The synthesis of polyethylmethacrylate as starting materials for the preparation of highly cross-linked organic solids containing high atom fractions of carbon is described. Treatment of bromo- and iodoaromatic compounds with (trimethylsilyl)acetylene (TMSA) in the presence of palladium(0) and copper(I) in amine solvents yields (trimethylsilyl)ethynyl-substituted aromatics. The TMS protecting groups can be removed by hydrolysis with mild base. Compounds prepared by using this technique include 1,3-diethynylbenzene, 2,5-diethynylthiophene, 1,3-diethynyltetrafluorobenzene, 1,4-diethynyltetrafluorobenzene, 2-ethynylthiazole, 2,4-diethynylthiazole, 2,7-diethynylnaphthalene, hexakis((trimethylsilyl)ethynyl)benzene, tetraethynylthiophene, 2,5-bis((trimethylsilyl)ethynyl)-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene, 2,5-bis(4-(2-thienyl)butadiynyl)-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene, and 2,5-bis(4-(2-thienyl)butadiynyl)-3,4-diethynylthiophene.

**Introduction**

We are engaged in a project aimed at the preparation of organic solids containing a high density of strong, directed carbon–carbon bonds. Our objective in this project is to relate the molecular-level structure of the solids to their macroscopic physical properties and to determine if it is possible to replicate in these materials some of the remarkable range of properties exhibited by pure allotropes of carbon (diamond: hardness, high thermal conductivity) (graphite: electrical conductivity, lubricity). We expect high-carbon, densely cross-linked organic solids to display high thermal stability and a high degree of hardness. Our strategy for the preparation of these materials involves the initial syntheses of low molecular weight poly(di-ethynylbenzenes) by a route involving cyclotrimerization polymerization. The Hercules process also used suitable end-capping groups such as 2 to limit molecular weight. Soviet workers have also extensively developed the cyclotrimerization polymerization of diethynyl aromatics.

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Commercialization of materials derived from diethynylbenzene and other acetylenic precursors was explored at both General Electric and Hercules. The absence of an inexpensive route to the monomers, together with the limitation of a low elongation-to-break of the finished materials, discouraged their full development. A parallel effort to develop acetylene-containing polymers as thermoset resins resulted in the development of

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(1) This work was supported by the National Science Foundation, Grant CHE 85-08702.
acylene-terminated imide oligomers such as the Thermid-600 series. These materials have excellent thermal stability but their high cost and difficulty in curing have restricted their development.

Classical methods for the synthesis of terminal aryl-acetylenes involve the manipulation of preformed two-carbon units. Most useful among these are the Vilsmeier reaction, the halogenation-dehydrohalogenation of vinyl aromatics and ketones, and the dehydrohalogenation of β,β-dihalo olefins. This latter reaction was employed for the preparation of diethynylbenzene in the research of both General Electric and Hercules. A number of reactions also introduce ethynyl moieties directly into aromatic rings. The most widely accepted of these methods has been the Stephens-Castro reaction between an aromatic halide and a protected cuprous acetylide in refluxing pyridine. Difficulty in removing protective groups has been a limitation of this method. An alternative to the Stephens-Castro method—the coupling between arylcopper reagents and (iodoethynyl)trimethylsilane at low temperatures—is limited by the necessity to form the organocopper reagents. The palladium-catalyzed reaction of alkynylzinc reagents with aryl halides yields terminal and internal ethynyl aromatic compounds and does not require protection of the alkynyl groups but does require as reactant an aryl iodide or activated aryl bromide. A system of palladium(0) and copper(I) catalytically couples acetylenes and aryl iodides. Haghighi and Lau improved this reaction by using (trimethylsilyl)acetylene (TMSA). This improvement yields stable, readily manipulated trimethylsilyl-protected ethynyl aromatics as intermediates; mild basic hydrolysis removes the TMS group. Electron-withdrawing groups on the aryl ring facilitate the reaction; electron-donating groups are detrimental. This method offers the advantages of simplicity, ease of workup, and high yields. Vollhardt and co-workers first demonstrated multiple replacement of halogens on the same molecule by using this reaction. We chose this route to polyethynyl aromatics for these reasons and because of the wide range of suitably substituted haloaromatics available as starting materials. TMSA is expensive and 2-methyl-3-butyn-2-ol has been proposed as an alternative, but deprotection requires hydroxide base in high boiling solvent.

Results and Discussion

Ethynylbenzenes. We prepared 1,3-diethynylbenzene (1) by the reaction of 1,3-dibromotetrafluorobenzene with TMSA using dichlorobis(benzonitrile)palladium, triphenylphosphine, and copper(I) iodide as catalyst. The TMS-protected intermediate (6) is an air- and moisture-stable solid. Treatment of compound 6 with a catalytic amount of base in methanol removes the protecting groups. Compound 1 is a clear colorless liquid that discolors upon prolonged standing. Compound 1 may be purified by distillation at moderate temperatures and under high vacuum. (Note: Our initial attempt to distill 1 at temperatures of up to 110 °C and at aspirator pressures resulted in an exothermic reaction followed by an explosion. Compound 1 and all other volatile polyethynyl aromatics should be distilled at high vacuum and at temperatures of less than 60 °C in well-shielded equipment. Only limited quantities should be distilled, stored, or manipulated as pure (undiluted) material. All of the deprotected ethynyl aromatics mentioned in this paper should be treated as potentially explosive materials.)

The same chemistry can be extended to the preparation of higher poly- and persubstituted acetylenic aromatic compounds. Reaction of hexadiodobenzene (8) with TMSA yielded 9 in 1% isolated yield and the related 10 in 14% yield. Compound 9 is only produced after prolonged reflux of the reaction mixture, and these conditions result in competitive reduction of the halogens and formation of 10. The reaction yields other mixed substituted and reduced products (of higher R). These compounds were not characterized. Vollhardt has previously reported a synthesis of 9 from hexabromobenzene in 27% yield.

Derivatives of Tetrafluorobenzene. We expect polymers prepared from (fluorophenyl)acetylenes to have lower water permeability, and perhaps greater thermal stability, than polymers from analogous phenylacetylenes. The preparation of 1,4-diethynyltetrafluorobenzene by the coupling of the lithium salt of TMSA with hexafluorobenzene followed by basic hydrolysis of the protecting groups has been described by Walton. Application of the same palladium/copper chemistry described above to commercially available 1,4-dibromotetrafluorobenzene (11)...

(10) For a review of the development of Thermid-600 and of other acetylene terminated oligomers, see: Hergenrother, P. M. In Reactive Oligomers; ACS Symposium Series 282; American Chemical Society: Washington, DC, 1986: p 1-16.
followed by deprotection of 12 yields 1,4-diethynyltetrafluorobenzene (13) in 90% overall yield.

Since we were aware that para-substituted diethylbenzyl monomers might yield rigid rod polymers with limited solubility, we were particularly interested in preparing monomers in which the two ethynyl groups were meta. Several attempts to brominate 1,2,3,5-tetrafluorobenzene yielded only starting material, but 1,2,3,5-tetrafluorobenzene (14) reacted cleanly with periodic acid in hot concentrated sulfuric acid when a variation of the method of Mattern(28) was used and yielded 1,3-diido-2,4,5,6-tetrafluorobenzene (15). The conversion of 15 to 1,3-bis((trimethylsilyl)ethynyl)tetrafluorobenzene (16) then proceeded smoothly by using the palladium/copper catalyst system. Removal of the TMS protecting groups with KOH in methanol yielded 1,3-diethynyl-2,4,5,6-tetrafluorobenzene (17) as a colorless liquid. Compound 17 could be purified by vacuum transfer, but attempts to distill it at aspirator pressure resulted in an explosive decomposition.

**Ethynylpentfluorobenzene** (20) (an end-capping agent in the polymerization) was prepared by using a similar procedure from bromopentafluorobenzene (18).

**Derivatives of Thiophene.** The synthesis of simple diethylbenzylthiophenes such as 2,5-diethylthiophene(29) (23) could be accomplished by using procedures analogous to those described for the phenyl derivatives.

The reaction of tetraiodothiophene(30) (24) with a 2 equiv of TMSA at room temperature resulted in the clean formation of 2,5-bis((trimethylsilyl)ethynyl)-3,4-diiodothiophene (25) in 84% isolated yield (Scheme I). Attempts to derivatize 25 further by, for example, treatment with CuCN in DMF resulted in decomposition. Reaction of 25 with 2 equiv of TMSA did, however, yield tetrakis-((trimethylsilyl)ethynyl)thiophene (26) in 45% yield. Compound 26 could also be prepared directly from 24 by treatment with 4.5–6 equiv of TMSA. Compound 26 was isolated as stable but slightly light-sensitive white crystals. Deprotection of the four acetylene groups could be accomplished by treatment with dilute KOH in degassed methanol. Tetraethylthiophene (27) was isolated in 91% yield after rapid chromatography on silica with hexanes. Compound 27 is a white crystalline material which rapidly turns black upon standing in air. (Note: Compound 27 is sensitive to heat and shock and attempts to sublime it under high vacuum resulted in an explosive decomposition. Compound 27 is the least stable compound described in this work and great caution is advised in its preparation and handling.) Solutions of 27 in chlorinated solvents deposit insoluble black crystals upon standing. These crystals were not examined further.

More complicated ethynyl monomers are also accessible by the same general route. For example, reaction of 2,5-bis((trimethylsilyl)ethynyl)-3,4-diiodothiophene (25) with an excess of 2-methyl-3-butyn-2-ol(31) in the presence of the same palladium/copper catalyst system resulted in the isolation of the doubly protected tetraethylthiophene (28) (as light-sensitive crystals in 86% yield). The presence of the two different protecting groups allows for selective deprotection. Thus, treatment of 28 with a catalytic amount of KOH in methanol at room temperature permits the essentially quantitative isolation of compound 29, in which the TMS protecting groups alone have been removed. Coupling of 29 with an excess of 2-ethylthiophene(31) using standard Glaser coupling conditions followed by chromatography allowed the isolation of the end-capped derivative 30 together with higher oligomers, from which 30 could be easily separated by chromatography. The removal of the acetone protecting groups has been described previously(32). This reaction is less effective than the removal of TMS protecting groups and requires further refinement.

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(31) 2-Ethynylthiophene may be prepared by the route described in this paper for 2,5-diethynylthiophene and using 2-bromothiophene as the starting material. For alternative routes, see ref 29.
prolonged reflux in the presence of solid KOH and a high boiling solvent. Nevertheless, the deprotection could be accomplished in good yield by following the evolution of acetone (by GC) from the reaction. Compound 31 was recovered as orange air-stable crystals.

**Derivatives of Thiazole.** The thermal stability of the thiazole nucleus has been exploited in the preparation of the well-known poly(benzothiazole) engineering plastics.33 These materials are stable at temperatures up to 400 °C. For this reason and to provide a comparison with the diethynylthiophene case, we attempted the preparation of several acetylenic thiazoles. Although a great variety of halogenated thiazoles have been reported,34 the number of useful commercially available examples is limited. Freshly distilled 2-bromothiazole (32) reacted quickly with TMSA under palladium/copper catalysis to yield 2-((trimethylsilyl)ethynyl)thiazole (33) in 65% isolated yield. Compound 33 was isolated as a pale yellow oil that darkened upon standing in air or in light. Removal of the protecting group was accomplished as before by treatment of 33 with a catalytic amount of base in methanol. 2-Ethynylthiophene (34) was recovered as a volatile unstable oil. An alternative route to 34 was devised starting from 2-iodothiazole.35

The preparation of a diethynylthiazole derivative was complicated by the low reactivity of both the 4 and 5 positions of the ring toward halogen replacement.34 Thus, attempted reaction of 2,5-dibromothiazole with TMSA in the presence of catalyst resulted primarily in decomposition with production of only small quantities of mono-substituted (probably in the 2 position) product. We did find, however, that 2,4-dibromothiazole (38) (prepared from the corresponding diol (37) by reaction with PdCl₂)36 reacted rapidly with TMSA and yielded quantitatively a monosubstituted product (presumably 2-((trimethylsilyl)ethyl)4-bromothiazole). Prolonged reflux of the reaction mixture (>36 h) yielded the desired protected derivative (39). The later stages of the reaction were complicated by decomposition and the protected diethynylated thiazole was only recoverable in ~20% yield after chromatography on alumina. The product could neither be crystallized or distilled. Deprotection of the TMS groups was accomplished as before and the desired 2,4-diethynylthiazole (40) was isolated as a yellow oil (which rapidly turned dark upon standing) in 62% yield.

**Ethynyl Naphthalenes.** The synthesis of 1-ethynyl-naphthalene is summarized in Table I. The preparation of a suitable diethynl naphthalene proved to be more troublesome. Although 1,4-dibromonaphthalene is commercially available, we felt that the rigid rod-like character of any polymer prepared from a monomer having the two ethynyl groups in this configuration would result in poor solubility. We therefore settled upon the preparation of the 2,7 derivative. We prepared 2,7-dibromonaphthalene (41) by treatment of the commercially available 2,7-di-hydroxynaphthalene (40) with triphenylphosphine/Br₂ complex.37 This reaction was complicated by the contamination of the product by triphenylphosphine oxide. We therefore give a reliable procedure for this synthesis in the Experimental Section. The syntheses of the protected (42) and deprotected 2,7-diethynyl naphthalene (43) are summarized in Table I.

**Conclusions**

This work describes a simple route to poly- and per-acetylenic aromatics through the palladium/copper-catalyzed reaction between an activated aromatic halide and a protected acetylene. The intermediate protected acetylenic aromatics were then deprotected by basic hydrolysis. We have found that any combination of reagents that generates a bis(triphenylphosphine)palladium(0) complex in solution (palladium chloride plus 2 equiv of triphenylphosphine or bis(benzonitrile)palladium chloride plus 2 equiv of triphenylphosphine) works equally well as the catalytic species. Copper(I) iodide or copper(II) acetate is the most suitable choice for the copper reagent.

We have examined both TMSA and 2-methyl-3-butyne-2-ol as protected acetylenes for the reaction. Despite its high cost, TMSA is the most suitable choice as the protected acetylene because it forms stable crystalline TMSA-protected intermediates and the TMS groups may be removed by very mild basic hydrolysis.

Both aromatic bromides and iodides are suitable as precursors to the aromatic acetylenes. In certain cases (as in the attempted preparation of hexakis((trimethylsilyl)ethyl)benzene (9)), we found that iodo-substituted aromatics underwent a side reaction in which reduction rather than substitution of the iodines occurred. Electron- withdrawing groups on the ring facilitated substitution of both bromo and iodo substituents, whereas electron-donating groups were detrimental. In certain cases (as in the preparation of compounds 25 and 28), we were able to take advantage of the variations in reactivity between halogens in the same molecule to selectively substitute at certain positions.

We isolated acetylenic substituted molecules by mild basic hydrolysis of the protected intermediates. We found that attempted distillation of many of the free acetylenes even at moderate temperatures resulted in an explosive decomposition. All of the liquid acetylenes, however, could be purified by vacuum transfer at room temperatures, and the solid materials could be purified by recrystallization or sublimation.

**Experimental Section**

**General.** Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded as KBr disks or as thin films on NaCl plates. UV spectra were recorded as 10⁻⁵ M solutions in heptane. ¹H NMR spectra were recorded at 80 MHz or 300 MHz and ¹³C NMR spectra were recorded at 75 MHz. Mass spectra were recorded at 70 eV or by GC/MS on a HP 5990A spectrometer. Elemental analyses were obtained by Galbraith Laboratories, Nashville, TN. (Trimethylsilyl)acetylene (TMSA), copper(I) iodide, dichloro-bis(benzonitrile)palladium(II), 2,5-dibromothiophene, 1,2,3,5-tetrafluorobenzene, 2-aminothiophene, 2-bromo thio phene, and 2,7-dihydroxynaphthalene were obtained from Aldrich and were used without further purification. Silica gel (70–230 mesh) was obtained from Fluka. Disisopropylamine (Aldrich) and piperidine (Aldrich) were distilled from KOH before use. Diethyl ether and tetrahydrofuran (THF) were distilled from purum sodium benzophenone dimethyl solution before use. Hexafluorobenzene (8) was prepared from benzene by the method of Mattern38 in 45% yield. Tetrasilodithiophene (24) was prepared from thiophene by the

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(35) The synthesis of 2-iodothiazole (36) from 2-aminothiazole (35) has been reported by Travaglì (Travaglì, G. Gazz. Chim. Ital. 1948, 72, 599–599). The conversion of 2-aminothiazole to 2-iodothiazole is low and in our hands was never greater than 40%. Nevertheless the low cost of 2-aminothiazole, together with the enhanced reactivity of the iodo derivative, make this route attractive. We therefore give a procedure for the preparation of 2-iodothiazole in the Experimental Section.
method of Steinkopf\(^{(28)}\) in 75% yield. All reactions, except where indicated, were carried out under an atmosphere of argon.

**General Procedure for the Synthesis of TMS Acetylene Derivatives.** Synthesis of 1,3-Bis((trimethylsilyl)-ethynyl)benzene (6). To a solution of 1,3-dibromobenzene (5) (10.0 g, 48 mmol) in freshly distilled disopropylamine (50 mL) were added dichlorobis(benzonitrile)palladium(II) (1.86 g, 2.4 mmol), triphenylphosphine (1.26 g, 4.8 mmol), and copper(II) acetate hydrate (0.47 g, 2.4 mmol) in portions by passing a rapid stream of argon through it. TMSA (10.4 g, 14.6 mL, 2.2 equiv) was added over 1 h at room temperature to the clear yellow-green solution. The solution changed color rapidly to a yellow-brown with the formation of a heavy precipitate. The solvent was removed at reduced pressure and the residue was taken up in methylene chloride. Extraction with water (twice), drying of the organic layer, and the clear yellow solution was diluted to 40 mL. The solution was heated at reflux for 20 min until GC analysis indicated that the reaction was complete. The reaction mixture was cooled to room temperature and the residue was dissolved in methylene chloride, washed with water, and finally dried with MgSO\(_4\). The residue was chromatographed on silica gel with hexanes. After the elution of several lower substituted ethynyl compounds, a pale yellow band was removed from the column. The yield was 4.2 g, 95%.

Further elution yielded 9 (5 mg, 1%) as a pale yellow solid.

**Compound 9:** mp >300 °C; IR (KBr) 2980, 2920, 2150, 1400, 1250, 940, 850, 760 cm\(^{-1}\); \(^{1}H\) NMR (80 MHz, CDCl\(_3\)) \(\delta 0.23\) (s); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 102.5, 105.0, 101.3\); mass spectrum (EI, exact mass), calculated for C\(_{12}\)H\(_{19}\)BrN\(_2\)SIO: m/z 308.1, 264.1, found 308.1, 264.1; UV max (log \(\varepsilon\)) 275 (4.2), 280 (4.5), 284 (5.1), 268 (4.5), 252 (4.3) nm. Compound 10: pale yellow crystals, mp 155-157 °C; IR (KBr) 2975, 2895, 2810, 1420, 1290, 1250, 1210, 1010, 955, 850, 760, 705, 635 cm\(^{-1}\); \(^{1}H\) NMR (80 MHz, CDCl\(_3\)) \(\delta 7.50\) (1 H, 15 \(\delta\)), 0.28 (s, 4 H); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta 132.5, 128.9, 127.9, 125.6, 105.1, 103.9, 101.9, 100.9, 1.5, 1.3, 1.40; mass spectrum (EI, m/z (rel intensity)) 558 (M\(^{+}\), 8.35), 543 (3.7), 455 (6.2), 425 (2.3), 397 (2.2), 381 (2.1), 37 (100); UV max (log \(\varepsilon\)) 270 (4.73), 286 (4.98), 298 (4.56), 308 (4.53), 322 (4.49) nm. Anal. Calcld for C\(_{12}\)H\(_{14}\)BrSIO: C, 66.66; H, 8.24. Found: C, 66.58; H, 8.21.

**1,3-Diiodotetrafluorobenzene** (15). To a cooled solution of concentrated H\(_2\)SO\(_4\) (50 mL) was added in portions periodic acid (HIO\(_4\)) (7.5 g, 33 mmol). To this clear solution was added in portions finely ground KI (16.4 g, 100 mmol). An exothermic reaction took place with the evolution of iodine vapor and the formation of a dark solution. 1,3,3,5-Tetrafluorobenzene (14) (5 g, 33 mmol) was added dropwise and the reaction mixture was heated at 70 °C for 4 h. Upon cooling, the solution was poured carefully onto crushed ice (200 g) and filtered to remove excess iodine. The filtrate consisted of an orange aqueous layer and a heavy dark oil. Diethyl ether (200 mL) was added to dissolve the oil and the organic layer was separated, washed with 10% sodium thiosulfate solution and water, and dried over magnesium sulfate. The solvent was removed, leaving an orange oil that was further purified by passing it through a short column of silica gel, using hexanes as the eluting solvent. Removal of the solvent yielded 1,3-diiodotetrafluorobenzene (7.1 g) as a colorless liquid in 61% yield (based on 85% pure starting material from Aldrich), bp 140 °C (10 Torr); mass spectrum (EI), m/z (rel intensity) 156 (9.0). Anal. Calcld for C\(_{12}\)H\(_{12}\)I\(_2\)F\(_4\): C, 56.14; H, 5.26. Found: C, 56.16; H, 5.24. Compound 16 was purified by chromatography with hexanes on silica. It formed white needles in 92% yield, mp 55-57 °C; IR (KBr), 2980, 2920, 2050, 1505, 1260, 990, 850 cm\(^{-1}\); \(^{1}H\) NMR (80 MHz, CDCl\(_3\)) \(\delta 0.25\) (s); mass spectrum (EI, m/z (rel intensity)) 342 (18.2), 329 (10.1), 328 (26.4), 327 (100) (9.0). Anal. Calcld for C\(_{12}\)H\(_{13}\)BrSIO: C, 65.14; H, 5.29. Found: C, 56.11; H, 5.36. Compound 16 was partially purified by recrystallization from hexanes.

**1,3-Di(ethynyl)tetrafluorobenzene** (13). Removal of the TMS protecting groups was accomplished as for the synthesis of 1,3-diethynylbenzene described above. The yield of compound 13 (as white crystals after chromatography on silica gel) was 95%: mp 132-134 °C (lit.\(^{(25)}\) mp 132-134 °C); IR (KBr), 2985, 2120, 1480 cm\(^{-1}\); \(^{1}H\) NMR (80 MHz, CDCl\(_3\)) \(\delta 3.45\) (s); mass spectrum (EI, m/z (rel intensity)) 198 (100, M\(^{+}\)), 167 (5.7), 145 (8.5), 109 (1.1), 99 (5.5).

**1,3-Di(ethynyl)tetrafluorobenzene** (17): yield 91% after purification by vacuum distillation at 55 °C and 1.0 Torr; IR (film on NaCl) 3010, 2130, 1480 cm\(^{-1}\); \(^{1}H\) NMR (80 MHz, CDCl\(_3\)) \(\delta 3.50\) (s). Anal. Calcld for C\(_{12}\)H\(_{13}\)F\(_{14}\): C, 60.60; H, 1.01. Found: C, 60.68; H, 0.94.

**((Trimethylsilyl)ethynyl)pentfluorobenzene** (19) was prepared by treatment of pentfluorobenzom (18) with 1.1

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\(\text{(28)}\) It appears that any combination of reagents that generates a bis(triarylphosphine)phosphate(palladium(II)) complex in solution works equally well as the catalytic species. We have used palladium(II) chloride plus 2 equiv of triarylphosphine, bis(benzonitrile)palladium(II) chloride plus 2 equiv of triphenylphosphine, or bis(triethylphosphine)palladium(II) dichloride. The choice of copper iodide is also flexible. The original reports describe the use of copper iodide. Economics and co-workers, however, report that the use of copper(II) acetate hydrate lessens the formation of colloidal palladium formed.\(^{(2)}\)


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High Carbon Materials from Acetylenic Precursors
equiv of TMSA under the same conditions described for 12 and 16: bp 97 ºC (13 Torr); 1H NMR (80 MHz, CDCl3) δ 0.14 (s); mass spectrum (EI), m/z (rel intensity) 264 (M+, 31.0), 249 (100). Anal. Calcd for C11H6F6Si: C, 50.00; H, 3.41. Found: C, 50.22; H, 3.45.

**Table I. Preparation of TMS-Protected and Deprotected Polyethynyl Aromatics**

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<th>aryl halide</th>
<th>equiv TMSA</th>
<th>conditions</th>
<th>reactn time (h)</th>
<th>protected yield, %</th>
<th>deprotected yield, %</th>
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<td>6</td>
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</table>

*The following conditions were used for the substitution reactions: A. The concentrations of palladium(0) and of copper(I) were 2 mol % with respect to replaceable halogen. The solvent was diisopropylamine. The TMSA was added at 0 ºC. The reaction time included 1 h of heating at reflux (84 ºC) at the end of the reaction period. B. The concentrations of palladium(0) and of copper(I) were 8% with respect to the available halogen. TMSA was added at 0 ºC. A mixture of diisopropylamine and piperidine (1:1) at reflux was used as the solvent. C. The concentrations of palladium(0) and of copper(I) were 2 mol % with respect to replaceable halogen. The solvent was diisopropylamine. The reaction time included 1 h at room temperature and the remainder at reflux. *The reported yields are isolated yields. Only iodine atoms are replaced. "Only bromine atoms are replaced. Removal of the TMS groups was carried out by stirring the protected derivatives with 1% KOH in methanol for 25 min at room temperature.

for the synthesis of 1,3-diethynylbenzene described above: yield 96%; mp 80–81 ºC (lit. 29 mp 82.5–83.5 ºC); 1H NMR (80 MHz, CDCl3) δ 7.02 (s, 2 H), 0.17 (s, 18 H); 13C NMR (75 MHz, CDCl3) δ 132.2, 124.5, 99.9, 99.1, 0.38. Anal. Calcd for C11H6F6Si: C, 60.90; H, 7.29; S, 11.58. Found: C, 60.23; H, 7.29; S, 11.58.

2,5-Diethynylbenzene (22). Ethynylpentfluorobenzene (20). Basic hydrolysis of 19 yielded 20 in 95% yield: bp 129–131 ºC (lit. 30 bp 50–52 ºC, 37 Torr); IR (NaCl) 3310, 2135 cm⁻¹; 1H NMR (CDCl3) δ 3.55.

2,5-Bis((trimethylsilyl)ethynyl)thiophene (22). The synthesis of 22 from 2,5-dibromothiophene (21) was carried out as
The solvent was removed at reduced pressure and the residue dissolved in the minimum amount (~15 mL) of 10% THF/methylene chloride. This solution was applied to a column of neutral alumina (Broekman Activity I 180–200 mesh) packed in methylene chloride. The column was eluted first with methylene chloride to remove traces of starting material and then the product was removed from the column by eluting with 10% THF/methylene chloride. Compound 28 was recovered as colorless cubic crystals that darkened upon standing. The yield was 3.59 g (86%). An analytical sample was obtained as white crystals by recrystallization from methanol. A mixture of 29 (0.16 g, 0.1 mmol) and TMSA (0.44 mL, 3.64 mmol) was added to a solution of 25 (0.2 g, 0.28 mmol) in diisopropylamine (120 mL) followed by the desired compound 26 as off-white and slightly orange oil that solidified upon standing: yield 0.20 g (40%); IR (KBr) 2920, 2895, 1450, 1410, 3670, 3570 cm⁻¹; UV (CH₂Cl₂) max 345 (4.02) nm. Anal. Calcd for C₂₉H₂₄N₂S₂: C, 70.80; H, 3.99.

The solution was stirred at room temperature for 25 min. The solvent was removed at reduced pressure, and the residue was taken up in 100 mL of diethyl ether, washed with water, and dried with magnesium sulfate. The ether was removed to yield compound 29 in quantitative yield. The compound could be further purified by rapid chromatography on neutral alumina using 10% THF in methylene chloride as the eluting solvent. The purified compound was obtained as pale yellow crystals: IR (KBr) 3420, 3140, 1630, 1570, 1550, 1540 cm⁻¹; UV (CH₂Cl₂) max 360 (4.34) nm. Anal. Calcd for C₂₉H₂₄N₂S₂: C, 72.97; H, 6.65. Found: C, 73.08; H, 6.65.

2-Butadiynyl-3,4-bis(3-hydroxy-3-methyl-1-butylnyl)thiophene (30). A solution was prepared of CuCℓ (190 mg, 10 mmol) and TMEDA (0.2 mL) in reagent-grade acetone. A steady stream of oxygen was bubbled through the solution for 10 min. A mixture of 29 (0.3 g, 1 mmol) and 2-ethylthiophene (0.87 g, 8 mmol) in acetone (3 mL) was added, the reaction was allowed to proceed for 4 h, while a steady stream of oxygen was bubbled through it. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in methylene chloride and applied to a silica gel column packed in methylene chloride. Elution with methylene chloride removed first 1,4-bis(2-thienyl)butadiyne as a pale yellow band. Changing the solvent to 10% THF in methylene chloride removed the desired compound 30 as an orange oil that solidified upon standing: yield 0.20 g (40%); IR (KBr) 3400, 2920, 2920, 2840, 2210, 1660, 1560 cm⁻¹; UV (CH₂Cl₂) max 368 (4.4), 243 (4.06), 212 (4.3), 325 (4.37), 340 (4.34) nm. Anal. Calcd for C₃₀H₂₅N₂S₄: C, 71.53; H, 6.79. Found: C, 71.61; H, 7.83.

2-Butadiynyl-3,4-bis(3-hydroxy-3-methyl-1-butylnyl)thiophene (31). To a sample of 30 (75 mg, 0.15 mmol) in toluene (30 mL) was added KOH (75 mg, 1.33 mmol). The reaction flask was fitted with a Dean–Stark trap and heating was begun. A mixture of toluene and acetone was removed by distillation and the toluene was replaced by degassed toluene when necessary. After 2 h, the heating was discontinued and the organic solution was extracted with water and dried with magnesium sulfate and the toluene removed. The bright yellow product was chromatographed on silica gel with methylene chloride as the solvent to yield 31 as a pale yellow, light-sensitive yellow crystals. The yield was 38 mg (62%); IR (KBr) 3300, 2920, 2510, 1520, 870 cm⁻¹; UV (CH₂Cl₂) max 342 (4.32), 243 (5.2), 214 (5.0), 189 (4.3), 158 (4.6), 131 (4.0) nm. Anal. Calcd for C₂₉H₂₄N₂S₄: C, 73.86; H, 2.04. Found: C, 73.52; H, 1.73.

2-Iodothiazole (36). To a mixture of concentrated H₂SO₄ (20 mL) and water (50 mL) cooled to ~5 °C was added 2-aminothiazole (35) (10 g, 0.1 mol). To the dark red solution was added NaNO₂ (7.3 g, 0.1 mol) (dissolved in the minimum amount of chilled water) dropwise over a period of 1 h. The rate of reaction was slow, but the reaction was allowed to proceed for 1 h.
addition was such that the temperature did not rise above -2 °C. The solution was stirred for 1 h. A solution of 1 (20 g, 0.12 mol) in water (50 mL) was added and the solution was allowed to stir for 1 h, with the temperature at room temperature, and finally at 70 °C for 30 min. The dark solution was filtered. To the filtrate was added enough dilute sodium bicarbonate to make the solution basic. The solution was extracted with diethyl ether (three 100-mL portions), and the organic layers were combined, washed with water, and dried over MgSO4. The solvent was removed to yield the crude product as a dark oil. The material was purified by distillation at reduced pressure (bp 117 °C at 40 Torr): yield 8.4 g (40%); IR (film on NaCl): 3020, 2950, 2895 cm⁻¹; 1H NMR (80 MHz, CDCl₃) δ 7.93 (d, J = 3.6 Hz, 1 H), 7.92 (d, J = 3.6 Hz, 1 H); mass spectrum (EI), m/z (rel intensity) 211 (M⁺, 100), 172 (92), 135 (53), 107 (53), 77 (25).  

2-((Trimethylsilyl)ethynyl)thiazole (33). To a solution of freshly distilled 2-bromothiazole (5 g, 30 mmol) were added 2-ethynylthiophene, 4298-52-6. The solution was degassed by means of a rapid stream of argon and to the solution was added TMSA (3.9 g, 1.2 mmol). The solution was heated at about 100 °C. The material was isolated by filtration and washed with small amounts of cold ethanol. Final recrystallization from ethanol: yield 62%, mp 140–142 °C (lit. mp 140–141 °C). 1-(Trimethylsilyl)ethynyl)naphthalene (42) and 2,7-Bis((trimethylsilyl)ethynyl)naphthalene (46). The syntheses of these compounds were analogous to the preparation of the protected diisopropylbenzene reported above. The monosubstituted product was formed at room temperature from 1-bromonaphthalene (41), while the disubstituted compound (prepared from 2,7-dibromonaphthalene (45)) required gentle heating. 1-(Trimethylsilyl)ethynyl)naphthalene was obtained as a dark oil using a similar procedure: IR (film on NaCl) 3295, 2950, 2220, 1505, 1248, 1050, 870, 640 cm⁻¹; 1H NMR (80 MHz, CDCl₃) δ 7.93 (d, J = 3.6 Hz, 1 H), 7.92 (d, J = 3.6 Hz, 1 H); mass spectrum (EI), m/z (rel intensity) 211 (M⁺, 100), 172 (92), 135 (53), 107 (53), 77 (25).  

1-Ethynylnaphthalene (43). Deprotections of the naphtho derivatives were carried out as described for 1,3-diethynylbenzene. Compound 43 was obtained as a colorless oil in 95% yield: IR (film on NaCl) 3295 (vs), 3050 (vw), 2955 (s), 2925 (m), 2895 (w), 2140 (w), 1585 (s), 1505 (m), 1390 (s), 1248 (w), 1080 (m), 1040 (w), 830 (s), 800 (s), 770 (v), 650 (s), 640 (s), 630 (s), 520 (s), 460 (s), 420 (s); 1H NMR (80 MHz, CDCl₃) δ 7.93 (d, J = 3.6 Hz, 1 H), 7.92 (d, J = 3.6 Hz, 1 H); mass spectrum (EI), m/z (rel intensity) 109 (M⁺, 100), 82 (15.6), 69 (44.7), 58 (26.7).  

2.4-Diethynylthiophene (40) was prepared from 39 as a colorless oil using a similar procedure: 1H NMR (80 MHz, CDCl₃) δ 7.4 (s, 1 H), 3.55 (s, 1 H), 3.49 (s, 1 H); mass spectrum (EI), m/z (rel intensity) 133 (M⁺, 100), 108 (34), 94 (45.5), 53 (23.8). This compound was too sensitive to be submitted for elemental analysis.  

2,7-Dibromonaphthalene (45). A 1000-mL round-bottomed flask was charged with triphenylphosphine (144 g, 0.55 mol) and 2,7-dibromonaphthalene (113.7 g, 0.35 mol), in a dry box to prevent polymerization. The suspension was cooled to 0 °C and to this mixture was added bromine (88 g, 28.2 mL, 0.55 mol) dropwise such that the temperature remained below 5 °C. A heavy white precipitate was formed (an overhead stirrer was necessary at this point to ensure efficient mixing). To this mixture was added dropwise 2,7-dihydroxynaphthalene (44) (40 g, 0.25 mol) as a solution in acetonitrile (200 mL). The precipitate became even thicker and stirring was maintained only with difficulty. The mixture was heated to 70 °C at which point the precipitate dissolved and heating was continued for 30 min. The flask was fitted with an air-cooled distillation head and the acetonitrile was removed at atmospheric pressure. The temperature was then gradually raised to 250 °C. Evolution of HBr appeared to begin at about 190 °C and the HBr was trapped by means of a beaker filled with cold NaOH solution. The temperature was maintained at 250 °C for 50 min, and the dark oil was allowed to cool approximately to 100 °C, at which point it was poured into a flask containing 500 mL of absolute ethanol. The flask was stoppered and allowed to sit overnight. A dark crystalline mass of crude 2,7-dibromonaphthalene was formed (scraping of the inside of the flask was necessary to induce crystallization). The product was isolated by filtration and washed with small amounts of cold ethanol. Final recrystallization from ethanol: yield 62%, mp 140–142 °C (lit. mp 140–141 °C).