# Synthesis and Characterization of Diastereoisomerically Pure Tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4-carboxylic Acid Derivatives

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The synthesis and detailed NMR analysis of diastereoisomerically pure samples of 4-methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4-carboxylic acid (**2**), tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4-carboxylic acid (**6**) and their *tert*-butyl esters are reported. Mixtures containing two isomers of the methyl esters of these compounds were obtained by a twofold, sequential *Diels-Alder* reaction between cyclopentadiene, and methyl methacrylate or methyl acrylate, respectively. Pure diastereoisomers of the acids were prepared by selective hydrolysis of their methyl esters.

**Introduction.** – Derivatives of tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-4-ene[1]) have gained increasing interest as starting materials for the preparation of specialty polymers as indicated by numerous patents relating to this topic. The excellent mechanical properties of these materials combined with their high VIS and UV transparency makes them particularly suitable for applications like substrates for compact discs, optical fibers, and lenses. An important product for these applications has been commercialized as *Arton*® by *JSR*. More recently, polymers based on the tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-4-ene structure have shown great promise as a platform from which to design chemically amplified photoresists for 193-nm microlithography [1–4]. This application demands polymers with both high transparency at the exposure wavelength, and good mechanical and chemical stability, especially against reactive-ion etching [5]. It has been found experimentally that a high C/H ratio in the empirical formula of the polymer is required to meet the latter requirement [6]. In the past, this was achieved through incorporation of aromatic moieties, but aromatics absorb strongly at 193 nm so their use is essentially precluded. Incorporation of alicyclic structures provides a means to meet both the etch resistance and the transparency requirements. The tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-4-ene ring system is, therefore, an attractive basis for the design of such systems.

The tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-4-ene skeleton is accessible by two sequential *Diels-Alder* reactions with cyclopentadiene. As early as 1938, *Alder* and *Windemuth* described the first synthesis of the fully saturated basic structure '1,4:5,8-bis-*endo*-methylene-decalin' [7]. Even earlier, *Alder* and *Stein* concluded from their experiments on the polymerization of cyclopentadiene that the sequential addition of cyclopentadiene to a dienophile occurs in a specific way so that diastereoisomers are generated only in the very first *Diels-Alder* addition [8]. Several years later, *Soloway* established the complete configuration of tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-4-ene by an

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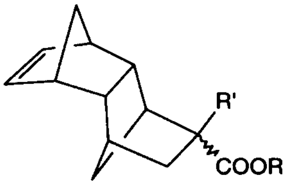
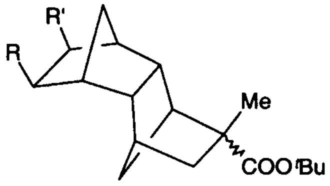
[1]) *Chemical Abstracts: 1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene* [21635-90-5].

elegant derivatization experiment [9]. Generalizing his findings, he concluded that the repeated addition of cyclopentadiene always occurs in an *exo*-fashion relative to the preceding norbornene unit such that any two adjacent methylene bridges point in opposite directions with respect to their decalin unit.

Application to photoresist technology requires synthesis of polymers derived from tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodec-4-ene derivatives bearing a polar functionality, including for example, acid-sensitive *t*-Bu esters. This functionality is required to provide the light-induced solubility-switching function, control of adhesion, adjustment of $T_g$, *etc.* [5]. Methyl 4-methyltetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodec-9-ene-4-carboxylate (**1**)2) and methyl tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodec-9-ene-4-carboxylate (**5**)3) are valuable precursors to the functionalized monomers required for the design of 193-nm photoresists. The synthesis of these and closely related compounds has been subject to several patents [10][11], and it has also been mentioned briefly in the open literature (including the direct preparation of the *t*-Bu ester **7** from *tert*-butyl acrylate and (di)cyclopentadiene) [4][12]. The use of methacrylate derivatives for the preparation of photoresist polymers has been mentioned as well [2]. However, none of these publications gives any analytical data for the monomers or indicates the configuration of these compounds. In light of the older literature mentioned above, it is likely that diastereoisomers only result from the formation of the first norbornene unit by addition of cyclopentadiene to methacrylate or acrylate, respectively. Nevertheless, because of the technological importance of these monomers, it was both interesting and useful to us to obtain isomerically pure compounds, to elucidate their configuration, and to establish the assignment of the $^1$H- and $^{13}$C-NMR signals of the different isomers in more detail. On the one hand, this is the first step in order to judge possible influences of isomer mixtures and isomer ratios on the polymer properties, and, on the other hand, it is the basis for more extensive chemical variation of these interesting monomers.



**1** R = Me, R' = Me
**2** R = H, R' = Me
**3** R = *t*-Bu, R' = Me
**6** R = H, R' = H
**7** R = *t*-Bu, R' = H



**4a** R = OH, R' = H
**b** R = H, R' = OH

In this paper, we present the preparation and detailed analytical data for the diastereoisomerically pure acids and *tert*-butyl esters derived from **1** and **5**. In addition,

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2) *Chemical Abstracts: 1,2,3,4,4a,5,8,8a-octahydro-2-methyl-1,4:5,8-dimethanonaphthalene-2-carboxylic acid methyl ester* [58732-15-3].

3) *Chemical Abstracts: 1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene-2-carboxylic acid methyl ester* [41596-02-5].

we describe, as an example, the hydroboration product **4x**, which may be used as precursor for the introduction of an acrylate unit or other polymerizable groups.

**Results and Discussion.** – As starting materials for our investigations, we prepared the methyl esters **1** and **5** by a twofold *Diels-Alder* addition of cyclopentadiene to methyl methacrylate or methyl acrylate, respectively. The two major complications in this *Diels-Alder* reaction are the formation of tri(cyclopentadiene) (which is difficult to remove from the product by distillation because of its very similar boiling point) and the formation of polymeric material. Tri(cyclopentadiene) formation was reduced successfully by using (somewhat counter-intuitively) an excess of the dienophile in the reaction. This leads to increased formation of the bicyclic derivative, but this compound can be isolated easily and re-used as starting material for the reaction. The formation of polymeric by-products was reduced significantly by using freshly cracked cyclopentadiene as starting material instead of di(cyclopentadiene) (as proposed in [10–12]) and especially at longer reaction times, by the addition of a radical scavenger. A relatively long reaction time combined with limiting the temperature to 180° proved to be the most successful preparation method for **1**. In the case of **5**, good results were also obtained with significantly shorter reaction times at higher temperature.

GC Analysis of the products of the *Diels-Alder* reaction shows the presence of significant amounts of two isomers. The ratio of the two isomers varies with reaction temperature, giving decreasing amounts of the *exo*-isomer **1x** and increasing amounts of **5x** with increasing temperature[4]). We observed that a diastereoisomerically pure sample of the *endo*-isomer **1n** with the sterically less accessible ester group could be recovered after incomplete hydrolysis of **1**. This led us to use selective hydrolysis in order to obtain isomerically pure samples of the acids **2** and **6** (*Schemes 1* and *2*). As can be seen from *Fig. 1*, under suitable conditions, the rate of hydrolysis of the two isomers is very different, which makes it possible to obtain the two isomers easily in high purity and satisfying yield.

The isomers of **2** and **6** were converted to the *tert*-butyl esters either *via* the acid chloride (for **7x**) or *via* the formation of a mixed anhydride of the carboxylic acid with $(CF_3CO)_2O$ (TFAA) in toluene or dry THF [13]. Compound **6n** could be esterified *via* the acid chloride as well, but the product showed *ca.* 10% epimerization at the stereogenic center C(4). The acid-chloride pathway was not successful for **2** and gave dark-colored material in this case.

Finally, the *tert*-butyl ester **3x** was converted to the alcohol **4x**, giving rise to a 1:1 mixture of two regioisomers **4xa** and **4xb**.

The configuration and the assignment of the $^1$H-NMR signals of all isomers was determined by proton correlation spectroscopy (COSY) complemented by several nuclear-*Overhauser*-effect (NOE) difference experiments [14]. *J* Values were extracted from the 1D-NMR spectra. The results of the $^1$H-NMR experiments are summarized in *Schemes 1* and *2*. The COSY experiments show no coupling between protons at C(2) and C(7) with those at C(3) and C(6), but coupling with those at C(1) and C(8). This indicates a 90° arrangement of H–C(2) and H–C(7) relative to H–C(3) and H–C(6) and consequently an *anti*-position for H–C(2) and H–C(7) relative to H–C(12) but

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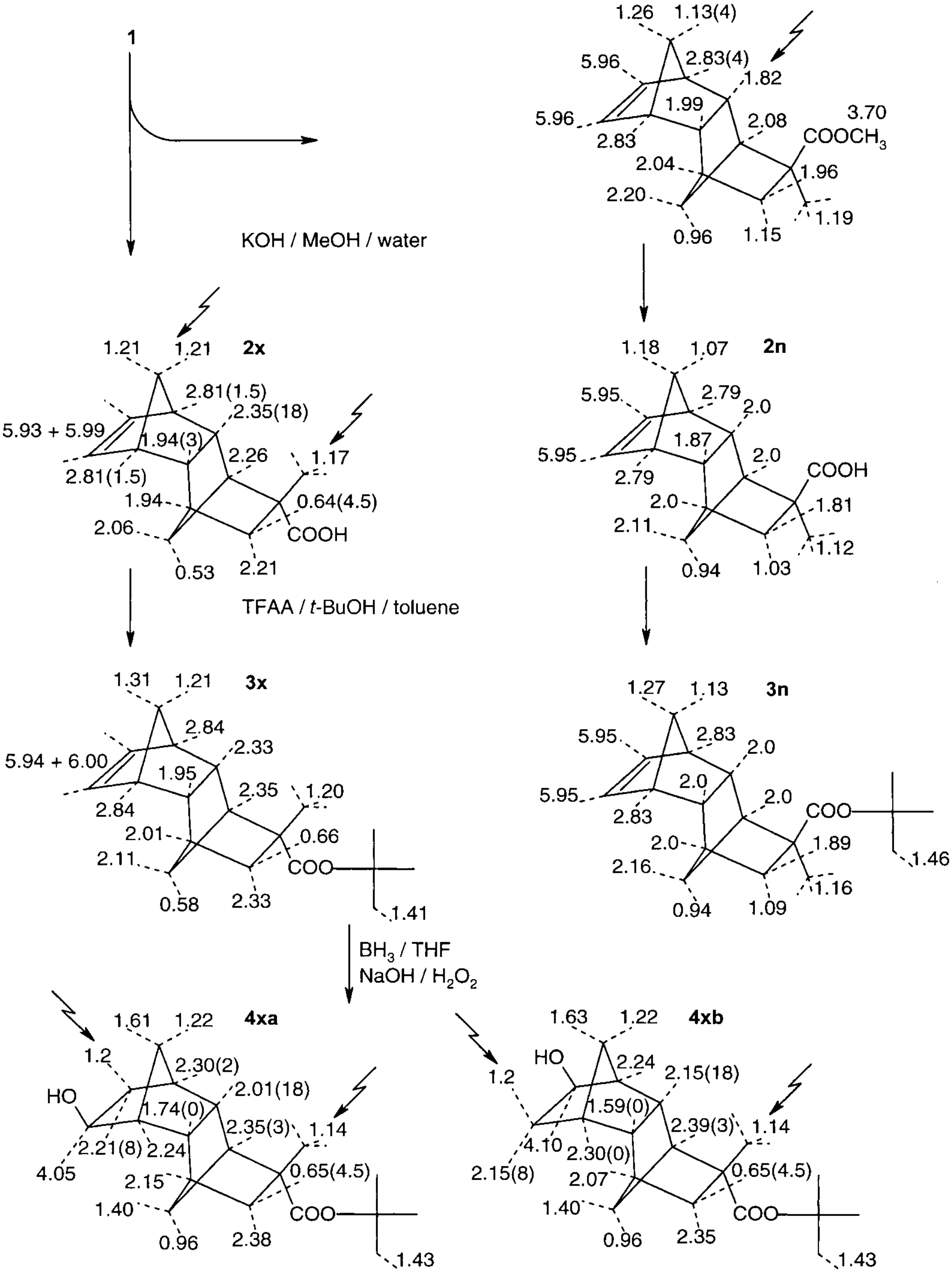
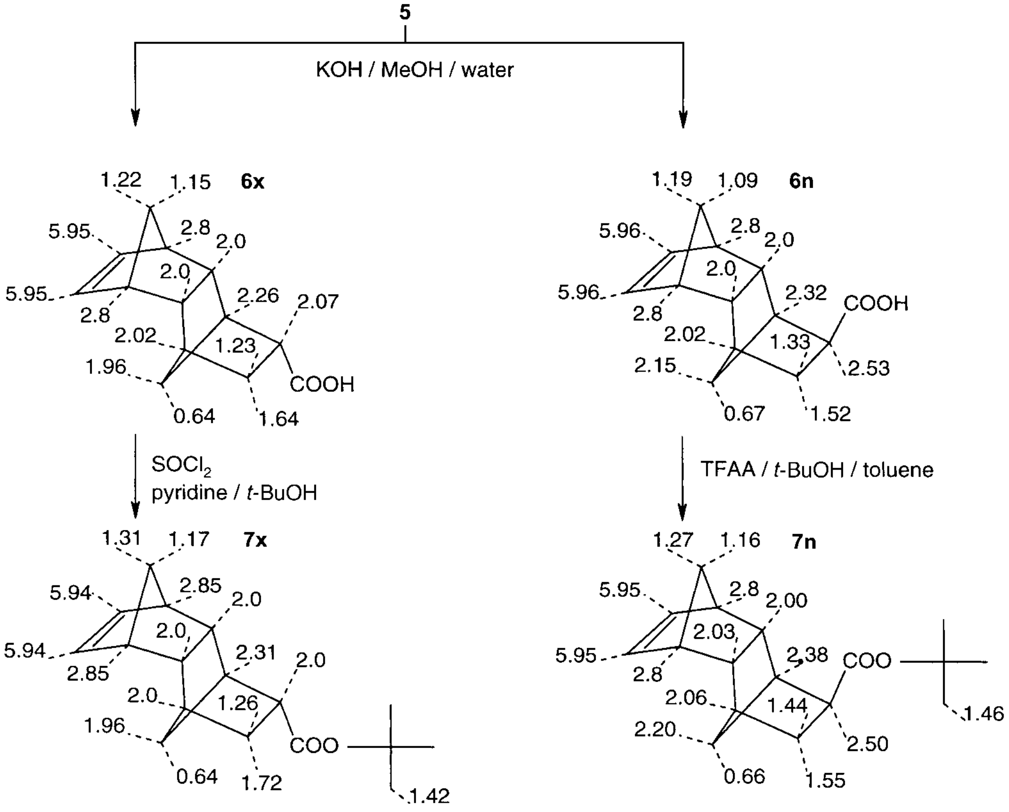
[4]) Here, *endo* and *exo* (**n**, **x**) refer to the orientation of the carboxylic acid or carboxylate group.

Scheme 1. *Assignment of* $^1$*H-NMR Chemical Shifts for Derivatives of Methyl 4-Methyltetracyclo[6.2.1.1*$^{3,6}$*.0*$^{2,7}$*]-dodec-9-ene-4-carboxylate* (**1**). NOEs [%] for irradiation at the indicated positions are given in parentheses.



Scheme 2. *Assignment of* $^{1}$*H-NMR Chemical Shifts for Derivatives of Methyl Tetracyclo[6.2.1.1*$^{3,6}$*.0*$^{2,7}$*]dodec-9-ene-4-carboxylate* (**5**)



*syn*-position relative to H–C(11). A small coupling is also observed for H–C(2) and H–C(7) with $H_{syn}$–C(12) (*W*-arrangement), providing additional support for the proposed configuration. In the case of the derivatives of **5**, the coupling between H–C(3) and H–C(4) clearly indicates the configuration at C(4) as well. As an example, part of the COSY spectrum of **2x** is shown in *Fig. 2*. $^{13}$C-NMR Signals were either assigned by $^{1}$H,$^{13}$C-heteronuclear shift correlation (HETCOR) or by a *J*-modulated spin-echo experiment (APT), and by analogy to the assignments determined with HETCOR. Some HETCOR experiments were performed in the presence of a shift reagent ([Eu(fod)]) in order to distinguish between H–C(2) and H–C(7), and C(2) and C(7), respectively. The $^{13}$C-NMR data for the carboxylic acids and *tert*-butyl esters are summarized in *Table 1*. The configurations of the two compounds **1n** and **3x** were additionally verified by X-ray crystallography (*Fig. 3* and *Table 2*).

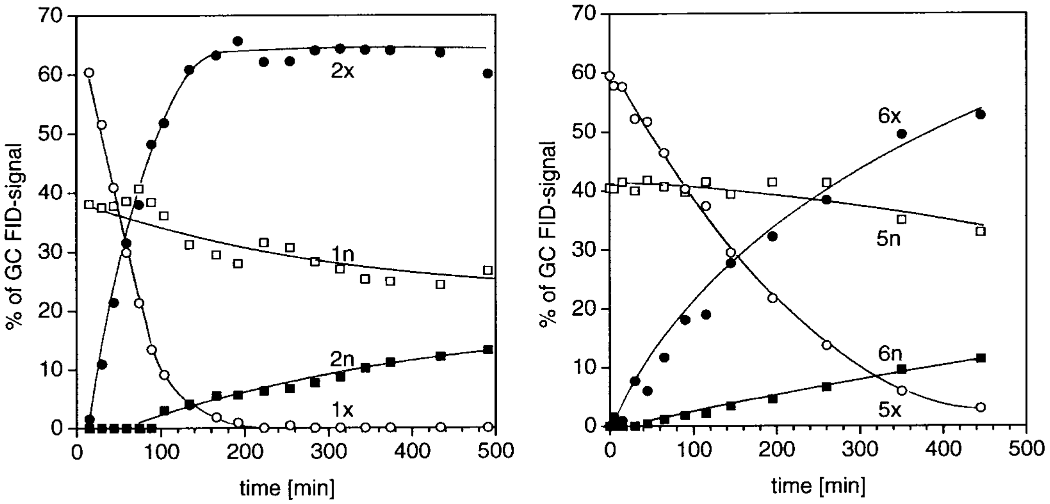


Fig. 1. *Hydrolysis kinetics for* **1** (10 g) *in 20 ml of MeOH/5 ml of $H_2O$/6 g of KOH under reflux* (left) *and for* **5** (10 g) *in 20 ml of MeOH/5 ml of $H_2O$/3 g of KOH at 22 ± 1°* (right)

## Experimental Part

*General.* All solvents, KOH (85%), *t*-BuOH, and pyridine were obtained from *EM Science* in reagent-grade quality. Methyl methacrylate (99%; stabilized with 10–100 ppm MEHQ), methyl acrylate (99%; stabilized with 100 ppm MEHQ), 4-(*tert*-butyl)catechol, $(CF_3CO)_2O$, $BH_4 \cdot THF$ (1M soln. in THF), and $[Eu(fod)_3]$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate were purchased from *Aldrich*. Di(cyclopentadiene) (technical grade) was purchased from *Lancaster* and $SOCl_2$ (99.5%) from *Acros*. The samples of **1** and **6** used in the derivatization steps were obtained as a gift from *Japan Synthetic Rubber Co. Ltd.* as a mixture of *ca.* 60% *exo*- and 40% *endo*-product. All chemicals were used as received with the following exceptions: *t*-BuOH and pyridine were dried over $CaH_2$ and distilled prior to use. Cyclopentadiene was obtained by cracking di(cyclopentadiene) at 200°, distilled over a 30-cm *Vigreux* column and collected in a round-bottomed flask cooled with dry ice. Bulb-to-bulb distillations were performed with a *Büchi B-580* glass oven. M.p.: *Mel-Temp II*, *Laboratory Devices*; uncorrected. GC: *Hewlett Packard 5890 Series II* with cap. column *HP-5* (crosslinked 5% PH ME siloxane) and flame-ionization detector (FID); temp. ramp from 50 to 100° over 1 min, followed by a ramp from 100 to 200° over 10 min; all purity indications are based on GC analysis. FT-IR: *Nicolet Avatar 360*; in $cm^{-1}$. 1D and 2D $^1H$- and $^{13}C$-NMR: *Varian Unity plus* ($^1H$: 300 MHz, $^{13}C$: 75.5 MHz), *Varian Unity Inova 500* ($^1H$: 500 MHz, $^{13}C$: 125.5 MHz), and *Bruker AMX-500* ($^1H$: 500 MHz); chemical shifts $\delta$ in ppm relative to TMS, coupling constants $J$ in Hz. All $^1H$ signals were assigned by homonuclear shift correlation (COSY). Chemical-ionization mass spectra (CI-MS): *Finnigan MAT TSQ 700*, $CH_4$ was used as reactand gas, values as $m/z$ (rel. int. %). X-Ray crystal-structure analysis[5]): the data were collected using the $\omega$-scan technique with a 1.2° scan range in $\omega$ on a *Siemens P4* diffractometer, equipped with a *Nicolet LT-2* low-temp. device and a graphite monochromator with $MoK_\alpha$ radiation ($\lambda = 0.71073$ Å). Details of crystal data and structure refinement are listed in *Table 2*. Check reflections were remeasured periodically to monitor instrument and crystal stability. A small correction (< 1%) was applied to the data. The data were corrected for Lp effects but not for absorption. Data reduction, decay correction, structure solution, and refinement were performed using the SHELXTL/PC software package [15]. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H-atoms. The H-atom positions were observed in a $\Delta F$

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[5]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-117232 (**1n**) and CCDC-117231 (**3x**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

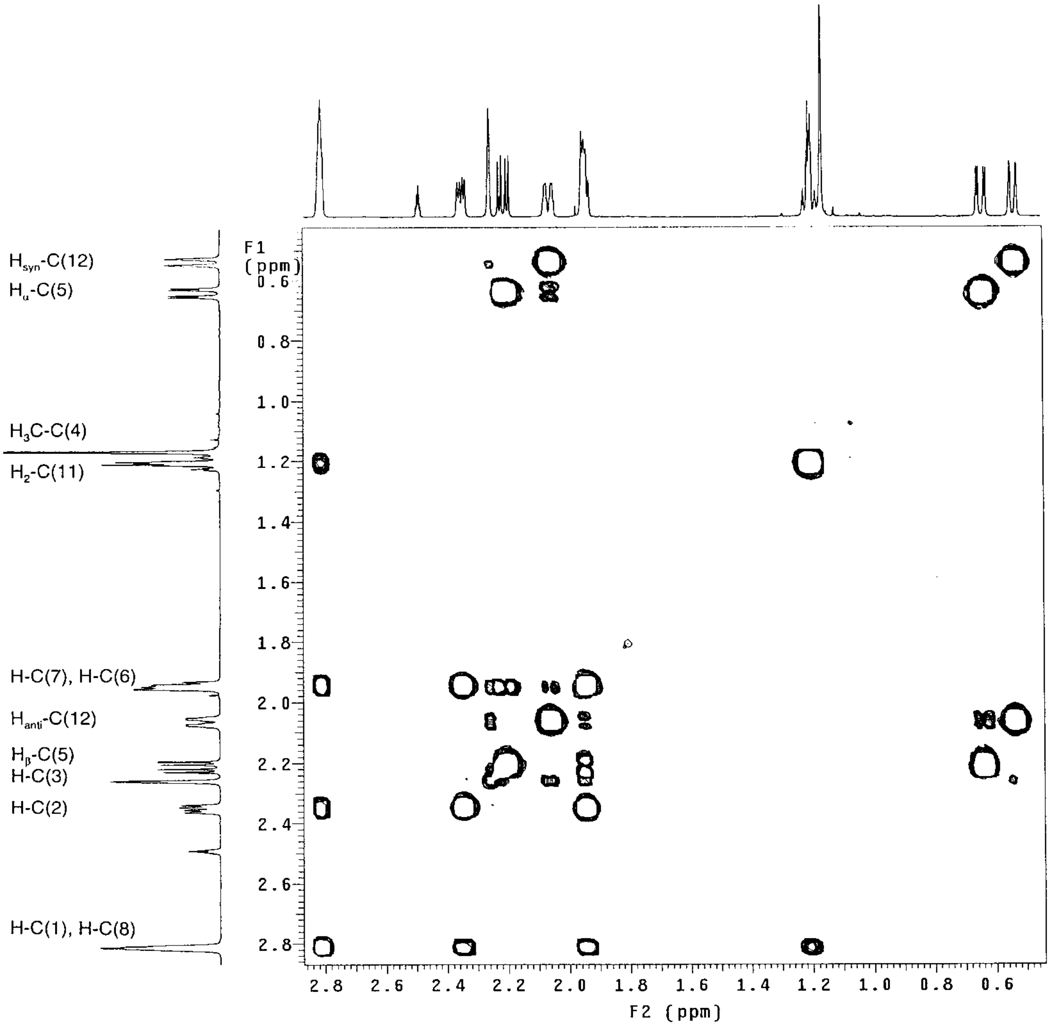


Fig. 2. *Part of the COSY spectrum of* **2x**

map and refined with isotropic displacement parameters. The function, $\Sigma w(|F_o|^2-|F_c|^2)^2$, was minimized, where $w=1/[(\sigma(F_o))^2+(a\times P)^2+(b\times P)]$ and $P=(|F_o|^2+2|F_c|^2)/3$. The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr}=kF_c/[1+EXTI)\times F_c^2\ \lambda^3/(\sin 2\theta)]^{0.25}$ where $k$ is the overall scale factor. The value for *EXTI* is listed in *Table 2*. Neutral-atom-scattering factors and values used to calculate the linear absorption coefficient are from the *International Tables for X-Ray Crystallography* (1992) [16]. All figures were generated using SHELXTL/PC [15].

*Methyl 4-Methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4-carboxylate* (**1**). A 250-ml stainless-steel reactor (*Parr Instrument Company*) was charged with methyl methacrylate (21.5 ml, 0.2 mol), cyclopentadiene (25 ml, 0.3 mol), and 4-(*tert*-butyl)catechol (350 mg, 2 mmol), put into an oil bath that was preheated to 180° and left at this temp. for 16 h. Twofold distillation of the crude product over a 30-cm *Vigreux* column gave 17.9 g of a mixture of 90% methyl *endo*/*exo*-2-methylbicyclo[2.2.1]hept-5-ene-2-carboxylate (48% yield relative to methyl methacrylate) and 10% di(norbornene) (2 mmHg, 25–34°), 3.1 g of an intermediate fraction containing mainly

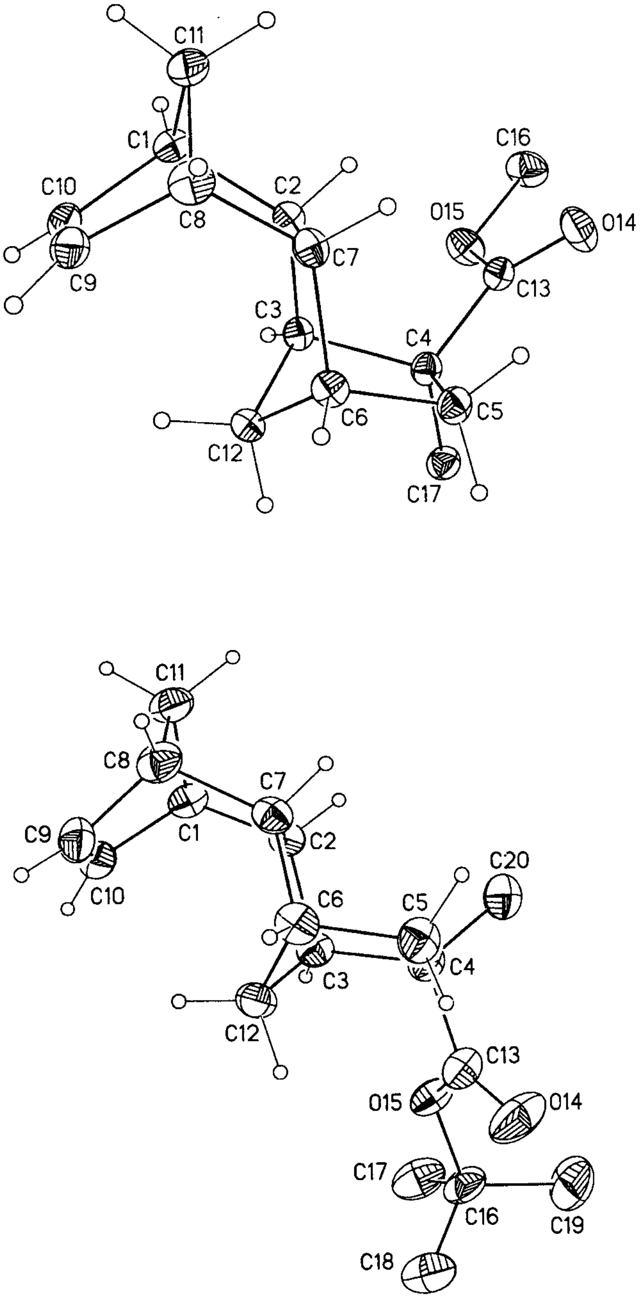
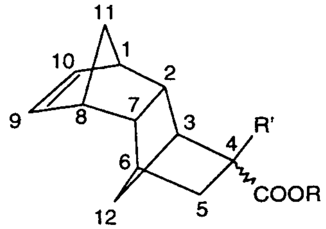


Fig. 3. *X-Ray crystallography structures of* **1n** (top) *and* **3x** (bottom). The thermal ellipsoids are scaled to the 30% probability level. The H-atoms are drawn to an arbitrary scale. The H-atoms of the Me groups have been omitted for clarity.

Table 1. *$^{13}$C-NMR Chemical Shifts*



| C-Atom | **2x** | **2n** | **3x** | **3n** | **6x** | **6n** | **7x** | **7n** |
|---|---|---|---|---|---|---|---|---|
| C(1), C(8) | 46.1,<br>46.2 | 46.2,<br>46.3 | 46.6,<br>46.8 | 46.6,<br>46.7 | 45.9,<br>46.0 | 46.0,<br>46.3 | 46.4,<br>46.5 | 46.6,<br>46.8 |
| C(2), C(7) | 40.8,<br>38.8 | 44.7,<br>46.4 | 41.3,<br>39.3 | 44.9,<br>46.7 | 47.6,<br>47.9 | 43.0,<br>47.9 | 48.2,<br>48.6 | 43.2,<br>48.2 |
| C(3) | 45.2 | 47.4 | 45.7 | 48.1 | 42.0 | 41.3 | 42.6 | 42.2 |
| C(4) | 50.5 | 51.9 | 52.0 | 52.9 | 48.1 | 47.2 | 49.7 | 48.5 |
| C(5) | 43.6 | 42.4 | 44.0 | 42.5 | 35.7 | 33.8 | 36.2 | 33.9 |
| C(6) | 47.5 | 38.8 | 48.3 | 39.2 | 37.2 | 38.2 | 37.6 | 38.8 |
| C(9), C(10) | 135.2,<br>136.0 | 135.5,<br>135.8 | 135.4,<br>136.0 | 135.5,<br>135.8 | 135.1,<br>135.2 | 135.5 | 135.2,<br>135.3 | 135.6,<br>135.7 |
| C(11) | 52.9 | 52.9 | 53.4 | 53.2 | 52.6 | 52.6 | 53.0 | 52.9 |
| C(12) | 34.1 | 31.5 | 34.3 | 31.7 | 31.7 | 35.2 | 31.8 | 35.5 |
| C=O | 179.5 | 178.4 | 178.2 | 177.1 | 176.2 | 175.1 | 175.1 | 174.0 |
| $H_3C$–C(4) | 21.3 | 26.0 | 21.6 | 26.2 | – | – | – | – |
| $Me_3$*C* | – | – | 79.4 | 79.4 | – | – | 79.5 | 79.6 |
| *$Me_3$*C | – | – | 27.9 | 28.0 | – | – | 28.0 | 28.2 |

tri(cyclopentadiene), and the slightly lower-boiling **1n**, and 7.1 g (15% yield relative to methyl methacrylate) of 95% pure **1** as a 5:4 *endo*/*exo* mixture (1 mgHg, 59–67°).

*Kinetic Study of Hydrolysis of* **1**. Compound **1** (10 g, 0.043 mol) was added under $N_2$ to a soln. of KOH (6.0 g, 0.09 mol) in MeOH/$H_2O$ (20 ml/5 ml) at reflux temp. After different time intervals, a few drops of the mixture were removed and neutralized with 1N HCl. The product mixture in each sample was extracted with AcOEt and analyzed by GC.

*Methyl (1α,2α,3β,6β,7α,8α)-4β-Methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4α-carboxylate* (**1n**). KOH (60 g, 0.9 mol) in MeOH/$H_2O$ (200 ml/50 ml) was heated to reflux under $N_2$. Compound **1** (100 g, 0.43 mol) was added, and heating was continued for 3 h. The mixture was then diluted with $H_2O$ (350 ml), extracted three times with $Et_2O$ (300 ml). The combined $Et_2O$ extracts were washed with $H_2O$, dried ($Na_2SO_4$), and concentrated. The residue was recrystallized from petroleum ether (70 ml) by cooling with dry ice to yield 44.3 g (44.3% relative to the total amount of **1**) of large, colorless crystals of 96% purity. M.p. 52–54°. FT-IR (KBr): 3050*m*, 2970*s*, 2920*m*, 1728*s*, 1450*m*, 1270*m*, 1195*m*, 1145*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 0.96 (*dm*, $^2J = 10.0$, $H_{syn}$–C(12)); 1.13 (*dm*, $^2J = 7.8$, $H_{syn}$–C(11)); 1.15 (*dd*, $^2J = 12.4$, $^3J(5\beta,6) = 4.4$, $H_\beta$–C(5)); 1.19 (*s*, Me–C(4)); 1.26 (*dt*, $^2J = 7.8$, $^3J(1,11anti) = {}^3J(8,11anti) = 1.8$, $H_{anti}$–C(11)); 1.82 (*dd*, $^3J(2,7) = 8.2$, $^3J(1,2) = 3.8$, H–C(2)); 1.96 (*dd*, $^2J = 12.4$, $^4J(5\alpha,12anti) = 3.0$, $H_\alpha$–C(5)); 1.99 (*dd*, $^3J(2,7) = 8.2$, $^3J = 4.0$, H–C(7)); 2.04 (br. *d*, $^3J(5\beta,6) = 4.4$, H–C(6)); 2.08 (br. *s*, H–C(3)); 2.20 (*ddm*, $^2J = 10.0$, $^4J(5\alpha,12anti) = 3.0$, $H_{anti}$–C(12)); 2.83 (*m*, H–C(1), H–C(8)); 3.70 (*s*, MeO); 5.96 (*m*, H–C(9), H–C(10)). NOE Difference experiment for the assignment of $H_{syn}$–C(11) and $H_{anti}$–C(11) with irradiation at H–C(2) (1.82 ppm): 4% NOE for $H_{syn}$–C(11) and 4% for H–C(1), no effect for $H_{anti}$–C(11). $^{13}$C-NMR (75.5 MHz, $CDCl_3$, HETCOR): 26.1 (*Me*–C(4)); 31.6 (C(12)); 39.0 (C(6)); 42.8 (C(5)); 45.2 (C(2)); 46.5, 46.6, 46.8 (C(1), C(7), C(8)); 48.0 (C(3)); 51.5 (MeO); 52.5 (C(4)); 53.0 (C(11)); 135.6, 135.8 (C(9), C(10)); 178.2 (COO). HETCOR in the presence of [Eu(fod)$_3$]: stronger upfield shift for H–C(2) than for H–C(7). CI-MS: 249 (21, $[M + \mathrm{Me}]^+$), 233 (100, $[M + \mathrm{H}]^+$), 201 (6, $[M + \mathrm{H} - \mathrm{CH_3OH}]^+$). The X-ray crystal structure is shown in *Fig. 3* (top). For crystal data and refinement parameters, see *General* and *Table 2*.

Table 2. *Crystal Data and Structure Refinement*

| | **1n** | **3x** |
|---|---|---|
| Empirical formula | $C_{15}H_{20}O_2$ | $C_{18}H_{26}O_2$ |
| Formula weight | 232.31 | 274.39 |
| Temperature | 183(2) K | 198(2) K |
| Crystal system | triclinic | monoclinic |
| Space group | P-1 | $P2_1/c$ |
| Unit-cell dimensions *a* [Å] | 6.1731(5) | 6.1912(9) |
| *b* [Å] | 9.497(1) | 23.154(3) |
| *c* [Å] | 11.200(1) | 10.668(1) |
| *α* [°] | 75.57(1) | 90.0 |
| *β* [°] | 76.63(1) | 91.618(9) |
| *γ* [°] | 86.05(1) | 90.0 |
| *V* | 615.8(1) | 1528.7(3) |
| *Z* | 2 | 4 |
| Density (calc.) [$Mg/m^3$] | 1.25 | 1.19 |
| Absorption coefficient [$mm^{-1}$] | 0.081 | 0.075 |
| *F*(000) | 252 | 600 |
| Crystal size [mm] | 0.85 × 0.39 × 0.31 | 0.52 × 0.42 × 0.37 |
| *θ* Range [°] for data collection | 2.2 to 25.0 | 2.1 to 30.0 |
| Reflections collected | 2550 | 8995 |
| Independent reflections | 2087 | 4455 |
| *R*(int) | 0.014 | 0.037 |
| Data/parameters | 2087/235 | 4454/286 |
| Goodness-of-fit on $F^2$ | 1.044 | 1.018 |
| Final *R* indices [$I > 2\sigma(I)$] (*R*1, *wR*2) | 0.0382, 0.0919 | 0.0461, 0.105 |
| *R* Indices (all data) (*R*1, *wR*2) | 0.0501, 0.101 | 0.0763, 0.121 |
| Extinction coefficient (*EXTI*) | $7.3(7) \times 10^{-5}$ | $4.2(3) \times 10^{-5}$ |
| Largest diff. peak and hole [$e \cdot A^{-3}$] | 0.22, −0.16 | 0.29, −0.16 |

*(1α,2α,3β,6β,7α,8α)-4α-Methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4β-carboxylic Acid* (**2x**). The aq. phase from the preceding reaction was acidified with half-conc. HCl (150 ml). The precipitate was filtered off, recrystallized from EtOH/$H_2O$ (800 ml/200 ml), and dried under vacuum at 50° to yield 28.0 g (30% relative to the total amount of **1**) of the acid as fine, slightly yellow crystals of 98% purity. M.p. (AcOEt) 202–205°. FT-IR (KBr): 3050*m*, 2960*s*, 2930*s*, 2880*m*, 2810*m*, 2670*m*, 1690*s*, 1450*m*, 1305*m*, 1285*m*, 940*m*, 755*m*. $^1$H-NMR (500 MHz, ($D_6$)DMSO): 0.53 (*d*, $^2J = 10.5$, $H_{syn}$−C(12)); 0.64 (*dd*, $^2J = 12.3$, $^4J(5\alpha,12anti) = 2.8$, $H_\alpha$−C(5)); 1.17 (*s*, Me−C(4)); 1.21 (*m*, 2 H−C(11)); 1.94 (*m*, H−C(7), H−C(6)); 2.06 (*dm*, $^2J = 10.5$, $H_{anti}$−C(12)); 2.21 (*dd*, $^2J = 12.3$, $^3J(5\beta,6) = 4.9$, $H_\beta$−C(5)); 2.26 (br. *s*, H−C(3)); 2.35 (*dd*, $^3J(2,7) = 8.3$, $^3J(1,2) = 3.9$, H−C(2)); 2.81 (*m*, H−C(1), H−C(8)); 5.93, 5.99 (2*dd*, $^3J(9,10) = 5.6$, $^3J(1,10) \approx {}^3J(8,9) \approx 3.5$, H−C(9), H−C(10)); 11.93 (*s*, COOH). NOE Difference experiment for the assignment of H−C(2) and H−C(7) with irradiation at the Me group at C(4) (1.17 ppm): NOE of 18% for H−C(2) and 3% for H−C(7). Additional NOEs were observed for $H_\alpha$−C(5) (4.5%), H−C(3) (3%), and H−C(1) and H−C(8) (1.5%). Some of the NOE has to be attributed to unavoidable simultaneous irradiation at $CH_2$(11) (1.21 ppm). $^{13}$C-NMR (125.5 MHz, ($D_6$)DMSO, HETCOR): 21.3 (Me); 34.1 (C(12)); 38.8 (C(7)); 40.8 (C(2)); 43.6 (C(5)); 45.2 (C(3)); 46.1, 46.2 (C(1), C(8)); 47.5 (C(6)); 50.5 (C(4)); 52.9 (C(11)); 135.2, 136.0 (C(9), C(10)); 179.5 (COO). CI-MS: 219 (100, $[M + H]^+$), 201 (52, $[M + H - H_2O]^+$), 173 (48, $[M + H - H_2O - CO_2]^+$).

*(1α,2α,3β,6β,7α,8α)-4β-Methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4α-carboxylic Acid* (**2n**). Compound **1n** (25 g, 0.11 mol) was heated under reflux with KOH (30 g, 0.45 mol) in MeOH/$H_2O$ (100 ml/25 ml) for 64 h. The mixture was diluted with $H_2O$ (200 ml) and extracted with $Et_2O$ (200 ml). The aq. phase was acidified with half-conc. HCl (200 ml), and the precipitate was isolated by filtration, dried, and recrystallized from heptane (700 ml): 18.8 g (80%) of large, transparent crystals were obtained (99% pure). M.p. 167–170°. FT-IR (KBr):

3070*w*, 3030*w*, 2970*s*, 2940*m*, 2920*m*, 2870*m*, 2680*w*, 1695*s*, 1285*m*, 1180*m*, 920*m*, 900*m*, 750*m*, 725*m*. $^{1}$H-NMR (300 MHz, (D$_6$)DMSO): 0.94 (br. *d*, $^{2}J = 10.8$, H$_{syn}$−C(12)); 1.03 (*dd*, $^{2}J = 12.3$, $^{3}J(5\beta,6) = 4.5$, 1 H, H$_\beta$−C(5)); 1.07 (*d*, $^{2}J = 7.8$, H$_{syn}$−C(11)); 1.12 (*s*, Me−C(4)); 1.18 (br. *d*, $^{2}J = 7.8$, H$_{anti}$−C(11)); 1.81 (*dd*, $^{2}J = 12.3$, $^{4}J(5\alpha,12anti) = 2.7$, H$_\alpha$−C(5)); 1.87 (*dd*, $^{3}J(2,7) = 8.1$, $^{3}J(7,8) = 3.9$, H−C(7)); 1.94 – 2.0 (*m*, H−C(3), H−C(6), H−C(2)); 2.11 (br. *d*, $^{2}J = 10.8$, $^{4}J(5\alpha,12anti) \approx 1.0$, H$_{anti}$−C(12)); 2.79 (br. *s*, H−C(1), H−C(8)); 5.95 (*m*, H−C(9), H−C(10)); 12.00 (*s*, COOH). $^{13}$C-NMR (75.5 MHz, (D$_6$)DMSO, HETCOR): 26.0 (Me); 31.5 (C(12)); 38.8 (C(6)); 42.4 (C(5)); 44.7 (C(2)); 46.2, 46.3, 46.4 (C(1), C(7), C(8)); 47.4 (C(3)); 51.9 (C(4)); 52.9 (C(11)); 135.4, 135.8 (C(9), C(10)); 178.4 (COOH). CI-MS: 219 (100, $[M + \mathrm{H}]^+$), 201 (44, $[M + \mathrm{H} - \mathrm{H_2O}]^+$).

tert-*Butyl (1α,2α,3β,6β,7α,8α)-4α-Methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4β-carboxylate* (**3x**) [13]. Compound **2x** (21.8 g, 0.1 mol) was dispersed in toluene (100 ml) under N$_2$. The soln. was cooled to 10°, and (CF$_3$CO)$_2$O (17.6 ml, 0.125 mol) was added dropwise over 20 min. After stirring for 1 h at r.t., the mixture was again cooled with ice, and dry *t*-BuOH (19 ml, 0.2 mol, diluted with 1 ml toluene) was added dropwise. Stirring was continued overnight at r.t. The soln. was cooled one more time with ice, and 2M NaOH (100 ml) was added dropwise followed by 100 ml of H$_2$O. The org. phase was separated, and the aq. phase was extracted with Et$_2$O (2 × 100 ml). The combined org. phases were washed with H$_2$O (3 × 50 ml), dried (Na$_2$SO$_4$), and concentrated giving a yellow oil. Twofold recrystallization from EtOH yielded 7.6 g (28%) of the 99% pure **3x**. Several-mm long prisms were obtained by slowly evaporating the solvent over several days. M.p. 74 – 76°. FT-IR (KBr): 2965*s*, 2950*s*, 1710*s*, 1450*m*, 1365*m*, 1280*m*, 1150*s*, 1115*m*, 1100*m*, 850*m*, 750*m*. $^{1}$H-NMR (500 MHz, CDCl$_3$): 0.58 (*d*, $^{2}J = 10.5$, H$_{syn}$−C(12)); 0.66 (*dd*, $^{2}J = 12.3$, $^{4}J(5\alpha,12anti) = 3.3$, H$_\alpha$−C(5)); 1.20 (*s*, Me−C(4)); 1.20 – 1.33 (*m*, $^{2}J = 7.8$, 2 H−C(11)); 1.41 (*s*, *t*-Bu); 1.95 (*dd*, $^{3}J(2,7) = 8.4$, $^{3}J(7,8) = 3.9$, H−C(7)); 2.01 (*dm*, $^{3}J(5exo,6) = 4.8$, H−C(6)); 2.11 (*dq*, $^{2}J = 10.5$, $^{3}J(3,12anti) \approx {}^{3}J(6,12anti) \approx {}^{4}J(5\alpha,12anti) \approx 2.5$, H$_{anti}$−C(12)); 2.33 (*m*, $^{3}J(5\alpha,5\beta) = 12.3$, $^{3}J(2,7) = 8.4$, $^{3}J(5\beta,6) = 4.8$, $^{3}J(1,2) = 4.0$, H−C(2), H−C(3), H$_\beta$−C(5)); 2.84 (*m*, H−C(1), H−C(8)); 5.94, 6.00 (2*dd*, $^{3}J(9,10) = 5.7$, $^{3}J(1,10) \approx {}^{3}J(8,9) \approx 3.3$, H−C(9), H−C(10)). $^{13}$C-NMR (75.5 MHz, CDCl$_3$, APT): 21.6 Me−C(4)); 27.9 (*Me*$_3$C); 34.3 (C(12)); 39.3 (C(7)); 41.3 (C(2)); 44.0 (C(5)); 45.7 (C(3)); 46.6, 46.8 (C(1), C(8)); 48.3 (C(6)); 52.0 (C(4)); 53.4 (C(11)); 79.4 (Me$_3$*C*); 135.4, 136.0 (C(9), C(10)); 178.2 (C=O). CI-MS: 275 (12, $[M + \mathrm{H}]^+$), 259 (4), 247 (12), 219 (100, $[M + \mathrm{H} - \text{isobutene}]^+$), 217 (10), 201 (11, $[M + \mathrm{H} - (t\text{-BuOH})]^+$), 173 (7, $[M + \mathrm{H} - \text{isobutene} - \mathrm{CO}]^+$), 153 (3, $[M + \mathrm{H} - \text{isobutene} - \mathrm{C_5H_6}]^+$). The X-ray crystal structure is shown in *Fig. 3* (bottom). For crystal data and refinement parameters, see *General* and *Table 2*.

tert-*Butyl (1α,2α,3β,6β,7α,8α)-4β-Methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4α-carboxylate* (**3n**) [13]. The analogous procedure as described for **3x**, followed by distillation over a 15-cm *Vigreux* column (1 mm Hg, 76 – 80°) gave **3n** as a colorless oil in 31% yield and 99% purity. FT-IR (film): 3050*w*, 2965*s*, 2925*m*, 2870*m*, 1720*s*, 1480*m*, 1455*m*, 1365*m*, 1280*m*, 1155*s*, 1140*s*, 1125*m*, 1110*m*, 850*m*, 750*m*. $^{1}$H-NMR (300 MHz, CDCl$_3$): 0.94 (*d*, $^{2}J = 11.1$, H$_{syn}$−C(12)); 1.09 (*dd*, $^{2}J = 12.3$, $^{3}J(5\beta,6) = 4.5$, H$_\beta$−C(5)); 1.13 (*d*, $^{2}J = 7.8$, H$_{syn}$−C(11)); 1.16 (*s*, Me−C(4)); 1.27 (*dt*, $^{2}J = 7.8$, $^{3}J(1,11anti) \approx {}^{3}J(8,11anti) \approx 1.8$, H$_{anti}$−C(11)); 1.46 (*s*, *t*-Bu); 1.89 (*dd*, $^{2}J = 12.3$, $^{4}J(5\alpha,12anti) = 2.7$, H$_\alpha$−C(5)); 2.00 – 2.03 (*m*, H−C(2), H−C(3), H−C(6), H−C(7)); 2.16 (*dq*, $^{2}J = 11.1$, $^{3}J(3,12anti) \approx {}^{3}J(6,12anti) \approx {}^{4}J(5\alpha,12anti) \approx 2.5$, H$_{anti}$−C(12)); 2.83 (*m*, H−C(1), H−C(8)); 5.95 (*m*, H−C(9), H−C(10)). $^{13}$C-NMR (75.5 MHz, CDCl$_3$, HETCOR): 26.2 (Me−C(4)); 28.0 (*Me*$_3$C); 31.7 (C(12)); 39.2 (C(6)); 42.5 (C(5)); 44.9 (C(2)); 46.6, 46.7 (2 ×) (C(1), C(7), C(8)); 48.1 (C(3)); 52.9 (C(4)); 53.2 (C(11)); 79.4 (Me$_3$*C*); 135.5, 135.8 (C(9), C(10)); 177.1 (COO). CI-MS: 275 (11, $[M + \mathrm{H}]^+$), 219 (100, $[M + \mathrm{H} - \text{isobutene}]^+$), 201 (19, $[M + \mathrm{H} - (t\text{-BuOH})]^+$).

*Mixture of* tert-*Butyl (1α,2α,3β,6β,7α,8α)-9α-Hydroxy- and (1α,2α,3β,6β,7α,8α)-10α-Hydroxy-4α-methyltetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodecane-4β-carboxylate* (**4xa** and **4xb**, resp.) [17]. A soln. of **3x** (27.4 g, 0.1 mol) in dry THF (150 ml) was cooled to 0° under N$_2$, and 1 equiv. of BH$_4$ (1M soln. in THF) was added dropwise over *ca.* 30 min. The soln. was stirred at r.t. overnight, then NaOH (16 g in 80 ml of H$_2$O) and 30% H$_2$O$_2$ (56 ml) were added slowly. Stirring was continued for 2 h. The mixture was then diluted with 2N HCl (175 ml) and sat. NaCl soln. (175 ml), the org. phase was separated and the aq. phase extracted with Et$_2$O (3 × 100 ml). The combined org. phases were washed with sat. NaCl soln. (100 ml), dried (Na$_2$SO$_4$), and concentrated. The residue was dried extensively under high vacuum at 50° and then recrystallized from heptane (60 ml): 25.4 g (87%) of the 1:1 mixture were obtained as a white solid in 96% purity. FT-IR: 3320*s*, 3040*w*, 2970*s*, 2945*s*, 2900*m*, 2880*m*, 1721*s*, 1455*m*, 1368*m*, 1280*m*, 1160*s*, 1140*s*, 1100*m*, 1040*m*, 990*m*, 850*m*. $^{1}$H-NMR (500 MHz, CDCl$_3$): 0.65 (2*dd*, $^{2}J = 12.6$, $^{4}J(5\alpha,12anti) = 2.6$, H$_\alpha$−C(5)); 0.96 (2*d*, $^{2}J = 11.8$, H$_{syn}$−C(12)); 1.14 (2*s*, Me−C(4)); 1.16 – 1.23 (*m*, $^{2}J(11syn,11anti) = 9.6$, H$_{syn}$−C(11),H$_\alpha$−C(10) of **4xa**, H$_\alpha$−C(9) of **4xb**); 1.40 (*m*, H$_{anti}$−C(12)); 1.43 (2*s*, *t*-Bu); 1.59 (*dd*, $^{3}J(2,7) = 9.8$, $^{3}J(7,8) = 4.6$, 0.5 H, H−C(7) of **4xb**); 1.60 – 1.65 (2*dt*, $^{2}J = 9.6$, $^{3}J(1,11anti) \approx {}^{3}J(8,11anti) \approx 1.4$, H$_{anti}$−C(11)); 1.67 (*s*, OH); 1.74 (*ddd*, $^{3}J(2,7) = 10.0$, $^{3}J(7,8) = 5.0$, $^{4}J(7,12syn) < 1.0$, 0.5 H, H−C(7) of **4xa**); 2.01 (*ddd*, $^3J(2,7) = 10.0$, $^3J(1,2) = 4.6$, $^4J(2,12\mathit{syn}) < 1.0$, 0.5 H, H−C(2) of **4xa**); 2.07 (*dm*, $^3J(5\beta,6) = 5.0$, 0.5 H, H−C(6) of **4xa**); 2.11–2.17 (*m*, 1.5 H, H−C(6) of **4xa**, H−C(2) of **4xb**, $H_\beta$−C(9) of **4xb**); 2.21 (*ddd*, $^2J = 13.8$, $^3J(9\beta,10\beta) = 6.4$, $^4J(10\beta,11\mathit{syn}) = 2.6$, 0.5 H, $H_\beta$−C(10) of **4xa**); 2.24 (*m*, 1 H, H−C(8) of **4xa**, H−C(1) of **4xb**); 2.30 (*m*, 1 H, H−C(1) of **4xa**, H−C(8) of **4xb**); 2.33–2.40 (2*dd*, $^2J = 12.6$, $^3J(5\beta,6) = 5.0$, $H_\beta$−C(5)); 2.35, 2.39 (2*s*, H−C(3)); 4.05 (*d*, $^3J(9\beta,10\beta) = 6.4$, 0.5 H, $H_\beta$−C(9) of **4xa**); 4.10 (*d*, $^3J(9\beta,10\beta) = 6.2$, 0.5 H, $H_\beta$−C(10) of **4xa**). NOE Difference experiment for the assignment of protons at C(2) andC(7) with irradiation at the Me group at C(4) (1.14 ppm): NOE of 18% for H−C(2) and no effect for H−C(7). Additional NOEs were observed for $H_\alpha$−C(5) (4.5%), $H_\beta$−C(9) of **4xb** and $H_\beta$−C(10) of **4xa** (*ca.* 8%), H−C(1) of **4xa** and H−C(8) of **4xb** (2%) and H−C(3) (3%). Some of the NOEs have to be attributed to unavoidable simultaneous irradiation at $H_\alpha$−C(10) of **4xa** and $H_\alpha$−C(9) of **4xb** (1.16–1.23 ppm). $^{13}$C-NMR (75.5 MHz, $CDCl_3$, HETCOR): 22.1, 22.2 (Me−C(4)); 27.8 (*Me*$_3$C); 35.0, 35.1 (C(12)); 37.0 (C(6) of **4xa**); 37.4 (C(9) of **4xb**); 37.9 (C(10) of **4xa**); 38.0 (C(6) of **4xb**); 38.2, 38.4 (C(11)); 39.9 (C(2) of **4xa**); 40.1 (C(1) of **4xa**, C(8) of **4xb**); 40.9 (C(2) of **4xb**); 43.0, 43.2 (C(5)); 43.5, 44.6 (C(3)); 47.3 (C(7) of **4xb**); 48.2 (C(7) of **4xa**); 49.6, 49.7 (C(8) of **4xa**, C(1) of **4xb**); 51.5, 51.6 (C(4)); 70.2, 70.4 (C−OH); 79.6 (Me$_3$*C*); 178.1 (COO). CI-MS: 293 (23, $[M+H]^+$), 275 (25, $[M+H-H_2O]^+$), 265 (6), 247 (4), 237 (60, $[M+H-\text{isobutene}]^+$), 219 (100, $[M+H-(t\text{-BuOH})]^+$), 191 (18, $[M+H-(t\text{-BuOH})-CO]^+$), 173 (5, $[M+H-(t\text{-BuOH})-CO-H_2O]^+$).

*Methyl Tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4-carboxylate* (**5**). A 250-ml stainless-steel reactor (*Parr Instrument Company*) was charged with methyl acrylate (18 ml, 0.2 mol), cyclopentadiene (25 ml, 0.3 mol), and 4-(*tert*-butyl)catechol (350 mg, 2 mmol), put into an oil bath that was preheated to 230°, and left at this temp. for 2 h. The reactor was immediately opened at high temp. and the crude product was distilled two times over a 30-cm *Vigreux* column giving 12.0 g (39% yield relative to methyl acrylate) of a 99% pure *endo*/*exo*-mixture of methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (2 mm Hg, 28–31°), 1.3 g, of an intermediate fraction containing mainly tri(cyclopentadiene) and the slightly lower-boiling **5n**, and 12.4 g (28% yield relative to methyl acrylate) of 96% pure **5** as a 1 : 2 *endo*/*exo*-mixture (2 mm Hg, 69–77°).

*Kinetic Study of Hydrolysis of* **5**. Compound **5** (10 g, 0.046 mol) was added under $N_2$ to a soln. of KOH (3.0 g, 0.045 mol) in MeOH/$H_2O$ (20 ml/5 ml) at 22°. Small samples were removed and analyzed as described for **1**.

*(1α,2α,3β,6β,7α,8α)-Tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4β-carboxylic Acid* (**6x**). Compound **5** (100 g, 0.46 mol) was added to a soln. of KOH (30 g, 0.45 mol) in MeOH/$H_2O$ (200 ml/50 ml) at $22 \pm 2°$. The mixture was stirred at this temp. for 5 h, diluted with $H_2O$ (350 ml), and extracted with $Et_2O$ (3 × 300 ml). The aq. phase was acidified with half-conc. HCl (100 ml), the precipitate was filtered off and recrystallized two times from EtOH/$H_2O$ (400 ml/200 ml): 32.6 g (35% with respect to the total amount of **5**) of fine white crystals were obtained (99% pure). M.p. 145–148°. FT-IR (KBr): 3050*m*, 2970*s*, 2925*m*, 2740*w*, 2670*w*, 2570*w*, 1710*s*, 1690*s*, 1415*m*, 1310*m*, 1290*m*, 1250*m*, 1230*m*, 940*m*, 750*m*. $^1$H-NMR (500 MHz, ($D_6$)DMSO): 0.64 (*d*, $^2J = 10.3$, $H_{syn}$−C(12)); 1.15, 1.22 (2*d*, $^2J = 7.6$, 2 H−C(11)); 1.23 (*ddd*, $^2J = 12.0$, $^3J(4,5\alpha) = 8.8$, $^4J(5\alpha,12\mathit{anti}) = 2.5$, $H_\alpha$−C(5)); 1.64 (*dt*, $^2J = 12.0$, $^3J(4,5\beta) = {}^3J(5\beta,6) = 4.5$, $H_\beta$−C(5)); 1.96–2.01 (*m*, H−C(2), H−C(7), $H_{anti}$−C(12)); 2.02 (*d*, $^3J(5\beta,6) = 4.5$, H−C(6)); 2.07 (*ddd*, $^3J(4,5\alpha) = 8.8$, $^3J(4,5\beta) = 4.5$, $^4J(4,12\mathit{anti}) = 1.2$, H−C(4)); 2.26 (br. *s*, $^3J(3,12) < 1$, H−C(3)); 2.81, 2.83 (2*d*, $^3J(1,2) = {}^3J(7,8) = 1.4$, H−C(1), H−C(8)); 5.95 (*m*, H−C(9), H−C(10)); 11.89 (*s*, COOH). $^{13}$C-NMR (75.5 MHz, ($D_6$)DMSO, HETCOR): 31.7 (C(12)); 35.7 (C(5)); 37.2 (C(6)); 42.0 (C(3)); 45.9, 46.0 (C(1), C(8)); 47.6, 47.9 (C(2), C(7)); 48.1 (C(4)); 52.6 (C(11)); 135.1, 135.2 (C(9), C(10)); (176.2 (COOH). CI-MS: 205 (100, $[M+H]^+$), 187 (20, $[M+H-H_2O]^+$).

*(1α,2α,3β,6β,7α,8α)-Tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-ene-4α-carboxylic Acid* (**6n**). The combined $Et_2O$ extracts from the preceding reaction were washed with small amounts of $H_2O$, dried ($Na_2SO_4$), and concentrated. The residual oil (containing *ca.* 80% of **5n**) was subjected to hydrolysis for a second time with KOH/MeOH/$H_2O$ (30 g/100 ml/25 ml) for 16 h at r.t. The mixture was diluted with $H_2O$ (200 ml) and acidified with half-conc. HCl (100 ml). The precipitate was filtered off and recrystallized (3 ×) from AcOEt yielding 15.7 g (17%) of large, colorless crystals. M.p. 148–150°. FT-IR (KBr): 3035*m*, 2965*s*, 2945*s*, 2875*m*, 2730*w*, 2620*w*, 2560*w*, 1705*s*, 1420*m*, 1315*m*, 1230*m*, 940*m*, 750*m*, 720*m*. $^1$H-NMR (300 MHz, ($D_6$)DMSO): 0.67 (*d*, $^2J = 10.2$, $H_{syn}$−C(12)); 1.09, 1.19 (2*d*, $^2J = 7.7$, 2 H−C(11)); 1.33 (*ddd*, $^2J = 12.0$, $^3J(4,5\alpha) = 4.5$, $^4J(5\alpha,12\mathit{anti}) = 3.0$, $H_\alpha$−C(5)); 1.52 (*td*, $^2J \approx {}^3J(4,5\beta) \approx 11.5$, $^3J(5\beta,6) = 4.5$, $H_\beta$−C(5)); 1.95–1.99 (*m*, H−C(2), H−C(7)); 2.02 (*d*, $^3J(5\beta,6) = 4.5$, H−C(6)); 2.15 (*dm*, $^2J = 10.2$, $H_{anti}$−C(12)); 2.32 (*d*, $^3J(3,4) = 4.0$, H−C(3)); 2.53 (*dt*, $^3J(4,5\beta) = 11.1$, $^3J(3,4) \approx {}^3J(4,5\alpha) \approx 4.5$, H−C(4)); 2.80, 2.83 (2 br. *s*, H−C(1), H−C(8)); 5.96 (*m*, H−C(9), H−C(10)); 11.95 (*s*, COOH). $^{13}$C-NMR (75.5 MHz, ($D_6$)DMSO, HETCOR): 33.8 (C(5)); 35.2 (C(12)); 38.2 (C(6)); 41.3 (C(3)); 43.0 (C(2)); 46.0, 46.3 (C(1), C(8)); 47.2 (C(4)); 47.9 (C(7)); 52.6 (C(11)); 135.5 (C(9), C(10)); 175.1 (COOH). CI-MS: 205 (97, $[M+H]^+$), 187 (100, $[M+H-H_2O]^+$).

tert-*Butyl (1α,2α,3β,6β,7α,8α)-Tetracyclo[6.2.1.*$1^{3,6}$*.*$0^{2,7}$*]dodec-9-ene-4β-carboxylate* (**7x**) [18]. $SOCl_2$ (5.5 ml, 0.075 mol) was added to **6x** (10.2 g, 0.05 mol), and the mixture was heated to 100° for 30 min under a slight flow of $N_2$. The slightly yellow liquid was transferred to an addition funnel, diluted with 5 ml of $CH_2Cl_2$, and added dropwise under $N_2$ and ice cooling to a soln. of *t*-BuOH (9.6 ml, 0.1 mol) in pyridine (25 ml). The soln. was allowed to come to r.t. and then refluxed for 30 min. After stirring overnight, the mixture was poured onto ice, the product was extracted with $Et_2O$ (3 × 100 ml), and the combined org. phases were washed with 1N HCl (3 × 75 ml), sat. $NaHCO_3$ (50 ml) and $H_2O$ (50 ml), dried, and concentrated. Bulb-to-bulb distillation (3 mm Hg, 170° oven temp.) gave 10.5 g (80%) of **7x** as a colorless oil, which solidified upon standing (95% pure). M.p. (EtOH) 44–46°. FT-IR (KBr): 3040*w*, 2955*s*, 2930*m*, 2870*w*, 1715*s*, 1475*w*, 1370*m*, 1285*m*, 1245*m*, 1225*m*, 1150*s*, 1030*w*, 850*m*, 755*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.75 (*d*, $^2J = 10.8$, $H_{syn}-C(12)$); 1.17 (br. *d*, $^2J = 7.8$, $H_{syn}-C(11)$); 1.26 (*ddd*, $^2J = 12.0$, $^3J(4,5\alpha) = 8.7$, $^4J(5\alpha,12anti) = 2.7$, $H_\alpha-C(5)$); 1.31 (*dt*, $^2J = 7.8$, $^3J(1,11anti) \approx {}^3J(8,11anti) \approx 1.8$, $H_{anti}-C(11)$); 1.42 (*s*, 9 H, *t*-Bu); 1.72 (*dt*, $^2J = 12.0$, $^3J(4,5\beta) \approx {}^3J(5\beta,6) \approx 4.8$, 1 H, $H_\beta-C(5)$); 1.98–2.07 (*m*, H–C(2), H–C(4), H–C(6), H–C(7), $H_{anti}-C(12)$); 2.31 (br. *s*, H–C(3)); 2.85 (*m*, H–C(1), H–C(8)); 5.94 (*m*, H–C(9), H–C(10)). $^{13}$C-NMR (75.5 MHz, $CDCl_3$, APT): 28.0 ($Me_3$C); 31.8 (C(12)); 36.2 (C(5)); 37.6 (C(6)); 42.6 (C(3)); 46.4, 46.5 (C(1), C(8)); 48.2, 48.6 (C(2), C(7)); 49.7 (C(4)); 53.0 (C(11)); 79.5 ($Me_3C$); 135.2, 135.3 (C(9), C(10)); 175.1 (COO). CI-MS: 261 (9, $[M+H]^+$), 205 (100, $[M+H-\text{isobutene}]^+$).

tert-*Butyl (1α,2α,3β,6β,7α,8α)-Tetracyclo[6.2.1.*$1^{3,6}$*.*$0^{2,7}$*]dodec-9-ene-4α-carboxylate* (**7n**) [13]. The analogous procedure as described for **3x** followed by bulb-to-bulb distillation (2 mm Hg, 140° oven temp.) gave **7n** as a colorless oil in 85% yield and 95% purity. FT-IR (film): 3050*w*, 2960*s*, 2875*m*, 1725*s*, 1475*m*, 1460*m*, 1365*m*, 1215*m*, 1150*s*, 1105*m*, 850*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 0.66 (*d*, $^2J = 10.2$, $H_{syn}-C(12)$); 1.16 (br. *d*, $^2J = 8.0$, $H_{syn}-C(11)$); 1.27 (*dt*, $^2J = 8.0$, $^3J(1,11anti) \approx {}^3J(8,11anti) \approx 1.5$, $H_{anti}-C(11)$); 1.44 (*m*, $H_\alpha-C(5)$); 1.46 (*s*, *t*-Bu); 1.55 (*ddd*, $^2J = 12.3$, $^3J(4,5\beta) = 10.5$, $^4J(5\beta,6) = 4.5$, $H_\beta-C(5)$); 2.00 (*dd*, $^3J(2,7) = 8.4$, $^3J(1,2) = 3.6$, H–C(2)); 2.03 (*dd*, $^3J(2,7) = 8.4$, $^3J(7,8) = 3.6$, H–C(7)); 2.06 (*m*, H–C(6)); 2.20 (*dq*, $^2J = 10.2$, $^3J(3,12anti) \approx {}^3J(6,12anti) \approx {}^4J(5\alpha,12anti) \approx 2.5$, $H_{anti}-C(12)$); 2.38 (br. *d*, $^3J(3,4) = 4.5$, H–C(3)); 2.50 (*dt*, $^3J(4,5\beta) = 10.5$, $^3J(3,4) \approx {}^3J(4,5\alpha) \approx 5.0$, H–C(4)); 2.82, 2.86 (2 br. *s*, H–C(1), H–C(8)); 5.95 (*m*, H–C(9), H–C(10)). $^{13}$C-NMR (75.5 MHz, $CDCl_3$, HETCOR): 28.2 ($Me_3$C); 33.9 (C(5)); 35.5 (C(12)); 38.8 (C(6)); 42.2 (C(3)); 43.2 (C(2)); 46.6, 46.8 (C(1), C(8)); 48.2 (C(7)); 48.5 (C(4)); 52.9 (C(11)); 79.6 ($Me_3C$); 135.6, 135.7 (C(9), C(10)); 174.0 (COO). HETCOR in the presence of $[Eu(fod)_3]$: stronger upfield shift for H–C(2) than for H–C(7). CI-MS: 261 (12, $[M+H]^+$), 205 (100, $[M+H-\text{isobutene}]^+$), 187 (19, $[M+H-(t\text{-BuOH})]^+$).

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