Supporting Information

[3-(2,2-Dimethyl-[1,3]dioxolane-4-yl)-hex-3-ene-1,5-diynyl]trimethylsilane (3): To a solution of **2** (47 mg, 0.2 mmol) in DCM (1 mL) was added Et_3N (74 µl, 0.5 mmol) and DMAP (86 mg, 0.7 mmol) at 0 ^oC and the reaction was stirred for 30 min. Methanesulfonyl chloride (21 µl, 0.3 mmol) was then added. Stirring was continued for 1.5 h at rt and the reaction quenched with a saturated aqueous solution of $NaHCO_3$ (2 mL). The resulting mixture extracted with DCM (3 x 2 mL), washed with brine (6 mL), dried over magnesium sulphate, filtered and concentrated *in vacuo*. Column chromatography eluting with Et_2O (7%)/PE afforded the inseparable diastereoisomeric enediynes **3** (17 mg, *E*:*Z* 5:3, 38%) as a clear yellow oil. ν_{max} (film)/cm^{-1} 3299, 3054, 2305, 1265; ^1H NMR (300 MHz, $CDCl_3$) δ_H 6.15 (d, 1H *J* 2.5, **minor**), 5.98 (d, 1H, *J* 2.5, **major**), 5.43 (t, 1H, *J* 7.0, **major**), 4.40 (t, 1H, *J* 7.0, **minor**), 4.10-3.91 (m, 2H), 3.09 (d, 1H, *J* 2.5, **minor**), 3.00 (d, 1H, *J* 2.5, **major**), 1.68 (s, 3H, **major**), 1.46 (s, 3H, **major**), 1.45 (s, 3H, **minor**), 1.35 (s, 3H, **minor**), 0.28 (s, 9H); ^{13}C (75MHz, $CDCl_3$) δ_C 137.3 (C, **major**), 136.1 (C, **minor**), 126.4 (C, **minor**), 118.1 (CH, **major**), 115.8 (CH, **minor**), 110.8 (C, **major**), 104.0 (C, **major**), 101.9 (C, **minor**), 89.2 (CH, **major**), 85.5 (CH, **minor**), 81.3 (C, **minor**), 79.4 (C, **major**), 77.8 (CH, **minor**), 75.3 (CH, **major**), 69.5 (CH_2, **minor**), 68.6 (CH_2, **major**), 30.5 (C), 27.0 (CH_3, **major**), 26.7 (CH_3, **major**), 26.6 (CH_3, **minor**), 26.2 (CH_3, **minor**), 0.1 (3 x CH_3, **minor**), 0.0 (3 x CH_3, **major**); *m/z* 248 ($M+H^+$, 41%), 233 (100%), 218 (18%); HRMS $(M+H)^+$ cald. for $C_{14}H_{20}O_2Si$ 248.1232, found *m/z* 248.1230.

[3-(2,2-Dimethyl-[1,3]dioxolane-4-yl)-7,7-dimethoxy-hept-3-ene-1,5-diynyl]-trimethylsilane (4): To a solution of **2** (100 mg, 0.4 mmol) in trimethylorthoformate (5.5 mL, 49.6 mmol) was added zinc chloride (51 mg, 0.4 mmol). The reaction was allowed to warm to 140 ^oC in a Dean-Stark apparatus. The reaction mixture was then filtered through celite and washed with EtOAc (3 x 5 mL) and the filtrate concentrated *in vacuo*. Flash chromatography eluting with Et_2O (5%)/PE gave the endiyne **4** (29.5 mg, 25%) as a yellow oil. ν_{max} (film)/cm^{-1} 3054, 2305, 1265; ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.88 (s, 1H), 5.12 (s, 1H), 4.36 (t, 1H, *J* 7.0), 3.99 (dd, 1H, *J* 8.0, 7.0), 3.69 (dd, 1H, *J* 8.0, 7.0), 3.21 (s, 6H), 1.24 (s, 3H), 1.20 (s, 3H), 0.00 (s, 9H); ^{13}C (75MHz, $CDCl_3$) δ_C 135.4 (C), 114.9 (CH), 110.8 (C), 105.0 (C), 100.4 (C), 93.8 (CH), 90.8 (C), 83.3 (C), 76.9 (CH), 69.3 (CH_2), 52.9 (2 x CH_3), 26.5 (CH_3), 26.2 (CH_3), 0.0 (3 x CH_3); *m/z* 322 ($M+H^+$, 11%), 307, 291, 264, 249, 233; HRMS $(M+H)^+$ cald. for $C_{17}H_{26}O_4Si$ 322.1600, found *m/z* 322.1620.

7-^{t}Butyldimethylsilyloxy-3,5-heptadiyne-1,2-diol (6): To **5** (0.320 g, 1.51 mmol) in pyrrolidine (1.5 mL) at 0 ^oC was added ^{t}butyldimethylsilylpropargyl alcohol (0.462 g, 2.72 mmol) and CuI (0.029 g, 0.15 mmol). The reaction mixture was stirred for 1 h and quenched with a saturated aqueous solution of NH_4Cl (5 mL). The mixture was extracted with Et_2O (3 x 5 mL), washed with brine (5 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Flash column chromatography eluting with EtOAc (20%)/PE gave **6** (0.299 g, 78%) as a brown oil. ν_{max} (film)/cm^{-1} 3367, 2955, 2930, 2885, 2858, 2146, 1087; ^1H NMR (300 MHz, $CDCl_3$) δ_H 4.40 (1H, t, *J* 4.6), 4.26 (2H, s), 3.66-3.56 (2H, m), 2.26 (1H, s br), 1.95 (1H, s br), 0.78 (9H, s), 0.00 (6H, s); ^{13}C (75MHz, $CDCl_3$) δ_C 79.1 (C), 76.7 (C), 70.8 (C), 68.9 (C), 66.6 (CH_2), 64.0 (CH), 52.4 (CH_2), 26.1 (3 x CH_3), 18.7 (C), -4.8 (2 x CH_3); MS (EI) 254, 223, 179, 167, 149.

7-^{t}Butyldiphenylylsilyloxy-3,5-heptadiyne-1,2-diol (7): To **5** (0.113 g, 0.53 mmol) in pyrrolidine (1.5 mL) at 0 ^oC was added ^{t}butyldiphenylsilylpropargyl alcohol (0.155 g, 0.53 mmol) and CuI (0.010 g, 0.05 mmol). The reaction mixture was stirred for 1 h and quenched with a saturated aqueous solution of NH_4Cl (5 mL). The mixture was extracted with Et_2O (3 x 5 mL), washed with brine (5 mL), dried over magnesium sulphate, filtered and concentrated *in vacuo*. Flash column chromatography eluting with EtOAc (30%)/PE gave **7** (0.108 g, 54%) as an orange oil. ν_{max} (film)/cm^{-1} 3427, 2103; ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.62-7.58 (4H, m), 7.38-7.28 (6H, m), 4.42-4.39 (1H, m), 4.31-4.29 (3H, m), 3.70-3.58 (2H, m), 3.28 (1H, s br), 2.87 (1H, s br), 0.77 (9H, s); ^{13}C (75MHz, $CDCl_3$) δ_C 136 (4 x CH), 133.0 (C), 130.4 (2 x CH), 128.2 (4 x CH), 78.6 (C), 76.9 (C), 70.8 (C), 69.2 (C), 66.6 (CH_2), 64.0 (CH), 53.4 (CH_2), 27.0 (3 x CH_3), 19.6 (C); M/S (EI) 377, 303, 273, 199, 181, 137, 77; HRMS ($M+NH_4^+$) cald for $C_{23}H_{26}O_3Si$ 396.1995, found *m/z* 396.1995.

7-^{t}Benzyloxy-3,5-heptadiyne-1,2-diol (8): To **5** (0.153 g, 0.72 mmol) in pyrrolidine (1.5 mL) at 0 ^oC was added ^{t}benzylpropargyl alcohol (0.117 g, 0.80 mmol) and CuI (0.015 g, 0.08 mmol) and the reaction was stirred for 6 h. The mixture was diluted with EtOAc (3 mL) and washed with a 10% aqueous solution of $CuSO_4$ (2 mL). The aqueous layer was extracted with EtOAc (3 x 3 mL) and the combined organic extracts was washed with brine (5 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Flash column chromatography eluting with EtOAc (10%)/PE gave **8** (0.041 g, 25%) as an orange oil. ν_{max} (film)/cm^{-1} 3416, 3055, 2915, 2885, 2858, 2170; ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.30-7.25 (5H, m), 4.53 (2H, s), 4.46 (1H, dd, *J* 4.1), 4.17 (2H, s), 3.70-3.64 (2H, m), 2.30 (1H, s br), 1.72 (1H, s br); ^{13}C (75MHz, $CDCl_3$) δ_C 136.9 (C), 128.5 (2 x CH), 128.16 (2 x CH), 128.11 (CH),

76.6 (C), 76.3 (C), 71.8 (CH_2), 70.3 (C), 70.1 (C), 66.1 (CH_2), 63.6 (CH), 57.4 (CH_2), 26.1 (3 x CH_3), 18.7 (C), -4.8 (2 x CH_3); MS (EI) 182, 169, 141, 91.

4-^{t}Butyldimethylsilyloxy-but-3-yn-dimethylphosphonate (11): To **10** (0.565 g, 2.15 mmol) was added trimethylphosphite (2 mL) and the reaction was heated at 140 ^{o}C for 1 h and excess of trimethylphosphite was removed by distillation. Flash column chromatography eluting with EtOAc (25%)/PE afforded **11** (0.354 g, 59%) as colourless oil. ν_{max} (film)/cm^{-1} 3054, 2987, 2305, 1421; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 4.20 (2H, dt, J_{P-H} 5.3, J_{H-H} 2.3), 3.72 (6H, d, J_{P-H} 7.9), 2.70 (2H, dt, J_{P-H} 21.9, J_{H-H} 2.3), 0.79 (9H, s), 0.00 (6H, s); ^{13}C (75MHz, $CDCl_3$) δ_C 81.8 (d, J 10.3, C), 74.6 (d, J 14.9, C), 53.9 (CH_3), 53.8 (CH_3), 52.2 (d, J 2.9, CH_3), 26.1 (3 x CH_3), 18.6 (C), 17.5 (d, J 146.6, CH_2), -4.9 (2 x CH_3); MS (EI) 277, 261, 247, 235, 205, 149, 137, 93, 79, 52; HRMS (M+NH_4^+) cald for $C_{12}H_{25}O_4SiP$ 310.1604, found *m/z* 310.1600.

1-Bromo-2-trimethylsilylethynyl-3,4-isopropylidenedioxy-but-1-ene(14):
To bromometyltriphenylphosphonium bromide (0.545 g, 1.25 mmol) in THF (10 mL) at -78 ^{o}C was added 0.5 M solution of KHMDS in toluene (2.5 mL, 1.25 mmol) and the reaction was stirred for 1 h. **12** (0.285 g, 1.25 mmol) in THF (5 mL) was added and the mixture was stirred for 5 min and quenched with a saturated aqueous solution of NH_4Cl (5 mL). The mixture was extracted with Et_2O (2 x 5 mL), washed with brine (5 mL), dried over magnesium sulphate, filtered and concentrated *in vacuo*. Flash column chromatography eluting with Et_2O (1%)/PE gave **14** (0.270 g, 71%) as an orange oil. ν_{max} (film)/cm^{-1} 3436, 2685, 1606; ; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.57 (1H, s), 4.85 (1H, dd, *J* 7.3, 6.4), 4.00 (1H, dd, *J* 8.3, 6.4), 3.69 (1H, dd, *J* 8.3, 7.3), 1.30 (3H, s), 1.24 (3H, s), 0.00 (9H, s); ^{13}C (75MHz, $CDCl_3$) δ_C 128.4 (C), 118.0 (CH), 110.7 (C), 100.2 (C), 99.1 (C), 74.8 (CH), 68.0 (CH_2), 26.6 (CH_3), 26.5 (CH_3), 0.0 (3 x CH_3); MS (EI) 304, 302, 289, 287, 231, 229, 193, 139, 137, 135, 107, 73, 72; HRMS (M-H) cald for $C_{12}H_{19}O_2Si$ 302.0338, found *m/z* 302.0336.

1-^{t}Butyldimethylsilyloxy-5-trimethylsilylethynyl-6,7,isopropylidenedioxy-hept-4-en-2-yne (15): To **14** (120 mg, 0.40 mmol) in THF (3 mL) was added $Pd(dba)_2$ (9 mg, 0.02 mmol), PPh_3 (11 mg, 0.004 mmol) and CuI (8 mg, 0.04 mmol) and the reaction was stirred for 15 min. Et_3N (0.115 mL, 0.80 mmol) and ^{t}butyldimethylsilylpropargyl alcohol (82 mg, 0.48 mmol) in THF (2 mL) were added and the reaction was refluxed for 1 h and quenched with a saturated aqueous solution of NH_4Cl (3 mL). The Mixture was extracted with Et_2O (3 x 5 mL), washed with brine (5 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Flash column chromatography eluting with Et_2O (2%)/ PE gave **15** (81 mg, 54%) as a brown oil. ν_{max} (film)/cm^{-1} 3436, 1638, 14.21; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.83 (1H, t, *J* 2.0), 4.91 (1H, dd, *J* 7.7, 6.5), 4.31 (2H, d, *J* 2.0), 3.96 (1H, dd, *J* 8.3, 6.5), 3.67 (1H, dd, *J* 7.7, 8.3), 1.29 (3H, s), 1.23 (3H, s), 0.71 (9H, s), 0.00 (9H, s), -0.07 (6H, s); ^{13}C (75MHz, $CDCl_3$) δ_C 133.7 (C), 119.0 (CH), 110.4 (C), 102.1 (C), 101.3 (C), 99.7 (C), 80.5 (C), 74.8 (CH), 68.3 (CH_2), 52.6 (CH_2), 26.6 (CH_3), 26.5 (CH_3), 26.0 (3 x CH_3), 18.5 (C), 0.0 (2 x CH_3), -4.9 (3 x CH_3); MS (EI) 377, 277, 247, 203, 147, 120, 84, 73, 49; HRMS (M+NH_4)$^+$ cald. for $C_{21}H_{36}O_2Si_2$ 410.2547, found *m/z* 410.2553.

4-(2,2-Dibromo-vinyl)-2,2-dimethyl-[1,3]-dioxolane[18] (18): To a solution of 1,2-5,6-diisopropylidene-D-mannitol **17** (25 g, 95 mmol) in DCM (350 mL) and aqueous sodium bicarbonate (4mL) was added portionwise sodium periodate (41 g, 190 mmol) over 20 min. Then the reaction mixture was stirred for 2 h and filtered through a pad of magnesium sulfate. DCM was then evaporated under vacum to give the D-glyceraldehyde acetonide. Meanwhile, to a solution of carbon tetrabromide (25.50 g, 77 mmol) in DCM (100 mL) at 0 ^{o}C, was added triphenylphosphine (40.3 g, 154 mmol). The reaction mixture was stirred for 30 min and a solution of the D-glyceraldehyde acetonide (24.7 g, 190 mmol) in DCM (250 mL) was added over a period of 30 min. Stirring was continued for 1 h and the suspension was then poured into PE (2 L) giving a precipitation of an orange/brown semi-crystalline mass. The supernatant liquid was decanted, and the resulting solid was washed with Et_2O (100 mL) and PE (100 mL). The filtrate was concentrated *in vacuo* to give an oil contaminated with triphenylphosphine oxide. Column chromatography eluting with Et_2O 5%/PE gave the vinyl dibromide **18** (7.09 g, 75%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.53 (d, 1H, *J* 7.6), 4.72 (t, 1H, *J* 6.5), 4.18 (dd, 1H, *J* 8.4, 6.3), 3.68 (dd, 1H, *J* 8.4, 6.5), 1.42 (s, 3H), 1.38 (s, 3H); ^{13}C (75MHz, $CDCl_3$) δ_C 137 (CH), 110.0 (C), 92.6 (C), 76.1 (CH), 68.0 (CH_2), 26.6 (CH_3), 25.6 (CH_3); HRMS (M+H)$^+$ cald. for $C_7H_{10}O_2Br_2Si$ 284.9125, found *m/z* 284.9124.

(2,2-Dimethyl-[1,3]dioxolan-4-yl)-propynoic acid methyl ester[18] (19): To a solution of dibromide **18** (10.0 g, 35.0 mmol) in THF (170 mL) at –78 ^{o}C was added *n*-BuLi (32.0 mL of a 2.3 M solution in hexanes, 73.4 mmol) over 30 min. The stirring was continued for 2 h and then methyl chloroformate (5.4 mL, 69.9 mmol) was added slowly. After stirring for 30 min, the reaction was warmed to rt and quenched by the addition of a saturated solution of $NaHCO_3$. The mixture was extracted with Et_2O (3 x 150 mL), the organics combined and washed with brine (75 mL), dried over magnesium sulphate and then concentrated *in vacuo*. Column chromatography eluting with Et_2O (10%)/PE gave the titled compound **19** (5.1 g, 79%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 4.80 (1H, dd, *J* 6.5, 5.5), 4.18 (1H, dd, *J* 8.3, 6.5), 4.02 (1H, dd, *J* 8.3, 5.5), 3.77 (3H, s), 1.48 (3H, s), 1.37 (3H, s);

^{13}C (75MHz, $CDCl_3$) δ_C 153.4 (C=O), 111.2 (C), 84.8 (C), 76.7 (C), 69.2 (CH_2), 64.9 (CH), 52.8 (CH_3), 26.0 (CH_3), 25.7 (CH_3); *m/z* 185 ($M+H^+$, 7%), 157, 137, 129, 111, 97, 83, 69, 61.

3-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-3-iodo-acrylic acid methyl ester (20): A solution **19** (1.00 g, 5.4 mmol), sodium iodide (1.22 g, 8.1 mmol) and acetic acid (3.0 mL, 50.1 mmol) in acetonitrile (120 mL) was heated at 115 ^oC. The stirring was continued for 90 min at this temperature. The reaction mixture was carefully poured into a saturated solution of $NaHCO_3$ (50 mL) and ether (150 mL). The resulting suspension was extracted with Et_2O (3 x 100 mL), washed with a saturated solution of $NaHCO_3$ (50 mL) and brine (50 mL), dried over magnesium sulphate and concentrated *in vacuo*. Column chromatography eluting with Et_2O (10%)/PE gave the vinyl iodide **20** (1.23 g, 95%) as a yellow oil; $[\alpha]_D^{22}$ +40.1 (*c* 1.01 in $CHCl_3$); ν_{max} (film)/cm^{-1} 2988, 2950, 2880, 1732, 1630; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.87 (d, 1H, *J* 1.6), 4.74 (t, 1H, *J* 6.8), 4.34 (dd, 1H, *J* 8.6, 6.8), 3.81 (dd, 1H, *J* 8.6, 6.8), 3.76 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H); ^{13}C (75MHz, $CDCl_3$) δ_C 164.8 (C=O), 123.2 (CH), 118.5 (C), 111.7 (C), 82.9 (CH), 69.9 (CH_2), 51.7 (CH_3), 26.0 (CH_3), 25.8 (CH_3); HRMS $(M+H)^+$ cald. for $C_9H_{13}O_4I$ 312.99368, found *m/z* 312.99371; Anal. Calcd for CHIO: C, 34.64; H, 4.20. Found: C, 34.37; H, 4.21.

3-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-5-trimethylsilanyl-pent-2-en-4-ynoic acid methyl ester[9e,17] (21): A degassed solution of **20** (3.0 g, 9.60 mmol), triethylamine (4.0 mL, 28.80 mmol) and trimethylsilylacetylene (1.9 mL, 13.50 mmol) in acetonitrile (75 mL) was added to a suspension of CuI (183 mg, 0.96 mmol) and $Pd(PPh_3)_4$ (555 mg, 0.48 mmol) in acetonitrile (10 mL) at rt. The reaction was continued for 2 h and a mixture of saturated solution of NH_4Cl (20 mL) and Et_2O (100 mL) was added. The reaction mixture was extracted with Et_2O (3 x 100 mL), washed with brine (50 mL), dried over magnesium sulphate and concentrated *in vacuo*. Column chromatography eluting with Et_2O (10%)/PE gave the titled compound **21** (2.5 g, 91%) as a yellow oil. $[\alpha]_D^{22}$ +32.6 (*c* 1.01 in $CHCl_3$) (Lit.[30] $[\alpha]_D^{25}$ 39.6 (*c* 1.01 in $CHCl_3$)); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.37 (d, 1H, *J* 1.5), 4.61 (dt, 1H, *J* 6.8, 1.5), 4.25 (dd, 1H, *J* 8.5, 6.8), 3.92 (dd, 1H, *J* 8.5, 6.8), 3.74 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 0.23 (s, 9H); ^{13}C (75MHz, $CDCl_3$) δ_C (ppm) 165.2 (C=O), 136.9 (CH), 123.7 (C), 110.9 (C), 109.0 (C), 99.4 (C), 77.7 (CH), 69.1 (CH_2), 51.4 (CH_3), 26.2 (CH_3), 25.8 (CH_3), -0.4 (3 x CH_3); HRMS $(M+H)^+$ cald. for $C_{14}H_{22}O_4Si$ 283.13656, found *m/z* 283.13657

3-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-5-trimethylsilanyl-pent-2-en-4-yn-1-ol[9e,17] (22): To a solution of **21** (2.5 g, 8.7 mmol) in THF (35 mL) at -78 ^oC was added DIBAL (21.8 mL of a 1 M solution in toluene, 21.8 mmol) dropwise. The stirring was continued for 3 h until completion and then saturated Rochelle salt solution (10 mL) was added. The reaction mixture was extracted with Et_2O (2 x 30 mL), washed with brine (2 x 10 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Flash chromatography eluting with Et_2O (40%)/PE gave the allylic alcohol **22** (2.2 g, 98%) as a yellow oil. $[\alpha]_D^{22}$ +29.6 (*c* 2.07 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.25 (t, 1H, *J* 6.4), 4.49 (t, 1H, *J* 6.8), 4.40 (d, 2H, *J* 6.4), 4.14 (dd, 1H, *J* 8.3, 6.8), (dd, 1H, *J* 8.3, 6.8), 1.62 (s br, 1H), 1.46 (s, 3H), 1.40 (s, 3H), 0.20 (s, 9H, CH_3); ^{13}C (75MHz, $CDCl_3$) δ_C 138.8 (CH), 123.7 (C), 110.2 (C), 103.0 (C), 99.2 (C), 78.0 (CH), 68.9 (CH_2), 61.3 (CH_2), 26.5 (CH_3), 26.2 (CH_3), 0.00 (3 x CH_3); HRMS $(M+H)^+$ cald. for $C_{13}H_{23}O_3Si$ 183.14165, found *m/z* 183.14159.

3-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-pent-2-en-4-yn-1-ol (24): To a solution of **22** (200 mg, 0.8 mmol) in dry THF (5 mL) was added tetrabutylammonium fluoride (1.6 ml of a 1 M solution in THF, 1.6 mmol) and the reaction stirred for 20 min at 0 ^0C. The reaction was poured into H_2O (2 mL). The mixture was extracted with Et_2O (3 x 15 mL) and the combined organics washed with brine (5 mL), dried over magnesium sulfate and concentrated *in vacuo*. Column chromatography eluting with Et_2O 50%/PE afforded **24** (122 mg, 85%) as a yellow oil. $[\alpha]_D^{22}$ +17.1 (*c* 1.04 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3411, 3284, 2987, 2940, 2882, 2361, 1457; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 6.33 (t, 1H, *J* 6.4), 4.53 (dd, 1H, *J* 7.1, 6.4), 4.42 (d, 2H, *J* 6.4), 4.17 (dd, 1H, *J* 8.3, 6.4), 3.90 (dd, 1H, *J* 8.3, 7.1), 3.23 (s, 1H), 1.67 (br s, 1H), 1.47 (s, 3H), 1.40 (s, 3H); ^{13}C (75MHz, $CDCl_3$) δ_C 139.2 (CH), 122.6 (C), 110.2 (C), 84.8 (C), 78.1 (CH), 77.6 (CH), 68.7 (CH_2), 60.9 (CH_2), 26.3 (CH_3), 25.9 (CH_3); HRMS $(M+H)^+$ cald. for $C_{10}H_{14}O_3$ 183.10211, found *m/z* 183.10223.

[3-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-3-ethynyl-oxiranyl]-methanol (25): To a suspension of powdered molecular sieves 4Å (2.3 g) in DCM (6 mL) cooled at -25 ^oC was added Ti (IV) isopropoxide (1.13 ml, 3.78 mmol) and D-(-)-diethyl tartrate (0.650 ml, 3.78 mmol) and the reaction mixture was stirred for 30 min. A prepared solution of 5.2 M *tert*-butyl hydroperoxide (18 mL, 94.5 mmol) in DCM (12 mL) was added dropwise and the reaction was stirred for 10 min. **24** (3.447 g, 18.9 mmol) was then added dropwise and the reaction mixture was allowed to warm to – 6 ^oC and stirred for 96 h. The reaction was quenched with saturated solution of sodium thiosulfate (50 mL) and diluted with Et_2O (50 mL). The resultant precipitate was filtered through celite and washed with Et_2O. The filtrate was extracted with Et_2O, washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. Column chromatography eluting with Et_2O (40%)/PE gave **25** (3.2 g, 81%) as a colourless oil. $[\alpha]_D^{22}$ +62.5 (*c* 1.1 in $CHCl_3$), ν_{max} (film)/cm^{-1} 3452, 3271, 2987, 2921, 2889, 2119, 1377;^{1}H NMR

(500 MHz, $CDCl_3$) δ_H 4.13 (dd, 1H, *J* 8.7, 6.3), 4.04 (dd, 1H, *J* 8.7, 6.3), 3.93 (t, 1H, *J* 6.3), 3.90 (dd, 1H, *J* 12.4, 4.4), 3.78 (dd, 1H, *J* 12.4, 6.2), 3.28 (dd, 1H, *J* 6.2, 4.4), 2.67 (br s, 1H), 2.45 (s, 1H), 1.42 (s, 3H), 1.31 (s, 3H); ^{13}C (125 MHz, $CDCl_3$) δ_C 110.8 (C), 77.2 (C), 76.6 (CH), 75.7 (CH), 66.6 (CH_2), 61.7 (CH_2), 61.2 (CH), 55.1 (C), 26.05 (CH_3), 25.1 (CH_3); HRMS $(M+H)^+$ cald. for $C_{10}H_{14}O_4$ 199.09703, found *m/z* 199.09602; Anal calcd for CHO: C, 60.59; H, 7.12. Found: C, 60.70; H, 7.12.

4-[3-(2,2-dibromo-vinyl)-2-ethynyl-oxiranyl]-2,2-dimethyl [1,3]dioxolane (27): To **25** (0.50 g, 2.52 mmol) in DCM (13 mL) at 0 ^oC was added Dess-Martin periodinane (2.02 g, 5.04 mmol) in one portion. The stirring was continued at 0 ^oC for 30 min and the reaction mixture was poured into a mixture of a saturated aqueous solution of sodium thiosulfate (5 mL) and a saturated aqueous solution of $NaHCO_3$ (5 mL). Then Et_2O (100 mL) was added and the mixture stirred for 30 min. The mixture was extracted with Et_2O (3 x 50 mL), washed with brine (2 x 10 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude epoxy-aldehyde **26** was seen to be of sufficient purity (without flash chromatography) for use in the next stage.
To a solution of carbon tetrabromide (1.68 g, 5.04 mmol) in DCM (50 mL) was added triphenylphosphine (1.32 g, 5.04 mmol) and the reaction mixture was stirred for 15 min at -78 ^oC. A solution of the crude epoxy-aldehyde **26** and Et_3N (0.53 mL, 3.78 mmol) in DCM (30 mL) was added dropwise *via* cannula. The stirring was continued for 10 min and the reaction quenched with a saturated aqueous solution of $NaHCO_3$. The reaction mixture was extracted with DCM, washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The resulting crude product was transferred on silica gel previously neutralised with 0.2% of Et_3N. Flash column chromatography eluting with Et_2O 10%/PE gave the epoxy-dibromoalkene **27** (0.47 g, 53%) as a colourless oil. $[\alpha]_D^{22}$ +94 (*c* 1.0 in $CHCl_3$); vmax (cm^{-1}) 3225, 2917, 2856, 2172, 1465; ^1H NMR (400 MHz, $CDCl_3$) δ_H 6.39 (d, 1H, *J* 7.9), 4.15 (dd, 1H, *J* 10.4, 9.2), 4.034 (dd, 1H, *J* 9.2, 5.7), 4.032 (dd, 1H, 10.4, 5.7), 3.78 (d, 1H, *J* 7.9), 2.50 (s, 1H), 1.42 (3H, s), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 132.4 (CH), 111.0 (Me_2C), 96.7 (CBr_2), 77.2 (C), 76.5 (C), 75.9 (CH), 66.8 (CH_2), 60.2 (CH), 57.0 (C), 26.2 (CH_3), 25.3 (CH_3); HRMS $(M+H)^+$ cald. for $C_{11}H_{12}Br_2O_3$ 350.9231, found *m/z* 350.9230.

(3-chloroprop-1-ynyl)trimethylsilane[32] (31): To propargyl chloride **30** (5.0 mL, 69 mmol) in THF (200 mL) at -78 ˚C was added a 1.4 M solution of n-BuLi in hexane (25 mL, 35 mmol) dropwise over 2 h. TMSCl (8.8 mL, 69 mmol) was then added dropwise and the solution allowed to warm to rt and stirred for 1 h. The reaction mixture was quenched by adding it to H_2O (200 mL), then Et_2O (200 mL) was added and the layers separated. The aqueous layer was then washed with Et_2O (2 × 200 mL) and the combined organic extracts washed with H_2O (100 mL), brine (100 mL), and dried over magnesium sulfate. Concentration *in vacuo*, followed by purification *via* distillation (bp 135 ˚C) gave **31** (4.8 g, 48%) as a colourless oil. ν_{max}(film)/cm^{-1} 2962, 2183, 1269, 1029; ^1H NMR (300 MHz; $CDCl_3$) δ_H 4.13 (s, 2H), 0.18 (s, 9H); ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 99.6 (C), 91.8 (C), 30.7 (CH_2), -0.4 (3 x CH_3).

(3-chloroprop-1-ynyl)triethylsilane[33]: To propargyl chloride **30** (2.5 mL, 34.6 mmol) in THF (100 mL) at -78 ˚C was added a 1.4 M solution of n-BuLi in hexane (12.5 mL, 17.5 mmol) dropwise over 2 h. TESCl (5.8 mL, 34.6 mmol) was then added dropwise and the solution allowed to warm to rt and stirred for 1 h. The reaction mixture was quenched by adding it to H_2O (100 mL), then Et_2O (100 mL) was added and the layers separated. The aqueous layer was then washed with Et_2O (2 × 100 mL) and the combined organic extracts washed with H_2O (50 mL), brine (50 mL), and dried over magnesium sulphate. Concentration *in vacuo* and subsequent column chromatography eluting with 100% PE gave the title compound (2.4 g, 37%) as a colourless oil. ν_{max}(film)/cm^{-1} 2959, 2179, 1029; ^1H NMR (300 MHz; $CDCl_3$) δ_H 4.15 (s, 2H, CH_2), 0.99 (t, 9H, *J* 7.9), 0.61 (q, 6H, *J* 7.8); ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 100.8 (C), 89.5 (C), 30.8 (CH_2), 7.3 (3 x CH_3), 4.1 (3 x CH_2).

***tert*-Butyl-(3-Chloro-prop-1-ynyl)-dimethylsilane:** To propargyl chloride **30** (5.0 mL, 69 mmol) in THF (200 mL) at -78 ˚C was added a 2.18 M solution of n-BuLi (16 mL, 35 mmol) dropwise over 2 h. A 2 M solution of TBSCl in THF (34.5 mL, 69 mmol)) was then added dropwise *via* cannula and the reaction was allowed to warm to rt and stirred for 1 h. The reaction was quenched with H_2O (200 mL), extracted with Et_2O (2 x 200 mL), washed with brine (100 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Column chromatography eluting with 100% PE gave the title compound (5.5 g, 42%) as a colourless oil. ν_{max} (cm^{-1}) 2916, 2198 1450, 1257, 1033, 817; ^1H NMR (300 MHz; $CDCl_3$) δ_H (300 MHz, $CDCl_3$) 4.14 (s, 2H), 0.94 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ_C 100.3 (C), 90.2 (C), 30.7 (CH_2), 25.9 (C), 16.4 (3 x CH_3), -4.8 (2 x CH_3).

4-Hydroxy-but-2-ynal diethyl acetal[31] (41): To a solution of (propargyloxy)trimethylsilane (30.0 g, 234 mmol) in THF (150 mL) was added a 1 M THF-solution of ethylmagnesium bromide (234 mL, 234 mmol). The reaction was stirred for 30 min and a solution of phenyl orthoformate (41.8 g, 212 mmol) in THF (110 mL) was added. Stirring was continued for 16 h then the reaction quenched with a saturated solution of NH_4Cl (200 mL) and H_2O (200 mL), extracted with Et_2O (2 x 200 mL), washed with NaOH (4 M solution, 3 x 100 mL) dried over

magnesium sulfate and concentrated *in vacuo*. The residue was then dissolved in methanol (530 mL) and potassium carbonate (29.3 g, 212 mmol) was added at 0 ˚C and the mixture stirred for 10 min. The solution was concentrated *in vacuo* then H_2O (200 mL) was added. The mixture was extracted with EtOAc (3 x 150 mL), dried over magnesium sulfate and concentrated in vacuo. Distillation of the residue under vacuum (bp 88˚C; 1 mmHg) gave **41** (23.7 g, 70%) as a colourless oil. ν_{max} (cm^{-1}) 3424, 1120; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.26 (d, 1H, *J* 1.3), 4.28 (dd, 2H, *J* 6.2, 1.3), 3.70 (dq, 2H, *J* 7.2, 9.4), 3.55 (dq, 2H, *J* 7.2, 9.4), 2.30 (s br, 1H), 1.19 (t, 6H, *J* 7.2); ^{13}C NMR (300 MHz; $CDCl_3$) δ_C (75 MHz, $CDCl_3$) 91.6 (CH), 84.2 (C), 81.1 (C), 61.3 (CH_2), 51.1 (CH_2), 15.4 (CH_3).

4-Chloro-1,1-diethoxy-but-2-yne[34] (42): To a solution of the alcohol **41** (10.0 g, 63 mmol) and triethylamine (26.4 mL, 190 mmol) in ether (320 mL) was added dropwise methanesulfonyl chloride (5.5 mL, 70 mmol) at 0 ˚C. Stirring was continued for 1 h and then the reaction quenched with a saturated aqueous solution of $NaHCO_3$ (120 mL), extracted with Et_2O (2 x 60 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was dissolved in chloroform (310 mL) with tetra-n-butylammonium chloride (41.0 g, 126 mmol). The reaction was refluxed for 1 h. Concentration of the mixture *in vacuo* gave the crude residue to which Et_2O (200 mL) was added. The solution was washed with H_2O (100 mL), then brine (2 x 100 mL), dried over magnesium sulfate and concentrated *in vacuo* to furnish the pure propargylic chloride **42** as a yellow oil (8.9 g, 80%). ν_{max} (cm^{-1}) 2971, 2901, 2888, 2238; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.23 (t, 1H, *J* 1.3), 4.13 (d, 2H, *J* 1.3), 3.69 (dq, 2H, *J* 7.2, 9.3), 3.53 (dq, 2H, *J* 7.2, 9.3), 1.18 (t, 6H, *J* 7.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 91.1 (CH), 81.6 (C), 79.9 (C), 60.9 (2 x CH_2), 29.7 (CH_2), 14.9 (2 x CH_3); HRMS $(M+H)^+$ cald. for $C_8H_{13}O_2Cl$ 175.0520, found *m/z* 175.0518.

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