Supplementary Information

(*E*)-5-*tert*-Butyldimethylsilyloxy-pent-1-enyl-1-boronic acid 10
Catecholborane (5.7ml, 53mmol) was added dropwise over 10min to a stirred solution of the alkyne **9** (10.2g, 53mmol) in dry THF (40ml) at room temperature, under a nitrogen atmosphere. The solution was heated under reflux for 14h, then cooled and concentrated *in vacuo* to leave a yellow oil. Purification by distillation under reduced pressure gave (*E*)-5-*tert*-butyldimethylsilyloxy-pent-1-enyl-1-benzodioxaborole (12.7g, 77%) as a colourless oil, b.p. 142°C (0.3mm/Hg); ν_{max}(film)/cm^{-1} 2929, 2856; δ_H (400MHz, $CHCl_3$) 0.07 (6H, s, Si(CH_3)$_2$), 0.91 (9H, s, SiC(CH_3)$_3$), 1.69-1.77 (2H, m, CH_2CH$_2$OTBS), 2.34-2.40 (2H, m, CH_2CH=CH), 3.67 (2H, t, *J* 6.2Hz, CH_2OTBS), 5.82 (1H, d, *J* 18.1Hz, CH=C*H*B), 7.03-7.11 (3H, m, C*H*=CHB, 2 x Ar*H*), 7.20-7.24 (2H, m, 2 x Ar*H*); δ_C (68MHz, $CHCl_3$) -5.3 (q), 18.3 (s), 25.9 (q), 31.2 (t), 32.4 (t), 62.3 (t), 112.2 (d), 116.7 (br d), 122.4 (d), 148.2 (s), 157.3 (d). A mixture of the benzodioxaborole (1.0g, 3.2mmol) and water (20ml) was stirred vigorously at room temperature for 4h. The resulting suspension was filtered and the precipitate was then recrystallised from water (10ml). The crystals were dissolved in ether (20ml) and washed with brine (20ml). The organic fraction was dried and concentrated *in vacuo* to give the boronic acid **10** (0.7g, 87%) as a colourless solid, m.p. 68°C (H_2O); ν_{max}(sol $CHCl_3$)/cm^{-1} 3416, 2954; δ_H (400MHz, $CHCl_3$) 0.06 (6H, s, Si(CH_3)$_2$), 0.90 (9H, s, SiC(CH_3)$_3$), 1.62-1.72 (2H, m, CH_2CH$_2$OTBS), 2.21-2.31 (2H, m, CH_2CH=CH), 3.65 (2H, t, *J* 6.2Hz, CH_2OTBS), 5.55 (1H, d, *J* 18.6Hz, CH=C*H*B(OH)$_2$), 6.99 (1H, dt, *J* 18.6 and 6.5Hz, C*H*=CHB(OH)$_2$); δ_C (68MHz, $CHCl_3$) -5.3 (q), 18.3 (s), 25.9 (q), 31.3 (t), 32.0 (t), 62.5 (t), 122.2 (br d), 157.2 (d); which was used without further purification.

(*E*,*E*)-11-*tert*-Butyldimethylsilyloxy-undeca-5,7-dien-1-ol 12a
Palladium acetate (0.27g, 1.1mmol) was added in one portion to a stirred solution of triphenylphosphine (1.3g, 4.6mmol) in THF (40ml) at room temperature, under a nitrogen atmosphere. The mixture was stirred at room temperature for 10min and then added in one portion to a stirred mixture of the vinyl iodide **11** (2.6g, 12mmol), the boronic acid **10** (3.7g, 15mmol) in THF (115ml) and aqueous lithium hydroxide solution (2M, 80ml), at room temperature, under a nitrogen atmosphere. The mixture was heated to 40°C for 16h and then cooled and diluted with ether (200ml) and water (200ml). The separated aqueous extract was re-extracted with ether (2 x 100ml) and the combined organic extracts were then washed with brine (200ml), dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 30% ether in light petroleum (b.p. 40-60°C) to give the diene **12a** (2.9g, 82%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 3356, 2930; δ_H (400MHz, $CHCl_3$) 0.05 (6H, s, Si(CH_3)$_2$), 0.90 (9H, s, SiC(CH_3)$_3$), 1.45-1.49 (2H, m, CH_2), 1.54-1.63 (4H, m, 2 x CH_2), 2.07-2.14 (4H, m, 2 x CH_2), 3.59-3.66 (4H, m, 2 x CH_2O), 5.54-5.60 (2H, m, 2 x =C*H*), 6.00-6.03 (2H, m, 2 x =C*H*); δ_C (68MHz, $CHCl_3$) -5.3 (q), 18.3 (s), 25.5 (t), 26.0 (q), 28.8 (t), 32.2 (t), 32.2 (t), 32.4 (t), 62.6 (t), 62.8 (t), 130.5 (d), 130.7 (d), 131.8 (d), 132.0 (d); m/z (EI) 241.1619 (M^+ -^{t}Bu, $C_{13}H_{25}O_2Si$ requires 241.1624).

(*E*,*E*)-1-Acetoxy-11-*tert*-butyldimethylsilyloxy-undeca-5,7-diene 12b
Acetic anhydride (0.85ml, 9.0mmol) was added dropwise over 2min to a stirred solution of the alcohol **12a** (1.8g, 7.5mmol), triethylamine (1.6ml, 11.2mmol), and 4-dimethylaminopyridine (50mg, 0.41mmol) in dry dichloromethane (70ml), at 0°C, under a nitrogen atmosphere. The mixture was stirred at 0°C for 4h and then diluted with dichloromethane (70ml) and water (100ml). The separated aqueous extract was re-extracted with dichloromethane (2 x 100ml) and the combined organic extracts were then washed with brine (100ml), dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the acetate **12b** (1.9g, 91%) as a colourless oil; ν_{max}(film)/cm^{-1} 1742, 1471; δ_H (270MHz, $CHCl_3$) 0.03 (6H, s, Si(CH_3)$_2$), 0.88 (9H, s, SiC(CH_3)$_3$), 1.37-1.48 (2H, m, CH_2), 1.53-1.65

(4H, m, 2 x CH_2), 2.02 (3H, s, COCH_3), 2.03-2.14 (4H, m, 2 x CH_2), 3.59 (2H, t, *J* 6.3Hz, CH_2OTBS), 4.04 (2H, t, *J* 6.6Hz, CH_2OAc), 5.45-5.62 (2H, m, 2 x =C*H*), 5.93-6.03 (2H, m, 2 x =C*H*); δ_C (68MHz, $CHCl_3$) -5.4 (q), 18.2 (s), 20.9 (q), 25.6 (t), 25.9 (q), 28.0 (t), 28.8 (t), 32.0 (t), 32.4 (t), 62.4 (t), 64.3 (t), 130.4 (d), 130.8 (d), 131.4 (d), 132.0 (d), 171.0 (s); m/z (EI) 283.1731 (M^+ -^{t}Bu, $C_{15}H_{27}O_3Si$ requires 283.1729).

(*E*,*E*)-1-Acetoxy-undeca-5,7-dien-11-ol 13a

A solution of tetra-*n*-butylammonium fluoride (7.4ml) in THF (1.0M, 7.4mmol) was added dropwise over 5min to a stirred solution of the silyl ether **12b** (1.9g, 6.7mmol) in THF (33ml), at 0°C, under a nitrogen atmosphere. The mixture was stirred at 0°C for 30min and then room temperature for 90min. Ether (100ml) and water (100ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 100ml) and the combined organic extracts were then washed with brine (200ml), dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 70% ether in light petroleum (b.p.40-60°C), to give the alcohol **13a** (1.1g, 79%) as a colourless oil; (Found C, 68.7; H, 10.1%. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.8%); ν_{max}(film)/cm^{-1} 3414, 2935, 1739, 1463; δ_H (400MHz, $CHCl_3$) 1.34-1.41 (2H, m, CH_2), 1.53-1.61 (4H, m, 2 x CH_2), 1.97 (3H, s, COCH_3), 1.99-2.10 (4H, m, 2 x CH_2), 3.55 (2H, t, *J* 6.4Hz, CH_2OH), 3.99 (2H, t, *J* 6.6Hz, CH_2OAc), 5.44-5.54 (2H, m, 2 x =C*H*), 5.90-5.99 (2H, m, 2 x =C*H*); δ_C (100MHz, $CHCl_3$) 20.7 (q), 25.4 (t), 27.9 (t), 28.6 (t), 31.9 (t), 32.0 (t), 61.9 (t), 64.2 (t), 130.5 (d), 130.5 (d), 131.5 (d), 131.5 (d), 171.1 (s); m/z (EI) 208.1461 (M^+ -H_2O, $C_{13}H_{20}O_2$ requires 208.1463).

(*E*,*E*)-1-Acetoxy-11-bromo-undeca-5,7-diene 13b

A solution of triphenylphosphine (2.1g, 7.9mmol) in dichloromethane (10ml) was added dropwise over 10min to a stirred solution of the alcohol **13a** (1.1g, 5.3mmol) and carbon tetrabromide (2.6g, 7.9mmol) in dry dichloromethane (20ml), at 0°C, under a nitrogen atmosphere. The mixture was stirred at 0°C for 30min and then concentrated in vacuo to leave a yellow oil. The oil was purified by chromatography on silica, eluting with a gradient of 10 to 50% ether in light petroleum (b.p. 40-60°C), to give the bromide **13b** (1.4g, 89%) as a colourless oil; (Found C, 54.4; H, 7.8%. $C_{13}H_{21}O_2Br$ requires C, 54.2; H, 7.4%); ν_{max}(film)/cm^{-1} 1739, 1436; δ_H (400MHz, $CHCl_3$) 1.43-1.49 (2H, m, CH_2), 1.60-1.67 (2H, m, CH_2), 1.90-1.97 (2H, m, CH_2), 2.05 (3H, s, COCH_3), 2.07-2.12 (2H, m, CH_2), 2.19-2.25 (2H, m, CH_2), 3.41 (2H, t, J 6.7Hz, CH_2Br), 4.06 (2H, t, J 6.7Hz, CH_2OAc), 5.49-5.61 (2H, m, 2 x =CH), 5.97-6.09 (2H, m, 2 x =CH); δ_C (100MHz, $CHCl_3$) 20.7 (q), 25.4 (t), 27.9 (t), 30.6 (t), 31.8 (t), 32.0 (t), 32.9 (t), 64.0 (t), 129.6 (d), 130.3 (d), 131.5 (d), 132.1 (d), 170.7 (s); m/z (EI) 288.0728 (M^+, $C_{13}H_{21}O_2Br$ requires 288.0704).

(*E*,*E*)-11-Bromoundeca-5,7-dien-1-al 14

A suspension of the acetate **13b** (1.4g, 4.5mmol), potassium carbonate (1.3g, 9.0mmol) and methanol (30ml) was stirred vigorously at room temperature for 2h and then concentrated *in vacuo*. Ether (50ml) and water (50ml) were added and the organic layer was then separated. The aqueous layer was re-extracted with ether (2 x 50ml) and the combined organic fractions were then washed with brine (100ml), dried and concentrated *in vacuo* to leave (*E*,*E*)-11-bromoundeca-5,7-dien-1-ol (1.1g, 97%) as a colourless oil; ν_{max}(film)/cm^{-1} 3334, 2932, 2858, 1435, 1269, 1249, 1060, 988; δ_H (400MHz, $CHCl_3$) 1.43-1.50 (2H, m, CH_2), 1.56-1.63 (2H, m, CH_2), 1.91-1.98 (2H, m, CH_2), 2.08-2.14 (2H, m, CH_2), 2.20-2.25 (2H, m, CH_2), 3.42 (2H, t, *J* 6.7Hz, CH_2Br), 3.66 (2H, t, *J* 6.4Hz, CH_2OH), 5.48-5.68 (2H, m, 2 x =C*H*), 5.98-6.10 (2H, m, 2 x =C*H*); δ_C (68MHz, $CHCl_3$) 25.2 (t), 30.6 (t), 31.9 (t), 32.0 (t), 32.1 (t), 33.1 (t), 62.3 (t), 129.6 (d), 130.1 (d), 131.5 (d), 132.5 (d); m/z (EI) 247.0515 (M^+, $C_{11}H_{18}OBr$ requires 247.0521); which was used without further purification. Dess-Martin periodinane (2.9g, 6.7mmol) was added in one portion to a stirred solution of the alcohol (1.1g, 4.5mmol) in dry dichloromethane (40ml), at 0°C, under a nitrogen atmosphere. The mixture was

warmed to room temperature where it was stirred for 30min. Aqueous sodium thiosulphate (5%, 10ml) was added, and the mixture was stirred vigorously for 10min. The mixture was neutralised with saturated aqueous potassium carbonate and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 40ml) and the combined organic fractions were then washed with brine (50ml), dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the aldehyde **14** (1.0g, 89%) as a colourless oil; ν_{max}(film)/cm^{-1} 2838, 1723, 1463, 990; δ_H (270MHz, $CHCl_3$) 1.61-1.71 (2H, m, C*H*$_2$), 1.81-1.92 (2H, m, C*H*$_2$), 2.00-2.20 (4H, m, 2 x C*H*$_2$), 2.37 (2H, dt, *J* 7.3 and 1.7Hz, C*H*$_2$CHO), 3.34 (2H, t, *J* 6.9Hz, C*H*$_2$Br), 5.42-5.53 (2H, m, 2 x =C*H*), 5.90-6.04 (2H, m, 2 x =C*H*), 9.69 (1H, t, *J* 1.7Hz, C*H*O); δ_C (68MHz, $CHCl_3$) 21.4 (t), 30.6 (t), 31.5 (t), 31.9 (t), 33.0 (t), 42.9 (t), 130.1 (d), 130.9 (d), 131.2 (d), 131.2 (d), 202.0 (d); m/z (EI) 165.1276 (M^+ -HBr, $C_{11}H_{17}O$ requires 165.1279).

(*E*,*E*)-1-Bromo-3-hydroxy-trideca-7,9-dien-1-yne 15
A solution of ethynylmagnesium bromide (12ml) in THF (0.5M, 6.0mmol) was added dropwise over 5min to a stirred solution of the aldehyde **14** (1.0g, 4.0mmol) in dry THF (20ml), at 0°C, under a nitrogen atmosphere. The mixture was allowed to warm to room temperature where it was stirred for 30min. Ether (50ml) and saturated aqueous ammonium chloride solution (50ml) were added, and the organic layer was then separated. The aqueous extract was re-extracted with ether (2 x 50ml) and the combined organic fractions were then washed with brine (100ml), dried and concentrated *in vacuo* to leave the alcohol **15** (1.1g, 98%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 3385, 3294, 989; δ_H (400MHz, $CHCl_3$) 1.52-1.61 (2H, m, C*H*$_2$), 1.72-1.79 (2H, m, C*H*$_2$), 1.91-1.98 (2H, m, C*H*$_2$), 2.10-2.15 (2H, m, C*H*$_2$), 2.20-2.26 (2H, m, C*H*$_2$), 2.48 (1H, s, ≡C-H), 3.42 (2H, t, *J* 6.7Hz, C*H*$_2$Br), 4.38-4.41 (1H, m, C*H*OH), 5.49-5.63 (2H, m, 2 x =C*H*), 5.99-6.10 (2H, m, 2 x =C*H*); δ_C (100MHz, $CHCl_3$) 24.5 (t), 30.7 (t), 31.9 (t), 32.1 (t), 33.0 (t), 36.9 (t), 61.9 (d), 72.6 (d), 84.9 (s), 129.7 (d), 130.3 (d), 131.5 (d), 132.2 (d); m/z (EI) 270.0617 (M^+, $C_{13}H_{19}OBr$ requires 270.0619).

(*E*,*E*)-11-Bromo-3-oxo-trideca-7,9-dien-1-yne 16a
Dess-Martin periodinane (2.4g, 5.6mmol) was added in one portion to a stirred solution of the alcohol **15** (1.0g, 3.7mmol) in dry dichloromethane (37ml), at 0°C, under a nitrogen atmosphere. The mixture was warmed to room temperature where it was stirred for 30min. Aqueous sodium thiosulphate (5%, 10ml) was added and the mixture was stirred vigorously for 10min. The mixture was neutralised with saturated aqueous potassium carbonate and the organic layer was then separated. The aqueous extract was re-extracted with dichloromethane (2 x 40ml) and the combined organic fractions were then washed with brine (50ml), dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the ketone **16a** (0.81g, 82%) as a colourless oil; ν_{max}(film)/cm^{-1} 3274, 2933, 2093, 1682, 990; δ_H (270MHz, $CHCl_3$) 1.70-1.81 (2H, m, C*H*$_2$), 1.86-1.97 (2H, m, C*H*$_2$), 2.03-2.12 (2H, m, C*H*$_2$), 2.16-2.25 (2H, m, C*H*$_2$), 2.57 (2H, t, *J* 7.3Hz, C*H*$_2$CO), 3.24 (1H, s, ≡C-H), 3.38 (2H, t, *J* 6.7Hz, C*H*$_2$Br), 5.46-5.57 (2H, m, 2 x =C*H*), 5.94-6.09 (2H, m, 2 x =C*H*); δ_C (68MHz, $CHCl_3$) 23.1 (t), 30.7 (t), 31.4 (t), 32.0 (t), 33.1 (t), 44.5 (t), 78.4 (d), 81.3 (s), 130.3 (d), 131.1 (d), 131.2 (d), 131.3 (d), 187.0 (s); m/z (EI) 266.0308 (M^+ -H_2, $C_{13}H_{15}OBr$ requires 266.0306).

(*E*,*E*)-11-Iodo-3-oxo-trideca-7,9-dien-1-yne 16b
A suspension of the bromide **16a** (0.80g, 3.0mmol) and sodium iodide (1.3g, 9.0mmol) in acetone (15ml) was stirred at room temperature for 16h, under a nitrogen atmosphere, and then concentrated *in vacuo*. Ether (50ml) and water (50ml) were added and the organic layer was separated. The aqueous extract was re-extracted with ether (2 x 50ml) and the combined organic fractions were then washed with brine (50ml), dried and concentrated *in vacuo* to leave the iodide **16b** (0.94g, quantitative)

as a colourless oil; ν_{max}(film)/cm^{-1} 1682, 1435, 990; δ_H (270MHz, $CHCl_3$) 1.65-1.77 (2H, m, CH_2), 1.80-1.90 (2H, m, CH_2), 2.00-2.15 (4H, m, 2 x CH_2), 2.53 (2H, t, *J* 7.3Hz, CH_2CO), 3.12 (2H, t, *J* 6.9Hz, CH_2I), 3.25 (1H, s, ≡C-H), 5.40-5.54 (2H, m, 2 x =C*H*), 5.91-6.05 (2H, m, 2 x =C*H*); δ_C (68MHz, $CHCl_3$) 6.4 (t), 22.9 (t), 31.2 (t), 31.5 (t), 32.8 (t), 44.4 (t), 78.4 (d), 81.2 (s), 129.9 (d), 130.9 (d), 131.0 (d), 131.2 (d), 186.7 (s); which was used without further purification.

2-(*tert*-Butyldiphenylsilyloxy-propan-1'-yl)-furan 27b

tert-Butyldiphenylsilyl chloride (1.2ml, 4.8mmol) was added dropwise, over 10min, to a stirred solution of the alcohol **27a** (0.50g, 4.0mmol),[1] 4-dimethylaminopyridine (50mg, 0.40mmol) and triethylamine (0.72ml, 5.2mmol) in dry dichloromethane (20ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was stirred at 0^{o}C for 1h and then allowed to warm to room temperature where it was stirred for a further 16h. Dichloromethane (20ml) and water (20ml) were added and the organic layer was separated. The aqueous fraction was re-extracted with dichloromethane (2x30ml) and the combined organic extracts were then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 10% ether in light petroleum (b.p. 40-60^{o}C), to give the silyl ether **27b** (1.4g, 97%) as a colourless oil; δ_H (400MHz, $CHCl_3$) 1.08 (9H, s, SiC(CH_3)$_3$), 1.89-1.95 (2H, m, CH_2CH$_2$OTBDPS), 2.78 (2H, t, *J* 7.5Hz, CH_2CH$_2$CH$_2$OTBDPS), 3.72 (2H, t, *J* 6.1Hz, CH_2OTBDPS), 5.96-5.97 (1H, m, OC=C*H*), 6.28-6.29 (1H, m, OCH=C*H*), 7.30-7.31 (1H, m, OC*H*=), 7.38-7.46 (6H, m, 6 x SiPh*H*), 7.68-7.70 (4H, m, 4 x SiPh*H*); δ_C (68MHz, $CHCl_3$) 19.2 (s), 24.4 (t), 26.8 (q), 30.9 (t), 62.9 (t), 104.8 (d), 110.0 (d), 127.6 (d), 129.5 (d), 133.9 (s), 135.5 (d), 140.7 (d), 155.9 (s); m/z (EI) 307.1154 (M$^+$ -^{t}Bu, $C_{19}H_{19}O_2Si$ requires 307.1154).

3-*tert*-Butyldimethylsilyloxy-propan-1-al 28b

Pyridinium chlorochromate (16g, 74mmol) was added portionwise over 10min to a stirred suspension of the alcohol **28a** (9.4g, 49mmol)[2] and silica (30g), in dry dichloromethane (100ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was allowed to warm to room temperature where it was stirred for 4h. The mixture was concentrated *in vacuo* to leave a fine powder which was subjected to chromatography on silica, eluting with 10% ether in light petroleum (b.p. 40-60^{o}C), to give the aldehyde **28b** (5.6g, 60%) as a colourless oil; ν_{max}(film)/cm^{-1} 1730; δ_H (250MHz, $CHCl_3$) 0.07 (6H, s, Si(CH_3)$_2$), 0.89 (9H, s, SiC(CH_3)$_3$), 2.60 (2H, td, *J* 6.0 and 2.1Hz, CH_2CHO), 3.99 (2H, t, *J* 6.0Hz, CH_2OTBS), 9.81 (1H, t, *J* 2.1Hz, C*H*O); δ_C (68MHz, $CHCl_3$) -5.2 (q), 18.5 (s), 26.1 (q), 46.8 (t), 57.6 (t), 202.2 (d); m/z (EI) 188.1219 (M$^+$, $C_9H_{20}O_3Si$ requires 188.1223).

(*E*)-4-*tert*-Butyldimethylsilyloxy-1-iodo-prop-1-ene 29

Potassium *tert*-butoxide (3.2g, 28mmol) was added portionwise over 5min to a stirred suspension of iodomethyltriphenylphosphonium iodide (14.4g, 27mmol) in dry THF (150ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was allowed to warm to room temperature where it was stirred for 30min. The mixture was cooled to -60^{o}C and then a solution of the aldehyde **28b** (3.4g, 18mmol) in THF (20ml) was added dropwise over 10min. The mixture was allowed to warm to -40^{o}C over 2h and then concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 10% ether in light petroleum (b.p. 40-60^{o}C), to give the vinyl iodide **29** (5.0g, 97%) as a yellow oil; δ_H (270MHz, $CHCl_3$) 0.07 (6H, s, Si(CH_3)$_2$), 0.90 (9H, s, SiC(CH_3)$_3$), 2.37 (2H, app q, *J* 6.6Hz, =CHCH_2), 3.69 (2H, t, *J* 6.6Hz, CH_2OTBS), 6.24-6.29 (2H, m, C*H*=C*H*I); δ_C (100MHz, $CHCl_3$) -5.8 (q), 18.2 (s), 25.7 (q), 38.3 (t), 61.1 (t), 83.6 (d), 138.2 (d); m/z (EI) 297.0181 (M$^+$-Me, $C_9H_{18}IOSi$ requires 297.0173).

5-(3'-*tert*-Butyldiphenylsilyloxy-propan-1'-yl)-2-(4'-hydroxy-but-1'-en-1'-yl)-furan 31b

A solution of *t*-butyllithium (1.1ml) in pentane (1.7M, 1.8mmol) was added dropwise over 5min to a stirred solution of the furan **27b** (0.55g, 1.5mmol) in dry

THF, at -78°C, under a nitrogen atmosphere. The resulting furyllithium **30a** was allowed to warm to -20°C over 3h and then tributyltin chloride (0.57ml, 2.1mmol) was added dropwise over 2min. The resulting furylstannane **30b**[3] was allowed to warm to room temperature over 3h and then (*bis*)-triphenylphosphine palladium (II) chloride (53mg, 0.07mmol) was added in one portion. A solution of the iodide **29** (0.34g, 1.2mmol) in THF (5ml) was added in one portion and the mixture was heated under reflux for 16h and then cooled to room temperature. Ether (50ml) and water (50ml) were added and the organic layer was separated. The aqueous fraction was re-extracted with ether (2 x 50ml) and the combined organic extracts were then washed with brine (200ml), dried and concentrated *in vacuo* to leave the coupled product **31a** as a yellow oil. The oil was re-dissolved in methanol (20ml) and then pyridinium *p*-toluenesulphonate (0.94g, 3.0mmol) was added in one portion. The mixture was stirred at room temperature for 24h and then concentrated *in vacuo*. Ether (50ml) and water (50ml) were added to the residue and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 50ml) and the combined organic fractions were then washed with brine (200ml), dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with a gradient of 20 to 50% ether in light petroleum (b.p. 40-60°C), to give the alcohol **31b** (0.21g, 40%) as a yellow oil; ν_{max}(film)/cm^{-1} 3345, 1588; δ_H (400MHz, $CHCl_3$) 1.08 (9H, s, SiC(C*H*$_3$)$_3$), 1.89-1.96 (2H, m, C*H*$_2$CH$_2$OTBDPS), 2.72-2.80 (4H, m, =CHC*H*$_2$, C*H*$_2$CH$_2$CH$_2$OTBDPS), 3.74 (2H, t, *J* 6.1Hz, C*H*$_2$OTBDPS), 3.78 (2H, t, *J* 6.5Hz, C*H*$_2$OH), 5.50 (1H, dt, *J* 11.7 and 7.4Hz, =C*H*CH$_2$), 5.98 (1H, d, *J* 3.2Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$OTBDPS), 6.19 (1H, d, *J* 3.2Hz, =CHC(O)=C*H*), 6.26 (1H, d, *J* 11.7Hz, C*H*=CHCH$_2$), 7.37-7.46 (6H, m, 6 x Ph*H*), 7.67-7.73 (4H, m, 4 x Ph*H*); δ_C (100MHz, $CHCl_3$) 19.2 (s), 24.5 (t), 26.8 (q), 30.7 (t), 32.9 (t), 62.3 (t), 62.9 (t), 106.6 (d), 110.2 (d), 119.6 (d), 124.6 (d), 127.6 (d), 129.5 (d), 133.8 (s), 135.5 (d), 151.4 (s), 155.2 (s); m/z (EI) 434.2279 (M^+, $C_{27}H_{34}O_3Si$ requires 434.2277).

5-(3'-*tert*-Butyldiphenylsilyloxy-propan-1'-yl)-2-(4'-hydroxy-butan-1'-yl)-furan 32

A solution of the alkene **31b** (2.8g, 6.5mmol) in methanol (30ml) was stirred with palladium (II) hydroxide on carbon (100mg, 20% Pd) at room temperature for 6h, under an atmosphere of hydrogen. The suspension was filtered through a short plug of celite, and the residue was then washed with ether (100ml). The combined filtrate was concentrated *in vacuo* to leave the alkane **32** (2.7g, 96%) as a colourless oil; ν_{max}(film)/cm^{-1} 3358, 1567; δ_H (400MHz, $CHCl_3$) 1.08 (9H, s, SiC(C*H*$_3$)$_3$), 1.60-1.73 (4H, m, C*H*$_2$C*H*$_2$CH$_2$OH), 1.86-1.93 (2H, m, C*H*$_2$CH$_2$OTBDPS), 2.63 (2H, t, *J* 7.1Hz, C*H*$_2$CH$_2$CH$_2$CH$_2$OH), 2.72 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$OTBDPS), 3.67 (2H, t, *J* 6.5Hz, C*H*$_2$OTBDPS), 3.73 (2H, t, *J* 6.2Hz, C*H*$_2$OH), 5.84 (1H, d, *J* 3.0Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$OTBDPS), 5.87 (d, *J* 3.0Hz, 1H, HOCH$_2$CH$_2$CH$_2$CH$_2$C(O)=C*H*), 7.37-7.46 (6H, m, 6 x Ph*H*), 7.67-7.70 (4H, m, 4 x Ph*H*); δ_C (91MHz, $CHCl_3$) 19.1 (s), 24.2 (t), 24.3 (t), 26.7 (q), 27.6 (t), 30.8 (t), 31.9 (t), 62.1 (t), 62.9 (t), 105.0 (d), 105.0 (d), 127.5 (d), 129.4 (d), 133.8 (s), 135.4 (d), 153.9 (s), 154.0 (s); m/z (EI) 379.1721 (M^+-^{t}Bu, $C_{23}H_{27}O_3Si$ requires 379.1729); which was used without further purification.

2-(4'-Acetoxy-butan-1'-yl)-5-(3'-*tert*-Butyldiphenylsilyloxy-propan-1'-yl)-furan 33a

Acetic anhydride (0.70ml, 7.4mmol) was added dropwise over 2min to a stirred solution of the alcohol **32** (2.6g, 6.2mmol), triethylamine (1.3ml, 9.3mmol), and 4-dimethylaminopyridine (38mg, 0.31mmol) in dry dichloromethane (60ml), at 0°C, under a nitrogen atmosphere. The mixture was stirred at 0°C for 6h and then diluted with dichloromethane (50ml) and water (100ml). The separated aqueous fraction was re-extracted with dichloromethane (2 x 100ml) and the combined organic extracts were then washed with brine (100ml), dried and concentrated *in vacuo*. The residue was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the acetate **33a** (2.1g, 74%) as a colourless oil; ν_{max}(film)/cm^{-1} 1738; δ_H (360MHz, $CHCl_3$) 1.11 (9H, s, SiC(C*H*$_3$)$_3$),

1.69-1.73 (4H, m, C*H*$_2$C*H*$_2$CH$_2$OAc), 1.90-1.95 (2H, m, C*H*$_2$CH$_2$OTBDPS), 2.08 (3H, s, COC*H*$_3$), 2.61-2.66 (2H, m, C*H*$_2$CH$_2$CH$_2$CH$_2$OAc), 2.76 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$OTBDPS), 3.76 (2H, t, *J* 6.2Hz, C*H*$_2$OTBDPS), 4.12 (2H, t, *J* 6.2Hz, C*H*$_2$OAc), 5.87 (1H, d, *J* 2.8Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$OTBDPS), 5.90 (1H, d, *J* 2.8Hz, AcOCH$_2$CH$_2$CH$_2$CH$_2$C(O)=C*H*), 7.39-7.46 (6H, m, 6 x Ph*H*), 7.71-7.74 (4H, m, 4 x Ph*H*); δ_C (91MHz, CHCl$_3$) 19.2 (q), 20.9 (s), 24.4 (t), 24.5 (t), 26.8 (q), 27.6 (t), 28.0 (t), 30.9 (t), 63.0 (t), 64.2 (t), 105.1 (d), 105.3 (d), 127.6 (d), 129.5 (d), 133.9 (s), 135.5 (d), 153.7 (s), 154.2 (s), 171.1 (s); m/z (EI) 421.1828 (M^+-^{t}Bu, $C_{25}H_{29}O_4Si$ requires 421.1835).

2-(4'-Acetoxy-butan-1'-yl)-5-(3'-hydroxy-propan-1'-yl)-furan 33b
A solution of tetra-*n*-butylammonium fluoride (3.0ml) in THF (1.0M, 3.0mmol) was added dropwise over 5min to a stirred solution of the silyl ether **33a** (1.2g, 2.5mmol) in dry THF (50ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was stirred at 0^{o}C for 10min and then at room temperature for 2h. Ether (100ml) and water (100ml) were added and the organic layer was separated. The aqueous fraction was re-extracted with ether (2 x 100ml) and the combined organic extracts were then washed with brine (200ml), dried and concentrated *in vacuo*. The residue was purified by chromatography on silica, eluting with 80% ether in light petroleum (b.p.40-60^{o}C), to give the alcohol **33b** (0.58g, 96%) as a colourless oil; (Found C, 64.7; H, 8.7%. $C_{13}H_{20}O_4$ requires: C, 65.0; H, 8.4%); ν_{max}(film)/cm^{-1} 3405, 1738; δ_H (400MHz, CHCl$_3$) 1.64-1.69 (4H, m, C*H*$_2$C*H*$_2$CH$_2$OAc), 1.84-1.91 (2H, m, C*H*$_2$CH$_2$OH), 2.04 (3H, s, COC*H*$_3$), 2.60 (2H, t, *J* 6.8Hz, C*H*$_2$CH$_2$CH$_2$CH$_2$OAc), 2.67 (2H, t, *J* 7.4Hz, C*H*$_2$CH$_2$CH$_2$OH), 3.67 (2H, t, *J* 6.4Hz, C*H*$_2$OH), 4.07 (2H, t, *J* 6.3Hz, C*H*$_2$OAc), 5.86 (1H, d, *J* 3.0Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$OH), 5.88 (1H, d, *J* 3.0Hz, AcOCH$_2$CH$_2$CH$_2$CH$_2$C(O)=C*H*); δ_C (91MHz, CHCl$_3$) 20.8 (q), 24.2 (t), 24.3 (t), 27.4 (t), 27.8 (t), 30.9 (t), 61.6 (t), 64.1 (t), 105.2 (d), 105.2 (d), 153.7 (s), 153.7 (s), 171.2 (s); m/z (EI) 240.1368 (M^+, $C_{13}H_{20}O_4$ requires 240.1362).

2-(4'-Acetoxy-butan-1'-yl)-5-(3'-bromo-propan-1'-yl)-furan 33c
A solution of triphenylphosphine (0.94g, 3.6mmol) in dichloromethane (5ml) was added dropwise over 5min to a stirred solution of the alcohol **33b** (0.58g, 2.4mmol) and carbon tetrabromide (1.2g, 3.6mmol) in dry dichloromethane (20ml) at 0^{o}C under a nitrogen atmosphere. The mixture was stirred at 0^{o}C for 15min and then concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60^{o}C), to give the bromide **33c** (0.69g, 95%) as a colourless oil; (Found C, 51.8; H, 6.4%. $C_{13}H_{19}O_3Br$ requires: C, 51.5; H, 6.3%); ν_{max}(film)/cm^{-1} 1731, 785; δ_H (360MHz, CHCl$_3$) 1.63-1.68 (4H, m, C*H*$_2$C*H*$_2$CH$_2$OAc), 2.02 (3H, s, COC*H*$_3$), 2.11-2.17 (2H, m, C*H*$_2$CH$_2$Br), 2.55-2.61 (2H, m, C*H*$_2$CH$_2$CH$_2$CH$_2$OAc), 2.73 (2H, t, *J* 7.1Hz, C*H*$_2$CH$_2$CH$_2$Br), 3.39 (2H, t, *J* 6.6Hz, C*H*$_2$Br), 4.03-4.07 (2H, m, C*H*$_2$OAc), 5.85 (1H, d, *J* 2.8Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$Br), 5.89 (1H, d, *J* 2.8Hz, AcOCH$_2$CH$_2$CH$_2$CH$_2$C(O)=C*H*); δ_C (91MHz, CHCl$_3$) 20.8 (q), 24.4 (t), 26.3 (t), 27.4 (t), 27.9 (t), 31.0 (t), 32.7 (t), 64.0 (t), 105.3 (d), 106.0 (d), 152.2 (s), 154.1 (s), 170.8 (s); m/z (EI) 302.0521 (M^+, $C_{13}H_{19}O_3Br$ requires 302.0518).

5-(3'-Bromo-propan-1'-yl)-2-(4'-hydroxy-butan-1'-yl)-furan 34a
A suspension of the acetate **33c** (0.66g, 2.2mmol) and potassium carbonate (0.64g, 4.4mmol) in methanol (20ml) was stirred vigorously at room temperature for 4h and then concentrated *in vacuo*. Ether (50ml) and water (50ml) were added and the organic layer was separated. The aqueous layer was re-extracted with ether (2 x 50ml) and the combined organic fractions were then washed with brine (100ml), dried and concentrated *in vacuo* to leave the alcohol **34a** (0.56g, 98%) as a colourless oil; (Found C, 50.7; H, 6.7; Br, 30.5%. $C_{11}H_{17}O_2Br$ requires: C, 50.6; H, 6.6; Br, 30.6%); ν_{max}(film)/cm^{-1} 3353, 1613, 783; δ_H (360MHz, CHCl$_3$) 1.57-1.71 (4H, m, C*H*$_2$C*H*$_2$CH$_2$OH), 2.10-2.19 (2H, m, C*H*$_2$CH$_2$Br), 2.59 (2H, t, *J* 7.0Hz, C*H*$_2$CH$_2$CH$_2$CH$_2$OH), 2.73 (2H, t, *J* 7.2Hz, C*H*$_2$CH$_2$CH$_2$Br), 3.41 (2H, t, *J* 6.6Hz, C*H*$_2$Br), 3.62 (2H, t, *J* 6.5Hz, C*H*$_2$OH), 5.86 (1H, d, *J* 3.0Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$Br), 5.90 (1H, d, *J* 3.0Hz, HOCH$_2$CH$_2$CH$_2$CH$_2$C(O)=C*H*);

δ_C (91MHz, $CHCl_3$) 24.2 (t), 26.3 (t), 27.6 (t), 31.0 (t), 32.0 (t), 32.9 (t), 62.3 (t), 105.2 (d), 106.0 (d), 152.1 (s), 154.5 (s); m/z (EI) 260.0411 (M^+, $C_{11}H_{17}O_2Br$ requires 260.0412); which was used without further purification.

5-(3'-Bromo-propan-1'-yl)-2-(4'-oxo-butan-1'-yl)-furan 34b
Dess-Martin periodinane (1.8g, 4.2mmol) was added in one portion to a stirred solution of the alcohol **34a** (0.56g, 2.1mmol) in dry dichloromethane (30ml), at 0°C, under a nitrogen atmosphere. The mixture was warmed to room temperature where it was stirred for 20min. Aqueous sodium thiosulphate (5%, 20ml) was added and the mixture was then stirred vigorously for 10min. The mixture was neutralised with saturated aqueous potassium carbonate and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 40ml) and the combined organic fractions were then washed with brine (50ml), dried and concentrated *in vacuo*. The residue was purified by chromatography on silica, eluting with 30% ether in light petroleum (b.p. 40-60°C), to give the aldehyde **34b** (0.39g, 70%) as a colourless oil; ν_{max}(film)/cm^{-1} 1725, 790; δ_H (360MHz, $CHCl_3$) 1.88-1.96 (2H, m, CH_2CH_2CHO), 2.09-2.17 (2H, m, CH_2CH_2Br), 2.45 (2H, td, *J* 7.3 and 1.3Hz, CH_2CHO), 2.60 (2H, t, *J* 7.3Hz, $CH_2CH_2CH_2CHO$), 2.72 (2H, t, *J* 7.2Hz, $CH_2CH_2CH_2Br$), 3.39 (2H, t, *J* 6.6Hz, CH_2Br), 5.86 (1H, d, *J* 3.0Hz, CH=C(O)$CH_2CH_2CH_2Br$), 5.89 (1H, d, *J* 3.0Hz, $OCHCH_2CH_2CH_2C(O)$=CH), 9.71 (1H, t, *J* 1.3Hz, CHO); δ_C (90.6MHz, $CHCl_3$) 20.5 (t), 26.3 (t), 27.0 (t), 30.8 (t), 32.8 (t), 42.8 (t), 105.8 (d), 106.0 (d), 152.5 (s), 153.3 (s), 201.7 (d); m/z (EI) 258.0251 (M^+, $C_{11}H_{15}O_2Br$ requires 258.0255).

5-(3'-Bromo-propan-1'-yl)-2-(4'-hydroxy-hex-5'-yn-1'-yl)-furan 34c
A solution of ethynylmagnesium bromide (4.4ml) in THF (0.5M, 2.2mmol) was added dropwise over 5min to a stirred solution of the aldehyde **34b** (0.38g, 1.5mmol) in dry THF (15ml), at 0°C, under a nitrogen atmosphere. The mixture was allowed to warm to room temperature where it was stirred for 30min. Ether (50ml) and saturated aqueous ammonium chloride solution (50ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 50ml) and the combined organic fractions were washed with brine (100ml), then dried and concentrated *in vacuo*. The residue was purified by chromatography on silica, eluting with 40% ether in light petroleum (b.p. 40-60°C), to give the alcohol **34c** (0.35g, 84%) as a pale yellow oil; (Found C, 54.4; H, 6.1%. $C_{13}H_{17}O_2Br$ requires: C, 54.7; H, 6.0%); ν_{max}(film)/cm^{-1} 3356, 3294, 2114, 786; δ_H (360MHz, $CHCl_3$) 1.72-1.80 (4H, m, CH_2CH_2CHOH), 2.10-2.19 (2H, m, CH_2CH_2Br), 2.46 (1H, d, *J* 2.0Hz, ≡C-H), 2.61 (2H, t, *J* 6.1Hz, $CH_2CH_2CH_2CHOH$), 2.74 (2H, t, *J* 7.1Hz, $CH_2CH_2CH_2Br$), 3.41 (2H, t, *J* 6.6Hz, CH_2Br), 4.35-4.39 (1H, m, $CHOH$), 5.88 (1H, d, *J* 3.0Hz, CH=C(O)$CH_2CH_2CH_2Br$), 5.91 (1H, d, *J* 3.0Hz, $HOCHCH_2CH_2CH_2C(O)$=CH); δ_C (91MHz, $CHCl_3$) 23.4 (t), 26.3 (t), 27.4 (t), 30.9 (t), 32.9 (t), 36.7 (t), 61.7 (d), 72.9 (d), 84.7 (s), 105.3 (d), 106.0 (d), 152.2 (s), 154.1 (s); m/z (EI) 284.0405 (M^+, $C_{13}H_{17}O_2Br$ requires 284.0412).

5-(3'-Bromo-propan-1'-yl)-2-(4'-oxo-hex-5'-yn-1'-yl)-furan 35a
Dess-Martin periodinane (0.75g, 1.7mmol) was added in one portion to a stirred solution of the alcohol **34c** (0.32g, 1.1mmol) in dry dichloromethane (15ml), at 0°C, under a nitrogen atmosphere. The mixture was warmed to room temperature where it was stirred for 30min. Aqueous sodium thiosulphate (5%, 20ml) and dichloromethane (20ml) were added, and the mixture was then stirred vigorously for 10min. The mixture was neutralised with saturated aqueous potassium carbonate and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 30ml) and the combined organic fractions were washed with brine (50ml), then dried and concentrated *in vacuo*. The residue was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the ketone **35a** (0.28g, 88%) as a colourless oil; ν_{max}(film)/cm^{-1} 3270, 2092, 1684, 787; δ_H (360MHz, $CHCl_3$) 1.94-2.02 (2H, m, CH_2CH_2CO), 2.11-2.19 (2H, m, CH_2CH_2Br), 2.61 (2H, app t, *J* 7.2Hz, $CH_2CH_2CH_2CO$), 2.62 (2H, app t, *J* 7.3Hz, CH_2CO), 2.74 (2H, t, *J* 7.2Hz,

C*H*$_2$CH$_2$CH$_2$Br), 3.24 (1H, s, ≡C-H), 3.41 (2H, t, *J* 6.6Hz, C*H*$_2$Br), 5.88 (1H, d, *J* 3.0Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$Br), 5.91 (1H, d, *J* 3.0Hz, O=CCH$_2$CH$_2$CH$_2$C(O)=C*H*); δ_C (91MHz, $CHCl_3$) 22.0 (t), 26.3 (t), 26.9 (t), 31.0 (t), 32.8 (t), 44.4 (t), 78.5 (d), 81.2 (s), 106.0 (d), 106.1 (d), 152.6 (s), 153.2 (s), 186.6 (s); m/z (EI) 282.0259 (M^+, $C_{13}H_{15}O_2Br$ requires 282.0255).

5-(3'-Iodo-propan-1'-yl)-2-(4'-oxo-hex-5'-yn-1'-yl)-furan 24
A suspension of the bromide **35a** (0.13g, 0.45mmol), sodium iodide (0.20g, 1.3mmol) and potassium carbonate (3mg, 0.02mmol) in acetone (5ml) was stirred at room temperature for 14h, under a nitrogen atmosphere, and then concentrated *in vacuo*. Ether (50ml) and water (50ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 50ml) and the combined organic fractions were washed with brine (50ml), then dried and concentrated *in vacuo* to leave the iodide **24** (0.15g, quantitative) as a colourless oil; ν_{max}(film)/cm^{-1} 3269, 2092, 1681, 786; δ_H (360MHz, $CHCl_3$) 1.96-2.05 (2H, m, C*H*$_2$CH$_2$CO), 2.09-2.17 (2H, m, C*H*$_2$CH$_2$I), 2.63 (2H, app t, *J* 7.0Hz, C*H*$_2$CH$_2$CH$_2$CO), 2.64 (2H, app t, *J* 7.3Hz, C*H*$_2$CO), 2.71 (2H, t, *J* 7.0Hz, C*H*$_2$CH$_2$CH$_2$I), 3.21 (2H, app t, *J* 6.8Hz, C*H*$_2$I), 3.22 (1H, app s, ≡C-H), 5.90 (1H, d, *J* 2.9Hz, C*H*=C(O)CH$_2$CH$_2$CH$_2$I), 5.93 (1H, d, *J* 2.9Hz, O=CCH$_2$CH$_2$CH$_2$C(O)=C*H*); δ_C (91MHz, $CHCl_3$) 5.9 (t), 22.0 (t), 26.9 (t), 28.6 (t), 31.6 (t), 44.4 (t), 78.5 (d), 81.3 (s), 105.9 (d), 106.1 (d), 152.4 (s), 153.2 (s), 186.6 (s); m/z (EI) 330.0100 (M^+, $C_{13}H_{15}O_2I$ requires 330.0116); which was used without further purification.

2-(4'-Oxo-hex-5'-yn-1'-yl)-5-(3'-propan-1'-yl)-furan 35b
A solution of triethylborane (14µl) in hexanes (1M, 0.014mmol) was added in one portion to a stirred solution of the iodide **24** (45mg, 0.14mmol) and tri-*n*-butyltin hydride (46µl, 0.17mmol) in dry toluene (14ml), at 0^{o}C, under an argon atmosphere. The mixture was stirred at 0^{o}C for 48h and then concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 5% ether in light petroleum (b.p. 40-60^{o}C), to give the corresponding hydrocarbon **35b** (10mg, 37%) as a colourless oil; ν_{max}(film)/cm^{-1} 3261, 2092, 1682, 781; δ_H (360MHz, $CHCl_3$) 0.96 (3H, t, *J* 7.4Hz, CH$_2$C*H*$_3$), 1.61-1.67 (2H, m, C*H*$_2$CH$_3$), 1.98-2.04 (2H, m, C*H*$_2$CH$_2$CO), 2.55 (2H, t, *J* 7.5Hz, C*H*$_2$), 2.63 (2H, app t, *J* 7.0Hz, C*H*$_2$), 2.64 (2H, app t, *J* 7.1Hz, C*H*$_2$), 3.22 (1H, s, ≡C-H), 5.86 (1H, d, *J* 2.8Hz, C*H*=C(O)CH$_2$CH$_2$CH$_3$), 5.89 (1H, d, *J* 2.8Hz, O=CCH$_2$CH$_2$CH$_2$C(O)=C*H*); δ_C (90.6MHz, $CHCl_3$) 13.7 (q), 21.4 (t), 22.2 (t), 27.0 (t), 30.0 (t), 44.5 (t), 78.4 (d), 81.3 (s), 105.1 (d), 105.9 (d), 152.7 (s), 155.0 (s), 186.8 (s); m/z (EI) 204.1152 (M^+, $C_{13}H_{16}O_2$ requires 204.1150).

1-[5'-(3''-*tert*-Butyldiphenylsilyloxy-propan-1''-yl)-2'-furanyl]-2-methylcyano-benzene 39a
A solution of *t*-butyllithium (3.9ml) in pentane (1.7M, 6.6mmol) was added dropwise over 10min to a stirred solution of the furan **27b** (2.0g, 5.5mmol) in dry THF, at -78^{o}C, under a nitrogen atmosphere. The resulting furyllithium **30a** was allowed to warm to -20^{o}C over 3h and then tributyltin chloride (2.1ml, 7.7mmol) was added dropwise over 10min. The resulting pale yellow solution of **30b** was allowed to warm to room temperature over 3h. (*bis*)-Triphenylphosphine palladium (II) chloride (0.19g, 0.27mmol) and a solution of 2-iodobenzeneacetonitrile (1.1g, 4.5mmol) in dry THF (25ml) were added and the mixture was heated under reflux for 16h. The cooled mixture was diluted with ether (100ml) and water (100ml), and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 100ml) and the combined organic fractions were dried and concentrated *in vacuo* to leave a brown oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60^{o}C), to give the nitrile **39a** (1.9g, 89%) as a yellow oil; ν_{max}(film)/cm^{-1} 3070, 2250; δ_H (250MHz, $CHCl_3$) 1.08 (9H, s, SiC(C*H*$_3$)$_3$), 1.91-2.02 (2H, m, C*H*$_2$CH$_2$OTBDPS), 2.85 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$OTBDPS), 3.75 (2H, t, *J* 6.1Hz, C*H*$_2$OTBDPS), 3.95 (2H, s, C*H*$_2$CN), 6.10 (1H, d, *J* 3.3Hz, ArC(O)=CHC*H*), 6.48 (1H, d, *J* 3.3Hz, ArC(O)=C*H*), 7.34-7.43 (8H, m, 6 x

SiPh*H* + 2 x Ar*H*), 7.49-7.53 (1H, m, Ar*H*), 7.58-7.62 (1H, m, Ar*H*), 7.66-7.74 (4H, m, 4 x SiPh*H*); δ_C (68MHz, $CHCl_3$) 19.2 (s), 23.1 (t), 24.5 (t), 26.8 (q), 30.8 (t), 62.8 (t), 107.1 (d), 109.7 (d), 118.0 (s), 126.1 (s), 127.6 (d), 127.8 (d), 127.9 (d), 128.3 (d), 129.6 (d), 129.6 (d), 133.8 (s), 135.5 (d), 150.6 (s), 156.6 (s); m/z (EI) 422.1585 (M^+-^{t}Bu, $C_{27}H_{24}NO_2Si$ requires 422.1576).

1-[5'-(3''-Hydroxy-propan-1''-yl)-2'-furanyl]-2-methylcyano-benzene 39b
A solution of *tetra-n*-butylammonium fluoride (29ml) in THF (1M, 29mmol) was added dropwise over 10min to a stirred solution of the silyl ether **39a** (3.4g, 7.2mmol) and *p*-toluenesulphonic acid (2.7g, 14mmol) in THF (140ml), at 0°C, under a nitrogen atmosphere. The solution was allowed to warm to room temperature over 12h and then ether (100ml) and water (100ml) were added. The organic layer was separated and the aqueous fraction was re-extracted with ether (2 x 100ml). The combined organic extracts were dried and then concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 60% ether in light petroleum (b.p. 40-60°C), to give the alcohol **39b** (1.3g, 75%) as a colourless oil; (Found C, 74.4; H, 6.5%. $C_{15}H_{15}NO_2$ requires: C, 74.7; H, 6.3%); ν_{max}(film)/cm^{-1} 3414, 2251, 1595; δ_H (250MHz, $CHCl_3$) 1.44 (1H, t, *J* 6.1Hz, O*H*), 1.94-2.05 (2H, m, CH_2CH$_2$OH), 2.84 (2H, t, *J* 7.4Hz, CH_2CH$_2$CH$_2$OH), 3.75 (2H, dt, *J* 6.1 and 6.1Hz, CH_2OH), 3.98 (2H, s, CH_2CN), 6.17 (1H, d, *J* 3.3Hz, ArC(O)=CHC*H*), 6.51 (1H, d, *J* 3.3Hz, ArC(O)C*H*), 7.28-7.41 (2H, m, 2 x Ar*H*), 7.48 (1H, dd, *J* 7.1 and 1.7Hz, Ar*H*), 7.61 (1H, dd, *J* 7.7 and 1.8Hz, Ar*H*); δ_C (68MHz, $CHCl_3$) 23.0 (t), 24.3 (t), 30.7 (t), 61.4 (t), 107.1 (d), 109.5 (d), 118.1 (s), 125.8 (s), 127.6 (d), 127.7 (d), 128.2 (d), 129.7 (d), 129.9 (s), 150.6 (s), 156.2 (s); m/z (EI) 241.1117 (M^+, $C_{15}H_{15}NO_2$ requires 241.1103).

1-[5'-(3''-Bromo-propan-1''-yl)-2'-furanyl]-2-methylcyano-benzene 40a
A solution of triphenylphosphine (0.96g, 3.7mmol) in dichloromethane (5ml) was added dropwise over 5min to a stirred solution of the alcohol **39b** (0.59g, 2.5mmol) and carbon tetrabromide (1.2g, 2.5mmol) in dry dichloromethane (25ml), at 0°C, under a nitrogen atmosphere. The mixture was stirred at 0°C for 30min, then concentrated *in vacuo* to leave a brown oil, which was poured into petrol (25ml). The resulting suspension was filtered and the residue was then washed with petrol (50ml). The combined filtrates were concentrated *in vacuo* to leave a yellow oil which was then purified by chromatography on silica, eluting with a gradient of 10 to 40% ether in light petroleum (b.p. 40-60°C), to give the bromide **40a** (0.63g, 85%) as a colourless oil; (Found C, 59.1; H, 4.7; Br, 26.1%. $C_{15}H_{14}BrNO$ requires: C, 59.2; H, 4.6; Br, 26.3%); ν_{max}(film)/cm^{-1} 2250, 1595, 733; δ_H (250MHz, $CHCl_3$) 2.21-2.32 (2H, m, CH_2CH$_2$Br), 2.92 (2H, t, *J* 7.2Hz, CH_2CH$_2$CH$_2$Br), 3.48 (2H, t, *J* 6.4Hz, CH_2Br), 3.98 (2H, s, CH_2CN), 6.22 (1H, d, *J* 3.3Hz, ArC(O)CHC*H*), 6.52 (1H, d, *J* 3.3Hz, ArC(O)C*H*), 7.29-7.42 (2H, m, 2 x Ar*H*), 7.49 (1H, dd, *J* 7.6 and 1.9Hz, Ar*H*), 7.61 (1H, dd, *J* 7.7 and 1.8Hz, Ar*H*); δ_C (68MHz, $CHCl_3$) 23.0 (t), 26.3 (t), 30.6 (t), 32.7 (t), 107.8 (d), 109.5 (d), 117.8 (s), 125.9 (s), 127.6 (d), 127.8 (d), 128.1 (d), 129.6 (d), 129.7 (s), 150.8 (s), 154.5 (s); m/z (EI) 303.0264 (M^+, $C_{15}H_{14}BrNO$ requires 303.0259).

1-[5'-(3''-Bromo-propan-1''-yl)-2'-furanyl]-2-(2'''-hydroxybut-3'''-yn-1'''-yl)-benzene 41
A solution of di-*iso*-butylaluminium hydride (1.4ml) in toluene (1.5M, 2.1mmol) was added dropwise over 5min to a stirred solution of the nitrile **40a** in toluene (20ml), at -78°C, under a nitrogen atmosphere. The mixture was allowed to warm to 0°C over 4.5h and then aqueous methanol (50% v/v, 3ml) was added dropwise over 2min. The mixture was allowed to warm to room temperature and then silica (8g) and ethyl acetate (10ml) were added. The mixture was stirred at room temperature for 30min and then filtered through a short plug of silica and washed with ether (100ml). The combined filtrates were concentrated *in vacuo* to leave the corresponding aldehyde **40b** as a yellow oil. The oil was dissolved in dry THF (20ml) and then cooled to -78°C, under a nitrogen atmosphere. A solution of ethynylmagnesium chloride (3.8ml) in THF (0.5M, 1.9mmol) was added dropwise over 5min, and the resulting mixture was allowed to warm to room temperature

over 2h. Ether (50ml) and water (50ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 50ml) and the combined organic extracts were washed with brine, then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60^{o}C), to give the alcohol **41** (0.38g, 60%) as a colourless oil; ν_{max}(film)/cm^{-1} 3415, 3290, 761; δ_H (270MHz, $CHCl_3$) 2.21-2.31 (2H, m, CH_2CH$_2$Br), 2.48 (1H, d, *J* 2.0Hz, ≡C-H), 2.88 (2H, t, *J* 7.3Hz, CH_2CH$_2$CH$_2$Br), 3.21 (1H, dd, *J* 13.9 and 7.6Hz, C*H*HCHOH), 3.31 (1H, dd, *J* 13.9 and 5.6Hz, CH*H*CHOH), 3.46 (2H, t, *J* 6.6Hz, CH_2Br), 4.58-4.62 (1H, m, C*H*OH), 6.16 (1H, d, *J* 3.3Hz, ArC(O)CHC*H*), 6.47 (1H, d, *J* 3.3Hz, ArC(O)C*H*), 7.24-7.38 (3H, m, 3 x Ar*H*), 7.56 (1H, dd, *J* 7.6 and 2.0Hz, Ar*H*); δ_C (68MHz, $CHCl_3$) 26.5 (t), 30.9 (t), 32.9 (t), 42.5 (t), 62.5 (d), 73.4 (d), 84.5 (s), 107.8 (d), 109.0 (d), 127.1 (d), 127.5 (d), 127.9 (d), 130.5 (s), 132.0 (d), 133.2 (s), 152.4 (s), 153.9 (s); m/z (EI) 332.0393 (M^+, $C_{17}H_{17}BrO_2$ requires 332.0412).

1-[5'-(3''-Bromo-propan-1''-yl)-2'-furanyl]-2-(2'''-oxo-but-3'''-yn-1'''-yl)-benzene 42

Dess-Martin periodinane (0.72g, 1.7mmol) was added in one portion to a stirred solution of the alcohol **41** (0.37g, 1.2mmol) in dry dichloromethane (12ml) at 0^{o}C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature where it was stirred for 2h. Aqueous sodium thiosulphate solution (5%, 10ml) was added and the mixture was then stirred vigorously for 20min. The mixture was neutralised with saturated aqueous potassium carbonate solution and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 20ml) and the combined organic extracts were washed with brine (30ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60^{o}C), to give the ynone **42** (0.19g, 50%) as a colourless oil; ν_{max}(film)/cm^{-1} 3272, 2093, 1682, 760; δ_H (250MHz, $CHCl_3$) 2.18-2.29 (2H, m, CH_2CH$_2$Br), 2.87 (2H, t, *J* 7.2Hz, CH_2CH$_2$CH$_2$Br), 3.21 (1H, s, ≡C-H), 3.46 (2H, t, *J* 6.5Hz, CH_2Br), 4.11 (2H, s, CH_2CO), 6.15 (1H, d, *J* 3.3Hz, ArC(O)CHC*H*), 6.47 (1H, d, *J* 3.3Hz, ArC(O)C*H*), 7.25-7.38 (3H, m, 3 x Ar*H*), 7.59 (1H, dd, *J* 7.8 and 1.7Hz, Ar*H*); δ_C (68MHz, $CHCl_3$) 26.9 (t), 31.2 (t), 33.4 (t), 51.4 (t), 80.0 (d), 81.6 (s), 108.2 (d), 109.2 (d), 127.9 (d), 128.0 (d), 128.2 (d), 129.2 (s), 131.3 (s), 132.8 (d), 152.5 (s), 154.7 (s), 185.1 (s); m/z (EI) 330.0251 (M^+, $C_{17}H_{15}BrO_2$ requires 330.0255).

1-[5'-(3''-Iodo-propan-1''-yl)-2'-furanyl]-2-(2'''-oxo-but-3'''-yn-1'''-yl)-benzene 36

A suspension of the bromide **42** (91mg, 0.27mmol), potassium carbonate (20mg, 0.14mmol) and sodium iodide (120mg, 0.81mmol) in acetone (5ml) was stirred at room temperature for 14h, under a nitrogen atmosphere. The mixture was concentrated *in vacuo,* and then ether (20ml) and water (20ml) were added. The organic layer was separated and the aqueous fraction was re-extracted with ether (2x20ml). The combined organic extracts were washed with brine (30ml), then dried and concentrated *in vacuo* to leave the iodide **36** (80mg, 77%) as a colourless oil; ν_{max}(film)/cm^{-1} 3275, 2093, 1682, 760; δ_H (270MHz, $CHCl_3$) 2.14-2.24 (2H, m, CH_2CH$_2$I), 2.82 (2H, t, *J* 7.3Hz, CH_2CH$_2$CH$_2$I), 3.22 (1H, app s, ≡C-H), 3.23 (2H, app t, *J* 6.5Hz, CH_2I), 4.12 (2H, s, CH_2CO), 6.15 (1H, d, *J* 3.3Hz, ArC(O)CHC*H*), 6.47 (1H, d, *J* 3.3Hz, ArC(O)C*H*), 7.22-7.38 (3H, m, 3 x Ar*H*), 7.60 (1H, dd, *J* 7.8 and 1.7Hz, Ar*H*); δ_C (68MHz, $CHCl_3$) 6.0 (t), 28.8 (t), 31.4 (t), 60.0 (t), 79.5 (d), 81.2 (s), 107.9 (d), 108.8 (d), 127.5 (d), 127.6 (d), 127.8 (d), 128.8 (s), 130.9 (s), 132.3 (d), 152.1 (s), 154.1 (s), 184.7 (s); m/z (EI) 378.0116 (M^+, $C_{17}H_{15}O_2$ requires 378.0117); which was used without further purification.

2-(2'-*tert*-Butyldimethylsilyloxy-ethan-1'-yl)-cyclohexan-1-one 50

A mixture of the hemi-aminal **49** (1.0g, 5.1mmol)[4] and hydrochloric acid (1M, 5.6ml) was stirred and heated under reflux for 5h, and then cooled to room temperature. Dichloromethane (50ml) and water (50ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 50ml) and the combined organic extracts were washed with saturated aqueous sodium bicarbonate solution (50ml), then dried and concentrated *in vacuo* to leave a yellow oil. A solution of the oil, triethylamine (1.1ml, 7.7mmol) and 4-dimethylaminopyridine (31mg, 0.26mmol) in dry dichloromethane (25ml) was stirred at room temperature for 30min, and then cooled to 0°C. *tert*-Butyldimethylsilyl chloride (0.85g, 5.6mmol) was added portionwise over 5min and the mixture was allowed to warm to room temperature where it was stirred for 16h. Dichloromethane (50ml) and water (50ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 50ml) and the combined organic extracts were washed with brine (50ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 10% ether in light petroleum (b.p. 40-60°C), to give the cyclohexanone **50** (0.85g, 65%) as a colourless oil; (Found C, 65.6; H, 11.4%. $C_{14}H_{28}O_2Si$ requires C, 65.5; H, 11.1%); ν_{max}(film)/cm^{-1} 1711, 775; δ_H (250MHz, $CHCl_3$) 0.04 (6H, s, Si(CH_3)$_2$), 0.89 (9H, s, SiC(CH_3)$_3$), 1.29-1.43 (2H, m, CH_2), 1.62-1.73 (2H, m, CH_2), 1.83-2.16 (4H, m, 2 x CH_2), 2.30-2.56 (3H, m, CH + CH_2), 3.65 (2H, td, *J* 6.4 and 2.2Hz, CH_2OTBS); δ_C (68MHz, $CHCl_3$) -5.1 (q), 18.5 (s), 25.4 (t), 26.2 (q), 28.4 (t), 32.7 (t), 34.5 (t), 42.4 (t), 47.3 (t), 61.1 (t), 213.4 (s); m/z (EI) 199.1157 (M$^+$-^{t}Bu, $C_{10}H_{19}O_2Si$ requires 199.1154).

2-(2'-*tert*-Butyldimethylsilyloxy-ethan-1'-yl)-cyclohex-6-en-1-yl-trifluoromethanesulphonate 51

Diisopropylamine (0.86ml, 6.6mmol) was added dropwise over 5min to a stirred solution of *n*-butyllithium (10ml) in THF (0.55M, 5.5mmol), at -78°C, under a nitrogen atmosphere. The mixture was stirred at -78°C for 15min and then at room temperature for 15min. The mixture was cooled to -78°C and then a solution of the ketone **50** (1.0g, 3.9mmol) in THF (20ml) was added dropwise over 10min. The mixture was allowed to warm to room temperature over 2h, and was then re-cooled to -78°C. A solution of *N*-phenyl *bis*-trifluoromethanesulfonimide (1.5g, 4.3mmol) in THF (10ml) was added dropwise over 10min, and the resulting mixture was allowed to warm to 0°C over 3h. Ether (50ml) and water (50ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2x50ml) and the combined organic extracts were washed with brine (50ml), and then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 10% ether in light petroleum (b.p. 40-60°C), to give the triflate **51** (1.5g, 99%) as a colourless oil; ν_{max}(film)/cm^{-1} 1681; δ_H (400MHz, $CHCl_3$) 0.06 (6H, s, Si(CH_3)$_2$), 0.90 (9H, s, SiC(CH_3)$_3$), 1.48-1.65 (4H, m, 2 x CH_2), 1.89-2.03 (2H, m, CH_2), 2.16-2.19 (2H, m, CH_2), 2.58-2.63 (1H, m, CH), 3.68-3.73 (2H, m, CH_2OTBS), 5.77 (1H, t, *J* 4.1Hz, =CH); δ_C (100MHz, $CHCl_3$) -5.5 (q), -5.5 (q), 18.2 (s), 18.8 (t), 24.2 (t), 25.8 (q), 27.8 (t), 34.3 (d), 34.4 (t), 60.3 (t), 118.7 (d), 129.2 (m), 152.5 (s); m/z (EI) 373.1103 (M$^+$-Me, $C_{14}H_{24}O_4F_3SSi$ requires 373.1107).

1-[5'-(3''-*tert*-Butyldiphenylsilyloxy-propan-1''-yl)-2'-furanyl]-2-(2'''-hydroxy-ethan-1'''-yl)-cyclohex-6-ene 52b

A solution of *t*-butyllithium (11.6ml) in pentane (1.7M, 19.8mmol) was added dropwise over 15min to a stirred solution of the furan **27b** (6.0g, 16.5mmol) in dry THF (160ml), at -78°C, under a nitrogen atmosphere. The mixture was allowed to warm to -20°C over 3h and then *tri*-butyltin chloride (6.3ml, 23.1mmol) was added dropwise over 2min. The mixture containing the stannane **30b** was allowed to warm to room temperature over 3h and then (*bis*)-triphenylphosphine palladium (II) chloride (0.58g, 0.83mmol) and a solution of the triflate **51** (5.5g, 14.9mmol) in THF (80ml) were added. The mixture was heated under reflux for 5h and then cooled to room temperature. Ether (250ml) and water (250ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with

ether (2 x 250ml) and the combined organic extracts were washed with brine (400ml), dried and concentrated *in vacuo* to leave the coupled product **52a** as a yellow oil. The oil was re-dissolved in methanol (200ml) and then pyridinium *p*-toluenesulfonate (10.0g, 39.8mmol) was added in one portion. The resulting mixture was stirred at room temperature for 48h and then concentrated *in vacuo*. Ether (250ml) and water (250ml) were added and the organic layer was separated. The aqueous fraction was re-extracted with ether (2 x 250ml) and the combined organic extracts were washed with brine (400ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with a gradient of 20 to 50% ether in light petroleum (b.p. 40-60^{o}C), to give the alcohol **52b** (6.1g, 85%) as a colourless oil; ν_{max}(film)/cm^{-1} 3332, 1960, 1889, 1824, 1652, 700; δ_H (360MHz, $CHCl_3$) 1.07 (9H, s, SiC(C*H*$_3$)$_3$), 1.63-1.70 (4H, m, =CHCH$_2$C*H*$_2$C*H*$_2$), 1.75-1.81 (1H, m, C*H*HCH$_2$OH), 1.87-1.94 (3H, m, C*H*$_2$CH$_2$OTBDPS + CH*H*CH$_2$OH), 2.18-2.23 (2H, m, =CHC*H*$_2$), 2.63-2.68 (1H, m, C*H*CH$_2$CH$_2$OH), 2.75 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$OTBDPS), 3.72 (2H, t, *J* 6.0Hz, C*H*$_2$OH), 3.73 (2H, t, *J* 6.3Hz, C*H*$_2$OTBDPS), 5.92 (1H, d, *J* 3.2Hz, =CC(O)C*H*), 6.14 (1H, d, *J* 3.2Hz, =CC(O)CHC*H*), 6.18 (1H, t, *J* 4.1Hz, =C*H*CH$_2$), 7.36-7.45 (6H, m, 6 x Ph*H*), 7.66-7.70 (4H, m, 4 x Ph*H*); δ_C (68MHz, $CHCl_3$) 17.3 (t), 19.2 (s), 24.5 (t), 25.1 (t), 25.8 (t), 26.8 (q), 30.0 (d), 30.9 (t), 36.7 (t), 61.3 (t), 63.0 (t), 104.5 (d), 106.2 (d), 121.9 (d), 127.6 (d), 129.5 (d), 131.7 (s), 133.9 (s), 135.5 (d), 153.4 (s), 154.4 (s); m/z (EI) 488.2748 (M^{+}, $C_{31}H_{40}O_3Si$ requires 488.2747).

2-(2'''-Acetoxy-ethan-1'''-yl)-1-[5'-(3''-*tert*-butyldiphenylsilyloxy-propan-1''-yl)-2'-furanyl]-cyclohex-6-ene 52c

Acetic anhydride (0.58ml, 6.2mmol) was added dropwise over 2min to a stirred solution of the alcohol **52b** (2.5g, 5.1mmol), triethylamine (1.1ml, 7.6mmol), and 4-dimethylaminopyridine (31mg, 0.25mmol) in dry dichloromethane (50ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was stirred at 0^{o}C for 6h, and then dichloromethane (100ml) and water (100ml) were added. The organic layer was separated and the aqueous fraction was then re-extracted with dichloromethane (2 x 50ml). The combined organic extracts were washed with brine (100ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60^{o}C), to give the acetate **52c** (2.6g, 96%) as a colourless oil; (Found C, 74.6; H, 8.0%. $C_{33}H_{42}O_4Si$ requires: C, 74.7; H, 8.0%); ν_{max}(film)/cm^{-1} 1741, 740, 703; δ_H (360MHz, $CHCl_3$) 1.07 (9H, s, SiC(C*H*$_3$)$_3$), 1.62-1.81 (5H, m, =CHCH$_2$C*H*$_2$C*H*$_2$ + C*H*HCH$_2$OAc), 1.89-2.01 (3H, m, C*H*$_2$CH$_2$OTBDPS + CH*H*CH$_2$OAc), 2.09 (3H, s, COC*H*$_3$), 2.19-2.23 (2H, m, =CHC*H*$_2$), 2.56-2.60 (1H, m, C*H*CH$_2$CH$_2$OAc), 2.75 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$OTBDPS), 3.73 (2H, t, *J* 6.2Hz, C*H*$_2$OTBDPS), 4.14 (1H, d, *J* 5.5Hz, C*H*HOAc), 4.16 (1H, d, *J* 5.5Hz, CH*H*OAc), 5.93 (1H, d, *J* 3.1Hz, =CC(O)C*H*), 6.08 (1H, d, *J* 3.1Hz, =CC(O)CHC*H*), 6.20 (1H, t, *J* 4.0Hz, =C*H*CH2), 7.36-7.46 (6H, m, 6 x Ph*H*), 7.67-7.69 (4H, m, 4 x Ph*H*); δ_C (68MHz, $CHCl_3$) 17.2 (t), 19.1 (s), 20.9 (q), 24.4 (t), 25.0 (t), 25.5 (t), 26.8 (q), 30.3 (d), 30.8 (t), 32.2 (t), 62.9 (t), 63.0 (t), 104.3 (d), 106.1 (d), 122.0 (d), 127.5 (d), 129.5 (d), 131.1 (s), 133.8 (s), 135.4 (d), 153.1 (s), 154.5 (s), 170.9 (s); m/z (EI) 530.2854 (M^{+}, $C_{33}H_{42}O_4Si$ requires 530.2852).

2-(2'''-Acetoxy-ethan-1'''-yl)-1-[5'-(3''-chloro-propan-1''-yl)-2'-furanyl]-cyclohex-6-ene 53a

A solution of tetra-*n*-butylammonium fluoride (5.6ml) in THF (1.0M, 5.6mmol) was added dropwise over 5min to a stirred solution of the silyl ether **52c** (2.5g, 4.7mmol) in THF (50ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was allowed to warm to room temperature where it was stirred for 90min. Ether (100ml) and water (100ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 100ml) and the combined organic extracts were washed with brine (200ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 80% ether in light petroleum (b.p.40-60^{o}C), to give 2-(2-(5-(3-chloropropyl)furan-2-yl)cyclohex-2-enyl)ethyl acetate (1.4g, 98%) as a colourless

oil; (Found C, 69.4; H, 8.5%. $C_{17}H_{24}O_4$ requires: C, 69.0; H, 8.3%); ν_{max}(film)/cm^{-1} 3428, 1738, 1594, 781; δ_H (250MHz, $CHCl_3$) 1.60-1.78 (5H, m, =CHCH$_2$C*H*$_2$C*H*$_2$ + C*H*HCH$_2$OAc), 1.89-2.02 (3H, m, C*H*$_2$CH$_2$OH + CH*H*CH$_2$OAc), 2.08 (3H, s, COC*H*$_3$), 2.13-2.22 (2H, m, =CHC*H*$_2$), 2.54-2.61 (1H, m, C*H*CH$_2$CH$_2$OAc), 2.71 (2H, t, *J* 7.3Hz, C*H*$_2$CH$_2$CH$_2$OH), 3.69 (2H, t, *J* 6.4Hz, C*H*$_2$OH), 4.12 (1H, d, *J* 5.6Hz, C*H*HOAc), 4.15 (1H, d, *J* 5.6Hz, CH*H*OAc), 5.98 (1H, d, *J* 3.1Hz, =CC(O)C*H*), 6.09 (1H, d, *J* 3.1Hz, =CC(O)CHC*H*), 6.19 (1H, t, *J* 4.0Hz, =C*H*CH$_2$); δ_C (68MHz, $CHCl_3$) 17.1 (t), 20.9 (q), 24.3 (t), 25.0 (t), 25.4 (t), 30.2 (d), 30.9 (t), 32.2 (t), 61.8 (t), 63.1 (t), 104.3 (d), 106.3 (d), 122.2 (d), 131.3 (s), 153.2 (s), 154.1 (s), 171.2 (s); m/z (EI) 292.1675 (M^+, $C_{17}H_{24}O_4$ requires 292.1675). *N*-Chlorosuccinimide (0.82g, 6.1mmol) was added in one portion to a stirred solution of the alcohol (1.2g, 4.1mmol), triphenylphosphine (1.6g, 6.1mmol) and potassium carbonate (0.12g, 0.80mmol) in dry dichloromethane (80ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was stirred at 0^{o}C for 30min and then concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60^{o}C), to give the chloride **53a** (1.2g, 94%) as a colourless oil; ν_{max}(film)/cm^{-1} 1738, 1594, 782; δ_H (360MHz, $CHCl_3$) 1.62-1.78 (5H, m, =CHCH$_2$C*H*$_2$C*H*$_2$ + C*H*HCH$_2$OAc), 1.94-1.98 (1H, m, CH*H*CH$_2$OAc), 2.08 (3H, s, COC*H*$_3$), 2.08-2.14 (2H, m, C*H*$_2$CH$_2$Cl), 2.17-2.20 (2H, m, =CHC*H*$_2$), 2.54-2.59 (1H, m, C*H*CH$_2$CH$_2$OAc), 2.78 (2H, t, *J* 7.2Hz, C*H*$_2$CH$_2$CH$_2$Cl), 3.57 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 4.12 (1H, d, *J* 5.6Hz, C*H*HOAc), 4.14 (1H, d, *J* 5.6Hz, CH*H*OAc), 6.00 (1H, d, *J* 3.1Hz, =CC(O)C*H*), 6.09 (1H, d, *J* 3.1Hz, =CC(O)CHC*H*), 6.20 (1H, t, *J* 4.1Hz, =C*H*CH$_2$); δ_C (91MHz, $CHCl_3$) 17.2 (t), 20.9 (q), 25.1 (t), 25.2 (t), 25.5 (t), 30.3 (d), 30.9 (t), 32.2 (t), 44.1 (t), 63.0 (t), 104.4 (d), 107.0 (d), 122.5 (d), 131.3 (s), 152.8 (s), 153.6 (s), 171.0 (s); m/z (EI) 310.1334 (M^+, $C_{17}H_{23}O_3Cl$ requires 310.1336).

1-[5'-(3''-Chloro-propan-1''-yl)-2'-furanyl]-2-(2'''-hydroxy-ethan-1'''-yl)-cyclohex-6-ene 53b

A suspension of the acetate **53a** (1.1g, 3.5mmol), potassium carbonate (1.6g, 10.5mmol) and methanol (35ml) was stirred vigorously at room temperature for 16h, and then concentrated *in vacuo*. Ether (50ml) and water (50ml) were added and the organic layer was then separated. The aqueous layer was re-extracted with ether (2x50ml) and the combined organic extracts were washed with brine (100ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 80% ether in light petroleum (b.p. 40-60^{o}C), to give the alcohol **53b** (0.89g, 94%) as a colourless oil; (Found C, 67.0; H, 8.1%. $C_{15}H_{21}O_2Cl$ requires: C, 67.0; H, 7.9%); ν_{max}(film)/cm^{-1} 3355, 1644, 1594, 782; δ_H (360MHz, $CHCl_3$) 1.63-1.78 (5H, m, =CHCH$_2$C*H*$_2$C*H*$_2$ + C*H*HCH$_2$OH), 1.85-1.90 (1H, m, CH*H*CH$_2$OH), 2.07-2.14 (2H, m, C*H*$_2$CH$_2$Cl), 2.18-2.21 (2H, m, =CHC*H*$_2$), 2.61-2.65 (1H, m, C*H*CH$_2$CH$_2$OH), 2.77 (2H, t, *J* 7.2Hz, C*H*$_2$CH$_2$CH$_2$Cl), 3.58 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 3.70-3.73 (2H, m, C*H*$_2$OH), 6.00 (1H, d, *J* 3.1Hz, =CC(O)C*H*), 6.15 (1H, d, *J* 3.1Hz, =CC(O)CHC*H*), 6.19 (1H, t, *J* 4.0Hz, =C*H*CH$_2$); δ_C (91MHz, $CHCl_3$) 17.2 (t), 25.1 (t), 25.1 (t), 25.7 (t), 29.9 (d), 30.9 (t), 36.5 (t), 44.1 (t), 61.1 (t), 104.5 (d), 107.0 (d), 122.2 (d), 131.5 (s), 152.7 (s), 153.7 (s); m/z (EI) 268.1220 (M^+, $C_{15}H_{21}O_2Cl$ requires 268.1230).

1-[5'-(3''-Chloro-propan-1''-yl)-2'-furanyl]-2-(2'''-oxo-ethan-1'''-yl)-cyclohex-6-ene 53c

Dess-Martin periodinane (0.82g, 2.0mmol) was added in one portion to a stirred solution of the alcohol **53b** (0.40g, 1.3mmol) in dry dichloromethane (13ml), at 0^{o}C, under a nitrogen atmosphere. The mixture was stirred at 0^{o}C for 30min, then dichloromethane (20ml) and aqueous sodium thiosulphate (5%, 10ml) were added and the resulting heterogeneuos mixture was stirred vigorously at room temperature for 10min. The mixture was neutralised with saturated aqueous potassium carbonate and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 40ml) and the combined organic extracts were washed with brine (50ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica,

eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the aldehyde **53c** (0.30g, 76%) as a colourless oil; ν_{max}(film)/cm^{-1} 1722, 1594, 784; δ_H (360MHz, $CHCl_3$) 1.54-1.78 (4H, m, =CHCH$_2$C*H*$_2$C*H*$_2$), 2.04-2.12 (2H, m, C*H*$_2$CH$_2$Cl), 2.18-2.21 (2H, m, =CHC*H*$_2$), 2.58-2.69 (2H, m, C*H*$_2$CHO), 2.76 (2H, t, *J* 7.2Hz, C*H*$_2$CH$_2$CH$_2$Cl), 3.12-3.15 (1H, m, C*H*CH$_2$CHO), 3.55 (2H, td, *J* 6.4 and 1.4Hz, C*H*$_2$Cl), 5.99 (1H, d, *J* 3.0Hz, =CC(O)C*H*), 6.04 (1H, d, *J* 3.0Hz, =CC(O)CHC*H*), 6.23 (1H, t, *J* 3.8Hz, =C*H*CH$_2$), 9.76 (1H, d, *J* 1.2Hz, C*H*O); δ_C (90.6MHz, $CHCl_3$) 17.1 (t), 24.8 (t), 25.1 (t), 26.8 (t), 27.7 (d), 30.8 (t), 44.0 (t), 48.2 (t), 104.6 (d), 107.0 (d), 123.4 (d), 129.7 (s), 152.9 (s), 153.1 (s), 201.8 (d); m/z (EI) 268.1076 (M^+, $C_{15}H_{19}O_2Cl$ requires 268.1073).

1-[5'-(3''-Chloro-propan-1''-yl)-2'-furanyl]-2-(2'''-hydroxy-but-3'''-yn-1'''-yl)-cyclohex-6-ene 53d

A solution of ethynylmagnesium bromide (3.4ml) in THF (0.5M, 1.7mmol) was added dropwise over 5min to a stirred solution of the aldehyde **53c** (0.29g, 1.1mmol) in dry THF (11ml), at 0°C, under a nitrogen atmosphere. The mixture was allowed to warm to room temperature where it was stirred for 30min. Ether (50ml) and saturated aqueous ammonium chloride solution (50ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 50ml) and the combined organic extracts were washed with brine (100ml), then dried and concentrated *in vacuo* to leave a mixture of diastereoisomers (3:2 ratio) of the alcohol **53d** (0.30g, 94%) as a colourless oil; ν_{max}(film)/cm^{-1} 3362, 3297, 2248, 1594, 784, 733; δ_H (360MHz, $CHCl_3$) (major diastereoisomer) 1.64-1.70 (3H, m), 1.75-1.81 (1H, m), 1.87-2.01 (2H, m), 2.10-2.21 (4H, m, C*H*$_2$CH$_2$Cl + =CHC*H*$_2$), 2.58 (1H, d, *J* 2.1Hz, ≡C-H), 2.74-2.80 (1H, m, C*H*CH$_2$CHOH), 2.79 (2H, app t, *J* 7.2Hz, C*H*$_2$CH$_2$CH$_2$Cl), 3.58 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 4.48 (1H, br s, C*H*OH), 6.01 (1H, d, *J* 3.1Hz, =CC(O)C*H*), 6.22 (1H, t, *J* 4.0Hz, =C*H*CH$_2$), 6.26 (1H, d, *J* 3.1Hz, =CC(O)CHC*H*); δ_H (360MHz, $CHCl_3$) (minor diastereoisomer) 1.61-1.70 (3H, m), 1.77-1.89 (2H, m), 1.98-2.24 (5H, m), 2.48 (1H, d, *J* 2.1Hz, ≡C-H), 2.77-2.80 (1H, m, C*H*CH$_2$CHOH), 2.79 (2H, app t, *J* 7.2Hz, C*H*$_2$CH$_2$CH$_2$Cl), 3.58 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 4.48 (1H, br s, C*H*OH), 6.00 (1H, d, *J* 3.1Hz, =CC(O)C*H*), 6.21 (1H, t, *J* 4.0Hz, =C*H*CH$_2$), 6.24 (1H, d, *J* 3.1Hz, =CC(O)CHC*H*); δ_C (91MHz, $CHCl_3$) (major diastereoisomer) 17.2 (t), 25.0 (t), 25.2 (t), 25.8 (t), 30.4 (t), 30.9 (d), 40.9 (t), 44.1 (t), 63.3 (d), 73.7 (d), 84.7 (s), 104.7 (d), 107.1 (d), 122.5 (d), 130.8 (s), 152.9 (s), 153.5 (s); δ_C (91MHz, $CHCl_3$) (minor diastereoisomer) 17.1 (t), 25.1 (t), 25.2 (t), 25.4 (t), 29.4 (d), 30.9 (t), 41.5 (t), 44.1 (t), 60.3 (d), 72.8 (d), 85.2 (s), 104.9 (d), 107.1 (d), 122.4 (d), 131.0 (s), 152.8 (s), 153.4 (s); m/z (EI) 292.1237 (M^+, $C_{17}H_{21}O_2Cl$ requires 292.1230).

1-[5'-(3''-Chloro-propan-1''-yl)-2'-furanyl]-2-(2'''-oxo-but-3'''-yn-1'''-yl)-cyclohex-6-ene 53e

Dess-Martin periodinane (0.17g, 0.40mmol) was added in one portion to a stirred solution of the alcohol **53d** (80mg, 0.27mmol) in dry dichloromethane (5ml), at 0°C, under a nitrogen atmosphere. The mixture was warmed to room temperature where it was stirred for 30min. Dichloromethane (10ml) and aqueous sodium thiosulphate (5%, 10ml) were added and the mixture was then stirred vigorously for 10min. The mixture was neutralised with saturated aqueous potassium carbonate and the organic layer was then separated. The aqueous fraction was re-extracted with dichloromethane (2 x 10ml) and the combined organic extracts were washed with brine (20ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the ketone **53e** (69mg, 87%) as a colourless oil; ν_{max}(film)/cm^{-1} 3273, 2091, 1680, 1594, 784; δ_H (360MHz, $CHCl_3$) 1.58-1.73 (4H, m, =CHCH$_2$C*H*$_2$C*H*$_2$), 2.07-2.15 (2H, m, C*H*$_2$CH$_2$Cl), 2.18-2.21 (2H, m, =CHC*H*$_2$), 2.72-2.89 (4H, m, C*H*$_2$CH$_2$CH$_2$Cl + C*H*$_2$CO), 3.19-3.23 (1H, m, C*H*CH$_2$CHO), 3.27 (1H, s, ≡C-H), 3.58 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 6.01 (1H, d, *J* 3.1Hz, =CC(O)C*H*), 6.12 (1H, d, *J* 3.1Hz, =CC(O)CHC*H*), 6.25 (1H, t, *J* 3.9Hz, =C*H*CH$_2$); δ_C (91MHz, $CHCl_3$) 16.9 (t), 24.9 (t), 25.1 (t), 26.1 (t), 29.3 (d), 30.8 (t), 44.0 (t), 49.5 (t), 78.6 (d), 81.4 (s), 104.6 (d), 107.0 (d), 123.4 (d), 129.4 (s),

152.8 (s), 153.2 (s), 186.6 (s); m/z (EI) 290.1083 (M^+, $C_{17}H_{19}O_2Cl$ requires 290.1074).

1-[5'-(3''-Iodo-propan-1''-yl)-2'-furanyl]-2-(2'''-oxo-but-3'''-yn-1'''-yl)-cyclohex-6-ene 47

A suspension of the chloride **53e** (0.15g, 0.52mmol), sodium iodide (0.39g, 2.6mmol) and potassium carbonate (4mg, 0.01mmol) in 2-butanone (5ml) was heated to 80°C for 10h, under a nitrogen atmosphere, and then cooled to room temperature. Ether (20ml) and water (20ml) were added and the organic layer was then separated. The aqueous fraction was re-extracted with ether (2 x 20ml) and the combined organic extracts were washed with brine (30ml), then dried and concentrated *in vacuo* to leave a yellow oil. The oil was purified by chromatography on silica, eluting with 20% ether in light petroleum (b.p. 40-60°C), to give the *iodide* **47** (0.13g, 66%) as a yellow oil; ν_{max}(film)/cm^{-1} 3270, 2092, 1681, 783; δ_H (360MHz, $CHCl_3$) 1.57-1.73 (4H, m, =CHCH$_2$C*H*$_2$C*H*$_2$), 2.09-2.20 (4H, m, C*H*$_2$CH$_2$I + =CHC*H*$_2$), 2.70-2.88 (4H, m, C*H*$_2$CH$_2$CH$_2$I + C*H*$_2$CO), 3.18-3.22 (1H, m, C*H*CH$_2$CHO), 3.20 (2H, app t, *J* 6.8Hz, C*H*$_2$I), 3.29 (1H, s, ≡C-H), 6.01 (1H, d, *J* 3.2Hz, =CC(O)C*H*), 6.11 (1H, d, *J* 3.2Hz, =CC(O)CHC*H*), 6.24 (1H, t, *J* 4.0Hz, =C*H*CH$_2$); δ_C (91MHz, $CHCl_3$) 5.9 (t), 17.0 (t), 24.9 (t), 26.1 (t), 28.7 (t), 29.3 (d), 31.6 (t), 49.5 (t), 78.6 (d), 81.5 (s), 104.6 (d), 107.2 (d), 123.5 (d), 129.4 (s), 152.8 (s), 152.8 (s), 186.6 (s); m/z (EI) 382.0438 (M^+, $C_{17}H_{19}O_2I$ requires 382.0430).

5-(*tert*-Butyl-diphenyl-silanyloxy)-pentan-2-ol 65b

A solution of 1,4-pentanediol **65a** (1.10g, 10.6mmol) in tetrahydrofuran (25ml) was added dropwise over 10 min, to a stirred suspension of sodium hydride (60% in mineral oil, 0.39g, 9.8mmol) (previously washed with pentane (3 x 25ml)) in tetrahydrofuran (50ml) at 0°C, under a nitrogen atmosphere. The mixture was stirred at room temperature for 30 min, and then *tert*-butyldiphenylsilyl chloride (2.50ml, 9.61mmol) was added dropwise, over 5 min at 0°C. The mixture was stirred at room temperature for 2 h, and then diethyl ether (20ml) and water (20ml) were added. The separated aqueous phase was extracted with diethyl ether (3 x 20ml) and the combined organic extracts were dried over sodium sulphate and then concentrated *in vacuo*. The residue was purified by flash column chromatography (30% Et_2O, 70% petrol) on silica gel, to give the silyl ether **65b** (3.60g, 98%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3617, 3418, 1067; δ_H (400MHz, $CDCl_3$), 1.07 (9H, s, SiC(C*H*$_3$)$_3$), 1.20 (3H, d, *J* 6.0Hz, CHC*H*$_3$), 1.27 (1H, br s, O*H*), 1.48-1.70 (4H, m, C*H*$_2$C*H*$_2$), 3.70 (2H, t, *J* 6.0Hz, C*H*$_2$OTBDPS), 3.84 (1H, tq, *J* 7.0 and 6.0Hz, C*H*OH), 7.40-7.46 (6H, m, 6 x Ar*H*), 7.70-7.72 (4H, m, 4 x Ar*H*); δ_C (100MHz, $CDCl_3$), 19.1 (s), 23.4 (q), 26.8 (q), 28.9 (t), 36.2 (t), 64.2 (t), 67.8 (d), 127.6 (d), 129.6 (d), 133.6 (s), 135.6 (d); m/z (ES) 365.1945 (M + Na^+, $C_{21}H_{30}O_2SiNa$ requires 365.1913).

2-[5-(*tert*-Butyl-diphenyl-silanyloxy)-pentane-2-sulfonyl]-benzothiazole 66

2-Mercaptobenzothiazole (0.74g, 4.4mmol) and triphenylphosphine (1.23g, 4.7mmol) were added sequentially, to a stirred solution of the alcohol **65b** (1.0g, 2.95mmol) in tetrahydrofuran (33ml) at 0°C, under a nitrogen atmosphere. The mixture was stirred at 0°C for 5 min, and then diethyl azodicarboxylate (0.80ml, 4.4mmol) was added dropwise over 15 min. The yellow mixture was stirred at room temperature for 24 h and then diethyl ether (6ml), water (6ml) and brine (8ml) were added. The separated aqueous phase was extracted with diethyl ether (3 x 50ml) and the combined organic extracts were dried over sodium sulphate and then concentrated *in vacuo*. The residue was purified by flash column chromatography (5% Et_2O, 95% petrol) on silica gel, to give 2-[4-(*tert*-butyl-diphenyl-silanyloxy)-1-methyl-butylsulfanyl]-benzothiazole (1.44g, 99%) as a colourless oil; δ_H (400MHz, $CDCl_3$), 1.04 (9H, s, SiC(C*H*$_3$)$_3$), 1.51 (3H, d, *J* 7.0Hz, CHC*H*$_3$), 1.73-1.79 (2H, m, C*H*$_2$CH$_2$OTBDPS), 1.83-1.91 (2H, m, C*H*$_2$CH$_2$CH$_2$OTBDPS), 3.71 (2H, t, *J* 5.5Hz, C*H*$_2$OTBDPS), 4.00 (1H, tq, *J* 7.0 and 6.5Hz, C*H*CH$_3$), 7.28-7.44 (8H, m, 8 x Ar*H*), 7.66 (4H, dd, *J* 7.5 and 1.5Hz, 4 x Ar*H*), 7.75 (1H, dd, *J* 8.0 and 0.5Hz, Ar*H*), 7.86 (1H, app d, *J* 8.0Hz, Ar*H*); δ_C

(100MHz, $CDCl_3$), 19.2 (s), 21.5 (q), 26.9 (q), 29.9 (t), 33.2 (t), 44.4 (d), 63.5 (t), 120.9 (d), 121.5 (d), 124.2 (d), 126.0 (d), 127.7 (d), 129.6 (d), 135.6 (d), 135.3 (s), 137.2 (s), 153.4 (s), 166.6 (s); m/z (ES) 492.1840 ($M + H^+$, $C_{29}H_{33}NOS_2Si$ requires 492.1851).

Brine (20ml) was added to a solution of 3-chloroperoxybenzoic acid (70-75% in H_2O, 34.0g, 138mmol) in dichloromethane (50ml) at room temperature. The separated organic phase was then added dropwise, over 10 min, to a stirred solution of the above sulfide (30g, 60mmol) and sodium hydrogen carbonate (24.0g, 290mmol) in dichloromethane (150ml), at -40°C. The stirred mixture was allowed to warm to room temperature over 12 h, and then dichloromethane (100ml) and saturated aqueous sodium thiosulphate solution (200ml) were added. The separated aqueous phase was extracted with dichloromethane (3 x 50ml) and the combined organic extracts were then washed with water (5 x 200ml) and brine (5 x 100ml), dried and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% Et_2O, 80% petrol) on silica gel, to give the sulfone **66** (29.9g, 93%) as a colourless oil; δ_H (400MHz, $CDCl_3$), 0.96 (9H, s, $SiC(CH_3)_3$), 1.45 (3H, d, *J* 7.0Hz, $CHCH_3$), 1.44-1.64 (2H, m, $CH_2CH_2OTBDPS$), 1.68-1.78 (2H, m, $CH_2CH_2CH_2OTBDPS$), 3.65 (2H, t, *J* 6.0Hz, $CH_2OTBDPS$), 3.66 (1H, app t, *J* 7.0Hz, $CHCH_3$), 7.33-7.43 (6H, m, 6 x Ar*H*), 7.57-7.65 (6H, m, 6 x Ar*H*), 8.01 (1H, ddd, *J* 7.5, 1.0, and 0.5Hz, Ar*H*), 8.21 (1H, ddd, *J* 8.0, 1.0, 0.5Hz, Ar*H*); δ_C (100MHz, $CDCl_3$), 12.8 (q), 19.0 (s), 25.9 (t), 26.7 (q), 29.2 (t), 59.6 (d), 63.0 (t), 122.2 (d), 125.5 (d), 127.5 (d), 127.7 (d), 129.9 (d), 129.6 (d), 133.5 (s), 136.9 (s), 135.5 (d), 153.0 (s), 165.1 (s); m/z (ES) 546.1571 ($M + Na^+$, $C_{28}H_{33}NO_3S_2SiNa$ requires 546.1569).

_Z_-3 and _E_-3 Isomers of (2_E_)-Ethyl 3-(2-(7-(2,2-dimethyl-1,1-diphenylpropoxy)-4-methylhept-3-enyl)phenyl)acrylate 68a

Sodium hexamethyldisilazane (2.0M in THF, 1.70ml, 3.40mmol) was added dropwise over 10 min, to a stirred solution of the sulfone **66** (1.6g, 3.0mmol) in tetrahydrofuran (24ml) at -78°C, under a nitrogen atmosphere. The yellow solution was stirred at -78°C for 45 min and then a solution of the aldehyde **67a** (0.62g, 2.7mmol)[5] in tetrahydrofuran, (12ml) was added dropwise over 30 min. The mixture was stirred at -78°C for 2 h and then allowed to warm to room temperature over 12h. Saturated aqueous ammonium chloride solution (10ml) was added, and the separated aqueous phase was then extracted with diethyl ether (3 x 50ml). The combined organic extracts were dried over magnesium sulphate and concentrated *in vacuo*. The residue was purified by flash column chromatography (5% EtOAc, 95% petrol) on silica gel, to give a 2:3 mixture of *Z* and *E* isomers of the alkene **68a** (0.42g, 38%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 1703, 1634; δ_H (400MHz, $CDCl_3$), 1.05 (9H, 2 x s, $SiC(CH_3)_3$), 1.33 (3H, m, OCH_2CH_3), 1.44 (3H, s, $CH=CCH_3$), 1.47-1.67 (2H, m, $CH_2CH_2OTBDPS$), 1.98-2.10 (2H, m, $CH_2CH_2CH_2OTBDPS$), 2.18-2.34 (2H, m, $ArCH_2CH_2$), 2.71-2.82 (2H, m, $ArCH_2$), 3.57-3.67 (2H, m, $CH_2OTBDPS$), 4.25 (2H, 2 x q, *J* 7.0Hz, OCH_2CH_3), 5.16 (1H, 2 x t, *J* 7.0Hz, $CH=CCH_3$), 6.35 (1H, 2 x d, *J* 16.0Hz, ArCH=C*H*), 7.13-7.30 (3H, m, 3 x Ar*H*), 7.32-7.45 (6H, m, 6 x Ar_H), 7.54 (1H, 2 x dd, *J* 7.0 and 1.0Hz, Ar*H*), 7.62-7.70 (4H, m, 4 x Ar*H*), 8.01 (1H, 2 x d, *J* 16.0Hz, Ar*H*); δ_C (100MHz, $CDCl_3$), 14.3 (q), 15.8 (s), 19.1 (q), 19.2 (q), 26.8 (q), 26.9 (q), 29.7 (t), 30.0 (t), 30.3 (t), 30.8 (t), 33.4 (t), 33.5 (t), 34.4 (t), 35.7 (t), 60.4 (t), 60.5 (t), 63.3 (t), 63.6 (t), 119.2 (d), 119.3 (d), 122.9 (d), 126.4 (d), 126.5 (d), 127.5 (2C d), 129.5 (d), 129.9 (d), 130.1 (d), 130.9 (d), 132.9 (s), 133.0 (s), 134.0 (s), 134.1 (s), 135.5 (2C d), 135.6 (2C d), 136.0 (s), 136.1 (s), 138.0 (s), 138.1 (s), 141.9 (d), 142.1 (d), 167.0 (s); m/z (ES) 483.2349 (M^+ -^{t}Bu, $C_{31}H_{35}O_3Si$ requires 483.2355).

_Z_-3 and _E_-3 Isomers of (2_E_)-Ethyl 3-(2-(7-hydroxy-4-methylhept-3-enyl)phenyl)acrylate 68b

A solution of tetra-*n*-butylammonium fluoride (0.16g, 0.50mmol) in tetrahydrofuran (1ml) was added dropwise over 10 min, to a stirred solution of the silyl ether **68a** (0.12g, 0.30mmol) in tetrahydrofuran (2ml) at 0°C, under a nitrogen atmosphere. The pink solution was allowed to warm to room temperature over 3 h and then diethyl ether (2ml) and water (2ml) were added dropwise. The separated

aqueous phase was extracted with diethyl ether (3 x 30ml) and the combined organic extracts were then dried and concentrated *in vacuo*. The residue was purified by flash column chromatography (30% Et_2O, 70% petrol) on silica gel, to give i) the *Z*-3 isomer of the alcohol (0.021g, 25%)(eluted first) as a colourless oil; (Found C, 71.2; H, 7.9%. $C_{19}H_{25}ClO_2$ requires C, 71.1; H, 7.9%); ν_{max}(sol $CHCl_3$)/cm^{-1}, 3623, 1706, 1633; δ_H (400MHz, $CDCl_3$), 1.26 (3H, t, *J* 7.0Hz, OCH_2CH_3), 1.53 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2OH), 1.62 (3H, s, $CH=CCH_3$), 1.90 (1H, br s, O*H*), 2.00 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2OH$), 2.20 (2H, dt, *J* 8.0 and 7.5Hz, $ArCH_2CH_2$), 2.70 (2H, td, *J* 8.0 and 1.0Hz, $ArCH_2$), 3.52 (2H, t, *J* 6.5Hz, CH_2OH), 4.19 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.16 (1H, app t, *J* 7.5Hz, $CH=CCH_3$), 6.30 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.19 (3H, m, 3 x Ar*H*), 7.50 (1H, dd, *J* 7.0 and 2.0Hz, Ar*H*), 7.99 (1H, d, *J* 16.0Hz, $ArCH$=CH); δ_C (100MHz, $CDCl_3$), 14.3 (q), 23.3 (q), 28.0 (t), 30.4 (t), 31.0 (t), 34.0 (t), 60.7 (t), 62.4 (t), 119.1 (d), 124.3 (d), 126.4 (d), 129.0 (d), 130.1 (d), 130.3 (d), 132.9 (s), 136.0 (s), 142.1 (s), 142.5 (d), 167.2 (s); m/z (ES) 325.1793 ($M + Na^+$, $C_{19}H_{26}O_3Na$ requires 325.1779); and ii) the *E*-3 isomer of the alcohol (0.045g, 52%)(eluted second) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3623, 1706, 1633; δ_H (400MHz, $CDCl_3$), 1.34 (3H, t, *J* 7.0Hz, OCH_2CH_3), 1.52 (4H, br s, $CH=CCH_3$ + O*H*), 1.64 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2OH), 2.03 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2OH$), 2.27 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.78 (2H, t, *J* 7.5Hz, $ArCH_2$), 3.60 (2H, t, *J* 6.5Hz, CH_2OH), 4.27 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.21 (1H, t, *J* 7.0Hz, $CH=CCH_3$), 6.36 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.18-7.32 (3H, m, 3 x Ar*H*), 7.56 (1H, app d, *J* 7.5Hz, Ar*H*), 8.02 (1H, d, *J* 16.0Hz, $ArCH$=CH); δ_C (100MHz, $CDCl_3$), 14.3 (q), 15.8 (q), 29.9 (t), 30.7 (t), 33.3 (t), 35.8 (t), 60.5 (t), 62.7 (t), 119.3 (d), 123.3 (d), 126.4 (d), 126.5 (d), 129.9 (d), 130.2 (d), 133.0 (s), 136.0 (s), 141.8 (s), 142.3 (d), 167.1 (s); m/z (ES) 325.1764 ($M + Na^+$, $C_{19}H_{26}O_3Na$ requires 325.1779).

_Z_-3 and _E_-3 Isomers of (2_E_)-Ethyl 3-(2-(7-chloro-4-methylhept-3-enyl)phenyl)acrylate 69a

a) _Z_-3 Isomer

N-Chlorosuccinimide (0.07g, 0.5mmol) was added in one portion, to a stirred solution of the *Z*-alcohol **68b** (0.105g, 0.347mmol), triphenylphosphine (0.12g, 0.47mmol) and potassium carbonate (0.02g, 0.14mmol) in dichloromethane (10ml) at 0°C, under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 h and then concentrated *in vacuo*. The residue was purified by flash column chromatography (10% Et_2O, 90% petrol) on silica gel, to give the chloride **69a** (0.11g, 96%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 1706, 1633; δ_H (400MHz, $CDCl_3$), 1.28 (3H, t, *J* 7.0Hz, OCH_2CH_3), 1.59 (3H, d, *J* 1.0Hz, $CH=CCH_3$), 1.64 (2H, tt, *J* 7.0 and 6.5Hz, CH_2CH_2Cl), 2.01 (2H, t, *J* 7.0Hz, $CH_2CH_2CH_2Cl$), 2.20 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.72 (2H, t, *J* 7.0Hz, $ArCH_2$), 3.36 (2H, t, *J* 6.5Hz, CH_2Cl), 4.20 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.17 (1H, app t, *J* 7.5Hz, $CH=CCH_3$), 6.29 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.20-7.35 (3H, m, 3 x Ar*H*), 7.48 (1H, dd, *J* 7.5 and 1.0Hz, Ar*H*), 7.94 (1H, d, *J* 16.0Hz, $ArCH$=CH); δ_C (100MHz, $CDCl_3$), 11.6 (q), 14.4 (q), 30.2 (t), 30.8 (t), 35.0 (t), 38.2 (t), 44.4 (t), 60.6 (t), 120.2 (d), 125.2 (d), 126.8 (d), 127.0 (d), 130.1 (d), 130.3 (d), 133.1 (s), 137.5 (s), 140.1 (s), 141.5 (d), 166.8 (s); m/z (ES) 321.1598 ($M + H^+$, $C_{19}H_{26}ClO_2$ requires 321.1621).

b) _E_-3 Isomer

The corresponding *E*-chloride **69a** was prepared from the *E*-alcohol **68b** using an identical procedure (98%) and showed: ν_{max}(sol $CHCl_3$)/cm^{-1}, 1706, 1633; δ_H (400MHz, $CDCl_3$), 1.35 (3H, t, *J* 7.0Hz, OCH_2CH_3), 1.50 (3H, app s, $CH=CCH_3$), 1.83 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.09 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.27 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.79 (2H, t, *J* 7.0Hz, $ArCH_2$), 3.46 (2H, t, *J* 6.5Hz, CH_2Cl), 4.27 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.22 (1H, tq, *J* 7.5 and 1.0Hz, $CH=CCH_3$), 6.37 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.16-7.36 (3H, m, 3 x Ar*H*), 7.56 (1H, app d, *J* 7.5Hz, Ar*H*), 8.02 (1H, d, *J* 16.0Hz, $ArCH$=CH); δ_C (100MHz, $CDCl_3$), 14.3 (q), 15.7 (q), 29.9 (t), 30.6 (t), 33.3 (t), 36.6 (t), 44.6 (t), 60.5 (t), 119.3 (d), 124.1 (d), 126.5 (d), 126.6 (d), 129.9 (d), 130.2 (d), 133.0 (s), 134.6 (s), 141.7 (s), 142.1 (d), 167.0 (s); m/z (ES) 343.1430 ($M + Na^+$, $C_{19}H_{25}ClO_2Na$ requires 343.1435).

_Z_-3 and _E_-3 Isomers of (2_E_)-3-(2-(7-Chloro-4-methylhept-3-enyl)phenyl)acrylaldehyde 69b

a) _Z_-3 Isomer

Diisobutylaluminium hydride (1.0M in hexanes, 6.28ml, 6.28mmol) was added dropwise over 10 min, to a stirred solution of the *Z*-ester **69a** (0.96g, 3.0mmol) in dichloromethane (50ml) at -78^{o}C under a nitrogen atmosphere. The mixture was stirred at -78^{o}C for 4 h and then saturated aqueous Rochelle's salt (50ml) was added at 0^{o}C. The separated aqueous phase was extracted with dichloromethane (3 x 100ml) and the combined organic extracts were dried and then concentrated *in vacuo*. The residue was purified by flash column chromatography (30% Et_2O, 70% petrol) on silica gel to give the corresponding *Z*-alcohol (0.72g, 86%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3611, 1600; δ_H (400MHz, $CDCl_3$), 1.69 (3H, s, CH=CCH_3), 1.77 (2H, m, CH_2CH_2Cl), 2.12 (2H, t, *J* 7.5Hz, CH_2CH_2CH_2Cl), 2.30 (2H, dt, *J* 8.0 and 7.0Hz, ArCH_2CH_2), 2.73 (2H, t, *J* 8.0Hz, ArCH_2), 3.47 (2H, t, *J* 7.0Hz, CH_2Cl), 4.35 (2H, dd, *J* 6.0 and 1.0Hz, CH_2OH), 5.28 (1H, t, *J* 7.0Hz, C*H*=CCH$_3$), 6.28 (1H, dt, *J* 16.0 and 6.0Hz, ArCH=C*H*), 6.90 (1H, app d, *J* 16.0Hz, ArC*H*=CH), 7.14-7.25 (3H, m, 3 x Ar*H*), 7.47 (1H, dd, *J* 6.0 and 2.5Hz, Ar*H*); δ_C (100MHz, $CDCl_3$), 23.2 (q), 28.9 (t), 29.4 (t), 30.8 (t), 33.6 (t), 44.8 (t), 63.9 (t), 125.6 (d), 126.2 (d), 126.3 (d), 127.7 (d), 128.7 (d), 129.7 (d), 130.2 (d), 134.3 (s), 135.4 (s), 139.6 (s); m/z (ES) 301.1342 (M + Na$^+$, $C_{17}H_{23}ClONa$ requires 301.1335).

Activated manganese (IV) oxide (4.34g, 50.5mmol) was added portionwise over 5 mins, to a stirred solution of the *Z*-alcohol (0.70g, 2.5mmol) in dichloromethane (50ml) at room temperature, under a nitrogen atmosphere. The mixture was stirred at room temperature for 21 h, then filtered through celite with ethyl acetate (200ml) and concentrated *in vacuo*. The residue was purified by flash column chromatography (30% Et_2O, 70% petrol) on silica gel, to give the *Z*-aldehyde **69b** (0.62g, 89%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 1673, 1622; δ_H (400MHz, $CDCl_3$), 1.68 (3H, d, *J* 1.0Hz, CH=CCH_3), 1.74 (2H, m, CH_2CH_2Cl), 2.10 (2H, t, *J* 7.5Hz, CH_2CH_2CH_2Cl), 2.36 (2H, dt, *J* 7.5 and 7.0Hz, ArCH_2CH_2), 2.86 (2H, t, *J* 7.5Hz, ArCH_2), 3.45 (2H, t, *J* 6.5Hz, CH_2Cl), 5.26 (1H, app t, *J* 7.0Hz, C*H*=CCH$_3$), 6.70 (1H, dd, *J* 16.0 and 7.5Hz, ArCH=C*H*), 7.25-7.33 (2H, m, 2 x Ar*H*), 7.39 (1H, ddd, *J* 7.5, 7.0 and 1.0Hz, Ar*H*), 7.62 (1H, dd, *J* 8.0 and 1.0Hz, Ar*H*), 7.85 (1H, d, *J* 16.0Hz, ArC*H*=CH), 9.76 (1H, d, *J* 7.5Hz, C*H*O); δ_C (100MHz, $CDCl_3$), 23.2 (q), 28.7 (t), 30.0 (t), 30.6 (t), 33.5 (t), 44.6 (t), 124.9 (d), 126.8 (d), 126.9 (d), 129.6 (d), 130.5 (d,), 131.1 (d), 132.4 (s), 134.9 (s), 142.1 (s), 150.1 (d), 193.8 (d); m/z (ES) 277.1335 (M + H$^+$, $C_{17}H_{22}ClO$ requires 277.1359).

b) _E_-3 Isomer

The corresponding *E*-chloride **69b** was prepared from the *E*-ester **69a** using an identical procedure and showed: (*E*-alcohol, 85%); ν_{max}(sol $CHCl_3$)/cm^{-1}, 3609, 1601; δ_H (400MHz, $CDCl_3$), 1.52 (3H, app s, CH=CCH_3), 1.84 (2H, tt, *J* 7.5 and 7.0Hz, CH_2CH_2Cl), 2.10 (2H, t, *J* 7.5Hz, CH_2CH_2CH_2Cl), 2.26 (2H, dt, *J* 8.0 and 7.5Hz, ArCH_2CH_2), 2.70 (2H, t, *J* 8.0Hz, ArCH_2CH_2), 3.47 (2H, t, *J* 7.0Hz, CH_2Cl), 4.36 (2H, dd, *J* 5.5 and 1.5Hz, ≡C-*H*), 5.23 (1H, tq, *J* 7.5 and 1.0Hz, C*H*=CCH$_3$), 6.27 (1H, dt, *J* 15.5 and 5.5Hz, ArCH=C*H*), 6.70 (1H, dt, *J* 15.5 and 1.5Hz, ArC*H*=CH), 7.11-7.23 (3H, m, 3 x Ar*H*), 7.46 (1H, dd, *J* 7.5 and 2.0Hz, Ar*H*); δ_C (100MHz, $CDCl_3$), 15.8 (q), 28.7 (t), 29.6 (t), 32.3 (t), 36.6 (t), 44.7 (t), 63.9 (t), 124.7 (d), 126.3 (d), 126.4 (d), 127.6 (d), 129.7 (d), 130.3 (d), 130.9 (d), 134.3 (s), 135.4 (s), 139.6 (s); m/z (ES) 301.1330 (M + Na$^+$, $C_{17}H_{23}ClONa$ requires 301.1335).

(*E*-aldehyde, 87%); ν_{max}(sol $CHCl_3$)/cm^{-1}, 1674, 1621; δ_H (400MHz, $CDCl_3$), 1.49 (3H, d, *J* 0.5Hz, CH=CCH_3), 1.83 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.10 (2H, t, *J* 7.5Hz, CH_2CH_2CH_2Cl), 2.30 (2H, dt, *J* 7.5 and 7.0Hz, ArCH_2CH_2), 2.83 (2H, t, *J* 7.0Hz, ArCH_2), 3.46 (2H, t, *J* 6.5Hz, CH_2Cl), 5.22 (1H, tq, *J* 7.5 and 0.5Hz, C*H*=CCH$_3$), 6.69 (1H, dd, *J* 15.5 and 7.5Hz, ArCH=C*H*), 7.22-7.30 (2H, m, 2 x Ar*H*), 7.37 (1H, ddd, *J* 7.5, 7.0 and 1.5Hz, Ar*H*), 7.61 (1H, dd, *J* 7.5 and 1.5Hz, Ar*H*), 7.82 (1H, d, *J* 15.5Hz, ArC*H*=CH), 9.74 (1H, d, *J* 7.5Hz, C*H*O); δ_C (100MHz, $CDCl_3$), 15.8 (q), 30.0 (t), 30.6 (t), 33.3 (t), 36.6 (t), 44.5 (t), 123.9 (d), 126.8 (d), 126.9 (d), 129.7 (d), 130.5 (d), 131.0 (d), 132.4 (s), 135.0 (s), 142.1 (s),

150.1 (d), 193.8 (d); m/z (ES) 299.1195 ($M + Na^+$, $C_{17}H_{21}ClONa$ requires 299.1173).

_Z_-3 and _E_-3 Isomers of (1_E_)-1-(2-(7-Chloro-4-methylhept-3-enyl)phenyl)pent-1-en-4-yn-3-ol 70a

a) _Z_-3 Isomer

Ethynylmagnesium bromide (0.5M in THF, 0.64ml, 0.32mmol) was added dropwise over 5 min, to a stirred solution of the *Z*-aldehyde **69b** (0.06g, 0.2mmol) in tetrahydrofuran (5ml) at -78°C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature over 22 h, and then diethyl ether (5ml) and saturated aqueous ammonium chloride (5ml) were added. The separated aqueous phase was extracted with diethyl ether (3 x 25ml) and the combined organic extracts were then washed with brine (20ml), dried and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% Et_2O, 80% petrol) on silica gel, to give the *Z*-propargylic alcohol **70a** (0.064g, 98%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3594, 3305, 1601; δ_H (400MHz, $CDCl_3$), 1.44 (3H, s, CH=CC*H*$_3$), 1.79 (2H, tt, *J* 7.5 and 7.0Hz, C*H*$_2$CH$_2$Cl), 1.94 (1H, d, *J* 6.0Hz, O*H*), 2.04 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$Cl), 2.19 (2H, dt, *J* 7.5 and 7.0Hz, ArCH$_2$C*H*$_2$), 2.58 (1H, t, *J* 2.0Hz, ≡C-*H*), 2.66 (2H, t, *J* 7.5Hz, ArC*H*$_2$), 3.41 (2H, t, *J* 7.0Hz, C*H*$_2$Cl), 4.99-5.05 (1H, m, C*H*OH), 5.15 (1H, t, *J* 7.0Hz, C*H*=CCH$_3$), 6.13 (1H, dd, *J* 15.5 and 6.0Hz, ArCH=C*H*), 7.02-7.20 (4H, m, ArC*H*=CH + 3 x Ar*H*), 7.38 (1H, dd, *J* 7.0 and 1.5Hz, Ar*H*); δ_C (100MHz, $CDCl_3$), 23.2 (q), 28.9 (t), 29.5 (t), 30.7 (t), 33.6 (t), 44.8 (t), 63.0 (d), 74.6 (d), 83.2 (s), 125.5 (d), 126.2 (d), 126.4 (d), 128.1 (d), 129.0 (d), 129.8 (d), 130.0 (d), 134.3 (s), 134.5 (s), 140.0 (s); m/z (ES) 325.1355 ($M + Na^+$, $C_{19}H_{23}ClONa$ requires 325.1335).

b) _E_-3 Isomer

The corresponding *E*-alkyne **70b** was prepared from the *E*-aldehyde **69b** using an identical procedure (98%) and showed: ν_{max}(sol $CHCl_3$)/cm^{-1}, 3594, 3305, 1648; δ_H (400MHz, $CDCl_3$), 1.51 (3H, app s, CH=CC*H*$_3$), 1.59 (1H, br s, O*H*), 1.83 (2H, tt, *J* 7.5 and 6.5Hz, CH$_2$CH$_2$Cl), 2.10 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$Cl), 2.26 (2H, dt, *J* 7.5 and 7.0Hz, ArCH$_2$C*H*$_2$), 2.65 (1H, d, *J* 2.0Hz, ≡C-*H*), 2.71 (2H, t, *J* 7.5Hz, ArC*H*$_2$), 3.46 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 5.06-5.12 (1H, m, C*H*OH), 5.23 (1H, tq, *J* 7.0 and 1.0Hz, C*H*=CCH$_3$), 6.21 (1H, dd, *J* 15.5 and 6.0Hz, ArCH=C*H*), 7.07-7.25 (4H, m, ArC*H*=CH + 3 x Ar*H*), 7.47 (1H, dd, *J* 7.0 and 2.0Hz, Ar*H*); δ_C (100MHz, $CDCl_3$), 15.8 (q), 29.5 (t), 30.6 (t), 33.3 (t), 36.6 (t), 44.6 (t), 62.9 (d), 74.6 (d), 84.5 (s), 124.5 (d), 126.2 (d), 126.3 (d), 128.1 (d), 128.9 (d), 129.7 (d), 130.0 (d), 134.3 (s), 134.6 (s), 140.0 (s).

_Z_-3 and _E_-3 Isomers of (1_E_)-1-(2-(7-Chloro-4-methylhept-3-enyl)phenyl)pent-1-en-4-yn-3-one 71a

a) _Z_-3 Isomer

Activated manganese (IV) oxide (0.3g, 3.3mmol) was added portionwise over 5 mins, to a stirred solution of the *Z*-secondary alcohol **70a** (0.05g, 0.17mmol) in dichloromethane (5ml) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 18 h, then filtered through celite with dichloromethane (50ml) and warm ethyl acetate (50ml), and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% Et_2O, 80% petrol) on silica gel, to give the *Z*-acetylenic ketone **71a** (0.04g, 81%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2101, 1635, 1598; δ_H (400MHz, $CDCl_3$), 1.65 (3H, d, *J* 1.0Hz, CH=CC*H*$_3$), 1.70 (2H, tt, *J* 7.5 and 6.5Hz, C*H*$_2$CH$_2$Cl), 2.04 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$Cl), 2.32 (2H, dt, *J* 7.5 and 7.0Hz, ArCH$_2$C*H*$_2$), 2.83 (2H, t, *J* 7.5Hz, ArC*H*$_2$), 3.34 (1H, s, ≡C-*H*), 3.40 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 5.23 (1H, app t, *J* 7.0Hz, C*H*=CCH$_3$), 6.75 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.21-7.32 (2H, m, 2 x Ar*H*), 7.37 (1H, ddd, *J* 7.5, 7.0 and 1.5Hz, Ar*H*), 7.60 (1H, dd, *J* 7.5 and 1.5Hz, Ar*H*), 8.26 (1H, d, *J* 16.0Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 23.2 (q), 28.8 (t), 30.1 (t), 30.6 (t), 33.5 (t), 44.6 (t), 79.1 (d), 80.1 (s), 124.7 (d), 126.7 (d), 128.6 (d), 130.2 (d), 130.5 (d), 131.2 (d), 132.3 (s), 135.0 (s), 142.6 (s), 147.2 (d), 177.6 (s); m/z (ES) 301.1367 ($M + H^+$, $C_{19}H_{22}ClO$ requires 301.1359).

b) _E_-3 Isomer

The corresponding *E*-ketone **71a** was prepared from the *E*-alcohol **70a** using an identical procedure (86%) and showed: ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2101, 1635, 1598; δ_H (400MHz, $CDCl_3$), 1.51 (3H, app s, CH=CC*H3*), 1.83 (2H, m, C*H*$_2$CH$_2$Cl), 2.12 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$Cl), 2.32 (2H, dt, *J* 7.5 and 7.0Hz, ArCH$_2$C*H*$_2$), 2.86 (2H, t, *J* 7.0Hz, ArC*H*$_2$), 3.35 (1H, s, ≡C-*H*), 3.47 (2H, t, *J* 6.5Hz, C*H*$_2$Cl), 5.24 (1H, tq, *J* 7.5 and 1.0Hz, C*H*=CCH$_3$), 6.77 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.21-7.31 (2H, m, 2 x Ar*H*), 7.39 (1H, ddd, *J* 7.5, 7.0 and 1.0Hz, Ar*H*), 7.62 (1H, dd, *J* 7.5 and 1.0Hz, Ar*H*), 8.28 (1H, d, *J* 16.0Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 15.8 (q), 30.2 (t), 30.6 (t), 33.4 (t), 36.6 (t), 44.5 (t), 79.1 (d), 80.9 (s), 123.9 (d), 126.8 (d), 128.8 (d), 130.6 (d), 131.0 (d), 131.2 (d), 132.6 (s), 134.9 (s), 142.3 (s), 147.2 (d), 172.9 (s); m/z (ES) 323.1173 ($M + Na^+$, $C_{19}H_{21}ClONa$ requires 323.1173).

_Z_-3 and _E_-3 Isomers of (1_E_)-1-(2-((7-Iodo-4-methylhept-3-enyl)phenyl)pent-1-en-4-yn-3-one 73a

a) _Z_-3 Isomer

Sodium iodide (220mg, 1.5mmol) was added in one portion, to a stirred solution of the *Z*-3 isomer of the chloride **71a** (115mg, 0.38mmol) and potassium carbonate (2mg, 0.01mmol) in 2-butanone (6ml) at room temperature under a nitrogen atmosphere. The mixture was heated under reflux for 24 h, then cooled to room temperature and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% Et_2O, 90% petrol) on silica gel to give the iodide **73a** (0.129g, 87%) as a yellow oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2102, 1635, 1598; δ_H (400MHz, $CDCl_3$), 1.64 (3H, s, CH=CC*H*$_3$), 1.74 (2H, tt, *J* 7.5 and 7.0Hz, C*H*$_2$CH$_2$I), 1.97 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$I), 2.33 (2H, dt, *J* 7.5 and 7.5Hz, ArCH$_2$C*H*$_2$), 2.84 (2H, t, *J* 7.5Hz, ArC*H*$_2$), 3.04 (2H, t, *J* 7.0Hz, C*H*$_2$I), 3.34 (1H, s, ≡C-*H*), 5.22 (1H, t, *J* 7.5Hz, C*H*=CCH$_3$), 6.75 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.22-7.29 (2H, m, 2 x Ar*H*), 7.37 (1H, ddd, *J* 7.5, 7.0 and 1.5Hz, Ar*H*), 7.60 (1H, dd, *J* 7.5 and 1.5Hz, Ar*H*), 8.26 (1H, d, *J* 16.0Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 6.5 (t), 23.3 (q), 30.2, (t), 31.7 (t), 32.4 (t), 33.6 (t), 79.2 (d), 80.2 (s), 124.8 (d), 126.8 (d), 126.9 (d), 128.7 (d), 130.6 (d), 131.2 (d), 132.3 (s), 134.9 (s), 142.6 (s), 147.3 (d), 177.7 (s); m/z (ES) 393.0742 ($M + H^+$, $C_{19}H_{22}IO$ requires 393.0715).

b) _E_-3 Isomer

The corresponding *E*-iodide **72a** was prepared from the *E*-chloride **71a** using an identical procedure (89%) and showed: (Found C, 58.3; H, 5.3%. $C_{19}H_{21}IO$ requires C, 58.2; H, 5.4%); ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2102, 1635, 1598; δ_H (400MHz, $CDCl_3$), 1.40 (3H, app s, C*H*=CCH$_3$), 1.74-1.83 (2H, m, C*H*$_2$CH$_2$I), 2.00 (2H, t, *J* 7.5Hz, C*H*$_2$CH$_2$CH$_2$I), 2.23 (2H, dt, *J* 7.5 and 7.0Hz, ArCH$_2$C*H*$_2$), 2.79 (2H, t, *J* 7.0Hz, ArC*H*$_2$), 3.02 (2H, t, *J* 7.0Hz, C*H*$_2$I), 3.26 (1H, s, ≡C-*H*), 5.15 (1H, tq, *J* 7.5 and 1.0Hz, C*H*=CCH$_3$), 6.68 (1H, d, *J* 16.0Hz, ArCH=C*H*), 7.15-7.21 (2H, m, 2 x Ar*H*), 7.29 (1H, ddd, *J* 7.5, 7.0, 1.0Hz, Ar*H*), 7.53 (1H, dd, *J* 7.5 and 1.0Hz, Ar*H*), 8.18 (1H, d, *J* 16.0Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 6.6 (t), 15.8 (q), 30.2, (t), 31.4 (t), 33.4 (t), 40.0 (t), 79.2 (d), 80.1 (s), 124.1 (d), 126.7 (d), 126.8 (d), 128.8 (d), 130.5 (d), 131.2 (d), 132.2 (s), 134.6 (s), 142.6 (s), 147.2 (d), 177.7 (s); m/z (ES) 415.0563 ($M + Na^+$, $C_{19}H_{21}IONa$ requires 415.0537).

_Z_-3 and _E_-3 Isomers of (2_E_)-Ethyl 3-(2-((7-(2,2-dimethyl-1,1-diphenylpropoxy)-4-methylhept-3-enyl)-4-methoxyphenyl)acrylate 68c

Sodium hexamethyldisilazane (2.0M in THF, 9.0ml, 18mmol) was added dropwise over 10 min, to a stirred solution of the sulfone **66** (8.25g, 16.0mmol) and the aldehyde **67b** (3.75g, 14mmol)[5] in tetrahydrofuran (50ml) at -78°C, under a nitrogen atmosphere. The yellow mixture was stirred at -78°C for 3 h and then allowed to warm to room temperature over 12 h. Saturated aqueous ammonium chloride (30ml) was added, and the separated aqueous phase was then extracted with diethyl ether (3 x 50ml). The combined organic extracts were dried and concentrated *in vacuo*. The residue was purified by flash colomn chromatography (5% EtOAc, 95% petrol) on silica gel, to give a 2:3 mixture of *Z* and *E* isomers of the alkene **67c** (3.30g, 55%) as a colourless oil ν_{max}(sol $CHCl_3$)/cm^{-1}, 1706, 1631; δ_H (400MHz, $CDCl_3$), 1.02, 1.07 (9H, 2 x s, SiC(C*H*$_3$)$_3$), 1.31 (3H, 2 x t, *J* 7.0Hz,

OCH_2CH_3), 1.48-1.69 (5H, m, $CH{=}CCH_3$ + $CH_2CH_2OTBDPS$), 2.02 (2H, 2 x t, *J* 6.0Hz, $CH_2CH_2CH_2OTBDPS$), 2.17-2.29 (2H, m, $ArCH_2CH_2$), 2.72 (2H, 2 x t, *J* 7.0Hz, $ArCH_2$), 3.61 (2H, 2 x t, J 6.5Hz, $CH_2OTBDPS$), 3.81 (3H, 2 x s, OCH_3), 4.24 (2H, 2 x q, *J* 7.0Hz, OCH_2CH_3), 5.16 (1H, 2 x tq, *J* 7.0 and 1.0Hz, $CH{=}CCH_3$), 6.26 (1H, 2 x d, *J* 16.0Hz, ArCH=CH), 6.73-6.78 (3H, m, 3 x ArH), 7.32-7.45 (6H, m, 6 x ArH), 7.53 (1H, 2 x d, *J* 8.5Hz, ArH), 7.62-7.84 (4H, m, 4 x ArH), 7.95 (1H, 2 x d, *J* 16.0Hz, ArCH=CH); δ_C (100MHz, $CDCl_3$), 14.4 (q), 16.0 (t), 19.2 (s), 19.3 (s), 23.4 (q), 26.8 (q), 26.9 (q), 28.1 (t), 29.7 (t), 30.0 (t), 31.0 (q), 33.7 (t), 33.8 (t), 35.8 (t), 55.3 (q), 55.4 (q), 60.3 (t), 60.4 (t), 63.7 (t), 63.8 (t), 112.2 (d), 112.3 (d), 115.1 (d), 115.2 (d), 116.7 (d), 116.8 (d), 122.9 (d), 123.9 (d), 125.5 (s), 125.6 (s), 127.6 (2C d), 127.7 (2C d), 128.0 (d), 128.1 (d), 129.5 (d), 1297 (d), 134.1 (s), 134.2 (s), 135.6 (2C d), 135.7 (2C d), 136.2 (s), 136.3 (s), 141.7 (d), 141.8 (d), 144.0 (s), 144.1 (s), 161.0 (s), 161.1 (s), 167.4 (s), 167.5 (s).

_Z_-3 and _E_-3 Isomers of (2_E_)-Ethyl 3-(2-((7-hydroxy-4-methylhept-3-enyl)-4-methoxyphenyl)acrylate 68d

A solution of tetra-*n*-butylammonium fluoride (0.090g, 0.30mmol) in tetrahydrofuran (1.5ml) was added dropwise over 10 min, to a stirred solution of the silyl ether **68c** (0.130g, 0.2mmol) in tetrahydrofuran (2ml) at 0°C, under a nitrogen atmosphere. The pink solution was allowed to warm to room temperature over 3 h and then diethyl ether (5ml) and water (5ml) were added at 0°C. The separated aqueous phase was extracted with diethyl ether (3 x 25ml) and the combined organic extracts were then dried and concentrated *in vacuo*. The residue was purified by flash column chromatography (35% Et_2O, 65% petrol) on silica gel, to give i) the *Z*-3 isomer of the alcohol (0.024g, 32%)(eluted first) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3623, 3513, 1699, 1629; δ_H (400MHz, $CDCl_3$), 1.33 (3H, t, *J* 7.0Hz, OCH_2CH_3), 1.62 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2OH), 1.70 (3H, s, $CH{=}CCH_3$), 2.08 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2OH$), 2.25 (2H, dt, *J* 8.0 and 7.0Hz, $ArCH_2CH_2$), 2.74 (2H, t, *J* 8.0Hz, $ArCH_2$), 3.59 (2H, t, *J* 6.5Hz, CH_2OH), 3.82 (3H, s, OCH_3), 4.25 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.23 (1H, t, *J* 7.0Hz, $CH{=}CCH_3$), 6.28 (1H, d, *J* 16.0Hz, ArCH=CH), 6.72 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.76 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.55 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 8.00 (1H, d, *J* 16.0Hz, ArCH=CH); δ_C (100MHz, $CDCl_3$), 14.3 (q), 23.3 (q), 27.9 (t), 30.4 (t), 31.0 (t), 34.2 (t), 55.3 (q), 60.5 (t), 62.5 (t), 112.3 (d), 115.2 (d), 116.4 (d), 124.2 (d), 125.4 (s), 127.9 (d), 136.0 (s), 142.0 (d), 144.2 (s), 161.1 (s); m/z (ES) 355.1880 ($M + Na^+$, $C_{20}H_{28}O_4Na$ requires 355.1880); and ii) the *E*-3 isomer of the alcohol (0.028g, 37%)(eluted second) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3621, 1700, 1630; δ_H (400MHz, $CDCl_3$), 1.33 (3H, t, *J* 7.0Hz, OCH_2CH_3), 1.53 (3H, s, $CH{=}CCH_3$), 1.64 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2OH), 2.03 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2OH$), 2.26 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.76 (2H, t, *J* 7.5Hz, $ArCH_2$), 3.59 (2H, t, *J* 6.5Hz, CH_2OH), 3.82 (3H, s, OCH_3), 4.25 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.21 (1H, t, *J* 7.0Hz, $CH{=}CCH_3$), 6.27 (1H, d, *J* 16.0Hz, ArCH=CH), 6.71 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.76 (1H, dd, *J* 9.0 and 2.5Hz, $CH_3OCCHCH$), 7.54 (1H, d, *J* 9.0Hz, $CH_3OCCHCH$), 7.95 (1H, d, *J* 16.0Hz, ArCH=CH); δ_C (100MHz, $CDCl_3$), 14.3 (q), 15.8 (q), 29.8 (t), 30.6 (t), 33.5 (t), 35.8 (t), 55.2 (q), 60.3 (t), 62.6 (t), 112.1 (d), 115.2 (d), 116.7 (d), 123.2 (d), 125.6 (s), 128.0 (d), 136.0 (s), 141.7 (d), 143.9 (s), 160.9 (s), 167.4 (s); m/z (ES) 355.1880 ($M + Na^+$, $C_{20}H_{28}O_4Na$ requires 355.1880).

_Z_-3 and _E_-3 Isomers of (2_E_)-Ethyl 3-(2-(7-chloro-4-methylhept-3-enyl)-4-methoxyphenyl)acrylate 69c

a) _Z_-3 Isomer

N-Chlorosuccinimide (0.80g, 6.0mmol) was added in one portion, to a stirred solution of the *Z*-alcohol **68d** (1.40g, 4.3mmol), triphenylphosphine (1.45g, 5.6mmol) and potassium carbonate (0.12g, 0.9mmol) in dichloromethane (50ml) at 0°C, under a nitrogen atmosphere. The solution was stirred at 0°C for 4 h and then concentrated *in vacuo*. The residue was purified by flash column chromatography (15% Et_2O, 85% petrol) on silica gel, to give the chloride **69c** (1.34g, 90%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 1703, 1630; δ_H (400MHz, $CDCl_3$), 1.33 (3H,

t, *J* 7.0Hz, OCH_2CH_3), 1.66 (3H, d, *J* 1.0Hz, $CH=CCH_3$), 1.73 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.08 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.27 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.76 (2H, t, *J* 7.5Hz, $ArCH_2$), 3.43 (2H, t, *J* 6.5Hz, CH_2Cl), 3.82 (3H, s, OCH_3), 4.26 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.24 (1H, app t, *J* 7.0Hz, $CH=CCH_3$), 6.27 (1H, d, *J* 16.0Hz, ArCH=CH), 6.73 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.77 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.54 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 7.95 (1H, d, *J* 16.0Hz, ArCH=CH); δ_C (100MHz, $CDCl_3$), 14.4 (q), 23.2 (q), 28.8 (t), 29.9 (t), 30.7 (t), 33.7 (t), 44.7 (t), 55.3 (q), 60.3 (t), 112.3 (d), 115.2 (d), 116.8 (d), 125.1 (d), 125.9 (s), 128.1 (d), 134.7 (s), 141.6 (d), 143.8 (s), 161.0 (s), 167.4 (s); m/z (ES) 351.1713 ($M + H^+$, $C_{20}H_{28}ClO_3$ requires 351.1721).

b) *E*-3 Isomer

The corresponding *E*-chloride **69c** was prepared from the *E*-alcohol **68d** using an identical procedure (91%) and showed: ν_{max}(sol $CHCl_3$)/cm^{-1}, 1698, 1631; δ_H (400MHz, $CDCl_3$), 1.33 (3H, t, *J* 7.0Hz, OCH_2CH_3), 1.52 (3H, d, *J* 1.0Hz, $CH=CCH_3$), 1.83 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.09 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.27 (2H, dt, *J* 8.0 and 7.5Hz, $ArCH_2CH_2$), 2.76 (2H, t, *J* 8.0Hz, $ArCH_2$), 3.46 (2H, t, *J* 6.5Hz, CH_2Cl), 3.82 (3H, s, OCH_3), 4.26 (2H, q, *J* 7.0Hz, OCH_2CH_3), 5.21 (1H, tq, *J* 7.5 and 1.0Hz, $CH=CCH_3$), 6.27 (1H, d, *J* 16.0Hz, ArCH=CH), 6.72 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.77 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.55 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 7.96 (1H, d, *J* 16.0Hz, ArCH=CH); δ_C (100MHz, $CDCl_3$), 14.4 (q), 15.8 (q), 29.9 (t), 30.7 (t), 33.5 (t), 36.6 (t), 44.6 (t), 55.3 (q), 60.3 (t), 112.2 (d), 115.3 (d), 116.8 (d), 124.1 (d), 125.6 (s), 128.0 (d), 134.7 (s), 144.6 (d), 143.8 (s), 161.0 (s), 167.4 (s); m/z (ES) 351.1720 ($M + H^+$, $C_{20}H_{28}ClO_3$ requires 351.1721).

_Z_-3 and _E_-3 Isomers of (2_E_)-3-(2-(7-Chloro-4-methylhept-3-enyl)-4-methoxyphenyl)acrylaldehyde 69d

a) _Z_-3 isomer

Diisobutylaluminium hydride (1.0M in hexanes, 3.5ml, 3.50mmol) was added dropwise over 10 min, to a stirred solution of the ester **69c** (0.58g, 1.65mmol) in dichloromethane (30ml) at -78°C under a nitrogen atmosphere. The mixture was stirred at -78°C for 3 h and then saturated aqueous Rochelle's salt (30ml) was added at 0°C. The separated aqueous phase was extracted with dichloromethane (3 x 50ml) and the combined organic extracts were dried and then concentrated *in vacuo*. The residue was purified by flash column chromatography (30% Et_2O, 70% petrol) on silica gel, to give the corresponding alcohol (0.47g, 92%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3610, 1607; δ_H (400MHz, $CDCl_3$), 1.68 (3H, s, $CH=CCH_3$), 1.76 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.11 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.26 (2H, dt, *J* 8.0 and 7.0Hz, $ArCH_2CH_2$), 2.67 (2H, t, *J* 8.0Hz, $ArCH_2$), 3.45 (2H, t, *J* 6.5Hz, CH_2Cl), 3.80 (3H, s, OCH_3), 4.32 (2H, dd, *J* 6.0 and 1.5Hz, CH_2OH), 5.25 (1H, app t, *J* 7.0Hz, $CH=CCH_3$), 6.17 (1H, dt, *J* 15.5 and 6.0Hz, ArCH=CH), 6.69 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.74 (1H, dd, *J* 8.0 and 2.5Hz, $CH_3OCCHCH$), 6.80 (1H, app d, *J* 15.5Hz, ArCH=CH), 7.41 (1H, d, *J* 8.0Hz, $CH_3OCCHCH$); δ_C (100MHz, $CDCl_3$), 23.2 (q), 28.8 (t), 29.3 (t), 30.7 (t), 33.8 (t), 44.8 (t), 55.2 (q), 64.1 (t), 111.8 (d), 114.9 (d), 125.5 (d), 127.2 (d), 128.0 (s), 128.1 (d), 128.4 (d), 134.3 (s), 141.1 (s), 159.1 (s); m/z (ES) 291.1507 (M^+ - OH, $C_{18}H_{24}ClO$ requires 291.1510).

Activated manganese (IV) oxide (5.80g, 66.7mmol) was added portionwise over 5 mins, to a stirred solution of the above alcohol (1.03g, 3.34mmol) in dichloromethane (50ml) at room temperature, under a nitrogen atmosphere. The solution was stirred at room temperature for 20 h and then filtered through celite with ethyl acetate (200ml) and concentrated *in vacuo*. The residue was purified by flash column chromatography (40% Et_2O, 60% petrol) on silica gel, to leave the *Z*-aldehyde **69d** (0.83g, 81%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 1671, 1598; δ_H (400MHz, $CDCl_3$), 1.67 (3H, s, $CH=CCH_3$), 1.74 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.09 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.31 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.80 (2H, t, *J* 7.0Hz, $ArCH_2$), 3.43 (2H, t, *J* 6.5Hz, CH_2Cl), 3.85 (3H, s, OCH_3), 5.24 (1H, app t, *J* 7.5Hz, $CH=CCH_3$), 6.60 (1H, dd, *J* 16.0 and 8.0Hz, ArCH=CH), 6.77 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.81 (1H, dd, *J* 8.0 and 2.5Hz,

$CH_3OCCHCH$), 7.60 (1H, d, *J* 8.0Hz, $CH_3OCCHCH$), 7.73 (1H, d, *J* 16.0Hz, $ArCH$=CH), 9.68 (1H, d, *J* 8.0Hz, CHO); δ_C (100MHz, $CDCl_3$), 23.2 (q), 28.7 (t), 29.9 (t), 30.5 (t), 33.6 (t), 44.6 (t), 55.4 (q), 112.6 (d), 115.5 (d), 124.8 (d), 124.9 (s), 127.4 (d), 128.7 (d), 135.0 (s), 144.4 (s), 149.8 (d), 161.9 (s), 193.8 (s); m/z (ES) 329.1280 ($M + Na^+$, $C_{18}H_{23}ClO_2Na$ requires 329.1279).

b) *E*-3 Isomer

The corresponding *E*-aldehyde **69d** was prepared from the *E*-ester **69c** using an identical procedure and showed: (*E*-alcohol, 87%); ν_{max}(sol $CHCl_3$)/cm^{-1}, 3610, 1607; δ_H (400MHz, $CDCl_3$), 1.53 (3H, app s, CH=CCH_3), 1.84 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.11 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.26 (2H, dt, *J* 8.0 and 7.5Hz, $ArCH_2CH_2$), 2.67 (2H, t, *J* 8.0Hz, $ArCH_2$), 3.47 (2H, t, *J* 6.5Hz, CH_2Cl), 3.80 (3H, s, OCH_3), 4.33 (2H, dd, *J* 6.0 and 1.5Hz, CH_2OH), 5.23 (1H, tq, *J* 7.5 and 1.0Hz, CH=CCH_3), 6.17 (1H, dt, *J* 15.5 and 6.0Hz, ArCH=C*H*), 6.68 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.74 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 6.81 (1H, app d, *J* 15.5Hz, $ArCH$=CH), 7.41 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$); δ_C (100MHz, $CDCl_3$), 15.8 (q), 29.3 (t), 30.7 (t), 33.5 (t), 36.7 (t), 44.6 (t), 55.2 (q), 64.2 (t), 111.7 (d), 114.9 (d), 124.6 (d), 127.2 (d), 128.0 (d), 128.1 (s), 128.6 (d), 134.3 (s), 141.1 (s), 159.1 (s); m/z (ES) 331.1422 ($M + Na^+$, $C_{18}H_{25}ClO_2Na$ requires 331.1441).

(*E*-aldehyde, 81%); ν_{max}(sol $CHCl_3$)/cm^{-1}, 1671, 1595; δ_H (400MHz, $CDCl_3$), 1.51 (3H, app s, CH=CCH_3), 1.83 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.11 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.30 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.80 (2H, t, *J* 7.0Hz, $ArCH_2$), 3.46 (2H, t, *J* 6.5Hz, CH_2Cl), 3.85 (3H, s, OCH_3), 5.22 (1H, tq, *J* 7.5 and 1.0Hz, CH=CCH_3), 6.61 (1H, dd, *J* 15.5 and 7.5Hz, ArCH=C*H*), 6.76 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.81 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.60 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 7.73 (1H, d, *J* 15.5Hz, $ArCH$=CH), 9.68 (1H, d, *J* 7.5Hz, CHO); δ_C (100MHz, $CDCl_3$), 15.8 (q), 29.9 (t), 30.6 (t), 33.4 (t), 36.6 (t), 44.5 (t), 55.4 (q), 112.4 (d), 115.6 (d), 123.9 (d), 125.0 (s), 127.4 (d), 128.6 (d), 128.7 (s), 144.4 (s), 149.8 (d), 161.9 (s), 193.8 (s); m/z (ES) 329.1297 ($M + Na^+$, $C_{18}H_{23}ClO_2Na$ requires 329.1279).

***Z*-3 and *E*-3 Isomers of (1*E*)-1-(2-(7-Chloro-4-methylhept-3-enyl)-4-methoxyphenyl)pent-1-en-4-yn-3-ol 70b**

a) *Z*-3 isomer

Ethynylmagnesium bromide (0.5M in THF, 7.8ml, 3.9mmol) was added dropwise over 5 min, to a stirred solution of the aldehyde **69d** (0.80g, 2.6mmol) in tetrahydrofuran (45ml) at -78°C, under a nitrogen atmosphere. The mixture was allowed to warm to room temperature over 20 h, and then diethyl ether (30ml) and saturated aqueous ammonium chloride (50ml) were added at room temperature. The separated aqueous phase was extracted with diethyl ether (3 x 80ml) and the combined organic extracts were then washed with brine (20ml), dried and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% Et_2O, 80% petrol) on silica gel, to give the alkyne **70b** (0.86g, 99%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3593, 3305, 1606; δ_H (400MHz, $CDCl_3$), 1.68 (3H, d, *J* 1.0Hz, CH= CCH_3), 1.75 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.00 (1H, d, *J* 6.5Hz, OH), 2.10 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.27 (2H, dt, *J* 8.0 and 7.5Hz, $ArCH_2CH_2$), 2.64 (1H, d, *J* 2.0Hz, ≡C-*H*), 2.68 (2H, t, *J* 8.0Hz, $ArCH_2$), 3.45 (2H, t, *J* 6.5Hz, CH_2Cl), 3.80 (3H, s, OCH_3), 5.04-5.09 (1H, m, HOC*H*), 5.25 (1H, app t, *J* 7.5Hz, CH=CCH_3), 6.11 (1H, dd, *J* 15.5 and 6.0Hz, ArCH=C*H*), 6.70 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.74 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.02 (1H, d, *J* 15.5Hz, $ArCH$=CH), 7.42 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$); δ_C (100MHz, $CDCl_3$), 23.2 (q), 29.4 (t), 30.7 (t), 33.8 (t), 35.2 (t), 44.8 (t), 55.2 (q), 63.1 (d), 77.2 (d), 83.0 (s), 108.1 (d), 115.0 (d), 124.6 (d), 126.9 (d), 127.2 (s), 127.4 (d), 129.6 (d), 134.4 (s), 145.0 (s), 159.5 (s); m/z (ES) 355.1434 ($M + Na^+$, $C_{20}H_{25}ClO_2Na$ requires 355.1441).

b) *E*-3 Isomer

The corresponding *E*-alkyne **70b** was prepared from the *E*-aldehyde **69d** using an identical procedure (93%) and showed: ν_{max}(sol $CHCl_3$)/cm^{-1}, 3591, 3305, 1608; δ_H (400MHz, $CDCl_3$), 1.53 (3H, app s, CH=CCH_3), 1.84 (2H, tt, *J* 7.5 and 7.0Hz, CH_2CH_2Cl), 2.01 (1H, d, *J* 6.5Hz, OH), 2.11 (2H, t, *J* 7.0Hz, $CH_2CH_2CH_2Cl$), 2.27

(2H, dt, *J* 8.0 and 7.5Hz, $ArCH_2CH_2$), 2.64 (1H, d, *J* 2.0Hz, ≡C-*H*), 2.69 (2H, t, *J* 8.0Hz, $ArCH_2$), 3.46 (2H, t, *J* 7.5Hz, CH_2Cl), 3.80 (3H, s, OCH_3), 5.03-5.09 (1H, m, C*H*OH), 5.22 (1H, tq, *J* 7.5 and 1.0Hz, C*H*=CCH_3), 6.11 (1H, dd, *J* 15.5 and 6.0Hz, ArCH=C*H*), 6.69 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.74 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.02 (1H, d, *J* 15.5Hz, ArC*H*=CH), 7.42 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$); δ_C (100MHz, $CDCl_3$), 15.8 (q), 29.4 (t), 30.7 (t), 33.5 (t), 36.6 (t), 44.6 (t), 55.2 (q), 63.1 (d), 74.5 (d), 83.0 (s), 111.8 (d), 115.0 (d), 124.5 (d), 126.9 (d), 127.2 (s), 127.4 (d), 129.6 (d), 134.3 (s), 141.6 (s), 159.5 (s); m/z (ES) 355.1423 ($M + Na^+$, $C_{20}H_{25}ClO_2Na$ requires 355.1441).

_Z_-3 and _E_-3 Isomers of (1_E_)-1-(2-(7-Chloro-4-methylhept-3-enyl)-4-methoxyphenyl)pent-1-en-4-yn-3-one 71b

a) _Z_-3 Isomer

Activated manganese (IV) oxide (4.34g, 49.9mmol) was added portionwise over 5 mins, to a stirred solution of the *Z*-alcohol **70b** (0.83g, 2.5mmol) in dichloromethane (45ml) at room temperature, under a nitrogen atmosphere. The solution was stirred at room temperature for 23 h, then filtered through celite with dichloromethane (50ml) and warm ethyl acetate, (100ml) and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% Et_2O, 80% petrol) on silica gel, to give the ketone **71b** (0.04g, 86%) as a colourless oil; ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2101, 1630, 1596; δ_H (400MHz, $CDCl_3$), 1.66 (3H, d, *J* 1.0Hz, CH=CCH_3), 1.72 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.06 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.32 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.81 (2H, t, *J* 7.0Hz, $ArCH_2$), 3.30 (1H, s, ≡C-H), 3.42 (2H, t, *J* 6.5Hz, CH_2Cl), 3.85 (3H, s, OCH_3), 5.24 (1H, app t, *J* 7.5Hz, C*H*=CCH_3), 6.67 (1H, d, *J* 16.0Hz, ArCH=C*H*), 6.77 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.80 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.60 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 8.20 (1H, d, *J* 16.0Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 23.3 (q), 28.8 (t), 30.1 (t), 30.7 (t), 33.8 (t), 44.7 (t), 55.4 (q), 78.7 (d), 80.3 (s), 112.7 (d), 115.6 (d), 124.7 (d), 124.9 (s), 126.4 (d), 128.6 (d), 135.0 (s), 145.1 (s), 147.0 (d), 162.1 (s), 177.6 (s); m/z (ES) 331.1433 ($M + H^+$, $C_{20}H_{24}ClO_2$ requires 331.1459).

b) _E_-3 Isomer

The corresponding *E*-ketone **71b** was prepared from the *E*-alcohol **70b** using an identical procedure (88%) and showed: ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2101, 1631, 1594; δ_H (400MHz, $CDCl_3$), 1.51 (3H, app s, CH=CCH_3), 1.83 (2H, tt, *J* 7.5 and 6.5Hz, CH_2CH_2Cl), 2.10 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2Cl$), 2.31 (2H, dt, *J* 7.5 and 7.0Hz, ArCH2C*H*2), 2.81 (2H, t, *J* 7.0Hz, $ArCH_2$), 3.20 (3H, s, ≡C-H), 3.45 (2H, t, *J* 6.5Hz, CH_2Cl), 3.85 (3H, s, OCH_3), 5.22 (1H, tq, *J* 7.5 and 1.0Hz, C*H*=CCH_3), 6.68 (1H, d, *J* 15.5Hz, ArCH=C*H*), 6.76 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.80 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.60 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 8.21 (1H, d, *J* 15.5Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 15.8 (q), 30.1 (t), 30.6 (t), 33.6 (t), 36.6 (t), 44.4 (t), 55.4 (q), 78.7 (d), 80.2 (s), 112.5 (d), 115.6 (d), 123.9 (d), 124.8 (s), 126.4 (d), 128.6 (d), 134.9 (s), 145.1 (s), 146.9 (d), 162.1 (s), 177.6 (s); m/z (ES) 331.1456 ($M + H^+$, $C_{20}H_{24}ClO_2$ requires 331.1459).

_Z_-3 and _E_-3 Isomers of (1_E_)-1-(2-((7-Iodo-4-methylhept-3-enyl)-4-methoxyphenyl)pent-1-en-4-yn-3-one 73b

a) _Z_-3 Isomer

Sodium iodide (270mg, 1.8mmol) was added in one portion, to a stirred solution of the Z-3 isomer of the chloride **71b** (115mg, 0.34mmol) and potassium carbonate (3mg, 0.02mmol) in 2-butanone (6ml) at room temperature under a nitrogen atmosphere. The mixture was heated under reflux for 23 h, then cooled to room temperature and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% Et_2O, 90% petrol) on silica gel, to give the iodide **73b** (0.135g, 92%) as a yellow solid; m.p = 80-81°C (Petrol); ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2101, 1631, 1596; δ_H (400MHz, $CDCl_3$), 1.65 (3H, d, J 1.0Hz, CH=CCH_3), 1.76 (2H, tt, *J* 7.5 and 7.0Hz, CH_2CH_2I), 2.00 (2H, t, *J* 7.5Hz, $CH_2CH_2CH_2I$), 2.34 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.82 (2H, t, *J* 7.0Hz, $ArCH_2$), 3.05 (2H, t, *J* 7.0Hz, CH_2I), 3.30 (1H, s, ≡C-*H*), 3.85 (3H, s, OCH_3), 5.23 (1H, app t, *J* 7.5Hz, C*H*=CCH_3), 6.68 (1H, d, *J* 16.0Hz, ArCH=C*H*), 6.78 (1H, d, *J* 2.5Hz,

CH_3OCCHC), 6.81 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.60 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 8.20 (1H, d, *J* 16.0Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 6.5 (t), 23.2 (q), 30.2, (t), 31.7 (t), 32.4 (t), 33.7 (t), 55.5 (q), 78.8 (d), 80.3 (s), 112.7 (d), 115.7 (d), 124.8 (d), 124.9 (s), 126.4 (d), 128.7 (d), 134.9 (s), 145.0 (s), 147.0 (d), 162.1 (s), 180.1 (s); m/z (ES) 445.0610 ($M + Na^+$, $C_{20}H_{23}IO_2Na$ requires 445.0640).

b) *E*-3 Isomer

The corresponding *E*-iodide **72b** was prepared from the *E*-chloride **71b** using an identical procedure (95%) and showed a yellow oil: ν_{max}(sol $CHCl_3$)/cm^{-1}, 3297, 2101, 1634, 1592; δ_H (400MHz, $CDCl_3$), 1.50 (3H, app s, CH=CCH_3), 1.87 (2H, tt, *J* 7.5 and 7.0Hz, CH_2CH_2I), 2.05 (2H, t, *J* 7.0Hz, C$H_2CH_2CH_2I$), 2.30 (2H, dt, *J* 7.5 and 7.0Hz, $ArCH_2CH_2$), 2.81 (2H, t, *J* 7.0Hz, ArCH_2), 3.09 (2H, t, *J* 7.5Hz, CH_2I), 3.30 (1H, s, ≡C-H), 3.85 (3H, s, OCH_3), 5.24 (1H, tq, *J* 7.5 and 1.0Hz, C*H*=CCH_3), 6.68 (1H, d, *J* 16.0Hz, ArCH=C*H*), 6.76 (1H, d, *J* 2.5Hz, CH_3OCCHC), 6.80 (1H, dd, *J* 8.5 and 2.5Hz, $CH_3OCCHCH$), 7.60 (1H, d, *J* 8.5Hz, $CH_3OCCHCH$), 8.20 (1H, d, *J* 16.0Hz, ArC*H*=CH); δ_C (100MHz, $CDCl_3$), 6.5 (t), 15.8 (q), 30.1, (t), 31.4 (t), 33.5 (t), 40.0 (t), 55.4 (q), 78.8 (d), 80.2 (s), 112.5 (d), 115.6 (d), 124.1 (d), 124.8 (s), 126.4 (d), 128.6 (d), 134.6 (s), 145.0 (s), 146.9 (d), 162.1 (s), 177.6 (s); m/z (ES) 445.0629 ($M + Na^+$, $C_{20}H_{23}IO_2Na$ requires 445.0640).

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