Synthesis of Cyclo-1,3-dien-5-ynes**

Henning Hopf* and Anke Krüger[a]

Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday

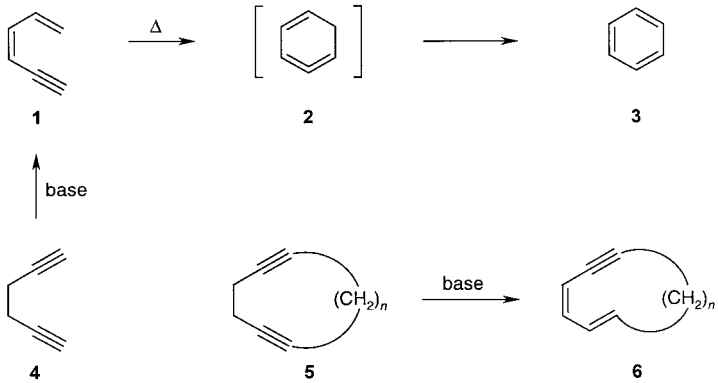
Abstract: Cyclo-1,3-dien-5-ynes with ring sizes from 10 to 14 (**6a–e**) have been prepared for the first time by using a five-step synthesis starting from the alkynols **7a–e**. The final ring-closure was achieved by McMurry coupling of the α,ω-dialdehydes **12a–e** with the complex $TiCl_3(DME)_{1.5}$. Thermal isomerization of the cyclodienynes leads to the corresponding benzocycloalkenes, and it has been shown that the ring size has a considerable influence on the temperature necessary for thermocylization.

Keywords: alkynes · bridged furans · cyclodienynes · cyclization · McMurry coupling

Introduction

The thermal cyclization of hexa-1,3-dien-5-yne (**1**) to benzene (**3**) is the "dihydro variant" of the celebrated Bergman cyclization.[2] At temperatures above 200 °C this electrocyclization begins with the formation of isobenzene (**2**, cyclohexa-1,2,4-triene),[3] which subsequently stabilizes itself by a hydrogen shift process to **3**.[4–7] (Scheme 1).

Whereas in the Bergman cyclization of hex-3-en-1,5-diynes the cycloaromatization requires the "addition" of external hydrogen atoms (which may be furnished either by simple hydrogen donors, such as cyclohexa-1,4-diene, or also by very complex ones, such as DNA[2]), the substrate **1** is "self sufficient", no external hydrogen source being necessary for its cyclization. Having studied the mechanism of the **1** → **3** cyclization in great detail[4, 5] and having, furthermore, used this process for the synthesis of a number of novel aromatic hydrocarbons,[5, 8] we became interested in incorporating the hexa-1,3-dien-5-yne unit into cyclic ring systems. Since the terminal carbon atoms of **1** have to be joined during the isomerization step, it appears reasonable to assume that the interconnection of these positions through a molecular bridge should facilitate the process. Comparable experiments have been carried out for the Bergman cyclization, and it has been shown that the cyclization temperature required can be reduced significantly (from ca. 200 °C for the parent hydrocarbon[9] to room temperature for cyclodeca-1,5-diyne-3-ene, for example[10]). Before we began our preparative efforts to find a route to the cyclo-1,3-dien-5-ynes, we carried out semiempirical calculations[11] on the stability of these unsaturated hydrocarbons. According to these estimates, the ring strain in cyclodeca-1,3-dien-5-yne ($C_{10}H_{12}$) should be sufficiently low to permit the isolation of this hydrocarbon. In fact, this compound is the only currently known isolable member of this series, having been prepared by Hanack and coworkers many years ago.[12] However, the reaction sequence published at that time is quite elaborate and not easily adapted to other ring sizes. In this paper, we report on a general synthesis of the cyclo-1,3-dien-5-ynes with ring sizes of between ten and fourteen members, and present exploratory experiments on their thermal cyclization.



Scheme 1. The thermal cyclization of hexa-1,3-dien-5-yne (**1**) to benzene (**3**).

Results and Discussion

Since the base-catalyzed isomerization of hexa-1,5-diyne (**4**) to **1** is a very well known process in hydrocarbon chemistry—it is in fact the fundamental process of Sondheimer's annulene

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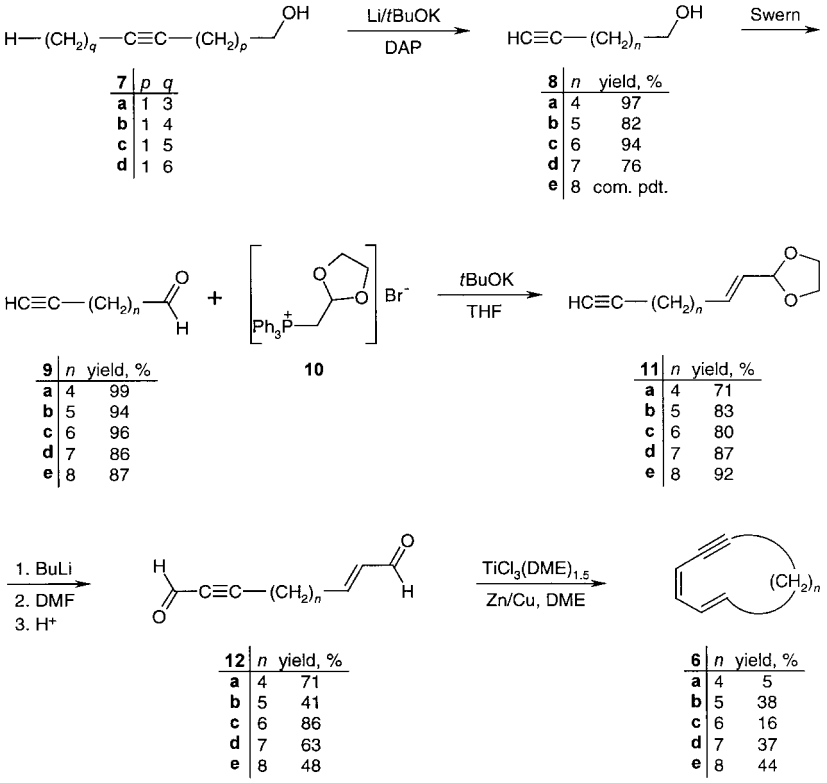
chemistry[13] and has also been studied extensively from the mechanistic viewpoint[14]—we initially thought that it should be effortlessly adaptable to converting cyclo-1,5-diynes **5** into their conjugated isomers **6**. The starting materials **5** are now readily available, thanks to the synthetic efforts of Gleiter and co-workers.[15] As a model compound, cycloundeca-1,5-diyne (**5**, $n = 5$) was selected. However, to our surprise, all isomerization reactions, with a large variety of bases and different conditions, failed.[16] Either the starting cyclodiyne did not rearrange at all, or isomerization would set in uncontrollably, leading to a product mixture containing numerous isomerization products that could not be separated. After a series of other unsuccessful approaches—including inter alia pinacolization, Barbier and Sonogashira coupling reactions, and ring-closing metathesis of appropriately functionalized precursor systems[11]—the sequence summarized in Scheme 2 was finally successful.

The starting materials were the alkynols **7**, all of them readily available commercially or from propargyl alcohol by standard treatments. These were first subjected to an acetylene zipper reaction[17] by using Abrams' method, which involves treatment of the acetylenic alcohols with lithium powder and potassium *tert*-butoxide in 1,3-diaminopropane (DAP).[18] The advantage of this variant over Brown's classical procedure[17] is the improved safety and the consistently good to excellent yield of the desired terminal alkynols; yields in the 80–100% range are typically achieved after purification by distillation; this permits preparation of the starting materials on the multigram scale. Subsequent Swern oxidation[19] of **8a–e** afforded the corresponding aldehydes **9a–e**, which could be used without further purification, again in good yield. However, these intermediates are unstable toward oxygen and can only be stored for prolonged periods when kept under argon. The higher homologues of **9** crystallize on standing in the freezer.

The next step involved chain elongation with the ylide prepared from the phosphonium salt **10**, a process often used to prepare α,ω-unsaturated aldehydes.[20] In contrast to the procedures reported in the literature, work up was carried out under neutral conditions to avoid removal of the protecting group. The yields of the ketals **11**, isolated as colorless oils, were around 80%, and they were produced as mixtures of *E* and *Z* isomers in ca. 2.5:1 ratios (GC analysis). It was not possible to separate the diastereomers by preparative gas chromatography but, when solutions of them in tetrahydrofuran were treated with aqueous oxalic acid, the deprotected *E* aldehydes were generated in a pure state. This observation was put to use when the derivatives **11** were subjected to a second chain extension step to give the dialdehydes **12**. The ketals **11** were metallated with butyl lithium in diethyl ether, and the resulting acetylides were quenched with DMF. Work up under acidic conditions removed the protecting group and induced $Z \rightarrow E$ isomerization, resulting in the formation of the dialdehydes **12**, which, after rapid chromatographic purification at low temperature, were obtained as colorless oils. They could only be stored for a limited time under argon in the refrigerator and, hence, should be used as quickly as possible.

The synthesis of the desired cyclo-1,3-dien-5-ynes **6** was finally accomplished by means of a McMurry-type coupling of **12**, by using $TiCl_3(DME)_{1.5}$ (DME = dimethoxyethane) as the titanium source and a zinc/copper couple as the reducing agent.[21] Whereas **6a** and **6b** were formed even at room temperature, the higher homologues required boiling DME. The yields of the cyclodienynes (see Scheme 2) do not show any particular trend. For the lower members of the series, their low thermal stabilities (see below) and their high volatilities certainly contributed to a yield reduction. Complete removal of the solvent was only possible with heavy losses of product. We also noted the formation of higher-molecular-weight material, but found no evidence that this was produced by the formation of dimers or trimers. The products **6a–e** were characterized by the usual spectroscopic methods as described in the Experimental Section. The assignment of the (1*E*,3*Z*) stereochemistry shown in Scheme 2 is largely based on the coupling constants between the olefinic protons. Whereas the coupling constants between the protons at C-3 and C-4 amount to 10.5 ± 0.5 Hz, constants of 15.8 ± 0.1 Hz are observed between the protons at



7	p	q
a	1	3
b	1	4
c	1	5
d	1	6

8	n	yield, %
a	4	97
b	5	82
c	6	94
d	7	76
e	8	com. pdt.

9	n	yield, %
a	4	99
b	5	94
c	6	96
d	7	86
e	8	87

11	n	yield, %
a	4	71
b	5	83
c	6	80
d	7	87
e	8	92

12	n	yield, %
a	4	71
b	5	41
c	6	86
d	7	63
e	8	48

6	n	yield, %
a	4	5
b	5	38
c	6	16
d	7	37
e	8	44

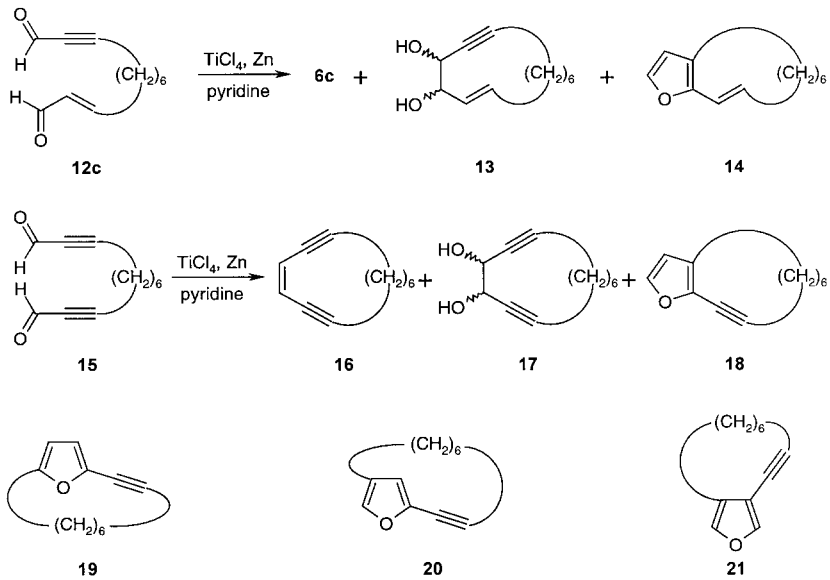
Scheme 2. The preparation of the cyclodienynes **6**.

C-1 and C-2. Furthermore, the ^{1}H NMR spectrum of (7*Z*,9*E*)-octadeca-7,9-dien-5-yne, an open-chain model for the cyclodienynes **6**, has recently become available.[22] For this dienyne, a value of 10.3 Hz was observed for J_{cis} and one of 15.4 Hz for J_{trans}; this is in excellent agreement with the data for the cyclic hydrocarbons **6**.

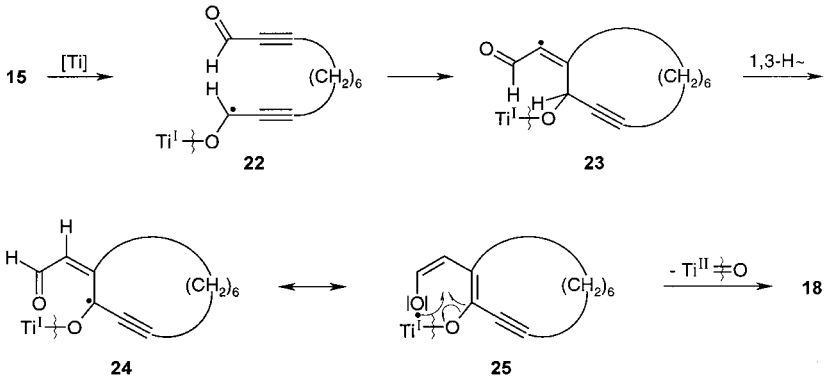
Over all five steps, the hydrocarbons **6** could be prepared in isolated yields between 2% ($n=4$) and 22% ($n=8$), no optimization so far having been attempted. Because of their *trans*-configured double bonds, the dienynes **6** are inherently chiral. However, attempts to resolve them on a chiral column (cyclodextrin)[23] have so far met with failure. Whether this is due to a low enantiomerization barrier or to not yet having found the right resolution conditions is unknown at present.

Interestingly, when other conditions for the McMurry coupling were applied, different results were obtained. For example, in a qualitative experiment under the conditions proposed by Lenoir[24] ($TiCl_4$, Zn powder, pyridine, terahydrofuran), **12c** provided a complex mixture comprising **6c** and two oxygen-containing compounds. Structures **13** and **14** (Scheme 3) were assigned to these, largely on the basis of GC/MS analysis. Although they could not be obtained in pure form, we are confident about our structure assignment, largely because of the similarity of their spectroscopic and analytical data to those of the acetylene **18** (see below). To reduce the complexity of the product mixture, we replaced **12c** with the more symmetrical dialdehyde **15** in a second experiment. In this case the McMurry coupling provided the corresponding products **16** (2.6%), **17** (16%), and **18** (7%). Again, it was easy to assign a furan structure to the last product, but the ring positions in which the bridging alkynyl chain was anchored were not initially obvious. Comparison with the NMR spectra of model compounds,[25] however, indicated that structure **18** must be correct. For the alternative **19** a coupling constant of about 3.4 Hz would be expected for the furan-ring hydrogen atoms, whereas in **20** it should amount to 0.9 Hz and in **21** to 1.5 Hz. For **18** a value of 1.8 Hz was observed.

Although no mechanistic studies were undertaken to elucidate the mechanism of formation of the unexpected "furanophanes", we believe that the interpretation offered in Scheme 4 for **18** is reasonable.



Scheme 3. Furan formation during McMurry coupling of the unsaturated dialdehydes **12** and **15**.



Scheme 4. Mechanism of furan formation.

The process begins with the formation of radical **22** on the surface of the activated titanium. This intermediate may be reduced a second time to provide the corresponding diyl, which can collapse to the intermediate that, on hydrolysis, will furnish the diol **17** or the endiyne **16**. Alternatively, the radical centre in **22** may be trapped intramolecularly by the unreduced ynal function to provide the cyclic radical **23**. This stabilizes itself through a 1,3-hydrogen shift, and the resulting radical **24** ↔ **25** can undergo terminal ring-closure to **18** by deoxygenation. It seems likely that the cyclization products **6c**, **13**, and **14** are produced by a similar mechanism in the case of **12c**.

The anticipated thermal cyclizations of the monocyclic precursor hydrocarbons **6** to the corresponding benzocycloalkenes were studied in a series of exploratory experiments by heating the starting materials in tetradeuterio-*ortho*-dichlorobenzene and monitoring the cycloaromatization by ^{1}H NMR spectroscopy. As shown in Scheme 5—and already mentioned above—the ten-membered ring system **6a** already begins to aromatize at room temperature.

As expected, the higher homologues require higher temperatures, a trend that has also been observed in the Bergman cyclization of cyclic endiynes.[10] For a thorough understanding of the cyclization process it will now be necessary to

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6a-e

26	n	$T_{cycl.}$, °C
a	4	room temp.
b	5	100
c	6	150
d	7	210
e	8	>210

Scheme 5. Thermal cyclization of the cyclodienynes **6** to the benzocycloalkenes **26**.

investigate the kinetics of the reaction. We hope to report on these results in due course.

Experimental Section

General remarks: All moisture-sensitive reactions were carried out in flame-dried glassware under nitrogen or argon. When necessary, commercially available reagents and solvents were purified and dried by standard methods immediately prior to use. IR: Nicolet 320 FT-IR spectrometer. UV/Vis: HP 8452 A Diode Array spectrophotometer. ^{1}H and ^{13}C NMR: Bruker AC 200 or Bruker DRX 400 spectrometer at 200.1 and 50.3, or 400.1 and 100.6 MHz, respectively; chemical shifts refer to TMS as internal standard, while NMR signal assignments were performed with the aid of COSY and COLOQ experiments. MS: Finnigan MAT 8430. GC/MS: Carlo Erba HRGC 5160 in combination with a Finnigan 4515 mass spectrometer; HRMS: Finnigan MAT 8430 with the peak-matching method. Elemental analyses: Institute of Inorganic and Analytical Chemistry of the Technical University of Braunschweig. Undec-10-yn-1-ol (**8e**) is a commercial product (Lancaster Synthesis) and was used without further purification.

General procedure for the preparation of the alkynols 8: Lithium powder was placed under nitrogen in a three-necked flask, and 1,3-diaminopropane was added. The mixture was stirred at 80 °C for 2 h; during which the initial blue color faded and a pale grey suspension was formed. After this had cooled to RT, potassium *tert*-butoxide was added, and the mixture was stirred for 15 min. The alkynol **7** was added and, after 2 h at RT, the orange reaction mixture was cautiously poured into ice water (50 mL). After extraction with chloroform (4 × 50 mL), the combined organic layers were washed with water, 10% aq. HCl, satd. $NaHCO_3$ solution, and saturated brine solution, then dried over sodium sulfate. After removal of the solvent at reduced pressure, the crude product was purified by distillation. Although the products **8** have all been described in the literature, the analytical data are incomplete and were recorded under different conditions. We have therefore repeated/completed these data for the whole set of homologous compounds **8**.

Hept-6-yn-1-ol (8a): This compound was synthesized according to the general procedure: Li (0.42 g, 60 mmol), diaminopropane (30 mL), *t*BuOK (3.9 g, 35 mmol), and **7a** (1.0 g, 9.0 mmol) provided **8a** (0.97 g, 8.66 mmol, 97%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.36-1.65$ (m, 6H; 2-H, 3-H, 4-H), 1.93 (t, 1H; $^4J = 2.6$ Hz, 7-H), 2.18 (dt, $^3J = 6.7$, $^4J = 2.6$ Hz, 2H; 5-H), 3.62 (t, $^3J = 6.3$ Hz, 2H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-5), 24.8 (C-3 or C-4), 28.2 (C-3 or C-4), 32.1 (C-2), 62.7 (C-1), 68.3 (C-7), 84.4 (C-6); IR (film): $\tilde{\nu} = 3300$ (vs), 2940 (vs), 2864 (s), 2117 (w), 1433 (m), 1401 (m), 1073 (m), 1052 (m), 626 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (2.49), 220 (0.79), 276 nm (0.65); MS (70 eV, EI): *m/z* (%): 112 $[M]^+$ (2), 97 (14), 93 (11), 83 (17), 79 (100), 67 (31), 55 (59).

Oct-7-yn-1-ol (8b): This compound was synthesized according to the general procedure: Li (2.21 g, 0.32 mol), diaminopropane (160 mL), *t*BuOK (20.6 g, 0.19 mol), and **7b** (5.94 g, 47 mmol) provided **8b** (4.87 g, 38.6 mmol, 82%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.33-1.54$ (m, 8H; 2-H, 3-H, 4-H, 5-H), 1.89 (t, $^4J = 2.6$ Hz, 1H; 8-H), 2.01–2.16 (m, 2H; 6-H), 3.52–3.59 (m, 2H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-6), 25.2 (C-5), 28.3 (C-3 or C-4), 28.4 (C-3 or C-4), 32.5 (C-2), 62.7 (C-1), 68.2 (C-8), 84.5 (C-7); IR (film): $\tilde{\nu} = 3348$ (s, br), 3301 (vs), 2937 (vs), 2861 (vs), 2117 (w), 1463 (m), 1433 (m), 1328 (m), 1074 (m), 1056 (m), 1033 (m), 1002 (m), 726 (m), 628 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (2.52), 208 (1.72), 226 nm (1.16); MS (70 eV, EI): *m/z* (%): 125 $[M-H]^+$ (1), 107 (24), 93 (48), 79 (100), 67 (62), 55 (39), 43 (9).

Non-8-yn-1-ol (8c): This compound was synthesized according to the general procedure: Li (3.08 g, 0.44 mol), diaminopropane (220 mL), *t*BuOK (28.6 g, 0.26 mol), and **7c** (9.16 g, 65.6 mmol) provided **8c** (8.57 g, 61.2 mmol, 94%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.20-1.53$ (m, 10H; 2-H to 6-H), 1.70 (br s, 1H; OH), 1.88 (t, $^4J = 2.7$ Hz, 1H; 9-H), 2.12 (dt, $^3J = 6.8$, $^4J = 2.6$ Hz, 2H; 7-H), 3.56 (t, $^3J = 6.5$ Hz, 2H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-7), 25.6 (C-6), 28.3, 28.6, 28.8 (C-3, C-4, C-5), 32.6 (C-2), 62.8 (C-1), 68.1 (C-9), 84.6 (C-8); IR (film): $\tilde{\nu} = 3350$ (s, br), 3310 (s), 3302(s), 2934 (vs), 2859 (s), 2118 (w), 1464 (w), 1058 (w), 625 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 202$ (2.22), 222 (1.76), 244 nm (1.48); MS (70 eV, EI): *m/z* (%): 121 $[M-H_3O]^+$ (2), 107 (28), 79 (100), 67 (59), 55 (71).

Dec-9-yn-1-ol (8d): This compound was prepared according to the general procedure: Li (1.54 g, 0.22 mol), diaminopropane (110 mL), *t*BuOK (14.3 g, 0.13 mol), and **7d** (5.05 g, 32.0 mmol) provided **8d** (3.86 g, 25.1 mmol, 76%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.22-1.55$ (m, 12H; 2-H to 7-H), 1.90 (t, $^4J = 2.6$ Hz, 1H; 10-H), 2.00 (br s, 1H; OH), 2.14 (dt, $^3J = 6.9$, $^4J = 2.6$ Hz, 2H; 8-H), 3.57 (t, $^3J = 6.6$ Hz, 2H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-8), 25.6 (C-7), 28.4, 28.6, 29.0, 29.2 (C-3, C-4, C-5, C-6), 32.7 (C-2), 62.8 (C-1), 68.1 (C-10), 84.7 (C-9); IR (film): $\tilde{\nu} = 3346$ (s, br), 3312 (s), 2933 (vs), 2858 (vs), 2118 (w), 1465 (m), 1433 (m), 628 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 202$ (2.04), 214 (1.55), 244 nm (1.26); MS (70 eV, EI): *m/z* (%): 155 $[M+H]^+$ (1), 121 (11), 107 (18), 93 (56), 79 (100), 67 (80), 55 (88).

General procedure for the preparation of the aldehydes 9: A solution of anhydrous DMSO in anhydrous dichloromethane (10 mL) was slowly added to a solution of oxalyl chloride in anhydrous dichloromethane (100 mL) at −60 °C. The mixture was stirred for 10 min, and a solution of the alkynols **8** in anhydrous dichloromethane (20 mL) was added. After this had been stirred for 30 min at −60 °C, triethylamine was added, and the reaction mixture was allowed to warm to 0 °C. After addition of diethyl ether (150 mL) and water (100 mL), the layers were separated, and the aqueous phase was extracted carefully with diethyl ether (3 × 100 mL). The combined organic layers were washed with 15% aq. HCl, 5% aq. soda solution, and saturated brine, then dried with sodium sulfate. After removal of the solvent in vacuo, the crude product was purified by distillation. Although the products **9** have all been described in the literature, the analytical data are incomplete and were recorded under different conditions. We have therefore repeated/completed these data for the whole set of homologous compounds **9**.

Hept-6-yn-al (9a): This compound was prepared according to the general procedure: oxalyl chloride (2.1 mL, 23.1 mmol), DMSO (3.6 mL), NEt_3 (14 mL, 0.1 mol), and **8a** (2.36 g, 21 mmol) produced **9a** (2.29 g, 20.8 mmol, 98%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.42-1.77$ (m, 4H; 3-H, 4-H), 1.91 (t, $^4J = 2.6$ Hz, 1H; 7-H), 2.14 (dt, $^3J = 6.8$, $^4J = 2.6$ Hz, 2H; 5-H), 2.40 (t, $^3J = 7.1$ Hz, 2H; 2-H), 9.69 (pseudo s, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.1$ (C-5), 21.0 (C-3 or C-4), 27.7 (C-3 or C-4), 43.2 (C-2), 68.7 (C-7), 83.7 (C-6), 202.0 (C-1); IR (film): $\tilde{\nu} = 3297$ (s), 2943 (s), 2868 (s), 2117 (w), 1712 (vs), 1655 (m), 1649 (m), 1638 (m), 1461 (m), 1433 (m), 1413 (m), 1356 (m), 1331 (m), 1291 (m), 1234 (m), 1198 (m), 1140 (m), 1080 (m), 635 cm^{-1} (s). UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (2.45), 220 (1.85), 276 nm (1.07); MS (70 eV, EI): *m/z* (%): 111 $[M+H]^+$ (100), 110 $[M]^+$ (15), 109 (46), 93 (76), 83 (48), 79 (26), 77 (16), 67 (57), 55 (60).

Oct-7-yn-al (9b): This compound was prepared according to the general procedure: oxalyl chloride (1.5 mL, 16.5 mmol), DMSO (2.5 mL), NEt_3 (10 mL, 71.4 mmol), and **8b** (1.8 g, 14.3 mmol) provided **9b** (1.67 g, 13.5 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.36-1.62$ (m, 6H; 3-H, 4-H, 5-H), 1.88 (t, $^4J = 2.5$ Hz, 1H; 8-H), 2.13 (dt, $^3J = 6.9$, $^4J = 2.7$ Hz, 2H; 6-H), 2.38 (dt, $^3J = 7.3$, $^3J = 1.6$ Hz, 2H; 2-H), 9.71 (t, $^3J = 1.5$ Hz, 1H; 1-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 18.1$ (C-6), 21.5 (C-5), 28.0 (C-3 or C-4), 28.1 (C-3 or C-4), 43.6 (C-2), 68.4 (C-8), 84.1 (C-7), 202.4 (C-1); IR (film): $\tilde{\nu} = 3298$ (s), 2939 (vs), 2862 (s), 2117 (w), 1710 (vs), 1464 (m), 1433 (m), 1412 (m), 1363 (m), 1352 (m), 1270 (m), 1245 (m), 1206 (m), 1176 (m), 1133 (s), 1087 (m), 630 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (2.67), 222 nm (2.39); MS (70 eV, EI): *m/z* (%): 124 $[M]^+$ (7), 109 (10), 101 (20), 95 (72), 80 (100), 67 (35), 60 (35), 55 (83).

Non-8-yn-al (9c): This compound was prepared according to the general procedure: oxalyl chloride (2.3 mL, 24.4 mmol), DMSO (3.9 mL), NEt_3 (15 mL, 107 mmol), and **8c** (3.1 g, 22.1 mmol) provided **9c** (2.94 g, 21.3 mmol, 96%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.27-1.65$ (m, 8H; 3-H to 6-H), 1.88 (t, $^4J = 2.6$ Hz, 1H; 9-H), 2.12 (dt, $^3J = 6.8$, $^4J = 2.6$ Hz, 2H; 7-H), 2.37 (dt, $^3J = 7.4$, $^3J = 1.7$ Hz, 2H; 2-H), 9.70 (t, $^3J = 1.7$ Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.2$ (C-7), 21.8 (C-6), 28.1, 28.3, 28.5 (C-3, C-4, C-5), 43.7 (C-2), 68.2 (C-9), 84.4 (C-8), 202.5 (C-1); IR (film): $\tilde{\nu} = 3299$ (s), 2937 (vs), 2861 (s), 2117 (w), 1710 (vs), 1464 (m), 1433 (m), 1401 (m), 1355 (m), 1328 (m), 1296 (m), 1259 (m), 1234 (m), 1172 (m), 1133 (s), 1092 (m), 632 cm^{-1} (s). UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (2.83), 236 (2.18), 266 nm (1.76); MS (70 eV, EI): *m/z* (%): 138 $[M]^+$ (1), 109 (12), 94 (29), 79 (100), 67 (63), 55 (61).

Dec-9-yn-al (9d): This compound was prepared according to the general procedure: oxalyl chloride (1.5 mL, 16.5 mmol), DMSO (2.2 mL), NEt_3 (9.7 mL. 69 mmol), and **8d** (2.2 g, 14.3 mmol) provided **9d** (1.87 g, 12.3 mmol, 86%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.29-1.65$ (m, 10H; 3-H to 7-H), 1.92 (t, $^4J = 2.6$ Hz, 1H; 10-H), 2.16 (dt, $^3J = 6.9$, $^4J = 2.6$ Hz, 2H; 8-H), 2.40 (dt, $^3J = 7.2$, $^3J = 0.8$ Hz, 2H; 2-H), 9.76 (t, $^3J = 0.8$ Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-8), 22.0 (C-7), 28.3, 28.4, 28.7, 29.0 (C-3 to C-6), 43.8 (C-2), 68.1 (C-10), 84.5 (C-9), 202.7 (C-1); IR (film): $\tilde{\nu} = 3294$ (m), 2935 (vs), 2869 (s), 2117 (w), 1725 (vs), 1465 (m), 1432 (m), 1411 (m), 1391 (m), 723 cm^{-1} (m); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (2.59), 222 (1.45), 238 nm (1.24); MS (70 eV, EI): *m/z* (%): 153 $[M+H]^+$ (42), 135 (91), 107 (40), 97 (63), 81 (68), 67 (100), 55 (80).

Undec-10-yn-al (9e): This compound was prepared according to the general procedure: oxalyl chloride (4.4 mL, 48.4 mmol), DMSO (7.4 mL), NEt_3 (29.0 mL, 0.21 mol), and **8e** (7.0 g, 41.7 mmol) provided **9e** (6.04 g, 36.4 mmol, 86%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.30-1.63$ (m, 12H; 3-H to 8-H), 1.92 (t, $^4J = 2.6$ Hz, 1H; 11-H), 2.15 (dt, $^3J = 6.9$, $^4J = 2.6$ Hz, 2H; 9-H), 2.40 (dt, $^3J = 7.4$, $^3J = 1.8$ Hz, 2H; 2-H), 9.72 (t, $^3J = 1.8$ Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-9), 22.0 (C-8), 28.4, 28.6, 28.8, 29.0, 29.1 (C-3 to C-7), 43.8 (C-2), 68.1 (C-11), 84.6 (C-10, 202.7 (C-1); IR (film): $\tilde{\nu} = 3286$ (m), 2934 (vs), 2924 (vs), 2850 (s), 2138 (w), 1726 (vs), 1465 (m), 1363 (m), 1158 (m), 1134 (m), 1128 (m), 1121 (m), 698 (m), 670 cm^{-1} (m); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (2.83), 228 (2.47), 256 nm (1.58); MS (70 eV, EI): *m/z* (%): 167 $[M+H]^+$ (17), 133 (20), 117 (36), 109 (32), 95 (63), 91 (60), 81 (100), 67 (97), 55 (76).

General procedure for the preparation of the 1,3-dioxolanes 11: The phosphonium salt **10**[20] was placed under nitrogen in a three-necked, flame-dried flask, then anhydrous THF (200 mL) was added. Potassium *tert*-butoxide was added to the suspension with ice cooling (color change to deep yellow), and the mixture was stirred for 30 min. A solution of the aldehyde **9** in anhydrous THF (50 mL) was added over 20 min, and the reaction mixture was stirred for 6 h at room temperature. After decomposition with water (250 mL), the product was isolated by careful extraction with pentane (5 × 100 mL). The organic phases were combined, reduced to approximately one third of the original volume and passed through a short silica gel column (removal of the triphenylphosphine oxide). After the column had been washed with pentane, the solvent was removed in vacuo, and the remaining brown oil was purified by flash chromatography on silica gel with pentane/diethyl ether (10:1, *v*/*v*); the products **11** were obtained as colorless oils. For the NMR data only the signals for the main (*E*) isomer are given.

(*E*,*Z*)-2-Oct-1-en-7-ynyl-[1.3]dioxolane (11a): This compound was prepared according to the general procedure: **10** (30.3 g, 70.7 mmol), *t*BuOK (7.6 g, 68.0 mmol), and **9a** (2.9 g, 26.4 mmol) provided **11a** (3.37 g, 18.7 mmol, 71%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.52$ (m, 4H; 4-H, 5-H), 1.92 (t, $^4J = 2.6$ Hz, 1H; 8-H), 2.08–2.24 (m, 4H; 3-H, 6-H), 3.82–4.06 (m, 4H; CH_2 dioxolane ring), 5.15–5.98 (m, 3H; -OCHO-, 1-H, 2-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.1$ (C-6), 27.2 (C-3), 27.7, 28.4 (C-4, C-5), 64.9 (CH_2 dioxolane ring), 68.3 (C-8), 84.2 (C-7), 99.1 (-OCHO-), 126.2 (C-1), 136.9 (C-2); IR (film): $\tilde{\nu} = 3290$ (s), 2941 (s), 2868 (m), 2115 (w), 2093 (w), 1655 (m), 1455 (m), 1435 (m), 1401 (m), 1377 (m), 1275 (s), 1186 (s), 1082 (s), 1041 (s), 983 (m), 886 (m), 634 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 208$ nm (3.68); MS (70 eV, EI): *m/z* (%): 180 $[M]^+$ (3), 179 (24), 135 (27), 133 (25), 121 (28), 107 (37), 105 (44), 99 (28), 91 (47), 79 (28), 73 (100), 67 (58), 55 (48).

(*E*,*Z*)-2-Non-1-en-8-ynyl-[1.3]dioxolane (11b): This compound was prepared according to the general procedure: **10** (32.2 g, 75.1 mmol), *t*BuOK (8.08 g, 72.4 mmol), and **9b** (3.48 g, 28.1 mmol) provided **11b** (4.50 g, 23.2 mmol, 83%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.40-1.60$ (m, 6H; 4-H, 5-H, 6-H), 1.93 (t, $^4J = 2.6$ Hz, 1H; 9-H), 2.13–2.44 (m, 4H; 3-H, 7-H), 3.83–4.04 (m, 4H; CH_2 dioxolane ring), 5.15–5.96 (m, 3H; -OCHO-, 1-H, 2-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-7), 27.6 (C-3), 28.2 (2 signals), 28.9 (C-4, C-5, C-6), 64.9 (CH_2 dioxolane ring), 68.2 (C-9), 84.8 (C-8), 99.2 (-OCHO-), 126.0 (C-1), 137.3 (C-2); IR (film): $\tilde{\nu} = 3290$ (m), 2937 (vs), 2888 (s), 2861 (s), 2117 (w), 1463 (m), 1430 (m), 1347 (m), 1224 (s), 1212 (s), 1128 (s), 1102 (s), 1042 (s), 985 (s), 625 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (3.88), 228 nm (2.08); MS (70 eV, EI): *m/z* (%): 193 $[M-H]^+$ (3), 179 (4), 155 (22), 137 (4), 125 (8), 113 (47), 99 (100), 86 (14), 79 (10), 73 (32), 69 (12), 55 (12); elemental analysis calcd (%) for $C_{12}H_{18}O_2$: C 74.19, H 9.34; found C 74.13, H 9.14.

(*E*,*Z*)-2-Dec-1-en-9-ynyl-[1.3]dioxolane (11c): This compound was prepared according to the general procedure: **10** (11.9 g, 27.7 mmol), *t*BuOK (3.0 g, 26.9 mmol), and **9c** (1.43 g, 10.4 mmol) provided **11c** (1.72 g, 8.27 mmol, 80%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.15-1.62$ (m, 8H; 4-H to 7-H), 1.91 (t, $^4J = 2.5$ Hz, 1H; 10-H), 2.01–2.18 (m, 4H; 3-H, 8-H), 3.83–4.00 (m, 4H; CH_2 dioxolane ring), 5.13–5.98 (m, 3H; -OCHO-, 1-H, 2-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-8), 27.7 (C-3), 28.3, 28.5, 29.3, 31.9 (C-4 to C-7), 64.9 (CH_2 dioxolane ring), 68.1 (C-10), 84.8 (C-9), 99.2 (-OCHO-), 125.9 (C-1), 137.5 (C-2); IR (film): $\tilde{\nu} = 3291$ (m), 2934 (vs), 2888 (s), 2859 (s), 2117 (w), 1464 (w), 1430 (w), 1347 (w), 1211 (w), 1127 (s), 1106 (s), 1047 (m), 995 (w), 626 cm^{-1} (m); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (3.84), 218 (2.24), 276 nm (2.18); MS (70 eV, EI): *m/z* (%): 208 $[M]^+$ (1), 169 (19), 152 (6), 125 (11), 113 (56), 99 (100), 86 (18), 73 (48), 55 (31); elemental analysis calcd (%) for $C_{13}H_{20}O_2$: C 74.95, H 9.68; found C 74.38, H 9.76.

(*E*,*Z*)-2-Undec-1-en-10-ynyl-[1.3]dioxolane (11d): This compound was prepared according to the general procedure: **10** (16.7 g, 38.9 mmol), *t*BuOK (4.20 g, 37.6 mmol), and **9d** (2.25 g, 14.8 mmol) provided **11d** (2.86 g, 12.88 mmol, 87%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.33$ (m, 4H; 6-H, 7-H), 1.42 (m, 4H; 5-H, 8-H), 1.54 (m, 2H; 4-H), 1.96 (t, $^4J = 2.6$ Hz, 1H; 11-H), 2.20 (m, 4H; 3-H, 9-H), 3.89–4.08 (m, 4H; CH_2 dioxolane ring), 5.43–5.57 (m, 2H; -OCHO-, 1-H), 5.78 (dt, $^3J = 7.7$, $^3J = 11.0$ Hz, 1H; 2-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-9), 27.7 (C-3), 28.4 (C-4), 28.5, 28.8, 28.9, 29.3 (C-5 to C-8), 64.9 (CH_2 dioxolane ring), 68.0 (C-11), 84.6 (C-10), 99.1 (-OCHO-), 125.7 (C-1), 137.6 (C-2); IR (film): $\tilde{\nu} = 3298$ (m), 2932 (vs), 2890 (s), 2117 (w), 1465 (w), 1430 (w), 1347 (w), 1212 (w), 1126 (m), 1108 (m), 1052 (m), 959 (w), 723 cm^{-1} (w); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ nm (3.80), 216 (2.09); MS (70 eV, EI): *m/z* (%): 221 $[M-H]^+$ (5), 179 (6), 155 (5), 125 (9), 113 (47), 99 (100), 93 (25), 81 (83), 79 (42), 73 (41), 55 (70); elemental analysis calcd (%) for $C_{14}H_{22}O_2$: C 75.63, H 9.97; found C 75.45, H 9.97.

(*E*,*Z*)-2-Dodec-1-en-11-ynyl-[1.3]dioxolane (11e): This compound was prepared according to the general procedure: **10** (30.3 g, 70.6 mmol), *t*BuOK (7.6 g, 68.1 mmol), and **9e** (4.38 g, 26.4 mmol) provided **11e** (5.7 g, 24.2 mmol, 92%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.28-1.62$ (m, 12H; 4-H to 9-H), 1.92 (t, $^4J = 2.6$ Hz, 1H; 12-H), 2.04–2.20 (m, 4H; 3-H, 10-H), 3.80–4.07 (m, 4H; CH_2 dioxolane ring), 5.15–5.99 (m, 3H; -OCHO-, 1-H, 2-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.3$ (C-10), 27.7 (C-3), 28.4, 28.7, 28.9, 29.0, 29.2, 29.4 (C-4 to C-9), 64.9 (CH_2 dioxolane ring), 68.0 (C-12), 84.7 (C-11), 99.2 (-OCHO-), 125.8 (C-1), 137.6 (C-2); IR (film): $\tilde{\nu} = 3291$ (m), 2929 (vs), 2857 (vs), 2117 (w), 1719 (m), 1465 (m), 1430 (m), 1347 (m), 1210 (m), 1126 (s), 1110 (s), 1057 (s), 996 (m), 958 (s), 722 (m), 625 cm^{-1} (s); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 192$ (3.87), 218 nm (2.72); MS (70 eV, EI): *m/z* (%): 236 $[M]^+$ (2), 193 (8), 179 (6), 155 (14), 125 (10), 113 (45), 99 (100), 73 (27), 55 (8); elemental analysis calcd (%) for $C_{15}H_{24}O_2$: C 76.23, H 10.23; found C 75.24, H 10.07.

General procedure for the preparation of the dialdehydes 12: A solution of the alkyne **11** in anhydrous diethyl ether (200 mL) was placed in a three-necked flask under nitrogen. A solution of *n*-butyl lithium (1.6 M) in hexane was added at −50 °C, and the mixture was stirred for 30 min at this temperature, before being taken down to −70 °C to cause precipitation of the acetylide. *N*,*N*-Dimethylformamide was added in one portion, and the reaction mixture was allowed to warm to 10–15 °C, which resulted in dissolution of the precipitate. After 2 h, the product mixture was hydrolyzed with sulfuric acid/ice water, then the two-phase mixture was stirred vigorously overnight. Neutralization with $NaHCo_3$ solution, separation of the organic phase, careful extraction of the aqueous phase with diethyl ether, and drying of the combined organic phase with sodium sulfate concluded the workup. The solvent was removed by rotary evaporation and

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the remaining yellow oil was purified by column chromatography on silica gel (pentane/ether = 2:1, *v*/*v*). The dialdehydes **12** were obtained as colorless, unstable oils, which did not give satisfactory elemental analyses.

Dec-2-en-8-ynedial (12a): This compound was prepared according to the general procedure: **11a** (3.2 g, 17.8 mmol), *n*BuLi (1.6 M, 11.3 mL, 18.1 mmol), DMF (1.64 g, 22.5 mmol), and H_2SO_4 (96 %, 4.4 g) in ice water (90 mL) provided **12a** (2.07 g, 12.6 mmol, 71 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.58–1.71 (m, 4H; 5-H, 6-H), 2.30–2.47 (m, 4H; 4-H, 7-H), 6.10 (ddt, ^3J = 15.6, ^3J = 7.9, ^4J = 1.5 Hz, 1H; 2-H), 6.81 (dt, ^3J = 6.7, ^3J = 15.6 Hz, 1H; 3-H), 9.15 (t, ^5J = 0.8 Hz, 1H; 10-H), 9.48 (d, ^3J = 7.9 Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.9 (C-7), 26.8, 26.9 (C-5, C-6), 32.0 (C-4), 81.9 (C-9), 98.0 (C-8), 133.3 (C-2), 157.4 (C-3), 177.0 (C-10), 193.8 (C-1); IR (film): $\tilde{\nu}$ = 2943 (s), 2866 (s), 2281 (s), 2236 (s), 2203 (s), 1694 (vs), 1691 (vs), 1463 (m), 1418 (s), 1396 (s), 1355 (s), 1286 (s), 1243 (s), 1210 (s), 1138 (s), 1088 (m), 1077 (m), 1021 (m), 981 (s), 905 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 218 (4.03), 230 (3.86, sh), 244 nm (3.12, sh).

Undec-2-en-9-ynedial (12b): This compound was prepared according to the general procedure: **11b** (4.4 g, 22.7 mmol), *n*BuLi (1.6 M, 14.7 mL, 23.5 mmol), DMF (2.1 g, 28.8 mmol), and H_2SO_4 (96 %, 5.0 g) in ice water (100 mL) provided **12b** (1.66 g, 9.33 mmol, 41 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39–1.67 (m, 6H; 5-H, 6-H, 7-H), 2.21–2.62 (m, 4H; 4-H, 8-H), 5.78–6.16 (m, 1H; 2-H), 6.76–7.10 (m, 1H; 3-H), 9.14 (t, ^5J = 0.8 Hz, 1H; 11-H), 9.46 (d, ^3J = 7.9 Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.5 (C-8), 27.2 (2 signals), 28.2 (C-5, C-6, C-7), 32.4 (C-4), 81.8 (C-10), 98.7 (C-9), 133.0 (C-2), 158.4 (C-3), 177.2 (C-11), 194.2 (C-1); IR (film): $\tilde{\nu}$ = 3022 (m), 2937 (vs), 2863 (s), 2281 (w), 2235 (m), 2202 (s), 1692 (vs), 1670 (vs), 1458 (m), 1426 (m), 1390 (m), 1373 (m), 1236 (s), 1168 (m), 1139 (s), 1093 (m), 1072 (m), 1017 (m), 979 (m), 756 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 218 nm (3.93); MS (70 eV, EI): *m*/*z* (%): 178 [*M*]$^+$ (1), 177 (2), 149 (20), 135 (32), 121 (46), 107 (72), 91 (68), 79 (100), 67 (43), 55 (89).

Dodec-2-en-10-ynedial (12c): This compound was prepared according to the general procedure: **11c** (3.0 g, 14.4 mmol), *n*BuLi (1.6 M, 9.1 mL, 14.6 mmol), DMF (1.33 g, 18.2 mmol), and H_2SO_4 (96 %, 2.5 g) in ice water (65 mL) provided **12c** (2.39 g, 12.4 mmol, 86 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30–1.60 (m, 8H; 5-H to 8-H), 2.31 (pseudo qd, ^3J = 7.1, ^3J = 7.1, ^4J = 1.5 Hz, 2H; 4-H), 2.38 (dt, ^3J = 6.9, ^5J = 0.8 Hz, 2H; 9-H), 6.07 (ddt, ^3J = 15.7, ^3J = 7.9, ^4J = 1.5 Hz, 1H; 2-H), 6.81 (dt, ^3J = 6.9, ^3J = 15.6, 1H; 3-H), 9.13 (br s, 1H; 12-H), 9.46 (d, ^3J = 7.9 Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.0 (C-9), 27.3, 27.5, 28.4, 28.5 (C-5 to C-8), 32.5 (C-4), 81.7 (C-10), 98.9 (C-11), 133.0 (C-2), 158.5 (C-3), 177.1 (C-12), 194.0 (C-1); IR (film): $\tilde{\nu}$ = 2935 (vs), 2860 (s), 2280 (w), 2235 (w), 2201 (s), 1690 (vs), 1670 (vs), 1464 (w), 1448 (s), 1390 (w), 1159 (m), 1138 (m), 978 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 220 (4.14), 248 (3.11, sh), 266 nm (2.78, sh); MS (70 eV, EI): *m*/*z* (%): 193 [*M*+H]$^+$ (5), 192 [*M*]$^+$ (1), 191 (4), 173 (4), 161 (19), 149 (21), 133 (36), 135 (36), 121 (52), 107 (51), 91 (67), 81 (100), 67 (57), 55 (75); HRMS: *m*/*z* calcd for $C_{12}H_{16}O_2$ 192.1150; found 192.1150.

Tridec-2-en-11-ynedial (12d): This compound was prepared according to the general procedure: **11d** (2.7 g, 12.2 mmol), *n*BuLi (1.6 M, 7.9 mL, 12.7 mmol), DMF (1.13 g, 15.5 mmol), and H_2SO_4 (3.0 g, 96 %) in ice water (60 mL) provided **12d** (1.57 g, 7.63 mmol, 63 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.18–1.57 (m, 10H; 5-H to 9-H), 2.22–2.64 (m, 4H; 4-H, 10-H), 5.73–6.15 (m, 1H; 2-H), 6.55–6.97 (m, 1H; 3-H), 9.15 (t, ^5J = 0.8 Hz, 1H; 13-H), 9.48 (d, ^3J = 7.9 Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.0 (C-10), 27.4, 27.7, 28.6, 28.7, 28.9 (C-5 to C-9), 32.6 (C-4), 81.7 (C-12), 99.2 (C-11), 132.9 (C-2), 158.9 (C-3), 177.2 (C-13), 194.3 (C-1); IR (film): $\tilde{\nu}$ = 2932 (vs), 2858 (s), 2281 (w), 2235 (m), 2201 (s), 1690 (vs), 1670 (vs), 1465 (m), 1423 (m), 1283 (m), 1235 (m), 1139 (m), 976 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 222 nm (4.18), 248 (3.03, sh); MS (70 eV, EI): *m*/*z* (%): 205 [*M* – H]$^+$ (1), 204 (1), 183 (6), 171 (5), 159 (4), 145 (8), 131 (100), 117 (84), 91 (79), 79 (36), 67 (28).

Tetradec-2-en-12-ynedial (12e): This compound was prepared according to the general procedure: **11e** (0.52 g, 2.2 mmol), *n*BuLi (1.6 M, 1.4 mL, 2.2 mmol), DMF (0.20 g, 2.76 mmol), and H_2SO_4 (96 %, 0.4 g) in ice water (10 mL) provided **12e** (234 mg, 1.06 mmol, 48 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.31–1.83 (m, 12H; 5-H to 10-H), 2.26–2.58 (m, 4H; 4-H, 11-H), 6.10 (ddt, ^3J = 15.6, ^3J = 7.9, ^4J = 1.5 Hz, 1H; 2-H), 6.84 (dt, ^3J = 6.8, ^3J = 15.6 Hz, 1H; 3-H), 9.16 (t, ^5J = 0.8 Hz, 1H; 14-H), 9.50 (d, ^3J = 7.9 Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.1 (C-11), 27.4, 27.7, 28.7, 28.8, 29.0, 29.1 (C-5 to C-10), 32.6 (C-4), 81.7 (C-13), 99.2 (C-12), 133.0 (C-2), 158.8 (C-3), 177.2 (C-14), 194.1 (C-1); IR (film): $\tilde{\nu}$ = 2930 (vs), 2857 (s), 2280 (w), 2236 (w), 2201 (m), 1691 (vs), 1670 (vs), 1466 (m), 1422 (m), 1283 (m), 1231 (m), 1139 (m), 977 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 220 (4.00), 246 nm (3.04, sh).

General procedure for the preparation of the cyclo-1,3-dien-5-ynes 6: A flame-dried three-necked flask (1 L) was charged under argon with $TiCl_3(DME)_{1.5}$, prepared according to [21], and with a zinc/copper couple. The two components were mixed thoroughly. Freshly distilled DME was added, and the mixture was heated under reflux for 5 h, during which time it turned black. The suspension was cooled to room temperature, and a solution of the bisaldehyde **12** in DME (20 mL) was added slowly by means of a motor-driven syringe (ca. 30 h). The reaction mixture was stirred until the substrate **12** had been consumed completely, while the process was monitored by GC analysis. After dilution with pentane (250 mL), the product mixture was filtered through silica gel, and the column was washed carefully with pentane. The organic solvents were removed in vacuo, and the remaining oil was purified by preparative thick-layer chromatography on silica gel with pentane. The cyclodienynes **6** were isolated as colorless oils. In all cases the volatile products contained varying amounts of solvent (DME, as shown by ^{1}H NMR analysis); this made the determination of elemental analyses impossible.

Cyclodeca-1,3-dien-5-yne (6a): This compound was prepared according to the general procedure: $TiCl_3(DME)_{1.5}$ (13.0 g, 44.9 mmol), Zn/Cu couple (17.1 g, 0.27 mol), and **12a** (1.6 g, 9.78 mmol) in DME (220 mL) provided **6a** (60 mg, 0.45 mmol, 5 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71 (m, 4H; 8-H, 9-H), 2.10 (m, 2H; 10-H), 2.18 (m, 2H; 7-H), 5.28 (dm, ^3J = 10.2 Hz, 1H; 4-H), 5.53 (dm, ^3J = 15.9 Hz, 1H; 2-H), 6.31 (m, 1H; 1-H), 6.41 (dm, ^3J = 10.2 Hz, 1H; 3-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.9 (C-7), 26.9, 30.8 (C-8, C-9), 33.0 (C-10), 84.1 (C-5), 97.5 (C-6), 112.0 (C-4), 123.1 (C-2), 141.8 (C-1), 142.6 (C-3); IR (film): $\tilde{\nu}$ = 2934 (vs), 2864 (s), 2251 (w), 2205 (w), 1720 (vs), 1679 (vs), 1449 (m), 1408 (m), 1392 (m), 1351 (m), 1326 (m), 1260 (m), 1232 (m), 1212 (m), 1167 (m), 1140 (m), 1099 (m), 1079 (m), 1031 (m), 1013 (m), 914 (m), 733 (s), 647 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 192 (3.94), 212 (3.52, sh), 226 nm (3.29); MS (GC/MS): *m*/*z* (%): 132 [*M*]$^+$ (80), 115 (24), 104 (100), 91 (65), 78 (17), 65 (16).

Cycloundeca-1,3-dien-5-yne (6b): This compound was prepared according to the general procedure: $TiCl_3(DME)_{1.5}$ (5.2 g, 17.9 mmol), Zn/Cu couple (3.8 g, 58 mmol), and **12b** (0.4 g, 2.2 mmol) in DME (220 mL) provided **6b** (121 mg, 0.83 mmol, 38 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.34 (m, 2H; 10-H), 1.49 (m, 2H; 8-H), 1.60 (m, 2H; 9-H), 2.08 (m, 2H; 11-H), 2.28 (m, 2H; 7-H), 5.34 (dm, ^3J = 10.6 Hz, 1H; 4-H), 5.61 (dm, ^3J = 15.7 Hz, 1H; 2-H), 5.87 (m, 1H; 1-H), 6.33 (dm, ^3J = 10.5 Hz, 1H; 3-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.7 (C-7), 22.0 (C-9), 23.9 (C-10), 26.4 (C-8), 32.2 (C-11), 82.8 (C-5), 93.5 (C-6), 111.2 (C-4), 125.6 (C-2), 137.9 (C-1), 140.9 (C-3); IR (film): $\tilde{\nu}$ = 3018 (m), 2929 (vs), 2860 (s), 2219 (w), 2205 (w), 2170 (w), 1682 (s), 1648 (m), 1456 (m), 1443 (m), 1346 (m), 1018 (m), 968 (m), 921 (m), 765 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 198 (3.77), 242 (3.56), 268 nm (3.52); MS (GC/MS): *m*/*z* (%): 146 [*M*]$^+$ (5), 145 (6), 131 (28), 117 (100), 104 (36), 91 (66), 78 (28), 65 (15).

Cyclododeca-1,3-dien-5-yne (6c): This compound was prepared according to the general procedure: $TiCl_3(DME)_{1.5}$ (11.0 g, 37.9 mmol), Zn/Cu couple (14.6 g 0.22 mol), and **12c** (1.6 g, 8.33 mmol) in DME (220 mL) provided **6c** (210 mg, 1.31 mmol, 16 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.47 (m, 6H; 8-H, 9-H, 10-H), 1.60 (m, 2H; 11-H), 2.11 (m, 2H; 12-H), 2.21 (m, 2H; 7-H), 5.34 (d, ^3J = 11.0 Hz, 1H; 4-H), 5.75 (dm, ^3J = 15.8 Hz, 1H; 2-H), 6.10 (dm, ^3J = 11.0 Hz, 1H; 3-H), 6.41 (dm, ^3J = 15.8 Hz, 1H; 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.7 (C-7), 25.6, 25.7, 27.1, 27.2, 32.4 (C-8 to C-12), 80.7 (C-5), 94.8 (C-6), 108.8 (C-4), 125.1 (C-2), 138.4 (C-1), 138.6 (C-3); IR (film): $\tilde{\nu}$ = 2927 (vs), 2858 (s), 2208 (w), 1712 (m), 1683 (m), 1656 (m), 1459 (m), 1445 (m), 1348 (m), 1320 (m), 1132 (m), 1117 (m), 1110 (m), 1091 (m), 1050 (m), 1024 (m), 970 (m), 911 (m), 733 cm^{-1} (m); UV/Vis (MeCN): λ_{max}(lg ε) = 244 (3.54), 264 nm (3.55); MS (GC/MS): *m*/*z* (%): 160 [*M*]$^+$ (6), 145 (7), 131 (39), 117 (100), 104 (27), 91 (91), 79 (41), 65 (17).

Cyclotrideca-1,3-dien-5-yne (6d): This compound was prepared according to the general procedure: $TiCl_3(DME)_{1.5}$ (5.74 g, 19.8 mmol), Zn/Cu couple (4.19 g, 64 mmol), and **12d** (0.5 g, 2.43 mmol) in DME (150 mL) provided **6d** (156 mg, 0.90 mmol, 37 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.13–1.57 (m, 10H; 8-H to 12-H), 2.13–2.49 (m, 4H; 7-H, 13-H), 5.22 (dm, ^3J = 10.1 Hz, 1H; 4-H), 5.99–6.85 (m, 3H; 1-H, 2-H, 3-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.9 (C-7), 25.4, 25.7, 26.1, 27.6, 29.1, 30.1 (C-8 to

C-13), 78.8 (C-5), 98.4 (C-6), 108.4 (C-4), 126.6 (C-2), 135.1 (C-1), 139.2 (C-3); IR (film): $\tilde{\nu}$ = 3017 (w), 2931 (vs), 2859 (vs), 2204 (w), 1683 (m), 1645 (m), 1462 (m), 1449 (m), 1347 (m), 1322 (m), 1108 (m), 1080 (m), 1051 (m), 1012 (m), 985 (m), 734 cm^{-1} (m); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 264$ (3.67), 268 nm (3.87); MS (GC/MS): *m/z* (%): 174 $[M]^+$ (23), 145 (23), 131 (64), 117 (70), 105 (36), 91 (100), 79 (45), 67 (26).

Cyclotetradeca-1,3-dien-5-yne (6e): This compound was prepared according to the general procedure: $TiCl_3(DME)_{1.5}$ (0.84 g 2.89 mmol), Zn/Cu couple (1.12 g, 17.1 mmol), and **12e** (0.14 g, 0.64 mmol) in DME (50 mL) provided **6e** (53 mg, 0.28 mmol, 44%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 – 1.66 (m, 12H; 8-H to 13-H), 2.21 (m, 2H; 14-H), 2.41 (m, 2H; 7-H), 5.29 (dm, ^3J = 10.4 Hz, 1H; 4-H), 5.94 (dm, ^3J = 15.7 Hz, 1H; 2-H), 6.42 (m, 1H; 3-H), 6.76 (m, 1H; 1-H); IR (film): $\tilde{\nu}$ = 2933 (vs), 2929 (vs), 2859 (vs), 2280 (w), 2234 (m), 2203 (m), 1707 (s), 1702 (s), 1695 (s), 1671 (s), 1641 (m), 1462 (m), 1426 (m), 1361 (m), 1322 (m), 1215 (m), 1205 (m), 1137 (m), 1091 (m), 1064 (m), 985 (m), 631 cm^{-1} (m); UV/Vis (MeCN): $\lambda_{max}(\lg \varepsilon) = 194$ (4.26), 214 (3.70, sh), 268 nm (3.79); MS (GC/MS): *m/z* (%): 188 $[M]^+$ (36), 145 (28), 131 (42), 117 (57), 105 (43), 91 (100), 79 (44), 67 (22).

McMurry coupling of the dialdehyde 15 under Lenoir conditions:[24] Anhydrous THF (200 mL) was placed under nitrogen in a flame-dried, three-necked flask (500 mL), and titanium(IV) chloride (0.93 mL, 8.43 mmol) was added at 0 °C. The color of the solution changed to intense yellow. Zinc dust (1.01 g, 15.47 mmol) and anhydrous pyridine (0.52 g, 6.63 mol) were added. The color of the initially grey suspension changed to dark brown within 15 min. A solution of **15** (1.26 g, 6.63 mmol) in anhydrous THF (90 mL) was added over 4 h, and the reaction mixture was stirred overnight at room temperature. After hydrolysis with aqueous potassium carbonate solution (35 mL, 25%), the solid precipitate was removed by filtration and decomposed by treatment with HCl (2 N, 120 mL). The resulting solution (combined with the mother liquors) was extracted with pentane, and the organic phases were combined, washed successively with saturated bicarbonate solution and brine, then dried with $MgSO_4$. The solvent was removed in vacuo, and the resulting oily product mixture was separated by column chromatography on silica gel with pentane/diethyl ether (1:1, *v/v*) to provide two fractions: a) cyclododeca-3,11-diyne-1,2-diol (**17**) as a waxy solid: yield: 240 mg, 16%, 1.25 mmol; m.p. 25 – 30 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.53 (m, 8H; 6-H to 9-H), 2.20 – 2.32 (m, 4H; 5-H, 10-H), 4.33 (m, 2H; 1-H, 2-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.0 (C-5, C-10), 25.5, 26.2 (C-6 to C-9), 67.7 (C-1, C-2), 78.7 (C-4, C-11), 87.9 (C-3, C-12); IR (KBr): $\tilde{\nu}$ = 3389 (vs, br), 2935 (vs), 2857 (s), 2235 (m), 1716 (m), 1711 (m), 1702 (m), 1446 (m), 1432 (m), 1334 (m), 1273 (m), 1268 (m), 1241 (m), 1237 (m), 1161 (m), 1140 (m), 1057 (vs), 1011 (m), 1002 cm^{-1} (m); MS (GC/MS, 70 eV): *m/z* (%): 192 $[M]^+$ (1), 173 (1), 164 (2), 145 (2), 131 (3), 117 (5), 105 (8), 95 (16), 79 (16), 70 (100), 55 (15). b) the 2,3-bridged furan **18** as a colorless oil: yield: 71 mg, 7%, 0.41 mmol; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.54 – 1.83 (m, 8H; 8-H, 9-H, 10-H, 11-H), 2.45 (m, 2H; 7-H or 12-H), 2.60 (m, 2H; 7-H or 12-H), 6.18 (d, ^3J = 1.8 Hz, 1H; 4-H), 7.16 (d, ^3J = 1.8 Hz, 1H; 5-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.1 (C-7), 24.3, 25.1, 25.2, 27.9 (C-8 to C-12), 76.2 (C-5), 101.5 (C-6), 113.4 (C-3), 131.2 (C-2), 133.4 (C-1), 140.8 (C-4); IR (film): $\tilde{\nu}$ = 2930 (vs), 2906 (s), 2863 (s), 2227 (w), 2215 (w), 1678 (w), 1583 (w), 1085 (m), 740 cm^{-1} (m); MS (70 eV, EI): *m/z* (%): 174 $[M]^+$ (88), 159 (24), 146 (53), 131 (100), 117 (45), 105 (20), 91 (56), 77 (33), 63 (17), 51 (19). The formation of cyclododeca-3-ene-1,5-diyne (**16**; ca. 2.6% by GC analysis) was inferred by comparison of the spectral data with those reported in ref. [10b].

When the same coupling experiment was carried out with **12c** in THF at room temperature, a complex product mixture **13**/**14** (85:15, GC analysis) was obtained, which could not be fully characterized. The following analytical data were obtained: Cyclodeca-3-en-11-yne-1,2-diol (**13**): GC/MS (40 eV): *m/z* (%): 193 $[M - H]^+$ (1), 175 (2), 163 (2), 147 (7), 133 (10), 123 (12), 110 (20), 91 (28), 83 (44), 70 (100), 57 (48), 41 (32), identical to the spectrum reported in ref. [10]. 4,5,6,7,8,9-Hexahydrocyclodeca[*b*]furan (**14**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.17 – 1.65 (m, 8H; 9-H to 12-H), 1.90 – 2.07 (m, 2H; 13-H), 2.10 – 2.28 (m, 2H; 8-H), 5.78 – 5.93 (m, 1H; 7-H), 6.07 – 6.00 (m, 2H; 4-H, 6-H), 7.16 (d, ^3J = 1.8 Hz, 1H; 5-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.8, 23.5, 23.6, 26.1, 28.2 (C-9 to C-13), 31.8 (C-8), 111.0 (C-6), 113.5 (C-4), 119.9 (C-3), 120.9 (C-2), 139.9 (C-5), 141.4 (C-7); GC/MS (40 eV): *m/z* (%): 176 $[M]^+$ (68), 161 (9), 147 (25), 133 (68), 119 (25), 105 (28), 91 (100), 77 (33), 65 (19), 55 (19). When the reaction was carried out in THF under reflux, **6c** was obtained in place of the diol **13** (ratio **6c**/**14** 56:44, GC analysis). Compound **6c** was identified by its mass spectrum, which could be superimposed on that obtained above.

Thermal cyclization of the cyclodienynes 6: A solution of **6** (10^{-4} M) in perdeuterated *o*-dichlorobenzene was placed in an NMR tube under nitrogen, and the tube was heated in an oil bath at the temperature given in Scheme 5. Product formation was monitored by ^{1}H NMR spectroscopy, and the benzocycloalkenes **26** were identified by their NMR spectroscopic data, with the commercially available **26a** (tetralin) used as a reference compound.

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