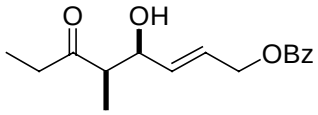
Experimental. Toluene was distilled for sodium/ benzophenone. DMF was dried by prolonged standing over molecular sieves and degassed by purging with a flow of Ar. CH_2Cl_2 and *i*Pr_2NEt was distilled from CaH_2. Ammonium formate was recrystallized from MeOH and stored in a descicator. All other solvents and reagents were used as purchased from commercial sources.

Standard Conditions for the Pd catalysed Formate Reduction of Allyl benzoates of disubstituted double bonds:

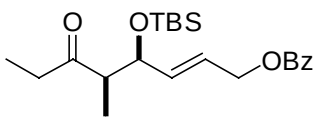
$Pd_2(dba)_3$ (0.03 mmol) and n-Bu_3P (0.24 mmol) were added to a 23 ^oC suspension of HCO_2NH_4 (2.2 mmol) in toluene (1 mL) was added. The dark purple solution turned orange over the course of 10 minutes at which point a solution of allyl benzoate (1.0 mmol) in toluene (1 mL) was added via canula. The resulting suspension was placed in a 105 ^oC oil bath until TLC analysis revealed consumption of allyl acetate. The mixture is then diluted with water, extracted three times with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated to dryness. The residue is then pruified by flash chromatography.

Benzoic acid 4R*-hydroxy-5R*methyl-6-oxo-oct-2-enyl ester (10a).



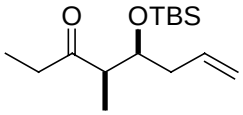
$TiCl_4$ (920 μL, 8.40mmol) was added to a -78 ^oC solution of 3-pentanone (490 μL, 4.64 mmol) in CH_2Cl_2 (5 mL) to give a bright yellow suspension. After two minutes, iPr_2EtN (800 μL, 4.64 mmol) was added to give a deep red solution. After 20 minutes, a solution of **5** (400 mg, mmol) in CH_2Cl_2 (6 mL) was added via canula. After 120 minutes the reaction was quenched by careful addition of saturated $NaHCO_3$ at -78^oC. After warming to 23^oC, the mixture was extracted three times with CH_2Cl_2. The organic layers were washed with brine, filtered through cotton and concentrated to dryness. The majority of the material was converted to silyl ether **10b** without further purification and a small sample was puried for characterization by flash chromatography (30% EtOAc/ hexanes) to yield the title compound as a colourless liquid. R_f =0.24 (30 % EtOAc/ hexanes); 1H NMR (CDCl3) δ; 1.05 (t, *J*=7Hz, 3H), 1.15 (d, *J*=7Hz, 3H), 2.43-2.64 (m, 2H), 2.65-2.73 (m, 1H), 2.90 (d, *J*=3Hz, 1H), 4.50-4.55 (m, 1H), 4.84 (dt, *J*=6, 1Hz, 2H), 5.80 (ABX, ddt, *J*= 16, 5, 1Hz, 1H), 5.98 (ABX, dtd, *J*=19, 6, 1.5 Hz, 7.44 (t, *J*=7.5 Hz, 2H), 7.57 (tt, *J*=7.5, 1.5 Hz, 1H), 8.03-8.07 (m, 2H), ;13C NMR (100 MHz, CDCl3) δ; IR (neat, cm^{-1}) 3475, 2968, 2932, 1722, 1278, 1111.

Benzoic acid 4R*-*t*-Butyldimethylsiloxy-5R*-methyl-6-oxo-oct-2-enyl ester (10b).



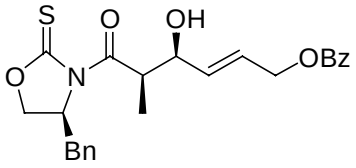
Imidizole (289 mg, 4.24 mmol) and DMF (2 mL) were added to unpurified **10a**. TBDMSCl (639 mg, 4.24 mmol) was added and the resulting solution was stirred at 23^{o}C for 16 hours. The mixture was treated with water and extracted three times with Et_2O. The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to dryness. The residue was purified by flash chromatography (20% EtOAc/ hexanes) to yield the title compounds as a colorless liquid (759 mg, 92% over two steps). R_f =0.47 (20 % EtOAc/ hexanes); 1H NMR (CDCl3) δ; 0.02 (s, 3H), 0.05 (s, 3H), 0.88 (s, 9H), 0.98 (t, *J*=7Hz, 3H), 1.10 (d, *J*=7HZ, 3H), 2.40-2.55 (m, 2H), 2.69 (quin., *J*=7Hz, 1H0, 4.33 (t, *J*=3Hz, 1H), 4.78 (d, *J*=3 Hz, 2H), 5.78-5.83 (m, 2H), 7.41 (t, *J*=7.5 Hz, 2H), 7.54 (tt, *J*=7.5, 1.3 Hz, 1H), 7.99-8.04 (m, 2H);13C NMR (100 MHz, CDCl3) δ -5.03, -4.24, 7.33, 12.65, 18.07, 25.74, 36.60, 52.57, 64.49, 74.34, 125.27, 128.35, 129.57, 132.94, 135.78, 166.2, 213.39; IR (neat, cm^{-1}) 2944, 2862, 1724, 1457, 1372, 1265, 1115, 1071, 980, 836; Elemental Analysis: Calculated: %C=67.65, %H=8.77, Found: %C=68.05, %H, 9.06.

5S*-*t*-Butyldimethylsiloxy-4R*-methyl-oct-7-en-3-one (11).



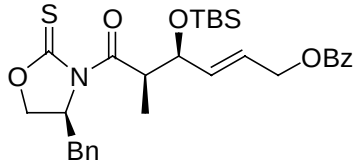
Allyl benzoate **10b** (200 mg, 0.51 mmol) was subjected to the stadard conditions for Pd catalyzed formate reduction. The residue was purified by flash chromatography (5% EtOAc/ hexanes → 10% EtOAc/ hexanes) to yield the title compound as a color less liquid (135 mg, 98%). R_f =0.61 (10 % EtOAc/ hexanes); ^{1}H NMR (CDCl3) δ; 0.03 (s, 3H), 0.05 (s, 3H), 0.85 (t, *J*=8Hz, 3H), 0.87 (s, 9H), 1.01 (t, *J*=7 Hz, 3H), 1.07 (d, *J*=7 Hz, 3H), 2.09-2.18 (m, 1H), 2.20-2.30 (m, 1H), 2.40-2.56 (m, 2H), 2.65 (dt, *J*=13, 6 Hz, 1H), 3.99 (q, *J*=5.5 Hz, 1H), 4.98-5.06 (m, 2H), 5.72-5.84 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ -4.68, -4.27, 7.52, 12.45, 18.03, 25.81, 35.76, 39.84, 50.72, 72.88, 117.32, 134.63, 214.03; IR (neat, cm^{-1}) 2935, 1734, 1454, 1375, 1235, 1064.

Benzoic acid 6-(4S-benzyl-2-thioxo-oxazolidin-3-yl)-4-hydroxy-5R-methyl-6-oxo-hex-2-enyl ester (13a).



$TiCl_4$ (210 μL, 1.91 mmol) was added to a 0°C solution of **12** (238 mg, 0.956 mmol) in CH_2Cl_2 (4 mL) to give a yellow solid mass sticking to the stir bar. After 10 minutes, iPr_2EtN (183 μL, 1.05 mmol) was added to give a deep red solution. After 30 minutes, this solution was cooled to -78°C and a solution of **5** (200 mg, 1.05 mmol) in CH_2Cl_2 (1 mL). After 90 minutes the reaction was quenched by addition of saturated $NaHCO_3$ at -78°C. After warming to 23°C, the mixture was extracted three times with CH_2Cl_2. The organic layers were washed with brine, filtered through cotton and concentrated to dryness. The residue was purified by flash chromatography (15% EtOAc/ hexanes→20% EtOAc/ hexanes→30% EtOAc/ hexanes) to yield the title compound as a colourless liquid (373 mg, 84%) plus **12** (36 mg, 15%) and **5** (50 mg, 25%). 1H NMR (CDCl3) δ 1.23, (d, *J*=7 Hz, 3H), 2.76 (dd, *J*=13, 10Hz, 1H0, 2.89 (bs, 1H), 3.27 (dd, *J*=13, 3.5 Hz, 1H), 4.24-4.35 (m, 2H), 4.72 (bs, 1H), 4.87 (d, *J*=16Hz, 2H), 4.92-5.0 (m, 2H), 5.94 (ABX, dd, *J*=16, 5Hz, 1H), 6.06 (ABX, dt, *J*=16, 5.5 Hz, 1H), 7.20 (AB, *J*=7Hz, 2H), 7.26-7.36 (m, 3H), 7.40 (t, *J*=7.5 Hz, 2H), 7.54, (t, *J*=7.5Hz, 1H), 8.04 (AB, *J*=7Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 11.01, 37.68, 42.12, 60.06, 64.57, 70.20, 71.84, 123.20, 127.41, 128.29, 128.97, 129.32, 129.56, 130.02, 132.91, 133.26, 135.04, 166.2, 176.81, 185.27; IR (neat, cm^{-1}) 3458, 2974, 1715, 1671, 1603, 1447, 1311, 1179, 972; HRMS Calculated for $C_{24}H_{25}O_5NS^+$ (MH^+): 439.1456, Found: 439.1453.

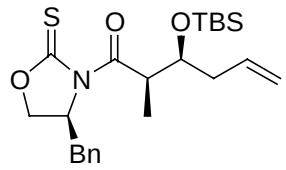
Benzoic acid 6-(4S-benzyl-2-thioxo-oxazolidin-3-yl)-4R-*t*-Butyldimethylsiloxy-5R-methyl-6-oxo-hex-2-enyl ester (13b).



To a –10°C solution of **13a** (710 mg, 1.62 mmol) in CH_2Cl_2 (9 ml) was added 2,6-lutidine (207 μL, 1.78 mmol) was added TBSOTf (371 μL, 1.62 mmol). The resulting solution was warmed to 23°C and after 13 hours, was treated with saturated $NaHCO_3$. The mixture was extracted three times with CH_2Cl_2, washed with brine, filtered through cotton and concentrated to dryness. The residue was purified by flash chromatography (15 % EtOAc/ hexanes) to yield the title compound as a colorless liquid (642 mg, 72%). R_f =0.15 (10% EtOAc/ hexanes); 1H NMR (CDCl3) δ 0.05 (s, 3H), 0.081 (s, 3H), 0.91 (s, 9H), 1.25 (d, *J*=7 Hz, 3H), 2.60 (ABX, dd, *J*=13, 11 Hz, 1H0, 3.28 (ABX, dd, *J*=13, 3 Hz, 1H), 4.18-4.30 (m, 2H0, 4.58 (t, *J*=7 Hz, 1H), 4.81 (qd, *J*=13, 6 Hz, 2H), 4.88-5.00 (m, 2H), 5.92 (ABX, dt, *J*=10, 6 Hz, 1H), 6.03 (ABX, dd, *J*=17, 7 Hz, 1H), 7.16, (d, *J*=7Hz, 2H), 7.24-7.37 (m, 5H), 7.50 (t, *J*=8 Hz, 1H0, 7.98 (d, *J*=8Hz, 2H); 13C NMR

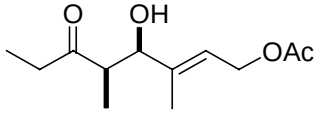
(100 MHz, CDCl3) δ -4.79, -4.00, 13.32, 18.16, 25.81, 37.83, 43.88, 60.07, 64.55, 70.01, 74.55, 126.02, 127.37, 128.31, 129.03, 129.29, 130.07, 132.90, 135.43, 135.57, 166.22, 175.79, 185.30; IR (neat, cm^{-1}): 2959, 1718, 1456, 1369, 1314, 1266, 1185, 1146, 1113, 1068, 1023, 951, 839.

1-(4S-benzyl-2-thioxo-oxazolidin-3-yl)-3S-*tert*butyldimethylsiloxy-2(R)-methyl-hex-5-en-1-one (11).



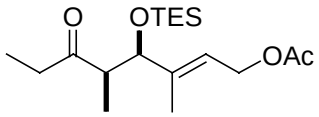
Allyl benzoate **10b** (77 mg, 0.13 mmol) was subjected to the stadard conditions for Pd catalyzed formate reduction. A TLC after 5 minutes in the 105°C oil bath revealed complete consumtion of **10b**. The residue was purified by flash chromatography (8% EtOAc/ hexanes → 10% EtOAc/ hexanes) to yield the title compound as a color less liquid (52 mg, 86%). R_f =() (10 % EtOAc/ hexanes); ^{1}H NMR (CDCl3) δ; 0.09 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 1.23 (d, *J*= 6.8 Hz, 3H), 2.39 (t, *J*=5.8 Hz, 2H), 2.65 (ABX, dd, *J*=13.1, 10.7 Hz, 1H), 3.35 (ABX, dd, *J*=13.2, 3.3 Hz, 1H), 4.20-4.30 (m, 3H), 4.81 (quint., *J*=7 Hz, 1H), 4.88-4.95 (m, 1H), 5.03-5.11 (m, 2H), 5.84-5.96 (m, 1H), 7.21-7.31 (m, 3H), 7.31-7.37 (m, 2H) ; ^{13}C NMR (100 MHz, CDCl3) δ -4.49, -3.94, 14.01, 18.14, 25.89, 37.82, 40.71, 42.74, 60.09, 69.88, 72.81, 117.53, 127.39, 129.04, 129.30, 134.61, 135.44, 176.58, 184.89; IR (neat, cm^{-1}) 2942, 1704, 1686, 1466, 1351, 1309, 1194, 1152.

Acetic acid (E)-4R*-hydroxy-3,5R*-dimethyl-6-oxo-oct-2-enyl ester (16a).



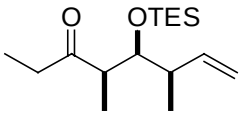
$TiCl_4$ (1.77 mL, 16.2 mmol) was added to a -78 °C solution of 3-pentanone (940 μL, 8.90 mmol) in CH_2Cl_2 (17 mL) to give a bright yellow suspension. After five minutes, iPr_2EtN (1.55 mL, 8.90 mmol) was added to give a deep red solution. After 20 minutes, a solution of **4** (575 mg, 4.05 mmol) in CH_2Cl_2 (3 mL) was added via canula. After 90 minutes the reaction was quenched by addition of saturated $NaHCO_3$ at -78°C. After warming to 23°C, the mixture was extracted five times with CH_2Cl_2. The organic layers were washed with brine, filtered through cotton and concentrated to dryness. The residue was purified by flash chromatography (30% EtOAc/ hexanes) to yield the title compound as a colourless liquid (795 mg, 86%). R_f =0.14 (20 % Ethylacetate/ hexanes); 1H NMR (CDCl3) δ 1.05 (t, *J*=3.5 Hz, 3H), 1.07 (t, *J*=3.5 Hz, 3H), 1.67 (s, 3H), 2.05 (s, 3H), 2.44-2.64 (m, 1H), 2.54 (qd, *J*=17, 7.1 Hz, 1H), 2.74 (qd, *J*=7.3, 3.5 Hz, 1H), 2.95 (d, *J*=2.5 Hz, 1H), 4.37, (s, 1H), 4.65 (d, *J*=7 Hz, 2H), 5.69 (tt, *J*=7, 1.3 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 7.50, 9.87, 13.62, 20.88, 34.96, 47.61, 60.83, 74.46, 120.13, 139.41, 171.02, 215.88; IR (neat) 3483, 2974, 2929, 1737, 1718, 1461, 1372, 1236, 1021; HRMS calculated for $C_{12}H_{21}O_4^+$ (MH^+): 229.1440, found: 229.1444.

Acetic acid (E)-4R*-triethylsiloxy-3,5R*-dimethyl-6-oxo-oct-2-enyl ester (16b).



2,6-lutidine (347 μL, 2.41 mmol), and TESOTf (495 μL, 2.19 mmol) were added to a -10°C solution of **11a** (500 mg, 2.19 mmol) in CH_2Cl_2 (10 mL). After 45 minutes, the mixture was treated with saturated $NaHCO_3$. The mixture was extracted three times with CH_2Cl_2, washed with brine, filtered through cotton and concentrated to dryness. The residue was purified by flash chromatography (5% EtOAc/ hexanes → 15% EtOAc/ hexanes) to yield the title compound as a colorless liquid (613 mg, 82%). R_f 0.54 (20 % Ethyl acetate/ hexanes); 1H NMR (CDCl3) δ 0.56 (q, *J*=8 Hz, 6H), 0.92 (t, *J*=8 Hz, 9H), 0.98 (t, *J*=7.2 Hz, 3H), 1.09 (d, *J*= 6.8 Hz, 3H), 1.67 (s, 3H), 2.03 (s, 3H), 2.40 (dq, *J*=7.2, 2.2 Hz, 2H), 2.72 (quint, *J*= 7.1 Hz, 1H), 4.19 (d, *J*=7.3 Hz, 1H), 4.56 (d, *J*=7.0 Hz, 2H), 5.47 (tt, *J*= 7, 1.1 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 4.74, 6.77, 7.35, 12.09, 12.75, 20.84, 35.89, 50.79, 60.60, 78.69, 121.04, 141.70, 170.87, 213.52; IR (neat): 2968, 1741, 1456, 1372, 1230, 1068, 1016; Elemental Analysis: Calculated: %C=63.11, %H=10.00, Found: %C=63.19, %H=9.80.

5S*-triethylsiloxy-4R*,6R*-dimethyl-oct-7-en-3-one (11).



A solution of n-Bu_3P (3.6 μL, mmol) in toluene (36 μL) was added via syringe to a mixture of **10** (100mg, 0.303 mmol), HCO_2NH_4 (42 mg, 0.667 mmol) and $P_2(dba)_3$ (13.9 mg, mmol) in DMF (500 μL). The resulting mixture was warmed to 50°C. After 16 hours, water was added and the mixture extracted three times with Et_2O. The organic layer were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated to dryness. The residue was purified by flash chromatography (2% Et_2O/ hexanes) to yield the title compounds as a colorless oil (65 mg, 75%). R_f (20 % Ethyl acetate/ hexanes); 1H NMR (CDCl3) δ 0.60 (q, *J*= 8 Hz, 6H), 0.95 (t, *J*= 8 Hz, 9H), 0.97 (d, *J*=6.8 Hz, 3H), 1.03 (t, *J*= 7.3 Hz, 3H), 1.09 (d, *J*=7.1 Hz, 3H), 2.22 (sextet, *J*= 6.8 Hz, 1H), 2.47 (q, *J*=7.3, 2H), 2.66 (quint, *J*=7.1 Hz, 1H), 3.96 (t, *J*=5.7 Hz, 1H), 5.00 (d, *J*=9.1, 1H), 5.02 (d, *J*=17.2, 1H), 5.77 (ddd, *J*= 17.2, 10, 7.5 Hz); 13C NMR (100 MHz, CDCl3) δ 5.30, 6.98, 7.65, 12.34, 15.43, 35.06, 43.00, 49.93, 76.29, 114.50, 141.57, 214.02.