0, *J*_t = 9.0, HC-3), 2.36 (dt, 1 H, *J*_d = 8.8, *J*_t = 9.5, HC-3), 2.09 (ddt, 1 H, *J*_d = 14.2, 11.0, *J*_t = 9.0, HC-2), 2.03 (t, 1 H, *J* = 10.7, HC-5), 1.90 (dd, 1 H, *J* = 9.3, 6.6, HC-8a), 1.48 (dddd, 1 H, *J* = 12.0, 8.5, 3.4, 1.7, HC-2).¹³C NMR: (126 MHz, D₂O, pH 9.7)

78.1 (C-7), 73.2 (C-1), 72.8 (C-8), 72.3 (C-8a), 69.3 (C-6), 54.3 (C-5), 50.3 (C-3), 31.9 (C-2).

MS: (FAB)190 ([M+H]⁺, 100), 188 (27), 155 (54), 152 (23), 135 (36), 119 (97).HRMS: Calcd. for (C₈H₁₆NO₄): 190.1079.

Found:

Rotation: $[\alpha]_D^{23}$ -5.31 ° (c 0.83, H₂O, pH 9.7)Rotation: $[\alpha]_D^{23}$ -3.10 ° (c 1.86, MeOH)TLC: *R*_f 0.24 (CHCl₃/MeOH/NH₄OH)

(1*R*,2*R*,3*R*,7*R*,7*aR*)-1,2,7-Triacetoxy-3-(acetoxymethyl)hexahydro-1*H*-pyrrolizine ((-)-37)

Acetic anhydride (0.3 mL) was added to a solution of amine (-)-4 (3.9 mg, 0.021 mmol) in dry pyridine (0.3 mL) and the reaction mixture maintained at ambient temperature. After 24 h, the volatiles were removed under high vacuum (10^{-2} mm Hg) and the residue was purified by chromatography [EtOAc/hexanes 1:1 (70 mL) then 2:1 (1 x 10 cm SiO₂)] to provide 7.2 mg (97%) of (-)-37 as a colorless oil.

Analytical Data for (-)-37:

¹H NMR: (500 MHz, CDCl₃)

5.23 (t, 1 H, *J* = 5.9, HC-2), 5.23-5.20 (m, 1 H, HC-7), 5.16 (t, 1 H, *J* = 5.9, HC-1), 4.11 and 4.09 (two dd, 1 H, *J* = 11.5, 5.6, HC-8), 3.40 (dd, 1 H, *J* = 5.6, 2.9, HC-7a), 3.20 (ddd, 1 H, *J* = 11.7, 9.5, 6.3, HC-5), 3.03 (dd, 1 H, *J* = 11.5, 5.6, HC-3), 2.91 (ddd, 1 H, *J* = 11.5, 7.3, 4.2, HC-5), 2.22-2.09 (m, 1 H, HC-6), 2.09 (s, 6 H, HC-2'), 2.06 (s, 3 H, HC-2'), 2.04 (s, 3 H, HC-2'), 1.91-1.85 (m, 1 H, HC-6)

¹³C NMR: (126 MHz, CDCl₃)

170.8 (C-1'), 170.6 (C-1'), 170.4 (C-1'), 169.9 (C-1'), 77.8 (C-1), 77.5 (C-2), 77.1 (C-7), 73.1 (C-7a), 66.7 (C-3), 64.8 (C-8), 52.7 (C-5), 30.3 (C-6), 21.0 (C-2'), 20.9 (C-2'), 20.8 (C-2').

IR: (CDCl₃)

2951 (w), 2941 (w), 2934 (w), 1742 (s), 1437 (w), 1371 (m), 1234 (s), 1122 (w), 1084 (w), 1046 (m), 985 (w), 914 (w), 883 (w), 681 (w), 668 (w), 654 (w), 649 (w).

MS: (FAB)

359 ([M+H]⁺, 22), 358 (M⁺, 100), 298 (55), 178 (17), 79 (13).

HRMS: Calcd. for (C₁₆H₂₅NO₈): 359.1580.

Found: 359.1580.

Rotation: [α]_D²³ -8.61° (*c* 0.72, CHCl₃)

TLC: R_f 0.20 (EtOAc/hexanes 2:1)

SFC: t_R (-)-**37**, 2.83 min (98.3%); (+)-**37**, 3.38 min (1.7%) (Chiracel OD, 150 bar, 40 °C, 1.5% MeOH in CO₂, 3.0 mL min⁻¹).

Crystal Structure of Nitroso Acetal ($\pm$)-26a

The following was made available by Dr. Scott Wilson, X-ray Crystallographic Laboratory, University of Illinois at Urbana-Champaign. The structure was solved and refined by Xiping Su, University of Illinois at Urbana-Champaign.

Crystal Preparation and Structure Refinement Summary.

The synthesis was carried out by reaction of the corresponding ketone with L-selectride in THF at $-74\text{ }^{\circ}\text{C}$. Crystals were grown from ethyl acetate and hexane by diffusion crystallization at $-20\text{ }^{\circ}\text{C}$ for two days. The data crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber with the (0 0 1) scattering planes roughly normal to the spindle axis.

Systematic conditions suggested the unambiguous space group P-1. Structure was solved by direct methods.⁸ The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2 .⁹ The highest peaks in the final difference Fourier map were in the vicinity of atom O(42); the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed independence on amplitude or resolution.

Table 1. Crystal Data and Structure Refinement for alcohol **26a**.

Empirical formula	$\text{C}_{42}\text{H}_{49}\text{NO}_7\text{Si}$	
Formula weight	707.91	
Temperature	198(2) K	
Wavelength	0.71073 Å	
Crystal system	?	
Space group	?	
Unit cell dimensions	$a = 9.0421(2)\text{ Å}$	$\alpha = 78.013(2)\text{ deg}$
from ? reflns with	$b = 14.7020(3)\text{ Å}$	$\beta = 78.004(2)\text{ deg}$
$2\theta = ?$	$c = 15.3401(4)\text{ Å}$	$\gamma = 78.371(2)\text{ deg}$
	$V = 1924.31(8)\text{ Å}^3$	$Z = 2$
Density (calculated)	1.222 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
Crystal size	? x ? x ? mm	

Theta range for data collection	1.38 to 25.03 deg
Index ranges	-10<=h<=10, -17<=k<=17, -18<=l<=12
Collection method	?
Reflections collected	10069 [R(int) = 0.0843]
Independent reflections	6607 [4431 obs, I > 2sigma(I)]
Refinement (shift/err=-0.007)	Full-matrix least-squares on F ²
Data / restraints / parameters	6605 / 0 / 463
Goodness-of-fit on F ²	1.268
Final R indices (obs data)	R1 = 0.1227, wR2 = 0.2426
R indices (all data)	R1 = 0.1785, wR2 = 0.2897
calc $w=1/[\sigma^2(F_o^2)+(0.0403P)^2+9.4319P]$	
where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.233 and -0.480 e.Å ⁻³

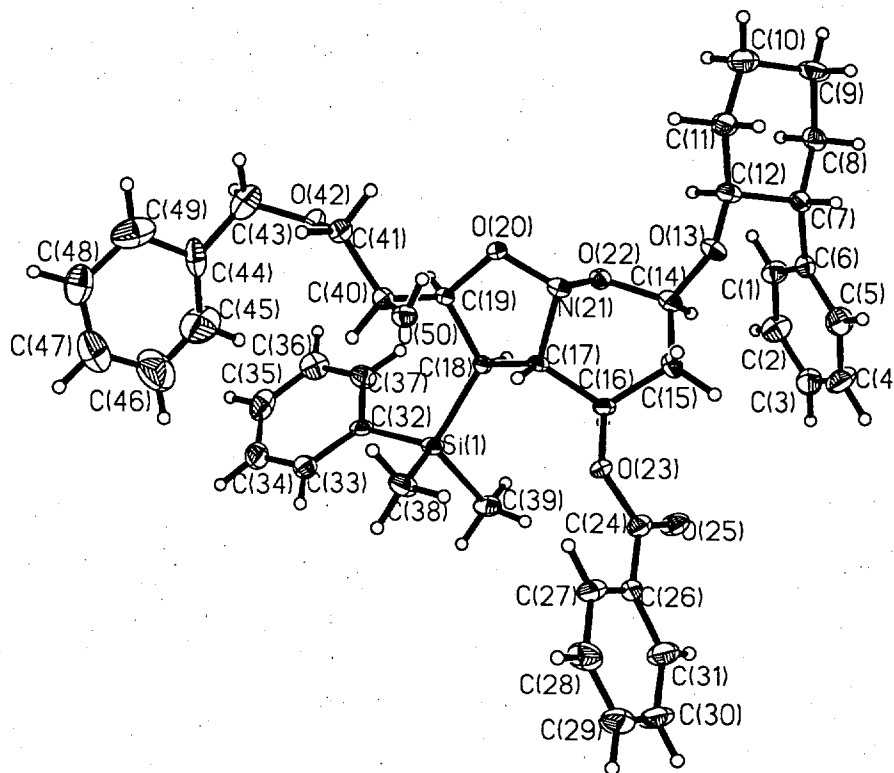


Figure 1. SHELXTL¹⁰ plot of alcohol **26a** showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms. Disordered atoms were omitted for clarity.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for alcohol **26a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U(\text{eq})$
Si(1)	-2093(2)	-2333(1)	3081(1)	28(1)
C(1)	-508(9)	-6842(5)	541(5)	38(2)
C(2)	158(9)	-6225(6)	-173(5)	44(2)
C(3)	-740(10)	-5658(6)	-767(5)	48(2)
C(4)	-2272(11)	-5703(7)	-642(5)	57(2)
C(5)	-2933(9)	-6322(6)	88(5)	47(2)
C(6)	-2043(8)	-6898(5)	683(4)	28(2)
C(7)	-2789(8)	-7535(4)	1501(4)	30(2)
C(8)	-1863(9)	-8531(5)	1635(5)	35(2)
C(9)	-2677(10)	-9175(5)	2423(5)	47(2)
C(10)	-2919(10)	-8782(5)	3296(5)	49(2)
C(11)	-3821(9)	-7776(5)	3182(5)	39(2)
C(12)	-3006(8)	-7138(4)	2376(5)	29(2)
O(13)	-3990(5)	-6227(3)	2306(3)	30(1)
C(14)	-3207(8)	-5453(4)	2108(4)	28(2)
C(15)	-4353(8)	-4569(4)	1853(5)	30(2)
C(16)	-3853(7)	-3724(4)	2068(4)	23(1)
C(17)	-3732(7)	-3851(4)	3064(4)	23(1)
C(18)	-2311(7)	-3625(4)	3292(4)	23(1)
C(19)	-2308(7)	-4206(4)	4250(4)	23(1)
O(20)	-3082(5)	-5000(3)	4257(3)	28(1)
N(21)	-3749(6)	-4865(4)	3479(4)	27(1)
O(22)	-2531(5)	-5367(3)	2844(3)	25(1)
O(23)	-4975(5)	-2878(3)	1889(3)	27(1)
C(24)	-4900(8)	-2437(5)	1012(5)	32(2)
O(25)	-3989(6)	-2732(3)	400(3)	39(1)
C(26)	-6070(8)	-1572(4)	911(5)	29(2)
C(27)	-7165(8)	-1290(5)	1623(5)	36(2)
C(28)	-8200(9)	-469(5)	1476(6)	47(2)
C(29)	-8118(10)	88(6)	627(6)	51(2)
C(30)	-7034(10)	-185(5)	-71(6)	53(2)

C(31)	-5999(10)	-1008(5)	50(5)	45(2)
C(32)	-495(8)	-2219(4)	3636(4)	28(2)
C(33)	-428(9)	-1361(5)	3893(5)	38(2)
C(34)	783(10)	-1246(6)	4257(5)	46(2)
C(35)	1950(9)	-1996(6)	4412(5)	47(2)
C(36)	1907(9)	-2846(6)	4183(6)	50(2)
C(37)	712(8)	-2941(5)	3792(5)	38(2)
C(38)	-3921(8)	-1585(5)	3498(5)	40(2)
C(39)	-1500(10)	-1974(5)	1841(5)	43(2)
C(40)	-3190(7)	-3712(4)	5041(4)	25(1)
C(41)	-2885(8)	-4283(5)	5956(4)	32(2)
O(42)	-1305(5)	-4372(3)	6004(3)	36(1)
C(43)	-1084(11)	-4208(7)	6838(6)	63(3)
C(44)	-1576(9)	-3192(6)	6974(6)	48(2)
C(45)	-1394(13)	-2420(9)	6354(8)	83(4)
C(46)	-1806(17)	-1579(10)	6503(10)	109(5)
C(47)	-2422(13)	-1414(8)	7347(9)	79(3)
C(48)	-2693(10)	-2107(8)	8061(7)	61(3)
C(49)	-2276(11)	-3055(8)	7885(7)	70(3)
O(50)	-4776(5)	-3495(3)	5016(3)	30(1)

Table 3. Bond lengths [Å] for alcohol 26a.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Si(1)-C(39)	1.859(7)	Si(1)-C(38)	1.862(8)	Si(1)-C(32)	1.873(7)
Si(1)-C(18)	1.904(6)	C(1)-C(6)	1.376(10)	C(1)-C(2)	1.385(10)
C(1)-H(1A)	0.95	C(2)-C(3)	1.379(11)	C(2)-H(2A)	0.95
C(3)-C(4)	1.372(11)	C(3)-H(3A)	0.95	C(4)-C(5)	1.398(11)
C(4)-H(4A)	0.95	C(5)-C(6)	1.382(10)	C(5)-H(5A)	0.95
C(6)-C(7)	1.524(9)	C(7)-C(8)	1.529(9)	C(7)-C(12)	1.533(9)
C(7)-H(7A)	1.00	C(8)-C(9)	1.527(10)	C(8)-H(8A)	0.99
C(8)-H(8B)	0.99	C(9)-C(10)	1.524(11)	C(9)-H(9A)	0.99
C(9)-H(9B)	0.99	C(10)-C(11)	1.533(10)	C(10)-H(10A)	0.99
C(10)-H(10B)	0.99	C(11)-C(12)	1.541(9)	C(11)-H(11A)	0.99
C(11)-H(11B)	0.99	C(12)-O(13)	1.448(7)	C(12)-H(12A)	1.00

O(13)-C(14)	1.407(7)	C(14)-O(22)	1.430(8)	C(14)-C(15)	1.526(9)
C(14)-H(14A)	1.00	C(15)-C(16)	1.522(8)	C(15)-H(15A)	0.99
C(15)-H(15B)	0.99	C(16)-O(23)	1.455(7)	C(16)-C(17)	1.524(8)
C(16)-H(16A)	1.00	C(17)-N(21)	1.497(7)	C(17)-C(18)	1.513(9)
C(17)-H(17A)	1.00	C(18)-C(19)	1.538(8)	C(18)-H(18A)	1.00
C(19)-O(20)	1.474(7)	C(19)-C(40)	1.539(9)	C(19)-H(19A)	1.00
O(20)-N(21)	1.408(7)	N(21)-O(22)	1.493(7)	O(23)-C(24)	1.362(8)
C(24)-O(25)	1.205(8)	C(24)-C(26)	1.485(9)	C(26)-C(27)	1.385(10)
C(26)-C(31)	1.403(10)	C(27)-C(28)	1.380(10)	C(27)-H(27A)	0.95
C(28)-C(29)	1.383(11)	C(28)-H(28A)	0.95	C(29)-C(30)	1.360(11)
C(29)-H(29A)	0.95	C(30)-C(31)	1.377(10)	C(30)-H(30A)	0.95
C(31)-H(31A)	0.95	C(32)-C(37)	1.383(10)	C(32)-C(33)	1.414(9)
C(33)-C(34)	1.381(10)	C(33)-H(33A)	0.95	C(34)-C(35)	1.383(11)
C(34)-H(34A)	0.95	C(35)-C(36)	1.376(12)	C(35)-H(35A)	0.95
C(36)-C(37)	1.382(11)	C(36)-H(36A)	0.95	C(37)-H(37A)	0.95
C(38)-H(38A)	0.98	C(38)-H(38B)	0.98	C(38)-H(38C)	0.98
C(39)-H(39A)	0.98	C(39)-H(39B)	0.98	C(39)-H(39C)	0.98
C(40)-O(50)	1.411(7)	C(40)-C(41)	1.525(9)	C(40)-H(40A)	1.00
C(41)-O(42)	1.424(8)	C(41)-H(41A)	0.99	C(41)-H(41B)	0.99
O(42)-C(43)	1.410(9)	C(43)-C(44)	1.514(12)	C(43)-H(43A)	0.99
C(43)-H(43B)	0.99	C(44)-C(45)	1.336(13)	C(44)-C(49)	1.446(13)
C(45)-C(46)	1.27(2)	C(45)-H(45A)	0.95	C(46)-C(47)	1.35(2)
C(46)-H(46A)	0.95	C(47)-C(48)	1.350(14)	C(47)-H(47A)	0.95
C(48)-C(49)	1.435(14)	C(48)-H(48A)	0.95	C(49)-H(49A)	0.95
		O(50)-H(50)	0.84		

Table 4. Bond Angles [deg] for alcohol 26a.

Bond Angle	Angle (°)	Bond Angle	Angle (°)
C(39)-Si(1)-C(38)	110.6(4)	C(39)-Si(1)-C(32)	107.3(3)
C(38)-Si(1)-C(32)	111.5(3)	C(39)-Si(1)-C(18)	107.2(3)
C(38)-Si(1)-C(18)	111.2(3)	C(32)-Si(1)-C(18)	108.8(3)
C(6)-C(1)-C(2)	122.0(7)	C(6)-C(1)-H(1A)	119.0(4)
C(2)-C(1)-H(1A)	119.0(5)	C(3)-C(2)-C(1)	119.0(7)
C(3)-C(2)-H(2A)	120.5(5)	C(1)-C(2)-H(2A)	120.5(5)
C(4)-C(3)-C(2)	120.1(7)	C(4)-C(3)-H(3A)	120.0(5)
C(2)-C(3)-H(3A)	120.0(5)	C(3)-C(4)-C(5)	120.3(8)
C(3)-C(4)-H(4A)	119.9(5)	C(5)-C(4)-H(4A)	119.9(5)
C(6)-C(5)-C(4)	120.1(7)	C(6)-C(5)-H(5A)	119.9(4)
C(4)-C(5)-H(5A)	119.9(5)	C(1)-C(6)-C(5)	118.4(7)
C(1)-C(6)-C(7)	121.8(6)	C(5)-C(6)-C(7)	119.7(6)
C(6)-C(7)-C(8)	112.0(6)	C(6)-C(7)-C(12)	112.1(5)
C(8)-C(7)-C(12)	108.5(5)	C(6)-C(7)-H(7A)	108.0(4)
C(8)-C(7)-H(7A)	108.0(4)	C(12)-C(7)-H(7A)	108.0(4)
C(9)-C(8)-C(7)	111.2(6)	C(9)-C(8)-H(8A)	109.4(4)
C(7)-C(8)-H(8A)	109.4(4)	C(9)-C(8)-H(8B)	109.4(5)
C(7)-C(8)-H(8B)	109.4(4)	H(8A)-C(8)-H(8B)	108.0
C(10)-C(9)-C(8)	110.4(6)	C(10)-C(9)-H(9A)	109.6(5)
C(8)-C(9)-H(9A)	109.6(5)	C(10)-C(9)-H(9B)	109.6(4)
C(8)-C(9)-H(9B)	109.6(4)	H(9A)-C(9)-H(9B)	108.1
C(9)-C(10)-C(11)	110.3(6)	C(9)-C(10)-H(10A)	109.6(5)
C(11)-C(10)-H(10A)	109.6(5)	C(9)-C(10)-H(10B)	109.6(4)
C(11)-C(10)-H(10B)	109.6(4)	H(10A)-C(10)-H(10B)	108.1
C(10)-C(11)-C(12)	110.8(6)	C(10)-C(11)-H(11A)	109.5(4)
C(12)-C(11)-H(11A)	109.5(4)	C(10)-C(11)-H(11B)	109.5(5)
C(12)-C(11)-H(11B)	109.5(4)	H(11A)-C(11)-H(11B)	108.1
O(13)-C(12)-C(7)	110.4(5)	O(13)-C(12)-C(11)	105.9(5)
C(7)-C(12)-C(11)	110.8(5)	O(13)-C(12)-H(12A)	109.9(3)
C(7)-C(12)-H(12A)	109.9(4)	C(11)-C(12)-H(12A)	109.9(4)
C(14)-O(13)-C(12)	114.4(5)	O(13)-C(14)-O(22)	112.8(5)
O(13)-C(14)-C(15)	107.5(5)	O(22)-C(14)-C(15)	110.8(5)
O(13)-C(14)-H(14A)	108.6(3)	O(22)-C(14)-H(14A)	108.6(3)

C(15)-C(14)-H(14A)	108.6(4)	C(16)-C(15)-C(14)	109.0(5)
C(16)-C(15)-H(15A)	109.9(3)	C(14)-C(15)-H(15A)	109.9(4)
C(16)-C(15)-H(15B)	109.9(4)	C(14)-C(15)-H(15B)	109.9(4)
H(15A)-C(15)-H(15B)	108.3	O(23)-C(16)-C(15)	110.5(5)
O(23)-C(16)-C(17)	106.2(5)	C(15)-C(16)-C(17)	111.9(5)
O(23)-C(16)-H(16A)	109.4(3)	C(15)-C(16)-H(16A)	109.4(4)
C(17)-C(16)-H(16A)	109.4(3)	N(21)-C(17)-C(18)	104.7(5)
N(21)-C(17)-C(16)	108.6(5)	C(18)-C(17)-C(16)	117.9(5)
N(21)-C(17)-H(17A)	108.4(3)	C(18)-C(17)-H(17A)	108.4(3)
C(16)-C(17)-H(17A)	108.4(3)	C(17)-C(18)-C(19)	101.0(5)
C(17)-C(18)-Si(1)	117.3(4)	C(19)-C(18)-Si(1)	119.3(4)
C(17)-C(18)-H(18A)	106.0(3)	C(19)-C(18)-H(18A)	106.0(3)
Si(1)-C(18)-H(18A)	106.0(2)	O(20)-C(19)-C(18)	104.3(5)
O(20)-C(19)-C(40)	106.9(5)	C(18)-C(19)-C(40)	116.7(5)
O(20)-C(19)-H(19A)	109.6(3)	C(18)-C(19)-H(19A)	109.6(3)
C(40)-C(19)-H(19A)	109.6(3)	N(21)-O(20)-C(19)	111.3(4)
O(20)-N(21)-O(22)	103.1(4)	O(20)-N(21)-C(17)	105.0(4)
O(22)-N(21)-C(17)	102.5(4)	C(14)-O(22)-N(21)	107.6(4)
C(24)-O(23)-C(16)	116.6(5)	O(25)-C(24)-O(23)	122.9(6)
O(25)-C(24)-C(26)	125.1(6)	O(23)-C(24)-C(26)	112.0(6)
C(27)-C(26)-C(31)	119.7(6)	C(27)-C(26)-C(24)	123.4(6)
C(31)-C(26)-C(24)	116.9(6)	C(28)-C(27)-C(26)	119.8(7)
C(28)-C(27)-H(27A)	120.1(5)	C(26)-C(27)-H(27A)	120.1(4)
C(27)-C(28)-C(29)	120.3(8)	C(27)-C(28)-H(28A)	119.9(5)
C(29)-C(28)-H(28A)	119.9(5)	C(30)-C(29)-C(28)	119.9(7)
C(30)-C(29)-H(29A)	120.0(5)	C(28)-C(29)-H(29A)	120.0(5)
C(29)-C(30)-C(31)	121.3(8)	C(29)-C(30)-H(30A)	119.4(5)
C(31)-C(30)-H(30A)	119.4(5)	C(30)-C(31)-C(26)	119.0(8)
C(30)-C(31)-H(31A)	120.5(5)	C(26)-C(31)-H(31A)	120.5(4)
C(37)-C(32)-C(33)	115.7(6)	C(37)-C(32)-Si(1)	123.2(5)
C(33)-C(32)-Si(1)	121.2(5)	C(34)-C(33)-C(32)	122.1(7)
C(34)-C(33)-H(33A)	118.9(5)	C(32)-C(33)-H(33A)	118.9(4)
C(33)-C(34)-C(35)	119.9(7)	C(33)-C(34)-H(34A)	120.1(5)
C(35)-C(34)-H(34A)	120.1(5)	C(36)-C(35)-C(34)	119.5(7)
C(36)-C(35)-H(35A)	120.3(5)	C(34)-C(35)-H(35A)	120.3(5)
C(35)-C(36)-C(37)	120.0(8)	C(35)-C(36)-H(36A)	120.0(5)

C(37)-C(36)-H(36A)	120.0(5)	C(36)-C(37)-C(32)	122.9(7)
C(36)-C(37)-H(37A)	118.6(5)	C(32)-C(37)-H(37A)	118.6(4)
Si(1)-C(38)-H(38A)	109.5(2)	Si(1)-C(38)-H(38B)	109.5(2)
H(38A)-C(38)-H(38B)	109.5	Si(1)-C(38)-H(38C)	109.5(2)
H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5
Si(1)-C(39)-H(39A)	109.5(3)	Si(1)-C(39)-H(39B)	109.5(3)
H(39A)-C(39)-H(39B)	109.5	Si(1)-C(39)-H(39C)	109.5(2)
H(39A)-C(39)-H(39C)	109.5	H(39B)-C(39)-H(39C)	109.5
O(50)-C(40)-C(41)	111.2(5)	O(50)-C(40)-C(19)	111.3(5)
C(41)-C(40)-C(19)	112.2(5)	O(50)-C(40)-H(40A)	107.3(3)
C(41)-C(40)-H(40A)	107.3(4)	C(19)-C(40)-H(40A)	107.3(3)
O(42)-C(41)-C(40)	109.6(5)	O(42)-C(41)-H(41A)	109.7(3)
C(40)-C(41)-H(41A)	109.7(4)	O(42)-C(41)-H(41B)	109.7(3)
C(40)-C(41)-H(41B)	109.7(4)	H(41A)-C(41)-H(41B)	108.2
C(43)-O(42)-C(41)	112.4(6)	O(42)-C(43)-C(44)	114.2(7)
O(42)-C(43)-H(43A)	108.7(4)	C(44)-C(43)-H(43A)	108.7(5)
O(42)-C(43)-H(43B)	108.7(5)	C(44)-C(43)-H(43B)	108.7(5)
H(43A)-C(43)-H(43B)	107.6	C(45)-C(44)-C(49)	117.1(9)
C(45)-C(44)-C(43)	127.1(9)	C(49)-C(44)-C(43)	115.8(9)
C(46)-C(45)-C(44)	124.9(12)	C(46)-C(45)-H(45A)	117.6(8)
C(44)-C(45)-H(45A)	117.6(7)	C(45)-C(46)-C(47)	120.2(13)
C(45)-C(46)-H(46A)	119.9(8)	C(47)-C(46)-H(46A)	119.9(8)
C(46)-C(47)-C(48)	123.2(11)	C(46)-C(47)-H(47A)	118.4(8)
C(48)-C(47)-H(47A)	118.4(6)	C(47)-C(48)-C(49)	116.5(9)
C(47)-C(48)-H(48A)	121.8(6)	C(49)-C(48)-H(48A)	121.8(6)
C(48)-C(49)-C(44)	118.0(8)	C(48)-C(49)-H(49A)	121.0(6)
C(44)-C(49)-H(49A)	121.0(6)	C(40)-O(50)-H(50)	109.5(3)

Table 5. Dihedral Angles [deg] for alcohol **26a**.

Dihedral Angle	Angle (°)	Dihedral Angle	Angle (°)
C(6)-C(1)-C(2)-C(3)	-0.8(12)	C(1)-C(2)-C(3)-C(4)	0.5(13)
C(2)-C(3)-C(4)-C(5)	0.1(14)	C(3)-C(4)-C(5)-C(6)	-0.5(14)
C(2)-C(1)-C(6)-C(5)	0.4(11)	C(2)-C(1)-C(6)-C(7)	-176.3(7)
C(4)-C(5)-C(6)-C(1)	0.3(12)	C(4)-C(5)-C(6)-C(7)	177.0(8)
C(1)-C(6)-C(7)-C(8)	-48.1(9)	C(5)-C(6)-C(7)-C(8)	135.3(7)
C(1)-C(6)-C(7)-C(12)	74.2(8)	C(5)-C(6)-C(7)-C(12)	-102.5(8)
C(6)-C(7)-C(8)-C(9)	-176.6(6)	C(12)-C(7)-C(8)-C(9)	59.2(8)
C(7)-C(8)-C(9)-C(10)	-59.2(9)	C(8)-C(9)-C(10)-C(11)	56.7(9)
C(9)-C(10)-C(11)-C(12)	-56.2(9)	C(6)-C(7)-C(12)-O(13)	60.7(7)
C(8)-C(7)-C(12)-O(13)	-175.1(5)	C(6)-C(7)-C(12)-C(11)	177.7(6)
C(8)-C(7)-C(12)-C(11)	-58.1(7)	C(10)-C(11)-C(12)-O(13)	177.2(6)
C(10)-C(11)-C(12)-C(7)	57.5(8)	C(7)-C(12)-O(13)-C(14)	-100.5(6)
C(11)-C(12)-O(13)-C(14)	139.5(6)	C(12)-O(13)-C(14)-O(22)	-70.0(7)
C(12)-O(13)-C(14)-C(15)	167.6(5)	O(13)-C(14)-C(15)-C(16)	153.2(5)
O(22)-C(14)-C(15)-C(16)	29.6(7)	C(14)-C(15)-C(16)-O(23)	-176.2(5)
C(14)-C(15)-C(16)-C(17)	-58.1(7)	O(23)-C(16)-C(17)-N(21)	135.1(5)
C(15)-C(16)-C(17)-N(21)	14.4(7)	O(23)-C(16)-C(17)-C(18)	-106.1(6)
C(15)-C(16)-C(17)-C(18)	133.2(6)	N(21)-C(17)-C(18)-C(19)	-36.8(6)
C(16)-C(17)-C(18)-C(19)	-157.6(5)	N(21)-C(17)-C(18)-Si(1)	-168.2(4)
C(16)-C(17)-C(18)-Si(1)	70.9(6)	C(39)-Si(1)-C(18)-C(17)	-76.1(5)
C(38)-Si(1)-C(18)-C(17)	45.0(6)	C(32)-Si(1)-C(18)-C(17)	168.1(5)
C(39)-Si(1)-C(18)-C(19)	161.5(5)	C(38)-Si(1)-C(18)-C(19)	-77.5(6)
C(32)-Si(1)-C(18)-C(19)	45.7(6)	C(17)-C(18)-C(19)-O(20)	28.3(6)
Si(1)-C(18)-C(19)-O(20)	158.4(4)	C(17)-C(18)-C(19)-C(40)	-89.4(6)
Si(1)-C(18)-C(19)-C(40)	40.8(7)	C(18)-C(19)-O(20)-N(21)	-9.7(6)
C(40)-C(19)-O(20)-N(21)	114.5(5)	C(19)-O(20)-N(21)-O(22)	93.4(5)
C(19)-O(20)-N(21)-C(17)	-13.6(6)	C(18)-C(17)-N(21)-O(20)	32.0(6)
C(16)-C(17)-N(21)-O(20)	158.8(5)	C(18)-C(17)-N(21)-O(22)	-75.4(5)
C(16)-C(17)-N(21)-O(22)	51.4(6)	O(13)-C(14)-O(22)-N(21)	-82.6(6)
C(15)-C(14)-O(22)-N(21)	37.9(6)	O(20)-N(21)-O(22)-C(14)	167.4(4)
C(17)-N(21)-O(22)-C(14)	-83.6(5)	C(15)-C(16)-O(23)-C(24)	-80.6(7)
C(17)-C(16)-O(23)-C(24)	157.8(5)	C(16)-O(23)-C(24)-O(25)	1.9(9)
C(16)-O(23)-C(24)-C(26)	-178.6(5)	O(25)-C(24)-C(26)-C(27)	175.4(7)

O(23)-C(24)-C(26)-C(27)	-4.0(10)	O(25)-C(24)-C(26)-C(31)	-6.9(11)
O(23)-C(24)-C(26)-C(31)	173.7(6)	C(31)-C(26)-C(27)-C(28)	1.4(11)
C(24)-C(26)-C(27)-C(28)	179.1(7)	C(26)-C(27)-C(28)-C(29)	-1.9(12)
C(27)-C(28)-C(29)-C(30)	1.4(13)	C(28)-C(29)-C(30)-C(31)	-0.4(14)
C(29)-C(30)-C(31)-C(26)	-0.1(13)	C(27)-C(26)-C(31)-C(30)	-0.4(12)
C(24)-C(26)-C(31)-C(30)	-178.2(7)	C(39)-Si(1)-C(32)-C(37)	-89.2(6)
C(38)-Si(1)-C(32)-C(37)	149.5(6)	C(18)-Si(1)-C(32)-C(37)	26.5(7)
C(39)-Si(1)-C(32)-C(33)	88.5(6)	C(38)-Si(1)-C(32)-C(33)	-32.8(6)
C(18)-Si(1)-C(32)-C(33)	-155.8(5)	C(37)-C(32)-C(33)-C(34)	1.5(10)
Si(1)-C(32)-C(33)-C(34)	-176.3(6)	C(32)-C(33)-C(34)-C(35)	-2.6(11)
C(33)-C(34)-C(35)-C(36)	1.5(12)	C(34)-C(35)-C(36)-C(37)	0.6(12)
C(35)-C(36)-C(37)-C(32)	-1.7(12)	C(33)-C(32)-C(37)-C(36)	0.6(10)
Si(1)-C(32)-C(37)-C(36)	178.4(6)	O(20)-C(19)-C(40)-O(50)	-51.5(6)
C(18)-C(19)-C(40)-O(50)	64.7(7)	O(20)-C(19)-C(40)-C(41)	73.7(6)
C(18)-C(19)-C(40)-C(41)	-170.1(5)	O(50)-C(40)-C(41)-O(42)	-171.7(5)
C(19)-C(40)-C(41)-O(42)	63.0(7)	C(40)-C(41)-O(42)-C(43)	135.2(7)
C(41)-O(42)-C(43)-C(44)	-69.4(9)	O(42)-C(43)-C(44)-C(45)	-39.1(13)
O(42)-C(43)-C(44)-C(49)	142.9(7)	C(49)-C(44)-C(45)-C(46)	-1(2)
C(43)-C(44)-C(45)-C(46)	-178.9(12)	C(44)-C(45)-C(46)-C(47)	3(2)
C(45)-C(46)-C(47)-C(48)	-3(2)	C(46)-C(47)-C(48)-C(49)	1(2)
C(47)-C(48)-C(49)-C(44)	1.4(13)	C(45)-C(44)-C(49)-C(48)	-1.3(12)
C(43)-C(44)-C(49)-C(48) 176.9(8)			

Crystal Structure of Nitroso Acetal (-)-27a

The following was made available by Dr. Scott Wilson, X-ray Crystallographic Laboratory, University of Illinois at Urbana-Champaign.

Crystal Preparation and Structure Refinement Summary.

The data crystal was mounted using epoxy to a thin glass fiber with the (0 1 0) scattering planes roughly normal to the spindle axis. Systematic conditions suggested the ambiguous space group. The structure was solved by direct methods.⁸ The proposed model includes disordered positions for atoms Si(1) and C(9-16); primary site occupancy converged at 0.66(2). Disordered positions were refined with idealized 1,2- and 1,3-interatomic distances using an effective standard deviation of 0.01 Å. Displacement parameters for disordered Si atoms were constrained to be equivalent. Displacement parameters for disordered C atoms separated by less than bonding distances were restrained to be similar with an effective standard deviation of 0.01. Phenyl rings were refined as ideal rigid groups. H atoms were included as riding idealized contributors. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F².⁹ The Flack parameter¹¹ supported the enantiomer choice. The highest peaks in the final difference Fourier map were in the vicinity of atom Si(1); the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

Table 6. Crystal Data and Structure Refinement for alcohol (-)-27a.

Empirical formula	C ₄₃ H ₆₁ NO ₇ Si ₂	
Formula weight	760.11	
Temperature	299(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 12.253(3) Å	alpha = 90 deg
from 3070 reflns with	b = 11.032(2) Å	beta = 96.36(3) deg
5<=theta<=52	c = 16.489(3) Å	gamma = 90 deg
	V = 2215.0(8) Å ³	Z = 2

Density (calculated)	1.140 Mg/m ³
Absorption coefficient	1.097 mm ⁻¹
Crystal size	0.54 x 0.20 x 0.07 mm
Theta range for data collection	4.28 to 52.74 deg
Index ranges	-12<=h<=12, -10<=k<=10, -7<=l<=16
Collection method	ω and ϕ scans
Reflections collected	3982 [R(int) = 0.0638]
Independent reflections	3661 [3501 obs, I > 2 σ (I)]
Absorption correction	Semi-empirical from ψ -scans
Max. and min. transmission	0.9673 and 0.3464
Refinement (shift/err=-0.079)	Full-matrix least-squares on F ²
Data / restraints / parameters	3661 / 148 / 519
Goodness-of-fit on F ²	1.032
Final R indices (obs data)	R1 = 0.1004, wR2 = 0.2468
R indices (all data)	R1 = 0.1023, wR2 = 0.2540
calc $w=1/[\sigma^2(F_o^2)+(0.2302P)^2+0.8624P]$	
where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.04(7)
Extinction coefficient	0.016(2)
Largest diff. peak and hole	0.688 and -0.524 e/Å ⁻³

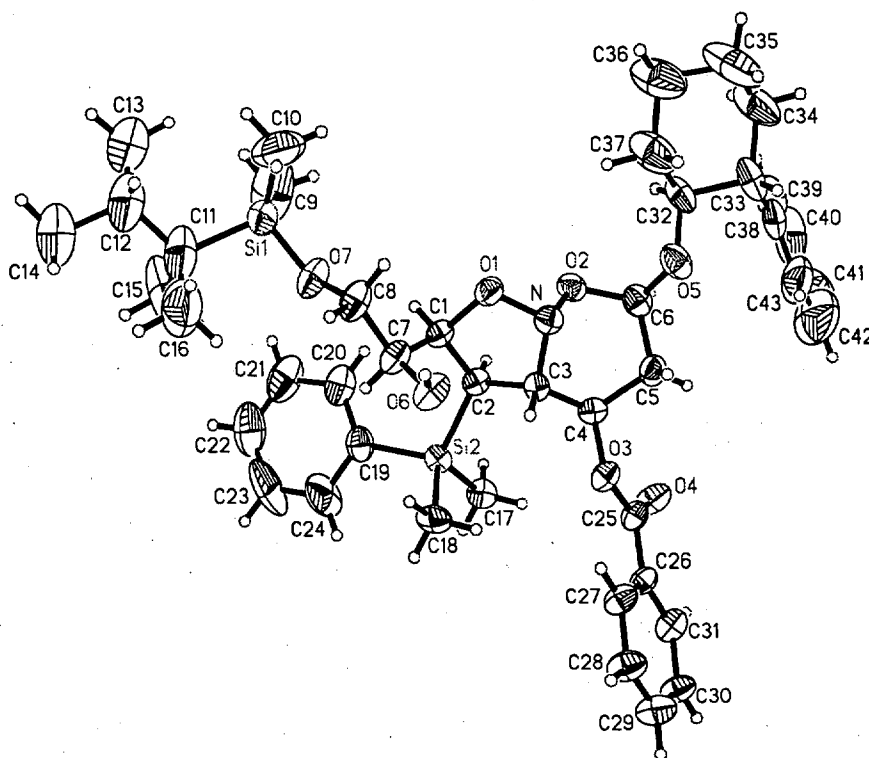


Figure 2. SHELXTL¹⁰ plot of alcohol (-)-**27a** showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms. Disordered atoms were omitted for clarity.

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for alcohol (-)-**27a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U(\text{eq})$
N	6272(4)	3977(6)	-421(3)	51(2)
O(1)	7162(4)	4046(6)	177(3)	60(1)
C(1)	6807(5)	4449(7)	957(4)	44(2)
C(2)	5633(5)	4918(7)	726(4)	48(2)
C(3)	5282(5)	4092(7)	5(4)	45(2)
C(4)	4335(5)	4519(7)	-585(4)	46(2)
C(5)	4562(6)	4341(8)	-1480(4)	59(2)