Three-Carbon Ring Expansion by Cyclopropane Insertion: Macrocyclic Musks from Readily Available C-12 Starting Materials

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1. General Details

Flash chromatography: silica gel 60 (*Merk*), grain size 0.040–0.063 mm. IR Spectra: *Perkin-Elmer 1600 Series FT-IR* spectrometer. NMR Spectra: *Bruker ARX-300* (300/75 MHz) and *Avance DRX 600* (600/150 MHz); chemical shifts (δ , ppm) relative to CD(H)Cl₃ (7.27/77.00 ppm); for complete assignments of ¹H NMR signals COSY, TOCSY, NOESY, ROESY 2D- or 1D-NMR methods were applied; for complete assignments of ¹³C NMR signals HMBC, HSQC, and HSQC-TOCSY 2D-NMR methods were employed. GC/MS: *Hewlett Packard HP-5971 Series* (mass-selective detector; EI, 70 eV).

2. General procedure for the addition of Grignard reagents to cycloalk-3-en-1-ones.

A freshly prepared solution of the corresponding magnesium bromide (42 mmol) in dry THF (80 mL) was added at 0 °C to a suspension of the substrate ketone (30 mmol) and CeCl₃ (30 mmol) in dry THF (75 mL). The resulting mixture was allowed to warm to room temperature within 30 min and was subsequently quenched with saturated NH₄Cl (150 mL) and then poured into a separatory funnel containing ether (200 mL). The organic layer was separated, and the aqueous phase extracted with ether (3 × 150 mL). The combined organic layers were washed with saturated NH₄Cl and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel. An analytical sample was distilled (*Kugelrohr*).

(*E*)-1-Cyclopropylcyclododec-3-enol (10)

The reaction of (*E*)-3-cyclododecenone (6.0 g, 33.3 mmol) with cyclopropyl magnesium bromide following the general procedure afforded 7.3 g (98%) of the title compound as a colorless oil.

IR (film) 3445, 3083, 2925, 2851, 1462, 1444, 1349, 1299, 1197, 1144 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.65–5.45 (m, 2H), 2.24–2.21 (m, 2H), 2.14–2.07 (m, 2H), 1.61–1.26 (m, 15H), 1.01–0.86 (m, 1H), 0.44–0.28 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 134.5, 125.6, 73.0, 43.1, 37.3, 33.3, 28.5, 27.1, 26.1, 25.2, 24.4, 20.5, 19.1, 0.3, –0.4; MS *m/z* (rel intensity) 222 (3), 151 (12), 137 (9), 123 (8), 109 (8), 97 (45), 84 (68), 69 (100). Anal. Calcd for C₁₅H₂₆O (222.37): C, 81.02; H, 11.78. Found: C, 80.89; H, 11.91.

(E)-1-Cyclopropylcyclotridec-3-enol

The reaction of (*E*)-3-cyclotridecenone¹ (2.5 g, 12.9 mmol) with cyclopropyl magnesium bromide following the general procedure afforded 3.0 g (99%) of the title compound as a colorless oil.

IR (film) 3446, 3083, 3004, 2931, 2858, 1461, 1445, 1059, 971 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.53–5.33 (m, 2H), 2.18 (d, J = 6.6 Hz, 2H), 2.07–1.89 (m, 2H), 1.62–1.20 (m, 17H), 1.02–0.85 (m, 1H), 0.40–0.28 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.4, 126.2, 72.6, 43.1, 38.5, 32.3, 27.7, 27.6, 27.4, 25.1, 24.9, 24.6, 20.5, 19.3, 0.2, –0.1; MS m/z (rel intensity) 236 (1), 218 (2), 151 (10), 137 (7), 123 (8), 97 (51), 84 (73), 69 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}$ (236.40): C, 81.29; H, 11.93. Found: C, 81.42; H, 11.99.

(Z)-1-Cyclopropylcyclooct-3-enol

The reaction of (*Z*)-3-cyclooctenone^{2,3} (3.5 g, 28.2 mmol) with cyclopropyl magnesium bromide following the general procedure afforded 4.1 g (87%) of the title compound as a colorless oil.

IR (film) 3442, 3082, 3016, 2928, 2857, 1464, 1446, 1050, 1002, 942, 771 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.81–5.52 (m, 2H), 2.35 (dd, J = 12.9, 8.4 Hz, 1H), 2.23–2.10 (m, 3H), 1.64–1.39 (m, 7H), 1.00–0.91 (m, 1H), 0.40–0.27 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 132.4, 127.1, 74.7, 38.5, 37.1, 29.4, 26.5, 22.3, 20.4, 0.1, –0.1; MS m/z (rel intensity) 166 (3), 137 (7), 123 (10), 111 (12), 97 (81), 84 (40), 69 (100). HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{O}$ m/z 166.1358, found m/z 166.1358.

(E)-1-Isopropenylcyclododec-3-enol (9d)

The reaction of (*E*)-3-cyclododecenone (3.0 g, 16.6 mmol) with isopropenyl magnesium bromide following the general procedure afforded 3.6 g (96%) of the title compound as a colorless oil.

IR (film) 3398, 2926, 2852, 1462, 1446, 1372, 1120 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.66–5.47 (m, 2H), 4.92 (s, 1H), 4.85–4.83 (m, 1H), 2.53 (dd, J = 14.5, 8.1 Hz, 1H), 2.26 (dd, J = 14.5, 5.4 Hz, 1H), 2.12–2.01 (m, 2H), 1.78–1.21 (m, 18H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.3, 134.7, 125.7, 110.2, 76.7, 41.4, 34.8, 33.2, 28.3, 27.0, 25.5, 24.9, 24.5, 19.3, 18.8; MS m/z (rel intensity) 222 (3), 179 (5), 151 (4), 137 (9), 123 (12), 109 (14), 97 (39), 84 (56), 69 (100). HRMS (EI) calcd for $\text{C}_{15}\text{H}_{26}\text{O}$ m/z 222.1984, found m/z 222.1983.

(E)-1-[(Z)-Propen-1-yl]cyclododec-3-enol (9e)

The reaction of (*E*)-3-cyclododecenone (3.8 g, 21.1 mmol) with (*Z*)-propen-1-yl magnesium bromide following the general procedure afforded 4.5 g (97%) of the title compound as a colorless oil.

IR (film) 3368, 3012, 2929, 2849, 1552, 1346, 1160, 1009 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.61–5.38 (m, 4H), 2.38 (d, J = 7.0 Hz, 2H), 2.10 (q, J = 6.6 Hz, 2H), 1.87 (d, J = 5.3 Hz, 3H), 1.67–1.22 (m, 15H);

^{13}C NMR (75 MHz, CDCl_3) δ 136.1, 134.8, 126.3, 125.3, 75.8, 44.6, 37.8, 33.2, 28.4, 27.0, 26.0, 25.0, 24.3, 19.1, 14.3; MS m/z (rel intensity) 222 (1), 179 (2), 165 (2), 151 (4), 137 (4), 123 (6), 109 (6), 97 (33), 84 (42), 69 (100). HRMS (EI) calcd for $\text{C}_{15}\text{H}_{26}\text{O}$ m/z 222.1984, found m/z 222.1982.

(*E*)-1-[(*E*)-Propen-1-yl]cyclododec-3-enol

The reaction of (*E*)-3-cyclododecenone (2.6 g, 14.4 mmol) with (*E*)-propen-1-yl magnesium bromide following the general procedure afforded 2.9 g (90%) of the title compound as a colorless oil.

IR (film) 3359, 3013, 2930, 2847, 1471, 1442, 1345, 1160, 1008 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.62–5.36 (m, 4H), 2.38 (d, $J = 7.1$ Hz, 2H), 2.09 (q, $J = 6.6$ Hz, 2H), 1.88 (d, $J = 5.5$ Hz, 3H), 1.65–1.21 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.2, 132.6, 126.4, 125.0, 75.7, 39.1, 37.4, 35.8, 26.9, 26.4, 25.5, 22.1, 21.9, 19.9, 14.0; MS m/z (rel intensity) 222 (1), 179 (1), 165 (2), 151 (3), 137 (4), 123 (5), 109 (7), 97 (36), 84 (45), 69 (100). HRMS (EI) calcd for $\text{C}_{15}\text{H}_{26}\text{O}$ m/z 222.1984, found m/z 222.1982.

(*E*)-1-(2-Methylpropen-1-yl)cyclododec-3-enol (9f)

The reaction of (*E*)-3-cyclododecenone (2.5 g, 13.9 mmol) with 2-methylpropen-1-yl magnesium bromide following the general procedure afforded 3.2 g (99%) of the title compound as a colorless oil.

IR (film) 3415, 2926, 2854, 1461, 1376, 1119, 982 cm^{-1} ; ^1H NMR (300 MHz, C_6D_6) δ 5.61–5.43 (m, 2H), 5.31–5.29 (m, 1H), 2.44 (dd, $J = 13.8, 5.0$ Hz, 1H), 2.34 (dd, $J = 13.1, 6.6$ Hz, 1H), 2.06 (q, $J = 5.4$ Hz, 2H), 1.91 (d, $J = 1.2$ Hz, 3H), 1.66 (d, $J = 1.3$ Hz, 3H), 1.86–1.22 (m, 15H); ^{13}C NMR (75 MHz, C_6D_6) δ 134.4, 134.3, 131.5, 126.4, 74.7, 45.4, 38.5, 33.5, 28.7, 27.3, 26.5, 24.8, 24.4, 19.5, 19.0, 18.9; MS m/z (rel intensity) 236 (1), 218 (6), 175 (3), 147 (4), 133 (7), 119 (14), 105 (17), 98 (21), 83 (100). HRMS (EI) calcd for $\text{C}_{16}\text{H}_{28}\text{O}$ m/z 236.2140, found m/z 236.2141.

(*E*)-2-Methylcyclododec-3-enone

A solution of (*E*)-3-cyclododecenone (6.0 g, 33.3 mmol) in dry DMSO (20 mL) was added dropwise to a solution of *tert*-BuOK (3.7 g, 33.3 mmol) in dry DMSO (40 mL). The yellow solution was stirred for 15 min at room temperature and subsequently cooled to 0 °C at which methyl iodide (6.1 mL, 33.3 mmol) was added in one portion. After 5 min the yellow color of the solution disappeared and stirring was continued for 1 h at room temperature. The mixture was quenched with saturated NH_4Cl (150 mL) and then poured into a separatory funnel containing ether (200 mL). The organic layer was separated, and the aqueous phase extracted with ether (3 $\times$ 150 mL). The combined organic layers were washed with water, saturated NH_4Cl and brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 5% ethyl acetate in hexanes) affording 4.0 g (62%) of the title compound as a colorless oil. An analytical sample was distilled (Kugelrohr).

IR (film) 3011, 2932, 2860, 1707, 1463, 1366, 1196, 1046, 977 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.54–5.48 (m, 1H), 5.34–5.25 (m, 1H), 3.84–3.46 (m, 1H), 2.57 (ddd, $J = 13.9, 6.2, 5.4$ Hz, 1H), 2.31 (ddd, $J = 13.9, 10.1, 5.4$ Hz, 1H), 1.98–1.75 (m, 2H), 1.68–1.53 (m, 2H), 1.47–1.15 (m, 10H), 1.12 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 214.5, 130.7, 130.5, 41.6, 41.5, 26.8, 26.4, 24.8, 23.7, 23.6, 23.5, 22.9, 18.4; MS m/z (rel intensity) 194 (8), 151 (4), 137 (4), 123 (5), 109 (10), 95 (26), 81 (63), 68 (100). HRMS (EI) calcd for $\text{C}_{13}\text{H}_{22}\text{O}$ m/z 194.1671, found m/z 194.1669.

(1*R**,2*R**,3*E*)-1-Cyclopropyl-2-methylcyclododec-3-enol

The reaction of (*E*)-2-methylcyclododec-3-enone (2.3 g, 11.8 mmol) with cyclopropyl magnesium bromide carried out at $-30\text{ }^\circ\text{C}$ (!) following the general procedure afforded 2.4 g (86%) of the title compound as a colorless oil. A minor amount of the (1*RS*,2*SR*)-isomer (ca. 10%) was evident from GC/MS analysis.

IR (film) 3665, 3082, 3005, 2926, 2850, 1460, 1446, 1382, 982 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.50–5.33 (m, 1H), 5.29–5.15 (m, 1H), 2.99–2.87 (m, 1H), 2.53–2.40 (m, 1H), 1.91–1.78 (m, 1H), 1.60–1.05 (m, 14H), 1.02 (d, $J = 6.9$ Hz, 3H), 0.60–0.14 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 132.6, 130.0, 74.1, 39.4, 37.9, 27.0, 25.6, 24.2, 24.1, 24.0, 22.3, 18.7, 17.4, 15.4, 0.9, -0.8 ; MS m/z (rel intensity) 236 (2), 151 (12), 137 (7), 123 (6), 109 (8), 97 (44), 84 (49), 69 (100). HRMS (EI) calcd for $\text{C}_{16}\text{H}_{28}\text{O}$ m/z 236.2140, found m/z 236.2142.

3. General procedure for the regioselective cyclopropanation of allyl alcohols.

To a solution of the appropriate allyl alcohol (10 mmol) in dry benzene (100 mL) was treated with diethylzinc (9.1 mL of 1.1 M in toluene, 10 mmol). The resulting mixture was cooled to $5\text{ }^\circ\text{C}$ at which diiodomethane (2.0 mL, 25 mmol) was added dropwise via syringe. The progress of the reaction was monitored by TLC. After 1–3 h the mixture became cloudy and the reaction was quenched with saturated NH_4Cl (100 mL) and then poured into a separatory funnel containing ether (150 mL). The organic layer was separated, and the aqueous phase extracted with ether ($3 \times 100\text{ mL}$). The combined organic layers were washed with saturated NH_4Cl and brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel. An analytical sample was distilled (Kugelrohr).

(*E*)-1-(1-Methylcyclopropyl)cyclododec-3-enol

The cyclopropanation of (*E*)-1-isopropenylcyclododec-3-enol (**9d**) (3.0 g, 13.5 mmol) following the general procedure afforded 2.9 g (92%) of the title compound as a colorless oil.

IR (film) 3464, 3080, 3001, 2926, 2851, 1459, 1380, 1026, 1015, 982 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.63–5.44 (m, 2H), 2.21–2.02 (m, 4H), 1.59–1.12 (m, 15H), 1.09 (s, 3H), 0.68–0.56 (m, 2H), 0.25–0.20 (m, 1H), 0.12–0.07 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 133.8, 126.2, 75.4, 40.0, 34.9, 32.8, 27.5, 26.7, 26.2, 24.5, 24.4, 23.6, 21.3, 19.5, 10.9, 8.8; MS m/z (rel intensity) 236 (1),

218 (2), 147 (4), 133 (7), 119 (6), 111 (19), 98 (36), 83 (100). Anal. Calcd for $C_{16}H_{28}O$ (236.40): C, 81.29; H, 11.93. Found: C, 81.46; H, 12.07.

(*E*)-1-(*cis*-2-Methylcyclopropyl)cyclododec-3-enol

The cyclopropanation of (*E*)-1-[(*Z*)-propen-1-yl]cyclododec-3-enol (**9e**) (3.7 g, 16.6 mmol) following the general procedure afforded 3.3 g (85%) of the title compound as a colorless oil.

IR (film) 3479, 3064, 2926, 2850, 1461, 1446, 1386, 1014, 981 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.65–5.44 (m, 2H), 2.38–2.30 (m, 2H), 2.14–2.07 (m, 2H), 1.65–1.24 (m, 15H),

0.96–0.78 (m, 5H), 0.60–0.49 (m, 1H), 0.32–0.15 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.5, 125.5, 74.2, 45.9, 37.0, 33.2, 28.4, 27.0, 26.1, 25.0, 24.3, 24.2, 19.2, 13.5, 10.4, 6.7; MS m/z (rel intensity) 236 (1), 218 (2), 165 (5), 151 (6), 137 (4), 119 (3), 111 (27), 98 (35), 83 (100). Anal. Calcd for $C_{16}H_{28}O$ (236.40): C, 81.29; H, 11.93. Found: C, 81.25; H, 12.09.

(*E*)-1-(*trans*-2-Methylcyclopropyl)cyclododec-3-enol

The cyclopropanation of (*E*)-1-[(*E*)-propen-1-yl]cyclododec-3-enol (2.3 g, 10.3 mmol) following the general procedure afforded 1.9 g (78%) of the title compound as a colorless oil.

IR (film) 3475, 3065, 2925, 2850, 1461, 1445, 1385, 1014, 981 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.63–5.36 (m, 2H), 2.37–2.28 (m, 2H), 2.14–2.07 (m, 2H), 1.66–1.19 (m, 15H),

0.98–0.80 (m, 5H), 0.61–0.48 (m, 1H), 0.29–0.12 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.2, 125.9, 74.4, 43.3, 39.4, 31.5, 25.1, 25.0, 24.3, 24.0, 22.8, 22.5, 19.2, 14.0, 10.6, 6.4; MS m/z (rel intensity) 236 (1), 218 (2), 165 (5), 151 (5), 137 (3), 119 (3), 111 (24), 98 (43), 83 (100). Anal. Calcd for $C_{16}H_{28}O$ (236.40): C, 81.29; H, 11.93. Found: C, 81.36; H, 12.12.

(*E*)-1-(2,2-Dimethylcyclopropyl)cyclododec-3-enol

The cyclopropanation of (*E*)-1-(2-methylpropen-1-yl)cyclododec-3-enol (**9f**) (2.4 g, 10.2 mmol) using ether (!) as solvent following the general procedure afforded 1.98 g (78%) of the title compound as a colorless oil.⁴

IR (film) 3483, 2990, 2926, 2862, 1460, 1446, 1373, 1124, 981 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.63–5.46 (m, 2H), 2.36 (d, J = 6.5 Hz, 2H), 2.12 (q, J = 5.0 Hz, 2H), 1.61–1.23 (m, 15H), 1.27 (s, 3H), 1.04 (s, 3H), 0.69 (dd, J = 9.2, 6.3 Hz, 1H), 0.40 (dd, J = 6.3, 4.0 Hz, 1H), 0.30 (dd, J = 9.2, 4.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.2, 125.9, 74.1, 43.1, 39.3, 33.2, 33.1, 31.5, 28.9, 28.3, 27.0, 26.1, 25.1, 24.3, 19.9, 19.2, 14.4; MS m/z (rel intensity) 250 (6), 232 (5), 189 (10), 161 (5), 135 (14), 125 (29), 112 (35), 97 (100). Anal. Calcd for $C_{17}H_{30}O$ (250.42): C, 81.54; H, 12.07. Found: C, 81.44; H, 12.01.

4. General procedure for silylether formation.

A solution of the cyclopropyl alcohol (10 mmol), DMAP (0.19 g, 1.5 mmol), and Et₃N (2.1 mL, 15 mmol) in DMF (40 mL) was cooled to 0 °C and TMSCl (1.5 mL, 12 mmol) was added via syringe. The resulting cloudy solution was stirred for 1 h at room temperature and then poured into a separatory funnel containing ether (100 mL) and saturated NH₄Cl (100 mL). The organic layer was separated, and the aqueous phase extracted with ether (3 × 100 mL). The combined organic layers were washed with saturated NH₄Cl and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was filtered through a pad of silica gel. The silyl ethers **7** were immediately subjected to FVP without further purification.

(*E*)-1-Cyclopropyl-1-trimethylsilyloxycyclododec-3-ene (**3**)

The reaction of (*E*)-1-cyclopropylcyclododec-3-enol (6.8 g, 30.6 mmol) following the general procedure afforded 8.9 g (99%) of the title compound as a colorless oil. An analytical sample was distilled (Kugelrohr).

IR (film) 3085, 2924, 2852, 1462, 1445, 1358, 1300, 1250, 1207, 1181, 1156 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.45–5.36 (m, 2H), 2.22–2.10 (m, 2H), 2.08–1.99 (m, 2H), 1.58–1.18 (m, 14H), 0.89 (m, 1H), 0.38–0.19 (m, 4H), 0.01 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 133.9, 126.6, 77.4, 43.6, 38.0, 33.3, 28.3, 27.2, 26.4, 25.2, 22.7, 20.9, 19.7, 2.9, 1.0, 0.5; MS *m/z* (rel intensity) 294 (5), 195 (4), 183 (5), 169 (100), 141 (9), 130 (3), 73 (75). HRMS (EI) calcd for C₁₈H₃₄OSi *m/z* 294.2379, found *m/z* 294.2377. Anal. Calcd for C₁₈H₃₄OSi (294.55): C, 73.40; H, 11.63. Found: C, 73.52; H, 11.70.

(*E*)-1-Cyclopropyl-1-trimethylsilyloxycyclotridec-3-ene (**7b**)

The reaction of (*E*)-1-cyclopropylcyclotridec-3-enol (2.4 g, 10.2 mmol) following the general procedure afforded 3.1 g (99%) of the title compound as a colorless oil (GC purity > 99%).

IR (film) 3084, 2931, 2859, 1461, 1446, 1249, 1072, 974, 838 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.52–5.30 (m, 2H), 2.27–2.10 (m, 2H), 2.04–1.93 (m, 2H), 1.68–1.17 (m, 16H), 1.02–0.87 (m, 1H), 0.38–0.27 (m, 4H), 0.02 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 133.9, 127.2, 77.1, 43.6, 38.6, 32.4, 27.8, 27.6, 27.5, 25.1, 25.0, 24.7, 20.9, 19.8, 2.8, 0.8, 0.7; MS *m/z* (rel intensity) 308 (5), 183 (4), 169 (100), 143 (9), 73 (90). HRMS (EI) calcd for C₁₉H₃₆OSi *m/z* 308.2535, found *m/z* 308.2534.

(*Z*)-1-Cyclopropyl-1-trimethylsilyloxycyclooct-3-ene (**7c**)

The reaction of (*Z*)-1-cyclopropylcyclooct-3-enol (3.8 g, 22.8 mmol) following the general procedure afforded 5.4 g (99%) of the title compound as a colorless oil (GC purity > 98%).

IR (film) 3084, 3018, 2932, 2857, 1465, 1446, 1250, 1071, 838 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.81–5.51 (m, 2H), 2.34 (dd, *J* = 12.7, 8.6 Hz, 1H), 2.19 (dd, *J* = 12.7, 7.4 Hz, 1H), 2.07–2.01 (m, 2H), 1.63–1.35 (m, 6H), 1.02–0.89 (m, 1H), 0.39–0.27 (m, 4H), 0.08 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 131.8, 128.3, 79.2, 38.4, 38.3, 29.7, 26.6, 22.8, 20.9, 2.7, 0.8, 0.6; MS *m/z* (rel intensity) 238 (2),

195 (6), 169 (100), 141 (18), 73 (96). HRMS (EI) calcd for $C_{14}H_{26}OSi$ m/z 238.1753, found m/z 238.1751.

(*E*)-1-(1-Methylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene (7d)

The reaction of (*E*)-1-(1-methylcyclopropyl)cyclododec-3-enol (2.7 g, 11.4 mmol) following the general procedure afforded 3.5 g (99%) of the title compound as a colorless oil (GC purity > 99%).

IR (film) 3081, 2925, 2851, 1459, 1379, 1249, 1073, 980, 837; 1H NMR (300 MHz, $CDCl_3$) δ 5.59–5.47 (m, 2H), 2.24–2.02 (m, 4H), 1.62–1.22 (m, 14H), 1.08 (s, 3H), 0.68–0.56 (m, 2H), 0.24–0.20 (m, 1H), 0.14–0.09 (m, 1H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.0, 126.5, 80.2, 39.0, 36.0, 33.5, 28.7, 27.1, 26.4, 25.2, 24.5, 22.7, 22.0, 20.0, 11.7, 10.2, 2.9; MS m/z (rel intensity) 308 (3), 253 (9), 183 (33), 169 (26), 144 (18), 73 (100). HRMS (EI) calcd for $C_{19}H_{36}OSi$ m/z 308.2535, found m/z 308.2538.

(*E*)-1-(*cis*-2-Methylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene (7e)

The reaction of (*E*)-1-(*cis*-2-methylcyclopropyl)cyclododec-3-enol (2.6 g, 11.0 mmol) following the general procedure afforded 3.3 g (98%) of the title compound as a colorless oil (GC purity > 99%).

IR (film) 3069, 2928, 2852, 1461, 1446, 1250, 1091, 1067, 977, 837 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.62–5.41 (m, 2H), 2.42–2.34 (m, 2H), 2.16–2.02 (m, 2H), 1.64–1.23 (m, 14H), 1.20 (d, J = 6.5, 3H), 0.92–0.82 (m, 1H), 0.81–0.70 (m, 1H), 0.51 (td, J = 12.6, 3.9, 1H), 0.32–0.18 (m, 1H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.7, 126.9, 78.1, 46.3, 39.7, 32.6, 27.5, 27.1, 26.8, 24.9, 24.6, 24.5, 19.6, 13.4, 10.8, 7.6, 1.3; MS m/z (rel intensity) 308 (4), 183 (52), 169 (8), 155 (15), 73 (100). HRMS (EI) calcd for $C_{19}H_{36}OSi$ m/z 308.2535, found m/z 308.2537.

(*E*)-1-(*trans*-2-Methylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene

The reaction of (*E*)-1-(*trans*-2-methylcyclopropyl)cyclododec-3-enol (1.8 g, 7.6 mmol) following the general procedure afforded 2.3 g (97%) of the title compound as a colorless oil (GC purity > 98%).

IR (film) 3068, 2925, 2850, 1461, 1446, 1250, 1089, 1067, 977, 837 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.62–5.35 (m, 2H), 2.40–2.32 (m, 2H), 2.15–2.08 (m, 2H), 1.66–1.19 (m, 14H), 1.21 (d, J = 6.6, 3H), 0.86–0.67 (m, 2H), 0.63–0.47 (m, 1H), 0.29–0.11 (m, 1H), 0.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.9, 127.0, 78.3, 44.8, 39.4, 33.2, 28.7, 27.1, 26.4, 24.6, 24.2, 22.6, 20.6, 13.4, 10.7, 7.2, 3.1; MS m/z (rel intensity) 308 (3), 183 (48), 169 (9), 155 (17), 73 (100). HRMS (EI) calcd for $C_{19}H_{36}OSi$ m/z 308.2535, found m/z 308.2533.

(*E*)-1-(2,2-Dimethylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene (7f)

The reaction of (*E*)-1-(2,2-dimethylcyclopropyl)cyclododec-3-enol (1.3 g, 5.2 mmol) following the general procedure afforded 1.7 g (99%) of the title compound as a colorless oil (GC purity > 99%).

IR (film) 2926, 2863, 1461, 1446, 1372, 1250, 1080, 981 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.61–5.45 (m, 2H), 2.35 (d, J = 5.7 Hz, 2H), 2.16–2.06 (m, 2H), 1.61–1.23 (m, 14H), 1.22 (s, 3H), 1.02 (s, 3H), 0.66 (dd, J = 9.0, 6.2 Hz, 1H), 0.41 (dd, J = 6.2, 3.6 Hz, 1H), 0.25 (dd, J = 9.0, 3.6 Hz, 1H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 133.7, 127.0, 78.7, 44.7, 39.3, 33.2, 32.9, 29.3, 28.2, 27.1, 26.5, 25.1, 24.6, 20.4, 19.7, 16.1, 15.2, 1.3; MS m/z (rel intensity) 322 (11), 279 (8), 197 (16), 169 (12), 141 (9), 107 (6), 91 (10), 73 (100). HRMS (EI) calcd for $\text{C}_{20}\text{H}_{38}\text{OSi}$ m/z 322.2692, found m/z 322.2691.

(1*R,2*R**,3*E*)-1-Cyclopropyl-2-methyl-1-trimethylsilyloxycyclododec-3-ene (7g)**

The reaction of (1*R**,2*R**,3*E*)-1-cyclopropyl-2-methylcyclododec-3-enol (1.8 g, 7.6 mmol) following the general procedure afforded 2.0 g (87%) of the title compound as a colorless oil (GC purity > 97%).

IR (film) 3085, 3005, 2935, 2864, 1462, 1364, 1249, 1167, 1072, 966, 838 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.47–5.34 (m, 1H), 5.18–5.04 (m, 1H), 2.96–2.86 (m, 1H), 2.52–2.39 (m, 1H), 1.89–1.77 (m, 1H), 1.51–1.06 (m, 14H), 0.99 (d, J = 6.9 Hz, 3H), 0.59–0.20 (m, 5H), 0.09 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 133.4, 129.5, 78.8, 40.9, 34.8, 27.2, 25.7, 24.5, 24.1, 22.4, 22.3, 18.1, 16.1, 16.0, 2.5, 1.8, 1.3; MS m/z (rel intensity) 308 (3), 183 (8), 169 (83), 141 (10), 73 (100). HRMS (EI) calcd for $\text{C}_{19}\text{H}_{36}\text{OSi}$ m/z 308.2535, found m/z 308.2535.

5. General procedure for the thermal three-carbon ring expansion by FVP.^{5,6}

The FVP-device consists of an electrically heatable tube furnace (one meter-long), a condenser unit with a cooling trap at the outlet side and a kugelrohr oven as the evaporation unit at the inlet side. A quartz tube (110 cm long, 2.5 cm i. d., no fillings were used), which fitted into the furnace, was connected to a trap (cooled with liquid N_2) on one side and to a bulb placed in the kugelrohr oven on the other. The starting material was placed in the bulb equipped with a capillary inlet device for the inert flow gas (a flow of N_2 was adjusted from 0.8–1.4 L/h) and a magnetic stirrer. After evacuation of the apparatus with a high-vacuum oil pump ($2\text{--}4 \times 10^{-2}$ mbar) the starting material was distilled directly through the preheated reactor tube (1–3 g/h). After all of the starting material had been distilled, the apparatus was vented and the frozen products were transferred to a bulb using Et_2O as solvent. The resulting solution was dried over anhydrous MgSO_4 and evaporated under reduced pressure. The residue was dissolved in EtOH and treated with 1% HCl to cleave the TMS-group. Workup in the usual manner followed by flash chromatography on silica gel (1–10% EtOAc in hexane) provided analytically pure compounds.

(E)-Cyclopentadec-6-enone (5) and 5-Vinylcyclotridecanone (6)

FVP of (*E*)-1-cyclopropyl-1-trimethylsilyloxycyclododec-3-ene (**3**) (4.60 g, 15.6 mmol) at 530 °C following the general procedure afforded 2.43 g (70%) of **5** and 0.35 g (10%) of **6**. Physical and spectral data of **5** are in accordance with literature data.⁷

Data of **5**: IR (film) 2930, 2857, 1711, 1460, 1444, 1364, 1251, 1070, 976 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 5.37–5.27 (m, 2H), 2.38 (t, *J* = 6.7 Hz, 2H), 2.34 (t, *J* = 8.1 Hz, 2H), 2.08–2.02 (m, 4H), 1.65–1.56 (m, 4H), 1.46–1.41 (m, 2H), 1.40–1.33 (m, 2H), 1.32–1.20 (m, 8H); ¹³C NMR (150 MHz, CDCl₃) δ 212.1, 131.8, 130.6, 42.7, 42.4, 31.71, 31.65, 28.4, 28.2, 27.23, 27.20, 27.19, 26.5, 23.8, 23.7; MS *m/z* (rel intensity) 222 (49), 179 (7), 165 (17), 151 (12), 137 (15), 123 (19), 109 (44), 98 (82), 81 (86), 67 (96), 55 (100). Anal. Calcd for C₁₅H₂₆O (222.37): C, 81.02; H, 11.78. Found: C, 80.88; H, 11.90.

Data of **6**: IR (film) 3078, 2934, 2861, 1706, 1462, 1444, 1420, 1365, 1248, 1216. ¹H NMR (600 MHz, CDCl₃) δ 5.59 (ddd, *J* = 17.0, 10.2, 7.3 Hz, 1H), 5.97 (dd, *J* = 17.0, 1.2 Hz, 1H), 4.94 (dd, *J* = 10.2, 1.2 Hz, 1H), 2.53 (ddd, *J* = 15.5, 9.3, 3.4 Hz, 1H), 2.44 (td, *J* = 8.0, 4.1 Hz, 2H), 2.34 (ddd, *J* = 15.5, 8.3, 4.5 Hz, 1H), 1.99 (m, 1H), 1.78–1.53 (m, 4H), 1.44–1.22 (m, 14H); ¹³C NMR (150 MHz, CDCl₃) δ 212.9, 143.6, 113.7, 42.2, 42.1, 40.3, 32.5, 31.2, 26.7, 26.04, 26.00, 25.1, 23.5, 23.4, 21.1; HRMS (EI) for C₁₅H₂₆O: calcd 222.1984; found 222.1989. Anal. Calcd for C₁₅H₂₆O (222.37): C, 81.02; H, 11.78. Found: C, 81.19; H, 11.99.

(Z)-Cyclopentadec-6-enone (8a)

FVP of (*Z*)-1-cyclopropyl-1-trimethylsilyloxycyclododec-3-ene (**7a**) (2.53 g, 8.6 mmol) at 530 °C following the general procedure afforded 1.32 g (69%) of the title compound as a colorless oil. Physical and spectral data are in accordance with literature data.⁷ GC/MS analysis provided evidence for the presence of 5-vinylcyclotridecanone (**6**) (8%).

IR (film) 2928, 2857, 1712, 1461, 1443, 1350, 1246, 1070, 971 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.36–5.27 (m, 2H), 2.45–2.32 (m, 4H), 2.09–1.99 (m, 4H), 1.68–1.55 (m, 4H), 1.46–1.17 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 212.5, 130.6, 129.4, 42.9, 41.1, 28.9, 28.1, 27.4, 27.3, 27.1, 27.0, 26.5, 26.2, 24.0, 23.0; MS *m/z* (rel intensity) 222 (45), 193 (5), 179 (6), 165 (12), 151 (12), 137 (15), 125 (20), 111 (46), 98 (78), 81 (83), 67 (100). Anal. Calcd for C₁₅H₂₆O (222.37): C, 81.02; H, 11.78. Found: C, 80.91; H, 11.83.

(E)-Cyclohexadec-6-enone (8b)

FVP of (*E*)-1-cyclopropyl-1-trimethylsilyloxycyclotridec-3-ene (**7b**) (1.65 g, 5.3 mmol) at 530 °C following the general procedure afforded 0.90 g (71%) of the title compound as a colorless oil. ¹H NMR of the crude product provided evidence for the presence of a minor amount of 5-vinylcyclotetradecanone (ca. 10%).

IR (film) 2927, 2854, 1712, 1459, 1447, 1368, 1261, 968 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.39–5.29 (m, 2H), 2.43 (t, *J* = 6.3 Hz, 2H), 2.38–2.32 (m, 2H), 2.08–2.00 (m, 4H), 1.69–1.53 (m, 4H), 1.46–1.15 (m,

14H); ^{13}C NMR (75 MHz, CDCl_3) δ 212.5, 131.8, 130.2, 43.1, 41.1, 32.2, 32.0, 28.6, 28.5, 28.0, 27.7, 27.6, 26.9, 26.5, 24.1, 22.8; MS m/z (rel intensity) 236 (23), 152 (5), 137 (7), 123 (9), 111 (14), 95 (48), 81 (63), 67 (82), 55 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}$ (236.40): C, 81.29; H, 11.93. Found: C, 81.23; H, 11.89.

(Z)-Cycloundec-6-enone (8c)⁸

(Z)-1-Cyclopropyl-1-trimethylsilyloxycyclooct-3-ene (**7c**) (2.10 g, 8.8 mmol) was pyrolyzed at 560 °C to afford 1.30 g (89% recovery) of crude product. Flash chromatography of the hydrolyzed crude product (silica gel, 2% ethyl acetate in hexanes) afforded a fraction (0.88 g) containing the title compound accompanied with two unidentified side products in a 2:1:1 ratio. Hydrogenation of this mixture in the presence of Pd/C and co-injection (GC/MS) with an authentic sample of cycloundecanone (purchased from *Fluka*) provided evidence for the initial formation of the title compound.

(E)-2-Methylcyclopentadec-6-enone (8d)

FVP of (*E*)-1-(1-methylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene (**7d**) (2.10 g, 6.8 mmol) at 520 °C following the general procedure afforded 1.55 g (72%) of the title compound as a colorless oil.

IR (film) 2929, 2855, 1711, 1459, 1447, 1370, 968 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.35–5.29 (m, 2H), 2.56–2.48 (m, 1H), 2.45 (dd, J = 7.6, 6.1 Hz, 1H), 2.32–2.22 (m, 1H), 2.14–1.90 (m, 4H), 1.72–1.62 (m, 2H), 1.56–1.42 (m, 2H), 1.41–1.17 (m, 12H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 215.4, 131.7, 130.6, 46.2, 40.4, 31.7, 31.6, 31.3, 27.9, 27.5, 27.4, 27.3, 26.8, 26.6, 23.1, 14.9; MS m/z (rel intensity) 236 (12), 165 (5), 151 (4), 139 (7), 123 (9), 109 (26), 95 (47), 81 (60), 67 (69), 55 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}$ (236.40): C, 81.29; H, 11.93. Found: C, 81.19; H, 11.91.

(E)-4-Methylcyclopentadec-6-enone (8e)

FVP of (*E*)-1-(*cis*-2-methylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene (**7e**) (1.80 g, 5.8 mmol) at 520 °C following the general procedure afforded 0.55 g (41%) of the title compound as a colorless oil. Alternatively, FVP of the diastereoisomeric (*E*)-1-(*trans*-2-methylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene (1.15 g, 3.7 mmol) at the same temperature afforded 0.35 g (41%) of the title compound as a colorless oil.

IR (film) 2928, 2856, 1708, 1458, 970 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.37–5.32 (m, 2H), 2.44–2.32 (m, 4H), 2.17–1.97 (m, 4H), 1.88–1.13 (m, 15H), 0.94 (d, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.4, 132.2, 129.3, 42.7, 40.4, 40.1, 32.9, 31.7, 30.2, 28.2, 27.1, 27.1, 27.2, 26.5, 23.7, 20.3; MS m/z (rel intensity) 236 (12), 151 (4), 136 (5), 125 (6), 109 (10), 97 (30), 81 (51), 67 (52), 55 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}$ (236.40): C, 81.29; H, 11.93. Found: C, 81.25; H, 11.88.

(E)-4,4-Dimethylcyclopentadec-6-enone (8f)

FVP of (*E*)-1-(2,2-dimethylcyclopropyl)-1-trimethylsilyloxycyclododec-3-ene (**7f**) (1.10 g, 3.4 mmol) at 510 °C following the general procedure afforded 0.43 g (50%) of the title compound as a colorless oil.

IR (film) 2929, 2858, 1710, 1459, 1447, 1385, 1366, 1120, 969 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.41–5.35 (m, 2H), 2.38 (t, $J = 6.5$ Hz, 2H), 2.35–2.29 (m, 2H), 2.05 (q, $J = 5.6$ Hz, 2H), 1.94 (d, $J = 5.8$ Hz, 2H), 1.65–1.56 (m, 2H), 1.47–1.41 (m, 2H), 1.40–1.19 (m, 10H), 0.91 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.5, 133.0, 127.5, 45.3, 42.7, 37.6, 34.8, 32.8, 31.8, 28.3, 27.6, 27.0, 26.8, 26.7, 26.1, 23.7; MS m/z (rel intensity) 250 (6), 235 (4), 163 (7), 125 (68), 112 (46), 97 (37), 81 (43), 69 (55), 55 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{O}$ (250.42): C, 81.54; H, 12.07. Found: C, 81.63; H, 12.15.

(E)-5-Methylcyclopentadec-6-enone (8g)

FVP of (1*R**,2*R**,3*E*)-1-cyclopropyl-2-methyl-1-trimethylsilyloxycyclododec-3-ene (**7g**) (1.80 g, 3.6 mmol) at 520 °C following the general procedure afforded 0.51 g (61%) of the title compound as a colorless oil.

IR (film) 2928, 2857, 1710, 1459, 1365, 970 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 5.30 (ddd, $J = 15.3, 8.9, 4.9$ Hz, 1H), 5.16 (ddd, $J = 15.3, 8.4, 1.1$ Hz, 1H), 2.44–2.32 (m, 3H), 2.28–2.23 (m, 1H), 2.14–2.07 (m, 2H), 1.96–1.90 (m, 1H), 1.68–1.16 (m, 16H), 0.97 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 213.3, 136.6, 129.8, 43.0, 42.6, 37.3, 36.9, 31.8, 28.4, 27.3, 27.23, 27.20, 26.7, 23.4, 23.5, 21.7; MS m/z (rel intensity) 250 (6), 235 (4), 163 (7), 125 (68), 112 (46), 97 (37), 81 (43), 69 (55), 55 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}$ (236.40): C, 81.29; H, 11.93. Found: C, 81.23; H, 11.90.

1-Cyclopropylcyclododec-11-en-1-one (11) and Bicyclo[10.3.0]pentadecan-2-one (12).

FVP of (*E*)-1-cyclopropylcyclododec-3-enol (**10**) (1.50 g, 6.7 mmol) at 530 °C following the general procedure, but without treatment of the crude product with 1% HCl in EtOH afforded **5** (75 mg, 5%), **12** (150 mg, 10%),⁹ and **11** (0.98 g, 65%) in that order.

Data of **11**: IR (film) 3078, 3009, 2977, 2926, 2855, 1699, 1641, 1464, 1386, 1302, 1195 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 5.87–5.74 (m, 1H), 5.02–4.90 (m, 2H), 2.53 (t, $J = 7.2$ Hz, 2H), 2.03 (q, $J = 7.5$ Hz, 2H), 1.92 (m, 1H), 1.60 (quint., $J = 7.2$ Hz, 2H), 1.37 (quint., $J = 7.5$ Hz, 2H), 1.28–1.22 (m, 10H), 1.02–0.97 (m, 2H), 0.88–0.80 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 211.0, 139.0, 113.9, 43.4, 33.6, 29.3, 29.1, 29.0, 28.8, 23.9, 20.1, 10.3; MS m/z (rel intensity) 222 (1), 151 (4), 137 (5), 97 (16), 84 (100), 69 (80). Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{O}$ (222.37): C, 81.02; H, 11.78. Found: C, 80.96; H, 11.81.

Data of **12**: IR (film) 2932, 2864, 1713, 1460, 1445, 1205, 998 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 3.03–2.85 (m, 2H), 2.23–1.95 (m, 4H), 1.91–1.78 (m, 1H), 1.77–1.53 (m, 5H), 1.43–1.06 (m, 14H); ^{13}C NMR (150 MHz, CDCl_3) δ 213.3, 55.3, 43.3, 40.8, 31.8, 27.3, 26.32, 26.31, 25.9, 25.0, 24.1, 24.0, 22.9, 22.3, 21.6.

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