DOI: 10.1002/chem.201001250

VIP

Preparation of Highly Hindered Polyenes with *tert*-Butyl Groups in Internal Positions**

Markus Betz,[a] Henning Hopf,*[a] Ludger Ernst,[b] Peter G. Jones,[c] and Yoshio Okamoto[d]

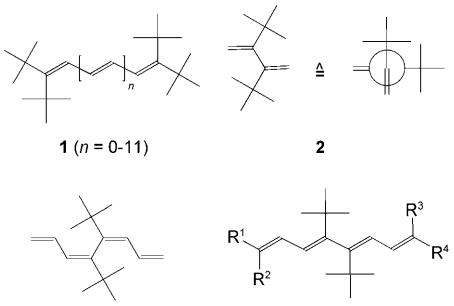
In memory of Professor Wilfried A. König

Abstract: The conjugated tetraenes **3** and **4a–c** have been prepared and shown to possess an orthogonal structure. This was not only demonstrated by their spectroscopic properties and X-ray structural analysis of solid representatives (e.g., **4a–c**) but also by the resolution of these chiral compounds by GC and HPLC chromatography using various chiral selector systems. The chemical behavior of the typical tetraene **4a** has been studied using bromination, hydrogenation, epoxidation, and photo equilibration reactions.

Keywords: bromination · chirality · conjugation · epoxidation · polyolefins · tetraenes

Introduction

In the two preceding papers of this series we described the preparation and structural properties of long oligoenes **1**, which were stabilized by placing *tert*-butyl groups in their α- and ω-positions;[2] in several of these molecules we also replaced up to four double bonds by acetylene moieties, creating oligoene/oligoyne hybrids[1] (Scheme 1).



4	R^1	R^2	R^3	R^4
a	*t*Bu	*t*Bu	*t*Bu	*t*Bu
b	*t*Bu	H	*t*Bu	*t*Bu
c	*t*Bu	H	H	*t*Bu

Scheme 1. Terminally and "internally" *tert*-butylated oligoenes.

Single-crystal X-ray structural analysis of the hydrocarbons **1** revealed that most of the molecules studied have a planar structure.[2] This situation should be vastly different if the bulky blocking groups are bonded to interior positions of the polyolefin. In this case they would not only prevent an "external attack" on the normally highly reactive polyene chain,[3] but would also cause intramolecular repulsive forces, eventually leading to nonplanar polyolefins in which the lateral overlap of the p orbitals would be impaired or even completely removed. This could not only lead to reduced—or even annihilated—conjugation; but also to a chiral oligo- or polyolefin. Applied to the most famous poly-

[a] Dr. M. Betz, Prof. Dr. H. Hopf
Institut für Organische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
Fax: (+49) 531-391-5388
E-mail: H.Hopf@tu-bs.de

[b] Prof. Dr. L. Ernst
NMR-Laboratorium der Chemischen Institute der
Technischen Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
Fax: (+49) 531-391-8192

[c] Prof. Dr. P. G. Jones
Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig
Postfach 3329, 38023 Braunschweig (Germany)
Fax: (+49) 531-391-5387

[d] Prof. Dr. Y. Okamoto
EcoTopia Science Institute, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3188

[**] Highly hindered olefins and polyolefins, XVI. Part XV: ref. [1].

olefin, "polyacetylene"[4] this would mean "insulation" towards the attack of external reagents, that is, stabilization, but only at the price of reduced electric conductivity if these polyolefins are employed as substrates for molecular metals.[5] In fact, one of the simplest conjugated hydrocarbons carrying internal *tert*-butyl substituents, 2,3-di-*tert*-butyl-buta-1,3-diene (**2**, 2,2,5,5-tetramethyl-3,4-bismethylenhexane) has already been described by Backer and co-workers in the late 1930s.[6] Structural work on this hydrocarbon was performed much later and demonstrated the orthogonal geometry of the molecule: as determined by X-ray structural elucidation the dihedral angle between the two planes passing through the two double bonds of **2** amounts to 96°,[7] whereas an angle of 101.5° is obtained from a gas-phase electron diffraction (GED) study of the molecule.[8] Clearly, the Newman representation of **2** (right half of the formula in Scheme 1) is a more realistic representation of the molecule. Note that orthogonal **2** is a chiral molecule possessing a chiral axis, just like numerous allenes, biphenyls or spirocompounds.[9]

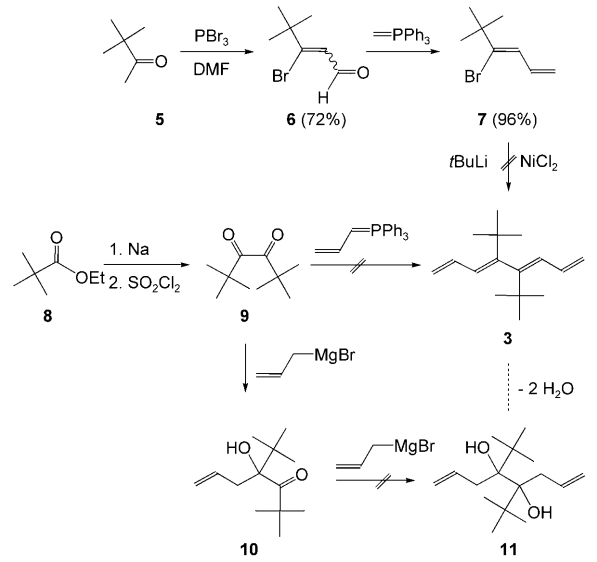
Because the preparation of internally substituted oligoenes is hence an interesting question in its own right, but could also be of considerable practical importance (organic metals stabilized by bulky or functional groups), we decided to prepare higher vinylogues of **2**. In this publication we not only describe the synthesis of the (formally) conjugated tetraene **3** (3,4-di-*tert*-butyl-octa-1,3,5,7-tetraene), but also of a few of its derivatives **4a–c** carrying *tert*-butyl groups both terminally and internally.

Results and Discussion

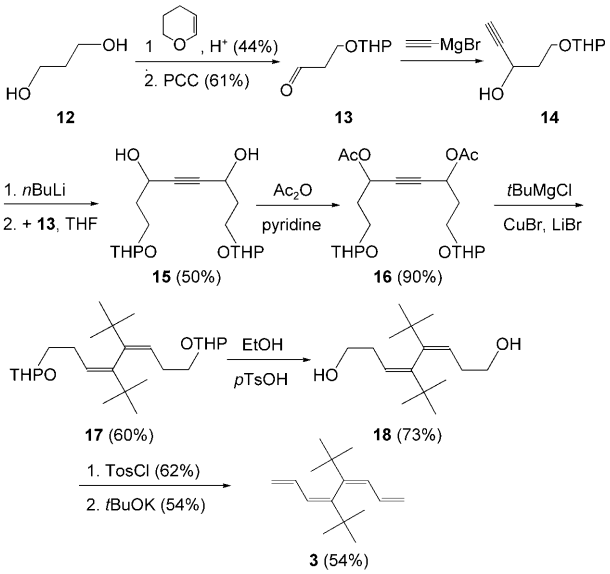
Synthesis: Since **3** is structurally a simple molecule, we hoped that we could prepare it by a short synthesis using simple reagents and transformations. As it turned out, all of our initial attempts, a selection of which is summarized in Scheme 2, failed.

Although the bromodiene **7** could be obtained easily from *tert*-butyl methyl ketone **5** via the intermediate α,β-unsaturated aldehyde **6**[10] in good yields, we were unable to homocouple two of these molecules to **3**. Although we could detect the hydrocarbon by GC/MS analysis of the complex product mixture, we failed to isolate the target molecule therefrom. Likewise, double Wittig olefination of the diketone **9** with the ylid generated from allyltriphenylphosphonium bromide did not furnish the target molecule. The reaction of **9** with allyl magnesium bromide started hopefully and yielded the tertiary alcohol **10**, which, disappointingly, could not be induced to react a second time with the Grignard reagent, however. The intended double dehydration of the desired diol **11** could hence not be performed.

After these failures we decided to concentrate our efforts on a multistep synthesis in which the carbon framework of **3** was first generated step by step and the complete set of double bonds was only produced at the very end of the sequence. This approach is summarized in Scheme 3.



Scheme 2. Failed attempts to prepare 4,5-di-*tert*-butyl-octa-1,3,5,7-tetraene (**3**).



Scheme 3. Successful preparation of 4,5-di-*tert*-butyl-octa-1,3,5,7-tetraene (**3**).

The rather involved route began with propane-1,3-diol (**12**), which was first monoprotected to the corresponding tetrahydropyranyl (THP) ether, which in a subsequent oxidation step with pyridinium chlorochromate (PCC) provided **13**, a previously described aldehyde.[11,12] The next intermediate, propargyl alcohol **14**, obtained from **13** by ethynylation with an acetylene Grignard, is also a known compound.[13,14] When the former was treated with excess *n*-butyl lithium in THF and the resulting organolithio species quenched with **13**, the symmetrical diol **15**, a highly viscous, colorless oil, was produced. With its four stereogenic centers this compound should be formed as a mixture of diastereomers, and this is indeed the case as shown by its ^{13}C NMR

spectrum (multiple signals for the majority of carbon atoms); no attempt, however, was made to separate these stereoisomers.

For the next step, *tert*-butylation, as described by us previously,[15] the two hydroxyl groups of **15** first had to be converted into better leaving groups. This was accomplished by esterification of **15** with acetic anhydride in pyridine. The diacetate **16**, formed in good yield (90%), was then subjected to the reagent produced from *tert*-butyl magnesium bromide and CuBr/LiBr.[15] The desired diene **17** was obtained in 60% yield as a highly viscous oil. We believe that the configuration of the two new double bonds is that shown in Scheme 3; however, this could not be derived unambiguously from its spectroscopic data (see experimental section), but follows from the crystal structure determination of the diol **18** (see below), isolated in 73% yield after the protecting groups of **17** had been removed by acid cleavage. The bis-THP ether **17** contains three stereogenic centers (two chiral centers, one chiral axis), and is hence produced as a diastereomeric mixture by the above transformation. The conversion of **16** into **17** involves two consecutive S_N2'-substitution processes, taking place via an allenic intermediate. This can be isolated as the main product if the substitution is carried out with substoichiometric amounts of the metal organic reagent; its spectroscopic data are given in the experimental section.

Since the direct dehydration of **18** with *p*-toluene sulfonic acid or sodium hydrogensulfate failed, the diol was first converted into its bis-tosylate (62%). When this was treated with potassium *tert*-butoxide in diethyl ether at room temperature double elimination took place and yielded the tetraene **3** in 54% yield. The hydrocarbon is a colorless oil, which forms a glasslike polymer when exposed neat to air for several weeks at room temperature. Its structure follows from the usual spectroscopic and analytical data as well as its chiroptical properties (see below).

Particularly revealing is its electronic spectrum (see below), which shows a single absorption maximum at 228 nm, much shorter than expected for a conjugated tetraene: the fully conjugated parent hydrocarbon octa-1,3,5,7-tetraene displays the typical "finger pattern" of absorption maxima between 267 and 304 nm, the last two bands being the most intense,[16] and its derivative carrying four *tert*-butyl substituents in its 1- and 8-position shows a very similar pattern with the four bands shifted to the range between 300 and 342 nm.[2] In fact, the absorption of **3** resembles more that observed for its "half" 1,1-di-*tert*-butylbuta-1,3-diene ($\lambda_{max}=242$ nm, single maximum).[17] Parent buta-1,3-diene absorbs at 217 nm, and its 1,1,4,4-tetramethyl derivative also at 228 nm.[18] We conclude from these data, that the two diene subsystems of **3** are practically uncoupled and that the hydrocarbon possesses an orthogonal, chiral structure.

The ^{1}H NMR spectrum of **3** also deserves comment. Its olefinic region (Figure 1) shows a highly second-order four-proton spin system. Its second-order character is caused mainly by the closeness of the chemical shifts of 2-H and 3-H. The spectrum needed an iterative analysis in order to obtain the chemical shifts and coupling constants (Table 1). The coupling constant of highest interest, J(2-H, 3-H), was determined to be 10.75 Hz, slightly larger than the corresponding value in 1,3-butadiene (10.41 Hz).[19] This shows that the two butadiene halves of **3** are essentially planar, at least as much as in butadiene itself. Hence, the conceivable unfavorable interaction between 2-H and 5-*t*Bu (or between 7-H and 4-*t*Bu) does not play a major role. It is prevented by the twist of the molecule about the C4–C5 bond as discussed above. It should be noted that the *Z*,*Z*-configuration of **3** shown in Scheme 3 does not follow from these data. We assume that the configuration shown is correction because the stereochemistry of precursor diol **18** was established by X-ray structural analysis (see below).

All other spectroscopic and analytical data of **3** are collected in the experimental section and agree with the proposed structure.

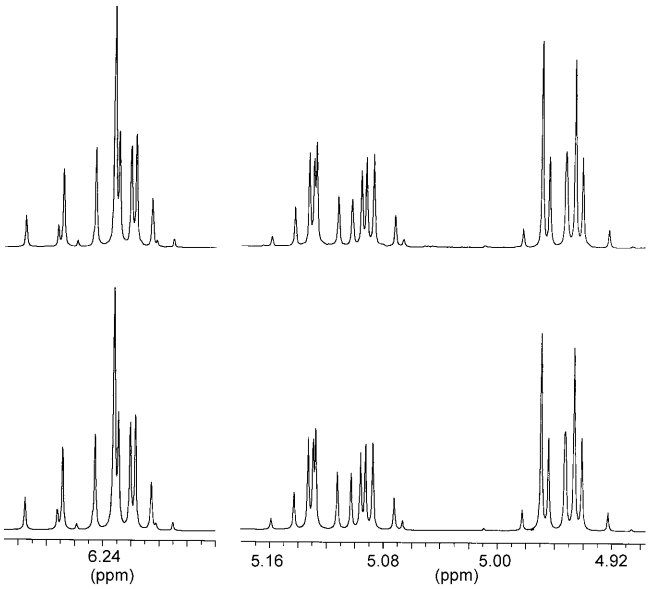


Figure 1. Olefinic region of the ^{1}H NMR spectrum of **3** (400 MHz, solvent $CDCl_3$; top: experimental spectrum, bottom: simulated spectrum).

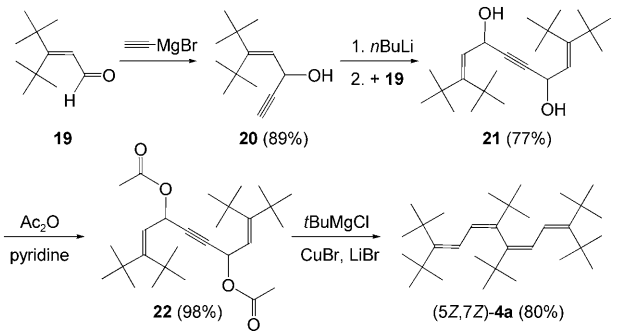
Table 1. ^{1}H NMR chemical shifts and coupling constants of **3**[a] compared to butadiene.[b]

Proton	δ(**3**) [ppm]	δ(butadiene) [ppm]	Protons	J(HH) in **3** [Hz]	J(HH) in butadiene [Hz]
1*E*	4.955	5.02	1*E*, 1*Z*	2.09	1.74
1*Z*	5.110	5.13	1*E*, 2	10.12	10.17
2	6.244	6.23	1*E*, 3	−0.79	−0.86
3	6.224	6.23	1*Z*, 2	16.98	17.05
*t*Bu	1.146		1*Z*, 3	−0.83	−0.83
			2, 3	10.75	10.41

[a] Solvent $CDCl_3$, reference TMS, observation frequency 400 MHz, quality of fit: $R=0.22\%$. [b] From reference [19]; solvent CCl_4, reference cyclohexane converted to the TMS scale using $\delta(C_6H_{12})=1.40$ ppm, compare with reference [20]).

Although with the synthesis of **3** we had been successful in preparing the double vinylogue of the parent hydrocarbon **2**, we did not have enough material to study its chemical properties and because of its oily nature we were unable to carry out an X-ray diffraction study. Since the compound was also somewhat labile (see above), we decided to introduce *tert*-butyl groups at the ends of its olefinic system as well, that is, use the same approach employed for the stabilization of the parent polyolefin.[2]

Towards this end the α,β-unsaturated ketone **19**, available from our previous work in multigram quantities[1,2] was ethynylated to provide the propargyl alcohol **20** (89%, Scheme 4). When this was metalated as described above for

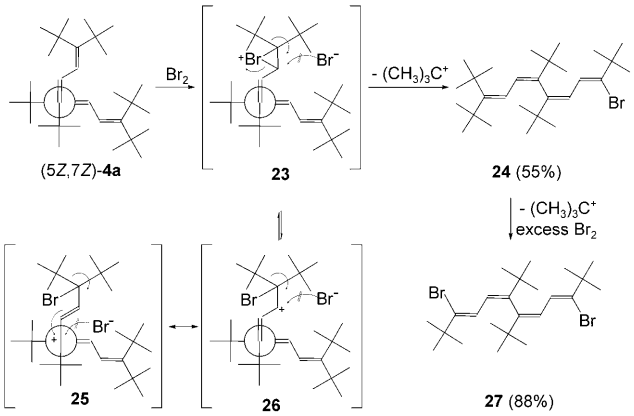


Scheme 4. Preparation of the terminally and internally *tert*-butylated tetraene (5*Z*,7*Z*)-**4a**.

the **14**→**15** conversion, and the formed organolithio intermediate quenched by the addition of **19**, the diol **21** was isolated (77%) as a mixture of diastereomers as shown by its ^{1}H NMR spectrum (see Experimental Section). The conversion of **21** via **22** into the tetraene **4a** was routine (see Scheme 4), and we were pleased to obtain this hydrocarbon not only in gram amounts, but also as a stable, crystalline material.

The structure determination of **4a** was carried out by the usual spectroscopic and analytical methods, in particular by single-crystal X-ray diffraction, the required crystals being obtained by slow high-vacuum sublimation. As discussed below, **4a** possesses an orthogonal structure and is therefore chiral.

Chemical behavior of highly *tert*-butylated octatetraenes: With sufficient amounts of **4a** in hand, the first experiment we tried was its bromination. As in the case of 1,2,3-tri-*tert*-butylbuta-1,3-diene, another "orthogonal diene" studied by us earlier,[17,21] we found that the intuitively expected electrophilic addition had not taken place, but that **4a** had undergone a substitution reaction yielding the monobromide **24** (55%) when one equivalent of bromine was used. If a threefold excess of bromine is used, the dibromide **27** is formed in good yield (88%). It appears likely that **24** is an intermediate en route to **27**. This double substitution product could not be converted into a more highly brominated product, as shown by repeating the process under rougher reaction conditions (large excess of bromine, extended reaction time). The separation of the product mixture containing the substrate **4a** and varying amounts of **24** and **27** was accomplished by column chromatography on silver nitrate impregnated silica gel (Scheme 5).



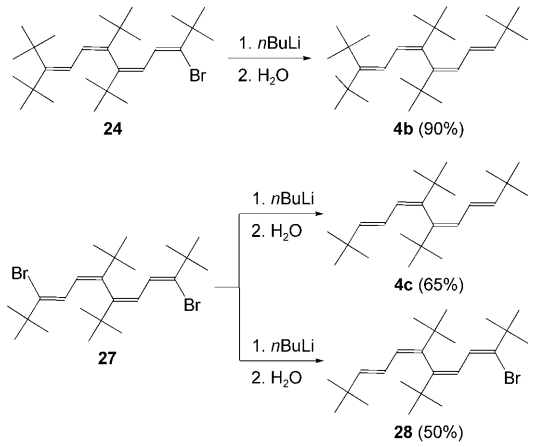
Scheme 5. The bromination of (5*Z*,7*Z*)-**4a**.

Whereas the structure of **24** could be derived by two-dimensional NMR analysis and its other spectroscopic data (see Experimental Section), the dibromide **27** on high vacuum sublimation provided crystals suitable for an X-ray structural analysis (see below). It shows that the two diene "halves" of **27** indeed adopt an orthogonal configuration with respect to each other. The extensive 2D-NMR experiments on **24** (COSY, HSQC, HMBC, NOESY) allowed us to determine constitution, configuration, and conformation of the molecule. Nuclear Overhauser effects were observed between all *tert*-butyl protons and their respective *cis*-proton at the same double bond. The NOE between 4-H and the 3-*tert*-butyl group established the *Z* configuration of the C3=C4 double bond. Moreover, a NOESY cross-peak was found between 8-H and the (*Z*)-*tert*-butyl protons at C-10, in accordance with an *s-trans* conformation at the C8–C9 bond. Yet no NOE was discernible between protons in the different halves of the molecule in agreement with an orthogonal conformation at the C6–C7 bond.

Formally the above substitution resembles the *ipso*-substitution in highly alkylated benzene derivatives. For example on bromination of *tert*-butyl benzene small amounts of bromobenzene are generated,[22] and in the case of 1,3,5-tri-*tert*-butylbenzene the *ipso*-substitution product bromo-3,5-di-*tert*-butylbenzene is the main product.[23] If the addition–elimination mechanism postulated for these cases is applied to **4a**, the picture summarized in Scheme 5 results. According to molecular models and PM3 calculations, the terminal double bonds of **4a** are more accessible to an attacking external reagent than the internal ones, and as a primary intermediate the bromonium ion **23** could be formed. Any *trans*-attack by bromide ion is prevented by the severely crowded environment, and therefore **23** stabilizes itself by loss of a *tert*-butyl cation. In fact, the trapping product of this leaving

group with bromide, that is, *tert*-butylbromide, could be detected in the product mixture of this experiment by GC/MS analysis as well as ^{1}H NMR spectroscopy (singlet at $\delta =$ 1.81 ppm). We could not find any evidence for the also possible production of isobutene. Even if the cyclic structure **23** opened up to the allyl cation **25**↔**26**, no additional room for external bromide trapping would become available, the *ipso*-substitution route still being the most favorable one. Both vinyl bromides, **24** and **27**, are, in principle, useful for further transformations; in particular it would be of interest to incorporate them into larger structures by metal-mediated coupling and cross-coupling reactions. The "polyacetylenes" thus obtained might well possess a helical structure. The reason for the observed stereospecific formation of both **24** and **27** is unclear at present. It could well be that during the product-forming step from, for example, **23** or **26**, the incoming bromine substituent might find it sterically easier to point towards the next double bond in a *cisoid* fashion. If the *tert*-butyl substituent were to replace the bromine atom, we might expect strong steric interactions between the bulky substituent and the neighboring olefinic hydrogen atom.

Tetraenes with a smaller number of *tert*-butyl substituents, namely **4b** and **4c**, are readily available from **24** and **27** by halogen–metal exchange followed by hydrolysis. Although this process is slow and required heating in a THF/hexane solvent mixture (probably because of steric hindrance again), the two debrominated hydrocarbons **4b** and **4c** could be prepared in good yields (90 and 65%, respectively; Scheme 6).



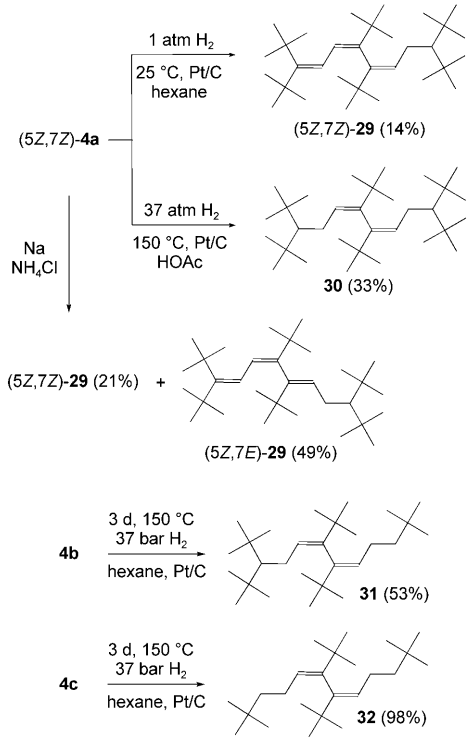
Scheme 6. Debromination of the bromides **24** and **27**.

On slow recrystallization from ethanol, single crystals of **4b** and **4c** were obtained which allowed X-ray structural determination (see below). As expected, both compounds show a twisted structure; their full spectroscopic and analytical details can be found in the Experimental Section.

When the debromination of **27** was performed at −78 °C (excess *n*-butyl lithium) and the resulting intermediate quenched with water, the monobromide **28** was isolated in 50% yield; its structure follows from the spectroscopic data (see Experimental Section).

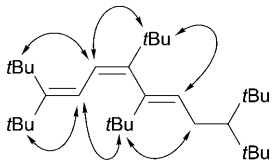
We next turned to the hydrogenation of the highly *tert*-butylated octatetraenes **4a–c**. In a first series of experiments catalytic hydrogenation reactions over various precious metal catalysts were carried out.

Whereas **4a** did not add hydrogen when Pd on charcoal or in situ prepared Pt (from PtO_2) was used, hydrogen uptake took place over Pt/C although it proceeded very slowly and provided the monohydrogenated triene (5*Z*,7*Z*)-**29** after one week at 1 atm of hydrogen pressure at room temperature in 14% yield only. Although a doubly hydrogenated product was also produced in trace amounts (hints from the MS data), we could not separate and identify it. Analytically pure triene was obtained by recrystallizing the hydrocarbon several times from ethanol; the crystals were suitable for an X-ray structure determination (see below). The other spectroscopic data are given in the Experimental Section. Under more rigorous conditions (37 atm H_2 pressure, 150 °C, acetic acid, 3 days) the two terminal double bonds of **4a** were saturated and the hydrocarbon **30** was isolated in 33% yield. Again, recrystallization from ethanol provided single crystals of X-ray quality and the structure of the diene in the solid state is reported below. Both hydrocarbons have the expected orthogonal structure (Scheme 7).



Scheme 7. Hydrogenation of (5*Z*,7*Z*)-**4a** under different conditions.

Comparable results were obtained when **4a** was subjected to the conditions of a Birch reduction (liquid ammonia, sodium, ammonium chloride, THF). In this case, two reduc-



(5*Z*,7*E*)-**29**

Scheme 8. Structure-relevant NOEs observed in (5*Z*,7*E*)-**29**.

tion products are formed, both being trienes according to their mass spectra. The first one is the 5*Z*,7*Z*-diasteromer of **29** already discussed above (21%) and the second one its 5*Z*,7*E*-isomer (49%, see Scheme 7). The hydrocarbons could be separated by column chromatography on silver nitrate impregnated silica gel, and their structures determined by NMR spectroscopy (NOESY spectra). As the structure of (5*Z*,7*Z*)-**29** was also determined by X-ray diffraction, only the NOEs relevant for the structure of (5*Z*,7*E*)-**29** are given in Scheme 8.

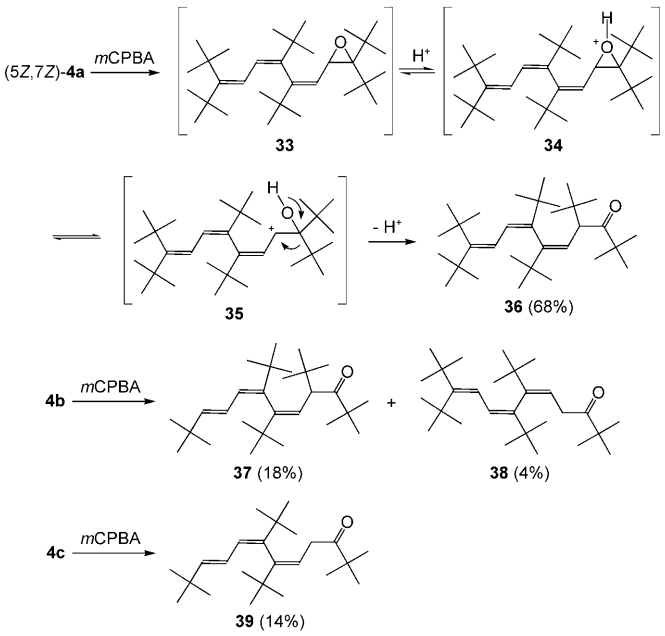
After these results with **4a**, the hydrogenation of **4b** and **4c** offered no surprises. Under high pressure conditions the two "internal" dienes were produced in 53 and 98% yield, respectively (Scheme 7). Not only do the higher yields and the milder conditions—the unpolar hexane serving as the solvent—in these cases indicate less steric shielding, but according to a GC/MS analysis of the hydrogenation mixture a monoene was also produced in trace amounts; its concentration was, however, so small that its structure could not be derived from its NMR spectra.

In summary, the hydrogenation experiments demonstrate that these oligoenes posses an "external part" at which the reducing agent (hydrogen plus catalyst surface) can more or less readily attack and an inner unsaturated core which is so strongly sterically protected that it survives even severe hydrogenation conditions. The unsaturation is "buried" by a saturated sheet and survives chemical transformations, that is, we are dealing with a "hidden functionality".

The terminal double bonds of the tetraenes **4** also reacted in the next series of experiments performed: epoxidations. To our surprise, however, we could not isolate the expected adducts. As shown in Scheme 9, in all cases ketones with a rearranged carbon skeleton were produced.

We nevertheless assume that an epoxide, **33**, generated at the periphery of **4a**, is produced initially and that this opens up under the acidic conditions via **34** and **35**; a terminating Wagner–Meerwein shift of a *tert*-butyl substituent finally provides the isolated ketone **36**. Since this product possesses two stereogenic elements (an axis and a center) it should be formed as a mixture of two diastereomers. This is indeed the case as shown by ^{1}H NMR analysis, and although the two products, formed in 9:1 ratio, could be separated by column chromatography, no attempt was made to establish their exact stereostructure. To avoid the presence of acid during epoxidation, we repeated the process using dimethyldioxirane as the oxidation reagent. However, in this case no epoxidation of **4a** was observed.

Tetraene **4b** offers the interesting possibility to study two competing oxidation reactions, since its two terminal double bonds are differently substituted. Evidently, the more electron-rich double bond is attacked preferentially and **37** is formed as the main product. Since this contains two stereo-



Scheme 9. Epoxidation of (5*Z*,7*Z*)-**4a**, **4b**, and **4c**.

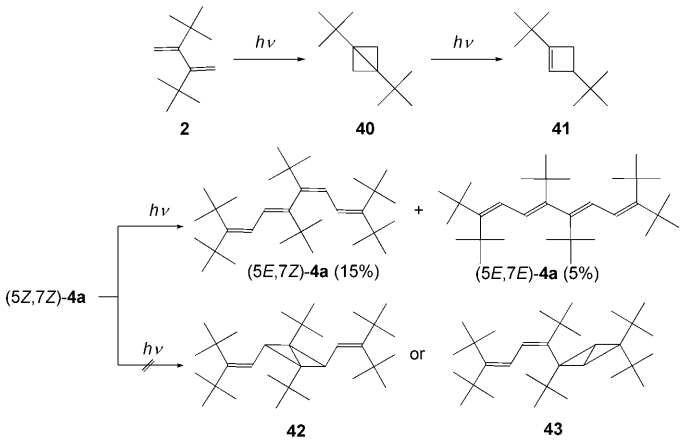
genic elements, a mixture of diasteromers is produced (ratio 1:9 as shown by ^{1}H NMR analysis). In this case, however, a separation of the two isomers failed. When the alternative terminal double bond is attacked, the isomeric ketone **38** is produced. For its formation a proton shift must have been faster than the migration of a *tert*-butyl group.

In **4c** the termini of the tetraene are equally substituted again and one product, ketone **39**, is produced on epoxidation, as expected. The structures of all these new compounds follow from their spectroscopic data which are listed in the Experimental Section.

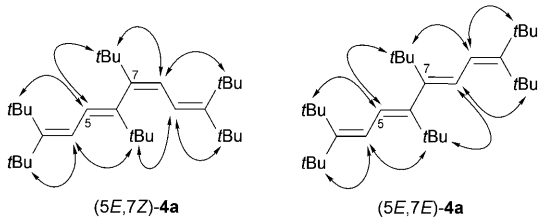
In one of our earlier studies on the preparation of *tert*-butylated di- and oligoenes, we described the photochemical behavior of **2**.[24] It was found that this hydrocarbon, on direct irradiation with a high-pressure mercury lamp, cyclized to the bicyclobutane derivative **40**. The surprisingly high yield of 60% was attributed by us to the orthogonal structure of **2**. On further irradiation the central bond of **40** is cleaved and by a 1,2-hydrogen shift the cyclobutene derivative **41** is produced (Scheme 10)

To investigate whether the "extended" oligoenes **3** and **4** show a comparable behavior, we selected (5*Z*,7*Z*)-**4a** as a model compound and irradiated it in hexane for three days with a 150 W low-pressure mercury lamp. Two products were formed and they could be separated by repeated recrystallization from ethanol. These hydrocarbons were the 5*E*,7*Z* and 5*E*,7*E* isomers of the substrate (5*Z*,7*Z*)-**4a**, and not cyclization products such as **42** and **43**, as demonstrated by their NOESY-spectra (see Scheme 11).

According to B3LYP-DFT calculations[25] (5*E*,7*Z*)-**4a** is 16 kJ mol^{-1} and (5*E*,7*E*)-**4a** is 26 kJ mol^{-1} less stable than the substrate. No hints could be derived from the photolysate that **42** or **43** had been produced during irradiation. Fol-



Scheme 10. Photoisomerization of (5*Z*,7*Z*)-**4a**.



Scheme 11. NOEs observed in (5*E*,7*Z*)-**4a** and (5*E*,7*E*)-**4a**.

lowing the photoreaction by continuous monitoring (TLC analysis) did not reveal any additional products at shorter reaction times.

The structures of 4a–c, 18, 27, (5*Z*,7*Z*)-29, and 30 in the solid state: All compounds crystallize solvent-free and without imposed crystallographic symmetry; the asymmetric unit of compounds **18** and **27** consists of two independent molecules. Approximate twofold symmetry (r.m.s. deviations in brackets) is displayed by the molecules **4a** (0.1 Å), **4c** (0.2 Å), **18** (first molecule only, 0.1 Å), **27** (both molecules; 0.07, 0.08 Å), and **30** (0.04 Å).

Molecular structures are presented in Figures 2–5. Table 2 presents a summary for all structures of molecular dimensions along the central C_8 chain. The most striking feature is the geometry associated with the central single bond C4–C5. The torsion angles (absolute values) about this bond lie in the range 77 to 93°, thus demonstrating that the double *tert*-butyl substitution has forced the orthogonality of the two halves of the chain. The bond length itself ranges from 1.495 to 1.511 Å (av. 1.503 Å), which may be compared with typical values for the system C=**C**–**C**=C quoted as 1.455 Å for conjugated and 1.478 Å for nonconjugated systems.[26] The formally analogous bond lengths C2–C3, when lying between two double bonds as in compounds **4a–c**, **27** and (one half of) **29**, correspond well to the conjugated value, because the torsion angles about this bond are essentially zero. The extra elongation of C4–C5 may be attributed to the steric effects of the bulky substituents; compare with the bond

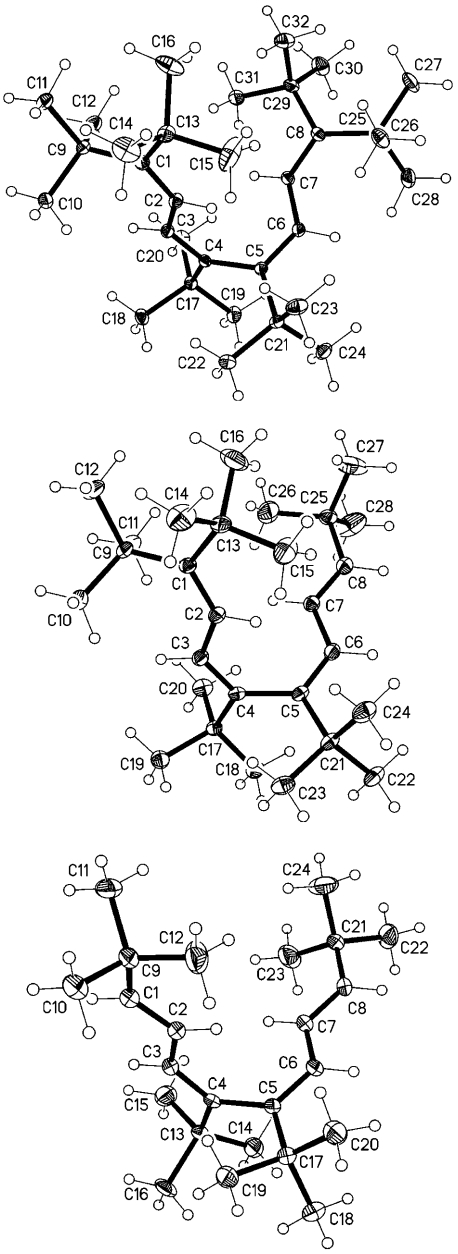


Figure 2. The molecular structures of compounds **4a** (top), **4b** (middle), and **4c** (bottom) in the crystal. Ellipsoids represent 30% probability levels for **4a** and **4b** and 50% for **4c**.

lengths C1=C2, which are significantly longer if C1 bears two *tert*-butyl substituents. The double bonds C3=C4 are shorter, effectively isolated double bonds, in compounds **18**, (one half of) **29**, and **30** than in the other molecules. Bond angles are consistent with some of the trends noted in our polyene and mixed polyene/polyyne systems;[1,2] thus the angles C1-C2-C3 are extremely wide (>130°) if C1 bears two *tert*-butyl substituents, and angles C2-C3-C4 are also consistently wider than the ideal 120° by some 6°. The angles C3-C4-C5 at the center of the chain are however close to ideal.

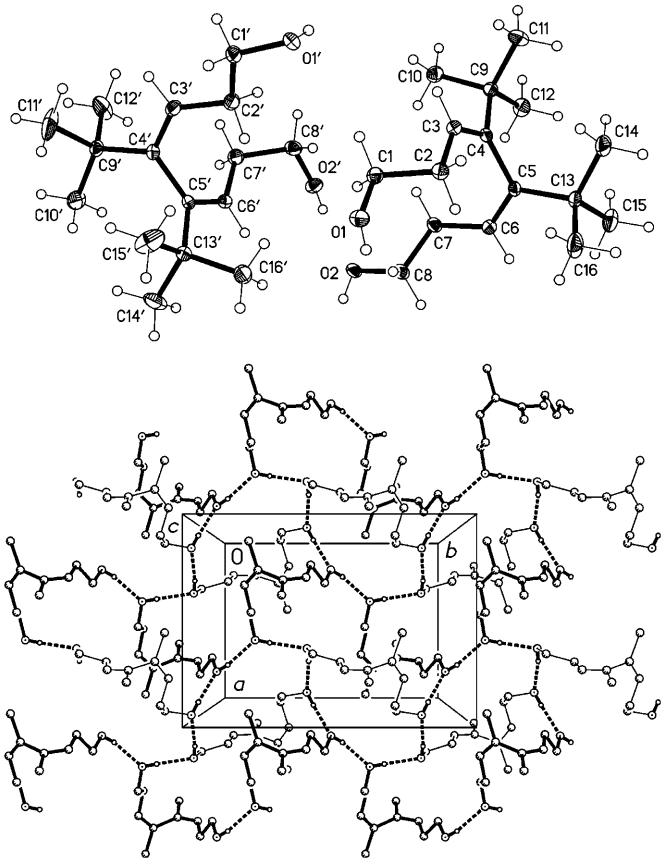


Figure 3. Top: The two independent molecules of compound **18** in the crystal. Ellipsoids represent 50% probability levels. Bottom: Packing diagram of compound **18** in the region $z \approx {}^1/_4$; thick dashed lines indicate hydrogen bonds. Molecule 1 is drawn with thick and molecule 2 with thin bonds. Hydrogen atoms not involved in H bonds are omitted. The 19-membered rings (see text) are seen as a horizontal series along the *yz* faces and the 33-membered rings across the center of the cell.

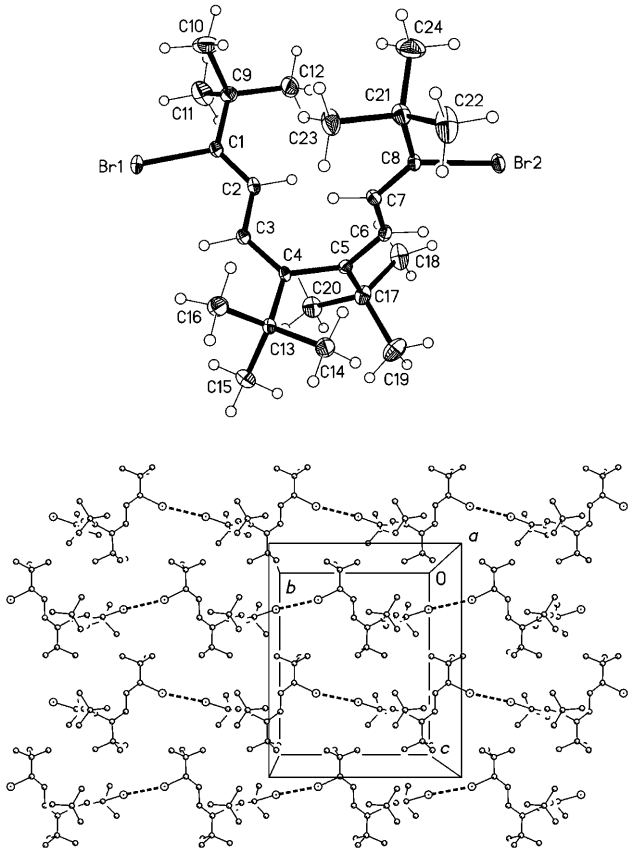


Figure 4. Top: One of two independent molecules of compound **27** in the crystal. Ellipsoids represent 30% probability levels. Bottom: Packing diagram of compound **27**; thick dashed lines indicate bromine–bromine contacts. This is the region at $x \approx {}^1/_8$ and contains only the second independent molecule (see text).

The two independent molecules of **18** differ primarily in the conformation of the C-C-C-OH chains, for which the torsion angles are extended ($\approx \pm 180°$) except for C6′-C7′-C8′-O2′ 75.4°. For compound **27**, differences in torsion angles combine to make the r.m.s. deviation of a least-squares fit 0.32 Å, reducing to 0.11 Å if only the atoms Br1, Br2, C1–8, C13, C17 are considered.

The packing of the rod-shaped molecules of our polyene and mixed polyene/polyyne systems[1,2] often involved parallel molecular chains (which were generally linear) and associated layer structures. The more equidimensional form of the molecules studied here, associated with the orthogonality about C4–C5, renders the packing devoid of special features unless other functional groups are present. For compound **18** (Figure 3, bottom) each of the four independent OH groups forms one classical hydrogen bond to another OH group as the acceptor. Each independent molecule, considered alone, forms an undulating chain of graph set $C(11)$ with overall direction parallel to the *y* axis. The combination of both chains leads to a corrugated layer structure parallel to the *xy* plane. The layer contains two topologically different types of rings; rings of graph set $R_5^5(19)$ involving the complete backbone of molecule 2, and larger rings $R_3^3(33)$ involving two backbones of molecule 1 and one of molecule 2.

The packing of compound **27** is determined largely (ignoring borderline C–H···Br contacts) by the Br···Br interactions Br1···Br2 3.5907(7) and Br1′···Br2′ 3.5597(7) Å, with all C–Br···Br angles in the range 165–175°. Each independent molecule thereby forms chains of molecules related by *y* axis translation, neighboring chains forming layers at $x \approx {}^1/_8, {}^7/_8$ (molecule 2), ${}^3/_8, {}^5/_8$ (molecule 1; Figure 4, bottom).

Chirality of 3, 4b, and 4c: Excluding the *meso*-forms, all nonplanar di- and oligoenes are chiral. This is evident for butadiene, the only achiral conformations of which are its *syn*- and the *anti*-forms. As soon as the dihedral angle between the two double bonds differs from 0 or 180°, chirality is generated. Whether, however, optically active enantiomers can be isolated depends on the racemization barrier (activation energy for rotation about the single bond connecting the double bounds). In fact, resolvable derivatives of chiral dienes have been known for a long time, the most famous examples coming from the classical studies of Kö-

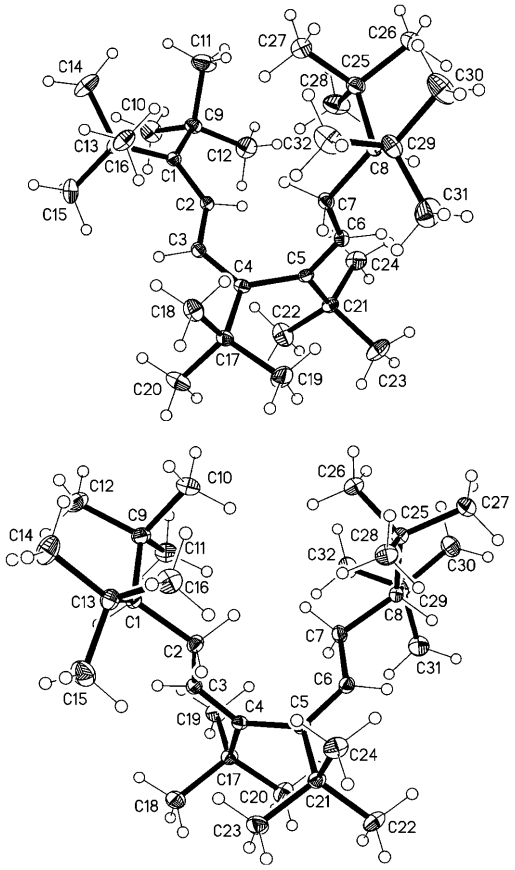


Figure 5. The molecular structures of compounds **29** (*Z*,*Z* isomer; top) and **30** in the crystal. Ellipsoids represent 30% probability levels.

brich and of Mannschreck and involve polyhalogenated di- and trienes.[27,28]

As far as we are aware, we are presenting here the first experimental proof that nonplanar conjugated tetraenes are chiral and can be resolved by either gas chromatography or HPLC on chiral phases. For this purpose the di-*tert*-butylated octatetraene **3** and the two derivatives **4b** and **4c** were resolved by various chromatographic methods using different chiral selectors.

Beginning with the tetraenes **4b** and **4c**, these could be resolved by analytical gas chromatography on a capillary column coated with 6-*O*-TBDMS-2,3-di-*O*-methyl-β-cyclodextrin. As shown in Figure 6 in both cases base-line separation was accomplished.[29]

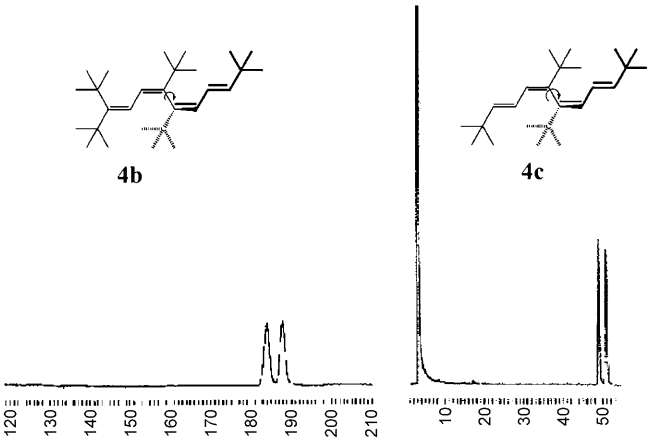


Figure 6. Gas chromatographic separation of the two enantiomers of the tetraenes **4b** and **4c** with 6-*O*-TBDMS-2,3-di-*O*-methyl-β-cyclodextrin as chiral selector.

These separations were carried out at 150°C, the highest operating temperature of the used columns, showing that

Table 2. Selected geometric parameters [bond lengths in Å, bond angles and torsion angles in °] for the central carbon chains of compounds **4a**, **4b**, **4c**, **18**, **27**, (*Z*,*Z*)-**29** and **30**. The chains are numbered from C1 to C8. Values for both halves of the chain, which are in general chemically equivalent unless otherwise stated, are presented together (e.g., C1−C2 with C7−C8).

	C1−C2	C2−C3	C3−C4	C4−C5	C1-C2-C3	C2-C3-C4	C3-C4-C5	C1-C2-C3-C4	C2-C3-C4-C5	C3-C4-C5-C6
4a	1.359(1)	1.460(1)	1.352(1)	1.503(1)	131.5(1)	125.7(1)	121.2(1)	173.5(1)	0.7(1)	−78.9(1)
	1.356(1)	1.457(1)	1.350(1)		131.3(1)	124.7(1)	121.1(1)	169.5(1)	3.4(1)	
4b[a]	1.354(2)	1.451(2)	1.353(2)	1.496(2)	131.7(2)	125.0(2)	120.6(2)	163.9(2)	−0.9(2)	−77.3(2)
	1.332(2)	1.460(2)	1.336(2)		123.4(2)	126.7(2)	119.8(1)	178.8(2)	4.4(2)	
4c	1.342(4)	1.458(4)	1.355(4)	1.511(4)	124.2(3)	125.9(3)	118.9(2)	−174.3(3)	0.0(4)	−91.8(3)
	1.343(4)	1.456(4)	1.364(4)		124.0(3)	125.0(3)	118.3(2)	176.9(3)	0.7(4)	
18	1.518(3)	1.500(3)	1.332(3)	1.506(3)	112.0(2)	127.2(2)	120.8(2)	−130.6(2)	−1.1(3)	87.9(2)
	1.503(3)	1.508(3)	1.333(3)		115.2(2)	127.4(2)	120.8(2)	−126.0(2)	0.5(3)	
	1.504(3)	1.501(3)	1.334(3)	1.507(3)	110.8(2)	127.4(2)	119.1(2)	−157.7(2)	1.0(3)	−80.7(3)
	1.523(3)	1.497(3)	1.340(3)		113.0(2)	126.7(2)	119.0(2)	134.9(2)	1.8(3)	
27	1.338(5)	1.442(5)	1.344(5)	1.495(5)	127.7(4)	125.2(4)	120.0(4)	−178.0(4)	−8.1(6)	90.4(5)
	1.331(5)	1.440(5)	1.356(5)		127.4(4)	125.3(4)	119.7(3)	177.8(4)	−3.8(6)	
	1.336(5)	1.442(5)	1.338(5)	1.499(5)	127.9(4)	125.6(4)	119.8(4)	−175.9(4)	3.1(6)	−92.4(5)
	1.331(5)	1.451(5)	1.349(5)		127.9(4)	124.1(4)	119.3(4)	−171.9(5)	1.4(6)	
(*Z*,*Z*)-**29**[b]	1.351(2)	1.459(2)	1.348(2)	1.504(2)	131.7(2)	125.5(2)	120.9(1)	−162.9(2)	4.4(3)	88.2(2)
	1.553(2)	1.502(2)	1.337(2)		115.6(1)	127.4(2)	119.5(1)	−166.6(2)	−0.4(3)	
30	1.552(1)	1.509(1)	1.334(1)	1.507(1)	115.8(1)	126.4(1)	120.4(1)	176.7(1)	−0.9(2)	−86.1(1)
	1.550(1)	1.507(1)	1.334(1)		115.6(1)	126.2(1)	120.3(1)	180.0(1)	−0.3(1)	

[a] The two halves of the molecule are not equivalent; C1 bears two *tert*-butyl substituents, C8 only one. [b] The two halves of the molecule are not equivalent; C1=C2 is a double bond, C7−C8 a single bond.

the two hydrocarbons are configurationally stable at least up to this temperature. Various attempts to resolve the enantiomers on a preparative GC scale failed. On the above column the two signals overlap far too strongly to allow a successful separation. Turning to cellulose-tris-(3,5-dimethylphenylcarbamate) as the chiral selector, a material that has been used for the separation of numerous racemates, including hydrocarbons and molecules with an axis of chirality[30] also failed, although many different conditions (variation of solvents and solvent mixtures) were tried.

Finally, the Nagoya group was able to separate **4c** on a Chiralpak OT(+)-column, which employs (+)-poly(triphenylmethylmethacrylate) as the chiral selector.[31] The result of a preparative HPLC separation of **4c** with ethanol as solvent at 0 °C is shown in Figure 7.

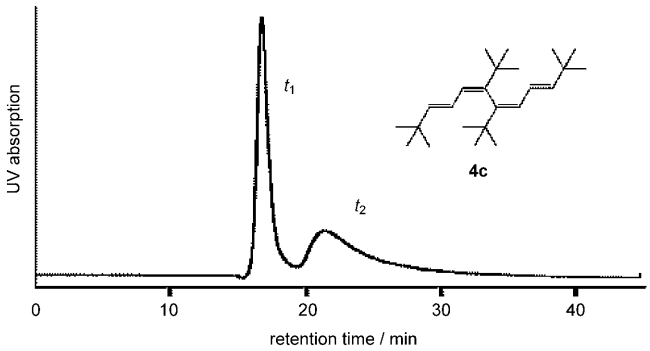


Figure 7. Separation of **4c** by preparative HPLC on Chiralpak OT(+); solvent: ethanol, flow rate 0.2 mL min^{-1}, 0 °C.

Altogether 3 mg of the first fraction, and 1 mg of the second were obtained. As shown by analytical HPLC analysis, the enantiomeric excess of the first fraction exceeded 99 %, whereas the second fraction had an *ee* of ≈95 %. The specific rotation of the first fraction $[\alpha]_D^{20}$ was determined as +130°.

Preparative gas chromatography on a 6-*O*-TBDMS-2,3-di-*O*-methyl-β-cyclodextrin impregnated column turned out to be the method of choice for separation of the di-*tert*-butylated tetraene **3**. In this case a specific rotation of $[\alpha]_D^{20} = \pm 284°$ was measured.

For two of the tetraenes prepared in this study the absolute configuration was determined by the exciton chirality method: **3** and **4b**.[32] The necessary CD and UV spectra are shown in Figures 8 and 9, respectively, and the assignment of the absolute configurations is given in Table 3. It is evident from the UV spectra that the two chromophores of these hydrocarbons are not in conjugation (see above). In both cases the dextrorotatory enantiomer is thus in the *S* configuration.

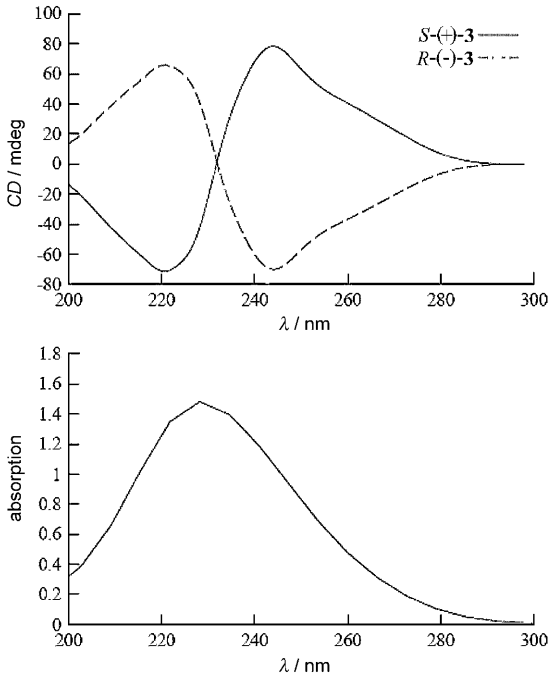


Figure 8. Top: CD spectrum of hydrocarbon **3** in hexane at room temperature; conc. of *S*-(+)-**3**: 10.2 μg mL^{-1}, conc. of *R*-(−)-**3**: 8.6 μg mL^{-1}. Bottom: UV spectrum of **3** in hexane.

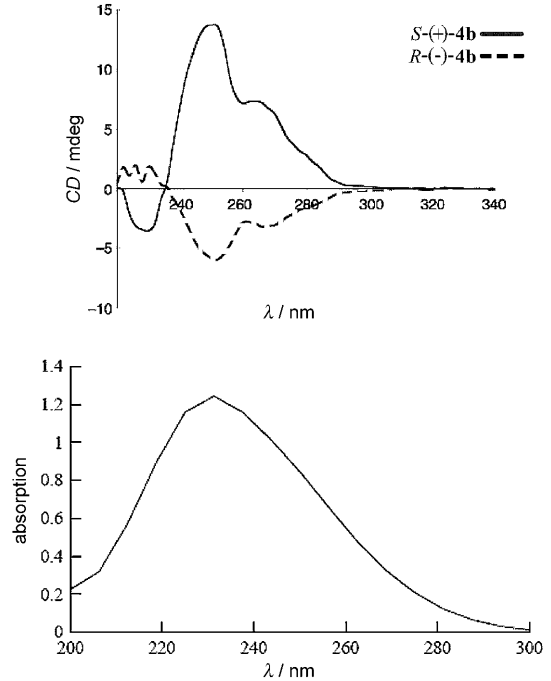
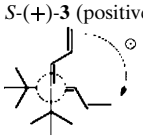
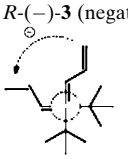
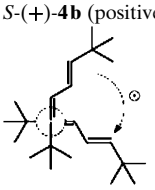
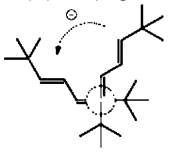


Figure 9. Top: CD spectrum of hydrocarbon **4b** in ethanol at room temperature. Bottom: UV spectrum of **4b** in ethanol.

Experimental Section

General: Melting points: below 200 °C: Büchi 510 melting point apparatus; above 200 °C: Kofler apparatus. The m.p. are uncorrected. NMR:

Table 3. Assignment of the absolute configurations of **3** and **4b**.

	UV λ_{max} [nm]	CD λ_{ext} [nm] (ψ [mdeg])	
S-(+)-**3** (positive exciton chirality)			
	228	244.2 (84.2) 231.9 (0.0) 221.4 (−75.9)	A = 160.1 mdeg
R-(−)-**3** (negative exciton chirality)			
	228	244.2 (−73.4) 232.3 (0.0) 220.4 (69.3)	A = −142.7 mdeg
S-(+)-**4b** (positive exciton chirality)			
	232 192	251 (13.8) 236 (0.0) 229 (−3.5)	A = 17.3 mdeg
R-(−)-**4b** (negative exciton chirality)			
	232 192	251 (−5.8) 236 (0.0) 226 (1.9)	A = −7.7 mdeg

Bruker AC-200: ^{1}H NMR (200.1 MHz), ^{13}C NMR (50.3 MHz); Bruker AM-400 and DRX-400: ^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) in deuteriochloroform. ^{1}H chemical shifts in ppm to high frequency of internal tetramethylsilane, ^{13}C chemical shifts relative to $CDCl_3$ (δ = 77.01 ppm). IR: Nicolet 320 FT-IR spectrometer as KBr pellets or thin films; ATR-IR: Bruker Tensor 27 Spectrometer. UV/Vis: HP 8452 A Diode Array spectrophotometer; Varian Cary 100 BIO. MS: Finnigan MAT 8430 (EI, 70 eV and FAB). GC/MS: Finnigan MAT 4515 (EI, 40 eV) attached to a Carlo Erba HRGC 5160. Analytical enantioselective GC: Carlo Erba Fractovap 2150 with a 25 m fused silica capillary column with octakis-(2,6-di-*O*-methyl-3-*O*-pentyl-γ-cyclodextrin or heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin in OV-1701 (1:1; w/w) as the stationary phase. Preparative enantioselective GC: Varian 1400 with heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin/SE-52 (1:1; w/w) on Chromosorb W-HP. Optical rotation: Propol polarimeter (Dr. Kernchen). CD: AVIV Model 215 Circular Dichroism Spectrometer (University of Hamburg); JASCO-1595 CD-Spectrometer (Nagoya University). HPLC columns for enantioselective chromatography: Chiracell OD-H; Chiralpak OT(+) using a Merck L-4250 or JASCO MD-2010 UV/Vis detector. Elemental analyses: Institut für Pharmazeutische Chemie, TU Braunschweig. X-ray analysis: Siemens R3; Stoe STADI-4; Bruker SMART 1000 CCD. The X-ray data were processed and refined with the SHELXS-86 and SHELXS-93 programs, respectively.

The aldehydes **13**[11,12] and **19**[16] and the alcohol **14**[14] were prepared according to the procedure described in the literature; all other reagents were commercial compounds.

1,8-Bis-(tetrahydropyran-2-yloxy)-oct-4-yne-3,6-diol (15): A solution of *n*BuLi (1.6 M) in hexane (18.4 mL, 29.5 mmol) was added under nitrogen to a solution of the propargyl alcohol **14** (2.47 g, 13.4 mmol) in anhydrous THF (70 mL) at 0 °C . The mixture was heated to reflux for 1 h and after cooling to 0 °C a solution of aldehyde **13** (2.33 g, 14.75 mmol) in anhydrous THF (10 mL) was added. The reaction mixture was stirred at room temperature and subsequently hydrolyzed with sat. ammonium chloride solution in water (100 mL). The phases were separated and the aqueous phase was carefully extracted with diethyl ether (4×30 mL). The combined organic phases were dried ($MgSO_4$) and the solvent removed by distillation. The raw product was purified by column chromatography (silica gel; hexane/diethyl ether 1:1). Yield: 2.29 g (50 %); colorless oil; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.43–1.83 (m, 12 H; 10-, 11-, 12-, 15-, 16-, 17-H), 1.93–2.06 (m, 4 H; 2-, 7-H), 3.54–4.03 (m, 8 H; 1-, 8-, 13-, 18-H), 4.58–4.63 ppm (m, 4 H; 3-, 6-, 9-, 14-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 99.01, 99.00, 98.81 (d, C-9, -14), 85.39, 85.36 (s, C-4, -5), 64.27, 64.21 (t, C-1, -8), 62.46, 62.44, 62.14, 62.12 (t, C-13, -18), 60.31, 60.16 (d, C-3, -6), 37.09, 37.04 (t, C-2, -7), 30.47, 30.43 (t, C-10, -15), 25.22, 25.19 (t, C-12, -17), 19.46, 19.27 ppm (t, C-11, -16); IR (ATR): $\tilde{\nu}$ = 3042 (br, w), 2940 (m), 2872 (m), 1440 (m), 1352 (m), 1201 (m), 1136 (m), 1118 (s), 1062 (s), 1020 (s), 981 (s), 904 (m), 867 (m), 809 cm^{-1} (m); ESI-MS: *m/z*: 366.1 [M^++H+Na] (25), 365.1 [M^++Na] (100); UV (acetonitrile): λ_{max} (log ε) = 191 nm (3.05); HRMS/ESI: $C_{18}H_{30}O_6Na$: calcd 365.1940; found: 365.1933.

3,6-Diacetoxy-1,8-bis-(tetrahydropyran-2-yloxy)-oct-4-yne (16): A mixture of **15** (1.48 g, 4.32 mmol), acetic anhydride (50 mL), and pyridine (6 mL, 74 mmol) was left at RT for 12 h under nitrogen. After neutralization with aqueous bicarbonate solution, the reaction mixture was extracted with diethyl ether (4×30 mL portions), and the combined organic phases dried over magnesium sulfate. The oil obtained after solvent removal in vacuo was purified by column chromatography on silica gel (hexane/diethyl ether 1:1). Colorless oil, yield: 1.66 g (90 %); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.48–1.87 (m, 12 H; 10-, 11-, 12-, 19-, 20-, 21-H), 1.98–2.17 (m, 4 H; 2-, 7-H), 2.072 and 2.075 (s, 6 H; 15-, 17-H), 3.42–3.91 (m, 8 H; 1-, 8-, 13-, 22-H), 4.56–4.59 (m, 2 H; 9-, 18-H), 5.52–5.63 ppm (m, 2 H; 3-, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.70, 169.68 (s, C-14, -16), 98.68, 98.64 (d, C-9, -18), 82.77 (s, C-4, -5), 62.93, 62.85, 61.94, 61.91 (t, C-1, -18, -13, -22), 61.36, 61.26, 61.24 (d, C-3, -6), 34.94, 34.86 (t, C-2, -7), 30.49, 30.45 (t, C-10, -19), 25.39 (t, C-12, 21), 20.92 (q, C-15, -17), 19.23, 19.18 ppm (t, C-11, -20); IR (ATR): $\tilde{\nu}$ = 2942 (m), 2871 (w), 1739 (s), 1439 (w), 1369 (m), 1222 (s), 1200 (w), 1160 (m), 1119 (m), 1076 (m), 1035 (s), 1017 (s), 981 (s), 961 (s), 903 (m), 868 (m), 814 cm^{-1} (m); ESI-MS: *m/z* (%): 450 [M^++H+Na] (22), 449 [M^++Na] (100); UV (acetonitrile): λ_{max} (log ε) = 193 nm (3.15); HRMS/ESI: $C_{22}H_{34}O_8Na$ (449.22): calcd 449.2151; found: 449.2154.

(3*Z*,5*Z*)-4,5-Di-*tert*-butyl-1,8-bis-(tetrahydropyran-2-yloxy)-octa-3,5-diene (17): A solution of *tert*-butyl magnesium chloride in anhydrous diethyl ether (150 mL) was prepared from magnesium turnings (6.9 g, 0.28 mol) and *tert*-butylchloride (9.4 mL, 86 mmol). The Grignard solution was added under nitrogen at −50 °C to a suspension of anhydrous CuBr (3.51 g, 24.5 mmol) and LiBr (2.12 g, 24.4 mmol) in THF (50 mL). After stirring at this temperature, a solution of **16** (2.26 g, 5.30 mmol) in THF (50 mL) was added at −70 °C. After 1 h stirring at this temperature more Grignard solution was added (prepared from magnesium (7.3 g, 0.3 mol), *tert*-butylchloride (10 mL, 91.8 mmol) at −70 °C. After stirring for 16 h at room temperature, saturated aqueous ammonium chloride solution was added for hydrolysis. The hydrolysate was filtered to remove any solid precipitates, the phases were separated, and the aqueous phase was washed with diethyl ether (3×30 mL). The combined organic phases were dried with magnesium sulfate and the solvent was removed by rotary evaporation. The remaining oily residue was purified by silica gel column chromatography with hexane/diethyl ether 8:2 as the eluent. Yield: 1.35 g (60 %); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.11 (s, 18 H; 15-, 17-H), 1.52–1.86 (m, 12 H; 10-, 11-, 12-, 19-, 20-, 21-H), 2.17–2.24 (m, 4 H; 2-, 7-H), 3.33–3.89 (m, 8 H; 1-, 8-, 13-, 22-H), 4.59 (t, J = 3.5 Hz, 2 H; 9-, 18-H), 5.54 ppm (t, J = 7.0 Hz, 2 H; 3-, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 149.65, 149.61 (s, C-4, -5), 122.99, 122.86 (d, C-3, -6), 98.60, 98.56 (d, C-9, -18), 67.21, 67.14 (t, C-1, -8), 61.94, 61.89 (t, C-13, -22), 35.34 (s, C-14, -16), 32.15 (q, C-15, -17), 31.26 (t, C-2, -7), 30.63 (t, C-10, -19), 25.51 (t, C-12, -21), 19.43, 19.40 ppm (t, C-11, -20); IR (ATR): $\tilde{\nu}$ = 2945 (m), 2900 (m), 2868 (m), 1471 (w), 1388 (w), 1362 (w), 1200 (m), 1138 (m), 1119 (m), 1075 (m), 1028 (s), 986 (m), 967 (m), 870 (m), 813 cm^{-1} (m); MS (70 eV): *m/z* (%): 422 [M^+] (<1), 192 (3), 179 (8), 164 (16), 149 (13), 119 (14), 105 (14), 85 (100), 67 (12), 57 (74); ESI/MS : *m/z* (%): 445 [M^++Na] (100), 446 [M^++Na+H] (28); UV (acetonitrile): λ_{max} (log ε) = 193 nm (4.23); HRMS/ESI: *m/z* calcd for: $C_{26}H_{46}O_4Na$: 445.3294; found: 445.3293.

3-Acetoxy-4-*tert*-butyl-1,8-bis-(tetrahydropyran-2-yloxy)-octa-4,5-diene: With shorter reaction times and/or insufficient amounts of the metal organic reagent in the preparation of **17**, the mono-*tert*-butylated intermediate could be isolated. Colorless oil; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta =$ 1.06, 1.07 (s, 9H; 17-H), 1.50–1.85 (m, 12H; 10-, 11-, 12-, 19-, 20-, 21-H), 2.01, 2.02 (s, 3H; 15-H), 1.91–2.06 (m, 2H; 2-H), 2.33 (q, $J = 6.9$ Hz, 2H; 7-H), 3.31–3.38 (m, 2H; 1-H), 3.44–3.89 (m, 6H; 8-, 13-, 22-H), 4.55–4.61 (m, 2H; 9-, 18-H), 5.37 (t, $J = 6.9$ Hz, 1H; 6-H), 5.51–5.55 ppm (m, 1H; 3-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$ 202.26, 202.23, 202.20, 202.17 (s, C-5), 170.07, 170.01 (s, C-14), 113.44, 113.40, 113.34, 113.29 (s, C-4), 98.60, 98.53, 98.47, 98.37 (d, C-9, -18), 92.15, 92.12 (d, C-6), 68.55, 68.22 (d, C-3), 66.64, 66.62 (t, C-8), 64.07, 63.87 (t, C-1), 61.94, 61.88, 61.60 (t, C-13, -22), 35.08 (t, C-2), 33.15 (s, C-16), 30.45 (t, C-10, -19), 29.68, 29,63 (t, C-7), 29.32, 29.28 (q, C-17), 25.29 (t, C-12, -21), 21.15 (q, C-15), 19.32, 19.28, 19.25, 19.09 ppm (t, C-11, -20); IR (ATR): $\tilde{\nu} =$2943 (m), 2869 (w), 1735 (m), 1440 (w), 1366 (m), 1233 (s), 1201 (m), 1138 (m), 1120 (s), 1078 (m), 1064 (m), 1030 (s), 984 (m), 906 (m), 813 cm^{-1} (m); MS (70 eV): *m/z* (%): 424 [M^+] (<1), 178 (8), 165 (8), 121 (4), 85 (100), 67 (7), 57 (12), 43 (9); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 192 nm (4.22); elemental analysis calcd (%) for $C_{24}H_{40}O_6$ (424.6): C 67.89, H 9.50; found: C 67.51, H 9.64.

(3*Z*,5*Z*)-4,5-Di-*tert*-butylocta-3,5-diene-1,8-diol (18): The diene **17** (660 mg, 1.56 mmol) was heated under nitrogen in the presence of *p*-toluenesulfonic acid (10 mg, 0.05 mmol) in ethanol (30 mL) for 2 h under reflux. The solvent was removed in vacuo, and the solid residue purified by silica gel column chromatography with diethyl ether: 290 mg (73%) of **18** as colorless plates. M.p. 108 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta =$ 1.11 (s, 18H; 10-, 12-H), 2.02–2.09 (m, 2H; 2-, 7-H_A), 2.30–2.39 (m, 2H; 2-, 7-H_B), 2.69 (s, 2H; -OH), 3.57–3.63 (m, 2H; 1-, 8-H_A), 3.67–3.72 (m, 2H; 1-, 8-H_B), 5.50 ppm (dd, $J = 9.5$, 4.3 Hz, 2H; 3-, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$ 150.74 (s, C-4, -5), 123.43 (d, C-3, -6), 62.60 (t, C-1, -8), 35.60 (s, C-9, -11), 34.10 (t, C-2, -7), 32.09 (q, C-10, -12); IR (ATR): $\tilde{\nu} =$3295 (m), 3027 (w), 2958 (s), 2904 (m), 2867 (m), 1475 (m), 1460 (m), 1388 (m), 1361 (m), 1226 (w), 1195 (m), 1054 (s), 1022 (s), 947 (m), 731 (m), 655 (s), 607 cm^{-1} (m); MS (70 eV): *m/z* (%): 236 [M^+] (5), 180 (4), 179 (8), 165 (9), 164 (20), 149 (18), 137 (6), 135 (10), 121 (15), 105 (15), 93 (12), 81 (8), 69 (9), 57 (100), 55 (11); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 192 nm (4.21); elemental analysis calcd (%) for $C_{16}H_{30}O_2$ (254.43): C 75.54, H 11.89; found: C 75.49, H 11.98; X-ray structural analysis: see below.

(3*Z*,5*Z*)-4,5-Di-*tert*-butyl-1,8-bis-(toluene-4-sulfonyloxymethyl)-octa-3,5-diene: A mixture of the diol **18** (160 mg, 0.63 mmol) and *p*-toluenesulfonyl chloride (900 mg, 4.72 mmol) in pyridine (8 mL) was stirred for 16 h under nitrogen at room temperature. After completion of the reaction, the mixture was poured into saturated aqueous bicarbonate solution (50 mL), the aqueous phase was extracted with ether thoroughly, and the combined organic phases were dried ($MgSO_4$). After solvent removal by rotary evaporation the oily residue was purified by column chromatography (silica gel, hexane/dichloromethane 1:1). Yield: 0.22 g (62%) of the ditosylate; colorless oil; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta =$1.00 (s, 18H; 17-, 19-H), 2.13–2.19 (m, 4H; 2-, 7-H), 2.44 (s, 6H; 15-, 26-H), 3.89–4.00 (m, 4H; 1-, 8-H), 5.35 (t, $J = 6.9$ Hz, 2H; 3-, 6-H), 7.34 (*AA'*XX', 4H; 11-,13-, 22-, 24-H), 7.77 ppm (AA'*XX'*, 4H; 10-, 14-, 21-, 25-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$151.30 (s, C-4, -5), 144.61 (s, C-9, -20), 133.91 (s, C-12, -23), 129.73 (d, C-11, -13, -22, -24), 127.70 (d, C-10, -14, -21, -25), 120.75 (d, C-3, -6), 69.83 (t, C-1, -8), 35.33 (s, C-16, -18), 31.81 (q, C-17, -19), 30.10 (t, C-2, -7), 21.42 ppm (q, C-15, -26); IR (ATR): $\tilde{\nu} =$2965 (w), 2901 (w), 2867 (w), 1598 (w), 1467 (w), 1356 (s), 1173 (s), 1097 (w), 1055 (m), 963 (m), 908 (s), 835 (m), 813 (s), 757 (m), 731 (m), 661 cm^{-1} (s); ESI/MS : *m/z* (%): 586 [M^+ + Na + H], 585 [M^+ + Na]; UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 197 (4.69), 224 nm (4.38); HRMS (ESI): *m/z* calcd for $C_{30}H_{42}O_6S_2Na$: 585.2321; found: 585.2327.

(3*Z*,5*Z*)-4,5-Di-*tert*-butylocta-1,3,5,7-tetraene (3): A solution of the above ditosylate (0.380 g, 0.675 mmol) in anhydrous diethyl ether (50 mL) was stirred under nitrogen at room temperature for 2 d in the presence of potassium *tert*-butoxide (1.0 g, 8.91 mmol) The progress of the reaction was monitored by TLC analysis. The reaction mixture was hydrolyzed with aqueous bicarbonate solution (50 mL), the phases were separated, and the aqueous phase was thoroughly extracted with diethyl ether (3× 100 mL). The combined organic phases were dried ($MgSO_4$), the solvent was removed in vacuo, and the remaining oil purified by column chromatography (hexane): 80 mg (54%) of **3** as a colorless oil. On standing, the hydrocarbon polymerized within several weeks yielding a glassy polymer. ^{1}H NMR (400.1 MHz, $CDCl_3$): see Table 1; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$151.95 (s, C-4, -5), 136.32 (d, C-2, -7), 127.71 (d, C-3, -6), 115.28 (t, C-1, -8), 35.96 (s, C-9, -11), 31.73 ppm (q, C-10, -12); IR (ATR): $\tilde{\nu} =$3084 (w), 2965 (m), 2868 (w), 1717 (w), 1624 (w), 1474 (w), 1391 (w), 1364 (m), 1195 (w), 1158 (w), 1089 (m), 1043 (s), 997 (s), 899 (s), 663 cm^{-1} (s); GC/MS (70 eV): *m/z* (%): 218 [M^+] (<1), 145 (6), 131 (5), 119 (13), 105 (26), 91 (11), 77 (6), 57 (100), 41 (17); UV (hexane): λ_{max} ($\log\varepsilon$) = 228 nm (4.53); elemental analysis calcd (%) for $C_{16}H_{26}$ (218.4): C 88.00 H 12.00; found: C 87.21 H 12.10; specific rotation: $[\alpha]_D^{20} = +284 \pm 3$ ($c = 0.34$ in hexane, $l = 0.1$ dm), -280 ± 1 ($c = 0.33$ in hexane, $l = 0.1$ dm).

5-*tert*-Butyl-6,6-dimethylhept-4-en-1-yn-3-ol (20): A solution of ethynyl magnesium bromide (85.6 mL, 42.8 mmol) in THF (50 mL) was added under nitrogen to a solution of the aldehyde **19** (6.0 g, 35.7 mmol)[33] in anhydrous THF (100 mL) at 0 °C over a period of 30 min. After stirring for 2 h at 0 °C, the reaction mixture was hydrolyzed by the addition of an ice-cold saturated ammonium chloride solution (100 mL). The aqueous phase was separated, thoroughly extracted with diethyl ether (3× 100 mL), and the combined organic phases were dried over magnesium sulfate. After solvent removal in vacuo, the solid residue was purified by column chromatography (silica gel; dichloromethane). Yield: 6.2 g (89%), colorless solid; m.p. 60–61 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta =$ 1.23, 1.34 (s, 9H; 7-, 9-H), 1.83 (s, 1H; OH), 2.50 (d, $J = 2.0$ Hz, 1H; 1-H), 5.42 (d, $J = 9.8$ Hz, 1H; 4-H), 5.51 ppm (dd, $J = 9.8$, 1.2 Hz, 1H; 3-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$157.15 (s, C-5), 124.5 (d, C-4), 84.58 (s, C-2), 72.91 (d, C-1), 60.55 (d, C-3), 38.64, 37.47 (s, C-6/8), 33.93, 31.58 ppm (q, C-7/9); IR (KBr): $\tilde{\nu} =$3355 (s), 3278 (s), 3013 (w), 2979 (m), 2960 (s), 2925 (m), 2877 (w), 1610 (w), 1394 (w), 1369 (w), 1020 (s), 697 (m), 674 (m), 670 (m), 653 cm^{-1} (s); GC/MS (70 eV): *m/z* (%): 194 [M^+] (<1), 139 (23), 137 (3), 126 (8), 123 (13), 111 (31), 105 (54), 97 (4), 95 (20), 91 (15), 84 (50), 69 (37), 67 (17), 59 (24), 57 (100), 55 (19), 43 (15), 41 (28); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 198 nm (4.02); elemental analysis calcd (%) for $C_{13}H_{22}O$ (194.36): C 80.35, H 11.41; found: C 80.42, H 11.62.

3,10-Di-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,9-dien-6-yne-5,8-diol (21): A solution of *n*-butyl lithium (25.4 mL, 40.6 mmol) in hexane (1.6 M) was slowly added to a solution of **20** (3.6 g, 18.5 mmol) in anhydrous diethyl ether (100 mL) at 0 °C. After the mixture had been heated to reflux for 1 h, it was cooled to −78 °C and a solution of the aldehyde **19** (4.0 g, 23.8 mmol) in anhydrous ether (20 mL) was added. The mixture was warmed to room temperature, stirred for 12 h, and hydrolyzed with saturated aqueous ammonium chloride solution (80 mL). The phases were separated, the aqueous phase was extracted carefully with diethyl ether (150 mL), and the combined organic phases were dried over magnesium sulfate. After solvent removal the solid residue was purified by column chromatography (silica gel; dichloromethane, then diethyl ether) and recrystallization (dichloromethane/hexane). Yield: 5.2 g (77%), slightly yellow, amorphous solid; m. p. 112 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta =$ 1.205, 1.208, 1.32 (s, 36H; 1-, 12-, 14-, 16-H), 1.92 (s, 1H; OH), 5.38 (d, $J = 9.5$ Hz, 2H; 4-, 9-H), 5.53 ppm (d, $J = 9.5$ Hz, 2H; 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$156.24, 156.20 (s, C-3, -10), 124.92, 124.88 (d, C-4, -9), 88.50 (s, C-6, -7), 60.82 (d, C-5, -8), 38.64, 37.44 (s, C-2, -11, -13, -15), 33.87, 33.85, 31.64 (q, C-1, -12, -14, -16); IR (KBr): $\tilde{\nu} =$3386 (s), 2959 (s), 2918 (s), 2875 (m), 1392 (m), 1371 (m), 1216 (m), 1017 cm^{-1} (s); MS (CI, NH_3, pos.): *m/z* (%): 380 [$M^+ + NH_4$] (13), 346 (10), 345 (36), 322 (3), 289 (43), 271 (73), 261 (6), 233 (100), 186 (35), 177 (13), 169 (11), 126 (5), 121 (3), 111 (3); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 200 nm (4.34); elemental analysis calcd (%) for $C_{24}H_{42}O_2$ (362.64): C 79.50H, 11.68; found: C 79.38, H 11.70.

5,8-Diacetoxy-3,10-di-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,9-dien-6-yne (22): As described above for **16**, from the diol **21** (3.7 g, 10.1 mmol), acetic anhydride (40 mL) and pyridine (2.2 mL, 27.2 mmol) **22** was prepared. The raw product was purified by column chromatography (silica gel, dichloromethane): 4.43 g (98%) of **22**, colorless crystals. m.p. 82 °C;

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.19, 1.20, 1.31 (s, 36H; 1-, 12-, 14-, 20-H), 2.08 (s, 6H; 16-, 18-H), 5.35, 5.37 (d, J = 9.4 Hz, 2H; 4-, 9-H), 6.46 ppm (d, J = 9.4 Hz, 2H; 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.66, 169.62 (s, C-15, -17), 157.53, 157.44 (s, C-3, -10), 120.72, 120.66 (d, C-4, -9), 82.97, 82.89 (s, C-6, -7), 62.94, 62.89 (d, C-5, -8), 38.89, 37.42 (s, C-2, -11, -13, -19), 33.52, 31.64 (q, C-1, -12, -14, -20), 21.19 ppm (q, C-16, -18); IR (KBr): $\tilde{\nu}$ = 3018 (w), 2961 (s), 2920 (w), 2877 (w), 1750 (s), 1393 (m), 1370 (m), 1013 cm^{-1} (s); MS (70 eV): *m/z* (%): 446 [M^+] (6), 389 (5), 347 (37), 306 (3), 307 (15), 287 (12), 273 (24), 249 (21), 231 (66), 203 (10), 175 (8), 149 (8), 137 (8), 123 (15), 111 (13), 57 (100), 41 (16); UV (acetonitrile): λ_{max} (log ε) = 202 nm (4.34); elemental analysis calcd (%) for $C_{28}H_{46}O_4$ (446.73): C 75.29, H 10.38; found: C 75.35, H 10.50.

(5*Z*,7*Z*)-2,2,11,11-Tetramethyl-3,6,7,10-tetra-*tert*-butyldodeca-3,5,7,9-tetraene ((5*Z*,7*Z*)-4a): As described above for the conversion of **18** to **3**, the metal organic alkylating reagent was prepared from magnesium turnings (4.9 g, 0.20 mol), *tert*-butyl bromide (6.7 mL, 61.5 mmol) in diethyl ether (50 mL) and CuBr (2.5 g, 17 mmol) and LiBr (1.5 g, 17 mmol) in THF (150 mL). This reagent was used to *tert*-butylate **22** (2.3 g, 5.1 mmol) in THF (20 mL). After stirring for 12 h at room temperature the process was complete (monitoring by TLC), and the reaction mixture was hydrolyzed by the addition of saturated aqueous ammonium chloride solution (150 mL). Most of the solvent was removed by rotary evaporation, the obtained concentrated product solution filtered through a pad of silica gel, and the final product obtained by gradient high vacuum sublimation at 100 °C/0.011 mbar. Yield: 1.8 g (80 %) as colorless crystals; m.p. 166 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.13 (s, 18H; 1-, 12-H = terminal (*E*)-*t*Bu), 1.15 (s, 18H; 16-, 18-H), 1.36 (s, 18H; 14-, 20-H = terminal (*Z*)-*t*Bu), 5.87 (d, J = 11.1 Hz, 2H; 4-, 9-H), 6.73 (d, J = 11.1 Hz, 2H; 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 153.01 (s, C-3, -10), 148.91 (s, C-6, -7), 125.44 (d, C-5, -8), 122.89 (d, C-4, -9), 39.16 (s, C-2, -11 = terminal (*E*)-*t*Bu), 37.39 (s, C-13, -19 = terminal (*Z*)-*t*Bu), 36.48 (s, C-15, -17), 33.68 (q, C-14, -20 = terminal (*Z*)-*t*Bu), 32.07 ppm (q, C-1, -12 = terminal (*E*)-*t*Bu), 31.94 (q, C-16, -18); IR (KBr): $\tilde{\nu}$ = 3003 (w), 2956 (s), 2924 (m), 2907 (m), 2869 (m), 1637 (w), 1389 (w), 1364 cm^{-1} (m); MS (70 eV): *m/z* (%): 442 [M^+] (17), 386 (16), 343 (2), 330 (3), 274 (6), 273 (18), 203 (4), 181 (7), 131 (7), 109 (13), 83 (19), 69 (25), 57 (100); UV (acetonitrile): λ_{max} (log ε) = 238 (4.25, sh), 246 (4.30), 254 nm (4.23, sh); elemental analysis calcd (%) for $C_{32}H_{58}$ (442.83): C 86.80, H 13.20; found: C 86.81, H 13.35; X-ray structure analysis: see main section and below.

Bromination of (5*Z*,7*Z*)-4a—synthesis of (3*Z*,5*Z*,7*Z*)-3-bromo-6,7,10-tri-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,5,7,9-tetraene (24): A solution of bromine (0.42 g, 2.63 mmol) in CCl_4 (5 mL) was slowly added to a solution of **4a** (1.0 g, 2.26 mmol) in CCl_4 (80 mL) at 0 °C. Even after 12 h at room temperature the color of the solution was still red, indicating the slow rate of the reaction. The reaction mixture was washed with aqueous bisulfite solution (25 mL), the phases were separated and after thorough extraction of the aqueous layer with diethyl ether (3 × 100 mL) the combined organic fractions were dried over magnesium sulfate. The solvent was removed in vacuo and the resulting solid raw product was purified by column chromatography (silver nitrate impregnated silica gel; hexane). Yield: 0.577 g (55 %), colorless plates; m.p. 73 °C (150 mg (15 %) of the starting tetraene **4a** was recovered); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.13 (s, 9H; 10-*t*Bu(*E*)), 1.15 (s, 9H; 3-*t*Bu), 1.16 (s, 9H; 7-*t*Bu), 1.17 (s, 9H; 6-*t*Bu), 1.36 (s, 9H; 10-*t*Bu(*Z*)), 5.83 (d, J = 11.1 Hz, 1H; 9-H), 6.19 (d, J = 9.7 Hz, 1H; 4-H), 6.52 (d, J = 9.7 Hz, 1H; 5-H), 6.74 ppm (d, J = 11.1 Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 154.87 (s, C-6), 154.12 (s, C-10), 148.84 (s, C-7), 139.61 (s, C-3), 126.13 (d, C-8), 125.12 (d, C-5), 123.88 (d, C-4), 122.34 (d, C-9), 39.77 (s, C_q of 3-*t*Bu), 39.22 (s, C_q of 10-*t*Bu(*E*)), 37.44 (s, C_q of 10-*t*Bu(*Z*)), 36.82 (s, C_q of 6-*t*Bu), 36.14 (s, C_q of 7-*t*Bu), 33.67 (q, CH_3 of 10-*t*Bu(*Z*)), 32.04 (q, CH_3 of 10-*t*Bu(*E*)), 31.96 (q, CH_3 of 6-*t*Bu), 31.93 (q, CH_3 of 7-*t*Bu), 29.77 ppm (q, CH_3 of 3-*t*Bu); IR (KBr): $\tilde{\nu}$ = 2966 (s), 2921 (m), 2909 (m), 2869 (m), 1390 (w), 1363 cm^{-1} (m); MS (70 eV): *m/z* (%): 466/464 [M^+] (20/21), 410 (4), 409/407 (18/19), 353/351 (28/31), 326 (2), 297/295 (3/4), 271 (4), 245/243 (9/9), 215 (3), 173 (4), 164 (8), 159 (3), 121 (3), 83 (16), 57 (100), 41 (13); UV (acetonitrile): λ_{max} (log ε) = 246 nm (4.48), 260 (4.42, sh); HRMS: *m/z* calcd for $C_{28}H_{49}Br$: 464.3018; found: 464.3014.

Bromination of (5*Z*,7*Z*)-4a—synthesis of (3*Z*,5*Z*,7*Z*,9*Z*)-3,10-dibromo-6,7-di-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,5,7,9-tetraene (27): According to the above procedure, **4a** (3.0 g, 6.75 mmol) in CCl_4 (75 mL) was treated with bromine (3.3 g, 20.63 mmol) in CCl_4 (10 mL). Since in this case the reaction was slow (TLC monitoring on $AgNO_3$-treated silica gel; hexane) another portion of bromine (0.300 g, 1.88 mmol) was added and the mixture stirred for another day at room temperature. After solvent removal the remainder was purified by sublimation (50 °C, 0.011 mbar). Yield: 2.92 g (88 %), colorless plates; m.p. 98 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15 (s, 18H; 1-, 12-H), 1.17 (s, 18H; 14-, 16-H), 6.16 (d, J = 9.8 Hz, 2H; 4-, 9-H), 6.52 ppm (d, J = 9.7 Hz, 2H; 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 154.72 (s, C-6, -7), 140.55 (s, C-3, -10), 125.69 (d, C-5, -8), 123.43 (d, C-4, -9), 39.87 (s, C-2, -11), 36.53 (s, C-13, -15), 31.99 (q, C-14, -16), 29.79 ppm (q, C-1, -12); IR (KBr): $\tilde{\nu}$ = 2869 (w), 2908 (w), 2936 (m), 2968 (s), 3053 (w), 1392 (w), 1385 (w), 1363 (m), 1262 (s), 1225 (m), 785 cm^{-1} (m); MS (70 eV): *m/z* (%): 490/488/486 [M^+] (7/15/8), 433/431/429 (< 1/1/ < 1), 373/375/377 (1/2/1), 337 (2), 295/293 (3/1), 215 (2), 199 (2), 173 (3), 159 (5), 128 (3), 105 (3), 91 (3), 83 (2), 57 (100), 41 (15); UV (acetonitrile): λ_{max} (log ε) = 246 (4.41), 254 nm (4.37, sh); HRMS: *m/z* calcd for $C_{24}H_{40}Br_2$: 486.1497; found: 486.1500; X-ray structural analysis: see below and main section. The formation of *tert*-butyl bromide as a reaction product was established by ^{1}H NMR spectroscopy (singlet at δ = 1.81 ppm, *t*Bu) and GC/MS analysis (*m/z* = 135 and 133 [M^+] and comparison with the data of an authentic sample.

(5*Z*,7*Z*)-3,6,7-Tri-*tert*-butyl-2,2,11,11-tetramethyl-dodeca-3,5,7,9-tetraene (4b): A solution of *n*BuLi in hexane (30 mL, 48 mmol, 1.6 M) was added under nitrogen and ice cooling to a solution of the bromide **24** (0.74 g, 1.59 mmol) in anhydrous THF (50 mL). The reaction mixture was heated to reflux for 2 h and then hydrolyzed under ice cooling with saturated aqueous bicarbonate solution (50 mL). The phases were separated, the aqueous phase thoroughly extracted with diethyl ether (3 × 100 mL) and the combined organic layers were dried ($MgSO_4$). After solvent removal by rotary evaporation the solid residue was purified by column chromatography ($AgNO_3$ impregnated silica gel; hexane) and gradient sublimation (110 °C, 0.6 mbar). Yield: 552 mg (90 %), colorless plates; m.p. 61 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.97 (s, 9H; 12-H), 1.122 (s, 9H; 16-H), 1.125 (s, 9H; 1-H), 1.16 (s, 9H; 18-H), 1.36 (s, 9H; 14-H), 5.59 (d, J = 15.5 Hz, 1H; 10-H), 5.87 (dd, J = 10.5 Hz, 15.5 Hz, 1H; 9-H), 5.87 (d, J = 10.9 Hz, 1H; 4-H), 6.13 (d, J = 10.5 Hz, 1H; 8-H), 6.72 ppm (d, J = 10.9 Hz, 1H; 5-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 153.03 (s, C-3), 149.11 (s, C-6), 148.84 (s, C-7), 143.03 (d, C-10), 126.44 (d, C-8), 126.14 (d, C-5), 125.16 (d, C-9), 122.89 (d, C-4), 39.10 (s, C-2), 37.41 (s, C-13), 36.16, 36.13 (s, C-15/17), 33.61 (q, C-14), 33.16 (s, C-11), 32.05 (q, C-1), 31.89, 31.88 (q, C-16/18), 29.85 ppm (q, C-12); IR (KBr): $\tilde{\nu}$ = 2994 (m), 2953 (s), 2926 (m), 2904 (m), 2867 (m), 1390 (w), 1363 (m), 974 cm^{-1} (m); MS (70 eV): *m/z* (%): 386 [M^+] (42), 329 (26), 273 (100), 246 (5), 231 (3), 217 (17), 203 (8), 189 (5), 165 (8), 133 (5), 109 (23), 95 (3), 83 (10), 69 (5), 57 (95), 41 (13); UV (acetonitrile): λ_{max} (log ε) = 238 (4.54), 258 nm (4.40, sh); elemental analysis calcd (%) for $C_{28}H_{50}$ (386.68): C 86.97, H 13.03; found: C 86.82, 13.25; X-ray structural analysis: see below and main section.

(3*E*,5*Z*,7*Z*,9*E*)-6,7-Di-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,5,7,9-tetraene (4c): A solution of *n*BuLi in hexane (40 mL, 64 mmol, 1.6 M) was added under nitrogen and ice cooling to a solution of the dibromide **27** (2.9 g, 5.94 mmol) in anhydrous THF (100 mL). After heating under reflux for 2 h, the reaction mixture was cooled to room temperature and a saturated aqueous solution of ammonium chloride (100 mL) was added for hydrolysis. After the usual work-up (see above, experiment 14) the resulting raw hydrocarbon was purified by recrystallization from ether/ethanol or by sublimation (47 °C, 0.001 mbar). Yield: 1.3 g (65 %) of **4c**, colorless plates; m.p. 55 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.99 (s, 18H; 1-, 12-H), 1.14 (s, 18H; 14-, 16-H), 5.60 (d, J = 15.5 Hz, 2H; 3-, 10-H), 5.89 (dd, J = 10.4, 15.5 Hz, 2H; 4-, 9-H), 6.15 ppm (d, J = 10.4 Hz, 2H; 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 149.19 (s, C-6, -7), 143.12 (d, C-3, -10), 127.04 (d, C-5, -8), 125.23 (d, C-4, -9), 35.86 (s, C-13, -15), 33.16 (s, C-2, -11), 31.88 (q, C-14, -16), 29.88 ppm (q, C-1, -12); IR (KBr): $\tilde{\nu}$ = 3041 (w), 3022 (w), 2967 (s), 2956 (s), 2903 (m), 2865 (m), 1638 (m), 1475 (m), 1460 (m), 1390 (w), 1360 (m), 1316 (w), 1258 (w), 1228 cm^{-1} (m); MS (70 eV): *m/z* (%): 330 [M^+] (96), 315 (8), 274 (32),

259 (40), 245 (24), 231 (77), 217 (98), 189 (24), 175 (35), 161 (79), 133 (29), 105 (26), 95 (12), 91 (17), 83 (22), 69 (21), 57 (100), 43 (20), 41 (55); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 222 (4.49, sh), 232 (4.60), 250 nm (4.43, sh); elemental analysis calcd (%) for $C_{24}H_{42}$ (330.58): C 87.19, H 12.81; found: C 87.20, H 12.93; specific rotation $[\alpha]_D^{20} = \pm 130 \pm 2°$ (c = 0.19 in hexane l = 0.1 dm), ±135.3° (c = 0.3 in hexane, l = 1 dm); X-ray structural analysis: see below and main section.#

(3*Z*,5*Z*,7*Z*,9*E*)-3-Bromo-6,7,10-tri-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,5,7,9-tetraene (28): A solution of *n*BuLi in hexane (6.25 mL, 10 mmol, 1.6 M) was added under nitrogen to a solution of the dibromide **27** (100 mg, 0.205 mmol) in anhydrous THF (30 mL) at −78 °C . The reaction mixture was stirred for 30 min at −78 °C and subsequently hydrolyzed by addition of a saturated ammonium chloride solution (20 mL). After the usual work-up (see above, preparation of **4b**) the raw product was purified by column chromatography ($AgNO_3$ impregnated silica gel; hexane). Yield:42 mg (50 %), colorless oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (s, 9H; 12-H), 1.05 (s, 9H; 16-H), 1.08 (s, 9H; 1-H), 1.10 (s, 9H; 14-H), 5.54 (d, J = 15.5 Hz, 1H; 10-H), 5.77 (dd, J = 10.5, 15.5 Hz, 1H; 9-H), 6.07 (d, J = 10.5 Hz, 1H; 8-H), 6.13 (d, J = 9.7 Hz, 1H; 4-H), 6.45 ppm (d, J = 9.7 Hz, 1H; 5-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 154.93 (s, C-6), 149.05 (s, C-7), 144.02 (d, C-10), 139.70 (s, C-3), 127.03 (d, C-8), 125.60 (d, C-5), 124.65 (d, C-9), 123.95 (d, C-4), 39.78 (s, C-2), 36.55 (s, C-13), 35.84 (s, C-15), 33.23 (s, C-11), 31.94 (q, C-14), 31.90 (q, C-16), 29.82 (q, C-12), 29.78 ppm (q, C-1); IR (KBr): $\tilde{\nu}$ = 2868 (s), 2905 (s), 2963 (s), 1572 (w), 1477 (m), 1463 (m), 1391 (m), 1362 (s), 1262 (m), 1227 (m), 1196 (m), 975 cm^{-1} (m); MS (70 eV): *m/z* (%): 410/408 [M^+] (65/68), 395/393 (5/4), 353/351 (9/9), 339/337 (8/8), 325/323 (5/4), 311/309 (8/8), 297/295 (12/13), 285/282 (5/7), 257 (5), 241/239 (4/4), 215 (7), 187/185 (4), 173 (8), 159 (14), 133 (5), 95 (4), 83 (7), 57 (100), 41 (15); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 238 (4.35), 254 nm (4.23, sh); HRMS: *m/z* calcd for $C_{24}H_{41}Br$: 408.2392; found: 408.2401.

Hydrogenation of 4a to (5*Z*,7*Z*)-3,6,7,10-tetra-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,5,7-triene ((5*Z*,7*Z*)-29): A suspension of the tetraene **4a** (0.200 g, 0.45 mmol), and Pt on C (20 mg) in hexane (20 mL) was hydrogenated at room temperature for 7 d under normal pressure. The catalyst was removed by filtration through a pad of silica gel, and the solvent was removed in vacuo. The raw hydrogenation product was purified by column chromatography (silver nitrate impregnated silica gel; hexane), yielding 170 mg of hydrogenated products and 30 mg of substrate **4a** (15 %). Threefold recrystallization from ethanol provided (5*Z*,7*Z*)-**29** (29 mg, 14 %) as colorless needles. M.p. 96 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.93, 0.98 (s, 9H each; 12-, 20-H), 1.0–1.1 (m, 1H; 10-H), 1.11 (s, 9H; 1-H), 1.15 (s, 9H; 16-H), 1.20 (s, 9H; 18-H), 1.37 (s, 9H; 14-H), 1.83 (dt, J = 18.5, ≈4.6 Hz, 1H; 9-H$_A$), 1.92 (ddd, J = 4.1, 6.1, 18.5 Hz, 1H; 9-H$_B$), 5.46 (dd, J = 4.3, 6.1 Hz, 1H; 8-H), 5.91 (d, J = 11.3 Hz, 1H; 4-H), 6.69 ppm (d, J = 11.3 Hz, 1H; 5-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 152.85 (s, C-3), 149.30 (s, C-6), 146.30 (s, C-7), 131.89 (d, C-8), 125.91 (d, C-5), 122.38 (d, 4-C), 58.58 (d, C-10), 39.06 (s, C-2), 37.40 (s, C-13), 36.74, 36.57 (s, C-11/19), 35.86 (s, C-15), 35.65 (s, C-17), 33.69 (q, C-14), 32.34 (q, C-1), 32.25 (q, C-18), 32.02 (q, C-16), 31.28, 31.11 (q, C-12/20), 30.67 ppm (t, C-9); IR (KBr): $\tilde{\nu}$ = 3008 (s), 2962 (s), 2904 (s), 2867 (s), 1476 (s), 1392 (s), 1365 (s), 1212 cm^{-1} (m); MS (70 eV): *m/z* (%): 444 [M^+] (9), 387 (24), 275 (7), 205 (7), 163 (2), 135 (5), 109 (4), 91 (4), 83 (10), 69 (7), 57 (100), 41 (21); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 198 (4.06), 254 (4.32, sh), 260 nm (4.33); elemental analysis calcd (%) for $C_{32}H_{60}$ (444.8): C 86.40, H 13.60; found: C 86.14 H 13.81; X-ray structural analysis: see below and main section.

Hydrogenation of 4a to (5*Z*,7*Z*)-3,6,7,10-tetra-*tert*-butyl-2,2,11,11-tetramethyldodeca-5,7-diene (30): A suspension of **4a** (0.130 g, 0.29 mmol) and Pt on C (20 mg) in glacial acetic acid (5 mL) was hydrogenated at 150 °C for 3 d at a hydrogen pressure of 37 atm. The solvent was removed by distillation and the remaining solid residue recrystallized several times from ethanol. Yield: 43 mg (33 %) as colorless needles; m.p. 107 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98, 0.99 (s, 18H each; 1-, 12-, 14-, 20-H), 1.13 (s, 18H; 16-, 18-H), 1.17 (dd, J = 5.3, 3.7 Hz, 2H; 3-, 10-H), 1.93 (ddd, J = 19.1, 5.3, 4.7 Hz, 2H; 4-, 9-H$_A$), 2.00 (ddd, J = 19.1, 4.9, 3.7 Hz, 2H; 4-, 9-H$_B$), 5.35 ppm ("t", J ≈ 4.8 Hz, 2H; 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 146.94 (s, C-6, -7), 132.16 (d, C-5, -8), 59.11 (d, C-3, -10), 36.76, 36.74 (s, C-2, -11, -13, -19), 35.00 (s, C-15, -17), 32.86 (q, C-16, -18), 31.13, 31.09 (q, C-1, -12, -14, -20), 30.11 ppm (t, C-4, -9); IR (KBr): $\tilde{\nu}$ = 2970 (s), 2959 (s), 2923 (m), 2910 (m), 2870 (m), 1488 (w), 1474 (m), 1459 (w), 1394 (m), 1385 (w), 1367 cm^{-1} (m); MS (70 eV): *m/z* (%): 446 [M^+] (5), 389 (40), 375 (3), 333 (100), 319 (25), 278 (7), 277 (35), 263 (54), 249 (4), 221 (10), 207 (46), 193 (30), 179 (20), 165 (11), 151 (38), 137 (64), 123 (53), 97 (31), 83 (50), 71 (77); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 198 nm (4.26); elemental analysis calcd (%) for $C_{32}H_{62}$ (446.8): C 86.01 H; 13.99; found: C 86.07, H 14.33; X-ray structural analysis: see below and main section.

Birch reduction of (5*Z*,7*Z*)-4a—formation of (5*Z*,7*E*)-29: Ammonia (50 mL) was condensed into a three-necked flask and small pieces of sodium (1.0 g, 43.5 mmol) were added. After stirring the intensely blue solution for 30 min (5*Z*,7*Z*)-**4a** (0.200 g, 0.45 mmol) in THF (5 mL) and ammonium chloride (1.0 g, 18.7 mmol) were added. After stirring for 10 min the reaction mixture was brought to room temperature, while the ammonia evaporated. Ice water (50 mL) was carefully added to the remaining solid (**caution!** there may be traces of sodium left over) and the suspension extracted carefully with diethyl ether (3 × 30 mL). The solvent was removed in vacuo and the raw product was purified by column chromatography ($AgNO_3$ impregnated silica gel; hexane). Yield: 98 mg (49 %) of the triene (5*Z*,7*E*)-**29**, 41 mg (21 %) of (5*Z*,7*Z*)-**29**, and 30 mg of a mixture of hydrocarbons (*m/z* = 446), the composition of which was not determined; m.p. 95 °C; data for (5*Z*,7*E*)-**29**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.01, 1.02 (s, 9 H each, 12-, 20-H), 1.07 (t, J = 4.2 Hz, 1H; 10-H), 1.12 (s, 9H; 16-H), 1.169 (s, 9H; 18-H), 1.171 (s, 9H; 1-H), 1.35 (s, 9H; 14-H), 2.23–2.37 (m, 2H; 9-H), 5.01 (t, J = 5.4 Hz, 1H; 8-H), 6.10 (d, J = 10.4 Hz, 1H; 4-H), 6.53 ppm (d, J = 10.4 Hz, 1H; 5-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 154.03 (s, C-6), 152.91 (s, C-3), 143.66 (s, C-7), 133.99 (d, C-8), 124.18 (d, C-5), 122.94 (d, C-4), 60.99 (d, C-10), 39.11 (s, C-2), 37.45 (s, C-13), 36.86 (s, C-11, -19), 36.78 (s, C-15), 35.23 (s, C-17), 33.48 (q, C-14), 32.17 (q, C-1), 31.74 (q, C-16), 31.19, 31.14 (q, C-12, -20), 29.99 (q, C-18), 29.96 ppm (t, C-9); IR (ATR): $\tilde{\nu}$ = 2952 (s), 2903 (m), 2868 (m), 1477 (m), 1460 (m), 1392 (m), 1364 (s), 1237 (m), 1211 (m), 1193 (m), 664 cm^{-1} (m); MS (70 eV): *m/z* (%): 444 [M^+] (5), 387 (7), 332 (5), 331 (19), 275 (4), 219 (2), 205 (6), 83 (11), 69 (7), 57 (100); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 197 (4.13), 257 nm (4.27); HRMS: *m/z* calcd for $C_{32}H_{60}$: 444.4695; found: 444.4694.

Hydrogenation of 4b to (5*Z*,7*Z*)-3,6,7-tri-*tert*-butyl-2,2,11,11-tetramethyldodeca-5,7-diene (31): Using the same procedure as for the hydrogenation of **4a** to give **30**, the tetraene **4b** (0.191 g, 0.49 mmol) in hexane (5 mL) was hydrogenated over Pt/C (20 mg) for 3 d at 150 °C and 37 atm pressure. After purification by column chromatography, **31** (100 mg, 53 %) was obtained as a colorless oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.85 (s, 9H; 12-H), 0.97, 0.99 (s, 9H each; 1-, 14-H), 1.09 (s, 9H; 16-H), 1.13 (s, 9H; 18-H), 1.15–1.17 (m, 1H; 3-H), 1.18–1.28 (m, 2H; 10-H), 1.85–1.91 (m, 4H; 4-, 9-H), 5.35–5.41 ppm (m, 2H; 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 148.09 (s, C-7), 146.81 (s, C-6), 131.87 (d, C-5), 127.11 (d, C-8), 58.90 (d, C-3), 44.05 (t, C-10), 36.83, 36.61 (s, C-2, -13), 35.09 (s, C-17), 35.06 (s, C-15), 32.79 (q, C-18), 32.38 (q, C-16), 31.23, 31.17 (q, C-1, -14), 29.49 (q, C-12), 26.28, 30.58 (t, C-4, -9), 30.40 ppm (s, C-11); IR (ATR): $\tilde{\nu}$ = 2953 (s), 2904 (m), 2868 (m), 1475 (m), 1393 (m), 1364 (s), 1227 (w), 1196 cm^{-1} (w); GC/MS (70 eV): *m/z* (%): 388 [M^+] (11), 332 (3), 331 (13), 276 (15), 275 (72), 219 (9), 135 (6), 111 (6), 83 (23), 57 (100); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 193 (4.21), 197 nm (4.16).

Hydrogenation of 4c to (5*Z*,7*Z*)-6,7-di-*tert*-butyl-2,2,11,11-tetramethyldodeca-5,7-diene (32): Using the same procedure as for the hydrogenation of **4a** to give **30**, compound **4c** (227 mg, 0.69 mmol) was hydrogenated in hexane (5 mL) over Pt/C (20 mg) at 150 °C and 37 atm of hydrogen pressure: diene **32** (220 mg, 95 %) was obtained as a colorless oil; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.79 (s, 18H; 1-, 12-H), 1.02 (s, 18H; 14-, 16-H), 1.03–1.18 (m, 4H; 3-, 10-H), 1.69–1.84 (m, 4H; 4-, 9-H), 5.32 ppm (dd, 2H; J = 6.2, 7.9 Hz, 5-, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 147.31 (s, C-6, -7), 126.75 (d, C-5, -8), 43.74. (t, C-3, -10), 34.83 (s, C-13, -15), 32.04 (q, C-14, -16), 30.10 (s, C-2, -11), 29.22 (q, C-1, -12), 25.95 ppm (t, C-4, -9); IR (ATR): $\tilde{\nu}$ = 2952 (s), 2904 (m), 2867 (m), 1709 (w), 1472 (m), 1391 (m), 1363 cm^{-1} (s); GC/MS (70 eV): *m/z* (%): 334 [M^+] (19), 277 (29), 263 (9), 235 (15), 221 (47), 207 (22), 194 (23),

179 (11), 151 (8), 137 (16), 123 (20), 95 (8), 83 (9), 71 (6), 57 (100), 55 (5), 43 (9); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 192 nm (3.95).

Epoxidation of 4a to (5*Z*,7*Z*)-4,6,7,10-tetra-*tert*-butyl-2,2,11,11-tetramethyldodeca-5,7,9-trien-3-one (36): *m*-Chloroperbenzoic acid (136 mg, 0.45 mmol) was added to a solution of **4a** (200 mg, 0.45 mmol) in dichloromethane (15 mL) and the mixture stirred for 1 h at room temperature. The solvent was removed in vacuo and the remainder purified by column chromatography (silica gel; hexane/dichloromethane 9:1) yielding two diastereomers of **36**: diastereomer I (131 mg, 63%) as a colorless solid (m.p. 74°C) and diastereomer II (19 mg, 5%) as a colorless oil; 49 mg (25%) of the starting material **4a** was recovered.

*Diastereomer I of **36***: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (s, 9H; 14-H), 1.12 (s, 9H; 18-H), 1.18 (s, 9H; 1-H), 1.19 (s, 9H; 12-H), 1.24 (s, 9H; 16-H), 1.36 (s, 9H; 20-H), 3.58 (d, J = 10.3 Hz, 1H; 4-H), 5.79 (d, J = 10.3 Hz, 1H; 5-H), 5.94 (d, J = 11.9 Hz, 1H; 9-H), 6.80 ppm (d, J = 11.9 Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 219.68 (s, C-3), 153.26 (s, C-10), 148.23 (s, C-6), 147.09 (s, C-7), 128.90 (d, C-5), 128.56 (d, C-8), 123.47 (d, C-9), 56.5 (d, C-4), 44.49 (s, C-2), 39.19 (s, C-11), 37.43 (s, C-13), 37.32, 37.29 (s, C-13, -19), 35.87 (s, C-15), 33.79 (q, C-20), 32.83 (q, C-16), 32.68 (q, C-18), 32.02 (q, C-12), 29.29 (q, C-14), 28.02 ppm (q, C-1); IR (ATR): $\tilde{\nu}$ = 2955 (s), 2904 (m), 2870 (m), 1685 (m), 1476 (m), 1462 (m), 1391 (m), 1364 (s), 1211 (s), 1192 (m), 1051 (m), 996 (m), 928 (m), 670 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 459 [M^++1] (45), 404 (2), 402 (17), 374 (25), 346 (15), 318 (23), 289 (17), 261 (100), 233 (12), 219 (15), 205 (29), 153 (10), 133 (6), 109 (9), 85 (21), 83 (32); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 192 (4.20), 260 nm (4.35); elemental analysis calcd (%) for $C_{32}H_{58}O$ (458.83): C 83.77, H 12.74; found: C 83.64 H 12.80.

*Diastereomer II of **36***: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.02, 1.10, 1.12, 1.13 (s, 9H each; 1-, 12-, 14-, 16-H), 1.26 (s, 9H; 18-H), 1.34 (s, 9H; 20-H), 3.61 (d, J = 10.5 Hz, 1H; 4-H), 5.69 (d, J = 11.8 Hz, 1H; 9-H), 5.86 (d, J = 10.5 Hz, 1H; 5-H), 6.79 (d, J = 11.8 Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 219.56 (s, C-3), 153.06 (s, C-10), 148.55 (s, C-6), 147.39 (s, C-7), 127.94, 127.70 (d, C-5, -8), 122.68 (d, C-9), 54.53 (d, C-4), 44.22 (s, C-2), 39.05 (s, C-11), 37.27, 37.02, 36.01, 35.44 (s, C-13, -15, -17, -19), 33.67 (q, C-12), 32.54, 32.49, 31.55, 29.59, 28.75 (q, C-1, -14, -16, -18, -20); IR (ATR): $\tilde{\nu}$ = 2959 (s), 2923 (s), 2870 (m), 1690 (s), 1478 (m), 1391 (m), 1364 (s), 1212 (s), 1193 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 458 [M^+] (4), 317 (8), 261 (20), (2), 205 (14), 177 (5), 135 (6), 109 (7), 83 (17), 69 (8), 57 (100), 55 (9); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 195 (4.02), 254 (4.26), 260 nm (4.26); HRMS: *m*/*z* calcd for $C_{32}H_{50}O$: 458.4488; found: 458.4493.

Epoxidation of 4b to (5*Z*,7*Z*)-4,6,7-tri-*tert*-butyl-2,2,11,11-tetramethyldodeca-5,7,9-trien-3-one (37) and (5*Z*,7*Z*)-6,7,10-tri-*tert*-butyl-2,2,11,11-tetramethyldodeca-5,7,9-trien-3-one (38): As described under the epoxidation of **4a** to give **36**, the tetraene **4b** (200 mg, 0.517 mmol) was epoxidized for 1 h at RT in dichloromethane (15 mL) with *m*-chloroperbenzoic acid (156 mg, 0.515 mmol). After work-up and chromatographic purification (silica gel, hexane/dichloromethane 1:1) were obtained: ketone **37** (39 mg, 18%) as an oily mixture of diastereomers, ketone **38** (8 mg, 4%) as a colorless solid (m.p. 70°C), and unreacted substrate **4b** (50 mg, 25%).

(5Z,7Z)-4,6,7-tri-tert-*butyl-2,2,11,11-tetramethyldodeca-5,7,9-trien-3-one (**37**)*: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (s, 9H; 14-H), 1.00 (s, 9H; 12-H), 1.12 (s, 9H; 16-H), 1.18 (s, 9H; 1-H), 1.20 (s, 9H; 18-H), 3.57 (d, J = 10.5 Hz, 1H; 4-H), 5.53 (d, J = 15.3 Hz, 1H; 10-H), 5.81 (d, J = 10.5 Hz, 1H; 5-H), 6.01 (dd, J = 10.9, 15.3 Hz, 1H; 9-H), 6.12 ppm (d, J = 10.9 Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 219.58 (s, C-3), 148.32 (s, C-6), 147.89 (s, C-7), 142.79 (d, C-10), 129.11 (d, C-8), 128.92 (d, C-5), 126.48 (d, C-9), 56.5 (d, C-4), 44.53 (s, C-2), 37.18 (s, C-13), 35.32 (s, C-17), 33.28 (s, C-11), 32.70 (q, C-18), 32.61 (q, C-16), 29.72 (q, C-12), 29.46 (q, C-14), 28.02 ppm (q, C-1); IR (film): $\tilde{\nu}$ = 2962 (s), 2906 (s), 2870 (m), 1691 (m), 1476 (m), 1465 (m), 1392 (m), 1365 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 403 [M^++1] (<1), 318 (6), 289 (7), 261 (55), 233 (4), 205 (64), 191 (6), 135 (7), 91 (4), 83 (16), 57 (100); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 192 (4.04), 246 nm (4.31); HRMS: *m*/*z* calcd for $C_{28}H_{50}O$: 402.3862; found: 402.3859.

(5Z,7Z)-6,7,10-tri-tert-*butyl-2,2,11,11-tetramethyldodeca-5,7,9-trien-3-one (**38**)*: M.p. 70°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.08, 1.12, 1.14, 1.16 (s, 9H each; 1-, 12-, 14-, 16-H), 1.35 (s, 9H; 18-H), 2.94 (dd, J = 5.1, 19.2 Hz, 1H; 4-H_A), 3.25 (dd, J = 7.9, 19.2 Hz, 1H; 4-H_B), 5.84 (d, J = 11.2 Hz, 1H; 9-H), 5.87 (dd, J = 5.1, 7.9 Hz, 1H; 5-H), 6.73 ppm (d, J = 11.2 Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 214.14 (s, C-3), 153.79 (s, C-10), 150.63 (s, C-6), 148.48 (s, C-7), 126.27 (d, C-8), 122.06 (d, C-9), 119.11 (d, C-5), 43.95 (s, C-2), 39.12 (s, C-11), 38.13 (t, C-4), 37.41, 36.42, 35.78 (s, C-13, -15, -17), 33.64 (q, C-18), 32.09, 31.92, 31.97 (q, C-12, -14, -16), 28.56 ppm (q, C-1); IR (KBr): $\tilde{\nu}$ = 3442 (w), 2870 (m), 2907 (m), 2928 (m), 2965 (s), 1709 (m), 1478 (m), 1467 (m), 1365 (m), 1213 (m), 1066 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 402 [M^+] (4), 345 (6), 289 (16), 261 (24), 205 (25), 189 (12), 133 (11), 85 (11), 57 (100), 41 (21); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 194 (3.98), 258 nm (4.15); HRMS: *m*/*z* calcd for $C_{28}H_{50}O$: 402.3862; found: 402.3853.

Epoxidation of 4c to (5*Z*,7*Z*)-6,7-di-*tert*-butyl-2,2,11,11-tetramethyldodeca-5,7,9-trien-3-one (39): As described above (experiment 23) the tetraene **4c** (200 mg, 0.606 mmol) was epoxidized in dichloromethane (15 mL) with *m*-chloroperbenzoic acid (183 mg, 0.604 mmol; reaction time 3 h). After work-up (see above) were isolated: ketone **39** (30 mg, 14%, colorless oil) and 30 mg (15%) of the substrate **4c**. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.96 (s, 9H; 12-H), 1.08 (s, 9H; 1-H), 1.13 (s, 9H; 16-H), 1.14 (s, 9H; 14-H), 2.91 (dd, J = 5.1, 18.7 Hz, 1H; 4-H_A), 3.30 (dd, J = 8.5, 18.7 Hz, 1H; 4-H_B), 5.57 (d, J = 15.6 Hz, 1H; 10-H), 5.85 (dd, J = 5.1, 8.5 Hz, 1H; 5-H), 5.88 (dd, J = 10.7, 15.7 Hz, 1H; 9-H), 6.12 ppm (d, J = 10.7 Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 214.24 (s, C-3), 150.91 (s, C-6), 148.86 (s, C-7), 143.58 (d, C-10), 127.19 (d, C-8), 119.81 (d, C-5), 44.00 (s, C-2), 38.18 (t, C-4), 36.15 (s, C-13), 35.44 (s, C-15), 33.24 (s, C-11), 32.08 (q, C-14), 31.89 (q, C-16), 29.72 (q, C-12), 26.49 ppm (q, C-1); IR (film): $\tilde{\nu}$ = 2964 (s), 2906 (s), 2870 (s), 1710 (s), 1677 (m), 1478 (s), 1466 (s), 1393 (m), 1365 (s), 1227 (m) 1198 (m), 1065 (m), 981 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 346 [M^+] (7), 289 (37), 233 (16), 231 (5), 205 (9), 189 (6), 135 (6), 133 (7), 85 (12), 69 (4), 57 (100), 55 (7), 41 (18); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 194 (4.04), 240 nm (4.23); elemental analysis calcd (%) for $C_{24}H_{42}O$ (346.64): C 83.17, H 12.21; found: C 83.17 H 12.25.

Photoisomerization of 4a: In a quartz NMR tube a solution of 5*Z*,7*Z*-**4a** (100 mg, 0.226 mmol) in hexane (2 mL) was irradiated for 3 d with a 150 W low-pressure mercury lamp. Removal of the solvent and recrystallization from ethanol provided two diastereomers.

*(5*E*,7*Z*)-2,2,11,11-tetramethyl-3,6,7,10-tetra*-tert-*butyldodeca-3,5,7,9-tetraene ((5*E*,7*Z*)-**4a**)*: Yield: 15 mg (15%); m.p. 65°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15 (s, 18H; 18-, 20-H), 1.22 (s, 9H; 16-H),1.25 (s, 9H; 1-H), 1.32 (s, 9H; 14-H), 1.36 (s, 9H; 12-H), 6.04 (d, J = 10.5 Hz, 1H; 9-H), 6.17 (d, J = 11.3 Hz, 1H; 5-H), 6.49 (d, J = 11.3 Hz, 1H; 4-H), 6.56 ppm (d, J = 10.5 Hz, 1H; 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 153.89 (s, C-7), 153.85 (s, C-3), 153.20 (s, C-10), 145.98 (s, C-6), 126.84 (d, C-5), 124.11 (d, C-8), 122.80 (d, C-9), 120.48 (d, C-4), 39.37 (s, C-2), 39.07 (s, C-19), 37.46 (s, C-11), 37.24 (s, C-13), 36.92 (s, C-17), 35.08 (s, C-15), 33.54 (q, C-14), 33.47 (q, C-12), 32.12, 31.65 (q, C-18, -20), 32.06 (q, C-1), 31.19 ppm (q, C-16); IR (KBr): $\tilde{\nu}$ = 2953 (s), 2903 (s), 2869 (m), 1476 (m), 1391 (m), 1363 (s), 1213 (s), 1193 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 442 [M^+] (15), 385 (15), 329 (6), 301 (2), 273 (30), 245 (8), 203 (11), 133(6), 109 (11), 83 (15), 57 (100); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 244 (4.47), 259 nm (4.41, sh); HRMS: *m*/*z* calcd for $C_{32}H_{58}$: 442.4539; found: 442.4534.

*(5*E*,7*E*)-2,2,11,11-tetramethyl-3,6,7,10-tetra*-tert-*butyldodeca-3,5,7,9-tetraene ((5*E*,7*E*)-**4a**)*: Yield: 5 mg (5%); m. p. 123°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.22 (s, 18H; 16-, 18-H), 1.24 (s, 18H; 1-, 20-H), 1.33 (s, 18H; 12-, 14-H), 6.15 (d, J = 11.0 Hz, 2H; 5-, 8-H), 6.43 ppm (d, J = 11.0 Hz, 2H; 4-, 9-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 153.21 (s, C-3, -10), 151.93 (s, C-6, -7), 125.72 (d, C-5, -8), 120.77 (d, C-4, -9), 39.31 (s, C-2, -19), 37.19 (s, C-11, -13), 35.41 (s, C-15, -17), 33.40 (q, C-12, -14), 32.07 (q, C-1, -20), 31.27 ppm (q, C-16, -18); IR (ATR): $\tilde{\nu}$ = 3015 (m), 2987 (m), 2953 (s), 2900 (s), 2864 (m), 1479 (m), 1453 (m), 1390 (m), 1362 (s), 1234 (m), 1214 (s), 1193 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 442 [M^+] (7), 385 (7), 273 (8), 245 (5), 203 (6), 139 (4), 109 (9), 83 (12), 57 (100); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 246 (4.49), 260 nm (4.48); HRMS: *m*/*z* calcd for $C_{32}H_{58}$: 442.4539; found: 442.4533.

Table 4. Crystallographic data for compounds **4a**, **4b**, **4c**, **18**, **27**, (*Z*,*Z*)-**29** and **30**.

	4a	**4b**	**4c**	**18**	**27**	(*Z*,*Z*)-**29**	**30**
formula	$C_{32}H_{58}$	$C_{28}H_{50}$	$C_{24}H_{42}$	$C_{16}H_{30}O_2$	$C_{24}H_{40}Br_2$	$C_{32}H_{60}$	$C_{32}H_{62}$
M_r	442.78	386.68	330.58	254.40	488.38	444.80	446.82
habit	colorless tablet	colorless tablet	colorless plate	colorless tablet	colorless tablet	colorless prism	colorless tablet
cryst. size (mm)	0.4×0.3×0.2	0.25×0.2×0.08	0.5×0.25×0.07	0.3×0.3×0.17	0.15×0.13×0.10	0.25×0.2×0.15	0.4×0.3×0.2
crystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	*Cc*	$P2_12_12_1$	$P2_1/c$	*Pbca*	$P\bar{1}$
a [Å]	8.6943(8)	9.072(2)	18.630(4)	8.7348(8)	29.578(4)	11.480(2)	8.7800(12)
b [Å]	11.8507(11)	11.884(2)	11.838(2)	12.0757(11)	12.0343(14)	15.661(2)	11.7302(16)
c [Å]	15.5774(14)	12.707(2)	10.587(2)	30.160(3)	14.6191(18)	33.685(5)	15.928(2)
α [°]	82.849(3)	101.075(6)	90	90	90	90	86.785(6)
β [°]	89.937(3)	90.646(6)	100.693(4)	90	90.699(5)	90	84.032(6)
γ [°]	68.991(3)	91.046(6)	90	90	90	90	70.598(5)
V [Å^3]	1485.0	1344.0	2294.4	3181.3	5203.3	6056.5	1538.5
Z	2	2	4	8	8	8	2
ρ_{calcd} [Mg m^{-3}]	0.990	0.955	0.957	1.067	1.247	0.976	0.965
μ [mm^{-1}]	0.05	0.05	0.05	0.07	3.1	0.05	0.05
F(000)	500	436	744	1136	2032	2016	500
T [°C]	−140	−140	−140	−140	−140	−140	−140
$2\theta_{max}$	60	56.6	56.6	57.4	56.6	53.8	60
reflns measured	23100	13823	7994	33534	61759	51304	17651
independent reflns	8559	6598	2846	4601	12876	6206	8818
R_{int}	0.028	0.036	0.159	0.048	0.075	0.062	0.027
parameters	307	268	229	363	493	307	307
restraints	0	0	61	33	118	0	0
wR (F^2, all reflns)	0.147	0.170	0.172	0.117	0.120	0.163	0.129
R [$F>4\sigma(F)$]	0.049	0.058	0.068	0.044	0.047	0.053	0.045
S	1.03	1.06	1.03	1.07	0.94	1.03	1.04
max. $\Delta\rho$ [e Å^{-3}]	0.38	0.32	0.52	0.38	0.68	0.32	0.33

X-ray structure determinations: Numerical details are presented in Table 4. Data collection and reduction: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Measurements were performed with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed for the brominated derivative **27** only, on the basis of multi-scans (program SADABS). Structure refinement: The structures were refined anisotropically against F^2 (program SHELXL-97[34]). Hydroxyl hydrogen atoms were refined freely but with OH distance restraints; other H atoms were included as rigid methyl groups or with a riding model. Special features: For **4c** and **18**, which crystallize in noncentrosymmetric space groups, anomalous scattering was negligible and Friedel opposite reflections were therefore merged. For **18**, the *tert*-butyl group at C9′ is disordered over two positions; the disordered methyl groups were refined ideally staggered using a riding model.

CCDC-745687 (**4a**), -745688 (**4b**), -745689 (**4c**), -745690 (**18**), -745691 (**27**), -745692 (**29**), -745693 (**30**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the Fonds der Chemischen Industrie for continuous support of our studies.

[1] P. Kilickiran, H. Hopf, I. Dix, P. G. Jones, *Eur. J. Org. Chem.* **2010**, 4035–4045.
[2] D. Klein, P. Kiliçkiran, C. Mlynek, H. Hopf, I. Dix, P. G. Jones, *Chem. Eur. J.* **2010**, *16*, 10507–10522.
[3] For a summary of the literature, see H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**, ch. 7.1, pp. 103–111.
[4] H. Shirakawa, *Angew. Chem.* **2001**, *113*, 2642–2648; *Angew. Chem. Int. Ed.* **2001**, *40*, 2574–2580.
[5] A. G. MacDiarmid, *Angew. Chem.* **2001**, *113*, 2649–2659; *Angew. Chem. Int. Ed.* **2001**, *40*, 2581–2590; A. J. Heeger, *Angew. Chem.* **2001**, *113*, 2660–2682; *Angew. Chem. Int. Ed.* **2001**, *40*, 2591–2611.
[6] H. J. Backer, *Recl. Trav. Chim. Pays-Bas* **1939**, *58*, 643–661.
[7] W. R. Roth, O. Adamczak, R. Breuckmann, H.-W. Lennartz, R. Boese, *Chem. Ber.* **1991**, *124*, 2499–2521.
[8] a) M. Trætteberg, P. Bakken, H. Hopf, R. Hänel, *Chem. Ber.* **1994**, *127*, 1469–1478; b) M. Trætteberg, H. Hopf, H. Lipka, R. Hänel, *Chem. Ber.* **1994**, *127*, 1459–1467.
[9] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, pp. 1119–1190.
[10] Z. Arnold, A. Holy, *Collect. Czech. Chem. Commun.* **1961**, *26*, 3059–3073.
[11] T. Koźluk, L. Cottier, G. Descotes, *Tetrahedron* **1981**, *37*, 1875–1880.
[12] B. Danieli, G. Lesma, G. Palmisano, S. Tollari, *J. Chem. Soc. Perkin Trans. 1* **1984**, 1237–1240.
[13] T. Wirth, S. Blechert, *Synlett* **1994**, 717–718.
[14] M. M. Hann, M. D. de Marquez, V. Thailer, *J. Chem. Res. Miniprint* **1988**, 0401–0409.
[15] H. Hopf, H. Lipka, *Chem. Ber.* **1991**, *124*, 2075–2084.
[16] F. Sondheimer, D. A. Ben-Efraim, R. Wolovsky, *J. Am. Chem. Soc.* **1961**, *83*, 1675–1681.
[17] a) H. Hopf, R. Haenel, P. G. Jones, P. Bubenitschek, *Angew. Chem.* **1994**, *106*, 1444–1445; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1369–1370; b) R. Hänel, Ph.D. dissertation, Braunschweig, **1995**.
[18] J. C. Lunt, F. Sondheimer, *J. Chem. Soc.* **1950**, 2957–2961.
[19] R. T. Hobgood, J. H. Goldstein, *J. Mol. Spectrosc.* **1964**, *12*, 76–86.
[20] R. K. Harris, A. V. Cunliffe, *Org. Magn. Reson.* **1977**, *9*, 483–488.
[21] H. Hopf, R. Hänel, M. Trætteberg, *Nachr. Chem. Tech. Lab.* **1994**, *42*, 856–862.
[22] a) P. B. D. de La Mare, T. J. Harvey, *J. Chem. Soc.* **1957**, 131–136; b) P. B. D. de La Mare, J. T. Harvey, M. Hassan, S. Varma, *J. Chem. Soc.* **1958**, 2756–2759.

[23] P. D. Bartlett, M. Roha, R. M. Stiles, *J. Am. Chem. Soc.* **1954**, *76*, 2349–2353.
[24] H. Hopf, H. Lipka, M. Trætteberg, *Angew. Chem.* **1994**, *106*, 232–233; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 204–205.
[25] We thank Doz. Dr. J. Grunenberg (University of Braunschweig) for carrying out these calculations for us.
[26] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1-S19.
[27] a) G. Köbrich, A. Mannschreck, R. A. Misra, G. Rissmann, M. Rösner, W. Zündorf, *Chem. Ber.* **1972**, *105*, 3794–3806; b) G. Köbrich, B. Kolb, A. Mannschreck, R. A. Misra, *Chem. Ber.* **1973**, *106*, 1601–1611; c) A. Mannschreck, V. Jonas, H.-O. Bädecker, H.-L. Elbe, G. Köbrich, *Tetrahedron Lett.* **1974**, *15*, 2153–2156; d) H.-O. Bödecker, V. Jonas, B. Kolb, A. Mannschreck, G. Köbrich, *Chem. Ber.* **1975**, *108*, 3497–3508; e) G. Becher, A. Mannschreck, *Chem. Ber.* **1981**, *114*, 2365–2368; f) G. Becher, A. Mannschreck, *Chem. Ber.* **1983**, *116*, 264–272; g) M. Rösner, G. Köbrich, *Angew. Chem.* **1974**, *86*, 775–776; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 741–742.
[28] a) G. Köbrich, H. Büttner, *Tetrahedron* **1969**, *25*, 2223–2228; b) G. Köbrich, H. Büttner, *J. Organomet. Chem.* **1969**, *18*, 117–134.
[29] We thank Professors W. A. König and St. H. von Reuß (University of Hamburg) for their help in resolving several of our chiral oligoolefins on various cyclodextrin phases.
[30] Y. Okamoto, E. Yashima, *Angew. Chem.* **1998**, *110*, 1072–1095; *Angew. Chem. Int. Ed.* **1998**, *37*, 1020–1043; for a more recent reference, see: T. Ikai, Y. Okamoto, *Chem. Rev.* **2009**, *109*, 6077–6101.
[31] a) Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata, R. Noyori, H. Takaya, *J. Am. Chem. Soc.* **1981**, *103*, 6971–6973; b) C. G. Knudsen, S. C. Carey, W. H. Okamura, *J. Am. Chem. Soc.* **1980**, *102*, 6355–6358.
[32] N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*, Oxford University Press, Oxford, **1983**.
[33] D. Fischer, Ph.D. dissertation, Braunschweig, **2000**.
[34] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.

Received: May 10, 2010
Published online: December 1, 2010

