Mechanistic Dichotomy in CpRu(CH₃CN)₃PF₆ Catalyzed Enyne Cycloisomerizations.

Supplementary Material

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4.4-Bis(methoxycarbonyl)-oct-6(E)-en-1-yne 2a

To a solution of alkyne 1a (200 mg, 1.17 mmol) and cesium carbonate (570 mg, 1.75 mmol) in acetone (3 mL) was added (*E*)-crotyl bromide (240 μ L, 2.35 mmol) and the resulting suspension refluxed for 12h. The reaction mixture was diluted with diethyl ether (5 mL), filtered, the solid residue washed with diethyl ether (2 x 5 mL) and the filtrate concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded 2a (245 mg, 93%) as a colorless liquid. Ratio of *E:Z* isomers determined using ¹H-NMR by integration of the propargylic methine: a doublet at 2.71 ppm for (*E*)-2a and a doublet at 2.77 ppm for (*Z*)-2b.

IR (film): 3289, 2999, 2956 2858, 1740, 1438, 1285, 1212, 1136, 1055, 973 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.54 (dm, J = 15.1 Hz, 1H), 5.15 (dm, J = 15.1 Hz, 1H), 3.67 (s, 6H), 2.71 (d, J = 2.7 Hz, 2H), 2.67 (d, J = 7.5 Hz, 2H), 1.96 (t, J = 2.7 Hz, 1H), 1.5 (d, J = 7.5 Hz, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 170.2, 130.6, 123.7, 78.8, 71.3, 56.9, 52.6, 35.2, 22.4, 18.0.

4,4-Bis(methoxycarbonyl)-oct-6(Z)-en-1-yne 2b

Utilizing the procedure described for 2a, 2b (300 mg, 91%) was prepared from alkyne 1a (250 mg, 1.46 mmol), cesium carbonate (710 mg, 2.18 mmol) and (Z)-crotyl bromide (300 μ L, 2.94 mmol) in acetone (5 mL).

IR (film): 3285, 2959 2855, 1739, 1436, 1262, 1212, 1136, 1053, 951, 834 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.59 (dm, J = 10.8 Hz, 1H), 5.12 (dm, J = 10.8 Hz, 1H), 3.68 (s, 6H), 2.77 (d, J = 6.8 Hz, 2H), 2.73 (d, J = 2.7 Hz, 2H), 1.96 (t, J = 2.7 Hz, 1H), 1.58 (d, J = 6.8 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 170.2, 129.0, 122.8, 79.0, 71.3, 56.9, 52.7, 35.2, 29.3, 12.8.

5,5-Bis(ethoxycarbonyl)-non-7-en-1-yne 2c

To a solution of alkyne **1b** (100 mg, 0.471 mmol) and cesium carbonate (300 mg, 0.921 mmol) in acetone (3 mL) was added crotyl bromide (100 μL, 0.980 mmol) and the resulting suspension heated at reflux for 12h. The reaction mixture was diluted with diethyl ether (5 mL), filtered, the solid residue washed with diethyl ether (2 x 5 mL) and the filtrate concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether:diethyl ether afforded **2c** (114 mg, 91%) as a colorless liquid. The ratio of *E:Z* isomers determined using ¹H-NMR by integration of the allylic methine: a doublet at 2.48 ppm for (*E*)-**2c** and a doublet at 2.58 ppm for (*Z*)-**2c**.

IR (film): 3289, 2999, 2956 2858, 1740, 1438, 1285, 1212, 1136, 1055, 973 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.43 (dm, J = 15.2 Hz, 1H), 5.16 (dm, J = 15.2 Hz, 1H), 4.08 (m, 4H), 2.48 (d, J = 7.3 Hz, 2H), 2.10-2.00 (m, 4H), 1.88 (t, J = 2.3 Hz, 1H), 1.55 (d, J = 7.6 Hz, 3H), 1.15 (t, J = 7.4 Hz, 6H). 13 C-NMR (125 MHz, CDCl₃): δ 170.6, 129.8, 124.1, 83.2, 68.5, 61.3, 56.8, 35.8, 31.1, 17.8, 13.9, 13.6.

4,4-Bis(phenylsulfonyl)-oct-6-en-1-yne 2d

To a solution of alkyne 1c (250 mg, 0.749 mmol) in DMF (5 mL), at 0 °C, was added 60% sodium hydride (35 mg, 0.875 mmol). After the effervescence had stopped, to the reaction mixture was added a solution of crotyl bromide (125 mg, 0.926 mmol). After stirring at room temperature for 12h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (25 mL), water (25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 1:1 petroleum ether: diethyl ether afforded a 4.6:1 mixture of (E)- and (Z)-2d (215 mg, 74% yield). Ratio of E:Z isomers was determined using 1 H-NMR by integration of the propargylic methine: a doublet at 3.15 ppm for (E)-2d and a doublet at 3.09 ppm for (Z)-2d.

IR (film): 3275, 3066, 2968, 2927, 1447, 1332, 1311 1147, 1078, 726, 687 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 8.11 (d, J = 7.9 Hz, 4H), 7.71 (t, J = 7.9 Hz, 2H), 7.58 (t, J = 7.9 Hz, 2H), 5.75-5.61 (m, 2H), 3.15 (d, J = 2.8 Hz, 2H), 3.05 (d, J = 6.6 Hz, 2H), 2.09 (t, J = 2.8 Hz, 1H), 1.73 (d, J = 6.6 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 136.5, 134.7, 132.5, 131.6, 128.5, 121.4, 89.0, 74.2, 32.2, 20.7, 18.2. HRMS Calc'd for C₂₀H₁₉O₄S₂ (M - H⁺): 387.0725. Found: 387.0734.

Additional signals for the Z-isomer: 1 H-NMR (500 MHz, CDCl₃): δ 3.20 (d, J = 2.8 Hz, 2H), 3.09 (d, J = 4.9 Hz, 2H), 2.10 (t, J = 2.8 Hz, 1H), 1.61 (d, J = 4.9 Hz, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 131.5, 128.6, 75.9.

4,4-Bis(phenylsulfonyl)-8-methyl-non-7-en-1-yne 2e

To a solution of alkyne **1c** (250 mg, 0.749 mmol) in DMF (5 mL), at 0 °C, was added 60% sodium hydride (35 mg, 0.875 mmol). After the effervescence had stopped, to the reaction mixture was added a solution of 5-bromo-2-methyl-pent-2-ene (150 mg, 0.920 mmol). After stirring at room temperature for 12h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (25 mL), water (25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 1:1 petroleum ether: diethyl ether afforded **2e** (268 mg, 86% yield).

IR (film): 3275, 3066, 2968, 2927, 1447, 1332, 1311 1147, 1078, 726, 687 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 8.12 (d, J = 7.5 Hz, 4H), 7.74 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 7.5 Hz, 2H), 5.56 (t, J = 7.2 Hz, 1H), 3.26 (d, J = 2.8 Hz, 2H), 2.50 (dd, J = 9.0 and 7.5 Hz, 2H), 2.30 (m, 2H), 2.11 (t, J = 2.8 Hz, 1H), 1.70 (s, 3H), 1.68 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 136.5, 134.7, 131.3, 128.6, 102.7, 94.5, 89.3, 74.0, 28.7, 25.7, 17.9. HRMS Calc'd for $C_{21}H_{22}O_4S_2$: 402.0960. Found: 402.0954.

Methyl 5,5-bis(methoxycarbonyl)-non-7(Z)-en-2-ynoate 3a

To a solution of di-*iso*-propylamine (74 μL, 0.522 mmol) in THF (2 mL), at -78 °C, was added 1.6M *n*-butyllithium (0.325 mL, 0.520 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution enyne **2b** (100 mg, 0.446 mmol) in THF (2 mL). After stirring at -78 °C for 1h, the reaction mixture was treated with methyl chloroformate (50 μL, 0.646 mmol), stirred at -78 °C for 30 min. then warmed to room temperature. The reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded **3a** (72 mg, 58%) as a colorless liquid.

IR (film): 3020, 2959, 2243, 1739, 1719, 1436, 1262, 1212, 1079, 951, 824, 753 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.68 (dm, J = 11.0 Hz, 1H), 5.16 (dm, J = 11.0 Hz, 1H), 3.77 (s, 6H), 3.75 (s, 3H), 2.94 (s, 2H), 2.84 (d, J = 7.6 Hz, 2H), 1.67 (d, J = 6.9 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 169.8, 153.6, 129.6, 122.3, 83.9, 75.1, 56.5, 53.0 52.6, 29.7, 22.7, 12.9.

4,4-Bis(methoxycarbonyl)-1-trimethylsilyl-oct-6(Z)-en-1-yne 3b

To a solution of di-*iso*-propylamine (74 μ L, 0.522 mmol) in THF (2 mL), at -78 °C, was added 1.6M *n*-butyllithium (0.325 mL, 0.520 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution enyne **2b** (100 mg, 0.446 mmol) in THF (2 mL). After stirring at -78 °C for 1h, the reaction mixture was treated with chlorotrimethylsilane (75 μ L, 0.592 mmol), stirred at -78

°C for 30 min. then warmed to room temperature. The reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether: diethyl ether afforded **3b** (104 mg, 78% yield) as a colorless liquid.

IR (film): 2957, 2180, 1739, 1741, 1437, 1292, 1251, 1210, 1028, 845 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.62 (dm, J = 10.8 Hz, 1H), 5.13 (dm, J = 10.8 Hz, 1H), 3.70 (s, 6H), 2.80 (d, J = 7.7 Hz, 2H), 2.77 (s, 2H), 1.63 (d, J = 6.8 Hz, 3H), 0.98 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 170.4, 129.0, 123.1, 101.6, 88.0, 57.2, 52.7, 29.5, 23.8, 12.9, -0.1.

4,4-Bis(methoxycarbonyl)-7-cyclohexyl-hept-6(E)-en-1-yne 4a

To a solution of alkyne 1a (100 mg, 0.588 mmol), tetrakis(triphenylphosphine) palladium(0) (28 mg, 0.024 mmol), *N,O*-bis(trimethylsilyl)acetamide (30 μL, 0.121 mmol) and 60% sodium hydride (26 mg, 0.650 mmol) in THF (3 mL) was added a solution of 1-acetoxy-1-cyclohexyl-2-propene (90 mg, 0.500 mmol) in THF (1 mL). After stirring at room temperature for 8h, the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate, dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether: diethyl ether afforded 4a (118 mg, 81% yield) as a colorless liquid.

IR (film): 3291, 2925, 2852, 1740, 1438, 1290, 1205, 1058, 973 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.48 (dd, J = 15.5 and 6.9 Hz, 1H), 5.15 (dt, J = 15.5 and 7.5 Hz, 1H), 3.69 (s, 6H), 2.74 (d, J = 2.6 Hz, 2H), 2.69 (d, J = 7.5 Hz, 2H), 1.98 (t, J = 2.6 Hz, 1H), 1.92-1.83 (m, 1H), 1.69-1.57 (m 5H), 1.26-0.96 (m, 5H). ¹³C-NMR (125 MHz, CDCl₃): δ 170.2, 142.2, 120.0, 78.9, 71.3, 57.2, 52.6, 35.3, 26.1, 25.8, 22.5.

4,4-Bis(methoxycarbonyl)-7-cyclobutyl-hept-6(E)-en-1-yne 4b

To a solution of alkyne **1a** (50 mg, 0.294 mmol), tetrakis(triphenylphosphine) palladium(0) (14 mg, 0.012 mmol), N, O-bis(trimethylsilyl)acetamide (15 μ L, 0.060 mmol) and 60% sodium hydride (13 mg, 0.325 mmol) in THF (1 mL) was added a solution of 1-acetoxy-1-cyclobutyl-2-propene (40 mg, 0.263 mmol) in THF (1 mL). After stirring at room temperature for 8h, the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate, dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether: diethyl ether afforded **4b** (58 mg, 84% yield) as a colorless liquid. IR (film): 3294, 2956, 2850, 1738, 1438, 1288, 1203, 1057, 973 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.67 (dd, J = 15.2 and 6.8 Hz, 1H), 5.11 (dtd, J = 15.2, 7.5 and 1.2 Hz, 1H), 3.71 (s, 6H), 2.76 (d, J = 2.5 Hz, 2H), 2.71 (d, J = 7.5 Hz, 2H), 2.08-2.00 (m, 3H),

1.99 (t, J = 2.5 Hz, 1H), 1.86-1.70 (m, 4H). ¹³C-NMR (125 MHz, CDCl₃): δ 170.3, 140.7, 120.4, 78.9, 71.3, 57.2, 52.7, 35.2, 28.6, 22.6, 18.5.

4,4-Bis(methoxycarbonyl)-12,12-dimethoxy-dodec-6(E)-en-1-yne 4c

To a solution of alkyne **1a** (50 mg, 0.294 mmol), tetrakis(triphenylphosphine) palladium(0) (14 mg, 0.012 mmol), N, O-bis(trimethylsilyl)acetamide (15 μ L, 0.060 mmol) and 60% sodium hydride (13 mg, 0.325 mmol) in THF (1 mL) was added a solution of 3-acetoxy-8,8-dimethoxy-1-octene(60 mg, 0.261 mmol) in THF (1 mL). After stirring at room temperature for 8h, the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate, dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether: diethyl ether afforded **4c** (66 mg, 75% yield) as a colorless liquid. IR (film): 3293, 3308, 2930, 2859, 1735, 1439, 1288, 1210, 1058, 971 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.58 (dt, J = 15.2 and 7.1 Hz, 1H), 5.18 (dt, J = 15.2 and 7.5 Hz, 1H), 4.36 (t, J = 6.5 Hz, 1H), 3.75 (s, 6H), 3.33 (s, 6H), 2.79 (d, J = 2.2 Hz, 2H), 2.76 (d, J = 7.5 Hz, 2H), 2.08-2.00 (m, 2H), 2.01 (t, J = 2.2 Hz, 1H), 1.84-1.70 (m, 2H), 1.40-1.26 (m, 4H).

4,4-Bis(phenylsulfonyl)-6-methyl-oct-6-en-1-yne 5

To a solution of tiglyl carbonate (100 mg, 0.690 mmol), Pd₂dba₃•CHCl₃ (15 mg, 0.019 mmol) and triphenylphosphine (23 mg, 0.088 mmol) in methylene chloride (3 mL) was added a solution of alkyne 1c (200 mg, 0.599 mmol) and triethylamine (92 µL, 0.66 mmol) in methylene chloride (3 mL). After stirring at room temperature for 6h, the solution was washed with 1N hydrochloric acid (15 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 1:1 petroleum ether: diethyl ether afforded a 12:1 mixture of 5 and its regioisomer (171 mg, 71% yield). Ratio of primary to secondary attack was determined using ¹H-NMR by integration of the olefinic proton: a quartet at 5.60 ppm for primary attack (5) and a singlet at 4.54 ppm for the two protons of the terminal methylene resulting from secondary attack.

IR (film): 3273, 3065, 2922, 1448, 1335, 1311 1146, 1077, 728, 687 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 8.07 (d, J = 7.5 Hz, 4H), 7.73 (t, J = 7.5 Hz, 2H), 7.59 (t, J = 7.5 Hz, 2H), 5.60 (q, J = 7.6 Hz, 1H), 3.36 (d, J = 2.8 Hz, 2H), 3.16 (s, 2H), 2.08 (t, J = 2.8 Hz, 1H), 1.76 (s, 3H), 1.68 (d, J = 7.6 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 137.5, 134.6, 131.7, 128.4, 128.1, 127.9, 90.1, 75.3, 49.2, 38.7, 22.5, 16.9, 13.9. Anal. Calc'd for $C_{21}H_{22}O_4S_2$: C, 62.66; H, 5.51; S, 15.93. Found: C, 62.57; H, 5.43; S, 16.24.

6,6-Bis(methoxycarbonyl)-dec-8-en-1-yne 6

To a solution of diethyl crotylmalonate (100 mg, 0.573 mmol) and cesium carbonate (350 mg, 1.07 mmol) in acetone (5 mL) was added 5-iodopent-1-yne (250 mg, 1.29 mmol) and the resulting suspension heated at reflux for 12h. The reaction mixture was diluted with diethyl ether (5 mL), filtered, the solid residue washed with diethyl ether (2 x 5 mL) and the filtrate concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether:diethyl ether afforded $\bf 6$ (123 mg, 85%) as a colorless liquid. Ratio of $\bf E:\bf Z$ isomers determined using ¹H-NMR by integration of the propargylic methine: a doublet of doublets at 2.55 ppm for ($\bf E$)- $\bf 6$ and a doublet at 2.65 ppm for ($\bf Z$)- $\bf 6$.

IR (film): 3293, 2954, 1735, 1436, 1378, 1271, 1202, 1134, 1091, 1016, 970 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.52 (dm, J = 15.1 Hz, 1H), 5.22 (dm, J = 15.1 Hz, 1H), 3.69 (s, 6H), 2.55 (dd, J = 7.5 and 0.9 Hz, 2H), 2.16 (dt, J = 7.0 and 2.5 Hz, 2H),1.99-1.89 (m, 2H), 1.97 (t, J = 2.5 Hz, 1H), 1.62 (d, J = 6.1 Hz, 3H), 1.47-1.35 (m, 2H). 13 C-NMR (125 MHz, CDCl₃): δ 171.8, 129.9, 124.4, 83.7, 68.6, 57.5, 52.3, 35.8, 31.4, 23.2, 18.5, 17.9.

4-Methyl-N-(3-methyl-but-2-enyl)-N-(prop-2-ynyl)-benzenesulfonamide 8a

To a suspension of amine 7a (290 mg, 1.03 mmol) in DMF (5 mL) was added 60% sodium hydride (45 mg, 1.13 mmol). After the effervescence had stopped, crotyl bromide (180 μL, 1.56 mmol) followed by sodium iodide (15 mg, 0.10 mmol) was added. After stirring at room temperature for 2h, the solution was quenched with 1N sodium bisulfate (25 mL) and extracted with diethyl ether (3 x 25 mL). The combined organic extracts were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded 8a (223 mg, 79%) as a colorless liquid.

IR (film): 3276, 2972, 2923, 1598, 1446, 1346, 1161, 1093, 896, 814, 743, 660 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 7.71 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 5.07 (tt, J = 7.3 and 1.3 Hz, 1H), 4.04 (d, J = 2.4 Hz, 2H), 3.78 (d, J = 7.3 Hz, 2H), 2.40 (s, 3H), 1.96 (t, J = 2.4 Hz, 1H), 1.69 (s, 3H), 1.59 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 143.3, 139.0, 136.1, 129.3, 127.7, 117.9, 77.0, 73.3, 43.9, 35.3, 25.8, 21.5, 17.8.

N-But-3-ynyl-4-methyl-N-(3-methyl-but-2-enyl)-benzenesulfonamide 8b

To a suspension of amine **7b** (50 mg, 0.169 mmol) in DMF (1 mL) was added 60% sodium hydride (8 mg, 0.20 mmol). After the effervescence had stopped, crotyl bromide (30 μL, 0.26 mmol) followed by sodium iodide (3 mg, 0.02 mmol) was added. After stirring at room temperature for 2h, the solution was quenched with 1N sodium bisulfate (5 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic extracts were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded **8b** (40 mg, 82%) as a colorless liquid.

IR (film): 3290, 2971, 2926, 2870, 1599, 1450, 1341, 1158, 1094, 982, 924, 815, 743, 723, 655 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 7.66 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 4.98 (tt, J = 7.0 and 1.4 Hz, 1H), 3.80 (d, J = 7.0 Hz, 2H), 3.22 (t, J = 7.6 Hz, 2H), 2.43 (td, J = 7.6 and 2.5 Hz, 2H), 2.40 (s, 3H), 1.94 (t, J = 2.5 Hz, 1H), 1.65 (s, 3H), 1.60 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 143.2, 137.3, 136.9, 129.6, 127.1, 118.8, 81.2, 69.9, 46.0, 45.8, 25.7, 21.4, 19.5, 17.8. Anal Calc'd for C₁₆H₂₁NO₂S: C, 65.95; H, 7.26; N, 4.81. Found: C, 66.11; H, 7.12; N, 4.76.

1-(1-Phenylprop-2-ynyloxy)-3-methyl-but-2-ene 8c

To a suspension of 60% sodium hydride (180 mg, 4.5 mmol) in dimethoxyethane (20 mL) was added alcohol 7c (500 μ L, 4.11 mmol). The resulting orange suspension was stirred at room temperature for 5 min. and crotyl bromide (700 μ L, 6.07 mmol) followed by sodium iodide (60 mg, 0.40 mmol) was added. After stirring at room temperature for 5h, the solution was quenched with 1N sodium bisulfate (25 mL) and extracted with diethyl ether (2 x 25 mL). The combined organic extracts were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether afforded 8c (640 mg, 78%) as a colorless liquid.

IR (film): 3291, 3064, 3031, 2973, 2914, 2860, 1672, 1494, 1452, 1379, 1057, 757, 698, 652 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 7.52 (dm, J = 7.3 Hz, 2H), 7.36 (tm, J = 7.3 Hz, 2H), 7.31 (m, 1H), 5.38 (m, 1H), 5.18 (d, J = 2.0 Hz, 1H), 4.16 (dd, J = 11.3 and 6.8 Hz, 1H), 4.11 (dd, J = 11.3 and 7.5 Hz, 1H), 2.63 (d, J = 2.0 Hz, 1H),1.75 (s, 3H), 1.68 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 138.3, 138.2, 128.4, 128.3, 127.4, 120.3, 81.9, 75.3, 70.0, 64.6, 25.8, 18.0. HRMS Calc'd for C₁₄H₁₅O (M - H⁺): 199.1123. Found: 199.1128.

3-(4-Methoxybenzyloxy)-7-methyl-oct-6-en-1-yne

To a solution of aldehyde **9a** (250 mg, 2.23 mmol) in THF (10 mL), at -78 °C, was added 0.5M ethynylmagnesium bromide (6 ml, 3.0 mmol). The resulting solution was slowly warmed to 0 °C and stirred for 1h. The reaction mixture was quenched with 1N sodium bisulfate (50 mL) and extracted with diethyl ether (3 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded the propargyl alcohol (284 mg, 85%) as a colorless liquid.

¹H-NMR (500 MHz, CDCl₃): 5.10 (tt, J = 7.2 and 1.4 Hz, 1H), 4.34 (td, J = 7.3 and 2.1 Hz, 1H), 2.45 (d, J = 2.1 Hz, 1H), 2.15 (q, J = 7.3 Hz, 1H), 2.00 (br s, 1H), 1.73 (m, 2H), 1.67 (s, 3H), 1.61 (s, 3H).

To a solution of the propargyl alcohol (284 mg, 1.92 mmol) in dimethoxyethane (10 mL), at 0 °C, was added 0.5M potassium hexamethyldisilamide (4 mL, 2.0 mmol). The resulting

yellow solution was treated with 4-methoxybenzyl chloride (0.40 mL, 2.95 mmol). After 12h at 80 °C, the solution was quenched with 1N sodium bisulfate (25 mL) and extracted with diethyl ether (3 x 15 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 10:1 petroleum ether: diethyl ether afforded the titled compound (221 mg, 43%) as a colorless liquid.

¹H-NMR (500 MHz, CDCl₃): 7.33 (d, J = 8.3 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 5.11 (tt, J = 7.3 and 1.3 Hz, 1H), 4.77 (d, J = 11.2 Hz, 1H), 4.46 (d, J = 11.2 Hz, 1H), 4.09 (td, J = 7.0 and 2.0 Hz, 1H), 3.84 (s, 3H), 2.51 (d, J = 2.0 Hz, 1H), 2.19 (q, J = 7.5 Hz, 1H), 2.00 (br s, 1H), 1.81 (m, 2H), 1.71 (s, 3H), 1.64 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 159.2, 132.4, 129.9, 129.6, 123.2, 113.7, 83.0, 73.7, 70.1, 55.2, 35.7, 25.7, 23.7, 17.7.

Ethyl 4-hydroxy-8-methyl-non-7-en-2-ynoate 11b

To a solution of di-*iso*-propylamine (0.75 mL, 5.35 mmol) in THF (10 mL), at -78 °C, was added 1.5M *n*-butyllithium (3.5 mL, 5.25 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution ethyl propiolate (0.54 mL, 5.33 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with aldehyde **9a** (500 mg, 4.46 mmol), stirred at -78 °C for 30 min. then warmed to room temperature. The reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded **11b** (674 mg, 72 %) as a colorless liquid.

IR (film): 3414, 2969, 2929, 2236, 1714, 1447, 1368, 1248, 1066, 1025, 752 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): 5.13 (tt, J = 7.3 and 1.3 Hz, 1H), 4.51 (t, J = 6.5 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.23-2.14 (m, 3H), 1.82 (qd, J = 6.5 and 3.0 Hz, 2H), 1.71 (s, 3H), 1.65 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 153.4, 133.3, 122.6, 87.3, 76.5, 62.1, 61.6, 36.7, 25.7, 23.5, 17.7, 13.9.

3,7-Dimethyl-oct-6-en-1-yn-3-ol 11c

To a solution of ketone **9b** (0.50 mL, 3.39 mmol) in THF (10 mL), at -78 °C, was added 0.5M ethynylmagnesium bromide (10 ml, 5.0 mmol). The resulting solution was slowly warmed to 0 °C and stirred for 1h. The reaction mixture was quenched with 1N sodium bisulfate (50 mL) and extracted with diethyl ether (3 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded propargyl alcohol **11c** (490 mg, 95%) as a colorless liquid.

IR (film): 3396, 3308, 2972, 2930, 2859, 1451, 1376, 1120, 1021, 808 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): 5.19 (tt, J = 7.3 and 1.4 Hz, 1H), 2.49 (s, 1H), 2.32 (dq, J = 14.2 and 7.3 Hz,

1H), 2.20 (dq, J = 14.2 and 7.3 Hz, 1H), 1.75-1.70 (m, 2H), 1.72 (d, J = 1.4 Hz, 3H), 1.68 (s, 3H), 1.52 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 132.7, 123.6, 87.7, 71.5, 68.3, 43.1, 29.8, 25.7, 23.5, 17.7.

Ethyl 4-hydroxy-4-methyl-tridec-7(E)-en-2-ynoate 11e

To a solution of di-iso-propylamine (1.2 mL, 8.56 mmol) in THF (25 mL), at -78 °C, was added 1.4M *n*-butyllithium (5.8 mL, 8.12 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution ethyl propiolate (0.66 mL, 6.80 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with ketone **9c** (910 mg, 5.42 mmol), stirred at -78 °C for 30 min. and then warmed to room temperature. The reaction mixture was diluted with diethyl ether (50 mL), washed with 1N sodium bisulfate (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded **11e** (1.13 mg, 78 %) as a colorless liquid.

IR (film): 3414, 2958, 2927, 2856, 2238, 1715, 1450, 1368, 1245, 1033, 969 752 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.52 (dt, J = 15.4 and 6.6 Hz, 1H), 5.44 (dt, J = 15.4 and 6.6 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 2.56 (br s, 1H), 2.32-2.17 (m, 2H), 2.27 (dt, J = 7.1 and 6.8 Hz, 2H), 1.79 (t, J = 7.8 Hz, 2H), 1.54 (s, 3H), 1.38-1.24 (m, 6H), 1.32 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 153.5, 131.8, 128.8, 90.1, 75.4, 68.1, 62.1, 42.4, 32.5, 31.3, 29.1, 29.0, 27.8, 22.5, 14.0 13.9. HRMS. Calc'd for $C_{16}H_{25}O_{3}$ (M - H+): 265.1804. Found: 265.1807.

Ethyl 4-methyl-4-hydroxy-non-7(Z)-en-2-ynoate 11f

To a solution of di-*iso*-propylamine (0.75 mL, 5.35 mmol) in THF (10 mL), at -78 °C, was added 1.5M *n*-butyllithium (3.5 mL, 5.25 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution ethyl propiolate (0.54 mL, 5.33 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with *cis*-heptenone **9d** (500 mg, 4.46 mmol), stirred at -78 °C for 30 min. and then warmed to room temperature. The reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded **11f** (777 mg, 83 %) as a colorless liquid.

IR (film): 3415, 2983, 2936, 2237, 1712, 1452, 1369, 1250, 1135, 1030 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): 5.53 (dq, J = 11.0 and 6.7 Hz, 1H), 5.44 (dm, J = 11.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.44 (br s, 1H), 2.38 (m 1H), 2.24 (dd, J = 8.4 and 7.7 Hz, 2H), 1.67 (d, J = 6.7 Hz, 3H), 1.56 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ

153.5, 129.2, 125.3, 90.0, 75.5, 68.2, 62.1, 42.3, 29.0, 22.3, 14.0, 12.8. HRMS Calc'd for $C_{12}H_{18}O_3$: 210.1256. Found: 210.2152.

Ethyl 8-methyl-4-(trimethylsilyloxy)-non-7-en-2-ynoate 12b

To a solution of alcohol **11b** (300 mg, 2.17 mmol) in methylene chloride (10 ml) was added 2,6-lutidine (0.85 mL, 7.29 mmol) followed by *tert*-butyldimethylsilyl triflate (0.85 mL, 3.70 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (25 mL), washed with 1N hydrochloric acid (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 2% diethyl ether: petroleum ether afforded silyl ether **12b** (569 mg, 81 %) as a colorless liquid.

IR (film): 2957, 2951, 2859, 2237, 1717, 1472, 1365, 1246, 1095, 1052, 839, 779 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): 5.11 (tt, J = 7.1 and 1.4 Hz, 1H), 4.48 (t, J = 6.6 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.15 (m, 2H), 1.76 (m, 2H), 1.71 (d, J = 1.4 Hz, 3H), 1.63 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H), 0.92 (s, 9H), 0.17 (s, 3H), 0.13 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 153.5, 132.7, 123.0, 88.6, 76.1, 62.1, 61.9, 37.9, 25.7, 23.5, 18.1, 17.9, 14.0, -4.6, -5.2. Anal Calc'd for C₁₈H₃₂O₃Si: C, 66.62; H, 9.94. Found: C, 66.39; H, 9.75.

3,7-Dimethyl-3-(tert-butyldimethylsilyloxy)-oct-6-en-1-yne 12c

To a solution of alcohol **11c** (200 mg, 1.32 mmol) in methylene chloride (1 ml) was added 2,6-lutidine (0.50 mL, 4.42 mmol) followed by *tert*-butyldimethylsilyl triflate (0.50 mL, 2.18 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (25 mL), washed with 1N hydrochloric acid (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 2% diethyl ether: petroleum ether afforded silyl ether **12c** (284 mg, 81 %) as a colorless liquid.

IR (film): 3310, 2957, 2931, 2858, 1442, 1371, 1253, 1174, 1108, 994, 838, 777 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): 5.16 (tt, J = 7.4 and 1.3 Hz, 1H), 2.44 (s, 1H), 2.26-2.12 (m, 2H), 1.71 (s, 3H), 1.70-1.58 (m, 2H), 1.65 (s, 3H), 1.47 (s, 3H), 0.89 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 131.6, 124.0, 88.1, 71.9, 68.9, 45.1, 30.9, 25.9, 25.7, 23.3, 18.0, 17.5, -2.9, -3.2.

Methyl 4,8-Dimethyl-4-(tert-butyldimethylsilyloxy)-non-7-en-2-ynoate 12d

To a solution of alkyne 12c (100 mg, 0.376 mmol) in THF (4 ml) was added 1.0M n-butyllithium (0.4 mL, 0.4 mmol). After stirring at -78 °C for 30 min., methyl chloroformate (50 μ L, 0.660 mmol) was added and the reaction mixture warmed to room temperature. After an addition 30 min., the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash

chromatography eluting with 2% diethyl ether: petroleum ether afforded silyl ether 12d (109 mg, 89 %) as a colorless liquid.

IR (film): 2957, 2931, 2859, 2233, 1752, 1722, 1436, 1254, 1171, 1046, 837, 778 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): 5.14 (tt, J = 7.1 and 1.1 Hz, 1H), 3.80 (s, 3H), 2.26-2.10 (m, 2H), 1.72-1.65 (m, 2H), 1.70 (s, 3H), 1.64 (s, 3H), 1.51 (s, 3H), 0.90 (s, 9H), 0.23 (s, 3H), 0.21 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 154.0, 132.0, 123.5, 91.5, 75.8, 68.9, 52.7, 44.5, 30.1, 25.6(2), 23.2, 18.0, 17.5, -3.0, -3.3. HRMS Calc'd for $C_{17}H_{29}O_{3}Si$ (M+ - CH₃): 309.1885. Found: 309.1891.

Ethyl 4-methyl-4-(tert-butyldimethylsiloxy)-tridec-7(E)-en-2-vnoate 12e

To a solution of alcohol **11e**(400 mg, 1.50 mmol) in methylene chloride (15 ml) was added 2,6-lutidine (0.59 mL, 5.06 mmol) followed by *tert*-butyldimethylsilyl triflate (0.59 mL, 2.57 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3% diethyl ether: petroleum ether afforded silyl ether **12e** (501 mg, 88 %) as a colorless liquid.

R (film): 2957, 2930, 2857, 2239, 1717, 1472, 1368, 1245, 1174, 1100, 1034, 837, 778 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.46 (dt, J = 15.4 and 5.9 Hz, 1H), 5.42 (dt, J = 15.4 and 5.7 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.25-2.12 (m, 2H), 1.98 (dt, J = 7.2 and 6.8 Hz, 2H), 1.79 (ddd, J = 10.3, 5.9 and 3.3 Hz, 2H), 1.50 (s, 3H), 1.39-1.26 (m, 6H), 1.33 (t, J = 7.2 Hz, 3H), 0.90 (s, 9H), 0.89 (t, J = 7.2 Hz, 3H), 0.22 (s, 3H), 0.20 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 153.5, 130.9, 129.2, 91.0, 76.1, 68.8, 61.9, 44.5, 32.6, 31.4, 30.2, 29.2, 27.6, 25.7, 22.5, 18.0, 14.1, 14.0, -3.0, -3.3.

Ethyl 4-methyl-4-(tert-butyldimethylsiloxy)-non-7(Z)-en-2-ynoate 12f

To a solution of alcohol **11f** (315 mg, 1.50 mmol) in methylene chloride (15 ml) was added 2,6-lutidine (0.59 mL, 5.06 mmol) followed by *tert*-butyldimethylsilyl triflate (0.59 mL, 2.57 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3% diethyl ether: petroleum ether afforded silyl ether **12f** (428 mg, 88 %) as a colorless liquid. ¹H-NMR (500 MHz, CDCl₃): 5.48 (dq, J = 11.0 and 6.4 Hz, 1H), 5.41 (dm, J = 11.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.34-2.25 (m, 1H), 2.24-2.16 (m, 1H), 1.71 (t, J = 8.4 Hz, 1H), 1.64 (d, J = 6.4 Hz, 3H), 1.52 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H), 0.90 (s, 9H), 0.23 (s, 3H), 0.21 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 153.5, 129.5, 124.4, 90.9, 76.2, 68.9,

61.9, 44.2, 30.1, 25.6, 22.0, 18.0, 14.0, 12.7, -3.0, -3.3. HRMS Calc'd for $C_{18}H_{32}O_3Si: 324.2121$. Found: 324.2122

2-(3-Methylbut-2-enyl)-cyclohexanone 13a

To a solution of di-*iso*-propylamine (1.9 mL, 13.6 mmol) in THF (50 mL), at -78 °C, was added 1.4M *n*-butyllithium (9.3 mL, 13.0 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution of cyclohexanone (2 g, 11.8 mmol) in THF (10 mL). After stirring at -78 °C for 1h, the reaction mixture was slowly added to a solution of 4-methylpent-3-enyl bromide (1.6 mL, 14.1 mmol) in THF (5 mL), stirred at -78 °C for 30 min. and then warmed to room temperature. After 4h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 7:1 petroleum ether: diethyl ether afforded **13a** (1.01 g, 51 %) as a colorless liquid.

IR (film): 2931, 2860, 1712, 1448, 1377, 1313, 1128 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.09 (tq, J = 7.6 and 1.3 Hz, 1H), 2.46-2.38 (m, 2H), 2.35-2.26 (m, 2H), 2.17-2.10 (m, 1H). 2.09-2.02 (m, 1H), 1.98 (dt, J = 14.3 and 7.6 Hz, 1H), 1.89-1.84 (m, 1H), 1.74-1.64 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.41-1.33 (m, 1H). ¹³C-NMR (125 MHz, CDCl₃): δ 213.3, 132.9, 122.0, 51.1, 42.0, 33.4, 28.0, 27.8, 25.8, 25.0, 17.8.

cis-4-(tert-Butyl)-2-(3-methylbut-2-enyl)-cyclohexanone 13b

To a solution of di-*iso*-propylamine (2.9 mL, 20.7 mmol) in THF (50 mL), at -78 °C, was added 1.4M *n*-butyllithium (14.8 mL, 20.7 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution of 4-*t*-butylcyclohexanone (3 g, 19.4 mmol) in THF (25 mL). After stirring at -78 °C for 1h, the reaction mixture was slowly added to a solution of 4-methylpent-3-enyl bromide (3.4 mL, 29.1 mmol) in THF (5 mL), stirred at -78 °C for 30 min. and then warmed to room temperature. After 4h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 20:1 petroleum ether: diethyl ether gave first *cis-13b* (1.30 g, 30 %) followed by *trans-13b* (245 mg, 6%).

IR (film): 2963, 2869, 1716, 1447, 1366, 1226, 1175, 1134, 982, 843 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.09 (tq, J = 7.7 and 1.1 Hz, 1H), 2.48-2.27 (m, 4H), 2.19-2.13 (m, 1H), 2.10 (ddd, J = 12.8, 5.8 and 3.2 Hz, 1H), 1.92 (dt, J = 14.8 and 7.3 Hz, 1H), 1.70 (s, 3H), 1.62 (s, 3H), 1.57 (dt, J = 12.1 and 2.9 Hz, 1H), 1.45 (qd, J = 12.8 and 4.8 Hz, 1H), 1.13 (q,

J = 12.8 Hz, 1H), 0.92 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 213.4, 132.8, 122.1, 50.2, 47.0, 41.6, 34.6, 28.7, 27.8, 27.6, 27.4, 25.8, 17.8.

trans-4-(tert-Butyl)-2-(3-methylbut-2-enyl)-cyclohexanone trans-13b

IR (film): 2964, 2869, 1712, 1445, 1366, 1329, 1226 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.03 (tq, J = 6.8 and 1.3 Hz, 1H), 2.47-2.36 (m, 2H), 2.32-2.19 (m, 3H), 2.01 (m, 1H), 1.85 (m, 1H), 1.70 (s, 3H), 1.64 (s, 3H), 1.63-1.55 (m, 2H), 1.46 (m, 1H), 0.90 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 215.7, 133.5, 121.1, 49.4, 47.0, 41.2, 38.5, 32.3, 30.5, 29.8, 27.4, 26.9, 17.9.

1-(Ethoxycarbonylethynyl)-2-(3-methylbut-2-enyl)-cyclohexan-1-ol 14a

To a solution of di-*iso*-propylamine (0.32 mL, 2.28 mmol) in THF (25 mL), at -78 °C, was added 1.4M *n*-butyllithium (1.6 mL, 2.24 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution of ethyl propiolate (0.27 mL, 2.66 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with **13a** (250 mg, 1.49 mmol), stirred at -78 °C for 30 min. and then warmed to room temperature. The reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether affords cyclohexanol **Z-15a** (69 mg, 17 %) followed by **E-14a**. (160 mg, 40%) as a colorless liquid.

IR (film): 3463, 2934, 2859, 2230, 1715, 1448, 1368, 1241, 1035, 752 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.28 (tq, J = 7.2 and 1.3 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.88 (br s, 1H), 2.54 (dt, J = 14.4 and 7.7 Hz, 1H), 2.09 (m, 1H), 1.92 (dt, J = 14.4 and 6.7 Hz, 1H), 1.76-1.68 (m, 3H), 1.74 (s, 3H), 1.72 (s, 3H), 1.62-1.53 (m, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.22 (m, 2H). ¹³C-NMR (125 MHz, CDCl₃): δ 154.3, 134.9, 123.9, 89.2, 79.0, 74.3, 62.8, 48.9, 40.6, 31.4, 30.7, 26.6, 26.1, 24.3, 18.7, 14.8. HRMS Calc'd for C₁₆H₂₄O₃: 264.1725. Found: 264.1722.

1-(Ethoxycarbonylethynyl)-2-(3-methylbut-2-enyl)-cyclohexan-1-ol cis-14a

IR (film): 3487, 2935, 2860, 2233, 1714, 1447, 1368, 1243, 1039, 977, 752 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.20 (tq, J = 7.4 and 1.4 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.37 (dm, J = 13.0 Hz, 1H), 2.17 (dt, J = 14.4 and 9.1 Hz, 1H), 2.04 (dm, J = 13.6 Hz,, 1H), 1.76-1.68 (m, 2H), 1.73 (s, 3H), 1.67 (s, 3H), 1.66-1.52 (m, 4H), 1.33 (t, J = 7.1 Hz, 3H), 1.27 (m, 2H). ¹³C-NMR (125 MHz, CDCl₃): δ 154.4, 134.4, 123.1, 91.9, 76.2, 70.9, 62.8, 46.5, 39.6, 30.3, 26.7, 26.4, 25.7, 21.4, 18.6, 14.7.

1-(Ethoxycarbonylethynyl)-4-(tert-butyl)-2-(3-methylbut-2-enyl)-cyclohexan-1-ol 14b

To a solution of di-*iso*-propylamine (0.85 mL, 6.10 mmol) in THF (30 mL), at -78 °C, was added 1.4M *n*-butyllithium (4.3 mL, 6.02 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution of ethyl propiolate (0.69 mL, 6.80 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with **13b** (900 mg, 4.05 mmol), stirred at -78 °C for 30 min. and then warmed to room temperature. The reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded cyclohexanol **14b** (989 mg, 83 %) as a colorless liquid.

IR (film): 3458, 2964, 2869, 2231, 1715, 1447, 1367, 1239, 1109, 1041, 860, 752 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.29 (tq, J = 7.5 and 1.3 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.96 (br s, 1H), 2.48 (dt, J = 14.5 and 8.1 Hz, 1H), 2.13 (dt, J = 12.8 and 3.3 Hz, 1H), 1.92 (dt, J = 14.5 and 6.0 Hz, 1H), 1.78-1.70 (m, 1H), 1.74 (s, 3H), 1.73 (s, 3H), 1.64-1.57 (m, 1H), 1.56 (td, J = 13.4 and 3.2 Hz, 1H), 1.46-1.36 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.10 (tt, J = 11.9 and 2.8 Hz, 1H),1.02 (q, J = 12.4 Hz, 1H), 0.88 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 153.5, 134.3, 123.2, 88.4, 78.4, 73.6, 61.9, 48.0, 47.1, 39.9, 32.2, 31.2, 27.5, 25.9, 24.4, 22.6, 18.0, 14.0. HRMS Calc'd for C₂₀H3₂O₃: 320.2351. Found: 320.2342.

<u>1-(Ethoxycarbonylethynyl)-4-(*tert*-butyl)-1-(*tert*-butyldimethylsiloxy)-2-(3-methylbut-2-enyl)-cyclohexan-1-ol **15b**</u>

To a solution of alcohol **14b** (710 mg, 2.22 mmol) in methylene chloride (4 mL) was added 2,6-lutidine (1.0 mL, 8.58 mmol) followed by *tert*-butyldimethylsilyl triflate (0.90 mL, 3.9 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3% diethyl ether: petroleum ether afforded silyl ether **15b** (830 mg, 86 %) as a colorless liquid. **15b** was characterized as a 2:1 mixture of conformations.

IR (film): 2956, 2860, 2230, 1717, 1472, 1366, 1237, 1114, 1086, 1041, 838, 778 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.15 (tq, J = 7.7 and 1.2 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.57 (dd, J = 13.5 and 6.8 Hz, 1H), 2.13 (dt, J = 12.5 and 3.2 Hz, 1H), 1.83-1.75 (m, 2H), 1.72 (s, 3H), 1.70 (m, 1H), 1.64 (s, 3H), 1.55 (td, J = 13.4 and 4.7 Hz, 1H), 1.45-1.36 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.08-1.01 (m, 2H), 0.90 (s, 9H), 0.87 (s, 9H), 0.24 (s, 3H), 0.20 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 153.5, 134.4, 122.9, 89.0, 79.4, 74.0, 61.8, 50.0, 46.9, 41.4, 32.5, 29.3, 27.6, 27.4, 25.8, 25.7, 24.7, 18.0, 17.8, 14.0, -2.7, -3.3. Anal. Calc'd for $C_{26}H_{46}O_{3}Si$: C, 71.83; H, 10.67. Found: C, 71.61; H, 10.68.

Additional signals for minor conformation: 1 H-NMR (500 MHz, CDCl₃): δ 2.40 (dd, J = 14.0 and 5.0 Hz, 1H), 2.09 (dt, J = 12.5 and 3.2 Hz, 1H), 1.92 (dt, J = 14.5 and 6.0 Hz, 1H), 0.93 (s, 9H), 0.86 (s, 9H), 0.26 (s, 3H), 0.21 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 123.0, 61.8, 48.1, 46.8, 40.4, 32.3, 30.4, 29.0, 27.5, 26.5, 25.9, 25.8, 17.8, -3.2, -3.3.

1-Trimethylsilyl-7,11-dimethyl-dodeca-6E,10-diene-1-yne-3-one 20a

To a solution of di-*iso*-propylamine (0.46 mL, 3.30 mmol) in THF (3 mL), at -78 °C, was added 1.6 M *n*-butyllithium (2.4 mL, 3.84 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution N,O-dimethyl hydroxyacetamide (322 mg, 3.12 mmol). After stirring at -78 °C for 2h, the reaction mixture was slowly added over 15 min. to a solution of geranyl bromide (550 mg, 2.53 mmol) in THF (2 mL) and HMPA (1 mL). After an additional 2h, the reaction mixture was diluted with 1:1 diethyl ether: petroleum ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 12:1 petroleum ether: diethyl ether afforded the amide **19a** (369 mg, 61%) as a slightly yellow liquid.

¹H-NMR (300 MHz, CDCl₃): δ 5.14 (tt, J = 7.0 and 1.5 Hz, 1H), 5.08 (tt, J = 6.9 and 1.5 Hz, 1H), 3.68 (s, 3H), 3.18 (s, 3H), 2.44 (m, 2H), 2.33 (p, J = 7.5 Hz, 2H), 2.05 (m, 2H), 1.98 (m, 2H), 1.68 (s, 3H), 1.62 (s, 3H), 1.59 (s, 3H).

To a solution of trimethylsilylacetylene (0.33 mL, 2.32 mmol) in THF (5 mL), at -78 °C, was slowly added 1.6 M *n*-butyllithium (1.4 mL, 2.24 mmol). After 30 min., the reaction mixture was added to a solution of the amide (369 mg, 1.54 mmol) in THF (2 mL) at -78 °C. After 1h at -78 °C, the reaction mixture was warmed to room temperature, quenched with 1N sodium bisulfate (25 mL) and extracted with diethyl ether (3 x 25 mL). The combined extracts were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether afforded ketone **20a** (302 mg, 70%) as a colorless liquid.

IR (film): 2965, 2918, 2151, 1679, 1253, 1109, 847, 761 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.02 (m, 2H), 2.53 (t, J = 7.6 Hz, 2H), 2.30 (q, J = 7.5 Hz, 2H), 2.00 (m, 2H), 1.92 (m, 2H), 1.62 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H) 0.18 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 187.4, 136.6, 131.2, 124.0, 121.8, 101.9, 97.5, 45.3, 39.5, 26.6, 25.6, 22.5, 17.5, 15.9, -0.9.

1-Trimethylsilyl-7,11-dimethyl-dodeca-6Z,10-diene-1-yne-3-one 20b

To a solution of di-iso-propylamine (0.46 mL, 3.30 mmol) in THF (3 mL), at -78 °C, was added 1.6 M *n*-butyllithium (2.4 mL, 3.84 mmol). The solution was warmed to 0 °C for 15

min., then recooled to -78 °C. To the reaction mixture was slowly added a solution N,O-dimethyl hydroxyacetamide (322 mg, 3.12 mmol). After stirring at -78 °C for 2h, the reaction mixture was slowly added over 15 min. to a solution of neryl bromide (550 mg, 2.53 mmol) in THF (2 mL) and HMPA (1 mL). After an additional 2h the reaction mixture was diluted with 1:1 diethyl ether: petroleum ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 12:1 petroleum ether: diethyl ether afforded the amide **19b** (337 mg, 54%) as a slightly yellow liquid.

¹H-NMR (300 MHz, CDCl₃): δ 5.10 (m, 2H), 3.67 (s, 3H), 3.18 (s, 3H), 2.43 (m, 2H), 2.32 (m, 2H), 2.06 (m, 4H), 1.69 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H).

To a solution of trimethylsilylacetylene (0.30 mL, 2.11 mmol) in THF (5 mL), at -78 °C, was slowly added 1.6 M *n*-butyllithium (1.25 mL, 2.00 mmol). After 30 min., the reaction mixture was added to a solution of the amide (323 mg, 1.35 mmol) in THF (2 mL) at -78 °C. After 1h at -78 °C, the reaction mixture was warmed to room temperature, quenched with 1N sodium bisulfate (25 mL) and extracted with diethyl ether (3 x 25 mL). The combined extracts were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether afforded ketone **20b** (257 mg, 68%) as a colorless liquid.

IR (film): 2965, 2927, 2151, 1679, 1252, 1105, 846, 762 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.02 (m, 2H), 2.53 (t, J = 7.6 Hz, 2H), 2.30 (q, J = 7.5 Hz, 2H), 2.00 (m, 2H), 1.92 (m, 2H), 1.62 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H) 0.18 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 187.6, 136.8, 131.7, 124.1, 122.7, 102.0, 97.8, 45.7, 34.1, 26.4, 25.7, 22.4, 17.6, 14.0, -0.8.

Ethyl 4,8-dimethyl-4-hydroxy-non-7-en-2-ynoate

To a solution of di-*iso*-propylamine (0.85 mL, 6.06 mmol) in THF (20 mL), at -78 °C, was added 1.5M *n*-butyllithium (4.0 mL, 6.0 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution of ethyl propiolate (0.50 mL, 4.93 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with ketone **9b** (500 mg, 3.97 mmol), stirred at -78 °C for 30 min. then warmed to room temperature. The reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded the title compound (730 mg, 82 %) as a colorless liquid.

IR (film): 3455, 2981, 2933, 2236, 1715, 1449, 1369, 1250, 1121, 1033, 752 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): 5.14 (tt, J = 7.3 and 1.1 Hz, 1H), 3.80 (s, 3H), 2.26-2.20 (m,

2H), 1.72-1.67 (m, 2H), 1.70 (s, 3H), 1.64 (s, 3H), 1.51 (s, 3H), 0.90 (s, 9H), 0.23 (s, 3H), 0.20 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 153.5, 133.0, 123.2, 90.2, 75.4, 68.2, 62.0, 42.5, 29.0, 25.7, 23.4, 17.7, 13.9. HRMS Calc'd for $C_{12}H_{18}O_3$: 210.1256. Found: 210.1257.

7-Methyl-1-trimethylsilyl-oct-6-en-1-yn-3-one 20c

To a solution of trimethysilylacetylene (1.5 mL, 10.6 mmol) in THF (25 mL), at -78 °C, was slowly added 1.5 M *n*-butyllithium (7.0 mL, 10.5 mmol). After 30 min., the reaction mixture was added to a solution of aldehyde **9a** (1.0 g, 8.92 mmol) in THF (5 mL) at -78 °C. After 1h at -78 °C, the reaction mixture was warmed to room temperature, quenched with 1N sodium bisulfate (25 mL) and extracted with diethyl ether (3 x 25 mL). The combined extracts were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded the propargyl alcohol (1.72 g, 92%) as a colorless liquid.

¹H-NMR (500 MHz, CDCl₃): δ 5.13 (tt, J = 7.3 and 1.2 Hz, 1H), 4.36 (t, J = 6.4 Hz, 1H), 2.16 (q, J = 7.4 Hz, 2H), 1.90 (br s, 1H), 1.73 (q, J = 7.3 Hz, 2H), 1.69 (s, 3H), 1.63 (s, 3H), 0.17 (s, 9H).

To a stirred solution of the alcohol (1.0 g, 4.76 mmol) in methylene chloride (50 mL) was added PCC (1.25 g, 5.80 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (100 mL) and filtered through a pad of silica, The filtrate was concentrated *in vacuo* and chromatographed eluting with 3:1 petroleum ether: diethyl ether to afford ketone **20c** (890 mg, 90%) as a slightly yellow liquid.

IR (film): 2966, 2923, 2154, 1680, 1447, 1408, 1379, 1253, 1100, 846, 762 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.00 (tt, J = 7.3 and 1.2 Hz, 1H), 2.51 (t, J = 7.3 Hz, 2H), 2.27 (q, J = 7.3 Hz, 2H), 1.61 (s, 3H), 1.55 (s, 3H), 0.17 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 187.4, 133.0, 129.1, 101.8, 97.5, 45.3, 25.5, 22.6, 17.5, -0.9.

3-(4,5-trans-Diphenyl-[1,3]dioxolan-2-yl)-7-methyl-1-trimethylsilyl-oct-6-en-1-yne 22

To a solution of ketone **20c** (500 mg, 2.40 mmol) and the hydrobenzoin bis-TMS ether (1.3 g, 3.62 mmol) in methylene chloride (25 mL), at 0 °C, was added trimethylsilyl **21** trifluoromethanesulfonate (20 μL, 0.110 mmol). After stirring at 0 °C for 5h, the reaction mixture was washed with 1N sodium bicarbonate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 2% diethyl ether: petroleum ether ketal **22** (708 mg, 73 %) as a colorless liquid.

IR (film): 3033, 2962, 2925, 1454, 1251, 1190, 1095, 1040, 1025, 862, 844, 761, 698 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 7.43-7.32 (m, 10H), 7.29 (m, 2H), 5.28 (tt, J = 7.4 and 1.4 Hz, 1H), 5.13 (d, J = 8.4 Hz, 1H), 4.72 (d, J = 8.4 Hz, 1H), 2.43 (m, 2H), 2.17 (m, 2H), 1.76 (s, 3H), 1.71 (s, 3H), 0.29 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 137.6, 135.7, 132.2, 128.5, 128.4, 128.3, 128.2, 127.2, 126.7, 124.4, 104.2, 103.5, 89.5, 86.5, 86.2, 40.0, 25.7, 22.4, 17.7, -0.2.

Methyl 4-(4,5-trans-diphenyl-[1,3]dioxolan-2-yl)-8-methyl-non-7-en-2-ynoate 23

To a solution of alkyne **22** (350 mg, 0,866 mmol) in diethyl ether (5 mL), at 0 °C, was added 0.9M methyllithium (1,1 mL, 0.99 mmol). After stirring at 0 °C for 1h, methyl chloroformate (80 μL, 1.04 mmol) was added and the reaction mixture warmed to room temperature. After an additional 2h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 10:1 petroleum ether: diethyl ether afforded alkynoate **23** (212 mg, 63 %) as a colorless liquid.

IR (film): 3034, 2954, 2824, 2236, 1721, 1497, 1455, 1435, 1251, 1190, 1018, 763, 750, 699 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 7.41-7.35 (m, 8H), 7.32 (m, 2H), 7.28 (m, 2H), 5.25 (t, J = 7.2 Hz, 1H), 5.09 (d, J = 8.6 Hz, 1H), 4.76 (d, J = 8.6 Hz, 1H), 3.89 (s, 3H), 2.43 (m, 2H), 2.22 (m, 2H), 1.76 (s, 3H), 1.70 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 153.6, 136.4, 134.7, 132.7, 128.8, 128.6, 128.5, 128.4, 126.8, 122.7, 103.2, 86.5, 86.4, 85.0, 75.0, 52.9, 39.6, 25.7, 22.0, 17.7. Anal Calc'd for C₂₅H₂₆O₄: C, 76.90; H, 6.71. Found: C, 76.74; H, 6.60.

$\underline{\text{Undec-5}(E)\text{-en-2-one}}$

To a solution of decenal (4.0g, 25.9 mmol) in diethyl ether (100 mL), at -78 °C, was slowly added 2.0M methylmagnesium bromide (15 mL, 45 mmol) and the resulting tan solution allowed to slowly warm to room temperature. After 3h, the solution was poured into cold 3N ammonium chloride (100 mL) and separated. The ether layer was washed with brine (50 mL), dried (MgSO₄) and concentrated *in vacuo*. Kugelrohr distillation affords the propargyl alcohol (4.0 g, 691 %) as a colorless liquid.

IR (film): 3346, 2960, 2926, 1458, 1376, 1125, 1083, 968 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.46 (dt, J = 15.4 and 6.1 Hz, 1H), 5.44 (dt, J = 15.4 and 6.0 Hz, 1H), 4.82 (sixtet, J = 6.2 Hz, 1H), 2.10 (m, 2H), 1.99 (td, J = 6.6 and 6.1 Hz, 2H), 1.53 (m, 2H), 1.39-1.26 (m, 6H), 1.21 (d, J = 6.2 Hz, 3H), 0.90 (t, J = 6.6 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 131.1, 129.6, 67.8, 38.9, 32.5, 31.4, 29.2, 29.0, 23.4, 22.5, 14.1.

To a stirred solution of the alcohol (1.10 g, 6.47 mmol) in methylene chloride (70 mL) was added PCC (1.6 g, 7.42 mmol). After stirring at room temperature for 8h, the solution was diluted with diethyl ether (100 mL) and filtered through a pad of silica, The filtrate was

concentrated *in vacuo* and chromatographed eluting with 3:1 petroleum ether: diethyl ether to afford the title ketone(960 mg, 88%) as a colorless liquid.

IR (film): 2958, 2926, 2858, 1720, 1438, 1360, 1161, 970 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.45 (dt, J = 15.6 and 6.0 Hz, 1H), 5.38 (dt, J = 15.6 and 6.2 Hz, 1H), 2.50 (t, J = 7.3 Hz, 2H), 2.27 (q, J = 7.0 Hz, 2H), 2.15 (s, 3H), 1.97 (q, J = 7.0 Hz, 2H), 1.38-1.22 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 208.6, 131.6, 128.1, 43.5, 32.4, 31.3, 30.0, 29.1, 26.8, 22.5, 14.0.

3,7,11-Trimethyl-1-trimethylsilyl-dodeca-6(E),10-dien-1-yn-3-ol 24a

To a solution of ketone **20a** (2.0 g, 7.25 mmol) in diethyl ether (70 mL), at 0 °C, was slowly added 1.5M methyllithium•lithium bromide (7.3 mL, 11.0 mmol). After 4h at 0 °C, the solution was poured into cold 3N ammonium chloride (100 mL) and separated. The ether layer was washed with brine (50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether afforded propargyl alcohol **24a** (1.88 g, 89 %) as a colorless liquid.

IR (film): 3374, 2965, 2928, 2857, 2167, 1449, 1375, 1251, 1120, 925, 843, 760, 699, 637 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.21 (t, J = 7.1 Hz, 1H), 5.10 (t, J = 6.8 Hz, 1H), 2.37-2.22 (m, 2H), 2.21-2.16 (m, 1H), 2.09 (q, J = 6.8 Hz, 1H), 2.01 (dd, J = 7.9 and 7.1 Hz, 1H), 1.72-1.63 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.62 (s, 3H), 1.48 (s, 3H), 0.18 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 136.0, 131.4, 124.2, 123.8, 109.5, 87.4, 68.6, 43.3, 39.7, 29.7, 26.6, 25.7, 23.6, 17.6, 16.0, -0.1.

3,7,11-Trimethyl-1-trimethylsilyl-dodeca-6(Z),10-dien-1-yn-3-ol 24b

To a solution of ketone **20b** (2.0 g, 7.25 mmol) in diethyl ether (70 mL), at 0 °C, was slowly added 1.5M methyllithium•lithium bromide (7.3 mL, 11.0 mmol). After 4h at 0 °C, the solution was poured into cold 3N ammonium chloride (100 mL) and separated. The ether layer was washed with brine (50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 10% diethyl ether: petroleum ether afforded propargyl alcohol **24b** (1.67 g, 79 %) followed by desilylated alkyne **25b** (251 mg, 16%) as a colorless liquid. IR (film): 3374, 2965, 2930, 2858, 2167, 1450, 1376, 1251, 1117, 925, 843, 760 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.21 (t, J = 7.0 Hz, 1H), 5.15 (m, 1H), 2.35-2.25 (m, 1H), 2.25-2.17 (m, 5H), 1.72-1.63 (m, 2H), 1.72 (s, 3H), 1.70 (s, 3H), 1.63 (s, 3H), 1.49 (s, 3H), 0.19 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 136.1, 131.6, 124.6, 124.3, 109.3, 87.5, 68.6, 43.5, 31.9, 29.8, 26.5, 25.7, 23.5, 23.4, 17.7, -0.1.

3,7,11-Trimethyl-dodeca-6(E),10-dien-1-yn-3-ol 25a

To a solution of **24a** (R²=TMS) (1.88 g, 6.43 mmol) in THF (5 mL) was added 1.0M tetrabutylammonium fluoride (7.7 mL, 7.7 mmol). After stirring at room temperature for 1h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N hydrochloric acid (25 mL), brine (25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 10% diethyl ether: petroleum ether afforded propargyl alcohol **25a** (1.34 g, 95 %) as a colorless liquid.

IR (film): 3396, 3308, 2969, 2928, 2857, 1450, 1376, 1153, 1111, 909, 838, 651, 630 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.20 (t, J = 7.0 Hz, 1H), 5.10 (t, J = 6.9 Hz, 1H), 2.48 (s, 1H), 2.38-2.28 (m, 1H), 2.27 (s, 1H), 2.24-2.16 (m, 1H), 2.09 (dd, J = 7.1 and 6.8 Hz, 1H), 2.01 (t, J = 7.9 Hz, 1H), 1.78-1.64 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.62 (s, 3H), 1.52 (s, 3H), . ¹³C-NMR (125 MHz, CDCl₃): δ 136.2, 131.5, 124.1, 123.5, 87.6, 71.4, 68.3, 43.1, 39.7, 29.8, 26.6, 25.7, 23.4, 17.7, 16.0.

3,7,11-Trimethyl-dodeca-6(Z),10-dien-1-yn-3-ol 25b

To a solution of **24b** (R²=TMS) (1.60 g, 5.47 mmol) in THF (5 mL) was added 1.0M tetrabutylammonium fluoride (8.3 mL, 8.3 mmol). After stirring at room temperature for 1h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N hydrochloric acid (25 mL), brine (25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 10% diethyl ether: petroleum ether afforded propargyl alcohol **25b** (1.06 g, 88 %) as a colorless liquid.

IR (film): 3406, 3309, 2966, 2930, 2858, 1450, 1376, 1251, 1146, 1114, 910, 843 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.19 (t, J = 7.0 Hz, 1H), 5.14 (m, 1H), 2.47 (s, 1H), 2.35-2.26 (m, 1H), 2.25-2.16 (m, 2H), 2.20-2,06 (m, 4H), 1.76-1.69 (m, 2H), 1.72 (s, 3H), 1.71 (s, 3H), 1.63 (s, 3H), 1.52 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 136.2, 131.5, 124.3, 124.2, 87.5, 71.4, 68.2, 43.4, 31.9, 29.8, 26.5, 25.7, 23.4, 23.3, 17.6.

3-(tert-Butyldimethylsiloxy)-3,7,11-trimethyl-dodeca-6(Z),10-dien-1-yne 26a

To a solution of alcohol **25a** (250 mg, 1.13 mmol) in methylene chloride (15 ml) was added 2,6-lutidine (0.44 mL, 3.77 mmol) followed by *tert*-butyldimethylsilyl triflate (0.44 mL, 1.92 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 1% diethyl ether: petroleum ether afforded silyl ether **26a** (313 mg, 83 %) as a colorless liquid

IR (film): 3310, 2957, 2930, 2857, 1462, 1370, 1253, 1173, 1106, 1046, 838, 776 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.18 (t, J = 7.1 Hz, 1H), 5.13 (t, J = 7.1 Hz, 1H), 2.44 (s, 1H), 2.28-2.14 (m, 2H), 2.11 (m, 2H), 2.01 (t, J = 7.0 Hz, 2H), 1.71 (s, 3H), 1.68-1.60 (m, 2H),

1.65 (s, 3H), 1.63 (s, 3H), 1.48 (s, 3H), 0.90 (s, 9H), 0.21 (s 6H). 13 C-NMR (125 MHz, CDCl₃): δ 136.2, 131.3, 124.4, 123.9, 88.2, 71.9, 68.9, 45.1, 39.7, 30.9, 26.7, 25.7, 23.2, 18.1, 17.7, 15.9, -2.9, -3.1. HRMS Calc'd for $C_{21}H_{38}OSi$: 334.2692. Found: 334.2688.

3-(tert-Butyldimethylsiloxy)-3,7,11-trimethyl-dodeca-6(E),10-dien-1-yne 26b

To a solution of alcohol **25b** (1.0 g, 4.55 mmol) in methylene chloride (40 ml) was added 2,6-lutidine (18 mL, 15.5 mmol) followed by *tert*-butyldimethylsilyl triflate (1.8 mL, 7.72 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 1% diethyl ether: petroleum ether afforded silyl ether **26b** (1.42 g, 93 %) as a colorless liquid

IR (film): 3310, 2958, 2930, 2857, 1462, 1371, 1252, 1174, 1103, 1046, 994, 837, 777 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.18 (t, J = 7.0 Hz, 1H), 5.15 (m, 1H), 2.43 (s, 1H), 2.28-2.14 (m, 2H), 2.08 (m, 4H), 1.71 (s, 6H), 1.69-1.60 (m, 2H), 1.64 (s, 3H), 1.47 (s, 3H), 0.90 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 135.3, 131.4, 124.8, 124.3, 88.1, 71.9, 68.9, 45.4, 31.9, 31.0, 26.6, 25.7, 25.6, 23.4, 23.2, 18.0, 17.6, -2.9, -3.2. HRMS Calc'd for $C_{21}H_{38}OSi$: 334.2692. Found: 334.2687.

Methy 4-(tert-butyldimethylsiloxy)-4,8,12-trimethyl-trideca-7(E),11-dien-2-ynoate 27a

To a solution of alkyne **26a** (200 mg, 0.599 mmol) in THF (6 mL), at -78 °C, was added 1.6M *n*-butyllithium (0.42 mL, 0.672 mmol). After stirring at -78 °C for 30 min., the solution was warmed to 0 °C, methyl chloroformate (100 μL, 1.16 mmol) added and the reaction mixture slowly warmed to room temperature. After an additional 1h, the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether afforded alkynoate **27a** (168 mg, 72 %) as a colorless liquid.

IR (film): 2956, 2930, 2858, 2234, 1722, 1434, 1372, 1252, 1172, 1107, 1046, 1022, 837, 778 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.15 (t, J = 7.2 Hz, 1H), 5.11 (tt, J = 7.0 and 1.3 Hz, 1H), 3.80 (s, 3H), 2.28-2.12 (m, 2H), 2.08 (m, 2H), 2.01 (m, 2H), 1.72-1.66 (m, 2H), 1.70 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H), 1.51 (s, 3H), 0.90 (s, 9H), 0.23 (s 3H), 0.21 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 153.9, 135.6, 131.3, 124.3, 123.3, 91.5, 75.8, 68.9, 52.7, 44.5, 39.7, 30.1, 26.7, 25.7, 25.6, 23.1, 18.0, 17.7, 15.9, -3.0, -3.3. HRMS Calc'd for C₂₃H₄₀O₃Si : 392.2747. Found: 392.2742.

Methy 4-(tert-butyldimethylsiloxy)-4,8,12-trimethyl-trideca-7(Z),11-dien-2-ynoate 27b

To a solution of alkyne **26b** (600 mg, 1.79 mmol) in THF (15 mL), at - 78 °C, was added 1.6M n-butyllithium (1.3 mL, 0.672 mmol). After stirring at -78 °C for 30 min. the solution was warmed to 0 °C, methyl chloroformate (100 μ L, 1.16 mmol) added and the reaction mixture warmed to room temperature. After an additional 1h, the solution was diluted with diethyl ether (50 mL), washed with 1N sodium bisulfate (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether afforded alkynoate **27b** (603 mg, 86 %) as a colorless liquid.

IR (film): 2957, 2931, 2858, 2234, 1722, 1435, 1253, 1172, 1104, 1046, 837, 778 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.15 (t, J = 7.5 Hz, 1H), 5.13 (m, 1H), 3.80 (s, 1H), 2.28-2.18 (m, 1H), 2.18-2.08 (m, 1H), 2.06 (m, 4H), 1.71 (s, 6H), 1.71-1.62 (m, 2H), 1.62 (s, 3H), 1.50 (s, 3H), 0.90 (s, 9H), 0.22 (s, 3H), 0.20 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 153.9, 135.7, 131.5, 124.3, 124.2, 91.4, 75.8, 68.9, 52.6, 44.8, 31.9, 30.2, 26.5, 25.7, 25.6, 23.4, 23.0, 18.0, 17.6, -3.0, -3.3. HRMS Calc'd for $C_{22}H_{37}O_{3}Si$ (M+- CH₃): 377.2512. Found: 377.2512.

Ethyl 2,2,5-trimethyl-hex-4-enoate

To a solution of di-*iso*-propylamine (5.9 mL, 42.1 mmol) in THF (200 mL), at -78 °C, was added 1.6M *n*-butyllithium (26 mL, 41.6 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution of ethyl isobutyrate (5 mL, 37.4 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with prenyl bromide (4.5 mL, 39.0 mmol), stirred at -78 °C for 30 min. and then warmed to room temperature. After 10h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Kugelrohr distillation afforded the titled compound (5.37 g, 78 %) as a colorless liquid.

IR (film): 2977, 2932, 1731, 1472, 1449, 1385, 1310, 1252, 1129, 1032 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.09 (t, J = 7.5 Hz, 1H) 4.12 (q, J = 7.1 Hz, 2H), 2.23 (d, J = 7.5 Hz, 2H), 1.71 (s, 3H), 1.62 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.17 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 177.9, 134.0, 119.9, 60.2, 42.7, 38.7, 26.0, 24.8, 17.9, 14.2.

Ethyl 2,2,6-trimethyl-hept-5-enoate

To a solution of di-*iso*-propylamine (5.9 mL, 42.1 mmol) in THF (200 mL), at -78 °C, was added 1.6M *n*-butyllithium (26 mL, 41.6 mmol). The solution was warmed to 0 °C for 15 min., then recooled to -78 °C. To the reaction mixture was slowly added a solution of ethyl isobutyrate (5 mL, 37.4 mmol). After stirring at -78 °C for 1h, the reaction mixture was treated with 4-methylpent-3-enyl bromide (4.5 mL, 33.6 mmol), stirred at -78 °C for 30 min.

and then warmed to room temperature. After 10h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Kugelrohr distillation afforded the titled compound (4.93 g, 74 %) as a colorless liquid.

IR (film): 2975, 2931, 1730, 1474, 1282, 1176, 1128, 1027 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.08 (tq, J = 7.2 and 1.4 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 1.91 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.54 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.17 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 177.9, 131.6, 124.0, 60.1, 42.0, 40.7, 25.6, 25.1, 23.7, 17.5, 14.2. Anal. Calc'd for C₁₂H₂₂O₂: C, 74.96, H, 9.68 . Found: C, 74.90, H, 9.73.

2,2,5-Trimethyl-hex-4-enal

To a solution of ethyl 2,2,5-trimethyl-hex-4-enoate (4.0 g, 21.7 mmol) in diethyl ether (200 mL) at 0 °C, was slowly added lithium aluminum hydride (1.7 g, 44.8 mmol). After stirring at 0 °C for 4h, the grey suspension was quenched by careful addition of wet magnesium sulfate. After rapidly stirring for 1h, the solids were removed by filtration, washed with diethyl ether (200 mL) and concentrated *in vacuo* to afford the alcohol as a clear colorless liquid (2.97 g, 96%)

IR (film): 3356, 2965, 2927, 2871, 1472, 1454, 1378, 1045 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.21 (tq, J = 7.6 and 1.1 Hz, 1H) 3.31 (s, 2H), 1.95 (d, J = 7.6 Hz, 2H), 1.73 (s, 3H), 1.67 (br s, 1H), 1.63 (s, 3H), 0.88 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 133.4, 120.6, 71.9, 36.9, 36.2, 26.0, 23.9, 17.8.

To a solution of the alcohol (2.3 g, 16.2 mmol) in methylene chloride (160 mL) was added PCC (4.2 g, 19.5 mmol). After stirring at room temperature for 4h, the solution was diluted with diethyl ether (100 mL), filtered through a pad of silica, washed with diethyl ether (100 mL) and the filtrate carefully concentrated *in vacuo*. Kugelrohr distillation afforded the titled aldehyde (1.38 g, 61%) as a colorless liquid.

IR (film): 2969, 2930, 2872, 2701, 1727, 1468, 1378, 1157, 1066, 882 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 9.48 (s, 1H), 5.06 (t, J = 7.1 Hz, 1H), 2.16 (d, J = 7.1 Hz, 2H), 1.70 (s, 3H), 1.61 (s, 3H), 1.04 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 206.4, 134.7, 118.6, 46.5, 35.5, 25.9, 21.1, 17.8.

2,2,6-Trimethyl-hept-5-enal

To a solution of ethyl 2,2,5-trimethyl-hept-5-enoate (4.0 g, 20.2 mmol) in diethyl ether (200 mL) at 0 °C, was slowly added lithium aluminum hydride (1.5 g, 39.5 mmol). After stirring at 0 °C for 4h, the gray suspension was quenched by careful addition of wet magnesium sulfate. After rapidly stirring for 1h, the solids were removed by filtration, washed with

diethyl ether (200 mL) and concentrated in vacuo to afford the alcohol as a clear colorless liquid (2.96 g, 94%)

IR (film): 3356, 2964, 2927, 2871, 1473, 1454, 1378, 1051 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.13 (t, J = 7.2 Hz, 1H), 3.34 (s, 2H), 1.96 (m, 2H), 1.70 (s, 3H), 1.63 (s, 3H), 1.28 (m, 2H), 0.91 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 131.2, 125.0, 71.9, 38.7, 35.1, 25.7, 23.8, 22.5, 17.6.

To a solution of the alcohol (2.5 g, 16.0 mmol) in methylene chloride (200 mL) was added PCC (4.1 g, 16.0 mmol). After stirring at room temperature for 6h, the solution was diluted with diethyl ether (100 mL), filtered through a pad of silica, washed with diethyl ether (100 mL) and the filtrate carefully concentrated *in vacuo*. Kugelrohr distillation afforded the titled aldehyde (1.85 g, 75%) as a colorless liquid.

IR (film): 2968, 2929, 2871, 2695, 1728, 1470, 1378, 1101, 1058 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 9.47 (s, 1H), 5.07 (tq, J = 7.2 and 1.2 Hz, 1H), 1.91 (m, 2H), 1.69 (s, 3H), 1.59 (s, 3H), 1.52 (m, 2H), 1.08 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 206.2, 132.2, 123.7, 45.8, 37.5, 25.6, 23.0, 21.3, 17.6.

Methyl 4,4,7-trimethyl-oct-6-en-2-ynoate 28a

To a suspension of chloromethyltriphenylphosphonium chloride (950 mg, 2.75 mmol) and piperidine (0.27 mL, 2.72 mmol) in diethyl ether (10 mL), was added 1.6M n-butyllithium (1.7 mL, 2.72 mmol) and the resulting orange solution stirred at rt for 2h. 2,2,5-Trimethyl-hex-4-enal (350 mg, 2.5 mmol) in diethyl ether (5 mL) was added and the reaction mixture stirred for an additional 10h. The solution was diluted with diethyl ether (25 mL), washed with 1N hydrochloric acid (3 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. The triphenylphosphine oxide by-product was removed by filtration through a pad of silica, eluting with 2% diethyl ether :petroleum ether to afford a 2:1 mixture of E:Z vinyl chlorides. 1 H-NMR (500 MHz, CDCl₃): δ 5.94 (d, J = 8.0 Hz, 1H (Z)), 5.93 (d, J = 13.5 Hz, 1H (E)), 5.87 (d, J = 13.6 Hz, 1H (E)), 5.65 (d, J = 8.0 Hz, 1H (Z)), 5.18 (tq, J = 7.5 and 1.3 Hz, 1H (Z)), 5.13 (tq, Z = 7.5 and 1.5 Hz, 1H (Z)), 2.20 (d, Z = 7.5 Hz, 2H (Z)), 2.00 (d, Z = 7.5 Hz, 2H (Z)), 1.75 (s, 3H (Z and Z)), 1.64 (s, 3H (Z)), 1.63 (s, 3H (Z)), 1.21 (s, 6H (Z)), 1.03 (s, 6H (Z))

To a solution of the crude vinyl chloride in diethyl ether (15 mL), at 0 °C, was added a solution of 1.6M *n*-butyllithium (3.1 mL, 4.96 mmol). After 3h at 0 °C, methyl chloroformate (0.45 mL, 5.24 mmol) was added and the reaction mixture warmed to room temperature. After an additional 5h, the reaction mixture was diluted with diethyl ether (25 mL), washed with 1N hydrochloric acid (3 x 25 mL), dried (MgSO₄) and concentrated *in*

vacuo. Flash chromatography eluting with 5% diethyl ether: petroleum ether affords alkynoate 28a (314 mg, 64%) as a colorless liquid.

IR (film): 2972, 2932, 2234, 1717, 1435, 1385, 1289, 1247, 1218, 1030, 753 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.26 (tq, J = 7.5 and 1.3 Hz, 1H), 3.77 (s, 3H), 2.19 (d, J = 7.5 Hz, 2H), 1.76 (s, 3H), 1.64 (s, 3H), 1.25 (s, 6H). 13 C-NMR (125 MHz, CDCl₃): δ 154.4, 134.9, 119.5, 96.2, 72.5, 52.5, 40.5, 31.9, 27.7, 25.9, 18.0. HRMS Calc'd for $C_{12}H_{18}O_{2}$: 194.1307. Found: 194.1280.

Methyl 4,4,8-trimethyl-non-7-en-2-ynoate 28b

To a suspension of chloromethyltriphenylphosphonium chloride (3.25 mg, 9.36 mmol) and piperidine (0.925 mL, 9.35 mmol) in diethyl ether (20 mL), was added 1.6M n-butyllithium (5.8 mL, 9.28 mmol) and the resulting orange solution stirred at rt for 2h. 2,2,6-Trimethylhept-5-enal (1.3 g, 8.44 mmol) in diethyl ether (5 mL) was added and the reaction mixture stirred for an additional 10h. The solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (3 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. The triphenylphosphine oxide by-product was removed by filtration through a pad of silica, eluting with 2% diethyl ether :petroleum ether to afford a 2:1 mixture of E:Z vinyl chlorides. 1 H-NMR (500 MHz, CDCl₃): δ 5.95 (d, J = 8.0 Hz, 1H (Z)), 5.90 (d, J = 13.6 Hz, 1H (Z)), 5.87 (d, J = 13.6 Hz, 1H (Z)), 5.62 (d, J = 8.0 Hz, 1H (Z)), 5.12 (t, J = 7.5 Hz, 1H (Z)), 5.09 (t, J = 7.5 Hz, 1H (Z)), 1.61 (s, 3H (Z)), 1.61 (s, 3H (Z)), 1.52 (m, 2H (Z)), 1.33 (m, 2H (Z)), 1.22 (s, 6H (Z)), 1.05 (s, 6H (Z)).

To a solution of the crude vinyl chloride in diethyl ether (40 mL), at 0 °C, was added a solution of 1.6M *n*-butyllithium (11.0 mL, 17.6 mmol). After 3h at 0 °C, methyl chloroformate (15.1 mL, 17.6 mmol) was added and the reaction mixture warmed to room temperature. After an additional 5h, the reaction mixture was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (3 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether affords alkynoate **28b**(1.19 g, 67%) as a colorless liquid.

IR (film): 2971, 2928, 2870, 2233, 1717, 1435, 1377, 1312, 1263, 1237, 1029, 753 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.11 (tq, J = 7.2 and 1.1 Hz, 1H), 3.75 (s, 3H), 2.12 (m, 2H), 1.68 (s, 3H), 1.62 (s, 3H), 1.47 (m, 2H), 1.26 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 154.3, 131.9, 123.6, 95.8, 72.8, 52.4, 42.4, 31.3, 28.1, 25.6, 23.9, 17.6. HRMS Calc'd for C₁₃H₁₉O₂ (M - H⁺): 207.1385. Found: 207.1381.

6-Bromo-hept-5(Z)-en-2-one

Using a modification of the procedure reported by Satoh *et al*,²¹ to a solution of 1.0M *B*-bromo-9-BBN (60 mL, 60,0 mmol) in methylene chloride, at room temperature, was added propyne (4.8 mL). After 1h, methyl vinyl ketone (15 mL, 180 mmol) was added and the resulting brown solution was stirred at room temperature for 4h and then concentrated *in vacuo*. The resulting thick oil was dissolved in toluene (10 mL), 2N sodium hydroxide (10 mL) was added and the solution heated at reflux for 10h. The solution was cooled to room temperature, diluted with diethyl ether (250 mL), washed with 2N sodium hydroxide (200 mL), brine (200 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 5:1 petroleum ether: diethyl ether afforded the titled ketone (6.49 g, 57%) as a slightly yellow liquid.

IR (film): 2922, 2850, 1718, 1360, 1165, 1109 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.61 (td, J = 6.9 and 1.3 Hz, 1H), 2.50 (t, J = 7.2 Hz, 2H), 2.35 (m, 2H), 2.22 (d, J = 1.3 Hz, 3H), 2.11 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ 207.7, 127.0, 123.3, 41.9, 29.6, 28.5, 25.6.

7-Bromo-3-methyl-1-trimethylsilyl-oct-6(Z)-en-1-yn-3-ol

To a solution of trimethysilylacetylene (1.8 mL, 12.6 mmol) in THF (25 mL), at -78 °C, was slowly added 1.6 M *n*-butyllithium (7.9 mL, 12.56 mmol). After 30 min., the reaction mixture was added to a solution of the above ketone (2.0 g, 10.53 mmol) in THF (5 mL) at -78 °C. After 1h at -78 °C, the reaction mixture was warmed to room temperature, quenched with 1N sodium bisulfate (100 mL) and extracted with diethyl ether (3 x 50 mL). The combined extracts were dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded the titled propargyl alcohol (2.94 g, 97%) as a colorless liquid.

IR (film): 3396, 2959, 2925, 2859, 2267, 1684, 1447, 1373, 1301, 1251, 1139, 917, 843, 760 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.70 (td, J = 6.9 and 1.3 Hz, 1H), 2.50 (dd, J = 9.2 and 6.9 Hz, 2H), 2.30 (s, 3H), 1.75 (dt, J = 9.0 and 6.9 Hz, 2H), 1.65 (br s, 1H), 1.51 (s, 3H), 0.19 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 128.1, 122.8, 108.9, 87.9, 68.1, 41.9, 29.7, 28.7, 22.1, -0.1.

7-Bromo-3-methyl-3-(tert-butyldimethylsiloxy)-1-trimethylsilyl-oct-6(Z)-en-1-yne

To a solution of the above alcohol (2.0 g, 6.94 mmol) in methylene chloride (35 ml) was added 2,6-lutidine (2.7 mL, 22.4 mmol) followed by *tert*-butyldimethylsilyl triflate (2.7 mL, 11.8 mmol). After stirring at room temperature for 2h, the solution was diluted with diethyl ether (50 mL), washed with 1N hydrochloric acid (2 x 50 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with petroleum ether afforded the titled silyl ether (2.65 g, 95 %) as a colorless liquid.

IR (film): 2958, 2936, 2857, 2168, 1664, 1472, 1369, 1300, 1251, 1176, 1151, 1113, 1036, 994, 877, 839, 777 cm⁻¹. ¹H-NMR (500 MHz, CDCl₃): δ 5.68 (t, J = 6.9 Hz, 1H), 2.35 (m, 2H), 2.29 (s, 3H), 1.67 (m, 2H), 1.45 (s, 3H), 0.89 (s, 9H), 0.20 (s, 6H), 0.19 (s, 9H). ¹³C-NMR (125 MHz, CDCl₃): δ 128.8, 122.2, 109.9, 88.4, 69.0, 43.4, 30.9, 28.7, 27.2, 25.7, 18.0, -0.1, -3.0, -3.1. Anal. Calc'd for C₁₈H₃₅BrOSi₂: C, 53.57; H, 8.74. Found: C, 53.65; H, 8.72.

<u>3-Methyl-3-(*tert*-butyldimethylsiloxy</u>)-7-(<u>trideuteromethyl</u>)-1-trimethylsilyl-oct-6(*Z*)-en-1-yne

To a solution of the above vinyl bromide (600 mg, 1.49 mmol) in diethyl ether (15 mL), at -78 °C, was added 1.7M *tert*-butyllithium (1.9 mL, 3.28 mmol) and the resulting yellow solution warmed to 0 °C. after 30 min, copper(+1) iodide (570 mg, 3.0 mmol) was added and the green reaction mixture rapidly stirred for an additional 30 min. Trideuteromethyl iodide (0.28 mL, 4.47 mmol) was added and stirring continued for 8h. The reaction mixture was diluted with petroleum ether (150 mL) and washed with 1N sodium bisulfate (100 mL), 5% aqueous ammonium hydroxide (100 mL), brine (100 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with petroleum ether afforded the titled silyl ether (360 mg, 71 %) as a colorless liquid.

IR (film): 2959, 2936, 2858, 2167, 1472, 1369, 1252, 1170, 1105, 1043, 995, 883, 839, 776 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): δ 5.68 (t, J = 7.2 Hz, 1H), 2.18 (m, 2H), 1.71 (s, 3H), 1.66-1.54 (m, 2H), 1.44 (s, 3H), 0.89 (s, 9H), 0.20 (s, 6H), 0.19 (s, 9H). 13 C-NMR (125 MHz, CDCl₃): δ 131.4, 124.3, 110.3, 89.0, 69.2, 45.1, 30.9, 25.7, 25.6, 23.5, 18.1, 17.5, -0.2, -3.0, -3.1. HRMS Calc'd for $C_{15}H_{26}D_{3}OSi_{2}$ (M⁺ - t-Bu): 284.1942. Found: 284.1950.

3-Methyl-3-(tert-butyldimethylsiloxy)-7-(trideuteromethyl)-oct-6(Z)-en-1-yne

To a solution of the above alkyne (360 mg, 1.06 mmol) in methanol (10 mL) was added potassium carbonate (500 mg, 3.62 mmol) and the resulting suspension stirred at room temperature for 12h. The reaction mixture was filtered and the solid washed with diethyl ether (3 x 25 mL). The filtrate was washed with water (3 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 2% diethyl ether: petroleum ether afforded the titled terminal alkyne (250 mg, 88%) as a colorless liquid.

IR (film): 3310, 2957, 2931, 2858, 1442, 1371, 1253, 1174, 1108, 994, 838, 777 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): 5.16 (t, J = 7.1 Hz, 1H), 2.44 (s, 1H), 2.24-2.12 (m, 2H), 1.71 (s, 3H), 1.70-1.58 (m, 2H) 1.47 (s, 3H), 0.89 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 131.6, 124.1, 88.2, 71.9, 68.9, 45.1, 30.9, 25.7, 25.6, 23.3, 18.0, 17.5,

-2.9, -3.2.

Methyl 4-methyl-4-(*tert*-butyldimethylsilyloxy)-8-(trideuteromethyl)-non-7(Z)-en-2-ynoate **49**

To a solution of the above alkyne (250 mg, 0.933 mmol) in THF (10 ml) was added 1.6M n-butyllithium (0.64 mL, 1.02 mmol). After stirring at -78 °C for 30 min., methyl chloroformate (110 μ L, 1.42 mmol) was added and the reaction mixture warmed to room temperature. After an addition 30 min., the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried (MgSO₄) and concentrated *in vacuo*. Flash chromatography eluting with 2% diethyl ether: petroleum ether afforded silyl ether 49 (262 mg, 86 %) as a colorless liquid.

IR (film): 2957, 2931, 2859, 2233, 1752, 1722, 1436, 1254, 1171, 1046, 837, 778 cm⁻¹. 1 H-NMR (500 MHz, CDCl₃): 5.14 (t, J = 7.1 Hz, 1H), 3.80 (s, 3H), 2.26-2.10 (m, 2H), 1.72-1.65 (m, 2H), 1.70 (s, 3H), 1.51 (s, 3H), 0.90 (s, 9H), 0.23 (s, 3H), 0.21 (s, 3H). 13 C-NMR (125 MHz, CDCl₃): δ 154.0, 132.0, 123.5, 91.5, 75.8, 68.9, 52.6, 44.5, 30.1, 25.6(2), 23.2, 18.0, 17.6, -3.0, -3.3.