

A Novel and Highly Efficient Two-Carbon Ring Expansion

Georg Rüedi,* Matthias Nagel,[†] and Hans-Jürgen Hansen

Organisch-Chemisches Institut der Universität, CH-8057 Zürich, Switzerland

*[†]Swiss Federal Laboratories for Materials Testing and Research (EMPA),
CH-8600 Dübendorf, Switzerland*

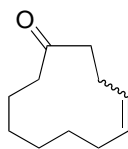
Supporting Information

Experimental

General. TLC: glass plates covered with silica gel 60 F_{254} (Merck) or Polygram Alox N/UV₂₅₄ (Macherey-Nagel); visualization by UV light or by spraying with ‘mostain’ solution ((NH₄)₆Mo₇O₂₄·4H₂O (40 g), Ce(SO₄)₂ (0.8 g), 10% H₂SO₄ soln. (800 ml)) and heating (blue spots). Column chromatography (CC) and flash chromatography (FC): silica gel 60 (Merk), grain size 0.040–0.063 mm, or aluminium oxide, Fluka, type 5016 A basic, Brockmann grade IV, or Alox ICN Alumina N neutral, Brockmann grade III. mp (not corrected): Mettler FP 5/52. IR Spectra: Perkin-Elmer 1600 Series FT-IR spectrometer; wave numbers in cm⁻¹. NMR Spectra: Bruker ARX-300 (300/75 MHz), Avance DRX 500 (500/125 MHz), and Avance DRX 600 (600/150 MHz); chemical shifts (δ , ppm) relative to CD(H)Cl₃ (7.27/77.00 ppm), coupling constants J in Hz; 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 and HSQC 2D-NMR methods were employed. MS: Varian SSQ 700; Ionization by EI (70 eV) or CI (NH₃): m/z , rel. intensities (%). GC/MS: Hewlett Packard HP-5971 Series (mass-selective detector; EI, 70 eV) and HP-5890 Series II (GC); carrier gas He; WCOT capillary column HP-5; 25 m × 0.3 mm, 0.2 μ m. GC conditions: injector temp. 280°, starting temp. 60° over 2 min, rate 20°/min, term. temp. 250° over 5 min.

General Procedure for DGPTI of 3-Vinylcycloalkanones 1b–f. The thermo-isomerization 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.), which fitted into the furnace, was connected to a trap (cooled with liquid N₂) on one side and to a bulb placed in the kugelrohr oven on the other. The starting material (typically 1–2 g) was placed in the bulb equipped with a capillary inlet device for the inert flow gas (N₂) and a magnetic stirrer. After evacuation of the apparatus with a high-vacuum oil pump 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 Et₂O as solvent. The resulting solution was dried over anhydrous MgSO₄ and evaporated under reduced pressure.

The following parameters are typical for the DGPTI process: (i) the kugelrohr oven was heated up to 140–160 °C; (ii) a flow of N₂ was adjusted from 0.8–1.4 L/h; (iii) the reactor tube was heated up to 580–630 °C; (iv) the high-vacuum was adjusted from 2–4×10⁻² mbar.



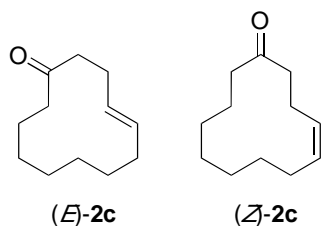
(*E/Z*)-**2b**

(*E/Z*)-Cycloundec-4-enone (2b).

3-Vinylcyclononanone (**1b**) (0.86 g, 5.17 mmol) was thermo-isomerized at 620 °C. The dark yellow crude product was purified by column chromatography (hexane/AcOEt (50:1) as eluent) to afford **2b** (0.30 g, 35%) as a colorless oil (*E:Z* = 1.3:1).

IR (film) 2933vs, 2858s, 1702vs, 1461m, 1446m, 1410w, 1366m, 1215w, 1201w, 1144w, 1122w, 1053w, 981m cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.49–5.26 (m, H–C(4,5)), 2.50–2.46 (m, CH₂(2)), 2.41–2.36 (m, CH₂(3,11)), 2.09–1.95 (m, CH₂(6)), 1.61–1.55 (m, CH₂(10)), 1.47–1.22 (m, CH₂(7,8,9)); ¹³C NMR (75 MHz, CDCl₃): δ 214.0 (s), 213.3 (s), 132.7 (d), 131.4 (d), 128.7 (d), 128.1 (d), 42.5 (t), 41.5 (t), 40.4 (t), 34.0 (t), 30.6 (t), 26.7 (t), 25.9 (t), 25.2 (t), 24.5 (t), 24.2 (t), 23.8 (t), 22.3 (t); EI-MS of (*E*)-**2b**: 166 (48, *M*⁺), 137 (12, [*M* – CHO]⁺), 123 (33, [*M* – CHO – CH₂]⁺), 109 (43, [*M* – CHO – 2 CH₂]⁺), 98 (70), 81 (66), 67 (100), 55 (89).

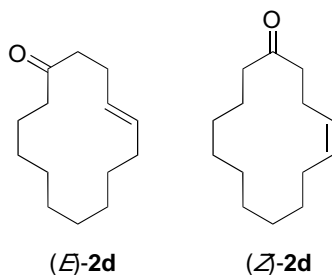
EI-MS of (Z)-**2b**: 166 (32, M^+), 137 (12, $[M - \text{CHO}]^+$), 123 (31, $[M - \text{CHO} - \text{CH}_2]^+$), 111 (40), 98 (62), 81 (57), 67 (100), 55 (82).



(E)- and (Z)-Cyclododec-4-enone (2c).

3-Vinylcyclodecanone (**1c**) (1.30 g, 7.21 mmol) was thermo-isomerized at 610 °C. The dark yellow crude product was purified by column chromatography (hexane/AcOEt (30:1) as eluent) to give (E)-**2c** (0.56 g, 43%) as a colorless oil, followed by (Z)-**2c** (0.33 g, 25%) as a colorless oil. Data of (E)-**2c**: IR (film) 3025w, 2925vs, 2853vs, 1712vs, 1457s, 1438s, 1363m, 1290w, 1219m, 1110m, 1050w, 975vs, 948m, 918m, 733s cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 5.41–5.33 (m, H-C(4,5)), 2.43–2.39 (m, $\text{CH}_2(2,12)$), 2.37–2.33 (m, $\text{CH}_2(3)$), 2.03–2.00 (m, $\text{CH}_2(6)$), 1.66 (quint, $J = 6.0$ Hz, $\text{CH}_2(11)$), 1.44–1.38 (m, $\text{CH}_2(7)$), 1.35–1.29 (m, $\text{CH}_2(8)$), 1.28–1.23 (m, $\text{CH}_2(9,10)$); ^{13}C NMR (150 MHz, CDCl_3): δ 212.9 (s, C(1)), 134.4 (d, C(5)), 128.0 (d, C(4)), 42.5 (t, C(12)), 41.5 (t, C(2)), 31.9 (t, C(6)), 29.4 (t, C(3)), 26.9 (t, C(8)), 25.3 (t, C(10)), 25.0 (t, C(7)), 24.6 (t, C(9)), 21.1 (t, C(11)); EI-MS: 180 (100, M^+), 151 (27, $[M - \text{CHO}]^+$), 137 (46, $[M - \text{CHO} - \text{CH}_2]^+$), 123 (65, $[M - \text{CHO} - 2 \text{CH}_2]^+$), 111 (50), 95 (81), 81 (89), 67 (96), 55 (70).

Data of (Z)-**2c**: IR (film) 3002m, 2927vs, 2856vs, 1710vs, 1460s, 1440s, 1361m, 1216m, 1181w, 1096m, 976m, 917m, 732s, 712s cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.41–5.25 (m, H-C(4,5)), 2.54–2.39 (m, $\text{CH}_2(2,12)$), 2.11 (q, $J = 6.3$ Hz, $\text{CH}_2(3)$), 1.69 (q, $J = 6.3$ Hz, $\text{CH}_2(6)$), 1.49–1.17 (m, 10 H); ^{13}C NMR (75 MHz, CDCl_3): δ 211.7 (s, C(1)), 131.4 (d, C(5)), 128.1 (d, C(4)), 43.2 (t, C(12)), 38.9 (t, C(2)), 26.63 (t), 26.57 (t), 24.9 (t), 24.5 (t), 23.54 (t), 23.51 (t), 19.7 (t); EI-MS: 180 (78, M^+), 151 (21, $[M - \text{CHO}]^+$), 137 (35, $[M - \text{CHO} - \text{CH}_2]^+$), 123 (49), 111 (50), 95 (80), 81 (92), 67 (100), 55 (82).

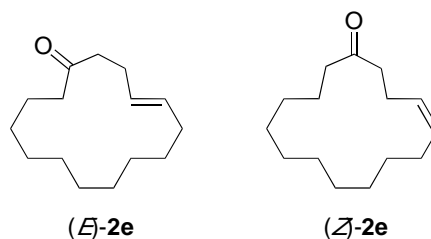


(E)- and (Z)-Cyclotetradec-4-enone (2d).

3-Vinylcyclododecanone (**1d**) (4.82 g, 23.14 mmol) was thermo-isomerized at 600 °C. The pale yellow crude product was purified by column chromatography (hexane/AcOEt (40:1) as eluent) to give (*E*)-**2d** (2.75 g, 57%), followed by (*Z*)-**2d** (1.35 g, 28%). Both (*E*)- and (*Z*)-**2d** could be crystallized from 60:1 hexane/AcOEt to afford in either case colorless needles.

Data of (*E*)-**2d**: mp 40 °C (60:1 hexane/AcOEt). IR (KBr) 3030w, 2928vs, 2848s, 1703vs, 1456m, 1431s, 1407m, 1361m, 1213m, 1185w, 1092w, 1003w, 977m, 967m cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 5.41–5.30 (m, H–C(4,5)), 2.51 (t, ³*J*(2,3) = 5.7 Hz, CH₂(2)), 2.41 (t, ³*J*(14,13) = 6.2 Hz, CH₂(14)), 2.32 (q, *J* = 6.5 Hz, CH₂(3)), 2.00 (q, *J* = 5.9 Hz, CH₂(6)), 1.68–1.64 (m, CH₂(13)), 1.38–1.32 (m, 4 H), 1.24–1.12 (m, 8 H); ¹³C NMR (150 MHz, CDCl₃): δ 211.4 (s, C(1)), 131.9 (d, C(5)), 130.1 (d, C(4)), 42.2 (t, C(14)), 42.0 (t, C(2)), 30.8 (t, C(6)), 27.2 (t, C(7)), 26.9 (t), 26.8 (t, C(3)), 26.0 (t), 25.9 (t), 24.9 (t), 24.4 (t, C(8)), 24.2 (t, C(13)); EI-MS: 208 (11, *M*⁺), 165 (10, [*M* – CHO – CH₂]⁺), 151 (7), 121 (12), 109 (23), 95 (42), 81 (55), 67 (82), 55 (100). Anal. Calcd for C₁₄H₂₄O: C, 80.71; H, 11.61. Found: C, 80.45; H, 11.47.

Data of (*Z*)-**2d**: mp 58–59 °C (60:1 hexane/AcOEt). IR (KBr) 3006w, 2923vs, 2846vs, 1701vs, 1465s, 1452m, 1429m, 1405s, 1356s, 1263m, 1203m, 1158w, 1128w, 1112w, 1067w, 850w, 732s, 704m cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 5.49–5.41 (m, H–C(4)), 5.40–5.30 (m, H–C(5)), 2.45 (t, ³*J*(2,3) = 7.4 Hz, CH₂(2)), 2.40 (t, ³*J*(14,13) = 6.7 Hz, CH₂(14)), 2.33 (q, *J* = 7.7 Hz, CH₂(3)), 2.07 (q, *J* = 7.4 Hz, CH₂(6)), 1.67 (quint, *J* = 6.7 Hz, CH₂(13)), 1.41 (quint, *J* = 7.0 Hz, CH₂(7)), 1.35–1.32 (m, 4 H), 1.29–1.22 (m, 6 H); ¹³C NMR (150 MHz, CDCl₃): δ 212.5 (s, C(1)), 131.4 (d, C(5)), 128.5 (d, C(4)), 42.7 (t, C(14)), 41.7 (t, C(2)), 27.8 (t, C(7)), 26.6 (t), 26.13 (t), 26.07 (t), 25.8 (t), 25.6 (t), 25.4 (t, C(6)), 23.5 (t, C(13)), 22.3 (t, C(3)); EI-MS: 208 (15, *M*⁺), 165 (12, [*M* – CHO – CH₂]⁺), 151 (10), 121 (18), 109 (30), 95 (62), 81 (75), 67 (98), 55 (100). Anal. Calcd for C₁₄H₂₄O: C, 80.71; H, 11.61. Found: C, 80.72; H, 11.52.

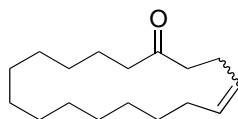


(E)- and (Z)-Cyclopentadec-4-enone (2e).

3-Vinylcyclotridecanone (**1e**) (1.80 g, 8.09 mmol) was thermo-isomerized at 600 °C. The pale yellow crude product was purified by column chromatography (hexane/AcOEt (60:1) as eluent) to give pure (*E*)-**2e** (0.79 g, 44%) as a colorless oil, followed by a mixed fraction of (*E/Z*)-**2e** (0.67 g, 37%) as a colorless oil (*E:Z* = 2:1).

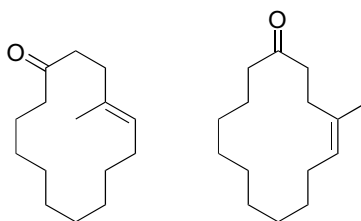
Data of (*E*)-**2e**: IR (film) 3027w, 2927vs, 2855vs, 1714vs, 1459s, 1441s, 1406s, 1367s, 1292w, 1207w, 1124m, 1073m, 970vs, 917w, 733s cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 5.44–5.36 (m, H–C(4,5)), 2.48 (t, $^3J(2,3) = 5.9$ Hz, $\text{CH}_2(2)$), 2.40 (t, $^3J(15,14) = 7.0$ Hz, $\text{CH}_2(15)$), 2.32 (q, $J = 5.3$ Hz, $\text{CH}_2(3)$), 2.02 (q, $J = 5.4$ Hz, $\text{CH}_2(6)$), 1.63 (quint, $J = 6.8$ Hz, $\text{CH}_2(14)$), 1.39–1.32 (m, 6 H), 1.30–1.17 (m, 8 H); ^{13}C NMR (150 MHz, CDCl_3): δ 211.6 (s, C(1)), 132.1 (d, C(5)), 129.5 (d, C(4)), 42.8 (t, C(2)), 42.6 (t, C(15)), 31.3 (t, C(6)), 28.2 (t), 27.6 (t), 27.4 (t, C(3)), 27.3 (t), 26.7 (t), 26.4 (t), 26.1 (t), 26.0 (t), 21.9 (t, C(14)); EI-MS: 222 (60, M^+), 193 (48, $[M - \text{CHO}]^+$), 179 (20, $[M - \text{CHO} - \text{CH}_2]^+$), 165 (18), 151 (14), 135 (23), 121 (30), 109 (45), 95 (87), 81 (94), 67 (97), 55 (100).

Data of (*Z*)-**2e**: ^1H NMR (300 MHz, CDCl_3): δ 5.54–5.35 (m, H–C(4,5)), 2.50–2.45 (m, $\text{CH}_2(11)$), 2.40 (t, $^3J(15,14) = 6.9$ Hz, $\text{CH}_2(15)$), 2.32 (t, $J = 6.0$ Hz, $\text{CH}_2(3)$), 2.09 (m, $\text{CH}_2(6)$), 1.67–1.22 (m, 14 H); ^{13}C NMR (75 MHz, CDCl_3): δ 211.2 (s, C(1)), 131.2 (d, C(5)), 128.1 (d, C(4)), 43.1 (t, C(15)), 41.8 (t, C(2)), 27.3 (t), 27.1 (t), 27.0 (t), 26.8 (t), 26.43 (t), 26.37 (t), 25.8 (t), 25.7 (t), 23.7(t), 22.4 (t); EI-MS: 222 (99, M^+), 193 (47, $[M - \text{CHO}]^+$), 179 (63, $[M - \text{CHO} - \text{CH}_2]^+$), 165 (50), 151 (39), 135 (70), 123 (78), 109 (85), 95 (94), 81 (95), 67 (100), 55 (95).

(E/Z)-**2f****(E/Z)-Cycloheptadec-4-enone (2f).**

3-Vinylcyclopentadecanone (**1f**) (1.72 g, 6.87 mmol) was thermo-isomerized at 600 °C. The yellow crude product was purified by column chromatography (hexane/AcOEt (40:1) as eluent) to afford **2f** (1.29 g, 75%) as a colorless oil (*E:Z* = 1.7:1).

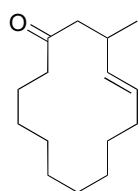
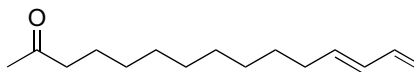
IR (film) 2962vs, 2855vs, 1714vs, 1459m, 1407m, 1365m, 1204w, 1079w, 969m, 915m, 733m cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.43–5.35 (m, H-C(4,5)), 2.50–2.45 (m, $\text{CH}_2(2)$), 2.44–2.35 (m, $\text{CH}_2(17)$), 2.34–2.26 (m, $\text{CH}_2(3)$), 2.07–1.95 (m, $\text{CH}_2(6)$), 1.65–1.57 (m, $\text{CH}_2(16)$), 1.39–1.28 (m, 18 H); ^{13}C NMR (75 MHz, CDCl_3): δ 211.3 (s), 211.0 (s), 131.7 (d), 131.1 (d), 128.7 (d), 127.9 (d), 43.2 (t), 42.9 (t), 42.4 (t), 41.9 (t), 31.6 (t), 28.5 (t), 28.3 (t), 27.8 (t), 27.6 (t), 27.5 (t), 27.4 (t), 27.23 (t), 27.15 (t), 27.1 (t), 27.01 (t), 26.96 (t), 26.90 (t), 26.8 (t), 26.7 (t), 26.3 (t), 23.5 (t), 23.2 (t); EI-MS of (*E*)-**2f**: 250 (63, M^+), 221 (10, $[M - \text{CHO}]^+$), 207 (9, $[M - \text{CHO} - \text{CH}_2]^+$), 193 (5), 179 (4), 151 (7), 135 (14), 123 (15), 109 (28), 95 (50), 81 (61), 67 (79), 55 (100); EI-MS of (*Z*)-**2f**: 250 (70, M^+), 221 (8, $[M - \text{CHO}]^+$), 207 (9, $[M - \text{CHO} - \text{CH}_2]^+$), 193 (2), 179 (3), 165 (4), 151 (7), 135 (10), 123 (13), 109 (24), 95 (54), 81 (59), 67 (75), 55 (100).

(E)-**4a**(Z)-**4a****(E)- and (Z)-4-Methylcyclotetradec-4-enone (4a).**

3-(isopropenyl)cyclododecanone (**3a**) (1.43 g, 6.43 mmol) was thermo-isomerized at 600 °C. The colorless crude product was purified by column chromatography (hexane/AcOEt (50:1) as eluent) to give pure (*E*)-**4a** (0.29 g, 20%), followed by a larger mixed fraction of (*E/Z*)-**4a** (0.54 g, 38%). Finally, pure (*Z*)-**4a** (0.41 g, 29%) was obtained as a third fraction, which could be crystallized from hexane to afford colorless needles.

Data of (*E*)-**4a**: IR (film) 2931vs, 2856vs, 1702vs, 1442m, 1425m, 1360m, 1221w, 875w, 732w cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.13 (td, $^3J(5,6) = 7.4$ Hz, $J = 1.1$ Hz, H-C(5)), 2.54 (t, $^3J(2,3) = 6.0$ Hz, $\text{CH}_2(2)$), 2.43 (t, $^3J(14,13) = 6.1$ Hz, $\text{CH}_2(14)$), 2.36 (t, $^3J(3,2) = 6.1$ Hz, $\text{CH}_2(3)$), 1.99 (q, $J = 6.9$ Hz, $\text{CH}_2(6)$), 1.62 (s, CH_3), 1.62 (quint, $J = 5.9$ Hz, $\text{CH}_2(13)$), 1.38–1.10 (m, 12 H); ^{13}C NMR (75 MHz, CDCl_3): δ 210.6 (s, C(1)), 133.4 (s, C(4)), 126.5 (d, C(5)), 41.1 (t, C(14)), 39.8 (t, C(2)), 33.4 (t), 27.6 (t), 26.4 (t), 25.6(t), 25.4 (t), 25.2 (t), 24.8 (t), 24.3 (t), 22.3 (t), 19.7 (q, CH_3); EI-MS: 222 (8, M^+), 164 (15, $[M - \text{CHO} - 2 \text{CH}_2]^+$), 152 (12), 134 (16, $[M - \text{CHO} - 4 \text{CH}_2]^+$), 109 (31), 95 (58), 81 (51), 67 (70), 55 (100).

Data of (*Z*)-**4a**: mp 69–70 °C (hexane). IR (KBr) 2960s, 2929vs, 2853vs, 1701vs, 1465m, 1451m, 1408m, 1349m, 1268m, 1208w, 1071w, 877m, 752w, 706w cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 5.12 (t, $^3J(5,6) = 7.7$ Hz, H-C(5)), 2.50 (t, $^3J(2,3) = 7.8$ Hz, $\text{CH}_2(2)$), 2.39 (t, $^3J(14,13) = 6.8$ Hz, $\text{CH}_2(14)$), 2.29 (t, $^3J(3,2) = 7.8$ Hz, $\text{CH}_2(3)$), 1.99 (q, $J = 7.2$ Hz, $\text{CH}_2(6)$), 1.69 (d, $^4J(\text{CH}_3,5) = 1.0$ Hz, CH_3), 1.68 (quint, $J = 7.1$ Hz, $\text{CH}_2(13)$), 1.39–1.22 (m, 12 H); ^{13}C NMR (150 MHz, CDCl_3): δ 212.8 (s, C(1)), 134.6 (s, C(4)), 126.6 (d, C(5)), 42.9 (t, C(14)), 40.2 (t, C(2)), 28.1 (t), 26.9 (t), 26.4 (t), 26.3 (t, C(6)), 26.1 (t, C(3)), 25.80 (t), 25.78 (t), 25.5 (t), 23.8 (t, C(13)), 23.5 (q, CH_3); EI-MS: 222 (5, M^+), 164 (24, $[M - \text{CHO} - 2 \text{CH}_2]^+$), 152 (23), 137 (25), 108 (91), 93 (90), 82 (98), 67 (100), 55 (99). Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{O}$: C, 81.02; H, 11.78. Found: C, 80.86; H, 11.73.

(*E*)-**4b**(*E*)-**5b**

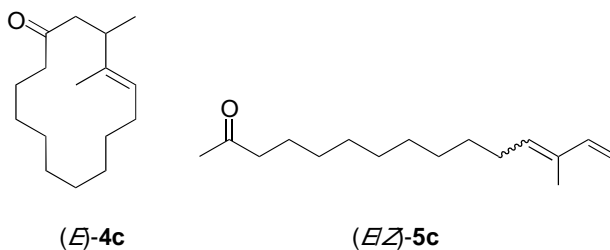
(*E*)-3-Methylcyclotetradec-4-enone (4b) and (*E*)-Pentadec-12,14-dien-2-one (5b).

(*E/Z*)-3-(1-Propenyl)cyclododecanone (**3b**) (5.70 g, 25.63 mmol) was thermo-isomerized at 580 °C. The yellow-orange crude product mixture was purified by column chromatography (hexane/AcOEt (70:1) as eluent) to give recovered starting material (1.08 g, 19%), **4b** (3.14 g, 55%), and open-chain dienone **5b** (0.57 g, 10%) which solidifies below 17 °C. An analytical sample of **4b** was crystallized from hexane affording colorless needles.

Data of **4b**: mp 48 °C (hexane). IR (KBr) 2925vs, 2858vs, 1703vs, 1456s, 1432m, 1408s, 1365s, 1276m, 1163m, 971vs, 742m cm^{-1} ; ^1H NMR (600 MHz, CDCl_3): δ 5.33 (ddd, $^3J(5,4) = 15.4$ Hz,

$^3J = 8.2$ Hz, $^3J = 2.6$ Hz, H–C(5)), 5.26 (dd, $^3J(4,5) = 15.4$ Hz, $^3J(4,3) = 7.8$ Hz, H–C(4)), 2.83–2.77 (m, H–C(3)), 2.48 (dd, $^2J = 16.3$ Hz, $^3J(2_a,3) = 11.2$ Hz, H_a–C(2)), 2.45, 2.35 (2 ddd, $^2J = 16.8$ Hz, $^3J = 8.4$ Hz, $^3J = 4.2$ Hz, CH₂(14)), 2.28 (dd, $^2J = 16.3$ Hz, $^3J(2_b,3) = 3.0$ Hz, H_b–C(2)), 2.11–2.04, 1.93–1.86 (2 m, CH₂(6)), 1.75–1.66, 1.59–1.52 (2 m, CH₂(13)), 1.42–1.38 (m, 1 H), 1.39–1.32 (m, 10 H), 1.15–1.07 (m, 1 H), 1.02 (d, $^3J(\text{CH}_3,3) = 7.0$ Hz, CH₃); ^{13}C NMR (150 MHz, CDCl₃): δ 210.8 (s, C(1)), 135.4 (d, C(4)), 129.9 (d, C(5)), 50.2 (t, C(2)), 42.0 (t, C(14)), 32.9 (d, C(3)), 31.1 (t, C(6)), 27.4 (t, C(7)), 26.5 (t), 25.8 (t), 25.3 (t), 25.2 (t), 24.4 (t), 23.3 (t, C(13)), 21.3 (q, CH₃); EI-MS: 222 (10, M^+), 137 (8, $[M - \text{CHO} - 4 \text{CH}_2]^+$), 123 (11), 109 (20), 95 (40), 81 (45), 67 (81), 55 (100). Anal. Calcd for C₁₅H₂₆O: C, 81.02; H, 11.78. Found: C, 81.11; H, 11.61.

Data of **5b**: mp 17 °C. IR (film) 3085w, 3015s, 2927vs, 2855vs, 1718vs, 1463s, 1410m, 1359s, 1163s, 1004s, 987s, 949m, 897w, 719w cm⁻¹; ^1H NMR (600 MHz, CDCl₃): δ 6.30 (ddd, $^3J_{\text{trans}} = 16.5$ Hz, $^3J_{\text{cis}} = 10.2$ Hz, $^3J(14,13) = 9.7$ Hz, H–C(14)), 6.04 (ddd, $^3J(13,12) = 15.2$ Hz, $^3J(13,14) = 9.7$ Hz, $^4J = 0.6$ Hz, H–C(13)), 5.70 (td, $^3J(12,13) = 15.2$ Hz, $^3J(12,11) = 6.9$ Hz, H–C(12)), 5.08 (dd, $^2J = 0.6$ Hz, $^3J_{\text{trans}} = 16.5$ Hz, 1 H), 4.94 (dd, $^2J = 0.6$ Hz, $^3J_{\text{cis}} = 10.2$ Hz, 1 H), 2.41 (t, $^3J(3,4) = 7.5$ Hz, CH₂(3)), 2.13 (s, CH₃), 2.07 (q, $J = 7.2$ Hz, CH₂(11)), 1.56 (quint, $J = 7.3$ Hz, CH₂(4)), 1.38 (quint, $J = 7.0$ Hz, CH₂(10)), 1.29–1.24 (m, 10 H); ^{13}C NMR (150 MHz, CDCl₃): δ 209.3 (s, C(2)), 137.3 (d, C(14)), 135.5 (d, C(12)), 130.8 (d, C(13)), 114.5 (t, C(15)), 43.8 (t, C(3)), 32.5 (t, C(11)), 29.8 (q, CH₃), 29.38 (t), 29.35 (t), 29.34 (t), 29.30 (t), 29.13 (t), 29.08 (t), 23.8 (t, C(4)); EI-MS: 222 (46, M^+), 164 (21), 135 (24), 125 (30), 109 (28), 95 (39), 81 (64), 67 (75), 55 (48), 43 (100).



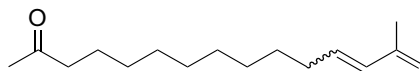
(E)-3,4-Dimethylcyclotetradec-4-enone (4c) and (E/Z)-13-Methylpentadec-12,14-dien-2-one (5c).

(E/Z)-3-(1-Methyl-1-propenyl)cyclododecanone (**3c**) (2.50 g, 10.58 mmol) was thermoisomerized at 580 °C. The colorless crude product mixture was purified by column

chromatography (hexane/AcOEt (70:1) as eluent) to give recovered starting material (0.63 g, 25%), followed by **4c** (1.15 g, 46%) as a colorless oil, and **5c** (0.53 g, 21%, *E:Z* = 1:1) which solidifies below 21 °C.

Data of **4c**: IR (film) 2931vs, 2859vs, 1713vs, 1458s, 1407m, 1364s, 1275w, 1211w, 1154w, 1111m, 1049w, 878w, 738w cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 5.19 (td, ³*J*(5,6) = 6.8 Hz, *J* = 0.7 Hz, H–C(5)), 2.88–2.79 (m, H–C(3)), 2.68 (dd, ²*J* = 15.4 Hz, ³*J*(2_a,3) = 11.8 Hz, H_a–C(2)), 2.43–2.38 (m, CH₂(14)), 2.16 (dd, ²*J* = 15.4 Hz, ³*J*(2_b,3) = 3.1 Hz, H_b–C(2)), 2.09–1.98, 1.98–1.89 (2 m, CH₂(6)), 1.70–1.58, 1.55–1.47 (2 m, CH₂(13)), 1.57 (s, Me–C(4)), 1.40–1.10 (m, 12 H), 1.02 (d, ³*J*(Me–C(3),3) = 7.0 Hz, Me–C(3)); ¹³C NMR (150 MHz, CDCl₃): δ 210.6 (s, C(1)), 137.9 (s, C(4)), 125.9 (d, C(5)), 48.3 (t, C(2)), 41.2 (t, C(14)), 39.6 (d, C(3)), 28.1 (t), 26.6 (t, C(6)), 25.78 (t), 25.76 (t), 25.73 (t), 24.8 (t), 24.6 (t), 22.1 (t, C(13)), 21.0 (q, Me–C(3)), 12.4 (q, Me–C(4)); EI-MS: 236 (70, *M*⁺), 193 (30, [*M* – CHO – CH₂]⁺), 165 (62), 149 (69), 137 (75), 123 (89), 109 (100), 95 (96), 81 (99), 67 (98), 55 (96).

Data of (*E/Z*)-**5c**: mp 21 °C. IR (film) 2927vs, 2854vs, 1718vs, 1456vs, 1359vs, 1227m, 1167s, 1065w, 989s, 963vs, 911m, 733s cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 6.35–6.08 (m, 1 H), 5.80–5.14 (m, 1 H), 5.15–4.91 (m, CH₂(15)), 2.41 (t, ³*J*(3,4) = 7.4 Hz, CH₂(3)), 2.12 (s, Me–C(2)), 2.12–2.08 (m, CH₂(11)), 1.79–1.77 (m, Me–C(13)), 1.56 (quint, *J* = 7.1 Hz, CH₂(4)), 1.37–1.28 (m, 12 H); ¹³C NMR (75 MHz, CDCl₃): δ 209.1 (s, C(2)), 138.7 (s), 138.6 (s), 134.5 (d), 133.4 (d), 132.1 (d), 132.0 (d), 110.1 (t), 43.7 (t, C(3)), 33.1 (t), 32.7 (t), 29.6 (q), 29.4 (t), 29.2 (t), 29.1 (t), 29.0 (t), 28.9 (t), 25.7 (t), 12.7 (q), 12.4 (q).



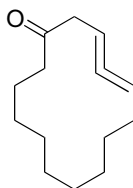
(*EZ*)-**5d**

(*E/Z*)-14-Methylpentadec-12,14-dien-2-one (5d).

3-(2-Methyl-1-propenyl)cyclododecanone (**3d**) (0.95 g, 4.02 mmol) was thermo-isomerized at 590 °C. The colorless crude product mixture was purified by column chromatography (hexane/AcOEt (70:1) as eluent) to give recovered starting material (0.27 g, 28%) and, as a second fraction, **5d** (0.36 g, 38%) as a colorless liquid (*E:Z* = 1:1).

IR (film) 3017s, 2928vs, 2854vs, 1720vs, 1459s, 1410s, 1358s, 1224m, 1165s, 987m, 963m, 881m, 720m cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 6.22–5.97 (m, 1 H), 5.85–5.56 (m, 1 H), 4.85

(s, CH₂(15)), 2.41 (t, ³J(3,4) = 7.4 Hz, CH₂(3)), 2.12 (s, Me–C(2)), 2.11–2.04 (m, CH₂(11)), 1.75, 1.73 (2 s, Me–C(14)), 1.56 (quint, *J* = 7.2 Hz, CH₂(4)), 1.39–1.28 (m, 12 H); ¹³C NMR (75 MHz, CDCl₃): δ 209.1 (s, C(2)), 142.1 (s), 134.6 (d), 131.9 (d), 130.9 (d), 129.5 (d), 113.9 (t), 43.7 (t, C(3)), 32.7 (t), 32.6 (t), 29.7 (q), 29.6 (t), 29.5 (t), 29.3 (t), 29.24 (t), 29.20 (t), 29.1 (t), 29.0 (t), 28.9 (t), 27.4 (t), 22.3 (t), 18.6 (q), 18.0 (q).



7

Cyclotetradeca-3,4-dienone (7).

3-Ethynylcyclododecanone (**6**) (1.12 g, 5.43 mmol) was thermo-isomerized at 540 °C. The crude product mixture was purified by column chromatography (hexane/AcOEt (70:1) as eluent) to give, as a first fraction, recovered starting material (0.87 g, 78%), followed by **7** (146 mg, 13%) as a colorless oil.

IR (film) 2935vs, 2858vs, 1962w, 1707vs, 1469s, 1446s, 1414m, 1360m, 1266m, 1071w, 1019w cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.36–5.26 (m, H–C(3)), 5.15–5.07 (m, H–C(5)), 3.24 (ddd, ²*J* = 16.4 Hz, ³*J*(2_a,3) = 10.4 Hz, ⁵*J*(2_a,5) = 0.8 Hz, H_a–C(2)), 2.97 (ddd, ²*J* = 16.4 Hz, ³*J*(2_b,3) = 8.9 Hz, ⁵*J*(2_b,5) = 2.5 Hz, H_b–C(2)), 2.61–2.30 (m, CH₂(14)), 2.03–1.91 (m, CH₂(6)), 1.73–1.65 (m, CH₂(13)), 1.40–1.15 (m, 12 H); ¹³C NMR (75 MHz, CDCl₃): δ 209.5 (s, C(1)), 205.2 (s, C(4)), 91.2 (d, C(3)), 84.6 (d, C(5)), 42.7 (t, C(2)), 41.3 (t, C(14)), 28.8 (t), 27.0 (t), 26.9 (t), 26.3 (t), 25.9 (t), 25.8 (t), 25.6 (t), 23.3 (t); EI-MS: 206 (43, *M*⁺), 177 (10, [*M* – CHO]⁺), 163 (21, [*M* – CHO – CH₂]⁺), 149 (30), 135 (26), 121 (29), 107 (100), 93 (68), 81 (80), 67 (59), 55 (70).