2. Tetraethynylethenes: Fully Cross-Conjugated π-Electron Chromophores and Molecular Scaffolds for All-Carbon Networks and Carbon-Rich Nanomaterials

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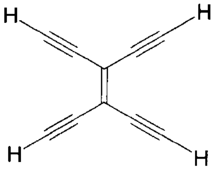
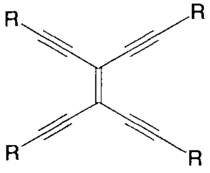
The preparation of tetraethynylethene (3,4-diethynylhex-3-ene-1,5-diyne) **1** as well as of a great diversity of differentially mono-, di-, and triprotected derivatives by newly developed synthetic routes is described. These fully cross-conjugated molecules are versatile building blocks and precursors to two-dimensional all-C networks and novel C-rich nanoarchitecture with unusual structural and electronic properties, such as perethynylated expanded radialenes, or molecular wires and polymers with the novel polytriacetylene backbone. A key step in all of these routes was the *Corey-Fuchs* dibromoolefination of aldehydes and ketones. Dibromoolefination of silyl-protected penta-1,4-diyn-3-ones yielded the corresponding dibromomethylidene derivatives which, by twofold Pd-catalyzed alkyne coupling, were transformed into tetraethynylethene derivatives. In routes to tetraethynylethenes with free *cis*- or *trans*-enediyne moieties, dibromoolefination of aldehyde groups produced geminal dibromoethenes which, upon elimination/metallation with LDA followed by quenching with H^+ or other electrophiles, yielded free or substituted ethynyl groups in high yields. Tetra- and triprotected tetraethynylethenes are rather stable compounds that could be isolated in pure form, whereas derivatives with two or more free $\equiv$C–H termini were only stable in dilute solution and polymerized rapidly in pure form. A *trans*-bis-deprotected, *trans*-bis(triisopropylsilyl)-protected derivative represented an exception and could be isolated as stable crystals. X-Ray analysis revealed that the two bulky $(i\text{-Pr})_3Si$ groups isolate the reactive chromophores from one another in the crystal and prevent intermolecular reactions. The structures of several tetraethynylethenes were revealed in high-quality X-ray crystal structures.

1. Introduction. – In 1987, we started a program aimed at the preparation of novel molecular and polymeric carbon allotropes and carbon-rich nanoarchitecture with unusual structural, electronic, and optical properties [1–3]. As molecular targets, we selected the cyclo[*n*]carbons, *n*-membered monocyclic rings of sp-hybridized C-atoms [1] [4]. As synthetically accessible polymeric targets, we identified two-dimensional C-networks in which the C_{10}-fragment of the fully cross-conjugated tetraethynylethene (3,4-diethynylhex-3-ene-1,5-diyne; **1**) represents the repeating unit [2] [3]. At the beginning of this work, **1** was elusive, and only a few derivatives (**2**–**5**) had been described [5–7]. The first tetraethynylethene derivative **2** was reported in 1969 by *Hori* and coworkers [5], and the persilylated and peralkylated derivatives **3**–**5** were prepared in the mid-seventies by *Hauptmann* [6]. In 1991, *Hopf et al.* [7] summarized this early synthetic work (*Scheme 1*) and reported the X-ray crystal structure of **2**. To get access to the desired C-networks, we developed a novel synthesis of tetraethynylethenes and prepared the parent compound **1** by this route [8].



1



2 R = Ph
3 R = Me
4 R = Me_3C
5 R = Me_3Si

Since the preliminary communication on **1** in 1991, synthetic routes to tetraethynylethenes with essentially any desired substitution and protection pattern have been worked out. Starting from this versatile molecular construction kit, oxidative acetylenic coupling provided access to perethynylated dehydroannulenes [9], expanded radialenes [10], molecular wires [11], and polymers with the novel polytriacetylene (PTA) backbone [12]. These compounds incorporate extended C-cores and are of interest as materials with unusual structural and electronic properties or as specific intermediates on the way to infinite all-C-networks.

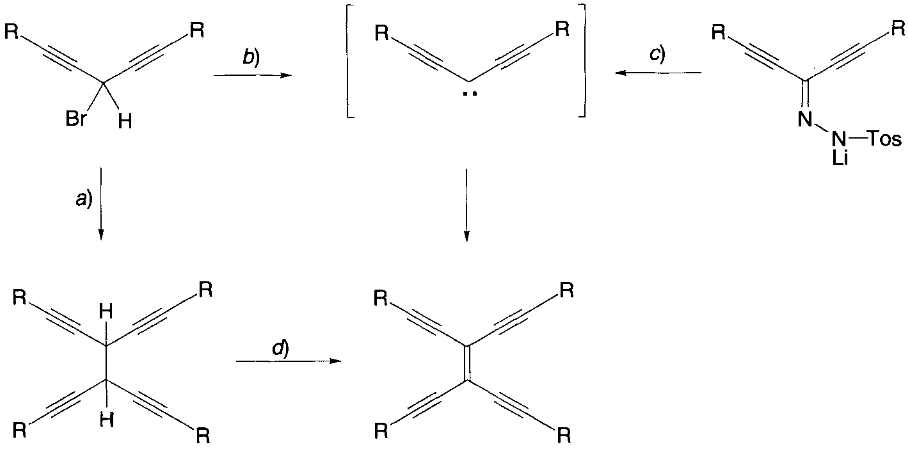
Prior to the synthesis of tetraethynylethene (**1**), *Vollhardt* and coworkers had reported the synthesis of hexaethynylbenzene as a potential precursor for the formation of a two-dimensional all-C-network by oxidative acetylenic coupling [2] [13a]. In the meantime, a variety of other perethynylated molecules have been prepared and explored for similar purposes [13b–h].

In this paper, we provide a full account on the synthesis and properties of tetraethynylethene (**1**) and a great diversity of derivatives which should find increasing use in acetylenic C-scaffolding and the construction of nanomaterials.

2. Results and Discussion. – 2.1. *Early Routes to Tetraethynylethene Derivatives.* Tetrakis(phenylethynyl)ethene (**2**) was prepared in good yield by dimerization of bis(phenylethynyl)methylene carbene, formed by α-elimination of 3-bromo-1,5-diphenylpenta-1,4-diyne (*Scheme 1*, route *b*) [5] [7]. Whereas the *Bamford-Stevens* reaction failed to give **2**, derivatives **4** and **5** could be prepared in low yield by this method (*Scheme 1*, route *c*) [6c]. The most versatile of the early routes involved a reductive dimerization of 3-bromopenta-1,4-diynes under *Finkelstein* conditions followed by dehydrogenation (*Scheme 1*, route *a*) [6a, b]. Since none of these approaches had yielded the parent compound **1**, and since the preparation of differentially substituted or protected tetraethynylethenes by these methods would be difficult due to the formation of product mixtures, a new synthesis was developed.

2.2. *Tetraethynylethene* (**1**) *and Geminally Bis-deprotected Derivatives.* The new synthetic route, which provided access to both **1** and geminally bis-deprotected tetraethynylethenes (*Scheme 4*) started from 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-one (**14**). The 1,5-disubstituted penta-1,4-diyn-3-ones **14**–**17** were conveniently prepared by $BaMnO_4$ or pyridinium chlorochromate (PCC) oxidation of the corresponding penta-1,4-diyn-3-ols **10**–**13** which, in turn, were obtained by addition of lithium acetylides (formed from **6**–**9**) to 3-(trimethylsilyl)prop-2-ynal (*Scheme 2*).

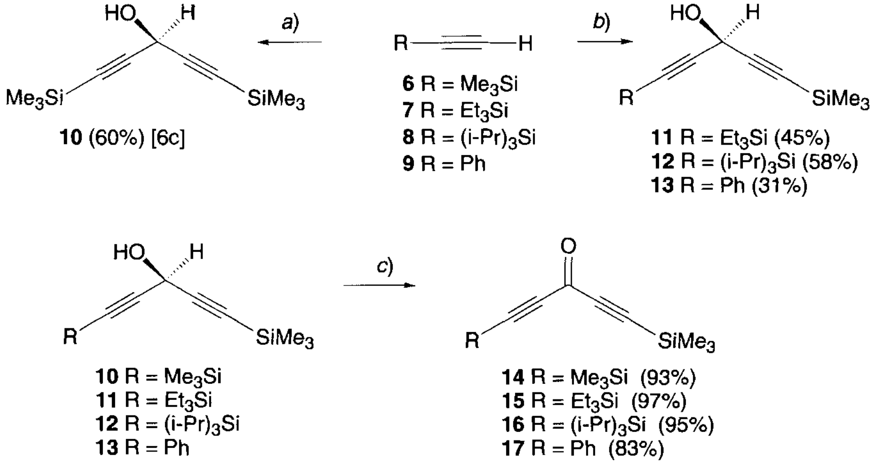
Scheme 1. *Early Synthetic Routes to Tetraethynylethenes*



2 R = Ph (routes *a*, *b*)
3 R = Me (route *a*)
4 R = Me_3C (routes *a*, *c*)
5 R = Me_3Si (routes *a*, *c*)

a) KI, acetone; 17–30%. *b*) *t*-BuOK, THF, 1-methylpyrrolidin-2-one; 73%. *c*) *Δ*; *ca.* 4%. *d*) BuLi, *t*-BuOCl; 36–45%.

Scheme 2. *Syntheses of Penta-1,4-diyn-3-ols and Penta-1,4-diyn-3-ones*



10 (60%) [6c]

6 R = Me_3Si
7 R = Et_3Si
8 R = $(i\text{-}Pr)_3Si$
9 R = Ph

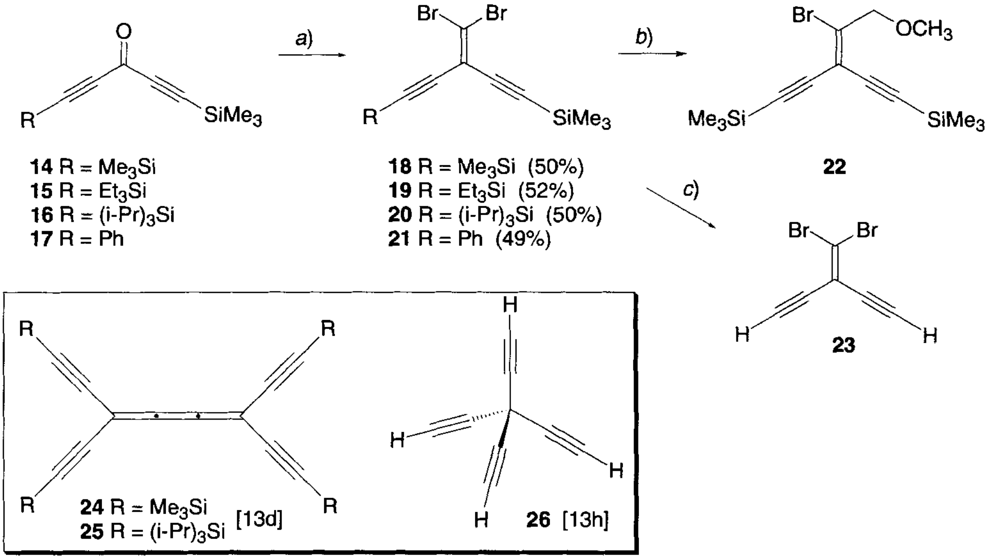
11 R = Et_3Si (45%)
12 R = $(i\text{-}Pr)_3Si$ (58%)
13 R = Ph (31%)

10 R = Me_3Si
11 R = Et_3Si
12 R = $(i\text{-}Pr)_3Si$
13 R = Ph

14 R = Me_3Si (93%)
15 R = Et_3Si (97%)
16 R = $(i\text{-}Pr)_3Si$ (95%)
17 R = Ph (83%)

a) 1) BuLi, THF, 0°, then EtOCHO; 2) sat. aq. NH_4Cl soln. *b*) 1) BuLi, 0°, then $Me_3SiC{\equiv}CCHO$; 2) sat. aq. NH_4Cl soln. *c*) $BaMnO_4$, CH_2Cl_2 (**14**) or PCC, CH_2Cl_2, *Celite*, molecular sieves (4 Å) (**15**–**17**).

In the route to **1** (*Scheme 4*, below), ketone **14** was converted according to the method of *Corey* and *Fuchs* [14] into the corresponding 3-(dibromomethylidene) derivative **18**. The 3-(dibromomethylidene)penta-1,4-diynes such as **18**–**21** (*Scheme 3*) are not only versatile intermediates in the preparation of tetraethynylethenes, they were also used as starting materials in the synthesis of other C-rich compounds. Compound **18** and the corresponding bis(triisopropylsilyl) derivative were the direct precursors in the one-step preparation of the persilylethynylated [3]cumulenes **24** and **25** [13d], and *Feldman et al.* used **18** as the starting material in their elegant synthesis of tetraethynylmethane (**26**) [13h]. Their utility in the preparation of polyfunctional materials was illustrated by the conversion of **18** into methyl ether **22** [15]. In the synthesis of tetraethynylmethane (**26**), such functionalization was also demonstrated by condensing monolithiated **18** with gaseous formaldehyde [13h]. Compound **18** could also be deprotected to give the free alkyne **23**.



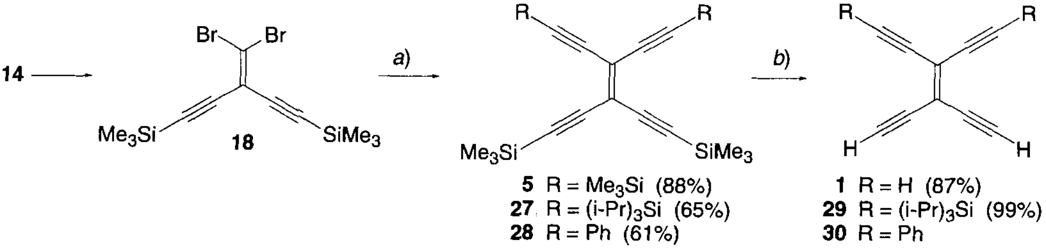
Scheme 3. *Synthesis of 3-(Dibromomethylidene)penta-1,4-diynes, Starting Materials in the Syntheses of the C-Rich Molecules* **24**–**26**

a) CBr_4, PPh_3, benzene. *b*) BuLi, THF, –95°, then $MeOCH_2Cl$; 24%. *c*) K_2CO_3, MeOH; 65%.

The $[Pd(PPh_3)_4]$-catalyzed alkynylation [16] of **18** was successfully carried out with acetylenes **6**, **8**, and **9** to give the tetraethynylethenes **5**, **27**, and **28**, respectively, in good yields (*Scheme 4*). Removal of the Me_3Si protecting groups with catalytic amounts of K_2CO_3 in MeOH smoothly afforded the desired free alkynes **1**, **29**, and **30**. Compound **1**, like **23** (*Scheme 3*), is quite volatile, and great care is required to prevent material losses upon drying.

The free alkynes **1**, **29**, and **30** differ substantially in their physical properties and stabilities. Tetraethynylethene (**1**) is fairly soluble in pentane and crystallizes out of this

Scheme 4. *Synthesis of* **1** *and Geminally Bis-deprotected Tetraethynylethenes*



a) **6** (or **8** or **9**), $[Pd(PPh)_3]_4$, CuI, $BuNH_2$, C_6H_6. *b*) K_2CO_3, MeOH; yield of **30** not determined due to instability.

solvent at −10° as white plates. At 25°, it turns rapidly brown, even in the absence of O_2, and polymerizes to a black solid with a metallic luster; the same process happens slowly in solution to give a brown precipitate. However, the elemental composition of this polymer does not correspond to a multiple of $C_{10}H_4$, but rather to a polymer incorporating H_2O and O_2 (correct elemental analysis for $(C_{10}H_4 \cdot H_2O \cdot O_2)_n$) as confirmed by the presence of a broad, medium-intensity absorption around 3426 cm^{-1} in the FT-IR spectrum of the powder in KBr. Similarly, the triisopropylsilyl derivative **29** decomposes at 25° in the neat state, although much more slowly than **1**. A dramatic decrease in stability is observed for **30**; the neat oil polymerizes to a hard black mass within a few s, requiring all manipulations with this compound to be made in solution. The strongly enhanced reactivity of **30**, as compared to **1**, is due to the Ph rings which stabilize the intermediates (and the corresponding transition states) of anionic, cationic, or radical polymerizations. For similar reasons, styrene ($PhCH{=}CH_2$) is well known to polymerize more readily than ethylene ($CH_2{=}CH_2$).

The remarkably simple FT-IR spectrum of **1** (*Fig. 1*) in $CDCl_3$ shows a characteristic strong C−H stretching band at 3307 cm^{-1}, together with a weak C≡C stretching band at 2102 cm^{-1}. We initially ascribed the strong absorptions at 653 and 632 cm^{-1} to coupled C−H bending modes in **1** [8], and this assignment found support in a high-level theoretical study by *Schaefer* and coworkers [17]. The UV spectrum of **1** in MeOH (*Fig. 2*) shows the end absorption at *ca.* 330 nm; it resembles the spectrum of the Me_3Si derivative **5** [6a], although the absorption bands for **1** are shifted to higher energy by 20–35 nm and are somewhat broader. Similar effects upon deprotection are seen in the comparison of the spectra of **27** and **29**. In the spectra of the Ph derivatives, the fine structure of the individual bands is considerably reduced as compared to the spectra of **1** and **5**. Also, as a result of the extended conjugation, the end absorption is shifted to longer wavelengths and appears at 385 (**30**) and 405 nm (**28**; *Fig. 3*).

The X-ray crystal-structure analysis of **5** (*Fig. 4*) shows a nearly planar molecule with a maximum deviation from the least-squares plane through the tetraethynylethene framework (including the 4 Si-atoms) of 0.032(9) Å. The tetraethynylethene framework itself is planar within 0.007(8) Å. The molecule is slightly distorted: the C(3′)−C(3)−C(2) angle is 125.3(7)°, a value similar to those calculated for other unstrained *cis*-enediynes [18], while the C(3′)−C(3)−C(4) angle is unusually small with a value of 118.2(7) Å. This distortion presumably results from crystal packing effects in the solid [13a]. The bond lengths in **5**

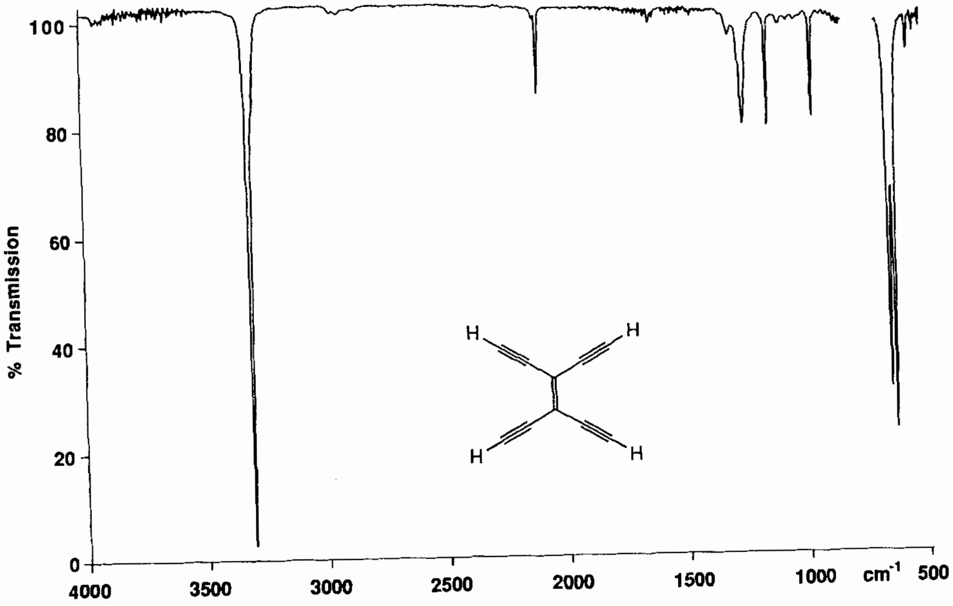


Fig. 1. *FT-IR Spectrum of* **1** *in dilute* CCl_4 *solution*

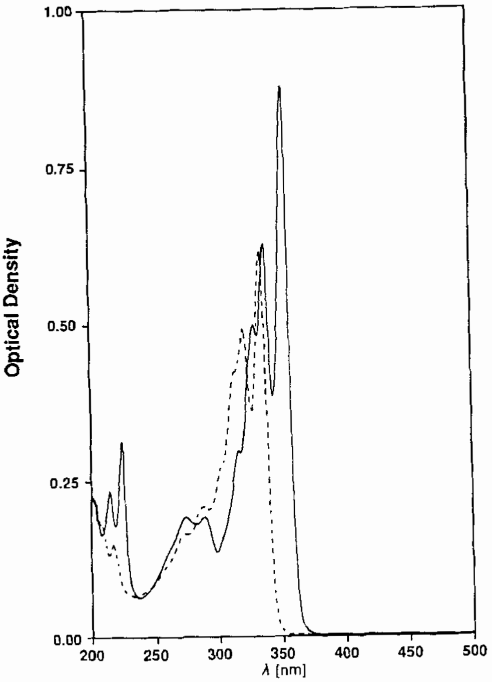


Fig. 2. *Electronic absorption spectra of* **5** (–) *and* **1** (----) *in MeOH. T* 25°, $d = 1$ cm, $c = 2.33 \cdot 10^{-5}$ M.

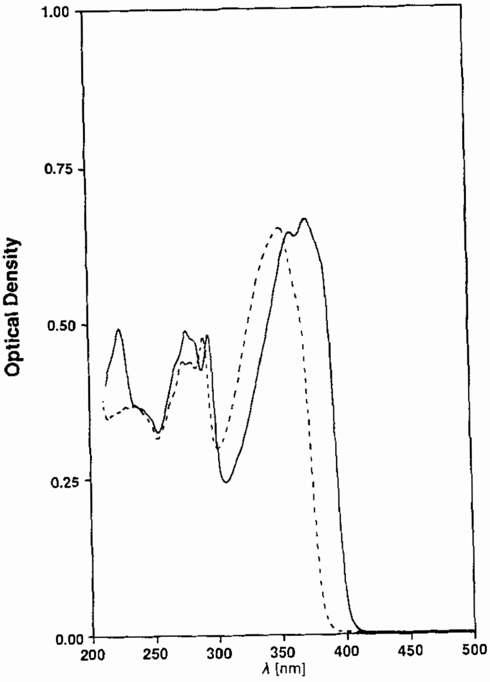


Fig. 3. *Electronic absorption spectra of* **28** (–) *and* **30** (----) *in MeOH. T* 25°, $d = 1$ cm, $c = 2.09 \cdot 10^{-5}$ M.

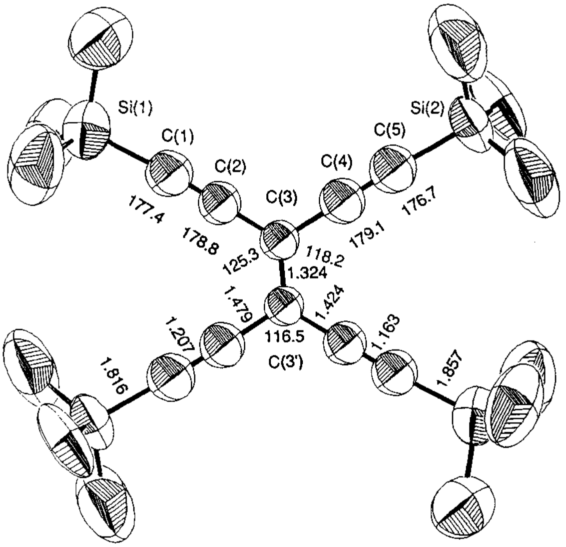
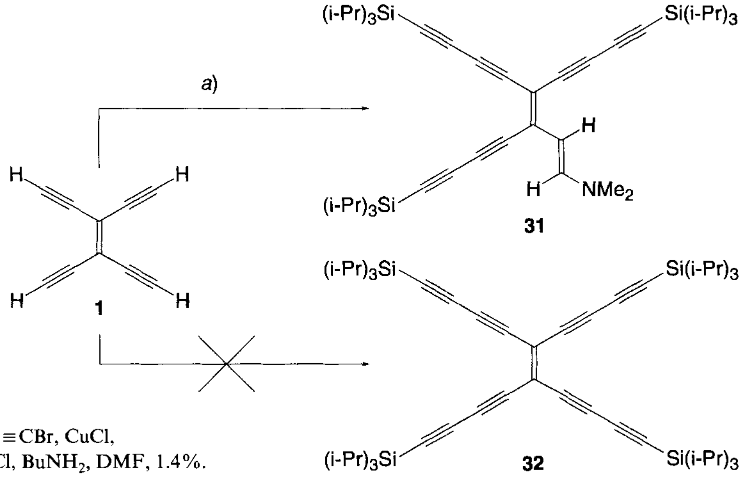


Fig. 4. *X-Ray crystal structure of* **5**. Arbitrary numbering.

are within the normal range for C=C and C≡C bonds and do not deviate greatly from those calculated for a perfectly D_{2h}-symmetrical $C_{10}H_4$ molecule **1** [17] [19].

Compound **1** is the only known isomer of molecular formula $C_{10}H_4$. It did not undergo a double *Bergman* cycloaromatization reaction [20] to naphthalene upon prolonged refluxing in toluene. We attempted to further extend its π-electron system by alkyne homologation through a *Cadiot-Chodkievicz* reaction [21] with 1-bromo-2-(triisopropylsilyl)ethyne [21] (*Scheme 5*). Surprisingly, amine **31** was obtained in a very poor

Scheme 5. *Attempted Formation of Tetrakis[4-(triisopropylsilyl)buta-1,3-diynyl]ethene* (**32**)

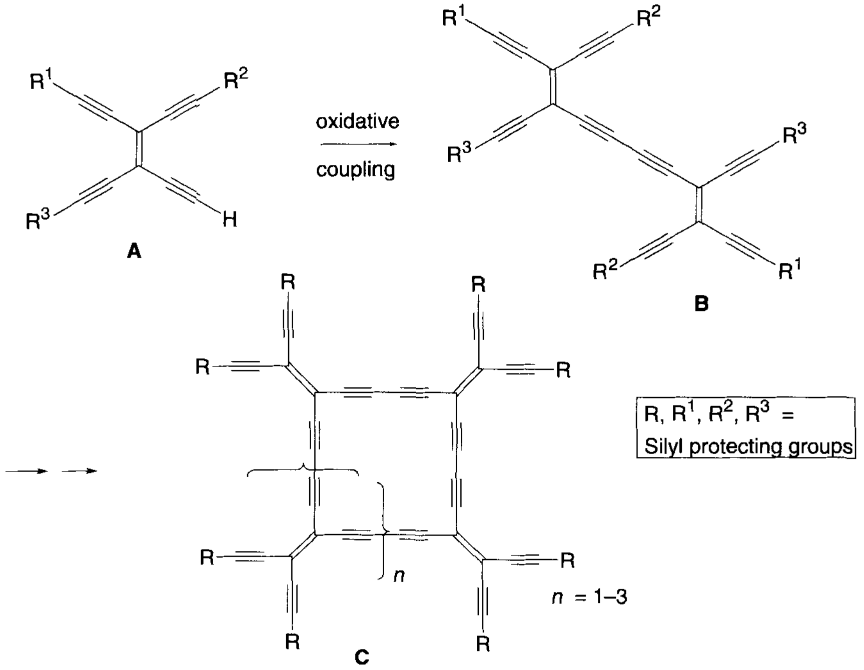


a) $(i\text{-}Pr)_3SiC{\equiv}CBr$, CuCl, $NH_2OH \cdot HCl$, $BuNH_2$, DMF, 1.4%.

yield instead of the expected tetrakis[4-(triisopropylsilyl)buta-1,3-diynyl]ethene (**32**). We believe that **32** was formed, but extended reaction time or the presence of an excess of $BuNH_2$ led to polymerization of the product. It seems peculiar that the dimethylamino derivative **31** was isolated, and no product containing the BuNH group. Presumably, the $BuNH_2$ addition product was formed, but it was too unstable and polymerized rapidly. The dimethylamine needed to form **31** was probably present as an impurity in the DMF used for the reaction. We had previously observed a peculiarly enhanced reactivity of large conjugated alkynes toward addition of amines during *Cadiot-Chodkievicz* couplings [22]. Compound **31** is surprisingly stable, and its electron-impact (EI) mass spectrum shows the molecular ion at *m/z* 709 as the base peak.

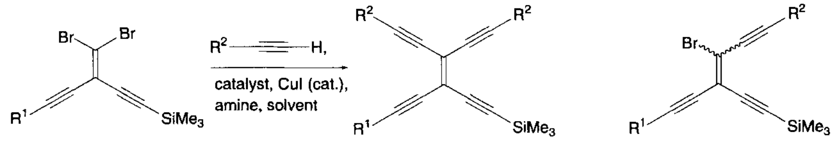
2.3. *Mono-deprotected Tetraethynylethenes.* Mono-deprotected tetraethynylethenes **A** were of interest, since they provided access to extended cross-conjugated dimeric chromophores **B** through oxidative coupling (*Scheme 6*) [23]. The latter compounds served as building blocks in the construction of the expanded radialenes **C** (*Scheme 6*) and as reference compounds in the evaluation of the competition between linear and cross-conjugation in these large C-cores [10].

Scheme 6. *Oxidative Coupling of Monodeprotected Tetraethynylethenes* **A** *to Extended Dimeric Cross-Conjugated π-Electron Systems* **B**, *Precursors to the Perethynylated Expanded Radialenes* **C** [10]



The preparation of the mono-deprotected tetraethynylethenes **41**–**44** followed the synthetic route shown for **1** in *Scheme 4*. In the first step, the protected acetylenes **7**–**9** and **33** were coupled to the 3-(dibromomethylidene)penta-1,4-diynes **19** or **20** to provide a series of differentially tetrasubstituted tetraethynylethenes, **34**–**38** (*Table 1*). Good yields

Table 1. *Preparation of Tetrasubstituted Tetraethynylethenes from Unsymmetrically Protected 3-(Dibromomethylidene)penta-1,4-diynes*



19, 20

34–38

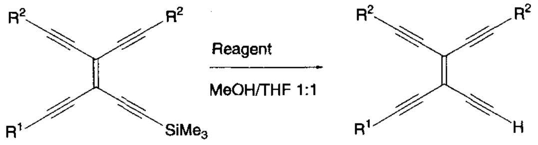
39 R^1 = Et_3Si, R^2 = $(i\text{-}Pr)_3Si$
40 R^1 = R^2 = Me_3Si

Starting materials					Solvent	Amine	Product	Yield [%]
	R^1		R^2	Catalyst				
19	Et_3Si	**8**	$(i\text{-}Pr)_3Si$	$[PdCl_2(PPh_3)_2]$	C_6H_6	$(i\text{-}Pr)_2NEt$	**34**	47
19	Et_3Si	**7**	Et_3Si	$[Pd(PPh_3)_4]$	C_6H_6	$BuNH_2$	**35**	44
20	$(i\text{-}Pr)_3Si$	**9**	Ph	$[PdCl_2(PPh_3)_2]$	C_6H_6	$(i\text{-}Pr)_2NEt$	**36**	38
20	$(i\text{-}Pr)_3Si$	**8**	$(i\text{-}Pr)_3Si$	$[PdCl_2(PPh_3)_2]$	Et_3N	Et_3N	**37**	70
20	$(i\text{-}Pr)_3Si$	**33**	CMe_2OH	$[PdCl_2(PPh_3)_2]$	C_6H_6	$(i\text{-}Pr)_2NEt$	**38**	27

were usually obtained with $[PdCl_2(PPh_3)_2]/CuI$ as catalyst and $(i\text{-}Pr)_2NEt$ as amine in benzene. Under alternative coupling conditions, the amine (Et_3N) was also employed as solvent. Separation of the tetraethynylethenes from mono-coupled products such as **39** and **40** and butadiynes (*e.g.* $(i\text{-}Pr)_3SiC{\equiv}C{-}C{\equiv}CSi(i\text{-}Pr)_3$), resulting from undesired homocoupling of the acetylenes, was best achieved by chromatography on reversed-phase SiO_2.

Formation of the mono-deprotected derivatives **43** and **44** from **36** and **37** by removal of Me_3Si in the presence of alkyne-protecting $(i\text{-}Pr)_3Si$ groups was readily accomplished with K_2CO_3 in MeOH/THF 1:1 (*Table 2*) [24]. We were delighted to find that the Me_3Si groups in **34** and **35** could also be removed selectively in the presence of Et_3Si groups to give mono-deprotected **41** and **42** [10]. This was best accomplished under kinetic control by stirring **34** or **35** for 2–5 min in MeOH/THF 1:1 containing a few drops of 1N aq.

Table 2. *Synthesis of Mono-deprotected Tetraethynylethenes*



34–37

41–44

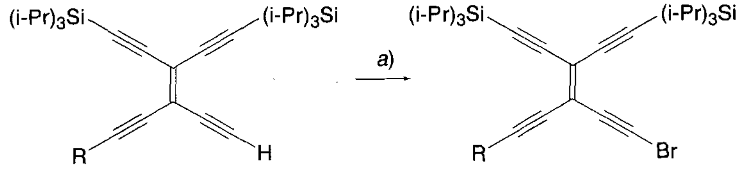
	R^1	R^2	Reagent	Product	Yield [%]
34	Et_3Si	$(i\text{-}Pr)_3Si$	1N aq. NaOH[a]	**41**	98
35	Et_3Si	Et_3Si	1N aq. NaOH[a]	**42**	89
36	$(i\text{-}Pr)_3Si$	Ph	K_2CO_3	**43**	57
37	$(i\text{-}Pr)_3Si$	$(i\text{-}Pr)_3Si$	K_2CO_3	**44**	98

[a] Addition of a few drops and stirring for 2–5 min at 20°.

NaOH. Stirring the mixture for longer periods of time also led to the cleavage of the Et_3Si groups. In the presence of $(i\text{-}Pr)_3Si$ groups only, alkyne-protecting Et_3Si groups were most efficiently removed with K_2CO_3 in MeOH. F^- Sources such as Bu_4NF in wet THF finally removed the $(i\text{-}Pr)_3Si$ groups. The sequential deprotection of **34** to **41**, to **29** (*Scheme 4*), and ultimately to tetraethynylethene **1** is the first known example of a sequential and differential deprotection of three silylated alkynyl residues in one molecule.

As illustrated by the reaction shown in *Scheme 5*, brominated alkynes are useful substrates in *Cadiot-Chodkievicz* heterocoupling reactions. We were able to prepare the mono (**45**) and dibromo (**46**) derivatives by brominating the corresponding tetraethynylethenes **44** and **29** with *N*-bromosuccinimide (NBS) in acetone in the presence of $AgNO_3$ (*Scheme 7*) [25]. However, all attempts to perform heterocoupling reactions with the brominated tetraethynylethenes **45** and **46** have failed so far.

Scheme 7. *Synthesis of Brominated Tetraethynylethenes*



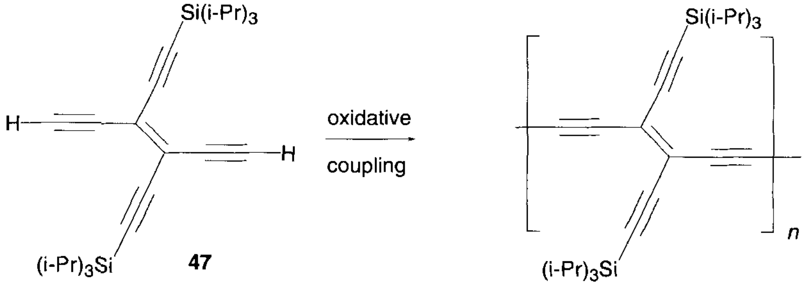
44 R = (i-Pr)3Si
29 R = H

45 R = (i-Pr)3Si (57%)
46 R = Br (62%)

a) NBS, $AgNO_3$, acetone.

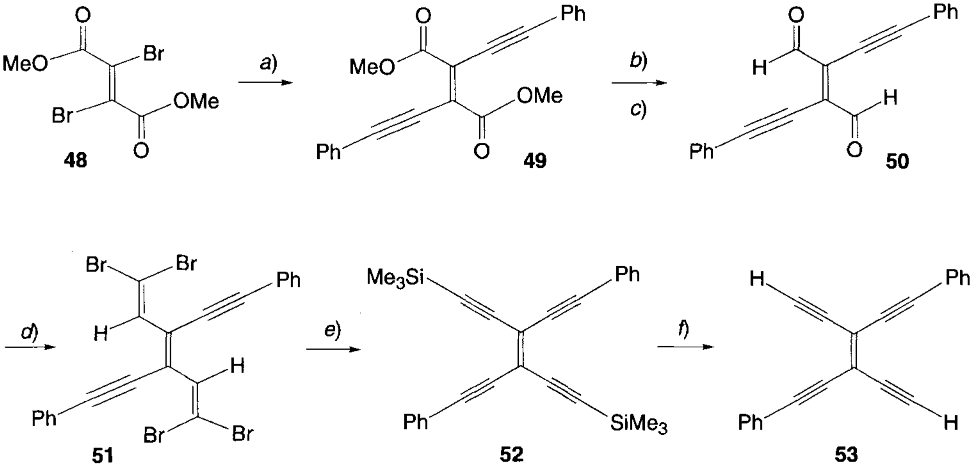
2.4. trans-*Bis(triisopropylsilyl)-Protected and* trans-*Bis-deprotected Tetraethynylethenes.* The preparation of *trans*-bis-deprotected tetraethynylethenes was of significant interest, since these compounds represented suitable monomers for the oxidative polymerization to polytriacetylenes (PTA's), previously elusive [26] linearly conjugated single-strand polymers with an all-C-backbone. The successful synthesis of **47** indeed allowed the first preparation of molecular wires of multinanometer length [11] and longer-chain oligomers with the PTA backbone [12] (*Scheme 8*).

Scheme 8. *Preparation of Polytriacetylenes by Oxidative Polymerization of* trans-*Bis-deprotected Tetraethynylethene* **47** [11] [12]



47

Scheme 9. *Preparation of the Diphenyl-Substituted* trans-*Bis-deprotected Tetraethynylethene* **53**



a) $PhC{\equiv}CSnBu_3$, $[PdCl_2(PPh_3)_2]$, THF; 90%. *b*) Diisobutylaluminium hydride (DIBAL-H), THF, –78°. *c*) PCC, CH_2Cl_2, *Celite*, molecular sieves (4 Å); 80% (steps *b* and *c*). *d*) CBr_4, Zn, PPh_3, CH_2Cl_2; 17%. *e*) Lithium diisopropylamide (LDA), Et_2O, –78°, then Me_3SiCl, 20°, 84%. *f*) K_2CO_3, MeOH.

As the first *trans*-bis-deprotected tetraethynylethene, we prepared the diphenyl derivative **53** (*Scheme 9*). The Pd-catalyzed addition of stannylated phenylacetylene [27] to dimethyl 2,3-dibromofumarate (**48**) in THF was slow and, depending on the reaction scale, took up to a week to proceed to completion. The desired diester **49** was readily separated from the Sn-containing by-products by recrystallization. Reduction of **49** with DIBAL-H followed by PCC oxidation afforded dialdehyde **50** which was subjected to the dibromoolefination reaction to give **51**. Whereas an extra equiv. of PPh_3 served as the required reducing agent in the dibromoolefinations shown in *Scheme 3*, Zn powder was the reducing agent in the formation of **51**. Elimination of HBr and metallation was best achieved with LDA in THF, and the resulting bright-green dianion was quenched with Me_3SiCl to give **52**. Deprotection of **52** with K_2CO_3 in MeOH proceeded quantitatively to yield the free alkyne **53** as a highly unstable oil (^{1}H-NMR (360 MHz, $CDCl_3$): 3.66 ppm (${\equiv}C{-}H$); IR ($CHCl_3$): 3302 cm^{-1} (${\equiv}C{-}H$)). Similar to the geminal bis(phenylethynyl) derivative **30** (*Scheme 4*), compound **53** is only stable at 20° in dilute solutions of $CHCl_3$ or CCl_4. Upon concentration, even at – 5°, as well as in the solid state, decomposition occurs instantaneously.

Upon recrystallization of **52** from $CHCl_3$, crystals suitable for X-ray structure analysis were obtained which showed a perfectly planar arrangement of the entire conjugated C-skeleton including the two Ph rings (*Fig. 5*) [23].

Following the strategy for the preparation of **53**, a very general route to multigram quantities of *trans*-bis(triisopropylsilyl)-protected tetraethynylethene derivatives, including the free *trans*-enediyne **47**, was developed (*Scheme 10*) [11]. This route started with the Pd^{II}-catalyzed addition of $(i\text{-}Pr)_3SiC{\equiv}CSnBu_3$ to dimethyl dibromofumarate (**48**) in THF to give the diprotected *trans*-enediyne **54** in a very slow conversion (9 days).

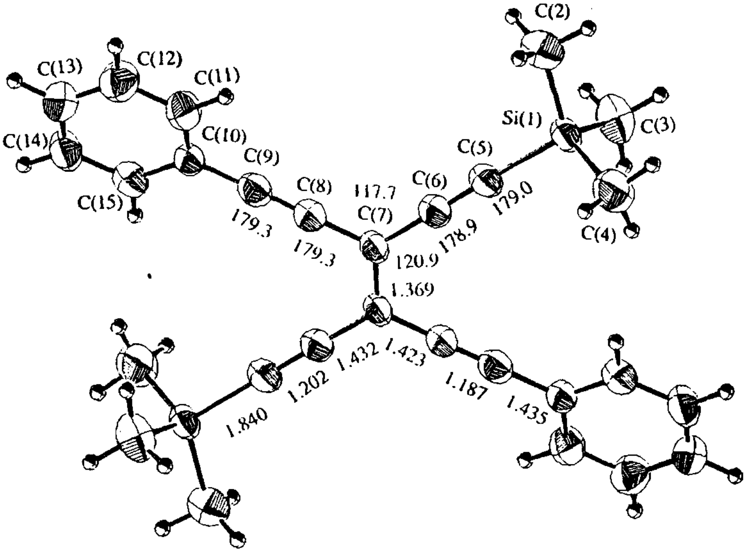
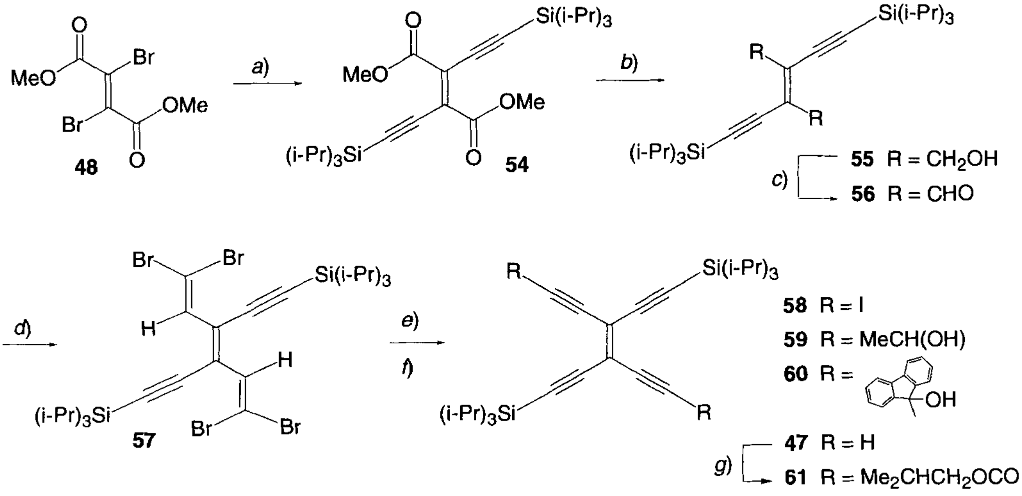


Fig. 5. *X-Ray crystal structure of* **52**. Arbitrary numbering.

Scheme 10. *Preparation of* trans-*Bis(triisopropylsilyl)-Protected Tetraethynylethene Derivatives*



a) $(i\text{-Pr})_3SiC{\equiv}CSnBu_3$, $[PdCl_2(PPh_3)_2]$, THF, or $(i\text{-Pr})_3SiC{\equiv}CH$ (**8**), $[PdCl_2(PPh_3)_2]$, CuI, Et_3N; 92 and 90%, resp. *b*) DIBAL-H, CH_2Cl_2, 0°; 95%. *c*) PCC, CH_2Cl_2, *Celite*, molecular sieves (4 Å); 85%. *d*) CBr_4, PPh_3, Zn, CH_2Cl_2; 94%. *e*) LDA (6 equiv.), THF, –78°. *f*) Sat. aq. NH_4Cl soln. →**47** (95%); I_2→**58** (23%); MeCHO→**59** (47%); fluorenone→**60** (79%). *g*) 1.6 M BuLi in hexane, Et_2O, –78°, then isobutyl chloroformate; 65%.

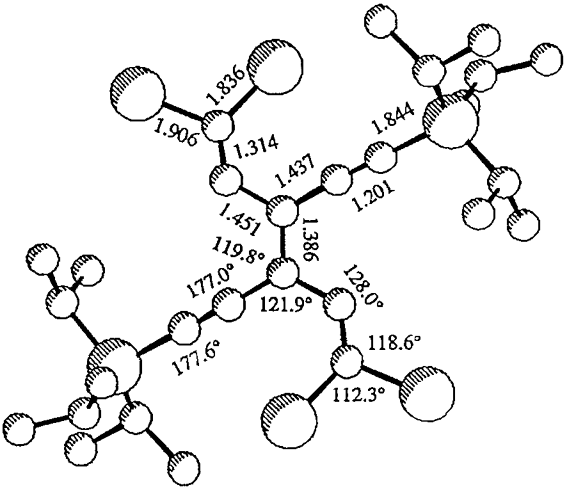
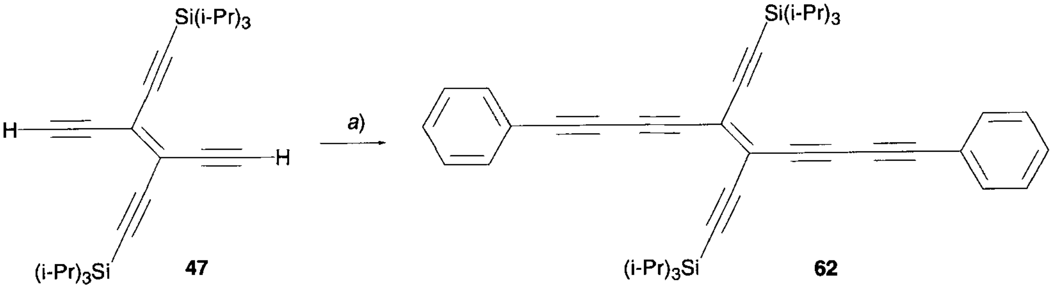


Fig. 6. *X-Ray crystal structure of tetrabromide* **57**

Alternatively, the reaction was performed in good yield in 18 h using $(i\text{-}Pr)_3SiC{\equiv}CH$ and $[PdCl_2(PPh_3)_2]/CuI$ as catalyst in pure Et_3N. Reduction (DIBAL-H) to diol **55** followed by PCC oxidation afforded the dialdehyde **56**, and dibromoolefination gave tetrabromide **57** which was characterized by X-ray analysis (*Fig. 6*). Elimination/metallation with LDA produced the purple dianion which was quenched either with NH_4Cl to give free *trans*-enediyne **47** or with mildly reactive electrophiles such as I_2, acetaldehyde, and 9*H*-fluoren-9-one to give compounds **58**–**60**. More reactive electrophiles such as i-BuOCOCl could not be used in this reaction, since they reacted with the $(i\text{-}Pr)_2NH$ formed, and **47** became the major product. However, by starting from pure **47** and deprotonating with BuLi, the formed dianion could be safely quenched with i-BuOCOCl to give diester **61** in good yield. Upon oxidative coupling with a large excess of phenylacetylene, **47** was transformed in 70% yield into the extended linearly conjugated chromophore **62** (*Scheme 11*).

Scheme 11. *Extension of the Linearly Conjugated π-Chromophore of* **47** *through Oxidative Coupling*



a) PhC≡CH (**9**), CuCl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), acetone, air; 70%.

Compounds **58**–**61** were deprotected with Bu$_4$NF in wet THF; however, solutions of the formed free *trans*-enediynes decomposed rapidly upon concentration. This is in agreement with the findings for other tetraethynylethene derivatives with more than one free terminal alkyne residue which all are too unstable to be isolated and kept in pure form (such as **1**, the geminally bis-deprotected derivatives **29** and **30**, *trans*-enediyne **53**, and the *cis*-bis-deprotected derivatives **63** and **64** (see below, *Scheme 12*)). Similarly, *trans*-hex-3-ene-1,5-diyne could not be isolated and is even unstable in solution [26]. In sharp contrast, the *trans*-bis(triisopropylsilyl)-protected free *trans*-enediyne **47** is an air-stable solid which melts at 76°. The origin of this remarkable stability was revealed by its X-ray crystal-structure analysis (*Fig. 7*) [11]. The molecules are aligned in a herringbone fashion (*Fig. 7b*) with the reactive free ethynyl groups pointing towards the silyl groups of neighboring molecules. The (i-Pr)$_3$Si groups provide a matrix which efficiently insulates the individual reactive chromophores in the crystal. Such an 'insulating effect' of (i-Pr)$_3$Si groups was also found to stabilize crystals of the per[(triisopropylsilyl)-ethynylated] tetrahydro[12]annulene **65b** (see below, *Scheme 12*) [3] [9].

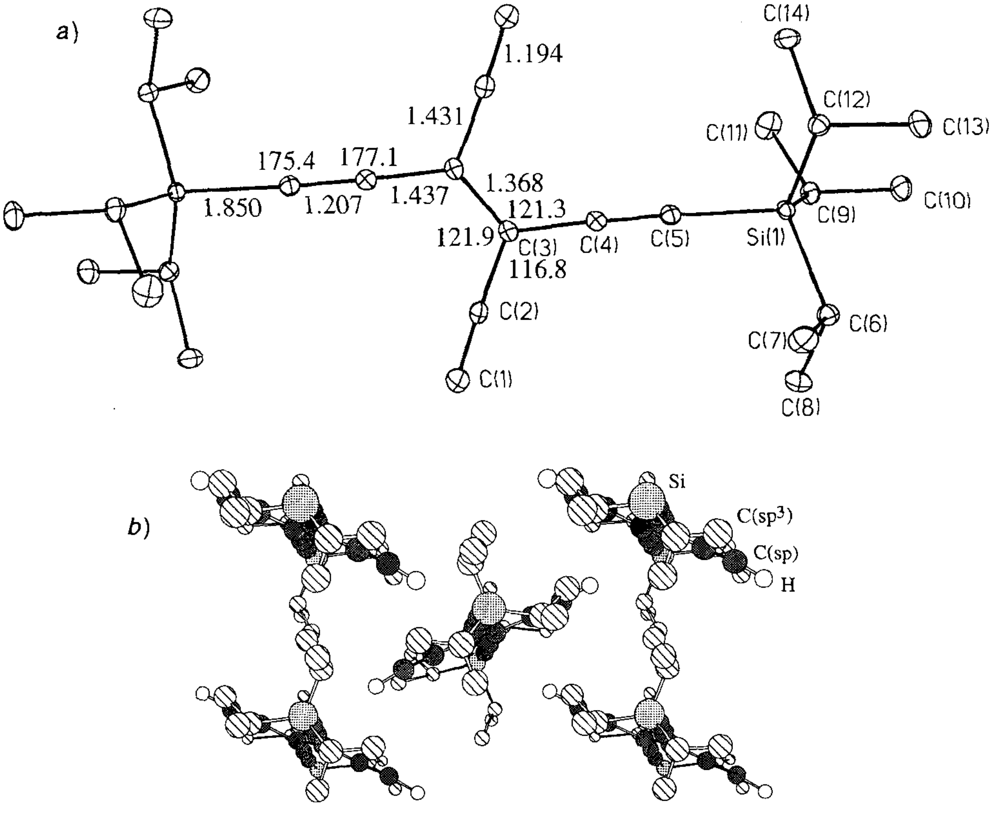


Fig. 7. a) *X-Ray crystal structure of* trans-*enediyne* **47**; b) *crystal packing of* **47** *showing the herringbone alignment of the molecules.* Arbitrary numbering.

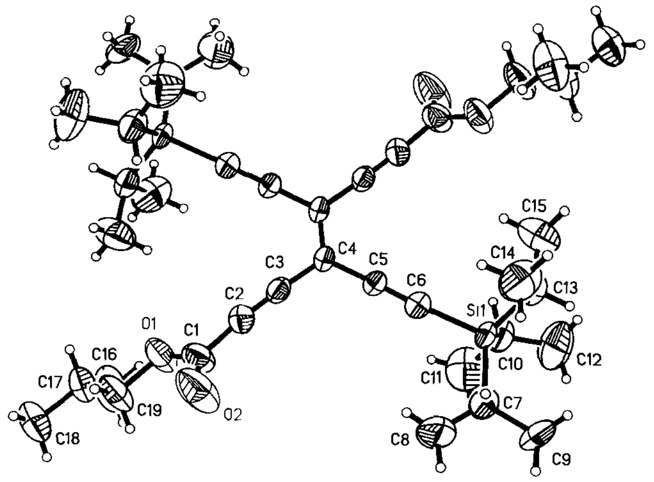


Fig. 8. *X-Ray crystal structure of diisobutyl ester* **61**. Selected bond lengths [Å] and bond angles [°]: C(2)–C(3) 1.173(8), C(3)–C(4) 1.436(7), C(4)–C(5) 1.426(6), C(5)–C(6) 1.204(6), C(4)–C(4A) 1.353(11), C(1)–C(2)–C(3) 175.9(6), C(2)–C(3)–C(4) 176.7(5), C(3)–C(4)–C(4A) 121.4(4), C(3)–C(4)–C(5) 116.5(5), C(4A)–C(4)–C(5) 122.0(5), C(4)–C(5)–C(6) 178.2(6), C(5)–C(6)–Si(1) 174.8(4).

In the crystal structure of the bis(isobutyl ester) **61** (*Fig. 8*), the oxycarbonyl groups are twisted out of the plane of the tetraethynylethene backbone because of steric hindrance between the ester residue and the neighboring (i-Pr)$_3$Si group. The angle between the least-squares planes passing through C(2), C(1), O(1), O(2), and the tetraethynylethene fragment is 42(1)°. Crystals of the extended chromophore **62** suitable for X-ray analysis were grown out of hexane. The conjugated C-frame in **62** (*Fig. 9a*) is nearly planar with a maximum deviation from the least-squares plane passing through the entire C-chromophore of 0.22 Å. The distance between the C_p atoms of the Ph groups at the termini of this molecular rod is 19.37 Å; force-field calculations had predicted a distance of 19.4 Å [28]. Crystal-packing analysis showed (*Fig. 9b*) that the Ph rings of adjacent molecules do stack, with a centroid-to-centroid distance of 3.8 Å. This interaction forms molecular 'chains' in the crystal. These chains stack in rows perpendicular to each other, which describes the two-dimensional structure. The three-dimensional structure can be described by stacking the planes of perpendicular chains, creating planes of 'conjugated C-backbone' surrounded on top and bottom by silyl groups (*Fig. 9c*). In future work, we plan to change, through substitution, the ionization potentials of the two 'end-capping' phenyl groups in **62** to strengthen the interaction between the stacking rings and, therefore, along the molecular chains in the crystal.

2.5. cis-*Bis-deprotected Tetraethynylethenes*. The perethynylated dehydroannulenes **65a, b** and **66a, b** (*Scheme 12*) are macrocyclic precursors to two-dimensional all-carbon networks [2] [3]. The construction of these interesting C-cores required the preparation of *cis*-bis-deprotected tetraethynylethenes **63** and **64** as starting materials [9]. These compounds proved by far the most difficult to prepare of all the tetraethynylethene derivatives described in this paper.

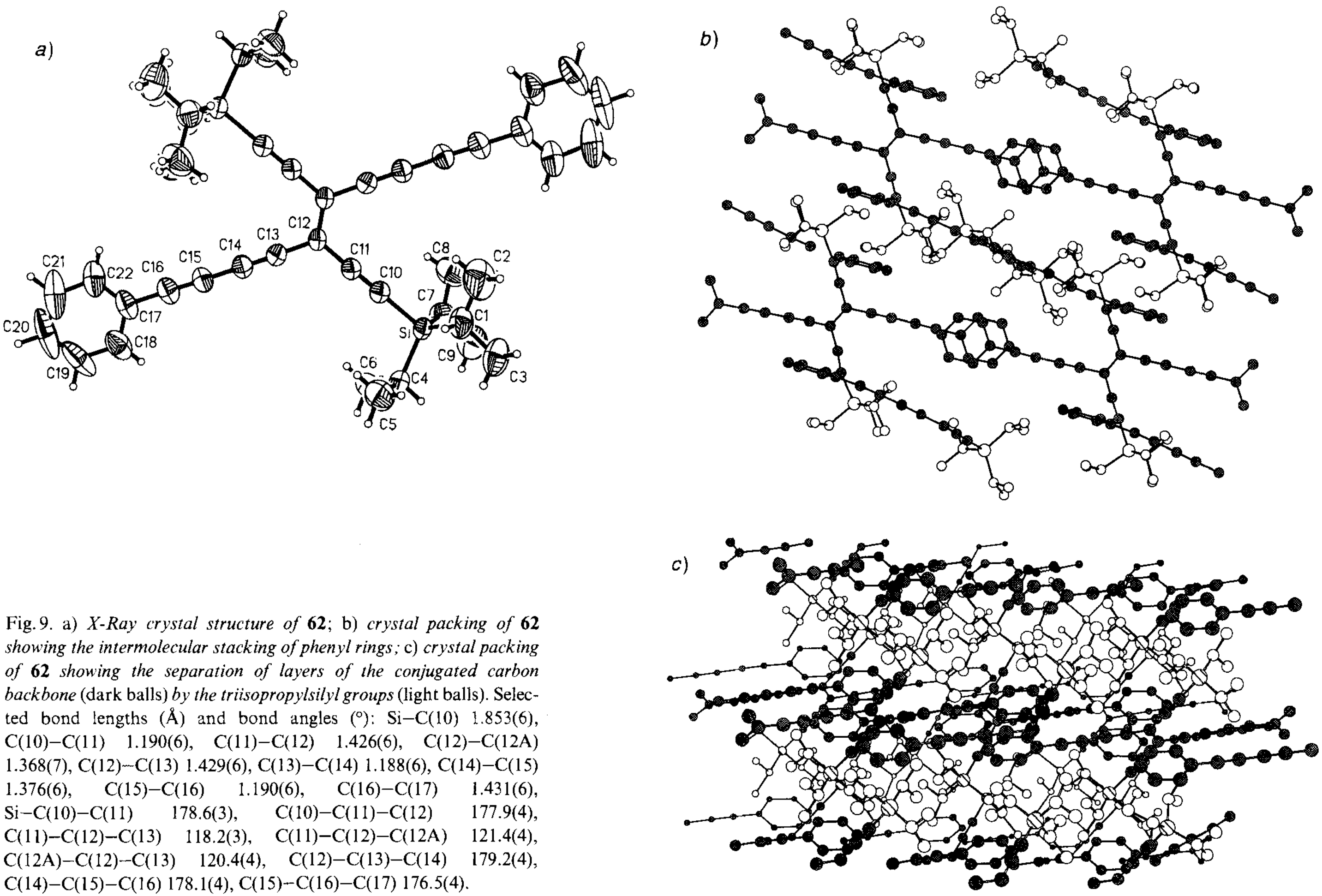
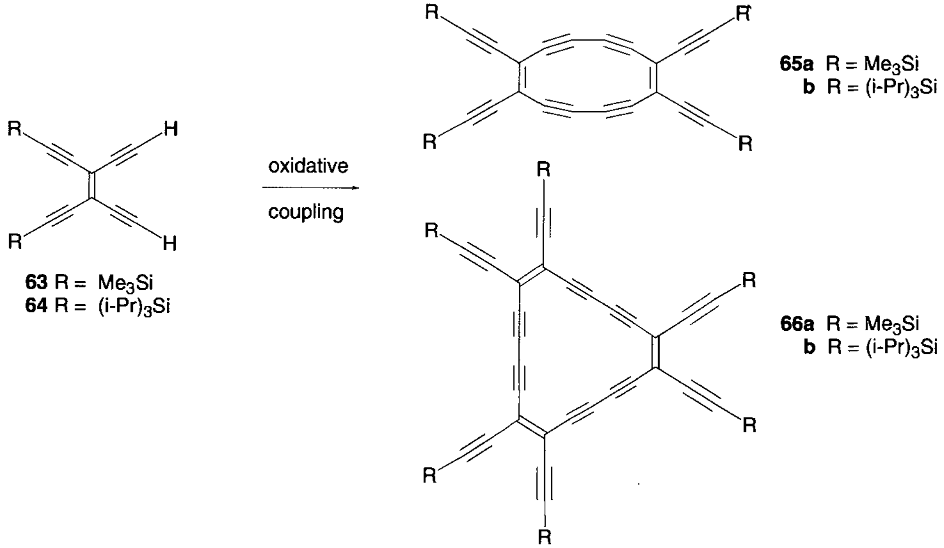


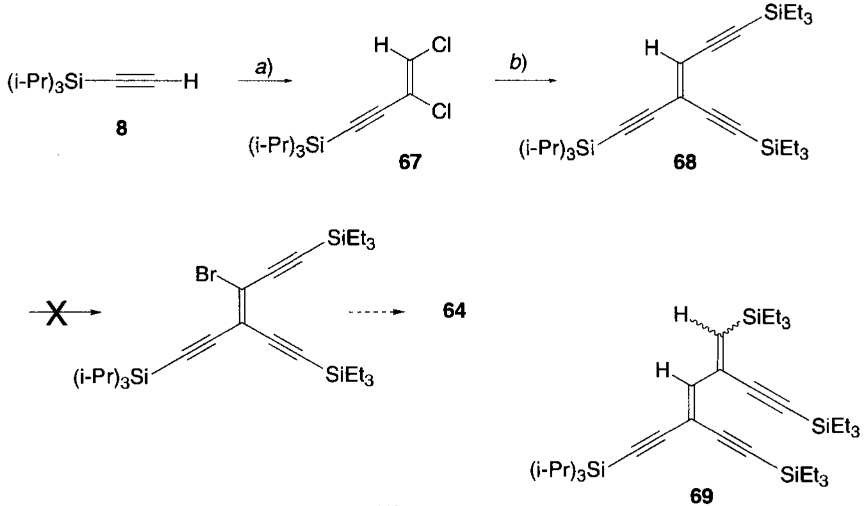
Fig. 9. a) *X-Ray crystal structure of* **62**; b) *crystal packing of* **62** *showing the intermolecular stacking of phenyl rings*; c) *crystal packing of* **62** *showing the separation of layers of the conjugated carbon backbone* (dark balls) *by the triisopropylsilyl groups* (light balls). Selected bond lengths (Å) and bond angles (°): Si–C(10) 1.853(6), C(10)–C(11) 1.190(6), C(11)–C(12) 1.426(6), C(12)–C(12A) 1.368(7), C(12)–C(13) 1.429(6), C(13)–C(14) 1.188(6), C(14)–C(15) 1.376(6), C(15)–C(16) 1.190(6), C(16)–C(17) 1.431(6), Si–C(10)–C(11) 178.6(3), C(10)–C(11)–C(12) 177.9(4), C(11)–C(12)–C(13) 118.2(3), C(11)–C(12)–C(12A) 121.4(4), C(12A)–C(12)–C(13) 120.4(4), C(12)–C(13)–C(14) 179.2(4), C(14)–C(15)–C(16) 178.1(4), C(15)–C(16)–C(17) 176.5(4).

Scheme 12. cis-*Bis-deprotected Tetraethynylethenenes as Precursors to Perethynylated Dehydroannulenes and, Ultimately, to Two-Dimensional All-Carbon Networks*



The first attempt to synthesize **64** is shown in *Scheme 13*. The alkynyl *Grignard* reagent prepared from **8** was reacted with 1,1,2-trichloroethylene using the sterically demanding catalyst [PdCl$_2$(dppb)] described by *Minato et al.* [30], and the *cis*-dichloride **67** was obtained in 85% yield. The special catalyst was required, since standard Pd-catalyzed alkyne-coupling reactions on 1,1,2-trichloroethylene occur at the mono-chlorinated

Scheme 13. *Attempted Preparation of* cis-*Bis-deprotected Tetraethynylethene* **64** via *Triethynylethene Intermediates*

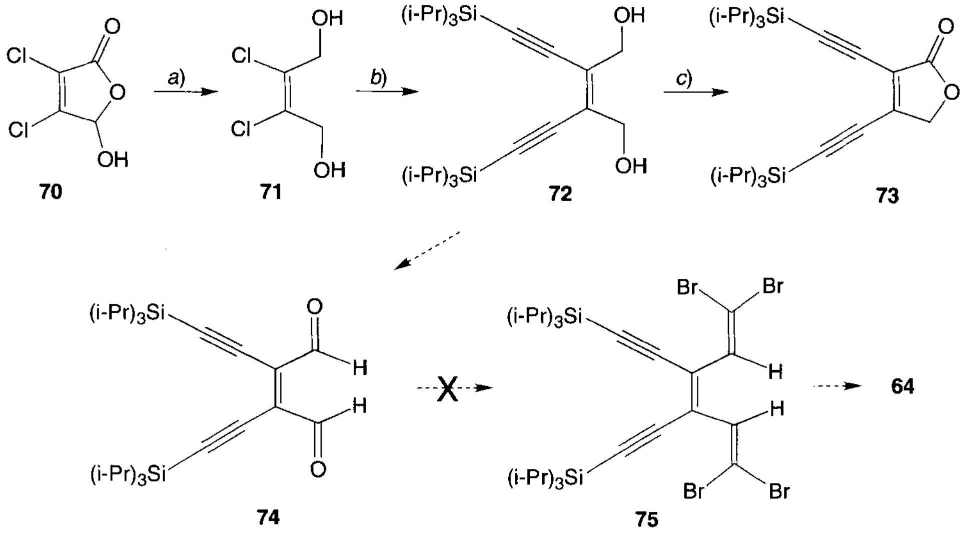


a) MeMgBr, Et$_2$O, then Cl$_2$C=CHCl, [PdCl$_2$(dppb)] (dppb = bis(diphenylphosphino)butane), −78°→0°; 85%. *b*) Et$_3$SiC≡CH (**7**), [PdCl$_2$(PPh$_3$)$_2$], CuI, BuNH$_2$; 72%.

position [31]. The double alkynylation to **68** was complicated by concentration-dependent side-reactions. At low concentrations, good yields of the desired triyne **68** were obtained. At higher concentrations, however, a second product with very similar chromatographic behavior appeared. On the basis of known side-products encountered in the coupling of alkynes to *trans*-dichloroethene [16], we tentatively assigned structure **69** to this by-product, although the material was too unstable for characterization. This route to **64** was finally abandoned, when it was found that the deprotonation of **68** with BuLi, even at −100°, led to significant isomerization. Trapping the formed anion with various reagents (*N*-bromosuccinimide) (NBS), Br_2, I_2, D_2O, acetone) produced no desirable products.

The next synthetic approach to the free *cis*-enediyne **64** was based on the strategy that was successfully applied to the preparation of the free *trans*-enediyne **47** (*Scheme 10*). The key intermediate in this route was dialdehyde **74** (*Scheme 14*) which we hoped to transform *via* the tetrabromo derivative **75** into **64**. For the preparation of dialdehyde **74**, mucochloric acid (**70**) was exhaustively reduced to give *cis*-2,3-dichlorobut-2-ene-1,4-diol (**71**) [32], which was then coupled with $(i\text{-Pr})_3SiC{\equiv}CH$ (**8**) to the protected *cis*-enediyne-diol **72**. However, PCC oxidation of **72** did not give the desired dialdehyde **74** but rather the dialkynyl-lactone **73**. Oxidation with pyridinium dichromate (PDC) also yielded predominantly **73** (*ca.* 30%) together with *ca.* 10% of a very unstable bright-yellow compound that could have been dialdehyde **74**. Since dibromoolefination reactions with this compound did not produce any isolable products, this route was finally abandoned.

Scheme 14. *Attempted Preparation of* cis-*Bis-deprotected Tetraethynylethene* **64** via *Dialdehyde* **74**

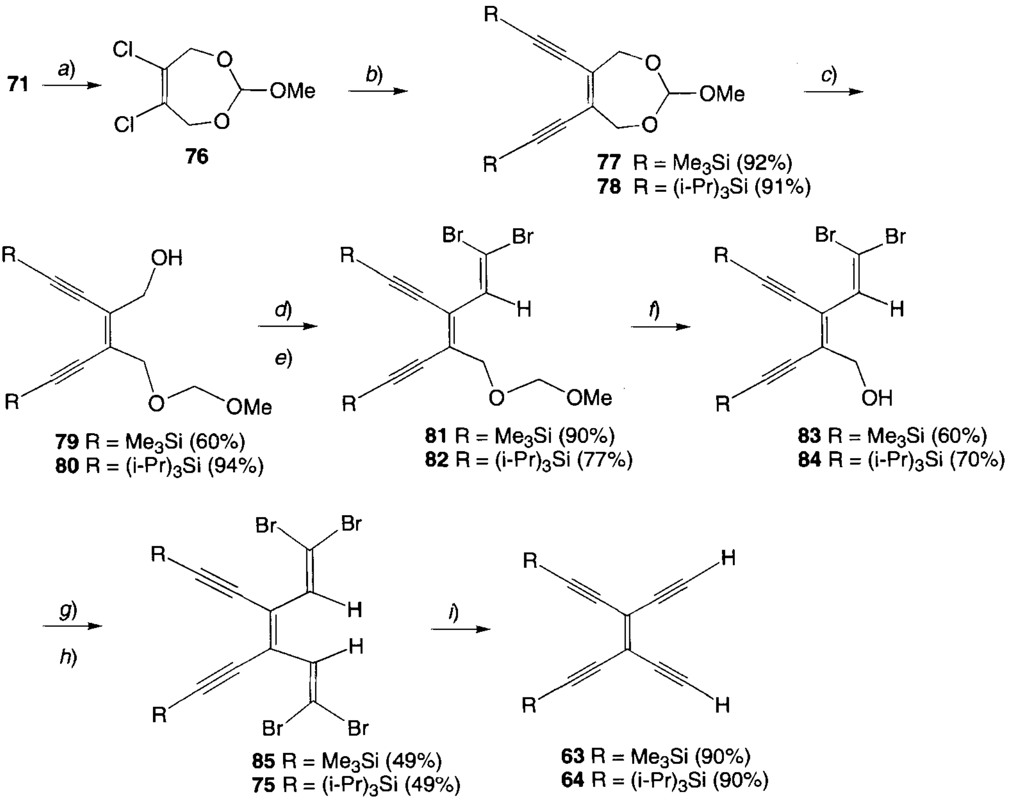


a) $LiAlH_4$, Et_2O; 29%. *b*) $(i\text{-Pr})_3SiC{\equiv}CH$ (**8**), $[PdCl_2(PPh_3)_2]$, CuI, $BuNH_2$, PhH; 64%. *c*) PCC, CH_2Cl_2, *Celite*, molecular sieves (4 Å); 91%.

To avoid the problems associated with the preparation and reactivity of dialdehyde **74**, a route to the free *cis*-enediynes **63** and **64** was chosen by which the key intermediates

75 and **85** were prepared by sequential introduction of the two dibromomethylidene residues (*Scheme 15*). Dichloride **71** was transformed into orthoester **76** which was ethynylated with **6** and **8** to give **77** and **78**, respectively. Orthoesters **77** and **78** are rather unstable compounds with a strong tendency to hydrolyze to the corresponding *cis*-diethynyl-dimethanol derivatives. The monoprotected diols **79** and **80** were formed by reduction of **77** and **78** with DIBAL-H following a procedure by *Takasu et al.* [33]. Oxidation of **79** and **80** with PDC yielded solutions of the corresponding monoaldehydes as very unstable compounds which could neither be concentrated nor stored at room temperature for more than a few min. Even in dilute solution at – 20°, the aldehydes decomposed within a few h to a mixture of products. Dibromoolefination of the monoaldehydes at 0° yielded the moderately stable dibromides **81** and **82** as yellow oils. These and all subsequent compounds on the way to the target free *cis*-enediynes **63** and **64** had to be kept free of acid and out of light, otherwise isomerization to the corresponding *trans*-isomers occurred.

Scheme 15. *Synthesis of the* cis-*Bis-deprotected Tetraethynylethenes* **63** *and* **64**



a) $(MeO)_3CH$, camphorsulfonic acid (CSA), CH_2Cl_2; 66%. *b*) $Me_3SiC{\equiv}CH$ (**6**) or $(i\text{-}Pr)_3SiC{\equiv}CH$ (**8**), $[PdCl_2(PPh_3)_2]$, CuI, $BuNH_2$, PhH. *c*) DIBAL-H, CH_2Cl_2, –78°. *d*) PDC, CH_2Cl_2. *e*) CBr_4, PPh_3, Zn, CH_2Cl_2. *f*) *B*-bromo-1,3,2-benzodioxaborole ('*B*-bromocatecholborane'), CH_2Cl_2, 0°. *g*) PDC, CH_2Cl_2. *h*) CBr_4, PPh_3, Zn, CH_2Cl_2. *i*) LDA, THF, –78°, then NH_4Cl.

Removal of the methoxymethyl protecting group in **81** and **82** provided difficult. Standard acidic methods induced almost complete *cis-trans*-isomerization. Trimethylsilyl halides such as Me_3SiBr [33] produced some deprotected product, along with an equal amount of isomerized starting material. The only reagent which effected deprotection without any appreciable isomerization was *B*-bromocatecholborane [34]. The yields of alcohols **83** and **84** were generally between 60 and 70%, with the remainder of the mass balance being decomposition products (rather than isomerized compound). The alcohols were oxidized with PDC and dibromoolefinated to yield the tetrabromo derivatives **85** and **75**, respectively. Whereas Me_3Si-protected **85** is a solid, the $(i\text{-}Pr)_3Si$ derivative **75** is a yellow oil. These tetrabromides are highly susceptible to isomerization. When a sample of **75** was allowed to sit on the lab bench for several h, yellow crystals started forming from the oil. X-Ray analysis showed these crystals to be the *trans*-tetrabromide **57** (*Fig. 6*). Isomerization can be kept to a minimum, if the *cis*-tetrabromides are kept rigorously free of acid and away from light. Dilute solutions of **85** or **75** could be kept over $NaHCO_3$ at – 20° in the freezer for periods of over 2 weeks without detectable isomerization occurring.

The conversion of tetrabromides **85** and **75** into dilithiated **63** and **64** was accompanied by some spectacular color changes which aided in monitoring the progress of the reaction. Upon addition of the first drops of LDA to a dilute solution of the tetrabromide in THF at – 78°, the mixture turned pale green. This green color deepened upon further LDA addition and then turned deep blue. When all elimination and metallation was terminated, the solution was deep purple. At this moment, sat. aqueous NH_4Cl solution or 0.1M aqueous HCl was added to give a pale brown solution. Isolation of the *cis*-bis-deprotected tetraethynylethenes **63** and **64** proved very difficult. The $(i\text{-}Pr)_3Si$ derivative **64** was obtained in TLC-pure form as colorless solution in hexanes which eventually darkened upon concentration. The compound was isolated as an orange oil which showed the expected ^1H- and ^{13}C-NMR spectra along with a few peaks in the aromatic region. If a benzene solution of **64** was heated at reflux for a few h, little change was seen in the NMR spectra. However, when the oily compound was heated neat above 50° in an attempted bulb-to-bulb distillation, it decomposed immediately. The ^1H-NMR spectrum of the resulting black tar showed a multitude of peaks in the aromatic region, suggesting the formation of large insoluble aromatic compounds. *Bergman* cycloaromatization [20] could be excluded as decomposition mechanism at such a low temperature; this type of cyclization occurs spontaneously at ambient temperature only when the terminal alkyne C-atoms in a *cis*-enediyne are within 3.2 Å of each other [20c]. Force-field calculations [28] gave values of 4.38 Å and 4.37 Å for the distances between the two alkyne C-termini in the free *cis*-enediyne moieties of **63** and **64**, respectively. These distances are too large for the *Bergman* reaction to occur at 50° and below.

The Me_3Si-protected derivative **63** was even less stable. Concentration of its hexane solution led to a black tarry mass. This black oily solid was extracted with hexanes to yield a mixture of low-weight soluble polymers along with some undecomposed starting material. Filtration over SiO_2 (hexanes) led to the recovery of small amounts of **63**. Even at – 20° in the dark, some coloring of dilute solutions of **63** occurred, along with the appearance of a fluorescent spot on the TLC plate and a series of aromatic peaks in the ^{13}C-NMR spectrum.

Because of these stability problems, the hexane solutions of the bis-deprotected tetraethynylethenes **63** and **64** were always prepared *in situ* for use in cyclization reactions to the dehydroannulenes **65** and **66** [9]. Since the characterization of **63** and **64** was necessarily incomplete due to the instability of the pure compounds, their transformation into annulenes **65b** and **66a**, which were both characterized by X-ray analysis, provided additional conclusive proof for their formation [9] [35].

3. Conclusion. – The first synthesis of unprotected tetraethynylethene **1** was accomplished by a novel synthetic route. A great diversity of tetraethynylethene derivatives of almost any substitution and protection pattern were prepared, and these compounds now serve as versatile molecular building blocks in C-scaffolding and the construction of acetylenic C-rich nanometer-sized structures on the way to all C-networks [3]. Although they possess two *cis*-enediyne moieties, *Bergman*-cycloaromatization reactions do not represent a decomposition pathway in tetraethynylethene derivatives. Tetra- and trisubstituted tetraethynylethenes are rather stable molecules, whereas derivatives with two and more free $\equiv$C—H termini are only stable in dilute solution and tend to polymerize rapidly in neat form. *trans*-Bis-deprotected *trans*-bis(triisopropylsilyl)-protected derivative **47** is an exception and forms stable crystals. Its X-ray crystal-structure analysis showed that this surprising stability is due to the presence of the bulky $(i\text{-Pr})_3$Si groups which isolate the reactive chromophores in the crystal and prevent intermolecular reactions. The construction of extended linear and macrocyclic C-rich chromophores with the components of the 'tetraethynylethene molecular construction kit' introduced in this paper will be the subject of forthcoming reports.

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Experimental Part

General. Reagents and solvents were purchased reagent grade and used without further purification. CH_2Cl_2, Et_3N, and $BuNH_2$ were distilled over CaH_2, and THF and Et_2O over sodium benzophenone ketyl prior to use. DMF was dried over alumina, activity I, and maintained under vacuum (10^{-2} Torr) for 5 min to remove most amine impurities. Benzene and TMEDA were stored over molecular sieves (4 Å). Anh. $MgSO_4$ was used as the drying agent after workup in all the experiments. Evaporation and concentration *in vacuo* was done at H_2O-aspirator pressure. Stannylacetylenes were prepared following the standard literature preparations [36]. Dimethyl 2,3-dibromofumarate (**48**) was prepared according to [37]. All reactions were performed in standard glassware under an inert atmosphere of N_2 or Ar. A positive pressure of the protecting gas was essential for high yields in all Pd-catalyzed coupling reactions. Column chromatography: silica gel *60* (230–400 mesh) or reversed-phase (C_{18}) silica gel (230–400 mesh) from *E. Merck*; flash chromatography = FC. Thin layer chromatography (TLC): glass or plastic sheets coated with silica gel *60* F_{254} from *E. Merck*, and reversed-phase (C_{18}) TLC glass plates from *Aldrich*; visualization by UV light and anisaldehyde stain. M.p.: *Electrothermal* or *Büchi* (Dr. *Tottoli*) apparatus; uncorrected. UV/VIS Spectra: *Varian-Cary-2300* and *Varian-Cary-5* spectrophotometers; λ_{max} in nm (ε). IR Spectra (cm^{-1}): *Perkin-Elmer-1600-FTIR* or *Perkin-Elmer-PE-580* instrument. ^{1}H- and ^{13}C-NMR: *Bruker-AM500*, *-AM400*, *-AM360*, *-AM300*, *-AF200*, and *Varian-Gemini-200* and *-300* spectrometers at 296 or 300 K; Me_4Si as internal standard for ^{1}H, solvent peaks as reference for ^{13}C; *J* in Hz; if not indicated otherwise, in $CDCl_3$. MS (*m*/*z* (%)): *VG-7070-EHF* (UC Riverside) and *VG-Tribrid* (ETHZ) instruments for EI; *VG-ZAB-1FHF* (UC Riverside) or *VG-ZAB-2SEQ* (ETHZ) instruments for FAB in a 3-nitrobenzyl alcohol matrix; laser-desorption time-of-flight (LD-TOF) MS on a *Bruker-Reflex-TOF* instrument; for molecules with 3 and 4 Br-atoms, the expected isotopic patterns were observed; for molecular ions with 4 Br-atoms, only the most intense peak of the molecular-ion cluster is given, and for molecular ions and fragment ions with 3 Br-atoms, the two most intense peaks. Elemental analyses were effected by *Desert Analytics*, Tucson, AZ, and by the Mikrolabor in the Laboratorium für Organische Chemie at ETHZ. Chemical Abstracts Registry Service (CAS) or the *Beilstein* program AUTONOM assisted in naming new compounds.

UV/VIS Spectroscopy. Solns. of **1**, **29**, **30**, and **53** for UV/VIS were obtained from solns. of **5**, **27**, **28**, and **52** of known concentration in MeOH by treatment with K_2CO_3 (5 mg) for 10 min and finally adding 36% aq. HCl soln. (10 µl) to eliminate the absorption below 220 nm due to the CO_3^{2-} ion. Absorption coefficients ε were calculated based on the assumed quantitative deprotection of the Me_3Si group in the precursors.

1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ol (**10**) [6c]. A soln. of $Me_3SiC{\equiv}CH$ (**6**; 9.82 g, 14.1 ml, 100 mmol) in THF (500 ml) was cooled to 0° and 1.6M BuLi in hexane (62.5 ml, 0.1 mol) added dropwise over 10 min. After 15 min, ethyl formate (3.70 g, 4.1 ml, 50 mmol) was added dropwise and the soln. stirred further for 30 min at 0° and then quenched with sat. aq. NH_4Cl soln. The org. phase was washed (H_2O, then sat. aq. NaCl soln.) and dried. Evaporation and distillation under reduced pressure gave **10** (6.78 g, 60%). Pale yellow oil. B.p. 56–57°/0.06 Torr ([6c]: 76°/0.2 Torr). IR (CCl_4): 3595 (O–H), 2180 (C≡C). ^{1}H-NMR (360 MHz): 0.11 (*s*, 18 H); 3.04 (br. *s*, 1 H); 5.04 (*d*, $J = 6.4$, 1 H). ^{13}C-NMR (90.6 MHz, gated-decoupled): −0.44 (*qm*, $J = 120.1$); 52.7 (*d*, $J = 151.4$); 89.4 (*s*); 101.8 (*d*, $^2J = 10.0$).

1-(Triethylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-ol (**11**). A soln. of $Et_3SiC{\equiv}CH$ (**7**; 13 ml, 72.6 mmol) in THF (500 ml) was cooled to 0° and 1.4M BuLi in hexane (51.8 ml, 73.0 mmol) added. After stirring for 15 min, $Me_3SiC{\equiv}CCHO$ (8.05 g, 63.8 mmol) was added dropwise and the soln. stirred for 1 h at 0°. After quenching with sat. aq. NH_4Cl soln., the org. phase was washed (H_2O, then sat. aq. NaCl soln.) and dried. Distillation under reduced pressure gave **11** (8.66 g, 45%). Pale yellow oil. B.p. 110–112°/0.3–0.4 Torr. IR (neat): 3462 (O–H), 2176 (C≡C). ^{1}H-NMR (360 MHz): 0.15 (*s*, 9 H); 0.59 (*q*, $J = 7.9$, 6 H); 0.97 (*t*, $J = 7.9$, 9 H); 2.35 (*s*, 1 H); 5.07 (*s*, 1 H). ^{13}C-NMR (90.6 MHz, gated-decoupled): −0.4 (*q*, $J = 120.1$); 4.1 (*t*, $J = 120.4$); 7.3 (*tq*, $J = 126.2, 4.4$); 52.9 (*d*, $J = 151.9$); 87.2 (*s*); 89.4 (*s*); 102.0 (*d*, $J = 9.9$); 103.2 (*d*, $J = 10.1$). EI-MS (70 eV): 266 (21, M^+), 251 (20, $[M - Me]^+$), 237 (54, $[M - Et]^+$), 209 (50, $[M - Et - C_2H_4]^+$), 155 (100). HR-MS: 266.1513 (M^+, $C_{14}H_{26}OSi_2^+$, calc. 266.1522).

1-(Triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-ol (**12**). A soln. of $(i\text{-}Pr)_3SiC{\equiv}CH$ (**8**; 22.1 ml, 98.5 mmol) in THF (500 ml) was cooled to 0° and 2.1M BuLi in hexane (46.9 ml, 98.4 mmol) added over 5 min. After stirring for 15 min, $Me_3SiC{\equiv}CCHO$ (11.3 g, 89.5 mmol) in THF (50 ml) was added dropwise and the soln. stirred for 30 min at 0°. Workup as described for **11** and distillation afforded **8** (8.18 g, 44.9 mmol) and **12** (9.54 g, 58% based on converted starting material). Pale yellow oil. B.p. 130–144°/0.6 Torr. IR (neat): 3386 (O–H), 2160 (C≡C). ^{1}H-NMR (360 MHz): 0.14 (*s*, 9 H); 1.05 (*s*, 21 H); 2.28 (*s*, 1 H); 5.06 (*s*, 1 H). ^{13}C-NMR (90.6 MHz): −0.4, 11.1, 18.5, 52.9, 86.2, 89.3, 102.2, 104.0. EI-MS (20 eV): 308 (6, M^+), 263 (20, $[M - 3\,Me]^+$), 235 (11, $[M - Me_3Si]^+$), 73 (100, Me_3Si^+). HR-MS: 308.1992 (M^+, $C_{17}H_{32}OSi_2^+$, calc. 308.1991).

1-Phenyl-5-(trimethylsilyl)penta-1,4-diyn-3-ol (**13**). A soln. of $PhC{\equiv}CH$ (**9**; 3.6 ml, 32.55 mmol) in THF (250 ml) was cooled to 0° and 1.6M BuLi in hexane (20.0 ml, 32.0 mmol) added. After stirring for 15 min, $Me_3SiC{\equiv}CCHO$ (4.47 g, 35.4 mmol) was added dropwise and the soln. stirred for 1 h. Workup as described for **11** and FC (SiO_2, hexane/CH_2Cl_2 1:1, then 2:3, then 1:2) gave **13** (2.30 g, 31%). Pale orange oil. IR (neat): 3342 (O–H), 2235, 2178 (C≡C). ^{1}H-NMR (300 MHz): 0.22 (*s*, 9 H); 2.38 (*d*, $J = 7.5$, 1 H); 5.35 (*d*, $J = 7.5$, 1 H); 7.32–7.36 (*m*, 3 H); 7.46–7.49 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): −0.3; 53.1; 84.4; 85.9; 89.8; 101.7; 122.0; 128.3; 128.8; 131.9. EI-MS (20 eV): 228 (19, M^+), 227 (28, $[M - H]^+$), 213 (89, $[M - Me]^+$), 185 (100, $[M - Me - CO]^+$), 138 (86, $[M - OH - Me_3Si]^+$), 73 (76, Me_3Si^+). HR-MS: 228.0960 (M^+, $C_{14}H_{16}OSi^+$, calc. 228.0970).

1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-one (**14**) [6c] [38]. A suspension of **10** (23.95 g, 107 mmol) and $BaMnO_4$ [39] (38.44 g, 150 mmol) in CH_2Cl_2 (500 ml) was stirred at 20° for 15 h. The dark manganese salts were filtered through *Celite*, and evaporation of the dried filtrate afforded **14** (22.13 g, 93%). Pale yellow crystals. M.p. 47–49° ([6c]: 51°). IR ($CHCl_3$): 2153 (C≡C), 1614 (C=O). ^{1}H-NMR (360 MHz): 0.17 (*s*, 18 H). ^{13}C-NMR (90.6 MHz): −1.13; 98.8; 102.3; 159.8.

1-(Triethylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-one (**15**). To a mixture of **11** (8.07 g, 30.28 mmol), *Celite* (11 g), and molecular sieves (4 Å; 11 g) in CH_2Cl_2 (250 ml) was added PCC (9.63 g, 44.68 mmol). After stirring for 6 h at r.t., the mixture was passed through a plug (SiO_2, CH_2Cl_2) and the filtrate evaporated: **15** (7.81 g, 97%). Yellow oil. IR (CCl_4): 2160 (C≡C), 1629 (C=O). ^{1}H-NMR (360 MHz): 0.18 (*s*, 9 H); 0.62 (*q*, $J = 7.9$, 6 H); 0.95 (*t*, $J = 7.9$, 9 H). ^{13}C-NMR (90.6 MHz): −1.1; 3.6; 7.06; 97.7; 98.9; 102.6; 103.9; 159.8. CI-MS: 265 (100, MH^+), 249 (8, $[M - Me]^+$), 235 (12, $[M - Et]^+$). HR-MS: 265.1441 (MH^+, $C_{14}H_{25}OSi_2^+$, calc. 265.1444).

1-(Triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-one (**16**). To a mixture of **12** (4.86 g, 15.75 mmol), *Celite* (5 g), and molecular sieves (4 Å; 5 g) in CH_2Cl_2 (400 ml) was added PCC (5.3 g, 24.59 mmol). After stirring for 21 h at r.t., workup as described for **15** gave **16** (4.61 g, 95%). Orange oil. IR (neat): 2159 (C≡C), 1636 (C=O). ^{1}H-NMR (360 MHz): 0.19 (*s*, 9 H); 1.07 (*s*, 21 H). ^{13}C-NMR (90.6 MHz): −1.0; 11.0; 18.4; 98.0; 99.2; 102.8; 105.0;

160.0. EI-MS (70 eV): 306 (5, M^+), 263 (100, $[M - \text{i-Pr}]^+$), 73 (61, Me_3Si^+). HR-MS: 306.1835 (M^+, $\text{C}_{17}\text{H}_{30}\text{OSi}_2^+$, calc. 306.1835).

1-Phenyl-5-(trimethylsilyl)penta-1,4-diyn-3-one (**17**). To a mixture of **13** (148.9 mg, 0.652 mmol), *Celite* (*ca.* 0.5 g), and molecular sieves (4 Å; *ca.* 0.5 g) in CH_2Cl_2 (25 ml) was added PCC (255 mg, 1.183 mmol). After stirring for 14 h at r.t., workup as described for **15** gave **17** (122.6 mg, 83%). Orange oil. IR (neat): 2206, 2147 (C≡C), 1623 (C=O). ^{1}H-NMR (200 MHz): 0.28 (*s*, 9 H); 7.34–7.52 (*m*, 3 H); 7.59–7.64 (*m*, 2 H). ^{13}C-NMR (50.3 MHz): −1.0; 89.2; 91.6; 99.2; 102.7; 119.4; 128.7; 131.3; 133.4; 160.6. EI-MS: 226 (44, M^+), 211 (19, $[M - \text{Me}]^+$), 183 (100, $[M - \text{Me} - \text{CO}]^+$). HR-MS: 226.0832 ($M^+$, $\text{C}_{14}\text{H}_{14}\text{OSi}$, calc. 226.0814).

3-(Dibromomethylidene)-1,5-bis(trimethylsilyl)penta-1,4-diyne (**18**). To a soln. of **14** (18.92 g, 85 mmol) and CBr_4 (36.48 g, 0.11 mmol) in benzene (1 l) was added PPh_3 (57.7 g, 0.22 mol). After stirring at 20° for 12 h, hexane (500 ml) was added to the suspension and the mixture filtered through *Celite*. Evaporation of the filtrate gave a pale yellow semi-solid which was triturated with hexane and filtered. After evaporation, FC (SiO_2, hexane) of the residual oil gave **18** (16.21 g, 50%). Colorless oil. R_f 0.44 (SiO_2, hexane). IR (CCl_4): 2156, 2133 (C≡C). ^{1}H-NMR (360 MHz): 0.23 (*s*, 18 H). ^{13}C-NMR (90.6 MHz): −0.45; 100.1; 102.6; 110.5; 114.3. EI-MS (20 eV): 376/378/380 (4/8/6, M^+), 361/363/365 (7/11/6, $[M - \text{Me}]^+$), 145 (100, $[M - 2\ \text{Br} - \text{Me}_3\text{Si}]^+$), 73 (73, Me_3Si^+). HR-MS: 375.9298 (M^+, $\text{C}_{12}\text{H}_{18}\text{Br}_2\text{Si}_2^+$, calc. 375.9314). Anal. calc. for $\text{C}_{12}\text{H}_{18}\text{Br}_2\text{Si}_2$ (378.25): C 38.10, H 4.80; found: C 37.86, H 4.82.

3-(Dibromomethylidene)-1-(triethylsilyl)-5-(trimethylsilyl)penta-1,4-diyne (**19**). To a soln. of **15** (5.0 g, 19 mmol) in benzene (250 ml) was added CBr_4 (8.3 g, 25 mmol) and PPh_3 (13.0 g, 49.6 mmol). After stirring for 24 h, workup as described for **18** gave **19** (4.16 g, 52%). Yellow oil. IR (neat): 2155, 2132 (C≡C). ^{1}H-NMR (360 MHz): 0.20 (*s*, 9 H); 0.65 (*q*, $J = 7.9$, 6 H); 1.02 (*t*, $J = 7.9$, 9 H). ^{13}C-NMR (90.6 MHz): −0.4; 4.2; 7.4; 100.3; 100.5; 101.3; 102.4; 110.0; 114.5. EI-MS (20 eV): 418/420/422 (14/29/16, M^+), 389/391/393 (48/100/54, $[M - \text{Et}]^+$), 361/363/365 (15/31/17, $[M - \text{C}_2\text{H}_4 - \text{Et}]^+$). HR-MS: 417.9759 ($M^+$, $\text{C}_{15}\text{H}_{24}\text{Br}_2\text{Si}_2^+$, calc. 417.9784).

3-(Dibromomethylidene)-1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyne (**20**). To a soln. of **16** (2.22 g, 7.24 mmol) in benzene (90 ml) was added CBr_4 (3.10 g, 9.34 mmol) and PPh_3 (4.90 g, 18.69 mmol). After stirring for 24 h, workup as described for **18** gave **20** (1.68 g, 50%). Yellow oil. IR (neat): 2159 (C≡C). ^{1}H-NMR (360 MHz): 0.20 (*s*, 9 H); 1.09 (*s*, 21 H). ^{13}C-NMR (90.6 MHz): −0.2; 11.2; 18.6; 99.7; 100.4; 102.0; 102.4; 109.5; 114.7. EI-MS (20 eV): 460/462/464 (6/12/7, M^+), 417/419/421 (36/73/41, $[M - \text{i-Pr}]^+$), 375/377/379 (8/17/9, $[M - \text{i-Pr} - \text{C}_3\text{H}_6]^+$), 229 (19, $[M - 2\ \text{Br} - \text{Me}_3\text{Si}]^+$), 73 (100, Me_3Si^+). HR-MS: 460.0253 (M^+, $\text{C}_{18}\text{H}_{30}\text{Br}_2\text{Si}_2$, calc. 460.0254).

3-(Dibromomethylidene)-1-phenyl-5-(trimethylsilyl)penta-1,4-diyne (**21**). To a soln. of PPh_3 (2.52 g, 9.6 mmol) in CH_2Cl_2 (25 ml) at 0° was added CBr_4 (1.59 g, 4.79 mmol). After a precipitate formed, **17** (459 mg, 2.03 mmol) was added in CH_2Cl_2 (2 ml). After stirring for 24 h, workup as described for **18** yielded **21** (380 mg, 49%). IR (neat): 2203, 2153 (C≡C). ^{1}H-NMR (300 MHz): 0.28 (*s*, 9 H); 7.35–7.39 (*m*, 3 H); 7.53–7.56 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): −0.4; 85.9; 95.8; 100.1; 102.6; 109.1; 114.2; 122.1; 128.4; 129.1; 131.6. EI-MS (20 eV): 380/382/384 (55/100/56, M^+), 365/367/369 (20/43/22, $[M - \text{Me}]^+$), 286/288 (51/51, $[M - \text{Br} - \text{Me}]^+$), 207 (62, $[M - 2\ \text{Br} - \text{Me}]^+$), 73 (12, Me_3Si^+). HR-MS: 379.9233 (M^+, $\text{C}_{15}\text{H}_{14}\text{Br}_2\text{Si}^+$, calc. 379.9233).

4-Bromo-5-methoxy-1-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-3-en-1-yne (**22**). A soln. of **18** (1.632 g, 4.315 mmol) in THF (25 ml) was cooled to −95° using a liquid N_2/acetone bath. Dropwise addition of 1.2M BuLi in hexane (7.2 ml, 8.629 mmol) over 100 s resulted in a dark mixture. After stirring for 10 min, MeOCH_2Cl (1 ml, 13.0 mmol) was added and the soln. warmed to r.t. within 15 h. The reaction was quenched with sat. aq. NH_4Cl soln. and the org. layer washed with H_2O and sat. aq. NaCl soln. Chromatography (SiO_2, hexane/CH_2Cl_2 1:1) gave **22** (361 mg, 24%). Red-brown oil. IR (neat): 2156 (C≡C). ^{1}H-NMR (200 MHz): 0.20 (*s*, 9 H); 0.22 (*s*, 9 H); 3.31 (*s*, 3 H); 4.45 (*s*, 2 H). ^{13}C-NMR (50.2 MHz): −0.55; 57.56; 73.49; 98.28; 100.48; 100.67; 101.12; 110.94; 142.42. EI-MS: 342/344 (4/4, M^+), 263 (100, $[M - \text{Br}]^+$), 73 (34, Me_3Si^+). HR-MS: 342.0493 (M^+, $\text{C}_{14}\text{H}_{23}\text{BrOSi}_2^+$, calc. 342.0471).

3-(Dibromomethylidene)penta-1,4-diyne (**23**). A soln. of **18** (185 mg, 0.49 mmol) in MeOH (25 ml) was stirred with K_2CO_3 (100 mg, 0.72 mmol) at 20° for 15 min. The soln. was poured into a stirred mixture of pentane H_2O, and the org. phase washed with H_2O and sat. aq. NaHCO_3 soln. and dried. Evaporation below 20° afforded **23** (79 mg, 65%). Highly volatile white crystals. R_f (SiO_2, hexane) 0.29. M.p. > 35°. IR (CCl_4): 3306 (≡C−H), 2117 (C≡C). ^{1}H-NMR (360 MHz): 3.52 (*s*, 2 H). ^{13}C-NMR (90.6 MHz; gated-decoupled): 79.5 (*dd*, $J = 50.7$, 1.4); 84.4 (*d*, $J = 256.7$); 111.7 (*t*, $J = 3.6$); 112.5 (*t*, $J = 4.9$). EI-MS (20 eV): 232/234/236 (52/100/52, M^+), 153/155 (24/32, $[M - \text{Br}]^+$), 74 (56, $[M - 2\ \text{Br}]^+$). HR-MS: 231.8530 (M^+, $\text{C}_6\text{H}_2\text{Br}_2^+$, calc. 231.8524).

1,6-Bis(trimethylsilyl)-3,4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**5**) [6a]. To a soln. of **18** (2.37 g, 6.3 mmol) in benzene (100 ml) was added sequentially BuNH_2 (1.83 g, 2.5 ml, 25 mmol), CuI (114 mg, 0.6 mmol), and $[\text{Pd}(\text{PPh}_3)_4]$ (346 mg, 0.3 mmol). Then, $\text{Me}_3\text{SiC{\equiv}CH}$ (**6**; 1.47 g, 2.1 ml, 15 mmol) was added and the mixture stirred at 20° for 24 h. The soln. was diluted with hexane, extracted with 0.1M aq. HCl, washed with H_2O and sat. aq. $NaHCO_3$ soln., and dried. Evaporation gave an orange-brown solid which was dissolved in hexane (50 ml), and the black insoluble precipitate was filtered. Evaporation and recrystallization from MeOH gave **5** (2.28 g, 88%). Tan plates, M.p. 199–201° ([6a]: 203–205°). UV/VIS (MeOH): 214 (15600), 224 (18300), 262 (sh, 8600), 270 (10800), 285 (10200), 315 (sh, 15600), 326 (24800), 335 (30300), 350 (39400). IR (CCl_4): 2164, 2145 (C≡C). ^{1}H-NMR (360 MHz): 0.23 (*s*, 36 H). ^{13}C-NMR (90.6 MHz, gated-decoupled): –0.2 (*qm*, *J* = 120.2); 101.0 (*s*); 105.3 (*decet*, *J* = 2.6); 118.8 (*s*). EI-MS (70 eV): 412 (100, M^+), 397 (5, $[M - Me]^+$), 381 (9, $[M - Me - CH_4]^+$), 73 (96, Me_3Si^+). HR-MS: 412.1882 (M^+, $C_{22}H_{36}Si_4^+$, calc. 412.1894). X-Ray: *Fig. 4*.

1-(Triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**27**). As described for **5**, with **18** (7.57 g, 20 mmol), benzene (250 ml), $BuNH_2$ (5.85 g, 7.9 ml, 80 mmol), CuI (381 mg, 2 mmol), $[Pd(PPh_3)_4]$ (1.16 g, 1 mmol), and $(i\text{-}Pr)_3SiC{\equiv}CH$ (**8**; 8.21 g, 10.1 ml, 45 mmol). After 48 h at 20°, evaporation (no extraction) gave a brown oil. FC (SiO_2, hexane) yielded **27** (7.50 g, 65%) as pale brown crystals which were recrystallized from $MeOH/CH_2Cl_2$. White platelets. R_f (SiO_2, hexane) 0.24. M.p. 156–157°. UV/VIS (MeOH): 213 (14800), 223 (16100), 274 (10800), 288 (10700), 316 (sh, 16200), 328 (26700), 336 (32700), 351 (44900). IR (CCl_4): 2159, 2143 (C≡C). ^{1}H-NMR (360 MHz): 0.20 (*s*, 18 H); 1.10 (*s*, 42 H). ^{13}C-NMR (90.6 MHz): –0.34; 11.2; 18.7; 101.2; 102.2; 103.7; 104.7; 117.0; 118.9. EI-MS (70 eV): 580 (100, M^+), 537 (2, $[M - i\text{-}Pr]^+$), 495 (7, $[M - i\text{-}Pr - C_3H_6]^+$), 453 (7, $[M - i\text{-}Pr - 2\,C_3H_6]^+$). HR-MS: 580.3750 ($M^+$, $C_{34}H_{60}Si_4^+$, calc. 580.3772). Anal. calc. for $C_{34}H_{60}Si_4$ (581.20): C 70.26, H 10.41; found: C 70.25, H 10.39.

1-Phenyl-3-(phenylethynyl)-6-(trimethylsilyl)-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**28**). As described for **5**, with **18** (1.44 g, 3.81 mmol), benzene (50 ml), $BuNH_2$ (1.46 g, 2.0 ml, 20 mmol), CuI (76 mg, 0.4 mmol), $[Pd(PPh_3)_4]$ (230 mg, 0.2 mmol), and $PhC{\equiv}CH$ (**9**, 817 mg, 0.9 ml, 8.0 mmol; 24 h at 20°). The orange-brown oil obtained after drying and evaporation was subjected to FC (SiO_2, hexane, then hexane/CH_2Cl_2 99:1, 98:2, 95:5, and 9:1), and recrystallization from EtOH (95%) afforded **28** (984 mg, 61%). Off-white fibrous needles. M.p. 112.5–113.5°. UV/VIS (MeOH): 219 (sh, 20800), 225 (23300), 238 (sh, 17400), 245 (sh, 16800), 249 (sh, 16400), 271 (sh, 20900), 278 (23100), 283 (sh, 22500), 295 (22800), 358 (30500), 372 (31500), 380 (sh, 29700). IR (CCl_4): 2199, 2143 (C≡C), 1596 (C=C). ^{1}H-NMR (360 MHz): 0.24 (*s*, 18 H); 7.3–7.35 (*m*, 6 H); 7.5–7.55 (*m*, 4 H). ^{13}C-NMR (90.6 MHz): –0.26; 87.0; 99.1; 101.3; 105.1; 116.6; 119.5; 122.4; 128.3; 129.1; 131.8. EI-MS (70 eV): 420 (100, M^+), 405 (4, $[M - Me]^+$). HR-MS: 420.1713 (M^+, $C_{28}H_{28}Si_2^+$, calc. 420.1729). Anal. calc. for $C_{28}H_{28}Si_2$ (420.71): C 79.94, H 6.71; found: C 80.15, H 6.75.

Tetraethynylethene (= *3,4-Diethynylhex-3-ene-1,5-diyne*; **1**). A soln. of **5** (1.25 g, 3.0 mmol) in MeOH (50 ml) was stirred with solid K_2CO_3 (200 mg, 1.44 mmol) for 15 min at 20°. The mixture was poured into pentane/H_2O and the org. phase washed with more H_2O and dried. Evaporation gave **1** (325 mg, 87%) as *very volatile* white platelets, becoming dark within 5 min at 20°. UV/VIS (MeOH): 242 (sh, 4850), 250 (5300), 264 (5500), 286 (sh, 13800), 295 (sh, 19800), 301 (22900), 313 (25800). IR (CCl_4): 3307 (≡C–H), 2102 (C≡C), 653, 632 (≡C–H, bend.). ^{1}H-NMR (360 MHz, CD_3COCD_3): 4.38 (*s*, 4 H). ^{13}C-NMR (90.6 MHz, gated-decoupled, CD_3COCD_3): 80.1 (*d*, *J* = 50.6); 89.8 (, *J* = 257.4); 119.1 (*m*). DEI-MS (50 eV): 124 (84, M^+), 98 (61, $[M - C_2H_2]^+$), 74 (100, $[M - C_4H_2]^+$). HR-MS: 124.0311 (M^+, $C_{10}H_4^+$, calc. 124.0313).

Thermal Polymerization of **1**. Crystals of **1** (*ca.* 10 mg) were left in the air at 20° for 2 weeks. The initially white crystals turned rapidly brown (within min) and more slowly to a shiny metallic black. IR (CCl_4): 3426 (br., O–H), 2925 (C–H), 2132 (br., C≡C), 1615 (br., C=C). Anal. calc. for $(C_{10}H_4 \cdot O_2 \cdot H_2O)_n$ ($n \cdot 174.16$): C 68.97, H 3.47, O 27.56; found: C 69.01, H 3.18, O 27.81.

4-Ethynyl-1-(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**29**). To a stirred soln. of **27** (620 mg, 1.07 mmol) in THF (3 ml) and MeOH (50 ml) was added K_2CO_3 (500 mg, 3.61 mmol). After 20 min, TLC (SiO_2, hexane/CH_2Cl_2 9:1) showed quantitative conversion of **27** (R_f 0.44) to **29** (R_f 0.36). The mixture was poured into hexane/0.1M aq. HCl and the org. phase washed with H_2O and sat. aq. $NaHCO_3$ soln., dried, and evaporated: **29** (461 mg, 99%). Unstable pale-yellow oil. UV/VIS (MeOH): 217 (11600), 273 (sh, 10200), 288 (12400), 303 (sh, 15600), 314 (sh, 24100), 320 (27500), 334 (34300). IR (CCl_4): 3302 (≡C–H), 2152, 2096 (C≡C). ^{1}H-NMR (360 MHz): 1.10 (*s*, 42 H); 3.49 (*s*, 2 H). ^{13}C-NMR (90.6 MHz, gated-decoupled): 11.2 (*dm*, *J* = 119.7); 18.5 (*qm*, *J* = 126.3); 80.2 (*dd*, *J* = 49.7, 1.7); 86.5 (*d*, *J* = 255.3); 102.7 (*s*); 102.9 (*s*); 115.6 (*t*, *J* = 5.0); 121.4 (*t*, *J* = 2.9). EI-MS (20 eV): 436 (43, M^+), 393 (100, $[M - i\text{-}Pr]^+$), 351 (21, $[M - i\text{-}Pr - C_3H_6]^+$), 309 (10, $[M - i\text{-}Pr - 2\,C_3H_6]^+$), 267 (10, $[M - i\text{-}Pr - 3\,C_3H_6]^+$). HR-MS: 436.2966 ($M^+$, $C_{28}H_{44}Si_2^+$, calc. 436.2981).

4-Ethynyl-1-phenyl-3-(phenylethynyl)hex-3-ene-1,5-diyne (**30**). A soln. of **28** (413 mg, 0.98 mmol) in MeOH was stirred with solid K_2CO_3 (100 mg, 0.72 mmol) for 30 min at 20°. TLC (SiO_2, hexane/CH_2Cl_2 1:1) showed quantitative conversion of **28** (R_f 0.45) to **30** (R_f 0.35). The mixture was poured into pentane/H_2O and the org. phase washed with more H_2O, dried, and concentrated to 5 ml. CCl_4 (20 ml) was added and the soln. concentrated to 0.5 ml. Addition of CD_3COCD_3 (0.5 ml) gave a soln. of highly unstable **30** for NMR analysis. UV/VIS (MeOH):

229 (17200), 237 (17300), 241 (sh, 17100), 248 (sh, 15900), 267 (sh, 18000), 274 (20600), 280 (20600), 290 (22400), 350 (30700), 361 (sh, 26300). IR (CCl_4): 3307 (≡C–H), 2196 (C≡C), 1598 (C=C). ^{1}H-NMR (360 MHz, CD_3COCD_3): 4.11 (*s*, 2 H); 7.35–7.45 (*m*, 6 H); 7.5–7.55 (*m*, 4 H). ^{13}C-NMR (90.6 MHz, CD_3COCD_3): 80.8; 86.7; 88.6; 99.5; 115.6; 120.7; 122.5; 129.0; 129.9; 132.3. DEI-MS (50 eV): 276 (100, M^+). HR-MS: 276.0932 (M^+, $C_{22}H_{12}^+$, calc. 276.0939).

*(E)-*N,N*-Dimethyl-8-(triisopropylsilyl)-3,4-bis[4-(triisopropylsilyl)buta-1,3-diynyl]octa-1,3-diene-5,7-diyn-1-amine* (**31**). To a soln. of $(i\text{-}Pr)_3SiC{\equiv}CBr$ [22] (1.31 g, 5 mmol) in DMF (40 ml) was added sequentially $NH_2OH \cdot HCl$ (21 mg, 0.3 mmol), CuCl (10 mg, 0.1 mmol), and $BuNH_2$ (731 mg, 1.0 ml, 10 mmol). A soln. of **1** (101.9 mg, 0.82 mmol) in DMF (4 ml) was added and the mixture stirred at 20° for 15 h, then poured into Et_2O/H_2O. The org. phase was washed with more H_2O and sat. aq. NaCl soln. After drying and evaporation, FC (SiO_2, hexane then hexane/CH_2Cl_2 9:1) gave a bright orange fraction which was further purified by a 2nd FC (SiO_2, hexane/AcOEt 95:5); **31** (8.0 mg, 1.4%). Orange oil. ^{1}H-NMR (360 MHz): 1.0–1.2 (*m*, 63 H); 2.98 (*s*, 6 H); 5.64 (*d*, *J* = 12.8, 1 H); 7.19 (*d*, *J* = 12.8, 1 H). ^{13}C-NMR (90.6 MHz): 11.65; 11.70; 18.68; 18.71; 30.06; 30.43; 71.54; 73.30; 78.73; 85.04; 85.38; 89.11; 90.07; 90.35; 90.45; 92.74; 92.90; 93.27; 97.83; 125.77; 142.16; 150.02. EI-MS (20 eV): 709 (100, M^+), 666 (3, $[M - i\text{-}Pr]^+$). HR-MS: 709.4936 (M^+, $C_{45}H_{71}NSi_3^+$, 709.4894).

1-(Triethylsilyl)-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]-3-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**34**). A soln. of **19** (3.04 g, 7.23 mmol) in benzene (80 ml) was carefully degassed and $(i\text{-}Pr)_2NEt$ (5 ml, 28.7 mmol) added while bubbling Ar through the soln. After 30 min, $[PdCl_2(PPh_3)_2]$ (251 mg, 0.358 mmol), CuI (60 mg, 0.315 mmol), and $(i\text{-}Pr)_3SiC{\equiv}CH$ (**8**; 4.8 ml, 21.40 mmol) was sequentially added. After stirring at r.t. for 92 h, the dark soln. was diluted with hexane, washed with 0.1M aq. HCl, H_2O, and sat. aq. $NaHCO_3$ soln., and dried. The crude product was filtered through a plug (SiO_2, hexanes), and FC (reversed-phase SiO_2, $MeCN/CH_2Cl_2$ 2:1) gave **34** (2.103 g, 47%). Tan solid. M.p. 122–124°. UV/VIS (hexane): 215 (8000), 225 (12700), 263 (sh, 3000), 274 (6900), 289 (6800), 315 (10800), 329 (23500), 337 (32100), 353 (48800). IR (neat): 2157, 2141, 2061 (C≡C). ^{1}H-NMR (360 MHz): 0.17 (*s*, 9 H); 0.61 (*q*, *J* = 7.9, 6 H); 0.97 (*t*, *J* = 7.9, 9 H); 1.07 (2*s*, 42 H). ^{13}C-NMR (90.6 MHz): –0.4; 4.2; 7.4; 11.15; 11.18; 18.62; 18.64; 101.57; 101.98; 102.29; 102.71; 102.95; 103.61; 103.67; 104.6; 117.1; 118.2. EI-MS (70 eV): 622 (24, M^+), 537 (5, $[M - i\text{-}Pr - C_3H_6]^+$), 509 (15, $[M - i\text{-}Pr - C_3H_6 - C_2H_4]^+$), 73 (100, Me_3Si^+). HR-MS: 622.4223 (M^+, $C_{37}H_{66}Si_4^+$, calc. 622.4241).

1,6-Bis(triethylsilyl)-3-[(triethylsilyl)ethynyl]-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**35**). As described for **34**, a carefully degassed soln. of **19** (1.99 g, 4.73 mmol), $BuNH_2$ (1.87 ml, 18.9 mmol), $[Pd(PPh_3)_4]$ (273 mg, 0.236 mmol), CuI (90 mg, 0.47 mmol), and $Et_3SiC{\equiv}CH$ (**7**; 1.91 ml, 10.66 mmol) in benzene (60 ml) was prepared while bubbling Ar through. After stiring at r.t. under Ar for 48 h, workup as described for **34** and FC (reversed-phase SiO_2, $MeCN/CH_2Cl_2$ 1:1) afforded **35** (1.132 g, 44%). Yellow solid. UV/VIS (hexane): 208 (10800), 219 (13100), 228 (16800), 260 (sh, 7900), 264 (sh, 8500), 273 (11000), 276 (sh, 9600), 287 (11200), 304 (sh, 8000), 315 (sh, 15000), 328 (24400), 337 (31500), 353 (43900). IR (neat): 2162, 2141 (C≡C). ^{1}H-NMR (360 MHz): 0.18 (*s*, 9 H); 0.63 (*m*, 18 H); 0.97 (*m*, 27 H). ^{13}C-NMR (90.6 MHz): –0.4; 4.2; 7.4; 100.8; 101.4; 102.5; 102.7; 102.8; 102.9; 103.1; 104.9; 117.8; 118.3. EI-MS (20 eV): 538 (100, M^+), 73 (11, Me_3Si^+). HR-MS: 538.3284 (M^+, $C_{31}H_{54}Si_4$, calc. 538.3302).

1-Phenyl-3-(phenylethynyl)-6-(triisopropylsilyl)-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**36**). As described for **34**, a carefully degassed soln. of **20** (764 mg, 1.652 mmol), $(i\text{-}Pr)_2NEt$ (1.1 ml, 6.3 mmol), $[PdCl_2(PPh_3)_2]$ (58 mg, 0.083 mmol), CuI (31 mg, 0.163 mmol), and $PhC{\equiv}CH$ (**9**; 0.7 ml, 6.37 mmol) in benzene (30 ml) was prepared while bubbling Ar through. After stirring at r.t. under Ar for 48 h, workup as described for **34** and FC (reversed phase SiO_2, hexane then hexane/CH_2Cl_2 5:1) gave **36** (315 mg, 38%). Dark oil. UV/VIS (hexane): 226 (17800), 240 (15400), 247 (14800), 252 (sh, 13900), 271 (sh, 16000), 279 (sh, 18000), 297 (18700), 359 (19200), 373 (20100), 384 (17900). IR (neat): 2200, 2183, 2142 (C≡C). ^{1}H-NMR (300 MHz): 0.28 (*s*, 9 H); 1.13 (*s*, 21 H); 7.34–7.37 (*m*, 6 H); 7.51–7.56 (*m*, 4 H). ^{13}C-NMR (75.5 MHz): –0.2; 11.3; 18.6; 86.9; 87.3; 98.7; 101.9; 102.4; 103.5; 104.7; 117.1; 118.4; 122.56; 122.64; 128.2; 128.3; 129.0; 131.8. EI-MS (70 eV): 504 (100, M^+), 461 (40, $[M - i\text{-}Pr]^+$), 419 (16, $[M - i\text{-}Pr - C_3H_6]^+$), 73 (39, Me_3Si^+). HR-MS: 504.2648 (M^+, $C_{34}H_{40}Si_2^+$, calc. 504.2668).

1,6-Bis(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**37**). A carefully degassed soln. of **20** (1.00 g, 2.16 mmol), $[PdCl_2(PPh_3)_2]$ (58 mg, 0.083 mmol), CuI (30 mg, 0.160 mmol), and $(i\text{-}Pr)_3SiC{\equiv}CH$ (**8**; 1.0 g, 1.2 ml, 5.4 mmol) in Et_3N (35 ml) was prepared while bubbling Ar through. After stirring at r.t. under Ar for 36 h, workup and plug filtration as described for **34** and FC (reversed-phase SiO_2, $MeCN/CH_2Cl_2$ 1:1) gave **36** (1.10 g, 70%). Colorless crystals. M.p. 174–175°. UV/VIS (hexane): 216 (13600), 226 (16800), 263 (sh, 7800), 278 (12100), 293 (12400), 319 (sh, 17300), 332 (29900), 340 (37000), 355 (52200), 337 (820). IR (neat): 2158 (C≡C). ^{1}H-NMR (360 MHz): 0.16 (*s*, 9 H); 1.06 (*s*, 21 H); 1.07 (*s*, 21 H); 1.08 (*s*, 21 H). ^{13}C-NMR (90.6 MHz): –0.4; 11.16; 11.18; 11.25; 18.61; 18.64; 101.7; 101.9; 102.3; 102.6; 103.58; 103.65; 103.72; 104.53; 117.2; 117.3. Anal. calc. for $C_{40}H_{72}Si_4$ (665.36): C 72.21, H 10.91; found: C 72.52, H 11.13.

2,8-Dimethyl-5-{3-(triisopropylsilyl)-1-[(triisopropylsilyl)ethynyl]prop-2-ynylidene}nona-3,6-diyne-2,8-diol (**38**). As described for **34**, a carefully degassed soln. of **20** (5.058 g, 10.938 mmol), (i-Pr)$_2$NEt (7.6 ml, 43.63 mmol), $[(PPh_3)_2PdCl_2]$ (331 mg, 0.472 mmol), CuI (23 mg, 0.121 mmol), and HOC(Me)$_2$C≡CH (**33**; 4.2 ml, 42.99 mmol) in benzene (80 ml) was prepared while bubbling Ar through. After stirring at r.t. under Ar for 64 h, workup as described for **34** and FC (SiO_2, hexane/AcOEt 3:1) gave **38** (1.374 g, 27%). Dark oil. IR (neat): 3373 (O–H), 2207, 2147 (C≡C). ^{1}H-NMR (200 MHz): 0.18 (*s*, 9 H); 1.07 (*s*, 21 H); 1.52 (*s*, 6 H); 1.55 (*s*, 6 H); 2.62 (*s*, 2 H). ^{13}C-NMR (50.3 MHz): –0.5; 11.1; 18.5; 30.9; 31.1; 65.5; 79.3; 79.6; 101.4; 101.8; 103.0; 103.1 (2 x); 104.0; 116.8; 117.6. EI-MS (70 eV): 468 (27, M^+), 73 (100, Me_3Si^+). HR-MS: 468.2935 (M^+, $C_{28}H_{44}O_2Si_2^+$, calc. 468.2880).

(E)- and (Z)-3-Bromo-6-(triethylsilyl)-1-(triisopropylsilyl)-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**39**). As described for **34**, a carefully degassed soln. of **19** (2.703 g, 6.430 mmol), (i-Pr)$_2$NEt (4.0 ml, 22.96 mmol), $[PdCl_2(PPh_3)_2]$ (100 mg, 0.142 mmol), CuI (27 mg, 0.142 mmol), and (i-Pr)$_3$SiC≡CH (**8**; 4.3 ml, 19.17 mmol) in benzene (30 ml) was prepared while bubbling Ar through. After stirring at r.t. under Ar for 10 h, workup and plug filtration as described for **34** and FC (reversed-phase SiO_2, MeCN/CH_2Cl_2 2:1) gave **39** (913 mg, 27%). IR (neat): 2156, 2130, 2062 (C≡C). ^{1}H-NMR (200 MHz): 0.20 (*s*, 9 H); 0.23 (*s*, 9 H); 0.67 (*m*, 12 H); 1.02 (*m*, 18 H); 1.11 (*s*, 42 H). ^{13}C-NMR (75.4 MHz): –0.4; 4.2; 7.4; 11.2; 18.6; 99.5; 100.3; 101.29; 101.51; 101.57; 102.54; 103.5 (2 ×); 104.1; 105.9; 108.06; 108.37; 114.16; 114.37; 115.55; 115.64. EI-MS (70 eV): 520/522 (9/11, M^+), 435/437 (7/7, $[M - \text{i-Pr} - C_3H_6]^+$), 319 (100, $[M - Br - C_9H_{14}]^+$), 73 (44, Me_3Si^+). HR-MS: 520.2005 (M^+, $C_{26}H_{45}BrSi_3^+$, calc. 520.2013).

3-Bromo-1,6-bis(trimethylsilyl)-4-[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**40**). As described for **34**, a carefully degassed soln. of **18** (519 mg, 1.372 mmol), $BuNH_2$ (0.5 ml, 5.059 mmol), $[PdCl_2(PPh_3)_2]$ (100 mg, 0.142 mmol), CuI (27 mg, 0.142 mmol), and Me$_3$SiC≡CH (**6**; 0.4 ml, 2.830 mmol) in benzene (25 ml) was prepared while bubbling Ar through. After stirring at r.t. under Ar for 14 h, workup and plug filtration as described for **34** and FC (SiO_2, hexane) gave **40** (31 mg, 6%). Brown oil. IR (neat): 2157, 2134 (C≡C). ^{1}H-NMR (300 MHz): 0.22 (*s*, 9 H); 0.23 (*s*, 9 H); 0.24 (*s*, 9 H). ^{13}C-NMR (75.5 MHz): –0.4; –0.3; 99.99; 100.86; 101.32; 101.60; 106.4; 110.3; 114.7; 116.1. EI-MS (70 eV): 394/396 (31/34, M^+), 316 (15, $[M + H - Br]^+$), 301 (17, $[M + H - Br - Me]^+$), 227 (100, $[M - Br - Me - Me_3Si]^+$), 73 (14 Me_3Si^+). HR-MS: 394.0597 (M^+, $C_{17}H_{27}BrSi_3$, calc. 394.0604).

3-Ethynyl-1-(triethylsilyl)-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**41**). A soln. of **34** (478 mg, 0.766 mmol) and 1M aq. NaOH (8 drops) in MeOH/THF 1:1 (200 ml) was stirred at r.t. for 2.5 min. Then the mixture was poured into pentane/H_2O 1:1 and the org. phase washed with H_2O and sat. aq. $NaHCO_3$ soln. Drying and evaporation gave **41** (418 mg, 98%). Unstable oil. IR (CCl_4): 3306 (≡C–H), 2157, 2139, 2099 (C≡C). ^{1}H-NMR (360 MHz): 0.61 (*q*, $J = 7.9$, 6 H); 0.98 (*t*, $J = 7.9$, 9 H); 1.07 (*s*, 21 H); 1.08 (*s*, 21 H); 3.42 (*s*, 1 H). ^{13}C-NMR (90.6 MHz): 4.2; 7.5; 11.17; 11.18; 18.56; 18.63; 80.8; 85.7; 102.06; 102.25; 102.87; 103.20; 103.40; 103.51; 116.2; 119.9. EI-MS (70 eV): 550 (64, M^+), 507 (59, $[M - \text{i-Pr}]^+$), 465 (20, $[M - \text{i-Pr} - C_3H_6]^+$), 73 (100, Me_3Si^+). HR-MS: 550.3832 (M^+, $C_{34}H_{58}Si_3^+$, calc. 550.3846).

3-Ethynyl-1,6-bis(triethylsilyl)-4-[(triethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**42**). The reaction of **35** (194 mg, 0.360 mmol) and 1M aq. NaOH (8 drops) in MeOH/THF 1:1 (20 ml), as described for **41**, afforded **42** (149 mg, 89%). Unstable yellow-orange oil. R_f (SiO_2, hexane) 0.23. ^{1}H-NMR (360 MHz): 0.62 (*q*, $J = 7.8$, 18 H); 0.99 (*t*, $J = 7.8$, 27 H); 3.45 (*s*, 1 H). EI-MS (70 eV): 466 (26, M^+), 352 (79, $[M - 2\ Et - 2\ C_2H_4]^+$), 323 (100, $[M - 3\ Et - 2\ C_2H_4]^+$). HR-MS: 466.2908 ($M^+$, $C_{28}H_{46}Si_3^+$, calc. 466.2907).

3-Ethynyl-6-phenyl-4-(phenylethynyl)-1-(triisopropylsilyl)hex-3-ene-1,5-diyne (**43**). A mixture of **36** (104 mg, 0.206 mmol) and K_2CO_3 (100 mg, 0.724 mmol) in MeOH/THF 1:1 (15 ml) was stirred at r.t. for 30 min, then poured into pentane/H_2O, washed with H_2O and sat. aq. $NaHCO_3$ soln., dried, and evaporated: **43** (51 mg, 57%). Red oil. IR (neat): 3286 (≡C–H), 2197, 2136 (C≡C). ^{1}H-NMR (300 MHz): 1.11 (*s*, 21 H); 3.60 (*s*, 1 H); 7.35–7.37 (*m*, 6 H); 7.51–7.57 (*m*, 4 H). ^{13}C-NMR (75.4 MHz): 11.3; 18.6; 80.9; 85.78; 85.83; 86.58; 86.95; 98.9; 102.9; 103.2; 115.9; 119.6; 122.4; 128.22; 128.36: 129.08; 129.16; 131.88; 131.94. EI-MS (70 eV): 432 (100, M^+), 389 (80, $[M - \text{i-Pr}]^+$), 347 (23, $[M - \text{i-Pr} - C_3H_6]^+$). HR-MS: 432.2295 ($M^+$, $C_{31}H_{32}Si^+$, calc. 432.2273).

3-Ethynyl-1,6-bis(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**44**). Reaction of **37** (305 mg, 0.458 mmol) and K_2CO_3 (305 mg, 2.207 mmol) in MeOH/THF 1:1 (125 ml) as described for **43** afforded **44** (266 mg, 98%) as oil that crystallized upon standing. M.p. 77–78°. IR (neat): 3307 (≡C–H), 2156 (C≡C). ^{1}H-NMR (360 MHz): 1.08 (*s*, 63 H); 3.41 (*s*, 1 H). ^{13}C-NMR (90.6 MHz, gated-decoupled): 11.2 (*d*, $J = 128$); 18.6 (*q*, $J = 189$); 81.0 (*d*, $J = 49.90$); 85.5 (*d*, $J = 254.9$); 102.0; 102.90; 102.93; 102.99; 103.29; 103.54; 116.2; 119.4. EI-MS (70 eV): 592 (45, M^+), 549 (61, $[M - \text{i-Pr}]^+$), 381 (100, $[M - \text{i-Pr} - 4\ C_3H_6]^+$). HR-MS: 592.4290 ($M^+$, $C_{37}H_{64}Si_3^+$, calc. 592.4316).

1-Bromo-6-(triisopropylsilyl)-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**45**). To **44** (338 mg, 0.570 mmol) in acetone (6 ml) was added NBS (121 mg, 0.681 mmol) and $AgNO_3$ (5.7 mg, 0.034 mmol). The mixture was stirred for 3 h at 25°, then washed with H_2O and sat. aq. NaCl soln., dried, and evaporated: **45** (218 mg, 57%). Oil. IR (neat): 2186, 2151 (C≡C). ^{1}H-NMR (360 MHz): 1.066 (*s*, 21 H); 1.072 (*s*, 21 H); 1.081 (*s*, 21 H). ^{13}C-NMR (90.6 MHz): 11.19; 11.21; 11.24; 18.57; 18.63; 18.67; 50.3; 77.97; 101.8; 102.60; 102.85; 103.29; 103.36; 103.64; 116.6; 119.3. EI-MS (70 eV): 670/672 (5/5, M^+), 549 (8, $[M - Br - C_3H_6]^+$). 507 (4, $[M - Br - 2\ C_3H_6]^+$), 465 (20, $[M - Br - 3\ C_3H_6]^+$), 269 (100, $[M - Br - Si - 7\ C_3H_6]^+$). HR-MS: 670.3444 ($M^+$, $C_{37}H_{63}BrSi_3^+$, calc. 670.3421).

1-Bromo-3-(bromoethynyl)-6-(triisopropylsilyl)-4-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**46**). As described for **45**, with **29** (148 mg, 0.339 mmol), NBS (144 mg, 0.809 mmol), $AgNO_3$ (75 mg, 0.441 mmol), and acetone (5 ml, 1 h): **46** (125 mg, 62%). Very unstable brown oil. R_f (hexane/CH_2Cl_2 1:1) 0.60. IR (neat): 2179, 2146 (C≡C). ^{1}H-NMR (360 MHz, C_6D_6): 1.11 (*s*, 42 H). ^{13}C-NMR (90.6 MHz, C_6D_6): 11.5; 18.7; 61.8; 77.6; 103.40; 103.43; 117.8; 121.2.

Dimethyl 2,3-Bis(phenylethynyl)fumarate (**49**). To a degassed soln. of **48** (13.6 g, 45 mmol) and $PhC{\equiv}CSnBu_3$ (39.2 g, 100 mmol) in THF (50 ml) was added $[PdCl_2(PPh_3)_2]$ (1.5 g, 2 mmol), and the resulting mixture was stirred at r.t. for 4 d. Evaporation gave an oil which was passed through a plug of SiO_2, first with hexanes (*ca.* 1.5 l) to remove residual tin and diphenylbutadiyne impurities, then with CH_2Cl_2. Evaporation yielded an oil which, upon standing overnight at – 5°, crystallized. The crystals were separated from residual oily tin impurities and washed with hexanes: **49** (14 g, 90%). Bright yellow crystals. M.p. 82°. IR (KBr): 2204 (C≡C), 1655 (C=O). ^{1}H-NMR (200 MHz): 3.92 (*s*, 6 H); 7.37 (*m*, 6 H); 7.53 (*m*, 4 H). ^{13}C-NMR (50.3 MHz): 53.0; 85.1; 105.1; 122.2; 126.7; 128.4; 129.6; 132.0; 163.9. EI-MS (20 eV): 344 (100, M^+), 329 (11, $[M - Me]^+$). Anal. calc. for $C_{22}H_{16}O_4$ (344.37): C 76.73, H 4.68; found: C 76.74, H 4.68.

2,3-Bis(phenylethynyl)fumaraldehyde (**50**). To a soln. of **49** (14 g, 40 mmol) in THF (100 ml) at – 78° was added 1.0M DIBAL-H in hexanes (200 ml, 200 mmol). After 2 h, the soln. was allowed to warm to r.t. and sufficient MeOH (*ca.* 80 ml) was added to cause the mixture to become very thick. Filtration through a medium glass frit gave a clear soln. which, upon evaporation, yielded the crude dimethanol as a thick sticky oil. ^{1}H-NMR (200 MHz): 4.60 (*s*, 4 H); 7.30 (*m*, 6 H); 7.48 (*m*, 4 H). ^{13}C-NMR (50.3 MHz): 67.6; 85.9; 101.4; 122.3; 127.8; 128.0; 129.5; 131.4. The oil was immediately dissolved in dry CH_2Cl_2 (300 ml), and PCC (26 g, 120 mmol), *Celite* (20 g), and molecular sieves (4 Å) (20 g) were added. The resulting suspension was stirred for 3 h, then passed through a pad of SiO_2 (CH_2Cl_2) to yield **50** (9.1 g, 80%). An anal. pure sample was prepared by recrystallization from hexanes. Bright orange solid. M.p. 146°. IR (KBr): 2198 (C≡C), 1692 (C=O). ^{1}H-NMR (200 MHz): 7.37 (*m*, 6 H); 7.56 (*m*, 4 H); 10.44 (*s*, 2 H). ^{13}C-NMR (50.3 MHz): 80.8; 110.0; 121.1; 128.8; 129.5; 131.8; 136.6; 189.0. EI-MS (20 eV): 284 (70, M^+), 282 (100, $[M - 2\ H]^+$). Anal. calc. for $C_{20}H_{12}O_2$ (284.32): C 84.49, H 4.25; found: C 84.40, H 4.28.

*(*E*)-1,1,6,6-Tetrabromo-3,4-bis(phenylethynyl)hexa-1,3,5-triene* (**51**). A mixture of CBr_4 (42 g, 127 mmol), PPh_3 (34 g, 130 mmol), and Zn dust (8.32 g, 127 mmol) in dry CH_2Cl_2 (800 ml) was stirred at r.t. for 24 h. The suspension was then cooled to – 78°, and **50** (9.1 g, 32 mmol) dissolved in CH_2Cl_2 (50 ml) was added at once. The resulting soln. was warmed slowly to r.t. over 8 h, hexane (600 ml) was added and the resulting thick suspension filtered. Evaporation of the filtrate yielded a dark solid which was dissolved in a minimum of boiling CH_2Cl_2, and cooling to – 5° led to the almost immediate precipitation of **51** (3.2 g, 17%). Yellow-orange solid. M.p. 176°. IR (KBr): 2194 (C≡C). ^{1}H-NMR (200 MHz): 7.38 (*m*, 6 H); 7.51 (*m*, 4 H); 7.80 (*s*, 2 H). ^{13}C-NMR (50.3 MHz): 84.9; 95.0; 107.0; 122.5; 126.9; 128.6; 129.4; 131.3; 133.6. EI-MS (20 eV): 596 (100, M^+). Anal. calc. for $C_{22}H_{12}Br_4$ (595.96): C 44.34, H 2.03; found: C 44.25, H 2.06.

*(*E*)-1,6-Diphenyl-3,4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**52**). To a soln. of **51** (3.2 g, 5.4 mmol) in dry Et_2O (400 ml) at – 78° was added slowly 2.0M LDA in THF (11 ml, 22 mmol). After 40 min, the bright-green soln. was slowly warmed to r.t., and Me_3SiCl (1.3 g, 12 mmol) was added. The now colorless soln. was stirred for 3 h, quenched with sat. aq. NH_4Cl soln., extracted with H_2O and sat. aq. NaCl soln., and dried. Evaporation gave a dark residue which was passed through a short pad of SiO_2 (CH_2Cl_2). Evaporation to *ca.* 5 ml, and cooling to – 5° slowly gave crystalline **52** (1.9 g, 84%). Pale yellow solid. M.p. 150° (dec.). UV/VIS (MeOH): 232 (sh, 17700), 246 (18600), 256 (18900), 274 (24400), 380 (23500). IR (KBr): 2205, 2141 (C≡C). ^{1}H-NMR (360 MHz): 0.27 (*s*, 18 H); 7.36 (*m*, 6 H); 7.54 (*m*, 4 H). ^{13}C-NMR (90.6 MHz): – 0.2; 87.2; 98.8; 101.1; 105.4; 118.1; 122.5; 128.3; 129.0; 131.9. EI-MS (20 eV): 420 (100, M^+, $C_{28}H_{28}Si_2^+$), 405 (65, $[M - Me]^+$). X-Ray: *Fig. 5*.

*(*E*)-3,4-Diethynyl-1,6-diphenylhex-3-ene-1,5-diyne* (**53**). A soln. of **52** (0.2 g, 0.48 mmol) and K_2CO_3 (20 mg, 0.14 mmol) was stirred for 20 min, then poured into hexane and extracted with H_2O. The org. phase was dried and concentrated to *ca.* 10 ml, then CCl_4 (10 ml) was added and the soln. further concentrated to *ca.* 1 ml (→ continuous darkening presumably due to beginning product decomposition). An aliquot of this soln. was added to $CDCl_3$ for NMR analysis. UV/VIS (MeOH): 224 (18900), 242 (19700), 250 (19600), 256 (19600), 272 (sh, 15800), 358 (25800), 380 (21400). IR ($CHCl_3$): 3302 (≡C–H), 2210 (C≡C). ^{1}H-NMR (360 MHz): 3.66 (*s*, 2 H); 7.37 (*m*, 6 H); 7.55 (*m*, 4 H). ^{13}C-NMR (90.6 MHz): 80.1; 86.7, 99.5; 117.7; 122.1; 128.4; 129.3; 131.9 (1 peak masked).

Dimethyl 2,3-Bis[(triisopropylsilyl)ethynyl]fumarate (**54**). *a*) To a degassed soln. of **48** (25 g, 83 mmol) and $(i\text{-}Pr)_3SiC{\equiv}CSnBu_3$ (118 g, 250 mmol) in THF (100 ml) was added $[PdCl_2(PPh_3)_2]$ (1.5 g, 2 mmol), and the resulting soln. was stirred at r.t. for 9 d. Evaporation afforded an oil which was passed through a plug (SiO_2) first with hexanes to remove residual tin compounds followed by CH_2Cl_2. Evaporation and standing overnight at – 5° led to the formation of a solid which was separated from residual oil and recrystallized from MeOH to give **54** (38.5 g, 92%). Buff-colored crystals. M.p. 55°. IR (KBr): 2170 (C≡C), 1750 (C=O). ^{1}H-NMR (200 MHz): 1.00 (*s*, 42 H); 3.72 (*s*, 6 H). ^{13}C-NMR (50.3 MHz): 11.2; 18.5; 52.7; 100.3; 109.8; 127.3; 163.7. EI-MS (70 eV): 504 (6, M^+), 461 (100, $[M - i\text{-}Pr]^+$). Anal. calc. for $C_{28}H_{48}O_4Si_2$ (504.86): C 66.61, H 9.58; found: C 66.80, H 9.81.

b) To a degassed soln. of **48** (1.00 g, 3.31 mmol) and $(i\text{-}Pr)_3SiC{\equiv}CH$ (**8**; 1.51 g, 8.30 mmol) in Et_3N (35 ml) was added $[PdCl_2(PPh_3)]$ (116 mg, 0.166 mmol) and CuI (40 mg, 0.210 mmol). After 18 h stirring at r.t., the mixture was diluted with Et_2O (50 ml) and washed with sat. aq. NaCl soln. (2 × 50 ml). The combined aq. phase was subsequently extracted with Et_2O (50 ml), the combined org. phase dried and evaporated, and the resulting dark oil passed through a plug (SiO_2) first with hexanes ro remove 1,4-bis(triisopropylsilyl)butadiyne, then with hexanes/CH_2Cl_2 2:1. Evaporation afforded **54** (1.50 g, 90%) which was recrystallized from MeOH.

(E)*-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diol* (**55**). To a soln. of **54** (38.5 g, 76.3 mmol) in CH_2Cl_2 (100 ml) at 0° was added 1.0M DIBAL-H in hexanes (380 ml, 380 mmol), and the soln. was warmed slowly to r.t., then stirred for 3 h. The mixture was carefully poured into dilute ice-cold aq. NH_4Cl soln. and became very thick. More CH_2Cl_2 (100 ml) was added, the resulting soln. filtered through a medium glass frit, and the collected solid washed with CH_2Cl_2 (3 × 100 ml). The combined org. fractions were evaporated, and recrystallization from hexane yielded **55** (32.5 g, 95%). Colorless solid. M.p. 66°. IR (KBr): 3350 (O–H), 2150 (C≡C). ^{1}H-NMR (200 MHz): 1.10 (*s*, 42 H); 1.95 (*t*, *J* = 6.7, 2 H); 4.20 (*d*, *J* = 6.7, 4 H). ^{13}C-NMR (50.3 MHz): 11.3; 18.8; 63.7; 102.4; 108.7; 130.9. EI-MS (70 eV): 448 (5, M^+), 430 (2, $[M - H_2O]^+$), 387 (27, $[M - i\text{-}Pr - H_2O]^+$). Anal. calc. for $C_{26}H_{48}O_2Si_2$ (448.84): C 69.58, H 10.78; found: C 69.78, H 10.74.

2,3-Bis[(triisopropylsilyl)ethynyl]fumaraldehyde (**56**). To a soln. of **55** (32.5 g, 72 mmol) in CH_2Cl_2 (400 ml) was added PCC (50 g, 233 mmol), *Celite* (25 g), and molecular sieves (4 Å; 25 g). The soln. was stirred at r.t. for 6 h and filtered through a plug (SiO_2, CH_2Cl_2). Evaporation followed by recrystallization from hexane afforded **56** (27.4 g, 85%). Yellow solid. M.p. 45°. IR (KBr): 2170 (C≡C), 1700 (C=O). ^{1}H-NMR (200 MHz): 1.12 (*s*, 42 H); 10.35 (*s*, 2 H). ^{13}C-NMR (50.3 MHz): 11.3; 18.7; 96.7; 116.7; 138.7; 189.3. EI-MS (70 eV): 444 (32, M^+), 401 (100, $[M - i\text{-}Pr]^+$). HR-MS: 444.2869 (M^+, $C_{26}H_{44}O_2Si_2^+$, calc. 444.2880).

(E)*-1,1,6,6-Tetrabromo-3,4-bis[(triisopropylsilyl)ethynyl]hexa-1,3,5-triene* (**57**). A mixture of CBr_4 (78.8 g, 238 mmol), PPh_3 (62.2 g, 238 mmol), and Zn dust (15.4 g, 236 mmol) in dry CH_2Cl_2 (620 ml) was prepared at 0° and stirred at 0° for 2 h before warming to r.t. (*Caution:* exothermicity of ylide formation at high concentrations.) After 24 h stirring at r.t., the suspension was again cooled to 0° and **56** (21.1 g, 47.7 mmol) in CH_2Cl_2 (100 ml) added at once. The resulting soln. was warmed slowly to r.t. over 18 h and the resulting thick suspension filtered through SiO_2 and evaporated to yield a deep-yellow solid. The solid was dissolved in a minimum amount of CH_2Cl_2, then hexane was added to precipitate the remaining phosphine oxide which was removed by filtration. Recrystallization from MeOH/CH_2Cl_2 yielded **57** (34 g, 94%). Pale-yellow crystals. M.p. 85–87°. IR (KBr): 2150 (C≡C). ^{1}H-NMR (200 MHz): 1.12 (*s*, 42 H); 7.70 (*s*, 2 H). ^{13}C-NMR (50.3 MHz): 11.5; 18.9; 95.2; 100.8; 112.5; 129.1; 134.0. EI-MS (70 eV): 756 (M^+). Anal. calc. for $C_{28}H_{44}Br_4Si_2$ (756.45): C 44.46, H 5.86; found: C 44.48, H 5.79. X-Ray: *Fig. 6*.

(E)*-3,4-Diethynyl-1,6-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**47**). To a soln. of **57** (1.0 g, 1.3 mmol) in dry THF (400 ml) was added slowly a soln. of LDA in THF (14.9 ml, 7.8 mmol; prepared by the addition of 1.6M BuLi in hexane (4.9 ml) to a soln. of $(i\text{-}Pr)_2NH$ (0.8 g) in THF (10 ml) at 0°). The soln. turned bright green, then blue, and finally purple, indicating complete reaction of **57**. After 10 min, sat. aq. NH_4Cl soln. (5 ml) was added and the now pale yellow soln. diluted with hexane and extracted with H_2O (2 ×). The hexane layer was filtered through a pad of SiO_2 and concentrated to 5 ml from which crystals were obtained after standing at – 20° for 12 h: **47** (0.54 g, 95%). M.p. 76° (dec.). UV/VIS ($CHCl_3$): 264 (5100), 277 (4600), 328 (20400), 342 (26000). IR (KBr): 3280 (≡C–H), 2170, 2100 (C≡C). ^{1}H-NMR (200 MHz): 1.11 (*s*, 42 H); 3.48 (*s*, 2 H). ^{13}C-NMR (50 MHz): 11.5; 18.8; 80.6; 86.6; 102.8; 103.6; 119.1. EI-MS (70 eV): 436 (17, M^+), 393 (100, $[M - i\text{-}Pr]^+$). Anal. calc. for $C_{28}H_{44}Si_2$ (436.83): C 76.99, H 10.15; found: C 77.13, H 9.99. X-Ray: *Fig. 7*.

(E)*-1,6-Diiodo-3,4-bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne* (**58**). To the THF soln. of dilithiated **47** at – 78° prepared from **57** (1.0 g, 1.3 mmol) as described above, one crystal of I_2 was added and the soln. warmed slowly to r.t. After stirring for 4 h, the soln. had turned pale brown and was diluted with hexane, extracted with H_2O (2 ×), filtered through a pad of SiO_2 (hexane), and evaporated to yield crude **58** which was recrystallized from MeOH: 0.2 g, 23%. M.p. 88–90°. IR (KBr): 2180, 2150 (C≡C). ^{1}H-NMR (200 MHz): 1.09 (*s*, 42 H). ^{13}C-NMR (125.7 MHz): – 3.35; 11.2; 18.7; 90.9; 102.5; 103.0; 120.0. EI-MS (70 eV): 688 (75, M^+), 254 (100, I_2^+). Anal. calc. for $C_{28}H_{42}I_2Si_2$ (688.63): C 48.84, H 6.15; found: C 49.23, H 6.16.

(E)-5,6-Bis[(triisopropylsilyl)ethynyl]dec-5-ene-3,7-diyne-2,9-diol (**59**). To the THF soln. of dilithiated **47** at – 78° prepared from **57** (1.0 g, 1.3 mmol) as described above, acetaldehyde (0.5 ml, 10 mmol) was added. The soln. immediately turned pale-yellow. After 1 h, the soln. was diluted with hexane, extracted with H_2O (2 ×), filtered through a pad of SiO_2 (CH_2Cl_2), and evaporated. Recrystallization from hexane yielded **59** (0.32 g, 47%). M.p. 104–106° (dec.). IR (KBr): 3360 (O–H), 2180, 2150 ($C{\equiv}C$). ^{1}H-NMR (200 MHz): 1.10 (*s*, 42 H); 1.49 (*d*, $J = 6.5$, 6 H); 1.91 (*d*, $J = 6.0$, 2 H); 4.68 (*quint.*, $J \approx 6.0$, 2 H). ^{13}C-NMR (50.3 MHz): 11.4; 19.9; 24.0; 59.2; 81.9; 100.0; 102.8; 103.4; 117.8. EI-MS (70 eV): 524 (13, M^+), 506 (1, $[M - H_2O]^+$), 28 (100, CO^+). Anal. calc. for $C_{32}H_{52}O_2Si_2$ (524.94): C 73.22, H 9.98; found: C 73.82, H 9.80.

9,9′-{(E)-3,4-Bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne-1,6-diyl}bis[9H-fluoren-9-ol] (**60**). To the THF soln. of dilithiated **47** at – 78° prepared from **57** (1.0 g, 1.3 mmol) as described above, 9*H*-fluoren-9-one (0.5 g, 2.8 mmol) was added (→pale yellow). After 18 h, the soln. was diluted with hexane, extracted with H_2O (3 ×), filtered through a pad of SiO_2 (CH_2Cl_2), and evaporated. Recrystallization from hexane (3 ×) afforded pure **60** (0.82 g, 79%). M.p. 174–175°. IR (KBr): 3455 (O–H), 2222, 2155 ($C{\equiv}C$). ^{1}H-NMR (500 MHz): 0.97 (*s*, 42 H); 2.65 (*s*, 2 H); 7.33 (*td*, $J = 7.3, 1.2$, 4 H); 7.40 (*td*, $J = 7.3, 1.2$, 4 H); 7.62 (*d*, $J = 7.5$, 4 H); 7.70 (*d*, $J = 7.9$, 4 H). ^{13}C-NMR (125.7 MHz): 11.4; 18.5; 75.1; 80.7; 98.0; 102.9; 103.0; 117.0; 120.1; 124.4; 128.5; 129.7; 139.2; 146.5. EI-MS (70 eV): 796 (M^+), 778 ($[M - H_2O]^+$). Anal. calc. for $C_{54}H_{60}Si_2O_2$ (797.25): C 81.35, H 7.58; found: C 81.19, H 7.73.

Diisobutyl (E)-4,5-Bis[(triisopropylsilyl)ethynyl]oct-4-ene-2,6-diynedioate (**61**). To **47** (0.44 g, 1.0 mmol) in dry Et_2O (100 ml) at – 78° was added 1.6M BuLi in hexane (2 ml, 3.2 mmol; →light yellow-brown). After 10 min, isobutyl chloroformate (1.0 g, 7.3 mmol) was added and the mixture allowed to warm slowly to r.t. The soln. was diluted with hexane, extracted with H_2O, filtered through a pad of SiO_2 (CH_2Cl_2), and evaporated. Recrystallization from hexane (2 ×) gave white **61** (0.41 g, 65%). M.p. 81° (dec.). IR (KBr): 2222 ($C{\equiv}C$), 1705 (C=O). ^{1}H-NMR (500 MHz): 0.95 (*d*, $J = 6.8$, 12 H); 1.09 (*s*, 42 H); 1.97 (*sept.*, $J = 6.8$, 2 H); 3.97 (*d*, $J = 7$, 4 H). ^{13}C-NMR (125.7 MHz): 11.06; 18.51; 18.90; 27.55; 72.25; 81.04; 88.40; 100.6; 107.4; 111.8; 153.2. EI-MS (70 eV): 636 (< 1, M^+, $C_{38}H_{60}O_4Si_2^+$), 593 (38, $[M - \text{i-Pr}]^+$), 467 (100, $[M - (CH_3)_2CCH - 2\ \text{i-Pr} - CO]^+$). X-Ray: *Fig. 8*.

(E)-1,10-Diphenyl-5,6-bis[(triisopropylsilyl)ethynyl]dec-5-ene-1,3,7,9-tetrayne (**62**). To **47** (0.44 g, 1.0 mmol) in acetone, open to the air, was added $PhC{\equiv}CH$ (**9**; 0.5 g, 5 mmol), followed by CuCl (10 mg, 0.1 mmol) and TMEDA (0.05 ml, 0.3 mmol). Within 1 h, the soln. had turned bright yellow, and after 18 h, hexane was added. The soln. was extracted with H_2O (3 ×), filtered through a pad of SiO_2 (hexane), and evaporated to give crude product contaminated with diphenylbutadiyne. A 2nd filtration (SiO_2, hexane) afforded a bright yellow fraction which, after recrystallization, yielded **62** (0.45 g, 70%). Bright yellow fluorescent crystals. M.p. 142–143°. UV/VIS ($CHCl_3$): 256 (36700), 275 (28100), 290 (25300), 306 (20000), 325 (15600), 394 (34000), 422 (35500), 479 (1600). IR (KBr): 2220 ($C{\equiv}C$). ^{1}H-NMR (200 MHz): 1.16 (*s*, 42 H); 7.37 (*m*, 6 H); 7.50 (*m*, 4 H). ^{13}C-NMR (127.7 MHz): 11.2, 18.6; 74.2; 79.0; 84.6; 86.9; 101.8; 104.2; 119.8; 121.5; 128.5; 129.9; 132.5. LD-TOF-MS (negative-ion mode): 637 (M^-). Anal. calc. for $C_{44}H_{52}Si_2$ (637.07): C 82.96, H 8.22; found: C 82.94, H 8.15. X-Ray: *Fig. 9*.

Deprotection of **58**–**61**. To a soln. of *trans*-bis(triisopropylsilyl)-protected derivative (5 mmol) in THF (25 ml) was added H_2O (1 ml) and 1.0M Bu_4NF in THF (11 ml, 11 mmol). The mixture was stirred at 0° until TLC showed complete deprotection (after *ca.* 2 h), then diluted with hexane (100 ml), and extracted exhaustively with H_2O to remove the THF. Concentration gave rapid decomposition; however, oxidative acetylene coupling in polymerizations could be done with the deprotected compounds without isolation.

(Z)-1,2-Dichloro-4-(triisopropylsilyl)but-1-en-3-yne (**67**). To a soln. of $(\text{i-Pr})_3SiC{\equiv}CH$ (**8**; 10.0 g, 55 mmol) in dry Et_2O (200 ml) at – 78° was added 2.0M MeMgBr in Et_2O (30 ml, 60 mmol). The mixture was warmed to r.t., then refluxed for 1 h, cooled again to – 78° at which temp. $[PdCl_2(dppb)]$ (1.51 g, 2.75 mmol) and $Cl_2C{=}CHCl$ (21.7 g, 165 mmol) were added. After 2 h, the soln. was warmed to 0°, kept at this temp. for 10 h, then poured into sat. aq. NH_4Cl soln., extracted (H_2O), dried, and evaporated. The resulting yellow oil was filtered through a plug of SiO_2 (hexane, then CH_2Cl_2). Evaporation gave **67** (13.0 g, 85%). IR (neat): 2144 ($C{\equiv}C$). ^{1}H-NMR (200 MHz): 1.09 (*s*, 21 H); 6.66 (*s*, 1 H). ^{13}C-NMR (90.6 MHz): 11.2; 18.5; 96.5; 100.0; 117.1; 125.1. EI-MS (70 eV): 276/278 (10/7, M^+), 233/235 (100/65, $[M - \text{i-Pr}]^+$). HR-MS: 276.0887 (M^+, $C_{13}H_{22}Cl_2Si^+$, calc. 276.0868).

(E)-1-(Triethylsilyl)-4-[(triethylsilyl)ethynyl]-6-(triisopropylsilyl)hex-3-ene-1,5-diyne (**68**). To a degassed soln. of **67** (5 g, 18 mmol) in benzene (850 ml) was added sequentially $BuNH_2$ (10 g, 137 mmol), $[PdCl_2(PPh_3)_2]$ (0.8 g, 1 mmol), CuI (0.35 g, 2 mmol), and $Et_3SiC{\equiv}CH$ (**7**; 5.04 g, 36 mmol), and the mixture was stirred for 3 d. The residue obtained after evaporation was dissolved in hexane and filtered through a plug of SiO_2 (hexane). Evaporation gave crude product contaminated with 5% bis(triethylsilyl)butadiyne as an orange oil which was purified by FC (SiO_2, hexane): **68** (6.3 g, 72%). Yellow oil. IR (KBr): 2155 ($C{\equiv}C$). ^{1}H-NMR (200 MHz): 0.62 (*m*, 12 H); 0.95 (*m*, 18 H); 1.07 (*s*, 21 H); 6.13 (*s*, 1 H). ^{13}C-NMR (90.6 MHz): 4.24; 4.26; 7.36; 7.43; 11.2; 18.5; 94.7;

98.9; 102.0; 103.0; 104.5; 105.9; 116.0; 123.7. EI-MS (70 eV): 484 (71, M^+), 441 (41, $[M - \text{i-Pr}]^+$), 371 (100, $[M - \text{i-Pr} - C_3H_6 - C_2H_4]^+$). HR-MS: 484.3341 ($M^+$, $C_{29}H_{52}Si_3^+$, calc. 484.3377).

(Z)-2,3-Dichlorobut-2-ene-1,4-diol (**71**) [40]. To an ice-cold soln. of $LiAlH_4$ (10 g, 263 mmol) in dry Et_2O (1200 ml) was added slowly over 1 h mucochloric acid (**70**; 40 g, 237 mmol) in Et_2O (200 ml). The suspension was stirred for 5 h, then quenched by careful addition of H_2O (10 ml), followed by 2.0M aq. NaOH (20 ml) and H_2O (30 ml). The mixture was filtered, the collected aluminium salts were washed with Et_2O (500 ml) and the dried org. liquors evaporated. Recrystallization (CH_2Cl_2) yielded **71** (9.5 g, 29%). White needles. M.p. 89–90° ([40]: 88°).

(Z)-2,3-Bis[(triisopropylsilyl)ethynyl]but-2-ene-1,4-diol (**72**). To a degassed soln. of **71** (5.0 g, 32 mmol) was added sequentially $BuNH_2$ (12 g, 164 mmol), $[PdCl_2(PPh_3)_2]$ (0.5 g, 0.7 mmol), CuI (0.3 g, 1.6 mmol), and $(\text{i-Pr})_3SiC{\equiv}CH$ (**8**; 17 g, 96 mmol). The mixture was stirred at r.t. for 2 d and then filtered through a plug of SiO_2 (hexane then CH_2Cl_2). The solid obtained by evaporation of CH_2Cl_2 was recrystallized from hexane to yield **72** (9 g, 64%). Brown-yellow crystals. M.p. 53–54°. IR (KBr): 3420 (O–H), 2133 (C≡C). ^{1}H-NMR (500 MHz): 1.02 (*m*, 42 H); 3.39 (*s*, 2 H); 4.28 (*s*, 4 H). ^{13}C-NMR (125.7 MHz): 11.2; 18.6; 62.2; 99.9; 107.4; 131.2. EI-MS (70 eV): 448 (M^+), 387 ($[M - \text{i-Pr} - H_2O]^+$). Anal. calc. for $C_{26}H_{48}O_2Si_2$ (448.84): C 69.58, H 10.78; found: C 69.64, H 10.72.

3,4-Bis[(triisopropylsilyl)ethynyl]furan-2(5H)-one (**73**). To a soln. of **72** (1 g, 2.2 mmol) in CH_2Cl_2 was added PCC (1.5 g, 7 mmol), *Celite* (1.5 g), and molecular sieves (4 Å; 1.5 g), and the mixture was stirred for 3 h. Filtration through a plug of SiO_2 (CH_2Cl_2) followed by evaporation yielded **73** (0.89 g, 91%). White solid. M.p. 49–50°. IR (KBr): 2155 (C≡C), 1777 (C=O). ^{1}H-NMR (200 MHz): 1.10 (*s*, 42 H); 4.80 (*s*, 2 H). ^{13}C-NMR (125.6 MHz): 11.00; 11.08; 18.50; 18.55; 71.4; 95.2; 96.1; 105.5; 114.3; 119.5; 145.0; 170.1. EI-MS (70 eV): 444 (2, M^+), 401 (100, $[M - \text{i-Pr}]^+$). Anal. calc. for $C_{26}H_{44}O_2Si_2$ (444.81): C 70.21, H 9.97; found: C 70.62, H 9.52.

5,6-Dichloro-4,7-dihydro-2-methoxy-1,3-dioxepine (**76**). A soln. of **70** (9 g, 53 mmol), $(MeO)_3CH$ (12 g, 114 mmol), and camphorsulfonic acid (45 mg, 0.2 mmol) in CH_2Cl_2 (50 ml) was stirred for 2 d at r.t., then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Recrystallization from pentane yielded **76** (7 g, 66%). Hygroscopic volatile solid. M.p. 52–53°. ^{1}H-NMR (200 MHz): 3.35 (*s*, 3 H); 4.22 (*d*, J = 14, 2 H); 4.56 (*d*, J = 14, 2 H); 5.34 (*s*, 1 H). ^{13}C-NMR (50.3 MHz): 54.1; 64.9; 112.9; 128.2. EI-MS (70 eV): 198 (M^+). Anal. calc. for $C_6H_8Cl_2O_3 \cdot 0.5\ CH_2Cl_2$ (241.50): C 32.33, H 3.76; found: C 31.25, H 3.74.

4,7-Dihydro-2-methoxy-5,6-[(trimethylsilyl)ethynyl]-1,3-dioxepine (**77**). To a degassed soln. of **76** (5.2 g, 26.1 mmol), $BuNH_2$ (10 g, 137 mmol), $[PdCl_2(PPh_3)_2]$ (0.92 g, 1.3 mmol), and CuI (0.5 g, 2 mmol) in benzene (150 ml) was added $Me_3SiC{\equiv}CH$ (**6**; 6.4 g, 65 mmol), and the mixture was stirred under TLC control (SiO_2, hexane/Et_2O 10:1) for 15 h. Filtration through a plug of SiO_2 (CH_2Cl_2) and evaporation yielded **77** (7.74 g, 92%) as a brown oil which, for anal. purposes, was further purified by chromatography (SiO_2, hexane/CH_2Cl_2 1:1). Yellow oil. IR (neat): 2144 (C≡C). ^{1}H-NMR (500 MHz): 0.20 (*s*, 18 H); 3.37 (*s*, 3 H); 4.16 (*d*, J = 14.1, 2 H); 4.52 (*d*, J = 14.1, 2 H); 5.31 (*s*, 1 H). ^{13}C-NMR (125.7 MHz): – 0.2; 53.6; 63.0; 101.7; 102.5; 113.1; 128.9. EI-MS (70 eV): 322 (4, M^+), 263 (85, $[M - MeOCO]^+$), 73 (100, Me_3Si^+). HR-MS: 322.1427 (M^+, $C_{16}H_{26}O_3Si_2^+$, calc. 322.1420).

4,7-Dihydro-2-methoxy-5,6-bis[(triisopropylsilyl)ethynyl]-1,3-dioxepine (**78**). To a degassed soln. of **76** (5.4 g, 27 mmol), $BuNH_2$ (10 g, 137 mmol), $[PdCl_2(PPh_3)_2]$ (1 g, 1.4 mmol), and CuI (0.5 g, 2 mmol) in benzene (150 ml) was added $(\text{i-Pr})_3SiC{\equiv}CH$ (**8**; 12.35 g, 68 mmol), and the mixture was stirred for 24 h. Filtration through a plug of SiO_2 (CH_2Cl_2) and evaporation yielded a dark oil which was purified by FC (SiO_2, hexane until **8** was completely eluted, then hexanes/CH_2Cl_2 1:1): **78** (12 g, 91%). Yellow oil. IR (neat): 2133 (C≡C). ^{1}H-NMR (200 MHz): 1.07 (*s*, 42 H); 3.37 (*s*, 3 H); 4.22 (*d*, J = 15, 2 H); 4.59 (*d*, J = 15, 2 H); 5.32 (*s*, 1 H). ^{13}C-NMR (50.3 MHz): 11.3; 18.8; 53.8; 64.5; 100.0; 104.1; 113.5; 128.2. EI-MS (70 eV): 409 (M^+). HR-MS: 490.3274 (M^+, $C_{28}H_{50}O_3Si_2^+$, calc. 490.3298).

(Z)-3-(Methoxymethoxymethyl)-5-(trimethylsilyl)-2-[(trimethylsilyl)ethynyl]pent-2-en-4-yn-1-ol (**79**). At – 78°, 1.0M DIBAL-H in hexanes (72 ml, 72 mmol) was added rapidly to **77** (7.74 g, 24 mmol) in CH_2Cl_2 (50 ml). After 20 min, the soln. was warmed rapidly to 0° and stirred at 0° for 20 min. The soln. was quenched by careful addition to H_2O (50 ml). CH_2Cl_2 (50 ml) was added and the mixture filtered, after which the org. phase was evaporated to give 96% pure **79** (4.61 g, 60%) as a pale-yellow oil which was used without further purification in the subsequent reaction. Anal. pure **79** was obtained as a colorless oil by FC (SiO_2, gradient from pure hexane to pure Et_2O). IR (neat): 3438 (O–H), 2249, 2149 (C≡C). ^{1}H-NMR (500 MHz): 0.195 (*s*, 9 H); 0.196 (*s*, 9 H); 2.59 (*s*, 1 H); 3.38 (*s*, 3 H); 4.21 (*s*, 2 H); 4.23 (*d*, J = 5, 2 H); 4.64 (*s*, 2 H). ^{13}C-NMR (125.7 MHz): – 0.11, – 0.09, 55.5; 60.9; 64.7; 95.3; 102.0; 103.37; 103.41; 104.1; 127.5; 133.0. EI-MS (20 eV): 324 (1, M^+), 262 (66, $[M - MeOCH_2OH]^+$), 73 (100, Me_3Si^+). HR-MS: 324.1569 (M^+, $C_{16}H_{28}O_3Si_2^+$, calc. 324.1577).

(Z)-3-(Methoxymethoxymethyl)-5-(triisopropylsilyl)-2-[(triisopropylsilyl)ethynyl]pent-2-en-4-yn-1-ol (**80**). At – 78°, 1.0M DIBAL-H in hexanes (45 ml, 45 mmol) was added rapidly to **78** (7.35 g, 15 mmol) in CH_2Cl_2 (150 ml). After 15 min, the mixture was warmed rapidly to 0° and stirred at 0° for 15 min. The mixture was worked up as described for **79** to give 96% pure **80** (7.0 g, 94%) as a pale-yellow oil which, for anal. purpose, was further purified

by FC (SiO_2, CH_2Cl_2). Colorless oil. IR (neat): 3440 (O–H), 2146, 2127 (C≡C). ^{1}H-NMR (200 MHz): 1.07 (*s*, 42 H); 3.38 (*s*, 3 H); 4.24 (*s*, 2 H); 4.240 (*d*, $J = 5$, 2 H); 4.66 (*s*, 2 H). ^{13}C-NMR (50.3 MHz): 11.4; 18.9; 55.7; 62.0; 66.2; 95.9; 99.5; 101.1; 105.6; 106.6; 126.8; 132.5. EI-MS (70 eV): 492 (1, M^+), 430 (68, $[M - MeOCH_2OH]^+$), 115 (100, $(i\text{-}Pr)_2Si^+$). HR-MS: 492.3476 (M^+, $C_{28}H_{52}O_3Si_2^+$, calc. 492.3455).

(Z)-1,1-Dibromo-4-(methoxymethoxymethyl)-6-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]hexa-1,3-dien-5-yne (**81**). Alcohol **79** (4.91 g, 15 mmol) was added to a soln. of PDC in CH_2Cl_2 (*ca.* 90 mmol; prepared by stirring CrO_3 (9 g) and pyridine (14.3 g) in CH_2Cl_2 (225 ml) for 20 min). After 3 h, the dark mixture was filtered through a plug of SiO_2 (CH_2Cl_2) to yield a bright yellow soln. Extraction with 20% aq. $CuSO_4$ soln. and concentration to 50 ml yielded a soln. of the unstable aldehyde which was poured directly into a 0°-cold soln. of dibromoolefination reagent (prepared by stirring CBr_4 (15 g, 45 mmol), PPh_3 (12 g, 45 mmol), and Zn powder (2.9 g, 45 mmol) for 28 h in CH_2Cl_2 (800 ml)). After 4 h, the mixture was filtered through a plug of SiO_2 (CH_2Cl_2). Evaporation yielded **81** (6.45 g, 90%). Unstable orange oil. IR (KBr): 2136 (C≡C). ^{1}H-NMR (200 MHz): 0.176 (*s*, 9 H); 0.187 (*s*, 9 H); 3.36 (*s*, 3 H); 4.10 (*s*, 2 H); 4.61 (*s*, 2 H); 7.13 (*s*, 1 H). ^{13}C-NMR (50 MHz): –0.4; –0.3; 55.3; 64.9; 94.8; 95.4; 99.9; 103.6; 103.7; 105.1; 126.5; 129.8; 131.1. EI-MS (70 eV): 476/478/480 (5/11/7, M^+), 431/433/435 (5/11/7, $[M - MeOCH_2]^+$), 73 (Me_3Si^+). HR-MS: 475.9822 (M^+, $C_{17}H_{26}Br_2O_2Si_2^+$, calc. 475.9839).

(Z)-1,1-Dibromo-4-(methoxymethoxymethyl)-6-(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]hexa-1,3-dien-5-yne (**82**). As described for **81**, with **80** (6.93 g, 14.1 mmol), PDC (*ca.* 90 mmol), and CH_2Cl_2 (225 ml; 1 h). The soln. of aldehyde (50 ml) was added to a soln. of dibromoolefination reagent (45 mmol) in CH_2Cl_2 (800 ml). Workup yielded **82** (7 g, 77%). Orange oil. IR (neat): 2131 (C≡C). ^{1}H-NMR (360 MHz): 1.08 (*s*, 21 H); 1.09 (*s*, 21 H); 3.36 (*s*, 3 H); 4.12 (*s*, 2 H); 4.63 (*s*, 2 H); 7.15 (*s*, 1 H). ^{13}C-NMR (90.6 MHz): 11.17; 11.21; 18.63; 18.68; 55.4; 66.4; 94.7; 95.7; 100.9; 101.9; 102.4; 105.7; 125.9; 129.1; 132.3. EI-MS (70 eV): 644/646/648 (3/6/4, M^+), 449/451 (5/5, $[M - Br - i\text{-}Pr - C_3H_6 - MeO]^+$), 115 (100, $(i\text{-}Pr)_2SiH^+$). HR-MS: 644.1661 (M^+, $C_{29}H_{50}Br_2Si_2O_2^+$, calc. 644.1717).

(Z)-5,5-Dibromo-2,3-bis[(trimethylsilyl)ethynyl]penta-2,4-dien-1-ol (**83**). To a soln. of **81** (6.45 g, 13.5 mmol) in dry CH_2Cl_2 (100 ml) at 0° was added *B*-bromocatecholborane (2.7 g, 13.6 mmol). After 2 h, deprotection was completed (TLC (SiO_2, CH_2Cl_2)), and sat. aq. $NaHCO_3$ soln. was carefully added. The mixture was stirred rapidly for 30 min, extracted with H_2O (3 ×), filtered through a pad of SiO_2 (CH_2Cl_2), and evaporated. Chromatography (SiO_2, CH_2Cl_2) gave **83** (3.5 g, 60%). Unstable yellow oil. IR (neat): 3408 (O–H), 2134 (C≡C). ^{1}H-NMR (500 MHz): 0.21 (*s*, 9 H); 0.23 (*s*, 9 H); 1.92 (*t*, $J = 6.7$, 1 H); 4.18 (*d*, $J = 6.7$, 2 H); 7.08 (*s*, 1 H). ^{13}C-NMR (50 MHz): –0.02; 0.10; 61.6; 95.4; 100.6; 103.4; 104.0; 106.6; 125.5; 131.6; 133.3. EI-MS (70 eV): 432/434/436 (2/4/2, M^+), 336/338 (5/5, $[M - Br - OH]^+$), 73 (100, Me_3Si^+). HR-MS: 431.9568 (M^+, $C_{15}H_{22}Br_2OSi_2^+$, calc. 431.9577).

(Z)-5,5-Dibromo-2,3-bis[(triisopropylsilyl)ethynyl]penta-2,4-dien-1-ol (**84**). To a soln. of **82** (6.5 g, 10 mmol) in dry CH_2Cl_2 (100 ml) was added 0.2M *B*-bromocatecholborane (1.98 g, 10 mmol) in CH_2Cl_2 (50 ml). After 1 h, H_2O was added and the soln. stirred for 25 min. The org. layer was washed with sat. aq. $NaHCO_3$ soln., H_2O, and sat. aq. NaCl soln., dried, and evaporated: **84** (4.2 g, 70%). Yellow oil. IR (neat): 3437 (O–H), 2142 (C≡C). ^{1}H-NMR (360 MHz): 1.081 (*s*, 21 H); 1.089 (*s*, 21 H); 2.01 (*s*, 1 H); 4.16 (*s*, 2 H); 7.06 (*s*, 1 H). ^{13}C-NMR (90.6 MHz): 11.11; 11.21; 18.50; 18.65; 62.1; 95.0; 100.5; 101.9; 103.6; 104.3; 124.0; 131.7; 132.1. EI-MS (70 eV): 600/602/604 (M^+), 478/480 ($[M - Br - i\text{-}Pr]^+$), 401 ($[M - i\text{-}Pr - 2\,Br]^+$). HR-MS: 600.1467 ($M^+$, $C_{27}H_{46}Si_2OBr_2^+$, calc. 600.1454).

(Z)-1,1,6,6-Tetrabromo-3,4-bis[(trimethylsilyl)ethynyl]hexa-1,3,5-triene (**85**). Alcohol **83** (3.5 g, 8 mmol) was added to a soln. of PDC (*ca.* 60 mmol; prepared by stirring CrO_3 (6 g) and pyridine (9 g) in CH_2Cl_2 (150 ml) for 15 min). The dark mixture was stirred for 1 h. Filtration through a plug of SiO_2 (CH_2Cl_2) and evaporation to 50 ml yielded a bright yellow soln. which was poured into a 0°-cold soln. of dibromoolefination reagent (prepared by stirring CBr_4 (8 g, 24 mmol), PPh_3 (6.3 g, 24 mmol), and Zn (1.6 g, 24 mmol) in CH_2Cl_2 (700 ml) for 25 h). After 1 h, filtration through a plug of SiO_2 (CH_2Cl_2) yielded **83** contaminated with *ca.* 10% (*E*)-isomer. Chromatography (SiO_2, hexanes) gave pure **85** (2.3 g, 49%). Colorless solid. M.p. 72°. IR (KBr): 2133 (C≡C). ^{1}H-NMR (500 Hz): 0.24 (*s*, 18 H); 6.98 (*s*, 2 H). ^{13}C-NMR (125.7 MHz): –0.3; 96.1; 100.3; 107.6; 127.3; 131.7. EI-MS (70 eV): 588 (10, M^+), 509/507 (8/8, $[M - Br]^+$), 73 (100, Me_3Si^+). Anal. calc. for $C_{16}H_{20}Br_4Si_2$ (588.12): C 32.68, H 3.43; found: C 32.96, H 3.16.

(Z)-1,1,6,6-Tetrabromo-3,4-bis[(triisopropylsilyl)ethynyl]hexa-1,3,5-triene (**75**). Alcohol **84** (2.8 g, 4.7 mmol) was added to a soln. of PDC (*ca.* 30 mmol; prepared by stirring CrO_3 (3 g) and pyridine (4.8 g) in CH_2Cl_2 (100 ml) for 15 min), and the mixture was stirred for 1 h. Filtration through a plug of SiO_2 (CH_2Cl_2) and evaporation to 50 ml yielded a bright-yellow soln. which was poured into a 0°-cold soln. of dibromoolefination reagent (prepared by stirring CBr_4 (4.6 g, 14 mmol), PPh_3 (3.7 g, 14 mmol), and Zn (1 g, 15 mmol) in CH_2Cl_2 (600 ml) for 25 h). After stirring for 1 h, the soln. was filtered through a plug of SiO_2 (CH_2Cl_2) to yield **75** contaminated with *ca.* 10% of (*E*)-isomer. The isomers were separated by chromatography (SiO_2, hexanes) yielding **75** (1.71 g,

49%) as an oil which is extremely sensitive towards photochemical or acid-catalyzed isomerization and is best stored in hexanes over $NaHCO_3$ in the dark at – 20°. IR (neat): 2133 (C≡C). ^{1}H-NMR (360 MHz): 1.12 (*s*, 42 H); 6.96 (*s*, 2 H). ^{13}C-NMR (90.6 MHz): 11.3; 18.7; 95.0; 100.5; 112.3; 128.7; 133.6. EI-MS (20 eV): 756 (M^+), 589/591 ([M – Br – 2 i-Pr]$^+$). HR-MS: 751.9724 (M^+, $C_{28}H_{44}Br_4Si_2^+$, calc. 751.9717).

(Z)-3,4-Diethynyl-1,6-bis(trimethylsilyl)hex-3-ene-1,5-diyne (**63**). To a soln. of **85** (0.588 g, 1.0 mmol) in dry THF (100 ml) at – 78° was added freshly prepared 1.0M LDA in THF (7 ml, 7 mmol). The mixture turned deep purple when the formation of dilithiated **63** was completed. After 15 min, sat. aq. NH_4Cl soln. was added (which immediately froze). The mixture was warmed rapidly to r.t., the brown mixture poured into hexane (100 ml), and the org. layer extracted with 0.1M aq. HCl soln., H_2O, and sat. aq. NaCl soln. Evaporation at 0° (due to product volatility and instability) gave **63** (0.24 g, 90%), which decomposed rapidly even during weighing. IR (neat): 3311 (≡C–H), 2155, 2100 (C≡C). ^{1}H-NMR (200 MHz): 0.24 (*s*, 18 H); 3.55 (*s*, 2 H). ^{13}C-NMR (90.6 MHz): – 0.57; 79.6; 86.4; 100.1; 106.0; 118.3.

(Z)-3,4-Diethynyl-1,6-bis(triisopropylsilyl)hex-3-ene-1,5-diyne (**64**). As described for **63**, with **75** (1.71 g, 2.26 mmol), THF (220 ml), and 1.0M LDA in THF (15.8 ml, 15.8 mmol). Workup with pentane (100 ml) instead of hexane. The pentane extract was filtered through a plug of SiO_2 (hexanes) before evaporation: **64** (0.89 g, 90%) as an unstable yellow oil which turned orange as decomposition occurred. IR (neat): 3305 (≡C–H), 2144, 2095 (C≡C). ^{1}H-NMR (200 MHz): 1.08 (*s*, 42 H); 3.51 (*s*, 2 H). ^{13}C-NMR (90.6 MHz): 11.2; 18.6; 80.6; 85.8; 102.6; 103.8; 117.7. EI-MS (70 eV): 436 (1, M^+), 393 (2, [M – i-Pr]$^+$), 309 (100, [M – i-Pr – 2 C_3H_6]$^+$). HR-MS: 436.3026 (M^+, $C_{28}H_{44}Si_2^+$, calc. 436.2981).

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