Experimental

General. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Alkyllithium reagents were obtained from FMC. Pyridine, methyl iodide, triethylamine, and *N*,*N*-dimethylformamide (DMF) were distilled over calcium hydride, and stored over 4 Å molecular sieves. Toluene and benzene were distilled over CaH_2. Methylene chloride and hexanes were distilled. Ethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine and diisopropylethylamine (Hünig's base) were distilled over CaH_2. MeOH was dried over oven dried 3 Å molecular sieves. Gravity column chromatography, silica gel plugs, and flash chromatography were performed using 230-400 mesh silica gel from EM Science. Thin layer chromatography was preformed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. Combustion analyses were obtained from Atlantic Microlab, Inc., P. O. Box 2288, Norcross, GA 30091.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Using the Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).[1] To an oven-dried round bottom flask equipped with a water cooled West condenser and magnetic stir bar or to a screw cap pressure tube with a magnetic stir bar were added the aryl halide, a palladium catalyst such as bis(triphenylphosphine)palladium(II) dichloride (3-5 mol % per halide), and copper(I) iodide (6-10 mol % per halide). Triphenylphosphine was used in some reactions to keep the palladium in solution. The vessel was then sealed with a rubber septum (flask) or capped (tube) under a N_2 atmosphere. A solvent system of THF and/or benzene and/or methylene chloride was added depending on the solubility of the aryl halide. Then base, triethylamine or diisopropylethylamine, was added. Finally, the terminal alkyne (1-1.5 mol %

per halide) was added and the reaction was heated until complete. Upon completion of the reaction, the reaction mixture was quenched with water, a saturated solution of NH_4Cl, or brine. The organic layer was diluted with methylene chloride or Et_2O and washed with water, a saturated solution of NH_4Cl, or brine (3×). The combined aqueous layers were extracted with methylene chloride or Et_2O (2×). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each material.

General Procedure for the Iodination of Triazenes.[2] To an oven-dried screw cap tube was added the corresponding triazene and iodomethane. The mixture was degassed by slowly bubbling nitrogen for more than 15 min. After flushing with nitrogen, the tube was capped and heated at 120 °C overnight. The reaction mixture was cooled and diluted with hexane. The mixture was passed through a plug of silica gel. After evaporation of the solvent in vacuo, purified product was obtained by chromatography. Eluents and other slight modifications are described below for each material.

4,4¢-Di(ethynylphenyl)-1-(thioacetyl)benzene (4) (JMT-I-27). See the general procedure for the Pd/Cu coupling reaction. The compounds used were copper(I) iodide (0.042 g, 0.22 mmol), bis(dibenzylideneacetone)palladium(0) (0..063 g, 0.11 mmol), triphenylphosphine (0.115 g, 0.44 mmol), **3** (0.64 g, 2.3 mmol) 1-ethynyl-4-(ethynylphenyl)benzene (0.44 g, 2.2 mmol), diisopropylethylamine (1.7 mL, 10.0 mmol), and THF (10 mL) at 50° C for 3 h. The residue purified by flash liquid chromatography using silica gel (1:1 hexanes: methylene chloride) yielding 0.57 g (74%) of the titled compound. IR (KBr) 3435.9, 3138.5, 2215.4, 1697.4, 1656.4, 1507.7, 1379.5, 1353.8, 1128.2, 1107.7, 1015.4, 943.6, 838.6, 828.1, 759.0, 756.7, 692.0, 620.5 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) δ 7.54-7.50 (m, 2 H), 7.39 (d, *J*=8.5 Hz, 2 H), 7.34 (d, *J*=2 Hz, 3 H), 7.24 (d, *J*=8.5 Hz, 2 H), 7.16 (br s, 1 H), 7.03-6.98 (m, 3 H), 1.81 (s, 3 H). ^{13}C NMR (400 MHz, C_6D_6) δ 190.94, 134.24, 132.01, 131.62, 131.58, 128.91, 128.35, 127.21, 126.96, 124.12, 123.60, 123.28, 122.93, 91.87, 91.01, 90.90, 89.52, 29.55. HRMS calcd for $C_{23}H_{16}SO$: 352.0922. Found 352.0921.

1-Diethyltriazenyl- 4-ethynylphenylbenzene (7) (JMT-I-42). See the general procedure for the Pd/Cu coupling reaction. **6** (2.56 g, 10.0 mmol), phenylacetylene (1.21 mL, 11.0 mmol), bis(dibenzylideneacetone)palladium(0) (0.26 g, 0.280 mmol), copper(I) iodide (0.21 g, 11.0 mmol), triphenylphosphine (0.83 g, 2.75 mmol), and diisopropylethylamine (7.65 mL, 44.0 mmol) were reacted in THF (10 mL) at room temperature for 2 d and 70 °C for 3 d. An additional portion of phenylacetylene (0.60 mL, 5.5 mmol) was added and the mixture was stirred at 70 °C for 1 d. The crude product was purified by flash chromatography on silica gel (hexane-ether 19:1) to afford desired product (2.64 g, 95%) as a yellow oil. FTIR (neat) 2976, 2359, 2213, 1594, 1393, 1237, 1201, 1162, 1097, 841, 756, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.51 (dd, *J* = 7.7, 1.7 Hz, 2 H), 7.48 (dt, *J* = 8.5, 1.6 Hz, 2 H), 7.38 (dt, *J* = 8.5, 1.6 Hz, 2 H), 7.36-7.26 (m, 3 H), 3.76 (q, *J* = 7.2 Hz, 2 H), 1.26 (br t, 3 H). ^{13}C NMR ($CDCl_3$) δ 151.1, 132.3, 131.5, 128.3, 128.0, 123.6, 120.4, 119.4, 90.1, 89.1. (Two carbons are missing due to the quadropolar effect of nitrogen.) HRMS calcd for $C_{18}H_{19}N_3$: 277.1579. Found: 277.1582.

Bis(3,5-diiodophenyl)methane (JMT-II-7). To a solution of bis(3,5-dibromophenyl)methane (484 mg, 1.0 mmol) in dry THF (1.0 mL) was added under nitrogen at -78 °C *n*-butyllithium (1.58 M in hexane, 3.2 mL, 5.0 mmol). The solution was stirred at -78 °C for 1 h. After chlorotrimethylsilane (1.27 mL, 10.0 mmol) was added, the solution was stirred at -78 °C for 30 min and at room temperature overnight. The solution was poured into water and extracted with ether. The extract was dried over magnesium sulfate. After filtration, the solvent was evaporated in vacuo to afford a brown oil. The oil was separated by flash chromatography on silica gel (hexane-ethyl acetate 19:1) to afford bis(3,5-bistrimethylsilylphenyl)methane (377 mg) as a yellow oil. The oil contained a small amount of impurity but it was used for next reaction without further purification. To a solution of bis(3,5-bistrimethylsilylphenyl)methane (332 mg, 0.73 mmol) in carbon tetrachloride (10 mL) was added at room temperature iodine monochloride (0.16 mL, 3.2 mmol) in carbon tetrachloride (5.0 mL). The solution was stirred at room temperature for 1 h and poured into an aqueous solution of sodium thiosulfate. The aqueous solution was extracted with dichloromethane. The solution was dried over magnesium sulfate. After filtration, the solvent was evaporated in vacuo to afford a brown oil. The oil was washed with a small amount of dichloromethane to afford the desired product (209 mg, 36%) as a white solid. Mp 219-221 °C. FTIR (KBr) 1560, 1542, 1412, 1384, 712 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.91 (s, 2 H), 7.42 (t, *J* = 1.5 Hz, 4 H), 7.42 (d, *J* = 1.5, 4 H), 3.71 (s, 2 H). ^{13}C NMR ($CDCl_3$) δ 143.6, 137.1, 94.8, 39.8. HRMS calcd for $C_{13}H_8I_4$: 671.6805. Found: 671.6802.