A New Approach to the Nazarov Reaction via Sequential Electrocyclic Ring Opening and Ring Closure

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Supporting Information: Experimental procedures, physical data and NMR spectra for **5a-h**, **6a-e**, **g**, **h**, **7f**, **8b-e**, **g**, **9a**, **b**, **g**, **10h**, and synthetic intermediates (57 pages).

General Information. Reactions were carried out in flame-dried glassware under a positive nitrogen 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 from calcium hydride, tetrahydrofuran, diethylether and benzene from sodium/benzophenone ketyl, toluene from sodium metal. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F₂₅₄ (Merck). Flash chromatography column were packed with 230-400 mesh silica gel (Silicycle). Proton nuclear magnetic resonance spectra (¹H NMR) were recorded at 400 MHz or 500 MHz and coupling constants (*J*) are reported in Hertz (Hz). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 100 MHz or 125 MHz and are reported (ppm) relative to the center line of the triplet from chloroform-*d* (77.23 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.

2-(Triisopropylsiloxy)-1,3-butadiene (5a). Methyl vinyl ketone (0.41 mL, 5.0 mmol) was dissolved in anhydrous CH₂Cl₂ (40 mL). The temperature of the solution was dropped to -78°C. Freshly distilled 2,6-lutidine (0.87 mL, 7.5 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (1.5 mL, 5.5 mmol) was added dropwise and the solution was stirred at -78°C for 4 h. The reaction was allowed to warm to room temperature before being quenched with a mixture of triethylamine (20 mL) and H₂O (20 mL). The aqueous layer was extracted with CH₂Cl₂ (20 mL). The organic layer was washed with H₂O (2 x 20 mL) and brine (20 mL) and dried (Na₂SO₄). The solvent was removed and the crude oil purified by flash column chromatography (silica gel, hexanes:EtOAc:TEA 25:1:1) to yield 2-(triisopropylsiloxy)-1,3-butadiene (463 mg, 2.0 mmol, 41 %) as a colorless oil: *R*_f 0.72 (hexanes/EtOAc 8:1); IR (thin film) 2946, 2893, 2868, 1586, 1464, 1375, 1303, 1060, 1009, 883, 684 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.23 (dd, *J* = 17.2, 10.8 Hz, 1H) 5.63 (dd, *J* = 17.2, 2.4 Hz, 1H), 5.13 (br d, *J* = 10.4 Hz, 1H), 4.38 (s, 1H), 4.32 (s, 1H), 1.25-1.34 (m, 3H), 1.16 (d, *J* = 7.0 Hz, 18H); ¹³C NMR (125 MHz, CDCl₃) δ 155.6, 135.2, 114.6, 95.3, 18.3, 13.1; HRMS (EI, M⁺) for C₁₃H₂₆OSi calcd 226.1753, found: *m/z* 226.1754.

(3E)-4-Isopropyl-2-(triisopropylsiloxy)-1,3-butadiene (5b). 5-Methyl-(3E)-hexene-2-one (0.26 mL, 2.0 mmol) was dissolved in anhydrous THF (5.0 mL). The temperature of the solution was dropped to 0°C. Freshly distilled triethylamine (0.70 mL, 5.0 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (0.59 mL, 2.2 mmol) was added dropwise and the solution was stirred at 0°C for 2 h. The reaction was quenched with a mixture of triethylamine (1 mL), hexanes (5 mL), and saturated NaHCO₃.

solution (5 mL). The organic layer was washed with H₂O (2 x 5 mL) and brine (5 mL) and dried (MgSO₄). The solvent was removed to yield (3*E*)-4-isopropyl-2-(triisopropylsiloxy)-1,3-butadiene, **5b**, (535 mg, 2.0 mmol, 100 %) as a colorless oil: *R*_f 0.84 (hexanes/EtOAc 8:1); IR (thin film) 2960, 2868, 1589, 1464, 1306, 1026, 883, 678 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.06 (dd, *J* = 15.5, 6.5 Hz, 1H), 5.82 (dd, *J* = 15.5, 1.0 Hz, 1H), 4.23 (s, 1H), 4.19 (s, 1H), 2.36 (app. octet, *J* = 7.0 Hz, 1H), 1.20-1.28 (m, 3H), 1.11 (d, *J* = 7.5 Hz, 18H), 1.02 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 155.6, 138.5, 124.9, 93.1, 30.5, 22.2, 18.0, 12.8; HRMS (EI, M⁺) for C₁₆H₃₂OSi calcd 268.2222, found: *m/z* 268.2219.

(3*E*)-3-Methyl-4-phenyl-2-(triisopropylsiloxy)-1,3-butadiene (5c). α-Methyl-*trans*-cinnamaldehyde (1.4 mL, 10.0 mmol) was dissolved in freshly distilled THF (25 mL). The temperature of the reaction mixture was dropped to -78°C before adding MeLi (1.6 M, 6.3 mL, 10 mmol) dropwise by syringe. The reaction mixture was stirred at low temperature for 3 h and then quenched by the addition of saturated NH₄Cl solution. The organic layer was washed with H₂O (20 mL) and brine (20 mL). The aqueous layer was extracted with Et₂O (2 x 20 mL) and the combined organic layers were dried (MgSO₄). The solvent was removed and the crude oil was purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 3-methyl-4-phenyl-(3*E*)-butene-2-ol (1.6 g, 9.8 mmol, 98 %) as a pale yellow oil: *R*_f 0.38 (hexanes/EtOAc 2:1); IR (thin film) 3347, 2974, 1947, 1806, 1600, 1443, 1074, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (app. t, *J* = 7.5 Hz, 2H), 7.28 (app. d, *J* = 6.5 Hz, 2H), 7.22 (app. t, *J* = 7.0 Hz, 1H), 6.53 (br s, 1H), 4.39 (q, 1H, *J* = 6.5 Hz), 1.89 (d, 3H, *J* = 1.0 Hz), 1.60 (br s, 1H), 1.38 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 141.6, 137.6, 128.9, 128.1, 126.4, 124.4, 73.6, 21.8, 13.4; HRMS (EI, M⁺) for C₁₁H₁₄O calcd 162.1045, found: *m/z* 162.1045.

3-Methyl-4-phenyl-(3*E*)-butene-2-ol (1.56 g, 9.6 mmol) was dissolved in freshly distilled CH₂Cl₂ (30 mL). To the solution was added powdered 4 Å molecular sieves (7 g). The temperature of the reaction mixture was dropped to 0°C before adding NMO (1.7 g, 14.4 mmol) in one portion. At low temperature, tetrapropylammonium perruthenate (0.17 g, 0.48 mmol) was next added in three equal portions. The reaction was left to stir at room temperature for 3 h before being quenched by filtration through a silica gel plug. The solvent was removed and the crude material purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 3-methyl-4-phenyl-(3*E*)-butene-2-one (1.3 g, 8.1 mmol, 85 %) as a white solid: m.p. 36-37.5 °C; *R*_f 0.49 (hexanes/EtOAc 2:1); IR (thin film) 3056, 2999, 2961, 2925, 1956, 1666, 1626, 1245, 1006 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.52 (s, 1H), 7.42-7.45 (m, 4H), 7.34-7.38 (m, 1H), 2.48 (s, 3H), 2.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 200.3, 139.6, 137.8, 135.9, 129.7, 128.5, 128.4, 25.8, 12.9; HRMS (EI, M⁺) for C₁₁H₁₂O calcd 160.0888, found: *m/z* 160.0884; Anal. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.50; H, 7.62.

3-Methyl-4-phenyl-(3*E*)-butene-2-one (0.20 g, 1.2 mmol) was dissolved in anhydrous THF (3.5 mL). The temperature of the solution was dropped to 0°C. Freshly distilled triethylamine (0.43 mL, 3.1 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (0.40 mL, 1.5 mmol) was added dropwise and the solution was stirred at 0°C for 2 h. The reaction was quenched with a mixture of triethylamine (0.5 mL), hexanes (2.5 mL), and saturated NaHCO₃ solution (5 mL). The organic layer was washed with H₂O (2 x 5 mL) and brine (5 mL) and dried (MgSO₄). The solvent was removed to yield (3*E*)-3-methyl-4-phenyl-2-(triisopropylsiloxy)-1,3-butadiene, **5c**, (371 mg, 1.17

mmol, 94%) as a colorless oil: R_f 0.75 (hexanes/EtOAc 8:1); IR (thin film) 3022, 2944, 2866, 1600, 1589, 1463, 1124, 1021 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35 (t, $J = 7.5$ Hz, 2H), 7.29 (d, $J = 7.0$ Hz, 2H), 7.23 (t, $J = 7.0$ Hz, 1H), 7.18 (br s, 1H), 4.59 (d, $J = 1.5$ Hz, 1H), 4.44 (d, $J = 1.0$ Hz, 1H), 2.00 (d, $J = 1.0$ Hz, 3H), 1.26-1.34 (m, 3H), 1.15 (d, $J = 7.5$ Hz, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.8, 138.2, 133.0, 129.3, 128.0, 127.1, 126.4, 92.0, 18.1, 14.7, 12.9; HRMS (EI, M^+) for $\text{C}_{20}\text{H}_{32}\text{OSi}$ calcd, 316.2222, found: m/z 316.2218.

1-Triisopropylsiloxy-1-(cyclohexen-1-yl)-ethene (5d). 1-Acetyl-1-cyclohexene (0.13 mL, 1.0 mmol) was dissolved in anhydrous THF (2.5 mL). The temperature of the solution was dropped to 0°C . Freshly distilled triethylamine (0.35 mL, 2.5 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (0.29 mL, 1.1 mmol) was added dropwise and the solution was stirred at 0°C for 2 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 to yield 1-(triisopropylsiloxy)-1-(cyclohexen-1-yl)-ethene, **5d**, (278 mg, 0.99 mmol, 99%) as a colorless oil: R_f 0.76 (hexanes/EtOAc 8:1); IR (thin film) 2943, 2867, 1591, 1464, 1288, 1017, 883 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.32 (br s, 1H), 4.31 (s, 1H), 4.18 (s, 1H), 2.12-2.16 (m, 4H), 1.64-1.70 (m, 2H), 1.56-1.60 (m, 2H), 1.20-1.28 (m, 3H), 1.11 (d, $J = 7.0$ Hz, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.1, 133.1, 125.1, 88.6, 25.5, 25.1, 22.8, 22.1, 18.1, 12.9; HRMS (EI, M^+) for $\text{C}_{17}\text{H}_{32}\text{OSi}$ calcd 280.2222, found: m/z 280.2220.

1-Triisopropylsiloxy-1-(cyclopenten-1-yl)-ethene (5e). The above procedure was used in the synthesis of **5e** starting with 1-acetyl-1-cyclopentene (0.11 mL, 1.0 mmol). The reaction yielded 1-(triisopropylsiloxy)-1-(cyclopenten-1-yl)-ethene, **5e**, (266 mg, 1.0 mmol, 100%) as a pale yellow oil: R_f 0.76 (hexanes/EtOAc 8:1); IR (thin film) 2945, 2867, 1586, 1464, 1363, 1014, 883 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.06 (br s, 1H), 4.26 (s, 1H), 4.24 (s, 1H), 2.44 (app. t, $J = 7.5$ Hz, 4H), 1.94 (pent, $J = 7.5$ Hz, 2H), 1.20-1.28 (m, 3H), 1.11 (d, $J = 7.0$ Hz, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.3, 141.3, 128.5, 91.6, 32.9, 32.2, 23.6, 18.1, 12.8; HRMS (EI, M^+) for $\text{C}_{16}\text{H}_{30}\text{OSi}$ calcd 266.2066, found: m/z 266.2067.

(1E,3Z)-1-Phenyl-3-(triisopropylsiloxy)-1,3-heptadiene (5f). N-morpholino cinnamide¹ (0.23 g, 1.0 mmol) was dissolved in freshly distilled THF (10 mL). The temperature of the reaction mixture was dropped to -78°C before adding $n\text{BuLi}$ (1.6 M in hexanes, 0.72 mL, 1.1 mmol) dropwise by syringe. The reaction mixture was stirred at low temperature for 3 h before being quenched by the addition of saturated NH_4Cl solution. The organic layer was washed with H_2O (10 mL) and brine (10 mL). The aqueous layer was extracted with Et_2O (2 x 10 mL) and the combined organic layers were dried (MgSO_4). The solvent was removed and the crude oil purified by flash column chromatography (silica gel, hexanes:EtOAc 8:1) to yield 1-phenyl-(1E)-heptene-3-one (0.053 g, 0.28 mmol, 27 % [unoptimized]) as a white solid: m.p. $34-36^\circ\text{C}$; R_f 0.48 (hexanes/EtOAc 8:1); IR (thin film) 3023, 2954, 2939, 2864, 1650, 1464, 1452, 984, 745, 688 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.54-7.57 (m, 3H), 7.39-7.41 (m, 3H), 6.75 (d, $J = 16.5$ Hz, 1H), 2.67 (t, $J = 7.5$ Hz, 2H), 1.67 (pent, $J = 7.5$ Hz, 2H), 1.39 (sextet, $J = 7.5$ Hz, 2H), 0.95 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.6, 142.3, 134.6, 130.3, 128.9, 128.2, 126.3, 40.7, 26.5, 22.5, 13.9; HRMS (EI, M^+) for $\text{C}_{13}\text{H}_{16}\text{O}$

calcd 188.1201, found: m/z 188.1201; Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.74; H, 8.73.

1-Phenyl-(*IE*)-heptene-3-one (0.086 g, 0.49 mmol) was dissolved in anhydrous THF (1.5 mL). The temperature of the solution was dropped to 0°C. Freshly distilled triethylamine (0.17 mL, 1.2 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (0.17 mL, 0.62 mmol) was added dropwise and the solution was stirred at 0°C for 2 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 to yield (*IE*,3*Z*)-1-phenyl-3-(triisopropylsiloxy)-1,3-heptadiene (164 mg, 0.47 mmol, 97%) as a colorless oil: R_f 0.76 (hexanes/EtOAc 8:1); IR (thin film) 3025, 2946, 2867, 1618, 1464, 1062 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.5 Hz, 2H), 7.31 (app. t, J = 8.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 15.5 Hz, 1H), 6.56 (d, J = 15.5 Hz, 1H), 4.90 (t, J = 7.5 Hz, 1H), 2.18 (q, J = 7.5 Hz, 2H), 1.42 (sextet, J = 7.5 Hz, 2H), 1.22-1.30 (m, 3H), 1.16 (d, J = 7.0 Hz, 18H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 137.4, 128.6, 128.1, 127.1, 126.5, 126.3, 115.3, 28.3, 22.8, 18.1, 14.0, 13.9; HRMS (EI, M^+) for $C_{22}H_{36}OSi$ calcd, 344.2535, found: m/z 344.2535.

(*IE*,3*Z*)-2-Methyl-1-phenyl-3-(triisopropylsiloxy)-1,3-heptadiene (5g). α -Methyl-*trans*-cinnamaldehyde (1.4 mL, 10.0 mmol) was dissolved in freshly distilled Et_2O (40 mL). The temperature of the reaction mixture was dropped to -78°C before adding $nBuLi$ (1.45 M in hexanes, 7.1 mL, 10.3 mmol) dropwise by syringe. The reaction mixture was stirred at low temperature for 4 h and then quenched by the addition of 0.5 M HCl (aq) at room temperature. The organic layer was washed with H_2O (2 x 30 mL) and brine (30 mL). The aqueous layer was extracted with Et_2O (2 x 30 mL) and the combined organic layers were dried ($MgSO_4$). The solvent was removed and the crude oil was purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 2-methyl-1-phenyl-(*IE*)-heptene-3-ol (1.3 g, 6.6 mmol, 66 %) as a colorless oil: R_f 0.24 (hexanes/EtOAc 8:1); IR (thin film) 3349, 3024, 2956, 2860, 1446, 1011 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.18-7.37 (m, 5H), 6.49 (br s, 1H), 4.18 (t, J = 6.6 Hz, 1H), 1.87 (d, J = 1.2 Hz, 3H), 1.65 (app. q, J = 6.5 Hz, 2H), 1.59 (br s, 1H), 1.24-1.44 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 137.6, 128.9, 128.1, 126.4, 125.7, 78.2, 34.8, 28.0, 22.6, 14.0, 13.1; HRMS (EI, m^+) for $C_{14}H_{20}O$ calcd 204.1514, found: m/z 204.1510.

2-Methyl-1-phenyl-(*IE*)-heptene-3-ol (2.1 g, 10.3 mmol) was dissolved in freshly distilled CH_2Cl_2 (30 mL). To the solution was added powdered 4 Å molecular sieves (7 g). The temperature of the reaction mixture was dropped to 0°C before adding NMO (1.8 g, 31 mmol) in one portion. At low temperature, tetrapropylammonium perruthenate (0.17 g, 0.50 mmol) was next added in three equal portions. The reaction was left to stir at room temperature for 5 h before being quenched by filtration through a silica gel plug. The solvent was removed and the crude material purified by gradient column chromatography (silica gel, hexanes:EtOAc 50:1, 40:1, 30:1, 20:1) to yield (*IE*)-2-methyl-1-phenyl-heptene-3-one (1.6 g, 7.8 mmol, 76 %) as a colorless oil: R_f 0.42 (hexanes/EtOAc 8:1); IR (thin film) 3057, 2958, 2932, 2872, 1667 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.52 (br q, J = 1.2 Hz, 1H), 7.31-7.43 (m, 5H), 2.80 (t, J = 7.5 Hz, 2H), 2.07 (d, J = 1.5 Hz, 3H), 1.68 (pent, J = 7.5 Hz, 2H), 1.40 (sextet, J = 7.2 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 138.3,

137.5, 136.1, 129.7, 128.4, 128.4, 37.4, 27.1, 22.5, 13.9, 13.2; HRMS (EI, M⁺) for C₁₄H₁₈O calcd 202.1358, found: m/z 202.1363.

(*1E*)-2-Methyl-1-phenyl-heptene-3-one (0.20 g, 1.0 mmol) was dissolved in anhydrous THF (2.5 mL). The temperature of the solution was dropped to 0°C. Freshly distilled triethylamine (0.35 mL, 2.5 mmol) was added dropwise to the reaction mixture. Triisopropylsilyl trifluoromethanesulfonate (0.32 mL, 1.2 mmol) was added dropwise and the solution was stirred at 0°C for 4 h. The reaction was quenched with a mixture of triethylamine (0.5 mL), hexanes (2.5 mL), and saturated NaHCO₃ solution (5 mL). The organic layer was washed with H₂O (2 x 5 mL) and brine (5 mL) and dried (MgSO₄). The solvent was removed to yield (*1E,3Z*)-2-methyl-1-phenyl-3-(triisopropylsiloxy)-hepta-1,3-diene, **5g**, (16:1, (*1E,3Z*):(*1E,3E*); 0.33 g, 0.93 mmol, 93 %) as a pale yellow oil: R_f 0.75 (hexanes/EtOAc 8:1); IR (thin film) 3022, 2958, 2867, 1622, 1464, 1090 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.26-7.28 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.86 (s, 1H), 4.97 (t, *J* = 7.0 Hz, 1H), 2.19 (q, *J* = 7.0 Hz, 2H), 1.99 (s, 3H), 1.43 (sextet, *J* = 7.5 Hz, 2H), 1.22-1.30 (m, 3H), 1.14 (d, *J* = 7.0 Hz, 18H), 0.96 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 152.0, 138.4, 134.9, 129.1, 128.0, 126.2, 125.3, 111.1, 28.5, 23.0, 18.1, 15.5, 14.1, 13.9; HRMS (EI, M⁺) for C₂₃H₃₈OSi calcd, 358.2692, found: m/z 358.2684.

(3E)-2-(triisopropylsiloxy)-6-phenyl-1,3-hexadiene (5h). 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 being quenched by the addition of hexanes (25 mL). The addition of hexanes precipitated a white solid, which was removed by filtration. The solvent was removed and the crude oil was purified by flash column chromatography (silica gel, hexanes:EtOAc 15:1) to yield 6-phenyl-(*3E*)-hexene-2-one (0.09 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, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 198.5, 147.0, 140.6, 131.7, 128.5, 128.3, 126.2, 34.4, 34.1, 26.9; HRMS (EI, M⁺) for C₁₂H₁₄O 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 temperature of the solution was dropped to 0°C. 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 NaHCO₃ solution (5 mL). The organic layer was washed with H₂O (2 x 5 mL) and brine (5 mL) and dried (MgSO₄). The solvent was removed to yield (*3E*)-2-(triisopropylsiloxy)-6-phenyl-1,3-hexadiene, **5h**, (0.25 g, 0.84 mmol, 98%) as a clear, colorless oil: R_f 0.82 (hexanes:EtOAc 8:1); IR (thin film) 3028, 2944, 2867, 1589, 1464, 1321, 1028, 883, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 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 (dt, *J* = 7.5, 7.5 Hz, 2H), 1.16-1.27 (m, 3H), 1.10 (d, *J* = 6.6 Hz, 18H); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₁H₃₄OSi calcd 330.2379, found: m/z 330.2375.

1,1-Dichloro-2-(ethenyl)-2-triisopropylsilyloxycyclopropane (6a). Siloxy diene, **5a**, (0.46 g, 2.0 mmol) was dissolved in CHCl₃ (0.2 mol, 16 mL). Benzyltriethylammonium chloride (0.13 g, 0.60 mmol) was added to the reaction mixture. A solution of 50 % NaOH aq. (0.37 mol, 19.5 mL) was then added in one portion and the reaction was vigorously stirred at room temperature for 4 h. The reaction was quenched by dilution with CH₂Cl₂ (20 mL) and H₂O (20 mL). The organic layer was washed with H₂O (2 x 20 mL). The aqueous layer was extracted with CH₂Cl₂ (2 x 20 mL) and the combined organic layers were dried (MgSO₄). The solvent was removed and the crude oil was purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield 1,1-dichloro-2-(ethenyl)-2-triisopropylsilyloxycyclopropane (0.57 g, 1.86 mmol, 93 %) as a pale yellow oil: *R_f* 0.69 (hexanes/EtOAc 10:1); IR (thin film) 2946, 2893, 2868, 1464, 1228, 1070, 883, 682 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.09 (ddd, *J* = 1.0, 10.5, 17.0 Hz, 1H), 5.37 (d, *J* = 10.5 Hz, 1H), 5.32 (d, *J* = 17.0 Hz, 1H), 1.88 (d, *J* = 8.5 Hz, 1H), 1.69 (dd, *J* = 1.0, 8.5 Hz, 1H), 1.07-1.16 (m, 21H); ¹³C NMR (125 MHz, CDCl₃) δ 135.9, 118.4, 65.4, 64.6, 32.4, 18.3, 18.2, 13.0; HRMS (EI, [M-Cl]⁺) for C₁₄H₂₆OSiCl calcd 273.1441, found: *m/z* 273.1445.

1,1-Dichloro-2-(3-methyl-[*IE*]-buten-1-yl)-2-triisopropylsilyloxycyclopropane (6b). The aforementioned method was also employed in the synthesis of **6b** starting with (3*E*)-4-isopropyl-2-(triisopropylsiloxy)-1,3-butadiene (0.23 g, 0.84 mmol). The reaction was quenched after 1 h and the crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield 1,1-dichloro-2-(3-methyl-*trans*-buten-1-yl)-2-triisopropylsilyloxycyclopropane (0.28 g, 0.80 mmol, 95 %) as a colorless oil: *R_f* 0.78 (hexanes/EtOAc 20:1); IR (thin film) 2961, 2868, 1668, 1464, 1219, 1080, 970, 883, 769, 683 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.72 (d, *J* = 15.5 Hz, 1H), 5.66 (dd, *J* = 15.5, 6.0 Hz, 1H), 2.38 (app. octet, *J* = 6.5 Hz, 1H), 1.84 (d, *J* = 8.5 Hz, 1H), 1.61 (dd, *J* = 8.5, 1.0 Hz, 1H), 1.04-1.14 (m, 21H), 1.02 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.9, 124.7, 65.8, 64.3, 32.3, 31.1, 22.2, 22.0, 18.3, 18.2, 13.0; HRMS (EI, [M-Cl]⁺) for C₁₇H₃₂ClOSi calcd 315.1911, found: *m/z* 315.1895.

(*IE*)-1,1-Dichloro-2-(1-phenylpropen-2-yl)-2-triisopropylsilyloxycyclopropane (6c). The same method was employed in the synthesis of **6c** starting with (*IE*)-2-methyl-1-phenyl-3-(triisopropylsiloxy)-1,3-butadiene (0.30 g, 0.95 mmol). The reaction was quenched after 3 h and the crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield (*IE*)-1,1-dichloro-2-(1-phenylpropen-2-yl)-2-triisopropylsilyloxycyclopropane (0.30 g, 0.76 mmol, 80 %) as a colorless oil: *R_f* 0.58 (hexanes/EtOAc 20:1); IR (thin film) 3024, 2945, 2867, 1495, 1257, 1076, 700, 690 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.24-7.28 (m, 3H), 6.49 (s, 1H), 2.13 (s, 3H), 2.14 (d, *J* = 8.5 Hz, 1H), 1.78 (d, *J* = 8.5 Hz, 1H), 1.06-1.18 (m, 21H); ¹³C NMR (125 MHz, CDCl₃) δ 136.7, 135.8, 129.4, 128.9, 128.2, 127.0, 68.7, 64.8, 32.0, 18.0, 18.0, 16.0, 12.8; HRMS (EI, M⁺) for C₂₁H₃₂Cl₂OSi calcd 398.1599, found: *m/z* 398.1600.

1,1-Dichloro-2-(1-cyclohexenyl)-2-triisopropylsilyloxycyclopropane (6d). The same method was employed in the synthesis of **6d** starting with 1-triisopropylsiloxy-1-(cyclohexen-1-yl)-ethene (0.12 g, 0.45 mmol). The reaction was quenched after 20 min. and the crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield 1,1-dichloro-2-(1-cyclohexenyl)-2-triisopropylsilyloxycyclopropane (0.16 g, 0.43 mmol,

96 %) as a colorless oil: R_f 0.63 (hexanes/EtOAc 20:1); IR (thin film) 2943, 2867, 1464, 1249, 1099, 1081, 1069, 883, 682 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.70 (app. septet, $J = 2.0$ Hz, 1H), 2.38-2.45 (m, 1H), 2.11-2.19 (m, 1H), 2.04-2.09 (m, 2H), 1.92 (d, $J = 8.0$ Hz, 1H), 1.64-1.71 (m, 2H), 1.62 (d, $J = 8.0$ Hz, 1H), 1.56-1.64 (m, 2H), 1.07-1.16 (m, 21H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.8, 127.4, 67.3, 65.1, 31.5, 26.0, 25.3, 22.6, 22.3, 18.2, 18.2, 13.0; HRMS (EI, M^+) for $\text{C}_{17}\text{H}_{32}\text{OSiCl}_2$ calcd 362.1599, found: m/z 362.1599.

1,1-Dichloro-2-(1-cyclopentenyl)-2-triisopropylsilyloxycyclopropane (6e). The same method was employed in the synthesis of **6e** starting with 1-triisopropylsiloxy-1-(cyclopenten-1-yl)-ethene (0.15 g, 0.58 mmol). The reaction was quenched after 20 min. and the crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield 1,1-dichloro-2-(1-cyclopentenyl)-2-triisopropylsilyloxycyclopropane (0.20 g, 0.57 mmol, 97 %) as a colorless oil: R_f 0.63 (hexanes/EtOAc 20:1); IR (thin film) 2946, 2868, 1464, 1265, 1243, 1099, 1068, 883, 683 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.68 (app. pent., $J = 2.0$ Hz, 1H), 2.58-2.65 (m, 1H), 2.42-2.48 (m, 1H), 2.34-2.39 (m, 2H), 1.88-2.00 (m, 2H), 1.92 (d, $J = 8.0$ Hz, 1H), 1.70 (d, $J = 8.0$ Hz, 1H), 1.05-1.15 (m, 21H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.6, 131.0, 65.3, 63.0, 33.0, 32.8, 32.4, 23.9, 18.2, 18.2, 13.0; HRMS (EI, $[\text{M}-\text{Cl}]^+$) for $\text{C}_{17}\text{H}_{30}\text{OSiCl}$ calcd 313.1754, found: m/z 313.1755.

cis-1,1-Dichloro-2-(1-phenyl-[*IE*]-propen-2-yl)-3-propyl-2-triisopropylsilyloxycyclopropane (6g). The same method was employed in the synthesis of **6g** starting with (*IE*,3*Z*)-1-phenyl-3-(triisopropylsiloxy)-1,3-heptadiene (0.10 g, 0.28 mmol). The reaction was quenched after 1.5 h, and the crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield (*IE*)-1,1-dichloro-2-(1-phenylpropen-2-yl)-3-propyl-2-triisopropylsilyloxycyclopropane (0.11 g, 0.24 mmol, 87 %) as a colorless oil: R_f 0.69 (hexanes/EtOAc 25:1); IR (thin film) 3027, 2947, 2868, 1630, 1464, 1257, 884, 682 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.36 (t, $J = 7.5$ Hz, 2H), 7.25-7.29 (m, 3H), 6.61 (s, 1H), 2.11 (d, $J = 1.5$ Hz, 3H), 1.86-1.88 (m, 1H), 1.57-1.65 (m, 4H), 1.08-1.14 (m, 21H), 1.03 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.8, 136.2, 131.4, 128.9, 128.3, 127.0, 70.8, 69.2, 38.8, 26.8, 21.6, 18.3, 18.1, 16.8, 14.0, 13.9; HRMS (EI, M^+) for $\text{C}_{24}\text{H}_{38}\text{Cl}_2\text{OSi}$ calcd 440.2069, found: m/z 440.2078.

(*IE*)-1,1-Dichloro-2-(4-phenyl-1-butenyl)-2-triisopropylsilyloxycyclopropane (6h). The same method was employed in the synthesis of **6h** starting with (*IE*)-2-(triisopropylsiloxy)-6-phenyl-1,3-hexadiene (0.26 g, 0.80 mmol). The reaction was quenched after 2 h and the crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 50:1) to yield (*IE*)-1,1-dichloro-2-(4-phenyl-1-butenyl)-2-triisopropylsilyloxycyclopropane (0.27 g, 0.65 mmol, 72 %) 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) δ 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 (dt, $J = 7.0, 7.0$ 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) δ 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, $[\text{M}-\text{Cl}]^+$) for $\text{C}_{22}\text{H}_{34}\text{OSiCl}$ calcd 377.2068, found: m/z 377.2066.

1-Phenyl-4-chloro-octa-1,4-dien-3-one (7f). The 2-siloxy-diene, **5f**, (0.12 g, 0.35 mmol) was dissolved in anhydrous toluene (0.1 M, 3.5 mL). CHCl_3 (0.11 mL, 1.43 mmol) was then added and the temperature was dropped to 0°C . Potassium *tert*-butoxide (0.16 g, 1.4 mmol) was added in portions at 0°C . The reaction was allowed to stir at low temperature for 1 h before CHCl_3 (0.057 mL, 0.71 mmol) and potassium *tert*-butoxide (0.08 g, 0.70 mmol) were added once again. The reaction was quenched by pouring into ice water after 1 h stirring at room temperature. The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The organic layer was washed with H_2O (2 x 10 mL) and dried (MgSO_4). The crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc 10:1) to yield 1-phenyl-4-chloro-octa-1,4-dien-3-one (0.045 g, 0.19 mmol, 55 %) as a white solid: m.p. $69\text{--}70^\circ\text{C}$; R_f 0.40 (hexanes/EtOAc 8:1); IR (thin film) 3028, 2962, 2932, 2873, 1666, 1617, 1576, 1330, 759 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.83 (d, $J = 15.6\text{ Hz}$, 1H), 7.66–7.69 (m, 2H), 7.44–7.49 (m, 4H), 7.12 (t, $J = 7.2\text{ Hz}$, 1H), 2.49 (q, $J = 7.2\text{ Hz}$, 2H), 1.65 (sextet, $J = 7.5\text{ Hz}$, 2H), 1.07 (t, $J = 7.5\text{ Hz}$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 184.1, 145.3, 141.0, 134.6, 134.0, 130.7, 128.9, 128.5, 120.5, 31.7, 21.2, 13.9; HRMS (EI, M^+) for $\text{C}_{14}\text{H}_{15}\text{ClO}$ calcd, 234.0811, found: m/z 234.0805; Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{ClO}$: C, 71.64; H, 6.44. Found: C, 71.31; H, 6.49.

2-Chloro-cyclopentenone (9a). 1,1-Dichloro-2-(ethenyl)-2-triisopropylsilyloxycyclopropane, **6a**, (0.10 g, 0.35 mmol) was dissolved in CH_2Cl_2 (0.05 M, 7.0 mL). AgBF_4 (0.10 g, 0.52 mmol) was added in one portion and the reaction mixture stirred at room temperature. The reaction was quenched after 24 h stirring by filtration through a pad of celite and silica gel. This compound was only observed as the major product in a crude reaction mixture. The product was not isolated since it readily decomposed during attempted purification by silica gel or alumina chromatography. Its presence was implied by partial spectral data: R_f 0.12 (hexanes/EtOAc 8:1); ^1H NMR (500 MHz, CDCl_3) δ 7.60 (t, $J = 3.0\text{ Hz}$, 1H), 2.68–2.71 (m, 2H), 2.53–2.58 (m, 2H).

5-Chloro-3-isopropyl-cyclopentenone (8b) and 2-Chloro-4-isopropyl-cyclopentenone (9b). 1,1-Dichloro-2-(3-methyl-*trans*-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **6b**, (0.12 g, 0.33 mmol) was dissolved in CH_2Cl_2 (0.05 M, 6.6 mL). AgBF_4 (0.096 g, 0.50 mmol) was added in one portion and the reaction mixture stirred at room temperature. The reaction was quenched after 4 h stirring at room temperature, by filtration through a pad of celite and silica gel. The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 50:1, 30:1, 25:1, 15:1, 10:1) to yield 5-chloro-3-isopropyl-cyclopentenone, **8b**, (0.017 g, 0.11 mmol, 33 %), 2-chloro-4-isopropyl-cyclopentenone, **9b**, (0.010 g, 0.06 mmol, 19 %) and small amounts of 2-hydroxy-4-*I*-propylcyclopentenone³ (presumed to result from capture of the Nazarov 2-siloxy-cyclopentenyl cation by adventitious water).

5-Chloro-3-isopropyl-cyclopentenone (8b). This compound was isolated as a pale yellow oil: R_f 0.28 (hexanes/EtOAc 8:1); IR (thin film) 2968, 2933, 2875, 1719, 1610, 1174, 878, $859, 757\text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3) δ 6.01 (dd, $J = 3.0, 2.0\text{ Hz}$, 1H), 4.28 (dd, $J = 7.0, 3.0\text{ Hz}$, 1H), 3.22 (dddd, $J = 19.0, 7.0, 2.0, 1.0\text{ Hz}$, 1H), 2.78 (dddd, $J = 19.0, 2.5, 2.0, 1.0\text{ Hz}$, 1H), 2.65 (sept., $J = 7.0\text{ Hz}$, 1H), 1.20 (d, $J = 7.0\text{ Hz}$, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.3, 185.6, 125.5, 54.2, 40.7, 32.4, 20.7; HRMS (EI, M^+) for $\text{C}_8\text{H}_{11}\text{ClO}$ calcd 158.0498, found: m/z 158.0500.

2-Chloro-4-isopropyl-cyclopentenone (9b). This compound was isolated as a colorless oil: R_f 0.39 (hexanes/EtOAc 8:1); IR (thin film) 2962, 2930, 2873, 1725, 1625, 1597, 1466, 1296, 1273, 959, 884 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.55 (d, $J = 2.5$ Hz, 1H), 2.76 (dddd, $J = 6.5, 6.0, 2.0, 2.0$ Hz, 1H), 2.60 (dd, $J = 19.0, 6.5$ Hz, 1H), 2.24 (dd, $J = 19.0, 2.0$ Hz, 1H), 1.79 (app. octet, $J = 7.0$ Hz, 1H), 0.98 (d, $J = 7.0$ Hz, 3H), 0.96 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.7, 159.9, 135.8, 44.9, 37.5, 31.8, 19.8, 19.7; HRMS (EI, M^+) for $\text{C}_8\text{H}_{11}\text{ClO}$ calcd 158.0498, found: m/z 158.0494.

2-Hydroxy-4-isopropyl-2-cyclopentenone. This compound was isolated in variable low yields under the previously mentioned reaction conditions: R_f 0.14 (hexanes/EtOAc 8:1); IR (thin film) 3351, 2960, 2931, 2873, 1699, 1652, 1396, 1240, 1199, 1105 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.53 (d, $J = 3.5$ Hz, 1H), 5.49 (br. s, 1H), 2.63 (dddd, $J = 6.0, 6.0, 3.0, 1.5$ Hz, 1H), 2.51 (dd, $J = 19.5, 6.0$ Hz, 1H), 2.14 (dd, $J = 19.5, 1.5$ Hz, 1H), 1.70 (app. octet, $J = 6.5$ Hz, 1H), 0.95 (d, $J = 6.5$ Hz, 3H), 0.93 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 203.4, 152.6, 132.0, 41.3, 36.7, 32.2, 19.8, 19.7; HRMS (EI, M^+) for $\text{C}_8\text{H}_{12}\text{O}_2$ calcd 140.0837, found: m/z 140.0838.

5-Chloro-2-methyl-3-phenyl-cyclopentenone (8c). The above procedure was used in the preparation of **8c** starting with (*E*)-1,1-dichloro-2-(1-phenylpropen-2-yl)-2-triisopropylsilyloxycyclopropane, **6c**, (0.08 g, 0.20 mmol). The reaction was quenched after 48 h stirring at room temperature. The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 20:1, 15:1, 10:1, 8:1, 5:1) to yield 5-chloro-2-methyl-3-phenyl-cyclopentenone (0.04 g, 0.17 mmol, 87 %) as an off-white solid: m.p. 99–100°C; R_f 0.26 (hexanes/EtOAc 8:1); IR (thin film) 3056, 2943, 1702, 1615, 1352, 762, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47–7.55 (m, 5H), 4.43 (dd, $J = 7.2, 2.8$ Hz, 1H), 3.51 (ddq, $J = 18.0, 6.8, 2.0$ Hz, 1H), 3.14 (ddq, $J = 18.4, 2.0, 2.0$ Hz, 1H), 2.05 (t, $J = 2.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.5, 163.8, 135.3, 134.7, 130.6, 129.1, 128.0, 53.2, 40.7, 10.6; HRMS (EI, M^+) for $\text{C}_{12}\text{H}_{11}\text{ClO}$ calcd 208.0469, found: m/z 208.0467; Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{ClO}$: C, 69.74; H, 5.36. Found: C, 69.75; H, 5.50.

$\Delta^{1,6}$ -8-Chloro-bicyclo[4.3.0]nonen-7-one (8d). The above procedure was used in the preparation of **8d** starting from 1,1-dichloro-2-(1-cyclohexenyl)-2-triisopropylsilyloxycyclopropane, **6d**, (0.11 g, 0.29 mmol). The reaction was quenched after 30 h stirring at room temperature. The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 50:1, 30:1, 25:1, 20:1, 10:1) to yield $\Delta^{1,6}$ -8-chloro-bicyclo[4.3.0]nonen-7-one (0.022 g, 0.13 mmol, 45 %) as a colorless oil: R_f 0.13 (hexanes/EtOAc 8:1); IR (thin film) 2933, 2863, 1713, 1643, 1399, 1279, 731 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.26 (dd, $J = 7.0, 2.5$ Hz, 1H), 3.12 (app. dd, $J = 18.5, 7.0$ Hz, 1H), 2.68 (app. d, $J = 19.0$ Hz, 1H), 2.26–2.41 (m, 2H), 2.14–2.24 (m, 2H), 1.74–1.79 (m, 2H), 1.66–1.72 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 203.1, 171.3, 137.2, 53.6, 41.6, 28.6, 22.1, 21.7, 20.4; HRMS (EI, M^+) for $\text{C}_9\text{H}_{11}\text{OCl}$ calcd 172.0469, found: m/z 172.0466.

$\Delta^{1,5}$ -3-Chloro-bicyclo[3.3.0]octen-2-one (8e). The above procedure was used in the preparation of **8e** starting from 1,1-dichloro-2-(1-cyclopentenyl)-2-triisopropylsilyloxycyclopropane, **6e**, (0.12 g, 0.33 mmol). The reaction was quenched after 48 h stirring at room temperature. The crude material was purified by gradient column

chromatography (silica gel, hexanes:EtOAc 50:1, 30:1, 25:1, 20:1, 10:1) to yield $\Delta^{1,5}$ -3-chloro-bicyclo[3.3.0]octen-2-one (0.038 g, 0.24 mmol, 73 %) as a colorless oil: R_f 0.11 (hexanes/EtOAc 8:1); IR (thin film) 2925, 2855, 1709, 1631, 1387, 732 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.54 (dd, $J = 6.5, 2.5$ Hz, 1H), 3.20 (app. dd, $J = 18.5, 6.4$ Hz, 1H), 2.71 (app. d, $J = 19.0$ Hz, 1H), 2.56-2.61 (m, 2H), 2.43-2.48 (m, 2H), 2.38 (app. pent, $J = 6.4$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 195.9, 184.1, 146.7, 59.3, 37.8, 32.5, 27.3, 25.2; HRMS (EI, M^+) for $\text{C}_8\text{H}_9\text{OCl}$ calcd 156.0342, found: m/z 156.0341.

5-Chloro-2-methyl-3-phenyl-4-propyl-cyclopentenone (8g) and 2-Chloro-5-methyl-4-phenyl-3-propyl-cyclopentenone (9g). The above procedure was used in the preparation of **8g** and **9g** starting from (*IE*)-1,1-dichloro-2-(1-phenyl-propen-2-yl)-3-propyl-2-triisopropylsilyloxycyclopropane, **6g**, (0.10 g, 0.23 mmol). The reaction was quenched after 1 h stirring at room temperature. Purification by gradient column chromatography (silica gel, hexanes:EtOAc 20:1, 15:1, 10:1, 8:1, 5:1) yielded **8g(cis)** : **9g(cis)** : **8g(trans)** : **9g(trans)** (7.7 : 4.5 : 3 : 1, 87 %).³ Products **9g(cis)** and **8g(trans)** were inseparable by standard techniques.

Major product **8g(cis)** could be converted to the more stable **8g(trans)** by stirring in Et_2O in the presence of DBU to give a 12 : 1 mixture in favor of the *trans* diastereomer.

5-Chloro-2-methyl-3-phenyl-4-propyl-cyclopentenone (8g(cis)). This sample was isolated as a colorless oil: R_f 0.29 (hexanes/EtOAc 8:1); IR (thin film) 3059, 2959, 2932, 2872, 1713, 1624, 1346, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.44-7.50 (m, 3H), 7.34-7.40 (m, 2H), 4.64 (d, $J = 6.5$ Hz, 1H), 3.55-3.58 (m, 1H), 1.92 (d, $J = 2.0$ Hz, 3H), 1.56-1.62 (m, 2H), 1.19-1.26 (m, 2H), 0.80 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.9, 168.5, 134.9, 134.5, 129.5, 128.7, 127.4, 59.9, 45.3, 32.0, 20.1, 13.8, 9.8; HRMS (EI, M^+) for $\text{C}_{15}\text{H}_{17}\text{ClO}$ calcd 248.0968, found: m/z 248.0968.

2-Chloro-5-methyl-4-phenyl-3-propyl-cyclopentenone (9g(cis)). The sample was contaminated with (**8g(trans)**), thus complete spectral data could not be reported: R_f 0.35 (hexanes/EtOAc 8:1); Partial ^1H NMR (500 MHz, CDCl_3) δ 4.20 (d, $J = 7.0$ Hz, 1H), 2.86 (pent, $J = 7.5$ Hz, 1H), 2.64 (ddd, $J = 14.0, 9.5, 7.0$ Hz), 2.13 (ddd, $J = 14.5, 9.5, 5.5$ Hz, 1H), 1.39-1.56 (m, 2H), 0.91 (t, $J = 7.5$ Hz, 3H), 0.75 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 203.1, 172.4, 137.2, 132.6, 128.7, 127.8, 127.6, 51.5, 44.3, 31.6, 19.9, 14.1, 12.2.

5-Chloro-2-methyl-3-phenyl-4-propyl-cyclopentenone (8g(trans)). The sample was contaminated with (**9g(cis)**), thus complete spectral data could not be reported: R_f 0.35 (hexanes/EtOAc 8:1); ^1H NMR (500 MHz, CDCl_3) δ 7.43-7.51 (m, 3H), 7.35-7.37 (m, 2H), 4.05 (d, $J = 2.5$ Hz, 1H), 3.41 (app. d, $J = 10.0$ Hz, 1H), 1.91 (d, $J = 2.0$ Hz, 3H), 1.66 (dddd, $J = 14.0, 10.5, 6.5, 3.0$ Hz, 1H), 1.35-1.50 (m, 2H), 1.20-1.30 (m, 1H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.7, 169.3, 134.8, 134.4, 129.7, 128.7, 127.8, 58.6, 51.9, 34.6, 20.0, 13.9, 9.8.

2-Chloro-5-methyl-4-phenyl-3-propyl-cyclopentenone (9g(trans)). This sample was isolated as a colorless oil: R_f 0.41 (hexanes/EtOAc 8:1); IR (thin film) 3027, 2962, 2931, 2873, 1723, 1618, 1455, 703 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.37 (m, 2H), 7.28-7.32 (m, 1H), 7.11-7.13 (m, 2H), 3.49 (d, $J = 3.0$ Hz, 3H), 2.58 (ddd, $J = 13.5, 9.5, 7.5$ Hz,

1H), 2.44 (qd, $J = 7.5, 2.5$ Hz, 1H), 2.07 (ddd, $J = 14.5, 9.0, 5.5$ Hz, 1H), 1.49-1.56 (m, 1H), 1.38-1.44 (m, 1H), 1.29 (d, $J = 7.5$ Hz, 3H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 203.1, 173.0, 140.3, 131.8, 129.4, 127.9, 127.8, 56.0, 50.1, 31.3, 20.3, 15.5, 14.2; HRMS (EI, M^+) for $\text{C}_{15}\text{H}_{17}\text{ClO}$ calcd 248.0968, found: m/z 248.0973.

2,3,4,5-Tetrahydrocyclopenta[*a*]naphthalen-1-one (10h). The above procedure was used in the preparation of **10h** from (*1E*)-1,1-dichloro-2-(4-phenyl-1-buten-1-yl)-2-triisopropylsilyloxycyclopropane, **6h**, (0.09 g, 0.22 mmol). The reaction was quenched after 18 h stirring at room temperature. The crude material was purified by gradient column chromatography (silica gel, hexanes:EtOAc 20:1, 15:1, 10:1, 8:1, 5:1) to yield 2,3,4,5-tetrahydrocyclopenta[*a*]naphthalen-1-one (0.028 g, 0.15 mmol, 63 %) 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) δ 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) δ 202.8, 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 $\text{C}_{13}\text{H}_{12}\text{O}$ calcd 184.0888, found: m/z 184.0886. (Data are in accord with previously published literature values.⁴)

References

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Compound 5a
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Apr 19 2006 sweep width: 5999Hz acq.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
 spectrometer:d601 file:/mnt/d600/home13/westnmt/nmrdata/T_Granny/TNG8/TNG8-MVK_TIPS.fid

Pulse Sequence: s2pul

Compound 5a
 125 MHz 1D ¹³C in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Apr 19 2006 sweep width: 3375Hz acq.time: 1.9s relax.time: 0.1s # scans: 64 d1g.res.: 0.3 Hz/pt hz/mm:136.3
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG8/TNG8-MVK_TRIPS_13C.fid

Pulse Sequence: s2pul

Compound 5b
 400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
 date: Apr 17 2006 sweep width: 4802Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm: 20.0
 spectrometer: d601 file: /mnt/d600/home13/westnmt/nmrdata/T_Granny/TNG8/TNG8-11a.fid

Pulse Sequence: s2pul

Compound 5b
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Mar 6 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 304 dig.res.: 0.5 Hz/pt hz/mm:140.9
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-62a_APT.fid

Pulse Sequence: apt

Compound 5c
 500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Jan 28 2006 sweep width: 6002Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm: 21.1
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-32a_TIPS.fid

Pulse Sequence: s2pul

Compound 5c
 125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Sep 7 2005 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 152 d1g.res.: 0.5 Hz/pt hz/mm: 119.2
 spectrometer: d601 file: /mnt/d600/home13/westmnr/nmrdata/T_Granny/TNG6/TNG6-46a_APT.fid

Pulse Sequence: apt

Compound 5d

Pulse Sequence: s2pul

500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
date: Nov 17 2005 sweep width: 6002Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 d1g.res.: 0.1 Hz/pt hz/mm:22.2
spectrometer:d601 file:/mnt/d600/home13/westmr/nmrdata/T_Granny/TNG6/TNG6-70a.fld

Compound 5d
 125 MHz APT 1h CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Nov 22 2005 sweep width: 22516Hz acq.time: 2.0s relax.time: 0.1s # scans: 568 d1g.res.: 0.3 Hz/pt hz/mm: 93.8
 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG6-78a_APT.fid
 spectrometer: d601

Pulse Sequence: apt

Compound 5e
 500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Nov 22 2005 sweep width: 6001Hz acq.time: 3.0s # scans: 16 d1g.res.: 0.1 Hz/pt hz/mm: 25.0
 spectrometer: d601 file: /mnt/d600/home13/westnmt/nmrdata/T_Granny/TNG6/TNG6-79a.fid

Pulse Sequence: s2pul

Compound 5e
 125 MHz APt in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Nov 22 2005 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 368 dig.res.: 0.5 Hz/pt hz/mm:140.9
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG6/TNG6-79a_Apt.fld

Pulse Sequence: apt

Compound 5f
 500 MHz 1D 1H CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Dec 3 2005 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pk hz/mm:25.0
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/r_Granny/TNG6/TNG6-88a.f1d

Pulse Sequence: s2pu1

Compound 5f
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Dec 6 2005 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 888 dig.res.: 0.5 Hz/pt hz/mm: 113.6
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG6/TNG6-88a_APT.fid

Pulse Sequence: apt

Pulse Sequence: s2pul

Compound 5g
 125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Apr 20 2006 sweep width: 33755Hz acq.time: 1.9s relax.time: 0.1s # scans: 632 dig.ref: 0.3 Hz/pt hz/mm: 140.6
 file: /mnt/d600/home13/westnmt/nmrdata/T_Granny/TNG8/2006.04.20.us_TNG8-17b_C13_1D.fid
 spectrometer: d601

Pulse Sequence: szpul

Compound 5h
 400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
 date: Feb 21 2006 sweep width: 4802Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.0
 spectrometer:d601 file:/mnt/d600/home13/westnmt/nmrdata/T_Granny/TNG7/TNG7-46a.fld

Pulse Sequence: szpul

Compound 5h
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Mar 6 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 336 dig.res.: 0.5 Hz/pt hz/mm:140.9
 spectrometer:d601 file:/mnt/d600/home13/westnmt/nmrdata/TNG7/TNG7-63a_APT.fid

Pulse Sequence: apt

Compound 6a
 500 MHz 1D 1H NMR CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Jul 28 2005 sweep width: 6002Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 d1g.res.: 0.1 Hz/pt hz/mm: 25.0
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG6/TNG6-10a.fid

Pulse Sequence: s2pu1

Compound 6a
 100 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm) Temp 26.8 C -> actual temp = 27.0 C, asw400 probe
 date: Apr 17 2006 sweep widch: 26954Hz acq.time: 2.5s relax.time: 0.1s # scans: 16588 dig.res.: 0.2 Hz/pt hz/mm:112.3
 file:/mnt/d600/home13/westnmt/nmrdata/r/granny/TNG8-TNG8-13a_13c.fid
 spectrometer:d601

Pulse Sequence: szpul

Compound 6b
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Mar 7 2006 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 d1g.res.: 0.1 Hz/pt hz/mm: 25.0
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-66a.fld

Pulse Sequence: s2pul1

Compound 6b
 125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Mar 8 2006 sweep width: 33755Hz acq.time: 1.9s relax.time: 0.1s # scans: 1048 d1g.res.: 0.3 Hz/pt hz/mm: 140.6
 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-66a_13C.fid
 Spectrometer: d601

Pulse Sequence: szpul

Compound 6c
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Sep 7 2005 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 d1g.res.: 0.1 Hz/pt hz/mm: 20.3
 spectrometer: d601 file: /mnt/d600/home13/weschnr/nmrdata/1_granny/TMG6/TMG6-48b.fid

Pulse Sequence: s2pul

Compound 6c
 125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Feb 27 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 416 dig.res.: 0.5 Hz/pt hz/mm:122.7
 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-35b_TIPS_APF.fid
 spectrometer:d601

Pulse Sequence: apt

Compound 6d
 400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
 date: Mar 21 2006 sweep width: 4802Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm: 20.0
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-79a.fid

Pulse Sequence: szpul

Compound 6d
 125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Mar 22 2006 sweep width: 3375Hz acq.time: 1.9s relax.time: 0.1s # scans: 3972 d1g.res.: 0.3 Hz/pt hz/mm: 123.9
 spectrometer: d601 file: /mnt/d600/home13/westnmt/nmrdata/Tf_Granny/TNG7/TNG7-79a_13C.fid

Pulse Sequence: szpul

Compound 6e
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Mar 22 2006 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 0 d1g.res.: 0.1 Hz/pt hz/mm: 25.0
 spectrometer: d601 file: /mnt/d600/home13/westnmt/nmrdata/T_Granny/TNG7/TNG7-84a.fid

Pulse Sequence: s2pul

Compound 6e
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Mar 22 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 0 dig.res.: 0.5 Hz/pt hz/mm:120.1
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TMG7/TMG7-84a_APT.fid

Pulse Sequence: apt

Compound 6g
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Apr 1 2006 sweep width: 5999Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 d1g.res.: 0.1 Hz/pt hz/nm: 19.4
 spectrometer: d601 file: /mnt/d600/home13/westnmc/nmrdata/T_Granny/TNG7/TNG7-97c.fld

Pulse Sequence: szpul

Compound 6g
 125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Apr 1 2006 sweep width: 33755Hz acq.time: 1.9s relax.time: 0.1s # scans: 144 dig.res.: 0.3 Hz/pt hz/mm: 114.4
 file: /mnt/d600/home13/westmt/nmrdata/r_Granny/TNG7/TNG7-97a_13C.fid
 spectrometer: d601

Pulse Sequence: szpul

Compound 6h
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Mar 8 2006 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 d1g.res.: 0.1 Hz/pt hz/mm:22.5
 spectrometer:d601 file:/mnt/d600/home13/westmr/nmrdata/T_NGranny/TNG7/TNG7-67a.fld

Pulse Sequence: s2pul

Compound 6h
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Mar 8 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 1336 dig.res.: 0.5 Hz/pt hz/mm: 140.9
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-67a_APT.fid

Pulse Sequence: apt

Compound 8b
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Apr 12 2006 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dtg.res.: 0.1 Hz/pt hz/mm: 25.0
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG8-8d.fid

Pulse Sequence: szpu1

Compound 8b
 125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Apr 13 2006 sweep width: 33755Hz acq.time: 1.9s relax.time: 0.1s # scans: 1564 d1g.res.: 0.3 Hz/pt hz/nm: 134.8
 file: /mnt/d600/home13/westnmr/nmrdata/r_Granny/TN08/TN08-8d_13c.fid
 spectrometer: d601

Pulse Sequence: szpul

Compound 9b
 400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
 date: Apr 18 2006 sweep width: 4802Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 d1g.res.: 0.1 Hz/pt hz/mm:20.0
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG8/TNG8-14a.fid

Pulse Sequence: s2pul1

Compound 9b
125 MHz 1D C13 1n CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw5004 probe
date: Apr 13 2006 sweep width: 33755Hz acq.time: 1.9s relax.time: 0.1s # scans: 19464 dig.res.: 0.3 Hz/pt hz/mm: 140.6
spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG8/TNG8-8b_13C.fid

Pulse Sequence: szpul

2-Hydroxy-4-isopropyl-2-cyclopentenone
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Apr 14 2006 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:19.0
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TMG8-10c_1500.fid

Pulse Sequence: s2pul

2-Hydroxy-4-isopropyl-2-cyclopentenone
 125 MHz APF in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Apr 14 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 1248 dig.res.: 0.5 Hz/pt hz/mm:140.9
 spectrometer:d601 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG8/TNG8-10c_APF.fid

Pulse Sequence: apt

Compound 8d
 500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C
 date: Apr 18 2006 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16
 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG8/TNG8-3c.fld
 spectrometer:d601

dig.res.: 2.9 Hz/pt hz/mm:25.0

Pulse Sequence: s2pul

Compound 8d
 125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Apr 18 2006 sweep width: 33827Hz acq.time: 2.5s relax.time: 0.1s # scans: 624 d1g.ref.: 0.3 Hz/pt hz/mm: 140.9
 file: /mnt/d600/home13/westmt/nmrdata/T-granny/TNG8/TNG8-3C_13C.fid
 spectrometer: d601

Pulse Sequence: szpul

Compound 8e
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
date: Apr 14 2006 sweep width: 5999Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm: 20.3
spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG8/TNG8-4b.fid

Pulse Sequence: szpul

8e

Compound 8e
 125 MHz 1D C13 In CDCl3 (ref. to CDC13 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Apr 5 2006 sweep width: 33827Hz acq.time: 2.5s relax.time: 0.1s # scans: 784 d1g.res.: 0.3 Hz/pt hz/mm: 140.9
 file:/mnt/d600/home13/westnmt/nmrdata/T_Granny/TNG7/TNG7-87a_13C_.fid
 spectrometer:d601

Pulse Sequence: s2pul

Compound 8g(trans)
 500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Jan 16 2006 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
 spectrometer:d601 file:/mnt/d600/home13/westnmt/nmrdata/T_Granny/TMG7/TMG7-20e.fld

Pulse Sequence: s2pul

Compound 8g(trans)
 125 MHz APF 1n CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Jan 16 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 808 dig.res.: 0.5 Hz/pt hz/mm: 136.1
 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-20e_APF.fid
 spectrometer:d601

Pulse Sequence: apt

Compound 9g(cis)
 500 MHz ID in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Jan 16 2006 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm: 21.9
 spectrometer: d601 file: /mnt/d600/home13/westnmt/nmrdata/T_NG7/TNG7-20c.fid

Pulse Sequence: s2pul

Compound 9g(cis)
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 date: Feb 15 2006 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 1544 dig.res.: 0.5 Hz/pt hz/mm: 140.9
 file:/mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-20c_Apt.fid

Pulse Sequence: apt

Compounds 9g(trans) and 8g(cis)
 500 MHz 1D 1h CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
 date: Mar 6 2006 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm: 21.7
 spectrometer: d601 file: /mnt/d600/home13/westnmr/nmrdata/T_Granny/TNG7/TNG7-20d_F10-11.fid

Pulse Sequence: szpul

Compounds 9g(trans) and 9g(cis)
 125 MHz 1D C13 in CDCl3 (ref. to CDC13 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
 date: Apr 19 2006 sweep width: 33755Hz acq.time: 1.9s relax.time: 0.1s # scans: 25916 dig.res: 0.3 Hz/pt hz/mm:121.0
 file:/mnt/d600/home13/westnmt/nmrdata/r_Granny/TMG7/2006.04.19.u5_TMG7-2006_C13_1D.fid
 spectrometer:d601

Pulse Sequence: s2pul