Supporting Information

Nickel-Catalyzed Addition of Dimethylzinc to Aldehydes Across Alkynes and 1,3-Butadiene: an Efficient Four-Component Connection Reaction

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Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel 60F₂₅₄). Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Distillation were carried out in a Kugelrohr apparatus and boiling points are meant to refer to the oven temperature. Proton and carbon NMR data were obtained with either a JEOL-GX400, Varian 300, or Gemini 200 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303. Combustion analyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within ± 0.4 %.

Solvents and Reagents. Tetrahydrofuran (THF) and ether were dried and distilled from sodium/benzophenone ketyl immediately prior to use under nitrogen atmosphere. Dichloromethane and triethylamine were distilled over calcium hydride. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) was distilled over calcium sulfate and calcium hydride, respectively, under reduced pressure. Acetone was distilled over potassium carbonate and hexane over sodium. Aldehydes were distilled

under reduced pressure prior to use. Dimethylzinc, diethylzinc, triethylborane (1.0 M in hexane; KANTO CHEMICAL), Ni(acac)₂ (Aldrich), and Ni(cod)₂ (KC) were used as received. Butadiene was purchased as a compressed gas in a pressurized cylinder (Tokyo Kasei Kogyo) and the gas was liquefied in a flask by cooling at -78 °C (dry ice-isopropanol) prior to use. Isoprene, 3-hexyne, diphenylacetylene, dimethyl acetylenedicarboxylate acid, 1-phenyl-1-butyne, 1-(trimethylsilyl)-1-propyne, 3-pentyn-1-ol were used as received (TKK).

General Procedure for the Four-Component Connection Reaction: (run 7, Table 1):

Into a flask containing Ni(acac)₂ (25.7 mg, 0.1 mmol) purged with N₂ were successively added THF (5 ml), 3-hexyne (98.6 mg, 1.2 mmol), 1,3-butadiene (0.11 ml, 1.2 mmol), 2-furaldehyde (96.1 mg, 1.0 mmol), and dimethylzinc (2.4 ml, 1 M in hexane) via syringes at room temperature. The homogeneous solution was stirred at room temperature for 2 h under N₂ and then quenched by adding 2 M HCl (25 ml). The mixture was extracted twice with ethyl acetate and the combined organic extracts were washed with sat. NaHCO₃ and with sat. NaCl, dried (MgSO₄), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane:ethyl acetate = 16:1, v/v) to give **1d** in 76% yield (189 mg) and **2b** in 15% yield (25 mg). *R_f* (**1d**) = 0.46, *R_f* (**2b**) = 0.39 (hexane:ethyl acetate = 4:1, v/v). **(3E,6E)-6-Ethyl-1-(2-furyl)-7-methyl-3,6-nonadiene-1-ol (1d)**: IR (neat) 3361 (s), 2963 (s), 1010 (m), 734 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.7 Hz, 3 H), 0.95 (t, *J* = 7.7 Hz, 3 H), 1.60 (s, 3 H), 1.98 (q, *J* = 7.7 Hz, 2 H), 2.02 (q, *J* = 7.7 Hz, 2 H), 2.56 (m, 2 H), 2.72 (d, *J* = 6.2 Hz, 2 H), 4.68 (t, *J* = 6.2 Hz, 1 H), 5.36 (dt, *J* = 15.4, 7.1 Hz, 1 H), 5.52 (dt, *J* = 15.4, 6.2 Hz, 1 H), 6.22 (br d, *J* = 3.3 Hz, 1 H), 6.31 (dd, *J* = 1.8, 3.3 Hz, 1 H), 7.36 (br d, *J* = 1.8 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.3, 13.6, 17.5, 24.8, 30.9, 35.3, 39.0, 67.3, 106.0, 110.1, 124.7, 131.3, 131.4, 133.1, 141.9, 156.3; HRMS calcd for C₁₆H₂₄O₂: 248.1776, found *m/z* (relative intensity) 248.1777 (M⁺, 41),

230 (18), 152 (100), 136 (22).

(3E,6E)-6-Ethyl-7-methyl-1-phenyl-3,6-nonadien-1-ol (1a): IR (neat) 3404 (s), 1454 (s), 1375 (m), 1028 (m), 970 (m), 910 (s), 735 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.5$ Hz, 3 H), 0.95 (t, $J = 7.5$ Hz, 3 H), 1.60 (s, 3 H), 1.99 (q, $J = 7.5$ Hz, 2 H), 2.02 (q, $J = 7.5$ Hz, 2 H), 2.41 (dt, $J = 7.7, 13.9$ Hz, 1 H), 2.48 (ddd, $J = 5.1, 6.2, 13.9$ Hz, 1 H), 2.72 (d, $J = 6.2$ Hz, 2 H), 4.68 (dd, $J = 5.1, 7.7$ Hz, 1 H), 5.35 (ddd, $J = 6.2, 7.7, 15.4$ Hz, 1 H), 5.51 (dt, $J = 15.4, 6.2$ Hz, 1 H), 7.23 - 7.37 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.3, 13.6, 17.6, 24.8, 27.1, 35.2, 42.8, 73.5, 125.4, 125.9, 127.4, 128.4, 131.3, 131.4, 133.0, 144.1; HRMS calcd for $\text{C}_{18}\text{H}_{26}\text{O}$: 258.1984, found m/z (relative intensity) 258.1973 (M^+ , 4), 256 (3), 240 (2), 107 (100), 99 (9).

(3E,6Z)-1,6,7-Triphenyl-3,6-octadien-1-ol (1b): IR (neat) 3404 (s), 3026 (s), 1597 (m), 1491 (s), 1441 (s), 1026 (s), 972 (s), 910 (s), 762 (s), 733 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.82 (br s, 1 H), 2.15 (s, 3 H), 2.40 (dt, $J = 14.1, 7.0$ Hz, 1 H), 2.46 (ddd, $J = 5.5, 7.7, 14.1$ Hz, 1 H), 3.27 (d, $J = 6.0$ Hz, 2 H), 4.60 (dd, $J = 5.5, 7.0$ Hz, 1 H), 5.40 (br ddd, $J = 7.0, 7.7, 15.2$ Hz, 1 H), 5.57 (dt, $J = 15.2, 6.0$ Hz, 1 H), 6.91 - 7.34 (m, 15 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 38.4, 42.7, 73.3, 125.7, 125.8, 126.5, 127.3, 127.6, 128.3, 129.2, 129.6, 131.5, 134.5, 135.4, 143.3, 143.9, 144.4; HRMS calcd for $\text{C}_{26}\text{H}_{26}\text{O}$: 354.1984, found m/z (relative intensity) 355 ($\text{M}^+ + 1$, 20), 354.1960 (M^+ , 64), 336 (6), 233 (19), 107 (100).

(3E,6Z)-6,7-Dicarbomethoxy-1-phenyl-3,6-octadien-1-ol (1c): IR (neat) 3444 (s), 2952 (s), 1722 (s), 1434 (s), 1211 (s), 1053 (m), 765 (m), 702 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.04 (s, 3 H), 2.33 (br s, 1 H), 2.38 (dt, $J = 13.9, 8.1$ Hz, 1 H), 2.48 (dt, $J = 13.9, 4.8$ Hz, 1 H), 3.18 (d, $J = 6.6$ Hz, 1 H), 3.19 (d, $J = 6.6$ Hz, 1 H), 3.76 (s, 3 H), 3.77 (s, 3 H), 4.67 (dd, $J = 4.8, 8.1$ Hz, 1 H), 5.47 (dm, $J = 15.4$ Hz, 1 H), 5.57 (dt, $J =$

15.4, 6.6 Hz, 1 H), 7.24 - 7.36 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.6, 34.4, 42.7, 51.9, 73.2, 125.7, 127.3, 128.3, 128.5, 130.3, 133.4, 136.2, 143.9, 168.8, 169.1; HRMS calcd for $\text{C}_{18}\text{H}_{22}\text{O}_5$: 318.1467, found m/z (relative intensity) 318.1439 (M^+ , <1), 314 (1), 287 (2), 212 (56), 180 (100).

(4*E*,7*E*)-7-Ethyl-8-methyl-1-phenyl-4,7-decadien-2-ol (1e): IR (neat) 3394 (s), 2869 (s), 1602 (m), 1496 (s), 1454 (s), 1373 (s), 1269 (m), 1031 (s), 970 (s), 742 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.94 (t, $J = 7.5$ Hz, 3 H), 0.96 (t, $J = 7.5$ Hz, 3 H), 1.62 (s, 3 H), 1.70 (br s, 1 H), 2.01 (q, $J = 7.5$ Hz, 2 H), 2.03 (q, $J = 7.5$ Hz, 2 H), 2.15 (m, 1 H, coalescing to dd, $J = 7.3, 13.9$ Hz, by irradiation at 3.81), 2.28 (m, 1 H, coalescing to dd, $J = 6.2, 13.9$ Hz, by irradiation at 3.81), 2.70 (dd, $J = 7.7, 13.6$ Hz, 1 H), 2.74 (d, $J = 5.9$ Hz, 2 H), 2.79 (dd, $J = 5.1, 13.6$ Hz, 1 H), 3.81 (m, 1 H), 5.42 (ddd, $J = 6.2, 7.3, 15.4$ Hz, 1 H), 5.50 (dt, $J = 15.4, 5.9$ Hz, 1 H), 7.20 - 7.34 (m, 5 H); HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{O}$: 272.2140, found m/z (relative intensity) 273 (M^++1 , 20), 272.2104 (M^+ , 100), 254 (4), 215 (23), 181 (11).

(3*E*,6*E*)-1-Cyclohexyl-6-ethyl-7-methyl-3,6-nonadien-1-ol (1f): IR (neat) 3381 (s), 2926 (s), 1450 (s), 1373 (m), 1028 (m), 970 (s), 893 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.94 (t, $J = 7.5$ Hz, 3 H), 0.96 (t, $J = 7.5$ Hz, 3 H), 0.98 - 1.37 (m, 12 H), 1.62 (s, 3 H), 1.64 - 1.78 (m, 4 H), 1.85 (m, 1 H), 2.01 (q, $J = 7.5$ Hz, 2 H), 2.03 (q, $J = 7.5$ Hz, 2 H), 2.07 (m, 1 H), 2.27 (m, 1 H), 2.74 (d, $J = 5.9$ Hz, 2 H), 3.33 (dt, $J = 3.6, 9.2$ Hz, 1 H), 5.39 (ddd, $J = 5.9, 7.7, 15.4$ Hz, 1 H), 5.48 (dt, $J = 15.4, 6.2$ Hz, 1 H); HRMS calcd for $\text{C}_{18}\text{H}_{32}\text{O}$: 264.2453, found m/z (relative intensity) 265 (M^++1 , 20), 264.2479 (M^+ , 100), 246 (6), 217 (15).

(3*E*,6*E*)-1-*t*-Butyl-7-methylnona-3,6-dien-1-ol (1g): IR (neat) 3445 (s), 2870 (s), 1454 (s), 1364 (s), 1240 (m), 1072 (s), 1007 (s), 970 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3)

δ 0.91 (s, 9 H), 0.94 (t, $J = 7.7$ Hz, 3 H), 0.95 (t, $J = 7.7$ Hz, 3 H), 0.98 (s, 3 H), 1.91 (ddd, $J = 8.2, 10.1, 14.1$ Hz, 1 H), 2.01 (q, $J = 7.7$ Hz, 2 H), 2.03 (q, $J = 7.7$ Hz, 2 H), 2.31 (br ddd, $J = 1.7, 4.8, 14.1$ Hz, 1 H), 2.74 (d, $J = 5.9$ Hz, 2 H), 3.19 (dd, $J = 1.7, 10.6$ Hz, 1 H), 5.41 (br ddd, $J = 4.8, 8.2, 15.4$ Hz, 1 H), 5.49 (dt, $J = 15.4, 5.9$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.3, 13.6, 17.5, 24.8, 25.8, 30.9, 34.5, 35.3, 35.4, 78.3, 127.5, 131.2, 131.5, 132.4; HRMS calcd for $\text{C}_{16}\text{H}_{30}\text{O}$: 238.2297, found m/z (relative intensity) 238.2323 (M^+ , 30), 151 (3), 136 (5), 123 (100).

1-[5-Ethyl-6-methyl-(2*E*,5*E*)-octadienyl]cyclohexanol (1h): IR (neat) 3385 (s), 2932 (s), 1448 (s), 1375 (m), 1263 (m), 1151 (m), 970 (s) cm^{-1} ; ^1H NMR (400 MHz, C_6D_6) δ 0.96 (t, $J = 7.5$ Hz, 3 H), 0.98 (t, $J = 7.5$ Hz, 3 H), 1.09 - 1.52 (m, 9 H), 1.63 (s, 3 H), 1.64 - 1.69 (m, 2 H), 2.00 (q, $J = 7.5$ Hz, 4 H), 2.07 (dd, $J = 5.9, 7.0$ Hz, 2 H), 2.75 (d, $J = 5.9$ Hz, 2 H), 5.45 (dt, $J = 15.2, 5.9$ Hz, 1 H), 5.54 (ddd, $J = 5.9, 7.0, 15.2$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.3, 13.7, 17.6, 22.3, 24.9, 25.9, 27.1, 35.4, 37.5, 45.4, 71.1, 124.7, 131.1, 131.6, 133.1; HRMS calcd for $\text{C}_{17}\text{H}_{30}\text{O}$: 250.2297, found m/z (relative intensity) 251 ($\text{M}^+ + 1$, 23), 250.2319 (M^+ , 100), 233 (50), 232 (90).

(3*E*,6*E*)-6-Ethyl-1,7-diphenyl-3,6-octadien-1-ol (1i; a mixture with (3*E*,6*E*)-1,6-diphenyl-7-methyl-3,6-nonadien-1-ol): IR (neat) 3393 (s), 2964 (s), 1599 (m), 1491 (s), 1441 (s), 1373 (m), 1026 (m), 970 (m), 766 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, $J = 7.3$ Hz, 3 H), 1.85 (q, $J = 7.3$ Hz, 2 H), 1.90 (s, 3 H), 2.04 (br s, 1 H), 2.50 (m, 2 H), 2.90 (d, $J = 6.0$ Hz, 2 H), 4.72 (br t, $J = 6.2$ Hz, 1 H), 5.47 (br ddd, $J = 6.6, 7.3, 15.2$ Hz, 1 H), 5.59 (br dt, $J = 15.2, 6.0$ Hz, 1 H), 7.06 - 7.37 (m, 10 H), ^{13}C NMR (100 MHz, CDCl_3) δ 13.5, 21.0, 26.2, 34.3, 42.7, 73.7, 125.9, 127.5, 128.1, 128.4, 132.1, 132.2, 134.9, 144.0, 145.2; HRMS calcd for $\text{C}_{22}\text{H}_{16}\text{O}$: 306.1984, found m/z (relative intensity) 307 ($\text{M}^+ + 1$, 27), 306.1992 (M^+ , 100), 291 (18), 288 (52).

(3E,6Z)-6-Methyl-1-phenyl-7-trimethylsilylocta-3,6-dien-1-ol (1j; a mixture with (3E)-7-methyl-1-phenyl-6-trimethylsilyl-3,6-octadien-1-ol): IR (neat) 3360 (s), 2910 (s), 1612 (m), 1454 (s), 1248 (s), 1028 (m), 968 (m), 856 (s), 835 (s), 756 (s), 700 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9 H), 1.63 (q, *J* = 1.5 Hz, 3 H), 1.74 (q, *J* = 1.5 Hz, 3 H), 2.03 (d, *J* = 3.1 Hz, 1 H), 2.44 (br dt, *J* = 13.9, 7.3 Hz, 1 H), 2.49 (br ddd, *J* = 5.3, 6.4, 13.9 Hz, 1 H), 2.80 (d, *J* = 6.2 Hz, 2 H), 4.69 (ddd, *J* = 3.1, 5.3, 7.3 Hz, 1 H), 5.35 (br ddd, *J* = 6.4, 7.3, 15.4 Hz, 1 H), 5.50 (br dt, *J* = 15.4, 6.2 Hz, 1 H), 7.24 - 7.37 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃), **major isomer** δ 0.38, 17.5 (C8), 23.0 (C6-Me), 38.3 (C5), 42.7 (C2), 73.5 (C1), 125.7 (C4), 125.8, 127.4, 128.3, 128.6 (C7), 131.7 (C3), 143.4, 143.9 (C6); **minor isomer** δ 0.69, 21.1 (C8), 25.3 (C7-Me), 34.7 (C5), 42.8 (C2), 73.5 (C1), 124.9 (C4), 125.8, 127.4, 128.3, 129.6 (C6), 133.8 (C3), 143.9, 144.6 (C7); HRMS calcd for C₁₈H₂₈OSi: 288.1909, found *m/z* (relative intensity) 289 (M⁺+1, 3), 288.1899 (M⁺, 7), 270 (5), 182 (100).

(3E,6E)-6,7-Dimethyl-1-phenyl-3,6-nonadiene-1,9-diol (1k; a mixture with (3E)-7-isopropylidene-1-phenyl-3-octene-1,8-diol): IR (neat) 3360 (s), 2880 (s), 1454 (m), 1039 (s), 970 (m), 758 (m), 700 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.68 (s, 3 H), 1.71 (s, 3 H), 2.33 (t, *J* = 6.8 Hz, 2 H), 2.40 - 2.48 (m, 2 H), 2.74 (d, *J* = 5.9 Hz, 2 H), 3.63 (t, *J* = 6.8 Hz, 2 H), 4.68 (dd, *J* = 1.8, 5.5 Hz, 1 H), 5.39 (br ddd, *J* = 7.3, 9.2, 15.4 Hz, 1 H), 5.48 (br dt, *J* = 15.4, 5.9 Hz, 1 H), 7.22 - 7.37 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃) **major isomer** δ 18.2 (C6-Me), 18.4 (C7-Me), 35.9 (C8), 38.0 (C5), 42.6 (C2), 61.0 (C9), 73.6 (C1), 125.9, 126.1 (C6), 127.5, 128.2 (C4), 128.4, 129.8 (C7), 131.7 (C3), 144.1; **minor isomer** δ 20.6 (Me), 35.8 (C7), 37.8 (C5), 42.6 (C2), 61.1 (C8), 73.6 (C1), 125.9, 126.3 (C6), 127.5, 128.4, 129.4, 132.2 (C3), 144.0; HRMS calcd for C₁₇H₂₄O₂: 260.1776, found *m/z* (relative intensity) 260.1772 (M⁺, 7), 243 (20), 242 (100), 228 (89).

(3E,6Z)-7-Methyl-1-phenyl-6-[2-(2-pyridinyloxy)-ethyl]-3,6-octadien-1-ol (1l; a mixture with (3E,6E)-6,7-dimethyl-1-phenyl-9-(2-pyridyloxy)-3,6-nonadien-1-ol): IR (neat) 3381 (s), 1597 (s), 1477 (s), 1433 (s), 1315 (s), 1288 (s), 779 (s), 700 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.67 (s, 3 H), 1.73 (s, 3 H), 2.37 - 2.48 (m, 2 H), 2.52 (t, *J* = 7.3 Hz, 2 H), 2.73 (d, *J* = 5.9 Hz, 2 H), 4.30 (t, *J* = 7.3 Hz, 2 H), 4.68 (m, 1 H), 5.47 (br ddd, *J* = 6.2, 7.3, 15.2 Hz, 1 H), 5.54 (dt, *J* = 15.4, 5.9 Hz, 1 H), 6.70 (d, *J* = 8.4 Hz, 1 H), 6.82 (br dd, *J* = 5.3, 6.8 Hz, 1 H), 7.23 - 7.35 (m, 5 H), 7.54 (ddd, *J* = 2.2, 6.8, 8.4 Hz, 1 H), 8.10 (br dd, *J* = 2.2, 5.3 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) **major isomer** δ 20.4 (Me), 20.6 (Me), 32.5 (C7), 36.5 (C5), 42.9 (C2), 64.6 (C8), 73.6 (C1), 111.2, 116.5, 125.8, 126.0, 126.4 (C4), 127.3, 128.4, 128.9 (C6), 132.4 (C3), 138.5, 144.1, 146.9, 164.0; **minor isomer** δ 18.3 (C6-Me), 18.6 (C7-Me), 34.4 (C8), 37.9 (C5), 42.7 (C2), 64.2 (C9), 73.6 (C1), 111.2, 116.5, 125.5 (C6), 125.9, 126.4 (C4), 127.4, 128.4, 129.0 (C7), 132.0 (C3), 138.5, 144.4, 146.9, 164.0; HRMS calcd for C₂₂H₂₇NO₂: 337.2042, found *m/z* (relative intensity) 338 (M⁺+1, 22), 337.2039 (M⁺, 100), 224 (23), 176 (40).

(6E)-Ethyl-3,7-dimethyl-1-phenyl-3,6-nonadien-1-ol (1m); a mixture of 3E and 3Z in 1:1 ratio: IR (neat) 3418 (s), 2968 (s), 1674 (m), 1454 (s), 1379 (m), 756 (m), 700 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, *J* = 7.3 Hz, 3 H), 0.96 (t, *J* = 7.3 Hz, 3 H), 1.62 (s, 3 H), 1.73 (s, 3 H), 1.99 (q, *J* = 7.3 Hz, 2 H), 2.05 (q, *J* = 7.3 Hz, 2 H), 2.12 (br s, 1 H), 2.33 (dd, *J* = 9.5, 13.6 Hz, 1 H), 2.42 (dd, *J* = 4.0, 13.6 Hz, 1 H), 2.76 (d, *J* = 7.0 Hz, 2 H), 4.75 (dd, *J* = 4.0, 9.5 Hz, 1 H), 5.20 (t, *J* = 7.0 Hz, 1 H), 7.23 - 7.37 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.3, 13.6, 16.2, 17.6, 25.0, 27.1, 30.9, 50.5, 71.3, 125.8, 127.3, 128.4, 128.6, 130.6, 131.1, 132.6, 144.3; HRMS calcd for C₁₉H₂₈O: 272.2140, found *m/z* (relative intensity) 272.2149 (M⁺, 69), 270 (100), 254 (32).

6,7,8,9-Tetramethoxycarbonyl-1-phenyldeca-3,6,8-trien-1-ol (3'); IR (neat) 3437 (s),

3032 (w), 2953 (m), 1728 (s), 1435 (w), 1242 (m), 1057 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.30 (s, 3 H), 2.38 (dt, $J = 13.9, 7.3$ Hz, 1 H), 2.49 (dt, $J = 13.9, 8.1$ Hz, 1 H), 3.50 (dm, $J = 5.9$ Hz, 1 H), 3.67 (s, 3 H), 3.69 (s, 3 H), 3.74 (s, 6 H), 4.67 (br dd, $J = 7.3, 8.1$ Hz, 1 H), 5.55 (dt, $J = 15.5, 7.3$ Hz, 1 H), 5.63 (dt, $J = 15.5, 5.9$ Hz, 1 H), 7.22 - 7.34 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.1, 33.3, 42.9, 52.1, 52.2, 52.3, 73.0, 125.6, 127.2, 128.2, 128.6, 129.5, 132.6, 140.6, 142.0, 143.8, 165.5, 165.7, 167.8, 168.1; HRMS calcd for $\text{C}_{24}\text{H}_{28}\text{O}_9$: 460.1733. Found m/z (relative intensity): 460.1716 (M^+ , 15), 442 ($\text{M}^+ - \text{H}_2\text{O}$, 96), 429 (100).

(*E*)-2-Ethyl-3-methyl-1-phenyl-2-penten-1-ol (3a): IR (neat) 3383 (s), 2964 (s), 1448 (s), 1373 (m), 1020 (s), 754 (m), 700 (s) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.78 (t, $J = 7.6$ Hz, 3 H), 1.04 (t, $J = 7.6$ Hz, 3 H), 1.78 (br s, 1 H), 1.84 (s, 3 H), 1.91 (br q, $J = 7.6$ Hz, 1 H), 2.01 – 2.19 (m, 3 H), 5.82 (br s, 1 H), 7.19 - 7.38 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.8, 15.6, 17.4, 20.3, 27.5, 72.7, 125.6, 126.6, 128.0, 134.8, 135.5, 143.3; HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{O}$: 204.1514. Found m/z (relative intensity): 204.1545 (M^+ , 33), 175 (100), 157 (41).

3-Methyl-1-phenyl-2-trimethylsilyl-2-buten-1-ol (3b): IR (neat) 3466 (s), 2897 (s), 1605 (s), 1493 (s), 1448 (s), 1248 (s), 1009 (s), 839 (s), 748 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.02 (s, 9 H), 1.80 (d, $J = 3.7$ Hz, 1 H), 1.84 (s, 3 H), 1.97 (s, 3 H), 5.80 (d, $J = 3.7$ Hz, 1 H), 7.19 - 7.35 (m, 5 H); HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$: 234.1440. Found m/z (relative intensity): 234.1434 (M^+ , 100), 232 (21), 219 (61).

Preparation of 2-(3-Pentynyloxy)pyridine (4g): Into a round-bottom flask was placed NaH (480 mg; a 60% dispersion in oil, 12 mmol). The dispersion was washed with hexane (2 x 2 ml) to remove the oil under N_2 . To the flask was added DMF (25 ml) and heterogeneous mixture was cooled to 0°C , into which was added dropwise 3-

pentyn-1-ol (0.92 ml, 10 mmol). After stirring for 30 min at 0 °C, 2-fluoropyridine (1.0 ml, 12 mmol) was added dropwise and stirred at same temperature for 10 h. The mixture was partitioned into ethyl acetate (50 ml) and water (50 ml). The organic layer was washed with brine, dried (MgSO₄), and concentrated *in vacuo*. The residue was distilled (80 °C/5 mm Hg) to give **4g** in 52 % yield. ¹H NMR (200 MHz, CDCl₃) δ 1.82 (t, *J* = 3.0 Hz, 3 H), 2.62 (tq, *J* = 7.0, 3.0 Hz, 2 H), 4.37 (t, *J* = 7.0 Hz, 2 H), 6.75 (br d, *J* = 8.5 Hz, 1 H), 6.85 (br t, *J* = 8.5 Hz, 1 H), 7.56 (br t, *J* = 8.5 Hz, 1 H), 8.14 (br d, *J* = 8.5 Hz, 1 H).

Preparation of 1,ω-Dienynes **5**

2-(2,4-Pentadienyl)-2-(2-propynyl)malonic Acid Diethyl Ester (5a) and **2-(2-Butynyl)-2-(2,4-pentadienyl)malonic Acid Diethyl Ester (5b)**:^{1,2} To a solution of 1,4-pentadien-3-ol (9.73 ml, 100 mmol, Aldrich) was added conc. HCl (25 ml, 300 mmol) at 0 °C and the mixture was stirred at the same temperature for 2 h. The mixture was extracted with pentane and the organic layer was successively washed with water and sat. NaHCO₃ and dried over MgSO₄. After distillation of the solvent under atmospheric pressure, the residue was distilled (70 °C/100 mmHg) to give the 1-chloro-2,4-pentadiene (75%).

Into a round-bottom flask was placed NaH (1.44 g; a 60% dispersion in oil, 36 mmol). The dispersion was washed with hexane (2 x 5 ml). Into the flask were added THF (120 ml) and DMSO (10 ml), and the heterogeneous mixture was cooled to 0 °C. Into this was added dropwise a solution of diethyl malonate (9.7 ml, 65 mmol/THF 10 ml) at same temperature. After 1 h, a solution of 1-chloro-2,4-pentadiene (3.1 ml, 30mmol) in THF (10 ml) was added dropwise at the same temperature. The resulting mixture was allowed to warm to ambient temperature, stirred for 16 h. Into this mixture was added water (50 ml). THF was removed *in vacuo* and the resulting oil was dissolved in ether. The organic layer was washed with

water dried (MgSO₄), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 64/1, v/v) to provide 2-(2,4-pentadienyl)malonic acid diethyl ester (70 %).

In a round-bottom flask was placed NaH (250 mg; a 60% dispersion in oil, 6.25 mmol). The dispersion was washed with hexane as above. Into the flask were added THF (30 ml) and DMSO (5 ml). This heterogeneous mixture was cooled to 0 °C. To this was added dropwise a solution of 2-(2,4-pentadienyl)malonic acid diethyl ester (1.13 g, 5 mmol) in THF (5 ml) at the same temperature. After 1 h, either a solution of propargyl bromide (1.12 ml, 10 mmol) in THF (5 ml) or a solution of 1-bromo-2-butyne (0.88 ml, 10 mmol) in THF (5 ml) was added dropwise. The mixture was allowed to warm to ambient temperature, and stirred for 2 h. After addition of water (25 ml), THF was removed *in vacuo* and a resulting oil was partitioned between ether and water. The organic layer was washed with water, dried (MgSO₄), and the solvent was removed *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5a** in 79% yield. Distillation (110 °C/0.3 mmHg) furnished **5b** in 73% yield. **5a**: IR (neat) 3292 (m), 1736 (s), 1192 (s), 1007 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.25 (t, *J* = 7.0 Hz, 6 H), 2.02 (t, *J* = 2.6 Hz, 1 H), 2.79 (d, *J* = 2.6 Hz, 2 H), 2.83 (br d, *J* = 7.8 Hz, 2 H), 4.21 (q, *J* = 7.0 Hz, 4 H), 5.02 (br d, *J* = 10.6 Hz, 1 H), 5.13 (br d, *J* = 16.5 Hz, 1 H), 5.50 (dt, *J* = 15.2, 7.8 Hz, 1 H), 6.16 (br dd, *J* = 10.6, 15.2 Hz, 1 H), 6.27 (dt, *J* = 16.5, 10.6 Hz, 1 H). Anal. Calcd for C₁₅H₂₀O₄: C, 68.16; H, 7.63. Found: C, 68.50; H, 7.43. **5b** is a known compound (RN 222549-37-3): IR (neat) 1738 (s), 1603 (m), 1211 (s), 1055 (s) cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.26 (t, *J* = 7.0 Hz, 6 H), 1.77 (t, *J* = 2.0 Hz, 3 H), 2.73 (q, *J* = 2.0 Hz, 2 H), 2.81 (br d, *J* = 8.0 Hz, 2 H), 4.20 (q, *J* = 7.0 Hz, 4 H), 5.02 (br d, *J* = 10.2 Hz, 1 H), 5.13 (br d, *J* = 16.5 Hz, 1 H), 5.52 (dt, *J* = 15.0, 8.0 Hz, 1 H), 6.14 (br dd, *J* = 10.2, 15.0 Hz, 1 H), 6.28 (dt, *J* = 16.5, 10.2 Hz, 1 H).

2-(3-Pentynyl)-2-(2,4-pentadienyl)malonic Acid Dimethyl Ester (5m) is prepared

from 2-(2,4-pentadienyl)malonic acid dimethyl ester (as above) and 1-bromo-3-pentyne (Aldrich) under similar way to give **5a** and **5b**. **5m**: IR (neat) 2955 (s), 1732 (s), 1437 (s), 1271 (s), 1202 (s), 1178 (s), 1084 (m), 1013 (m), 974 (m) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.75 (s, 3 H), 2.08 – 2.02 (m, 4 H), 2.68 (d, $J = 7.8$ Hz, 2 H), 3.72 (s, 6 H), 5.02 (d, $J = 10.2$ Hz, 1 H), 5.13 (d, $J = 16.6$ Hz, 1 H), 5.49 (dt, $J = 7.8, 14.9$ Hz, 1 H), 6.09 (dd, $J = 10.2, 14.9$ Hz, 1 H), 6.28 (dt, $J = 16.6, 10.2$ Hz, 1 H); HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4$: 264.1362. Found m/z (relative intensity): 264.1353 (M^+ , 100), 249 (12).

***N*-2-Butynyl-*N*-(2*E*,4-pentadienyl)-*p*-toluenesulfonamide (5c):**³ Into a mixture of *p*-toluenesulfonamide (3.77 g, 22 mmol) and potassium carbonate (2.76 g, 20 mmol) in acetone (20 ml) was added dropwise 1-chloro-2,4-pentadiene (2.1 ml, 20 mmol) at room temperature. The mixture was refluxed for 23 h under N_2 and then poured into water. Extraction with dichloromethane, drying over MgSO_4 , concentration *in vacuo*, followed by purification by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) provided *N*-(2,4-pentadienyl)-*p*-toluenesulfonamide in 44 % isolated yield.

Into a flask containing NaH (400 mg; a 60% dispersion in oil, 10 mmol; washed with hexane as above) was added DMF (50 ml) and then was added dropwise a solution of *N*-(2,4-pentadienyl)-*p*-toluenesulfonamide (1.90 g, 8.0 mmol) in DMF (10 ml) at 0 °C. After stirring for 1 h, 1-bromo-2-butyne (1.05 ml, 12 mmol) was added dropwise via syringe. The mixture was allowed to warm to ambient temperature and stirred for 20 h, and then poured into water. Extracts with ethyl acetate were dried over MgSO_4 and concentrated *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5c** in 90% yield. **5c**: ^1H NMR (300 MHz, CDCl_3) δ 1.56 (t, $J = 2.0$ Hz, 3 H), 2.42 (s, 3 H), 3.83 (br d, $J = 8.0$ Hz, 2 H), 4.00 (q, $J = 2.0$ Hz, 2 H), 5.11 (br d, $J = 10.3$ Hz, 1 H), 5.20 (br d, $J = 16.5$ Hz, 1 H), 5.58 (dt, $J = 15.0, 8.0$ Hz, 1 H), 6.22 (br dd, $J = 10.3, 15.0$ Hz, 1 H), 6.33 (dt, $J = 16.5, 10.3$ Hz, 1 H), 7.31 (d, $J = 8.4$ Hz, 2 H), 7.72 (d, $J = 8.4$ Hz, 2 H). Anal. Calcd for

C₁₆H₁₉NO₂S: C, 66.41; H, 6.62; N, 4.84; S, 11.08. Found: C, 66.80; H, 6.82; N, 4.49; S, 11.48.

5-(2-Butynyloxy)-(1,3E)-pentadiene (5d) and 1-[(2E,4)-Pentadienyloxy]-3-phenyl-2-propyne (5e):⁴ Into a flask containing NaH (680 mg; a 60% dispersion in oil, 17 mmol; washed with hexane as above) was added THF (30 ml) and the mixture was cooled to 0 °C. To this solution was added dropwise either a solution of 2-butyne-1-ol (1.12 ml, 15 mmol) in 10 ml THF, or a solution of 1-phenyl-1-propyne-3-ol (15 mmol) in 10 ml THF at the same temperature. The resulting mixture was allowed to warm at room temperature and stirred for 1 h. This mixture was cooled again to 0 °C, and into this a solution of 1-chloro-2,4-pentadiene (1.79 ml, 17 mmol) in 10 ml THF was added dropwise via syringe. The mixture was allowed to warm to ambient temperature, and stirred for 22 h. The mixture was poured onto ice-water and extracted with ether. The organic phase was washed with sat. NH₄Cl and with sat. NaHCO₃, and dried over MgSO₄. The solvent was removed *in vacuo* and the residue was purified by distillation (90°C/5 mmHg) to give **5d** in 73% yield or by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5e** in 94% yield. **5d**: IR (neat) 1605 (m), 1074 (s), 1005 (s), 907 (s) cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.88 (t, *J* = 2.0 Hz, 3 H), 4.08 (br d, *J* = 7.0 Hz, 2 H), 4.13 (q, *J* = 2.0 Hz, 2 H), 5.12 (br d, *J* = 11.0 Hz, 1 H), 5.22 (br d, *J* = 16.5 Hz, 1 H), 5.78 (br dt, *J* = 15.0, 7.0 Hz, 1 H), 6.27 (br dd, *J* = 11.0, 15.0 Hz, 1 H), 6.36 (dt, *J* = 16.5, 11.0 Hz, 1 H). Anal. Calcd for C₉H₁₂O: C, 79.37; H, 8.88. Found: C, 79.08; H, 8.58. **5e** is a known compound (RN 478176-03-3): IR (neat) 1603 (m), 1076 (s), 1005 (s), 756 (s), 691 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.19 (d, *J* = 6.0 Hz, 2 H), 4.39 (s, 2 H), 5.14 (br d, *J* = 10.3 Hz, 1 H), 5.24 (br d, *J* = 15.6 Hz, 1 H), 5.81 (br dt, *J* = 12.2, 6.0 Hz, 1 H), 6.33 (dd, *J* = 10.3, 12.2 Hz, 1 H), 6.37 (dt, *J* = 15.6, 10.3 Hz, 1 H), 7.28 – 7.36 (m, 3 H), 7.40 – 7.50 (m, 2 H).

5-(3-Pentynyloxy)-(1,3E)-pentadiene (5j) is prepared from 1-chloro-2,4-pentadiene and 3-pentyn-1-ol under similar way to give **5d** and **5e**. **5j**: IR (neat) 3086 (w), 2918 (s), 2858 (s), 1728 (w), 1605 (w), 1605 (w), 1439 (m), 1360 (m), 1113 (s), 1005 (m), 970 (m), 908 (w) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.78 (br s, 3 H), 2.42 (br t, $J = 6.8$ Hz, 2 H), 3.52 (t, $J = 6.8$ Hz, 2 H), 4.05 (d, $J = 6.4$ Hz, 2 H), 5.10 (d, $J = 10.4$ Hz, 1 H), 5.22 (d, $J = 16.6$ Hz, 1 H), 5.77 (dt, $J = 14.9, 6.4$ Hz, 1 H), 6.26 (dd, $J = 10.4, 14.9$ Hz, 1 H), 6.35 (dt, $J = 16.6, 10.4$ Hz, 1 H); HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{O} - \text{CH}_3$: 135.0810. Found m/z (relative intensity): 135.0644 (M - CH_3 , 100), 122 (18), 105 (20).

2-[(2E,4)-Pentadienyl]-2-(3-pentynyl)malonic Acid Diethyl Ester (5g): A solution of 3-pentyn-1-ol (3.0 ml, 33 mmol, Aldrich) and triethylamine (4.6 ml, 33 mmol) in dichloromethane (50 ml) was cooled to 0 °C. To this solution was added *p*-toluenesulfonyl chloride (5.72 g, 30 mmol) at the same temperature. The resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was washed with sat. NaHCO_3 and with brine. The organic phase was dried over MgSO_4 and the solvent was removed *in vacuo*. Distillation of the residue (160 °C /0.2 mmHg) provided 3-pentynyl tosylate in 86% yield.

NaH (280 mg; a 60% dispersion in oil, 6.9 mmol) placed in a flask was washed with hexane under N_2 . To the flask were added THF (30 ml) and DMSO (5 ml) via syringe and the mixture was cooled to 0 °C. To this mixture was added dropwise a solution of 2-(2,4-pentadienyl)malonic acid diethyl ester (1.2 ml, 5.7 mmol) in THF (10 ml) at the same temperature. After being allowed to warm to room temperature and stirred for 1 h, a solution of 3-pentyl tosylate (1.64 g, 6.9 mmol) in THF (10 ml) was added dropwise into this mixture. The mixture was heated at reflux for 28 h. Into this mixture was added ice and THF was removed *in vacuo*. The residual oil was partitioned between ether and water. The organic layer was washed with water, dried (MgSO_4), and concentrated *in vacuo*. The residue was purified by column

chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5g** in 62% yield. **5g**: IR (neat) 1732 (s), 1603 (m), 1188 (s), 1082 (s), 1007 (s) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.25 (t, J = 6.8 Hz, 6 H), 1.75 (br s, 3 H), 2.06 – 2.17 (m, 4 H), 2.68 (br d, J = 7.6 Hz, 2 H), 4.18 (q, J = 6.8 Hz, 4 H), 5.03 (br d, J = 10.6 Hz, 1 H), 5.12 (br d, J = 16.6 Hz, 1 H), 5.53 (dt, J = 15.0, 7.6 Hz, 1 H), 6.10 (br dd, J = 10.6, 15.0 Hz, 1 H), 6.27 (br dt, J = 16.6, 10.6 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 3.4, 14.0, 14.1, 32.0, 36.0, 57.2, 61.2, 76.0, 77.9, 116.3, 127.7, 134.8, 136.4, 170.5; HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: 292.1675. Found m/z (relative intensity): 292.1660 (M^+ , 13), 247 (100).

***N*-[*(2E,4)*-Pentadienyl]-*N*-(3-pentynyl)-*p*-toluenesulfonamide (**5h**):** NaH (1.8 g; 60% dispersion in oil, 12 mmol) placed in a flask was washed with hexane under N_2 . Into the flask were added THF (50 ml) and DMSO (5 ml) and the mixture was cooled to 0 °C. To this solution was added dropwise a solution of *N*-(2,4-pentadienyl)-*p*-toluenesulfonamide (2.37 g, 10 mmol) in THF (10 ml) at the same temperature. This solution was allowed to warm to room temperature and stirred for 1 h and then, into which were added 3-pentynyl tosylate (2.86 g, 12 mmol, dissolved in 10 ml THF) and sodium iodide (0.48 g, 12 mmol). The mixture was refluxed for 43 h and then poured into water. The ethereal extracts were washed with water, dried (MgSO_4), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5h** in 45% yield. **5h**: ^1H NMR (200 MHz, CDCl_3) δ 1.74 (t, J = 3.0 Hz, 3 H), 2.38 (tq, J = 8.0, 3.0 Hz, 2 H), 2.42 (s, 3 H), 3.23 (t, J = 8.0 Hz, 2 H), 3.87 (d, J = 7.0 Hz, 2 H), 5.08 (br d, J = 10.0 Hz, 1 H), 5.17 (br d, J = 16.6 Hz, 1 H), 5.50 (dt, J = 14.0, 7.0 Hz, 1 H), 6.12 (br dd, J = 10.0, 14.0 Hz, 1 H), 6.27 (dt, J = 16.6, 10.0 Hz, 1 H), 7.29 (d, J = 8.4 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H); HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$: 303.1293. Found m/z (relative intensity): 303.1284 (M^+ , 4), 250 (100), 212 (13).

***N*-[**(3*E*,5)**-hexadienyl]-*N*-(2-butynyl)-*p*-toluenesulfonamide (**5i**):^{5,6}** Into a mixture of *p*-toluenesulfonamide (6.85 g, 40 mmol) and potassium carbonate (2.76 g, 20 mmol) in acetone (20 ml) was added dropwise propargyl bromide (1.8 ml, 20 mmol) at room temperature and the mixture was refluxed for 21 h. The mixture was poured into water and extracted with ether. The organic extract was dried (MgSO₄) and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide *N*-(2-butynyl)-*p*-toluenesulfonamide in 35 % yield.

A solution of lithium diisopropylamide (LDA) was prepared by the slow addition of *n*-BuLi (60 ml, 96 mmol, 1.6 M in hexane) to a solution of diisopropylamine (13.5 ml, 96 mmol) in THF (160 ml) at -78 °C. To this solution was added dropwise hexamethylphosphotriamide (18.1 ml, 104 mmol). After stirring at -78 °C for 30 min, methyl sorbate (10.5 ml, 80 mmol) was added over 2 h and stirring was continued for an additional hour at -78 °C. Then the dark-red mixture was siphoned into a rapidly stirred solution of acetic acid (13.7 ml, 240 mmol) in H₂O (288 ml) at 0 °C. The resultant solution was extracted with pentane. The combined extracts were washed with water and then with sat. NaHCO₃. The organic phase was dried over MgSO₄ and the solvent removed *in vacuo*. The residue was distilled (80 °C / 20 mmHg) to give methyl 3,5-hexadienoate in 99 % yield.

A solution of methyl 3,5-hexadienoate (3.79 g, 30 mmol) in ether (10 ml) was added into suspension of LiAlH₄ (910.8 mg, 24 mmol) in ether (50 ml) at 0 °C. After being stirred for 1 h at same temperature, the mixture was quenched by addition of a mixture of THF/H₂O (2:1, 30 ml), and then 2M HCl (30 ml). The mixture was extracted with ethyl acetate and the combined extracts were washed with brine, dried (MgSO₄), and concentrated *in vacuo*. The residue was distilled (80 °C/10 mmHg) to give 3,5-hexadien-1-ol in 78 % yield.

N-(2-butynyl)-*p*-toluenesulfonamide (1.56 g, 7 mmol) and triphenylphosphine (3.67

g, 14 mmol) were dissolved in THF (20 ml). To this solution were added dropwise 3,5-hexadien-1-ol (0.59 g, 6 mmol) and diethyl azodicarboxylate (2.09 g, 12 mmol, 40% in toluene) at room temperature, and the mixture was stirred for 4 h. The solvents were removed *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5i** in 63 % yield. **5i**: ¹H NMR (200 MHz, CDCl₃) δ 1.56 (t, *J* = 3.0 Hz, 3 H), 2.36 (q, *J* = 7.0 Hz, 2 H), 2.41 (s, 3 H), 3.20 (t, *J* = 7.0 Hz, 2 H), 4.04 (q, *J* = 3.0 Hz, 2 H), 5.02 (br d, *J* = 10.0 Hz, 1 H), 5.12 (br d, *J* = 15.8 Hz, 1 H), 5.62 (dt, *J* = 15.8, 7.0 Hz, 1 H), 6.12 (br dd, *J* = 10.0, 15.8 Hz, 1 H), 6.29 (dt, *J* = 15.8, 10.0 Hz, 1 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.72 (d, *J* = 8.5 Hz, 2 H). Anal. Calcd for C₁₇H₂₁NO₂S: C, 67.29; H, 6.98; N, 4.62; S, 10.57. Found: C, 67.65; H, 6.60; N, 4.48; S, 10.97.

***o*-[*(2E,4-Pentadienyloxy)*(trimethylsilylethynyl)benzene (**5k**): and *o*-[*(2E,4-Pentadienyloxy)*(phenylethynyl)benzene (**5l**):**^{7,8} Into a mixture of bis-(triphenylphosphine)palladium(II) dichloride (221 mg, 0.3 mmol) and copper(I) iodide (171.4 mg, 0.9 mmol) in benzene (50 ml) was added 2-iodophenol (2.2 g, 10 mmol), either ethynyltrimethylsilane (2.1 ml, 15 mmol) or ethynylbenzene (1.6 ml, 15 mmol), and diisopropylamine (1.4 ml, 10 mmol). The resulting solution was stirred at room temperature for 2 h. The mixture was passed through a short pad of celite and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate and the solution was washed with water, dried (MgSO₄), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide either *o*-(trimethylsilylethynyl)phenol in 99% yield or *o*-phenylethynylphenol in 99% yield.

Into a mixture of *o*-(trimethylsilylethynyl)phenol (1.93 g, 10 mmol) and potassium carbonate (1.52 g, 11 mmol) in acetone (30 ml) were added potassium iodide (0.17 g, 1 mmol) in one portion and 1-chloro-2,4-pentadiene (1.2 ml, 11 mmol) dropwise at room

temperature. The mixture was refluxed for 5 h. After being passed through a short pad of celite, washed with ethyl acetate, the filtrate was concentrated *in vacuo*. The residue was dissolved in ether and the solution was washed with sat. NaHCO₃ and with brine, dried (MgSO₄), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5k** in 53 % yield. Alkylation of 2-phenylethynylphenol (1.94 g, 10 mmol) with 1-chloro-2,4-pentadiene was undertaken in a similar way to give **5l** in 86% yield. **5k**: IR (neat) 2458 (s), 1595 (s), 1114 (s), 1005 (s), 842 (s), 750 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.26 (s, 9 H), 4.64 (d, *J* = 5.0 Hz, 2 H), 5.13 (br d, *J* = 10.6 Hz, 1 H), 5.25 (br d, *J* = 16.6 Hz, 1 H), 5.92 (dt, *J* = 15.0, 5.0 Hz, 1 H), 6.37 (br dd, *J* = 10.6, 15.0 Hz, 1 H), 6.48 (br dt, *J* = 16.6, 10.6 Hz, 1 H), 6.85 (br d, *J* = 8.0 Hz, 1 H), 6.89 (br t, *J* = 8.0 Hz, 1 H), 7.26 (br t, *J* = 8.0 Hz, 1 H), 7.45 (br d, *J* = 8.0 Hz, 1 H); HRMS calcd for C₁₆H₂₀OSi: 256.1283. Found *m/z* (relative intensity): 256.1273 (M⁺, 100), 242 (18), 241 (80). **5l**: IR (neat) 1593 (s), 1107 (s), 1003 (s), 754 (s), 691 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.68 (d, *J* = 5.0 Hz, 2 H), 5.12 (br d, *J* = 10.0 Hz, 1 H), 5.20 (br d, *J* = 16.4 Hz, 1 H), 5.96 (dt, *J* = 14.6, 5.0 Hz, 1 H), 6.37 (br dd, *J* = 10.0, 14.6 Hz, 1 H), 6.48 (br dt, *J* = 16.4, 10.0 Hz, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 6.96 (t, *J* = 8.0 Hz, 1 H), 7.20 – 7.45 (m, 4 H), 7.46 – 7.63 (m, 3 H); HRMS calcd for C₁₉H₁₆O: 260.1201. Found *m/z* (relative intensity): 260.1204 (M⁺, 100), 259 (49), 246 (6), 233 (15).

3-Hydroxy-1,4,4-triphenyl-(6*E*,8)-nonadien-1-yne (5f):⁹ Into a mixture of palladium(II) acetate (68 mg, 0.3 mmol), 1,1'-bis(diphenylphosphino)ferrocene (166 mg, 0.3 mmol) and lithium chloride (250 mg, 6 mmol) in THF (30 ml) were added 1,4-pentadien-3-ol (0.58 ml, 6 mmol), diphenylacetaldehyde (0.89 ml, 5 mmol, Aldrich), triethylamine (0.84 ml, 6 mmol), and triethylborane (12 ml, 12 mmol, 1 M in hexane) via syringe under nitrogen atmosphere. The resulting solution was stirred at 50 °C for 24 h. After the reaction completes, the most portion of the solvents was removed with

a rotary evaporator, and the residual solution is diluted with ethyl acetate (30 mL). The organic phase is washed with 2 M HCl (20 mL), sat-NaHCO₃ (30 mL), and brine (30 mL), and then dried over magnesium sulfate, filtered, and concentrated. The residue is purified by means of flash column chromatography over silica gel (eluent; hexane:ethyl acetate = 16:1 v/v) to provide 2,2-diphenyl-(4*E*,6)-heptadienal in 92% yield.

A solution of lithium acetylide was prepared by the addition of *n*-BuLi (2 ml, 3.3 mmol, 1.6 M in hexane) to a solution of phenylacetylene (0.36 ml, 3.3 mmol) in THF (5 ml) at -78 °C. A solution of 2,2-diphenyl-(4*E*,6)-heptadienal (787 mg, 3 mmol) dissolved in THF (5 ml) was added dropwise to the lithium acetylide solution at -78 °C, and the reaction mixture was stirred at ambient temperature for 3 h. The mixture was quenched by the addition of 1 M HCl (4 ml) at 0 °C and diluted with diethyl ether (25 ml). The organic phase was washed with 1 M HCl (25 mL), sat-NaHCO₃ (25 mL), and brine (25 mL), and then dried over magnesium sulfate, filtered, and concentrated. The residue is purified by means of flash column chromatography over silica gel (eluent; hexane:ethyl acetate = 16:1 v/v) to provide **5f** in 69 % yield. **5f**: IR (neat) 3422 (s), 3057 (s), 2926 (m), 2199 (w), 1663 (w), 1595 (m), 1495 (m), 1445 (m), 1034 (m), 762 (s), 698 (s) cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 3.15 (d, *J* = 7.7 Hz, 2 H), 4.95 (d, *J* = 10.6 Hz, 1 H), 5.07 (d, *J* = 16.4 Hz, 1 H), 5.22 (dt, *J* = 14.9, 7.7 Hz, 1 H), 5.30 (d, *J* = 8.9 Hz, 1 H), 6.13 (dd, *J* = 10.6, 14.9 Hz, 1 H), 6.17 (dt, *J* = 16.4, 10.6 Hz, 1 H), 7.30 (m, 15 H); HRMS calcd for C₂₇H₂₄O: 364.1827. Found *m/z* (relative intensity): 364.1809 (M⁺, 100), 347 (5), 346 (15).

7-(2-Butynyloxy)-6,6-diphenyl-(1,3*E*)-heptadiene (5n): To a solution of 2,2-diphenyl-(4*E*,6)-heptadienal (2.62 g, 10 mmol) dissolved in ethanol (50 ml) was added NaBH₄ (0.38 g, 10 mmol) and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* and the residue was dissolved in diethyl ether (50

ml). The solution was washed with 2M HCl (30 ml), and then the aqueous phase was extracted with diethyl ether (3 x 30 ml). Combined organic extracts was washed with sat-NaHCO₃ (25 mL), and brine (30 mL), and then dried over magnesium sulfate, filtered, and concentrated. The residue is purified by means of flash column chromatography over silica gel (eluent; hexane:ethyl acetate = 16:1 v/v) to provide 2,2-diphenyl-(4*E*,6)-heptadien-1-ol in 88 % yield.

Into a flask containing NaH (420 mg; a 60% dispersion in oil, 10 mmol; washed with hexane) was added DMF (20 ml) and the mixture was cooled to 0 °C. To this solution was added dropwise a solution of 2,2-diphenyl-(4*E*,6)-heptadien-1-ol (2.31 g, 8.7 mmol) in 5 ml DMF at the same temperature. The resulting mixture was allowed to warm at room temperature and stirred for 3 h. This mixture was cooled again to 0 °C, and into this a solution of 1-bromo-2-butyne (0.85 ml, 9.6 mmol, Aldrich) in 5 ml DMF was added dropwise via syringe. The mixture was allowed to warm to ambient temperature, and stirred for 24 h. The mixture was poured onto ice-water 30 mL and extracted with pentane 30 mL. The organic phase was washed with sat. NH₄Cl and with sat. NaHCO₃, and dried over MgSO₄. The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **5n** in 27% yield. **5n**: IR (neat) 3057 (w), 2918 (m), 2243 (w), 1712 (s), 1599 (w), 1495 (m), 1447 (s), 1360 (m), 1259 (m), 1090 (s), 1028 (m), 758 (s), 700 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.83 (br s, 3 H), 3.02 (d, *J* = 7.4 Hz, 2 H), 4.00 – 4.06 (m, 4 H), 4.93 (d, *J* = 10.2 Hz, 1 H), 5.06 (d, *J* = 16.7 Hz, 1 H), 5.39 (dt, *J* = 14.6, 7.4 Hz, 1 H), 6.10 (dd, *J* = 10.2, 14.6 Hz, 1 H), 6.20 (dt, *J* = 16.7, 10.2 Hz, 1 H), 7.13 – 7.43 (m, 10 H); HRMS calcd for C₂₃H₂₄O: 316.1827. Found *m/z* (relative intensity): 316.1825 (M⁺, 2), 264 (6), 249 (100).

General Procedure for the Ni-Catalyzed Cyclization of 1,ω-Dienyne (run 2, Table 4): To a homogeneous solution of Ni(acac)₂ (25.6 mg, 0.1 mmol) and 1,ω-dienyne **5h**

(303 mg, 1 mmol) in dry THF (5 ml) were successively added benzaldehyde (212 mg, 2 mmol) and dimethylzinc (2.4 ml, 1 M in hexane). The mixture was stirred at room temperature for 1 h under N₂. The reaction mixture was poured into ice water and 2M HCl (5 ml) was added, then the mixture was extracted with ethyl acetate (2 x 20 ml). The combined organic extracts were washed with sat. NaHCO₃ and with sat. NaCl, dried (MgSO₄), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane:ethyl acetate = 12:1, v/v) to give **6h** in 96% yield (408 mg). $R_f(\mathbf{6h}) = 0.20$ (hexane:ethyl acetate = 4:1, v/v).

(2*S,4'*S*')-4,4-Diethoxycarbonyl-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-(1*Z*)-**

ethylidenecyclopentane (6a): a mixture of two diastereomers in a ratio of 11:1; IR (neat): 3530 (s), 1724 (s), 1157 (s), 970 (s), 912 (s), 700 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, major isomer) δ 1.23 (t, $J = 7.1$ Hz, 3 H), 1.24 (t, $J = 7.1$ Hz, 3 H), 1.53 (ddm, $J = 2.4, 7.1$ Hz, 3 H), 1.98 (dd, $J = 6.6, 13.2$ Hz, 1 H), 2.20 (d, $J = 2.9$ Hz, 1 H), 2.40 (ddd, $J = 6.6, 7.7, 13.6$ Hz, 1 H), 2.47 (br dt, $J = 13.6, 5.0$ Hz, 1 H), 2.64 (ddd, $J = 1.5, 8.4, 13.2$ Hz, 1 H), 2.77 (br d, $J = 15.8$ Hz, 1 H), 3.01 (dq, $J = 15.8, 2.4$ Hz, 1 H), 3.35 (br dd, $J = 6.6, 8.4$ Hz, 1 H), 4.17 (q, $J = 7.1$ Hz, 2 H), 4.18 (q, $J = 7.1$ Hz, 2 H), 4.68 (ddd, $J = 2.9, 4.8, 7.7$ Hz, 1 H), 5.41 (ddd, $J = 5.0, 6.6, 15.2$ Hz, 1 H), 5.43 (dq, $J = 1.5, 7.1$ Hz, 1 H), 5.46 (dm, $J = 15.2$ Hz, 1 H), 7.24 – 7.37 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃, major isomer) δ 14.1, 14.2, 40.9, 41.5, 42.6, 42.7, 59.1, 61.4, 61.5, 73.6, 119.1, 125.5, 125.8, 127.4, 128.4, 136.0, 140.6, 144.0, 171.6, 171.9; HRMS calcd for C₂₃H₃₀O₅: 386.2093. Found m/z (relative intensity): 386.2104 (M⁺, 2), 368 (38), 280 (81), 206 (100), 117 (16).

(2*S,4'*S*')-4,4-Diethoxycarbonyl-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-1-**

isopropylidenecyclopentane (6b): a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3466 (s), 1732 (s), 1252 (s), 1194 (s), 972 (m), 702 (s) cm⁻¹; ¹H NMR (300 MHz,

CDCl₃, major isomer) δ 1.23 (t, J = 7.1 Hz, 3 H), 1.24 (t, J = 7.1 Hz, 3 H), 1.57 (s, 3 H), 1.66 (s, 3 H), 2.09 (dd, J = 5.1, 13.2 Hz, 1 H), 2.28 (d, J = 2.9 Hz, 1 H), 2.37 (dt, J = 13.9, 8.1 Hz, 1 H), 2.44 (br dt, J = 13.9, 4.8 Hz, 1 H), 2.57 (dd, J = 8.4, 13.2 Hz, 1 H), 2.83 (d, J = 16.7 Hz, 1 H), 2.96 (d, J = 16.7 Hz, 1 H), 3.33 (br dd, J = 5.1, 8.4 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 4.67 (ddd, J = 2.9, 4.8, 8.1 Hz, 1 H), 5.32 (dddm, J = 4.8, 8.1, 15.4 Hz, 1H), 5.42 (dd, J = 6.2, 15.4 Hz, 1 H), 7.24 – 7.37 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃, major isomer) δ 14.1, 20.9, 21.5, 38.4, 40.8, 43.0, 44.1, 59.4, 61.4, 61.6, 73.5, 125.4, 125.8, 126.1, 127.3, 128.3, 133.1, 136.7, 144.1, 171.9, 172.3; HRMS calcd for C₂₄H₃₂O₅: 400.2550. Found m/z (relative intensity): 400.2229 (M⁺, 2), 382 (31), 220 (40), 178 (65), 105 (100).

(4*S,4'*S**)-3-Isopropylidene-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine (6c):** IR (neat) 3524 (s), 1597 (m), 1344 (s), 1159 (s), 1045 (s), 970 (m), 760 (m), 655 (s) cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 1.19 (br s, 3 H), 1.30 (br s, 3 H), 1.89 (s, 3 H), 2.24 (br ddd, J = 5.9, 7.3, 13.6 Hz, 1 H), 2.30 (br dt, J = 13.6, 7.3 Hz, 1 H), 2.85 (dddm, J = 2.2, 6.8, 7.3 Hz, 1 H), 2.96 (dd, J = 6.8, 9.3 Hz, 1 H), 3.29 (dd, J = 2.2, 9.3 Hz, 1 H), 3.60 (br d, J = 13.8 Hz, 1 H), 3.96 (d, J = 13.8 Hz, 1 H), 4.42 (ddm, J = 5.9, 7.3 Hz, 1 H), 5.17 (dd, J = 7.3, 15.2 Hz, 1 H), 5.27 (br dt, J = 15.2, 7.3 Hz, 1 H), 6.81 (d, J = 8.2 Hz, 2 H), 7.09 – 7.27 (m, 5 H), 7.76 (d, J = 8.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 20.5, 21.2, 21.6, 42.4, 44.1, 50.4, 54.2, 73.7, 125.9, 126.1, 126.5, 127.6, 128.0, 128.4, 129.7, 130.0, 132.6, 133.6, 143.6, 143.9; HRMS calcd for C₂₄H₂₈O₂NS: 394.1814. Found m/z (relative intensity): 394.1814 (M⁺-OH, 10), 262 (54), 138 (82), 121 (51), 91 (100).

(4*S,4'*S**)-3-Isopropylidene-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydrofuran (6d):** IR (neat) 3422 (s), 1053 (s), 970 (m), 700 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.58 (s, 3 H), 1.64 (s, 3 H), 2.04 (br s, 1 H), 2.46 (ddd, J = 2.9, 5.9, 7.7 Hz, 2 H), 3.29

(m, 1 H), 3.71 (dd, $J = 2.9, 8.6$ Hz, 1 H), 3.85 (dd, $J = 5.9, 8.6$ Hz, 1 H), 4.23 (br d, $J = 12.5$ Hz, 1 H), 4.32 (br d, $J = 12.5$ Hz, 1 H), 4.69 (dd, $J = 5.9, 7.7$ Hz, 1 H), 5.41 (br dt, $J = 15.4, 7.7$ Hz, 1 H), 5.52 (dd, $J = 7.7, 15.4$ Hz, 1 H), 7.24 – 7.37 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.9, 21.2, 42.5, 45.7, 70.2, 73.6, 74.6, 123.7, 125.6, 125.9, 127.5, 128.4, 134.0, 134.6, 144.0; HRMS calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2$: 258.1620. Found m/z (relative intensity): 258.1620 (M^+ , 8), 240 (8), 107 (100), 95 (15), 77 (24).

(4*S,4'*S*'*)-3-[(1*Z*)-Phenylethylidene]-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydrofuran (6e)**: a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3404 (s), 1599 (m), 1034 (s), 972 (s), 764 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , major isomer) δ 1.99 (br s, 3 H), 2.20 (d, $J = 2.3$ Hz, 1 H), 2.54 (br t, $J = 6.4$ Hz, 2 H), 3.46 (br dt, $J = 3.9, 6.6$ Hz, 1 H), 3.69 (dd, $J = 3.9, 8.4$ Hz, 1 H), 3.96 (dd, $J = 6.6, 8.4$ Hz, 1 H), 4.11 (br d, $J = 13.2$ Hz, 1 H), 4.30 (br d, $J = 13.2$ Hz, 1 H), 4.73 (br dt, $J = 2.3, 6.4$ Hz, 1 H), 5.53 (br dt, $J = 15.4, 6.4$ Hz, 1 H), 5.59 (dd, $J = 6.6, 15.4$ Hz, 1 H), 7.10 – 7.37 (m, 10 H); ^1H NMR (400 MHz, CDCl_3 , minor isomer) δ 1.96 (br s, 3 H), 2.16 (br s, 1 H), 2.52 (t, $J = 6.4$ Hz, 2 H), 3.47 (br dt, $J = 3.9, 6.6$ Hz, 1 H), 3.70 (dd, $J = 3.9, 8.4$ Hz, 1 H), 3.94 (dd, $J = 6.6, 8.4$ Hz, 1 H), 4.11 (br d, $J = 13.2$ Hz, 1 H), 4.29 (br d, $J = 13.2$ Hz, 1 H), 4.73 (br t, $J = 6.4$ Hz, 1 H), 5.52 (br dt, $J = 15.4, 6.4$ Hz, 1 H), 5.58 (dd, $J = 6.6, 15.4$ Hz, 1 H), 7.10 – 7.37 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3 , major isomer) δ 20.8, 42.4, 46.2, 70.6, 73.8, 74.2, 125.9, 126.5, 126.8, 127.1, 127.6, 128.2, 128.4, 129.5, 133.7, 137.5, 143.3, 143.9; ^{13}C NMR (100 MHz, CDCl_3 , minor isomer) δ 20.8, 42.3, 46.2, 70.7, 73.7, 74.2, 125.9, 126.5, 126.8, 127.1, 127.6, 128.2, 128.4, 129.5, 133.7, 137.5, 143.3, 143.9; HRMS calcd for $\text{C}_{22}\text{H}_{24}\text{O}_2\text{NS}$: 320.1776. Found m/z (relative intensity): 320.1791 (M^+ , 27), 147 (15), 105 (100), 95 (25), 78 (17).

Structure Confirmation of the Minor Isomer of 6e; 1) Oxidation of 6e with PCC: A solution of **6e** (8:1 ratio) (288 mg, 0.9 mmol) in dichloromethane (5 mL) was added into

a solution of PCC (646 mg, 3 mmol) in dichloromethane (5 mL) under N₂ at 0 °C and the mixture was stirred for additional 2 h at the same temperature. The reaction mixture was diluted with 10 ml of ether and filtered with suction through a celite pad on a glass filter. The filter cake was washed with ether several times. The combined organic extracts were washed with 2M HCl (5 ml), sat. NaHCO₃ (5 ml), and sat. NaCl (10 ml) and dried (MgSO₄). The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel (hexane:ethyl acetate = 12:1, v/v) to give a ketone as a single isomer in 48% yield. **3-[(1Z)-Phenylethylidene]-4-[4-oxo-4-phenyl-(1E)-butenyl]tetrahydrofuran**: IR (neat) 1684 (s), 1209 (s), 1036 (s), 935 (m), 700 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3 H), 3.56 (br ddd, *J* = 3.2, 6.5, 7.5 Hz, 1 H), 3.75 (dd, *J* = 3.2, 8.9 Hz, 1 H), 3.78 (br d, *J* = 6.5 Hz, 2 H), 4.02 (dd, *J* = 6.5, 8.9 Hz, 1 H), 4.14 (br d, *J* = 13.0 Hz, 1 H), 4.35 (br d, *J* = 13.0 Hz, 1 H), 5.65 (br dd, *J* = 7.5, 15.3 Hz, 1 H), 5.86 (br dt, *J* = 15.3, 6.5 Hz, 1 H), 7.11 – 7.62 (m, 8 H), 7.92 – 8.02 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 20.7, 42.3, 46.4, 70.7, 74.1, 123.5, 126.8, 127.1, 128.2, 128.3, 128.7, 129.8, 133.1, 133.8, 136.7, 137.2, 143.5, 198.2. HRMS calcd for C₂₂H₂₂O₂: 318.1620. Found *m/z* (relative intensity): 318.1630 (M⁺, 100), 288 (15). **2) Reduction of the ketone with NaBH₄**: To a solution of 3-[(1Z)-phenylethylidene]-4-[4-oxo-4-phenyl-(1E)-butenyl]tetrahydrofuran (0.4 mmol) dissolved in MeOH (2 ml) was added NaBH₄ (30 mg, 0.8 mmol) and the mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue was dissolved in ethyl acetate (10 ml). The solution was washed with 2M HCl (5 ml), sat. NaHCO₃ (5 ml), and sat. NaCl (5 ml), and dried (MgSO₄), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane:ethyl acetate = 8:1, v/v) to provide a mixture of **6e** in 1:1 ratio in 80% yield.

(3S*,4'S*)-3-[4-Hydroxy-4-phenyl-(1E)-butenyl]-5,5-diphenyl-2-[(1Z)-phenylethylidene] cyclopentanol (6f): a mixture of two diastereomers in a ratio of 4:1; mp 67.0 - 68.0 °C (hexane-dichloromethane); IR (KBr disk) 3356 (s), 3057 (s), 2928

(s), 1684 (m), 1599 (s), 1493 (s), 1447 (s), 1269 (m), 972 (s), 912 (m), 756 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , major isomer) δ 1.89 (s, 3 H), 2.52 (t, $J = 7.1$ Hz, 2 H), 2.64 (dd, $J = 7.7, 12.1$ Hz, 1 H), 2.74 (dd, $J = 9.5, 12.1$ Hz, 1 H), 3.13 (br q, $J = 8.4$ Hz, 1 H), 4.71 (t, $J = 7.1$ Hz, 1 H), 4.76 (s, 1 H), 5.47 (dt, $J = 15.1, 7.1$ Hz, 1 H), 5.71 (dd, $J = 8.4, 15.1$ Hz, 1 H), 6.99 – 7.46 (m, 20 H); ^{13}C NMR (100 MHz, CDCl_3 , major isomer) δ 22.7, 31.6, 42.5, 43.1, 59.0, 73.8, 78.8, 125.4, 125.9, 126.4, 126.9, 127.2, 127.5, 127.8, 128.0, 128.2, 128.4, 128.7, 137.4, 137.8, 140.2, 143.7, 144.0, 144.3, 145.8; HRMS calcd for $\text{C}_{35}\text{H}_{34}\text{O}_2 - \text{H}_2\text{O}$: 468.2403. Found m/z (relative intensity): 468.2476 ($\text{M}^+ - \text{H}_2\text{O}$, 100), 107 (61), 77 (57).

(2S*,4'S*)-4,4-Diethoxycarbonyl-2-[4-hydroxy-4-phenyl-(1E)-butenyl]-1-isopropylidenecyclohexane (6g) : a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3468 (m), 2928 (m), 1732 (s), 1435 (m), 1242 (s), 1200 (m), 1051 (w), 700 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.51 (m, 2 H), 1.60 (br s, 3 H), 2.01 (dd, $J = 3.3, 9.5$ Hz, 1 H), 2.33 (dd, $J = 8.8, 13.7$ Hz, 1 H), 2.17 (dd, $J = 6.2, 13.9$ Hz, 2 H), 2.25 (m, 2 H), 2.36 (m, 1 H), 2.40 (dt, $J = 13.9, 2.7$ Hz, 1 H), 2.49 (br dt, $J = 14.3, 3.8$ Hz, 1 H), 2.68 (ddd, $J = 7.3, 9.2, 13.7$ Hz, 1 H), 2.80 (ddd, $J = 5.9, 9.2, 13.7$ Hz, 1 H), 3.47 (m, 1 H), 3.59 (m, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 5.17 (dddd, $J = 2.6, 5.9, 8.8, 15.4$ Hz, 1 H), 5.41 (br dd, $J = 4.2, 15.4$ Hz, 1 H), 7.15 – 7.32 (m, 5 H); ^{13}C NMR (100MHz, CDCl_3) δ 19.9, 20.1, 22.4, 31.4, 32.1, 35.8, 38.4, 41.3, 52.5, 70.2, 125.4, 125.8, 126.3, 128.4, 128.5, 135.2, 142.4, 172.8, (minor) 36.1, 40.7, 125.3, 135.5; HRMS calcd for $\text{C}_{25}\text{H}_{34}\text{O}_5$: 414.2406. Found m/z (relative intensity): 415 ($\text{M}^+ + 1$, 44), 414.2408 (M^+ , 84), 396 ($\text{M}^+ - \text{H}_2\text{O}$), 242 (100), 105 (33). Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{O}_5$: C, 72.43; H 8.27. Found: C, 72.44; H, 8.29.

(3S*,4'S*)-4-Isopropylidene-3-[4-hydroxy-4-phenyl-(1E)-butenyl]-N-(p-toluenesulfonyl)piperidine (6h): mp 92.0 – 93.0 °C (hexane – dichloromethane); IR (KBr disk) 3460 (m), 1340 (s), 1169 (s), 1103 (m), 932 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.61 (s, 6 H), 2.08 – 2.24 (m, 2 H), 2.32 (dd, $J = 3.7, 11.4$ Hz, 1 H), 2.40 (s, 3

H), 2.43 – 2.51 (m, 3 H), 3.37 (m, 1 H), 3.76 (m, 1 H), 3.78 (dm, $J = 11.4$ Hz, 1 H), 4.73 (br dd, $J = 5.5, 7.0$ Hz, 1 H), 5.50 (ddt, $J = 1.5, 15.6, 7.1$ Hz, 1 H), 5.67 (br dd, $J = 5.7, 15.6$ Hz, 1 H), 7.24 – 7.36 (m, 5 H), 7.30 (d, $J = 8.2$ Hz, 2 H), 7.62 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.9, 20.1, 21.5, 25.4, 39.8, 42.7, 47.1, 51.1, 73.7, 125.9, 126.8, 127.2, 127.4, 127.7, 128.4, 129.6, 133.4, 134.0, 143.3, 144.1; HRMS calcd for $\text{C}_{25}\text{H}_{31}\text{O}_3\text{NS}$: 425.2025. Found m/z (relative intensity): 425.2042 (M^+ , 1), 407 (2), 319 (100), 278 (17).

(4*S,4'*S**)-3-Isopropylidene-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)piperidine (6i)** : IR (neat) 3445 (s), 2856 (s), 1599 (s), 1495 (s), 1454 (s), 1159 (s), 1043 (s), 916 (s), 816 (s), 744 (s), 702 (s), 658 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.62 (d, $J = 1.5$ Hz, 3 H), 1.74 (s, 3 H), 1.77 - 1.86 (m, 2 H), 2.37 (tm, $J = 6.8$ Hz, 1 H), 2.42 (s, 3 H), 2.43 (tm, $J = 6.8$ Hz, 1 H), 2.59 (dt, $J = 2.9, 12.1$ Hz, 1 H), 2.90 (d, $J = 13.6$ Hz, 1 H), 3.36 (m, 1 H), 3.52 (dm, $J = 12.1$ Hz, 1 H), 4.41 (d, $J = 13.6$ Hz, 1 H), 4.58 (tm, $J = 6.6$ Hz, 1 H), 5.20 (ddt, $J = 1.8, 15.4, 7.0$ Hz, 1 H), 5.31 (dd, $J = 5.1, 15.4$ Hz, 1 H), 7.21 - 7.33 (m, 7 H), 7.66 (dt, $J = 8.1, 2.0$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.0, 20.2, 21.5, 30.3, 37.2, 42.1, 42.5, 44.3, 73.7, 125.8, 126.5, 127.5, 127.7, 128.3, 128.5, 129.6, 134.3, 134.5, 143.3, 143.9; HRMS calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_3\text{S}$: 425.2025, Found m/z (relative intensity) 425.2014 (M^+ , 51), 424 (47), 410 (68), 407 (100).

(2*S,4'*S**)-3-Isopropylidene-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydropyran (6j)**: IR (neat) 3422 (m), 3028 (w), 2955 (s), 1740 (m), 1452 (m), 1240 (m), 1105 (s), 1047 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.65 (br s, 3 H), 1.67 (br s, 3H), 2.18 (br s, 1 H), 2.22 (br d, $J = 14.5$ Hz, 1 H), 2.35 (br d, $J = 14.5$ Hz, 1 H), 2.45 (dm, $J = 5.3$ Hz, 1 H), 2.49 (dm, $J = 7.0$ Hz, 1 H), 3.17 (br s, 1 H), 3.28 (dm, $J = 10.6$ Hz, 1 H), 3.48 (br d, $J = 11.0$ Hz, 1 H), 3.91 (br d, $J = 11.0$ Hz, 1 H), 3.97 (dm, $J = 10.6$ Hz, 1 H),

4.69 (dd, $J = 5.3, 7.0$ Hz, 1 H), 5.43 (br dt, $J = 15.4, 7.1$ Hz, 1 H), 5.75 (br dt, $J = 15.4, 6.0$ Hz, 1 H), 7.23 – 7.37 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.5, 19.8, 27.1, 41.8, 42.8, 68.7, 72.7, 73.6, 124.7, 125.8, 127.3, 127.5, 128.3, 135.1, 144.1; Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_2$: C, 79.37; H, 8.88. Found: C, 79.20; H, 8.84.

(3S*,4'S*)-3-[4-hydroxy-4-phenyl-(1E)-butenyl]-(4Z)-(1-trimethylsilylethylidene)-chroman (6k): IR (neat) 3381 (m), 3030 (m), 2953 (s), 1589 (s), 1481 (s), 1304 (s), 1250 (s), 1038 (s), 837 (s), 754 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.11 (s, 9 H), 1.84 (s, 3 H), 2.34 (m, 1 H), 3.57 (m, 1 H), 4.20 (d, $J = 3.1, 10.8$ Hz, 1 H), 4.36 (d, $J = 2.0, 10.8$ Hz, 1 H), 4.45 (ddd, $J = 3.1, 4.8, 7.9$ Hz, 1 H), 5.40 (ddt, $J = 1.5, 15.8, 7.8$ Hz, 1 H), 5.57 (dd, $J = 5.5, 15.8$ Hz, 1 H), 6.75 (dd, $J = 1.1, 7.7$ Hz, 2 H), 6.81 (dd, $J = 1.1, 7.7$ Hz, 2 H), 7.31 – 7.14 (m, 7 H); ^{13}C NMR (100 MHz, CDCl_3) δ 0.7, 18.7, 39.7, 42.8, 71.3, 73.2, 115.6, 119.3, 123.7, 125.8, 127.3, 127.3, 128.0, 128.3, 128.5, 129.5, 130.5, 132.3, 143.7, 153.9; HRMS calcd for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{Si}$: 378.2015. Found m/z (relative intensity): 379 ($\text{M}^{++} + 1$, 39), 378.2017 (M^+ , 100), 107 (50), 73 (58).

(3S*,4'S*)-3-[4-hydroxy-4-phenyl-(1E)-butenyl]-(4Z)-(1-phenylethylidene)chroman (6l): IR (neat) 3391 (s), 2872 (s), 1738 (w), 1601 (m), 1574 (m), 912 (w), 824 (w), 748 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.13 (s, 3 H), 2.34 – 2.44 (m, 2 H), 3.57 (m, 1 H), 4.32 (dd, $J = 2.8, 11.0$ Hz, 1 H), 4.42 (dd, $J = 2.2, 11.0$ Hz, 1 H), 4.49 (m, 1 H), 5.50 (ddt, $J = 1.5, 15.4, 7.7$ Hz, 1 H), 5.66 (dd, $J = 5.3, 15.4$ Hz, 1 H), 6.40 (ddd, $J = 1.3, 7.0, 8.3$ Hz, 1 H), 6.52 (dd, $J = 1.5, 8.3$ Hz, 1 H), 6.74 (dd, $J = 1.3, 8.4$ Hz, 1 H), 7.18 – 7.40 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.1, 22.3, 22.7, 38.1, 39.7, 42.5, 42.8, 70.4, 71.5, 73.3, 116.3, 119.4, 121.1, 125.6, 125.9, 126.0, 126.8, 128.3, 128.6, 129.1, 130.9, 131.2, 131.9, 132.1, 143.7, 144.4, 154.0; HRMS calcd for $\text{C}_{27}\text{H}_{26}\text{O}_2$: 382.1933. Found m/z (relative intensity): 383 ($\text{M}^{++} + 1$, 34), 382.1917 (M^+ , 100), 275 (33), 107 (47).

(4S*,4'R*)-3-Isopropylidene-4-[4-hydroxy-6-phenyl-(1E)-hexenyl]-N-(p-toluenesulfonyl)pyrrolidine (6ca): IR (neat) 3449 (s), 1340 (s), 1157 (s), 1092 (s), 1016 (s), 972 (m) cm^{-1} ; ^1H NMR (400 MHz, C_6D_6) δ 1.21 (s, 3 H), 1.35 (s, 3 H), 1.58 (dm, $J = 12.8$ Hz, 1 H), 1.63 (dm, $J = 12.8$ Hz, 1 H), 1.87 (m, 1 H, coalescing to br dd, $J = 6.6$, 13.6 Hz, by irradiation at 5.22), 1.89 (s, 3 H), 1.94 (m, 1 H, coalescing to br dd, $J = 4.4$, 13.6 Hz, by irradiation at 5.22), 2.60 (br dt, $J = 13.6$, 8.1 Hz, 1 H), 2.73 (br ddd, $J = 6.6$, 8.1, 13.6 Hz, 1 H), 2.89 (br dt, $J = 2.2$, 6.6 Hz, 1 H), 2.98 (dd, $J = 6.6$, 9.2 Hz, 1 H), 3.34 (dd, $J = 2.2$, 9.2 Hz, 1 H), 3.36 (ddm, $J = 4.4$, 6.6 Hz, 1 H), 3.60 (br d, $J = 13.6$ Hz, 1 H), 4.00 (br d, $J = 13.6$ Hz, 1 H), 5.22 (ddd, $J = 6.6$, 9.2, 15.4 Hz, 1 H), 5.28 (ddd, $J = 6.6$, 15.4 Hz, 1 H), 6.80 (d, $J = 8.1$ Hz, 2 H), 7.07 – 7.22 (m, 5 H), 7.76 (d, $J = 8.1$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 21.3, 21.6, 32.1, 38.5, 40.6, 44.3, 50.4, 54.3, 70.3, 125.9, 126.3, 126.5, 128.0, 128.5, 129.7, 130.1, 132.6, 133.6, 134.6, 142.1, 143.6; HRMS calcd for $\text{C}_{26}\text{H}_{33}\text{O}_3\text{NS}$: 439.2181. Found m/z (relative intensity): 439.2114 (M^+ , 3), 438 (2), 305 (100), 238 (33), 105 (16).

(4S*,4'S*)-3-Isopropylidene-4-[4-cyclohexyl-4-hydroxy-(1E)-butenyl]-N-(p-toluenesulfonyl)pyrrolidine (6cb): IR (neat) 3447 (s), 1340 (s), 1159 (s), 970 (s), 710 (s) cm^{-1} ; ^1H NMR (400 MHz, C_6D_6) δ 0.96 – 1.29 (m, 6 H), 1.21 (s, 3 H), 1.38 (s, 3 H), 1.54 – 1.88 (m, 5 H), 1.90 (s, 3 H), 1.94 (dddm, $J = 7.3$, 9.2, 13.2 Hz, 1 H), 2.05 (dddm, $J = 3.1$, 6.2, 13.2 Hz, 1 H), 2.94 (br ddd, $J = 2.0$, 6.6, 7.3 Hz, 1 H), 3.02 (dd, $J = 6.6$, 9.2 Hz, 1 H), 3.18 (ddd, $J = 3.1$, 5.3, 9.2 Hz, 1 H), 3.35 (dd, $J = 2.0$, 9.2 Hz, 1 H), 3.61 (br d, $J = 13.6$ Hz, 1 H), 4.00 (br d, $J = 13.6$ Hz, 1 H), 5.27 (dd, $J = 7.3$, 15.0 Hz, 1 H), 5.37 (ddd, $J = 6.2$, 7.3, 15.0 Hz, 1 H), 6.81 (d, $J = 8.2$ Hz, 2 H), 7.77 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 21.3, 21.6, 26.2, 26.4, 26.6, 28.2, 29.2, 37.4, 43.2, 44.3, 50.5, 54.3, 75.1, 126.4, 127.1, 128.0, 129.7, 130.2, 132.6, 133.2, 143.6; HRMS calcd for $\text{C}_{24}\text{H}_{35}\text{O}_3\text{NS}$: 417.2338. Found m/z (relative intensity): 417.2376 (M^+ , 4), 416 (4), 305 (100), 262 (40), 107 (21).

(4S*,4'S*)-3-Isopropylidene-4-[4-*tert*-butyl-4-hydroxy-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine (6cc): a mixture of two diastereomers in a ratio of 12:1; IR (neat) 3553 (s), 1346 (s), 1159 (s), 1094 (s), 970 (s), 710 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, major isomer) δ 0.90 (s, 9 H), 1.55 (br s, 3 H), 1.58 (br s, 3 H), 1.88 (ddd, *J* = 7.3, 10.6, 13.9 Hz, 1 H), 2.27 (ddd, *J* = 2.2, 5.3, 13.9 Hz, 1 H), 2.43 (s, 3 H), 3.11 (dd, *J* = 6.4, 9.2 Hz, 1 H), 3.18 (dd, *J* = 2.2, 10.6 Hz, 1 H), 3.29 (br t, *J* = 6.4 Hz, 1 H), 3.33 (dd, *J* = 2.2, 9.2 Hz, 1 H), 3.57 (br d, *J* = 13.6 Hz, 1 H), 3.90 (br d, *J* = 13.6 Hz, 1 H), 5.42 (dd, *J* = 6.4, 15.2 Hz, 1 H), 5.46 (ddd, *J* = 5.3, 7.3, 15.2 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃, major isomer) δ 20.5, 21.3, 21.6, 25.8, 34.7, 35.1, 44.3, 50.4, 54.3, 78.5, 126.5, 128.0, 128.1, 129.7, 130.3, 132.6, 133.2, 143.6; HRMS calcd for C₂₂H₃₃O₃NS: 391.2181. Found *m/z* (relative intensity): 391.2134 (M⁺, 3), 374 (2), 305 (100), 236 (56), 108 (23).

3-Isopropylidene-4-[4-hydroxy-4,4-pentamethylene-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine (6cd): IR (neat) 3533 (s), 1242 (m), 1015 (m), 972 (m), 710 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.34 – 1.58 (m, 10 H), 1.56 (br s, 3 H), 1.57 (br s, 3 H), 2.10 (d, *J* = 7.3 Hz, 2 H), 2.43 (s, 3 H), 3.13 (dd, *J* = 7.3, 9.5 Hz, 1 H), 3.30 (dd, *J* = 2.6, 9.5 Hz, 1 H), 3.30 (m, 1 H), 3.58 (br d, *J* = 13.4 Hz, 1 H), 3.89 (br d, *J* = 13.4 Hz, 1 H), 5.35 (dd, *J* = 7.3, 15.0 Hz, 1 H), 5.47 (dt, *J* = 15.0, 7.3 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 20.5, 21.3, 21.5, 22.2, 25.8, 37.5, 44.3, 45.2, 50.4, 54.4, 71.1, 125.5, 126.3, 128.0, 129.6, 130.3, 133.0, 133.8, 143.5; HRMS calcd for C₂₃H₃₃O₃NS: 403.2181. Found *m/z* (relative intensity): 403.2174 (M⁺, 1), 305 (100), 262 (36), 99 (25), 91 (39).

(2*E*)-(1-Phenylethylidene)-3-[4-hydroxy-4,4-pentamethylene-(1*E*)-butenyl]-5,5-diphenylcyclopentanol (6fd): major isomer: mp 43.0 - 44.0 °C (hexane -

dichloromethane); IR (KBr disk) 3422 (w), 3057 (w), 2932 (s), 1599 (w), 1493 (m), 1447 (m), 1005 (m), 970 (m), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.39 – 1.64 (m, 10 H), 1.95 (br s, 3 H), 2.21 (d, $J = 7.0$ Hz, 2 H), 2.69 (dd, $J = 8.1, 12.3$ Hz, 1 H), 2.79 (dd, $J = 9.7, 12.3$ Hz, 1 H), 3.18 (dt, $J = 9.7, 8.1$ Hz, 1 H), 4.78 (s, 1 H), 5.58 (dt, $J = 15.0, 7.0$ Hz, 1 H), 5.68 (dd, $J = 8.1, 15.0$ Hz, 1 H), 7.01 – 7.44 (m, 15 H); ^{13}C NMR (100 Hz, CDCl_3) δ 20.4, 22.3, 25.8, 29.7, 37.5, 42.0, 43.3, 45.3, 45.3, 59.0, 71.2, 78.8, 124.9, 125.9, 126.4, 127.0, 127.2, 127.9, 128.0, 128.1, 128.2, 128.7, 137.3, 138.1, 140.5, 143.8, 144.4, 145.8; HRMS calcd for $\text{C}_{34}\text{H}_{38}\text{O}_2 - \text{H}_2\text{O}$: 460.2766. Found m/z (relative intensity): 460.2792 ($\text{M}^+ - \text{H}_2\text{O}$, 100), 99 (32). **minor isomer:** ^1H NMR (400 MHz, CDCl_3) δ 1.10 - 1.72 (m, 10 H), 1.92 (ddd, $J = 1.1, 7.3, 12.5$ Hz, 1H), 1.98 (br s, 3 H), 2.30 (ddd, $J = 1.1, 2.6, 12.5$ Hz, 1 H), 3.29 (dd, $J = 9.5, 12.5$ Hz, 1 H), 3.68 (br dd, $J = 8.4, 9.5$ Hz, 1 H), 4.82 (dd, $J = 8.4, 15.4$ Hz, 1 H), 5.02 (s, 1 H), 5.43 (br ddt, $J = 15.4, 7.3$ Hz, 1 H), 7.13-7.39 (m, 15 H).

(2E)-(1-Phenylethylidene)-3-[4-hydroxy-4,4-dimethyl-(1E)-butenyl]-5,5-

diphenylcyclopentanol (6fe): a mixture of two diastereomers in a ratio of 3:1; mp 64.0 - 65.0 $^{\circ}\text{C}$ (hexane - dichloromethane); IR (KBr disk) 3395 (m), 3055 (w), 2968 (m), 1599 (w), 1493 (m), 1375 (m), 1055 (m), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.21 (s, 6 H, major isomer), 1.25 (s, 6 H, minor isomer), 1.95 (d, $J = 1.1$ Hz, 3 H, major isomer), 2.17 (br s, 3 H, minor isomer), 2.23 (d, $J = 7.3$ Hz, 2 H), 2.70 (ddm, $J = 8.1, 2.3$ Hz, 1 H), 2.80 (dd, $J = 9.7, 12.3$ Hz, 1 H), 3.18 (dt, $J = 9.7, 8.1$ Hz, 1 H), 4.78 (s, 1 H), 5.58 (dt, $J = 15.0, 7.3$ Hz, 1 H), 5.69 (dd, $J = 8.1, 15.0$ Hz, 1 H), 7.01 – 7.44 (m, 15 H); ^{13}C NMR (100 Hz, CDCl_3 , major isomer is assigned) δ 20.3, 29.1, 41.9, 43.2, 46.8, 59.0, 70.6, 78.8, 125.4, 125.9, 126.4, 127.0, 127.2, 127.8, 128.0, 128.2, 128.7, 137.4, 138.1, 140.4, 143.7, 144.3, 145.8; HRMS calcd for $\text{C}_{31}\text{H}_{34}\text{O}_2 - \text{H}_2\text{O}$: 420.2453. Found m/z (relative intensity): 420.2445 ($\text{M}^+ - \text{H}_2\text{O}$, 100).

(1S*,4'R*)-2-Isopropylidene-1-[4-hydroxy-6-phenyl-(1E)-hexenyl]-5,5-

dicarbomethoxycyclohexane (6ma): a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3466 (m), 2928 (m), 1732 (s), 1435 (m), 1242 (s), 1200 (m), 1051 (w), 700 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , major isomer is assigned) δ 1.60 (br s, 3 H), 1.70 (br s, 3 H), 1.72 - 1.78 (m, 2 H), 2.02 (dm, $J = 13.9$ Hz, 1 H), 2.04 (ddm, $J = 8.8$, 13.9 Hz, 1 H), 2.17 (dm, $J = 13.9$ Hz, 2 H), 2.25 (m, 1 H), 2.36 (m, 1 H), 2.40 (dt, $J = 13.9$ Hz, 1 H), 2.49 (br d, $J = 13.9$ Hz, 1 H), 2.68 (ddm, $J = 9.2$, 13.7 Hz, 1 H), 2.80 (ddd, $J = 5.9$, 9.2, 13.7 Hz, 1 H), 3.47 (br s, 1 H), 3.59 (m, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 5.17 (dddm, $J = 5.9$, 8.8, 15.4 Hz, 1 H), 5.41 (br dd, $J = 4.2$, 15.4 Hz, 1 H), 7.15 - 7.32 (m, 5 H); ^{13}C NMR (100MHz, CDCl_3 , major isomer is assigned) δ 19.9, 20.1, 22.4, 31.4, 32.1, 35.8, 38.4, 41.3, 52.5, 70.2, 125.4, 125.8, 126.3, 128.4, 128.5, 135.2, 142.4, 172.8; HRMS calcd for $\text{C}_{25}\text{H}_{34}\text{O}_5$: 414.2406. Found m/z (relative intensity): 414.2408 (M^+ , 84), 396 ($\text{M}^+ - \text{H}_2\text{O}$), 242 (100), 105 (33).

(1S*,4'S*)-2-Isopropylidene-1-[4-hydroxy-4-cyclohexyl-(1E)-hexenyl]-5,5-

dicarbomethoxycyclohexane (6mb): IR (neat) 3555 (m), 2926 (s), 1732 (s), 1450 (s), 1242 (s), 1200 (s), 1087 (m), 978 (m), 756 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.99 - 1.33 (m, 6 H), 1.55 - 1.76 (m, 5 H), 1.61 (br s, 3 H), 1.70 (s, 3 H), 1.85 (d, $J = 3.1$ Hz, 1 H), 1.96 (dd, $J = 9.2$, 13.9 Hz, 1 H), 1.99 (dd, $J = 9.2$, 13.9 Hz, 1 H), 2.17 (dd, $J = 5.9$, 13.9 Hz, 1 H), 2.20 - 2.29 (m, 2 H), 2.36 (m, 1 H), 2.40 (dm, $J = 13.9$ Hz, 1 H), 2.50 (br dt, $J = 14.7$, 3.7 Hz, 1 H), 3.31 (ddm, $J = 5.5$, 11.7 Hz, 1 H), 3.48 (m, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 5.19 (dddm, $J = 5.5$, 9.2, 15.4 Hz, 1 H), 5.40 (dm, $J = 15.4$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.9, 20.1, 22.4, 26.3, 26.4, 26.6, 28.4, 29.1, 31.4, 35.9, 37.9, 38.5, 43.4, 52.5, 75.0, 125.3, 127.0, 128.7, 134.9, 172.7, 172.8; HRMS calcd for $\text{C}_{23}\text{H}_{36}\text{O}_5$: 392.2563. Found m/z (relative intensity): 392.2539 (M^+ , 60), 265 (71), 239 (100), 113 (39).

(1S*,4'S*)-2-Isopropylidene-1-[4-hydroxy-4-*tert*-butyl-(1*E*)-hexenyl]-5,5-dicarbomethoxycyclohexane (6mc): IR (neat) 3553 (s), 2959 (s), 1724 (s), 1437 (s), 1290 (s), 1252 (s), 1202 (s), 1088 (s), 980 (s), 698 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (s, 9 H), 1.61 (br s, 3 H), 1.70 (s, 3 H), 1.84 (br d, *J* = 2.7 Hz, 1 H), 1.85 (ddm, *J* = 9.7, 13.7 Hz, 1 H), 1.87 (ddm, *J* = 10.3, 13.7 Hz, 1 H), 2.17 (dm, *J* = 13.9 Hz, 1 H), 2.23 - 2.30 (m, 2 H), 2.36 (dm, *J* = 14.3 Hz, 1 H), 2.41 (dm, *J* = 13.9 Hz, 1 H), 2.50 (dm, *J* = 14.3 Hz, 1 H), 3.19 (ddm, *J* = 2.7, 10.3 Hz, 1 H), 3.49 (m, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 5.19 (ddm, *J* = 9.7, 15.4 Hz, 1 H), 5.41 (dm, *J* = 15.4 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 19.9, 20.1, 22.3, 25.9, 31.4, 34.6, 35.8, 35.9, 38.4, 52.5, 78.3, 125.3, 127.8, 128.7, 134.9, 172.7, 172.8; HRMS calcd for C₂₁H₃₄O₅: 366.2406. Found *m/z* (relative intensity): 366.2424 (M⁺, 38), 309 (17), 280 (100), 265 (16), 127 (13), 91 (14).

2-[4-hydroxy-4-pentamethylene-(1*E*)-butenyl]-4,4-dicarbomethoxy isopropylidenecyclohexane (6md): IR (neat) 3474 (m), 2932 (s), 1734 (s), 1437 (s), 1242 (s), 1088 (m), 978 (m), 733 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.19 - 1.67 (m, 11 H), 1.61 (br s, 3 H), 1.70 (s, 3 H), 2.09 (d, *J* = 7.3 Hz, 2 H), 2.16 (dm, *J* = 13.2 Hz, 1 H), 2.18 (d, *J* = 13.2 Hz, 1 H), 2.25 (dm, *J* = 13.9 Hz, 1 H), 2.36 (dm, *J* = 14.7 Hz, 1 H), 2.41 (dm, *J* = 13.9 Hz, 1 H), 2.50 (dm, *J* = 14.7 Hz, 1 H), 3.49 (m, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 5.29 (dtm, *J* = 7.3, 15.4 Hz, 1 H), 5.40 (dm, *J* = 15.4 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 19.9, 20.1, 22.3, 22.4, 26.0, 31.4, 36.0, 37.4, 37.8, 38.7, 45.4, 52.6, 71.1, 124.6, 125.1, 128.8, 135.8, 172.5, 172.8; HRMS calcd for C₂₂H₃₄O₅: 378.2406. Found *m/z* (relative intensity): 378.2389 (M⁺, 30), 361 (21), 265 (32), 239 (94), 99 (100).

4,4-Diethoxycarbonyl-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-(1*Z*)-2-butyldene-cyclopentane (6m): IR (neat) 3466 (s), 1732 (s), 1258 (s), 1194 (s), 1063 (s), 970 (m),

700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.91 (t, $J = 7.7$ Hz, 3 H), 1.23 (t, $J = 7.3$ Hz, 3 H), 1.25 (t, $J = 7.3$ Hz, 3 H), 1.64 (br s, 3 H), 1.96 (qm, $J = 7.7$ Hz, 2 H), 2.10 (dd, $J = 4.8, 13.0$ Hz, 1 H), 2.32 (d, $J = 2.9$ Hz, 1 H), 2.39 (ddd, $J = 6.2, 7.7, 13.9$ Hz, 1 H), 2.43 (dddm, $J = 6.2, 7.7, 13.9$ Hz, 1 H), 2.55 (dd, $J = 8.4, 13.0$ Hz, 1 H), 2.81 (d, $J = 16.7$ Hz, 1 H), 2.98 (d, $J = 16.7$ Hz, 1 H), 3.35 (dddm, $J = 4.8, 6.2, 8.4$ Hz, 1 H), 4.17 (q, $J = 7.3$ Hz, 2 H), 4.18 (q, $J = 7.3$ Hz, 2 H), 4.67 (ddd, $J = 2.9, 6.2, 7.7$ Hz, 1 H), 5.33 (br ddd, $J = 6.2, 7.7, 15.4$ Hz, 1 H), 5.45 (dd, $J = 6.2, 15.4$ Hz, 1 H), 7.22 – 7.36 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 12.5, 14.1, 18.3, 27.5, 38.8, 40.8, 43.0, 43.8, 59.2, 61.5, 61.6, 73.6, 125.4, 125.8, 127.3, 128.4, 131.7, 132.6, 137.1, 144.1, 172.0, 172.4. Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{O}_5$: C, 72.43; H 8.27. Found: C, 72.18; H, 8.28.

3-[(1*E*)- α -Phenethylidene]-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydrofuran

(**6n**) : a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3418 (s), 1599 (m), 1028 (m), 968 (m), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , major isomer) δ 1.94 (s, 3 H), 2.15 (dt, $J = 13.9, 8.4$ Hz, 1 H), 2.25 (dddm, $J = 4.4, 6.2, 13.9$ Hz, 2 H), 3.45 (m, 1 H), 3.65 (dd, $J = 3.9, 8.4$ Hz, 1 H), 3.91 (dd, $J = 6.2, 8.4$ Hz, 1 H), 4.35 (dd, $J = 4.4, 8.4$ Hz, 1 H), 4.44 (br d, $J = 13.6$ Hz, 1 H), 4.48 (d, $J = 13.6$ Hz, 1 H), 4.99 (ddd, $J = 6.2, 8.4, 15.0$ Hz, 1 H), 5.30 (dd, $J = 8.4, 15.0$ Hz, 1 H), 7.17 - 7.35 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3 , major isomer) δ 21.6, 42.9, 45.9, 70.8, 73.1, 74.8, 125.8, 126.5, 127.4, 127.7, 128.2, 128.3, 128.7, 134.0, 137.6, 143.2, 143.9; HRMS calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_2\text{S}$: 320.1776, found m/z (relative intensity): 320.1792 (M^+ , 23), 302 (15), 214 (52), 183 (100), 108 (86).

2-Isopropylidene-4-oxa-1,6,6-triphenylundeca-8,10-dien-1-ol (7): IR (neat) 3477 (m), 3026 (m), 2916 (m), 1653 (w), 1601 (w), 1495 (m), 1447 (m), 1092 (s), 1009 (s), 901 (s), 756 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.75 (s, 3 H), 1.89 (s, 3 H), 2.84 (dd, $J = 7.3, 13.7$ Hz, 1 H), 2.94 (d, $J = 8.3$ Hz, 1 H), 3.00 (dd, $J = 7.3, 13.7$ Hz, 1

H), 3.59 (d, $J = 10.6$ Hz, 1 H), 3.72 (d, $J = 8.5$ Hz, 1 H), 3.85 (d, $J = 8.5$ Hz, 1 H), 4.10 (d, $J = 10.6$ Hz, 1 H), 4.92 (d, $J = 10.5$ Hz, 1 H), 5.02 (d, $J = 16.8$ Hz, 1 H), 5.20 (dt, $J = 15.0, 7.3$ Hz, 1 H), 5.60 (d, $J = 8.3$ Hz, 1 H), 5.95 (dd, $J = 10.5, 15.0$ Hz, 1 H), 6.15 (dt, $J = 16.8, 10.5$ Hz, 1 H), 7.00 (d, $J = 7.1$ Hz, 2 H), 7.06 (d, $J = 7.1$ Hz, 2 H), 7.13 - 7.33 (m, 11 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 39.8, 50.3, 68.5, 72.2, 75.8, 115.2, 125.3, 126.1, 126.2, 127.5, 127.7, 127.8, 127.9, 128.0, 130.2, 130.4, 133.7, 134.0, 136.9, 143.8, 145.6, 145.8; HRMS calcd for $\text{C}_{31}\text{H}_{34}\text{O}_2$: 438.2559. Found m/z (relative intensity): 439 ($\text{M}^+ + 1$, 29), 438.2581 (M^+ , 100), 421 ($\text{M}^+ - \text{H}_2\text{O}$, 35).

(4E)-7,7-Diethoxycarbonyl-1-phenyl-4-undecen-9-yn-1-ol (8): IR (neat) 3443 (s), 1732 (s), 1192 (s), 1028 (s), 972 (m), 702 (s) cm^{-1} ; ^1H NMR (400 MHz, C_6D_6) δ 0.91 (t, $J = 7.0$ Hz, 3 H), 0.92 (t, $J = 7.0$ Hz, 3 H), 1.46 (t, $J = 2.6$ Hz, 3 H), 1.62 (ddt, $J = 5.1, 15.2, 7.3$ Hz, 1 H), 1.75 (dq, $J = 15.2, 7.3$ Hz, 1 H), 2.04 (q, $J = 7.3$ Hz, 2 H), 3.15 (q, $J = 2.6$ Hz, 2 H), 3.17 (d, $J = 6.8$ Hz, 2 H), 3.99 (q, $J = 7.0$ Hz, 4 H), 4.41 (dd, $J = 5.1, 7.3$ Hz, 1 H), 5.51 (br dt, $J = 15.0, 7.3$ Hz, 1 H), 5.63 (br dt, $J = 15.0, 6.8$ Hz, 1 H), 7.05 – 7.30 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 3.4, 14.1, 22.9, 28.9, 35.2, 38.5, 57.3, 61.4, 61.5, 73.5, 73.8, 78.6, 124.1, 125.9, 127.5, 128.5, 134.7, 144.7, 170.2. Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{O}_5$: C, 71.48; H 7.82. Found: C, 71.27; H 7.70.

Structure Determination of Products

The structure of **6c**, **6h**, and **6i** was determined unequivocally by means of X-ray crystallographic analyses.¹⁸ A piperidine derivative **6h** formed a nice crystalline solid that is suitable for X-ray analysis, while **6c** and **6i** were obtained as heavy oil. Accordingly, these two nitrogen heterocycles were converted into the 3,5-dinitrobenzoic acid esters, which formed crystalline solids suitable for X-ray analysis. The Chem3DTM perspective views of **6h** and a 3,5-dinitrobenzoic acid ester of **6c** from the ORTEP diagram programs are shown in Figure 1, which clearly reveals that, irrespective of the ring size of heterocycles, the products are *syn* with respect to the two stereogenic centers: the heterocycle methine carbon and the OH-bearing carbon.

Figure 1. The Chem3D™ Presentation of X-Ray Structures of **6h** (a) and a 3,5-Dinitrobenzoic Acid Ester of **6c** (b). For clarity, all protons except those on the stereogenic centers are omitted.

Figure 2. NOE Increments (%) Observed for Products.

The reaction is also stereoselective with respect to the exocyclic double bonds (100% selectivity in all cases), the methyl group of Me_2Zn being placed *cis* to the newly formed single bond between the alkyne and the diene moieties. For example, the *Z* structure of **6a** and **6e** was deduced on the basis of NOE experiments (Fig 2). The H_a and H_b of **6a** and **6e** appeared separately in the 400 MHz ^1H NMR spectra, the H_b protons being characteristically split further by a long-range coupling with the ring methine proton and resonating at lower fields (3.01 and 4.30 ppm, respectively) than the H_a protons (2.77 and 4.11 ppm, respectively). Individual irradiation at the H_a and H_b protons of **6a** caused an increment in the area intensity of the vinylic proton of the ethylidene group by 8.9 and 8.0%, respectively, while no increments were observed for the methyl protons on the same carbon. Similarly, **6e** showed NOE's only between the

Ha,b protons and the *o*-protons of the benzene ring.

The mode of stereoselectivity across the triple bond for the intermolecular four-component connection reaction turned out to be the same as that for the intramolecular reaction. The dienol products **1a-l** were stereochemically homogeneous and were characterized by the (3*E*,6*Z*)-geometry, the structure of which was verified by the NOE experiments; e.g. irradiation of **1b** at the C5 methylene protons caused increments in the area intensities of the olefinic C3-H proton (3.9 %) and the C7-Me protons (5.8 %) (Fig 2). For convenience, here, the *E* and *Z* assignment was made regarding the priority order of the substituents on the original alkynes **4a~g** as the lowest in the Cahn-Ingold-Prelog convention.

Despite extensive efforts (flash column chromatography over silica gel and GPC), the minor isomers of **6** could not be separated from the major isomers. They frequently showed absorptions pairwise in the ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra, suggesting that they are diastereomeric to each other.

Based on the chemical transformation shown in Scheme 1, it is confirmed that they are diastereomeric to each other with respect to the two stereogenic centers, the cycloalkane methine carbon and the OH-bearing carbon and not with respect to the double bond geometries. An 8:1 mixture of **6e** was oxidized to a ketone, which was spectroscopically homogeneous, concluding that the exocyclic double bond and the C2 side chain double bond are stereochemically homogeneous. Furthermore, reduction of the ketone provided a 1:1 mixture of **6e**, the ¹H and ¹³C NMR spectra of which were completely superimposable to those of the starting **6e** except the resonance intensities.

Scheme 1. Confirmation of the Structure of the Minor Isomer of **6e**.

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¹H NMR spectra of products

5j

5k

5I

5m