Interrupted Nazarov Reactions Using Dichlorocyclopropanes: A Novel Mode of Arene Trapping

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Supporting Information: Part 1–Experimental procedures and physical data for **5a-i, 1a-i, 4a-f, 2h, 6i, 8a-e, 10a, 11a, 12b-e** and synthetic intermediates, as well as ORTEP structures for **6i**, **12d** and **12e** (29 pages); **Part 2–**NMR spectra (99 pages) for **5a-i, 1a-i, 4a-f, 2h, 6i**, **8a-e**, **10a**, **11a**, **12b-e** and synthetic intermediates.

Part 1

General Information. Reactions were carried out in flame-dried glassware under a positive argon atmosphere unless otherwise stated. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes or cannulae. Solvents were distilled before use: methylene chloride (CH_2Cl_2) from calcium hydride, tetrahydrofuran (THF) and diethyl ether (Et_2O) from sodium/benzophenone ketyl, and toluene from sodium metal. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F_{254} (Merck). Flash chromatography columns were packed with 230-400 mesh silica gel (Silicycle) or ~150 mesh activated, neutral, Brockmann I, standard grade aluminum oxide (Sigma-Aldrich). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 400 MHz or 500 MHz and coupling constants (*J*) are reported in Hertz (Hz). Standard notation was used to describe the multiplicity of signals observed in ^{1}H NMR spectra: broad (br), apparent (app), multiplet (m), singlet (s), doublet (d), triplet (t), etc. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz or 125 MHz and are reported (ppm) relative to the center line of the triplet from chloroform-*d* (77.26 ppm). Infrared (IR) spectra were measured with a Mattson Galaxy Series FT-IR 3000 spectrophotometer. Mass spectra were determined on a PerSeptive Biosystems Mariner high-resolution electrospray positive ion mode spectrometer.

(*3E*)-2-(Triisopropylsiloxy)-6-phenyl-1,3-hexadiene, 5a.[1]

1-(Triphenylphosphoranylidene)-2-propanone (0.32 g, 1.0 mmol) was dissolved in freshly distilled THF (10 mL). Hydrocinnamaldehyde (0.13 mL, 1.0 mmol) was added dropwise to the reaction mixture at room temperature. The colorless solution was allowed to stir at room temperature for 18 h before dilution with hexanes (25 mL). The addition of hexanes precipitated a white solid, which was removed by filtration. The solvent was removed under pressure and the crude oil was purified by flash column chromatography (silica gel, hexanes:EtOAc 15:1) to yield 6-phenyl-(*3E*)-hexene-2-one (0.090 g, 0.52 mmol, 52 %) as a colorless oil: R_f 0.22 (hexanes/EtOAc 8:1); IR (thin film) 3028, 2928, 2858, 1697, 1675, 1627, 1360, 1255, 976, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) □ 7.29-7.33 (m, 2H), 7.18-7.24 (m, 3H), 6.82 (dt, *J* = 16.0, 6.8 Hz, 1H), 6.10 (dt, *J* = 16.0, 1.6 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.53-2.59 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 198.5, 147.0, 140.6, 131.7, 128.5, 128.3, 126.2, 34.4, 34.1, 26.9; HRMS (EI, M^+) for $C_{12}H_{14}O$ calcd 174.1045, found: m/z 174.1043.

6-Phenyl-(*3E*)-hexene-2-one (0.15 g, 0.86 mmol) was dissolved in anhydrous THF (3.0 mL). The solution was cooled to 0°C, and freshly distilled triethylamine (0.30 mL, 2.1 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (0.24 mL, 0.95 mmol) was added dropwise and the solution was stirred at 0°C for 2.5 h. The reaction was quenched with a mixture of triethylamine (0.5 mL), hexanes (2.5 mL), and saturated $NaHCO_3$ solution (5 mL). The organic layer was washed with H_2O (2 x 5 mL) and brine (5 mL) and dried ($MgSO_4$). The solvent was removed and the crude oil was purified by flash column chromatography (alumina, hexanes:EtOAc:TEA 50:1:1) to yield (*3E*)-2-(triisopropylsiloxy)-6-phenyl-1,3-hexadiene, **5a**, (0.25 g, 0.84 mmol, 98%) as a clear, colorless oil: R_f 0.82 (alumina, hexanes:EtOAc 8:1); IR (thin film) 3028, 2944, 2867, 1589, 1464, 1321, 1028, 883, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) □ 7.25-7.30 (m, 2H), 7.15-7.20 (m, 3H), 6.09 (dt, *J* = 15.3, 6.9 Hz, 1H), 5.90 (dt, *J* = 15.3, 1.2 Hz, 1H), 4.22 (s, 1H), 4.17 (s, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.42 (app q, *J* = 7.5 Hz, 2H), 1.16-1.27 (m, 3H), 1.10 (d, *J* = 6.6 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 155.3, 141.8, 130.5, 128.5, 128.4, 128.3, 125.8, 93.2, 35.7, 33.9, 18.1, 12.8; HRMS (EI, M^+) for $C_{21}H_{34}OSi$ calcd 330.2379, found: m/z 330.2375.

(*3E*)-2-(Triisopropylsiloxy)-6-(3-methoxy-phenyl)-1,3-hexadiene, 5b. DMSO (0.12 mL, 1.7 mmol) was added to a solution of oxalyl chloride (0.13 mL, 1.5 mmol) in CH_2Cl_2 (8 mL) at –78 ºC.[2] The reaction mixture was stirred for 10 min. before adding 3-(3-methoxyphenyl)-propanol (0.17 g, 1.0 mmol) in CH_2Cl_2 (2 mL) *via* cannula. The reaction was stirred for 15 min. before adding triethylamine (0.52 mL, 3.7 mmol) dropwise *via* syringe. The reaction was then allowed to stir for another 15 min. before transferring a solution of (triphenylphosphoranylidene)-2-propanone (0.60 g, 1.9 mmol) in CH_2Cl_2 (5 mL) to the stirring reaction mixture at –78ºC. The reaction was allowed to warm slowly to room temperature and stirred until disappearance of starting material was observed by TLC analysis (hexanes/EtOAc 2:1). The reaction was then diluted with Et_2O (15 mL). The cloudy organic layer was then washed with H_2O (2 x 25 mL) and brine (25 mL). The organic layer was dried ($MgSO_4$) and filtered. The solvent was removed and the crude oil purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 6-(3-methoxy-phenyl)-(*3E*)-hexene-2-one (0.16 g, 0.78 mmol, 78 %) as a colorless oil: R_f 0.53 (hexanes/EtOAc 2:1); IR (thin film) 3003, 2939, 2836, 1696, 1674, 1602, 1257 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.21 (t, *J* = 8.0 Hz, 1H), 6.82 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.73-6.79 (m, 3H), 6.10 (dt, *J* = 16.0, 1.5 Hz, 1H), 3.80 (s, 3H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.55 (app q, *J* = 7.0 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.5, 159.8, 147.0, 142.3, 131.7, 129.5, 120.7, 114.2, 111.4, 55.1, 34.4, 34.0, 26.9; HRMS (EI, M^+) for $C_{13}H_{16}O_2$ calcd 204.1150, found: m/z 204.1152.

6-(3-Methoxy-phenyl)-(*3E*)-hexene-2-one (0.15 g, 0.76 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.23 mL, 0.84 mmol) under the previously outlined conditions to obtain (*3E*)-2-(triisopropylsiloxy)-6-(3-methoxy-phenyl)-1,3-hexadiene, **5b**, (0.27 g, 0.76 mmol) as a clear, colorless oil: R_f 0.87 (alumina, hexanes:EtOAc 4:1); IR (thin film) 2944, 2867, 1586, 1490, 1464, 1320, 1260, 1152, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.19 (td, *J* = 7.5, 1.0 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.72-6.74 (m, 2H), 6.09 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.91 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.22 (s, 1H), 4.17 (s, 1H), 3.80 (s, 3H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.43 (app qd, *J* = 7.5, 1.0 Hz, 2H), 1.19-1.26 (m, 3H), 1.10 (d, *J* = 7.5 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) 159.6, 155.2, 143.4, 130.5, 129.2, 128.4, 120.9, 114.2, 111.2, 83.2, 55.1, 35.7, 33.8, 18.1, 12.8; HRMS (EI, M^+) for $C_{22}H_{36}O_2Si$ calcd 360.2485, found: m/z 360.2482.

(*3E*)-2-(Triisopropylsiloxy)-6-(4-methoxy-phenyl)-1,3-hexadiene, 5c. The previously outlined procedure was used in the synthesis of **5c** starting with 3-(4-methoxyphenyl)-propanol (0.18 g, 1.1 mmol). The reaction was diluted with Et_2O (15 mL) after 48 h. stirring at room temperature. The crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 6-(4-methoxy-phenyl)-(*3E*)-hexene-2-one (0.12 g, 0.61 mmol, 56 %) as a colorless oil: R_f 0.44 (hexanes/EtOAc 2:1); IR (thin film) 3004, 2934, 2836, 1674, 1626, 1513, 1361, 1248, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.81 (dt, J = 16.0, 7.0 Hz, 1H), 6.09 (dt, J = 16.0, 1.5 Hz, 1H), 3.80 (s, 3H), 2.74 (t, J = 7.5 Hz, 2H), 2.52 (app q, J = 7.0 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 158.0, 147.2, 132.7, 131.7, 129.2, 113.9, 55.2, 34.4, 33.5, 26.8; HRMS (EI, M^+) for $C_{13}H_{16}O_2$ calcd 204.1150, found: m/z 204.1150.

6-(4-Methoxy-phenyl)-(*3E*)-hexene-2-one (0.20 g, 1.0 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.30 mL, 1.1 mmol) under the previously outlined conditions to obtain (*3E*)-2-(triisopropylsiloxy)-6-(4-methoxy-phenyl)-1,3-hexadiene, **5c**, (0.36 g, 1.0 mmol) as a clear, colorless oil: R_f 0.78 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2944, 2867, 1588, 1513, 1464, 1320, 1247, 1029 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (app d, J = 8.5 Hz, 2H), 6.82 (app d, J = 8.5 Hz, 2H), 6.08 (dt, J = 15.0, 7.0 Hz, 1H), 5.89 (dt, J = 15.0, 1.0 Hz, 1H), 4.22 (s, 1H), 4.16 (s, 1H), 3.79 (s, 3H), 2.67 (t, J = 7.5 Hz, 2H), 2.39 (app q, J = 7.5 Hz, 2H), 1.18-1.28 (m, 3H), 1.10 (d, J = 7.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ158.0, 155.6, 134.2, 130.9, 129.6, 128.6, 114.0, 93.4, 55.5, 35.0, 34.4, 18.3, 13.1; HRMS (EI, M^+) for $C_{22}H_{36}O_2Si$ calcd 360.2485, found: m/z 360.2486.

(*3E*)-2-(Triisopropylsiloxy)-6-(2-methylphenyl)-1,3-hexadiene, 5d. The previously outlined procedure was used in the synthesis of **5d** starting with 3-(2-methylphenyl)-propanol (0.15 g, 1.0 mmol). The crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 6-(2-methyl-phenyl)-(*3E*)-hexene-2-one (0.14 g, 0.72 mmol, 72 %) as a colorless oil: R_f 0.55 (hexanes/EtOAc 2:1); IR (thin film) 3016, 2940, 1675, 1626, 1361, 1254, 976, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.11-7.17 (m, 4H), 6.86 (dt, J = 16.5, 6.5 Hz, 1H), 6.12 (dt, J = 16.0, 1.5 Hz, 1H), 2.78 (t, J = 7.5 Hz, 2H), 2.52 (app q, J = 6.5 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5,

147.2, 138.8, 135.8, 131.6, 130.3, 128.6, 126.4, 126.1, 32.9, 31.8, 26.9, 19.3; HRMS (EI, M^+) for $C_{13}H_{16}O$ calcd 188.1201, found: m/z 188.1201.

6-(2-Methyl-phenyl)-(*3E*)-hexene-2-one (0.16 g, 0.85 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.25 mL, 0.94 mmol) under the previously outlined conditions to obtain (*3E*)-2-(triisopropylsiloxy)-6-(2-methyl-phenyl)-1,3-hexadiene, **5d**, (0.29 g, 0.85 mmol, 100 %) as a clear, colorless oil: R_f 0.93 (alumina, hexanes:EtOAc 4:1); IR (thin film) 2945, 2867, 1589, 1463, 1321, 1027, 883, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.11-7.16 (m, 4H), 6.14 (dt, *J* = 15.0, 7.0 Hz, 1H), 5.93 (d, *J* = 15.5 Hz, 1H), 4.24 (s, 1H), 4.19 (s, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.40 (app q, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.22-1.30 (m, 3H), 1.12 (d, *J* = 7.5 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 155.3, 139.9, 135.8, 130.6, 130.1, 128.9, 128.4, 125.9, 125.9, 93.1, 32.9, 32.7, 19.3, 18.1, 12.8; HRMS (EI, M^+) for $C_{22}H_{36}OSi$ calcd 344.2535, found: m/z 344.2530.

(*3E*)-2-(Triisopropylsiloxy)-6-(2-bromophenyl)-1,3-hexadiene, 5e. The previously outlined procedure was used in the synthesis of **5e** starting with 3-(2-bromophenyl)-propanol (0.21 g, 1.0 mmol). The crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 5:1) to yield 6-(2-bromophenyl)-(*3E*)-hexene-2-one (0.18 g, 0.70 mmol, 70 %) as a colorless oil: R_f 0.46 (hexanes/EtOAc 2:1); IR (thin film) 3010, 2931, 2862, 1674, 1626, 1471, 1360, 1254, 1023, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.56 (d, *J* = 8.0 Hz, 1H), 7.25 (app t, *J* = 7.0 Hz, 1H), 7.20 (app d, *J* = 8.0 Hz, 1H), 7.09 (app t, *J* = 7.5 Hz, 1H), 6.84 (dt, *J* = 16.0, 6.5 Hz, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.56 (app q, *J* = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 198.5, 146.5, 139.9, 132.9, 131.9, 130.3, 128.0, 127.6, 124.3, 34.7, 32.6, 26.9; HRMS (EI, M^+) for $C_{12}H_{13}OBr$ calcd 252.0150, found: m/z 252.0143.

6-(2-Bromophenyl)-(*3E*)-hexene-2-one (0.42 g, 1.7 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.45 mL, 1.7 mmol) under the previously outlined conditions to yield (*3E*)-2-(triisopropylsiloxy)-6-(2-bromophenyl)-1,3-hexadiene, **5e**, (0.57 g, 1.4 mmol, 83 %) as a clear, colorless oil: R_f 0.79 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2944, 2866, 1589, 1470, 1321, 1025, 883, 748, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) □ 7.53 (app d, *J* = 8.0 Hz, 1H), 7.20-7.22 (m, 2H), 7.03-7.07 (m, 1H), 6.10 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.91 (dt, *J* = 15.2, 1.2 Hz, 1H), 4.23 (s, 1H), 4.18 (s, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.43 (app

qd, *J* = 8.0, 1.2 Hz), 1.19-1.29 (m, 3H), 1.11 (d, *J* = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 155.1, 140.8, 132.7, 130.4, 129.8, 128.6, 127.4, 127.2, 124.3, 93.2, 35.8, 32.0, 18.0, 12.7; HRMS (EI, M^+) for $C_{21}H_{33}OSiBr$ calcd 408,1484, found: m/z 408,1494.

(*3E*)-2-(Triisopropylsiloxy)-6-(4-triisopropylsiloxyphenyl)-1,3-hexadiene, 5f. The previously outlined procedure was used in the synthesis of **5f** starting with 3-(4-hydroxyphenyl)-propanol (0.30 g, 2.0 mmol). The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 5:1) to yield 6-(4-hydroxyphenyl)-(*3E*)-hexene-2-one (0.095 g, 0.50 mmol, 25 %) as a colorless oil: R_f 0.28 (hexanes/EtOAc 2:1); IR (thin film) 3347, 3020, 2924, 2855, 1665, 1614, 1515, 1447, 1363, 1365, 1227, 974, 832 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) □ 7.04 (app d, *J* = 8.5 Hz, 2H), 6.83 (dt, *J* = 16.0, 6.5 Hz, 1H), 6.78 (app d, *J* = 8.5 Hz, 2H), 6.10 (d, *J* = 16.5 Hz, 1H), 5.45 (br s, 1H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.51 (app q, *J* = 7.5 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 199.0, 154.1, 147.5, 132.6, 131.6, 129.4, 115.4, 34.4, 33.5, 26.9; HRMS (EI, M^+) for $C_{12}H_{14}O_2$ calcd 190.0994, found: m/z 190.0994.

6-(4-Hydroxyphenyl)-(*3E*)-hexene-2-one (0.089 g, 0.47 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.25 mL, 0.94 mmol) under the previously outlined conditions to obtain (*3E*)-2-(triisopropylsiloxy)-6-(4-triisopropylsiloxyphenyl)-1,3-hexadiene, **5f**, (0.15 g, 0.31 mmol, 66 %) as a clear, colorless oil: R_f 0.86 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2944, 2867, 1510, 1464, 1263, 1028, 917, 883 685 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) □ 7.01 (app d, *J* = 8.5 Hz, 2H), 6.78 (app d, *J* = 8.5 Hz, 2H), 6.09 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.86 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.21 (s, 1H), 4.15 (s, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.38 (app q, *J* = 8.0 Hz, 2H), 1.18-1.28 (m, 6H), 1.10 (d, *J* = 7.0 Hz, 18H), 1.09 (d, *J* = 7.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 155.3, 154.0, 134.1, 130.6, 129.2, 128.4, 119.6, 93.1, 34.9, 34.2, 18.1, 17.9, 12.8, 12.7; HRMS (EI, M^+) for $C_{30}H_{54}O_2Si_2$ calcd 502.3662, found: m/z 502.3669.

(*3E*)-2-(Triisopropylsiloxy)-6-(2-furyl)-1,3-hexadiene, 5g. The previously outlined procedure was used in the synthesis of **5g** starting with 3-(2-furyl)-propanol (0.13 g, 1.0 mmol). The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 6-(2-furyl)-(*3E*)-hexene-2-one (0.075 g, 0.46 mmol, 46 %) as a

colorless oil: R_f 0.48 (hexanes/EtOAc 2:1); IR (thin film) 2919, 1734, 1675, 1627, 1361, 1255, 1010, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 2.0 Hz, 1H), 6.81 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.29 (dd, *J* = 3.5, 2.0 Hz, 1H), 6.11 (dt, *J* = 16.5, 1.5 Hz, 1H), 6.02 (d, *J* = 3.0 Hz, 1H), 2.82 (t, *J* = 7.0 Hz, 2H), 2.59 (app q, *J* = 7.0 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 154.1, 146.3, 141.1, 131.7, 110.1, 105.4, 30.7, 26.8, 26.5; HRMS (EI, M^+) for $C_{10}H_{12}O_2$ calcd 164.0837, found: m/z 164.0838.

6-(2-Furyl)-(*3E*)-hexene-2-one 0.36 g, 2.2 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.59 mL, 2.2 mmol) under the previously outlined conditions to obtain (*3E*)-2-(triisopropylsiloxy)-6-(2-furyl)-1,3-hexadiene, **5g**, (0.62 g, 1.9 mmol, 88 %) as a pale yellow oil: R_f 0.80 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2944, 2867, 1591, 1464, 1321, 1027, 883, 727, 684 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 1.5, 0.5 Hz, 1H), 6.27 (dd, *J* = 3.5, 2.0 Hz, 1H), 6.09 (dt, *J* = 15.0, 7.0 Hz, 1H), 5.99 (dd, *J* = 2.0, 1.0 Hz, 1H), 5.91 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.23 (s, 1H), 4.18 (s, 1H), 2.74 (t, *J* = 7.0 Hz, 2H), 2.45 (app q, *J* = 6.5 Hz, 2H), 1.19-1.27 (m, 3H), 1.10 (d, *J* = 7.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 155.2, 140.8, 130.0, 128.7, 110.0, 105.0, 93.4, 30.5, 27.8, 18.0, 12.8; HRMS (EI, M^+) for $C_{19}H_{32}O_2Si$ calcd 320.2172, found: m/z 320.2174.

(*3E*)-3-Methyl-6-phenyl-2-(triisopropylsiloxy)-1,3-hexadiene, 5h.

(Carbethoxyethylidene)triphenylphosphorane (0.72 g, 2.0 mmol) was added to a solution of hydrocinnamaldehyde (0.26 mL, 2.0 mmol) in CH_2Cl_2 (7 mL) at room temperature. After 18 h. stirring, the reaction was diluted with Et_2O (15 mL). The organic layer was washed with H_2O (2 x 15 mL) and brine (15 mL) and dried ($MgSO_4$). After filtration and evaporation of solvent under reduced pressure, the crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 8:1) to yield ethyl 2-methyl-5-phenyl-2*E*-pentenoate (0.30 g, 1.4 mmol, 69 %) as a colorless oil: R_f 0.64 (hexanes/EtOAc 2:1); IR (thin film) 2981, 2930, 1709, 1650, 1266, 1116, 1081, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.32 (m, 2H), 7.17-7.23 (m, 3H), 6.81 (tq, *J* = 7.2, 1.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.49 (app q, *J* = 7.5 Hz, 2H), 1.79 (dt, *J* = 1.2, 1.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 141.1, 140.8, 128.3, 128.2 (2 C), 126.0, 60.3, 34.6, 30.5, 14.2, 12.2; HRMS (EI, M^+) for $C_{14}H_{18}O_2$ calcd 218.1307, found: m/z 218.1306.

N,*O*-Dimethylhydroxylamine hydrochloride (1.18 g, 12.1 mmol) was dissolved in CH_2Cl_2 (50 mL) and the temperature lowered to 0ºC. Dimethylaluminum chloride (12.10 mL, 12.1 mmol) was then added to the reaction mixture dropwise *via* syringe. The reaction mixture was stirred for 1 h. during which it was slowly allowed to warm to room temperature. A solution of ethyl 2-methyl-5-phenyl-*2E*-pentenoate (0.29 g, 1.3 mmol) in CH_2Cl_2 (50 mL) was then added to the reaction flask dropwise *via* cannula. The reaction was allowed to stir at room temperature for 48 h. before being quenched by the addition of H_2O (50 mL). The aqueous and organic layers were separated after 10 min. of vigorous stirring. The aqueous layer was extracted with Et_2O (2 x 25 mL) and the combined organic layers were then washed with brine (50 mL). The organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation to yield an orange oil.

The crude material was subsequently re-dissolved in Et_2O (14 mL) and the solution was cooled to –78ºC. MeLi (1.6M in Et_2O, 2.0 mmol, 1.3 mL) was added dropwise *via* syringe, during which the reaction mixture changed color from pale orange to dark red. The reaction was quenched at –78ºC after stirring for 45 min. Aqueous HCl (1.0M, 10 mL) was added dropwise and the aqueous and organic layers were subsequently separated. The aqueous layer was extracted with Et_2O (2 x 15 mL) and the combined organic layers washed with brine (15 mL). The organic layer was dried ($MgSO_4$), filtered, and the solvent removed by rotary evaporation to yield a pale yellow oil. The crude material was purified by gradient column chromatography (hexanes/EtOAc 10:1, 9:1, 7:1, 5:1, 3:1) to provide 3-methyl-6-phenyl-*3E*-hexen-2-one (0.17 g, 0.90 mmol, 68 %) as a clear, colorless oil: R_f 0.60 (hexanes/EtOAc 2:1); IR (thin film) 3027, 2927, 2859, 1668, 1642, 1367, 1277, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) □ 7.31 (app t, *J* = 7.5 Hz, 2H), 7.19-7.23 (m, 3H), 6.65 (tq, *J* = 7.5, 1.5 Hz, 1H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.57 (app q, *J* = 7.5 Hz, 2H), 2.28 (s, 3H), 1.73 (d, *J* = 0.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 199.8, 142.2, 141.0, 138.2, 128.5, 128.3, 126.2, 34.7, 30.9, 30.3, 25.4; HRMS (EI, M^+) for $C_{13}H_{16}O$ calcd 188.1201, found: m/z 188.1202.

3-Methyl-6-phenyl-*3E*-hexen-2-one (0.14 g, 0.73 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.20 mL, 0.73 mmol) under the previously outlined conditions to yield (*3E*)-3-methyl-6-phenyl-2-(triisopropylsiloxy)-1,3-hexadiene, **5h**, (0.57 g, 1.4 mmol, 83 %) as a clear, colorless oil: R_f 0.79 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2945, 2867, 1590, 1463, 1299, 1021, 883, 697 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$) δ 7.25-7.29 (m, 2H), 7.16-7.21 (m, 3H), 6.13 (app t, *J* = 7.2 Hz, 1H), 4.36 (d, *J* = 0.8 Hz, 1H), 4.24 (d, *J* = 0.8 Hz, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.47 (app q, *J* = 7.6 Hz, 2H), 1.72 (s, 3H), 1.17-1.27 (m, 3H), 1.09 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 141.9, 131.5, 128.4, 128.3, 127.3, 125.7, 90.0, 35.7, 30.1, 18.1, 13.3, 12.8; HRMS (EI, M^+) for $C_{22}H_{36}OSi$ calcd 344.2535, found: m/z 344.2528.

(*3E*)-3-Methyl-6-(3-methoxyphenyl)-2-(triisopropylsiloxy)-1,3-hexadiene, 5i. DMSO (0.36 mL, 5.2 mmol) was added to a solution of oxalyl chloride (0.39 mL, 4.5 mmol) in CH_2Cl_2 (24 mL) at –78 ºC.[2] The reaction mixture was stirred for 10 min. before adding 3-(3-methoxyphenyl)-propanol (0.46 g, 2.8 mmol) in CH_2Cl_2 (6 mL) *via* cannula. The reaction was stirred for 15 min. before the addition of triethylamine (1.5 mL, 11.1 mmol) dropwise *via* syringe. The reaction was then allowed to stir for another 15 min. before transferring a solution of (carbethoxyethylidene)triphenylphosphorane (1.5 g, 4.2 mmol) in CH_2Cl_2 (15 mL) to the stirring reaction mixture at –78ºC. The reaction was slowly allowed to warm to room temperature and stirred until the disappearance of starting material was observed by TLC analysis (hexanes/EtOAc 2:1). The reaction was then diluted with Et_2O (15 mL). The cloudy organic layer was then washed with H_2O (2 x 25 mL) and brine (25 mL). The organic layer was dried ($MgSO_4$) and filtered. The solvent was removed and the crude oil purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield ethyl 2-methyl-5-(3-methoxyphenyl)-*2E*-pentenoate (0.33 g, 1.3 mmol, 48 %) as a colorless oil: R_f 0.56 (hexanes/EtOAc 2:1); IR (thin film) 2981, 2938, 1710, 1650, 1602, 1489, 1264, 1153, 1114, 1080, 1051 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (app dt, *J* = 7.5, 1.0 Hz, 1H), 6.76-6.82 (m, 3H), 6.75 (s, 1H), 4.19 (q, *J* = 7.5 Hz, 2H), 3.80 (s, 3H), 2.73 (t, *J* = 8.5 Hz, 2H), 2.49 (app q, *J* = 8.0 Hz, 2H), 1.80 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 159.7, 142.9, 140.8, 129.4, 128.5, 120.7, 114.1, 111.4, 60.4, 55.1, 34.8, 30.5, 14.3, 12.3; HRMS (EI, M^+) for $C_{15}H_{20}O_3$ calcd 248.1412, found: m/z 248.1409.

N,*O*-Dimethylhydroxylamine hydrochloride (0.16 g, 1.6 mmol) was dissolved in CH_2Cl_2 (20 mL) and the temperature lowered to 0ºC. Dimethylaluminum chloride (1.6 mL, 1.6 mmol) was then added to the reaction mixture dropwise *via* syringe. The reaction mixture was stirred for 1 h. during which it was slowly warmed to room temperature. A solution of ethyl 2-methyl-5-(3-methoxyphenyl)-*2E*-pentenoate (0.08 g, 0.32 mmol) in

CH_2Cl_2 (12 mL) was then added to the reaction flask dropwise *via* cannula. The reaction was allowed to stir at room temperature for 48 h. before being quenched by the addition of H_2O (50 mL). The aqueous and organic layers were separated after 10 min. of vigorous stirring. The aqueous layer was extracted with Et_2O (2 x 25 mL) and the combined organic layers were then washed with brine (50 mL). The organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation to yield a yellow oil.

The crude material was subsequently re-dissolved in Et_2O (5 mL) and the temperature dropped to –78ºC. MeLi (1.6M in Et_2O, 0.25 mL, 0.4 mmol) was added dropwise *via* syringe. The reaction was quenched after 2 h. stirring at low temperature by the addition of HCl aq. (1.0M, 10 mL). The aqueous and organic layers were subsequently separated, and the aqueous layer extracted with Et_2O (2 x 15 mL). The combined organic layers were then washed with brine (15 mL). The organic layer was dried ($MgSO_4$), filtered, and the solvent removed by rotary evaporation to yield a pale yellow oil. The crude material was purified by flash column chromatography (hexanes/EtOAc 10:1) to isolate 3-methyl-6-(3-methoxyphenyl)-*3E*-hexen-2-one (0.038 g, 0.17 mmol, 54 %) as a clear, colorless oil: R_f 0.53 (hexanes/EtOAc 2:1); IR (thin film) 3000, 2928, 1668, 1642, 1602, 1489, 1265, 1152, 1051, 780, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.22 (app td, J = 7.6, 0.4 Hz, 1H), 6.77-6.75-6.81 (m, 3H), 6.64 (tq, J = 6.8, 1.2 Hz, 1H), 3.81 (s, 3H), 2.77 (t, J = 7.6 Hz, 2H), 2.57 (app q, J = 8.0 Hz, 2H), 2.29 (s, 3H), 1.74 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 199.6, 159.6, 142.5, 142.1, 138.0, 129.4, 120.6, 114.1, 111.2, 55.0, 34.6, 30.6, 25.3, 11.0; HRMS (EI, M^+) for $C_{14}H_{18}O_2$ calcd 218.1307, found: m/z 218.1308.

3-Methyl-6-(3-methoxyphenyl)-*3E*-hexen-2-one (0.11 g, 0.49 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.13 mL, 0.49 mmol) under the previously outlined conditions to yield (*3E*)-3-methyl-6-(3-methoxyphenyl)-2-(triisopropylsiloxy)-1,3-hexadiene, **5i** (0.15 g, 0.40 mmol, 81 %) as a clear, colorless oil: R_f 0.79 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2945, 2867, 1586, 1464, 1299, 1260, 1152, 1021, 883, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.19 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.72-6.76 (m, 2H), 6.13 (t, J = 7.2 Hz, 1H), 4.37 (s, 1H), 4.24 (s, 1H), 3.80 (s, 3H), 2.69 (t, J = 8.0 Hz, 2H), 2.47 (app q, J = 7.6 Hz, 2H), 1.74 (d, J = 0.8 Hz, 3H), 1.17-1.26 (m, 3H), 1.09 (d, J = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) 159.5, 157.4, 143.5, 131.3, 129.1, 127.1,

120.8, 114.1, 111.0, 89.9, 55.0, 35.6, 29.9, 18.0, 13.2, 12.7; HRMS (EI, M^+) for $C_{23}H_{38}O_2Si$ calcd 374.2641, found: m/z 374.2644.

(*1E*)-1,1-Dichloro-2-(4-phenyl-1-butenyl)-2-triisopropylsilyloxycyclopropane, 1a.[1] Siloxy diene **5a** (0.29 g, 0.87 mmol) was dissolved in $CHCl_3$ (0.087 mol, 7.0 mL). The $CHCl_3$ does not need to be freshly distilled or pre-dried for this reaction. Benzyltriethylammonium chloride (0.059 g, 0.26 mmol) was added to the reaction mixture. A solution of 50 % aq. NaOH (0.16 mol, 6.5 mL) was then added in one portion and the reaction was vigorously stirred at room temperature for 30 min. The reaction was then diluted with H_2O (20 mL) and CH_2Cl_2 (20 mL) at 0ºC. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were then washed with H_2O (2 x 20 mL) and dried ($MgSO_4$). After filtration, the solvent was removed and the crude oil purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield (*1E*)-1,1-dichloro-2-(4-phenyl-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.31 g, 0.76 mmol, 87 %) as a colorless oil: R_f 0.70 (hexanes/EtOAc 20:1); IR (thin film) 3027, 2944, 2867, 1463, 1222, 1083, 883, 697, 683 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.27-7.30 (m, 2H), 7.17-7.21 (m, 3H), 5.82 (d, *J* = 15.5 Hz, 1H), 5.75 (dt, *J* = 15.0, 6.5 Hz, 1H), 2.73 (t, *J* = 9.0 Hz, 2H), 1.46 (app q, *J* = 7.0 Hz, 2H), 1.81 (d, *J* = 8.5 Hz, 1H), 1.61 (d, *J* = 8.5 Hz, 1H), 1.04-1.10 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 141.6, 134.3, 128.7, 128.6, 128.3, 126.2, 65.7, 64.2, 35.4, 33.9, 32.5, 18.3, 18.2, 13.0; HRMS (EI, $[M-Cl]^+$) for $C_{22}H_{34}OSiCl$ calcd 377.2068, found: m/z 377.2066.

(*1E*)-1,1-Dichloro-2-(4-(3-methoxyphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane, 1b. The same method was employed in the synthesis of **1b** starting with siloxy diene **5b** (0.26 g, 0.73 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 30 min. and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield (*1E*)-1,1-dichloro-2-(4-(3-methoxyphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.24 g, 0.54 mmol, 75 %) as a clear, colorless oil: R_f 0.40 (hexanes/EtOAc 50:1); IR (thin film) 2945, 2867, 1602, 1585, 1465, 1261, 1083, 883, 772, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.20 (t, *J* = 8.0 Hz, 1H), 6.73-6.79 (m, 3H), 5.82 (d, *J* = 15.5 Hz, 1H), 5.74 (dt, *J* = 15.5, 6.5 Hz, 1H), 3.80 (s, 3H), 2.70 (t, *J* = 8.5

Hz, 2H), 2.46 (app q, *J* = 7.5 Hz, 2H), 1.82 (d, *J* = 8.5 Hz, 1H), 1.62 (dd, *J* = 8.0, 1.0 Hz, 1H), 1.04-1.12 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) 159.7, 142.9, 134.0, 129.3, 128.1, 120.7, 114.2, 111.2, 65.4, 64.0, 55.1, 35.2, 33.5, 32.2, 18.0, 17.9, 12.8; HRMS (ESI, $[M+H]^+$) for $C_{23}H_{37}O_2SiCl_2$ calcd 443.1934, found: m/z 443.1937.

(*1E*)-1,1-Dichloro-2-(4-(4-methoxyphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane, 1c. The same method was employed in the synthesis of **1c** starting with siloxy diene **5c** (0.36 g, 1.0 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 20 min. and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 20:1) to yield (*1E*)-1,1-dichloro-2-(4-(4-methoxyphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.39 g, 0.88 mmol, 88 %) as a clear, colorless oil: R_f 0.26 (hexanes/EtOAc 50:1); IR (thin film) 2945, 2867, 1613, 1513, 1464, 1247, 1040, 883 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.09 (app d, *J* = 8.4 Hz, 2H), 6.83 (app d, *J* = 8.4 Hz, 2H), 5.81 (dd, *J* = 15.2, 0.8 Hz, 1H), 5.74 (dt, *J* = 15.2, 6.4 Hz, 1H), 3.79 (s, 3H), 2.67 (t, *J* = 6.8 Hz, 2H), 2.42 (app q, *J* = 6.4 Hz, 2H), 1.81 (d, *J* = 8.4 Hz, 1H), 1.62 (dd, *J* = 8.4, 0.8 Hz, 1H), 1.03-1.12 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) 157.9, 134.2, 133.4, 129.2, 127.9, 113.8, 64.0, 65.9, 55.2, 34.3, 33.9, 32.2, 18.0, 17.9, 12.8; HRMS (EI, M^+) for $C_{23}H_{36}O_2SiCl_2$ calcd 442.1862, found: m/z 442.1872.

(*1E*)-1,1-Dichloro-2-(4-(2-methylphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane, 1d. The same method was employed in the synthesis of **1d** starting with siloxy diene **5d** (0.29 g, 0.85 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 30 min. and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 20:1) to yield (*1E*)-1,1-dichloro-2-(4-(2-methylphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.19 g, 0.45 mmol, 53 %) as a clear, colorless oil: R_f 0.67 (hexanes/EtOAc 50:1); IR (thin film) 2945, 2967, 1463, 1222, 1083, 883, 683 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.10-7.18 (m, 4H), 5.86 (dd, *J* = 15.5, 0.5 Hz, 1H), 5.80 (dt, *J* = 15.5, 6.0 Hz, 1H), 2.71 (br t, *J* = 7.5 Hz, 2H), 2.42 (app q, *J* = 6.5 Hz, 2H), 2.31 (s, 3H), 1.85 (d, *J* = 8.0 Hz, 1H), 1.64 (dd, *J* = 8.0, 1.0 Hz, 1H), 1.06-1.14 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) 139.5, 135.8, 134.3, 130.2, 128.6, 127.9, 126.1, 126.0, 65.4, 64.0, 32.5, 32.4, 32.2,

19.2, 18.0, 18.0, 12.8; HRMS (ESI, $[M+H]^+$) for $C_{23}H_{37}OSiCl_2$ calcd, 427.1985 found: m/z 427.1986.

(*1E*)-1,1-Dichloro-2-(4-(2-bromophenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane, 1e. The same method was employed in the synthesis of **1e** starting with siloxy diene **5e** (0.57 g, 1.4 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 45 min. and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 20:1) to yield (*1E*)-1,1-dichloro-2-(4-(2-bromophenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.49 g, 1.0 mmol, 72 %) as a clear, colorless oil: R_f 0.48 (hexanes/EtOAc 50:1); IR (thin film) 2944, 2866, 1470, 1221, 1083, 1024, 882, 749, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.18-7.24 (m, 2H), 7.04-7.08 (m, 1H), 5.85 (dd, *J* = 15.5, 1.0 Hz, 1H), 5.77 (dt, *J* = 15.5, 6.5 Hz, 1H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.46 (app q, *J* = 6.5 Hz, 2H), 1.84 (d, *J* = 8.5 Hz, 1H), 1.63 (dd, *J* = 8.0, 0.5 Hz, 1H), 1.05-1.12 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) 140.5, 133.7, 132.9, 130.2, 128.3, 127.7, 127.4, 124.4, 65.4, 64.0, 35.4, 32.2, 32.1, 18.0, 18.0, 12.8; HRMS (ESI, $[M+Na]^+$) for $C_{22}H_{33}OSiBrCl_2Na$ calcd 513.0753, found: m/z 513.0754.

(*1E*)-1,1-Dichloro-2-(4-(4-triisopropylsiloxyphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane, 1f. The same method was employed in the synthesis of **1f** starting with siloxy diene **5f** (0.15 g, 0.31 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 40 min. and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 20:1) to yield (*1 E*)-1,1-dichloro-2-(4-(4-triisopropylsiloxyphenyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.14 g, 0.24 mmol, 77 %) as a clear, colorless oil: R_f 0.40 (hexanes/EtOAc 50:1); IR (thin film) 3029, 2945, 2867, 1609, 1510, 1463, 1264, 1083, 917, 883, 684 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.01 (app d, *J* = 8.0 Hz, 2H), 6.79 (app d, *J* = 8.0 Hz, 2H), 5.81 (dd, *J* = 15.5, 0.5 Hz, 1H), 5.73 (dt, *J* = 15.5, 6.5 Hz, 1H), 2.60-2.69 (m, 2H), 2.41 (app q, *J* = 7.0 Hz, 2H), 1.80 (d, *J* = 8.5 Hz, 1H), 1.61 (dd, *J* = 8.5, 0.5 Hz, 1H), 1.21-1.30 (m, 3H), 1.10 (d, *J* = 7.5 Hz, 18H), 1.04-1.07 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.2, 134.3, 133.6, 129.1, 127.8, 119.7, 64.0, 34.4, 33.9, 32.2, 18.0, 18.0, 17.9, 12.8, 12.7; HRMS (ESI, $[M+H]^+$) for $C_{31}H_{55}O_2Si_2Cl_2$ calcd 585.3112, found: m/z 585.3112.

(*1E*)-1,1-Dichloro-2-(4-(2-furyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane, 1g. The same method was employed in the synthesis of **1g** starting with siloxy diene **5g** (0.084 g, 0.26 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 7 min. and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 20:1) to yield (*1E*)-1,1-dichloro-2-(4-(2-furyl)-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.10 g, 0.25 mmol, 95 %) as a clear, yellow oil: R_f 0.53 (hexanes/EtOAc 50:1); IR (thin film) 2945, 2867, 1669, 1597, 1464, 1223, 1083, 883, 729, 683 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.29-7.30 (m, 1H), 6.27 (dd, *J* = 2.0, 3.5 Hz, 1H), 5.99 (dd, *J* = 3.0, 0.5 Hz, 1H), 5.82 (dd, *J* = 16.0, 1.0 Hz, 1H), 5.75 (dt, *J* = 15.5, 6.5 Hz, 1H), 2.69-2.79 (m, 2H), 2.48 (app q, *J* = 7.0 Hz, 2H), 1.81 (d, *J* = 8.5 Hz, 1H), 1.63 (dd, *J* = 8.5, 1.0 Hz, 1H), 1.02-1.15 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) 155.0, 140.9, 133.5, 128.4, 110.1, 105.1, 63.9, 32.3, 30.4, 27.4, 18.0, 18.0, 12.8; HRMS (ESI, $[M+H]^+$) for $C_{20}H_{33}O_2SiCl_2$ calcd 403.1621, found: m/z 403.1621.

(*2E*)-1,1-Dichloro-2-(5-phenyl-2-penten-2-yl)-2-triisopropylsilyloxycyclopropane, 1h. The same method was employed in the synthesis of **1h** starting with siloxy diene **5h** (0.24 g, 0.69 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 45 min. and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield (*2E*)-1,1-dichloro-2-(5-phenyl-2-penten-2-yl)-2-triisopropylsilyloxycyclopropane (0.27 g, 0.63 mmol, 91 %) as a clear, colorless oil: R_f 0.68 (hexanes/EtOAc 50:1); IR (thin film) 2945, 2868, 1464, 1256, 1087, 1071, 884, 686 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.26-7.29 (m, 2H), 7.17-7.20 (m, 3H), 5.47 (tq, *J* = 7.0, 1.0 Hz, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.36-2.43 (m, 2H), 1.92 (d, *J* = 8.5 Hz, 1H), 1.87 (d, *J* = 1.0 Hz, 3H), 1.62 (d, *J* = 8.5 Hz, 1H), 1.04-1-14 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) 141.6, 133.6, 129.3, 128.3, 128.3, 125.9, 68.2, 64.7, 35.0, 31.7, 29.3, 18.0, 17.9, 14.4, 12.7; HRMS (ESI, $[M+Na]^+$) for $C_{23}H_{36}OSiCl_2Na$ calcd 449.1805, found: m/z 449.1799.

(*2E*)-1,1-Dichloro-2-(5-(3-methoxyphenyl)-2-penten-2-yl)-2-triisopropylsilyloxycyclopropane, 1i. The same method was employed in the synthesis of **1i** starting with siloxy diene **5i** (0.13 g, 0.34 mmol). The reaction mixture was diluted with H_2O/CH_2Cl_2 after 1.5 h. and the crude material purified by flash column chromatography

(silica gel, hexanes:EtOAc 20:1) to yield (*2E*)-1,1-dichloro-2-(5-(3-methoxyphenyl)-2-penten-2-yl)-2-triisopropylsilyloxycyclopropane (0.14 g, 0.30 mmol, 88 %) as a clear, colorless oil: R_f 0.56 (hexanes/EtOAc 50:1); IR (thin film) 2945, 2867, 1602, 1585, 1464, 1257, 1084, 1046, 883, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 6.74-6.78 (m, 2H), 6.73 (s, 1H), 5.47 (tq, *J* = 7.0, 1.0 Hz, 1H), 3.80 (s, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.36-2.42 (m, 2H), 1.92 (d, *J* = 8.5 Hz, 1H), 1.88 (s, 3H), 1.63 (d, *J* = 8.5 Hz, 1H), 1.04-1.14 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 159.7, 143.2, 133.6, 129.3 (2 C), 120.7, 114.2, 111.1, 68.2, 64.7, 55.1, 35.1, 31.7, 29.2, 18.0, 17.9, 14.4, 12.7; HRMS (ESI, $[M+Na]^+$) for $C_{24}H_{38}O_2SiCl_2Na$ calcd 479.1910, found: m/z 479.1909.

2,3,4,5-Tetrahydrocyclopenta[*a*]napthalen-1-one, 4a.[1] (*1E*)-1,1-dichloro-2-(4-phenyl-1-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **1a**, (0.17 g, 0.42 mmol) was dissolved in acetonitrile (0.05 M, 8.3 mL). $AgBF_4$ (0.082 g, 0.42 mmol) was added in one portion and the reaction flask was equipped with a reflux condenser. The reaction was stirred at reflux for 12 h. and was then allowed to cool to room temperature. The reaction mixture was then filtered through a short pad of celite and silica gel. After removal of the solvent, the crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 5:1) to yield 2,3,4,5-tetrahydrocyclopenta[*a*]napthalen-1-one (0.062 g, 0.34 mmol, 80 %) as an off-white solid: m.p. 102-104°C; R_f 0.07 (hexanes/EtOAc 8:1); IR (thin film) 3067, 2947, 2933, 2906, 2841, 1683, 1629, 1435, 765 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 8.24 (d, *J* = 7.5 Hz, 1H), 7.17-7.25 (m, 3H), 2.96 (t, *J* = 8.0 Hz, 2H), 2.68-2.70 (m, 2H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.57-2.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 206.1, 174.8, 134.9, 134.4, 129.1, 127.8, 127.5, 126.7, 123.9, 35.9, 29.2, 27.6, 27.1; HRMS (EI, M^+) for $C_{13}H_{12}O$ calcd 184.0888, found: m/z 184.0886.

7-Methoxy-2,3,4,5-tetrahydro-cyclopenta[*a*]napthalen-1-one, 4b. The previously outlined procedure was used in the preparation of **4b** from (*1E*)-1,1-dichloro-2-(4-(3-methoxyphenyl)-1-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **1b**, (0.13 g, 0.29 mmol). The reaction was cooled to room temperature after 7 h. stirring at reflux. The crude material was purified by column chromatography (silica gel, hexanes:EtOAc 5:1) to yield **4b** (0.033 g, 0.15 mmol, 53

%) as an off-white solid: m.p. 93-97°C; R_f 0.15 (hexanes/EtOAc 8:1); IR (thin film) 2935, 2838, 1680, 1607, 1502, 1253, 1037, 872 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 8.18 (d, *J* = 8.5 Hz, 1H), 6.74-6.80 (m, 2H), 3.81 (s, 3H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.65-2.67 (m, 2H), 2.63 (t, *J* = 8.5 Hz, 2H), 2.55-2.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 206.2, 172.3, 159.2, 136.4, 134.7, 125.1, 122.2, 114.0, 111.0, 55.2, 35.9, 29.1, 28.0, 26.9; HRMS (EI, M^+) for $C_{14}H_{14}O_2$ calcd 214.0994, found: m/z 214.0996.

8-Methoxy-2,3,4,5-tetrahydro-cyclopenta[*a*]napthalen-1-one, 4c. The previously outlined procedure was used in the preparation of **4c** from (*1E*)-1,1-dichloro-2-(4-(4-methoxyphenyl)-1-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **1c**, (0.17 g, 0.38 mmol). The reaction was cooled to room temperature after 24 h. stirring at reflux. The crude material was purified by column chromatography (silica gel, hexanes:EtOAc 5:1) to yield **4c** (0.043 g, 0.20 mmol, 53 %) as an off-white solid: m.p. 98-101°C; R_f 0.13 (hexanes/EtOAc 8:1); IR (thin film) 2937, 2838, 1692, 1607, 1495, 1218, 1041 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.89 (d, *J* = 2.5 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.76 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.83 (s, 3H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.68-2.69 (m, 2H), 2.63 (t, *J* = 8.5 Hz, 2H), 2.57-2.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 206.0, 175.5, 158.5, 134.8, 130.0, 128.2, 126.4, 113.8, 109.1, 55.4, 35.8, 29.9, 27.4, 26.8; HRMS (EI, M^+) for $C_{14}H_{14}O_2$ calcd 214.0994, found: m/z 214.0995.

6-Methyl-2,3,4,5-tetrahydro-cyclopenta[*a*]napthalen-1-one, 4d. The previously outlined procedure was used in the preparation of **4d** from (*1E*)-1,1-dichloro-2-(4-(2-methylphenyl)-1-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **1d**, (0.06 g, 0.14 mmol). The reaction was cooled to room temperature after 7 h. stirring at reflux. The crude material was purified by column chromatography (silica gel, hexanes:EtOAc 5:1) to yield **4d** (0.022 g, 0.11 mmol, 79 %) as an off-white solid: m.p. 95-97°C; R_f 0.18 (hexanes/EtOAc 8:1); IR (thin film) 2949, 2922, 2902, 1682, 1635, 1476, 1428, 1378, 1044, 949, 795 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 8.16 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.65-2.68 (m, 4H), 2.56-2.58 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 206.1, 174.2, 135.0, 134.9, 132.6, 129.9, 129.0, 126.1, 121.9, 35.9, 29.0, 26.8, 23.6, 20.0; HRMS (EI, M^+) for $C_{14}H_{14}O$ calcd 198.1045, found: m/z 198.1047.

6-Bromo-2,3,4,5-tetrahydro-cyclopenta[*a*]napthalen-1-one, 4e. The previously outlined procedure was used in the preparation of **4e** from (*1E*)-1,1-dichloro-2-(4-(2-bromophenyl)-1-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **1e**, (0.23 g, 0.48 mmol). The reaction was cooled to room temperature after 24 h. stirring at reflux. The crude material was purified by column chromatography (silica gel, hexanes:EtOAc 5:1) to yield **4e** (0.61 g, 0.23 mmol, 48 %) as a white solid: m.p. 92-95ºC; R_f 0.12 (hexanes/EtOAc 8:1); IR (thin film) 2922, 1688, 1637, 1554, 1464, 1430, 1384, 1167, 1114, 941, 796, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.26 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.67-2.71 (m, 4H), 2.59-2.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.3, 175.2, 134.2, 133.6, 131.9, 131.0, 127.9, 123.6, 123.0, 35.9, 28.8, 27.2, 26.5; HRMS (EI, M^+) for $C_{13}H_{11}OBr$ calcd 261.9993, found: m/z 261.9994.

8-Hydroxy-2,3,4,5-tetrahydro-cyclopenta[*a*]napthalen-1-one, 4f. The previously outlined procedure was used in the preparation of **4f** from (*1E*)-1,1-dichloro-2-(4-(4-triisopropylsiloxyphenyl)-1-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **1f**, (0.13 g, 0.22 mmol). The reaction was cooled to room temperature after 48 h. stirring at reflux. The crude material was purified by column chromatography (silica gel, hexanes:EtOAc 3:1) to yield **4f** (0.017 g, 0.085 mmol, 39 %) as a white solid: m.p. 197-200ºC; R_f 0.21 (hexanes/EtOAc 2:1); IR (thin film) 3225, 2922, 2810, 1655, 1625, 1451, 1397, 1235, 895, 833 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.96 (d, *J* = 2.5 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.08 (br s, 1H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.68-2.71 (m, 2H), 2.65 (t, *J* = 8.5 Hz, 2H), 2.60-2.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 207.0, 176.6, 154.9, 134.6, 129.6, 128.4, 125.8, 114.4, 111.0, 35.8, 29.3, 27.4, 26.6; HRMS (EI, M^+) for $C_{13}H_{12}O_2$ calcd 200.0837, found: m/z 200.0837.

5-Chloro-2-methyl-3-(2-phenylethyl)-cyclopent-2-en-1-one, 2h. The previously outlined procedure was used in the preparation of **2h** from (*2E*)-1,1-dichloro-2-(5-phenyl-2-penten-2-yl)-2-triisopropylsilyloxycyclopropane, **1h**, (0.064 g, 0.15 mmol). The reaction was cooled to room temperature after 6 h. stirring at reflux. The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 25:1, 20:1, 15:1, 10:1, 8:1, etc.) to yield **2h** (0.034 g, 0.14 mmol, 97 %) as a white solid: m.p. 41-43ºC; R_f 0.19 (hexanes/EtOAc 8:1);

IR (thin film) 3027, 2924, 1711, 1642, 1454, 1385, 751, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 4.21 (dd, *J* = 6.5, 2.5 Hz, 1H), 3.07 (br dd, *J* = 18.5, 6.5 Hz, 1H), 2.84-2.87 (m, 2H), 2.71-2.80 (m, 2H), 2.67 (br d, *J* = 18.5 Hz, 1H), 1.63 (t, *J* = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 169.6, 140.1, 135.1, 128.7, 128.2, 126.6, 52.9, 40.7, 33.0, 32.8, 8.2; HRMS (EI, M^+) for $C_{14}H_{15}OCl$ calcd 234.0811, found: m/z 234.0809.

2-Chloro-7-methoxy-9b-methyl-2,3,3a,4,5,9b-hexahydro-cyclopenta[*a*]napthalen-1-one, 6i. The previously outlined procedure was used in the preparation of **6i** from (*2E*)-1,1-dichloro-2-(5-(3-methoxyphenyl)-2-penten-2-yl)-2-triisopropylsilyloxycyclopropane, **1i**, (0.049 g, 0.11 mmol). The reaction was cooled to room temperature after 18 h. stirring at reflux. The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 10:1, 9:1, 8:1, 7:1, etc.) to yield **6i** (0.026 g, 0.098 mmol, 89 %) as a white solid: m.p. 98-100°C; R_f 0.25 (hexanes/EtOAc 8:1); IR (thin film) 2928, 2863, 1750, 1608, 1499, 1453, 1260, 1244, 1037, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 1H), 6.76 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 4.25 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.77 (s, 3H), 2.87 (ddd, *J* = 18.4, 12.4, 6.4 Hz, 1H), 2.76 (ddd, *J* = 17.6, 6.0, 2.8 Hz, 1H), 2.51 (ddd, *J* = 12.8, 8.4, 5.6 Hz, 1H), 2.25 (dddd, *J* = 18.0, 5.6, 3.6, 3.6 Hz, 1H), 1.90-2.08 (m, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 158.1, 136.2, 130.1, 126.2, 113.8, 113.0, 56.9, 55.0, 49.3, 39.8, 33.7, 26.9, 24.9, 20.8; HRMS (ESI, $[M+Na]^+$) for $C_{15}H_{17}O_2ClNa$ calcd 287.0809, found: m/z 287.0809.

(*2Z, 4E*)-1-(2-Methylphenyl)-7-phenyl-3-(triisopropylsiloxy)-2,4-heptadiene, 8a. Dimethyl 4-(2-methylphenyl)-2-oxobutylphosphonate[3] (0.26 g, 0.96 mmol) was dissolved in THF (2 mL). This solution was transferred by cannula to a suspension of NaH (0.020 g, 0.88 mmol) in THF (1 mL) at 0°C. The reaction was allowed to stir for 10 min at low temperature before removal of the ice bath and subsequent stirring at room temperature for 30 min. Hydrocinnamaldehyde (0.053 mL, 0.40 mmol) in THF (2 mL) was then transferred by cannula to the reaction mixture, which was allowed to stir for another 18 h before the addition of glacial acetic acid. The crude material was then filtered through a short pad of silica gel (EtOAc) and the solvent removed under reduced pressure to provide a yellow oil.

The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 10:1, 9:1, 8:1, 7:1, etc.) to yield 1-(2-methylphenyl)-7-phenyl-*(4E)*-hepten-3-one as a clear, colorless oil: R_f 0.62 (silica gel, hexanes:EtOAc 2:1); IR (thin film) 3062, 3026, 2931, 2860, 1696, 1670, 1629, 1495, 1454, 977, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.30 (pseudo t, *J* = 7.0 Hz, 2H), 7.11-7.23 (m, 7H), 6.85 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.13 (dt, *J* = 16.0, 1.5 Hz, 1H), 2.90-2.93 (m, 2H), 2.76-2.81 (m, 4H), 2.54 (app. q, *J* = 7.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.5, 146.2, 140.7, 139.3, 135.9, 130.7, 130.3, 128.6, 128.5, 128.3, 126.2, 126.2, 126.1, 40.4, 34.4, 34.1, 27.5, 19.3; HRMS (EI, M^+) for $C_{20}H_{22}O$ calcd 278.1670, found: m/z 278.1671.

1-(2-Methylphenyl)-7-phenyl-*(4E)*-hepten-3-one (0.090 g, 0.32 mmol) was dissolved in anhydrous THF (1.0 mL). The solution was cooled to 0ºC, and freshly distilled triethylamine (0.11 mL, 0.80 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (0.094 mL, 0.35 mmol) was added dropwise and the solution was stirred at 0ºC for 1.5 h. The reaction was quenched with a mixture of triethylamine (0.5 mL), hexanes (2.5 mL), and saturated $NaHCO_3$ solution (5 mL). The organic layer was washed with H_2O (2 x 5 mL) and brine (5 mL) and dried ($MgSO_4$). The solvent was removed and the crude oil purified by flash column chromatography (alumina, hexanes:EtOAc:TEA 50:1:1) to yield (*2Z, 4E*)-1-(2-methylphenyl)-7-phenyl-3-(triisopropylsiloxy)-2,4-heptadiene, **8a**, (0.12 g, 0.27 mmol, 86 %) as a clear, colorless oil: R_f 0.81 (alumina, hexanes:EtOAc 8:1); IR (thin film) 3026, 2944, 2866, 1651, 1462, 1014, 883, 742, 698, 682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.28 (t, *J* = 8.5 Hz, 2H), 7.10-7.20 (m, 7H), 5.90 (d, *J* = 15.5 Hz, 1H), 5.85 (dd, *J* = 15.5, 6.0 Hz, 1H), 4.74 (t, *J* = 7.0 Hz, 1H), 3.45 (d, *J* = 7.0 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.43 (app. q, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 1.10-1.19 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.6, 141.7, 139.8, 136.3, 130.0, 129.6, 128.7, 128.6, 128.4, 128.3, 126.0, 126.0, 125.9, 109.5, 35.7, 34.0, 30.1, 19.5, 18.2, 13.8; HRMS (EI, M^+) for $C_{29}H_{42}OSi$ calcd 434.3005, found: m/z 434.3004.

(*2Z, 4E*)-1-(3-Methoxyphenyl)-7-phenyl-3-(triisopropylsiloxy)-2,4-heptadiene, 8b. The previously outlined procedure was used in the synthesis of **8b** starting with dimethyl 4-(3-methoxyphenyl)-2-oxobutylphosphonate[3] (0.29 g, 1.0 mmol) and hydrocinnamaldehyde (0.069 mL, 0.53 mmol). The crude material was purified by gradient column

chromatography (silica gel, hexanes:EtOAc 10:1, 9:1, 8:1, 7:1, etc.) to yield 1-(3-methoxyphenyl)-7-phenyl-*(4E)*-hepten-3-one as a clear, colorless oil: R_f 0.57 (silica gel, hexanes:EtOAc 2:1); IR (thin film) 3027, 2935, 2860, 1695, 1671, 1629, 1602, 1491, 1454, 1260, 1153, 1050, 976, 781, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.18-7.24 (m, 4H), 6.86 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.76-6.77 (m, 2H), 6.13 (dt, *J* = 16.0, 1.0 Hz, 1H), 3.81 (s, 3H), 2.91-2.94 (m, 2H), 2.84-2.88 (m, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.55 (app. q, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 159.7, 146.3, 142.9, 140.7, 130.7, 129.5, 128.5, 128.3, 126.2, 120.7, 114.2, 111.4, 55.2, 41.6, 34.4, 34.1, 30.1; HRMS (EI, M^+) for $C_{20}H_{22}O_2$ calcd 294.1620, found: m/z 294.1618.

1-(3-Methoxyphenyl)-7-phenyl-*(4E)*-hepten-3-one (0.40 g, 0.14 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.072 mL, 0.27 mmol) under the previously outlined conditions to yield (*2Z, 4E*)-1-(3-methoxyphenyl)-7-phenyl-3-(triisopropylsiloxy)-2,4-heptadiene, **8b**, (0.040 g, 0.09 mmol, 63 %) as a clear, colorless oil: R_f 0.63 (alumina, hexanes:EtOAc 8:1); IR (thin film) 3027, 2944, 2866, 1601, 1490, 1465, 1454, 1258, 1149, 1015, 884, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.2 Hz, 2H), 7.20-7.24 (m, 4H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.80 (br s, 1H), 6.76 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.95 (d, *J* = 15.2 Hz, 1H), 5.90 (dd, *J* = 15.6, 5.6 Hz, 1H), 4.86 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.49 (d, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.47 (m, 2H), 1.12-1.23 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 149.6, 143.3, 141.6, 129.5, 129.2, 128.8, 128.4, 128.3, 125.8, 120.8, 114.0, 111.2, 109.9, 55.1, 35.6, 33.9, 32.2, 18.1, 13.8; HRMS (EI, M^+) for $C_{29}H_{42}O_2Si$ calcd 450.2954, found: m/z 450.2955.

(*2Z, 4E*)-1-(3-Methoxyphenyl)-6-methyl-3-(triisopropylsiloxy)-2,4-heptadiene, 8c. The previously outlined procedure was used in the synthesis of **8c** starting with dimethyl 4-(3-methoxyphenyl)-2-oxobutylphosphonate[3] (0.46 g, 1.6 mmol) and isobutyraldehyde (0.060 mL, 0.66 mmol). The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 10:1, 9:1, 8:1, 7:1, etc.) to yield 1-(3-methoxyphenyl)-6-methyl-*(4E)*-hepten-3-one (0.087 g, 0.38 mmol, 57 %) as a pale yellow oil: R_f 0.66 (silica gel, hexanes:EtOAc 2:1); IR (thin film) 2962, 2871, 1672, 1602, 1491, 1260, 1153, 1051, 982, 780 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.0 Hz, 1H), 6.74-6.81 (m, 4H), 6.05 (dd, *J* = 16.0, 1.5 Hz, 1H), 3.80 (s, 3H), 2.85-2.93 (m, 4H), 2.46 (qqdd, *J* = 7.0, 7.0, 7.0, 1.5

Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 199.8, 159.7, 153.7, 143.0, 129.4, 127.5, 120.7, 114.2, 111.3, 55.1, 41.6, 31.1, 30.2, 21.3; HRMS (EI, M^+) for $C_{15}H_{20}O_2Si$ calcd 232.1463, found: m/z 232.1459.

1-(3-Methoxyphenyl)-6-methyl-*(4E)*-hepten-3-one (0.042 g, 0.18 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.054 mL, 0.20 mmol) under the previously outlined conditions to yield (*2Z, 4E*)-1-(3-methoxyphenyl)-6-methyl-3-(triisopropylsiloxy)-2,4-heptadiene, **8c**, (0.043 g, 0.11 mmol, 62 %) as a clear, colorless oil: R_f 0.75 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2947, 2867, 1610, 1490, 1465, 1258, 1149, 1014, 883, 682 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.20 (t, *J* = 7.6 Hz, 1H), 6.82 (br d, *J* = 7.6 Hz, 1H), 6.79 (br s, 1H), 6.74 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.88 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.82 (d, *J* = 15.6 Hz, 1H), 4.84 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 3.48 (d, *J* = 6.8 Hz, 2H), 2.35 (app oct, *J* = 6.4 Hz, 1H), 1.20-1.30 (m, 3H), 1.15 (d, *J* = 6.4 Hz, 18H), 1.02 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 159.6, 149.8, 143.5, 137.0, 129.2, 125.9, 120.8, 114.1, 111.1, 109.4, 55.1, 32.2, 30.8, 22.3, 18.1, 13.7; HRMS (EI, M^+) for $C_{24}H_{40}O_2Si$ calcd 388.2797, found: m/z 388.2800.

(*2Z, 4E*)-1-(3-Methoxyphenyl)-3-(triisopropylsiloxy)-2,4-heptadiene, 8d. The previously outlined procedure was used in the synthesis of **8d** starting with dimethyl 4-(3-methoxyphenyl)-2-oxobutylphosphonate[3] (0.55 g, 1.92 mmol) and propionaldehyde (0.058 mL, 0.80 mmol). The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 10:1, 9:1, 8:1, 7:1, etc.) to yield 1-(3-methoxyphenyl)-*(4E)*-hepten-3-one (0.17 g, 0.78 mmol, 97 %) as a clear, colorless oil: R_f 0.65 (silica gel, hexanes:EtOAc 2:1); IR (thin film) 2966, 2936, 1671, 1696, 1628, 1602, 1491, 1455, 1260, 1153, 1051, 978, 781 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) □ 7.20 (t, *J* = 7.5 Hz, 1H), 6.88 (dt, *J* = 16.0, 6.5 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.73-6.76 (m, 2H), 6.10 (dt, *J* = 16.0, 1.5 Hz, 1H), 3.80 (s, 3H), 2.85-2.94 (m, 4H), 2.21 (app. pent, *J* = 7.5 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 199.6, 159.7, 149.0, 143.0, 129.4, 129.4, 120.7, 114.1, 111.3, 55.1, 41.5, 30.1, 25.6, 12.4; HRMS (EI, M^+) for $C_{14}H_{18}O_2$ calcd 218.1307, found: m/z 218.1301.

1-(3-Methoxyphenyl)-*(4E)*-hepten-3-one (0.11 g, 0.52 mmol) in THF (4 mL) was added by cannula to a stirring solution of LDA (0.58 mmol) in THF (4 mL) at -78ºC.[4] The reaction

was allowed to stir at low temperature for 40 min before the dropwise addition of triisopropylsilyl trifluoromethanesulfonate (0.15 mL, 0.58 mmol) by syringe. The reaction was slowly allowed to warm to room temperature and was quenched by the addition of triethylamine (1 mL), hexanes (5 mL), and saturated $NaHCO_3$ solution (10 mL). The organic layer was washed with H_2O (2 x 5 mL) and brine (5 mL) and dried ($MgSO_4$). The solvent was removed and the crude oil purified by flash column chromatography (alumina, hexanes:EtOAc:TEA 50:1:1) to yield (*2Z, 4E*)-1-(3-methoxyphenyl)-3-(triisopropylsiloxy)-2,4-heptadiene, **8d**, as the major product in a mixture of *2Z:2E* (6.5:1) isomers (0.14 g, 0.38 mmol, 73 %): R_f 0.76 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2962, 2868, 1601, 1464, 1356, 1258, 1149, 1051, 884, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) □ 7.19 (t, *J* = 8.0 Hz, 1H), 6.71-6.82 (m, 3H), 5.92 (dt, *J* = 15.2, 6.4 Hz, 1H), 5.85 (d, *J* = 15.6 Hz, 1H), 4.82 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.46 (d, *J* = 7.2 Hz, 2H), 2.10 (app pent, *J* = 6.8 Hz, 2H), 1.18-1.28 (m, 3H), 1.14 (d, *J* = 6.8 Hz, 18H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 159.6, 149.7, 143.5, 131.6, 129.2, 127.9, 120.8, 114.0, 111.2, 109.2, 55.1, 32.2, 25.3, 18.1, 13.7, 13.4; HRMS (EI, M^+) for $C_{23}H_{38}O_2Si$ calcd 374.2641, found: m/z 374.2638.

(*1E, 3Z*)-5-(3-Methoxyphenyl)-1-phenyl-3-(triisopropylsiloxy)-1,3-pentadiene, 8e. The previously outlined procedure was used in the synthesis of **8e** starting with dimethyl 4-(3-methoxyphenyl)-2-oxobutylphosphonate (0.20 g, 0.71 mmol) and benzaldehyde (0.030 mL, 0.29 mmol). The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 10:1, 9:1, 8:1, 7:1, etc.) to yield 5-(3-methoxyphenyl)-1-phenyl-*(1E)*-penten-3-one (0.077 g, 0.29 mmol, 100 %) as a white solid: m.p. 41-44ºC; R_f 0.53 (silica gel, hexanes:EtOAc 2:1); IR (thin film) 3027, 2937, 2835, 1690, 1662, 1611, 1493, 1450, 1260, 1153, 1051, 782 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.56 (d, *J* = 16.5 Hz, 1H), 7.53-7.54 (m, 2H), 7.39-7.41 (m, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81 (br s, 1H), 6.77 (dd, *J* = 8.0, 3.0 Hz, 1H), 6.75 (d, *J* = 16.5 Hz, 1H), 3.81 (s, 3H), 3.01 (br s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 199.2, 159.8, 142.9, 142.7, 134.5, 130.5, 129.5, 129.0, 128.3, 126.2, 120.7, 114.2, 111.4, 55.2, 42.3, 30.2; HRMS (EI, M^+) for $C_{18}H_{18}O_2$ calcd 266.1307, found: m/z 266.1305; Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.40; H, 6.96. 5-(3-Methoxyphenyl)-1-phenyl-*(1E)*-penten-3-one (0.11 g, 0.41 mmol) was treated with triisopropylsilyl trifluoromethanesulfonate (0.12 mL, 0.45 mmol) under the previously

outlined conditions to yield (*1E, 3Z*)-5-(3-methoxyphenyl)-1-phenyl-3-(triisopropylsiloxy)-1,3-pentadiene, **8e**, (0.13 g, 0.31 mmol, 75 %) as a clear, colorless oil: R_f 0.81 (alumina, hexanes:EtOAc 8:1); IR (thin film) 2945, 2867, 1600, 1490, 1465, 1359, 1258, 1149, 1049, 1014, 884, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) □ 7.40 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.21-7.26 (m, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.82 (br s, 1H), 6.80 (d, *J* = 15.6 Hz, 1H), 6.77 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 5.10 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.57 (d, *J* = 7.2 Hz, 2H), 1.28-1.38 (m, 3H), 1.21 (d, *J* = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 159.7, 149.9, 142.9, 137.1, 129.3, 128.6, 127.7, 127.5, 127.4, 126.4, 120.9, 114.1, 112.9, 111.4, 55.1, 32.5, 18.1, 13.9; HRMS (EI, M^+) for $C_{27}H_{38}O_2Si$ calcd 422.2641, found: m/z 422.2641.

3-(2-Methylbenzyl)-2,3,4,5-tetrahydrocyclopenta[*a*]naphthalen-1-one, 10a, and 3-(2-methylbenzyl)-4,5-dihydro-3a*H*-cyclopenta[*a*]naphthalen-1(9b*H*)-one, 11a. (*2Z, 4E*)-1-(2-Methylphenyl)-7-phenyl-3-(triisopropylsiloxy)-2,4-heptadiene, **8a**, (0.092 g, 0.21 mmol) was dissolved in $CHCl_3$ (0.021 mol, 1.7 mL). The $CHCl_3$ does not need to be freshly distilled or pre-dried for this reaction. Benzyltriethylammonium chloride (0.014 g, 0.060 mmol) was added to the reaction mixture. A solution of 50 % aq. NaOH (0.040 mol, 1.6 mL) was then added in one portion and the reaction was vigorously stirred at room temperature for 12 min. The reaction was then diluted with H_2O (5 mL) and CH_2Cl_2 (5 mL) at 0ºC. The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were then washed with H_2O (2 x 10 mL) and dried ($MgSO_4$). After filtration, the solvent was removed to provide a brown-orange oil.

The crude oil was re-dissolved in acetonitrile (0.05 M, 4.2 mL). $AgBF_4$ (0.041 g, 0.21 mmol) was added in one portion and the reaction flask was equipped with a reflux condenser. The reaction was stirred at reflux for 20 h and was then allowed to cool to room temperature. The reaction mixture was then filtered through a short pad of celite/silica gel. After removal of the solvent, the crude material was purified by gradient column chromatography (silica gel, 1%□ 2%□ 4%□ 6%□ 8%□ 10% EtOAc in hexanes) to yield **10a** (0.030 g, 0.10 mmol, 50 %) and **11a** (0.011 g, 0.040 mmol, 18 %) as an off-white solid and a yellow oil, respectively.

3-(2-Methylbenzyl)-2,3,4,5-tetrahydrocyclopenta[*a*]naphthalen-1-one, 10a: R_f 0.32 (hexanes/EtOAc 8:1); IR (thin film) 3060, 2928, 2693, 1490, 1385, 764, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.5 Hz, 1H), 7.17-7.28 (m, 7H), 3.23-3.27 (m, 1H), 3.19 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.96 (pseudo t, *J* = 7.5 Hz, 2H), 2.73 (ddd, *J* = 18.0, 8.5, 8.5 Hz, 1H), 2.64 (dd, *J* = 18.5, 6.5 Hz, 1H), 2.55 (ddd, *J* = 19.0, 7.5, 7.5 Hz, 1H), 2.51 (dd, *J* = 14.0, 10.0 Hz, 1H), 2.38 (s, 3H), 2.35 (dd, *J* = 19.0, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 177.0, 137.6, 136.0, 135.0, 134.5, 130.6, 129.1, 129.0, 128.0, 127.5, 126.8, 126.7, 126.2, 124.3, 42.6, 41.1, 37.1, 27.8, 25.4, 19.6; HRMS (EI, M^+) for $C_{21}H_{20}O$ calcd 288.1514, found: m/z 288.1513.

3-(2-Methylbenzyl)-4,5-dihydro-3a*H*-cyclopenta[*a*]naphthalen-1(9b*H*)-one, 11a: R_f 0.27 (hexanes/EtOAc 8:1); IR (thin film) 3021, 2929, 1701, 1616, 1493, 1453, 1172, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.14-7.25 (m, 6H), 7.08 (d, *J* = 7.5 Hz, 1H), 5.71 (app q, *J* = 1.5 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.65 (d, *J* = 17.5 Hz, 1H), 3.65 (d, *J* = 7.0 Hz, 1H), 3.37 (app q, *J* = 6.0 Hz, 1H), 2.68 (ddd, *J* = 15.5, 6.0, 4.0 Hz, 1H), 2.54 (ddd, *J* = 15.0, 9.0, 4.5 Hz, 1H), 2.27 (s, 3H), 1.98-2.09 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 181.6, 137.5, 136.3, 135.2, 132.5, 131.0, 130.6, 129.9, 127.8, 127.3, 126.6, 126.4, 126.3, 50.5, 43.4, 35.8, 27.0, 26.5, 19.4; HRMS (EI, M^+) for $C_{21}H_{20}O$ calcd 288.1514, found: m/z 288.1515.

Compound 12b. The previously outlined procedure was used in the preparation of **12b** from (*2Z, 4E*)-1-(3-methoxyphenyl)-7-phenyl-3-(triisopropylsiloxy)-2,4-heptadiene, **8b**, (0.10 g, 0.22 mmol). The crude material was purified by gradient column chromatography (silica gel, 1% 2% 4% 6% 8% 10% EtOAc in hexanes) to yield **12b** (0.043 g, 0.12 mmol, 57 %) as a white solid: m.p. 111-114ºC; R_f 0.25 (hexanes/EtOAc 8:1); IR (thin film) 3025, 2930, 2856, 1751, 1605, 1496, 1260, 1154, 1122, 1034, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.72 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.67 (d, *J* = 2.5 Hz, 1H), 4.51 (br d, *J* = 7.5 Hz, 1H), 3.77 (s, 3H), 3.33 (s, 1H), 3.32 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.10 (dd, *J* = 17.5, 5.0 Hz, 1H), 2.90-2.92 (m, 1H), 2.74 (app. t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 8.0 Hz, 1H), 1.68-1.81 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 159.5, 140.8, 135.1, 128.6, 128.6, 128.3, 126.8, 126.2,

113.9, 113.3, 60.2, 55.2, 55.1, 41.9, 40.3, 33.8, 33.7, 32.1; HRMS (ESI, $[M+Na]^+$) for $C_{21}H_{21}O_2ClNa$ calcd 363.1122, found: m/z 363.1121.

Compound 12c. The previously outlined procedure was used in the preparation of **12c** from (*2Z, 4E*)-1-(3-methoxyphenyl)-6-methyl-3-(triisopropylsiloxy)-2,4-heptadiene, **8c**, (0.034 g, 0.10 mmol). The crude material was purified by gradient column chromatography (silica gel, 1% 2% 4% 6% 8% 10% EtOAc in hexanes) to yield **12c** (0.018 g, 0.065 mmol, 65 %) as a white solid: m.p. 102-104ºC; R_f 0.30 (hexanes/EtOAc 8:1); IR (thin film) 2962, 1749, 1606, 1498, 1470, 1260, 1038, 810 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.04 (d, *J* = 8.5 Hz, 1H), 6.73 (dd, *J* = 8.5, 3.5 Hz, 1H) 6.68 (d, *J* = 3.0 Hz, 1H), 4.44 (br d, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 3.48 (br s, 1H), 3.35 (d, *J* = 17.0 Hz, 1H), 3.05-3.12 (m, 2H), 1.88 (d, *J* = 11.0 Hz, 1H), 1.43 (dqq, *J* = 11.0, 6.5, 6.5 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.1, 159.5, 135.1, 128.7, 127.1, 113.8, 113.2, 60.1, 55.2, 54.0, 50.0, 38.1, 32.3, 28.3, 21.5, 20.2; HRMS (ESI, $[M+Na]^+$) for $C_{16}H_{19}O_2ClNa$ calcd 301.0966, found: m/z 301.0968.

Compound 12d. The previously outlined procedure was used in the preparation of **12d** from (*2Z, 4E*)-1-(3-methoxyphenyl)-3-(triisopropylsiloxy)-2,4-heptadiene, **8d**, (0.074 g, 0.20 mmol). The crude material was purified by gradient column chromatography (silica gel, 1% 2% 4% 6% 8% 10% EtOAc in hexanes) to yield **12d** (0.044 g, 0.017 mmol, 84 %) as a white solid: m.p. 111-114ºC; R_f 0.25 (hexanes/EtOAc 8:1); IR (thin film) 2960, 2933, 1755, 1606, 1497, 1463, 1258, 1122, 1036, 895 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.03 (d, *J* = 8.5 Hz, 1H), 6.73 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.68 (d, *J* = 3.0 Hz, 1H), 4.49 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 3.34 (s, 1H), 3.33 (dd, *J* = 17.5, 1.5 Hz, 1H), 3.13 (dd, *J* = 17.5, 4.5 Hz, 1H), 2.89-2.91 (m, 1H), 2.20 (t, *J* = 8.0 Hz, 1H), 1.40-1.50 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 205.2, 159.5, 135.2, 128.6, 127.0, 114.0, 113.2, 60.3, 55.2, 54.9, 44.3, 40.0, 32.2, 25.0, 12.1; HRMS (ESI, $[M+Na]^+$) for $C_{15}H_{17}O_2ClNa$ calcd 287.0809, found: m/z 287.0811.

Compound 12e. The previously outlined procedure was used in the preparation of **12e** from (*1E, 3Z*)-5-(3-methoxyphenyl)-1-phenyl-3-(triisopropylsiloxy)-1,3-pentadiene, **8e**, (0.079 g,

0.19 mmol). The crude material was purified by gradient column chromatography (silica gel, 1% 2% 4% 6% 8% 10% EtOAc in hexanes) to yield **12e** (0.035 g, 0.11 mmol, 59 %) as a white solid: m.p. 109-112ºC; R_f 0.25 (hexanes/EtOAc 8:1); IR (thin film) 2927, 2854, 1748, 1606, 1497, 1277, 1261, 1120, 1038, 794, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.28 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.75 (d, *J* = 2.5 Hz, 1H), 4.39 (dd, *J* = 7.5, 1.0 Hz, 1H), 3.89 (br s, 1H), 3.80 (s, 3H), 3.66 (s, 1H), 3.45 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.38 (dd, *J* = 17.5, 4.5 Hz, 1H), 3.17-3.19 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.5, 159.7, 140.1, 135.0, 129.1, 129.0, 127.2, 126.6, 126.5, 114.0, 113.6, 60.0, 55.3, 53.6, 46.3, 43.5, 32.1; HRMS (ESI, $[M+Na]^+$) for $C_{19}H_{17}O_2ClNa$ calcd 335.0809, found: m/z 335.0807.

References

1. The spectral data, including ^1H and ^{13}C NMR spectra, have previously been reported: T. N. Grant, F. G. West, *J. Am. Chem. Soc.* **2006**, *128*, 9348.
2. This procedure was adapted from a one-pot Swern oxidation/Wittig olefination sequence: R. E. Ireland, D. W. Norbeck, *J. Org. Chem.* **1985**, *50*, 2198.
3. K. Mitoshi, T. Nakae, S. Sakuyama, M. Nishizaki, Y. Odagaki, H. Nakai, N. Hamanaka, *Bioorg. Med. Chem.* **1997**, *5*, 1621-1647.
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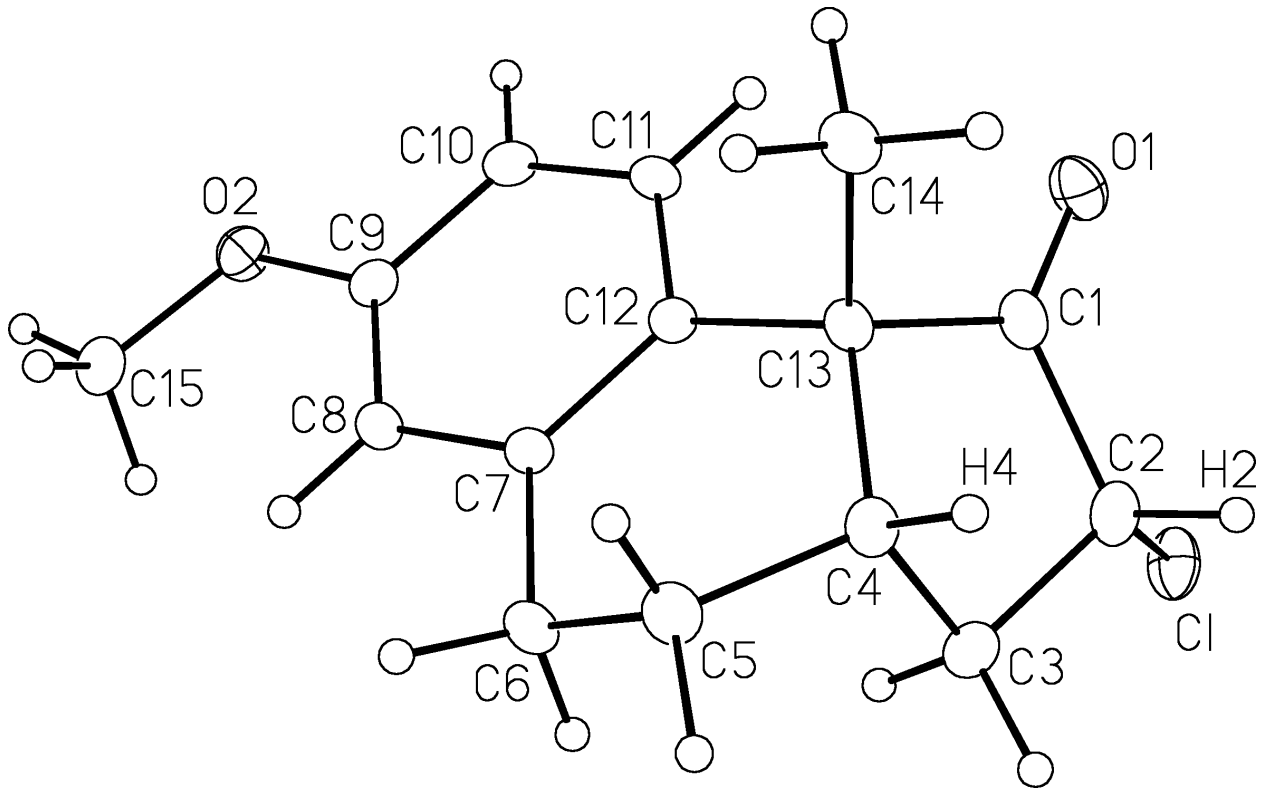
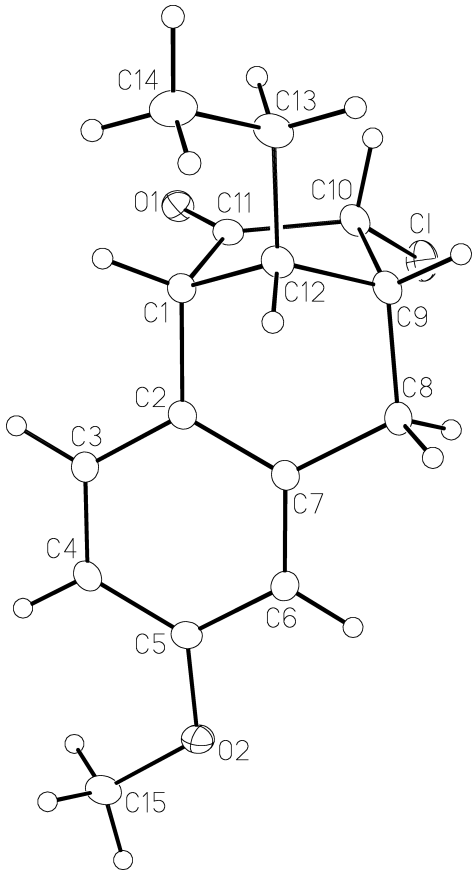
ORTEP Structure for Cyclization Product **6i**



ORTEP Structure for Cyclization Product **12d**



ORTEP Structure for Cyclization Product **12e**