An Iterative Approach to *cis*-Oligodiacetylenes

Christoph Kosinski,[a] Andreas Hirsch,*[a] Frank W. Heinemann,[b] and Frank Hampel[a]

Dedicated to Professor Michael Hanack on the occasion of his 70th birthday

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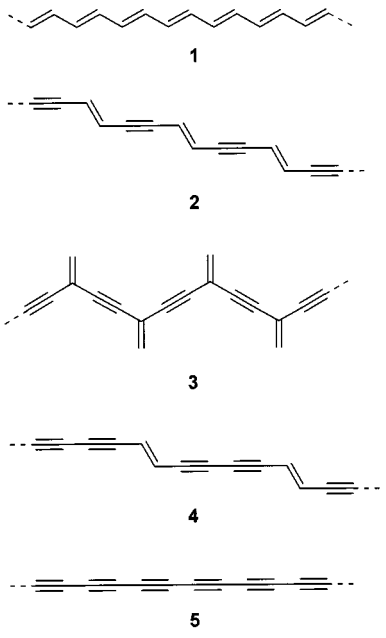
Phenyl-terminated *cis*-oligodiacetylenes such as **18**, containing a π-conjugated backbone with four triple and three double bonds, were synthesized using Pd-catalysed Sonogashira coupling reactions. Compound **18** represents the longest *cis*-oligoenyne system to date, but it suffers from the drawback of *cis*/*trans* isomerization observed in solution. In order to avoid *cis*/*trans* isomerization in such *cis*-oligodicacetylenes, the ene moieties within the oligomeric backbone were locked by incorporation into ring systems. 1,2-Dibromocyclopentene was used as an olefinic building block for this purpose, permitting the iterative synthesis of the *cis*-oligodiacetylenes **27** and **28**, possessing the same π-conjugated backbone as **18**. Unlike that compound, however, **27** and **28** are stable both in solution and in the solid state. Whereas X-ray crystallography revealed a completely planar structure for **27** in the single crystal, NMR and computational investigations suggest that a preferred helical conformation is likely in solution.

Introduction

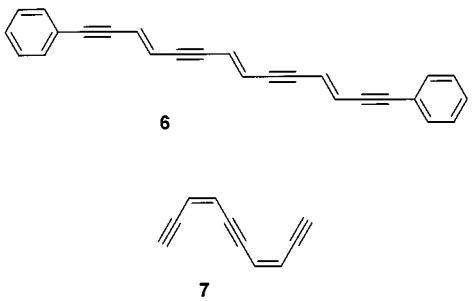
Linear polymers with π-conjugated carbon scaffolds are predicted to have special electronic and optical properties.[1,2] Stepwise reduction in saturation of the carbon scaffold, starting with polyacetylene **1**,[3] produces the hypothetical carbon allotrope carbyne **5**,[4,5] via polydiacetylene **2**[6] or polytriacetylene **4**.[7] Another π-conjugated carbon scaffold is represented by the cross-conjugated system **3**.[8]



1 **2** **3** **4** **5**

[a] Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestr. 42, 91054 Erlangen, Germany
Fax: (internat.) + 49-(0)9131/852-6864
E-mail: hirsch@organik.uni-erlangen.de
[b] Institut für Anorganische Chemie der Universität Erlangen-Nürnberg
Egerlandstr. 1, 91058 Erlangen, Germany

The synthesis of π-conjugated oligomers[2,9] is also of interest because it is anticipated that these oligomers should be important components of molecular electronic devices. Moreover, they can serve as constrained model systems, the spectroscopic properties of which can be extrapolated to enable the electronic, optical, thermal, and morphological properties of the corresponding polymers[4,10] to be predicted. Polydiacetylenes **2** have not been investigated to the same extent as other linear oligomers of π-conjugated, nonaromatic, all-carbon backbones, presumably due to the fact that it is difficult to find a topochemically controlled synthesis of their π-conjugated backbone.[9] The first studies of the synthesis of the polydiacetylenes go back to Slysh, Georgiana, and Desai in 1960,[11] who investigated the polymerization of butadiyne (diacetylene), C_4H_2. The first systematic series of *trans*-enyne oligomers, dating back to 1986, was published by Wudl and Bittler,[12] who reported the synthesis of *tert*-butyl-endcapped oligomers. The *tert*-butyl endcaps were found to be essential for sufficient thermal stability, with the oligomers displaying no particular sensitivity to air and light, as is generally observed in the case of oligoenes. In 1992, Lindsell produced the phenyl-endcapped *trans*-enyne oligomer **6**.[13] In 1992, Bergman's group published the synthesis of the longest all-*cis* oligomer **7** so far, together with its *cis,trans* and *trans,trans* isomers.[14]



6 **7**

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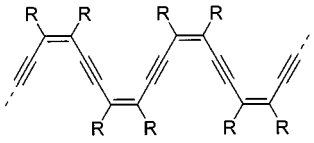
The number of synthetic approaches to *cis*-enyne oligomers is very limited.[13,14] Here we introduce our new iterative approach for a homologous series of *cis*-oligoacetylenes **8**.

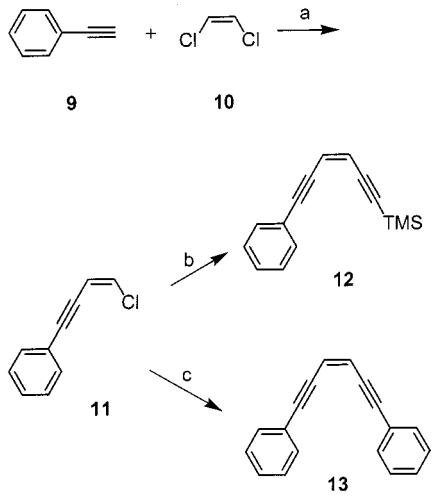


8

R = H or (cyclo)alkyl groups

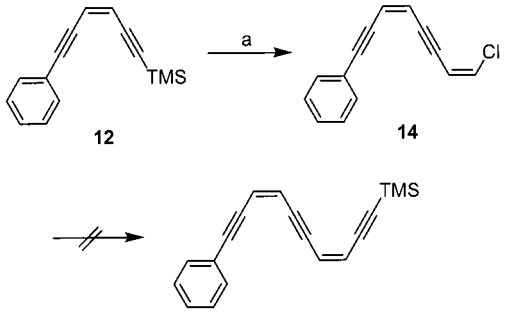
Results and Discussion

Our strategy for the construction of *cis*-enyne oligomers is based on the Sonogashira Pd-catalysed sp-sp^2 coupling of terminal acetylenes with vinyl halides in the presence of an amine and CuI.[15] Use of the phenyl group as the endcap turned out to be favourable for this approach, as it caused an increase in the reactivity of the π-conjugated carbon chain. The synthesis of a first series of *cis*-enyne oligomers started with the coupling of phenylacetylene **9** and 2.0 equiv. of (*Z*)-1,2-dichloroethene (**10**) (Scheme 1), producing **11**[16] in 76% yield. Subsequently, **11** was treated with phenylacetylene (**9**) to yield [(3*Z*)-6-phenylhex-3-ene-1,5-diynyl]benzene (**13**) (87%). Treatment of **11** with TMS-acetylene gave **12**[17] in up to 84% yield.



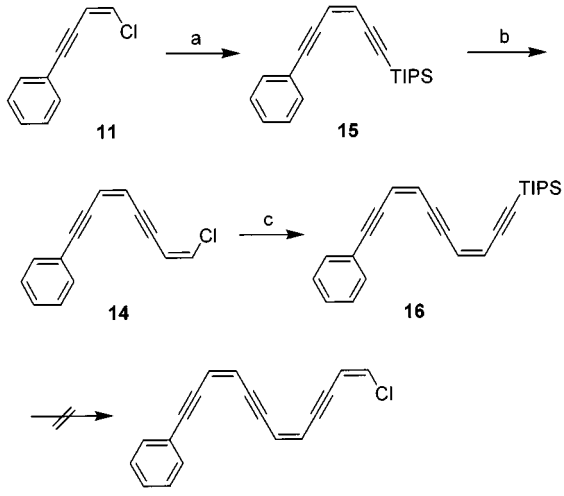
Scheme 1. Synthesis of **12** and **13**: a) $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 24 h, 76%; b) TMS-acetylene (1.3 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 48 h, 84%; c) · **9** (1.0 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 24 h, 87%

The next step involved the cleavage of the TMS protecting group by the action of a solution of potassium carbonate in methanol to afford the terminal alkyne intermediate. This was coupled in situ with 1.5 equiv. of (*Z*)-1,2-dichloroethene (**10**) under Sonogashira conditions to give **14** in up to 42% yield (Scheme 2).



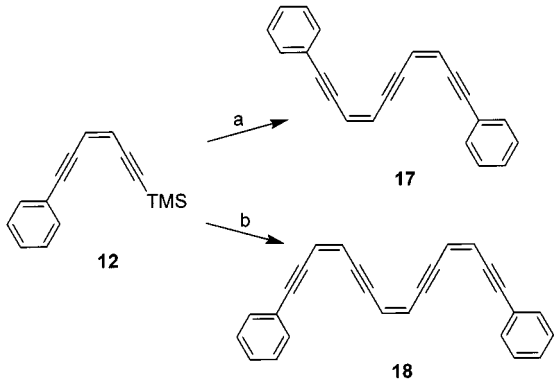
Scheme 2. Synthesis of **14**: a) K_2CO_3, CH_3OH/H_2O, room temp., 6 h, then **10** (1.9 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 100 h, 42% (2 steps)

We refrained from purification and characterisation of the unprotected alkynes because of the poor stability of these compounds. Further experiments to elongate the chain by coupling with TMS-acetylene were unsuccessful. Since the instability of the products precluded purification, we modified the synthesis route and decided to use TIPS instead of TMS as protecting group. Analogously to the synthesis of **12**, the chloride **11** was coupled with TIPS-acetylene to generate **15** in 94% yield (Scheme 3). Removal of the TIPS protecting group with TBAF and coupling of the product with (*Z*)-1,2-dichloroethene (**10**) afforded **14** in up to 41% yield. Subsequent treatment of **14** with TIPS-acetylene produced **16** in 41% yield, but further coupling steps were unsuccessful.

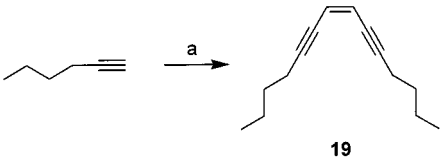


Scheme 3. Preparation of **16**: a) TIPS-acetylene (1.2 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 72 h, 94%; b) TBAF, THF/H_2O, 3 h, then **10** (1.4 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 100 h, 41% (2 steps); c) TIPS-acetylene (1.5 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 20 h, 41%

When we started from **12**, however, we were able to synthesize the *cis*-oligoeneynes **17** and **18** in yields of 29% and 6%, respectively (Scheme 4). Compound **18** is longer than **7**[14] and is the all-*cis* isomer of the all-*trans*-**6** synthesized by Lindsell.[13] To extend the range of compounds available for comparative purposes, we also synthesized **19**, from 1-hexyne and (*Z*)-1,2-dichloroethene (**10**), in 80% yield (Scheme 5).[18]



Scheme 4. Synthesis of **17** and **18**: a) K_2CO_3, CH_3OH/H_2O, room temp., 6 h, then **11** (1.2 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 24 h, 29% (2 steps); b) K_2CO_3, CH_3OH/H_2O, room temp., 6 h, then **10** (0.4 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 72 h, 6% (2 steps)



Scheme 5. Synthesis of **19**: a) **10** (0.5 equiv.), $Pd(PPh_3)_4$, CuI, nBuNH$_2$, C_6H_6, room temp., 80 h, 80%

Although the generation of a series of *cis*-oligoenynes proved successful, it must be noted that their isolation and handling posed some difficulties. The instability of these systems is evident from the observed *cis*/*trans* isomerization and ease of polymerization. A clear example of *cis*/*trans* isomerization is provided by compound **18**. The ^{1}H NMR signals of the hydrogen atoms of the central double bond give a singlet at $\delta = 7.96$, while two doublets at $\delta = 5.94$ and 6.70 are observed for the hydrogen atoms of the outer double bonds. The coupling constant is 12.0 Hz, typical for *cis* double bonds. After only a short time, however, changes can be observed in the ^{1}H NMR spectrum of **18**. Alongside the old signals, new peaks appear at $\delta = 7.39$ (singlet) for the central double bond and at $\delta = 6.39$ and 7.01 (two doublets with the typical *trans* coupling constant of 16.1 Hz) for the outer double bonds. We also observed changes in the chemical shifts of the olefinic carbon atoms in the ^{13}C NMR spectrum: The carbon atoms of the central bond in the all-*cis* isomer resonated at $\delta = 128.67$ and those of the outer double bonds at $\delta = 107.80$ and 138.09; the corresponding values for the all-*trans* isomer are $\delta = 126.66$, 108.48, and 140.52, respectively. In the ^{1}H NMR spectrum of **17**, we unexpectedly found only one peak for the four olefinic hydrogen atoms at $\delta = 6.14$. As anticipated, however, the ^{13}C NMR spectrum contained two peaks for the four olefinic carbon atoms at $\delta = 118.98$ and 119.97 and three peaks for the acetylenic C atoms at $\delta = 87.23$, 94.98, and 98.27.

In order to circumvent these problems associated with instability and isomerization, we decided to use cyclic double bond moieties − a well established concept used among other things for the synthesis of platyrins from the group of the porphyrins.[19] This should simultaneously prevent both polymerization, thanks to steric obstruction, and also *cis*/*trans* isomerization of the double bond (Figure 1). As the cyclic olefin we used 1,2-dibromocyclopentene (**20**).[20]

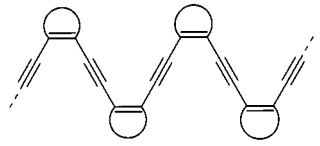
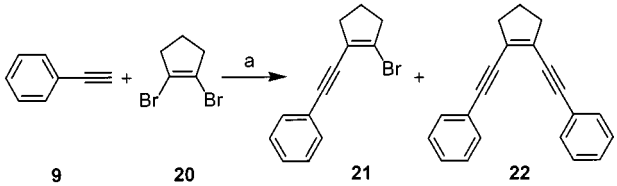


Figure 1. Stabilisation of the enyne backbones in *cis*-polydiacetylenes by introduction of ene moieties into a ring system

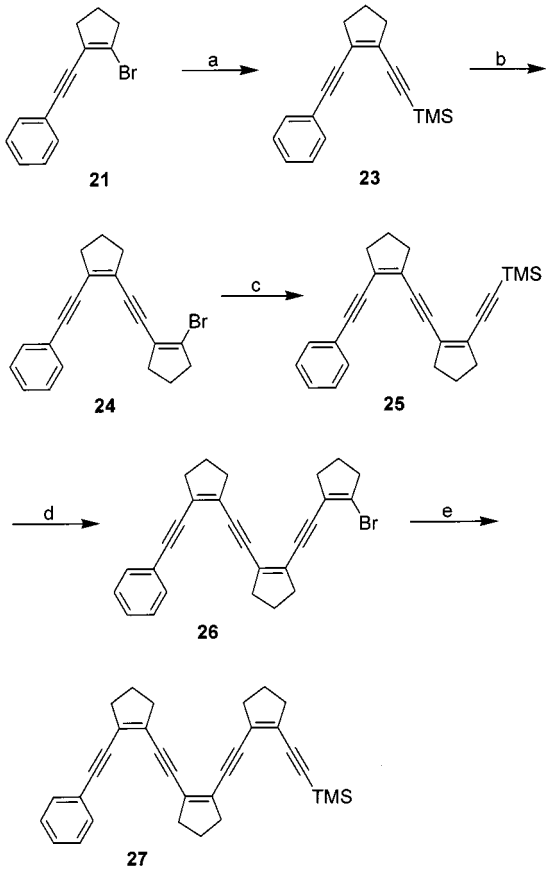
The change in the ethylene component had the further advantage of enabling us to use $PdCl_2(PPh_3)_2$ as the catalyst instead of $Pd(PPh_3)_4$; this produced better results than those found in the synthesis of the "naked" chain. Like the synthesis of the "naked" *cis*-enyne chains, that of the "protected" chain started with the coupling of phenylacetylene (**9**) with 1,2-dibromocyclopentene (**20**). In contrast with the synthesis described above, this technique always afforded a mixture of the products **21** and **22**, together with small amounts of (4-phenylbuta-1,3-diinyl)benzene, which was separated by column chromatography with hexane/dichloromethane (15:1 and 10:1; Scheme 6).



Scheme 6. Preparation of **21** and **22**: a) $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 6 h

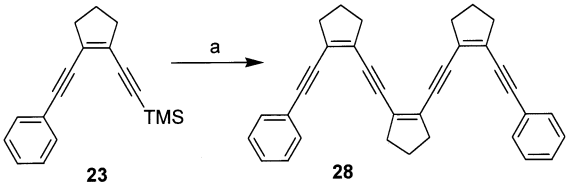
Compound **21** was coupled with 4.0 equiv. of TMS-acetylene in a Sonogashira reaction to afford **23** in 91% yield (Scheme 7). Before the chain was elongated further, the TMS group was cleaved by treatment with methanolic potassium carbonate solution. The reaction proceeded almost quantitatively, but we refrained from isolation and characterization of the product because of the instability of the deprotected form. Coupling of **23** with 1.2 equiv. of 1,2-dibromocyclopentene (**20**) resulted in **24**. The yield after two steps was 36%. A yield of 99% was obtained for the coupling of **24** with TMS-acetylene to give **25**. Removal of the TMS protecting group and coupling with 1.1 equiv. of 1,2-dibromocyclopentene (**20**) gave **26** in a yield of 22%. In the next step, compound **27** was obtained in 81% yield on treatment of **26** with 6.0 equiv. of TMS-acetylene.

We obtained **28** in 9% yield from **23**, by removal of the TMS group and subsequent Sonogashira coupling with 0.45 equiv. of 1,2-dibromocyclopentene (**20**) (Scheme 8).



Scheme 7. Synthesis of **27**: a) TMS-acetylene (4.0 equiv.), $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 24 h, 91%; b) K_2CO_3, CH_3OH/H_2O, room temp., 16 h, then **20** (1.2 equiv.), $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 20 h, 36% (2 steps); c) TMS-acetylene (4.0 equiv.), $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 48 h, 99%; d) K_2CO_3, CH_3OH/H_2O, room temp., 36 h, then **20** (1.1 equiv.), $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 72 h, 22% (2 steps); e) TMS-acetylene (6.0 equiv.), $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 72 h, 81%

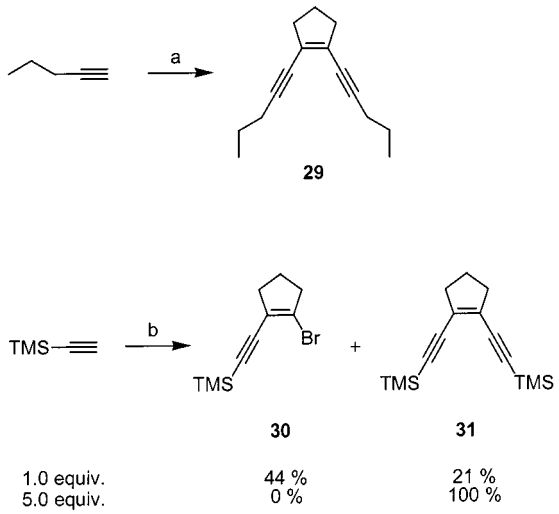
Compound **24** was generated as a by-product in this reaction (19% yield).



Scheme 8. Preparation of **28**: a) K_2CO_3, CH_3OH/H_2O, room temp., 20 h, then **20** (0.45 equiv.), $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 20 h, 9% (2 steps)

We obtained compound **29** in 87% yield from 1,2-dibromocyclopentene (**20**), by coupling with 1-pentyne. Depending on the amount of **20** used, coupling with TMS-acetylene would produce either a mixture of the two products **30** and **31**, or **31** exclusively (Scheme 9).

All products were purified by column chromatography and were completely characterized by IR, UV/Vis, ^{1}H NMR, ^{13}C NMR, MS, and microanalysis. The UV spectra of selected molecules are shown in Figure 2. In general,



Scheme 9. Synthesis of **29**, **30** and **31**: a) **20** (0.25 equiv.), $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 48 h, 87%; b) **20**, $PdCl_2(PPh_3)_2$, CuI, nBuNH$_2$, C_6H_6, room temp., 18 h

compounds with larger π-conjugated systems exhibit bathochromic shifts and increases in extinction coefficients. This is evident in the colour of the compounds either in solution or as solids; the colours become more intense and change from white or yellow (compounds **21**, **22**, **23**, **24**, and **25**, for example) to brownish (**26** and **28**) or orange (**27**). Figure 2, a), shows spectra of selected examples with "naked" chains (**19** and **13**) and with "protected" chains (**29** and **22**). A comparison of the spectra demonstrates that the presence of the cyclopentene ring has a negligible influence on the UV absorption, since **19** and **13** have spectra very similar to those of **29** and **22**, respectively. Only a weak increase in absorbance can be discerned. The use of phenyl groups, which conjugate with the π-system of the diacetylene, in place of alkyl groups has a much greater influence on the absorption. In this case, both the absorbance and the peak wavelengths increase. The shift of the maxima with increasing chain length is shown in Figure 2, b). Compounds **24** and **26** have essentially similar UV spectra, but that of **21** is quite different, presumably because it lacks an enediyne moiety.

Finally, we can see in Figure 2, c), that the substitution of one phenyl group by a TMS protecting group (no conjugation with the π-system) in the compounds with highest chain length (**27** and **28**) has a strong effect on absorbances and peak maxima, but only a limited influence on the relative appearance of the UV spectra.

The IR stretching modes of all the acetylenes synthesized appear between 2130 and 2218 cm^{-1}. The olefinic valence vibrations appear from 1628−1677 cm^{-1} and are in general much more easily observable in the "naked" chains than in the "protected" ones. The *cis*-olefinic deformation modes always appear at 744 cm^{-1} for **19** and between 678 and 700 cm^{-1} for the other compounds.

The ^{13}C NMR signals of the acetylenic carbon atoms appear between δ = 83 and 98 for C atoms bonded to sp^2-hybridized carbon atoms, δ = 100−103 for those from the

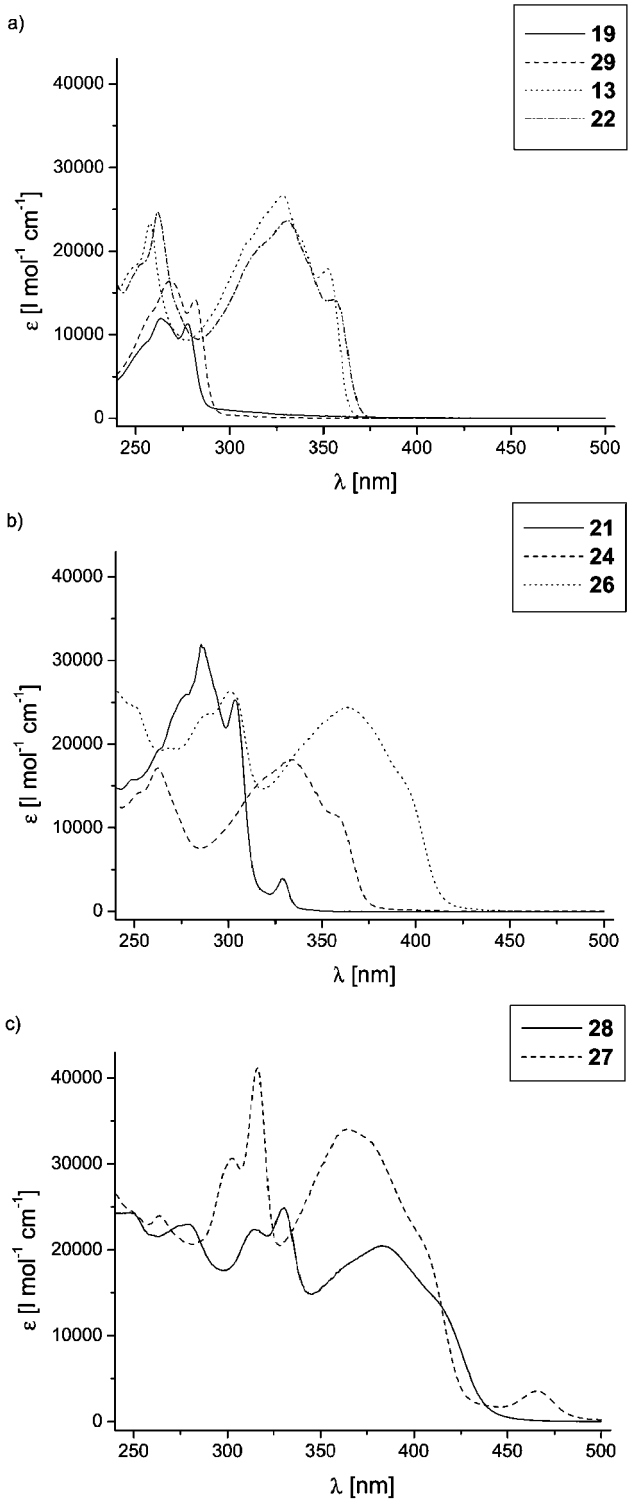


Figure 2. The UV spectra of selected compounds (further details in the text)

TMS- and TIPS-acetylene groups, and δ = 77 to 78 for acetylenic atoms bound to sp^3-hybridized C atoms (compounds **19** and **29**). For the olefinic carbon atoms, there is a general trend towards upfield shifting of the olefinic C atoms of the "naked" chain (δ = 112−129) relative to the C atoms of the "protected" diacetylenes (δ = 124−132).

The compounds with three cyclopentene rings (**26**, **27**, and **28**) display interesting behaviour in solution, in comparison with their smaller homologues. This is shown in the ^{1}H NMR spectra of molecules **27** and **28** (Figure 3). The hydrogen atoms of the two outer cyclopentene rings A of the symmetrical compound **28** have chemical shifts of δ = 1.73 and 2.46 and are shifted to a higher field than those of the rings in the centre (δ = 1.92 or 2.61).

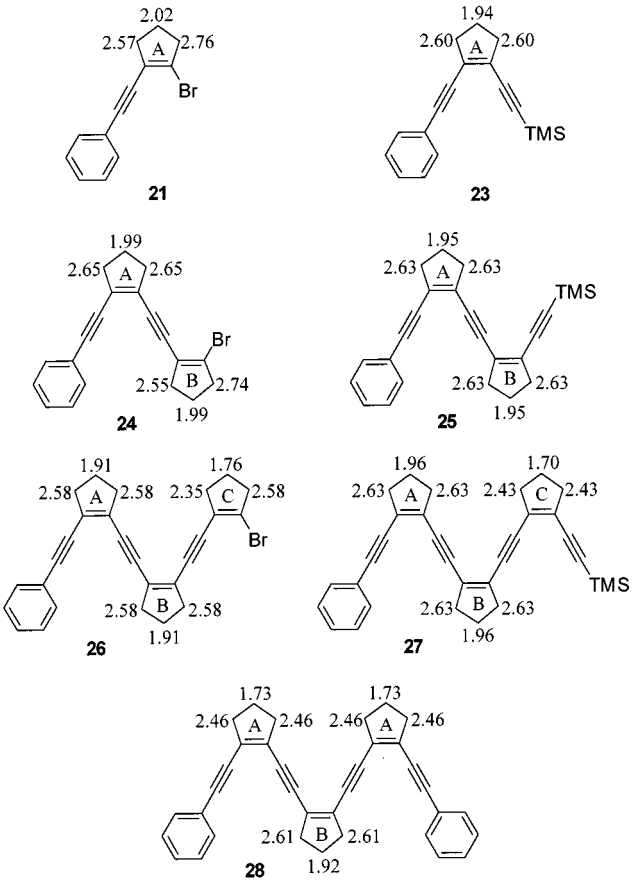


Figure 3. The ^{1}H NMR shifts of the cyclopentene rings of compounds **21**, **23**, **24**, **25**, **26**, **27**, and **28**; upfield shifts of the cyclopentene C ring signals of **26** and **27** and of the A ring signals of the symmetrical compound **28** are apparent

Different behaviour is observed in the unsymmetrical compound **27**. In this case, the hydrogen atoms of the cyclopentenes A and B show the same chemical shifts, δ = 1.96 and 2.63. It is conspicuous that the chemical shifts of the hydrogen atoms of the cyclopentenes A in compound **28** are almost identical to the shifts of those of ring C in compound **27** (δ = 1.70 or 2.43), and they are shifted upfield relative to those of ring B. The best explanation for this behaviour is the adoption of a helical conformation by compounds **27** and **28** (Figure 4).

Many organic molecules are helical.[21] The conformation of natural biopolymers is stabilized by, among other things, localised non-covalent interactions such as hydrogen bonding, hydrophobic, and van der Waals forces.[22] In nonbiological macromolecules, particularly when dissolved in polar solvents, these forces are relatively unimportant.[23] In this case, the structure of the molecules arises from nonspecific

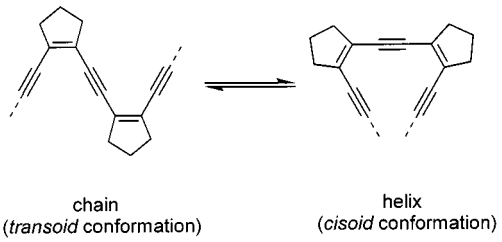


Figure 4. The backbone can adopt a *transoid* or a *cisoid* conformation by rotation about the triple bond

forces such as solvophobic interactions[24] and π−π interaction[25] of aromatic units. Moore has recently observed that certain phenylene-ethylene oligomers undergo a cooperative conformational transition in solution, from a random state to a putative helical structure stabilized by the π-stacking of aromatic residues.[26]

In the PM3-calculated helical conformers of **27** and **28**, both cyclopentenes A of **28** and ring C of **27** lie directly over phenyl rings (Figure 5) and so are situated in the shielding region due to the diamagnetic ring current. This consequently results in a weak upfield shifting of these proton signals.

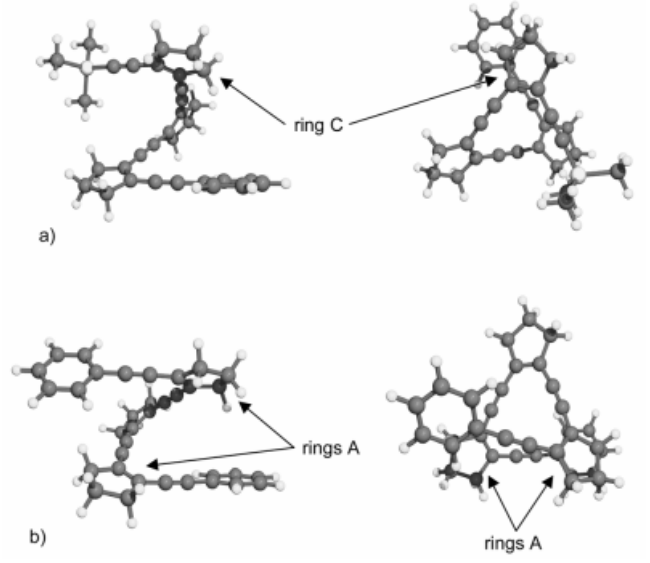


Figure 5. POV-ray representations of the PM3-optimized structures of **27** (a) and **28** (b) in the helical conformation (grey = carbon, white small = hydrogen, white large = silicon; left: side view of the helix; right: view through the helix; the spatial proximity to the phenyl rings of the cyclopentene A ring in **28** and the C ring in **27** is apparent

Compound **26** shows similar behaviour to its short-chain homologues **21** and **24** in the protons at the cyclopentene ring C. The signal of the methylene group in the centre, for example, shows an upfield shift [δ = 1.76, compared to δ = 1.91 in the A and B rings and δ = 2.02 (**21**) and δ = 1.99 (**24**)], an indication that molecule **26** is present in helical form. The same pattern is observed for the other methylene group in the C ring. In the "naked" chain compound **18**, the ^{1}H NMR signals of the two outer double bond hydrogen atoms are observed upfield (δ = 5.94 and 6.70) of those of the centre double bond (δ = 7.96). This may be an indication of a helical conformation in this molecule in solution. However, this result should not be overemphasised, as no "naked" chain compounds analogous to **26** and **27** have been prepared.

According to PM3 calculations[27] on compounds **27** and **28**, the helical conformation is favoured over the chain by about 1.9 and 1.3 kcal/mol respectively. In contrast, the chain form of compound **26** is about 1.5 kcal/mol more stable than the helix. These values are similar to the error limits intrinsic to the method and they are too low to allow ascertainment of which of these conformations would occur in the gas phase. Another interesting result appeared when we optimized the structure of **22** with ab initio methods[28] [the calculations were performed at the standard MP2(fc)/6-311+G(d,p) level using Gaussian98 Rev. A.5]. According to these calculations, the whole molecule, including the cyclopentene ring, should have a flat structure.

Recrystallization of compound **22** by diffusion of hexane into a dichloromethane solution produced crystals suitable for X-ray analysis. This structural analysis of **22**, which crystallised in the monoclinic system, confirms this unexpected result [Figure 6, a) and b)]. The cyclopentene ring has a flat structure and, furthermore, the molecule as a whole is almost flat, as predicated by the calculation. Only one phenyl ring shows a slight twist out of the molecular plane. The planar structure of the molecule permits efficient packing [Figure 6, c) and d)] of the molecules within the unit cell to form a "herringbone" pattern. The distance between each layer amounts to 462.3 pm, which allows only weak van der Waals forces between the molecules.

Compound **27** crystallised out of [D_2]dichloromethane with one molecule of CD_2Cl_2 in every formula unit (Figure 7). The molecule and the solvent are located on the crystallographic mirror plane of the space group $Pmn2_1$ of the orthorhombic system. The molecules crystallize in alternately repeating layers [Figure 7, c)]. The TMS groups within each layer all point in the same direction, but the TMS groups in the adjacent layers point in the opposite direction, to achieve the highest possible packing efficiency. Because of this arrangement of the molecules within the crystal, the intermolecular distance between apparent stacking partners [Figure 7, b)] comes to 710.7 pm, significantly greater than that found in **22**. This is also more than double the distance associated with the usual π−π stacking separation observed in aromatic[29] compounds and graphite (335.4 pm).[30] At this distance, only very weak van der Waals forces and π−π interactions are to be expected.

In the X-ray analysis of **22** and **27**, the planar structure of the molecule is noteworthy: It provides evidence of full conjugation of the π-backbone of both compounds within the crystal. Another indication of the distinct conjugation of the π-backbone is given by comparison of the C−C bond lengths within the crystal. Whereas the lengths of the double and triple bonds lie in the usual ranges (120−121 pm for the triple bonds, 134−136 pm for the nonaromatic double bonds and 137−139 pm for the aromatic C−C bonds), the single bonds of the chain are significantly

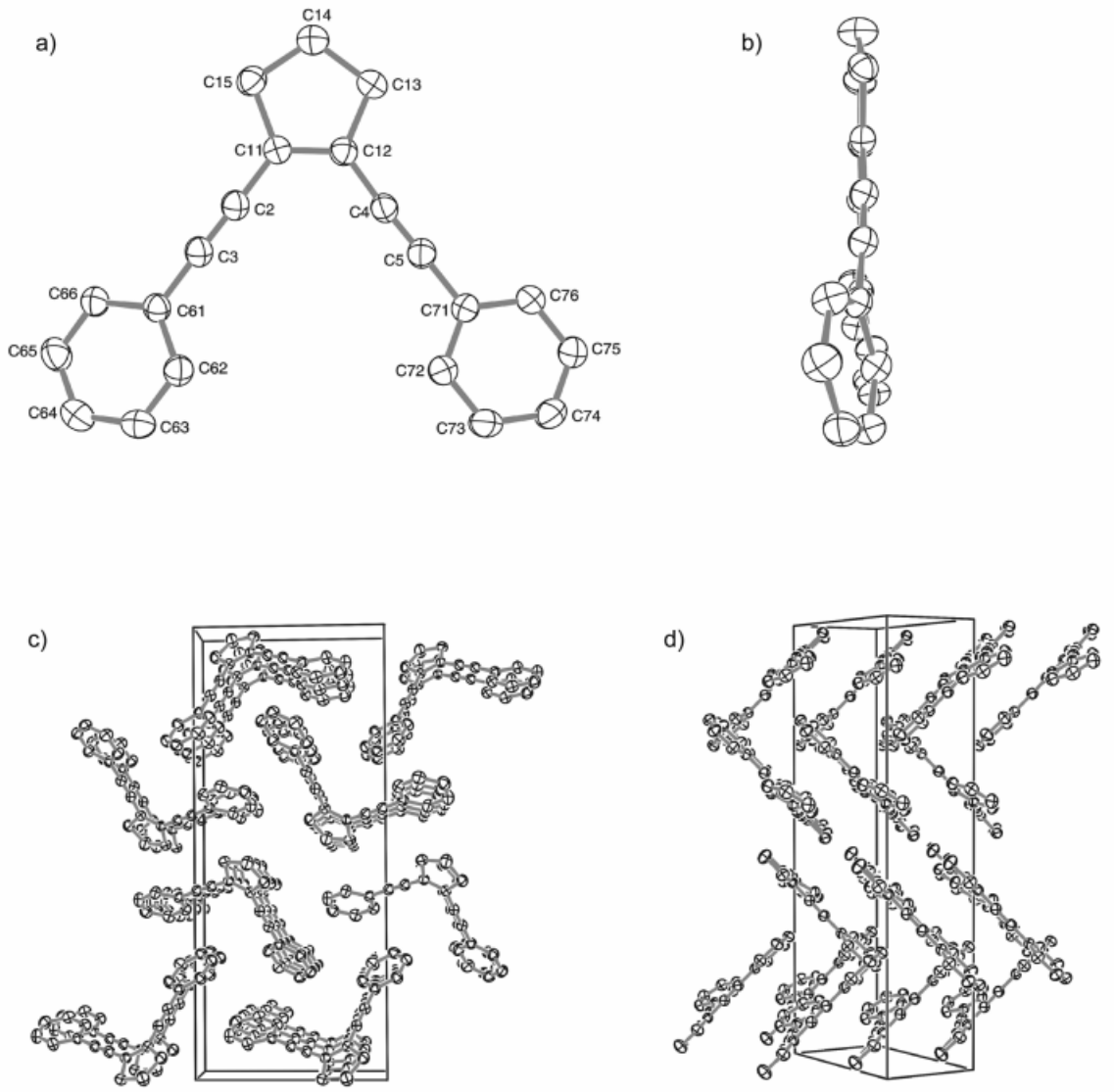


Figure 6. X-ray crystal structure of compound **22** (hydrogen atoms omitted for clarity): a) view of the molecule plane; b) side view; c) and d) arrangement of the molecules within the unit cell; selected bond lengths [Å] and angles [°]: C(3)−C(61) 1.432(3), C(2)−C(3) 1.199(3), C(2)−C(11) 1.420(3), C(11)−C(12) 1.346(3), C(11)−C(15) 1.503(3), C(14)−C(15) 1.510(3); C(2)−C(3)−C(61) 176.6(2), C(3)−C(2)−C(11) 178.0(2), C(12)−C(11)−C(2) 125.4(2), C(2)−C(11)−C(15) 123.3(2), C(12)−C(11)−C(15) 111.3(2), C(11)−C(15)−C(14) 104.5(2), C(13)−C(14)−C(15) 108.0(2)

shorter, 141−143 pm instead of the usual 154 pm. The C−C single bonds of the cyclopentene rings are of normal length (150−154 pm). The C−Si bond lengths of **27** are the typical 185−186 pm.

Conclusion

The longest oligoenyne described up to now was (*Z*,*Z*)-deca-3,7-diene-1,5,9-triyne (**7**), synthesized by Bergman in 1992.[14] By using cyclic 1,2-dibromocyclopentene as a conformationally locked olefinic building block, we have been able to synthesize stable phenyl-terminated *cis*-oligoenynes containing backbones with up to seven conjugated triple and double bonds, in an iterative approach based on Pd-catalysed Sonogashira coupling reactions. Whereas these molecules are completely planar in the solid state, both NMR and computational investigations suggest that a preferred helical conformation is likely in solution. The synthesis of even longer oligoenynes is currently underway.

Experimental Section

General Remarks: ^{1}H NMR and ^{13}C NMR: Jeol JNM EX 400 and Jeol JNM GX 400. − MS: Varian MAT 311 A (EI), Micromass ZabSpec (FAB). − IR: Bruker FT-IR Vector 22. − UV/Vis: Shimadzu UV 3102 PC. − Elemental analysis: EA 1110 CHNS, CE Instruments. − Melting point apparatus: IA 9100, Electrothermal (values are uncorrected). − Preparative HPLC: Shimadzu Class LC10, SIL 10A, SPD 10A, CBM 10A, LC 8A, FRC 10A (Nucleosil, 5 μm, 200 × 4). − Analytical HPLC: Shimadzu Class LC10, SIL 10A, SPD-M10A, CBM 10A, LC 10AT (Nucleosil, 5 μm, 250 × 21). − TLC: Merck, silica gel 60 F 254 nm, viewing by UV or by staining with molybdophosphoric acid and cerium sulfate in

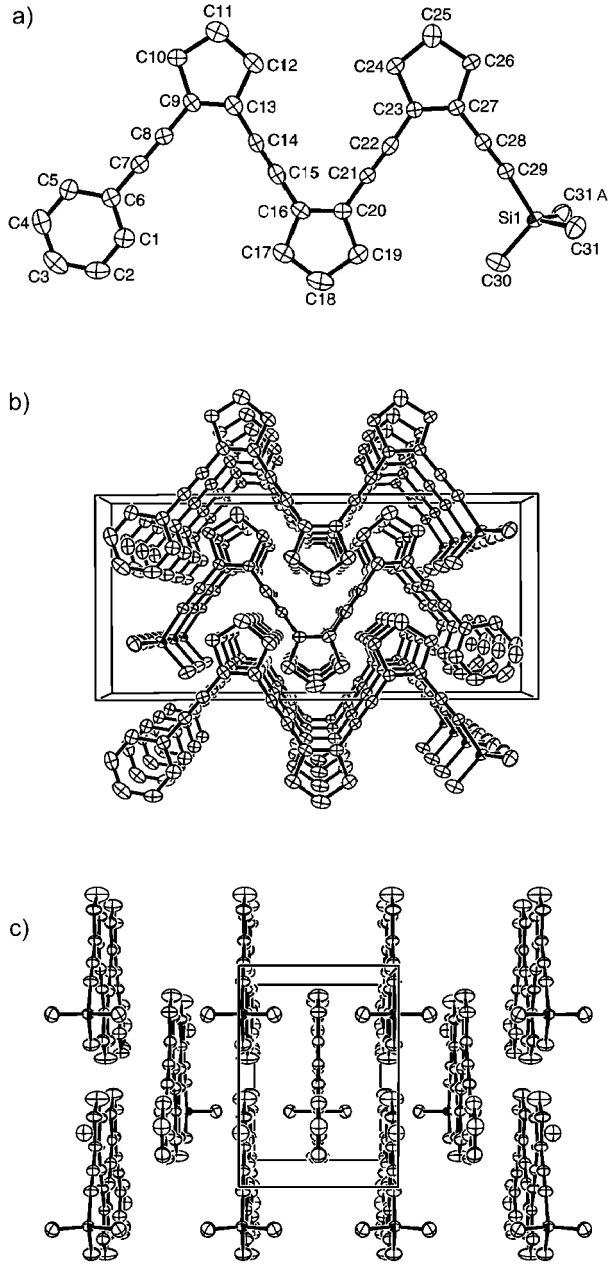


Figure 7. X-ray crystal structure of compound **27** (hydrogen atoms and solvent molecules omitted for clarity): a) view of the molecule plane; b) and c) arrangement of the molecules within the unit cell; selected bond lengths [Å] and angles [°]: C(20)−C(21) 1.410(5), C(21)−C(22) 1.211(5), C(22)−C(23) 1.398(5), C(23)−C(27) 1.361(5), C(27)−C(28) 1.414(5), C(28)−C(29) 1.195(5), Si(1)−C(29) 1.858(4), Si(1)−C(30) 1.850(5), C(23)−C(24) 1.535(6), C(24)−C(25) 1.518(8), C(25)−C(26) 1.528(7), C(26)−C(27) 1.518(6); C(21)−C(22)−C(23) 176.7(4), C(27)−C(23)−C(22) 126.7(3), C(23)−C(27)−C(28) 125.3(4), C(29)−C(28)−C(27) 179.7(4), C(27)−C(23)−C(24) 111.1(3), C(23)−C(27)−C(26) 110.7(3), C(25)−C(24)−C(23) 105.1(4), C(24)−C(25)−C(26) 107.2(5), C(27)−C(26)−C(25) 105.8(4), C(28)−C(29)−Si(1) 173.9(4), C(30)−Si(1)−C(29) 106.8(2)

H_2SO_4 (aq) or with $KMnO_4$ (aq). − Materials and solvents were obtained from commercial suppliers and were dried and purified according to literature methods.[31] Products were isolated whenever possible by flash column chromatography (FC) (silica gel 60, particle size 0.04−0.063 nm, Merck). The semiempirical PM3 calculations were carried out with the PC software package VAMP 7.0a[32] and HyperChem 5.1 or HyperChem 6.0. IUPAC names were generated with the software package ACDLabs Chem Sketch for WINDOWS 4.02. In the assignment of the NMR signals of protected chains, the numbering of the carbon atoms always starts at the acetylenic carbon atom connected to the *ipso*-carbon atom of the phenyl group, irrespective of the IUPAC nomenclature. The numbering of the carbon atoms of the unprotected chain corresponds to IUPAC nomenclature.

General Procedure I for the Sonogashira Coupling: A vinyl halide component, the acetylene compound, and lastly nBuNH$_2$ (5−6 equiv.) were added to a solution of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ (4−10 mol %) and CuI (4−10 mol %) in benzene (2−3 mL/mmol). The reaction mixture was stirred for 18−100 h (TLC monitoring) and was transferred to a separating funnel. The organic layer was washed with 10% hydrochloric acid (2 × 40 mL), saturated $NaHCO_3$ (aq) (1 × 30 mL), and brine (1 × 50 mL), dried with Na_2SO_4 and filtered. Evaporation of the solvent gave the crude product (usually brown oil), which was purified by FC or HPLC.

General Procedure II for the Removal of TMS Protecting Group: The TMS-protected compound was dissolved in 1 mL of THF and the resulting solution was diluted with methanol (2−3 mL/mmol). A few drops of water were added to the solution, which was then cooled to 0 °C. K_2CO_3 (about 6−8 equiv.) was added. The mixture was stirred for 30 min at 0 °C, and then for 6−36 h at room temperature (TLC monitoring). The reaction mixture was then poured into a separating funnel containing 100 mL of diethyl ether and 50 mL of iced H_2O. The organic layer was washed with iced H_2O (4 × 25 mL) and brine (1 × 30 mL), dried with Na_2SO_4, and filtered. The solution was concentrated under vacuum and used directly in the next step.

[(3*Z*)-4-Chlorobut-3-en-1-ynyl]benzene (11):[16] Compound **11** was synthesized according to general procedure I, with phenylacetylene (2.50 g) and (*Z*)-1,2-dichloroethene (4.75 g). Product **11** was purified by column chromatography with hexane as eluent. Yield 3.03 g (76%) yellow oil (R_f = 0.42 in pentane). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.08 (d, ^3J = 7.4 Hz, 1 H, 3-CH_{olef}), 6.43 (d, ^3J = 7.6 Hz, 1 H, 4-CH_{olef}), 7.33 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.50 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 83.25 (C_{acet}-2), 97.40 (C_{acet}-1), 112.06 (C_{olef}-3), 122.67 (C_{ar}-1), 128.23 (C_{olef}-4), 128.32 (C_{ar}-4), 128.72 (C_{ar}-2, C_{ar}-2′), 131.65 (C_{ar}-3, C_{ar}-3′). − IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3083, 3027, 2204, 1953, 1599, 1581, 1489, 1441, 1342, 1264, 1188, 1070, 1028, 984, 916, 806, 756, 722, 690, 636. − MS (70 eV, EI): m/z (%) = 162 (100) $[M]^+$, 127 (83) $[M - Cl]^+$.

Trimethyl[(3*Z*)-6-phenylhex-3-ene-1,5-diynyl]silane (12):[17] Compound **12** was synthesized according to general procedure I, with **11** (1.30 g) and TMS-acetylene (1.03 g). Product **12** was isolated by flash column chromatography, with pentane as eluent. Yield 1.52 g (84%) yellow oil (R_f = 0.20 in pentane). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.24 (s, 9 H, CH_3), 5.87 (d, ^3J = 11.0 Hz, 1 H, 3-CH_{olef}), 6.05 (d, ^3J = 10.7 Hz, 1 H, 4-CH_{olef}), 7.32 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.47 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = −0.12 (CH_3), 87.07 (C_{acet}-5), 97.57 (C_{acet}-6), 102.18 (C_{acet}-1), 103.35 (C_{acet}-2), 119.33, 120.67 (C_{olef}-3, C_{olef}-4), 123.04 (C_{ar}-1), 128.30 (C_{ar}-4), 128.61 (C_{ar}-2, C_{ar}-2′), 131.77 (C_{ar}-3, C_{ar}-3′). − IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3056, 2960, 2899, 2195, 2145, 1881, 1715, 1676, 1598, 1489, 1443, 1395, 1251, 1051, 1027, 999, 961, 845, 757, 690, 633. − MS (70 eV, EI): m/z (%) = 224 (68) $[M]^+$, 209 (100) $[M - CH_3]^+$, 193 (14), 165 (15), 105 (15), 83 (22), 43 (17).

[(3*Z*)-6-Phenylhex-3-ene-1,5-diynyl]benzene (13):[17] Compound **13** was synthesized according to general procedure I, with **11** (0.22 g) and phenylacetylene (0.14 g). Product **13** was isolated by flash column chromatography, with hexane as eluent. Yield 0.26 g (87%) yellow solid (R_f = 0.16 in pentane). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.10 (s, 2 H, 3-C*H*$_{olef}$, 4-C*H*$_{olef}$), 7.33 (m, 6 H, 2 × 2-C*H*$_{ar}$, 2′-C*H*$_{ar}$, 4-C*H*$_{ar}$), 7.52 (m, 4 H, 2 × 3-C*H*$_{ar}$, 3′-C*H*$_{ar}$). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 87.29 (C_{acet}-2, C_{acet}-5), 97.57 (C_{acet}-1, C_{acet}-6), 119.42 (C_{olef}-3, C_{olef}-4), 123.10 (2 × C_{ar}-1), 128.36 (2 × C_{ar}-4), 128.61 (2 × C_{ar}-2, C_{ar}-2′), 131.66 (2 × C_{ar}-3, C_{ar}-3′). − IR (NaCl): ṽ [cm^{-1}] = 3080, 3058, 2216, 2180, 1713, 1674, 1597, 1572, 1488, 1441, 1401, 1263, 1176, 1157, 1069, 1030, 996, 915, 757, 689. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 257.5 (23400), 328.5 (26625), 352.0 (17875). − MS (70 eV, EI): *m*/*z* (%) = 228 (100) [M]$^+$, 126 (25), 28 (27). − $C_{18}H_{12}$ (228.29): calcd. C 94.70, H 5.30; found C 94.09, H 5.74; m.p. 34 °C.

[(3*Z*,7*Z*)-8-Chloroocta-3,7-diene-1,5-diynyl]benzene (14): General procedure II was carried out, with **12** (0.80 g) and K_2CO_3 (3.72 g). The crude product was used in the next step according to general procedure I, with (*Z*)-1,2-dichloroethene (0.66 g). Product **14** was isolated by flash column chromatography, with hexane/chloroform (10:1) as eluent. Yield 0.32 g (42%) yellow solid (R_f = 0.38 in pentane/chloroform = 10:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.09 (m, 3 H, 3-C*H*$_{olef}$, 4-C*H*$_{olef}$, 7-C*H*$_{olef}$), 6.45 (d, ^3J = 7.3 Hz, 1 H, 8-C*H*$_{olef}$), 7.31 (m, 3 H, 2-C*H*$_{ar}$, 2′-C*H*$_{ar}$, 4-C*H*$_{ar}$), 7.47 (m, 2 H, 3-C*H*$_{ar}$, 3′-C*H*$_{ar}$). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 87.01 (C_{acet}-2), 90.92 (C_{acet}-6), 94.92 (C_{acet}-5), 98.14 (C_{acet}-1), 112.06 (C_{olef}-7), 118.66, 120.52 (C_{olef}-3, C_{olef}-4), 122.95 (C_{ar}-1), 128.27 (C_{ar}-4), 128.65 (C_{ar}-2, C_{ar}-2′), 129.20 (C_{olef}-8), 132.01 (C_{ar}-3, C_{ar}-3′). − IR (NaCl): ṽ [cm^{-1}] = 3082, 2199, 2176, 1677, 1597, 1554, 1489, 1442, 1400, 1332, 1268, 1217, 1130, 1070, 1028, 981, 916, 857, 783, 756, 723, 690, 670. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 248.5 (48670), 261.0 (46940), 272.5 (25020), 290.0 (38540), 308.0 (56700), 329.0 (50350), 348.5 (2985). − MS (70 eV, EI): *m*/*z* (%) = 212 (100) [M]$^+$, 176 (90) [M − Cl]$^+$, 151 (29). − $C_{14}H_9Cl$ (212.68): calcd. C 79.06, H 4.91; found C 84.81, H 5.38; m.p. 76 °C.

Triisopropyl[(3*Z*)-6-phenylhex-3-ene-1,5-diynyl]silane (15): Compound **15** was synthesized according to general procedure I, with **11** (1.56 g) and TIPS-acetylene (2.10 g). Product **15** was isolated by flash column chromatography, with hexane as eluent. Yield 2.80 g (94%) yellowish oil (R_f = 0.45 in pentane). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.10 [s, 21 H, C*H*(C*H*$_3$)$_2$], 5.90 (d, ^3J = 11.0 Hz, 1 H, 3-C*H*$_{olef}$), 6.05 (d, ^3J = 10.5 Hz, 1 H, 4-C*H*$_{olef}$), 7.30 (m, 3 H, 2-C*H*$_{ar}$, 2′-C*H*$_{ar}$, 4-C*H*$_{ar}$), 7.45 (m, 2 H, 3-C*H*$_{ar}$, 3′-C*H*$_{ar}$). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 11.26 [*C*H(CH$_3$)$_2$], 18.64 [CH(*C*H$_3$)$_2$], 87.09 (C_{acet}-5), 97.16 (C_{acet}-6), 99.94 (C_{acet}-1), 103.97 (C_{acet}-2), 119.46, 120.17 (C_{olef}-3, C_{olef}-4), 123.08 (C_{ar}-1), 128.20 (C_{ar}-4), 128.49 (C_{ar}-2, C_{ar}-2′), 131.71 (C_{ar}-3, C_{ar}-3′). − IR (NaCl): ṽ [cm^{-1}] = 2943, 2891, 2865, 2194, 2141, 1676, 1598, 1568, 1489, 1463, 1394, 1366, 1050, 1017, 997, 953, 918, 883, 784, 755, 678. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 261.0 (7500), 307.0 (22670), 327.0 (21410). − MS (70 eV, EI): *m*/*z* (%) = 308 (43) [M]$^+$, 265 (100) [M − C_3H_7]$^+$, 237 (21), 223 (24), 195 (40), 104 (33), 59 (20). − $C_{21}H_{28}Si$ (308.54): calcd. C 81.75, H 9.15; found C 81.18, H 9.09.

Triisopropyl[(3*Z*,7*Z*)-10-phenyldeca-3,7-diene-1,5,9-triynyl]silane (16): Compound **15** was synthesized according to general procedure I, with **14** (0.32 g) and TIPS-acetylene (0.41 g). Product **16** was isolated by flash column chromatography, with hexane/chloroform (10:1) as eluent. Yield 0.79 g (41%) yellow oil (R_f = 0.23 in hexane/chloroform = 15:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.08 [s, 21 H, C*H*(C*H*$_3$)$_2$], 5.89−6.11 (m, 4 H, C*H*$_{olef}$), 7.31 (m, 3 H, 2-C*H*$_{ar}$, 2′-C*H*$_{ar}$, 4-C*H*$_{ar}$), 7.46 (m, 2 H, 3-C*H*$_{ar}$, 3′-C*H*$_{ar}$). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 11.21 [*C*H(CH$_3$)$_2$], 18.57 [CH(*C*H$_3$)$_2$], 87.21 (C_{acet}-9), 94.63, 95.00 (C_{acet}-5, C_{acet}-6), 97.94 (C_{acet}-10), 100.68 (C_{acet}-1), 103.93 (C_{acet}-2), 119.15, 119.83, 120.25, 120.34 (C_{olef}-3, C_{olef}-4, C_{olef}-7, C_{olef}-8), 123.04 (C_{ar}-1), 128.28 (C_{ar}-4), 128.59 (C_{ar}-2, C_{ar}-2′), 131.86 (C_{ar}-3, C_{ar}-3′). − IR (NaCl): ṽ [cm^{-1}] = 33042, 2943, 2890, 2865, 2197, 2137, 1673, 1598, 1489, 1463, 1406, 1384, 1240, 1136, 1071, 1022, 997, 918, 883, 754, 678. − UV/Vis (cyclohexane): λ_{max} [nm] = 227.0, 275.0, 344.0, 368.5. − MS (70 eV, EI): *m*/*z* (%) = 358 (64) [M]$^+$, 315 (100) [M − C_3H_7]$^+$, 272 (72) [315 − C_3H_7]$^+$, 257 (23) [272 − CH_3]$^+$, 245 (44), 238 (51), 202 (22), 129 (35), 99 (27), 69 (19), 57 (37), 43 (36).

[(3*Z*,7*Z*)-10-Phenyldeca-3,7-diene-1,5,9-triynyl]benzene (17): General procedure II was carried out, with **12** (0.15 g) and K_2CO_3 (0.74 g). The crude product was used in the next step according to general procedure I, with **11** (0.13 g). The product **17** was isolated by flash column chromatography, with pentane as eluent. Yield 0.05 g (29%) brownish oil (R_f = 0.09 in pentane). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.14 (s, 4 H, C*H*$_{olef}$), 7.20−7.53 (m, 10 H, C*H*$_{ar}$). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 87.23 (C_{acet}-2, C_{acet}-9), 94.98 (C_{acet}-5, C_{acet}-6), 98.27 (C_{acet}-1, C_{acet}-10), 118.98, 119.97 (C_{olef}-3, C_{olef}-4, C_{olef}-7, C_{olef}-8), 122.89 (2 × C_{ar}-1), 128.14 (2 × C_{ar}-4), 128.50 (2 × C_{ar}-2, C_{ar}-2′), 131.92 (2 × C_{ar}-3, C_{ar}-3′). − IR (NaCl): ṽ [cm^{-1}] = 3034, 2925, 2192, 2164, 1675, 1598, 1489, 1442, 1408, 1130, 1070, 1029, 932, 915, 757, 689. − MS (70 eV, EI): *m*/*z* (%) = 278 (58) [M]$^+$, 276 (100), 228 (12), 226 (13), 138 (17). − $C_{22}H_{14}$ (278.35): calcd. C 94.93, H 5.07; found C 92.78, H 5.00.

[(3*Z*,7*Z*,11*Z*)-14-Phenyltetradeca-3,7,11-triene-1,5,9,13-tetraynyl]benzene (18): General procedure II was carried out, with **12** (0.34 g) and K_2CO_3 (1.68 g). The crude product was used in the next step according to general procedure I, with (*Z*)-1,2-dichloroethene (0.06 g). Product **18** was isolated first by flash column chromatography, with pentane/chloroform (12:1) as eluent, and then by preparative HPLC, with heptane/dichloromethane (95:5) as eluent. Yield 0.03 g (6%) yellow solid (R_f = 0.21 in pentane/chloroform = 12:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.94 (d, ^3J = 12.0 Hz, 2 H, 3-C*H*$_{olef}$, 12-C*H*$_{olef}$), 6.70 (d, ^3J = 12.0 Hz, 2 H, 4-C*H*$_{olef}$, 11-C*H*$_{olef}$), 7.32 (m, 6 H, 2 × 2-C*H*$_{ar}$, 2′-C*H*$_{ar}$, 4-C*H*$_{ar}$), 7.48 (m, 4 H, 2 × 3-C*H*$_{ar}$, 3′-C*H*$_{ar}$), 7.96 (s, 2 H, 7-C*H*$_{olef}$, 8-C*H*$_{olef}$). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 88.51, 88.99, 92.48 (C_{acet}-2, C_{acet}-5, C_{acet}-6, C_{acet}-9, C_{acet}-10, C_{acet}-13), 96.49 (C_{acet}-1, C_{acet}-14), 107.80 (C_{olef}-3, C_{olef}-12), 123.41 (2 × C_{ar}-1), 128.39 (2 × C_{ar}-4), 128.43 (2 × C_{ar}-2, C_{ar}-2′), 128.67 (C_{olef}-7, C_{olef}-8), 131.43 (2 × C_{ar}-3, C_{ar}-3′), 138.09 (C_{olef}-4, C_{olef}-11). − IR (KBr): ṽ [cm^{-1}] = 3619, 2956, 2189, 1598, 1489, 1441, 1250, 1069, 1028, 952, 913, 838, 755, 689. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] 235.0 (21330), 350.0 (32015). − MS (FAB): *m*/*z* = 330 [M + 2 H]$^+$, 252 [330 − C_6H_6]$^+$. − $C_{26}H_{16}$ (328.41): calcd. C 95.09, H 4.91; found C 92.74, H 5.63; m.p. 175 °C.

(7Z)-Tetradec-7-ene-5,9-diyne (19):[18] Compound **19** was synthesized according to general procedure I, with 1-hexyne (0.35 g) and (*Z*)-1,2-dichloroethene (0.21 g). Product **19** was isolated by flash column chromatography, with pentane as eluent. Yield 0.32 g (80%) yellow oil (R_f = 0.27 in pentane). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, 6 H, ^3J = 7.2 Hz, 1-C*H*$_3$, 14-C*H*$_3$), 1.48 (m, 8 H, 2-C*H*$_2$, 3-C*H*$_2$, 12-C*H*$_2$, 13-C*H*$_2$), 2.37 (t, ^3J = 6.8 Hz, 4-C*H*$_2$, 11-C*H*$_2$), 5.70 (s, 2 H, 7-C*H*$_{olef}$, 8-C*H*$_{olef}$). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 13.60 (*C*H$_3$-1, *C*H$_3$-14), 19.43 (*C*H$_2$-4, *C*H$_2$-11), 21.88 (*C*H$_2$-2, *C*H$_2$-13), 30.70 (*C*H$_2$-3, *C*H$_2$-12), 78.28 (C_{acet}-6, C_{acet}-9), 97.83 (C_{acet}-5, C_{acet}-10), 118.93 (C_{olef}-7, C_{olef}-8). − IR (NaCl): ṽ [cm^{-1}] = 3026, 2958, 2932, 2872, 2218, 1677, 1577, 1466, 1429, 1398, 1379, 1326, 1250, 1161, 1107, 745. −

UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 263.5 (11950), 277.5 (11320). − MS (70 eV, EI): *m/z* (%) = 188 (92) $[M]^+$, 145 (27) $[M - C_3H_7]^+$, 131 (93), 117 (100), 105 (31), 103 (31), 91 (97), 79 (25), 77 (48), 65 (20), 63 (24), 57 (23), 51 (27), 43 (28), 41 (53), 39 (35), 29 (21), 27 (30).

[(2-Bromocyclopent-1-en-1-yl)ethynyl]benzene (21) and {[2-(Phenylethynyl)cyclopent-1-en-1-yl]ethynyl}benzene (22): Compounds **21** and **22** were synthesized according to general procedure I, with phenylacetylene (3.19 g) and 1,2-dibromocyclopentene (7.77 g). Products **21** and **22** were purified by column chromatography, with a mixture of hexane/dichloromethane (15:1) as eluent. Yield **21** 6.18 g (80%) yellow oil (R_f = 0.55 in hexane/dichloromethane, 15:1), **22** 1.19 g (20%) white solid (R_f = 0.28 in hexane/dichloromethane, 15:1).

Compound 21: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.02 (quint, 2 H, ^3J = 7.6 Hz, CH_2-b), 2.57 (t, ^3J = 7.6 Hz, 2 H, CH_2-a), 2.76 (t, ^3J = 7.6 Hz, 2 H, CH_2-c), 7.34 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.50 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 22.50 (*C*H_2-b), 35.88 (*C*H_2-a), 40.35 (*C*H_2-c), 84.89 (C_{acet}-2), 95.25 (C_{acet}-1), 123.08 (C_{ar}-1), 124.19 (C_{olef}-4), 127.77 (C_{olef}-3), 128.27 (*C*H_{ar}-4), 128.36 (*C*H_{ar}-2, *C*H_{ar}-2′), 131.61 (*C*H_{ar}-3, *C*H_{ar}-3′). − IR (NaCl): ṽ [cm^{-1}] = 3060, 2954, 2851, 2218, 2203, 2151, 1594, 1487, 1442, 1319, 1069, 1026, 931, 755, 689. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 285.5 (31960), 303.5 (25300), 329.0 (3910). − MS (70 eV, EI): *m/z* (%) = 248 (83) $[M^{81}Br]^+$, 246 (84) $[M^{79}Br]^+$, 167 (87), 165 (100), 152 (72), 139 (29), 83 (30), 82 (30), 43 (25). − $C_{13}H_{11}Br$ (247.13): calcd. C 63.18, H 4.49; found C 59.64, H 4.20.

Compound 22: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.02 (quint, 2 H, ^3J = 7.6 Hz, CH_2-b), 2.69 (t, ^3J = 7.6 Hz, 4 H, CH_2-a, CH_2-c), 7.31 (m, 6 H, 2 × 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.51 (m, 4 H, 2 × 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 23.18 (*C*H_2-b), 36.99 (*C*H_2-a, *C*H_2-c), 86.30 (C_{acet}-2, C_{acet}-5), 96.64 (C_{acet}-1, C_{acet}-6), 123.41 (2 × C_{ar}-1), 128.25 (2 × *C*H_{ar}-4), 128.28 (2 × *C*H_{ar}-2, *C*H_{ar}-2′), 130.31 (C_{olef}-3, C_{olef}-4), 131.59 (2 × *C*H_{ar}-3, *C*H_{ar}-3′). − IR (KBr): ṽ [cm^{-1}] = 3077, 2925, 2851, 2359, 2184, 1596, 1487, 1439, 1363, 1277, 1155, 1066, 1027, 989, 915, 839, 755, 689, 591, 528, 447, 431. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 229.5 (19180), 261.5 (24642), 332.0 (23645), 356.0 (14194). − MS (70 eV, EI): *m/z* (%) = 268 (100) $[M]^+$, 252 (38) $[M - CH_2]^+$. − $C_{21}H_{16}$ (268.36): calcd. C 93.99, H 6.01; found C 93.27, H 5.86; m.p. 87 °C.

Trimethyl{[2-(phenylethynyl)cyclopent-1-en-1-yl]ethynyl}silane (23): Compound **23** was synthesized according to general procedure I, with **21** (6.00 g) and TMS-acetylene (9.53 g). Product **23** was isolated by flash column chromatography, with hexane/dichloromethane (20:1) as eluent. Yield 5.84 g (91%) yellowish solid (R_f = 0.24 in hexane/dichloromethane, 20:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.23 [s, 9 H, Si(CH_3)$_3$], 1.94 (quint, 2 H, ^3J = 7.6 Hz, CH_2-b), 2.60 (m, 4 H, CH_2-a, CH_2-c), 7.30 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.45 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 0.03 [Si(*C*H_3)$_3$], 23.14 (*C*H_2-b), 36.79 (*C*H_2-a, *C*H_2-c), 86.08 (C_{acet}-2), 96.71 (C_{acet}-3), 101.54 (C_{acet}-6), 101.98 (C_{acet}-5), 123.37 (C_{ar}-1), 128.26 (*C*H_{ar}-4), 128.35 (*C*H_{ar}-2, *C*H_{ar}-2′), 130.31 (C_{olef}-3), 131.65 (*C*H_{ar}-3, *C*H_{ar}-3′), 131.75 (C_{olef}-4). − IR (KBr): ṽ [cm^{-1}] = 2959, 2850, 2139, 1600, 1489, 1442, 1350, 1250, 1130, 1069, 1028, 995, 913, 844, 756, 690. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 239.0 (19627), 311.0 (28857), 332.0 (24389). − MS (70 eV, EI): *m/z* (%) = 264 (100) $[M]^+$, 249 (85). − $C_{18}H_{20}Si$ (264.44): calcd. C 81.76, H 7.62; found C 82.28, H 7.83; m.p. 46 °C.

({2-[(2-Bromocyclopent-1-en-1-yl)ethynyl]cyclopent-1-en-1-yl}ethynyl)benzene (24): General procedure II was carried out, with **23** (2.49 g) and K_2CO_3 (7.81 g). The crude product was used in the next step according to general procedure I, with 1,2-dibromocyclopentene (2.55 g). Product **24** was isolated by flash column chromatography, with hexane/dichloromethane (5:1) as eluent. Yield 0.90 g (36%) yellow solid (R_f = 0.43 in hexane/dichloromethane, 5:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.99 (2 × quint, 4 H, ^3J = 7.6 Hz, CH_2-b, CH_2-e), 2.55 (m, 2 H, CH_2-d), 2.65 (t, ^3J = 7.6 Hz, 4 H, CH_2-a, CH_2-c), 2.74 (t, ^3J = 7.6 Hz, 2 H, CH_2-f), 7.29 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.48 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 22.54 (*C*H_2-e), 23.20 (*C*H_2-b), 35.95 (*C*H_2-d), 36.90, 37.10 (*C*H_2-a, *C*H_2-c), 40.46 (*C*H_2-f), 86.30 (C_{acet}-2), 91.87, 92.04 (C_{acet}-5, C_{acet}-6), 96.84 (C_{acet}-1), 123.42 (*C*H_{ar}-1), 124.37 (C_{olef}-8), 128.17 (*C*H_{ar}-4), 128.25 (*C*H_{ar}-2, *C*H_{ar}-2′), 130.00, 130.81 (C_{olef}-3, C_{olef}-4, C_{olef}-7), 131.85 (*C*H_{ar}-3, *C*H_{ar}-3′). − IR (KBr): ṽ [cm^{-1}] = 3442, 2923, 2851, 2197, 1715, 1595, 1488, 1439, 1362, 1312, 1289, 1203, 1119, 1084, 1070, 1025, 970, 918, 878, 810, 756, 694, 591, 534, 500, 439. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 262.5 (17132), 334.0 (18140). − MS (70 eV, EI): *m/z* (%) = 338 (100) $[M^{81}Br]^+$, 336 (100) $[M^{79}Br]^+$, 256 (17) $[M - Br]^+$, 241 (32), 229 (36), 215 (25), 202 (17), 115 (20), 85 (19), 71 (29), 57 (51), 43 (40). − $C_{20}H_{17}Br$ (337.26): calcd. C 71.23, H 5.08; found C 70.93, H 5.13; m.p. 71 °C.

Trimethyl[(2-{[2-(phenylethynyl)cyclopent-1-en-1-yl]ethynyl}cyclopent-1-en-1-yl)ethynyl]silane (25): Compound **25** was synthesized according to general procedure I, with **24** (0.65 g) and TMS-acetylene (0.75 g). Product **25** was isolated by flash column chromatography, with hexane/dichloromethane (10:1) as eluent. Yield 0.67 g (99%) yellowish solid (R_f = 0.18 in hexane/dichloromethane, 10:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.15 [s, 9 H, Si(CH_3)$_3$], 1.95 (2 × quint, 4 H, ^3J = 7.7 Hz, CH_2-b, CH_2-e), 2.63 (m, 8 H, CH_2-a, CH_2-c, CH_2-d, CH_2-f), 7.28 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.44 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 0.01 [Si(*C*H_3)$_3$], 23.18 (*C*H_2-b, *C*H_2-e), 36.99, 37.08, 37.12, 37.21 (*C*H_2-a, *C*H_2-c, *C*H_2-d, *C*H_2-f), 86.43 (C_{acet}-2), 93.11, 93.37 (C_{acet}-5 and C_{acet}-6), 96.82 (C_{acet}-1), 101.57 (C_{acet}-10), 102.23 (C_{acet}-9), 123.50 (*C*H_{ar}-1), 128.17 (*C*H_{ar}-4), 128.25 (*C*H_{ar}-2, *C*H_{ar}-2′), 130.07, 130.18, 130.40 (C_{olef}-3, C_{olef}-4, C_{olef}-7, C_{olef}-8), 131.77 (*C*H_{ar}-3, *C*H_{ar}-3′). − IR (KBr): ṽ [cm^{-1}] = 3442, 2955, 2924, 2853, 2130, 1600, 1488, 1442, 1374, 1253, 1241, 1069, 1027, 968, 916, 844, 750, 687, 621, 563, 524, 438. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 231.0 (10347), 281.5 (9396), 351.5 (13001), 377.0 (8619). − MS (70 eV, EI): *m/z* (%) = 354 (100) $[M]^+$, 339 (33) $[M - CH_3]^+$, 311 (27), 295 (52), 279 (42), 265 (23), 252 (22), 73 (91), 59 (49). − $C_{25}H_{26}Si$ (354.56): calcd. C 84.69, H 7.39; found C 83.41, H 7.53; m.p. 101 °C.

{[2-({2-[(2-Bromocyclopent-1-en-1-yl)ethynyl]cyclopent-1-en-1-yl}ethynyl)cyclopent-1-en-1-yl]ethynyl}benzene (26): General procedure II was carried out, with **25** (0.77 g) and K_2CO_3 (1.93 g). The crude product was used in the next step according to general procedure I, with 1,2-dibromocyclopentene (0.54 g). Product **26** was isolated by flash column chromatography, with hexane/dichloromethane (5:1) as eluent. Yield 0.90 g (36%) yellow-brownish solid (R_f = 0.36 in hexane/dichloromethane, 5:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.76 (quint, 2 H, ^3J = 7.6 Hz, CH_2-h), 1.91 (t, ^3J = 7.6 Hz, 4 H, CH_2-b, CH_2-e), 2.35 (t, ^3J = 7.6 Hz, 2 H, CH_2-g). 2.58 (t, 10 H, ^3J = 7.6 Hz, CH_2-a, CH_2-c, CH_2-d, CH_2-f, CH_2-i), 7.22 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.39 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 22.36 (*C*H_2-h), 23.18 (*C*H_2-b, *C*H_2-e), 35.91 (*C*H_2-g), 37.06, 37.17, 37.30 (*C*H_2-a, *C*H_2-c, *C*H_2-d, *C*H_2-f), 40.37 (*C*H_2-i), 86.54 (C_{acet}-2), 92.09, 92.18, 93.33, 93.59 (C_{acet}-5, C_{acet}-6, C_{acet}-9, C_{acet}-10), 96.84 (C_{acet}-1), 123.42 (*C*H_{ar}-1), 124.47 (C_{olef}-12), 127.92 (C_{olef}-11), 128.06

(CH_{ar}-4), 128.16 (CH_{ar}-2, CH_{ar}-2′), 129.98, 130.37, 130.40, 130.68 (C_{olef}-3, C_{olef}-4, C_{olef}-7, C_{olef}-8), 131.81 (CH_{ar}-3, CH_{ar}-3′). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3474, 2963, 2952, 2922, 2849, 2183, 2156, 1735, 1604, 1488, 1442, 1378, 1312, 1281, 1210, 1083, 1028, 909, 753, 688, 594, 523, 417. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 300.5 (26250), 364.0 (24360). − MS (70 eV, EI): *m/z* (%) = 428 (78) $[M^{81}Br]^+$, 426 (76) $[M^{79}Br]^+$, 347 [M − Br]$^+$, (100), 317 (16), 303 (19), 294 (30). − $C_{27}H_{23}Br$ (427.38): calcd. C 75.88, H 5.42; found C 74.73, H 5.44; m.p. 119 °C.

Trimethyl({2-[(2-{[2-(phenylethynyl)cyclopent-1-en-1-yl]ethynyl}-cyclopent-1-en-1-yl)ethynyl]cyclopent-1-en-1-yl}ethynyl)silane (27): Compound **27** was synthesized according to general procedure I, with **26** (0.09 g) and TMS-acetylene (0.12 g). Product **27** was isolated by flash column chromatography, with hexane/dichloromethane (5:1) as eluent. Yield 0.07 g (81%) orange solid (R_f = 0.42 in hexane/dichloromethane, 5:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.20 [s, 9 H, Si(CH_3)$_3$], 1.70 (quint, 2 H, ^3J = 7.6 Hz, CH_2-h), 1.96 (quint, 4 H, ^3J = 7.6 Hz, CH_2-b, CH_2-e), 2.43 (t, ^3J = 7.6 Hz, 4 H, CH_2-g, CH_2-i), 2.63 (m, 8 H, CH_2-a, CH_2-c, CH_2-d, CH_2-f), 7.27 (m, 3 H, 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.44 (m, 2 H, 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 0.00 [Si(CH_3)$_3$], 22.93(CH_2-h), 23.13 (CH_2-b, CH_2-e), 36.79, 36.93 (CH_2-g, CH_2-i), 37.03, 37.10, 37.25, 37.38 (CH_2-a, CH_2-c, CH_2-d, CH_2-f), 86.44 (C_{acet}-2), 93.41, 93.49 (C_{acet}-5, C_{acet}-6, C_{acet}-9, C_{acet}-10), 96.83 (C_{acet}-1), 101.67 (C_{acet}-14), 101.93 (C_{acet}-13), 123.35 (CH_{ar}-1), 128.01 (CH_{ar}-4), 128.12 (CH_{ar}-2, CH_{ar}-2′), 129.90, 130.03, 130.16, 130.33 (C_{olef}-3, C_{olef}-4, C_{olef}-7, C_{olef}-8, C_{olef}-11), 131.82 (CH_{ar}-3, CH_{ar}-3′), 132.04 (C_{olef}-12). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3442, 2957, 2926, 2852, 2131, 1718, 1636, 1489, 1443, 1385, 1249, 1177, 1095, 845, 756, 687. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 264.0 (23960), 302.5 (30650), 316.0 (41225), 364.5 (34085), 465.5 (3560). − MS (70 eV, EI): *m/z* (%) = 444 (100) [M]$^+$, 371 (17) [M − TMS]$^+$, 73 (65). − $C_{32}H_{32}Si$ (444.69): calcd. C 86.43, H 7.25; found C 83.53, H 7.08; m.p. 169 °C.

({2-[(2-{[2-(Phenylethynyl)cyclopent-1-en-1-yl]ethynyl}cyclopent-1-en-1-yl)ethynyl]cyclopent-1-en-1-yl}ethynyl)benzene (28): General procedure II was carried out, with **23** (1.60 g) and K_2CO_3 (4.93 g). The crude product was used in the next step according to general procedure I, with 1,2-dibromocyclopentene (0.62 g). Product **28** was isolated by flash column chromatography, with hexane/dichloromethane (5:1) as eluent. Yield 0.11 g (9%) bright brownish solid (R_f = 0.18 in hexane/dichloromethane, 5:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.73 (quint, 4 H, ^3J = 7.6 Hz, CH_2-b, CH_2-h), 1.92 (quint, 2 H, ^3J = 7.6 Hz, CH_2-e), 2.46 (2 × tr, 8 H, ^3J = 7.6 Hz, CH_2-a, CH_2-c, CH_2-g, CH_2-i), 2.61 (t, ^3J = 7.6 Hz, 4 H, CH_2-d, CH_2-f), 7.22 (m, 6 H, 2 × 2-CH_{ar}, 2′-CH_{ar}, 4-CH_{ar}), 7.40 (m, 4 H, 2 × 3-CH_{ar}, 3′-CH_{ar}). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 22.99 (CH_2-b, CH_2-h), 23.23 (CH_2-e), 36.99, 37.04 (CH_2-a, CH_2-c, CH_2-g, CH_2-i), 37.32 (CH_2-d, CH_2-h), 86.61 (C_{acet}-2, C_{acet}-13), 93.50, 93.83 (C_{acet}-5, C_{acet}-6, C_{acet}-9, C_{acet}-10), 96.84 (C_{acet}-1, C_{acet}-14), 123.53 (2 × C_{ar}-1), 128.00 (2 × CH_{ar}-4), 128.14 (2 × CH_{ar}-2, CH_{ar}-2′), 130.33, 130.50 (2 × C_{olef}-3, 2 × C_{olef}-4, C_{olef}-7), 131.86 (2 × CH_{ar}-3, CH_{ar}-3′). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3441, 2924, 2850, 1628, 1488, 1442, 1385, 1122, 754, 688. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 250.0 (24310), 279.5 (22967), 315.0 (22395), 330.5 (24901), 382.5 (20473). − MS (FAB): *m/z* = 448 [M]$^+$. − $C_{35}H_{28}$ (448.61): calcd. C 93.71, H 6.29; found C 88.82, H 6.48; m.p. 158 °C.

1,2-Di(1-pentynyl)cyclopent-1-ene (29): Compound **29** was synthesized according to general procedure I, with 1-pentyne (0.36 g) and 1,2-dibromocyclopentene (0.30 g). Product **29** was isolated by flash column chromatography, with hexane/dichloromethane (10:1) as eluent. Yield 0.23 g (87%) yellow oil (R_f = 0.42 in hexane/dichloromethane, 10:1). − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.00 (t, 6 H, ^3J = 7.3 Hz, CH_3-1, CH_3-12), 1.55 (sextet, 4 H, ^3J = 7.1, ^3J = 7.3 Hz, CH_2-2, CH_2-11), 1.85 (quint, 2 H, ^3J = 7.6 Hz, CH_2-b), 2.35 (t, ^3J = 7.1 Hz, 4 H, 3-CH_2, 10-CH_2), 2.46 (t, ^3J = 7.6 Hz, 4 H, CH_2-a, CH_2-c). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 13.38 (CH_3-1, CH_3-12), 21.75 (CH_2-3, CH_2-10), 22.17 (CH_2-2, CH_2-11), 22.87 (CH_2-b), 36.90 (CH_2-a, CH_2-c), 77.53 (C_{acet}-5, C_{acet}-8), 96.60 (C_{acet}-4, C_{acet}-9), 129.09 (C_{olef}-6, C_{olef}-7). − IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2962, 2934, 2871, 2213, 1458, 1380, 1353, 1276. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 268.0 (16369), 281.5 (14217). − MS (70 eV, EI): *m/z* (%) = 200 (100) [M]$^+$, 171 (25) [M − C_2H_5]$^+$, 157 (10) [171 − CH_2]$^+$, 143 (15) [157 − CH_2]$^+$, 129 (25) [143 − CH_2]$^+$, 115 (13) [129 − CH_2]$^+$, 91 (11). − $C_{15}H_{20}$ (200.32): calcd. C 89.94, H 10.06; found C 88.91, H 9.99.

[(2-Bromocyclopent-1-en-1-yl)ethynyl](trimethyl)silane (30) and Trimethyl({2-[(trimethylsilyl)ethynyl]cyclopent-1-en-1-yl}ethynyl)-silane (31): Compounds **30** and **31** were synthesized according to general procedure I, with TMS-acetylene (0.33 g) and 1,2-dibromocyclopentene (0.76 g). Products **30** and **31** were purified by column chromatography, with a mixture of hexane/dichloromethane (20:1) as eluent. Yield **30** 0.36 g (44%) yellow oil (R_f = 0.49 in hexane), **31** 0.18 g (21%) yellowish solid (R_f = 0.22 in hexane).

Compound 30: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.20 [s, 9 H, Si(CH_3)$_3$], 1.95 (quint, 2 H, ^3J = 7.6 Hz, CH_2-b), 2.46 (t, ^3J = 7.6 Hz, 2 H, CH_2-a), 2.68 (t, ^3J = 7.6 Hz, 2 H, CH_2-c). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 22.46 (CH_2-b), 35.84 (CH_2-a), 40.31 (CH_2-c), 100.15 (C_{acet}-1), 101.00 (C_{acet}-2), 124.23 (C_{olef}-4), 128.81 (C_{olef}-3). − IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2960, 2854, 2150, 1720, 1609, 1441, 1311, 1250, 1039, 936, 844, 760, 700. − MS (70 eV, EI): *m/z* (%) = 244 (27) $[M^{81}Br]^+$, 242 (26) $[M^{79}Br]^+$, 229 (100) $[M^{81}Br - CH_3]^+$, 227 (97) $[M^{79}Br - CH_3]^+$, 147 (35), 145 (26), 139 (34), 137 (34), 105 (46), 74 (22), 43 (20).

Compound 31: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.19 [s, 18 H, Si(CH_3)$_3$], 1.87 (quint, 2 H, ^3J = 7.6 Hz, CH_2-b), 2.51 (t, ^3J = 7.6 Hz, 4 H, CH_2-a, CH_2-c). − ^{13}C NMR (105.5 MHz, $CDCl_3$, 25 °C): δ = 0.03 [Si(CH_3)$_3$], 23.11 (CH_2-b), 36.65 (CH_2-a, CH_2-c), 101.20 (C_{acet}-1, C_{acet}-6), 102.06 (C_{acet}-2, C_{acet}-5), 131.74 (C_{olef}-3, C_{olef}-4). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2961, 2924, 2852, 2193, 2135, 1442, 1408, 1330, 1249, 1180, 1015, 844, 758, 698, 618, 556, 478. − UV/Vis (CH_2Cl_2): λ_{max} (ε) [nm] = 282.5 (23252), 297.5 (22011). − MS (70 eV, EI): *m/z* (%) = 260 (80) [M]$^+$, 245 (78) [M − CH_3]$^+$, 171 (45), 157 (18), 115 (35), 73 (100), 59 (21), 45 (25). − $C_{15}H_{24}Si_2$ (260.53): calcd. C 69.15, H 9.26; found C 68.87, H 9.34; m.p. 39 °C.

X-ray Crystallography Study

Crystal Data for 22: $C_{21}H_{16}$, monoclinic, space group $P2_1/n$, a = 5.8013(12), b = 25.336(5), c = 10.741(2) Å, β = 91.40(3), V = 1578.3(6) Å^3, Z = 4, μ = 0.064 mm^{-1}, D_x = 1.129 Mg/m^3, F(000) = 568. Data were collected at 173(2) K with a Nonius Kappa CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å, range for data collection θ = 3.07 to 26.36°, index ranges $0 \le h \le 7$, $0 \le k \le 31$, $-13 \le l \le 13$), 3190 reflections collected, 3190 independent reflections (R_{int} = 0.0000), 1695 reflections [$I > 2\sigma(I)$]. Absorption correction method was applied.[33] The structure was solved by direct methods and refined using full-matrix, least-squares procedures on F^2 (SHELXL93),[34] data/restraints/parameters = 3188/0/191, goodness-of-fit on F^2 = 1.014, final R indices $R1$ = 0.0581 [$I > 2\sigma(I)$], $wR2$ = 0.1652 (all data) for 191 refined parameters, largest diff. peak and hole: 0.1644 and −0.145 e·A^{-3}.

Crystal Data for 27: $C_{33}H_{32}Cl_2D_2Si$, orthorhombic, space group $Pmn2_1$ (no. 31), a = 7.107(1), b = 20.988(2), c = 9.917(1) Å, V =

1479.2(3) Å^3, $Z = 2$, $\mu = 0.279$ mm^{-1}, $D_x = 1.194$ Mg/m^3, yellow plate, crystal size $0.70 \times 0.55 \times 0.15$ mm, $F(000) = 560$. Data were collected at 200 K with a Siemens P4 diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator, ω-scans with 4.0 °min^{-1}, $3.8 \le 2\theta \le 56.0°$, index ranges $-9 \le h \le 9$, $-27 \le k \le 27$, $-13 \le l \le 13$); 4072 reflections collected, 3854 unique reflections ($R_{int} = 0.0136$), 2731 observed reflections [$F_o \ge 4.0\sigma(F)$]. A ψ-scan absorption correction was applied ($T_{min} = 0.687$, $T_{max} = 0.715$). The structure was solved by direct methods and refined using full-matrix, least-squares procedures on F^2 (SHELXTL NT 5.10);[35] final R values $R1 = 0.0496$ ($F_o \ge 4.0\sigma(F)$], $wR2 = 0.0905$ (all data) for 268 refined parameters, absolute structure parameter $x = -0.07(9)$,[36] largest diff. peak and hole: 0.206 and -0.276 e·A^{-3}. All hydrogen atom positions were derived from a difference Fourier synthesis and refined with a fixed common isotropic displacement parameter.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156865 (**22**) and -157538 (**27**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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