Completely Spirocyclopropanated Macrocyclic Oligodiacetylenes and Their Permethylated Analogues: Preparation and Properties

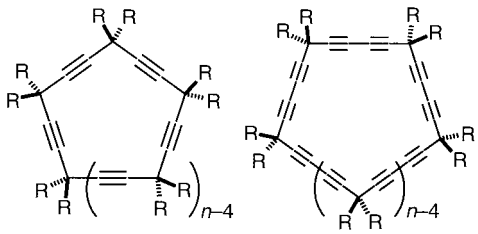
Armin de Meijere* and Sergei I. Kozhushkov[a]

Abstract: The acyclic dehydrotrimer (**12**) and -hexamer (**28**) of 1,1-diethynyl-2,2,3,3-tetramethylcyclopropane were prepared from 1-chloro-1-(trimethylsilylethynyl)-2,2,3,3-tetramethylcyclopropane (**4**) in six and nine steps, respectively, in 36 and 8% overall yield, respectively, using Cadiot–Chodkiewicz or Hay coupling procedures as key steps. Mono-*tert*-butyldimethylsilyl (TBDMS) protection of the acyclic dehydrotrimer (**20**) and -hexamer (**23**) of 1,1-diethynylcyclopropane followed by Hay coupling and protiodesilylation furnished the acyclic dehydrohexamer (**23**) and -dodecamer (**29**) in 35 and 56% overall yield, respectively. Subsequent cyclizing oxidative dimerization of **12** or cyclization of **28** using a modified Glaser protocol produced the first completely permethylspirocyclopropanated macrocyclic oligodiacetylene, compound **30** in 49 and 21% yield, respectively. The cyclic dehydrohexa- (**31**) and dehydrododecamer (**32**) have been prepared from **23** and **29** in 49 and 7% yield by applying the same protocol. The macrocycle **32** is particularly interesting in that it contains 60 carbon atoms in the inner ring, and indeed a decomposition mode consecutively cleaving off ethylene units from it as well as from **31** and tetramethylethylene from the permethylated exp-[6]rotane **30** has been proved by differential scanning calorimetry with evolved gas analysis. The thermal decomposition of these "exploding" [6]rotanes **31** and **30** set on at 100 and 135 °C, respectively, and release energies of 478 and 285 kcal · mol^{-1}, respectively, significantly more than the energy release of the explosive hexogen with 143 kcal mol^{-1}.

Keywords: alkynes · cyclooligomerization · small ring systems · spiro compounds · thermal decomposition

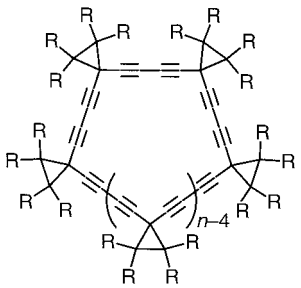
Introduction

After a rather quiet period following the classical work of Sondheimer et al.,[1] the synthesis of macrocyclic oligoacetylenes with a capacity for cyclic electronic interaction and the investigation of their properties has become an actively pursued area of acetylene chemistry again.[2] Among the many systems studied, the macrocyclic structurally homoconjugated oligoacetylenes such as the so-called "pericyclynes" **1a**,[3, 4] expanded **2a**[5] and spirocyclopropanated pericyclynes **1b**,[6] and expanded [*n*]rotanes **2b**[7] were of special interest to evaluate the potential effects of homoconjugation and cyclic homoconjugation, particularly in neutral molecules.[8] The spirocyclopropanated analogues are more intriguing from this point of view, as the highest occupied molecular orbitals (HOMOs) of a cyclopropane ring[9] are much closer in energy to the π-MOs of an acetylene unit than are the σ-MOs of a *gem*-dimethylcarbon group.



1a R = Me
1b R,R = CH_2–CH_2

2a R = Me
2b R,R = CH_2–CH_2



3a R = Me
3b R,R = CH_2–CH_2

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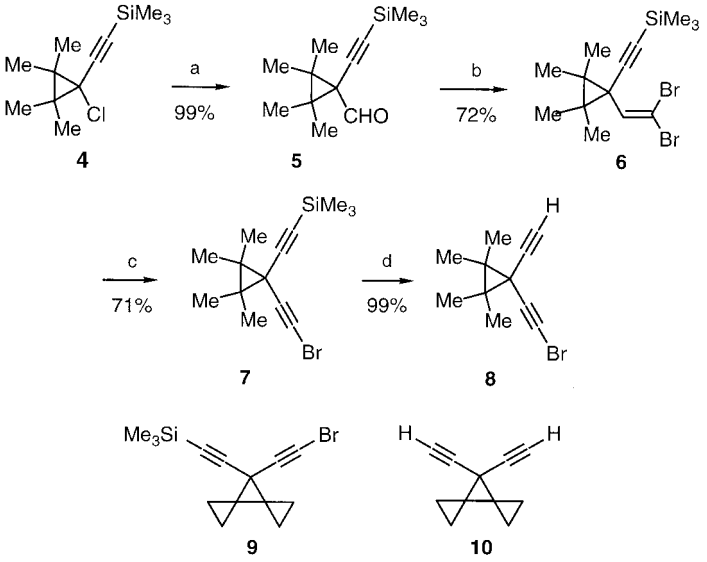
All these compounds are extremely high-energy molecules. For example, a striking feature common to all of the "blown-up" [*n*]rotanes **2b** is their shock sensitivity: When struck too hard with a spatula, a pestle, or a falling ball, they go off with a flame and yield a cloud of black soot.[7] The composition of the black soot formed in such destructive processes is of special interest.[10] For example, not only have amorphous carbon and graphite, but also ordered tube- and onion-type carbon layers along with the evolution of methane and hydrogen gas been detected upon an analogous explosive thermal decomposition of a cyclic oligoyne with aromatic connectors.[11] However, only amorphous carbon with small graphitic areas was found in the explosion products of the butadiyne-expanded [*n*]rotanes **2b**, and traces of C_{60} fullerene were detected by mass spectrometry after the explosion of exp-[6]rotane **2b** (*n* = 6).[12] To be able to quantify and identify all of the gaseous products formed in these explosions,[13] we have elaborated a new approach to the expanded [*n*]rotanes **2b** as well as some permethylated analogues **3a**, and investigated a possible synthetic route towards perspirocyclopropanated exp-[*n*]rotanes **3b**. Herein we report the synthetic aspects of these investigations.

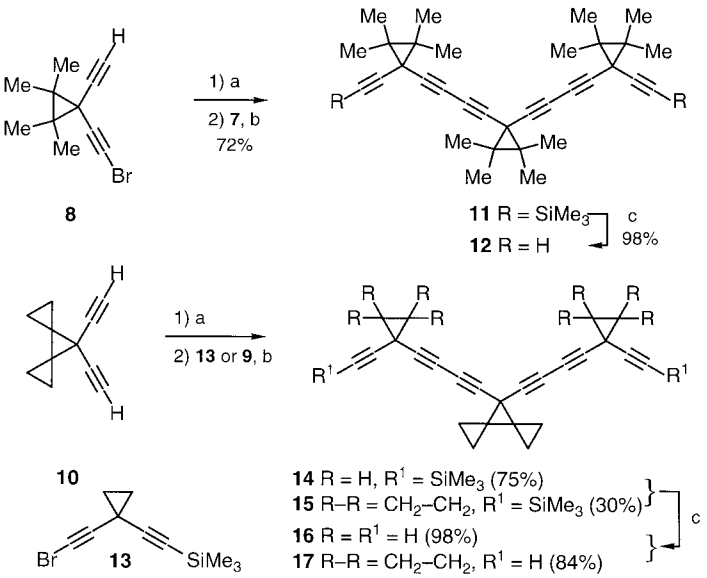


Scheme 1. The basic building blocks for butadiyne-expanded permethylated and perspirocyclopropanated [*n*]rotanes. a) *n*BuLi, Et_2O, −78 °C, 0.5 h, 20 °C, 1 h, then DMF, −10 °C; b) CBr_4, Ph_3P, Zn, CH_2Cl_2, 20 °C, 72 h; c) *t*BuOK, THF, −78 °C, 5 h; d) $KF \cdot 2H_2O$, DMF, 20 °C, 3 h.

Results and Discussion

According to previous experience,[7] a reasonable approach to macrocycles of type **3** containing butadiyne moieties is by oxidative coupling of one, two or more open-chain dehydrooligomers of the corresponding parent 1,4-diyne applying the $CuCl/Cu(OAc)_2$/pyridine system,[14] and the success then depends on the availability of an appropriate building block for the corresponding acyclic dehydrooligomers. The starting material for the butadiyne-expanded permethylated [*n*]rotanes **3a**, the bromodiethynylcyclopropane **8**, was obtained starting from 1-chloro-1-(trimethylsilylethynyl)tetramethylcyclopropane (**4**).[15] Lithiation of **4** by halogen–metal exchange with *n*-butyllithium and subsequent treatment with dimethylformamide followed by Corey–Fuchs olefination[16] and dehydrobromination with potassium *tert*-butoxide in tetrahydrofuran, gave 1-(bromoethynyl)-1-(trimethylsilylethynyl)tetramethylcyclopropane (**7**) in 51% overall yield. This diyne was cleanly protiodesilylated to give the 1-bromo-1,4-diyne **8** (99% yield) (Scheme 1). An analogous access to the 7,7-diethynyldispiro[2.0.2.1]heptanes **9** and **10** has previously been published in another context.[17]

Starting from the building blocks **7**—**10** and **13**[7] and using two standard operations, namely the Cadiot–Chodkiewicz coupling via intermediate copper derivatives[18] and protiodesilylation under various conditions, it was possible to construct the immediate precursors to the permethylated **3a** and spirocyclopropanated **3b** exploded [*n*]rotanes, namely the open-chain oligoynes **12**, **16**, and **17** in 71, 74, and 25% yield, respectively (Scheme 2). The approach to exploded [*n*]rotanes of types **2b** and **3a** by oxidative ring closure of a single prefabricated open-chain dehydrooligomer would certainly be far more selective than the previously reported synthesis by oxidative assembly of more than one building block.[7] Potential starting materials for this approach containing an



Scheme 2. Preparation of acyclic 1,1-diethynylcyclopropane dehydrotrimers **12**, **16** and **17**. a) MeLi, Et_2O or THF, 0 °C, 1 h, then CuCl, THF, 0 °C, 2 h; b) Py, 20 °C, 5 h; c) $KF \cdot 2H_2O$, DMF/H_2O 10:1, 20 °C, 3 h.

even number of 1,1-diethynylcyclopropane units, may be efficiently prepared from the acyclic dehydrotrimers **12** and **20**[7] applying the Hay coupling protocol[19, 20] as a key step (Scheme 3). The trimethylsilyl residue does not provide sufficient protection when long-chain acyclic dehydrooligomers of 1,4-diynes are to be made.[7] Deprotonation of **12** and **20** with one equivalent of *n*-butyllithium followed by treatment with *tert*-butyldimethylsilyl chloride furnished the monosilylated dehydrotrimers **18** and **21** in 52 and 48% yield, respectively, along with the bissilylated compounds **19** and **22** (21 and 29% yield, respectively). Partial protiodesilylation of the latter provided some more **18** and **21** after chromatographic separation, albeit in moderate yields (Scheme 3, yields of compounds **18**, **21**, and **24** are given as obtained

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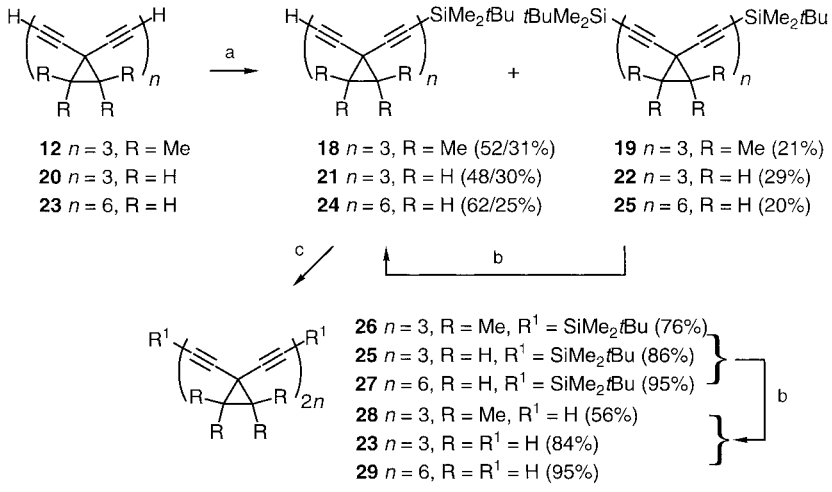


Scheme 3. Preparation of acyclic oligoynes **23**, **28**, **29** by Hay coupling of **18**, **21**, **24** and subsequent desilylation. a) *n*BuLi (1 equiv), THF, −78 °C, 1 h, then TBDMSCl, −78 → 20 °C; b) KOH, nBu_4NF, THF, 20 °C, 0.5–72 h; c) CuCl·TMEDA, O_2, acetone, 20 °C, 1 h.

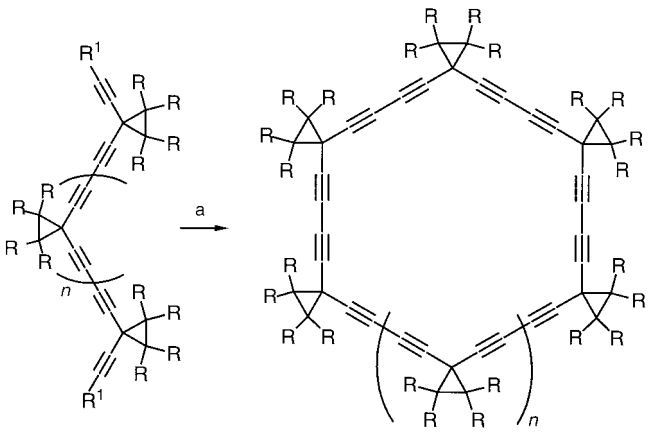
along the routes a and b), as the complete desilylation is a competing process.

The oxidative dimerization of the monosilylated dehydrotrimers **18** and **21** according to the Hay coupling protocol provided the corresponding bisprotected dehydrohexamers **26** and **25** in 76 and 86% yield, respectively. The latter was subjected to the desilylation–silylation cycle described above to give the monoprotected acyclic dehydrohexamer **24** which was dimerized again to yield the bissilylated dehydrododecamer **27** almost quantitatively. All three coupling products **25**–**27** were completely deprotected to **23**, **28**, and **29** which could be used directly for oxidative cyclization. With increasing chain length as well as with the methyl substitution on the cyclopropane rings the rate of desilylation and the solubility of the products in all organic solvents decreased significantly. These problems of solubility of the starting materials as well as of the products and the limited stabilities of the higher open-chain deprotected dehydrooligomers make the subsequent duplicative stepwise assembly less advantageous.

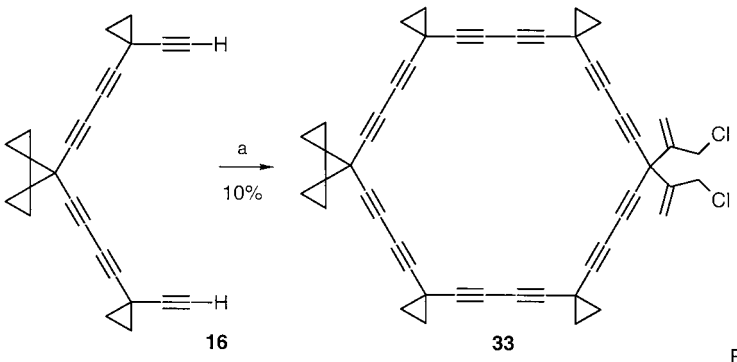
In close analogy to the previously reported preparation of the exp-[*n*]rotanes **2b**,[7] the cyclizations and cocyclizations of **11**, **12**, **28**, **23**, and **29** were performed by adding the solution of the respective starting material in pyridine over a period of three days to a slurry of cuprous chloride and cupric acetate in pyridine, and the reaction mixtures were stirred at ambient temperature for an additional four days. As protiodesilylation does occur under the applied conditions,[7] all three acyclic permethylated dehydrooligomers **11**, **12**, and **28** were subjected to the cyclization conditions. But cyclodehydrodimerization of the silylated permethyldehydrotrimer **11** gave a lower yield of the permethyl-exp-[6]rotane **30** (37%) than that of its desilylated analogue **12** (49%), and the yield of **30** obtained by oxidative cyclization of the acyclic hexamer **28** was even lower (21%) (Scheme 4). This phenomenon must have to do with the fact that the acyclic higher permethylated dehydrooligomers unexpectedly have an increased tendency to decompose when kept at room temperature in the syringe pump for extended times. When the acyclic dehydrohexamer **23** was oxidatively cyclized, an increased yield (49%) of the butadiyne-expanded [6]rotane **31** (cf.[7]) was obtained along with the expanded [12]rotane **32** (5%) containing an inner ring of 60 carbon atoms. But the yield of the latter in its preparation from the acyclic dehydrododecamer **29** (7%) suffered from the fact that the corresponding starting material slowly decomposed in solution in the syringe pump.

Apparently, the current methodology does not at all allow one to prepare macrocyclic oligodiacetylenes which would be even more highly strained than the butadiyne-expanded [*n*]rotanes **30**–**32**; no cyclic dehydrooligomers were isolated upon the attempted oxidative coupling of the 7,7-diethynyldispiro[2.0.2.1]heptane dehydrotrimers **15** and **17**.

In the case of the dehydrotrimer **16** with only one dispiro[2.0.2.1]heptane unit, the residue obtained after work-up of the reaction mixture exploded violently upon touching it with a plastic spatula. Column chromatography of the post-explosion mixture furnished one also highly explosive product in low yield (10%), the NMR data of which indicated a cyclic structure of type **33**, in which one dispiro[2.0.2.1]heptane moiety had been retained and a second one had undergone threefold ring opening by formal addition of chlorine with twofold cyclopropyl to allyl rearrangement (Scheme 5). However, it is difficult to say whether



Scheme 4. Two- and one-component assemblies of permethyl-exp-[6]rotane **30** and one-component accesses to exp-[6]rotanes **31**, **32**. a) CuCl, $Cu(OAc)_2$, Py, 20 °C, seven days, slow inverse addition of **11**, **12**, **28**, **23** or **29** over three days.



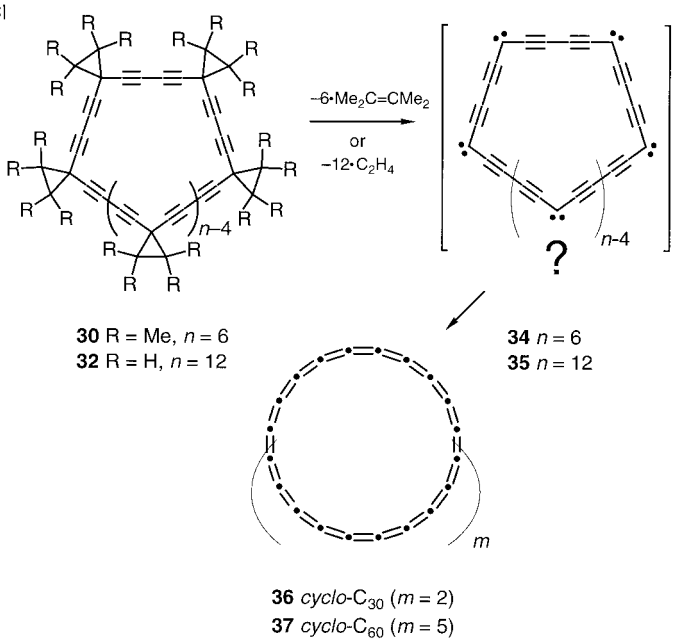
Scheme 5. Attempted synthesis of spirocyclopropanated butadiyne-expanded [*n*]rotane from the acyclic precursor **16**. a) CuCl, $Cu(OAc)_2$, Py, 20 °C, seven days, slow inverse addition of **16** over three days.

33 was the main reaction product or only a by-product which survived the explosion.

The cyclic permethyl-exp-[6]rotane **30** was characterized by its diagnostically simple ^{1}H and ^{13}C NMR spectra (see Experimental Section). Attempts to determine its molecular mass by mass spectrometry with any of the available routine ionization methods (EI, CI, DCI, FD) failed, as the compounds apparently decomposed irregularly in the inlet system of the mass spectrometer. Its molecular mass could successfully be determined by the MALDI-TOF-MS[21] method using a 9-nitroanthracene matrix, and was found to be 887.9 (**30** + Na: calcd for $C_{66}H_{72}Na$ 888.23). Unfortunately, all attempts to grow good quality crystals of the compounds **30**, **32**, and **33** for X-ray crystal structure analyses were unsuccessful (cf.[7b]).

A more detailed investigation of the thermal behavior of the "exploding" [*n*]rotanes by differential scanning calorimetry (DSC) measurements performed in aluminum crucibles with a perforated lid under an argon atmosphere[13] revealed that slow decomposition of exp-[6]rotane **31** starts already at 100 °C and an explosive quantitative decomposition sets on at 154 °C with an energy release of $\Delta H_{decomp} = 478$ kcal · mol^{-1}. The permethylated exp-[6]rotane **30** is thermally less labile and its decomposition is moderated with an onset at 135 °C and a maximum decomposition rate at 194.5 °C with $\Delta H_{decomp} = 285$ kcal · mol^{-1}. For example, ΔH_{decomp} of the well-known explosive hexogen (1,3,5-trinitro-1,3,5-triazacyclohexane, RDX) determined under similar experimental conditions was only 143 kcal · mol^{-1}.

Applying an evolved gas analysis (EGA) technique upon the thermal decomposition of **30** and **31** in different heatable optical cells with rapid scan FT-IR spectroscopy monitoring, the formation of only methane, ethylene, and acetylene could be detected in the case of **31**, and the only gaseous product evolved upon the decomposition of permethyl-exp-[6]rotane **30** was tetramethylethylene. The latter fact leads one to conclude that the spirocyclopropane moieties in these expanded [*n*]rotanes fragment only externally and leave carbene moieties behind. Indeed, the MALDI-TOF mass spectra of several exp-[*n*]rotanes **2b** show fragment ions with $M^+ - 28$.[7a] Thus, if this fragmentation in an exp-[*n*]rotane were to continue *n* times, a cyclic C_n carbon cluster would be left over. It remains to be seen, whether a C_{30} and a C_{60} cluster **36** and **37**, respectively, will be detected in the mass spectrum of permethylated exp-[6]rotane **30** and exp-[12]rotane **32** (Scheme 6).[22] It will also be of interest to obtain clues about the structure of carbon clusters generated in this way and their further fate by such mass spectrometric methods as "ion chromatography".[23]



Scheme 6. Potential approaches to *cyclo*-C_{30} **36** and *cyclo*-C_{60} **37** carbon clusters.

Experimental Section

General aspects: 1-Chloro-1-(trimethylsilylethynyl)-2,2,3,3-tetramethylcyclopropane (**4**),[15] 7-(bromoethynyl)-7-(trimethylsilylethynyl)dispiro[2.0.2.1]-heptane (**9**),[17] 7,7-diethynyldispiro[2.0.2.1]heptane (**10**),[17] 1-(bromoethynyl)-1-(trimethylsilylethynyl)cyclopropane (**13**),[7b] and 3:3,8:8,13:13-trisethanopentadeca-1,4,6,9,11,14-hexayne (**20**)[7b] were prepared according to published procedures. All other chemicals were used as commercially available (Merck, Acrõs, BASF, Bayer, Degussa AG, and Hüls AG). CuCl was dried before use by heating at 100 °C under reduced pressure (0.1 Torr) overnight. All reactions were performed under argon. Organic extracts were dried with $MgSO_4$. All operations in anhydrous solvents were performed under argon in flame-dried glassware. Anhydrous diethyl ether and THF were obtained by distillation from sodium benzophenone ketyl, Me_3SiCl from magnesium, acetone from K_2CO_3, TMEDA, pyridine and DMF from CaH_2, and dichloromethane from P_4O_{10}. ^{1}H and ^{13}C NMR: Spectra were recorded at 250 (^{1}H), and 62.9 (^{13}C, multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) measurements) MHz with a Bruker AM 250 instrument in $CDCl_3$, $CHCl_3/CDCl_3$ as internal reference; δ in ppm, J in Hz. Melting points were determined on a Büchi 510 capillary melting point apparatus, values are uncorrected. TLC analyses were performed on precoated sheets, 0.25 mm Sil G/UV_{254} (Macherey-Nagel). Silica gel grade 60, 230—400 mesh, was used for column chromatography (Merck).

1-Formyl-1-(trimethylsilylethynyl)-2,2,3,3-tetramethylcyclopropane (5): A solution of 1-chloro-1-(trimethylsilylethynyl)-2,2,3,3-tetramethylcyclopropane (**4**)[15] (11.44 g, 50 mmol) in anhydrous Et_2O (100 mL) was treated with *n*BuLi (60 mmol, 23.35 mL of a 2.57 M solution in hexane) at −78 °C. After stirring for an additional 30 min at this temperature, the solution was allowed to warm to ambient temperature, stirred for 1 h, and then cooled to −10 °C. DMF (9.22 mL) was added dropwise, the resulting mixture was allowed to warm to ambient temperature, poured into ice-cold water (200 mL) and extracted with Et_2O (3 × 50 mL). The combined organic solutions were washed with brine (50 mL), dried, and concentrated under

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reduced pressure to give **5** (11.01 g, 99%) as a colorless solid, which was used without further purification. An analytical sample was obtained by crystallization from hexane (m.p. 70–72 °C). ^{1}H NMR: $\delta = 9.68$ (s, 1H; CHO), 1.35 (s, 6H; 2 CH_3), 1.29 (s, 6H; 2 CH_3), 0.18 ppm (s, 9H; 3 CH_3); ^{13}C NMR: $\delta = 0.2$ (3 CH_3), 20.9, 17.1 (2 CH_3), 199.0 (CH), 41.3 (2 C), 103.9, 88.9, 42.4 ppm (C); elemental analysis calcd (%) for $C_{13}H_{22}OSi$ (222.40): C 70.20, H 9.97; found: C 70.44, H 10.19.

1-(2,2-Dibromoethenyl)-1-(trimethylsilylethynyl)-2,2,3,3-tetramethylcyclopropane (6): Zinc (14.61 g, 223.5 mmol), triphenylphosphane (58.62 g, 223.5 mmol), and carbon tetrabromide (74.12 g, 223.5 mmol) were mixed in anhydrous CH_2Cl_2 (450 mL) at −20 °C, and the mixture then stirred at room temperature for 30 h. To the resulting mixture, aldehyde **5** (12.43 g, 55.89 mmol) was added, and stirring was continued for an additional 72 h. The reaction mixture was then poured into pentane (800 mL), and the insoluble materials were removed by filtration. The insoluble fraction was carried through two additional cycles of dichloromethane extraction and pentane precipitation to remove all of the olefinic product. Evaporation of the solvent under reduced pressure gave compound **6** (15.22 g, 72%) as a slightly yellow oil in almost pure form. As column chromatography of **6** was accompanied by significant decomposition (up to 80% of the material), only an analytical sample was purified, $R_f = 0.44$ (pentane); ^{1}H NMR: $\delta =$ 6.37 (s, 1H; =CH), 1.20 (s, 6H; 2 CH_3), 1.03 (s, 6H; 2 CH_3), 0.14 ppm (s, 9H; 3 CH_3); ^{13}C NMR: $\delta = 0.3$ (3 CH_3), 19.6, 18.3 (2 CH_3), 134.6 (CH), 30.4 (2 C), 104.8, 96.2, 84.4, 31.5 ppm (C); elemental analysis calcd (%) for $C_{14}H_{22}Br_2Si$ (378.23): C 44.45, H 5.86; found; C 44.11, H 6.13.

1-(Bromoethynyl)-1-(trimethylsilylethynyl)-2,2,3,3-tetramethylcyclopropane (7): Sublimed potassium *tert*-butoxide (12.43 g, 111 mmol) was added in portions to a solution of dibromoalkene **6** (20.80g, 55 mmol) in anhydrous THF (600 mL) at −78 °C over a period of 2 h. The resulting reaction mixture was stirred at −78 °C for an additional 5 h, and then poured into H_2O (1 L). The aqueous layer was extracted with pentane (3 × 300 mL), and the combined extracts were washed with 5% HCl and 5% $NaHCO_3$ aqueous solutions (400 mL each), water (3 × 250 mL), and dried. After evaporation of the solvent, the crude bromodiyne **7** (15.29 g, 94%) was purified by column chromatography (120 g of silica gel, 40 × 4 cm column, hexane) to give **7** (11.58 g, 71%) as a slightly yellow semisolid, $R_f = 0.44$, m.p. ca. 25 °C; ^{1}H NMR: $\delta = 1.17$ (s, 6H; 2 CH_3), 1.16 (s, 6H; 2 CH_3), 0.14 ppm (s, 9H; 3 CH_3); ^{13}C NMR: $\delta = 0.1$ (3 CH_3), 19.1, 19.0 (2 CH_3), 33.0 (2 C), 103.5, 85.4, 78.1, 38.6, 24.3 ppm (C); elemental analysis calcd (%) for $C_{14}H_{21}BrSi$ (297.30): C 56.55, H 7.12; found: C 56.29, H 7.35.

Cadiot–Chodkiewicz coupling: general procedure (GP) 1: Methyllithium (27.6 mmol, 18.0 mL of a 1.53 M solution in Et_2O) was added at 0 °C over 30 min to a solution of bromodiacetylene **8** or dicetylene **10** (13.8 mmol) in anhydrous ether (for **8**) or THF (for **10**) (50 mL), and the mixture was stirred at this temperature for additional 30 min. In the case of **8**, diethyl ether was carefully removed under vacuum and replaced by anhydrous THF (40 mL) at −20 °C. CuCl (2.732 g, 27.6 mmol) was added at −20 °C to this solution, and the mixture was stirred at 0 °C for an additional 2 h. The THF was then carefully removed under vacuum (**CAUTION**: copper acetylides can be explosive when dry) and replaced by anhydrous pyridine (80 mL), and a solution of **7** (for **8**) or **9**, **13** (for **10**) in THF (40 mL) was added dropwise at 0 °C over a period of 2 h. After additional stirring at 20 °C for 3 h, the resulting mixture was poured into ice cold 15% HCl (160 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 300 mL). The combined extracts were washed with 5% $NaHCO_3$ solution, water (100 mL each), dried, and concentrated under reduced pressure. The crude products were taken up with CH_2Cl_2, preabsorbed on silica gel (20 g) and purified by column chromatography.

1,15-Bis(trimethylsilyl)-3:3,8:8,13:13-tris(1,1,2,2-tetramethylethano)pentadeca-1,4,6,9,11,14-hexayne (11): The crude product mixture obtained from **8** (3.11 g, 13.8 mmol) and **7** (8.21 g, 27.6 mmol) according to GP1 gave, after column chromatography (150 g of silica gel, 40 × 4 cm column, hexane/benzene 4:1), **11** (5.74 g, 72%) as a colorless solid, $R_f = 0.42$, m.p. 153–155 °C (MeOH/hexane, decomp). ^{1}H NMR: $\delta = 1.19$ (s, 24H; 8 CH_3), 1.16 (s, 12H; 4 CH_3), 0.14 ppm (s, 18H; 6 CH_3); ^{13}C NMR: $\delta = 0.1$ (6 CH_3), 19.3, 19.25, 19.1, (4 CH_3), 34.5 (4 C), 103.2, 85.7, 76.1, 74.8, 66.6, 65.9, 36.0, 24.0 (2 C), 24.0 ppm (C); elemental analysis calcd (%) for $C_{39}H_{54}Si_2$ (578.99): C 80.90, H 9.40; found: C 81.06, H 9.52.

1,15-Bis(trimethylsilyl)-3:3,13:13-bisethano-8:8-(bicyclopropyl-1,1′-diyl)-pentadeca-1,4, 6,9,11,14-hexayne (14): The crude product mixture obtained from **10**[17] (1.35 g, 9.49 mmol) and 7-(bromoethynyl)-7-(trimethylsilylethynyl)cyclopropane (**13**)[7b] (4.56 g, 18.92 mmol) according to GP1 gave, after column chromatography (150 g of silica gel, 40 × 4 cm column, hexane/benzene 20:3), **14** (3.27 g, 75%) as a colorless solid, $R_f = 0.33$, m.p. 130–132 °C (MeOH, decomp); ^{1}H NMR: $\delta = 1.27$ (s, 8H; 4 CH_2), 1.21–1.10 and 0.95–0.85 (m, AA′BB′, 8H; 4 CH_2), 0.16 ppm (s, 18H; 6 CH_3); ^{13}C NMR: $\delta =$ -0.8 (6 CH_3), 21.3, 6.6 (4 CH_2), 105.3, 81.5, 79.0, 75.2, 65.0, 61.6, 32.7, 4.0 (2 C), 16.4 ppm (C); elemental analysis calcd (%) for $C_{31}H_{34}Si_2$ (462.78): C 80.46, H 7.41; found: C 80.30, H 7.30.

1,15-Bis(trimethylsilyl)-3:3,8:8,13:13-tris(bicyclopropyl-1,1′-diyl)pentadeca-1,4,6,9,11, 14-hexayne (15): The crude product mixture obtained from **10**[17] (2.275 g, 16 mmol) and **9**[17] (9.385 g, 32 mmol) according to GP1 gave, after column chromatography (150 g of silica gel, 40 × 4 cm column, hexane/benzene 4:1), **15** (2.73 g, 30%) as a colorless solid, $R_f = 0.37$, m.p. 177–178 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: $\delta = 1.22–1.07$ and 0.91–0.86 (m, AA′BB′, 24H; 12 CH_2), 0.13 ppm (s, 18H; 6 CH_3); ^{13}C NMR: $\delta =$ 0.1 (6 CH_3), 6.72, 6.68, 6.4 (4 CH_2), 32.1 (4 C), 102.9, 81.7, 76.7, 75.9, 64.9, 64.4, 16.5, 15.49 ppm (2 C), 15.52 (C); elemental analysis calcd (%) for $C_{39}H_{42}Si_2$ (566.90): C 82.62, H 7.47; found: C 82.53, H 7.58.

Desilylation of trimethylsilyl-protected acetylenes: general procedure (GP) 2: The respective trimethylsilyl-substituted acetylene was added to a solution of three equivalents of $KF \cdot 2H_2O$ per trimethylsilyl group in DMF, and the reaction mixture was stirred at room temperature for 3 h. The resulting mixture was poured into water and extracted with benzene (3 × 80 mL). The combined organic layers were washed with 5% HCl, 5% $NaHCO_3$ solution, H_2O (50 mL each), dried, and concentrated under reduced pressure. The products were purified as indicated below.

1-(Bromoethynyl)-1-ethynyl-2,2,3,3-tetramethylcyclopropane (8): The reaction mixture obtained from the desilylation of **7** (4.0 g, 13.45 mmol) with $KF \cdot 2H_2O$ (3.90 g, 41.4 mmol) in DMF (50 mL) according to GP2 gave essentially pure **8** (3.0 g, 99%) as a colorless oil, which was used without further purification. An analytical sample was obtained by column chromatography (hexane/benzene 3:1, $R_f = 0.41$); m.p. 33–35 °C; ^{1}H NMR: $\delta = 2.13$ (s, 1H; ≡CH), 1.18 (s, 6H; 2 CH_3), 1.17 ppm (s, 6H; 2 CH_3); ^{13}C NMR: $\delta = 19.1$, 19.0 (2 CH_3), 81.5 (CH), 32.6 (2 C), 78.0, 69.0, 38.7, 23.9 ppm (C); elemental analysis calcd (%) for $C_{11}H_{13}Br$ (225.12): C 56.68, H 5.82; found: C 56.41, H 5.89.

3:3,8:8,13:13-Tris(1,1,2,2-tetramethylethano)pentadeca-1,4,6,9,11,14-hexayne (12): The reaction mixture obtained from the desilylation of **11** (8.53 g, 14.73 mmol) with $KF \cdot 2H_2O$ (8.32 g, 88.38 mmol) in DMF (250 mL) according to GP2 gave essentially pure **12** (6.28 g, 98%) as a colorless solid, which was used without further purification. An analytical sample was obtained by column chromatography, $R_f = 0.38$ (hexane/benzene 3:1); m.p. 150–153 °C (decomp.); ^{1}H NMR: $\delta = 2.15$ (s, 2H; 2 ≡CH), 1.21 (s, 12H; 4 CH_3), 1.19 ppm (s, 24H; 8 CH_3); ^{13}C NMR: $\delta = 19.3$, 19.2, 19.1 (4 CH_3), 81.3 (2 CH), 34.1 (4 C), 85.0, 76.0, 69.3, 66.4, 66.0, 36.1, 22.9 (2 C), 24.0 ppm (C); elemental analysis calcd (%) for $C_{33}H_{38}$ (434.63): C 91.19, H 8.81; found: C 90.87, H 9.06.

3:3,13:13-Bisethano-8:8-(bicyclopropyl-1,1′-diyl)pentadeca-1,4,6,9,11,14-hexayne (16): The reaction mixture obtained from the desilylation of **14** (3.19 g, 6.9 mmol) with $KF \cdot 2H_2O$ (3.90 g, 41.4 mmol) in DMF (50 mL) according to GP2 gave essentially pure **16** (2.15 g, 98%) as a colorless solid, which was used without further purification. An analytical sample was obtained by crystallization from wet MeOH; m.p. 102–104 °C; ^{1}H NMR: $\delta = 1.98$ (s, 2H; 2 ≡CH), 1.28 (s, 8H; 4 CH_2), 1.21–1.16 and 0.89–0.85 ppm (m, AA′BB′, 8H; 4 CH_2); ^{13}C NMR: $\delta = 20.6$, 6.6 (4 CH_2), 83.8 (2 CH), 78.6, 75.3, 65.4, 64.8, 62.0, 32.8, 3.0 (2 C), 16.3 ppm (C); elemental analysis calcd (%) for $C_{25}H_{18}$ (318.39): C 94.30, H 5.70; found: C 93.78, H 5.11.

Preparation of *tert*-butyldimethylsilyl-protected acetylenes: general procedure (GP) 3: *n*BuLi (10 mmol, 6.62 mL of a 1.51 M solution in hexane) at −78 °C was added over 30 min to a solution of the respective oligoacetylene **12**, **20**, or **23** (10 mmol) in anhydrous THF (250 mL), and the resulting mixture was stirred for an additional 30 min. After this, *tert*-butyldimethylsilyl chloride (TBDMSCl) (1.58 g, 10.5 mmol) was added in one portion as a 50% solution in toluene, and the reaction mixture was allowed to warm to ambient temperature. After 15 min of stirring at this temperature, the mixture was poured into ice-cold water (200 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with 5% $NaHCO_3$ solution (100 mL), H_2O (100 mL), dried, and concentrated under reduced pressure. The residue was taken up with benzene and adsorbed on

silica gel (20 g). The products were separated by column chromatography on silica gel.

Monoprotection of 3:3,8:8,13:13-tris(1,1,2,2-tetramethylethano)pentadeca-1,4,6,9,11,14-hexayne (12): Column chromatography (200 g of silica gel, 40×4 cm column, hexane/benzene 3:1) of the crude product mixture obtained from the oligoyne **12** (4.65 g, 10.7 mmol) and TBDMSCl (1.69 g, 11.2 mmol) according to GP3 gave the starting material **12** (464 mg, 10%, $R_f = 0.39$), 1-(*tert*-butyldimethylsilyl)-3:3,8:8,13:13-tris(1,1,2,2-tetramethylethano)pentadeca-1,4,6,9,11,14-hexayne (**18**) (3.057 g, 52%), and 1,15-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13-tris(1,1,2,2-tetramethylethano)-pentadeca-1,4,6,9,11,14-hexayne (**19**) (1.49 g, 21%).

18: colorless solid; $R_f = 0.52$; m.p. 143–145 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: $\delta = 2.14$ (s, 1H; ≡CH), 1.20 (s, 12H; 4 CH_3), 1.19 (s, 18H; 6 CH_3), 1.18 (s, 6H; 2 CH_3), 0.91 (s, 9H; 3 CH_3), 0.08 ppm (s, 6H; 2 CH_3); ^{13}C NMR: $\delta = 19.4$, 19.3 (4 CH_3), 26.1 (3 CH_3), 19.2, 19.1, −4.4 (2 CH_3), 83.8 (CH), 36.1, 34.7, 34.1 (2 C), 103.6, 81.3, 76.3, 75.9, 75.0, 74.7, 69.3, 66.6, 66.4, 66.0, 65.8, 24.1, 24.0, 22.9, 16.6 ppm (C); elemental analysis calcd (%) for $C_{39}H_{52}Si$ (548.90): C 85.33, H 9.55; found: C 84.65, H 9.46.

19: colorless solid; $R_f = 0.62$; m.p. 165–166 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: $\delta = 1.19$ (s, 24H; 8 CH_3), 1.18 (s, 12H; 4 CH_3), 0.91 (s, 18H; 6 CH_3), 0.08 ppm (s, 12H, 4 CH_3); ^{13}C NMR: $\delta = 26.1$ (6 CH_3), 19.33, 19.28, 19.2, −4.4 (4 CH_3), 34.6 (4 C), 103.6, 83.8, 76.2, 74.8, 66.6, 65.8, 36.0, 24.1, 16.6 (2 C), 24.0 ppm (C); elemental analysis calcd (%) for $C_{45}H_{66}Si_2$ (663.15): C 81.50, H 10.03; found: C 81.72, H 10.09.

Monoprotection of 3:3,8:8,13:13-trisethanopentadeca-1,4,6,9,11,14-hexayne (20): Column chromatography (100 g of silica gel, 40×3 cm column, hexane/benzene 3:1) of the crude product mixture obtained from the oligoyne **20**[7b] (2.67 g, 10 mmol) and TBDMSCl (1.58 g, 10.5 mmol) according to GP3 gave the starting material **20** (400 mg, 15%, $R_f = 0.27$), 1-(*tert*-butyldimethylsilyl)-3:3,8:8,13:13-trisethanopentadeca-1,4,6,9,11,14-hexayne (**21**) (1.827 g, 48%), and 1,15-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13-trisethanopentadeca-1,4,6,9,11,14-hexayne (**22**) (1.44 g, 29%).

21: colorless oil; $R_f = 0.38$; ^{1}H NMR: $\delta = 1.98$ (s, 1H; ≡CH), 1.30 (s, 4H; 2 CH_2), 1.27 (s, 4H; 2 CH_2), 1.26 (s, 4H; 2 CH_2), 0.89 (s, 9H; 3 CH_3), 0.06 ppm (s, 6H; 2 CH_3); ^{13}C NMR: $\delta = 26.0$ (3 CH_3), −4.7 (2 CH_3), 21.4, 21.3, 20.6 (2 CH_2), 83.6 (CH), 105.9, 79.7, 79.1, 78.6, 77.5, 77.1, 65.8, 62.5, 62.3, 61.7, 61.3, 16.5, 4.0, 3.8, 2.9 ppm (C); elemental analysis calcd (%) for $C_{27}H_{28}Si$ (380.58): C 85.21, H 7.42; found: C 84.91, H 7.58.

22: colorless solid; $R_f = 0.51$; m.p. 99–100 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: $\delta = 1.30$ (s, 4H; 2 CH_2), 1.27 (s, 8H; 4 CH_2), 0.89 (s, 18H; 6 CH_3), 0.05 ppm (s, 12H; 4 CH_3); ^{13}C NMR: $\delta = 26.0$ (6 CH_3), −4.7 (4 CH_3), 21.4 (4 CH_2), 21.3 (2 CH_2), 105.9, 79.8, 79.1, 77.2, 62.5, 61.3, 16.6, 4.0 (2 C), 3.8 ppm (C); elemental analysis calcd (%) for $C_{33}H_{42}Si_2$ (494.84): C 80.09, H 8.56; found: C 79.95, H 8.73.

Monoprotection of 3:3,8:8,13:13,18:18,23:23,28:28-hexakisethanotriaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (23): Column chromatography (300 g of silica gel, 20×7 cm column, hexane/benzene 1:1) of the crude product mixture obtained from the oligoyne **23** (2.39 g, 4.5 mmol) and TBDMSCl (712 mg, 4.7 mmol) according to GP3 gave the starting material **23** (188 mg, 8%, $R_f = 0.38$), 1-(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28-hexakisethanotriaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (**24**) (1.81 g, 62%), and 1,30-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28-hexakisethanotriaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (**25**) (686 mg, 20%).

24: colorless solid; $R_f = 0.49$; m.p. 125–127 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: $\delta = -1.88$ (s, 1H; ≡CH), 1.21 (s, 16H; 8 CH_2), 1.19 (s, 4H; 2 CH_2), 1.18 (s, 4H; 2 CH_2), 0.81 (s, 9H; 3 CH_3), 0.03 ppm (s, 6H; 2 CH_3); ^{13}C NMR: $\delta = 26.0$ (3 CH_3), −4.7 (2 CH_3), 21.36 (6 CH_2), 21.32 (4 CH_2), 20.6 (2 CH_2), 83.5 (CH), 62.3, 3.7 (4 C), 77.56, 65.5 (3 C), 105.8, 79.7, 79.0, 78.6, 77.7, 77.6, 77.2, 77.0, 62.6, 62.4, 62.2, 61.7, 61.4, 4.0, 2.9 ppm (C).

25: colorless solid; $R_f = 0.57$; m.p. 142–144 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: $\delta = 1.30$ (s, 16H; 8 CH_2), 1.27 (s, 8H; 4 CH_2), 0.89 (s, 18H; 6 CH_3), 0.05 ppm (s, 12H; 4 CH_3); ^{13}C NMR: $\delta = 26.0$ (6 CH_3), −4.7 (4 CH_3), 21.44, 21.39, 21.3 (4 CH_2), 77.6, 62.2, 3.8 (4 C), 105.1, 79.7, 79.1, 77.8, 77.6, 62.5, 62.2, 61.3, 16.5, 4.0 ppm (2 C); elemental analysis calcd (%) for $C_{54}H_{54}Si_2$ (759.15): C 85.43, H 7.17; found: C 85.60, H 7.31.

Desilylation of *tert*-butyldimethylsilyl-protected acetylenes: general procedure (GP) 4: An aqueous 2 M KOH solution (2 mL) and TBAF (2 mL of a 1 M solution in THF) were added to a solution of the respective bisprotected oligoyne **19**, **22**, **25**–**27** (7 mmol) in THF (100 mL), and the resulting mixture was vigorously stirred at ambient temperature with TLC monitoring for the indicated time. After this, the resulting mixture was poured into half-saturated aqueous NH_4Cl solution (150 mL) and extracted with THF (3×150 mL or 3×500 mL for **26**, **27**). The combined organic layers were washed with 5% $NaHCO_3$ solution, H_2O (100 mL each), dried, and concentrated under reduced pressure. The residue was taken up with THF, adsorbed on silica gel (20 g) and separated by column chromatography on silica gel (GP4a) or purified as indicated below (GP4b).

Partial desilylation of 1,15-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13-tris(1,1,2,2-tetramethylethano)pentadeca-1,4,6,9,11,14-hexayne (19): Column chromatography (100 g of silica gel, 40×3 cm column, hexane/benzene 3:1) of the crude product mixture obtained from the oligoyne **19** (1.52 g, 2.29 mmol) according to GP4a (4.5 h) gave unreacted **19** (382 mg, 25%), monoprotected oligoyne **18** (391 mg, 31%), and completely deprotected **12** (298 mg, 30%).

Partial desilylation of 1,15-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13-trisethanopentadeca-1,4,6,9,11,14-hexayne (22): Column chromatography (100 g of silica gel, 40×3 cm column, hexane/benzene 3:1) of the crude product mixture obtained from the oligoyne **22** (3.55 g, 7.17 mmol) according to GP4a (30 min) gave unreacted **22** (854 mg, 24%), monoprotected oligoyne **21** (820 mg, 30%), and completely deprotected **20** (668 mg, 35%).

Partial desilylation of 1,30-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28-hexakisethanotriaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (25): Column chromatography (100 g of silica gel, 40×3 cm column, hexane/benzene 1:1) of the crude product mixture obtained from the oligoyne **25** (743 mg, 0.98 mmol) according to GP4a (40 min) gave unreacted **25** (75 mg, 10%), monoprotected oligoyne **24** (160 mg, 25%), and completely deprotected **23** (105 mg, 20%).

Desilylation of 1,30-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28-hexakis(1,1,2,2-tetramethylethano)triaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (26): The crude product obtained from protected oligoyne **26** (4.68 g, 4.27 mmol) according to GP4b (72 h) was crystallized from $CHCl_3$ to give **28** (2.08 g, 56%) as a colorless powder; m.p. > 154 °C (decomp); ^{1}H NMR: $\delta = 2.14$ (s, 2H; 2 ≡CH), 1.20 (s, 18H; 6 CH_3), 1.18 ppm (s, 54H; 18 CH_3); ^{13}C NMR: $\delta = 19.3$ (16 CH_3), 19.2, 19.1 (4 CH_3), 84.3 (2 CH), 36.3, 36.2, 34.1 (4 C), 81.3, 77.6, 76.0, 75.2, 69.3, 67.9, 66.4, 66.3, 66.0, 26.1 25.6, 24.0 ppm (2 C); elemental analysis calcd (%) for $C_{66}H_{74}$ (867.28): C 91.40, H 8.60; found: C 90.99, H 8.95.

Desilylation of 1,30-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28-hexakisethanotriaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (25): The crude product obtained from the protected oligoyne **25** (2.04 g, 2.68 mmol) according to GP4b (2 h) was crystallized from MeOH/$CHCl_3$ to give **23** (1.19 g, 84%) as a colorless powder; explosion point 140 °C; ^{1}H NMR: $\delta = 1.98$ (s, 2H; 2 ≡CH), 1.30 (s, 16H; 8 CH_2), 1.28 ppm (s, 8H; 4 CH_2); ^{13}C NMR: $\delta = 21.38$, 21.36, 20.7 (4 CH_2), 83.7 (2 CH), 65.5, 3.8 (4 C), 78.7, 77.72, 77.66, 77.4, 77.2, 62.33, 62.25, 62.2, 61.7, 3.0 ppm (2 C); elemental analysis calcd (%) for $C_{42}H_{26}$ (530.63): C 95.06, H 4.94; found: C 94.86, H 5.24.

Desilylation of 1,60-bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28,33:33,38:38,43:43,48:48,53:53,58:58-dodecakisethanohexaconta-1,4,6,9,11,14,16,19,21,24,26,29,31,34,36,39,41,44,46,49,51,54,56,59-tetracosayne (27): Almost pure 3:3,8:8,13:13,18:18,23:23,28:28,33:33,38:38,43:43,48:48,53:53,58:58-dodecakisethanohexaconta-1,4,6,9,11,14,16,19,21,24,26,29,31,34,36,39,41,44,46,49,51,54,56,59-tetracosayne (**29**) (1.64 g, 95%) was obtained as a colorless powder from protected oligoyne **27** (2.10 g, 1.63 mmol) according to GP4b (1 h). An analytical sample was obtained by crystallization from $CHCl_3$; > 130 °C (decomp); ^{1}H NMR: $\delta = 1.99$ (s, 2H; 2 ≡CH), 1.31 (br s, 32H; 16 CH_2), 1.29 (s, 8H; 4 CH_2), 1.25 ppm (s, 8H; 4 CH_2); ^{13}C NMR: $\delta = 21.4$ (br, 20 CH_2), 20.7 (4 CH_2), 84.1 (2 CH), 77.8, 62.3, 3.8 (several indistinguishable C), 78.8, 77.2, 65.5, 3.0 ppm (2 C); elemental analysis calcd (%) for $C_{84}H_{50}$ (1059.24): C 95.24, H 4.76; found: C 95.30, H 5.15.

Hay coupling: general procedure (GP) 5: A solution of TMEDA·CuCl (freshly prepared from TMEDA (1.56 g, 2.02 mL, 13.38 mmol) and CuCl (4.04 g, 40.8 mmol) in anhydrous acetone (70 mL) according to the published procedure[24]) was added to a solution of the respective monoprotected oligoacetylene **18**, **21**, or **24** (13.43 mmol) in anhydrous acetone (120 mL), and an intensive stream of anhydrous oxygen was passed through the resulting mixture with stirring at ambient temperature for 1 h.

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After this, the resulting mixture was poured into a 1:1 half-saturated NH_4Cl solution (150 mL) and extracted with THF (3 × 100 mL). The combined organic layers were washed with 5% HCl, 5% $NaHCO_3$ solutions and H_2O (100 mL each), dried, and concentrated under reduced pressure. The residue was crystallized from a mixture of MeOH/$CHCl_3$ (**25**, **26**) or washed with Et_2O (**27**).

1,30-Bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28-hexakis(1,1,2,2-tetramethylethano)triaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (26): From the TBDMS-protected oligoyne **18** (4.83 g, 8.8 mmol), **26** (3.67 g, 76%) was obtained according to GP5 after crystallization as a colorless solid; m.p. 151–154 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: δ = 1.23 (s, 12H; 4 CH_3), 1.17 (br s, 60H; 20 CH_3), 0.88 (s, 18H; 6 CH_3), 0.06 ppm (s, 12H; 4 CH_3); ^{13}C NMR: δ = 19.3 (16 CH_3), 26.0 (6 CH_3), 19.21, 19.15, −4.5 (4 CH_3), 36.2, 36.1, 36.0 (4 C), 103.5, 83.7, 76.2, 75.2, 75.11, 75.10, 74.6, 69.4, 69.2, 66.6, 66.4, 65.7, 25.5, 24.0, 23.9, 16.5 ppm (2 C); elemental analysis calcd (%) for $C_{78}H_{102}Si_2$ (1095.78): C 85.49, H 9.38; found: C 85.18, H 9.51.

1,30-Bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28-hexakisethanotriaconta-1,4,6,9,11,14,16,19,21,24,26,29-dodecayne (25): From the TBDMS-protected oligoyne **21** (5.10 g, 13.4 mmol), **25** (4.36 g, 86%) was obtained according to GP5 after crystallization as a colorless solid.

1,60-Bis(*tert*-butyldimethylsilyl)-3:3,8:8,13:13,18:18,23:23,28:28,33:33,38:38,43:43,48:48,53:53,58:58-dodecakisethanohexaconta-1,4,6,9,11,14,16,19,21,24,26,29,31,34,36,39,41,44,46,49,51,54,56,59-tetracosayne (27): From the TBDMS-protected oligoyne **24** (1.94 g, 3.0 mmol), **27** (1.84 g, 95%) was obtained according to GP5 as a colorless solid; m. p. 165–168 °C (MeOH/$CHCl_3$, decomp); ^{1}H NMR: δ = 1.31 (br s, 48H; 24 CH_2), 0.89 (s, 18H; 6 CH_3), 0.06 ppm (s, 12H; 4 CH_3); ^{13}C NMR: δ = 26.0 (6 CH_3), −4.7 (4 CH_3), 21.4 (br s, 24 CH_2), 3.8 (10 C), 105.9, 79.8, 79.1, 77.2, 62.6, 61.32, 53.7, 16.6, 4.0 (2 C), 62.55, 62.26 ppm (several C); elemental analysis calcd (%) for $C_{96}H_{78}Si_2$ (1287.75): C 89.53, H 6.11; found: C 89.40, H 6.21.

Oxidative coupling of oligoacetylenes: general procedure (GP) 6: A solution of the respective oligoacetylene (3.75 mmol) in anhydrous pyridine (50 mL) was added dropwise over 72 h to a slurry of CuCl (5.72 g, 57.77 mmol) and $Cu(OAc)_2$ (14.39 g, 79.22 mmol) in anhydrous, oxygen-free pyridine (1250 mL) at 20 °C. The reaction mixture was stirred for an additional four days, and then concentrated HCl (1250 mL) was added at −5 to −10 °C; during this addition the reaction mixture was cooled with a dry ice/acetone bath. The aqueous layer was extracted with CH_2Cl_2 (4 × 250 mL), and the combined extracts were washed with ice-cold 5% HCl (2 × 250 mL), 5% $NaHCO_3$ solution, water (250 mL each), dried and concentrated under reduced pressure. The products were isolated by crystallization from an appropriate solvent or taken up with THF, adsorbed on silica gel and purified by column chromatography on silica gel. (**CAUTION**: the isolated products should neither be heated too high nor scratched with a spatula too harshly, as they may suddenly decompose to leave only black soot).

1,1,2,2,9,9,10,10,16,16,17,17,23,23,24,24,30,30,31,31,37,37,38,38-Tetracosamethylhexaspiro[2.4.2.4.2.4.2.4.2.4.2.4]dotetraconta-4,6,11,13,18,20,25,27,32,34,39,41-dodecayne (30): a) The reaction mixture obtained from **11** (1.74 g, 3.0 mmol) according to GP6 was adsorbed on 20 g of silica gel from THF (50 mL) and purified by chromatography on silica gel (200 g, 30 × 7 cm column, hexane/benzene 3:1) to give **30** (480 mg, 37%) as a colorless powder, R_f = 0.29, m.p. 194.5 °C (decomp; DSC). ^{1}H NMR (C_6D_6): δ = 1.03 ppm (s, 72H, 24 CH_3); ^{13}C NMR (C_6D_6): δ = 19.2 (24 CH_3), 76.1, 67.8, 35.7 (12 C), 24.9 ppm (6 C); MS (MALDI-TOF): *m/z* (%): 887.9 (100) [*M* + Na^+]; calcd. for $C_{66}H_{72}Na$: 888.23. b) The crude product mixture obtained from **12** (1.09 g, 2.5 mmol) according to GP6 was adsorbed on 20 g of silica gel from THF (50 mL) and purified by chromatography on silica gel (200 g, 30 × 7 cm column, hexane/benzene 3:1) to give **30** (531 mg, 49%). c) The crude product mixture obtained from **28** (2.15 g, 2.48 mmol) according to GP6 was adsorbed on 40 g of silica gel from THF (100 mL) and purified by chromatography on silica gel (300 g, 30 × 7 cm column, hexane/benzene 2:1) to give **30** (448 mg, 21%), R_f = 0.46.

Hexaspiro[2.4.2.4.2.4.2.4.2.4.2.4]dotetraconta-4,6,11,13,18,20,25,27,32,34,39,41-dodecayne (31) and dodecaspiro[2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4.2.4]tetraoctaconta-4,6,11,13,18,20,25,27,32,34,39,41,46,48,53,55,60,62,67,69,74,76,81,83-tetracosayne (32): a) The crude product mixture obtained from **23** (955 mg, 1.8 mmol) according to GP6 was adsorbed on 20 g of silica gel from THF (100 mL) and purified by chromatography on silica gel (200 g, 30 × 7 cm column, hexane/benzene 1:1) to give **31** (468 mg, 49%), R_f = 0.38, and **32** (48 mg, 5%), R_f = 0.16. Their physical and spectroscopic properties were identical to the published ones.[7b] b) The crude product mixture obtained from **29** (1.06 g, 1.0 mmol) according to GP6 was adsorbed on 20 g of silica gel from THF (100 mL) and purified by chromatography on silica gel (200 g, 30 × 7 cm column, hexane/benzene 1:1) to give **31** (73 mg, 7%).

Oxidative coupling of 3:3,13:13-bisethano-8:8-(bicyclopropyl-1,1′-diyl)-pentadeca-1,4,6,9,11,14-hexayne (16): The residue obtained from **16** (1.26 g, 3.96 mmol) according to GP6 exploded violently upon touching it with a plastic spatula. The post-explosion mixture was taken up in THF (50 mL), adsorbed on silica gel (20 g) and purified by chromatography on silica gel (200 g, 30 × 7 cm column, hexane/benzene 2:1) to give, according to its ^{1}H and ^{13}C NMR spectra, 26,26-bis(3-chloropropen-2-yl)heptaspiro-[2.0.2.0.4.2.4.2.9.2.4.2.4]tetratetraconta-8,10,15,17,22,24,27,29,34,36,41,43-dodecayne (**33**) (135 mg, 10%); R_f = 0.27; ^{1}H NMR: δ = 4.65 (br s, 2H; =CH_2), 4.51 (br s, 2H; =CH_2), 3.23 (br s, 4H; 2 CH_2Cl), 1.29 (s, 16H; 8 CH_2), 1.18–1.10 and 0.92–0.88 ppm (m, AA′BB′, 8H; 4 CH_2); ^{13}C NMR (C_6D_6): δ = 21.1, 20.8, 16.4 (4 CH_2), 101.6, 45.7 (2 CH_2), 80.2, 78.2, 77.0, 69.2, 63.5, 63.1, 4.3 (4 C), 150.0, 70.1 (2 C), 40.0, 16.3 ppm (C).

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