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Synthesis and reactions of two stereoisomeric [4.5.5.5]fenestranes with bridgehead substituents

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ABSTRACT

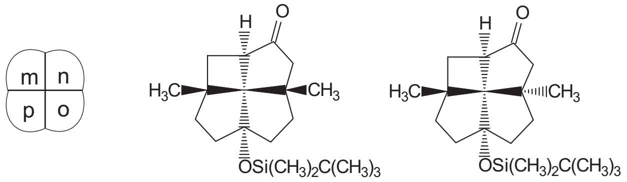
The [4.5.5.5]fenestranes **2** and **3** with two different functionalities were prepared in seven steps with overall yields of 5% and 10%, respectively. For introduction of a bridgehead double bond the removal of the tertiary hydroxy group was investigated in the two stereoisomeric hydroxyketones **12** and **15**. Whereas the dehydration readily occurred in **12**, a ring opening reaction was observed for **15**.

1. Introduction

As discussed in the preceeding paper, fenestranes with tetracylic scaffolds containing a central carbon being part of four rings as in **1** are of theoretical as well as of synthetic interest.[1] The preparation of natural products and the creative development of methods by which such structures are formed in a few steps find continuous attention.[2–5] In addition, fenestranes of interest for the study of planarizing distortions in $C(C)_4$ substructures, forming the central part in fenestranes.[6] Semiempirical, DFT calculations and X-ray analyses of some fenestranes prepared clearly show, that two opposite bond angles across the quaternary carbon are larger than 109.4°.[1] As mentioned earlier, ring contraction, inversion at the bridgehead C atoms, bridgehead double bonds and alkyl substituents at the peripheral bridgehead C centres have been identified as those parameters, which enhance the opening of two opposite bond angles in the central $C(C)_4$ moiety.[7]

2. Results and discussion

In order to implement the above mentioned three features we prepared the stereoisomeric [4.5.5.5]fenestranes **2** and **3** bearing methyl groups in bridgehead positions and a protected hydroxy group and explored some methods for the introduction of a bridgehead double bond (Scheme 1).



1 **2** **3**

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Scheme 1. General formulae of fenestranes and the two stereoisomers prepared.

Ethyl 4-methylpent-4-enoate **4**, prepared from 2-methylallylic alcohol and *ortho*-ethyl acetate was submitted to a Claisen condensation. Saponification and decarboxylation gave the dienone **5**, which was treated with ethyne to give **6** (Scheme 2).

After masking the tertiary hydroxy group with TBDMSiCl, **7** was submitted to the Pauson–Khand cyclocarbonylation.[8] This cyclocarbonylation reaction gave the expected stereoisomeric bicyclo [3.3.0]enones **8** and **9** in yields of 89% and 79%, respectively. In addition the saturated byproducts **10** and **11** were isolated in a total yield of 20% with the *trans*-isomer **11** being obtained pure (Scheme 2).

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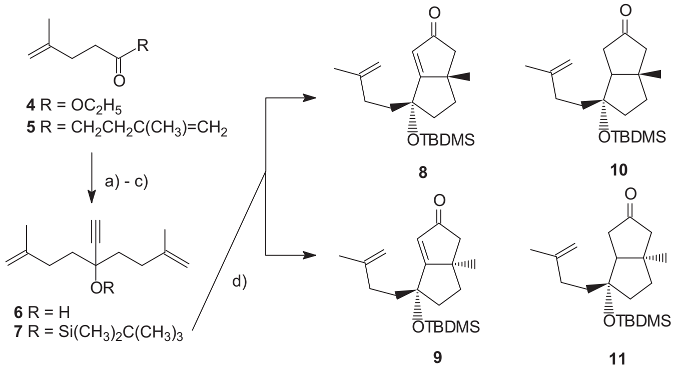
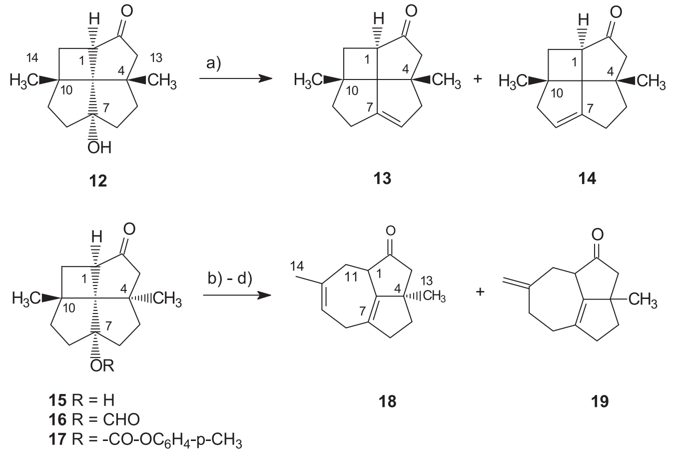


Scheme 2. (a) C_2H_5ONa; (b) $HC{\equiv}CMgCl$; (c)TBDMSi–OSO_2CF_3; (d) $Co_2(CO)_8$, NMO.

The photoinduced ene–enone cycloaddition of the pure isomers **8** and **9** gave the bifunctionlized fenestranes **2** and **3**, respectively.[9] An X-ray analysis of **3** provided detailed information about its structure.[10] The bond angles C1–C12–C7 and C4–12–C10 are 128.9° and 122.8°, respectively. The bond length C10–C14 of 1.616 Å is significantly longer than that of C4–C12 (1.524 Å). In addition, the bond angle C12–C10–C14 is 134°, whereas C12–C4–C13 is only 112°. Earlier MM^+ (and AM1) calculations for **15** gave bond angles for C1–C12–C7 of 126° (133°) and C4–C12–C10 of 126° (125°); recent DFT-results showed values for these bond angles just 1° larger (129.8° and 123.8°)[11] than those observed in the X-ray structure analysis.

With the aim to further enhance the planarizing distortions in the fenestranes **2** and **3** the introduction of a bridgehead double bond was investigated. Desilylation was achieved by the conventional method and gave the hydroxyketones **12** and **15**, respectively (Scheme 3). The hydroxy group at the tertiary position C7 is well suited for introduction of a bridgehead double bond. Treatment of **12** with MsCl and base at rt readily led to dehydration and gave a mixture of the fenestrenones **13** and **14**. The regioisomers were separated and the position of the bridgehead double bond extracted from 2D-NMR and NOE spectra (cf. Supplement, Tables 3 and 4).

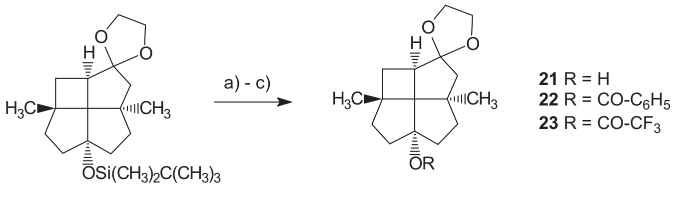


Scheme 3. Reactions of the fenestranes **12** and **15**. (a) DMAP, Et_3N, MsCl; (b) DMAP, Et_3N, MsCl; (c) $(CH_3)_2NCH(OCH_3)_2$, $C_6H_5CH_3$; (d) DMAP, pyridine, $CH_3C_6H_5OC(S)Cl$.

Dehydration of **15** under the same conditions led to a ring opening reaction rather than to the desired *cis*,*trans*,*cis*,*cis*-[4.5.5.5] fenestrenone.[9] The tricyclic compounds **18** and **19**, obtained in a ratio 1:1.5, were separated and their structures assigned by 2D-NMR and NOE spectra (cf. Supplement, Tables 5 and 6). This reaction is interpreted in terms of a tertiary carbenium ion formed at C(7), which leads via ring opening to another tertiary carbenium ion and deprotonoation to **18** and **19**. Derivatives of triquinane possibly formed from the tertiary carbenium ion at C(12) via 1,2 rearrangement from C(7) are not observed.[1] It is apparent that the attempted dehydration in the *cis*,*trans*,*cis*,*cis*-[4.5.5.5]fenestranol **15** leads to a release rather than built up of strain. According to our semiempirical calculations **15** is more strained than **12** by almost 20 kcal/mol.

In further pursuit to introduce a bridgehead double bond, **15** was heated with DMF-dimethylacetal[12] and gave the isomeric tricyclic compounds **18** and **19** in modest yield as well as a small amount of the formate **16**. When **15** was treated with *p*-*O*-tolylthionocarbonyl chloride[13,14] the carbonate **17** rather than the expected thionocarbonate was obtained. Pyrolysis of this compound at 220 °C in vacuo gave again a mixture of the tricyclic compounds **18** and **19**, however in a ratio of 5:1.

In view of the result that the attempts to form a bridgehead double in **15** by conventional methods leads to ring opening reactions, we considered fragmentation reactions via photoinduced H-abstraction in the α-position to the tertiary hydroxy group. In order to prevent photocleavage of the carbonyl group the ketal **20** was prepared. After desilylation the hydroxy group in **21** was transformed into the benzoate **22** and trifluoroacetate **23** (Scheme 4). Photolysis of **22** or **23** in hexane or acetonitrile with a low pressure lamp was very slow and led only to complex mixtures of products.



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Scheme 4. Formation of **21**–**23** from the ketal **20**. (a) TBAF• $(H_2O)_3$; (b) DMAP, C_6H_5N, C_6H_5COCl; (c) DMAP, C_6H_5N, $(CF_3CO)_2O$.

However it should be noticed that the MS spectra of **21** and **22** show a strong peak for m/z=246, which is compatible with the desired elimination product.

3. Concluding remarks

As described in the preceeding paper X the two regioisomeric bridgehead olefins **13** and **14** are readily formed from the 7-hydroxy-*cis*,*cis*,*cis*,*cis*[4.5.5.5]fenestrane-2-one **12**. In the case of the stereoisomeric 7-hydroxy-*cis*,*trans*,*cis*,*cis*[4.5.5.5]fenestrane-2-one **15** elimination reactions led to the tricyclic compounds **18** and **19** via a ring opening reaction. The rearrangement to the triquinane structure was not observed.[1]

Despite of extensive experimental efforts no fenestrane has hitherto been observed with opposite bond angles both larger than 130°.

4. Experimental

4.1. General

All reactions are performed under an Ar or N_2 atmosphere. Chemicals, most of them of purum quality, were purchased from commercial suppliers and used without further purification. After work up, the organic phases were dried over $MgSO_4$ and the residue purified by flash chromatography (FC) or column chromatography (CC) with the eluent given. Thin layer chromatography was performed on silica gel plates SIL G/UV_{254} (Macherey and Nagel) with hexane–EtOAc (ratio given) as eluent if not stated otherwise. GC analyses were performed on a Hewlett Packard HP-5890 instrument with an HP-5 Ultra capillary column (length 10 m, i.d.

0.2 mm, 0.11 μm thickness of the film) and He with a flow of 0.75 mL/min with a temperature program 40–220 °C (3°/min), t_R in min. Preparative HPLC was performed with an ET, 250/1/2″, Nucleosil. 50-7 715004 silica gel column (Macherey and Nagel, 7 μm, i.d. 10 mm) flow: 12 mL/min and a pressure of 20–40 bar; the eluent is given. IR (recorded on a Perkin–Elmer-782 IR-spectrophotometer in $CHCl_3$) in cm^{-1}, if not stated otherwise; relative intensities of selected bands are indicated as vs (very strong), s (strong), m (medium) sh (shoulder) and NMR spectra (recorded on Bruker AM 300 [^{1}H, 300 MHz (a), 500 MHz (b), DRX500; ^{13}C, 75 MHz (a), AM 300, 125 MHz (b), DRX500]) were measured in $CDCl_3$. Chemical shifts, measured with $CDCl_3$ as internal lock, are given relative to $Si(CH_3)_4$ in δ (ppm) for ^{1}H NMR and ^{13}C NMR. Coupling constants are given in Hertz and multiplicities are indicated as s (singlet), d (doublet) t (triplet), q (quartet), m (multiplet), br s (broad singlet) and st (stack). The multiplicities for the ^{13}C–^{1}H couplings were extracted from DEPT measurements, those for the ^{13}C–^{19}F interactions were apparent in the ^{13}C spectra. Mass spectra (MS), determined on a Varian MAT CH7A (70 eV, EI) and a Fisons Autospec Q spectrometer, are reported for selected peaks (intensities >10%) in units of m/z and in relative intensities to the base peak. GC–MS were performed on a VG Autospec spectrometer. UV/vis spectra are measured on a Hewlett–Packard 8451A Diode array spectrophotometer. The position of the absorption bands are given in [nm], the extinction coefficients in [M^{-1} cm^{-1}]; shoulders are indicated as sh.

4.1.1. Ethyl 4-methylpent-4-enoate ***4***. A solution of β-methylallyl alcohol (36.06 g, 0.5 mol) and *ortho*-ethyl acetate (167.5 g, 1 mol) was treated with propionic acid (0.5 mL) and heated to 120 °C. The ethanol formed was distilled off via a Vigreux column (30 cm). After 45 min the temperature of the oil bath was slowly raised to 180 °C and maintained there until the head temperature reached 120 °C. The reaction mixture was treated at 0 °C with 1 M HCl (140 mL), stirred for 30 min at rt, worked up and distilled in vacuo to give **18** (47.71 g, 67%).

Bp (62–64 °C/15 mbar, 62–64 °C/12 Torr);[15] R_f=0.32 (25:1); GC: t_R=4.7 (purity ~98.5%). IR: 1730vs, 1450m, 1375m, 1300m, 1285m, 1180s, 895m. ^{1}H NMR (a): 4.74 (s, 1H), 4.69 (s, 1H), 4.13 (q, J=7.1, 2H), 2.41–2.49 (m, 2H), 2.30–2.37 (m, 2H), 1.74 (s, 3H), 1.25 (t, J=7.1, 3H). ^{13}C NMR (a): 173.3 (s), 144.1 (s), 110.3 (t), 60.3 (t), 32.7 (t), 32.6 (t), 22.4 (q), 14.2 (q). MS: 142 (M^+, 32), 97 (24), 96 (34), 69 (100), 68 (21).

4.1.2. 2,8-Dimethylnona-1,8-dien-5-one ***5***. Freshly distilled **4** (28.44 g, 0.2 mol) was shaken with NaOEt (freshly prepared from Na and an equimolar amount of abs EtOH by reflux in abs Et_2O for 16 h under Ar, removal of the solvent and drying at HV) under Ar until a half solid yellow gel had formed. In partial vacuo (600 mm) the mixture was heated to 120 °C to give a liquid suspension. The EtOH formed was removed in vacuo (150 mm) via a Vigreux column (15 cm) for 6 h. At rt the reddish transparent mass was emulgated in NaOH (300 mL 0.5 M) and refluxed overnight. After slow addition of 4 M HCl (24 mL) at rt and stirring for 15 min (strong evolution of CO_2) the yellowish clear mixture was 3× extracted with Et_2O (100 mL each). Further work up and distillation over a Vigreux column (5 cm) at 15 mbar gave **5** (11.40 g, 69%) with a strongly aromatic odour.

Bp: 102–104 °C (15 mbar); R_f=0.50 (10:1); GC: R_t=13.9 (purity >99.8%). ^{1}H NMR (a): 4.73 (s, 2H), 4.65 (s, 2H), 2.57 (~t, J=7.4, 4H), 2.28 (~br t, J=7.4, 4H), 1.72 (s, 6H). ^{13}C NMR (a): 209.8 (s), 144.5 (s), 110.2 (t), 41.0 (t), 31.5 (t), 22.6 (q). IR: 2930m, 1715vs, 1650s, 1447s. MS: 166 (M^+, 4), 97 (25), 69 (91), 55 (34), 41 (100).

4.1.3. 2,8-Dimethyl-5-ethinylnona-1,8-dien-5-ol ***6***. A solution of n-C_4H_9MgCl (ca. 2.8 M) in THF was prepared from Mg (5.83 g, 0.24 mol) and n-C_4H_9Cl (24.0 g, 0.24 mol) under Ar. A solution of ethyne in THF was prepared by introducing ethyne (purified via bubbling through concd H_2SO_4 and passing over P_2O_5 on glass wool and KOH pellets) via a frit into THF (120 mL abs). The saturated solution was cooled to −5 °C and dropped via syringe into the Grignard solution (45 min) at a temperature <0 °C. A stream of ethyne was maintained during this procedure. The greyish suspension was further stirred for 30 min under ethyne; subsequently a solution of **5** (16.63 g, 100 mL) in THF (20 mL) was added during 15 min. After stirring for 2 h at rt the greyish–black mixture was poured onto 300 mL icecold, satd NH_4Cl solution, the organic phase separated and the aqueous phase 3× extracted with pentane. The organic phase was washed with 100 mL solutions of satd NaH_2PO_4 and $NaHCO_3$. After drying over Na_2SO_4 sicc and evaporation of the solvents, the crude product was purified by CC on silica gel (100 g,) with pentane–ether (10:1) as eluent to give **6** (18.03 g, 94%) as an almost colourless, viscous oil. R_f=0.23 (10:1); GC: t_R=18.8 (purity ~98.5%). ^{1}H NMR (a): 4.75 (br s, 4H), 2.51 (s, 1H), 2.16–2.39 (m, 5H), with s (OH), 1.74–1.90 (m, 10H), 1.77 (s, 6H). ^{13}C NMR (a): 145.8 (s), 110.2 (t), 86.1 (s), 73.1 (d), 71.2 (s), 39.9 (t), 32.4 (t), 22.6 (q). IR: 3290vs, 2930s, 1640s, 1440s, 882vs, 626s. MS; 192 (M^+, 0.1), 191 (0.3), 177 (12), 159 (68), 146 (24), 145 (47), 132 (23), 131 (64), 123 (61), 122 (14), 121 (43), 119 (81), 118 (60), 117 (78), 109 (37), 107 (72), 106 (54), 105 (83), 103 (39), 97 (21), 95 (78), 94 (28), 93 (67), 92 (43), 91 (83), 81 (68), 80 (25), 79 (74), 78 (25), 77 (60), 70 (54), 69 (72), 68 (32), 67 (83), 65 (24), 57, 55 (100), 53 (89).

4.1.4. 2,8-Dimethyl-5-ethinyl-5-tert-butyldimethylsilyloxy-nona-1,8-diene ***7***. To a solution of **6** (9.62 g, 50 mmol) in THF (100 mL abs) at −10 °C was dropped *tert*-butyldimethylsilyltriflate (14.93 mL, 65 mmol) during 10 min. After warming to rt the solution was stirred for 2 h, poured onto ice-H_2O (300 g) and treated with pentane (100 mL). The aqueous phase was extracted 2× with pentane (100 mL each). The organic phase was washed with satd NaCl (50 mL), dried over $MgSO_4$ and filtered over 2 cm Celite®. The crude yellowish oil (18.93 g) was purified by filtration through silica gel (100 g) with hexane as eluent to give after drying in vacuo 7 (15.79 g, 103%) as colourless oil.

R_f=0.60 (25:1); GC: t_R=29.9 (purity ~96.5%). ^{1}H NMR (a): 4.89–4.73 (m, 4H), 2.48 (s, 1H), 2.15–2.23 (m, 4H), 1.74–1.83 (m, 10H), 1.76 (s, 6H), 0.90 (s, 9H), 0.20 (s, 6H); impurity: [(t-Bu)$(Me)_2$Si$]_2$O, ca. 4%. ^{13}C NMR (a): 145.9 (s), 109.6 (t), 87.0 (s), 73.5 (s), 71.7 (d), 41.0 (t), 32.5 (t), 25.8 (q), 22.7 (q), 18.2 (s), −2.9 (q); impurty: [(t-Bu)$(Me)_2$Si$]_2$O. IR ($CHCl_3$): 2940s, 2930s, 2860s, 1255s, 1130sh, 1095s, 1050s, 890s, 840vs. MS: 306 (M^+, 0.5), 305 (0.8), 249 (62), 237 (37), 231 (23), 193 (35), 181 (60), 180 (17), 179 (33), 175 (39), 173 (57), 147 (23), 131 (39), 119 (32), 105 (65), 93 (28), 91 (27), 83 (46), 81 (29), 77 (32), 76 (38), 75 (57), 73 (100), 69 (24), 59 (32).

4.1.5. cis- and trans-8-(3-Methylbut-3-enyl-)-8-tert-butyldimethylsilyloxy-bicyclo[3.3.0]-oct-1-en-3-one ***8*** *and* ***9***. To a solution of **7** (7.67 g, 25 mmol) in THF and CH_2Cl_2 (1:1, 200 mL abs), degassed with Ar, was added $Co_2(CO)_8$ (9.83 g, 28.75 mmol, 1.15 mol equiv) in one portion and stirred at rt for 2 h. The solution of NMO (13.18 g, 112.5 mmol, 4.5 mol equiv) in THF and CH_2Cl_2 (1:1, 240 mL abs) was added to this complex within 4 h and stirring continued for 60 h at rt. The reaction mixture was filtered over 5 cm sea sand and 5 cm silica gel and rinsed with ether. After evaporation of the solvents the viscous oil was dissolved in EtOAc (50 mL) and treated with silica gel (20 g). The powder, obtained after removal of the solvent was poured onto silica gel (250 g) and CC with hexane–EtOAc (10:1) gave a product, which was 2× rechromatographed to give **8**/**9** (3.91 g, 47%) as a mixture (ratio 1:2.15) and **10**/**11** (3.93:1; 1.75 g, 21%) as a solid mixture. The isomeric mixture **8**/**9** was dissolved in MeOH (16 mL) and left overnight at −70 °C and gave the crystalline *trans*-isomer **9**. Recrystallisation from MeOH (12 mL) at −70 °C gave **9** (2.64 g, 32%) as white crystals. The *cis*-isomer **8** (1.12 g, 13%) was obtained from the combined mother liquors by evaporation of the solvent as brownish oil.

For analysis a sample of **8** was chromatographed on silica gel impregnated with 30% $AgNO_3$ (hexane–EtOAc=10:1) under exclusion of light in a water-cooled column. R_f=0.25 (10:1). GC: t_R=43.7 (purity ~95.0%). UV/vis (hexane): λ_{max} (ε) 236 (2’600), 220 nm (sh, 2’100). ^1H NMR (a): 5.95 (s, 1H), 4.69 (s, 1H), 4.65 (s, 1H), 2.40 (~s, 2H), 1.65–2.35 (st, 13H) with 1.71 (s, 3H), 1.21 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (a): 209.4 (s), 197.4 (s), 145.5 (s), 125.3 (d), 109.8 (t), 80.1 (s), 53.8 (t), 48.7 (s), 41.5 (t), 39.7 (t), 35.7 (t), 32.5 (t), 26.1 (q), 25.7 (q), 22.6 (q), 18.2 (s), −2.5 (q), −2.6 (q). IR: 2960s, 2940s, 1705vs, 1260s, 1110s, 1055s, 838s. MS: 334 (M^+, 0.1), 319 (0.8), 277 (49), 145 (88), 75 (100), 73 (43).

For analysis a sample of **9** was purified as described for **8**. Mp: 58–59 °C; R_f=0.27 (10:1) GC: t_R=44.0 (purity ~98.5%). UV/vis (hexane): λ_{max} (ε) 234 (2’600), 219 nm (sh, 2’100). ^1H NMR (a): 5.90 (s, 1H), 4.72 (s, 1H), 4.68 (s, 1H), 2.42 (A, J_{AB}=17.6, 1H), 2.33 (B, J_{AB}=17.6, 1H), 2.21–2.29 (m, 2H), 2.06–2.19 (m, 1H), 1.87–2.04 (m, 3H), 1.67–1.80 (m, 4H), 1.73 (s, 3H), 1.18–1.39 (m, 4H), 1.36 (s, 3H), 0.88 (s, 9H), 0.16 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (a): 210.4 (s), 193.5 (s), 145.2 (s), 123.9 (d), 109.9 (t), 78.0 (s), 52.7 (t), 50.6 (s), 40.8 (t), 39.2 (t), 35.4 (t), 32.5 (t), 26.5 (q), 25.8 (q), 22.7 (q), 18.2 (s), −2.2 (q), −2.4 (q). IR: 1705vs, 1055s, 839s. MS: 334 (M^+, 1), 306 (36), 305 (42), 279 (54), 278 (90), 277 (63), 266 (35), 265 (67), 259 (26), 251 (25), 249 (29), 235 (38), 231 (13), 223 (34), 222 (43), 221 (54), 217 (23), 209 (39), 207 (36), 203 (40), 195 (20), 186 (26), 185 (76), 184 (25), 183 (70), 179 (21), 171 (30), 170 (27), 169 (21), 165 (36), 161 (33), 160 (24), 159 (53), 157 (44), 151 (22), 149 (21), 147 (34), 146 (40), 145 (100), 144 (28), 143 (66), 133 (47), 131 (46), 130 (26), 129 (50), 128 (20), 119 (60), 118 (15), 117 (40), 115 (37), 107 (68), 106 (17), 105 (69), 103 (25), 95 (26), 93 (55), 91 (63), 81 (32), 80 (12), 79 (46), 78 (20), 77 (64), 76 (52), 75 (86), 74 (44), 73 (68), 69 (29), 67 (27), 65 (24), 61 (30), 59 (52), 58 (31), 57 (54), 56 (22), 55 (63), 53 (33).

Attempts to obtain the *cis*-isomer **10** from the mother liquor by crystallisation off the *trans*-isomer did not lead to **10** sufficiently pure for obtaining analytical data. R_f=0.35 (10:1). GC: t_R=42.8 (purity <50.0%).

A pure sample of **11** was obtained from the isomeric mixture by crystallisation in MeOH at −70 °C and recrystallisation from EtOAc at −20 °C. Mp: 63–64 °C; R_f=0.35 (10:1) GC: t_R=43.0 (purity >99.8%). ^1H NMR (a): 4.69 (s, 1H), 4.65 (s, 1H), 2.45–2.57 (m, 1H), 2.09–2.33 (st, 5H), 1.82–2.03 (st, 3H), 1.48–1.78 (st, 7H), 1.71 (s, 3H), 1.35 (s, 3H), 0.91 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (a): 218.8 (s), 145.7 (s), 109.5 (t), 87.5 (s), 57.5 (d), 53.2 (t), 46.0 (s), 41.4 (t), 38.8 (t), 38.8 (t), 36.4 (t), 32.2 (t), 30.5 (q), 26.1 (q), 22.7 (q), 18.4 (s), −2.2 (q), −2.2 (q). IR: 2920s, 2890s, 2860s, 1740vs, 1053s, 836vs. MS: 336 (M^+, 4), 281 (23), 280 (74), 279 (100), 267 (22), 239 (38), 223 (52), 187 (60), 147 (43), 145 (44), 131 (37), 119 (32), 107 (39), 105 (36), 95 (20), 93 (24), 75 (48), 73 (40). HRMS: *m*/*z* $[M]^+$ calcd for $C_{20}H_{36}O_2Si$: 336.2484; found: 336.2481.

4.1.6. cis,cis,cis,cis-4,10-Dimethyl-7-tert-butyldimethyl-silyloxytetracyclo-[5.4.1.0^{4,12}.0^{10,12}]dodeca-2-one **2**[8]. In a flame-dried reaction flask (200 mL), a solution of **8** (0.93 g, 2.75 mmol) in hexane (200 mL) was degassed with Ar for 15 min. The colourless solution was irradiated with a 15 W low pressure Hg lamp through a filter of quartz glass and cooling with H_2O for 50 min. The yellow clear solution was evaporated to dryness and the turbid oil purified by CC on silica gel (100 g) with hexane–EtOAc (25:1) to give colourless crystalline **2** (0.83 g, 89%). For the analyses a sample was crystallized from hexane at −20 °C (colourless cubes). Mp: 80–81 °C; R_f=0.3 (15:1); GC: t_R=43.3 (purity >99.8%). ^1H NMR (b): 3.04 (dd, J=10.4, 5.1, 1H), 2.45 (A, J_{AB}=18.5, 1H), 2.40 (B, J_{AB}=18.5, 1H), 2.04–2.13 (m, 2H), 1.68–1.96 (st, 6H), 1.52–1.61 (m, 2H), 1.25 (s, 3H), 1.19 (s, 3H), 0.87 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (b): 222.3 (s), 92.7 (s), 72.7 (s), 53.7 (t), 46.3 (s), 45.5 (s), 44.1 (t), 43.3 (t), 42.0 (d), 41.4 (t), 37.9 (t), 36.0 (t), 25.8 (q), 25.6 (q), 23.2 (q), 18.2 (s), −2.8 (q), −2.9 (q); for 2D-NMR- and NOE-results see Supplement, Table 1. IR: 2962s, 1720s, 1256vs, 1090s, 1060s, 1040s, 1010s. MS: 334 (M^+, 0.5), 278 (56), 277 (100), 185 (53), 145 (44), 133 (24). Anal. Calcd for $C_{20}H_{34}O_2Si$ (334.57): C, 71.80; H, 10.24. Found 71.55; 10.22.

4.1.7. cis,trans,cis,cis-4,10-Dimethyl-7-tert-butyldimethylsilyl-oxy-tetra-cyclo[5.4.1.0^{4,12}.0^{10,12}]dodeca-2-one ***3***[8]. Photolysis of a solution of **9** (1.01 g, 3.0 mmol) in hexane (200 mL) for 70 min gave after CC crystalline **3** (0.797 g, 79%). For analysis a sample was crystallized from hexane at −20 °C to give colourless needles.

Mp: 73–75 °C; R_f=0.40 (15:1); GC: t_R=44.2 (purity >99.8%). ^1H NMR (b): 2.82 (A, J_{AB}=17.7, 1H), 2.50 (d, J=8.6, 1H), 2.34 (dt, J=14.4, 9.0, 1H), 2.10–2.19 (st, 2H), 2.04 (B, J_{AB}=17.7, 1H), 1.90–2.00 (st, 2H), 1.70 (dd, J=11.3, 9.0, 1H), 1.56 (dd, J=11.3, 9.6, 1H), 1.51 (d, J=11.7, 1H), 1.42–1.48 (m, 1H), 1.27–1.36 (m, 1H), 1.18 (s, 3H), 1.02 (s, 3H), 0.84 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (b): 225.6 (s), 86.4 (s), 72.3 (s), 51.3 (t), 50.0 (s), 49.0 (s), 44.0 (t), 40.6 (d), 38.6 (t), 37.4 (t), 34.2 (t), 31.4 (t), 27.0 (q), 26.3 (q), 25.8 (q), 18.1 (s), −1,9 (q), −2.4 (q); For 2D-NMR- and NOE-results see Supplement, Table 2. IR: 1720s, 1150s, 1064vs, 1030s, 1002s. MS: 334 (M^+, 8), 277 (69), 223 (10), 145 (26), 105 (22), 91 (30), 75 (100), 73 (64), 59. Anal. Calcd for $C_{20}H_{34}O_2Si$ (334.57): C 71.80, H 10.24. Found 71.59; 10.23.

4.1.8. cis,cis,cis,cis-4,10-Dimethyl-7-hydroxy-tetracyclo-[5.4.1.0^{4,12}.0^{10,12}]dodeca-2-one ***12***[9]. The *tert*-butyldimethylsilyl group was removed by treatment of a solution of TBAF-trihydrate (3.15 g, 10 mmol, 5 equiv) in abs THF (40 mL) (stirred over 10 g freshly activated molecular sieve (4 Å) for 30 min) with a slowly added solution of **2** (0.67 g, 2.0 mmol) in abs THF (20 mL). After 2 h stirring at rt the mixture was poured onto ice (75 g) and Et_2O (75 mL). The aqueous phase was extracted 3× with Et_2O (25 mL each) and the combined organic phases treated with brine (20 mL) and dried over $MgSO_4$. The orange oil was purified by CC over silica gel (50 g) with hexane–EtOAc (2:1) to give **12** (0.40 g, 91%) as a white powder. For analysis a sample was crystallized from hexane; the elemental analysis was performed with a sample sublimed 2× in vacuo at 120 °C. Mp 228–232 °C (decomp.); R_f=0.27 (2:1); GC: t_R=33.1 (purity >99.8%). ^1H NMR: 3.00 (dd, J=10.7, 5.5, 1H), 2.46 (s, 2H), 2.09–2.23 (st, 2H), 1.55–2.01 (st, 9H), 1.28 (s, 3H), 1.21 (s, 3H). ^{13}C NMR: 222.00 (s), 90.6 (s), 71.3(s), 53.1 (t), 47.2 (s), 45.8 (s), 44.3 (t), 43.2 (t), 41.8 (t), 41.5 (d), 38.6 (t), 35.9 (t), 25.5 (q), 22.9 (q). IR: 2940s, 2860s, 1720vs, 1254s,1090s, 1053s, 1003s. MS: 221 (12), 220 (M^+, 86), 205 (52), 203 (18), 202 (100), 187 (52), 178 (21), 177 (31), 175 (20), 174 (52), 165 (27), 164 (30), 161 (37), 160 (89), 159 (68), 152 (28), 151 (65), 150 (33), 149 (45), 148 (34), 147 (58), 146 (31), 145 (90), 137 (61), 136 (48), 135 (64), 134 (22), 133 (79), 132 (56), 131 (45), 123 (87), 122 (25), 121 (33), 120 (22), 119 (68), 118 (26), 117 (29), 110 (43), 109 (38), 108 (21), 107 (37), 105 (58), 95 (41), 93 (37), 91 (49), 81 (28), 79 (37), 77 (22), 67 (28), 55 (33). Anal. Calcd for $C_{14}H_{20}O_2$ (220.32): C, 76.32; H, 9.15. Found 75.52; 9.20.

4.1.9. cis,trans,cis,cis-4,10-Dimethyl-7-hydroxytetracyclo-[5.4.1.0^{4,12}.0$^{10,12-}$]dodeca-2-one ***17***[9]. As described above, deprotection of **3** (0.797 g, 2.40 mmol) induced by 3.76 g (12.0 mmol, 5 equiv) in THF (80 mL) gave after work up and flash chromatography **10b** (0.46 g, 88%) as colourless powder. For analysis a sample was crystallized from hot hexane, for elemental analysis a sample was crystallized from hot hexane, for elemental analysis a sample was additionally sublimed 2× in vacuo at 120 °C. Mp: 238–242 °C (decomp.); R_f=0.30 (2:1); GC: t_R=32.2 (purity >99.8%). ^1H NMR: 2.83 (A, J_{AB}=17.7, 1H), 2.55 (d, J=8.8, 1H), 2.35 (dt, J=14.7, 9.0, 1H), 2.20 (dd, J=11.8, 8.8, 1H), 1.94–2.13 (st, 4H), 2.09 (B, J_{AB}=17.7, 1H), 1.30–1.79 (st, 6H) with 1.55 (d, J=11.8, 1H) and (br s, 1H, OH-Proton), 1.20 (s, 3H), 1.05 (s, 3H). ^{13}C NMR: 225.2 (s), 84.7 (s), 71.3 (s), 51.0 (t), 50.9 (s), 49.0 (s), 42.5 (t), 40.2 (d), 39.3 (t), 36.8 (t), 34.2 (t), 31.1 (t), 26.9 (q), 25.7 (q).

IR: 2960s, 2955s, 2860s, 1730vs. MS: 220 (M^+, 5) 202 (95), 187 (21), 163 (20), 161 (18), 160 (96), 159 (53), 149 (21), 147 (25), 146 (19), 145 (100), 132 (20), 131 (35), 77 (31), 67 (25), 55 (50). Anal. Calcd for $C_{14}H_{20}O_2$ (220.32): C, 76.32; H, 9.15. Found 76.32; 9.19.

4.1.10. cis,cis,cis,cis-4,10-Dimethyltetracyclo[5.4.1.$0^{4,12}$.$0^{10,12}$] dodec-6-en-2-one ***13***[8] *and cis,cis,cis,cis-4,10-dimethyltetracyclo[5.4.1.$0^{4,12}$.$0^{10,12}$] dodec-7-en-2-one* ***14***[8]. A solution of **12** (0.35 g, 1.6 mmol) and DMAP (0196 g, 1.6 mmol, 1.0 equiv) in abs CH_2Cl_2 (20 mL) was cooled to −10 °C. After addition of Et_3N (1.35 mL, 9.6 mmol, 6 equiv) and MsCl (0.37 mL, 4.8 mmol, 3.0 equiv) in 5 min, the mixture was stirred for 15 min, warmed to rt and stirred for 1 h. The orange, clear mixture was poured onto ice-water (60 g) and treated with Et_2O (60 mL). The aqueous phase was extracted 3× with Et_2O (20 mL each), the combined organic phase washed with 1% HCl (20 mL), 1% $NaHCO_3$ (20 mL), H_2O (10 mL) and dried over Na_2SO_4. The crude, oily product (0.347 g) was dissolved in EtOAc–Et_2O (1:1) and purified by CC on silica gel (50 g) with hexane–ether (20:1) to give **8b**:**9b** (0.26 g, 80%) as turbid product in a ratio=1:2.6. HPLC (20:1) gave first crystalline **13** and **14** as a semisolid oil.

Compound **13**: Mp: 45–46 °C; R_f=0.64 (2:1); GC: t_R=24.6 (purity ~99.0%). ^1H NMR (b): 5.24 (br s, 1H), 2.71 (A, J_{AB}=19.2, 1H), 2.61–2.68 (m, 1H), 2.35–2.50 (st, 5H) with 2.46 (B, J_{AB}=19.2, 1H), 2.14 (dd, J=12.6, 10.5, 1H), 1.90–1.97 (m, 1H), 1.84 (dd, J=12.6, 4.4, 1H), 1.69–1.88 (m, 1H), 1.22 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (b): 222.7 (s), 152.3 (s), 116.6 (d), 71.8 (s), 53.4 (t), 53.3 (t), 48.9 (s), 47.0 (d), 46.2 (s), 44.4 (t), 33.3 (t), 25.1 (q), 24.8 (t), 23.4 (q); for 2D-NMR- and NOE-results see Supplement, Table 3. IR: 2905s, 2875s, 2843s, 1722vs, 1190s, 1170s. MS: 203 (9), 202 (M^+, 50), 160 (36), 159 (33), 147 (26), 145 (35), 133 (46), 132 (100), 131 (40), 119 (35), 118 (19), 117 (73), 115 (22), 105 (24), 91 (38), 77 (16). HRMS: m/z $[M]^+$ calcd for $C_{14}H_{18}O$: 202.1357; found: 202.1354.

Compound **14**: Mp: 29–31 °C; R_f=0.64 (2:1) GC: t_R=25.1 (purity ~98.5%). ^1H NMR: 5.38 (br s, 1H), 2.79–2.86 (m, 1H), 2.71 (dd, J=10.4, 4.6, 1H), 2.53–2.62 (st, 2H) with 2.56 (A, J_{AB}=18.5, 1H), 2.42 (B, J_{AB}=18.5, 1H), 2.21–2.29 (st, 3H), 1.76–1.94 (st, 3H), 1.21 (s, 3H), 1.14 (s, 3H). ^{13}C NMR: 222.1 (s), 150.1 (s), 120.6 (d), 74.4 (s), 55.6 (t), 52.3 (t), 51.1 (d), 45.5 (s), 43.9 (s), 43.3 (t), 37.1 (t), 24.6 (q), 22.0 (t), 19.9 (q); for 2D-NMR- and NOE-results see Supplement Table 4. IR: 2905s, 2890s, 2860s, 2842s, 1725vs, 1445s, 1255s. MS: 203 (14), 202 (M^+, 47), 160 (40), 146 (20), 145 (32), 133 (41), 132 (100), 131 (52), 117 (74), 115 (16), 105 (26), 91 (30). HRMS: m/z $[M]^+$ calcd for $C_{14}H_{18}O$: 202.1357; found: 202.1361.

4.1.11. 4,10-Dimethyltricyclo[5.4.1.$0^{4,12}$]dodeca-7(12),9-dien-2-one ***18*** *and 4-methyltricyclo[5.4.1.$0^{4,12}$]dodeca-7(12),10(14)-dien-2-one* ***19***. As described for **12** a mixture of **15** (0.40 g, 1.82 mmol) DMAP (25.0 mg, 0.18 mmol, 0.10 equiv) and Et_3N (2.02 mL, 14.5 mmol, 8.0 equiv) was cooled to −10 °C, treated with MsCl (0.57 mL, 7.30 mmol, 4.0 equiv), stirred at 0 °C for 30 min and worked up. The crude product (0.504 g, yellow, turbid oil) was dissolved in Et_2O (50 mL) and treated with 5 g silica gel. The dried material was poured onto silica gel (50 g) and eluted with hexane–EtOAc (25:1) to give the isomers **18** and **19** (0.0939 g, 26%) as a mixture in a ratio of 1:1.47. In addition 41.0 mg (10%) of slightly impure **15** was isolated. The isomers were separated by CC on silica gel (20 g), impregnated with 30% $AgNO_3$ under exclusion of light to give first **18**. Further purification was achieved by HPLC (hexane–EtOAc=25:1) and gave **18** and **19** as colourless oils, which became yellowish after extended storage at −20 °C.

Compound **18**: R_f=0.67 (3:1); GC: t_R=28.0 (purity ~98.5%). ^1H NMR 5.49–5.54 (m, 1H), 2.87–2.97 (m, 1H), 2.77–2.85 (m, 1H), 2.60–2.75 (st, 2H), 2.39 (A, J_{AB}=18.3, 1H), 2.30–2.36 (m, 1H), 2.16–2.28 (m, 2H), 2.12 (B, J_{AB}=18.3, 1H), 1.99–2.05 (m, 1H), 1.80–1.89 (st, 4H) with 1.84 (s, 3H), 1.12 (s, 3H). ^{13}C NMR: 219.9 (s), 145.5 (s), 137.3 (s), 131.8 (s), 122.3 (d), 54.4 (t), 50.6 (s), 45.9 (d), 40.1 (t), 37.1 (t), 33.4 (t), 28.9 (t), 26.5 (q), 24.6 (q); for 2D-NMR results see Supplement Table 5. IR: 2930s, 2870s, 2848s, 1740vs, 1712s, 1160s. MS: 203 (17), 202 (M^+, 100), 160 (44), 159 (28), 158 (29), 145 (85), 143 (20), 131 (56), 117 (20), 84 (25), 71 (24), 57 (29). HRMS: m/z $[M]^+$ calcd for $C_{14}H_{18}O$: 202.1357; found: 202.1354.

Compound **19**: R_f=0.67 (2:1); GC: t_R=26.9 (purity ~84.0%). ^1H NMR (a): 4.84 (s, 2H), 2.63–2.88 (st, 3H), 2.12–2.58 (st, 7H) with 2.38 (A, J_{AB}=18.0, 1H) and 2.19 (B, J_{AB}=18.0, 1H), 1.95–2.10 (st, 2H), 1.77–1.91 (m, 1H), 1.09 (s, 3H); contains ~13% **18** as impurity. ^{13}C NMR (a): 220.0 (s), 148.6 (s), 145.7 (s), 135.3 (s), 111.8 (t), 54.3 (t), 50.7 (s), 48.0 (d), 40.3 (t), 38.0 (t), 37.7 (t), 36.5 (t), 30.1 (t), 24.1 (q); signals of **18** are present; for 2D-NMR results see Supplement Table 6. IR: 2925s, 2858s, 1740vs. GC–MS: 203 (18), 202 (M^+, 100), 160 (40), 159 (22), 158 (45), 146 (20), 145 (74), 143 (32), 131 (68), 118 (29), 117 (30), 105 (25), 91 (24). HRMS: m/z $[M]^+$ calcd for $C_{14}H_{182}$: 202.1357; found: 202.1354.

Further attempts for elimination reactions with **15**.

4.1.12. cis,trans,cis,cis,-4,10-Dimethyltricylo-7-oxyformyl-[5.4.1.$0^{4,12}$] dodeca-7(12),9-dien-2-one ***16***. In a flask bearing a Soxhlet-extractor, charged with freshly activated molecular sieve (4 Å), a mixture of **15** (0.223 g, 1.0 mmol) and DMF-dimethylacetal (0.80 mL, 6.0 mmol, 6.0 equiv) in toluene (120 mL) was heated for 64 h under Ar. The residue obtained after complete removal of the solvent was purified by CC on silica gel (40 g) with hexane–EtOAc (4:1) to give **18** and **19** (0.026 g, 13%) in a ratio of 1:2.51 and the formate **16** (17.6 mg, 7%) as a solid and the slightly impure educt **15** (0.166 g, 76%).

Compound **16**: Mp 129–131 °C; R_f=0.34 (4:1); GC: t_R=35.2 (purity ~92.5%). ^1H NMR (a): 8.03 (d, J=0.8, 1H), 2.86 (A, J_{AB}=18.0, 1H), 2.62–2.76 (st, 3H), 2.05–2.28 (st, 4H), with 2.11 (B, J_{AB}=18.0, 1H), 1.37–1.78 (st, 5H), 1.22 (s, 3H), 0.96 (s, 3H). ^{13}C NMR: 223.8 (s), 160.3 (d), 92.1 (s), 71.9 (s), 50.6 (t), 50.1 (s), 48.9 (s), 40.9 (d), 40.6 (t), 37.5 (t), 35.1 (t), 34.2 (t), 30.9 (t), 26.7 (q), 25.6 (q). IR: 1735sh, 1725s, 1267vs, 1100s, 1020s. MS: 248 (M^+, 10), 220 (10), 203 (44), 202 (100), 187 (63), 161 (43), 160 (92), 159 (20), 147 (23), 146 (17) 145 (77), 132 (26), 131 (52), 119 (28), 105 (31), 91 (24). HRMS: m/z $[M]^+$ calcd for $C_{15}H_{20}O_3$: 248.1412; found: 248.1408.

4.1.13. cis,trans,cis,cis,-4,10-Dimethyltricylo-7-p-O toluenecar-bonyloxy-[5.4.1.$0^{4,12}$]dodeca-7(12),9-dien-2-one ***17***[8]. To a solution of **15** (0.22 g, 1.0 mmol) and DMAP (0.244 g, 2.0 mmol, 2 equiv) in abs pyridine (10 mL) was dropwise added at 0 °C a solution of *p-O*-toluenethionocarbonylchloride (0.60 mL, 4.0 mmol, 4.0 equiv) in abs dioxane (1.0 mL). The mixture was heated in the dark to 80 °C for 20 h. To the brownish-red, clear solution was added at rt 1 M NaOH (20 mL) and Et_2O (30 mL). The aqueous phase was 2× extracted with Et_2O (10 mL each), the combined organic phases were treated with 1 M HCl (10 mL), satd $NaHCO_3$ (10 mL) solution and brine (10 mL). The dark brown solution was dried over $MgSO_4$, treated with charcoal (1 g) and filtered over Celite®. After removal of the solvent the orange crystalline residue was purified by CC on silica gel (60 g, hexane–EtOAc=5:1) to give **17** (0.111 g, 31%) as yellow crystals. Mp: 87–89 °C; R_f=0.48 (2:1). ^1H NMR (a): 7.14–7.28 (m, 2H), 7.01–7.06 (m, 2H), 2.61–2.91 (st, 4H) including 2.87 (A, J_{AB}=18.0, 1H), 2.09–2.43 (st, 7H) with 2.35 (s, 3H) and 2.13 (B, J_{AB}=18.0, 1H), 1.55–1.82 (st, 4H), 1.38–1.51 (m, 1H), 1.24 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (a): 223.9 (s), 152.6 (s), 148.9 (s), 135.6 (s), 129.9 (d), 120.8 (d), 94.0 (s), 71.9 (s), 50.6 (t), 50.5 (s), 49.0 (s), 41.1 (d), 40.0 (t), 37.0 (t), 34.5 (t), 34.2 (t), 30.9 (t), 26.8 (q), 25.7 (q), 20.8 (t). IR: 1772sh, 1740s, 1268vs, 1102s, 1020s, 990sh. MS: 354 (M^+, 6), 203 (84), 202 (85), 162 (29), 161 (100), 160 (77), 159 (28), 158 (22), 131 (23), 119 (23), 108 (20), 105 (45). HRMS: m/z $[M]^+$ calcd for $C_{22}H_{26}O_4$: 354.1831; found: 354.1817.

4.1.14. Pyrolysis of ***17***. The inner surface of a flask (25 mL) was coated with **17** (68.0 mg, 0.19 mmol) by evaporation of an Et_2O

solution (10 mL). The flask was heated in vacuo (15 mbar) to 220 °C for 20 min. The pyrolysate was dissolved in Et$_2$O (30 mL) and the solution extracted 1 M NaOH (3× each with 10 mL). After further work up and CC on silica gel (6 g, hexane–EtOAc=20:1) a 5.01:1 mixture of **18** and **19** (10.2 mg, 26%) was obtained.

*4.1.15. Ethyleneketal (**20**) of cis,trans,cis,cis-4,10-dimethyl-7-tert-butyldimethylsilyloxytetra-cyclo[5.4.1.0^{4,12}.0^{10,12}]-dodeca-2-one **15**.* The reaction of **15** (0.334 g, 1.0 mmol) was performed in ethylene glycol (0.28 mL, 5.0 mmol, 5 equiv) and *p*-TsOH (0.01 g, 0.05 mmol, 0.05 equiv) in benzene (25 mL) with a Dean–Stark apparatus. After 16 h reflux and cooling Et$_2$O (30 mL) was added and the solution washed with a satd NaHCO$_3$-solution (10 mL) and H$_2$O (2× with 10 mL each). The residue was purified by CC on silica gel (40 g, hexane–EtOAc=25:1) to give partially crystalline **20** (0.26 g, 69%) and **15** (55.2 mg (17%). Mp: 18–22 °C; R_f=0.32 (20:1); GC: t_R=48.8 (purity >99.8%). ^{1}H NMR (a): 3.83–3.99 (m, 3H), 3.64–3.77 (m, 1H), 2.47 (A, J_{AB}=13.2, 1H), 3H), 1.56–1.72 (st, 2H) with 1.68 (B, J_{AB}=13.2, 1H), 1.15–1.52 (st, 10H) with 1.29 (s, 3H) and 1.18 (s, 3H), 0.88 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (a): 124.3 (s), 85.8 (s), 75.2 (s), 63.5 (t), 63.3 (t), 50.1 (s), 49.5 (s), 46.5 (t), 45.5 (t), 38.7 (d), 38.4 (t), 37.8 (t), 31.4 (t), 29.9 (t), 26.0 (q), 25.9 (q), 25.9 (q), 18.1 (s), −1.9 (q), −2.3 (q). IR: 2950s, 1260s, 1165w, 1085s, 1020s; for 2D-NMR results see Supplement Table 6. MS: 378 (M$^+$, 34), 377 (13), 322 (36), 321 (100), 309 (15), 292 (22), 277 (59), 276 (51), 247 (16), 246 (34), 245,235 (26), 203 (20), 185 (22), 160 (33), 159 (20), 145 (27), 141 (39), 119 (27), 105 (20), 75 (62), 74 (56). HRMS: *m*/*z* [M]$^+$ calcd for C$_{22}$H$_{38}$O$_3$Si: 378.2590; found: 378.2591.

*4.1.16. Desilylation of **20**.* As described for the desilylation of **15** a mixture prepared of TBAF-trihydrate (3.55 g, 11.25 mmol, 5.0 equiv) and **20** (0.85 g, 2.25 mmol) was stirred at rt for 18 h. Work up and CC over silica gel (50 g, hexane–EtOAc=2:1) gave **21** (0.592 g, 99%) as a viscous oil. For analysis a sample was rechromatographed to give an oil, which slowly crystallized at −20 °C within 2 weeks. Mp: 73–74 °C; R_f=0.32 (2:1); GC: t_R=38.9 (purity >99.8%). ^{1}H NMR (a): 3.77–3.95 (m, 3H), 3.64–3.75 (m, 1H), 2.46 (A, J_{AB}=13.3, 1H), 2.33 (dt, J=14.7, 9.0, 1H), 2.16 (d, J=6.6, 1H), 1.57–2.05 (st, 7H) with (br s, 1H, OH-Proton) and 1.67 (B, J_{AB}=13.2, 1H), 1.17–1.54 (st, 10H) with 1.28 (s, 3H) und 1.18 (s, 3H). ^{13}C NMR (a): 124.0 (s), 84.3 (s), 74.3 (s), 63.5 (t), 63.4 (t), 50.6 (s), 50.1 (s), 46.3 (t), 44.2 (t), 38.8 (t), 38.1 (d), 37.3 (t), 31.1 (t), 29.0 (t), 25.9 (q), 25.4 (q). IR: 2950vs, 2930sh, 2910s, 2890s, 1472s, 1320s, 1312s, 175s, 1108s, 1068s, 1032sh, 1020vs, 953s. MS: 264 (M$^+$, 34), 246 (24), 196 (28), 194 (10), 193 (35), 178 (71), 160 (100), 145 (33). HRMS: *m*/*z* [M]$^+$ calcd for C$_{16}$H$_{24}$O$_3$: 264.1725; found: 264.1717.

*4.1.17. Benzoate **22**.* To a solution of **21** (0.265 g, 1.0 mmol) and DMAP (0.244 g, 2.0 mmol, 2.0 equiv) in abs pyridine (20 mL) was dropwise added benzoylchloride (0.46 mL, 4.0 mmol, 4 equiv) at rt and stirred for 1 h. The suspension containing a precipitate was refluxed for 20 h. The clear, brown solution was treated with NaOH (30 mL) at 0 °C. After addition of Et$_2$O (60 mL) and extraction of the aqueous phase with Et$_2$O (3× with 20 mL each), the organic phases were treated with satd NH$_4$Cl solution (20 mL), satd Na$_2$CO$_3$ solution (20 mL) and H$_2$O (10 mL). After drying over MgSO$_4$ and removal of pyridine in vacuo the dark brown oil (0.377 g) was purified by CC over silica gel (40 g, hexane–ether=10:1) to give **22** (0.3.3 g, 82%) as a slightly yellow material. Colourless plates were obtained by crystallisation from MeOH at −20 °C. Mp: 93–94 °C; R_f=0.54; (2:1). UV/vis (hexane): λ_{max} (ε): 274 (1’200), 280sh (1’000), 230 (21’400). ^{1}H NMR (a): 7.99–8.05 (m, 2H), 7.50–7.58 (m, 1H), 7.38–7.47 (m, 2H), 3.90–4.04 (m, 3H), 3.70–3.84 (m, 1H), 2.71–2.89 (st, 2H), 2.45–2.59 (m, 2H), 2.08–2.30 (st, 2H), 1.85–1.96 (m, 1H), 1.67–1.80 (m, 2H), 1.33–1.60 (st, 7H) including 1.36 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (a): 165.7 (s), 132.6 (d), 131.6 (s), 129.5 (d), 128.3 (d), 123.9 (s), 91.5 (s), 75.2 (s), 63.7 (t), 63.5 (t), 50.1 (s), 49.5 (s), 46.2 (t), 41.8 (t), 39.2 (d), 38.1 (t), 34.6 (t), 31.0 (t), 29.9 (t), 25.6 (q), 25.5 (q). IR: 2960s, 2950s, 1715vs, 1320s, 1297vs, 1290s, 1128s, 1110s, 1010sh, 1000m. MS: 368 (M$^+$, 8), 246 (48), 191 (10), 161 (20), 160 (100), 145 (32), 131 (15), 105 (54), 84 (30), 56 (44), 55 (62). HRMS: *m*/*z* [M]$^+$ calcd for C$_{23}$H$_{28}$O$_4$: 368.1987; found: 368.1986.

*4.1.18. Trifluoroacetate **23**.* To a solution of **21** (0.049 g, 0.19 mmol) and DMAP (0.049 g, 0.38 mmol, 2.0 equiv) in abs pyridine (10 mL) at 0 °C was added dropwise (CF$_3$CO)$_2$O. After stirring at 0 °C for 1 h the reaction mixture was added to ice-H$_2$O (10 g), the solution extracted with Et$_2$O (30 mL) and the aqueous phase treated Et$_2$O (3× with 10 mL each). The organic phase was treated with satd NH$_4$Cl solution (10 mL), satd Na$_2$CO$_3$ solution (10 mL) and H$_2$O (5 mL). After drying over MgSO$_4$ and removal of the solvent the remaining pyridine was removed in vacuo. CC of the yellow oil (0.106 g) over silica gel (10 g) gave **23** (0.056 g, 83%) as a colourless oil, which slowly crystallized (1 week) to give thin needles. Mp: 50–51 °C; R_f=0.62 (2:1). UV/vis (hexane): λ_{max} (ε): 264 (sh, 12). ^{1}H NMR (a): 3.83–3.99 (m, 3H), 3.65–3.79 (m, 1H), 2.45–2.76 (st, 3H), 2.36 (d, J=7.4, 1H), 2.13–2.27 (st, 2H), 1.84–1.93 (m, 1H), 1.66–1.77 (m, 2H), 1.25–1.59 (st, 7H) with 1.34 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (a): 156.6 (q, J_{C-F}=41.2), 123.5 (s), 113.8 (q, J_{C-F}=284.9), 95.9 (s), 74.8 (s), 63.7 (t), 63.5 (t), 50.0 (s), 49.8 (s), 46.0 (t), 41.5 (t), 39.0 (d), 37.6 (t), 33.6 (t), 30.8 (t), 29.8 (t), 25.5 (q), 24.9 (q). IR: 2955s, 2945s, 2910s, 2900s, 2885s, 2860s, 1765s, 1375s, 1165vs, 1110s, 1080s, 1055s, 1012s, 990s. MS: 360 (M$^+$, 9), 247 (16), 246 (31), 160 (100), 145 (35), 131 (20). HRMS: *m*/*z* [M]$^+$ calcd for C$_{18}$H$_{23}$O$_4$F$_3$: 360.1548; found: 360.1531.

*4.1.19. General procedure for photolysis of **22** and **23**.* A solution of solution of **22** or **23** (20 mg) in hexane (40 mL) or CH$_3$CN in a quartz flask was degassed under ultrasound and Ar and irradiated with a 15 W low pressure Hg lamp for 6–40 h with or without a Pyrex filter. The progress of the reactions (very slow) was controlled by TLC. The solution was evaporated to dryness, treated with Et$_2$O (10 mL) and washed with a satd Na$_2$CO$_3$ solution (2× with 5 mL each) and H$_2$O (1× with 5 mL). The dried organic phase was filtered over 5 cm silica gel to give a yellow sticky oil. This crude mixture was directly submitted to HPLC.

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Supplementary data

The 2D-NMR spectra of the compounds **2**, **3**, **13**, **14**, **18** and **19** are given in the Tables 1–6. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.03.086.

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