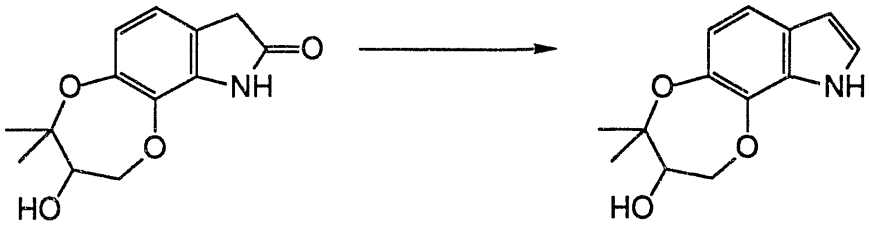
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Supporting Information for *J. Am. Chem. Soc.*, **1993**, 115(20), 9323-9324, DOI: 10.1021/ja00073a072

CUSHING
9323-9324

J. Am. Chem. Soc. v 115
p. 9323 Cushing

Supplementary material



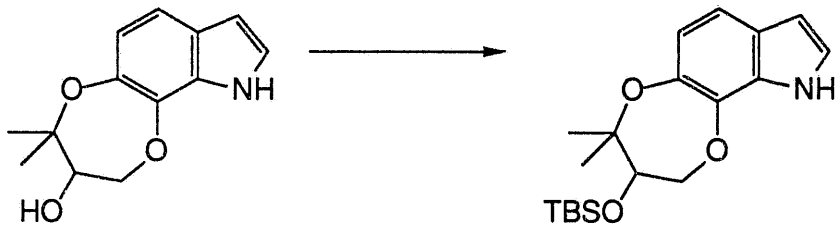
i

^{1}H NMR (300MHz) ($CDCl_3$) δTMS; 1.22(3H, s); 1.56(3H, s); 3.03(1H, d, J = 11,4Hz, D_2O exch.); 3.63(1H, ddd, J = 4.0, 0.9, 11.3Hz); 4.19(1H, dd, J = 0.9, 12.3Hz); 4.31(1H, dd, J = 4.0, 12.3Hz); 6.49(1H, dd, J = 2.2, 3.1Hz); 6.78(1H, d, J = 8.4Hz); 7.16-7.19(2H, m); 8.29(1H, s, D_2O exch.).

IR(KBr) 3340,2984,1580,1504,1444,1338,1224,1133,1057,814, 753cm-1

microanalysis calc'd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00; Found: C, 67.16; H, 6.63; N, 5.79.

m.p. 202-205°C

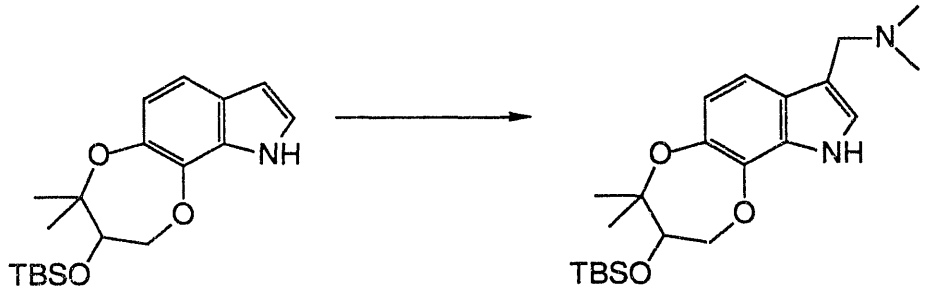


^{1}H NMR (300Hz) ($CDCl_3$) δTMS; 0.14(6H, s); 0.89(9H, s); 1.12(3H, s); 1.48(3H, s); 3.88(1H, dd, J = 9.2, 11.5Hz); 3.98(1H, dd, J = 3.2, 9.2Hz); 4,22(1H, dd, J = 3.2, 11.5Hz); 6.48(1H, dd, J = 2.2, 3.1Hz); 6.76(1H, d, J = 8.4Hz); 7.14(2H, ddd, J = 2.4, 3.4, 3.5Hz); 8.21(1H, s, D_2O exch.)

IR(neat) 3412,2936,1500,1438,1234,1093,833cm-1.

f9324-m2

m.p. 118-119°C



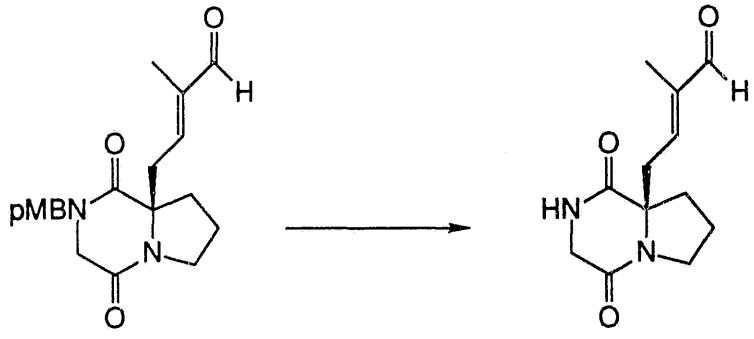
6

^{1}H NMR (300Hz) ($CDCl_3$) δTMS; 0.90(9H, s); 1.13(3H, s); 1.48(3H,s); 2.28(6H, s); 3.58(2H, s); 3.58(2H, s); 3.88(1H, dd, J = 9.2, 11.4Hz); 3.98(1H, dd, J = 3.2, 9.1Hz); 4.21(1H, dd, J = 3.2, 11.5Hz); 6.76(1H, d, J = 8.4Hz); 8.44(1H, s, D_2O exch.)

IR (neat) 2932,1502,1458,1360,1251,1218,1093,837,777cm-1.

microanalysis calc'd for $C_{22}H_{36}N_2O_3Si$: C, 65.31; H, 8.97; N, 6.92; found: C, 65.09; H, 8.77; N, 6.73.

m.p. 152°C



3

^{1}H NMR (300MHz) ($CDCl_3$) δ TMS 1.76(3H, s); 1.99-2.10(2H, br s); 2.17-2.26(2H, m); 2.78(1H, dd, J = 7.3, 14.5Hz); 2.90(1H, dd, J = 8.0, 14.8Hz); 3.54-3.63(1H, m); 3.84(1H, dt, J = 12.3, 8.4Hz); 3.95(1H, d½ABq, J = 3.4, 17.6Hz); 4.10(1H, ½ABq, J = 17.6 Hz); 6.55(1H, t, J = 7.2Hz); 7.96(1H, br s, D_2O exch.); 9.45(1H, s),

IR (neat) 3246, 1684, 1448, 1326, 1107 cm^{-1}.

$[\alpha]_{25}^{D} = -1.51/1.92x10^{-2} = -78.4(CH_2Cl_2, c = 0.164)$

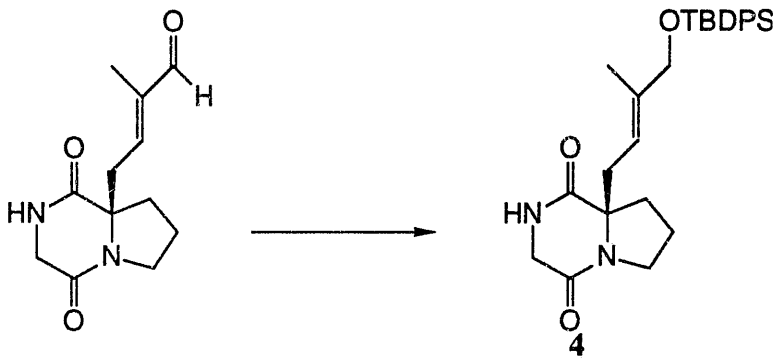
J-9324-1173.

IR (neat) 3246, 1684, 1448, 1326, 1107 cm^{-1}.

$[\alpha]_{25}^{D} = -1.51/1.92x10^{-2} = -78.4(CH_2Cl_2, c = 0.164)$

microanalysis calc'd for.$C_{12}H_{15}N_2O_3$ C, 61.00; H, 6.83; N, 11.86; found: C, 60.88; H, 6.66; N, 11.71.

EI HRMS 236.1155 ($C_{12}H_{15}N_2O_3$ requires 236.11609).



4

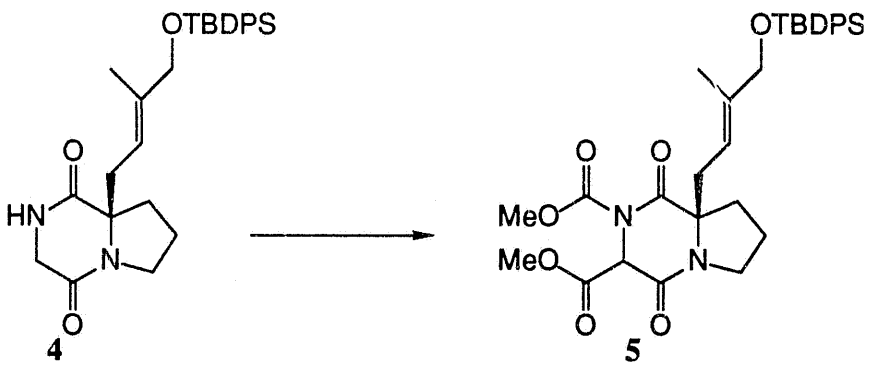
^1H NMR (300MHz) ($CDCl_3$) δ 1.03(9H, s); 1.54(3H, s); 1.92-2.19(4H, m); 2.49(1H, dd, J = 8.6, 14.1Hz); 2.58(1H, dd, J = 7.5, 14.1Hz); 3.44-3.53(1H, m); 3.73(1H, d½ABq, J = 4.1, 16.9Hz); 3.78-3.85(1H, m); 4.01(2H, s); 4.06(1H, ½ABq, J = 16.9Hz); 5.56-5.62(1H, m); 6.38(1H, d, J = 3.7Hz, D_2O exch.); 7.32-7.43(6H, m); 7.62(4H, dd, J = 1.8, 7.6Hz).

IR (neat) 3232(br) 2930, 2857, 1664, 1446, 1435, 1113, 822, 733, 702 cm^{-1}.

$[\alpha]_{25}^{D} = -1.24/1.92x10^{-2} = -63.3(CDCl_3, c = 0.0822)$

microanalysis cacl'd for $C_{28}H_{36}N_2O_3Si$ C,70.55; H, 7.61; N, 5.88; found C, 70.60; H, 7.56; N, 5.91.

m.p. 132°C.



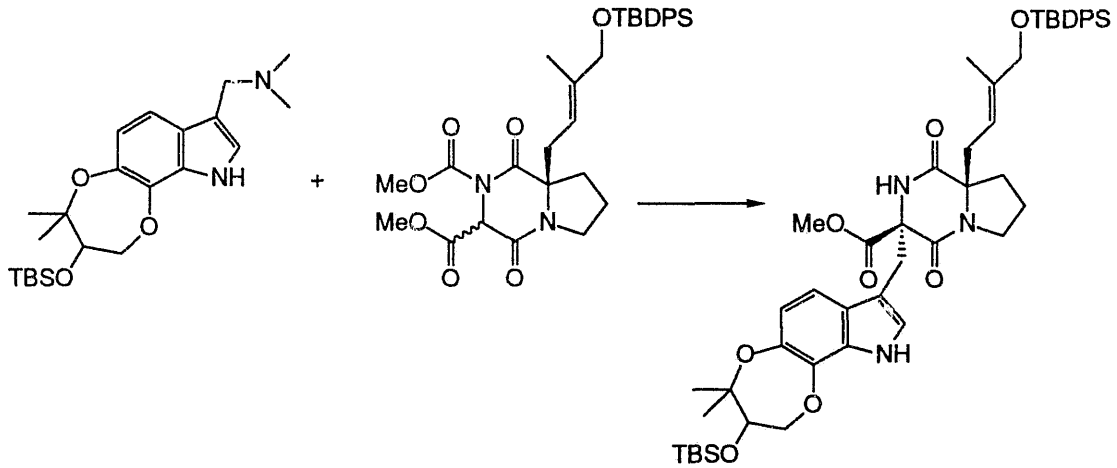
4 5

J-9324-mf

^{1}H NMR (300MHz) ($CDCl_3$) δ 1.04(9H, s); 1.40(3H, s); 1.86-2.03(2H, m); 2.12-2.31(2H, m); 2.55(1H, d, J = 7.4Hz); 3.43-3.52(1H, m); 3.74-3.82(1H, m); 3.83(3H, s); 3.88(3H, s); 4.03(2H, br s); 5.48-5.53(2H, m); 7.34-7.41(6H, m); 7.57-7.66(4H, m).

IR (neat) 2960, 1790, 1740, 1681, 1430, 1366, 1272, 1223, 1109, 735, 705 cm^{-1}.

microanalysis cacl'd for $C_{32}H_{40}N_2O_7Si$ C,68.06 H, 7.14; N, 4.96; found C, 67.87; H, 7.27; N, 4.77.



6 **5** **7**

^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.10(6H, s); 0.115(3H, s); 0.12(3H, s); 0.87(9H, s); 0.88(9H, s); 1.02(18H, s); 1.096(3H, s); 1.10(3H, s); 1.45(3H, s); 1.46(3H, s); 1.54(6H, s); 1.60-1.88(6H, m); 2.02-2.11(2H, m): 2.92(2H, dd, J = 7.1, 14.4Hz); 2.44(2H, dd, J = 8.1, 14.5Hz); 3.32-3.44(4H, m); 3.60(3H, s); 3.62(3H, s); 3.72-3.93(8H, m); 3.98(4H, br s); 4.18(2H, dd, J = 2.9, 8.4Hz); 5.43(2H, m); 6.38(1H, s, D_2O exch.); 6.41(1H, s, D_2O exch.); 6.74(1H, d, J = 8.5Hz); 6.75(1H, d, J = 8.5Hz); 6.89(1H, d, J = 2.3Hz); 6.92(1H, d, J = 2.3Hz); 7.08(2H, d, J = 8.5Hz); 7.33-7.41(12H, m); 7.61-7.63(8H, m); 8.43(1H, d, J = 2.9Hz, D_2O exch.); 8.64(1H, d, J =1.9Hz, D_2O exch.).

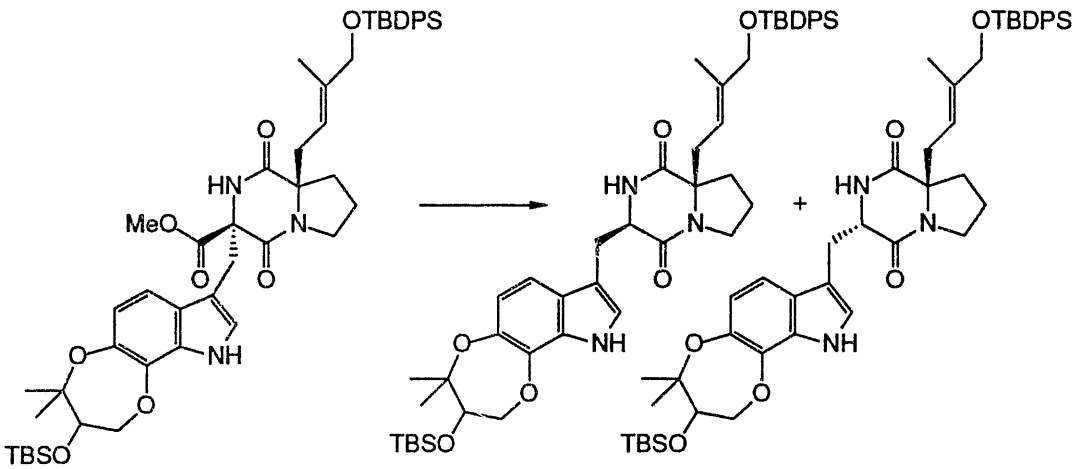
IR (neat) 3281(br), 2954, 2932, 2856, 1747, 1670, 1665, 1649, 1431, 1251, 1224, 1109, 1088, 733, 706 cm-^{1}.

EI HRMS 893.4457($C_{50}H_{67}N_3O_8Si_2$ requires 893.4467).

J-9324-m5

microanalysis calc'd for $C_{50}H_{67}N_3O_8Si_2$ C, 67.16; H, 7.55; N, 4.70; found C, 66.93; H, 7.36; N, 4.51.

m.p.106-108°C.



^{1}H NMR (300MHz) ($CDCl_3$) (syn, mixture of two diastereomers) δTMS 0.146(6H, s); 0.904(18H, s); 1.04(18H, s); 1.126(3H, s); 1.13(3H, s); 1.48(6H, s); 1.64(6H, s); 1.94-2.06(6H, m); 2.20-2.24(2H, m); 2.36-2.46(2H, m); 2.60-2.72(2H, m); 2.98(2H, dd, J = 11.6, 14.1Hz); 3.44-3.57(4H, m); 3.88(2H, dd, J = 6.7,9.2Hz); 3.97(2H, dd, J = 3.1, 9.1Hz); 4.02-4.06(2H, m); 4.10(4H, s); 4.17-4.25(4H, m); 5.58(2H, m); 5.68(2H, br s, D_2O exch.); 6.75(2H, d, J = 8.5Hz); 6.86(1H, d, J = 2.2Hz): 6.88(1H, J = 2.2Hz); 7.14(2H, d, J = 8.4Hz); 7.26-7.44(12H, m); 7.60-7.64(8H, m); 8.04(1H, s, D_2O exch.); 8.06(1H, s, D_2O exch.).

syn diastereomers separated;

^{1}H NMR (300MHz) ($CDCl_3$) (syn #1, less polar) δTMS 0.12(3H, s); 0.13(3H, s); 0.88(9H, s); 1.03(9H, s); 1.11(3H, s); 1.46(3H, s); 1.63(3H, s); 1.92-2.04(3H, m); 2.18-2.23(1H, m); 2.39(1H, dd, J = 7.2, 14.2Hz); 2.64(1H, dd, J = 8.7, 14.2Hz); 2.99(1H, dd, J = 11.4, 14.2Hz); 3.42-3.46(1H, m); 3.51(1H, dd, J = 2.7, 14.2Hz); 3.85(1H, dd, J = 9.2, 11.3Hz); 3.94(1H, dd, J = 3.0, 9.Hz); 3.99-4.06(1H, m); 4.08(2H, s); 4.11-4.15(1H, m); 4.19(1H, dd, J = 3.0, 11.3Hz); 5.58(1H, t, J = 7.8Hz);

J-9324-M6

5.76(1H, d, J = 2.7Hz, D_2O exch.); 6.73(1H, d, J = 8.4Hz); 6.85(1H, d, J = 2.1Hz); 7.11(1H, d, J = 8.5Hz); 7.26-7.42(6H, m); 7.57-7.63(4H, m); 8.15(1H, s, D_2O exch.).

^1H NMR (300MHz) ($CDCl_3$) (syn #2, more polar) δTMS 0.12(3H, s); 0.14(3H, s); 0.88(9H, s); 1.03(9H, s); 1.11(3H, s); 1.46(3H, s); 1.62(3H, s); 1.91-2.04(3H, m); 2.18-2.22(1H, m); 2.36(1H, dd, J = 7.3, 14.2Hz); 2.60(1H, dd, J = 8.6, 14.3Hz); 2.97(1H, dd, J = 11.3, 14.2Hz); 3.41-3.44(1H, m); 3.50(1H, dd, J = 3.1, 14.2Hz); 3.86(1H, dd, J = 9.3, 11.3Hz); 3.95(1H, dd, J = 3.0, 9.1Hz); 3.99-4.03(1H, m); 4.08(2H, s); 4.14-4.16(1H, m); 4.20(1H, dd, J = 2.9, 11.6Hz); 5.56(1H, t, J =7.5Hz); 5.72(1H, d, J = 2.6Hz, D_2O exch.); 6.73(1H, d, J = 8.4Hz); 6.84(1H, d, J = 2.1Hz); 7.11(1H, d, J = 8.4Hz); 7.26-7.42(6H, m); 7.57-7.62(4H, m); 8.07(1H, s, D_2O exch.).

^1H NMR (300MHz) ($CDCl_3$) (anti, mixture of two diastereomers) δTMS 0.14(6H, s); 0.16(6H, s); 0.90(18H, s); 1.04(9H, s); 1.045(9H, s); 1.09(3H, s); 1.13(3H, s); 1.47(6H, s); 1.53(3H, m); 1.54(3H, m); 1.97-2.17(8H, m); 2.47-2.62(4H, m); 2.78-2.88(2H, m); 3.54-3.65(4H, m); 3.82-3.99(6H,m); 4.02(4H, s); 4.21(2H, dd, J = 3.1, 11.0Hz); 4.35-4.39(2H, m); 5.52-5.54(2H, m); 5.69(2H, br s, D_2O exch.); 6.60(1H, d, J = 8.4Hz); 6.63(1H, d, J = 8.4Hz): 6.89(2H, d, J = 2.1Hz); 6.98(2H, d, J = 8.4Hz); 7.36-7.42(12H, m); 7.62-7.69(4H, m); 8.08(2H, br s, D_2O exch.).

IR (neat) (anti) 3289(br), 2929, 2855, 1666, 1444, 1428, 1254, 1222, 1111, 857, 836, 704 cm-1.

IR (neat) (syn) 3274(br), 2929, 2858, 1666, 1651, 1453, 1428, 1250, 1224, 1112, 1052, 858, 838, 777 cm-1.

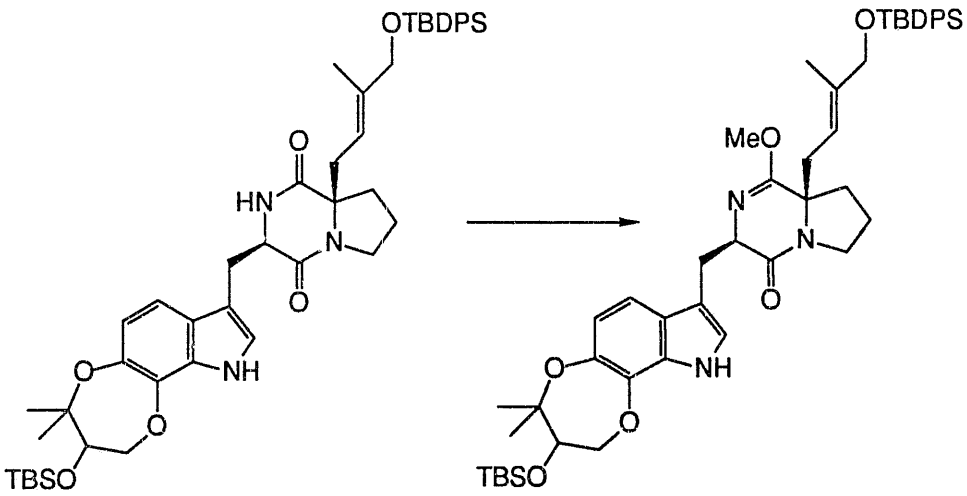
microanalysis cacl'd for $C_{49}H_{65}N_3O_6Si_2$(syn) C, 68.94; H, 7.84; N, 5.02; Found C,69.06; H, 7.76; N, 5.03.

m.p. (syn) 167-168°C.

microanalysis cacl'd for $C_{48}H_{65}N_3O_6Si_2$(anti) C, 68.94; H, 7.84; N, 5.02; Found C,68.76; H, 7.60; N, 4.82.

m.p.(anti) 95-99°C

J-9324-117



^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.120(12H, s); 0.875(18H, s); 1.02(18H, s); 1.06(3H, s); 1.07(3H, s); 1.45(12H, s); 1.65-2.08(12H, m); 3.07-3.15(2H, m); 3.26(2H, dd, J = 6.2, 12.6Hz); 3.32-3.40(2H, m); 3.61(6H, s); 3.70-3.86(2H, m); 3.91-3.95(4H, m); 3.99(2H, s); 4.15(2H, dd, J = 3.6, 11.7Hz); 4.36-4.40(2H, m); 5.37-5.44(2H, br m); 6.69(2H, d, J = 8.4Hz); 7.01(2H, d, J = 1.7Hz); 7.15(2H, d, J = 8.4Hz); 7.26-7.41(12H, m); 7.58-7.62(8H, m); 8.06(2H, s, D_2O exch.).

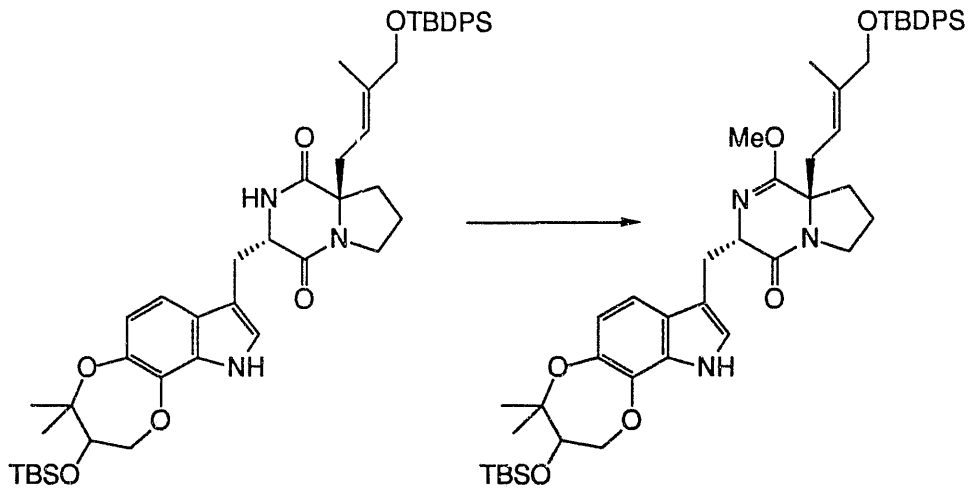
IR (neat) 3292, 2932, 1687, 1643, 1447, 1251, 1218, 1109, 837 cm^{-1}.

MS (EI) 849 *m/e* (rel intensity) 849 (M^+, 8.9) 361 (26) 360 (95) 167(100).

microanalysis calc'd for $C_{49}H_{67}N_3O_6Si_2$; C, 69.02; H, 7.94; N, 4.94; Found: C, 69.02; H, 7.88; N, 4.79.

m.p. 74-76°C.

J-9324-178



^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.13(3H, s); 0.14(9H, s); 0.89(18H, s); 1.03(9H, s); 1.04(9H, s); 1.087(3H, s); 1.093(3H, s); 1.28-1.43(3H, m); 1.48(3H, s); 1.50(6H, s); 1.79-1.89(4H, m); 2.24-2.38(4H, m); 3.22-3.42(6H, m); 3.60(3H, s); 3.62(3H, s); 3.68-3.76(2H, m); 3.79-3.87(2H, m); 3.94(2H, d, J = 3.4Hz); 3.97(4H, br s); 4.15-4.20(2H, m); 4.26-4.32(2H, m); 5.41(2H, t, J = 7.8Hz); 6.701(1H, d, J = 8.5Hz); 6.703(2H, d, J = 8.4Hz); 6.96(1H, d, J = 2.6Hz); 6.97(1H, d, J = 2.6Hz); 7.28(2H, d, J = 8.5Hz); 7.32-7.44(12H, m); 7.60-7.64(8H, m); 7.97(2H, br s, D_2O exch.).

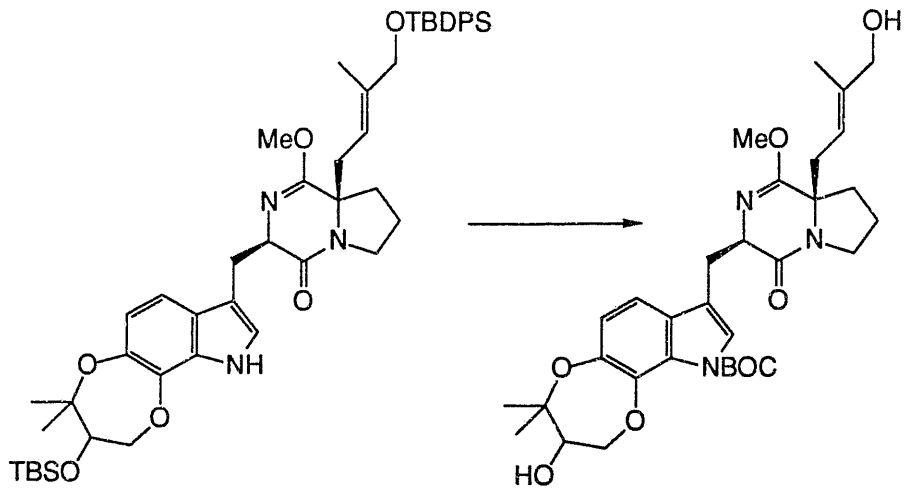
IR (neat) 3304, 2930, 1695, 1645, 1447, 1249, 1221, 836 cm^{-1}.

EI HRMS 849.4550 ($C_{49}H_{67}N_3O_6Si_2$ requires 849.4568)

microanalysis calc'd for $C_{49}H_{67}N_3O_6Si_2$: C, 69.22; H, 7.94; N, 4.94; found C, 59.06; H, 8.04; N, 4.89.

m.p. 54-58°C.

J-9324-M19



8a

^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 1.18(6H, s); 1.52(3H, s); 1.53(1H, s); 1.56(1H, s); 1.57(21H, s); 1.61-2.07(10H, m); 2.14(2H, dd, J = 8.6, 14.5Hz); 2.85(2H, br s, D_2O Exch.); 2.92-3.01(2H, m); 3.18-3.35(6H, m); 3.56(2H, br s, D_2O exch.); 3.62(3H, s); 3.64(3H, s); 3.88(4H, br s); 3.91-4.00(2H, m); 4.25(4H, br s); 4.30-4.39(2H, m); 4.98-5.01(2H, m); 6.87(1H, d, J = 8.3Hz); 6.88(1H, d, J = 8.3Hz): 7.16(1H, d, J = 8.3Hz); 7.17(1H, d, J= 8.3Hz); 7.34(1H, s); 7.35(1H, s).

^{13}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 13.44, 19.47, 19.68, 23.51, 23.63, 25.13, 25.32, 27.86, 30.34, 30.52, 34.38, 34.84, 35.12, 35.26, 43.38, 43.63, 52.63, 52.70, 62.03, 62.40, 65.26, 65.45, 67.67, 67.76, 70.63, 75.37, 82.57, 82.64, 114.53, 114.73, 116.75, 116.88, 118.18, 118.32, 119.04, 119.12, 126.34, 128.04, 128.10, 129.94, 130.07, 138.64, 138.71, 140.68, 146.15, 148.49, 161.32, 161.50, 168.53, 168.66

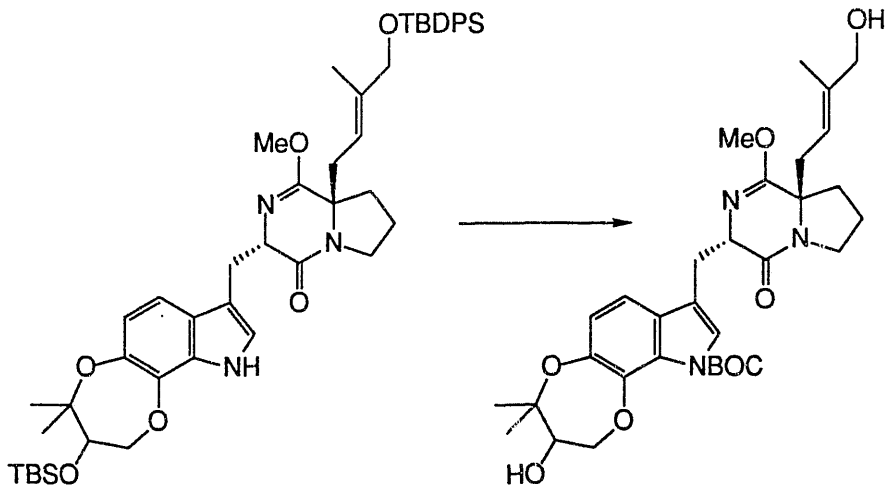
IR (neat) 3390(br), 2976, 1752, 1692, 1632, 1491, 1453, 1371, 1251, 1158, 733 cm^{-1}.

microanalysis calc'd for $C_{32}H_{43}N_3O_8$; C, 64.30; H, 7.25; N, 7.03; found: C, 64.12; H, 7.41; N, 6.88.

EI HRMS m/e 597.3065 ($C_{32}H_{43}N_3O_8$ requires 597.3050).

m.p. 72-85°C.

J-9324-1M10



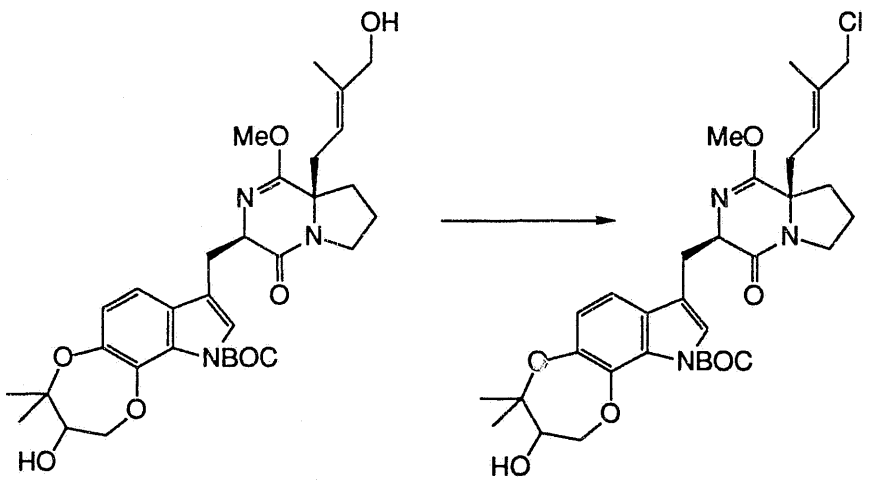
8b

^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 1.16(3H, s); 1.18(3H, s); 1.51(3H, s); 1.52(3H, s); 1.55(6H, s); 1.57(18H, s); 1.60-2.14(10H, m, 2H D_2O exch.);2.22-2.37(4H, m); 3.06-3.18(3H, m, 1H D_2O exch.); 3.26-3.36(5H, m, 1H D_2O exch.); 3.55(3H, s); 3.56(2H, br s); 3.60(3H, s); 3.63-3.72(2H, m); 3.89(4H, m); 4.18-4.23(2H, m); 4.25(4H, br s); 5.21-5.27(2H, m); 6.857(1H, d, J = 8.3Hz); 6.861(1H, d, J = 8.3Hz); 7.22(2H, d, J = 8.3Hz); 7.24(2H, s).

IR (neat) 3401(br), 2976, 1747, 1692, 1632, 1496, 1436, 1371, 1251, 1158, 733 cm^{-1}.

EI HRMS 597.3050 ($C_{32}H_{43}N_3O_8$ requires 597.3050)

m.p.72-80°C.



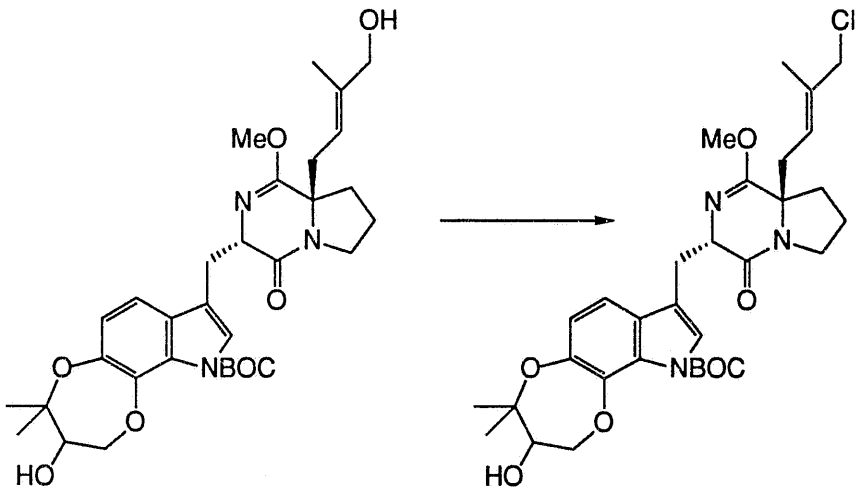
J-9324-mll

^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 1.17(6H, S); 1.52(6H, s); 1.57(18H, s); 1.65(6H, s); 1.73-2.20(12H, s); 2.84(2H, dd, J = 9.0, 14.4Hz); 3.06(1H, br s, D_2O exch.); 3.10(1H, br s, D_2O exch.); 3.26-3.36(4H, m); 3.55-3.58(4H, m); 3.62(2H, s); 3.63(2H, s); 3.91(4H, s); 3.95-4.05(2H, m); 4.24-4.25(4H, m); 4.30-4.36(2H, m); 5.28(2H, m); 6.88(2H, d, J = 8.3Hz); 7.14(1H, d, J = 8.3Hz); 7.15(1H, d, J = 8.3Hz); 7.376(1H,s); 7.384(1H, s).

IR (neat) 3403, 2979, 1750, 1716, 1642, 1348, 1154 cm^{-1}.

EI HRMS 615.2709 ($C_{32}H_{42}N_3O_7Cl$ requires 615.2711).

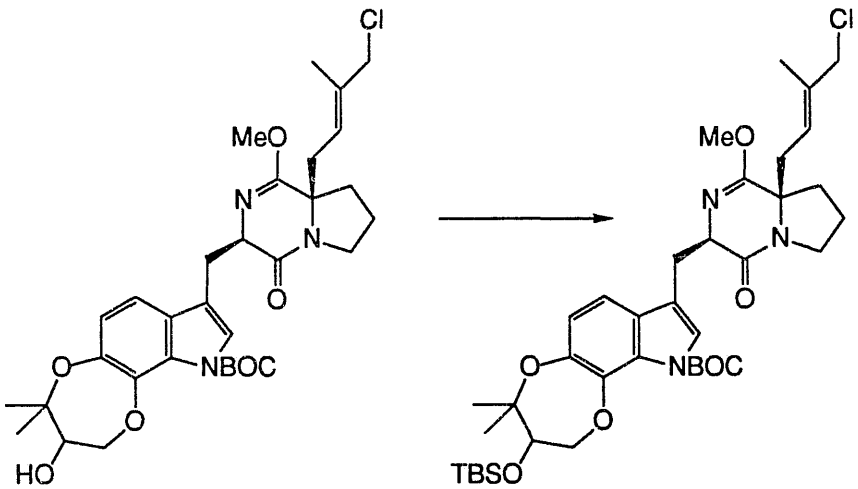
microanalysis calc'd for $C_{32}H_{42}N_3O_7Cl$ C, 62.38; H, 6.87; N, 6.82; found C, 62.53; H, 6.86; N, 6.67.



^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 1.17(3H, s); 1.18(3H, s); 1.52(3H, s); 1.54(3H, s); 1.57(18H, s); 1.65(6H, s); 1.71-1.92(6H, m); 2.24-2.39(4H, m); 3.03-3.19(4H, m, 2H D_2O exch.); 3.28-3.37(4H, m); 3.56(3H, s); 3.60(3H, s); 3.59-3.75(4H, m); 3.89(4H, s); 4.21-4.29(6H, m); 5.35(2H, t, J = 7.5Hz); 6.86(1H, d, J = 8.3Hz); 6.87(1H, d, J = 8.3Hz); 7.23(2H, d, J = 8.3Hz); 7.22(1H, s); 7.27(1H, s).

IR (neat) 3412(br), 2976, 1752, 1698, 1638, 1365, 1251, 1158 cm^{-1}.

EI HRMS 615.2714 ($C_{32}H_{42}N_3O_7Cl$ requires 615.2711)



9a

^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.12(6H, s); 0.13(6H, s); 0.88(18H, s); 1.06(6H, s); 1.47(6H, s); 1.59(18H, s); 1.65(6H, s); 1.78-1.98(8H, s); 2.02-2.12(4H, m); 2.86(2H, dd, J = 9.0, 14.6Hz); 3.31-3.34(2H, m); 3.33(2H, dd, J = 4.0, 13.6Hz); 3.62(3H, s); 3.64(3H, s); 3.71-3.79(2H, m); 3.73(1H, dd, J = 4.2, 9.8Hz); 3.77(1H, dd, J = 4.4, 9.7Hz);

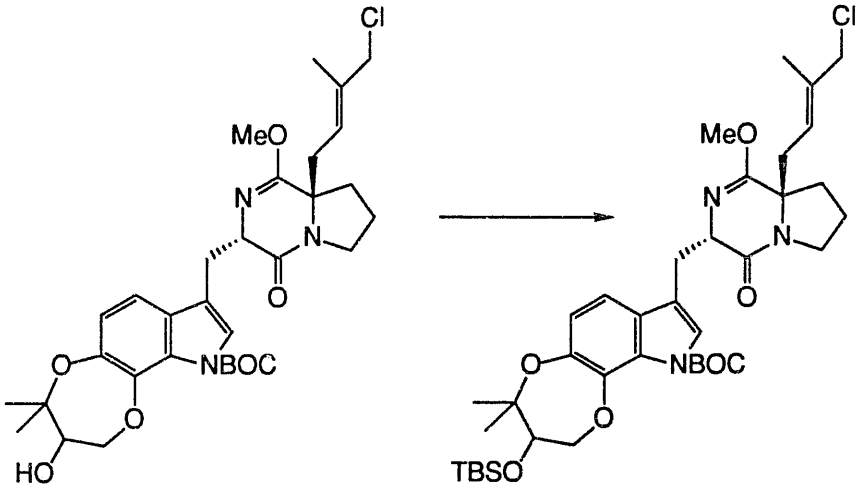
3.92(4H, s); 3.94-4.01(4H, m); 4.15(2H, dd, J = 3.8, 12.4Hz); 4.32-4.37(2H, m); 5.28-5.30(2H, m); 6.87(2H, d, J = 8.3Hz); 7.12(2H, d, J = 8.3Hz); 7.13(1H, d, J = 8.3Hz); 7.38(2H, s).

IR (neat) 2930, 1750, 1691, 1652, 1494, 1424, 1366, 1248, 1159, 1088 cm^{-1}.

MS (EI) 729 *m/e* (rel intensity) 731 (M+2, 2.1) 729 (M^+, 4.2) 629 (9.4) 361 (24.1) 360 (100) 167(94.8) 57.2 (63).

microanalysis calc'd for $C_{38}H_{56}N_3O_7SiCl$; C, 62.49; H, 7.73; N, 5.75; found: C, 62.57; H, 7.71, N, 5.55.

J-9324-M13



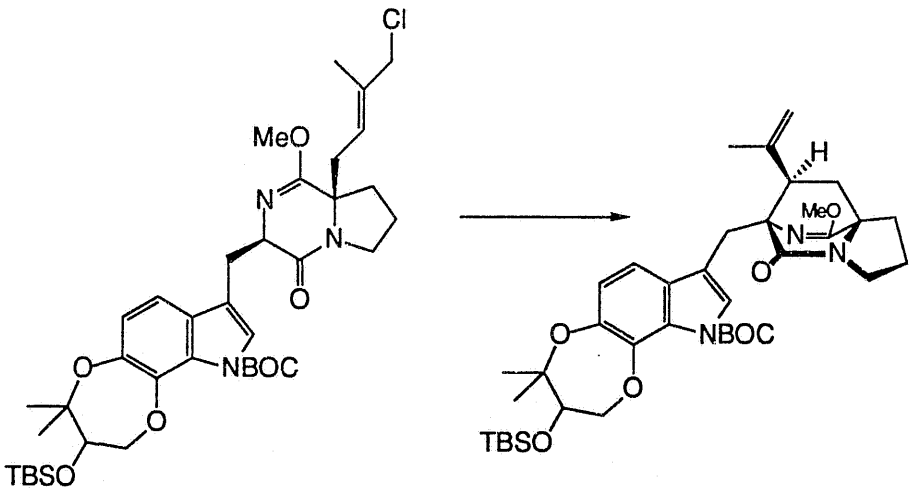
9b

^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.12(6H, s); 0.13(6H, s); 0.87(18H, s); 1.05(3H, s); 1.06(3H, s); 1.47(6H, s); 1.50-1.53(2H, m); 1.58(18H, s); 1.65(6H, s); 1.72-1.91(4H, m); 2.21-2.37(4H, m); 3.06-3.19(2H, m); 3.28-3.36(4H, m); 3.56(3H, s); 3.60(3H, s); 3.63-3.87(4H, m): 3.89(4H, s); 3.93(2H, dd, J = 3.9, 9.8Hz); 4.13-4.18(2H, m); 4.22-4.35(2H, m); 5.30-5.40(2H, m); 6.85(1H, d, J = 8.3Hz); 6.86(1H, d, J = 8.3Hz); 7.19-7.26(4H, m).

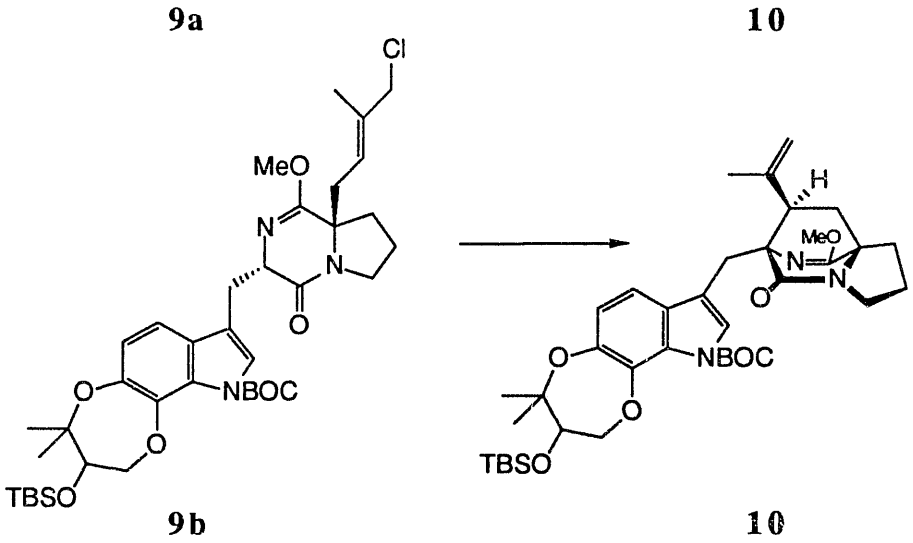
IR (neat) 2949, 1751, 1693, 1652, 1493, 1424, 1369, 1250, 1156, 1086 cm^{-1}.

microanalysis calc'd for $C_{38}H_{56}N_3O_7SiCl$; C, 62.49; H, 7.73; N, 5.75; found: C, 62.29; H, 7.61; N, 5.76.

EI HRMS 729.3555($C_{38}H_{56}N_3O_7SiCl$ requires 729.3576)



J-9324-m14



^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.12(6H, s); 0.13(6H, s); 0.872(9H, s); 0.875(9H, s); 1.46(6H, s); 1.58(18H, s); 1.61(3H, s); 1.64(3H, s); 1.72-2.03(8H, m); 2.25-2.42(2H, m); 2.47(2H, dd, J = 5.1, 9.7Hz); 2.54(2H, dd, J = 5.8, 9.7Hz); 3.05(1H, ½ ABq, J = 15.0Hz); 3.07(1H, ½ ABq, J = 15.0Hz); 3.31-3.53(6H, m); 3.57(3H, s); 3.64(3H, s); 3.73-3.89(2H, m); 3.94(2H, dd, J = 3.7, 9.7Hz); 4.17(2H, dd, J = 3.1, 11.6Hz); 4.62(1H, s); 4.75(1H, s); 4.78(1H, s); 4.85(1H, s); 6.82(2H, d, J = 8.4Hz); 7.31(1H, d, J = 8.4Hz); 7.38(1H, d, J = 8.4Hz); 7.44(1H, s); 7.52(1H, s).

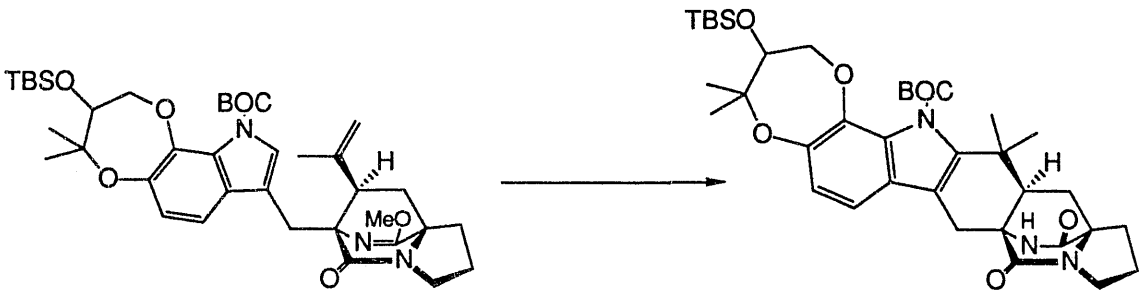
IR (neat) 2935, 1752, 1684, 1637, 1496, 1418, 1365, 1350, 1250, 1220, 1156, 1083 cm^{-1}.

EI HRMS m/e 693.3834 ($C_{38}H_{55}N_3O_7Si$ requires 693.3809).

microanalysis calc'd for $C_{38}H_{55}N_3O_7Si$ C, 65.77; H, 7.99; N, 6.05; found C, 65.85; H, 7.99; N, 5.91.

m.p.105-108°C.

J-9324-1115



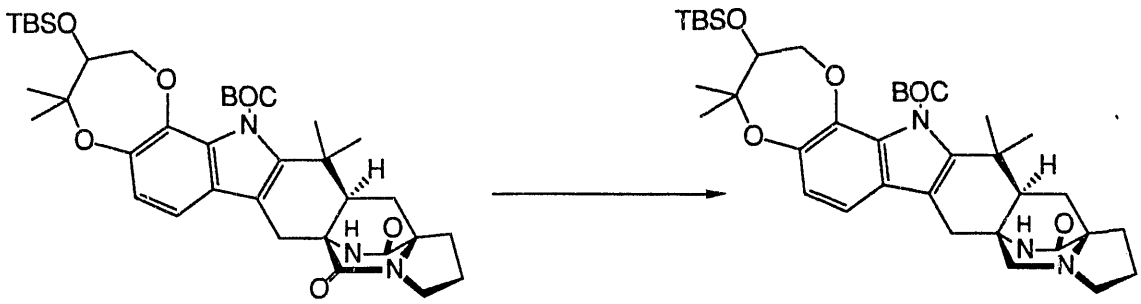
^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.081(6H,s); 0.11(6H, s); 0.87(9H, s); 0.88(9H, s); 1.08(3H, s); 1.17(3H, s); 1.26(3H, s); 1.27(3H, s); 1.34(3H, s); 1.35(3H, s); 1.44(3H, s); 1.46(3H, s); 1.56(9H, s); 1.58(9H, s); 1.81–1.90(2H, m); 1.96–2.06(6H, m); 2.20(2H, dd, J = 10.3, 13.5Hz); 2.52–2.60(4H, m); 2.78(2H, dt, J = 6.5, 12.9Hz); 3.36–3.49(2H, m); 3.51–3.57(2H, m); 3.51–3.57(2H, m); 3.63–3.84(4H, m); 3.88–3.92(2H, m); 4.04–4.16(2H, m); 6.24(1H, s, D_2O exch.); 6.26(1H, s, D_2O exch.) 6.78(1H, d, J = 8.3Hz); 6.80(1H, d, J =8.5Hz); 6.98(1H, d, J = 8.2Hz); 6.99(1H, d, J = 8.4Hz).

^{13}C NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ –5.2, –5.1, –5.0, –4.5, –4.3, 17.6. 18.7, 19.3, 19.7, 19.9, 24.3,.25.5, 25.6, 26.9, 26.2, 27.2, 27.8, 27.9, 28.3, 28.5, 29.1, 31.1, 36.2, 43.8, 50.5, 50.6, 53.3, 54.8, 55.7, 59.4, 60.16, 60.22, 66.3, 67.6, 71.1, 72.7, 75.9, 78.0, 80.5, 84.1, 84.3, 108.3, 112.4, 112.5, 113.6, 117.9, 118.5, 124.6, 124.9, 128.7, 128.9, 129.4, 137.7, 138.3, 139.4, 139.6, 143.0, 143.2, 152.9, 153.0, 168.3, 174.1.

IR(neat) 3214, 2928, 2856, 1745, 1556, 1496, 1443, 1368, 1252, 1233, 1154, 1141, 1091, 1052, 994, 859, 838, 777, 733.

MS (EI) 679 *m/e* (rel intensity) 679 (M^+, 0.3) 580 (20.4) 579 (51) 73(100).

EI HRMS m/e 679.3661 ($C_{37}H_{53}N_3O_7Si$ requires 679.3653).

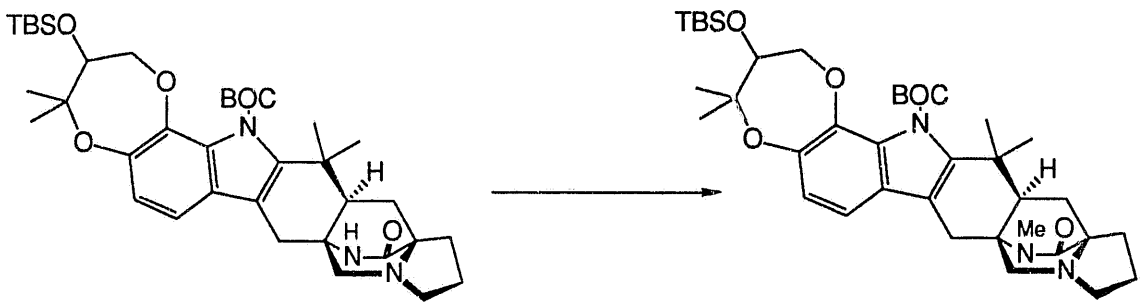


11

^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.085(6H, s); 0.11(6H, s); 0.87((H, s); 0.88(9H, s); 1.12(3H, s); 1.15(3H, s); 1.23(3H, s); 1.24(3H, s); 1.36(3H, s); 1.37(3H, s); 1.45(6H, s); 1.59(9H, s); 1.61(9H, s); 1.88–1.92(3H, s); 1.97–2.10(2H, m); 2.17–2.26(2H, m); 2.54–2.63(2H, m); 2.70(2H, ½ ABq, J = 15.5Hz); 2.829(1H, ½ ABq, J =15.4Hz); 2.835(1H, ½ ABq, J = 15.6Hz); 3.06–3.09(2H, m); 3.45–3.49(2H, m); 3.67–3.85(4H, m); 3.90(2H, dd, J = 3.4, 8.7Hz); 4.09–4.18(2H, m); 6.03(2H, s, D_2O exch.); 6.78(1H, d, J = 8.3Hz); 6.79(1H, d, J =8.3Hz); 6.89(2H, d, J = 8.3Hz); IR(neat) 3227, 2928, 1746, 1683, 1597, 1371, 1254, 1233, 1154, 1138, 1090, 836.

MS (EI) 665 *m/e* (rel intensity) 665 (M^+, 0.3) 565 (30.6) 521 (40.1) 164(100).

EI HRMS m/e 665.38365 ($C_{37}H_{55}N_3O_6Si$ requires).



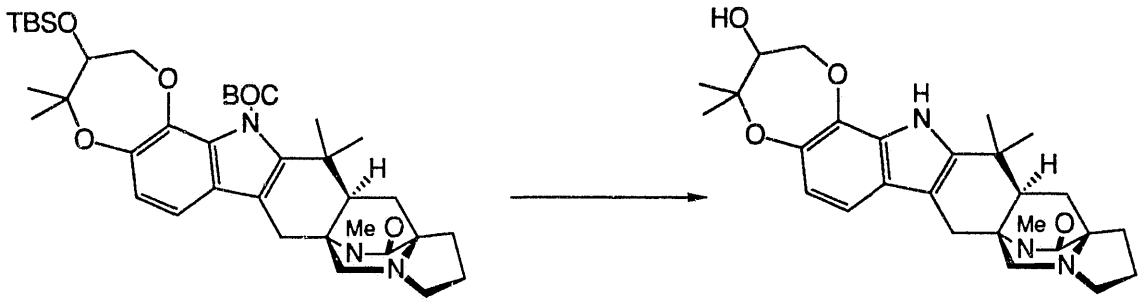
^{1}H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 0.089(6H, s); 0.11(6H, s); 0.87(9H, s); o.88(9H, s); 1.13(3H, s); 1.15(3H, s); 1.36(3H, s); 1.37(3H, s); 1.46(6H, s); 1.59(9H, s); 1.61(9H, s); 1.86–2.06(10H, m); 2.09–2.20(6H, m); 2.61–2.70(2H, m); 2.747(1H, ½ ABq, J = 15.4Hz); 2.754(1H, ½ ABq, J = 15.4Hz); 2.30–3.05(2H, m); 3.05(6H, s); 3.14(2H, ½ ABq, J = 15.4Hz); 3.39(2H, d, J = 10.5Hz); 3.74–3.85(2H,

m); 3.89–3.93(2H, m); 4.07–4.18(2H, m); 6.797(1H, d, J = 8.3Hz); 6.804(1H, d, J = 8.3Hz); 6.93(2H, d, J = 8.3Hz).

IR(neat) 2921, 1747, 1665, 1496, 1371, 1251, 1235, 1158, 1142, 1108, 1093, 837, 755.

MS (EI) 679 *m/e* (rel intensity) 679 (M^+, 2.1) 579(4.2) 520(4.2) 178 (100).

EI HRMS m/e 679.4008 ($C_{38}H_{57}N_3O_6Si$ requires 679.4017).



12

^1H NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 1.21((3H, s); 1.23(3H, s); 1.29(2H, s); 1.32(3H, s); 1.42(3H, s); 1.45(3H, s); 1.54(6H, s); 1.88–2.00(10H, m); 2.07–2.22(6H, m); 2.63–2.72(2H, m); 2.79(1H, ½ ABq, J = 15.1Hz); 2.80(1H, ½ ABq, J = 15.1Hz); 3.01–3.07(4H, m, 2H D_2O exch.); 3.07(6H, s); 3.17(1H, ½ ABq, J = 15.1Hz); 3.19(1H, ½ ABq, J = 15.4Hz); 3.37–3.43(2H, m); 3.62(2H, br. s); 4.20(2H, dd, J = 4.4, 12.3Hz); 4.29(1H, dd, J = 4.0, 12.3Hz); 4.31(1H, dd, J = 4.0, 12.3Hz); 6.750(1H, d, J = 8.4Hz); 6.753(1H, d, J = 8.3Hz); 7.01(2H, d, J = 8.4Hz); 8.01(2H, s, D_2O exch.).

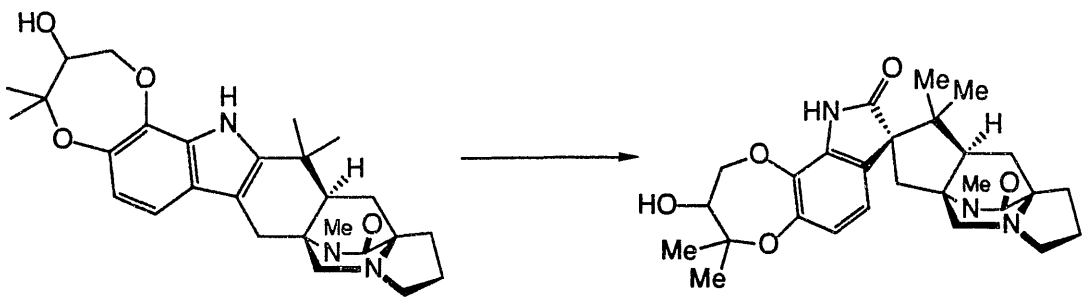
^{13}C NMR (300MHz) ($CDCl_3$) (mixture of two diastereomers) δ 14.0, 20.8, 22.6, 23.9, 24.4, 24.5, 24.7, 25.1, 27.7, 27.9, 30.2, 30.3, 31.3, 34.4, 45.9, 54.3, 57.4, 60.0, 60.2, 64.0, 71.0, 75.5, 76.6, 77.0, 77.4, 79.5, 104.6, 112.2, 116.17, 116.22, 125.0, 129.2, 137.2, 140.4, 141.6, 171.0, 174.3.

IR (neat) 3324, 2954, 1654, 1507, 1474, 1365, 1235, 1071, 1049, 908, 733.

MS (EI) 465 *m/e* (rel intensity) 465 (M^+, 9.7) 406 (14.5) 287 (11.8) 178 (100).

EI HRMS m/e 465.2625 ($C_{27}H_{35}N_3O_4Si$ requires 465.2628).

J-9324-m18



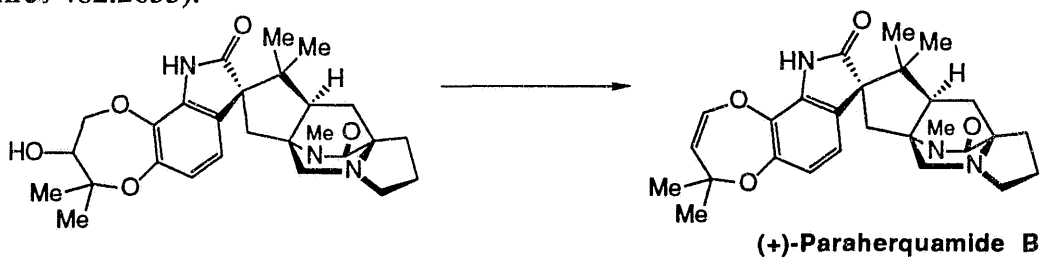
12 13

^{1}H NMR (300MHz) ($CDCl_3$) mixture of two diastereomers δ TMS 0.80(3H, s); 0.83(3H, s); 1.08(3H, s); 1.10(3H, s); 1.22(3H, s); 1.26(3H, s); 1.50(3H, s): 1.52(3H, s); 1.40–1.60(8H, m); 1.77–1.93(8H, m); 2.05–2.21(2H, m); 2.55–2.71(4H, m); 3.02–3.10(4H, m); 3.06(6H, s); 3.63(4H, br s, 2H D_2O exch.); 4.05–4.24(4H, m); 6.60(1H, d, J = 8.1Hz); 6.62(1H, d, J = 8.2Hz); 6.78(1H, d, J = 8.1Hz); 6.79(1H, d, J = 8.2Hz); 7.42(1H, s, D_2O exch.); 7.45(1H, s, D_2O exch.)

IR (neat) 3333, 2974, 2933, 1703, 1651, 1646, 1631, 1456, 1395, 1323, 1200, 1046 903 728 cm^{-1}

MS (EI) 481 *m/e* (rel intensity) 481 (M^+, 0.7) 422 (20.7) 421 (15) 135 (48).133 (100).

CI HRMS m/e481($C_{27}H_{35}N_3O_5$ requires 481.2578), [M + H] 482.2645($C_{27}H_{36}N_3O_5$ requires 482.2655).



(+)-Paraherquamide B

13 2

^{1}H NMR (300MHz) ($CDCl_3$) δ TMS 0.82(3H, s); 1.09(3H, s); 1.40(3H, s); 1.41(3H, s); 1.64(1H, dd, J = 9.7, 12.4Hz); 1.73–1.92(4H, m); 1.82(1H, ½ ABq, J = 15.5Hz); 2.16(1H, dd, J = 8.6, 17.8Hz); 2.54–2.59(1H, m); 2.61(1H, ½ ABq, J = 11.1Hz); 2.66(1H, ½ ABq, J = 15.5Hz); 3.03–3.10(2H, m); 3.05(3H, s); 3.60(1H, ½ ABq, J =

11.1Hz); 4.87(1H, d, J = 7.7Hz); 6.30(1H, d, J = 7.7Hz); 6.64(1H, d, J = 8.2Hz); 6.78(1H, d, J = 8.2Hz); 8.5(1H, br s, D_2O exch.).

^{13}C NMR (300MHz) ($CDCl_3$) δ 20.7(q); 23.8(q); 26.2(q); 28.2(q); 28.8(t); 29.8(t); 29.9(q); 37.2(t); 46.1(s); 52.8(d); 53.8(t); 59.5(t); 63.0(s); 65.2(s); 67.4(s); 79.7(s); 115.0(d); 117.2(d); 120.3(d); 125.3(s); 132.5(s); 135.3(s); 139.0(d); 146.0(s); 172.9(s); 183.1(s).

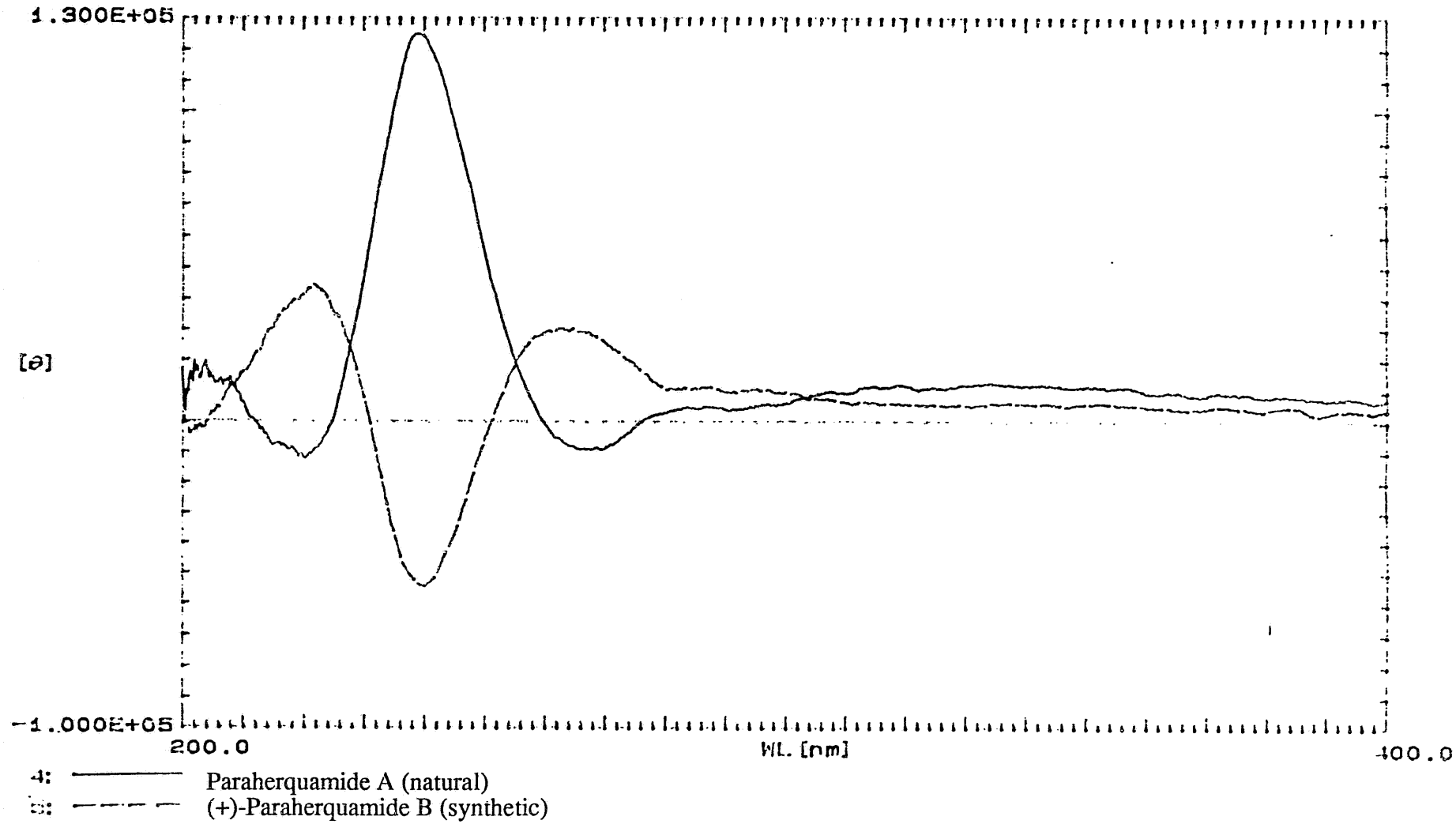
IR (neat) 3190, 2974, 2933, 1703, 1697, 1651, 1631, 1503, 1456, 1328, 1195, 1046 728 cm^{-1}.

u.v. λ_{max} 226nm (ε = 30200).

$[\alpha]_{25}^{D}$ = + 0.4/7.75x10-3 = + 51.6($CHCl_3$, c = 0.008)

MS (EI) 463 *m/e* (rel intensity) 463 (M^+, 0.5) 404 (15.6) 135 (41.5) 133 (100).

EI HRMS m/e 463.2456 ($C_{27}H_{33}N_3O_4$ requires 463.2471).



J-9324-1020

CD Spectra (CH_2Cl_2)