Intramolecular Diels–Alder Reactions, 2[+]

Studies on the Synthesis of Natural Products with Bicyclo[4.4.0]decene Skeleton: Synthesis and Uncatalysed Intramolecular Diels–Alder Reactions of the Decatrienone Substrates

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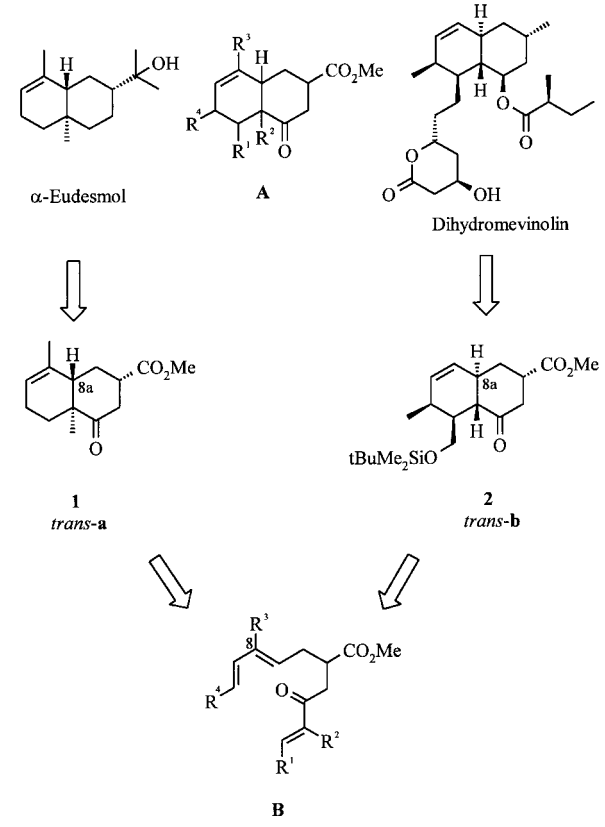
Starting from enones **7** and **8** siloxydienes **9** and **12** were synthesized. Cyclopropanation and subsequent alkylation with sorbyl bromide provided tetrasubstituted siloxycyclopropanes **15** and **16** in good overall efficiency. Their ring cleavage with fluoride reagents gave 1,7,9-decatrienones **5** and **17**; the latter was converted into the protected compound **6**. The thermal intramolecular Diels–Alder reactions of **5** and **6** were compared with those of related trienones **3** and **4**. Octalones **1**, **2**, **21**, and **22** were formed as mixtures of three or four diastereomers. Thus, for the stereoselective construction of natural products such as α-eudesmol or dihydromevinolin alternative reaction conditions for the cycloaddition step have to be developed.

Introduction

The intramolecular Diels−Alder reaction has served as a powerful tool for the construction of fused ring systems with one six-membered ring and has been employed frequently in stereoselective syntheses of polycyclic natural products.[3] Earlier we reported a fast and flexible synthesis of octalone derivatives using an intramolecular Diels−Alder reaction as the key step.[4] We demonstrated that variably substituted octalones **A** (Scheme 1) are very suitable precursors for the production of sesquiterpenes such as α-eudesmol,[4c] or for the synthesis of the fused bicyclic portion of the compactin/mevinolin type structures, as found in dihydromevinolin[4d] (Scheme 1). α-Eudesmol, a bicyclic sesquiterpene of the eudesmane type, has been isolated from over 40 plant species, mainly from Australian gum trees.[5] As a component of eucalyptus oil it is of commercial interest.[5d] Dihydromevinolin is a natural product of pharmaceutical importance.[6a] Like mevinolin[6b] and compactin,[6c] it is a potent inhibitor of 3-hydroxy-3-methylglutaryl coenzyme-A-reductase, an enzyme which controls the rate-determining step in cholesterol biosynthesis. The required connection of the rings is *trans* in both targets. The configuration of α-eudesmol calls for a *trans* relationship of the methoxycarbonyl group and 8a-H in the octalone precursor **1** (*trans*-**a**), whereas dihydromevinolin requires *cis* positioning of both substituents in **2** (*trans*-**b**). The stereogenic centres of the target molecules are thereby formed exclusively, or almost exclusively, in the cycloaddition step



Trienone	R^1	R^2	R^3	R^4
3	H	Me	H	H
4	H	Me	Me	H
5	Me	H	H	Me
6	CH_2OSiMe_2tBu	H	H	Me

Scheme 1

[+] Part 1: Ref.[4b]

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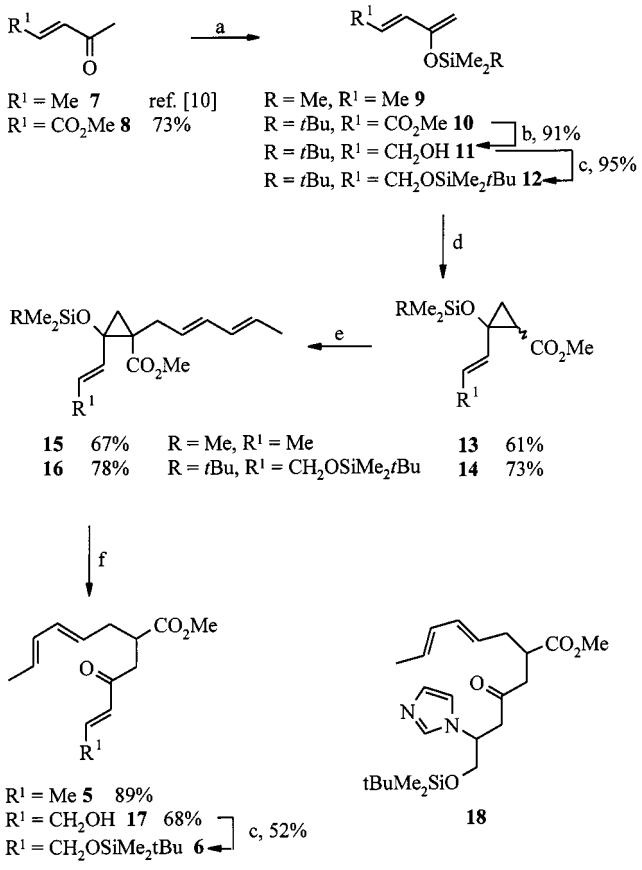
of trienones **B**. Since these syntheses were performed with racemates, all chiral compounds are provided as mixtures of both enantiomers; for clarity, only one enantiomer is depicted in the schemes. In extensive studies[1][2] we found that the stereochemical outcome of the cycloaddition step depends not only on the nature of the trienone substrate, but can be crucially influenced by the reaction conditions. In this paper we describe the synthesis of the Diels–Alder precursors **5**[7] and **6**, and the uncatalysed cycloaddition reactions of the trienones **3**–**6**, whereas subsequent reports will deal with Lewis acid promoted reactions and applications to the synthesis of α-eudesmol and dihydromevinolin.

Results and Discussion

Synthesis of the Trienones

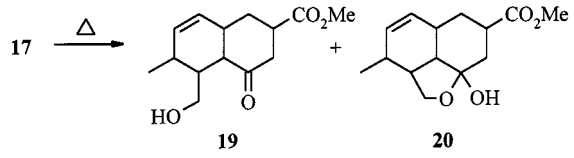
Both 2-methyl-substituted 1,7,9-decatrien-3-ones **3** and **4**[4b] (Scheme 1) were employed in the studies on the Diels–Alder reaction for the α-eudesmol pathway. Trienone **4** is a precursor of this sesquiterpene, whereas analogue **3** lacking the 8-methyl group was included to probe the influence of the 8-methyl group on the stereoselectivity of the cycloaddition reaction. The intramolecular [4+2]-cycloaddition reactions of trienones **5** and **6** were investigated in preliminary studies on the approach towards dihydromevinolin. In this program, initial focus was given on the dimethyl-substituted trienone **5**, a readily accessible model compound. Later we turned to 1-oxymethyl-substituted 1,7,9-decatrien-3-ones, which are potential precursors of dihydromevinolin. Here, first experiments on the uncatalysed intramolecular Diels–Alder reaction were performed on the siloxymethyl-substituted trienone **6**. The syntheses of substrates **5** and **6** are illustrated in Scheme 2.

Enones **7** and **8**[8][9] were converted into the siloxydienes **9**[10] and **10** with TMS–Cl or TBDMS–Cl, respectively, following a standard protocol.[11] Siloxydienecarboxylate **10** was transformed to bissiloxypentadiene **12** in two steps by means of a LAH reduction/TBDMS protection sequence. Cyclopropanation of siloxydienes **9** and **12** with methyl diazoacetate[12] under copper- or rhodium-catalysis proceeded smoothly in 61–73% yield. Stereoselective alkylation[4b,13] of cyclopropanecarboxylates **13** and **14** with sorbyl bromide[14] provided compounds **15** and **16** in good yields. Desilylation and ring opening to the trienones **5** and **17** were achieved smoothly by treating trimethylsiloxycyclopropane **15** with $NEt_3 \cdot 3\,HF$[15] and the TBDMS-protected compound **16** with tetrabutylammonium fluoride (TBAF). Both silyl groups in the latter were cleaved off in this step to provide hydroxymethyl-substituted trienone **17**. This substrate was subjected to the conditions of cycloaddition, where it was found to furnish an inseparable mixture of hydroxymethyloctalones **19** and lactols **20** (Scheme 3).[16] Since this mixture complicated the stereochemical analysis considerably, it was necessary to protect the hydroxy group in the precursor **17**. Reaction with TBDMS–Cl/imidazole (Scheme 2) furnished the desired siloxymethyltrienone **6** along with the imidazole adduct **18** as a by-product.[17]



a: $ClSiMe_3$ or $ClSiMe_2tBu$, NEt_3, NaI, CH_3CN, room temp. – b: $LiAlH_4$, Et_2O, 0 °C. – c: $ClSiMe_2tBu$, imidazole, DMF, room temp. – d: N_2CHCO_2Me, $Cu(acac)_2$/EtOAc/100 °C (for **9**) or $Rh_2(OAc)_4/CH_2Cl_2$/room temp. (for **12**). – e: (i) LDA, THF, –78 °C, (ii) (*E*,*E*)-1-bromo-2,4-hexadiene, –78 °C. – f: $NEt_3 \cdot 3HF/CH_2Cl_2$/–25 °C (R = Me) or TBAF/THF/0 °C (R = *t*Bu).

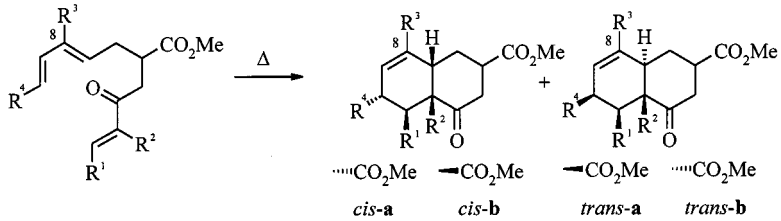
Scheme 2



Scheme 3

Intramolecular Diels–Alder Reactions

The results of the uncatalysed intramolecular Diels–Alder reactions (Scheme 4) are summarized in Table 1. Four possible diastereomers can arise from the intramolecular cycloaddition reaction, two products of the *endo*-approach of diene and dienophile, *cis*-**a** and *cis*-**b**, and the two *exo*-products *trans*-**a** and *trans*-**b**. Four possible transition states for the formation of these diastereomers are depicted in Scheme 5. Within the *endo*- and *exo*-series, the transition states differ in the conformation of the tether that links diene and dienophile. Provided that the methoxycarbonyl group adopts the sterically favoured equatorial posi-



R^1, R^3, R^4 = H, R^2 = Me	**3**	**21**
R^1, R^4 = H, R^2, R^3 = Me	**4**	**1**
R^1, R^4 = Me, R^2, R^3 = H	**5**	**22**
R^1 = CH_2OSiMe_2tBu, R^2, R^3 = H, R^4 = Me	**6**	**2**

Scheme 4

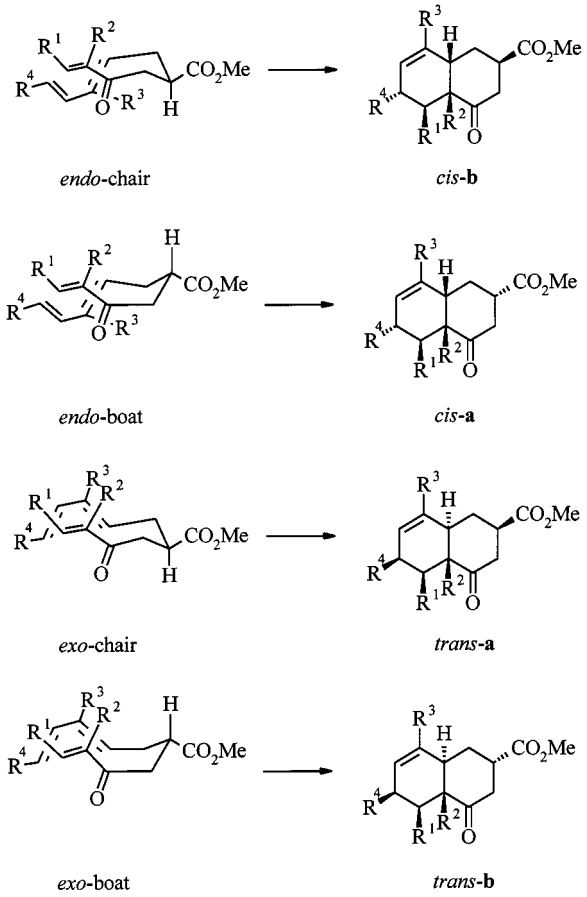
Table 1. Intramolecular Diels–Alder reactions of trienones **3**–**6**

Entry	Trienone	Octalone	Conditions	Yield [%]	Diastereomeric Ratio *cis*-**a** / *cis*-**b** / *trans*-**a** / *trans*-**b**
1[a]	**3**	**21**	80–110°C	41	45 : 16 : 39 : 0
2[a]	**4**	**1**	80–110°C	73	50 : 12 : 38 : 0
3	**5**	**22**	110°C	81	23 : 30 : 36 : 11
4	**6**	**2**	110°C	79	30 : 35 : 21 : 14

[a] Ref.[4b]

tion on the folded chain, two boat-transition states, leading to *cis*-**a** and *trans*-**b**, and two chair-transition conformations, forming *cis*-**b** and *trans*-**a**, can be formulated. Generally, a moderate preference for the products of an *endo*-approach of diene and dienophile, *cis*-**a** and *cis*-**b**, was found (Table 1). The **a/b** ratio among the *cis*- and the *trans*-isomers, however, differs with the substitution pattern of the trienones. Within the *cis*-series, the 2-methyl-substituted trienones **3** and **4** favour the *cis*-**a** forming, *endo*-boat transition state, whereas substrates **5** and **6** show a slight preference for the *endo*-chair folding, which leads to *cis*-**b**. A strong preference for *endo*-boat transition states in the intramolecular Diels–Alder reactions of 1,7,9-decatrien-3-ones is quite common.[3] In a semiquantitative approach to this phenomenon, Roush and Coe[18] found that *endo*-boat transition states are indeed energetically favoured. However, this effect can be easily overridden by substitution effects as the differences in enthalpy are small. Within the *trans*-series, the *exo*-chair product *trans*-**a** is formed exclusively from the 2-methyl-substituted trienones **3** and **4**, and predominantly from the substrates **5** and **6**. The desired diastereomer of the α-eudesmol precursor, *trans*-**1a**, is formed in only 38% (entry 2).

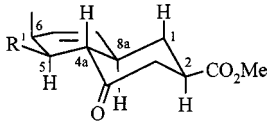
Application of high pressure (9 kbar/31–36°C) or ultrasound (175 kHz/24–45°C) provided similar diastereomeric ratios.[16] The steric influence of the methyl group at C-8 in the uncatalysed cycloaddition reaction (entry 1) is only minor. Diastereomers *trans*-**22b** (entry 3) and *trans*-**2b** (entry 4), which possess the relative configuration of the target molecule dihydromevinolin, represent only 11 and 14%, respectively, of the isolated products, which, of course, was very unsatisfactory. However, as the trienones contain two possible coordination sites, we expected drastic changes of the diastereoselectivity by application of Lewis acid catalysts in the cycloaddition step. The following report discloses the results of our studies on the Lewis acid catalysed intramolecular Diels–Alder reaction of trienones **3**, **4**, and **5**.[19]

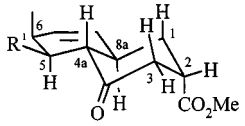


Scheme 5

Configurational Assignment

Octalones **21** and **1** are known.[4b] The assignment of the individual isomers of octalones **22** and **2** was based on their NMR spectra (Scheme 6). ^{13}C-NMR data were available for all diastereomers of octalone **22**. The bridgehead carbons of *trans*-fused 6/6-ring systems usually resonate at higher chemical shift values than their *cis*-fused counterparts.[20] Based on the values for C-8a, the isomers of **22** could be grouped into the *cis*- and the *trans*-series. In addition, the 4a-proton of *trans*-**2a** exhibits the expected *trans*-diaxial couplings with 5-H and 8a-H. In contrast, the 4a-protons of the *cis*-fused systems show one large diaxial and one small coupling, which also confirmed the conformation of the A- and the B-ring as depicted in Scheme 6. Within the *cis*- and the *trans*-fused series of **22**, the **a**-isomers were identified by the axial position of their proton at C-2, whereas the equatorial 2-protons of the **b**-isomers show the expected downfield shift. Similar criteria were used to assign the **a**- and **b**-isomers of octalone **2**. Here, the grouping of the four isomers into the *cis*- and *trans*-fused series was based on the ^{1}H-NMR shift of the 6-methyl group. Both *trans*-isomers possess an axially positioned 6-methyl group, which is evident from their upfield chemical shifts in relation to the equatorial 6-methyl groups of *cis*-**a** and *cis*-**b**.



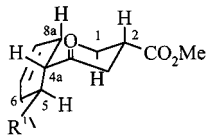


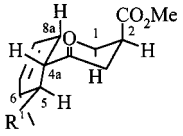
R^1 = Me *trans*-**22a**
δ(2-H) = 2.82 (tt, *J* = 4.5, 12.5 Hz)
δ(1-H_{ax}) = 1.66 (q, *J* = 12.5 Hz)
δ(C-8a) = 43.3

R^1 = Me *trans*-**22b**
δ(2-H) = 3.11 (m_c)
δ(1-H_{ax}) = 1.72 (ddd, *J* = 6, 13, 14 Hz)
δ(3-H) = 2.70 (td, *J* = 3, 13 Hz)
2.65 (ddd, *J* = 1, 7, 13 Hz)
δ(C-8a) = 40.9

R^1 = CH_2OSiMe_2tBu *trans*-**2a**
δ(2-H) = 2.83 (tt, *J* = 4.5, 12.5 Hz)
δ(4a-H) = 2.36 (br. t, *J* = 10.5 Hz)
δ(6-Me) = 0.94 (d, *J* = 7 Hz)

R^1 = CH_2OSiMe_2tBu *trans*-**2b**
δ(2-H) = 3.18 (m_c)
δ(1-H_{ax}) = 1.72 (ddd, *J* = 6, 12, 13.5 Hz)
δ(6-Me) = 0.95 (d, *J* = 7 Hz)





R^1 = Me *cis*-**22a**
δ(2-H) = 2.66 (ddt, *J* = 4, 5, 12.5 Hz)
δ(4a-H) = 2.24 (dd, *J* = 5, 12 Hz)
δ(C-8a) = 37.7

R^1 = Me *cis*-**22b**
δ(2-H) = 3.08 (m_c)
δ(4a-H) = 2.25 (dd, *J* = 5, 10.5 Hz)
δ(C-8a) = 34.6

R^1 = CH_2OSiMe_2tBu *cis*-**2a**
δ(2-H) = 2.65 (tt, *J* = 3.5, 13 Hz)
δ(6-Me) = 1.06 (d, *J* = 7 Hz)

R^1 = CH_2OSiMe_2tBu *cis*-**2b**
δ(2-H) = 2.97 (tt, *J* = 5, 7 Hz)
δ(6-Me) = 1.06 (d, *J* = 7 Hz)

Scheme 6

Experimental Section

General: All reactions with air- and moisture-sensitive compounds were performed under Ar or N_2 atmosphere in flame-dried glassware. All solvents were purified and dried by standard methods prior to use. − Conventional column chromatography: silica gel 60 (0.063−0.200 mm, E. Merck) or neutral alumina (6% H_2O, activity III, Macherey & Nagel); flash chromatography: silica gel 60 (0.040−0.063 mm, E. Merck). − TLC: Polygram Sil G/UV_{254} or Polygram Alox N/UV_{254} (Macherey & Nagel). − Short-path distillation: Büchi Kugelrohr GKR-50. − ^{1}H (^{13}C) NMR: Bruker AC 200, AC 300, WM 300, or ARX 300; 200 (50.3) MHz, or 300 (75.5) MHz; solvent: $CDCl_3$; internal standards: chloroform or TMS. − IR: Perkin−Elmer IR-325, IR-197 or Nicolet 205. − Melting points (not corrected): Büchi SMP-20 or Gallenkamp MPD 350. − Elemental analysis: Mikroanalytische Laboratorien der Institute für Organische Chemie der Technischen Hochschule Darmstadt and der Technischen Universität Dresden.

Methyl (*E*)-4-(*tert*-Butyldimethylsiloxy)-2,4-pentadienoate (10): To a solution of methyl (*E*)-4-oxo-2-pentenoate (**8**) (15.0 g, 0.117 mol) and NEt_3 (16.8 g, 0.166 mol) in CH_3CN (135 mL) was added dropwise a solution of TBDMS−Cl (25.0 g, 0.166 mol) in CH_3CN (120 mL) at 0°C, followed by a solution of dry NaI (20.0 g, 0.133 mol) in CH_3CN (250 mL). The mixture was stirred at room temp. for 3 d, then poured into an ice-cold mixture of pentane (500 mL) and satd. $NaHCO_3$ (500 mL). The top (pentane) layer was separated, and the two bottom layers were extracted with pentane (3× 100 mL). The combined pentane extracts were washed with water (100 mL), dried ($MgSO_4$), and concentrated. Bulb-to-bulb distillation (60−70°C/0.02 Torr) yielded silyl enol ether **10** as a colourless oil (20.7 g, 73%). − IR (neat): $\tilde{\nu}$ = 2960−2860 cm^{-1} (C−H), 1720 (CO_2Me), 1635 (C=CH_2), 1590 (C=C), 1250 (Si−C). − ^{1}H NMR (300 MHz): δ = 7.01 (d, *J* = 15.5 Hz, 1 H, 3-H), 6.09 (d, *J* = 15.5 Hz, 1 H, 2-H), 4.60, 4.58 (2 d, *J* = 0.5 Hz, 2× 1 H, *trans*-5-H, *cis*-5-H), 3.69 (s, 3 H, CO_2Me), 0.92 (s, 9 H, *t*Bu), 0.14 (s, 6 H, $SiMe_2$). − ^{13}C NMR (75.5 MHz): δ = 167.3 (s, *C*O_2Me), 153.6 (s, C-4), 142.7 (d, C-3), 116.7 (d, C-2), 102.7 (t, C-5), 51.5 (q, CO_2*Me*), 25.8 (q, Si*CMe*$_3$), 16.3 (s, Si*C*Me_3), −4.7 (q, $SiMe_2$). − $C_{12}H_{22}O_3Si$ (242.4): calcd. C 59.46, H 9.15; found C 59.64, H 9.21.

(*E*)-4-(*tert*-Butyldimethylsiloxy)-2,4-pentadien-1-ol (11): To a suspension of $LiAlH_4$ (2.80 g, 73.8 mmol) in ether (200 mL) was added dropwise at −5 to 0°C over a period of 2.5 h a solution of ester **10** (20.0 g, 82.5 mmol) in ether (200 mL). After stirring for 1 h at 0°C the mixture was carefully hydrolysed under vigorous stirring and ice cooling by dropwise addition of satd. NH_4Cl solution (100 mL). The aqueous phase was extracted with ether (3× 100 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated, after which the crude product (18.1 g) was distilled (kugelrohr 70−100°C/0.015 Torr) to afford alcohol **11** as a colourless oil (16.1 g, 91%). − IR (neat): $\tilde{\nu}$ = 3350 cm^{-1} (O−H), 2960, 2940, 2900, 2860 (C−H), 1655, 1590 (C=C), 1250 (Si−C). − ^{1}H NMR (300 MHz): δ = 6.03 (m_c, 2 H, 2-H, 3-H), 4.23 (br. s, 2 H, 5-H), 4.14 (m_c, 2 H, 1-H), 2.66 (br. s, 1 H, OH), 0.89 (s, 9 H, *t*Bu), 0.11 (s, 6 H, $SiMe_2$). − ^{13}C NMR (75.5 MHz): δ = 154.3 (s, C-4), 129.1, 128.5 (2 d, C-2, C-3), 95.6 (t, C-5), 62.5 (t, C-1), 25.6 (q, Si*CMe*$_3$), 16.1 (s, Si*C*Me_3), −4.7 (q, $SiMe_2$). − $C_{11}H_{22}O_2Si$ (214.4): calcd. C 61.63, H 10.34; found C 61.78, H 10.43.

(*E*)-1,4-Bis(*tert*-butyldimethylsiloxy)-2,4-pentadiene (12): To a solution of alcohol **11** (16.5 g, 77.0 mmol) and imidazole (13.1 g, 192 mmol) in DMF (40 mL) was added dropwise over a period of 15 min a solution of TBDMS−Cl (13.9 g, 92.2 mmol) in DMF (20 mL). The mixture was stirred for 19 h at room temp., then poured into a mixture of ether (200 mL) and brine (200 mL). The

organic phase was washed with brine (2× 150 mL), dried ($MgSO_4$), and concentrated to afford a yellowish oil (26.9 g). Distillation (kugelrohr 100−120°C/0.02 Torr) furnished bissiloxydiene **12** as a colourless, waxy solid (24.0 g, 95%), m. p. 30°C. − IR (neat): $\tilde{\nu}$ = 2960, 2930, 2890, 2860 cm^{-1} (C−H), 1590 (C=C), 1250 (Si−C). − ^1H NMR (300 MHz): δ = 6.06 (m_c, 2 H, 2-H, 3-H), 4.27 (m_c, 4 H, 1-H, 5-H), 0.97, 0.92 (2 s, 2× 9 H, 2 *t*Bu), 0.19, 0.07 (2 s, 2× 6 H, 2 $SiMe_2$). − ^{13}C NMR (75.5 MHz): δ = 154.7 (s, C-4), 129.8, 127.1 (2 d, C-2, C-3), 95.0 (t, C-5), 62.9 (t, C-1), 25.8, 25.7 (2 q, 2 $SiCMe_3$), 18.3, 18.2 (2 s, 2 $SiCMe_3$), −4.8, −5.3 (2 q, 2 $SiMe_2$). − $C_{17}H_{36}O_2Si_2$ (328.6): calcd. C 62.13, H 11.04; found C 62.10, H 11.39.

***trans*/*cis*-Methyl 2-[(*E*)-1-Propenyl]-2-(trimethylsiloxy)-1-cyclopropanecarboxylate (13):** To a mixture of (*E*)-2-(trimethylsiloxy)-1,3-pentadiene (**9**) (1.41 g, 9.02 mmol) and $Cu(acac)_2$ (47.0 mg, 0.180 mmol) was added at 100°C over a period of 1.5 h a solution of methyl diazoacetate (991 mg, 9.92 mmol) in EtOAc (5 mL). After evaporation of the solvent in vacuo the residue was filtered through alumina (pentane). The filtrate was concentrated and distilled (kugelrohr, 70°C/0.5 Torr) to provide cyclopropane **13** (*trans*/*cis* = 67:33) as a colourless oil (1.26 g, 61%). − IR (neat): $\tilde{\nu}$ = 3020−2920 cm^{-1} (C−H), 1730 (CO_2Me), 1665 (C=C), 1250 (Si−C). − *trans*-**13**: ^1H NMR (300 MHz): δ = 5.73 (qd, *J* = 6.5, 15 Hz, 1 H, 2′-H), 5.51 (qd, *J* = 1.5, 15 Hz, 1 H, 1′-H), 3.63 (s, 3 H, CO_2Me), ABX system (δ_A = 1.43, δ_B = 1.39, δ_X = 2.05, J_{AX} = 7.5 Hz, J_{BX} = 9 Hz, J_{AB} = 6 Hz, 3 H, 1-H, 3-H), 1.69 (dd, *J* = 1.5, 6.5 Hz, 3 H, 3′-H), 0.12 (s, 9 H, $SiMe_3$). − ^{13}C NMR (75.5 MHz): δ = 171.2 (s, *C*O_2Me), 128.5, 126.1 (2 d, C-1′, C-2′), 63.0 (s, C-2), 51.6 (q, CO_2*Me*), 29.9 (d, C-1), 21.5 (t, C-3), 17.6 (q, C-3′), 0.9 (q, $SiMe_3$). − *cis*-**13**: ^1H NMR (300 MHz): δ = 5.65 (qd, *J* = 6.5, 15 Hz, 1 H, 2′-H), 5.24 (qd, *J* = 1.5, 15 Hz, 1 H, 1′-H), 3.64 (s, 3 H, CO_2Me), 1.93 (dd, *J* = 8, 10 Hz, 1 H, 1-H), 1.66 (dd, *J* = 1.5, 6.5 Hz, 3 H, 3′-H), 1.33−1.29 (m, 2 H, 3-H), 0.12 (s, 9 H, $SiMe_3$). − ^{13}C NMR (75.5 MHz): δ = 169.5 (s, *C*O_2Me), 133.4, 124.4 (2 d, C-1′, C-2′), 62.5 (s, C-2), 51.5 (q, CO_2*Me*), 28.3 (d, C-1), 20.5 (t, C-3), 17.6 (q, C-3′), 0.9 (q, $SiMe_3$). − $C_{11}H_{20}O_3Si$ (228.4): calcd. C 57.86, H 8.83; found C 57.83, H 8.57.

***trans*/*cis*-Methyl 2-(*tert*-Butyldimethylsiloxy)-2-[(*E*)-3-(*tert*-butyldimethylsiloxy)-1-propenyl]-1-cyclopropanecarboxylate (14):** To a mixture of siloxydiene **12** (2.00 g, 6.09 mmol) and $Rh_2(OAc)_4$ (30 mg, 0.068 mmol) in CH_2Cl_2 (5 mL) was added over a period of 4 h a solution of methyl diazoacetate (1.30 g, 13.0 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was concentrated and filtered through alumina (pentane). The filtrate was concentrated and distilled (kugelrohr, 100−130°C/0.02 Torr) to give siloxycyclopropane **14** (*trans*/*cis* = 66:34) as a colourless oil (1.79 g, 73%). − IR (neat): $\tilde{\nu}$ = 2950, 2930, 2890, 2860 cm^{-1} (C−H), 1730 (CO_2Me), 1250 (Si−C). − *trans*-**14**: ^1H NMR (300 MHz): δ = 5.88 (td, *J* = 4.5, 15.5 Hz, 1 H, 2′-H), 5.74 (td, *J* = 1.5, 15.5 Hz, 1 H, 1′-H), 4.17 (dd, *J* = 1.5, 5.0 Hz, 2 H, 3′-H), 3.63 (s, 3 H, CO_2Me), ABX system (δ_A = 1.50, δ_B = 1.46, δ_X = 2.09, J_{AX} = 7.5 Hz, J_{BX} = 9.5 Hz, J_{AB} = 6 Hz, 3 H, 1-H, 3-H), 0.87, 0.86 (2 s, 2× 9 H, 2 *t*Bu), 0.11, 0.09 (2 s, 2× 6 H, 2 $SiMe_2$). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 171.2 (s, *C*O_2Me), 130.1, 128.2 (2 d, C-1′, C-2′), 63.3 (t, C-3′), 62.9 (s, C-2), 51.8 (q, CO_2*Me*), 30.5 (d, C-1), 26.0, 25.9 (2 q, 2 $SiCMe_3$), 22.2 (t, C-3), 18.0 (s, 2 $SiCMe_3$), −3.5, −5.8 (2 q, 2 $SiMe_2$). − *cis*-**14**: ^1H NMR (300 MHz): δ = 5.71 (td, *J* = 4.5, 15.5 Hz, 1 H, 2′-H), 5.58 (td, *J* = 1.5, 15.5 Hz, 1 H, 1′-H), 4.15 (partially obscured m, 2 H, 3′-H), 3.64 (s, 3 H, CO_2Me), 1.84−1.72 (m, 2 H, 1-H, *trans*-3-H), 1.26−1.22 (m, 1 H, *cis*-3-H), 0.88, 0.86 (2 s, 2× 9 H, 2 *t*Bu), 0.12, 0.08 (2 s, 2× 6 H, $SiMe_2$). − ^{13}C NMR (75.5 MHz): δ = 169.5 (s, *C*O_2Me), 132.2, 128.4 (2 d, C-1′, C-2′), 62.8 (t, C-3′), 61.9 (s, C-2), 51.8 (q, CO_2*Me*), 29.1 (d, C-1), 25.8, 25.7 (2 q, 2 $SiCMe_3$), 20.2 (t, C-3), 18.4 (s, 2 $SiCMe_3$), −3.4, −3.7 (2 q, 2 $SiMe_2$). − $C_{20}H_{40}O_4Si_2$ (400.7): calcd. C 59.94, H 10.06; found C 59.73, H 10.23.

General Procedure for the Preparation of the Tetrasubstituted Cyclopropanes 15 and 16: To a solution of LDA (1.5 equiv., generated from diisopropylamine and *n*BuLi at −78°C, 20 min reaction time) in THF (5−10 mL/mmol LDA) was added the methyl cyclopropanecarboxylate **13** or **14** (1 equiv.). After stirring for 2 h at −78°C, 1-bromo-2,4-hexadiene (1.5−2.5 equiv.) was added, and stirring was continued at −78°C for 16−26 h, followed by quenching with satd. NH_4Cl solution and extraction with EtOAc or ether. The combined organic extracts were washed with water, dried ($MgSO_4$), and concentrated. Excess 1-bromo-2,4-hexadiene was removed by bulb-to-bulb distillation (50−60°C/0.5−0.02 Torr), and the residue was purified as described. The products contain 15−20% of the respective (2*E*,4*Z*)- and (2*Z*,4*E*)-hexadienyl isomers, which could not be separated from the desired (2*E*,4*E*)-isomers.

Methyl 1-[(*E*,*E*)-2,4-Hexadienyl]-*c*-2-[(*E*)-1-propenyl]-*t*-2-(trimethylsiloxy)-*r*-1-cyclopropanecarboxylate (15) was prepared from cyclopropane **13** (2.00 g, 8.76 mmol), LDA (13.1 mmol) and 1-bromo-2,4-hexadiene (2.82 g, 17.5 mmol); 18 h reaction time. The crude product was filtered through alumina (hexane), followed by distillation (kugelrohr, 100−130°C/0.02 Torr) to give **15** (1.80 g, 67%) as a pale yellow oil. − IR (neat): $\tilde{\nu}$ = 3010 cm^{-1} (=C−H), 2940 (C−H), 1720 (CO_2Me), 1620 (C=C), 1250 (Si−C). − ^1H NMR (300 MHz): δ = 6.08−5.90 (m, 2 H, hexadienyl-3-H, -4-H), 5.68 (qd, *J* = 7, 16 Hz, 1 H, propenyl-2-H), 5.61−5.50 (m, 2 H, hexadienyl-2-H, -5-H), 5.41 (dd, *J* = 2, 16 Hz, 1 H, propenyl-1-H), 3.60 (s, 3 H, CO_2Me), 2.92, 2.13 (2 dd, *J* = 6.5, 15.5 Hz each, 2× 1 H, hexadienyl-1-H), 1.77−1.68 (m, 7 H, hexadienyl-6-H, propenyl-3-H, *cis*-3-H), 0.98 (d, *J* = 6.5 Hz, 1 H, *trans*-3-H), 0.14 (s, 9 H, $SiMe_3$). − ^{13}C NMR (75.5 MHz): δ = 172.3 (s, *C*O_2Me), 131.5, 131.4, 129.4, 128.4, 127.3, 126.3 (6 d, =CH), 64.9 (s, C-2), 51.7 (q, CO_2*Me*), 36.2 (s, C-1), 31.9 (t, hexadienyl-C-1), 24.0 (t, C-3), 18.2, 17.5 (2 q, hexadienyl-C-6, propenyl-C-3), 0.93 (q, $SiMe_3$). − $C_{17}H_{28}O_3Si$ (308.5): calcd. C 66.19, H 9.15; found C 66.05, H 9.05.

Methyl *t*-2-(*tert*-Butyldimethylsiloxy)-*c*-2-[(*E*)-3-(*tert*-butyldimethylsiloxy)-1-propenyl]-1-[(*E*,*E*)-2,4-hexadienyl]-*r*-1-cyclopropanecarboxylate (16) was prepared from cyclopropane **14** (6.80 g, 17.0 mmol), LDA (22.5 mmol) and 1-bromo-2,4-hexadiene (6.80 g, 42.2 mmol); 26 h reaction time. The crude product was purified by chromatography on alumina (hexane/EtOAc, 100:1) to provide **16** (6.38 g, 78%) as a pale yellow oil. − IR (neat): $\tilde{\nu}$ = 3020 cm^{-1} (=C−H), 2950, 2930, 2860 (C−H), 1720 (CO_2Me), 1650, 1595 (C=C), 1250 (Si−C). − ^1H NMR (300 MHz): δ = 6.07−5.95 (m, 2 H, hexadienyl-3-H, -4-H), 5.77 (td, *J* = 4.5, 15.5 Hz, 1 H, propenyl-2-H), 5.67 (br. d, *J* = 15.5 Hz, 1 H, propenyl-1-H), 5.56 (m_c, 2 H, hexadienyl-2-H, -5-H), 4.12 (dd, *J* = 1.5, 4.5 Hz, 2 H, propenyl-3-H), 3.59 (s, 3 H, CO_2Me), 2.92 (dd, *J* = 6.5, 15.5 Hz, 1 H, hexadienyl-1-H), 2.23 (dd, *J* = 7.0, 15.5 Hz, 1 H, hexadienyl-1-H), 1.82 (d, *J* = 6 Hz, 1 H, *cis*-3-H), 1.80 (d, *J* = 6 Hz, 3 H, hexadienyl-6-H), 1.01 (d, *J* = 6 Hz, 1 H, *trans*-3-H), 0.893, 0.887 (2 s, 2× 9 H, 2 *t*Bu), 0.11, 0.08 (2 s, 2× 6 H, $SiMe_2$). − ^{13}C NMR (75.5 MHz): δ = 172.2 (s, *C*O_2Me), 131.79, 131.76, 130.8, 128.7, 128.5, 127.6 (6 d, =CH), 64.7 (s, C-2), 63.3 (t, propenyl-C-3), 52.0 (q, CO_2*Me*), 37.5 (s, C-1), 32.0 (t, hexadienyl-C-1), 26.1 (q, 2 $SiCMe_3$), 24.1 (t, C-3), 18.5, 18.4 (2 s, 2 $SiCMe_3$), 18.2 (q, hexadienyl-C-6), −3.1, −3.3, −5.1 (3 q, 2 $SiMe_2$). − $C_{26}H_{48}O_4Si_2$ (480.8): calcd. C 64.95, H 10.06; found C 64.76, H 10.28.

Methyl (4*E*,6*E*)-2-[(*E*)-2-Oxo-3-pentenyl]-4,6-octadienoate (5): To a solution of siloxycyclopropane **15** (1.73 g, 5.61 mmol) in CH_2Cl_2 (80 mL) was added at −25°C $NEt_3 \cdot 3\,HF$ (4.24 g, 26.3 mmol).

Table 2. ^{1}H NMR (300 MHz) data [δ values, *J* (Hz)] of octalones **22**

H[a]	*cis*-**22a**	*cis*-**22b**	*trans*-**22a**	*trans*-**22b**
7-H	5.63 (ddd, *J* = 2.5, 5, 10)	5.60 (ddd, *J* = 2.5, 5, 10)	5.70 (ddd, *J* = 2.5, 5, 10)	5.68 (ddd, *J* = 2.5, 5, 18)
8-H	5.47 (d, *J* = 10)	5.51 (td, *J* = 1.5, 10)	5.40 (td, *J* = 1.5, 10)	5.38 (td, *J* = 1.5, 10)
CO_2Me	3.67 (s)	3.68 (s)	3.69 (s)	3.67 (s)
2-H	2.66 (ddt, *J* = 4, 5, 12.5)	3.08 (m_c)	2.82 (tt, *J* = 4.5, 12.5)	3.11 (m_c)
3-H_{ax}	2.54−2.31 (m)	2.63−2.55[b] (m)	2.66 (dt, *J* = 1, 12.5)	2.70[b] (td, *J* = 3, 13)
3-H_{eq}	2.54−2.31 (m)	2.40[b] (dd, *J* = 6.5, 14.5)	2.52 (ddd, *J* = 2, 5, 12.5)	2.65[b] (ddd, *J* = 1, 7, 13)
8a-H	2.54−2.31 (m)	2.63−2.55 (m)	2.30−1.90 (m)	2.39−1.95 (m)
4a-H	2.24 (dd, *J* = 5, 12)	2.25 (dd, *J* = 5, 10.5)	2.30−1.90 (m)	2.39−1.95 (m)
1-H_{eq}	2.06 (d, *J* = 13.5)	2.15−2.05 (m)	2.30−1.90 (m)	2.39−1.95 (m)
5-H	1.89−1.54 (m)	1.90−1.60 (m)	2.30−1.90 (m)	2.39−1.95 (m)
6-H	1.89−1.54 (m)	1.90−1.60 (m)	2.30−1.90 (m)	2.39−1.95 (m)
1-H_{ax}	1.89−1.54 (m)	1.90−1.60 (m)	1.66 (q, *J* = 12.5)	1.72 (ddd, *J* = 6, 13, 14)
6-Me	1.01 (d, *J* = 7)	1.02 (d, *J* = 7)	1.03 (d, *J* = 7)	1.05 (d, *J* = 7)
5-Me	0.83 (d, *J* = 7)	0.87 (d, *J* = 6.5)	0.85 (d, *J* = 7)	0.84 (d, *J* = 7)

[a] Integrals are in accordance with the expected values. − [b] Assignments are interchangeable within the column.

After stirring for 2 h at −25°C, water (80 mL) was added, followed by extraction of the aqueous layer with CH_2Cl_2 (3× 40 mL), washing of the combined organic phases with water (100 mL), drying with Na_2SO_4 and concentration. The crude material was filtered through silica gel (hexane/EtOAc, 2:1), and the resulting product **5** was obtained as a pale yellow oil [1.18 g, 89%, purity ca. 85% due to the presence of (2*E*,4*Z*)- and (2*Z*,4*E*)-hexadienyl isomers] and used without further purification. − The spectroscopic data of compound **5** are identical with those reported.[7]

Methyl (4*E*,6*E*)-2-[(*E*)-5-Hydroxy-2-oxo-3-pentenyl]-4,6-octadienoate (17): To a solution of siloxycyclopropane **16** (2.00 g, 4.16 mmol) in THF (15 mL) was added at 0°C dropwise over a period of 20 min a solution of TBAF · 3 H_2O (3.50 g, 11.1 mmol) in THF (40 mL). The reaction mixture was stirred for 5 min at 0°C, diluted with ether (100 mL) and water (100 mL). The organic layer was washed with water (3× 100 mL), dried ($MgSO_4$), and concentrated. Purification of the crude product on silica gel (hexane/EtOAc, 1:1) provided trienone **17** as a colourless oil [713 mg, 68%, purity ca. 80% due to the presence of (2*E*,4*Z*)- and (2*Z*,4*E*)-hexadienyl isomers]. − IR (neat): ṽ = 3450 cm^{-1} (O−H), 3020 (=C−H), 2970−2840 (C−H), 1730 (CO_2Me), 1690, 1670 (C=O), 1630, 1620 (C=C). − ^{1}H NMR (300 MHz): δ = 6.90 (td, *J* = 4, 16, 1 H, 4′-H), 6.35 (td, *J* = 2, 16 Hz, 1 H, 3′-H), 6.03−5.98 (m, 2 H, 5-H, 6-H), 5.61 (qd, *J* = 6.5, 13 Hz, 1 H, 7-H), 5.40 (br. td, *J* = 6.5, 13 Hz, 1 H, 4-H), 4.33 (br. s, 2 H, 5′-H), 3.66 (s, 3 H, CO_2Me), 3.05−2.95 (m, 3 H, 1′-H, OH, 2-H), 2.66 (m_c, 1 H, 1′-H), 2.40 (td, *J* = 6.5, 14 Hz, 1 H, 3-H), 2.28 (td, *J* = 7, 14 Hz, 1 H, 3-H), 1.73 (d, *J* = 6.5 Hz, 3 H, 8-H). − ^{13}C NMR (75.5 MHz): δ = 198.1 (s, C=O), 175.2 (s, *C*O_2Me), 145.6 (d, C-4′), 133.2, 130.9, 128.3, 127.6, 126.6 (5 d, C-3′, C-4, C-5, C-6, C-7), 61.5 (t, C-5′), 51.7 (q, CO_2*Me*), 41.0 (t, C-1′), 40.0 (d, C-2), 34.6 (t, C-3), 17.8 (q, C-8). − $C_{14}H_{20}O_4$ (252.3): calcd. C 66.65, H 7.99; found C 66.62, H 8.15.

Methyl (4*E*,6*E*)-[(*E*)-5-(*tert*-Butyldimethylsiloxy)-2-oxo-3-pentenyl]-4,6-octadienoate (6): Oxoester **6** was prepared according to the procedure for the synthesis of bissiloxydiene **12**, using trienone **17** (280 mg, 1.11 mmol), TBDMS−Cl (200 mg, 1.33 mmol) and imidazole (190 mg, 2.79 mmol). After workup and gradient elution chromatography on silica gel (hexane/EtOAc, 20:1−1:1), **6** was obtained as a pale yellow oil [210 mg, 52%, purity ca. 85% due to the presence of (2*E*,4*Z*)- and (2*Z*,4*E*)-hexadienyl isomers], followed by the imidazole-adduct **18** (1:1 mixture of diastereomers, 133 mg, 28%). − Analytical and spectroscopic data of **6**: IR (neat): ṽ = 3050 cm^{-1} (=C−H), 2950−2850 (C−H), 1730 (CO_2Me), 1690, 1670 (C=O), 1630 (C=C), 1250 (Si−C). − ^{1}H NMR (300 MHz): δ = 6.85 (td, *J* = 3.5, 15.5 Hz, 1 H, 4′-H), 6.33 (td, *J* = 2, 15.5 Hz, 1 H, 3′-H), 6.05−5.93 (m, 2 H, 5-H, 6-H), 5.65−5.52 (m, 1 H, 7-H), 5.44−5.35 (m, 1 H, 4-H), 4.33 (dd, *J* = 2, 3.5 Hz, 2 H, 5′-H), 3.65 (s, 3 H, CO_2Me), 3.40−2.93 (m, 2 H, 1′-H, 2-H), 2.64 (m_c, 1 H, 1′-H), 2.44−2.35, 2.31−2.22 (2 m, 2 H, 3-H), 1.71 (d, *J* = 6 Hz, 3 H, 8-H), 0.90 (s, 9 H, *t*Bu), 0.06 (s, 6 H, $SiMe_2$). − ^{13}C NMR (75.5 MHz): δ = 198.1 (s, C=O), 175.2 (s, *C*O_2Me), 145.8 (d, C-4′), 133.4, 131.3, 128.5, 127.7, 127.1 (5 d, C-3′, C-4, C-5, C-6, C-7), 62.4 (t, C-5′), 51.9 (q, CO_2*Me*), 41.3 (t, C-1′), 40.3 (d, C-2), 34.9 (t, C-3), 26.0 (q, Si*C*Me_3), 18.5 (s, Si*C*Me_3), 18.1 (q, C-8), −5.3 (q, $SiMe_2$). − $C_{20}H_{34}O_4Si$ (366.6): calcd. C 65.53, H 9.35; found C 65.58, H 9.42. − Analytical and spectroscopic data of *methyl (4E,6E)-[(E)-5-(tert-butyldimethylsiloxy)-4-(1-imidazolyl)-2-oxopentenyl]-4,6-octadienoate* (**18**): IR (neat): ṽ = 3100, 3020 cm^{-1} (=C−H), 2950−2860 (C−H), 1730 (CO_2Me), 1715 (C=O), 1250 (Si−C). − ^{1}H NMR (300 MHz): δ = 7.57 (br. s, 1 H, imidazole-2-H), 7.04, 7.00 (2 br. s, 2× 1 H, imidazole-4-H, -5-H), 6.07−5.95 (m, 2 H, 5-H, 6-H), 5.71−5.58 (m, 1 H, 7-H), 5.43−5.34 (m, 1 H, 4-H), 4.69 (m_c, 1 H, 4′-H), 3.83−3.81 (m, 2 H, 5′-H), 3.68, 3.65 (2 s, 2× 1.5 H, CO_2Me), 3.15−2.77, 2.55−2.18 (2 m, 4 H, 3 H, 3′-H, 1′-H, 2-H, 3-H), 2.64 (m_c, 1 H, 1′-H), 1.77 (d, *J* = 7 Hz, 3 H, 8-H), 0.91, 0.90 (2 s, 2× 4.5 H, *t*Bu), 0.08, 0.02, 0.00 (3 s, 1.5 H, 1.5 H, 3 H, $SiMe_2$). − ^{13}C NMR (75.5 MHz): δ = 205.1 (s, C=O), 174.6, 174.4 (2 s, *C*O_2Me), 136.6 (d, imidazole-C-2), 133.4, 130.8, 128.4, 128.9, 126.4, 126.3 (6 d, imidazole-C-4, C-4, C-5, C-6, C-7), 117.5 (d, imidazole-C-5), 65.2, 65.0 (2 t, C-5′), 51.7

Table 3. ^{13}C NMR (75.5 MHz) data (δ values) of octalones **22**

C	*cis*-**22a**	*cis*-**22b**	*trans*-**22a**	*trans*-**22b**
C-4 (s)	212.2	211.0	210.0	209.0
CO_2Me (s)	173.7	174.2	173.5	174.1
C-7 (d)	127.6	127.9	134.4	134.3
C-8 (d)	133.8	133.9	127.0	127.7
C-4a (d)	56.4	55.9	52.6	53.1
CO_2*Me* (q)	52.0	52.1	51.9	52.0
C-3 (t)	40.7	39.3	44.5	43.3
C-2 (d)	42.7	41.0	44.1	42.0
C-8a (d)	37.7	34.6	43.3	40.9
C-6 (d)	38.3	38.1	29.9	30.3
C-5 (d)	33.3	33.4	34.1	34.5
C-1 (t)	31.7	30.5	35.2	34.1
6-Me (q)	19.6	20.0	15.6	16.0[a]
5-Me (q)	16.3	16.9	15.6	15.8[a]

[a] Assignments are interchangeable within the column.

Table 4. ^{1}H NMR (300 MHz) data [δ, *J* (Hz)] of octalones **2**

H[a]	*cis*-**2a**	*cis*-**2b**	*trans*-**2a**	*trans*-**2b**
7-H	5.50 (br. d, *J* = 10)	5.56[b] (td, *J* = 2, 10)	5.71 (ddd, *J* = 2.5, 5, 10)	5.69 (ddd, *J* = 2.5, 5, 10)
8-H	5.67 (ddd, *J* = 2, 4.5, 10)	5.51[b] (ddd, *J* = 2, 3, 10)	5.40 (td, *J* = 1.5, 10)	5.39 (td, *J* = 1.5, 10)
CO_2Me	3.69 (s)	3.69 (s)	3.70 (s)	3.68 (s)
2-H	2.65 (tt, *J* = 3.5, 13)	2.97 (tt, *J* = 5, 7)	2.83 (tt, *J* = 4.5, 12.5)	3.18 (m_c)
3-H_{ax}	2.84 (dd, *J* = 13, 13.5)	2.73−2.68[c,d] (m)	2.64 (dt, *J* = 1, 12.5)	2.73−2.68[b,d] (m)
3-H_{eq}	3.04−2.97[b] (m)	2.67 (br. dd, *J* = 5, 15.5)	2.51 (ddd, *J* = 1.5, 5, 12.5)	2.58−2.49[b,d] (m)
8a-H	2.47−2.37[b] (m)	2.58−2.49[c,d] (m)	2.50−2.40[b] (m)	2.49−1.80[d] (m)
4a-H	2.47−2.37 (m)	2.18−2.13 (m)	2.36 (br. t, *J* = 10.5)	2.49−1.80[d] (m)
1-H_{eq}	2.06 (br. d, *J* = 13.5)	2.18−2.13 (m)	2.11 (ddd, *J* = 3, 5.5, 11)	2.49−1.80[d] (m)
5-H	1.96−1.82 (m)	1.85 (m_c)	2.18 (br. d, *J* = 10.5)	2.49−1.80[d] (m)
6-H	1.78−1.71 (m)	2.54 (br. quint, *J* = 7)	2.20−2.10[b,d] (m)	1.64 (m_c)
1-H_{ax}	1.96−1.82 (m)	1.96 (ddd, *J* = 4.5, 8.5, 13)	1.66 (q, *J* = 12.5)	1.72 (ddd, *J* = 6, 12, 13.5)
6-Me	1.06 (d, *J* = 7)	1.06 (d, *J* = 7)	0.94 (d, *J* = 7)	0.95 (d, *J* = 7)
5-CH_2	3.67 (dd, *J* = 2, 10)	3.59 (dd, *J* = 4.5, 10)	4.03 (dd, *J* = 3, 10)	4.09 (dd, *J* = 3.5, 10)
	3.46 (dd, *J* = 7, 10)	3.44 (dd, *J* = 8.5, 10)	3.66 (dd, *J* = 8.5, 10)	3.66 (dd, *J* = 9, 10)
CMe_3	0.87 (s)	0.87 (s)	0.86 (s)	0.85 (s)
$SiMe_2$	0.03, 0.00 (2 s)	0.03, 0.02 (2 s)	0.03, 0.00 (2 s)	0.03, 0.00 (2 s)

[a] Integrals are in accordance with the expected values. − [b,c] Assignments are interchangeable within the column. − [d] Signal is partially obscured by signals of other diastereomer(s).

Table 5. ^{13}C NMR (75.5 MHz) data (δ values) of octalones **2**[a]

C	*cis*-**2a**	*cis*-**2b**	*trans*-**2a**
C-4 (s)	211.9	210.1	210.0
CO_2Me (s)	174.1	174.4	173.7
C-7 (d)	127.9	127.6	127.0
C-8 (d)	133.5	134.7	134.6
5-CH_2 (t)	64.3	64.2	61.0
C-4a (d)	54.3	51.1[b]	48.8
CO_2*Me* (q)	52.1	52.0[b]	52.1
C-3 (t)	41.3	41.4	44.5
C-2 (d)	43.2[b]	40.1[c]	43.3
C-8a (d)	42.3[b]	41.3[c]	44.2[b]
C-6 (d)	32.3	33.6	31.5
C-5 (d)	38.4[b]	41.2[c]	37.6[b]
C-1 (t)	31.8	31.4	35.5
6-Me (q)	20.3	21.0	16.4
C*Me*$_3$ (q)	26.0	25.9	25.8
CMe_3 (s)	18.4	18.3	18.1
$SiMe_2$ (2 q)	−5.67	−5.6	−5.5
	−5.75	−5.8	−5.7

[a] Data for *trans*-**2b** were not obtained due to the low amount available. − [b,c] Assignments are interchangeable within the column.

(q, CO_2*Me*), 44.2, 44.1, 43.5, 43.3 (4 t, C-1′, C-3′), 39.9, 39.7 (2 d, C-2), 34.4 (t, C-3), 25.6, 25.5 (2 q, SiC*Me*$_3$), 18.0 (s, Si*C*Me_3), 17.8 (q, C-8), −5.9, −6.0 (2 q, $SiMe_2$). − $C_{23}H_{38}N_2O_4Si$ (434.7): calcd. C 63.56, H 8.81, N 6.45; found C 62.27, H 8.82, N 6.08.

Methyl 1,2,3,4,4a,5,6,8a-Octahydro-5,6-dimethyl-4-oxo-2-naphthalenecarboxylate (22): A solution of trienone **5** (270 mg, 1.14 mmol) in toluene (80 mL) was refluxed for 2 days and then concentrated in vacuo. The diastereomeric ratio of the crude material was determined as *cis*-**22a**/*cis*-**22b**/*trans*-**22a**/*trans*-**22b** = 23:30:36:11. Flash chromatography (hexane/EtOAc, 8:1) provided the following fractions as colourless oils: *trans*-**22a** (70 mg), *cis*-**22a** (23 mg), *cis*-**22b** and *trans*-**22b** (1:1, 34 mg), and *cis*-**22b** (35 mg). The total yield of octalone **22** was 162 mg (81%). − IR (neat): ṽ = 3050, 2955−2850 cm^{-1} (C−H), 1730 (CO_2Me), 1700 (C=O), 1650 (C=C). − $C_{14}H_{20}O_3$ (236.3): calcd. C 71.16, H 8.53; found C 70.84, H 8.63. − For ^{1}H-NMR data see Table 2. − For ^{13}C-NMR data see Table 3.

Methyl 5-(*tert*-Butyldimethylsiloxymethyl)-1,2,3,4,4a,5,6,8a-octahydro-6-methyl-4-oxo-2-naphthalenecarboxylate (2): A solution of trienone **6** (160 mg, 0.436 mmol) in toluene (50 mL) was refluxed for 24 h and then concentrated in vacuo. The diastereomeric ratio of the crude material was determined as *cis*-**2a**/*cis*-**2b**/*trans*-**2a**/*trans*-**2b** = 30:35:21:14. Purification on silica gel (hexane/EtOAc, 20:1) provided the following fractions as colourless oils: *trans*-**2a** (28 mg), *cis*-**2a** [70 mg, contained ca. 37% (2*E*,4*Z*)- and (2*Z*,4*E*)-hexadienyl isomers], *cis*-**2a** and *cis*-**2b** and *trans*-**2b** [20:64:16, 44 mg, impurified with ca. 9% (2*E*,4*Z*)- and (2*Z*,4*E*)-hexadienyl isomers]. The total yield of octalone **2** was 142 mg [79%, impurified with ca. 20% (2*E*,4*Z*)- and (2*Z*,4*E*)-hexadienyl isomers]. − IR (neat): ṽ = 3020 cm^{-1} (=C−H), 2980−2820 (C−H), 1730 (CO_2Me), 1710 (C=O), 1545 (C=C), 1250 (Si−C). − $C_{20}H_{34}O_4Si$ (366.6): calcd. C 65.53, H 9.35; found C 65.33, H 9.43. − For ^{1}H-NMR data see Table 4. − For ^{13}C-NMR data see Table 5.

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