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Synthesis of Unsymmetrically Substituted 1,3-Butadiynes and 1,3,5-Hexatriynes via Alkylidene Carbenoid Rearrangements

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Unsymmetrically substituted 1,3-butadiynes and 1,3,5-hexatriynes are synthesized in four steps from commercially available aldehydes or carboxylic acids. The key step in this process involves a Fritsch−Buttenberg−Wiechell rearrangement, in which an alkylidene carbenoid intermediate subsequently rearranges to the desired polyyne. This rearrangement proceeds under mild conditions, and it is tolerant of a range of functionalities. In general, the procedurally facile formation of the dibromoolefinic precursors, in combination with the effectiveness of the rearrangement step, makes this procedure an attractive alternative to traditional methods for di- and triyne synthesis that utilize palladium or copper catalysis.

Introduction

The 1,3-butadiynyl and 1,3,5-hexatriynyl moieties are versatile and useful building blocks in organic synthesis that have been exploited for their rigid and conjugated nature.[1] Butadiynes, in particular, have been widely utilized as substructures in the formation of new photonic materials,[2] oligomers and polymers,[3] macrocycles,[4] and supramolecular scaffolds.[5] Diynes and triynes have a rich history as precursors for single-crystal polydiacetylene formation via topochemical polymerization reactions, the only method known to give such materials.[6] Furthermore, di- and triynes are, perhaps somewhat surprisingly, quite common constituents of natural products.[7]

Symmetrically substituted 1,3-butadiynes are relatively straightforward to synthesize using Hay,[8] Eglinton/Galbraith,[9] or related protocols, which proceed via oxidative homocoupling of terminal acetylenes with Cu(I)/Cu(II) catalysis.[10] These conditions are not suitable, however, for the synthesis of unsymmetrically substituted 1,3-butadiynes. The oxidative coupling of two or more different acetylenic precursors affords a mixture of products, and separation is invariably tedious and difficult. A more substantial challenge is encountered in the formation of both symmetrical and unsymmetrical 1,3,5-hexatriynes via oxidative coupling because the reactivity (acidity) of the two precursors, a terminal acetylene and diacetylene, differ appreciably. Thus, attempts to assemble the triyne skeleton via oxidatively coupling these two groups usually leads first to homocoupling of the diacetylene (to give the symmetrical tetrayne) followed by diyne formation via homocoupling of the acetylene.[10a,11]

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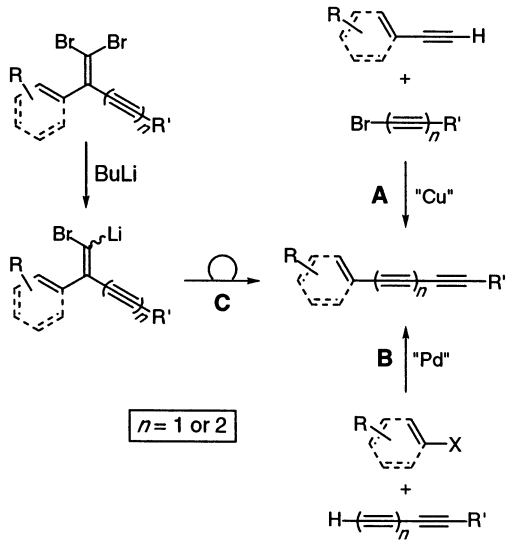
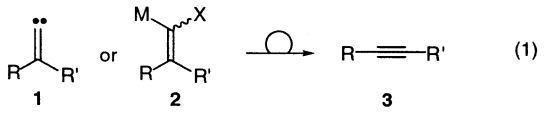
CHART 1



Thus, homocoupling is generally an inefficient method for the synthesis of triynes.

As a result of the challenges outlined above for homocoupling reactions, the cross-coupling of terminal acetylenes with alkynyl bromides or iodides, the Cadiot−Chodkiewicz coupling (Chart 1, route A),[12] has often been useful for accessing unsymmetrical 1,3-diynes[13] as well as symmetrical and unsymmetrical 1,3,5-hexatriynes.[14] Such molecules have also been realized via the palladium-catalyzed cross-coupling reaction of terminal alkynes with aryl halides or triflates, such as the Sonogashira reaction (Chart 1, route B).[15] The predominant limitation of these and related methods in the synthesis of di- and triynes,[16] however, is that they all require the prior synthesis of a terminal alkyne for one or both of the coupling partners. This situation becomes problematic in the case of terminal diynes or triynes, which are quite often unstable to isolation and must therefore be generated and utilized in situ.[17]

The chemistry of alkylidene carbenes and carbenoid species has a rich and diverse history. Dependent upon reaction conditions and substrate, a free carbene (**1**) can undergo addition reactions to olefins, bond insertion reactions, or, as shown in eq 1, rearrangements to afford



(1)

an alkyne (**3**). In the case of carbenoid species **2**, the latter mode of reactivity, rearrangement to an alkyne product, ordinarily dominates, a reaction deemed the Fritsch−Buttenberg−Wiechell (FBW) rearrangement when R = R′ = aryl.[18] This transformation has been a well-utilized technique for the formation of tolans.[19,20] We have recently reported the modification of this method and have demonstrated that it is suitable for the formation of polyynes via alkyne migration in carbene/carbenoid intermediates.[21,22] These initial studies suggested that, in addition to the well-established propensity for aryl and olefin migration in an alkylidene carbenoid species,[19b] 1,2-alkyne migrations could also be quite successful. As a result, we envisioned 1,1-dibromoolefins as precursors to di- and triynes **3** as shown in Chart 1, route C. This reaction would involve a sequence of lithium halogen exchange with a suitable 1,1-dibromoolefin to give the carbene/carbenoid intermediate, followed by rearrangement to the desired polyyne.

We now report the successful synthesis of functionalized, unsymmetrical 1,3-butadiynes[23] and 1,3,5-hexatriynes via this method.[24] Beginning with commercially available

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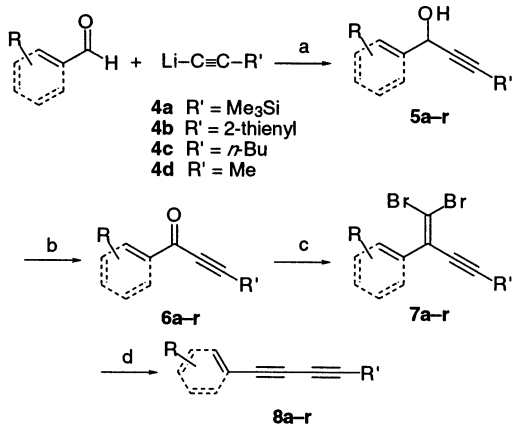
(24) For a preliminary account of these results, see: Chernick, E. T.; Eisler, S.; Tykwinski, R. R. *Tetrahedron Lett.* **2001**, *42*, 8575−8578.

SCHEME 1[a]



[a] Reagents and conditions: (a) Et_2O, −78 °C; (b) PCC, Celite, molecular sieves (4 Å), CH_2Cl_2, rt; (c) PPh_3 (2 equiv), CBr_4, CH_2Cl_2 at rt or C_6H_6 at reflux; (d) *n*-BuLi, −78 to −40 °C, hexanes.

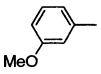
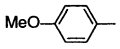
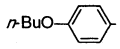
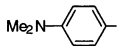
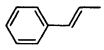
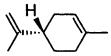
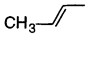
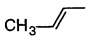
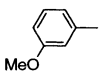
aryl or vinyl aldehydes and carboxylic acids (or acid chlorides), these polyynes are achieved in four facile steps, with the carbenoid rearrangement proceeding under mild conditions and generally in good to excellent yields. As this method has not been successfully executed in all cases, however, the scope and limitation of this protocol are also discussed.

Results and Discussion

The synthetic sequence toward unsymmetrically substituted 1,3-butadiynes begins with condensation of a slight excess of the appropriate lithium acetylide with an aryl carboxaldehyde in Et_2O at −78 °C (Scheme 1).[25] As a result of the slight excess of the acetylide, complete reaction with the aldehyde can generally be effected, and the resultant alcohols **5** can be isolated pure and in high yield following aqueous workup (Table 1).

Oxidation from alcohol **5** to ketone **6** is normally accomplished with PCC at rt in CH_2Cl_2. Reaction times are less than 1 h for most derivatives, and concentration of the reaction mixture, followed by filtration through a short plug of silica, affords the crude ketone. The ketone is normally of sufficient purity to be carried on to the subsequent dibromoolefination step. The ketones can, however, be isolated pure by column chromatography, as demonstrated for a number of the examples in Table 1. The oxidation of several alcohols was particularly difficult with PCC (e.g., **5k**, **5n**, **5o**). As a result, $BaMnO_4$ was employed as the oxidant,[26] with more satisfactory results. As this reaction is done in CH_2Cl_2, filtration of the reaction solution through Celite to remove the insoluble barium salts affords a CH_2Cl_2 solution of the ketone suitable to be carried on to the dibromoolefination step without additional purification or manipulation. In two cases, the aniline and pyridine derivatives **5g** and **5j**, we were unable to successfully complete the oxidation procedure due to the chemical instability of these substrates.

TABLE 1. Isolated Yields for Compounds 5−8

compd	R	R'	5 yield (%)[a]	6 yield (%)	7 yield (%)	8 yield (%)
a		Me_3Si	64	—[a]	44[c,d]	93
b		Me_3Si	96	83[a]	39[c,e]	79
c		Me_3Si	90	—[a]	59[c,d]	43
d		Me_3Si	76	76[a]	48[c,d]	75
e		Me_3Si	97	—[a]	47[c,d]	82
f		Me_3Si	69	—[a]	38[c,e]	79
g		Me_3Si	91	—	—	—
h		Me_3Si	85	—[a]	34[c,d]	54
i		Me_3Si	97	87[a]	85[d]	91
j		Me_3Si	50	—	—	—
k		Me_3Si	95	36[a] 94[b]	26[c,e]	28
l		Me_3Si	81	96[b]	77[c,d]	95
m		Me_3Si	63	85[b]	27[d]	46
n		Me_3Si	39	89[b]	—	—
o			80	35[a] 82[b]	—	—
p		*n*-Bu	88	46[a]	7[c,d]	92
q		*n*-Bu	94	82[a]	16[c,d]	86
r		Me	98	73[a]	17[d]	41

[a] Using PCC in CH_2Cl_2. [b] Using $BaMnO_4$ in CH_2Cl_2. [c] Yield over two steps from alcohol, without isolation of intermediate ketone. [d] Dibromoolefination reaction in CH_2Cl_2 at rt. [e] Dibromoolefination reaction in C_6H_6 at 80 °C.

The well-established dibromoolefination method using PPh_3/CBr_4 was employed to provide derivatives **7**.[27] For

(25) A similar route has been utilized by others; inter alia, see: (a) Brown, R. F. C.; Jackson, W. R.; McCarthy, T. D. *Tetrahedron* **1994**, *50*, 5469−5488. (b) Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S.; Papagni, A.; Torchio, M. *Tetrahedron Lett.* **1993**, *34*, 7943−7946.

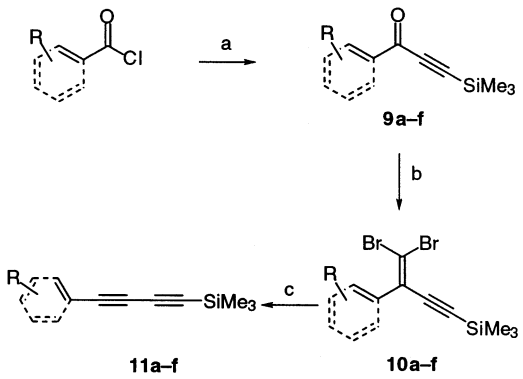
(26) Lange, T.; van Loon, J.-D.; Tykwinski, R. R.; Schreiber, M.; Diederich, F. *Synthesis* **1996**, 537−550.

sterically unhindered ketones, the dibromoolefinations can generally be completed at rt in CH_2Cl_2 in 1−2 h. For ketones **6b**, **6f**, and **6k**, however, reactions were sluggish at rt in CH_2Cl_2 and were therefore carried out in benzene under reflux. In all cases, the dibromoolefinic products are considerably less polar than the ketone precursors, as well as any byproducts of the reaction, and can therefore be quickly and easily purified by column chromatography.

During the course of this study, it became apparent that the dibromoolefination step is the weakest link in this synthetic sequence. The first 1,3-butadiyne derivatives that we targeted were terminated at one end with a trimethylsilyl group (entries **a**−**m**, Table 1) since this alkyne protecting group nicely allows for further synthetic elaboration of the resultant diynes. In these cases, reasonable to good yields of the desired dibromoolefinic products could be achieved, whether beginning with either the pure ketone or the crude product directly from the oxidation reaction. As it turns out, however, the presence of the trimethylsilyl group also appears to play a significant role in the success of the dibromoolefination reactions. In cases where this group has been replaced by either an alkyl or aryl moiety, the yields from the dibromoolefination reaction are dramatically reduced (e.g., **7p**−**r**), and in some cases we have been unable to effect this transformation at all (entries **7n** and **7o**). To date, this remains the predominant limitation of our methodology.[28]

The conversion of the dibromoolefins to the desired diynes **8** has been consistently more successful in hexanes, as opposed to more polar solvents such as Et_2O or THF.[29,30] Thus, diyne formation is effected by the dropwise addition of *n*-BuLi to a hexanes solution of **7** cooled to −78 °C. The mixture is subsequently warmed to ca. −20 °C over 0.5−1 h to ensure complete rearrangement of the carbenoid intermediate[31] and then quenched by the addition of an aqueous NH_4Cl solution. If *strictly* anhydrous reaction conditions have been maintained during the rearrangement, the diyne is generally the sole product as observed by TLC analysis.[32] The diynes can thus be isolated pure, in good to excellent yields, by passing the concentrated reaction mixture through a plug of silica to remove any polar baseline material. As

SCHEME 2[a]



[a] Reagents and conditions: (a) $Me_3SiC{\equiv}CSiMe_3$, $AlCl_3$, CH_2Cl_2, 0 to 25 °C; (b) PPh_3 (2 equiv), CBr_4, CH_2Cl_2; (c) *n*-BuLi, hexanes, −78 to −40 °C.

demonstrated in Table 1, the carbenoid rearrangement process allows a range of pendant groups to be appended to the diyne skeleton, including aromatic hydrocarbon (**8a**,**b**), electron-rich and -poor aryl (**8c**−**f**,**k**,**p**),[33] heteroaryl (**8h**,**i**,**q**,**r**), alkyl (**8p**−**r**), and vinyl (**8l**,**m**) functionalities.

Scheme 2 outlines an alternate pathway to aryl 1,3-diynes that exploits readily available carboxylic acid chlorides. Friedel−Crafts acylation of aryl or vinyl acid chlorides with bis(trimethylsilyl)acetylene easily afforded ketones **9a**−**f** in good to excellent yields (Table 2).[34] Dibromoolefination of **9a**−**f** under standard conditions generated **10a**−**f**. Subjecting dibromides to *n*-BuLi at −78 °C according to the standard protocol described above afforded **11a**−**e** in good to excellent yields. This route allowed formation of functionalized diacetylenes such as the azo diyne **11c**, trimethoxyarene **11d**, and thienyl-terminated enediyne **11e**. Frustratingly, rearrangement of butadienyl derivative **11f** was unsuccessful, regardless of the conditions employed. For this substrate, unreacted dibromoolefin **10f** was recovered, along with the product derived from protonation of the intermediate carbenoid species, but no diyne could be detected in the reaction mixture. In view of the facile rearrangement of vinyl dibromides **7l**, **7m**, and **10e**, the inability to effect an analogous rearrangement on **10f** is surprising and remains unexplained.

The traditional difficulties encountered in the synthesis of unsymmetrical triacetylenes led us to extend our general protocol in this direction, as outlined in Scheme 3. Friedel−Crafts acylation of the appropriate acyl chloride with 1,4-bis(trimethylsilyl)-1,3-butadiyne provided diynones **12a**−**f** (Table 3). Ketones **12a**−**c**, with pendant aryl functionality, showed somewhat limited stability. Although they could be isolated, decomposition was

(27) (a) Corey, E. J.; Fuchs, P. L. *Tetrahedron. Lett.* **1972**, 3769−3772. (b) Posner, G.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* **1975**, 1373−1376. (c) Ramirez, F.; Desai, N. B.; McKelvie, N. *J. Am. Chem. Soc.* **1962**, *84*, 1745−1747. (d) Neidlein, R.; Winter, M. *Synthesis* **1998**, 1362−1366. (e) Anthony, J.; Boldi, A. M.; Rubin, Y.; Hobi, M.; Gramlich, V.; Knobler, C. B.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 13−45.

(28) A recent report offers one potential solution to this problem; see: Rezaei, H.; Normant, J. F. *Synthesis* **2000**, 109.

(29) Köbrich had extensively studied solvent effects in aryl- and alkyl-substituted alkylidene carbenes; see: Köbrich, G.; Buck, P. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; Chapter 2.

(30) A full investigation of the mechanistic aspects of these reactions is under way and will be published in due course. Preliminary evidence suggests that collapse of the carbenoid intermediate is consistent with that expected on the basis of the results of Curtin and Bothner-By, which is to say that the group that is *trans* to the bromide atom in the intermediate **2** is the one that migrates; see: Curtin, D. Y.; Flynn, E. W.; Nystrom, R. F. *J. Am. Chem. Soc.* **1958**, *90*, 4599. Bothner-By, A. A. *J. Am. Chem. Soc.* **1955**, *77*, 3293. See also ref 20a.

(31) Using TLC to monitor these reactions is problematic, as warming of the sample in the capillary tube used for TLC application can lead to the inaccurate observation that the reaction has reached completion.

(32) Experimental evidence suggests that lithium−halogen exchange is faster than quenching of the BuLi by adventitious water in the reaction medium. As a result, any water that is present results in protonation of the carbenoid intermediate, which severely complicates purification due to very similar retention times on chromatographic supports.

(33) The low yield for **8c** results from the presence of the *o*-alkoxy substituent; see: Köbrich, G.; Trapp, H. *Chem. Ber.* **1966**, *99*, 680−688.

(34) (a) Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, *37*, 45−56. (b) Suzuki, R.; Tsukuda, H.; Watanabe, N.; Kuwatani, Y.; Ueda, I. *Tetrahedron* **1998**, *54*, 2477−2496.

TABLE 2. Isolated Yields for Compounds 9−11

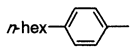
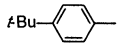
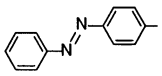
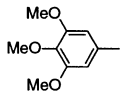
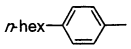
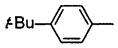
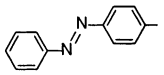
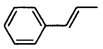
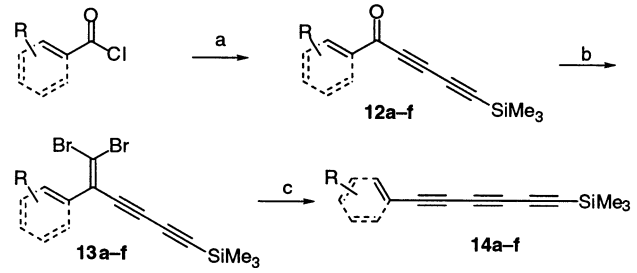
compd	R	9 yield (%)	10 yield (%)	11 yield (%)
a		90	79	70
b		78	61	88
c		43	83	61
d		91	91	51
e		62	67	55
f		66	41	—

TABLE 3. Isolated Yields for Compounds 12−14

compd	R	12 yield (%)	13 yield (%)	14 yield (%)
a		—	21[a]	41
b		—	24[a]	98
c		—	8[a]	46
d		45	72	82
e		69	75	74
f		65	40	76

[a] Yield over two steps from acid chloride, without isolation of intermediate ketone.

SCHEME 3[a]

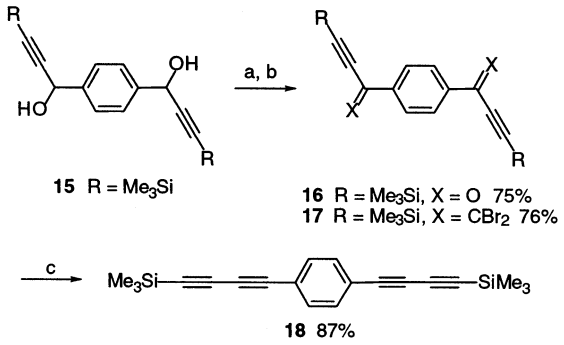


[a] Reagents and conditions: (a) $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$, $AlCl_3$, CH_2Cl_2, 0 to 25 °C; (b) PPh_3 (2 equiv), CBr_4, CH_2Cl_2; (c) *n*-BuLi, hexanes, −78 to −40 °C.

always observed when manipulations were carried out under ambient conditions. Thus, these compounds were expeditiously carried on to the dibromoolefination step in CH_2Cl_2 at rt, following workup. Although the dibromoolefinic products **13a−c** are relatively stable, overall yields for these derivatives remained low for the two-step process. Conversely, enediynones **12d−f** were considerably more stable and could be isolated in good yields and characterized in all cases. The enhanced stability of **12d−f** also afforded increased yields for dibromoolefins **13d−f**, which were isolated in 40−75% yield. Carbenoid rearrangement of **13a−f** to triynes **14a−f** was accomplished in the same manner as outlined for diyne formation above. Yields from these rearrangements were moderate to excellent, with olefinic derivatives consistently formed in higher yields. It should be noted that unlike the formation of azo diyne **11c**, which proceeded without isomerization of the azo moiety, triyne **14c** was isolated and characterized as a mixture of its *E*- and *Z*-stereoisomers.

This general sequence of reactions is applicable to the assembly of larger, extended polyyne systems as outlined in Scheme 4. Diol **15** is easily produced in 88% yield as a mixture of stereoisomers via the condensation of $Li{-}C{\equiv}C{-}SiMe_3$ with terephthaldehyde. Oxidation with

SCHEME 4[a]



[a] Reagents and conditions: (a) PCC, Celite, molecular sieves (4 Å), CH_2Cl_2, rt; (b) PPh_3 (2 equiv), CBr_4, CH_2Cl_2, rt; (c) *n*-BuLi, hexanes, −78 to −40 °C.

PCC, followed by dibromoolefination, gave the tetrabromide **17** in 57% yield over the two steps from **15**. Subjecting **17** to 2.4 equiv of *n*-BuLi afforded 1,4-bis(4-trimethylsilyl-1,3-butadiynyl)benzene (**18**) in 87% yield as a colorless, quite stable, crystalline solid. The formation of **18** nicely demonstrates the ability to scale-up the rearrangement protocol: this reaction produced nearly 2 g of **18**.

Single crystals of **18** were easily grown from a concentrated solution in hexanes at 4 °C. X-ray crystallographic analysis of **18** shows the butadiynyl segments to be nearly linear, as expected for an sp-hybridized carbon system (Figure 1). The most notable feature of the solid-state structure is the parallel solid-state alignment of neighboring molecules, in a manner potentially suitable for topochemical polymerization. Analysis of the packing parameters shows that the stacking angle between neighboring molecules is $\theta = 49°$, near the optimal value of 45° required for a 1,4-polymerization process.[35] The stacking distance at d = 5.9 Å and distance between reacting atoms R = 4.4 Å (C7 to C4 of the neighboring molecule), however, are both outside the ideal values of

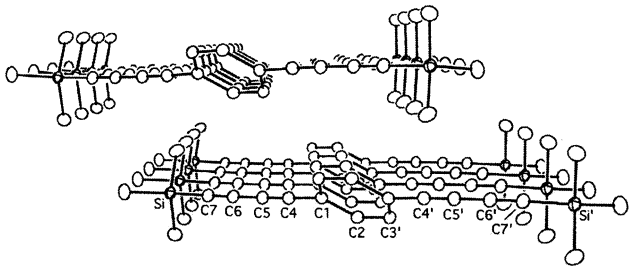
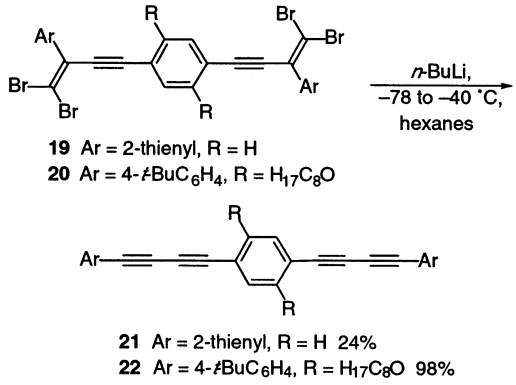


FIGURE 1. ORTEP drawing (20% probability level) of **18** demonstrating solid-state packing. Selected bond lengths (Å) and angles (deg): C(1)−C(4) 1.432(3), C(4)−C(5) 1.196(3), C(5)−C(6) 1.377(3), C(6)−C(7) 1.208(3); C(1)−C(4)−C(5) 178.8-(2), C(4)−C(5)−C(6) 178.7(2), C(5)−C(6)−C(7) 179.6(2), C(6)−C(7)−Si 178.57(19).

SCHEME 5



$d \approx 5$ Å and $R < 4$ Å, respectively. Thus, the observed stability of **18** in the solid state can be attributed, at least in part, to the inability of the compound to undergo topochemical polymerization.

The syntheses of two functionalized, extended polyyne systems are described in Scheme 5. Tetrabromide **19** derives from the condensation of the bis(lithium) acetylide of 1,4-(diethynyl)benzene with 2-thiophene carboxaldehyde, followed by PCC oxidation and dibromoolefination under standard conditions. The tetrabromide **19** was isolated in 33% yield, over two steps from the diol, with the moderate yield primarily the result of the problematic isolation of the relatively insoluble solid **19** from the reaction mixture. Rearrangement of tetrabromide **19** to tetrayne **21** was accomplished by the addition of *n*-BuLi at −78 °C and then allowing the reaction mixture to warm to approximately −10 °C to increase the solubility of **19** and facilitate the rearrangement. The rigid tetrayne **21** proved to be a nearly insoluble solid, which hampered isolation and purification. Nonetheless, it could be obtained in 24% yield as a yellow solid that has been identified by its ^{1}H NMR spectrum, which demonstrates its symmetrical structure, and by mass spectrometry, which shows the expected parent signal at *m*/*z* 338.

The tetrabromide **20** is obtained as a stable oil via the two-step sequence of the Friedel−Crafts acylation of 1,4-di(octyloxy)-2,5-bis(trimethylsilylethynyl)benzene with 4-*tert*-butylbenzoyl chloride, followed by dibromoolefination in CH_3CN. Although the octyloxy side chains and the *tert*-butyl end groups greatly enhanced the solubility of **20**, yields from the dibromoolefination step remained frustratingly low (∼20%), regardless of the conditions employed. Solubility did, however, have a dramatic effect on the yield of the rearrangement step, and the highly fluorescent, stable tetrayne **22** was produced in nearly quantitative yield from tetrabromide **20**.

Conclusions

In summary, the carbenoid rearrangement described herein provides a facile route to a range of aryl diyne and triyne systems. This synthetic route offers several attractive features versus more commonly employed palladium coupling methods including (1) the wide range of commercially available aryl and vinyl aldehydes and carboxylic acid precursors, (2) tolerance of a range of chemical functionalities, and (3) generally rapid reaction times and easy purification/isolation that often allow for all four transformations of the di- or triyne synthesis to be accomplished within a single day. The most significant limitation of this method, to date, is the variability encountered in the conversion of ynones into the requisite dibromoolefinic precursors. Whereas this step generally proceeds in good yield for derivatives of trimethylsilyl-substituted substrates, other end groups are not as well tolerated.

Experimental Section

General Information. Reagents were purchased reagent grade from commercial suppliers and used without further purification. Et_2O and benzene were distilled from sodium/benzophenone ketyl, and hexanes and dichloromethane were distilled from CaH_2 immediately prior to use. Anhydrous $MgSO_4$ was used as the drying agent after aqueous workup. 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. For simplicity, the coupling constants of the aryl protons for *para*-substituted phenyl groups have been reported as pseudo-first-order, even though they are second-order spin systems. For mass spectral analyses, low-resolution data are provided in cases where M^+ is not the base peak; otherwise, only high-resolution data are provided.

General Procedure for Alcohol Formation. To trimethylsilylacetylene (1.23 g, 12.5 mmol, 1.25 equiv) in Et_2O (50 mL) at −78 °C was added *n*-BuLi (2.5 M in hexanes, 4.8 mL, 12 mmol, 1.2 equiv). After the mixture was stirred for 30 min, the appropriate aldehyde (10 mmol, 1 equiv) in Et_2O (5 mL) was added. The reaction mixture was slowly warmed to ca. −10 °C until the reaction was judged complete by TLC analysis. The reaction was quenched with saturated aq NH_4Cl at −78 °C, and the organic layer was washed with brine (2 × 50 mL) and dried ($MgSO_4$). The resulting alcohol could generally be used without further purification.

General Procedure for Ketone Formation via Oxidation Using PCC. To the appropriate alcohol (4 mmol) in CH_2Cl_2 (50 mL) were added sequentially Celite (equal amount by mass to that of PCC), molecular sieves (4 Å, equal amount by mass to that of PCC), and PCC (5 mmol, 1.25 equiv). After being stirred at rt until the reaction was judged complete by TLC analysis, the solution was filtered through a plug of silica (CH_2Cl_2), and the solvent was evaporated to give the corresponding ketone. The ketone was of sufficient purity to be carried directly to the dibromoolefination step without further

(35) Shirakawa, H.; Masuda, T.; Takeda, K. In *The Chemistry of Triple-bonded Functional Groups*; Patai, S., Ed.; John Wiley and Sons: New York, 1994; Vol. 2, Suppl. 2, pp 992−994.

purification, or could be isolated pure by column chromatography (hexanes/CH_2Cl_2, 1:1).

General Procedure for Ketone Formation via Oxidation Using $BaMnO_4$. To the appropriate alcohol (4 mmol) in CH_2Cl_2 (50 mL) was added barium manganate (3 equiv). After being stirred at rt until the reaction was judged complete by TLC analysis, the solution mixture was filtered through a pad of Celite. The solvent was evaporated to give the corresponding ketone.

General Procedure for Ketone Formation via Friedel–Crafts Acylation. The formation of **9a**–**f** and **12a**–**f** was accomplished as reported for similar derivatives.[34] Commercially available acid chlorides were used except for 4-phenylazobenzoyl chloride, 3-(2-thienyl)acryloyl chloride, and sorbyl chloride, which were made from the commercially available carboxylic acid.

General Procedure for Acid Chloride Formation. To the appropriate carboxylic acid (1 equiv) was added thionyl chloride (6 equiv). After the mixture was stirred for 24 h, the excess thionyl chloride was evaporated, and the acid chloride was used directly in the next step without further purification.

General Procedure for Dibromoolefin Formation. Literature procedures were followed as referenced.[27] In some cases, and to date unexplained, reactions conducted under reported conditions would fail to go to completion using the normal amounts of PPh_3 and CBr_4. In these cases, an additional equivalent of both PPh_3 and CBr_4 would be added to force the reaction to completion.

General Procedure for Diyne Formation.[36] Unless otherwise noted, the following procedure was followed. To the appropriate dibromoolefin (0.368 mmol) in dry hexanes (10 mL) at −78 °C was added dropwise over 10 min 1.1−1.2 equiv of *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol). The mixture was warmed to approximately −40 °C for 30 min, recooled to −78 °C, and quenched with a saturated aq solution of NH_4Cl. Et_2O was added (∼50 mL), and the organic layer was separated, washed with a saturated aq solution of NH_4Cl, and dried over magnesium sulfate. Solvent removal in vacuo and passing the residue through a short plug of silica gel with the solvent system detailed for each product afforded the desired diyne. If necessary, additional purification could be achieved via flash column chromatography.

[4-(1-Naphthyl)-1,3-butadiynyl]trimethylsilane (8a). Dibromoolefin **7a** (757 mg, 1.85 mmol) was reacted with *n*-BuLi (1.0 mL, 2.5 M in hexanes, 2.5 mmol) as per the general procedure to give diyne **8a** (430 mg, 93%) as a yellow oil: R_f = 0.3 (hexanes); IR (CH_2Cl_2 cast) 3058, 2959, 2199, 2098, 1585, 1505, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.73 (dd, J = 7.2, 1.1 Hz, 1H), 7.57 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.51 (ddd, J = 8.1, 6.8, 1.4 Hz, 1H), 7.40 (dd, J = 8.3, 7.2 Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (125 MHz, APT, $CDCl_3$) δ 134.0, 133.0, 132.2, 129.7, 128.3, 127.1, 126.6, 126.0, 125.1, 119.0, 91.7, 88.0, 78.8, 75.1, −0.2; EI HRMS m/z calcd for $C_{17}H_{16}Si$ (M^+) 248.1021, found 248.1019.

[4-(1-Pyrenyl)-1,3-butadiynyl]trimethylsilane (8b). Dibromoolefin **7b** (177 mg, 0.367 mmol) was reacted in hexanes (20 mL) at −50 °C (rather than −78 °C due to decreased solubility of dibromoolefin **7b**) with *n*-BuLi (0.16 mL, 2.5 M in hexanes, 0.40 mmol) to give **8b** (92.8 mg, 79%) as a bright yellow solid: mp 124−125 °C; R_f = 0.8 (CH_2Cl_2/hexanes, 1:1); IR ($CHCl_3$ cast) 3046, 2195, 2095, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, J = 9.0 Hz, 1H), 8.10 (m, 4H), 7.98 (m, 3H), 7.92 (t, J = 9.0 Hz, 1H), 0.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.5, 131.8, 131.0, 130.8, 130.6, 128.8, 128.7, 127.0, 126.3, 125.9, 125.8, 125.1, 124.3, 124.1, 123.9, 115.4, 92.2, 88.4, 79.6, 76.3, −0.2; EI HRMS m/z calcd for $C_{23}H_{18}Si$ (M^+) 322.1178, found 322.1174.

[4-(2-Methoxyphenyl)-1,3-butadiynyl]trimethylsilane (8c). Dibromoolefin **7c** (82.0 mg, 0.211 mmol) was reacted with *n*-BuLi (0.10 mL, 2.5 M in hexanes, 0.25 mmol) as per the general procedure to give diyne **8c** (20.6 mg, 43%) as a yellow oil: R_f = 0.7 (hexanes/CH_2Cl_2, 1:1); IR (CH_2Cl_2 cast) 2959, 2836, 2204, 2103, 1594, 1273 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 1H), 7.30 (m, 1H), 6.86 (m, 2H), 3.86 (s, 3H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, APT, $CDCl_3$) δ 161.6, 134.5, 130.7, 120.4, 110.6, 91.0, 88.1, 77.9, 73.3, 55.8, −0.2 (one coincident peak not observed); EI HRMS m/z calcd for $C_{14}H_{16}OSi$ (M^+) 228.0971, found 228.0967.

[4-(3-Methoxyphenyl)-1,3-butadiynyl]trimethylsilane (8d). Dibromoolefin **7d** (152 mg, 0.392 mmol) was reacted with *n*-BuLi (0.16 mL, 2.5 M in hexanes, 0.40 mmol) as per the general procedure to give diyne **8d** (67.3 mg, 75%) as a colorless oil: R_f = 0.8 (hexanes/CH_2Cl_2, 1:1); IR ($CHCl_3$ cast) 3004, 2959, 2207, 2102, 1596, 1574, 1251 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, J = 8.2, 7.7 Hz, 1H), 7.07 (ddd, J = 1.1, 1.4, 7.7 Hz, 1H), 6.98 (dd, J = 1.4, 2.6 Hz, 1H), 6.91 (ddd, J = 8.2, 2.6, 1.1 Hz, 1H), 3.77 (s, 3H), 0.22 (s, 9H); ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 159.2, 129.5, 125.2, 122.3, 117.2, 116.1, 90.7, 87.7, 76.6, 73.9, 55.2, −0.4; EI HRMS m/z calcd for $C_{14}H_{16}OSi$ (M^+) 228.0971, found 228.0966. Anal. Calcd for $C_{14}H_{16}OSi$: C, 73.63; H, 7.06. Found: C, 73.69; H, 6.99.

[4-(4-Methoxyphenyl)-1,3-butadiynyl]trimethylsilane (8e). Dibromoolefin **7e** (139 mg, 0.358 mmol) was reacted with *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol) as per the general procedure to give diyne **8e** (67.2 mg, 82%) as a yellow oil. Spectral data were consistent with those reported by Haley.[37]

[4-(4-*n*-Butoxyphenyl)-1,3-butadiynyl]trimethylsilane (8f). Dibromoolefin **7f** (200 mg, 0.464 mmol) was reacted with *n*-BuLi (0.19 mL, 2.5 M in hexanes, 0.48 mmol) as per the general procedure to give diyne **8f** (99 mg, 79%) as a yellow solid: mp 68−69 °C; R_f = 0.9 (hexanes/Et_2O, 4:1); IR (CH_2Cl_2 cast) 2956, 2940, 2871, 2203, 2101, 1602, 1508, 1257 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.96 (t, J = 7.2 Hz, 2H), 1.76 (m, 2H), 1.48 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 160.1, 134.3, 114.7, 113.0, 89.8, 88.2, 77.2, 73.0, 67.9, 31.2, 19.2, 13.8, −0.3; MS (EI, 70 eV) m/z 270.1 (M^+, 78), 199.1 ([M − C_4H_8 − CH_3]$^+$, 100); EI HRMS m/z calcd for $C_{17}H_{22}OSi$ (M^+) 270.1440, found 270.1436.

[4-(2-Furyl)-1,3-butadiynyl]trimethylsilane (8h). Dibromoolefin **7h** (126 mg, 0.362 mmol) was reacted with *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol) as per the general procedure to give diyne **8h** (37.1 mg, 54%) as a light yellow oil that slowly decomposes, even if kept refrigerated: R_f = 0.9 (hexanes/CH_2Cl_2, 1:1); IR (CH_2Cl_2 cast) 2960, 2201, 2104, 1251 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.43 (dd, J = 2.0, 0.1 Hz, 1H), 6.77 (dd, J = 3.3, 0.7 Hz, 1H), 6.43 (dd, J = 3.3, 0.7 Hz, 1H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, APT, CD_2Cl_2) δ 145.4, 136.5, 119.1, 111.6, 94.6, 87.2, 79.2, 66.4, −0.4; MS (EI, 70 eV) m/z 188.1 (M^+, 44), 173.0 ([M − CH_3]$^+$, 100); EI HRMS m/z calcd for $C_{11}H_{12}OSi$ (M^+) 188.0658, found 188.0662.

[4-(2-Thienyl)-1,3-butadiynyl]trimethylsilane (8i). Dibromoolefin **7i** (582 mg, 1.60 mmol) was reacted with *n*-BuLi (0.77 mL, 2.5 M in hexanes, 1.93 mmol) as per the general procedure to give diyne **8i** (298 mg, 91%) as a light brown oil that slowly decomposes, even if kept refrigerated: R_f = 0.9 (CH_2Cl_2/hexanes, 1:1); IR ($CHCl_3$ cast) 3107, 2960, 2194, 2101, 1251 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.31 (m, 2H), 7.10 (m, 1H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, APT, CD_2Cl_2) δ 134.7, 128.9, 127.2, 121.7, 93.0, 87.6, 78.3, 69.8, −0.4; MS (EI, 70 eV) m/z 204.0 (M^+, 37), 189.0 ([M − CH_3]$^+$, 100); EI HRMS m/z calcd for $C_{11}H_{12}SSi$ (M^+) 204.0429, found 204.0424.

(4-Ferrocenyl-1,3-butadiynyl)trimethylsilane (8k). To dibromoolefin **7k** (153 mg, 0.373 mmol) in dry hexanes (10 mL) at −78 °C was added dropwise over 10 min 1 equiv of *n*-BuLi (0.16 mL, 2.5 M in hexanes, 0.40 mmol). The mixture was

(36) The general experimental details and characterization for all alcohols, ketones, and dibromoolefin precursors are detailed in the Supporting Information.

(37) Wan, W. B.; Haley, M. M. *J. Org. Chem.* **2001**, *66*, 3893−3901.

warmed to −20 °C and cooled to −78 °C, and an additional 1/4 equiv of *n*-BuLi (0.04 mL, 2.5 M in hexanes) was added. Workup as per the general procedure and purification via column chromatography (hexanes/CH_2Cl_2, 2:1) gave diyne **8k** (32 mg, 28%) as an orange oil: $R_f = 0.7$ (hexanes/CH_2Cl_2, 1:1); IR (CH_2Cl_2 cast) 2925, 2205, 2102, 1249 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.49 (t, $J = 1.8$ Hz, 2H), 4.25 (s, 5H), 4.24 (t, $J = 1.8$ Hz, 2H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 88.7, 87.6, 77.3, 72.3, 70.5, 70.2, 69.4, 62.5, −0.3; EI HRMS *m/z* calcd for $C_{17}H_{18}SiFe$ (M^+) 306.0527, found 306.0530.

(6-Phenylhex-5-ene-1,3-diynyl)trimethylsilane (8l). Dibromoolefin **7l** (610 mg, 1.59 mmol) was reacted with *n*-BuLi (0.76 mL, 2.5 M in hexanes, 1.9 mmol) as per the general procedure to give diyne **8l** (338 mg, 95%) as a yellow oil: $R_f =$ 0.4 (hexanes); IR ($CHCl_3$ cast) 3030, 2959, 2925, 2191, 2092, 1605, 1492, 1448 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 5H), 7.08 (d, $J = 16.2$ Hz, 1H), 6.16 (d, $J = 16.2$ Hz, 1H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 145.1, 135.6, 129.3, 128.8, 126.4, 106.3, 91.3, 88.0, 76.5, 76.3, −0.4; MS (EI, 70 eV) *m/z* 224.1 (M^+, 50), 209.1 ($[M - CH_3]^+$, 100); EI HRMS *m/z* calcd for $C_{15}H_{16}Si$ (M^+) 224.1021, found 224.1020. Anal. Calcd for $C_{15}H_{16}Si$: C, 80.29; H, 7.19. Found: C, 80.06; H, 7.16.

[4-(*S*)-(−)-Perillyl-1,3-butadienyl]trimethylsilane (8m). Dibromoolefin **7m** (131 mg, 0.324 mmol) was reacted with *n*-BuLi (0.16 mL, 2.5 M in hexanes, 0.40 mmol) as per the general procedure to give diyne **8m** (37 mg, 46%) as a pale yellow oil which solidified into a yellow solid upon refrigeration: mp 52−54 °C; $R_f = 0.3$ (hexanes); IR (CH_2Cl_2 cast) 3082, 2960, 2198, 2098, 1676, 1645 cm^{-1}; $[\alpha]^{22}_D$ −17.2° ($c = 0.0029$, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 6.29 (m, 1H), 4.73 (m, 1H), 4.69 (m, 1H), 2.20 (m, 3H), 2.10 (m, 1H), 2.03 (m, 1H), 1.80 (m, 1H), 1.71 (s, 3H), 1.45 (m, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 148.8, 138.7, 119.1, 109.2, 89.4, 88.1, 78.5, 72.0, 39.8, 31.3, 28.9, 27.0, 20.6, −0.4; MS (EI, 70 eV) *m/z* 242.1 (M^+, 51); EI HRMS *m/z* calcd for $C_{16}H_{22}Si$ (M^+) 242.1491, found 242.1491.

1-(3-Methoxyphenyl)-1,3-octadiyne (8p). Dibromoolefin **7p** (121 mg, 0.325 mmol) was reacted with *n*-BuLi (0.23 mL, 1.6 M in hexanes, 0.37 mmol) as per the general procedure to give diyne **8p** (63.3 mg, 92%) as a yellow oil: $R_f = 0.6$ (hexanes/CH_2Cl_2, 2:1); IR (CH_2Cl_2 cast) 3072, 3002, 2958, 2242, 2152, 1601, 1594, 1574, 1489, 1427 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, $J = 8.0$ Hz, 1H), 7.05 (dd, $J = 1.0$, 1.5 Hz, 1H), 6.98 (dd, $J = 2.6$, 1.5 Hz, 1H), 6.87 (ddd, $J = 8.0$, 2.6, 1.0 Hz, 1H), 3.77 (s, 3H), 2.35 (t, $J = 7.0$ Hz, 2H), 1.55 (m, 2H), 1.45 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 159.2, 129.5, 125.1, 123.1, 117.2, 115.7, 84.9, 74.6, 74.2, 65.0, 55.3, 30.3, 21.9, 19.3, 13.5; EI HRMS *m/z* calcd for $C_{15}H_{16}O$ (M^+) 212.1201, found 212.1200.

1-(2-Thienyl)-1,3-octadiyne (8q). Dibromoolefin **7q** (70.9 mg, 0.204 mmol) was reacted with *n*-BuLi (0.15 mL, 1.6 M in hexanes, 0.24 mmol) as per the general procedure to give diyne **8q** (32.9 mg, 86%) as a yellow oil: $R_f = 0.7$ (hexanes); IR (CH_2Cl_2 cast) 3106, 2957, 2931, 2871, 2231, 2151, 1465, 1425 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, $J = 3.7$, 1.1 Hz, 1H), 7.23 (dd, $J = 5.1$, 1.1 Hz, 1H), 6.94 (dd, $J = 5.1$, 3.7 Hz, 1H), 2.36 (t, $J = 7.0$ Hz, 2H), 1.54 (m, 2H), 1.44 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 133.8, 127.9, 127.0, 122.5, 87.0, 78.5, 67.6, 64.9, 30.2, 21.9, 19.4, 13.5; EI HRMS *m/z* calcd for $C_{12}H_{12}S$ (M^+) 188.0660, found 188.0662.

1-(2-Thienyl)-1,3-pentadiyne (8r). Dibromoolefin **7r** (76.6 mg, 0.250 mmol) was reacted with *n*-BuLi (0.12 mL, 2.5 M in hexanes, 0.30 mmol) as per the general procedure to give diyne **8r** (14.8 mg, 41%) as a colorless oil: $R_f = 0.5$ (hexanes); IR ($CHCl_3$ cast) 3105, 2912, 2850, 2236, 2150, 1426 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, $J = 3.7$, 1.2 Hz, 1H), 7.25 (dd, $J = 5.2$, 1.2 Hz, 1H), 6.94 (dd, $J = 5.2$, 3.7 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, APT, $CDCl_3$) δ 133.9, 128.0, 127.0, 122.4, 82.6, 78.6, 67.2, 64.3, 4.8; EI HRMS *m/z* calcd for C_9H_6S (M^+) 146.0190, found 146.0188.

[4-(4-*n*-Hexylphenyl)-1,3-butadiynyl]trimethylsilane (11a). Dibromoolefin **10a** (170 mg, 0.384 mmol) was reacted with *n*-BuLi (0.16 mL, 2.5 M in hexanes, 0.40 mmol) as per the general procedure to give diyne **11a** (76.1 mg, 70%) as a colorless oil: $R_f = 0.6$ (hexanes); IR ($CHCl_3$ cast) 3029, 2958, 2204, 2103, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.3$ Hz, 2H), 2.57 (t, $J = 7.7$ Hz, 2H), 1.57 (m, 2H), 1.27 (m, 6H), 0.86 (m, 3H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 132.6, 128.5, 118.4, 90.1, 88.0, 77.1, 73.5, 36.0, 31.6, 31.1, 28.9, 22.5, 14.0, −0.4; MS (EI, 70 eV) *m/z* 282.2 (M^+, 65), 267.2 ($[M - CH_3]^+$, 100); EI HRMS *m/z* calcd for $C_{19}H_{26}Si$ (M^+) 282.1804, found 282.1796. Anal. Calcd for $C_{19}H_{26}Si$: C, 80.78; H, 9.28. Found: C, 80.73; H, 9.54.

[4-(4-*tert*-Butylphenyl)-1,3-butadiynyl]trimethylsilane (11b). Dibromoolefin **10b** (152 mg, 0.367 mmol) was reacted with *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol) as per the general procedure to give diyne **11b** (82.2 mg, 88%) as a yellow crystalline solid. Spectral data were consistent with those reported by Haley.[37]

[4-(4-Trimethylsilyl-1,3-butadiynyl)phenyl]phenyldiazene (11c). Dibromoolefin **10c** (170 mg, 0.369 mmol) was reacted with *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol) as per the general procedure to give diyne **11c** (67.6 mg, 61%) as a red solid: mp 103−104 °C; $R_f = 0.7$ (hexanes/CH_2Cl_2, 2:1); IR (CH_2Cl_2 cast) 2960, 2202, 2102, 1404, 1278, 1253, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, $J = 8.3$, 1.8 Hz, 2H), 7.86 (d, $J = 8.7$ Hz, 2H), 7.62 (d, $J = 8.7$ Hz, 2H), 7.50 (m, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.5, 152.3, 133.5, 131.4, 129.1, 123.9, 123.0, 122.9, 92.2, 87.7, 76.4, 76.4, −0.2; MS (EI, 70 eV) *m/z* 302.1 (M^+, 89), 297.0 ($[M - C_6H_3N_2]^+$, 100); EI HRMS *m/z* calcd for $C_{19}H_{18}N_2Si$ (M^+) 302.1239, found 302.1245. Anal. Calcd for $C_{19}H_{18}N_2Si$: C, 75.45; H, 6.00; N, 9.26. Found: C, 74.92; H, 5.92; N, 9.18.

[4-(3,4,5-Trimethoxyphenyl)-1,3-butadiynyl]trimethylsilane (11d). Dibromoolefin **10d** (255 mg, 0.569 mmol) was reacted with *n*-BuLi (0.27 mL, 2.5 M in hexanes, 0.68 mmol) as per the general procedure, and purification by column chromatography (SiO_2, hexanes/CH_2Cl_2, 4:1) gave diyne **11d** (83.1 mg, 51%) as a yellow solid: mp 75−78 °C; $R_f = 0.2$ (hexanes/CH_2Cl_2, 1:1); IR ($CHCl_3$ cast) 2959, 2203, 2095, 1249, 1130 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 2H), 3.84 (s, 3H), 3.82 (s, 6H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 153.0, 140.0, 116.1, 109.9, 90.6, 87.7, 76.8, 73.3, 60.9, 56.1, −0.4; EI HRMS *m/z* calcd for $C_{16}H_{20}O_3Si$ (M^+) 288.1182, found 288.1179. Anal. Calcd for $C_{16}H_{20}O_3Si$: C, 66.63; H, 6.99. Found: C, 66.73; H, 7.03.

[6-(2-Thienyl)hex-5-ene-1,3-diynyl]trimethylsilane (11e). Dibromoolefin **10e** (679 mg, 1.74 mmol) was reacted with *n*-BuLi (0.84 mL, 2.5 M in hexanes, 2.1 mmol) as per the general procedure to give diyne **11e** (221 mg, 55%) as a yellow oil: $R_f = 0.3$ (hexanes); IR (CH_2Cl_2 cast) 2959, 2188, 2093, 1593, 1425, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, $J = 5.1$ Hz, 1H), 7.16 (d, $J = 15.9$ Hz, 1H), 7.05 (d, $J = 3.6$ Hz, 1H), 6.99 (dd, $J = 5.1$, 3.6 Hz, 1H), 5.95 (d, $J = 15.9$ Hz, 1H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 140.8, 137.7, 128.0, 127.9, 126.4, 105.3, 91.6, 88.0, 76.7, 76.3, −0.4; MS (EI, 70 eV) *m/z* 230.1 (M^+, 55), 215.0 ($[M - CH_3]^+$, 100); HRMS *m/z* calcd for $C_{13}H_{14}SSi$ (M^+) 230.0586, found 230.0586. Anal. Calcd for $C_{13}H_{14}SSi$: C, 67.77; H, 6.13. Found: C, 67.50; H, 6.27.

[6-(4-*n*-Hexylphenyl)-1,3,5-hexatriynyl]trimethylsilane (14a). Dibromoolefin **13a** (171 mg, 0.366 mmol) was reacted with *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol) as per the general procedure to give triyne **14a** (46.4 mg, 41%) as a light yellow oil: $R_f = 0.7$ (hexanes); IR (CH_2Cl_2 cast) 3029, 2957, 2928, 2856, 2176, 2075, 1604, 1509, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, $J = 8.2$ Hz, 2H), 7.12 (d, $J = 8.2$ Hz, 2H), 2.59 (t, $J = 7.8$ Hz, 2H), 1.60 (m, 2H), 1.28 (m, 6H), 0.87 (m, 3H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 145.4, 133.1, 128.7, 117.9, 88.8, 88.2, 77.4, 73.8, 66.6, 61.9, 36.1, 31.7, 31.1, 28.9, 22.6, 14.1, −0.4; MS (EI, 70 eV) *m/z* 306.2 (M^+, 96), 291.2 ($[M - CH_3]^+$, 100); EI HRMS *m/z* calcd for $C_{21}H_{26}Si$ (M^+) 306.1804, found 306.1817. Anal. Calcd for $C_{21}H_{26}Si$: C, 82.29; H, 8.55. Found: C, 81.82; H, 8.74.

[6-(4-*tert*-Butylphenyl)-1,3,5-hexatriynyl]trimethylsilane (14b). Dibromoolefin **13b** (80.6 mg, 0.184 mmol) was reacted with *n*-BuLi (0.08 mL, 2.5 M in hexanes, 0.20 mmol) as per the general procedure to give triyne **14b** (50.0 mg, 98%) as a yellow solid: mp 78−80 °C; R_f = 0.9 (hexanes/CH_2Cl_2, 2:1); IR ($CHCl_3$ cast) 2962, 2903, 2181, 2169, 2075, 1652, 1599, 1504, 1462, 1407 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 1.30 (s, 9H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 153.5, 132.9, 125.6, 117.7, 88.8, 88.2, 77.3, 73.8, 66.6, 61.9, 35.0, 31.1, −0.4; MS (EI, 70 eV) *m*/*z* 278.1 (M^+, 49), 263.1 ([M − CH_3]$^+$, 100); EI HRMS *m*/*z* calcd for $C_{19}H_{22}Si$ (M^+) 278.1491, found 278.1497.

[4-(6-Trimethylsilyl-1,3,5-hexatriynyl)phenyl]phenyldiazene (14c). Dibromoolefin **13c** (54.7 mg, 0.113 mmol) was reacted with *n*-BuLi (0.04 mL, 2.5 M in hexanes, 0.10 mmol) as per the general procedure to give triyne **14c** (16.8 mg, 46%) as a bright orange solid, a mixture of *E*- and *Z*-isomers: mp 88−89 °C; R_f = 0.6 (hexanes/CH_2Cl_2, 4:1); IR (CH_2Cl_2 cast) 2959, 2167, 2075, 1248, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.3, 2.1 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.50 (m, 3H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ (major isomer) 152.7, 152.6, 134.0, 131.6, 129.2, 123.3, 123.1, 123.0, 89.9, 88.0, 77.3, 76.5, 68.1, 61.4, −0.5; MS (EI, 70 eV) *m*/*z* 326.1 (M^+, 93), 221.1 ([M − $C_6H_5N_2$]$^+$, 100); EI HRMS *m*/*z* calcd for $C_{21}H_{18}N_2Si$ (M^+) 326.1239, found 326.1241.

(8-Phenyloct-7-ene-1,3,5-triynyl)trimethylsilane (14d). Dibromoolefin **13d** (420 mg, 1.03 mmol) was reacted with *n*-BuLi (0.49 mL, 2.5 M in hexanes, 1.2 mmol) as per the general procedure to give diyne **14d** (210 mg, 82%) as an orange/yellow oil: R_f = 0.3 (hexanes); IR ($CHCl_3$ cast) 3030, 2959, 2162, 2073, 1601, 1448 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 5H), 7.15 (d, J = 16.3 Hz, 1H), 6.18 (d, J = 16.3 Hz, 1H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 146.5, 135.4, 129.6, 128.8, 126.6, 105.8, 89.4, 88.2, 76.8, 76.5, 67.5, 61.9, −0.5; MS (EI, 70 eV) *m*/*z* 248.1 (M^+, 59), 233.1 ([M − CH_3]$^+$, 100); EI HRMS *m*/*z* calcd for $C_{17}H_{16}Si$ (M^+) 248.1021, found 248.1018. Anal. Calcd for $C_{17}H_{16}Si$: C, 82.20; H, 6.49. Found: C, 82.19; H, 6.78.

[8-(2-Thienyl)oct-7-ene-1,3,5-triynyl]trimethylsilane (14e). Dibromoolefin **13e** (459 mg, 1.11 mmol) was reacted with *n*-BuLi (0.53 mL, 2.5 M in hexanes, 1.3 mmol) as per the general procedure to give triyne **14e** (209 mg, 74%) as a yellow solid: mp 55−56 °C; R_f = 0.3 (hexanes); IR (CH_2Cl_2 cast) 2959, 2898, 2161, 2083, 2061, 1589, 1425, 1311, 1288, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 5.7 Hz, 1H), 7.23 (d, J = 15.6 Hz, 1H), 7.07 (d, J = 3.6 Hz, 1H), 7.00 (dd, J = 5.7, 3.6 Hz, 1H), 5.95 (d, J = 15.9 Hz, 1H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, APT, $CDCl_3$) δ 140.6, 139.0, 128.5, 128.0, 126.9, 104.7, 89.6, 88.1, 76.9, 76.5, 67.8, 61.8, −0.5; MS (EI, 70 eV) *m*/*z* 254.1 (M^+, 80), 239.0 ([M − CH_3]$^+$, 100); EI HRMS *m*/*z* calcd for $C_{15}H_{14}SSi$ (M^+) 254.0586, found 254.0590.

(Undeca-7,9-diene-1,3,5-triynyl)trimethylsilane (14f). Dibromoolefin **13f** (104 mg, 0.279 mmol) was reacted with *n*-BuLi (0.13 mL, 2.5 M in hexanes, 0.34 mmol) as per the general procedure to give diyne **14f** (45.0 mg, 76%) as a pale yellow solid: mp 48−49 °C; R_f = 0.5 (hexanes); IR ($CHCl_3$ cast) 2958, 2924, 2853, 2162, 2074 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.74 (dd, J = 15.6, 10.8 Hz, 1H), 6.11 (dd, J = 14.7, 10.8 Hz, 1H), 5.90 (dq, J = 14.7, 6.3 Hz, 1H), 5.46 (d, J = 15.6 Hz, 1H), 1.79 (d, J = 6.3 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, APT, $CDCl_3$) δ 147.4, 135.9, 130.9, 106.3, 89.2, 88.3, 77.2, 76.0, 67.3, 62.0, 18.6, −0.4; MS (EI, 70 eV) *m*/*z* 212.1 (M^+, 96), 197.1 ([M − CH_3]$^+$, 100); EI HRMS *m*/*z* calcd for $C_{14}H_{16}Si$ (M^+) 212.1021, found 212.1019.

1,4-Bis(4-trimethylsilyl-1,3-butadiynyl)benzene (18). Dibromoolefin **17** (4.12 g, 6.46 mmol) was reacted with *n*-BuLi (6.2 mL, 2.5 M in hexanes, 15.5 mmol) as per the general procedure to give tetrayne **18** (1.79 g, 87%) as colorless crystals: mp 187−188 °C; R_f = 0.4 (hexanes); IR ($CHCl_3$ cast) 2957, 2209, 2105, 1400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 4H), 0.21 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 122.3, 92.4, 87.5, 76.7, 75.9, −0.5; MS (EI, 70 eV) *m*/*z* 318.1 (M^+, 75), 303.1 ([M − CH_3]$^+$, 100); EI HRMS *m*/*z* calcd for $C_{20}H_{22}Si_2$ (M^+) 318.1260, found 318.1261. Anal. Calcd for $C_{20}H_{22}Si_2$: C, 75.40; H, 6.96. Found: C, 75.01; H, 6.89.

1,4-Bis[4-(2-thienyl)-1,3-butadiynyl]benzene (21). The bis(dibromoolefin) **19** (37.6 mg, 0.057 mmol) was stirred in 7 mL of dry hexanes at −78 °C, and *n*-BuLi (0.24 mL, 2.5 M in hexanes, 1.4 mmol) was added. The heterogeneous mixture was then warmed to about −10 °C for several minutes and then cooled to −78 °C before workup. Addition of $CH_2Cl_2$was required to solubilize the product for workup. Recrystallization (hexanes/CH_2Cl_2) yielded **21** (4.5 mg, 24%) as a shiny light-brown solid: mp 261 °C dec; R_f = 0.7 (hexanes/CH_2Cl_2, 1:1); IR (microscope) 3101, 2202, 2143, 1663 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.48 (s 4H), 7.37 (d, J = 4.4 Hz, 4H), 7.01 (m, 2H); ^{13}C NMR (100 MHz, APT, CD_2Cl_2) δ 135.2, 132.8, 129.7, 127.7, 122.9, 121.9, 83.2, 77.8, 76.4, 76.3; EI HRMS *m*/*z* calcd for $C_{22}H_{10}S_2$ (M^+) 338.0224, found 338.0220.

1,4-Bis[4-(4-*tert*-butylphenyl)-1,3-butadiynyl]-2,5-bis(octyloxy)benzene (22). Dibromoolefin **20** (16 mg, 0.016 mmol) was reacted with *n*-BuLi (0.01 mL, 2.5 M in hexanes, 0.031 mmol) as per the general procedure to give tetrayne **22** (10.7 mg, 98%) as a yellow waxy solid: mp 118−119 °C; R_f = 0.8 (hexanes/EtOAc, 9:1); IR (CH_2Cl_2 cast) 2924, 2209, 2143, 1603, 1467, 1262, 1221 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 4H), 7.34 (d, J = 8.6 Hz, 4H), 6.94 (s, 2H), 3.96 (t, J = 6.6 Hz, 4H), 1.80 (quint, J = 6.8 Hz, 4H), 1.47 (m, 4H), 1.30 (s, 18H), 1.27 (m, 16H), 0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 152.7, 132.3, 125.5, 118.8, 117.7, 113.6, 83.5, 79.7, 77.6, 73.6, 69.8, 34.9, 31.8, 31.1, 29.3, 29.26, 29.1, 26.0, 22.7, 14.1; EI HRMS *m*/*z* calcd for $C_{50}H_{62}O_2$ (M^+) 694.4750, found 694.4742.

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Supporting Information Available: General experimental and spectroscopic details for precursor alcohols, ketones, and dibromoolefins, ^1H and ^{13}C NMR spectra for all unpublished products, and X-ray crystallographic data for compound **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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