Synthesis of *cis*-fused Carbo-Bicycles by Domino Enyne Cross Metathesis / Intramolecular Diels-Alder Reaction

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Supporting Information

Experimental Procedures and Characterization Data

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General Information. NMR spectra were recorded on a *BRUKER* DRX 500 (500 MHz) and AM 400 (400 MHz) spectrometer. Shifts reported are relative to the internal residual proton signal of solvent CDCl_3 (7.26 ppm). Coupling constants *J* are reported in hertz and refer to apparent peak multiplicities. Abbreviations used for describing ^1H -NMR spectra are as follows: s = singlet, d = doublet, t = triplet, br = broad signal. Stereochemical assignments were done using COSY, HMQC and NOE experiments. Diastereomeric ratios were determined by ^1H -NMR. Mass spectra were recorded on a *FINNIGAN* MAT 95 SQ with an ionisation potential of 70 eV and are reported as percent relative intensity to the base peak. IR spectra were recorded on a *NICOLET* FTIR-Spectrometer Magna 750. Flash chromatography was done on *ICN* silica gel 60 (0.04-0.063 mm) and analytical TLC was done on aluminium-backed *E. Merck* silica gel 60 plates with a 254 nm fluorescent indicator. THF and ether were distilled from sodium/benzophenone under nitrogen. CH_2Cl_2 was distilled from Siccapent. Solvents for workups and chromatography were distilled prior to use. Except for metathesis reactions with catalysts **2** or **3**, all reactions were run under an atmosphere of nitrogen in oven-dried glassware. Commercially available chemicals were used without further purification.

Metathesis catalysts used for the following synthetic procedures:

Method **A** for the synthesis of hexahydroindenes **14** - **17**:

In a 5 ml screw cap glass vial equipped with a magnetic stirring bar the α,ω -diene (1 eq; 0.2-0.4 mmol), alkyne (1.2-1.35 eq) and catalyst **1** (7.5 mol %) were dissolved in CH_2Cl_2 (0.2 M α,ω -diene solution) under an N_2 -atmosphere. After being stirred at room temperature for 24 h, the reaction mixtures were concentrated in vacuo. The oily residues were dissolved in a mixture of 5 ml MtBE and 10 ml hexane and filtered over a small plug of silica. After washing using 20 ml of the same solvent mixture, the combined filtrates were concentrated in vacuo. The residues were dissolved in 5 ml toluene and heated to 80 °C under N_2 -atmosphere for 24 h. After removal of the solvent under reduced pressure, the residues were subjected to flash chromatography (using silica and the eluent system given). The purified hexahydroindenes **14-17** were obtained as mixtures of major diastereomer **a** and minor diastereomers **b**, **c** (ratios given below). The characteristic ^1H -NMR-signals of H-1 and H-4 are assigned for all isomers found. ^{13}C -data are given only for the major diastereomer **a**, except for C-1, C-4 and C-9 signals, which are given and assigned also for the minor diastereomers, if possible.

6-Acetoxymethyl-1-(tert-butyldimethylsilanyloxy)-2,3,4,7,8,9-hexahydro-1H-indene-9-carboxylic acid methyl ester (14a,b)

According to method **A** propargyl acetate **9** (49 mg, 0.5 mmol) and α,ω -diene **4** (117 mg, 0.412 mmol) were converted using catalyst **1** (25 mg, 7.5 mol %). After final chromatography

(SiO_2 , hexane/MtBE 30:1), the title compound **14a,b** (68 mg, 0.177 mmol, 59 %, **a:b** = 5:1) was obtained as a colourless oil.

^1H -NMR (500.132MHz; CDCl_3): $\delta(\text{ppm})$ = -0.02 - 0.01 (m, 6H), 0.87 (s, 9H), 1.40-1.72 (m, 3H), 1.90-2.07 (m, 7H), 2.12-2.19 (m, 1H), 2.78-2.87 (br, 1H, H-4b), 2.90-2.97 (br, 1H, H-4a), 4.23 (d, $J=5$ Hz, 1H, H-1b), 4.36 (pseudo-t, $J=8$ Hz, 1H, H-1a), 4.43 (s, 2H), 5.64-5.68 (m, 1H)

^{13}C -NMR (125.8MHz; CDCl_3): $\delta(\text{ppm})$ = -5.2 (CH_3), -4.8 (CH_3), 18.1 (C), 20.9 (CH_2), 21.0 (CH_3), 23.1 (CH_2), 25.7 (CH_3), 28.3 (CH_2), 32.9 (CH_2), 40.3 (CH, C-4a), 41.8 (CH, C-4b), 51.8 (CH_3), 54.6 (C, C-9a), 59.9 (C, C-9b), 68.1 (CH_2), 76.4 (CH, C-1b), 79.6 (CH, C-1a), 127.3 (CH), 132.1 (C), 171.0 (C), 176.9 (C)

IR: (cm^{-1}) 777 (m), 838 (s), 1119 (s), 1248 (s), 1740 (s), 2930 (m), 2954 (s)

EI-MS (90°C): m/z = 382 (M^+), 325 (100%), 265 (40), 233 (8), 159 (5), 131 (40), 73 (26)

HR-MS: ($\text{C}_{20}\text{H}_{34}\text{O}_5\text{Si}$, $\text{M}^+ - \text{CH}_3$) calcd 367.1941, found 367.1940

NOE H-4a $\leftrightarrow$ H-1a: 1.2 %; no further NOEs related to H-4a have been found.

6-Acetoxymethyl-1-(tert-butyldimethylsilanyloxy)-2,3,4,7,8,9-hexahydro-1H-indene-9-carbonitrile (15a,b,c)

According to method **A** propargyl acetate **9** (69 mg, 0.7 mmol) and α,ω -

diene **5** (136 mg, 0.54 mmol) were converted using catalyst **1** (25 mg, 7.5 mol %). After final chromatography (SiO_2 , hexane/MtBE 30:1), the title compound **15a,b,c** (38 mg, 0.08 mmol, 20 %, **a:b:c** = 14:1:2) was obtained as a colourless oil.

¹H-NMR (500.132MHz; CDCl₃): δ(ppm)= 0.04-0.16 (m, 6H), 0.87-0.95 (m, 9H), 1.44-1.74 (m, 3H), 1.94-2.27 (m, 8H), 2.69-2.78 (br, 1H, H-4a,b), 2.95-3.05 (br, 1H, H-4c), 4.02-4.06 (m, 1H, H-1c), 4.33 (d, J=5 Hz, 1H, H-1b), 4.46-4.53 (m, 3H, signal contains H-1a), 5.69-5.72 (m, 1H)

¹³C-NMR (125.8MHz; CDCl₃): δ(ppm)= -4.8 (CH₃), 18.1 (C), 21.0 (CH₃), 21.8 (CH₂), 22.8 (CH₂), 25.8 (CH₃), 27.8 (CH₂), 31.5 (CH₂), 41.5 (CH, C-4a), 44.1 (C, C-9a), 67.7 (CH₂), 78.8 (CH, C-1a), 124.0 (C), 125.4 (CH), 132.7 (C), 170.9 (C)

IR: (cm⁻¹) 779 (m), 839 (s), 1130 (m), 1229 (s), 1251 (m), 1377 (w), 1741 (s), 2223 (w), 2930 (m), 2955 (m)

EI-MS (60°C): m/z= 339 (M⁺-2), 292 (8), 232 (25), 158 (9), 131 (20), 117 (100%), 75 (30)

HR-MS: (C₁₉H₃₁O₃NSi, M⁺ - *tert*-butyl) calcd 292.1369, found 292.1371

NOE H-4a ↔ H-1a: 1.3 %; no further NOEs related to H-4a have been found.

3-(*tert*-Butyldimethylsilanyloxy)-6-(2-methoxycarbonyl-ethyl)-2,3,4,7,8,9-hexahydro-1*H*-indene-9-carboxylic acid methyl ester (16a,b)

According to method A methyl pent-4-ynoate **10** (55 mg, 0.49 mmol) and α,ω-diene **4** (110 mg, 0.39 mmol) were converted using catalyst **1** (25

mg, 7.5 mol %). After final chromatography (SiO₂, hexane/MtBE 30:1), the title compound **16a,b** (99 mg, 0.25 mmol, 64 %, **a:b** = 5:1) was obtained as a colourless oil.

¹H-NMR (500.132MHz; CDCl₃): δ(ppm)= -0.06 – 0.06 (m, 6H), 0.86 (s, 9H), 1.31-1.39 (m, 1H), 1.46-1.55 (m, 1H), 1.56-1.67 (m, 1H), 1.77-2.13 (m, 5H), 2.18-2.27 (m, 2H), 2.35-2.41 (m, 2H), 2.68-2.77 (br, 1H, H-4b), 2.82-2.89 (br, 1H, H-4a), 3.63 (s, 3H), 3.65 (s, 3H), 4.18 (d, J=5 Hz, 1H, H-1b), 4.34 (pseudo-t, J=8 Hz, 1H, H-1a), 5.33-5.37 (m, 1H, H-5a), 5.59 (s, 1H, H-5b)

¹³C-NMR (125.8MHz; CDCl₃): δ(ppm)= -5.2 (CH₃), -4.8 (CH₃), 18.0 (C), 21.1 (CH₂), 25.5 (CH₂), 25.7 (CH₃), 28.8 (CH₂), 32.6 (CH₂), 32.7 (CH₂), 32.8 (CH₂), 40.5 (CH, C-4a), 42.0 (CH, C-4b), 51.5 (CH₃), 51.7 (CH₃), 54.4 (C, C-9a), 59.7 (C, C-9b), 76.5 (CH, C-1b), 79.6 (CH, C-1a), 123.6 (CH), 135.4 (C), 173.9 (C), 177.1 (C)

IR: (cm⁻¹) 776 (m), 838 (s), 1119 (m), 1166 (m), 1250 (s), 1435 (m), 1739 (s), 2929 (m), 2952 (m)

EI-MS (150°C): m/z= 381 (M⁺-CH₃), 339 (100%), 205 (40), 131 (22), 105 (20), 89 (20), 73 (30)

HR-MS: (C₂₀H₃₃O₅Si, M⁺-CH₃) calcd 381.2097, found 381.2099

NOE H-4a ↔ H-1a: 1.2 %; no further NOEs related to H-4a have been found.

3-(*tert*-Butyldimethylsilanyloxy)-6-(2-methoxycarbonyl-ethyl)-2,3,4,7,8,9-hexahydro-1*H*-indene-9-carbonitrile (17a,b,c)

According to method A methyl pent-4-ynoate **10** (56 mg, 0.5 mmol) and α,ω-diene **5** (100 mg, 0.398 mmol) were converted using catalyst **1** (25 mg, 7.5 mol %). After final chromatography (SiO₂, hexane/MtBE 30:1), the title compound **17a,b,c** (49 mg, 0.135 mmol, 34 %, **a:b:c** = 10:1:2) was obtained as a colourless oil.

¹H-NMR (500.132MHz; CDCl₃): δ(ppm)= 0.02-0.08 (m, 6H), 0.85-0.95 (m, 9H), 1.37-1.70 (m, 3H), 1.89-2.05 (m, 4H), 2.18-2.28 (m, 1H), 2.30-2.36 (m, 2H), 2.44 (t, J=7 Hz, 2H), 2.63-2.71 (br, 1H, H-4a,b), 2.89-2.96 (br, 1H, H-4c), 3.66 (s, 3H), 3.98-4.03 (m, 1H, H-1c), 4.29-4.33 (m, 1H, H-1b), 4.45-4.51 (m, 1H, H-1a), 5.38-5.42 (m, 1H, H-5a,c), 5.02 (s, 1H, H-5b)

¹³C-NMR (125.8MHz; CDCl₃): δ(ppm)= -4.8 (CH₃), 18.07 (C), 21.9 (CH₂), 25.2 (CH₂), 25.8 (CH₃), 28.2 (CH₂), 32.5 (3xCH₂), 41.7 (CH, C-4a), 42.0 (CH, C-4c), 43.0 (CH, C-4b), 44.1 (C, C-9a), 47.6 (C, C-9c), 51.6 (CH₃), 75.6 (CH, C-1b), 78.4 (CH, C-1c), 78.9 (CH, C-1a), 121.9 (C), 124.3 (CH), 136.0 (C), 173.7 (C)

IR: (cm⁻¹) 779 (m), 839 (s), 1132 (s), 1253 (m), 1437 (w), 1740 (s), 2232 (w), 2929 (m), 2954 (s)

EI-MS (110°C): m/z= 362 (M⁺-1), 348 (3), 306 (100%), 274 (10), 247 (5), 173 (18), 131 (10), 73 (30)

HR-MS: (C₁₉H₃₀O₃NSi = M⁺-CH₃) calcd 348.1995, found 348.2001

NOE H-4a ↔ H-1a: 1.2 %; no further NOEs related to H-4a have been found.

Method **B** for the synthesis of hexahydroindenes **18** and **19**:

In a 5 ml screw cap glass vial equipped with a magnetic stirring bar the α,ω-diene (1 eq; 0.2-0.4 mmol), alkyne (1.2-1.35 eq) and catalyst **3** (5 mol %) were dissolved in CH₂Cl₂ (0.2 M α,ω-diene solution). After being stirred at 45 °C for 24 h, the reaction mixtures were concentrated in vacuo. The oily residues were dissolved in a mixture of 5 ml MtBE and 10 ml hexane and filtered over a small plug of silica. After washing using 20 ml of the same solvent mixture the combined filtrates were concentrated in vacuo. The residues were dissolved in 5 ml toluene and heated to 80 °C under N₂-atmosphere for 24 h. After removal of the solvent under reduced pressure, the residues were subjected to flash chromatography (using silica and the eluent system given). The purified hexahydroindenes **18** and **19** were obtained as mixtures of major diastereomeric pairs **a** and minor diastereomeric pairs **b**, **c** (ratios given below). The characteristic ¹H-NMR-signals of H-1 and H-4 are assigned for all isomers found in the product mixture. ¹³C-data are given only for the major diastereomeric pair, except for C-1, C-4, C-5, C-6 and C-9 signals, which are given and assigned also for the minor diastereomers, if possible. In ¹³C-spectra partial extra signal duplication occurred because of the side chain epimeric mixture.

6-(1-Acetoxy-butyl)-1-(tert-butyldimethylsilanyloxy)-2,3,4,7,8,9-hexahydro-1H-indene-9-carboxylic acid methyl ester (18a,b)

According to method **B** hex-1-yn-3-yl acetate **11** (56 mg, 0.4 mmol) and α,ω-diene **4** (93 mg, 0.31 mmol) were converted using catalyst **3** (10 mg, 5 mol %). After final chromatography (SiO₂,

hexane/MtBE 30:1), the title compound **18a,b** (91 mg, 0.21 mmol, 69 %, **a:b** = 14:1) was obtained as a slightly brown coloured oil.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 0.0 (s, 6H), 0.83-0.94 (m, 12H), 1.15-1.45 (m, 3H), 1.46-1.70 (m, 5H), 1.86-2.18 (m, 7H), 2.77-2.86 (br, 1H, H-4b), 2.87-2.97 (br, 1H, H-4a), 3.65 (s, 3H, OMe-a), 3.76 (s, 3H, OMe-b), 4.18-4.22 (m, 1H, H-1b), 4.32-4.39 (m, 1H, H-1a), 5.05-5.15 (m, 1H), 5.55-5.63 (m, 1H, H-5a,b)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) -5.2 (CH₃), -4.8 (CH₃), 13.9 (CH₃), 18.1 (C), 18.7 (CH₂), 20.8 (CH₂), 21.1 (CH₂), 21.4 (CH₃), 25.8 (CH₃), 28.4 (CH₂), 32.9 (CH₂), 34.5 (CH₂), 40.3 (CH, C-4a), 51.7 (CH₃), 54.7 (C, C-9a), 77.8 (CH), 79.6 (CH, C-1a), 127.2 (CH), 135.1 (C), 170.4 (C), 177.1 (C)

IR: (cm⁻¹) 776 (m), 837 (m), 1020 (w), 1118 (m), 1239 (s), 1370 (m), 1463 (w), 1734 (s), 2857 (w), 2931 (m), 2956 (m)

EI-MS (100°C): m/z= 409 (M⁺-CH₃), 367 (100%), 307 (90), 279 (12), 196 (12), 173 (14), 117 (20), 89 (24), 73 (30)

HR-MS: (C₂₂H₃₇O₅Si; M⁺-CH₃) calcd 409.2410, found 409.2411

NOE H-4a $\leftarrow \rightarrow$ H-1a: 0.7 %; no further NOEs related to H-4a have been found.

6-(1-Acetoxy-butyl)-1-(tert-butyldimethylsilanyloxy)-2,3,4,7,8,9-hexahydro-1H-indene-9-carbonitrile (19a,b,c)

diene **4** (108 mg, 0.43 mmol) were converted using catalyst **3** (13.5 mg, 5 mol %). After final chromatography (SiO₂, hexane/MtBE 30:1), the title compound **19a,b,c** (108 mg, 0.27 mmol, 64 % **a:b:c** 10:1:5) was obtained as a slightly brown coloured oil.

¹H-NMR (500 MHz; CDCl₃): δ (ppm) 0.00-0.08 (m, 6H), 0.81-0.97 (m, 12H), 1.20-1.75 (m, 8H), 1.88-2.26 (m, 5H), 2.65-2.73 (br, 1H, H-4a,b), 2.94-3.02 (br, 1H, H-4c), 3.98-4.04 (m, 1H, H-1c), 4.30 (d, J=5Hz, 1H, H-1b), 4.48 (pseudo-t, J=6Hz), 1H, H-1a), 5.10-5.22 (m, 1H), 5.65-5.75 (m, 1H, H-5-a,b,c)

¹³C-NMR (125.8 MHz; CDCl₃): δ (ppm) -4.8 (CH₃), 14.0 (CH₃), 18.1 (C), 18.64 (CH₂), 18.77 (CH₂), 18.80 (CH₂), 20.1 (CH₂), 20.5 (CH₂), 21.40 (CH₃), 21.53 (CH₃), 21.7 (CH₂), 22.0 (CH₂), 25.8 (CH₃), 26.5 (CH₂), 27.8 (CH₂), 28.0 (CH₂), 29.1 (CH₂), 31.41 (CH₂), 31.49 (CH₂), 33.1 (CH₂), 34.4 (CH₂), 34.8 (CH₂), 41.22 (CH, C-4a), 41.34 (CH, C-4b), 41.8 (CH, C-4c), 44.22 (C, C-9a), 44.30 (C, C-9a), 47.9 (C, C-9c), 76.7 (CH, C-1c), 77.66 (CH), 77.69 (CH), 78.75 (CH, C-1b), 78.86 (CH, C-1a), 122.1 (C), 123.4 (CH, C-5b), 124.1 (C), 125.7 (CH, C-5a), 126.2 (CH, C-5c), 134.4 (C, C-6c), 135.6 (C, C-6a), 135.8 (C, C-6b), 170.49 (C), 170.52 (C)

IR: (cm⁻¹) 777 (m), 836 (m), 1018 (w), 1241 (s), 1468 (m), 1731 (s), 2229 (w), 2857 (w), 2931 (m), 2955 (m)

EI-MS (100°C): m/z= 391 (M⁺), 334 (5), 274 (100%), 247 (15), 173 (25), 128 (20)

HR-MS: (C₂₂H₃₇O₃SiN; M⁺) calcd 391.2309, found 391.2317

NOE H-4a $\leftarrow \rightarrow$ H-1a: 0.4 %; no further NOEs related to H-4a have been found.

One-pot method C for the synthesis of hexahydroindenes 20 - 23:

In a 5 ml screw cap glass vial equipped with a magnetic stirring bar the α,ω -diene (1 eq; 0.2-1.0 mmol), alkyne (1.2-1.35 eq) and catalyst **3** (5 – 7.5 mol %) were dissolved in CH₂Cl₂ (0.2 M α,ω -diene solution). After being stirred at 45 °C for 24 h, the reaction mixtures were concentrated in vacuo. The oily residues were subjected to flash chromatography (using silica and the eluent system given). The purified hexahydroindenes **20 - 23** were obtained as mixtures of major diastereomer **a** and minor diastereomers **b**, **c** (ratios given below). The characteristic ¹H-NMR-signals of H-1 and H-4 are assigned for all isomers found in the product mixture. ¹³C-data are given only for the major diastereomer **a**, except for C-1, C-4 and C-9 signals, which are given and assigned also for the minor diastereomers, if possible.

6-Phenyl-1-(*tert*-butyldimethylsilanyloxy)-2,3,4,7,8,9-hexahydro-1*H*-indene-9-carboxylic acid methyl ester (20a,b)

According to method C phenyl acetylene **12** (36 mg, 0.35 mmol) and α,ω -diene **4** (80 mg, 0.28 mmol) were converted using catalyst **3** (9 mg, 5 mol %). After final chromatography (SiO₂, hexane/MtBE 100:1), the title compound **20a,b**

(37 mg, 0.095 mmol, 34 %, **a:b** = 5:1) was obtained as an inseparable mixture with starting material **4** (40 mg, 0.14 mmol, 50 %) forming a slightly brown coloured oil. Spectroscopic data were collected with product enriched samples obtained by repeated column chromatography.

¹H-NMR (500.132MHz; CDCl₃): δ (ppm)= 0.00-0.03 (s, 6H), 0.90 (s, 9H), 1.47-1.80 (m, 3H), 1.89-2.16 (m, 2H), 2.22-2.36 (m, 1H), 2.45-2.54 (m, 2H), 2.92-3.00 (br, 1H, H-4b), 3.08-3.16 (br, 1H, H-4a), 3.65 (s, 3H), 4.29 (d, J=5Hz, 1H, H-1b), 4.48 (m, 1H, H-1a), 6.07 (d, J = 5.5Hz, 1H), 7.17-7.42 (m, 5H)

¹³C-NMR (125.8MHz; CDCl₃): δ (ppm)= -4.8 (CH₃), 18.1 (C), 21.5 (CH₂), 24.7 (CH₂), 25.8 (CH₃), 28.7 (CH₂), 33.0 (CH₂), 41.1 (CH, C-4a), 51.8 (CH₃), 54.4 (C, C-9a), 79.8 (CH, C-1a), 125.1 (CH), 126.3 (CH), 126.8 (CH), 128.2 (CH), 135.8 (C), 141.9 (C), 177.1 (C)

IR: (cm⁻¹) 776 (m), 837 (m), 1091 (m), 1118 (m), 1251 (m), 1463 (w), 1727 (s), 2929 (m), 2953 (m)

EI-MS (140°C): m/z = 386 (M⁺), 329 (100%), 325 (20), 227 (35), 195 (70), 91 (15), 89 (45), 73 (50)

HR-MS: (C₂₂H₃₁O₃Si; M⁺-CH₃) calcd 371.2042, found 371.2044

NOE H-4a $\leftrightarrow$ H-1a: 1.3 %; no further NOEs related to H-4a have been found.

6-Phenyl-1-(*tert*-butyldimethylsilanyloxy)-2,3,4,7,8,9-hexahydro-1*H*-indene-9-carbonitrile(21a,c)

According to method C phenyl acetylene **12** (41 mg, 0.4 mmol) and α,ω -diene **5** (82 mg, 0.32 mmol) were converted using catalyst **3** (10 mg, 5 mol %). After final chromatography (SiO₂, hexane/MtBE 100:1), the title compound **21a,c**

(102 mg, 0.29 mmol, 90 %, **a:c** = 5:1) was obtained as a slightly brown coloured oil.

¹H-NMR (500.132MHz; CDCl₃): δ (ppm)= 0.07 - 0.23 (m, 6H), 0.89-0.98 (m, 9H), 1.49-1.82 (m, 3H), 1.97-2.18 (m, 3H), 2.33-2.76 (m, 2H), 2.86-2.96 (br, 1H, H-4a), 3.14-3.21 (br, 1H, H-4c), 4.09 (pseudo-t, J=4.5Hz, 1H, H-1c), 4.56 (pseudo-t, J=8Hz, 1H, H-1a), 6.02-6.08 (m, 1H, H-5a,c), 7.22-7.42 (m, 5H)

¹³C-NMR (125.8MHz; CDCl₃): δ (ppm)= -4.7 (CH₃), 18.1 (C), 22.4 (CH₂), 24.5 (CH₂), 25.8 (CH₃), 28.2 (CH₂), 31.6 (CH₂), 42.1 (CH, C-4a), 42.4 (CH, C-4c), 44.0 (C, C-9a), 47.5 (C, C-9c), 78.4 (CH, C-1c), 79.0 (CH, C-1a), 124.21 (CH), 124.26 (C), 125.3 (CH), 127.3 (CH), 128.4 (CH), 136.6 (C), 141.3 (C)

IR: (cm⁻¹) 778 (m), 838 (s), 1130 (m), 1253 (w), 1472 (w), 1599 (w), 2232 (w), 2929 (m), 2955 (s)

EI-MS (90°C): m/z = 353 (M⁺), 338 (3), 296 (100%), 269 (30), 195 (35), 167 (40), 128 (30), 91 (25), 73 (43)

HR-MS: (C₂₂H₃₁ONSi) calcd 353.2175, found 353.2172

NOE H-4a $\leftrightarrow$ H-1a: 1.0 %; no further NOEs related to H-4a have been found.

6-(4-Methoxyphenyl)-1-(*tert*-butyldimethylsilyloxy)-2,3,4,7,8,9-hexahydro-1*H*-indene-9-carboxylic acid methyl ester (22a,b)

According to method **C** 4-methoxyphenyl acetylene **13** (169 mg, 1.28 mmol) and α,ω -diene **4** (284 mg, 1.0 mmol) were converted using catalyst **3** (48 mg, 7.5 mol %). After final chromatography

(SiO₂, hexane/MtBE 100:1), the title compound **22a,b** (266 mg, 0.64 mmol, 64 %, **a:b** = 9:1) was obtained as a pale yellow oil.

¹H-NMR (500 MHz; CDCl₃): δ (ppm) -0.02 - 0.10 (m, 6H), 0.87-0.93 (m, 9H), 1.48-1.57 (m, 1H), 1.62-1.77 (m, 2H), 1.90-2.10 (m, 2H), 2.19-2.31 (m, 1H), 2.37-2.51 (m, 2H), 2.88-2.98 (br, 1H, H-4b), 3.05-3.13 (br, 1H, H-4a), 3.67 (s, 3H), 3.80 (s, 3H), 4.27 (d, *J*=5Hz, 1H, H-1b), 4.39-4.45 (pseudo-t, *J*=5.5Hz, 1H, H-1a), 5.89-5.93 (d, *J*=12 Hz, 1H, H-5b), 5.96-5.99 (d, *J*=6Hz, 1H, H-5a), 6.84 (d, *J*=9Hz, 2H), 7.32 (d, *J*=9Hz, 2H)

¹³C-NMR (125.8 MHz; CDCl₃): δ (ppm) -5.1 (CH₃), -4.8 (CH₃), 18.1 (C), 21.5 (CH₂), 24.7 (CH₂), 25.79 (CH₃), 25.85 (CH₃), 25.92 (CH₃), 28.8 (CH₂), 33.00 (CH₂), 41.1 (CH, C-4a), 51.8 (CH₃), 54.4 (C, C-9a), 55.3 (CH₃), 79.8 (CH, C-1a), 113.6 (CH), 124.6 (CH, C-5a), 126.2 (CH), 134.5 (C), 135.1 (C), 158.6 (C), 177.1 (C)

IR: (cm⁻¹) 776 (s), 835 (s), 1038 (m), 1115 (m), 1178 (m), 1248 (s), 1463 (w), 1512 (s), 1608 (m), 1725 (s), 2858 (w), 2929 (w), 2952 (m)

EI-MS (100°C): *m/z* = 416 (M⁺), 359 (100%), 225 (65), 199 (50), 89 (42), 73 (38)

HR-MS: (C₂₄H₃₆O₄Si) calcd 416.2382, found 416.2381

NOE H-4a $\leftrightarrow$ H-1a: 2.3 %; no further NOEs related to H-4a have been found.

6-(4-Methoxyphenyl)-1-(*tert*-butyldimethylsilyloxy)-2,3,4,7,8,9-hexahydro-1*H*-indene-9-carbonitrile (23a,b,c)

According to method **C** 4-methoxyphenyl acetylene **13** (92 mg, 0.7 mmol) and α,ω -diene **5** (155 mg, 0.62 mmol) were converted using catalyst **3** (33 mg, 7.5 mol %). After final chromatography (SiO₂, hexane/MtBE 100:1), the title compound **23a,b,c** (147 mg, 0.384 mmol, 62 %, **a:b:c** = 20:1:4) was obtained as a slightly yellow oil.

¹H-NMR (500 MHz; CDCl₃): δ (ppm) 0.07 - 0.19 (m, 6H), 0.87-0.95 (m, 9H), 1.40-1.60 (m, 1H), 1.63-1.81 (m, 2H), 1.98-2.15 (m, 3H), 2.40-2.67 (m, 2H), 2.86-2.93 (br, 1H, H-4a,b), 3.02-3.09 (br, 1H, H-4c), 3.81 (s, 3H), 4.09 (pseudo-t, *J*=3.5Hz, 1H, H-1c), 4.38 (d, *J*=5Hz, 1H, H-1b), 4.52-4.58 (pseudo-t, *J*=5Hz, 1H, H-1a), 5.92-5.98 (m, 1H, H-5)

¹³C-NMR (125.8 MHz; CDCl₃): δ (ppm) -4.7 (CH₃), 18.1 (C), 22.4 (CH₂), 24.5 (CH₂), 25.8 (CH₃), 27.2 (CH₂ isomer c), 28.2 (CH₂), 29.5 (CH₂ isomer c), 31.6 (CH₂), 33.2 (CH₂ isomer c), 42.2 (CH, C-4a), 42.5 (CH, C-4c), 44.0 (C, C-9a), 55.4 (CH₃), 78.4 (CH, C-1c), 79.0 (CH, C-1a), 113.8 (CH), 122.6 (CH, C-5a), 124.3 (C), 126.33 (CH), 126.39 (CH), 133.9 (C), 135.9 (C), 159.0 (C)

IR: (cm⁻¹) 777 (m), 833 (s), 1037 (m), 1129 (m), 1181 (m), 1256 (s), 1471 (w), 1513 (s), 1607 (m), 2223 (w), 2857 (w), 2929 (m), 2955 (m)

EI-MS (130°C): m/z = 383 (M^+), 355 (5), 326 (100%), 299 (12), 251 (14), 225 (30), 197 (50), 128 (25), 58 (60)

HR-MS: ($C_{23}H_{33}O_2NSi$) calcd 383.2281, found 383.2287

NOE H-4a $\leftrightarrow$ H-1a: 1.7 %; no further NOEs related to H-4a have been found.

Synthesis of Ketones 24 – 28:

6-(1-Acetoxybutyl)-2,3,4,7,8,9-hexahydro-1*H*-indene-1-one-9-carboxylic acid methyl ester (24)

The TBS-ether **18a,b** (128 mg, 0.3 mmol) and TBAF*3H₂O (126 mg, 0.45 mmol) were dissolved in 4 ml THF and stirred at room temperature for 45 min. Then the reaction mixture was diluted with 15 ml MtBE, extracted with 10 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 5 ml dry CH₂Cl₂. After addition of molecular sieves (4A) and PCC (97 mg, 0.45 mmol) at 0 °C, the reaction mixture was stirred for 2 h at room temperature, then diluted with 20 ml MtBE and filtered through a Florisil plug. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **24** (64 mg, 0.21 mmol, 69 %) as a mixture of C-6 α epimers forming a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ (ppm) 0.85-0.93 (m, 3H), 1.12-1.32 (m, 2H), 1.43-1.65 (m, 2H), 1.66-1.74 (m, 1H), 1.80-2.08 (m, 7H), 2.19-2.44 (m, 3H), 3.21-3.28 (br, 1H, H-4), 3.71 (s, 3H), 5.09-5.14 (m, 1H), 5.62-5.66 (m, 1H)

¹³C-NMR (125.8 MHz; CDCl₃): δ (ppm) 13.9 (CH₃), 18.63 (CH₂), 18.75 (CH₂), 20.3 (CH₂), 20.7 (CH₂), 21.28 (CH₃), 21.30 (CH₃), 23.91 (CH₂), 24.07 (CH₂), 27.03 (CH₂), 27.10 (CH₂), 34.55 (CH₂), 34.61 (CH₂), 36.6 (CH₂), 36.9 (CH₂), 40.54 (CH, C-4), 41.60 (CH, C-4), 52.7 (CH₃), 58.92 (C, C-9), 59.04 (C, C-9), 77.18 (CH), 77.26 (CH), 125.1 (CH, C-5), 125.7 (CH, C-5), 136.9 (C, C-6), 137.2 (C, C-6), 170.3 (C), 171.54 (C), 171.65 (C), 214.60 (C, C-1), 214.69 (C, C-1) (signal duplication due to side chain epimeric mixture)

IR: (cm⁻¹) 1023 (w), 1044 (w), 1058 (w), 1237 (s), 1371 (w), 1434 (w), 1731 (s), 1750 (m), 2874 (w), 2958 (m)

EI-MS (100°C): m/z = 308 (M^+), 248 (100%), 219 (15), 189 (45), 141 (12), 91 (15)

HR-MS: ($C_{15}H_{20}O_3$; M^+ -HOAc) calcd 248.1412, found 248.1413

No NOEs related to H-4 have been found.

6-(1-Acetoxybutyl)-2,3,4,7,8,9-hexahydro-1*H*-indene-1-one-9-carbonitrile (25)

The TBS-ether **19a,b,c** (117 mg, 0.3 mmol) and TBAF*3H₂O (126 mg, 0.45 mmol) were dissolved in 4 ml THF and stirred at room temperature for 15 min. Then the reaction mixture was diluted with 15 ml MtBE, extracted with 10 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 5 ml dry CH₂Cl₂. After addition of molecular sieves (4A) and PCC (97 mg, 0.45 mmol) at 0 °C, the reaction mixture was stirred for 4 h at room temperature, then diluted with 20 ml MtBE and filtered through a Florisil plug. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **25** (55 mg, 0.2 mmol, 87 % referring to *cis*-fused isomers **19a,b**) as a mixture of C-6 α epimers forming a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 0.87-0.94 (m, 3H), 1.13-1.37 (m, 2H), 1.45-1.69 (m, 2H), 1.71-1.81 (m, 1H), 1.88-2.11 (m, 6H), 2.12-2.24 (m, 1H), 2.33-2.51 (m, 3H), 3.08-3.19 (br, 1H, H-4), 5.09-5.17 (m, 1H), 5.63-5.72 (m, 1H)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 13.8 (CH₃), 18.7 (CH₂), 20.1 (CH₂), 20.5 (CH₂), 21.24 (CH₃), 24.51 (CH₂), 24.59 (CH₂), 26.84 (CH₂), 26.90 (CH₂), 34.53 (CH₂), 34.66 (CH₂), 35.62 (CH₂), 35.92 (CH₂), 41.34 (CH, C-4), 41.45 (CH, C-4), 46.8 (C, C-9), 76.8 (CH), 77.36 (CH), 118.8 (C), 122.9 (CH, C-5), 123.5 (CH, C-5), 137.4 (C, C-6), 137.8 (C, C-6), 170.3 (C), 208.77 (C, C-1), 208.88 (C, C-1) (signal duplication due to side chain epimeric mixture)

IR: (cm⁻¹) 1024 (w), 1238 (ss), 1371 (w), 1434 (w), 1466 (w), 1731 (s), 1752 (s), 2238 (w), 2874 (w), 2936 (w), 2959 (w)

EI-MS (100°C): m/z= 275 (M⁺), 233 (65), 215 (100%), 186 (22), 173 (20), 145 (20)

HR-MS: (C₁₆H₂₁O₃N) calcd 275.1521, found 275.1530

No NOEs related to H-4 have been found.

6-Phenyl-2,3,4,7,8,9-hexahydro-1*H*-indene-1-one-9-carbonitrile (**26**)

The TBS-ether **21a,c** (106 mg, 0.3 mmol) and TBAF*3H₂O (126 mg, 0.45 mmol) were dissolved in 4 ml THF and stirred at room temperature for 5 min. Then the reaction mixture was diluted with 15 ml MtBE, extracted with 10 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 5 ml dry CH₂Cl₂. After addition of molecular sieves (4A) and PCC (97 mg, 0.45 mmol) at 0 °C, the reaction mixture was stirred for 2.5 h at room temperature, then diluted with 20 ml MtBE and filtered through a Florisil plug. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **26** (38 mg, 0.16 mmol, 65 % referring to *cis*-fused isomer **21a**) as a slightly yellow oil.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 1.82-1.93 (m, 1H), 2.14 (t, J = 7Hz, 2H), 2.44-2.55 (m, 4H), 2.59-2.68 (m, 1H), 3.30-3.36 (m, 1H, H-4), 6.03-6.08 (m, 1H, H-5), 7.26-7.39 (m, 5H)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 23.7 (CH₂), 24.9 (CH₂), 27.1 (CH₂), 35.9 (CH₂), 42.1 (CH, C-4), 46.4 (C, C-9), 118.9 (C), 122.6 (CH), 125.2 (CH), 127.8 (CH), 128.5 (CH), 137.9 (C), 140.4 (C), 208.8 (C)

IR: (cm⁻¹) 698 (w), 752 (w), 1140 (w), 1446 (w), 1752 (s), 2238 (w), 2929 (w), 2951 (w)

EI-MS (100°C): m/z= 237 (M⁺, 100%) 208 (20), 195 (20), 180 (25), 158 (30), 104 (50), 91 (25), 77 (18)

HR-MS: (C₁₆H₁₅NO) calcd 237.1154, found 237.1152

No NOEs related to H-4 have been found.

6-(4-Methoxyphenyl)-2,3,4,7,8,9-hexahydro-1*H*-indene-1-one-9-carboxylic acid methyl ester (**27**)

The TBS-ether **22a,b** (247 mg, 0.59 mmol) and TBAF*3H₂O (223 mg, 0.8 mmol) were dissolved in 8 ml THF and stirred at room temperature for 18 h. Then the reaction mixture was diluted with 25 ml MtBE, extracted with 15 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 10 ml dry CH₂Cl₂. After addition of molecular sieves (4A) and PCC (190 mg, 0.88 mmol) at 0 °C, the reaction mixture was stirred for 18 h at room temperature, then diluted with 30 ml MtBE and filtered through a Florisil plug. Removal of the solvent and purification of the

residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **27** (113 mg, 0.38 mmol, 64 %) as a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 1.75-1.84 (m, 1H), 2.04-2.11 (m, 1H), 2.14-2.42 (m, 1H), 2.30-2.50 (m, 5H), 3.40-3.46 (br, 1H, H-4), 3.73 (s, 3H), 3.81 (s, 3H), 5.95-5.98 (m, 1H), 6.83-6.88 (m, 2H), 7.26-7.32 (m, 2H)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 24.16 (CH₂), 24.31 (CH₂), 27.5 (CH₂), 37.0 (CH₂), 41.4 (CH, C-4), 52.7 (CH₃), 55.4 (CH₃), 58.7 (C, C-9), 113.8 (CH), 123.2 (CH, C-5), 126.2 (CH), 133.7 (C), 136.8 (C), 159.1 (C), 176.7 (C), 214.8 (C, C-1)

IR: (cm⁻¹) 829 (w), 1036 (w), 1181 (m), 1221 (s), 1257 (m), 1361 (m), 1514 (m), 1713 (s), 1750 (m), 2840 (w), 2957 (w)

EI-MS (115°C): m/z= 300 (M⁺), 241 (100%), 199 (5), 185 (6), 134 (8)

HR-MS: (C₁₈H₂₀O₄) calcd 300.1362, found 300.1367

No NOEs related to H-4 have been found.

6-(4-Methoxyphenyl)-2,3,4,7,8,9-hexahydro-1*H*-indene-1-one-9-carbonitrile (**28**)

The TBS-ether **23a,b,c** (265 mg, 0.69 mmol) and TBAF*3H₂O (232 mg, 0.83 mmol) were dissolved in 9 ml THF and stirred at room temperature for 20 min. Then the reaction mixture was diluted with 25 ml MtBE, extracted with 15 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 14 ml dry CH₂Cl₂. After addition of molecular sieves (4A) and PCC (224 mg, 1.04 mmol) at 0 °C, the reaction mixture was stirred for 18 h at room temperature, then diluted with 30 ml MtBE and filtered through a Florisil plug. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **28** (133 mg, 0.5 mmol, 86 % referring to *cis*-fused isomers **23a,b**) as a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 1.81-1.91 (m, 1H), 2.10-2.15 (m, 2H), 2.42-2.52 (m, 4H), 2.54-2.63 (m, 1H), 3.28-3.34 (br, 1H, H-4), 3.81 (s, 3H), 5.94-5.98 (m, 1H), 6.87 (d, J=9Hz, 2H), 7.30 (d, J=9Hz, 2H)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 23.8 (CH₂), 25.0 (CH₂), 27.3 (CH₂), 35.9 (CH₂), 42.2 (CH, C-4), 46.6 (C, C-9), 55.40 (CH₃), 113.9 (CH), 119.0 (C), 121.0 (CH, C-5), 126.4 (CH), 133.0 (C), 137.3 (C), 159.4 (C), 209.1 (C, C-1)

IR: (cm⁻¹) 797 (s), 825 (s), 1030 (s), 1240 (m), 1259 (m), 1512 (m), 1605 (w), 1749 (s), 2237 (w), 2836 (w), 2962 (w)

EI-MS (140°C): m/z= 267 (M⁺=100%), 239 (6), 226 (4), 211 (15), 188 (10), 134 (30)

HR-MS: (C₁₇H₁₇O₂N) calcd 267.1259, found 267.1261

No NOEs related to H-4 have been found.

Synthesis of Trienes 29 - 34 by Enyne Cross Metathesis:

General Procedure for the synthesis of the trienes 29 - 34:

In a 5 ml screw cap glass vial equipped with a magnetic stirring bar the α,ω -diene (1 eq; 0.2-1.0 mmol), alkyne (1.2-1.35 eq) and catalyst (5 – 7.5 mol %) were dissolved in CH_2Cl_2 (0.2 M α,ω -diene solution). After being stirred at room temperature (using 7.5 mol % of Grubbs 1 catalyst **1**; referred to as method **A**) or alternatively at 45 °C (using 5 mol % of either Grubbs 2 catalyst **2** or phosphine free catalyst **3**; referred to as method **B**) for 24 h, the reaction mixtures were concentrated in vacuo. The oily residues were subjected to flash chromatography (using silica and the eluent system given). The purified trienes **29** - **34** were obtained as *E/Z*-mixtures (ratios given below).

(*E/Z*)-9-Acetoxymethyl-3-(*tert*-butyldimethylsilanyloxy)-2-methylene-deca-7,9-dienoic acid methyl ester (**29**)

According to the general procedure propargyl acetate **9** (47 mg, 0.48 mmol) and α,ω -diene **7** (119 mg, 0.4 mmol) were converted using catalyst **1** (25 mg, 7.5 mol %) at room temperature (method **A**). After final

chromatography (SiO_2 , hexane/MtBE 30:1), the title compound **29** (95 mg, 0.24 mmol, 60 %, *E:Z*=1:1.3) was obtained as a slightly brown oil.

¹H-NMR (400MHz; CDCl_3): δ (ppm)= -0.02 (s, 6H), 0.06 (s, 6H), 0.92 (s, 18H), 1.36-1.68 (m, 8H), 2.00-2.27 (m, 4H), 2.09 (s, 3H), 2.11 (s, 3H), 3.76 (s, 6H), 4.56 (s, 2H), 4.60 (m, 2H), 4.72 (s, 2H), 5.06 (s, 1H), 5.09 (s, 1H), 5.12 (s, 1H), 5.24 (s, 1H), 5.56 (dt, $J_1 = 12\text{Hz}$, $J_2 = 7\text{Hz}$, 1H-*Z*), 5.69 (dt, $J_1 = 16\text{Hz}$, $J_2 = 7\text{Hz}$, 1H-*E*), 5.79 (d, $J = 12\text{Hz}$, 1H-*Z*), 5.93 (s, 2H), 6.06 (d, $J = 16\text{Hz}$, 1H-*E*), 6.24 (s, 1H)

¹³C-NMR (100.6MHz; CDCl_3): δ (ppm)= -1.0 (CH_3), -0.7 (CH_3), 18.0 (C), 20.8 (CH_3), 24.4 (CH_2), 25.2 (CH_2), 25.8 (CH_3), 28.6 (CH_2), 32.7 (CH_2), 37.1 (CH_2), 37.2 (CH_2), 51.6 (CH_3), 64.0 (CH_2), 66.8 (CH_2), 69.93 (CH), 69.97 (CH), 115.3 (CH_2), 115.9 (CH_2), 124.4 (CH_2), 126.3 (CH), 129.2 (CH), 131.3 (CH), 134.4 (CH), 139.9 (C), 140.3 (C), 143.75 (C), 143.78 (C), 166.5 (C), 170.48 (C), 170.58 (C)

IR: (cm^{-1}) 776 (s), 836 (ss), 1092 (ss), 1143 (m), 1227 (s), 1251 (s), 1630 (w), 1719 (ss), 1744 (ss), 2930 (m), 2952 (m)

EI-MS (120°C): m/z = 396 (M^+), 339 (65), 279 (35), 229 (25), 173 (45), 145 (58), 117 (70), 89 (80), 73 (100%)

HR-MS: ($\text{C}_{21}\text{H}_{35}\text{O}_5\text{Si}$) calcd 396.2332, found 396.2339

(*E/Z*)-3-(*tert*-Butyldimethylsilanyloxy)-2,9-dimethylene-dodec-7-enedioic acid dimethyl ester (**30**)

According to the general procedure methyl pent-4-ynoate **10** (68 mg, 0.63 mmol) and α,ω -diene **7** (156 mg, 0.52 mmol) were converted using catalyst **1** (32 mg, 7.5 mol %) at room temperature

(method **A**). After final chromatography (SiO_2 , hexane/MtBE 30:1), the title compound **30** (141 mg, 0.34 mmol, 65 %, *E:Z*=1:1.5) was obtained as a slightly brown oil.

¹H-NMR (500.132MHz; CDCl_3): δ (ppm)= -0.04 (s, 3H), -0.03 (s, 3H), 0.04 (s, 3H), 0.05 (s, 3H), 0.88 (s, 18H), 1.35-1.65 (m, 8H), 2.01-2.23 (m, 4H), 2.29-2.44 (m, 4H), 2.49 (m, 4H), 3.64 (s, 3H), 3.66 (s, 3H), 3.73 (s, 6H), 4.59 (m, 2H), 4.82 (s, 1H), 4.84 (s, 1H), 4.89 (s, 1H), 4.97 (s, 1H), 5.46 (dt, $J_1 = 12\text{Hz}$, $J_2 = 7\text{Hz}$, 1H-*Z*), 5.67 (dt, $J_1 = 16\text{Hz}$, $J_2 = 7\text{Hz}$, 1H-*E*), 5.72 (d, $J = 12\text{Hz}$, 1H-*Z*), 5.89 (s, 2H), 6.02 (d, $J = 16\text{Hz}$, 1H-*E*), 6.22 (s, 2H)

¹³C-NMR (125.8MHz; CDCl₃): δ(ppm)= -5.0 (CH₃), -4.7 (CH₃), 18.2 (C), 24.6 (CH₂), 25.4 (CH₂), 25.9 (CH₃), 27.3 (CH₂), 27.9 (CH₂), 28.6 (CH₂), 32.3 (CH₂), 32.7 (CH₂), 33.0 (CH₂), 37.25 (CH₂), 37.49 (CH₂), 51.53 (CH₃), 51.58 (CH₃), 51.71 (CH₃), 70.09 (CH), 70.15 (CH), 113.6 (CH₂), 113.9 (CH₂), 124.57 (CH₂), 124.62 (CH₂), 129.2 (CH), 130.3 (CH), 131.7 (CH), 133.2 (CH), 143.76 (C), 143.92 (C), 144.6 (C), 166.7 (C), 173.61 (C), 173.76 (C)

IR: (cm⁻¹) 776 (m), 837 (s), 1092 (s), 1257 (m), 1437 (m), 1630 (w), 1720 (ss), 1742 (s), 2930 (m), 2952 (m)

EI-MS (90°C): m/z= 410 (M⁺), 353 (100%), 339 (8), 289 (10), 229 (20), 173 (30), 145 (20), 89 (65), 73 (63)

HR-MS: (C₂₂H₃₈O₅Si) calcd 410.2489, found 410.2489

(E,Z)-10-Acetoxy-3-(tert-butyldimethylsilanyloxy)-2,9-dimethylene-tridec-7-enoic acid methyl ester (31)

According to the general procedure hex-1-yn-3-yl acetate **11** (46 mg, 0.33 mmol) and α,ω-diene **7** (82 mg, 0.27 mmol) were converted using catalyst **3** (10.5 mg, 5 mol %) at 45 °C (method **B**). After final

chromatography (SiO₂, hexane/MtBE 30:1), the title compound **31** (98 mg, 0.224 mmol, 83 %, *E:Z*=1.3:1) was obtained as a slightly brown oil.

¹H-NMR (400 MHz; CDCl₃): δ(ppm) -0.02 (s, 3H), 0.06 (s, 3H), 0.87-0.92 (m, 12H), 1.20-1.52 (m, 6H), 1.52-1.70 (m, 2H), 1.96-2.12 (m, 4H), 2.12-2.22 (m, 1H), 3.75 (s, 3H), 4.56-4.63 (m, 1H), 4.96 (s, 1H-*E*), 5.00-5.03 (m, 1H), 5.15-5.21 (m, 1H), 5.41-5.46 (m, 1H-*E*), 5.55-5.63 (m, 1H-*Z*), 5.75-5.85 (m, 1H), 5.89-5.92 (m, 1H), 5.97 (d, *J*=16Hz, 1H-*E*), 6.21-6.24 (m, 1H)

¹³C-NMR (100.6 MHz; CDCl₃): δ(ppm) -0.9 (CH₂), -0.6 (CH₂), 13.75 (CH₃), 13.77 (CH₃), 18.1 (C), 18.54 (CH₂), 18.74 (CH₂), 21.2 (CH₃), 24.5 (CH₂), 25.3 (CH₂), 25.8 (CH₃), 28.6 (CH₂), 32.9 (CH₂), 35.4 (CH₂), 36.2 (CH₂), 37.28 (CH₂), 37.36 (CH₂), 51.6 (CH₃), 70.04 (CH), 70.11 (CH), 73.8 (CH), 76.7 (CH), 112.5 (CH₂), 114.5 (CH₂), 124.5 (CH₂), 125.7 (CH), 128.8 (CH), 131.3 (CH), 134.7 (CH), 143.4 (C), 143.8 (C), 143.9 (C), 145.3 (C), 166.7 (C), 170.2 (C) (signal duplication due to side chain epimeric mixture)

IR: (cm⁻¹) 776 (m), 836 (m), 1093 (m), 1237 (s), 1370 (w), 1720 (s), 1741 (s), 2857 (w), 2930 (m), 2956 (m)

EI-MS (110°C): m/z= 438 (M⁺), 381 (5), 321 (100%), 229 (10), 187 (14), 173 (16), 134 (20), 117 (22), 89 (30), 73 (40)

HR-MS: (C₂₄H₄₂O₅Si) calcd 438.2802, found 438.2812

(E,Z)-10-Acetoxy-3-(tert-butyldimethylsilanyloxy)-2-cyano-9-methylene-trideca-1,7-diene (32)

According to the general procedure hex-1-yn-3-yl acetate **11** (50 mg, 0.36 mmol) and α,ω-diene **8** (79 mg, 0.3 mmol) were converted using catalyst **2** (13 mg, 5 mol %) at 45 °C (method **B**). After final chromatography (SiO₂,

hexane/MtBE 30:1), the title compound **32** (98 mg, 0.18 mmol, 60 %, *E:Z*=1.1:1) was obtained as a slightly brown oil.

¹H-NMR (400 MHz; CDCl₃): δ(ppm) 0.02-0.10 (m, 6H), 0.87-0.93 (m, 12H), 1.22-1.48 (m, 6H), 1.48-1.72 (m, 2H), 2.00-2.08 (m, 3H), 2.98-2.16 (m, 1H), 2.17-2.26 (m, 1H), 4.19-4.25 (m, 1H), 4.96 (s, 1H-*Z*), 5.04 (s, 1H), 5.15-5.22 (m, 1H), 5.41-5.46 (m, 1H-*E*), 5.55-5.63 (m, 1H-*Z*), 5.75-5.87 (m, 1H), 5.93 (s, 1H), 5.98 (d, *J*=16Hz, 1H-*E*)

^{13}C -NMR (100.6 MHz; CDCl_3): $\delta(\text{ppm})$ -0.9 (CH_3), -0.7 (CH_3), 13.7 (CH_3), 18.0 (C), 18.5 (CH_2), 18.7 (CH_2), 21.1 (CH_3), 24.07 (CH_2), 24.13 (CH_2), 24.8 (CH_2), 25.63 (CH_3), 25.72 (CH_3), 28.3 (CH_2), 32.7 (CH_2), 35.4 (CH_2), 36.13 (CH_2), 36.19 (CH_2), 36.22 (CH_2), 72.6 (CH), 73.7 (CH), 76.5 (CH), 112.87 (CH_2), 112.90 (CH_2), 114.5 (CH_2), 117.2 (C), 126.3 (CH), 127.40 (C), 129.0 (CH_2), 129.28 (CH), 129.31 (CH), 130.6 (CH), 134.0 (CH), 143.5 (C), 145.1 (C), 170.20 (C), 170.23 (C) (signal duplication due to side chain epimeric mixture)
IR: (cm^{-1}) 778 (m), 1095 (m), 1243 (s), 1364 (w), 1741 (s), 2226 (w), 2857 (w), 2930 (m)
EI-MS (100°C): m/z = 405 (M^+), 321 (100%), 224 (15), 187 (14), 173 (30), 134 (15),
HR-MS: ($\text{C}_{23}\text{H}_{39}\text{O}_3\text{NSi}$) calcd 405.2699, found 405.2691

(*E/Z*)-3-(*tert*-Butyldimethylsilanyloxy)-2-methylene-9-phenyl-deca-7,9-dienoic acid methyl ester (33**)**

According to the general procedure phenyl acetylene **12** (31 mg, 0.3 mmol) and α,ω -diene **7** (75 mg, 0.25 mmol) were converted using catalyst **3** (10 mg, 5 mol %) at 45 °C (method **B**). After final chromatography (SiO_2 , hexane/MtBE 100:1), the title compound **33** (90 mg, 0.225 mmol, 90 %, $E:Z=2:1$) was obtained as a slightly brown oil.

^1H -NMR (400 MHz; CDCl_3): $\delta(\text{ppm})$ -0.02 (s, 3H), 0.05 (s, 3H), 0.99 (s, 9H), 1.35-1.69 (m, 4H), 2.06-2.16 (m, 2H), 3.73 (s, 3H), 4.54-4.63 (m, 1H), 5.04-5.06 (m, 1H-*E*), 5.11-5.13 (m, 1H-*Z*), 5.16-5.18 (m, 1H-*E*), 5.51-5.53 (m, 1H-*Z*), 5.58-5.72 (m, 1H), 5.88-5.92 (m, 1H), 6.12 (d, $J=12\text{Hz}$, 1H-*Z*), 6.21-6.24 (m, 1H), 6.27 (d, $J=16\text{Hz}$, 1H-*E*), 7.27-7.42 (m, 5H)

^{13}C -NMR (100.6 MHz; CDCl_3): $\delta(\text{ppm})$ -1.0 (CH_3), -0.7 (CH_3), 18.3 (C), 24.3 (CH_2), 25.2 (CH_2), 25.8 (CH_3), 28.5 (CH_2), 32.6 (CH_2), 37.1 (CH_2), 37.4 (CH_2), 51.6 (CH_3), 70.02 (CH), 70.08 (CH), 114.53 (CH_2), 114.68 (CH_2), 124.51 (CH_2), 124.57 (CH_2), 126.5 (CH), 127.25 (CH), 127.44 (CH), 128.0 (CH), 128.18 (CH), 128.22 (CH), 128.9 (CH), 131.5 (CH), 134.20 (CH), 134.28 (CH), 140.68 (C), 140.83 (C), 143.83 (C), 143.87 (C), 144.5 (C), 148.1 (C), 166.7 (C)

IR: (cm^{-1}) 775 (m), 836 (m), 1093 (m), 1258 (w), 1438 (w), 1719 (s), 2857 (w), 2929 (w), 2952 (w)

EI-MS (100°C): m/z = 400 (M^+), 343 (100%), 268 (8), 209 (10), 173 (10), 156 (18), 89 (25), 73 (20), 57 (8)

HR-MS: ($\text{C}_{24}\text{H}_{36}\text{O}_3\text{Si}$) calcd 400.2434, found 400.2431

(*E,Z*)-8-(*tert*-Butyldimethylsilanyloxy)-9-cyano-2-phenyl-deca-1,3,9-triene (34**)**

According to the general procedure phenyl acetylene **12** (29 mg, 0.28 mmol) and α,ω -diene **8** (63 mg, 0.24 mmol) were converted using catalyst **3** (10 mg, 5 mol %) at 45 °C (method **B**). After final chromatography (SiO_2 , hexane/MtBE 100:1), the title compound **34** (77 mg, 0.21 mmol, 88 %, $E:Z=1:2$) was obtained as a slightly brown oil.

^1H -NMR (400 MHz; CDCl_3): $\delta(\text{ppm})$ 0.02-0.08 (m, 6H), 0.89-0.94 (m, 9H), 1.33-1.47 (m, 2H), 1.56-1.71 (m, 2H), 2.08-2.19 (m, 2H), 4.15-4.26 (m, 1H), 5.07-5.09 (m, 1H-*E*), 5.13 (s, 1H-*Z*), 5.18-5.20 (m, 1H-*E*), 5.53-5.55 (m, 1H-*Z*), 5.57-5.72 (m, 1H), 5.87 (s, 1H-*Z*), 5.90 (s, 1H-*Z*), 5.92 (s, 1H-*E*), 5.94 (s, 1H-*E*), 6.17 (d, $J=12\text{Hz}$, 1H-*Z*), 6.31 (d, $J=16\text{Hz}$, 1H-*E*), 7.27-7.43 (m, 5H)

^{13}C -NMR (100.6 MHz; CDCl_3): $\delta(\text{ppm})$ -4.9 (CH_3), -4.7 (CH_3), 18.2 (C), 24.0 (CH_2), 24.8 (CH_2), 25.75 (CH_3), 25.86 (CH_3), 28.2 (CH_2), 32.5 (CH_2), 36.17 (CH_2), 36.25 (CH_2), 71.2 (CH), 72.7 (CH), 114.92 (CH_2), 114.99 (CH_2), 117.3 (C), 125.3 (CH), 126.6 (CH), 127.4 (CH), 127.5 (CH), 127.6 (C), 128.1 (CH), 128.30 (CH), 128.33 (CH), 129.12 (CH_2), 129.19

(CH₂), 129.6 (CH), 132.1 (CH), 133.57 (CH), 133.66 (CH), 140.75 (C), 140.91 (C), 143.6 (C), 145.0 (C)

IR: (cm⁻¹) 777 (s), 837 (s), 1106 (m), 1259 (m), 1472 (w), 2224 (w), 2857 (m), 2930 (m), 2952 (m)

EI-MS (100°C): m/z= 367 (M⁺), 310 (100%), 208 (8), 156 (8), 91 (10), 75 (50)

HR-MS: (C₂₃H₃₃NOSi) calcd 367.2331, found 367.2333

Synthesis of Hexahydronaphthalinones **35** - **38**:

7-(Acetoxymethyl)-3,4,5,8,9,10-hexahydro-2H-naphthalin-1-one-10-carboxylic acid methyl ester (**35**)

The TBS-protected triene **29** (119 mg, 0.3 mmol) and TBAF*3H₂O (168 mg, 0.6 mmol) were dissolved in 4 ml THF and stirred at room temperature for 4 h. Then the reaction mixture was diluted with 15 ml MtBE, extracted with 10 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 10 ml dry CH₂Cl₂. After addition of Dess-Martin periodinane (254 mg, 0.6 mmol) at 0 °C, the reaction mixture was stirred for 2 h at room temperature, then diluted with 20 ml MtBE and filtered through a silica plug. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **35** (50 mg, 0.18 mmol, 60 %) as a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 1.66-1.78 (m, 3H), 1.78-1.87 (m, 1H, H-3), 1.91-1.99 (m, 1H, H-4), 2.00-2.10 (m, 4H), 2.16-2.25 (m, 1H, H-8), 2.35-2.45 (m, 3H), 3.23-3.28 (br, 1H, H-5), 3.73 (s, 3H), 4.36-4.46 (m, 2H), 5.45-5.49 (m, 1H, H-6)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 21.0 (CH₃), 22.8 (CH₂), 23.1 (CH₂), 27.2 (CH₂), 28.4 (CH₂), 39.7 (CH, C-5), 40.6 (CH₂), 52.7 (CH₃), 58.7 (C, C-10), 67.7 (CH), 127.0 (CH, C-6), 134.5 (C, C-7), 170.9 (C), 173.0 (C), 207.0 (C, C-1)

IR: (cm⁻¹) 1022 (m), 1223 (ss), 1432 (w), 1709 (s), 1733 (s), 2868 (w), 2930 (w)

EI-MS (100°C): m/z= 264 (M⁺), 220 (100%), 188 (38), 161 (85), 132 (50), 105 (58), 91 (90)

HR-MS: (C₁₄H₁₇O₄; M⁺-CH₃) calcd 249.1127, found 249.1126

No NOEs related to H-5 have been found.

7-[2-(Methoxycarbonyl)-ethyl]-3,4,5,8,9,10-hexahydro-2H-naphthalin-1-one-10-carboxylic acid methyl ester (**36**)

The TBS-protected triene **30** (112 mg, 0.27 mmol) and TBAF*3H₂O (155 mg, 0.54 mmol) were dissolved in 4 ml THF and stirred at room temperature for 24 h. Then the reaction mixture was diluted with 15 ml MtBE, extracted with 10 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 10 ml dry CH₂Cl₂. After addition of Dess-Martin periodinane (127 mg, 0.3 mmol) at 0 °C, the reaction mixture was stirred for 2 h at room temperature, then diluted with 20 ml MtBE and filtered through a silica plug. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **36** (43 mg, 0.15 mmol, 54 %) as a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 1.62-1.73 (m, 3H), 1.74-1.81 (m, 1H), 1.85-1.97 (m, 2H), 2.11-2.22 (m, 1H), 2.22-2.28 (m, 2H), 2.30-2.48 (m, 5H), 3.14-3.19 (br, 1H, H-5), 3.63 (s, 3H), 3.71 (s, 3H), 5.13-5.17 (m, 1H, H-6)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 22.6 (CH₂), 25.3 (CH₂), 27.5 (CH₂), 28.6 (CH₂), 32.2 (CH₂), 32.6 (CH₂), 39.8 (CH, C-5), 40.6 (CH₂), 51.6 (CH₃), 52.6 (CH₃), 58.7 (C, C-10), 123.4 (CH, C-6), 137.8 (C, C-7), 173.2 (C), 173.6 (C), 207.3 (C, C-1)

IR: (cm⁻¹) 846 (w), 1029 (w), 1066 (w), 1154 (m), 1230 (s), 1433 (w), 1709 (s), 1733 (s), 2931 (w), 2950 (w)

EI-MS (100°C): m/z= 294 (M⁺), 234 (100%), 203 (10), 175 (12), 147 (45), 105 (15), 91 (18)

HR-MS: (C₁₆H₂₂O₅) calcd 294.1467, found 294.1466

No NOEs related to H-5 have been found.

7-(1-Acetoxybutyl)-3,4,5,8,9,10-hexahydro-2H-naphthalin-1-one-10-carboxylic acid methyl ester (37)

The TBS-protected triene **33** (101 mg, 0.3 mmol) and TBAF*3H₂O (167 mg, 0.6 mmol) were dissolved in 4 ml THF and stirred at room temperature for 4 h. Then the reaction mixture was diluted with 15 ml MtBE, extracted with 10 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced pressure, was dissolved in 10 ml dry CH₂Cl₂.

After addition of Dess-Martin periodinane (254 mg, 0.6 mmol) at 0 °C, the reaction mixture was stirred for 2 h at room temperature, then diluted with 20 ml MtBE and filtered through a plug of silica gel. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **37** (48 mg, 0.15 mmol, 50 %) as a mixture of side chain epimers forming a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 0.88 (t, J=7Hz, 3H), 1.07-1.31 (m, 2H), 1.41-1.74 (m, 6H), 1.76-1.85 (m, 1H, H-3), 1.86-1.96 (m, 1H, H-4), 1.99-2.07 (m, 4H), 2.11-2.22 (m, 1H, H-8), 2.33-2.44 (m, 3H), 3.17-3.28 (br, 1H, H-5), 3.71 (s, 3H), 5.04-5.14 (m, 1H), 5.39-5.46 (m, 1H, H-6)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 13.82 (CH₃), 13.88 (CH₃), 18.56 (CH₂), 18.62 (CH₂), 20.5 (CH₂), 21.27 (CH₃), 21.34 (CH₃), 21.37 (CH₂), 22.68 (CH₂), 22.78 (CH₂), 27.1 (CH₂), 27.4 (CH₂), 28.2 (CH₂), 28.5 (CH₂), 34.3 (CH₂), 34.8 (CH₂), 39.58 (CH, C-5), 39.74 (CH, C-5), 40.52 (CH₂), 40.73 (CH₂), 52.62 (CH₃), 52.68 (CH₃), 58.5 (C, C-10), 58.9 (C, C-10), 77.1 (CH), 77.6 (CH), 125.8 (CH, C-6), 127.1 (CH, C-6), 137.6 (C, C-7), 170.4 (C), 173.1 (C), 206.9 (C, C-1) (signal duplication due to side chain epimeric mixture)

IR: (cm⁻¹) 986 (w), 1025 (w), 1143 (w), 1239 (s), 1371 (w), 1719 (s), 2873 (w), 2957 (w)

EI-MS (110°C): m/z= 322 (M⁺), 262 (75), 203 (100%), 173 (40), 105 (40), 91 (62)

HR-MS: (C₁₆H₂₂O₅; M⁺-HOAc) calcd 262.1569, found 262.1571

No NOEs related to H-5 have been found.

7-Phenyl-3,4,5,8,9,10-hexahydro-2H-naphthalin-1-one-10-carboxylic acid methyl ester (38)

The TBS-protected triene **31** (107 mg, 0.27 mmol) and TBAF*3H₂O (153 mg, 0.55 mmol) were dissolved in 4 ml THF and stirred at room temperature for 4 h. Then the reaction mixture was diluted with 15 ml MtBE, extracted with 10 ml saturated NaHCO₃-solution and washed with brine. The residue, obtained after drying with MgSO₄ and removal of solvent under reduced

pressure, was dissolved in 10 ml dry CH₂Cl₂. After addition of Dess-Martin periodinane (233 mg, 0.55 mmol) at 0 °C, the reaction mixture was stirred for 2 h at room temperature, then

diluted with 20 ml MtBE and filtered through a silica plug. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **38** (41 mg, 0.14 mmol, 53 %) as a waxy white solid.

¹H-NMR (500 MHz; CDCl₃): δ(ppm) 1.71-1.89 (m, 4H), 1.98-2.08 (m, 1H, H-4), 2.38-2.50 (m, 3H), 2.50-2.56 (m, 1H, H-9), 2.63-2.72 (m, 1H, H-8), 3.38-3.43 (br, 1H, H-5), 3.75 (s, 3H), 5.82-5.85 (m, 1H, H-6), 7.21-7.40 (m, 5H)

¹³C-NMR (125.8 MHz; CDCl₃): δ(ppm) 22.9 (CH₂), 24.5 (CH₂), 27.8 (CH₂), 28.8 (CH₂), 40.5 (CH, C-5), 40.7 (CH₂), 52.7 (CH₃), 58.5 (C, C-10), 125.1 (CH), 125.7 (CH, C-6), 127.3 (CH), 128.3 (CH), 138.0 (C), 141.0 (C), 173.2 (C), 207.2 (C, C-1)

IR: (cm⁻¹) 697 (m), 756 (m), 1065 (m), 1221 (s), 1445 (w), 1710 (s), 2865 (w), 2932 (m)

EI-MS (110°C): m/z= 284 (M⁺), 225 (100%), 196 (8), 91 (8)

HR-MS: (C₁₈H₂₀O₃; M⁺) calcd 284.1412, found 284.1414

No NOEs related to H-5 have been found.

Stereochemical assignments for *cis*-fused hexahydronaphthalinones **34-38** were made on the basis of NOE-measurements, molecular modelling and very similar NMR shifts of

bridgehead protons and carbons compared to *cis*-fused hexahydroindenones **24-28**. Molecular modelling was carried out using a PC Spartan AM1 geometry optimization. According to this, the bridgehead protons of *cis*-fused isomers should not show any NOE related to non-vicinal protons in the chair-like ring bearing the ketone function. In contrast to this, in the *trans*-fused isomers this ring should be rather boat-like and strong NOE between bridgehead H-5 and H-2 is expected.

One-pot-procedure for the synthesis of hexahydronaphthalinone **37**:

The hydroxy- α,ω -diene **6** (60 mg, 0.4 mmol), hex-1-yn-3-yl acetate **11** (70 mg, 0.5 mmol) and catalyst **3** (12.5 mg, 5 mol %) were dissolved in 2 ml CH₂Cl₂. After stirring at 45 °C in a closed screw cap glass vial for 24 h, 6 ml CH₂Cl₂ and Dess-Martin periodinane (339 mg, 0.8 mmol) were added at 0 °C and stirring was continued for further 2 h at room temperature. Then the reaction mixture was diluted with 20 ml MtBE and filtered through a plug of silica gel. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **37** (64 mg, 0.2 mmol, 50 %) as a mixture of C-7 α -epimers forming a waxy white solid.

One-pot-procedure for the synthesis of hexahydronaphthalinone **38**:

The hydroxy- α,ω -diene **6** (60 mg, 0.4 mmol), phenyl acetylene **12** (50 mg, 0.5 mmol) and catalyst **3** (12.5 mg, 5 mol %) were dissolved in 2 ml CH₂Cl₂. After stirring at 45 °C in a closed screw cap glass vial for 24 h, 6 ml CH₂Cl₂ and Dess-Martin periodinane (339 mg, 0.8 mmol) were added at 0 °C and stirring was continued for further 2 h at room temperature. Then the reaction mixture was diluted with 20 ml MtBE and filtered through a plug of silica gel. Removal of the solvent and purification of the residue by flash chromatography (SiO₂, Hexan:MtBE 10:1) yielded *cis*-ketone **38** (80 mg, 0.28 mmol, 70 %) forming a waxy white solid.

^{13}C -NMR of compound **14** (diastereomer a)

^{13}C -NMR of compound **15** (diastereomer a)

^{13}C -NMR of compound **16** (diastereomers a + b)

^{13}C -NMR of compound **17** (diastereomers a +c)

^{13}C -NMR of compound **18** (diastereomer a)

^{13}C -NMR of compound **19** (diastereomers a,b,c; side chain epimeric mixture)

^{13}C -NMR of compound **21** (diastereomer a)

^{13}C -NMR of compound **22** (diastereomer a)

^{13}C -NMR of compound **23** (diastereomers a + c)

^{13}C -NMR of compound **24** (pair of side chain epimers)

^{13}C -NMR of compound **25** (pair of side chain epimers)

^1H -NMR of compound **25** (pair of side chain epimers)

^{13}C -NMR of compound **26**

^1H -NMR of compound **26**

^{13}C -NMR of compound **27**

¹H-NMR of compound **27**

^{13}C -NMR of compound **28**

^1H -NMR of compound **28**

28

Spectrum 01x40702c

^{13}C -NMR of compound **29** (E/Z-mixture)

^1H -NMR of compound **29** (E/Z-mixture)

^{13}C -NMR of compound **30** (E/Z-mixture)

¹H-NMR of compound **30** (E/Z-mixture)

CCCC(C(=O)OC)C(=C)C/C=C/C(C(=O)OC)C(=C)CCCC(C(=O)OC)C(=C)C(=O)OC

^1H -NMR of compound **31** (E/Z, lk/ul-mixture)

^{13}C -NMR of compound **32** (E/Z,1k/ul-mixture)

^1H -NMR of compound **32** (E/Z, lk/ul-mixture)

¹³C-NMR of compound **33** (E/Z-mixture)

^1H -NMR of compound **33** (E/Z-mixture)

^{13}C -NMR of compound **34** (E/Z-mixture)

^1H -NMR of compound **34** (E/Z-mixture)

^{13}C -NMR of compound **35**

¹H-NMR of compound **35**

^{13}C -NMR of compound **36**

^1H -NMR of compound **36**

36

^{13}C -NMR of compound **37** (side chain epimeric mixture)

¹H-NMR of compound **37** (side chain epimeric mixture)

37

Spectrum 373306101

^{13}C -NMR of compound **38**