1,3-Diethynylallenes: Carbon-Rich Modules for Three-Dimensional Acetylenic Scaffolding

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

Regioselective Pd^0-catalyzed cross-coupling of substrates, which bear bispropargylic leaving groups with silyl-protected alkynes, has provided access to a variety of 1,3-diethynylallenes, a new family of modules for three-dimensional acetylenic scaffolding. In enantiomerically pure form, these C-rich building blocks could provide access – by oxidative oligomerization – to a fascinating new class of helical oligomers and polymers with all-carbon backbones (*Fig. 2*). In the first of two routes, a bispropargylic epoxide underwent ring opening during S_N2'-type cross-coupling, and the resulting alkoxide was silyl-protected, providing 1,3-diethynylallenes (±)-**8**, (±)-**12** (*Scheme 3*), and (±)-**15** (*Scheme 5*). A more general approach involved bispropargylic carbonates or esters as substrates (*Scheme 6–8*), and this route was applied to the preparation of a series of 1,3-diethynylallenes to investigate how their overall stability against undesirable [2 + 2] cycloaddition is affected by the nature of the substituents at the allene moiety. The investigation showed that the 1,3-diethynylallene chromophore is stable against [2 + 2] cycloaddition only when protected by steric bulk and when additional π-electron delocalization is avoided. The regioselectivity of the cross-coupling to the bispropargylic substrates is entirely controlled by steric factors: attack occurs at the alkyne moiety bearing the smaller substituent (*Schemes 9* and *10*). Oxidative *Hay* coupling of the terminally mono-deprotected 1,3-diethynylallene (±)-**49** afforded the first dimer **50**, probably as a mixture of two diastereoisomers (*Scheme 12*). Attempts to prepare a silyl-protected tetraethynylallene by the new methodology failed (*Scheme 13*). Control experiments (*Schemes 14–16*) showed that the Pd^0-catalyzed cross-coupling to butadiyne moieties in the synthesis of this still-elusive chromophore requires forcing conditions under which rapid [2 + 2] cycloaddition of the initial product cannot be avoided.

1. Introduction. – Oxidative coupling of small acetylenic modules has facilitated the assembly of well-defined molecular architecture extending into one, two, and three dimensions [1–3]. For example, (*E*)-diethynylethenes (**1**, DEEs, (*E*)-hex-3-ene-1,5-diynes) and tetraethynylethenes (**2**, TEEs, 3,4-diethynylhex-3-ene-1,5-diynes) (*Fig. 1*) have provided monodisperse rod-like poly(triacetylene) oligomers with lengths of up to 18 nm, which have allowed insight into the chain-length dependency of extended linear π-electron conjugation and hold promise as potential molecular wires [4]. Similarly, linear oligomers made from derivatives of 1,4-diethynyl- (**3**) and 1,1,4,4-tetraethynylbutatriene (**4**) would also afford flat and rod-like structures. Acetylenic scaffolding starting from (±)-1,3-diethynylallene ((±)-**5**; (±)-hepta-3,4-diene-1,6-diyne) and 1,1,3,3-tetraethynylallene (**6**; *Fig. 1*), on the other hand, would provide access to three-dimensional structures due to the inherent twist of the allene moiety. Whereas silylated derivatives of peralkynylated butatriene **4** have been reported [5], the ethynylated allenes (±)-**5** and **6** have remained elusive, despite intensive efforts aimed at their preparation [6]. During an attempted preparation of tetraethynylmethane, evidence for the formation of 1,1,3-triethynylallene in a mixture of products was obtained [7]; also, mono-alkynylated allenes are well-known [8]. The major

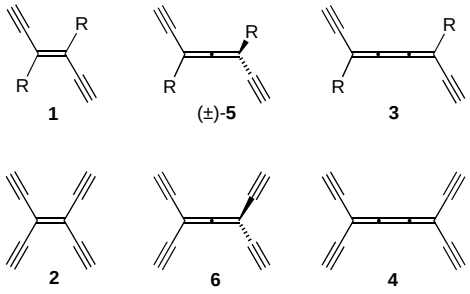


Fig. 1. *Carbon-rich modules for acetylenic scaffolding*

problems encountered in previous attempts to synthesize the novel C-rich building blocks (±)-**5** and **6** were their high tendency for rearrangement and facile [2 + 2] cycloaddition, which occurred readily even at room temperature [6].

Here, we describe the synthesis of the first racemic 1,3-diethynylallenes, derivatives of the parent compound (±)-**5** (for a preliminary communication of parts of this work, see [9]). We show that appropriate derivatives of (±)-**5** possess sufficient stability for terminal alkyne deprotection and subsequent oxidative coupling, generating the first oligomeric derivatives. Due to the inherent 90° twist of the allene moiety, oxidative coupling of these compounds in enantiomerically pure form promises to provide access to a fascinating new class of three-dimensional helical oligomers and polymers. A model of the helical structure of a dodecamer with (*S*)-1,3-diethynylallene repeating units was generated by semi-empirical calculations (AM1, Austin model 1) [10]. As shown in *Fig. 2*, substituents on the allene backbone (H-atoms in the model) are all oriented toward the outside of the (*P*)-helix. This indicates possibilities such as helix stabilization by attachment of substituents undergoing H-bonding or aromatic interactions. Nonracemic helical polymers are attracting increasing interest for potential applications ranging from materials exhibiting circularly polarized electroluminescence [11] to dopants for cholesteric liquid-crystalline phases [12]. Many approaches to such advanced materials have relied upon side-chain chirality to induce the desired helicity in a conformationally labile polymer backbone [13]. The incorporation of rigid chiral units such as the 1,3-diethynylallenes directly into the main chain offers the possibility for generating more-defined structures with a stabilized helical conformation (for some recent examples, see [14]).

2. Results and Discussion. – 2.1. *Synthesis of 1,3-Dialkynylallenes.* 2.1.1. *Pd Catalysis in the Formation of Allene–Acetylene C(sp²)–C(sp) Bonds.* Pd^0-catalyzed cross-couplings of alkynes with suitably functionalized $C(sp^2)$-centers have been well-developed, and several particularly versatile protocols have seen widespread use [15]. Especially convenient are the *Sonogashira* conditions, under which the acetylene partner is a Cu^I species generated *in situ* from CuI and an amine base [16].

Most transition-metal-catalyzed cross-couplings proceed through initial oxidative addition of, *e.g.*, the vinyl or aryl halide to generate the intermediate Pd^{II} species (*Scheme 1*). For the coupling of allenyl (as opposed to vinyl) moieties, a variant protocol involving S_N2'-type displacement of a propargylic leaving group can be

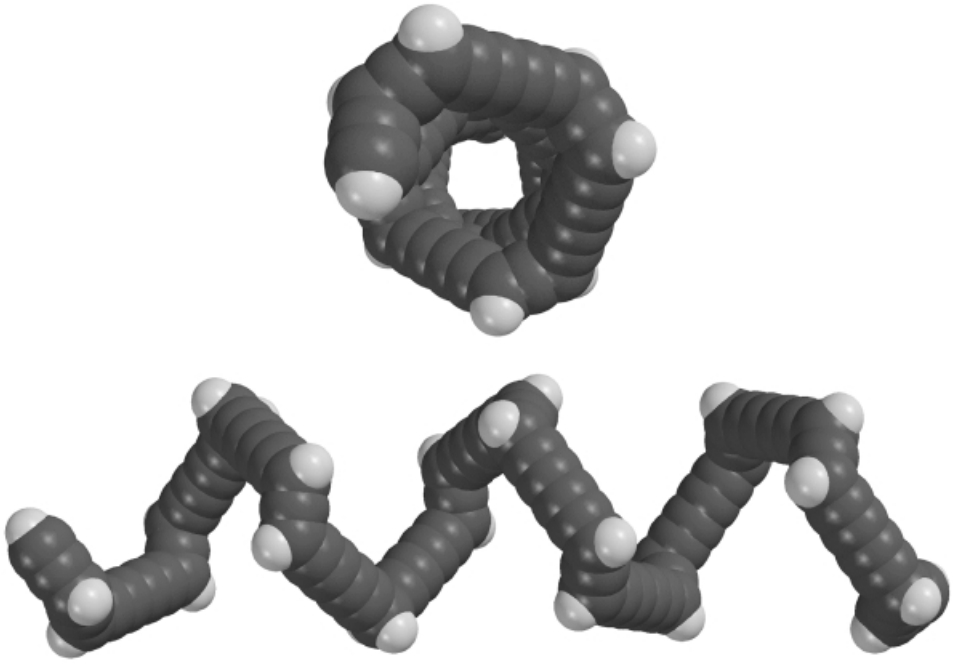


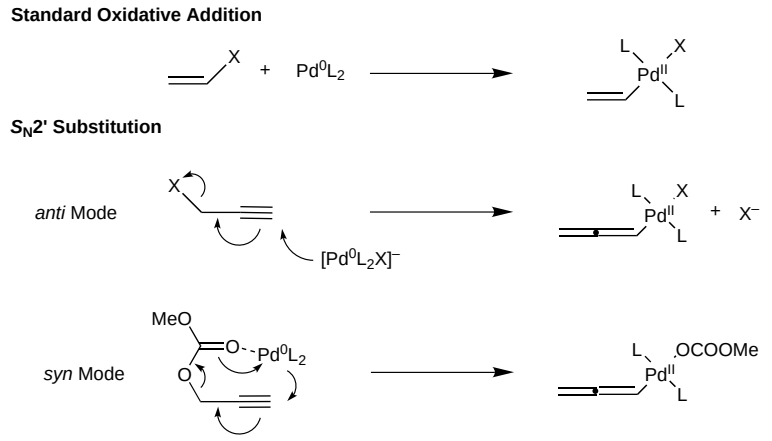
Fig. 2. *Views of the computer-generated* (AM1) *(*P*)-configured helical structure for a dodecamer obtained by oxidative coupling of (*S*)-1,3-diethynylallene*

employed [17]. This method has proven valuable in the preparation of alkynylallenes from substrates bearing propargylic leaving groups such as halides, epoxides, acetates, and carbonates [18–21]. Whether Pd^0 attack occurs *syn* or *anti* to the leaving group (*Scheme 1*) is relevant when considering the transfer of stereochemical information from the C-atom bearing the leaving group to the newly formed allene. Either mode might occur through the more nucleophilic anionic Pd^0 complex as proposed by *Armatore* and *Jutand* (shown for the *anti* mode) [22], while the *syn* mode would involve prior precoordination of the metal to the acyl leaving group.

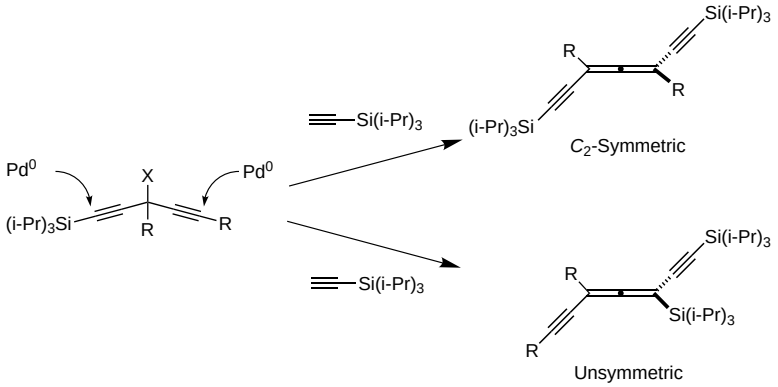
Given an appropriate regiochemical bias, application of these conditions to bispropargylic precursors should yield the desired C_2-symmetric 1,3-diethynylallenes (*Scheme 2*).

2.1.2. *1,3-Diethynylallenes by the Epoxide Route.* In a first approach, we targeted the bispropargylic epoxide (±)-**7** (*Scheme 3*), which would undergo ring opening, concomitant with the attack of the Pd^0 species, generating an allenylpalladium(II) intermediate. In these experiments, the zinc acetylide $(i\text{-}Pr)_3Si-C\equiv C-ZnCl$ was used as the alkyne partner, thus generating an intermediate zinc alkoxide after coupling, which could be silylated directly with $(t\text{-}Bu)Me_2SiOTf$ ($Tf = SO_2CF_3$) to give the desired C_2-symmetrical allene [23]. In a higher-yielding protocol, the standard *Sonogashira* conditions are employed, which formally generate the more-active Cu^I acetylide *in situ*, allowing the coupling to proceed at room temperature and with short reaction times. Under these more weakly basic conditions, the epoxide opening

Scheme 1. *Pd⁰-Catalyzed Cross-Coupling Modes of Vinyl and Allenyl Substrates*



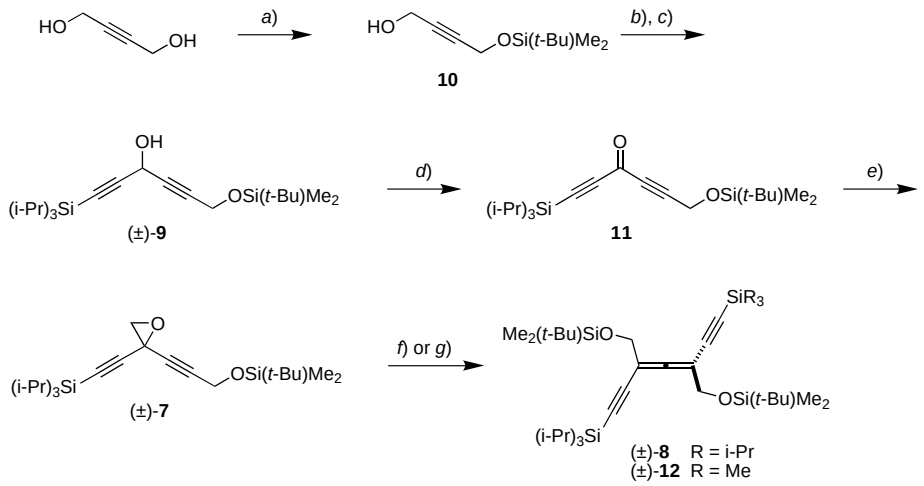
Scheme 2. *Regioselectivity in the Cross-Coupling of Bispropargylic Substrates*



generates the alcohol (rather than the zinc alkoxide), so the addition of imidazole is necessary to efficiently protect the newly created hydroxymethyl side chain as the (*t*-Bu)Me_2Si ether (*Scheme 3*). Just 2 mol-% of [$Pd(PPh_3)_4$] as catalyst were sufficient to produce 1,3-diethynylallene (±)-**8** in 52% yield after 6 h at room temperature. In later couplings of similar substrates, the use of higher catalyst loads (typically 5 mol-%) resulted in significantly shorter reaction times and generally higher yields, so this result should be considered nonoptimized.

A first synthesis of bispropargylic epoxide (±)-**7** started with the formation of bispropargylic alcohol (±)-**9**, which was obtained by two different routes. In one approach, (*t*-Bu)$Me_2SiOCH_2-C{\equiv}CLi$ (prepared from the corresponding alkyne [24] with BuLi in THF at $-78°$) was added to $(i\text{-Pr})_3Si-C{\equiv}C-CHO$ [6b][25] in THF to provide (±)-**9** in 45% yield. Transmetallation of the lithiated alkyne with $MgBr_2 \cdot OEt_2$ did not enhance the yield of (±)-**9**. Alternatively, commercially available but-2-yne-1,4-diol was monoprotected with (*t*-Bu)Me_2SiCl to give **10** [26]. Oxidation with MnO_2

Scheme 3. *Synthesis of 1,3-Diethynylallenes* (±)-**8** *and* (±)-**12**



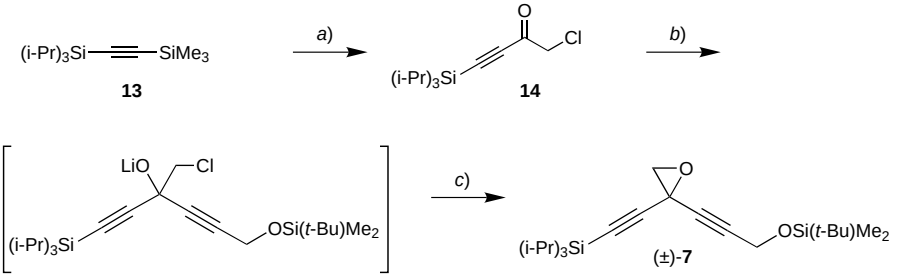
a) (*t*-Bu)Me_2SiCl, NaH, THF, r.t.; 65%. *b*) MnO_2, Et_2O, r.t. *c*) (i-Pr)$_3$Si−C≡CLi, THF, −78° → r.t.; 34% (from **10**). *d*) MnO_2, Et_2O, r.t.; 77%. *e*) MeLi · LiBr, CH_2I_2, THF, −78° → r.t.; 79%. *f*) (i-Pr)$_3$Si−C≡CH, (i-Pr)$_2$NH, [Pd(PPh_3)$_4$], CuI, CH_2Cl_2, r.t., then (*t*-Bu)Me_2SiCl, 1*H*-imidazole, r.t.; 52%. *g*) Me_3Si−C≡CH, (i-Pr)$_2$NH, [Pd(PPh_3)$_4$], CuI, $(CH_2Cl)_2$, r.t., then (*t*-Bu)Me_2SiCl, 1*H*-imidazole, r.t.; 53%.

provided the corresponding propargylic aldehyde to which (i-Pr)$_3$Si−C≡CLi was added to furnish (±)-**9**. Oxidation of (±)-**9** afforded ketone **11**, which was transformed into epoxide (±)-**7** with CH_2I_2/MeLi · LiBr [27]. The C_2-symmetric 1,3-diethynylallene (±)-**8** was subsequently obtained in 52% yield as described above, and its structure was established by X-ray crystallography [9]. Alternatively, coupling of (±)-**7** with Me_3Si−C≡CH afforded the differentially protected derivative (±)-**12** in a similar yield.

In view of the rather modest yields obtained in the preparation of epoxide (±)-**7**, a more direct and higher-yielding approach to this key intermediate was developed (*Scheme 4*). *Lewis* acid-catalyzed acylation of differentially protected acetylene **13** (prepared in 90% yield from (i-Pr)$_3$Si−C≡CH and Me_3SiCl) with $ClCH_2COCl$ gave chloro ketone **14** [28] in nearly quantitative yield, without need for chromatographic purification. Addition of (*t*-Bu)Me_2SiOCH_2−C≡CLi gave the intermediate alkoxide, and epoxide-ring closure was effected by addition of DMF to promote the nucleophilic substitution. Addition of *t*-BuOK (0.5 equiv.) served to compensate for adventitious H_2O in the DMF and to promote substitution by switching from Li^+ to the less coordinating K^+ ion as the counterion. Conversion to epoxide (±)-**7** was sufficiently clean that only quick filtration through SiO_2 was required to give material of reasonable analytical purity.

Subsequently, we became interested in preparing the C_2-symmetric bis-Me_3Si-protected allene (±)-**15**. We hoped to smoothly remove the more-labile Me_3Si protecting groups in (±)-**15** (as compared to the (i-Pr)$_3$Si groups in (±)-**8**) without disturbing the (*t*-Bu)Me_2Si ether residues and thus allow the preparation of oligomeric materials under the *Glaser-Hay* coupling conditions developed in our group for the preparation of long poly(triacetylene) oligomers [4a][29]. However, the greater

Scheme 4. *Alternative Synthesis of Epoxide* (±)-**7**



a) $ClCH_2COCl$, $AlCl_3$, CH_2Cl_2, 0° → r.t.; 97%. *b*) (*t*-Bu)$Me_2SiOCH_2-C{\equiv}CLi$, THF, −78° → r.t. *c*) *t*-BuOK, DMF, r.t.; 82% (from **14**).

lability of the Me_3Si protecting group also led to substantially reduced yields in the preparation of the required epoxide (±)-**16** by both routes described above.

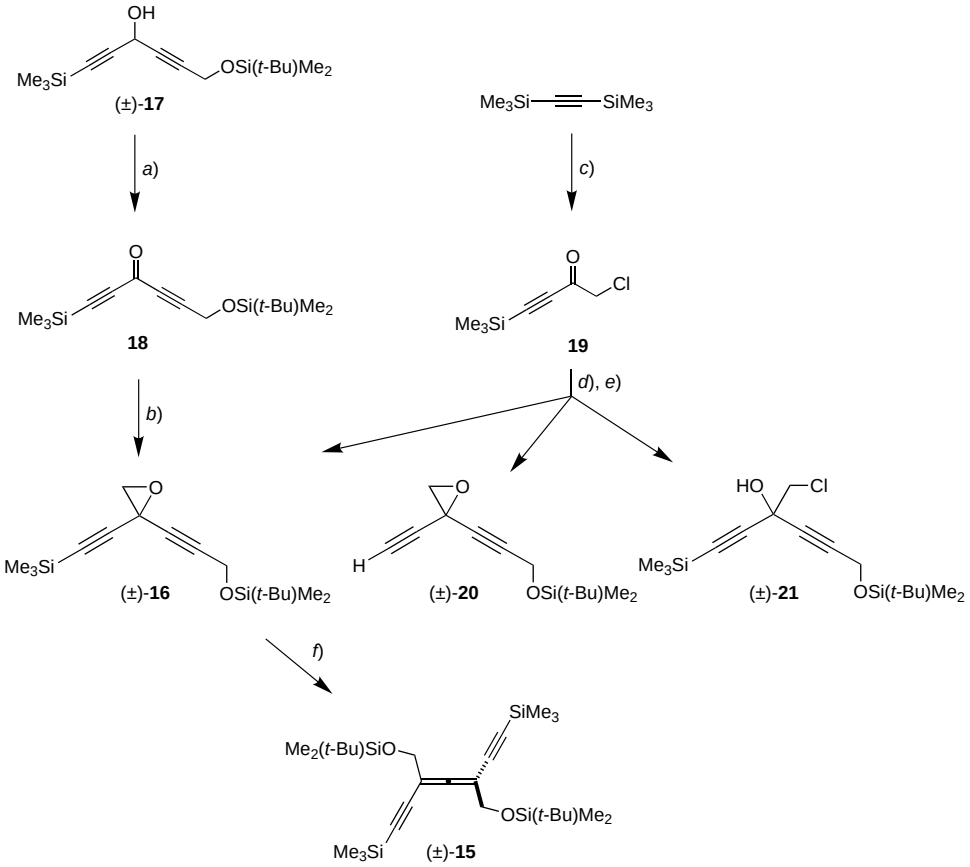
Addition of (*t*-Bu)$Me_2SiOCH_2-C{\equiv}CLi$ to $Me_3Si-C{\equiv}C-CHO$ provided bispropargylic alcohol (±)-**17**, which was oxidized with $BaMnO_4$ [30] to the corresponding ketone **18** (*Scheme 5*). As a result of the lability of the Me_3Si protecting group, ketone **18** was particularly susceptible to protodesilylation during chromatographic purification. Oxirane formation as described above afforded (±)-**16** in only 39% yield. By the alternative route, chloro ketone **19** [31] was obtained in good yield, but the lability of the Me_3Si group caused substantial problems in the epoxide-forming step, since this reaction proceeds through an intermediate alkoxide, to which the silyl group is readily transferred. Indeed, the isolated product mixture was found to include the desired epoxide (±)-**16**, protodesilated epoxide (±)-**20**, and compound (±)-**21** resulting from incomplete epoxide formation. Once isolated, epoxide (±)-**16** was readily converted to 1,3-diethynylallene (±)-**15** under standard conditions.

2.1.3. *A General Route to 1,3-Diethynylallenes.* The structural limitations of the epoxide-opening route could be circumvented with acetate or carbonate as the leaving group for the formation of the allenylpalladium intermediate. This is illustrated by the synthesis of (±)-**22** in *Scheme 6*. Propargyl alcohol (±)-**23** was oxidized to give ketone **24**, to which lithiated oct-1-yne was added to provide bispropargylic alcohol (±)-**25**. While the corresponding acetate (±)-**26** could be formed under standard conditions in 69% yield, aliphatic amine bases or pyridine proved generally unsuitable for the preparation of carbonates from bispropargylic alcohols. On the other hand, formation of the lithium alkoxide with BuLi or LHMDS (lithium hexamethyldisilazide), followed by addition of methyl chloroformate [18c], provided carbonate (±)-**27** in good yield (71%).

While acetate (±)-**26** could be converted by Pd^0-mediated cross-coupling to 1,3-dialkynylallene (±)-**22** in 66% yield after 4 h reflux in THF, carbonate (±)-**27** provided the target compound in 94% yield by stirring for 30 min at room temperature in CH_2Cl_2 (a better solvent for the catalyst at ambient temperature).

Upon isolation in pure form, (±)-**22** became prone to the thermal [2 + 2] cyclodimerization known to occur readily in allenes with extended π-electron conjugation [32]. This process had not been observed with the sterically hindered

Scheme 5. *Synthesis of 1,3-Diethynylallene* (±)-**15**

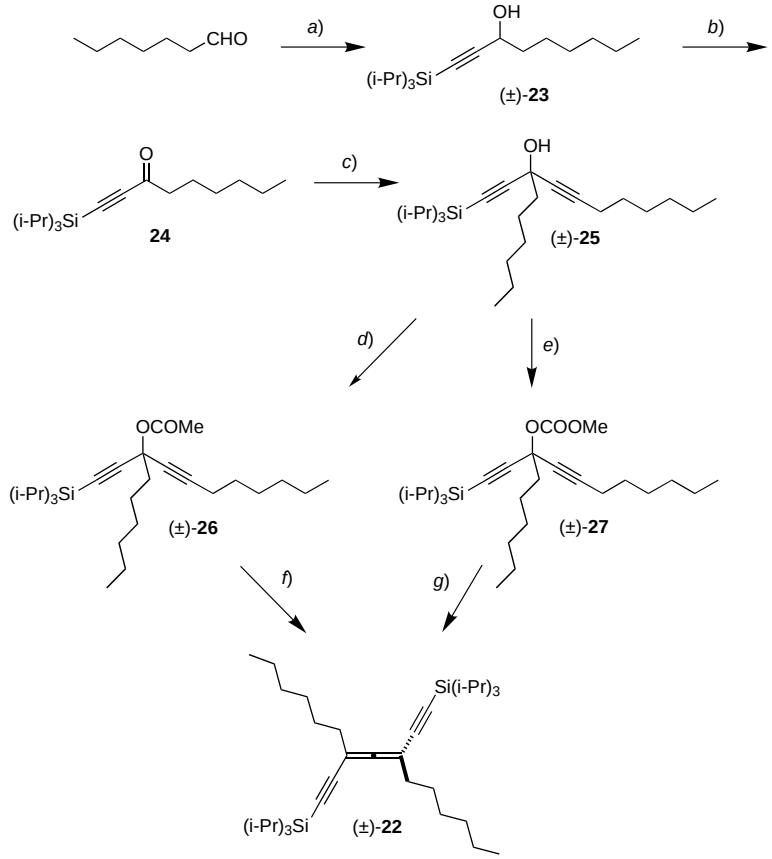


a) $BaMnO_4$, CH_2Cl_2, r.t.; 93%. *b*) MeLi·LiBr, CH_2I_2, THF, $-78° \rightarrow$ r.t.; 39%. *c*) $ClCH_2COCl$, $AlCl_3$, CH_2Cl_2, $0° \rightarrow$ r.t.; 78%. *d*) (*t*-Bu)Me_2SiOCH_2–C≡CLi, THF, $-78° \rightarrow -40°$. *e*) *t*-BuOK, DMF, $-40° \rightarrow -20°$; 23% (**16**), 9% ((±)-**20**), 26% ((±)-**21**) (from **19**). *f*) Me_3Si–C≡CH, (i-Pr)$_2$NH, [$Pd(PPh_3)_4$], CuI, CH_2Cl_2, r.t., then (*t*-Bu)Me_2SiCl, 1*H*-imidazole, r.t.; 63%.

allene (±)-**8**, but, for (±)-**22**, the half-life was on the order of 1–2 d at room temperature. Storage at low temperature did not entirely suppress the dimerization although the monomer was stable over several months when diluted with hexane and kept in the freezer at $-30°$. NMR Analysis indicated that the dimerized product consists of several inseparable stereoisomers. That this material is a dimer of 1,3-diethynylallene (±)-**22** was established by mass spectrometry and microanalysis, but since the inseparable mixture of isomers does not give clear structural data, further rearrangements of the presumed initial [2 + 2] cycloadduct cannot be ruled out [6b].

To explore the influence of different substituents on the thermal stability against [2 + 2] cycloaddition, the new route developed for (±)-**22** was applied to the synthesis of other 1,3-diethynylallenes. The preparation of (±)-**28** started from 3-(4-methoxyphenyl)prop-1-yne (**29**) [33] (*Scheme 7*). The corresponding acetylide was added to

Scheme 6. *Synthesis of 1,3-Diethynylallene* (±)-**22**

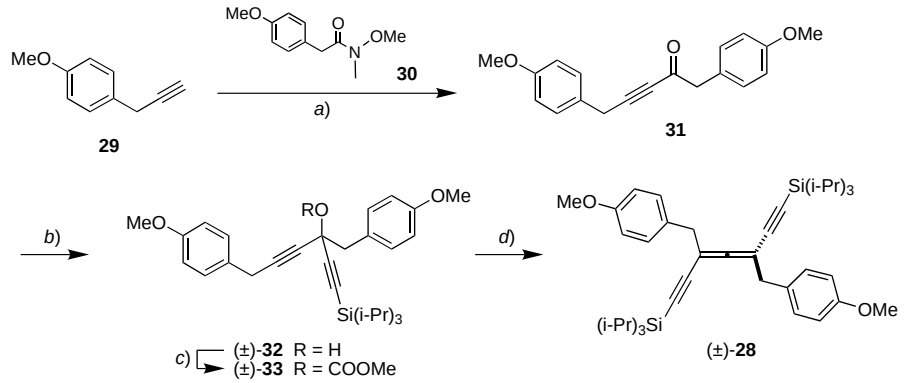


a) (i-Pr)$_3$Si–C≡CLi, THF, –78°→r.t.; 79%. *b*) Me_2SO, $(COCl)_2$, Et_3N, CH_2Cl_2, –78°; 94%. *c*) $Me(CH_2)_5C{\equiv}CLi$, THF, –78°→r.t.; 66%. *d*) Ac_2O, Et_3N, 4-(dimethylamino)pyridine (DMAP), CH_2Cl_2, r.t.; 69%. *e*) BuLi, THF, –78°, then MeOCOCl, r.t.; 71%. *f*) (i-Pr)$_3$Si–C≡CH, (i-Pr)$_2$NH, [Pd(PPh$_3$)$_4$], CuI, THF, Δ; 66%. *g*) (i-Pr)$_3$Si–C≡CH, (i-Pr)$_2$NH, [Pd(PPh$_3$)$_4$], CuI, CH_2Cl_2, r.t.; 94%.

Weinreb amide **30** to provide ketone **31**. Addition of (i-Pr)$_3$Si–C≡CLi led to tertiary alcohol (±)-**32**, which was transformed into methyl carbonate (±)-**33**. Allene formation as described for (±)-**22** gave the target compound (±)-**28** in 52% yield. Intermediates on the route to (±)-**28** proved rather unstable to extended storage even at low temperature, presumably because of the acidity of the doubly activated benzylic groups. Also, the final 1,3-diethynylallene, which was isolated as a clear oil, showed only borderline stability.

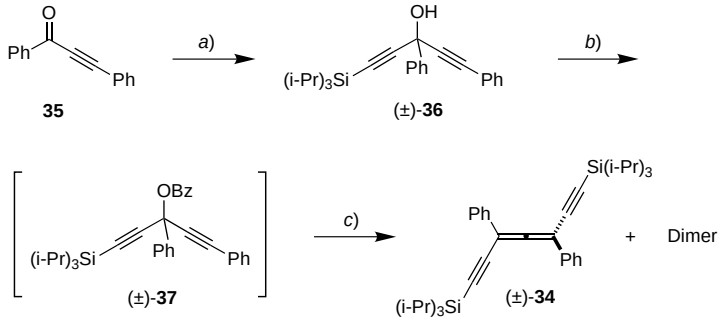
When the allene fragment is substituted by Ph residues, thereby further extending its π-electron conjugation and reducing the steric shielding, the stability decreases dramatically. The preparation of 1,3-diethynyl-1,3-diphenylallene (±)-**34** proved quite challenging due to instability of the intermediates in the synthetic route (*Scheme 8*).

Scheme 7. *Synthesis of 1,3-Diethynylallene* (±)-**28**



a) BuLi, THF, −78°, then **30**, −78° → r.t.; 67%. *b*) (i-Pr)$_3$Si−C≡CLi, THF, −78° → r.t.; 56%. *c*) LiHMDS, THF, −78°, then MeOCOCl, −78° → r.t.; 71%. *d*) (i-Pr)$_3$Si−C≡CH, (i-Pr)$_2$NH, [Pd(PPh$_3$)$_4$], CuI, CH_2Cl_2, r.t.; 52%.

Scheme 8. *Synthesis of the Thermally Unstable 1,3-Diethynylallene* (±)-**34**



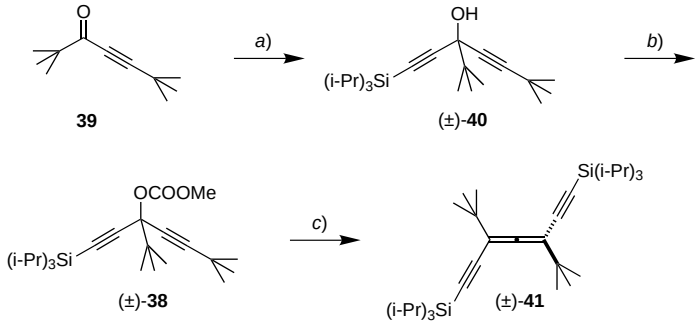
a) (i-Pr)$_3$Si−C≡CLi, THF, −78° → r.t.; 92%. *b*) BuLi, PhCOCl (BzCl), THF, −78° → r.t. *c*) (i-Pr)$_3$Si−C≡CH, (i-Pr)$_2$NH, [Pd(PPh$_3$)$_4$], CuI, THF, Δ; 38% (combined yield of (±)-**34** and dimer, starting from (±)-**36**).

Addition of (i-Pr)$_3$Si−C≡CLi to 1,3-diphenylprop-2-yn-1-one (**35**) [34] provided the bispropargylic alcohol (±)-**36**. Both the methyl carbonate and the diethyl phosphate of (±)-**36** proved unstable in solution even at low temperatures. The corresponding acetate and benzoate could not be isolated, but were sufficiently stable to be used in the formation of the allene. Thus, benzoate (±)-**37** was prepared *in situ*, followed by immediate application of the cross-coupling conditions to give (±)-**34**. However, the half-life of this allene with regard to cyclodimerization was only a few minutes in neat form at room temperature, which precluded isolation in pure form. These experiments clearly demonstrate that bulky side chains that do not extend the π-conjugation of the allene system are required to prevent the approach of the two allene units and to mitigate the undesired thermal [2 + 2] cycloaddition to an appreciable extent.

2.2. *Regiochemical Studies.* From the outset of this investigation, we assumed that the primary factor in determining the regioselectivity (*Scheme 2*) in the formation of the allenylpalladium intermediate and, ultimately, the 1,3-diethynylallene formed

would be the difference in steric bulk between the two alkyne substituents rather than the difference in electronic factors. Thus, attack of the Pd^0 species at (±)-**7** (*Scheme 3*) or (±)-**16** (*Scheme 5*) occurs at the acetylene bearing the smaller (*t*-Bu)Me_2SiOCH_2 substituent and not at the silyl-protected ((i-Pr)$_3$Si or Me_3Si) alkyne. To test this hypothesis further, we investigated 1,3-dialkynylallene formation starting from carbonate (±)-**38**, in which the two alkynyl residues are substituted with (i-Pr)$_3$Si and Me_3C groups, respectively. Starting from ketone **39** [35], we prepared by the established protocol alcohol (±)-**40** and carbonate (±)-**38** (*Scheme 9*).

Scheme 9. *Cross-Coupling of the Hindered Carbonate* (±)-**38**

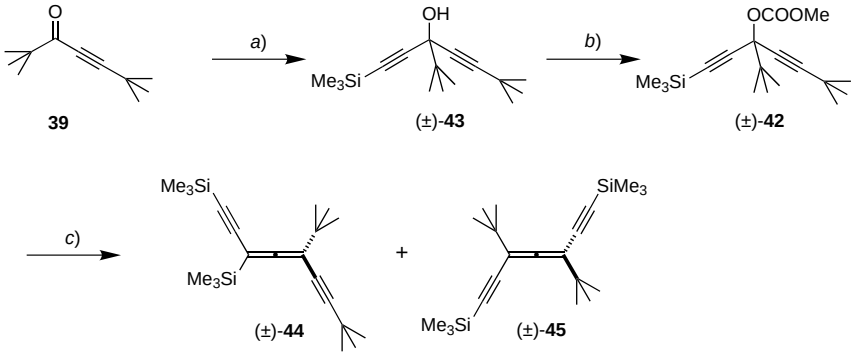


a) (i-Pr)$_3$Si−C≡CLi, THF, −78° → r.t.; 89%. *b*) LiHMDS, THF, −78°, then MeOCOCl, −78° → r.t.; 94%. *c*) (i-Pr)$_3$Si−C≡CH, (i-Pr)$_2$NH, [Pd(PPh$_3$)$_4$], CuI, $(CH_2Cl)_2$, 70°; 32%.

The following cross-coupling reaction with (i-Pr)$_3$Si−C≡CH proved extremely sluggish even after heating, with the Pd catalyst turning to a black, inactive precipitate after low conversion. Air should be rigorously excluded to prevent oxidative coupling of (i-Pr)$_3$Si−C≡CH, since the separation of the resulting buta-1,3-diyne from the desired allene proved extremely difficult. The attack by Pd^0 occurred with complete regioselectivity at the alkyne moiety substituted with the smaller Me_3C group, affording the stable, C_2-symmetric 1,3-diethynylallene (±)-**41** in 32% yield (92% based on recovered starting material). The sluggish reaction and the low yield demonstrate, however, that the increase in steric bulk at the site of Pd-attack is clearly hindering formation of the allenylpalladium intermediate and subsequent cross-coupling.

To further explore the role of steric *vs.* electronic factors in the regioselectivity, we replaced the (i-Pr)$_3$Si group in carbonate (±)-**38** with the smaller Me_3Si group, which is similar to the Me_3C group in steric bulk (*Scheme 10*). Preparation of carbonate (±)-**42** was accomplished *via* the established route starting from ketone **39** [35] *via* alcohol (±)-**43**, and cross coupling with Me_3Si−C≡CH in $(CH_2Cl)_2$ at 70° proceeded smoothly to complete conversion. The 1,3-diethynylallene products isolated in 71% yield consisted of a *ca.* 5 : 2 mixture of C_1-symmetric (±)-**44** and C_2-symmetric isomer (±)-**45**. This ratio is (qualitatively speaking) easily accounted for by the slightly reduced steric demand imposed by the Me_3Si group with the longer C(sp)−Si bond and rules out any significant electronic bias for attack in the cross-coupling.

Scheme 10. *Inverted Regioselectivity in the Cross-Coupling of Carbonate* (±)-**42**



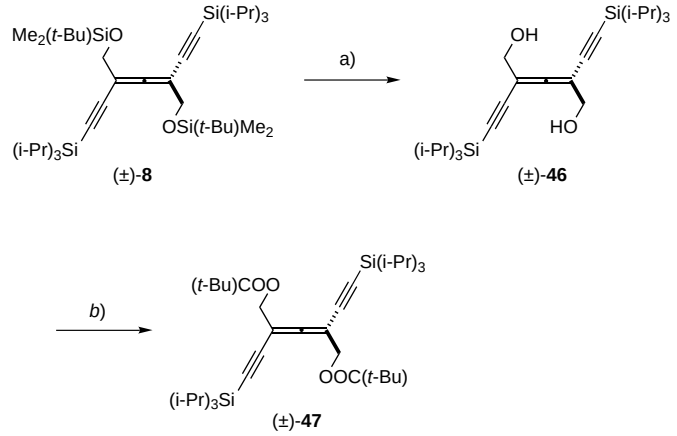
a) (i-Pr)$_3$Si−C≡CLi, THF, −78° → r.t.; 72% (includes preparation of crude **39**). *b*) LiHMDS, THF, −78°, then MeOCOCl, −78° → r.t.; 90%. *c*) Me$_3$Si−C≡CH, (i-Pr)$_2$NH, [Pd(PPh$_3$)$_4$], CuI, (CH$_2$Cl)$_2$, 70°; 71% (combined yield).

While this result was satisfying in itself, it does place some constraints upon the design of future systems, in which we would generally like to use bulkier side chains to prevent allene dimerization, yet sterically less-demanding alkyne protection to allow more-facile deprotection for subsequent oligomerization *via* oxidative coupling.

2.3. *Chemical Transformations with 1,3-Diethynylallenes: Preparation of the First Dimer.* The first target in our investigations was the formation of a 1,3-diethynylallene dimer, thereby establishing the feasibility of the oxidative acetylenic coupling required to ultimately reach the new helical oligomers and polymers (*Fig. 2*). We initially chose (±)-**8** as the precursor in view of its stability and good accessibility *via* the epoxide route (*Scheme 4*). However, (±)-**8** bears silyl-protecting groups on the side chains as well as the alkynyl moieties, which precludes straightforward alkyne deprotection, as required for oxidative coupling. Therefore, we intended to exchange the silyl ether by another *O*-protecting group (*Scheme 11*). The (*t*-Bu)Me$_2$Si group could, indeed, be removed with TsOH in MeOH/Et$_2$O to yield diol (±)-**46**, which is stable only in very dilute solution. Upon concentration, dimerization occurs within minutes. Therefore, the crude diol, isolated as an oil after workup, was immediately trapped with pivaloyl chloride in CH$_2$Cl$_2$ in the presence of Et$_3$N. The first acylation seems to proceed rather smoothly (TLC), but the second one is appreciably slower, and side products start to form with increasing reaction time. Pure diacetylated allene (±)-**47** was isolated, although its instability prevented further use in alkyne deprotection and subsequent oxidative coupling.

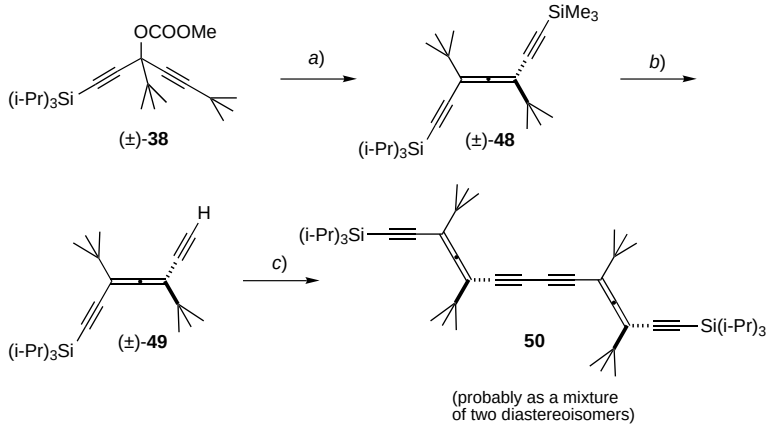
We subsequently decided to prepare the desired dimer starting from unsymmetrically protected 1,3-diethynylallene (±)-**48** (*Scheme 12*). Cross-coupling between carbonate (±)-**38** and Me$_3$Si−C≡CH provided (±)-**48** as a stable compound that was mono-deprotected with K$_2$CO$_3$ in MeOH/THF to give ethynyl derivative (±)-**49**. Oxidative coupling under *Hay* conditions proceeded slowly and afforded the desired diallene **50** in 72% yield. The isolated product decomposes only slowly at ambient

Scheme 11. *Exchange of the* O*-Protecting Groups in 1,3-Diethynylallene* (±)-**8**



a) TsOH, MeOH/Et_2O, r.t. *b*) Me_3CCOCl, Et_3N, CH_2Cl_2, 0° → r.t.; 49% (from (±)-**8**).

Scheme 12. *Synthesis of Diallene* **50**



a) $Me_3Si-C\equiv CH$, $(i\text{-}Pr)_2EtN$, $[Pd(PPh_3)_4]$, CuI, $(CH_2Cl)_2$, 80°. *b*) K_2CO_3, MeOH/THF 1:1, r.t.; 57% (from (±)-**38**). *c*) CuCl, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), air, molecular sieves (4 Å), $CHCl_3$, r.t.; 72%.

atmosphere to a much more-polar compound, but it does not dimerize. Stored in an inert atmosphere, it seems completely stable.

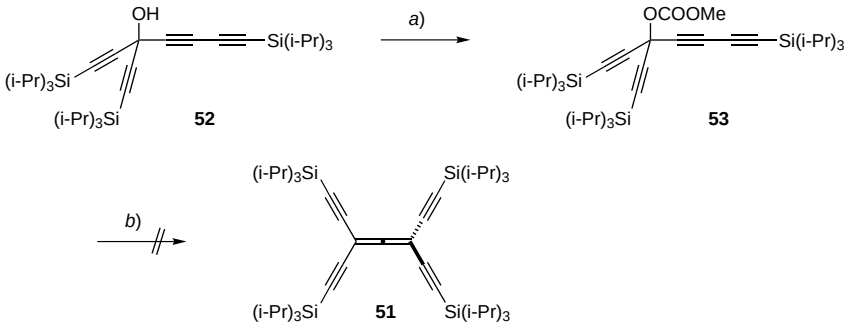
Support for the formation of **50** was provided by the electron-impact mass spectrum (EI-MS), which depicted the molecular ion $M+$ at m/z 710.5 (52%) as an intense ion, besides characteristic fragment ions at 695.5 (11, $[M-Me]^+$), 667.4 (16, $[M-Pr]^+$), 653.4 (46, $[M-t\text{-}Bu]^+$), 553.3 (5, $[M-(i\text{-}Pr)_3Si]^+$), 57.1 (89, $t\text{-}Bu^+$), and 44.0 (100, Pr^+). Starting from racemic (±)-**49**, the formation of two diastereoisomers, one *meso* compound and one pair of enantiomers, was expected. However, the ^1H- and ^{13}C-NMR spectra ($CDCl_3$) show only one set of peaks (*i.e.*, 13 ^{13}C and two ^1H resonances). Also,

all attempts to separate the diastereoisomers by HPLC have failed so far. Nevertheless, we believe that the existence of only one set of NMR resonances is pure coincidence, and that the isolated compound **50** is composed of a mixture of two diastereoisomers. Full clarity will be reached in this matter when oxidative coupling is conducted with enantiomerically pure 1,3-diethynylallenes, which is our next objective in this project.

2.4. *Attempted Synthesis of Tetraethynylallene.* Tetraethynylallene (**6**) and its silylated derivatives have remained elusive despite intensive past efforts aimed at their preparation in our group [6b]. These compounds are expected to be unstable toward dimerization in analogy to the diphenyl derivative (±)-**34**, but we hoped that the newly developed methodology described above would allow their synthesis and subsequent characterization, at least in solution.

On the way to (i-Pr)$_3$Si-protected tetraethynylallene **51**, we started from alcohol **52** [6b], which was transformed into carbonate **53** (*Scheme 13*). However, the carbonate failed to react under the standard cross-coupling conditions at room temperature, and heating gave incomplete conversion to two less-polar products, the minor of which could be consistent with the dimer of **51**, although no clean spectral data were obtained to support this conclusion.

Scheme 13. *Attempted Synthesis of Tetraethynylallene* **51**



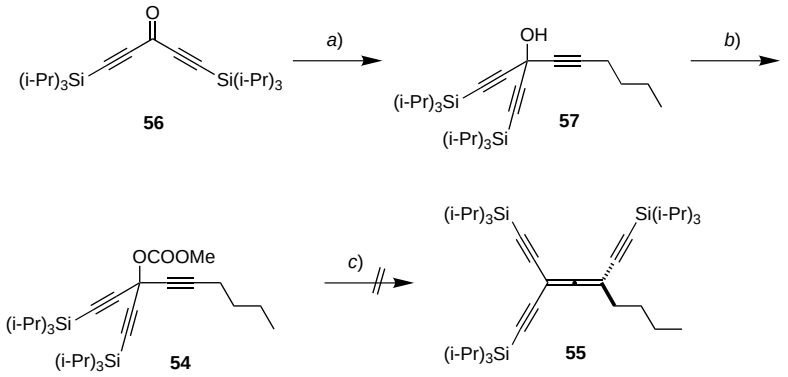
a) LiHMDS, THF, −78°, then MeOCOCl, −78° → r.t.; 84%. *b*) (i-Pr)$_3$Si−C≡CH, (i-Pr)$_2$NH, [Pd(PPh$_3$)$_4$], CuI, (CH$_2$Cl)$_2$, Δ.

In analyzing this failure, we note that two structural elements have been changed from the previously used substrates. First, one of the three residues at the tertiary center, which, in previous substrates, was generally an alkyl group, is now an additional alkynyl group, making the leaving group trispropargylic. Second, the acetylene moiety to undergo Pd-attack is now part of a buta-1,3-diyne fragment, and this might cause a sufficiently large electronic perturbation to disfavor the attack. Preparing and cross-coupling substrates that separate these two elements might give insight into the problems encountered in the attempted preparation of tetraethynylallene.

The first target was trispropargylic carbonate **54**, which was expected to give triethynylallene **55** after coupling (*Scheme 14*). Ketone **56** [6b] was transformed into alcohol **57** and subsequently into the desired carbonate, which proved to be unstable to concentration and chromatography, but could be prepared cleanly in solution, then taken directly to the cross-coupling step. This resulted in the formation of several

products, including one likely candidate for the targeted triethynylallene, but this largely decomposed to another product on attempted isolation. This behavior is consistent with allene formation and dimerization, as observed with the diphenyl and expected for the tetraethynyl derivative.

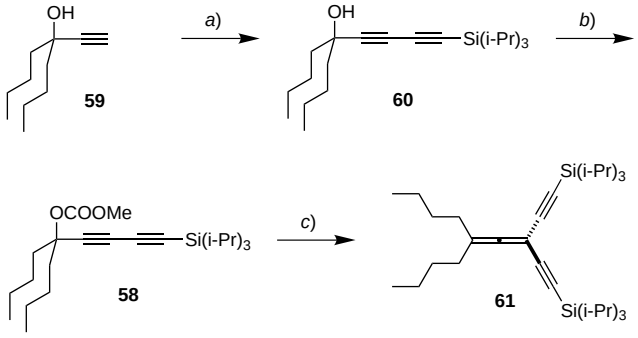
Scheme 14. *Attempted Synthesis of Triethynylallene* **55**



a) $Me(CH_2)_3C{\equiv}CLi$, THF, $-78° \rightarrow$ r.t.; 75%. *b*) LiHMDS, THF, $-78°$, then MeOCOCl, $-78° \rightarrow$ r.t. *c*) $(i\text{-}Pr)_3Si{-}C{\equiv}CH$, $(i\text{-}Pr)_2NH$, $[Pd(PPh_3)_4]$, CuI, THF, Δ.

Carbonate **58** was subsequently prepared from propargyl alcohol **59** [36] *via* **60** to test the reactivity of buta-1,3-diyne fragments in the cross-coupling reaction (*Scheme 15*). Attack of Pd required heating to attain appreciable reaction rates. However, once the reaction was initiated, conversion to product was clean and 1,1-diethynylallene **61** was obtained in excellent (97%) yield.

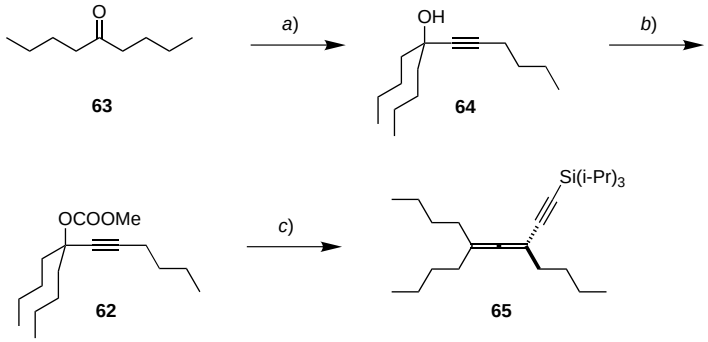
Scheme 15. *Synthesis of 1,1-Diethynylallene* **61**



a) $(i\text{-}Pr)_3Si{-}C{\equiv}CBr$ [37], $NH_2OH{\cdot}HCl$, $PrNH_2$, EtOH, CuCl, r.t.; 93%. *b*) LiHMDS, THF, $-78°$, then MeOCOCl, $-78° \rightarrow$ r.t.; 71%. *c*) $(i\text{-}Pr)_3Si{-}C{\equiv}CH$, $(i\text{-}Pr)_2NH$, $[Pd(PPh_3)_4]$, CuI, $(CH_2Cl)_2$, 70°; 97%.

For direct comparison of the reaction rates for cross-coupling to acetylene and butadiyne fragments, carbonate **62** was also prepared (*via* **63** → **64** → **62**; *Scheme 16*). In this case, cross-coupling proceeded readily at room temperature and alkynylallene **65** was isolated in 94% yield.

Scheme 16. *Synthesis of Alkynylallene* **65**



a) $Me(CH_2)_3C{\equiv}CLi$, THF, $-78° \rightarrow$ r.t. *b*) LiHMDS, THF, $-78°$, then MeOCOCl, $-78° \rightarrow$ r.t.; 67% (from **63**). *c*) $(i\text{-}Pr)_3Si{-}C{\equiv}CH$, $(i\text{-}Pr)_2NH$, $[Pd(PPh_3)_4]$, CuI, $(CH_2Cl)_2$, r.t.; 94%.

The comparison between the cross-coupling reactivity of **58** and **62** clearly shows that attack of Pd at the butadiyne fragment is less favorable, compared with attack at an acetylene moiety, requiring higher temperatures for conversion. This finding may also explain why carbonate **53** (*Scheme 13*) is much less reactive than analog **54** (*Scheme 14*). Thus, the attempt to synthesize the most delicate tetraethynylallene chromophore *via* this cross-coupling method appears disadvantageous: attack of Pd at the butadiyne moiety requires forcing conditions, while the product, with its high propensity to undergo [2 + 2] cycloaddition, is likely to exhibit extreme sensitivity to heat.

3. Conclusions. – Regioselective Pd^0-catalyzed cross-coupling of substrates bearing bispropargylic leaving groups with silyl-protected alkynes has provided access to a variety of 1,3-diethynylallenes, a new family of C-rich modules for three-dimensional acetylenic scaffolding. Extensive investigation showed that the 1,3-diethynylallene chromophore is stable only against [2 + 2] cycloaddition, when protected by steric bulk, and when additional π-electron delocalization is avoided. Compounds (±)-**8** and (±)-**41** with bulky alkyl groups attached to the allene fragment are representatives of thermally stable derivatives, whereas the diphenyl derivative (±)-**34** is a good example for an unstable derivative undergoing rapid [2 + 2] cycloaddition at ambient temperature. *Hay* coupling of (±)-**49** led to the first 1,3-diethynylallene dimer **50**, demonstrating that the formation of oligomers and polymers with a helical backbone (*Fig. 2*) by oxidative oligomerization is in reach, once a protocol for the optical resolution of the 1,3-diethynylallenes has been worked out. Attempts to apply the new cross-coupling methodology to the formation of a silyl-protected tetraethynylallene failed. Control experiments showed that the Pd^0-catalyzed cross-coupling to butadiyne moieties in the synthesis of this still-elusive chromophore requires forcing conditions under which rapid [2 + 2] cycloaddition of the initial product cannot be avoided.

Now that the methods for preparing 1,3-diethynylallenes are well-established, the focus will be on isolating them in enantiomerically pure form. One option for isolation of enantiomerically pure compounds is derivatization of racemic material with chiral

side chains, followed by separation of the diastereoisomers. An obvious candidate for such experiments is diol (±)-**46** (*Scheme 11*), which could be esterified with optically active carboxy derivatives. Another option is to prepare enantiomerically pure bispropargylic carbonates and attempt to transfer this atom-centered chirality to the axial chirality of the allene according to the stereoselective modes of attack outlined in *Scheme 1*. It is clear that such an endeavor will require many additional new methods. But the prospect of preparing fascinating new helical oligomers and polymers (*Fig. 2*) with promising chiroptical properties fully warrants these synthesis investments.

Experimental Part

General. Reagents and solvents were purchased as reagent-grade and used without further purification unless otherwise stated. THF and Et_2O were freshly distilled from sodium benzophenone ketyl, and CH_2Cl_2 was freshly distilled from CaH_2. (i-Pr)$_2$NH and Et_3N were distilled over KOH and stored over activated molecular sieves (4 Å). All reactions were performed in oven-dried or flame-dried glassware under an inert atmosphere (N_2; for Pd-catalyzed reactions: Ar) unless otherwise stated. Evaporation and concentration *in vacuo* was performed at $\leq 30°$/*ca.* 10 Torr. Further drying of the new compounds was carried out at *ca.* 10^{-2} Torr. Chromatography refers to flash chromatography (FC) on SiO_2 *60* (0.02–0.063 mm) from *Fluka*; head pressure of *ca.* 0.3 bar. TLC: *Polygram SIL G/UV$_{254}$* SiO_2-coated plates from *Macherey-Nagel*; visualization by UV light (254 nm) or by coloring with an anisaldehyde soln. (98% EtOH (198 ml), conc. H_2SO_4 (7 ml), AcOH (2 ml), and anisaldehyde (5 ml)). M.p.: *Büchi B-540* melting-point apparatus; uncorrected. UV/VIS (λ_{max} [nm], (ε [M^{-1} cm^{-1}]): *Varian-CARY 500 Scan* spectrophotometer with a 1-cm cell at r.t. IR ([cm^{-1}], KBr or film): *Perkin-Elmer 1600 FT-IR* spectrometer. NMR (^{1}H, ^{13}C; δ [ppm], J [Hz]): *Varian Gemini 200*, *Varian Gemini 300*, or *Bruker 500* MHz spectrometer at 298 K with residual solvent peaks as internal reference. MS (*m/z* (%)): EI mass spectra were recorded on a *VG-Tribid* instrument operating at 70 eV, and HR-MALDI mass spectra on an *IonSpec Fourier Transform* (FT) instrument. Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für Organische Chemie* at *ETH Zürich*.

*(±)-6-[(*tert*-Butyl)dimethylsilyloxy]-1-(triisopropylsilyl)hexa-1,4-diyn-3-ol* ((±)-**9**). *Method A:* BuLi (1.71 ml of a 1.6M soln. in hexane, 2.73 mmol) was added dropwise to (*t*-Bu)Me$_2$SiOCH$_2$–C≡CH [24] (503 mg, 2.96 mmol) in THF (10 ml) at −78°. After 30 min, (i-Pr)$_3$Si–C≡C–CHO [6b][25] (478 mg, 2.28 mmol) in THF (2 ml) was added *via* cannula. After 45 min, the reaction was quenched by dropwise addition of sat. aq. NH_4Cl soln. (1 ml) and allowed to warm to r.t. The mixture was partitioned between Et_2O and sat. aq. NH_4Cl soln. (1:1, 50 ml), the phases were separated, and the aq. layer was extracted with Et_2O (3 × 20 ml). The combined org. phases were washed with sat. aq. NaCl soln. (10 ml), dried ($MgSO_4$), and concentrated *in vacuo*. FC (SiO_2; CH_2Cl_2/hexane 1:1) afforded (±)-**9** (393 mg, 45%). Clear oil. R_f (SiO_2; hexane/AcOEt 10:1) 0.30. IR (film): 3385, 2944, 2861, 2172, 1461, 1386, 1364, 1292, 1256, 1133, 1089, 1036, 997, 961, 883, 836, 778, 733, 672. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.25 (*dt*, J = 7.8, 1.8, 1 H); 4.36 (*d*, J = 1.8, 2 H); 2.13 (*d*, J = 7.8, 1 H); 1.08 (*s*, 21 H); 0.91 (*s*, 9 H); 0.13 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.7; 85.9; 82.9; 81.9; 52.6; 51.6; 25.8; 18.5; 18.2; 11.1; −5.1. EI-MS: 380.2 ($M+$). Anal. calc. for $C_{21}H_{40}O_2Si_2$ (380.7): C 66.25; H 10.59; found: C 66.44, H 10.58.

Method B: MnO_2 (15 g) was added at r.t. to **10** [26] (3.00 g, 15 mmol) in Et_2O (15 ml). After stirring overnight, additional MnO_2 (15 g) and Et_2O (10 ml) were added, and stirring was continued for 24 h. The mixture was filtered through *Celite*, washing with Et_2O, and the filtrate was dried ($MgSO_4$). Evaporation *in vacuo* gave 1.75 g of the propargylic aldehyde as a clear oil, which was used without further purification. BuLi (8.69 ml of a 1.6M soln. in hexane, 13.9 mmol) was added at −78° to (i-Pr)$_3$Si–C≡CH (2.96 ml, 13.2 mmol) in THF (25 ml). After 15 min, the soln. was warmed to r.t. and stirred for another 15 min. After recooling to −78°, the crude propargylic aldehyde (1.75 g, 8.8 mmol) in THF (10 ml) was added rapidly *via* syringe. After warming to r.t., the mixture was partitioned between sat. aq. NH_4Cl soln. (50 ml) and Et_2O (50 ml), the aq. phase was extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 5:1) gave (±)-**9** (1.95 g, 34%).

*6-[(*tert*-Butyl)dimethylsilyloxy]-1-(triisopropylsilyl)hexa-1,4-diyn-3-one* (**11**). MnO_2 (3.8 g) was added at r.t. to (±)-**9** (1.90 g, 5.00 mmol) in Et_2O, and the mixture was stirred for 3 h. Filtration through *Celite*, evaporation *in vacuo*, and FC (SiO_2; hexanes/AcOEt 10:1) gave **11** (1.46 g, 77%). Clear oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.53. IR (film): 2946, 2866, 2228, 2139, 1633, 1461, 1361, 1256, 1200, 1100, 983, 883, 833, 779.

^{1}H-NMR (300 MHz, $CDCl_3$): 4.50 (*s*, 2 H); 1.11 (*s*, 18 H); 1.09 (*s*, 3 H); 0.91 (*s*, 9 H); 0.15 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.9; 104.6; 97.5; 91.0; 84.9; 51.5; 25.6; 18.4; 18.1; 11.0; −5.2. EI-MS: 378.2 (6, M^+), 321.2 (100, $[M-CMe_3]^+$). Anal. calc. for $C_{21}H_{38}O_2Si_2$ (378.7): C 66.60, H 10.11; found: C 66.83, H 10.16.

*(±)-2-[2-({[(*tert*-Butyl)dimethylsilyl]oxy}methyl)ethynyl]-2-[(triisopropylsilyl)ethynyl]oxirane* ((±)-**7**). *Method A:* MeLi·LiBr (3.12 ml of a 1.5M soln. in Et_2O, 4.68 mmol) was added dropwise at −78° to **11** (1.36 g, 3.60 mmol) and CH_2I_2 (0.38 ml, 4.68 mmol) in THF (15 ml). The mixture was slowly warmed to r.t. over 2 h, while epoxide formation was monitored by TLC. After 1 h at r.t., the mixture was partitioned between sat. aq. NH_4Cl soln. (25 ml) and Et_2O (25 ml), the aq. phase was extracted with Et_2O (2 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 20:1) provided (±)-**7** (1.11 g, 79%). Pale-yellow, somewhat unstable oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.49. IR (film): 2945, 2862, 2241, 2167, 1464, 1367, 1292, 1264, 1099, 929, 882, 837, 779, 678. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.34 (*s*, 2 H); 3.14 (*s*, 2 H); 1.07 (*s*, 21 H); 0.90 (*s*, 9 H); 0.12 (*s*, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 102.3; 84.9; 81.2; 80.8; 57.4; 51.6; 39.8; 25.7; 18.5; 18.2; 11.0; −5.2. EI-MS: 392 (M^+). Anal. calc. for $C_{22}H_{40}O_2Si_2$ (392.7): C 67.28, H 10.27; found: C 67.18, H 10.26.

Method B: BuLi (1.56 ml of a 1.6M soln. in hexane, 2.5 mmol) was added at −78° to (*t*-Bu)Me_2-$SiOCH_2$–C≡CH (425 mg, 2.5 mmol) in THF (5 ml), and the soln. was stirred for 30 min at this temp. Ketone **14** (518 mg, 2.0 mmol) in THF (2 ml) was added rapidly *via* syringe, and the mixture was warmed to r.t. over 1 h. Dry DMF (4 ml) and *t*-BuOK (100 mg, 1 mmol) were added, and the deep-red mixture was stirred 2 h at r.t. The mixture was partitioned between sat. aq. NH_4Cl soln. (25 ml) and Et_2O (25 ml), the aq. phase was extracted with Et_2O (2 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and filtration (SiO_2; hexanes/AcOEt 10:1) gave nearly pure (±)-**7** (643 mg, 82%).

*(±)-3,5-Bis({[(*tert*-butyl)dimethylsilyl]oxy}methyl)-1,7-bis(triisopropylsilyl)hepta-3,4-diene-1,6-diyne* ((±)-**8**). A soln. of (±)-**7** (785 mg, 2.0 mmol), (i-Pr)$_3$Si–C≡CH (0.67 ml, 3.0 mmol), and (i-Pr)$_2$NH (0.56 ml, 4.0 mmol) in CH_2Cl_2 (4 ml) was sparged with Ar. $[Pd(PPh_3)_4]$ (46 mg, 0.04 mmol) and CuI (15 mg, 0.08 mmol) were added sequentially with further sparging with Ar after each addition. After 6 h, 1*H*-imidazole (204 mg, 3.0 mmol) and (*t*-Bu)Me_2SiCl (393 mg, 2.6 mmol) were added sequentially with additional CH_2Cl_2 (5 ml). After 2 h, the mixture was filtered through *Celite* with hexanes and the filtrate evaporated *in vacuo*. FC (SiO_2; hexanes/CH_2Cl_2 4:1) yielded (±)-**8** (720 mg, 52%). Clear oil, which solidified upon storage at −30°. R_f (SiO_2; hexanes/CH_2Cl_2 4:1) 0.45. M.p. 56–57°. IR (film): 2944, 2891, 2863, 2147, 1944, 1464, 1388, 1361, 1333, 1254, 1111, 994, 878, 833, 779, 667. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.20 (*s*, 4 H); 1.07 (*s*, 42 H); 0.89 (*s*, 18 H), 0.08 (*s*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 214.9; 98.7; 95.9; 95.1; 64.1; 25.7; 18.5; 18.1; 11.2; −5.4; −5.5. EI-MS: 688 (M^+). Anal. calc. for $C_{39}H_{76}O_2Si_4$ (689.4): C 67.95, H 11.11; found: C 67.85, H 11.13. X-Ray: see [9].

*(±)-3,5-Bis({[(*tert*-butyl)dimethylsilyl]oxy}methyl)-1-(triisopropylsilyl)-7-(trimethylsilyl)hepta-3,4-diene-1,6-diyne* ((±)-**12**). A soln. of (±)-**7** (196 mg, 0.50 mmol), Me_3Si–C≡CH (206 µl, 0.75 mmol), and (*i*-Pr)$_2$NH (140 µl, 1.0 mmol) in $(CH_2Cl)_2$ (2.5 ml) was sparged with Ar. $[Pd(PPh_3)_4]$ (29 mg, 0.025 mmol) and CuI (9.5 mg, 0.050 mmol) were added sequentially with further sparging with Ar after each addition. After 1 h, 1*H*-imidazole (51 mg, 0.75 mmol) and (*t*-Bu)Me_2SiCl (98 mg, 0.65 mmol) were added sequentially. After 2 h, the mixture was filtered through *Celite* with hexanes and the filtrate evaporated *in vacuo*. FC (SiO_2; hexanes/CH_2Cl_2 4:1) afforded (±)-**12** (161 mg, 53%). Clear oil. R_f (SiO_2; hexanes/CH_2Cl_2 4:1): 0.33. IR (film): 2957, 2891, 2859, 2149, 1943, 1463, 1387, 1359, 1251, 1112, 1004, 882, 841, 777, 677. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.21 (*s*, 2 H); 4.20 (*s*, 2 H); 1.07 (*s*, 21 H); 0.90 (*s*, 18 H); 0.18 (*s*, 9 H); 0.09 (*s*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 214.5; 98.5; 98.4; 96.8; 95.9; 95.6; 95.3; 64.3; 63.7; 25.8; 18.6; 18.2; 11.2; −0.2; −5.2; −5.3; −5.4. EI-MS: 604.3 (M^+). Anal. calc. for $C_{33}H_{64}O_2Si_4$: C 65.49, H 10.66; found: C 65.76, H 10.81.

1-(Triisopropylsilyl)-2-(trimethylsilyl)acetylene (**13**) [28]. BuLi (32.8 ml of a 1.6M soln. in hexane, 52.5 mmol) was added at −78° to (i-Pr)$_3$Si–C≡CH (11.2 ml, 50.0 mmol) in THF (50 ml). After stirring for 15 min at this temp. and 15 min at r.t., the mixture was recooled, and Me_3SiCl (6.98 ml, 55.0 mmol) was added *via* syringe. After stirring 1 h at −78°, the mixture was warmed to r.t. and stirred an additional 2 h before being partitioned between H_2O (100 ml) and Et_2O (100 ml). The aq. phase was extracted with Et_2O (2 × 100 ml), and the combined org. phases were dried ($MgSO_4$) and evaporated *in vacuo*. Vacuum distillation afforded **13** (12.73 g, 90%). Clear liquid. R_f (SiO_2; hexane) 0.52. IR (film) 2959, 2944, 2896, 2867, 1464, 1383, 1250, 996, 883, 859, 842, 767, 676. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.07–1.05 (*m*, 21 H); 0.17 (*s*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 116.2; 110.2; 18.6; 11.1; 0.0.

1-Chloro-4-(triisopropylsilyl)but-3-yn-2-one (**14**) [28]. Compound **13** (1.27 g, 5.0 mmol) and $ClCH_2COCl$ (0.40 ml, 5.0 mmol) in CH_2Cl_2 (10 ml) were added over 10 min at 0° to $AlCl_3$ (0.87 g, 6.5 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at r.t. for 30 min , then 1M HCl (25 ml) was added. The mixture was extracted with Et_2O (3 × 50 ml) and the combined extracts were dried ($MgSO_4$). Evaporation *in vacuo* provided nearly

pure **14** (1.25 g, 97%), which was used without further purification in the next conversion. Yellow oil. R_f (SiO_2; hexanes/AcOEt 10:1): 0.47. IR (film) 2946, 2868, 2152, 1692, 1682, 1464, 1214, 1105, 995, 883, 858, 836, 788, 681. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.21 (*s*, 2 H); 1.13–1.10 (*m*, 21 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 178.5; 101.5; 101.3; 49.4; 18.3; 10.8.

*(±)-6-[(*tert*-Butyl)dimethylsilyloxy]-1-(trimethylsilyl)hexa-1,4-diyn-3-ol* ((±)-**17**). BuLi (10.1 ml of a 1.6M soln. in hexane, 16.2 mmol) was added dropwise to (*t*-Bu)Me_2SiOCH_2–C≡CH (2.98 g, 17.5 mmol) in THF (60 ml) at −78°. After 30 min, Me_3Si–C≡C–CHO (1.70 g, 13.5 mmol) in THF (12 ml) was added *via* cannula. After 40 min, the reaction was quenched by dropwise addition of sat. aq. NH_4Cl soln. (5 ml) and allowed to warm to r.t. The mixture was partitioned between Et_2O (100 ml) and sat. aq. NH_4Cl soln. (100 ml). The aq. phase was extracted with Et_2O (3 × 75 ml), and the combined org. phases were washed with sat. aq. NaCl soln. (50 ml), dried ($MgSO_4$), and concentrated *in vacuo*. FC (SiO_2; CH_2Cl_2/hexane 7:3 → 9:1 gradient) afforded (±)-**17** (2.91 g, 73%). Pale-yellow oil. IR (film): 3383, 2956, 2928, 2889, 2856, 2178, 1464, 1367, 1294, 1250, 1133, 1089, 1042, 964, 839, 778, 761. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.12 (*dt*, *J* = 7.8, 1.8, 1 H); 4.37 (*d*, *J* = 1.8, 2 H); 2.17 (*d*, *J* = 7.8, 1 H); 0.91 (*s*, 9 H); 0.18 (*s*, 9 H); 0.13 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 101.6; 89.6; 83.2; 81.8; 52.5; 51.6; 25.7; 18.1; −0.5; −5.3. EI-MS: 296.1 (M^+). Anal. calc. for $C_{15}H_{28}O_2Si_2$ (296.6): C 60.75, H 9.52; found: C 60.94, H 9.42.

*6-[(*tert*-Butyl)dimethylsilyloxy]-1-(trimethylsilyl)hexa-1,4-diyn-3-one* (**18**). $BaMnO_4$ (0.79 g, 90% tech. grade, 2.75 mmol) was added in one portion to (±)-**17** (0.164 g, 0.55 mmol) in CH_2Cl_2 (7 ml) at r.t. After 3.5 h, the mixture was filtered through a pad of *Celite* with hexane/CH_2Cl_2 1:1 (200 ml). Concentration of the filtrate *in vacuo* provided **18** (0.152 g, 93%), which was of sufficient purity for subsequent transformations. FC (SiO_2; hexanes/CH_2Cl_2 7:3) provided a sample for anal. characterization. Yellow oil. IR (film): 2958, 2930, 2891, 2858, 2228, 2147, 2097, 1633, 1472, 1361, 1256, 1200, 1106, 983, 839, 778, 722. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.50 (*s*, 2 H); 0.92 (*s*, 9 H); 0.25 (*s*, 9 H); 0.15 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.2; 102.3; 99.6; 91.6; 84.9; 51.6; 25.6; 18.1; 1.1; −5.4. EI-MS: 294.0 (0.5, M^+), 237.1 (74, $[M - Me_3C]^+$), 209.1 (100, $[M - Me_3C - CO]^+$). The tendency for protodesilylation during purification precluded collection of accurate microanalysis data.

1-Chloro-4-(trimethylsilyl)but-3-yn-2-one (**19**) [31]. A soln. of Me_3Si–C≡C–$SiMe_3$ (2.24 ml, 10 mmol) and $ClCH_2COCl$ (0.80 ml, 10 mmol) in CH_2Cl_2 (10 ml) was added over 10 min at 0° to $AlCl_3$ (1.33 g, 10 mmol) in CH_2Cl_2 (20 ml). After stirring at r.t. for 30 min, 1M HCl (25 ml) were added at 0°. The mixture was extracted with Et_2O (3 × 50 ml) and the combined extracts were dried ($MgSO_4$). Evaporation *in vacuo* and bulb-to-bulb distillation gave **19** (1.36 g, 78%). Clear oil. R_f (SiO_2; hexane/AcOEt 10:1) 0.40. IR (film): 2964, 2892, 2155, 1698, 1677, 1398, 1254, 1215, 1106, 867, 847, 785, 763, 615. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.22 (*s*, 2 H); 0.26 (*s*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 178.3; 103.3; 99.9; 49.5; −1.0.

*(±)-2-[2-({[(*tert*-Butyl)dimethylsilyl]oxy}methyl)ethynyl]-2-[(trimethylsilyl)ethynyl]oxirane* ((±)-**16**). Method A: MeLi·LiBr (1.65 ml of a 1.5M soln. in Et_2O, 2.47 mmol) was added dropwise to **18** (519 mg, 1.77 mmol) and CH_2I_2 (185 µl, 2.29 mmol) in THF (6 mol) at −78°. The soln. was allowed to warm to r.t over 3 h and, after 1.5 h at r.t., it was poured into sat. aq. NH_4Cl soln. (10 ml). The phases were separated, and the aq. phase was extracted with Et_2O (3 × 20 ml). The combined org. phases were washed with sat. aq. NaCl soln. (10 ml), dried ($MgSO_4$), and concentrated *in vacuo*. FC (SiO_2; hexanes/CH_2Cl_2 7:3) provided relatively unstable (±)-**16** (212 mg, 39%), which slowly decomposed at −20° under N_2. Pale-yellow oil. IR (film): 2957, 2929, 2899, 2858, 2169, 1472, 1364, 1294, 1258, 1097, 1014, 931, 875, 839, 778, 761. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.34 (*s*, 2 H); 3.18–3.10 (*AB*, *J* = 6.6, 2 H); 0.91 (*s*, 9 H); 0.18 (*s*, 9 H); 0.13 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 100.2; 88.5; 81.6; 80.6; 57.2; 51.6; 39.7; 25.7; 18.1; −0.6; −5.3. EI-MS: 308.2 (1.5, M^+), 251.1 (93, $[M - Me_3C]^+$), 205.1 (100, $[M - Me_3C–CH_2O–O]^+$). Anal. calc. for $C_{16}H_{28}O_2Si_2$ (308.6): C 62.28, H 9.15; found: C 61.09, H 9.19.

Method B: BuLi (3.75 ml of a 1.6M soln. in hexane, 6.0 mmol) was added at −78° to (*t*-Bu)Me_2-$SiOCH_2$–C≡CH (1.02 g, 6.0 mmol) in THF (10 ml), and the soln. was stirred for 30 min at this temp. After rapid addition of **19** (874 mg, 5.0 mmol) in THF (2 ml) *via* syringe, the mixture was warmed to −40° over 30 min. Dry DMF (5 ml) and *t*-BuOK (280 mg, 2.5 mmol) were added, and the mixture darkened to deep reddish-brown as it was warmed to −20°. After stirring 30 min at −20°, the mixture was partitioned between sat. aq. NH_4Cl soln. (50 ml) and Et_2O (50 ml). The aq. phase was extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$) and evaporated *in vacuo*. FC (SiO_2; hexanes/AcOEt 20:1 → 10:1) provided (±)-**16** (357 mg, 23%) in addition to (±)-**20** (111 mg, 9%) and (±)-**21** (450 mg, 26%).

*(±)-3,5-Bis({[(*tert*-butyl)dimethylsilyl]oxy}methyl)-1,7-bis(trimethylsilyl)hepta-3,4-diene-1,6-diyne* ((±)-**15**). A soln. of (±)-**16** (62 mg, 0.20 mmol), Me_3Si–C≡CH (42 µl, 0.30 mmol) and $(i\text{-}Pr)_2NH$ (56 µl, 0.40 mmol) in CH_2Cl_2 (1.0 ml) was sparged with Ar. $[Pd(PPh_3)_4]$ (11.6 mg, 0.01 mmol) and CuI (3.8 mg, 0.02 mmol) were added sequentially with further sparging with Ar after each addition. After 1 h, 1*H*-imidazole (20 mg,

0.30 mmol) and (*t*-Bu)Me_2SiCl (39 mg, 0.26 mmol) were added sequentially. After 2 h, the mixture was filtered through *Celite* with hexanes and the filtrate evaporated *in vacuo*. FC (SiO_2; hexanes/CH_2Cl_2 4:1) provided (±)-**15** (66 mg, 63%). Clear oil. R_f (SiO_2; hexanes/AcOEt 4:1) 0.26. IR (film): 2958, 2929, 2897, 2856, 2151, 1944, 1472, 1360, 1251, 1111, 1006, 910, 841, 777, 759. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.20 (*s*, 4 H); 0.90 (*s*, 18 H); 0.17 (*s*, 18 H); 0.09 (*s*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$) 214.6; 98.8; 96.6; 95.6; 63.8; 25.8; 18.3; −0.2; −5.3; −5.4. EI-MS; 520.4 (M^+). Anal. calc. for $C_{27}H_{52}O_2Si_4$ (521.1): C 62.24, H 10.06; found: C 62.51, H 10.04.

(±)-1-(Triisopropylsilyl)non-1-yn-3-ol ((±)-**23**). BuLi (6.56 ml of a 1.6M soln. in hexane, 10.5 mmol) was added at −78° to (i-Pr)$_3$Si−C≡CH (2.24 ml, 10.0 mmol) in THF (10 ml). The mixture was stirred for 15 min at this temp., then warmed to r.t. and stirred for another 15 min. After recooling to −78°, heptanal (1.54 ml, 11.0 mmol) was added, and the mixture was stirred for 30 min at this temp. After warming to r.t., the mixture was partitioned between sat. aq. NH_4Cl soln. (25 ml) and Et_2O, the org. phase was extracted with Et_2O (25 ml), and the combined org. extracts were dried ($MgSO_4$). Evaporation *in vacuo* and bulb-to-bulb distillation gave (±)-**23** (2.33 g, 79%). Clear oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.31. IR (film): 3333, 2933, 2862, 2164, 1462, 1385, 1333, 1264, 1123, 1041, 1015, 995, 918, 877, 677. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.38 (*q*, *J* = 6.1, 1 H); 1.77–1.65 (*m*, 3 H); 1.51–1.28 (*m*, 8 H); 1.07 (*s*, 21 H); 0.89 (*t*, *J* = 6.6, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 109.1; 85.3; 63.0; 37.9; 31.7; 28.9; 25.1; 22.5; 18.5; 14.0; 11.1. EI-MS: 296 (M^+). Anal. calc. for $C_{18}H_{36}OSi$ (296.8): C 72.90, H 12.24; found: C 73.00, H 12.27.

1-(Triisopropylsilyl)non-1-yn-3-one (**24**). Me_2SO (0.65 ml, 9.1 mmol) was added at −78° to $(COCl)_2$ (0.65 ml, 7.3 mmol) in CH_2Cl_2 (15 ml), and the soln. was stirred for 10 min. A soln. of (±)-**23** (1.80 g, 6.07 mmol) in CH_2Cl_2 (5 ml) was added dropwise over 10 min and, after stirring for 10 min, Et_3N (2.54 ml, 18.2 mmol) was added. The mixture was stirred for 30 min at −78° and 30 min at r.t. before being diluted with CH_2Cl_2 (20 ml) and washed with sat. aq. NH_4Cl soln. (20 ml). Evaporation *in vacuo* left a residue, which was taken up in Et_2O (25 ml) and washed with H_2O (3 × 10 ml). Drying ($MgSO_4$) and evaporation *in vacuo* gave nearly pure **24** (1.70 g, 94%). Pale-yellow oil. R_f (SiO_2; hexanes/AcOEt 20:1) 0.44. IR (film) 2944, 2862, 2144, 1677, 1462, 1210, 1133, 1087, 1072, 1015, 995, 882, 677. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.55 (*t*, *J* = 7.5, 2 H); 1.73–1.62 (*m*, 2 H); 1.35–1.28 (*m*, 6 H); 1.11 (*s*, 3 H); 1.10 (*s*, 18 H); 0.88 (*t*, *J* = 6.4, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 188.1; 104.3; 95.3; 45.5; 31.4; 28.5; 24.1; 22.3; 18.3; 13.8; 10.9. EI-MS: 294 (M^+). Anal. calc. for $C_{18}H_{34}OSi$ (294.6): C 73.40, H 11.63; found: C 73.43, H 11.54.

(±)-3-Hexyl-1-(triisopropylsilyl)undeca-1,4-diyn-3-ol ((±)-**25**). BuLi (3.71 ml of a 1.6M soln. in hexane, 5.93 mmol) was added at −78° to oct-1-yne (0.84 ml, 5.68 mmol) in THF (10 ml). After 15 min, the mixture was warmed to r.t. and stirred for additional 15 min. After recooling to −78°, **24** (1.52 g, 5.16 mmol) in THF (5 ml) was added, and the mixture was stirred for 30 min. After warming to r.t., the mixture was partitioned between sat. aq. NH_4Cl soln. (50 ml) and Et_2O (50 ml), the aq. phase was extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 20:1) gave (±)-**25** (1.37 g, 66%). Clear oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.32. IR (film): 3456, 2933, 2862, 2236, 2164, 1467, 1379, 1323, 1067, 995, 877, 672. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.35 (*s*, 1 H); 2.24 (*t*, *J* = 6.8, 2 H); 1.93–1.84 (*m*, 2 H); 1.65–1.23 (*m*, 16 H); 1.10 (*s*, 21 H); 0.91 (*t*, *J* = 6.9, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 108.5; 84.1; 83.5; 81.1; 64.1; 44.0; 31.6; 31.2; 28.9; 28.3; 24.6; 22.4; 18.5; 18.4; 13.9; 11.0 (3 resonances missing due to overlap). EI-MS: 404 (M^+). Anal. calc. for $C_{26}H_{48}OSi$: C 77.16, H. 11.95; found: C 76.87, H 11.77.

(±)-1-Hexyl-1-[(triisopropylsilyl)ethynyl]non-2-ynyl Acetate ((±)-**26**). Ac_2O (0.28 ml, 3.0 mmol) was added at 0° to (±)-**25** (405 mg, 1.0 mmol), Et_3N (0.7 ml, 5.0 mmol), and DMAP (*ca.* 5 mg) in CH_2Cl_2 (3 ml). The mixture was stirred at r.t. for 12 h and then partitioned between sat. aq. NH_4Cl soln. (20 ml) and Et_2O (20 ml). The aq. phase was extracted with Et_2O (2 × 20 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 20:1) gave (±)-**26** (308 mg, 69%). Clear oil. R_f (SiO_2; hexanes/AcOEt 20:1) 0.30. IR (film): 2933, 2862, 2246, 2164, 1759, 1462, 1364, 1221, 1072, 1010, 918, 882, 677. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.21 (*t*, *J* = 6.9, 2 H); 2.05–1.97 (*m*, 2 H); 2.03 (*s*, 3 H); 1.64–1.18 (*m*, 16 H); 1.06 (*s*, 21 H); 0.91–0.85 (*m*, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.0; 104.6; 85.7; 85.6; 77.8; 68.4; 42.7; 31.6; 31.2; 28.8; 28.3; 28.2; 24.2; 22.4; 21.4; 18.6; 18.4; 13.9; 11.1 (2 resonances missing due to overlap). EI-MS: 446 (M^+). Anal. calc. for $C_{28}H_{50}O_2Si$ (446.8): C 75.27, H 11.28; found: C 75.26, H 11.14.

(±)-1-Hexyl-1-[(triisopropylsilyl)ethynyl]non-2-ynyl Methyl Carbonate ((±)-**27**). BuLi (0.34 ml of a 1.6M soln. in hexane, 0.55 mmol) was added at −78° to (±)-**25** (202 mg, 0.50 mmol) in THF (2 ml). After stirring for 15 min at this temp., MeOCOCl (58 µl, 0.75 mmol) was added, and the mixture was stirred at r.t. for 30 min. The mixture was partitioned between H_2O (25 ml) and Et_2O (25 ml), the aq. phase was extracted with Et_2O (2 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 20:1) gave (±)-**27** (165 mg, 71%). Clear oil. R_f (SiO_2; hexanes/AcOEt 20:1) 0.34. IR (film): 2934, 2862, 2247, 2174, 1770, 1464, 1436, 1253, 1144, 1075, 997, 952, 883, 788, 678. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.78 (*s*, 3 H);

2.24 (*t*, *J* = 7.2, 2 H); 2.09–2.01 (*m*, 2 H); 1.67–1.28 (*m*, 16 H); 1.09 (*s*, 21 H); 0.90 (*t*, *J* = 6.6, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.9; 104.0; 86.3; 77.3; 71.0; 54.4; 42.9; 31.6; 31.2; 28.7; 28.3; 28.1; 24.2; 22.4; 18.6; 18.4; 13.9; 11.0 (3 resonances missing due to overlap). EI-MS: 462 (M^+). Anal. calc. for $C_{28}H_{50}O_3Si$ (462.8): C 72.67, H 10.89; found: C 72.77, H 10.84.

(±)-3,5-Dihexyl-1,7-bis(triisopropylsilyl)hepta-3,4-diene-1,6-diyne ((±)-**22**). A soln. of (±)-**27** (46 mg, 0.10 mmol), (i-Pr)$_3$Si–C≡CH (34 µl, 0.15 mmol) and (i-Pr)$_2$NH (28 µl, 0.20 mmol) in CH_2Cl_2 (1.0 ml) was sparged with Ar. [Pd(PPh$_3$)$_4$] (5.8 mg, 5.0 µmol) and CuI (1.9 mg, 10 µmol) were added sequentially with further sparging with Ar after each addition. After stirring for 30 min, the yellow soln. was diluted with hexanes and filtered through SiO_2. Evaporation *in vacuo* and FC (SiO_2; hexanes) provided (±)-**22** (54 mg, 94%). Clear oil. R_f (SiO_2; hexanes) 0.60. IR (film): 2927, 2851, 2133, 1933, 1464, 1380, 1154, 1072, 990, 883, 672. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.15 (*t*, *J* = 7.1, 4 H); 1.58–1.43 (*m*, 4 H); 1.40–1.22 (*m*, 12 H); 1.07 (*s*, 42 H); 0.88 (*t*, *J* = 6.6, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 216.2; 101.7; 92.6; 91.8; 34.1; 31.6; 28.2; 27.4; 22.4; 18.5; 14.0; 11.2. EI-MS: 568.6 (M^+). Anal. calc. for $C_{37}H_{68}Si_2$ (569.1): C 78.09, H 12.04; found: C 78.22, H 12.08.

N-*Methoxy*-N-*methyl-2-(4-methoxyphenyl)acetamide* (**30**). Pyridine (1.45 ml, 18.0 mmol) was added *via* syringe to 2-(4-methoxyphenyl)acetyl chloride (1.22 ml, 8.0 mmol) and *N,O*-dimethylhydroxylamine hydrochloride (878 mg, 0.9 mmol) at 0° in CH_2Cl_2. After stirring for 1 h at r.t., the mixture was taken up in H_2O (25 ml) and Et_2O (25 ml). The aq. phase was extracted with Et_2O (3 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and bulb-to-bulb distillation provided **30** (1.48 g, 88%). Clear oil. R_f (SiO_2; hexanes/AcOEt 1:1) 0.27. IR (film): 2933, 2831, 1662, 1610, 1508, 1462, 1380, 1246, 1174, 1031, 1005, 821, 790. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.25–7.19 (*m*, 2 H); 6.87–6.83 (*m*, 2 H); 3.77 (*s*, 3 H); 3.70 (*s*, 2 H); 3.60 (*s*, 3 H); 3.17 (*s*, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 172.7; 158.5; 130.2; 126.9; 113.8; 61.1; 55.0; 38.2; 32.0. EI-MS: 209 (M^+). Anal. calc. for $C_{11}H_{15}NO_3$ (209.2): C 63.14, H 7.23, N 6.69; found: C 63.11, H 7.14, N 6.70.

1,5-Bis(4-methoxyphenyl)pent-3-yn-2-one (**31**). BuLi (4.69 ml of a 1.6M soln. in hexane, 7.5 mmol) was added at −78° to **29** [33] (1.02 g, 7.0 mmol) in THF (15 ml). After stirring for 15 min at this temp. and 15 min at r.t., the mixture was recooled to −78° and **30** (1.36 g, 6.5 mmol) in THF (2 ml) was added dropwise *via* syringe. The mixture was immediately brought to 0° and, after stirring for 1 h, warmed to r.t. The mixture was partitioned between sat. aq. NH_4Cl soln. (25 ml) and Et_2O (25 ml), the aq. phase was extracted with Et_2O (2 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 5:1) gave **31** (1.28 g, 67%). Pale-yellow oil which eventually solidified. R_f (SiO_2; hexanes/AcOEt 5:1) 0.21. M.p. 76.5–77°. IR (film): 2995, 2954, 2841, 2210, 1667, 1611, 1513, 1456, 1303, 1250, 1178, 1033, 818. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.19–7.06 (*m*, 4 H); 6.91–6.79 (*m*, 4 H); 3.80 (*s*, 6 H); 3.77 (*s*, 2 H); 3.66 (*s*, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 185.5; 158.9; 158.7; 130.8; 128.9; 126.1; 125.1; 114.1; 114.0; 93.4; 81.9; 55.2; 55.1; 51.2; 24.3. EI-MS: 294 (100, M^+). Anal. calc. for $C_{19}H_{18}O_3$ (294.4): C 77.53, H 6.16; found: C 77.26, H 6.42.

(±)-3-(4-Methoxybenzyl)-6-(4-methoxyphenyl)-1-(triisopropylsilyl)hexa-1,4-diyn-3-ol ((±)-**32**). BuLi (2.28 ml of a 1.6M soln. in hexane, 3.64 mmol) was added at −78° to (i-Pr)$_3$Si–C≡CH (0.75 ml, 3.36 mmol) in THF (10 ml). After 15 min, the mixture was warmed to r.t. and stirred for an additional 15 min. After recooling to −78°, **31** (825 mg, 2.80 mmol) in THF (2 ml) was added *via* syringe, and the mixture was stirred for 30 min. After warming to r.t., the mixture was partitioned between sat. aq. NH_4Cl soln. (25 ml) and Et_2O (25 ml), the aq. phase was extracted with Et_2O (3 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 10:1) gave (±)-**32** (750 mg, 56%) besides recovered **31** (190 mg). Pale-yellow oil. R_f (SiO_2; hexanes/AcOEt 5:1) 0.26. IR (film): 3448, 2943, 2865, 2236, 2164, 1611, 1513, 1464, 1249, 1177, 1036, 883, 824, 672. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.29 (*d*, *J* = 8.7, 2 H); 7.19 (*d*, *J* = 8.7, 2 H); 6.83 (*d*, *J* = 8.7, 2 H); 6.80 (*d*, *J* = 8.7, 2 H); 3.80 (*s*, 3 H); 3.79 (*s*, 3 H); 3.57 (*s*, 2 H); 3.16 (*s*, 2 H); 2.58 (br. *s*, 1 H); 1.06 (*s*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.0; 158.5; 132.1; 129.0; 128.3; 127.3; 113.9; 113.4; 107.5; 85.2; 83.0; 82.6; 64.2; 55.2; 55.1; 48.8; 24.0; 18.4; 11.0. EI-MS: 476 (M^+). HR-MALDI-MS: 499.2644 ([M + Na]$^+$, $C_{30}H_{40}NaO_3Si^+$; calc. 499.2644).

(±)-1-(4-Methoxybenzyl)-4-(4-methoxyphenyl)-1-[(triisopropylsilyl)ethynyl]but-2-ynyl Methyl Carbonate ((±)-**33**). LHMDS (1.20 ml of a 1M soln. in hexane, 1.20 mmol) was added at −78° to (±)-**32** (477 mg, 1.00 mmol) in THF (5 ml). After stirring for 30 min at this temp., MeOCOCl (100 µl, 1.30 mmol) was added *via* syringe. The mixture was warmed to r.t. and, after 30 min, partitioned between sat. aq. NH_4Cl soln. (25 ml) and Et_2O (25 ml). The aq. phase was extracted with Et_2O (2 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 10:1) gave (±)-**33** (380 mg, 71%). Pale-yellow syrup. R_f (SiO_2; hexanes/AcOEt 5:1) 0.32. IR (film): 2943, 2862, 2246, 2174, 1766, 1610, 1513, 1462, 1436, 1248, 1174, 1031, 990, 677. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.27 (*d*, *J* = 8.3, 2 H); 7.16 (*d*, *J* = 8.3, 2 H); 6.82 (*d*, *J* = 8.7, 2 H); 6.77 (*d*, *J* = 8.7, 2 H); 3.80 (*s*, 3 H); 3.78 (*s*, 3 H); 2.77 (*s*, 3 H); 3.57 ('*s*', 2 H); 3.31 ('*s*', 2 H); 1.05 (*s*, 21 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 159.0; 158.4; 152.9; 132.3; 129.0; 128.0; 126.5; 113.8; 113.2; 103.2; 88.0; 85.2; 79.0;

70.9; 55.2; 55.1; 54.5; 47.4; 24.1; 18.4; 11.0. EI-MS: 534.3 (M^+). HR-MALDI-MS: 459.2717 ([M – MeOOCO]$^+$, $C_{30}H_{39}O_2Si^+$; calc. 459.2719).

(±)-3,5-Bis(4-methoxybenzyl)-1,7-bis(triisopropylsilyl)hepta-3,4-diene-1,6-diyne ((±)-**28**). A soln. of (±)-**33** (160 mg, 0.30 mmol), (i-Pr)$_3$Si–C≡CH (101 µl, 0.45 mmol), and (i-Pr)$_2$NH (84 µl, 0.60 mmol) in CH_2Cl_2 (1.5 ml) was sparged with Ar. [Pd(PPh$_3$)$_4$] (17.3 mg, 15.0 µmol) and CuI (5.7 mg, 30 µmol) were added sequentially with further sparging with Ar after each addition. After stirring for 1 h, the yellow soln. was diluted with hexanes and filtered through *Celite*. Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 20:1) provided (±)-**28** (100 mg, 52%). Clear oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.47. IR (film): 2943, 2851, 2133, 1939, 1611, 1512, 1464, 1303, 1248, 1174, 1039, 883, 815, 677. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.00 (*d*, *J* = 8.7, 4 H); 6.75 (*d*, *J* = 8.7, 4 H); 3.78 (*s*, 6 H); 3.34 ('*s*', 2 H); 3.33 ('*s*', 2 H); 1.03 (*s*, 42 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 216.9; 158.4; 130.2; 130.0; 113.6; 101.0; 93.9; 93.2; 55.1; 39.8; 18.4; 11.1. EI-MS: 640.3 (M^+). HR-EI-MS: 640.4129 (M^+, $C_{41}H_{60}O_2Si_2^+$; calc. 640.4132).

1,3-(Diphenyl)prop-2-yn-1-one (**35**) [34]. BuLi (6.88 ml of a 1.6M soln. in hexane, 11.0 mmol) was added at –78° to phenylacetylene (1.10 ml, 10.0 mmol) in THF (20 ml). After 15 min, the mixture was warmed to r.t. and stirred for additional 15 min. After recooling to –78°, PhCHO (1.22 ml, 12.0 mmol) was added *via* syringe. After warming to r.t. and stirring for 30 min, the mixture was partitioned between sat. aq. NH_4Cl soln. (50 ml) and Et_2O (50 ml). The aq. phase was extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* provided the propargyl alcohol (2.30 g) containing an excess of PhCHO. The alcohol was dissolved in Et_2O (20 ml), and MnO_2 (5.0 g) was added at r.t. After stirring for 3 h, the mixture was filtered through *Celite* with Et_2O, and the filtrate was dried ($MgSO_4$). Evaporation *in vacuo* and application of high vacuum (10^{-2} Torr) overnight gave **35** (2.05 g, 99%) as a liquid, which, on storage, crystallized. Pale-yellow solid. R_f (SiO_2; hexanes/AcOEt 5:1) 0.42. M.p. 45–47°. IR (film): 2199, 1642, 1600, 1580, 1490, 1450, 1316, 1286, 1209, 1172, 1012, 996, 758, 698. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.25–8.20 (*m*, 2 H); 7.69–7.36 (*m*, 8 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 177.8; 136.7; 134.0; 132.9; 130.7; 129.4; 128.54; 128.48; 119.9; 92.9; 86.8.

(±)-1,3-Diphenyl-5-(triisopropylsilyl)penta-1,4-diyn-3-ol ((±)-**36**). BuLi (3.75 ml of a 1.6M soln. in hexane, 6.0 mmol) was added at –78° to (i-Pr)$_3$Si–C≡CH (1.23 ml, 5.5 mmol) in THF (10 ml). After 15 min, the mixture was warmed to r.t. and stirred for an additional 15 min. After recooling to –78°, **35** (1.03 g, 5.0 mmol) in THF (5 ml) was added *via* syringe. After warming to r.t. and stirring for 30 min, the mixture was partitioned between sat. aq. NH_4Cl soln. (50 ml) and Et_2O (50 ml). The aq. phase was extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 10:1) gave (±)-**36** (1.79 g, 92%). Clear oil. R_f (SiO_2; hexanes/AcOEt 5:1) 0.43. IR (film): 3539, 3447, 3067, 2943, 2865, 2226, 2174, 1490, 1450, 1063, 1015, 940, 883, 756, 693. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.97–7.92 (*m*, 2 H); 7.53–7.33 (*m*, 8 H); 3.01 (*s*, 1 H); 1.16 (*s*, 21 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 141.9; 131.9; 128.8; 128.6; 128.5; 128.3; 126.0; 122.2; 107.0; 89.4; 87.1; 84.7; 65.8; 18.5; 11.1. EI-MS: 388 (M^+). Anal. calc. for $C_{26}H_{32}OSi$ (388.6): C 80.36, H 8.30; found: C 80.45, H 8.32.

(±)-3,5-Diphenyl-1,7-bis(triisopropylsilyl)hepta-3,4-diene-1,6-diyne ((±)-**34**). BuLi (0.46 ml of a 1.6M soln. in hexane, 0.75 mmol) was added at –78° to (±)-**36** (194 mg, 0.50 mmol) in THF (5 ml). After 15 min, the mixture was warmed to r.t. and stirred for additional 15 min. PhCOCl (58 µl, 0.50 mmol) was added, and stirring was continued for 30 min. Subsequently, (i-Pr)$_3$Si–C≡CH (168 µl, 0.75 mmol) and (i-Pr)$_2$NH (140 µl, 1.00 mmol) were added, and the soln. was purged with Ar. [Pd(PPh$_3$)$_4$] (29 mg, 25.0 µmol) and CuI (9.5 mg, 50 µmol) were added sequentially with further sparging with Ar after each addition. After heating to reflux for 3 h in a preheated oil bath, the mixture was diluted with hexane and filtered through *Celite*. The bulk of the solvent was evaporated *in vacuo* at r.t. and in the absence of light, and the residual few ml were quickly removed under high vacuum (10^{-2} Torr). The residue was immediately purified by FC (SiO_2; hexanes/CH_2Cl_2 10:1) to give, after solvent evaporation as above, (±)-**34** (48 mg) and dimeric material (58 mg; 38% total cross-coupled product). Immediate characterization of (±)-**34** was required. R_f (SiO_2; hexanes/AcOEt 10:1) 0.65. IR (film): 2944, 2862, 2144, 1944, 1595, 1492, 1462, 1385, 1241, 1062, 990, 882, 759, 676. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.65–7.62 (*m*, 2 H); 7.40–7.27 (*m*, 8 H); 1.15 (*s*, 42 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 222.6; 132.7; 128.7; 128.2; 126.8; 98.7; 97.6; 97.3; 18.5; 11.2. EI-MS (dimer): 1104.7 (M^+). Anal. calc. for $C_{74}H_{104}Si_4$ (1106.0; dimer): C 80.36, H 9.48; found: C 80.17, H 9.34.

2,2,6,6-Tetramethylhepta-4-yn-3-one (**39**) [35]. BuLi (3.43 ml of a 1.6M soln. in hexane, 5.5 mmol) was added at –78° to 3,3-dimethylbut-1-yne (0.62 ml, 5.0 mmol) in THF (5 ml). After 15 min, the mixture was warmed to r.t. and stirred for an additional 15 min. After recooling to –78°, the soln. was transferred dropwise *via* cannula into a rapidly stirring soln. of *t*-BuCOCl (1.85 ml, 15 mmol) and CuCl (50 mg, 0.5 mmol) in THF (10 ml) at –78°. The mixture was stirred for 30 min at this temp., then warmed to 0°. Sat. aq. $NaHCO_3$ soln. (10 ml) was added, and the mixture was extracted with Et_2O (4 × 25 ml). The combined org. phases were

washed with sat. aq. $NaHCO_3$ soln. (50 ml) and dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 20:1) gave **39** (575 mg, 69%). Clear volatile oil. R_f (SiO_2; hexanes/AcOEt 20:1) 0.31. IR (film): 2972, 2872, 2205, 1728, 1674, 1478, 1456, 1365, 1278, 1251, 1200, 1113, 1015, 900, 749. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.29 (*s*, 9 H); 1.18 (*s*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 194.6: 103.0; 77.1; 44.6; 30.0; 27.8; 26.1.

*(±)-3-(*tert*-Butyl)-6,6-dimethyl-1-(triisopropylsilyl)hepta-1,4-diyn-3-ol* ((±)-**40**). BuLi (2.59 ml of a 1.6M soln. in hexane, 4.15 mmol) was added at −78° to (i-Pr)$_3$Si−C≡CH (0.85 ml, 3.80 mmol) in THF (5 ml). After stirring for 15 min, the mixture was warmed to r.t. and stirred for an additional 15 min. The soln. was recooled to −78°, and **39** (575 mg, 3.46 mmol) in THF (2 ml) was added *via* syringe. After 15 min, the mixture was allowed to warm to r.t. and was partitioned between conc. aq. NH_4Cl soln. (50 ml) and Et_2O (50 ml). The aq. phase was extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* gave anal. pure (±)-**40** (1.07 g, 89%). Clear oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.44. IR (film): 3467, 2967, 2236, 2164, 1459, 1363, 1261, 1123, 1072, 1005, 973, 883, 749, 672. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.23 (br. *s*, 1 H); 1.21 (*s*, 9 H); 1.11 (*s*, 9 H); 1.08 (*s*, 21 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 107.7; 92.6; 84.3; 78.7; 71.0; 39.7; 30.7; 27.5; 24.8; 18.6; 11.2. EI-MS: 348.3 (M^+). Anal. calc. for $C_{22}H_{40}OSi$ (348.7): C 75.79, H 11.56; found: C 75.64, H 11.64.

*(±)-1-(*tert*-Butyl)-4,4-dimethyl-1-[(triisopropylsilyl)ethynyl]pent-2-ynyl Methyl Carbonate* ((±)-**38**). LHMDS (1.76 ml of a 1M soln. in hexane, 1.76 mmol) was added at −78° to (±)-**40** (560 mg, 1.60 mmol) in THF (5 ml). After stirring for 15 min at this temp. and 15 min at r.t., the soln. was recooled to −78° and MeOCOCl (148 µl, 1.92 mmol) was added *via* syringe. After 15 min, the mixture was warmed to r.t. and, after 30 min, partitioned between sat. aq. NH_4Cl soln. (25 ml) and Et_2O (25 ml). The aq. phase was extracted with Et_2O (2 × 25 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexanes/AcOEt 20:1) gave (±)-**38** (610 mg, 94%). Colorless crystalline solid. R_f (SiO_2; hexanes/AcOEt 10:1) 0.55. IR (film): 2966, 2862, 2236, 2174, 1769, 1462, 1436, 1364, 1254, 1149, 1072, 964, 908, 877, 672. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.76 (*s*, 3 H); 1.21 (*s*, 9 H); 1.15 (*s*, 9 H); 1.07 (*s*, 21 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.9; 103.1; 94.5; 86.9; 77.3; 75.0; 54.3; 40.4; 30.5; 27.5; 24.8; 18.5; 11.2. EI-MS: 406.4 (M^+). Anal. calc. for $C_{24}H_{42}O_3Si$ (406.7): C 70.88, H 10.41; found: C 70.84, H 10.40.

*(±)-3,5-Di(*tert*-butyl)-1,7-bis(triisopropylsilyl)hepta-3,4-diene-1,6-diyne* ((±)-**41**). A soln. of (±)-**38** (203 mg, 0.50 mmol), (i-Pr)$_3$Si−C≡CH (168 µl, 0.75 mmol), and (i-Pr)$_2$NH (140 µl, 1.00 mmol) in $(CH_2Cl)_2$ (2.5 ml) was sparged with Ar. [Pd(PPh$_3$)$_4$] (58 mg, 50 µmol) and CuI (9.5 mg, 50 µmol) were added sequentially with further sparging with Ar. An Ar-flushed reflux condenser was added, and the dark-purple mixture was heated to 70° in a preheated oil bath. After 1 h, conversion was less than 50%, but the Pd appeared to have precipitated almost entirely as a black solid, so the reaction was halted to prevent oxidative dimerization of (i-Pr)$_3$Si−C≡CH. The mixture was filtered through *Celite* with hexanes, and evaporation *in vacuo*, followed by FC (SiO_2; hexanes), provided (±)-**41** (82 mg, 32%) besides 132 mg recovered (±)-**38**. Colorless crystalline solid. R_f (SiO_2; hexanes) 0.60. M.p. 106.5–107°. IR (film): 2963, 2866, 2141, 1460, 1359, 1241, 1118, 1072, 990, 882, 754, 718, 677. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.13 (*s*, 18 H); 1.08 (*s*, 42 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 213.3; 103.4; 100.6; 93.8; 35.2; 28.8; 18.5; 11.2. EI-MS: 512.3 (M^+). Anal. calc. for $C_{33}H_{60}Si_2$ (513.0): C 77.26, H 11.79; found: C 77.05, H 11.89.

*(±)-3-(*tert*-Butyl)-6,6-dimethyl-1-(trimethylsilyl)hepta-1,4-diyn-3-ol* ((±)-**43**). BuLi (5.0 ml of a 1.6M soln. in hexane, 8.0 mmol) was added at −78° to Me$_3$Si−C≡CH (1.06 ml, 7.5 mmol) in THF (10 ml). After stirring for 15 min, the mixture was warmed to r.t. and stirred for additional 15 min. The soln. was recooled to −78°, and crude **39** (737 mg, 4.43 mmol) in THF (2 ml) was added *via* syringe. After 15 min, the mixture was allowed to warm to r.t. and was partitioned between conc. aq. NH_4Cl soln. (50 ml) and Et_2O (50 ml). The aq. phase was extracted with Et_2O (3 × 50 ml), and the combined org. phases were dried ($MgSO_4$). Evaporation *in vacuo* followed by FC (SiO_2; hexanes/AcOEt 10:1) gave (±)-**43** (950 mg, 72% (including the preparation of crude **39**). White waxy solid. M.p. 31–32.5°. R_f (SiO_2; hexanes/AcOEt 10:1) 0.36. IR (film): 3477, 2969, 2903, 2882, 2236, 2164, 1477, 1456, 1363, 1251, 1072, 973, 862, 843, 760. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.25 (*s*, 1 H); 1.22 (*s*, 9 H); 1.09 (*s*, 9 H); 0.17 (*s*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 105.5; 92.7; 87.8; 78.4; 70.9; 39.9; 30.7; 27.3; 24.7; −0.2. EI-MS: 249.3 ([M − Me]$^+$). Anal. calc. for $C_{16}H_{28}OSi$ (264.5): C 72.66, H 10.67; found: C 72.69, H 10.70.

*(±)-1-(*tert*-Butyl)-4,4-dimethyl-1-[(trimethylsilyl)ethynyl]pent-2-ynyl Methyl Carbonate* ((±)-**42**). LHMDS (1.1 ml, 1.1 mmol) was added at −78° to (±)-**43** (264 mg, 1.0 mmol) in THF (2 ml). Reaction with MeOCOCl (93 µl, 1.2 mmol) and workup as described for (±)-**38** afforded (±)-**42** (290 mg, 90%). Colorless crystalline solid. R_f (SiO_2; hexanes/AcOEt 10:1) 0.41. M.p. 55–56°. IR (film): 2970, 2892, 2872, 2246, 2164, 1770, 1440, 1364, 1253, 1152, 1074, 963, 909, 862, 844. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.76 (*s*, 3 H); 1.21 (*s*, 9 H); 1.12 (*s*, 9 H); 0.16 (*s*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 153.0; 101.2; 94.4; 90.0; 77.1; 74.6; 54.3; 40.8; 30.5; 27.4; 24.8; −0.3. EI-MS: 322.2 (M^+). Anal. calc. for $C_{18}H_{30}O_3Si$ (322.5): C 67.03, H 9.38; found: C 67.12, H 9.38.

*(±)-5-(*tert*-Butyl)-8,8-dimethyl-1,3-bis(trimethylsilyl)nona-3,4-diene-1,6-diyne* ((±)-**44**) and *(±)-3,5-Di-(*tert*-butyl)-1,7-bis(trimethylsilyl)hepta-3,4-diene-1,6-diyne* ((±)-**45**). A soln. of (±)-**42** (161 mg, 0.50 mmol), $Me_3Si-C\equiv CH$ (106 µl, 0.75 mmol), and $(i\text{-}Pr)_2NH$ (140 µl, 1.00 mmol) in $(CH_2Cl)_2$ (2.5 ml) was sparged with Ar. $[Pd(PPh_3)_4]$ (58 mg, 50 µmol) and CuI (9.5 mg, 50 µmol) were added sequentially with further sparging with Ar. An Ar-flushed reflux condenser was added, and the dark-purple mixture was heated to 70° in a preheated oil bath. After 1 h, the mixture was filtered through *Celite* with hexanes. Evaporation *in vacuo* and FC (SiO_2; hexanes) provided (±)-**44** and (±)-**45** as a 5:2 mixture (ratio from ^{1}H-NMR; 123 mg, 71% combined yield). Careful additional FC (SiO_2; hexanes) allowed partial separation of the isomers for anal. purposes.

Data of (±)-**44**: Colorless oil. R_f (SiO_2; hexanes) 0.29. IR (film): 2966, 2903, 2872, 2135, 1913, 1477, 1460, 1362, 1250, 1051, 843, 758, 698, 638. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.23 (*s*, 9 H); 1.09 (*s*, 9 H); 0.18 (*s*, 9 H); 0.17 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 216.7; 103.2; 99.0; 97.5; 96.2; 86.9; 71.5; 34.5; 31.0; 29.0; 28.2; 0.0; −2.0. EI-MS: 344.2 (M^+). Anal. calc. for $C_{21}H_{36}Si_2$ (344.7): C 73.18, H 10.53; found: C 73.28, H 10.40.

Data of (±)-**45**: White Solid. R_f (SiO_2; hexanes) 0.32. M.p. 55–56°. IR (film): 2964, 2892, 2871, 2142, 1917, 1476, 1460, 1363, 1249, 1116, 1082, 842, 758, 699, 639. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.12 (*s*, 18 H); 0.18 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 212.2; 103.4; 98.6; 97.8; 35.4; 28.8; −0.1. EI-MS: 344.2 (M^+). Anal. calc. for $C_{21}H_{36}Si_2$ (344.7): C 73.18, H 10.53; found: C 73.20, H 10.60.

(±)-2,4-Bis[(triisopropylsilyl)ethynyl]pent-2,3-diene-1,5-diyl Bis(2,2-dimethylpropionate) ((±)-**47**). To (±)-**8** (245 mg, 0.36 mmol) in Et_2O (3 ml) and MeOH (50 ml), a catal. amount of TsOH was added. After 2 h at r.t., the mixture was poured into sat. aq. $NaHCO_3$ soln. and extracted with Et_2O (70 ml). After careful evaporation *in vacuo* and rapid exposure to high vacuum, the resulting oil (crude (±)-**46**) was immediately taken up in CH_2Cl_2 (12 ml). The soln. was cooled to 0°, and Et_3N (0.75 ml, 5.4 mmol) and *t*-BuCOCl (0.64 ml, 5.2 mmol) were added. After 5 h at r.t., the mixture was washed with sat. aq. NH_4Cl soln. (2 × 20 ml). The org. phase was dried (filtered through cotton wool) and concentrated *in vacuo*. FC (SiO_2; hexane/CH_2Cl_2 1:1) gave (±)-**47** (111 mg, 49%). Unstable colorless oil. R_f (SiO_2; hexane/AcOEt 20:1) 0.30. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.61 (*s*, 4 H); 1.21 (*s*, 18 H); 1.07 (*s*, 42 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 214.6; 177.3; 96.7; 96.6; 92.5; 62.9; 38.8; 27.2; 18.6; 11.3. EI-MS: 627.7 (<1, $[M-H]^+$), 57.1 (100, Me_3C^+).

*(±)-3,5-Di(*tert*-butyl)-1-(triisopropylsilyl)-7-(trimethylsilyl)hepta-3,4-diene-1,6-diyne* ((±)-**48**). A soln. of (±)-**38** (0.60 g, 1.48 mmol) in $(i\text{-}Pr)_2EtN$ (5 ml) and $(CH_2Cl)_2$ (5 ml) was sparged with Ar. $[Pd(PPh_3)_4]$ (0.17 g, 0.15 mmol), CuI (0.03 g, 0.15 mmol), and a first portion of $Me_3Si-C\equiv CH$ (0.1 ml, 0.71 mmol) were added sequentially with further Ar-sparging after each addition. An Ar-flushed reflux condenser was added, and the dark mixture was heated to 80° in a preheated oil bath. During the reaction, additional $Me_3Si-C\equiv CH$ (0.6 ml, 4.20 mmol) was added in portions of 0.1 or 0.05 ml. After 5 h, the mixture was diluted with hexanes (100 ml), filtered through *Celite*, and concentrated *in vacuo*. FC (SiO_2; hexanes) yielded a pale-yellow oil. For anal. characterization, $Me_3Si-C\equiv C-C\equiv C-SiMe_3$, formed by oxidative homocoupling, was partially separated by careful FC (*ca.* 72% estimated yield of (±)-**48** determined by ^{1}H-NMR integration after subtracting the amount of butadiyne). R_f (SiO_2; hexane) 0.40. UV/VIS (cyclohexane): 201 (24100), 236 (39700), 246 (41500). IR (film): 2963, 2866, 2141, 1460, 1391, 1362, 1250, 1117, 1084, 996, 874, 842, 760, 714, 675. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*, 9 H); 1.12 (*s*, 9 H); 1.08 (*s*, 21 H); 0.20 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 212.0; 103.7; 102.8; 100.3; 97.5; 94.0; 35.6; 35.4; 28.9 (2×); 18.7; 11.4; 0.2. EI-MS: 428.4 (17, M^+), 385.4 (100, $[M-Pr]^+$), 372.4 (64, $[M-Me_3C]^+$). Anal. calc. for $C_{27}H_{48}Si_2$ (428.9): C 75.62, H 11.28; found: C 75.68, H 11.37.

*(±)-3,5-Di(*tert*-butyl)-1-(triisopropylsilyl)hepta-3,4-diene-1,6-diyne* ((±)-**49**). To (±)-**48** (243 mg, 0.57 mmol) in THF (6 ml), K_2CO_3 (88 mg, 0.64 mmol) and MeOH (6 ml) were added, and the mixture was stirred at r.t. for 2 h under N_2. The soln. was diluted with CH_2Cl_2 and washed with sat. aq. NH_4Cl soln. The org. layer was filtered through cotton wool and evaporated *in vacuo*. The resulting pale-yellow oil was purified *via* FC (SiO_2; hexanes) to give (±)-**49** (157 mg, 57% from (±)-**38**). Colorless oil. R_f (SiO_2; hexanes) 0.32. UV/VIS (hexane): 198 (sh, 18100), 225 (30300), 233 (34600), 243 (sh, 19400). IR (film): 3314, 2964, 2866, 2143, 1461, 1392, 1362, 1243, 1223, 1108, 1070, 1018, 996, 883, 864, 756, 679, 641. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.98 (*s*, 1 H); 1.14 (*s*, 9 H); 1.14 (*s*, 9 H); 1.08 (*s*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 212.3; 104.1; 101.7; 99.9; 94.3; 80.1; 77.6; 35.4; 35.4; 29.0; 28.9; 18.8; 11.4. EI-MS: 356.3 (14, M^+), 313.2 (100, $[M-Pr]^+$). Anal. calc. for $C_{24}H_{40}Si$ (356.67): C 80.82, H 11.30; found: C 80.94, H 11.29.

*3,5,10,12-Tetrakis(*tert*-butyl)-1,14-bis(triisopropylsilyl)tetradeca-3,4,10,11-tetraene-1,6,8,13-tetrayne* (**50**). To (±)-**49** (21 mg, 0.059 mmol) in $CHCl_3$ (3 ml), a few grains of molecular sieves (4 Å), TMEDA (13 µl, 0.082 mmol), and CuCl (3 mg, 0.030 mmol) were added. The mixture was stirred at r.t. under air, while evaporated solvent was replaced. After 30 h, CH_2Cl_2 (25 ml) was added, and the mixture was washed with sat. aq. NH_4Cl soln. (3 × 20 ml). The org. layer was filtered through cotton wool and concentrated *in vacuo*. FC (SiO_2; hexanes) yielded **50** (15 mg, 72%). White solid. R_f (SiO_2; hexane) 0.49. M.p. 110–118°. UV/VIS

(hexane): 222 (sh, 40900), 249 (sh, 75400), 255 (sh, 80300), 261 (85400), 277 (25700), 296 (26300), 316 (22400). IR (KBr): 2963, 2865, 2142, 1464, 1394, 1363, 1241, 1108, 1069, 1018, 996, 883, 863, 754, 678. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.14 (*s*, 36 H); 1.08 (*s*, 42 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 214.2; 104.6; 102.4; 99.6; 94.9; 76.9; 75.3; 35.9; 35.5; 29.0; 28.9; 18.7; 11.3. EI-MS: 710.5 (52, M^+), 695.5 (11, $[M-CH_3]^+$), 667.4 (16, $[M-C_3H_7]^+$), 653.4 (46, $[M-Me_3C]^+$), 57.1 (89, Me_3C^+), 44.0 (100, $C_3H_7^+$). Anal. calc. for $C_{48}H_{78}Si_2$ (711.3): C 81.05, H 11.05; found: C 81.03, H 11.16.

Methyl 5-(Triisopropylsilyl)-1,1-bis[(triisopropylsilyl)ethynyl]penta-2,4-diynyl Carbonate (**53**). LHMDS (0.60 ml of a 1M soln. in hexane, 0.60 mmol) was added at $-78°$ to **52** [6b] (300 mg, 0.50 mmol) in THF (5 ml). Reaction with MeOCOCl (50 µl, 0.65 mmol) and workup as described for (±)-**38** provided **53** (275 mg, 84%). Colorless oil. R_f (SiO_2; hexanes/AcOEt 20:1) 0.39. IR (film): 2944, 2862, 2226, 2102, 1772, 1464, 1257, 1221, 1137, 1019, 995, 918, 883, 785, 679. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.81(*s*, 3 H); 1.08 (*s*, 63 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 152.0; 99.25; 88.4; 88.3; 69.8; 69.3; 55.1; 18.5; 11.2; 11.1 (3 alkynyl resonances missing due to overlap). EI-MS; 654.5 (M^+). HR-MALDI-MS: 579.4241 ($[M-MeOCOO]^+$, $C_{36}H_{63}Si_3^+$; calc. 579.4243).

1-Triisopropylsilyl-3-[(triisopropylsilyl)ethynyl]nona-1,4-diyn-3-ol (**57**). BuLi (1.0 ml of a 1.6M soln. in hexane, 1.6 mmol) was added at $-78°$ to hex-1-yne (0.17 ml, 1.5 mmol) in THF (5 ml). Reaction with **56** [6b] (0.40 g, 1.0 mmol) and workup as described for (±)-**32** provided **57** (353 mg, 75%). Clear oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.37. IR (film): 3456, 2943, 2866, 2236, 2174, 1464, 1159, 1072, 1017, 918, 883, 677. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.70 (*s*, 1 H); 2.24 (*t*, $J=6.6$, 2 H); 1.34–1.60 (*m*, 4 H); 1.08 (*s*, 42 H); 0.90 (*t*, $J=7.1$, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 104.8; 83.9; 83.7; 78.5; 54.6; 30.1; 21.7; 18.5; 18.3; 13.5; 11.1. EI-MS: 472.4 (M^+). Anal. calc. for $C_{29}H_{52}OSi_2$ (472.9): C 73.66, H 11.08; found: C 73.65, H 11.11.

5-Ethynylnonan-5-ol (**59**) [36]. HC≡C–MgBr (10 ml of a 0.5M soln. in Et_2O, 5.0 mmol) was added at $-78°$ to nonan-5-one (0.86 ml, 5.0 mmol) in THF (50 ml). After stirring for 15 min, the mixture was warmed to r.t. and stirring was continued for 1 h. Sat. aq. NH_4Cl soln. (50 ml) was added, and the mixture was extracted with Et_2O (4 × 50 ml). The combined org. phases were dried ($MgSO_4$) and evaporated *in vacuo*. Bulb-to-bulb distillation gave 680 mg (81% crude yield) of the product containing only traces of an impurity with higher R_f-value. FC (SiO_2; hexanes/AcOEt 5:1) gave pure **59** (420 mg, 50%). R_f (SiO_2; hexanes/AcOEt 5:1) 0.41. IR (film): 3408, 3311, 2956, 2867, 2107, 1468, 1459, 1379, 1259, 1139, 1036, 996, 899, 625. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.42 (*s*, 1 H); 1.98 (*s*, 1 H); 1.69–1.25 (*m*, 12 H); 0.92 (*t*, $J=7.1$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 87.0; 72.1; 71.1; 41.5; 26.2; 22.8; 14.0.

5-Butyl-1-(triisopropylsilyl)nona-1,3-diyn-5-ol (**60**). A soln. of **59** (420 mg, 2.5 mmol), $NH_2OH\cdot HCl$ (347 mg, 5.0 mmol), and $PrNH_2$ (0.82 ml, 10 mmol) in 95% EtOH (10 ml) was sparged at r.t. with Ar for 5 min. CuCl (25 mg, 0.25 mmol) and (i-Pr)$_3$Si–C≡C–Br [37] (732 mg, 2.8 mmol) were added sequentially, and sparging with Ar was continued for several min. After stirring for 12 h, H_2O (50 ml) was added, and the mixture was extracted with Et_2O (4 × 50 ml). The combined extracts were dried ($MgSO_4$), and evaporation *in vacuo* followed by FC (SiO_2; hexanes/AcOEt 10:1), gave **60** (810 mg, 93%). Colorless crystals. R_f (SiO_2; hexanes/AcOEt 10:1) 0.36. M.p. 74–75°. IR (film): 3328, 2943, 2863, 2215, 2098, 1460, 1382, 1230, 1142, 1113, 1042, 992, 880, 672. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.07 (*s*, 1 H); 1.70–1.61 (*m*, 4 H); 1.54–1.26 (*m*, 8 H); 1.08 (*s*, 21 H); 0.92 (*t*, $J=7.1$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 89.1; 84.1; 79.6; 71.7; 69.5; 41.5; 26.2; 22.7; 18.4; 13.8; 11.2. EI-MS: 348.2 (M^+). Anal. calc. for $C_{22}H_{40}OSi$ (348.7): C 75.79, H 11.56; found: C 75.95, H 11.59.

1,1-Dibutyl-5-(triisopropylsilyl)penta-2,4-diynyl Methyl Carbonate (**58**). LHMDS (1.43 ml of a 1M soln. in hexane, 1.43 mmol) was added at $-78°$ to **60** (454 mg, 1.30 mmol) in THF (5 ml). Reaction with MeOCOCl (120 µl, 1.56 mmol) and workup as described for (±)-**38** provided **58** (376 mg, 71%) besides 52 mg of recovered **60**. Colorless oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.52. IR (film): 2958, 2862, 2092, 1758, 1462, 1441, 1380, 1253, 1112, 995, 882, 790, 677. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.76 (*s*, 3 H); 2.05–1.82 (*m*, 4 H); 1.52–1.23 (*m*, 8 H); 1.08 (*s*, 21 H); 0.92 (*t*, $J=7.1$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 153.3; 88.9; 85.2; 80.8; 75.0; 71.6; 54.4; 37.9; 25.9; 22.6; 18.5; 13.9; 11.2. EI-MS: 406.3 (M^+). Anal. calc. for $C_{24}H_{42}O_3Si$ (406.7): C 70.88, H 10.41; found: C 70.73, H 10.54.

5-Butyl-1-(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]nona-3,4-dien-1-yne (**61**). A soln. of **58** (122 mg, 0.30 mmol), (i-Pr)$_3$Si–C≡CH (101 µl, 0.45 mmol), and (i-Pr)$_2$NH (84 µl, 0.60 mmol) in $(CH_2Cl)_2$ (1.5 ml) was sparged with Ar. $[Pd(PPh_3)_4]$ (17.3 mg, 15 µmol) and CuI (5.7 mg, 30 µmol) were added sequentially with further sparging with Ar. An Ar-flushed reflux condenser was added, and the mixture was heated to 70° in a preheated oil bath. After 30 min, the mixture was diluted with hexanes and filtered through SiO_2. Evaporation *in vacuo* and FC (SiO_2; hexanes) provided **61** (150 mg, 97%). Colorless oil. R_f (SiO_2; hexanes) 0.42. IR (film): 2944, 2862, 2155, 1933, 1464, 1382, 1241, 1191, 1073, 996, 883, 675. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.06 (*t*, $J=6.6$, 4 H); 1.51–1.26 (*m*, 8 H); 1.09–1.07 (*m*, 42 H); 0.89 (*t*, $J=7.1$, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 214.3; 108.4;

100.6; 90.1; 77.7; 32.1; 29.3; 22.0; 18.6; 13.9; 11.3. EI-MS: 512.4 (M^+). Anal. calc. for $C_{33}H_{60}Si_2$: C 77.26, H 11.79; found: C 77.15, H 11.72.

5-Butylundec-6-yn-5-ol (**64**). BuLi (4.06 ml of a 1.6M soln. in hexane, 6.5 mmol) was added at $-78°$ to hex-1-yne (0.67 ml, 6.0 mmol) in THF (10 ml). Reaction with **63** (0.86 ml, 5.0 mmol) and workup as described for (±)-**32** (but no FC needed) provided **64** (1.02 g, 91%) as an oil, which was used without further purification. R_f (SiO_2; hexanes/AcOEt 10:1) 0.31. IR (film): 3415, 2957, 2935, 2862, 2236, 1467, 1379, 1328, 1139, 1028, 995. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.19 (*t*, *J* = 6.9, 2 H); 1.84 (br. *s*, 1 H); 1.62–1.54 (*m*, 4 H); 1.52–1.27 (*m*, 15 H); 0.91 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 84.6; 83.2; 71.3; 42.0; 30.8; 26.5; 22.9; 21.9; 18.3; 14.0; 13.5. EI-MS: 224.2 (M^+). Anal. calc. for $C_{15}H_{28}O$ (224.4): C 80.29, H 12.58; found: C 80.31, H 12.49.

1,1-Dibutylhept-2-ynyl Methyl Carbonate (**62**). LHMDS (1.1 ml of a 1M soln. in hexane, 1.1 mmol) was added at $-78°$ to **64** (224 mg, 1.0 mmol) in THF (2 ml). Reaction with MeOCOCl (93 µl, 1.2 mmol) and workup as described for (±)-**38** provided **62** (190 mg, 67%; from **63**). Colorless oil. R_f (SiO_2; hexanes/AcOEt 10:1) 0.44. IR (film): 2958, 2934, 2867, 2242, 1756, 1463, 1440, 1379, 1252, 1155, 1128, 962, 941, 880, 791. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.71 (*s*, 3 H); 2.21 (*t*, *J* = 6.8, 2 H); 2.01–1.78 (*m*, 4 H); 1.56–1.24 (*m*, 12 H); 0.891 (*t*, *J* = 7.2, 6 H); 0.886 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 153.4; 87.0; 81.6; 79.2; 54.0; 38.2; 30.6; 26.2; 22.7; 21.8; 18.4; 14.0; 13.5. EI-MS: 205.3 (M – H – MeOOCO]$^+$). Anal. calc. for $C_{17}H_{30}O_3$ (282.4): C 72.30, H 10.71; found: C 72.43, H 10.76.

3,5-Dibutyl-1-(triisopropylsilyl)nona-3,4-diene-1-yne (**65**). A soln. of **62** (85 mg, 0.30 mmol), $(i\text{-}Pr)_3Si{-}C{\equiv}CH$ (101 µl, 0.45 mmol), and $(i\text{-}Pr)_2NH$ (84 µl, 0.60 mmol) in $(CH_2Cl)_2$ (1.5 ml) was sparged with Ar. [$Pd(PPh_3)_4$] (17.3 mg, 15 µmol) and CuI (5.7 mg, 30 µmol) were added sequentially with further sparging with Ar. After stirring for 30 min at r.t., the yellow soln. was diluted with hexanes and filtered through SiO_2. Evaporation *in vacuo* and FC (SiO_2; hexanes) provided **65** (110 mg, 94%). Clear oil. R_f (SiO_2; hexanes) 0.62. IR (film): 2957, 2864, 2142, 1946, 1464, 1380, 1073, 1015, 996, 883, 675. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.08 (*t*, *J* = 7.3, 2 H); 2.00–1.94 (*m*, 4 H); 1.52–1.29 (*m*, 12 H); 1.08–1.06 (*m*, 21 H); 0.901 (*t*, *J* = 7.2, 6 H); 0.889 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 206.8; 105.5; 104.4; 90.6; 89.6; 33.8; 32.3; 30.2; 29.7; 22.2; 22.0; 18.6; 14.0; 13.9; 11.4. EI-MS: 388.4 (M^+). Anal. calc. for $C_{26}H_{48}Si$ (388.8): C 80.33, H 12.44; found: C 80.28; H 12.39.

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