147. Synthesis and Structure of [4.5.5.5]Fenestranes (= Tetracyclo[5.4.1.$0^{4,12}$.$0^{9,12}$]dodecanes)

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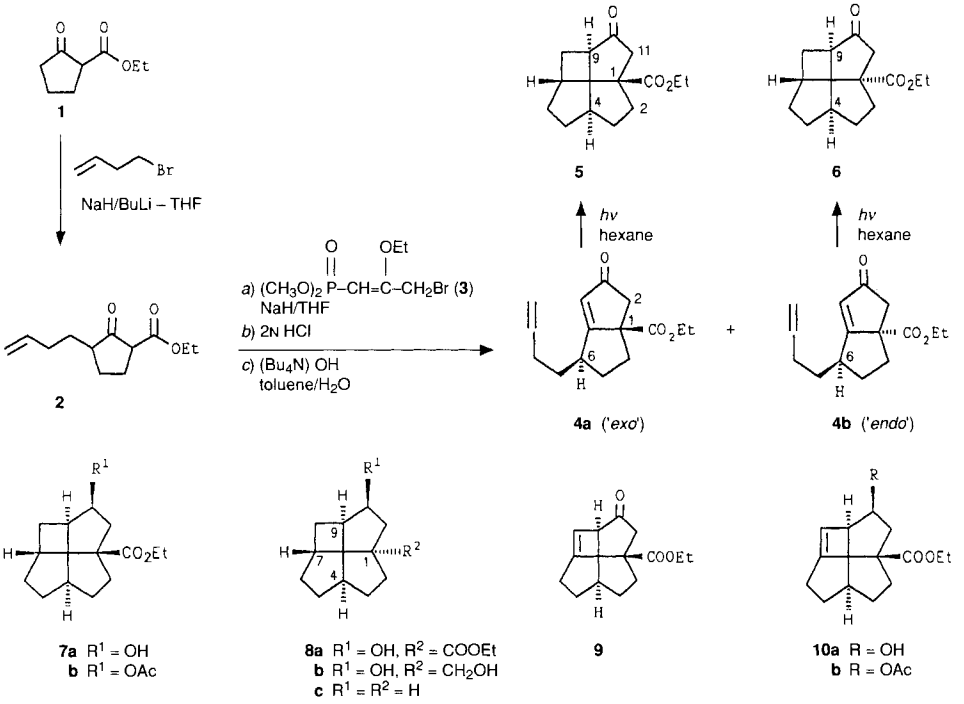
The preparation and the X-ray structure analysis of *cis,trans,cis,cis*-10-hydroxy-[4.5.5.5]fenestrane-1-methanol (**8b**) is reported. The measured bond angles and bond lengths of the central $C(C)_4$ fragment are better reproduced by calculations with the AM1 than by the MNDO method.

Introduction. – The tetracyclic fenestranes, where four rings share a central C-atom, are a unique class of hydrocarbons, because two opposite bond angles in the central $C(C)_4$ substructure are consistently larger than 109° 28′. This type of deformation may be enhanced by ring contraction and by incorporation of *trans*-fused bicyclo[*m.n.o*]alkane subunits. Whereas computational analyses of the deformation space of $C(C)_4$ fragments in fenestranes and related hydrocarbons are readily available [1], the investigation of their structure and their chemistry depends strongly on efficient syntheses of this class of compounds. Our recent success in the preparation of a variety of highly functionalized fenestranes provided crystalline compounds amenable to a detailed structural analysis. We report here the X-ray structure analysis of a [4.5.5.5]fenestrane containing a *trans*-fused bicyclo[3.3.0]octane subunit. The results are compared with data from AM1 calculations.

Synthesis of the [4.5.5.5]Fenestranes. – The key step for the preparation of the stereoisomeric [4.5.5.5]fenestranes **5** and **6** was an intramolecular enone-olefin photocycloaddition. The configurationally isomeric 6-(butenyl)bicyclo[3.3.0]oct-4-en-3-ones **4a** and **4b** were obtained from ethyl 2-oxocyclopentanecarboxylate **1** in 4 steps with an overall yield of 30 and 3%, respectively (*Scheme 1*). Photoreaction of **4a** and **4b** (formed from **2** and **3**) with a low-pressure Hg lamp gave **5** and **6**, respectively, as single isomers [2]. Reduction of **5** with $NaBH_4$ occurred stereoselectively and gave **7a**, from which **7b** was obtained. The latter material was identical with material prepared by hydrogenation of **10b** which was obtained from **9** [3] *via* **10a**. Reduction of **6** with $NaBH_4$ gave **8a** as a single isomer, whereas reaction of **6** as well as of **8a** with $LiAlH_4$ gave the crystalline diol **8b**.

The structure of the stereoisomers **4a** and **4b** was established by detailed NMR analysis. The $^{13}C,^{1}H$ connectivities and the $^{1}H,^{1}H$-coupling interactions are based on hetero-COSY and COSY measurements (*cf. Exper. Part*). According to NOE experiments for **4a**, the tertiary *H*–C(6) is located *trans* to the COOEt group and 'sees on the same side' $H^{\bullet}_{trans}$–C(7) and H_{trans}–C(8), the latter of which interacts with H_{trans}–C(2). In **4b**,

Scheme



H–C(6) is placed *cis* to the COOEt group, because it interacts with H_{cis}–C(7), which interferes with H_{cis}–C(8), but not with H_{trans}–C(8), which itself 'sees' H_{trans}–C(2).

The structure of fenestrane **5** is based upon the well established stereochemical course of photochemically induced [2 + 2] enone-olefin cycloadditions, particularly those leading to fenestranes [4], and is supported by NOE results. In the rather complex spectrum, the expected *cis*-relationship between H–C(4) and H–C(9) is apparent, but the signals overlap partially with the signal of H_{trans}–C(11). In **6**, the *cis*-arrangement of H–C(4) and H–C(9) H with the COOEt group was established by hetero-NOE measurements [2]. The structure of **6** was eventually established *via* an X-ray structure analysis of **8b** (see below).

The structural relationship between **5** and the product prepared by hydrogenation of **9** (→ **5**) was established by comparison of **7b** and the product obtained from hydrogenation of **10b**. NOE Measurements with **10b** revealed the *cis*-relationship of H–C(4), H–C(9), and H–C(10) [3]. The AcO and the COOEt group are, therefore, *cis* to each other.

The remarkable selectivity in the $NaBH_4$ reduction of the carbonyl group in **5**, **6**, and **9** giving **7a**, **8a**, and **10a**, respectively, as single products may be interpreted in terms of *Baldwin*'s rules [5]. In **5**, as well as in **9**, the approach of the hydride from the β-face is severely hindered by the COOEt group: There is additional hindrance in **5** from the cyclobutane moiety with its bridgehead H-atom. The result of the reduction of **6**, giving a

trans-disubstituted cyclopentane ring suggests that the COOEt group provides less steric hindrance to the approach of the hydride than the cyclobutane moiety at the opposite face.

X-Ray Structure Analysis of 8b. – To gain information about the structural features of the molecule and in particular of the central $C(C)_4$ subunit, an X-ray structure analysis of the crystalline diol **8b** was performed (*Fig. 1*). The asymmetric unit (space group $P2_1/c$)

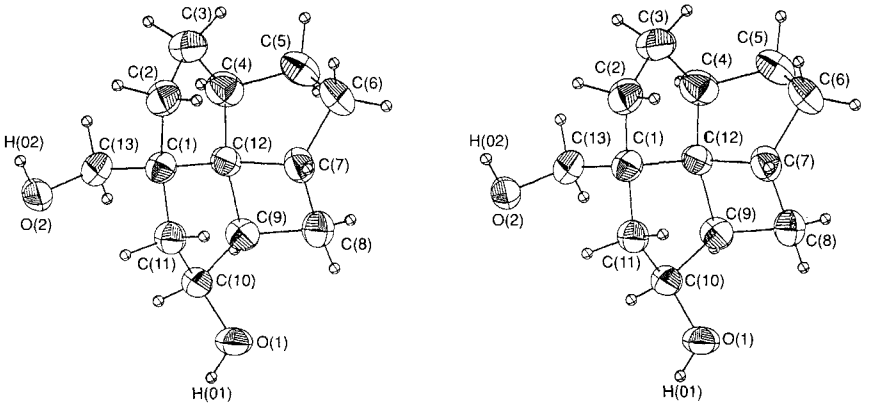


Fig. 1. *Stereoscopic view of* **8b** (molecule I) *with thermal ellipsoids representing 50% probability density* (298 K). Plot generated with PEANUT [6].

contains two molecules I and II, which differ slightly in their dimensions (*cf. Table 1*)[1]). The PEANUT plot [6] of molecule I clearly shows the *trans*-relationship of the bridgehead CH_2OH and the OH group, which had been deduced from NMR measurements (see above). Also, the presence of a *trans*-bicyclo[3.3.0]octane subunit is confirmed. In both molecules, most C–C bonds in the periphery fall into the range expected for regular bond distances.

The bond angles C(4)–C(12)–C(9) ($\alpha = 132.4(4)°$) and C(1)–C(12)–C(7) ($\beta = 119.5(4)°$) at the central C-atom are clearly larger than those found in molecules like neopentane [7] (*cf. Table 1*). The larger opening of the bond angle α might be due to the larger flexibility of the tertiary bridgeheads in comparison with the quaternary center. In this way, the distortion imposed on β by the CH_2 and CH_2CH_2 chains connecting C(7) with C(9) and C(4), respectively, is transferred to the bond angle α. The large bond angle C(2)–C(1)–C(11) (124.3(4)°) at the quaternary bridgehead is also noteworthy. In view of the computational results obtained for a variety of structures containing *trans*-bicyclo[3.3.0]octane substructures, two large bond angles at the bridgeheads might be a general feature of these structures (see below).

The unit cell contains 8 molecules, 4 of type I and 4 of type II, which are arranged in two layers parallel to the *ab* plane at $c \approx 0$ and $c \approx 0.5$, each containing 4 molecules. In each layer, the enantiomers of molecule I as well as II are H-bonded to each other. In

[1]) According to AM1 calculations for molecule I and II in fixed geometries, the molecules differ by 13.0 kJ/mol in strain energy.

Table 1. *Bond Angles* [°] *and Lengths* [Å] *of* **8b** *with Standard Deviations* (*cf. Exper. Part*)

Bond angle	Molecule I	Molecule II	Bond length	Molecule I	Molecule II
C(2)–C(1)–C(11)	124.3(4)	124.0(4)	C(1)–C(2)	1.525(6)	1.526(6)
C(2)–C(1)–C(12)	100.6(4)	99.9(4)	C(1)–C(11)	1.516(6)	1.502(6)
C(2)–C(1)–C(13)	109.5(4)	109.9(4)	C(1)–C(12)	1.509(6)	1.520(6)
C(11)–C(1)–C(12)	102.2(4)	101.6(3)	C(1)–C(13)	1.530(7)	1.530(6)
C(11)–C(1)–C(13)	109.0(4)	110.3(4)	C(2)–C(3)	1.548(7)	1.539(7)
C(12)–C(1)–C(13)	110.1(4)	109.4(4)	C(3)–C(4)	1.563(7)	1.558(7)
C(1)–C(2)–C(3)	102.2(4)	103.1(4)	C(4)–C(5)	1.520(7)	1.533(7)
C(2)–C(3)–C(4)	108.5(4)	107.9(4)	C(4)–C(12)	1.518(6)	1.531(6)
C(3)–C(4)–C(5)	114.3(5)	112.7(5)	C(5)–C(6)	1.525(8)	1.504(8)
C(3)–C(4)–C(12)	100.5(4)	101.1(4)	C(6)–C(7)	1.540(7)	1.531(7)
C(5)–C(4)–C(12)	106.4(4)	105.9(4)	C(7)–C(8)	1.537(6)	1.537(7)
C(4)–C(5)–C(6)	103.5(4)	104.2(4)	C(7)–C(12)	1.565(6)	1.573(6)
C(5)–C(6)–C(7)	104.0(4)	104.6(4)	C(8)–C(9)	1.515(6)	1.539(7)
C(6)–C(7)–C(8)	116.9(4)	116.6(4)	C(9)–C(10)	1.562(6)	1.541(6)
C(6)–C(7)–C(12)	107.4(4)	107.6(4)	C(9)–C(12)	1.560(6)	1.527(6)
C(8)–C(7)–C(12)	89.7(4)	88.8(4)	C(10)–C(11)	1.536(6)	1.544(6)
C(7)–C(8)–C(9)	89.9(4)	89.1(3)			
C(8)–C(9)–C(10)	114.3(4)	115.0(4)			
C(8)–C(9)–C(12)	90.7(3)	90.5(3)			
C(10)–C(9)–C(12)	102.0(3)	102.8(3)			
C(9)–C(10)–O(1)	113.2(4)	115.3(4)			
C(9)–C(10)–C(11)	107.2(4)	107.0(4)			
C(11)–C(10)–O(1)	111.2(4)	113.9(4)			
C(1)–C(11)–C(10)	102.6(4)	102.2(4)			
C(1)–C(12)–C(4)	106.5(4)	106.1(4)			
C(1)–C(12)–C(7)	119.7(4)	119.2(4)			
C(1)–C(12)–C(9)	107.6(4)	107.4(4)			
C(4)–C(12)–C(7)	103.9(4)	103.6(4)			
C(4)–C(12)–C(9)	132.0(4)	132.7(4)			
C(7)–C(12)–C(9)	87.2(3)	88.2(3)			
C(1)–C(13)–O(2)	113.4(4)	113.3(4)			

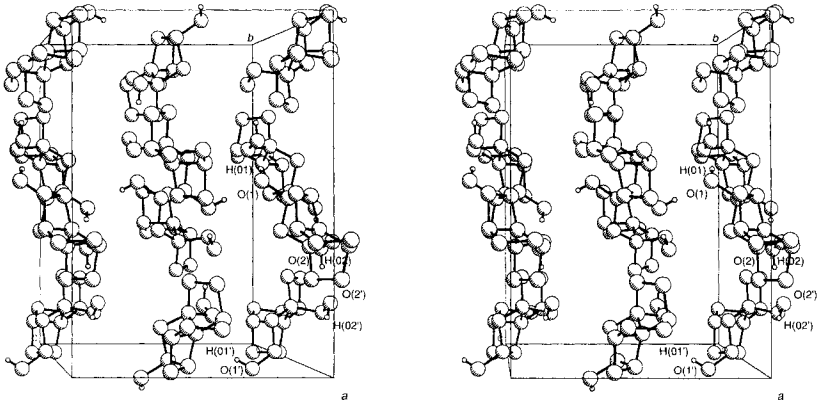


Fig. 2. *Stereoview of the crystal packing of compound* **8b**

type-I molecules, the H-bonds are formed by interactions of the secondary >CH–O*H* of one chiral form with O-atoms of the primary $-CH_2-OH$ group of its antipode. *Vice versa*, the antipodes of set II are H-bonded to each other by interactions between the primary CH_2-OH and the secondary *O*H groups. The type-I and type-II molecules are held together in each layer by additional H-bonds between the primary CH_2OH/CH_2OH groups. The interlayer H-bonds are formed by interactions of the secondary OH groups of both type-II molecules of one layer with those of type-I molecules in the next layer (*cf. Fig. 2*).

AM1 Analysis of Stereoisomeric Fenestranes Containing 4- and 5-Membered Rings. – We observed that the MNDO analyses of the parent [4.4.5.5]- and [4.4.4.5]fenestranes reproduce the measured bond angles α and β at the central C-atom within 1° [1b] [8]. Much to our surprise, the MNDO results overestimated in the *c,c,c,t*-[4.5.5.5]fenestrane **8b** these bond angles by 3 and 7°, respectively (*Table 2*). Further calculations by the AM1 and the PM3 method showed that the experimental geometry of the C-skeleton of this fenestrane is reproduced with the much smaller deviation of 2°. Also, the values for $\Delta H_f°$ are very similar and lower than those obtained by MNDO calculations.

Table 2. *Bond Angles* α *and* β [°] (*cf.* text) *of* **8b**, *Obtained from X-Ray Structure Analysis and Computational Results*

	α	β	$\Delta H_f°$ [kJ/mol]
X-Ray	132.7	119.2	–
MNDO	135.5	126.2	–327.8
AM1	135.1	121.4	–383.9
PM3	133.3	121.2	–372.1

In view of the observation that AM1 results provide more reliable bond angles for fenestranes than MNDO calculations, we analyzed the geometry of the six stereoisomers of [5.5.5.5]fenestranes (see **11–14**) and the structural prerequisites for large bond angles (*Table 3*). From a systematic exploration of the deformation space of the $C(C)_4$ fragment in this class of compounds, it was concluded that the bond-angle opening could be enhanced by ring contraction, introduction of bridgehead double bonds, formation of certain stereoisomers, and replacement of the bridgehead H-atoms by bulky substituents [9] [10].

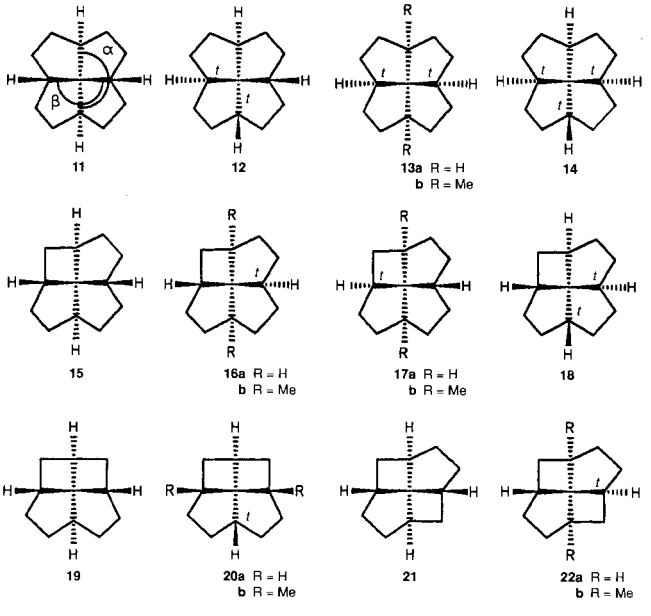
It is apparent from the data of *Table 3* that the spread of the opposite bond angles in the stereoisomeric [5.5.5.5]fenestranes **11–14** increases with the number of *trans*-bicyclo[3.3.0]octane subunits, thus predicting for the all-*trans*-isomer a geometry close to planarity. However, the total strain energy in the all-*trans*-isomer is much larger than the bond energy of a single C–C bond. Since a large proportion of this strain is located in the central $C(C)_4$ subunit [1b], it might be expected that this molecule decomposes by homolysis of one bond of the $C(C)_4$ substructure leading eventually to tricyclic compounds. More realistic structures are the *c,c,t,t*- and the *c,t,c,t*-isomers **12** and **13a**, respectively, for which bond angles in the range of 130–140° are predicted. Since the strain energies are less than 300 kJ/mol, these molecules are attractive targets for synthesis[2]). The bond

[2]) Part of the Ph. D. Thesis of *R. Guidetti-Grept.*

Table 3. *Computational Bond Angles and Strain Energies of Selected Fenestranes.* According to frequency analyses, all structures are energy-minimal.

[*m.n.o.p*]-Fenestrane	Ring fusions[a])		Bond angles [°][b])		Strain energy[c])
			α	β	
5.5.5.5	*cccc*	**11**	113.8	113.8	2.6
	tccc	(*cf.* **8c**)	118.3	126.7	78.7
	cctt	**12**	136.5	134.4	290.7
	ctct	**13a**	137.5	130.6	242.6
	cttt	**14**	154.9	153.6	532.1
	tttt		178.4	177.8	733.8
4.5.5.5	*cccc*	**15**	120.3	120.2	89.8
	ctcc	**16a**	134.0	121.9	162.4
	ccct	**17a**	141.2	120.1	246.1
	cttc	**18**	149.8	133.5	350.7
4.4.5.5	*cccc*	**19**	127.0	122.2	229.6
	cctc	**20a**	125.2	136.2	275.2
4.5.4.5	*cccc*	**21**	126.6	126.6	224.8
	ctcc	**22a**	149.6	119.1	347.2

[a]) *c* and *t* refer to *cis*- and *trans*-bicyclo[*x.y.*0]alkane subunits.
[b]) AM1 results [11].
[c]) HOF (AM1) – Σ average bond energies [12] in kJ/mol.



angles at the bridgehead in those stereoisomers that contain *trans*-bicyclo[3.3.0]octane subunits are consistently larger than in the all-*cis* isomer **11**. In view of the bridgehead geometry observed in the X-ray structure of **8b**, a bond angle > 120° seems to be a general structural feature of *trans*-bicyclo[3.3.0]octanes. The 19 1,5-dialkyl-substituted *trans*-

fused bicyclo[3.3.0]octane substructures found in the *Cambridge Structural Data Base* have average bond angles at the bridgehead of 126.4° (3.6) and 127.0 (6.3), respectively. This is further supported by an AM1 calculation for *trans*-1,5-dimethyl-bicyclo-[3.3.0]octane, which gave a bond angle of 124° for C(2)–C(1)–C(8), and also by the results obtained for **12–14**, **16–18**, as well as **20** and **22**.

Comparison of the bond angles in **15** with those in **11** reveals that ring contraction leads to an enhanced spread of angles. Depending on the size of the *trans*-bicyclo[*m.n.*0]alkane substructure as in **16a** and **17a**, respectively, one of the bond angles in the $C(C)_4$ fragment becomes even larger, whereas the other is hardly affected[3]). As expected, the presence of two adjacent *trans*-bicyclo[3.3.0]octane subunits, as in **18**, leads to two large opposite bond angles in the central $C(C)_4$ structure.

For fenestranes constructed of two four- and two five-membered rings, two 'sequence' isomers are possible (**19** and **21**, resp.). In both cases, α and β are slightly smaller than those found in a derivative of *c,c,c,c*-[4.4.4.5]fenestrane[4]). Inversion at one bridgehead leads to the *c,c,t,c*-[4.4.5.5]fenestrane (**20a**) and the *c,t,c,c*-[4.5.4.5]isomer **22a** respectively, which each contain one *trans*-fused subunit. For both compounds, one large bond angle is predicted, whereas for the opposite angle, there should even be a decrease. The strain in **22a** is certainly due to the presence of a *trans*-biyclo[3.2.0]heptane subunit. It is also related to the large value of the bond angle in the $C(C)_4$ fragment, which generally contributes to the overall strain in a systematic way [1b]. In several cases, substituent effects were explored in order to enhance the opening of the opposite bond angles. The AM1 results for **13b**, **16b**, **17b**, **20b**, and **22b** show that two bridgehead Me groups, *cis* to each other, do affect the bond angles in the central $C(C)_4$ fragment only marginally.

Concluding Remarks. – The successful synthesis of stereoisomeric [4.5.5.5]fenestranes by intramolecular photoinduced olefin-enone [2 + 2] cycloaddition allowed to perform a detailed structural analysis. According to the X-ray structure of **8b**, the structural adjustment to the presence of a *trans*-bicyclo[3.3.0]octane subunit (*cf.* **16**) was achieved in such a way, that the bond angles at the bridgehead C-atoms of this substructure become larger than those in the corresponding all-*cis*-isomer (*cf.* **15**). AM1 results indicate, that two large bond angles at the bridgeheads of *trans*-bicyclo[3.3.0]octanes might be a general feature of such bicyclic structures.

The hydrogenation of **10b** occurs exclusively at the sterically more hindered side (**10b** → **7b**). The reversal of this remarkable stereoselectivity would lead to a *c,c,c,t*-[4.5.5.5]stereoisomer (*cf.* **17**) with a *trans*-bicyclo[3.2.0]heptane subunit. The topological difference of the bridgehead double bond merits further investigation. The deviation of the opposite bond angles α and β in fenestrane **8b** from the value found in a regular tetrahedron by 10–23° indicates, that the geometry of a $C(C)_4$ fragment is rather robust. According to the computational results, some stereoisomers of the [4.5.5.5]- and [5.5.5.5]fenestranes have, nevertheless, bond angles larger than 130°. These are attractive targets for further syntheses.

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[3]) It should be noted, that no *trans*-bicyclo[3.2.0]heptane was hitherto prepared. A case, where a *trans*-bicyclo-[3.2.0]heptane subunit is mechanistically plausible, was reported [10].

[4]) For the X-ray structure of a derivative of **19**, see [8].

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Experimental Part

General. Org. solvents used for reactions were dried and distilled. Reactions were not optimized with respect to yield. If not stated otherwise, mixtures were worked up by pouring on ice/H_2O, extracting 3 times with Et_2O, drying ($MgSO_4$) the org. phase, and evaporation. TLC: *Alugram SIL* (*Macherey* and *Nagel*): Column chromatography (CC; lowbar): silica gel for flash chromatography (FC) 30–60 μm (*J. T. Baker*). Anal. GC: capillary column *SE-54*, 20 m. IR Spectra (cm^{-1}): if not stated otherwise, in $CHCl_3$; *Perkin-Elmer* spectrometer *PE 782*. NMR Spectra: in $CDCl_3$; *Bruker-AM300* (300 MHz) or *-AM400* (400 MHz) instrument; assignments based on $^{13}C,^1H$- and $^1H,^1H$ correlations; NOE: irradiated proton/proton(s) with signal enhancement; *c* = *cis* and *t* = *trans* to the COOEt group; chemical shifts in δ[ppm] downfield from TMS as an internal standard, (stack = heavily overlapping signals), coupling constants *J* in Hz. Mass Spectra (MS): *Varian-MAT-CH7A* instrument; signals (*m*/*z*) in % of the most intense peak. Elemental analyses were performed by *D. Manser*, Mikroanalytisches Labor, ETH Zürich.

Ethyl 3-(But-3-enyl)-2-oxocyclopentanecarboxylate (**2**). A soln. of **1** (10 g, 64 mmol) in THF (30 ml) was slowly added to a suspension of NaH (1.54 g, 64 mmol) at 0° and stirred for 15 min. After cooling to −78°, 2.3M BuLi (28 ml, 64 mmol) was added slowly and the soln. allowed to warm to −30°. After cooling to −60°, 4-bromobut-1-ene (8.64 g, 64 mmol) in THF (20 ml) was added. After stirring overnight at r.t., the mixture was worked up and purified by CC: 8.39 g (63%) of **2**. TLC (hexane/Et_2O 2:1): R_f 0.43. B.p. 102°/6·10^{-2} Torr. IR: 3001*m*, 2980*s*, 2940*m*, 1750*vs*, 1725*vs*, 1645*m*, 1135*s*, 920*s*. ^1H-NMR: 1.29 (*m*, 3 H); 1.42–1.60 (stack, 2 H); 1.75–2.00 (stack, 2 H); 2.00–2.4 (stack, *ca.* 5 H); 2.1–3.35 (2*m*, 1 H); 4.20 (*m*, 2 H); 4.95–5.1 (*m*, 2 H); 5.70–5.88 (*m*, 1 H). ^{13}C-NMR: Isomer **A**: 14.18 (*q*); 25.14 (*t*); 27.31 (*t*); 28.81 (*t*); 31.45 (*t*); 48.65 (*d*); 56.07 (*d*); 61.35 (*t*); 115.39 (*t*); 137.75 (*d*); 169.50 (*s*); isomer **B**: 14.41 (*q*); 25.12 (*t*); 25.12 (*t*); 27.61 (*t*); 29.12 (*t*); 31.45 (*t*); 48.17 (*d*); 54.19 (*d*); 61.35 (*t*); 115.33 (*t*); 137.25 (*d*); 169.44 (*s*).

Ethyl rel-(*1*R,*6*R)- *and* rel-(*1*S,*6*R)-*6-(But-3-enyl)-3-oxobicyclo[3.3.0]oct-4-ene-1-carboxylate* (**4a** and **4b**, resp.). To a suspension of NaH (0.571 g, 23.8 mmol) in THF (100 ml) was added at 0° a soln. of **2** (5 g, 23.8 mmol) in THF (25 ml). After 15 min, a soln. of dimethyl (3-bromo-2-ethoxyprop-1-enyl)phosphonate [13] (**3**; 6.83 g, 25 mmol) in THF (25 ml), was slowly added. After stirring overnight at r.t., the soln. was evaporated and worked up. The crude material (11.5 g) was dissolved in acetone (300 ml) and treated with 2N HCl (5 ml) at r.t. for 1 h. After neutralisation with $NaHCO_3$ soln. and evaporation, the mixture was worked up with AcOEt. To the crude material (9.7 g) in toluene (200 ml) were added H_2O (200 ml) and 40% $(Bu_4N)OH$ soln. (13 ml). After stirring at r.t. the mixture was worked up and purified by CC (hexane/Et_2O 4:6): 2.84 g (48%) of **4a** and 0.284 g (4.8%) of **4b**.

4a: M.p. 48°. TLC (hexane/Et_2O 1:2): R_f 0.43. GC (*SE-54*, 20 m, 160°): t_R 5.65 min. IR: 3005*m*, 2980*m*, 2940*m*, 1715*vs*, 1630*s*, 1460*w*, 1440*w*, 1185*s*, 1160*m*. ^1H-NMR: 6.02 (*s*, H–C(4)); 2.72 (*d*, *J* = 19, H_c–C(2); corr. to H_t–C(2)); 2.3 (*d*, *J* = 19, H_t–C(2); corr. to H_c–C(2)); 1.39 (*ddd*, H_t–C(8); corr. to H_c–C(8); H_c–C(7), H_t–C(7); 2.7 *dd*, H_c–C(8); corr. to H_t–C(8), H_c–C(7), H_t–C(7), H–C(6)); 1.7–1.82 (*m*, H_c–C(7); corr. to H_t–C(7), H_c–C(8), H_t–C(8), H–C(6)); 2.2–2.28 (*m*, H_t–C(7); corr. to H_c–C(7), H_c–C(8), H_t–C(8), H–C(6)); 2.8–2.91 (*m*, H–C(6); corr. to H_c–C(7), H_t–C(7), CH_2(1′)); 4.21 (*m*, CH_3CH_2O; corr. to CH_3CH_2O); 1.21 (*t*, CH_3CH_2O; corr. to CH_3CH_2O); 1.51–1.62 (*m*, CH_2(1′); corr. to CH_2(2′), H–C(6)); 2.1–2.18 (*m*, CH_2(2′); corr. to H–C(3′), CH_2(4′)); 5.76 (*m*, H–C(3′); corr. to CH_2(2′), CH_2(4′)); 5.01 (*m*, CH_2(4′); corr. to H–C(3′), CH_2(2′)). NOE: H_t–C(8)/H_c–C(8), H_t–C(2), H_t–C(7); H_c–C(7)/H_t–C(7), H_c–C(8), CH_2(1′); H_t–C(7)/H_c–C(7), H_t–C(8), H–C(6); H–C(6)/H_t–C(7), CH_2(1′), H–C(4); CH_2(1′)/H_c–C(7), CH_2(2′), H–C(6). ^{13}C-NMR: 189.0 (C(5)); 127.5 (CH(4)); 208.8 (C(3)); 48.7 (CH_2(2)); 60.3 (C(1)); 33.5 (CH_2(8)); 32.4 (CH_2(7)); 38.8 (CH(6)); 172.9 (*C*OOEt); 61.6 (CH_3CH_2O); 14.0 (CH_3CH_2O); 34.4 (CH_2(1′)); 32.4 (CH_2(2′)); 137.6 (CH(3′)); 115.4 (CH_2(4′)). MS: 248 (90, M^+), 220 (51), 207 (55), 202 (52), 194 (33), 191 (22), 179 (56), 178 (36), 177 (47), 176 (39), 175 (100), 174 (70), 166 (16), 161 (20), 157 (26), 148 (28), 147 (82), 146 (51), 133 (89), 132 (51), 131 (43), 119 (46), 117 (36), 107 (29), 105 (90), 93 (39), 92 (31), 91 (62), 79 (31), 67 (26), 55 (34). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.57, H 8.34.

4b: TLC (hexane/Et_2O 1:2): R_f 0.45. GLC (*SE-54*, 20 m, 160°): t_R 6.29 min. IR: 2980*m*, 2970*m*, 2938*m*, 1715*vs*, 1630*s*, 1180*s*, 920*m*. ^1H-NMR: 5.96 (*s*, H–C(4), corr. to H_c–C(2)); 2.89 (*d*, *J* = 18.2, H_c–C(2), corr. to H_t–C(2)); 2.29 (*d*, *J* = 18.2, H_t–C(2), corr. to H_c–C(2)); 2.65–2.78 (*dd*, H_c–C(8); corr. to H_t–C(8), H_c–C(7), H_t–C(7)); *ca.*

1.45–1.55 (*m*, H_t–C(8); corr. to H_c–C(8), H_c–C(7), H_t–C(7)); 2.35–2.47 (*m*, H_c–C(7), corr. to H_c–C(8), H_t–C(8), H_t–C(7), *H*–C(6)); 1.57–1.70 (*m*, H_t–C(7); corr. to H_c–C(8), H_t–C(8), H_c–C(7), *H*–C(6)); 2.88 (*m*, H–C(6); corr. to H_c–C(7), H_t–C(7), H_A–C(1′), H_B–C(1′)); 4.12 (*m*, CH_3CH_2O; corr. to CH_3CH_2O); 1.20 (*t*, CH_3CH_2O; corr. to CH_3CH_2O); 1.80–1.92 (*m*, H_A–C(1′); corr. to *H*–C(6), CH_2(2′), H_B–C(1′)); *ca.* 1.40–1.50 (*m*, H_B–C(1′); corr. to *H*–C(6), CH_2(2′)); 2.05–2.25 (*m*, CH_2(2′); corr. to H_A–C(1′), H_B–C(1′), *H*–C(3′), CH_2(4′)); 5.75–5.90 (*m*, H–C(3); corr. to CH_2(2′), CH_2(4′)); 4.95–5.10 (*m*, CH_2(4′); corr. to *H*–C(3′), CH_2(2′)). NOE: H_c–C(2)/H_t–C(2); H_t–C(2)/H_c–C(2), H_t–C(8); H_c–C(8)/H_t–C(8), H_c–C(7); H_t–C(8)/H_c–C(8), H_t–C(2); H_c–C(7)/H_t–C(7), H_c–C(8), H–C(6); H_t–C(7)/(H_c–C(7), H_B–C(1′), CH_2(2′); H–C(6)/H_c–C(7), H_A–C(1′), CH_2(2′); H_A–C(1′)/H–C(6), H_B–C(1′), CH_2(2′), H–C(4); H_B–C(1′)/H_t–C(7), H_A–C(1′), CH_2(2′); H–C(3′)/CH_2(2′), CH_2(1′)(?), CH_2(4′); CH_2(4′)/CH_2(2′), H–C(3′). ^{13}C-NMR: 190.0 (*s*, C(5)); 124.5 (*d*, CH(4)); 208.7 (*s*, C(3)); 48.1 (*t*, CH_2(2)); 60.2 (*s*, C(1)); 32.3 (*t*, CH_2(8)); 30.8 (*t*, CH_2(7)); 37.7 (*d*, CH(6)); 173 (*s*, *C*OOEt); 61.6 (*t*, CH_3CH_2O); 14.0 (*q*, CH_3CH_2O); 32.1 (*t*, CH_2(1′)); 32.0 (*t*, CH_2(2′)); 137.7 (*d*, H–C(3′)); 115.3 (*t*, CH_2(4′)). MS: 248 (10, M^+), 207 (67), 206 (22), 179 (36), 175 (39), 147 (60), 146 (13), 133 (67), 132 (23), 131 (20), 121 (23), 119 (16), 105 (96), 103 (15), 95 (32), 93 (100), 83 (13), 81 (19), 79 (37), 77 (31), 67 (32), 65 (16), 57 (15), 55 (32), 53 (13), 41 (46). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.22, H 8.16.

Ethyl rel-(*1*R,*4*R,*7*R,*9*R)-*10-Oxotetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodecane-1-carboxylate* (**5**). A soln. of **4a** (0.70 g, 2.8 mmol) in degassed hexane (HPLC quality; 70 ml) was irradiated in a quartz vessel with a 125-W low-pressure Hg lamp for 1.5 h. CC (hexane/Et_2O 1:2) gave 0.616 g of **5** (89%). Colourless oil. TLC (hexane/Et_2O 1:2): R_f 0.47. GC (*SE-54*, 20 m, 160°): t_R 5.54 min. IR: 2905*m*, 2860*m*, 1728*vs*, 1460*m*, 1450*m*, 1370*m*, 1320*m*, 1295*m*, 1283*m*, 1270*s*, 1252*m*, 1248*m*, 1185*s*, 1180*s*, 1145*m*, 1130*s*, 1115*m*, 1020*m*. ^{1}H-NMR: 1.29 (*t*, *J* = 7.0, 3 H); 1.58–1.75 (stack, 4 H); 1.8–1.9 (stack, 2 H); 2.01–2.18 (stack, 3 H); 2.18–2.35 (*m*, 1 H); 2.38 (*dd*, 17.3, 1.5, 1 H); 2.40–2.50 (*m*, 1 H); 2.55–2.65 (stack, 2 H); 3.08 (*dd*, *J* = 17.3, 0.8, 1 H); 4.17 (*q*, *J* = 7.0, 1 H). ^{13}C-NMR: 14.1 (*q*); 25.2 (*t*); 31.9 (*t*), 32.5 (*t*); 34.6 (*t*); 39.7 (*t*); 39.9 (*d*); 48.0 (*d*); 50.2 (*t*); 52.3 (*d*); 55.6 (*s*); 60.6 (*t*); 68.7 (*s*); 175.2 (*s*); 218.7 (*s*). MS: 248 (40, M^+), 220 (24), 202 (21), 178 (20), 175 (100), 174 (60), 147 (37), 146 (26), 133 (24), 131 (21), 119 (14), 107 (18), 105 (31), 91 (31), 79 (13), 55 (24). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.36, H 7.97.

Ethyl rel-(*1*S,*4*R,*7*R,*9*R)-*10-Oxotetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodecane-1-carboxylate* (**6**). As described for **5**, irradiation of 0.2 g (0.81 mmol) of **4b** gave 0.1725 g (86%) of **6**. TLC (hexane/Et_2O 1:1): R_f 0.39. IR: 3001*m*, 2950*s*, 2870*m*, 1740*vs*, 1480*w*, 1470*m*, 1460*m*, 1445*m*, 1420*w*, 1370*w*, 1302*m*, 1295*w*, 1272*w*, 1240*w*, 1180*s*, 1143*s*, 1125*w*, 1079*w*, 1055*w*, 1050*m*, 1030*m*, 915*w*, 860*w*. ^{1}H-NMR: 1.20 (*t*, 3 H); 1.25–1.38 (stack, 2 H); 1.41–1.55 (*m*, 1 H); 1.6–1.75 (*m*, 1 H); 1.75–1.92 (stack, 3 H); 2.1–2.4 (stack, 4 H); 2.48 (*d*, *J* = 15.9, 1 H); 2.63 (*d*, *J* = 15.9, 1 H); 2.63–2.75 (*dd*, 1 H); 2.78–2.81 (*d*, 1 H); 4.10 (*q*, 2 H). ^{13}C-NMR: 14.03 (*q*); 25.3 (*t*); 27.6 (*t*); 29.15 (*t*); 32.33 (*t*); 33.12 (*t*); 39.43 (*d*); 42.75 (*d*); 45.53 (*d*); 45.94 (*t*); 59.12 (*s*); 60.85 (*t*); 72.27 (*s*); 175.8 (*s*); 221.3 (*s*). MS: 248 (51, M^+), 220 (44), 207 (11), 206 (*100*), 205 (*100*), 202 (22), 191 (57), 179 (27), 177 (29), 176 (22), 175 (96), 174 (57), 166 (17), 160 (23), 148 (15), 147 (64), 146 (53), 133 (66), 132 (77), 131 (77), 119 (36), 117 (33), 105 (71), 93 (24), 92 (18), 91 (83), 81 (21), 79 (28), 77 (28), 55 (20). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.36, H 8.25.

Ethyl rel-(*1*R,*4*R,*7*R,*9*R,*10*S)-*10-Hydroxytetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodecane-1-carboxylate* (**7a**). Keto-ester **5** (0.08 g, 0.3 mmol) was treated with $NaBH_4$ (18.5 mg, 0.5 mmol) in MeOH (2 ml). Workup and CC yielded 53 mg (70.9%) of **7a**. TLC (hexane/Et_2O 1:2): R_f 0.47. GC: (*SE-54*, 20 m, 160°): t_R 5.22 min. IR: 3450*w*, 2980*m*, 2940*s*, 2870*m*, 1680*s*, 1450*m*, 1430*m*, 1370*m*, 1320*s*, 1302*m*, 1290*m*, 1272*s*, 1175*w*, 1180*s*, 1155*s*, 1110*m*, 1100*m*, 1065*m*, 1050*m*, 1025*m*, 1000*w*, 862*w*. ^{1}H-NMR: 1.25 (*t*, 3 H); 1.38–1.48 (stack, 2 H); 1.54–1.77 (stack, 6 H); 1.78–1.85 (*m*, 1 H); 1.98–2.27 (stack, 5 H); 2.27–2.34 (*m*, 1 H); 3.98 (*d*, 1 H); 4.05–4.15 (*m*, 1 H); 4.15–4.25 (*m*, 1 H); 4.39 (*m*, 1 H). ^{13}C-NMR: 14.22 (*q*); 18.79 (*t*); 29.91 (*t*); 31.75 (*t*); 33.27 (*t*); 40.33 (*t*); 41.23 (*d*); 47.56 (*d*); 48.06 (*t*); 52.19 (*d*); 61.06 (*t*); 63.23 (*s*); 75.15 (*s*); 77.21 (*d*); 179.80 (*s*). MS: 251 (5), 250 (28), 233 (14), 206 (63), 278 (32), 277 (27), 260 (19), 259 (*100*), 258 (26), 133 (31), 132 (18), 131 (22), 130 (12), 121 (22), 119 (20), 117 (37), 105 (39), 93 (25), 91 (49), 79 (33), 77 (19). Anal. calc. for $C_{15}H_{22}O_3$ (250.34): C 71.97, H 8.86; found: C 71.82, H 9.07.

Ethyl rel-(*1*S,*4*R,*7*R,*9*R,*10*S)-*10-Hydroxytetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodecane-1-carboxylate* (**8a**). Keto-ester **6** (0.15 g, 0.6 mmol) was reduced with $NaBH_4$ (0.035 g, 0.9 mmol) in MeOH (5 ml). Workup and CC yielded 11.2 mg (75%) of **8a**. M.p. 64–66°. TLC (hexane/Et_2O 1:1): R_f 0.43. GC: *SE-54* (20 m, 160°): t_R 6.88 min. IR: 3608*w*, 2942*vs*, 2860*m*, 1715*vs*, 1520*w*, 1510*w*, 1470*m*, 1460*m*, 1445*w*, 1390*w*, 1368*w*, 1300*m*, 1295*m*, 1288*m*, 1272*m*, 1190*s*, 1180*s*, 1155*s*, 1120*s*, 1100*m*, 1070*m*, 1005*m*, 1020*s*. ^{1}H-NMR: 1.20–1.35 (stack, 5 H); 1.38–2.2 (stack, 10 H); 2.20–2.3 (*dd*, 1 H); 2.35–2.5 (stack, 2 H); 4.1 (*t*, 3 H); 4.75 (*dd*, 1 H). ^{13}C-NMR: 14.161 (*q*); 20.07 (*t*); 28.16 (*t*); 29.34 (*t*); 32.66 (*t*); 34.48 (*t*); 37.27 (*d*); 38.27 (*d*); 39.19 (*t*); 43.37 (*d*); 60.24 (*t*); 61.44 (*s*); 73.67 (*s*); 77.55 (*d*). MS: 250 (2, M^+), 232 (11), 206 (26), 204 (11), 178 (13), 177 (*100*), 176 (19), 160 (12), 159 (79), 158 (25), 131 (22), 119 (21), 117 (26), 107 (13), 105 (29), 93 (23), 91 (41), 79 (27), 77 (14). Anal. calc. for $C_{15}H_{22}O_3$ (250.34): C 71.97, H 8.86; found: C 71.55, H 8.71.

rel-(*1S,4R,7R,9R,10S*)-*10-Hydroxytetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodecane-1-methanol* (**8b**). Under reflux **6** (0.15 g, 0.605 mmol) was reduced with $LiAlH_4$ (0.035 g, 0.925 mmol) in Et_2O (10 ml). The isolated, solid material gave, after crystallization from $CHCl_3$, 0.092 g (73%) of **8b**. M.p. 145°. IR (KBr): 3280*s* (br.), 2982*s*, 2978*s*, 2977*s*, 2840*s*, 1480*m*, 1463*m*, 1450*m*, 1440*m*, 1370*w*, 1345*w*, 1340*w*, 1310*w*, 1270*w*, 1250*w*, 1230*w*, 1185*w*, 1150*m*, 1105*m*, 1080*m*, 1068*s*, 1050*s*, 1039*s*, 1020*s*, 990*m*, 968*w*, 953*w*, 938*w*, 925*w*. ^{1}H-NMR: ((D$_5$)pyridine): 1.1–1.35 (stack, 2 H); 1.35–1.50 (stack, 2 H); 1.50–1.7 (stack, 2 H); 2.0–2.15 (stack, 2 H); 2.15–2.35 (stack, 2 H); 2.5–2.75 (stack, 3 H); 2.9–3.0 (*dd*, *J* = 11.7, 6.85, 1 H); 3.5–3.59 (*dd*, *J* = 10.82, 1.65, H$_a$); 3.6–3.68 (*dd*, *J* = 10.89, 1.54 H$_b$); 5.35–5.45 (*dd*, *J* = 16.0, 7.8, 1 H); 5.9 (br., 2 H). ^{13}C-NMR: 19.79 (*t*); 26.08 (*t*); 28.69 (*t*); 31.99 (*t*); 33.32 (*t*); 36.33 (*d*); 37.26 (*t*); 38.19 (*d*); 42.13 (*d*); 56.39 (*s*); 63.91 (*t*); 74.0 (*s*); 76.08 (*d*). MS: 208 (0.006, M^+), 190 (3), 178 (29), 160 (12), 159 (61), 149 (16), 135 (25), 134 (27), 133 (41), 131 (27), 119 (19), 117 (29), 107 (20), 105 (23), 95 (23), 93 (21), 91 (38), 81 (11), 79 (25), 77 (12).

Ethyl rel-(*1S,4R,9R*)-*10-Oxotetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodec-7-ene-1-carboxylate* (**9**). A soln. of 0.20 g (0.81 mmol) of ethyl 6-(but-3-inyl)-3-oxobicyclo[3.3.0]oct-4-ene-1-carboxylate in 0.5 mol of *t*-BuOMe was irradiated in a quartz flask with a low-pressure Hg lamp. After separation of some polymeric material, the solvent was evaporated: 0.19 g of a greenish oil, which was purified by CC (hexane/*t*-BuOMe 6:4): 0.114 g (57%) of **9**. TLC (hexane/*t*-BuOMe 6:4): R_f 0.36. GC (100°): t_R 23.50 min. IR: 3310*w*, 3000*w*, 2950*m*, 2870*w*, 1725*s*, 1460*w*, 1455*w*, 1445*w*, 1400*w*, 1368*w*, 1265*m*, 1190*m*, 1025*m*. ^{1}H-NMR: 2.55 (*m*, H$_c$–C(2), corr. to *H$_t$*–C(2), *H$_c$*–C(3), *H$_t$*–C(3)); 1.63 (*m*, H$_t$–C(2); corr. to *H$_c$*–C(2), *H$_c$*–C(3), *H$_t$*–C(3)); 1.79 (*m*, H$_c$–C(3); corr. to *H$_c$*–C(2), *H$_t$*–C(2), *H$_t$*–C(3)); 2.16 (*m*, H$_t$–C(3); corr. to *H$_c$*–C(2), *H$_t$*–C(2), *H$_c$*–C(3), *H*–C(4)); 2.60 (*m*, H–C(4); corr. to *H$_t$*–C(3), *H$_c$*–C(5), *H$_t$*–C(5)); 1.90 (*m*, H$_c$–C(5); corr. to *H*–C(4), *H$_t$*–C(5), C*H*$_2$(6)); 2.14 (*m*, H$_t$–C(5); corr. to *H*–C(4), *H$_c$*–C(5), C*H*$_2$(6)); 2.22 (*m*, H$_c$–C(6); corr. to *H$_c$*–C(5), *H$_t$*–C(5), *H*–C(9)); 2.13 (*m*, H$_t$–C(6); corr. to *H$_c$*–C(5), *H$_t$*–C(5), *H*–C(9)); 5.97 (*s*, H–C(8); corr. to C*H*$_2$(6); *H*–C(9)); 2.98 (*m*, H–C(9); corr. to C*H*$_2$(6), *H*–C(8), *H$_c$*–C(11), *H$_t$*–C(11)); 3.18 (*dd*, H$_c$–C(11); corr. to *H*–C(9), *H$_t$*–C(11), CH$_3$C*H*$_2$O); 2.56 (*dd*, H$_t$–C(11); corr. to *H*–C(9), *H$_c$*–C(11), CH$_3$C*H*$_2$O); 4.17 (*dq*, 1 H, CH$_3$C*H*$_2$O; corr. to C*H*$_3$CH$_2$O); 4.11 (*dq*, 1 H, CH$_3$C*H*$_2$O; corr. to C*H*$_3$CH$_2$O); 1.26 (*t*, C*H*$_3$CH$_2$O; corr. to CH$_3$C*H*$_2$O). ^{13}C-NMR: 53.67 (*s*, C(1)); 38.42 (*t*, CH$_2$(2)); 33.16 (*t*, CH$_2$(3)); 42.71 (*d*, CH(4)); 37.40 (*t*, CH$_2$(5)); 26.76 (*t*, CH$_2$(6)); 161.41 (*s*, C(7)); 125.84 (*d*, CH(8)); 53.39 (*d*, CH(9)); 214.03 (*s*, C(10)); 51.42 (*t*, CH$_2$(11)); 70.41 (*σ*, C(12)); 174.95 (*s*, *C*OOEt); 60.93 (*t*, CH$_3$*C*H$_2$O); 14.20 (*q*, *C*H$_3$CH$_2$O). MS (GC/MS): 246 (7, M^+), 218 (15), 190 (20), 173 (27), 146 (29), 145 (100), 144 (30), 131 (24), 130 (52), 129 (42), 128 (25), 118 (20), 117 (92), 116 (22), 115 (44), 105 (35), 91 (73), 79 (28), 77 (42), 65 (33).

Ester **5** *from* **9**. A soln. of **9** (0.05 g, 0.2 mmol) in MeOH was hydrogenation over Pd/C to give, after FC chromatography, 0.044 g (87%) of **5**.

Ethyl rel-(*1R,4R,9R,10S*)-*10-Hydroxytetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodec-7-ene-1-carboxylate* (**10a**). A soln. of **9** (1.0 g, 3.3 mol) in anh. MeOH (33 ml) was treated with $NaBH_4$ (0.19 g, 4.85 mmol). After 1 h, the solvent was evaporated and the residue dissolved in Et_2O. After workup and FC (hexane/*t*-BuOMe 6:4), 0.426 (52%) of **10a** were obtained. TLC (hexane/*t*-BuOMe 6:4): R_f 0.19. GC (100°): t_R 25.90 min. IR: 3440*m*, 3000*s*, 2920*s*, 2870*m*, 1711*s*, 1695*s*, 1445*m*, 1430*m*, 1370*m*, 1330*w*, 1310*m*, 1300*m*, 1280*m*, 1260*s*, 1190*s*, 1130*s*, 1110*s*. ^{1}H-NMR: 5.87 (*q*, *J* = 1.5, 1 H); 4.15 (*dq*, *J* = 10.9, 7.4, 1 H); 4.14 (*dq*, *J* = 10.9, 7.4, 1 H); 4.12 (*m*, 1 H); 3.71 (br. *s*, 1 H); 2.96 (*m*, 1 H); 2.61 (*d*, *J* = 14.3, 1 H); 2.47 (*dt*, *J* = 12.9, 7.4, 1 H); 2.38 (*dq*, *J* = 7.4, 4.5, 1 H); 2.29–2.15 (*m*, 2 H); 2.08–1.83 (*m*, 4 H); 1.74 (*m*, 1 H); 1.61 (*ddd*, *J* = 12.9, 7.4, 6.3, 1 H); 1.30 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR: 178.6 (*s*); 158.7 (*s*); 125.4 (*d*); 70.6 (*s*); 70.6 (*d*); 61.1 (*t*); 56.8 (*s*); 55.3 (*d*); 50.2 (*t*); 45.2 (*d*); 37.2 (*t*); 35.2 (*t*); 32.3 (*t*); 26.6 (*t*); 14.2 (*q*). MS: 248 (27, M^+), 220 (16), 219 (21), 218 (17), 202 (28), 192 (40), 175 (93), 174 (94), 173 (51), 161 (27), 160 (28), 157 (44), 147 (56), 146 (100), 145 (86), 133 (58), 132 (27), 131 (68), 130 (26), 129 (40), 128 (26), 119 (36), 118 (24), 117 (61), 115 (26), 107 (33), 105 (35), 93 (22), 91 (60), 84 (20), 79 (24), 77 (28), 55 (20).

Ethyl rel-(*1R,4R,9R,10S*)-*10-Acetoxytetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodec-7-ene-1-carboxylate* (**10b**). To a soln. of **10a** (0.55 g, 2.2 mmol) in abs. Et_2O (20 ml) was added pyridine (0.52 g, 6.6 mmol) and AcBr (495 µl, 6.6 mmol) in abs. Et_2O (5 ml). After stirring overnight at r.t., the mixture was worked up and the crude material purified by FC (hexane/*t*-BuOMe 4:1): 0.341 g (53%) of **10b**. TLC (hexane/*t*-BuOMe 6:4): R_f 0.49. GC (100°): t_R 27.47 min. IR: 3060*w*, 3005*m*, 2940*s*, 2870*m*, 1730*vs*, 1480*w*, 1455*m*, 1430*m*, 1375*m*, 1370*m*, 1258*vs*, 1132*m*, 1108*m*, 1080*m*, 1027*m*. ^{1}H-NMR: 5.58 (*m*, 1 H); 4.87 (*ddd*, *J* = 5.9, 5.5, 2.9, 1 H); 4.13 (*q*, *J* = 7.0, 2 H); 2.93 (*m*, 1 H); 2.78 (*dd*, *J* = 14.2, 2.9, 1 H); 2.48 (*m*, 1 H); 2.32 (*qd*, *J* = 8.5, 2.9, 1 H); 2.23–2.05 (*m*, 3 H); 2.00 (*s*, 3 H); 1.98 (*dd*, *J* = 14.2, 5.5, 1 H); 1.95 (*m*, 1 H); 1.86 (*m*, 1 H); 1.78 (*ddd*, *J* = 12.5, 7.4, 5.2, 1 H); 1.67 (*dddd*, *J* = 12.5, 7.4, 5.2, 2.9, 1 H); 1.27 (*t*, *J* = 7.0, 3 H). ^{13}C-NMR: 176.3 (*s*); 170.8 (*s*); 159.8 (*s*); 122.1 (*d*); 74.3 (*s*); 73.4 (*d*); 60.4 (*t*); 55.9 (*s*); 51.8 (*d*); 45.5 (*d*); 44.2 (*t*); 37.7 (*t*); 35.9 (*t*); 30.7 (*t*); 27.1 (*t*); 21.1 (*q*); 14.3 (*q*). MS: 290 (14, M^+), 249 (18), 248 (81), 230 (14), 220 (12), 219 (22), 203 (29), 202 (72), 190 (12), 175 (46), 174 (100), 173 (40), 160 (24), 157 (63), 156 (26), 147 (16), 146 (36), 145 (33), 133 (16), 131 (7), 129 (22), 117 (29). Anal. calc. for $C_{17}H_{22}O_4$ (290.36): C 70.32, H 7.64; found: C 69.99, H 7.74.

Ethyl rel-*(1R,4R,7R,9R,10S)-10-Acetoxytetracyclo[5.4.1.0^{4,12}.O^{9,12}]dodecane-1-carboxylate* (**7b**). A sample of **10b** (0.06 g, 0.21 mmol) in MeOH (6 ml) was hydrogenated over Pd/C and gave, after FC (hexane/*t*-BuOMe 4:1), 0.038 g (62%) of **7b**. TLC (hexane/*t*-BuOMe 6:4): R_f 0.47. GC (100°): t_R 27.5 min. IR: 2950*s*, 2870*m*, 1720*vs*, 1480*w*, 1460*m*, 1450*m*, 1375*m*, 1320*m*, 1250*vs*, 1182*m*, 1170*m*, 1150*m*, 1135*m*, 1120*m*, 1080*w*, 1050*m*, 1030*m*, 910*w*. ^{1}H-NMR: 5.25 (*dd*, *J* = 12.5, 5.9, 1 H); 4.17 (*dq*, *J* = 10.7, 7.0, 1 H); 4.11 (*dq*, *J* = 10.7, 7.0, 1 H); 2.83 (*dd*, *J* = 14.0, 5.9, 1 H); 2.59 (*q*, *J* = 5.9, 1 H); 2.43–2.31 (*m*, 2 H); 2.20–2.06 (*m*, 2 H); 2.04 (*s*, 3 H); 2.01 (*m*, 1 H); 1.93 (*dd*, *J* = 14.0, 5.9, 1 H); 1.92–1.81 (*m*, 2 H); 1.75 (*m*, 1 H); 1.69–1.58 (*m*, 2 H); 1.55–1.42 (*m*, 2 H); 1.28 (*t*, *J* = 7.0, 3 H). ^{13}C-NMR: 175.8 (*s*); 170.8 (*s*); 77.4 (*d*); 72.3 (*s*); 60.2 (*t*); 59.9 (*s*); 52.6 (*d*); 46.0 (*d*); 42.0 (*t*); 41.4 (*t*); 39.8 (*d*); 35.5 (*t*); 35.6 (*t*); 35.3 (*t*); 21.1 (*q*); 20.3 (*t*); 14.3 (*q*). MS (23°): 292 (20, M^+), 233 (36), 232 (98), 206 (17), 205 (25), 204 (40), 203 (35), 186 (18), 178 (30), 177 (14), 160 (33), *159* (100), 158 (54), 149 (16), 133 (16), 131 (28), 130 (16), 119 (72), 118 (44), 117 (38), 105 (34), 91 (32), 43 (26). Anal. calc. for $C_{17}H_{24}O_4$ (292.38): C 69.84, H 8.27; found: C 69.98, H 8.27.

X-Ray Structure Analysis of **8b**. Compound **8b** was obtained by recrystallization from hot $CHCl_3$. The fragment to be measured (*ca.* 0.3 × 0.3 × 0.3 mm^3) was cut from one of the colorless crystals trying to get the best single crystal available. On an *Enraf-Nonius-CAD4* diffractometer, 4380 diffraction intensities ($-16 \geq h \geq 16$, $0 \geq k \geq 16$, $0 \geq l \geq 12$) were recorded, using graphite-monochromated Mo$K\alpha$ radiation to $\sin\Theta/\lambda_{max} = 0.59$ Å^{-1} ($\Theta_{max} = 25°$). The intensity of (−2 0 −2) was recorded every 180 reflections and showed a decrease of 3.5% during the experiment (exposure time 72 h). Data reduction was carried out according to the procedure developed by *Hoppe* [14]. Data were corrected for decay, *Lorentz*, and polarisation effects, but no absorption correction was applied. Equivalent reflections were merged and reflections inconsistent with reflection conditions rejected. From the remaining 3990 unique reflections, 1873 with $F > 6\sigma(F)$ were considered observed. The structure was solved using the direct-methods package SHELXS86 [15], and 284 parameters were refined by full-matrix least-squares on *F* with SHELX76 [16]. Non-H-atoms were refined anisotropically, while the two pairs of hydroxy H-atoms were attached with a fixed distance of 0.85 Å to the corresponding O-atoms and refined isotropically. The remaining H-atoms were attached using a riding model with C–H = 0.98 Å. For the final weighting scheme, *R*, R_w, goodness of fit, and, max. shift/e.s.d., see *Table 4*. Max. peak and the min. through in final difference *Fourier* synthesis were 0.29 (near C(5′)) and −0.24 (near C(2′)). Atomic scattering factors were obtained from [17]. Bond angles and lengths are given in *Table 1* and crystallographic data in *Table 4*. Supplementary material was deposited with the *Cambridge Crystallographic Data Centre*.

Table 4. *Crystallographic Data for* **8b**

Molecular formula	$C_{13}O_2H_{20}$	Range/indices (*h*, *k*, *l*)	−16 16, 0 16, 0 12
Molecular weight	208.17	Θ_{max} [°]	25
Crystal system	monoclinic	No. of reflections	
Space group	$P2_1/c$	between stds.	180
Cell dimensions		Total unique data	3990
a [Å]	13.861(7)	Observed data, $I > 6\sigma(I)$	1873
b [Å]	15.22(2)	Abs. coeff. μ [cm^{-1}]	0.45
c [Å]	10.88(1)	Decay [%]	3.5
β [°]	98.19(6)	No. of variables	284
V [Å^3]	2273.12	Weighting scheme applied	$w = 0.8126/[\sigma^2(F) + 0.001(F^2)]$
Z	8	$R\ \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0627
d_{calc} [g/cm^3] (25%)	1.22	$R_w\ [\Sigma\omega(\|F_o\|-\|F_c\|)^2/\Sigma\omega\|F_o\|^2]^{1/2}$	0.0636
Crystal dimensions [mm^3]	0.3 × 0.3 × 0.3	Goodness of fit	1.583
Radiation [Å]	λ(MoK_α) 0.71069	Δ/σ(max)	0.002

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