Samarium(II)-mediated 4-*exo*-trig cyclisation. A stereocontrolled approach to the core of Pestalotiopsin A.

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***rel*-(3*R*)-(*rel*-(1*R*)-3,3-Dimethyl-2-oxo-cyclobutyl)-dihydrofuran-2(3*H*)-one 7**

To a stirred solution of **6** (101 mg, 0.55 mmol) in CH_2Cl_2 (5.5 ml) at room temperature was added 4Å molecular sieves (10 mg), *N*-methyl morpholine *N*-oxide (256 mg, 2.19 mmol), and TPAP (8 mg, 0.02 mmol). After 3 h, the reaction mixture was poured onto a short column of silica gel and eluted with 50% EtOAc in petroleum ether (40-60°C). Concentration *in vacuo* gave the cyclobutanone **7** (100 mg, 0.55 mmol, 100%) as a clear colourless oil: υ_{max} (soln. in $CHCl_3$)/cm^{-1} 3028s (C-H), 2949s, 1756s (C=O), 1709s (C=O), 1656m, 1530m, 1467m, and 1367m; δ_H (400 MHz, $CDCl_3$) 4.41 (1H, td, *J* 8.9, 1.9, 1H from CH_2O), 4.24-4.18 (1H, m, 1H from CH_2O), 3.98-3.92 (1H, m, $(Me)_2CCH_2CH$), 3.00-2.94 (1H, m, $CHCH_2$), 2.39-2.32 (1H, m, 1H from CH_2CH_2O), 2.19-2.08 (1H, m, 1H from CH_2CH_2O), 2.05 (1H, apparent t, *J* 11.0, 1H from $(Me)_2CCH_2$), 1.91-1.86 (1H, m, 1H from $(Me)_2CCH_2$), 1.30 (3H, s, 3H from $C(CH_3)_2$) and 1.16 (3H, s, 3H from $C(CH_3)_2$); δ_C (100 MHz, $CDCl_3$) 214.8 (C=O), 177.5 (C=O), 66.8 (CH_2O), 58.1 ($C(CH_3)_2$), 53.7 ($(Me)_2CCH_2CH$), 37.7 ($CHCH_2$), 28.7 ($(Me)_2CCH_2$), 26.1 (CH_2CH_2O), 24.0 ($C(CH_3)_2$) and 21.2 ($C(CH_3)_2$); *m/z* (EI mode) 182 (26%), 154 (11), 126 (35), 111(12), 82 (35), 70 (100) and 41 (27) (Found M^+, 182.0943. $C_{10}H_{14}O_3$ requires *M*, 182.0943).

General procedure for the addition of alkyl ytterbium reagents to 7:

***rel*-(1*S*, 4*R*, 5*R*)-4-(2-Hydroxy ethyl)-1,7,7-trimethyl-2-oxa-bicyclo[3.2.0]heptan-3-one 9a**

To a stirred solution of $Yb(OTf)_3$ (185 mg, 0.30 mmol) in THF (7.2 ml) at –78°C was added MeLi.LiBr (0.24 ml, 0.30 mmol, 1.26 M in THF) and the mixture left for 40 min. A solution of the cyclobutanone **7** (27 mg, 0.15 mmol) in THF (0.35 ml) at –78 °C was then added dropwise *via* cannula to the purple solution of the organoytterbium reagent also at -–78 °C. After 35 min, aqueous saturated $NaHCO_3$ (1 ml) was added and the aqueous layer separated and extracted with $CHCl_3$ (4 x 15 ml), the organic layers dried ($MgSO_4$) and

concentrated *in vacuo* to give the crude **9a** as a clear colourless oil. Purification by column chromatography (eluting with 50% EtOAc in petroleum ether (bp 40-60°C)) gave pure **9a** as a clear oil (20 mg, 0.10 mmol, 68%): υ_{max} (soln. in $CHCl_3$)/cm^{-1} 3480br.m (O-H), 3028s, (C-H), 2959s (C-H), 1750s (C=O), 1519s, 1477s and 1425s; δ_H (400 MHz, $CDCl_3$) 3.86-3.74 (2H, m, C*H*$_2$OH), 2.66 (1H, t, *J* 7.7, COCH), 2.55 (1H, td, *J* 8.0, 1.0, $(Me)_2CCH_2CH$), 2.02 (1H, dd, *J* 12.2, 8.8, 1H from $(Me)_2CCH_2$), 1.93-1.85 (1H, m, 1H from CH_2CH_2OH), 1.83-1.74 (1H, m, 1H from CH_2CH_2OH), 1.54 (1H, dd, *J* 12.2, 7.1, 1H from $(Me)_2CCH_2$), 1.36 (3H, s, CH_3), 1.15 (3H, s, 3H from $C(CH_3)_2$), and 1.04 (3H, s, 3H from $C(CH_3)_2$); δ_C (100 MHz, $CDCl_3$) 181.0 (C=O), 92.3 (*C*OC(O)), 60.8 (CH_2OH), 46.3 (*C*HC(O)), 40.7 ($C(CH_3)_2$), 40.9 ($(Me)_2CCH_2CH$), 38.1 ($(Me)_2CCH_2$), 35.4 (CH_2CH_2OH), 25.8 ($C(CH_3)_2$), 22.4 ($C(CH_3)_2$), and 19.7 (CH_3); *m/z* (CI mode, isobutane) 199 (100%), 181 (18), 155 (4), 142 (5), 115 (15), and 69 (3) (Found $(M+H)^+$, 199.1334. $C_{11}H_{19}O_3$ requires *M*, 199.1334).

***rel*-(1*S*, 4*R*, 5*R*)-4-(2-Hydroxy ethyl)-7,7-dimethyl-1-vinyl-2-oxa-bicyclo[3.2.0]heptan-3-one 9b**

Lactone **9b** was obtained as a clear, colourless oil: ν_{max} (soln. in $CHCl_3$)/cm^{-1} 3627br.s (OH), 3023s, 1756s (C=O), 1519s, 1425s, 1230s and 1204s; δ_H (400 MHz, $CDCl_3$) 6.02 (1H, dd, *J* 17.3, 11.0, C*H*=CH_2), 5.34 (1H, d, *J* 17.3, *trans* 1H from CH=C*H*$_2$), 5.23 (1H, d, *J* 11.0, *cis* 1H from CH=C*H*$_2$), 3.80-3.72 (2H, m, C*H*$_2$OH), 2.83 (1H, t, *J* 8.2, $(Me)_2CCH_2CH$), 2.67 (1H, t, *J* 7.8, C*H*C(O)), 2.01 (1H, dd, *J* 12.1, 8.8, 1H from $(Me)_2CCH_2$), 1.86-1.68 (2H, m, C*H*$_2$CH$_2$OH), 1.57 (1H, dd, *J* 12.0, 7.6, 1H from $(Me)_2CCH_2$), 1.15 (3H, s, CH_3) and 1.06 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 180.6 (C=O), 134.4 (*C*H=CH_2), 116.5 (CH=*C*H$_2$), 93.2 (*C*OC(O)), 60.7 (CH_2OH), 45.5 (*C*HC(O)), 42.3 ($C(CH_3)_2$), 39.3 ($(Me)_2CCH_2CH$), 37.4 (CCH_2CH), 34.5 (CH_2CH_2OH), 26.1 (CH_3) and 22.3 (CH_3); *m/z* (CI mode, isobutane) 211 (100%), 193 (17), 167 (5), 154 (7), 136 (3), 115 (9), 107 (2) and 79 (2) (Found $(M+H)^+$, 211.1334. $C_{12}H_{19}O_3$ requires *M*, 211.1334).

***rel*-(1*R*, 4*R*, 5*R*)-4-(2-Hydroxy ethyl)-7,7-dimethyl-1-isopropenyl-2-oxa-bicyclo[3.2.0]heptan-3-one 9c**

Lactone **9c** was obtained as a colourless oil: ν_{max} (soln. in $CHCl_3$)/cm^{-1} 3485w (OH), 3012s, 1756s (C=O), 1519s, 1424s, 1230s, 1010m and 926s; δ_H (400 MHz, $CDCl_3$) 5.04 (1H, s, 1H from CH_2=), 4.88 (1H, s, 1H from CH_2=), 3.85-3.73 (2H, m, C*H*$_2$OH), 3.01 (1H, t, *J* 8.2, C*H*$CH_2C(Me)_2$), 2.67 (1H, t, *J* 8.0, C*H*C(O)O), 1.94 (1H, dd, *J* 12.0, 8.9, 1H from C*H*$_2C(Me)_2$), 1.88-1.70 (2H, m, C*H*$_2$CH$_2$OH), 1.77 (3H, s, C*H*$_3$C=), 1.51 (1H dd, *J* 12.0, 7.5, 1H from C*H*$_2C(Me)_2$), 1.15 (3H, s, Me) and 1.04 (3H, s, Me); δ_C (100 MHz, $CDCl_3$)

180.2 (C=O), 142.2 (*C*=CH_2), 113.4 (C=*C*H_2), 96.5 (*C*OC(O)), 60.6 (CH_2OH), 45.7 (*C*HC(O)), 41.0 (*C*$(Me)_2$), 36.9 (*C*$H_2C(Me)_2$), 36.5 (*C*$HCH_2C(Me)_2$), 34.3 (*C*H_2CH_2OH), 25.1 (Me), 22.9 (Me) and 19.0 (*C*H_3C=); *m/z* (CI mode, isobutane) 225 (100%), 207 (27), 168 (55), 150 (54), 138 (20), and 115 (30) (Found: $(M+H)^+$, 225.1492. $C_{13}H_{21}O_3$ requires *M*, 225.1491).

***rel*-(1*S*, 4*R*, 5*R*)-4-(2-Hydroxy ethyl)-1-[3-methyl-but-3-enyl]-7,7-dimethyl-2-oxa-bicyclo[3.2.0]heptan-3-one 9d**

Lactone **9d** was obtained as a colourless oil: ν_{max} (soln. in $CHCl_3$)/cm^{-1} 3496m (OH), 2965s, 1751s (C=O), 1467s, 1383s and 1183m; δ_H (400 MHz, $CDCl_3$) 4.73 (1H, s, 1H from CH_2=), 4.68 (1H, s, 1H from CH_2=), 3.87-3.74 (2H, m, C*H*$_2$OH), 2.66 (1H, t, *J* 7.8, CHCO), 2.53 (1H, t, *J* 7.6, C*H*$CH_2C(Me)_2$), 2.19-2.12 (1H, m, 1H from C*H*$_2CH_2$), 2.06-1.88 (4H, m, 1H from C*H*$_2C(Me)_2$, 1H from C*H*$_2CH_2OH$, 1H from C*H*$_2CH_2$ and 1H from CH_2C*H*$_2$), 1.81-1.64 (2H, m, 1H from C*H*$_2CH_2OH$ and 1H from CH_2C*H*$_2$), 1.74 (3H, s, C*H*$_3$C=), 1.50 (1H dd, *J* 12.2, 6.9, 1H from C*H*$_2C(Me)_2$), 1.22 (3H, s, Me) and 1.11 (3H s, Me); δ_C (100 MHz, $CDCl_3$) 181.3 (C=O), 145.3 (*C*=CH_2), 110.1 (C=*C*H_2), 93.9 (*C*OC(O)), 61.0 (*C*H_2OH), 46.4 (*C*HC(O)O), 41.3 (*C*$(Me)_2$), 39.8 (*C*$HCH_2C(Me)_2$), 38.3 (*C*$H_2C(Me)_2$), 35.2 (*C*H_2CH_2OH), 33.2 (CH_2*C*H_2), 31.7 (*C*H_2CH_2), 25.5 (Me), 23.7 (Me) and 22.8 (*C*H_3C=); *m/z* (CI mode, isobutane) 253 (100%), 235 (20), 196 (30), 179 (20) and 115 (15) (Found: $(M+H)^+$ 253.1800. $C_{15}H_{25}O_3$ requires *M*, 253.1804).

***rel*-(1*R*, 4*R*, 5*R*)-4-(2-Hydroxyethyl)-1-[1-(2-benzyloxy ethyl) vinyl]-7,7-dimethyl-2-oxa-bicyclo[3.2.0]heptan-3-one 9e**

Lactone **9e** was obtained as a colourless oil: ν_{max} ($CDCl_3$ soln.)/cm^{-1} 3691m (OH), 3617m, 3154s, 2981s, 2963s, 1758s (C=O), 1641m (C=C), 1604m, 1561m, 1468s and 1382s; δ_H (400 MHz, $CDCl_3$) 7.39-7.28 (5H, m, 5 x ArCH), 5.15 (1H, s, 1H from C=C*H*$_2$), 5.02 (1H, s, 1H from C=C*H*$_2$), 4.55 (AB system, 1H, d, *J* 11.9, 1H from PhC*H*$_2$), 4.51 (AB system, 1H, d, *J* 11.9, 1H from PhC*H*$_2$), 3.83-3.71 (2H, m, C*H*$_2$OH), 3.70-3.59 (2H, m, C*H*$_2$OBn), 3.02 (1H, app. t, *J* 8.2, $(Me)_2CCH_2$C*H*), 2.67 (1H, app. t, *J* 7.9, C*H*C(O)), 2.51-2.44 (1H, m, 1H from C*H*$_2CH_2$OBn), 2.36-2.28 (1H, m, 1H from C*H*$_2CH_2$OBn), 1.94 (1H, dd, *J* 12.0, 9.0, 1H from $(Me)_2$CC*H*$_2$), 1.87-1.66 (2H, m, C*H*$_2CH_2OH$), 1.51 (1H, dd, *J* 12.0, 7.5, 1H from $(Me)_2$CC*H*$_2$), 1.15 (3H, s, CH_3) and 1.02 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 180.2 (C=O), 143.4 (C=), 138.5 (ArC), 128.6 (2 x ArCH), 127.9 (2 x ArCH), 127.8 (ArCH), 113.8 (=CH_2), 96.8 (*C*OC(O)), 73.1 (Ph*C*H_2), 69.0 (CH_2O), 60.7 (CH_2O), 45.8 (*C*HC(O)), 41.5 (*C*$(CH_3)_2$), 37.1 ($(Me)_2$C*C*H_2), 36.8 ($(Me)_2CCH_2$*C*H), 34.3 (*C*H_2CH_2OH), 31.8

(CH_2CH_2OBn), 25.5 (CH_3) and 23.1 (CH_3); *m/z* (CI mode, isobutane) 345 (13%), 327 (13), 270 (11), 253 (20), 235 (49), 223 (19), 197 (22), 167 (11), 149 (11), 138 (16), 109 (11), 91 (100) (Found M^+, 344.1989. $C_{21}H_{28}O_4$ requires *M*, 344.1980).

_p_-Nitro benzoic acid-2-(*rel*-(1*S*, 4*R*, 5*R*)-1,7,7-trimethyl-2-oxa-3-oxo-bicyclo[3.2.0]hept-4-yl) ethyl ester 11

To a stirred solution of lactone **9a** (15 mg, 0.08 mmol) in pyridine (0.5 ml) at room temperature was added *p*-nitrobenzyl chloride (21 mg, 0.12 mmol) and the reaction mixture stirred for 3 days. Aqueous saturated $NaHCO_3$ (1 ml) was then added and the aqueous layer separated and extracted with $CHCl_3$ (4 x 10 ml). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to give **11** as a yellow solid (23 mg, 0.07 mmol, 88%). Recrystallisation (EtOH) gave white crystals suitable for crystallographic analysis (mp 146-147°C): υ_{max} (soln. in $CDCl_3$)/cm^{-1} 3154s, 2980s (C-H), 1756s (C=O), 1724s (C=O), 1646m, 1614m, 1567m, 1530s and 1383s; δ_H (400 MHz, $CDCl_3$) 8.31 (2H, apparent d, *J* 8.8, ArH), 8.21 (2H, apparent d, *J* 8.8, ArH), 4.56-4.46 (2H, m, CH_2O), 2.66-2.58 (2H, m, CHC(O) and $(Me)_2CCH_2CH$), 2.24-2.16 (1H, m, 1H from CH_2CH_2O), 2.08-1.96 (2H, m, 1H from $(Me)_2CCH_2$ and 1H from CH_2CH_2O), 1.55 (1H, dd, *J* 12.2, 7.0, 1H from $(Me)_2CCH_2$), 1.37 (3H, s, $CH_3COC(O)$), 1.16 (3H, s, 3H from $C(CH_3)_2$), and 1.06 (3H, s, 3H from $C(CH_3)_2$); δ_C (100 MHz, $CDCl_3$) 179.5 (C=O), 164.5 (C=O), 150.6 (ArC), 135.4 (ArC), 131.0 (2 x ArCH), 123.8 (2 x ArCH), 91.8 ($COC(O)$), 63.4 (CH_2O), 46.0 ($CHC(O)$), 41.0 ($C(CH_3)_2$), 40.2 ($(Me)_2CCH_2CH$), 38.1 ($(Me)_2CCH_2$), 31.4 (CH_2CH_2O), 25.8 ($C(CH_3)_2$), 22.5 ($C(CH_3)_2$) and 19.8 (CH_3); *m/z* (CI mode, isobutane) 348 (100%), 318 (6), 291 (2), 181 (5), 163 (2) and 150 (2) (Found $(M+H)^+$, 348.1450. $C_{18}H_{22}O_6N$ requires *M*, 348.1447) (Found: C, 62.29; H, 6.10; N, 3.91. $C_{18}H_{21}O_6N$ requires C, 62.24; H, 6.09; N, 4.03%).

***rel*-(1*S*, 4*R*, 5*R*)-4-(2-*tert*-butyldiphenylsilyloxy ethyl)-7,7-dimethyl-1-vinyl-2-oxa-bicyclo[3.2.0]heptan-3-one 12**

To a stirred solution of **9b** (9 mg, 0.04 mmol) in DMF (0.2 ml) at room temperature was added imidazole (9 mg, 0.13 mmol) and TBDPSCl (17 µl, 0.07 mmol). After 43 h a further quantity of imidazole (4 mg, 0.06 mmol) and TBDPSCl (8 µl, 0.03 mmol) was added. After a further 12 h, aqueous saturated $NaHCO_3$ (0.5 ml) was added and the aqueous layer extracted with 50% EtOAc in petroleum ether (40-60°C). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give a cloudy oil. Purification by column chromatography (eluting with 5% EtOAc in petroleum ether (40-60°C)) gave **12** as a clear,

colourless oil (14 mg, 0.03 mmol, 73%): ν_{max} (soln. in $CHCl_3$)/cm^{-1} 2990m, 1762m (C=O), 1475s, 1387s and 1099s; δ_H (400 MHz, $CDCl_3$) 7.67-7.63 (4H, m, 4 x ArCH), 7.47-7.37 (6H, m, 6 x ArCH), 5.95 (1H, dd, *J* 17.3, 11.0, C*H*=CH_2), 5.27 (1H, dd, *J* 17.3, 1.3, *trans* 1H from CH=CH_2), 5.16 (1H, dd, *J* 11.0, 1.3, *cis* 1H from CH=CH_2), 3.80-3.74 (1H, m, 1H from CH_2OH), 3.71-3.66 (1H, m, 1H from CH_2OH), 2.84 (1H, t, *J* 8.2, $(Me)_2CCH_2CH$), 2.68 (1H, dd, *J* 10.3, 4.9, C*H*C(O)), 2.00-1.91 (2H, m, 1H from CH_2CH_2OH and 1H from $(Me)_2CCH_2$), 1.60-1.52 (2H, m, 1H from CH_2CH_2OH and 1H from $(Me)_2CCH_2$), 1.11 (3H, s, CH_3), 1.06 (9H, s, $C(CH_3)_3$) and 1.05 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 180.5 (C=O), 135.7 (4 x ArCH), 134.5 (CH=), 133.6 (2 x ArC), 129.9 (2 x ArCH), 127.9 (4 x ArCH), 116.3 (=CH_2), 92.7 (*C*OC(O)), 61.9 (CH_2OH), 45.4 (*C*HC(O)), 42.1 ($C(CH_3)_2$), 38.3 ($(Me)_2CCH_2CH$), 37.4 ($(Me)_2CCH_2$), 34.2 (CH_2CH_2OH), 27.0 (3 x $C(CH_3)_3$), 26.1 (CH_3), 22.3 (CH_3) and 20.0 (CSi); *m/z* (CI mode, isobutane) 449 (27%), 391 (30), 371 (100), 335 (7), 293 (4), 199 (6) and 107 (3) (Found $(M+H)^+$, 449.2513. $C_{28}H_{37}O_3Si$ requires *M*, 449.2512).

***rel*-(1*S*, 3*R*, 4*R*, 5*R*)-4-(2-*tert*-butyldiphenylsilyloxy ethyl)-7,7-dimethyl-1-vinyl-2-oxa-bicyclo[3.2.0]heptan-3-ol 13**

To a stirred solution of **12** (39 mg, 0.09 mmol) in CH_2Cl_2 (0.45 ml) at –78°C was added DIBAL-H (76 µl, 0.11 mmol, 1.5 M in toluene) dropwise. After 3.5 h, aqueous saturated $NaHCO_3$ (1 ml) was added and the aqueous layer separated and extracted with CH_2Cl_2 (3 x 10 ml) and dried ($MgSO_4$). Concentration *in vacuo* gave a 2:1 mixture of lactols as a clear, colourless oil [diastereoisomers were inseparable by chromatography] (34 mg, 0.08 mmol, 86%): ν_{max} (soln. in $CHCl_3$)/cm^{-1} 3603m (OH), 1643m, 1464s, 1380s and 1094s; δ_H (400 MHz, $CDCl_3$) 7.69-7.65 (8H, m, 4 x ArCH of major and 4 x ArCH of minor), 7.46-7.38 (12H, m, 6 x ArCH of major and 6 x ArCH of minor), 6.10 (1H, dd, *J* 17.3, 10.8, C*H*=CH_2 of minor), 5.97 (1H, dd, *J* 17.2, 10.8, C*H*=CH_2 of major), 5.69 (1H, dd, *J* 6.6, 5.0, C*H*OH of minor), 5.50 (1H, dd, *J* 3.7, 1.2, C*H*OH of major), 5.26 (1H, dd, *J* 17.3, 1.9, *trans* 1H from CH=CH_2 of minor), 5.18 (1H, dd, *J* 17.2, 2.0, *trans* 1H from CH=CH_2 of major), 5.10 (1H, dd, *J* 10.8, 1.9, *cis* 1H from CH=CH_2 of minor), 5.03 (1H, dd, *J* 10.8, 2.0, *cis* 1H from CH=CH_2 of major), 3.74-3.65 (4H, m, 2H from CH_2O of major, 2H from CH_2O of minor), 3.08 (1H, d, *J* 6.6, OH of minor), 2.93 (1H, d, *J* 3.7, OH of major), 2.58-2.51 (2H, m, $(Me)_2CCH_2CH$ of major and $(Me)_2CCH_2CH$ of minor), 2.37-2.25 (1H, m, C*H*CHOH of minor), 2.20 (1H, t, *J* 7.7, C*H*CHOH of major), 2.03 (1H, dd, *J* 11.4, 7.6, 1H from $(Me)_2CCH_2$ of major), 1.87-1.79 (2H, m, 1H from CH_2CH_2OH, 1H from $(Me)_2CCH_2$ both minor), 1.72 (1H, dd, *J* 11.4, 9.0, 1H from $(Me)_2CCH_2$ of major), 1.68-1.59 (1H, m, 1H

from C*H*$_2$CH$_2$OH of major), 1.52-1.41 (3H, m, 1H from C*H*$_2$CH$_2$OH of major, 1H from C*H*$_2$CH$_2$OH of minor and 1H from (Me)$_2$CC*H*$_2$ of minor), 1.06 (18H, s, 9H from C(CH$_3$)$_3$ of major, 9H from C(CH$_3$)$_3$ of minor), 1.07-1.05 (9H, obscured singlets, 6H from C(CH$_3$)$_2$ of major, 3H from C(CH$_3$)$_2$ from minor) and 1.01 (3H, s, 3H from C(CH$_3$)$_2$ of minor); δ_C (100 MHz, CDCl$_3$) 138.8 (HC=, minor), 137.8 (HC=, major), 135.6 (8 x ArCH, major and minor), 133.8 (2 x ArC, major), 133.5 (2 x ArC, minor), 129.7 (2 x ArCH, minor), 129.6 (2 x ArCH, major), 127.7 (4 x ArCH, major), 127.6 (4 x ArCH, minor), 113.4 (=CH$_2$, major), 113.3 (=CH$_2$, minor), 107.7 (CHOH, major), 102.1 (CHOH, minor), 94.7 (*C*(O)CH(OH), major), 90.3 (*C*(O)CH(OH), minor), 62.9 (CH$_2$O, minor), 62.5 (CH$_2$O, major), 49.5 (*C*HCHOH, major), 48.6 (*C*HCHOH, minor), 42.3 ((Me)$_2$CCH$_2$*C*H, major), 41.5 ((Me)$_2$CCH$_2$*C*H, minor), 40.4 ((Me)$_2$*C*, minor), 39.3 ((Me)$_2$*C*, major), 37.1 ((Me)$_2$C*C*H$_2$, minor), 36.4 ((Me)$_2$C*C*H$_2$, major), 35.2 (*C*H$_2$CH$_2$O, major), 31.6 (*C*H$_2$CH$_2$O, minor), 27.3 (CH$_3$, major), 26.8 (6 x SiC(*C*H$_3$)$_3$, major and minor, CH$_3$ minor), 23.4 (CH$_3$, minor), 22.5 (CH$_3$, major) and 19.2 (2 x CSi, major and minor); *m/z* (FAB mode) 473 (40%), 433 (60), 319 (35), 199 (95), 177 (72), 135 (100) and 107 (48) (Found: (M+Na)$^+$ 473.2490. C$_{28}$H$_{38}$O$_3$SiNa requires *M*, 473.2488).

.Table 1. Crystal data and structure refinement for **11**.

Identification code	km0500 **11**	
Empirical formula	$C_{18}H_{21}NO_6$	
Formula weight	347.36	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.5693(6) Å	α= 85.814(11)°.
	b = 7.6665(10) Å	β= 81.746(10)°.
	c = 19.936(2) Å	γ = 62.170(12)°.
Volume	878.70(18) $Å^3$	
Z	2	
Density (calculated)	1.313 Mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
Absorption correction	None	
F(000)	368	
Crystal size	0.40 x 0.35 x 0.18 mm^3	
θ range for data collection	3.0 to 30.0°.	
Index ranges	$-9 \le h \le 8$, $-10 \le k \le 1$, $-27 \le l \le 27$	
Reflections collected	6176	
Independent reflections	5116 [R(int) = 0.0435]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5116 / 0 / 229	
Goodness-of-fit on F^2	0.996	
R indices [2504 $I>2\sigma(I)$]	R1 = 0.0506, wR2 = 0.1252	
R indices (all data)	R1 = 0.1339, wR2 = 0.1550	
Largest diff. peak and hole	0.19 and -0.23 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5080(2)	9549(2)	1202(1)	56(1)
O(2)	7678(2)	7916(2)	1908(1)	81(1)
O(3)	2562(2)	6949(2)	3542(1)	59(1)
O(4)	-638(3)	7011(3)	4117(1)	85(1)
0(5)	6150(3)	8268(3)	6402(1)	90(1)
O(6)	3325(3)	8072(3)	7017(1)	86(1)
N(1)	4396(3)	8082(2)	6471(1)	60(1)
C(1)	1395(3)	12622(3)	1183(1)	53(1)
C(2)	2594(3)	10346(3)	1174(1)	46(1)
C(3)	1605(3)	10330(3)	1920(1)	46(1)
C(4)	1068(4)	12501(3)	1965(1)	62(1)
C(5)	5684(3)	8684(3)	1802(1)	54(1)
C(6)	3602(3)	8813(3)	2271(1)	48(1)
C(7)	3652(3)	6796(3)	2355(1)	57(1)
C(8)	1856(3)	6748(3)	2905(1)	58(1)
C(9)	1163(3)	7070(3)	4104(1)	51(1)
C(10)	2064(3)	7307(2)	4715(1)	46(1)
C(11)	3947(3)	7670(3)	4663(1)	52(1)
C(12)	4705(3)	7921(3)	5240(1)	55(1)
C(13)	3566(3)	7808(2)	5859(1)	47(1)
C(14)	1714(3)	7420(3)	5927(1)	60(1)
C(15)	972(3)	7172(3)	5349(1)	59(1)
C(16)	2777(4)	13650(4)	868(1)	87(1)
C(17)	-933(4)	13491(4)	908(1)	87(1)
C(18)	2305(4)	9242(3)	632(1)	72(1)

Table 3. Bond lengths [Å] and angles [°] for **11**.

O(1)-C(5)	1.344(2)	C(2)-C(3)	1.537(2)
O(1)-C(2)	1.4602(19)	C(3)-C(6)	1.511(2)
O(2)-C(5)	1.203(2)	C(3)-C(4)	1.538(3)
O(3)-C(9)	1.3232(19)	C(5)-C(6)	1.508(2)
O(3)-C(8)	1.455(2)	C(6)-C(7)	1.528(2)
O(4)-C(9)	1.201(2)	C(7)-C(8)	1.503(3)
0(5)-N(1)	1.214(2)	C(9)-C(10)	1.485(2)
O(6)-N(1)	1.2097(18)	C(10)-C(11)	1.378(2)
N(1)-C(13)	1.472(2)	C(10)-C(15)	1.383(2)
C(1)-C(16)	1.507(3)	C(11)-C(12)	1.375(2)
C(1)-C(17)	1.523(3)	C(12)-C(13)	1.369(2)
C(1)-C(2)	1.544(2)	C(13)-C(14)	1.368(2)
C(1)-C(4)	1.544(2)	C(14)-C(15)	1.372(3)
C(2)-C(18)	1.505(2)		
C(5)-O(1)-C(2)	111.78(13)	O(2)-C(5)-O(1)	120.59(17)
C(9)-O(3)-C(8)	117.66(14)	O(2)-C(5)-C(6)	128.20(17)
O(6)-N(1)-0(5)	123.38(17)	O(1)-C(5)-C(6)	111.21(14)
O(6)-N(1)-C(13)	118.54(17)	C(5)-C(6)-C(3)	102.42(13)
0(5)-N(1)-C(13)	118.06(15)	C(5)-C(6)-C(7)	110.73(14)
C(16)-C(1)-C(17)	110.28(18)	C(3)-C(6)-C(7)	113.91(14)
C(16)-C(1)-C(2)	117.99(16)	C(8)-C(7)-C(6)	113.26(15)
C(17)-C(1)-C(2)	111.31(16)	O(3)-C(8)-C(7)	106.26(14)
C(16)-C(1)-C(4)	116.81(17)	O(4)-C(9)-O(3)	123.70(17)
C(17)-C(1)-C(4)	110.76(16)	O(4)-C(9)-C(10)	124.08(16)
C(2)-C(1)-C(4)	88.01(12)	O(3)-C(9)-C(10)	112.22(14)
O(1)-C(2)-C(18)	107.32(14)	C(11)-C(10)-C(15)	119.48(16)
O(1)-C(2)-C(3)	103.37(12)	C(11)-C(10)-C(9)	121.52(14)
C(18)-C(2)-C(3)	122.64(15)	C(15)-C(10)-C(9)	119.00(15)
O(1)-C(2)-C(1)	110.57(13)	C(12)-C(11)-C(10)	119.95(15)
C(18)-C(2)-C(1)	121.33(15)	C(13)-C(12)-C(11)	119.17(16)
C(3)-C(2)-C(1)	89.67(12)	C(14)-C(13)-C(12)	122.23(17)
C(6)-C(3)-C(2)	105.84(13)	C(14)-C(13)-N(1)	119.20(15)
C(6)-C(3)-C(4)	117.33(15)	C(12)-C(13)-N(1)	118.56(16)
C(2)-C(3)-C(4)	88.44(12)	C(13)-C(14)-C(15)	118.09(16)
C(3)-C(4)-C(1)	89.64(13)	C(14)-C(15)-C(10)	121.07(16)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	42(1)	69(1)	51(1)	-2(1)	1(1)	-22(1)
O(2)	48(1)	93(1)	98(1)	-1(1)	-25(1)	-24(1)
O(3)	56(1)	81(1)	44(1)	3(1)	-9(1)	-36(1)
O(4)	78(1)	138(2)	70(1)	-4(1)	-4(1)	-77(1)
0(5)	86(1)	148(2)	62(1)	-9(1)	-10(1)	-72(1)
O(6)	93(1)	119(1)	46(1)	-14(1)	7(1)	-52(1)
N(1)	62(1)	67(1)	46(1)	-5(1)	-3(1)	-26(1)
C(1)	57(1)	54(1)	49(1)	3(1)	-9(1)	-26(1)
C(2)	45(1)	54(1)	41(1)	-4(1)	-7(1)	-23(1)
C(3)	42(1)	53(1)	42(1)	-1(1)	-3(1)	-21(1)
C(4)	66(1)	53(1)	51(1)	-9(1)	-2(1)	-15(1)
C(5)	47(1)	55(1)	58(1)	-6(1)	-12(1)	-20(1)
C(6)	52(1)	51(1)	38(1)	-5(1)	-9(1)	-20(1)
C(7)	68(1)	53(1)	46(1)	-2(1)	-11(1)	-23(1)
C(8)	70(1)	64(1)	49(1)	6(1)	-18(1)	-36(1)
C(9)	52(1)	55(1)	51(1)	4(1)	-4(1)	-29(1)
C(10)	42(1)	41(1)	50(1)	2(1)	-3(1)	-17(1)
C(11)	50(1)	66(1)	43(1)	6(1)	-1(1)	-31(1)
C(12)	50(1)	68(1)	53(1)	7(1)	-4(1)	-33(1)
C(13)	46(1)	46(1)	43(1)	0(1)	-2(1)	-17(1)
C(14)	54(1)	76(1)	47(1)	0(1)	7(1)	-32(1)
C(15)	51(1)	79(1)	55(1)	2(1)	2(1)	-39(1)
C(16)	99(2)	72(2)	95(2)	7(1)	-1(1)	-47(1)
C(17)	74(1)	76(2)	96(2)	10(1)	-37(1)	-16(1)
C(18)	92(2)	79(2)	51(1)	-7(1)	-19(1)	-42(1)

Table 5. Torsion angles [°] for **11**.

C(5)-O(1)-C(2)-C(18)	-116.48(16)	C(2)-C(3)-C(6)-C(5)	21.81(17)
C(5)-O(1)-C(2)-C(3)	14.43(17)	C(4)-C(3)-C(6)-C(5)	-74.78(17)
C(5)-O(1)-C(2)-C(1)	109.18(16)	C(2)-C(3)-C(6)-C(7)	-97.79(16)
C(16)-C(1)-C(2)-O(1)	30.8(2)	C(4)-C(3)-C(6)-C(7)	165.62(14)
C(17)-C(1)-C(2)-O(1)	159.77(16)	C(5)-C(6)-C(7)-C(8)	170.15(14)
C(4)-C(1)-C(2)-O(1)	-88.69(14)	C(3)-C(6)-C(7)-C(8)	-75.06(18)
C(16)-C(1)-C(2)-C(18)	-96.1(2)	C(9)-O(3)-C(8)-C(7)	175.93(14)
C(17)-C(1)-C(2)-C(18)	32.8(2)	C(6)-C(7)-C(8)-O(3)	-68.68(19)
C(4)-C(1)-C(2)-C(18)	144.38(17)	C(8)-O(3)-C(9)-O(4)	0.4(3)
C(16)-C(1)-C(2)-C(3)	134.98(18)	C(8)-O(3)-C(9)-C(10)	-178.97(14)
C(17)-C(1)-C(2)-C(3)	-96.06(17)	O(4)-C(9)-C(10)-C(11)	-169.81(18)
C(4)-C(1)-C(2)-C(3)	15.48(13)	O(3)-C(9)-C(10)-C(11)	9.6(2)
O(1)-C(2)-C(3)-C(6)	-22.45(16)	O(4)-C(9)-C(10)-C(15)	9.7(3)
C(18)-C(2)-C(3)-C(6)	98.59(19)	O(3)-C(9)-C(10)-C(15)	-170.87(15)
C(1)-C(2)-C(3)-C(6)	-133.54(13)	C(15)-C(10)-C(11)-C(12)	-0.9(3)
O(1)-C(2)-C(3)-C(4)	95.56(14)	C(9)-C(10)-C(11)-C(12)	178.67(16)
C(18)-C(2)-C(3)-C(4)	-143.40(17)	C(10)-C(11)-C(12)-C(13)	-0.1(3)
C(1)-C(2)-C(3)-C(4)	-15.53(13)	C(11)-C(12)-C(13)-C(14)	1.1(3)
C(6)-C(3)-C(4)-C(1)	122.58(15)	C(11)-C(12)-C(13)-N(1)	-179.94(15)
C(2)-C(3)-C(4)-C(1)	15.53(13)	O(6)-N(1)-C(13)-C(14)	-4.3(3)
C(16)-C(1)-C(4)-C(3)	-136.03(18)	0(5)-N(1)-C(13)-C(14)	174.27(17)
C(17)-C(1)-C(4)-C(3)	96.61(17)	O(6)-N(1)-C(13)-C(12)	176.63(16)
C(2)-C(1)-C(4)-C(3)	-15.46(13)	0(5)-N(1)-C(13)-C(12)	-4.7(3)
C(2)-O(1)-C(5)-O(2)	178.62(16)	C(12)-C(13)-C(14)-C(15)	-1.1(3)
C(2)-O(1)-C(5)-C(6)	-0.51(19)	N(1)-C(13)-C(14)-C(15)	179.97(17)
O(2)-C(5)-C(6)-C(3)	167.12(19)	C(13)-C(14)-C(15)-C(10)	0.1(3)
O(1)-C(5)-C(6)-C(3)	-13.84(18)	C(11)-C(10)-C(15)-C(14)	0.9(3)
O(2)-C(5)-C(6)-C(7)	-71.1(2)	C(9)-C(10)-C(15)-C(14)	-178.67(17)
O(1)-C(5)-C(6)-C(7)	107.96(16)		

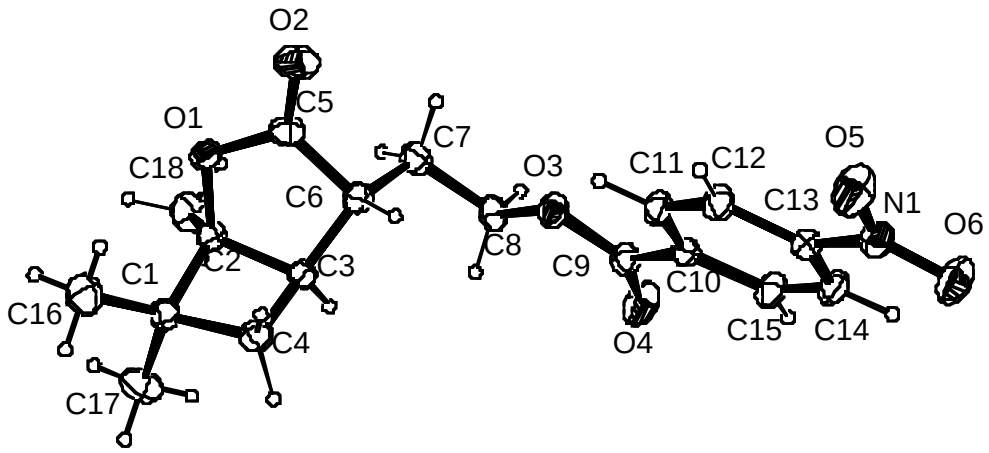

Figure. Molecular drawing of **11** showing atom numbering and 20% probability ellipsoids for non-hydrogen atoms