Expanded Radialenes with Bicyclo[4.3.1]decatriene Units: New Precursors to Cyclo[*n*]carbons

Yoshito Tobe,* Rui Umeda, Naruhito Iwasa, and Motohiro Sonoda[a]

Abstract: A new method for the formation of conjugated polyynes has been developed based on both the rearrangement of vinylidenes to alkynes and the [2+1] cheletropic fragmentation of dialkynylmethylenebicyclo[4.3.1]deca-1,3,5-triene derivatives. A model study of the photolysis of simple dialkynylmethylenebicyclo[4.3.1]deca-1,3,5-trienes resulted in cheletropic fragmentation followed by 1,2-migration to give the corresponding linear polyynes, although undesired isomerization to methylenebicyclo[5.3.0]triene derivatives took place concurrently. Expanded [3]-, [4]-, [5]-, and [6]radialene derivatives with exocyclic bicyclo[4.3.1]decatriene units were prepared by oxidative coupling of the monomeric units as precursors to the corresponding cyclo[*n*]carbons, monocyclic forms of carbon clusters. The spectroscopic properties of the expanded radialenes were investigated in connection with cross conjugation of the core π system and with its perturbation by the extraannular bicyclic π system. In negative-mode laser-desorption time-of-flight (LD-TOF) mass spectra, the expanded radialenes exhibited peaks due to the corresponding cyclo[*n*]carbon anions (n = 18, 24, 30, and 36) formed by the stepwise loss of the aromatic indane fragments.

Keywords: alkynes · carbenes · cyclo[*n*]carbons · cycloreversion · radialenes

Introduction

Cyclo[*n*]carbons, defined as *n*-membered monocyclic rings of all-carbon molecules, have been attracting considerable interest from several points of view. First, although their unique cyclic structure among the various forms of carbon allotropes has been indicated by spectroscopic methods,[1] detailed geometrical, electronic, and vibrational information, which is also important with regard to aromaticity/antiaromaticity of dehydroannulenes, has not yet been elucidated. Next, it is thought likely that cyclo[*n*]carbons play a key role during the early stages of fullerene formation.[2] Moreover, it has been proposed that cyclo[12]carbon and cyclo[18]carbon serve as precursors of the hitherto unknown, two-dimensional carbon networks called graphyne and graphdiyne, respectively.[3]

Cyclo[*n*]carbons can be produced by laser vaporization of graphite, but with little selectivity in cluster-size distribution. It would be advantageous for size- and shape-selectivity to generate cyclo[*n*]carbons from the corresponding precursors that have monocyclic frameworks of the desired carbon numbers. In this context, a number of precursors of cyclo[*n*]carbons have been prepared by utilizing a retro-Diels–Alder reaction,[4] decarbonylation,[5] and decomposition of aminotriazoles.[6] We have developed our own method based on the retro [2+2] fragmentation of [4.3.2]propellatrienes to form a C(sp)–C(sp) bond by extruding an aromatic fragment, indane, and applied it to the formation of cyclo[*n*]carbons.[7] Despite the advantages of this retro [2+2] approach, such as the ease of fragmentation and the kinetic stability of the precursors, a few disadvantages exist. For example, the preparation of the propellane unit requires lengthy sequences and is laborious. Moreover, owing to the relatively small angle (ca. 90°) between the triple bonds of the diethynyl[4.3.2]propellatriene unit, only the cyclic dehydrotrimer and dehydrotetramer were obtained; larger cyclic dehydrooligomers such as the dehydropentamer and dehydrohexamer, with 30- and 36-membered rings, respectively, were not obtained. In addition to these methods, the [2+1] cheletropic fragmentation of cyclopropane-containing oligodiacetylenes, such as cyclic dehydrooligomers of diethynyl[4.4.1]propellatetraenes[8] incorporated in a fullerene structure, and 1,1-diethynyltetramethylcyclopropane,[9] have been investigated by mass spectrometry, aiming at the generation of cyclo[5*n*]carbons.

It has been well documented that vinylidenes equilibrate with acetylenes at high temperature.[10] Similarly, alkylidene carbenes generated by the photolysis of alkylidenecyclopro-

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[a] Prof. Dr. Y. Tobe, R. Umeda, N. Iwasa, Dr. M. Sonoda
Department of Chemistry, Faculty of Engineering Science
Osaka University
and CREST, Japan Science and Technology Corporation (JST)
Toyonaka, Osaka 560-8531 (Japan)
Fax: (+81) 6-6850-6229
E-mail: tobe@chem.es.osaka-u.ac.jp

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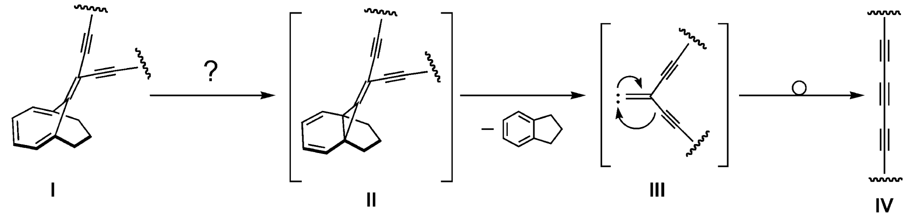
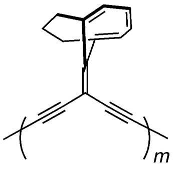
pane derivatives rearranged to alkynes.[11] Moreover, Tykwinski developed an ingenious method for the preparation of polyynes by use of the rearrangement of dialkynylvinylidenoids generated from the corresponding dibromoalkenes.[12] On the basis of these previous results, we planned to develop a new method for generating cyclo[*n*]carbons utilizing the vinylidene-to-acetylene rearrangement. To this end, we designed the dialkynylmethylenebicyclo[4.3.1]deca-1,3,5-triene unit **I** as the key unit of the precursor.[13] That is, we envisioned that extrusion of an aromatic fragment (indane) from **I** would produce dialkynylvinylidene **III**, presumably via the corresponding propelladiene-type valence isomer **II**, and would then isomerize to form a hexatriyne unit **IV** (Scheme 1). The observations underlying our design of the carbene precursor **I** are the following: i) Thermally induced fragmentation of dihalomethano[10]annulenes has been reported to form dihalocarbenes by elimination of naphthalene,[14] although the mechanism, that is, whether or not the corresponding [4.4.1]propellatetraene is involved, is not clear.[14b] ii) Photolysis of cyclopropane-containing propellanes has been recognized as a method for forming free carbenes,[15] including such peculiar species as homocubylidene.[15c] The cyclic dehydrooligomers **V** of **I** would then serve as precursors of cyclo[*n*]carbons. Since the bicyclic unit **I** would be more readily prepared than the previously employed precursor [4.3.2]propellatriene units, we expected that this method would provided ready access to cyclo[*n*]carbons. In addition, since the C(sp)-C(sp^2)-C(sp) bond angle of the exo methylene carbon of **I** must be nearly 120°, large cyclic dehydrooligomers such as pentamers and hexamers (**V**: $m = 5, 6$) would be obtained, providing a route to large cyclo[*n*]carbons. The corresponding large cyclic dehydrooligomers were not obtained from the diethynyl[4.3.2]propellatriene unit.[7b,e]



Scheme 1. Proposed pathway for the formation of a polyyne unit.



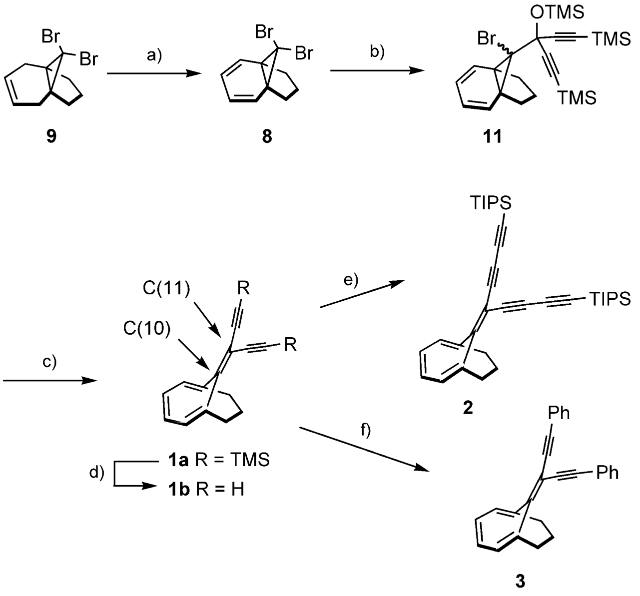
V

The cyclic dehydrooligomers **V** possess expanded radialene structures that have attracted a great deal of interest with regard to their cross conjugation.[16] Since the π segments in **V** are not linearly conjugated (i.e., cross-conjugated), **V** must possess considerable kinetic stability. In addition, in the oligomers **V**, the radialene π system would suffer from perturbation of the bridged cycloheptatriene system connected to the periphery of the radialene framework.

Herein we report the synthesis of dialkynylmethylenebicyclo[4.3.1]decatriene derivatives **1a**, **1b**, **2**, and **3**, the X-ray structural characterization of **1b**, and the photolysis of **1a**, **2**, and **3** as a model study of the photochemical [2+1] fragmentation to form corresponding linear polyynes. We also report the synthesis and spectral properties of cyclic dehydrooligomers **4**–**7**, which have expanded radialene structures, and their cheletropic fragmentation in negative-mode laser-desorption mass spectra to provide the corresponding cyclo[*n*]carbon anions ($n = 18, 24, 30$, and 36).

Results and Discussion

Synthesis and structure of monomer unit: Dibromo[4.3.1]propelladiene **8** was prepared by treatment of dibromopropellane **9**, which had been prepared by dibromocarbene addition to dihydroindane,[17] with pyridinium hydrobromide perbromide followed by dehydrobromination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Halogen–lithium exchange of **8** with *n*BuLi at −100 °C followed by treatment with 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-one (**10**)[18] and then with TMSCl afforded adduct **11** (Scheme 2).[19] Although the

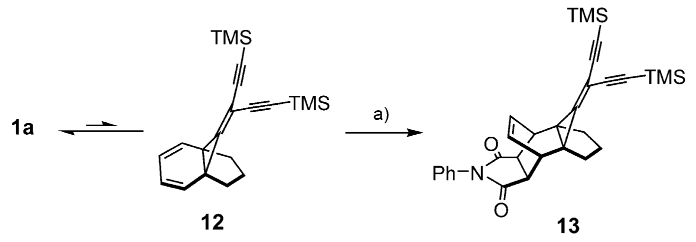


Scheme 2. a) i) $C_5H_5N{\cdot}HBr_3$, C_5H_5N, CH_2Cl_2, RT; ii) DBU, toluene, 42 °C, 35 %. b) *n*BuLi, −100 °C, then $(TMS\text{-}C{\equiv}C)_2C{=}O$ (**10**), −70 °C, then TMSCl, THF, 46 %. c) *t*BuLi, pentane, −110 °C, then TMSCl, 80 %. d) $LiOH{\cdot}H_2O$, THF, RT, 100 %. e) TIPS-C≡C-Br (**14**), CuCl, $NH_2OH{\cdot}HCl$, aq. $EtNH_2$, THF-MeOH (1:2), RT, 63 %. f) PhI, $PdCl_2(PPh_3)_2$, CuI, Et_3N, RT, 91 %.

spectral data (^{1}H NMR and ^{13}C NMR) of the product indicated that it was a single isomer, its configuration was not determined. A second halogen–lithium exchange of **11** with *t*BuLi effected the elimination to give **1a** in 80% yield.

The ^{13}C NMR spectrum of the product was consistent with the open form **1a**, not the closed isomer **12** with a propelladiene form, since it does not exhibit the quaternary sp^3 carbon signal present in propelladienes **8** and **11**. Instead, the bridgehead carbon signal appears at $\delta = 138.6$ ppm. In addition, the ^{13}C NMR spectrum of **1a** indicates that the exocyclic double bond is considerably polarized, since one of the protons resonates at substantially lower field (C(10) $\delta = 167.0$ ppm) than the other (C(11) $\delta = 93.1$ ppm). Neuenschwander et al. reported that the electron-withdrawing groups caused polarization of the exocyclic double bond of heptafulvene derivatives, thereby leading to large chemical-shift differences in the ^{13}C NMR spectra of the double bond.[20] Accordingly, the polarization of the double bond of **1a** can be ascribed to the weak electron-withdrawing effect of the ethynyl groups. Alternatively, the bond-angle strain caused by the relatively short methylene bridge may also contribute to the polarization in **1a**, since Itô et al. demonstrated that the ^{13}C NMR signals of the carbonyl carbon of 2,7-methylene-brigded tropones exhibited downfield shifts with decreasing length of the methylene bridge.[21]

In analogy to the previously reported [2+2+2] cycloaddition of the 1,6-methano[10]annulenes with dienophiles,[22] the reaction of **1a** with *N*-phenylmaleimide in refluxing toluene afforded adduct **13** as a sole product in 81% yield (Scheme 3). Nevertheless, this result is consistent with the bridged-triene structure of **1a**, since, just as for cycloheptatriene itself, the valence tautomer, which is in equilibrium with **1a**, is the more reactive diene in the Diels–Alder reaction.



Scheme 3. a) *N*-phenylmaleimide, toluene, reflux, 81%

Desilylation of **1a** with LiOH•H$_2$O afforded **1b** and a subsequent Cadiot–Chodkiewicz reaction[23] with bromoalkyne **14** gave the bisbutadiynyl derivative **2** as a pale yellow solid in 63% yield. The diphenyl derivative **3** was prepared by Sonogashira cross coupling[24] of **1b** with iodobenzene (Scheme 2).

Bicyclo[4.3.1]decatrienes **1a**, **1b**, **2**, and **3** are bridgehead dienes, compounds possessing two distorted bridgehead double bonds. In order to elucidate the deformation of the bridgehead double bond and clarify the effect of strain on the structure of the bicyclic framework, an X-ray structure analysis of **1b** was carried out (Figure 1). A single crystal of **1b** suitable for X-ray crystallographic analysis was obtained by recrystallization from *n*-hexane.

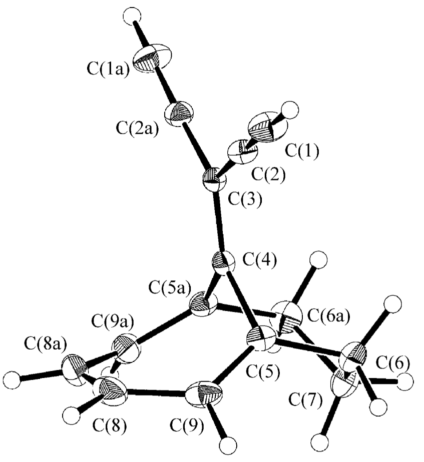


Figure 1. ORTEP drawing of **1b** with arbitrary numbering. Selected bond lengths [Å] and bond angles [°]: C(1)–C(2) 1.186(2), C(2)–C(3) 1.441(1), C(3)–C(4) 1.342(2), C(4)–C(5) 1.464(1), C(5)–C(6) 1.509(1), C(5)–C(9) 1.350(1), C(6)–C(7) 1.551(1), C(8)–C(8a) 1.356(3), C(8)–C(9) 1.441(2), C(1)-C(2)-C(3) 177.8(1), C(2)-C(3)-C(2a) 117.6(1), C(2)-C(3)-C(4) 121.19(6), C(3)-C(4)-C(5) 130.05(5), C(5)-C(4)-C(5a) 99.8(1), C(4)-C(5)-C(6) 110.85(8), C(4)-C(5)-C(9) 116.53(10), C(5)-C(6)-C(7) 106.78(9), C(5)-C(9)-C(8) 122.2(1), C(6)-C(5)-C(9) 128.14(10), C(6)-C(7)-C(6a) 113.8(1), C(8a)-C(8)-C(9) 124.16(7).

The bond lengths and angles of the bicyclic framework in **1b** are similar to those of [4]troponophane **15**.[21] Similarly, both cycloheptatriene moieties of **1b** and **15** possess a tub form. As shown in Figure 2, the seven-membered ring of **1b** is bent more severely than that of **15**. Since the exocyclic double bond of **1b** is nearly perpendicular to the plane C(5)-C(9)-C(9a)-C(5a), its conjugation with the cycloheptatriene π-system is not efficient. This is in accordance with the fact that **1a**, **1b**, **2**, and **3** do not exhibit absorption bands in the visible region, while unbridged methylenecycloheptatriene derivatives, including **18** and **20** described later, exhibit characteristic absorptions around 400 nm.[25] These results suggest that the large polarization of the exocyclic double bond is mainly due to the strain around the bridge top (C(5)-C(4)-C(5a) = 99.8°), which is caused by the relatively short methylene bridge rather than the conjugation of the cycloheptatriene moiety with the electron-withdrawing ethynyl groups. The torsional angles of the bridgehead double bond of **1b** are depicted in Figure 3. The twisting or torsion parameter (ϕ) represents the deviation from copla-

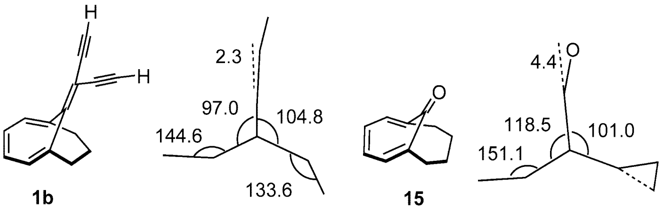


Figure 2. Angles between the least-squares planes of **1b** and **15**.

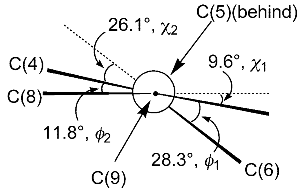
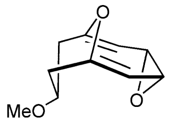


Figure 3. Torsional angles of the bridgehead double bonds in **1b**.

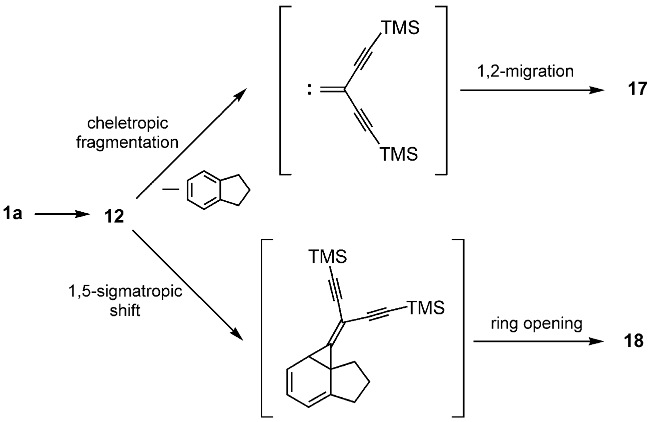
narity of the two p-type orbitals, and the out-of-plane bending parameter (χ) is regarded as a measure of the extent of rehybridization.[26] The angle of twisting parameter τ, represented by $(\phi_1 + \phi_2)/2$, of **1b** is 20.1°, which is larger than that reported for the bridgehead diene **16** ($\tau = 11.6°$),



16

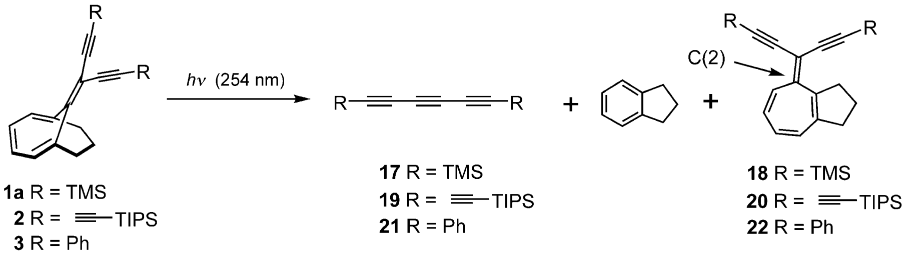
which has an oxabicyclo[4.3.1]decatriene framework.[27] The difference is probably due to the wider angle of the oxygen bridge of **16** (101.9°) than that of **1b** (99.8°), which reduces the distortion of the double bond. On the other hand, the angle of the vinylidene carbon (C(2)-C(3)-C(2a)) of **1b** (117.6°) is slightly larger than those reported for other ethynylethenes, which typically show angles of around 115°.[28a–e]

Photolysis of model compounds: As model studies to test the photochemical cheletropic fragmentation of the dialkylmethylenebicyclo[4.3.1]decatrienes, acyclic compounds **1a**, **2**, and **3** were irradiated with a low pressure mercury lamp in an ice bath (Scheme 4). Photolysis of **1a** in *n*-hexane afforded bis(trimethylsilyl)hexatriyne (**17**)[7a,29,30] in 43% isolated yield together with indane (45% yield detected by GC). In addition, the isomerization product **18** of the starting material was obtained in 30% isolated yield as a brown oil. The structure of **18** was elucidated on the basis of its NMR and UV/Vis spectra. The salient features of the NMR spectrum include four vinyl proton signals at $\delta = 6.90$ (d, 1H), 6.37 (dd, 1H), and 6.12–6.21 (m, 2H) ppm and eight vinyl carbon signals at 151.3, 145.1, 144.9, 134.4, 132.0, 130.5, 128.7, and 93.5 ppm. It should be pointed out that, although the ^{13}C NMR chemical shifts of the exocyclic double bond of **18** indicate its polarization as in the case of **1a**, the signal for C(2) is not as much downfield shifted as that of **1a**; this implies the presence of a steric effect in the latter. The UV/Vis spectrum of **18** (*n*-hexane) exhibits a strong absorption at 385 nm ($\varepsilon = 3300$), which is consistent with the heptafulvene chromophore.[25] The formation of **18** can be explained in terms of a 1,5-sigmatropic shift of a cyclopropane bond of the propelladiene intermediate **12**, the valence isomer of **1a**, followed by electrocyclic ring opening of the norcaradiene moiety (Scheme 5).



Scheme 5. Mechanism of the fragmentation and isomerization reactions of **1a**.

Irradiation of the extended system **2** in *n*-hexane yielded decapentayne derivative **19**[7a,29] in 59% isolated yield together with the isomerization product **20** in 24% yield as a brown oil. The structure of **20** was also confirmed on the basis of the NMR and UV/Vis spectroscopic data as in the case of **18**. In the electronic absorption spectrum, **20** exhibits a maximum at 428 nm ($\varepsilon = 19400$). In contrast, irradiation of a solution of diphenyl derivative **3** in diethyl ether afforded diphenylhexatriyne (**21**)[31] in slightly lower yield (37%). We were not able to isolate the isomerization product **22**, because it polymerized rapidly when a solution containing **22** was concentrated. Therefore, a solution of **3** in [D$_8$]THF was irradiated under similar conditions, and the photolysate was analyzed by ^1H NMR and liquid-chromatography mass spectroscopy (LCMS). The ^1H NMR spectrum exhibited four vinyl proton signals corresponding to **22** at $\delta = 7.02$–7.09 (m, 1H), 6.38–6.42 (m, 1H), and 6.19–6.27 (m, 2H) ppm and three methylene signals from the five-membered ring of **22** at $\delta = 3.28$ (t, 2H), 2.62 (t, 2H), and 1.91 (quintet, 2H) ppm in addition to the signals of the methylene and aromatic protons of indane and **21**. In the LCMS, an LC peak corresponding to the molecular ion was observed at $m/z = 335$ [M^++H]; this indicated that the product was an isomer of

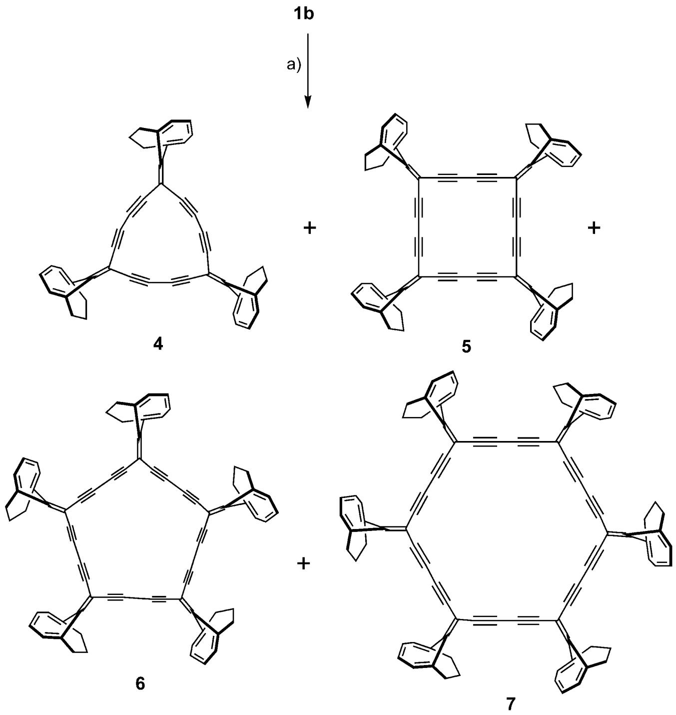


Scheme 4. Cheletropic fragmentation and isomerization by photolysis of **1a**, **2**, and **3**.

the starting material **3**. These results are consistent with the structure formulated for **22**.

Thus the model study showed that photochemical fragmentation took place, as we had expected, to yield linear polyynes. However, because of the formation of the rearrangement products, it was not as efficient as the [2+2] fragmentation of the [4.3.2]propellatrienes.[7a,e] The photochemical fragmentation, therefore, was not investigated for cyclic dehydrooligomers of diethynylmethylenebicyclo[4.3.1]decatriene with expanded radialene frameworks.

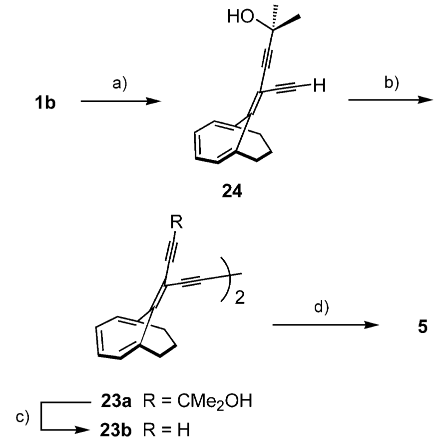
Synthesis of cyclic dehydrooligomers: Macrocyclic dehydrooligomers of **1b** with expanded radialene structures were prepared by its copper(II)-mediated oxidative coupling under dilution conditions. We obtained cyclic dehydrotetramer **5** as the major product (33%) together with cyclic dehydrotrimer **4**, dehydropentamer **6**, and dehydrohexamer **7** in 3%, 15%, and 7% yield, respectively (Scheme 6).



Scheme 6. a) $Cu(OAc)_2$, pyridine, RT, **4** 3%, **5** 33%, **6** 15%, **7** 7%. Only one of the diastereomers is shown for reasons of clarity.

The expanded [3]radialene **4**, which should be considerably strained,[16c,e] is one of the relatively rare members of this class of compounds. It is also worth noting that large macrocycles **6** and **7** were obtained from **1b**, whereas only dehydrotrimer and dehydrotetramer were isolated from the oxidative coupling of the cyclobutene-containing diethynyl[4.3.2]propellatrienes under similar conditions.[7b,e] Solutions of radialenes **4**–**7** could be stored in a cold and dark place for a few months, but after removal of the solvent the solid materials, in particular [3]radialene **4**, tend to decompose more rapidly, in contrast to our initial expectation regarding their kinetic stability.

To obtain even-number cyclic dehydrooligomers, oxidative coupling of dehydrodimer **23b** was examined (Scheme 7). First, one of the terminal alkynyl groups of **1b** was selectively protected by a 2-hydroxypropyl group by treatment with *n*BuLi (1.2 equiv) followed by acetone to afford **24** in 81% yield. Oxidative coupling of **24** under Hay conditions[32] gave bis-protected dehydrodimer **23a**, and removal of the protective group gave **23b** as a stable yellow solid. Oxidative coupling of **23b** under dilution conditions formed cyclic dehydrotetramer **5** exclusively in 91% yield.

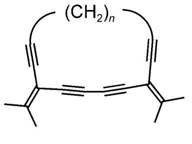


Scheme 7. a) *n*BuLi, THF, −78°C, then acetone, 81%. b) CuCl, TMEDA, O_2, acetone, RT, 93%. c) KOH, benzene, reflux, 93%, d) $Cu(OAc)_2$, pyridine, RT, 91%. Only one of the isomers is shown for reasons of clarity.

The expanded radialenes **4**–**7** exhibit poor solubility in organic solvents, which is minimal to allow spectral characterizations by ^1H NMR, ^{13}C NMR, and UV/Vis spectroscopy.

^{13}C NMR spectra of cyclic dehydrooligomers: The ^{13}C NMR spectra of **4**–**7** indicate clearly that these are mixtures of diastereomers. In particular, several signals are observed for the tertiary sp^2 carbons of the bicyclic triene framework and the bridgehead sp^2 carbons. The ^{13}C NMR chemical shifts of the radialene double bonds suggest that the polarization of the double bonds increases with increasing ring size of the expanded radialene framework (from **4** to **7**). Namely, the chemical shifts of the endocyclic carbons move up field slightly (93.2 to 91.9 ppm), while those of the exocyclic carbons exhibit noticeable downfield shift (160.5 to 170.5 ppm). The same trend was also observed for alkynyl-substituted radialenes by Diederich et al.[16a,e] Selected ^{13}C NMR chemical shift data for expanded radialenes **4**–**7** are shown in Table 1.

Tykwinski et al. studied the effect of strain imposed by the different lengths of the methylene linkage of the cross-conjugated macrocycles **25** by ^{13}C NMR spectroscopy and



25 *n* = 2-5, 7

Table 1. Selected ^{13}C NMR (CDCl$_3$) chemical shifts data (in ppm) of alkene and alkyne carbon atoms in expanded radialenes.

Compound	4		5		6		7	
C(alkyne) δ	77.8	90.3	76.0	79.1	75.3	76.4	75.1	76.3
C(alkene) δ	93.2	160.5	92.3	166.3	92.1	169.3	91.9	170.5

X-ray analysis.[28b] With decreasing number of methylene linkages, the ^{13}C NMR signals of the endocyclic sp^2 carbons of **25** exhibited slight upfield shifts, while those of the sp carbons moved downfield as a result of increased ring strain. These observations were attributed to the increasing p-character of the σ bonds of the endocyclic sp^2 carbons, which imparts more s-character to the double bonds, with decreasing ring size. The bicyclic triene framework of **4**–**7** exerts similar strain effects because of the small bond angle at the bridge top carbon. Perhaps, the effect of both ring systems counteracts the polarization of the exocyclic double bond, thereby reducing the difference between the chemical shifts of the double bond of **4** ($\Delta\delta$ = 67.3 ppm) compared with those of less-strained macrocycles (e.g., **7** $\Delta\delta$ = 78.6 ppm). On the other hand, the ^{13}C NMR chemical shifts of the sp carbons in expanded radialenes **4**–**7** exhibit steady downfield shifts with decreasing ring size. Particularly, one of the sp carbons of the most-strained **4** appeared at considerably lower field (90.3 ppm) than other (**5**–**7**) signals (76–79 ppm).

Electronic-absorption spectra of cyclic dehydrooligomers: The UV/Vis spectra of **4**–**7** in CHCl$_3$ are shown in Figure 4. Although the preparations and purifications were carried out with great care to protect the products from light, the prepared radialenes **4**–**7** exhibited very week absorptions around 460 nm due to the corresponding isomer having the methylenecycloheptatriene moiety produced by photoisomerization like those of **18**, **20**, and **22**. However, taking the large absorption coefficient of the chromophore in **18** and **20** into account, the proportion of the isomerized moiety must be negligible.

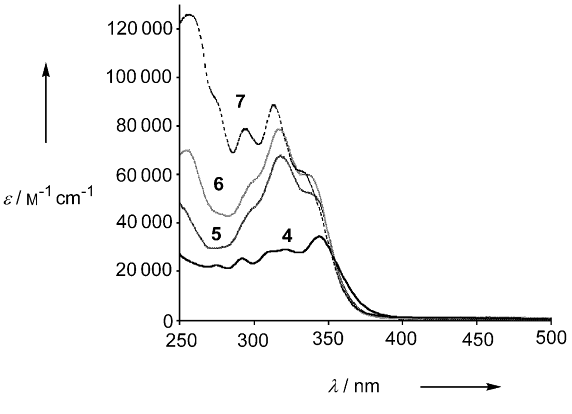
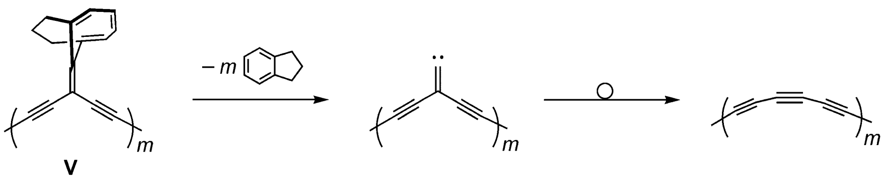


Figure 4. UV/Vis spectra of cyclic dehydrooligomers **4**–**7** in CHCl$_3$.

Recently, Tykwinski et al.[28] reported the electronic effect of cross conjugative interactions in enyne macrocycles. Expanded radialenes and dendralenes are composed of two distinct π-electron systems that are perpendicular to each other. One system represents in-plane p orbitals in the macrocycle, the absorptions of which due to homoconjugation are assigned to the bands at around 260 nm. The other system includes out-of-plane p orbitals in the macrocycle, the absorption bands of which due to the linearly conjugated ene-yne-yne-ene chromophore are expected to occur in a lower energy region than those of the former system. However, it is difficult to discuss the electronic absorptions of **4**–**7** due to homoconjugation of the in-plane p orbitals around 260 nm, since they possess bicyclic triene chromophores, which also absorb in the same region. The out-of-plane absorptions (300–350 nm) do not shift to longer wavelengths with increasing ring size. Conversely, they exhibit small blue shifts on going from **4** to **7** (**4** 344, 318 nm; **5** 340 (*sh*), 318 nm; **6** 337 (*sh*), 317 nm; **7** 334 (*sh*), 313 nm). This is probably due to the decreasing planarity of the macrocycles, which would reduce the overlap of p orbitals in the ene-yne-yne-ene system, since it has been reported that an expanded [6]radialene adopts a chair conformation of the macrocycle.[16e] Although the spectral shapes of **5**–**7** are similar, the spectrum of [3]radialene **4** is apparently different. That is, the relative intensity of the longest-wavelength absorption maximum of **4** is strong, while its molar absorption coefficient is smaller [λ_{max} (ε) = 344 (34500) nm] than those of **5**–**7**. Diederich et al. also reported similar behavior of expanded [3]radialenes.[16c,e] This unusual trend of expanded [3]radialenes might be explained in terms of the effect of strain in the macrocycle on the geometries of the ground and excited states of the molecules. Namely, the excited state geometry of **4** might be reminiscent of that of the ground state due to the geometrical constraint, thereby facilitating the 0–0 transition from S$_0$.

Laser-desorption time-of-flight mass spectra of cyclic dehydrooligomers: With the expanded radialenes **4**–**7** in hand, we investigated the extrusion of indane fragments to produce the vinylidenes that would isomerize to the corresponding cyclo[*n*]carbons (*n* = 18, 24, 30, and 36) (Scheme 8).

To this end, laser-desorption time-of-flight mass spectra of **4**–**7** were measured. As shown in Figure 5a–d, the negative-mode laser-desorption mass spectra of **4**–**7** exhibited peaks due to the cyclo[*n*]carbon anions (*n* = 18, 24, 30, and



Scheme 8. Generation of cyclo[*n*]carbons from **V** via of vinylidenes.

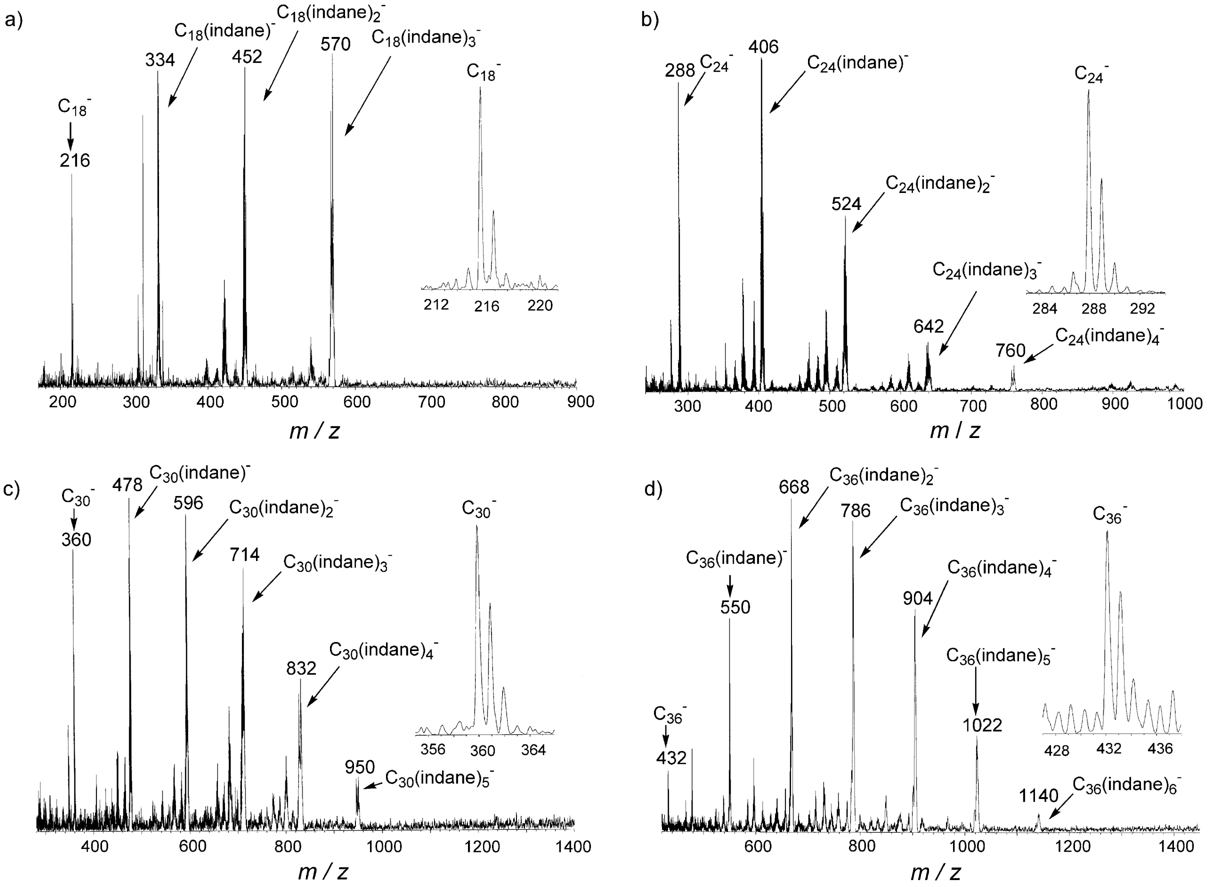


Figure 5. Laser-desorption time-of-flight mass spectra of cyclic dehydrooligomers a) **4** [C_{18}(indane)$_3$], b) **5** [C_{24}(indane)$_4$], c) **6** [C_{30}(indane)$_5$], and d) **7** [C_{36}(indane)$_6$]. Insets: Expansion of the carbon anion peaks.

36) formed by the stepwise loss of the aromatic indane fragments.[33]

At present, we do not have spectroscopic evidence regarding the structures of the carbon cluster anions thus produced. But it is reasonable to assume that these possess cyclocarbon structures given their stability relative to the vinylidenes and the results of the photolysis of acyclic model compounds **1a**, **2**, and **3**. If this is the case, the formation of C_{36}^- represents the first example of a cyclo[36]carbon generated from an organic precursor. Although the intensities of the parent peak relative to those of the fragments depend on the conditions of ionization, relatively strong peaks of C_{18}^-, C_{24}^-, and C_{30}^- were observed. By contrast, C_{36}^-, which was produced by the loss of six indane fragments from **7**$^-$, was only weakly observed (Figure 5d). This may be an indication of the formation of carbon cluster anions of different structures, since the monocyclic form of carbon clusters are most stable within the C_{10}–C_{30} range. Proof would be given by photoelectron spectroscopy of the carbon anions,[7d] which we are planning to carry out in due course.

Conclusion

As an approach to all-carbon molecules from stable precursors, we prepared diethynylmethylenebicyclo[4.3.1]decatriene derivatives **1a**, **2**, and **3**. The model study of the photolysis for acyclic compounds **1a**, **2**, and **3** by UV irradiation revealed that cheletropic fragmentation followed by 1,2-migration gave the corresponding linear polyynes, although undesired isomerization took place concurrently. We prepared the expanded radialenes **4**–**7** by copper(II)-mediated oxidative coupling of **1b** under dilute conditions. In the electronic spectra of **4**–**7**, the absorptions did not exhibit large bathochromic shifts with increasing ring size of the macrocycles **4**–**7**; this indicated the presence of cross-conjugative interactions of the ene-yne-yne-ene chromophores. Laser-desorption mass spectra of the radialenes **4**–**7** exhibited, in the negative mode, peaks due to the corresponding cyclo[*n*]carbon anions ($n = 18$, 24, 30, and 36) formed by the loss of the aromatic indane fragments. It is worth noting that the formation of C_{36}^- from the expanded [6]radialene **7** represents the first example of cyclo[36]carbon generated from an organic precursor.

Experimental Section

General: ^{1}H NMR spectra were recorded at 30 °C and at 270 or 300 MHz and ^{13}C NMR spectra at 67.8, 75, or 125 MHz on a Varian Unity Inova500, a Varian Mercury300, or a JEOL JNM-GSX-270 in $CDCl_3$ and with Me_4Si or residual solvent as an internal standard, unless otherwise stated. IR spectra were recorded by using KBr disks with a JASCO FTIR-410. Electronic spectra were recorded on a HITACHI U-3310 spectrometer. Mass-spectral analyses were performed on a JEOL JMS-DX303HF or a JMS-700 spectrometer for EI and FAB ionization. LCMS analyses were undertaken with a Shimadzu LCMS2010 with an APCI ionizer. For most of the MALDI-TOF mass measurements, a Shimadzu/Kratos AXIMA-CFR spectrometer was employed. Elemental analyses were performed on a Perkin–Elmer 2400II analyzer. Melting points were measured with a hot-stage apparatus and are uncorrected. Column chromatography and TLC were performed with Merck silica gel 60 (70–230 mesh ASTM) and Merck silica gel 60 F_{254}, respectively. Flash chromatography was performed with Fuji Silysia silica gel (BW-300). Analytical GC was carried out on a Shimadzu GC-8A gas chromatograph equipped with a flame-ionization detector. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph by using 600×20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as eluent. All reagents were obtained from commercial suppliers and used as received. Solvents were dried (drying agent in parentheses) and distilled prior to use: THF ($LiAlH_4$ followed by sodium benzophenone ketyl), benzene (CaH_2), pyridine (KOH), acetone (K_2CO_3), pentane (CaH_2).

10,10-Dibromo[4.3.1]propella-2,4-diene (8): Pyridinium hydrobromide perbromide (85.3 g, 0.267 mol) was added to a mechanically stirred solution of **9** (51.9 g, 0.178 mol) in CH_2Cl_2 (645 mL) and pyridine (27 mL). After the mixture had been stirred at room temperature for 2.5 h, an aqueous solution of sodium thiosulfate (0.2 M, ca. 1000 mL) was added, and the reaction mixture was extracted with ether. The organic layer was separated and washed with aqueous sodium thiosulfate (0.2 M) and dried over $MgSO_4$. Removal of the solvent in vacuo afforded 85.9 g of the tetrabromide as a colorless solid, which was employed in the following reaction without further purification.

A solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (144.6 g, 0.950 mol) in toluene (75 mL) was added dropwise over 1.5 h to a mechanically stirred solution of the tetrabromide in toluene (550 mL) under a nitrogen atmosphere. The mixture was stirred at 40 °C for 7 days, then diluted with water (500 mL) and extracted with ether. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave a brown solid, which was purified by chromatography (*n*-hexane) followed by recrystallization from methanol to afford propelladiene **8**[15b,e,f] (19.3 g, 35 %) as a colorless solid.

Ketone adduct 11: A solution of *n*BuLi in *n*-hexane (25.2 mL, 1.50 M) was added dropwise over 3 h to a solution of dibromide **8** (10.1 g, 34.7 mmol) dissolved in THF (70 mL) at −100 °C under a nitrogen atmosphere. After the mixture had been stirred for 2 h at −100 °C, a solution of 1,5-bis(trimethylsilyl)penta-1,4-dien-3-one (**10**)[18] (14.1 g, 62.6 mmol) in THF (50 mL) was added dropwise over 1 h. After being stirred for 2 h, the mixture was slowly warmed to room temperature, then chlorotrimethylsilane (TMSCl; 7.5 g, 69.3 mmol) was added dropwise over 15 min. After being stirred for 1.5 h at room temperature, the mixture was poured into saturated $NaHCO_3$ solution and extracted with ether. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, purification by chromatography (*n*-hexane) gave **11** (7.2 g, 42 %) as a pale yellow solid. The NMR spectra of the product revealed that it consisted of a single diastereomer. **11**: m.p. 87–88 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.04$ (dd, $J = 7.1$, 2.5 Hz, 2H), 5.87 (dd, $J = 7.1$, 2.5 Hz, 2H), 2.99–2.92 (m, 2H), 1.87–1.67 (m, 4H), 0.30 (s, 9H), 0.20 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 128.3$ (d), 122.3 (d), 106.0 (s), 89.3 (s), 70.8 (s), 48.2 (s), 47.8 (s), 35.8 (t), 29.6 (t), 1.5 (q), −0.4 (q); IR (KBr): $\tilde{\nu} = 3033$, 2960, 2901, 2875, 2163, 1451, 1377, 1250, 1105, 1076, 1036, 925, 763, 751, 730, 704 cm^{-1}; MS (FAB) *m*/*z*: 426 $[M^+ + H - Br]$; elemental analysis calcd (%) for $C_{24}H_{37}OSi_3Br$: C 57.00, H 7.38; found: C 56.89, H 7.41.

10-{Bis[(trimethylsilyl)ethynyl]methylene}bicyclo[4.3.1]deca-1,3,5-triene (1a): A solution of *t*BuLi in pentane (2.41 mL, 1.47 M) was added dropwise over 20 min to a solution of the ketone adduct **11** (1.59 g, 3.14 mmol) in THF (38 mL) and pentane (38 mL) at −110 °C. After being stirred for 2 h at −110 °C, the reaction mixture was warmed up slowly to room temperature, followed by addition of TMSCl (630 mg, 0.63 mmol). After 1 h, water was added, and the reaction mixture was extracted with ether. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, purification by chromatography (*n*-hexane) afforded **1a** (842 mg, 80 %) as a colorless solid. **1a**: m.p. 85–86 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.47$–6.45 (m, 2H), 5.97–5.95 (m, 2H), 2.59 (dt, $J = 11.5$, 5.2 Hz, 2H), 2.33–2.27 (m, 2H), 2.13–1.88 (m, 2H), 0.17 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.0$ (s), 138.6 (s), 127.0 (d), 114.6 (d), 99.7 (s), 95.0 (s), 93.1 (s), 50.5 (t), 36.6 (t), 0.0 (q); IR (KBr): $\tilde{\nu} = 3037$, 2954, 2854, 2153, 1655, 1561, 1457, 1334, 1245, 1048, 983, 843, 757, 727, 699 cm^{-1}; UV/Vis (*n*-hexane): λ_{max} (ε) = 258 nm (16500); MS (EI) *m*/*z*: 336 $[M^+]$; elemental analysis calcd (%) for $C_{21}H_{28}Si_2$: C 74.93, H 8.46; found: C 74.83, H. 8.46.

10-(Diethynylmethylene)bicyclo[4.3.1]deca-1,3,5-triene (1b): A solution of $LiOH \cdot H_2O$ (43.6 mg, 1.04 mmol) in H_2O (4 mL) was added over 10 min with stirring to a solution of **1a** (350 mg, 1.04 mmol) in THF (11 mL) at room temperature, followed by addition of THF (11 mL). After 3 h, the mixture was diluted with water and extracted with diethyl ether. The organic layer was washed with saturated $NaHCO_3$ solution and brine, and dried over $MgSO_4$. Removal of the solvent afforded **1b** (205 mg, 100 %) as a colorless solid. **1b**: m.p. 59–61 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.52$–6.49 (m, 2H), 6.04–6.01 (m, 2H), 2.92 (s, 2H), 2.62 (dt, $J = 11.6$, 5.0 Hz, 2H), 2.38–2.32 (m, 2H), 2.17–1.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.0$ (s), 139.0 (s), 127.3 (d), 114.9 (d), 90.8 (s), 78.5 (s), 78.0 (d), 50.9 (t), 36.7 (t); IR (KBr): $\tilde{\nu} = 3272$, 3036, 3002, 2953, 2921, 2853, 2100, 1657, 1561, 1440, 1357, 1331, 1265, 1047, 951, 876, 831, 796, 743, 683 cm^{-1}; UV/Vis (*n*-hexane): λ_{max} (ε) = 246 nm (17600); MS (EI) *m*/*z*: 192 $[M^+]$; elemental analysis calcd (%) for $C_{15}H_{12}$: C 93.71, H 6.29; found: C 93.36, H 6.29.

10-{Bis[(triisoproylylsilyl)butadiynyl]methylene}bicyclo[4.3.1]deca-1,3,5-triene (2): A solution of **1b** (39 mg, 0.20 mmol) in methanol/THF (3 mL, 2:1, *v*/*v*) was added dropwise over 6 min to a mixture of $NH_2OH \cdot HCl$ (73 mg, 1.02 mmol), 70 % aqueous solution of ethylamine (256 mg, 3.98 mmol), and CuCl (20 mg, 0.20 mmol) dissolved in methanol/THF (6 mL, 2:1, *v*/*v*) at 0 °C under a nitrogen atmosphere. After being stirred at room temperature for 30 min, a solution of 1-bromo-2-(triisopropylsilyl)ethyne (**14**)[30] (175 mg, 0.66 mmol) in methanol/THF (5 mL, 2:1, *v*/*v*) was added. The reaction mixture was stirred for 2.5 h at room temperature. During the reaction, the flask was covered with aluminum foils to protect the products from light. After HCl (50 mL, 0.5 N) had been added, the mixture was extracted with ether. The organic layer was washed with saturated $NaHCO_3$ solution and brine, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, purification by flash chromatography (*n*-hexane) afforded **2** (71 mg, 63 %) and the monosubstitution product (8 mg, 10 %) as pale yellow solids. **2**: m.p. 146–147 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.50$–6.47 (m, 2H), 6.02–5.99 (m, 2H), 2.60 (dt, $J = 11.5$, 4.9 Hz, 2H), 2.39–2.33 (m, 2H), 2.17–2.09 (m, 1H), 2.02–1.94 (m, 1H), 1.09 (brs, 42H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.9$ (s), 138.4 (s), 127.5 (d), 115.2 (d), 91.2 (s), 89.5 (s), 88.1 (s), 75.6 (s), 69.9 (s), 50.8 (t), 37.2 (t), 18.5 (q), 11.3 (d); IR (KBr): $\tilde{\nu} = 3039$, 2944, 2866, 2200, 2095, 1634, 1462, 1385, 1335, 1070, 1016, 997, 918, 882, 793, 737, 680 cm^{-1}; UV/Vis (*n*-hexane): λ_{max} (ε) = 306 (19600), 288 (19200), 269 (15400), 256 nm (13300); MS (FAB) *m*/*z*: 552 $[M^+]$; elemental analysis calcd (%) for $C_{37}H_{52}Si_2$: C 80.36, H 9.48; found: C 80.20, H 9.64.

Monosubstitution product: m.p. 67–69 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.51$–6.48 (m, 2H), 6.03–5.97 (m, 2H), 2.92 (s, 1H), 2.67–2.56 (m, 2H), 2.39–2.32 (m, 2H), 2.17–2.06 (m, 1H), 2.02–1.94 (m, 1H), 1.08 (brs, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.0$ (s), 138.8 (s), 138.6 (s), 127.5 (d), 127.3 (d), 115.3 (d), 114.8 (d), 91.0 (s), 89.6 (s), 87.9 (s), 78.3 (d), 77.9 (s), 75.4 (s), 70.5 (s), 50.9 (t), 37.1 (t), 36.8 (t), 18.6 (q), 11.3 (d); IR (KBr): $\tilde{\nu} = 3299$, 3033, 2944, 2866, 2203, 2094, 1651, 1561, 1461, 1335, 1074, 1018, 995, 915, 883, 856, 838, 795, 735, 681 cm^{-1}; MS (FAB) *m*/*z*: 372 $[M^+]$.

10-[Bis(phenylethynyl)methylene]bicyclo[4.3.1]deca-1,3,5-triene (3): $PdCl_2(PPh_3)_2$ (73 mg, 0.104 mmol) and CuI (40 mg, 0.21 mmol) were added under an argon atmosphere to a solution of iodobenzene (835 mg, 4.09 mmol) in Et_3N (100 mL), which had been degassed thoroughly by bubbling argon for 2 h. After the mixture had been stirred at room temperature for 5 min, a solution of **1b** (198 mg, 1.03 mmol) in degassed Et_3N (50 mL) was added dropwise over 20 min. After 20 h, the solvent was removed under reduced pressure. The residue was subjected to chromatography (*n*-hexane/diethyl ether 10:0 to 9:1) to afford **3** (323 mg, 91 %) as a pale yellow solid, together with iodobenzene (401 mg). **3**: m.p. 110–111 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.46 (m, 4H), 7.32–

7.28 (m, 6H), 6.53–6.52 (m, 2H), 6.06–6.04 (m, 2H), 2.71 (dt, J = 11.5, 5.1 Hz, 2H), 2.38 (ddd, J = 11.5, 5.1, 1.2 Hz, 2H), 2.20–2.12 (m, 1H), 2.09–1.94 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 165.0 (s), 139.2 (s), 131.8 (d), 128.1 (d), 127.2 (d), 123.3 (s), 115.1 (d), 92.9 (s), 89.7 (s), 84.7 (s), 50.9 (t), 36.9 (t); IR (KBr): $\tilde{\nu}$ = 3040, 2918, 2850, 1654, 1490, 1441, 1340, 1317, 1100, 1069, 960, 916, 885, 839, 800, 755, 736, 690 cm^{-1}; UV/Vis (n-hexane): $\lambda_{\max}$ (ε) = 275 nm (37700); MS (EI) m/z: 344 [M^+]; elemental analysis calcd (%) for C$_{27}$H$_{20}$: C 94.15, H 5.85; found: C 93.75, H 5.67.

[2+2+2] Cycloadduct 13: A solution of **1a** (43 mg, 0.13 mmol) and N-phenylmaleimide (24 mg, 0.14 mmol) in toluene (2.0 mL) was heated at reflux with stirring under a nitrogen atmosphere. After 7 h, the solvent was removed under reduced pressure. The residue was purified by flash chromatography (n-hexane/ether 9:1) followed by preparative HPLC to afford the adduct **13** (53 mg, 81 %) as a colorless solid. **13**: m.p. 213–215 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.46–7.33 (m, 3H), 7.18–7.13 (m, 2H), 6.09–6.03 (m, 2H), 3.61 (brs, 2H), 3.31 (brs, 2H), 2.03–1.96 (m, 2H), 1.91–1.69 (m, 3H), 1.60–1.44 (m, 1H), 0.19 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 177.8 (s), 154.2 (s), 131.8 (s), 131.3 (d), 129.1 (d), 128.6 (d), 126.4 (d), 103.2 (s), 100.0 (s), 94.5 (s), 40.7 (d), 35.1 (d), 34.9 (s), 27.8 (t), 27.7 (t), 0.1 (q); IR (KBr): $\tilde{\nu}$ = 3057, 2958, 2899, 2863, 2154, 1776, 1714, 1597, 1499, 1387, 1249, 1221, 1183, 1036, 978, 957, 842, 750, 737, 699 cm^{-1}; LD-TOF MS (negative ion mode) m/z: 509.2 [M^-]; elemental analysis calcd (%) C$_{31}$H$_{35}$NO$_2$Si$_2$: C 73.04, H 6.92; found: C 72.74, H 6.99.

Photolysis of 1a: Nitrogen was bubbled into a solution of **1a** (40.0 mg, 0.12 mmol) in n-hexane (3 mL) in a quartz tube. The solution was irradiated in an ice bath with a 60 W low-pressure mercury lamp for 6 h. The solvent and indane were removed by evaporation, and the products were separated by preparative HPLC to afford **17** (14.0 mg, 46 %) as a colorless solid and **18** (14.6 mg, 30 %) as a reddish brown oil. The quantity of indane formed was determined by calibrated GC with undecane as an internal standard. **18**: ^{1}H NMR (270 MHz, CDCl$_3$): δ = 6.90 (dd, J = 9.7, 2.1 Hz, 1H), 6.37 (d, J = 9.7 Hz, 1H), 6.21–6.12 (m, 2H), 3.14 (t, J = 7.4 Hz, 2H), 2.63 (t, J = 7.4 Hz, 2H), 1.86 (quin, J = 7.4 Hz, 2H), 0.21 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 151.3 (s), 145.1 (s), 144.9 (s), 134.4 (d), 132.0 (d), 130.5 (d), 128.7 (d), 104.8 (s), 103.7 (s), 100.4 (s), 99.8 (s), 93.5 (s), 38.7 (t), 38.3 (t), 24.0 (t), 0.1 (q), −0.2 (q); IR (KBr): $\tilde{\nu}$ = 3025, 2957, 2925, 2852, 2136, 1542, 1249, 1041, 945, 842, 758 cm^{-1}; UV/Vis (n-hexane): $\lambda_{\max}$ (ε) = 385 nm (3300); MS (EI) m/z: 336 [M^+]; HRMS (EI) calcd for C$_{21}$H$_{28}$Si$_2$: 336.1730; found: 336.1750.

Photolysis of 2: Irradiation of **2** (40.0 mg, 0.072 mmol) in n-hexane (3 mL) was conducted as described above for 6 h. The products were separated by flash chromatography (n-hexane) to afford **19** (18.3 mg, 59 %) as a pale yellow solid and a mixture of the starting material **2** and its isomer **20** (11.7 mg). The amount of **20** (24 %) was estimated by ^{1}H NMR integration of the vinyl proton of **20** relative to that of **2** for the mixture. The mixture was further irradiated as described above to consume **2** completely. Pure sample **20** was thus isolated in 12 % yield after chromatography followed by preparative HPLC. Indane was detected in the crude products by ^{1}H NMR (irradiation in [D$_8$]THF) and by GC. **20**: ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.13–7.07 (m, 1H), 6.48–6.44 (m, 1H), 6.30 (dt, J = 5.4, 4.5 Hz, 2H), 3.14 (t, J = 7.2 Hz, 2H), 2.65 (t, J = 7.2 Hz, 2H), 1.90 (quin, J = 7.2 Hz, 2H), 1.01 (brs, 42H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 155.9 (s), 147.7 (s), 146.5 (s), 135.2 (d), 133.1 (d), 131.8 (d), 130.6 (d), 91.3 (s), 90.4 (s), 90.2 (s), 90.0 (s), 81.6 (s), 80.9 (s), 74.9 (s), 74.1 (s), 39.3 (t), 38.7 (t), 24.0 (t), 18.6 (q), 11.40 (d), 11.39 (d); IR (KBr): $\tilde{\nu}$ = 3028, 2942, 2865, 2174, 2089, 1529, 1458, 1289, 1242, 1072, 996, 882, 763, 678, 661 cm^{-1}; UV/Vis (n-hexane): $\lambda_{\max}$ (ε) = 428 (19400), 304 (12700), 285 (13700), 270 nm (11100); MS (EI) m/z: 552 [M^+].

Photolysis of 3: Irradiation of **3** (38.0 mg, 0.109 mmol) in diethyl ether (3 mL) was conducted as described above for 10 h. The products were separated by flash chromatography (n-hexane) to afford **21** (9.0 mg, 37 %) as a pale yellow solid. Indane was detected in the crude products by ^{1}H NMR (irradiation in [D$_8$]THF) and by GC. **21** was detected in the crude products by ^{1}H NMR (irradiation in [D$_8$]THF) and by LCMS (m/z: 335 [M^++H]).

Cyclic dehydrooligomers 4–7: Compound **1b** (280 mg, 1.46 mmol) in pyridine (150 mL) was added through a Hershberg dropping funnel over 21 h to a suspension of Cu(OAc)$_2$ (3.98 g, 22.0 mmol) in pyridine (300 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h, with all apparatus covered with aluminum foil to shield the mixture from light. The solvent was concentrated to ca. 200 mL, and the mixture was passed through a column of silica gel (CHCl$_3$). Most of the solvent was removed under reduced pressure to leave ca. 20 mL. The poorly soluble dehydrotetramer **5** was filtered off and washed with ether and CHCl$_3$. The solid was purified by flash chromatography (CHCl$_3$) to afford **5** (89 mg) as an orange solid. The filtrate was concentrated under reduced pressure, diluted with HCl (100 mL, 0.5 N), and extracted with CHCl$_3$. The organic layer was washed with saturated NaHCO$_3$ solution and brine, and dried over MgSO$_4$. After most of the solvent had been removed under reduced pressure, the mixture was again passed through a column of silica gel (CHCl$_3$). The solvent was removed by evaporation, and the products were separated by preparative HPLC. Further purification by flash chromatography (CHCl$_3$) afforded dehydrotrimer **4** (8 mg, 3 %) as a red solid, dehydrotetramer **5** (3 mg, combined yield 33 %) as an orange solid, dehydropentamer **6** (42 mg, 15 %) as a reddish orange solid, and dehydrohexamer **7** (20 mg, 7 %) as a yellow solid. **4**: decomposed gradually from ca. 150 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.47–6.41 (m, 6H), 5.96–5.91 (m, 6H), 2.58–2.47 (m, 6H), 2.32–2.24 (m, 6H), 2.14–1.85 (m, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 160.59 (s), 160.52 (s), 160.47 (s), 138.76 (s), 138.69 (s), 138.66 (s), 138.60 (s), 127.65 (d), 127.63 (d), 115.32 (d), 93.20 (s) and two small peaks at 93.23 (s) and 93.18 (s), 90.25 (s), 90.20 (s), 77.80 (s) and a small peak at 77.82 (s), 51.05 (t), 36.88 (t); IR (KBr): $\tilde{\nu}$ = 3037, 2939, 2848, 2187, 1660, 1455, 1349, 1071, 1046, 963, 955, 843, 814, 736 cm^{-1}; UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 344 (34500), 321 (29100), 312 (28300), 275 nm (22600); LD-TOF MS (negative ion mode) m/z: 569.9 [M^-].

5: decomposed gradually from ca. 140 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.49–6.42 (m, 8H), 5.99–5.94 (m, 8H), 2.64–2.48 (m, 8H), 2.36–2.26 (m, 8H), 2.16–1.86 (m, 8H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 166.30 (s), 138.79 (s), 138.77 (s), 138.66 (s), 138.62 (s) and two small peaks 138.72 and 138.70, 127.64 (d), 127.61 (d), 115.29 (d), 92.30 (s), 79.11 (s), 76.01 (s), 51.00 (t), 37.02 (t); IR (KBr): $\tilde{\nu}$ = 3036, 2939, 2914, 2849, 2208, 1650, 1436, 1351, 1074, 1048, 965, 955, 838, 733 cm^{-1}; UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 340 (sh, 51700), 318 nm (67600); LD-TOF MS (negative ion mode) m/z: 760.1 [M^-].

6: decomposed gradually from ca. 160 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.51–6.45 (m, 10H), 6.03–5.98 (m, 10H), 2.69–2.52 (m, 10H), 2.40–2.28 (m, 10H), 2.17–1.90 (m, 10H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 169.30 (s), 138.78 (s), 138.72 (s), 138.64 (s), 138.56 (s), 127.59 (d), 127.52 (d), 115.34 (d), 115.29 (d), 92.06 (s), 76.42 (s), 76.41 (s), 75.31 (s), 75.28 (s), 50.91 (t), 37.22 (t); IR (KBr): $\tilde{\nu}$ = 3035, 2936, 2914, 2849, 2210, 1644, 1436, 1347, 1080, 954, 906, 879, 838, 733 cm^{-1}; UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 337 (sh, 59700), 317 nm (78600); LD-TOF MS (negative ion mode) m/z: 950.2 [M^-].

7: decomposed gradually from ca. 140 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.51–6.44 (m, 12H), 6.02–5.96 (m, 12H), 2.67–2.52 (m, 12H), 2.39–2.28 (m, 12H), 2.16–1.89 (m, 10H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 170.53 (s), 138.73 (s), 138.70 (s), 138.57 (s), 127.55 (d) and a small peak at 127.47 (d), 115.24 (d), 91.92 (s), 76.28 (s), 76.15 (s), 75.13 (s), 50.84 (t), 37.20 (t); IR (KBr): $\tilde{\nu}$ = 3034, 2932, 2914, 2850, 2212, 1638, 1436, 1345, 1087, 953, 907, 837, 793, 734 cm^{-1}; UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 334 (sh, 60800), 313 (88500), 294 nm (78800); LD-TOF MS (negative ion mode) m/z: 1140.3 [M^-].

Singly protected bicyclic triene 24: A solution of nBuLi in n-hexane (5.3 mL, 1.59 M) was added dropwise over 40 min to a solution of **1b** (1.47 g, 7.65 mmol) in THF (140 mL) cooled to −78 °C under an argon atmosphere. After 2 h, acetone (0.63 g, 10.3 mmol) was added dropwise over 5 min. The reaction mixture was stirred at −78 °C for 1 h and then slowly warmed up to room temperature. The mixture was poured into saturated NaHCO$_3$ solution and extracted with ether. The organic layer was washed with brine and dried over MgSO$_4$. After removal of the solvent under reduced pressure, purification by flash chromatography (n-hexane/EtOAc 9:1 to 5:5) yielded **24** (1.54 g, 81 %) as a yellow oil, the doubly protected product (0.26 g, 10 %) as a pale yellow solid, and unreacted **1b** (90 mg). **24**: ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.51–6.50 (m, 2H), 6.04–6.00 (m, 2H), 2.91 (s, 1H), 2.68–2.54 (m, 2H), 2.34–2.31 (m, 2H), 2.18–1.91 (m, 3H), 1.55 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 166.49 (s), 139.02 (s), 138.98 (s), 127.30 (d), 127.08 (d), 114.94 (d), 114.82 (d), 94.57 (s), 91.15 (s), 78.92 (s), 77.47 (d), 65.48 (s), 50.83 (t), 36.79 (t), 36.60 (t), 31.32 (q); IR (KBr): $\tilde{\nu}$ = 3392, 3287, 3034, 2981, 2933, 2852, 2101, 1441, 1363, 1338, 1270, 1165, 950, 896, 838, 752, 730 cm^{-1}; MS (EI) m/z: 250 [M^+]; HRMS (EI) calcd for $C_{18}H_{18}O$: 250.1358; found: 250.1364.

Doubly protected product: m.p. 126–127 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.47–6.45 (m, 2H), 5.98–5.96 (m, 2H), 2.57 (dt, J = 11.4, 5.1 Hz, 2H), 2.19–1.85 (m, 4H), 1.52 (s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 164.97 (s), 138.99 (s), 127.05 (d), 114.80 (d), 94.12 (s), 91.54 (s), 77.34 (s), 65.44 (s), 50.72 (t), 36.62 (t), 31.34 (q), 31.33 (q); IR (KBr): $\tilde{\nu}$ = 3341, 3033, 2979, 2936, 2852, 1655, 1561, 1455, 1375, 1361, 1288, 1231, 1167, 1140, 952, 904, 838, 731 cm^{-1}; MS (EI) m/z: 308 [M^+]; HRMS (EI) calcd for $C_{21}H_{24}O_2$: 308.1776; found: 308.1760.

Doubly protected bicyclic triene dehydrodimer 23a: A mixture of CuCl (1.01 g, 9.74 mmol) and tetramethylethylenediamine (385 mg, 3.31 mmol) in acetone (20 mL) was stirred at room temperature for 1 h, and the blue skim of this mixture was used as a catalyst. The catalyst solution (7.5 mL) was added dropwise over 10 min to an air-saturated solution of **24** (1.54 g, 6.16 mmol) in acetone (120 mL), and the reaction mixture was stirred at room temperature for 17 h while air was bubbled through a needle immersed in the solution. After HCl (200 mL, 0.5 N) had been added, the acetone was evaporated in vacuo, and the residue was extracted with ether. The organic layer was washed with saturated NaHCO$_3$ solution and brine, and dried over MgSO$_4$. After removal of the solvent under reduced pressure, purification by flash chromatography (n-hexane/EtOAc 9:1 to 7:3) afforded **23a** (1.43 g, 93 %) and recovered **24** (40 mg). **23a**: m.p. 89–90 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.47–6.45 (m, 4H), 6.01–5.96 (m, 4H), 2.63–2.52 (m, 4H), 2.36–2.28 (m, 4H), 2.17–1.88 (m, 6H), 1.52 (s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 168.23 (s), 138.81 (s), 138.71 (s), 127.27 (d), 127.23 (d), 115.26 (d), 114.71 (d), 94.91 (s), 91.59 (s), 76.80 (s), 76.26 (s), 74.37 (s), 65.45 (s), 50.78 (t), 37.10 (t), 36.68 (t), 31.31 (q), 31.29 (q); IR (KBr): $\tilde{\nu}$ = 3386, 3034, 2980, 2934, 2850, 2215, 1654, 1439, 1363, 1335, 1266, 1166, 951, 838, 729 cm^{-1}; MS (EI) m/z: 498 [M^+]; HRMS (EI) calcd for $C_{36}H_{34}O_2$: 498.2559; found: 498.2557.

Bicyclic triene dehydrodimer 23b: Powdered KOH (12 mg, 0.21 mmol) was added with stirring to a solution of **23a** (90 mg, 0.18 mmol) in benzene (25 mL). The mixture was heated at 95 °C so that the solvent slowly distilled out. After completion of the reaction (monitored by HPLC), the mixture was cooled to room temperature and HCl (100 mL, 0.5 N) was added. The mixture was extracted with ether, and the organic layer was washed with saturated NaHCO$_3$ solution followed by brine and dried over MgSO$_4$. Removal of the solvent gave **23b** (64 mg, 93 %) as a pale yellow solid. **23b**: decomposed gradually from ca. 160 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.49–6.47 (m, 4H), 6.02–5.99 (m, 4H), 2.91 (s, 2H), 2.60 (dt, J = 11.6, 5.1 Hz, 4H), 2.37–2.32 (m, 4H), 2.15–2.08 (m, 2H), 2.05–1.89 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 169.9 (s), 138.9 (s), 138.7 (s), 127.5 (d), 127.3 (d), 115.3 (d), 114.9 (d), 91.2 (s), 78.3 (d), 77.8 (s), 74.7 (s), 50.9 (t), 37.1 (t), 36.8 (t); IR (KBr): $\tilde{\nu}$ = 3275, 3036, 2939, 2914, 2848, 1640, 1433, 1330, 1222, 1046, 951, 903, 839, 795, 741, 684 cm^{-1}; UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 323 (15200), 305 (19000), 285 nm (17300); MS (EI) m/z: 382 [M^+]; elemental analysis calcd (%) for $C_{32}H_{22}$: C 94.20, H 5.80; found: C 93.95, H 5.77.

Oxidative coupling of 23b: Compound **23b** (101 mg, 0.26 mmol) in pyridine (250 mL) was added through a Hershberg dropping funnel over 20 h to a suspension of Cu(OAc)$_2$ (3.84 g, 21.1 mmol) in pyridine (200 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 h, with all apparatus covered with aluminum foil to shield it from light. The solvent was concentrated to ca. 200 mL, and the mixture was passed through a column of silica gel (CHCl$_3$). After removal of the solvent, the crude product was purified by flash chromatography (CHCl$_3$) followed by preparative HPLC to afford **5** (91 mg, 91 %) as an orange solid.

Crystal data for 1b: Crystal dimensions 0.42 × 0.42 × 0.34 mm, orthorhombic, space group $Pnma$ (#62), ρ_{calcd} = 1.150 g cm^{-3}, Z = 4, a = 13.0782(2), b = 12.3136(2), c = 6.8979(1) Å, V = 1110.84 Å^3, $2\theta_{\max}$ = 55°, Mo$_{K\alpha}$ radiation (λ = 0.71069 Å), T = −100 °C. Of the 20913 reflections that were collected, 1329 were unique. The structure was solved by direct methods (SIR92) and expanded by using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 1329 of all reflections ($2\theta < 54.96$) and 99 variable parameters, and converged with R = 0.079, R_w = 0.090. CCDC-208630 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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