Synthesis of Vinylallenes by Conjugate 1,6-, 1,8-, 1,10- and 1,12-Addition Reactions of Organocuprates with Acetylenic Michael Acceptors and Their Use as Dienes in Intermolecular Diels-Alder Reactions

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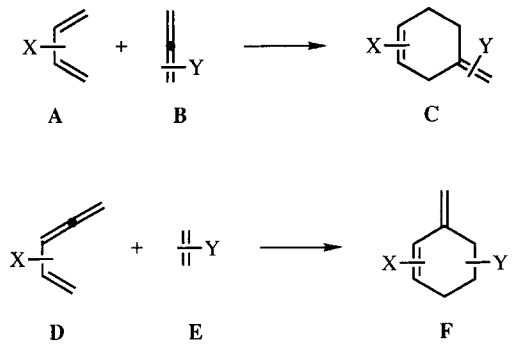
Various vinylallenes were synthesized by conjugate cuprate additions to acetylenic Michael acceptors. Thus, 1,6-addition reactions with 2-en-4-ynoates **1**, **3**, and **5a**, respectively, furnished vinylallenes **2**, **4**, and **7** after regioselective electrophilic capture of the allenyl enolates formed. Likewise, 1,8-addition to 2,4-dien-6-ynoates **8a** and **10** gave the vinylallenes **9** and **11**, whereas the 1,10-addition of Me_2CuLi to 2,4,6-trien-8-ynoate **12** provided allene **13**, and the analogous 1,12-addition to 2,4,6,8-tetraen-10-ynoate **14** furnished the polyene **15**. These vinylallenes are valuable dienophiles in regio- and stereoselective Diels-Alder reactions, as evidenced by the formation of the cycloaddition products **16**–**24**. In the presence of Lewis acids, vinylallene **4a** presumably rearranges to a cyclopentadiene derivative which then forms the cycloadducts **25** and **26**.

1. Introduction

Due to the fact that it allows the selective formation of two carbon-carbon bonds and up to four centers of chirality in a single step, the Diels-Alder reaction belongs to the most important transformations in organic chemistry[1]. Nowadays, it seems impossible to keep up with the numerous applications of this cycloaddition for the synthesis of simple as well as highly complicated target molecules. Likewise, the mechanism of the Diels-Alder reaction has been studied extensively since it is a prototype of pericyclic reactions.

Among the many different dienes and dienophiles employed in Diels-Alder reactions, allenes have played only a minor role so far[1,2]. In most cases, they were used as dienophiles (**B**) and converted into cycloadducts of type **C** by reaction with dienes **A**[1–3]. If the allene bears another conjugated double bond, however, it can be used as diene component (**D**), and the Diels-Alder reaction with dienophiles **E** then gives products of type **F**. A prominent but rather special example of the latter reaction type is the cycloaddition of bisallenes to alkynes to give quinodimethanes which then dimerize to cyclophanes[2,4]. However, there is only a limited number of examples for the use of vinylallenes as dienes in inter-[1,2,5] and intramolecular [4 + 2] cycloadditions[1,2,6].

Compared to ordinary conjugated dienes, the use of vinylallenes as diene component in Diels-Alder reactions is advantageous from the viewpoint of both reactivity and selectivity[1,2,5–7]. Thus, Bond[7c] showed by ab-initio calculations that the equilibrium between the *s-trans* and *s-cis* conformers of vinylallenes is more on the side of the *s-cis* isomer than for 1,3-dienes; consequently, vinylallenes exhibit a higher reactivity in [4 + 2] cycloadditions. In another seminal contribution, Reich et al.[5f] demonstrated that Diels-Alder reactions of unfunctionalized vinylallenes take place with high regio-, *exo-endo*-, and facial selectivity, allowing control of the stereochemistry of the cyclohexene ring and the exocyclic double bond formed. Here the reaction of a vinylallene with an unsymmetrical dienophile proceeds predominantly or (in many cases) exclusively via transition state **G** to furnish the isomer **H** with the smallest interaction between the largest substituents A and X.



Like their use in cycloaddition reactions, the synthetic availability of vinylallenes was limited in scope and/or efficiency so far. Many of the known methods like addition, substitution, isomerization, sigmatropic rearrangement, and olefination reactions[2–6,8] can only be applied to sim-

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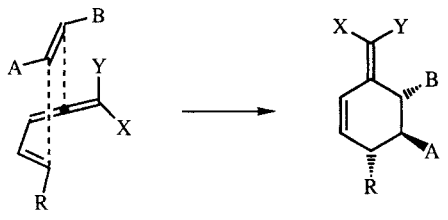


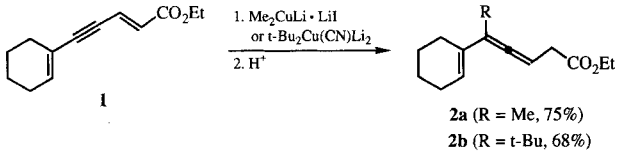
G H

Size: A > B
X > Y

ple unfunctionalized vinylallenes or compounds with a rigid substitution pattern. During our previous work concerning conjugate addition reactions of organocopper reagents[9] with acetylenic Michael acceptors[10], we were able to show that highly functionalized vinylallenes are readily accessible by 1,6-cuprate additions to 2-en-4-ynoates[6k,10b,h,k] and 1,8-additions to 2,4-dien-6-ynoates[10d]. In view of the advantages of vinylallenes as diene component in Diels-Alder reactions, we therefore initiated an extensive study of the synthesis of functionalized vinylallenes by our methods and their use in [4 + 2] cycloadditions[11]. The results of this work are presented here.

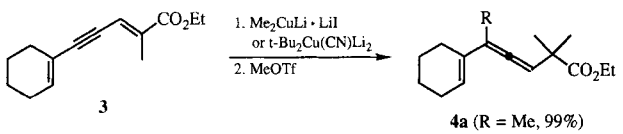
2. Synthesis of Vinylallenes

The Michael acceptors employed in this investigation are either known compounds or were prepared by Wittig-Horner-Wadsworth-Emmons (WHWE) olefinations (for details see Experimental). As found earlier[10b], 2,6-dien-4-ynoate **1** reacts with lithium dimethylcuprate ($Me_2CuLi \cdot LiI$) at the triple bond with 1,6-addition exclusively, and the protonation of the allenyl enolate also takes place regioselectively at C-2 to give vinylallene **2a** in 75% yield. Likewise, 1,6-addition of $tBu_2Cu(CN)Li_2$ furnished compound **2b** (68% yield). In order to synthesize the corresponding vinylallenes **4** with two methyl groups at C-2, the Michael acceptor **3** was treated with the cuprate and methyl triflate; also this electrophile reacts regioselectively at C-2 of the allenyl enolates[6k,10e] to provide allenes **4a** (99%) and **4b** (58% yield), respectively.



1

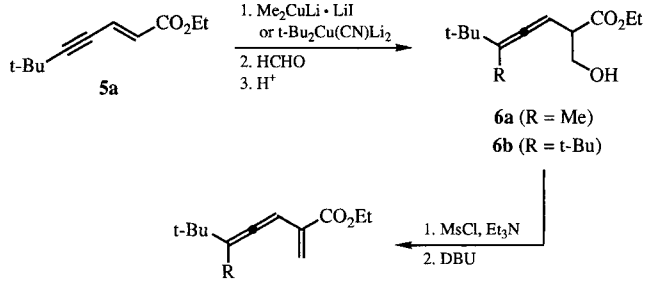
2a (R = Me, 75%)
2b (R = t-Bu, 68%)



3

4a (R = Me, 99%)
4b (R = t-Bu, 58%)

Structurally different vinylallenes are accessible by 1,6-cuprate addition to simple 2-en-4-ynoates, followed by regioselective aldol reaction at C-2 and dehydration[10e,h,k]. For example, 1,6-addition of $Me_2CuLi \cdot LiI$ to enyne **5a** and treatment of the enolate with formaldehyde led to hydroxy ester **6a**, and subsequent mesylation and elimination with DBU gave vinylallene **7a**. Attempts to isolate this compound, however, resulted in a spontaneous Diels-Alder reaction affording cycloadduct **20** (see below). In contrast to this, the vinylallene **7b** formed analogously from $tBu_2Cu(CN)Li_2$ was isolated in 77% yield.

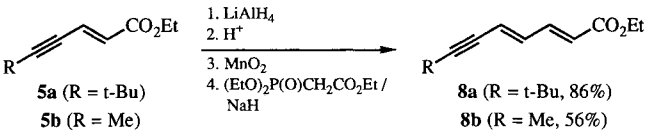


5a

6a (R = Me)
6b (R = t-Bu)

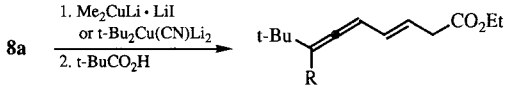
7a (R = Me)
7b (R = t-Bu, 77%)

Another direct route to vinylallenes is the 1,8-cuprate addition to 2,4-dien-6-ynoates, followed by regioselective protonation of the vinylogous allenyl enolate with pivalic acid[10d]. The Michael acceptors **8** required are readily prepared from enynoates **5** by reduction with $LiAlH_4$, reoxidation to the aldehydes with activated manganese dioxide, and WHWE olefination. This sequence gave overall yields of 86% for **8a** and 56% for **8b** and is by far more effective than a direct olefination of acetylenic aldehydes with the C_4-building block ethyl 4-(diethoxyphosphoryl)-2-butenoate. The reactions of dienynoate **8a** with $Me_2CuLi \cdot LiI$ or $tBu_2Cu(CN)Li_2$ and protonation with pivalic acid all took place with the desired regioselectivities to furnish vinylallenes **9a** (90%) and **9b** (72% yield) as only isolable products (the latter was obtained as a 70:30 mixture of *E*/*Z* isomers).



5a (R = t-Bu)
5b (R = Me)

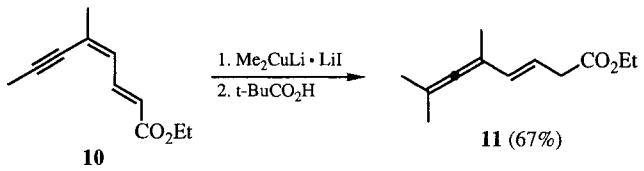
8a (R = t-Bu, 86%)
8b (R = Me, 56%)



9a (R = Me, 90%)
9b (R = t-Bu, 72%)

Similarly, the substrate **10** was prepared from commercially available (*Z*)-3-methyl-2-penten-4-yn-1-ol by methylation at the acetylenic terminus, oxidation to the aldehyde and WHWE reaction. Also this Michael acceptor reacts with lithium dimethylcuprate at the triple bond exclusively,

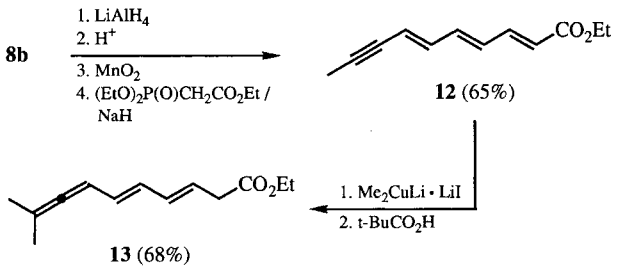
and regioselective protonation provided the 1,8-adduct **11** in 67% yield.



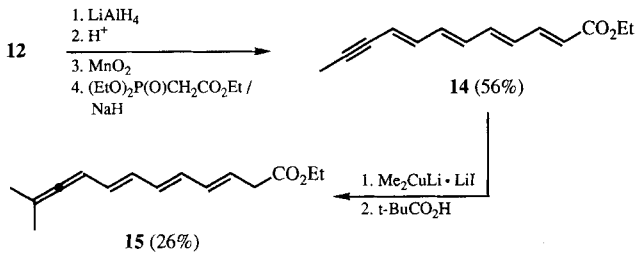
10 **11** (67%)

In view of the high regioselectivities observed in these conjugate cuprate addition reactions in favor of the attack at the triple bond of the Michael acceptors, it seemed of interest to explore the scope and limitations of 1,*n*-additions of this type with increasing distance between triple bond and acceptor substituent. These transformations would not only shed more light on mechanistic details of conjugate cuprate additions but could also lead to vinylogous vinylallenes which might be valuable diene components for Diels-Alder reactions. Of course, the number of possible regioisomeric products is rising with increasing length of the conjugate system; in the case of the 2,4-dien-6-ynoates **8** and **10**, the cuprate could attack at C-3, C-5, or C-7, and the vinylogous allenyl enolates formed in the latter case possess four reactive positions (enolate oxygen, C-2, C-4, C-6).

The Michael acceptor required for a possible 1,10-addition, 2,4,6-trien-8-ynoate **12**, was obtained from **8b** in 65% yield by the chain extension technique employed earlier, i.e. by reduction, reoxidation, and WHWE olefination. Also this substrate reacts with $Me_2CuLi \cdot LiI$ regioselectively at the triple bond, and protonation with pivalic acid again takes place at C-2 to furnish the 1,10-adduct, 3,5,7,8-tetraenoate **13**, in 68% yield.

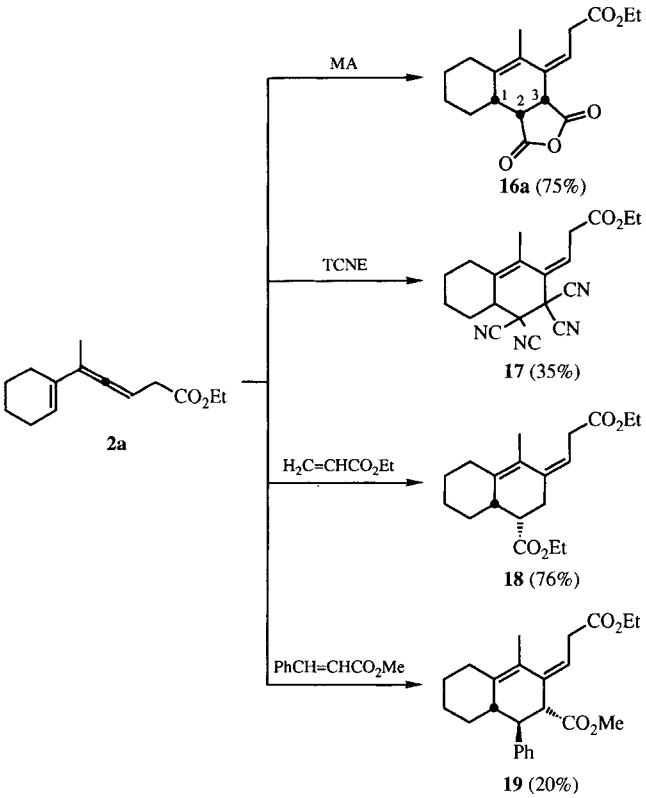


One more step towards a conjugate 1,12-addition turned out to be feasable. Transformation of **12** into the 2,4,6,8-tetraen-10-ynoate **14** with the reliable chain-extension sequence proceeded without difficulty (56% yield), and treatment of this Michael acceptor with lithium dimethylcuprate and pivalic acid provided allene **15**, i.e. the product resulting from regioselective attack of the cuprate at C-11 and of the proton source at C-2. Here, the limits of the 1,*n*-cuprate addition reactions with acetylenic Michael acceptors seem to be reached since the yield of **15** drops to 26%; however, this is probably not due to a loss of regioselectivity (polyene **15** is still the only isolable reaction product) but rather to a decrease of the stabilities of starting material and product with increasing length of the conjugated system.



3. Diels-Alder Reactions

Having several vinylallenes with different steric and electronic properties in hand, we were able to examine their utility as diene components in [4 + 2] cycloadditions in detail. First, we investigated the reactions of vinylallene **2a** with different dienophiles in order to gather basic information on the stereochemical course and the reactivity of these transformations. Thus, treatment of **2a** with maleic anhydride (MA) resulted in a complete consumption of the starting materials within one day at room temperature, and cycloadduct **16a** was obtained in 75% yield as only reaction product.



The assignment of the (*Z*) configuration to the exocyclic double bond and the determination of the relative configuration of the three centers of chirality of **16a** are based on the NMR data and an X-ray structure analysis[11a]. Thus,

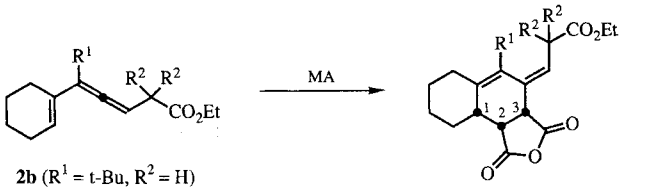
coupling constants $^3J_{1,2}$ = 5.8 Hz and $^3J_{2,3}$ = 9.2 Hz were found which turned out to be typical of *endo* Diels-Alder adducts of this type. Another interesting and frequently observed feature is the existence of diastereotopic hydrogen atoms at the CH_2CO_2Et group. Thus, the cycloaddition takes place with complete *endo* and facial selectivity via a transition state of type **G** with the maximal distance between the CH_2CO_2Et group of the vinylallene and the anhydride part of the dienophile. This facial selectivity was also observed in the [4 + 2] cycloadditions of vinylallene **2a** to other dienophiles, for example with tetracyanoethylene (TCNE) which gave the bicyclic compound **17** (35% yield after 3 d at room temperature).

In the case of unsymmetrical dienophiles, however, the regioselectivity of the cycloaddition has also to be considered besides the *exo-endo* and facial selectivities. The regioselectivity of Diels-Alder reactions of unsymmetrical dienes with dienophiles can often be explained by consideration of the frontier-orbital coefficients of the reactants; usually, the regioisomer originating from large-large and small-small interactions of the frontier orbitals is favored over that with large-small interactions[12]. In the case of vinylallenes, however, the HOMO coefficients at the termini of the diene part are very similar[13]; therefore, the regioselectivity of the reaction with an unsymmetrical dienophile is not determined by electronic but rather by steric interactions which (according to transition state **G**) favor the cycloadduct with the maximal distance between the largest substituents of the reactants.

The reaction of **2a** with the rather unreactive dienophile ethyl acrylate had to be carried out in toluene at reflux temperature for 5 h in order to achieve complete consumption of the vinylallene, and the cycloaddition product was obtained in 76% yield as a 83:17 mixture of isomers. The structure **18** was assigned to the crystalline major isomer by NMR spectroscopy and an X-ray structure analysis[11a]. Thus, as expected from the considerations made above, the *endo* isomer with the largest distance between the groups A = CO_2Et and X = CH_2CO_2Et according to transition state **G** was formed predominantly. The characteristic coupling constants are $^3J_{1,2}$ = 6.4 Hz and $^3J_{2,3}$ = 9.4/3.0 Hz, and NOE effects between 1-H and 2-H, 2-H and 3-H, and 3-H and 1′-H, respectively, prove the regio- and relative stereochemistry of the molecule. The structure of the minor isomer, on the other hand, could not be deduced unambiguously from the spectroscopic data available. However, for two reasons this can be assumed to be the *exo* isomer of **18**: (i) In no other case examined here regioisomers or facial isomers were observed, and (ii) ethyl acrylate possesses only one carbonyl group capable of secondary orbital interactions, so that the *endo*-selectivity should be lower than that of dienophiles with two secondary orbital interactions like maleic anhydride[1,12].

A different behavior was expected and also observed with the dienophile methyl cinnamate. Here, the phenyl group is sterically more demanding than the ester function (A values: Ph: 2.7; CO_2Me: 1.3[14]); thus, if the model **G** were still valid, the phenyl group should adopt the most distant position relative to the CH_2CO_2Et group of the vinylallene. Since methyl cinnamate is even less reactive as dienophile than ethyl acrylate, it took 3 days at reflux temperature in toluene in order to consume the diene completely; from the complex product mixture the major isomer was isolated in 20% yield by column chromatography. Obviously, a considerable amount of the vinylallene is polymerized under the rather harsh reaction conditions, and this undesired pathway is also responsible for the "missing" material in the other Diels-Alder reactions examined here since in all of these transformations the starting vinylallene was consumed completely. The crystalline cycloadduct was characterized by NMR spectroscopy and X-ray structure analysis and turned out to be compound **19**; the coupling constants $^3J_{1,2}$ = 8.5 Hz and $^3J_{2,3}$ = 11.1 Hz are in accordance with the *trans-trans* arrangement of the corresponding hydrogen atom. Thus, the cycloaddition does indeed proceed with the regio- and stereochemical course expected from the model transition state **G**.

In order to examine the influence of the substitution pattern on the stereochemistry and the rate of the cycloaddition, we also treated the vinylallenes **2b**, **4a**, and **4b** with maleic anhydride. In all three cases, the cycloadducts **16b–d** were formed exclusively, demonstrating clearly that the *exo-endo-*, regio-, and facial selectivities are not affected by bulky substituents at C-2 and C-5 of the vinylallene; i.e. transition state **G** is valid. The similarity of the structures is evident from the characteristic coupling constants ($^3J_{1,2}$ = 5.1–6.0 Hz and $^3J_{2,3}$ = 8.9–9.2 Hz) and the corresponding chemical shifts (see Experimental). In terms of the reactivity and chemical yield, however, considerable differences were encountered. Thus, whereas vinylallenes **2a**, **2b**, and **4a** react completely with maleic anhydride within 1–3 days at room temperature, refluxing in toluene for several hours is necessary in order to complete the cycloaddition of the sterically most crowded substrate **4b**. Likewise, moderate chemical yields in the range of 26–33% were observed for cycloadducts **16b–d**, indicating that polymerization is prevailing with decreasing reactivity of the vinylallene as diene.

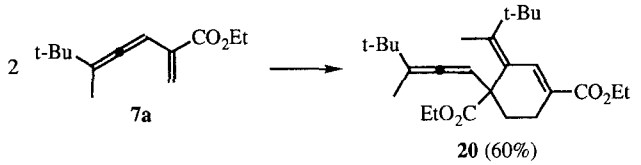


2b (R^1 = t-Bu, R^2 = H)
4a (R^1 = Me, R^2 = Me)
4b (R^1 = t-Bu, R^2 = Me)

16b (R^1 = t-Bu, R^2 = H, 33%)
16c (R^1 = Me, R^2 = Me, 26%)
16d (R^1 = t-Bu, R^2 = Me, 26%)

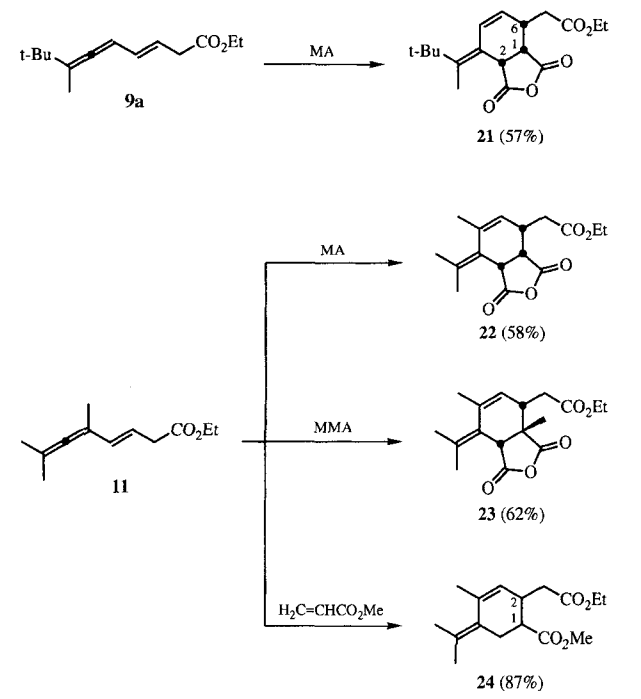
We then turned our attention to Diels-Alder reactions of the structurally different vinylallenes **7**. Also here, dramatic differences in reactivity were found. Thus, attempts to isolate vinylallene **7a** failed because it reacts even at 5°C both as diene and dienophile to give cycloadduct **20** as a 70:30 mixture of two isomers (60% yield). The NMR-spectroscopic data show that both isomers possess the same regiochemistry; thus, they differ in the relative configuration with regard to the center and axis of chirality. Whereas the facial

selectivity is in accordance with transition state **G**, the regioselectivity is contrary to this model. Since the frontier orbital coefficients do not favor one regioisomer over the other (see above), a satisfactory explanation for this behavior cannot be given at present.



Surprisingly, our attempts to react vinylallene **7a** with other dienophiles failed. For example, heating of **7a** with a large excess of maleic anhydride or ethyl acrylate did not yield any mixed cycloaddition products, but only compound **20**. The twofold *tert*-butyl-substituted vinylallene **7b**, on the other hand, is so unreactive that no cycloaddition with itself or with other dienophiles (e.g., maleic anhydride) could be observed. Upon standing in contact with air, however, a rather rapid epoxidation at the vinylic double bond takes place[11b].

The 1,8-addition products **9a** and **11** turned out to be more versatile diene components for Diels-Alder reactions. For example, vinylallene **9a** reacted with maleic anhydride in refluxing toluene within 30 h to provide cycloadduct **21** exclusively (57% yield). As observed in the transformations of vinylallenes **2** and **4**, the reaction proceeds with complete *endo* and facial selectivity on the sterically less crowded diastereotopic side of the vinylallene. The configuration of **21** was proven by an X-ray structure analysis and is in accordance with the coupling constants $^3J_{1,2}$ = 9.2 Hz and $^3J_{1,6}$ = 5.1 Hz.



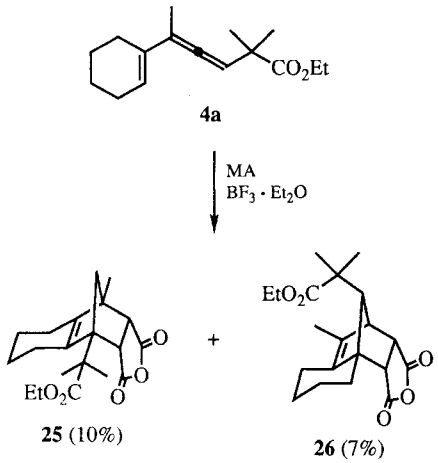
The analogous reaction of vinylallene **11** with maleic anhydride was complete after 19 h at room temperature and furnished the bicyclic product **22** in 58% yield. The *endo* configuration follows from the similarity of the characteristic coupling constants ($^3J_{1,2}$ = 9.2 Hz and $^3J_{1,6}$ = 5.8 Hz) with those of **21**. With the unsymmetrical dienophile methylmaleic anhydride (MMA), the reaction proceeds also regioselectively; the cycloadduct obtained in 62% yield has structure **23**, as indicated by the occurrence of the ^{1}H-NMR resonance of 2-H as a singlet and by NOE effects between the methyl group at C-1 and both 2-H and 6-H. Thus, also these reactions seem to proceed as suggested by transition state **G**.

In these three cases, the cycloadducts **21**–**23** were formed exclusively since no isomers could be detected in the crude product mixtures. The reaction of vinylallene **11** with methyl acrylate, however, provided a 3:1 mixture of two isomeric products in 87% yield. The situation is similar to the formation of cycloadduct **18** since the NMR data indicate the same regiochemistry for both isomers; i.e. the *exo-endo* isomers **24** are formed. The coupling constant $^3J_{1,2}$ = 5.4 Hz observed for the major isomer is in accordance with a *cis* (*endo*) configuration.

The 1,10-addition product **13** is a particularly intriguing diene component for Diels-Alder reactions since the attack of the dienophile could occur at the vinylallene or 1,3-diene part of the molecule to give two different regioisomers. Likewise, three regioisomers could be formed from 1,12-adduct **15**. Although one case of a Diels-Alder reaction of a 1,2,4,6-tetraene (taking place at the vinylallene and not at the 1,3-diene moiety of the molecule) was reported[5d], our attempts to react these substrates with dienophiles failed; prolonged reaction times or elevated temperatures only caused complete polymerization of the allenes.

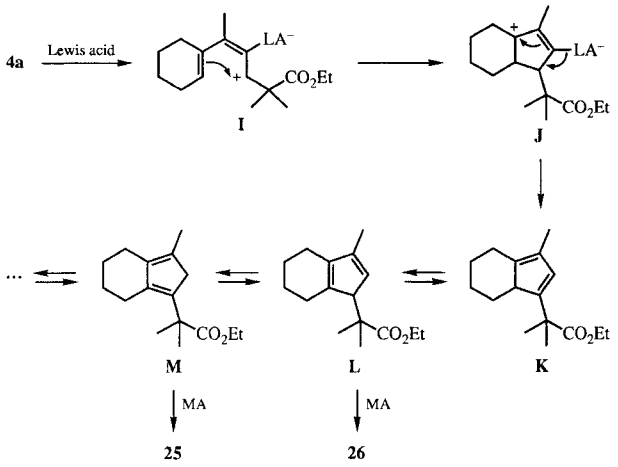
Finally, we also examined the use of Lewis acids as catalyst for Diels-Alder reactions of vinylallenes. The dramatic influence of Lewis acids on the rate and course of cycloadditions of 1,3-dienes to dienophiles is well documented[1,12]; in contrast to this, Lewis-acid catalyzed [4 + 2] cycloadditions of vinylallenes have hardly been examined[6e]. Of the different vinylallenes synthesized in this work, compounds with hydrogen atoms adjacent to the ester group cannot be used for this purpose because β-allenic carbonyl compounds are rapidly isomerized by Lewis acids[10e] (as well as by strong proton acids and bases[10,15]) to the thermodynamically more stable conjugated dienes. Thus, we were restricted to vinylallenes **4** bearing two methyl groups at C-2 and therefore examined the Lewis acid mediated reaction of **4a** with maleic anhydride.

Treatment of these reactants with boron trifluoride etherate for 2 h at room temperature led to a complete consumption of the vinylallene, and after chromatographic purification two cycloaddition products were isolated in 10% and 7% yield. Inspection of the NMR spectra showed immediately that none of them was the expected cycloadduct **16c**; by extensive 1D- and 2D-NMR studies as well as an X-ray structure analysis, the structures **25** and **26** were assigned to the two products (for details see Experimental). Interest-



ingly, a variation of the Lewis acid does not affect the course of the reaction, but only the product yields; for example, with $SbCl_3$ 13% of **25** and 2% of **26** were isolated.

The bicyclic norbornene core of both cycloaddition products makes it tempting to assume a cyclopentadiene derivative as precursor which might have been formed by rearrangement of the vinylallene **4a** in the presence of the Lewis acid. A possible mechanistic scenario starts with an attack of the Lewis acid at the central allenic carbon atom of **4a** to give species **I** which then cyclizes to intermediate **J**. Loss of the Lewis acid and hydrogen transfer lead to cyclopentadiene **K** which should exist in five tautomeric forms; of these, the Diels-Alder reaction of tautomer **L** with maleic anhydride should give cycloadduct **26** whereas **M** should yield **25**. According to this scheme, five tautomeric cyclopentadienes and therefore five isomeric Diels-Alder products are conceivable. The experimental observation of only two cycloadducts might be attributed to a higher stability and/or reactivity of **L** and **M** with respect to the other tautomers.



4. Conclusion

In this work the synthesis of various vinylallenes by conjugate 1,6-, 1,8-, 1,10- and 1,12-cuprate addition reactions with suitable acetylenic Michael acceptors and the regioselective electrophilic capture of the enolates are described. In all cases, the cuprate attacks regioselectively the triple bond of the Michael acceptor, even if this is separated from the acceptor substituent by four double bonds. In the context of our earlier work on transformations of this kind[10], these results can be summarized in the following rule: *A Michael acceptor with any permutation of conjugated double and triple bonds reacts with a cuprate regioselectively at that triple bond that is closest to the acceptor substituent.*

The vinylallenes obtained by 1,6- and 1,8-addition reactions are valuable diene components for Diels-Alder cycloadditions since they react with various dienophiles with complete regio- and facial selectivities and high *endo* selectivity. In most cases only one of up to four possible diastereomers is formed with complete control of the stereochemistry of the exocyclic double bond and the relative configuration of the centers of chirality at the cyclohexene ring. With the exception of cycloadduct **20**, these reactions seem to proceed via a transition state of type **G** which is characterized by minimal steric interactions between the largest substituents of diene and dienophile. Our work demonstrates that this model, which has been proposed by Reich et al.[5f] for [4+2] cycloadditions of simple unfunctionalized vinylallenes, is also valid for most Diels-Alder reactions of elaborated functionalized vinylallenes and can therefore be used for the reliable prediction of the course of these transformations.

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Experimental

General Information: See ref.[10]. The major component of a mixture of isomers is marked with an asterisk (*). – Some vinylallenes are very susceptible to oxidation and/or polymerization; therefore, correct elemental analyses could not be obtained in all cases.

General Procedure for the Preparation of Allenes by Conjugate Cuprate Addition to Acetylenic Michael Acceptors: To a suspension of 1.5–2.0 equiv. of copper(I) iodide or copper(I) cyanide in diethyl ether 3.0–4.0 equiv. of the organolithium compound in diethyl ether (MeLi) or pentane (*t*BuLi) were added dropwise at −20 to −30 °C under argon. After stirring at this temperature for 15 min 1.0 equiv. of the Michael acceptor in diethyl ether was added. If necessary the temperature was then allowed to rise to 0 °C and was kept there until the reaction was complete (monitoring by TLC and GC).

Workup Procedure A: The mixture was cooled to −80 °C and transferred via a teflon tube to a stirred solution of pivalic acid (4.0–5.0 equiv.) in diethyl ether, which was kept at −80 °C. After warming up to room temp. water was added and the mixture was filtered through Celite. The organic layer was washed with a saturated $NaHCO_3$ solution to remove the pivalic acid and dried with $MgSO_4$. After removal of the solvent in vacuo the crude product was purified by kugelrohr distillation or column chromatography.

Workup Procedure B: The mixture was hydrolyzed with a saturated NH_4Cl solution at −20 °C and treated further as described under A.

Workup Procedure C: The mixture was cooled to −100 °C and 5 equiv. of methyl triflate were added slowly. After stirring at this

temperature for 15 min the mixture was warmed up to −20 °C before an excess of saturated $NaHCO_3$ solution was added. It was then warmed to room temp., filtered through Celite (elution with pentane) and treated further as described under A.

Workup Procedure D: An excess of paraformaldehyde was heated in a separate flask to 180 °C, and the formaldehyde produced was transferred via a glass tube to the reaction mixture which was kept at −20 to −30 °C. After 1 h at this temperature a saturated NH_4Cl solution was added and the mixture was treated further as described under A.

Ethyl 5-(1-Cyclohexenyl)-6,6-dimethyl-3,4-heptadienoate (**2b**): Prepared from 1.94 g (10.0 mmol) of **1**[10b] in 75 ml of diethyl ether, 1.34 g (15.0 mmol) of CuCN in 75 ml of diethyl ether, and 18.2 ml (30.0 mmol) of *t*BuLi (1.65 M in pentane); workup procedure B. The crude product was purified by kugelrohr distillation (130 °C/0.03 Torr); yield: 1.80 g (68%) of **2b** as a colorless oil. − IR: $\tilde{\nu}$ = 2960−2910 cm^{-1} (s, CH), 1950 (w, C=C=C), 1730 (s, C=O). − ^1H NMR: δ = 1.02 [s, 9H, $C(CH_3)_3$], 1.19 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 1.50−1.66 (m, 4H, 4′-H, 5′-H), 2.03−2.08 (m, 4-H, 3′-H, 6′-H), 2.98 (d, J = 7.1 Hz, 2H, 2-H), 4.12 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 5.22 (t, J = 7.1 Hz, 1H, 3-H), 5.58−5.60 (m, 1H, 2′-H). − ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 22.4, 23.1 (2−, C-4′, C-5′), 25.6, 30.6 (2−, C-3′, C-6′), 30.2 [+, $C(CH_3)_3$], 34.1 (×, C-6), 35.8 (−, C-2), 60.6 (−, OCH_2CH_3), 84.4 (+, C-3), 118.7 (×, C-5), 125.5 (+, C-2′), 133.5 (×, C-1′), 171.8 (×, C-1), 202.6 (×, C-4). − MS: *m/z* (%) = 262 (40) [M^+], 67 (100). − $C_{17}H_{26}O_2$ (262.4): calcd. C 77.82, H 9.99; found C 77.95, H 10.17.

Ethyl 5-(1-Cyclohexenyl)-2-methyl-2-penten-4-ynoate (**3**): Analogously to the synthesis of **1**[10b], 3-(1-cyclohexenyl)propynal was prepared from 5.30 g (50.0 mmol) of 1-ethynylcyclohexene, 18.8 ml (45.0 mmol) of *n*BuLi (2.4 M in hexane) and 4.8 ml (62.5 mmol) of DMF[16]. The crude aldehyde was then subjected to a WHWE olefination with 11.9 g (50.0 mmol) of ethyl 2-(diethoxyphosphoryl)propionate in 50 ml of THF and 1.50 g (50.0 mmol) of NaH (80% in paraffin oil) in 50 ml of THF. The crude product was purified by column chromatography (diethyl ether/cyclohexane, 1:4) and kugelrohr distillation (125 °C/0.15 Torr) to furnish 8.09 g (74%) of **3** as a colorless liquid. − IR: $\tilde{\nu}$ = 2990−2950 cm^{-1} (s, CH), 2180 (w, C≡C), 1710 (s, C=O). − ^1H NMR: δ = 1.29 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.56−1.68 (m, 4H, 4′-H, 5′-H), 2.04 (s, 3H, 2-CH_3), 2.11−2.19 (m, 4H, 3′-H, 6′-H), 4.20 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 6.21 (m, 1H, 2′-H), 6.74 (s, 1H, 3-H). − ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 15.2 (+, 2-CH_3), 21.4, 22.1 (2−, C-4′, C-5′), 25.9, 29.0 (2−, C-3′, C-6′), 60.8 (−, OCH_2CH_3), 83.8 (×, C-4), 103.8 (×, C-5), 120.0 (+, C-3), 120.8 (×, C-1′), 136.9 (+, C-2′), 137.6 (×, C-2), 167.3 (×, C-1). − MS: *m/z* (%) = 218 (100) [M^+], 189 (56). − $C_{14}H_{18}O_2$ (218.3): calcd. C 77.03, H 8.31; found C 76.95, H 8.25.

Ethyl 5-(1-Cyclohexenyl)-2,2-dimethyl-3,4-hexadienoate (**4a**): From 4.96 g (22.8 mmol) of **3** in 100 ml of diethyl ether, 6.86 g (36.0 mmol) of CuI in 100 ml of diethyl ether, 45.0 ml (72.0 mmol) of MeLi (1.6 M in diethyl ether), and 8.9 ml (80.0 mmol) of methyl triflate; workup procedure C. Chromatography with diethyl ether/cyclohexane (1:3) provided 5.61 g (99%) of **4a** as a colorless liquid. − IR: $\tilde{\nu}$ = 2980−2840 cm^{-1} (s, CH), 1940 (w, C=C=C), 1730 (s, C=O). − ^1H NMR: δ = 1.22 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.25 (s, 6H, 2-CH_3), 1.50−1.67 (m, 4H, 4′-H, 5′-H), 1.81 (d, J = 2.6 Hz, 3H, 6-H), 2.01−2.12 (m, 4H, 3′-H, 6′-H), 4.10 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.42 (m, 1H, 3-H), 5.65−5.68 (m, 1H, 2′-H). − ^{13}C NMR: δ = 14.0 (+, OCH_2CH_3), 16.2 (+, 2-CH_3), 22.3, 22.8 (2−, C-4′, C-5′), 25.1 (+, C-6), 25.9, 26.8 (2−, C-3′, C-6′), 43.0 (×, C-2), 60.5 (−, OCH_2CH_3), 98.4 (+, C-3), 105.7 (×, C-5), 122.7 (+, C-2′), 133.3 (×, C-1′), 176.4 (×, C-1), 202.5 (×, C-4). − MS: *m/z* (%) = 248 (69) [M^+], 48 (100). − $C_{16}H_{24}O_2$ (248.4): calcd. C 77.38, H 9.74; found C 77.68, H 10.09.

Ethyl 5-(1-Cyclohexenyl)-2,2,6,6-tetramethyl-3,4-heptadienoate (**4b**): Prepared from 2.18 g (10.0 mmol) of **3** in 50 ml of diethyl ether, 1.34 g (15.0 mmol) of CuCN in 50 ml of diethyl ether, 18.2 ml (30.0 mmol) of *t*BuLi (1.65 M in pentane), and 8.20 g (50.0 mmol) of methyl triflate. The crude product was purified by column chromatography (diethyl ether/cyclohexane, 1:3) to give 1.68 g (58%) of **4b** as a slightly yellow oil. − IR: $\tilde{\nu}$ = 2980−2860 cm^{-1} (s, CH), 1950 (w, C=C=C), 1730 (s, C=O). − ^1H NMR: δ = 1.10 [s, 9H, $C(CH_3)_3$], 1.24 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.28 (s, 6H, 2-CH_3), 1.54−1.79 (m, 4H, 4′-H, 5-H′), 2.06−2.10 (m, 4H, 3′-H, 6′-H), 4.11 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.32 (s, 1H, 3-H), 5.60−5.63 (m, 1H, 2′-H). − ^{13}C NMR: δ = 14.1 (+, OCH_2CH_3), 22.0, 23.2 (2−, C-4′, C-5′), 25.3, 25.4 (2+, 2-CH_3), 25.6, 30.7 (2−, C-3′, C-6′), 30.2 [+, $C(CH_3)_3$], 34.1 (×, C-6), 42.7 (×, C-2), 60.5 (−, OCH_2CH_3), 97.7 (+, C-3), 120.3 (×, C-5), 125.1 (+, C-2′), 133.5 (×, C-1′), 176.6 (×, C-1), 199.7 (×, C-4). − MS: *m/z* (%) = 290 (35) [M^+], 57 (100). − $C_{19}H_{30}O_2$ (290.4): HRMS: calcd. 290.2246, found 290.2253.

Ethyl 2-Hexen-4-ynoate (**5b**)[17]: To a solution of 2.94 g (30.0 mmol) of methyl 2-butynoate[18] in 150 ml of diethyl ether 33 ml (33.0 mmol) of DIBAH (1.0 M in hexane) was added slowly at −100 °C. In a second flask 7.84 g (35.0 mmol) of ethyl (diethoxyphosphoryl)acetate in 50 ml of THF was added dropwise to a suspension of 1.40 g (35.0 mmol) of NaH (60% in paraffin oil) in 50 ml of THF. After 10 min the solution of the WHWE reagent was cooled to −80 °C and transferred via a teflon tube to the other flask. The mixture was warmed to room temp. and stirred for 90 min. After acidification with 2 N HCl the layers were separated; the aqueous layer was extracted several times with diethyl ether and the combined organic layers were dried with $MgSO_4$. The solvent was removed in vacuo, the crude product was filtered through silica gel (diethyl ether/cyclohexane, 1:3) and purified by kugelrohr distillation (40−50 °C/0.1 Torr), furnishing 4.02 g (97%) of **5b** as a colorless liquid.

Ethyl 5,6,6-Trimethyl-2-methylene-3,4-heptadienoate (**7a**): Prepared from 2.70 g (15.0 mmol) of **5a**[19] in 75 ml of diethyl ether, 4.28 g (22.5 mmol) of CuI in 75 ml of diethyl ether, 24.3 ml (45.0 mmol) of MeLi (1.85 M in diethyl ether), and 8.00 g (0.27 mol) of paraformaldehyde; workup procedure D. Purification of the crude product by column chromatography (diethyl ether/cyclohexane, 1:1) gave 2.62 g (77%) of **6a** (colorless solid, 1:1 mixture of diastereomers). A solution of 1.36 g (6.0 mmol) of **6a** and 1.12 g (11.1 mmol) of triethylamine in 30 ml of dichloromethane was treated at −50 °C with 0.86 g (7.5 mmol) of methanesulfonylchloride and stirred for 30 min at room temp. Then 3.67 g (24.1 mmol) of DBU was added. After stirring at room temp. for 30 min 30 ml diethyl ether was added and the mixture was washed with 1 N HCl and water and dried with $MgSO_4$. Attempts to isolate allene **7a** resulted in the formation of the cycloaddition product **20**.

Ethyl 6,6-Dimethyl-2-methylene-5-(1,1-dimethylethyl)-3,4-heptadienoate (**7b**): Crude hydroxy ester **6b** was obtained from 1.80 g (10.0 mmol) of **5a**[19] in 50 ml of diethyl ether, 1.34 g (15.0 mmol) of CuCN in 50 ml of diethyl ether, 18.0 ml (30.0 mmol) of *t*BuLi (1.67 M in pentane), and 8.00 g (0.27 mol) of paraformaldehyde according to workup procedure D. In analogy to the preparation of **7a**, it was dissolved in 45 ml of dichloromethane and the solution was treated with 1.69 g (16.7 mmol) of triethylamine, 1.29 g (11.3 mmol) of methanesulfonylchloride and 5.47 g (36.0 mmol) of DBU. After column chromatography with diethyl ether/cyclohexane (1:5),

1.93 g (77%) of **7b** was isolated as a colorless liquid. – IR: $\tilde{\nu}$ = 3020–2860 cm^{-1} (s, CH), 1930 (w, C=C=C), 1720 (s, C=O). – ^1H NMR: δ = 1.13 [s, 18H, $C(CH_3)_3$], 1.24 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 4.15 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.63 (d, *J* = 1.4 Hz, 1H, 3-H), 5.93 (s, 1H, 1'-H), 5.95 (d, *J* = 1.4 Hz, 1H, 1'-H). – ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 32.0 [+, $C(CH_3)_3$], 35.6 [×, $C(CH_3)_3$], 60.7 (–, OCH_2CH_3), 90.1 (+, C-3), 120.8 (–, C-1'), 124.7 (×, C-5), 135.7 (×, C-2), 166.3 (×, C-1), 204.4 (×, C-4). – MS: *m/z* (%) = 250 (10) [M^+], 57 (100). – A correct elemental analysis could not be obtained because **7b** is readily oxidized by air at the terminal double bond to give the corresponding oxirane.

Ethyl 8,8-Dimethyl-2,4-nonadien-6-ynoate (**8a**): A suspension of 0.38 g (10.0 mmol) of $LiAlH_4$ in 20 ml of diethyl ether was cooled to –60°C, and 1.80 g (10.0 mmol) of **5a**[19] in 20 ml of diethyl ether was added dropwise. After stirring for 1 h at –60°C, 2 ml of a saturated NH_4Cl solution was added and the mixture was warmed up to room temp. and filtered through Celite; the residue was washed with diethyl ether, the combined filtrates were dried with $MgSO_4$, and the solvent was removed in vacuo. A solution of the crude alcohol thus obtained in 10 ml of diethyl ether was added to a thoroughly stirred suspension of 17.4 g (0.20 mol) of activated MnO_2 (Merck), and the mixture was stirred for 16 h at room temp. The mixture was then filtered through Celite and the solvent was removed in vacuo. The following WHWE olefination was carried out as in the preparation of **5b** with 2.24 g (10.0 mmol) of ethyl (diethoxyphosphoryl)acetate in 10 ml of THF, 0.30 g (10.0 mmol) of NaH (80% in paraffin oil) in 10 ml of THF and the crude aldehyde in 10 ml of THF. Purification of the crude product by column chromatography (diethyl ether/hexane, 1:20) furnished 1.77 g (86%) of **8a** as a colorless oil. – IR: $\tilde{\nu}$ = 3020–2860 cm^{-1} (s, CH), 2200 (s, C≡C), 1710 (s, C=O). – ^1H NMR: δ = 1.25 [s, 9H, $C(CH_3)_3$], 1.29 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 4.19 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.88 (d, *J* = 15.3 Hz, 1H, 2-H), 5.95 (d, *J* = 15.4 Hz, 1H, 5-H), 6.56 (ddd, *J* = 15.4/11.3/0.5 Hz, 1H, 4-H), 7.24 (ddd, *J* = 15.3/11.3/0.5 Hz, 1H, 3-H). – ^{13}C NMR: δ = 14.3 (+, OCH_2CH_3), 28.3 (×, C-8), 30.8 [+, $C(CH_3)_3$], 60.4 (–, OCH_2CH_3), 78.0 (×, C-6), 105.9 (×, C-7), 120.4 (+, C-5), 122.0 (+, C-2), 137.4 (+, C-4), 143.4 (+, C-3), 166.7 (×, C-1). – MS: *m/z* (%) = 206 (81) [M^+], 91 (100). – $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.80; found C 75.35, H 8.68.

Ethyl 2,4-Octadien-6-ynoate (**8b**): The preparation was carried out as for **8a**, using 15.5 g (0.11 mol) of **5b** in 200 ml of diethyl ether, 4.16 g (0.11 mol) of $LiAlH_4$ in 100 ml of diethyl ether, 191 g (2.2 mol) of activated MnO_2 in 500 ml of diethyl ether, 24.6 g (0.11 mol) of ethyl (diethoxyphosphoryl)acetate in 100 ml of THF, and 4.40 g (0.11 mol) of NaH (60% in paraffin oil) in 100 ml of THF. The crude product was filtered through silica gel (diethyl ether/cyclohexane, 1:5) and purified further by kugelrohr distillation (70°C/0.3 mbar); yield 9.10 g (56%) of **8b** as a colorless liquid. – IR: $\tilde{\nu}$ = 3020–2860 cm^{-1} (s, CH), 2220 (s, C≡C), 1710 (s, C=O). – ^1H NMR: δ = 1.23 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.95 (d, *J* = 2.5 Hz, 3H, 8-H), 4.14 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.84 (d, *J* = 15.5 Hz, 1H, 2-H), 5.88 (dq, *J* = 14.8/2.5 Hz, 1H, 5-H), 6.51 (dd, *J* = 15.5/11.3 Hz, 1H, 3-H), 7.19 (dd, *J* = 14.8/11.3 Hz, 1H, 4-H). – ^{13}C NMR: δ = 4.5 (+, C-8), 14.1 (+, OCH_2CH_3), 60.2 (–, OCH_2CH_3), 78.6 (×, C-6), 93.2 (×, C-7), 120.2, 122.1 (2+, C-2, C-5), 137.5 (+, C-4), 143.2 (+, C-3), 166.5 (×, C-1). – MS: *m/z* (%) = 164 (70) [M^+], 135 (100). – $C_{10}H_{12}O_2$ (164.2): calcd. C 73.15, H 7.37; found C 73.27, H 7.51.

Ethyl 7,8,8-Trimethyl-3,5,6-nonatrienoate (**9a**): From 0.41 g (2.0 mmol) of **8a** in 10 ml of diethyl ether, 0.48 g (2.5 mmol) of CuI in 10 ml of diethyl ether, 3.3 ml (5.0 mmol) of MeLi (1.5 M in diethyl ether), and 1.02 g (10.0 mmol) of pivalic acid in 10 ml of diethyl ether; workup procedure A. The crude product was purified by kugelrohr distillation (70–80°C/0.05 Torr); yield 0.40 g (90%) of **9a** as a colorless liquid. – IR: $\tilde{\nu}$ = 2960–2860 cm^{-1} (s, CH), 1940 (w, C=C=C), 1735 (s, C=O). – ^1H NMR: δ = 1.04 [s, 9H, $C(CH_3)_3$], 1.26 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.69 (d, *J* = 2.7 Hz, 3H, 7-CH_3), 3.08 (d, *J* = 7.1 Hz, 2H, 2-H), 4.14 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.64 (dt, *J* = 15.2/7.1 Hz, 1H, 3-H), 5.72 (dq, *J* = 10.2/2.7 Hz, 1H, 5-H), 5.93 (dd, *J* = 15.2/10.2 Hz, 1H, 4-H). – ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 14.8 (+, 7-CH_3), 29.0 [+, $C(CH_3)_3$], 33.7 (×, C-8), 38.1 (–, C-2), 60.6 (–, OCH_2CH_3), 93.2 (+, C-5), 109.8 (×, C-7), 121.4 (+, C-4), 131.0 (+, C-3), 171.7 (×, C-1), 203.8 (×, C-6). – MS: *m/z* (%) = 222 (10) [M^+], 57 (100). – $C_{14}H_{22}O_2$ (222.3): calcd. C 75.63, H 9.97; found C 75.43, H 10.12.

Ethyl 8,8-Dimethyl-7-(1,1-dimethylethyl)-3,5,6-nonatrienoate (**9b**): Prepared from 1.03 g (5.0 mmol) of **8a** in 25 ml of diethyl ether, 0.90 g (10.0 mmol) of CuCN in 25 ml of diethyl ether, 11.6 ml (20.0 mmol) of *t*BuLi (1.7 M in pentane), and 2.55 g (25.0 mmol) of pivalic acid in 20 ml of diethyl ether; workup procedure A. Purification by kugelrohr distillation (110°C/0.03 mbar) gave 0.95 g (72%) of **9b** as a colorless liquid (70:30 mixture of *E*/*Z* isomers). – IR: $\tilde{\nu}$ = 2960–2860 cm^{-1} (s, CH), 1920 (w, C=C=C), 1740 (s, C=O). – ^1H NMR: δ = 1.14*/1.15 [2s, 18H, $C(CH_3)_3$], 1.18/1.22* (2 t, 2 × *J* = 7.2 Hz, 3H, OCH_2CH_3), 3.05*/3.15 (2 d, 2 × *J* = 7.3 Hz, 2H, 2-H), 4.10*/4.11 (2 q, 2 × *J* = 7.2 Hz, 2H, OCH_2CH_3), 5.25–5.92 (m, 3H, 3-H, 4-H, 5-H). – ^{13}C NMR: δ = 14.2*/14.3 (2+, OCH_2CH_3), 32.2 [+, $C(CH_3)_3$], 33.3/38.2* (2–, C-2), 35.1/35.2* [2 ×, $C(CH_3)_3$], 60.6 (–, OCH_2CH_3), 90.6/94.7* (2+, C-5), 119.3/120.9* (2+, C-4), 122.6/122.8* (2 ×, C-7), 128.8/131.1 (2+, C-3), 171.7/171.9* (2×, C-1), 205.8*/207.2 (2×, C-6). – MS: *m/z* (%) = 264 (9) [M^+], 57 (100). – $C_{17}H_{28}O_2$ (264.4): calcd. 264.2089, found 264.2089.

Ethyl 5-Methyl-2,4-octadien-6-ynoate (**10**): Analogously to the preparation of **8a**, 3.30 g (30.0 mmol) of (*Z*)-3-methyl-2-hexen-4-yn-1-ol[20] was oxidized to the corresponding aldehyde with 41.4 g (0.60 mol) of activated MnO_2 in 200 ml of diethyl ether, and the WHWE olefination was carried out with 6.72 g (30.0 mmol) of ethyl (diethoxyphosphoryl)acetate in 30 ml of THF and 1.20 g (30.0 mmol) of NaH (60% in paraffin oil) in 30 ml of THF. The crude product was filtered through silica gel (diethyl ether/cyclohexane, 1:2) and purified further by kugelrohr distillation (90°C/0.04 Torr) to provide 4.83 g (91%) of **10** as a colorless oil. – IR: $\tilde{\nu}$ = 3020–2860 cm^{-1} (s, CH), 2240 (s, C≡C), 1710 (s, C=O). – ^1H NMR: δ = 1.23 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.90, 1.99 (2 s, 6H, 5-CH_3, 8-H), 4.14 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.78 (d, *J* = 15.5 Hz, 1H, 2-H), 6.20 (d, *J* = 11.4 Hz, 1H, 4-H), 7.64 (dd, *J* = 15.5/11.4 Hz, 1H, 3-H). – ^{13}C NMR: δ = 4.6 (+, C-8), 14.2 (+, OCH_2CH_3), 15.2 (+, 5-CH_3), 60.1 (–, OCH_2CH_3), 78.3 (×, C-6), 95.3 (×, C-7), 120.4 (+, C-2), 129.5 (×, C-5), 132.0 (+, C-4), 142.1 (+, C-3), 167.2 (×, C-1). – MS: *m/z* (%) = 178 (68) [M^+], 149 (100). – $C_{11}H_{14}O_2$ (178.2): calcd. C 74.13, H 7.92; found C 74.24, H 8.01.

Ethyl 5,7-Dimethyl-3,5,6-octatrienoate (**11**): From 0.89 g (5.0 mmol) of **10** in 25 ml of diethyl ether, 1.90 g (10.0 mmol) in CuI in 25 ml of diethyl ether, 13.8 ml (20.0 mmol) of MeLi (1.45 M in diethyl ether), and 2.55 g (25.0 mmol) of pivalic acid in 20 ml of diethyl ether; workup procedure A. Purification by kugelrohr distillation (140°C/0.15 Torr); yield 0.65 g (67%) of **11** as a colorless liquid. – IR: $\tilde{\nu}$ = 2980–2850 cm^{-1} (s, CH), 1950 (w, C=C=C), 1730 (s, C=O). – ^1H NMR: δ = 1.18 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 1.60 (s, 6H, 7-CH_3), 1.68 (s, 3H, 5-CH_3), 3.03 (dd, *J* = 7.1/1.4 Hz, 2H, 2-H), 4.06 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3),

5.46 (dt, J = 15.7/7.1 Hz, 1H, 3-H), 5.99 (dt, J = 15.7/1.4 Hz, 1H, 4-H). – ^{13}C NMR: δ = 14.1 (+, OCH_2CH_3), 20.4 (+, 7-CH_3), 26.9 (+, 5-CH_3), 38.2 (–, C-2), 60.5 (–, OCH_2CH_3), 94.1, 97.3 (2×, C-5, C-7), 118.6 (+, C-3), 133.6 (+, C-4), 171.9 (×, C-1), 204.5 (×, C-6). – MS: *m/z* (%) = 194 (51) [M^+], 121 (100). – $C_{12}H_{18}O_2$ (194.3): calcd. C 74.19, H 9.34; found C 74.41, H 9.58.

Ethyl 2,4,6-Decatrien-8-ynoate (**12**): As in the preparation of **8a**, 9.10 g (55.5 mmol) of **8b** in 100 ml of diethyl ether was treated with 2.09 g (55.0 mmol) of $LiAlH_4$ in 100 ml of diethyl ether, 96.7 g (1.1 mol) of activated MnO_2 in 400 ml of diethyl ether, 14.5 g (65.0 mmol) of ethyl (diethoxyphosphoryl)acetate in 50 ml of THF, and 2.60 g (65.0 mmol) of NaH (60% in paraffin oil) in 50 ml of THF. The crude product was purified by column chromatography (diethyl ether/cyclohexane, 1:20); yield 6.74 g (65%) of **12** as orange crystals (m.p. 47–48 °C). – IR: $\tilde{\nu}$ = 3020–2860 cm^{-1} (s, CH), 2210 (s, C≡C), 1700 (s, C=O). – ^{1}H NMR: δ = 1.22 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.93 (d, J = 2.5 Hz, 3H, 10-H), 4.13 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.64–5.72 (m, 1H, 7-H), 5.83 (d, J = 15.2 Hz, 1H, 2-H), 6.21–6.35, 6.44–6.52 (2 m, 3H, 4-H, 6-H), 7.21 (dd, J = 15.2/11.1 Hz, 1H, 3-H). – ^{13}C NMR: δ = 4.7 (+, C-10), 14.3 (+, OCH_2CH_3), 60.3 (–, OCH_2CH_3), 79.1 (×, C-9), 92.1 (×, C-8), 122.1 (+, C-7), 131.0 (+, C-2), 137.5, 139.4, 139.5, 143.8 (4+, C-3, C-4, C-5, C-6), 166.9 (×, C-1). – MS: *m/z* (%) = 190 (46) [M^+], 115 (100). – $C_{12}H_{14}O_2$ (190.2): calcd. C 75.89, H 8.79; found C 76.22, H 8.89.

Ethyl 9-Methyl-3,5,7,8-decatetraenoate (**13**): Prepared from 0.95 g (5.0 mmol) of **12** in 25 ml of diethyl ether, 1.90 g (10.0 mmol) of CuI in 25 ml of diethyl ether, 12.5 ml (20.0 mmol) of MeLi (1.6 M in diethyl ether), and 2.55 g (25.0 mmol) of pivalic acid in 20 ml of diethyl ether; workup procedure A. Purification by column chromatography (diethyl ether/cyclohexane, 1:5) gave 0.70 g (68%) of **13** as a yellow oil. – IR: $\tilde{\nu}$ = 2980–2860 cm^{-1} (s, CH), 1950 (w, C=C=C), 1740 (s, C=O). – ^{1}H NMR: δ = 1.18 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.64 (d, J = 2.7 Hz, 6H, 9-CH_3), 3.03 (d, J = 6.7 Hz, 2H, 2-H), 4.06 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.58–5.67 (m, 2H, 3-H, 7-H), 5.85–5.94, 6.02–6.10 (2 m, 3H, 4-H, 5-H, 6-H). – ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 20.3 (+, 9-CH_3), 38.1 (–, C-2), 60.6 (–, OCH_2CH_3), 92.4 (+, C-7), 96.5 (×, C-9), 123.9, 129.3, 129.6, 133.6 (4+, C-3, C-4, C-5, C-6), 171.5 (×, C-1), 205.9 (×, C-8). – MS: *m/z* (%) = 206 (92) [M^+], 91 (100). – $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.79; found C 75.22, H 8.89.

Ethyl 2,4,6,8-Dodecatetraen-10-ynoate (**14**): The preparation was carried out as for **8a**, using 2.85 g (15.0 mmol) of **12** in 10 ml of diethyl ether, 0.57 g (15.0 mmol) of $LiAlH_4$ in 30 ml of diethyl ether, 26.1 g (0.30 mol) of activated MnO_2 in 200 ml of diethyl ether, 3.36 g (15.0 mmol) of ethyl (diethoxyphosphoryl)acetate in 15 ml of THF, and 0.60 g (15.0 mmol) of NaH (60% in paraffin oil) in 20 ml of THF. Chromatographic purification (diethyl ether/cyclohexane, 1:20) gave 1.80 g (56%) of **14** as orange crystals (m.p. 104–106 °C). – IR: $\tilde{\nu}$ = 3020–2860 cm^{-1} (s, CH), 2210 (s, C≡C), 1700 (s, C=O). – ^{1}H NMR: δ = 1.22 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.93 (d, J = 2.5 Hz, 3H, 12-H), 4.13 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.60 (dq, J = 15.3/2.5 Hz, 1H, 9-H), 5.81 (d, J = 15.3 Hz, 1H, 2-H), 6.21–6.36 (m, 3H), 6.47 (dd, J = 15.3/10.6 Hz, 1H), 6.49 (dd, J = 14.8/10.6 Hz, 1H), 7.22 (dd, J = 15.0/11.2 Hz, 1H, 3-H). – ^{13}C NMR: δ = 4.7 (+, C-12), 14.3 (+, OCH_2CH_3), 60.3 (–, OCH_2CH_3), 79.4 (×, C-10), 91.4 (×, C-11), 114.4 (+, C-9), 121.2 (+, C-2), 131.1, 132.9, 136.0, 139.9, 140.0 (5+, C-4, C-5, C-6, C-7, C-8), 144.0 (+, C-3), 167.0 (×, C-1). – MS: *m/z* (%) = 216 (65) [M^+], 128 (100). – $C_{14}H_{16}O_2$ (216.3): calcd. C 77.75, H 7.46; found C 77.82, H 7.72.

Ethyl 11-Methyl-3,5,7,9,10-dodecapentaenoate (**15**): From 648 mg (3.0 mmol) of **14** in 10 ml of diethyl ether, 1.14 g (6.0 mmol) of CuI in 15 ml of diethyl ether, 8.0 ml (12.0 mmol) of MeLi (1.6 M in diethyl ether), and 1.53 g (15.0 mmol) of pivalic acid in 10 ml of diethyl ether; workup procedure A. Purification by column chromatography (diethyl ether/cyclohexane, 1:10); yield 182 mg (26%) of **15** as a yellow solid (m.p. 60–63 °C). – IR: $\tilde{\nu}$ = 2980–2860 cm^{-1} (s, CH), 1940 (w, C=C=C), 1740 (s, C=O). – ^{1}H NMR: δ = 1.25 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.70 (d, J = 2.7 Hz, 6H, 11-CH_3), 3.13 (d, J = 6.6 Hz, 2H, 2-H), 4.13 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.68–5.76 (m, 2H, 3-H, 9-H), 5.98–6.18 (m, 5H, 4-H, 5-H, 6-H, 7-H, 8-H). – ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 20.5 (+, 11-CH_3), 38.3 (–, C-2), 60.7 (–, OCH_2CH_3), 92.9 (+, C-9), 96.6 (×, C-11), 124.8, 130.0, 130.4, 131.0, 132.6, 134.0 (6+, C-3, C-4, C-5, C-6, C-7, C-8), 171.6 (×, C-1), 206.2 (×, C-10). – MS: *m/z* (%) = 232 (100) [M^+]. – $C_{15}H_{20}O_2$ (232.4): HRMS: calcd. 232.1468; found 232.1466.

4-(2-Ethoxycarbonylethylidene)-5-methylbicyclo[4.4.0]dec-5-ene-2,3-dicarboxylic Anhydride (**16a**): A mixture of 661 mg (3.0 mmol) of **2a** and 294 mg (3.0 mmol) of maleic anhydride in 30 ml toluene was stirred for 24 h at room temp. The solvent was removed in vacuo and the crude product was crystallized from ethanol; yield 720 mg (75%) of **16a** as colorless needles (m.p. 103–104 °C). – IR: $\tilde{\nu}$ = 2920–2850 cm^{-1} (s, CH), 1835, 1760, 1705 (s, C=O). – ^{1}H NMR: δ = 1.25 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.25–1.40, 1.50–1.68, 1.71–1.82, 2.20–2.35 (4 m, 8H, 7-H, 8-H, 9-H, 10-H), 1.81 (s, 3H, 5-CH_3), 2.02–2.20 (m, 1H, 1-H), 3.09 (dd, J = 18.0/8.6 Hz, 1H, 2′-H), 3.23 (dd, J = 18.0/5.5 Hz, 1H, 2′-H), 3.31 (dd, J = 9.2/5.8 Hz, 1H, 2-H), 3.84 (d, J = 9.2 Hz, 1H, 3-H), 4.14 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.66 (dd, J = 8.6/5.5 Hz, 1H, 1′-H). – ^{13}C NMR: δ = 14.1 (+, OCH_2CH_3), 17.4 (+, 5-CH_3), 21.2, 21.6, 24.3, 25.0 (4–, C-7, C-8, C-9, C-10), 34.8 (–, C-2′), 36.4 (+, C-1), 45.2 (+, C-2), 51.5 (+, C-3), 60.9 (–, OCH_2CH_3), 122.5 (+, C-1′), 126.5, 133.7, 139.3 (3×, C-4, C-5, C-6), 171.1, 171.7, 171.8 (3×, C=O, C-3′). – The NMR resonances were assigned by means of ^{1}H,^{1}H and ^{1}H,^{13}C COSY spectra. – MS: *m/z* (%) = 318 (24) [M^+], 272 (100). – $C_{18}H_{22}O_5$ (318.4): calcd. C 67.91, H 6.97; found C 67.80, H 6.98. – The relative configuration was confirmed by an X-ray structure analysis[11a].

4-(2-Ethoxycarbonylethylidene)-5-(1,1-dimethylethyl)-bicyclo[4.4.0]dec-5-ene-2,3-dicarboxylic Anhydride (**16b**): A solution of 786 mg (3.0 mmol) of **2b** and 392 mg (4.0 mmol) of maleic anhydride in 20 ml of benzene was stirred for 3 d at room temp. After removal of the solvent in vacuo, the crude product was purified by crystallization from ethanol; yield 258 mg (33%) of **16b** as colorless needles (m.p. 108–109 °C). – IR: $\tilde{\nu}$ = 3020–2880 cm^{-1} (s, CH), 1860, 1780, 1730 (s, C=O). – ^{1}H NMR: δ = 1.22 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.30–1.49, 1.63–1.71, 1.81–2.24 (3 m, 8H, 7-H, 8-H, 9-H, 10-H), 2.71–2.78 (m, 1H, 1-H), 3.04 (dd, J = 16.8/8.2 Hz, 1H, 2′-H), 3.13 (dd, J = 16.8/6.4 Hz, 1H, 2′-H), 3.52 (dd, J = 8.9/5.1 Hz, 1H, 2-H), 4.11, 4.12 (2 q, 2 × J = 7.1 Hz, 2H, OCH_2CH_3), 4.13 (d, J = 8.9 Hz, 1H, 3-H), 5.66 (dd, J = 8.2/6.4 Hz, 1H, 1′-H). – ^{13}C NMR: δ = 14.7 (+, OCH_2CH_3), 20.7, 23.0, 26.0 (3–, C-7, C-8, C-9, C-10), 31.2 [+, $C(CH_3)_3$], 34.2 [×, $C(CH_3)_3$], 37.2 (–, C-2′), 41.1 (+, C-1), 46.4 (+, C-2), 54.4 (+, C-3), 61.1 (–, OCH_2CH_3), 123.6 (+, C-1′), 136.5, 140.1, 141.9 (3×, C-4, C-5, C-6), 171.2, 173.1, 173.5 (3×, C=O, C-3′). – MS: *m/z* (%) = 360 (<1) [M^+], 66 (100). – $C_{21}H_{28}O_5$ (360.5): calcd. C 69.98, H 7.83; found C 69.69, H 7.76.

4-(2-Ethoxyarbonyl-2,2-dimethylethylidene)-5-methylbicyclo-[4.4.0]dec-5-ene-2,3-dicarboxylic Anhydride (**16c**): A solution of 155 mg (0.6 mmol) of **4a** and 69 mg (0.7 mmol) of maleic anhydride in 5 ml of benzene was stirred for 24 h at room temp. After removal of the solvent in vacuo, the crude product was purified by column

chromatography (diethyl ether/cyclohexane, 1:2) furnishing 56 mg (26%) of **16c** as a yellow oil. Crystallization of a sample from ethanol gave colorless crystals (m.p. 97–98°C). – IR: $\tilde{\nu}$ = 3020–2880 cm^{-1} (s, CH), 1850, 1770, 1730 (s, C=O). – ^1H NMR: δ = 1.19 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.30, 1.39 (2 s, 6H, 2′-CH_3), 1.42–1.88, 2.04–2.32 (2 m, 9H, 1-H, 7-H, 8-H, 9-H, 10-H), 1.69–1.70 (m, 3H, 5-CH_3), 3.29 (dd, *J* = 9.1/6.0 Hz, 1H, 2-H), 3.73 (d, *J* = 9.1 Hz, 1H, 3-H), 3.90, 4.16 (2 dq, 2 × *J* = 10.8/7.1 Hz, 2H, OCH_2CH_3), 5.43 (s, 1H, 1′-H). – ^{13}C NMR: δ = 14.1 (+, OCH_2CH_3), 17.9 (+, 5-CH_3), 21.1, 21.5, 23.9, 24.5 (4–, C-7, C-8, C-9, C-10), 27.1, 27.4 (2+, 2′-CH_3), 37.2 (+, C-1), 43.4 (×, C-2′), 45.6 (+, C-2), 53.6 (+, C-3), 60.7 (–, OCH_2CH_3), 128.1, 131.9, 137.5 (3×, C-4, C-5, C-6), 136.0 (+, C-1′), 171.7, 172.0 (2×, C=O), 179.2 (×, C-3′). – MS: *m/z* (%) = 346 (2) [M^+], 159 (100). – $C_{20}H_{26}O_5$ (346.4): calcd. C 69.34, H 7.59; found C 69.21, H 7.53.

4-(2-Ethoxycarbonyl-2,2-dimethylethylidene)-5-(1,1-dimethylethyl)bicyclo[4.4.0]dec-5-ene-2,3-dicarboxylic Anhydride (**16d**): A solution of 870 mg (3.0 mmol) of **4b** and 392 mg (4.0 mmol) of maleic anhydride in toluene was heated at 110°C for 5 h. After removal of the solvent in vacuo, the crude product was purified by column chromatography (diethyl ether/cyclohexane, 1:3) furnishing 308 mg (26%) of **16d**. Crystallization of a sample from ethanol gave colorless needles (m.p. 117–118°C). – IR: $\tilde{\nu}$ = 3020–2880 cm^{-1} (s, CH), 1850, 1770, 1720 (s, C=O). – ^1H NMR: δ = 1.13 [s, 9H, $C(CH_3)_3$], 1.25 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.30, 1.38 (2 s, 6H, 2′-CH_3), 1.39–2.28 (m, 8H, 7-H, 8-H, 9-H, 10-H), 2.70–2.78 (m, 1H, 1-H), 3.26 (dd, *J* = 9.0/5.4 Hz, 1H, 2-H), 3.82 (d, *J* = 9.0 Hz, 1H, 3-H), 4.05–4.19 (m, 2H, OCH_2CH_3), 5.48 (s, 1H, 1′-H). – ^{13}C NMR: δ = 14.0 (+, OCH_2CH_3), 19.5, 20.0, 22.0, 25.0 (4–, C-7, C-8, C-9, C-10), 23.1, 29.2 (2+, 2′-CH_3), 31.0 [+, $C(CH_3)_3$], 33.7 [×, $C(CH_3)_3$], 40.8 (+, C-1), 44.1 (×, C-2′), 44.8 (+, C-2), 55.8 (+, C-3), 60.7 (–, OCH_2CH_3), 131.3, 139.3, 140.4 (3×, C-4, C-5, C-6), 135.3 (+, C-1′), 171.6, 171.8, 175.7 (3×, C=O, C-3′). – NOE experiment: Irradiation at δ = 5.48 (1′-H) caused an intensity enhancement at δ = 3.82 (3-H). – MS: *m/z* (%) = 388 (3) [M^+], 56 (100). – $C_{23}H_{32}O_5$ (388.5): calcd. C 71.11, H 8.30; found C 71.11, H 8.35.

4,4,5,5-Tetracyano-3-(2-ethoxycarbonylethylidene)-2-methylbicyclo[4.4.0]dec-1-ene (**17**): A solution of 661 mg (3.0 mmol) of vinylallene **2a**, 384 mg (3.0 mmol) of TCNE and a small amount of hydroquinone in 30 ml of toluene was stirred for 3 d at room temp. After removal of the solvent in vacuo, the solid residue was washed with diethyl ether and crystallized from ethanol; 364 mg (35%) of **17** was obtained as colorless needles (m.p. 81–82°C). – IR: $\tilde{\nu}$ = 3000–2870 cm^{-1} (s, CH), 2260 (s, C≡N), 1740 (s, C=O). – ^1H NMR: δ = 1.28 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.48–2.01, 2.24–2.34, 2.80–2.88 (3 m, 8H, 7-H, 8-H, 9-H, 10-H), 2.03 (t, *J* = 1.5 Hz, 3H, 2-CH_3), 2.96–3.00 (m, 1H, 6-H), 3.35, 3.49 (2 dd, 2 × *J* = 18.0/7.5 Hz, 2H, 2′-H), 4.21 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 6.54 (t, *J* = 7.5 Hz, 1H, 1′-H). – ^{13}C NMR: δ = 14.1 (+, OCH_2CH_3), 18.9 (+, 2-CH_3), 25.0, 25.5 (2–, C-8, C-9), 29.4, 30.6 (2–, C-7, C-10), 35.4 (–, C-2′), 45.1 (+, C-6), 46.6, 48.0 (2×, C-4, C-5), 61.6 (–, OCH_2CH_3), 109.0, 109.7, 110.0, 111.3 (4×, CN), 121.6, 126.8, 136.8 (3×, C-1, C-2, C-3), 129.9 (+, C-1′), 168.9 (×, C-3′). – NOE experiment: Irradiation at δ = 3.35 (2′-H) caused an intensity enhancement at δ = 2.03 (2-CH_3). – MS: *m/z* (%) = 348 (12) [M^+], 40 (100). – $C_{20}H_{20}N_4O_2$ (348.4): calcd. C 68.95, H 5.79, N 16.08; found C 68.57, H 5.94, N 15.65.

Ethyl 4-(2-Ethoxycarbonylethylidene)-5-methylbicyclo[4.4.0]dec-5-ene-2-carboxylate (**18**): A solution of 853 mg (3.9 mmol) of allene **2a**, 1.1 ml (10.0 mmol) of ethyl acrylate and a small amount of hydroquinone in 25 ml of toluene was heated at reflux for 5 h. The solvent was removed in vacuo, and the crude product was purified by column chromatography (diethyl ether/cyclohexane, 1:10), furnishing 945 mg (76%) of **18** as a colorless oil which consisted of an 83:17 mixture of isomers. Colorless crystals of the major isomer (m.p. 75–76°C) were obtained by dissolving the oil in hexane and cooling of the solution to 5°C. – IR: $\tilde{\nu}$ = 2910–2850 cm^{-1} (s, CH), 1725 (s, C=O). – ^1H NMR: Major isomer: δ = 1.27 (t, *J* = 7.1 Hz, 6H, OCH_2CH_3), 1.29–1.45, 1.73–1.78, 1.78–1.85, 2.69–2.73 (4 m, 8H, 7-H, 8-H, 9-H, 10-H), 1.91 (s, 3H, 5-CH_3), 2.29 (dd, *J* = 12.8/3.0 Hz, 1H, 3-H), 2.45–2.51 (m, 2H, 1-H, 3-H), 2.82 (ddd, *J* = 9.4/6.4/3.0 Hz, 1H, 2-H), 3.19 (dd, *J* = 17.8/8.1 Hz, 1H, 2′-H), 3.34 (dd, *J* = 17.8/6.7 Hz, 1H, 2′-H), 4.14, 4.15 (2 q, 2 × *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.34 (pseudo-t, *J* = 7.4 Hz, 1H, 1′-H). Additional signals of the minor isomer: δ = 1.82 (s, 3H, 5-CH_3), 3.16 (dd, *J* = 17.5/6.9 Hz, 1H, 2′-H), 3.23 (dd, *J* = 17.5/7.3 Hz, 1H, 2′-H), 5.61 (pseudo-t, *J* = 7.2 Hz, 1H, 1′-H). – ^{13}C NMR: Major isomer: δ = 14.2, 14.3 (2+, OCH_2CH_3), 18.1 (+, 5-CH_3), 26.6, 28.0, 30.4, 31.5 (4–, C-7, C-8, C-9, C-10), 33.7 (–, C-3), 35.4 (–, C-2′), 41.4 (+, C-1), 45.5 (+, C-2), 60.1, 60.6 (2–, OCH_2CH_3), 115.9 (+, C-1′), 122.8, 140.4, 141.3 (3×, C-4, C-5, C-6), 172.3, 174.1 (2×, C-3′, C=O). Additional signals of the minor isomer: δ = 41.6 (+, C-1), 44.5 (+, C-2), 60.3, 60.3 (2–, OCH_2CH_3), 114.7 (+, C-1′), 138.6, 139.5 (2×, C-4, C-6), 173.5, 174.3 (2×, C-3′, C=O). – The NMR signals were assigned by means of $^1H,^1H$ and $^1H,^{13}C$ COSY spectra. – NOE experiments (irradiation at → intensity enhancement at): δ = 5.34 (1′-H) → 2.29 (3-H); 2.29 (3-H) → 2.82 (2-H) and 2.45–2.51 (1-H, 3-H); 2.82 (2-H) → 2.29 (3-H) and 2.45–2.51 (1-H, 3-H). – MS: *m/z* (%) = 320 (9) [M^+], 159 (100). – $C_{19}H_{28}O_4$ (320.4): calcd. C 71.22, H 8.81; found C 71.35, H 9.00. – The relative configuration of the crystalline major isomer was confirmed by an X-ray structure analysis[11a].

Methyl 4-(Ethoxycarbonylethylidene)-5-methyl-2-phenylbicyclo[4.4.0]dec-5-ene-3-carboxylate (**19**): A solution of 661 mg (3.0 mmol) of **2a**, 487 mg (3.0 mmol) of methyl cinnamate and a small amount of hydroquinone in 30 ml of toluene was heated at reflux for 3 d. The cooled mixture was filtered to remove the hydroquinone and the solvent was distilled off in vacuo. The crude product was purified by column chromatography (diethyl ether/hexane, 1:9); yield 230 mg (20%) of **19**. Crystallization of a sample from ethanol gave colorless crystals (m.p. 89–90°C). – IR: $\tilde{\nu}$ = 3080–2840 cm^{-1} (s, CH), 1730 (s, C=O). – ^1H NMR: δ = 1.24 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.13–1.36, 1.58–1.89, 2.75 (3 m, 8H, 7-H, 8-H, 9-H, 10-H), 1.97 (s, 3H, 5-CH_3), 2.06–2.19 (m, 1H, 1-H), 2.87 (dd, *J* = 11.1/8.5 Hz, 1H, 2-H), 3.18, 3.32 (2 dd, 2 × *J* = 17.6/7.0 Hz, 2H, 2′-H), 3.44 (s, 3H, OCH_3), 3.49 (dd, *J* = 11.1/1.0 Hz, 1H, 3-H), 4.13 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.16 (dt, *J* = 1.0/7.0 Hz, 1H, 1′-H), 7.09–7.29 (m, 5H, Ph). – ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 18.7 (+, 5-CH_3), 26.3, 27.3, 30.2, 33.5 (4–, C-7, C-8, C-9, C-10), 35.5 (–, C-2′), 47.0 (+, C-1), 51.2 (+, OCH_3), 51.5 (+, C-2), 55.0 (+, C-3), 60.6 (–, OCH_2CH_3), 116.0 (+, C-1′), 122.9 (×, Ph), 126.4, 128.1, 128.2 (3+, Ph), 139.4, 140.6, 143.5 (3×, C-4, C-5, C-6), 171.7, 173.1 (2×, C-3′, CO_2CH_3). – MS: *m/z* (%) = 382 (11) [M^+], 350 (100). – $C_{24}H_{30}O_4$ (382.5): calcd. C 75.36, H 7.91; found C 75.14, H 7.71. – The relative configuration of **19** was confirmed by an X-ray structure analysis[11a].

Diethyl 4-(3,4,4-Trimethyl-1,2-pentadienyl)-3-(1,2,2-trimethylpropylidene)-1-cyclohexene-1,4-dicarboxylate (**20**): Vinylallene **7a** (prepared from 2.70 g of **5a**) was kept for 18 h at 5°C, and the crude product was purified by column chromatography (diethyl ether/cyclohexane, 1:2) furnishing 749 mg (60%) of **20** as a yellow oil (70:30 mixture of isomers). – IR: $\tilde{\nu}$ = 3010–2870 cm^{-1} (s, CH),

1960 (w, C=C=C), 1730, 1710 (s, C=O). – ^{1}H NMR: δ = 0.88*/0.92 [2 s, 9H, 3′-C(CH$_3$)$_3$], 1.21–1.30 (m, 6H, OCH$_2$CH$_3$), 1.26 [s, 9H, 1″-C(CH$_3$)$_3$], 1.48/1.57* (2 d, 2 × *J* = 2.8 Hz, 3H, 3′-CH$_3$), 1.63*/1.65 (2 s, 3H, 1″-CH$_3$), 1.71–2.08, 2.11–2.51 (2 m, 4H, 5-H, 6-H), 4.09–4.29 (m, 4H, OCH$_2$CH$_3$), 5.36*/5.54 (2 q, 2 × *J* = 2.8 Hz, 1H, 1′-H), 7.91–7.94/7.97–8.00* (2 m, 1H, 2-H). – ^{13}C NMR: δ = 14.1/14.4 (2+, OCH$_2$CH$_3$), 15.1 (+, 1″-CH$_3$), 20.5*/21.0 (2+, 3′-CH$_3$), 20.7/20.9* (2–, C-5), 28.7*/28.9 [2+, 3′-C(CH$_3$)$_3$], 31.7 [+, 1″-C(CH$_3$)$_3$], 33.3*/33.5 (2×, C-4′), 35.3*/35.4 (2–, C-6), 37.0 (×, C-2″), 51.6/52.2* (2×, C-4), 60.1/60.9 (2–, OCH$_2$CH$_3$), 92.2/92.3* (2+, C-1′), 110.7/110.8* (2×, C-3′), 123.4/123.8*, 129.6*/131.2 (4×, C-3, C-1″), 135.3/136.5* (2+, C-2), 152.4/153.5* (2×, C-1), 167.8*/167.9, 176.7/176.9* (4×, C=O), 199.8/200.4 (2×, C-2′). – NOE experiment: Irradiation at δ = 7.91–8.00 (2-H) caused an intensity enhancement at δ = 1.26 [1″-C(CH$_3$)$_3$]. – MS: *m/z* (%) = 416 (10) [M$^+$], 307 (100). – $C_{26}H_{40}O_4$ (416.6): calcd. C 74.96, H 9.34; found C 74.69, H 9.70.

6-(Ethoxycarbonylmethyl)-3-(1,2,2-trimethylpropylidene)-4-cyclohexene-1,2-dicarboxylic Anhydride (**21**): A solution of 540 mg (2.4 mmol) of **9a**, 245 mg (2.5 mmol) of maleic anhydride and a trace of hydroquinone in 15 ml of toluene was heated at 110°C for 30 h. The solvent was removed in vacuo and the residue was washed with cold diethyl ether to give 434 mg (57%) of **21**. Crystallization of a sample from ethanol gave colorless thin needles (m.p. 60–62°C). – IR: ṽ = 3020–2860 cm^{-1} (s, CH), 1850, 1770, 1720 (s, C=O). – ^{1}H NMR: δ = 1.16 [s, 9H, C(CH$_3$)$_3$], 1.26 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH$_3$), 1.98 (s, 3H, 1″-CH$_3$), 2.69–2.83 (m, 2H, 1′-H, 6-H), 3.05 (dd, *J* = 16.5/8.6 Hz, 1H, 1′-H), 3.72 (dd, *J* = 9.2/5.1 Hz, 1H, 1-H), 4.15 (q, *J* = 7.1 Hz, 2H, OCH$_2$CH$_3$), 4.39 (d, *J* = 9.2 Hz, 1H, 2-H), 5.62 (dd, *J* = 9.9/3.1 Hz, 1H, 5-H), 6.67 (dd, *J* = 9.9/1.3 Hz, 1H, 4-H). – ^{13}C NMR: δ = 14.2 (+, OCH$_2$CH$_3$), 18.0 (+, 1″-CH$_3$), 30.4 [+, C(CH$_3$)$_3$], 30.6 (+, C-6), 35.1 (–, C-1′), 37.3 (×, C-2″), 44.5, 45.7 (2+, C-1, C-2), 60.7 (–, OCH$_2$CH$_3$), 119.4 (×, C-1″), 128.6, 130.8 (2+, C-1, C-2), 148.1 (×, C-3), 171.5, 172.1, 172.2 (3×, C-2′, C=O). – MS: *m/z* (%) = 320 (9) [M$^+$], 218 (100). – $C_{18}H_{24}O_5$ (320.4): calcd. C 67.48, H 7.55; found C 67.43, H 7.69. – The relative configuration of cycloadduct **21** was confirmed by an X-ray structure analysis.

6-(Ethoxycarbonylmethyl)-4-methyl-3-(1-methylethylidene)-4-cyclohexene-1,2-dicarboxylic Anhydride (**22**): A mixture of 352 mg (1.8 mmol) of **11** and 176 mg (1.8 mmol) of maleic anhydride in 10 ml of toluene was stirred for 19 h at room temp. After removal of the solvent in vacuo the residue was washed with cold diethyl ether; yield 305 mg (58%) of **22** as colorless needles (m.p. 121°C). – IR: ṽ = 3020–2860 cm^{-1} (s, CH), 1850, 1790, 1730 (s, C=O). – ^{1}H NMR: δ = 1.24 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH$_3$), 1.79, 1.92 (2 s, 6H, 1″-CH$_3$), 1.88 (t, *J* = 1.7 Hz, 3H, 4-CH$_3$), 2.53–2.63 (m, 1H, 6-H), 2.73 (dd, *J* = 17.1/6.9 Hz, 1H, 1′-H), 2.93 (dd, *J* = 17.1/9.0 Hz, 1H, 1′-H), 3.63 (dd, *J* = 9.2/5.8 Hz, 1H, 1-H), 4.14 (q, *J* = 7.1 Hz, 2H, OCH$_2$CH$_3$), 4.33 (d, *J* = 9.2 Hz, 1H, 2-H), 5.47 (dd, *J* = 3.5/1.7 Hz, 1H, 5-H). – ^{13}C NMR: δ = 14.2 (+, OCH$_2$CH$_3$), 21.2, 22.0, 23.0 (3+, 1″-CH$_3$, 4-CH$_3$), 32.1 (+, C-6), 34.9 (–, C-1′), 44.9, 45.9 (2+, C-1, C-2), 60.7 (–, OCH$_2$CH$_3$), 124.3, 134.7, 138.9 (3×, C-1″, C-3, C-4), 128.5 (+, C-5), 171.9, 172.2, 172.3 (3×, C-2′, C=O). – MS: *m/z* (%) = 292 (18) [M$^+$], 190 (100). – $C_{16}H_{20}O_5$ (292.3): calcd. C 65.74, H 6.90; found C 65.60, H 6.78.

6-(Ethoxycarbonylmethyl)-1,4-dimethyl-3-(1-methylethylidene)-4-cyclohexene-1,2-dicarboxylic Anhydride (**23**): A solution of 291 mg (1.5 mmol) of vinylallene **11**, 0.18 ml (2.0 mmol) of methylmaleic anhydride and a small amount of hydroquinone in 15 ml of toluene was heated at reflux for 16 h. The solvent was removed and the product **23** was crystallized from ethanol to give 286 mg (62%) of **23** as colorless crystals (m.p. 92–93°C). – IR: ṽ = 3020–2860 cm^{-1} (s, CH), 1860, 1790, 1730 (s, C=O). – ^{1}H NMR: δ = 1.23 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH$_3$), 1.43 (s, 3H, 1-CH$_3$), 1.79, 1.86 (2 s, 6H, 1″-CH$_3$), 1.87 (d, *J* = 2.2 Hz, 3H, 4-CH$_3$), 2.33–2.37 (m, 1H, 6-H), 2.50 (dd, *J* = 16.2/10.7 Hz, 1H, 1′-H), 2.78 (dd, *J* = 16.2/3.4 Hz, 1H, 1′-H), 3.90 (s, 1H, 2-H), 4.12 (q, *J* = 7.1 Hz, 2H, OCH$_2$CH$_3$), 5.38–5.39 (m, 1H, 5-H). – ^{13}C NMR: δ = 14.2 (+, OCH$_2$CH$_3$), 21.0, 21.8, 22.3, 22.8 (4+, 1″-CH$_3$, 4-CH$_3$, C-6), 34.3 (–, C-1′), 39.4 (+, 1-CH$_3$), 51.1 (×, C-1), 54.7 (+, C-2), 60.8 (–, OCH$_2$CH$_3$), 124.8, 134.9, 140.2 (3×, C-1″, C-3, C-4), 129.0 (+, C-5), 171.1, 172.5, 175.1 (3×, C-2′, C=O). – NOE experiment: Irradiation at δ = 1.43 (1-CH$_3$) caused intensity enhancements at δ = 2.33–2.37 (6-H) and 3.90 (2-H). – MS: *m/z* (%) = 306 (18) [M$^+$], 147 (100). – $C_{17}H_{22}O_5$ (306.4): calcd. C 66.65, H 7.24; found C 66.81, H 7.25.

Methyl 2-(Ethoxycarbonylmethyl)-4-methyl-5-(1-methylethylidene)-3-cyclohexene-1-carboxylate (**24**): A solution of 291 mg (1.5 mmol) of **11**, 0.26 ml (3.0 mmol) of methyl acrylate and a trace of hydroquinone in 10 ml of toluene was heated at 100°C for 24 h. The crude product obtained by removal of the solvent in vacuo was purified by column chromatography (diethyl ether/cyclohexane, 1:10), furnishing 363 mg (87%) of **24** as a colorless oil (75:25 mixture of diastereomers). – IR: ṽ = 3020–2860 cm^{-1} (s, CH), 1740 (C=O). – ^{1}H NMR: Major isomer: δ = 1.18 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH$_3$), 1.69, 1.81 (2 s, 6H, 1″-CH$_3$), 1.92 (s, 3H, 4-CH$_3$), 2.14–2.38 (m, 3H, 6-H, 1′-H), 2.52 (dd, *J* = 14.8/4.2 Hz, 1H, 6-H), 2.72 (ddd, *J* = 11.1/5.4/4.2 Hz, 1H, 1-H), 2.89–2.99 (m, 1H, 2-H), 3.58 (s, 3H, OCH$_3$), 4.06 (q, *J* = 7.1 Hz, 2H, OCH$_2$CH$_3$), 5.41 (d, *J* = 3.8 Hz, 1H, 3-H). Additional signals of the minor isomer: δ = 1.67, 1.78 (2 s, 6H, 1″-CH$_3$), 1.90 (s, 3-H, 4-CH$_3$), 2.14–2.38 (m, 4H, 1-H, 6-H, 1′-H), 2.57 (dd, *J* = 13.1/3.5 Hz, 1H, 6-H), 3.61 (s, 3H, OCH$_3$), 5.28 (m, 1H, 3-H). – ^{13}C NMR: δ = 14.1 (+, OCH$_2$CH$_3$), 22.8/23.2*, 23.3/23.4* (4+, 1″-CH$_3$), 24.5/24.8* (2+, 4-CH$_3$), 28.1*/31.5 (2–, C-6), 33.8*/35.3 (2+, C-2), 36.0*/39.4 (2–, C-1′), 43.1*/45.9 (2+, C-1), 51.3*/51.6 (2+, OCH$_3$), 60.2 (–, OCH$_2$CH$_3$), 128.1, 128.4, 128.4, 128.9, 130.4, 135.1 (6×, C-4, C-5, C-6), 128.3/128.6* (2+, C-3), 172.0/172.3* (2×, C-2′), 174.5*/175.2 (2×, CO$_2$CH$_3$). – NOE experiment: Irradiation at δ = 2.89–2.99 (2-H) caused intensity enhancements at δ = 2.72 (1-H) and 5.41 (3-H). – Decoupling experiment: Irradiation at δ = 2.89–2.99 (2-H) changed the signal at δ = 2.72 (1-H) to a dd with *J* = 11.1 and 4.2 Hz. – MS: *m/z* (%) = 280 (55) [M$^+$], 133 (100). – $C_{16}H_{24}O_4$ (280.4): HRMS: calcd. 280.1675; found 280.1675.

5-(1-Ethoxycarbonyl-1-methylethyl)-2-methyltricyclo[4.4.0.1^{2,5}]undec-1(6)-en-3,4-dicarboxylic Anhydride (**25**) *and 11-(1-Ethoxycarbonyl-1-methylethyl)-2-methyltricyclo[4.4.0.1^{3,6}]undec-1-en-4,5-dicarboxylic Anhydride* (**26**): A solution of 2.45 g (9.9 mmol) of vinylallene **4a**, 1.50 g (15.0 mmol) of maleic anhydride and a small amount of hydroquinone in 30 ml of dichloromethane was treated at 0°C with 3.8 ml (30.0 mmol) of $BF_3 \cdot OEt_2$. The mixture was stirred for 2 h at room temp., then diluted with diethyl ether and washed with a saturated $NaHCO_3$ solution. After drying with $MgSO_4$ and removal of the solvent in vacuo, the crude product was purified by column chromatography (diethyl ether/cyclohexane, 1:3), providing 353 mg (10%) of **25** and 240 mg (7%) of **26** as viscous oils. Crystallization from ethanol gave colorless crystals in both cases, m.p. 71°C (**25**) and 147°C (**26**).

25: IR: ṽ = 2980–2840 cm^{-1} (s, CH), 1860, 1770, 1720 (s, C=O). – ^{1}H NMR: δ = 1.19 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH$_3$), 1.20–1.55, 1.72–1.78, 1.96–2.06, 2.20–2.26 (4 m, 8H, 7-H, 8-H, 9-H, 10-H), 1.32, 1.41 (2 s, 6H, 1′-CH$_3$), 1.33 (d, *J* = 8.8 Hz, 1H, 11-H), 1.37

(s, 3H, 2-CH_3), 1.59 (d, J = 8.8 Hz, 1H, 11-H), 3.15 (d, J = 7.9 Hz, 1H, 3-H), 4.01 (d, J = 7.9 Hz, 1H, 4-H), 4.03–4.12 (m, 2H, OCH_2CH_3). – ^{13}C NMR: δ = 14.1 (+, OCH_2CH_3), 15.4 (+, 2-CH_3), 22.0, 22.7, 22.8, 25.5 (4–, C-7, C-8, C-9, C-10), 23.9, 24.5 (2+, 1′-CH_3), 44.3 (×, C-1′), 50.9 (+, C-4), 53.6 (×, C-2), 54.4 (+, C-3), 59.0 (–, C-11), 60.8 (–, OCH_2CH_3), 65.5 (×, C-5), 140.6 (×, C-6), 142.6 (×, C-1), 170.5, 171.0 (2×, C=O), 176.1 (×, C-2′). – MS: *m/z* (%) = 346 (3) [M^+], 175 (100). – $C_{20}H_{26}O_5$ (346.4): calcd. C 69.34, H 7.56; found C 69.52, H 7.69. – The configuration of **25** was confirmed by ^{1}H,^{1}H-, ^{1}H,^{13}C-COSY and NOESY spectra and an X-ray structure analysis.

26: IR: $\tilde{\nu}$ = 3000–2840 cm^{-1} (s, CH), 1840, 1780, 1720 (s, C=O). – ^{1}H NMR: δ = 1.02, 1.15 (2 s, 6H, 1′-CH_3), 1.24–1.50, 1.70–2.01, 2.37–2.44 (3 m, 8H, 7-H, 8-H, 9-H, 10-H), 1.26 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 1.66 (d, J = 2.1 Hz, 3H, 2-CH_3), 2.23 (s, 1H, 11-H), 3.14 (d, J = 4.7 Hz, 1H, 3-H), 3.35 (d, J = 7.7 Hz, 1H, 5-H), 3.64 (dd, J = 7.7/4.7 Hz, 1H, 4-H), 4.10 (q, J = 7.2 Hz, 2H, OCH_2CH_3). – ^{13}C NMR: δ = 12.9 (+, 2-CH_3), 14.1 (+, OCH_2CH_3), 21.4, 22.9, 23.3 (3–, C-8, C-9, C-10), 23.9, 27.8 (2+, 1′-CH_3), 28.7 (–, C-7), 42.1 (×, C-1′), 49.1 (+, C-4), 51.0 (+, C-3), 55.3 (+, C-5), 59.4 (×, C-6), 60.8 (–, OCH_2CH_3), 71.4 (+, C-11), 131.7 (×, C-2), 133.8 (×, C-1), 171.1, 171.9 (2×, C=O), 177.1 (×, C-2′). – MS: *m/z* (%) = 346 (1) [M^+], 175 (100). – $C_{20}H_{26}O_5$ (346.4): calcd. C 69.34, H 7.56; found C 69.41, H 7.71. – The configuration of **26** was confirmed by ^{1}H,^{1}H-, ^{1}H,^{13}C-COSY and NOESY spectra.

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