

Supporting Information

for:

Application of metathesis reaction in the synthesis of sterically congested medium-sized rings. A direct ring closing versus a double bond migration – ring closing process.

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1. General Information.....	S1
2. Metathesis reactions.....	S2
3. Syntheses of dienes.....	S10
4. References.....	S26

General Information

Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were recorded for CDCl₃ solutions at 200 MHz (¹H) or 50 MHz (¹³C) with Varian Gemini instrument or at 500 MHz (¹H) with Bruker AMX apparatus. Chemical shifts are reported in δ units, referenced for CDCl₃ (7.26 ppm for ¹H and 77.0 ppm for ¹³C). High resolution mass spectra (HRMS) were taken using AMD – 604 unit, electron ionisation (EI) at 70 eV or liquid secondary ion mass spectroscopy (LSIMS), or electrospray ionisation (ESI). HPLC analyses were performed using a Shimadzu LC-8A chromatograph provided with an analytical column (25/0.46 cm), Nucleosil 50/5 μm, or RP18 –Hypersil ODS 5 μm column, Besta Technik GmbH and a variable UV SPD – 6A detector, at 254 nm; a flow rate 1 mL/min. TLC was performed on aluminium sheets, Merck 60F 254. Merck silica gel, 230-400 mesh was used for flash column chromatography in a ratio 30 g per 1 g of organic material, if otherwise not indicated. Deactivated silica gel was prepared by pre-washing of a column with hexane

containing 2% of Et₃N (ca. 50 mL per 10 g of silica gel). Metathesis reactions and all air and/or moisture - sensitive reactions were performed in a flame-dried glassware under a positive pressure of argon, using anhydrous solvents. Benzene was distilled from Na-K alloy. Dichloromethane (DCM) and dichloroethylene were distilled over CaH₂. Triethylamine and pyridine were distilled over CaH₂ and stored over potassium hydroxide. Diisopropylamine was distilled over CaH₂ and stored over 4 Å molecular sieves. Commercially available mixtures of hexanes were redistilled before the use. *n*-Butyllithium was purchased from Aldrich and standardized by titration with 1,10-phenanthroline. Trimethylsilyl triflate was purchased from Aldrich and distilled prior to use. Tris(dibenzylideneacetone)dipalladium, palladium(II) acetate, 1,2-bis-(diphenylphosphino)-ethane and 1,4-bis-(diphenylphosphino)-butane and Grubbs' catalysts were purchased from Aldrich. Organic solutions were dried over anhydrous MgSO₄ and solvents were evaporated using rotary evaporator.

Metathesis reactions

General procedure I: A solution of diene in a chosen solvent, DCM, benzene or ethylene chloride (a half of the total volume needed for the final concentration, 0.01 M) was added to a stirred under argon solution of a Grubbs' catalyst (3-10 mol%) in the same solvent (half of the total volume). The mixture was heated at reflux temperature, under argon, until the starting material was consumed (by TLC analysis). After cooling, the solvent was evaporated (a rotary evaporator) and the residue was chromatographed on silica gel using an appropriate eluting system.

General procedure II: A solution of diene in a chosen solvent (a half of the total volume needed for the final concentration, 0.01 M) was added to a solution of Grubbs' catalyst **7** (5 mol%) and ruthenium hydride **9** (1-5 mol%) in the same solvent (a half of the total volume). The mixture was heated at reflux temperature, under argon, until starting material was consumed (by TLC analysis). Then the solvent was evaporated and the residue was chromatographed on silica gel using an appropriate eluting system.

***S*-tert-Butyl (3aR*,4R*,8aR*)-7,8a-dimethyl-1-oxo-1,2,3,3a,4,5,8,8a-octahydroazulene-4-carbothioate (5)**

a. Procedure I, using diene **3** (102.3 mg, 0.30 mmol), catalyst **7** (12.9 mg, 0.015 mmol) and DCE (30 mL); reaction time, 72 h; silica gel (0.5 g, 5% EtOAc/hexanes); product **5** (60.0 mg, 67% yield).

b. Procedure II, using diene **3** (69.9 mg, 0.208 mmol), catalyst **7** (8.8 mg, 0.010 mmol), ruthenium hydride **9** (11.9 mg, 0.010 mmol) and benzene (21 mL); reaction time, 6 h; silica gel (0.5 g, 5% EtOAc/hexanes); product **5** (61.2 mg, 100%).

c. Procedure I, using diene **10** (60.5 mg, 0.180 mmol), catalyst **7** (7.6 mg, 0.009 mmol) and benzene (18 mL); reaction time, 2 h; silica gel (5.0 g, 5% EtOAc/hexanes); product **5** (51.7 mg, 98% yield): ¹H NMR (200 MHz): 5.69 (br t, *J*=6.0 Hz, =CH, 1H), 2.95-2.85 [m, CHCOSC(CH₃)₃, 1H], 2.65-1.90 (m, 9H), 1.78 (s, C7-CH₃, 3H), 1.44 [s, COSC(CH₃)₃, 9H], 0.86 (s, C8a-CH₃, 3H) ¹³C NMR (50 MHz): 222.8 (C=O), 201.5 [COSC(CH₃)₃], 136.9 (CH=C), 123.4 (CH=C), 53.1, 52.8, 49.0, 48.0, 40.2, 35.4, 29.9, 29.6, 27.4, 24.0, 15.6. HRMS calc. for C₁₇H₂₆O₂S: 294.1653; found: 294.1651.

d. Procedure I, using diene **12** (71.5 mg, 0.204 mmol), catalyst **7** (8.7 mg, 0.010 mmol) and benzene (20.4 mL); reaction time, 72 h; silica gel (5.0 g, 5% EtOAc/hexanes); products: **5** (10.2 mg, 17% yield) and dimers of **12** (45.3 mg, 66%). Dimers of diene **12**: ¹H NMR (200 MHz): 5.52-5.32 (m, =CH, 2H), 4.92 (br s, =CH₂, 2H), 4.75 (br s, =CH₂, 2H), 2.78-1.95 (m, 18H), 1.78-1.20 (m, 10H) overlapping 1.65 (s, CH₃C=CH₂, 6H) and 1.55 [s, COSC(CH₃)₃, 18H], 1.09 (s, C2CH₃, 6H); ¹³C NMR (50 MHz): 222.4 (C=O), 202.9 [COSC(CH₃)₃], 141.4 [C(CH₃)=CH₂], 115.2 (=CH), 54.6, 54.2, 51.6, 48.5, 43.8, 42.9, 37.5, 32.6, 31.3, 30.8, 29.8 [COSC(CH₃)₃], 26.5, 24.6, 23.3, 20.1. HRMS (EI) calc. for C₄₀H₆₄O₄S₂: 672.4246; found: 672.4235.

e. Procedure II, using diene **12** (64.6 mg, 0.185 mmol), catalyst **7** (7.8 mg, 0.009 mmol), ruthenium hydride **9** (8.8 mg, 0.009 mmol) and benzene (18.5 mL); reaction time, 24 h; silica gel (5.0 g, 5% EtOAc/hexanes); products **5** (34.7 mg, 64%) and dimers of **12** (18.6 mg, 30%). Dimers of **12**: ¹H NMR (200 MHz): 5.52-5.32 (m, =CH, 2H), 4.92 (br s, =CH₂, 2H), 4.75 (br s, =CH₂, 2H), 2.78-1.95 (m, 18H), 1.78-1.20 (m, 10H) overlapping 1.65 (s, CH₃C=CH₂, 6H) and 1.55 [s, COSC(CH₃)₃, 18H], 1.09 (s, C2CH₃, 6H); ¹³C NMR (50 MHz): 222.4 (C=O), 202.9 [COSC(CH₃)₃], 141.4 [C(CH₃)=CH₂], 115.2 (=CH), 54.6, 54.2, 51.6, 48.5, 43.8, 42.9, 37.5, 32.6, 31.3, 30.8, 29.8 [COSC(CH₃)₃], 26.5, 24.6, 23.3, 20.1. HRMS (EI) calc. for C₄₀H₆₄O₄S₂: 672.4246; found: 672.4235.

***S*-tert-Butyl (3a*R**,4*R**,8a*R**)-7,8a-dimethyl-1-oxo-1,2,3,3a,4,5,8,8a-octahydroazulene-4-carbothioate (5) and *S*-tert-butyl (3a*R**,4*R**,9a*R**)-8,9a-dimethyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1*H*-cyclopenta[8]annulen-4-carbothioate (4)**

a. Procedure I, using thioester **11** (100.0 mg, 0.286 mmol), catalyst **7** (12.1 mg, 0.014 mmol, 5 mol%) and benzene (28.6 mL); reaction time, 72 h; silica gel (10 g, 5% EtOAc/hexanes);

products: **5** (28.6 mg, 34%) and **4** (35.2 mg, 40%). Product **4**: ^1H NMR (200 MHz): 5.46 (t, $J=5.7$ Hz, =CH, 1H), 2.96-2.80 (m, 1H), 2.76-1.90 (m, 10H), 1.70-1.30 (m, 1H) overlapping 1.53 (s, C8-CH₃, 3H) and 1.44 [s, COSC(CH₃)₃, 9H], 0.97 (s, C9a-CH₃, 3H); ^{13}C NMR (50 MHz): 221.0 (C=O), 202.6 [COSC(CH₃)₃], 133.0 (CH=C), 127.1 (CH=C), 56.2, 53.3, 48.1, 42.9, 37.8, 36.3, 29.6 [COSC(CH₃)₃], 28.0, 27.6, 26.4, 24.5, 19.0. HRMS calc. for C₁₈H₂₈O₂S: 308.1810; found: 308.1816.

b. Procedure II, using diene **11** (78.4, 0.224 mmol), catalyst **7** (9.3 mg, 0.011 mmol, 5 mol%), ruthenium hydride **9** (10.6 mg, 0.011 mmol, 5 mol%) and benzene (22 mL); reaction time, 24 h; silica gel (10 g, 5% EtOAc/hexanes); product **5** (56.6 mg, 86%).

***S*-tert-Butyl (4aR*,5R*,9aR*)-8,9a-dimethyl-1-oxo-2,3,4,4a,5,6,9,9a-octahydro-1H-benz[7]annulen-5-carbothioate (15)**

Procedure I, using diene **13** (68.9 mg, 0.197 mmol), catalyst **7** (8.4 mg, 0.001 mmol, 5 mol%) and benzene (20 mL); reaction time 16 h; silica gel (7.0 g, 7% EtOAc/hexanes); product **15** (34.6 mg, 57%): ^1H NMR (200 MHz): 5.59-5.44 (m, =CH, 1H), 2.92-2.76 (m, 1H), 2.75-1.94 (m, 7H) overlapping 2.39 (s, CH₂CCH₃=CH, 2H), 1.92-1.08 (m, 3H) overlapping 1.75 (s, C8-CH₃, 3H) and 1.44 [s, COSC(CH₃)₃, 9H] and 1.20 (s, C9a-CH₃, 3H); ^{13}C NMR (50 MHz): 214.5 (C=O), 201.2 [COSC(CH₃)₃], 139.1 [CCH₃=CH], 121.9 [CCH₃=CH], 55.3, 51.0, 50.3, 47.7, 38.7, 37.7, 29.8, 29.7, 27.7 [COSC(CH₃)₃], 26.3, 26.2, 19.2. HRMS calc. for C₁₈H₂₈O₂S: 308.1810; found 308.1806.

***S*-tert-Butyl (3aS*,4S*,9aR*)-8-methyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1H-cyclopenta[8]annulen-4-carbothioate (16)**

Procedure I, using thioester **14** (208.0 mg, 0.645 mmol), catalyst **7** (27.3 mg, 0.032 mmol) and benzene (65 mL); reaction time, 16 h; silica gel (20 g, 4% EtOAc/5% *tert*-BuOMe/hexane); product **16** (109.4 mg, 58%): ^1H NMR (200 MHz): 5.41 (br t, $J=7.2$ Hz, =CH, 1H), 2.85 (br t, $J=4.3$ Hz, 1H), 2.76-1.82 (m, 10H), 1.76-1.30 (m, 2H) overlapping 1.57 (s, CH₃, 3H) and 1.43 [s, COSC(CH₃)₃, 9H]; ^{13}C NMR (50 MHz): 218.9 (C=O), 202.2 [COSC(CH₃)₃], 134.9 (C=CH), 125.8 (C=CH), 54.2, 52.9, 48.1 [COSC(CH₃)₃], 42.6, 37.3, 30.1, 29.8 [COSC(CH₃)₃], 28.5, 27.2, 25.3, 25.1. HRMS calc. for C₁₇H₂₆O₂S: 294.1653; found: 294.1658.

***S*-tert-Butyl (3aR*,4R*,8aR*)-8a-methyl-1-oxo-1,2,3,3a,4,5,8,8a-octahydroazulene-4-carbothioate (21)**

a. Procedure I, using diene **17** (70.8 mg, 0.222 mmol), catalyst **6** (19 mg, 0.022 mmol, 10 mol%) and benzene (27 mL); reaction time, 72 h; silica gel (3% EtOAc/hexanes); product **21** (25 mg, 40%). Bicyclic product **22** was identify by HPLC-MS analysis and its content was estimated for 15%.

b. Procedure II, using diene **17** (69.1 mg, 0.215 mmol), catalyst **7** (9.1 mg, 0.011 mmol, 5 mol%) ruthenium hydride **9** (10.2 mg, 0.011 mmol, 5 mol%) and benzene (21.5 mL); reaction time 16 h; silica gel (3% EtOAc/hexanes); product **21** (22.8 mg, 38% yield, 77% pure by HPLC ($R_t = 11.17$ min, detector RI, 5% EtOAc/hexanes): ^1H NMR (200 MHz): 6.08-5.96 (m, =CH, 1H), 5.96-5.70 (m, =CH, 1H), 3.10-2.90 (m, 1H), 2.57-2.26 (m, 3H), 2.26-1.84 (m, 5H), 1.56-1.38 [m, COSC(CH₃)₃, 9H], 1.04-0.93 (m, 1H), 0.87 (s, C8a-CH₃, 3H); ^{13}C NMR (50 MHz): 220.9 (C=O), 201.5 [COSC(CH₃)₃], 130.5 (=CH), 128.3 (=CH), 53.2, 52.7, 49.7, 48.2, 35.6, 35.4, 30.4, 29.6, 24.4, 16.4. HRMS calc. for C₁₆H₂₄O₂SNa: 303.1389; found: 303.1408.

***S*-tert-Butyl (3aR*,4R*,9aR*)-6,6,9a-trimethyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1H-cyclopenta[8]annulen-4-carbothioate (23) and *S*-tert-butyl (2R*)-4,4-dimethyl-2-((1R*,2R*)-2-methyl-3-oxo-2-[(1E,Z)-prop-1-enyl] cyclopentyl)hex-5-carbothioate (24)**

a. Procedure I, using diene **18** (64.0 mg, 0.18 mmol), catalyst **7** (15.5 mg, 0.018 mmol, 10 mol%) and benzene (18 mL); reaction time, 72 h; silica gel (6.0 g, 5% EtOAc/hexanes); product **23** (30.8 mg, 52%). Product **23**: ^1H NMR (200 MHz): 5.41 (dt, $J=11.9$, 1.4 Hz, =CH, 1H), 5.08 (dt, $J=11.9$, 8.7 Hz, =CH, 1H), 3.01 [ddd, $J=13.0$, 6.0, 3.5 Hz, CHCOSC(CH₃)₃, 1H], 2.78-2.26 (m, 5H), 2.24-1.86 (m, 4H), 1.46 [s, COSC(CH₃)₃, 9H], 1.05 and 1.04 (s, C6-CH₃, 6H), 0.99 (s, C9a-CH₃, 3H); ^{13}C NMR (50 MHz): 220.2 (C=O), 202.2 [COSC(CH₃)₃], 143.4 (=CH), 120.5 (=CH), 52.7, 52.3, 48.2, 40.7, 39.1, 36.9, 33.2, 32.6, 29.6 [COSC(CH₃)₃], 29.0, 23.5, 18.9. HRMS (EI) calc. for C₁₉H₃₀O₂S: 322.1967; found: 322.1971.

b. Procedure II, using diene **18** (82.4 mg, 0.235 mmol), catalyst **7** (10.0 mg, 0.012 mmol, 5 mol%), ruthenium hydride **9** (11.2 mg, 0.012 mmol, 5 mol%) and benzene (23.5 mL); reaction time 16 h; silica gel (10 g, 5% EtOAc/hexanes); products: **23** (11.4 mg, 15%) and **24** (28.0 mg, 34%). Product **24**: ^1H NMR (200 MHz): 5.72 (dd, $J=17.8$, 6.8 Hz, 1H), 5.53 (dq, $J=15.5$, 6.3 Hz, 1H), 5.27 (d, $J=15.5$ Hz, 1H), 4.98 (d, $J=8.2$ Hz, 1H), 4.91 (s, 1H), 2.72-2.50 (m, 1H), 2.47-1.82 (m, 6H), 1.68 (dd, $J=6.1$, 1.3 Hz, CH=CHCH₃, 3H), 1.50-1.20 (m, 1H) overlapping 1.43 [s, COSC(CH₃)₃, 9H], 1.09 (s, C2-CH₃, 3H), 1.02 (s, C4a-CH₃, 6H); ^{13}C NMR (50 MHz): 220.2 (C=O), 203.2 [COSC(CH₃)₃], 147.2 (=CH), 133.7 (=CH), 126.4 (=CH), 111.5 (=CH₂), 54.7, 50.4, 49.7, 48.1, 41.4, 37.1, 36.3, 29.7 [COSC(CH₃)₃], 27.8, 26.6, 21.9, 18.4, 16.1. HRMS (ESI) calc. for C₂₁H₃₄O₂S: 373.2172; found: 373.2155.

***S-tert-Butyl* (4aR*,5R*,9aR*)-9a-methyl-1-oxo-2,3,4,4a,5,6,9,9a-octahydro-1H-benz[7]annulen-5-carbothioate (25)**

Procedure I, using diene **19** (56.8 mg, 0.169 mmol), catalyst **7** (7.2 mg, 0.008 mmol) and benzene (17 mL); reaction time, 16 h; silica gel (6.0 g, 4% EtOAc/hexanes); product, **25** (20.7 mg, 42%): ¹H NMR (200 MHz): 5.67-5.55 (m, =CH, 1H), 2.92-1.60 (m, 13H), 1.46 [s, COSC(CH₃)₃, 9H], 1.13 (s, C9a-CH₃, 3H); ¹³C NMR (50 MHz): 213.2 (C=O), 202.8 [COSC(CH₃)₃], 131.4 (=CH), 126.1 (=CH), 60.9, 54.9, 50.8, 48.1, 42.0, 37.3, 32.9, 29.7, 29.6

***S-tert-Butyl* (4aR*,5R*,10aR*)-7,7,10a-trimethyl-1-oxo-1,2,3,4,4a,5,6,7,10,10a-decahydrobenzo[8]annulene-5-carbothioate (26)**

Procedure I, using diene **20** (68.9 mg, 0.197 mmol), catalyst **7** (8.4 mg, 0.001 mmol, 5 mol%) and benzene (20 mL); reaction time, 16 h; silica gel (7.0 g, 7% EtOAc/hexanes); product, **26** (34.6 mg, 57%): ¹H NMR (500 MHz): 5.33-5.22 (m, =CH, 2H), 2.83 (dt, *J*=13.0, 4.8, 1H), 2.64 (dd, *J*=14.8, 13.2, 1H), 2.55 (dd, *J*=13.5, 8.2 Hz, 1H), 2.47 (dd, *J*=13.5, 8.2 Hz, 1H), 2.39 (dt, *J*=14.2, 6.8 Hz, 1H), 2.28 (ddd, *J*=13.0, 4.5, 2.9 Hz, 1H), 2.15-2.05 (m, 2H), 1.98-1.90 (m, 1H), 1.70-1.62 (m, 1H), 1.52-1.30 (m, 2H) overlapping 1.41 [s, COSC(CH₃)₃, 9H], 1.12 [s, C10a-CH₃, 3H], 0.96 [s, C7-(CH₃)₂, 3H], 0.93 [s, C7-(CH₃)₂, 3H]; ¹³C NMR (125 MHz): 213.3 (C=O), 202.8 [COSC(CH₃)₃], 141.3 (=CH), 121.9 (=CH), 57.6 [CHCOSC(CH₃)₃], 54.2, 48.1, 40.6, 40.5, 37.4, 37.2 [C(CH₃)₃], 33.2, 33.0, 29.6 [CHCOSC(CH₃)₃], 28.7, 28.1, 25.6, 21.4. HRMS (ESI) calc. for C₂₀H₃₂O₂SNa: 359.2015; found: 359.2030.

Methyl (3aR*,4R*,8aR*)-7,8a-dimethyl-1-oxo-1,2,3,3a,4,5,8,8a-octahydroazulene-4-carboxylate (32)

a. Procedure I, using ester **27** (78.4 mg, 0.282 mmol), catalyst **7** (12.0 mg, 0.014 mmol, 5 mol%) and benzene (28 mL); reaction time 16 h; silica gel (0.5 g, 5% EtOAc/hexanes); product, **32** (56.6 mg, 85%).

b. Procedure II, using ester **27** (62.5 mg, 0.225 mmol), catalyst **7** (9.5 mg, 0.011 mmol), ruthenium hydride **9** (10.7 mg, 0.011 mmol) and benzene (22.5 mL); reaction time, 30 min; silica gel (5% EtOAc/hexanes); product, **32** (49.9 mg, 94%): mp 52-54 °C; ¹H NMR (200 MHz): 5.81-5.67 (m, =CH, 1H), 3.66 (s, CO₂CH₃, 3H), 2.90-2.78 [m, CHCO₂CH₃, 1H], 2.68-2.28 (m, 4H), 2.27-1.86 (m, 5H), 1.78 (s, C7-CH₃, 3H), 0.76 (s, C8a-CH₃, 3H); ¹³C NMR (50 MHz): 221.0 (C=O), 174.2 (COOCH₃), 136.4 (C7), 124.2 (C6), 53.6, 51.4, 48.9, 43.1, 40.2,

35.3, 30.0, 27.6, 23.9, 14.2. Found: C 71.27; H 8.56. Calc. for C₁₄H₂₀O₃ (236.31): C 71.16; H 8.53.

Methyl (3aR*,4R*,8aR*)-7,8a-dimethyl-1-oxo-1,2,3,3a,4,5,8,8a-octahydroazulene-4-carboxylate (32) and methyl (3aR*,4R*,9aR*)-8,9a-dimethyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1H-cyclopent[8]annulen-4-carboxylate (33)

Procedure II, using diene **27** (74.6 mg, 0.268 mmol), catalyst **7** (11.3 mg, 0.013 mmol, 5 mol%), ruthenium hydride **9** (2.6 mg, 0.003 mmol, 1 mol%) and benzene (27.0 mL); reaction time 6 h; silica gel (10 g, 5% EtOAc/hexanes); products: **32** (27.9 mg, 38%) and **33** (24.2 mg, 36%). Product **33**: R_f=0.58 (5% EtOAc/hexane); ¹H NMR (500 MHz): 5.51 (t, *J*=6.4 Hz, =CH, 1H), 3.67 (s, CO₂CH₃, 3H), 2.83-2.75 [m, CHCO₂CH₃, 1H], 2.70-2.52 (m, 1H), 2.47-2.35 (m, 3H), 2.34-1.90 (m, 6H), 1.68-1.53 (m, 1H) overlapping 1.56 (s, C8-CH₃, 3H), 0.86 (s, C9a-CH₃, 3H); ¹³C NMR (50 MHz): 222.1 (C=O), 175.6 (COOCH₃), 132.7 (C8), 127.5 (C7), 53.2, 51.2, 45.6, 42.7, 37.7, 36.3, 27.6, 26.8, 26.3, 24.7, 18.0. HRMS (EI) calc. for C₁₅H₂₂O₃: 250.1569; found: 250.1562.

Methyl (3aR*,4S*,9aR*)-8,9a-Dimethyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1H-cyclopent[8]annulen-4-carboxylate (34)

Procedure I, using diene **29** (1.020 g, 3.76 mmol), catalyst **7** (93.4 mg, 0.11 mmol, 3 mol%) and DCM (367 mL); reaction time, 6 h; silica gel (30 g, 5% EtOAc/hexanes); product, ester **34** (871.4-889.6 mg, 96-98% yield, 94% pure by HPLC (R_t = 8.85 min, column RP18, detector RI): ¹H NMR (200 MHz): 5.55-5.39 (m, =CH, 1H), 3.67 (s, COOCH₃, 3H), 2.78-2.60 (m, 1H), 2.52-1.98 (m, 7H), 1.97-1.70 (m, 3H) overlapping 1.72 (br s, C8-CH₃, 3H), 1.68-1.40 (m, 1H), 0.92 (s, C9a-CH₃, 3H); ¹³C NMR (50 MHz): 221.0 (C=O), 175.8 (COOCH₃), 135.2 (C8), 126.0 (C7), 52.4, 51.6, 45.6, 42.2, 37.4, 35.8, 30.6, 27.2, 25.0, 22.8, 16.4. HRMS (EI) calc. for C₁₅H₂₂O₃: 250.1569; found: 250.1576.

Dimers of diene 28

Procedure I, using ester **28** (36.0 mg, 0.12 mmol), catalyst **7** (10.5 mg, 0.012 mmol) and benzene (12 mL); reaction time 72 h; silica gel (5.0 g, 5% EtOAc/hexanes); product, dimers of diene **28** (28.4 mg, 83%): ¹H NMR (200 MHz): 5.76-5.28 (m, =CH, 3H), 5.10 (dq, *J*=15.4, 1.6 Hz, 1H), 4.93 (br s, 1H), 4.86 (dd, *J*=6.2, 1.2 Hz, 1H), 3.46 (s, COOCH₃, 6H), 2.56-2.04 (m, 10H), 1.88-1.36 (m, 12H), 1.07 [s, C(2'')CH₃, 6H], 1.00 [s, C(2'')CH₃, 6H], 0.96 (s, C2'-CH₃, 6H); ¹³C NMR (50 MHz): 223.0 (C=O), 220.3 (C=O), 176.0 (COOCH₃), 175.6

(COOCH₃), 147.0, 132.9, 129.3, 126.4, 111.0, 54.4, 52.2, 51.0, 50.9, 49.2, 43.5, 43.3, 42.8, 42.7, 42.6, 38.9, 36.9, 36.5, 36.0, 27.5, 27.3, 26.2, 26.1, 24.6, 23.8, 18.4, 17.8, 13.9. HRMS calc. for C₃₄H₅₂O₆: 556.3764; found: 556.3764.

Methyl (3aR*,4R*,9aR*)-9a-Methyl-1-oxo-2,3,3a,4,5,6,9,9a-oktahydro-1H-cyclopent[8]annulen-4-carboxylate (35)

a. Procedure I, using diene **30** (42.0 mg, 0.159 mmol), catalyst **6** (3.9 mg, 0.005 mmol, 3 mol%) and benzene (16 mL); reaction time, 72 h; silica gel (0.5 g, 5% EtOAc/hexanes); product, **35** (19.8 mg, 56%).

b. Procedure II, using diene **30** (22.8 mg, 0.086 mmol), catalyst **7** (3.7 mg, 0.04 mmol, 5 mol%) ruthenium hydride **9** (4.1 mg, 0.004 mmol, 5 mol%) and benzene (16 mL); reaction time, 6 h; silica gel (0.5 g, 3% EtOAc/hexanes); product, **35** (5.4 mg, 28% yield, 94% pure by HPLC (R_t = 6.42 min, column RP18, detector RI, MeOH : H₂O = 6 : 4): ¹H NMR (500 MHz): 6.08-5.97 (m, =CH, 1H), 5.82-5.71 (m, =CH, 1H), 3.67 (s, COOCH₃, 3H), 2.90-2.84 (m, 1H), 2.66 (ddd, J=14.8, 8.6, 4.7 Hz, CHCOOCH₃, 1H), 2.50-2.33 (m, 3H), 2.25-2.06 (m, 3H), 2.04-1.97 (m, 1H), 1.96-1.87 (m, 1H), 0.76 (s, C9a-CH₃, 3H); ¹³C NMR (50 MHz): 221.0 (C=O), 174.2 (COOCH₃), 131.5 (=CH), 127.7 (=CH), 53.5, 51.5, 49.4, 42.9, 35.5, 35.2, 30.4, 24.2, 14.9. HRMS calc. for C₁₃H₁₈O₃: 222.1256; found: 222.1262.

Methyl (3aR*,4S*,9aR*)-9a-Methyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1H-cyclopent[8]annulen-4-carboxylate (36)

Procedure I, using diene **31** (31.0 mg, 0.117 mmol), catalyst **6** (2.9 mg, 0.003 mmol, 3 mol%) and DCM (12 mL); reaction time, 16 h; silica gel (0.5 g, 10% EtOAc/hexanes); product, **36** (26.2 mg, 94%): ¹H NMR (500 MHz): 5.77-5.70 (m, =CH, 1H), 5.65-5.59 (m, =CH, 1H), 3.67 (s, COOCH₃, 3H), 2.68 (ddd, J=10.2, 6.8, 5.3 Hz, CHCOOCH₃, 1H), 2.42-2.16 (m, 5H), 2.13-2.04 (m, 2H), 1.96-1.83 (m, 3H), 1.62-1.49 (m, 1H), 0.91 (s, CH₃, 3H); ¹³C NMR (50 MHz): 220.1 (C=O), 175.3 (COOCH₃), 132.2 (=CH), 126.7 (=CH), 52.2 (C9a), 51.3 (CHCOOCH₃), 45.2, 41.7, 35.4, 32.0, 29.9, 23.8, 22.6, 15.8 (CH₃). HRMS (EI) calc. for C₁₄H₂₀O₃Na: 236.1412; found: 236.1411.

(3aR*,4R*,9aR*)-4-(Hydroxymethyl)-9a-methyl-2,3,3a,4,5,6,9,9a-octahydro-1H-cyclopenta[8]annulen-1-on (41)

Procedure I, using diene **37** (38.0 mg, 0.16 mmol), catalyst **6** (3.9 mg, 0.016 mmol, 3 mol%) and benzene (16 mL); reaction time, 72 h; silica gel (3.0 g, 30%EtOAc/hexanes); product, **41**

(15.7 mg, 47%): ^1H NMR (200 MHz): 5.82-5.66 (m, =CH, 1H), 5.42-5.22 (m, =CH, 1H), 3.96 (dd, $J = 10.3, 3.2$ Hz, CH_2OH , 1H), 3.61 (dd, $J = 10.3, 8.7$ Hz, CH_2OH , 1H), 2.70-2.25 (m, 5H), 2.24-1.74 (m, 7H), 0.91 (m, C9a-CH₃, 3H); ^{13}C NMR (200 MHz): 221.0 (C=O), 134.3 (=CH), 123.7 (=CH), 64.2 (CH₂OH), 53.4, 46.6, 43.0, 36.2, 33.3, 28.7, 27.4, 23.6, 20.1. HRMS calc. for C₁₃H₂₀O₂: 208.1463; found: 208.1461.

[(3a*R,4*R**,9a*R**)-9a-Methyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1*H*-cyclopent[8]annulen-4-yl]methyl benzoate (42)**

Procedure I, using ester **38** (29.9 mg, 0.088 mmol), catalyst **6** (2.2 mg, 0.0026 mmol, 3 mol%) and benzene (9 mL); reaction time, 72 h; silica gel (1.0 g, 5% EtOAc/hexanes); product, **42** (4.9 mg, 18% yield, 78% pure by HPLC: ($R_t = 53.9$ min, Nucleosil, detector UV, 3% EtOAc/hexanes); ^1H NMR (200 MHz): 8.15-8.00 (m, C₆H₅, 2H), 7.65-7.40 (m, C₆H₅, 3H), 5.88-5.68 (m, =CH, 1H), 5.48-5.26 (m, =CH, 1H), 4.63 (dd, $J = 10.8, 4.3$ Hz, $\text{CH}_2\text{OCOC}_6\text{H}_5$, 1H), 4.28 (dd, $J = 10.8, 9.4$ Hz, $\text{CH}_2\text{OCOC}_6\text{H}_5$, 1H), 2.78-2.22 (m, 6H), 2.20-1.78 (m, 6H), 1.00 (s, CH₃, 3H); ^{13}C NMR (50 MHz): 220.6 (C=O), 166.6 (C₆H₅C=O), 134.1 (=CH), 133.0 (=CH), 130.2 (=CH), 129.5 (C^{IV}, C₆H₅), 128.4 (=CH), 123.9 (=CH), 66.5, 53.4, 42.9, 42.8, 36.2, 33.3, 28.7, 28.0, 23.6, 20.1. HRMS calc. for C₂₀H₂₄O₃: 312.1725; found: 312.1728.

(3a*R,4*S**,9a*R**)-4-(Hydroxymethyl)-9a-methyl-2,3,3a,4,5,6,9,9a-octahydro-1*H*-cyclopent[8]annulen-1-on (43)**

Procedure I, using diene **39** (30 mg, 0.127 mmol), catalyst **6** (3.1 mg, 0.004 mmol, 3 mol%) and DCM (13 mL); reaction time, 16 h; silica gel (6.0 g, 35% EtOAc/hexanes); product, **43** (26.1 mg, 99%): ^1H NMR (200 MHz): 5.80-5.49 (m, =CH, 2H), 3.73 (dd, $J = 10.6, 4.9$ Hz, CH_2OH , 1H), 3.62 (dd, $J = 10.6, 6.0$ Hz, CH_2OH , 1H), 2.49-2.20 (m, 4H), 2.20-1.70 (m, 6H), 1.64-1.42 (m, 2H) overlapping 1.57 (br s, 1H, -OH, disappears on exchange with D₂O), 0.87 (s, C9a-CH₃, 3H); ^{13}C NMR (50 MHz): 221.8 (C=O), 132.7 (=CH), 126.3 (=CH), 65.4 (CH₂OH), 52.2, 46.0, 36.6, 36.0, 32.5, 30.0, 24.2, 21.6, 16.1. HRMS calc. for C₁₃H₂₀O₂: 208.1463; found: 208.1456.

[(3a*R,4*S**,9a*R**)-9a-Methyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1*H*-cyclopent[8]annulen-4-yl]methyl benzoate (44)**

Procedure, I using diene **40** (94.0 mg, 0.276 mmol), catalyst **6** (6.8 mg, 0.008 mmol, 3 mol%) and DCM (28 mL); reaction was heated under reflux for 16 h; silica gel (1.0 g, 10% EtOAc/hexanes); product, **44** (colourless oil, 85.3 mg, 99%): ^1H NMR (200 MHz): 8.10-7.98

(m, C₆H₅, 2H), 7.66-7.38 (m, C₆H₅, 3H), 5.90-5.54 (m, =CH, 2H), 4.39 (dd, *J* = 11.3, 5.3 Hz, CH₂OCOC₆H₅, 1H), 4.29 (dd, *J* = 11.3, 5.5 Hz, CH₂OCOC₆H₅, 1H), 2.52-1.40 (m, 12H), 0.91 (s, CH₃, 3H); ¹³C NMR (50 MHz): 221.2 (C=O), 166.4 (C=O), 133.0 (=CH), 132.5 (=CH), 130.1 (C^{IV}, C₆H₅), 129.4 (=CH), 128.4 (=CH), 126.5 (=CH), 67.6, 52.1, 46.1, 36.0, 33.7, 32.5, 30.6, 24.2, 21.8, 16.0. HRMS (EI) calc. for C₂₀H₂₄O₃: 312.1722; found: 312.1725.

Syntheses of dienes

Hex-5-enoic acid¹

Aqueous H₂O₂ (30%, 227 mL, 2 mol) was added dropwise, within 30 min, maintaining the temperature at 20-25 °C, to a stirred mixture of cyclohexanone (98.0 g, 1 mol) and MeOH (100 mL). The mixture was then added dropwise, within 3 to 4 hrs, maintaining the temperature at 18-20 °C, to a solution of FeSO₄·6H₂O (278 g, 1 mol) and CuSO₄·5H₂O (250 g, 1 mol) in water (1.8 L). The mixture was then extracted with Et₂O (3 × 200 mL). The combined extracts were washed with 20% aq NaOH (3 × 100 mL). The alkaline extract was brought to pH 2 with 20% H₂SO₄ (ca. 250 mL) and the solution was extracted with Et₂O (3 × 200 mL). The combined extracts were washed with water (2 × 100 mL), brine (2 × 200 mL) and dried (MgSO₄). The solution was concentrated and then the residue was distilled in vacuo collecting the fraction at 87-90 °C/10 mmHg, to give hex-5-ene carboxylic acid (51.8 g, 42%, 94% pure by GC): ¹H NMR (200 MHz) 11.40-11.20 (m, 1H), 5.88-5.64 (m, 1H), 5.10-5.82 (m, 2H), 2.36 (t, *J*=7.6 Hz, 2H), 2.18-2.02 (m, 2H), 1.82-1.74 (m, 2H); ¹³C NMR (50MHz) 180.3, 137.4, 115.5, 33.3, 32.9, 23.7.

Methyl hex-5-enoate

Me₃SiCl (0.44 mL, 3.5 mmol) was added to a solution of hex-5-enoic acid (8.010 g, 70.0 mmol) in anhyd MeOH (140 mL). The mixture was heated under reflux for 4 h and then distilled at the atmospheric pressure. The fraction at 140-142 °C was collected to give the title compound (7.63 g, 85%): ¹H NMR (200 MHz) 5.90-5.68 (m, 1H), 5.12-4.90 (m, 2H), 3.67 (s, 3H), 2.32 (t, *J*=7.2, 2H), 2.47-2.28 (m, 2H), 1.85-1.63 (m, 2H); ¹³C NMR (50MHz) 174.0, 137.6, 115.3, 51.4, 33.2, 33.0, 24.0. Spectrum in agreement with that reported.²

S-tert-Butyl hex-5-enethioate

a. Thionyl chloride (8.9 mL, 0.12 mol) and a drop of DMF were added to a mixture of hex-5-enoic acid (11.7 g, 0.10 mol) and benzene (20 mL), stirred at rt. The solvent was evaporated and the residue was added dropwise to a mixture of *t*-BuSH (10.1 mL, 0.90 mol) and Et₃N (16.7 mL, 0.12 mol) and DCM (150 mL), stirred at 0 °C. The cooling bath was removed and, after 30 min, the mixture was washed consecutively with water (2 × 50 mL) and 5% HCl (2 × 50 mL), and dried. The solvent was evaporated and then the residue was distilled in vacuo collecting the fraction at 64-68 °C/1.7 mmHg to give the title product (light yellow oil, 14.7 g, 77% yield, 98% pure by GC).

b. ³ *tert*-BuSH (3.608 g, 40.0 mmol) was added at 0 °C, under argon, to a stirred mixture of Me₃Al (2 M in heptane, 20 mL, 40.0 mmol) and DCM (40 mL). The solution was warmed to rt in ca. 10 min and, after subsequent 30 min, recooled to 0 °C again and methyl hex-5-enoate² (2.560 g, 20.0 mmol) was added. The mixture was stirred at rt 14 h and then water (100 mL) and 3% HCl (50 mL) were added. The aq layer was separated and extracted with DCM (3 × 50 mL). The combined organic solutions were washed with 5% NaOH (3 × 30 mL) and dried. The solvent was evaporated to give the title product (3.68 g, 99% yield, 94% pure by GC): ¹H NMR (200 MHz): 5.88-5.64 (m, =CH, 1H), 5.10-4.92 (m, =CH₂, 2H), 2.46 [t, *J*=7.2 Hz, CH₂COSC(CH₃)₃, 2H], 2.16-2.00 (m, 2H), 1.82-1.64 (m, 2H), 1.45 [s, COSC(CH₃)₃, 9H]; ¹³C NMR (50MHz): 200.1 [COSC(CH₃)₃], 137.5 (=CH), 115.3 (=CH₂), 47.8 [COSC(CH₃)₃], 43.8, 32.8, 29.8 [COSC(CH₃)₃], 24.7. HRMS (ESI) calc. for C₁₀H₁₈OSNa: 209.0971; found: 209.0980.

Hept-5-enoic acid

A solution of *t*-BuOK (8.38 g, 19.0 mmol) in THF (80 mL) was added to a stirred at rt suspension of (4-carboxybutyl)triphenylphosphonium bromide⁴ (16.362 g, 36.9 mmol) in THF (20 mL). After 3 h, freshly distilled acetaldehyde (8 mL) in THF (20 mL) was added. After 1 h, the solvent was evaporated and residue was diluted with water (200 mL) and the solid material was filtered off. The filtrate was acidified with H₃PO₄ (100 mL, 1:1 = conc H₃PO₄:H₂O) and extracted with DCM (4 × 50 mL). The combined organic solutions were dried, the solvent was evaporated and the residue was distilled at 130-132 °C/27 mmHg to give hept-5-enoic acid as a yellow oil (2.305 g, 49%): ¹H NMR (200 MHz): 9.80-9.00 (br s, COOH, 1H), 5.60-5.20 (m, =CH, 2H), 2.36 (t, *J*=7.2 Hz, CH₂CO₂H, 2H), 2.20-1.96 (m, 2H), 1.82-1.55 (m, 5H). Reported distillation temp.⁵: 120-121 °C/16 mmHg.

S-tert-Butyl hept-5-enethioate

Thionyl chloride (2.2 mL, 29.4 mmol) and a drop of DMF were added to a mixture of hept-5-enoic acid (3.131 g, 24.5 mmol) and benzene (5 mL), stirred at rt. The solvent was evaporated and the residue was added dropwise to a mixture of *tert*-BuSH (3 mL, 26.9 mmol), Et₃N (4.9 mL, 35.0 mmol) and DCM (37 mL), stirred at 0 °C. The cooling bath was removed and, after 30 min, the mixture was washed consecutively with water (2 × 25 mL) and 5% HCl (1 × 10 mL), dried. The solvent was evaporated and the residue was distilled in vacuo collecting the fraction at 84-88 °C/2.0 mmHg to give the title product (colourless oil, 2.690 g, 55%): GC 13.3 and 13.2 (dr=7:1, 60-200 °C, 60 °C-1 min., 10 °C/min.); ¹H NMR (200 MHz): 5.60-5.25 (m, =CH, 2H), 2.45 [t, *J*=7.3 Hz, CH₂COSC(CH₃)₃, 2H], 2.20-1.90 (m, 2H), 1.82-1.50 (m, 5H), 1.45 [s, CH₂COSC(CH₃)₃, 9H]; ¹³C NMR (50 MHz): 175.7 [COSC(CH₃)₃], 129.3 (=CH), 124.9 (=CH), 47.7, 43.9, 29.8 [COSC(CH₃)₃], 25.9, 25.3, 12.7. HRMS (EI) calc. for C₁₁H₂₀OS: 200.1235; found: 200.1239.

***S*-(*tert*-Butyl) hept-6-enthioate**

Thionyl chloride (1.4 mL, 72.0 mmol) and a drop of DMF were added to a mixture of hept-6-enoic acid (2.00 g, 16.5 mmol) and benzene (3.3 mL), stirred at rt. The solvent was evaporated and the residue was added dropwise to a mixture of *tert*-BuSH (1.8 mL, 15.5 mmol), Et₃N (2.6 mL, 18.7 mmol) and DCM (25 mL), stirred at 0 °C. The cooling bath was removed and, after 30 min, the mixture was washed consecutively with water (2 × 20 mL) and 5% HCl (1 × 20 mL), and dried. The solvent was evaporated and the residue was distilled in vacuo collecting the fraction at 80-82 °C/2.0 mmHg to give the title product (colourless oil, 2.806 g, 92%): ¹H NMR (200 MHz): 6.00-5.5.80 (m, =CH, 1H), 5.14-4.92 (m, =CH₂, 2H), 2.53 [t, *J*=7.2 Hz, CH₂COSC(CH₃)₃, 2H], 2.24-2.04 (m, 2H), 1.90-1.30 (m, 4H) overlapping 1.54 [s, CH₂COSC(CH₃)₃, 9H]; ¹³C NMR (50 MHz): 200.2 [COSC(CH₃)₃], 138.3 (=CH), 114.7 (=CH), 47.7 [COSC(CH₃)₃], 44.4, 33.3, 29.7 [COSC(CH₃)₃], 28.1, 25.0. HRMS (EI) calc. for C₁₁H₂₀OS: 200.1235; found: 200.1240.

4,4-Dimethylhex-5-en-1-ol

To a suspension of Mg (2.413 g, 89.3 mmol) in Et₂O (75 mL), stirred at 0 °C, prenyl bromide (11.012 g, 74.4 mmol) in Et₂O (75 mL) was added dropwise at within 3 h. To the Grignard reagent thus prepared, oxetane (5.8 mL, 89.3 mmol) was added dropwise at 0 °C and the mixture was stirred at 0 °C for 3 h and then at rt for 16 h. The reaction was quenched with 20% HCl (30 mL) and the organic phase was separated. The aq phase was extracted with Et₂O (2 × 40 mL). The combined organic solutions was washed with brine (1 × 20 mL) and dried. The solvent was evaporated and the residue was distilled in vacuo collecting the fraction at

89-92 °C/10 mmHg to the title product (colourless oil, 5.911 g, 62%): ¹H NMR (200 MHz): 5.75 (dd, *J*=18.1, 10.1 Hz, =CH, 1H), 4.96-4.89 (m, =CH₂, 1H), 4.87 (dd, *J*=5.4, 1.4 Hz, =CH₂, 1H), 3.59 (t, *J*=6.3 Hz, CH₂OH, 2H), 1.65-1.22 (m, 4H), 0.97 (s, CH₃, 6H); ¹³C NMR (50 MHz): 148.1 (=CH), 110.5 (=CH₂), 63.6 (CH₂OH), 38.5, 37.2, 28.0, 26.7 (CH₃). Spectral data are in agreement with those reported.⁶

4,4-Dimethylhex-5-enoic acid

Jones' reagent (ca. 17.5 mL) was added dropwise to a stirred solution of 4,4-dimethylhex-5-en-1-ol (5.824 g, 45.6 mmol) in acetone (30 mL), until deep orange colour persisted. After 0.5 h, *i*-PrOH (ca. 0.5 mL) was added and the solvent was evaporated. The residue was diluted with water (100 mL) and extracted with hexanes (3 × 20 mL). The combined organic extracts were dried and the solvent was evaporated. The residue was distilled in vacuo collecting the fraction at 88-90 °C/3 mmHg to give the title product (colourless oil, 4.530 g, 70%): ¹H NMR (200 MHz): 11.60-10.80 (br s, COOH, 1H), 5.72 (dd, *J*=17.2, 10.9 Hz, =CH, 1H), 4.98 (m, *J*=10.9, 1.3 Hz, =CH₂, 1H), 4.91 (dd, *J*=10.9, 1.3 Hz, =CH₂, 1H), 2.35-2.18 (m, 2H), 1.73-1.55 (m, 2H), 1.00 (s, CH₃, 6H); ¹³C NMR (50 MHz): 180.8 (COOH), 146.8 (=CH), 111.6 (=CH₂), 36.7, 36.2 [C(CH₃)₂], 29.9, 26.7 (CH₃).

S-tert-Butyl 4,4-dimethylhex-5-enethioate

Thionyl chloride (4.5 mL, 60.0 mmol) and a drop of DMF were added to a mixture of 4,4-dimethylhex-5-enoic acid (7.110 g, 50.0 mmol) and benzene (10 mL), stirred at rt. The solvent was evaporated and the residue was added dropwise to a mixture of *tert*-BuSH (5.0 mL, 45.0 mmol) and Et₃N (8.4 mL, 60.0 mmol) and DCM (40 mL), stirred at 0 °C. The cooling bath was removed and, after 30 min, the mixture was washed consecutively with water (2 × 40 mL) and 5% HCl (1 × 25 mL), and dried. The solvent was evaporated and the residue was distilled in vacuo collecting the fraction at 94-96 °C/1.0 mmHg to give the title product (colourless oil, 10.715 g, 84%): ¹H NMR (200 MHz): 5.70 (dd, *J*=17.2, 11.0 Hz, =CH, 1H), 5.00-4.90 (m, =CH₂, 2H), 2.42-2.32 [m, CH₂COSC(CH₃)₃, 2H], 1.68-1.54 [m, CH₂CH₂COSC(CH₃)₃, 2H], 1.43 [s, COSC(CH₃)₃, 9H], 0.97 (s, CH₃, 6H); ¹³C NMR (50 MHz): 200.6 [COSC(CH₃)₃], 147.0 (=CH), 111.4 (=CH₂), 47.7 [C(CH₃)₂], 40.6, 37.5, 36.3, 29.8 [COSC(CH₃)₃], 26.5 (CH₃). HRMS (EI) calc. for C₁₂H₂₂OSNa: 237.1284; found: 237.1295.

{1(Z)-1-[(*tert*-Butylthio)hexa-1,5-dienyl]oxo}trimethylsilane (45)

S-(*tert*-Butyl) hex-5-enethioate⁷ (12.1 g, 65.0 mmol) was added dropwise to a solution LDA (78 mmol) [prepared from (*i*-Pr)₂NH (1.102 mL, 78 mmol) in THF (100 mL) and *n*-BuLi (2.5 M in hexanes, 31 mL, 78 mmol)], stirred at -78 °C. After 30 min, Me₃SiCl (9.89 mL, 78 mmol) was added. The solution was stirred at rt for 3 h and then the solvent was evaporated. The residue was diluted with hexanes (200 mL) and filtered through a pad of Celite. The solvent was evaporated and the residue was distilled at 79-82 °C/3 mmHg to give **45** [14.4 g, 87%, GC analysis of this product showed the presence of one isomer (Z) only]: ¹H NMR (200 MHz): 5.92-5.68 (m, CH=CH₂, 1H), 5.20 [t, *J* = 7.2 Hz, =CHCOSC(CH₃)₃, 1H], 5.10-4.90 (m, CH=CH₂, 2H), 2.37-2.20 (m, 2H), 2.18-2.00 (m, 2H), 1.37 [s, SC(CH₃)₃, 9H], 0.22 [s, Si(CH₃)₃, 9H]; ¹³C NMR (50 MHz): 145.5 [HC=CS(CH₃)₃OSi(CH₃)₃], 138.2 [HC=CS(CH₃)₃OSi(CH₃)₃], 119.8 (=CH), 114.7 (=CH₂), 46.3, 34.2, 31.8 [SC(CH₃)₃], 31.4, 28.7, 0.8 [Si(CH₃)₃], 0.3 [Si(CH₃)₃]. HRMS (EI) calc. for C₉H₁₇OSSi (M⁺-C₄H₉) 201.0769; found: 201.0758.

{1(Z)-1-[(*tert*-Butylthio)hepta-1,5-dienyl]oxo}trimethylsilane (48)

S-(*tert*-Butyl) hept-5-enethioate⁷ (2.695 g, 13.5 mmol) was added dropwise to a solution LDA (17.5 mmol) [prepared from (*i*-Pr)₂NH (2.5 mL, 17.5 mmol) in THF (22 mL) and *n*-BuLi (2.5 M in hexanes, 7.0 mL, 17.5 mmol)], stirred at -78 °C. After 30 min, Me₃SiCl (2.2 mL, 16.8 mmol) was added. The solution was stirred at rt for 3 h and then the solvent was evaporated. The residue was diluted with hexanes (28 mL) and filtered through a pad of Celite. The solvent was evaporated and the residue was distilled in vacuo collecting the fraction at 100-103 °C/2 mmHg to give **48** (3.040 g, 82% yield, 94% pure by GC) (GC analysis of this product showed the presence of four isomers, isomer ratio, 7 : 1, C5-C6, and 12 : 1, C1-C2: ¹H NMR (200 MHz): 5.60-5.5.26 (m, =CH, 2H), 5.21 [t, *J*=7.4 Hz, =CHCOSC(CH₃)₃, 1H], 2.35-1.85 (m, 4H), 1.70-1.55 (m, =CHCH₃, 3H), 1.37 [s, SC(CH₃)₃, 9H], 0.22 [s, Si(CH₃)₃, 9H]; separated signal of an isomer: 5.19 [t, *J*=7.4 Hz, =CHCOSC(CH₃)₃]; ¹³C NMR (50 MHz): 130.0 (=CH), 124.2 (=CH), 120.1, 46.3 [SC(CH₃)₃], 31.7, 31.3, 29.2, 27.3, 12.8, 0.2 [Si(CH₃)₃]. HRMS (EI) calc. for C₁₄H₂₈OSSi: 272.1630; found: 272.1626.

(1Z)-[1-[(*tert*-Butylthio)hepta-1,6-dienyloxy]trimethylsilane (47)

S-(*tert*-Butyl) hept-6-enethioate⁷ (3.648 g, 18.2 mmol) was added dropwise to a solution LDA (21.9 mmol) [prepared from (*i*-Pr)₂NH (3.1 mL, 21.9 mmol) in THF (23 mL) and *n*-BuLi (2.5 M in hexanes, 8.8 mL, 21.9 mmol)], stirred at -78 °C. After 30 min, Me₃SiCl (2.8 mL, 21.9

mmol) was added. The solution was stirred at rt for 3 h and the solvent was evaporated. The residue was diluted with hexanes (50 mL) and filtered through a pad of Celite. The solvent was evaporated and the residue was distilled in vacuo collecting the fraction at 100-102 °C/2 mmHg to give **47** (4.549 g, 92% yield, 98% pure by GC): ¹H NMR (200 MHz): 5.94-5.70 (m, CH=CH₂, 1H), 5.20 [t, *J*=7.4 Hz, =CHCOSC(CH₃)₃, 1H], 5.08-4.88 (m, CH=CH₂, 2H), 2.24-1.94 (m, 4H), 1.45-1.30 (m, 2H) overlapping 1.37 [s, SC(CH₃)₃, 9H], 0.21 [s, Si(CH₃)₃, 9H]; ¹³C NMR (50 MHz): 145.4 HC=CS(CH₃)₃OSi(CH₃)₃, 138.8 [HC=CS(CH₃)₃OSi(CH₃)₃], 120.4 (=CH), 114.4 (=CH₂), 46.3 [SC(CH₃)₃], 33.4, 31.8 [SC(CH₃)₃], 29.4, 28.7, 0.3 [Si(CH₃)₃]. HRMS (EI) calc. for C₁₄H₂₈OSiS: 272.1630; found: 272.1641.

(1E)-(1-(tert-Butylthio)-4,4-dimethylhexa-1,5-dienyloxy)trimethylsilane (46)

S-(tert-Butyl) 4,4-dimethylhex-5-enthioate⁷ (4.420 g, 20.6 mmol) was added dropwise to a solution LDA (24.8 mmol) [prepared from (*i*-Pr)₂NH (3.5 mL, 24.8 mmol) in THF (32 mL) and *n*-BuLi (9.9 mL, 24.8 mmol, 2.5 M in hexanes,)], stirred at -78 °C. After 30 min, Me₃SiCl (3.2 mL, 24.8 mmol) was added. The solution was stirred at rt for 3 h and then the solvent was evaporated. The residue was diluted with hexanes (54 mL) and filtered through a pad of Celite. The solvent was evaporated and the residue was distilled in vacuo collecting the fraction at 123-125 °C/0.1 mmHg to give **46** (4.607 g, 78% yield, isomer ratio 4.9:1 from ¹H NMR): ¹H NMR (200 MHz): 5.90-5.68 (m, CH=CH₂, 1H), 5.15 [t, *J* = 7.6 Hz, =CHCOSC(CH₃)₃, 1H], 4.98-4.84 (m, CH=CH₂, 2H), 2.21 (d, *J* = 7.6 Hz, CH₂, 2H), 1.36 [s, SC(CH₃)₃, 9H], 0.98 [s, C4-CH₃, 6H], 0.21 [s, Si(CH₃)₃, 6H]; separated signals of the minor isomer: 5.17 (t, *J* = 7.3 Hz, =C2H), 2.05 (d, *J* = 7.3 Hz, CH₂), 1.33 [s, SC(CH₃)₃]; ¹³C NMR (50 MHz): 148.2, 146.4, 116.9, 110.4, 46.5, 41.9, 37.5, 31.8, 31.5, 26.8, 26.7, 24.5, 0.38; separated signals of the minor isomer: 31.5, 0.88. HRMS (ESI) calc. for C₁₅H₃₀OSSiNa: 309.1679; found: 309.1686

***S*-tert-Butyl (2*R**)-2-[(1*R**,2*R**)-2-methyl-2-(2-methylprop-2-enyl)-3-oxocyclopentyl]hex-5-enthioate (3)**

2-Methylcyclopent-2-en-1-one (**49**) (0.96 g, 10.0 mmol) was added dropwise to a mixture of **45** (3.43 g, 12.0 mmol), Me₃SiOTf (100 μL, 0.5 mmol, 5 mol%) and anhyd DCM (30 mL), stirred under argon at -78 °C. Stirring at -78 °C was continued for 3 h and then 2-pyridinemethanol (72 μL, 0.75 mmol, 7.5 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (60 mL) and filtered through

deactivated silica gel (12 g). The solvent was evaporated in vacuo to give silyl enol ether 51 as a light yellow oil. A solution of this product and methyl 2-methylprop-2-enyl carbonate⁸ (**53**), (2.60 g, 20.0 mmol) in THF (12 mL) was added to a solution of Pd(OAc)₂ (112.0 mg, 0.5 mmol, 5 mol%) and dppb (213.1 mg, 0.5 mmol, 5 mol%) in THF (18 mL), and stirred under argon at rt. Stirring was continued for 120 h and then the solvent was evaporated. The residue was chromatographed on silica gel (3% EtOAc/hexanes) to give **3** as a light yellow oil (1.79 g, 86%): ¹H NMR (200 MHz): 5.90-5.66 (m, CH=CH₂, 1H), 5.10-4.92 (m, CH=CH₂, 2H), 4.85 (br s, CH₂=CCH₃, 1H), 4.69 (br s, CH₂=CCH₃, 1H), 2.69-2.49 (m, 2H), 2.47-2.23 (m, 2H), 2.22-1.92 (m, 5H), 1.84-1.30 (m, 3H) overlapping 1.58 (s, CH₂=CCH₃, 3H) and 1.48 [s, COSC(CH₃)₃, 9H], 1.02 (s, C2-CH₃, 3H); ¹³C NMR (50 MHz): 222.4 (C=O), 202.8 [COSC(CH₃)₃], 141.4 (CH₂=CCH₃), 137.8 (CH=CH₂), 115.3 (2 × =CH₂), 54.2, 51.7, 48.7, 43.8, 42.9, 37.5, 30.9, 30.7, 29.8 [COSC(CH₃)₃], 24.6, 23.3, 20.1. HRMS (EI) calc. for C₂₀H₃₂O₂S: 336.2123; found: 336.2125.

***S*-tert-Butyl (2*R**,5*E/Z*)-2-[(1*R**,2*R**)-2-methyl-2-(2-methyl-2-propenyl)-3-oxocyclopentyl]hept-5-enethioate (**11**)**

2-Methylcyclopent-2-en-1-one (**49**) (352.0 mg, 3.67 mmol) in DCM (13 mL) was added dropwise to a mixture of 48 (1.211 g, 4.40 mmol), Me₃SiOTf (36 μL, 0.18 mmol, 5 mol%) and anhyd DCM (20 mL), stirred under argon at -78 °C. Stirring at -78 °C was continued for 1 h and then 2-pyridinemethanol (26 μL, 0.33 mmol, 7.5 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (66 mL), and filtered through deactivated silica gel (6 g). The solvent was evaporated to give silyl enol ether **51** as a light yellow oil. A solution of this product and carbonate **53** (1.131 g, 8.80 mmol) in THF (5 mL) was added to a stirred solution of Pd(OAc)₂ (40.3 mg, 0.18 mmol, 5 mol%) and dppb (76.8 mg, 0.18 mmol, 5 mol%) in THF (15 mL). Stirring was continued 72 h at rt and then the solvent was evaporated. The residue was chromatographed on silica gel (2-5% EtOAc/hexanes) to give **11** (815.5 mg, 64%): ¹H NMR (200 MHz): 5.56-5.25 (m, =CH, 2H), 4.95 (br s, =CH, 1H), 4.85 (br s, =CH, 1H), 4.67 (br s, =CH, 1H), 2.70-2.48 (m, 2H), 3.79 (s, a contamination), 2.47-1.93 (m, 7H), 1.82-1.25 (m, 6H) overlapping 1.58 (br s, CH₂=CCH₃, 3H) and 1.49 [s, COSC(CH₃)₃, 9H], 1.02 (s, C2-CH₃, 3H); ¹³C NMR (50 MHz): 222.6 (C=O), 203.1 [COSC(CH₃)₃], 141.5 (CH₂=CCH₃), 129.5 (=CH), 124.8 (=CH), 115.3 (CH₂=CCH₃), 54.4, 51.7, 48.6, 43.8, 42.9, 37.5, 31.2, 29.7 [SC(CH₃)₃], 24.6, 24.2, 23.2, 20.0, 12.8. HRMS (EI) calc. for C₂₁H₃₄O₂S: 350.2280; found: 350.2274.

***S*-tert-Butyl (2*R**)-2-[(1*R**,2*R**)-2-methyl-2-(2-methyl-2-propenyl)-3-oxocyclopentyl]hept-6-enethioate (12)**

2-Methylcyclopent-2-en-1-one (**49**) (192 mg, 2.00 mmol) was added dropwise to a mixture of **47** (614.9 mg, 2.40 mmol), Me₃SiOTf (19.7 μl, 0.10 mmol, 5 mol%) and anhyd DCM (15 mL), stirred under argon at -78 °C. Stirring at -78 °C was continued for 3 h and then 2-pyridinemethanol (14.5 μl, 0.15 mmol, 7.5 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (30 mL) and filtered through deactivated silica gel (6 g). The solvent was evaporated to give silyl enol ether **51** as a light yellow oil. A solution of this product and carbonate **53** (520.0 mg, 4.00 mmol) in THF (5 mL) was added to a stirred solution of Pd(OAc)₂ (22.4 mg, 0.1 mmol, 5 mol%) and dppb (42.7 mg, 0.1 mmol, 5 mol%) in THF (10 mL). The mixture was heated under reflux for 6 h, cooled and the solvent was evaporated. The residue was chromatographed on silica gel (8 g, 2-5% EtOAc/hexanes) to give **12** as a light yellow oil (272.1 mg, 39%): ¹H NMR (200 MHz): 5.88-5.64 (m, =CH, 1H), 5.06-4.91 (m, CH=CH₂, 2H), 4.85 [br s, C(CH₃)=CH₂, 1H], 4.68 [br s, C(CH₃)=CH₂, 1H], 2.70-2.05 (m, 9H), 1.75-1.3 (m, 5H) overlapping 1.58 [s, (CH₃)C=CH₂, 3H] and 1.48 [s, COSC(CH₃)₃, 9H], 1.02 (s, C2-CH₃, 3H); ¹³C NMR (50 MHz): 222.4 (C=O), 202.9 [COSC(CH₃)₃], 141.4 [C(CH₃)=CH₂], 138.2 (CH=CH₂), 115.2 (=CH₂), 114.8 (=CH₂), 54.6, 51.6, 48.6, 43.8, 42.9, 37.5, 33.7, 30.8, 29.8 [SC(CH₃)], 25.9, 24.6, 23.3, 20.1. HRMS (EI) calc. for C₂₁H₃₄O₂S: 350.2280; found: 350.2274.

***S*-tert-Butyl (2*R**)-2-[(1*R**,2*R**)-2-methyl-2-(2-methyl-2-propenyl)-3-oxocyclohexyl]hex-5-enethioate (13)**

2-Methylcyclohex-2-en-1-one (**50**) (220.0 mg, 2.0 mmol) was added dropwise to a mixture of **45** (620.0 mg, 2.40 mmol), Me₃SiOTf (40 μl, 0.2 mmol, 10 mol%) and anhyd DCM (6 mL), stirred under argon at -78 °C. Stirring at -78 °C was continued for 20 h and then 2-pyridinemethanol (29 μl, 0.30 mmol, 15 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (12 mL) and filtered through deactivated silica gel (15 g). The solvent was evaporated to give silyl enol ether **51**. A solution of this product and carbonate **53** (520.0 mg, 4.0 mmol) in THF (6 mL) was added to a stirred solution of Pd(OAc)₂ (22.4 mg, 0.10 mmol, 5 mol%) and dppb (42.7 mg, 0.10 mmol) in THF (6 mL). The mixture was heated under reflux for 6 h, cooled and the solvent was evaporated. The residue was chromatographed on silica gel (3% EtOAc/hexanes) to give **13**

(154.1 mg, 22%): ^1H NMR (200 MHz): 5.88-5.64 (m, $\text{CH}=\text{CH}_2$, 1H), 5.12-4.92 (m, $\text{CH}=\text{CH}_2$, 2H), 4.84 [br s, $\text{C}(\text{CH}_3)=\text{CH}_2$, 1H], 4.64 [br s, $\text{C}(\text{CH}_3)=\text{CH}_2$, 1H], 2.70-2.26 (m, 7H), 2.24-1.40 (m, 7H) overlapping 1.62 [s, $\text{C}(\text{CH}_3)=\text{CH}_2$, 3H] and 1.44 [s, $\text{COSC}(\text{CH}_3)_3$, 9H], 1.02 (s, $\text{C}2'-\text{CH}_3$, 3H); ^{13}C NMR (50 MHz): 214.7 (C=O), 203.4 [$\text{COSC}(\text{CH}_3)_3$], 141.5 [$\text{C}(\text{CH}_3)=\text{CH}_2$], 137.6 ($\text{CH}=\text{CH}_2$), 115.6 ($=\text{CH}_2$), 115.3 ($=\text{CH}_2$), 52.9, 48.0, 44.5, 44.2, 38.4, 32.0, 29.7 [$\text{COSC}(\text{CH}_3)_3$], 28.2, 24.5, 23.8, 22.6, 20.8. HRMS (EI, m/z) calc. for $\text{C}_{21}\text{H}_{34}\text{O}_2\text{S}$: 350.2288; found: 350.2280.

***S*-tert-Butyl (2*S**)-2-[(1*R**,2*R**)-2-(2-methyl-2-propenyl)-3-oxocyclopentyl]-hex-5-enthioate (14)**

Cyclopent-2-en-1-one (**54**) (82.0 mg, 1.00 mmol) was added dropwise to a mixture of **45** (309.8 mg, 1.20 mmol) and Me_3SiOTf (10 μl , 0.05 mmol, 5 mol %), and anhyd DCM (3 mL), stirred under argon at -78 °C. Stirring at -78 °C was continued for 3 h and then 2-pyridinemethanol (7.2 μl , 0.075 mmol, 7.5 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (6 mL) and filtered through deactivated silica gel (1.5 g). The solvent was removed to give silyl enol ether **55**. A solution of this product and carbonate **53** (260.3 mg, 2.00 mmol) in THF (5 mL) was added to a stirred solution of $\text{Pd}_2(\text{dba})_3$ (45.8 mg, 0.050 mmol, 5 mol%) and dppe (119.0 mg, 0.30 mmol, 30 mol%) in THF (5 mL). The mixture was heated under reflux for 6 h, cooled and the solvent was evaporated. The residue was chromatographed on silica gel (5% EtOAc/hexanes) to give **14** (119.1 mg, 37%): ^1H NMR (200 MHz): 5.90-5.64 (m, $\text{CH}=\text{CH}_2$, 1H), 5.12-4.92 (m, $\text{CH}_2=$, 2H), 4.88-4.68 (m, $\text{CH}_2=$, 2H), 2.74-2.56 (m, 1H), 2.44-1.54 (m, 11H) overlapping 1.68 (s, $\text{CH}_3\text{C}=\text{CH}_2$, 3H), 1.52-1.20 (m, 1H) overlapping 1.46 [s, $\text{SC}(\text{CH}_3)_3$, 9H]; ^{13}C NMR (50 MHz): 219.5 (C=O), 202.8 [$\text{COSC}(\text{CH}_3)_3$], 142.6 ($\text{CH}_3\text{C}=\text{CH}_2$), 137.6 ($\text{CH}=\text{}$), 115.5 ($\text{CH}_2=$), 113.5 ($\text{CH}_2=$), 55.8, 49.7, 48.4 [$\text{COSC}(\text{CH}_3)_3$], 43.8, 37.9, 37.1, 31.5, 29.7 [$\text{COSC}(\text{CH}_3)_3$], 27.6, 23.5, 22.5. HRMS (EI) calc. for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{S}$: 322.1967; found: 322.1974.

***S*-tert-Butyl (2*R**)-2[(1*R**,2*R**)-2-allyl-2-methyl-3-oxocyclopentyl]hex-5-enthioate (17)**

2-Methylcyclopent-2-en-1-one (**49**) (1.0 mL, 10.0 mmol) was added dropwise to a mixture of **45** (3.102 g, 12.0 mmol), Me_3SiOTf (98 μl , 0.5 mmol) and anhyd DCM (90 mL), stirred under argon at -78 °C. Stirring at -78 °C was continued for 3 h and then 2-pyridinemethanol (72 μl , 0.75 mmol) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (90 mL) and filtered through deactivated silica gel (40 g).

The solvent was evaporated to give silyl enol ether **51** (3.612 g, 98%). A solution of this product (3.612 g, 9.80 mmol) and allyl methyl carbonate⁹ **52** (2.276 g, 19.6 mmol) in THF (24 mL) (prepared under argon) was added to a stirred solution of Pd₂(dba)₃ (274.7 mg) and dppe (956.2 mg, 2.4 mmol) in THF (48 mL). The mixture was heated under reflux for 6 h, cooled and the solvent was evaporated. The residue was chromatographed on silica gel (120 g, 3% EtOAc/hexanes) to give **17** (3.162 g, 68%): ¹H NMR (200 MHz): 5.90-5.50 (m, CH=CH₂, 2H), 5.10-4.92 (m, CH=CH₂, 4H), 2.70-2.25 (m, 4H), 2.20-1.85 (m, 5H), 1.80-1.55 (m, 3H), 1.49 [s, SC(CH₃)₃, 9H], 1.01 (s, C₂CH₃, 3H); ¹³C NMR (50 MHz): 221.9 (C=O), 202.9 [COSC(CH₃)₃], 137.8 (CH=CH₂), 133.8 (CH=CH₂), 118.7 (CH=CH₂), 115.3 (CH=CH₂), 54.0 [CHCOSC(CH₃)₃], 52.3 (C₂), 48.7 [COSC(CH₃)₃], 43.1, 39.8, 37.5, 30.8, 29.6 [COSC(CH₃)₃], 23.4, 18.7. HRMS (EI) calc. for C₁₉H₃₀O₂S: 322.1967; found: 322.1970.

***S*-tert-Butyl (2*R**)-2-[(1*R**,2*R**)-2-allyl-2-methyl-3-oxocyclopentyl]-4,4-dimethylhex-5-enthioate (18)**

2-Methylcyclopent-2-en-1-one (**49**) (1.0 g, 3.50 mmol) was added dropwise to a mixture of **46** (280.0 mg, 2.91 mmol), TrSbCl₆ (67.4 mg, 0.12 mmol, 4 mol%) and anhyd DCM (20 mL), stirred under argon at -78 °C. Stirring at -78 °C was continued for 1 h and then 2-pyridinemethanol (21 μL, 0.22 mmol, 7.5 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (40 mL) and filtered through deactivated silica gel (8 g). The solvent was evaporated to give silyl enol ether **51**. A solution of this product and carbonate **52** (676.7 mg, 5.83 mmol) in THF (10 mL) was added to a stirred solution of Pd₂(dba)₃ (80.1 mg, 0.09 mmol, 3 mol%) and dppe (200.2 mg, 0.53 mmol, 18 mol%) in THF (20 mL). The mixture was heated under reflux for 6 h, cooled and the solvent was evaporated. The residue was chromatographed on silica gel (3% EtOAc/hexanes) to give **18** (704.4 mg, 69%): ¹H NMR (200 MHz): 5.82-5.48 (m, =CH, 1H) overlapping 5.72 (dd, *J*= 17.5, 10.6 Hz, 1H), 5.20-4.86 (m, =CH₂, 4H), 2.72-2.52 (m, 1H), 2.44-2.22 (m, 3H), 2.21-1.50 (m, C₄-CH₃, 6H), 1.45 [s, COSC(CH₃)₃, 9H], 1.02 (s, 6H), 0.99 (s, C₂-CH₃, 3H); ¹³C NMR (50 MHz): 221.6 (C=O), 203.4 [COSC(CH₃)₃], 147.1 (=CH), 133.6 (=CH), 118.9 (=CH₂), 111.6 (=CH₂), 52.6, 50.6, 48.4, 44.8, 41.8, 40.2, 37.2, 37.1, 29.7 [C(CH₃)₃], 27.9, 26.6, 22.4, 18.2. HRMS (EI) calc. for C₂₁H₃₄O₂S: 350.2280; found: 350.2283.

***S*-tert-Butyl (2*R**)-2-[(1*R**,2*R**)-2-allyl-2-methyl-3-oxocyclohexyl]-hex-5-enthioate (19)**

2-Methylcyclohex-2-en-1-one (**50**) (441 mg, 4.00 mmol) was added dropwise to a mixture of **45** (1.241 g, 4.8 mmol), Me₃SiOTf (79 μl, 0.4 mmol, 10 mol%) and anhyd DCM (12 mL),

stirred under argon at $-78\text{ }^{\circ}\text{C}$. Stirring at $-78\text{ }^{\circ}\text{C}$ was continued for 20 h and then 2-pyridinemethanol (50 μl , 0.52 mmol, 13 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (24 mL) and filtered through deactivated silica gel (6 g). The solvent was evaporated in vacuo to give silyl enol ether **51**. A solution of this product and carbonate **52** (928.0 mg, 8.0 mmol) in THF (mL) was added to a stirred solution of $\text{Pd}_2(\text{dba})_3$ (109.9 mg, 0.12 mmol, 3 mol%) and dppe (286.9 mg, 0.72 mmol) in THF (10 mL). The mixture was heated at $60\text{ }^{\circ}\text{C}$ for 30 h, cooled and the solvent was evaporated. The residue was chromatographed on silica gel (5% EtOAc/hexanes) to give **19** (927.4 mg, 69%): ^1H NMR (200 MHz): 5.86-5.60 (m, $\text{CH}=\underline{\text{C}}\text{H}_2$, 2H), 5.20-4.80 (m, $\text{C}\underline{\text{H}}=\text{CH}_2$, 4H), 2.72-2.43 (m, 2H), 2.41-1.34 (m, 12H) overlapping 1.44 [s, $\text{SC}(\text{CH}_3)_3$, 9H] and 1.02 (s, $\text{C}2'-\text{CH}_3$, 3H), ^{13}C NMR (50 MHz): 214.0 (C=O), 203.1 [$\text{COSC}(\text{CH}_3)_3$], 137.6 ($\text{C}\underline{\text{H}}=\text{CH}_2$), 134.1 ($\text{C}\underline{\text{H}}=\text{CH}_2$), 118.5 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 115.6 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 53.4 (C2'), 52.6, 48.1 [$\text{COSC}(\text{CH}_3)_3$], 44.2, 40.7, 38.6, 32.0, 29.7 [$\text{COSC}(\underline{\text{C}}\text{H}_3)_3$], 28.0, 24.2, 22.6, 20.4. HRMS (EI) calc. for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{S}$: 336.2123; found: 336.2122.

***S*-tert-Butyl (2*R**)-2-[(1*R**,2*R**)-2-allyl-2-methyl-3-oxocyclohexyl]-4,4-dimethyl hex-5-enethioate (20)**

2-Methylcyclohex-2-en-1-one (**50**) (441.0 mg, 4.0 mmol) was added dropwise to a mixture of **46** (1.375 g, 4.8 mmol), Me_3SiOTf (79 μl , 0.4 mmol, 10 mol%) and anhyd DCM (12 mL), stirred under argon at $-78\text{ }^{\circ}\text{C}$. Stirring at $-78\text{ }^{\circ}\text{C}$ was continued for 20 h and then 2-pyridinemethanol (58 μl , 0.6 mmol, 15 mol%) was added. The mixture was allowed to warm to rt (in ca. 30 min) and then it was diluted with hexanes (24 mL) and filtered through deactivated silica gel (6 g). The solvent was evaporated to give silyl enol ether **51**. A solution of this product and carbonate **52** (928 mg, 7.99 mmol) in THF (12 mL) was added to a stirred solution of $\text{Pd}_2(\text{dba})_3$ (109.9 mg, 0.12 mmol, 3 mol%) and dppe (286.9 mg, 0.72 mmol, 18 mol%) in THF (10 mL). The mixture was heated at $60\text{ }^{\circ}\text{C}$ for 30 h, cooled and the solvent was evaporated. The residue was chromatographed on silica gel (5% EtOAc/hexanes) to give **20** (902.7 mg, 62%): ^1H NMR (200 MHz): 5.96-5.60 (m, $\text{C}\underline{\text{H}}=\text{CH}_2$, 2H), 5.24-4.88 (m, $\text{C}\underline{\text{H}}=\text{CH}_2$, 4H), 2.77 (br s, 0.5 \times 1H), 2.72 (br s, 0.5 \times 1H), 2.58-2.20 (m, 4H), 2.10-1.48 (m, 6H), 1.46-1.30 (m, 9H) overlapping 1.42 [s, $\text{COSC}(\text{CH}_3)_3$, 9H], 1.06 (s, $\text{C}4-\text{CH}_3$, 3H), 1.01 (s, $\text{C}4-\text{CH}_3$, 3H), 0.97 (s, $\text{C}2'-\text{CH}_3$, 3H); ^{13}C NMR (50 MHz): 214.1 (C=O), 203.0, [$\text{COSC}(\text{CH}_3)_3$], 147.2 ($\text{C}\underline{\text{H}}=\text{CH}_2$), 134.4 ($\text{C}\underline{\text{H}}=\text{CH}_2$), 118.4 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 111.8 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 53.7, 49.7, 47.8, 46.3,

40.7, 38.9, 38.6, 37.4, 29.7 [COSC(CH₃)₃], 28.1, 25.8, 24.7, 21.7, 20.3. HRMS (EI) calc. for C₂₄H₃₆O₂S: 364.2436; found: 364.2424.

***S*-tert-Butyl (2*R**,4*E/Z*)-2-[(1*R**,2*R**)-2-methyl-2-(2-methylprop-2-enyl)-3-oxocyclopentyl]hex-4-enethioate (10)**

A solution of thioester **3** (180.6 mg, 0.54 mmol) in benzene (4 mL) was added to a solution of ruthenium hydride **9** (5.1 mg, 0.054 mmol, 1 mol%) in benzene (4 mL), and the mixture was heated under reflux for 10 min (GC indicated the substrate consumption). The solvent was evaporated and residue was chromatographed on silica (5% EtOAc/hexane) to give **10** as a yellow oil (157.1 mg, 87%; *E:Z* = 2.6 : 1 by GC): ¹H NMR (400 MHz): 5.57-5.32 (m, =CH₂, 2H), 4.88-4.82 (m, =CH₂, 1H), 4.70-4.66 (m, =CH₂, 1H), 2.69-2.52 (m, 2H), 2.47-2.04 (m, 8H), 1.66-1.61 (m, 3H), 1.60-1.56 (m, 3H), 1.45 [s, COSC(CH₃)₃, 9H], 1.03 and 1.02 (2s, =CHCH₃, 3H); ¹³C NMR (50 MHz): 222.6 (C=O), 202.4 [COSC(CH₃)₃], 141.5 [C(CH₃)=CH₂], 127.8 (=CH), 126.9 (=CH), 126.2 (=CH), 126.0 (=CH), 115.2 [C(CH₃)=CH₂], 55.1, 54.7, 51.6, 48.5, 43.7, 42.5, 37.5, 34.8, 29.7 [SC(CH₃)], 28.9, 24.6, 23.4, 23.3, 20.2, 17.8. HRMS (ESI) calc. for C₂₀H₃₂O₆Na: 336.2123; found: 336.2126.

Methyl (2*S)-2-[(1*R**,2*R**)-2-methyl-2-(2-methylprop-2-enyl)-3-oxocyclopentyl]hex-5-enoate (27) and methyl (2*R**)-2-[(1*R**,2*R**)-2-methyl-2-(2-methylprop-2-enyl)-3-oxocyclopentyl]hex-5-enoate (29)**

A mixture of thioester **3** (635 mg, 1.89 mmol) and MeOK in MeOH (freshly prepared from K, 0.515 g, 13.2 mg atom, and MeOH, 3 mL) was heated under reflux for 30 h, cooled and poured into water (30 mL). The product was isolated with toluene and chromatographed on silica gel (80 g, 3% EtOAc/hexanes, 100 : 1), to give **27** (210-221 mg, 40-42%) and **29** (237-258 mg, 45-49%); TLC (10% EtOAc/hexanes, R_f 0.22 and 0.17, respectively).

27: ¹H NMR (200 MHz): 5.90-5.66 (m, CH=CH₂, 1H), 5.10-4.92 (m, CH=CH₂, 2H), 4.83 (br s, CH₂=CCH₃, 1H), 4.63 (br s, CH₂=CCH₃, 1H), 3.70 (s, CO₂CH₃, 3H), 2.62-2.29 (m, 4H), 2.28-2.05 (m, 2H), 2.04-1.80 (m, 2H), 1.78-1.58 (m, 3H), 1.56 (br. s, CH₂=CCH₃, 3H), 1.54-1.36 (m, 1H), 0.96 (s, C2-CH₃, 3H); ¹³C NMR (50 MHz): 222.5 (C=O), 175.6 (CO₂CH₃), 141.5 (CH₂=CCH₃), 137.5 (CH=CH₂), 115.4 (=CH₂), 115.4 (=CH₂), 51.5, 51.4, 46.1, 43.8, 43.0, 37.3, 31.5, 29.8, 24.5, 23.6, 19.5. HRMS calc. for C₁₇H₂₆O₃: 278.1882; found: 278.1884.

29: ¹H NMR (200 MHz): 5.90-5.66 (m, CH=CH₂, 1H), 5.10-4.92 (m, CH₂=CCH₃, 2H), 4.86 (br s, CH₂=CCH₃, 1H), 4.69 (br s, CH₂=CCH₃, 1H), 3.69 (s, CO₂CH₃, 3H), 2.74-2.39 (m, 2H),

2.38-2.09 (m, 4H), 2.08-1.74 (m, 4H), 1.73-1.56 (m, 2H), 1.52 (br. s, CH₂=CCH₃, 3H), 0.88 (s, C₂-CH₃, 3H); ¹³C NMR (50 MHz): 222.2 (C=O), 175.6 (CO₂CH₃), 141.9 (CH₂=CCH₃), 137.3 (CH=CH₂), 115.9 (=CH₂), 115.5 (=CH₂), 51.4, 51.4, 47.0, 45.6, 43.3, 37.1, 31.8, 30.8, 23.9, 23.3, 19.1. HRMS calc. for C₁₇H₂₆O₃: 278.1882, found: 278.1886.

Methyl (2R*)-2-[(1R*,2R*)-2-allyl-2-methyl-3-oxocyclopentyl]-4,4-dimethylhex-5-enoate (28)

The mixture of thioester **18** (204.0 mg, 0.58 mmol) and MeOK in MeOH (prepared from K, 272 mg, 6.98 mg atom and MeOH, 3 mL) was heated under reflux for 6 h, cooled and poured into water (20 mL). The product was isolated with toluene and chromatographed on silica gel (5% EtOAc/hexanes) to give ester **28** (137 mg, 82%): ¹H NMR (200 MHz): 5.78-5.40 (m, =CH, 2H), 5.07-4.82 (m, =CH₂, 4H), 3.63 (s, COOCH₃, 3H), 2.52 (m, 4H), 2.20-1.68 (m, 4H), 1.65-1.24 (m, 2H), 1.02 (s, C₂'-CH₃, 3H), 0.97 [s, C₄-(CH₃)₂, 6H]; ¹³C NMR (50 MHz): 221.9 (C=O), 176.3 (CO₂CH₃), 147.0 (=CH), 133.6 (=CH), 118.8 (=CH₃), 111.1 (=CH₃), 52.3, 51.1, 43.6, 42.8, 42.6, 39.5, 37.1, 36.7, 27.6, 26.0, 23.9, 18.0. HRMS calc. for C₁₈H₂₈O₃: 292.2038; found: 292.2046.

Methyl (2R*)-2-[(1R*,2R*)-2-allyl-2-methyl-3-oxocyclopentyl]hex-5-enoate (30) and methyl (2S*)-2-[(1R*,2R*)-2-allyl-2-methyl-3-oxocyclopentyl]hex-5-enoate (31)

The mixture of thioester **17** (330 mg, 1.02 mmol) and MeOK in MeOH (prepared from 0.73 g K, 18.7 mg atom and 8 mL MeOH) was heated under reflux for 3.5 h, cooled and poured into water (10 mL). The product was isolated with hexanes and chromatographed on silica gel (33 g, 3% EtOAc/hexanes) to give **30** (124 mg, 46%) and **31** (113 mg, 42%).

30: ¹H NMR (200 MHz): 5.85-5.35 (m, =CH, 2H), 5.15-4.85 (m, =CH₂, 4H), 3.65 (s, COOCH₃, 3H), 2.55-2.20 (m, 4H), 2.15-1.55 (m, 5H), 1.53-1.20 (m, 3H), 0.89 (s, C₂'-CH₃, 3H); ¹³C NMR (50 MHz): 221.6 (C=O), 175.4 (COOCH₃), 137.3 (=CH), 133.5 (=CH), 118.7 (=CH₂), 115.2 (=CH₂), 51.9, 51.2, 45.9, 43.1, 39.7, 37.2, 31.2, 29.9, 23.6, 18.2. HRMS calc. for C₁₆H₂₄O₃: 264.1725; found: 264.1734.

31: ¹H NMR (200 MHz): 5.90-5.45 (m, =CH, 2H), 5.18-4.90 (m, =CH₂, 4H), 3.70 (s, COOCH₃, 3H), 2.58-2.24 (m, 4H), 2.22-1.60 (m, 5H), 1.58-1.25 (m, 3H), 0.94 (s, C₂'-CH₃, 3H); ¹³C NMR (50 MHz): 221.8 (C=O), 175.6 (COOCH₃), 137.4 (=CH), 133.6 (=CH), 118.8 (=CH₂), 115.4 (=CH₂), 52.0, 51.3, 46.0, 43.2, 39.8, 37.4, 31.3, 30.0, 23.7, 18.3. HRMS calc. for C₁₆H₂₄O₃: 264.1725; found: 264.1713.

(2*R)-2-[(1*R**,2*R**)-2-Allyl-2-methyl-3-oxocyclopentyl]hex-5-enyl benzoate (38)**

DIBALH (1.5 M in toluene, 3 mL, 4.5 mmol) was added to a solution of thioestr 3 (203 mg, 0.63 mmol) in DCM (10 mL), stirred at -78 °C. Stirring at -78 °C was continued for 1 h and then the mixture was allowed to warm to rt. After 24 h, MeOH (6 mL) and 10% aqueous tartaric acid (30 mL) were added. The mixture was extracted with DCM (3×25 mL). The combined organic extracts were dried and the solvent was evaporated to give (1*R**,2*R**,3*R**)- and (1*S**,2*R**,3*R**)-2-allyl-3-[1-(hydroxymethyl)pent-4-enyl]-2-methylcyclopentanols (bright yellow oil, 138 mg, 94%):

^1H NMR (200 MHz): 6.11-5.68 (m, =CH, 2H), 5.20-4.90 (m, =CH₂, 4H), 3.86 (dd, $J = 8.4$, 8.4 Hz, $\underline{\text{C}}\text{HOH}$, 0.3×1H), 3.76 (dd, $J = 5.3$, 1.5 Hz, $\underline{\text{C}}\text{HOH}$, 0.7×1H), 3.70-3.50 (m, $\underline{\text{C}}\text{H}_2\text{OH}$, 2H), 2.42-1.85 (m, 6H), 1.80 (s, OH, 2H, disappears on exchange with D₂O), 1.75-1.07 (m, 6H), 0.82 (s, C2-CH₃, 0.3×3H), 0.80 (s, C2-CH₃, 0.7×3H), (diastereomer ratio ca. 2 : 1); ^{13}C NMR (50 MHz): 138.9 (=CH), 136.4 (=CH), 136.0 (=CH), 117.5 (=CH₂), 116.8 (=CH₂), 114.6 (=CH₂), 81.1 ($\underline{\text{C}}\text{HOH}$), 78.3 ($\underline{\text{C}}\text{HOH}$), 64.3 ($\underline{\text{C}}\text{H}_2\text{OH}$), 63.8 ($\underline{\text{C}}\text{H}_2\text{OH}$), 48.2, 46.3, 44.9, 44.0, 43.8, 41.4, 40.4, 40.2, 39.7, 31.6, 31.5, 30.7, 29.7, 29.2, 28.3, 27.6, 24.8, 22.7, 18.3, 14.1, 13.5. HRMS calc. for C₁₅H₂₆O₂: 238.1933; found: 238.1939.

To a solution of these alcohols (96 mg, 0.40 mmol) in DCM (3 mL), pyridine (65 μL , 8.05 mmol) and benzoyl chloride (68 μL , 0.6 mmol) were added. The mixture was stirred for 3 h at rt, diluted with DCM (10 mL) and washed with water (3×10 mL). The water layer was extracted with DCM (2×10 mL). The combined organic extracts were dried and evaporated. The residue was chromatographed on silica gel (15% EtOAc/hexanes) to give monobenzoates, (1*R**,2*R**,3*R**)- and (1*S**,2*R**,3*R**)-2-allyl-3-[1-(benzoyloxymethyl)pent-4-enyl]-2-methylcyclopentanols (oil, 114 mg, 82%, diastereomer ratio 7:3, by integration of $\underline{\text{C}}\text{H}_2\text{OBz}$ signals in the ^1H NMR spectrum, 3.86 and 3.79 ppm).

^1H NMR (200 MHz): 8.10-7.95 (m, C₆H₅, 2H), 7.68-7.13 (m, C₆H₅, 3H), 6.12-5.70 (m, =CH, 2H), 5.18-4.90 (m, =CH₂, 4H), 4.37 (dd, $J = 11.1$, 5.0 Hz, $\underline{\text{C}}\text{H}_2\text{OCOC}_6\text{H}_5$, 1H), 4.25 (dd, $J = 11.1$, 4.6 Hz, $\underline{\text{C}}\text{H}_2\text{OCOC}_6\text{H}_5$, 1H), 3.86 (dd, $J = 8.4$, 8.4 Hz, $\underline{\text{C}}\text{HOH}$, 0.3×1H), 3.79 (dd, $J = 5.1$, 1.3 Hz, $\underline{\text{C}}\text{HOH}$, 0.7×1H), 2.40-1.30 (m, 12H) overlapping 1.71 (s, OH, 1H), 0.89 (s, C2'-CH₃, 0.33×3H), 0.86 (s, C2'-CH₃, 0.66×3H); ^{13}C NMR (50 MHz): 166.6 ($\underline{\text{C}}\text{H}_2\text{OCOC}_6\text{H}_5$), 138.5, 136.1, 135.5, 132.8, 130.2, 129.5, 128.3, 117.7, 116.9, 114.8, 81.1, 78.5, 66.5, 48.4, 46.6, 45.8, 45.1, 44.3, 41.5, 37.1, 31.3, 30.7, 29.0, 28.1, 25.5, 22.8, 18.2, 13.5. HRMS (LSIMS) calc. for C₂₂H₃₀O₃Na: 365.2087; found: 365.2098.

To a solution of these benzoates (112 mg, 0.33 mmol) in acetone (5 mL), Jones' reagent (ca. 3 mL) was added dropwise until deep orange colour persisted. After 0.5 h, *i*-PrOH (0.2 mL) was added the solution was diluted with hexanes (10 mL), washed with water (2 × 10 mL) and brine (1 × 10 mL), dried and evaporated. The residue was chromatographed on silica gel (5% EtOAc/hexanes) to give **38** (84 mg, 76%): ¹H NMR (200 MHz): 8.10-7.95 (m, C₆H₅, 2H), 7.65-7.40 (m, C₆H₅, 3H), 5.95-5.72 (m, =CH, 1H), 5.66-5.44 (m, =CH, 1H), 5.11-4.87 (m, =CH₂, 4H), 4.47 (dd, *J* = 11.4, 5.0 Hz, CH₂OCOC₆H₅, 1H), 4.28 (dd, *J* = 11.4, 5.0 Hz, CH₂OCOC₆H₅, 1H) 2.60-1.92 (m, 9H), 1.76-1.42 (m, 3H), 0.99 (s, C2'-CH₃, 3H); ¹³C NMR (50 MHz): 222.3 (C=O), 166.5 (CH₂OCOC₆H₅), 138.1, 133.8, 133.0, 130.1, 129.5, 128.4, 118.6 (=CH₂), 115.1 (=CH₂), 65.5, 52.0, 42.6, 41.8, 37.6, 37.3, 30.8, 27.9, 22.7, 18.2. HRMS calc. for C₂₂H₂₈O₃: 340.2038, found: 340.2037.

(2*R,3*R**)-2-Allyl-3-[(1*S**)-1-(hydroxymethyl)pent-4-enyl]-2-methylcyclopentanone (37)**

Ester **38** (180 mg, 0.53 mmol) in MeOH (5 mL) was added to a solution of KOH (296 mg, 5.27 mmol) in MeOH (5 mL). The mixture was stirred at rt for 2 h, and then it was diluted with water (10 mL) and was extracted with DCM (3 × 10 mL). The organic extract was dried and evaporated. The residue was chromatographed on silica gel (20% EtOAc/hexanes) to give alcohol **37** (oil, 109 mg, 87%). ¹H NMR (200 MHz): 5.92-5.50 (m, =CH, 2H), 5.16-4.90 (m, =CH₂, 4H), 3.68 (d, *J* = 4.4 Hz, CH₂OH, 2H), 2.62-1.88 (m, 8H), 1.74-1.15 (m, 4H), 1.53 (s, 1H, disappears on exchange with D₂O), 0.92 (s, CH₃, 3H); ¹³C NMR (50 MHz): 223.0 (C=O), 138.5 (=CH), 134.9 (=CH), 118.2 (=CH₂), 114.8 (=CH₂), 62.8, 51.9, 41.9, 41.8, 40.0, 37.6, 31.0, 27.3, 22.7, 18.1. HRMS calc. for C₁₅H₂₄O₂: 236.1776; found: 236.1771.

(2*S)-2-[(1*R**,2*R**)-2-Allyl-2-methyl-3-oxocyclopentyl]hex-5-enyl benzoate (40)**

DIBALH (1.5 M in toluene, 12.8 mL, 19.25 mmol) was added to a solution of ester 31 (727 mg, 2.75 mmol) in DCM (35 mL), stirred at -78 °C. Stirring at -78 °C was continued for 1 h and at rt for 6 h. MeOH (20 mL) and 10% aqueous tartaric acid (140 mL) were then added and the mixture was extracted with DCM (3 × 50 mL). The combined extract was dried and the solvent was evaporated. The residue was chromatographed on silica gel (35% EtOAc/hexanes) to give diols, (1*R**,2*R**,3*R**)- and (1*S**,2*R**,3*R**)-3-[(1*S**)-1-(hydroxymethyl)pent-4-enyl]-2-methyl-2-allylcyclopentan-1-ols (oil, 612 mg, 93%): ¹H NMR (200 MHz): 6.10-5.70 (m, =CH, 2H), 5.20-4.90 (m, =CH₂, 4H), 3.98-3.68 (m, CH₂OH, 2H), 3.58-3.46 (m, CHOH, 1H), 2.42-2.20 (m, 2H), 2.18-1.82 (m, 4H), 1.78-1.36 (m, 7H). 0.88 (s,

C2-CH₃, 0.4×3H), 0.81 (s, C2-CH₃, 0.6×3H), (diastereomer ratio ca. 3 : 2 based on integration of the C2-CH₃ signals); ¹³C NMR (50 MHz): 138.9 (=CH), 138.7 (=CH), 136.4 (=CH), 135.7 (=CH), 117.7 (=CH₂), 116.8 (=CH₂), 114.7 (=CH₂), 114.6 (=CH₂), 80.9, 79.0, 74.6, 63.9, 63.1, 48.3, 46.7, 45.4, 45.1, 41.7, 40.0, 39.7, 31.2, 30.9, 30.6, 30.2, 30.1, 29.5, 25.2, 23.2, 18.0, 13.8. MS (EI, m/z): 97 (57), 95 (65), 93 (58), 81 (100), 79 (57), 67 (70), 55 (74), 41 (86). HRMS (ES) calc. for C₁₅H₂₆O₂Na: 261.1825 (M+Na)⁺; found: 261.1823.

To a solution of these diols (540 mg, 2.26 mmol) in DCM (3 mL), pyridine (380 μL, 4.6 mmol, 2 equiv.) and benzoyl chloride (395 μL, 3.4 mmol, 1.5 equiv.) were added. The mixture was stirred at rt for 3 h and poured into water (30 mL). The usual workup (DCM) gave a crude product which was chromatographed on silica gel (15% -30% EtOAc/hexanes) to give (1*R**,2*R**,3*R**)- and (1*S**,2*R**,3*R**)-3-[(1*S**)-1-(benzoiloxymethyl)pent-4-enyl]-2-methyl-2-allylcyclopentan-1-ols (oil, 671 mg, 86%): ¹H NMR (200 MHz): 8.12-7.96 (m, C₆H₅, 2H), 7.64-7.38 (m, C₆H₅, 3H), 6.15-5.68 (m, =CH, 2H), 5.24-4.90 (m, =CH₂, 4H), 4.46 (dd, *J* = 11.3, 3.5 Hz, CH₂OCOC₆H₅, 1H), 4.38-4.08 (m, CH₂OCOC₆H₅, 1H), 3.88 (dd, *J* = 8.4, 8.4 Hz, CHOH, 0.4×1H), 3.80 (d, *J* = 5.7 Hz, CHOH, 0.6×1H), 2.46-2.26 (m, 2H), 2.24-1.78 (m, 5H), 1.88 (s, OH, 1H, disappears on exchange with D₂O), 1.76-1.38 (m, 5H), 0.91 (s, C2'-CH₃, 0.4×3H), 0.87 (s, C2'-CH₃, 0.6×3H), (diastereomer ratio 3 : 2); ¹³C NMR (50 MHz): 166.7 (CH₂OCOC₆H₅), 138.5, 136.3, 135.7, 132.9, 130.3, 129.5, 128.4, 117.8, 117.0, 114.8, 80.7, 78.4, 66.4, 48.5, 46.5, 46.0, 45.3, 44.5, 41.6, 37.6, 36.6, 31.1, 31.0, 30.9, 30.6, 29.1, 25.1, 23.4, 18.0, 13.2. HRMS calc. for C₂₂H₃₀O₃: 342.2195 (M⁺), found: 342.2200.

To a solution of these monobenzoates (651 mg, 1.89 mmol) in acetone (20 mL), Jones' reagent (ca. 5 mL) was added dropwise until orange colour persisted. After 0.5 h *i*-PrOH (0.5 mL) was added. The usual workup gave **40** (oil, 504 mg, 78%): ¹H NMR (200 MHz): 8.08-7.96 (m, C₆H₅, 2H), 7.66-7.40 (m, C₆H₅, 3H), 5.94-5.46 (m, =CH, 2H), 5.16-4.90 (m, =CH₂, 4H), 4.48 (dd, *J*=11.5, 3.7 Hz, CH₂OCOC₆H₅, 1H), 4.32 (dd, *J*=11.5, 4.4 Hz, CH₂OCOC₆H₅, 1H), 2.68-2.52 (m, 1H), 2.50-1.82 (m, 8H), 1.80-1.44 (m, 3H), 0.99 (s, C2-CH₃, 3H); ¹³C NMR (50 MHz): 222.4 (C=O), 166.5 (CH₂OCOC₆H₅), 138.0, 134.2, 133.0, 130.1, 129.5, 128.4, 118.5 (=CH₂), 115.2 (=CH₂), 64.5, 51.9, 42.7, 42.2, 38.0, 37.8, 30.9, 29.5, 23.6, 18.2. HRMS calc. for C₂₂H₂₈O₃: 340.2038 (M⁺); found: 340.2044.

(2*R,3*R**)-2-Allyl-3-[(1*S**)-1-(hydroxymethyl)pent-4-enyl]-2-methylcyclopentanone (39)**

Benzoate **40** (154 mg, 0.441 mmol) was added to a solution of KOMe in MeOH, prepared by from potassium (120 mg) and MeOH (10 mL). The mixture was heated under reflux for 2 h,

cooled, diluted with water (10 mL) and extracted with DCM (3 × 10 mL). The combined organic extract were dried and the solvent was evaporated. The residue was chromatographed on silica gel (EtOAc/*t*-BuOMe/hexanes = 1/1/3) to give **39** (84 mg, 82%): IR (film): 3452 cm⁻¹ (-OH), 1736 cm⁻¹ (-C=O); ¹H NMR (200 MHz): 5.95-5.67 (m, =CH, 1H), 5.65-5.45 (m, =CH, 1H), 5.15-4.90 (m, =CH₂, 4H), 3.90-3.60 (m, CH₂OH, 2H), 2.60-2.43 (m, 1H), 2.40-1.90 (m, 6H), 1.76-1.42 (m, 4H), 1.40-1.08 (m, 2H), 0.94 (s, C₂-CH₃, 3H); ¹³C NMR (50 MHz): 138.4 (=CH), 134.2 (=CH), 118.4 (=CH₂), 114.9 (=CH₂), 62.1, 51.8, 42.3, 40.2, 37.7, 31.1, 28.7, 23.2, 18.2. HRMS calc. for C₁₅H₂₄O₂: 236.1776; found: 236.1778.

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