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Domino 6π-Electrocyclization/Diels–Alder Reactions on 1,6-Disubstituted (*E*,*Z*,*E*)-1,3,5-Hexatrienes: Versatile Access to Highly Substituted Tri- and Tetracyclic Systems

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Abstract: The (*E*,*Z*,*E*)-1,3,5-hexatrienes **1a**, **2a**,**b** and **3b** undergo 6π-electrocyclization within 15–30 min upon heating to 200–215 °C. While the cyclohexene-annelated products **8a**,**b** were stable, the analogous cyclopentene- and cycloheptene-annelated derivatives **7a** and **9b** easily underwent dehydrogenation to the corresponding aromatic compounds **10a** and **12b** during the work-up. The cyclohexadiene derivatives **8a**,**b** were employed in thermal Diels–Alder reactions with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (PTAD) and tetracyanoethylene (TCNE) to give the expected [4+2] cycloadducts **13a** and **14a** in good yields (60 and 78 %). The initially formed cycloadduct of **8a** and dimethyl acetylenedicarboxylate (DMAD) underwent a subsequent retro-Diels–Alder reaction to give the tetrahydronaphthalene **11b** (47 %). Under high pressure (10 kbar), the cycloadduct **15a** was formed at room temperature and could be isolated in 44 % yield. TCNE and *N*-phenylmaleimide with **8a** under high pressure also led to the [4+2] cycloadducts **14a** and **16a** in good yields (60 and 77 %). The 6π-electrocyclization and subsequent Diels–Alder reaction, when performed as a one-pot domino process, provided direct access to Diels–Alder products of intermediately formed 6π-electrocyclization products, for example from the 1,3,5-hexatrienes **1a**,**b**, **2a**,**b**, **3b** and TCNE to the corresponding tricyclic products **17a**,**b**, **14a**,**b**, **18b** in moderate to good yields (27–80 %) depending on the nature of the alkoxycarbonyl group. Such sequential reactions with *N*-phenylmaleimide, maleic anhydride, dimethyl maleate and fumarodinitrile, the latter two under high pressure (10 kbar), worked as well to yield **16b** (70 %), **19a**,**b** (19, 32 %) and **20b** (39 %) and **21b** (76 %), respectively. With PTAD, however, the hexatrienes **2a**,**b** reacted at ambient temperature without 6π-electrocyclization to give the formal [4+2] cycloadducts **27a**,**b** (48 and 46 %), most probably via zwitterionic intermediates **23a**,**b** and **25a**,**b**.

Keywords: cross-coupling · cycloaddition · domino reactions · palladium · pericyclic reactions

Introduction

Palladium-catalyzed cross-coupling reactions often proceed in excellent yields, even when performed with oligohaloalkene and -arene derivatives.[1] Using this Heck methodology, alkenylations of appropriately 1,2-difunctionalized cycloalkenes give rise to 1,3,5-hexatrienes with a central cycloalkene moiety, which are valuable intermediates for the synthesis of a broad spectrum of cyclic and bicyclic compounds.[2] Symmetrical (*E*,*Z*,*E*)-1,3,5-hexatrienes with two identical substituents in the 1,6-position can be obtained by twofold Heck reaction of 1,2-dibromocycloalkenes with various alkenes. Some of these hexatrienes have been utilized to prepare interesting bicyclic β-amino acids,[2b] strained 1,6-oxygen bridged cyclodeca-1,5-dienes[2c] as well as highly functionalized cyclodecenones and cycloundecenones.[2d] Unsymmetrically 1,6-disubstituted 1,3,5-hexatrienes can be obtained by a sequence of chemoselective Stille cross-coupling of a 2-bromocycloalk-1-enyl triflate with an alkenylstannane at the site of the triflate leaving group and a subsequent Heck coupling on the resulting 2-bromo-1,3-butadiene.[2f,g]

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The symmetrical as well as the unsymmetrical 1,3,5-(*E*,*Z*,*E*)-hexatrienes do undergo thermal 6π-electrocyclizations affording ring-annelated cyclohexadienes.[2a,f,g] These should be adequate dienes for Diels–Alder reactions[3] with suitable dienophiles which would lead to functionalized tri- and tetracyclic compounds. We therefore set out to further optimize conditions for the thermal 6π-electrocyclizations of symmetrically 1,6-disubstituted (*E*,*Z*,*E*)-hexatrienes **1**–**3** with five- to seven-membered rings incorporated, and study Diels–Alder reactions for the thus formed ring-annelated cyclohexadienes with various dienophiles.

Results and Discussion

These cycloalkene derivatives **1**–**3** adopt s-*trans*,s-*trans* conformations as was disclosed by an X-ray crystal structure analysis of the 1,6-bis(methoxycarbonyl)ethenyl-substituted cyclohexene derivative **2b** (Figure 1).[4] Such 1,3,5-hexatrienes thus require elevated temperatures to undergo 6π-electrocyclization.[2a,f,g]

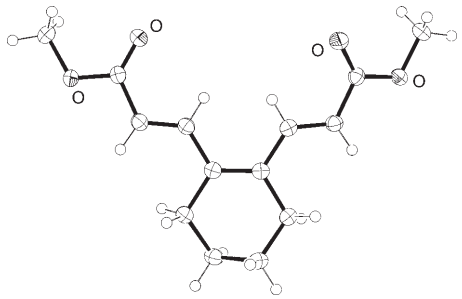
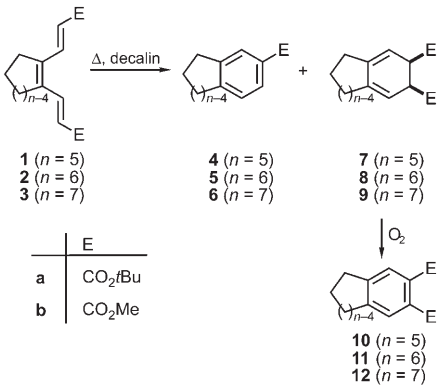


Figure 1. Structure of dimethyl cyclohexene-1,2-bisacrylate (**2b**) in the crystal. $C_{14}H_{18}O_4$, monoclinic crystals of space group $P2(1)/n$, $Z=4$, cell dimensions $a=7.7673(8)$, $b=15.8849(14)$, $c=11.1147(11)$ Å, $\alpha=90$, $\beta=108.609(8)$, $\gamma=90°$, $V=1299.6(2)$ Å^3.[4]

Upon heating the 1,6-bis(*tert*-butoxycarbonyl)-substituted hexatriene **2a** in deoxygenated decalin at 215 °C for 1 h, the monosubstituted tetrahydronaphthalene **5a** instead of the expected disubstituted hexahydronaphthalene **8a** was formed in 47 % yield (Scheme 1; Table 1, entry 1). With a heating period of 30 min, the expected ring-annelated cyclohexadiene **8a** and the monosubstituted tetrahydronaphthalene **5a** could be isolated in 30 and 19 % yield, respectively (entry 2). By further shortening of the heating time to 15 min, the yield of **8a** increased to 55 %, and that of **5a** dropped to 14 %. In addition, a fraction consisting mainly of the starting material **2a** was obtained (entry 3). These observations indicate that **5a** is a secondary product formed from **8a** at the high temperature. As the primary product **8b** from the methoxycarbonyl-substituted cyclohexene-derived hexatriene **2b** should be thermally more stable than **8a**, **2b** was also heated at 215 °C for 15 min, and indeed, the cyclization product **8b** was obtained in 50 % yield (entry 6). According to the thin-layer chromatogram of the crude product, the



Scheme 1. 6π-Electrocyclizations of symmetrically 1,6-dialkoxycarbonyl-substituted hexatrienes. For details see Table 1.

Table 1. 6π-Electrocyclizations of symmetrically 1,6-dialkoxycarbonyl-substituted hexatrienes.

Entry	Hexatriene	*T* [°C]	*t* [min]	Yield (%)[a] Arene **4**, **5** or **6**	Diene **7**, **8** or **9**	Arene **10** or **12**
1	**2a**	215	60	47	–	–
2	**2a**	215	30	19	30	–
3	**2a**	215	15	14	55	–[b]
4	**1a**	210	15	18	–	50
5	**1a**	180	75	–	30[c]	–
6	**2b**	215	15	–[d]	50	–
7	**3b**	210	30	38	32 (45:55)[e]	

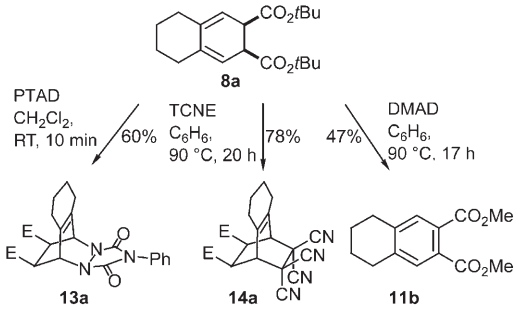
[a] Isolated yields. [b] In addition, a fraction containing the hexatriene **2a**, the cyclization product **8a** and at least one more unidentified product, was isolated. [c] Silica gel and solvents for chromatography were degassed. [d] Not isolated. [e] Mixture containing **9b** and **12b**; The ratio is given in brackets.

monosubstituted tetrahydronaphthalene **5b** had also been formed, but it was not isolated in this case. The cyclohexadiene derivatives **8a**,**b** turned out to be reasonably insensitive towards oxygen, as they aromatized only partly within several days to the tetrahydronaphthalene derivatives **11a**,**b** when exposed to air at ambient temperature.

However, the five-membered ring-derived hexatriene **1a**, when heated in decalin at 210 °C for 15 min, only gave the indane-5,6-dicarboxylate (**10a**) in 50 % yield along with the monosubstituted indane **4a** (18 %, entry 4). Apparently, the cyclization product **7a** had completely aromatized during work-up. When **1a** was heated at 180 °C for 75 min and the products purified by chromatography on carefully degassed silica gel eluting with degassed solvents, the primary cyclization product **7a** could be isolated in 30 % yield (entry 5), and proved to be very sensitive toward air-oxygen.

At last, when the methoxycarbonyl-substituted cycloheptene-derived hexatriene **3b** was heated in decalin at 210 °C for 30 min, 38 % of the monosubstituted aromatized product **6b** and 32 % of an inseparable 45:55 mixture of the primary cyclization product **9b** and the disubstituted aromatized product **12b** were obtained (entry 7). The mixture completely aromatized to **12b** when it was stirred in diethyl ether in the presence of silica gel for 14 h.

To test, whether the ring-annelated cyclohexadienes **7**–**9** with their tetrasubstituted 1,3-diene units would be suited for Diels–Alder reactions after all, a solution of the hexahydronaphthalene (**8a**) in dichloromethane was treated at ambient temperature with a solution of one equivalent of 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (PTAD) which is well known as one of the most potent dienophiles.[5] The prompt disappearance of the deep-red color of PTAD was the first indication that the reaction was successful, and indeed the tetracyclic Diels–Alder adduct **13a** was obtained in 60% yield (Scheme 2). The expected *endo*,*syn*-configuration of

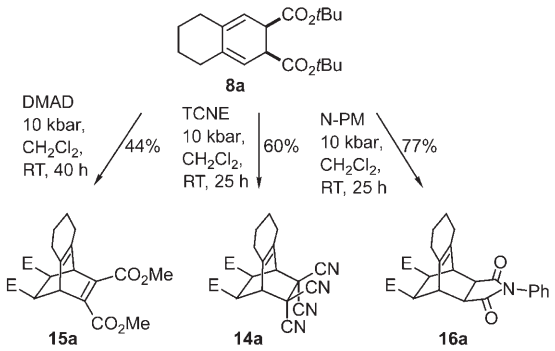


Scheme 2. Thermal Diels–Alder reactions of di-*tert*-butyl hexahydronaphthalenedicarboxylate (**8a**). E = CO_2tBu.

13a was assigned on the basis of its NMR data in comparison with those of an analogous adduct of **8b** and *N*-phenylmaleimide, for which an X-ray crystal structure was obtained at a later stage (see below, Figure 2). However, neither **8a** nor **8b** underwent a [4+2] cycloaddition with the dienophiles methyl acrylate, dimethyl fumarate and tetraethyl ethenetetracarboxylate upon heating in benzene at 90–110 °C for 15 h. Either no conversion or decomposition of the starting material was observed. This failure cannot be due to steric hindrance since tetracyanoethylene (TCNE), another highly reactive dienophile, upon heating together with the hexahydronaphthalene **8a** in benzene at 90 °C after 20 h furnished the tricyclic adduct **14a** in 78% yield.

Finally, when dimethyl acetylenedicarboxylate (DMAD) was heated with **8a** in benzene at 90 °C for 17 h, the tetrahydronaphthalene **11b**, apparently the product of a [4+2] cycloaddition and subsequent retro-Diels–Alder reaction,[6] was isolated in 47% yield. This is not surprising, as facile retro-Diels–Alder reactions with formation of dimethyl phthalate derivatives is often observed for bicyclo[2.2.2]octadienedicarboxylates formed by Diels–Alder reaction of DMAD with a cyclohexa-1,3-diene.[7b–e]

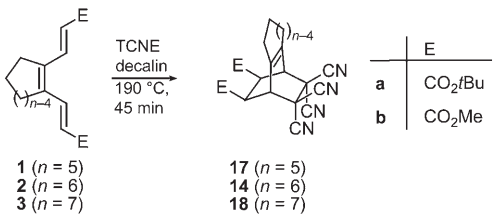
It is also well known that this cycloreversion can be prevented by carrying out the Diels–Alder reaction under high pressure at lower temperatures.[7e–g] Indeed, when the reaction of **8a** with DMAD was performed under a pressure of 10 kbar in dichloromethane at ambient temperature, the expected cyclohexane-annelated bicyclo[2.2.2]octadiene **15a** was isolated after 40 h in 44% yield (Scheme 3). Under high pressure (10 kbar), the cycloadducts of TCNE and *N*-phenylmaleimide (N-PM) to **8a**, the bicyclo[2.2.2]octene derivatives **14a** and **16a**, were formed at ambient temperature in 60 and 77% yield, respectively (Scheme 3).



Scheme 3. Diels–Alder reactions of di-*tert*-butyl hexahydronaphthalenedicarboxylate (**8a**) under high pressure. N-PM = *N*-Phenylmaleimide, E = CO_2tBu.

However, the less reactive dienophiles dimethyl fumarate, dimethyl maleate, tetraethyl ethenetetracarboxylate and fumarodinitrile did not react with **8a** in dichloromethane under a pressure of 10 kbar within 23.5–25 h, at least not at ambient temperature (see below, Scheme 5).

Although successful for the cyclohexane-annelated cyclohexadienes **8a**,**b**, these [4+2] cycloadditions would hardly be feasible for the cyclopentane- and cycloheptane-annelated cyclohexadienes **7** and **9** which so readily are oxidized to the corresponding aromatic compounds upon isolation. The most clever way to avoid exposure of such dienes to oxygen would be to trap them by an added dienophile as they are formed. This sequence of 6π-electrocyclization and [4+2] cycloaddition would constitute a new variant of a domino reaction, a class of transformations which has become increasingly important in recent years.[8] In spite of the foreseeable possibility that an added dienophile might react with one of the diene units in a 1,3,5-hexatriene before the latter would undergo the 6π-electrocyclization, a test was run with the hexatriene **2a** and TCNE. After heating these components in decalin at 190 °C for 45 min, the known tricyclic product **14a** was obtained in 55% yield (Scheme 4; Table 2, entry 2). Thus, the electrocyclization of **2a** must be significantly faster than its direct reaction with TCNE, and the yield in this 6π-electrocyclization Diels–Alder domino reaction was significantly higher than the overall yield in the two-step

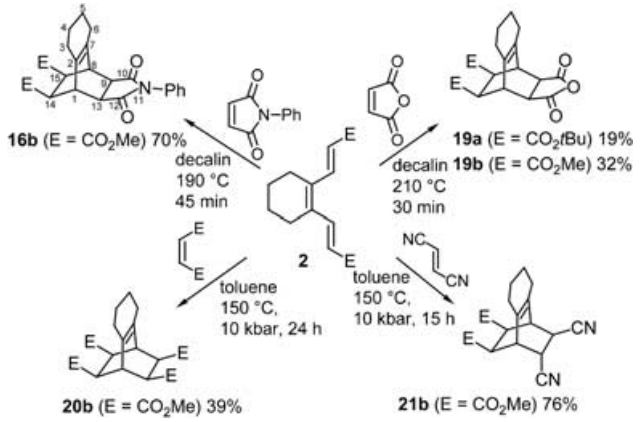


Scheme 4. 6π-Electrocyclization of (*E*,*Z*,*E*)-1,3,5-hexatrienes and ensuing Diels–Alder reaction with TCNE as a one pot-procedure. For details see Table 2.

Table 2. 6π-Electrocyclization of (*E*,*Z*,*E*)-1,3,5-hexatrienes and subsequent Diels–Alder reaction with TCNE as a one pot-procedure.

Entry	Hexatriene	Product	Yield (%)[a]
1	**1a**	**17a**	27
2	**2a**	**14a**	55
3	**1b**	**17b**	69
4	**2b**	**14b**	75
5	**3b**	**18b**	80

[a] Isolated yields.



Scheme 5. One-pot electrocyclization/Diels–Alder cascade of **2** with *N*-phenylmaleimide, maleic anhydride, dimethyl maleate, and fumarodinitrile.

procedure, which was 43% at best. While this new domino reaction performed with the cyclopentene-derived hexatriene **1a** and TCNE gave the corresponding tricycloundecene cycloadduct **17a** in only 27% yield (entry 1), all three methoxycarbonyl-substituted hexatrienes **1b**–**3b** with TCNE formed the tricyclic products **17b**, **14b** and **18b** in much better yields (69–80%) (entries 3–5).

The 6π-electrocyclization/Diels–Alder cascades of hexatrienes **2** with *N*-phenylmaleimide and maleic anhydride were successful as well. Again the bis(methoxycarbonyl)-substituted system **2b** gave better yields (70 and 32%) for **16b** and **19b**, respectively. Recrystallization of **16b** from hexane/dichloromethane furnished crystals suitable for an X-ray structure analysis, and this ultimately established the relative configuration at C-9,10,11,12 as being 9,10-*endo*, 11,12-*syn* (Figure 2).[4,9] This conforms with the Alder *endo* rule, and with the expectation that the steric bulk of the alkoxycarbonyl groups on the cyclohexadienes **8** should direct the dienophile to attack from the opposite side of the *cis*-configured substituents.

The yields with maleic anhydride were consistently lower, and with tetramethyl ethenetetracarboxylate as a dienophile no cycloadduct, but only the hexahydronaphthalene **8a** was formed from **2a** even with this cascade mode and at the higher temperature of 190°C. The cycloadducts **20b** and **21b** were obtained in 39 and 76% yield, respectively, by heating **2b** with dimethyl maleate and fumarodinitrile, respectively, at 150°C, under a pressure of 10 kbar. Both structures were confirmed by X-ray crystallography (Figure 2).

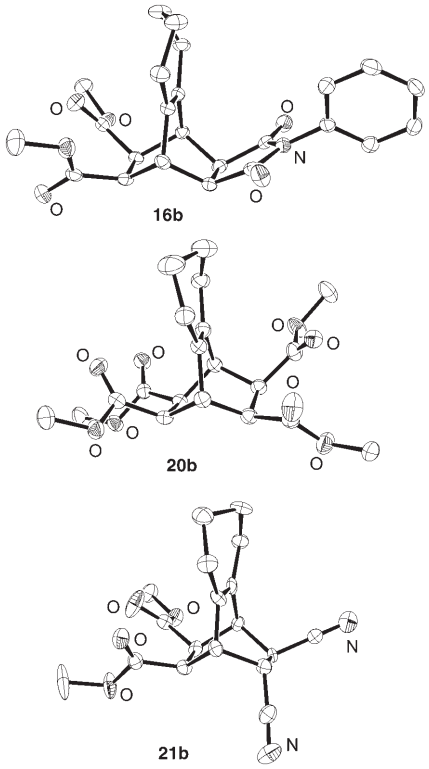
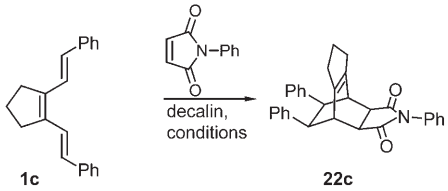


Figure 2. Structures of **16b**, **20b**, and **21b** in the crystals. **16b**: $C_{24}H_{25}NO_6$, monoclinic crystals of space group $P2_1/c$, $Z=4$, cell dimensions $a=13.0344(16)$, $b=13.3520(13)$, $c=13.1948(16)$ Å, $\alpha=90$, $\beta=113.848(9)$, $\gamma=90°$, $V=2100.3(4)$ Å^3.[4] **20b**: $C_{20}H_{26}O_8$, orthorhombic crystals of space group $Fdd2$, $Z=16$, cell dimensions $a=20.900(4)$, $b=45.789(9)$, $c=8.0983(16)$ Å, $\alpha=90$, $\beta=90$, $\gamma=90°$, $V=2100.3(4)$ Å^3.[4] **21b**: $C_{36}H_{40}N_4O_8$, monoclinic crystals of space group Cc, $Z=4$, cell dimensions $a=24.227(5)$, $b=15.323(3)$, $c=8.9994(18)$ Å, $\alpha=90$, $\beta=94.78(3)$, $\gamma=90°$, $V=3329.2(12)$ Å^3.[4]

In an attempted reaction of the distyryl-substituted cyclopentene **1c** with TCNE by heating the components in decalin for 45 min at 190°C, only decomposition of the hexatriene was observed. However, *N*-phenylmaleimide under the same conditions gave the expected tetracyclic product **22c** in 24% yield along with 51% of an inseparable 6:1 mixture of the starting material **1c** and the corresponding electrocyclization product (Scheme 6; Table 3, entry 1). Evidently, the 6π-electrocyclization of the 1,6-diphenyl-substituted hexatriene **1c** proceeds more slowly than that of the dialkoxycarbonyl-substituted analogues. Consequently, upon



Scheme 6. 6π-Electrocyclization and Diels–Alder reaction as a one-pot sequence with 1,2-distyrylcyclopentene (**1c**) and *N*-phenylmaleimide. For details see Table 3.

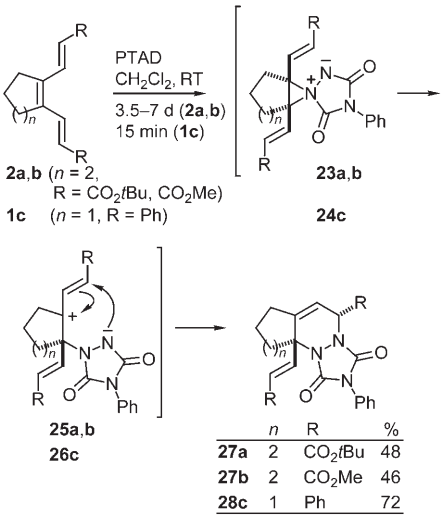
Table 3. 6π-Electrocyclization and Diels–Alder reaction as a one-pot sequence with 1,2-distyrylcyclopentene (**1c**) and *N*-phenylmaleimide.

Entry	*T* [°C]	*t* [h]	Yield[a] **22c** (%)
1	190	0.75	24[b]
2	210	4	61

[a] Isolated yields. [b] In addition, 51% of a 6:1-mixture of the hexatriene **1c** and the 6π-electrocyclization product **7c** was isolated.

prolonged (4 h) heating at higher temperature (210°C), this system gave the product **22c** in 61% yield (entry 2).

Since the extremely potent dienophile *N*-phenyltriazolinedione (PTAD) is not thermally stable enough, it cannot be employed in the one-pot conversion of (*E*,*Z*,*E*)-hexatrienes to Diels–Alder products of the thermally formed cyclohexadienes. Nevertheless it was tested towards potential Diels–Alder reactions with the hexatrienes **2a** and **2b** themselves. Applied towards **2a**,**b** in dichloromethane at ambient temperature, the color of PTAD did not disappear instantaneously, but slowly upon stirring the solutions for 3.5 and 7 d, respectively. With addition of a second equivalent of PTAD at an interval, the tricyclic products **27a** and **27b** were isolated in 48 and 46% yield, respectively (Scheme 7). The



	n	R	%
27a	2	CO_2tBu	48
27b	2	CO_2Me	46
28c	1	Ph	72

Scheme 7. Formal Diels–Alder reactions of (*E*,*Z*,*E*)-1,3,5-hexatrienes **2a**,**b** and **1c** with PTAD.

structure of **27b** was rigorously proved by X-ray structure analysis (Figure 3),[4] ultimately establishing the configurations at the stereogenic centers C-2 and C-9 which conform with the theoretical expectations.

With 1,2-distyrylcyclopentene (**1c**), PTAD in dichloromethane at ambient temperature reacted instantaneously, and within 15 min gave the same type of tricyclic cycloadduct **28c** in 72% isolated yield.

For comparison, the hexatriene **2a** did not react with *N*-phenylmaleimide at ambient temperature and not even within 14 h at 130°C, a temperature at which the 6π-electrocyclization of the hexatriene is not fast enough to form sig-

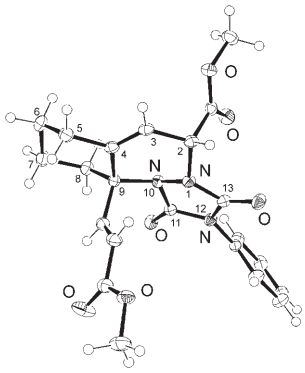


Figure 3. Structure of **27b** in the crystal. $C_{22}H_{23}N_3O_6$, triclinic crystals of space group $P\bar{1}$, $Z=2$, cell dimensions $a=8.1683(6)$, $b=8.5521(6)$, $c=14.9543(11)$ Å, $\alpha=80.583(6)$, $\beta=89.993(6)$, $\gamma=84.631(6)°$, $V=1025.93(13)$ Å^3.[4]

nificant amounts of the cyclohexadiene **8a**, which does react with *N*-phenylmaleimide (see above). Since the hexatrienes **2a**,**b** and **1c** are s-*trans*,s-*trans*-oriented, this lack of reactivity is not surprising. Their successful reactions with PTAD, however, must be rationalized in terms of a non-concerted process. It is well known that PTAD does undergo cycloadditions via zwitterionic intermediates at ambient temperature or even below.[10,11] In fact, PTAD has been shown to act as an electrophile and attack tetrasubstituted (nucleophilic) double bonds particularly well to form detectable aziridiniumimides[12] which, after ring opening, undergo further transformations.[13] In the case of **2a**,**b** and **1c**, electrophilic attack of PTAD should be most favorable at the central double bond to form the aziridiniumimides **23a**,**b**, **24c** and these, via the ring-opened zwitterions **25a**,**b**, **26c**, would close the more favorable six-membered ring to give, what looks like Diels–Alder adducts, **27a**,**b**, **28c**.

Conclusion

The one-pot transformation of (*E*,*Z*,*E*)-1,3,5-hexatrienes **1** and **2** to ring-annelated cyclohexa-1,3-dienes with ensuing [4+2] cycloadditions of dienophiles found in this study, constitutes a new domino process by which a remarkable increase of molecular complexity is achieved. With this process, by variation of the starting materials, a wide variety of functionally substituted tricyclic skeletons should be accessible.

Experimental Section

General methods: ^{1}H NMR: Bruker AM 250 (250 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to chloroform ($\delta=7.26$) as internal reference. ^{13}C NMR: Bruker AW 250 (62.9 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to chloroform ($\delta=77.0$); the multiplicity of the signals was determined by the DEPT (62.9 MHz) technique and quoted as (+) for CH_3 and CH groups, (−) for CH_2 groups and (C_{quat}) for quaternary carbon atoms. IR spectra: Bruker IFS 66. Low-resolution EI mass spectra: Finnigan MAT 95, ionizing voltage 70 eV.

High-resolution mass spectra: Finnigan MAT 95; preselected ion peak matching at $R \sim 10000$ to be within ± 2 ppm of the exact masses. The high-pressure reactions were carried in an Andreas Hofer high pressure press (max. 14 kbar). Elemental analyses: Mikroanalytisches Labor des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen, Germany. Melting points are uncorrected. Solvents for extraction and chromatography were of technical grade and distilled before use. All reactions were carried out under dry nitrogen in oven- and/or flame-dried glassware. Benzene and decalin were distilled from sodium. Dichloromethane was distilled from CaH_2.

(*E*,*Z*,*E*)-1,3,5-Hexatrienes **1a–c**,[2a] **2a**,**b**[2b] and **3a**[2h] as well as PTAD[14] were prepared according to literature procedures.

General procedure for the 6π-electrocyclization of (*E*,*Z*,*E*)-1,3,5-hexatrienes (GP 1): A thick-walled Pyrex bottle containing a magnetic stirring bar, was charged with a solution of the respective hexatriene (**1a**, **2a**, **2b** or **3b**) in decalin, and the mixture was purged with nitrogen in an ultrasonic bath for 10 min. The bottle was sealed with a screw cap, and the solution was stirred for the given time at the given temperature. The reaction mixture was cooled down to room temperature and was separated as such or after concentration in vacuo (50 °C, 0.01 Torr) by column chromatography (CC).

Reactions towards the 6π-electrocyclization of *tert*-butyl (*E*)-3-{2-[(*E*)-2-(*tert*-butoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (2a)

a) According to GP 1, the hexatriene **2a** (33 mg, 0.10 mmol) in decalin (10 mL) after 60 min at 215 °C was concentrated in vacuo at 50 °C, CC of the residue on silica gel (9 g, pentane/diethyl ether 20:1) afforded *tert*-butyl 5,6,7,8-tetrahydronaphthalene-2-carboxylate (**5a**) as a colorless oil (11 mg, 47 %). $R_f = 0.58$.[2f]

b) According to GP 1, the hexatriene **2a** (200 mg, 0.598 mmol) was heated in decalin (10 mL) and after 30 min at 215 °C was subjected to CC on silica gel (48 g, hexane/diethyl ether 20:1) to afford fraction I: tetrahydronaphthalene **5a** as a colorless oil (26 mg, 19 %). $R_f = 0.50$.

Fraction II: Di-*tert*-butyl 2,3,5,6,7,8-hexahydronaphthalene-*cis*-2,3-dicarboxylate (**8a**) as a colorless solid (60 mg, 30 %). M.p. 61–63 °C; $R_f = 0.26$; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.40$ (s, 18H, $C(CH_3)_3$], 1.42–1.54 [m, 4H, 6(7)-H], 2.22 [m, 4H, 5(8)-H], 3.33 [m, 2H, 2(3)-H], 5.65 [m, 2H, 1(4)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 24.46$ [−, 2C, C-6(7)], 27.90 [+, 6C, $C(CH_3)_3$], 30.87 [−, 2C, C-5(8)], 42.07 [+, 2C, C-2(3)], 80.35 [C_{quat}, 2C, $C(CH_3)_3$], 118.03 [+, 2C, C-1(4)], 135.50 [C_{quat}, 2C, C-4a(8a)], 170.93 (C_{quat}, 2C, CO_2); IR (KBr): $\nu = 3004$ (C-H), 2973 (C-H), 2928, 2863, 2837, 1739 (C=O), 1479, 1456, 1436, 1395, 1369, 1338, 1312, 1283, 1250, 1219, 1156, 1135, 1039, 1005, 980, 943, 910, 876, 849, 823, 797, 750, 689, 579, 519 cm^{-1}; MS (70 eV): *m*/*z* (%): 334 (3) [M^+], 278 (5) [$M^+ - C_4H_9$], 261 (1) [$M^+ - OC_4H_8$], 224 (2), 222 (23) [$M^+ - 2C_4H_8$], 178 (26) [$M^+ - CO_2 - 2C_4H_8$], 159 (1), 133 (13) [$M^+ - 2CO_2 - C_4H_9 - C_4H_8$], 104 (4), 91 (9), 57 (100) [$C_4H_9^+$], 41 (2); HRMS: calcd for $C_{20}H_{30}O_4$ (334.4): 334.2144 (correct mass).

c) According to GP 1, the hexatriene **2a** (200 mg, 0.598 mmol) was heated in decalin (10 mL) and after 15 min at 215 °C was subjected to CC on silica gel (48 g, hexane/diethyl ether 20:1) to afford fraction I: tetrahydronaphthalene **5a** as a colorless oil (20 mg, 14 %). $R_f = 0.50$.

Fraction II: Hexahydronaphthalene **8a** as a colorless solid (110 mg, 55 %). $R_f = 0.26$.

Fraction III: A mixture containing the hexatriene **2a**, the cyclization product **8a** and at least one more product (33 mg). $R_f = 0.18$.

Reactions towards the 6π-electrocyclization of *tert*-butyl (*E*)-3-{2-[(*E*)-2-(*tert*-butoxycarbonyl)ethenyl]-1-cyclopent-1-yl}acrylate (1a):

a) According to GP 1, hexatriene **1a** (100 mg, 0.312 mmol) in decalin (5 mL) after 15 min at 210 °C was subjected to CC on silica gel (53 g, pentane/diethyl ether 20:1) to afford fraction I: *tert*-Butyl indane-5-carboxylate (**4a**) as a colorless solid (12 mg, 18 %). M.p. 40–41 °C; $R_f = 0.53$; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.59$ [s, 9H, $C(CH_3)_3$], 2.10 (quin, $J =$ 7.4 Hz, 2H, 2-H), 2.93 [t, $J = 7.4$ Hz, 4H, 1(3)-H], 7.24 (d, $J = 8.1$ Hz, 1H, 7-H), 7.79 (d, $J = 7.8$ Hz, 1H, 6-H), 7.83 (s, 1H, 4-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 25.43$ (−, C-2), 28.21 [+, 3C, $C(CH_3)_3$], 32.53 (−, C-1), 32.93 (−, C-3), 80.54 [C_{quat}, $C(CH_3)_3$], 123.96 (+, C-7), 125.27 (+, C-6), 127.67 (+, C-4), 130.04 (C_{quat}, C-5), 144.29 (C_{quat}, C-7a), 149.32 (C_{quat}, C-3a), 166.21 (C_{quat}, CO_2); IR (KBr): $\nu = 3004$ (C-H), 2981 (C-H), 2959, 2843, 1705 (C=O), 1610, 1577, 1457, 1438, 1393, 1369, 1335, 1300, 1280, 1257, 1153, 1103, 1036, 908, 876, 850, 819, 767 cm^{-1}; MS (70 eV): *m*/*z* (%): 218 (2) [M^+], 162 (2) [$M^+ - C_4H_8$], 145 (2) [$M^+ - OC_4H_9$], 117 (54) [$M^+ - CO_2C_4H_9$], 115 (100), 89 (4), 77 (1), 57 (10) [$C_4H_9^+$], 41 (1); HRMS: calcd for $C_{14}H_{18}O_2$ (218.3): 218.1307 (correct mass).

Fraction II: Di-*tert*-butyl indane-5,6-dicarboxylate (**10a**) as a colorless solid (50 mg, 50 %). M.p. 59 °C; $R_f = 0.22$; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.57$ [s, 18H, $C(CH_3)_3$], 2.09 (quin, $J = 7.5$ Hz, 2H, 2-H), 2.92 [t, $J =$ 7.5 Hz, 4H, 1(3)-H], 7.46 [s, 2H, 4(7)-H]; ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): $\delta = 25.37$ (−, C-2), 28.07 [+, 6C, $C(CH_3)_3$], 32.66 [−, 2C, C-1(3)], 81.36 [−, 2C, $C(CH_3)_3$], 124.59 [+, 2C, C-4(7)], 132.22 [−, 2C, C-5(6)], 146.88 [−, 2C, C-3a(7a)], 167.26 [−, 2C, CO_2]; IR (KBr): $\nu = 2977$ (C-H), 1718 (C=O), 1613 (C=C), 1569, 1456, 1367, 1288, 1257, 1169, 1119, 1011, 893, 849, 780 cm^{-1}; MS (70 eV): *m*/*z* (%): 318 (3) [M^+], 263 (2), 207 (42), 189 (100) [$M^+ - C_4H_8 - OC_4H_9$], 162 (18), 117 (18), 57 (13) [$C_4H_9^+$]; HRMS: calcd for $C_{19}H_{26}O_4$ (318.4): 318.1831 (correct mass).

b) According to GP 1, the hexatriene **1a** (100 mg, 0.312 mmol) in decalin (5 mL) after 75 min at 180 °C was subjected to CC on degassed silica gel with degassed solvents (53 g, pentane/diethyl ether 20:1) to afford di-*tert*-butyl 2,3,5,6-tetrahydro-1*H*-indene-*cis*-5,6-dicarboxylate (**7a**) as a colorless oil (30 mg, 30 %), which was very sensitive to oxidative dehydrogenation. $R_f = 0.22$; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.43$ [s, 18H, $C(CH_3)_3$], 1.69 (quin, $J = 7.1$ Hz, 2H, 2-H), 2.28–2.37 [m, 4H, 1(3)-H], 3.49 [m, 2H, 5(6)-H], 5.69 [m, 2H, 4(7)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): $\delta = 25.00$ (−, C-2), 27.94 [+, 6C, $C(CH_3)_3$], 30.90 [−, 2C, C-1(3)], 43.07 [+, 2C, C-5(6)], 80.46 [C_{quat}, 2C, $C(CH_3)_3$], 113.49 [+, 2C, C-4(7)], 140.84 [C_{quat}, 2C, C-3a(7a)], 171.22 (C_{quat}, 2C, CO_2); MS (70 eV): *m*/*z* (%): 320 (3) [M^+], 264 (3) [$M^+ - C_4H_8$], 247 (1) [$M^+ - OC_4H_9$], 208 (8) [$M^+ - 2C_4H_8$], 191 (2) [$M^+ - C_4H_8 - OC_4H_9$], 189 (2), 164 (16) [$M^+ - CO_2 - 2C_4H_8$], 137 (4), 119 (9) [$M^+ - 2CO_2 - C_4H_9 - C_4H_8$], 95 (4), 91 (6), 57 (100) [$C_4H_9^+$], 41 (11); HRMS: calcd for $C_{19}H_{28}O_4$ (320.4): 320.1988 (correct mass).

Dimethyl 2,3,5,6,7,8-hexahydronaphthalene-*cis*-2,3-dicarboxylate (8b): According to GP 1, the hexatriene **2b** (200 mg, 0.800 mmol) in decalin (10 mL) after 15 min at 215 °C was subjected to CC on silica gel (48 g, pentane/diethyl ether 3:1) to afford hexahydronaphthalene **8b** as a colorless oil (100 mg, 50 %). $R_f = 0.50$.[2a]

Electrocyclization of methyl (*E*)-3-{2-[(*E*)-2-methoxycarbonylethenyl]cyclohept-1-enyl}acrylate (3b): According to GP 1, the hexatriene **3b** (62 mg, 0.23 mmol) in decalin (5 mL) after 30 min at 210 °C was subjected to CC on silica gel (35 g, pentane/diethyl ether 10:1 → 4:1) to afford fraction I: methyl 6,7,8,9-tetrahydro-5*H*-benzocycloheptene-2-carboxylate (**6b**) as a colorless solid (18 mg, 38 %). M.p. 28–30 °C; $R_f = 0.69$ (pentane/diethyl ether 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.65$ [m, 4H, 6(8)-H], 1.83 (m, 2H, 7-H), 2.83 [m, 4H, 5(9)-H], 3.89 (s, 3H, CH_3), 7.15 (d, $J =$ 7.6 Hz, 1H, 4-H), 7.73–7.77 [m, 2H, 1(3)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 27.91$ (−, C-6), 28.04 (−, C-8), 32.55 (−, C-7), 36.44 (−, C-5), 36.65 (−, C-9), 51.88 (+, CH_3), 127.39 (+, C-4), 127.70 (C_{quat}, C-2), 129.08 (+, C-3), 129.97 (+, C-1), 143.58 (C_{quat}, C-4a), 149.06 (C_{quat}, C-9a), 167.32 (C_{quat}, CO_2); IR (KBr): $\nu = 2924$ (C-H), 2852, 1722 (C=O), 1605, 1574, 1498, 1438, 1361, 1334, 1281, 1254, 1201, 1140, 1113, 984, 907, 864, 847, 831, 766, 740 cm^{-1}; MS (70 eV): *m*/*z* (%): 204 (100) [M^+], 189 (3) [$M^+ - CH_3$], 174 (7), 173 (52) [$M^+ - OCH_3$], 162 (7), 145 (53) [$M^+ - CO_2CH_3$], 131 (8), 115 (10), 103 (4), 91 (9), 67 (5); HRMS: calcd for $C_{13}H_{16}O_2$ (204.3): 204.1150 (correct mass).

Fraction II: A 45:55 mixture of dimethyl 2,3,6,7,8,9-hexahydro-5*H*-benzocycloheptene-2,3-dicarboxylate (**9b**) and dimethyl 6,7,8,9-tetrahydro-5*H*-benzocycloheptene-2,3-dicarboxylate (**12b**) as a colorless oil (20 mg, 32 %). $R_f = 0.33$ (pentane/diethyl ether 4:1). Compound **9b**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.44$–1.53 [m, 4H, 6(8)-H], 1.71–1.75 (m, 2H, 7-H), 2.27 [m, 4H, 5(9)-H], 3.53 [m, 2H, 2(3)-H], 3.67 (s, 6H, CH_3), 5.78 [m, 2H, 1(4)-H].

The mixture containing **9b** and **12b** was dissolved in diethyl ether (5 mL). A small amount of silica gel was added, and the mixture was stirred at ambient temperature for 14 h. The silica gel was filtered off, and the solvent was removed in vacuo. The residue (19 mg) obtained was the

completely aromatized product **12b** as a colorless solid. M.p. 76–78 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.49–1.65 [m, 4H, 6(8)-H], 1.79–1.84 (m, 2H, 7-H), 2.83 [m, 4H, 5(9)-H], 3.88 (s, 6H, CH_3), 7.45 [s, 2H, 1(4)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 27.64 [–, 2C, C-6(8)], 32.40 (–, C-7), 36.33 [–, 2C, C-5(9)], 52.48 (+, 2C, CH_3), 129.41 [C_{quat}, 2C, C-2(3)], 129.45 [+, 2C, C-1(4)], 147.06 [C_{quat}, 2C, C-4a(9a)], 168.31 (C_{quat}, 2C, CO_2); IR (KBr): ν = 2998 (C-H), 2957, 2934, 2899, 2847, 1727 (C=O), 1608, 1561, 1453, 1433, 1405, 1342, 1301, 1241, 1224, 1203, 1133, 979, 932, 906, 886, 855, 830, 789, 764, 633, 584 cm^{-1}; MS (70 eV): *m*/*z* (%): 262 (36) [M^+], 248 (1), 231 (100) [M^+-OCH_3], 212 (3), 189 (4), 152 (4), 128 (2), 111 (4), 91 (2), 59 (1) [$CO_2CH_3^+$], 43 (2); HRMS: calcd for $C_{15}H_{18}O_4$ (262.3): 262.1205 (correct mass).

Di-*tert*-butyl 10,12-dioxo-11-phenyl-9,11,13-triazatetracyclo[6.5.2.0^{2,7}.0^{9,13}]-pentadec-2(7)-ene-14,15-dicarboxylate (13a): A solution of PTAD (42 mg, 0.24 mmol) in dichloromethane (1 mL) was added dropwise within 10 min under stirring to a solution of the hexahydronaphthalene **8a** (83 mg, 0.25 mmol) in dichloromethane (1 mL). The solvent was removed in vacuo, and the residue was purified by CC on silica gel (18 g, pentane/diethyl ether 3:1) to yield **13a** as a colorless solid (74 mg, 60%). M.p. 147–148 °C; R_f = 0.53; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.45 [s, 18H, $C(CH_3)_3$], 1.49–1.70 [m, 4H, 4(5)-H], 2.09–2.30 [m, 4H, 3(6)-H], 3.43 [s, 2H, 14(15)-H], 4.88 [s, 2H, 1(8)-H], 7.33–7.44 (m, 5H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.15 [–, 2C, C-4(5)], 27.30 [–, 2C, C-3(6)], 27.99 [+, 6C, $C(CH_3)_3$], 45.25 [+, 2C, C-14(15)], 56.41 [+, 2C, C-1(8)], 81.74 [C_{quat}, 2C, $C(CH_3)_3$], 125.39 (+, 2C, Ar-C), 128.30 (+, Ar-C), 129.09 (+, 2C, Ar-C), 131.25 (C_{quat}, Ar-C), 132.69 [C_{quat}, 2C, C-2(7)], 156.78 [C_{quat}, 2C, C-10(12)], 168.38 (C_{quat}, 2C, CO_2); IR (KBr): ν = 3080 (C-H), 2985 (C-H), 2972 (C-H), 2933, 2836, 1775, 1740 (C=O), 1716 (C=O), 1596, 1505, 1459, 1392, 1349, 1340, 1296, 1278, 1252, 1222, 1166, 1149, 1073, 1023, 1004, 982, 962, 909, 851, 836, 773, 733, 713, 689, 638, 546, 505 cm^{-1}; MS (70 eV): *m*/*z* (%): 509 (17) [M^+], 453 (9) [$M^+-C_4H_8$], 397 (15) [$M^+-2C_4H_8$], 380 (28) [$M^+-OC_4H_9-C_4H_8$], 281 (100) [$M^+-H_9C_4O_2CCHCHCO_2C_4H_9$], 220 (33), 203 (61), 177 (62), 159 (9), 134 (36), 131 (12), 91 (17), 57 (93) [$C_4H_9^+$], 41 (12); HRMS: calcd for $C_{28}H_{35}N_3O_4$ (509.6): 509.2526 (correct mass).

Di-*tert*-butyl 11,11,12,12-tetracyanotricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-9,10-dicarboxylate (14a): A Pyrex tube equipped with a magnetic stirring bar was charged with hexahydronaphthalene **8a** (150 mg, 0.448 mmol), TCNE (57 mg, 0.45 mmol) and benzene (1 mL), the mixture was purged with nitrogen in an ultrasonic bath for 10 min, the tube sealed with a screw cap, and the solution stirred at 90 °C for 20 h. The mixture was cooled down to ambient temperature and concentrated in vacuo. After CC on silica gel (22 g, pentane/diethyl ether 5:1) **14a** was obtained as a colorless solid (162 mg, 78%). M.p. 188–189 °C; R_f = 0.36; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 [s, 18H, $C(CH_3)_3$], 1.69 [m, 4H, 4(5)-H], 2.25 [m, 4H, 3(6)-H], 3.35 [s, 2H, 1(8)-H], 3.49 [s, 2H, 9(10)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 21.68 [–, 2C, C-4(5)], 27.90 [+, 6C, C-(CH_3)$_3$], 28.72 [–, 2C, C-3(6)], 41.51 [+, 2C, C-1(8)], 43.01 [C_{quat}, 2C, C-11(12)], 46.20 [+, 2C, C-9(10)], 82.89 [C_{quat}, 2C, $C(CH_3)_3$], 110.90 (C_{quat}, 2C, CN), 110.97 (C_{quat}, 2C, CN), 134.89 [C_{quat}, 2C, C-2(7)], 167.29 (C_{quat}, 2C, CO_2); IR (KBr): ν = 2977 (C-H), 2931, 2909, 2874, 2837, 2254 (C=N), 1748 (C=O), 1457, 1437, 1395, 1372, 1295, 1265, 1223, 1153, 992, 850, 835, 747 cm^{-1}; MS (70 eV): *m*/*z* (%): 462 (1) [M^+], 406 (2) [$M^+-C_4H_8$], 350 (9) [$M^+-2C_4H_8$], 332 (4) [$M^+-C_4H_9OH-C_4H_8$], 222 (1), 175 (4), 131 (2), 115 (1), 91 (4), 57 (100) [$C_4H_9^+$], 41 (6); elemental analysis calcd (%) for $C_{26}H_{30}N_4O_4$ (462.5): C 67.51, H 6.54, N 12.11; found C 67.47, H 6.23, N 11.89.

Reaction of hexahydronaphthalene 8a with dimethyl acetylenedicarboxylate: A Pyrex tube equipped with a magnetic stirring bar was charged with hexahydronaphthalene **8a** (78 mg, 0.23 mmol), dimethyl acetylenedicarboxylate (28 µL, 33 mg, 0.23 mmol) and benzene (1 mL), and the mixture was purged with nitrogen in an ultrasonic bath for 10 min, the tube sealed with a screw cap, and the solution stirred at 90 °C for 17 h. The mixture was cooled down to ambient temperature and concentrated in vacuo. After CC on silica gel (26 g, pentane/diethyl ether 3:1) dimethyl 5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylate (**11b**) was obtained (27 mg, 47%). R_f = 0.37.[13,15]

General procedure for Diels–Alder reactions under high pressure (GP 2): A solution of hexahydronaphthalene **8a** (80 mg, 0.24 mmol) and the respective dienophile (0.24 mmol) in dichloromethane was sealed in a Teflon tube, and the tube subjected to 10 kbar at ambient temperature for the stated time. The solvent was removed in vacuo, and the residue subjected to chromatography on silica gel.

11,12-Di-*tert*-butyl 9,10-dimethyl tricyclo[6.2.2.0^{2,7}]dodeca-2(7),9-diene-9,10,11,12-tetracarboxylate (15a): According to GP 2, hexahydronaphthalene **8a** (80 mg, 0.24 mmol) and dimethyl acetylenedicarboxylate in dichloromethane (0.5 mL) after 40 h and subsequent CC on silica gel (19 g, pentane/diethyl ether 3:1) gave **15a** as a colorless solid (50 mg, 44%). M.p. 63–65 °C; R_f = 0.42; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34–1.57 [m, 4H, 4(5)-H], 1.41 [s, 18H, $C(CH_3)_3$], 2.14 [m, 4H, 3(6)-H], 2.84 [s, 2H, 1(8)-H], 3.76 (s, 6H, CO_2CH_3), 3.83 [s, 2H, 11(12)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.60 [–, 4C, 3(4,5,6)-C], 28.09 [+, 6C, $C(CH_3)_3$], 46.26 [+, 2C, C-1(8)*], 47.46 [+, 2 C, C-11(12)*], 52.22 (+, 2C, CO_2CH_3), 80.65 [C_{quat}, 2C, $C(CH_3)_3$], 135.71 [C_{quat}, 2C, C-2(7)], 143.79 [C_{quat}, 2C, C-9(10)], 165.99 (C_{quat}, 2C, CO_2), 170.24 (C_{quat}, 2C, CO_2); IR (KBr): ν = 2981 (C-H), 2932, 1743 (C=O), 1638 (C=C), 1458, 1437, 1395, 1369, 1334, 1256, 1223, 1158, 1077, 952, 854, 822, 734 cm^{-1}; MS (DCI, NH_3, 200 eV): *m*/*z* (%): 494 (30) [M+NH_4^+], 477 (100) [M+H^+].

Di-*tert*-butyl 11,11,12,12-Tetracyanotricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-9,10-dicarboxylate (14a): According to GP 2, hexahydronaphthalene **8a** (100 mg, 0.30 mmol) and TCNE (38 mg, 0.30 mmol) in dichloromethane (1 mL) after 25 h and CC on silica gel (19 g, pentane/diethyl ether 5:1) gave **14a** (83 mg, 60%).

Di-*tert*-butyl 10,12-dioxo-11-phenyl-11-azatetracyclo[6.5.2.0^{2,7}.0^{9,13}]pentadec-2(7)-ene-14,15-dicarboxylate (16a): According to GP 2, hexahydronaphthalene **8a** (80 mg, 0.24 mmol) and *N*-phenylmaleimide (41 mg, 0.24 mmol) in dichloromethane (1 mL) after 25 h and CC on silica gel (19 g, pentane/diethyl ether 1:1) gave **16a** as a colorless solid (93 mg, 77%). M.p. 119–121 °C; R_f = 0.44; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38–1.59 [m, 2H, 4(5)-H], 1.43 [s, 18H, $C(CH_3)_3$], 1.60–1.68 [m, 2H, 4(5)-H], 1.91–1.97 [m, 2H, 3(6)-H], 2.16–2.22 [m, 2H, 3(6)-H], 2.95 [s, 2H, 1(8)-H], 3.02 [s, 2H, 9(13)-H], 3.28 [s, 2H, 14(15)-H], 7.15 (d, ^3J = 7.0 Hz, 2H, Ar-H), 7.34–7.48 (m, 3H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.69 [–, 2C, C-4(5)], 28.05 [+, 6C, $C(CH_3)_3$], 28.55 [–, 2C, C-3(6)], 39.72 [+, 2C, C-1(8)], 44.35 [+, 2C, C-9(13)], 46.63 [+, 2C, C-14(15)], 80.76 [C_{quat}, 2C, $C(CH_3)_3$], 126.26 (+, 2C, Ar-C), 128.61 (+, Ar-C), 129.17 (+, 2C, Ar-C), 131.69 (C_{quat}, Ar-C), 132.88 [C_{quat}, 2C, C-2(7)], 170.39 (C_{quat}, 2C, CO_2), 176.78 [C_{quat}, 2C, C-10(12)]; IR (KBr): ν = 2979 (C-H), 2932, 1739 (C=O), 1709 (C=O), 1501, 1456, 1392, 1365, 1331, 1294, 1237, 1165, 1146, 1004, 850, 740, 695 cm^{-1}; MS (70 eV): *m*/*z* (%): 507 (1) [M^+], 451 (3) [$M^+-C_4H_8$], 395 (100) [$M^+-2C_4H_8$], 377 (83) [$M^+-OC_4H_9-C_4H_9$], 349 (18) [$M^+-CO_2C_4H_9-C_4H_9$], 331 (1), 304 (9) [$M^+-HCO_2C_4H_9-CO_2C_4H_9$], 279 (2), 202 (2), 175 (33) [CH_2CONPh-$COCH_2^+$], 131 (19) [$M^+-CHCONPhCOCH-HCO_2C_4H_9-CO_2C_4H_9$], 91 (11), 57 (52) [$C_4H_9^+$], 41 (11); HRMS: calcd for $C_{30}H_{37}NO_6$ (507.6): 507.2621 (correct mass).

General procedure for the 6π-electrocyclization/Diels–Alder one-pot reaction of (*E*,*Z*,*E*)-1,3,5-hexatrienes (GP 3): A Pyrex bottle equipped with a magnetic stirring bar, a solution of the hexatriene (**1**, **2** or **3**) and one equivalent of the respective dienophile in decalin (10 mL) was purged with nitrogen in an ultrasonic bath for 10 min. The bottle was sealed with a screw cap, and the solution was stirred at the given temperature for the given time. The reaction mixture was cooled down to ambient temperature, and worked up as described.

Di-*tert*-butyl 10,10,11,11-Tetracyanotricyclo[5.2.2.0^{2,6}]undec-2(6)-ene-8,9-dicarboxylate (17a): According to GP 3, the hexatriene **1a** (176 mg, 0.549 mmol) and TCNE (70 mg, 0.55 mmol) after 45 min at 190 °C was subjected to chromatography on silica gel (22 g, pentane/diethyl ether 5:1) to yield **17a** as a colorless solid (66 mg, 27%). M.p. 167–169 °C; R_f = 0.45; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 [s, 18H, $C(CH_3)_3$], 2.11 (m, 2H, 4-H), 2.64 [m, 4H, 3(5)-H], 3.42 [s, 2H, 1(7)-H], 3.90 [s, 2H, 8(9)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 23.25 (–, C-4), 27.91 [+, 6C, $C(CH_3)_3$], 34.36 [–, 2C, C-3(5)], 42.10 [+, 2C, C-1(7)], 43.36 [C_{quat}, 2C, C-10(11)], 44.01 [+, 2C, C-8(9)], 83.10 [C_{quat}, 2C, $C(CH_3)_3$], 110.91

(C_{quat}, 4C, CN), 141.13 [C_{quat}, 2C, C-2(6)], 167.29 (C_{quat}, 2C, CO_2); IR (KBr): ν = 2985 (C-H), 2852, 2253 (C≡N), 1739 (C=O), 1725, 1473, 1457, 1394, 1371, 1352, 1331, 1297, 1259, 1232, 1217, 1146, 1113, 958, 842, 749 cm^{-1}; MS (DCI, NH_3, 200 eV): *m/z* (%): 914 (6) [$2M+NH_4^+$], 483 (32) [$M+NH_3+NH_4^+$], 466 (100) [$M+NH_4^+$]; elemental analysis calcd (%) for $C_{25}H_{28}N_4O_4$ (448.5): C 66.95, H 6.29, N 12.49; found C 67.27, H 6.00, N 12.31.

Di-*tert*-butyl 11,11,12,12-tetracyanotricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-9,10-dicarboxylate (14a): According to GP 3, the hexatriene **2a** (201 mg, 0.600 mmol) and TCNE (77 mg, 0.60 mmol) after 45 min at 190 °C and chromatography on silica gel (53 g, pentane/diethyl ether 5:1) yielded **14a** (154 mg, 55 %).

Dimethyl 10,10,11,11-tetracyanotricyclo[5.2.2.0^{2,6}]undec-2(6)-ene-8,9-dicarboxylate (17b): According to GP 3, the hexatriene **1b** (200 mg, 0.846 mmol) and TCNE (108 mg, 0.843 mmol) after 45 min at 190 °C and chromatography on silica gel (31 g, pentane/diethyl ether 1:3) yielded **17b** as a colorless solid (214 mg, 69 %). M.p. 187–189 °C; R_f = 0.45; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.05–2.17 (m, 2H, 4-H), 2.64–2.71 [m, 4H, 3(5)-H], 3.63 [s, 2H, 1(7)-H], 3.68 (s, 6H, CH_3), 3.96 (s, 2H, 8(9)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 23.10 (–, C-4), 34.28 [–, 2C, C-3(5)], 41.50 [+, 2C, C-1(7)], 43.17 [C_{quat}, 2C, C-10(11)], 43.56 [+, 2C, C-8(9)], 52.79 (+, 2C, CO_2CH_3), 110.71 (C_{quat}, 2C, CN), 110.74 (C_{quat}, 2C, CN), 141.40 [C_{quat}, 2C, C-2(6)], 168.94 (C_{quat}, 2C, CO_2); IR (KBr): ν = 2991 (C-H), 2959, 2913, 2854, 2256 (C≡N), 1747 (C=O), 1668, 1443, 1373, 1354, 1328, 1276, 1227, 1202, 1156, 1105, 1039, 1020, 1007, 953, 943, 905, 837, 794, 633, 598 cm^{-1}; MS (70 eV): *m/z* (%): 364 (3) [M^+], 333 (44) [M^+-OCH_3], 236 (37) [$M^+-(CN)_2CC(CN)_2$], 177 (72) [$M^+-(CN)_2CC(CN)_2-CO_2CH_3$], 176 (81) [$M^+-(CN)_2CC(CN)_2-HCO_2CH_3$], 165 (2), 145 (9), 117 (100) [$M^+-(CN)_2CC(CN)_2-HCO_2CH_3-CO_2CH_3$], 113 (20), 105 (16), 91 (8), 77 (2), 59 (19) [$CO_2CH_3^+$], 41 (2); elemental analysis calcd (%) for $C_{19}H_{16}N_4O_4$ (364.3): C 62.63, H 4.43, N 15.38; found C 62.40, H 4.56, N 15.19.

Dimethyl 11,11,12,12-tetracyanotricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene-9,10-dicarboxylate (14b): According to GP 3, the hexatriene **2b** (200 mg, 0.799 mmol) and TCNE (102 mg, 0.799 mmol) after 45 min at 190 °C and chromatography on silica gel (31 g, pentane/diethyl ether 1:3) yielded **14b** as a colorless solid (226 mg, 75 %). M.p. 185–186 °C; R_f = 0.56; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.71 [m, 4H, 4(5)-H], 2.28 [m, 4H, 3(6)-H], 3.56 [s, 2H, 1(8)-H*], 3.58 [s, 2H, 9(10)-H*], 3.70 (s, 6H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 21.64 [–, 2C, C-4(5)], 28.56 [–, 2C, C-3(6)], 40.77 [+, 2C, C-1(8)], 42.61 [C_{quat}, 2C, C-11(12)], 45.61 [+, 2C, C-9(10)], 52.66 (+, 2C, CO_2CH_3), 110.67 (C_{quat}, 2C, CN), 110.74 (C_{quat}, 2C, CN), 135.20 [C_{quat}, 2C, C-2(7)], 168.94 (C_{quat}, 2C, CO_2); IR (KBr): ν = 2959 (C-H), 2836, 2252 (C≡N), 1740 (C=O), 1437, 1349, 1297, 1258, 1224, 1198, 1167, 1131, 1102, 1043, 1006, 963, 908, 877, 817 cm^{-1}; MS (70 eV): *m/z* (%): 378 (6) [M^+], 347 (32) [M^+-OCH_3], 318 (1) [$M^+-HCO_2CH_3$], 291 (7), 259 (2) [$M^+-HCO_2CH_3-CO_2CH_3$], 250 (22) [$M^+-(CN)_2CC(CN)_2$], 247 (3), 206 (4), 190 (92) [$M^+-(CN)_2CC(CN)_2-HCO_2CH_3$], 166 (1), 159 (3), 131 (100) [$M^+-(CN)_2CC(CN)_2-HCO_2CH_3-CO_2CH_3$], 113 (16), 105 (20), 91 (15), 77 (5), 59 (26) [$CO_2CH_3^+$], 41 (3); elemental analysis calcd (%) for $C_{20}H_{18}N_4O_4$ (378.4): C 63.49, H 4.79, N 14.81; found C 63.55, H 4.57, N 14.74.

Dimethyl 12,12,13,13-tetracyanotricyclo[7.2.2.0^{2,8}]tridec-2(8)-ene-10,11-dicarboxylate (18b): According to GP 3, the hexatriene **3b** (110 mg, 0.416 mmol) and TCNE (54 mg, 0.42 mmol) after 45 min at 195 °C and chromatography on silica gel (31 g, pentane/diethyl ether 1:3) yielded **18b** as a colorless solid (131 mg, 80 %). M.p. 193–194 °C; R_f = 0.49; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.58–1.84 [m, 6H, 4(5,6)-H], [m, 4H, 3(7)-H], 3.50 [s, 2H, 1(9)-H], 3.64 [s, 2H, 10(11)-H], 3.69 (s, 6H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 25.48 [–, 2C, C-4(6)], 29.44 (–, C-5), 35.29 [–, 2C, C-3(7)], 40.62 [+, 2C, C-1(9)], 42.47 [C_{quat}, 2C, C-12(13)], 49.18 [+, 2C, C-10(11)], 52.75 (+, 2C, CO_2CH_3), 110.76 (C_{quat}, 2C, CN), 110.99 (C_{quat}, 2C, CN), 138.43 [C_{quat}, 2C, C-2(8)], 169.06 (C_{quat}, 2C, CO_2); IR (KBr): ν = 2930 (C-H), 2857, 2257 (C≡N), 1740 (C=O), 1457, 1437, 1364, 1349, 1323, 1298, 1260, 1240, 1222, 1197, 1101, 1024, 1007, 966, 823, 806, 701, 668, 610 cm^{-1}; MS (70 eV): *m/z* (%): 392 (4) [M^+], 361 (24) [M^+-OCH_3], 332 (2) [$M^+-HCO_2CH_3$], 305 (2), 273 (3) [$M^+HCO_2CH_3-CO_2CH_3$], 264 (11) [$M^+-(CN)_2CC(CN)_2$], 232 (6), 204 (100) [$M^+-(CN)_2CC(CN)_2-HCO_2CH_3$], 173 (3), 146 (10) [$M^+-(CN)_2CC(CN)_2-2CO_2CH_3$], 145 (86) [$M^+-(CN)_2CC(CN)_2-HCO_2CH_3-CO_2CH_3$], 117 (10), 105 (16), 91 (11), 77 (3), 59 (17) [$CO_2CH_3^+$], 41 (6); elemental analysis calcd (%) for $C_{21}H_{20}N_4O_4$ (392.4): C 64.28, H 5.14, N 14.28; found C 64.00, H 5.25, N 14.03.

Dimethyl 10,12-dioxo-11-phenyl-11-azatetracyclo[6.5.2.0^{2,7}.0^{9,13}]pentadec-2(7)-ene-14,15-dicarboxylate (16b): According to GP 3, the hexatriene **2b** (200 mg, 0.799 mmol) and *N*-phenylmaleimide (207 mg, 1.20 mmol) in 3 mL of decaline after 45 min at 190 °C and chromatography on silica gel (45 g, pentane/diethyl ether 1:2) yielded **16b** as colorless crystals (237 mg, 70 %). M.p. 138–140 °C; R_f = 0.31; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.45–1.66 [m, 4H, 4(5)-H], 1.89–2.18 [m, 4H, 3(6)-H], 3.00 [s, 2H, 1(8)-H], 3.08 [s, 2H, 9(13)-H], 3.27 [s, 2H, 14(15)-H], 3.57 (s, 6H, OCH_3), 7.12 (d, J = 6.7, 2H, Ar-H), 7.31–7.46 (m, 3H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.58 [–, 2C, C-4(5)], 28.33 [–, 2C, C-3(6)], 39.29 [+, 2C, C-1(8)], 43.82 [+, 2C, C-9(13)], 45.62 [+, 2C, C-14(15)], 51.70 (+, 2C, CO_2CH_3), 126.10 (+, 2C, Ar-C), 128.52 (+, Ar-C), 129.06 (+, 2C, Ar-C), 131.53 (C_{quat}, Ar-C), 133.12 [C_{quat}, 2C, C-2(7)], 171.84 (C_{quat}, 2C, CO_2), 176.28 [C_{quat}, 2C, C-10(12)]; IR (KBr): ν = 2953 (C-H), 2919, 2855, 2833, 1760, 1740 (C=O), 1718 (C=O), 1700, 1494, 1457, 1434, 1386, 1362, 1331, 1298, 1237, 1192, 1164, 1041, 755, 702, 622, 603 cm^{-1}; MS (70 eV): *m/z* (%): 423 (6) [M^+], 391 (100) [M^+-CH_3OH], 363 (59) [$M^+-HCO_2CH_3$], 331 (5) [$M^+-HCO_2CH_3-CH_3OH$], 304 (21) [$M^+-HCO_2CH_3-CO_2CH_3$], 303 (10) [$M^+-2HCO_2CH_3$], 254 (3), 218 (2), 217 (7) [$M^+-CH_2CONPhCOCH_2-OCH_3$], 190 (10), 175 (71) [$CH_2CONPhCOCH_2^+$], 156 (9), 132 (18), 131 (44), 113 (28), 104 (17), 91 (20), 59 (10) [$CO_2CH_3^+$], 55 (1); elemental analysis calcd (%) for $C_{24}H_{25}NO_6$ (423.5): C 68.07, H 5.95, N 3.31; found C 67.81, H 5.72, N 3.26.

Di-*tert*-butyl 10,12-dioxo-11-oxatetracyclo[6.5.2.0^{2,7}.0^{9,13}]pentadec-2(7)-ene-14,15-dicarboxylate (19a): According to GP 3, hexatriene **2a** (200 mg, 0.598 mmol) was treated with maleic anhydride (59 mg, 0.60 mmol) at 210 °C for 30 min. The reaction mixture was stored at −15 °C for 7 d. During this time, colorless crystals precipitated at the glass wall. After warming to ambient temperature, the solvent was carefully removed, and the precipitate was recrystallized from diethyl ether yielding **19a** (50 mg, 19 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35–1.52 [m, 4H, 4(5)-H], 1.39 [s, 18H, $C(CH_3)_3$], 1.85–1.94 [m, 2H, 3(6)-H], 2.09–2.19 [m, 2H, 3(6)-H], 2.86 [s, 2H, 1(8)-H], 3.15 [s, 2H, 9(13)-H], 3.17 [s, 2H, 14(15)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.31 [–, 2C, C-4(5)], 28.00 [+, 6C, $C(CH_3)_3$], 28.52 [–, 2C, C-3(6)], 39.27 [+, 2C, C-1(8)], 44.89 [+, 2C, C-9(13)*], 45.91 [+, 2C, C-14(15)*], 81.17 [C_{quat}, 2C, $C(CH_3)_3$], 133.76 [C_{quat}, 2C, C-2(7)], 169.95 [C_{quat}, 2C, C-10(12)*], 171.63 (C_{quat}, 2C, CO_2*); IR (KBr): ν = 2937 (C-H), 1866 (C=O), 1784 (C=O), 1734 (C=O), 1457, 1437, 1394, 1370, 1261, 1152, 1076, 948, 908, 845, 735 cm^{-1}; MS (70 eV): *m/z* (%): 432 (1) [M^+], 320 (100) [$M^+-2C_4H_8$], 302 (96) [$M^+-OC_4H_9-C_4H_9$], 274 (46) [$M^+-CO_2C_4H_9-C_4H_9$], 246 (15), 228 (8), 203 (12), 156 (13), 131 (42), 104 (14), 91 (13), 78 (2), 57 (93) [$C_4H_9^+$], 41 (18).

Dimethyl 10,12-dioxo-11-oxatetracyclo[6.5.2.0^{2,7}.0^{9,13}]pentadec-2(7)-ene-14,15-dicarboxylate (19b): According to GP 3, the hexatriene **2b** (200 mg, 0.799 mmol) was treated with maleic anhydride (78 mg, 0.80 mmol) at 210 °C for 30 min. After cooling to ambient temperature, the reaction mixture was stored at −15 °C for 2 d. During this time, colorless crystals precipitated at the glass wall. After warming to ambient temperature, the solvent was carefully removed, and the precipitate was washed with diethyl ether (15 mL) and dried in vacuo. The crystals turned out to be pure **19b** (90 mg, 32 %). M.p. 165–168 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.56 [m, 4H, 4(5)-H], 1.91–1.98 [m, 2H, 3(6)-H], 2.12–2.19 [m, 2H, 3(6)-H], 3.05 [s, 2H, 1(8)-H], 3.19 [s, 2H, 9(13)-H], 3.28 [s, 2H, 14(15)-H], 3.63 (s, 6H, OCH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.32 [–, 2C, C-4(5)], 28.42 [–, 2C, C-3(6)], 38.94 [+, 2C, C-1(8)], 44.58 [+, 2C, C-9(13)*], 45.12 [+, 2C, C-14(15)*], 51.96 (+, 2C, CO_2CH_3), 134.15 [C_{quat}, 2C, C-2(7)], 171.29 [C_{quat}, 2C, C-10(12)*], 171.42 (C_{quat}, 2C, CO_2*); IR (KBr): ν = 3002, 2952 (C-H), 2902, 2833, 1838 (C=O), 1781 (C=O), 1750 (C=O), 1731, 1433, 1370, 1320, 1239,

1206, 1131, 1081, 1033, 1000, 976, 945, 907, 845, 814, 752, 722, 696, 671, 627, 595 cm^{-1}; MS (70 eV): *m/z* (%): 348 (25) [M^+], 316 (100) [$M^+ - H_3OH$], 288 (43) [$M^+ - HCO_2CH_3$], 260 (27), 229 (4) [$M^+ - HCO_2CH_3 - CO_2CH_3$], 214 (9), 189 (14), 145 (9) [$CH_3CO_2CH_2CH$-$CO_2CH_3^+$], 131 (19), 113 (22), 104 (9), 85 (2), 59 (4) [$CO_2CH_3^+$].

Tetramethyl *endo*,*syn*-tricyclo[6.2.2.0]dodec-2(7)-ene-9,10,11,12-tetracarboxylate (20b): A solution of dimethyl cyclohex-1-ene-1,2-bis-(*E*)-acrylate (**2b**; 400 mg, 1.60 mmol) and dimethyl maleate (1.21 g, 8.4 mmol) in deoxygenated anhydrous toluene (2.00 mL) was sealed in a Teflon tube and heated at 150 °C under a pressure of 10 kbar for 15 h. After evaporation of the solvent in vacuo, the residue was subjected to CC on 50 g of silica gel (column 3.2×15 cm) eluting with pentane/diethyl ether 1:1 to yield **20b** (R_f=0.35) as a colorless solid (2.00 mL, 39 %). M.p. 143–145 °C. Good quality crystals for X-ray diffraction were grown from pentane/diethyl ether 1:1 by slow evaporation of solvents at 23 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.55 [m, 4H, 4(5)-H], 2.07 [m, 4H, 3(6)-H], 3.00 [s, 4H, 9(10,11,12)], 3.04 [s, 2H, 1(8)-H], 3.60 [s, 12H, CH_3]; ^{13}C NMR (75.5 MHz, $CDCl_3$, additional APT, HSQC): δ=22.70 [–, 2C, C-4(5)], 28.35 [–, 2C, C-3(6)], 39.83 [+, 2C, C-1(8)], 46.42 [+, 4C, C-9-(10,11,12)], 51.61 [+, 4C, CO_2CH_3], 133.01 [C_{quat}, 2C, C-2(7)], 172.13 [C_{quat}, 4C, C=O]; IR (KBr): ν=2992 (C-H), 2950, 2925, 2840, 1735 (C=O), 1559, 1436, 1362, 1339, 1316, 1275, 1250, 1207, 1174, 1161, 1127, 1109, 1067, 1038, 1012, 937, 920, 865, 845, 833, 819, 787, 732, 668, 649, 622, 592, 535 cm^{-1}; MS (70 eV): *m/z* (%): 394 (29) [M^+], 363 (50) [$M^+ - CH_3O$], 334 (53) [$M^+ - HCO_2CH_3$], 302 (43), 274 (100), 243 (33), 215 (56), 189 (19), 145 (25), 131 (50), 113 (57), 91 (21), 85 (7), 59 (44) [CO_2Me^+].

Dimethyl 11,12-dicyanotricyclo[6.2.2.0^{2,7}]dodec-2(7)-en-9,10-dicarboxylate (21b): A solution of dimethylcyclohexene-1,2-bisacrylate (**2b**; 150 mg, 0.60 mmol) and fumarodinitrile (258 mg, 3.30 mmol) in deoxygenated anhydrous toluene (2.00 mL) in a sealed Teflon tube were heated at 150 °C under a pressure of 10 kbar for 15 h. After removal of the solvent under reduced pressure, the residue was purified by CC on 25 g of silica gel (column 3.2×15 cm, diethyl ether/pentane 1:1) to yield **21b** (149 mg, 76 %) as a colorless solid. M.p. 132–134 °C, R_f=0.40; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.57–1.66 [m, 4H, 4(5)-H], 2.02–2.18 [m, 4H, 3(6)-H], 2.65 [dd, J_1=5.0 Hz, J_2=3.2 Hz, 1H, 11-H], 2.96 [dd, J_1=5.0 Hz, J_2=2.5 Hz, 1H, 12-H], 3.01 [dd, J_1=3.1 Hz, J_2=2.5 Hz, 1H, 1-H], 3.05 [t, J=2.5 Hz, 1H, 8-H], 3.10 [dd, J_1=10 Hz, J_2=2.5 Hz, 1H, 9(10)-H], 3.41 [dd, J_1=10 Hz, J_2=2.5 Hz, 1H, 10(9)-H], 3.61 [s, 6H, CH_3]; ^{13}C NMR (75.5 MHz, additional APT, HSQC, $CDCl_3$): δ=22.27 [–, C-4(5)], 22.31 [–, C-5(4)], 27.41 [–, C-3(6)], 28.50 [–, C-6(3)], 32.47 [+, C-11], 33.39 [+, C-12], 39.21 [+, C-1], 39.88 [+, C-8], 41.95 [+, C-9(10)], 44.99 [+, C-10(9)], 52.09 [+, CO_2CH_3], 52.12 [+, CO_2CH_3], 118.77 [C_{quat}, CN], 118.84 [C_{quat}, CN], 134.09 [C_{quat}, C-2(7)], 134.92 [C_{quat}, C-7(2)], 170.78 [C_{quat}, C=O], 171.01 [C_{quat}, C=O]; IR (KBr): ν=3007 (CN), 2947 (C-H), 2835, 2243 (CN), 1751 (C=O), 1676, 1436, 1356, 1338, 1318, 1289, 1262, 1203, 1166, 1131, 1091, 1031, 998, 962, 914, 838, 828, 764, 734, 649 cm^{-1}; MS (70 eV): *m/z* (%): 328 (15) [M^+], 297 (50) [$M^+ - CH_3O$], 296 (100) [$M^+ - CH_3OH$], 268 (14) [$M^+ - HCO_2CH_3$], 241 (10), 214 (4), 209 (16), 182 (16), 181 (18), 156 (4), 145 (6), 131 (41), 113 (60), 91 (17), 77 (5), 59 (24) [CO_2Me^+].

6π-Electrocyclization and subsequent Diels–Alder reaction of 1,2-distyrylcyclopentene (1c) with *N*-phenylmaleimide:

a) According to GP 3, the hexatriene **1c** (200 mg, 0.734 mmol) was treated with *N*-phenylmaleimide (127 mg, 0.734 mmol) at 190 °C for 45 min. After concentration in vacuo at 50 °C, CC on silica gel (30 g, pentane/diethyl ether 3:1) afforded fraction I: a 6:1 mixture of the starting material **1c**, and the 6π-electrocyclization product **7c** as a yellow oil (103 mg, 52 %). R_f=0.92.

Fraction II: 9,11-Dioxo-10,13,14-triphenyl-10-azatetracyclo[5.5.2.0^{2,6}.0^{8,12}]-tetradec-2(6)-ene (**22c**) as a colorless solid (78 mg, 24 %). M.p. 216–218 °C; R_f=0.08; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.01–2.16 (m, 2H, 4-H), 2.41–2.68 [m, 4H, 3(5)-H], 3.42 (s, 2H, 1(7)-H], 3.76 (s, 2H, 13(14)-H*], 3.81 (s, 2H, 8(12)-H*], 6.74–6.78 (m, 4H, Ar-H), 6.96–7.01 (m, 6H, Ar-H), 7.09–7.19 (m, 2H, Ar-H), 7.35–7.51 (m, 3H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ=23.44 (–, C-4), 34.91 [–, 2C, C-3(5)], 40.31 [+, 2C, C-1(7)], 46.37 [+, 2C, C-13(14)*], 49.80 [+, 2C, C-8(12)*], 125.51 (+, 2C, Ar-C), 126.18 (+, 2C, Ar-C), 127.30 (+, 4C, Ar-C), 128.50 (+, Ar-C), 128.84 (+, 4C, Ar-C), 129.13 (+, 2C, Ar-C), 131.81 (C_{quat}, Ar-C), 140.90 (C_{quat}, 2C, Ar-C), 141.63 [C_{quat}, 2C, C-2(6)], 177.02 [C_{quat}, 2C, C-9(11)]; IR (KBr): ν=3080 (C-H), 3059 (C-H), 3024, 2978 (C-H), 2947, 2913, 2847, 1774, 1716 (C=O), 1597, 1497, 1451, 1381, 1300, 1184, 1074, 1029, 793, 766, 754, 699, 691, 617, 560 cm^{-1}; MS (70 eV): *m/z* (%): 445 (2) [M^+], 341 (2), 271 (9) [$M^+ - CH_2CONPh$-$COCH$], 270 (10) [$M^+ - CH_2CONPhCOCH_2$], 243 (2), 194 (3) [$M^+ - CH_2CONPhCOCH - C_6H_5$], 180 (100) [PhCHCHPh$^+$], 165 (7), 118 (7) [$M^+ + CHCONPhCOCH - 2C_6H_5$], 91 (2), 55 (1); elemental analysis calcd (%) for $C_{31}H_{27}NO_2$ (445.6): C 83.57, H 6.11, N 3.14; found C 83.71, H 6.11, N 3.24.

b) According to GP 3, the hexatriene **1c** (200 mg, 0.734 mmol) was treated with *N*-phenylmaleimide (127 mg, 0.734 mmol) at 210 °C for 4 h. After concentration in vacuo at 50 °C, CC on silica gel (30 g, pentane/diethyl ether 3:1 → 1:1) afforded **22c** (198 mg, 61 %).

***tert*-Butyl (2*R**,9*S**)-9-[(*E*)-2′-*tert*-butoxycarbonylethenyl]-11,13-dioxo-12-phenyl-1,10,12-triazatricyclo[8.3.0.0^{4,9}]tridec-3-ene-2-carboxylate (27a)**: A solution of hexatriene **2a** (100 mg, 0.299 mmol) and PTAD (52 mg, 0.30 mmol) in dichloromethane (2 mL) was stirred at ambient temperature. After 1 d, another portion of PTAD (52 mg, 0.30 mmol) was added. After a total of 3.5 d, the solvent was removed in vacuo, and the residue subjected to chromatography on silica gel (22 g, hexane/ethyl acetate 3:1) to yield **27a** as a colorless solid (73 mg, 48 %). M.p. 145–146 °C; R_f=0.65; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.33–1.62 [m, 2H, 6(7)-H], 1.45 [s, 9H, $C(CH_3)_3$], 1.47 [s, 9H, $C(CH_3)_3$], 1.70–1.91 [m, 3H, 5(6,7)-H], 2.08–2.19 (m, 1H, 8-H), 2.33–2.38 (m, 1H, 8H), 3.30–3.35 (m, 1H, 5-H), 4.94 (dd, J=2.7, J=5.3 Hz, 1H, 2-H), 5.81–5.88 [m, 2H, 3(2′)-H], 6.92 (d, J=16.2 Hz, 1H, 1′-H), 7.31–7.52 (m, 5H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ=21.86 (–, C-7), 26.95 (–, C-6), 27.95 [+, 3C, C(CH_3)$_3$], 28.01 [+, 3C, C(CH_3)$_3$], 32.21 (–, C-8), 36.50 (–, C-5), 55.78 (+, C-2), 63.59 (C_{quat}, C-9), 81.15 [C_{quat}, $C(CH_3)_3$], 83.48 [C_{quat}, $C(CH_3)_3$], 114.09 (+, C-3), 125.58 (+, 2C, Ar-C), 127.42 (+, C-2′), 128.02 (+, Ar-C), 128.96 (+, 2C, Ar-C), 131.14 (C_{quat}, Ar-C), 139.29 (C_{quat}, C-4), 142.02 (+, C-1′), 152.04 (C_{quat}, C-11*), 152.85 (C_{quat}, C-13*), 164.71 (C_{quat}, CO_2), 165.91 (C_{quat}, CO_2); IR (KBr): ν=3071 (C-H), 3003 (C-H), 2979 (C-H), 2944, 2874, 2853, 1783, 1715 (C=O), 1652 (C=C), 1507, 1460, 1419, 1369, 1299, 1276, 1252, 1146, 986, 946, 843, 769, 750, 730, 706, 688 cm^{-1}; MS (70 eV): *m/z* (%): 509 (7) [M^+], 408 (100) [$M^+ - CO_2C_4H_9$], 380 (5), 352 (39) [$M^+ - CO_2C_4H_9 - C_4H_8$], 334 (4) [$M^+ - CO_2C_4H_9 - C_4H_9OH$], 233 (2), 177 (5), 159 (3), 131 (4), 91 (4) [$NC_6H_5^+$], 57 (31) [$C_4H_9^+$], 41 (5).

Methyl (2*R,9*S**)-9-[(*E*)-2′-methoxycarbonylethenyl]-11,13-dioxo-12-phenyl-1,10,12-triazatricyclo[8.3.0.0^{4,9}]tridec-3-ene-2-carboxylate (27b)**: A solution of hexatriene **2b** (100 mg, 0.400 mmol) and PTAD (70 mg, 0.40 mmol) in dichloromethane (2 mL) was stirred at ambient temperature. After 2 d another portion of PTAD (70 mg, 0.40 mmol) was added. After a total of 7 d the solvent was removed in vacuo, and the residue subjected to chromatography on silica gel (27 g, pentane/diethyl ether 1:3) to yield **27b** as colorless crystals (78 mg, 46 %). M.p. 163–165 °C; R_f=0.44; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.39–1.49 [m, 2H, 6(7)-H], 1.80–1.92 [m, 3H, 5(6,7)-H], 2.03–2.19 (m, 1H, 8-H), 2.35–2.40 (m, 1H, 8H), 3.29–3.35 (m, 1H, 5-H), 3.76 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 5.07 (dd, J=2.7, J=5.2 Hz, 1H, 2-H), 5.90–5.99 [m, 2H, 3(2′)-H], 7.03 (d, J=15.8 Hz, 1H, 1′-H), 7.34–7.53 (m, 5H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ=21.82 (–, C-7), 26.62 (–, C-6), 32.19 (–, C-8), 36.09 (–, C-5), 51.88 (+, CH_3), 53.02 (+, CH_3), 55.21 (+, C-2), 63.74 (C_{quat}, C-9), 113.63 (+, C-3), 125.61 (+, C-2′), 125.82 (+, 2C, Ar-C), 128.28 (+, Ar-C), 129.04 (+, 2C, Ar-C), 130.90 (C_{quat}, Ar-C), 139.63 (C_{quat}, C-4), 143.41 (+, C-1′), 152.24 (C_{quat}, C-11*), 152.95 (C_{quat}, C-13*), 165.85 (C_{quat}, CO_2), 167.37 (C_{quat}, CO_2); IR (KBr): ν=2956 (C-H), 2945, 2849, 1778, 1754 (C=O), 1734, 1714 (C=O), 1648 (C=C), 1494, 1411, 1310, 1277, 1239, 1200, 1176, 1141, 1088, 1064, 977, 852, 776, 760, 741, 690, 644 cm^{-1}; MS (70 eV): *m/z* (%): 425 (7) [M^+], 394 (2) [$M^+ - OCH_3$], 366 (100) [$M^+ - CO_2CH_3$], 334 (3) [$M^+ - HCO_2CH_3 - OCH_3$], 247 (2), 215 (4), 187 (7), 176 (4), 131 (6), 119 (9) [$CONC_6H_5^+$], 91 (12) [$NC_6H_5^+$], 77 (3) [$C_6H_5^+$], 59 (7) [$CO_2CH_3^+$], 41 (2).

2,11-Diphenyl-8-(2′-phenylethenyl)-1,9,11,triazatricyclo[7.3.0.0^{4,8}]dodec-3-ene-10,12-dione (28c): 1,2-Distyrylcyclopent-1-ene (202 mg, 0.74 mmol)

was added to a solution of phenyltriazolindione (195 mg, 1.11 mmol) in CH_2Cl_2 (4 mL). The color of the solution changed spontaneously from violet to brown. After evaporation of the solvent, the product **28c** (240 mg, 72%) was isolated by CC on 15 g of silica gel (column 1.0× 10 cm, pentane/diethyl ether 3:1) as a colorless solid: M.p. 184°C; R_f= 0.35; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.80–1.97 (m, 1H, CH_2), 2.00–2.14 (m, 1H, CH_2), 2.30–2.39 (m, 1H, CH_2), 2.50–2.61 (m, 2H, CH_2), 2.85–2.95 (m, 1H, CH_2), 5.62 (d, J=2.7 Hz,), 5.61 (d, J=2.7 Hz, CH), 5.81(d, J=2.7 Hz, =CH), 6.39 (d, J=15.8 Hz, 1H, =CH), 6.60 (d, J=16.2 Hz, 1H, =CH), 7.26–7.40 (m, 15H, Ph-CH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=20.68 (–, CH_2), 27.17 (–, CH_2), 37.29 (–, CH_2), 56.73 (+, CH), 67.59 (C_{quat}), 117.76 (+, =CH), 124.91 (+, =CH*), 125.20 (+, 2×Ph-CH), 126.89 (+, 2×Ph-CH), 127. 79 (+, Ph-CH*), 127.93 (+, 2×Ph-CH), 128.36 (+, Ph-CH*), 128.61 (+, 2×Ph-CH*), 128.68 (+, 3×Ph-CH), 128.82 (+, 2×Ph-CH), 131.12 (Ph-C_{quat}*), 134.71 (+, =CH*), 135.64 (Ph-C_{quat}*), 137.25 (Ph-C_{quat}*), 141.46 (C_{quat}*), 207.40 (C=O), 207.41 (C=O); IR (KBr): ν=3032 (C-H), 2979 (C-H), 2917, 1769 (C=O), 1711 (C=O), 1495, 1420, 1246, 1144, 1083, 983, 869, 750, 701, 573 cm^{-1}.

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[1] For reviews see: a) S. Bräse, A. de Meijere in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, 2nd ed., **2004**, pp. 217–315; b) A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411; c) R. F. Heck in *Comprehensive Organic Synthesis, Vol. 4* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, pp. 833–863; d) R. F. Heck, *Org. React.* **1982**, *27*, 345–390.

[2] a) K. Voigt, P. von Zezschwitz, K. Rosauer, A. Lansky, A. Adams, O. Reiser, A. de Meijere, *Eur. J. Org. Chem.* **1998**, 1521–1534; b) K. Voigt, A. Lansky, M. Noltemeyer, A. de Meijere, *Liebigs Ann. Chem.* **1996**, 899–911; c) P. von Zezschwitz, K. Voigt, A. Lansky, M. Noltemeyer, A. de Meijere, *J. Org. Chem.* **1999**, *64*, 3806–3812; d) P. von Zezschwitz, K. Voigt, M. Noltemeyer, A. de Meijere, *Synthesis* **2000**, 1327–1340; e) A. Lansky, O. Reiser, A. de Meijere, *Synlett* **1990**, 405–407; f) P. von Zezschwitz, F. Petry, A. de Meijere, *Chem. Eur. J.* **2001**, *7*, 4035–4046; g) H. W. Sünnemann, A. de Meijere, *Angew. Chem.* **2004**, *116*, 913–915; *Angew. Chem. Int. Ed.* **2004**, *43*, 895–897; h) R. von Essen, P. von Zezschwitz, D. Vidović, A. de Meijere, *Chem. Eur. J.* **2004**, *10*, 4341–4352.

[3] F. Fringuelli, A. Taticchi, *Dienes in the Diels–Alder Reaction*, Wiley, New York, **1990**.

[4] CCDC-268140 (**2b**), -249113 (**16b**), -268139 (**20b**), -272215 (**21b**) and -249114 (**23b**) 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/

[5] a) S. M. Weinreb, R. R. Staib, *Tetrahedron* **1982**, *38*, 3087–3128; b) L. A. Paquette, R. F. Doehner Jr., *J. Org. Chem.* **1980**, *45*, 5105–5113; c) C. J. Moody, *Adv. Heterocycl. Chem.* **1982**, *20*, 1–45; d) A. G. Leach, K. N. Houk, *Chem. Commun.* **2002**, 1243–1255.

[6] For retro-Diels–Alder reactions see: a) M.-C. Lasne, J.-L. Ripoll, *Synthesis* **1985**, 121–143; b) A. Ichihara, *Synthesis* **1987**, 207–222.

[7] a) K. Matsumoto, A. Sera, *Synthesis* **1985**, 999–1027; b) G. M. Rubottom, D. S. Krueger, *Tetrahedron Lett.* **1977**, 611–614; c) G. P. Gisby, S. E. Royall, P. G. Sammes, *J. Chem. Soc. Perkin Trans. 1* **1982**, 169–173; d) P. A. Harland, P. Hodge, *Synthesis* **1982**, 223–225; e) A. Ichihara, K. Murakami, S. Sakamura, *Tetrahedron* **1987**, *43*, 5245–5250; f) T. Suzuki, K. Kubomura, H. Fuchii, H. Takayama, *J. Chem. Soc. Chem. Commun.* **1990**, 1687–1689; g) W. G. Dauben, C. R. Kessel, K. H. Takemura, *J. Am. Chem. Soc.* **1980**, *102*, 6894–6896; h) W. G. Dauben, H. O. Krabbenhoft, *J. Am. Chem. Soc.* **1976**, *98*, 1992–1993.

[8] a) L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137–170; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131–163; b) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136.

[9] For the stereochemical notation of such oligocyclic systems see: H. Prinzbach, H. Fritz, H. Hagemann, D. Hunkler, S. Kagabu, G. Philippossian, *Chem. Ber.* **1974**, *107*, 1971–1987.

[10] a) W. Adam, O. De Lucchi, I. Erden, *Angew. Chem.* **1979**, *91*, 512–513; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 468–469; b) I. Erden, *Chem. Lett.* **1981**, 263–266; c) T. J. Katz, N. Acton, *J. Am. Chem. Soc.* **1973**, *95*, 2738–2739.

[11] a) I. Erden, A. de Meijere, *Tetrahedron Lett.* **1980**, *21*, 1837–1840; b) A. de Meijere, I. Erden, W. Weber, D. Kaufmann, *J. Org. Chem.* **1988**, *53*, 152–161.

[12] a) C. A. Seymour, F. D. Greene, *J. Am. Chem. Soc.* **1980**, *102*, 6384–6385; b) S. F. Nelsen, D. L. Kopp, *J. Am. Chem. Soc.* **1985**, *107*, 5548–5549.

[13] W. Adam, N. Carballeira, *J. Am. Chem. Soc.* **1984**, *106*, 2874–2882.

[14] M. J. Bausch, B. David, *J. Org. Chem.* **1992**, *57*, 1118–1124.

[15] R. L. Hillard III, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1977**, *99*, 4058–4069.

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