179. Synthesis and Structure of Functionalized Cyclododecadiynes and -dienes

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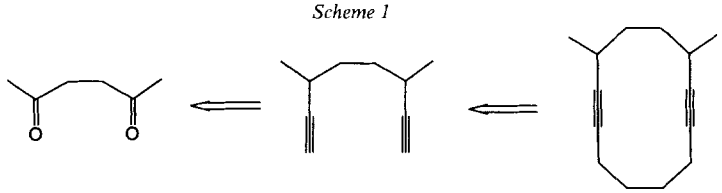
(14.VI.96)

The cyclododecadiynes **3b–d**, **8b–d**, and **10b–c** with functionalities in two propargylic positions, as well as the monofunctionalized diyne **13b** have been prepared from simple open-chain building blocks. In the DMPU (= *N*,*N*′-dimethylpropyleneurea)-assisted ring-closing alkylation of 1,7-diynes, the twelve-membered ring compounds have been prepared in yields of 16–55%. The preparation of the diene-diyne **15** and the cyclododeca-5,11-diyne-1,4-dione **18** are described.

1. Introduction. – The renaissance of the interest in medium-sized rings is due to the recognition that a substituted eight-membered ring is found in taxol [1], and that ene-diyne structures in ten-membered rings are the reactive functionality in anticancer compounds like calicheamycine [2] and dynemicine [3]. Also the interest in dihydroannulenes as building blocks for nanomaterials [4] as well as the chemistry of the so-called 'super'-phanes should be mentioned [5]. In many cases, the unsaturated medium-sized rings exhibit strong transannular reactivity forming the basis of their novel and intriguing chemistry.

For a study of transannular reactions with bi- and trifunctional reagents, we developed a method for the synthesis of symmetrically 1,4-functionalized cyclododeca-5,11-diynes and -5,11-dienes, which allows for the introduction of two additional C=C bonds. Our approach is based on building blocks with four C-atoms which are symmetrically extended by two C-atoms. The termini of the C_8 chains, *i.e.*, the 1,7-diynes, prepared in this manner, are then simultaneously coupled with another C_4 building block (*cf. Scheme 1*).

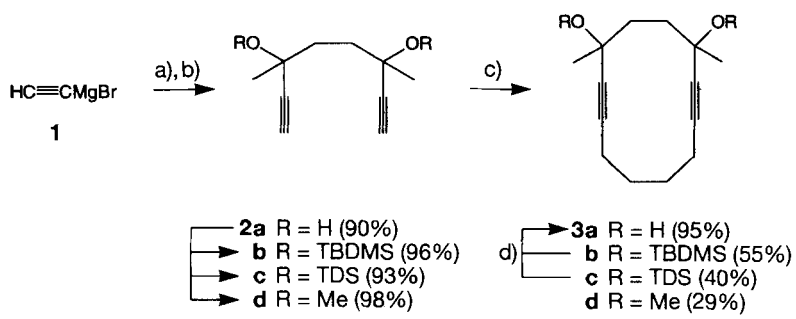
Scheme 1



This synthetic strategy has been used before for the preparation of unsubstituted cyclododecadiynes by *Gleiter* [6]. More recently, octadehydro[12]annulenes have been prepared by the oxidative dimerization of hex-3-ene-1,5-diynes, obtained by double coupling of an alkene with two C_2 fragments [7]. In all these cases, the termini of these alkadiynes provided the two functionalities for the cyclization reaction. We report here a short reliable synthesis of 3,6-disubstituted cyclododeca-1,7-diynes and their derivatives.

2. Results and Discussion. – When acetonylacetone (= hexane-2,5-dione) was reacted with 2 equiv. of HC≡CMgBr (**1**), the diyne-diol **2a** was obtained in a yield of 90% with a ratio *meso*/*rac* 54:46. After silylation of **2a** with (*tert*-butyl)dimethylsilyl trifluoromethanesulfonate (TBDMS triflate) or thexyldimethylsilyl (= (1,1,2-trimethylpropyl)dimethylsilyl) (TDS) chloride and deprotonation with BuLi, **2b** and **2c** were alkylated with 1,4-diiodo- or 1,4-dibromobutane in THF and in the presence of *N*,*N*′-dimethylpropyleneurea (DMPU) to give the cyclododecadiynes **3b** and **3c** in yields of 55 and 40%, respectively (*Scheme 2*). The reactions proceeded well in the presence of DMPU [8]; otherwise, only 5–10% of the desired products were obtained. In the case of **3b**, the addition of 1,4-dibromobutane and DMPU in one batch gave better results than a slow addition by syringe techniques, and all other alkylations were performed accordingly. Cyclization of **2d** at room temperature gave only 20% of **3d**, whereas the yield increased slightly to 29% at 50°. No cyclic product was obtained in the alkylation of the dibenzyl derivative of **2a** with 1,4-dibromobutane. Alkylation of **2b** with (*Z*)-1,4-dichlorobut-2-ene gave a very poor yield of the cyclized product. No cyclododecadiynes were obtained in the reaction of the di-MgBr salt of **2b** with hexane-2,5-dione. Only starting material could be recovered when the reaction was performed in the presence of $LiClO_4$ or additional $MgBr_2$.

Scheme 2



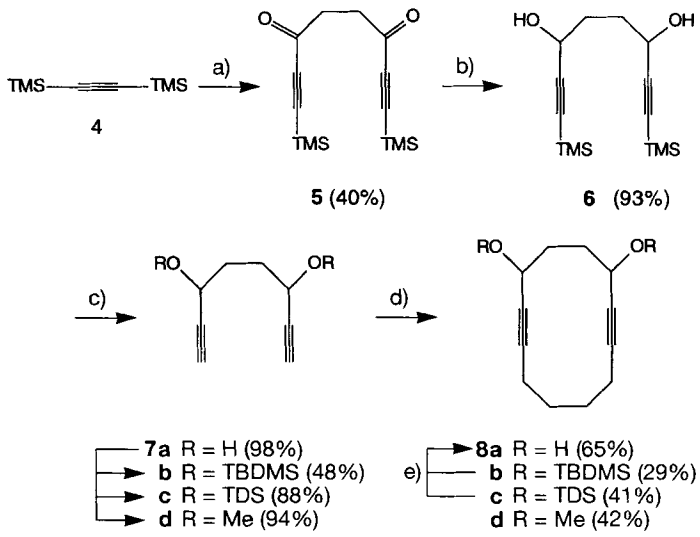
a) $MeCO(CH_2)_2COMe$, THF. b) TBDMS-triflate, Et_3N, THF; or TDS-Cl, imidazole, DMF; or 2 BuLi, MeI, DMSO, THF. c) 2 BuLi, DMPU, $X(CH_2)_4X$, X = I or Br, THF, r.t. d) TBAF, THF.

Also, the protection of the OH groups of **2a** seems to be important, as no cyclic products were obtained when **2a** was treated with 4 equiv. of BuLi, DMPU, and 1,4-dibromobutane under the same conditions. The diastereoisomers of **3b**, obtained in a ratio *meso*/*rac* 1:1, were separated by crystallization.

For the synthesis of cyclododeca-5,11-diynes with secondary OH groups in 1,4-positions, the sequence outlined below was pursued. The reaction of succinyl dichloride with bis(trimethylsilyl)ethyne **4** gave **5** in a yield of 40% (*Scheme 3*). Reduction with $NaBH_4$/$CeCl_3$ gave 93% of the diol **6** in a ratio *meso*/*rac* 1:1. After removal of the Me_3Si groups and protection of the OH groups in **7**, reaction of **7b** and **7c** with 1,4-dibromobutane in the presence of DMPU gave the cyclododecadiynes **8b** and **8c** in 29 and 41% yield, respectively. Cyclization of the dimethoxy derivative **7d** with 1,4-dibromobutane to give

8d was achieved under the same conditions in a yield of 42%. All these reactions were performed at room temperature, after it had been found that yields decrease at higher temperature.

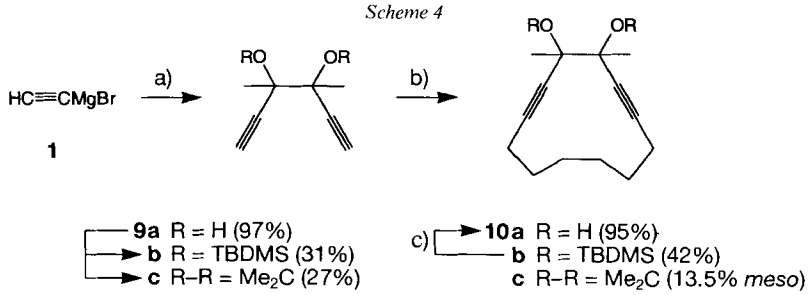
Scheme 3



a) $ClCOCH_2CH_2COCl$, $AlCl_3$, CH_2Cl_2. b) $NaBH_4/CeCl_3$. c) 1. $AgNO_3$/KCN, EtOH, H_2O; 2. TDS-Cl, imidazole, DMF; or TBDMS-Cl, imidazole, DMF; or 2 BuLi, MeI, DMSO, THF. d) 2 BuLi, DMPU, $Br(CH_2)_4Br$, THF, r.t. e) TBAF, THF.

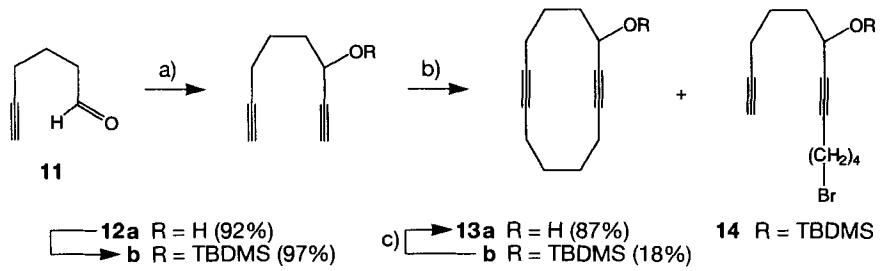
Modifiying this bifunctional approach, the 3,4-bis[(*tert*-butyl)dimethylsilyloxy]-cyclododeca-1,5-diyne **10b** was prepared from butane-2,3-dione *via* **9a** and **9b** (*Scheme 4*). Whereas both diastereoisomers of **9b** could be cyclized, only the *meso*-form of **10c** was obtained, when the mixture of the acetonides **9c** were reacted with 1,6-dibromohexane. In this case, a reaction temperature of 40–45° was necessary for the ring-forming dialkylation. Similarly, the monosubstituted cyclododeca-1,7-diyne **13b** was obtained from hex-5-ynal **11** *via* **12a** and **12b** at a temperature of 45–50° with a yield of 16% in the cyclization step (*Scheme 4*). The isolation of **14** as a by-product suggests that the (*t*-Bu)Me_2SiO group enhances the alkylation of the proximal alkyne.

Scheme 4



a) 1. MeCOCOMe, THF; 2. TBDMS-triflate, Et_3N, THF; or acetone, TsOH, C_6H_{12}. b) 2 BuLi, DMPU, $Br(CH_2)_6Br$, THF, 45–50°. c) TBAF, THF.

Scheme 5



a) 1. 1; 2. TBDMS-triflate, Et_3N, THF. b) BuLi, DMPU, $Br(CH_2)_4Br$, 45–50°, THF. c) TBAF, THF.

Structure Determination. The cyclic structures of **3a–d**, **8a–d**, and **10b** are supported by their ^{13}C-NMR spectra, which show two sets of six signals of equal intensity for the ring C-atoms of the *meso*- and racemic form. The *meso*-form of **10c** is apparent from the different chemical shifts in the ^1H-NMR spectrum for the two Me groups of the acetonide.

Further evidence for the twelve-membered ring systems is provided by the X-ray structure analysis of *rac*-**3a**, *rac*-**3b**, and *rac*-**8a** [9] [10], obtained by slow crystallization or chromatography. The stereoisomers of the diols **2a**, **3a**, **7a**, and **8a** were apparent from GC analyses with chiral phases (*cf. Exper. Part*).

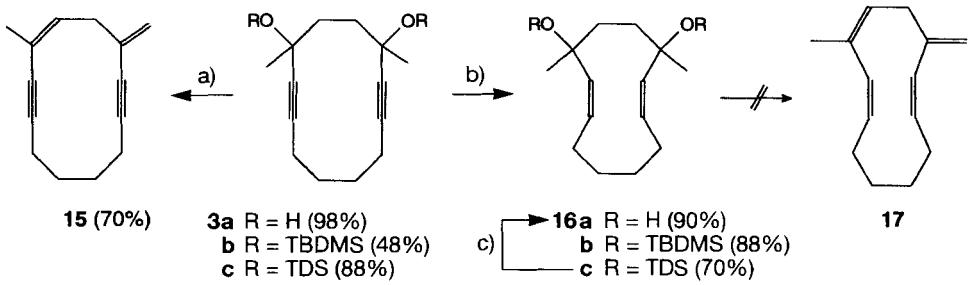
In the X-ray structure of *rac*-**3a**, *rac*-**3b**, and *rac*-**8a**, the geometry at the C≡C bond deviates slightly from a linear arrangement. Also, the dihedral angles C(4)–C(5)–C(6)–C(7) as well as C(10)–C(11)–C(12)–C(1) deviate from an ideal staggered arrangement. The bond lengths of the C≡C bonds are in the expected range of 1.18–1.19 Å. In all three compounds, **3a**, **3b**, and **8a**, the 'crossed' arrangements of the alkylene chains are similar to that described for unsubstituted cyclododecane [11]. These structures differ from those found for ten-, eleven-, and twelve-membered cyclic diynes containing exo- or endocyclic C=C bonds [12]. AM1 Calculations for *rac*-**3a** and *rac*-**8a** gave structural results which closely resemble those found in the X-ray structures of the racemic forms. The AM1 comparison of the racemates with the *meso*-forms of **3a** and **8a** indicate that the latter are less stable by 1–2 kcal/mol. These results form a solid basis for a detailed exploration of the conformational space of these compounds and the consequences for the transannular reactivity [6].

Transformations. When the diol **3a**, obtained by desilylation of **3b** or **3c**, was treated with MsCl, the diene-diyne **15** was formed directly. This compound was also obtained upon treatment of **3b** with Ac_2O and $FeCl_3$. The isomer containing two endocyclic, conjugated C=C bonds could not be observed under these conditions. Hydrogenation of **3b** or **3c** with *Lindlar* catalyst gave the (*Z*,*Z*)-dienes **16b** and **16c**, respectively, in high yield (*Scheme 6*). So far, our attempts to prepare the tetraene **17** or an isomeric tetraene from **16a**, readily available from **16c** under the conditions applied to **3a**, have failed.

Oxidation of the secondary OH groups in **8a** gave the diyne-dione **18** as a colorless liquid in high yield (*Scheme 7*). Reaction of the dimesylate **8e**, prepared from **8a**, with $LiAlH_4$ gave the known cyclododeca-1,7-diyne **19** [13] rather than the expected diallene **20**[1]).

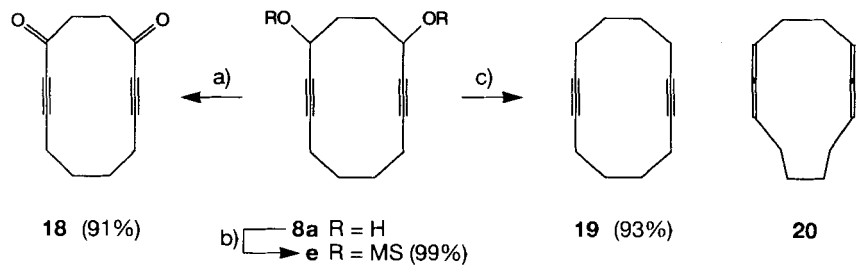
[1]) Cyclic diallenes and allen-ynes have been obtained from activated **3a**, **8a**, as well as from **13a** by Cu^I-induced alkylation *via* 1,3-substitution reactions [14].

Scheme 6



a) **3a**: MsCl, Et_3N; **3b**: Ac_2O, $FeCl_3$. b) **3b** or **3c**: H_2/*Lindlar* cat. c) TBAF, THF.

Scheme 7



a) **8a**: PCC, CH_2Cl_2. b) MsCl, Et_3N, CH_2Cl_2. c) **8e**: $LiAlH_4$, Et_2O.

3. Concluding Remarks. – The ring-closing double alkylation of the 1,7-diynes **2b–d** and the 1,5-diynes **9b–c** with 1,4-dibromo- or 1,4-diiodobutane and 1,6-dibromohexane, respectively, in the presence of DMPU leads to the bifunctionalized cyclododeca-1,7-diynes **3b–d** and **10b–c** in acceptable yields. The cyclododecadiynes **8b–c** and **13b** bearing secondary silyloxy groups have been obtained from the readily available 1,7-diynes **7a–c** and **12b**, respectively. This approach, which makes use of the alkylation of terminal dialkynes with 1,4-dibromobutane, 1,4-diiodobutane, and 1,6-dibromohexane in the presence of DMPU, provides a short and rather efficient route to cyclododecadiynes substituted in two propargylic positions[2]). The silyloxy groups in the propargylic positions enhance the ring-forming double alkylation of the terminal alkyne moieties. The transannular reactivity of these compounds with bi- and trifunctional reagents will now be elucidated.

This work has been supported by the *Swiss National Science Foundation* (project No. 20.37270.93 and 20.43565.95) and a fellowship from the *Stipendienfonds der Basler Chemischen Industrie*. *D. Lehmann*, *P. Hübscher*, and *A. Schild* have contributed with their remarkable experimental skills to the success of these investigations. We thank *A. Saxer* for thorough GC analyses.

[2]) We recently found that the repetition of the synthesis of cyclododeca-2,8-diyne-1,7-dione from hex-5-ynol, which we reported earlier [15], led to rather low yields.

Experimental Part

General. Abbreviations: TMS: trimethylsilyl; TDS: thexyl (= 2,3-dimethylbut-2-yl) dimethylsilyl; TBDMS: (*tert*-butyl)dimethylsilyl; DMPU: *N,N'*-dimethylpropylene urea; TBAF: tetrabutylammonium-fluoride trihydrate; TBME: *tert*-butyl methyl ether. Chemicals were purchased from commercial suppliers and used without further purification. BuLi (*Fluka*): 1.6M soln. in hexane. Reactions were normally performed under Ar or N_2. After workup by pouring the reaction mixture onto ice and extraction with Et_2O, the solns. were dried ($MgSO_4$). TLC: silica-gel plates *SIL G/UV$_{254}$* (*Macherey & Nagel*): eluent *1* (Et_2O), *2* (Et_2O/hexane), *3* (Et_2O/pentane), *4* (hexane/AcOEt), *5* (pentane), *6* (hexane). GC: *Hewlett-Packard-HP-5890* instrument, *HP-5-Ultra* capillary column (10 m × 0.2 mm); temp. program 40–220° (3°/min); t_R in min. Chiral analyses: *Hewlett-Packard-HP-5890* instrument, modified cyclodextrins as chiral stationary phase; variable temp. programs; column *A*: 10 m, 30% oktakis{2,3-di-(*O*-acetoxy)-6-*O*-[(*tert*-butyl)dimethylsilyl]}-γ-cyclodextrin in *OV-1701*; column *B*: 25 m, 34% heptakis[2,3,6-tri-(*O*-n-propyl)]-β-cyclodextrin in *OV-1701*; column *C*: 10 m, 100% heptakis[2,3-di-(*O*-acetoxy)-6-*O*-(thexyldimethylsilyl)]-β-cyclodextrin in *OV-1701*; column *D*: 25 m, 40% heptakis{2,3-di-(*O*-methyl)-6-*O*-[(*tert*-butyl)dimethylsilyl]}-β-cyclodextrin + 60% heptakis{2,3-di-(*O*-acetoxy)-6-*O*-[(*tert*-butyl)dimethylsilyl]}-β-cyclodextrin in *OV-1701*; column *E*: 20 m, 25% heptakis{2,3-di-(*O*-methyl)-6-*O*-[(*tert*-butyl)dimethylsilyl]}-β-cyclodextrin in *OV-1701*. Prep. HPLC: *715004 ET, 250/10, Nuc. 50-7* column (*Macherey-Nagel*); flow: 12 ml/min. M.p.: *Büchi 510* melting-point apparatus; uncorrected. IR Spectra: *Perkin-Elmer-872*-IR spectrophotometer; in $CHCl_3$. NMR Spectra: *Bruker-AC-300* (^1H, 300 MHz; ^{13}C, 75 MHz); in $CDCl_3$, if not mentioned otherwise; δ in ppm rel. to internal $CHCl_3$ (= 7.27 ppm) for ^1H-NMR and $CDCl_3$ (= 77.0 ppm) for ^{13}C-NMR; st = stack, heavily overlapping signals. MS: *Varian-MAT-CH7A* (70 eV, EI) and *Fisons Autospec-Q* spectrometer; in *m/z* (rel. intensity). GC/MS: *VG-Autospec* spectrometer.

Preparation of the Acyclic Diyne-diols **2a**, **7a**, *and* **9a**. *3,6-Dimethylocta-1,7-diyne-3,6-diol* (**2a**). Ethyne was bubbled through 100 ml of THF for 45 min at 0°. After addition of 18.68 ml (52.5 mmol) of EtMgBr, obtained from 1.90 g (80 mmol) of Mg and 8.10 g (75 mmol) of EtBr in THF, at temp. < +3° by syringe and stirring for 1 h, a soln. of 2 g (17.5 mmol) of hexane-2,5-dione in 8 ml of THF was added at −20°. After stirring for 12 h at r.t. and workup, a yellow powder was obtained, which, after crystallization from TBME/hexane, gave **2a** as a white powder in a yield of 2.69 g (92.5%). M.p. 83–84°. R_f (*1*) 0.54. GC: t_R 12.28 and 12.69 (54:46); column *A*: t_R 25.02 and 33.82 (48%, 1:1, *rac*), 27.18 (52%, *meso*). IR: 3510*s*, 3115*vs*, 2995*s*, 2940*s*, 1380*s*, 1285*s*, 1243*s*, 1110*s*, 1070*s*, 920*s*, 661*vs*, 643*vs*. ^1H-NMR: 1.48 (*s*, 6 H); 1.49 (*s*, 6 H); 1.77–2.05 (*m*, 8 H); 2.40 (*s*, 4 H); 2.79 (*s*, 2 H). ^{13}C-NMR: *rac*-**2a**: 29.96 (*q*); 38.41 (*t*); 67.73 (*s*); 71.90 (*d*); 87.50 (*s*); *meso*-**2a**: 30.68 (*q*); 38.59 (*t*); 67.89 (*s*); 72.10 (*d*); 87.28 (*s*). MS: 166 (0.5, M^+), 133 (81), 105 (57), 81 (37), 80 (96), 79 (100), 77 (51), 69 (82), 65 (30), 53 (45), 43 (59).

1,8-Bis(trimethylsilyl)octa-1,7-diyne-3,6-dione (**5**). To a soln. of 3.13 g (11.737 mmol) of $AlCl_3$ in 90 ml of CH_2Cl_2, a mixture of 4 g (23.5 mmol) of *bis(trimethylsilyl)ethyne* (**4**) and 1.82 g (11.74 mmol) of succinyl dichloride in 27 ml of CH_2Cl_2 was added at 0° over 30 min. After stirring for 30 min at 0°, a mixture of 30 ml of 10% HCl, 30 g of ice, and 3 g of NaCl was added and stirred for further 30 min. Extraction with CH_2Cl_2 gave solid crude product which, after chromatography with hexane/Et_2O (1:1), yielded 1.254 g (38%) of **5** as yellowish crystalline material. R_f (*4*, 1:1) 0.61. GC: T_R 33.38. IR: 2960*m*, 2915*w*, 2160*m*, 1675*vs*, 1252*vs*, 1105*vs*, 850*vs*. ^1H-NMR: 0.2 (*s*, 18 H); 2.88 (*s*, 4 H). ^{13}C-NMR: −0.87 (*q*); 38.50 (*t*); 98.70 (*s*); 101.39 (*s*); 184.65 (*s*). MS: 279 (3, $[M + 1]^+$), 278 (10, M^+), 264 (25), 263 (100), 235 (16), 133 (24), 126 (21), 125 (99), 97 (50), 73 (63).

1,8-Bis(trimethylsilyl)octa-1,7-diyne-3,6-diol (**6**). To a mixture of 0.815 g (2.19 mmol) of $CeCl_3 \cdot 7\ H_2O$ and 0.300 g (1.079 mmol) of **5** in 20 ml of MeOH, 0.087 g (2.3 mmol) of $NaBH_4$ was added in portions. After 20 min, addition of 4 ml of H_2O followed, and stirring was continued for 10 min. Workup gave 0.285 g (93%) of crude **6** which was desilylated directly. R_f (*2*, 1:1) 0.22. GC: t_R 33.82 and 33.95 (1:1). IR: 3600*s*, 3380*s*, 2960*vs*, 2870*s*, 2160*m*, 1382*s*, 1250*vs*, 1110*vs*, 1070*vs*, 1010*vs*, 845*vs*. ^1H-NMR: 0.16 (*s*, 18 H); 1.90 (*m*, 4 H); 2.70 (br. *s*, 2 H); 4.45 (*m*, 2 H). ^{13}C-NMR: isomer A: −0.16 (*q*); 33.16 (*t*); 62.23 (*d*); 89.67 (*s*); 106.29 (*s*); isomer B: −0.16 (*q*); 33.39 (*t*); 62.35 (*d*); 89.67 (*s*); 106.33 (*s*). MS: 280 (1, $[M - 2]^+$), 248 (22), 191 (21), 154 (20), 147 (47), 140 (25), 138 (35), 133 (23), 125 (25), 123 (81), 75 (51), 73 (100).

Octa-1,7-diyne-3,6-diol (**7a**). To a soln. of 0.348 g (1.079 mmol) of **6** in 8 ml of EtOH was added at 0° with vigorous stirring 0.734 g (4.32 mmol) of $AgNO_3$, dissolved in 7 ml of EtOH/H_2O 5:2. After 25 min, a soln. of 1.052 g (16.19 mmol) of KCN in 1.8 ml of H_2O was added, and stirring was continued for 45 min. Workup and extraction gave 0.146 g (98%) of crude **7a**. R_f (*2*, 2:1) 0.19. t_R 12.79; column *C*: t_R 80.33 and 93.43 (1:1, 47%, *rac*), 85.40 (53%, *meso*). IR: 3605*s*, 3380*s*, 3310*vs*, 2960*m*, 2942*m*, 2120*m*, 1250*s*, 1045*s*, 1005*s*, 640*s*. ^1H-NMR (CD_3OD): 1.82 (*t*, 4 H); 2.79 (*d*, 2 H); 4.34 (*d*, 2 H); no OH signal detected. ^{13}C-NMR (CD_3OD): isomer A: 34.42 (*t*); 62.11 (*d*); 73.72 (*d*); 85.81 (*s*); isomer B: 34.43 (*t*); 62.14 (*d*); 73.72 (*d*); 85.82 (*s*). MS: 121 (0.5, $[M - 17]^+$), 92 (10), 91 (63), 81 (12), 68 (24), 67 (16), 66 (100), 65 (28), 55 (71), 53 (16).

3,4-Dimethylhexa-1,5-diyne-3,4-diol (**9a**). Ethyne was bubbled through 60 ml of THF for 45 min at −5°. After addition of 40 ml (43.5 mmol) of BuMgBr, obtained from 1.11 g (45.7 mmol) of Mg and 4.03 g (43.5 mmol) of BuBr, in THF at temp. < −2° by syringe and stirring for 1 h, a soln. of 1 g (11.6 mmol) of butane-2,3-dione and 547 mg (2.3 mmol) of anh. $MgBr_2$ in 10 ml of THF was added at −25°. After stirring for 12 h at r.t., usual workup gave 1.5 g (97%) of **9a** which could be used without further purification. R_f (*1*) 0.58. GC: t_R 4.05 and 4.98 (1:1). IR: 3540*vs*, 3430*vs*, 3300*vs*, 2980*s*, 2960*s*, 2930*s*, 2120*m*, 1370*vs*, 1335*vs*, 1170*s*, 1150*vs*, 1110*vs*, 1060*vs*, 940*vs*, 830*s*, 640*vs*, 610*s*, 550*s*. ^{1}H-NMR: isomer A: 1.50 (*s*, 6 H); 2.50 (*s*, 2 H); 3.19 (*s*, 2 OH); isomer B: 1.58 (*s*, 6 H); 2.52 (*s*, 2 H); 3.32 (*s*, 2 OH). ^{13}C-NMR: isomer A: 22.97 (*q*); 73.42 (*s*); 73.53 (*d*); 84.26 (*s*); isomer B: 24.76 (*q*); 73.42 (*s*); 73.78 (*d*); 85.06 (*s*).

Preparation of the Acyclic Diynol **12a**. *Octa-1,7-diyn-3-ol* (**12a**). Ethyne was bubbled through 140 ml of THF for 30 min at 0°. After addition of 50 ml (73.4 mmol) of BuMgBr, obtained from 1.87 g (77 mmol) of Mg and 6.87 g (73.4 mmol) of BuBr, in THF at temp. < +3° by syringe and stirring for 1 h, a soln. of 1.9 g (19.8 mmol) of *hex-5-ynal* (**11**) in 5 ml of THF, was added at −20°. After stirring at r.t. for 12 h and workup, a yellow liquid was obtained, which, after chromatography, gave **12a** as colorless liquid in a yield of 2.18 g (92%). R_f (*2*, 1:1) 0.42. GC: t_R 9.54 (isothermic, 40°). IR: 3600*s*, 3400*m*, 3300*vs*, 2950*s*, 2940*s*, 2120*w*, 1070*s*, 1025*s*, 630*vs*. ^{1}H-NMR: 1.51–1.64 (*m*, 2 H); 1.66–1.77 (*m*, 2 H); 1.89 (*t*, 1 H); 2.13 (*td*, 2 H); 2.39 (*d*, 1 H); 3.12 (br. *d*, OH); 4.29 (*qd*, 1 H). ^{13}C-NMR: 17.99 (*t*); 23.89 (*t*); 36.35 (*t*); 61.48 (*d*); 68.89 (*d*); 73.08 (*d*); 84.01 (*s*); 84.71 (*s*). MS: 122 (4, M^+), 103 (37), 94 (63), 91 (30), 81 (68), 79 (75), 78 (61), 77 (57), 70 (40), 68 (40), 67 (60), 66 (76), 65 (60), 55 (100), 53 (76), 52 (50), 51 (52), 43 (41), 41 (60), 40 (58), 39 (80).

General Procedures for the Silylation of the Acyclic Hydroxy Compounds **2a**, **7a**, **9a**, *and* **12a**. *a*) Silylation was performed in THF (2 ml/mmol) with 2 equiv. of Et_3N and 1.5 equiv. of TBDMS-triflate at 0° for 1–2 h, followed by workup and chromatography. *b*) Silylation was performed in DMF (3 ml/mmol) with 20 equiv. of imidazole and 10 equiv. of TDS-Cl at 65° for 6 d, followed by workup and chromatography. *c*) Silylation was performed in DMF (2.5 ml/mmol) with 2 equiv. of imidazole and 1.5 equiv. of TBDMS-Cl at r.t. for 15 h, followed by workup and chromatography.

*3,6-Bis[(*tert*-butyl)dimethylsilyloxy]-3,6-dimethylocta-1,7-diyne* (**2b**). According to *a*), 1 g (6.024 mmol) of **2a** gave 2.28 g (96%) of **2b** as white crystals. M.p. 32–34°. R_f (*2*, 2:1) 0.72. GC: t_R 36.06. IR: 3302*s*, 2960*vs*, 2930*vs*, 2890*s*, 2860*vs*, 1471*s*, 1462*s*, 1250*vs*, 1170*s*, 1085*vs*, 1000*s*, 838*vs*. ^{1}H-NMR: 0.05 (*s*, 12 H); 0.70 (*s*, 18 H); 1.30 (*s*, 6 H); 1.60–1.72 (*m*, 4 H); 2.25 (*s*, 2 H). ^{13}C-NMR: isomer A: −2.77 (*q*); 18.18 (*s*); 25.83 (*q*); 31.26 (*q*); 40.19 (*t*); 68.80 (*s*); 72.02 (*d*); 88.24 (*s*); isomer B: −3.01 (*q*); 18.26 (*s*); 25.83 (*q*); 31.19 (*q*); 40.19 (*t*); 68.85 (*s*); 71.97 (*d*); 88.24 (*s*). MS: 391 (1, $[M - 3]^+$), 379 (1.5), 365 (2), 338 (8), 337 (28), 319 (8), 279 (2), 263 (8), 257 (10), 247 (10), 237 (14), 205 (20), 183 (46), 147 (71), 133 (20), 131 (26), 116 (25), 115 (27), 91 (30), 83 (26), 75 (79), 73 (100), 57 (11), 43 (11). Anal. calc. for $C_{22}H_{42}O_2Si_2$: C 66.93, H 10.72; found: C 66.84, H 10.51.

3,6-Dimethyl-3,6-bis[dimethyl(1,1,2-trimethylpropyl)silyloxy]octa-1,7-diyne (**2c**). According to *b*) 0.544 g (3.275 mmol) of **2a** gave 2.74 g (93%) of **2c** as colorless liquid. R_f (*5*) 0.44. GC: t_R 49.01. IR: 3300*m*, 2850*m*, 2120*m*, 1370*s*, 1255*vs*, 1170*s*, 1110*vs*, 1085*vs*, 1030*s*, 1000*s*, 840*vs*, 660*s*, 635*s*. ^{1}H-NMR: 0.236 (*s*, 6 H); 0.239 (*s*, 6 H); 0.832 (*s*, 12 H); 0.887 (*s*, 6 H); 0.909 (*s*, 6 H); 1.476 (*s*, 3 H); 1.479 (*s*, 3 H); 1.644 (*sept.*, 2 H); 1.76–1.96 (*m*, 4 H); 2.42 (*s*, 1 H); 2.43 (*s*, 1 H). ^{13}C-NMR: isomer A: −1.03 (*q*); 18.67 (*q*); 20.20 (*q*); 20.28 (*q*); 24.86 (*s*); 31.14 (*q*); 34.22 (*d*); 40.24 (*t*); 68.89 (*s*); 71.98 (*d*); 88.11 (*s*); isomer B: −0.78 (*q*); 18.64 (*q*); 20.23 (*q*); 20.27 (*q*); 24.86 (*s*); 31.05 (*q*); 34.19 (*d*); 40.24 (*t*); 68.94 (*s*); 72.04 (*d*); 88.11 (*s*). MS: 435 (0.1, $[M - 15]^+$), 366 (4), 365 (12), 302 (8), 291 (7), 281 (22), 218 (43), 217 (63), 207 (12), 149 (51), 148 (58), 147 (100), 135 (28), 134 (39), 133 (74), 117 (28), 85 (24), 84 (43), 75 (27), 73 (38), 57 (33), 43 (24).

*3,6-Bis[(*tert*-butyl)dimethylsilyloxy]octa-1,7-diyne* (**7b**). According to *c*) 0.996 g (7.22 mmol) of **7a** gave 1.262 g (48%) of **7b** as colorless liquid. R_f (*2*, 1:1) 0.79. GC: t_R 35.06. ^{1}H-NMR: 0.10 (*s*, 6 H); 0.13 (*s*, 6 H); 0.91 (*s*, 18 H); 1.85 (*m*, 4 H); 2.40 (*d*, 2 H); 4.42 (*m*, 2 H). ^{13}C-NMR: isomer A: −5.09 (*q*); 18.18 (*s*); 25.74 (*q*); 33.92 (*t*); 62.34 (*d*); 72.19 (*d*); 85.23 (*s*); isomer B: −4.61 (*q*); 18.18 (*s*); 25.74 (*q*); 33.97 (*t*); 62.48 (*d*); 72.19 (*d*); 85.23 (*s*). MS: 367 (0.2, $[M + 1]^+$), 366 (0.5, M^+), 311 (32), 310 (61), 309 (54), 244 (50), 243 (79), 235 (53), 209 (47), 189 (53), 177 (51), 169 (45), 157 (35), 149 (64), 148 (69), 147 (100), 133 (64), 119 (43), 115 (51), 103 (64), 83 (43), 77 (53), 75 (60), 73 (81).

3,6-Bis[dimethyl(1,1,2-trimethylpropyl)silyloxy]octa-1,7-diyne (**7c**). According to *b*) 0.544 g (3.275 mmol) of **7a** gave 2.74 g (93%) of **7c** as colorless oil. R_f (*2*, 1:1) 0.71. GC: t_R 48.02 and 48.13 (1:1). IR: 3310*s*, 2960*s*, 2865*s*, 2060*s*, 1465*s*, 1252*vs*, 1085*vs*, 834*vs*. ^{1}H-NMR: 0.106 (*s*, 6 H); 0.138 (*s*, 6 H); 0.148 (*s*, 6 H); 0.876 (*s*, 6 H); 0.899 (*s*, 6 H); 0.919 (*s*, 6 H); 1.64 (*qd*, 4 H); 1.84 (*sept.*, 2 H); 2.37 (*dd*, 2 H); 4.41 (*dm*, 2 H). ^{13}C-NMR: isomer A: −3.25 (*q*); 18.51 (*q*); 18.56 (*q*); 20.09 (*q*); 20.11 (*q*); 24.96 (*s*); 33.77 (*t*); 34.11 (*d*); 62.17 (*d*); 72.08 (*d*); 85.29 (*s*); isomer B: −3.25 (*q*); 18.58 (*q*); 20.20 (*q*); 24.97 (*s*); 33.94 (*t*); 34.15 (*d*); 62.28 (*d*); 72.08 (*d*); 85.29 (*s*). MS: 291 (1), 281 (2, $[M - TDS]^+$), 217 (13), 147 (19), 133 (47), 103 (100), 84 (32), 75 (34).

*3,4-Bis[(*tert*-butyl)dimethylsilyloxy]-3,4-dimethylhexa-1,5-diyne* (**9b**). According to *a*) 2 g (14.5 mmol) of **9a** gave 1.65 g (31%) of **9b** and 1.75 g (48%) of monosilylated by-product as colorless liquids. R_f (*2*, 1:1) 0.71. GC: t_R 32.21 and 32.44. IR: 3295*m*, 2890*s*, 2880*m*, 2850*m*, 2120*vw*, 1250*s*, 1150*s*, 1140*s*, 1115*s*, 835*s*. ^{1}H-NMR: isomer A: 0.20 (*s*, 12 H); 0.88 (*s*, 18 H); 1.55 (*s*, 6 H); 2.38 (*s*, 2 H); isomer B: 0.23 (*s*, 12 H); 0.89 (*s*, 18 H); 1.62 (*s*, 6 H); 2.45 (*s*, 2 H). ^{13}C-NMR: isomer A: −3.44 (*q*); −3.00 (*q*); 18.11 (*s*); 25.24 (*q*); 25.55 (*q*); 72.93 (*d*); 74.87 (*s*); 85.86 (*s*); isomer B: −3.06 (*q*); −2.97 (*q*); 18.11 (*s*); 25.62 (*q*); 25.74 (*q*); 26.19 (*q*); 73.21 (*d*); 74.94 (*s*); 86.88 (*s*). MS: 366 (2, M^+), 310 (20), 309 (72), 189 (32), 183 (20), 149 (22), 148 (38), 147 (100), 133 (20), 73 (42).

*3-[(*tert*-Butyl)dimethylsilyloxy]octa-1,7-diyne* (**12b**). According to *a*) 1.3 g (10.9 mmol) of **12a** gave 2.5 g (97%) of **12b** as colorless liquid. R_f (*3*, 1:2) 0.75. GC: t_R 18.27. IR: 3310v*s*, 2975v*s*, 2960v*s*, 2920v*s*, 2880v*s*, 2860v*s*, 2120*w*, 1360*s*, 1250v*s*, 1095v*s*, 1005*s*, 990*s*, 835v*s*, 635v*s*. ^{1}H-NMR: 0.11 (*s*, 3 H); 0.14 (*s*, 3 H); 0.90 (*s*, 9 H); 1.60–1.85 (*sept.*, 4 H); 1.95 (*t*, J = 2.94, 1 H); 2.23 (*td*, J_1 = 6.99, J_2 = 2.94, 2 H); 2.39 (*d*, J = 2.21, 1 H); 4.39 (*td*, J_1 = 6.99, J_2 = 2.21, 1 H). ^{13}C-NMR: −5.13 (*q*); −4.61 (*q*); 18.09 (*q*); 18.14 (*s*); 24.01 (*t*); 25.73 (*q*); 37.37 (*t*); 62.27 (*d*); 68.53 (*d*); 72.22 (*d*); 84.05 (*s*); 85.21 (*s*). MS: 221 (0.5, $[M - 15]^+$), 189 (34), 179 (30), 161 (11), 149 (39), 147 (73), 133 (20), 132 (25), 83 (22), 77 (19), 76 (34), 75 (100), 73 (26).

Methylation of the Acyclic Diols **2a** *and* **7a**. *3,6-Dimethyl-3,6-dimethoxyocta-1,7-diyne* (**2d**). After deprotonation of 1 g (6.02 mmol) of **2a** in 20 ml THF with 7.53 ml (12.05 mmol) BuLi at −25°, 9 ml of DMSO were added. After stirring for 30 min, 5.13 g (12.05 mmol) of MeI were added at 0°. The mixture was warmed to +10° for 1 h and to 45° for 1 h. Workup gave 1.16 g of **2d** as yellowish liquid, which was used without further purification. R_f (*2*, 2:1) 0.65. GC: t_R 13.07 and 13.19 (1.8:1); column *B*: t_R 79.31 (66.7%) and 81.47 (33.3%). IR: 3310v*s*, 2960v*s*, 2950v*s*, 2840*s*, 2120*w*, 1470*s*, 1465*s*, 1380*s*, 1290*s*, 1265*s*, 1175*s*, 1090v*s*. ^{1}H-NMR: 1.42 (*s*, 6 H); 1.85 (*m*, 4 H); 2.45 (*s*, 2 H); 3.36 (*s*, 6 H). ^{13}C-NMR: isomer A: 25.60 (*q*); 35.50 (*t*); 51.38 (*q*); 72.94 (*s*); 73.26 (*d*); 84.67 (*s*); isomer B: 25.60 (*q*); 35.55 (*t*); 51.38 (*q*); 72.89 (*s*); 73.31 (*d*); 84.62 (*s*). MS: 179 (8, $[M - 15]^+$), 178 (4), 147 (15), 128 (18), 115 (10), 91 (10), 83 (100), 42 (10).

3,6-Dimethoxyocta-1,7-diyne (**7d**). To a soln. of 0.284 g (2.05 mmol) of **7a** in 7 ml THF, 2.57 ml (4.12 mmol) of BuLi was added at −20° and stirred for 30 min. After addition of 3.1 ml (4.12 mmol) of DMSO and warming to 0°, 1.75 g (4.12 mmol) of MeI was added. Stirring was continued for 1 h at +10° and 1 h at +45°. Quenching with ice-cold sat. NaCl soln. and extraction with Et_2O gave, after evaporation of the solvent, 0.320 g (94%) of **7d** as colorless liquid. R_f (*3*, 2:1) 0.72. GC: t_R 9.194. IR: 3310v*s*, 2920*s*, 2900*s*, 2860*s*, 2825*s*, 2120*w*, 1465*s*, 1450*s*, 1335*s*, 1100v*s*, 950*s*, 635v*s*. ^{1}H-NMR: 1.90 (*t*, 2 H); 2.45 (*s*, 4 H); 3.41 (*s*, 6 H); 3.98 (*s*, 2 H). ^{13}C-NMR: isomer A: 30.94 (*t*); 56.38 (*q*); 70.47 (*d*); 74.01 (*d*); 82.20 (*s*); isomer B: 30.98 (*t*); 56.38 (*q*); 70.50 (*d*); 74.01 (*d*); 82.20 (*s*). MS: 166 (2, M^+), 164 (4), 134 (12), 108 (9), 107 (9), 102 (12), 94 (8), 76 (11), 70 (9), 68 (100), 42 (7), 38 (13).

4,5-Diethynyl-2,2,4,5-tetramethyl-1,3-dioxolane (**9c**). 1 g (7.25 mmol) of **9a**, 5 ml of acetone, and 310 mg of TsOH were dissolved in 12 ml of cyclohexane. After addition of 4-Å molecular sieve, the mixture was stirred for 3 d. Then 5 ml of Et_3N were added, and the mixture was filtered over silica gel with Et_2O/pentane (3:1). Workup and chromatography with Et_2O/hexane (1:1) gave 354 mg (27%) of **9c** as colorless liquid. R_f (*2*, 1:1) 0.63. GC: t_R 5.62 and 6.45 (1:1). IR: 3300*s*, 2980*m*, 2940*m*, 2120*w*, 1380*s*, 1250*s*, 1185*s*, 1120*s*, 1085*s*, 1070*s*, 1005*s*, 850*s*, 640*s*. ^{1}H-NMR: 1.42 (*d*, 3 H, *meso*); 1.54 (*s*, 6 H, *rac*); 1.56 (*s*, 6 H); 1.67 (*d*, 3 H, *meso*); 1.69 (*s*, 6 H); 2.59 (*s*, 2 H); 2.64 (*s*, 2 H). ^{13}C-NMR: *meso*-isomer: 24.08 (*q*); 27.40 (*q*); 29.33 (*q*); 74.79 (*d*); 79.42 (*s*); 83.66 (*s*); 110.48 (*s*); *rac*-isomer: 24.51 (*q*); 27.55 (*q*); 75.50 (*d*); 79.75 (*s*); 84.05 (*s*); 110.48 (*s*). MS: 164 (24), 163 (100, $[M - 15]^+$), 121 (24), 110 (54), 103 (52), 95 (45), 77 (24), 68 (17), 59 (47), 52 (38), 43 (66).

General Procedure for Cyclization. The precursors for cyclization were dissolved in THF (12 ml/mmol educt) and deprotonated with 2–2.5 equiv. of BuLi at −25°, then warmed to r.t. and stirred for 1 h. After addition of 2.5 equiv. of DMPU and 1.2 equiv. of the appropriate alkylating agent, stirring was continued for 2–7 d at either r.t. or 45–50°. After workup with sat. NH_4Cl soln., extraction with hexane/Et_2O (1:1), drying ($MgSO_4$), and filtration (silica gel, hexane/AcOEt (10:1)), the cyclic products were isolated by CC or HPLC with hexane/AcOEt in various compositions. Alkylating agents: *A1*: 1,4-dibromobutane, *A2*: 1,6-dibromohexane.

*3,6-Bis[(*tert*-butyl)dimethylsilyloxy]-3,6-dimethylcyclododeca-1,7-diyne* (**3b**). 4.0 g (10.15 mmol) of **2b** was cyclized at r.t. with *A1*. A white crystalline material was obtained. CC with hexane/AcOEt 100:1 gave 2.51 g (55%) of **3b** (*meso*/rac 1:1). In addition, 0.5 g (12%) of **2b** was recovered. Slow crystallization from Et_2O/hexane 1:1 gave octahedral crystals of *rac*-**3b**. M.p. (*rac*) 80°. R_f (*4*, 100:1) 0.49. GC: t_R 50.4. IR: 2960*s*, 2935v*s*, 2860*s*, 1250*s*, 1095v*s*, 840v*s*. ^{1}H-NMR: 0.15 (*s*, 12 H); 0.87 (*s*, 18 H); 1.37 (*s*, 6 H); 1.59–1.81 (*m*, 6 H); 1.81–1.89 (*m*, 2 H); 2.07–2.28 (*m*, 4 H). ^{13}C-NMR: *rac*- + *meso*-isomer: −3.01 (*q*); −2.95 (*q*); −2.94 (*q*); −2.89 (*q*); 17.97 (*s*); 17.99 (*s*); 18.77 (*t*); 18.81 (*t*); 25.72 (*q*); 25.78 (*q*); 27.04 (*t*); 30.44 (br. *q*); 41.86 (*t*); 70.18 (*s*); 83.85 (*s*); 83.88 (*s*); 85.15 (*s*); 85.19 (*s*); *rac*-isomer: −3.01 (*q*); −2.88 (*q*); 17.99 (*s*); 18.78 (*t*); 25.72 (*q*); 27.03 (*t*); 30.44 (br. *q*); 41.86 (*t*); 70.18 (*s*); 83.91 (*s*); 85.19 (*s*); *meso*-isomer: −2.94 (*q*); 17.98 (*s*); 18.82 (*t*); 25.72 (*q*); 27.03 (*t*); 30.05 (br. *q*); 41.86 (*t*); 70.18 (*s*); 83.88 (*s*); 85.15 (*s*). MS: 450 (0.3, $[M + 2]^+$), 449 (1.3, $[M + 1]^+$), 448 (3, M^+), 392 (50), 391 (100), 337

(38), 319 (34), 318 (60), 317 (100), 259 (57), 185 (62), 183 (80), 147 (61), 133 (25), 115 (30), 75 (47), 73 (60). Anal. calc. for $C_{26}H_{48}O_2Si_2$: C 69.57, H 10.77; found: C 69.48, H 10.68.

3,6-Dimethyl-3,6-bis[dimethyl(1,1,2-trimethylpropyl)silyloxy]cyclododeca-1,7-diyne (**3c**). Compound **2c** (0.917 g, 2.038 mmol) was cyclized at r.t. with *A1* 0.202 g (20%) **3c** was obtained after CC with hexane/AcOEt 100:1 as colorless liquid. *rac*-**3c** formed octahedral crystals by slow crystallization from Et_2O. In other experiments, a yield of up to 45% was obtained. M.p. (*rac*) 91°. R_f (*4*, 100:1) 0.51. IR: 2980*s*, 2945v*s*, 1250v*s*, 1085v*s*, 830*s*. ^{1}H-NMR: 0.21 (*s*, 12 H); 0.81 (*s*, 12 H); 0.88 (*s*, 6 H); 0.89 (*s*, 6 H); 1.37 (*s*, 6 H); 1.57–1.79 (*m*, 8 H); 1.79–1.90 (*m*, 2 H); 2.09–2.24 (*m*, 4 H). ^{13}C-NMR: −0.83 (*q*); −0.72 (*q*); 18.66 (*q*); 18.80 (*t*); 20.31 (*q*); 20.32 (*q*); 24.76 (*s*); 26.97 (*t*); 30.40 (*q*, weak); 34.26 (*d*); 41.94 (*t*); 70.36 (*s*); 84.02 (*s*); 85.22 (*s*); all measured ^{13}C-NMR spectra (*rac*- or *meso*-isomer or a mixture of them) showed only one set of signals. MS: 505 (0.1, $[M + 1]^+$), 504 (1, M^+), 489 (5), 419 (84), 366 (23), 365 (67), 347 (17), 345 (39), 275 (15), 261 (28), 259 (32), 245 (13), 211 (18), 205 (36), 185 (46), 149 (71), 147 (78), 133 (77), 127 (49), 116 (24), 91 (34), 84 (90), 75 (72), 73 (100). Anal. calc. for $C_{30}H_{56}O_2Si_2$: C 71.36, H 11,18; found: C 71.39, H 11.06.

3,6-Dimethoxy-3,6-dimethylcyclododeca-1,7-diyne (**3d**). Compound **2d** (411.3 mg, 2.12 mmol) was cyclized at 45° with *A1*. After CC with hexane/Et_2O 1:1, 90.7 mg (29.6%) **3d** was obtained as colorless liquid. The diastereoisomers could be separated by HPLC with hexane/AcOEt 10:1. *rac*-**3d** formed colorless crystals, the *meso*-isomer remained liquid. M.p. (*rac*) 50–51°. R_f (*2*, 1:10) 0.51. GC: t_R 33.49 and 33.78 (1:3), pure isomers: 34.04 (*meso*), 34.23 (*rac*). IR: 2940v*s*, 2920v*s*, 2910v*s*, 2870*s*, 2835*s*, 2240*w*, 1450*s*, 1435*s*, 1290*s*, 1250*s*, 1160*s*, 1080v*s*. ^{1}H-NMR: 1.34 (*s*, 6 H); 1.54–1.70 (*m*, 8 H); 2.24 (*t*, 4 H); 3.28 (*s*, 6 H). ^{13}C-NMR: *meso*-isomer: 18.73 (*t*); 26.96 (*t*); 31.56 (*t*); 37.79 (*t*); 51.32 (*q*); 74.91 (*s*); 81.72 (*s*); 85.59 (*s*); *rac*-isomer: 18.73 (*t*); 26.88 (*t*); 31.55 (*t*); 37.83 (*q*); 51.40 (*q*); 74.78 (*s*); 81.75 (*s*); 85.61 (*s*). MS: 248 (0.5, M^+), 233 (84), 218 (33), 217 (80), 204 (42), 202 (40), 186 (32), 177 (37), 176 (50), 174 (36), 173 (37), 163 (100), 161 (54), 145 (69), 143 (62), 131 (80), 129 (64), 115 (42), 105 (52), 91 (70), 79 (36), 77 (46), 43 (94). Anal. calc. for $C_{16}H_{24}O_2$: C 77.38, H9.74; found: C 77.33, H 9.58.

*3,6-Bis[(*tert*-butyl)dimethylsilyloxy]cyclododeca-1,7-diyne* (**8b**). Compound **7b** (1.262 g, 3.44 mmol) was cyclized at r.t. with *A1*. After CC with pentane/Et_2O 20:1, 0.423 g (29%) of **8b** was obtained as colorless liquid. The diastereoisomers 1:1 were separated by HPLC with hexane/AcOEt 100:1. R_f (*4*, 40:1) 0.34. GC: t_R 50.69 and 51.13 (1:1). IR: 2882v*s*, 2859v*s*, 2230*w*, 1450*s*, 1390*s*, 1355*s*, 1340*s*, 1292*s*, 1252v*s*, 1100v*s*, 1008*s*, 840v*s*. ^{1}H-NMR: 0.11 (*s*, 6 H); 0.13 (*s*, 6 H); 0.91 (*s*, 18 H); 1.66 (*sept.*, 4 H); 1.77 (*m*, 4 H); 2.25 (*td*, 4 H); 4.38 (*m*, 2 H). ^{13}C-NMR: *meso*-isomer: −4.96 (*q*); −4.49 (*q*); 17.85 (*t*); 18.25 (*s*); 25.82 (*q*); 26.99 (*t*); 34.64 (*t*); 34.67 (*t*); 62.83 (*d*); 62.97 (*d*); 82.39 (*s*); 82.41 (*s*); 83.50 (*s*); *rac*-isomer: −4.92 (*q*); −4.86 (*q*); −4.52 (*q*); −4.45 (*q*); 18.82 (*s*); 18.85 (*t*); 18.87 (*t*); 23.84 (*q*); 26.96 (*t*); 27.00 (*t*); 33.81 (*t*); 34.03 (*t*); 63.22 (*d*); 63.45 (*d*); 82.57 (*s*); 82.59 (*s*); 84.63 (*s*). GC-MS: 422 (0.2, $[M + 2]^+$), 421 (0.5, $[M + 1]^+$), 420 (1, M^+), 289 (15), 157 (8), 147 (11), 129 (8), 128 (7), 115 (8), 75 (100), 73 (42), 56 (9), 45 (9), 41 (21), 39 (12).

3,6-Bis[dimethyl(1,1,2-trimethylpropyl)silyloxy]cyclododeca-1,7-diyne (**8c**). Compound **7c** (2.0 g, 4.74 mmol) was cyclized at r.t. with *A1*. After CC with hexane/AcOEt 100:1, 0.968 g (41%) of **8c** was obtained as colorless liquid; 0.746 g (37%) **7c** could be recovered. R_f (*3*, 1:20) 0.62. GC: t_R 33.98 and 34.33 (1:1). IR: 2895*s*, 2870*s*, 2220*w*, 1710*m*, 1255*s*, 1092*s*, 838*s*. ^{1}H-NMR: 0.13–0.19 (*m*, 12 H); 0.85 (*d*, 12 H); 0.89 (*dd*, 12 H); 1.54–1.80 (*m*, 8 H); 1.80–1.91 (*m*, 2 H); 1.99–2.31 (*m*, 4 H); 4.40 (*m*, 2 H). ^{13}C-NMR: isomer A: −3.29 (*q*); −3.12 (*q*); 18.49 (*q*); 18.88 (*t*); 20.09 (*q*); 20.28 (*q*); 24.99 (*s*); 27.02 (*t*); 34.09 (*t*); 34.17 (*d*); 62.99 (*d*); 82.70 (*s*); 84.45 (*s*); isomer B: −3.24 (*q*); −3.04 (*q*); 18.56 (*q*); 18.88 (*t*); 20.19 (*q*); 20.34 (*q*); 24.99 (*s*); 27.02 (*t*); 34.11 (*t*); 34.17 (*d*); 63.28 (*d*); 82.76 (*s*); 84.47 (*s*). GC-MS: 478 (4, $[M + 2]^+$), 477 (13, $[M + 1]^+$), 476 (32, M^+), 449 (30), 448 (80), 317 (13), 231 (19), 215 (15), 75 (49), 73 (100), 59 (11).

3,6-Dimethoxycyclododeca-1,7-diyne (**8d**). Compound **7d** (0.302 g, 1.82 mmol) was cyclized at r.t. with *A1*. CC with hexane/Et_2O 1:2 and HPLC with hexane/AcOEt 4:1 gave 0.168 g (42%) of **8d** as colorless liquid. R_f (*2*, 2:1) 0.65. GC: t_R 31.91 and 32.36 (1:1). IR: 2910*s*, 2900*s*, 2880*s*, 2860*s*, 2820*s*, 2210*w*, 1345v*s*, 1250v*s*, 1160*s*, 1100v*s*, 950*s*, 640*s*. ^{1}H-NMR: 1.62–1.72 (*m*, 4 H); 1.82–2.04 (*m*, 8 H); 2.27 (*td*, 2 H); 3.37 (*s*, 3 H); 3.40 (*s*, 3 H). ^{13}C-NMR: 27.05 (*t*); 31.67 (*t*); 33.12 (*t*); 56.17 (*q*); 70.94 (*d*); 70.99 (*d*); 79.33 (*s*); 85.52 (*s*). GC-MS: 220 (1, M^+), 218 (8), 207 (16), 205 (100), 203 (91), 91 (35), 81 (50), 79 (39), 77 (23), 71 (20), 67 (19), 53 (21), 41 (37), 39 (20).

*3,4-Bis[(*tert*-butyl)dimethylsilyloxy]-3,4-dimethylcyclododeca-1,5-diyne* (**10b**). Compound **9b** (776 mg, 2.12 mmol) was cyclized at 50° with *A2*. After HPLC (hexane/AcOEt 100:1), 401 mg (42%) of **10b** could be isolated as a white powder. M.p. 89–91°. R_f (*4*, 1:1) 0.39. GC: t_R 51.64 and 51.75 (1:1). IR: 2950*s*, 2940v*s*, 2930v*s*, 2920v*s*, 2855*s*, 2320*w*, 1250*s*, 1170*s*, 1125v*s*, 1000*s*, 845v*s*. ^{1}H-NMR: 0.17 (*s*, 6 H); 0.18 (*s*, 6 H); 0.88 (*s*, 18 H); 1.48 (*s*, 6 H); 1.50–1.69 (*sept.*, 8 H); 2.24 (*m*, 4 H). ^{13}C-NMR: −3.29 (*q*); −2.98 (*q*); 18.04 (*t*); 18.14 (*s*); 25.56 (*q*); 25.65 (*t*); 25.71 (*q*); 25.92 (*q*); 26.35 (*t*); 75.71 (*s*); 84.33 (*s*); 84.98 (*s*). MS: 448 (1, M^+), 391 (2), 309 (35), 263 (18), 221 (29), 205 (17), 189 (31), 188 (17), 187 (100), 183 (17), 147 (90), 133 (17), 75 (47), 73 (54). Anal. calc. for $C_{26}H_{48}O_2Si_2$: C 69.59, H 10.79; found: C 69.87, H 10.64.

4,5-(Cyclodeca-1,9-diyne-1,10-diyl)-2,2,4,5-tetramethyl-1,3-dioxolane (**10c**). Compound **9c** (340 mg, 1.91 mmol) was cyclized at 50° with *A2*. After HPLC with hexane/AcOEt 10:1, 66.8 mg (13.5%) of *meso*-**10c** and 112 mg (11.7%) of dialkylated by-product were obtained as colorless liquids. R_f (*4*, 2:1) 0.62. GC: t_R 34.19. IR: 2930*vs*, 2920*vs*, 2900*vs*, 2860*vs*, 2240*m*, 1460*s*, 1430*s*, 1375*vs*, 1240*vs*, 1185*vs*, 1120*vs*, 1090*vs*, 1000*vs*, 900*s*, 860*s*. ^{1}H-NMR: 1.37 (*s*, 3 H); 1.45 (*s*, 6 H); 1.49–1.58 (*sept.*, 4 H); 1.58–1.66 (*sept.*, 4 H); 1.64 (*s*, 3 H); 2.23–2.31 (*m*, 4 H). ^{13}C-NMR: 18.15 (*t*); 24.37 (*q*); 25.23 (*t*); 26.15 (*t*); 27.51 (*q*); 29.36 (*q*); 80.48 (*s*); 81.95 (*s*); 86.37 (*s*); 109.41 (*s*). MS: 261 (3, $[M + 1]^+$), 260 (18, M^+), 245 (63), 218 (59), 204 (27), 203 (40), 202 (27), 163 (23), 160 (20), 159 (66), 145 (20), 131 (51), 129 (25), 119 (22), 117 (41), 105 (29), 91 (42), 79 (28), 77 (30), 43 (100). HR-MS: 260.1770 ($C_{17}H_{24}O_2^+$; calc. 260.1776).

*3-[(*tert*-Butyl)dimethylsilyloxy]cyclododeca-1,7-diyne* (**13b**). Compound **12b** (0.5 g, 2.12 mmol) was cyclized at 45–50° with *A1*. After HPLC (hexane/AcOEt 100:1), 112.3 mg (18%) of **13b** and 124.8 mg of the monoalkylated by-product **14** were obtained as colorless liquids. **13b**: R_f (*4*, 100:1) 0.73. GC: t_R 38.90. IR: 2880*s*, 2830*vs*, 2220*w*, 2160*w*, 1470*s*, 1462*s*, 1455*s*, 1360*s*, 1250*s*, 1080*vs*, 1040*s*, 1005*s*, 905*s*, 835*vs*. ^{1}H-NMR: 0.1 (*s*, 3 H); 0.11 (*s*, 3 H); 0.89 (*s*, 9 H); 1.58–1.88 (*sept.*, 6 H); 1.91–2.29 (*sept.*, 8 H); 4.39 (*m*, 1 H). ^{13}C-NMR: −4.71 (*q*); −4.46 (*q*); 18.29 (*s*); 18.66 (*t*); 18.88 (*t*); 18.94 (*t*); 23.99 (*t*); 25.84 (*q*); 26.91 (*t*); 27.55 (*t*); 37.33 (*t*); 63.50 (*d*); 81.23 (*s*); 82.60 (*s*); 84.65 (*s*); 85.19 (*s*). GC-MS: 290 (3, M^+), 275 (1), 233 (46), 160 (17), 159 (95), 158 (22), 157 (66), 131 (37), 129 (43), 117 (32), 115 (32), 91 (40), 77 (28), 75 (100), 73 (81), 59 (26), 41 (31). **14**: R_f (*2*, 1:10) 0.58. GC: t_R 43.37. IR: 3310*s*, 2950*vs*, 2920*vs*, 2878*vs*, 2250*w*, 2120*w*, 1470*s*, 1460*s*, 1380*s*, 1250*vs*, 1100*vs*, 1000*m*, 910*vs*, 835*vs*. ^{1}H-NMR: 0.11 (*s*, 3 H); 0.14 (*s*, 3 H); 0.91 (*s*, 9 H); 1.59–1.80 (*sept.*, 6 H); 1.96 (*t*, 1 H); 2.00 (*m*, 2 H); 2.25 (*qd*, 4 H); 3.44 (*t*, 2 H); 4.37 (*tt*, 1 H). ^{13}C-NMR: −5.01 (*q*); −4.49 (*q*); 17.84 (*s*); 18.15 (*t*); 18.23 (*t*); 24.29 (*t*); 25.81 (*q*); 26.99 (*t*); 31.57 (*t*); 31.66 (*t*); 37.84 (*t*); 62.66 (*d*); 68.39 (*d*); 82.33 (*s*); 83.58 (*s*); 84.26 (*s*). GC-MS: 357 (0.5, $[M - 15]^+$), 355 (0.5, $[M - 17]^+$), 305 (12), 303 (12), 241 (6), 239 (6), 159 (13), 139 (53), 136 (48), 131 (29), 117 (25), 91 (25), 79 (21), 75 (100), 73 (44), 41 (13).

Deprotection of the Cyclic Silyl Ethers **3b**, **3c**, **8b**, **8c**, **10b**, **13b**, *and* **16c**. Silyloxy compounds were deprotected by stirring with 6 equiv. of TBAF in THF for 6 d at r.t. For workup, the mixture was poured onto ice-water and extracted with Et_2O. The crude products were purified either by crystallization or by CC with AcOEt/hexane 2:1.

1,4-Dimethylcyclododeca-5,11-diyne-1,4-diol (**3a**). Deprotection of 0.449 g (1.0 mmol) of **3b** yielded, after crystallization from Et_2O, 0.217 g (98%) of **3a** as white solid. *rac*-**3a** (colorless orthorhombic crystals) could be separated from *meso*-**3a** (white crystal needles) by slow recrystallization from Et_2O. Similarly, **3c** gave **3a** in a yield of 95%. M.p. 144°. R_f (*4*, 1:2) 0.32. GC: t_R 33.16; column *D*: t_R 57.07 (57%); 59.31 and 59.96 (1:1, 43%). IR: 3600*s*, 2980*s*, 2930*vs*, 2862*s*, 2240*w*, 1330*s*, 1105*s*, 1080*vs*. ^{1}H-NMR (D_6(acetone)): 0.48 (*s*, 6 H); 0.87 (*m*, 4 H); 1.23 (*m*, 4 H); 1.30 (*d*, 4 H); 3.17 (*s*, 2 OH). ^{13}C-NMR (D_6(acetone)): *rac*- + *meso*-isomer: 18.88 (*t*); 18.90 (*t*); 27.54 (*t*); 30.05 (br. *q*); 41.15 (*t*); 41.18 (*t*); 68.40 (*s*); 68.51 (*s*); 82.71 (*s*); 82.73 (*s*); 86.24 (*s*); *rac*-isomer: 19.66 (*t*); 28.33 (*t*); 30.05 (br. *q*); 41.52 (*t*); 69.87 (*s*); 84.42 (*s*); 85.96 (*s*); *meso*-isomer: 19.38 (*t*); 28.04 (*t*); 30.05 (br. *q*); 41.45 (*t*); 69.13 (*s*); 83.57 (*s*); 86.31 (*s*). MS: 219 (1, $[M - 1]^+$), 201 (36), 192 (20), 188 (22), 187 (92), 174 (52), 173 (34), 160 (26), 159 (100), 145 (69), 131 (72), 117 (55), 105 (49), 91 (56), 79 (36), 43 (64). Anal. calc. for $C_{14}H_{20}O_2$: C 76.32, H 9.15; found: C 76.14, H 9.09.

Cyclododeca-5,11-diyne-1,4-diol (**8a**). Deprotection of 0.504 g (1.06 mmol) of **8c** gave, after CC with Et_2O/pentane 6:1, 0.107 g (53%) of **8a** as white powder. Crystallization from Et_2O gave *rac*-**8a** as clear orthorhombic crystals and *meso*-**8a** as turbid needles in a ratio of 1:1. Deprotection of **8b** gave **8a** in 65% yield. M.p. 154–155°. R_f (*3*, 6:1) 0.42. GC: t_R 35.12 and 35.17 (1:1), column *E*: t_R 75.95 and 76.79 (1:1, *rac*), 76.57 (*meso*). IR: 3280*vs*, 2895*m*, 2140*w*, 1440*s*, 1415*s*, 1060*s*, 1040*s*. ^{1}H-NMR: 0.71–0.80 (*m*, 4 H); 0.84–1.25 (*sept.*, 4 H); 1.15 (*m*, 2 H); 1.15–1.34 (*tm*, 2 H); 3.24 (*dd*, 2 H); 3.33–3.41 (*sept.*, 2 H). ^{13}C-NMR: *rac*-isomer: 19.12 (*t*); 27.67 (*t*); 34.56 (*t*); 62.69 (*d*); 83.96 (*s*); 84.64 (*s*); *rac*- + *meso*-isomer: 19.16 (*t*); 27.69 (*t*); 27.78 (*t*); 34.15 (*t*); 34.59 (*t*); 62.72 (*d*); 83.89 (*s*); 83.99 (*s*); 84.65 (*s*); 84.71 (*s*). MS: 193 (1, $[M + 1]^+$), 192 (2, M^+), 173 (13), 167 (32), 163 (24), 149 (100), 137 (67), 121 (58), 117 (72), 108 (56), 104 (22), 91 (73), 79 (55), 77 (51), 55 (35). Anal. calc. for $C_{12}H_{16}O_2$: C 74.97, H 8.39; found: C 74.91, H 8.49.

1,2-Dimethylcyclododeca-3,11-diyne-1,2-diol (**10a**). Deprotection of 117.8 mg (0.263 mmol) of **10b** gave after HPLC (hexane/AcOEt 2:1) 54.9 mg (95%) of the diastereoisomers (1:1) of **10a** as white powder. R_f (*4*, 2:1) isomer A: 0.30; isomer B: 0.26. GC: t_R isomer A: 32.952; isomer B: 33.938. IR: 3560*s*, 2940*vs*, 2860*vs*, 2240*m*, 1375*s*, 1340*s*, 1115*s*, 1075*s*, 910*vs*. ^{1}H-NMR: isomer A: 1.47 (*s*, 6 H); 1.51–1.70 (*st.*, 8 H); 2.29 (*m*, 4 H); 2.72 (br. *s*, 2 OH); isomer B: 1.51 (*s*, 6 H); 1.53–1.68 (*st.*, 8 H); 2.28 (*m*, 4 H); 2.43 (br. *s*, 2 OH). ^{13}C-NMR: isomer A: 17.89 (*t*); 22.41 (*q*); 25.48 (*t*); 26.14 (*t*); 74.24 (*s*); 83.50 (*s*); 85.18 (*s*); isomer B: 17.89 (*t*); 22.23 (*q*); 25.46 (*t*); 26.18 (*t*); 74.24 (*s*); 83.70 (*s*); 85.59 (*s*). MS: 220 (0.5, M^+), 119 (20), 109 (10), 105 (10), 97 (14), 95 (22), 93 (10), 91 (24), 84 (100), 82 (21), 79 (18), 77 (16), 69 (89), 67 (14), 55 (13), 53 (14), 43 (79), 41 (23).

Cyclododeca-2,8-diyn-1-ol (**13a**). Deprotection of 112.3 mg (0.387 mmol) of **13b** gave after HPLC (hexane/AcOEt 1:1) 59.7 mg (87%) of **13a** as white solid. M.p. 53–54°. R_f (*4*, 1:1) 0.65. GC: t_R 28.39. IR: 3590*m*, 3450*m*, 2900*s*, 2840*s*, 2220*w*, 1330*s*, 1055*s*, 1030*s*, 1000*s*. ^{1}H-NMR: 1.54–2.05 (*st.*, 9 H); 2.05–2.22 (*m*, 6 H); 4.36 (*d*, OH). ^{13}C-NMR: 18.67 (*t*); 18.78 (*t*); 18.83 (*t*); 23.85 (*t*); 26.69 (*t*); 27.32 (*t*); 36.35 (*t*); 62.96 (*d*); 81.06 (*s*); 81.39 (*s*); 82.02 (*s*); 85.97 (*s*). MS: 176 (2, M^+), 175 (16), 149 (20), 148 (100), 147 (97), 134 (29), 133 (86), 131 (25), 129 (25), 121 (20), 120 (89), 119 (36), 117 (28), 115 (26), 107 (23), 105 (49), 92 (28), 91 (70), 79 (35), 77 (32), 41 (20).

1,4-Dimethylcyclododeca-5,11-diene-1,4-diol (**16a**). Deprotection of 0.167 g (0.33 mmol) of *rac*-**16c** yielded, after CC with hexane/Et_2O 4:1, 66 mg (90.4%) of *rac*-**16a** as white powder. M.p. 136°. R_f (*2*, 4:1) 0.49. GC: t_R 32.08. IR: 3610*m*, 3320*m*, 2930*s*, 2910*m*, 2860*m*, 1635*w*, 1000*s*. ^{1}H-NMR: 1.39 (*s*, 6 H); 1.60 (*s*, 4 H); 1.82 (*m*, 4 H); 2.04 (*m*, 2 H); 2.22 (*s*, 1 H); 3.04 (*s*, 1 H); 3.62 (br., 2 OH); 5.28 (*s*, 2 H); 5.47 (*m*, 2 H). ^{13}C-NMR: 25.83 (*t*); 28.21 (*t*); 31.38 (*q*); 37.35 (*t*); 37.40 (*t*); 74.38 (*s*); 132.52 (*d*); 138.49 (*d*). MS: 206 (25, $[M - 18]^+$), 191 (74), 188 (72), 173 (65), 163 (88), 149 (57), 148 (73), 145 (50), 137 (54), 135 (66), 133 (66), 131 (56), 124 (64), 123 (60), 122 (76), 121 (67), 119 (57), 111 (44), 109 (69), 107 (89), 105 (58), 97 (83), 95 (98), 93 (98), 91 (63), 84 (60), 81 (93), 79 (74), 77 (53), 71 (67), 69 (70), 67 (67), 42 (100), 40 (65). Anal. calc. for $C_{14}H_{24}O_2$: C 74.95, H 10.78; found: C 74.75, H 10.59.

Transformations of the Cyclic Diynes. 3,6-Dimesyloxycyclododeca-1,7-diyne (**8e**). The cyclic dimesylate **8e** was prepared by reaction of 0.082 g (0.43 mmol) of **8a** with 0.216 g (1.88 mmol) of MsCl in 7 ml of CH_2Cl_2 in the presence of 0.234 g (2.31 mmol) of Et_3N at −5°. After stirring for 4 h at 0°, the mixture was treated with 2N HCl, neutralized with sat. $NaHCO_3$ soln., washed with sat. NaCl soln., and dried ($MgSO_4$). Evaporation of the solvent gave 0.121 g (99%) of **8e**, which was used without further purification. R_f 0.49 (*1*). ^{1}H-NMR: 1.55–1.86 (*m*, 4 H); 1.92–2.43 (*m*, 8 H); 3.092 (*s*, 3 H); 3.099 (*s*, 3 H); 5.15–5.34 (*m*, 2 H). ^{13}C-NMR: isomer A: 18.71 (*t*); 26.32 (*t*); 30.39 (*t*); 39.04 (*q*); 71.41 (*d*); 76.32 (*s*); 90.64 (*s*); isomer B: 18.72 (*t*); 26.33 (*t*); 30.81 (*t*); 39.07 (*q*); 71.49 (*d*); 76.35 (*s*); 90.66 (*s*). MS: 348 (0.5, M^+), 330 (2), 279 (29), 252 (10), 173 (30), 167 (61), 156 (21), 149 (82), 131 (33), 129 (33), 115 (26), 103 (25), 96 (94), 81 (76), 79 (100), 78 (69), 65 (59), 57 (24), 31 (37).

1-Methyl-4-methylidenecyclododeca-1-ene-5,11-diyne (**15**). To a suspension of 0.200 g (0.909 mmol) of **3a** in 15 ml CH_2Cl_2, THF was added until a clear soln. was obtained. After addition of 0.423 g of Et_3N and 0.458 g (4.0 mmol) of MsCl at −5°, the mixture was stirred at 0° for 5 h. Extraction with cold 2N HCl and neutralization with sat. $NaHCO_3$ soln. gave, after chromatography (hexane/Et_2O 2:1), 0.118 g (71%) of **15** as colorless liquid. R_f (*6*) 0.175. GC: t_R 26.62. IR: 2920*s*, 2895*m*, 2880*m*, 2850*m*, 2220*w*, 1438*s*, 910*vs*. ^{1}H-NMR: 1.62 (*dq*, 4 H); 1.70 (*s*, 3 H); 2.18 (*t*, 4 H); 2.90 (*d*, 2 H); 4.99 (*dd*, 2 H); 5.45 (*td*, 1 H). ^{13}C-NMR: 19.66 (*t*); 19.94 (*t*); 23.22 (*q*); 25.84 (*t*); 26.08 (*t*); 39.22 (*t*); 81.64 (*s*); 82.51 (*s*); 90.66 (*s*); 94.06 (*s*); 118.93 (*t*); 121.34 (*s*); 130.98 (*s*); 132.94 (*d*). GC-MS: 185 (2, $[M + 1]^+$), 184 (17, M^+), 156 (28), 155 (53), 154 (24), 153 (29), 142 (25), 141 (100), 128 (38), 115 (36), 77 (23), 39 (30).

*3,6-Bis[(*tert*-butyl)dimethylsilyloxy]-3,6-dimethylcyclododeca-1,7-diene* (**16b**). Hydrogenation of 0.050 g (0.111 mmol) of *rac*-**3b** in 5 ml of toluene over 0.140 g of *Lindlar* catalyst for 14 h gave, after filtration through *Celite* and CC with hexane, 0.045 g (88%) of *rac*-**16b** as colorless liquid. R_f (*6*) 0.81. GC: t_R 52.37. IR: 2960*s*, 2925*s*, 2860*s*, 1255*s*, 1110*s*, 1005*s*, 910*vs*, 835*s*. ^{1}H-NMR: 0.07 (*s*, 6 H); 0.10 (*s*, 6 H); 0.89 (*s*, 18 H); 1.35 (*s*, 6 H); 1.48 (*m*, 4 H); 1.81 (*ddd*, 4 H); 2.15 (*m*, 2 H); 2.33 (*m*, 2 H); 5.20–5.30 (*m*, 2 H); 5.40 (*d*, J_{cis} = 12.14, 2 H). ^{13}C-NMR: −2.19 (*q*); −1.85 (*q*); 18.29 (*s*); 25.99 (*q*); 27.34 (*t*); 28.53 (*t*); 31.40 (*q*); 37.82 (*t*); 76.36 (*s*); 130.02 (*d*); 137.42 (*d*). GC-MS: 454 (1, $[M + 2]^+$), 453 (3, $[M + 1]^+$), 452 (7, M^+), 305 (24), 263 (29), 189 (28), 187 (34), 147 (31), 75 (100), 73 (70).

3,6-Dimethyl-3,6-bis[dimethyl(1,1,2-trimethylpropyl)silyloxy]cyclododeca-1,7-diene (**16c**). Similarly, the hydrogenation of 0.234 g (0.463 mmol) of *rac*-**3c** gave 0.167 g (71%) of *rac*-**16c** as colorless liquid. R_f (*5*) 0.63. GC: t_R 52.52. IR: 2840*s*, 1640*w*, 1380*s*, 1255*vs*, 1190*s*, 1150*s*, 1090*vs*, 1015*vs*, 835*vs*. ^{1}H-NMR: 0.12 (*s*, 6 H); 0.14 (*s*, 6 H); 0.82 (*s*, 6 H); 0.83 (*s*, 6 H); 0.89 (*s*, 6 H); 0.91 (*s*, 6 H); 1.16–1.34 (*m*, 6 H); 1.36 (*s*, 6 H); 1.62–1.75 (*m*, 4 H); 2.07–2.34 (*m*, 4 H); 5.18–5.29 (*m*, 2 H); 5.44 (*d*, 2 H). ^{13}C-NMR: 0.09 (*q*); 0.47 (*q*); 18.67 (*q*); 18.69 (*q*); 20.34 (*q*); 20.37 (*q*); 24.99 (*s*); 27.28 (*t*); 28.46 (*t*); 31.51 (*q*); 33.97 (*d*); 34.15 (*d*); 38.15 (*t*); 76.69 (*s*); 129.71 (*d*); 137.48 (*d*). MS: 510 (1, $[M + 1]^+$), 509 (1, M^+), 424 (28), 423 (75), 333 (68), 269 (84), 263 (86), 249 (22), 217 (31), 215 (60), 189 (66), 187 (62), 149 (76), 147 (76), 145 (65), 139 (100), 133 (54), 131 (52), 109 (27), 97 (37), 95 (35), 83 (79), 75 (91), 73 (63), 69 (40).

Cyclododeca-5,11-diyne-1,4-dione (**18**). A mixture of 0.1165 g (0.54 mmol) of pyridinium chlorochromate in 4 ml of CH_2Cl_2 and 0.035 g (0.18 mmol) of **9a** in 0.3 ml of CH_2Cl_2 was stirred for 1 h at 0° and 3 h at r.t. Filtration (*Celite*) with Et_2O gave crude **18**. CC with pentane/Et_2O 1:4 led to 0.031 g (91%) of **18** as colorless liquid. R_f (*3*, 4:1) 0.44. IR: 2920*s*, 2210*s*, 1665*vs*, 1430*w*, 1425*w*. ^{1}H-NMR: 1.87 (*m*, 4 H); 2.49 (*m*, 4 H); 2.90 (*s*, 4 H). ^{13}C-NMR: 19.18 (*t*); 25.83 (*t*); 40.97 (*t*); 82.08 (*s*); 98.51 (*s*); 186.43 (*s*). MS: 188 (7, M^+), 160 (24), 146 (27), 134 (27), 133 (100), 132 (40), 117 (54), 116 (36), 106 (26), 105 (67), 104 (62), 92 (48), 80 (31), 79 (46), 78 (38), 66 (25).

Cyclododeca-1,7-diyne (**19**). Compound **8e** (0.095 g, 0.27 mmol) and 0.12 g (3.16 mmol) of $LiAlH_4$ were mixed in 4 ml Et_2O and refluxed for 3 h. The reaction was quenched at 0° by dropwise addition of sat. Na_2SO_4 soln.

Workup and chromatography with pentane gave 40.4 mg (93%) of **19** as colorless liquid. R_f (*2*, 1:1) 0.60. GC: t_R 20.85. IR: 3000*m*, 2940*m*, 2860*vs*, 2845*vs*, 1455*s*, 1440*s*, 1380*m*, 1365*m*, 1330*m*, 1260*s*, 1100*s*, 1015*s*. ^{1}H-NMR: 1.63 (*sept.*, 8 H); 2.04 (*sept.*, 8 H). ^{13}C-NMR: 19.13 (*t*); 27.16 (*t*); 81.52 (*s*). GC-MS: 160 (2, M^+), 159 (7), 145 (7), 132 (32), 131 (64), 117 (100), 104 (55), 91 (60), 77 (21), 65 (15), 53 (13), 51 (17), 41 (19).

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