A General Route to Fully Terminally tert-Butylated Linear Polyenes**

Dagmar Klein,^[a] Pinar Kiliçkiran,^[a] Cornelia Mlynek,^[a] Henning Hopf,^{*[a]} Ina Dix,^[a] and Peter G. Jones^[b]

Dedicated to Professor Pelayo Camps on the occasion of his 65th birthday

Abstract: Starting from the readily available α , β -unsaturated ketone, 3-*tert*-butyl-4,4-dimethyl-2-pentenal, higher vinylogues, and fully terminally *tert*-butylated polyolefins with up to 13 consecutive conjugated double bonds have been prepared by either McMurry dimerization or Wittig chain-elongation routes. The highly unsaturated conjugated π systems, which show a remarkable stability, have been characterized by spectroscopic methods and, in many cases, by X-ray structural analysis. The yields are high enough to allow for thorough chemical reactivity studies.

Introduction

Stabilization of polyolefins by substituent groups: Linearly conjugated olefins constitute one of the central classes of organic chemical compounds and they have been studied ever since organic chemistry became an exact natural science.^[2,3] Their importance ranges from 1,3-butadiene as a large-scale starting material in industrial organic chemistry^[4] to vitamin A, β -carotene, and numerous other retinoids^[5] and carotenoids,^[6] which play a crucial role in many biochemical processes, notably those in which light energy is converted into chemical energy and information (vision).^[7]

Furthermore, polyolefins have always played a pivotal role in the development of theoretical concepts of organic chemistry and in recent times have gained prominence as the parent compounds of organic metals; (doped) polyacety-lene is the most frequently investigated representative.^[8]

[b] Prof. P. G. Jones Institut für Anorganische und Analytische Chemie Technische Universität Braunschweig, Postfach 3329D-38023 Braunschweig (Germany)

[**] Highly hindered olefins and polyolefins, Part XIV; for Part XIII see reference [1].

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In spite of this century-old interest, much information is still lacking on oligo- and polymeric polyenes. This concerns both their structures-in the gas phase (for example, as determined by electron diffraction), solution (NMR spectroscopy), and the solid state (X-ray structural analysis)-and chemical behavior. It is, for example, surprising how rarely the reactions so typical of simple alkenes and alkadienes (electrophilic additions, cycloadditions, hydrogenation, polymerization, etc.) have been performed on the higher vinylogues of these parent systems. The reason that our ignorance grows so rapidly with the chain length is very simple: the unsubstituted polyolefins are a class of compounds very difficult to handle under normal laboratory conditions. They are thermally unstable and react readily with air. They polymerize and cross-link easily and often undergo cycloadditions with each other under mild conditions. Additionally, polyolefins are configurationally labile, which makes the isolation of pure diastereomers difficult, even when the most modern chromatographic methods are applied. These problems are already noticeable for structurally simple molecules, such as 1,3,5-hexatriene,^[9] and quickly become insurmountable with its higher vinylogues. Consequently, the classical early studies on the H(CH=CH)_nH hydrocarbons **1a** performed by Sondheimer and co-workers^[10] no longer fulfill present-day quality standards.

One often applied route to more stable polyolefins involves the introduction of substituents. This approach was first applied comprehensively by Nayler and Whiting^[11] and Bohlmann and Mannhardt^[12] who prepared numerous polyolefins **1b** with methyl groups at the terminal positions (Scheme 1; n = longest chain length prepared).

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 [[]a] D. Klein, P. Kiliçkiran, C. Mlynek, Prof. H. Hopf, I. Dix Institut für Organische Chemie, Technische Universität Braunschweig Hagenring 30, 38106 Braunschweig (Germany) Fax: (+49)531-391-5388 E-mail: H.Hopf@tu-bs.de

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Scheme 1. A selection of classical polyolefinic hydrocarbons.

Although these compounds show a pronounced increase in stability relative to **1a**, they are still reactive hydrocarbons, especially the higher members of the series. For example, Bohlmann's higher dimethyl derivatives **1b** (n > 3) all showed decomposition and polymerization on heating, which prevented the measurement of clearly defined melting points.^[12]

Another step toward the synthesis of longer polyenes (molecular wires) was developed by Kuhn, who incorporated two phenyl substituents at the α - and ω -positions and described a general route to polyolefins **1c** with up to 15 consecutive double bonds (Scheme 1).^[13] In this case, the terminal substituents are unsaturated and as a result they influence the electronic properties of the polyolefin chain (see discussion on electronic spectra and Table 1 below), which is a disadvantage if one wishes to study the effect of increasing chain length/unsaturation on the spectroscopic and chemical properties. However, incorporation of substituted-aryl groups provides a convenient way to create polarization of the unsaturated chain, if required.

The most popular group used for the stabilization of reactive organic molecules and intermediates is the *tert*-butyl substituent, as demonstrated by the two valence isomers tetrakis(*tert*-butyl)tetrahedrane and -cyclobutadiene studied by Maier et al.^[14] When bonded to a polyolefinic backbone, the *tert*-butyl moiety can exhibit vastly different effects, both from a reactivity and structural perspective.

As far as chemical behavior is concerned, *tert*-butyl groups will sterically protect the polyolefin chain from any attacking reagent, regardless of where they are positioned. They function as a "molecular fence" around the highly reactive π -conjugated backbone. This effect, which depends on the number of these bulky moieties, is particularly pronounced for terminally bonded *tert*-butyl groups because the α - and the ω -positions are the most reactive centers of the unsaturated chain.

The polyenes can adopt different conformations because the molecules 1a-c also contain σ -bonds around which rotation is possible. The extent of rotation is controlled by the placement of the *tert*-butyl substituents (terminal or internal) as discussed for the representative diene derivatives 2-5.

We have shown, by molecular-mechanics methods $(MM3)^{[15]}$ and ab initio Hartree–Fock (HF) calculations, that a *tert*-butyl group introduced into the 1-*trans* position (**2**) increases the steric-strain energy relative to the parent mole-



cule 1,3-butadiene, but that the potential-energy curves of the two compounds are rather similar; the transoid conformation is the most stable. On the other hand, if the tertbutyl moiety is introduced into the 2-position of 1,3-butadiene (3) a gauche conformation becomes the most stable, a result borne out by experiment (dihedral angle=32°, determined by electron diffraction of 3).^[16] For the dienes 4 and 5, which have two tert-butyl groups in the 1,1- and 2,3-positions, respectively, the results are even more pronounced. The calculated potential-energy curve for 4 favors the anti conformation, which is more stable by approximately 8 kJ mol^{-1} relative to the *gauche* conformation. For **5** this difference increases to approximately 55 kJ mol⁻¹ and makes an orthogonal structure much more favorable than a planar one. In fact, the experimentally determined dihedral angle amounts to 101.5° by gas-phase electron diffraction^[16] and 96.6° by single-crystal X-ray analysis.^[17] Extending these observations to the entire series of conjugated polyenes, we can state that terminally tert-butylated polyenes should prefer a planar structure, whereas introduction of an internal tert-butyl group should produce twisted polyolefins. Eventually completely orthogonal structures can be accessed, in which the double bonds are oriented in alternating, perpendicular planes, thus inhibiting any overlap between the respective π electrons.

Besides our own investigations on the preparation and structural properties of various *tert*-butylated conjugated dienes, extended oligo- and polyenes blocked by a single *tert*-butyl substituent at each end were described, more or less simultaneously, when we initiated our studies. These have largely been prepared by the two strategies discussed below.^[18]

Schrock and Knoll^[19] developed a route to the endcapped polyenes **10** by subjecting triene **6** to a catalytic ringopening oligomerization with the tungsten catalyst **7**. Cleavage of the more strained double bond of **6** led to metal-containing oligomers **8** (Scheme 2).

Addition of aldehydes, such as pivaldehyde, induced Wittig-type coupling with 8 to form 9, from which the 1,2bis(trifluoromethyl)benzene "protecting" group was cleaved by short-time pyrolysis. Although this approach could be extended as far as the decapentaenes (in 10: n=13), it yielded polydisperse mixtures that had to be separated by extensive chromatography. As a result, the overall yield of the differ-



Scheme 2. Preparation of polyolefins by metathesis reactions.

ent polyenes was low and only limited structural data (NMR spectra of representative hydrocarbons)^[20] and scarcely any chemical properties of the hydrocarbons **10** could be reported. Nevertheless, the amounts of various end-capped polyolefins prepared by this route were sufficient to carry out spectroscopic studies of radical cations generated radiolytically in Freon matrices, for example.^[21]

In a related ring-opening metathesis polymerization (ROMP) route, which used a Schrock catalyst system, Grubbs and Swager employed benzvalene as the starting material. After the polymerization step, the polymer obtained, which contained bicyclobutane units, was isomerized by treatment with heavy-metal ions (Hg^{2+} , Ag^+) to a mixture of polyenes (in the limiting case, polyacetylene). Compared with the Schrock and Knoll route, this process avoids the extrusion of a molecular fragment but, again, it is not a suitable method for the preparation of distinct polyenes in larger amounts.^[22]

Stepwise protocols that combine high efficiency with complete control of every step are preferable and were described by Müllen and co-workers.^[23] The routes to the hexaene **16** and octaene **18** presented in Scheme 3 are typical examples.

Stille coupling of vinyl iodide 11 with chlorodiene 12 yielded the extended polyunsaturated chloride 13, which could easily be converted into stannane 14, then iodide 15. Stille coupling of 14 and 15 provided 16 directly, whereas the Pd-catalyzed cross-coupling of 15 with the bis-stannane 17 led to 18, with the most stable all-*trans* isomer being formed in a final photoisomerization step.

Although this method gave the desired polyolefins in pure form and in sufficient amounts to collect all of the spectroscopic data and, in the case of **16**, the X-ray structure, it must be mentioned that the starting material for both **12** and **17**, 1,4-dichloro-1,3-butadiene, is not a readily available substrate. Like compound **6**, it has to be prepared from cyclooctatetraene, a hydrocarbon that has become expensive, although it is still available commercially.

The route to fully terminally *tert*-butylated polyolefins developed by us, and described herein in detail, avoids these



Scheme 3. Preparation of polyolefins bearing one terminal tert-butyl moiety.

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pitfalls. It uses simple substrates, nontoxic reagents and intermediates, does not require sophisticated chromatographic-separation techniques, and allows the synthesis of a comprehensive series of fully conjugated polyolefins (n=even or odd).

Results and Discussion

Synthesis of fully terminally *tert*-butylated polyolefins 30 (n = odd): The starting point of our polyene synthesis is 3-*tert*-butyl-4,4-dimethyl-2-pentenal (23), prepared in a four-step synthesis from pivaloyl chloride (19), as shown in Scheme 4.



Scheme 4. Preparation of the building block, tert-butyl-4,4-dimethyl-pent-2-enal (23).

Reaction of 19 with tert-butyl magnesium chloride yielded di-tert-butyl ketone 20 in 68% yield. When 20 was reacted with vinyl magnesium bromide, the expected allyl alcohol 21 was obtained in very good yield (90%), and subsequent treatment with thionyl chloride in pyridine at 0°C led to the isolation of chloride 22 in 58% yield. At higher reaction temperatures increasing amounts of the isomeric tertiary allylic chloride were produced. To convert 22 into aldehyde 23, we employed the method of Hass and Bender (KOH, isopropanol, 2-nitropropane)^[24] and obtained 23 in 66% yield. The pentenal can easily be prepared in 20 g batches by this route, enough for the chain-extension reactions described below. Surprisingly, compound 23 had not been reported at the beginning of our studies; we have since described its gas-phase conformation as determined by electron diffraction.^[25] As expected, compound 23 exists exclusively in the transoid conformation (shown in Scheme 4, full spectroscopic data are given in the Experimental Section).

The π system of **23** was first elongated by Wittig reaction with triphenyl phosphonium bromide **24** (Scheme 5). The vinylogous aldehyde **26**, obtained after acid-catalyzed hydrolysis of the initially formed acetal **25**, was then subjected to further chain-extension cycles with the same reagent until this protocol approached its limits with the aldehyde **27 f**. The Wittig reaction was performed at room temperature in most cases and the yield was excellent up to eight consecutive C=C double bonds (**27 f**, 90%). From this compound onwards the solubility of the aldehydes decreased dramatically and it was no longer possible to perform the reaction at room temperature. For the last two compounds in the series (**27 g** and **h**) reflux conditions were necessary, despite which significant amounts of the substrate aldehyde remained insoluble in the reaction mixture and the yields decreased. Workup was performed, in all cases, by simple column chromatography on silica gel and the aldehydes were stable as long as they were kept cold and under a nitrogen atmosphere. Nevertheless, the longest aldehydes prepared (**27 g** and **h**) displayed an increased tendency to form

> insoluble products (by polymerization) on standing. Clearly, the iterative approach to these aldehydes reached its limits at this point.

The structures of **26** and **27 a–h** were determined from their spectroscopic data and, in the case of **27 a**, **c**, and **d**, by X-ray crystal-structure analysis. The structural data are discussed below and summarized in the Experimental Section.

To prepare fully protected oligo- and polyenes with an odd number of double bonds from polyunsaturated aldehydes **23**,



Scheme 5. Homologation (vinylation) of aldehyde 23.

26, and **27 a–d**, the McMurry coupling reaction was used. Various protocols have been proposed in the literature for this reductive dimerization.^[26–28] We first tested these on the simple aldehyde **23** to find the optimum conditions for this class of compounds. The titanium(0) species generated by

zinc reduction of TiCl₄ in pyridine (Lenoir conditions) gave the best results. When the dimerization was carried out for shorter reaction times an intermediate product could be isolated, which was identified as a mixture of diastereomers of the pinacol **28** (Scheme 6). When **28** was reintroduced to the reduction conditions it was converted into the trienes (*E*)and (*Z*)-**29**. A 2:1 *E/Z* ratio of **29** was isolated directly when a solution of **23** in THF was heated at reflux temperature for longer reaction times.

The two diastereomers could be separated by gradienttemperature high-vacuum sublimation (at 0.05 mbar the Z and E isomers sublime at 90 and 115 °C, respectively). Structural assignment followed from the spectroscopic data and the single-crystal X-ray analyses (discussed below).

Under comparable conditions, the aldehydes 26 and 27a-d were reductively dimerized to the hydrocarbons 30a-e. The longest system, 30e, contains 13 consecutive double bonds; however, the yield drops rapidly (increased lability and poor solubility) and the purification of the material becomes increasingly difficult (separation of by-products becomes a problem) across the series. In the examples with a shorter chain length (30a-d) the yields are acceptable to good. The stability of these polyolefins will be addressed below.

Synthesis of fully terminally *tert*-butylated polyolefins 30 (n = even): The route discussed above does not allow the preparation of linear polyolefins with an even number of double bonds. To prepare these, we decided to synthesize an appropriate Wittig reagent and react it with the vinylogous aldehydes 26 and 27.

The required Wittig reagent was obtained from the phosphonium salt **35**, itself prepared by reaction of allylic bromide **31** with triphenylphosphine. Intermediate **31** was accessed by reaction of alcohol **21** with phosphorus tribromide in the presence of pyridine (Scheme 7).

Accompanying the bromination of 21, we noted the formation of small amounts of a quaternary hydrocarbon, to which we assigned structure 32 based on spectroscopic analysis of the material (see the Experimental Section). To rationalize the generation of 32, we propose that 21 is first dehydrated to the tertiary cation 33, followed by methyl migration to give the isomeric cation 34, then proton loss to furnish diene 32. The presence of two geminal tertbutyl moieties in 33 is thought





Scheme 6. Fully terminally *tert*-butylated polyolefins by McMurry dimerization.



Scheme 7. Fully terminally tert-butylated polyolefins by Wittig reaction.

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to induce migration to relieve steric strain.

The Wittig reaction with aldehydes **26**, **27b**, and **27d** proceeded without difficulties, although the yields of polyenes **30 f-h** were unsatisfactory. This is attributed, in part, to the expected formation of Z isomers during the chain-elongation process and to loss of material during the isolation and separation processes. In the case of **30 h**, only the 3-Z isomer could be obtained in analytically pure form. Detailed structures of these compounds are discussed below.

Stability of tert-butylated polyolefins 29 and 30: The polyenes described in this study are considerably more stable than any alkylated derivatives described to date in the literature. In pure form, no change is observed up to temperatures of approximately 50°C, either in solution or in the solid state, and when working with the polyenes no protection by an inert gas is necessary. From the triene (Z)-29 $(m.p. = 136 \degree C)$ to the undecaene **30d** $(m.p. = 257 \degree C)$ melting takes place without any visible change. Only for the tridecaene **30e** did we note decomposition (by polymerization), which began at 290 °C. The shorter homologues, with up to five consecutive double bonds, can be sublimed at 0.05 mbar-a property not shared by Kuhn's phenylpolyenes.^[29] When metal salts (FeCl₃) or metal oxides (Fe₂O₃) are added to solutions of the polyenes in THF or dichloromethane, an immediate color change to black is observed on mild heating (35°C), or at room temperature (for 7 or more double bonds: n > 5).

Hydrocarbons of medium-chain length (hexaene **30g** and heptaene **30b**) tend to include solvent molecules (dichloromethane, chloroform) in the solid state, shown by NMR spectroscopy and X-ray crystallography (see below). The solvent molecules, which are enclosed between the layers of the double-bond chains, are held very tightly in the crystal lattice and cannot be removed under high vacuum or by heating. From eight double bonds onwards, reproducible elemental analyses could not be obtained for the polyolefins, possibly because of incomplete combustion. A similar observation has been made by Müllen et al. for bis-*tert*-butylpo-lyenes.^[23]

The electronic spectra of selected *tert*-butyl-substituted aldehydes and polyolefins

UV/Vis spectra of polyenaldehydes 23, 26, and 27 a-h: UV/Vis spectra were determined for the series beginning with one (23) and ending with ten consecutive C=C double bonds (27h); representative examples are displayed in Figures 1 and 2.

As expected, the absorption maxima (λ_{max}) shift to longer wavelengths with increasing chain length; the color of the aldehydes changes from colorless to deep red. The absorption bands are very broad and show no vibrational fine structure. Bands from the $n \rightarrow \pi^*$ transitions are hidden under the $\pi \rightarrow \pi^*$ transition bands. Figure 3, summarizing all of the UV/Vis spectra measurements, shows that after approximately six double bonds the redshift trend begins to



Figure 1. Electronic spectra of the aldehydes 23 (---), 26 (----), and 27a (----) (in acetonitrile).



Figure 2. Electronic spectra of the polyenaldehydes 27b (----), c (-----), and d (----) (in acetonitrile).



Figure 3. Bathochromic shift of the absorption maximum of the polyenaldehydes **27** as a function of chain length.

decrease—a well-known phenomenon for polyenes—and aldehydes **27g** and **h** (n=8 and 9, respectively) absorb at nearly the same maximum. Very similar trends have been reported for analogous polyenals that contain a methyl^[30] or phenyl substituent^[31] at the ω -position, and also for various homologues of vitamin A aldehyde.^[32] The λ_{max} of the phenyl derivatives are shifted to longer wavelengths by 10– 40 nm, depending on the chain length, whereas the methyl compounds shift to shorter wavelengths.

UV/Vis spectra of polyenes 29 and 30 a-h: The UV/Vis spectra of polyenes have been discussed extensively in the chemical literature because of the importance of polyenes in biological chemistry, material science, and as model compounds for the theoretical interpretation of the relationship between color and constitution.^[33] Unsurprisingly, the absorption spectra of the all-trans compounds described herein are very similar to those of conjugated polyenes with other terminal substituents (see Table 1 below). The spectra display a profile characterized by three to four bands, with the maxima at the highest wavelengths being of greatest intensity. As in the case of the polyenals, the λ_{\max} are shifted bathochromically with increasing chain length. The distance between the maxima amounts to (1500 ± 150) cm⁻¹, independent of the stabilizing end groups, as is typical for such polyolefinic molecules.^[34] Figures 4 and 5 show typical absorption curves for a selection of polyenes prepared in this work and Table 1 contains the data from the groups of Kuhn (a phenyl substituent at either end),^[13,34] Sondheimer (unsubstituted),^[10] Bohlmann (a methyl substituent at each end),^[12] and our tetrakis(tert-butyl) derivatives.



Figure 4. Electronic spectra of 29 (----), 30 f (----), and 30 b (----) (in acetonitrile).

As can be seen in Table 1, the mesomeric effect of the phenyl substituent is considerably stronger than the hyperconjugative influence of the alkyl groups, even in the case of the fully *tert*-butylated polyenes. Kuhn's compounds show fluorescence in solution, whereas this effect is not observed for our *tert*-butyl-substituted hydrocarbons. Although hydrocarbon **30 h** has one Z-configured double bond, this stereochemi-



	Ph	н	Me	Ц.
п	(CH=CH) _n	(CH=CH) _n	(CH=CH) _n	
	Ph	Н	Me	n-2
	(in benzene) [nm]	(in isooctane) [nm]	(in hexane) [nm]	(in acetonitrile) [nm]
2	334	217	227	248
3	358	257	275	308
4	384	290	310	342
5	403	334	341	370
6	420	364	380	398
7	435	390	396	420
8	_	410	_	442
9	-	-	-	460
11	-	-	-	502 (in dichloromethane)
13	-	-	_	526 (in dichloromethane)



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Figure 5. Electronic spectra of 30b (----, acetonitrile), 30d (----, dichloromethane), and 30e (-----, dichloromethane).

cal feature apparently has only a weak influence on its electronic spectrum; qualitatively its UV spectrum correlates with lower and higher vinylogues. In a thorough study on the influence of solvents on the electronic spectra of several of these polyenes, it has been shown that **30c** is an excellent probe for the empirical determination of the polarizability of a wide variety of media.^[35]

X-ray structural analysis of selected aldehydes (27a, c, d) and polyolefins (29 and 30 a–c, f, g, and cis-30 h): The molecular structures of the aldehydes 27a, c, and d (Figures 6a, 7a, and 8a, respectively) have several common features. Torsion angles in the chains are as expected for *all-trans* systems, generally within $(180 \pm)10^\circ$. Chain lengths, expressed by the distance from the aldehyde carbon atom to the carbon atom on which the *tert*-butyl groups are located, are 7.40, 12.26, 14.74, and 14.80 Å for 27a, 27c, and the two independent forms of 27d, respectively. The disposition of the *tert*-butyl groups is such that 27a and 27c have approximate mirror symmetry (root mean square deviation (RMSD)= 0.10 and 0.13 Å, respectively). The two forms of 27d depart

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Figure 6. a) ORTEP plot of **27a**. Ellipsoids represent 30% probability levels. b) Packing diagram of **27a** in the region $z \approx \frac{1}{4}$. Hydrogen bonds of the form C–H…O are indicated by dashed lines. Hydrogen atoms not involved in hydrogen bonds and methyl carbon atoms are omitted.



Figure 7. a) ORTEP plot of **27c**. Ellipsoids represent 50% probability levels. b) Packing diagram of **27c**. Hydrogen atoms are omitted.

from this symmetry because of a bowing of the chain (C1-C7-C13=171 and 172°) and a nonideal torsion angle of 153° for C10'-C11'-C12'-C13' in form 2. The C–C bond lengths alternate in the polyene chains, between formal double and single bonds of approximately 1.35 and 1.44 Å, respectively (scatter approximately 0.01 Å; for individual values of these, and other dimensions, see the Supporting Information). The bond angles C–C=O are 125–126°; a search of the Cambridge Database^[36] gave an average of 125.9° for 37 occurrences of the acyclic fragment *trans*-CH=CH–CH=O. Moving along the chain, away from the aldehyde function, the next bond angle is approximately ideal (120–122°),



Figure 8. a) ORTEP plots of the two independent forms of **27d**. Ellipsoids represent 50% probability levels. b) Packing diagram of **27d**. Hydrogen atoms are omitted. Selected stacks of molecules 1 and 2 are indicated by the digits to the left of the stacks.

whereas all other angles are appreciably greater than 120° (122-126°). The final angle at (tBu)₂C=CH-CH is larger again (131-132°), presumably for steric reasons. Steric crowding is indicated by intramolecular H···H contacts as short as 1.85 Å between the *tert*-butyl groups. The Me₃C-C bonds are somewhat elongated at 1.55 Å (relative to the standard value of 1.52 Å for R_3C-C ,^[37] although the angles Me₃C-C-CMe₃ are not especially wide (122-123°). Taking 27 a as an example, the carbon atoms C9 (endo) and C13 (exo) lie in the mirror plane and, thus, short contacts (approximately 2 Å) must exist between H6 and two of the hydrogen atoms at C9, and also between H5 and one hydrogen atom at each of C14 and C15. The wide (tBu)₂C=CH-CH angle may serve to prevent very short contacts from the tertbutyl hydrogen atoms to H5. A Cambridge Database search gave only three hits for this moiety and all had relevant angles of 131-133° (reference codes ADAHUJ, LEWSUB10, and ZIFPAF).

The molecular packing of 27a (Figure 6b) is quite different from that of the other two aldehydes (Figures 7b and 8b). As would be expected in space group Pbca, there is no preferred chain direction; instead, the molecules associate to form broad layers at $z \approx \frac{1}{4}$, $\frac{3}{4}$, which involve weak hydrogen bonds of the form C-H...O (non-normalized $H2\cdots O = 2.74, H4\cdots O = 2.60, H5\cdots O = 2.73 \text{ Å}; \text{ the first two in-}$ teractions constitute a bifurcate system). For 27b (Figure 7b), parallel packing of the longer chains is clearly more important than C-H-O interactions because there are no H…O distances shorter than 2.89 Å. Each chain is surrounded by four others generated via various inversion centers, with the shortest C…C distances between chains at approximately 3.55 Å. Perhaps unexpectedly, the packing in 27c, with longer chains still, is a hybrid of the other two types (Figure 7b). The overall packing corresponds to the parallel-chain type but, in addition, there are two weak C-H-O

interactions H17 \cdots O = 2.74 and H7 \cdots O' 2.68 Å (not shown in Figure 8b).

The triene (*E*)-**29** (Figure 9a) displays crystallographic inversion symmetry, although the actual symmetry is close to 2/m (RMSD = 0.09 Å); the isomer (*Z*)-**29** (Figure 10a) has



Figure 9. a) ORTEP plot of (*E*)-**29**. Ellipsoids represent 50% probability levels. b) Packing diagram of (*E*)-**29**; layer at $x \approx \frac{1}{4}$. Hydrogen atoms are omitted.

no crystallographic symmetry, but has approximate mm2 symmetry (RMSD=0.19 Å). General features of molecular dimensions, including distortions and H···H contacts, are much as those described above. The triene chain of the Z isomer has particularly wide angles at C3 and C4 (126°), but there is little rotation about the central bond (torsion angle=3°). The packing of (E)-29 involves hexagonal layers (Figure 9b), whereas the corrugated layers in (Z)-29 involve a herringbone-type arrangement (Figure 10b).

The remaining *all-trans* polyenes 30a-c (n=odd), **f**, and **g** (n=even) all display crystallographic inversion symmetry (Figures 11 a, 12 a, 13 a, 14, and 15 a, respectively), although the true symmetry is, in most cases, close to 2/m (RMSD = 0.13, 0.05, 0.05, and 0.09 Å for 30a, **b**, **f**, and **g**, respectively). The exception is the longest-chain vinylogue 30c, which is distorted to a flattened-"S" shape (Figure 13 b). The general features of the molecular geometries of the polyene chains are similar to those described above for the aldehydes, except that the chain angles for 30c are marginally lower (C4-C5-C6=122°).

The packing patterns of **30a-c**, **f**, and **g** fall into two groups, depending on the space group. The solvent-free structures **30a**, **c**, and **f** all crystallize in $P\bar{1}$ with Z=1; thus, the chains are necessarily all parallel and the molecules form layers (Figure 11 b). The dichloromethane solvates **30b** and **g** crystallize in C2/c with Z=4; the packing, as viewed along the short *b* axis, appears to be similar to the $P\bar{1}$ struc-



Figure 10. a) ORTEP plot of (Z)-29. Ellipsoids represent 50% probability levels b) Packing diagram of (Z)-29; layer at $y \approx \frac{1}{4}$. Hydrogen atoms are omitted.



Figure 11. a) ORTEP plot of **30a**. Ellipsoids represent 30% probability levels. b) Packing diagram of **30a**, hydrogen atoms are omitted.

tures at first glance (see Figure 15b for 30g), but the molecules in the vertical rows are not parallel. Instead, they have angles of approximately 31 and 37° (for **30b** and **g**, respectively; calculated from the vectors from C1 to its symmetry equivalent in the same molecule). This can clearly be seen in the view parallel to the *c* axis for **30b** (Figure 12b), which also shows the voids where the disordered solvent molecules are located.



Figure 12. a) ORTEP plot of **30b**. Ellipsoids represent 50% probability levels. b) Packing diagram of **30b**, hydrogen atoms are omitted.



Figure 13. a) ORTEP plot of **30c**. Ellipsoids represent 50% probability levels. b: Side view of **30c** (arbitrary radii, hydrogen atoms are omitted).



Figure 14. ORTEP plot of **30 f**. Ellipsoids represent 50% probability levels.

Interestingly, in the case of **30h** we also isolated a *cis* isomer from the Wittig reaction and obtained single crystals suitable for X-ray analysis. Octaene *cis*-**30h** (Figure 16a), again, shows broadly similar features to its *all-trans* congeners (indeed, the chain angles are even wider; 131° at C4 and 127° at C6 and C8), but it would be unwise to overinter-



Figure 15. a) ORTEP plot of **30g**. Ellipsoids represent 50% probability levels. b) Packing diagram of **30g**, hydrogen atoms are omitted.



Figure 16. a) ORTEP plot of *cis*-**30h**. Ellipsoids represent 50% probability levels. b) Packing diagram of *cis*-**30h**, hydrogen atoms are omitted. Molecules with thick or thin bonds occupy the areas at $y \approx \frac{1}{2}$ or $\frac{1}{4}$, respectively.

pret these data in view of the unresolved disorder. The packing involves layers of molecules at intervals of $\frac{1}{4}$ along the *b* axis (Figure 16b).

Conclusion

Starting from the readily available building block 23, we have developed a general method for the preparation of oligoenes with up to 13 consecutive conjugated double bonds stabilized at their terminal positions by tert-butyl groups. Oligoenes with an odd number of double bonds can be prepared by McMurry coupling of the appropriate polyenals; the even-numbered double-bond derivatives by a Wittig approach. All of these compounds could be obtained in preparative amounts and, as a result, we can now begin to study their chemical properties. Structurally, these compounds prefer a planar arrangement, which allows optimal p-orbital overlap. All of these compounds are achiral. We emphasize this point because the introduction of the bulky tert-butyl moiety to the interior of these hydrocarbons prevents full conjugation and causes the formation of orthogonal polyenes. The resulting conformations possess sufficiently high rotational barriers to make these inner-substituted oligoenes chiral; these observations will be reported in a later publication of this series.

Experimental Section

General remarks: TLC: Commercial TLC-plates "Polygram Sil G/UV₂₅₄" by Macherey, Nagel & Co. (Düren). Column chromatography: Kieselgel 60 (70–230 mesh) by Merck (Darmstadt). M.p.: Büchi 530 melting-point apparatus, uncorrected. ¹H and ¹³C NMR spectroscopy: referenced to internal tetramethylsilane ($\delta_{\rm H}$ =0.00 ppm) or CDCl₃ ($\delta_{\rm C}$ =77.05 ppm), performed on Bruker AC-200 or WM-400 spectrometers. IR spectroscopy: recorded on a Nicolet 320 FTIR spectrometer. UV/Vis spectroscopy: recorded on Beckman UV 5230 and HP 8452A Diode Array spectrometers. EIMS: recorded on a Finnigan MAT 8430 spectrometer (70 eV). The following compounds were prepared according to literature methods: **20**,^[38] **21**,^[39] **22**,^[39] and **24**.^[40]

Compound 23: Freshly distilled 2-nitropropane (72.7 g, 73 mL, 0.82 mol) was added to a solution of potassium hydroxide (30.86 g, 0.55 mol) in water (70 mL) and isopropanol (230 mL) at RT.^[24] The mixture was stirred for 30 min and allyl chloride 22 (38.00 g, 0.20 mol) in isopropanol (80 mL) was added dropwise at RT. The reaction mixture was heated at reflux temperature for 6.5 h, cooled to RT, and hydrolyzed with ice water. The product mixture was extracted with diethyl ether, then the organic phases were combined and dried over anhydrous Na2SO4. The solvent was removed in vacuo and the resultant oil was distilled at 65°C/ 0.5 mbar to afford 23 as a colorless liquid (22.50 g, 66%). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.28$ (s, 9H; tBu), 1.49 (s, 9H; tBu), 5.96 (d, J =7.4 Hz, 1 H; 2-H), 10.50 ppm (d, J = 7.4 Hz, 1 H; 1-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 193.76$ (d, C1), 177.97 (C3), 126.62 (d, C2), 39.69 and 39.23 (C4, C6), 35.31, 30.96 ppm (q, CH_3); IR (film): $\tilde{\nu}\!=\!2963$ (vs), 1733 (vs), 1393 and 1368 (m), 1152 cm⁻¹ (m); UV/Vis (acetonitrile): see Figure 1; MS (EI, 70 eV): m/z (%): 167 (38) $[M^+-H]$, 127 (20), 57 (100); elemental analysis calcd (%) for C₁₁H₂₀O (168.27): C 78.51, H 11.98; found: C 78.12, H 12.03.

General procedure for the preparation of aldehydes 26 and 27: Under a nitrogen atmosphere, tBuOK (2.6 equiv) was added to a stirred suspension of phosphonium salt 24 (2.5 equiv) in anhydrous THF. An immediate color change of the mixture from colorless to yellow was observed. After stirring for 30 min, a solution of the respective aldehyde (1 equiv) in THF was added dropwise and the stirring was continued at RT for 6 h. Aqueous oxalic acid (1 M, 7 equiv) was added and the mixture was left to stir overnight. After the phases had separated, the aqueous layer was extracted with diethyl ether several times. The combined organic phases

were neutralized with saturated aqueous sodium bicarbonate solution, dried over anhydrous MgSO₄, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel. *Note:* When the reaction time was reduced to 2 h varying amounts of the diastereomer with the Z configuration at the C2=C3 double bond could be isolated. To ensure the formation of the most stable, *all-trans* configuration of the polyenaldehydes the reaction was always carried out for 6 h.

Compound **26**: According to the general procedure above, reaction of **23** (3.0 g, 18 mmol) in THF (30 mL), **24** (19.15 g, 44 mmol) in THF (90 mL), *t*BuOK (4.81 g, 43 mmol), and oxalic acid (15.76 g, 125 mmol) in water (125 mL), followed by silica-gel chromatography (ethyl acetate/hexane = 1:10), afforded **26** as a colorless solid (3.00 g, 86%). M.p. ≈5°C; ¹H NMR (400 MHz, CDCl₃): δ =1.27 (s, 9H; 7-H), 1.44 (s, 9H; 9-H), 5.99–6.05 (dd, *J*=7.6, 14.7 Hz, 1H; 2-H), 6.27 (d, *J*=11.8 Hz, 1H; 4-H), 7.80–7.86 (dd, *J*=11.8, 14.7 Hz, 1H; 3-H), 9.62 ppm (d, *J*=8.1 Hz, 1H; 1-H); ¹³C NMR (100 MHz, CDCl₃): δ =193.80 (d, C1), 169.88 (C5), 151.23 (d, C3), 131.09 (d, C2), 122.21 (d, C4), 39.82 and 38.63 (C6 and C8), 34.17 (q, C9), 31.31 ppm (q, C7); IR (film): $\tilde{\nu}$ =2960 (s), 1683 (vs), 1609 (s), 1394 and 1396 (m), 1145 (s), 978 cm⁻¹ (m); UV/Vis (acetonitrile): see Figure 1; MS (EI, 70 eV): *m*/*z* (%): 194 (2) [*M*]⁺, 138 (34), 123 (42), 57 (100); elemental analysis calcd (%) for C₁₃H₂₂O (194.31): C 80.36, H 11.41; found: C 79.97, H 11.23.

Compound 27a: According to the general procedure above, reaction of 26 (2.46 g, 12.7 mmol) in THF (25 mL), 24 (13.65 g, 31.8 mmol) in THF (60 mL), tBuOK (3.42 g, 30.5 mmol), and oxalic acid (11.34 g, 90.0 mmol) in water (90 mL), followed by silica-gel chromatography (ethyl acetate/ hexane=1:10), afforded 27a as a yellow solid (2.45 g, 88%). M.p. 30-31 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.25$ (s, 9H; 9-H), 1.41 (s, 9H; 11-H), 6.11-6.17 (m, 1H; 2-H), 6.16 (d, J=11.7 Hz, 1H; 6-H), 6.28-6.35 (dd, J=11.2, 14.4 Hz, 1H; 4-H), 7.19-7.26 (dd, J=11.2, 14.9 Hz, 1H; 3-H), 7.31-7.38 (dd, J=11.8, 14.4 Hz, 1 H; 5-H), 9.56 ppm (d, J=7.9 Hz, 1 H; 1-H); 13 C NMR (100 MHz, CDCl₃): $\delta = 193.43$ (d, C1), 164.93 (C7), 152.62 (d, C3), 142.12 (d, C5), 130.30 (d, C2), 129.18 (d, C4), 123.39 (d, C6), 39.44 and 38.37 (C8 and C10), 34.00 (q, C11), 31.49 ppm (q, C9); IR (film): $\tilde{v} = 2956$ (m), 1680 (vs), 1668 (vs), 1594 (vs), 1390 and 1368 (m), 1120 cm⁻¹ (s); UV/Vis (acetonitrile): see Figure 1; MS (EI, 70 eV): m/z(%): 220 (2) [M]⁺, 164 (33), 136 (17), 69 (13), 57 (100); elemental analysis calcd (%) for C13H22O (220.34): C 81.83, H 10.98; found: C 82.09, H 10.79.

Compound 27b: According to the general procedure above, reaction of 27a (1.15 g, 5.23 mmol) in THF (10 mL), 24 (5.60 g, 13.0 mmol) in THF (25 mL), tBuOK (1.40 g, 12.5 mmol), and oxalic acid (4.61 g, 36.0 mmol) in water (36 mL), followed by silica-gel chromatography (ethyl acetate/ hexane=1:10), afforded 27b as a yellow solid (1.17 g, 91%). M.p. 43-45°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.24$ (s, 9H; 11-H), 1.39 (s, 9H; 13-H), 6.11-6.17 (m, 2H; 2-H, 8-H), 6.17-6.23 (dd, J=10.8, 14.0 Hz, 1H; 6-H), 6.39-6.45 (dd, J=11.4, 14.8 Hz, 1H; 4-H), 6.75-6.82 (dd, J=10.8, 14.5 Hz, 1H; 5-H), 7.09-7.15 (dd, J=11.8, 14.3 Hz, 1H; 7-H), 7.11-7.27 (dd, *J*=11.2, 15.1 Hz, 1H; 3-H), 9.55 ppm (d, *J*=8.0 Hz, 1H; 1-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 193.40$ (d, C1), 162.25 (d, C9), 152.08 and 143.48 (C3, C5, C7), 130.86 (d, C6), 130.50 and 123.73 (2×d, C2, C8), 128.78 (d, C4), 39.33 and 38.27 (C10, C12), 33.96 (q, C13), 31.65 ppm (q, C11); IR (KBr): $\tilde{v} = 2958$ (m), 1677 (vs), 1580 (vs), 1192 cm⁻¹ (vs); UV/ Vis (acetonitrile): see Figure 2; MS (EI, 70 eV): m/z (%): 246 (32) [M]+, 189 (100), 133 (28), 57 (76); HRMS: m/z: calcd for $C_{17}H_{26}O$: 246.198 [M]+; found: 246.198.

Compound **27***c*: According to the general procedure above, reaction of **27b** (0.75 g, 2.85 mmol) in THF (5 mL), **24** (3.05 g, 7.11 mmol) in THF (15 mL), *t*BuOK (0.77 g, 6.83 mmol), and oxalic acid (2.52 g, 20.0 mmol) in water (20 mL), followed by silica-gel chromatography (ether/petroleum ether=3:10), afforded **27c** as a yellow solid (0.75 g, 96%). M.p. 89°C; ¹H NMR (400 MHz, CDCl₃): δ =1.24 (s, 9H; 13-H), 1.39 (s, 9H; 15-H), 6.11 (d, *J*=11.8 Hz, 1H; 10-H), 6.11–6.21 (m, 2H; 2-H, 8-H), 6.29–6.35 (dd, *J*=11.2, 14.7 Hz, 1H; 6-H), 6.41–6.47 (dd, *J*=11.3, 14.7 Hz, 1H; 4-H), 6.57–6.64 (dd, *J*=11.1, 14.7 Hz, 1H; 7-H), 6.69–6.75 (dd, *J*=11.2, 14.6 Hz, 1H; 5-H), 6.98–7.04 (dd, *J*=11.8, 14.3 Hz, 1H; 9-H), 7.11–7.18 (dd, *J*=11.3, 15.1 Hz, 1H; 3-H), 9.56 ppm (d, *J*=8.0 Hz,

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1 H; 1-H); ¹³C NMR (100 MHz, CDCl₃): δ = 193.47 (d, C1), 160.75 (C11), 152.01 (d, C3), 143.01 (d, C5), 139.68 (d, C7), 136.35 (d, C9), 131.56 and 130.59 (d, C2, C6, C8), 129.29 (d, C4), 123.91 (d, C10), 39.26 and 38.19 (C12, C14), 33.92 and 31.73 (2×q, C13, C15); IR (KBr): $\tilde{\nu}$ =2956 (m), 1673 (vs), 1568 (vs), 1390 and 1369 (m), 1151 (vs), 1012 cm⁻¹ (vs); UV/ Vis (acetonitrile): see Figure 2; MS (EI, 70 eV): *m/z* (%): 272 (40) [*M*]⁺, 215 (100), 188 (24), 159 (30), 57 (38); elemental analysis calcd (%) for C₁₉H₂₈O (272.43): C 82.04, H 10.73; found: C 82.50, H 10.47.

Compound 27d: According to the general procedure above, reaction of 27c (0.53 g, 1.95 mmol) in THF (4 mL), 24 (2.10 g, 4.87 mmol) in THF (10 mL), tBuOK (0.52 g, 4.67 mmol), and oxalic acid (1.72 g, 13.6 mmol) in water (14 mL), followed by silica-gel chromatography (ethyl acetate/ hexane = 1:6), afforded 27d as an orange-red solid (0.54 g, 93%). M.p. 127°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.23$ (s, 9H; 15-H), 1.38 (s, 9H; 17-H), 6.10 (d, J=11.9 Hz, 1H; 12-H), 6.13-6.19 (m, 2H; 2-H, 10-H), 6.27-6.33 (dd, J=11.2, 14.6 Hz, 1H; 8-H), 6.37 (dd, J=11.3, 14.6 Hz, 1H; 6-H), 6.40-6.47 (dd, J=11.3, 14.6 Hz, 1H; 4-H), 6.56 (m, 2H; 7-H, 9-H), 6.69-6.75 (dd, J=11.2, 14.6 Hz, 1H; 5-H), 6.92-6.98 (dd, J=11.9, 14.2 Hz, 1H; 11-H), 7.10-7.16 (dd, J=11.3, 15.1 Hz, 1H; 3-H), 9.56 ppm (d, J = 7.9 Hz, 1H; 1-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 193.26$ (C1), 159.70 (C15), 151.72 (d, C3), 142.81 (d, C5), 139.11 and 137.39 (2×d, C7, C9), 135.09 (d, C11), 131.82 and 130.96 (2×d, C2, C10), 131.25 (d, C8), 130.96 (d, C6), 128.38 (d, C4), 132.92 (d, C12), 39.10 and 38.04 (C14, C16), 33.79 (q, C17), 31.68 ppm (q, C15); IR (KBr): v=2957 (m), 1668 (vs), 1554 (vs), 1391 and 1367 (s), 1150 (vs), 1012 (vs), 1002 cm⁻¹ (vs); UV/Vis (acetonitrile): see Figure 2; MS (EI, 70 eV): m/z (%): 298 (60) $[M]^+$, 241 (100), 214 (20), 57 (54); HRMS: m/z: calcd for $C_{21}H_{30}O$: 298.230 [*M*]⁺; found: 298.229.

Compound 27e: According to the general procedure above, reaction of 27d (0.29 g, 0.97 mmol) in THF (7 mL), 24 (1.04 g, 2.43 mmol) in THF (15 mL), tBuOK (0.26 g, 2.34 mmol), and oxalic acid (0.86 g, 6.81 mmol) in water (7 mL), followed by silica-gel chromatography (dichloromethane), afforded 27 e as a red solid (0.30 g, 95%). M.p. 140-141 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.23$ and 1.37 (2×s, 2×9H; 17-H, 19-H), 6.08 (d, J=11.7 Hz, 1H; 14-H), 6.12-6.19 (m, 2H; 12-H, 2-H), 6.25-6.37 (m, 2H; 10-H, 8-H), 6.41-6.57 (m, 3H; 4-H, 6-H, 7-H), 6.53-6.57 (m, 2H; 9-H, 11-H), 6.72 (dd, J=14.7, 11.3 Hz, 1H; 5-H), 6.91 (dd, J=14.1, 12.0 Hz, 1H; 13-H), 7.14 (dd, J=15.0, 11.3 Hz, 1H; 3-H), 9.56 ppm (d, J = 7.9 Hz, 1H; 1-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 193.38$ (d, C1), 159.24 (C15), 151.81 (d, C3), 142.80 (d, C5), 139.11, 137.00, 136.20, 134.37, 132.04, 131.77, 131.68, 131.20, 130.62, 129.54 (d, C2, C4, C6, C7, C8, C9, C10, C11, C12, C13), 123.94 (d, C14), 39.07 and 38.01 (2×s; C16, C18), 33.77 and 31.70 ppm (2×q, C17, C19); IR (KBr): $\tilde{\nu}\!=\!2960$ (m), 1957 (m), 1667 (s), 1613 (m), 1542 (s), 1482 (w), 1392 (w), 1114 (s), 1105 (s), 1007 cm⁻¹ (vs); UV/Vis (chloroform): λ_{max} (log ε) = 422 nm (4.80); MS (EI, 70 eV): m/z (%): 324 (100) [M]⁺, 289 (35), 267 (88), 240 (20), 162 (100), 147 (42), 131 (58), 105 (44), 91 (100), 77 (66), 72 (66), 57 (79). The elemental analysis of this aldehyde was unsatisfactory, possibly because of the increased reactivity of 27 e.

Compound 27 f: According to the general procedure above, reaction of 27e (0.19 g, 0.58 mmol) in THF (7 mL), 24 (0.63 g, 1.47 mmol) in THF (15 mL), tBuOK (0.16 g, 1.41 mmol), and oxalic acid (0.52 g, 4.10 mmol) in water (4 mL), followed by silica-gel chromatography (dichloromethane), afforded 27 f as a red solid (0.18 g, 90%). M.p. 141-143°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.23$ and 1.37 (2×s, 2×9H; 19-H, 21-H), 6.08 (d, J=11.8 Hz, 1 H; 16-H), 6.12-6.18 (m, 2 H; 12-H, 14-H), 6.25-6.57 (m, 10H; 2-H, 4-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H), 6.72 (dd, J=11.2, 14.6 Hz, 1H; 5-H), 6.89 (dd, J=11.6, 13.0 Hz, 1H; 15-H), 7.14 (dd, *J*=11.3, 15.0 Hz, 1 H; 3-H), 9.56 ppm (d, *J*=7.9 Hz, 1 H; 1-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 193.37$ (d, C1), 158.78 (C17), 151.76 (d, C3), 142.76 (d, C5), 139.05 (d, C15), 136.96, 135.46, 133.94, 132.19, 132.16, 132.02, 131.91, 131.37, 130.66, 129.62 (d, C2, C4, C6, C7, C8, C9, C10, C11, C12, C13, C14), 123.98 (d, C16), 39.04 and 37.98 (2×s; C18, C20), 33.75 and 31.70 ppm (2×q, C19, C21); IR (KBr): $\tilde{\nu}$ =2957 (m), 1668 (s), 1600 (s), 1367 (w), 1139 (s), 1109 (vs), 1104 cm⁻¹ (m); UV/Vis (chloroform): λ_{max} (log ε) = 444 nm (4.83). During spectroscopic analysis the compound polymerized.

Compound 27g: Under a nitrogen atmosphere, tBuOK (0.140 g, 1.23 mmol) was added to a stirred suspension of phosphonium salt 24 (0.550 g, 1.29 mmol) in anhydrous THF (30 mL). An immediate color change of the mixture from colorless to yellow was observed. After stirring for 30 min, aldehyde 27 f (0.180 g, 0.514 mmol) in THF (20 mL) was added dropwise and the reaction mixture was heated at reflux temperature for 6 h. After cooling to RT, aqueous oxalic acid solution (1 M, 7 equiv) was added and the mixture was stirred overnight. After the phases had separated the aqueous layer was extracted with diethyl ether. The organic phases were combined and neutralized with saturated aqueous sodium bicarbonate solution. After removal of the solvent by rotary evaporation, the residue was purified by column chromatography on silica gel (ethyl acetate) to afford 27g as dark-red crystals (0.116g, 60%), poorly soluble in most common solvents. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 1.22$ and 1.32 (2×s, 2×9H; 21-H, 23-H), 6.05–6.51 (m, 14H; 2-H, 4-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 18-H), 6.66-6.95 (m, 2H; 5-H, 17-H), 7.13-7.26 (dd, J=15.0, 11.1 Hz, 1H; 3-H), 9.58 ppm (d, J = 7.9 Hz, 1H; 1-H); IR (KBr): $\tilde{\nu} = 2956$ (m), 1669 (s), 1612 (w), 1523 (s), 1463 (w), 1392 (w), 1132 (m), 1010 cm⁻¹ (vs); UV/Vis (chloroform): λ_{max} (log ε) = 456 (4.87), 472 nm (4.84, sh). The aldehyde could not be characterized fully; in the NMR solvent (CDCl₃) a fast color change from deep red to green-brown was noted, accompanied by a rapid loss of the aldehyde proton signal. A mass spectrum could not be obtained because of polymerization of the compound. The aldehyde group is at least partially responsible for the high reactivity of 27g, shown by the reaction of freshly prepared material with malononitrile, which led to the corresponding dinitrile (characterized spectroscopical $lv^{[42]}$).

Compound **27h**: According to the procedure described for **27g**, reaction of phosphonium salt **24** (0.199 g, 0.465 mmol) in THF (20 mL), **27g** (0.070 g, 0.186 mmol) in THF (35 mL), and *t*BuOK (0.050 g, 0.464 mmol) afforded the aldehyde **27h** as a dark-red solid (0.70 g, 53%). Compound **27h** is extremely insoluble in most organic solvents and during its (incomplete) spectroscopic characterization we noted extensive polymerization. ¹H NMR (400 MHz, CDCl₃): δ =1.23 and 1.37 (2×s, 2×9H; 23-H, 25-H), 6.10–6.95 (m, 16H; 2-H, 4-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H), 7.11–7.23 (dd, 1H; 3-H), 9.61 ppm (d, *J*=7.9 Hz, 1H; 1-H); UV/Vis (chloroform): λ_{max} (log ε)=468 nm (4.81). The nature of the compound was confirmed by Knoevenagel condensation with malononitrile, which gave the expected dinitrile in 30% yield. This derivative is much more stable than the starting material **27h** and could be characterized fully^[42].

McMurry reaction of aldehydes 23, 26, and 27 a-d

Compound 29: Under a nitrogen atmosphere at 0°C, zinc dust (4.67 g, 71.38 mmol) and anhydrous pyridine (2.72 g, 2.67 mL, 34.5 mmol) were added to a solution of TiCl₄ (6.77 g, 3.92 mL, 35.69 mmol) in anhydrous THF (90 mL). The mixture was stirred for 30 min at 0°C before a solution of aldehyde 23 (1.00 g, 5.95 mmol) in THF (50 mL) was added. The reaction mixture was stirred for 1.5 h at RT and subsequently heated at reflux temperature for 1.5 h. Hydrolysis with ice water, diethyl ether, and half-concentrated hydrochloric acid gave a clear aqueous phase from which the organic phase was separated. After extraction of the aqueous phase with diethyl ether (2×), the organic phases were combined, neutralized with saturated aqueous sodium bicarbonate solution, and dried over anhydrous Na2SO4. The solvent was removed in vacuo and the oily residue was purified by column chromatography on silica gel (pentane). Thermal gradient sublimation at 0.05 mbar provided two fractions: Fraction 1: (Z)-29 (0.21 g, 23%); fraction 2: (E)-29 (0.42 g 47%). Rinsing the chromatography column with dichloromethane provided a small amount of diol 28 as a mixture of diastereomers.

Compound (Z)-**29**: M.p. 136 °C; ¹H NMR (400 MHz, CDCl₃): δ =1.25 and 1.38 (2×s, 2×18H; 1-H, 10-H, 12-H, 14-H), 6.50–6.55 ppm (AA'XX', 4H; 4-H, 5-H, 6-H, 7-H); ¹³C NMR (100 MHz, CDCl₃): δ =157.11 (C3, C8), 126.22 and 117.92 (d, C4, C5, C6, C7), 39.48 and 37.67 (C2, C9, C11, C13), 33.54 and 31.74 ppm (q, C1, C10, C12, C14); IR (KBr): $\bar{\nu}$ =2955 (vs), 1625 (w), 1387 and 1364 cm⁻¹ (m); UV/Vis (acetonitrile): λ_{max} (log ε)=306 (4.38, sh), 294 (4.56), 284 nm (4.50); MS (EI, 70 eV): m/z (%): 304 (36) [M]⁺, 247 (10), 191 (64), 57 (100).

Compound (E)-**29**: M.p. 185 °C; ¹H NMR (400 MHz, CDCl₃): δ = 1.23 (s, 18H; 1-H, 10-H), 1.38 (s, 18H; 12-H, 14-H), 6.08–6.11 and 6.63–6.65 ppm (AA'XX, 4H; 4-H, 5-H, 6-H, 7-H); ¹³C NMR (100 MHz, CDCl₃): δ = 155.93 (C3), 131.72 (d, C5, C6), 124.15 (d, C4, C7), 38.81 (C2, C9), 37.72 (C11, C13), 33.74 (q, C12, C14), 31.85 ppm (q, C1, C10); IR (KBr): $\tilde{\nu}$ = 2956 (vs), 1598 (w), 1386, 1366 and 1355 (m-s), 984 cm⁻¹ (m); UV/Vis (acetonitrile): see Figure 4; MS (EI, 70 eV): *m/z* (%): 304 (24) [*M*]⁺, 247 (10), 191 (56), 57 (100); HRMS: *m/z*: calcd for C₂₂H₄₀ (304.54): C 86.76, H 13.24; found: C 86.54, H 13.32.

Compound **28** (mixture of diastereomers): M.p. 108°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.19$ (s, 18H; 1-H, 10-H), 1.34 (s, 18H; 12-H, 14-H), 1.99 (s, 2H; 5-H, 6-H), 4.86 and 5.43 ppm (AA'XX', 4H; 4-H, 5-H, 6-H, 7-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.92$ (C3, C8), 122.04 (d, C4, C7), 71.14 (d, C5, C6), 39.06 (C2, C9), 37.45 (C11, C13), 34.12 (q, C12, C14), 31.62 ppm (C1, C10); IR (KBr): $\tilde{\nu} = 3465$ (br, OH), 2957 (vs), 1624 (m), 1392, 1369 and 1363 (m), 1217 (m), 1011 cm⁻¹ (m); UV/Vis (acetonitrile): λ_{max} (log ε) = 198 nm (4.29); MS (EI, 70 eV): m/z (%): 339 (12) [*M*+H]⁺, 338 (50) [*M*]⁺, 321 (100), 247 (84); elemental analysis calcd (%) for C₂₂H₄₂O₂ (338.56): C 78.03, H 12.51; found: C 78.29, H 12.75.

Compound 30a: According to the procedure described for 29, reaction of TiCl₄ (5.76 g, 3.34 mL, 30.38 mmol) in THF (130 mL), zinc dust (3.97 g, 60.76 mmol), pyridine (2.12 g, 2.16 mL, 26.78 mmol), and aldehyde 26 (1.00 g, 5.15 mmol) in THF (60 mL), followed by chromatographic workup on silica gel (pentane), yielded 30 a as a pale-yellow solid (0.60 g, 65 %). M.p.184 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.23$ (s, 18H; 1-H, 14-H), 1.37 (s, 18H; 16-H, 18-H), 6.07 (d, J=11.7 Hz, 2H; 4-H, 11-H), 6.09-6.15 (AA'XX', 2H; 6-H, 9-H), 6.30-6.33 (AA'XX', 2H; 7-H, 8-H), 6.78–6.85 ppm (dd, J = 11.7, 14.2 Hz, 2H; 5-H, 10-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 157.26$ (C3, C12), 132.72 (d, C7, C8), 132.46 (d, C6, C9), 132.25 (d, C5, C10), 124.00 (d, C4, C11), 38.92 and 37.86 (C2, C13, C15, C17), 33.71 (q, C1, C14), 31.8 ppm (q, C16, C18); IR (KBr): $\tilde{v} = 2956$ (s), 1389, 1367 and 1355 (s), 995 cm⁻¹ (vs); UV/Vis (acetonitrile): λ_{max} (log ε) = 370 (4.95), 352 (4.99), 334 nm (4.79); MS (EI, 70 eV): m/z(%): 356 (66) [M]⁺, 299 (28), 242 (24), 57 (100); HRMS: m/z: calcd for C₂₆H₄₄: 356.344 [M]+; found: 356.344; elemental analysis calcd (%) for C₂₆H₄₄ (356.28): C 87.56, H 12.44; found: C 87.21, H 12.31.

Compound 30b: According to the procedure described for 29, reaction of TiCl₄ (7.63 g, 4.42 mL, 40.19 mmol) in THF (180 mL), zinc dust (5.26 g, 80.39 mmol), pyridine (2.81 g, 2.87 mL, 35.52 mmol), and aldehyde 27a (1.02 g, 4.61 mmol) in THF (90 mL), followed by chromatographic workup on silica gel (pentane), yielded 30b as orange plates (0.60 g, 64%) (recrystallized from dichloromethane/methanol). M.p. 178°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.23$ (s, 18H; 1-H, 18-H), 1.37 (s, 18H; 20-H, 22-H), 6.07 (d, J=11.7 Hz, 2H; 4-H, 15-H), 6.11-6.17 (dd, J=10.5, 14.3 Hz, 2H; 6-H, 13-H), 6.25-6.35 (m, 6H; 7-H, 8-H, 9-H, 10-H, 11-H, 12-H), 6.80–6.87 ppm (dd, J=11.8, 14.2 Hz, 2H; 5-H, 14-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 157.79$ (C3, C16), 133.60, 132.96, 132.39 (d, C7, C8, C9, C10, C11, C12), 132.76 (d, C5, C14), 132.44 (d, C6, C13), 124.04 (d, C4, C15), 38.97 (C2, C17), 37.91 (C19, C21), 33.73 (q, C20, C22), 31.76 ppm (q, C1, C18); IR (KBr): $\tilde{v} = 2955$ (s), 1392 and 1363 (m), 1217 (m), 998 cm⁻¹ (s); UV/Vis (acetonitrile): see Figure 5 < xfigr5; MS (EI, 70 eV): m/z (%): 408 (100) [M]⁺, 351 (21), 294 (38), 121 (17), 57 (91); HRMS: m/z: calcd for C₃₀H₄₈: 408.375 [M]⁺; found: 408.374; elemental analysis calcd (%) for C30H48 (408.79): C 83.35, H 11.22; found: C 83.49, H 11.37.

Compound **30***c*: According to the procedure described for **29**, reaction of TiCl₄ (1.80 g, 1.04 mL, 9.48 mmol) in THF (100 mL), zinc dust (1.04 g, 15.83 mmol), pyridine (0.56 g, 0.57 mL, 7.08 mmol), and aldehyde **27b** (0.250 g, 1.02 mmol) in THF (30 mL), followed by chromatographic workup on silica gel (pentane), yielded **30c** as a dark-red solid (0.194 g, 64%). M.p. 172 °C; ¹H NMR (400 MHz, CDCl₃): δ = 1.23 (s, 18H; 1-H, 22-H), 1.37 (s, 18H; 24-H, 26-H), 6.07 (d, *J* = 11.7 Hz, 2H; 4-H, 19-H), 6.11–6.17 (dd, *J* = 10.7, 14.3 Hz, 2H; 6-H, 17-H), 6.29–6.38 (m, 10H; 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H), 6.81–6.88 ppm (dd, *J* = 11.8, 14.2 Hz, 2H; 5-H, 18-H); ¹³C NMR (100 MHz, CDCl₃): δ = 157.91 (C3, C20), 133.92, 133.45, 133.23, 132.91, 132.35 (d, C7, C8, C9, C10, C11, C12, C13, C14, C15, C16), 132.96 (d, C5, C18), 132.41 (C6,

C17), 124.04 (d, C4, C19), 39.98 and 37.92 (C2, C21, C23, C25), 33.72 (q, C1, C12), 31.74 ppm (q, C24, C26); IR (KBr): $\tilde{\nu}$ =2954 (m), 1215 (m), 1005 cm⁻¹ (vs); UV/Vis (acetonitrile): λ_{max} (log ε)=460 (4.97), 432 (4.98), 408 (4.79), 390 (4.48, sh), 372 (4.15, sh), 330 (3.76), 266 nm (4.02); MS (EI, 70 eV): m/z (%): 460 (100) [M]⁺, 403 (14), 346 (22), 57 (76); HRMS: m/z: calcd for C₃₄H₅₂: 460.407 [M]⁺; found: 460.406.

Compound **30***d*: According to the procedure described for **29**, reaction of TiCl₄ (0.79 g, 0.46 mL, 4.16 mmol) in THF (40 mL), zinc dust (0.54 g, 8.32 mmol), pyridine (0.29 g, 0.28 mL, 3.67 mmol), and aldehyde **27c** (0.190 g, 0.71 mmol) in THF (20 mL), followed by chromatographic workup on silica gel (pentane/dichloromethane) and recrystallization (dichloromethane/methanol), yielded **30d** as a dark-red solid (0.080 g, 44%). M.p. 257°C; ¹H NMR (400 MHz, CDCl₃): δ =1.17 (s, 18H; 1-H, 26-H), 1.31 (s, 18H; 28-H, 30-H), 5.90 (d, *J*=11.7 Hz, 2H; 4-H, 23-H), 6.01–6.07 and 6.21 (m, 16H; 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H), 6.70–6.77 pm (m, 2H; 5-H, 22-H); IR (KBr): $\tilde{\nu}$ =2958 (m), 1689 (m), 1392 and 1367 (m), 1007 cm⁻¹ (vs); UV/vis (acetonitrile): see Figure 5; MS (EI, 70 eV): *m/z* (%): 512 (80) [*M*]⁺, 455 (10), 398 (12), 57 (100); HRMS: *m/z*: calcd for C₃₈H₅₆: 512.438 [*M*]⁺; found: 512.437.

Compound **30***e*: According to the procedure described for **29**, reaction of TiCl₄ (0.60 g, 0.35 mL, 3.12 mmol) in THF (45 mL), zinc dust (0.41 g, 6.32 mmol), pyridine (0.22 g, 0.23 mL, 2.97 mmol), and aldehyde **27d** (0.130 g, 0.44 mmol) in THF (20 mL), followed by chromatographic workup on silica gel (pentane/dichloromethane), yielded **30e** as a darkred oil (0.022 g, 18%), which contained several inseparable impurities. ¹H NMR (400 MHz, CDCl₃): δ =1.23 (s, 18H; 1-H, 30-H), 1.37 (s, 18H; 22-H, 34-H), 6.08 (d, *J*=11.5 Hz, 2H; 4-H, 27-H), 6.11–6.18 (dd, *J*=11.1, 13.9 Hz, 2H) and 6.25–6.39 (m, 20H; 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 23-H, 24-H, 25-H), 6.82–6.85 ppm (m, 2H; 5-H, 26-H); IR (KBr): $\tilde{\nu}$ =2953 (m), 1458 (m), 1388 and 1367 (m), 1216 (m), 1008 cm⁻¹ (vs); UVIVis (dichloromethane): see Figure 5; MS (EI, 70 eV): *m*/*z* (%): 564 (44) [*M*]⁺, 507 (10), 450 (4), 57 (100); HRMS: *m*/*z*: calcd for C₄₂H₆₀: 564.468 [*M*]⁺; found: 564.468.

Compound 31: Under nitrogen atmosphere and ice cooling, a solution of phosphorus tribromide (40.1 g, 0.148 mol) in ether (60 mL) was added slowly to a solution of allyl alcohol **21** (10.0 g, 58.72 mmol) and anhydrous pyridine (11.71 g, 12 mL, 0.148 mol) in ether (30 mL). The reaction mixture was stirred for 30 min at 0°C and then for 1 h at RT. After hydrolysis with ice water, the aqueous phase was extracted with diethyl ether. The organic phases were combined, neutralized with saturated aqueous sodium bicarbonate, and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo and the residual oil was purified by fractional distillation. The product **31** (6.35 g, 46%) distilled as a colorless oil at 59–62 °C and 0.8 mbar (100–105 °C/15 mm Hg)^[39]. In addition, the rearrangement product **32** (0.37 g, 4%) was isolated as a colorless oil (42 °C/ 0.8 mbar).

Compound 31: ¹H NMR (400 MHz, CDCl₃): $\delta = 1.20$ and 1.33 (2×s, 2× 9H; 5-H, 7-H), 4.28 (d, J=8.8 Hz, 2H; 1-H), 5.59 ppm (t, J=8.8 Hz, 1H; 2-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.62$ (C3), 121.34 (d, C2), 38.79 and 37.34 (C4, C6), 33.22 (t, C1), 33.27 and 31.54 ppm (2×q, C5, C7); IR (film): $\tilde{v} = 2960$ (vs), 1483 (m), 1608 (m), 1392 and 1367 (m), 1200 (m), 672 cm⁻¹ (m); UV/Vis (acetonitrile): $\lambda_{max} (\log \epsilon) = 228 \text{ nm } (4.14)$; MS (EI, 70 eV): m/z (%): 234/232 (36) $[M]^+$, 153 (4), 96 (100), 81 (86), 57 (98). Compound **32**: ¹H NMR (400 MHz, CDCl₃): $\delta = 0.92$ (s, 9H; 7-H), 1.17 (s, 3H; 9-H), 1.83 (s, 3H; 8-H), 4.79-4.96 (m, 2H; 1-H), 4.96-5.05 (m, 2H; 5-H), 6.31–6.38 ppm (dd, J = 11.0, 17.5 Hz, 1H, 4-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 149.89$ (C2), 144.28 (d, C4), 113.67 (t, C1), 111.82 (t, C5), 49.39 (C3), 36.02 (C6), 26.66 (q, C7), 24.31 (q, C8), 18.86 ppm (q, C9); IR (film): $\tilde{\nu} = 2960$ (vs), 1627 (m), 1395 and 1376 (m), 912 (m), 896 cm⁻¹ (m); UV/Vis (acetonitrile): λ_{max} (log ε) = 194 nm (3.92); MS (EI, 70 eV): m/z (%): 152 (2) [M]⁺, 137 (4), 96 (92), 81 (77), 67 (31), 57 (100). Compound 35: A mixture of allylbromide 31 (6.00 g, 25.74 mmol) and triphenylphosphine (7.87 g, 30 mmol) was stirred at 70 °C for 4 h. The resulting colorless crude product was washed with diethyl ether and dried under high vacuum to give 35 as colorless needles (10.45 g, 82 %). M.p. 223–235°C; ¹H NMR (400 MHz, CDCl₃; H–P decoupled): $\delta = 1.04$ and

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1.18 (2×s, 2×9H; 1-H, 13-H), 4.66 (d, J=7.5 Hz, 2H; 5-H), 5.26 (t, J=7.5 Hz, 1H; 4-H), 7.70–7.98 (m, 15H; Ar-H); ¹³C NMR (100 MHz, CDCl₃; C–P decoupled): δ =162.86 (C3), 135.21, 134.96, 133.89, 133.64, 130.37, 130.26 (d, Ar-C), 117.59 (q, C6, C10, C11), 108.28 (d, C4), 39.80 and 37.20 (C2, C12), 32.67 and 31.19 (2×q, C1, C13), 26.74 ppm (t, C5); IR (KBr): $\tilde{\nu}$ =2959 (s), 1588 (m), 1456 (vs), 1390 and 1368 (s), 1113 (vs), 746 cm⁻¹ (vs); UV/Vis (acetonitrile): λ_{max} (log ε)=196 (5.05), 268 nm (3.47); MS (EI, 70 eV): m/z (%): 414 (8) [M]⁺–HBr, 399 (42), 262 (100), 183 (72), 57 (32); elemental analysis calcd (%) for C₂₉H₃₆PBr (495.48): C 70.30, H 7.32, Br 16.13; found: C 69.70, H 7.18, Br 16.19.

Wittig reactions

Compound 30 f: Under nitrogen atmosphere, tBuOK (1.79 g, 16.0 mmol) was added to a solution of 35 (7.92 g, 16.0 mmol) in anhydrous THF (320 mL). After stirring the mixture for 30 min at RT, a solution of aldehyde 26 (1.61 g, 8.06 mmol) in THF (60 mL) was added. The reaction mixture was stirred for 2.5 h and then hydrolyzed with ice water. The aqueous phase was extracted with diethyl ether $(\times 2)$. The combined organic phases were dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The residue was filtered through a pad of silica gel (pentane) and the crude solid was recrystallized (dichloromethane/methanol) to give 30 f as colorless needles (0.51 g, 19%). M.p. 191°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.22$ (s, 18H; 1-H 12-H), 1.36 (s, 18H; 14-H, 16-H), 6.07 (d, J =11.6 Hz, 2H; 4-H, 9-H), 6.19-6.23 and 6.77-6.83 ppm (AA'XX', 4H; 5-H, 6-H, 7-H, 8-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 156.73$ (C3, C10), 132.69 (d, C6, C7), 131.78 (d, C5, C8), 123.97 (d, C4, C9), 38.86 and 37.79 (C2, C11, C13, C15), 33.66 (q, C14, C16), 31.77 ppm (q, C1, C12); IR (KBr): $\tilde{\nu} =$ 2954 (vs), 1609 (m), 1388, 1365 and 1351 (m), 1215 (m), 988 cm^{-1} (s); UV/Vis (acetonitrile): see Figure 4; MS (EI, 70 eV): m/z (%): 330 (44) $[M]^+$, 273 (22), 216 (40), 109 (46), 57 (100); HRMS: m/z: calcd for C₂₄H₄₂: 330.329 [M]+; found: 330.328; elemental analysis calcd (%) for $C_{24}H_{42}$ (330.58): C 87.20, H 12.80; found: C 86.81, H 13.11.

Compound 30g: According to the procedure described for 30 f, reaction of 35 (2.01 g, 4.06 mmol) in THF (100 mL), tBuOK (0.46 g, 4.06 mmol), and aldehyde 27b (0.50 g, 2.03 mmol) in THF (30 mL) afforded 30g (0.35 g, 45%) as a yellow solid. M.p. 89°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.23$ (s, 18H; 1-H, 16-H), 1.37 (s, 18H; 18-H, 20-H), 6.07 (d, J =11.7 Hz, 2H; 4-H, 13-H), 6.11-6.17 (dd, J=10.6, 14.3 Hz, 2H; 6-H, 11-H), 6.24-6.35 (AA'XX', 4H; 7-H, 8-H, 9-H, 10-H), 6.79–6.86 ppm (dd, J=11.7, 14.2 Hz, 2H; 5-H, 12-H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 157.54$ (C3, C14), 133.28 and 132.39 (d, C7, C8, C9, C10), 132.58 (d, C5, C12), 132.42 (d, C6, C11), 124.02 (d, C4, C13), 38.95 (C2, C15), 37.88 (C17, C19), 33.71 (q, C18, C20), 31.75 ppm (q, C1, C16); IR (KBr): $\tilde{\nu} = 2954$ (m), 1587 (m), 1390 and 1364 (m), 998 cm⁻¹ (vs); UV/Vis (acetonitrile): λ_{max} $(\log \varepsilon) = 398$ (5.00), 376 (5.00), 356 nm (4.80); MS (EI, 70 eV): m/z (%): 382 (100) [M]⁺, 325 (32), 268 (46), 57 (88); HRMS: m/z: calcd for C₂₈H₄₆: 382.359 $[M]^+$; found: 382.359; elemental analysis calcd (%) for C28H46 (382.31): C 78.38, H 10.71; found: C 78.13, H 10.98.

Table 2. Crystallo	graphic data for	compounds 27a,	c, d, (E)-29, (Z)	-29, 30 a, b, c, f,	g, and <i>cis</i> -30 h.						
Compound	27 a	27 c	27 d	(E)- 29	(Z)-29	30 a	30 b- CH ₂ Cl ₂	30 c	30 f	30 g-CH2Cl2	cis-30h
formula M _r	$C_{15}H_{24}O$ 220.24	$C_{19}H_{28}O$ 272.41	C ₂₁ H ₃₀ O 298.45	$C_{22}H_{40}$ 304.54	$C_{22}H_{40}$ 304.54	$C_{26}H_{44}$ 356.61	$C_{31}H_{50}Cl_2$ 493.61	$C_{34}H_{52}$ 460.76	$C_{24}H_{42}$ 330.58	$C_{29}H_{48}Cl_2$ 467.57	$C_{32}H_{50}$ 434.72
habit	colorless	yellow tablet	orange tablet	colorless	colorless, irregu-	pale-yellow	yellow	orange prism	colorless	yellow plate	orange
	prism			tablet	lar	tablet	tablet		prism		prism
crystal size [mm ³]	$0.9 \times 0.4 \times 0.2$	$0.45 \times 0.4 \times 0.15$	$0.4 \times 0.3 \times 0.15$	$0.6 \times 0.6 \times 0.4$	$0.9 \times 0.4 \times 0.3$	$0.8 \times 0.4 \times 0.15$	$0.9 \times 0.2 \times 0.1$	$0.45 \times 0.25 \times 0.13$	$0.4 \times 0.32 \times 0.24$	$0.9 \times 0.4 \times 0.06$	$0.3 \times 0.2 \times 0.1$
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	Pbca	$P\bar{1}$	C2/c	$P2_1/c$	Pbca	$P\bar{1}$	C2/c	$P\bar{1}$	$P\bar{1}$	C2/c	$P2_1/c$
$a \left[\stackrel{\circ}{A} \right]$	11.0360(16)	6.110(3)	22.848(6)	10.7846(14)	11.9708(12)	6.0870(8)	35.189(5)	6.0290(5)	6.0642(12)	32.312(5)	16.120(3)
$b \left[\AA ight]$	8.5697(16)	8.091(3)	8.374(2)	11.6744(16)	15.645(2)	8.1494(10)	8.1899(12)	8.1437(7)	6.5650(14)	8.1280(14)	15.560(3)
$c \left[\stackrel{\circ}{A} ight]$	31.212(5)	18.813(5)	40.531(10)	7.9545(16)	21.741(2)	12.6523(12)	11.3654(18)	16.1656(14)	14.330(3)	11.278(3)	11.7996(19)
α [•]	90	84.07(2)	90	90	90	89.267(8)	90	78.715(2)	88.776(14)	90	90
β [°]	90	86.72(2)	105.68(2)	94.104(12)	90	80.363(8)	105.534(10)	79.507(2)	86.868(16)	97.161(18)	104.013(4)
γ [°]	90	70.89(2)	90	90	90	81.314(10)	90	76.628(2)	79.527(16)	90	90
$V \left[{{ m \AA}^3} ight]$	2952	873.9	7466	1007.3	4071.8	611.6	3155.8	749.4	560.1	2939.0	2888.1
Ζ	8	2	16	2	8	1	4	1	1	4	4
$ ho_{ m calcd} [{ m Mgm}^{-3}]$	0.992	1.035	1.062	1.004	0.994	0.968	1.039	1.021	0.980	1.057	1.000
$\mu \ [mm^{-1}]$	0.06	0.06	0.06	0.06	0.06	0.05	0.22	0.06	0.05	0.23	0.06
F(000)	976	300	2624	344	1376	200	1080	256	186	1024	968
T [°C]	-100	-130	-130	-100	-100	-100	-100	-130	-100	-100	-130
$2 heta_{ m max}$	50	50	56.7	50	50	50	50	56	50	50	57
reflns measured	4296	4198	33428	3707	4032	3129	4421	8762	2161	3298	30496
reflns indep.	2602	3083	7651	1773	3583	2148	2780	3577	1960	2596	7319
$R_{ m int}$	0.022	0.037	0.108	0.025	0.018	0.011	0.019	0.077	0.015	0.022	0.16
parameters	152	187	409	106	211	124	187	160	115	178	332
restraints	0	0	0	0	0	0	74	0	0	142	339
$wR(F^2, all reflns)$	0.101	0.149	0.165	0.115	0.122	0.127	0.126	0.123	0.147	0.132	0.247
$R(F,>4\sigma(F))$	0.040	0.057	0.068	0.042	0.047	0.044	0.047	0.044	0.052	0.050	0.083
S	0.87	1.04	1.02	1.03	0.93	1.06	0.92	1.04	0.95	0.88	0.91
max. $\Delta \rho [e \text{ Å}^{-3}]$	0.13	0.14	0.31	0.16	0.18	0.22	0.21	0.30	0.17	0.15	0.76

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Compound 30h: According to the procedure described for 30 f, reaction of 35 (0.332 g, 0.67 mmol) in THF (15 mL), tBuOK (0.075 g, 0.34 mmol), and aldehyde 27d (0.100 g, 0.34 mmol) in THF (2.5 mL) afforded an inseparable E/Z mixture of **30h** as an orange solid (0.062 g, 43%). We were successful in obtaining single crystals (recrystallization from chlorobenzene) suitable for X-ray structural analysis. The sample contained crystals with both the E and Z configuration at the C3=C4 double bond, hence the structure is disordered in this part of the molecule (see below). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$, 1.08, 1.23, 1.37 (s, 4H; 1-H, 20-H, 22-H, 24-H), 6.02, 6.07 (d, J=11.42, J=11.7 Hz, 2H; 4-H, 17-H), 6.11-6.17 (dd, J=10.7, 14.2 Hz, 2H; 6-H, 15-H), 6.20-6.36 (m, 8H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H), 6.49-6.55 and 6.81-6.87 ppm (dd, J=11.3, 14.2 Hz, 1 H and dd, J=11.7, 14.2 Hz, 1 H; 5-H, 16-H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 157.78, 146.15 (C3, C18), 133.71, 133.36, 133.13,$ 132.96, 132.84, 132.68, 132.43, 132.39, 132.03, 130.49, 127.17, 124.04 (d, C4, C5, C6, C7, C8, C9, C10, C11, C12, C13, C14, C15, C16, C17), 44.37, 38.97, 37.91, 36.93 (C2, C19, C21, C23), 33.72, 31.74, 26.64, 23.76 ppm (q, C1, C20, C22, C24); IR (KBr): $\tilde{\nu} = 2955$ (s), 1391 and 1366 (m), 1216 (m), 1001 cm⁻¹ (vs); UV/Vis (acetonitrile): λ_{max} (log ε) = 250 (4.05), 356 (4.17), 374 (4.51), 392 (4.80), 416 (4.98), 442 nm (4.98); MS (EI, 70 eV): m/z (%): 434 (100) $[M]^+$, 337 (15), 320 (21), 57 (68); HRMS: m/z: calcd for C₃₂H₅₀: 434.391 [*M*]⁺; found: 434.390

X-ray structure determinations: Numerical details are presented in Table 2.

Data collection and reduction: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (27 d, 30 c, *cis*-30 h: Bruker SMART 1000 CCD; 27 c: Stoe STADI-4; others: Siemens P4, with appropriate low-temperature attachments). Measurements were performed with monochromated Mo_{Ka} irradiation ($\lambda = 0.71073$ Å). No absorption corrections were performed.

Structure refinement: The structures were refined anisotropically against F^2 (program SHELXL-97^[41]). Hydrogen atoms were included as rigid methyl groups or with a riding model.

Exceptions/special features of refinement: For all compounds that crystallized with solvent, the solvent was disordered; appropriate similarity restraints were used to improve refinement stability. A second structure of **30b** was determined as a deuteriochloroform hydrate and proved to be essentially isostructural to the first form; the data were of very limited quality and have been deposited as indicated below. Compound *cis*-**30h** was contaminated, both in solution (see discussion) and in the crystal, by a few percent of the *trans* isomer (seen as a difference in electron density of max. 0.75 e Å³); no appropriate disorder model could be refined. One *tert*-butyl group was also disordered over two positions.

CCDC-726529 (27a), 726530 (27c), 726531 (27d), 726532 ((*E*)-29), 726533 ((*Z*)-29), 726533 (30a), 726535 (30b), 726536 (30c), 726537 (30f), 726538 (30g), 726539(30h), and 726540 (30b (second form)) 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.

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