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Supplementary Information:
Asymmetric Synthesis of (-)-Swainsonine

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General Methods. All reactions were carried out under an atmosphere of nitrogen. Where necessary, reagents and solvents were purified according to methods contained in *Purification of Laboratory Chemicals*, 2nd ed. Perrin D.D., Amarego W.L.F., Perrin D.R., Pergamon Press Ltd., Oxford England (1981) or *Practical Textbook of Organic Chemistry*, 5th ed. Furnis B.S., Hannaford A.J., Smith P.W.G., Tatchell A.R., Longmann Scientific and Technical, London (1989). NMR spectra were obtained at either 300 or 500 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR on a Varian spectrometer and are referenced to the relevant solvent peak. Spectra are obtained as a $CDCl_3$ solution unless otherwise stated. ^{13}C NMR assignments (s, d, t and q) were made from DEPT experiments. Silica gel chromatography was performed using Merck GF 254 flash silica gel packed by the slurry method. Small scale separations (<2.0 g) were performed using either a 10 mm or a 20 mm diameter column, and large scale separations (>2.0g) were performed using a 50 mm diameter column, each with the stated solvent system. Melting points were obtained using a Gallenkamp MF-370 capillary tube melting point apparatus and are uncorrected. Specific rotations were measured using a 10 mm or a 50 mm cell, and a Jasco DIP-370 digital polarimeter. They are reported by the following convention: optical rotation [10^{-1}.deg.cm^3.g^{-1}](concentration, solvent). Mass spectra were obtained on a VG Quatro mass spectrometer (low resolution), and on a VG Autospec mass spectrometer (high resolution). In all cases exact masses were obtained in lieu of elemental analyses, and ^{1}H and ^{13}C NMR spectroscopy were used as criteria for purity.

(1*R*,7*aS*)-1-[3-[(4-Methoxyphenyl)methoxy]propyl]-5,7*a*-dihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (11).

The carbamate **10** (663 mg, 1.643 mmol) was dissolved in toluene (60 mL) then NaH (290 mg, 6.04 mmol) was added. The mixture was stirred at 45 ^{o}C for 18 h, then poured into water and extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give an oil. The pure product was obtained by column chromatography (increasing polarity from 5 % to 30 % Et_2O in DCM as eluant), which gave the title compound (370 mg, 1.220 mmol, 74.2 %) as a clear oil.

$[\alpha]_D^{25}$: -15 (c 1.0, $CHCl_3$).

MS (CI+) *m/z* 304 (9 %) (M+1) 302 (26 %) (M-1), HRMS (EI+) found 303.1464, calc for $C_{17}H_{21}NO_4$ 303.1471 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.45-2.00 (4H, m, H1' and H2'), 3.38-3.55 (2H, m, H3'), 3.70-3.80 (1H, m, H5a), 3.78 (3H, s, OCH_3), 4.40 (2H, s, $OC\underline{H}_2Ar$), 4.34-4.44 (1H, m, H5b), 4.64-4.76 (2H, m, H1 and H7*a*), 5.80-5.86 (1H, m, H6), 5.98-6.04 (1H, m, H7), 6.86 (2H, d, J=8.4 Hz, 2 x ArCH), 7.23 (2H, d, J=8.4 Hz, 2 x ArCH).

δ_C (75 MHz, $CDCl_3$): 25.8, 28.9 (t, C1' and C2'), 54.8 (t, C5), 55.2 (q, OCH_3), 68.3 (d, C7*a*), 68.9 (t, C3'), 72.4 (t, $O\underline{C}H_2Ar$), 78.5 (d, C1), 113.6 (d, 2 x ArCH), 126.4 (d, C6), 129.0 (d, 2 x ArCH), 130.2 (s, ArC), 131.4 (d, C7), 158.9 (s, ArC), 162.5 (s, C3).

(1*R*,6*R*,7*S*,7*aR*)-1-[3-[(4-Methoxyphenyl)methoxy]propyl]-tetrahydro-6,7-dihydroxy-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (12) and (1*R*,6*S*,7*R*,7*aR*)-1-[3-[(4-methoxyphenyl)methoxy]propyl]-tetrahydro-6,7-dihydroxy-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (13).

The oxazolidinone **11** (378 mg, 1.246 mmol) was dissolved in acetone (7 mL) then water (4.8 mL), NMO (336 mg, 2.866 mmol) and $K_2OsO_4.2H_2O$ (24 mg, 0.065 mmol) were added. The mixture was stirred at RT for 20 h, then all volatiles were removed *in vacuo* to give a black oil. Pure product was obtained by column chromatography (increasing polarity from 5 % to 10 % MeOH in DCM as eluant), which gave the title compound (356 mg, 1.055 mmol, 84.7 %) as a white solid. Two isomers were present in a 3:1 ratio. An analytical sample of the major isomer was isolated by preferential recrystallisation from hot DCM (40 mL) and pet. sp. (5-10 mL), which gave 177 mg as colourless needles.

Alternative method:

The oxazolidinone **11** (106 mg, 0.349 mmol) was dissolved in acetone (3.3 mL) then H_2O (1.8 mL), AD-mix-β (492 mg), $(DHQD)_2PHAL$ (11 mg, μ14 mol) and methane sulfonamide (66 mg, 0.822 mmol) were added. The mixture was stirred at RT for 6 d, then Na_2SO_3 (1.5 g) was added and the mixture stirred for 20 min. The mixture was poured into water (40 mL) and extracted with DCM (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* gave a semi solid. Column chromatography (increasing polarity from 2 % to 10 % MeOH in DCM as eluant) gave the mixture of title compounds (54 mg, 0.160 mmol, 45.9 %) as a white solid, and recovered **11** (48 mg, 0.158 mmol, 45.3 %) as a clear oil.

MS (CI+) *m/z* 338 (17 %) (M+1), HRMS (EI+) found 337.1505, calc for $C_{17}H_{24}NO_6$ 337.1525 (M+1).

12:

m.p. 146 ^oC

$[\alpha]_D^{25}$: -31.0 (c 1.77, $CHCl_3$).

δ_H (300 MHz, $CDCl_3$): 1.60-1.75 (1H, m, H2'a), 1.75-1.90 (1H, H2'b), 2.00-2.15 (1H, m, H1'a), 2.15-2.30 (1H, m, H1'b), 2.80 (1H, br. s, OH), 3.10 (1H, br. s, OH), 3.34-3.70 (5H, m, H5, H7*a* and H3'), 3.77 (3H, s, OCH_3), 3.98 (1H, br. s, H6), 4.35-4.45 (1H, m, H7), 4.40 (2H, s, O<u>C</u>H_2Ar), 4.59 (1H, app q, *J*=7.1 Hz, H1), 6.86 (2H, dt, *J*=8.7, 1.5 Hz, 2 x ArCH), 7.23 (2H, dt, *J*=8.7, 1.5 Hz, 2 x ArCH).

δ_C (75 MHz, $CDCl_3$): 26.3, 26.4 (t, C1' and C2'), 49.9 (t, C5), 55.2 (q, OCH_3), 65.1 (d, C7*a*), 69.3 (t, C3'), 70.8 (d, C6), 72.6 (t, O<u>C</u>H_2Ar), 73.6 (d, C7), 76.7 (d, C1), 113.8 (d, 2 x ArCH), 129.3 (d, 2 x ArCH), 130.2 (s, ArC), 159.2 (s, ArC), 163.0 (s, C3).

13:

δ_C (75 MHz, $CDCl_3$): *inter alia* 25.5, 26.5 (t, C1' and C2'), 52.8 (t, C5), 55.2 (q, OCH_3), 63.9 (d, C7*a*), 69.0 (t, C3'), 70.0 (d, C6), 70.9 (d, C7), 72.6 (t, O<u>C</u>H_2Ar), 76.2 (d, C1), 113.8 (d, 2 x ArCH), 129.4 (d, 2 x ArCH), 129.9 (s, ArC), 159.2 (s, ArC), 163.0 (s, C3).

(1*S*,6*R*,7*S*,7*aR*)-Tetrahydro-1-[3-[(4-methoxyphenyl)methoxy]propyl]-6,7-*bis*(phenylmethoxy)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (14) and (1*S*,6*S*,7*R*,7*aR*)-tetrahydro-1-[3-[(4-methoxyphenyl)methoxy]propyl]-6,7-*bis*(phenylmethoxy)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (15).

The diol **12** (177 mg, 0.525 mmol) was dissolved in dry THF (15 mL) then sodium hydride (75 mg, 1.575 mmol, 50 % dispersion in paraffin wax), benzylbromide (0.24 mL, 2.00 mmol) and tetrabutylammoniumiodide (38 mg, 0.105 mmol) were added. The mixture was stirred at RT for 2 d then poured into water (50 mL) and extracted with DCM (3 x 25 mL). The combined organic portions were dried ($MgSO_4$) filtered and evaporated *in vacuo* to give an oil. Pure product was obtained by column chromatography (increasing polarity from 30 % to 80 % EtOAc in pet. sp. as eluant), which gave the title compound (272 mg, 0.525 mmol, 100 %) as a clear oil. When starting with a mixture of the diols **12** and **13**, the mixture of products **14** and **15** may also be separated using this method.

14:

$[\alpha]_D^{23}$: -17 (c 1.18, $CHCl_3$).

MS (CI+) *m/z* 518 (25 %) (M+1), HRMS (CI+) found 518.2524, calc for $C_{31}H_{36}NO_6$ 518.2543 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.50-1.92 (3H, m, H1'a and H2'), 1.98-2.14 (1H, m, H1'b), 3.32 (1H, ddd, J=9.3, 7.5, 5.4 Hz, H3'a), 3.40-3.49 (2H, m, H5a and H3'b), 3.58-3.67 (2H, m, H5b and H7*a*), 3.79 (3H, s, OCH_3), 3.96 (1H, t, J=2.4 Hz, H7), 4.19 (1H, td, J=8.4, 2.7 Hz, H6), 4.37 (2H, s, $OC\underline{H}_2Ar$), 4.52-4.62 (4H, m, H1 and 1.5 x $OC\underline{H}_2Ph$), 5.04 (1H, d, J=11.7 Hz, 0.5 x $OC\underline{H}_2Ph$), 6.85 (2H, dt, J=8.4, 3.0 Hz, 2 x ArCH), 7.20 (2H, dt, J=8.4, 3.0 Hz, 2 x ArCH), 7.22-7.39 (10H, m, 2 x $OCH_2\underline{Ph}$).

δ_C (75 MHz, $CDCl_3$): 26.1 (t, C1'), 26.6 (t, C2'), 48.3 (t, C5), 55.2 (q, OCH_3), 63.8 (d, C7*a*), 69.2 (t, C3'), 72.5 (t, $O\underline{C}H_2Ar$), 72.6, 72.8 (t, 2 x $O\underline{C}H_2Ph$), 76.2 (d, C7), 76.2 (d, C1), 82.4 (d, C6), 113.7 (d, 2 x ArCH), 127.1, 127.3, 127.4, 128.0, 128.2, 128.5 (d, 2 x $OCH_2\underline{Ph}$), 129.2 (d, 2 x ArCH), 130.4 (s, ArC), 137.3, 137.9 (s, 2 x $OCH_2\underline{Ph}$), 159.1 (s, ArC), 162.2 (s, C3).

15:

$[\alpha]_D^{27}$: +65 (c 1.25, $CHCl_3$).

MS (ES+) *m/z* 518.3 (75 %) (M+1), HRMS (ES+) found 518.2565, calc for, $C_{31}H_{35}NO_6$ 518.2543 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.50 (4H, m, H1' and H2'), 3.30-3.50 (3H, m, H5a and H3'), 3.56 (1H, dd, *J*=9.3, 5.1 Hz, H7), 3.77 (3H, s, OCH_3), 3.74-3.82 (1H, m, H5b), 4.04-4.14 (2H, m, H6 and H7*a*), 4.30-4.70 (7H, m, H5, O$\underline{H_2}$Ar and 2 x O$\underline{H_2}$Ph), 6.84 (2H, d, *J*=8.4 Hz, 2 x ArCH), 7.18-7.38 (12 H, m, 2 x ArCH and 2 x $OCH_2\underline{Ph}$).

δ_C (75 MHz, $CDCl_3$): 26.2, 27.0 (t, C1' and C2'), 51.1 (t, C5), 55.2 (q, OCH_3), 62.9 (d, C7*a*), 69.0 (t, C3'), 71.7, 71.9, 72.5 (t, O$\underline{C}H_2$Ar and 2 x O$\underline{C}H_2$Ph), 74.9, 76.3, 76.9 (d, C1, C6 and C7), 113.6 (d, 2 x ArCH), 127.9, 128.0, 128.1, 128.1, 128.3, 128.4 (d, 2 x $OCH_2\underline{Ph}$), 129.0 (d, 2 x ArCH), 130.3 (s, ArC), 136.5, 137.0 (s, 2 x $OCH_2\underline{Ph}$), 158.9 (s, ArC), 161.2 (s, C3).

δ_H (500 MHz, d_6-benzene): 1.45-1.70 (4H, m, H1' and H2'), 3.10 (1H, dd, *J*=10.0, 5.0 Hz, H7), 3.16-3.24 (3H, m, H5a and H3'), 3.28 (3H, s, OCH_3) 3.52 (1H, t, *J*=5.0 Hz, H6), 3.74 (1H, dd, *J*=13.0, 5.0 Hz, H5b), 3.82 (1H, dd, *J*=9.0, 7.5 Hz, H7*a*), 4.00-4.28 (7H, m, H1, O$\underline{H_2}$Ar and 2 x O$\underline{H_2}$Ph), 6.76 (2H, dt, *J*=9.0, 2.0 Hz, 2 x ArCH), 7.10-7.22 (12H, m, 2 x ArCH and 2 x $OCH_2\underline{Ph}$).

δ_C (75 MHz, d_6-benzene): 26.8, 27.6 (t, C1' and C2'), 51.9 (t, C5), 54.9 (q, OCH_3), 63.2 (d, C7*a*), 69.5 (t, C3'), 71.7, 72.1, 72.8 (t, O$\underline{C}H_2$Ar and 2 x O$\underline{C}H_2$Ph), 75.8, 76.1, 78.4 (d, C1, C6 and C7), 114.1 (d, 2 x ArCH), 127.9, 128.0, 128.0, 128.1, 128.6, 128.6 (d, 2 x $OCH_2\underline{Ph}$), 129.4 (d, 2 x ArCH), 131.2 (s, ArC), 138.1, 138.3 (s, 2 x $OCH_2\underline{Ph}$), 159.6 (s, ArC), 161.4 (s, C3).

(2*R*,3*S*,4*R*)-2-[(1*R*)-1-Hydroxy-4-[(4-methoxyphenyl)methoxy]butyl]-3,4-*bis*(phenylmethoxy)pyrrolidine (17).

The oxazolidinone **14** (410 mg, 0.792 mmol) was dissolved in MeOH (8 mL), NaOH (200 mg, 5.00 mmol) dissolved in water (2 mL) was added. The mixture was placed in a teflon tube with a 100 bar pressure cap, then heated in a microwave reactor at 110 ^oC for 2 h. After cooling the mixture was poured into water (50 mL), then extracted with DCM (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), filtered and

evaporated *in vacuo* to give an oil. The pure product was obtained by column chromatography (increasing polarity from 5 % to 15 % MeOH in DCM as eluant), which gave the title compound (326 mg, 0.663 mmol, 83.7 %) as a clear oil.

$[\alpha]_D^{24}$: -25 (c 3.26, $CHCl_3$).

MS (CI+) *m/z* 492 (100 %) (M+1), HRMS (CI+) found 492.2769, calc for $C_{30}H_{38}NO_5$ 492.2750 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.40-1.54 (1H, m, H2'a), 1.60-1.90 (3H, m, H2'b and H3'), 2.70 (2H, br. s, NH and OH), 2.98 (1H, dd, *J*=6.3, 4.8 Hz, H2), 3.08 (1H, dd, *J*=11.1, 6.6 Hz, H5a), 3.18 (1H, dd, *J*=11.1, 6.6 Hz, H5b), 3.40 (2H, m, H4'), 3.78 (3H, s, OCH_3), 3.74-3.82 (1H, m, H1'), 4.00-4.10 (1H, m, H4), 4.15 (1H, t, *J*=4.2 Hz, H3), 4.43 (2H, s, $OC\underline{H_2}Ar$), 4.56 (2H, d, *J*=11.4 Hz, $OC\underline{H_2}Ph$), 4.62 (1H, d, *J*=12.0 Hz, $OC\underline{H_2}Ph$), 4.90 (1H, d, *J*=11.1 Hz, $OC\underline{H_2}Ph$), 6.87 (2H, dt, *J*=8.7, 2.1 Hz, 2 x ArCH), 7.22-7.38 (12H, m, 2 x ArCH and 2 x $OCH_2\underline{Ph}$).

δ_C (75 MHz, $CDCl_3$): 26.0, 31.6 (t, C2' and C3'), 48.2 (t, C5), 55.1 (q, OCH_3), 63.4 (d, C2), 69.9 (t, C4'), 71.1 (d, C1'), 71.9, 72.3, 73.4 (t, $O\underline{C}H_2Ar$ and 2 x $O\underline{C}H_2Ph$), 79.4 (d, C3), 80.1 (d, C4), 113.6 (d, 2 x ArCH), 127.4, 127.6, 127.8, 128.0, 128.3, 128.4 (d, 2 x $OCH_2\underline{Ph}$), 129.1 (d, 2 x ArCH), 130.4 (s, ArC), 137.8 (s, $OCH_2\underline{Ph}$), 137.9 (s, $OCH_2\underline{Ph}$), 159.0 (s, ArC).

(2*R*,3*S*,4*S*)-2-[(1*R*)-1-[[(1,1-Dimethylethyl)diphenylsilyl]oxy]-4-[(4-methoxyphenyl)methoxy]butyl]-3,4-*bis*(phenylmethoxy)pyrrolidine (18).

The amino alcohol **17** (326 mg, 0.663 mmol) was dissolved in CH_3CN (8 mL), then imidazole (100 mg, 1.441 mmol) and *tert*-butyldimethylsilylchloride (255 mg, 0.928 mmol) were added. The mixture was heated in a sealed tube at 65 ^oC for 3 d, then poured into sat. $NaHCO_3$ solution (50 mL) and extracted with DCM (3 x 30 mL). The combined organic portions were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give an oil. Pure product was obtained by column chromatography (increasing polarity from 2.5 % to 7.5 % MeOH in DCM as eluant), which gave the title compound (469 mg, 0.642 mmol, 96.9 %) as a clear gum.

$[\alpha]_D^{24}$: +3 (c 1.2, $CHCl_3$).

MS (ES+) *m/z* 730.3 (25 %) (M+1), HRMS (ES+) found 730.3942, calc for $C_{46}H_{56}NO_5Si$ 730.3928 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.04 (9H, s, $(CH_3)_3CSi$), 1.40-1.60 (4H, m, H2' and H3'), 1.86 (1H, br. s, NH), 3.02-3.16 (5H, m, H2, H5 and H4'), 3.81 (3H, s, OCH_3), 4.04-4.15 (2H, m, H3 and H4), 4.12 (1H, d, *J*=11.1 Hz, $OC\underline{H}_2Ph$), 4.20-4.28 (1H, m, H1'), 4.29 (2H, s, $OC\underline{H}_2Ph$), 4.56 (2H, s, $OC\underline{H}_2Ar$), 4.91 (1H, d, *J*=11.1 Hz, $OC\underline{H}_2Ph$), 6.87 (2H, dt, *J*=9.0, 2.7 Hz, 2 x ArCH), 7.16-7.44 (18H, m, 2 x ArCH, 2 x $OCH_2\underline{Ph}$, Ph_2Si), 7.64-7.70 (4H, m, Ph_2Si).

δ_C (75 MHz, $CDCl_3$): 19.4 (s, $(CH_3)_3\underline{C}Si$), 24.1 (t, C3'), 27.1 (q, $(\underline{C}H_3)_3CSi$), 30.1 (t, C2'), 48.2 (t, C5), 55.2 (q, OCH_3), 64.2 (d, C2), 70.2 (t, C4'), 71.3 (d, C1'), 72.2 (t, $O\underline{C}H_2Ar$), 72.3 (t, $O\underline{C}H_2Ph$), 72.5 (t, $O\underline{C}H_2Ph$), 77.1, 82.3 (d, C3 and C4), 113.6 (d, 2 x ArCH), 127.0, 127.3, 127.4, 127.4, 127.5, 127.9, 128.3 (d, Ph), 129.1 (d, 2 x ArCH), 129.4, 129.4 (d, Ph), 130.7 (s, ArC), 133.9, 134.8 (s, SiPh), 135.9, 136.0 (d, SiPh), 138.2, 139.1 (s, $OCH_2\underline{Ph}$), 159.0 (s, ArC).

(δ*R*,2*S*,3*S*,4*R*)-δ-[[(1,1-Dimethylethyl)diphenylsilyl]oxy]-3,4-*bis*(phenylmethoxy)-2-pyrrolidinebutanol (19).

The PMB ether **18** (484 mg, 0.663 mmol) was dissolved in CH_3CN (25 mL), then water (3.2 mL) and CAN (728 mg, 1.325 mmol) were added. The mixture was stirred at RT for 2h, then more CAN (350 mg, 0.637 mmol) was added. The mixture was stirred at RT for 1 h, then poured into sat. $NaHCO_3$ solution (75 mL) and extracted with DCM (3 x 40 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give an oil. The pure product was obtained by column chromatography (increasing polarity from 7.5 % to 20 % MeOH in DCM as eluant), which gave the title compound (371 mg, 0.608 mmol, 91.8 %) as a white foam.

m.p. 38-40 ^oC

$[\alpha]_D^{24}$: +12 (c 3.7, $CHCl_3$).

MS (CI+) *m/z* 610 (83 %) (M+1), HRMS (CI+) found 610.3357, calc for $C_{38}H_{48}NO_4Si$ 610.3353 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.07 (9H, s, $(CH_3)_3CSi$), 1.20-1.64 (4H, m, C2' and C3'), 3.00-3.44 (7H, m, C2, C5, C1', NH and 2 x OH), 4.03 (1H, d, *J*=10.8 Hz, $OC\underline{H}_2Ph$), 4.10-4.20

(2H, m, H3 and H4), 4.28 (1H, br. d, *J*=8.1 Hz, H4'), 4.56 (2H, s, OC$\underline{H}_2$Ph), 4.91 (1H, d, *J*=10.8 Hz, OC$\underline{H}_2$Ph), 7.10-7.44 (16H, m, 2 x OCH$_2\underline{Ph}$, Ph_2Si), 7.65 (4H, d, *J*=6.9 Hz, Ph_2Si).

δ_C (75 MHz, $CDCl_3$): 19.3 (s, $(CH_3)_3\underline{C}$Si), 26.0 (t, C2'), 27.0 (q, $(\underline{C}H_3)_3$CSi), 29.9 (t, C3'), 47.7 (t, C5), 62.1 (t, C1'), 64.2 (d, C2), 70.0 (d, C4'), 72.4 (t, O$\underline{C}H_2$Ph), 72.5 (t, OC$\underline{H}_2$Ph), 76.7, 82.1 (C3 and C4), 127.1, 127.4, 127.4, 127.4, 127.5, 127.7, 128.0, 128.3, 129.5, 129.6 (d, Ph), 133.5, 124.3 (s, SiPh), 135.9, 136.0 (d, SiPh), 137.8, 138.8 (OCH$_2\underline{Ph}$).

(1*S*,2*R*,8*R*,8*aS*)-Octahydro-1,2-*bis*(phenylmethoxy)-8-[[(1,1-dimethylethyl)diphenylsilyl]oxy]-indolizine (20).

The amino alcohol **19** (359 mg, 0.588 mmol) was dissolved in DCM (25 mL), then the solution was cooled to 0 ^oC. Carbontetrabromide (500 mg, 1.476 mmol) and triphenylphosphine (379 mg, 1.471 mmol) were added. The mixture was stirred at 0 ^oC for 15 min then triethylamine (4.0 mL, 28.7 mmol) was added. The mixture was stirred at 0 ^oC for 2 h, then left to stand at 4 ^oC for 20 h, before it was poured into water (60 mL) and extracted with DCM (3 x 30 mL). The combined organic portions were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give a black semi-solid. Pure product was obtained by column chromatography (increasing polarity from 5 % to 30 % EtOAc in pet. sp. as eluant), which gave the title compound (325 mg, 0.549 mmol, 93.4 %) as a clear gum.

$[\alpha]_D^{27}$: -10 (c 1.0, $CHCl_3$).

MS (CI+) *m/z* 592 (100 %) (M+1), HRMS (CI+) found 592.3256, calc for $C_{38}H_{46}NO_3Si$ 592.3247 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.07 (9H, s, $(CH_3)_3$CSi), 1.05-1.26 (1H, m, H7a), 1.34-1.48 (2H, m, H6), 1.70-1.90 (2H, m, H5a and H7b), 2.10 (1H, dd, *J*=8.7, 3.3 Hz, H8*a*), 2.47 (1H, dd, *J*=9.6, 8.1 Hz, H3a), 2.90 (1H, d, *J*=10.2 Hz, H5b), 3.24 (1H, dd, *J*=9.9, 3.3 Hz, H3b), 4.12-4.24 (2H, m, H2 and H8), 4.33 (1H, dd, *J*=5.1, 3.3 Hz, H1), 4.43 (1H, d, *J*=10.8 Hz, OC$\underline{H}_2$Ph), 4.56 (2H, AB system, *J*=12.0 Hz, OC$\underline{H}_2$Ph), 4.87 (1H, d, *J*=10.8 Hz, OC$\underline{H}_2$Ph), 7.16-7.48 (16H, m, 2 x OCH$_2\underline{Ph}$ and Ph_2Si), 7.69 (2H, dd, *J*=7.8, 1.2 Hz, PhSi), 7.73 (2H, dd, *J*=7.8, 1.2 Hz, PhSi).

δ_C (75 MHz, $CDCl_3$): 19.1 (s, $(CH_3)_3\underline{C}Si$), 23.5 (t, C6), 27.0 (q, $(\underline{C}H_3)_3CSi$), 34.1 (t, C7), 52.2 (t, C5), 58.1 (t, C3), 68.8 (d, C8), 71.9 (t, $O\underline{C}H_2Ph$), 73.1 (d, C8*a*), 74.0 (t, $O\underline{C}H_2Ph$), 77.7 (d, C2), 78.0 (d, C1), 126.9, 127.2, 127.4, 127.6, 127.7, 128.2, 129.3, 129.4 (d, Ph), 134.4, 134.7 (s, PhSi), 135.7, 135.8 (d, PhSi), 138.2, 138.8 (s, $OCH_2\underline{Ph}$).

(1*S*,2*R*,8*R*,8*aR*)-Octahydro-8-hydroxy-1,2-*bis*(phenylmethoxy)indolizine (21).

The indolizidine **20** (325 mg, 0.549 mmol) was dissolved in dry THF (20 mL) then dry TBAF (300 mg, 1.147 mmol) was added. The mixture was stirred at RT for 3 d, then TBAF (120 mg, 0.459 mmol) was added. The mixture was stirred at RT for 2 d, then poured into water (80 mL) and extracted with DCM (4 x 40 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give an oil. The pure product was obtained by column chromatography (increasing polarity from 5 % to 15 % MeOH in DCM as eluant), which gave the title compound (147 mg, 0.416 mmol, 75.8 %) as a colourless solid.

m.p. 78-80 ^oC.

$[\alpha]_D^{23}$: -103 (c 1.0, $CHCl_3$).

MS (CI+) *m/z* 354 (100 %) (M+1), HRMS (CI+) found 354.2083, calc for $C_{22}H_{28}NO_3$ 354.2069 (M+1).

δ_H (300 MHz, $CDCl_3$): 1.12 (1H, qd, *J*=12.6, 4.5 Hz, H7a), 1.50-1.76 (2H, m, H6), 1.80-2.02 (3H, m, H5a, H7b and H8*a*), 2.12 (1H, br. s, OH), 2.42 (1H, dd, *J*=10.2, 7.2 Hz, H3a), 2.91 (1H, br. d, *J*=10.5 Hz, H5b), 3.20 (1H, dd, *J*=10.2, 3.0 Hz, H3b), 3.90 (1H, ddd, *J*=11.1, 8.7, 4.5 Hz, H8), 4.00-4.12 (2H, m, H1 and H2), 4.49 (1H, d, *J*=12.0 Hz, $OC\underline{H}_2Ph$), 4.54 (1H, d, *J*=12.0 Hz, $OC\underline{H}_2Ph$), 4.59 (1H, d, *J*=12.0 Hz, $OC\underline{H}_2Ph$), 4.88 (1H, d, *J*=12.0 Hz, $OC\underline{H}_2Ph$), 7.22-7.40 (10H, m, 2 x $OCH_2\underline{Ph}$).

δ_C (75 MHz, $CDCl_3$): 23.0 (t, C6), 32.3 (t, C7), 51.4 (t, C5), 57.8 (t, C3), 66.4 (d, C8), 71.7 (t, $O\underline{C}H_2Ph$), 72.0 (d, C8*a*), 73.3 (t, $O\underline{C}H_2Ph$), 76.7, 76.8 (d, C1 and C2), 127.3, 127.5, 127.6, 128.0, 128.1, 128.3 (d, $OCH_2\underline{Ph}$), 138.0, 138.52 (s, $OCH_2\underline{Ph}$).

(1*S*,2*R*,8*R*,8*aR*)-Octahydro-1,2,8-indolizinetriol ((-)-swainsonine).

The indolizidine **21** (147 mg, 0.416 mmol) was dissolved in MeOH (10 mL) then $PdCl_2$ (59 mg, 0.333 mmol) was added. The mixture was stirred under an atmosphere of H_2 at

RT for 2 h, then the flask was flushed with N_2 before the mixture was filtered through celite. The solids were washed with MeOH (3 x 10 mL), then the filtrates were evaporated *in vacuo*. The residue was dissolved in water (2 mL) and applied to Dowex-1 basic ion-exchange resin (OH form), and eluted with water. Evaporation of the eluant afforded (-)-swainsonine (67 mg, 0.387 mmol, 93.0 %) as a colourless solid.

$[\alpha]_D^{26}$: -71 (c 0.56, MeOH).

MS (CI+) *m/z* 174 (100 %) (M+1), HRMS (ES+) found 174.1186, calc for $C_8H_{16}NO_3$ 174.1130 (M+1).

δ_H (300 MHz, D_2O): 1.13 (1H, qd, *J*=12.6, 4.8 Hz, H7a), 1.41 (1H, qt, *J*=13.5, 4.2 Hz, H6a), 1.62 (1H, br. d, *J*=13.6 Hz, H6b), 1.82 (1H, dd, *J*=7.8, 3.9 Hz, H8*a*), 1.85-2.00 (2H, m, H5a, H7b), 2.46 (1H, dd, *J*=11.1, 7.8 Hz, H3a), 2.75-2.85 (2H, m, H3b, H5b), 3.69 (1H, ddd, *J*=11.1, 9.6, 4.8 Hz, H8), 4.15 (1H, dd, *J*=6.0, 3.9 Hz, H1), 4.24 (1H, ddd, *J*=8.1, 6.0, 2.4 Hz, H2).

δ_C (75 MHz, D_2O): 22.2 (t, C6), 31.5 (t, C7), 50.6 (t, C5), 59.7 (t, C3), 65.2 (d, C8), 67.9 (C2), 68.5(C1), 71.8 (d, C8*a*).