Supporting information for

**Ring closing olefin metathesis and radical cyclization
as competing pathways**

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1 Experimental procedure and analytical data for 1a-d

Diallylcarbinols **1a-d** were prepared by addition of allylmagnesiumbromide to the corresponding ester or lactone following a procedure published previously.¹ **1a**¹ and **1b**² have been described in the literature. **1c** and **1d** were obtained from 4-allyl-hept-6-ene-1,4-diol (**11**) (synthesized by addition of allylmagnesiumbromide to γ -butyrolactone³):

4-(3-Benzyloxy-propyl)-hepta-1,6-dien-4-ol (**1c**).

To a solution of **11** (0.45 g, 2.6 mmol) in THF (10 mL) was added NaH (0.12 g, 3.0 mmol of a 60% dispersion in mineral oil), followed by benzyl bromide (0.40 mL, 3.3 mmol) at ambient temperature. The mixture was stirred at ambient temperature for three hours, diluted with ether (20 mL) and quenched with saturated aqueous NH₄Cl solution (20 mL). The organic layer was separated, washed with brine and dried with MgSO₄. After filtration, the solvent was removed in vacuo and the residue was purified by chromatography on silica with cyclohexane/MTBE (20:1 (v/v)) as eluent. Yield: 0.40 g (60%) of colourless **1c**. ¹H NMR (400 MHz, CDCl₃): δ 7.31–7.33 (5 H, H_{Ph}), 5.84 (dddd, 2 H, $J = 17.8, 10.3, 7.4, 7.4$, CH=CH₂), 5.12 (dm, 2 H, $J = 10.3$, CHH=CH), 5.10 (dm, 2 H, $J = 17.8$, CHH=CH), 4.47 (s, 2 H, CH₂Ph), 3.47 (t, 2 H, $J = 6.2$, CH₂OBn), 2.22 (d, 4 H, $J = 7.4$, CHH-CH=CH₂), 2.14 (s, 1 H, OH), 1.70 (tt, 2 H, $J = 6.2, 6.0$, CH₂CH₂OBn), 1.53 (t, 2 H, $J = 6.0$, CH₂COH). ¹³C NMR (100 MHz, CDCl₃): δ 138.3 (0, $C_{ipso-Ph}$), 133.8 (1, HC=CH₂), 128.3, 127.6 (1, C_{Ph}), 127.5 (1, $C_{para-Ph}$), 118.5 (2, H₂C=CH), 73.0 (0, COH), 72.8, 70.7 (2, CH₂O), 43.7 (2, CH₂CH=CH₂), 35.9 (2, CH₂CH₂OAc), 23.7 (2, OHCH₂). IR (neat, NaCl): 3440 (br w), 2930 (m), 2857 (m), 1100 (s), 914 (s) cm⁻¹. MS (EI, 70 eV): m/z 261 ($M^+ + 1$, 7%), 111 (18), 91 (100), 79 (10). Anal. Calcd. for C₁₇H₂₄O₂: C, 78.4%; H, 9.3%. Found: C, 78.1%; H, 9.5%.

Acetic acid 4-allyl-4-hydroxy-hept-6-enyl ester (1d).

To a solution of **11** (0.45g, 2.6 mmol) in CH_2Cl_2 (10 mL) was added Ac_2O (0.30 mL, 3.1 mmol), NEt_3 (0.70 mL, 5.2 mmol) and DMAP (10 mg, 3.5 mol%). After 6 hours at ambient temperature the mixture was diluted with ether (20 mL) and quenched with saturated aqueous NH_4Cl solution. The organic layer was separated, dried with MgSO_4 , filtered and evaporated. The residue was purified by chromatography on silica with cyclohexane/MTBE (5:1 v/v) as eluent. Yield: 0.47 g (84%) of **1d** as a colourless liquid. ^1H NMR (500 MHz, CDCl_3): δ 5.79 (dddd, 2 H, $J = 17.5, 10.2, 7.3, 7.3$, $\text{CH}=\text{CH}_2$), 5.10 (dm, 2 H, $J = 10.2$, $\text{CHH}=\text{CH}$), 5.09 (dm, 2 H, $J = 17.5$, $\text{CHH}=\text{CH}$), 4.01 (t, 2 H, $J = 6.5$, CH_2OAc), 2.20 (dd, 2 H, $J = 13.9, 7.3$, $\text{CHH}-\text{CH}=\text{CH}_2$), 2.17 (dd, 2 H, $J = 13.9, 7.3$, $\text{CHH}-\text{CH}=\text{CH}_2$), 2.00 (s, 3 H, CH_3), 1.65 - 1.71 (3 H, $\text{CH}_2\text{CH}_2\text{OAc}$, OH), 1.45 (2 H, CH_2COH). ^{13}C NMR (125 MHz, CDCl_3): δ 171.1 (0, $\text{C}=\text{O}$), 133.4 (1, $\text{HC}=\text{CH}_2$), 118.8 (2, $\text{H}_2\text{C}=\text{CH}$), 73.0 (0, COH), 64.7 (2, CH_2OAc), 43.6 (2, $\text{CH}_2\text{CH}=\text{CH}_2$), 35.1 (2, $\text{CH}_2\text{CH}_2\text{OAc}$), 22.7 (2, OHCCH_2), 20.9 (3, CH_3). IR (neat, NaCl): 3498 (br w), 2926 (w), 2869 (m), 1740 (s), 1245 (s) cm^{-1} . MS (EI, 70 eV): m/z 212 (M^+ , 5%), 134 (25), 110 (100), 67(30). Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_3$: C, 67.9%; H, 9.5%. Found: C, 67.9%; H, 9.5%.

2 Experimental procedure and analytical data for 3a-d

To a solution of the corresponding metathesis precursor **1a-d** (1.0 mmol) in CCl₄ (20 mmol, 1.9 mL) was added catalyst **B** (42 mg, 5 mol%). The mixture was heated to reflux for 16 hours. The solvent was evaporated, and the residue was purified by chromatography on silica with cyclohexane/MTBE mixtures as eluent.

4-tert-Butyl-cyclopentene-4-ol (3a). Obtained from **1a** (120 mg, 0.7 mmol) as a colourless liquid. Yield: 83 mg (83%). Chromatography: cyclohexane/MTBE 20:1 (v/v). Analytical data are identical to those described in the literature.¹

4-Chloromethyl-cyclopentene-4-ol (3b). Obtained from **1b** (100 mg, 0.6 mmol) as a colourless liquid. Yield: 58 mg (71%). Purification by Kugelrohr distillation (50°C, 0.2 mbar). Full characterization turned out to be very difficult due to rapid decomposition of the neat product. ¹H NMR (500 MHz, CDCl₃): δ 5.67 (s, 2 H, CH=CH), 3.67 (s, 2 H, CH₂Cl), 2.55 (d, 2 H, *J* = 16.2, CHH-CH=), 2.47 (d, 2 H, *J* = 16.2, CHH-CH=), 2.36 (s, 1 H, OH). ¹³C NMR (125 MHz, CDCl₃): δ 128.2 (1, HC=CH), 80.6 (0, COH), 53.9 (2, CH₂Cl), 45.1 (2, CH₂CH=). MS (EI, 70 eV): *m/z* 132 (M⁺, 10%), 115 (70), 106 (14), 97 (30), 83 (95), 79 (85), 55 (100).

4-(3-Benzyloxypropyl)-cyclopentene-4-ol (3c). Obtained from **1c** (94 mg, 0.4 mmol) as a colourless liquid. Yield: 59 mg (71%). Chromatography: cyclohexane/MTBE 10:1 (v/v). ¹H NMR (500 MHz, CDCl₃): δ 7.32 (4H, *H_{Ph}*), 7.26 (m, 1H, *H_{Ph}*), 5.67 (s, 2 H, CH=CH), 4.50 (s, 2 H, CH₂Ph), 3.52 (2 H, CH₂OBn), 2.44 (d, 2 H, *J* = 15.9, CHH-CH=), 2.36 (d, 2 H, *J* = 15.9, CHH-CH=), 1.71-1.80 (4 H, CH₂CH₂CO), 1.61 (s, 1 H, OH). ¹³C NMR (125 MHz, CDCl₃): δ 138.2 (0, *C_{ipso-Ph}*), 133.8, 128.7, 128.4, 127.7, 127.6 (1, *C_{Ph}*, HC=), 80.1 (0, COH), 73.0, 70.8 (2, CH₂O), 47.1 (2, CH₂CH=CH₂), 38.3 (2, CH₂CH₂OBn), 25.3 (2, OHCCCH₂).

4-(3-Acetoxypropyl)-cyclopentene-4-ol (3d). Obtained from **1d** (89 mg, 0.4 mmol) as a colourless liquid. Yield: 53 mg (68%). Chromatography: cyclohexane/MTBE 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃): δ 5.67 (s, 2 H, CH=CH), 4.07 (t, 2 H, *J* = 6.0, CH₂OAc), 2.43 (d, 2 H, *J* = 15.8, CHH-CH=), 2.35 (d, 2 H, *J* = 15.8, CHH-CH=), 2.02 (s, 3 H, CH₃), 1.81 (s, 1 H, OH), 1.75 (2 H, CH₂COAc), 1.69 (2 H, CH₂COH). ¹³C NMR (125 MHz, CDCl₃): δ 171.2 (0, CO₂Me), 128.6 (1, HC=CH), 80.9 (0, COH), 64.8 (2, CH₂OAc), 50.1 (3, OCH₃), 47.0 (2, CH₂CH=), 37.2 (CH₂COAc), 24.1 (CH₂COH), 20.1 (3, CH₃). IR (neat, NaCl): 3460 (br w), 2913 (w), 1735 (s), 1237 (s) cm⁻¹. MS (EI, 70 eV): *m/z* 185 (M⁺+1, 5%), 124 (17), 106 (14), 95 (100), 91 (63), 82 (76). Anal. Calcd. for C₁₀H₁₆O₃: C, 65.2%; H, 8.7%. Found: C, 64.8%; H, 8.6%.

3 Experimental procedure and analytical data for 7a

To a solution of **6a** (0.45 g, 1.7 mmol) in toluene (10 mL) was added Ru-catalyst **B** (58 mg, 4 mol%). The mixture was heated to reflux for 6 hours, the solvent was evaporated and the residue was purified by Kugelrohr distillation (0.3 mbar, 120°C) to give **8a** (0.28 g, 70%) as a colourless liquid. Analytical data are identical to those reported in the literature.⁴ ¹H NMR (500 MHz, CDCl₃): δ 7.62 (d, 4 H, J = 8.0, Ph), 7.45-7.40 (6 H, Ph), 6.09 (s (br), 2 H, -CH=), 1.89 (s, 4 H, -CH₂-). ¹³C NMR (125 MHz, CDCl₃): δ 135.8 (0, *ipso*C, Ph), 134.7, 131.0, 129.5, 127.9 (1, Ph, -CH=), 16.8 (2, -CH₂-).

4 Experimental procedure and analytical data for 8a,b

To a solution of the corresponding precursor **6** (3.6 mmol) in tetrachloromethane (6.9 mL) was added catalyst **A** (146 mg, 5 mol%) under an atmosphere of argon. The mixture was heated to reflux for 16 hours; the solvent was evaporated and the residue was purified by chromatography on silica using cyclohexane-MTBE mixtures as eluent.

Diphenyl-bis-(2,4,4,4-tetrachloro-butyl)-silane (8a). Obtained from **6a** (0.32 g, 1.2 mmol) as an unseparable 1:1 mixture of diastereoisomers. Yield: 0.45 g (64%). ¹H NMR (500 MHz, CDCl₃): δ 7.70-7.50 (2x 4 H, H_{Ph}), 7.50-7.30 (2x 6 H, H_{Ph}), 4.32-4.41 (2x 2 H, CHCl), 3.27 (dd, 2 H, J = 15.5, 6.0, HCHCCl₃), 3.19 (dd, 2 H, J = 15.7, 6.0, HCHCCl₃), 3.13 (dd, 2 H, J = 15.7, 5.5, HCHCCl₃), 3.12 (dd, 2 H, J = 15.5, 4.2, HCHCCl₃), 2.06-2.22 (2x 4 H, SiCH₂). ¹³C NMR (125 MHz, CDCl₃): δ 135.2, 135.0 (1, C_{Ph}), 133.0, 132.5 (0, C_{Ph}), 130.2, 130.1, 128.3, 128.1 (1, C_{Ph}), 96.5, 96.4 (0, CCl₃), 64.5, 64.1 (2, CH₂CCl₃), 55.4, 55.3 (1, CHCl), 26.0, 25.9 (2, SiCH₂). IR (neat, NaCl): 3070 (w), 1428 (s), 1112 (s), 950 (w), 777(m) cm⁻¹. MS: No M⁺ signal was observed using either EI or CI mode.

Dimethyl-bis-(2,4,4,4-tetrachloro-butyl)-silane (8b). Obtained from **6b** (0.50 g, 3.6 mmol) as an unseparable 1:1 mixture of diastereoisomers. Yield: 0.91 g (57%). ¹H NMR (400 MHz, CDCl₃): δ 4.41-4.50 (2x 2 H, CHCl), 3.34 (dd, 2 H, J = 15.6, 5.8, HCHCCl₃), 3.33 (dd, 2 H, J = 15.6, 5.8, HCHCCl₃), 3.13 (dd, 2 H, J = 15.6, 4.8, HCHCCl₃), 3.12 (dd, 2 H, J = 15.6, 5.3, HCHCCl₃), 1.41-1.56 (2x 4 H, SiCH₂), 0.26 (s, 6 H, SiMe₂), 0.24 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe). ¹³C NMR (100 MHz, CDCl₃): δ 96.6, 96.6 (0, CCl₃), 65.1, 65.0 (2, CH₂CCl₃), 55.7, 55.5 (1, CHCl), 28.2, 28.2 (2, SiCH₂), -1.5, -1.8, -2.0 (3, SiMe). IR (neat, NaCl): 2952 (w), 1416 (w), 1257 (m), 951 (m), 847 (s) cm⁻¹. MS: No M⁺ signal was observed using either EI or CI mode.

5 Experimental procedure and analytical data for 9

4-Methoxy-4-*tert*-butyl-hepta-1,6-diene (9). To a solution of **1a** (0.30 g, 1.8 mmol) in THF (5 mL) was added NaH (0.12 g, 3.0 mmol of a 60% dispersion in mineral oil). The mixture was heated to reflux for 0.5 h, cooled to ambient temperature, and MeI (0.13 mL, 2.0 mmol) was added. The mixture was heated to reflux for 4 hours, cooled to ambient temperature, diluted with ether, and quenched with a saturated aqueous solution of NH₄Cl. The organic layer was separated, washed with brine and dried with MgSO₄. After filtration, the solvent was evaporated and the residue was purified by Kugelrohr distillation (0.03 mbar, 25°C) to give **9** (0.22 g, 68%) as a colourless liquid. ¹H NMR (400 MHz, CDCl₃): δ 5.94 (dddd, 2 H, $J = 17.3, 10.3, 7.2, 7.2$, CH=CH₂), 5.04 (ddd, 2 H, $J = 10.3, 3.5, 1.5$, CHH=CH), 5.10 (dm, 2 H, $J = 17.3$, CHH=CH), 3.32 (s, 3 H, OCH₃), 2.44 (ddd, 4 H, $J = 7.0, 3.5, 1.5$, CHH-CH=CH₂), 0.96 (s, 9 H, ^tBu). ¹³C NMR (100 MHz, CDCl₃): δ 136.4 (1, HC=CH₂), 116.1 (2, H₂C=CH), 81.3 (0, COMe), 51.6 (3, OCH₃), 39.7 (0, CMe₃), 38.0 (2, CH₂CH=CH₂), 27.1 (3, CH₃). IR (neat, NaCl): 2961 (s), 1630 (w), 1083 (m), 909 (m) cm⁻¹. MS (EI, 70 eV): m/z 167 (M⁺-Me, <5%), 143 (35), 126 (25), 110 (100), 92 (90), 74 (80), 68 (75). Anal. Calcd. for C₁₂H₂₂O: C, 79.1%; H, 12.2%. Found: C, 78.9%; H, 12.2%.

6 Experimental procedure and analytical data for 10

4-Methoxy-4-*tert*-butyl-cyclopentene (6a). To a solution of **9** (0.11 g, 0.6 mmol) in CCl₄ (1.7 mL) was added Ru-catalyst **A** (23mg, 5 mol%). The mixture was heated to reflux for 16 hours, the solvent was evaporated and the residue was purified by Kugelrohr distillation (0.04 mbar, 50°C) to give **10** (60 mg, 71%) as a colourless liquid. ¹H NMR (500 MHz, CDCl₃): δ 5.64 (s, 2 H, CH=CH), 3.02 (s, 3 H, OCH₃), 2.49 (d, 2 H, $J = 17.0$, CHH-CH=), 2.22 (d, 2 H, $J = 17.0$, CHH-CH=), 0.89 (s, 9 H, ^tBu). ¹³C NMR (125 MHz, CDCl₃): δ 129.3 (1, HC=CH), 89.7 (0, COMe), 50.1 (3, OCH₃), 37.3 (0, CMe₃), 37.1 (2, CH₂CH=), 25.5 (3, CH₃). IR (neat, NaCl): 2955 (s), 2930 (s), 1196 (m), 1092 (s) cm⁻¹. MS (EI, 70 eV): m/z 123 (M⁺-OMe, 82%), 97 (100), 67 (98), 57 (50), 92 (90), 74 (80), 68 (75). Anal. Calcd. for C₁₀H₁₈O: C, 77.9%; H, 11.8%. Found: C, 77.8%; H, 11.7%.

7 NOE-Experiments

NOE-experiments were conducted as one-dimensional, gradient selected experiments at 600 MHz with a mixing time of 800 ms in CDCl_3 .

7.1 NOE-spectra for 2a (page S9)

1-D-NOE (600 MHz, CDCl₃). Irradiation at δ 0.96 (-C(CH₃)₃)

MP1135-noel_35Feb2003
Archive directory: /export/home/vnmr1/vnmr/sv/data
Sample directory: MP1135-noel_35Feb2003
File: NOESY1D_9_92p
Pulse Sequence: NOESY1D
Solvent: CDCl₃
Temp: 27.0 C / 300.1 K
INOVA-600 "eden"
Relax. delay 1.800 sec
Pulse 99.0 degrees
Mixing 0.000 sec
Acquisition 1.800 sec
Width 5898.0 Hz
64 repetitions
OBSERVE H1, 509.0311977 MHz
DATA PROCESSING 1.0 Hz
FT Size 32768
Total time 4 min, 12 sec

7.2 NOE-spectra for **2b**

Irradiation at δ 1.78 (H5') (page S11)

Irradiation at δ 2.06 (H2) (page S12)

1-D-NOE (600 MHz, CDCl₃). Irradiation at δ 1.78 (H5')

1-D-NOE (600 MHz, CDCl₃). Irradiation at δ 2.06 (H2)

7.3 NOE-spectra for 2c

Irradiation at δ 1.62 (H5')

2c (NOE's of H5')
page S14

Irradiation at δ 1.98 (H2)

2c (NOE of H²)
page S15

1-D-NOE (600 MHz, CDCl₃). Irradiation at δ 1.62 (H5')

1-D-NOE (600 MHz, CDCl₃). Irradiation at δ 1.98 (H2)

8 References:

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