Alkyne Migration in Alkylidene Carbenoid Species: A New Method of Polyyne Synthesis

Sara Eisler, Navjot Chahal, Robert McDonald, and Rik R. Tykwinski*[a]

Dedicated to Professor Ronald Caple on the occasion of his 65th birthday

Abstract: The synthesis of conjugated polyyne structures via a modification of the Fritsch–Buttenberg–Wiechell (FBW) rearrangement is reported. Our adaptation provides for the 1,2-migration of an alkyne in a carbene/carbenoid intermediate that is conveniently effected via lithium–halogen exchange with the appropriate dibromo-olefinic precursor. This rearrangement is quite rapidly accomplished under mild conditions (hexane solution, −78 °C), and the seemingly high migratory aptitude of the alkynyl moiety provides for efficient rearrangement. This, in turn, allows for multiple rearrangements in a single molecule, greatly facilitating the construction of highly unsaturated substrates. This procedure is exploited for the rapid synthesis of symmetrical and unsymmetrical 1,3,5-hexatriynes, extended polyynes, and aryl polyyne building blocks. Most significantly, many of these structures have been or would be difficult to access via more traditional transition metal catalyzed homo- or cross-coupling techniques.

Keywords: alkynes · carbenes · carbenoids · nanostructures · polyynes

Introduction

A great diversity of molecules with conjugated enyne and polyyne substructures have been proposed or realized,[1–4] including macrocycles,[5] liquid crystals,[6] oligomers,[7] and carbon networks.[4, 8] In addition to their engaging molecular structures, many of these carbon rich compounds have unique electronic, mechanical and structural characteristics, as well as other desirable materials properties.[4] Extended polyyne chains with a conjugated skeleton composed only of sp-hybridized carbon have been sought for many years.[9] Early work from the groups of Bohlmann, Jones, and Walton afforded several oligomeric series, with sp-carbon chains as long as -$(C\equiv C)_{16}$-, but characterization was limited.[10] More recent efforts toward the realization of polyynes and the penultimate sp-carbon allotrope carbyne, are motivated both by a fundamental interest in their unique linear, conjugated framework[11] and a more applied interest in their use as molecular wires to mediate communication between terminal metal centers.[12] As well, the synthesis of cyclic molecular carbon allotropes composed only of acetylenic carbon units has remained an active and challenging goal,[13] research inspired at least in part by the potential role of these cyclic molecules in the mechanism of fullerene formation.[14]

One of the oldest and perhaps most general routes toward the synthetic elaboration of an alkyne framework is oxidative coupling.[15] This methodology, developed by Glaser,[16] and later refined by Eglinton/Galbraith,[17] and Hay,[18] is used to combine two terminal alkynes via the an intervening Cu^I/Cu^{II} intermediate. These general methods have been used to make a range of symmetrical diynes and polyynes, as well as to close macrocyclic systems. Complementary to this is the Cadiot–Chodkiewicz reaction,[19] which couples a terminal acetylene and a haloacetylene to give unsymmetrical polyyne products, also via a cuprate intermediate. The recent development of numerous palladium catalyzed coupling protocols for alkynes has greatly expanded the realm of alkyne synthesis,[20] although their usefulness to date has been predominantly limited to the terminal functionalization of acetylenes and diacetylenes.

The major limitation to the above methods lies in the fact that they all require the prior synthesis of a terminal alkyne/polyyne as one or both of the synthetic precursors to an extended product. While this is not necessarily a problem for di- and even triacetylenes, the formation of longer acetylenic units without terminal functionality almost always affords a highly unstable species that is difficult or impossible to manipulate.

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[a] Prof. R. R. Tykwinski, S. Eisler, N. Chahal, Dr. R. McDonald
Department of Chemistry
University of Alberta
Edmonton, Alberta, T6G 2G2 (Canada)
Fax: (+1) 780 492-8231
E-mail: rik.tykwinski@ualberta.ca

Structural data and procedures for the synthesis of compounds **5a–j**, **6a–j**, **7a–j**, **12a**,**b**, **13a**,**b**, **15**, **17–19**, **21–23**, and **25–27**; ^1H and ^{13}C NMR spectra for all new compounds are available as Supporting Information at http://www.chemeurj.org/ or from the author.

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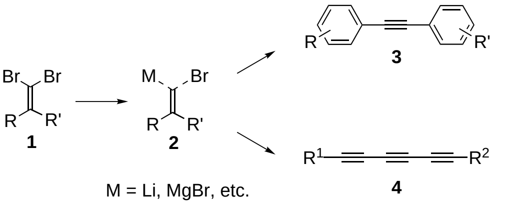
Several approaches are available that strive to circumvent the difficulties associated with the instability of terminal alkynes. For example, methods for the direct coupling of trialkylsilyl acetylenes have been developed, as have methods for the in situ generation and reaction of terminal alkynes under the appropriate coupling conditions.[21, 22] Other options include a variety of protocols in which the polyyne framework is completed in the final step of the synthesis through either elimination or extrusion of a suitable functional group. While these routes have afforded a number of interesting derivatives, in most cases their generality has yet to be established.[23] Thus, as the prevalence of extended acetylenic structures in organic chemistry continues to expand, there is a concurrent need for more versatile synthetic protocols.

The transformation of 1,1-dihalo-2,2-diarylalkenes **1** into tolans **3** was originally reported by Fritsch, Buttenberg, and Wiechell (Scheme 1).[24] This process, which is known to generally proceed through a carbenoid intermediate **2**, has become a well-established method for alkyne synthesis, and the general rearrangement now bears their names.[25] Over the course of the last century, this general transformation has been successfully applied to numerous systems in which the migrating group has been an aryl or heteroaryl moiety, a hydrogen atom, and to a lesser extent an alkenyl or alkyl group. Conspicuously absent from the above list is the ethynyl moiety, which to the best of our knowledge has not been demonstrated to migrate in a Fritsch–Buttenburg–Wiechell rearrangement.

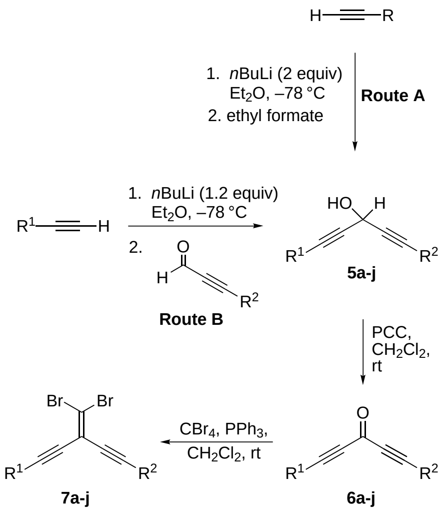


Scheme 1.

We have recently communicated that alkynes do indeed readily undergo 1,2-shifts in vinylidene carbenoid intermediates (e.g., **2** where R = R′ = -C≡C-R),[26] in a facile reaction that ultimately affords good yields of the desired polyyne **4**.[27, 28] The requisite 1,1-dibromo-2,2-diethynylethene precursors **1** are easily accessible and can be strategically functionalized in order to provide polyyne derivatives that would be difficult or impossible to access by other methods. In general, the rearrangements proceed without the substantial formation of by-products, allowing for facile purification and isolation of the desired product, often without column chromatography. In this paper, we report a full account of the synthetic utility of our new method, including the formation of linear polyynes, extended and highly unsaturated aryl polyyne building blocks, as well as the solid-state crystallographic analysis of two highly unsaturated polyyne derivatives, compounds **20** and **29**.

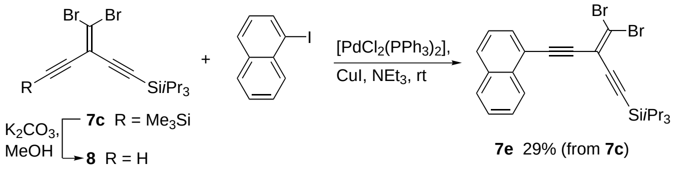
Results and Discussion

1,1-Dibromo-2,2-diethynylethenes (**7a–j**) are the backbone of this alkylidene carbene chemistry, and the general route for their synthesis based on the adaptation of known methods is shown in Scheme 2. Alcohols **5** can be made by either of two routes: Route A relies on the condensation of two equivalents of the appropriate lithium acetylide with ethyl formate to afford symmetrical derivatives **5a**,**b**,**f**, **g**, and **j**.[29] Route B provides unsymmetrical alcohols **5c–e** and **5h**,**i** via addition of the appropriately substituted lithium acetylide into an α,β-ethynyl aldehyde.[30] The alcohols **5a–j** can be effectively oxidized to the corresponding ketones **6a–j** with either PCC or $BaMnO_4$. PCC is generally more effective for larger scale reactions (i.e., >1 g), whereas $BaMnO_4$ provides a more procedurally facile formation of the ketone on smaller scales. It is worth noting that if the ketone product shows limited stability, the typically clean reaction mixture can simply be plugged through silica gel with CH_2Cl_2, and this solution carried on directly to the dibromo-olefination step, which is also conducted in CH_2Cl_2 (e.g., **5h** → **7h**). Vinyl bromides **7a–j** were then realized via the method of Corey and Fuchs.[30a, 31] This reaction is usually complete in less two hours, and affords good yields of the desired products, although reduced chemical stability for some derivatives resulted in lower yields.



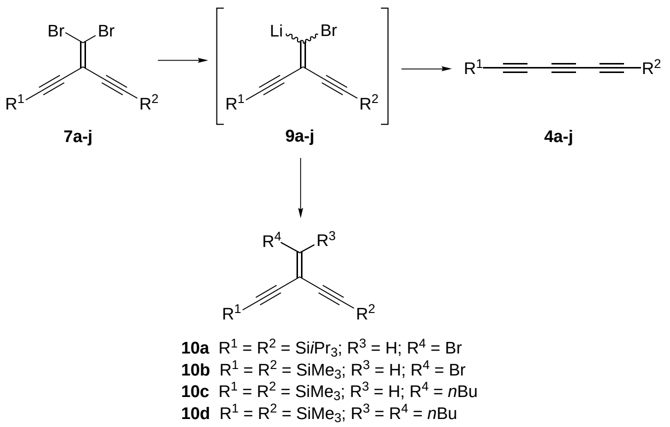
Scheme 2.

We envisioned an alternative entry into aryl substituted 1,1-dibromo-olefines via protiodesilylation of the differentially protected diyne **7c**, followed by palladium catalyzed cross-coupling of the terminal acetylene **8** with an iodo- or bromoarene [Eq. (1)].[32] The formation of **8** via reaction with K_2CO_3 in wet methanol proceeds without problem. Unfortunately, attempts to elaborate **8** under various cross-coupling conditions with iodoarenes have, to date, been ineffective. For example, the reaction of **8** with 1-iodonaphthalene using standard Sonogashira reaction conditions gave only 29% yield of the desired product **7e**. In general, these reactions provide low yields of the desired product, as well as numerous side products that make purification challenging. These results suggest that cross-coupling of the terminal alkyne of one molecule of **8** with the vinyl bromide moiety of a second equivalent of **8** effectively competes with the intended cross-coupling with the iodoarene.



(1)

Our initial attempts to induce 1,2-alkyne migration in a vinylidene carbene/carbenoid species employed dibromo-olefin **7a** (Scheme 3). Using conditions known to facilitate lithium halogen exchange in this molecule,[33] a THF solution of **7a** was treated with *n*BuLi at −78 °C and the solution slowly warmed to various temperatures. These reactions did not, however, afford appreciable amounts of **4a**, regardless of temperature or reaction time. While analysis of these product mixtures did suggest the formation of trace amounts of **4a**, as detected by mass spectral analysis, the protonated species **10a** was the only identifiable product. Likewise, reactions conducted in Et_2O and dioxane were equally unsuccessful (Table 2). Although disappointing, these results were not completely surprising, as vinyl lithium intermediates **9a** and **9b** generated in THF or Et_2O have been successfully trapped with electrophiles at low temperature.[33, 34]



Scheme 3.

Köbrich has previously demonstrated that solvent polarity can play a defining role in the success of the FBW rearrangement.[35] Assuming that the solvating ability of ethereal solvents was a stabilizing factor that prevented or retarded collapse of the vinyl lithium intermediate **9a**, the rearrangement was attempted in less polar, noncoordinating solvents. To our gratification, reactions conducted in hexanes, benzene, and cyclohexene all gave good yields of the triyne **4a** (Table 2).[36] Whereas the reaction in benzene was necessarily conducted at warmer temperatures (ca. −15 °C), reaction in hexanes or cyclohexene was most efficient when initiated at −78 °C.

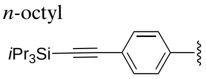
Table 2. Yield of triyne **7a** as a function of solvent.

Solvent	Yield [%]
THF	< 5
Et_2O	< 5
dioxane	< 5
hexane	70
benzene	80
cyclohexene	65

Thus, the optimized general procedure for this process has been established as the following. Vinyl bromide **7a** is dissolved in *rigorously* dried hexanes, cooled to −78 °C, and 1.2 equiv of *n*BuLi is slowly added over about two minutes. The reaction is warmed to about −10 °C over a period of 30 min to 1 h, and then quenched via addition of an aqueous NH_4Cl solution. The product, formed in high yield, can then be isolated pure following work-up by passing the crude product through a plug of silica gel.

The conditions employed for the successful rearrangement of **7a** have been less reliable with the bis(trimethylsilyl) derivative **7b**.[37] The overall yield for this rearrangement is typically lower and is also accompanied, unlike other rearrangements, by the formation of varying amounts of several by-products, identified by ^1H NMR spectroscopic and MS analysis as predominantly **10b**, **c**, and **d**. The rearrangement reaction with differentially protected **7c**, on the other hand, cleanly gave the triyne **4c**. This suggested that perhaps the presence of a triisopropylsilyl protected alkyne moiety was somehow important to facilitate the rearrangement. The rearrangement of 1-naphthyl derivative **7d** to the TMS protected triyne **4d** in 70% yield without by-products, however, showed that the presence of the TIPS-C≡C moiety is not a requirement. Comparable to the formation of **4d**, the rearrangement of TIPS protected dibromo-olefin **7e** provided a good yield of triyne **4e**. Thus, in addition to pendant trialkylsilyl functionality, aryl (**7d**, **e**, **h**, **j**) and alkyl (**7f**, **g**, **i**) substituents are clearly tolerated by the rearrangement conditions.[22a, 38] Also noteworthy is the formation of more elaborate aryl tetrayne building block **4h**, which features differential silyl protecting groups that would allow for further derivatization of this skeleton.

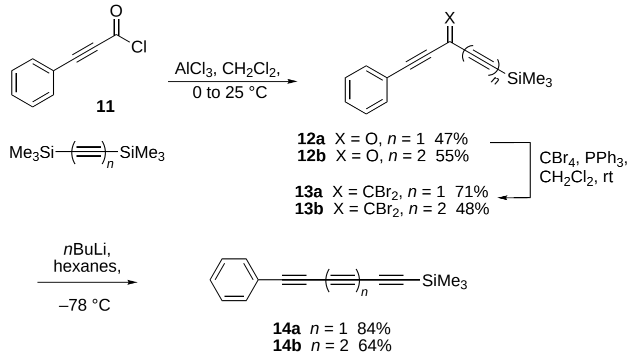
Table 1. Summary of synthetic yields for compounds **4**–**7**.

Cpd	R^1	R^2	**5** [%]	**6** [%]	**7** [%]	**4** [%]
a	iPr_3Si	iPr_3Si	[33]	[33]	[33]	70
b	Me_3Si	Me_3Si	[52]	[52]	[30a]	50
c	iPr_3Si	Me_3Si	[30a]	[30a]	[30a]	61
d	1-naphthyl	Me_3Si	60	54	54	70
e	1-naphthyl	iPr_3Si	55	47	82	62
f	*n*Bu	*n*Bu	92[53]	73[54]	40	80
g	*n*-octyl	*n*-octyl	76[55]	87[55]	54	66
h	Me_3Si		31	–	53[a]	61
i	Me_3Si	*n*Bu	98	57	60	82
j	2-thienyl	2-thienyl	40	50	47	64

[a] Two-step yield from alcohol.

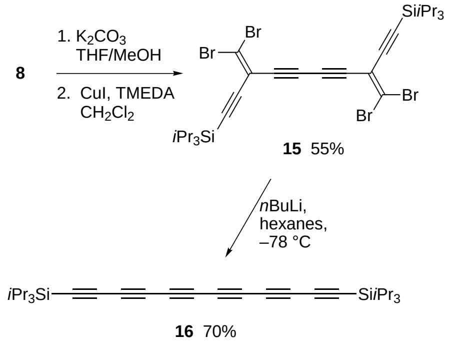
In general, the rearrangements in Table 1 are complete within minutes of *n*-BuLi addition, as monitored by TLC analysis. If the reaction is conducted under rigorous anhydrous conditions, there is minimal formation of non-polar byproducts. Empirical evidence suggests that lithium halogen exchange is a more rapid process than quenching of the BuLi by adventitious water. The presence of water in the reaction mixture does, however, result in in situ protonation of the intermediate carbenoid species, to give for example, **10a**. This significantly complicates purification of the desired triyne due to very similar retention times for the two species on common chromatographic supports and reemphasizes the need to maintain anhydrous reagents and reaction conditions.

Complementary to the route outlined above, Scheme 4 demonstrates the facile synthesis of an unsymmetrical tri- and tetrayne, beginning from the acid chloride **11**. Friedel–Crafts acylation of **11** with either bis(trimethylsilyl)acetylene or bis(trimethylsilyl)butadiyne gave ynones **12a** and **b**, respectively.[39] Dibromo-olefination then afforded **13a** and **b**, and subsequent rearrangement gave the triyne **14a** in 84 % yield and the tetrayne **14b** in 64 % yield. As acetylenic carboxylic acids are readily available via condensation of the appropriate lithium acetylide and CO_2,[40] this pathway nicely broadens the scope of polyyne products potentially accessible using this methodology.



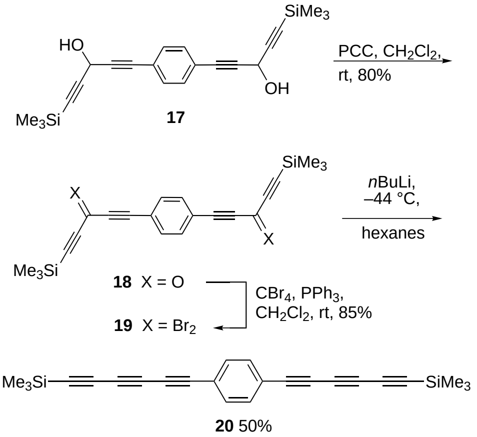
Scheme 4.

Our intention to exploit this method for formation of extended polyyne chains was explored via the assembly of dodecahexayne **16** (Scheme 5). The terminal alkyne of enediyne **8** was oxidatively homocoupled[15, 18] to give the dimer **15** as a yellow oil, which was easily purified by passing the reaction mixture through a plug of silica with hexanes. The moderate yield of **15** likely results from competition from Castro–Stevens coupling, in which the Cu-acetylide cross-couples with the dibromo-olefin moiety.[41, 42] To date, we have been unable to discover copper-catalyzed homocoupling conditions that can improve the yield of this or analogous reactions. Following the general procedure, tetrabromide **15** was rearranged with 2.4 equiv of *n*BuLi at low temperature. TLC analysis of the reaction mixture over time shows the progressive rearrangement of each vinyl bromide moiety, and, ultimately the 1,3,5,7,9,11-dodecahexayne (**16**) was the only nonpolar species observed by TLC analysis. After work-up, **16** was isolated as a yellow/orange solid in 70 % overall yield, representing an impressive 84 % yield for each rearrangement event.



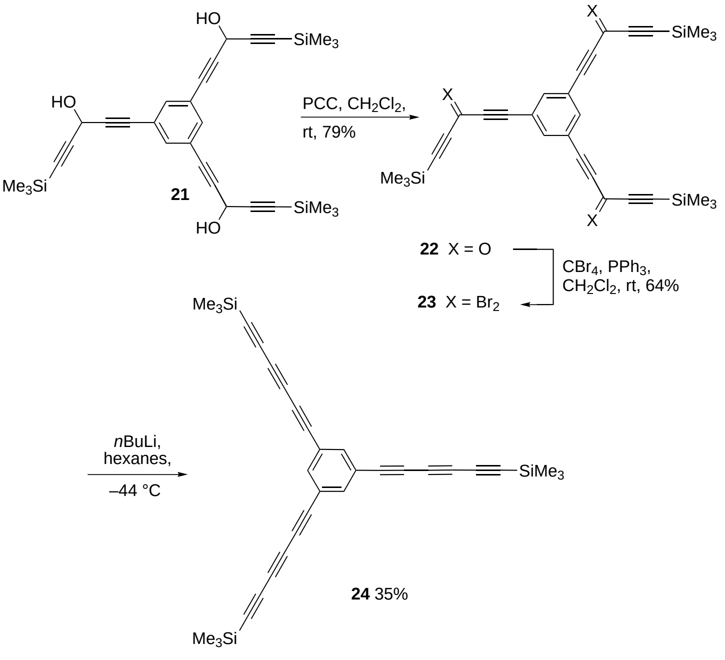
Scheme 5.

In addition to the synthesis of polyynes such as **16**, we expected that alkyne migration would allow us to explore the formation of highly unsaturated aryl-polyyne building blocks that would be difficult to achieve using established palladium catalyzed, cross-coupling conditions. This concept is demonstrated in Scheme 6 with hexayne **20**. Diol **17** was obtained as mixture of diastereomers from the condensation of the bis(lithium acetylide) of 1,4-diethynylbenzene with trimethylsilyl propargyl aldehyde. This diol was easily oxidized to the diketone **18**, and dibromo-olefination then provided tetrabromide **19**. Compound **19** is rather insoluble in hexanes at −78 °C, and the rearrangement was therefore initiated at −44 °C. Work-up and purification by column chromatography gave **20** in 50 % yield.



Scheme 6.

Tris(lithiation) of 1,3,5-triethynylbenzene in Et_2O followed by condensation with trimethylsilyl propargyl aldehyde gave the triol **21** in 42 % yield (Scheme 7). The PCC oxidation of **21** gave trione **22** as a stable colorless, solid, and subsequent dibromo-olefination gave hexabromide **23**. The three-fold rearrangement of **23** was initiated at −78 °C, and the heterogeneous solution was allowed to warm slowly to −10 °C over the course of an hour. Nonayne **24** was isolated in 35 % yield as a creme colored solid, representing an average of 70 % yield for each individual rearrangement.

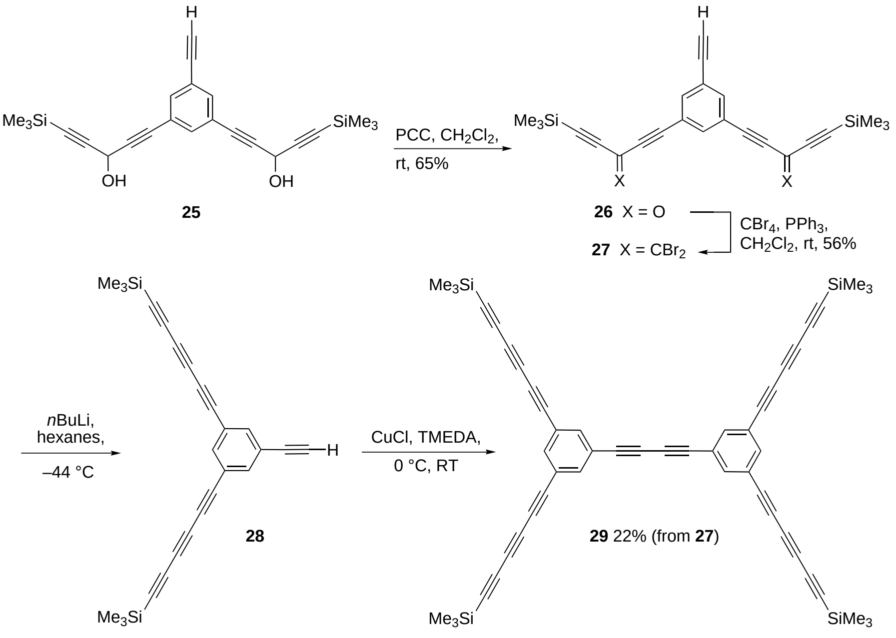


Scheme 7.

Whereas compound **24** is stable if left in a dilute hexane solution under refrigeration (4 °C), it decomposes over time if left neat.

The synthesis of triol **21** was always accompanied by the formation of moderate amounts of diol **25** (Scheme 8), the result of incomplete reaction of the precursor lithium acetylide with trimethylsilyl propargyl aldehyde. As the isolation of **25** was straightforward, it represented an opportunity to probe the scope of our new methodology. In particular, we sought to test the sequence of reactions in the presence of a terminal acetylene, in the pursuit of large carbon rich polyyne networks. Diol **25** was oxidized to dione **26** and dibromo-olefination gave **27** in a moderate 56 % yield. Anticipating that the deprotonation of the terminal acetylene would compete with lithium halogen exchange, 3.6 equivalents of *n*BuLi were utilized to form heptayne **28**, a molecule that shows reduced stability when neat. Compound **28** was then carried on to an oxidative coupling reaction under Hay conditions, to afford the extended tetradecayne **29**. In spite of its highly unsaturated, polyyne framework, **29** shows surprising stability, and could be fully characterized spectroscopically. In particular, the ^{13}C NMR spectrum of this highly symmetrical molecule shows the eight unique resonances for the sp-hybridized carbons. The electrospray mass spectrum in the presence of AgOTf distinctly shows the parent signal of $[\mathbf{28}+Ag]^+$ at *m*/*z* 887.

Solid-state characterization: Crystallization of **20** from a concentrated hexanes/CH_2Cl_2 solution via diffusion of MeOH at 4 °C afforded single crystals suitable for X-ray crystallographic analysis. Two crystallographically unique molecules are present in the unit cell. Both molecules show a slight, graceful curving of the individual triyne moieties (Figure 1). The observed bond angles and lengths for both molecules are, however, unremarkable. The solid state packing of **20** is shown from two different perspectives in Figure 1, and reveals a high degree of alignment along both the crystallographic *a*- and *b* axes. Along the *a* axis, alternating layers, individually composed of only crystallographically unique molecule A or molecule B, are observed. Within each layer, parallel alignment of neighboring molecules is present, and analysis of packing parameters with respect to topochemical polymerization along either of these layers demonstrates similar characteristics for the intermolecular arrangement. This analysis shows the closest intermolecular distance *R*1,6 (i.e., between C1 and C6), at 5.2 and 5.3 Å for molecules A and B, respectively, is well outside the desired range of 3.5 – 4 Å required for topochemical poly-



Scheme 8.

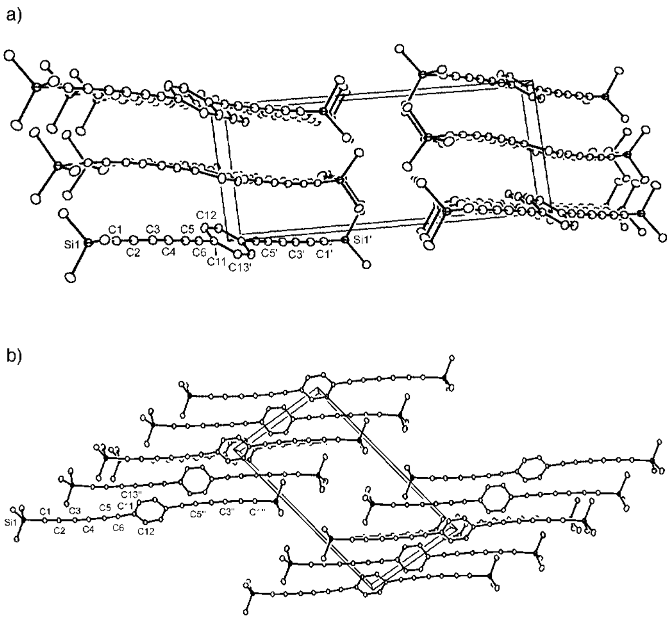


Figure 1. Illustration of crystal packing for compound **20** with the unit cell boundaries as indicated (hydrogen atoms have been omitted); a) view direction parallel to the crystallographic *a* axis, with atom labels for molecule A, and b) view direction parallel to the crystallographic *b* axis, with atom labels for molecule B.

merization.[43, 44] The stacking angle, ϕ, between molecules ($\approx 34^\circ$ in both cases) as well as the stacking distance, d, (9.1 Å in both cases) also deviate from their optimal values for 1,6-addition of $\phi = 27^\circ$ and $d = 7.5$ Å, respectively. Thus, polymerization in the solid state along the a-axis is not likely favorable.

A situation of pseudo-stacking between the crystallographically independent molecules is seen when viewing down the *b* axis. Stacking parameters indicate that from this crystallographic perspective, a 1,4-addition process is possible.[43, 45] The stacking angle $\phi = 45$ is optimal, and two intermolecular contacts $R1,4 = 4.0$ Å and $R3,6 \approx 3.9$ Å are both in the desired range (i.e., ≤ 4 Å). The stacking distance $d = 5.5$ Å is also reasonable for 1,4-addition. Indeed, warming the crystals to room temperature for periods of up to an hour results in a gradual darkening and the formation of an intractable solid.[46] It seems plausible, therefore, that the parallel alignment of the molecules in the solid state leads to their demise at ambient temperature, albeit apparently in a non-regioselective manner likely caused by competing 1,4- and 3,6-polymerization processes.

Single crystals of tetradecayne **29** suitable for X-ray analysis were grown by diffusion of MeOH into a hexanes/CH_2Cl_2 solution at $-10\,^\circ C$, and an ORTEP diagram is shown in Figure 2a. Although positional disorder increases toward the trimethylsilyl substituted termini of the individual triacetylene chains and hampers refinement of this structure, the overall solid state characteristics of this highly unsaturated molecule are still clearly evident. The two aryl rings of the molecule are nearly coplanar, whereas the four 3,5-triyne units gently bend above and below the aryl diyne plane. Analysis of the solid state packing shows that the aryl rings of neighboring are within 3° of coplanarity. They are separated at a distance of 3.4 Å and are offset in a manner expected for face to face π-stacking. Each such "face-to-face" pair of neighboring molecules is related by a center of inversion, affording an alternating packing motif to accommodate the bulk of the trimethylsilyl groups (Figure 2b). While the carbon atoms of neighboring butadiynyl groups approach at a distance that might allow for 1,4-addition in a topchemical polymerization reaction ($R1,4 = 4.2$ Å), the stacking angle of $\phi = 70^\circ$ is well outside of the range necessary for this to occur. Thus, single crystalline **29** remains reasonably stable at room temperature for periods of up to several days.

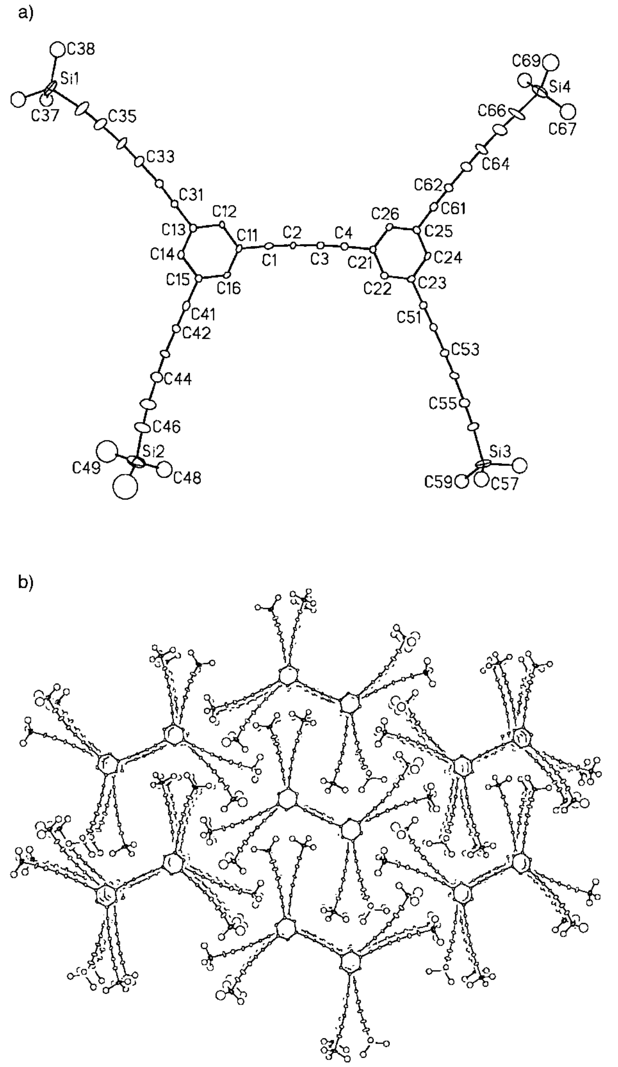


Figure 2. a) ORTEP drawing for compound **29**. b) View of crystal packing for **29** approximately along the crystal *a* axis (*n*-hexane solvent molecules and hydrogen atoms removed for clarity).

Conclusions

We have outlined the broad synthetic utility of an alkylidene carbene/carbenoid rearrangement for polyyne formation. The success of these reactions derives from the seemingly high migratory aptitude of the alkynyl group in alkylidene carbene/carbenoid intermediates, which are easily generated via lithium–halogen exchange between 1,1-dibromo-2,2-diethynylethenes and *n*BuLi. This rearrangement can be effected on a number of substrates, and it tolerates silyl, aryl, acetylenic, and alkyl substitution in the formation of symmetrical and unsymmetrical polyynes. Most significantly, the ability to accomplish up to three consecutive/sequential rearrangements within the same molecule in a single step has been demonstrated and promises to provide a synthetic route to a wider range of useful and interesting polyynes. The majority of the new polyyne derivatives show reasonable chemical stability, and in two cases, the origin of this (in)stability is explained via single crystal X-ray analysis and examination of solid state packing.

Experimental Section

General procedures and methods: Reagents were purchased reagent grade from commercial suppliers and used without further purification. THF, Et_2O, were distilled from sodium/benzophenone, hexane and benzene distilled from CaH. Dioxane and Gold label cyclohexene was purchased from Aldrich. 3-Trimethylsilylpropynal,[40] 1,3,5-triethynylbenzene,[47] 1-ethynylnaphthylene,[48] and 1-triisopropylsilylethynyl-4-trimethylsilylethynylbenzene[49] were made as previously reported. Evaporation and concentration in vacuo was done at H_2O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of N_2. A positive pressure of N_2 was essential to the success of all *n*BuLi reactions. Column chromatography: Silica gel 60 (230–400 mesh) from Rose Scientific Ltd. Thin-layer chromatography (TLC): plastic sheets covered with silica gel 60 F254 from Macherey-Nagel; visualization by UV light or $KMnO_4$ stain. M.p.; Gallenkamp apparatus; uncorrected. IR spectra (cm^{-1}): Nicolet Magna-IR 750 (neat) or Nic-Pan IR Microscope (solids). ^1H and ^{13}C NMR: Bruker AM300 or Varian Gemini-300, 400, and 500 at rt in CD_2Cl_2 or $CDCl_3$; solvent peaks (5.27 and 7.24 ppm for ^1H and 53.8 and 77.0 ppm, respectively, for ^{13}C) as reference. EI MS (*m*/*z*): Kratos MS50 instrument. Elemental analyses were effected by the Microanalytical Laboratory at the University of Alberta.

X-ray crystallographic studies: Unit cell parameters and intensity data were obtained on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The structures were solved by direct methods using SHELXS-86[50] and refined by full-matrix least squares on F^2 using SHELXL-93.[51] Hydrogen atoms were generated in idealized positions based on the sp^2 or sp^3 hybridization of their parent carbon atoms, and given displacement parameters 120% of the U_{eq} of their attached carbon atoms.

X-ray crystal data for 20: $C_{24}H_{22}Si_2$; $F_w = 366.60$; crystal dimensions: $0.38 \times 0.31 \times 0.04$ mm^3; crystal system: triclinic; space group $P\bar{1}$ (No. 2), $a = 7.1643(15)$, $b = 9.1375(19)$, $c = 17.305(4)$ Å; $\alpha = 98.116(4)$, $\beta = 92.197(4)$, $\gamma = 95.230(5)^\circ$; $V = 1115.3(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.092$ $g\,cm^{-3}$; $2\theta_{max} = 52.84^\circ$; absorption correction via Gaussian integration; $\mu = 0.163$ mm^{-1}, range of transmission factors = 0.9938–0.9402; total number of reflections = 4891; $R1(F) = 0.0699$ (2084 observed reflections with $F_o^2 \geq 2\sigma(F_o^2)$), $wR^2(F^2) = 0.1546$ for 235 variables and 4153 unique reflections with $F_o^2 \geq -3\sigma(F_o^2)$; $T = -80\,^\circ C$; scan mode: ω scans (0.2°) (25 s exposures); residual electron density = 0.311 and -0.228 e Å^{-3}.

X-ray crystal data for 29: $C_{55}H_{49}Si_4$; $F_w = 822.30$; crystal dimensions: $1.00 \times 0.10 \times 0.03$ mm^3; crystal system: monoclinic; space group $P2_1/c$ (No. 14), $a = 7.212(2)$, $b = 44.335(12)$, $c = 16.183(4)$ Å; $\beta = 93.463(5)^\circ$; $V = 5165(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.058$ $g\,cm^{-3}$; $2\theta_{max} = 50.00^\circ$; absorption correction via a multi-scan model (SADABS); $\mu = 0.147$ mm^{-1}, range of transmission factors = 0.9956–0.8666; total number of reflections = 21024; $R_1(F) = 0.1339$ (2960 observed reflections with $F_o^2 \geq 2\sigma(F_o^2)$); $wR^2(F^2) = 0.4207$ for 457 variables and 9108 unique reflections with $F_o^2 \geq -3\sigma(F_o^2)$; $T = -80\,^\circ C$; scan mode: ω scans (0.2°) (25 s exposures); residual electron density = 1.060 and -0.460 e Å^{-3}.

CCDC-197506 (**20**) and -197507 (**29**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

General procedure for alkyne rearrangements: Unless otherwise noted in the individual procedures below, a solution of the dibromo-olefin in hexanes under nitrogen was cooled to $-78\,^\circ C$. 1.1–1.2 equiv of *n*BuLi per dibromo-olefin moiety is slowly added over a period of ca. 2 min. The reaction mixture turned either a pale yellow or orange in color. Reactions were allowed to warm to approximately $-10\,^\circ C$ over a period of 0.5–1 h, unless otherwise noted. TLC analysis indicated that reactions were generally complete soon after addition of base (<10 min), although warming of the reaction solution in the TLC capillary tube can influence these analyses. The reactions were quenched at ca. $-5\,^\circ C$ with an aqueous NH_4Cl solution. Diethyl ether was added (50 mL), the organic layer separated, washed with aqueous NH_4Cl (2×50 mL), dried ($MgSO_4$), and the solvent removed in vacuo. Passing the crude reaction through a silica plug or flash column chromatography (silica gel) as necessary gave the desired products.

1,6-Bis(triisopropylsilyl)-1,3,5-hexatriyne (4a): *n*BuLi (2.17 M in hexanes, 0.17 mL, 0.37 mmol) was added to **7a** (0.201 g, 0.368 mmol) in hexanes (10 mL) according to the general procedure to produce **4a** (0.0989 g, 70%) as an off-white solid. $R_f = 0.8$ (hexanes). Spectral data were consistent with those reported by Rubin et al.[23a]

1,6-Bis(trimethylsilyl)-1,3,5-hexatriyne (4b): *n*BuLi (2.5 M in hexanes, 0.13 mL, 0.33 mmol) was added to **7b** (0.101 g, 0.266 mmol) in hexanes (5 mL) according to the general procedure to produce **4b** (0.029 g, 50%) as an off-white solid. $R_f = 0.67$ (hexanes). Spectral data were consistent with those reported by Tobe et al.[28]

1-(Triisopropylsilyl)-6-(trimethylsilyl)-1,3,5-hexatriyne (4c): *n*BuLi (2.17 M in hexanes, 0.20 mL, 0.43 mmol) was added to **7c** (0.200 g, 0.432 mmol) in hexanes (12 mL) according to the general procedure to produce **4c** (0.0802 g, 61%). $R_f = 0.7$ (hexanes). Spectral data were consistent with those reported by Rubin et al.[23a]

6-(1-Naphthyl)-1-(trimethylsilyl)-1,3,5-hexatriyne (4d): *n*BuLi (2.5 M in hexane, 0.080 mL, 0.20 mmol) was added to **7d** (0.0687 g, 0.159 mmol) at $0\,^\circ C$ in hexanes (6 mL) according to the general procedure to produce **4d** (0.0303 g, 70%) as a clear oil. $R_f = 0.43$ (hexanes); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.26$ (d, $J = 8.3$ Hz, 1H), 7.87 (d, $J = 8.2$ Hz, 1H), 7.84 (dd, $J = 7.2$, 1.4 Hz, 1H), 7.77 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.55 (m, 2H), 7.40 (dd, $J = 8.3$, 7.2 Hz, 1H), 0.22 (s, 9H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$, 25 °C): $\delta = 134.3$, 133.1, 133.0, 130.4, 128.6, 127.5, 126.9, 126.0, 125.2, 118.5, 89.8, 88.1, 78.9, 75.4, 68.1, 61.7, -0.5; IR (film): $\tilde{\nu} = 2959$, 2164, 2071, 1505 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 272 (91%) $[M^+]$, 257 (100%) $[M^+ - CH_3]$; HRMS: calcd for $C_{19}H_{16}Si$: 272.1021, found 272.1026; elemental analysis calcd (%) for $C_{19}H_{16}Si$ (272.4): C 83.77, H 5.92; found: C 83.65, H 6.06.

6-(1-Naphthyl)-1-(triisopropylsilyl)-1,3,5-hexatriyne (4e): *n*BuLi (2.5 M in hexane, 0.19 mL, 0.48 mmol) was added to **7e** (0.205 g, 0.396 mmol) in hexanes (11 mL) according to the general procedure to produce **4e** (0.0878 g, 62%) as an off-white solid. $R_f = 0.57$ (hexanes); m.p. 34–35 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.27$ (d, $J = 8.1$ Hz, 1H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.84 (d, $J = 6.5$ Hz, 1H), 7.76 (d, $J = 7.2$ Hz, 1H), 7.55 (m, 2H), 7.40 (dd, $J = 8.1$, 7.8 Hz, 1H), 1.10 (s, 21H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$, 25 °C): $\delta = 134.3$, 133.1, 132.9, 130.3, 128.6, 127.5, 126.8, 125.9, 125.2, 118.6, 89.8, 87.5, 79.0, 75.0, 68.5, 60.7, 18.6, 11.4; IR (film): $\tilde{\nu} = 2943$, 2182, 2163, 2069, 1462 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 356 (86%) $[M^+]$, 313 (100%) $[M^+ - i\text{Pr}]$; HRMS: calcd for $C_{25}H_{28}Si$: 356.1960, found 356.1963.

5,7,9-Tetradecatriyne (4f): *n*BuLi (2.5 M in hexane, 0.26 mL, 0.65 mmol) was added to **7f** (0.191 g, 0.552 mmol) hexanes (16 mL) according to the general procedure to produce **4f** (0.0821 g, 80%) as light yellow oil. $R_f = 0.53$ (hexanes); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 2.26$ (t, $J = 6.9$ Hz, 4H), 1.49 (m, 4H), 1.40 (m, 4H), 0.84 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (75.5 MHz, APT, $CDCl_3$, 25 °C): $\delta = 79.3$, 65.7, 60.4, 30.2, 22.0, 19.1, 13.5; IR (cast): $\tilde{\nu} = 2958$, 2216, 1465 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 186 (100%) $[M^+]$; HRMS: calcd for $C_{14}H_{18}$: 187.1487, found 187.1445.

8,10,12-Eicosatriyne (4g): *n*BuLi (2.5 M in hexane, 0.20 mL, 0.50 mmol) was added to **7g** (0.194 g, 0.422 mmol) in hexanes (12 mL) according to the general procedure to produce **4g** (0.0835 g, 66%) as a light brown oil. $R_f =$

0.59 (hexanes); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 2.31$ (t, $J = 7.0$ Hz, 4H), 1.52 (m, 4H), 1.40 (m, 4H), 1.25 (m, 16H), 0.86 (m, 6H); ^{13}C NMR (75.5 MHz, APT, CDCl$_3$, 25 °C): $\delta = 79.4$, 65.8, 60.4, 31.9, 29.2, 29.1, 28.9, 28.2, 22.7, 19.4, 14.1; IR (cast): $\tilde{\nu} = 2926$, 2855, 2216, 1466 cm^{-1}; MS (70 eV, EI): m/z (%): 298 (36%) [M^+]; HRMS: calcd for $C_{22}H_{34}$: 298.2661, found 298.2662.

[1-(Trimethylsilyl)-1,3,5-hexatriynyl]-[(4-triisopropylsilyl)ethynyl]benzene (4h): *n*BuLi (2.5 M in hexanes, 0.06 mL, 0.15 mmol) was added to **7h** (0.0578 g, 0.103 mmol) in hexanes (5 mL) according to the general procedure to produce **4h** (0.0254 g, 61%) as a yellow oil. $R_f = 0.5$ (hexanes); ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 7.41$ (m, 4H), 1.11 (s, 21H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, APT, CDCl$_3$, 25 °C): $\delta = 132.7$, 131.9, 124.9, 120.5, 106.2, 94.5, 89.6, 88.0, 76.4, 76.0, 67.8, 61.4, 18.7, 11.4, -0.4; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 2958$, 2891, 2154, 2076, 1506 cm^{-1}; MS (70 eV, EI): m/z (%): 402 (57%) [M^+], 359 (100%) [$M^+ - i$Pr]; HRMS: calcd for $C_{26}H_{34}Si_2$: 402.2199, found 402.2204.

1-(Trimethylsilyl)-1,3,5-decatriyne (4i): *n*BuLi (2.5 M in hexanes, 0.20 mL, 0.50 mmol) was added to **7i** (0.1484 g, 0.4100 mmol) in hexanes (10 mL) according to the general procedure to produce **4i** (0.0677 g, 82%) as a light yellow oil. $R_f = 0.54$ (hexanes); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 2.27$ (t, $J = 7.0$ Hz, 2H), 1.49 (m, 2H), 1.38 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl$_3$, 25 °C): $\delta = 88.3$, 85.4, 81.0, 65.4, 62.5, 59.9, 30.0, 21.9, 19.1, 13.5, -0.5; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 2960$, 2874, 2211, 2167, 2079 cm^{-1}; MS (70 eV, EI): m/z (%): 202 (31%) [M^+], 187 (100%) [$M^+ - CH_3$]; HRMS: calcd for $C_{13}H_{18}Si$: 202.1178, found 202.1180.

1,6-Bis(2-thienyl)-1,3,5-hexatriyne (4j): *n*BuLi (2.5 M in hexanes, 0.08 mL, 0.20 mmol) was added to **7j** (0.066 g, 0.17 mmol) in hexanes (5 mL) according to the general procedure to produce **4j** (0.0259 g, 64%) as a yellow solid. $R_f = 0.42$ (hexanes); m.p. 58–59 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.38$ (dd, $J = 1.2$, 3.9 Hz, 2H), 7.32 (dd, $J = 1.2$, 5.1 Hz, 2H), 6.98 (dd, $J = 3.9$, 5.1 Hz, 2H); ^{13}C NMR (100 MHz, APT, CDCl$_3$, 25 °C): $\delta =$ 135.6, 129.6, 127.3, 121.3, 78.6, 72.7, 68.5; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 3114$, 2187, 1433 cm^{-1}; MS (70 eV, EI): m/z (%): 238 (100) [M^+]; HRMS: calcd for $C_{14}H_6S_2$: 237.9911, found 237.9907.

3-(Bromomethylidene)-1,5-bis(triisopropylsilyl)penta-1,4-diyne (10a): *n*BuLi (1.6 M in hexanes, 0.15 mL, 0.24 mmol) was added to **7a** (0.106 g, 0.194 mmol) in THF or Et$_2$O (6 mL) at -78 °C, and the mixture was warmed to varying temperatures and then quenched with aqueous NH$_4$Cl. Dependent upon the final temperature of the reaction, varying amounts of **10a** were produced, with the yield decreasing substantially for reactions quenched at higher temperatures (>0 °C): $R_f = 0.85$ (hexanes); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 6.91$ (s, 1H), 1.09 (s, 21H), 1.06 (s, 21H); ^{13}C NMR (100 MHz, APT, CDCl$_3$, 25 °C): $\delta = 123.1$, 112.9, 102.3, 101.4, 98.9, 92.4, 18.5, 11.2; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 2943$, 2866, 2149, 1463 cm^{-1}; MS (70 eV, EI): m/z (%): 468 (24) [M^+], 425 (100) [$M^+ - i$Pr].

1-(Trimethylsilyl)-6-phenyl-1,3,5-hexatriyne (14a): *n*BuLi (2.5 M in hexanes, 0.15 mL, 0.38 mmol) was added to **13a** (0.145 g, 0.380 mmol) in hexanes (7 mL) according to the general procedure to produce **14a** (0.0711 g, 84%) as a clear oil. $R_f = 0.49$ (hexanes); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.50$ (d, $J = 6.9$ Hz, 2H), 7.36 (d, $J = 7.3$ Hz, 1H), 7.31 (t, $J = 7.3$ Hz, 2H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl$_3$, 25 °C): $\delta =$ 133.1, 129.8, 128.5, 120.8, 89.0, 88.0, 76.8, 74.3, 66.8, 61.6, -0.5; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 2960$, 2174, 2076, 1490 cm^{-1}; MS (70 eV, EI): m/z (%): 222 (35) [M^+], 207 (100) [$M^+ - CH_3$]; HRMS: calcd for $C_{15}H_{14}Si$: 222.0865, found 222.0865.

1-(Trimethylsilyl)-8-phenyl-1,3,5,7-octatetrayne (14b): *n*BuLi (2.5 M in hexanes, 0.13 mL, 0.33 mmol) was added to **13b** (0.112 g, 0.275 mmol) in hexanes (7 mL) according to the general procedure to produce **14b** (0.0432 g, 64%) as a clear oil. $R_f = 0.57$ (hexanes); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.51$ (dd, $J = 7.1$, 1.5 Hz, 2H), 7.39 (tt, $J = 7.4$, 1.5 Hz, 1H), 7.32 (m, 2H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, APT, CDCl$_3$, 25 °C): $\delta = 133.2$, 130.0, 128.6, 120.4, 88.8, 87.9, 76.9, 74.4, 67.2, 64.0, 62.2, 61.8, -0.6; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 2961$, 2195, 2132, 2059, 1491 cm^{-1}; MS (70 eV, EI): m/z (%): 246 (46) [M^+], 231 (100) [$M^+ - CH_3$]; HRMS: calcd for $C_{17}H_{14}Si$: 246.0865, found 246.0863.

1,12-Bis(triisopropylsilyl)-1,3,5,7,9,11-dodecahexayne (16): *n*BuLi (2.5 M in hexane, 0.22 mL, 0.55 mmol) was added to **15** (0.198 g, 0.254 mmol) in hexanes (16 mL) according to the general procedure to produce **16** (0.0816 g, 70%) as a yellow/orange solid. $R_f = 0.85$ (hexanes); m.p. 78–80 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 1.07$; ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 89.5$, 87.1, 62.8, 62.7, 62.5, 61.3, 18.6, 11.4; IR (CHCl$_3$ cast): $\tilde{\nu} = 2944$, 2158, 2127, 2067, 2030, 1462 cm^{-1}; MS (70 eV, EI): m/z (%): 458 (42) [M^+], 415 (100) [$M^+ - i$Pr]; HRMS: calcd for $C_{30}H_{42}Si_2$: 458.2825, found 458.2834 [M^+].

Bis-1,4-[6-(trimethylsilyl)-1,3,5-hexatriynyl]benzene (20): *n*BuLi (2.5 M in hexane, 0.24 mL, 0.60 mmol) was added to **19** (0.173 g, 0.252 mmol) at -44 °C in hexanes (15 mL) according to the general procedure to produce **20** (0.0463 g, 50%) as a pale yellow solid. $R_f = 0.42$ (hexanes); m.p. 180 °C (decomp.); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 7.44$ (s, 4H), 0.20 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 133.0$, 122.2, 90.2, 87.9, 77.2, 75.9, 68.4, 61.2, -0.5; IR (microscope): $\tilde{\nu} = 2956$, 2167, 2075 cm^{-1}; MS (70 eV, EI): m/z (%): 366 (98) [M^+], 351 (100) [$M^+ - CH_3$]; HRMS: calcd for $C_{24}H_{22}Si_2$: 366.1260; found 366.1265 [M^+].

Tris-1,3,5-[6-(trimethylsilyl)-1,3,5-hexatriynyl]benzene (24): *n*BuLi (2.5 M in hexane, 0.25 mL, 0.63 mmol) was added to **23** (0.174 g, 0.176 mmol) in hexanes (20 mL) according to the general procedure to produce **24** (0.0317 g, 35%) as a creme colored solid. $R_f = 0.5$ (hexanes); m.p. 160 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 7.65$ (s, 3H), 0.23 (s, 27H); ^{13}C NMR (75 MHz, APT, CDCl$_3$, 25 °C): $\delta = 138.1$, 122.8, 90.9, 87.6, 76.3, 74.1, 68.2, 60.9, -0.6; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 2960$, 2168, 2074, 1575 cm^{-1}; MS (70 eV, EI): m/z (%): 510 (100) [M^+]; HRMS: calcd for $C_{33}H_{30}Si_3$: 510.1655, found 510.1648 [M^+].

1-Ethynyl-3,5-bis[6-(trimethylsilyl)-1,3,5-hexatriynyl]benzene (28): *n*BuLi (2.5 M in hexanes, 0.25 mL, 0.63 mmol) was added to **27** (0.151 g, 0.0.213 mmol) in hexanes (25 mL) at -44 °C according to the general procedure. Following work-up, the reaction mixture was passed through a short column (silica gel, hexanes) to give the crude product **28** (0.06 g, ca. 70%) as a relatively unstable compound if taken to dryness, but of sufficient purity (>95%) to be taken on directly to the next step: $R_f = 0.38$ (hexanes); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 7.58$ (s, 3H), 3.12 (s, 1H), 0.22 (s, 18H); ^{13}C NMR (125 MHz, CDCl$_3$, APT, 25 °C): $\delta = 136.9$, 123.5, 122.1, 89.9, 87.7, 80.9, 79.5, 75.9, 74.1, 67.8, 60.9, 53.4, -0.5; IR (CDCl$_3$ cast): $\tilde{\nu} = 3299$, 2960, 2169, 2075, 1578 cm^{-1}; MS (EI, 70 eV) m/z (%): 390.1 (39) [M^+], 73.0 (100) [Me$_3$Si$^+$]; HRMS: calcd for $C_{26}H_{22}Si_2$: 390.1260, found 390.1258.

1,4-[Bis-1-[3,5-bis[6-(trimethylsilyl)-1,3,5-hexatriynyl]phenyl]butadiyne (29): Compound **28** (0.0295 g, 0.0755 mmol) was added to a solution of CuI (0.026 g, 0.14 mmol) and TMEDA (1 mL) in dichloromethane (35 mL). The reaction was followed by TLC and was completed within 30 minutes. Compound **29** was isolated by column chromatography (silica gel, hexanes) as a white solid (0.0092 g, 31%). $R_f = 0.31$ (hexanes); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 7.65$ (m, 6H), 0.23 (s, 36H); ^{13}C NMR (100 MHz, APT, CD$_2$Cl$_2$, 25 °C): $\delta = 137.9$, 137.7, 123.2, 122.7, 90.8, 87.6, 80.0, 76.2, 75.4, 74.2, 68.1, 60.8, -0.6; IR (CH$_2$Cl$_2$ cast): $\tilde{\nu} = 2959$, 2168, 2074, 1574 cm^{-1}; MS (ESI, nitromethane, AgOTf added): m/z (%): 887 (100) [M^++Ag].

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