Preparation and Some Subsequent Transformations of Tetraethynylmethane

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Abstract: Tetraethynylmethane (**1**) was synthesized in 10 steps and 33% overall yield from bis[(trimethysilyl)ethynyl] ketone. This route features (1) construction of the critical central quaternary center via the agency of a [3,3] sigmatropic shift and (2) installation of the fourth acetylene unit in a very sterically demanding environment. Alternative routes and model systems which were more informative than productive are also discussed. Finally, transition metal-mediated coupling of the rather unstable **1** (and derivatives) with unsaturated partners furnished a variety of relatively stable polylalkynylated species which could be manipulated without event.

The broad range of desirable bulk physical properties, including several "extremes", exhibited by the naturally occurring carbon allotropes diamond and graphite have generated intense interest in preparing related materials by rational synthesis.[1] However, limited access to a wide range of structurally interesting monomer units along with difficulties in polymerization/characterization techniques have hampered the development of general strategies for homogeneous carbon network synthesis, despite a plethora of imaginative proposals for novel carbon allotropes suggested from computational studies.[1a,2] We have recently prepared the high carbon content monomer tetraethynylmethane (TEM) (**1**)[3] as a prelude to studies directed toward carbon network synthesis which will exploit the facility by which alkynes engage in efficient carbon–carbon bond forming reactions with sp and sp^2 coupling partners.[4] In this full accounting of our synthesis studies, we describe the details of our successful route as well as the pitfalls encountered in unproductive alternative approaches which, when taken together, illustrate the possibilities and difficulties associated with "packing" four sp-hydridized carbons about a single sp^3 carbon atom. In addition, we describe several Cu- and Pd-mediated coupling reactions of a trisilylated derivative of TEM (and TEM itself) which illustrate the potential for carbon network construction that attends this monomer.

Materials approaching high bond density, high carbon content solids have been prepared by Whitesides,[1d,f,g] inter alia, using the Glaser-type coupling of *planar* polyalkynyl aromatics followed, in some instances, by thermal curing of the resultant polymer. These heterogeneous materials exhibit interesting bulk properties (e.g., hardness, conductivity) although the molecular level details of the bonding arrangement(s) (three-dimensional network or two-dimensional sheet?) remain to be elucidated. In separate studies directed toward the synthesis and iterative coupling of polyalkynyl alkanes and alkenes, Diederich[1a,7] and Scott[5] have developed several efficient strategies for the preparation of high carbon content polyalkynyl containing oligomers. As in the prior studies, the potential for network formation with these species has yet to be realized.

The nonplanar, nonconjugated nature of tetraethynylmethane makes it an attractive alternative candidate for three dimensional carbon allotrope synthesis, as recognized by Diederich,[1a] Alberts,[1j] and Bunz[6] in their prior efforts in this area. The Alberts and the Bunz synthesis strategies for TEM both faltered at introduction of the fourth acetylene unit and provide cautionary evidence about the inherent difficulties of introducing an alkyne into a hindered environment. In light of the Alberts work, we designed our synthesis approach to TEM with two key precepts paramount: (1) delivery of the fourth "alkyne precursor" appendage to the core carbon would occur in an *intramolecular* manner to deflect some of the problems Alberts encountered upon attempted intermolecular additions and (2) construction of the fourth alkyne would utilize "forcing" conditions in order to avoid issues of equilibration, etc., which frustrated the Bunz approach. Thus, the generalized strategy shown in Scheme 1 was born.[8] Initially,

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(1) Leading references to the approaches taken by different groups can be found in the following: (a) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101. (b) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354. (c) Visscher, G. T.; Nesting, D. C., Badding, J. V.; Bianconi, P. A. *Science* **1993**, *260*, 1496. (d) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489. (e) Archibald, T. G.; Malik, A. A.; Baum, K.; Unroe, M. R. *Macromolecules* **1991**, *24*, 5261. (f) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* **1988**, *21*, 3525. (g) Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3528. (h) Mathias, L. J.; Reichert, V. R., Muir, A. V. G. *Chem. Mater.* **1993**, *5*, 4. (i) McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993**, *259*, 1594. (j) Alberts, A. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 748. (k) Stille, J. K.; Rutherford, D. R. *Macromolecules*, **1988**, *21*, 3530. (l) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(2) (a) Stankevick, I. V.; Nikevov, M. V.; Bochvar, D. A. *Russ. Chem. Rev.* **1984**, *53*, 640. (b) Hoffmann, R.; Hughbanks, T.; Kertesz, M.; Bird, P. H. *J. Am. Chem. Soc.* **1983**, *105*, 4831. (c) Johnston, R. L.; Hoffman, R. *J. Am. Chem. Soc.* **1989**, *111*, 810. (d) Merz, K. M., Jr.; Hoffmann, R.; Balaban, A. T. *J. Am. Chem. Soc.* **1987**, *109*, 6742. (e) Baughman, R. H.; Eckhardt, H.; Kertesz, M. *J. Chem. Phys.* **1987**, *87*, 6687. (f) Nesper, R.; Vogel, K.; Blochl, P. E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 701.

(3) Feldman, K. S.; Kraebel, C. M.; Parvez, M. *J. Am. Chem. Soc.* **1993**, *115*, 3846.

(4) Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, pp 521–561.

(5) (a) Scott, L. T.; Cooney, M. J.; Johnels, D. *J. Am. Chem. Soc.* **1990**, *112*, 4054. (b) de Meijere, A.; Jaekel, F.; Simon, A.; Borrmann, H.; Kohler, J.; Johnels, D.; Scott, L. T. *J. Am. Chem. Soc.* **1991**, *113*, 3935. (c) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546.

(6) Bunz, U.; Vollhardt, K. P. C.; Ho, J. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1648.

(7) (a) Boldi, A. M.; Anthony, J.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1240. (b) Anthony, J.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 406. (c) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*. 4966. (d) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 1607. (e) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943. (f) van Loon, J.-D.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*. 1187, 1706. (g) Rubin, Y.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*. 698. (h) See also: Eastmond, R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4591.

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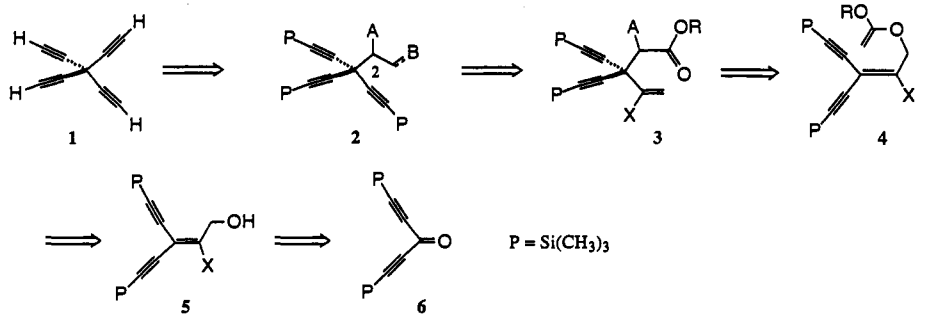
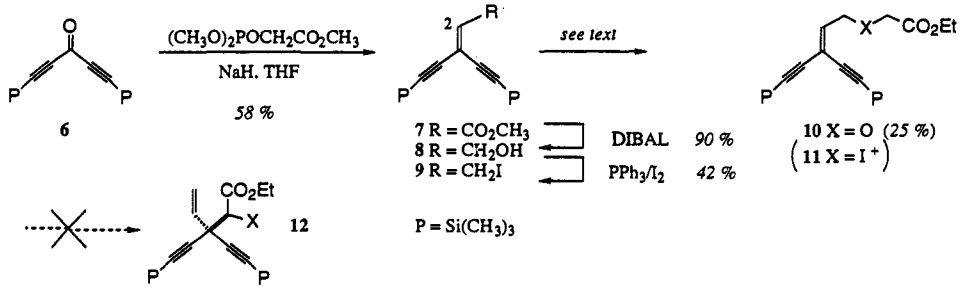
Scheme 1



Scheme 2



a [3,3] or [2,3] sigmatropic shift will be exploited to internally deliver the two-carbon fragment necessary for installation of the fourth alkyne (e.g., **4** → **3**), and in so doing set the core quaternary center. The groups A and B in TEM precursor **2** will be chosen to ensure that, in the final operation, the thermodynamic driving force of acetylene synthesis will compensate for the increase in steric strain sure to accompany rehybridization of C(2) from sp^3 to sp. The dialkynyl ketone **6** served as a starting point for Alberts' efforts[1j] and, in addition, has been used to great advantage by Diederich in several related projects in polyalkynylethene chemistry.[7] In the sections to follow, we will describe our synthesis of allylic alcohol **5** (X = H and Br) and our efforts to realize both [3,3] and [2,3] sigmatropic reorganizations of this substrate. The chemistry associated with the conversion of **2** to **1** has been detailed elsewhere.[11]

Results and Discussion

Our initial studies of the sigmatropic rearrangement approach utilized the model allylic alcohol **8** (Scheme 2) which lacked an oxidized functionality at C(2) and hence could only directly lead to triethynyl*ethenyl*methane derivative **20**, vida infra. Substrate **8** was readily available from ketone **6** as shown, with the proviso that the relatively nonpolar solvent THF was used in the Emmons–Horner coupling. Use of the more familiar solvent DMF led to polymerization, presumably via facile 1,6 anion addition to the first-formed unsaturated ester **7**. Product resubmission experiments support this contention. We originally planned to pursue [2,3] sigmatropic shifts with substrates derived from alcohol **8** due to the documented mildness of reaction conditions (relative to the [3,3] counterpart) and the design flexibility associated with the highly functionalized products anticipated to result. Toward this end, the alcohol **8**, could be converted to the ester **10** ($N_2CH_2CO_2Et/(RhOAc_2)_2$, 25%), but attempts to deprotonate this ester (LDA, NaH, *t*-BuOH) led to an uncharacterized, tarry residue. An alternative base-free approach which utilized the allylic iodide **9** was designed to proceed through the [2,3] shift precursor iodonium salt **11**. Unfortunately, this approach again met failure. A final attempt to effect [2,3] sigmatropic reorganization on a substrate derived from alcohol **8** which employed the Buchi protocol[9] [$Me_2NCH(OCH_3)_2$, heat] afforded only decomposition products reminiscent of the initial effort with **10**. These unrewarding experiments did, however, provide some insight into the base lability of this 1,1-dialkynylpropenyl system; in a control experiment, treatment of alcohol **8** with NaH in THF rapidly and exothermically resulted in a purple/black solution with complete disappearance of starting material (TLC).

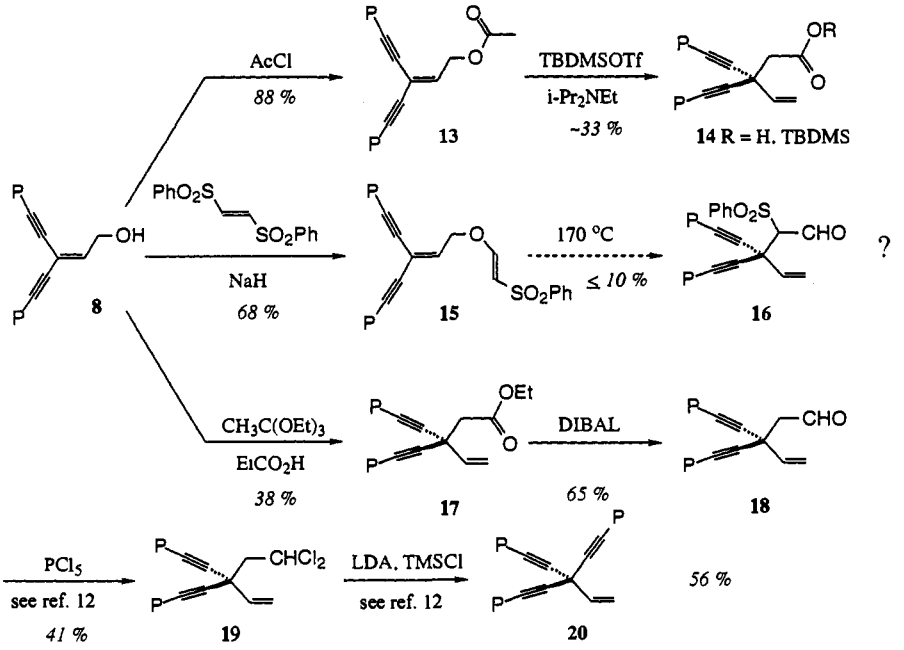
The prospects for quaternary carbon synthesis with allylic alcohol **8** were next explored through the agency of [3,3] sigmatropic reorganizations of derived enol ethers. The marked base lability of substrate **8** (or derivatives thereof) significantly narrowed the scope of possible Claisen-based strategies available. We eventually achieved varying degrees of success with the three procedures shown in Scheme 3. Thus, treatment of acetate **13** with TBDMSOTf and Hunig's base, followed by mild heating, afforded a low yield of the Claisen rearrangement products **14** following chromatography. In a similar manner, conversion of allylic alcohol **8** to the sulfone-substituted enol ether **15** and then heating to 170 °C in a sealed tube (PhH) led to trace amounts (≤10%) of the Claisen product **16**, which could not be obtained free of uncharacterized impurities. The alkylation of **8** with 1,2-bis(phenylsulfonyl)ethene was best accomplished by slow addition of solid NaH to a mixture of the reactants held below −10 °C; higher temperatures led immediately to (base-mediated?) decomposition of **8**. Both of these lines of inquiry were discontinued when it was observed that the acidic Johnson orthoester Claisen variant (**8** → **17**) cleanly furnished the desired alkenyl ester **17** in modest yield.[10] The remainder of the starting material could not be accounted for, although resubmission experiments with **17**, and independently **8**, suggested that neither of these species was destroyed upon exposure to propionic acid, although slow desilylation was observed. Thus, allylic alcohol **8** appears to be

(8) Cadiot et al. report a most direct approach to the synthesis of a material that they describe as tetra*propynyl*methane in 10% yield via the condensation of propynyl Grignard with CBr_4, in analogy with their synthesis of tetrapropynylsilane from the same Grignard and $SiCl_4$. Characterization data on this putative tetraalkyne is limited to IR (2210 cm^{-1}) and bp (36 °C, 2.8 mm) values. We have attempted to repeat this result and have in fact prepared an oil whose bp and IR (alkyne) values match the data indicated above. However, GC/MS and ^1H NMR analysis of this oil revealed it to be a mixture of not less than three components, each of which contains at least one bromine atom. Thus, we have not been able to synthesize tetrapropynylmethane by the Cadiot procedure: Masson, J.-C.; Quan, M. L.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1968**, 1085.

(9) Buchi, G.; Cushman, M.; Wuest, H. *J. Am. Chem. Soc.* **1974**, *96*, 5563.

(10) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.

Scheme 3



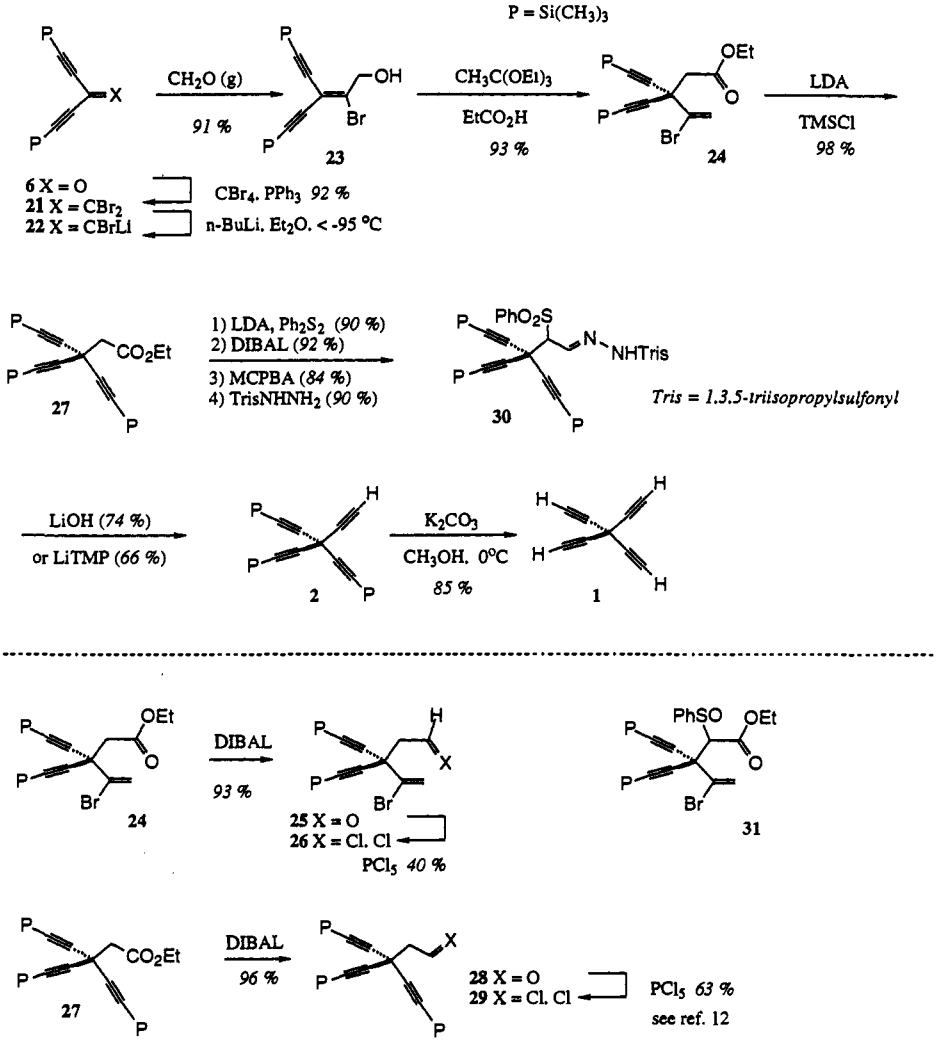
as surprisingly tolerant of acidic conditions as it is labile to base. In any event, with a source of dialkynyl ester **17** in hand, we next pursued the synthesis of the model compound triethynylethenylmethane **20** as a context to explore the conversion $-CH_2CO_2Et \rightarrow -C{\equiv}CH$. Several strategies have been reported for effecting such a conversion,[11] and the venerable dichloride elimination procedure (**19** → **20**) proved eminently serviceable in this case.[12] Trialkynylethenylmethane **20** is, to our knowledge, the first member of a new class of polyalkynylated hydrocarbons which features three acetylene and an additional unsaturated *carbon* appendage all attached to a central carbon atom core.

The encouraging results obtained in the model system described in Scheme 3 provided the impetus for explorations in the "real" system described in Scheme 4. The immediate goal in exploring this chemistry focused on introducing a higher level of oxidation in the 3,3-dialkynylpropenol substrate such that conversion of the Claisen-derived vinyl appendage to an alkyne unit would be facile. One straightforward solution which seemed unlikely to derail the chemistry developed so far utilizes the 1-bromo-3,3-dialkynylpropanol (**23**) as the Claisen precursor. The synthesis of this alcohol from ketone **6** was not a given, as incorporation of the bromide at C(2) would likely increase the base lability of the 3,3-dialkynylpropene moiety. After much experimentation, we were able to take advantage of contributions from both the Diederich (for the synthesis of **21**)[7g] and Braun[13] (for the alkylation procedure) laboratories to prepare bromoallylic alcohol **23** in reproducibly high yield. Attention to experimental detail is critical in this sensitive transformation, and parameters such as temperature, concentration, rate of gaseous formaldehyde addition, and stirring speed all must fall within narrow tolerances to achieve effective reaction. Once in hand, optimization studies on the Claisen rearrangement of alcohol **23** improved the yield from the modest value described in the model system (Scheme 3) to that shown in Scheme 4. The critical observation in these yield optimization studies was that the rate of product formation diminished as the reaction proceeded, allowing other adventitious, destructive (free radical?) processes to intervene. The rate attenuation was traced to a loss of propionic acid catalyst, presumably via triethyl orthoacetate-mediated esterification to afford ethyl propionate.[18b] Thus, incorporation of an antioxidant and slow continuous addition of propionic acid over 24 h led to dramatic improvements in yield. The bromoalkene moiety of Claisen product **24** was readily converted to the third alkyne unit of ester **27**, which itself was subjected to the similar dichloride elimination-based strategy for formation of the fourth alkyne. Unfortunately, this procedure failed with substrate **28**, as discussed in detail elsewhere.[11] In addition, treatment of the bromoalkenyl dichloride **26** with base (LDA, LiTMP) was equally unrewarding. Eventually, recourse was made to a modified version of Shibuya's acetylene synthesis for installation of this final alkyne, **30** → **2**.[14] This transformation was also burdened by its share of mechanistic surprises,[11] but ultimately proved quite reliable.

The trisilylated TEM derivative **2** was a completely shelf-stable white crystaline solid whose structural details were apparent from inspection of the results of a single-crystal X-ray study (Figure 1). In our original communication on this topic,[3] we reported that the X-ray structural analysis of **2** (performed at the University of Calgary) revealed unusually short alkyne bonds (ca. 1.16 Å) and elongated sp^3–sp bonds (ca. 1.48, 1.50 Å). More recently, Schaefer et al. challenged these values on the basis of high-level calculations (DZP SCF) on **2**, which indicated "normal" bond lengths for the alkynes (1.196, 1.188 Å).[15] This discrepancy between theory and experiment prompted us to revisit the crystal structure of **2**, with suprising results. Thus, single crystal diffraction studies on a new crystal of **2** at the University of Akron provided new bond length values (Figure 1) which were more in accord with the computional predictions than those reported previously. At present, the basis for the variance between the Calgary and the Akron structures remains a matter of speculation. However, we do note that further refinement[19a] of the Calgary coordinates at Akron led to normal bond distances. In any event, both the current crystal structure and the calculations are in accord and show a slightly lengthened sp^3–sp bond relative to standard values (e.g., 1.46 Å).[16] As a point of comparison, X-ray crystallographic analysis of the structurally related species

(11) (a) Shibasaki, M.; Torisawa, Y.; Ikegami, S. *Tetrahedron Lett.* **1982**, *23*, 4607. (b) Bartlett, P. A.; Greene, F. R., III; Rose, E. H. *J. Am. Chem. Soc.* **1978**, *100*, 4852.
(12) Feldman, K. S.; Weinreb, C. K.; Youngs, W. J.; Bradshaw, J. D. *J. Org. Chem.* **1994**, *59*, 1213.
(13) Mahler, H.; Braun, M. *Tetrahedron Lett.* **1987**, *28*, 5145.
(14) Kano, S.; Yokomatsu, T.; Shibuya, S. *J. Org. Chem.* **1978**, *43*, 4366.
(15) Ma, B.; Sulzbach, H. M.; Xie, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1994**, *116*, 3529.
(16) Gordon, A. J.; Ford, R. A. *The Chemists Companion*; John Wiley and Sons: New York, NY, 1972.

Scheme 4



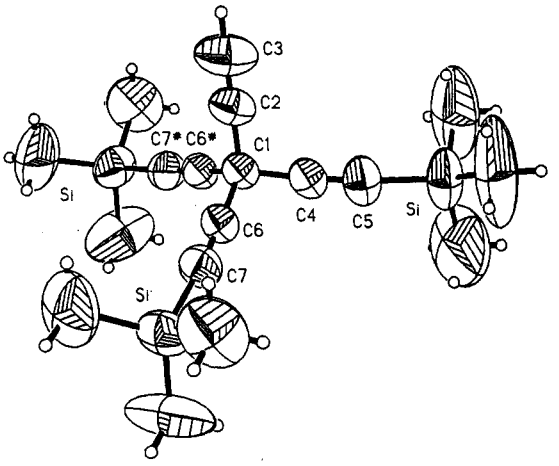


Figure 1. X-ray crystal structure of **2**. Selected bond lengths (Å) of **2** are as follows: C(1)–C(4), 1.482(8); C(1)–C(6) #1, 1.485(4); C(2)–C(3), 1.157 (8); C(6)–C(7), 1.198 (5); C(1)–C(6), 1.485(4); C(1)–C(2), 1.485(8); C(4)–C(5), 1.187(7).

tetracyanomethane revealed that the C–C bond is elongated by ~0.03 Å when measured against "standard" C–CN bond lengths,[16] but the CN bond remains of normal length.[17] Thus, it is plausible that steric crowding about the central carbon in both systems results in some geometric distortion as manifest in lengthening of the C_{sp^3}–C_{sp} bond.

(17) Britton, D. *Acta Crystallogr.* **1974**, *B30*, 1818.

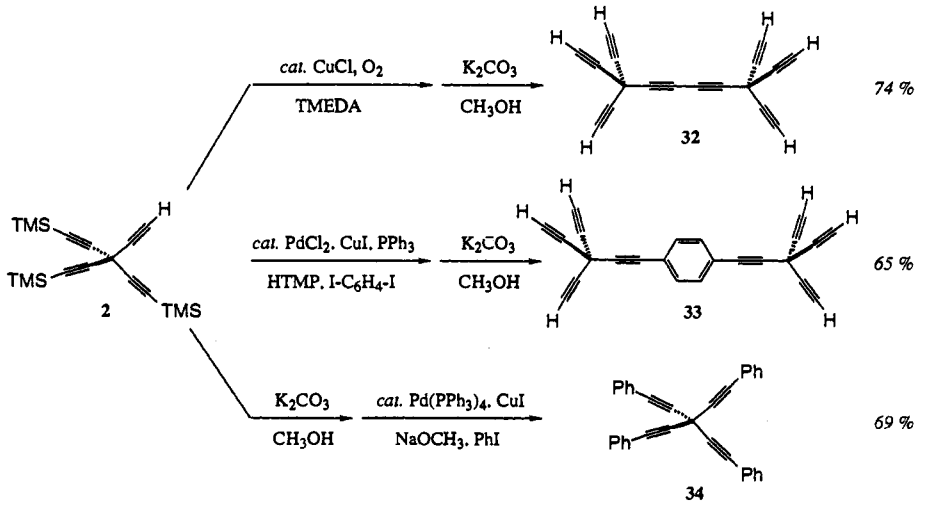
In any event, desilylation of **2** occurred smoothly to afford the title compound tetraethynylmethane (**1**) as a powdery white solid after solvent removal at 0 °C. Neat TEM is quite labile and cannot be manipulated at room temperature (in the presence or absence of H_2O, O_2) for more than a few minutes without onset of decomposition. Decomposition is marked by conversion to a brown oil which displays aliphatic but no alkynyl, alkenyl, or aromatic signals in the ^{13}C NMR, and remains otherwise uncharacterized. However, TEM can be stored as a dilute frozen benzene solution for months without evidence of decomposition.

Posner's modification of the Johnson orthoester Claisen strategy was explored briefly, in an effort to streamline the route.[18a] Thus, treatment of alcohol **23** with $PhS(O)CH_2C(OEt)_3$ under standard acidic catalysis afforded a modest (30%) yield of the sulfoxide **31** as a mixture of stereoisomers. Studies in this series were discontinued when repeated attempts to convert the phenylsulfinyl ester moiety to the requisite sulfonyl aldehyde functionality were not successful.

The eventual application of TEM (or derivatives) toward the synthesis of high carbon content networks of novel architecture will require efficient transition metal-mediated coupling of the terminal alkyne sites to other unsaturated functionalities. Toward this end, we have explored the Cu(I)-catalyzed oxidative dimerization of the trisilylated TEM derivative **2**, as well as Pd(0)-mediated Hagihara-type coupling of **1** and **2** with aryl iodides to

(18) (a) Posner, G. H.; Crouch, R. D.; Kinter, C. M.; Carry, J. C. *J. Org. Chem.* **1991**, *56*, 6981. (b) When the Claisen rearrangement of **8** was run with the nonvolatile acid 2,4,6-trimethylbenzoic acid as per ref 16a, the ethyl ester of this acid was isolated in high yield.

Scheme 5



afford phenyl-capped polyalkynyl products, Scheme 5. Thus, applying Hay's modification of Glaser coupling to terminal alkyne **2**, followed by desilylation of the coupled product, produced the TEM "dimer" **32**. Unlike TEM itself, the white crystalline dimer **32** could be stored under ambient conditions for days without noticeable decomposition. Similarly, TEM derivative **2** is a suitable substrate for coupling with 1,4-diiodobenzene and furnishes the "phenyl-spacer" version of the TEM dimer, **33**, following mild base-mediated desilylation. This compound appears to escape decomposition under short exposure (days) to ambient conditions as well. Finally, we probed the prospects for intercepting nascent TEM itself with phenyl iodide under the Hagihara protocol in competition with the previously described self-destruction. Freshly prepared TEM in methanol solution was added directly to the premixed coupling medium, leading ultimately to a good yield of the tetracoupled TEM derivative **34**. Tetrakis(phenylethynyl)methane (**34**) is a completely shelf-stable white crystalline solid. These scouting experiments demonstrate that both TEM itself and its silylated derivative **2** are competent partners in common acetylene-coupling methodologies and suggest that polymerization/oligomerization chemistry with **1** may be feasible.

In summary, we have developed a flexible experimental procedure for preparation of tetraethynylmethane and a variety of silylated and phenylated derivatives. Difficulties associated with compressing four formally sp-hydridized carbon atoms about a central core carbon dominated the execution of the synthesis and required less direct solutions to functional group manipulation problems than otherwise were anticipated. It is plausible that the geometric distortions associated with this structure contribute to the instability and chemical reactivity of TEM itself, although "end-capped" derivatives were significantly more robust. The synthesis of TEM (and derivatives) is amenable to preparation of hundreds of milligram lots per run and, hence, is a satisfactory source of reactive monomer for exploratory polymerization/oligomerization studies currently ongoing. The results of these investigations, especially with regard to novel properties of the derived materials, will be reported in due course.

Experimental Section

All reagents were obtained from the Aldrich Chemical Co. (Milwaukee, WI) unless otherwise stated. Et_2O and THF were purified by distillation from sodium/benzophenone ketyl under nitrogen. CH_2Cl_2, HTMP, and HDA were distilled from CaH_2 under N_2. Solvents for flash chromatography[20] (silica gel adsorbant) were distilled from CaH_2 prior to use. Moisture- and oxygen-sensitive reactions were carried out in predried glassware under Ar. Analytical TLC was performed using precoated silica gel (60 F_{254}) plates (E. Merck). The purity of all title compounds was judged to be ≥90% by ^1H and ^{13}C NMR determinations (see the supplementary material).

Methyl 5-(Trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-2-en-4-ynoate (7). A solution of bis[(trimethylsilyl)ethynyl]ketone **6**[19] (2.0 g, 9.0 mmol) in 20 mL of THF was added dropwise to a stirring slurry of the sodium salt of trimethyl phosphonoacetate, prepared from trimethyl phosphonoacetate (1.80 g, 9.9 mmol) and degreased sodium hydride (380 mg of 60% NaH suspension, 9.5 mmol), in 50 mL of THF held at −10 °C by an ice/salt bath. As addition proceeded, the reaction mixture became homogeneous and deeply orange colored. After 30 min, TLC analysis indicated consumption of **6**, and so the reaction mixture was poured into 100 mL of ice cold 1 M H_3PO_4 and extracted with 2 × 50 mL of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography on silica gel with 2% Et_2O/hexane as eluent to afford 1.44 g (58%) of ester **7** as a light yellow oil which solidified at −10 °C: IR (CCl_4) 2130, 1735 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.35 (s, 1H), 3.75 (s, 3H), 0.26 (s, 9H), 0.22 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.7, 132.4, 118.0, 106.1, 101.7, 99.5, 99.2, 51.6, −0.48; MS *m/z* (relative intensity) 278 (48), 263 (100), 204 (46). HRMS calcd for $C_{14}H_{22}O_2Si_2$ 278.1158, found 278.1156.

5-(Trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-2-en-4-ynol (8). A solution of DIBAL in toluene (24 mL of a 1.5 M solution, 36 mmol, 2.5 equiv) was added dropwise to a stirring solution of ester **7** (4.01 g, 14.4 mmol) in 100 mL of CH_2Cl_2 at −78 °C. After 10 min, TLC analysis indicated complete consumption of **7**, and so the reaction solution was poured into a mixture of ice cold Et_2O (100 mL) and 10% aqueous Rochelle's salt (100 mL). The aqueous layer was extracted with 2 × 50 mL of Et_2O, and the combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography with 15% Et_2O/hexane as eluent to afford 3.23 g of alcohol **8** as a viscous light yellow oil which darkened upon standing (90%): IR (CCl_4) 3610, 2122 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.45 (t, 1H, J = 7.1 Hz), 4.41 (d, 2H, J = 7.3 Hz), 1.60 (s, 1H), 0.21 (s, 9H), 0.18 (s, 9H); ^{13}C NMR (50 MHz , $CDCl_3$) δ 148.0, 107.1, 101.5, 100.4, 98.6, 93.6, 61.1, −0.29, −0.50; MS *m/z* (relative intensity) 250 (6), 235 (21), 206 (15); HRMS calcd for $C_{13}H_{22}OSi_2$ 250.1209, found 250.1199.

1-Iodo-5-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-2-en-4-yne (9). Iodine (183 mg, 0.72 mmol, 1.2 equiv) was added in one portion to a stirring, ice-cooled solution of alcohol **8** (150 mg, 0.6 mmol), PPh_3 (204 mg, 0.78 mmol, 1.3 equiv), and imidazole (102 mg, 1.5 mmol, 2.5 equiv) in 2 mL of CH_3CN. After 5 min, TLC indicated complete consumption of starting alcohol. The reaction solution was poured into half-saturated, ice cold $Na_2S_2O_3$ solutionand extracted with 2 × 10 mL of Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The brown residue was purified by flash chromatography using hexane as eluent to furnish 90 mg of iodide **9** as a colorless oil (42%): IR (CCl_4) 2155 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.53 (t, J = 8.9 Hz, 1H), 4.16 (d, J = 8.9 Hz, 2H), 0.25 (s,

(19) (a) Sheldrick, G. M. *J. Appl. Crystallogr.* manuscript in preparation. (b) Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.
(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

9H), 0.20 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.5, 110.9, 108.6, 106.9, 1.26, –0.25, –0.31; MS *m/z* (relative intensity) 345 ($M^+ - CH_3$, 2).

Ethyl [[5-(Trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-2-en-4-yn-1-yl]oxy]acetate (10). A solution of ethyl diazoacetate (85 μL, 0.81 mmol, 1.5 equiv) and alcohol **8** (135 mg, 0.54 mmol) in 3 mL of benzene was added dropwise over 5 h via a motor-driven syringe to a stirring solution of $(RhOAc)_2$ (12 mg, 0.03 mmol, 0.05 equiv) in 3 mL of benzene. After an additional 12 h of stirring at room temperature, this homogeneous green solution was filtered through a plug of silica gel and concentrated in vacuo, and the residue was purified by flash chromatography with 10% Et_2O/hexane as eluent to afford 46 mg of ether **10** as a yellow oil (25%): IR (CCl_4) 2156, 1758, 1738 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.44 (t, *J* = 6.8 Hz, 1H), 4.37 (d, *J* = 6.8 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.21 (s, 9H), 0.20 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.2, 144.7, 108.9, 101.3, 100.5, 98.5, 93.9, 66.9, 67.6, 60.9, 14.2, –0.31, –0.51; MS *m/z* (relative intensity) 336 (32), 249 (100); HRMS calcd for $C_{17}H_{29}Si_2O_3$ 336.1577, found 336.1584.

5-(Trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-2-en-4-ynyl Acetate (13). Pyridine (73 μL, 0.9 mmol, 1.5 equiv) and then acetyl chloride (52 μL, 0.73 mmol, 1.2 equiv) were added to an ice-cooled stirring solution of alcohol **8** (153 mg, 0.61 mmol) in 5 mL of CH_2Cl_2. After 5 min, TLC indicated complete consumption of starting alcohol, and so the solution was poured into ice cold 1 M H_3PO_4 and extracted with 2 × 20 mL of CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography using 5% Et_2O/hexane as eluent to yield 157 mg of acetate **13** as a colorless oil (88%): IR (CCl_4) 2156, 1746 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.38 (t, *J* = 6.8 Hz, 1H), 4.83 (d, *J* = 6.8 H_3, 2H), 2.07 (s, 3H), 0.22 (s, 9H), 0.20 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.7, 142.6, 109.1, 101.2, 99.4, 98.1, 94.2, 62.2, 20.8, –0.31; MS *m/z* (relative intensity) 292 (32), 249 (20); HRMS calcd for $C_{15}H_{24}Si_2O_2$ 292.1315, found 292.1311.

(*E*)-2-(Phenylsulfonyl)ethenyl 5-(Trimethylsilyl)-3-[(trimethylsilyl)-ethynyl]pent-2-en-4-ynyl Ether (15). Degreased NaH (35 mg, 0.88 mmol, 1.1 equiv) was added in portions over 15 min to a stirring, ice/rock salt-cooled solution/suspension of alcohol **8** (200 mg, 0.8 mmol) and 1,2-bis(phenylsulfonyl)ethylene (275 mg, 0.88 mmol, 1.1 equiv) in 3 mL of THF. After 16 h, TLC indicated a trace of remaining alcohol and a major, slightly faster moving compound (1:1 Et_2O/hexane). The crude reaction solution was poured into ice cold 1 M H_3PO_4 and extracted with 2 × 10 mL of Et_2O. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography with 1:1 Et_2O/hexane to furnish 225 mg of ether **15** as a viscous yellow oil (68%): IR (CCl_4) 2125, 1310, 1132 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.9 (m, 2H), 7.6 (m, 4H), 6.32 (t, *J* = 6.7 Hz, 1H), 5.76 (d, *J* = 12.3 Hz, 1H), 4.65 (d, *J* = 6.7 Hz, 2H), 0.23 (brs, 18 H); MS *m/z* (relative intensity) 416 (2); HRMS calcd for $C_{21}H_{28}Si_2O_3S$ 416.1298, found 416.1313.

Ethyl 3-Ethenyl-5-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-4-ynoate (17). A solution of alchohol **8** (2.1 g, 8.4 mmol) in 2 mL of triethyl orthoacetate was added over 6 h via syringe pump to a refluxing solution of 30 μL of propionic acid (0.4 mmol, 0.05 equiv) in 10 mL of triethyl orthoacetate. Reflux was continued for 36 h after addition. At this time, GLC analysis indicated consumption of alcohol **8**, and so the reaction solution was cooled to room temperature and poured into 50 mL of each of Et_2O and ice cold saturated $NaHCO_3$ solution. The aqueous layer was extracted with 2 × 20 mL of Et_2O, and the combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography with 5% Et_2O/hexane as eluent to furnish 1.03 g of ester **17** as a mobile light yellow oil (38%): IR (CCl_4) 2140, 1730 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.97 (dd 1H, *J* = 16.7, 9.7 Hz), 5.59 (dd, 1H, *J* = 16.6, 0.9 Hz), 5.20 (dd, 1H, *J* = 9.7, 1.1 Hz), 4.15 (q, 2H, *J* = 7.1 Hz), 2.76 (s, 2H), 1.27 (t, 3H, *J* = 7.3 Hz), 0.17 (s, 18H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.8, 137.6, 115.3, 103.4, 93.5, 60.6, 47.3, 14.2, –4.3; MS *m/z* (relative intensity) 320 (13), 305 (5), 233 (23); HRMS calcd for $C_{17}H_{28}O_2Si_2$ 320.1628, found 320.1643.

3-Ethenyl-5-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-4-ynal (18). A solution of DIBAL (2.13 mL of a 1.5 M solution in toluene, 3.2 mmol, 1.1 equiv) was added dropwise to a stirring solution of ester **17** (930 mg, 2.9 mmol) in 100 mL of CH_2Cl_2 at –78 °C. After 5 min, TLC analysis indicated that the starting ester was consumed, and so the solution was worked up as per **8**. The residue was purified by flash chromatography with 2% Et_2O/hexane as eluent to yield aldehyde **18** (524 mg, 65%) as a light brown oil: IR (CCl_4) 2135, 1728 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (t, 1H, *J* = 2.7 Hz), 5.82 (dd, 1H, *J* = 16.8, 9.5 Hz), 5.60 (d, 1H, *J* = 16.6 Hz), 5.24 (d, 1H, *J* = 9.5 Hz), 2.62 (d, 2H, *J* = 2.7 Hz), 0.18 (s, 18H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.2, 137.1, 115.8, 102.7, 53.7, 35.8, –0.25; MS *m/z* (relative intensity) 276 (1), 261 (5), 233 (13); HRMS calcd for $C_{15}H_{24}OSi_2$ 276.1366, found 276.1365.

1,1-Dichloro-3-ethenyl-5-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]-pent-4-yne (19). PCl_5 (281 mg, 1.35 mmol, 2.0 equiv) was added in one portion to a stirring solution of aldehyde **18** (184 mg, 0.67 mmol) in 5 mL of CH_2Cl_2 at –78 °C. After 5 min, TLC analysis indicated that aldehyde **18** was consumed. The reaction solution was poured into 50 mL of Et_2O and 50 mL of ice cold saturated $NaHCO_3$ solution, the aqueous phase was extracted with 2 × 25 mL of Et_2O, and the combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography with hexane as eluent to afford 91 mg (41%) of dichloride **19** as colorless oil: IR (CCl_4) 2140 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.97 (t, 1H, *J* = 5.6 Hz), 5.80 (dd, 1H, *J* = 16.6, 9.4 Hz), 5.61 (dd, 1H, *J* = 16.7, 0.6 Hz), 5.22 (dd, 1H, *J* = 9.4, 0.8 Hz), 2.69 (d, 2H, *J* = 5.8 Hz), 0.18 (s, 18 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.3, 115.9, 102.4, 89.9, 69.5, 54.9, 38.5, –0.21; MS *m/z* (relative intensity) 332 (.6), 330 (1), 253 (6); HRMS calcd for $C_{15}H_{24}Cl_2Si_2$ 330.0794, found 330.0781.

2-Bromo-5-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-2-en-4-yn-ol (23). A 250 mL Morton flash equipped with a Bernoulli stirrer and formadehyde generator was charged with 4.00 g of dibromide **21**[78] (10.6 mmol) and 100 mL of Et_2O. The solution was cooled to –95 °C (4:1:1 Et_2O/*i*-PrOH/acetone–liquid N_2) and *n*-BuLi (4.40 mL of a 2.5 M solution in hexane, 11.1 mmol, 1.05 equiv) was added dropwise over 5 min, resulting in a deep purple solution. After an additional 45 min at –95 °C, a stream of formaldehyde (2.50 g, 84.7 mmol, 8 equiv) entrained in Ar, generated by thermally cracking paraformaldehyde at 155 °C, was bubbled through the reaction solution. The Ar flow was modulated such that all the formaldehyde was added over 1 h. The solution was poured into 50 mL of ice cold 1 M H_3PO_4, and the aqueous solution was extracted with 2 × 50 mL of Et_2O. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography with 25% Et_2O/hexane as eluent to afford 3.17 g (91%) of alcohol **23** as a viscous orange/brown oil which solified at –15 °C: IR (CCl_4) 3590 cm^{-1}; ^{1}H NMR (200 MHz, (CDCl3) δ 4.61 (d, 2H, *J* = 6.9 Hz), 2.17 (t, 1H, *J* = 7.0 Hz), 0.24 (s, 9H), 0.22 (s, 9H); ^{13}C NMR (50 MHz, (CDCl3) δ 144.8, 109.0, 101.1, 100.5, 98.0, 65.2, –0.03, –0.40; MS *m/z* (relative intensity) 330 (8), 328 (8), 249 (7); HRMS calcd for $C_{13}H_{21}BrOSi_2$ 328.0315, found 328.0282.

Ethyl 3-(1-Bromoethenyl)-5-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]-pent-4-ynoate (24). Propionic acid (0.70 mL, 9.4 mmol, 1.02 equiv) was added dropwise via motor-driven syringe to a refluxing solution of alcohol **23** (3.03 gm, 9.2 mmol) in 17 mL of triethyl orthoacetate over 30 h with distillative removal (Dean-Stark condenser) of EtOH. The reaction solution was then cooled to room temperature and poured into 50 mL of hexane and 50 mL of ice cold saturated 1 M $NaHCO_3$, and the aqueous phase was extracted with 2 × 20 mL of hexane. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography with 3% Et_2O/hexane as eluent to yield 3.42 g of ester **24** (93%) as a light orange oil: IR (CCl_4) 2140, 1740 cm^{-1}; ^{1}H NMR (200 MHz, ($CDCl_3$) δ 6.36 (d, 1H, *J* = 0.9 Hz), 5.61 (d, 1H, *J* = 0.8 Hz), 4.08 (q, 2H, *J* = 7.1 Hz), 2.91 (s, 2H), 1.19 (t, 3H, *J* = 7.2 Hz), 0.11 (s, 18H); ^{13}C NMR (50 MHz, ($CDCl_3$) δ 168.2, 132.3, 120.3, 101.8, 89.8, 60.6, 45.9, 42.8, 14.2, –0.35; MS *m/z* (relative intensity) 400 (1), 398(1), 385 (3), 319 (100); HRMS calcd for $C_{17}H_{27}BrO_2Si_2$ 398.0733, found 398.0750.

3-(1-Bromoethenyl)-5-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]pent-4-ynal (25). A solution of DIBAL in toluene (1.49 mL of a 1.5 M solution, 2.24 mmol, 1.1 equiv) was added dropwise to a stirring solution of ester **23** (0.81 g, 2.0 mmol) in 20 mL of CH_2Cl_2 at –78 °C. After 5 min, TLC analysis indicated that starting ester was consumed. The solution was worked up as per **8**. The residue was purified by bulb-to-bulb distillation (145 °C/0.1 mm) to furnish 658 mg (93%) of aldehyde **25** as a light yellow oil: IR (CCl_4) 2130, 1730 cm^{-1}; ^{1}H NMR (200 MHz, ($CDCl_3$) δ 9.75 (t, 1H, *J* = 2.6 Hz), 6.36 (d, 1H, *J* = 2.2 Hz), 5.64 (d, 1H, *J* = 2.2 Hz), 2.76 (d, 2H, *J* = 2.7 Hz), 0.12 (s, 18H); ^{13}C NMR (50 MHz, ($CDCl_3$) δ 199.5, 131.9, 120.3, 101.2, 91.6, 52.9, 41.6 –0.41; MS *m/z* (relative intensity) 341 (5), 339 (3), 275 (13); HRMS calcd for $C_{15}H_{23}$-$BrOSi_2$ 354.0471, found 354.0471.

3-(1-Bromoethenyl)-1,1-dichloro-5-(trimethylsilyl)-3-[(trimethylsilyl)-ethynyl]pent-4-yne (26). PCl_5 (528 mg, 2.54 mmol, 2.0 equiv) was added

in two equal portions 30 min apart to a stirring solution of aldehyde **25** (450 mg, 1.27 mmol) in 20 mL of CH_2Cl_2 at −78 °C. TLC analysis indicated consumption of aldehyde 30 min after the second portion of PCl_5 was added. The reaction solution was poured into 50 mL of Et_2O and 50 mL of ice cold saturated $NaHCO_3$ solution, the aqueous phase was extracted with 2 × 25 mL of Et_2O, and the combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography with hexane as eluent to afford 206 mg of dichloride **26** (40%) as a colorless oil: IR (CCl_4) 2130 cm^{-1}; ^1H NMR (200 MHz, ($CDCl_3$) δ 6.44 (d, 1H, J = 2.1 Hz), 5.93 (t, 1H, J = 5.9 Hz), 5.70 (d, 1H, J = 2.2 Hz), 2.89 (d, 2H, J = 5.9 Hz), 0.20 (s, 18H); ^{13}C NMR (50 MHz, ($CDCl_3$) δ 131.9, 120.9, 101.0, 91.6, 69.1, 53.1, 44.0, −0.42; MS m/z (relative intensity) 413 (3), 412 (3), 411(3), 410 (7), 409 (2), 408 (4); HRMS calcd for $C_{15}H_{23}BrCl_2Si_2$ 407.9899, found 407.9882.

Ethyl 3,3-Bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)pent-4-ynoate (27). A solution of alkenyl bromide **24** (3.63 g, 9.09 mmol) in 15 mL of THF was added dropwise to a stirring solution of LDA [from *i*-Pr_2NH (7.0 mL, 50.0 mmol, 5.5 equiv) and *n*-BuLi (18.0 mL of a 2.5 M solution in hexane, 45.4 mmol, 5 equiv)] in 175 mL of THF at −78 °C. After 1 h at −78 °C and 30 min at −35 °C, TMSCl (6.7 mL, 45.5 mmol, 5 equiv) was added dropwise, and the solution was warmed to room temperature; 1 M H_3PO_4 (60 mL) was added, and after 10 min of stirring, the reaction solution was extracted with 3 × 60 mL of Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography using 2% Et_2O/hexane as eluent to afford 3.48 g (98%) of **27** as a light yellow oil which could be crystallized from pentane: mp 30–32 °C; IR (CCl_4) 2140, 1742 cm^{-1}; ^1H NMR (200 MHz, ($CDCl_3$) δ 4.18 (q, 2H, J = 7.2 Hz), 2.93 (s, 2H), 1.29 (t, 3H, J = 7.2 Hz), 0.17 (s, 27H); ^{13}C NMR (50MHz, ($CDCl_3$) δ 167.8, 101.6, 86.1, 60.6, 48.0, 27.9, 14.2, −0.40; MS m/z (relative intensity) 390 (23), 375(5); HRMS calcd for $C_{20}H_{34}O_2Si_3$ 390.1867, found 390.1877. Anal. Calcd for $C_{20}H_{34}O_2Si_3$: C, 61.51; H, 8.78. Found: C, 61.49; H, 8.33.

3,3-Bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)pent-4-ynal (28). A solution of DIBAL (1.65 mL of a 1.5 M solution in toluene, 2.47 mmol, 1.1 equiv) was added dropwise to a stirring solution of ester **27** (876 mg, 2.25 mmol) in 100 mL of CH_2Cl_2 at −78 °C. After 20 min, GLC analysis indicated that starting ester was consumed, and so the reaction solution was worked up as per **8**. The residue was purified by flash chromatography using 2% Et_2O/hexane as eluent to furnish aldehyde **28** (747 mg, 96%) as a light yellow oil which solidified to a waxy solid upon standing: IR (CCl_4) 2140, 1734 cm^{-1}; ^1H NMR (200 MHz, ($CDCl_3$) δ 9.85 (t, 1H, J = 2.7 Hz), 2.82 (d, 2H, J = 2.6 Hz), 0.18 (s, 27H); ^{13}C NMR (50 MHz, ($CDCl_3$) δ 199.4, 100.9, 87.8, 54.7, 26.6, −0.42; MS m/z (relative intensity) 346 (15), 331 (7), 303 (19); HRMS calcd for $C_{18}H_{30}OSi_3$ 346.1604, found 346.1605.

Ethyl 2-(Phenylthio)-3,3-bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)-pent-4-ynoate. A solution of ester **5** (2.2 g, 5.5 mmol) in 5.0 mL of THF was added dropwise to a stirring solution of LDA [from *i*-Pr_2NH (1.50 mL, 10.6 mmol, 1.8 equiv) and *n*-BuLi (4.1 mL of a 2.5 M solution in hexane, 10.3 mmol, 1.75 equiv)] in 18.0 mL of THF at −78 °C. After 1 h at −78 °C, the cold bath was removed and phenyl disulfide (2.3 g, 10.5 mmol, 1.8 equiv) in 5.0 mL of THF was added over 4 h via motor driven syringe. After 16 h of stirring at room temperature, 1 M H_3PO_4 (10 mL) was added and the reaction was extracted with 3 × 10 mL of Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the residue purified by flash chromatography using 2% Et_2O/hexane as eluent to afford 2.46 g (90%) of a yellow oil: IR (CCl_4) 2172, 1734 cm^{-1}; ^1H NMR (200 MHz, ($CDCl_3$) δ 7.55 (m, 2H), 7.22 (m, 3H), 4.14 (m, 2H), 3.84 (s, 1H), 1.21 (t, J = 7.14 Hz, 3H), 0.10 (s, 27H); ^{13}C NMR (50 MHz, ($CDCl_3$) δ 168.7, 135.2, 132.9, 128.9, 128.0, 100.1, 87.6, 62.5, 61.3, 33.9, 14.1, −0.41; MS m/z (relative intensity) 498 (1.5), 483 (3.9), 389 (65); HRMS calcd for $C_{26}H_{38}OSSi_3$ 498.1900, found 498.1876.

2-(Phenylthio)-3,3-bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)pent-4-ynal. A solution of DIBAL (3.8 mL of a 1.5 M solution in toluene, 5.7 mmol, 1.1 equiv) was added dropwise to a stirring solution of the above ester (2.56 g, 5.14 mmol) in 240 mL of CH_2Cl_2 at −78 °C. After 90 min the reaction was quenched with 10 mL of MeOH. The reaction was diluted with 100 mL of Et_2O and washed with 2 × 50 mL of 10% aqueous Rochelle's salt, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using 2 % Et_2O/hexane as eluent to furnish the title aldehyde (2.15 g, 92%) as a yellow oil: IR (CCl_4) 2176, 1724 cm^{-1}; ^1H NMR (200 MHz, ($CDCl_3$) δ 9.55 (d, J = 6.1 Hz, 1H), 7.53 (m, 2H), 7.29 (m, 3H), 3.60 (d, J = 5.8 Hz, 2H), 0.20 (s, 27H); ^{13}C NMR (90 MHz, ($CDCl_3$) δ 191.3, 133.4, 132.9, 129.2, 128.5, 98.8, 89.4, 67.0, 31.8, −0.45; MS m/z (relative intensity) 454 (3.9), 345 (65.8), 303 (63); HRMS calcd for $C_{24}H_{34}OSSi_3$ 454.1638, found 454.1609.

2-(Phenylsulfonyl)-3,3-bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)-pent-4-ynal. MCPBA (6.7 g, 43 mmol, 5.0 equiv) was added in one portion to a stirring solution of the above aldehyde (3.9 g, 8.6 mmol) in 180 mL of CH_2Cl_2 and stirred at ambient temperature overnight. The reaction was diluted with 75 mL of Et_2O, washed with 25 mL of a saturated Na_2SO_3 solution, 3 × 25 mL of a saturated $NaHCO_3$ solution, and once with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using 5% Et_2O/hexanes as the eluent to yield 3.5 g (84%) of the sulfone, which crystallized on standing, mp 61–63 °C: IR (CCl_4) 2963, 2176, 1730, 1344, 1160 cm^{-1}; ^1H NMR (200 MHz, ($CDCl_3$) δ 9.71 (d, J = 4.7 Hz, 1H), 7.90 (dd, J = 8.4, 1.3 Hz, 2H), 7.69 (tt, J = 7.1, 1.5 Hz, 1H), 7.57 (tt, J = 7.9, 1.0 Hz, 2H), 3.99 (d, J = 4.6 Hz, 1H), 0.20 (s, 27H); ^{13}C NMR (90 MHz, ($CDCl_3$) δ 189.7, 140.3, 134.4, 129.3, 129.0, 97.3, 90.8, 78.9, 29.1, −0.60; MS m/z (relative intensity) 486 (1.2), 471 (4.8), 345 (54.0); HRMS calcd for $C_{24}H_{34}O_3SSi_3$ 486.1536, found 486.1524.

2-(Phenylsulfonyl)-3,3-bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)-pent-4-ynal [(2,4,6-Triisopropylphenyl)sulfonyl]hydrazone (30). The above aldehyde (420 mg, 0.86 mmol) and (triisopropylphenyl)sulfonyl hydrazide (260 mg, 0.86 mmol) were dissolved in a minimum amount of CH_3CN. Two drops of concentrated HCl were added, and this solution was stirred for 16 h at ambient temperature. The reaction was concentrated in vacuo and the residue purified by flash chromatography using 20% Et_2O/hexanes as eluent to furnish hydrazone **30** (590 mg, 90%) as a beige solid, mp 162–163 °C: IR (CCl_4) 2962, 2172, 1160 cm^{-1}; ^1H NMR (300 MHz, ($CDCl_3$) δ 8.05 (s, 1H), 7.62 (dd, J = 8.2 Hz, 2H), 7.49 (t, J = 6.6 Hz, 1H), 7.29 (d, J = 7.5 Hz, 3H), 7.19 (d, J = 8.3 Hz, 1H), 4.02 (sept, J = 6.8 Hz, 2H), 3.96 (d, J = 8.3 Hz, 1H), 2.92 (sept, J = 6.8 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.7 Hz, 6H), 1.12 (d, J = 6.7 Hz, 6H), 0.17 (s, 27H); ^{13}C NMR (75 MHz, ($CDCl_3$) δ 153.4, 151.4, 139.9, 138.9, 133.6, 129.0, 128.6, 123.9, 98.1, 90.1, 74.6, 34.2, 29.8, 24.8, 24.7, 23.6, 23.58, −0.53; MS m/z (relative intensity) $M^+ - C_3H_7$ 723 (8.4), 625 (100), 499 (9.3), 303 (44.6); HRMS calcd for $C_{36}H_{51}N_2O_4S_2Si_3$ ($M^+ - C_3H_7$) 723.2598, found 723.2613. Anal. Calcd for $C_{39}H_{58}N_2O_4S_2Si_3$: C, 61.07; H, 7.63; S, 8.34. Found: C, 61.36; H, 7.50; S, 8.31.

3,3-Bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)pent-1,4-diyne (2). Method A. A solution of LiTMP [from tetramethylpiperidine (0.23 mL, 1.3 mmol, 3.5 equiv) and *n*-BuLi (0.50 mL of a 2.5 M solution in hexane, 1.2 mmol, 3.25 equiv) at −78 °C] in 25 mL of THF was added via cannula to a stirring solution of hydrazone **30** (300 mg, 0.39 mmol) in 170 mL of THF at −78 °C. After 1 h the cold bath was removed. Nitrogen evolution had ceased after 2 h, and at that time, 100 mL of 1M H_3PO_4 was added followed by 100 mL of pentane. The organic phase was washed with 3 × 100 mL of H_2O, 1 × 100 mL of saturated $NaHCO_3$ solution, and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using pentane as eluent to afford 82 mg (64%) of **2** as white crystals, mp 104–105 °C: IR (CCl_4) 3314, 2201, 2143.0 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 2.47 (s, 1H), 0.20 (s, 27H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 98.4, 85.6, 78.9, 68.9, 29.7, −0.51; MS m/z (relative intensity) 328 (6.8), 313 (4.0), 240 (36.4); HRMS calcd for $C_{18}H_{28}Si_3$ 328.1499, found 328.1527.

Method B. A solution of α-sulfonylhydrazone **30** (741 mg, 0.97 mmol) and $LiOH \cdot H_2O$ (244 mg, 5.8 mmol, 6.0 equiv) in 10.0 mL of Et_2O was stirred at room temperature. After 24 h the reaction was washed 3 × with H_2O and once with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting brown solid was purified by flash chromatography with 2% CH_2Cl_2/hexanes as eluent to furnish 236 mg (74%) of silylated tetraethynylmethane (TEM) **2.**

X-ray Crystallography. Unit cell dimensions of **2** were determined from 10 photographic reflections and least-squares refined using 21 reflections with 20° ≤ 2θ ≤ 30°. Data were collected from 3.5° to 50° in 2θ and were corrected for Lorentz and polarization effects. The structure was solved in both space groups *Pnma* (no. 62) and *Pna*2_1 (no. 33) by direct methods (SHELXTL-PC Version)[19b] and refined using SHELXL-93.[19a] The residual $R1$ was not appreciably smaller for *Pna*2_1 [$R1$ = 6.10% for $I > 2\sigma(I)$]; therefore, the higher space group *Pnma* [$R1$ = 6.96% $I > 2\sigma(I)$] was selected. However, it is noteworthy that in both space groups the C–C triple bond lengths are consistent. A mirror plane of symmetry (x, $^1/_4$, z Wyckoff letter c) was found to pass through C1, C2, C3, H3, C4, C5, Si1, C8, and H8A; hence, dependent anisotropic thermal parameters U_{12} and U_{23} were fixed at 0 for the non-hydrogen

atoms. Hydrogen atoms were placed in calculated positions 0.96 Å from carbon (0.93 Å for H3) using a riding model with fixed isotropic U values of 1.5 times that of the adjacent carbon (1.2 for H3). Details of data collection and structure refinement, atomic coordinates, selected bond lengths and angles, and anisotropic thermal parameters are given in the supplementary material.

3,3-Diethynylpenta-1,4-diyne (1). A solution of **2** (64 mg, 0.2 mmol) in 4.0 mL of MeOH was added to K_2CO_3 (13 mg, 0.1 mmol, 0.5 equiv). After 15 min the reaction was poured into 10 mL of H_2O. The aqueous phase was washed with 4 × 10 mL of pentane. The combined organic extracts were washed with brine, dried over Na_2SO_4 and silica gel, filtered, and concentrated in vacuo in an ice bath to afford 19 mg (85%) of an off-white solid: IR (CCl_4) 3298, 2145 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 1.85 (s); ^{13}C NMR (90 MHz, C_6D_6) δ 77.8, 70.1, 30.2; MS m/z (relative intensity) 112 (7.4), 87 (9.2), 74 (7.05).

3,3,8,8-Tetraethynyl-1,4,6,9-decatetrayne (32). A stirring blue solution of CuCl (7 mg, 0.07 mmol, 0.3 equiv) and TMEDA (3.0 μL, 0.02 mmol, 0.1 equiv) in 2.0 mL of acetone was purged/evacuated 3 × with O_2 leading to a blue-green solution. A solution of **2** (72 mg, 0.22 mmol) in 1.0 mL of acetone was added dropwise. After 16 h at ambient temperature, the reaction was diluted with 10 mL of Et_2O, washed three times with 5 mL of H_2O and once with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. A pure sample of the hexasilylated dimer was isolated in 78% yield (56 mg) by flash chromatography with 2% CH_2Cl_2/hexanes as eluent, mp 172 °C dec: IR 2194, 2167 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ –0.01 (s); ^{13}C NMR (75 MHz, C_6D_6) δ 98.0, 87.0, 75.2, 65.3, 30.2, –0.75; MS m/z (relative intensity) 654 (1), 639 (1), 351 (6). Anal. Calcd for $C_{36}H_{54}Si_6$: C, 65.98; H, 8.31. Found: C, 65.68; H, 8.38.

A solution of the hexasilylated dimer (56 mg, 0.09 mmol) and K_2CO_3 (12 mg, 0.09 mmol) in 1.0 mL of THF and 1.0 mL of MeOH was stirred at ambient temperature for 15 min. The reaction solution was poured into H_2O and the aqueous layer was washed with 4 × 10 mL of pentane. The combined organic phases were washed with brine, dried over Na_2SO_4 and silica gel, filtered, and concentrated in vacuo at 0 °C to yield 18 mg (95%) of **32** as an off-white solid, mp 151 °C dec: IR (C_6D_6) 3283, 2292, 2268, 2244 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 1.82 (s); ^{13}C NMR (50 MHz, C_6D_6) δ 98.2, 87.1, 76.6, 70.9, 30.2; CI MS m/z (relative intensity) 221 (15), 196 (2), 172 (2), 146 (3).

1,4-Bis(3,3-diethynylpenta-1,4-diynyl)benzene (33). A deoxygenated stirring solution of silylated TEM **2** (45 mg, 0.15 mmol), 1,4-diiodobenzene (24 mg, 0.07 mmol, 0.5 equiv), PPh_3 (2 mg, 0.07 mmol, 0.05 equiv), $PdCl_2$ (13 mg, 0.007 mmol, 0.05 equiv), and CuI (3 mg, 0.15 mmol, 0.1 equiv) in 0.5 mL of tetramethylpiperidine was held at 50 °C for 90 min. The reaction solution was cooled to room temperature, diluted with 10 mL of Et_2O, washed once with 5 mL of 1 M $CuSO_4$, 3 × 5 mL of H_2O, and once with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting beige solid was purified by flash chromatography with 5% CH_2Cl_2/hexanes as eluent to afford 37 mg (75%) of the hexasilylated phenyl diadduct as a white solid, mp 206 °C dec: IR ($CDCl_3$) 2193, 2160 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.44 (s, 4H), 0.21 (s, 54 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 131.7, 122.5, 98.7, 85.8, 85.7, 79.7, 23.7, –0.46; MS m/z (relative intensity) 730 (6), 715 (2), 657 (1), 633-(1). Anal. Calcd for $C_{42}H_{58}Si_6$: C, 68.96; H, 7.99. Found: C, 68.89; H, 8.04.

A stirring solution of above diadduct (28 mg, 0.038 mmol) in 0.5 mL of THF and 0.5 mL of MeOH was treated with K_2CO_3 (5 mg, 0.038 mmol, 1 equiv). After 30 min of stirring at ambient temperature the reaction was poured into 5 mL of H_2O and the aqueous layer was washed with 3 × 5 mL of Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4 and silica gel, filtered, and concentrated in vacuo at 0 °C to provide 10 mg (87%) of octayne **33** as a white solid, mp 227 °C dec: IR (CCl_4) 3310, 2241, 2146 cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 6.83 (s, 4H), 1.93 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 131.9, 122.2, 85.0, 81.0, 78.1, 70.2, 30.2; MS m/z (relative intensity) 298 (36), 272 (15), 246 (19).

3,3-Bis(2-phenylethynyl)-1,5-diphenylpent-1,4-diyne (34). A solution of silylated TEM **2** (27 mg, 0.08 mmol) and K_2CO_3 (5.5 mg, 0.04 mmol, 0.5 equiv) in 0.25 mL of MeOH was added to a solution, frozen in liquid N_2, of phenyl iodide (84 mg, 0.41 mmol, 5 equiv), $Pd(PPh_3)_4$ (10 mg, 0.008 mmol, 0.1 equiv), and CuI (3 mg, 0.016 mmol, 0.2 equiv) in 0.5 mL of DMF, followed by the addition of a solution of MeONa in MeOH [prepared from 60% NaH (16 mg, 400 μmol, 5 equiv) and 250 μL of MeOH]. The reaction vessel was rigorously deoxygenated by freeze–pump–thaw cycles and sealed. After warming to and stirring at ambient temperature for 16 h the reaction solution was diluted with 5 mL of CH_2Cl_2 and 5 mL of Et_2O. The organic layer was washed three times with 5 mL of H_2O and once with brine, dried over Na_2SO_4, filtered, concentrated in vacuo, and purified by flash chromatography with 2% CH_2Cl_2/pentane as eluent to furnish 23 mg (69%) of **34** as a white solid, mp 190 °C dec: IR (C_6D_6) 2233 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.58 (m, 8H), 7.34 (m, 12H); ^{13}C NMR (90 MHz, C_6D_6) δ 132.1, 128.8, 128.2, 122.0, 84.3, 80.5, 29.7; CI MS m/z (relative intensity) 416 (13), 339 (4), 315 (21). Anal. Calcd for $C_{33}H_{20}$: C, 95.16; H, 4.84. Found: C, 94.93; H, 4.92.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra for **7–10, 13, 15, 17, 18, 23–30,** and **32–34,** and tables of positional parameters, interatomic distances and angles, and anisotropic thermal parameters for the X-ray structural determination of **2** (40 pages); observed and calculated structure factors for **1** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.