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Synthesis of Hybrid Masked Triyne−Phenylene Axial Rods Containing (*E*)-*β*-Chlorovinylsilanes in the *π*-Conjugated Framework

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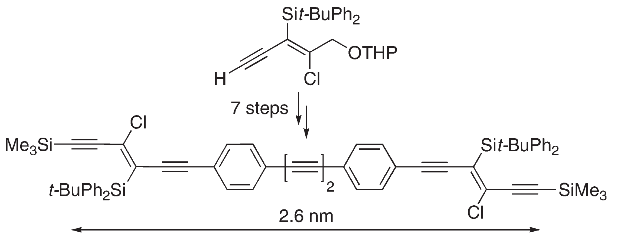

A two-directional synthesis of a masked hexayne **7**, in which two *β*-chlorovinylsilanes protect two of the internal alkynes, is reported. The key step involves the Pd-catalyzed oxidative dimerization of alkyne **10** to provide diyne **12**, which is elaborated into centrosymmetric masked hexayne **7** in four steps. Masked hexayne **7** is a constitutional isomer of masked hexayne **2**, which has been used as a monomer unit for oligoyne assembly. Although masked hexayne **7** was not as convenient a building block as **2** for application in oligoyne assembly, one of its precursors, namely alkyne **10**, could be used successfully in Sonogashira couplings, which allowed the incorporation of aromatic spacers and the formation of hybrid masked triyne-phenylenes **20** and **28**. Compounds **20** and **28** both contain removable end-groups, which will permit their application as building blocks for the assembly of classes of long-chain, *π*-conjugated rod-like molecules. Rod-like molecule **34**, which possesses a similar conjugated scaffold as **28**, was also prepared by using a similar strategy. Treatment of **34** with TBAF effected a 2-fold dechlorosilylation to provide a rigid rod molecule **35** in which two phenylene units interrupt an octayne scaffold.

Introduction

Linearly *π*-conjugated organic materials display optoelectronic properties that make them important candidates for molecular wires[1] in the emerging field of molecular electronics.[2] Our own research efforts in the area of *π*-conjugated materials have focused primarily on the synthesis of oligoynes.[3−7] These molecules represent clipped versions of carbyne,[8] an elusive allotrope of carbon, which has aroused considerable interest over the years, and, in many ways, represents the ultimate molecular wire.[9] The controlled preparation of oligoynes of any appreciable length (≥octayne), however, let alone of carbyne itself, presents a state-of-the-art synthetic challenge that has yet to find an efficient solution.[10] Working toward this goal, we have

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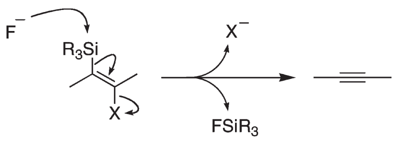
SCHEME 1. Action of Fluoride on a β-Halovinylsilane Generates an Alkyne

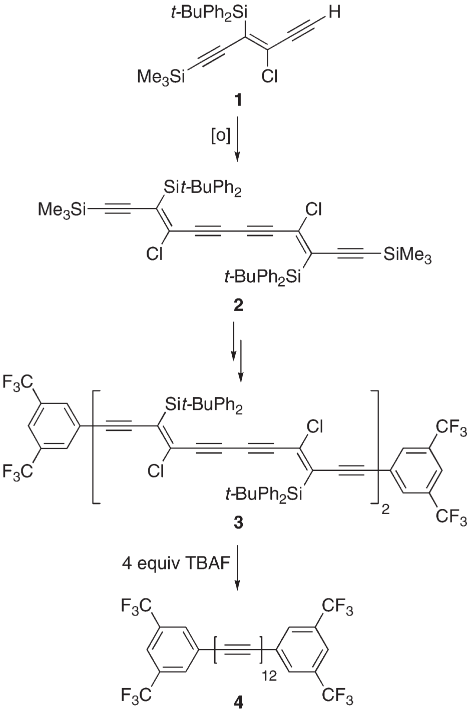


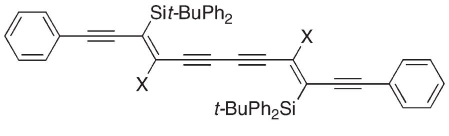
pioneered the use of β-halovinylsilanes[11] as masking groups[12] for alkynes in oligoyne assembly (Scheme 1).[3−7] This elimination approach[13] is particularly attractive since fluoride-induced release of the alkyne proceeds under mild conditions that do not affect the oligoyne product. Moreover, the oligoyne precursors themselves represent a new class of oligo(enediyne)s[14] containing heteroatom appendages (i.e., a halogen and a silyl substituent), which provide a useful means to modulate the optoelectronic properties of the π-conjugated backbone.

Our synthetic strategy generally begins with masked triyne **1** in which the central (*E*)-β-chlorovinylsilane serves to protect the internal alkyne. Dimerization of **1** provides a centrosymmetric masked hexayne **2**, which we have elaborated into aryl end-capped masked dodecayne **3** (Scheme 2).[5] Treatment of masked dodecayne **3** with TBAF effects a 4-fold dechlorosilylation to provide the corresponding dodecayne **4**, which is the longest aryl end-capped oligoyne reported to date.[15] Phenyl end-capped masked hexaynes based on β-chloro- (**5**) and β-fluorovinylsilanes (**6**) have also been prepared in a similar fashion to masked hexayne **2** (Figure 1), and unmasked to afford 1,12-diphenyldodeca-1,3,5,7,9,11-hexayne.[5,7] In the case of masked hexayne **6**, the unmasking can be performed by using a substoichiometric quantity of TBAF since a fluoride anion is regenerated in each elimination cycle.[7]

Having established an efficient route to a masked hexayne **2** in which the chloro substituents occupy "inside" positions, and the silyl groups "outside" positions,[3,5,6] we were keen to access its constitutional isomer **7** in which the chloro and silyl groups have been interchanged (Figure 2). We wanted to investigate how this structural change affects the efficiency of the synthesis of this alternative oligoyne building block, as well as the optoelectronic properties of the resulting masked hexayne. We now report the synthesis of masked hexayne **7**. While slightly longer than our route to its isomer **2** in terms of number of steps, the synthesis of **7** displays increased flexibility, which enables the introduction of aromatic spacer groups into the carbon-rich framework to generate hybrid masked phenylene−butadiynylene and masked phenylene−hexatriynylene π-conjugated building blocks.[16,17]

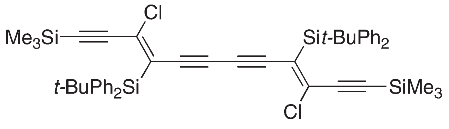
SCHEME 2. Assembly of Dodecayne 4 from Masked Triyne 1





5 (X = Cl), **6** (X = F)

FIGURE 1. Masked hexaynes in which two alkynes are protected as β-chloro- and β-fluorovinylsilanes.



7

FIGURE 2. Masked hexayne **7** is a constitutional isomer of masked hexayne **2**.

Results and Discussion

Our starting point in the synthesis of masked hexayne **7** was (*E*)-β-chlorovinylsilane **8**, which is readily prepared in

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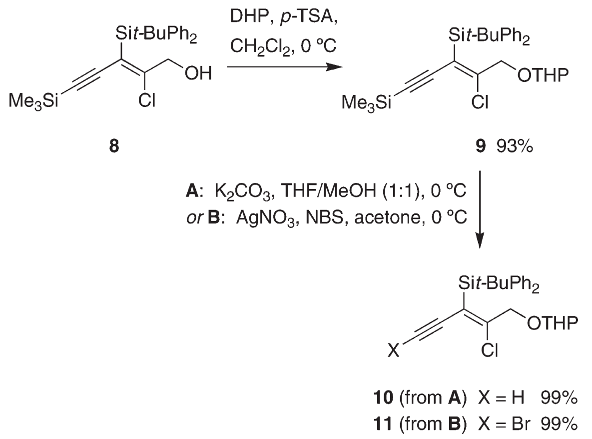
five steps from 1,4-bis(trimethylsilyl)buta-1,3-diyne and is a key intermediate in our synthesis of masked hexayne **2**.[3] For the synthesis of masked hexayne **7**, we first needed to process the alkyne in **8** and then elaborate the alcohol into a second alkyne, which would form the terminal units of our target molecule. Anticipating base-promoted 1,4-Brook rearrangement and subsequent elimination to the alkyne would be a problem when manipulating alcohol **8**, we chose to protect the alcohol functionality in **8** first as its THP ether; thus treatment of **8** with 3,4-dihydro-2*H*-pyran (DHP) in the presence of *p*-toluenesulfonic acid (*p*-TSA)[18] afforded the corresponding THP ether **9** in 93% yield. Removal of the TMS group in **9** could now be achieved under mildly basic conditions[19] to provide terminal alkyne **10** in 99% yield (Scheme 3). Since halo-alkynes are useful building blocks in alkyne coupling chemistry,[20,21] we also showed that TMS-protected alkyne **9** could be converted into the corresponding bromo-alkyne **11** in similarly excellent yield by reaction with 1 equiv each of silver(I) nitrate and NBS in acetone (Scheme 3).[22] A subsequent Cadiot−Chodkiewicz coupling[21] of **11** with phenylacetylene as the alkyne coupling partner was accomplished in 60% yield (see the Supporting Information).

Terminal alkyne **10** proved to be a rather poor substrate for homocoupling with use of the Eglinton−Glaser−Hay approach,[23] even under the reaction conditions that we have developed to avoid premature dechlorosilylation.[4,5] The desired dimerization product could be obtained in this way but only in poor yields (≤24%) and with poor recovery of starting material. We therefore turned our attention to palladium-catalyzed variants of this homocoupling reaction,[23−25] and were particularly attracted to the method of Zhang and co-workers, who reported excellent yields for a palladium-catalyzed oxidative homocoupling of alkynes, using ethyl bromoacetate as the promoter.[25] Treatment of a solution of terminal alkyne **10** in THF with DABCO (1.2 equiv), bis(triphenylphosphine)palladium(II) dichloride (5 mol %), copper(I) iodide (5 mol %), and ethyl bromoacetate (60 mol %) in the presence of air resulted in the formation of dimer **12** in excellent yield (Scheme 4). When ethyl bromoacetate was excluded from the reaction mixture, no dimerization product was observed. Interestingly, and in contrast to Zhang's observations, we also found that exposure of the reaction mixture to air was essential for the coupling to proceed.

SCHEME 3. Synthesis of Alkyne 10 and Bromo-alkyne 11



The THP protecting groups in the dimer **12** were removed by using PPTS in THF/ethanol (1:1) at 55 °C (Scheme 4),[26] to provide the diol **13**, which was poorly soluble in most organic solvents with the exception of dimethyl sulfoxide. With diol **13** in hand, we expected its conversion into our target masked hexayne **7** would be straightforward using our previously reported sequence of oxidation, dibromoolefination,[27,28] followed by a Fritsch−Buttenberg−Wiechell-like reaction;[27] however, this turned out not to be the case. Double allylic oxidation of diol **13** with manganese(IV) oxide proved to be surprisingly problematic: as well as forming the desired bis-aldehyde product **14**, a significant quantity (up to 25% by integration in the ^{1}H NMR spectrum of the crude reaction mixture) of an unknown byproduct was also obtained.[29] After screening a range of other oxidizing agents, it was found that treatment of diol **13** with PCC in dichloromethane in the presence of Celite and activated 5 Å molecular sieves[30] was effective in minimizing side reactions and provided the desired bis-aldehyde **14** in 87% yield. Bis-aldehyde **14** was then converted uneventfully into the corresponding bis-dibromoolefin **15** under standard conditions (Scheme 4).[28] The final step in the synthesis of masked hexayne **7** required the installation of the terminal alkyne groups. Using reaction conditions that we routinely employ to introduce the terminal alkyne in masked triyne **1**, tetrabromide **15** was treated with an excess (12 equiv) of LDA in THF at −78 °C; however, under these conditions, we observed rapid decomposition. Since the reaction of dibromoolefins with LDA generates an intermediate lithium acetylide, and the corresponding alkyne on aqueous workup, we attempted to trap this reactive intermediate by addition of chlorotrimethylsilane after 15 min; however, in contrast to carrying out a similar reaction, which we have used to prepare the bis-TMS end-capped masked triyne analogue of **1** in excellent yield,[3] this again failed to provide the desired compound. Fortunately a slight modification of the reaction conditions led to improved results: since chlorotrimethylsilane has been shown to be compatible with LDA at −78 °C,[31] we included this electrophile from the start of the reaction in order that it could act as an in situ quench for the generated

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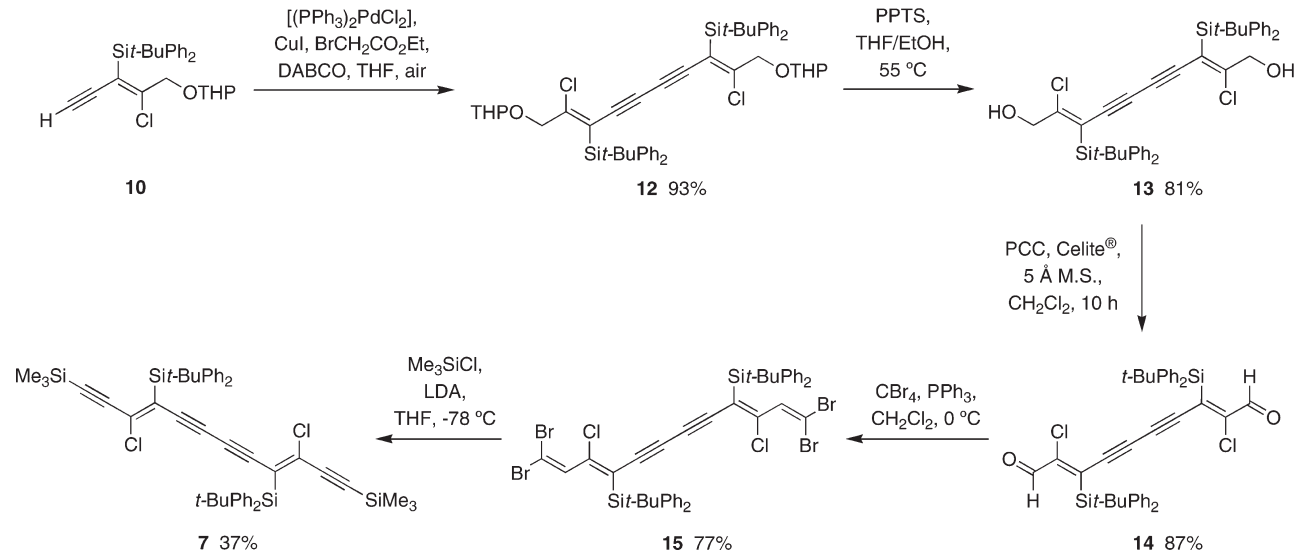
SCHEME 4. Synthesis of Masked Hexayne 7



lithium acetylide intermediates. In this way, masked hexayne **7** could be obtained in 37% yield after purification by column chromatography (Scheme 4).[32]

In summary, masked hexayne **7** was prepared from alcohol **8** in seven steps and 17% overall yield. By contrast, its constitutional isomer **2** can be accessed from **8** in only four steps with an overall yield of 52%. For these reasons, masked hexayne **7** is not as attractive a building block as **2** for oligoyne assembly. Contrasting the physical properties of these two isomers is interesting: masked hexayne **2** is generally isolated as pale yellow needles (mp 170 °C dec) whereas its constitutional isomer **7** is an amorphous yellow solid that exhibits a considerably lower melting point (mp 60−62 °C). The UV−vis absorption spectra for masked hexayne **7** and its constitutional isomer **2** are shown in Figure 3. In the case of this physical parameter, masked hexayne **7** shows a small bathochromic shift of 4 nm in $\lambda_{\max}$ compared with **2**; however, the spacing between the characteristic absorption bands in the spectra of these two isomers is the same; the positions of the silyl and chloro substituents along the π-conjugated framework do not seem to have a significant impact on these features of the UV−vis spectra. It is interesting to note, however, the difference in the relative intensities of the peaks in the two spectra: isomer **7**, with the chlorine atoms occupying "outside" positions and the silyl groups "inside" positions, exhibits molar absorptivities that are almost 2-fold higher than those for its constitutional isomer **2**.

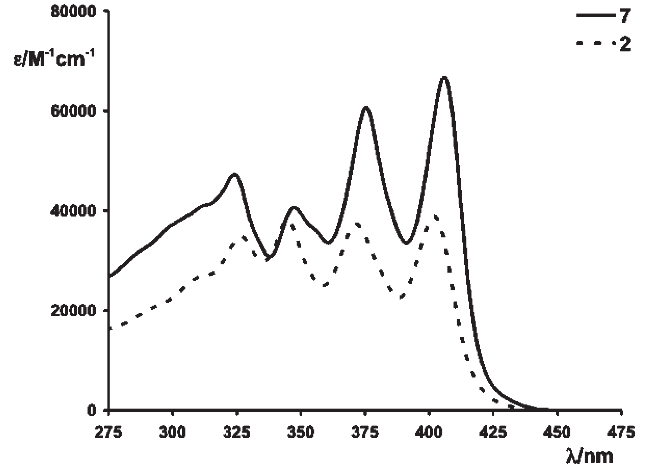


FIGURE 3. UV−vis spectra of masked hexaynes **7** (solid line) and **2** (dashed line).

Although masked hexayne **7** is a less convenient building block than **2** for the synthesis of oligoynes, the observation that one of its precursors, namely **10**, proved to be a good substrate in a Pd-catalyzed oxidative dimerization reaction suggested that this intermediate could be a useful coupling partner in a Sonogashira reaction.[33] The introduction of aromatic spacer groups between two masked triynes of the type contained in **1** should significantly alter the optoelectronic properties of the material, and potentially open the way to new and interesting classes of oligomers.[34] For example, aromatic spacer groups should reduce the efficiency of π-electron delocalization along the linear conjugated framework through competition with localized aromatic π-electron conjugation. This reduced delocalization is accompanied by a shift in electronic end absorptions to higher energy.[34] To investigate these proposals, we chose to introduce a phenylene spacer group between two of our masked triyne units. This was achieved by substituting the Pd-catalyzed homodimerization used to prepare diyne **12** with a double-Sonogashira cross-coupling reaction. Thus Sonogashira coupling of terminal alkyne **10** with 1,4-diiodobenzene (0.5 equiv) afforded the desired phenylene diethynylene **16** in 81% yield (Scheme 5). The THP protecting groups in **16** were removed by using PPTS to afford diol **17** in

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(32) Masked hexayne **7** was obtained in crude (~90% purity) form in 89% yield after column chromatography (1% → 2% Et_2O in hexane). It was poorly stable to long durations on silica, which accounts for the low isolated yield of **7**.

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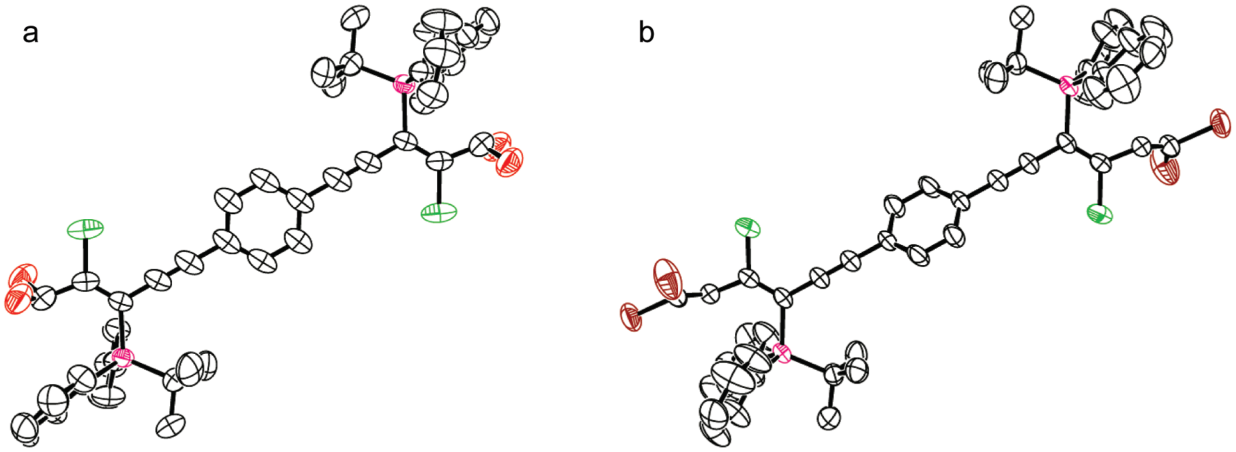
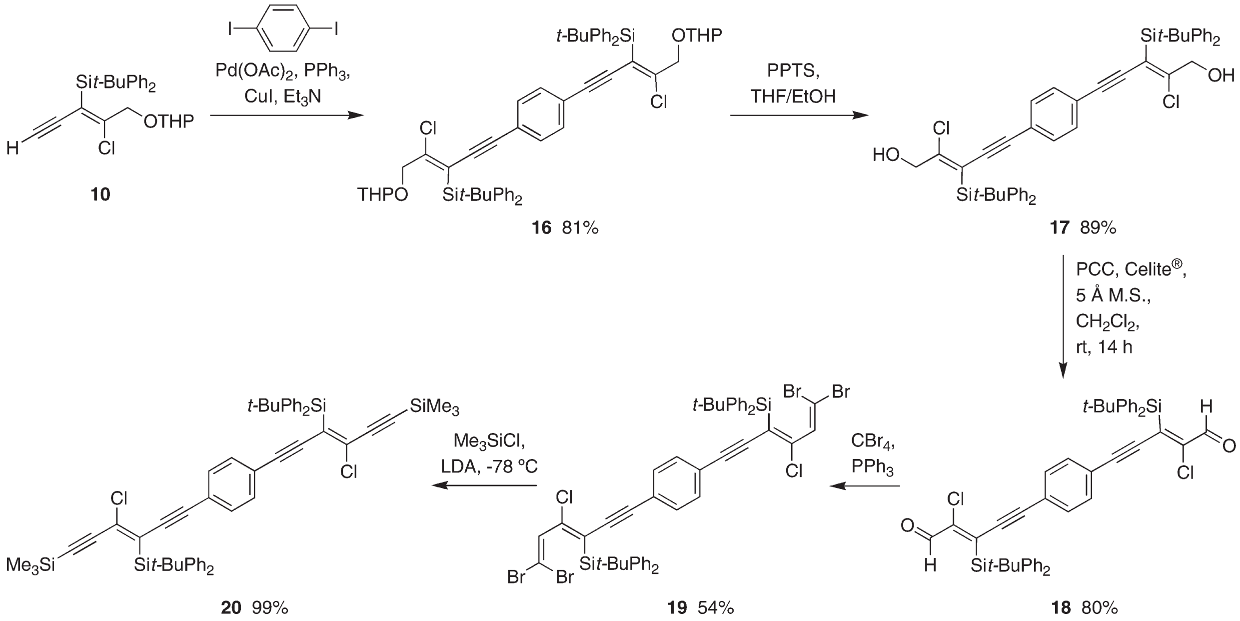


FIGURE 4. ORTEP plots of diol **17** (left) and tetrabromide **19** (right). Atomic displacement parameters at 293 K.

SCHEME 5. Synthesis of Hybrid Masked Triyne-phenylene 20

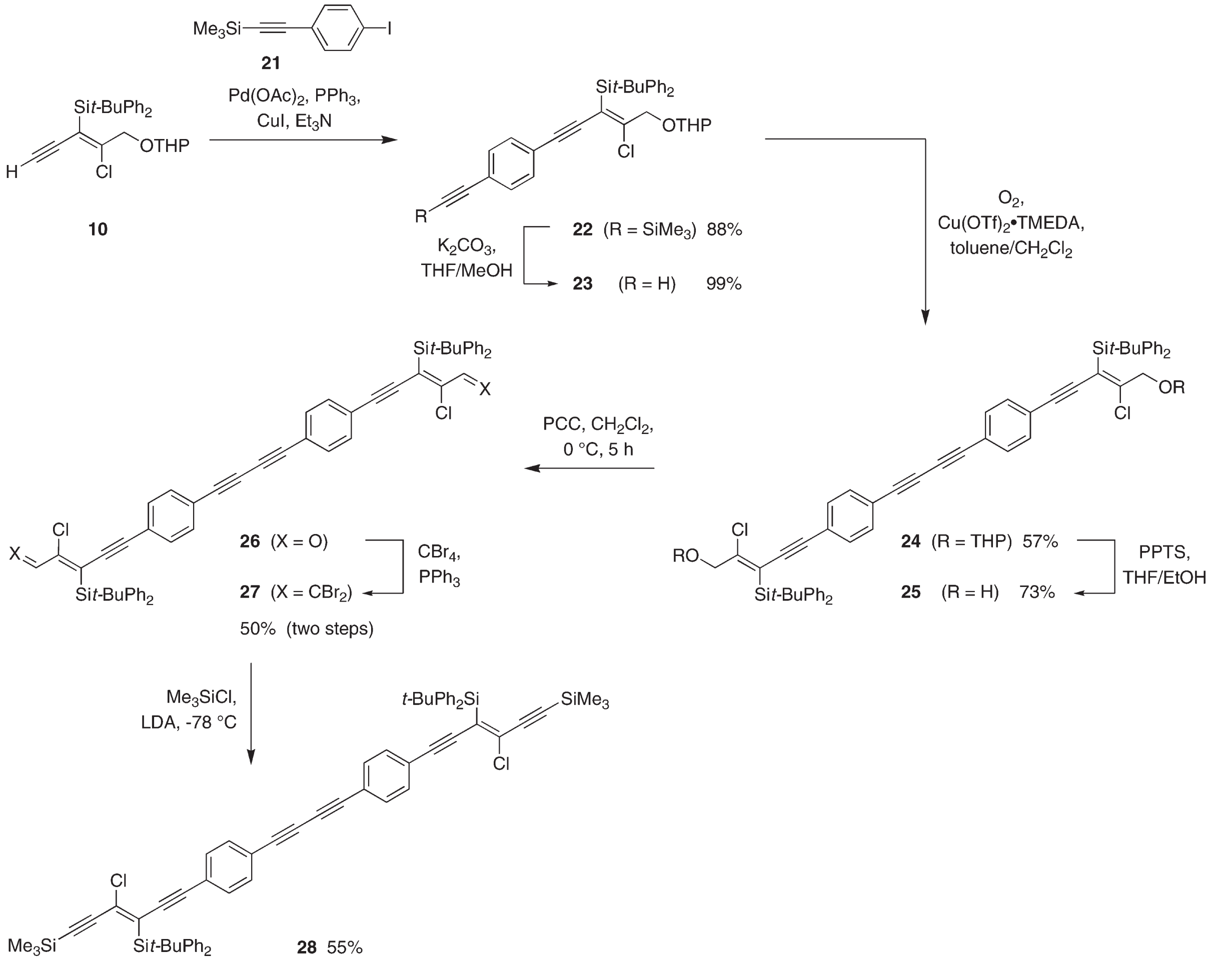


89% yield, allowing the same sequence that had been used to access masked hexayne **7** to be carried out on this new substrate. Reaction of diol **17** with PCC, in the presence of Celite and activated 5 Å molecular sieves, afforded bis-aldehyde **18** in 80% yield. Again, these reagents and reaction conditions were important to avoid the generation of the same type of side product described above in the synthesis of bis-aldehyde **14**. Bis-aldehyde **18** was next converted into its corresponding tetrabromide **19** by using carbon tetrabromide and triphenylphosphine (Scheme 5). The crystal structures of diol **17** and tetrabromide **19** were determined and these are shown as ORTEP plots in Figure 4.

In the case of diol **17**, four ellipsoids corresponding to the two oxygen atoms in the molecule are present in the solved X-ray structure showing that the two hydroxyl groups each occupy two positions, each with 50% probability. The relative orientation of the two β-chlorovinylsilane moieties is anti to each other across the π-conjugated framework. The phenylene spacer group is located in the plane of the π-conjugated framework to provide optimal overlap with the π-orbitals of the neighboring enyne units. In the case of tetrabromide **19**, the phenylene ring and the two 1,1-dibromoolefins are now not situated in the plane of the β-chlorovinylsilane moieties. This solid-state conformation suggests quite poor overlap of the π-orbitals along the chain and therefore a lower level of π-conjugation for this compound (at least in the solid state). A torsion angle of 61° is observed between each 1,1-dibromoolefin and its neighboring internal olefin; this presumably minimizes the 1,3-steric repulsions between the chlorine atom of the β-chlorovinylsilane unit and the cis-bromine atom of the proximal dibromoolefin.

Treatment of tetrabromide **19** with 12 equiv of LDA in THF at −78 °C in the presence of 10 equiv of chlorotrimethylsilane afforded hybrid masked triyne-phenylene **20** in excellent yield (Scheme 5). It would appear that incorporating the phenylene spacer group had resulted in an improved stability of the lithium intermediates generated in this reaction as well as the product itself (toward column chromatography) when compared with masked hexayne **7** whose synthesis and isolation had proven to be much more problematic.

SCHEME 6. Synthesis of Axial Rod 28



To investigate the scope of this type of reaction sequence further, we reacted alkyne **10** with 1-iodo-4-(trimethylsilylethynyl)benzene **21**[35] under Sonogashira coupling conditions to provide phenylene ethynylene **22** in good yield (Scheme 6). The trimethylsilyl group in **22** was removed in the usual fashion using anhydrous potassium carbonate in THF/methanol (Scheme 6). The resulting terminal alkyne in **23** was noticeably less stable than alkyne **10** and the product was therefore used immediately in the next synthetic step. Thus, terminal alkyne **23** was subjected to our modified Eglinton−Glaser−Hay coupling conditions with copper(II) triflate as the source of copper.[4−7] The triflate counteranion in this salt is weakly nucleophilic and therefore less susceptible to promoting a premature dechlorosilylation compared to other copper salts (e.g., copper chloride or acetate) commonly used in this type of homodimerization.[23] This coupling reaction afforded phenylene ethynylene **24**, in which the β-chlorovinylsilane moieties are now separated by a diphenylenebuta-1,3-diynyl spacer module. Using our now established methodology, the THP protecting groups of **24** were removed to afford diol **25** in 73% yield. Although diol **25** containing this much longer π-conjugated framework compared to our previous substrates exhibited poor solubility in most organic solvents, we were still able to perform a PCC oxidation to provide the corresponding bis-aldehyde **26** in good yield, although it was now necessary to perform this reaction at 0 °C to minimize the formation of side products (see above) with this more reactive substrate. In light of its increased lability, bis-aldehyde **26** was converted immediately into the corresponding tetrabromide **27** in good yield with carbon tetrabromide and triphenylphosphine. Finally reaction of bis-dibromoolefin **27** with LDA, once again with chlorotrimethylsilane as in situ quench, gave axial rod **28** in 55% yield (Scheme 6).

An alternative route to the above class of rigid rod molecule was developed starting from (*E*)-β-chlorovinylsilane **29**,[3] which is an intermediate in our synthesis of masked hexayne **2**. Treatment of dibromoolefin **29** with 6 equiv of LDA in THF at −78 °C, followed by addition of acetone, gave tertiary alcohol **30** in 89% yield (Scheme 7). The TMS group of **30** was cleaved selectively with anhydrous potassium carbonate in THF/methanol. The resulting terminal alkyne **31** was then cross-coupled with aryl iodide **21** under Sonogashira conditions to afford phenylene ethynylene **32** in 52% yield over two steps. A second TMS deprotection again proceeded uneventfully to afford terminal alkyne **33**, which was immediately subjected to our modified Eglinton−Glaser−Hay coupling conditions to provide the target axial rod **34** in 41% yield over two steps (Scheme 7). Rigid rod molecules **28** and **34** are approximately 2.6 nm in length

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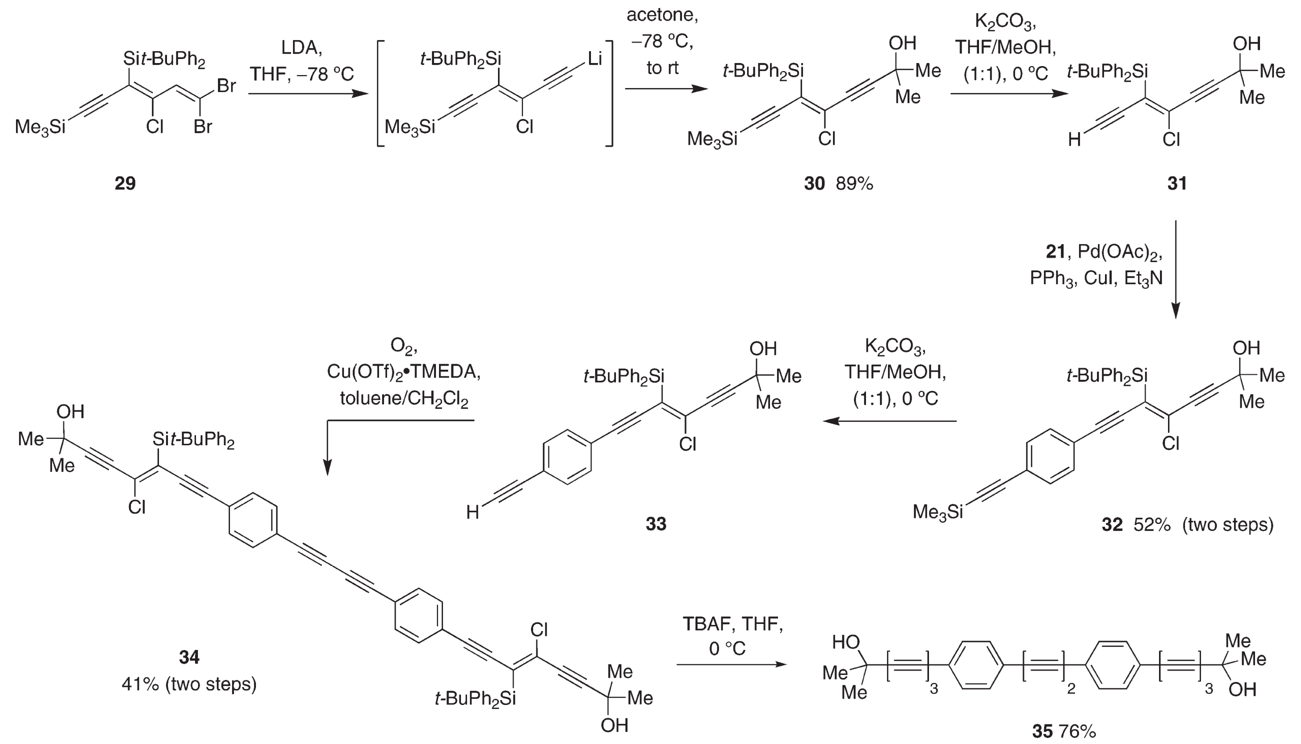
[35] Anderson, S. *Chem. Eur. J.* **2001**, *7*, 4706–4714.

SCHEME 7. Synthesis of Axial Rod 34 and Two-Fold Dechlorosilylation to 35



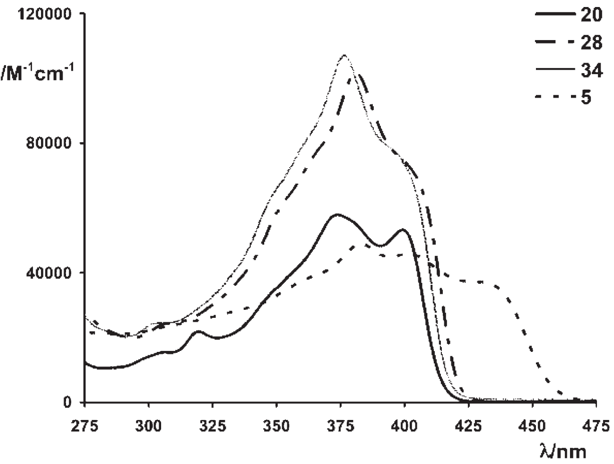


FIGURE 5. UV–vis spectra of phenylene-containing compounds **20**, **28**, and **34**, and masked hexayne **5**.

(measured from the terminal carbons in the conjugated scaffold) and, together with masked dodecayne **3**, represent the longest π-conjugated frameworks containing β-chlorovinylsilanes that have been prepared to date.

Since the dimethylmethanol end-capping groups present in **34** are much more robust to basic conditions than the TMS protecting groups used to end-cap the conjugated framework in compounds **7**, **20**, and **28**, rigid rod **34** provided us with an opportunity to effect elimination of the two β-chlorovinylsilanes without having to worry about generating compounds that possess unstable terminal hexatriynes (which would be produced were we to effect dechlorosilylation on compounds **20** and **28**). To this end, compound **34** was treated with TBAF under our standard conditions.[5] The 2-fold dechlorosilylation proceeded smoothly at 0 °C to provide compound **35** in which the two phenylene rings interrupt an octayne framework (Scheme 7).

TABLE 1. Absorption Peaks in the UV–Vis Spectra of 2, 5, 7, 20, 28, and 34

compd	λ_{max} (nm)	ε (M^{-1}cm^{-1})	compd	λ_{max} (nm)	ε (M^{-1}cm^{-1})
2	402	38 800	**20**	399	53 200
	372	37 300		383 sh	53 200
	345	38 100		374	57 900
	327	34 800		352 sh	36 500
	313 sh	27 000		320	21 900
5	430 sh	37 100	**28**	403 sh	72 100
	402	45 700		381	102 000
	383	48 900		355 sh	63 900
	364 sh	38 900	**34**	398 sh	76 500
7	406	66 600		377	107 000
	375	60 600		350 sh	65 700
	356 sh	35 900			
	348	40 600			
	324	47 300			
	314 sh	41 200			

The UV–vis spectra for **20**, which possesses a phenylene spacer group, and for molecular rods **28** and **34** are shown in Figure 5, along with the spectrum for phenyl end-capped masked hexayne **5**. The relevant signals in the UV–vis absorption spectra of target compounds **7**, **20**, **28**, and **34** are also summarized in Table 1 along with data for masked hexaynes **2** and **5**. Comparing the UV–vis spectrum of **5** with masked hexaynes **2** and **7**, which are of similar basic structure (see Figure 3), reveals the ability for the π-conjugated system to extend into the phenyl end-groups in **5** resulting in a bathochromic shift of λ_{max} (to 430 nm). Moving the phenyl units from the termini of the masked hexayne, as in **5**, to the middle, as in **20**, clearly interrupts the conjugation pathway in the masked hexayne, which has the effect of removing the characteristic profile for absorption associated with our masked hexaynes. As expected, the extinction coefficient, ε, of strong absorptions is enhanced by increasing the length of the π-conjugated framework (compare **20** with **28** and **34**), and changing the end-cap from trimethylsilyl to dimethylmethanol has little effect on the UV−vis absorption spectra.

Conclusions

We have shown that a modification in our synthesis of masked hexayne **2** allows access to its constitutional isomer **7** through a two-directional synthesis strategy. While masked hexayne **7** displays similar UV−vis properties to its isomer **2**, its synthesis is three steps longer and practically less straightforward. Bis-TMS end-capped hexayne **7** also proved to be more unstable than our "standard" masked hexayne **2**, which is likely to be mirrored in the relative stability of its bis-TMS deprotected building block that we would need for oligomerization studies. For these reasons, we believe that masked hexayne **2**, in which the chloro groups occupy "inside" positions and silyl groups "outside" positions, is the better building block for long-chain oligoyne assembly.[6,15] Where the route to masked hexayne **7** is attractive lies in the functionalization of the intermediates, specifically THP ether **10**, which has allowed us to incorporate other π-conjugated units (i.e., phenylene units) into the middle of the masked hexayne framework. Interrupting the linear conjugation of the masked hexayne has a significant effect on the optical properties of these hybrid products, as evidenced by their UV−vis spectra, and also increases the stability of some of these building blocks, which may be useful in future oligomerization studies. The solubility problems associated with some of the particularly long conjugated frameworks can be addressed in the future by judicious substitution on the aromatic units.

From a synthetic viewpoint, this study has shown that β-chlorovinylsilanes are stable to the conditions for the Sonogashira cross-coupling reaction and Cadiot−Chodkiewicz coupling. Moreover, the palladium-mediated oxidative coupling of alkyne **10** to provide dimer **12** proved to be an extremely efficient method for dimerizing this alkyne and may be a useful alternative for similar couplings where our modified Eglinton−Glaser−Hay coupling conditions fail. By introducing phenylene units into the π-conjugated framework, we were able to access a series of phenylene ethynylenes containing β-chlorovinylsilanes. Although this study has focused on assembling axial rod-like π-conjugated systems,[17] which contain masked alkynes in the form of the β-chlorovinylsilane moiety, we have shown previously that this alkyne masking group undergoes dechlorosilylation upon exposure to TBAF.[5] This oligoyne unmasking strategy was further verified by the synthesis of **35** from **34**, which demonstrates that these systems provide an entry into alkyne-rich π-conjugated frameworks that are not readily accessible by other means.[16] While compound **34** contains relatively robust dimethylmethanol end-capping groups, compounds **20** and **28** both contain more labile TMS end-capping groups. Since we have shown previously that this silyl protecting group can be removed without effecting dechlorosilylation of the internal β-chlorovinylsilane motifs, these compounds represent useful monomer precursors for oligomerization studies, which will be a focus for future work.

Experimental Section

(*E*)-3-*tert*-Butyldiphenylsilyl-4-chloro-5-tetrahydropyranyloxy-1-trimethylsilylpent-3-en-1-yne (9). *p*-TSA (11 mg, 0.060 mmol) was added to a solution of alcohol **8** (2.50 g, 5.85 mmol) in CH_2Cl_2 (60 mL) at 0 °C. After 5 min, 3,4-dihydro-2*H*-pyran (1.06 mL, 11.7 mmol) was added in one portion at 0 °C. After being stirred for 3 h, the reaction mixture was diluted with CH_2Cl_2 (40 mL) before being washed with $NaHCO_3$ solution (3 × 30 mL). The organic phase was separated, washed with H_2O (3 × 50 mL) and brine (3 × 50 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure. Purification of the residue by flash column chromatography (10% Et_2O in hexane) gave THP ether **9** as a white solid (2.78 g, 93%, single anomer); R_f 0.44 (10% Et_2O in hexane); mp 119−121.5 °C; IR (Nujol) 2131m (C≡C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 9H), 1.12 (s, 9H), 1.22−1.48 (stack, 5H), 1.52−1.71 (m, 1H), 3.04−3.27 (stack, 2H), 3.55 (d, *J* = 12.1 Hz, 1H), 3.73 (br s, 1H), 3.82 (d, *J* = 12.1 Hz, 1H), 7.29−7.46 (stack, 6H), 7.66−7.79 (stack, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.3 (CH_3), 18.2 (CH_2), 19.1 (C), 25.1 (CH_2), 27.3 (CH_3), 29.8 (CH_2), 60.5 (CH_2), 69.1 (CH_2), 97.5 (CH), 104.9 (C), 106.5 (C), 120.0 (C), 127.6 (CH), 127.8 (CH), 129.4 (CH), 129.5 (CH), 133.0 (C), 133.5 (C), 135.5 (CH), 135.7 (CH), 152.1 (C); MS (TOF ES+) *m*/*z* 533.0 ($[M + Na]^+$, 100%); HRMS (TOF ES+) calcd for $C_{29}H_{39}{}^{35}ClO_2Si_2Na$ $[M + Na]^+$ 533.2075, found 533.2084. Anal. Calcd for $C_{29}H_{39}ClO_2Si_2$: C, 68.13; H, 7.69. Found: C, 68.23; H, 7.78.

General Procedure for the K_2CO_3/MeOH-Mediated Deprotection of TMS-Alkynes: (*E*)-3-*tert*-Butyldiphenylsilyl-4-chloro-5-tetrahydropyranyloxy-pent-3-en-1-yne (10). Anhydrous K_2CO_3 (0.78 g, 5.7 mmol) was added to a solution of TMS-alkyne **9** (1.32 g, 2.58 mmol) in THF/MeOH (1:1, 25 mL) at 0 °C. After 3 h, NH_4Cl solution (20 mL) was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with brine (3 × 15 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure. Purification of the residue by flash column chromatography (5% Et_2O in hexane) gave alkyne **10** as a colorless oil (1.12 g, 99%, single THP anomer); R_f 0.47 (33% Et_2O in hexane); IR (film) 3286 s (H−C≡C), 2083 w cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 9H), 1.23−1.50 (stack, 5H), 1.54−1.75 (m, 1H), 3.06−3.32 (stack, 2H), 3.60 (d, *J* = 12.1 Hz, 1H), 3.70 (s, 1H), 3.76 (br s, 1H), 3.88 (d, *J* = 12.1 Hz, 1H), 7.29−7.50 (stack, 6H), 7.67−7.82 (stack, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.2 (CH_2), 19.1 (C), 25.1 (CH_2), 27.4 (CH_3), 29.8 (CH_2), 60.7 (CH_2), 69.0 (CH_2), 83.8 (C), 88.9 (CH), 97.6 (CH), 119.3 (C), 127.7 (CH), 127.9 (CH), 129.5 (CH), 129.6 (CH), 132.9 (C), 133.4 (C), 135.5 (CH), 135.7 (CH), 153.1 (C); MS (TOF ES+) *m*/*z* 461.2 ($[M + Na]^+$, 100%); HRMS (TOF ES+) calcd for $C_{26}H_{31}{}^{35}ClO_2SiNa$ $[M + Na]^+$ 461.1680, found 461.1683.

(2*E*,8*E*)-3,8-Di(*tert*-butyldiphenylsilyl)-2,9-dichloro-1,10-bis(tetrahydropyranyloxy)-deca-2,8-dien-4,6-diyne (12). DABCO (138 mg, 1.23 mmol), $[(PPh_3)_2PdCl_2]$ (36 mg, 0.051 mmol), and ethyl bromoacetate (70 μL, 0.63 mmol) were added to a stirred solution of alkyne **10** (450 mg, 1.03 mmol) in THF (12 mL) under N_2. CuI (10 mg, 0.053 mmol) was added. The reaction mixture was stirred under N_2 for 15 min before exposing the vessel to air. After 20 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and filtered through a short silica plug, eluting with 20% Et_2O in hexane (60 mL). The solvent was removed under reduced pressure and purification of the residue by flash column chromatography (20% Et_2O in hexane) afforded dimer **12**[36] as a white foam (367 mg, 93%); R_f 0.32 (33% Et_2O in hexane); IR (Nujol) 2923 s, 1460 s, 1122 m cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 18H), 1.23−1.48 (stack, 10H), 1.52−1.73 (m, 2H), 3.02−3.31

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(36) Bis-THP derivatives **12**, **16**, and **24** are presumably 1:1 mixtures of diastereoisomers even though there is no evidence for this in the NMR spectra for these compounds.

(stack, 4H), 3.59 (d, *J* = 12.5 Hz, 2H), 3.76 (br s, 2H), 3.86 (d, *J* = 12.5 Hz, 2H), 7.30−7.48 (stack, 12H), 7.67−7.82 (stack, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.3 (CH_2), 19.2 (C), 25.1 (CH_2), 27.4 (CH_3), 29.8 (CH_2), 60.8 (CH_2), 69.1 (CH_2), 85.0 (C), 85.2 (C), 97.7 (CH), 119.4 (C), 127.8 (CH), 128.0 (CH), 129.6 (CH), 129.7 (CH), 132.7 (C), 133.2 (C), 135.6 (CH), 135.7 (CH), 154.3 (C); MS (TOF ES+) *m*/*z* 897.5 ($[M+Na]^+$, 100%); HRMS (TOF ES+) calcd for $C_{52}H_{60}{}^{35}Cl_2O_4Si_2Na$ $[M + Na]^+$ 897.3305, found 897.3318.

General Procedure for the Deprotection of THP Ethers: (2*E*,8*E*)-3,8-Di(*tert*-butyldiphenylsilyl)-2,9-dichloro-deca-2,8-dien-4,6-diyn-1,10-diol (13). Bis-THP ether **12** (1.82 g, 2.07 mmol) was dissolved in THF/EtOH (1:1, 40 mL) and the resulting solution was heated with stirring at 55 °C. PPTS (0.10 g, 0.41 mmol) was added. After being stirred at 55 °C for 26 h, the reaction mixture was cooled to rt and H_2O (100 mL) was added. The resulting off-white precipitate was collected by suction filtration and washed with toluene (40 mL) to afford diol **13** as an off-white solid (0.97 g, 66%). More product was obtained from the filtrate: the organic layer of the combined filtrates was separated from the aqueous layer and dried ($MgSO_4$). The solvent was removed under reduced pressure followed by dissolution of the residue in CH_2Cl_2 (10 mL). The crude material was preadsorbed onto silica and purified by flash column chromatography (33% Et_2O in hexane) to give an off-white solid (0.22 g, 15%). The two samples of the diol **13** were combined (1.19 g, 81%); R_f 0.20 (50% Et_2O in hexane); mp 223−228 °C; IR ($CHCl_3$) 3563 m (O—H), 3534 m (O—H), 3442 br w (O—H), 2114 w (C≡C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 18H), 3.78 (s, 4H), 7.34−7.51 (stack, 12H), 7.67−7.82 (stack, 8H), O*H* resonances not observed; ^{13}C NMR (75 MHz, DMSO-d_6) δ 18.7 (C), 27.3 (CH_3), 63.8 (CH_2), 83.1 (C), 84.7 (C), 115.6 (C), 128.1 (CH), 130.0 (CH), 132.2 (C), 135.2 (CH), 158.9 (C); MS (TOF ES+) *m*/*z* 729.2 ($[M + Na]^+$, 100%); HRMS (TOF ES+) calcd for $C_{42}H_{44}{}^{35}Cl_2O_2Si_2Na$ $[M + Na]^+$ 729.2155, found 729.2143.

General Procedure for the PCC/Celite/5 Å Molecular Sieves-Mediated Oxidation of Diols to Enals: (2*E*,8*E*)-3,8-Di(*tert*-butyldiphenylsilyl)-2,9-dichloro-deca-2,8-dien-4,6-diyn-1,10-dial (14). Diol **13** (510 mg, 0.722 mmol) was added to a stirred suspension of Celite (250 mg) and freshly activated 5 Å molecular sieves (250 mg) in CH_2Cl_2 (3 mL). PCC (620 mg, 2.88 mmol) was then added in one portion at rt. After 10 h, the reaction mixture was diluted with CH_2Cl_2 (15 mL) and filtered through a short silica plug. The product was eluted with 33% Et_2O in hexane (100 mL), taking care not to bring through the dark band of Cr residues. Removal of the solvent under reduced pressure resulted in precipitation of a yellow solid of bis-aldehyde **14**, which was collected by suction filtration (430 mg, 87%); R_f 0.48 (40% Et_2O in hexane); UV (CH_2Cl_2) λ_{max}, nm (ε) 315 sh (10740), 331 (13150), 349 sh (10710), 375 (10370), 406 (9100); IR ($CHCl_3$) 1683 s (C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 18H), 7.34−7.52 (stack, 12H), 7.64−7.78 (stack, 8H), 9.21 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6 (C), 27.5 (CH_3), 91.3 (C), 97.8 (C), 128.5 (CH), 130.5 (CH), 132.5 (C), 135.5 (CH), 137.9 (C), 150.0 (C), 183.5 (CH); MS (TOF ES+) *m*/*z* 757.5 ($[M + Na + MeOH]^+$, 50%) 725.4 (100, $[M + Na]^+$); HRMS (TOF ES+) calcd for $C_{42}H_{40}{}^{35}Cl_2O_2Si_2Na$ $[M+Na]^+$ 725.1842, found 725.1840.

General Procedure for the Dibromoolefination of Aldehydes: (3*E*,9*E*)-4,9-Di(*tert*-butyldiphenylsilyl)-3,10-dichloro-1,1,12,12-tetrabromododeca-1,3,9,11-tetraen-5,7-diyne (15). A solution of PPh_3 (1.20 g, 4.56 mmol) in CH_2Cl_2 (5 mL) was added via a dropping funnel over 5 min to a cooled (0 °C) solution of CBr_4 (0.77 g, 2.3 mmol) in CH_2Cl_2 (5 mL), resulting in the formation of a golden yellow solution. After 1 h at 0 °C, a solution of aldehyde **14** (0.40 g, 0.57 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min. The dropping funnel was rinsed with additional CH_2Cl_2 (2 mL). After 1 h, hexane (50 mL) was added to the solution with vigorous stirring to precipitate the Ph_3P═O byproduct. The suspension was filtered through a silica plug and the plug was washed with 20% Et_2O in hexane (2 × 25 mL). The solvent was removed under reduced pressure to give bis-dibromide **15** as a yellow solid, which was used without further purification (0.44 g, 77%); R_f 0.27 (5% Et_2O in hexane); mp 126−128 °C; IR (Nujol) 2922 s, 1463 s, 1108 s, 700 s cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 18H), 6.51 (s, 2H), 7.36−7.50 (stack, 12H), 7.66−7.80 (stack, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4 (C), 27.8 (CH_3), 86.6 (C), 88.3 (C), 98.8 (C), 122.5 (C), 128.2 (CH), 130.0 (CH), 131.9 (C), 135.1 (CH), 135.8 (CH), 146.2 (C); MS (TOF ES+) *m*/*z* 1037.4 ($[M+Na]^+$, 100%), 577.5 (23); HRMS (TOF ES+) calcd for $C_{42}H_{40}{}^{79}Br_4{}^{35}Cl_2Si_2Na$ $[M+Na]^+$ 1032.8677, found 1032.8721. Anal. Calcd for $C_{44}H_{40}Br_4Cl_2Si_2$: C, 52.04; H, 3.97. Found: C, 51.93; H, 4.16.

General Procedure for the Synthesis of TMS-Alkynes from the Corresponding 1,1-Dibromoolefins: (3*E*,9*E*)-4,9-Di(*tert*-butyldiphenylsilyl)-3,10-dichloro-1,12-bis(trimethylsilyl)dodeca-3,9-dien-1,5,7,11-tetrayne (7). *n*-BuLi (1.96 mL of a 2.4 M solution in hexane, 4.6 mmol) was added over 5 min to a prechilled (0 °C) solution of *i*-Pr_2NH (0.64 mL, 4.9 mmol) in THF (5 mL). After 30 min, the resulting LDA solution was cooled to −78 °C and transferred via cannula to a cooled (−78 °C) solution of bis-dibromide **15** (398 mg, 0.394 mmol) and Me_3SiCl (0.50 mL, 3.9 mmol) in THF (5 mL). After 45 min, the resulting purple solution was quenched at −78 °C with NH_4Cl solution (20 mL) and allowed to warm to rt. The phases were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (3 × 20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford a viscous, orange oil. Purification by flash column chromatography (13% toluene in hexane) gave bis-TMS-alkyne **7** as a bright yellow solid (121 mg, 37%); R_f 0.32 (3% Et_2O in hexane); mp 60−62 °C; UV (CH_2Cl_2) λ_{max}, nm (ε) 290 sh (32700), 301sh (37400), 314 sh (41200), 324 (47300), 348 (40600), 356 sh (35900), 375 (60600), 406 (66600); IR ($CHCl_3$) 2964 m, 1489 m, 1109 s cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.27 (s, 18H), 1.15 (s, 18H), 7.33−7.46 (stack, 12H), 7.69−7.81 (stack, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.2 (CH_3), 19.6 (C), 27.5 (CH_3), 88.2 (C), 91.1 (C), 101.7 (C), 111.2 (C), 125.5 (C), 127.6 (CH), 129.4 (CH), 132.3 (C), 132.5 (C), 136.0 (CH); MS (TOF ES+) *m*/*z* 946.5 ($[M + {}^{109}Ag]^+$, 100%), 944.6 (43, $[M+{}^{107}Ag]^+$); HRMS (TOF ES+) calcd for $C_{50}H_{56}{}^{35}Cl_2Si_4{}^{107}Ag$ $[M + Ag]^+$ 945.1887, found 945.1862.

General Procedure for the Sonogashira Coupling. Aryl iodide (1.0 equiv) and terminal alkyne (1.0 equiv) were dissolved in Et_3N (0.1 M concentration) and the mixture was degassed with two freeze−thaw saturate with N_2 cycles. To this solution was added either [$Pd(OAc)_2$] (5 mol %) and PPh_3 (10 mol %) or [$(PPh_3)_2PdCl_2$] (5 mol %) and the mixture was again degassed with a freeze−thaw saturate with N_2 cycle. The reaction mixture was warmed to rt before adding CuI (2.5 mol %). The reaction mixture was carefully degassed by boiling briefly under reduced pressure and then flushing with N_2. After stirring at rt overnight, hexane was added, and the reaction mixture was filtered through Celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford the product.

(*E*)-1,4-Di[3′-*tert*-butyldiphenylsilyl-4′-chloro-5′-tetrahydropyranyloxypent-3′-en-1′-ynyl]benzene (16). Phenylene ethynylene **16** was synthesized according to the general procedure for the Sonogashira reaction. Alkyne **10** (2.310 g, 5.272 mmol) was coupled with 1,4-diiodobenzene (0.870 g, 2.64 mmol) in the presence of $Pd(OAc)_2$ (59 mg, 0.26 mmol), PPh_3 (138 mg, 0.520 mmol), and CuI (25 mg, 0.17 mmol) in Et_3N (50 mL). After 20 h, the reaction mixture was diluted with hexane (120 mL) and filtered through Celite. The solvent was removed under reduced pressure and purification of the residue by flash column chromatography (10% Et_2O in hexane) gave phenylene ethynylene **16**[36] as a white foam (2.060 g, 81%); R_f 0.74 (50% Et_2O in hexane); IR ($CHCl_3$) 2192 w (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 18H), 1.28−1.53 (stack, 10H), 1.58−1.78 (m, 2H), 3.06−3.37 (stack, 4H), 3.70 (d, J = 12.1 Hz, 2H), 3.85 (br s, 2H), 3.98 (d, J = 12.1 Hz, 2H), 7.33−7.54 (stack, 16H), 7.75−7.89 (stack, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.2 (CH_2), 19.2 (C), 25.1 (CH_2), 27.4 (CH_3), 29.8 (CH_2), 60.7 (CH_2), 69.3 (CH_2), 92.4 (C), 97.6 (CH), 99.7 (C), 119.7 (C), 123.5 (C), 127.8 (CH), 127.9 (CH), 129.5 (CH), 129.6 (CH), 131.1 (CH), 133.0 (C), 133.4 (C), 135.6 (CH), 135.7 (CH), 151.4 (C); MS (TOF ES+) m/z 1059.6 ($[M + {}^{109}Ag]^+$, 100%), 1057.6 (24, $[M + {}^{107}Ag]^+$), 428.9 (36); HRMS (TOF ES+) calcd for $C_{58}H_{64}{}^{35}Cl_2O_4Si_2{}^{107}Ag$ $[M + Ag]^+$ 1057.2771, found 1057.2747; Anal. Calcd for $C_{58}H_{64}Cl_2O_4Si_2$: C, 73.16; H, 6.77. Found: C, 73.19; H, 6.83.

(*E*)-1,4-Di[3′-*tert*-butyldiphenylsilyl-4′-chloro-5′-hydroxypent-3′-en-1′-ynyl]benzene (17). Diol **17** was synthesized according to the general procedure for the THP deprotection of THP ethers (see the synthesis of **13**). Bis-THP ether **16** (2.06 g, 2.17 mmol) was reacted under the standard conditions and after 24 h, the crude product was isolated by using the standard workup procedure. Purification of the crude product by flash column chromatography (25% Et_2O in hexane) gave diol **17** as colorless crystals (1.51 g, 89%); R_f 0.35 (50% Et_2O in hexane); mp > 140 °C dec; IR (Nujol) 3554 m (O−H), 3484 br m (O−H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.21 (s, 18H), 3.82 (s, 4H), 7.38−7.51 (stack, 16H), 7.74−7.84 (stack, 8H), O*H* resonances not observed; ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2 (C), 27.3 (CH_3), 65.6 (CH_2), 92.1 (C), 99.9 (C), 119.2 (C), 123.5 (C), 128.1 (CH), 129.9 (CH), 131.3 (CH), 133.3 (C), 135.6 (CH), 153.2 (C); MS (TOF ES+) m/z 805.7 ($[M + Na]^+$, 17%), 424.4 (100); HRMS (TOF ES+) calcd for $C_{48}H_{48}{}^{35}Cl_2O_2Si_2Na$ $[M + Na]^+$ 805.2468, found 805.2454. Anal. Calcd for $C_{48}H_{48}Cl_2O_2Si_2$: C, 73.54; H, 6.17. Found: C, 73.48; H, 6.07. Crystals suitable for X-ray analysis were obtained from the column eluent and confirm the structure of this compound (see the Supporting Information).

(*E*)-1,4-Di[3′-*tert*-butyldiphenylsilyl-4′-chloro-5′-oxo-pent-3′-en-1′-ynyl]benzene (18). Bis-aldehyde **18** was synthesized according to the general procedure for the PCC/Celite/5 Å molecular sieves-mediated oxidation of diols to enals (see the synthesis of **14**). Diol **17** (500 mg, 0.639 mmol) was reacted under the standard conditions, and after 14 h, the crude product was isolated by using the standard workup procedure to give bis-aldehyde **18** as a green foam, which was used without further purification (399 mg, 80%); R_f 0.59 (40% Et_2O in hexane); IR ($CHCl_3$) 2181s (C≡C), 1682s (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 18H), 7.33−7.57 (stack, 16H), 7.67−7.82 (stack, 8H), 9.27 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5 (C), 27.6 (CH_3), 93.6 (C), 114.3 (C), 123.9 (C), 128.3 (CH), 130.3 (CH), 131.8 (CH), 132.9 (C), 135.5 (CH), 139.2 (C), 147.5 (C), 183.8 (CH); MS (TOF ES+) m/z 801.3 ($[M + Na]^+$, 100%); HRMS (TOF ES+) calcd for $C_{48}H_{44}{}^{35}Cl_2O_2Si_2Na$ $[M + Na]^+$ 801.2155, found 801.2169. Anal. Calcd for $C_{48}H_{44}Cl_2O_2Si_2$: C, 73.92; H, 5.69. Found: C, 74.04; H, 5.78.

(*E*)-1,4-Di[3′-*tert*-butyldiphenylsilyl-4′-chloro-6′,6′-dibromo-hexa-3′,5′-dien-1′-ynyl]benzene (19). Bis-dibromide **19** was synthesized according to the general procedure for the dibromoolefination of aldehydes (see the synthesis of **15**). Bis-aldehyde **18** (357 mg, 0.459 mmol) was reacted with CBr_4 (607 mg, 1.83 mmol) and PPh_3 (960 mg, 3.66 mmol) under the standard conditions and the product was isolated by using the standard workup procedure; the product was eluted from the short silica plug with 10% Et_2O in hexane (60 mL). The solvent was removed under reduced pressure to give bis-dibromide **19** as a bright green foam (268 mg, 54%); R_f 0.33 (20% Et_2O in hexane); mp 85 °C dec; IR (film) 2858 s, 1591 m, 1428 s, 1107 s cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 1.27 (s, 18H), 6.66 (s, 2H), 7.10−7.25 (stack, 12H), 7.37 (s, 4H), 7.69−7.82 (stack, 8H); ^{13}C NMR (75 MHz, benzene-d_6) δ 19.6 (C), 28.3 (CH_3), 93.4 (C), 99.2 (C), 103.7 (C), 123.4 (C), 124.2 (C), 128.6 (CH), 130.3 (CH), 131.8 (CH), 132.7 (C), 135.9 (CH), 136.3 (CH), 144.2 (C). Satisfactory MS data could not be obtained for this compound. Crystals suitable for X-ray analysis were obtained from hexane and confirm the structure of this compound (see the Supporting Information).

(*E*)-1,4-Di[3′-*tert*-butyldiphenysilyl-4′-chloro-6′-trimethylsilyl-hex-3′-en-1′,5′-diynyl]benzene (20). Bis-TMS-alkyne **20** was synthesized according to the synthesis of TMS-alkynes from the corresponding 1,1-dibromoolefins (see the synthesis of **7**). Bis-dibromide **19** (229 mg, 0.210 mmol) was reacted under the standard conditions and after 1 h, the crude product was isolated with use of the standard workup conditions. Purification of the residue by flash column chromatography (2% Et_2O in hexane) gave bis-TMS-alkyne **20** as a pale yellow foam (190 mg, 99%); R_f 0.30 (3% Et_2O in hexane); UV (CH_2Cl_2) λ_{max}, nm (ε) 320 (21900), 352 sh (36500), 374 (57900), 383 sh (53200), 399 (53200); IR ($CHCl_3$) 2133 m (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ −0.23 (s, 18H), 1.25 (s, 18H), 7.34−7.49 (stack, 16H), 7.76−7.86 (stack, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.1 (CH_3), 19.8 (C), 27.7 (CH_3), 93.2 (C), 101.9 (C), 106.1 (C), 109.1 (C), 123.8 (C), 126.1 (C), 127.5 (CH), 129.3 (CH), 129.6 (C), 131.3 (CH), 132.8 (C), 136.0 (CH); MS (TOF ES+) m/z 1023.5 ($[M + {}^{109}Ag]^+$, 100%), 1021.5 (29, $[M + {}^{107}Ag]^+$), 749.3 (44, $[M\text{-}{}^tBuPh_2SiCl + Ag]^+$); HRMS (TOF ES+) calcd for $C_{56}H_{60}{}^{35}Cl_2Si_4{}^{107}Ag$ $[M + Ag]^+$ 1021.2200, found 1021.2235; HRMS (TOF ES+) calcd for $C_{56}H_{60}{}^{35}Cl_2Si_4{}^{109}Ag$ $[M + Ag]^+$ 1023.2197, found 1023.2195.

1,4-Di[4′-(7″-hydroxy-7″-methylocta-1″,3″,5″-triynyl)phenyl]-buta-1,3-diyne (35). TBAF (75 μL of a 1 M solution in THF, 0.08 mmol) was added to a solution of phenylene ethynylene **34** (19 mg, 0.019 mmol, see the Supporting Information) in THF (4 mL) at 0 °C. After 1 h, NH_4Cl solution (8 mL) was added at 0 °C and the reaction mixture was warmed to rt. The aqueous layer was extracted with Et_2O (3 × 8 mL) and the combined organic extracts were washed with H_2O (3 × 8 mL) and brine (3 × 8 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave phenylene-oligoyne **35** as an off-white solid, which was collected by suction filtration (7 mg, 76%); R_f 0.31 (70% Et_2O in hexane); UV (CH_2Cl_2) λ_{max}, nm (ε, normalized) 390 (0.93), 360.5 (1.00), 335 (0.58), 312 (0.31), 284 (0.40), 263 (0.50); ^1H NMR (300 MHz, acetone-d_6) δ 1.50 (s, 12H), 7.66 (s, 8H); MS (EI) m/z 462 ($[M]^+$, 100%), 447 (29, $[M - CH_3]^+$), 429 (11), 419 (12), 404 (25), 389 (7), 368 (9), 361 (11), 346 (15), 313 (11); HRMS (EI) calcd for $C_{34}H_{22}O_2$ M^+ 462.1620, found 462.1609.

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Supporting Information Available: General experimental details, experimental procedures, and compound characterization data for **11** and its Cadiot Chodkiewicz coupling product with phenyl acetylene, **22**, **24**−**28**, **32**, and **34**, X-ray data for **17** and **19**, scanned ^1H NMR spectra, and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.