End-Cap Stabilized Oligoynes: Model Compounds for the Linear sp Carbon Allotrope Carbyne

Thomas Gibtner,[a] Frank Hampel,[a] Jean-Paul Gisselbrecht,[b] and Andreas Hirsch*[a]

Abstract: Three series of differently 3,5-disubstituted α,ω-diphenylpolyynes Ar-(C≡C)$_n$-Ar ($n = 2, 4, 6, 8, 10$) were synthesized under optimized Cadiot–Chodkiewicz conditions, isolated and completely characterized. These compounds can be considered as model substances for the hypothetical one-dimensional carbon allotrope carbyne C_∞. The longest sp-carbon chain contains 20 atoms and is therefore the longest, purely organic polyyne studied with NMR techniques. Extinction coefficients over 600000 $\text{M}^{-1}\text{cm}^{-1}$ represent the highest measured quantitative values for that compound class so far. Comparisons with previous investigations and electrochemical studies allow the assignment of absorption for both wavelength regions structuring the UV/Vis spectra. Based on the trends in the spectroscopic behaviour of those molecules with increasing chain length, electronic as well as the NMR properties of carbyne are predicted, in line with our previously reported results. The observed stability properties promise the synthesis of even longer polyynes.

Keywords: alkynes · carbon allotropes · cross-coupling · dendrimers · electronic structure

Introduction

Carbon rich compounds and materials are currently an area of intensive research.[1–3] This was promoted inter alia by the discovery of the new carbon allotropes, the fullerenes,[4] which was honoured with the Nobel Prizes in chemistry in 1996.[1] Among the carbon rich compounds, the synthesis of the hypothetical polymeric sp carbon allotrope "carbyne" remains a demanding goal (Figure 1).[5, 6]

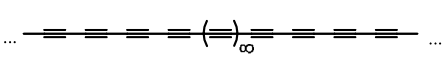

Figure 1. The polymeric sp carbon allotrope "carbyne".

This substance is as conceptually important as diamond (sp^3 lattice) and graphite (sp^2 lattice). Its precise physical and chemical characterization continues to present many challenges. For example, the possibility that carbyne might easily bend and generate other allotropes has stimulated considerable speculation,[5] but experimental evidence remains scant.

The first attempts to synthesize long sp carbon chains were undertaken by Bohlmann and Jones in the 1950s.[7, 8] As they were interested in the synthesis of di-, tri-, tetra-, and pentayne containing natural compounds, they initiated the systematical synthesis of several differently end-capped series of polyacetylenes with up to ten triple bonds.[8b, 9, 10] The direct correlation they observed between the size and bulkiness of the end groups and the stability of the sp carbon chains was later studied in detail by Wegner, during his investigations of topochemically controlled polymerizations of diacetylenic compounds.[11]

Due to the difficulty in handling the precursors to the polyynes, the classical elongation technique was only of limited scope. The synthesis of longer derivatives was possible after Walton and co-workers had introduced silylation as a protective method in acetylene coupling chemistry.[12–15] With the use of triethylsilyl as a protection group during iterative symmetrical and mixed Hay coupling reactions,[16] the synthesis of homologous series of unsubstituted and triethylsilyl substituted polyynes was reported,[12, 13] resulting in the longest sp carbon chain known to date (Et_3Si-(C≡C)$_{16}$-$SiEt_3$) which was characterized by UV/Vis spectroscopy.

A general approach to the synthesis of polyynes with an odd number of C≡C bonds has been developed by Diederich et al.[17] While the alternative Cadiot–Chodkiewicz method[18] often has the disadvantage of giving only a low yield of the desired coupling product,[7b, 18b, 19] the smooth elimination of

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two carbonyl groups from differently substituted 3-cyclobutene-1,2-diones under the "solution-spray flash vacuum pyrolysis" (SS-FVP) conditions allows the formation of corresponding alkynes in high yields.[17] In this way, the dodecahexayne TBDMS-$(C{\equiv}C)_6$-TBDMS (TBDMS: *tert*-butyldimethylsilyl) was obtained, which is the longest NMR-characterized purely organic oligoyne known to date.

Compounds in which unsaturated elemental carbon chains span two transition metal complex fragments[20] constitute another fundamental class of carbon-based molecular wires.[21] Such one-dimensional assemblies must by definition be composed only of sp-hybridized carbon.

The synthesis of polyynes containing up to ten triple bonds, which span two redox-active, chiral rhenium fragments, is described by Gladysz and co-workers.[22] The longest molecule, the decayne, which shows impressive stability even in the solid state at room temperature,[22b,c] is accessed by the use of a modified Cadiot–Chodkiewicz coupling[23] followed by a classic oxidative coupling reaction.[24] To date, this is the longest, completely characterized polyyne bearing transition metal end groups. Gladysz's group also reports the first structurally characterized hexayne that connects two platinum metal complex fragments, showing surprising crystallographic properties.[25]

We recently synthesized, under Krätschmer–Huffman conditions[26] in the presence of cyanogen $(CN)_2$, the α,ω-dicyanopolyynes $\mathbf{C_8N_2}$–$\mathbf{C_{18}N_2}$, which, in terms of their shape and their composition, come closest to carbyne.[5d,e] Together with the already known representatives of this compound class, NC-CN, NC-C≡C-CN, and NC-C≡C-C≡C-CN, they form a continuous homologous series of neutral rod-shaped molecules that possess the highest possible number of π electrons.[27]

In this paper, predictions of the properties of carbyne were put forward extrapolating our own and others' spectroscopic data.[5e] Here we report the iterative synthesis and detailed spectroscopic characterization including electrochemistry of several series of stable organic polyynes with up to ten C≡C bonds with different end-caps.

Results and Discussion

Synthesis: Due to the fact that oligoynes show a large decrease in stability with increasing chain length, stabilization is the crucial aspect in polyyne chemistry.[5d,e, 8–10, 12–14, 22c] As polymerization of polyacetylenic compounds can be considered as a function of the distance between such molecules,[11] we consequently decided to build up dumb-bell-shaped systems (Figure 2) where the carbon chains are kept at a distance by bulky, spherical end groups.[28, 29]

For this purpose, dendrimers[30] seemed to be the most suitable choice. Ideally, they are perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture, such as Fréchet's aromatic polyether dendrimers which are easily accessilbe through convergent procedures.[31, 32] Their synthesis up to the third generation was readily achieved in good to very good yields, according to the published procedures.[31, 33]

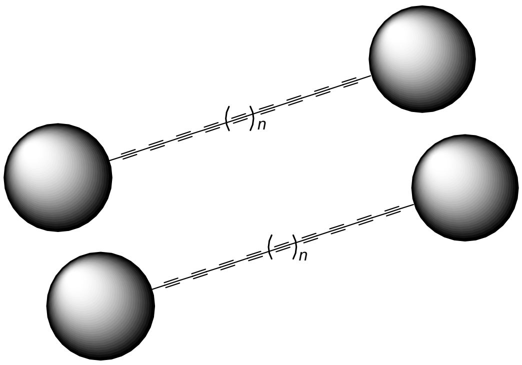
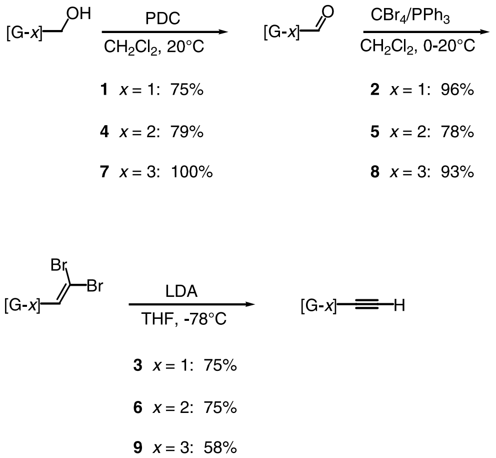


Figure 2. Dumb-bell-shaped polyynes with sterically demanding end-caps preventing cross-linking.

As various coupling reactions of the second generation bromide [G-2]-CH_2Br with lithiated[17, 34] and Grignard[35] trimethylsilylacetylene[36] at low temperatures did not result in the expected dendrimer substituted alkyne, we decided to generate the first yne-unit directly in the dendrimer core, applying Corey's and Fuchs' methodology (Scheme 1).[37]



Scheme 1. Synthesis of the dendrimer alkynes [G-*x*]-C_2H ($x = 1$ (**3**), 2 (**6**), 3 (**9**)) applying the Corey–Fuchs methodology.

Oxidation of [G-1]-CH_2OH with pyridinium dichromate (PDC)[38] in CH_2Cl_2 gave the aldehyde [G-1]-CHO (**1**) in 75% yield, which was transformed to the dibromo olefin [G-1]-$CHCBr_2$ (**2**) (96%). Finally, elimination with lithium diisopropylamide (LDA) gave the first generation dendrimer alkyne [G-1]-C_2H (**3**) in 75% yield. Although attempts to grow crystals of the highly viscous oils **1**, **2**, and **3** failed at room temperature, success was achieved in the cold (−20 °C) by overlaying the oils with MeOH. The crystals obtained were of sufficient quality for X-ray structure analysis. Figure 3 shows the structure of the first generation dendrimer alkyne **3**.

Scheme 2a outlines the synthesis of hexayne [G-1]-C_{12}-[G-1] (**15**). After bromination of **3** with *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of $AgNO_3$,[17, 39] the resulting bromo alkyne **11** was coupled in a modified Cadiot–Chodkiewicz reaction[23, 40] with H-C≡C-C≡C-$SiEt_3$ (**10**)[13] to give the triethylsilyl protected triyne **12** in only 7% yield. It was possible to isolate and separate **12** from the

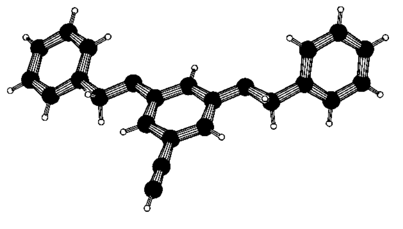


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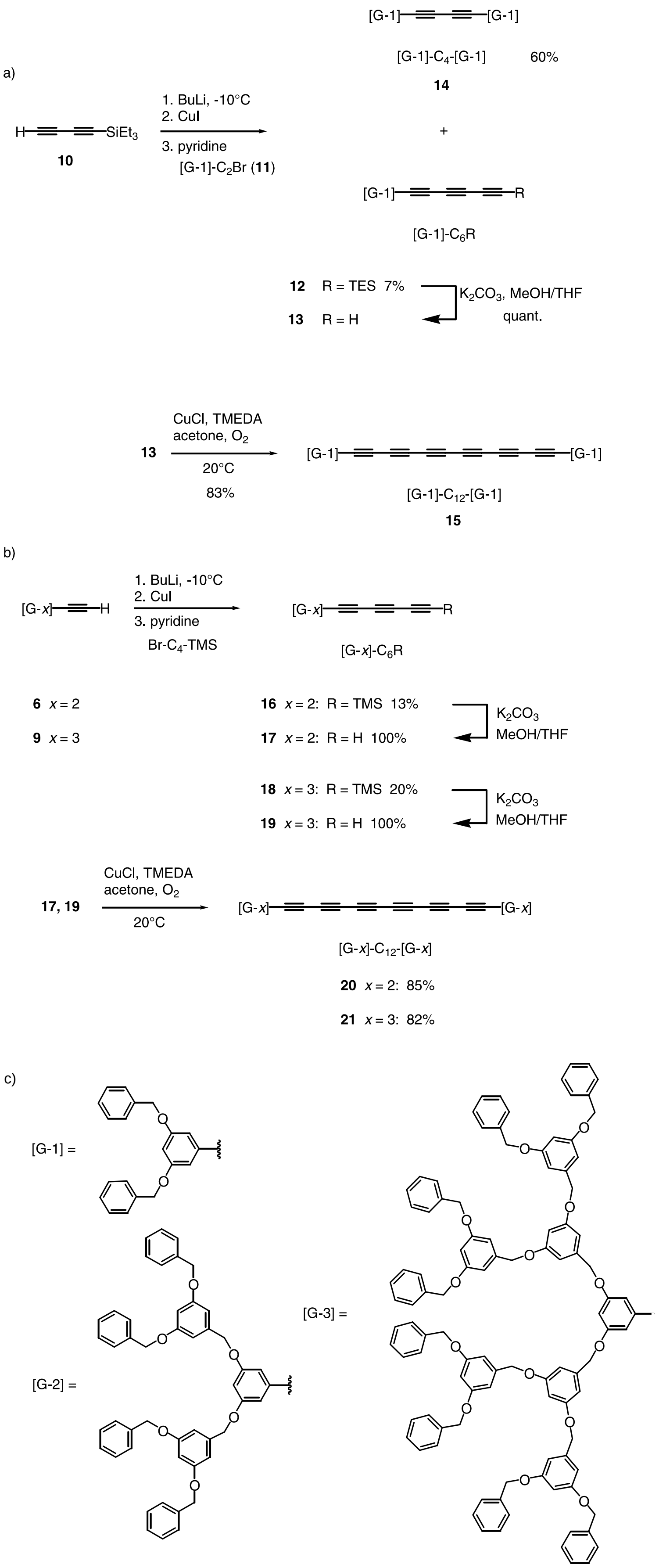
Figure 3. X-ray structure of **3**.

homo coupling side-product of the bromo acetylene compound, which often arose during Cadiot–Chodkiewicz reactions.[41] In our case, [G-1]-C_4-[G-1] (**14**) was the main product with 60% yield, probably because of extensive decomposition of the copper butadiynyl intermediate during the slow addition of the highly diluted solution of **11** with a syringe pump. In solution, **12** exhibited normal stability properties and no air sensitivity. However, during the evaporation of the solvent, it slightly decomposed to a dark brown oil. Nevertheless, **12** was completely characterized. Moreover, deprotection with K_2CO_3 in a wet MeOH/THF 1:1 solution was possible without decomposition. Crude **13** was then, without purification and charaterization, coupled to give the yellow hexayne **15** in good yield, which displayed the same stability profile as the triyne.

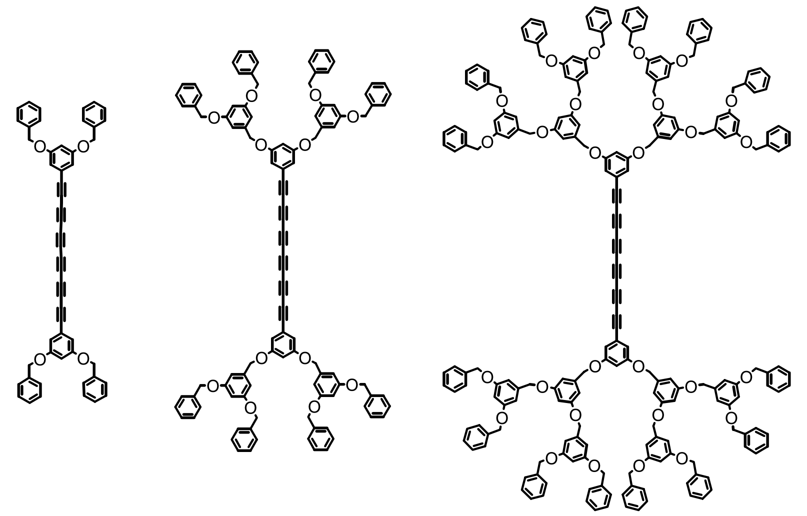
To see if the use of higher dendrimer generations would result in greater stability, almost the same reaction sequence was applied to the synthesis of the second and third generation C12 chains **20** and **21**, respectively (Scheme 2b). This time, the copper end-group acetylide and the bromo acetylene component (Br-C≡C-C≡C-TMS)[42] were coupled, resulting in higher cross-coupling yields. In Hay oxidative coupling reactions, [G-2]-C_4-[G-2] (**22**) but not [G-3]-C_4-[G-3] could be obtained from their corresponding starting materials [G-2]-C_2H (**6**) and [G-3]-C_2H (**9**), respectively. The likelihood of sterical hindrance in the latter case appeared to indicate a correlation between polyyne stability and dendrimer size. However, **20** and **21** did not show higher stability during evaporation or in the solid state. Both displayed similar behaviour to **15**. Indeed, independent of the steric demand of their end groups, all three hexaynes [G-*x*]-C_{12}-[G-*x*] ($x=1$ (**15**), 2 (**20**), 3 (**21**)) (Figure 4) formed indefinitely stable bright yellow solutions in CH_2Cl_2 at room temperature, but decomposed rather quickly upon evaporation.

Nevertheless, all of them were characterized by means of NMR and UV/Vis spectroscopy and mass spectrometry, showing strikingly similar properties. However, as a result of their solid state instability no further investigations were possible.

The more or less planar arrangement of the benzylic ether dendrimer fragments caused by unexpectedly strong aromatic $\pi-\pi$ interaction can explain this finding. We found support for this explanation in works about dendronized polymers.[43] According to these investigations, Fréchet[31] type dendrimers of at least the fourth



Scheme 2. a) Synthesis of dodecahexayne [G-1]-C_{12}-[G-1] (**15**). b) Synthesis of dodecahexaynes [G-2]-C_{12}-[G-2] (**20**) and [G-3]-C_{12}-[G-3] (**21**).



[G-1]-C$_{12}$-[G-1] **15** [G-2]-C$_{12}$-[G-2] **20** [G-3]-C$_{12}$-[G-3] **21**

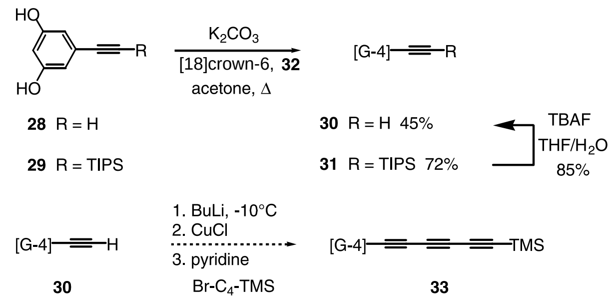
Figure 4. Series of Fréchet's benzylic dendrimer-protected C$_{12}$ carbon chains [G-x]-C$_{12}$-[G-x] ($x = 1, 2, 3$).

generation are required to form space-filling, three-dimensional structures, which would then keep encapsulated carbon chains a sufficient distance apart.

However, the realization of the synthesis of the fourth generation dendrimer alkyne [G-4]-C$_2$H (**30**), following the procedure described above, posed problems in respect of control of the reaction, purification and overall yields. We therefore sought to succeed in a new convergent approach, synthezising a dendrimer core building block which already bears one protected or unprotected acetylene unit and two OH groups for subsequent functionalization (Scheme 3).

For that purpose we needed to introduce a hydroxy protecting group right at the beginning of the synthesis of the building blocks. The *tert*-butyldimethylsilyl group proved to be ideal. It could be smoothly attached to the starting 3,5-dihydroxybenzaldehyde[44] (**23**) to give **24** in 90% yield. Within the Corey–Fuchs sequence, the aldehyde **24** could easily be converted to the corresponding dibromo olefin **25**, and then to the triisopropylsilyl (TIPS) protected and unprotected alkyne compounds **27** and **26**, respectively, in excellent yields. In the last step, **29** and **28** were obtained without any losses by the cleavage of the silylic OH protecting groups. As we were unsure about the kinetic stability of the 3,5-dihydroxyphenylacetylene (**28**) under the following basic reaction conditions (Scheme 4), we worked towards for the TIPS protected derivative **29**, in parallel.

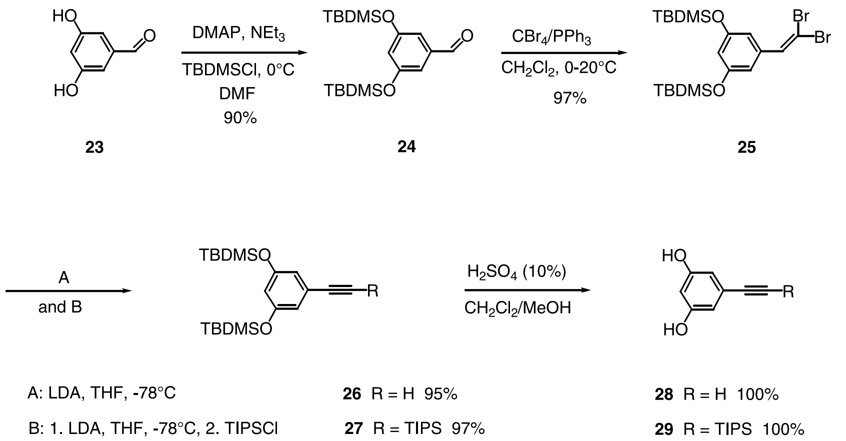
The fourth generation compounds **30** and **31** were obtained by the benzylation of the dihydroxy starting materials with the third generation bromide [G-3]-CH$_2$Br (**32**) in refluxing acetone. As expected, the yield of the unprotected alkyne **30** was much lower. The route via **31**, including the deprotection with tetrabutylammonium fluoride (TBAF) was more successful, with an overall yield of 62% over two steps.



Scheme 4. Synthesis of forth generation compounds **30** and **31**. Triyne **33** was not obtained in satisfactory yield.

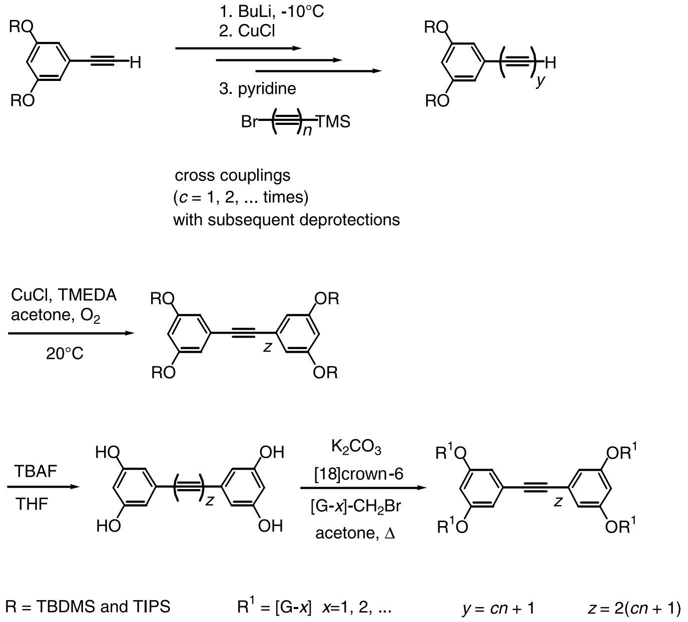
A variety of coupling conditions, besides those in Scheme 4, have been investigated, but none led to the cross-coupling product [G-4]-C$_6$TMS (**33**) in a satisfactory way. Either, only starting material was recovered after the usual work-up procedures, or, **33** could only be detected as a small component of an intractable product mixture by fast atom bombardment (FAB) mass spectrometry. All further attempts at improvement failed, thereby necessitating an alternative approach.

We therefore embarked on two different strategies. While we were testing another dendrimer type with a larger steric demand at lower generations, we simultaneously investigated a more convergent route with what we expected to be less difficult purification and sepa-



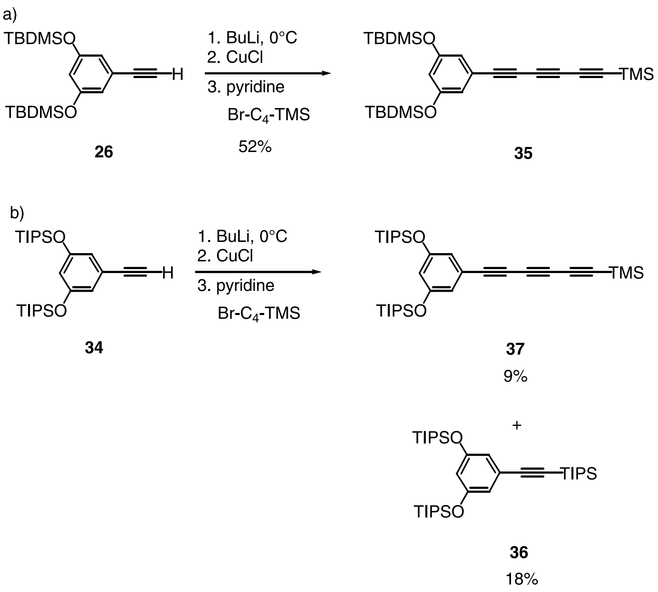
Scheme 3. Synthesis of the dendrimer core building blocks **28** and **29**.

ration procedures: namely, after the optimization of the cross-coupling conditions, we sought to extend the sp carbon chains from **26** and the analogously synthesized (Scheme 3) TIPS protected 3,5-dihydroxyphenylacetylene **34**[45] by iterative cross-coupling reactions and deprotections, followed by an oxidative homo coupling. After the cleavage of the silyl groups, the protection of the "naked" polyyne with dendrimers should take place in the last step (Scheme 5).



Scheme 5. Alternative, highly convergent synthesis strategy to dendrimer-protected polyynes.

In contrast to almost all published procedures of acetylene cross-coupling, we achieved the best results by adding highly concentrated bromo alkyne solutions in 1–2 min to the alkynyl copper species at ice water cooling, the reaction reaching completion after 20 to 30 minutes. During that time, the trimethylsilyl acetylene protecting group, which is rather sensitive to strong basic conditions, was only cleaved to a negligible extent, so that no side reactions, for example, a second cross-coupling, could occur. Signals corresponding to such products were observed in the FAB mass spectra of the crude product mixtures. Furthermore, only small quantities of polymerized, soot-like material were obtained after workup. The small amounts of starting materials which remained were separated by column chromatography without major problems. The resulting yields were about 50% for the first cross-coupling. We optimized the experimental protocol with **26** (Scheme 6a), expecting that it would be readily applicable to the other compounds. Application of the procedure proved to be successful in all further cases, except for **34**, where molecule **36** was found in addition to triyne **37** (Scheme 6b). We noticed the formation of **36** immediately after the addition of *n*BuLi to the mono alkyne **34**, which indicated a surprising and unusual cleavage of the silyl ether and subsequent reaction with the lithiated starting material.



Scheme 6. Synthesis of triynes **35** (a) and **37** (b). In the latter procedure, TIPS protected alkyne **36** was also obtained.

Unfortunately, the purification of **37** became very complicated, as the side product **36** revealed similar polarity. Two flash columns were necessary to achieve adequate separation. Therefore, the subsequent elongation process was continued only with **26**, with which no such problems had arisen.

To investigate variations of stability, and physical and chemical properties with increasing chain length, we continued building up series of sp carbon chains with two, four, and six C≡C bonds (Scheme 7a and b) bearing two different silyl protecting groups. The TMS cleavage/homo coupling sequence was used for triynes **35** and **37** which afforded the hexaynes **40** and **41** in 94% and 25% overall yields (Scheme 7a). In this case, the free acetylenic compounds **38** and **39** were purified by flash column chromatography. The significantly lower yield for **41** seems to stem from the decomposition of **39** during deprotection. With **40** and **41**, we had our most stable polyynes thus far. Upon drying, they formed yellow amorphous solids that gradually decomposed over a period of weeks to brown oils.

The synthesis of the octatetraynes **48** and **49** was initiated with a cross-coupling reaction under Hay conditions (Scheme 7b).[16] For that purpose, an excess of trimethylsilylacetylene was stirred together with each of the mono alkynes **26** and **34**, while the Hay catalyst was added in small portions.[25] In addition to the products of cross-coupling, **42** and **43**, which it was possible to isolate in good yields, the symmetrical butadiynes **44** and **45** were also obtained in significantly better yields. Compounds **42** and **43** could easily be converted to the unprotected, labile diacetylenes **46** and **47**. These were fully characterized, but showed significant decomposition after one week at −10°C, even when stored as a dilute stock solution. In the final Hay coupling, we obtained the tetraynes **48** and **49** as light coloured plates and as a light brown oil, respectively. Generally, the TBDMS derivatives (**44**, **48**, and **40**) more readily gave solids and powders upon drying, whereas the TIPS compounds (**45** and **49**), except for the hexayne **41**, remained highly viscous oils.

The next elongation reactions were only carried out with the TBDMS protected diyne **46** and triyne **38** (Scheme 8),

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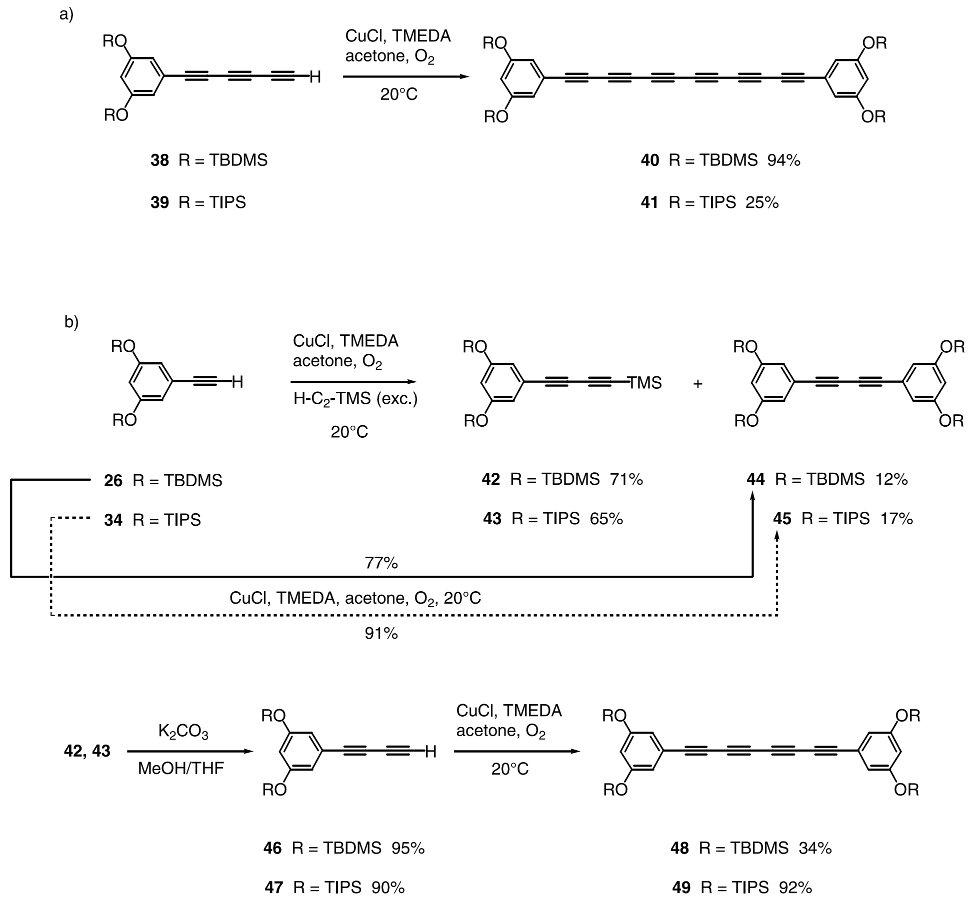


Scheme 7. Synthesis of TBDMS- and TIPS-protected series of sp carbon chains with six (a), and two and four C≡C bonds (b).

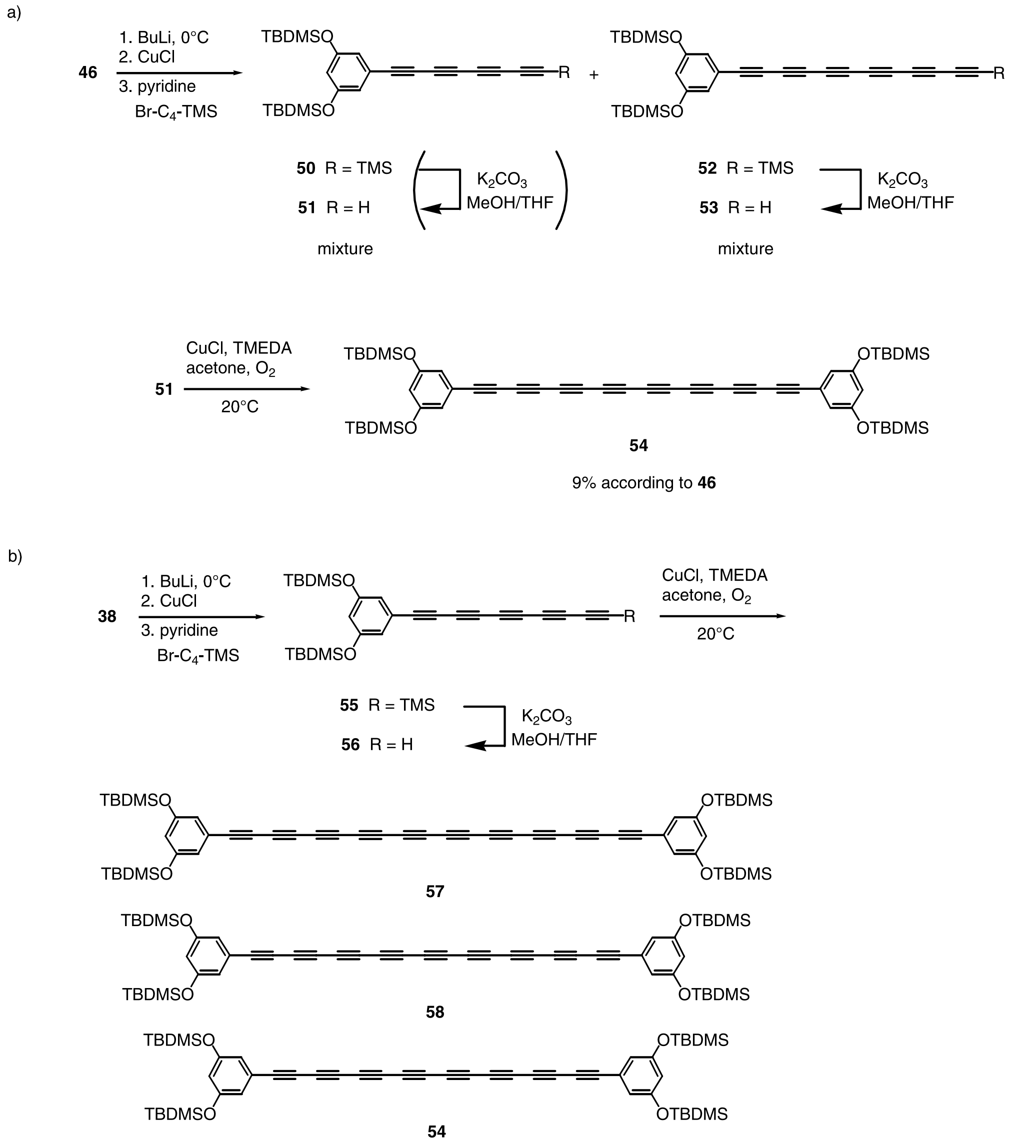
because of the aforementioned difficulty with the TIPS compound **34** during cross-coupling (Scheme 6b). Reaction of **46** under modified Cadiot–Chodkiewicz conditions afforded two fractions after workup. They represent a mixture of hexaynes **52** and **53**, and a mixture of tetrayne **50** with its deprotected derivative **51** (Scheme 8a). Due to the longer reaction time, a second cross-coupling occurs after **50** has been partially desilylated by pyridine. To minimize losses, we undertook no additional purification efforts with both fractions, which prevented further investigation of **52** and **50**. In the mixtures, **52** and **50** were converted to **53** and **51** respectively, which could only be characterized by mass and UV/Vis spectrometry. Unfortunately, there was only sufficient **53** to record its optical properties, but not to complete the oxidative homo-coupling. By contrast, **51** gave the hexadecaoctayne **54** under Hay conditions in 9% yield from **46**. Octayne **54** formed a slowly decomposing orange powder and exhibited extinction coefficients of more than $4 \times 10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$.

Treatment of **38** with our optimized cross-coupling technique gave the decapentayne **55**, from which eicosadecayne **57** can be prepared after deprotection to **56** (Scheme 8b). Interestingly, it emerged from FAB mass spectrometry that, besides **57**, two additional compounds had been formed whose masses were 24 and 48 Daltons lower. These compounds could not be separated, not even by HPLC. Due to the similar polarity, the orange-red colour of the product mixture, and the observed mass spectra, we presume that the two molecules are the octadecanonayne **58** and the hexadecaoctayne **54**. For the completion of the reaction, an unusually long time was necessary, probably corresponding to the lower acidity of the oligoacetylenic hydrogen in **56**. Therefore, a copper mediated cleavage of one acetylene unit could have occurred, providing a mixture of pentayne and tetrayne, thereby explaining the product distribution.

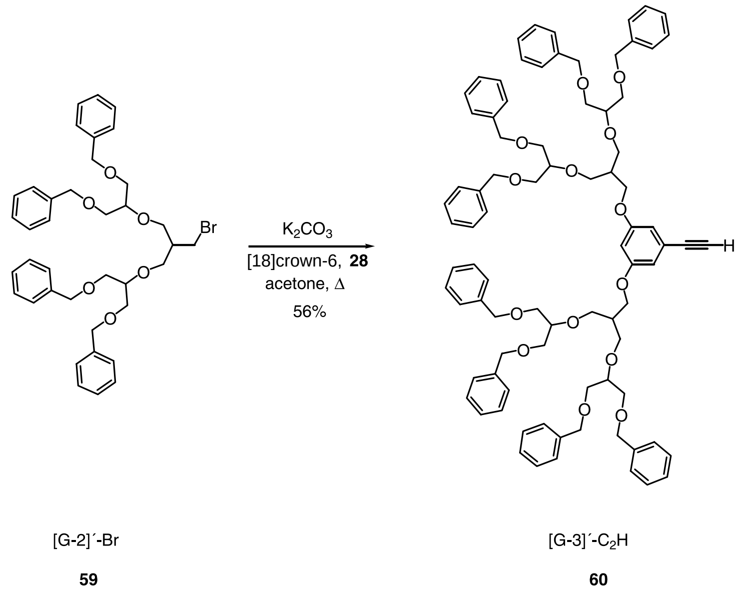
This first strategy allowed the synthesis and isolation of two series of differently silyl protected α,ω-tetrahydroxydiphenylpolyynes with up to eight C≡C bonds. We are currently investigating the synthesis of longer sp carbon chains and the final dendrimer protection step (Scheme 5).

Finally, following our second strategy, we were able to prepare and isolate molecules up to 20 carbon atoms in length (Figure 5). They represent the longest, purely organic polyynes that have been fully characterized. We achieved the required increase in steric shielding with lower generation dendrimers by using Fréchet's aliphatic polyether dendrimers.[46] Their preparation up to the second-generation alcohol proceeded very well.[46] After the bromination of this compound, a benzylation reaction between [G-2]′-Br (**59**) and **28** was conducted that gave [G-3]′-C_2H (**60**) in 56% yield (Scheme 9).

As shown in Scheme 10, the copper species derived from **60** was coupled with Br-C≡C-C≡C-TMS, affording **61** that was desilylated to **62**. The final, homo-coupling step led to another dodecahexayne [G-3]′-C_{12}-[G-3]′ (**63**) in reasonable yield. The cross-coupling was repeated with [G-3]′-C_6H (**62**). Again, because of a longer reaction time, the resulting cross-coupling product [G-3]′-C_{10}TMS (**64**) was deprotected by pyridine, simultaniously affording [G-3]′-$C_{10}H$ (**65**) in the crude product mixture after workup. Despite three-fold column chromatography, the separation of [G-3]′-C_{10}TMS (**64**), the slightly more polar [G-3]′-$C_{10}H$ (**65**), and some remaining starting material **62** was not successful. Therefore, the whole mixture was subjected to Hay coupling conditions, as we expected to separate the resulting, highly polar homo-coupling products more easily from **64**. Hence, we obtained two fractions in the subsequent purification step. One was pure [G-3]′-C_{10}TMS (**64**), characterized by FAB mass spectrometry and UV/Vis spectroscopy. The other consisted of a statistical mixture of homo-coupling products [G-3]′-C_{20}-[G-3]′ (**66**), [G-3]′-C_{16}-[G-3]′ (**67**), and [G-3]′-C_{12}-[G-3]′ (**63**) (Figure 5), that was readily separated by HPLC. Their orange-red (C20), orange (C16),



Scheme 8. Synthesis of polyynes **54** (a+b), **57**, and **58** (b).

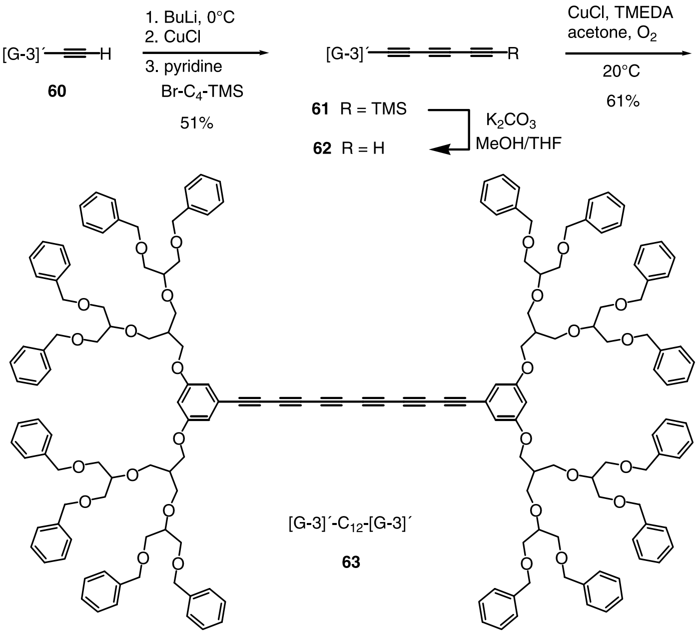


Scheme 9. Synthesis of dendrimer alkyne [G-3]′C_2H (**60**).

and yellow (C12) coloured solutions, directly eluted from the HPLC column, are shown in Figure 6.

The dendrimer capped polyynes proved to be rather stable. Only minute decomposition was observed in the solid state, to give more polar compounds within hours.[47] As a consequence, complete characterization of polyynes of such length was possible for the first time.

Analogous to the oxidative coupling of **56** (Scheme 8b), the corresponding reaction of [G-3]′-$C_{10}H$ (**65**) was also accompanied by partial loss of C2 units. This observation is to our knowledge unprecedented in



Scheme 10. Synthesis of dodecahexayne [G-3]′-C_{12}-[G-3]′ (**63**).

acetylene chemistry, but might be seen as a copper mediated retro-Hay coupling reaction. Therefore, [G-3]′-C_{20}-[G-3]′ (**66**) was not the only isolated product. [G-3]′-C_{18}-[G-3]′ (**68**) and [G-3]′-C_{16}-[G-3]′ (**67**) were also generated (Figure 5), for the same reasons as stated above. However, in contrast to the earlier case, the mixture was separated by HPLC. Unfortunately, the amount of [G-3]′-C_{18}-[G-3]′ (**68**) was insufficient for complete characterization, but we were able to record its FAB mass and UV/Vis spectra.

Chain length effects: The dumb-bell-shaped title compounds represent unique and formerly unavailable series of organic

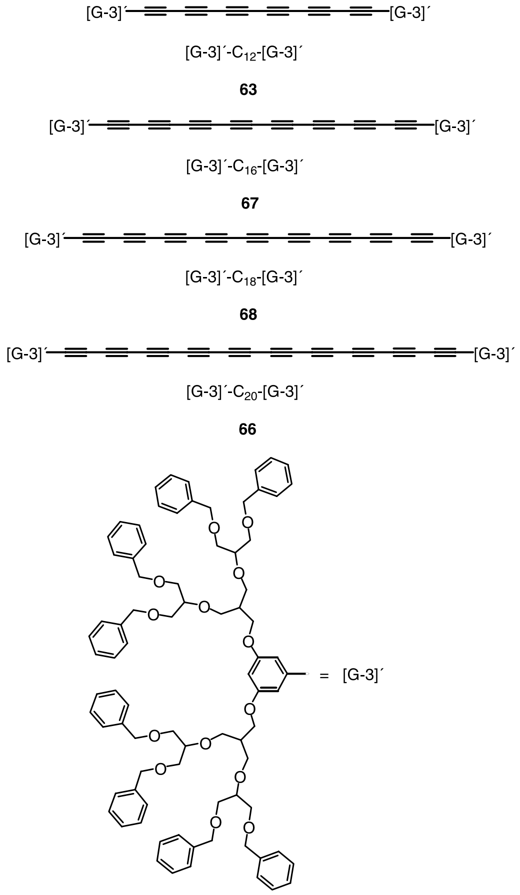


Figure 5. sp Carbon chains **63** and **66**–**68** protected with Fréchet's aliphatic polyether dendrimers.

polyynes that have been completely characterized. In the longest chain, the end-capping groups are linked by 10 C≡C and 11 C–C bonds. As noted in the introduction, only a few

Figure 6. Solutions of compounds [G-3]′-C_{20}-[G-3]′ (**66**), [G-3]′-C_{16}-[G-3]′ (**67**), and [G-3]′-C_{12}-[G-3]′ (**63**) in hexane/ethyl acetate 7:3.

comparable families of polyynediyl compounds with carbon, silicon or transition metal complex end groups have previously been isolated. These provide important opportunities to define the effect of chain length upon molecular properties. For infinite chains, two types of asymptotic structural limits are possible: 1) For large n there will be no bond length alternation in the interior of the chain. 2) The bond length equalization will never be complete, and the differencs in length between C–C and C≡C bonds will approach a certain limit. The former case implies a vanishing HOMO/LUMO energy gap ΔE,[48] which would make carbyne a black metal-like material. In the latter case, carbyne would be an insulator with a persistent energy gap ΔE.[48] The magnitude of ΔE would then depend on the extent of the remaining bond length alternation. Based on the present knowledge of the structures, including the longest polyynes M*-(C≡C)$_6$-M* (M* = platinum and iron transition metal complexes) structurally characterized to date,[25, 49] and on electronic properties of one-dimensional solids, it is likely that bond length alternation in carbyne persists, termed Peierls distortion in solid state physics.[48] This is additionally supported by theoretical studies of the parent system H-(C≡C)$_n$-H that predict two limiting values (1.1956 – 1.2031 and 1.3574 – 1.3726 Å)[50] and by our previously reported investigations on dicyanopolyynes.[5e] Bond length alternation is also expected by analogy to data on polyenes and polyacetylene, (CH=CH)$_n$,[51] which is an insulator in the undoped state.[52]

NMR spectra: The ^{13}C NMR spectra of the three series of polyynes are very characteristic and unambiguously allow structural confirmation of these carbyne model compounds (Figure 7). They include the spectra of the longest, purely organic carbon chains consisting of 16 and 20 atoms to be characterized with NMR techniques. Their key data are tabulated in Table 1.

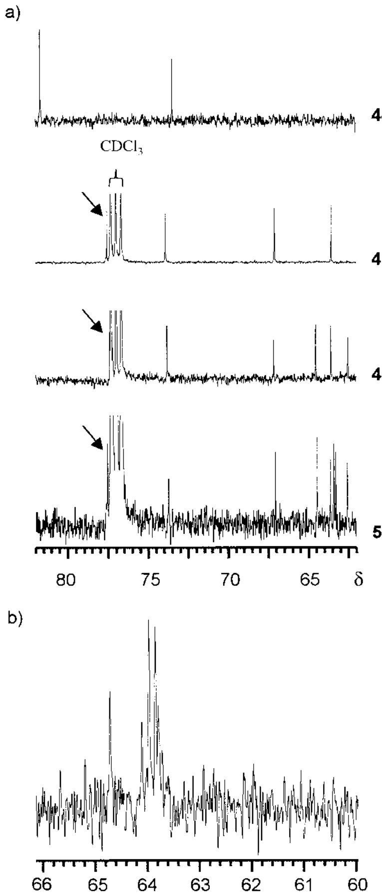


Figure 7. sp Carbon atom region in the ^{13}C NMR spectra (in CD$_2$Cl$_2$ and CDCl$_3$, respectively) of a) C4 (top) to C16 chain (bottom) of the TBDMS series. b) The area of $\delta = 63 – 65$ exhibits five sp-carbon signals, two with double intensity, for the dendronized C20 chain **66**.

In general, starting from the butadiynyl derivatives, two further sp carbon signals appear in the spectra for each additional C4 unit. In going from the tetrayne to the decayne, new signals appear in the very narrow region between $\delta = 62$ and 65. Compounds with the same chain length show almost identical chemical shifts independent of the groups connected to the conjugated framework. Only the resonances of the inner sp carbon atoms of the dendronized series are slightly shifted downfield. It is striking that the resonances of atoms C-1 to C-6 (except C-2 in **45** and **44**) have very similar chemical shifts irrespective of the carbon chain length. No significant shift of any atom is observed by increasing the number of C≡C bonds. Specifically, the signals are assigned as following: a) the first carbon atom C-1, which is bound to the aromatic system, always appears at $\delta = 73 – 74$; b) signals for the C-2 atoms are shifted most downfield between $\delta = 78$ and 82; c) the signals at $\delta = 67$ represent the C-3 atoms; the signals for d) the C-4 atoms and e) the C-5 atoms are observed very close to each other at $\delta = 64$; and f) signals for the C-6 atoms occur at highest field. All further signals for the longer carbon chains were recorded between the signals for sp atoms C-4 and C-6. They are tentatively assigned in Table 1.

Table 1. Summary of ^{13}C NMR chemical shifts (sp region) for polyynediyl compounds.

Compound	Solvent	R-C-1	R-C-2	R-C-3	R-C-4	R-C-5	R-C-6	Others[a]
45	CDCl$_3$	73.62	81.59					
49	CDCl$_3$	74.15	78.06	67.41	63.92			
41	CD$_2$Cl$_2$	73.68	78.10	67.12	63.76	64.62	62.86	
44	CD$_2$Cl$_2$	73.51	81.72					
48	CDCl$_3$	73.90	77.56	67.10	63.55			
40	CDCl$_3$	73.80	77.38	67.13	63.57	64.52	62.51	
54	CDCl$_3$	73.73	77.53	67.04	63.61	64.45	62.57	63.39 (C7), 63.30 (C8)
63	[D$_6$]acetone	73.64	79.30	67.11	64.04	64.75	63.53	
67	[D$_6$]acetone	73.52	79.55	67.07	63.97	64.68	63.65	63.89 (C7), 63.84 (C8)
66	[D$_6$]acetone	73.64	78.36	67.24	64.09	64.71	63.79	63.97 (C7/8), 63.84 (C9/10)

[a] This signals are assigned tentatively as an unambiguous determination was not possible.

The assignment was facilitated by comparison of the spectra with each other and with data available for other oligo- and polyynes (synthesized by Diederich,[17] Gladysz,[22c] and ourselves[5d,e]). Except for the signals of the sp C atoms adjacent or in close proximity to the end groups, such as C-1 and C-2 in our series, and C-3 in the rhenium complex-capped polyynes,[22] the signals of the inner sp C atoms appear in the narrow region between $\delta = 62$ and 67. This reinforces our earlier suggestion that the ^{13}C NMR spectra of polyynes R-(C≡C)$_n$-R with n reaching infinity will display one broad signal at $\delta = 63-64$,[5e] which therefore represents the expected chemical shift of the carbon allotrope carbyne.

UV/Vis spectra: The UV/Vis spectra of the TBDMS (**44**, **48**, **40**, **54**) and the dendrimer (**63**, **67**, **66**) series are shown in Figure 8 and 9, respectively.[53] Table 2 displays their most intriguing data. Strong fluorescence in CH_2Cl_2 solutions of all compounds, except **44**, was observed. The spectra of hexaynes **15**, **20**, and **21** which are end-capped with Fréchet's benzylic dendrimers show almost identical properties as hexaynes **40** and **63**.

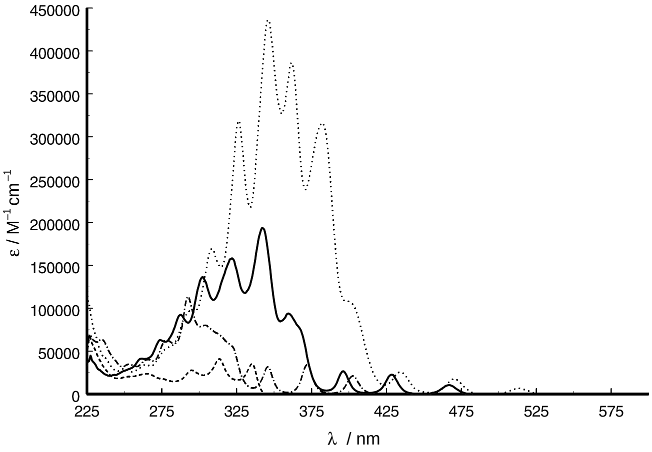


Figure 8. UV/Vis spectra (CH_2Cl_2) of the TBDMS series C4 (**44**: - - - -), C8 (**48**: •–•–), C12 (**40**: ——), and C16 (**54**: ••••).

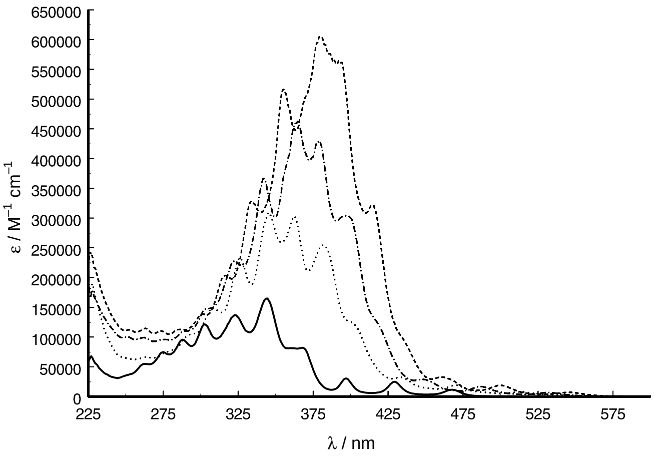


Figure 9. UV/Vis spectra (CH_2Cl_2) of the dentritic polyynes C12 (**63**: ——), C16 (**67**: ••••), C18 (**68**: •–•–), and C20 (**66**: - - - -).

Table 2. Key UV/Vis data for the TBDMS and the dendronized series.

Compound	λ_{max} [nm]	λ_{max} (region I) [nm]	$\lambda_{\varepsilon max}$ [nm]	ε_{max} [Mol^{-1}cm^{-1}]
44	336	275	314	40900
48	403	313	293	114000
40	467	367	342	193700
54	514	403	347	435200
63	469	368	345	164100
67	514	402	346	307900
68	532	420	364	459400
66	546	437	379	604600

All spectra exhibit the expected two regions of absorption with distinct bands showing vibrational fine structure. Whereas the extinctions of the higher wavelength bands (region II) differ only to a very small extent, the extinctions of the lower wavelength absorptions (region I) increase strongly with chain length (Table 2). They reach values of $435\,200\,\text{M}^{-1}\text{cm}^{-1}$ (**54**) and $604\,600\,\text{M}^{-1}\text{cm}^{-1}$ (**66**) for the longest derivatives within each series, representing the highest measured extinction coefficients for polyynes. Region II is only dominant for the butadiynyl compound **44** (Figure 8) with $\varepsilon_{max} = 40\,900\,\text{M}^{-1}\text{cm}^{-1}$.

Both wavelength regions can confidently be attributed to $\pi-\pi^*$ absorptions, as was also found for polyynediyls with different carbon end groups.[9a,b, 12–14] Polyynes, spanning two transition metal complexes, show $\pi \rightarrow \pi^*$ absorptions influenced by the metal d orbitals.[22b,c] Similar to our previously reported studies on α,ω-dicyanopolyynes,[5e] the HOMO–LUMO gaps decrease with increasing chain length, correlating well with the observed spectroscopic behaviour.

Transitions for wavelength region I deliver strongly increasing ε_{max} values and a bathochromic shift with increasing chain length (Table 2), corresponding to the spread of the HOMOs and LUMOs over the whole conjugated backbone (for further evidence, see below and the electrochemical part). Wavelength region II exhibits also a bathochromic shift, but, in contrast to region I, almost constant ε_{max} values which seem to be independent of the chain length. This behaviour might be caused by the aromatic end group displaying enhanced coefficients in the non degenerated HOMO and LUMO (AM1). This is due to the fact that one set of p orbitals is in conjugation with the parallel oriented p orbitals of the phenyl ring, whereas conjugation is impossible for the chain p orbitals perpendicular to the phenyl ring. This end-group effect becomes less important with increasing chain length. At the same time the energy difference between the HOMO (composed of chain p orbitals and the parallel oriented p orbitals of the phenyl ring) and the HOMO – 1 (composed of chain p orbitals perpendicular to the phenyl ring) decreases with increasing chain length. The same trend holds true for the LUMO and the LUMO+1.

Corresponding molecules from each series (Figure 8 and 9), exhibit close agreement in their key wavelength data (Table 2), which indicates a lack of dependence of the electronic properties of the α,ω-diphenylpolyynyl framework on the nature of the end groups. Nevertheless, the influence of the heavy dendrimer substituents becomes evident by comparing the extinction coefficients of chains of equal length. For the dendritic species, significantly lower values were recorded. This reduction in intensity and the lower resolution of the spectra can be attributed to a less rigid conjugated backbone, indicating a more pronounced propensity to chain bending caused by the high mass end groups.[54]

With increasing chain length, the longest-wavelength absorptions of both regions I are increasingly bathochromically shifted (Table 2), which is nicely illustrated by the colours of the compounds' solutions. While solutions of **44** and **48** are colourless and light yellow, respectively, corresponding solutions of the C12, C16, C18, and C20 chains deepen in colour from lemon yellow, to orange, and, finally, red orange (Figure 6). The magnitude of the bathochromic shift decreases with increasing n, however, no apparent saturation for λ_{max} of both regions is reached. The same behaviour has been observed by Bohlmann[9a,b] and Walton,[12–14] for series of polyynes containing bulky terminal end groups, and in our group for α,ω-dicyanopolyynes.[5d,e] The set of fine-structured absorptions of wavelength region I shown in Figures 8 and 9 can be correlated by means of the empirical Lewis–Calvin equation[55] commonly written as $\lambda^2 = kn$ (λ = wavelength of corresponding bands for polyynes containing n conjugated triple bonds). This equation was originally formulated for, and applied to, polyenes and was later used by Walton et al.[12–14] to describe the absorption behaviour of compounds R-(C≡C)$_n$-R, where R is H, silyl, alkyl, or aryl.

The plots of n versus the highest measured wavelengths (λ^2) for the TBDMS and dendrimer polyyne series (Figure 10) become good straight lines with constant slope k, which is distinctly higher per triple bond ($\approx 20 \times 10^3$ nm^2) than usually found.[5d,e]

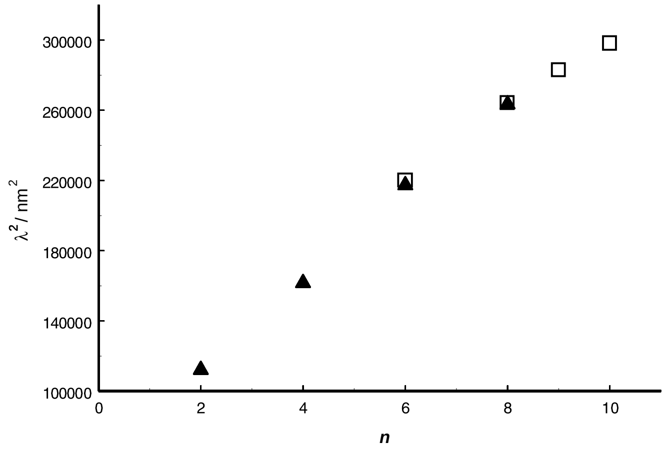


Figure 10. Lewis–Calvin plot ($\lambda^2 = kn$) for the TBDMS (▲) and the dendronized polyyne (□) series.

A further description of the spectroscopic behaviour, especially for long-chain compounds, is provided by the empirical equation $E_{exp} = a + b/n$.[52] As $n \rightarrow \infty$, E_{exp} (experimental optical absorption energy) tends to a limiting value a due to the decrease of end-group influence as n increases. This limiting value can be interpreted as the longest-wavelength absorption of the sp carbon allotrope carbyne.[5e] This is shown in Figure 11, where λ_{max} ($\propto {}^1/E_{exp}$) (region I) is plotted versus $1/n$.

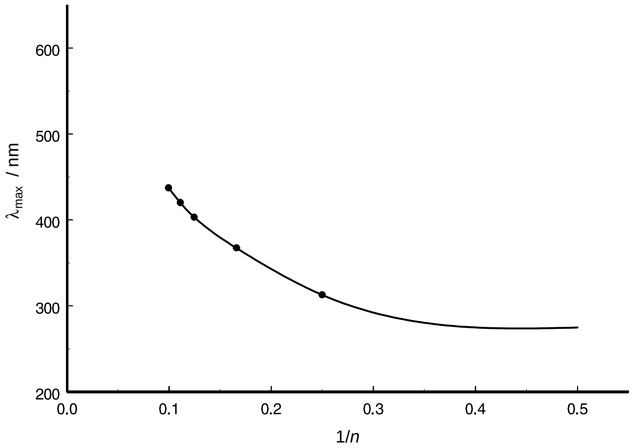


Figure 11. Plot of λ_{max} (region I) versus $1/n$. The values for $n = 2, 4, 6,$ and 8 are taken from the TBDMS series. The data for $n = 9$ and 10 are taken from the dendronized polyynes **68** and **66**.

Extrapolation for the values of the longest molecules which display an almost linear behaviour to $n \rightarrow \infty$ gives an estimated 569 nm as λ_{max} (region I) for RC$_\infty$R, where R holds for the TBDMS and the dendritic termini, respectively, and, consequently, as λ_{max} for hypothetical carbyne. This wavelength comes close to the value obtained from our previous estimations for the series R-(C≡C)$_\infty$-R (R = CN, *t*Bu, Et$_3$Si).[5e] Gladysz et al. presented a nearly identical result of 565 nm from an analogous plot, derived from rhenium complex end-capped polyynes.[22c] Also based on these model systems, carbyne should be a coloured insulating material.

IR and Raman spectra: IR and Raman data for the three series of polyynes are summarized in Table 3. Each IR spectrum was recorded from a KBr disc. Except for two compounds, **67** and **66**, all Raman spectra were measured in CH$_2$Cl$_2$. All IR spectra are dominated by the bands of the sp carbon chain end-capping groups. Whereas the silyl-functionalized derivatives exhibit a large number of sharp bands, the

Table 3. Key IR and Raman data for sp carbon chains [cm^{-1}].

Compound	IR $\tilde{\nu}_{C\equiv C}$ (KBr)	Raman $\tilde{\nu}_{C\equiv C}$ (CH$_2$Cl$_2$)
45	2150*vw*	2230*w*
49	2203*m*	2170*w*
	2137*vw*	2138*s*
41	2183*m*	
	2159*m*	
	2059*vw*	2060*m*
44	2148*vw*	2232*w*
48	2201*m*	2171*w*
	2136*vw*	2135s
40	2183*m*	
	2160*m*	
	2058*vw*	2060*m*
54	2194*m*	
	2112*s*	
	2009*vw*	2012*s*
63	2160*br s*	
	2057*vw*	2057*m*
67[a]		2013*m*
66[a]		1982*w*

[a] Available quantities too small, so no IR spectra could be recorded. Raman spectra were recorded in ethyl acetate.

dendronized compounds show significantly fewer, broad signals.

The IR $\tilde{\nu}_{C\equiv C}$ region is characteristically structured. Independent of the molecular mass, compounds of equal chain length show absorptions at almost equal wave numbers. The intensity and the total number of C≡C bands increases with chain length. A maximum of three bands is observed for the C12 and C16 silyl derivatives, whereas **63** displays only one broad absorption. With the exception of the C4 compounds, all spectra show a very weak band for the totally symmetrical vibration at lowest energy. On the other hand, these bands dominate the Raman spectra, as expected from IR selection rules. In the Raman spectra, a second band is observed only for C8 chains.

With increasing number of C≡C bonds, the energy of the totally symmetrical vibration decreases within each series, what is illustrated by the plots of $\tilde{\nu}_{C\equiv C_{sym}}$ versus $1/n$ in Figure 12 for the TBDMS and the dendronized series. Similar to the behaviour of λ_{max} in the UV/Vis spectra, these values tend to asymptotically reach a certain limit, which is determined by the degree of bond length equalization between single and triple bonds. These observations display an increasing cumulenic character with increasing chain length. However, these investigations in addition to calculation (PM3) as well as the UV/Vis investigations (see above) indicate that the bond length alternation persists with going to infinite chain lengths.[5e] Surprisingly, theoretical studies of vibrational spectra of polyynes appear to be scarce, precluding comparison,[56] but similar IR and Raman properties were observed by Gladysz and co-workers.[22c]

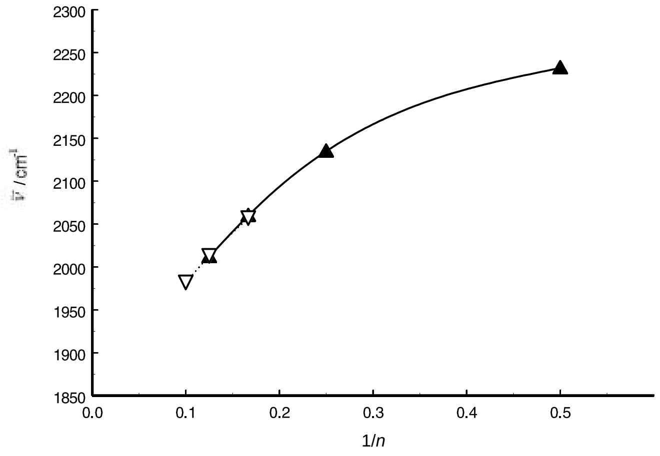


Figure 12. Plot of the Raman $\nu_{C\equiv C_{sym}}$ versus $1/n$ for the TBDMS (5) and the dendronized polyyne (▽) series.

Redox properties:[57] The electrochemical properties of the polyynes were studied by steady-state voltammetry and cyclic voltammetry (CV) in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as the supporting electrolyte. In CV, none of the compounds could be oxidized in the available potential range,[58] but were reduced in an irreversible step at low sweep rates as shown in Figure 13.

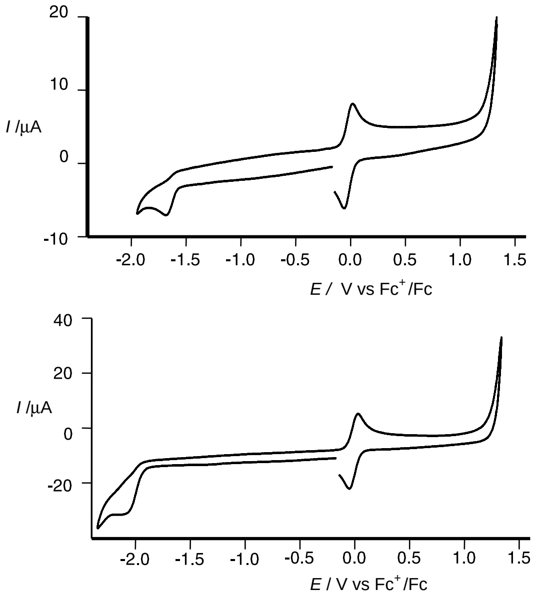


Figure 13. Cyclic voltammetry at $\nu = 0.1\ Vs^{-1}$ of **49** (bottom) and **41** (top) in the presence of ferrocene in CH_2Cl_2+0.1 M Bu_4NPF_6 on a glassy carbon working electrode.

However, by increasing the sweep rate, the reduction became more and more reversible as shown by the rising value of the peak current ratio $r = I_{pa}/I_{pc}$, which reaches almost unity at higher sweep rates (e.g. $r = 0.95$ at $10\ Vs^{-1}$ for **49** in Figure 14).

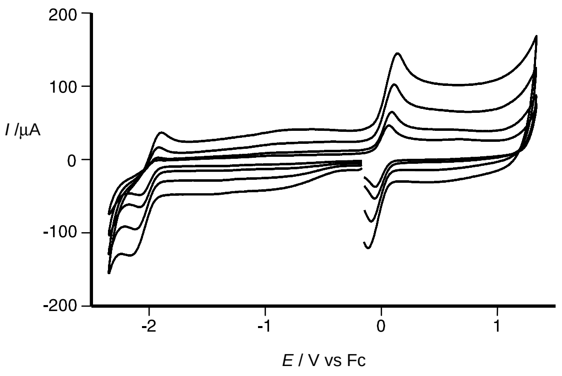


Figure 14. Cyclic voltammetry of **49** in the presence of ferrocene in CH_2Cl_2+0.1 M Bu_4NPF_6 on a glassy carbon working electrode at different sweep rates: 1, 2, 5 and $10\ Vs^{-1}$. The curves are uncorrected for ohmic drop, explaining the increasing values of ΔE_p with sweep rate.

Such characteristics clearly demonstrate that the first reduction step involves a reversible one-electron reduction followed by an irreversible chemical reaction ($E_{rev}C_{irrev}$ mechanism); this indicates that our linear polyynes are not able to stabilize the electrogenerated radical anion, which remains rather reactive. The observed reduction peak potentials are summarized in Table 4. These data show that the reduction potentials within the series are shifted to less negative potentials as the length of the conjugated system increases.

The values of the reduction peak potentials for chains of the same length are almost equal, independent of the terminal

Table 4. Cyclic voltammetric data at $v = 0.1\ \mathrm{V\,s^{-1}}$ of polyacetylenic derivatives observed on glassy carbon electrode in CH_2Cl_2+0.1M Bu_4NPF_6. Values given in V versus Fc/Fc$^+$.

Compound	E_{pc}
45	−2.65
49	−2.05
41	−1.66
44	−2.57
48	−2.00
40	−1.63
54	−1.38
63	−1.65
67	–
66	−1.25

groups. This also holds for the differences between the C4 and C8, and the C8 and C12 chains, respectively. With increasing number of π electrons within the TBDMS series, going from the butadiyne **44** to the hexadecaoctayne **54**, the reduction potential decreases drastically from −2.57 to −1.38 V. It is possible to observe a linear correlation between the reduction potential and 1/*n*, where *n* corresponds to the number of multiple bonds in the plane of the molecule including the phenyl rings (Figure 15a, Table 5). Similar behaviour is also observed by plotting the spectroscopic HOMO–LUMO gaps corresponding to the longest wavelength absorptions of the same compounds versus 1/*n* (Figure 15b, Table 5).

Linear dependence of redox potentials versus 1/*n* are quite usual and found for many such conjugated species.[59] In the case of oligomers, for example oligomers of poly(triacetylene), one observes linearity when *n* = degree of oligomerization.[60]

The influence of the C≡C bonds becomes obvious once the reduction potentials are compared with those recorded by Hoijtik and van Schooten for the corresponding α,ω-diphenylpolyenes.[61] Polarography measurements of Ph-$(C_2H_2)_n$-Ph ($n = 2, 3, 4, 5, 6$ the same number of multiple bonds between the two phenyl rings as in our series) were recorded. In this case, no CV spectra were run to check reversibility, but it emerges clearly,[61] that the observed half-wave potentials correspond to irreversible reductions. Going from 1,4-diphenylbutadiene to 1,12-diphenyldodecahexaene, the reduction potentials are shifted to less negative potentials by 0.46 V, whereas with the oligoynes, the observed shift is 0.94 V for the same increase in length. Hence, the larger number of π electrons (due to the presence of the triple bonds) results in much lower reduction potentials of the polyacetylenic compounds compared to the analogous polyene derivatives.

An analogous plot of the reduction potentials of the α,ω-diphenylpolyenes versus 1/*n*, including all conjugated double bonds in the molecular plane, also revealed a linear correlation, in agreement with the fact that electron transfer must occur to the LUMO orbital of both conjugated systems. We presume, that the presence of the remaining perpendicular π-electron molecular orbitals in the polyynes is reflected in the easier reduction of these compounds. Strong adsorption was observed by the C12 (**63**) and the C20 (**66**) dendritic species. Because of too little amount of the C16 (**67**) derivative, no electrochemical data was obtained for this compound.

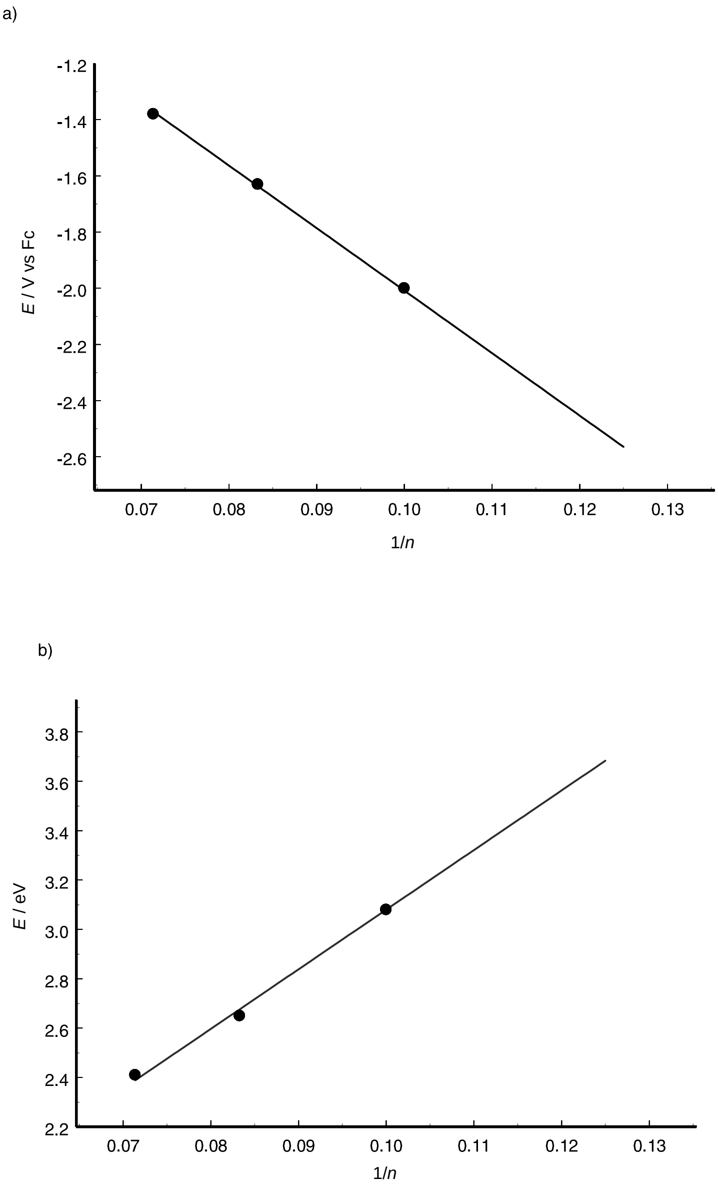


Figure 15. Plot of E_{pc} (a) and the HOMO–LUMO gap of the longest wavelength absorptions (b) versus 1/*n* for the polyacetylenic series **44** to **54**. *n* represents the total number of conjugated multiple bonds in the molecule (including the two phenyl rings).

Table 5. Longest-wavelength absorptions of the TBDMS polyacetylenic series, with corresponding eV values.

Compound	*n*	1/*n*	λ_{max} [nm]	[eV]
44	8	0.1250	336	3.69
48	10	0.1000	403	3.08
40	12	0.0833	467	2.65
54	14	0.0714	514	2.41

Conclusion

This work describes in detail the synthesis of three series of differently 3,5-disubstituted α,ω-diphenylpolyynes under optimized Cadiot–Chodkiewicz conditions, and their isolation and characterization, including electrochemical studies. These compounds can be considered as model substances for the hypothetical, and presumably unstable, linear sp carbon allotrope carbyne C_∞. The longest carbon chains, containing 16 and 20 atoms, respectively, represent the longest, purely organic polyynes studied with NMR and Raman spectroscopy as well as by electrochemistry. The dependence of the kinetic stability of polyynediyls on the nature of the end groups is highlighted in these studies. The size and shape of these end groups determines chain accessibility and, therefore, reactivity.[5d,e, 10, 12–14, 22c] The limiting factor for further progress in this field is the product stability. Generally, the TMS-protected chain precursor molecules display higher stability than the deprotected species. Consequently, our investigations will be extended to oxidative coupling procedures which avoid hydrogen-capped chains. A further line of research will be the loss of C2 units during Hay couplings.

All of our long symmetrical polyynes, even the series of hexaynes **15**, **20**, and **21**, exhibit an indefinite stability in solution and to air, whereas in the solid state their behaviour displays considerable variation. The hexaynes decompose upon drying to a brown-black polymerized material, presumably because planar arrangement of the benzylic ether dendrimer fragments allows chain–chain reactions to occur. The most stable of our compounds were the members of the TIPS and TBDMS polyyne series, which remained unchanged in the solid state for more than one month. Unfortunately, chains encapsulated by Fréchet's aliphatic ether dendrimers, including the longest molecule, with 20 sp carbon atoms, are more sensitive. However in this case, the instability is due to cleavage of benzylic ether groups of the dendrimer. Different ether groups are therefore a target of future investigations.

The UV/Vis spectra of the polyynes are bathochromically shifted with increasing chain length and are discussed in detail above. They exhibit the highest measured quantitative extinction coefficients within this compound class. The assignment of absorption bands in both wavelength regions was achieved by comparison with formerly reported results and was supported by the findings of our electrochemical investigations. In the latter, no reversible reduction steps were recorded (except for very high sweep rates); this indicates that the first reduction step is followed by an irreversible chemical reaction ($E_{rev}C_{irrev}$ mechanism). IR and Raman spectra exhibit the expected behaviour: They obey the alternate rule for point-symmetrical molecules and display increasing $C\equiv C$ bond vibration intensities with increasing carbon rod size. The energy of the Raman active vibration $\tilde{\nu}_{C\equiv C_{sym}}$ is decreasing with increasing chain length, asymptotically reaching a certain limit. Analysis of the spectroscopic behaviour of the polyynes (which proved to be independent of the end-capping groups) enables us to predict the properties of carbyne which are in close agreement with previously reported estimates.[5e, 22c] Considering the observed polyyne stability and taking into account the improved yields in the crucial synthesis steps, the route to even longer carbon chains is now open. The detection and characterization by means of UV/Vis spectroscopy and FAB mass spectrometry of the hydrogen-capped hexayne **53** suggests that the TBDMS C24 chain and even longer ones can be achieved soon.

Experimental Section

Crystallographic data for 3: Data were collected as summarized in Table 6. Cell parameters were determined and refined from 15 reflections. Space group was determined from systematic absences and subsequent least-squares refinements. Lorentz, polarization, and empirical absorption corrections were applied (ψ scans).

Table 6. Crystallographic data for **3**.

Compound	**3**
formula	$C_{22}H_{18}O_2$
diffractometer	Nonius MACH3
T [K]	173(2)
λ [Å]	0.71073
crystal system	orthorhombic
space group	$P2_12_12_1$
a [Å]	5.513(1)
b [Å]	12.726(3)
c [Å]	23.634(3)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	1658.2(5)
Z	4
ρ_{calcd} [Mg m^{-3}]	1.259
absorpt. coeff. [mm^{-1}]	0.079
crystal size [mm^3]	$0.15 \times 0.30 \times 0.35$
θ limit [°]	2.35 to 26.29
index ranges (h, k, l)	−6 to 6; −15 to 15; −29 to 29
reflections collected	3968
independent reflections	3348
reflections [$I > 2\sigma(I)$]	2034
data/restraints/parameters	3348/–/221
GOF on F^2	1.032
final R indices [$I > 2\sigma(I)$]	0.0671
	0.1605
R indices (all data)	0.1331
	0.2102
Δp (max) [e Å^{-3}]	0.259

The structures was solved by direct methods (SHELXS-86). The parameters were refined with all data by full-matrix-least-squares on F^2 (SHELXL-93).[62] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed in idealized positions (riding model). Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from literature.[63]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161416. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

General: ^1H NMR and ^{13}C NMR: JEOL JNM EX 400 and JEOL JNM GX 400 at room temperature (^1H: 400 MHz, ^{13}C: 100.5 MHz); MS: Varian MAT 311 a (EI), Finnigan MAT 900 (FAB); FT-IR: Bruker Vector 22; UV/Vis: Shimadzu UV 3102 PC; HPLC preparative: Shimadzu SIL10A, SPD10A, CBM10A, LC8A, FRC10A (Nucleosil, 7 µm, 21 × 250 mm, Macherey-Nagel); TLC (Riedel-de Haën, plates, silica gel 60 F_{254}). Apart from homo-coupling reactions, all reactions were performed under nitrogen in flame-dried glassware. Reagents used were commercially available reagent grade. K_2CO_3 was activated at 110 °C for 5 h and powdered before use. CuCl was washed with HCl (10%), water, ethanol, and Et_2O and dried in oil pump vacuum. The amines diisopropylamine and pyridine were distilled under reduced pressure and stored over 4 Å molecular sieves. Acetone, CH_2Cl_2, DMF, and THF were dried according to standard procedures. All reactions were monitored by TLC. Products were isolated where possible by flash column chromatography (silica gel 60, particle size 0.04–0.063 nm, Merck).

Compound 1: A solution of [G-1]-CH_2OH[31] (11.534 g, 36.0 mmol) in dry CH_2Cl_2 (40 mL) was slowly added to a vigorously stirred slurry of pyridinium dichromate (27.09 g, 72.0 mmol) in dry CH_2Cl_2 (70 mL) at room temperature. As soon as TLC control (silica gel, hexane/ethyl acetate 3:2) indicated complete reaction, the reaction mixture was filtered, and afterwards the solvent was removed by rotary evaporation. The residue was dissolved in Et_2O (100 mL) and washed with water (2 × 150 mL). The resulting aqueous phase was extracted with Et_2O (4 × 100 mL), and the combined organic phases were dried over Na_2SO_4. Recrystallization in Et_2O/pentane gave **1** as white solid (8.627 g, 27.0 mmol, 75 %). $R_f = 0.83$ (hexane/ethyl acetate 3:2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 9.89$ (s, 1H; C*H*O), 7.43–7.33 (m, 10H; Ph*H*), 7.10 (d, ^{3}J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.86 (t, ^{3}J(H,H) = 2.2 Hz, 1H; Ar*H*), 5.08 (s, 4H; $\mathrm{OC}H_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 191.80$ (1C; *C*HO), 160.39 (2C; Ar*C*$\mathrm{OCH_2}$), 138.43 (1C; Ar*C*), 136.24 (2C; Ph*C*), 128.68, 128.24, 127.56 (10C; Ph*C*H), 108.69 (1C; Ar*C*H), 108.32 (2C; Ar*C*H), 70.39 (2C; $C\mathrm{H_2O}$); IR (KBr): $\tilde{\nu} = 3066.5w$, $3031.7w$, $2935.1w$, $2827.7w$, $2735.0w$, $1688.2s$, $1608.4m$, $1594.2s$, $1498.4w$, $1450.4m$, $1384.3m$, $1351.3s$, $1298.2s$, $1258.5w$, $1218.2w$, $1174.6s$, $1060.8s$, $952.7m$, $831.2m$, $741.2m$, $720.4m$, 696.5 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 269 (8100), 326 nm (3400); MS (EI): m/z: 318 $[M]^+$, 227, 181, 91, 65.

Compound 2: PPh_3 (13.219 g, 50.4 mmol) was added at 0 °C to a solution of CBr_4 (8.358 g, 25.2 mmol) in dry CH_2Cl_2 (20 mL). At the same temperature, aldehyde **1** (4.0 g, 12.6 mmol), dissolved in dry CH_2Cl_2 (20 mL), was dropped slowly into the reaction mixture. The mixture was warmed to room temperature and the progress of the reaction was monitored by TLC (silica gel, hexane/ethyl acetate 4:1). Purification was achieved by filtering the reaction mixture through a silica gel plug (CH_2Cl_2). Evaporation of the solvent gave **2** as a colourless oil (5.73 g, 12.1 mmol, 96 %). $R_f = 0.91$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.37$–7.27 (m and s, 11H; 10 Ph*H* and C*H*$\mathrm{CBr_2}$), 6.72 (d, ^{3}J(H,H) = 2.0 Hz, 2H; Ar*H*), 6.58 (t, ^{3}J(H,H) = 2.0 Hz, 1H; Ar*H*), 4.96 (s, 4H; $\mathrm{OC}H_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 159.95$ (2C; Ar*C*$\mathrm{OCH_2}$), 136.82 (1C; Ar*C*), 136.62 (1C; *C*H$\mathrm{CBr_2}$), 136.58 (2C; Ph*C*), 128.53, 127.96, 127.40 (10C; Ph*C*H), 107.54 (2C; Ar*C*H), 102.64 (1C; Ar*C*H), 89.98 (1C; CH$C\mathrm{Br_2}$), 70.05 (2C; $C\mathrm{H_2O}$); IR (film): $\tilde{\nu} = 3028.7w$, $2935.7w$, $2876.9w$, $1593.4m$, $1577.5m$, $1496.5w$, $1454.7m$, $1379.3m$, $1308.2s$, $1218.2w$, $1165.3s$, $1046.9s$, $918.0w$, $825.2w$, $761.1m$, 678.2 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 (12700), 280 (sh, 10700), 310 nm (sh, 2200); MS (FAB+): m/z: 474 $[M]^+$, 344, 263, 181.

Compound 3: *n*BuLi (1.6 M in hexane, 5.76 mL, 9.49 mmol) was added with ice water cooling to a solution of diisopropylamine (961 mg, 9.49 mmol) in dry THF (10 mL) in a three-necked flask (100 mL). After 1 h, the resulting LDA solution was slowly dropped into **2** (1.5 g, 3.16 mmol), dissolved in dry THF (10 mL) at −78 °C. The temperature was kept at −78 °C and the reaction was monitored by TLC (silica gel, hexane/toluene 1:1). Due to its strong fluorescence, **3** could be differentiated from the starting material. By the careful addition of HCl (10 %, 10 mL), followed by hexane (40 mL), the reaction was quenched. The aqueous phase was extracted with hexane (4 × 50 mL), and the combined organic solutions were dried over Na_2SO_4. Column chromatography (silica gel, hexane/toluene 4:1) yielded **3** as a colourless oil (744 mg, 2.37 mmol, 75 %). $R_f = 0.89$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.37$–7.30 (m, 10H; Ph*H*), 6.73 (d, ^{3}J(H,H) = 2.0 Hz, 2H; Ar*H*), 6.61 (t, ^{3}J(H,H) = 2.0 Hz, 1H; Ar*H*), 4.96 (s, 4H; $\mathrm{OC}H_2$), 3.01 (s, 1H; $\mathrm{C{\equiv}C}$-*H*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 159.64$ (2C; Ar*C*$\mathrm{OCH_2}$), 136.51 (2C; Ph*C*), 128.58, 128.05, 127.49 (10C; Ph*C*H), 123.43 (1C; Ar*C*), 111.14 (2C; Ar*C*H), 103.81 (1C; Ar*C*H), 83.53 (1C; $C{\equiv}\mathrm{C}$-H), 76.95 (1C; $\mathrm{C}{\equiv}C$-H), 70.10 (2C; $C\mathrm{H_2O}$); IR (film): $\tilde{\nu} = 3288.6s$, $3089.7w$, $3065.0w$, $3032.7m$, $2931.9w$, $2872.1m$, $2109.1w$, $1588.9s$, $1498.1m$, $1454.4m$, $1431.2m$, $1376.2m$, $1342.5w$, $1320.3w$, $1293.9w$, $1250.4w$, $1214.2m$, $1160.6s$, $1055.7s$, $1029.4w$, $908.3w$, $834.2s$, $737.0s$, 697.7 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} = 247 (sh, 10900), 251 (11400), 257 (sh, 9800), 296 (3200), 303 (3200); MS (FAB+): m/z: 314 $[M]^+$, 223, 181.

Compound 11: A slurry of **3** (592 mg, 1.9 mmol) and $AgNO_3$ (97 mg, 0.57 mmol) in dry acetone (10 mL) was stirred for 15 min, before Et_2O (20 mL) and *N*-bromosuccinimide (471 mg, 2.6 mmol) were added. After TLC (silica gel, hexane/toluene 1:1) indicated quantitative reaction, the mixture was filtered through a short silica gel plug (CH_2Cl_2). The crude product was then purified via column chromatography (silica gel, CH_2Cl_2) to give **11** as a transparent brown oil (700 mg, 1.79 mmol, 94 %). $R_f = 0.62$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.38$–7.31 (m, 10H; Ph*H*), 6.68 (d, ^{3}J(H,H) = 1.7 Hz, 2H; Ar*H*), 6.60 (t, ^{3}J(H,H) = 1.7 Hz, 1H; Ar*H*), 4.98 (s, 4H; $\mathrm{OC}H_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 159.62$ (2C; Ar*C*$\mathrm{OCH_2}$), 136.48 (2C; Ph*C*), 128.60, 128.07, 127.47 (10C; Ph*C*H), 123.96 (1C; Ar*C*), 110.95 (2C; Ar*C*H), 103.81 (1C; Ar*C*H), 79.95 (1C; $C{\equiv}\mathrm{C}$-Br), 70.10 (2C; $C\mathrm{H_2O}$), 49.68 (1C; $\mathrm{C}{\equiv}C$-Br); MS (EI): m/z: 394 $[M+\mathrm{H}]^+$, 313, 181, 91, 65, 58, 43, 28.

Compounds 12 and 14: A flask was charged with **10** (269 mg, 1.64 mmol) and dry THF (5 mL) and cooled to −10 °C. Then *n*BuLi (1.6 M in hexane, 1.13 mL, 1.80 mmol) was added with stirring. After 25 min at 0 °C, CuI (312 mg, 1.64 mmol) was added. The cooling bath was removed and the mixture allowed to warm. After 1 h at room temperature, the mixture was cooled to −10 °C, and dry pyridine (11.3 mL, 140 mmol) was added. A solution of **11** (640 mg, 1.64 mmol) in dry THF (15 mL) was added dropwise over 100 min. As soon as TLC (silica gel, hexane/toluene 1:1) indicated no further progress, the reaction was quenched by addition of water (20 mL), diluted H_2SO_4 (10 mL), and CH_2Cl_2 (60 mL). The organic phase was dried over Na_2SO_4. Purification of the residual brown oil with column chromatography (silica gel, hexane/toluene 4:1 → 7:3 → 3:2 → 1:1 → toluene) gave **12** (56 mg (0.12 mmol, 7 %) as yellow-brown oil and **14** (314 mg (0.50 mmol, 60 %) as white solid.

Compound 12: $R_f = 0.84$ (hexane/toluene 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.40$–7.32 (m, 10H; PhH), 6.74 (d, ^{3}J(H,H) = 2.2 Hz, 2H; ArH), 6.65 (t, ^{3}J(H,H) = 2.2 Hz, 1H; Ar*H*), 5.00 (s, 4H; $\mathrm{OC}H_2$), 1.02 (t, ^{3}J(H,H) = 7.7 Hz, 9H; $\mathrm{Si(CH_2}CH_3\mathrm{)_3}$), 0.65 (q, ^{3}J(H,H) = 7.7 Hz, 6H; $\mathrm{Si(}CH_2\mathrm{CH_3)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 159.64$ (2C; Ar*C*$\mathrm{OCH_2}$), 136.29 (2C; Ph*C*), 128.62, 128.12, 127.47 (10C; Ph*C*H), 122.05 (1C; Ar*C*), 111.84 (2C; Ar*C*H), 105.08 (1C; Ar*C*H), 89.01 (1C; $\mathrm{C{\equiv}C\text{-}C{\equiv}C\text{-}}C{\equiv}\mathrm{C\text{-}Si(CH_2CH_3)_3}$), 87.47 (1C; $\mathrm{C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}}C\mathrm{\text{-}Si(CH_2CH_3)_3}$), 76.51 (1C; $\mathrm{C{\equiv}}C\mathrm{\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}Si(CH_2CH_3)_3}$), 73.95 (1C; $C\mathrm{{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}Si(CH_2CH_3)_3}$), 70.19 (2C; $C\mathrm{H_2O}$), 67.10 (1C; $\mathrm{C{\equiv}C\text{-}}C\mathrm{{\equiv}C\text{-}C{\equiv}C\text{-}Si(CH_2CH_3)_3}$), 60.85 (1C; $\mathrm{C{\equiv}C\text{-}C{\equiv}}C\mathrm{\text{-}C{\equiv}C\text{-}Si(CH_2CH_3)_3}$), 7.33 (3C; $\mathrm{Si(CH_2}C\mathrm{H_3)_3}$), 4.10 (3C; $\mathrm{Si(}C\mathrm{H_2CH_3)_3}$); IR (film): $\tilde{\nu} = 3004.5w$, $2261.6w$, $2144.1m$, $1698.2s$, $1436.0s$, $1227.8s$, $1092.5m$, $902.3m$, 785.0 cm^{-1} *w*; UV/Vis (toluene): λ_{max} (ε) = 249, 263, 285, 304, 324, 347 nm; MS (FAB+): m/z: 477 $[M+\mathrm{H}]^+$; MS (EI): m/z: 476 $[M]^+$, 181, 91, 65.

Compound 14: $R_f = 0.47$ (hexane/toluene 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.39$–7.30 (m, 20H; Ph*H*), 6.75 (d, ^{3}J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.64 (t, ^{3}J(H,H) = 2.2 Hz, 2H; Ar*H*), 5.01 (s, 8H; $\mathrm{OC}H_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$ 25 °C): $\delta = 159.67$ (4C; Ar*C*$\mathrm{OCH_2}$), 136.41 (4C; Ph*C*), 128.65, 128.12, 127.50 (20C; Ph*C*H), 122.99 (2C; Ar*C*), 111.38 (4C; Ar*C*H), 104.57 (2C; Ar*C*H), 81.55 (2C; $\mathrm{(R\text{-}C{\equiv}}C\mathrm{)_2}$), 73.49 (2C; $\mathrm{(R\text{-}}C\mathrm{{\equiv}C)_2}$), 70.20 (4C; $C\mathrm{H_2O}$); IR (KBr): $\tilde{\nu} = 3067.4w$, $3031.9w$, $2909.8w$, $2872.0w$, $2045.6w$, $1582.1s$, $1498.0w$, $1454.1w$, $1429.3m$, $1373.7m$, $1341.8m$, $1293.2m$, $1216.1w$, $1163.0s$, $1051.8m$, $1035.4m$, $906.8w$, $834.7m$, $747.8m$, $695.0m$, 675.8 cm^{-1} *w*; MS (FAB+): m/z: 627 $[M+\mathrm{H}]^+$; MS (EI): m/z: 626 $[M]^+$, 535, 444, 181, 91, 65.

Compounds 13 and 15: a) A spatula tip of K_2CO_3 was added to a stirred solution of **12** (56 mg, 0.12 mmol) in wet THF/MeOH (1:1, 10 mL). TLC (silica gel, hexane/toluene 1:1) indicated completeness of the reaction after a few minutes, whereupon the K_2CO_3 was separated with a short silica gel plug (CH_2Cl_2). Solvent was removed as much as possible and the deprotected triyne **13** ($R_f = 0.65$ (silica gel, hexane/toluene 1:1)) was, after addition of acetone (10 mL), used in reaction b) without characterization.

b) Tetramethylethylenediamine (TMEDA) (0.1 mL, 0.67 mmol) and CuCl (40 mg, 0.41 mmol) were added to the solution of triyne **13**. The resulting slurry was stirred in air, until TLC (silica gel, hexane/toluene 1:1) showed the disappearance of the starting material. Then, a small amount of hexane/CH_2Cl_2 4:1 was added, and purification of this mixture with column chromatography (silica gel, hexane/CH_2Cl_2 4:1) gave **15** as an unstable yellow solid (35 mg, 0.05 mmol, 83 % based on **12**). $R_f = 0.53$ (hexane/toluene 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.40$–7.35 (m, 20H; Ph*H*), 6.77 (d, ^{3}J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.69 (t, ^{3}J(H,H) = 2.2 Hz, 2H; Ar*H*), 5.01 (s, 8H; $\mathrm{OC}H_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 159.73$ (4C; Ar*C*$\mathrm{OCH_2}$), 136.24 (4C; Ph*C*), 128.68, 128.22, 127.51 (20C; Ph*C*H), 121.33 (2C; Ar*C*), 112.18 (4C; Ar*C*H), 105.80 (2C; Ar*C*H), 77.67 (2C; $\mathrm{(R\text{-}C{\equiv}}C\mathrm{\text{-}C{\equiv}C\text{-}C{\equiv}C)_2}$), 73.92 (2C; $\mathrm{(R\text{-}}C\mathrm{{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C)_2}$), 70.28 (4C; $C\mathrm{H_2O}$), 67.25 (2C; $\mathrm{(R\text{-}C{\equiv}C\text{-}}C\mathrm{{\equiv}C\text{-}C{\equiv}C)_2}$), 64.58 (2C; $\mathrm{(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}}C\mathrm{{\equiv}C)_2}$), 63.58 (2C; $\mathrm{(R\text{-}C{\equiv}C\text{-}C{\equiv}}C\mathrm{\text{-}C{\equiv}C)_2}$), 62.47 (2C; $\mathrm{(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}}C\mathrm{)_2}$); UV/Vis ($CH_2Cl_2$): λ_{max} = 228, 264, 277, 289, 302, 320, 343, 360 (sh), 369, 397, 429, 466; MS (FAB+): m/z: 723 $[M+\mathrm{H}]^+$.

Compound 4: A solution of [G-2]-CH_2OH[31] (3 g, 8.06 mmol) in dry CH_2Cl_2 (10 mL) was slowly added to a vigorously stirred slurry of pyridinium dichromate (3.034 g, 8.06 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C. As soon as TLC control (silica gel, hexane/ethyl acetate 3:2) indicated complete reaction, the reaction mixture was filtered through a silica gel plug (CH_2Cl_2). The product fraction obtained was washed with water (2 × 100 mL) and dried over Na_2SO_4. Column chromatography (silica gel, hexane/CH_2Cl_2 1:1) yielded **4** as white solid (2.364 g, 3.18 mmol, 79 %). $R_f = 0.84$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 9.86$ (s, 1H; C*H*O), 7.42–7.29 (m, 20H; Ph*H*), 7.06 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.82 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 6.66 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.58 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 5.02 (s, 8H; OC*H₂*), 5.01 (s, 4H; OC*H₂*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 191.80$ (1C; *C*HO), 160.25 (2C; Ar*C*OCH₂), 160.21 (4C; Ar*C*OCH₂), 138.63 (2C; Ar*C*), 138.39 (1C; Ar*C*), 136.68 (4C; Ph*C*), 128.60, 128.04, 127.54 (20C; Ph*C*H), 108.65 (1C; Ar*C*H), 108.30 (2C; Ar*C*H), 106.35 (4C; Ar*C*H), 101.67 (2C; Ar*C*H), 70.19 (2C; *C*H₂O), 70.12 (4C; *C*H₂O); IR (KBr): $\tilde{\nu}$ = 3062.2*m*, 3032.8*m*, 2904.4*m*, 2868.4*m*, 1688.3*s*, 1596.2*s*, 1498.9*w*, 1450.0*m*, 1377.8*s*, 1331.4*m*, 1303.0*m*, 1210.6*w*, 1160.5*s*, 1061.2*m*, 1040.0*m*, 826.9*m*, 744.1*w*, 730.7 cm^{-1} *m*; MS (FAB +): *m*/*z*: 743 [*M*+H]$^+$.

Compound 5: PPh_3 (6.715 g, 25.6 mmol) was added at 0 °C to a solution of CBr_4 (4.245 g, 12.8 mmol) in dry CH_2Cl_2 (5 mL). At the same temperature, aldehyde **4** (2.364 g, 3.2 mmol), dissolved in dry CH_2Cl_2 (20 mL), was dropped slowly into the reaction mixture. The mixture was warmed to room temperature and the progress of the reaction was monitored by TLC (silica gel, CH_2Cl_2). The reaction mixture was filtered through a silica gel plug (CH_2Cl_2). Evaporation and column chromatography (silica gel, CH_2Cl_2) gave the light yellow oil **5** (2.230 g, 2.48 mmol, 78 %); $R_f = 0.87$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$–7.31 (m and s, 21H; 20 Ph*H* and C*H*CBr₂), 6.73 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.65 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.56 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.55 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 5.02 (s, 8H; OC*H₂*), 4.96 (s, 4H; OC*H₂*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 160.16$ (4C; Ar*C*OCH₂), 159.58 (2C; Ar*C*OCH₂), 139.08 (2C; Ar*C*), 136.91 (1C; Ar*C*), 136.71 (4C; Ph*C*), 136.65 (1C; *C*HCBr₂), 128.58, 128.01, 127.53 (20C; Ph*C*H), 107.64 (2C; Ar*C*H), 106.29 (4C; Ar*C*H), 102.72 (1C; Ar*C*H), 101.56 (2C; Ar*C*H), 90.04 (1C; CH*C*Br₂), 70.09 (4C; *C*H₂O), 70.03 (2C; *C*H₂O); IR (film): $\tilde{\nu}$ = 3086.9*w*, 3061.5*w*, 3030.8*w*, 2928.1*w*, 2877.1*w*, 1595.9*s*, 1496.4*w*, 1449.9*m*, 1375.8*m*, 1338.4*w*, 1320.6*w*, 1156.5*s*, 1051.5*s*, 833.1*s*, 736.1*m*, 696.4 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 275 (16500), 286 nm (sh, 12900); MS (FAB +): *m*/*z*: 899 [*M*+H]$^+$; MS (EI): *m*/*z*: 898 [*M*]$^+$, 807, 596, 505, 392, 303, 211, 181, 91, 65.

Compound 6: *n*BuLi (1.6 M in hexane, 4.22 mL, 6.75 mmol) was added with ice water cooling to a solution of diisopropylamine (687 mg, 6.75 mmol) in dry THF (10 mL) in a three-necked flask (100 mL). After 1 h, the resulting LDA solution was slowly dropped into **5** (2.0 g, 2.2 mmol), dissolved in dry THF (10 mL) at −78 °C. The temperature was kept at −78 °C and the reaction was monitored by TLC (silica gel, CH_2Cl_2). Due to its strong fluorescence, **5** could be differentiated from the starting material. By the careful addition of HCl (10 %, 50 mL), then CH_2Cl_2 (100 mL), the reaction was quenched. The aqueous phase was extracted with CH_2Cl_2 (3 × 70 mL), and the combined organic solutions were dried over Na_2SO_4. Column chromatography (silica gel, toluene) yielded **5** as a white solid (1.222 g, 1.66 mmol, 75 %). $R_f = 0.57$ (toluene); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$–7.31 (m, 20H; Ph*H*), 6.71 (d, ^3J(H,H) = 2.0 Hz, 2H; Ar*H*), 6.65 (d, ^3J(H,H) = 2.0 Hz, 4H; Ar*H*), 6.58 (t, ^3J(H,H) = 2.0 Hz, 1H; Ar*H*), 6.57 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 5.01 (s, 8H; OC*H₂*), 4.93 (s, 4H; OC*H₂*), 3.03 (s, 1H; C≡C-*H*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 160.15$ (4C; Ar*C*OCH₂), 159.51 (2C; Ar*C*OCH₂), 138.92 (2C; Ar*C*), 136.71 (4C; Ph*C*), 128.58, 127.99, 127.53 (20C; Ph*C*H), 123.41 (1C; Ar*C*), 111.17 (2C; Ar*C*H), 106.29 (4C; Ar*C*H), 103.75 (1C; Ar*C*H), 101.59 (2C; Ar*C*H), 83.50 (1C; *C*≡C-H), 76.48 (1C; C≡*C*-H), 70.08 (4C; *C*H₂O), 69.97 (2C; *C*H₂O); IR (KBr): $\tilde{\nu}$ = 3285.2*m*, 3088.9*w*, 3063.5*w*, 3031.8*w*, 2925.1*w*, 2871.1*w*, 2109.2*w*, 1595.9*s*, 1497.4*w*, 1451.9*m*, 1374.8*m*, 1342.4*w*, 1320.6*w*, 1295.3*w*, 1156.5*s*, 1051.5*s*, 833.1*s*, 736.1*m*, 696.4 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 231 (36400), 255 (sh, 11400), 278 (sh, 5800), 284 (6800), 303 nm (3100); MS (FAB +): *m*/*z*: 739 [*M*+H]$^+$.

Compound 22: TMEDA (0.1 mL, 0.67 mmol) and CuCl (40 mg, 0.41 mmol) were added to a solution of **6** (80 mg, 0.11 mmol). The slurry was stirred in air, while the reaction progress was controlled with TLC (silica gel, toluene). After 4 d, water (20 mL) and HCl (10 %, 5 mL) were added, whereupon a colourless solid precipitated. Filtration and drying in the oil pump vacuum gave **22** as white solid (70 mg, 0.05 mmol, 88 %). $R_f = 0.44$ (toluene); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$–7.28 (m, 40H; Ph*H*), 6.72 (d, ^3J(H,H) = 2.1 Hz, 4H; Ar*H*), 6.64 (d, ^3J(H,H) = 2.5 Hz, 8H; Ar*H*), 6.60 (t, ^3J(H,H) = 2.1 Hz, 2H; Ar*H*), 6.56 (t, ^3J(H,H) = 2.5 Hz, 4H; Ar*H*), 5.01 (s, 16H; OC*H₂*), 4.93 (s, 8H; OC*H₂*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 160.14$ (8C; Ar*C*OCH₂), 159.53 (4C; Ar*C*OCH₂), 138.81 (4C; Ar*C*), 136.68 (8C; Ph*C*), 128.55, 127.99, 127.52 (40C; Ph*C*H), 122.95 (2C; Ar*C*), 111.38 (4C; Ar*C*H), 106.25 (8C; Ar*C*H), 104.52 (2C; Ar*C*H), 101.62 (4C; Ar*C*H), 81.58 (2C; (R-C≡*C*)₂), 73.59 (2C; (R-*C*≡C)₂), 70.06 (12C; *C*H₂O); IR (KBr): $\tilde{\nu}$ = 3031.4*w*, 2869.6*w*, 2145.7*w*, 1594.9*s*, 1497.6*w*, 1452.5*m*, 1375.6*m*, 1332.8*w*, 1298.0*w*, 1156.5*s*, 1054.6*m*, 830.8*m*, 736.6*m*, 696.7 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 266 (sh, 37600), 270 (sh, 38800), 277 (41000), 282 (sh, 37800), 297 (34600), 315 (45500), 337 nm (36000); MS (FAB +): *m*/*z*: 1475 [*M*]$^+$.

Compound 16: A flask was charged with **6** (4.002 g, 5.42 mmol) and dry THF (50 mL) and cooled to −78 °C. Then *n*BuLi (1.6 M in hexane, 3.73 mL, 5.97 mmol) was added with stirring. After 45 min, the cooling bath was warmed to −20 °C and CuI (1.033 g, 5.423 mmol) was added. The cooling bath was then removed and the mixture allowed to warm. After 15 min at room temperature, the mixture was cooled to −20 °C and dry pyridine (32 mL, 400 mmol) was added. A solution of Br-C≡C-C≡C-TMS[42] (1.194 g, 5.97 mmol) in dry THF (35 mL) was added dropwise with a syringe pump over 7 h. The mixture was then stirred for 5 d at room temperature. When TLC (silica gel, toluene) indicated no further progress, the reaction was quenched by addition of HCl (10 %, 100 mL) and CH_2Cl_2 (100 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic phases were washed with saturated solutions of NH_4Cl (100 mL) and NaCl (100 mL) before drying over Na_2SO_4. Purification with column chromatography (silica gel, hexane/toluene 1:1 → 2:3 → 3:7) yielded **16** as a brown oil (608 mg, 0.71 mmol, 13 %). $R_f = 0.73$ (toluene); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.35$–7.24 (m, 20H; PhH), 6.64 (d, ^3J(H,H) = 2.2 Hz, 2H; ArH), 6.57 (d, ^3J(H,H) = 2.2 Hz, 4H; ArH), 6.55 (t, ^3J(H,H) = 2.2 Hz, H; Ar*H*), 6.51 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 4.93 (s, 8H; OC*H₂*), 4.82 (s, 4H; OC*H₂*), 0.18 (s, 9H; Si(C*H₃*)₃); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 160.06$ (4C; Ar*C*OCH₂), 159.44 (2C; Ar*C*OCH₂), 138.66 (2C; Ar*C*), 136.62 (4C; Ph*C*), 128.47, 127.90, 127.43 (20C; Ph*C*H), 121.88 (1C; Ar*C*), 111.78 (2C; Ar*C*H), 106.16 (4C; Ar*C*H), 105.07 (1C; Ar*C*H), 101.55 (2C; Ar*C*H), 89.13 (1C; C≡C-C≡C-*C*≡C-Si(CH₃)₃), 88.01 (1C; C≡C-C≡C-C≡*C*-Si(CH₃)₃), 76.77 (1C; C≡*C*-C≡C-C≡C-Si(CH₃)₃), 73.96 (1C; *C*≡C-C≡C-C≡C-Si(CH₃)₃), 69.94 (6C; *C*H₂O), 66.92 (1C; C≡C-*C*≡C-C≡C-Si(CH₃)₃), 61.49 (1C; C≡C-C≡*C*-C≡C-Si(CH₃)₃), −0.61 (3C; C≡C-C≡C-C≡C-Si(*C*H₃)₃); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 248 (51000), 262 (64000), 271 (sh, 35300), 284 (21700), 303 (23300), 323 (32500), 346 nm (24300); MS (FAB +): *m*/*z*: 875 [*M*]$^+$, 859.

Compounds 17 and 20: a) A spatula tip of K_2CO_3 was added to a stirred solution of **16** (100 mg, 0.12 mmol) in wet THF/MeOH (1:1, 10 mL). TLC (silica gel, hexane/toluene 1:1) indicated completeness of the reaction after 80 min, whereupon water (20 mL), conc. HCl (1 mL), and CH_2Cl_2 (50 mL) were added. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic phases were dried over Na_2SO_4. After filtration, the solvent was removed until about 1 mL remained. The deprotected triyne **17** ($R_f = 0.60$, silica gel, toluene) was, after addition of acetone (10 mL), used in reaction b) without characterization.

b) A slurry of TMEDA (0.5 mL, 3.4 mmol) and CuCl (40 mg, 0.41 mmol) in dry acetone (10 mL) was stirred for 15 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the residue was washed with dry acetone (5 mL). To the resulting catalyst, a solution of **17** was added with a dropping funnel. TLC (silica gel, toluene) was used to monitor the reaction progress. At the end, the reaction was quenched with water (50 mL), CH_2Cl_2 (50 mL), followed by sufficient conc. HCl to redissolve the precipitated yellow product. The aqueous phase was extracted with CH_2Cl_2 (2 × 40 mL), and the combined organic phases were dried over Na_2SO_4. Column chromatography (silica gel, CH_2Cl_2) afforded **20** as a yellow solid (80 mg, 0.05 mmol, 85 %). $R_f = 0.45$ (toluene); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$–7.29 (m, 40H; Ph*H*), 6.72 (d, ^3J(H,H) = 2.4 Hz, 4H; Ar*H*), 6.62 (d, ^3J(H,H) = 2.1 Hz, 8H; Ar*H*), 6.56 (t, ^3J(H,H) = 2.1 Hz, 4H; Ar*H*), 6.55 (t, ^3J(H,H) = 2.4 Hz, 2H; Ar*H*), 5.01(s, 16H; OC*H₂*), 4.93 (s, 8H; OC*H₂*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 160.18 (8C; Ar*C*OCH₂), 159.56 (4C; Ar*C*OCH₂), 138.63 (4C; Ar*C*), 136.65 (8C; Ph*C*), 128.58, 128.02, 127.52 (40C; Ph*C*H), 121.97 (2C; Ar*C*), 112.19

(4C; Ar*C*H), 106.25 (8C; Ar*C*H), 105.12 (2C; Ar*C*H), 101.65 (4C; Ar*C*H), 77.33 (2C; (R-C≡*C*-C≡C-C≡C)$_2$), 73.96 (2C; (R-*C*≡C-C≡C-C≡C)$_2$), 70.11 (12C; *C*H$_2$O), 67.27 (2C; (R-C≡C-*C*≡C-C≡C)$_2$), 64.58 (2C; (R-C≡C-C≡C-*C*≡C)$_2$), 63.57 (2C; (R-C≡C-C≡*C*-C≡C)$_2$), 62.46 (2C; (R-C≡C-C≡C-C≡*C*)$_2$); UV/Vis (CH_2Cl_2): λ_{max} = 263, 275, 287, 302, 322, 343, 360, 368 (sh), 397, 428, 467; MS (FAB+): *m*/*z*: 1572 [*M*+H]$^+$.

Compound 7: A solution of [G-3]-CH_2OH[31] (9.87 g, 6.2 mmol) in dry CH_2Cl_2 (35 mL) was slowly added to a vigorously stirred slurry of pyridinium dichromate (4.655 g, 12.04 mmol) in dry CH_2Cl_2 (15 mL) at room temperature. After 2 d, TLC (silica gel, CH_2Cl_2) reaction control indicated complete reaction. The reaction mixture was filtered through a silica gel plug (CH_2Cl_2) to give **7** as a light yellow oil (9.86 g, 6.2 mmol, 100%). $R_f = 0.50$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.84 (s, 1H; C*H*O), 7.41–7.28 (m, 40H; Ph*H*), 7.06 (d, ^3J(H,H) = 2.0 Hz, 2H; Ar*H*), 6.84 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 6.66 (d, ^3J(H,H) = 2.2 Hz, 8H; Ar*H*), 6.64 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.56 (t, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.54 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 5.00 (s, 16H; OC*H*$_2$), 4.99 (s, 4H; OC*H*$_2$), 4.95 (s, 8H; OC*H*$_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 191.74 (1C; *C*HO), 160.24 (2C; Ar*C*OCH$_2$), 160.13 (8C; Ar*C*OCH$_2$), 160.07 (4C; Ar*C*OCH$_2$), 139.12 (4C; Ar*C*), 138.61 (2C; Ar*C*), 138.39 (1C; Ar*C*), 136.72 (8C; Ph*C*), 128.54, 127.97, 127.52 (40C; Ph*C*H), 108.57 (1C; Ar*C*H), 108.28 (2C; Ar*C*H), 106.38 (4C; Ar*C*H), 106.34 (8C; Ar*C*H), 101.68 (2C; Ar*C*H), 101.56 (4C; Ar*C*H), 70.17 (2C; *C*H$_2$O), 70.06 (8C; *C*H$_2$O), 69.97 (4C; *C*H$_2$O); IR (film): $\tilde{\nu}$ = 3442.0*s*, 3063.2*w*, 3031.6*w*, 2925.9*w*, 2871.3*w*, 1697.4*m*, 1595.5*s*, 1497.3*w*, 1451.0*s*, 1375.1*s*, 1343.3*w*, 1295.9*w*, 1214.2*w*, 1158.1*s*, 1053.7*s*, 832.7*m*, 737.2*m*, 696.9 cm^{-1} *w*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 229 (88600), 233 (sh, 72000), 269 (sh, 16200), 277 (19100), 284 (sh, 16700), 325 nm (3000); MS (FAB+): *m*/*z*: 1592 [*M*+H]$^+$.

Compound 8: PPh_3 (6.47 g, 24.65 mmol) was added at 0 °C to a solution of CBr_4 (4.14 g, 12.32 mmol) in dry CH_2Cl_2 (20 mL). At the same temperature, aldehyde **7** (9.8 g, 6.16 mmol), dissolved in dry CH_2Cl_2 (75 mL), was dropped slowly into the reaction mixture. The cooling bath was removed and the progress of the reaction was monitored by TLC (silica gel, CH_2Cl_2). After 17 h, the reaction mixture was poured into ice water (150 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 70 mL). The combined organic phases were dried over Na_2SO_4, and column chromatography (silica gel, CH_2Cl_2) yielded **8** as light yellow oil (10.02 g, 5.7 mmol, 93%). $R_f = 0.90$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.32–7.20 (m and s, 41H; 40 Ph*H* and C*H*CBr$_2$), 6.64 (d, ^3J(H,H) = 1.7 Hz, 2H; Ar*H*), 6.58 (d, ^3J(H,H) = 1.7 Hz, 8H; Ar*H*), 6.55 (d, ^3J(H,H) = 1.7 Hz, 4H; Ar*H*), 6.51 (t, ^3J(H,H) = 1.7 Hz, 1H; Ar*H*), 6.48 (t, ^3J(H,H) = 1.7 Hz, 4H; Ar*H*), 6.45 (t, ^3J(H,H) = 1.7 Hz, 2H; Ar*H*), 4.92 (s, 20H; OC*H*$_2$), 4.86 (s, 8H; OC*H*$_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 160.13 (8C; Ar*C*OCH$_2$), 160.06 (4C; Ar*C*OCH$_2$), 159.58 (2C; Ar*C*OCH$_2$), 139.15 (4C; Ar*C*), 139.06 (2C; Ar*C*), 136.89 (1C; Ar*C*), 136.72 (8C; Ph*C*), 136.63 (1C; *C*HCBr$_2$), 128.54, 127.96, 127.52 (40C; Ph*C*H), 107.64 (2C; Ar*C*H), 106.34 (12C; Ar*C*H), 102.71 (1C; Ar*C*H), 101.57 (6C; Ar*C*H), 90.05 (1C; CH*C*Br$_2$), 70.06 (10C; *C*H$_2$O), 69.97 (4C; *C*H$_2$O); IR (film): $\tilde{\nu}$ = 3062.6*w*, 3030.9*w*, 2926.0*w*, 2870.6*w*, 1595.6*s*, 1496.8*w*, 1450.9*s*, 1374.2*m*, 1295.6*w*, 1214.0*w*, 1157.4*s*, 1052.3*s*, 909.2*w*, 831.2*m*, 736.1*m*, 696.2 cm^{-1} *w*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 231 (97400), 233 (sh, 82400), 277 (25200), 285 nm (sh, 22000); MS (FAB+): *m*/*z*: 1747 [*M*]$^+$.

Compound 9: *n*BuLi (1.6 M in hexane, 6.8 mL, 10.83 mmol) was added with ice water cooling to a solution of diisopropylamine (1.1 g, 10.83 mmol) in dry THF (5 mL) in a three-necked flask (100 mL). After 1 h, the resulting LDA solution was slowly dropped into **8** (6.3 g, 3.61 mmol), dissolved in dry THF (15 mL). The temperature was kept at −78 °C, and the reaction was monitored by TLC (silica gel, CH_2Cl_2) at −78 °C. Due to its strong fluorescence, **9** could be differentiated from the starting material. By the careful addition of HCl (10%, 50 mL) followed by CH_2Cl_2 (100 mL), the reaction was quenched. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic solutions were dried over Na_2SO_4. Two-fold column chromatography (silica gel, CH_2Cl_2) gave the light yellow oil **9** (3.343 g, 2.1 mmol, 58%). $R_f = 0.87$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.40–7.24 (m, 40H; Ph*H*), 6.71 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.66 (d, ^3J(H,H) = 2.2 Hz, 8H; Ar*H*), 6.62 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.60 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 6.55 (t, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.53 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 5.00 (s, 16H; OC*H*$_2$), 4.94 (s, 8H; OC*H*$_2$), 4.91 (s, 4H; OC*H*$_2$), 3.00 (s, 1H; C≡C-*H*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 160.13 (8C; Ar*C*OCH$_2$), 160.06 (4C; Ar*C*OCH$_2$), 159.54 (2C; Ar*C*OCH$_2$), 139.15 (4C; Ar*C*), 138.92 (2C; Ar*C*), 136.74 (8C; Ph*C*), 128.56, 127.97, 127.53 (40C; Ph*C*H), 123.42 (1C; Ar*C*), 111.17 (2C; Ar*C*H), 106.34 (12C; Ar*C*H), 103.75 (1C; Ar*C*H), 101.59 (6C; Ar*C*H), 83.40 (1C; *C*≡C-H), 77.20 (1C; C≡*C*-H), 70.08 (10C; *C*H$_2$O), 69.98 (4C; *C*H$_2$O); IR (film): $\tilde{\nu}$ = 3282.8*m*, 3062.6*w*, 3030.9*w*, 2869.8*w*, 2108.8*w*, 1595.6*s*, 1497.0*w*, 1450.8*m*, 1374.1*m*, 1320.5*w*, 1295.0*w*, 1214.0*w*, 1155.9*s*, 1049.8*m*, 831.1*m*, 735.7*m*, 696.0 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 228 (84400), 229 (87900), 231 (77200), 257 (sh, 12900), 277 (sh, 15700), 283 (16500), 305 nm (sh, 3100); MS (FAB+): *m*/*z*: 1587 [*M*]$^+$.

Compound 18: A flask was charged with **9** (2.0 g, 1.26 mmol) and dry THF (12 mL) and cooled to −78 °C. Then *n*BuLi (1.6 M in hexane, 0.87 mL, 1.39 mmol) was added with stirring. After 45 min, the cooling bath was warmed to −20 °C and CuI (240 mg, 1.26 mmol) was added. The cooling bath was then removed and the mixture allowed to warm. After 15 min at room temperature, the mixture was cooled to −20 °C and dry pyridine (8 mL, 100 mmol) was added. A solution of Br-C≡C-C≡C-TMS[42] (279 mg, 1.39 mmol) in dry THF (24 mL) was added dropwise with a syringe pump over 1 h. The mixture was then stirred for 4 d at room temperature. When TLC (silica gel, toluene) indicated no further progress, the reaction was quenched by addition of HCl (10%, 100 mL) and CH_2Cl_2 (100 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic phases were washed with saturated solutions of NH_4Cl (100 mL) and NaCl (100 mL) before drying over Na_2SO_4. Purification with column chromatography (silica gel, toluene) yielded **18** as yellow oil(430 mg, 0.25 mmol, 20%). $R_f = 0.32$ (toluene); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.27–7.14 (m, 40H; Ph*H*), 6.58 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.53 (d, ^3J(H,H) = 2.2 Hz, 8H; Ar*H*), 6.49 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.49 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 6.43 (t, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.41 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 4.85 (s, 16H; OC*H*$_2$), 4.79 (s, 8H; OC*H*$_2$), 4.74 (s, 4H; OC*H*$_2$), 0.10 (s, 9H; C≡C-Si(C*H*$_3$)$_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 160.06 (8C; Ar*C*OCH$_2$), 159.98 (4C; Ar*C*OCH$_2$), 159.47 (2C; Ar*C*OCH$_2$), 139.10 (4C; Ar*C*), 138.67 (2C; Ar*C*), 136.68 (8C; Ph*C*), 128.47, 127.90, 127.46 (40C; Ph*C*H), 122.02 (1C; Ar*C*), 111.79 (2C; Ar*C*H), 106.27 (12C; Ar*C*H), 104.01 (1C; Ar*C*H), 101.56 (2C; Ar*C*H), 101.48 (4C; Ar*C*H), 89.25 (1C; C≡C-C≡C-*C*≡C-Si(CH$_3$)$_3$), 88.09 (1C; C≡C-C≡C-C≡*C*-Si(CH$_3$)$_3$), 76.85 (1C; C≡*C*-C≡C-C≡C-Si(CH$_3$)$_3$), 74.00 (1C; *C*≡C-C≡C-C≡C-Si(CH$_3$)$_3$), 69.94 (10C; *C*H$_2$O), 69.85 (4C; *C*H$_2$O), 66.99 (1C; C≡C-*C*≡C-C≡C-Si(CH$_3$)$_3$), 62.07 (1C; C≡C-C≡*C*-C≡C-Si(CH$_3$)$_3$), −0.60 (3C; C≡C-C≡C-C≡C-Si(*C*H$_3$)$_3$); UV/Vis (toluene): λ_{max} = 305, 324, 347, 365, 393, 426 nm; MS (FAB+): *m*/*z*: 1708 [*M*]$^+$.

Compounds 19 and 21: a) A spatula tip of K_2CO_3 was added to a stirred solution of **18** (110 mg, 0.06 mmol) in wet THF/MeOH (1:1, 10 mL). TLC (silica gel, CH_2Cl_2) indicated completeness of the reaction after 60 min, whereupon water (20 mL), conc. HCl (1 mL), and CH_2Cl_2 (20 mL) were added. The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic phases were dried over Na_2SO_4. After filtration, the solvent was removed until about 1 mL remained. The deprotected triyne **19** ($R_f = 0.58$, silica gel, CH_2Cl_2) was, after addition of acetone (10 mL), used in reaction b) without characterization.

b) A slurry of TMEDA (0.5 mL, 3.4 mmol) and CuCl (40 mg, 0.41 mmol) in dry acetone (10 mL) was stirred for 15 min, whereupon it was repeatedly filtered until no further solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (5 mL). The solution of **19** was added to the resulting catalyst with a dropping funnel. TLC (silica gel, CH_2Cl_2) was used to monitor the reaction progress. The reaction was quenched upon completion with water (10 mL), CH_2Cl_2 (50 mL), and conc. HCl (5 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 40 mL), and the combined organic phases were dried over Na_2SO_4. Two-fold column chromatography (silica gel, CH_2Cl_2) followed by HPLC separation (Nucleosil, toluene/CH_2Cl_2 7:3) gave **21** as a yellow oil (80 mg, 0.02 mmol, 82%). $R_f = 0.30$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.34–7.09 (m, 80H; Ph*H*), 6.66 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.59 (d, ^3J(H,H) = 2.2 Hz, 16H; Ar*H*), 6.53 (d, ^3J(H,H) = 2.2 Hz, 8H; Ar*H*), 6.49 (t, ^3J(H,H) = 2.2 Hz, 10H; Ar*H*), 6.46 (t, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 4.94 (s, 32H; OC*H*$_2$), 4.88 (s, 16H; OC*H*$_2$), 4.85 (s, 8H; OC*H*$_2$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 160.15 (16C; Ar*C*OCH$_2$), 160.09 (8C; Ar*C*OCH$_2$), 159.04 (4C; Ar*C*OCH$_2$), 139.13 (8C; Ar*C*), 138.63 (4C; Ar*C*), 136.73 (16C; Ph*C*), 128.58, 128.00, 127.55 (80C; Ph*C*H), 122.02 (2C; Ar*C*), 112.20 (4C; Ar*C*H), 106.36 (24C; Ar*C*H), 105.78 (2C; Ar*C*H), 101.67 (4C; Ar*C*H), 101.58 (8C; Ar*C*H), 77.41 (2C; (R-C≡*C*-C≡C-C≡C)$_2$), 74.00 (2C; (R-*C*≡C-C≡C-C≡C)$_2$), 70.09 (20C; *C*H$_2$O), 70.00 (8C; *C*H$_2$O), 67.30 (2C; (R-C≡C-*C*≡C-C≡C)$_2$), 64.46 (2C; (R-C≡C-C≡C-*C*≡C)$_2$), 63.57 (2C; (R-

C≡C-C≡*C*-C≡C)$_2$), 62.46 (2C; (R-C≡C-C≡C-C≡*C*)$_2$); UV/Vis (toluene): λ_{max} = 296, 316, 351, 377, 408 nm; MS (FAB +): *m/z*: 3269 $[M]^+$.

Compound 24: *tert*-Butyldimethylsilylchloride (543 mg, 3.60 mmol), dissolved in dry DMF (10 mL) was slowly added at 0 °C to a stirred solution of 3,5-dihydroxybenzaldehyde (225 mg, 1.63 mmol), 4-dimethylaminopyridine (135 mg, 1.10 mmol), and triethylamine (397 mg, 3.92 mmol) in dry DMF (10 mL). After 10 min, the resulting suspension was allowed to warm and the reaction was monitored with TLC (silica gel, ethyl acetate/hexane 1:1). After 18 h, water (40 mL) and Et_2O (40 mL) were added. The organic phase was washed with water (2 × 50 mL) and a saturated solution of NaCl (50 mL), before it was dried over Na_2SO_4. Purification with column chromatography (silica gel, CH_2Cl_2) yielded **24** as a transparent oil (540 mg, 1.47 mmol, 90 %). R_f = 0.57 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.84 (s, 1H; C*H*O), 6.93 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.57 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 0.97 (s, 18H; $\mathrm{Si(CH_3)_2C(C}H_3\mathrm{)_3}$), 0.20 (s, 12H; $\mathrm{Si(C}H_3\mathrm{)_2C(CH_3)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 191.83 (1C; *C*HO), 157.26 (2C; Ar*C*OSi), 138.33 (1C; Ar*C*), 118.42 (1C; Ar*C*H), 114.38 (2C; Ar*C*H), 25.61 (6C; $\mathrm{Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 18.19 (2C; $\mathrm{Si(CH_3)_2}C\mathrm{(CH_3)_3}$), −4.30 (4C; $\mathrm{Si(}C\mathrm{H_3)_2C(CH_3)_3}$); IR (film): $\tilde{\nu}$ = 2956.7*m*, 2931.7*m*, 2887.3*w*, 2859.9*m*, 1704.7*s*, 1589.4*s*, 1459.9*s*, 1384.5*m*, 1336.6*s*, 1258.6*m*, 1170.7*s*, 1031.8*m*, 1009.6*w*, 939.2*w*, 830.7*s*, 782.2 cm^{-1} *m*, 740.9*w*; MS (EI): *m/z*: 366 $[M]^+$, 309, 281, 267, 239, 73.

Compound 25: PPh_3 (1.469 g, 5.6 mmol) was added at 0 °C to a solution of CBr_4 (929 mg, 2.8 mmol) in dry CH_2Cl_2 (5 mL). At the same temperature, aldehyde **24** (510 mg, 1.4 mmol), dissolved in dry CH_2Cl_2 (14 mL), was dropped slowly into the reaction mixture. The cooling bath was removed and the progress of the reaction was monitored by TLC (silica gel, CH_2Cl_2). After 10 min, water (100 mL) and CH_2Cl_2 (50 mL) were added, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases were dried over Na_2SO_4, and column chromatography (silica gel, CH_2Cl_2) yielded **25** as transparent oil (713 mg, 1.37 mmol, 97 %). R_f = 0.73 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.33 (s, 1H; C*H*CBr$_2$), 6.63 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.31 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 0.95 (s, 18H; $\mathrm{Si(CH_3)_2C(C}H_3\mathrm{)_3}$), 0.18 (s, 12H; $\mathrm{Si(C}H_3\mathrm{)_2C(CH_3)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 156.47 (2C; Ar*C*OSi), 136.71 (1C; *C*HCBr$_2$), 136.60 (1C; Ar*C*), 113.43 (2C; Ar*C*H), 112.66 (1C; Ar*C*H), 89.44 (1C; CH*C*Br$_2$), 25.66 (6C; $\mathrm{Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 18.21 (2C; $\mathrm{Si(CH_3)_2}C\mathrm{(CH_3)_3}$), −4.39 (4C; $\mathrm{Si(}C\mathrm{H_3)_2C(CH_3)_3}$); IR (film): $\tilde{\nu}$ = 2957.7*m*, 2929.5*m*, 2898.3*w*, 2858.6*m*, 1580.7*s*, 1472.1*w*, 1432.6*m*, 1390.3*w*, 1362.7*w*, 1337.7*m*, 1257.4*m*, 1229.5*w*, 1169.1*s*, 1033.8*m*, 1014.7*w*, 939.0*w*, 830.6*s*, 812.1*w*, 781.3*m*, 741.8*w*, 688.1 cm^{-1} *w*; MS (EI): *m/z*: 522 $[M]^+$, 465, 329, 147, 139, 73.

Compound 27: *n*BuLi (1.6 M in hexane, 2.46 mL, 3.93 mmol) was added with ice water cooling to a solution of diisopropylamine (398 mg, 3.93 mmol) in dry THF (10 mL) in a three-necked flask (100 mL). After 1 h, the resulting LDA solution was slowly dropped into **25** (684 mg, 1.31 mmol), dissolved in dry THF (15 mL) at −78 °C. The temperature was kept at −78 °C, and the reaction was monitored by TLC (silica gel, CH_2Cl_2). Due to its strong fluorescence the elimination product could be differentiated from the starting material. When no further starting material could be observed, triisopropylsilylchloride (1.01 g, 5.24 mmol) was added with a syringe, and the mixture was allowed to warm to room temperature. After 1 h, the reaction was quenched by the careful addition of HCl (10 %, 50 mL) followed by CH_2Cl_2 (40 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL), and the combined organic solutions were dried over Na_2SO_4. Column chromatography (silica gel, CH_2Cl_2) gave the transparent oil **27** (658 mg, 1.3 mmol, 97 %). R_f = 0.78 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.54 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.28 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 1.10 (s, 21H; $\mathrm{Si(C}H\mathrm{(C}H_3\mathrm{)_2)_3}$), 0.95 (s, 18H; $\mathrm{Si(CH_3)_2C(C}H_3\mathrm{)_3}$), 0.17 (s, 12H; $\mathrm{Si(C}H_3\mathrm{)_2C(CH_3)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 156.26 (2C; Ar*C*OSi), 124.61 (1C; Ar*C*), 117.08 (2C; Ar*C*H), 112.99 (1C; Ar*C*H), 106.98 (1C; *C*≡C-TIPS), 89.99 (1C; C≡*C*-TIPS), 25.64 (6C; $\mathrm{Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 18.66 (6C; $\mathrm{Si(CH(}C\mathrm{H_3)_2)_3}$), 18.17 (2C; $\mathrm{Si(CH_3)_2}C\mathrm{(CH_3)_3}$), 11.32 (3C; $\mathrm{Si(}C\mathrm{H(CH_3)_2)_3}$), −4.43 (4C; $\mathrm{Si(}C\mathrm{H_3)_2C(CH_3)_3}$); IR (film): $\tilde{\nu}$ = 2957.3*m*, 2893.4*w*, 2863.9*m*, 2150.5*w*, 1578.3*s*, 1463.7*w*, 1427.1*m*, 1390.1*w*, 1345.6*m*, 1256.5*m*, 1169.7*s*, 1029.3*m*, 1015.3*m*, 856.6*w*, 832.1*s*, 781.5*m*, 669.2 cm^{-1} *w*; MS (EI): *m/z*: 518 $[M]^+$, 475, 433, 362, 305, 263, 160, 124, 73, 57, 41.

Compound 26: *n*BuLi (1.6 M in hexane, 60.1 mL, 96.1 mmol) was added with ice water cooling to a solution of diisopropylamine (9.724 g, 96.1 mmol) in dry THF (40 mL) in a three-necked flask (100 mL). After 1 h, the resulting LDA solution was slowly dropped into **25** (16.737 g, 32.03 mmol), dissolved in dry THF (150 mL) at −78 °C. The temperature was kept at −78 °C, and the reaction was monitored by TLC (silica gel, CH_2Cl_2). Due to its strong fluorescence **26** could be differentiated from the starting material. When no further starting material could be observed, careful addition of HCl (10 %, 110 mL), water (100 mL), and afterwards CH_2Cl_2 (300 mL) quenched the reaction. The aqueous phase was extracted with CH_2Cl_2 (2 × 150 mL), and the combined organic solutions were dried over Na_2SO_4. Column chromatography (silica gel, CH_2Cl_2) gave the transparent oil **26** (11.036 g, 30.43 mmol, 95 %). R_f = 0.72 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.59 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.34 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 2.99 (s, 1H; C≡C-*H*), 0.96 (s, 18H; $\mathrm{Si(CH_3)_2C(C}H_3\mathrm{)_3}$), 0.18 (s, 12H; $\mathrm{Si(C}H_3\mathrm{)_2C(CH_3)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 156.39 (2C; Ar*C*OSi), 123.07 (1C; Ar*C*), 117.22 (2C; Ar*C*H), 113.72 (1C; Ar*C*H), 83.53 (1C; *C*≡C-H), 76.51 (1C; C≡*C*-H), 25.62 (6C; $\mathrm{Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 18.17 (2C; $\mathrm{Si(CH_3)_2}C\mathrm{(CH_3)_3}$), −4.45 (4C; $\mathrm{Si(}C\mathrm{H_3)_2C(CH_3)_3}$); IR (film): $\tilde{\nu}$ = 3314.5*w*, 3296.2*w*, 2956.9*m*, 2931.5*m*, 2887.3*w*, 2859.8*m*, 2105.9*w*, 1580.7*s*, 1472.2*w*, 1428.6*m*, 1390.7*w*, 1362.2*w*, 1341.4*m*, 1298.2*w*, 1255.6*m*, 1225.8*w*, 1169.4*s*, 1136.6*w*, 1030.1*m*, 1007.2*m*, 978.9*w*, 939.2*w*, 833.1*s*, 814.7*w*, 781.8*m*, 742.4*w*, 671.2 cm^{-1} *w*; UV/Vis (hexane): λ_{max} (ε) = 211 (32000), 213 (sh, 30400), 244 (7800), 251 (8200), 295 nm (1600); MS (EI): *m/z*: 362 $[M]^+$, 347, 305, 263, 249, 73.

Compound 34:

A) Di-TIPS-benzaldehyde: Triisopropylsilylchloride (14.19, 73.58 mmol), dissolved in dry DMF (80 mL) was slowly added at 0 °C to a stirred solution of 3,5-dihydroxybenzaldehyde (4.62 g, 33.44 mmol), 4-dimethylaminopyridine (2.70 g, 22.07 mmol), and triethylamine (8.12 g, 80.27 mmol) in dry DMF (110 mL). After 10 min, the resulting suspension was allowed to warm, and the reaction was monitored with TLC (silica gel, ethyl acetate/hexane 1:1). After 20 h, water (100 mL) and Et_2O (150 mL) were added. The aqueous phase was extracted with Et_2O (2 × 100 mL), and the combined organic phases were washed with HCl (10 %, 2 × 50 mL) and water (100 mL), before drying over Na_2SO_4. Purification by column chromatography (silica gel, toluene) yielded the aldehyde as a transparent oil (11.3 g, 25.1 mmol, 75 %). R_f = 0.75 (ethyl acetate/hexane 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.84 (s, 1H; C*H*O), 6.96 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.66 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 1.29–1.23 (m, 6H; $\mathrm{Si(C}H\mathrm{(CH_3)_2)_3}$), 1.08 (d, ^3J(H,H) = 7.3 Hz, 36H; $\mathrm{Si(CH(C}H_3\mathrm{)_2)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 191.84 (1C; *C*HO), 157.61 (2C; Ar*C*OSi), 138.28 (1C; Ar*C*), 117.93 (1C; Ar*C*H), 113.98 (2C; Ar*C*H), 17.81 (12C; $\mathrm{Si(CH(}C\mathrm{H_3)_2)_3}$), 12.60 (6C; $\mathrm{Si(}C\mathrm{H(CH_3)_2)_3}$); IR (film): $\tilde{\nu}$ = 2946.1*s*, 2868.3*m*, 1705.8*m*, 1587.9*s*, 1459.5*m*, 1383.9*w*, 1339.9*m*, 1177.7*s*, 1033.1*w*, 1014.2*w*, 882.4*w*, 831.8*w*, 757.7*w*, 680.8 cm^{-1} *w*; MS (EI): *m/z*: 450 $[M]^+$, 407, 379, 351, 337, 154, 140, 126, 87, 73, 59.

B) Di-TIPS-phenyl-CHCBr$_2$: PPh_3 (26.06 g, 99.36 mmol) was added at 0 °C to a solution of CBr_4 (16.48 g, 49.68 mmol) in dry CH_2Cl_2 (80 mL). At the same temperature, the aldehyde obtained above (11.2 g, 24.84 mmol), dissolved in dry CH_2Cl_2 (150 mL), was dropped slowly into the reaction mixture. The cooling bath was removed and the progress of the reaction was monitored by TLC (silica gel, CH_2Cl_2). After 15 min, water (150 mL) and CH_2Cl_2 (100 mL) were added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were dried over Na_2SO_4, and column chromatography (silica gel, CH_2Cl_2) yielded the dibromoolefin as transparent oil (13.9 g, 22.9 mmol, 92 %). R_f = 0.97 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.34 (s, 1H; C*H*CBr$_2$), 6.66 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.41 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 1.25–1.20 (m, 6H; $\mathrm{Si(C}H\mathrm{(CH_3)_2)_3}$), 1.08 (d, ^3J(H,H) = 7.1 Hz, 36H; $\mathrm{Si(CH(C}H_3\mathrm{)_2)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 156.86 (2C; Ar*C*OSi), 136.85 (1C; *C*HCBr$_2$), 136.52 (1C; Ar*C*), 113.10 (2C; Ar*C*H), 112.37 (1C; Ar*C*H), 89.26 (1C; CH*C*Br$_2$), 17.90 (12C; $\mathrm{Si(CH(}C\mathrm{H_3)_2)_3}$), 12.64 (6C; $\mathrm{Si(}C\mathrm{H(CH_3)_2)_3}$); IR (film): $\tilde{\nu}$ = 2945.0*s*, 2867.4*m*, 1588.3*s*, 1462.7*m*, 1433.2*m*, 1388.5*w*, 1340.3*m*, 1228.9*w*, 1174.7*s*, 1034.7*m*, 1015.7*m*, 996.1*w*, 919.8*w*, 881.9*m*, 800.4*w*, 760.2*m*, 685.4 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 228 (30000), 230 (28200), 264 (sh, 15600), 270 (15900), 283 nm (sh, 11900); MS (EI): *m/z*: 606 $[M]^+$, 563, 535, 204, 115, 87, 73, 59, 43; MS (FAB +): *m/z*: 607 $[M+H]^+$, 563.

C) Compound **34**: *n*BuLi (1.6 M in hexane, 42.96 mL, 68.74 mmol) was added with ice water cooling to a solution of diisopropylamine (6.96 g, 68.74 mmol) in dry THF (30 mL) in a three-necked flask (100 mL). After 2 h, the resulting LDA solution was slowly dropped into the dibromoolefin (13.9 g, 22.91 mmol), dissolved in dry THF (100 mL) at −78 °C. The temperature was kept at –78 °C, and the reaction was monitored by TLC (silica gel, toluene). Due to its strong fluorescence the elimination product could be differentiated from the starting material. When no further starting material could be observed, careful addition of HCl (10 %, 100 mL), water (100 mL), and afterwards CH_2Cl_2 (100 mL) quenched the reaction. The aqueous phase was extracted with CH_2Cl_2 (2 × 150 mL), and the combined organic solutions were dried over Na_2SO_4. Column chromatography (silica gel, toluene) gave the transparent oil **34** (7.855 g, 17.58 mmol, 77 %). $R_f = 0.76$ (toluene); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 6.63$ (d, $^3J(\mathrm{H,H}) = 2.2$ Hz, 2H; Ar*H*), 6.46 (t, $^3J(\mathrm{H,H}) = 2.2$ Hz, 1H; Ar*H*), 3.06 (s, 1H; C≡C-*H*), 1.28–1.24 (m, 6H; $\mathrm{Si(C}H\mathrm{(CH_3)_2)_3}$), 1.10 (d, $^3J(\mathrm{H,H}) = 7.3$ Hz, 36H; $\mathrm{Si(CH(C}H_3\mathrm{)_2)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 157.34$ (2C; Ar*C*OSi), 123.45 (1C; Ar*C*), 117.20 (2C; Ar*C*H), 113.76 (1C; Ar*C*H), 83.84 (1C; *C*≡C-H), 76.88 (1C; C≡*C*-H), 18.05 (12C; $\mathrm{Si(CH(}C\mathrm{H_3)_2)_3}$), 13.04 (6C; $\mathrm{Si(}C\mathrm{H(CH_3)_2)_3}$); IR (film): $\tilde{\nu} = 3314.5$*m*, 2945.9*s*, 2893.0*w*, 2868.2*m*, 2105.3*w*, 1579.5*s*, 1463.7*w*, 1428.8*m*, 1388.5*w*, 1346.2*m*, 1249.5*w*, 1224.0*w*, 1176.4*s*, 1136.7*w*, 1070.8*w*, 1031.7*m*, 1010.6*m*, 919.9*w*, 882.7*m*, 858.0*w*, 811.7*w*, 760.4*m*, 684.2*m*, 645.2 cm^{-1} *w*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 227 (18000), 248 (13200), 254 (13500), 298 nm (3000); MS (EI): *m*/*z*: 446 $[M]^+$, 403, 375, 124, 59; MS (FAB+): *m*/*z*: 447 $[M+\mathrm{H}]^+$, 403.

Compound 28: H_2SO_4 (10 %, 1.3 mL) was added to a solution of **26** (1.5 g, 4.13 mmol) in $MeOH/CH_2Cl_2$ (1:1, 20 mL). The reaction was monitored with TLC (silica gel, ethyl acetate/hexane 1:1). After 65 h, the reaction was quenched by addition of water (40 mL) and Et_2O (40 mL). The aqueous phase was extracted with Et_2O (2 × 60 mL), and the combined organic phases were dried over Na_2SO_4. Purification by column chromatography (silica gel, ethyl acetate/hexane 1:1) gave **28** as white solid (553 mg, 4.13 mmol, 100 %). $R_f = 0.50$ (ethyl acetate/hexane 1:1); ^{1}H NMR (400 MHz, $[D_6]$acetone, 25 °C): $\delta = 8.51$ (s, 2H; O*H*), 6.47 (d, $^3J(\mathrm{H,H}) = 2.2$ Hz, 2H; Ar*H*), 6.40 (t, $^3J(\mathrm{H,H}) = 2.2$ Hz, 1H; Ar*H*), 3.50 (s, 1H; C≡C-*H*); ^{13}C NMR (100.5 MHz, $[D_6]$acetone, 25 °C): $\delta = 159.35$ (2C; Ar*C*OH), 124.38 (1C; Ar*C*), 111.17 (2C; Ar*C*H), 104.80 (1C; Ar*C*H), 84.39 (1C; *C*≡C-H), 77.96 (1C; C≡*C*-H); IR (KBr): $\tilde{\nu} = 3291.8$*s*, 2984.0*w*, 2111.7*w*, 1700.8*m*, 1596.5*s*, 1501.7*w*, 1439.1*m*, 1376.8*w*, 1334.7*m*, 1302.5*m*, 1196.1*w*, 1157.8*s*, 1043.2*w*, 1002.1*m*, 958.7*w*, 843.3*m*, 677.6*w*, 630.0 cm^{-1} *w*; MS (EI): *m*/*z*: 134 $[M]^+$.

Compound 29: H_2SO_4 (10 %, 0.1 mL) was added to a solution of **27** (60 mg, 0.12 mmol) in $MeOH/CH_2Cl_2$ 1:1 (2 mL). The reaction was monitored with TLC (silica gel, CH_2Cl_2). After 40 h, the reaction was quenched by addition of water (40 mL) and CH_2Cl_2 (40 mL). The aqueous phase was extracted with CH_2Cl_2 (20 mL), and the combined organic phases were dried over Na_2SO_4. Purification with column chromatography (silica gel, ethyl acetate/hexane 1:1) gave **29** as white solid (34 mg, 0.12 mmol, 100 %). $R_f = 0.58$ (ethyl acetate/hexane 1:1); ^{1}H NMR (400 MHz, $[D_6]$acetone, 25 °C): $\delta = 8.42$ (s, 2H; O*H*), 6.48 (d, $^3J(\mathrm{H,H}) = 2.2$ Hz, 2H; Ar*H*), 6.39 (t, $^3J(\mathrm{H,H}) = 2.2$ Hz, 1H; Ar*H*), 1.13 (s, 21H; $\mathrm{Si(C}H\mathrm{(C}H_3\mathrm{)_2)_3}$); ^{13}C NMR (100.5 MHz, $[D_6]$acetone, 25 °C): $\delta = 159.33$ (2C; Ar*C*OH), 125.32 (1 C; Ar*C*), 111.14 (2C; Ar*C*H), 108.64 (1C; *C*≡C-TIPS), 104.73 (1C; Ar*C*H), 89.31 (1C; C≡*C*-TIPS), 18.95 (6C; $\mathrm{Si(CH(}C\mathrm{H_3)_2)_3}$), 11.99 (3C; $\mathrm{Si(}C\mathrm{H(CH_3)_2)_3}$); IR (KBr): $\tilde{\nu} = 3313.3$*s*, 2942.9*s*, 2890.9*w*, 2864.4*m*, 2162.7*m*, 1616.5*w*, 1592.7*s*, 1506.6*m*, 1461.3*m*, 1365.8*w*, 1323.4*m*, 1302.4*w*, 1200.6*w*, 1147.9*s*, 1071.9*w*, 997.2*s*, 919.6*w*, 883.1*m*, 844.3*m*, 827.3*w*, 701.0*m*, 674.0*m*, 659.9 cm^{-1} *w*; MS (EI): *m*/*z*: 290 $[M]^+$, 247, 219, 205, 191, 177, 96, 75, 57, 45; MS (FAB+): *m*/*z*: 291 $[M+\mathrm{H}]^+$, 247, 219, 205, 191, 177.

Compound 31: K_2CO_3 (73 mg, 0.529 mmol) was added to a solution of [G-3]-Br[31] (700 mg, 0.423 mmol), **29** (61.4 mg, 0.212 mmol) and [18]crown-6 (11.2 mg, 0.042 mmol) in dry acetone (20 mL). The suspension was heated at reflux for 17 h. Water (60 mL) and CH_2Cl_2 (60 mL) were added, and the organic phase was dried over Na_2SO_4. Two-fold column chromatography (silica gel, CH_2Cl_2) afforded **31** as transparent oil (524 mg, 0.152 mmol, 72 %). $R_f = 0.27$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.38$–7.24 (m, 80H; Ph*H*), 6.72 (s, 4H; Ar*H*), 6.65 (s, 26H; Ar*H*), 6.54 (s, 12H; Ar*H*), 6.52 (s, 3H; Ar*H*), 4.97 (s, 36H; $\mathrm{C}H_2\mathrm{O}$), 4.92 (s, 20H; $\mathrm{C}H_2\mathrm{O}$), 4.88 (s, 4H; $\mathrm{C}H_2\mathrm{O}$), 1.10 (d, $^3J(\mathrm{H,H}) = 1.4$ Hz, 18H; $\mathrm{Si(CH(C}H_3\mathrm{)_2)_3}$), 0.89 (s, 3H; $\mathrm{Si(C}H\mathrm{(CH_3)_2)_3}$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 160.13$ (20C; Ar*C*OCH$_2$), 160.04 (8C; Ar*C*OCH$_2$), 159.53 (2C; Ar*C*OCH$_2$), 139.22 (12C; Ar*C*), 139.03 (2C; Ar*C*), 136.77 (16C; Ph*C*), 128.55, 127.94, 127.52 (80C; Ph*C*H), 124.89 (1C; Ar*C*), 111.21 (2C; Ar*C*H), 106.93 (1C; *C*≡C-$\mathrm{Si(CH(CH_3)_2)_3}$), 106.49 (4C; Ar*C*H), 106.44 (8C; Ar*C*H), 106.36 (16C; Ar*C*H), 103.13 (1C; Ar*C*H), 101.61 (14C; Ar*C*H), 90.45 (1C; C≡*C*-$\mathrm{Si(CH(CH_3)_2)_3}$), 70.06 (22 C; *C*H$_2$O), 69.95 (8C; *C*H$_2$O), 18.63 (6C; $\mathrm{Si(CH(}C\mathrm{H_3)_2)_3}$), 11.30 (3C; $\mathrm{Si(}C\mathrm{H(CH_3)_2)_3}$); IR (film): $\tilde{\nu} = 3063.0$*w*, 3030.3*w*, 2962.0*m*, 2862.6*w*, 2153.5*w*, 1593.8*s*, 1497.2*w*, 1446.9*s*, 1371.6*s*, 1342.4*w*, 1294.0*m*, 1262.7*w*, 1214.4*w*, 1162.3*s*, 1059.3*s*, 829.5*m*, 734.6*m*, 696.7*m*, 676.3 cm^{-1} *w*; MS (FAB+): *m*/*z*: 3443 $[M+\mathrm{H}]^+$.

Compound 30:

A) A mixture of **31** (641 mg, 0.186 mmol) and tetrabutylammonium fluoride (1.0 M in THF, 1.9 mL, 1.864 mmol) in THF/water 10:1 (11 mL) was heated at reflux, and the reaction was monitored by TLC (silica gel, CH_2Cl_2). After 4 d, saturated aqueous NaCl (40 mL) and CH_2Cl_2 (50 mL) were added. The aqueous phase was extracted with Et_2O (3 × 60 mL), and the combined organic layers were dried over Na_2SO_4. Column chromatography (silica gel, CH_2Cl_2) gave **30** as transparent oil (494 mg, 0.151 mmol, 85 %).

B) K_2CO_3 (90 mg, 0.653 mmol) was added to a solution of [G-3]-Br[31] (864 mg, 0.522 mmol), **28** (35 mg, 0.261 mmol), and [18]crown-6 (14 mg, 0.052 mmol) in dry acetone (15 mL). The suspension was heated at reflux for 24 h. Then water (60 mL) and CH_2Cl_2 (60 mL) were added, and the aqueous phase was extracted with CH_2Cl_2 (2 × 60 mL). The combined organic phases were dried over Na_2SO_4. Two-fold column chromatography (silica gel, first: CH_2Cl_2; second: CH_2Cl_2/hexane 9:1) afforded **30** as transparent oil (385 mg, 0.117 mmol, 45 %). $R_f = 0.76$ (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.41$–7.29 (m, 80H; Ph*H*), 6.71 (d, $^3J(\mathrm{H,H}) = 2.4$ Hz, 2H; Ar*H*), 6.67 (d, $^3J(\mathrm{H,H}) = 2.4$ Hz, 24H; Ar*H*), 6.66 (d, $^3J(\mathrm{H,H}) = 2.2$ Hz, 4H; Ar*H*), 6.61 (t, $^3J(\mathrm{H,H}) = 2.4$ Hz, 1H; Ar*H*), 6.57 (t, $^3J(\mathrm{H,H}) = 2.2$ Hz, 2H; Ar*H*), 6.55 (t, $^3J(\mathrm{H,H}) = 2.4$ Hz, 12H; Ar*H*), 5.00 (s, 36H; $\mathrm{C}H_2\mathrm{O}$), 4.95 (s, 20H; $\mathrm{C}H_2\mathrm{O}$), 4.91 (s, 4H; $\mathrm{C}H_2\mathrm{O}$), 3.07 (s, 1H; C≡C-*H*); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 160.48$ (20C; Ar*C*OCH$_2$), 160.39 (8C; Ar*C*OCH$_2$), 159.99 (2C; Ar*C*OCH$_2$), 139.80 (12C; Ar*C*), 139.56 (2C; Ar*C*), 137.31 (16C; Ph*C*), 128.85, 128.31, 127.94 (80C; Ph*C*H), 123.77 (1C; Ar*C*), 111.46 (2C; Ar*C*H), 106.67 (28C; Ar*C*H), 104.02 (1C; Ar*C*H), 101.78 (14C; Ar*C*H), 83.61 (1C; *C*≡C-H), 77.37 (1C; C≡*C*-H), 70.37 (22C; *C*H$_2$O), 70.24 (8C; *C*H$_2$O); IR (film): $\tilde{\nu} = 3285.7$*m*, 3064.0*w*, 3032.7*m*, 2930.1*s*, 2872.2*s*, 2101.2*w*, 1594.9*s*, 1497.4*w*, 1453.1*s*, 1374.1*s*, 1296.3*m*, 1214.9*m*, 1159.9*s*, 1053.2*s*, 910.5*w*, 833.5*m*, 737.1*m*, 697.6*m*, 632.3 cm^{-1} *w*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 231 (161800), 233 (182500), 236 (sh, 127200), 258 (19700), 278 (37200), 283 (37800), 304 nm (3400); MS (FAB+): *m*/*z*: 3285 $[M]^+$.

Compound 44: A slurry of TMEDA (0.4 mL, 2.6 mmol) and CuCl (153 mg, 1.56 mmol) in dry acetone (20 mL) was stirred for 5 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was purged with dry acetone (5 mL). To the resulting catalyst was added a solution of **26** (150 mg, 0.414 mmol) in dry acetone (8 mL) with a dropping funnel. TLC (silica gel, toluene) was used to monitor the reaction progress. Upon completion, the reaction was quenched with water (100 mL), HCl (10 %, 25 mL), and CH_2Cl_2 (100 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the combined organic phases were dried over Na_2SO_4. Purification by column chromatography (silica gel, toluene), followed by a second column (silica gel, hexane) yielded **44** as white solid (116 mg, 0.16 mmol, 77 %). $R_f = 0.81$ (toluene); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 6.63$ (d, $^3J(\mathrm{H,H}) = 2.2$ Hz, 4H; Ar*H*), 6.39 (t, $^3J(\mathrm{H,H}) = 2.2$ Hz, 2H; Ar*H*), 0.97 (s, 36H; $\mathrm{Si(CH_3)_2C(C}H_3\mathrm{)_3}$), 0.20 (s, 24H; $\mathrm{Si(C}H_3\mathrm{)_2C(CH_3)_3}$); ^{13}C NMR (100.5 MHz, CD_2Cl_2, 25 °C): $\delta = 157.04$ (4C; Ar*C*OSi), 122.95 (2C; Ar*C*), 117.82 (4C; Ar*C*H), 114.97 (2C; Ar*C*H), 81.72 (2C; (R-C≡*C*)$_2$), 73.51 (2C; (R-*C*≡C)$_2$), 25.77 (12C; $\mathrm{Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 18.48 (4C; $\mathrm{Si(CH_3)_2}C\mathrm{(CH_3)_3}$), –4.35 (8C; $\mathrm{Si(}C\mathrm{H_3)_2C(CH_3)_3}$); IR (KBr): $\tilde{\nu} = 2956.4$*m*, 2931.1*m*, 2887.2*w*, 2858.7*m*, 2148.1*w*, 1577.4*s*, 1471.7*w*, 1427.6*m*, 1390.3*w*, 1340.8*s*, 1260.8*m*, 1223.5*w*, 1168.6*s*, 1137.5*w*, 1030.3*m*, 1005.0*m*, 983.9*w*, 939.6*w*, 840.5*s*, 813.8*w*, 781.7*m*, 684.7 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 227 (67200), 252 (sh, 20400), 265 (23800), 275 (sh, 18200), 291 (sh, 21900), 295 (27900), 314 (40900), 336 nm (34500); MS (FAB+): *m*/*z*: 723 $[M]^+$, 523, 465, 329.

Compound 45: A slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 20 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of **34** (471 mg, 1.05 mmol) in dry acetone (15 mL) with a dropping funnel. TLC (silica gel, hexane) was used to monitor the reaction progress. After 3 h, the reaction was quenched with water (100 mL), HCl (10 %, 30 mL), and hexane (100 mL). The aqueous phase was extracted with hexane (2 × 100 mL). The combined organic

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phases were washed with HCl (10%, 2 × 50 mL) and water (50 mL) and dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane) gave **45** as transparent oil (427 mg, 0.48 mmol, 91%). $R_f = 0.18$ (hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): δ = 6.58 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.39 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 1.20–1.13 (m, 12H; Si(C*H*(CH$_3$)$_2$)$_3$), 1.01 (d, ^3J(H,H) = 7.3 Hz, 72H; Si(CH(C*H*$_3$)$_2$)$_3$); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25°C): δ = 156.86 (4C; Ar*C*OSi), 122.57 (2C; Ar*C*), 117.10 (4C; Ar*C*H), 114.12 (2C; Ar*C*H), 81.59 (2C; (R-C≡*C*)$_2$), 73.26 (2C; (R-*C*≡C)$_2$), 17.86 (24C; Si(CH(*C*H$_3$)$_2$)$_3$), 12.60 (12C; Si(*C*H(CH$_3$)$_2$)$_3$); IR (film): $\tilde{\nu}$ = 2945.2*s*, 2892.1*w*, 2867.5*m*, 2150.3*w*, 1582.1*s*, 1463.1*m*, 1426.2*m*, 1388.9*w*, 1344.6*m*, 1305.5*w*, 1241.5*w*, 1228.2*w*, 1178.4*s*, 1072.0*w*, 1031.8*m*, 1008.2*m*, 919.5*w*, 882.5*m*, 858.7*w*, 838.1*w*, 753.2*s*, 680.7 cm^{-1} *m*; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 227 (76300), 229 (73400), 254 (sh, 19800), 267 (23100), 276 (sh, 19900), 296 (28100), 315 (41100), 337 nm (34900); MS (FAB+): *m/z*: 891 [*M*]$^+$, 847.

Compound 35: A flask was charged with **26** (100 mg, 0.28 mmol) and dry, degassed THF (5 mL) and cooled to 0°C. *n*BuLi (1.6 M in hexane, 0.18 mL, 0.29 mmol) was added with stirring. After 1 h at 0°C, CuCl (28.4 mg, 0.29 mmol) was added. The cooling bath was removed and after 90 min the solvent was evaporated by oil pump vacuum until 1 mL remained. Dry, degassed pyridine (4.0 mL, 5.0 mmol) was then added and the solution cooled in an ice bath. A solution of Br-C≡C-C≡C-TMS[42] (83.1 mg, 0.41 mmol) in dry, degassed THF (2 mL) was added dropwise over 2 min with a syringe. As soon as TLC (silica gel, hexane) indicated no further progress (after 50 min), the reaction was quenched. HCl (10%, 20 mL), water (20 mL), and hexane (30 mL) were added. The aqueous phase was extracted with hexane (3 × 30 mL), and the combined organic phases were dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane) afforded **35** as light brown oil (70 mg, 0.143 mmol, 52%). $R_f = 0.22$ (hexane); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25°C): δ = 6.62 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.41 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 0.96 (s, 18H; Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 0.21 (s, 9H; Si(C*H*$_3$)$_3$), 0.18 (s, 12H; Si(C*H*$_3$)$_2$C(CH$_3$)$_3$); ^{13}C NMR (100.5 MHz, CD$_2$Cl$_2$, 25°C): δ = 157.06 (2C; Ar*C*OSi), 121.87 (1C; Ar*C*), 118.31 (2C; Ar*C*H), 115.68 (1C; Ar*C*H), 89.70 (1C; C≡C-C≡C-*C*≡C-Si(CH$_3$)$_3$), 87.93 (1C; C≡C-C≡C-C≡*C*-Si(CH$_3$)$_3$), 77.13 (1C; C≡*C*-C≡C-C≡C-Si(CH$_3$)$_3$), 73.73 (1C; *C*≡C-C≡C-C≡C-Si(CH$_3$)$_3$), 66.86 (1C; C≡C-*C*≡C-C≡C-Si(CH$_3$)$_3$), 61.53 (1C; C≡C-C≡*C*-C≡C-Si(CH$_3$)$_3$), 25.72 (6C; Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 18.45 (2C; Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), −0.52 (3C; C≡C-C≡C-C≡C-Si(*C*H$_3$)$_3$), −4.39 (4C; Si(*C*H$_3$)$_2$C(CH$_3$)$_3$); UV/Vis (CH$_2$Cl$_2$): λ_{max} = 249, 253 (sh), 261, 269 (sh), 284, 302, 323, 346 nm; MS (FAB+): *m/z*: 483 [*M*+H]$^+$.

Compounds 37 and 36: A flask was charged with **34** (258 mg, 0.58 mmol) and dry, degassed THF (10 mL) and cooled to 0°C. *n*BuLi (1.6 M in hexane, 0.38 mL, 0.60 mmol) was added with stirring. After 100 min at 0°C, CuCl (59.5 mg, 0.60 mmol) was added. The cooling bath was removed and after 60 min the solvent was evaporated by oil pump vacuum until 1 mL remained. Dry, degassed pyridine (9.0 mL, 11.6 mmol) was added and the solution cooled in an ice bath. A solution of Br-C≡C-C≡C-TMS[42] (232 mg, 1.15 mmol) in dry, degassed THF (7 mL) was added dropwise over 2 min with a syringe. As soon as TLC (silica gel, hexane) indicated no further progress (after 50 min), the reaction was quenched. HCl (10%, 30 mL), water (20 mL), and hexane (40 mL) were added. The aqueous phase was extracted with hexane (2 × 40 mL), and the combined organic phases were dried over Na_2SO_4. Purification by two-fold column chromatography (silica gel, hexane) gave **36** as transparent oil (63 mg, 0.104 mmol, 18%) and **37** as light brown oil (30 mg, 0.052 mmol, 9%).

Compound 36: $R_f = 0.28$ (hexane); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25°C): δ = 156.26 (2C; Ar*C*OSi), 124.61 (1C; Ar*C*), 117.08 (2C; Ar*C*H), 112.99 (1C; Ar*C*H), 106.98 (1C; *C*≡C-Si(CH(CH$_3$)$_2$)$_3$), 89.83 (1C; C≡*C*-Si(CH(CH$_3$)$_2$)$_3$), 18.65 (6C; Si(CH(*C*H$_3$)$_2$)$_3$), 17.88 (12C; Si(CH(*C*H$_3$)$_2$)$_3$), 12.61 (6C; Si(*C*H(CH$_3$)$_2$)$_3$), 11.32 (3C; Si(*C*H(CH$_3$)$_2$)$_3$); IR (film): $\tilde{\nu}$ = 2944.8*s*, 2867.5*s*, 2149.7*w*, 1576.8*s*, 1464.5*m*, 1427.2*m*, 1350.1*m*, 1247.9*w*, 1176.4*s*, 1031.0*w*, 1015.8*m*, 995.3*w*, 919.6*w*, 882.6*m*, 856.7*w*, 761.8 cm^{-1} *m*; UV/Vis (hexane): λ_{max} = 217, 255 nm; MS (FAB+): *m/z*: 603 [*M*]$^+$, 559.

Compound 37: $R_f = 0.26$ (hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): δ = 6.62 (d, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 6.46 (t, ^3J(H,H) = 2.2 Hz, 1H; Ar*H*), 1.24–1.18 (m, 6H; Si(C*H*(CH$_3$)$_2$)$_3$), 1.06 (d, ^3J(H,H) = 7.3 Hz, 36H; Si(CH(C*H*$_3$)$_2$)$_3$), 0.20 (s, 9H; Si(C*H*$_3$)$_3$); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25°C): δ = 157.46 (2C; Ar*C*OSi), 121.79 (1C; Ar*C*), 117.95 (2C; Ar*C*H), 115.28 (1C; Ar*C*H), 89.65 (1C; C≡C-C≡C-*C*≡C-Si(CH$_3$)$_3$), 87.95 (1C; C≡C-C≡C-C≡*C*-Si(CH$_3$)$_3$), 77.28 (1C; C≡*C*-C≡C-C≡C-Si(CH$_3$)$_3$), 73.64 (1C; *C*≡C-C≡C-C≡C-Si(CH$_3$)$_3$), 66.82 (1C; C≡C-*C*≡C-C≡C-Si(CH$_3$)$_3$), 61.57 (1C; C≡C-C≡*C*-C≡C-Si(CH$_3$)$_3$), 17.99 (12C; Si(CH(*C*H$_3$)$_2$)$_3$), 12.98 (6C; Si(*C*H(CH$_3$)$_2$)$_3$), −0.52 (3C; C≡C-C≡C-C≡C-Si(*C*H$_3$)$_3$); UV/Vis (hexane): λ_{max} = 207, 216 (sh), 223, 236 (sh), 250, 261, 269 (sh), 283, 301, 321, 345 nm; MS (FAB+): *m/z*: 567 [*M*]$^+$, 523.

Compound 38: Two spatula tips of K_2CO_3 were added to a stirred solution of **35** (2.65 g, 5.5 mmol) in wet THF/MeOH 1:1 (100 mL). TLC (silica gel, hexane) indicated completeness of the reaction after 70 min, whereupon water (30 mL), HCl (10%, 10 mL), and hexane (70 mL) were added. The aqueous phase was extracted with hexane (2 × 70 mL), and the combined organic phases were dried over Na_2SO_4. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane) to give **38** as an unstable transparent oil (2.03 g, 4.95 mmol, 90%). $R_f = 0.28$ (hexane); UV/Vis (hexane): λ_{max} = 219, 223, 242, 252, 261 (sh), 275, 291, 310, 331 nm; MS (FAB+): *m/z*: 411 [*M*+H]$^+$, 353, 311.

Compound 40: A slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 20 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of **38** (100 mg, 0.24 mmol) in dry acetone (30 mL) with a dropping funnel. TLC (silica gel, hexane) was used to monitor the reaction progress. After 2 h, the reaction was quenched with water (80 mL), HCl (10%, 20 mL), and hexane (100 mL). The aqueous phase was extracted with hexane (2 × 80 mL). The combined organic phases were washed with HCl (10%, 2 × 50 mL) and water (50 mL) and dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane) afforded **40** as yellow solid (93 mg, 0.11 mmol, 94%). $R_f = 0.07$ (hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): δ = 6.61 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.39 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 0.95 (s, 36H; Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 0.17 (*s*, 24H; Si(C*H*$_3$)$_2$C(CH$_3$)$_3$); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25°C): δ = 156.64 (4C; Ar*C*OSi), 120.94 (2C; Ar*C*), 118.24 (4C; Ar*C*H), 115.73 (2C; Ar*C*H), 77.38 (2C; (R-C≡*C*-C≡C-C≡C)$_2$), 73.80 (2C; (R-*C*≡C-C≡C-C≡C)$_2$), 67.13 (2C; (R-C≡C-*C*≡C-C≡C)$_2$), 64.52 (2C; (R-C≡C-C≡C-*C*≡C)$_2$), 63.57 (2 C; (R-C≡C-C≡*C*-C≡C)$_2$), 62.51 (2C; (R-C≡C-C≡C-C≡*C*)$_2$), 25.59 (12C; Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 18.17 (4C; Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), −4.45 (8C; Si(*C*H$_3$)$_2$C(CH$_3$)$_3$); IR (KBr): $\tilde{\nu}$ = 2955.5*m*, 2930.5*m*, 2895.7*w*, 2858.9*m*, 2182.6*w*, 2159.4*m*, 2057.9*w*, 1578.9*s*, 1471.4*w*, 1425.1*m*, 1372.5*s*, 1259.9*s*, 1171.0*s*, 1030.0*m*, 1004.7*m*, 987.2*w*, 939.1*w*, 831.3*s*, 813.9*w*, 781.6*m*, 741.0*w*, 680.7 cm^{-1} *w*; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 251 (sh, 27700), 262 (41400), 274 (63200), 288 (92500), 303 (135300), 322 (158600), 342 (193700), 360 (94000), 367 (sh, 77200), 396 (26700), 429 (22600), 467 nm (10500); MS (FAB+): *m/z*: 819 [*M*]$^+$.

Compound 39: A spatula tip of K_2CO_3 was added to a stirred solution of **37** (140 mg, 0.26 mmol) in wet THF/MeOH 1:1 (10 mL). TLC (silica gel, hexane) indicated completeness of the reaction after 25 min, whereupon water (20 mL), HCl (10%, 10 mL), and hexane (30 mL) were added. The aqueous phase was extracted with hexane (30 mL), and the combined organic phases were dried over Na_2SO_4. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane) to give a pure fraction of unstable **39** in hexane (≈100%). $R_f = 0.26$ (hexane); UV/Vis (hexane): λ_{max} = 238 (sh), 244 (sh), 252, 262 (sh), 275, 291, 310, 332 nm; MS (FAB+): *m/z*: 495 [*M*+H]$^+$, 451.

Compound 41: The solvent of the hexane fraction of **39** was evaporated, and the residue was dissolved in dry acetone (5 mL). A slurry of TMEDA (0.16 mL, 1.05 mmol) and CuCl (78 mg, 0.8 mmol) in dry acetone (5 mL) was stirred for 10 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (5 mL). To the resulting catalyst was added a solution of **39** (128 mg, 0.26 mmol) in dry acetone (5 mL) with a dropping funnel. TLC (silica gel, hexane) was used to monitor the reaction progress. Upon completion, the reaction was quenched with water (20 mL), HCl (10%, 30 mL), and hexane (80 mL). The aqueous phase was extracted with hexane (2 × 30 mL), and the combined organic phases were dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane) yielded **41** as a yellow solid (64 mg, 0.065 mmol, 25%). $R_f = 0.13$ (hexane); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25°C): δ = 6.69 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.53 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 1.28–1.20 (m, 12H; Si(C*H*(CH$_3$)$_2$)$_3$), 1.08 (d, ^3J(H,H) = 7.1 Hz, 72H; Si(CH(C*H*$_3$)$_2$)$_3$); ^{13}C NMR (100.5 MHz, CD$_2$Cl$_2$, 25°C): δ = 157.56 (4C; Ar*C*OSi), 121.09

(2 C; Ar*C*), 118.29 (4 C; Ar*C*H), 115.94 (1 C; Ar*C*H), 78.10 (2 C; (R-C≡*C*-C≡C-C≡C)$_2$), 73.68 (2 C; (R-*C*≡C-C≡C-C≡C)$_2$), 67.12 (2 C; (R-C≡C-*C*≡C-C≡C)$_2$), 64.62 (2 C; (R-C≡C-C≡C-*C*≡C)$_2$), 63.76 (2 C; (R-C≡C-C≡*C*-C≡C)$_2$), 62.86 (2 C; (R-C≡C-C≡C-C≡*C*)$_2$), 18.01 (24 C; Si(CH(*C*H$_3$)$_2$)$_3$), 13.00 (12 C; Si(*C*H(CH$_3$)$_2$)$_3$); IR (KBr): $\tilde{\nu}$ = 2944.9*s*, 2866.6*m*, 2182.8*m*, 2159.3*m*, 2058.7*w*, 1579.7*s*, 1462.0*m*, 1423.8*m*, 1373.9*m*, 1267.2*m*, 1176.0*s*, 1073.0*w*, 1031.0*m*, 1005.7*m*, 919.9*w*, 882.9*m*, 864.7*w*, 846.6*w*, 825.4*w*, 784.3*w*, 754.2*m*, 691.2 cm^{-1} *m*; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 249 (sh, 26200), 263 (sh, 43200), 275 (67500), 287 (94700), 303 (132600), 323 (155600), 344 (191400), 362 (90700), 368 (sh, 83100), 397 (26900), 429 (22800), 468 nm (10400); MS (FAB +): *m*/*z*: 988 [*M*+H]$^+$, 944.

Compounds 42 and 44: A three-necked flask (500 mL) with gas inlet and dropping funnel was charged with **26** (723 mg, 1.99 mmol) and trimethylsilylacetylene[36] (1.175 g, 11.96 mmol) in dry acetone (100 mL). A mixture of TMEDA (0.52 mL, 3.38 mmol) and CuCl (858 mg, 8.76 mmol) in dry acetone (80 mL) was stirred for 60 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). The solution of alkynes was purged with O$_2$ for 5 min and the catalyst solution was added over 15 min in five portions. O$_2$ was bubbled through the reaction mixture, and the reaction progress was monitored with TLC (silica gel, hexane). After 18 h, more trimethylsilylacetylene (235 mg, 3.98 mmol) was added. After 25 h, the reaction was quenched with HCl (10 %, 40 mL), water (60 mL), and hexane (100 mL). The aqueous phase was extracted with hexane (2 × 80 mL), and the combined organic layers were washed with HCl (10 %, 50 mL) and water (50 mL), before drying over Na$_2$SO$_4$. The residual brown oil was purified with column chromatography (silica gel, hexane) to give **42** as transparent oil (652 mg, 1.42 mmol, 71 %) and **44** as white solid (87 mg, 0.12 mmol, 12 %).

Compound 42: R_f = 0.31 (hexane); ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 6.68 (d, ^3J(H,H) = 2.2 Hz, 2 H; Ar*H*), 6.49 (t, ^3J(H,H) = 2.2 Hz, 1 H; Ar*H*), 0.99 (s, 18 H; Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 0.24 (s, 12 H; Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.23 (s, 9 H; Si(C*H*$_3$)$_3$); ^{13}C NMR (100.5 MHz, [D$_6$]acetone, 25 °C): δ = 157.63 (2 C; Ar*C*OSi), 123.09 (1 C; Ar*C*), 118.28 (2 C; Ar*C*H), 115.50 (1 C; Ar*C*H), 91.37 (1 C; CC-*C*≡C-Si(CH$_3$)$_3$), 88.50 (1 C; C≡C-C≡*C*-Si(CH$_3$)$_3$), 76.99 (1 C; C≡*C*-C≡C-Si(CH$_3$)$_3$), 74.21 (1 C; *C*≡C-C≡C-Si(CH$_3$)$_3$), 25.95 (6 C; Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 18.77 (2 C; Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), −0.49 (3 C; Si(*C*H$_3$)$_3$), −4.37 (4 C; Si(*C*H$_3$)$_2$C(CH$_3$)$_3$); IR (film): $\tilde{\nu}$ = 2957.7*m*, 2930.9*m*, 2898.0*w*, 2859.8*m*, 2209.3*m*, 2101.1*m*, 1578.7*s*, 1472.3*w*, 1463.6*w*, 1426.2*m*, 1390.9*w*, 1357.2*s*, 1299.0*w*, 1252.5*s*, 1225.0*w*, 1169.5*s*, 1030.3*m*, 1001.8*w*, 927.0*s*, 838.6*s*, 781.8*m*, 760.8*w*, 682.6*w*, 647.6*w*, 636.0 cm^{-1} *w*; UV/Vis (hexane): λ_{max} = 213 (sh), 218, 229, 241 (sh), 253, 267, 282, 299 nm; MS (FAB +): *m*/*z*: 459 [*M*+H]$^+$, 401.

Compound 44: R_f = 0.10 (hexane); spectroscopic data: see direct coupling reaction to **44**.

Compound 46: A spatula tip of K$_2$CO$_3$ was added to a stirred solution of **42** (615 mg, 1.34 mmol) in wet THF/MeOH 1:1 (20 mL). TLC (silica gel, hexane) indicated completeness of the reaction after 60 min, whereupon water (40 mL), HCl (10 %, 10 mL), and hexane (50 mL) were added. The aqueous phase was extracted with hexane (2 × 100 mL), and the combined organic phases were dried over Na$_2$SO$_4$. After filtration, the solvent was removed by rotary evaporation until 5 – 10 mL had remained. This solution was purified by column chromatography (silica gel, hexane) to give **46** as labile transparent oil (492 mg, 1.27 mmol, 95 %). R_f = 0.29 (hexane); UV/Vis (hexane): λ_{max} = 211, 220 (sh), 245, 257, 271, 286, 313 nm (sh); MS (FAB +): *m*/*z*: 387 [*M*+H]$^+$, 329.

Compounds 43 and 45: A three-necked flask (500 mL) with gas inlet and dropping funnel was charged with **34** (500 mg, 1.12 mmol) and trimethylsilylacetylene[36] (659 mg, 6.71 mmol) in dry acetone (80 mL). A mixture of TMEDA (0.3 mL, 1.90 mmol) and CuCl (483 mg, 4.92 mmol) in dry acetone (40 mL) was stirred for 30 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (5 mL). The solution of alkynes was purged with O$_2$ for 5 min and the catalyst solution was added over 7 min in four portions. O$_2$ was bubbled through the reaction mixture and the reaction progress was monitored with TLC (silica gel, hexane). After 3 h, more trimethylsilylacetylene (659 mg, 6.71 mmol) was added. After 17 h, the reaction was quenched with HCl (10 %, 50 mL) and hexane (100 mL). The aqueous phase was extracted with hexane (2 × 100 mL), and the combined organic layers were washed with HCl (10 %, 50 mL) and water (50 mL), before drying over Na$_2$SO$_4$. The residual brown oil was purified with column chromatography (silica gel, hexane) to give **43** as light brown oil (395 mg, 0.73 mmol, 65 %) and **45** as transparent oil (170 mg, 0.10 mmol, 17 %).

Compound 43: R_f = 0.22 (hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 6.70 (d, ^3J(H,H) = 2.2 Hz, 2 H; Ar*H*), 6.55 (t, ^3J(H,H) = 2.2 Hz, 1 H; Ar*H*), 1.35 – 1.30 (m, 6 H; Si(C*H*(CH$_3$)$_2$)$_3$), 1.12 (d, ^3J(H,H) = 7.3 Hz, 36 H; Si(CH(C*H*$_3$)$_2$)$_3$), 0.23 (s, 9 H; Si(C*H*$_3$)$_3$); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25 °C): δ = 157.63 (2 C; Ar*C*OSi), 123.14 (1 C; Ar*C*), 117.92 (2 C; Ar*C*H), 114.94 (1 C; Ar*C*H), 91.32 (1 C; C≡C-*C*≡C-Si(CH$_3$)$_3$), 88.52 (1 C; C≡C-C≡*C*-Si(CH$_3$)$_3$), 76.99 (1 C; C≡*C*-C≡C-Si(CH$_3$)$_3$), 74.51 (1 C; *C*≡C-C≡C-Si(CH$_3$)$_3$), 18.21 (12 C; Si(CH(*C*H$_3$)$_2$)$_3$), 13.32 (6 C; Si(*C*H(CH$_3$)$_2$)$_3$), −0.46 (3 C; Si(*C*H$_3$)$_3$); IR (film): $\tilde{\nu}$ = 2946.2*m*, 2893.7*w*, 2868.3*m*, 2208.8*w*, 2100.5*w*, 1577.3*s*, 1464.7*w*, 1425.9*m*, 1359.4*m*, 1251.4*w*, 1176.2*s*, 1071.0*w*, 1031.8*w*, 1015.1*w*, 1000.9*w*, 927.0*m*, 882.7*w*, 846.0*m*, 759.2*m*, 681.9 cm^{-1} *w*; UV/Vis (hexane): λ_{max} = 219, 229 (sh), 254, 267, 282, 299 nm; MS (FAB +): *m*/*z*: 543 [*M*]$^+$, 499.

Compound 45: R_f = 0.10 (hexane); spectroscopical data: see direct coupling reaction to **45**.

Compound 47: A spatula tip of K$_2$CO$_3$ was added to a stirred solution of **43** (238 mg, 0.44 mmol) in wet THF/MeOH 1:1 (10 mL). TLC (silica gel, hexane) indicated completeness of the reaction after 30 min, whereupon water (10 mL), HCl (10 %, 10 mL), and hexane (40 mL) were added. The aqueous phase was extracted with hexane (2 × 50 mL), and the combined organic phases were dried over Na$_2$SO$_4$. After filtration, the solvent was removed by rotary evaporation until 5 – 10 mL remained. This solution was purified by column chromatography (silica gel, hexane) to give a pure fraction of unstable **47** in hexane (≈100 %). R_f = 0.28 (hexane); UV/Vis (hexane): λ_{max} = 212, 245, 257, 271, 286, 306 nm (sh); MS (FAB +): *m*/*z*: 471 [*M*+H]$^+$, 427.

Compound 48: A slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 20 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of **46** (170 mg, 0.44 mmol) in dry acetone (10 mL) with a dropping funnel. TLC (silica gel, hexane) was used to monitor the reaction progress. After 18 h, the reaction was quenched with water (10 mL), HCl (10 %, 10 mL), and hexane (30 mL). The aqueous phase was extracted with hexane (40 mL), and the combined organic phases were dried over Na$_2$SO$_4$. Purification by column chromatography (silica gel, hexane → CH$_2$Cl$_2$/hexane 10:9) gave **48** as yellow plates (57 mg, 0.07 mmol, 34 %). R_f = 0.08 (hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 6.61 (d, ^3J(H,H) = 2.2 Hz, 4 H; ArH), 6.38 (t, ^3J(H,H) = 2.2 Hz, 2 H; ArH), 0.95 (s, 36 H; Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 0.17 (s, 24 H; Si(C*H*$_3$)$_2$C(CH$_3$)$_3$); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25 °C): δ = 156.55 (4 C; Ar*C*OSi), 121.37 (2 C; Ar*C*), 118.04 (4 C; Ar*C*H), 115.39 (2 C; Ar*C*H), 77.56 (2 C; (R-C≡*C*-C≡C)$_2$), 73.90 (2 C; (R-*C*≡C-C≡C)$_2$), 67.10 (2 C; (R-C≡C-*C*≡C)$_2$), 63.55 (2 C; (R-C≡C-C≡)$_2$), 25.59 (12 C; Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 18.17 (4 C; Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), −4.45 (8 C; Si(*C*H$_3$)$_2$C(CH$_3$)$_3$); IR (KBr): $\tilde{\nu}$ = 2955.8*m*, 2930.3*m*, 2885.9*m*, 2858.6*m*, 2201.0*m*, 2135.9*w*, 1579.6*s*, 1471.4*m*, 1425.1*m*, 1390.4*w*, 1356.1*s*, 1258.5*s*, 1201.2*w*, 1171.7*s*, 1053.2*s*, 1030.5*m*, 1005.0*m*, 939.2*w*, 904.3*m*, 829.9*s*, 813.2*w*, 781.6*m*, 740.2*w*, 678.0 cm^{-1} *m*; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 235 (64000), 253 (35000), 266 (40500), 278 (62300), 293 (114000), 305 (80300), 313 (sh, 69800), 346 (32000), 372 (34400), 403 nm (21500); MS (FAB +): *m*/*z*: 771 [*M*]$^+$, 713.

Compound 49: A slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 20 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of **47** (320 mg, 0.68 mmol) in dry acetone (10 mL) with a dropping funnel. TLC (silica gel, hexane) was used to monitor the reaction progress. After 18 h, the reaction was quenched with water (10 mL), HCl (10 %, 10 mL), and hexane (30 mL). The aqueous phase was extracted with hexane (40 mL), and the combined organic phases were dried over Na$_2$SO$_4$. Purification by column chromatography (silica gel, hexane → hexane/CH$_2$Cl$_2$ 19:1) yielded **49** as a light brown oil (292 mg, 0.31 mmol, 92 %). R_f = 0.04 (hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 6.65 (d, ^3J(H,H) = 2.2 Hz, 4 H; ArH), 6.49 (t, ^3J(H,H) = 2.2 Hz, 2 H; ArH), 1.27 – 1.18 (m, 12 H; Si(C*H*(CH$_3$)$_2$)$_3$), 1.8 (d, ^3J(H,H) = 7.3 Hz, 72 H; Si(CH(C*H*$_3$)$_2$)$_3$); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25 °C): δ = 157.28 (4C; Ar*C*OSi), 121.62 (2C; Ar*C*), 118.00 (4C; Ar*C*H), 115.35 (2C; Ar*C*H), 78.06 (2C; (R-C≡*C*-C≡C)$_2$), 74.15 (2C; (R-*C*≡C-C≡C)$_2$), 67.41 (2C; (R-C≡C-*C*≡C)$_2$), 63.92 (2C; (R-C≡C-C≡*C*)$_2$), 18.17 (24C; Si(CH(*C*H$_3$)$_2$)$_3$), 12.93 (12C; Si(*C*H(CH$_3$)$_2$)$_3$); IR (film): $\tilde{\nu}$ = 2945.7*s*, 2892.2*w*, 2967.6*m*, 2203.3*m*, 2136.5*w*, 1578.6*s*, 1463.6*m*, 1425.6*m*, 1389.6*w*, 1358.6*s*, 1249.4*w*, 1202.4*w*, 1177.6*s*, 1053.9*w*, 1031.6*m*, 1014.8*w*, 998.0*w*, 883.3*m*, 854.3*w*, 756.9*s*, 681.8 cm^{-1} *s*; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 237 (63 800), 254 (40 800), 266 (44 700), 280 (64 400), 295 (111 500), 305 (sh, 82 400), 313 (72 100), 347 (33 500), 373 (35 500), 404 nm (21 800); MS (FAB+): *m*/*z*: 939 $[M]^+$, 895.

Compounds 50 and 52: A Schlenk flask was charged with **46** (166 mg, 0.43 mmol) and dry, degassed THF (15 mL) and cooled to 0 °C. *n*BuLi (1.6 M in hexane, 0.28 mL, 0.45 mmol) was added with stirring. After 1 h at 0 °C, CuCl (44 mg, 0.45 mmol) was added. The cooloing bath was removed, and after 30 min the solvent was evaporated by oil pump vacuum until 4–5 mL remained. Dry, degassed pyridine (5 mL, 62 mmol) was added and the solution cooled to 0 °C. A solution of Br-C≡C-C≡C-TMS[42] (95 mg, 0.474 mmol) in dry, degassed THF (1 mL) was added dropwise over 1 minute with a syringe. As TLC (silica gel, hexane) indicated very slow reaction progress after 10 min, the cooling bath was removed, and, after 28 min, a second portion of pure Br-C≡C-C≡C-TMS[42] (95 mg, 0.474 mmol) was added. After 50 min, HCl (10 %, 50 mL), water (80 mL), and hexane (80 mL) were added. The aqueous phase was extracted with hexane (2 × 80 mL). The combined organic phases were washed with HCl (10 %, 100 mL) and water (2 × 100 mL) and dried over Na$_2$SO$_4$. Purification by column chromatography (silica gel, hexane) afforded two fractions, consisting of mixtures of **52** and **53** (fraction I), and **50** and **51** (fraction II): yields could not be determined. 1) **52** and **53** (fraction I): R_f = 0.39 (hexane); MS (FAB+): *m*/*z*: 555 $[M(\mathbf{52})+\mathrm{H}]^+$, 497 and 483 $[M(\mathbf{53})+\mathrm{H}]^+$, 425; 2) **50** and **51** (fraction II): R_f = 0.35 (hexane); MS (FAB+): *m*/*z*: 507 $[M(\mathbf{50})+\mathrm{H}]^+$, 449 and 435 $[M(\mathbf{51})+\mathrm{H}]^+$, 377.

Compound 51: The solvent of mixture **50**/**51** was removed by rotary evaporation until 2–3 mL remained, and wet THF/MeOH 1:1 (20 mL) and a spatula tip of K$_2$CO$_3$ were added with stirring. TLC (silica gel, hexane) indicated completeness of the reaction after 20 min, whereupon water (20 mL), HCl (10 %, 10 mL), and hexane (20 mL) were added. The aqueous phase was extracted with hexane (30 mL), and the combined organic phases were dried over Na$_2$SO$_4$. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane) to give pure **51** in hexane: yield could not be determined. R_f = 0.35 (hexane); UV/Vis (hexane): $\lambda_{\max}$ = 221, 229, 246, 258, 269, 279, 289, 305, 325, 348, 374 nm; MS (FAB+): *m*/*z*: 435 $[M+\mathrm{H}]^+$, 377.

Compound 53: The solvent of mixture **52**/**53** was removed by rotary evaporation until 2–3 mL remained, and wet THF/MeOH (1:1, 20 mL) and a spatula tip of K$_2$CO$_3$ were added with stirring. TLC (silica gel, hexane) indicated completeness of the reaction after 10 min, whereupon water (20 mL), HCl (10 %, 10 mL), and hexane (20 mL) were added. The aqueous phase was extracted with hexane (30 mL), and the combined organic phases were dried over Na$_2$SO$_4$. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane) to give pure **53** in hexane: yield could not be determined. R_f = 0.38 (hexane); UV/Vis (hexane): $\lambda_{\max}$ (ε) = 239 (sh), 253 (sh), 266, 276, 292, 311, 319 (sh), 334, 348 (sh), 373, 402, 436 nm; MS (FAB+): *m*/*z*: 483 $[M+\mathrm{H}]^+$, 425.

Compound 54: The solvent of the hexane fraction of **51** was removed by rotary evaporation until 2–3 mL remained, and dry acetone (7 mL) was added. A slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 20 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of **51** with a dropping funnel. TLC (silica gel, hexane) was used to monitor the reaction progress. After 1 h, the reaction was quenched with water (80 mL), HCl (10 %, 20 mL), and hexane (100 mL). The aqueous phase was extracted with hexane (2 × 80 mL). The combined organic phases were washed with HCl (10 %, 2 × 50 mL) and water (50 mL) and dried over Na$_2$SO$_4$. Purification by column chromatography (silica gel, hexane) gave **54** as orange solid (16 mg, 0.02 mmol, 9 % based on butadiyne **46**); R_f = 0.09 (hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 6.62 (d, ^3J(H,H) = 2.2 Hz, 4H; Ar*H*), 6.39 (t, ^3J(H,H) = 2.2 Hz, 2H; Ar*H*), 0.94 (s, 36H; Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 0.17 (s, 24H; Si(C*H*$_3$)$_2$C(CH$_3$)$_3$); ^{13}C NMR (100.5 MHz, CDCl$_3$, 25 °C): δ = 156.66 (4C; Ar*C*OSi), 120.76 (2C; Ar*C*), 118.29 (4C; Ar*C*H), 115.88 (2C; Ar*C*H), 77.53 (2C; (R-C≡*C*-C≡C-C≡C-C≡C)$_2$), 73.73 (2C; (R-*C*≡C-C≡C-C≡C-C≡C)$_2$), 67.04 (2C; (R-C≡C-*C*≡C-C≡C-C≡C)$_2$), 64.45 (2C; (R-C≡C-C≡C-*C*≡C-C≡C)$_2$), 63.61 (2C; (R-C≡C-C≡*C*-C≡C-C≡C)$_2$), 63.39 (2C; (R-C≡C-C≡C-C≡C-*C*≡C)$_2$), 63.30 (2C; (R-C≡C-C≡C-C≡C-C≡*C*)$_2$), 62.57 (2C; (R-C≡C-C≡C-C≡*C*-C≡C)$_2$), 25.59 (12C; Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 18.17 (4C; Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), −4.45 (8C; Si(*C*H$_3$)$_2$C(CH$_3$)$_3$); IR (KBr): $\tilde{\nu}$ = 2955.6*m*, 2929.0*m*, 2857.9*m*, 2193.7*m*, 2111.6*m*, 2008.5*w*, 1581.7*s*, 1462.4*w*, 1424.6*m*, 1391.1*m*, 1361.7*w*, 1314.1*m*, 1259.3*m*, 1173.5*s*, 1031.8*m*, 1005.1*w*, 907.2*w*, 830.3*s*, 813.8*w*, 782.1*m*, 738.9*w*, 677.3 cm^{-1} *w*; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 250 (30 100), 265 (33 700), 280 (sh, 55 600), 295 (sh, 96 000), 309 (169 600), 327 (318 400), 347 (435 200), 362 (386 500), 382 (316 100), 403 (sh, 103 500), 434 (28 800), 471 (17 700), 514 nm (6900); MS (FAB+): *m*/*z*: 867 $[M]^+$.

Compound 55: A Schlenk flask was charged with the degassed hexane fraction of **38** (28 mg, 0.066 mmol) and the solvent was removed by oil pump vacuum, until 4–5 mL remained. Dry, degassed THF (5 mL) was added, and the flask was cooled to 0 °C. *n*BuLi (1.6 M in hexane, 0.04 mL, 0.069 mmol) was dropped into the solution with stirring. After 45 min at 0 °C, CuCl (6.8 mg, 0.069 mmol) was added, and the cooling bath was removed. After 30 min, dry, degassed pyridine (3 mL, 37.1 mmol) was added followed by a solution of Br-C≡C-C≡C-TMS[42] (26 mg, 0.132 mmol) in dry, degassed THF (1 mL), which was added dropwise over 3 min with a syringe. As soon as TLC (silica gel, hexane) indicated no further progress, the reaction was quenched. After 50 min, HCl (10 %, 15 mL), water (15 mL), and hexane (20 mL) were added. The organic phase was washed with HCl (10 %, 50 mL) and water (50 mL) and dried over Na$_2$SO$_4$. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane) to give pure **55** in hexane: yield could not be determined. R_f = 0.23 (hexane); UV/Vis (hexane): $\lambda_{\max}$ = 236 (sh), 246 (sh), 253, 264, 274, 288, 295 (sh), 304, 313, 327 (sh), 338, 361, 390, 422 nm; MS (FAB+): *m*/*z*: 531 $[M+\mathrm{H}]^+$, 473.

Compound 56: The solvent of the hexane fraction of **55** was removed by rotary evaporation until 2–3 mL remained, and wet THF/MeOH 1:1 (10 mL) and a spatula tip of K$_2$CO$_3$ were added with stirring. TLC (silica gel, hexane) indicated completeness of the reaction after 25 min, whereupon water (20 mL), HCl (10 %, 10 mL), and hexane (30 mL) were added. The aqueous phase was extracted with hexane (30 mL), and the combined organic phases were dried over Na$_2$SO$_4$. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane) to give pure **56** in hexane: yield could not be determined. R_f = 0.24 (hexane); UV/Vis (hexane): $\lambda_{\max}$ = 219, 232, 243, 253 (sh), 258, 267, 282, 297, 307, 320 (sh), 330, 348 (sh), 354, 381, 412 nm; MS (FAB+): *m*/*z*: 459 $[M+\mathrm{H}]^+$.

Compounds 57, 58 and 54: The solvent of the hexane fraction of **56** was removed by rotary evaporation until 2–3 mL remained, and dry acetone (7 mL) was added. A slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 20 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of **56** with a dropping funnel. TLC (silica gel, hexane) was used to monitor the reaction progress. After 3 h, the reaction was quenched with water (80 mL), HCl (10 %, 20 mL), and hexane (100 mL). The aqueous phase was extracted with hexane (2 × 80 mL). The combined organic phases were washed with HCl (10 %, 2 × 50 mL) and water (50 mL) and dried over Na$_2$SO$_4$. Purification and separation attempts by column chromatography (silica gel, hexane) and HPLC (Nucleosil, hexane and petrol ether, respectively) only afforded a mixture of **57**, **58**, and **54** as red solid: yields could not be determined. R_f = 0.09 (hexane); MS (FAB+): *m*/*z*: 915 $[M(\mathbf{57})]^+$, 891 $[M(\mathbf{58})]^+$, 867 $[M(\mathbf{54})]^+$.

Compound 59: PPh$_3$ (193 mg, 0.74 mmol) was added at room temperature to a stirred solution of [G-2]′-ol[46] (362 mg, 0.59 mmol) and CBr$_4$ (244 mg, 0.74 mmol) in dry THF (2 mL). The reaction was monitored by TLC (silica gel, hexane/ethyl acetate 7:3). After 40 min, water (40 mL) and CH$_2$Cl$_2$ (40 mL) were added. The aqueous phase was extracted with CH$_2$Cl$_2$ (50 mL), and the combined organic phases were dried over Na$_2$SO$_4$. Column chromatography (silica gel, CH$_2$Cl$_2$ → hexane/ethyl acetate 4:1) yielded **59** as clear liquid (299 mg, 0.44 mmol, 75 %). R_f = 0.44 (hexane/ethyl acetate 4:1); 1H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.34–7.24 (m, 20H; PhH), 4.51 (s, 8H; ArCH2O), 3.69–3.63 (m, 6H; 4 $(CH_2)_2CHCH_2Br$, 2 $(CH_2)_2CHOCH_2CH$), 3.61–3.50 (m, 10H; 8 $ArCH_2OCH_2$, 2 CH_2Br), 2.28–2.21 (m, 1H; $(CH_2)_2CHCH_2Br$); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 138.26$ (4C; PhC), 128.34, 127.59, 127.55 (20C; PhCH), 78.50 (2C; $(CH_2)_2CHOCH_2$), 73.35 (4C; $ArCH_2O$), 70.09 (4C; $ArCH_2OCH_2$), 69.07 (2C; OCH_2CH), 42.00 (1C; $CHCH_2Br$), 33.59 (1C; CH_2Br); IR (film): $\tilde{\nu} = 3087.5$*w*, 3063.1*w*, 3029.7*m*, 2862.9*s*, 1604.4*w*, 1496.1*m*, 1473.4*w*, 1453.3*m*, 1365.8*m*, 1307.2*w*, 1261.0*m*, 1206.3*m*, 1101.4*s*, 1028.2*w*, 909.0*w*, 847.8*w*, 736.4*m*, 697.6 cm^{-1} *m*; MS (FAB +): *m/z*: 677 $[M]^+$, 391, 181.

Compound 60: K_2CO_3 (691 mg, 5.0 mmol) was added to a solution of **59** (2.69 g, 4.0 mmol), **28** (266 mg, 2.0 mmol), and [18]crown-6 (106 mg, 0.4 mmol) in dry acetone (50 mL). The suspension was heated at reflux, and the reaction progress was monitored by TLC (silica gel, hexane/ethyl acetate 7:3). After 38 h, more [18]crown-6 (106 mg, 0.4 mmol) was added. After 7 d, water (50 mL) and CH_2Cl_2 (50 mL) were added, and the aqueous phase was extracted with CH_2Cl_2 (2 × 90 mL). The combined organic phases were washed with water (100 mL) and dried over Na_2SO_4. Column chromatography (silica gel, hexane/ethyl acetate 4:1) afforded **60** as light brown oil (1.49 g, 1.12 mmol, 56 %). $R_f = 0.21$ (hexane/ethyl acetate 4:1); ^1H NMR (400 MHz, $[D_6]$acetone, 25 °C): $\delta = 7.34–7.21$ (m, 40H; PhH), 6.66 (d, $^3J(H,H) = 2.2$ Hz, 2H; ArH), 6.57 (t, $^3J(H,H) = 2.2$ Hz, 1H; ArH), 4.48 (s, 16H; $ArCH_2O$), 4.06 (d, $^3J(H,H) = 5.5$ Hz, 4H; CH_2OAr), 3.79–3.72 (m, 8H; $(CH_2)_2CHCH_2OAr$), 3.69–3.63 (m, 4H; $(CH_2)_2CHOCH_2CH$), 3.59–3.50 (m, 16H; $ArCH_2OCH_2$), 2.84 (s, 1H; C≡C-H), 2.31–2.28 (m, 2H; $(CH_2)_2CHCH_2OAr$); ^{13}C NMR (100.5 MHz, $[D_6]$acetone, 25 °C): $\delta = 161.16$ (2C; $ArCOCH_2$), 139.70 (8C; PhC), 129.01, 128.22, 128.10 (40C; PhCH), 124.44 (1C; ArC), 116.16 (2C; ArCH), 103.72 (1C; ArCH), 83.99 (1C; C≡C-H), 79.34 (4C; $(CH_2)_2CHOCH_2$), 78.72 (1C; C≡C-H), 73.62 (8C; $ArCH_2O$), 71.04 (8C; $ArCH_2OCH_2$), 68.83 (4C; OCH_2CHCH_2OAr), 67.02 (2C; $CHCH_2OAr$), 41.61 (2C; $CHCH_2OAr$); IR (film): $\tilde{\nu} = 3285.2$*m*, 3087.5*w*, 3063.1*w*, 3029.8*m*, 2906.3*s*, 2862.9*s*, 2107.8*w*, 1586.9*s*, 1495.9*w*, 1471.9*w*, 1453.8*m*, 1433.1*w*, 1366.3*m*, 1251.0*m*, 1205.8*w*, 1099.2*s*, 1028.2*w*, 910.5*w*, 847.2*m*, 736.3*s*, 697.3*m*, 666.0 cm^{-1} *w*; MS (FAB +): *m/z*: 1327 $[M]^+$, 1236, 781, 181.

Compound 61: A Schlenk flask was charged with **60** (896 mg, 0.68 mmol) and dry, degassed THF (23 mL) and cooled to 0 °C. *n*BuLi (1.6 M in hexane, 0.44 mL, 0.70 mmol) was added with stirring. After 1 h at 0 °C, CuCl (69.5 mg, 0.70 mmol) was added. The cooling bath was removed and after 30 min the solvent was evaporated by oil pump vacuum until 3–4 mL remained. Dry, degassed pyridine (8.0 mL, 99.0 mmol) was added and the solution cooled to 0 °C. A solution of Br-C≡C-C≡C-TMS[42] (149 mg, 0.74 mmol) in dry, degassed THF (2 mL) was added dropwise over 2 min with a syringe. When TLC (silica gel, hexane/ethyl acetate 7:3) indicated completion, the reaction was quenched. After 15 min, HCl (10 %, 30 mL), water (30 mL), and Et_2O (30 mL) were added. The aqueous phase was extracted with Et_2O (2 × 60 mL). The combined organic phases were washed with water (100 mL) and dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane/ethyl acetate 4:1 → 3:1 → 7:3) afforded **61** as light brown oil (502 mg, 0.35 mmol, 51 %). $R_f = 0.44$ (hexane/ethyl acetate 7:3); 1H NMR (400 MHz, $[D_6]$acetone, 25 °C): $\delta = 7.30–7.21$ (m, 40H; PhH), 6.73 (d, $^3J(H,H) = 2.2$ Hz, 2H; ArH), 6.63 (t, $^3J(H,H) = 2.2$ Hz, 1H; ArH), 4.8 (s, 16H; $ArCH_2O$), 4.07 (d, $^3J(H,H) = 5.6$ Hz, 4H; CH_2OAr), 3.79–3.70 (m, 8H; $(CH_2)_2CHCH_2OAr$), 3.69–3.65 (m, 4H; $(CH_2)_2CHOCH_2CH$), 3.59–3.50 (m, 16H; $ArCH_2OCH_2$), 2.31–2.28 (*m*, 2H; $(CH_2)_2CHCH_2OAr$), 0.23 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (100.5 MHz, $[D_6]$acetone, 25 °C): $\delta = 161.22$ (2C; $ArCOCH_2$), 139.66 (8C; PhC), 129.01, 128.13, 128.09 (40C; PhCH), 122.03 (1C; ArC), 111.98 (2C; ArCH), 105.78 (1C; ArCH), 90.22 (1C; C≡C-C≡C-C≡C-$Si(CH_3)_3$), 88.26 (1C; C≡C-C≡C-C≡C-$Si(CH_3)_3$), 79.35 (4C; $(CH_2)_2CHOCH_2$), 78.31 (1C; C≡C-C≡C-C≡C-$Si(CH_3)_3$), 73.64 (1C; C≡C-C≡C-C≡C-$Si(CH_3)_3$), 73.63 (8C; $ArCH_2O$), 71.04 (8C; $ArCH_2OCH_2$), 68.79 (4C; OCH_2CHCH_2OAr), 67.15 (1C; C≡C-C≡C-C≡C-$Si(CH_3)_3$), 67.14 (2C; $CHCH_2OAr$), 62.05 (1C; C≡C-C≡C-C≡C-$Si(CH_3)_3$), 41.55 (2C; $CHCH_2OAr$), −0.64 (3C; $Si(CH_3)_3$); UV/Vis (hexane/ethyl acetate 4:1): $\lambda_{max} = 248$, 260, 270 (sh), 284, 302, 321, 345 nm; MS (FAB +): *m/z*: 1447 $[M]^+$, 1356, 901, 181.

Compound 62: A spatula tip of K_2CO_3 was added to a stirred solution of **61** (404 mg, 0.28 mmol) in wet THF/MeOH 1:1 (20 mL). TLC (silica gel, hexane/ethyl acetate 7:3) indicated completeness of the reaction after 40 min, whereupon water (20 mL), HCl (10 %, 5 mL), and Et_2O (30 mL) were added. The aqueous phase was extracted with Et_2O (2 × 30 mL), and the combined organic phases were dried over Na_2SO_4. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to give **62** as an unstable brown oil (347 mg, 0.25 mmol, 90 %). $R_f = 0.34$ (hexane/ethyl acetate 7:3); UV/Vis (hexane/ethyl acetate 4:1): $\lambda_{max} = 247$, 253, 275, 292, 311, 333 nm; MS (FAB +): *m/z*: 1375 $[M]^+$, 1283.

Compound 63: A slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 15 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of **62** (61 mg, 0.04 mmol) in dry acetone (10 mL) with a dropping funnel. TLC (silica gel, hexane/ethyl acetate 7:3) was used to monitor the reaction progress. After 20 min, the reaction was quenched with water (25 mL), HCl (10 %, 15 mL), and Et_2O (60 mL). The aqueous phase was extracted with Et_2O (60 mL). The combined organic phases were washed with HCl (10 %, 50 mL) and water (50 mL) and dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane/ethyl acetate 4:1 → 7:3) gave **63** as yellow solid (37 mg, 0.01 mmol, 61 %). $R_f = 0.39$ (hexane/ethyl acetate 7:3); 1H NMR (400 MHz, $[D_6]$acetone, 25 °C): $\delta = 7.31–7.21$ (m, 80H; PhH), 6.77 (d, $^3J(H,H) = 2.2$ Hz, 4H; ArH), 6.66 (t, $^3J(H,H) = 2.2$ Hz, 2H; ArH), 4.48 (s, 32H; $ArCH_2O$), 4.08 (d, $^3J(H,H) = 5.6$ Hz, 8H; CH_2OAr), 3.79–3.71 (m, 16H; $(CH_2)_2CHCH_2OAr$), 3.70–3.65 (m, 8H; $(CH_2)_2CHOCH_2CH$), 3.59–3.50 (m, 32H; $ArCH_2OCH_2$), 2.33–2.27 (m, 4H; $(CH_2)_2CHCH_2OAr$); ^{13}C NMR (100.5 MHz, $[D_6]$acetone, 25 °C): $\delta = 161.27$ (4C; $ArCOCH_2$), 139.69 (16C; PhC), 129.02, 128.20, 128.11 (80C; PhCH), 121.22 (2C; ArC), 112.40 (4C; ArCH), 106.57 (2C; ArCH), 79.37 (8C; $(CH_2)_2CHOCH_2$), 79.30 (2C; $(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C)_2$), 73.65 (16C; $ArCH_2O$), 73.64 (2C; $(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C)_2$), 71.07 (16C; $ArCH_2OCH_2$), 68.79 (8C; OCH_2CHCH_2OAr), 67.24 (4C; $CHCH_2OAr$), 67.11 (2C; $(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C)_2$), 64.75 (2C; $(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C)_2$), 64.04 (2C; $(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C)_2$), 63.53 (2C; $(R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C)_2$), 41.57 (4C; $CHCH_2OAr$); IR (KBr): $\tilde{\nu} =$ 3062.9*w*, 3029.7*w*, 2921.6*m*, 2861.7*m*, 2160.0*m*, 2110.1*w*, 2057.0*w*, 1586.1*m*, 1496.3*w*, 1453.6*m*, 1431.2*w*, 1365.2*m*, 1263.0*m*, 1204.9*w*, 1172.0*w*, 1101.2*s*, 1028.2*w*, 908.3*w*, 838.9*w*, 736.7*m*, 698.1 cm^{-1} *m*; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 249 (sh, 34800), 262 (sh, 55200), 275 (74900), 289 (95100), 303 (121300), 323 (137300), 345 (164100), 368 (82400), 397 (30700), 431 (23400), 469 nm (11700); MS (FAB +): *m/z*: 2749 $[M]^+$, 2659.

Compounds 64, 66, 67 and 63: A Schlenk flask was charged with **62** (342 mg, 0.25 mmol) and dry, degassed THF (12 mL) and cooled to 0 °C. *n*BuLi (1.6 M in hexane, 0.16 mL, 0.26 mmol) was added with stirring. After 1 h at 0 °C, CuCl (25.6 mg, 0.26 mmol) was added. The cooling bath was removed and after 30 min the solvent was evaporated by oil pump vacuum until 5–6 mL remained. Dry, degassed pyridine (6.0 mL, 74.2 mmol) was added and the solution cooled to 0 °C. A solution of Br-C≡C-C≡C-TMS[42] (55 mg, 0.27 mmol) in dry, degassed THF (1 mL) was added dropwise over 2 min with a syringe. As TLC (silica gel, hexane/ethyl acetate 7:3) indicated very slow reaction progress, a second quantity of pure Br-C≡C-C≡C-TMS[42] (27.5 mg, 0.14 mmol) was added. After 50 min, HCl (10 %, 30 mL), water (40 mL), and Et_2O (80 mL) were added. The aqueous phase was extracted with Et_2O (2 × 80 mL). The combined organic phases were washed with HCl (10 %, 80 mL) and water (80 mL) and dried over Na_2SO_4. Separation and purification of the starting material (**62**) and the two products ([G-3]′-C_{10}TMS and [G-3]′-C_{10}H) by three-fold column chromatography (silica gel, hexane/ethyl acetate 4:1 → 3:1 → 7:3) was not successful. Therefore, the solvent mixture was removed by rotary evaporation until 10 mL remained and dry acetone (10 mL) was added. The mixture was then subjected to Hay coupling conditions. Hence, a slurry of TMEDA (0.5 mL, 3.3 mmol) and CuCl (1.0 g, 10.2 mmol) in dry acetone (50 mL) was stirred for 20 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (10 mL). To the resulting catalyst was added a solution of the mixture with a dropping funnel. TLC (silica gel, hexane/ethyl acetate 7:3) monitored the reaction progress. After 2 h, the reaction was quenched with water (80 mL), HCl (10 %, 20 mL), and Et_2O (100 mL). The aqueous phase was extracted with Et_2O (2 × 80 mL). The combined organic phases were washed with HCl (10 %, 2 × 50 mL) and water (50 mL) and dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane/ethyl acetate 4:1 → 7:3) gave a pure fraction of [G-3]′-C_{10}TMS (**64**) and a mixture, which was separated and purified by HPLC (Nucleosil, hexane/ethyl acetate 3:1) affording [G-3]′-C_{20}-[G-3]′ (**66**), [G-3]′-C_{16}-[G-3]′ (**67**), and [G-3]′-C_{12}-[G-3]′ (**63**) as red, orange, and yellow solids, respectively.

1) **[G-3]′-C$_{10}$TMS (64)**: yield could not be determined. $R_f = 0.43$ (hexane/ethyl acetate 7:3); UV/Vis (hexane/ethyl acetate 7:3): $\lambda_{max} = 248$, 265, 274, 289, 304, 314, 338, 363, 391, 423 nm; MS (FAB+): *m*/*z*: 1496 $[M{+}H]^+$.

2) **[G-3]′-C$_{20}$-[G-3]′ (66)** (HPLC fraction I): 17 mg (0.01 mmol, 5% based on **62**); $R_f = 0.39$ (hexane/ethyl acetate 7:3); ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): $\delta = 7.30$–7.23 (m, 80 H; Ph*H*), 6.77 (d, ^3J(H,H) = 2.2 Hz, 4 H; Ar*H*), 6.68 (t, ^3J(H,H) = 2.2 Hz, 2 H; Ar*H*), 4.48 (s, 32 H; ArC*H*$_2$O), 4.08 (d, ^3J(H,H) = 5.6 Hz, 8 H; C*H*$_2$OAr), 3.77–3.74 (m, 16 H; (C*H*$_2$)$_2$CHCH$_2$OAr), 3.72–3.64 (m, 8 H; (CH$_2$)$_2$C*H*OCH$_2$CH), 3.59–3.50 (m, 32 H; ArCH$_2$-OC*H*$_2$), 2.32–2.28 (m, 4 H; (CH$_2$)$_2$C*H*CH$_2$OAr); ^{13}C NMR (100.5 MHz, [D$_6$]acetone, 25 °C): $\delta = 161.31$ (4 C; Ar*C*OCH$_2$), 139.71 (16 C; Ph*C*), 129.04, 128.22, 128.13 (80 C; Ph*C*H), 121.04 (2 C; Ar*C*), 112.58 (4 C; Ar*C*H), 106.84 (2 C; Ar*C*H), 79.40 (8 C; (CH$_2$)$_2$*C*HOCH$_2$), 78.36 (2 C; (R-C≡*C*-C≡C-C≡C-C≡C-C≡C)$_2$), 73.68 (16 C; Ar*C*H$_2$O), 73.64 (2 C; (R-*C*≡C-C≡C-C≡C-C≡C-C≡C)$_2$), 71.11 (16 C; ArCH$_2$O*C*H$_2$), 68.84 (8 C; O*C*H$_2$CH-CH$_2$OAr), 67.33 (4 C; CH*C*H$_2$OAr), 67.24 (2 C; (R-C≡C-*C*≡C-C≡C-C≡C-C≡C)$_2$), 64.71 (2 C; (R-C≡C-C≡C-*C*≡C-C≡C-C≡C)$_2$), 64.09 (2 C; (R-C≡C-C≡*C*-C≡C-C≡C-C≡C)$_2$), 63.97 (4 C; (R-C≡C-C≡C-C≡C-*C*≡*C*-C≡C)$_2$), 63.84 (4 C; (R-C≡C-C≡C-C≡C-C≡C-*C*≡*C*)$_2$), 63.79 (2 C; (R-C≡C-C≡C-C≡*C*-C≡C-C≡C)$_2$), 41.60 (4 C; *C*HCH$_2$OAr); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 252 (sh, 112700), 263 (114900), 273 (110600), 288 (sh, 112700), 300 (137700), 316 (203400), 334 (328700), 355 (516200), 370 (sh, 505100), 379 (604600), 394 (561400), 415 (322600), 437 (sh, 88900), 461 (sh, 33000), 500 (19200), 546 nm (7400); MS (FAB+): *m*/*z*: 2798 $[M{+}H]^+$, 2707.

3) **[G-3]′-C$_{16}$-[G-3]′ (67)** (HPLC fraction II): 37 mg (0.01 mmol, 10% based on **62**); $R_f = 0.39$ (hexane/ethyl acetate 7:3); ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): $\delta = 7.32$–7.22 (m, 80 H; Ph*H*), 6.78 (d, ^3J(H,H) = 2.2 Hz, 4 H; Ar*H*), 6.68 (t, ^3J(H,H) = 2.2 Hz, 2 H; Ar*H*), 4.49 (s, 32 H; ArC*H*$_2$O), 4.08 (d, ^3J(H,H) = 5.6 Hz, 8 H; C*H*$_2$OAr), 3.80–3.73 (m, 16 H; (C*H*$_2$)$_2$CHCH$_2$OAr), 3.71–3.64 (m, 8 H; (CH$_2$)$_2$C*H*OCH$_2$CH), 3.60–3.51 (m, 32 H; ArCH$_2$-OC*H*$_2$), 2.33–2.27 (m, 4 H; (CH$_2$)$_2$C*H*CH$_2$OAr); ^{13}C NMR (100.5 MHz, [D$_6$]acetone, 25 °C): $\delta = 161.33$ (4 C; Ar*C*OCH$_2$), 139.73 (16 C; Ph*C*), 129.04, 128.24, 128.13 (80 C; Ph*C*H), 121.08 (2 C; Ar*C*), 112.53 (4 C; Ar*C*H), 106.77 (2 C; Ar*C*H), 79.55 (2 C; (R-C≡*C*-C≡C-C≡C-C≡C)$_2$), 79.40 (8 C; (CH$_2$)$_2$*C*HOCH$_2$), 73.68 (16 C; Ar*C*H$_2$O), 73.52 (2 C; (R-*C*≡C-C≡C-C≡C-C≡C)$_2$), 71.11 (16 C; ArCH$_2$O*C*H$_2$), 68.82 (8 C; O*C*H$_2$CHCH$_2$OAr), 67.29 (4 C; CH*C*H$_2$OAr), 67.07 (2 C; (R-C≡C-*C*≡C-C≡C-C≡C)$_2$), 64.68 (2 C; (R-C≡C-C≡C-*C*≡C-C≡C)$_2$), 63.97 (2 C; (R-C≡C-C≡*C*-C≡C-C≡C)$_2$), 63.89 (2 C; (R-C≡C-C≡C-C≡C-*C*≡C)$_2$), 63.84 (2 C; (R-C≡C-C≡C-C≡C-C≡*C*)$_2$), 63.65 (2 C; (R-C≡C-C≡C-C≡*C*-C≡C)$_2$), 41.60 (4 C; *C*HCH$_2$OAr); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 251 (sh, 65300), 264 (67000), 276 (sh, 74100), 291 (sh, 102100), 308 (149400), 326 (233300), 346 (307900), 363 (302100), 382 (254700), 402 (123500), 434 (32200), 470 (19500), 514 nm (8400); MS (FAB+): *m*/*z*: 2798 $[M{+}H]^+$, 2707.

4) **[G-3]′-C$_{12}$-[G-3]′ (63)** (HPLC fraction III): 15 mg (0.01 mmol, 5% based on **62**); $R_f = 0.39$ (hexane/ethyl acetate 7:3); spectroscopic data: see direct coupling reaction to [G-3]′-C$_{12}$-[G-3]′ (**63**).

Compound 65: The solvent of the hexane/ethyl acetate fraction of [G-3]′-C$_{10}$TMS (**64**) was removed by rotary evaporation until 2–3 mL remained, and wet THF/MeOH 1:1 (10 mL) and a spatula tip of K_2CO_3 were added with stirring. TLC (silica gel, hexane/ethyl acetate 7:3) indicated completeness of the reaction after 25 min, whereupon water (20 mL), HCl (10%, 10 mL), and Et_2O (30 mL) were added. The aqueous phase was extracted with Et_2O (30 mL), and the combined organic phases were dried over Na_2SO_4. After filtration, the solvent was removed by rotary evaporation until 5–10 mL remained. This solution was purified by column chromatography (silica gel, hexane/ethyl acetate 7:3) to give pure [G-3]′-C$_{10}$H (**65**) in hexane/ethyl acetate solution: yield could not be determined; $R_f = 0.34$ (hexane/ethyl acetate 7:3); UV/Vis (hexane/ethyl acetate 7:3): $\lambda_{max} = 247$, 256 (sh), 267 (sh), 283, 297, 309, 330 (sh), 355, 382, 414 nm; MS (FAB+): *m*/*z*: 1424 $[M{+}H]^+$.

Compounds 66, 68 and 67: The solvent of the hexane/ethyl acetate fraction of [G-3]′-C$_{10}$H (**65**) was removed by rotary evaporation until 2–3 mL remained, and dry acetone (7 mL) was added. A slurry of TMEDA (0.16 mL, 1.05 mmol) and CuCl (78 mg, 0.8 mmol) in dry acetone (5 mL) was stirred for 10 min, whereupon it was repeatedly filtered until no more solid precipitated in the filtrate. After each filtration, the filter cake was washed with dry acetone (5 mL). To the resulting catalyst was added a solution of [G-3]′-C$_{10}$H (**65**) with a dropping funnel. TLC (silica gel, hexane/ethyl acetate 7:3) monitored the reaction progress. After 2 h, the reaction was quenched with water (20 mL), HCl (10%, 30 mL), and Et_2O (80 mL). The aqueous phase was extracted with Et_2O (2 × 30 mL), and the combined organic phases were dried over Na_2SO_4. Purification by column chromatography (silica gel, hexane/ethyl acetate 7:3), followed by HPLC (Nucleosil, hexane/ethyl acetate 3:1) gave [G-3]′-C$_{20}$-[G-3]′ (**66**), [G-3]′-C$_{18}$-[G-3]′ (**68**), and [G-3]′-C$_{16}$-[G-3]′ (**67**) as red, red-orange and orange solids, respectively.

1) **[G-3]′-C$_{20}$-[G-3]′ (66)** (HPLC fraction I): 2 mg (0.001 mmol, 1% based on **62**); $R_f = 0.39$ (hexane/ethyl acetate 7:3); spectroscopic data: see other coupling reaction to [G-3]′-C$_{20}$-[G-3]′ (**66**).

2) **[G-3]′-C$_{18}$-[G-3]′ (68)** (HPLC fraction II): 2 mg (0.001 mmol, 1% based on **62**); $R_f = 0.39$ (hexane/ethyl acetate 7:3); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 251 (100300), 262 (99500), 276 (96300), 289 (sh, 110200), 303 (sh, 147200), 322 (227700), 342 (366800), 356 (sh, 376900), 364 (459400), 379 (430200), 397 (304100), 420 (sh, 115000), 449 (29000), 487 (17200), 532 nm (7100); MS (FAB+): *m*/*z*: 2822 $[M{+}H]^+$, 2731.

3) **[G-3]′-C$_{16}$-[G-3]′ (67)** (HPLC fraction III): 1 mg (0.001 mmol, 1% based on **62**); $R_f = 0.39$ (hexane/ethyl acetate 7:3); spectroscopic data: see other coupling reaction to [G-3]′-C$_{16}$-[G-3]′ (**67**).

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