Supplementary material

(E)-2-tributylstannylbut-2-ene-1,4-diol

To a THF solution (15 mL) of but-2-yn-1,4-diol (1.58 g, 30 mmol) and PdCl₂(PPh₃)₂ (420 mg, 2 mol %) was added dropwise a THF solution (20 mL) of tributyltin hydride (9.54 mL, 36 mmol) over a period of 1 h. The originally light yellow solution abruptly turned orange-brown. After stirring over 15 mn, THF was evaporated under vacuum. The crude product was then purified by flash chromatography (PE-Et₂O, 6/4 to 2/8) to yield 11.2 g of vinylstannane (99 %). IR (NaCl) 3300, 2940, 1457, 1027 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 0.84-0.93 (m, 15H), 1.23-1.35 (m, 6H), 1.43-1.53 (m, 6H), 1.64 (bt, J = 5.6 Hz, 1H), 1.73 (bt, J = 5.2 Hz, 1H), 4.18 (bt, J = 5.4 Hz, 2H), 4.36 (bd, J = 3.7 Hz, $^3J_{\text{Sn-H}} = 37$ Hz, 2H), 5.77 (m, $^3J_{\text{Sn-H}} = 67$ Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) 10.03 ($^1J_{\text{Sn-C}} = 332$ Hz, 3C), 13.74 (3C), 27.44 ($^3J_{\text{Sn-C}} = 58$ Hz, 3C), 29.18 ($^2J_{\text{Sn-C}} = 20$ Hz, 3C), 59.47, 63.30 ($^2J_{\text{Sn-C}} = 26$ Hz), 138.10 ($^2J_{\text{Sn-C}} = 20$ Hz), 149.22.

(E)-4-tert-butyldimethylsilyloxy-2-tributylstannylbut-2-en-1-ol 3

To a solution of (*E*)-2-tributylstannylbut-2-ene-1,4-diol (3.8 g, 10 mmol) in DMF (100 mL) at 0 °C was added imidazole (0.68 g, 10 mmol) and *tert*-butyldimethylsilylchloride (1.5 g, 10 mmol). The solution was stirred at 0 °C for 6 h then crushed ice (2.5 g) was added. The solution was diluted with Et₂O (200 mL), washed with saturated aqueous NH₄Cl solution (3 x 50 mL), dried over MgSO₄ and evaporated. The crude product was then purified by flash chromatography (light petroleum-Et₂O, 10/0 to 9/1; 3.23 g (65%). IR (NaCl) 3445.3, 2956.7, 2854.5, 1461.1, 1254.6, 1074.4, 837.1, 777.5 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) = 0.06 (s, 6H), 0.84-0.92 (m, 15H),0.88 (s, 9H), 1.28-1.53 (m, 12H), 1.80 (bt, J = 5.5 Hz, 1H), 4.20 (bd, J = 5.4 Hz, ⁴J_{Sn-H} = 15 Hz, 2H), 4.32 (bd, J = 5.5 Hz, J_{Sn-H} = 37 Hz, 2H), 5.68 (bt, J = 5.4 Hz, J_{Sn-H} = 69 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) -5.06 (2C), 10.12 (J_{Sn-C} = 332 Hz, 3C), 13.78 (3C), 13.38, 25.97 (3C), 27.47 (J_{Sn-C} = 58 Hz, 3C), 29.26 (J_{Sn-C} = 20 Hz, 3C), 60.83 (J_{Sn-C} = 61 Hz), 63.77 (J_{Sn-C} = 25 Hz), 138.82 (J_{Sn-C} = 18 Hz), 147.37.

Pent-3-yn-1-ol 4

To a solution of lithium (0.367 g, 0.0528 mol), ferric nitrate (15mg) and ammonia (200 mL) was added but-3-yn-1-ol (0.926 g, 13.2 mmol) at -40 °C. The mixture was stirred at -40°C for 2 h then methyliodide (4.11 mL, 66 mmol) was added. After 12 h, the reaction was quenched with saturated aqueous NH₄Cl solution. The aqueous layer was extracted with ethyl acetate (3 x 45 mL). The organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by flash chromatography (light petroleum-Et₂O, 6/4 to 4/6) to yield 3.75 g (56 %). IR (NaCl) 3340.7, 2918.9, 1429.8, 1046.1 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 1.82 (t, J = 2.6 Hz, 3H), 1.90 (bt, J = 6.1 Hz, 1H), 2.42 (m, J = 6.1/2.6 Hz, 2H); 3.69 (q, J = 6.1 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) 3.12, 22.68, 61.01, 75.62, 77.1

(E)-4-tributylstannylpent-3-en-1-ol 5

CuCN (0.639 g, 7.13 mmol) was suspended in freshly distilled THF (20 mL), cooled at -78°C and treated with BuLi in hexane (2.5 M, 5.7 mL, 14.3 mmol). The mixture was allowed to react until a homogenous solution was obtained. Then, at -78 °C, Bu₃SnH (3.78 mL, 14.3 mmol) was added dropwise via a syringe. Stirring was continued and, over ca. 10 mn, the solution yellowed and H₂ gas was liberated. Methanol (10.59 mL, 0.26 mol) was then added, and the mixture was allowed to warm to -40 °C and pent-3-yn-1-ol was added. The reaction was followed by TLC and guenched with a saturated aqueous NH₄Cl solution. The mixture was filtered and aqueous layer was extracted with ethyl acetate (4 x 45 mL). The organic layers were washed with a saturated aqueous NaCl solution, dried over MgSO₄ and concentrated under vacuum. The crude product (93/7 ratio of regioisomers) was purified by column chromatography on silica gel (petroleum ether-Et₂O, 8/2) to yield 0.79 g (84 %). IR (NaCl) 3328.1, 2921.3, 1457.9, 1046.0, 870.6 cm⁻¹, ¹H NMR (300 MHz, CDCl₃) 0.84-0.89 (m, 15H), 1.24-1.49 (m, 13H); 1.85 (d, J = 1.7 Hz, ${}^{3}J_{Sn-H} = 44$ Hz, 3H), 2.41 (m, 2H), 3.64 (bq, J = 6.4 Hz, 2H), 5.50 (m, J = 7/1.7 Hz, ${}^{3}J_{Sn-H} = 70$ Hz, 1H); ${}^{13}C$ NMR (50 MHz, CDCl₃) 9.12 (${}^{1}J_{\text{Sn-C}} = 322 \text{ Hz}, 3\text{C}$), 13.70 (3C), 19.28 (${}^{2}J_{\text{Sn-C}} = 41 \text{ Hz}$), 27.4 (${}^{3}J_{\text{Sn-C}} = 54 \text{ Hz}, 3\text{C}$), 29.2 $(^{2}J_{\text{Sn-C}} = 20 \text{ Hz}, 3\text{C}), 31.71 (^{3}J_{\text{Sn-C}} = 53 \text{ Hz}), 62.21, 135.84 (^{2}J_{\text{Sn-C}} = 28 \text{ Hz}), 142.13.$

(E)-4-iodopent-3-en-1-ol 6

To a solution of (E)-4-tributylstannylpent-3-en-1-ol $\mathbf{5}(0.355 \text{ g}, 0.95 \text{ mmol})$ in anhydrous

diethylether at 0 °C. The mixture was stirred 2 h at room temperature and quenched with 1M aqueous KF solution (2 mL) and acetone (2 mL). After stirring 2 h, the solution was filtered through a pad of celite. The aqueous layer was extracted with ethyl acetate (3 x 20 mL). The organic layers were washed with a saturated aqueous $Na_2S_2O_3$ solution, dried over MgSO₄ and concentrated under vacuum. The crude product was purified by chromatography (light petroleum, Et₂O, 9/1 to 0/10) to yield 2.20 g of vinyl iodide **6** (97%). The selectivity was attributed by ¹H NMR (200 MHz) (up to 95 %). After elimination of tin by-products, GC analysis gave a purity up to 98 % which was confirmed by ¹H NMR. IR (NaCl) 3355.0, 2948.1, 1635.8, 1426.5, 1051.9, 882.9; ¹H NMR (400 MHz, CDCl₃) 1.48 (bs,1H), 2.29 (m, 2H), 2.39 (d, J = 1.3 Hz, 3H), 3.64 (t, J = 6.2 Hz, 2H), 6.17 (tq, J = 7.5/1.3 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) 27.71, 33.85, 61.18, 96.04, 137.14.

(E)-4-iodopent-3-en-1-al 7

To a stirred solution of (*E*)-4-iodopent-3-en-1-ol **6** (0.1 g, 0.47 mmol) in CH₂Cl₂ (12 mL) at 0 °C was added Dess-Martin periodinane (0.26 g, 0.61 mmol). The reaction mixture was stirred under nitrogen at room temperature and followed by TLC. After disappearance of the starting material, the mixture was poured into a separating funnel containing saturated aqueous Na₂S₂O₃ / NaHCO₃ solution (26 mL, 1/1) and shaken vigorously for 5 mn. The aqueous layer was extracted with diethyl ether (3 x 20 mL) and the organic layers were washed with saturated aqueous NaHCO₃ solution, dried over MgSO₄ and concentrated under vacuum to give crude aldehyde **7** 97 mg (98%). ¹H NMR (400 MHz, CDCl₃) 2.37 (s, 3H), 3.15 (d, J = 7 Hz, 2H), 6.33 (t, J = 7 Hz, 1H), 9.60 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) 28.11, 44.91, 98.22, 129.64, 197.16.

1,1-dibromo-4-methylpent-1,3-diene 8

Carbon tetrabromide (24.87 g, 75 mmol), triphenylphosphine (19.67 g, 75 mmol) and zinc dust (4.69 g, 75 mmol) were placed in a dry 500 mL round-bottomed flask under a nitrogen atmosphere. The flask was cooled to 0 °C and CH₂Cl₂ (300 mL) was added to the mixture of the solids, giving a green suspension. The reaction mixture was allowed to warm room temperature and was then stirred for 24 h, after which time it was pink in colour. 3-methylbut-2-enal (2.89 mL, 30 mmol) was then added *via* syringe and the mixture stirred for a

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mL) added and the resultant solution was stirred. The residue was dissolved in CH_2Cl_2 (200mL) and then further pentane (500 mL). This was also filtered and the combined filtrates were concentrated to a colourless oil. This was triturated with pentane (20mL) and passed through a short silica column to remove triphenylphosphine oxide. After removal of solvents in vacuum, *gem*-dibromodiene **8** (5.95 g, 83 %) was obtained as a colourless oil. IR (NaCl) 3010, 2960, 2900, 2820, 1630, 1560, 1430, 1370, 1250, 850, 770, 650 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 1.74 (s, 3H), 1.78 (s, 3H), 5.83 (dqq, J = 10.6, 1.3, 1.3 Hz, 1H), 7.07 (d, J = 10.6 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) 19.42, 26.40, 88.61, 122.27, 133.57, 140.82.

1-trimethylstannyl-4-methylpent-3-en-1-yne

To a solution of 1,1-dibromo-4-methylpent-1,3-diene **8** (1g, 3.4 mmol) in THF (15 mL) under a nitrogen atmosphere at -78 °C, butyllithium (2.5 M, 2.86 mL, 7.1 mmol) was added dropwise. The clear yellow solution was stirred at -78 °C for 1.5 h. and then trimethylstannylchloride (0.71 g, 3.57 mmol) was added. After warming to room temperature the mixture was quenched with water (5 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with water (10 mL), dried over MgSO₄, filtered and concentrated under vacuum to give 0.73 g (88%). ¹H NMR (400 MHz, CDCl₃) 0.25 (s, ${}^2J_{\text{Sn-H}} = 59$ Hz, 9H), 1.74 (s, 3H), 1.87 (s, 3H), 5.25 (s, 1H); ¹³C NMR (50 MHz, CDCl₃) -7.68 (${}^1J_{\text{Sn-C}} = 404$ Hz), 21.06, 24.7, 94.84, 105.74, 107.30, 149.05.

2-[2-(tert-Butyldimethylsilyloxy)ethylidene]-6-iodohept-5-ene-1,3-diol 10

To a solution of (E)-4-*tert*-butyldimethylsilyloxy-2-tributylstannylbut-2-en-1-ol **3** (1.52 g, 3.09 mmol) in THF (50 mL) at -78° C was added dropwise n-BuLi (2.5 M, 2.72 mL, 6.81 mmol). The reaction mixture was warmed to -35° C for 2h and then cooled to -78° C then (E)-4-iodopent-3-en-1-al **7** (0.5 g, 2.38 mmol) was added dropwise. The solution was kept at -78° C for 1h and quenched with a saturated aqueous NH₄Cl solution. The aqueous layer was extracted with ethyl acetate (4 x 50 mL). The organic layers were washed with saturated aqueous NH₄Cl solution, dried over MgSO₄ and concentrated under vacuum. The crude product was then purified by flash chromatography (light petroleum-Et₂O, 3/7) giving 0.287 g (48%) of **10**. IR (NaCl) 3596, 3400, 2932, 2360, 1605, 1497, 1033, 837 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 0.08 (s, 6H), 0.89 (s, 9H), 2.14 (bd, J = 4.1 Hz, 1H), 2.30-2.46 (m, 2H), 2.38 (s,

6.16 (bt, J = 6.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) -5.17 (2C), 18.30, 25.93 (3C), 27.87, 36.88, 58.07, 59.47, 74.55, 95.84, 129.07, 136.82, 141.38.

2-[2-(tert-Butyldimethylsilyloxy)ethylidene]-1,3-diacetoxy-6-iodohept-5-ene 11

A solution of diol **10** (0.190 g, 0.46 mmol), acetic anhydride (0.173 mL, 1.84 mmol) and DMAP (4.6 mg) in pyridine (2 mL) was stirred overnight. The mixture was quenched with saturated aqueous NaHCO₃ solution. The aqueous layer was extracted with diethyl ether (3 x 10 mL) and the organic layers were washed with saturated aqueous CuSO4 solution (5 x 10 mL) and water (10 mL), dried over MgSO₄ and concentrated under vacuum to give 0.217 g (96%). IR (NaCl) 3465, 2932, 2856, 2361, 1742, 1638, 1465, 1432, 1371, 1230, 1026, 837, 778, 666 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 0.05 (s, 6H), 0.88 (s, 9H), 2.03 (s, 3H), 2.04 (s, 3H), 2.35-2.48 (m, 2H), 2.36 (s, 3H), 4.29 (d, J = 5.8 Hz, 2H), 4.60 (s, 2H), 5.22 (t, J = 6.4 Hz, 1H), 5.82 (t, J = 5.8 Hz, 1H), 6.06 (bt, J = 6.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) -5.17 (2C), 18.25, 20.88, 21.08, 25.88 (3C), 27.79, 34.46, 59.46, 59.50, 73.90, 96.36, 132.07, 134.70, 135.34, 169.84, 170.51.

2-[2-(*tert*-Butyldimethylsilyloxy)ethylidene]-1,3-diacetoxy-6,10-dimethylundecadi-5,9-en-7-yne 12

In a dry 10-mL Schlenk tube, vinyl iodide **11** (0.1 g, 0.2 mmol) in DMF (2 mL) was added PdCl₂(MeCN)₂ (2.6 mg, 0.01 mmol). The solution was degassed and 1-trimethylstannyl-4-methylpent-3-en-1-yne (0.073 g, 0.3 mol) was added and the reaction mixture immediately became black. The solution was stirred overnight and water (1 mL) was added. The aqueous layer was extracted with diethyl ether (3 x 5 mL). The organic layers were washed with water (2 x 5 mL), dried over MgSO₄ and concentrated under vacuum. Chromatography (PE-Et2O, 8/2) yielded 0.0895 g of **12** (99%). Products of inversion of configuration were not detected both by GC/MS and by 1 H NMR(300 MHz) spectroscopy. On this basis, the selectivity of the coupling is up to 99%. It should be noted that GC chromatogram exhibits minor impurities (<1%) that do not correspond to isomers of **12** (Cf GC chromatogram). 1 H NMR (400 MHz, CDCl₃) 0.03 (s, 6H), 0.86 (s, 9H), 1.78 (s, 3H), 1.79 (s, 3H), 1.85 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.38-2.53 (m, 2H), 4.28 (d, J = 5.8 Hz, 2H), 4.60 (s, 2H), 5.22 (t, J = 6.7 Hz, 1H), 5.31 (s, 1H), 5.66 (bt, J = 7.4 Hz, 1H), 5.82 (t, J = 5.8 Hz, 1H); 13 C NMR (100 MHz, CDCl₃)

-5.14 (2C), 17.81, 18.31, 20.91, 21.03, 21.18, 24.86, 25.92 (3C), 32.79, 59.58, 59.64, 74.65, 85.15, 94.18, 105.33, 121.15, 130.36, 132.41, 134.64, 148.05, 170.04, 170.68.

4-acetoxy-3-acetoxymethyl-7,11-dimethyldodecatri-2,6,10-en-8-yn-1-ol 13

To a solution of **12** (150 mg, 0.334 mmol) in THF (5 mL) was quickly added HF.Pyridine (0.153 mL, 0.5 mmol). The reaction was monitored by TLC. After disappearance of the starting material, the mixture was concentrated under vacuum. The crude product was then purified by flash chromatography (light petroleum-AcOEt, 6/4) (89 mg; 80%). 2 isomers were obtained in 95/5 ratio.

Major product

IR (NaCl) 3390, 2360, 1735, 1374, 1200, 1026; ${}^{1}H$ NMR (400 MHz, CDCl₃) 1.79 (d, J = 0.7 Hz, 3H), 1.80 (d, J = 1.2 Hz, 3H), 1.87 (d, J = 0.7 Hz, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.40-2.55 (m, 2H), 4.26 (d, J = 6.8 Hz, 2H), 4.64 (d, J = 12.4 Hz, 1H), 4.72 (d, J = 12.4 Hz, 2H), 5.22 (t, J = 6.7 Hz, 1H), 5.33 (d, J = 0.7 Hz, 1H), 5.66 (tq, J = 7.4, 1.2 Hz, 1H), 5.94 (t, J = 6.8 Hz, 1H); ${}^{13}C$ NMR (75 MHz, CDCl₃) 17.76, 20.92, 20.96, 21.11, 24.80, 32.79, 58.33, 59.54, 74.47, 85.22, 94.03, 105.20, 121.22, 130.13, 132.95, 134.28, 148.17, 170.13, 171.01.

Minor product

¹H NMR (400 MHz, CDCl₃) 1.79 (s, 3H), 1.80 (s, 3H), 1.87 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.50-2.55 (m, 2H), 4.17 (d, J = 12.8 Hz, 1H), 4.24 (d, J = 12.8 Hz, 1H), 4.69 (d, J = 6 Hz, 2H), 5.23 (t, J = 6.7 Hz, 1H), 5.33 (s, 1H), 5.66 (bt, J = 7.3, 2H); ¹³C NMR (75 MHz, CDCl₃) 17.77, 20.95, 20.98, 21.19, 24.82, 32.80, 58.13, 60.26, 74.85, 85.07, 94.13, 105.19, 124.26, 130.27, 135.27, 142.08, 148.11, 170.52, 171.29.

4-acetoxy-3-acetoxymethyl-7,11-dimethyldodecatri-2,6,10-en-8-ynal 2 (Taxifolial A)

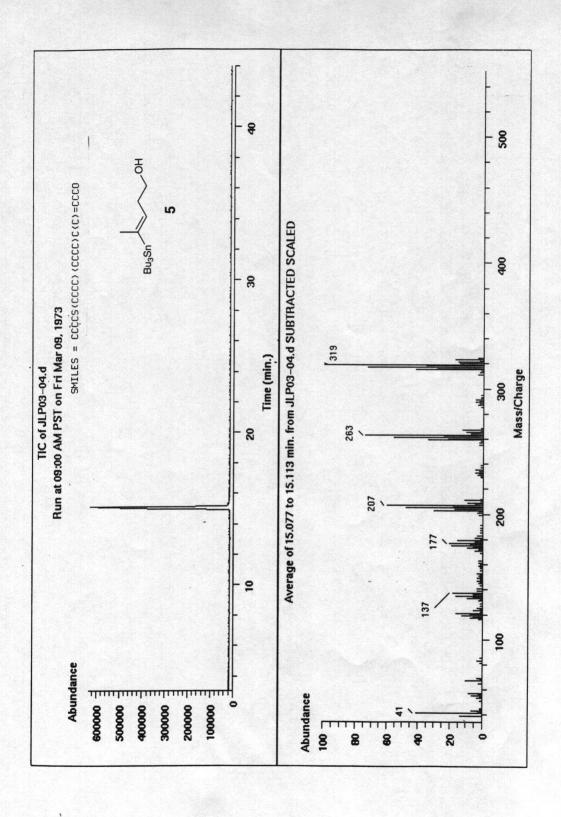
To a stirred solution of 13 (84/6) (6.5 mg, 0.0194 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added Dess-Martin periodinane (12.4 mg, 0.0291 mmol). The reaction mixture was stirred under argon at room temperature and monitored by TLC. After disappearance of the starting material, the mixture was poured into a separating funnel containing a saturated aqueous $Na_2S_2O_3/NaHCO_3$ solution (2 mL, 1/1) and shaken vigorously for 5 mn. The aqueous layer

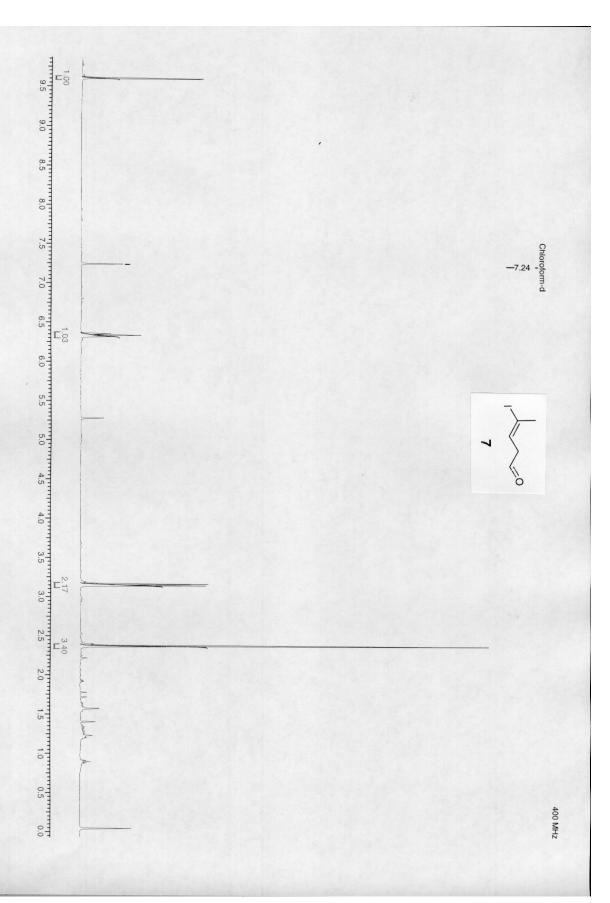
saturated aqueous NaHCO₃ solution, dried over MgSO₄ and concentrated under vacuum to give crude aldehyde **2** (6.20 mg, 96%). 1 H NMR (500 MHz, C₆D₆) 1.47 (s, 3H), 1.50 (s, 3H), 1.58 (s, 3H), 1.74 (s, 3H), 1.82 (s, 3H), 2.21 (m, 2H), 4.59 (d, J = 13.8 Hz, 1H), 4.76 (d, J = 13.8 Hz, 1H), 5.28 (t, J = 6.3 Hz, 1H), 5.43 (s, 1H), 5.83 (t, J = 7.4 Hz, 1H), 6.03 (d, J = 7.1 Hz, 1H), 9.86 (d, J = 7.1 Hz, 1H); %). 1 H NMR (300 MHz, CDCl₃) 1.80 (s, 3H), 1.81 (s, 3H), 1.87 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 2.53 (m, 2H), 5.00 (d, J = 13.8 Hz, 1H), 5.10 (d, J = 13.8 Hz, 1H), 5.32 (m, 1H), 5.33 (s, 1H), 5.67 (bt, J = 7.35 Hz, 1H), 6.12 (d, J = 7.1 Hz, 1H), 10.09 (d, J = 7.1 Hz, 1H); 13 C NMR (75 MHz, C₆D₆) 17.90, 20.13, 20.16, 20.98, 24.56, 32.79, 59.13, 72.98, 86.42, 94.55, 106.15, 122.48, 128.99, 129.72, 147.93, 154.00, 169.24, 169.56, 189.52.

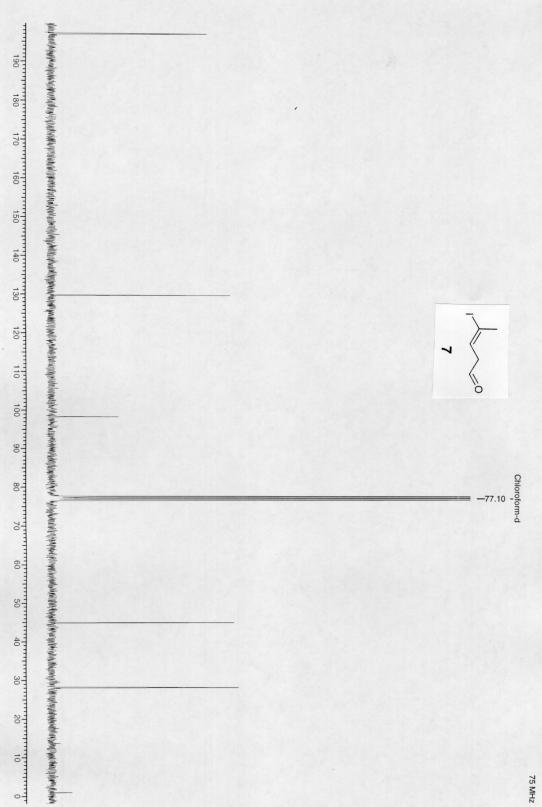
iso-Caulerpenyne

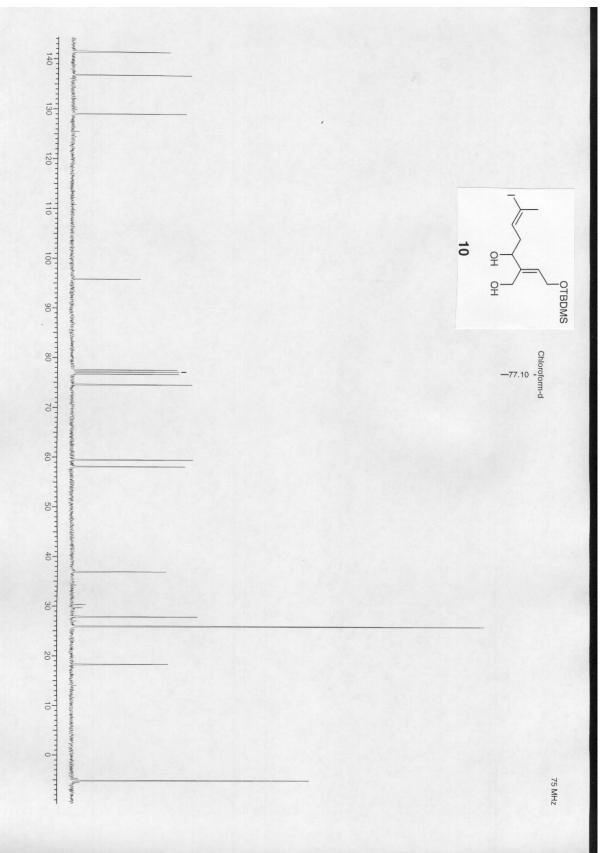
A solution of Taxifolial A **2** (44 mg, 0.132 mmol), KOAc (19.5 mg, 0.198 mmol), acetic anhydride (0.037 mL, 0.058 mmol) in benzene (3 mL) was heated at reflux for 48 h. After disappearance of the starting material, the mixture was concentrated under vacuum. The crude product was then purified by flash chromatography (hexane-Et₂O, 8/2) giving 43.6 mg (88%). 1 H NMR (500 MHz, CDCl₃) 1.79 (s, 3H), 1.80 (s, 3H), 1.86 (s, 3H), 2.02 (s, 3H), 2.19 (s, 6H), 2.36 (td, J = 7.3; 17.7, 1H), 2.54 (td, J = 7.3; 17.7, 1H), 5.18 (d, J = 7.3 Hz, 1H), 5.32 (s, 1H), 5.66 (bt, J = 7.3 Hz, 1H), 5.86 (t, J = 7.3 Hz, 1H), 7.22 (d, J = 7.3 Hz, 1H), 7.81 (s, 1H). 13 C NMR (125 MHz, CDCl₃) 17.79, 20.85, 20.89, 21.02, 21.16, 24.90, 32.00, 68.73, 85.20, 94.15, 103.59, 105.29, 116.85, 121.48, 129.89, 135.17, 137.63, 148.24, 167.23, 167.44, 170.03.

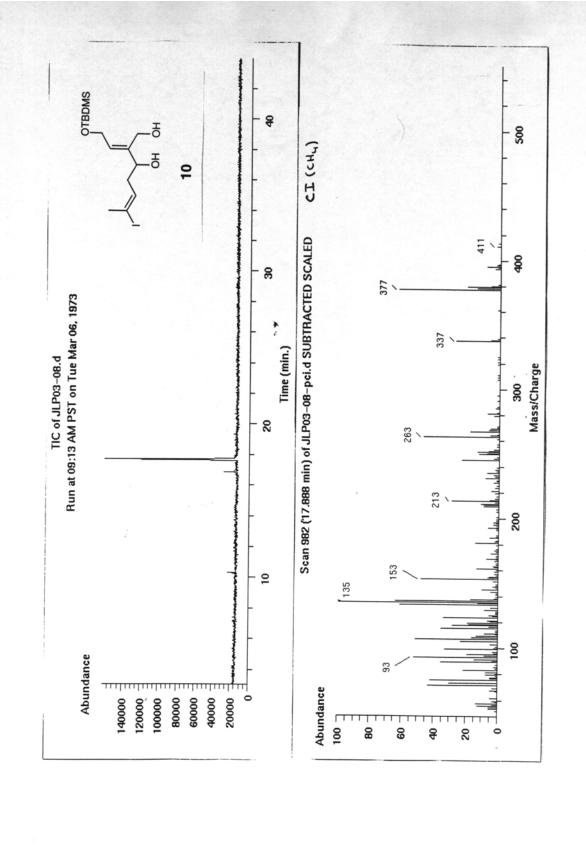
iso-caulerpenyne: Noesy analysis (see spectra)

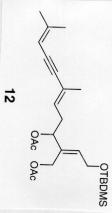




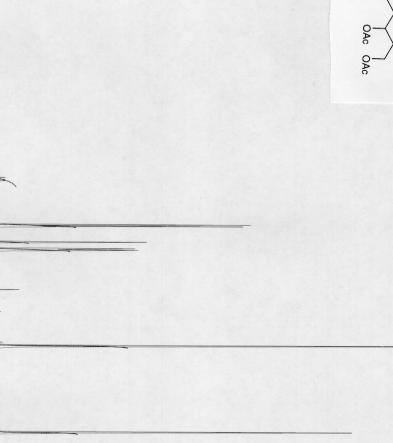








400 MHz



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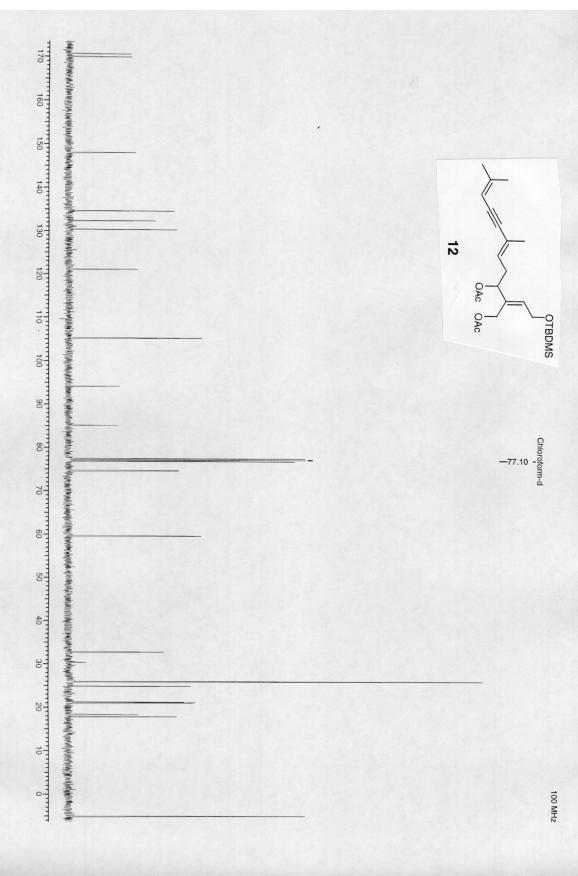
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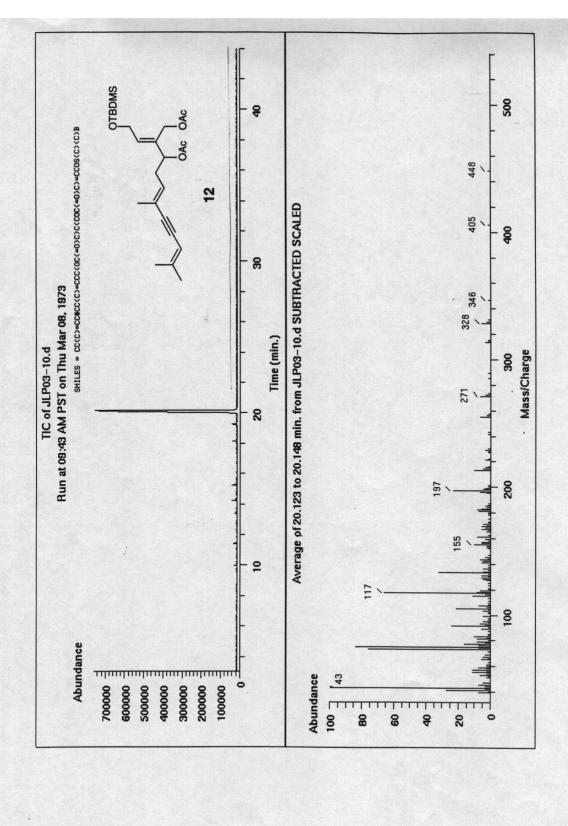
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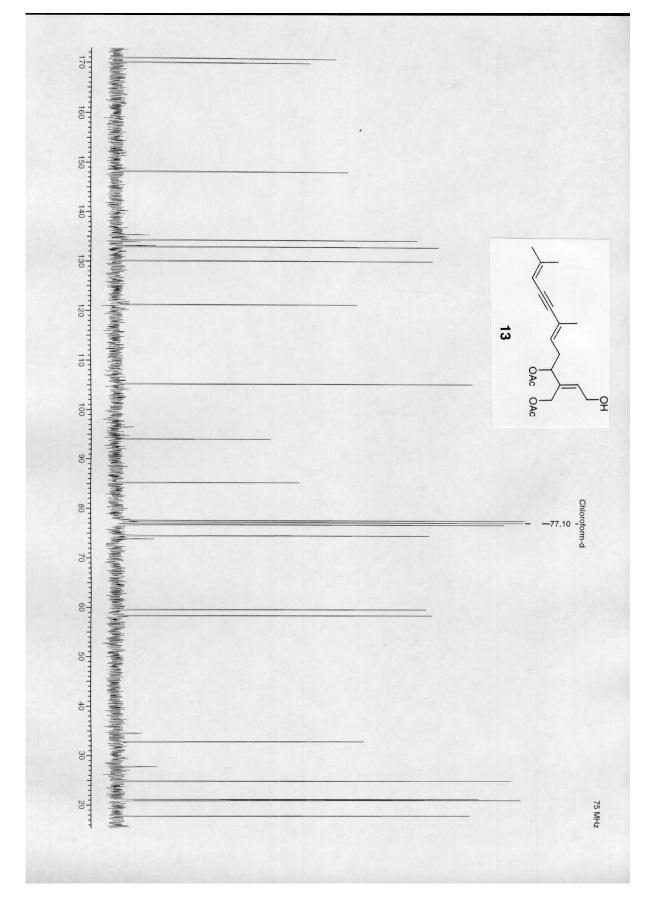
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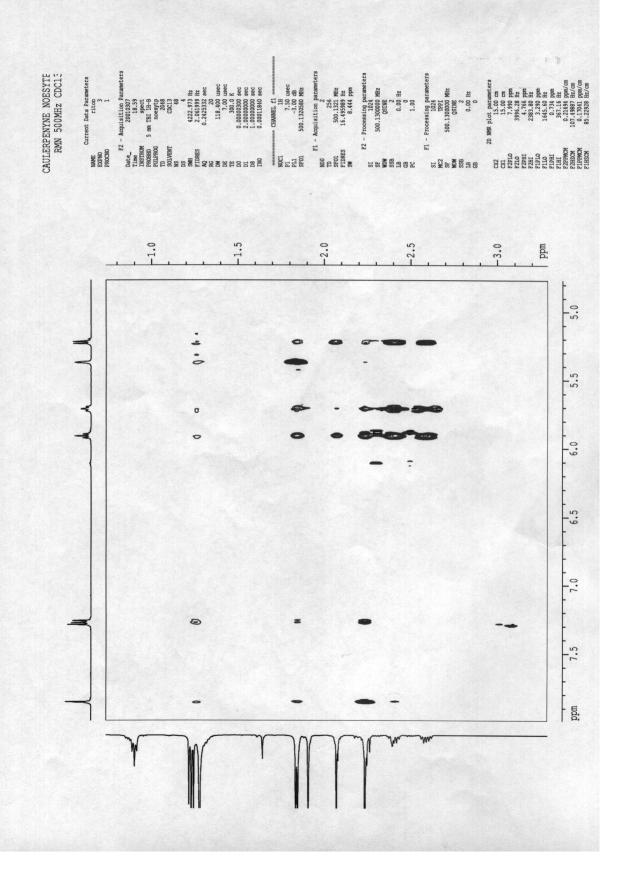
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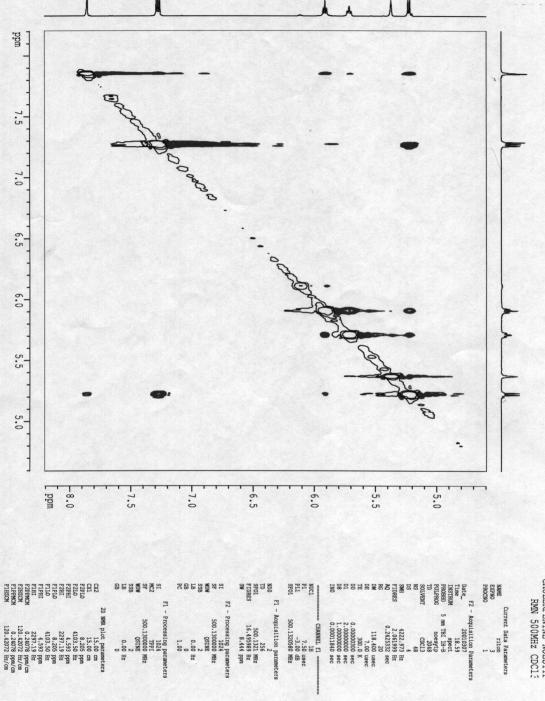






500 MHz





CAULERPENYNE NOESYTE RMN 500MHz CDC13