A Rhodium(I)-Catalyzed Formal Allenic Alder-ene Reaction for the Rapid and Stereoselective Assembly of Cross-Conjugated Trienes.

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Experimental Section

2-(2,3-Decadienyl)-2-(3-trimethylsilyl-2-propynyl)malonic acid diethyl ester (15). A solution of 2-(3-trimethylsilyl-2-propynyl) malonic acid diethyl ester (0.29 g, 1.1 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (44 mg, 60% dispersion in mineral oil, 1.1 mmol) in THF (10 mL). The resulting clear solution was stirred at rt for 20 min and PPh₃ (0.14 g, 0.26 mmol) was added. The flask was flushed with a stream of N₂ gas for 5 min Pd₂(dba)₃ (40 mg, 0.044 mmol) and phosphoric acid 2,3-decadienyl ester diethyl ester (0.30 g, 1.1 mmol) were added at 0 °C. The mixture was stirred at 0 °C for 2 h and quenched with sat. NH₄Cl solution (5 mL). The resulting mixture was extracted with ether, and the combined ether layers were washed with brine, dried (MgSO₄), and concentrated in vacuo to afford a yellow oil that was purified by flash chromatography (SiO₂, pentane : diethyl ether = 30 : 1) to afford title compound **15** as a colorless oil (0.187 g, 42%) : ¹H NMR (300 MHz, CDCl₃) δ 5.08-5.02 (m, 1 H), 4.91-4.82 (m, 1 H), 4.25-4.11 (m, 4 H), 2.85 (s, 2 H), 2.71 (dd, *J* = 2.3, 7.8 Hz, 2 H), 1.98-1.90 (m, 2 H), 1.39-1.19 (m, 14 H), 0.86 (t, *J* = 7.0 Hz), 0.10 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 205.9, 169.7, 101.5, 91.0, 88.0, 84.5, 61.5, 57.3, 32.4, 31.7, 29.2, 28.8,

23.9, 22.6, 14.1, -0.1; IR (neat) ν 1738, 1963, 2180, 2959, 2929 cm^{-1} ; EI-HRMS calcd for $\text{C}_{23}\text{H}_{38}\text{O}_4\text{Si}$ [M^+] m/z 406.2539, found 406.2537.

2-(2,3-Pentadienyl)-2-(3-trimethylsilyl-2-propynyl)malonic acid diethyl ester (17). 3-trimethylsilylpropargyl bromide (3.0 g, 15.7 mmol) was added to a solution of triethyl sodiomethanetricarboxylate (4.0 g, 15.7 mmol) in toluene : DMF (1 : 1, 50 mL) and the mixture was stirred and heated at 80 $^{\circ}\text{C}$ overnight. The resulting yellow suspension was cooled to rt, diluted with toluene (100 mL), washed with water, sat. Na_2CO_3 solution, and brine. The combined aqueous layers were back-extracted with toluene and the combined organic layers were dried (MgSO_4), filtered and concentrated to afford 2-ethoxycarbonyl-2-(3-trimethylsilyl-2-propynyl)malonic acid diethyl ester as a yellow oil (5.35 g, 99%).

This oil was dissolved in THF (20 mL) and added dropwise to a suspension of sodium ethoxide (1.30 g, 19.1 mmol) in THF (30 mL). After stirring at rt for 2 h the solution was acidified with 1N HCl and diluted with ether (150 mL), washed with water (30 mL), sat. NaHCO_3 solution, brine, dried (MgSO_4), concentrated and purified by flash chromatography (SiO_2 , hexanes : diethyl ether = 3 : 1) to afford 2-(3-trimethylsilyl-2-propynyl)malonic acid diethyl ester as a pale yellow oil (4.15 g, 100%).

A solution of 2-(3-trimethylsilyl-2-propynyl)malonic acid diethyl ester (0.14 g, 0.50 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (20 mg, 60% dispersion in mineral oil, 0.50 mmol) in THF (5 mL). The resulting clear solution was stirred at rt for 20 min and PPh_3 (0.032 g, 0.12 mmol) was added. The flask was flushed with a stream of N_2 gas for 5 min $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 0.01 mmol) and phosphoric acid diethyl ester 2,3-pentadienyl ester (0.11 g, 0.51 mmol) was added at 0 $^{\circ}\text{C}$. The mixture was stirred at 0 $^{\circ}\text{C}$ for 2 h and quenched with sat. NH_4Cl solution. The resulting mixture was extracted with ether, and the combined ether layers were washed with brine, dried (MgSO_4), and concentrated *in vacuo* to afford a yellow oil that was purified by flash chromatography (SiO_2 , pentane : diethyl ether = 10 : 1) to afford title compound **17** as a colorless oil (83 mg, 49%): ^1H NMR (300 MHz, CDCl_3) δ 5.05-5.01 (m, 1 H), 4.89-4.82 (m, 1 H), 4.23-4.12 (m, 4 H), 2.85 (s, 2 H), 2.71 (dd, J = 2.2, 7.8 Hz, 2 H), 1.60 (dd, J = 3.2, 7.0 Hz, 3 H), 1.25 (t, J = 7.1 Hz, 6 H), 0.10 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.8, 169.7, 101.4, 87.9, 85.5, 84.0, 61.5, 57.3, 32.2, 23.9, 14.2, 14.0, -0.1; IR (neat) ν

1738, 1963, 2180, 2960, 2928 cm^{-1} ; EI-HRMS calcd for $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Si}$ [M^+] m/z 336.1757, found 336.1770.

2-(2,3-Decadienyl)-2-(2-propynyl)malonic acid diethyl ester (11). A solution of 2-(2-propynyl)malonic acid diethyl ester (0.22 g, 1.1 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (44.0 mg, 60% dispersion in mineral oil, 1.1 mmol) in THF (5 mL). The resulting clear solution was stirred at rt for 20 min and PPh_3 (0.14 g, 0.260 mmol) was added. The flask was flushed with a stream of N_2 gas for 5 min $\text{Pd}_2(\text{dba})_3$ (40 mg, 0.04 mmol) and phosphoric acid 2,3-decadienyl ester diethyl ester (0.300 g, 1.10 mmol) was added at 0°C . The mixture was stirred at 0°C for 2 h and quenched with sat. NH_4Cl solution. The resulting mixture was extracted with ether, and the combined ether layers were washed with brine, dried (MgSO_4), and concentrated *in vacuo* to afford a yellow oil that was purified by flash chromatography (SiO_2 , pentane : diethyl ether = 10 : 1) to afford title compound **11** as a colorless oil (0.148 g, 41%) : ^1H NMR (300 MHz, CDCl_3) δ 5.09-5.02 (m, 1 H), 4.90-4.82 (m, 1 H), 4.26-4.11 (m, 4 H), 2.83 (d, $J = 2.7$ Hz, 2 H), 2.72 (dd, $J = 2.3, 7.8$ Hz, 2 H), 1.98-1.90 (m, 2 H), 1.38-1.18 (m, 8 H), 1.23 (t, $J = 7.1$ Hz, 6 H), 0.86 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.0, 169.7, 91.2, 84.3, 79.0, 71.2, 61.6, 57.0, 32.3, 31.7, 29.1, 28.8, 22.6, 22.5, 14.0; IR (neat) ν 1736, 1963, 3293 cm^{-1} ; EI-HRMS calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4$ [M^+] m/z 334.2144, found 334.2146.

2-(2,3-Pentadienyl)-2-(2-propynyl)malonic acid diethyl ester (13). Propargyl bromide (2.85 mL, 80% solution in toluene, 9.50 mmol) was added to a solution of

triethyl sodiomethanetricarboxylate (2.42 g, 9.50 mmol) in toluene : DMF (1 : 1, 24 mL) and the mixture was stirred and heated at 80 °C overnight. The resulting yellow suspension was cooled to rt, diluted with toluene (100 mL), washed with water, sat. Na₂CO₃ solution, and brine (2X). The combined aqueous layers were back-extracted with toluene and the combined organic layers were dried (MgSO₄), filtered and concentrated to afford 2-ethoxycarbonyl-2-(2-propynyl)malonic acid diethyl ester as a yellow oil (2.53 g, 100%).

This oil was dissolved in THF (6 mL) and added dropwise to a suspension of sodium ethoxide (0.800 g, 11.8 mmol) in THF (20 mL). After stirring at rt for 2 h the solution was acidified with 1N HCl and diluted with ether (150 mL), washed with water (30 mL), sat. NaHCO₃ solution, brine, dried (MgSO₄), concentrated and purified by flash chromatography (SiO₂, hexanes : diethyl ether = 3 : 1) to afford 2-(2-propynyl)malonic acid diethyl ester as a pale yellow oil (1.76 g, 95%).

A solution of 2-(2-propynyl)malonic acid diethyl ester (0.136 g, 0.503 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (20 mg, 60% dispersion in mineral oil, 0.503 mmol) in THF (5 mL). The resulting clear solution was stirred at rt for 20 min and PPh₃ (16 mg, 0.06 mmol) was added. The flask was flushed with a stream of N₂ gas for 5 min Pd₂(dba)₃ (9 mg, 0.01 mmol) and phosphoric acid diethyl ester 2,3-pentadienyl ester (0.11 g, 0.51 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 2 h and quenched with sat. NH₄Cl solution. The resulting mixture was extracted with ether, and the combined ether layers were washed with brine, dried (MgSO₄), and concentrated in vacuo to afford a yellow oil that was purified by flash chromatography (SiO₂, pentane : diethyl ether = 10 : 1) to afford title compound **13** as a colorless oil (37.7 mg, 28%) : ¹H NMR (300 MHz, CDCl₃) δ 5.05-5.01 (m, 1 H), 4.88-4.82 (m, 1 H), 4.25-4.10 (m, 4 H), 2.82 (d, *J* = 2.7 Hz, 2 H), 2.71 (dd, *J* = 2.2, 7.8 Hz, 2 H), 1.96 (t, *J* = 2.7 Hz, 1 H), 1.63 (dd, *J* = 3.2, 7.0 Hz, 3 H), 1.22 (t, *J* = 7.1 Hz, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 206.8, 169.6, 85.7, 83.9, 78.9, 71.2, 61.6, 57.0, 32.1, 22.5, 14.2, 14.0; IR (neat) ν 1736, 1967, 3287 cm⁻¹ ; EI-HRMS calcd for C₁₅H₂₀O₄ [M⁺] *m/z* 264.1362, found 264.1364.

2-(2-Butynyl)-2-(5,5,5-trideuterio-4-trideuteriomethyl-2,3-pentadienyl)malonic acid diethyl ester (6). A solution of 2-(2-butyne)malonic acid diethyl ester (0.390 g, 2.00 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (89.0 mg, 60% dispersion in mineral oil, 2.02 mmol) in THF (6 mL). The resulting clear solution was stirred at rt for 20 min and 5-bromo-1,1,1-trideuterio-2-trideuteriomethyl-2,3-pentadiene [prepared by bromination of 5,5,5-trideuterio-4-trideuteriomethyl-2,3-pentadien-1-ol (0.4 g, 3.8 mmol) with CBr_4 (1.4 g, 4.2 mmol) and PPh_3 (1.11 g, 4.2 mmol) in CH_2Cl_2 at 0°C] was added. The mixture was stirred at rt overnight and was quenched with sat. NH_4Cl solution, diluted with ether, washed with brine, sat. NaHCO_3 solution, and brine successively, dried (MgSO_4), concentrated and purified by flash chromatography (SiO_2 , hexanes : diethyl ether = 95 : 5) to afford title compound **6** as a colorless oil (0.260 g, 44%) : ^1H NMR (300 MHz, CDCl_3) δ 4.78 (t, J = 7.6 Hz, 1 H), 4.24-4.13 (m, 4 H), 2.78 (q, J = 2.4 Hz, 2 H), 2.69 (d, J = 7.6 Hz, 2 H), 1.74 (t, J = 2.4 Hz, 3 H), 1.24 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 203.9, 170.1, 94.7, 82.5, 78.4, 73.5, 61.3, 57.4, 32.4, 22.7, 19.5 (multiplet), 14.0, 3.4; IR (neat) ν 1736, 1968, 2982 cm^{-1} ; EI-HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{D}_6\text{O}_4$ [M^+] m/z . 298.2051, found 298.2057.

2-(2-Butynyl)-2-(4-methyl-2,3-pentadienyl)malonic acid diethyl ester (8). 1-Iodo-2-butyne (3.0 g, 16.7 mmol) was added to a solution of triethyl sodiomethanetricarboxylate (4.0 g, 15.7 mmol) in toluene : DMF (1 : 1, 40 mL) and the mixture was stirred and heated at 80°C overnight. The resulting yellow suspension was

cooled to rt, diluted with ether, washed with water, sat. Na_2CO_3 solution, and brine. The combined aqueous layers were back-extracted with ether and the combined ether layers were dried (MgSO_4), concentrated and purified by flash chromatography (SiO_2 , hexanes : diethyl ether = 5 : 1) to afford 2-(2-butynyl)-2-ethoxycarbonylmalonic acid diethyl ester as a yellow oil (4.06 g, 91%).

This oil was dissolved in THF (20 mL) and added dropwise to a suspension of sodium ethoxide (1.21 g, 17.9 mmol) in THF (20 mL). After stirring at rt for 2 h the solution was acidified with 1N HCl and diluted with ether, washed with water, sat. NaHCO_3 solution, brine, dried (MgSO_4), concentrated and purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 85 : 15) to afford 2-(2-butynyl)malonic acid diethyl ester as a pale yellow oil (2.48 g, 82%).

A solution of 2-(2-butynyl)malonic acid diethyl ester (0.38 g, 1.8 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (72 mg, 60% dispersion in mineral oil, 1.8 mmol) in THF (6 mL). The resulting clear solution was stirred at rt for 20 min and 1-bromo-4-methyl-2,3-pentadiene [prepared by bromination of 4-methyl-2,3-pentadien-1-ol (0.20 g, 2.0 mmol) with CBr_4 (0.74 g, 2.2 mmol) and PPh_3 (0.59 g, 2.2 mmol) in CH_2Cl_2 at 0 °C] was added. The mixture was stirred at rt overnight and was quenched with sat. NH_4Cl solution, diluted with ether, washed with brine, sat. NaHCO_3 solution, and brine successively, dried (MgSO_4), concentrated and purified by flash chromatography (SiO_2 , hexanes : diethyl ether = 9 : 1) to afford title compound **8** as a colorless oil (0.25 g, 48%) : ^1H NMR (300 MHz, CDCl_3) δ 4.80-4.74 (m, 1 H), 4.24-4.13 (m, 4 H), 2.78 (q, J = 2.4 Hz, 2 H), 2.69 (d, J = 7.6 Hz, 2 H), 1.74 (t, J = 2.4 Hz, 3 H), 1.65 (d, J = 2.8 Hz, 6 H), 1.24 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 203.9, 170.1, 95.0, 82.6, 78.4, 73.5, 61.3, 57.4, 32.5, 22.8, 20.4, 14.0, 3.4; IR (neat) ν 1732, 1970, 2981 cm^{-1} ; EI-HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$ [M^+] m/z . 292.1675, found 292.1688.

1-(2-Butynyloxy)-2,3-decadiene (25). A solution of 2,3-decadien-1-ol (0.3 g, 1.9 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (0.16 g, 60% dispersion in mineral oil, 3.8 mmol) in THF (10 mL). The resulting clear solution was stirred at rt for 20 min and 1-iodo-2-butyne was added. The mixture was stirred at rt overnight and was quenched with sat. NH_4Cl solution, diluted with ether, neutralized with 1 N HCl solution, washed with brine, sat. NaHCO_3 solution, and brine successively, dried (MgSO_4), concentrated and purified by flash chromatography (SiO_2 , pentane : ethyl ether = 30 : 1) to afford title compound **25** as a colorless oil (0.330 g, 82%) : ^1H NMR (300 MHz, CDCl_3) δ 5.19-5.13 (m, 2 H), 4.09 (q, $J = 2.2$ Hz, 2 H), 4.01 (dd, $J = 2.9, 6.3$ Hz, 2 H), 2.03-1.95 (m, 2 H), 1.83 (t, $J = 2.2$ Hz, 3 H), 1.40-1.21 (m, 8 H), 0.86 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.3, 92.0, 87.8, 82.3, 75.0, 68.1, 57.2, 31.6, 29.0, 28.7, 28.5, 22.6, 14.1, 3.6; IR (neat) ν 1963, 2924, 1079 cm^{-1} ; EI-HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{O}$ [$\text{M}-\text{H}^+$] m/z . 205.1592, found 205.1589.

N-(2,3-Decadienyl)-4-methyl-N-(2-propynyl)benzenesulfonamide (19). To a solution of 4-Methyl-N-(2-propynyl)benzenesulfonamide (2.09 g, 10.0 mmol), PPh_3 (3.54 g, 13.5 mmol) and 2,3-pentadien-1-ol (2.01 g, 13.0 mmol) in THF (30 mL) at 0 $^{\circ}\text{C}$ was added dropwise diisopropylazodicarboxylate (2.66 mL, 13.5 mmol). The resulting solution was allowed to slowly warm to rt and react for overnight. THF was removed in vacuo. The residue was dissolved in ethyl acetate and the resulting solution was washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 95 : 5) to afford **19** as a slightly yellow oil (3.42 g, 99%) : ^1H NMR (300 MHz, CDCl_3) δ 7.70 (d, $J = 8.2$ Hz, 2 H), 7.26 (d, $J = 8.2$ Hz, 2 H), 5.19-5.13 (m, 1 H), 4.99-4.93 (m, 1 H), 4.17 (dd, AB, $J = 2.4, 18.2$ Hz, 1 H), 4.09 (dd, AB, $J = 2.4, 18.2$ Hz, 1H), 3.85 (ddd, A B , $J = 2.4, 6.9, 14.0$ Hz, 1

H), 3.76 (ddd, A B , $J = 2.4, 6.9, 14.0$ Hz, 1 H), 2.39 (s, 3 H), 2.02-1.91 (m, 3 H), 1.39-1.18 (m, 8 H), 0.84 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.7, 143.5, 136.1, 129.4, 127.7, 92.8, 85.8, 76.5, 73.5, 46.2, 35.6, 31.6, 28.9, 28.7, 28.5, 22.5, 21.5, 14.0; IR (neat) ν 3278, 2926, 1964, 1350, 1163 cm^{-1} ; EI-HRMS calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_2\text{S}$ $[\text{M}^+]$ m/z . 345.1763, found 345.1770.

4-Methyl-N-(2,3-pentadienyl)-N-(2-propynyl)benzenesulfonamide (21). To a solution of 4-Methyl-N-(2-propynyl)benzenesulfonamide (0.50 g, 2.4 mmol), PPh_3 (0.85 g, 3.2 mmol) and 2,3-pentadien-1-ol (0.26 g, 3.1 mmol) in THF (10 mL) at 0 $^\circ\text{C}$ was added dropwise diisopropylazodicarboxylate (0.64 mL, 3.2 mmol). The resulting solution was allowed to slowly warm to rt and stirred overnight. THF was removed *in vacuo*. The residue was dissolved in ethyl acetate and the resulting solution was washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 95 : 5) to afford **21** as a colorless solid (0.61 g, 92%) : ^1H NMR (300 MHz, CDCl_3) δ 7.75-7.14 (m, 2 H), 7.30-7.26 (m, 2 H), 5.20-5.11 (m, 1 H), 4.99-4.91 (M, 1 H), 4.19 (dd, AB, $J = 2.5, 18.2$ Hz, 1 H), 4.12 (dd, AB, $J = 2.5, 18.2$ Hz, 1H), 3.87 (ddd, A B , $J = 2.3, 6.8, 14.1$ Hz, 1 H), 3.79 (ddd, A B , $J = 2.3, 6.8, 14.1$ Hz, 1 H), 2.42 (s, 3 H), 2.01 (t, $J = 2.5$ Hz, 1 H), 1.64 (dd, $J = 3.1, 7.1$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 206.6, 143.5, 136.3, 129.5, 127.7, 87.4, 85.3, 77.4, 73.4, 46.2, 35.7, 21.5, 14.0; IR (neat) ν 1966, 1160, 3269, 1597 cm^{-1} ; EI-HRMS calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$ $[\text{M}^+]$ m/z . 275.0980, found 275.0981.

N-2,3-Decadienyl-4-methyl-N-(3-trimethylsilyl-2-propynyl)benzenesulfonamide (23). To a solution of *N*-(2,3-Decadienyl)-4-methyl-*N*-(2-propynyl)benzenesulfonamide **19** (0.42 g, 1.2 mmol) in THF (10 mL) at -78 $^\circ\text{C}$ was added 1.6 M BuLi solution in hexanes (1.0 mL, 1.6 mmol). The mixture was stirred for 30 min at -78 $^\circ\text{C}$

and treated with trimethylsilyl chloride (0.32 mL, 2.4 mmol). The mixture was allowed to gradually warm to rt over 80 minutes and quenched with sat. NH_4Cl solution, diluted with ether, washed with brine, and dried (MgSO_4), filtered and concentrated to obtain a yellow oil. Purification by flash chromatography (SiO_2 , hexanes : ethyl acetate = 95 : 5) afforded the product as an off-white solid (0.38 g, 75%). : ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, J = 8.3 Hz, 2 H), 7.28 (d, J = 8.3 Hz, 2 H), 5.23-5.16 (m, 1 H), 5.03-4.97 (m, 1 H), 4.21 (d, AB, J = 18.4 Hz, 1 H), 4.14 (d, AB, J = 18.4 Hz, 1 H), 3.86 (ddd, A B , J = 2.3, 6.8, 18.0 Hz, 1 H), 3.78 (ddd, A B , J = 2.3, 6.8, 18.0 Hz, 1 H), 2.42 (s, 3 H), 2.01-1.96 (m, 2 H), 1.43-1.19 (m, 8 H), 0.88 (t, J = 6.5 Hz, 3 H), 0.00 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.7, 143.3, 136.1, 129.5, 127.7, 97.7, 92.7, 90.7, 85.9, 46.2, 36.6, 31.6, 28.9, 28.7, 28.5, 22.6, 21.5, 14.1, -0.5; IR (neat) ν 2925, 1964, 1351, 1164, 1094 cm^{-1} ; EI-HRMS calcd for $\text{C}_{23}\text{H}_{35}\text{NO}_2\text{SSi}$ [M^+] m/z 417.2160, found 417.2161.

5-Trimethylsilylmethylene-4-vinyl-3-cyclohexene-1,1-dicarboxylic acid diethyl ester (18). To a flame-dried test tube equipped with a magnetic stirring bar was added 2-(2,3-pentadienyl)-2-(3-trimethylsilylpropynyl)malonic acid diethyl ester (**17**, 41 mg, 0.13 mmol) and toluene (0.5 mL). The test tube was evacuated and charged with N_2 (this step was repeated 3 times) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (2.5 mg, 6×10^{-3} mmol) was

added. The mixture was stirred at rt for 1 h under N₂ atmosphere (1 atm). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO₂, hexanes : ethyl acetate = 9 : 1) to afford title compound **18** as a colorless oil (18.3 mg, 45%) : ¹H NMR (300 MHz, CDCl₃) δ 6.47 (dd, *J* = 10.8, 17.2 Hz, 1 H), 5.94 (t, *J* = 4.3 Hz, 1 H), 5.64 (s, 1 H), 5.32 (dd, *J* = 2.0, 17.2 Hz, 1 H), 5.06 (dd, *J* = 2.0, 10.8 Hz, 1 H), 4.27-4.09 (m, 4 H), 2.97 (s, 2 H), 2.74 (d, *J* = 4.3 Hz), 1.23 (t, *J* = 7.1 Hz), 0.18 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 146.1, 138.5, 136.0, 126.7, 124.3, 115.4, 61.4, 54.2, 35.8, 31.7, 14.0, 0.0; IR (neat) ν 1736, 1248, 1194, 1578, 2957 cm⁻¹; EI-HRMS calcd for C₁₈H₂₈O₄Si [M⁺] *m/z* 336.1757, found 336.1760.

4-(1-Heptenyl)-5-trimethylsilylmethylene-3-cyclohexene-1,1-dicarboxylic acid diethyl ester (16). To a flame-dried test tube equipped with a magnetic stirring bar was added 2-(2,3-decadienyl)-2-(3-trimethylsilyl-2-propynyl)malonic acid diethyl ester (**15**, 50 mg, 0.12 mmol) and toluene (0.5 mL). The test tube was evacuated and charged with N₂ (this step was repeated 3 times) and [Rh(CO)₂Cl]₂ (2.5 mg, 6 × 10⁻³ mmol) was added. The mixture was stirred at rt for 3 h under N₂ atmosphere (1 atm). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO₂, hexanes : ethyl acetate = 9 : 1) to afford title compound **16** as a colorless oil (29.5 mg, 60%, *E/Z* ratio = 3 : 1 determined by ¹H NMR). The *E/Z* isomers were separated by HPLC.

16-E : ¹H NMR (300 MHz, CDCl₃) δ 6.06 (d, *J* = 15.3 Hz, 1 H), 5.82 (t, *J* = 4.3 Hz, 1 H), 5.71 (td, *J* = 6.8, 15.3 Hz, 1 H), 5.61 (s, 1 H), 4.21-4.08 (m, 4 H), 2.94 (s, 2 H), 2.69 (d, *J* = 4.3 Hz, 2 H), 2.06 (q, *J* = 6.9 Hz, 2 H), 1.41-1.18 (m, 6 H), 1.21 (t, *J* = 7.0 Hz, 6 H), 0.87 (t, *J* = 6.9 Hz, 3 H), 0.14 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 146.7, 138.0, 132.4, 128.1, 126.3, 123.4, 61.4, 54.2, 35.9, 32.8, 31.7, 31.4, 29.0, 22.5, 14.0, 14.0, 0.1; IR (neat) ν 1736, 1247, 2926 cm⁻¹; EI-HRMS calcd for C₂₃H₃₈O₄Si [M⁺] *m/z* 406.2539, found 406.2553.

16-Z : ¹H NMR (300 MHz, CDCl₃) δ 5.91 (d, *J* = 11.2 Hz, 1 H), 5.66 (t, *J* = 4.0 Hz, 1 H), 5.61-5.49 (m, 1 H), 5.57 (s, 1 H), 4.24-4.10 (m, 4 H), 2.99 (s, 2 H), 2.74 (d, *J* = 4.0 Hz, 2 H), 2.02 (q, *J* = 6.9 Hz, 2 H), 1.44-1.22 (m, 6 H), 1.24 (t, *J* = 7.1 Hz, 6 H), 0.87 (t, *J* = 6.2 Hz, 3 H), 0.16 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 146.7, 136.3, 133.6, 127.6, 127.1, 125.6, 61.4, 54.3, 35.8, 31.6, 31.5, 29.4, 28.2, 22.5, 14.0, 0.0;

IR (neat) ν 1736, 1247, 1578, 2956, 2856 cm^{-1} ; EI-HRMS calcd for $\text{C}_{23}\text{H}_{38}\text{O}_4\text{Si}$ [M^+] m/z 406.2539, found 406.2547.

5-Methylene-4-vinyl-cyclohex-3-ene-1,1-dicarboxylic acid diethyl ester(14).

To a flame-dried test tube equipped with a magnetic stirring bar was added 2-(2,3-pentadienyl)-2-(2-propynyl)malonic acid diethyl ester (**13**, 39 mg, 0.15 mmol) and toluene (0.5 mL). The test tube was evacuated and charged with N_2 (this step was repeated 3 times) then $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1 mg, 3×10^{-3} mmol) was added. The mixture was stirred and heated at 90 $^\circ\text{C}$ for 1 h under N_2 atmosphere (1 atm). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 9 : 1) to afford title compound **14** as a colorless oil (27.6 mg, 71%) : ^1H NMR (300 MHz, CDCl_3) δ 6.37 (ddd, J = 1.1, 10.8, 17.3 Hz, 1 H), 5.86 (t, J = 4.2 Hz, 1 H), 5.34 (dd, J = 1.8, 17.3 Hz, 1 H), 5.09 (s, 1 H), 5.05 (dd, J = 1.8, 17.3 Hz, 1 H), 4.94 (s, 1 H), 4.22-4.10 (m, 4 H), 2.85 (s, 2 H), 2.73 (d, J = 4.2 Hz, 2 H), 1.20 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.8, 138.7, 136.4, 135.0, 124.3, 115.3, 112.4, 61.4, 54.1, 37.4, 31.8, 29.7, 14.1; IR (neat) ν 1734, 1244 cm^{-1} ; EI-HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4$ [M^+] m/z 264.1362, found 264.1362.

4-(1-Heptenyl)-5-methylene-3-cyclohexene-1,1-dicarboxylic acid diethyl ester

(12). To a flame-dried test tube equipped with a magnetic stirring bar was added 2-(2,3-decadienyl)-2-(2-propynyl)malonic acid diethyl ester (**11**, 53 mg, 0.16 mmol) and toluene (0.8 mL). The test tube was evacuated and charged with N_2 (this step was repeated 3 times) then $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1 mg, 3×10^{-3} mmol) was added. The mixture was stirred and heated at 90 $^\circ\text{C}$ for 1 h under N_2 atmosphere (1 atm). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 9 : 1) to afford title compound **12** as a colorless oil (42.9 mg, 80%, E/Z ratio = 3 : 1 determined by ^1H NMR). The E/Z isomers were separated by HPLC.

12-E : ^1H NMR (300 MHz, CDCl_3) δ 6.00 (dd, J = 1.1, 15.5 Hz, 1 H), 5.83-5.73 (m, 2 H), 5.07 (s, 1 H), 4.90 (s, 1 H), 4.19-4.08 (m, 4 H), 2.84 (s, 2 H), 2.70 (d, J = 4.1 Hz, 2 H), 2.04 (q, J = 6.7 Hz, 2 H), 1.41-1.23 (m, 6 H), 1.19 (t, J = 7.1 Hz, 6 H), 0.86 (t, J = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.8, 139.2, 136.0, 132.3, 127.4, 123.0,

112.1, 61.3, 54.1, 37.4, 32.8, 31.8, 31.4, 29.7, 29.0, 22.5, 14.0; IR (neat) ν 1736, 1243, 1181, 2927 cm^{-1} ; EI-HRMS calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4$ $[\text{M}^+]$ m/z 334.2144, found 334.2140.

12-Z : ^1H NMR (300 MHz, CDCl_3) δ 5.91 (dd, $J = 1.4, 11.3$ Hz, 1 H), 5.61 (t, $J = 4.8$ Hz, 1 H), 5.57 (td, $J = 7.3, 11.3$ Hz, 1 H), 5.00 (s, 1 H), 4.90 (s, 1 H), 4.23-4.12 (m, 4 H), 2.90 (s, 2 H), 2.76 (d, $J = 2.5$ Hz, 2 H), 1.38-1.15 (m, 6 H), 1.23 (t, $J = 7.1$ Hz, 6 H), 0.87 (t, $J = 6.5$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 1709, 139.5, 134.5, 133.8, 126.8, 125.5, 112.5, 61.3, 54.2, 37.1, 31.7, 31.5, 29.5, 28.3, 22.5, 14.0, 13.9; IR (neat) ν 1736, 1244, 1182, 1465, 2927 cm^{-1} ; EI-HRMS calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4$ $[\text{M}^+]$ m/z 334.2144, found 334.2137.

5-Ethylidene-4-isopropenyl-3-cyclohexene-1,1-dicarboxylic acid diethyl ester

(9). To a flame-dried test tube equipped with a magnetic stirring bar was added 2-(2-butynyl)-2-(4-methyl-2,3-pentadienyl)malonic acid diethyl ester (**8**, 40.0 mg, 0.14 mmol) and toluene (0.5 mL). The test tube was evacuated and charged with N_2 (this step was repeated 3 times) then $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (1 mg, 3×10^{-3} mmol) was added. The mixture was stirred and heated at $90\text{ }^\circ\text{C}$ for 1 h under N_2 atmosphere (1 atm). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 9 : 1) to afford title compound **9** as a colorless oil (28.0 mg, 70%) : ^1H NMR (300 MHz, CDCl_3) δ 5.53 (q, $J = 7.0$ Hz, 1 H), 5.45 (t, $J = 4.1$ Hz, 1 H), 4.90-4.89 (m, 1 H), 4.74 (d, $J = 1.9$ Hz, 1 H), 4.13 (q, $J = 7.1$ Hz, 4 H), 2.82 (s, 2 H), 2.65 (d, $J = 4.1$ Hz, 2 H), 1.78 (s, 3 H), 1.70 (d, $J = 7.0$ Hz, 3 H), 1.20 (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.1, 145.2, 143.1, 130.6, 123.4, 120.1, 114.1, 61.3, 54.1, 31.2, 30.7, 23.1, 14.0, 13.2; IR (neat) ν 1733, 1642, 1244 cm^{-1} ; EI-HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$ $[\text{M}^+]$ m/z 292.1675, found 292.1679.

5-(1-Deuterioethylidene)-4-(2,2-dideuterio-1-trideuteriomethylvinyl)-3-cyclohexene-1,1-dicarboxylic acid diethyl ester (7). To a flame-dried test tube equipped with a magnetic stirring bar was added 2-(2-butynyl)-2-(5,5,5-trideuterio-4-trideuteriomethyl-2,3-pentadienyl)malonic acid diethyl ester (**6**, 40.0 mg, 0.134 mmol) and toluene (0.5 mL). The test tube was evacuated and charged with N₂ (this step was repeated 3 times) then [Rh(CO)₂Cl]₂ (1.0 mg, 3.0 × 10⁻³ mmol) was added. The mixture was stirred and heated at 90 °C for 1 h under N₂ atmosphere (1 atm). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO₂, hexanes : ethyl acetate = 9 : 1) to afford title compound **7** as a colorless oil (25.0 mg, 63%) : ¹H NMR (300 MHz, CDCl₃) δ 5.45 (t, *J* = 4.1 Hz, 1 H), 4.13 (q, *J* = 7.1 Hz, 4 H), 2.82 (s, 2 H), 2.65 (d, *J* = 4.1 Hz, 2 H), 1.70 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 171.1, 144.9, 143.0, 130.5, 120.0, 61.3, 54.1, 31.2, 30.7, 14.0, 13.1; IR (neat) ν 1734, 1244, 1445, 2917 cm⁻¹; EI-HRMS calcd for C₁₇H₁₈D₆O₄ [M⁺] *m/z* . 298.2051, found 298.2053.

3-Ethylidene-4-(1-heptenyl)-3,6-dihydro-2H-pyran (26). To a flame-dried test tube equipped with a magnetic stirring bar was added 1-(2-butynyloxy)-2,3-decadiene (**25**, 46.0 mg, 0.22 mmol) and toluene (0.5 mL). The test tube was evacuated and charged with N₂ (this step was repeated 3 times) then [Rh(CO)₂Cl]₂ (4.6 mg, 0.01 mmol) was added. The mixture was stirred and heated at 90 °C for 1 h under N₂ atmosphere (1 atm). The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO₂, hexanes : ethyl ether = 3 : 1) to afford title compound **26** as a colorless oil (25.2

mg, 74%, E/Z ratio = 6 : 1 determined by ^1H NMR). The E/Z isomers were separated by flash chromatography (SiO_2 , hexanes : ethyl ether = 15 : 1).

26-E : ^1H NMR (300 MHz, CDCl_3) δ 6.05 (dd, J = 1.2, 15.4 Hz, 1 H), 5.80 (td, J = 6.8, 15.4 Hz, 1 H), 5.71 (t, J = 3.2 Hz, 1 H), 5.61 (q, J = 7.1 Hz, 1 H), 4.32 (s, 2 H), 4.24 (d, J = 2.1 Hz, 2 H), 2.07 (q, J = 6.8 Hz, 2 H), 1.67 (d, J = 7.1 Hz, 3 H), 1.44-1.17 (m, 6 H), 0.87 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.9, 132.9, 132.3, 126.9, 121.3, 119.0, 66.1, 64.4, 32.8, 31.4, 29.7, 29.0, 22.5, 14.0; IR (neat) ν 2924, 1132, 1452 cm^{-1} ; EI-HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ [M^+] m/z 206.1671, found 206.1671.

26-Z : ^1H NMR (300 MHz, CDCl_3) δ 5.91 (ddd, J = 1.7, 3.3, 11.4, 1 H), 5.61 (td, J = 7.3, 11.4, 1 H), 5.57 (s, broad, 1 H), 5.52 (dq, J = 0.7, 7.2 Hz, 1 H), 4.38 (s, 2 H), 4.29 (s, broad, 2 H), 2.16-2.08 (m, 2 H), 1.68 (d, J = 7.2 Hz), 1.41-1.25 (m, 6 H), 0.88 (t, J = 6.9 Hz, 3 H); IR (neat) ν 2924, 1132, 1451 cm^{-1} ; EI-HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ [M^+] m/z 206.1671, found 206.1670.

3-Methylene-1-(4-toluenesulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridine (22). To a dry NMR tube was added 4-methyl-N-(2,3-pentadienyl)-N-(2-propynyl)benzenesulfonamide (**21**, 26.3 mg, 0.096 mmol) and toluene- d_8 (0.5 mL). The NMR tube was evacuated and charged with N_2 (this step was repeated 3 times) then $[\text{Rh(CO)}_2\text{Cl}]_2$ (1 mg, 3×10^{-3} mmol) was added. The mixture was allowed to react at rt for 6 h until ^1H NMR shows complete consumption of starting material. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO_2 , pentane : ethyl ether = 1 : 1) to afford title compound **22** as a colorless oil (24.4 mg, 93%) : ^1H NMR (300 MHz, CDCl_3) δ 7.67 (d, J = 8.2 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 2 H), 6.31 (dd, J = 10.8, 17.2 Hz, 1 H), 5.76 (s, 1 H), 5.28 (dd, J = 1.5, 17.0 Hz, 1 H), 5.12 (s, 1 H), 5.28 (dd, J = 1.5, 10.8 Hz, 1 H), 5.02 (s, 1 H), 3.83-3.81 (m, 4 H), 2.42 (s, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.6, 136.5, 135.4, 133.7, 133.3, 129.5, 127.8, 121.5, 116.6, 112.1,

49.3, 45.7, 21.5; IR (neat) ν 1167, 1347, 1091 cm^{-1} ; EI-HRMS calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$ [M^+] m/z 275.0980, found 275.0985.

4-(1-Heptenyl)-3-methylene-1-(4-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (20). To a dry NMR tube was added N-(2,3-Decadienyl)-4-methyl-N-(2-propynyl)benzenesulfonamide (**19**, 32.2 mg, 0.093 mmol) and toluene- d_8 (0.5 mL). The NMR tube was evacuated and charged with N_2 (this step was repeated 3 times) then $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.7 mg, 0.002 mmol) was added. The mixture was allowed to react at rt for 6 h until ^1H NMR shows complete consumption of starting material. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 4 : 1) to afford title compound **20** as a colorless oil (24.4 mg, 90%, E/Z ratio = 6 : 1 measured by ^1H NMR). The *E* and *Z* isomers were separated by HPLC.

20-E : ^1H NMR (300 MHz, CDCl_3) δ 7.66 (d, $J = 8.2$ Hz, 2 H), 7.28 (d, $J = 8.2$ Hz, 2 H), 5.93 (dd, $J = 0.9, 15.4$ Hz, 1 H), 5.70 (td, $J = 6.8, 15.4$ Hz, 1 H), 5.66 (t, $J = 2.7$ Hz, 1 H), 5.10 (s, 1 H), 4.98 (s, 1 H), 3.80 (s, 4 H), 2.41 (s, 3 H), 2.06 (q, 6.8 Hz, 2 H), 1.43-1.21 (m, 6 H), 0.88 (t, $J = 6.2$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.5, 137.1, 135.1, 133.8, 133.5, 129.5, 127.8, 126.0, 120.3, 111.8, 49.4, 45.8, 32.7, 31.3, 28.8, 22.5, 21.5, 14.0; IR (neat) ν 1169, 1354, 2924 cm^{-1} ; EI-HRMS calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_2\text{S}$ [M^+] m/z 345.1763, found 345.1754.

20-Z : ^1H NMR (300 MHz, CDCl_3) δ 7.66 (d, $J = 8.2$ Hz, 2 H), 7.28 (d, $J = 8.2$ Hz, 2 H), 5.77 (dd, $J = 1.6, 11.4$ Hz, 1 H), 5.70 (td, $J = 7.2, 11.4$ Hz, 1 H), 5.51 (t, $J = 2.7$ Hz, 1 H), 5.01 (s, 1 H), 4.94 (s, 1 H), 3.84 (s, 4 H), 2.41 (s, 3 H), 1.92 (q, 6.8 Hz, 2 H), 1.43-1.20 (m, 6 H), 0.88 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.5, 137.4, 134.7, 133.8, 133.3, 129.6, 127.8, 125.1, 123.0, 112.1, 49.0, 45.5, 31.4, 29.5, 28.4, 22.5, 21.5, 14.0; IR (neat) ν 1169, 1351, 2924 cm^{-1} ; EI-HRMS calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_2\text{S}$ [M^+] m/z 345.1763, found 345.1748.

4-(1-Heptenyl)-1-(4-toluenesulfonyl)-3-trimethylsilanylmethylene-1,2,3,6-tetrahydropyridine (24). To a dry NMR tube was added *N*-2,3-decadienyl-4-methyl-*N*-(3-trimethylsilyl-2-propynyl)benzenesulfonamide (**23**, 20.6 mg, 0.049 mmol) and toluene- d_8 (0.5 mL). The NMR tube was evacuated and charged with N_2 (this step was repeated 3 times) then $[Rh(CO)_2Cl]_2$ (0.5 mg, 0.0012 mmol) was added. The mixture was allowed to react at rt for 5 h until 1H NMR shows complete consumption of starting material. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (SiO_2 , hexanes : ethyl acetate = 9 : 1) to afford title compound **24** as a colorless oil (17.5 mg, 85%, E/Z ratio = 5 : 1 measured by 1H NMR). The E and Z isomers were separated by HPLC.

E-24 : 1H NMR (300 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2 H), 7.32-7.29 (m, 2 H), 5.97 (dd, J = 1.2, 15.3 Hz, 1 H), 5.71-5.59 (m, 2 H), 5.66 (s, 1 H), 3.90 (dd, AB, J = 0.8, 14.0 Hz, 1 H), 3.86 (dd, AB, J = 0.8, 14.0 Hz, 1 H), 3.79 (broad d, J = 3.5 Hz, 2 H), 2.43 (s, 3 H), 2.07 (q, J = 6.9 Hz, 2 H), 1.44-1.22 (m, 6 H), 0.90 (t, J = 6.6 Hz, 3 H), 0.21 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6, 143.4, 137.3, 134.2, 133.8, 129.5, 127.9, 126.9, 126.8, 120.5, 48.2, 45.6, 32.7, 31.3, 28.9, 22.5, 21.4, 14.0, 0.01; IR (neat) ν 2955, 2855, 1584, 1352, 1167 cm^{-1} ; EI-HRMS calcd for $C_{23}H_{35}NO_2SSi$ [M^+] m/z 417.2160, found 417.2160.

Z-24 : 1H NMR (300 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2 H), 7.32-7.29 (m, 2 H), 5.78 (dd, J = 1.4, 11.4 Hz, 1 H), 5.63-5.52 (m, 2 H), 5.59 (s, 1 H), 3.93 (broad s, 2 H), 3.84-3.82 (m, 2 H), 2.43 (s, 3 H), 1.92 (q, 6.9 Hz, 2 H), 1.35-1.21 (m, 6 H), 0.88 (t, J = 6.7 Hz, 3 H), 0.21 (s, 9 H); IR (neat) ν 2955, 2926, 2856, 1597, 1352, 1168 cm^{-1} ; EI-HRMS calcd for $C_{23}H_{35}NO_2SSi$ [M^+] m/z 417.2160, found 417.2164.

Procedure for $[\text{RhCl(CO)}_2]_2$ Catalyzed Triene Formation. A flame dried 2-neck flask was charged with $[\text{RhCl(CO)}_2]_2$ (3.5 mg, 9.0×10^{-3} mmol) and flushed with a stream of nitrogen for 5 min. Allenyne **4** (56 mg, 0.10 mmol) in 5 mL of dry toluene was then added *via* syringe and the reaction mixture was immersed in a preheated 90°C sand bath. After 1 h TLC showed complete loss of starting material and the reaction was cooled to rt and concentrated under reduced pressure. Trienes **5E-Z** were purified by flash silica gel chromatography eluting with hexanes to afford 40 mg (0.14 mmol) of the triene in 72% yield as a 5 : 1 mixture of *E* : *Z* isomers. **Trimethyl-(2-oct-1-enyl-cyclohex-2-enylidenemethyl)-silane. 5E.** ^1H NMR (300 MHz, CDCl_3) δ : 6.13 (dd, 1H, $J = 15.4$ Hz), 5.92 (t, 1H, $J = 4.2$ Hz), 5.77 (dt, 1H, $J = 15.4, 6.8$ Hz), 5.52 (s, 1H), 2.46-2.42 (m, 2H), 2.22 (q, 2H, $J = 5.4$ Hz), 2.11 (q, 2H, $J = 6.9$ Hz), 1.74 (p, 2H, $J = 6.2$ Hz), 1.43-1.28 (m, 12 H), 0.90 (t, 3H, $J = 6.9$ Hz), 0.15 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ : 152.4, 138.7, 131.8, 129.5, 127.5, 123.1, 33.5, 32.1, 31.9, 29.9, 29.7, 29.5, 29.4, 26.6, 23.7, 22.9, 0.4. IR (neat) 2954, 2927, 2855, 1248, 841cm^{-1} .

Procedure for $[\text{RhCl(COD)}]_2$ Catalyzed Triene Formation. Allenyne **4** (47 mg, 0.17 mmol) was azeotroped with benzene (3 x 1 mL) and placed on a high-vac manifold for 20 min. Allenyne **4** was then diluted with 3 mL of dry 1,2-dichloroethane and the solution was degassed with a stream of N_2 for 5 min. To the reaction mixture was then added

[RhCl(COD)]₂ (4.5 mg, 9.1×10^{-3} mmol) and the reaction stirred at rt for 5 min during which time the reaction mixture turned a bright yellow color. To the reaction mixture was then added AgSbF₆ (5.9 mg, 1.7×10^{-2} mmol) after which the reaction turned a deep red color. After 15 min at rt TLC showed complete loss of starting material and the reaction mixture was diluted with 5 mL of Et₂O and filtered through a plug of celite 545[®]. The filtrate was concentrated under reduced pressure and the products purified by silica gel chromatography eluting with hexanes to afford 23 mg (0.12 mmol) of desilylated triene **5** as a 13 : 1 mixture of *E* : *Z* isomers in 67% yield. **6-Methylene-1-oct-1-enyl-cyclohexene. 5-E** ¹H NMR (300 MHz, CDCl₃) δ : 6.10 (d, 1H, *J* = 15.4 Hz), 5.88 (t, 1H, *J* = 3.8 Hz), 5.81 (dt, 1H, *J* = 15.4, 6.8 Hz), 4.97 (s, 1H), 4.79 (s, 1H), 2.35 (t, 2H, *J* = 6.1 Hz), 2.21 (q, 2H, *J* = 5.5 Hz), 2.09 (q, 2H, *J* = 6.9 Hz), 1.71 (p, 2H, *J* = 6.15 Hz), 1.43-1.19 (m, 8H), 0.89 (t, 3H, *J* = 6.5 Hz); ¹³C NMR (300 MHz, CDCl₃) δ : 144.0, 136.9, 131.6, 128.8, 127.2, 109.0, 33.2, 32.8, 29.7, 29.1, 26.7, 23.6, 22.9, 14.3; IR (neat) 2930, 2856, 1456 cm⁻¹; MS (GC/MS) *m/e* 204 (M⁺), 147, 133, 119, 105, 91, 84; HRMS calcd for C₁₅H₂₄ : 204.1878; found : 204.1880. **5-Z** : ¹H NMR (300 MHz, CDCl₃) δ 5.96 (d, 2H, *J* = 11.3 Hz), 5.70 (br s, 1H), 5.55 (dt, 1H, *J* = 11.3, 7.2 Hz), 4.87 (s, 1H), 4.75 (s, 1H), 2.41-2.36 (m, 2H), 2.23 (q, 2H, *J* = 5.1 Hz), 2.10 (q, 2H, *J* = 7.1 Hz), 1.74 (p, 2H, *J* = 6.2 Hz), 1.37-1.27 (m, 8H), 0.89 (t, 3H, *J* = 6.7 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 143.8, 134.4, 132.6, 129.4, 127.8, 109.1, 32.1, 31.7, 29.9, 28.9, 28.4, 26.2, 23.2, 22.6, 14.1; MS (GC/MS) *m/e* 204 (M⁺), 147, 133, 119, 105, 91, 79; IR (neat) 2925, 2854, 1455 cm⁻¹.

Procedure for [RhCl(CH₂CH₂)]₂ Catalyzed Triene Formation. Allenyne **4** (45 mg, 0.16 mmol) was azeotroped with benzene (3 x 1 mL) and placed on a high-vac manifold for 20 min. The allenyne **4** was then diluted with 3 mL of dry 1,2-dichloroethane and the solution degassed with a stream of N₂ for 5 min. To the reaction mixture was then added [RhCl(CH₂CH₂)]₂ (3.0 mg, 7.7×10^{-3} mmol) and stirred at rt for 5 min during which time the reaction turned to light gold. To the reaction mixture was then added AgSbF₆ (6.0 mg, 1.7×10^{-2} mmol) after which time the reaction mixture turned dark red. After 15 min at rt TLC showed complete loss of starting material and the reaction was diluted with 5 mL of Et₂O and filtered through a plug of Celite 545[®]. The filtrate was concentrated

under reduced pressure and the products purified by silica gel chromatography eluting with hexanes to afford 15.3 mg (7.5×10^{-2} mmol) of desilylated triene **5** as a 4 : 1 mixture of *E* : *Z* isomers in 46% yield.

General procedure for performing the Allenic Alder-ene reaction catalyzed by an Ir complex. To a flame-dried test tube was added the substrate (1 eq), dichloroethane (DCE, 0.50 mL/1 mmol of substrate). The test tube was evacuated and charged with N₂ (this step was repeated 3 times). A solution of AgBF₄ in DCE (0.05 M, 0.2 eq) was added to the test tube followed by immediate addition of [Ir(COD)Cl]₂ (0.1 eq). The mixture was heated at 60 °C for 5 min, cooled to 0 °C, diluted with hexanes and passed through a short SiO₂ column to remove the catalyst. Purification of the crude products by flash chromatography (SiO₂, hexanes : ethyl acetate = 9 : 1) afforded the desired products and the *E/Z* ratios were measured by ¹H NMR or by GC analysis.

Allenyne **4** (28 mg, 0.10 mmol) was treated under the general iridium conditions described above to afford triene **5** (16 mg, 57%) in an *E/Z* ratio of more than 20 : 1 (determined by ¹H NMR analysis).

Allenyne **15** (43 mg, 0.11 mmol) was treated to the general iridium conditions described above to afford triene **16** (29 mg, 67%) in an *E/Z* ratio of 180 : 1 (determined by GC analysis).

Allenyne **23** (40 mg, 0.096 mmol) was treated to the general iridium conditions described above to afford triene **24** (25 mg, 62%) in an *E/Z* ratio of more than 20 : 1 (determined by ^1H NMR analysis).

2-(3-Butynyl)-3,4-undecadien-1-ol (27). To a stirred solution of 5-hexyn-1-carboxylic acid (1.52 g, 13.6 mmol) in dichloromethane (13 mL) were added 4-dimethylaminopyridine (70 mg, 0.57 mmol) and 1-nonyn-3-ol (1.90 g, 13.6 mmol). The solution was cooled to 0 °C and 1,3-dicyclohexylcarbodiimide (2.81 g, 13.6 mmol) was added. The reaction was stirred at 0 °C for 5 min then warmed to rt and stirred for an additional 1 h. The precipitate was filtered off and the resulting filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel column using 5% ethyl acetate/hexanes as the eluant to afford hex-5-ynoic acid 1-hexyl-prop-2-ynyl ester as a yellow oil (2.62 g, 83%).

To a stirred solution of 5-hexynoic acid 1-hexyl-prop-2-ynyl ester (1.20 g, 5.13 mmol) in benzene (4 mL) were added triethylamine (1.44 mL, 10.26 mmol) and triisopropylsilyl trifluoromethanesulfonate (2.1 mL, 7.7 mmol). The solution was stirred at rt for 9 h. The two layers were separated and the bottom layer was extracted with benzene. The benzene layers were combined and concentrated. The crude material was purified by flash column chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to give 2-but-3-ynyl-undeca-3,4-dienoic acid methyl ester (1.38 g, 3.54 mmol) as a colorless oil.

This oil (1.38 g, 3.54 mmol) was dissolved in ether (7 mL) and the solution was cooled to 0 °C. To this solution was added lithium aluminum hydride (115 mg, 3.03 mmol). The reaction was stirred at 0 °C for 2 h. Water (115 μ L), 15% NaOH (115 μ L) and water (345 μ L) were added successively. The resulting white precipitate was filtered off and the filtrate was concentrated. The crude material was purified by flash chromatography using 15% ethyl acetate/hexanes as the eluant to afford title compound **27** as a colorless oil (631 mg, 81%): ^1H NMR (300 MHz, CDCl_3) δ 5.20 (dq, J = 2.0, 6.7 Hz, 1 H), 5.01-4.95 (m, 1 H), 3.64-3.51 (m, 2 H), 2.42-2.19 (m, 3 H), 2.05-1.95 (m, 3 H), 1.79-1.67 (m, 1 H), 1.61-1.51 (m, 2 H), 1.44-1.29 (m, 8 H), 0.89 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.3, 92.4, 91.0, 84.1, 68.5, 65.7, 41.2, 31.6, 29.8, 29.1, 28.9, 28.8, 22.6, 16.2, 14.0; IR (film) 3365, 3309, 2930, 2858, 2121, 1958, 1460, 1035 cm^{-1} .

3-(1-Heptenyl)-4-methylene-2-cyclohexenylmethanol (28). To a stirred solution of 2-(3-Butynyl)-3,4-undecadien-1-ol (**27**, 50 mg, 0.23 mmol) in 2 mL of CH_2Cl_2 was added chlorodicarbonylrhodium (I) dimer (4 mg, 0.01 mmol). The reaction was stirred at rt for 6 h. After removal of CH_2Cl_2 , the resulting crude material was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford **28-E** (27 mg, 54%) and **28-Z** (13 mg, 26%) as colorless oil.

28-E : ^1H NMR (300 MHz, CDCl_3) δ 6.11 (dt, $J = 1.2, 15.4$ Hz, 1 H), 5.86 (dt, $J = 6.8, 15.4$ Hz, 1 H), 5.80 (s, 1 H), 5.03 (s, 1 H), 4.86 (s, 1 H), 3.60 (t, $J = 5.7$ Hz, 1 H), 2.58-2.43 (m, 2 H), 2.38-2.29 (m, 1 H), 2.10 (q, $J = 6.8$ Hz, 2 H), 1.94-1.85 (m, 1 H), 1.55-1.40 (m, 4 H), 1.37-1.26 (m, 4 H), 0.90 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.4, 138.0, 132.2, 128.2, 126.9, 109.6, 66.8, 39.7, 32.9, 31.4, 31.0, 29.0, 26.2, 22.5, 14.0; IR (film) 3329, 2925, 2853, 1629, 1465, 1045 cm^{-1} ; EI-HRMS calcd for $\text{C}_{15}\text{H}_{24}\text{O}$ [M^+] m/z 220.1827, found 220.1832).

28-Z : ^1H NMR (300 MHz, CDCl_3) δ 5.98 (d, $J = 11.4$ Hz, 1 H), 5.63-5.54 (m, 2 H), 4.92 (s, 1 H), 4.81 (s, 1 H), 3.62 (t, $J = 4.8$ Hz, 2 H), 2.60-2.46 (m, 2 H), 2.41-2.30 (m, 1 H), 2.10 (qd, $J = 1.3, 6.9$ Hz, 2 H), 1.97-1.87 (m, 1 H), 1.58-1.48 (m, 1 H), 1.41-1.27 (m, 7 H), 0.88 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.4, 136.0, 133.1, 129.5, 127.5, 110.1, 69.7, 66.8, 39.5, 31.5, 30.4, 29.6, 28.4, 26.0, 22.5, 14.1; IR (film) 3329, 2925, 2853, 1465, 1045 cm^{-1} ; EI-HRMS calcd for $\text{C}_{15}\text{H}_{24}\text{O}$ [M^+] m/z 220.1827, found 220.1832.

2-(3-Butynyl)-3,4-hexadien-1-ol (29). To a stirred solution of 5-hexyn-1-carboxylic acid (1.49 g, 13.3 mmol) in dichloromethane (13 mL) were added 4-dimethylaminopyridine (163 mg, 1.33 mmol) and 3-butyn-2-ol (1.12 g, 16.0 mmol). The solution was cooled to 0 °C and 1,3-dicyclohexylcarbodiimide (3.30 g, 16.0 mmol) was added. The reaction was stirred at 0 °C for 5 min then warmed to rt and stirred for an additional 1 h. The precipitate was filtered off and the resulting filtrate was concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel column using 5% ethyl acetate/hexanes as the eluant to afford hex-5-ynoic acid 1-methyl-prop-2-ynyl ester as a yellow oil (1.77 g, 81%).

To a stirred solution of 5-hexynoic acid 1-methyl-prop-2-ynyl ester (700 mg, 4.27 mmol) in benzene (4 mL) were added triethylamine (1.20 mL, 8.54 mmol) and triisopropylsilyl trifluoromethanesulfonate (1.72 mL, 6.41 mmol). The solution was stirred at rt for 9 h. The two layers were separated and the bottom layer was extracted with benzene. The benzene layers were combined and concentrated. The crude material was purified by flash column chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford 2-(3-butynyl)-3,4-hexadienoic acid triisopropylsilyl ester (874 mg, 2.73 mmol) as a colorless oil.

2-(3-Butynyl)-3,4-hexadienoic acid triisopropylsilyl ester (874 mg, 2.73 mmol) was dissolved in ether (6 mL) and the solution was cooled to 0 °C. To this solution was added lithium aluminum hydride (75 mg, 1.98 mmol). The reaction was stirred at 0 °C for 2 h. Water (75 μL), 15% NaOH (75 μL) and water (225 μL) were added successively. The resulting white precipitate was filtered off and the filtrate was concentrated. The

crude material was purified by flash chromatography using 15% ethyl acetate/hexanes as the eluant to afford title compound **29** as a colorless oil (295 mg, 72%) : ^1H NMR (300 MHz, CDCl_3) δ 5.18-5.08 (m, 1 H), 4.98-4.87 (m, 1 H), 3.59-3.48 (m, 2 H), 2.41-2.14 (m, 3 H), 1.99 (bs, 1 H), 1.93 (t, $J = 2.7$ Hz, 1 H), 1.75-1.68 (m, 1 H), 1.65 (dd, $J = 3.2, 7.0$ Hz, 3 H), 1.56-1.44 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.1, 90.4, 86.7, 84.1, 68.4, 65.6, 41.0, 29.8, 16.0, 14.4; IR (film) 3356, 3300, 2922, 2860, 2110, 1961, 1726 cm^{-1} ; EI-HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ [M^+] m/z 150.1045, found 150.1039.

(4-Methylene-3-vinyl-cyclohex-2-enyl)-methanol (30). To a stirred solution of 2-(3-Butynyl)-3,4-hexadien-1-ol (**29**, 50 mg, 0.33 mmol) in 2 mL of CH_2Cl_2 was added chlorodicarbonylrhodium (I) dimer (6 mg, 0.02 mmol). The reaction was stirred at rt for 3 h. After removal of CH_2Cl_2 , the resulting crude material was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford 37 mg (80%) of **30** as a colorless oil : ^1H NMR (300 MHz, CDCl_3) δ 6.48 (ddt, $J = 1.0, 10.8, 17.2$ Hz, 1 H), 5.89 (s, 1 H), 5.41 (dd, $J = 1.9, 17.3$ Hz, 1 H), 5.10 (dd, $J = 1.9, 10.8$ Hz, 1 H), 5.03 (s, 1 H), 4.89 (s, 1 H), 3.61 (d, $J = 5.8$ Hz, 2 H), 2.53-2.44 (m, 2 H), 2.40-2.30 (m, 1 H), 1.95-1.86 (m, 1 H), 1.55-1.43 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.8, 138.2, 135.8, 128.1, 115.2, 109.8, 66.6, 39.6, 30.9, 26.0; IR (film) 3329, 2935, 2863, 1629, 1440, 1046 cm^{-1} ; EI-HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ [M^+] m/z 150.1045, found 150.1045.

2-(4-Trimethylsilyl-but-ynyl)-undeca-3,4-dien-1-ol (31). To a stirred solution of 2-(3-Butynyl)-3,4-undecadien-1-ol (**27**, 210 mg, 0.96 mmol) in 3 mL of THF at -78°C was added n-BuLi (2.5 M, 0.80 mL). The reaction was stirred for 10 min. Then chlorotrimethylsilane (0.37 mL, 2.9 mmol) was added. The reaction was stirred at -78°C for 50 min, then the reaction was warmed to rt and stirred for another 30 min. 10% HCl solution (3 mL) was added to the reaction solution and the mixture was stirred for 2 h at rt. The two layers were separated and the aqueous layer was extracted with ether. The organic layers were combined, dried (Na_2SO_4) and concentrated under vacuo. The resulting residue was purified by column chromatography to afford of 2-(4-trimethylsilyl-but-ynyl)-undeca-3,4-dien-1-ol (**31**) as a colorless oil (230 mg, 83%): ^1H NMR (300 MHz, CDCl_3) δ 5.192 (dq, $J = 2.0, 6.6$ Hz, 1 H), 5.03-4.93 (m, 1 H), 3.66-3.50 (m, 2 H), 2.40-2.23 (m, 3 H), 2.03-1.96 (m, 2 H), 1.72-1.52 (m, 3 H), 1.43-1.29 (m, 8 H), 0.89 (t, $J = 6.6$ Hz, 3 H), 0.14 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.4, 107.1, 92.4, 91.2, 84.8, 65.8, 41.4, 31.7, 30.2, 29.1, 29.0, 28.8, 22.6, 17.6, 14.0, 0.1; IR (film) 3338, 2960, 2923, 2167, 1956 cm^{-1} ; EI-HRMS calcd for $\text{C}_{18}\text{H}_{32}\text{OSi}$ [M^+] m/z 292.2222, found 292.2209.

(3-Hept-1-enyl-4-trimethylsilanylmethylene-cyclohex-2-enyl)-methanol (32).

To a stirred solution of 2-(4-Trimethylsilyl-but-3-ynyl)-undeca-3,4-dien-1-ol (**31**, 70 mg, 0.24 mmol) in 2 mL of 1,2-dichloroethane was added chlorodicarbonylrhodium(I) dimer

(5 mg, 0.01 mmol). The reaction was stirred at rt for 6 h. After removal of 1,2-dichloroethane, the resulting crude material was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford **32** (48 mg, 69%) as a 3:1 (determined by GC) mixture of *E* and *Z* isomers. The mixture was then subjected to HPLC to obtain **32-E** and **32-Z** in pure form.

A stirred solution of 2-(4-Trimethylsilyl-but-3-ynyl)-undeca-3,4-dien-1-ol (**31**, 55 mg, 0.19 mmol) in 2 mL of 1,2-dichloroethane was treated with chloro-1,5-cyclooctadiene iridium(I) dimer (12 mg, 0.018 mmol). Then a solution of silver tetrafluoroborate (0.05 M in 1,2-dichloroethane, 0.72 mL, 0.036 mmol) was added dropwise. The reaction was monitored by GC and stirred for 2 h at rt. The reaction solution was filter through a plug of silica gel and the resulting solution was concentrated to give **32-E** as a pale yellow oil (41 mg, 74%). The *E* to *Z* ratio was determined by GC to be greater than 99 : 1.

(32-E): ^1H NMR (300 MHz, CDCl_3) δ 6.13 (d, $J = 15.5$ Hz, 1 H), 5.82 (s, 1 H); 5.81 (dt, $J = 6.8, 15.5$ Hz, 1 H), 5.56 (s, 1 H), 2.61 (ddd, $J = 3.8, 5.8, 14.5$ Hz, 1 H), 2.55-2.47 (m, 1 H), 2.38-2.28 (m, 1 H), 2.11 (q, $J = 7.0$ Hz, 1 H), 1.96-1.87 (m, 1 H), 1.53-1.26 (m, 8 H), 0.90 (t, $J = 3.8$ Hz, 3 H), 0.1 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.6, 141.2, 132.3, 129.0, 127.1, 124.1, 66.8, 39.6, 32.9, 31.4, 30.1, 29.1, 26.3, 22.5, 14.0, 0.1; IR (film) 3389, 2916, 1665, 1244 cm^{-1} .

32-Z: ^1H NMR (300 MHz, CDCl_3) δ 5.98 (d, $J = 11.4$ Hz, 1 H); 5.61 (s, 1 H); 5.58 (dt, $J = 7.3, 11.4$ Hz, 1 H); 5.48 (s, 1 H); 3.61 (d, $J = 4.5$ Hz, 2 H); 2.63 (ddd, $J = 3.8, 6.0, 14.5$ Hz, 1 H); 2.57-2.50 (m, 1 H); 2.40-2.29 (m, 1 H); 2.08 (qd, $J = 1.5, 7.3$ Hz, 1 H); 1.99-1.90 (m, 1 H); 1.57-1.45 (m, 1 H), 0.1 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.3, 137.9, 133.0, 129.5, 128.2, 124.6, 66.8, 39.3, 31.5, 29.7, 29.5, 28.4, 26.1, 22.5, 14.1, 0.1; IR (film) 3353, 2953, 2924, 1571 cm^{-1} .