Supporting Information for:

Postulated Biogenesis of WS9885B and Progress Towards an Enantioselective Synthesis

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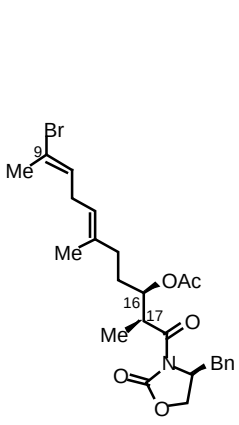

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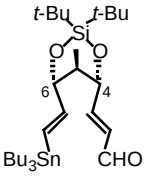

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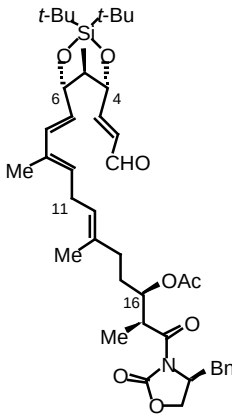

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Acetate bromide 9: $[\alpha]^{rt}_D$ +55.2 (*c* 1.0, $CHCl_3$); TLC: R_f = 0.55 [silica gel, hexanes : EtOAc (3:1)]; IR (film): $\tilde{\nu}_{max}$ = 1780, 1735, 1700 cm^{-1} (C=O); ^1H NMR (250 MHz, $CDCl_3$): δ = 7.33-7.18 (m, 5H, ArH), 5.81-5.74 (m, 1H, C-10), 5.20-5.14 (m, 1H, C-16), 5.09-5.02 (m, 1H, C-12), 4.59-4.50 (m, 1H, CHN), 4.31-4.25 (m, 1H, C*H*HOCON), 4.17-4.13 (m, 1H, CH*H*OCON), 4.01-3.91 (m, 1H, C-17), 3.27 (dd, 1H, C*H*HAr, *J* = 3.3, 13.2 Hz), 2.80-2.75 (m, 1H, CH*H*Ar), 2.71-2.66 (m, 2H, C-11), 2.22 (s, 3H, C-9 CH_3), 2.03 (s, 3H, $OCOCH_3$), 1.61 (s, 3H, C-13 CH_3), 1.20 (d, 3H, C-17, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.9, 170.8, 153.7, 135.4, 135.3, 130.6, 129.4, 128.9, 127.2, 121.4, 119.3, 73.0, 66.4, 55.8, 41.4, 37.9, 35.5, 30.3, 28.4, 23.1, 20.8, 15.9, 9.8; HRMS (MALDI-FTMS): *m/z* calcd for $[M + Na]^+$ 528.1362, found 528.1344.

Enal stannane 14: TLC: R_f = 0.50 [silica gel, hexanes : Et_2O (4:1)]; IR (film): $\tilde{\nu}_{max}$ = 1700 cm^{-1} (C=O); ^1H NMR (250 MHz, $CDCl_3$): δ = 9.63 (d, 1H, CHO, *J* = 8.0 Hz), 6.72 (dd, 1H, C-3, *J* = 2.9, 15.4 Hz), 6.47 (ddd, 1H, C-2, *J* = 1.8, 2.9, 15.4 Hz), 6.27 (dd, 1H, C-8, *J* = 1.8, 19.0 Hz), 5.87 (dd, 1H, C-7, *J* = 3.7, 19.0 Hz), 5.18-5.15 (m, 1H, C-4), 4.93-4.90 (m, 1H, C-6), 1.97-1.90 (m, 1H, C-5), 1.58-1.23 (m, 18H, *n*-$BuCH_2$), 1.09 (s, 9H, $SiC(CH_3)_3$), 1.08 (s, 9H, $SiC(CH_3)_3$), 0.93-0.85 (m, 9H, *n*-$BuCH_3$), 0.82 (d, 3H, C-5 CH_3, *J* = 6.9 Hz) ^{13}C NMR (62 MHz, $CDCl_3$): δ = 193.4, 158.2, 148.0, 131.2, 126.9, 78.8, 76.1, 40.0, 29.1, 28.6, 27.6, 27.2, 23.5, 20.8, 13.7, 9.5, 6.4; HRMS (FAB): *m/z* calcd for $[M + Na]^+$ 623.2924, found 623.2947.

Stille coupling product 15: $[\alpha]^{rt}_D$ +45.3 (*c* 1.0, $CHCl_3$); TLC: R_f = 0.73 [silica gel, hexanes : EtOAc (2:1)]; IR (film): $\tilde{\nu}_{max}$ = 1780, 1735, 1695 cm^{-1} (C=O); ^1H NMR (600 MHz, $CDCl_3$): δ = 9.64 (d, 1H, CHO, *J* = 7.9 Hz), 7.34-7.20 (m, 5H, Ph), 6.72 (dd, 1H, C-3, *J* = 2.8, 15.6 Hz), 6.48 (dd, 1H, C-2, *J* = 8.3, 15.3 Hz), 6.33 (d, 1H, C-8, *J* = 15.8 Hz), 5.50 (dd, 1H, C-7, *J* = 4.8, 15.4 Hz), 5.46 (m, 1H, C-10), 5.20-5.18 (m, 2H, C-4 and C-16), 5.12 (m, 1H, C-12), 5.02 (m, 1H, C-6), 4.57-4.54 (m, 1H, CHN), 4.28-4.26 (m, 1H, C*H*HOCON), 4.17-4.14 (m, 1H, CH*H*OCON), 4.00-3.96 (m, 1H, C-17), 3.27 (dd, 1H, C*H*HAr, *J* = 3.1, 13.6 Hz), 2.84-2.82 (m, 2H, C-11), 2.78-2.74 (m, 1H, CH*H*Ar), 2.03 (s, 3H, $OCOCH_3$), 2.00-1.95 (m, 2H, C-14), 1.92-1.88 (m, 1H, C-5), 1.78 (s, 3H, C-9 CH_3), 1.71-1.68 (m, 2H, C-15), 1.64 (s, 3H, C-13 CH_3), 1.21 (d, 3H, C-17 CH_3, *J* = 6.6 Hz), 1.09 (s, 9H, $SiC(CH_3)_3$), 1.08 (s, 9H, $SiC(CH_3)_3$), 0.86 (d, 3H, C-5 CH_3, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 174.0, 170.9, 158.0, 153.7, 135.4, 134.4, 134.2, 132.8, 131.2, 129.4, 128.9, 127.3, 122.8, 77.2, 76.1, 73.2, 66.3, 55.8, 41.4, 40.6, 37.9, 35.6, 30.4, 28.6, 27.6, 27.2, 23.5, 20.8, 20.7, 16.0, 12.5, 9.8, 6.4; HRMS (FAB): *m/z* calcd for $[M + Cs]^+$ 868.3221, found 868.3239.