Chem. *Eur*. *J*. **2001**

Supporting Information

Synthesis and Testing of Molecular Wires and Devices

James M. Tour,* Adam M. Rawlett, Masatoshi Kozaki, Yuxing Yao, Raymond C. Jagessar, Shawn M. Dirk, David W. Price, Mark A. Reed,* Chong-Wu Zhou, Jia Chen

Wenyong Wang, Ian Campbell*

1-Bromo-4-(trimethysilylethynyl)benzene.[16] See the general procedure for the Pd/Cu coupling reaction except that amine was added at 0 °C. The compounds used were 1-bromo-4-iodobenzene (2.83 g, 10.0 mmol), trimethylsilylacetylene (1.47 mL, 10.4 mmol), bis(triphenylphosphine)palladium(II) chloride (0.21 g, 0.30 mmol), copper(I) iodide (0.11 g, 0.60 mmol), benzene (13 mL), and triethylamine (5.6 mL, 40 mmol). The mixture was stirred at room temperature for 10 h. Flash chromatography (silica gel, hexane) afforded 2.37 g (95 %) of the title compound as a yellow oil with slight impurities. The compound was used for the next step without further purification. Spectral data were identical to that reported earlier.[16]

1-Ethynylphenyl-4-(trimethylsilylethynyl)benzene (2). See the general procedure for the Pd/Cu coupling reaction. The compounds used were copper(I) iodide (78 mg, 0.41 mmol), bis(triphenylphosphine)palladium(II) chloride (0.14 g, 0.20 mmol), 1-bromo-4-(trimethysilylethynyl)benzene (1.0 g, 4.0 mmol), phenylacetylene (0.60 mL, 5.5 mmol), triethylamine (2.0 mL, 14 mmol), and benzene (2 mL) at 80 ºC overnight. The resulting brown solid was eluted 2× through a 4 × 20-cm column of silica gel using hexanes as the eluent. The product was obtained as a crystalline white solid (1.08 g, 99 %). TLC R_f=0.28 (hexanes). IR (KBr) 3053, 2957, 2897, 2153, 1602, 1509, 1441, 1406, 1249, 866, 844, 757, 692, 628, 550, 529 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.512 (m, 2 H), 7.441 (m, 4 H), 7.336 (m, 3 H), 0.253 (s, 9 H), ^{13}C NMR ($CDCl_3$) δ 131.87, 131.60, 131.37, 128.45, 128.36, 123.34, 122.99, 122.89, 104.64, 96.21, 91.28, 89.01, -0.07. LRMS calcd for $C_{19}H_{18}Si$: 274 m/e. Found 274 (M^+), 259 [$(M-CH_3)^+$], 202 [$(M-C_3H_{10}Si)^+$].

1-Ethynyl-4-(ethynylphenyl)benzene. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were **2** (0.94 g, 3.4 mmol), K_2CO_3 (1.9 g, 14 mmol), methanol (2.5 mL), and methylene chloride (4 mL). The product was obtained as a pale yellow solid (0.63 g, 91 %). IR (KBr) 3278, 3079, 3062, 3053, 3033, 3017, 1602, 1500, 1440, 1406, 1265, 1249, 1181, 1111, 1101, 1070, 1025, 922, 842, 834, 759, 690, 666, 629, 548, 527, 460 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.515 (m, 2 H), 7.462 (m, 4 H), 7.341 (m, 3 H), 3.159 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 132.06, 131.64, 131.46, 128.52, 128.38, 123.79, 122.94, 121.86, 91.36, 88.82, 83.28, 78.85. LRMS calcd for $C_{16}H_{10}$: 202 m/e. Found 202 (M^+), 176 [$(M-C_2H_2)^+$], 150 [$(M-2C_2H_2)^+$], 101 [$(M-C_8H_5)^+$].

4,4′-Di(ethynylphenyl)-1-(thioacetyl)benzene (4). 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). 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 ºC for 3 d. An additional portion of phenylacetylene (0.60 mL, 5.5 mmol) was added and the mixture was stirred at 70 ºC 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.

1-(Ethynylphenyl)-4-iodobenzene (8). See the general procedure for the iodination of triazenes. **7** (2.51 g, 9.06 mmol) was stirred in iodomethane (10 mL) to afford **8** (2.46 g, 90%) as a white solid. The solid was recrystallized from ethanol to afford purified product (2.06 g, 75%) as white crystals. Mp 104-105 ºC. FTIR (KBr) 1493, 1385, 1004, 821, 758, 750, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.67 (dt, *J* = 8.5, 1.9 Hz, 2 H), 7.52-7.47 (m, 2 H), 7.36-7.30 (m, 3 H), 7.23 (dt, *J* = 8.5, 1.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 137.5, 133.1, 131.6, 128.5, 128.4, 122.9, 122.8, 94.1, 90.8, 88.5. HRMS calcd for $C_{14}H_9I$: 303.9749. Found: 303.9738.

11. See the general procedure for the Pd/Cu coupling reaction. **10**[20] (528 mg, 3.0 mmol), **9**[16] (990 mg, 3.3 mmol), bis(dibenzylideneacetone)palladium(0) (73 mg, 0.080 mmol), copper(I) iodide (63 mg, 0.33 mmol), triphenylphosphine (256 mg, 0.85 mmol), and diisopropylethylamine (2.29 mL, 13.2 mmol) were reacted in THF (10 mL) at room temperature for 2.5 d. The crude product was purified by flash chromatography on silica gel (hexane-dichloromethane 7:3) to afford desired product (841 mg, 81%) as a white solid. Mp 114 ºC. FTIR (KBr) 2150, 1694, 1504, 1384, 1248, 841 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2 H), 7.43 (s, 4 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 2.42 (s, 3 H), 0.24 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 193.2, 134.2, 132.2, 131.9, 131.5, 128.4, 124.2, 123.2, 123.0, 104.6, 96.5, 90.7, 90.5, 30.3, –0.1. HRMS calcd for $C_{21}H_{20}OSSi$: 348.1004. Found: 348.1004.

12. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. **11** (230 mg, 0.65 mmol) was desilylated with TBAF (1.0 M solution in THF, 0.72 mL, 0.72 mmol) and 48% hydrofluoric acid (0.045 mL, 1.40 mmol) in pyridine (4.0 mL) for 10 min according to Method B. The crude product was purified by flash chromatography on silica gel (hexane-ethyl acetate 9:1) to afford desired product (157 mg, 88%) as a pale yellow solid. Mp 113-115 ºC. FTIR (KBr) 3272, 1670, 1508, 1384, 1125, 833 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.53 (dt, *J* = 8.5, 1.9 Hz, 2 H), 7.46 (s, 4 H), 7.38 (dt, *J* = 8.5, 1.9 Hz, 1 H), 3.17 (s, 1 H), 2.42 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 193.4, 134.2, 132.2, 132.1, 131.5, 128.4, 124.2, 123.4, 122.2, 90.5, 90.4, 83.2, 79.1, 30.3. HRMS calcd for $C_{18}H_{12}OS$: 276.0609. Found: 276.0615.

14. See the general procedure for the Pd/Cu coupling reaction. **12** (319 mg, 0.43 mmol), **13**[20] (144 mg, 0.52 mmol), bis(dibenzylideneacetone)palladium(0) (13 mg, 0.023 mmol), copper(I) iodide (8 mg, 0.042 mmol), triphenylphosphine (33 mg, 0.11 mmol), and diisopropylethylamine (0.30 mL, 1.73 mmol) were stirred in THF (2.0 mL) at room temperature for 2 d. An additional portion of bis(dibenzylideneacetone)palladium(0) (13 mg, 0.023 mmol), copper(I) iodide (8 mg, 0.042 mmol) and triphenylphosphine (33 mg, 0.11 mmol) were then added. The mixture was stirred at room temperature another 2.5 d. The crude product was purified by flash chromatography on silica gel (hexane-ethyl acetate 8:2) to afford titled compound (307 mg, 81%) as a yellow solid. Mp 98-101 °C. FTIR (KBr) 2922, 2852, 2150, 1700, 1511, 1249, 1119, 862, 839 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.54 (dt, *J* = 8.4, 1.6 Hz, 2 H), 7.50 (s, 4 H), 7.45 (d, *J* = 7.9 Hz, 1 H), 7.42-7.37 (m, 4 H), 7.32 (dd, *J* = 7.9, 1.6, Hz, 1 H), 7.32 (d, *J* = 1.5 Hz, 1 H), 7.26 (dd, *J* = 7.9, 1.5 Hz, 1 H), 2.82 (t, *J* = 7.8, 2 H), 2.75 (t, *J* = 7.8, 2 H), 2.42 (s, 3 H), 1.70 (pent, *J* = 7.9 Hz, 2 H), 1.64 (pent, *J* = 8.0 Hz, 2 H), 1.45-1.13 (m, 36 H), 0.86 (t, *J* = 6.5 Hz, 6 H), 0.25 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 193.3, 145.7, 145.2, 134.2, 132.4, 132.2, 132.1, 131.9, 131.7, 131.6, 128.9, 128.6, 128.3, 124.3, 123.3, 123.3, 122.8, 122.8, 122.6, 103.6, 99.7, 94.7, 91.5, 90.8, 90.6, 90.5, 89.5, 34.7, 34.6, 32.0, 30.6, 30.6, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 22.7, 14.2, –0.01. HRMS calcd for $C_{61}H_{76}OSSi$: 884.5386. Found: 884.5386.

15. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. **14** (119 mg, 0.13 mmol) was desilylated with TBAF (1.0 M solution in THF, 0.14 mL, 0.14 mmol) and 48% hydrofluoric acid (0.009 mL, 0.29 mmol) in pyridine (1.5 mL) for 10 min according to Method B described above. The crude product was purified by flash chromatography on silica gel (hexane-ethyl acetate 19:1) to afford desired product (83 mg, 79%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.54 (dt, *J* = 8.4, 1.9 Hz, 2 H), 7.50 (s, 4 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.39 (d, *J* = 1.6 Hz, 1 H), 7.39 (dt, *J* = 8.4, 1.9 Hz, 1 H), 7.34 (br s, 1 H), 7.33 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.27 (dd, *J* = 8.0, 1.6 Hz, 1 H), 3.32 (s, 1 H), 2.82 (t, *J* = 7.4 Hz, 2 H), 2.77 (t, *J* = 7.6 Hz, 2 H), 2.43 (s, 3 H), 1.69 (pent, *J* = 7.4 Hz, 2 H), 1.64 (pent, *J* = 7.6 Hz, 2 H), 1.46-1.14 (m, 36 H), 0.86 (t, *J* = 6.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$) δ 193.3, 145.7, 145.2, 134.2, 132.9, 132.2, 132.1, 131.9, 131.6, 131.6, 128.9, 128.6, 128.3, 124.3, 123.6, 123.3, 122.9, 122.8, 122.7, 121.6, 94.4, 91.5, 90.7, 90.6, 90.5, 89.6, 82.1, 34.6, 34.3, 31.9, 31.6, 30.6, 30.5, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 22.7, 14.1. LRMS calcd for $C_{58}H_{68}OS$: 812. Found: 812. (This compound is too unstable to afford a HRMS.)

16. See the general procedure for the Pd/Cu coupling reaction. **15** (464 mg, 0.57 mmol), **8** (207 mg, 0.68 mmol), bis(dibenzylideneacetone)palladium(0) (17 mg, 0.029 mmol), copper(I) iodide (11 mg, 0.057 mmol), triphenylphosphine (38 mg, 0.145 mmol), and diisopropylethylamine (0.47 mL, 2.72 mmol) were stirred in THF (2.0 mL) at room temperature for 2 d. More bis(dibenzylideneacetone)palladium(0) (17 mg, 0.029 mmol), copper(I) iodide (11 mg, 0.057 mmol) and triphenylphosphine (38 mg, 0.145 mmol) were then added. The mixture was stirred at room temperature another 4 d. The crude product was purified by a recrystallization from hexane to afford desired product (369 mg, 66%) as a yellow solid. Mp 124-125 °C. FTIR (KBr) 2922, 1709, 1511, 1384, 836 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.57-7.43 (m, 13 H), 7.42-7.30 (m, 10 H), 2.84 (t, *J* = 7.4 Hz, 4 H), 2.42 (s, 3 H), 1.70 (p, *J* = 7.4 Hz, 4 H), 1.47-1.14 (m, 36 H), 0.90-0.78 (m, 6 H). ^{13}C NMR ($CDCl_3$) δ 193.3, 145.2, 137.5, 134.2, 133.1, 132.2, 131.9, 131.8, 131.7, 131.6, 131.6, 131.4, 129.0, 128.8, 128.4, 128.4, 124.3, 123.3, 123.3, 123.2, 123.1, 122.9, 122.8, 122.8, 122.5, 94.8, 94.4, 91.6, 91.4, 90.8, 90.6, 90.1, 89.7, 89.2, 34.7, 32.0, 30.6, 30.3, 29.8, 29.7, 29.7, 29.6, 29.4, 22.8, 14.2. HRMS calcd for $C_{72}H_{76}OS$: 988.5613. Found: 988.5630.

4-Bromo-(4′-ethyl)biphenyl (18). To a solution of 4,4'-dibromobiphenyl **(17)** (6.24 g, 20.0 mmol) in THF (100 mL) at -78 °C was added *n*-BuLi (12.4 mL, 20.0 mmol, 1.61 M in hexane) dropwise. The yellow slurry was stirred for 1 h and iodoethane was added. The mixture was allowed to warm to room temperature and stirred for 20 h. The mixture was poured into water. The organic layer was separated and washed with water (2×) and brine (1×). The combined aqueous solution was extracted with ether (2×). The combined organic fractions were dried over magnesium sulfate. Removal of solvent followed by flash chromatography (silica gel, hexane) gave desired product as a white solid (4.70 g, 90%). FTIR (neat) 2964, 2923, 2872, 1482, 1390, 1267, 1133, 1072, 1000, 815, 739 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.5 Hz, 2 H), 7.26 (d, *J* = 8.8 Hz, 2 H), 2.68 (q, *J* = 7.6 Hz, 2 H), 1.26 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.92, 140.14, 137.40, 131.89, 128.63, 128.51, 126.93, 121.28, 28.62, 15.65. HRMS calcd for $C_{14}H_{13}Br$: 260.0201. Found: 260.0204.

4-Ethyl-4′-thioacetylbiphenyl (19). See the general procedure for the conversion of aryl halide to arylthioacetate. The compounds used were **18** (0.784 g, 3.00 mmol) in ether (10 mL), *tert*-BuLi (2.6 mL, 6.0 mmol, 2.30 M in pentane) in ether (10 mL), sulfur powder (0.16 g, 5.0 mmol) in ether (5 mL), and acetyl chloride (0.43 mL, 6.0 mmol). Gravity chromatography (silica gel, hexane/ether 9/1) afforded desired material as a white solid (0.21

g, 27%). Mp 84-86 °C. FTIR (neat) 2964, 2923, 2872, 1703, 1482, 1395, 1354, 1123, 1097, 1005, 954, 815 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 7.44 (d, *J* = 8.1 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 2.68 (q, *J* = 7.6 Hz, 2 H), 2.43 (s, 3 H), 1.26 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.30, 144.04, 142.40, 137.54, 134.77, 128.43, 127.80, 127.15, 126.39, 30.24, 28.57, 15.57. HRMS calcd for $C_{16}H_{16}OS$: 256.0922. Found: 256.0918.

4-Bromo-(4′-propyl)biphenyl (20). To a solution of **17** (9.36 g, 30.0 mmol) in THF (150 mL) at -78 °C was added *n*-BuLi (18.8 mL, 30.0 mmol, 1.60 M in hexane) dropwise. The yellow slurry was stirred for 1.5 h and iodopropane was added. The mixture was allowed to warm to room temperature and stirred for 5 h. The mixture was poured into water and extracted with ether (2×). The organic fractions were dried over magnesium sulfate. Removal of solvent followed by flash chromatography (silica gel, hexane) gave product as a white solid (7.80 g, 94%). Mp 103-104 °C. FTIR (KBr) 2954, 2933, 2872, 1482, 1462, 1390, 1262, 1133, 1077, 1005, 826, 800, 739 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 7.9 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.1 Hz, 2 H), 2.62 (t, *J* = 7.6 Hz, 2 H), 1.67 (sext, *J* = 7.5 Hz, 2 H), 0.96 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.37, 140.13, 137.38, 131.86, 129.09, 128.62, 126.81, 121.24, 37.76, 24.61, 13.96. HRMS calcd for $C_{15}H_{15}Br$: 274.0357. Found: 274.0350.

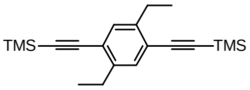
4-Allyl-4′-(propyl)biphenyl (21). A mixture of **20** (3.96 g, 14.4 mmol), tributylallyltin (4.97 g, 15.0 mmol), $Pd(dba)_2$ (0.248 g, 0.432 mmol), PPh_3 (0.453 g, 1.73 mmol), and BHT (four crystals) in toluene (20 mL) was heated to reflux for 21 h. The mixture was cooled to room temperature, filtered and concentrated in vacuo. The residue was diluted with ether and aqueous potassium fluoride (8 mL, 3 M) was added. The mixture was stirred for 15 min and filtered through a pad of celite. The filtrate was washed with water (2×) and dried over magnesium sulfate. Removal of solvent in vacuo followed by flash chromatography (silica gel, hexane) gave product as a white solid (2.55 g, 75 %). Mp 44-46 °C. FTIR (KBr) 3077, 3026, 2964, 2923, 2872, 1641, 1497, 1456, 1431, 1400, 1267, 1118, 1005, 995, 913, 831, 795, 739 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 6.07-5.94 (ddt, *J* = 17.0, 8.2, 6.7 Hz, , 1 H), 5.12 (dd, *J* = 17.0, 1.5 Hz, 1 H), 5.09 (dd, *J* = 8.2, 1.3 Hz, 1 H), 3.42 (d, *J* = 6.7 Hz, 2 H), 2.62 (t, *J* = 7.6 Hz, 2 H), 1.67 (sext, *J* = 7.5 Hz, 2 H), 0.97 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.85, 139.37, 139.09, 138.77, 137.74, 129.33, 129.23, 127.35, 127.19, 116.22, 40.26, 38.09, 24.96, 14.30. HRMS calcd for $C_{18}H_{20}$: 236.1565. Found: 236.1564.

1-(4′-Propylbiphenyl)-3-thioacetylpropane. A mixture of **21** (0.90 g, 3.8 mmol), thioacetic acid (0.44 mL, 6.0 mmol) and AIBN (0.005 g) in benzene (5 mL) was heated to reflux overnight.[22] After cooling to room temperature, the mixture was poured into water, extracted with ether (2×) and the extracts were dried over magnesium sulfate. Removal of solvent followed by flash chromatography (silica gel, hexane/ether = 20/1) gave the title compound as a white solid (0.75 g, 63%). FTIR (KBr) 2954, 2933, 2862, 1677, 1497, 1451, 1421, 1400, 1354, 1144, 1118, 954, 831, 790, 636 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.3 Hz, 2 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 2.91 (t, *J* = 7.3 Hz, 2 H), 2.71 (t, *J* = 7.6 Hz, 2 H), 2.61 (t, *J* = 7.6 Hz, 2 H), 2.33 (s, 3 H), 1.92 (p, *J* = 7.5 Hz, 2 H), 1.67 (sext, *J* = 7.4 Hz, 2 H), 0.96 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.55, 141.46, 139.75, 138.79, 138.20, 128.71, 128.67, 126.85, 126.66, 37.72, 34.50, 31.15, 30.71, 28.66, 24.62, 13.98. HRMS calcd for $C_{20}H_{24}OS$: 312.1548. Found: 312.1539.

1-(4′-Propylbiphenyl)-3-propanethiol (22). To a solution of 1-(4′-propylbiphenyl)-3-thioacetylpropane (0.50 g, 1.6 mmol) in ethanol (4 mL) was added water (4 mL) and potassium hydroxide (0.45 g, 8.0 mmol). The mixture was heated to reflux for 15 min. The mixture was cooled to room temperature. The solution was acidified with 3 N HCl and extracted with ether (3×). The extracts were dried over magnesium sulfate. Removal of solvent in vacuo followed by flash chromatography (silica gel, hexane) gave desired product as a white solid (0.31 g, 72%). Mp 32-33 °C. FTIR (KBr) 3026, 2954, 2923, 2862, 1497, 1456, 1400, 1374, 1344, 1292, 1256, 1185, 1118, 1005, 800, 739 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.1 Hz, 2 H), 7.23 (d, *J* = 8.5 Hz, 4 H), 2.75 (t, *J* = 7.5 Hz, 2 H), 2.61 (t, *J* = 7.6 Hz, 2 H), 2.56 (q, *J* = 7.4 Hz, 2 H), 1.96 (p, *J* = 7.3 Hz, 2 H), 1.67 (sext, *J* = 7.5 Hz, 2 H), 1.37 (t, *J* = 7.8 Hz, 2 H), 0.96 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.69, 140.10, 138.98, 138.41, 128.92, 128.91, 127.04, 126.86, 37.76, 35.51, 34.04, 24.63, 24.09, 13.98. HRMS calcd for $C_{18}H_{22}S$: 270.1442. Found: 270.1437.

24. See the general procedure for the Pd/Cu coupling reaction. The compounds used were 1,4-diiodobenzene (0.165 g, 0.500 mmol), **9**[16] (0.247 g, 1.40 mmol), Pd(dba)$_2$ (0.029 g, 0.05 mmol), copper(I) iodide (0.019 g, 0.10 mmol), PPh_3 (0.052 g, 0.20 mmol), THF (13 mL), and diisopropylethylamine (0.70 mL, 4.0 mmol). Flash chromatography (silica gel, hexane, then hexane/CH_2Cl_2 1/1) afforded desired product as a light brown solid (0.20 g, 94%). Mp 199-120 °C. FTIR (KBr) 1692, 1590, 1513, 1385, 1354, 1118, 1092, 1010, 964, 826, 621 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.5 Hz, 4 H), 7.50 (s, 4 H), 7.39 (d, *J* = 8.5, 4 H), 2.43 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.40, 134.22, 132.16, 131.62, 128.30, 124.21, 122.99, 90.65, 90.57, 30.29. HRMS calcd for $C_{26}H_{18}O_2S_2$: 426.0748. Found: 426.0740.

1,4-Diethyl-2,5-diiodobenzene. A mixture of 1,4-diethylbenzene (2.43 g, 18.1 mmol), iodine (6.13 g, 24.1 mmol), periodic acid (2.74 g, 12.0 mmol), acetic acid (12 mL) water (2.4 mL) and concentrated sulfuric acid (0.4 mL) was heated to 95 °C for 1 d. The mixture was cooled to room temperature and poured into water. The mixture was neutralized carefully with saturated aqueous sodium bicarbonate. The precipitate was collected by filtration and re-dissolved in ether. The ether solution was washed with aqueous sodium thiosulfate (1×), water (1×), brine (1×) and dried over magnesium sulfate. After filtration, removal of solvent in vacuo gave the title compound as a white solid (6.92 g, 99%). Mp 68-69 °C. FTIR (neat) 2964, 2933, 2862, 1462, 1380, 1349, 1318, 1046, 1036, 980, 882, 713, 667 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 2 H), 2.62 (q, J = 7.5 Hz, 4 H), 1.16 (t, J= 7.5 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.93, 138.70, 100.52, 33.26, 14.61.

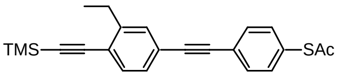


1,4-Diethyl-2,5-bis(trimethysilylethynyl)benzene. See the general procedure for the Pd/Cu coupling reaction. The compounds used were 1,4-diethyl-2,5-diiodobenzene (3.86 g, 10.0 mmol), trimethylsilylacetylene (3.53 mL, 25.0 mmol), bis(triphenylphosphine)palladium(II) chloride(0.35 g, 0.50 mmol), copper(I) iodide (0.19 g, 1.0 mmol), diisopropylethylamine (7 mL, 40 mmol), and THF (10 mL). Flash chromatography (silica gel, hexane) gave the title compound as yellow crystals (2.73 g, 84%). FTIR (neat) 2964, 2872, 2154, 1487, 1456, 1400, 1251, 1195, 1062, 897, 867, 841, 764, 708, 626 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (s, 2 H), 2.73 (q, J = 7.5 Hz, 4 H), 1.21 (t, J = 7.5 Hz, 6 H), 0.25 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.82, 131.76, 122.50, 103.78, 99.12, 27.10, 14.50, -0.02.

1,4-Diethyl-2,5-(diethynyl)benzene (26). See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were 1,4-diethyl-2,5-bis(trimethysilylethynyl)benzene (2.52 g, 7.70 mmol) and potassium carbonate (6.40 g, 46.2 mmol) in methanol (50 mL) for 1 d to afford titled compound as a yellow oil (1.29 g, 92%). FTIR (neat) 3290, 2971, 2933, 2875, 1491, 1457, 1239, 1061, 896 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 3.29 (s, 2 H), 2.75 (q, J = 7.6 Hz, 4 H), 1.22 (t, J = 7.6 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.99, 132.27, 121.88, 82.10, 81.68, 26.89, 14.63. HRMS calcd for $C_{14}H_{14}$: 182.1096. Found: 182.1088.

27. See the general procedure for the Pd/Cu coupling reaction. The compounds used were **26** (0.624 g, 3.42 mmol), **3** (1.95 g, 7.00 mmol), di(benzylidineacetone)palladium(0) (0.20 g, 0.35 mmol), triphenylphosphine (0.37 g, 1.4 mmol), copper(I) iodide (0.13 g, 0.70 mmol), diisopropylethylamine (4.9 mL, 28 mmol) and THF (10 mL). Flash chromatography (silica gel, hexane/CH_2Cl_2/ether = 12/6/1) gave desired product as a light yellow crystalline solid (1.19 g, 72%). Mp 154-158 °C. FTIR (neat) 2954, 2933, 2872, 1692, 1590, 1497, 1395, 1123, 949, 887, 826 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 4 H), 7.39 (d, J = 8.4 Hz, 4 H), 7.38 (s, 2 H), 2.83 (q, J = 7.5 Hz, 4 H), 2.42 (s, 6 H), 1.29 (t, J = 7.5 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.42, 143.66, 134.29, 132.08, 131.69, 128.11, 124.68, 122.42, 93.44, 89.88, 30.30, 27.20, 14.73. HRMS calcd for $C_{30}H_{26}O_2S_2$: 482.1374. Found: 482.1373.

28. To **27** (0.15 g, 0.31 mmol) and sodium hydroxide (0.740 g, 18.5 mmol) was added THF (20 mL) and water (4 mL). The mixture was stirred for 12 h. The solvent was decanted and the precipitate was washed with ether (5×). The solid was suspended in ether and acidified with 3 N HCl (10 mL). The organic layer was separated and washed with water (1×), brine (1×) and dried over magnesium sulfate. Removal of solvent in vacuo gave desired product as a yellow solid (0.11 g, 89%). FTIR (KBr) 2964, 2933, 2872, 2359, 2339, 1590, 1497, 1456, 1400, 1097, 1015, 897, 821 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.2 Hz, 4 H), 7.35 (s, 2 H), 7.23 (d, J = 8.4 Hz, 4 H), 3.52 (s, 2 H), 2.82 (q, J = 7.5 Hz, 4 H), 1.28 (t, J = 7.5 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.28, 132.94, 132.73, 132.42, 129.91, 123.33, 121.55, 94.59, 89.66, 28.27, 15.82. HRMS calcd for $C_{26}H_{22}S_2$: 398.1163. Found: 398.1167.



4-Ethynylphenyl-3′-ethyl-4′-trimethylsilylethynyl-1-thioacetylbenzene. See the general procedure for the Pd/Cu coupling reaction. **29**[20] (3.28 g, 10.0 mmol), **9**[16] (2.23 g, 12.7 mmol), bis(dibenzylideneacetone)palladium(0) (288 mg, 0.50 mmol), copper(I) iodide (0.190 g, 0.042 mmol), triphenylphosphine (655 mg, 2.50 mmol), and diisopropylethylamine (7.0 mL, 40.0 mmol) were stirred in THF (20.0 mL) at room temperature for 1 d. The crude product was purified by flash chromatography on silica gel (hexane-ethyl acetate 19:1) to afford desired product (3.00 g, 80%) as an orange oil. FTIR 2965, 2152, 1713, 1601, 1495, 1250, 1114, 864 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.52 (dt, J = 8.2, 1.6 Hz, 2 H), 7.39 (d, J = 7.8 Hz, 1 H), 7.38 (dt, J = 8.2, 1.6 Hz, 2 H), 7.35 (d, J = 1.4 Hz, 1 H), 7.27 (dd, J = 7.8, 1.4 Hz, 1 H), 2.78 (q, J = 7.6 Hz, 2 H), 2.42 (s, 3 H), 1.24 (t, J = 7.6 Hz, 3 H), 0.24 (s, 9 H). ^{13}C NMR ($CDCl_3$)

δ 193.3, 146.8, 134.2, 132.4, 132.2, 131.1, 128.8, 128.2, 124.4, 123.0, 122.6, 103.4, 100.0, 91. 1, 90.0, 30.3, 27.6, 14.4, 0.0. HRMS calcd for $C_{23}H_{24}OSSi$: 376.1317. Found: 376.1308.

30. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were (**31**) (940 mg, 2.5 mmol), pyridine (5.0 mL), concentrated hydrofluoric acid (48% in water, 0.18 mL, 5.60 mmol) and TBAF (1.0 M in THF, 2.75 mL, 2.75 mmol) at room temperature for 10 min. The crude product was then purified by flash column chromatography on silica gel (hexane-ether 19:1) to afford desired product (629 mg, 83%). Mp 97-98°C. FTIR (KBr) 3255, 2966, 1702, 1491, 1123, 956, 825 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ7.53 (dt, J = 8.4, 1.9 Hz, 2 H), 7.43 (d, J = 7.9 Hz, 1 H), 7.38 (dt, J = 8.4, 1.9 Hz, 2 H), 7.38 (d, J = 1.6 Hz, 1 H), 7.30 (dd, J = 7.9, 1.6 Hz, 1 H), 3.33 (s, 1 H), 2.81 (q, J = 7.6 Hz, 2 H), 2.42 (s, 3 H), 1.25 (t, J = 7.6 Hz, 3 H) ^{13}C NMR ($CDCl_3$) δ 193.4, 146.9, 134.2, 132.8, 132.2, 131.1, 128.9, 128.3, 124.3,123.4,

121.9, 90.9, 90.1, 82.4, 81.9, 30.3, 27.4, 14.5. HRMS calcd for $C_{20}H_{16}OS$: 304.0922. Found: 304.0920.

32. See the general procedure for the Pd/Cu coupling reaction. 1,3,5-Triiodobenzene (228 mg, 0.50 mmol), **30** (547 mg, 1.80 mmol), bis(dibenzylideneacetone)palladium(0) (43 mg, 0.075 mmol), copper(I) iodide (29 mg, 0.15 mmol), triphenylphosphine (98 mg, 0.37 mmol), and diisopropylethylamine (1.0 mL, 6.0 mmol) were stirred in THF (5.0 mL) at room temperature for 65 h. The crude product was washed with a small amount of ethyl acetate to afford a pale yellow solid (107 mg). The washings were combined, evaporated to dryness, and purified by a flash chromatography on silica gel (hexane-ethyl acetate 85:15) to afford another 219 mg yielding a total of 326 mg (66%) of titled compound. Mp 87-88 °C. FTIR (KBr) 1700, 1578, 1498, 1384, 1115, 827, 619 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.63 (s, 3 H), 7.55 (dt, *J* = 8.5, 1.9 Hz, 6 H), 7.49 (d, *J* = 7.9 Hz, 3 H), 7.43 (d, *J* = 1.6 Hz, 3 H), 7.39 (dt, *J* = 8.5, 1.9 Hz, 6 H), 7.36 (dd, *J* = 7.9, 1.6 Hz, 3 H), 2.90 (q, *J* = 7.5 Hz, 6 H), 2.43 (s, 9 H), 1.33 (t, *J* = 7.5 Hz, 9 H). ^{13}C NMR ($CDCl_3$) δ 193.4, 146.5, 134.3, 133.9, 132.3, 132.2, 131.2, 129.1, 128.3, 124.3, 124.2, 123.3, 122.1, 93.0, 91.0, 90.3, 89.2, 30.3, 27.7, 14.7. HRMS calcd for $C_{66}H_{48}O_3S_3$: 984.2766. Found: 984.2717.

Bis(4-bromophenyl)methanol (35). To a solution of 1,4-dibromobenzene (5.66 g, 24.0 mmol) in THF (50 mL) at -78 °C was added *n*-BuLi (14.6 mL, 22.0 mmol, 1.51 M in hexane) dropwise. The slurry was stirred for 40 min and added to a solution of 4-bromobenzylaldehyde (3.7 g, 20 mmol) in THF (40 mL) which was cooled at -78 °C. The yellow solution was allowed to warmed to room temperature and stirred for 2 h before pouring into water. The mixture was extracted with ethyl acetate (3×). The combined organic fractions were washed with water (2×) and dried over magnesium sulfate. Removal of solvents in vacuo followed by washing with hexane afforded titled compound as a white solid (5.89 g, 86%). Mp 112-113 °C. FTIR (KBr) 3323, 2903, 1590, 1482, 1400, 1328, 1190, 1113, 1072, 1041, 1010, 862, 810, 795 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 4 H), 7.21 (d, *J* = 8.3 Hz, 4 H), 5.74 (d, *J* = 3.3 Hz, 1 H), 2.21 (d, *J* = 3.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.23, 131.74, 128.21, 121.78, 75.03. HRMS calcd for $C_{13}H_{10}Br_2O$: 339.9098. Found: 339.9084.

Bis(4-bromophenyl)methane (36). To a solution of **35** (1.71 g, 5.00 mmol) in TFA (40 mL) was added sodium borohydride (1.89 g, 50.0 mmol) in small portions at room temperature over 10 min.[24] The resulting white slurry was stirred for 40 min before pouring into water. The suspension was carefully made alkaline with aqueous sodium hydroxide solution. The mixture was extracted with ether (3×). The combined organic fraction was washed with water (2×), brine (1×), and dried over magnesium sulfate. Removal of solvents followed by filtering through a short silica gel column (hexane) afforded desired product as a white solid (1.53 g, 94%). Mp 62-62.5 °C. FTIR (KBr) 2923, 2851, 1482, 1436, 1400, 1200, 1113, 1067, 1010, 856, 805, 780, 621 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 4 H), 7.01 (d, *J* = 8.3 Hz, 4 H), 3.86 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.46, 131.69, 130.64, 120.26, 40.71. HRMS calcd for $C_{13}H_{10}Br_2$: 323.9149. Found: 323.9147.

Bis(4-thioacetylphenyl)methane (37). See the general procedure for the conversion of aryl halides to arylthioacetates. The compounds used were **36** (0.978 g, 3.00 mmol) in THF (15 mL), *tert*-BuLi (8.7 mL, 15 mmol, 1.72 M in pentane) in ether (5 mL), sulfur powder (0.39 g, 12 mmol) in THF (15 mL), and acetyl chloride (1.07 mL, 15.0 mmol). Gravity chromatography (silica gel, hexane/ether 4/1) afforded desired product as a colorless oil (0.764, 81%). Mp 54-55 °C. FTIR (neat) 3395, 3026, 2923, 1703, 1595, 1492, 1431, 1405, 1354, 1118, 1092, 1015, 949, 805, 790, 610 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 4 H), 7.21 (d, *J* = 8.1 Hz, 4 H), 4.00 (s, 2 H), 2.39 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.10, 141.98, 134.70, 129.95, 125.81, 41.37, 30.24. HRMS calcd for $C_{17}H_{16}O_2S_2$: 316.0592. Found: 316.0583.

4′-Bromo-(4″-iodo)diphenylmethanol (38). See the preparation of **34.** The compounds used were 1,4-diiodobenzene (4.29 g, 13.0 mmol) in THF (50 mL), *n*-BuLi (8.0 mL, 12 mmol, 1.51 M in hexane), and 4-bromobenzylaldehyde (1.85 g, 10.0 mmol) in THF (40 mL). After workup, the solvent was removed in vacuo followed by washing with hexane to give desired compound as a white solid (3.53 g, 91%). Mp 119-120 °C. FTIR (KBr) 3333 (broad), 2903, 1590, 1482, 1400, 1328, 1292, 1190, 1113, 1072, 1036, 1005, 862, 831, 810, 790 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.5 Hz, 2 H), 7.20 (d, *J* = 8.7 Hz, 2 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 5.73 (d, *J* = 3.2 Hz, 1 H), 2.20 (d, *J* = 3.5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.92, 142.21, 137.70, 131.75, 128.44, 128.22, 121.79, 93.48, 75.12. HRMS calcd for $C_{13}H_{10}BrIO$: 389.8939. Found: 389.8930.

4′-Bromo-(4″-iodo)diphenylmethane (39). See the preparation of **35**. The compounds used were **38** (1.36 g, 3.50 mmol), sodium borohydride (1.32 g, 35.0 mmol), and TFA (30 mL). Flash chromatography (silica gel, hexane) afforded desired product as white needle-like crystals (1.23 g, 94%). Mp 68-70 °C. FTIR (KBr) 3036, 2923, 2851, 1482, 1436, 1395, 1200, 1108, 1067, 1010, 856, 800, 774 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 3.85 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.15, 139.42, 137.68, 131.71, 131.00, 130.68, 120.28, 91.71, 40.84. HRMS calcd for $C_{13}H_{10}BrI$: 371.9011. Found: 371.8996.

40. See the general procedure for the Pd/Cu coupling reaction. The compounds used were **39** (1.12 g, 3.00 mmol), 1-bromo-4-ethynylbenzene (0.58 g, 3.2 mmol), bis(dibenzylidineacetone)palladium(0) (0.086 g, 0.15 mmol), copper(I) iodide (0.057 g, 0.30 mmol), triphenylphosphine (0.157 g, 0.600 mmol), THF (20 mL), and diisopropylethylamine (2.1 mL, 12 mmol) at room temperature for 2 d. Flash chromatography (silica gel, hexane) afforded desired product as white crystals (1.17 g, 92%). Mp 151-153 °C. FTIR (KBr) 2215, 1508, 1482, 1385, 1067, 1005, 867, 826, 810, 780, 621 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 9.0 Hz, 2 H), 7.40 (d, *J* = 8.7 Hz, 2 H), 7.35 (d, *J* = 8.3 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 3.92 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.10, 139.48, 133.03, 131.85, 131.66, 131.64, 130.70, 129.01, 122.45, 122.31, 120.94, 120.22, 90.43, 88.23, 41.22. HRMS calcd for $C_{21}H_{14}Br_2$: 423.9462. Found: 423.9465.

41. See the general procedure for the conversion of aryl halide to arylthioacetate. The compounds used were **40** (0.852 g, 2.00 mmol) in THF (20 mL), *tert*-BuLi (6.0 mL, 10 mmol, 1.67 M in pentane) in ether (5 mL), sulfur powder (0.257 g, 8.00 mmol) in THF (10 mL), and acetyl chloride (0.71 mL, 10 mmol). Flash chromatography (silica gel, hexane/ether 4/1, then hexane/CH_2Cl_2 1/1) afforded desired product as a white solid (0.724 g, 87%). Mp 99-100 °C. FTIR (KBr) 1697, 1513, 1385, 1354, 1123, 1015, 959, 826, 785, 621 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2 H), 7.45 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.6 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 4.00 (s, 2 H), 2.42 (s, 3 H), 2.40 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.29, 193.51, 142.13, 140.98, 134.65, 134.23, 132.17, 131.93, 129.83, 129.15, 127.95, 125.66, 124.64, 120.93, 91.03, 88.52, 41.55, 30.30, 30.19. HRMS calcd for $C_{25}H_{20}O_2S_2$: 416.0905. Found: 416.0919.

Bis(4-diethyltriazenylphenyl)methane (43). To 4,4'-methylenedianiline (**42**) (19.83 g, 100 mmol) in water (80 mL) and concentrated hydrochloric acid (30 mL) was added sodium nitrite (15.18 g, 220 mmol) in water (120 mL) at 0 ºC. The reaction was stirred at 0 ºC for 30 min and then poured into a solution of potassium carbonate (165.85 g, 1200 mmol) and diethylamine (22.76 mL, 220 mmol) in water (500 mL) at 0 ºC. The reaction was stirred for 30 min at 0 ºC and then poured into water. The aqueous layer was extracted with diethyl ether (3 × 25 mL) and the organic layer was dried over magnesium sulfate and the product concentrated in vacuo to afford 17.30 g (47%) of the title compound as a viscous brown liquid. IR (neat) 3083, 3024, 2931, 1905, 1601, 1502, 1090, 1014, 854, 821, 787, 736, 700, 624 cm^{-1}. ^1H NMR (400 MHz, $CDC1_3$) δ 7.31 (d, *J* = 8.3 Hz, 4 H), 7.12 (d, *J* = 8.4 Hz, 4 H), 3.94 (s, 2 H), 3.72 (q, *J* = 7.2 Hz, 8 H), 1.23 (t, *J* = 7.1 Hz, 12 H). ^{13}C NMR (125 MHz, $CDC1_3$) δ 150.03, 138.76, 129.85, 120.98, 54.03, 41.60, 13.48.

Bis(4-iodophenyl)methane (44). See the general procedure for the iodination of triazenes. The title compound was prepared as above from **43** (9.15 g, 25 mmol) and iodomethane (25 mL) to yield 6.36 g (61%) of the title compound as a fluffy white solid. IR (KBr) 3025, 2919, 2848, 1898, 1477, 1394, 1196, 1105, 1056, 1003, 854, 798, 772, 617 cm^{-1}. ^{1}H NMR (400 MHz, $CDC1_3$) δ 7.58 (d, *J* = 8.3 Hz, 4 H), 6.88 (d, *J* = 8.4 Hz, 4 H), 3.83 (s, 2 H). ^{13}C NMR (100 MHz, $CDC1_3$) δ 140.15, 137.76, 131.15, 92.04, 41.07. LRMS calcd for $C_{13}H_{10}I_2$: 420. Found: 420.

45. See the general procedure for the Pd/Cu coupling reaction. **44** (84 mg, 0.20 mmol), **9**[16] (84 mg, 0.48 mmol), bis(dibenzylideneacetone)palladium(0) (12 mg, 0.021 mmol), copper(I) iodide (8 mg, 0.042 mmol), triphenylphosphine (30 mg, 0.10 mmol), and diisopropylethylamine (0.33 mL, 1.92 mmol) were stirred in THF (2.0 mL) at room temperature for 80 h. The crude product was purified by flash chromatography on silica gel (hexane-ethyl acetate 9:1) to afford titled compound (73 mg, 71%) as a yellow solid. Mp 173-174 °C. FTIR (KBr) 1701, 1508, 1385, 1118, 828 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.52 (dt, *J* = 8.3, 1.8 Hz, 4 H), 7.44 (d, *J* = 8.2 Hz, 4 H), 7.37 (dt, *J* = 8.3, 1.8 Hz, 4 H), 7.15 (d, *J* = 8.2 Hz, 4 H), 3.98 (s, 2 H), 2.41 (s, 6 H). ^{13}C NMR ($CDCl_3$) δ 193.5, 141.2, 134.2, 132.1, 131.9, 129.0, 127.9, 124.6, 120.9, 91.0, 88.5, 41.7, 30.3. HRMS calcd for $C_{33}H_{24}O_2S_2$: 516.1218. Found: 516.1207.

46. To a solution of 1,4-diiodobenzene (726 mg, 2.2 mmol) in dry THF (10 mL) was at -78 °C *n*-butyllithium (1.53 M in hexane, 1.37 mL, 2.1 mmol). The yellow suspension was stirred at -78 °C for 30 min and terephthaldehyde (134 mg, 1.0 mmol) in dry THF (5.0 mL) was added. After stirring at room temperature for 30 min, the suspension was poured into water. The solution was extracted with ether and dried over magnesium sulfate. After filtration, the solvent was evaporated in vacuo to afford a colorless oil. The oil was separated by flash chromatography on silica gel (hexane-ethyl acetate 7:3) to afford the desired product as a white solid (317 mg, 59%). The product was a 1:1 mixture of diastereomers. Mp 160-164 °C. FTIR (KBr) 3355, 1482, 1397, 1192, 1038, 1006, 799, 774 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 4 H), 7.29 (s, 4 H), 7.09 (d, *J* = 8.4 Hz, 4 H), 5.75 (s, 1 H), 5.74 (s, 1 H), 2.16 (s, 1 H), 2.15 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 143.2, 143.0, 137.6, 128.4, 126.8, 93.1, 75.4. HRMS calcd for $C_{20}H_{16}O_2I_2$: 541.9240. Found: 541.9216.

47. To trifluoroacetic acid (20 mL) was added under nitrogen at 0 ºC a mixture of **46** (542 mg, 1.0 mmol) and sodium borohydride (760 mg, 20.0 mmol).[24] The mixture was stirred at 0 °C for 1.5 h and poured into water. The solution was extracted with dichloromethane and washed with a saturated solution of sodium bicarbonate and brine. The solution was dried over magnesium sulfate. After filtration, the solvent was evaporated in vacuo to afford a white solid. The solid was crystallized from cyclohexane and purified by flash chromatography on silica gel to afford the desired product as a white solid (359 mg, 70%). Mp 141-142 °C. FTIR (KBr) 1511, 1480, 1426, 1398, 1181, 1003, 797, 752, 627, 471 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 4 H), 7.05 (s, 4 H), 6.91 (d, *J* = 8.2 Hz, 4 H), 3.86 (s, 4 H). ^{13}C NMR ($CDCl_3$) δ 140.8, 138.4, 137.5, 131.0, 129.0, 91.3, 41.0. HRMS calcd for $C_{20}H_{16}I_2$: 509.9342. Found: 509.9331.

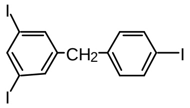
48. See the general procedure for the Pd/Cu coupling reaction. **47** (255 mg, 0.50 mmol), **9**[16] (201 mg, 1.1 mmol), bis(dibenzylideneacetone)palladium(0) (23 mg, 0.040 mmol), copper(I) iodide (20 mg, 0.10 mmol), triphenylphosphine (75 mg, 0.25 mmol), and diisopropylethylamine (0.70 mL, 4.0 mmol) were stirred in THF (4.0 mL) at room temperature for 65 h. The crude product was washed with a small amount of ethyl acetate to afford a yellow solid. The solid was dissolved in hot ethyl acetate and the solution was filtered. After the solvent was evaporated in vacuo, the title compound was afforded as a yellow solid (269 mg, 89%). Mp 188-190 °C (ethyl acetate). FTIR (KBr) 1692, 1560, 1508, 1384, 1112, 826, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.52 (dt, *J* = 8.5, 1.9 Hz, 4 H), 7.43 (d, *J* =

8.3 Hz, 4 H), 7.37 (dt, J = 8.5, 1.9 Hz, 4 H), 7.15 (d, J = 8.3 Hz, 4 H), 7.09 (s, 4 H), 3.95 (s, 4 H), 2.41 (s, 6 H). ^{13}C NMR ($CDCl_3$) δ 193.5, 141.9, 138.5, 134.2, 132.1, 131.8, 129.1, 129.0, 127.9, 124.7, 120.6, 91.1, 88.3, 41.5, 30.3. HRMS calcd for $C_{40}H_{30}O_2S_2$: 606.1687. Found: 606.1698.

4-Iodobenzaldehyde.[41] To a solution of 1,4-diiodobenzene (5.11 g, 0.015 mol) in diethyl ether (2.1 mL) at –78° C was added dropwise *n*-butyllithium (6.14 mL, 1.50 M in hexanes) over a period of 30 min. The reaction was stirred for 1 h. To this solution was added dropwise dry DMF (1.19 mL) over a period of 30 min. The reaction mixture was gradually allowed to warm to room temperature. The reaction mixture was quenched with distilled water and the mixture extracted with methylene chloride (3 × 70 mL). It was dried over sodium sulfate and the solvents were removed in *vacuo* to yield a yellow oil that solidified on cooling. The sample was purified by silica gel column chromatography using hexane/methylene chloride (1:1, v/v) to provide 2.50 g (70%) of the title compound as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (s, 1 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.87 (d, J = 8.37 Hz, 2 H). FABMS Calcd for C_7H_5IO: 232. Found: 232. ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.77, 135.56, 138.39, 191.23. Anal. Calcd for C_7H_5IO: C, 36.23; H, 2.17. Found. C, 36.46; H, 2.12.

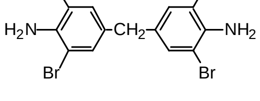
3,4',5-Triiododiphenylmethanol (49). To a solution of 1,3,5-triiodobenzene (3.37 g, 7.41 mmol) in dry THF (90 mL) at -78 ºC was added *n*-butyllithium (1.57 M in hexane, 5.18 mL, 8.14 mmol). The solution was stirred for 30 min and transferred via cannula into 4-iodobenzaldehyde (2.06 g, 8.88 mmol) in dry THF (50 mL) at -78 °C. The solution was stirred for 10 min and temperature was gradually raised to room temperature. The solution was poured into water and extracted with ether and washed with brine. 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 8:2) to afford desired product (2.32 g, 59%) as white crystals. Mp 146-147 °C. FTIR (KBr) 3416, 1567, 1540, 1410, 1384, 1167, 1038, 1005, 830 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.93 (t, *J* = 1.5 Hz, 1 H), 7.67 (dt, *J* = 8.7, 2.0 Hz, 2 H), 7.63 (dd, *J* = 1.5, 0.6 Hz, 2 H), 7.06 (dtd, *J* = 8.7, 2.0, 0.3 Hz, 2 H), 5.63 (d, *J* = 2.4 Hz, 1 H), 2.25 (d, *J* = 3.3 Hz, 1 H). ^{13}C NMR (CDCl$_3$) δ 147.1, 144.4, 142.2, 137.9, 134.7, 128.4, 95.0, 93.9, 74.3. HRMS calcd for $C_{13}H_9I_3O$: 561.7789. Found: 561.7798.



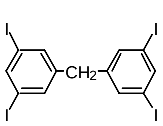
3,4',5-Triiododiphenylmethane. The procedure by Gribble was modified as follows.[24] To trifluoroacetic acid (50 mL) was added under nitrogen at room temperature sodium borohydride (1.05 g, 27.6 mmol). Before all of the sodium borohydride reacted with the trifluoroacetic acid, **49** (1.56 g, 2.78 mmol) in dichloromethane (50 mL) was added dropwise. The mixture was stirred for 1 h. Additional pieces of sodium borohydride (606 mg, 15.9 mmol) were added in portions over 6 h. The mixture was stirred for 1 h and then poured into ice water. The solution was neutralized by a careful addition of sodium hydroxide pellets. The solution was extracted with dichloromethane and washed with brine. The extract was dried over magnesium sulfate. After filtration, the solvent was evaporated in vacuo to afford a mixture of a yellow oil and a white solid. The mixture was washed with hexane-ethyl acetate (8:2) and filtered to afford a white solid (599 mg). The washings were combined, evaporated to dryness, and again purified by flash chromatography on silica gel (hexane-ethyl acetate 8:2) to afford another 145 mg yielding a total of 744 mg (49%) of desired compound in addition to the recovery of **49** (338 mg, 22%). Mp 147-148 °C. FTIR (KBr) 1571, 1539, 1482, 1418, 1384, 1006, 858, 787, 706 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.88 (t, *J* = 1.5 Hz, 1 H), 7.61 (dt, *J* = 8.6, 2.1 Hz, 2 H), 7.43 (d, *J* = 1.5 Hz, 2 H), 6.88 (dt, *J* = 8.6, 2.1 Hz, 2 H), 3.77 (s, 2 H). ^{13}C NMR (CDCl$_3$) δ 144.5, 143.1, 139.0, 137.8, 137.1, 130.9, 95.1, 92.1, 40.4. HRMS calcd for $C_{66}H_{48}O_3S_3$: 545.7838. Found: 545.7840.

50. See the general procedure for the Pd/Cu coupling reaction. **49** (295 mg, 0.54 mmol), **30** (587 mg, 1.93 mmol), bis(dibenzylideneacetone)palladium(0) (47 mg, 0.081 mmol), copper(I) iodide (30 mg, 0.16 mmol), triphenylphosphine (107 mg, 0.41 mmol), and diisopropylethylamine (1.13 mL, 6.5 mmol) were stirred in THF (5.0 mL) at room temperature for 3 d. The crude product was washed with a small amount of ethyl acetate to afford a pale brown solid (355 mg). The washings were combined, evaporated to dryness, and further purified by flash chromatography on silica gel (hexane-ethyl acetate 8:2) to afford a yellow oil. The oil was crystallized from ethyl acetate to afford another 125 mg yielding a total of 480 mg (83%) of desired product. Mp 132-134 ºC. FTIR (KBr) 2954, 2203, 1698, 1588, 1498, 1384, 1116, 827, 620 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.55-7.53 (m, 7 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 7.9 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.41 (d, *J* = 1.4 Hz, 2 H), 7.41-7.37 (m, 7 H), 7.33 (dd, *J* = 7.9, 1.4 Hz, 2 H), 7.34-7.31 (m, 3 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 4.00 (s, 2 H), 2.87 (q, *J* = 7.6 Hz, 4 H), 2.86 (q, *J* = 7.5 Hz, 2 H), 2.42 (s, 9 H), 1.31 (t, *J* = 7.6 Hz, 6 H), 1.30 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR ($CDCl_3$) δ 193.4, 146.4, 146.2, 141.3, 140.5, 134.4, 134.2, 132.4, 132.3, 132.2, 132.1, 131.9, 131.6, 131.2, 129.1, 129.0, 129.0, 128.4, 128.3, 128.3, 128.2, 124.4, 124.4, 124.0, 123.1, 122.8, 122.7, 122.4, 121.5, 94.7, 93.8, 91.2, 91.1, 90.2, 90.0, 88.6, 87.9, 41.4, 30.3, 27.7, 27.6, 14.6, 14.6. Anal. calcd for $C_{73}H_{54}O_3S_3$: C, 81.53; H, 5.06. Found: C, 81.48; H, 5.07.



Bis(3,5-dibromo-4-aminophenyl)methane. To 4,4'-diaminodiphenylmethylene (594 mg, 3.0 mmol) in a methanol/dichloromethane (1:1) solution (20 mL) was added dropwise bromine (0.77 mL, 15.0 mmol) in a methanol/dichloromethane (1:1) solution (20 mL). The mixture was stirred at room temperature for 3 h before poured into 1 N sodium hydroxide solution. The mixture was filtered to afford a white solid. The solid was washed with water and dried to give titled compound (1.45 g, 94%). Mp>250 °C. FTIR (KBr) 3424, 3315, 1618, 1472, 1060 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.14 (s, 4 H), 3.66 (s, 2 H). HRMS calcd for $C_{13}H_{10}N_2Br_4$: 509.7577, Found: 509.7600. Insolubility of the material inhibited obtaining other spectral characterization.

Bis(3,5-dibromophenyl)methane (51). To sodium nitrite (208 mg, 3.0 mmol) in sulfuric acid (5.0 mL) at 5 °C was added dropwise a suspension of bis(3,5-dibromo-4-aminophenyl)methane (514 mg, 1.0 mmol) in glacial acetic acid (5.0 mL). During the addition, the temperature was maintained below 10 °C. The mixture was stirred at 5 ºC for 30 min and a 50% aqueous solution of hypophosphorous acid (3.12 mL, 30 mmol) was added dropwise. After stirring for 30 min at 5 °C, the mixture was placed in a refrigerator for 1 d and then allowed to stand at room temperature overnight. The mixture was poured into water and extracted with ethyl acetate. The extract was washed with sodium bicarbonate solution and brine and dried over magnesium sulfate. After filtration, the solvent was evaporated in vacuo to afford a brown solid. The solid was crystallized from chloroform to afford desired product (109 mg, 23%) as a white solid. Mp 196 °C. FTIR (KBr) 3036, 1575, 1556, 1417, 1104, 849 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.54 (t, J = 1.7 Hz, 2 H), 7.21 (d, J = 1.7 Hz, 4 H), 3.82 (s, 2 H). ^{13}C NMR ($CDCl_3$) δ 143.1, 132.5, 130.7, 123.2, 40.4. HRMS calcd for $C_{13}H_8Br_4$: 479.7359. Found: 479.7357.



Bis(3,5-diiodophenyl)methane. 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}. ^{1}H 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.

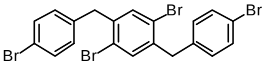
52. See the general procedure for the Pd/Cu coupling reaction. Bis(3,5-diiodophenyl)methane (170 mg, 0.25 mmol), **9**[16] (211 mg, 1.20 mmol), bis(dibenzylideneacetone)palladium(0) (29 mg, 0.050 mmol), copper(I) iodide (19 mg, 0.10 mmol), triphenylphosphine (66 mg, 0.25 mmol), and diisopropylethylamine (0.70 mL, 4.0 mmol) were stirred in THF (4.0 mL) at room temperature for 2 d. The crude product was dissolved in ethyl acetate and passed through a plug of silica gel. Then the crude solid was washed with a small amount of ethyl acetate, dissolved in hot ethyl acetate and filtered to afford titled compound (102 mg, 47%) as a pale yellow solid. Mp 177-178 °C. FTIR (KBr) 1701, 1593, 1486, 1385, 1118, 828 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.59 (t, *J* = 2.5 Hz, 2 H), 7.53 (dt, *J* = 8.3, 1.7 Hz, 8 H), 7.38 (dt, *J* = 8.3, 1.7 Hz, 8 H), 7.34 (d, *J* = 1.5 Hz, 4 H), 3.96 (s, 2

H), 2.41 (s, 12 H). ^{13}C NMR ($CDCl_3$) δ 193.3, 140.7, 134.2, 133.0, 132.2, 132.2, 128.4, 124.1, 123.7, 90.1, 89.5, 30.0. HRMS calcd for $C_{53}H_{36}O_4S_4$: 864.1496. Found: 864.1453.

53. See the general procedure for the Pd/Cu coupling reaction. Bis(3,5-diiodophenyl)methane (108 mg, 0.16 mmol), **30** (220 mg, 0.72 mmol), bis(dibenzylideneacetone)palladium(0) (18 mg, 0.032 mmol), copper(I) iodide (12 mg, 0.064 mmol), triphenylphosphine (42 mg, 0.16 mmol), and diisopropylethylamine (0.45 mL, 2.59 mmol) were stirred in THF (3.0 mL) at room temperature for 60 h. The crude product was dissolved in hexane-ethyl acetate (1:1) to afford a pale yellow solid. The solid was washed with a small amount of ethyl acetate to afford the desired product (107 mg, 49%) as a pale yellow solid. Mp 104-107 °C. FTIR (KBr) 1707, 1585, 1498, 1384, 1108, 826 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.57 (t, *J* = 1.3 Hz, 2 H), 7.54 (dt, *J* = 8.3, 1.7 Hz, 8 H), 7.48 (d, *J* = 8.0 Hz, 4 H), 7.41 (d, *J* = 1.3 Hz, 4 H), 7.38 (dt, *J* = 8.3, 1.7 Hz, 8 H), 7.35 (d, *J* = 1.3 Hz, 4 H), 7.33 (dd, *J* = 8.0, 1.3 Hz, 4 H), 4.00 (s, 2 H), 2.88 (q, *J* = 7.6 Hz, 8 H), 2.42 (s, 12 H), 1.31 (t, *J* = 7.6 Hz, 12 H). ^{13}C NMR ($CDCl_3$) δ 193.8, 146.8, 141.1, 134.6, 133.0, 132.6, 132.6, 132.3, 131.6, 129.4, 128.6, 124.8, 124.5, 123.5, 122.7, 94.1, 91.4, 90.6, 89.1, 41.3, 30.7, 28.0, 15.0. Anal. calcd for $C_{93}H_{68}O_4S_4$: C, 81.07; H, 4.97. Found: C, 81.16; H, 4.99.

2,5-Bis(*p*-bromobenzoyl)-1,4-dibromobenzene (56). To a suspension of aluminum chloride (2.67 g, 20.0 mmol) in CH_2Cl_2 (50 mL) at 0 °C was slowly added a solution of **54**[26] (3.25 g, 9.00 mmol) in CH_2Cl_2. The resultant yellow slurry was stirred for 10 min and a solution of 1-bromo-4-trimethylsilylbenzene (4.89 g, 21.3 mmol) in CH_2Cl_2 (15 mmol) was added. The mixture was stirred for 2 h at 0 °C and overnight at room temperature. The brown mixture was carefully poured into cold 1.5 N HCl solution. Dichloromethane (100 mL) was added to dissolve the precipitate and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2×). Combined organic fractions were washed with H_2O

(1×) and dried over magnesium sulfate. After filtration, the solvent was concentrated to ca. 100 mL and filtered through a short silica gel column [CH_2Cl_2/hexane (1/1)]. Removal of solvents followed by washing with hexane and ether afforded desired product as a white solid (3.25 g, 60%). Mp 254-256 °C. FTIR (KBr) 3097, 1677, 1585, 1400, 1385, 1339, 1246, 1067, 1010, 928, 882, 841, 749 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.9 Hz, 4 H), 7.65 (d, J = 9.0 Hz, 4 H), 7.58 (s, 2 H). ^{13}C NMR ($CDCl_3$, 50 °C, 100 MHz) 192.16, 142.94, 134.02, 133.08, 132.29, 131.42, 129.86, 118.54. HRMS calcd for $C_{20}H_{10}Br_4O_2$: 597.7414. Found: 597.7400.



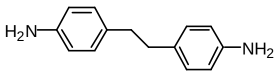
2,5-Bis(*p*-bromobenzyl)-1,4-dibromobenzene. To a suspension of **56** (2.11 g, 3.50 mmol) in CH_2Cl_2 (70 mL) was added dropwise trifluoromethanesulfonic acid (3.15 g, 21.0 mmol). The clear golden solution was cooled to 0 °C and a solution of triethylsilane (3.15 g, 17.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise.[22] The resulting light yellow solution was stirred at 0 °C for 10 min. Another portion of trifluoromethanesulfonic acid (3.15 g, 21.0 mmol) and triethylsilane (3.15 g, 17.5 mmol) was added by the above addition sequence at 0 °C. The obtained light yellow solution was allowed to warm to room temperature and stir for 3 h before pouring into saturated aqueous sodium carbonate (100 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (2×). The combined organic fractions were washed with H_2O (2×) and dried over magnesium sulfate. Removal of solvents followed by washing with hexane afforded desired product as a white solid (1.76 g, 88%). Mp 161-167 °C. FTIR (KBr) 1487, 1472, 1436, 1405, 1385, 1072, 1056, 1010, 897, 831, 774 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 4 H), 7.28 (s, 2 H), 7.03 (d, J = 8.4 Hz, 4 H), 3.97 (s, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.97, 137.63, 134.75, 131.76, 130.69, 123.74, 120.52, 40.59. HRMS calcd for $C_{20}H_{14}Br_4$: 569.7829. Found: 569.7834.

2,5-Bis(*p*-iodobenzyl)-1,4-diiodobenzene (57). To *tert*-BuLi (5.62 mL, 10.0 mmol, 1.78 M in pentane) in ether (5 mL) at -78 °C was added via cannula a solution of 2,5-bis(*p*-bromobenzyl)-1,4-dibromobenzene (0.574 g, 1.00 mmol) in THF (15 mL) dropwise. The brown slurry was stirred for 30 min and then warmed to 0 °C. The slurry was re-cooled to -78 °C and a solution of iodine (2.54 g, 10.0 mmol) in THF (10 mL) was added via cannula. The mixture was allowed to warmed to room temperature and stir for 1 h before pouring into an aqueous solution of sodium thiosulfate. The organic phase was separated. The aqueous layer was extracted with CH_2Cl_2 (2×). Combined organic fractions were washed with H_2O (2×) and dried over magnesium sulfate. Removal of solvents followed by washing with ethyl acetate afforded desired product as a white solid (0.442 g, 58%). Mp 210-213 °C. FTIR (KBr) 3149, 1482, 1431, 1400, 1385, 1354, 1185, 1041, 1005, 897, 815, 774 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 4 H), 7.53 (s, 2 H), 6.89 (d, *J* = 8.4 Hz, 4 H), 3.94 (s, 4 H). No ^{13}C could be obtained due to the limited solubility of **57**. HRMS calcd for $C_{20}H_{14}I_4$: 761.7274. Found: 761.7270.

58. See the general procedure for the Pd/Cu coupling reaction. The compounds used were **57** (0.38 g, 0.50 mmol), **9**[16] (0.44 g, 2.5 mmol), di(benzylidineacetone)palladium(0) (0.058 g, 0.10 mmol), copper(I) iodide (0.038 g, 0.20 mmol), triphenylphosphine (0.53 g, 0.20 mmol), THF (15 mL), and diisopropylethylamine (1.4 mL, 8.0 mmol) at room temperature. The mixture was stirred for 8 h. Another portion of di(benzylidineacetone)palladium(0) (0.029 g, 0.050 mmol) and PPh_3 (0.026 g, 0.10 mmol) in THF (5 mL) was added. The mixture was further stirred for 21 h. Flash chromatography (silica gel, hexane/CH_2Cl_2 1/1) gave desired product as a white solid (0.165 g, 35%). Mp 239-240 °C. FTIR (KBr) 1708, 1497, 1385, 1354, 1123, 1015, 854, 826, 621 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 4 H), 7.46 (d, *J* = 7.9 Hz, 8 H), 7.37 (d, *J* = 8.5 Hz, 4 H), 7.36 (d, *J* = 8.6 Hz, 4 H), 7.35 (s, 2 H), 7.24 (d, *J* = 8.3 Hz, 4 H), 4.19 (s, 4 H), 2.42 (s, 6 H), 2.41 (s, 6 H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ 193.53, 193.37, 140.72, 140.69, 134.32, 134.24, 133.34, 132.19, 132.11, 131.94, 129.10, 128.53, 127.94, 124.67, 124.12, 123.23, 120.89, 94.61, 91.17, 89.64, 88.56, 39.80, 30.36, 30.32. HRMS calcd for $C_{60}H_{42}O_4S_4$: 954.1966. Found: 954.1999. Anal. calcd for $C_{60}H_{42}O_4S_4$: C, 75.44; H, 4.43. Found: C, 75.52; H, 4.51.

59. See the general procedure for the Pd/Cu coupling reaction. The compounds used were **57** (0.076 g, 0.10 mmol), **30** (0.157 g, 0.500 mmol), di(benzylidineacetone)palladium(0) (0.012 g, 0.020 mmol), copper(I) iodide (0.0076 g, 0.040 mmol), triphenylphosphine (0.026 g, 0.10 mmol), THF (3 mL), and diisopropylethylamine (0.28 mL, 1.6 mmol) for 60 h at room temperature. Flash chromatography (silica gel, $CHCl_3$/hexane 1/1) afforded desired product as a green/yellow solid (0.060 g, 41%). Mp 159-162 °C. FTIR (KBr) 2964, 2933, 2872, 2205, 1708, 1595, 1508, 1400, 1385, 1349, 1118, 1087, 1015, 949, 892, 826, 613 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.1 Hz, 8 H), 7.48-7.43 (m, 6 H), 7.40-7.36 (m, 16 H), 7.32 (dd, J = 8.2, 1.7 Hz, 4 H), 7.25 (d, J = 8.1 Hz, 4 H), 4.25 (s, 4 H), 2.86 (q, J = 7.6 Hz, 4 H), 2.76 (q, J = 7.6 Hz, 4 H), 2.42 (s, 12 H), 1.29 (t, J = 7.6 Hz, 6 H), 1.21 (t, J = 7.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.31, 193.28, 146.19, 146.11, 140.53, 140.22, 134.21, 133.37, 132.27, 132.16, 132.04, 131.73, 131.16, 128.97, 128.94, 128.25, 128.14, 124.43, 124.32, 123.59, 123.15, 122.83, 122.68, 122.37, 121.26, 94.82, 93.72, 93.30, 91.21, 91.07, 90.32, 90.00, 87.77, 39.78, 30.45, 27.81, 27.75, 14.86, 14.77. LRMS calcd for $C_{100}H_{74}O_4S_4$: 1468. Found: 1468. Anal. calcd for $C_{100}H_{74}O_4S_4$: C, 81.82; H, 5.08. Found: C, 81.68; H, 5.13.



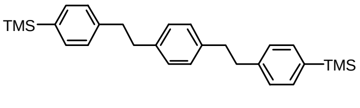
1,2-Bis(4'-aminophenyl)ethane. To a Parr flask was added **60** (5.45 g, 20.0 mmol), 10% palladium on activated carbon (274 mg), and ethanol (50 mL). The flask was purged with hydrogen and pressurized to 60 psi. The flask was shaken for 5 h at room temperature. After filtration, the solvent was evaporated in vacuo to afford desired compound (2.50 g, 59%) as a white solid. Mp >250 °C. ^{1}H NMR ($CDCl_3$) δ 6.95 (d, *J* = 8.2 Hz, 4 H), 6.61 (d, *J* = 8.2 Hz, 4 H), 3.47 (br, 4 H), 2.74 (s, 4 H).

1,2-Bis(4'-diethyltriazenylphenyl)ethane (61). To 1,2-bis(4'-aminophenyl)ethane (1.00 g, 4.72 mmol), hydrochloric acid (15 mL), and water (50 mL) was added at 0 ºC sodium nitrite (716 mg, 10.4 mmol) in water (2.0 mL). The solution was stirred for 30 min at 0 ºC and poured into potassium carbonate (10.4 g, 75.2 mmol), diethylamine (10 mL), and water (100 mL). An orange solid was removed by filtration and washed with water. After drying, the desired solid (1.59 g, 87%) was obtained. Mp 64-66ºC. FTIR (KBr) 2980, 2935, 1433, 1402, 1384, 1351, 1235, 1089, 841 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.30 (dt, *J* = 8.3, 2.0 Hz, 4 H), 7.11 (dt, *J* = 8.3, 2.0 Hz, 4 H), 3.73 (q, *J* = 7.2 Hz, 8 H), 2.87 (s, 4 H), 1.24 (t, *J* = 7.2 Hz, 12 H). ^{13}C NMR ($CDCl_3$) δ 149.4, 138.8, 128.9, 120.3, 37.7, 13.1 (br) (one carbon is missing due to the quadropolar effect of nitrogen.). HRMS calcd for $C_{22}H_{32}N_6$: 380.2688. Found: 380.2696.

1,2-Bis(4'-iodophenyl)ethane (62). See the standard procedure. The compounds used were **61** (800 mg, 2.48 mmol) and iodomethane (15 mL) at 120 °C overnight. After cooling, the reaction was diluted with hexane-ethyl acetate (1:1) and passed through a plug of silica gel. The solvent was evaporated in vacuo to afford desired compound (834 mg, 78%) as a yellow solid. Mp 150-151°C. FTIR (KBr) 1482, 1384, 1002, 816 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 4 H), 6.86 (d, *J* = 8.3 Hz, 4 H), 2.81 (s, 4 H). ^{13}C NMR ($CDCl_3$) δ 140.8, 137.4, 130.6, 91.2, 37.1. HRMS calcd for $C_{14}H_{12}I_2$: 433.9028. Found: 433.9027.

63. See the general procedure for the Pd/Cu coupling reaction. **62** (304 mg, 0.7 mmol), **9**[16] (296 mg, 1.68 mmol), bis(dibenzylideneacetone)palladium(0) (40 mg, 0.070 mmol), copper(I) iodide (27 mg, 0.14 mmol), triphenylphosphine (92 mg, 0.35 mmol), and diisopropylethylamine (0.97 mL, 5.6 mmol) were stirred in THF (10 mL) at room temperature for 2 d. The crude product was passed thorough a plug of silica gel (hexane-ethyl acetate 1:1) to afford a yellow solid. The solid was recrystallized from ethyl acetate to afford the desired compound (227 mg, 61%). FTIR (KBr) 1700, 1512, 1384, 1123, 828, 623 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.54 (dt, *J* = 8.5, 1.8 Hz, 4 H), 7.43 (dt, *J* = 8.3, 1.7 Hz, 4 H), 7.38 (dt, *J* = 8.5, 1.8 Hz, 4 H), 7.11 (dt, *J* = 8.3, 1.7 Hz, 4 H), 2.92 (s, 4 H), 2.42 (s, 6 H). ^{13}C NMR ($CDCl_3$) δ 193.5, 142.1, 134.2, 132.2, 131.7, 128.7, 127.9, 124.7, 120.5, 91.2, 88.4, 37.6, 30.3. HRMS calcd for $C_{34}H_{26}O_2S_2$: 530.1374. Found: 530.1366.

64. See the general procedure for the Pd/Cu coupling reaction. The compounds used were 1,4-diethynylbenzene (1.26 g, 10.0 mmol), 1-iodo-4-trimethylsilylbenzene (6.09 g, 22.0 mmol), di(benzylidineacetone)palladium(0) (0.57 g, 1.0 mmol), triphenylphosphine (0.53 g, 2.0 mmol), copper(I) iodide (0.38 g, 2.0 mmol), THF (40 mL), and diisopropylethylamine (13.9 mL, 80.0 mmol). The mixture was stirred at room temperature for 30 h. After workup, the residue was dissolved in CH_2Cl_2 and filtered through a silica gel column [hexane/CH_2Cl_2 (2/1)]. Removal of the solvent in vacuo followed by crystallization from hexane gave a pale yellow solid (2.86 g). The mother liquor was purified by flash chromatography to give another pale yellow solid (0.66 g). A total of 3.52 g (83%) of desired product was obtained. Mp 214-220 °C. FTIR (KBr) 3067, 3015, 2954, 2892, 1595, 1513, 1385, 1308, 1246, 1103, 846, 821, 754, 718, 682 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 12 H), 0.26 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.36, 133.31, 131.61, 130.74, 123.36, 123.18, 91.51, 89.59, -1.17. HRMS calcd for $C_{28}H_{30}Si_2$: 422.1886. Found: 422.1878.



1,4-Bis(2-(4´-trimethylsilylphenyl)ethyl)benzene. A mixture of **64** (1.27 g, 3.00 mmol) in ethanol (100 mL) and 37% hydrochloric acid (10 drops) was hydrogenated over Pd on carbon (0.2 g, 10% of Pd on carbon) at 60 psi for 21 h. The mixture was filtered and the residue was washed with ethyl acetate. Removal of solvent in vacuo gave desired compound as a white solid (1.26 g, 97%). Mp 168-173 °C. FTIR (KBr) 3067, 3015, 2954, 2923, 2851, 1600, 1513, 1451, 1395, 1246, 1108, 831, 754, 718, 692, 651 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 4 H), 7.20 (d, *J* = 7.9 Hz, 4 H), 7.14 (s, 4 H), 2.89 (s, 8 H), 0.29 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.66, 139.52, 137.61, 133.52, 128.45, 127.96, 38.07, 37.50, -0.96. HRMS calcd for $C_{28}H_{38}Si_2$: 430.2512. Found: 430.2497.

1,4-Bis(2-(4´-iodophenyl)ethyl)benzene (65). To a suspension of 1,4-bis(2-(4´-trimethylsilylphenyl)ethyl)benzene (1.13 g, 2.62 mmol) in carbon tetrachloride (60 mL) was added dropwise iodine monochloride (0.37 mL, 7.3 mmol). The mixture was stirred for 80 min and then decolorized with aqueous sodium thiosulfate. The mixture was extracted with methylene chloride (2×). The extracts were dried over magnesium sulfate. Removal of solvent in vacuo gave a white solid. The solid was re-dissolved in methylene chloride and passed through a short silica gel column to afford desired compound as a white solid (1.39 g, 98%). Mp 147-160 °C. FTIR (KBr) 3026, 2944, 2923, 2851, 1513, 1482, 1451, 1400, 1385, 1200, 1139, 1087, 1062, 1005, 815, 790, 759, 703, 610 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 4 H), 7.03 (s, 4 H), 6.88 (d, *J* = 8.2 Hz, 4 H), 2.83 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.39, 138.94, 137.35, 130.68, 128.50, 91.04, 37.41, 37.26. HRMS calcd for $C_{22}H_{20}I_2$: 537.9655. Found: 537.9634.

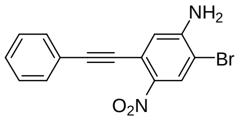
66. See the general procedure for the Pd/Cu coupling reaction. The compounds used were **65** (0.463 g, 0.860 mmol), **9**[16] (0.379 g, 2.15 mmol), di(benzylidineacetone)palladium(0) (0.049 g, 0.086 mmol), copper(I) iodide (0.033 g, 0.17 mmol), triphenylphosphine (0.090 g, 0.34 mmol), THF (15 mL), and diisopropylethylamine (0.91 mL, 5.2 mmol) for 24 h at room temperature. Flash chromatography (silica gel, CH_2Cl_2/hexane 2/1) afforded desired compound as a white solid (0.41 g, 75%). Mp 182 °C (decompose). FTIR (KBr) 2913, 2851, 1703, 1513, 1385, 1129, 1092, 1015, 949, 831, 821 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 4 H), 7.43 (d, *J* = 8.1 Hz, 4 H), 7.37

(d, *J* = 8.3 Hz, 4 H), 7.13 (d, *J* = 8.2 Hz, 4 H), 7.05 (s, 4 H), 2.89 (br s, 8 H), 2.42 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.28, 142.40, 138.83, 134.07, 131.99, 131.52, 128.51, 128.35, 127.69, 124.61, 120.24, 91.20, 88.16, 37.93, 37.25, 30.34. HRMS calcd for $C_{42}H_{34}O_2S_2$: 634.2000. Found: 634.1990.

67. See the general procedure for the Pd/Cu coupling reaction. A solution of bis(dibenzylidineacetone)palladium(0) (0.0770 g, 0.135 mmol) and triphenylphosphine (0.14 g, 0.54 mmol) in THF (5 mL) was added to a solution of **65** (0.724 g, 1.35 mmol), phenylacetylene (0.138 g, 1.35 mmol) and copper(I) iodide (0.050 g, 0.27 mmol) in THF (10 mL). The mixture was stirred for 19 h at room temperature. A solution of **9**[16] (0.44 g, 2.5 mmol), bis(dibenzylidineacetone)palladium(0) (0.015 g, 0.027 mmol) and triphenylphosphine (0.028 g, 0.11 mmol) in THF (5 mL) was added. The mixture was stirred for 28 h at room temperature and then poured into water. The mixture was extracted with methylene chloride (2×). The filtrate was dried over magnesium sulfate. Removal of solvent followed by flash chromatography (silica gel, CH_2Cl_2/hexane 1/1) and recrystallization from cyclohexane/CH_2Cl_2 afforded desired compound as a white solid (0.266 g, 35%). Mp 180-183 °C. FTIR (KBr) 2915, 2850, 2371, 2213, 1707, 1591, 1508, 1387, 1113, 1011, 946, 830 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2 H), 7.51 (dd, *J* = 7.8, 2.0 Hz, 2 H), 7.43 (d, *J* = 8.1 Hz, 4 H), 7.38-7.30 (m, 3 H), 7.13 (d, *J* = 8.3 Hz, 2 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 7.05 (s, 4 H), 2.89 (br s, 8 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.12, 142.28, 141.92, 138.74, 138.68, 133.94, 131.87, 131.39, 131.31, 128.38, 128.33, 128.22, 128.07, 127.87, 127.57, 124.49, 123.19, 120.49, 120.12, 91.09, 89.34, 88.77, 88.04, 37.79, 37.12, 30.20. HRMS calcd for $C_{40}H_{32}OS$: 560.2174. Found: 560.2157.

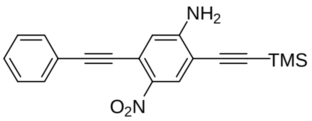
2-Bromo-4-nitro-5-(phenylethynyl)acetanilide (69). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2,5-dibromo-4-nitroacetanilide **(68)**[26] (3.0 g, 8.88 mmol), phenylacetylene (0.98 mL, 8.88 mmol), copper(I) iodide (0.17 g, 0.89 mmol), bis(triphenylphosphine)palladium(II) chloride (0.25 g, 0.44

mmol), triphenylphosphine (0.47 g, 1.78 mmol), diisopropylethylamine (6.18 mL, 35.52 mmol), and THF (25 mL) at room temperature for 1 d then 50 ºC for 12 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product) = 0.60. The reaction afforded 1.79 g (56% yield) of the desired product. IR (KBr) 3261.5, 3097.4, 2215.4, 1671.8, 1553.8, 1533.3, 1502.6, 1379.5, 1333.3, 1261.5, 1092.3, 1020.5, 892.3, 851.3, 753.8, 687.2, 651.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1 H), 8.39 (s, 1 H), 7.80 (br s, 1 H), 7.66-7.60 (m, 2 H), 7.43-7.36 (m, 3 H), 2.32 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 168.30, 139.81, 132.20, 129.49, 129.03, 128.49, 124.87, 122.21, 119.88, 117.49, 111.00, 98.64, 84.81, 25.33. HRMS calcd $C_{16}H_{11}N_2O_3Br$: 357.9953. Found: 357.9948.



2-Bromo-4-nitro-5-(phenylethynyl)aniline. To a 100 mL round bottom flask equipped with a magnetic stirbar, **69** (0.33 g, 0.92 mmol), potassium carbonate (0.64 g, 4.6 mmol), methanol (15 mL), and methylene chloride (15 mL) were added. The reaction was allowed to stir at room temperature for 1 h. The reaction mixture was quenched with water and extracted with methylene chloride (3×). The organic layers were combined and dried over magnesium sulfate. Solvents were removed in vacuo. No further purification needed. The reaction afforded 0.29 g (100% yield) of the titled compound as a yellow solid. IR (KBr) 3476.9, 3374.4, 3159.0, 1656.4, 1615.4, 1559.0, 1379.5, 1307.7, 1138.5, 1102.6, 892.3, 748.7, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1 H), 7.74-7.68 (m, 2 H), 7.52-7.46 (m, 3 H), 7.06 (s, 1 H), 4.93 (br s, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.55, 139.41, 132.02, 130.45, 129.25, 128.46, 122.46, 120.17, 118.38, 106.86, 96.94, 85.46. HRMS calcd: 317.9828. Found: 317.9841.

2´-Amino-4,4´-diphenylethynyl-5´-nitro-1-thioacetylbenzene (70). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-4-nitro-5-(phenylethynyl)aniline (0.10 g, 0.30 mmol) was coupled to **9**[16] (0.10 g, 0.56 mmol) as described above using copper(I) iodide (0.01 g, 0.03 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol), triphenylphosphine (0.02 g, 0.06 mmol), diisopropylethylamine (0.24 mL, 1.40 mmol), and THF (10 mL) in an oven dried round screw capped pressure tube equipped with a stirbar. The reaction mixture was allowed to react at 80 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.26. An additional hexanes wash gave yellow crystals of the desired compound, 0.80 g (67 % yield). IR (KBr) 3374.4, 3138.5, 2205.1, 1384.6, 1312.8, 1246.2, 1112.8, 825.6, 753.8, 692.3, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1 H), 7.59 (m, 2 H), 7.55 (d, J=8.0 Hz, 2 H), 7.42 (d, J=8.2 Hz, 2 H), 7.38 (m, 3 H), 6.92 (s, 1 H), 4.89 (br s, 2 H), 2.45 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 193.03, 150.99, 139.53, 134.36, 132.12, 132.08, 130.24, 129.23, 129.19, 128.441, 123.21, 122.55, 121.06, 118.01, 106.88, 97.66, 96.53, 85.98, 84.89, 30.51. HRMS calcd $C_{24}H_{16}N_2O_3S$: 412.0882. Found: 412.0882.

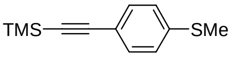


4-Nitro-3-phenylethynyl-6-trimethylsilylethynylaniline. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-bromo-4-nitro-5-(phenylethynyl)aniline (0.26 g, 0.83 mmol), trimethylsilylacetylene (0.17 mL, 1.25 mmol), copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.04 mmol), diisopropylethylamine (0.58 mL, 3.32 mmol), and THF (10 mL) at 75 °C for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/hexanes as the eluent. R_f = 0.72.

The reaction afforded 0.22 g (81 % yield) of the desired compound. IR (KBr) 3465.06, 3350.39, 3214.34, 2958.03, 2360.06, 2341.17, 2146.27, 1625.20, 1539.10, 1507.32, 1305.69, 1247.56, 1199.99, 1091.12, 878.19, 843.71, 756.00, 663.28, 472.37 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 7.65-7.60 (m, 2 H), 7.43-7.38 (m, 3 H), 6.91 (s, 1 H), 4.87 (br s, 2 H), 0.31 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.80, 139.68, 132.47, 130.77, 129.62, 128.85, 122.95, 121.37, 118.22, 107.50, 103.95, 99.08, 97.83, 86.32, 0.30. HRMS calcd $C_{19}H_{18}N_2O_2Si$: 334.1138. Found: 334.1135. This material was deprotected using the standard potassium carbonated protocol described above, and then further coupled with **3** by the Pd/Cu protocol to afford **70** in 82% yield. The spectra were identical to that described above for **70**.

2´-Acetamido-4,4´-diphenylethynyl-5´-nitro-1-thioacetylbenzene (71). See the general procedure for the Pd/Cu-catalyzed coupling reaction. **69** (0.10 g, 0.28 mmol) was coupled to **9**[16] (0.08 g, 0.45 mmol) as described above using copper(I) iodide (0.01 g, 0.02 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.01 mmol), triphenylphosphine (0.01 g, 0.04 mmol), diisopropylethylamine (0.19 mL, 1.12 mmol), and THF (10 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 80 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f = 0.40. The compound was further purified by a hexanes wash to give 0.10 g (82 % yield) of the desired compound as bright yellow crystals. IR (KBr) 3138.5, 2205.1, 1384.6, 1333.3, 1241.0, 1117.9, 953.8, 897.4, 825.6, 753.6, 687.2, 615.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H), 8.29 (s, 1 H), 8.06 (br s, 1 H), 7.62 (m, 2 H), 7.57 (d, J=8.4 Hz, 2 H), 7.46 (d, J=8.5 Hz, 2H), 7.38 (m, 3 H), 2.64 (s, 3 H), 2.32 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 192.77, 168.29, 143.82, 142.02, 134.51, 132.23, 132.17, 130.17, 129.47, 128.61, 128.46, 123.57, 122.27, 122.21, 120.70, 111.15, 99.43, 98.68, 85.55, 83.51, 30.58, 25.33. HRMS calcd $C_{26}H_{18}N_2O_4S$: 454.0987. Found: 454.0987.

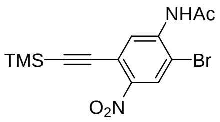
4-Iodophenyl methyl sulfide. 1,4-Diiodobenzene (6.60g, 20.0 mmol) was added to an oven-dried 2-neck round bottom flask equipped with a stir bar. Air was removed and nitrogen backfilled (3×). THF (2.5 mL) was then added under N_2 and the apparatus was cooled in a dry ice/acetone bath to –78°C. *tert*-BuLi (23.4 mL of 1.7 M solution) was then added drop wise over a period of 45 min. The mixture was allowed to stir for 30 min and sulfur (0.769 g, 24 mmol) was then added to the flask. This mixture was allowed to stir for 10 min and subsequently heated to 0°C and stirred for 10 min. The mixture was then cooled to –78°C and methyl iodide (1.87 mL, 30 mmol) added. The reaction was allowed to warm to room temperature overnight while maintaining stirring. The reaction was then quenched with water and washed with brine and methylene chloride (3×). Gravity column chromatography (silica gel with hexanes as eluent) afforded the desired product (3.14 g, 63 % yield). IR (KBr) 3070.5, 2910.5, 2851.5, 1883.0, 1469.0, 1426.3, 1381.1, 1092.3, 1000.2, 801.5, 482.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, *J*=8.6, 2.0 Hz, 2 H), 7.01 (dt, *J*=8.6, 2.0 Hz, 2 H), 2.48 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139, 138.06, 128.68, 90, 16.10. HRMS calc'd for C_7,H_7,S,I: 249.9313. Found: 249.9307.



4-Thiomethyl-1-(trimethylsilylethynyl)benzene. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 4-iodophenyl methyl sulfide (2.0 g, 8.0 mmol), bis(triphenylphosphine)palladium(II) chloride (0.281 g, 0.40 mmol), copper(I) iodide (0.15 g, 0.80 mmol), THF (30 mL), diisopropylethylamine (5.57 mL, 32.0 mmol), and trimethylsilylacetylene (1.47 mL, 10.4 mmol) at 50 °C for 10 h. Flash column chromatography (hexanes as eluent) afforded the desired product (1.74 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dt, *J*=8.6, 2.0 Hz, 2 H), 7.17 (dt, *J*=8.6, 2.0 Hz, 2 H), 2.50 (s, 3 H), 0.27 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.99, 132.63, 126.05, 119.78, 105.27, 94.56, 15.72, 0.39. IR (KBr) 3740.6, 3645.4, 3070.5, 3026.7, 2956.4, 2920.0, 2157.7, 1898.8, 1590.8, 1488.9, 1438.7, 1320.2, 1250.8, 1092.2, 1014.6. HRMS calculated for $C_{12}H_{16}SSi$: 220.0742. Found: 220.0737.

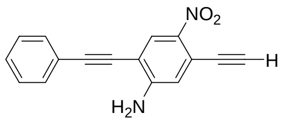
1-Ethynyl-4-thiomethylbenzene (72). See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were 4-thiomethyl-1-(trimethylsilylethynyl)benzene (0.29 g, 1.33 mmol), potassium carbonate (0.92 g, 6.63 mmol), methanol (20 mL), and methylene chloride (20 mL) for 2 h. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification.

73. 2-Bromo-4-nitro-5-(phenylethynyl)aniline (317 mg, 1.00 mmol), bis(triphenylphosphine)palladiumdichloride (35 mg, 0.05 mmol), copper(I) iodide (19 mg, 0.1 mmol), diisopropylethylamine (0.70 mL, 4.0 mmol), **72** (178 mg, 1.2 mmol), and THF (25 mL) were coupled according to the general coupling procedure except that **72** was dissolved in THF and transferred via cannula into the reaction. The reaction mixture was heated at 75 °C overnight. The crude product was then separated via flash chromatography (1:1 CH_2Cl_2/hexanes) to afford 143 mg (37%) as a yellow solid. IR (KBr) 3474.1, 3366.0, 2360.1, 2204.9, 1616.3, 1541.0, 1517.0, 1473.0, 1286.3, 1248.4, 1148.4, 1090.1, 814.8, 754.1, 686.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.60-7.53 (m, 2 H), 7.42 (d, *J* = 8.4, 2 H), 7.37-7.35 (m, 3 H), 7.21 (d, *J* = 8.5, 2 H) 4.85 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 141.1, 132.8, 132.5, 132.3, 132.1, 130.5, 129.6, 129.0, 128.9, 126.2, 126.1, 123.0, 121.1, 118.5, 118.3, 107.9, 97.7, 15.6. HRMS Calc'd for $C_{23}H_{16}N_2O_2S$: 384.0933. Found: 384.0932.



2-Bromo-4-nitro-5-(trimethylsilylethynyl)acetanilide. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were **68** (4.00 g, 11.84 mmol), trimethylsilylacetylene (1.30 mL, 11.8 mmol), copper(I) iodide (0.22 g, 1.18 mmol), bis(triphenylphosphine)palladium(II) chloride (0.41 g, 0.59 mmol), diisopropylethylamine (8.25 mL, 47.36 mmol), and THF (80 mL) at 70 ºC for 2 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 diethyl ether/hexanes as the eluent. R_f (product): 0.43. The reaction afforded 1.46 g (35 % yield, 54 % based on a recovered 1.44 g of starting material) of the desired product. IR (KBr) 3384.6, 3107.7, 3056.4, 2964.1, 2143.6, 1717.9, 1559.0, 1523.1, 1492.3, 1446.2, 1379.5, 1333.3, 1246.2, 1225.6, 1097.4, 846.2, 764.1, 712.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1 H), 8.29 (s, 1 H), 7.75 (br s, 1 H), 2.30 (s, 3 H), 0.27 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.38, 145.60, 140.82, 129.90, 126.63, 120.52, 112.46, 106.70, 100.03, 26.45, 0.93. HRMS Calcd $C_{13}H_{15}BrN_2O_3Si$: 354.0035. Found: 354.0034.

2-(Ethynylphenyl)-4-nitro-5-(trimethylsilylethynyl)acetanilide (74). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-4-nitro-5-(trimethylsilylethynyl)acetanilide (1.20 g, 3.38 mmol) was coupled to phenylacetylene (0.56 mL, 5.07 mmol) as described above using copper(I) iodide (0.06 g, 0.34 mmol), bis(triphenylphosphine)palladium(II) chloride (0.12 g, 0.17 mmol), diisopropylethylamine (2.36 mL, 13.52 mmol), and THF (25 mL) at 75 ºC for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.38. The reaction afforded 1.00 g (79 % yield) of the desired product. IR (KBr) 3384.6, 3128.2, 2953.8, 2215.4, 2153.8, 1707.7, 1543.6, 1523.1, 1497.4, 1456.4, 1384.6, 1338.5, 1225.6, 1169.2, 1112.8, 1051.3, 846.2, 748.7, 687.2, 620.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1 H), 8.21 (d, J=0.03 Hz, 1 H), 8.07 (br s, 1 H), 7.57-7.52 (m, 2 H), 7.47-7.39 (m, 3 H), 2.30 (s, 3 H), 0.29 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.35, 145.49, 142.99, 132.82, 131.01, 129.94, 129.34, 125.26, 122.25, 121.06, 112.98, 107.23, 100.90, 100.76, 83.10, 26.45, 0.96. HRMS Calcd $C_{21}H_{20}N_2O_3Si$: 376.1243. Found: 376.1235.



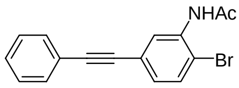
5-Ethynyl-2-(ethynylphenyl)-4-nitroaniline. See the general procedure for the deprotection of trimethylsilyl-protected alkynes. **74** (0.10 g, 0.27 mmol) was deprotected to the terminal alkyne and the free amine using the procedure described above using potassium carbonate (0.19 g, 1.35 mmol), methanol (15 mL), and methylene chloride (15 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.

5'-Amino-4,4'-diethynylphenyl-2'-nitro-1-thioacetylbenzene (75). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 5-ethynyl-2-(ethynylphenyl)-4-nitroaniline (0.08 g, 0.27 mmol), **3** (0.09 g, 0.32 mmol), copper(I) iodide (0.005 g, 0.01 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.01 mmol), diisopropylethylamine (0.20 mL, 1.08 mmol), and THF (20 mL) at 70 °C for 12 h. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/ hexanes as the eluent. $R_f = 0.32$. The reaction afforded 0.09 g (82 % yield over 3 steps) of the desired product as a yellow solid which turned yellowish-green upon standing. IR (KBr) 3466.7, 3364.1, 2205.1, 1702.6, 1615.4, 1548.7, 1507.7, 1476.9, 1307.7, 1246.2, 1117.9, 948.7, 912.8, 871.8, 820.5, 748.7, 682.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.61 (½ABq, *J*=8.4 Hz, 2H), 7.55 (m, 2 H), 7.41 (½ABq, *J*=8.4 Hz, 2 H), 7.41-7.35 (m, 3 H), 6.90 (s, 1 H), 4.93 (br s, 2 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.09, 150.93, 139.33, 134.98, 134.13, 132.46, 131.55, 130.06, 129.07, 128.49, 123.69, 121.94, 120.25, 117.91, 107.50, 97.51, 96.26, 87.50, 83.16, 30.45. HRMS Calcd $C_{24}H_{16}N_2O_3S$: 412.0882. Found: 412.0883.

1-Bromo-3-nitro-4-(trimethylsilylethynyl)benzene. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2,5-dibromonitrobenzene (1.37 g, 4.89 mmol), bis(triphenylphosphine)palladium(II) chloride (0.17 g, 0.25 mmol), copper(I) iodide (0.09g, 0.49 mmol), THF (30 mL), Hünig's base (3.41 mL, 19.56 mmol), and trimethylsilylacetylene (0.69 mL, 4.9 mmol) at 70 ^{o}C for 18 h. Due to difficulty in separation of products, full characterization was not achieved and the resulting mixture was carried on to the next reaction step. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J*=2.0 Hz, 1 H), 7.66 (dd, *J*=8.3, 2.0 Hz, 1 H), 7.49 (d, *J*=8.3 Hz, 1 H), 0.26 (s, 9 H).

2-Ethynyl-5-ethynylphenyl-1-nitrobenzene (77). 2,5-Dibromonitrobenzene **(76)** (4.0 g, 14.24 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.300 g, 0.427 mmol), copper(I) iodide (0.163g, 0.854 mmol), THF (30 mL), diisopropylethylamine (9.9 mL, 57.0 mmol), and trimethylsilylacetylene (2.21 mL, 15.66 mmol) were used at room temperature for 10 h following the general procedure for couplings. Flash column chromatography (silica gel using 2:1 hexanes/dichloromethane as eluent) afforded a mixture of products that was taken onto the next step. The product mixture (3.09 g), bis(triphenylphosphine)palladium(II) dichloride (0.217 g, 0.31 mmol), copper(I) iodide (0.118g, 0.62 mmol), THF (30 mL), diisopropylethylamine (7.2 mL, 41.44 mmol), and phenylacetylene (1.7 mL, 15.54 mmol) were used following the general procedure for couplings at 50 ºC for 15 h. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded a mixture of products that was taken onto the next step. The product mixture (1.95 g), potassium carbonate (4.2 g, 30.4 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product as an orange solid (1.23 g, 37% yield for three steps). IR (KBr) 3267.2, 3250.1, 3079.6, 2208.4, 2102.6, 1541.6, 1522.5, 1496.0, 1347.1, 1275.2, 900.9, 840.5, 825.0, 759.0, 688.0, 528.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.5 Hz, 1 H), 7.67 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.64 (d, *J* = 7.8 Hz, 1 H), 7.53 (m, 2 H), 7.37 (m, 3 H), 3.58 (s, 1 H). ^{13}*C* NMR (100 MHz, $CDCl_3$) δ 150.62, 135.82, 135.65, 132.24, 129.72, 128.97, 127.80, 125.51, 122.33, 117.01, 94.35, 87.04, 86.97, 78.82. HRMS calc'd for C_{16},H_9,N,O_2: 247.0633. Found: 247.0632.

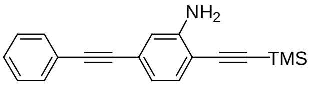
4,4'-Di(ethynylphenyl)-2'-nitro-1-thioacetylbenzene (78). See the standard procedure for Pd/Cu couplings. The compounds used were **77** (0.500 g, 2.02 mmol), **3** (0.675 g, 2.43 mmol), bis(dibenzylideneacetone)palladium(0) (0.232 g, 0.404 mmol), copper(I) iodide (0.077 g, 0.404 mmol), triphenylphosphine (0.212 g, 0.808 mmol), THF (10 mL), and diisopropylethylamine (0.7 mL, 4.04 mmol) at 50 ºC oil bath for 2 d. Column chromatography (silica gel using 2:1 dichloromethane/hexanes as eluent) afforded the desired product as an orange solid (0.381 g, 47% yield). IR (KBr) 3100, 2924, 2213.1, 1697.1, 1537.3, 1346.9, 1131.9, 831.9, 751.4, 684.9, 623.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 1.1, 0.3 Hz, 1 H), 7.70 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.61 (dt, *J* = 8.5, 1.9 Hz, 2 H), 7.54 (m, 2 H), 7.42 (dt, *J* = 8.5, 1.8 Hz, 2 H), 7.37 (m, 3 H), 2.43 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.10, 149.5, 135.30, 134.55, 134.27, 132.57, 131.84, 129.56, 129.26, 128.56, 127.65, 124.47, 123.40, 122.05, 117.5, 97.84, 93.82, 86.86, 86.31, 30.36. HRMS calculated for C_{24},H_{15},N,O_3, S: 397.0076. Found: 397.0773.



2-Bromo-5-(ethynylphenyl)acetanilide. See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2,5-Dibromoacetanilide (6.00 g, 17.76 mmol) was coupled to phenylacetylene (1.95 mL, 17.76 mmol) using copper(I) iodide (0.34 g, 1.78 mmol), bis(triphenylphosphine)palladium(II) chloride (0.62 g, 0.89 mmol), diisopropylethylamine (12.37 mL, 71.04 mmol), and THF (75 mL) at 75 ºC for 2.5 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. $R_f = 0.38$. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1

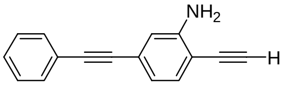
hexanes/ethyl acetate as the eluent. $R_f = 0.50$. The reaction afforded 1.79 g (32 % yield, 42 % based on a recovered 0.69 g of starting material) of the desired compound as a white solid. IR (KBr) 3282.1, 3159.0, 1661.5, 1559.0, 1507.7, 1461.5, 1405.1, 1379.5, 1271.8, 1107.7, 1066.7, 1015.4, 964.1, 892.3, 861.5, 820.5, 748.7, 682.1, 610.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (br s, 1 H), 7.92 (br s, 1 H), 7.55-7.49 (m, 2 H), 7.41-7.37 (m, 3 H), 7.32 (½ABq, *J*=8.3 Hz, 1 H), 7.20 (½ABq d, *J*= 6.4, *J*=1.8 Hz, 1 H), 2.25 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.15, 140.81, 133.62, 132.61, 130.32, 129.80, 127.70, 124.93, 123.33, 123.15, 111.69, 98.63, 84.65, 26.32. HRMS Calcd $C_{16}H_{12}BrNO$: 313.0102. Found: 313.0107.

3-Ethynylphenyl-6-(trimethylsilylethynyl)acetanilide (80). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-5-(ethynylphenyl)acetanilide (0.91 g, 2.90 mmol) was coupled to trimethylsilylacetylene (0.47 mL, 4.35 mmol) using copper(I) iodide (0.06 g, 0.29 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.15 mmol), diisopropylethylamine (2.02 mL, 11.60 mmol), and THF (20 mL) at 70 ºC for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. $R_f = 0.33$. The reaction afforded 0.81 g (84 % yield) of the desired compound as a yellow foam after drying in a vacuum atmosphere. IR (KBr) 3394.9, 3138.5, 2953.8, 2143.6, 1702.6, 1553.85, 1553.8, 1523.1, 1410.3, 1384.6, 1271.8, 1246.2, 1169.2, 1112.8, 1015.4, 846.2, 753.8, 687.2, 620.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (br s, 1 H), 7.91 (br s, 1 H), 7.55-7.49 (m, 2 H), 7.43-7.36 (m, 4 H), 7.15 (dd, *J*= 6.6, 1.5 Hz, 1 H), 2.24 (s, 3 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.09, 139.72, 132.62, 132.49, 130.27, 129.79, 128.06, 125.58, 123.63, 123.24, 112.98, 105.68, 99.09, 97.67, 85.26, 26.33, 1.28. HRMS Calcd $C_{21}H_{21}BrNOSi$: 331.1392. Found: 331.1391.



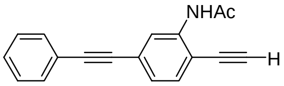
3-Ethynylphenyl-6-(trimethylsilylethynyl)aniline. A 100 mL round bottom flask equipped with a magnetic stirbar was charged with 3-ethynylphenyl-6-

(trimethylsilylethynyl)acetanilide (0.25 g, 0.75 mmol), hydrochloric acid (15 mL, 1.5 M), and THF (15 mL). The reaction mixture was heated to reflux for 2.5 h. The reaction progress was monitored by TLC. The reaction was quenched and extracted with water (3×) and diluted with methylene chloride. The organic layers were combined and dried over magnesium sulfate. Volatiles were removed in vacuo. Crude ^{1}H NMR and TLC showed two inseparable products with similar amine and aromatic resonances. Therefore, the crude reaction mixture was reacted further without purification.



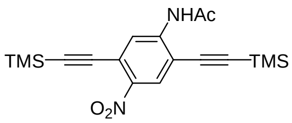
2-Ethynyl-5-(ethynylphenyl)aniline. See the general procedure for the deprotection of trimethylsilyl-protected alkynes. The compounds used were 3-ethynylphenyl-6-(trimethylsilylethynyl)aniline (0.22 g, 0.75 mmol) potassium carbonate (0.52 g, 3.75 mmol), methanol (15 mL), and methylene chloride (15 mL) for 2 h. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.

2´-Amino-4,4´-di(phenylethynyl)-1-thioacetylbenzene (81). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-ethynyl-5-(ethynylphenyl)aniline (0.16 g, 0.75 mmol), **3** (0.25 g, 0.90 mmol), copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.04 mmol), diisopropylethylamine (0.53 mL, 3.00 mmol), and THF (15 mL) at 45 ºC for 12 h. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:3 diethyl ether/hexanes as the eluent. R_f (product): 0.40. The reaction afforded 0.28 g (43% yield, over three steps) of the desired compound as a bright yellow solid. IR (KBr) 3138.5, 2205.1, 1702.6, 1610.3, 1384.6, 1117.9, 943.6, 825.6, 753.8, 692.3, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 4 H), 7.42-7.31 (m, 6 H), 6.92-6.87 (m, 2 H), 4.32 (br s, 2 H), 4.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.66, 148.20, 134.72, 132.40, 131.75, 128.89, 128.86, 128.84, 128383, 124.60, 124.10, 123.32, 121.49, 117.14, 108.58, 96.57, 91.32, 89.72, 85.78, 30.48. HRMS Calcd $C_{24}H_{17}NOS$: 367.1031. Found: 367.1032.

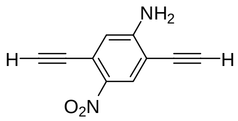


2-Ethynyl-5-(ethynylphenyl)acetanilide. See the general procedure for the deprotection of trimethylsilyl-protected alkynes. The compounds used were **80** (0.20 g, 0.60 mmol) potassium carbonate (0.25 g, 1.80 mmol), methanol (15 mL), and methylene chloride (15 mL) for 2 h. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.

2'-Acetamido-4,4'-di(phenylethynyl)-1-thioacetylbenzene (82). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-ethynyl-5-(ethynylphenyl)acetanilide (0.16 g, 0.60 mmol), **3** (0.20 g, 0.72 mmol) copper(I) iodide (0.01 g, 0.06 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.03 mmol), diisopropylethylamine (0.42 mL, 2.40 mmol), and THF (20 mL) at 70 ºC for 12 h. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 ethyl acetate/hexanes as the eluent. R_f (product): 0.35. The reaction afforded 0.12 g (50 % yield, two steps) of the desired compound as an off-white solid. IR (KBr) 3138.5, 2933.3, 1702.6, 1656.4, 1543.6, 1379.5, 1261.5, 1112.8, 1010.3, 948.7, 882.1, 820.5, 748.7, 682.1, 610.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (br s, 1 H), 7.96 (br s, 1 H), 7.58-7.52 (m, 4 H), 7.46 (½ABq, *J*=7.8 Hz, 1 H), 7.42-7.37 (m, 5 H), 7.23 (½ABq d, *J*= 8.1, 1.4 Hz, 1 H), 2.43 (s, 3 H), 2.27 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.62, 168.51, 139.39, 134.70, 132.48, 132.02, 131.88, 129.52, 129.09, 129.00, 126.87, 124.41, 124.25, 122.45, 122.27, 112.45, 98.38, 91.06, 90.61, 84.24, 30.48, 25.10. HRMS Calcd $C_{26}H_{19}NO_2S$: 410.1215. Found: 410.1212.



2,5-Bis(trimethylsilylethynyl)-4-nitroacetanilide. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were **68**[26] (0.60 g, 1.78 mmol), trimethylsilylacetylene (0.78 mL, 7.12 mmol), copper(I) iodide (0.07 g, 0.37 mmol), bis(triphenylphosphine)palladium(II) chloride (0.13 g, 0.18 mmol), diisopropylethylamine (2.48 mL, 14.24 mmol), and THF (20 mL) at 75 ºC for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 diethyl ether/hexanes as the eluent. R_f (product): 0.80. The reaction afforded 0.63 g (95% yield; 0.26 g of material as the product with the deprotected amino moiety instead of the acetamide was also obtained) of the desired product. IR (KBr) 3374.4, 3117.9, 2964.1, 2143.6, 1723.1, 1610.3, 1543.6, 1502.6, 1456.4, 1400.0, 1379.5, 1333.3, 1251.3, 1220.5, 1112.8, 882.1, 846.2, 759.0, 620.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1 H), 8.11 (s, 1 H), 8.07 (br s, 1 H), 2.25 (s, 3 H), 0.31 (s, 9 H), 0.26 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ169.27, 145.23, 143.53, 129.21, 124.94, 121.27, 112.68, 107.86, 107.26, 100.70, 98.57, 26.25, 1.08, 0.94. HRMS Calcd $C_{18}H_{24}N_2O_3Si_2$: 372.1325. Found: 372.1332.



2,5-Di(ethynyl)-4-nitroaniline. See the general procedure for the deprotection of trimethylsilyl-protected alkynes. The compounds used were 2,5-bis(trimethylsilylethynyl)-4-nitroacetanilide (0.60 g, 1.61 mmol), potassium carbonate (2.22 g, 16.10 mmol), methanol (40 mL), and methylene chloride (40 mL) for 2 h. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.

2,5-Diphenylethynyl-4',4''-dithioacetyl-4-nitroaniline (83). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2,5-

di(ethynyl)-4-nitroaniline (0.30 g, 1.61 mmol), **3** (1.09 g, 3.86 mmol) copper(I) iodide (0.06 g, 0.32 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.16 mmol), diisopropylethylamine (2.25 mL, 12.88 mmol), and THF (40 mL) at 50 °C for 2 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. $R_f = 0.52$. The reaction afforded 0.47g (57% over three steps) of the desired compound as a bright yellow solid. IR (KBr) 3476.9, 3364.1, 3117.9, 1687.2, 1625.6, 1543.6, 1507.7, 1476.9, 1384.6, 1307.7, 1246.2, 1117.9, 1010.3, 948.7, 825.6, 615.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.62 (½ABq, *J*=8.2 Hz, 2 H), 7.56 (½ABq, *J*=8.4 Hz, 2 H), 7.44 (½ABq, *J*=4.4 Hz, 2 H), 7.42 (½ABq, *J*=4.2 Hz, 2 H), 6.92 (s, 1 H), 4.90 (br s, 2 H), 2.45 (s, 3 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.00, 192.91, 150.99, 134.26, 134.25, 134.25, 134.13, 134.11, 132.45, 132.04, 130.16, 123.64, 123.09, 120.52, 118.01, 107.00, 96.59, 96.45, 87.44, 84.79, 30.44, 30.42. HRMS Calcd $C_{24}H_{17}NOS$: 487.0786. Found: 487.0792.

4-(Trimethylsilylethynyl)aniline. See the general procedure for the Pd/Cu cross couplings. The compounds used were 4-bromoaniline (6.88 g, 40 mmol), trimethylsilylacetylene (11.3 mL, 80 mmol), tetrakis(triphenylphosphine)palladium(0) (393 mg, 0.34 mmol), copper iodide (76 mg, 0.4 mmol) and diisopropylamine (40 mL) at 110-120° C for 12 h. The mixture was concentrated and filtered through a plug of silica get using 1:1 ethyl acetate/hexane. The filtrate was concentrated and purified on a silica gel column (1:5 ethyl acetate/hexane). IR (KBr) 3469, 3374, 2958, 2156, 2144, 1624, 1508, 1294, 1249 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2 H), 6.57 (d, *J* = 8.6 Hz, 2 H), 0.22 (s, 9 H).

4-Ethynylaniline. See the general procedure for the deprotection of trimethylsilyl alkynes. The compounds used were 4-(trimethylsilylethynyl)aniline (2.48 g, 13 mmol), potassium carbonate (11 g) and methanol (100 mL) for 12 h. Hexane was added to a highly concentrated ether solution to give fine crystals. The collected crystals were washed with hexane and dried in vacuo to afford 1.14 g (74 %) of the title compound. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.28 (d, *J* = 8.6 Hz, 2 H), 6.58 (d, *J* = 8.6 Hz, 2 H), 3.72- 3.88 (br, 2 H), 2.94 (s, 1 H). ^{13}C NMR (100 MHz, CDC1$_3$) δ 147.0, 133.5, 114.6, 111.4, 84.4, 74.9.

4'-Ethynylformanilide (84). A solution of 4-ethynylaniline (0.87 g, 6.0 mmol) in ethyl formate (40 mL) was heated to reflux for 24 h. After removal of the solvents by a rotary evaporation, another portion of ethyl formate (40 mL) was added and the solution was heated to reflux for 24 h. The evaporated residue was chromatographed on silica gel (1:2 ethyl acetate/hexane) to afford 0.65 g (75 %) of a slightly brown-white solid of the title compound. IR (KBr) 3292, 2107, 1686, 1672, 1601, 1536, 1407, 1314, 842, 668, 606 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.71 (d, *J* = 11.3 Hz, *a*), 8.38 (d, *J* = 1.5 Hz, *b*), 7.82-7.92 (br d, *J* = 10 Hz, *c*), 7.48 (dt, *J* = 14.5, 8.7 Hz, 3 H), 7.2 (br, *d*), 7.02 (d, *J* = 8.6 Hz, 1 H), 3.07 (s, *e*), 3.04 (s, *f*) where (a + b = 1 H, c + d = 1 H, e + f = 1 H).

85. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-bromo-4-nitro-5-(phenylethynyl)aniline (0.26 g, 0.83 mmol), **84** (0.15 g, 1.00 mmol), copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.04 mmol), diisopropylethylamine (0.58 mL, 3.32 mmol), and THF (25 mL) at 70 °C for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. R_f = 0.09. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of ethyl acetate as the eluent. R_f = 0.63. The reaction afforded an impure product of 0.23 g. The crude reaction product was taken on to the next synthetic step.

2´-Amino-4,4´-diphenylethynyl-5´-nitrobenzeneisonitrile (86). To an oven dried 100 mL round bottom flask equipped with a stirbar and a West condenser was added **85** (0.04 g, 0.10 mmol), triphenylphosphine (0.09 g, 0.33 mmol), triethylamine (0.04 mL, 0.39 mmol), carbon tetrachloride (0.03 mL, 0.31 mmol), and methylene chloride (10 mL).[31] The reaction was heated to 60 ºC for 5 h. The reaction mixture was cooled and quenched with water and extracted with methylene chloride (3×). Organic layers were combined and dried over $MgSO_4$. The volatiles were removed in vacuo. The crude reaction mixture was purified by gravity liquid chromatography using silica gel as the stationary phase and ethyl acetate as the eluent. R_f = 0.85. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.30. The reaction afforded 0.03 g (83 % yield, two steps) of the desired material. IR (KBr) 3450.62, 3358.15, 2925.78, 2855.52, 2200.00, 2114.03, 1618.06, 1542.38, 1506.39, 1432.51, 1367.16, 1309.39, 1246.34, 1203.57, 1144.72, 1097.07, 995.30, 835.22, 749.25, 470.10 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$) δ 8.32 (s, 1 H), 7.68-7.55 (m, 4 H), 7.45-7.37 (m, 5 H), 6.97 (s, 1 H), 4.89 (br s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.38, 133.03, 132.52, 132.07, 130.82, 129.74, 129.03, 128.89, 127.11, 126.98, 123.92, 122.86, 121.80, 118.54, 106.73, 98.30, 95.78, 86.36, 86.16. HRMS Calcd $C_{23}H_{13}N_3O_2$: 363.1008. Found: 363.1008.

1-Bromo-4-*n*-hexylbenzene. The procedure of Ranu et al. was followed.[33] In an 125 mL flask, bromine (0.52 mL, 10 mmol) was absorbed onto neutral, Brockmann grade I, alumina (10 g). 1-Phenylhexane (1.88 mL, 10 mmol) was absorbed onto neutral alumina (10 g) in a second 125 mL flask. The contents of both flasks were combined in a 250 mL flask equipped with a magnetic stirbar. The reaction was complete within 1 min when the dark orange color of the bromine became light yellow. The solid mass was then poured in a column that contained a short plug of silica gel. The desired product was eluted with methylene chloride to give 2.58 g of a 80:15:5 mixture (desired product: starting material: *ortho*-substituted product) as judged by ^1H NMR. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J*=8.2 Hz, 2 H), 7.03 (d, *J*=8.2 Hz, 2 H), 2.54 (t, *J*=7.5 Hz, 2 H), 1.60 (p, *J*=7.1 Hz, 2 H), 1.38-1.24 (m, 8 H), 0.92-0.84 (m , 3 H).

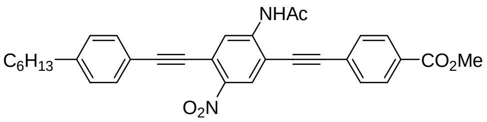
1-*n*-Hexyl-4-(trimethylsilylethynyl)benzene. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 1-bromo-4-*n*-hexylbenzene (7.23 g, 30.0 mmol) trimethylsilylacetylene (5.94 mL, 42.0 mmol), copper(I) iodide (0.69 g, 3.6 mmol), bis(triphenylphosphine)palladium(II) chloride (0.84 g, 1.2 mmol), triphenylphosphine (1.57 g, 6.0 mmol), triethylamine (30.36 mL, 300 mmol), and THF (30 mL) at 85 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and hexanes as the eluent. The reaction afforded 5.26 g (68 % yield) of the desired material. IR (KBr) 2923.1, 2851.3, 2158.2, 1923.1, 1507.7, 1461.5, 1405.1, 1246.2, 1220.5, 861.5, 835.9, 753.8, 600.0 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J*=8.0 Hz, 2 H), 7.07 (d, *J*=8.1 Hz, 2 H), 2.56 (t, *J*=7.7 Hz, 2 H), 1.62-1.50 (m, 2 H), 1.28 (br s, 8 H), 0.86 (br t, 3 H), 0.22 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.48, 131.75, 128.18, 120.17, 105.36, 93.15, 35.95, 31.76, 31.24, 28.95, 22.68, 14.18, 0.17. HRMS calcd $C_{17}H_{26}Si$: 258.1804. Found: 258.1793.

1-Ethynyl-4-*n*-hexylbenzene. See the general procedure for the deprotection of trimethylsilyl-protected alkynes. The compounds used were 1-*n*-hexyl-4-(trimethylsilylethynyl)benzene (0.18 g, 0.7 mmol), potassium carbonate (0.48 g, 3.5 mmol), methanol (10 mL), and methylene chloride (10 mL) for 2 h. The material was immediately reacted in the next step without additional purification or identification.

2-Bromo-5-(4′-*n*-hexylphenylethynyl)-4-nitroacetanilide (88). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were **68** (1.42 g, 4.21 mmol) 1-ethynyl-4-*n*-hexylbenzene (0.95 g, 3.83 mmol), copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.07 g, 0.38 mmol), diisopropylethylamine (2.69 mL, 15.38 mmol), and THF (20 mL) at 75 °C for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of methylene chloride as the eluent. R_f (product): 0.58. The reaction afforded 0.52 g (31% yield, two steps) of the desired material. IR (KBr) 3276.65, 3086.57, 3016.72, 2926.07, 2852.18, 2213.34, 1671.79, 1592.84, 1560.91, 1534.12, 1500.11, 1460.89, 1389.78, 1337.01, 1260.89, 1093.45, 1020.52, 894.33, 813.73, 743.88, 631.04, 464.48, 442.99 cm^{-1}. ^{1}H NMR (400 MHz, $CHCl_3$) δ 8.83 (s, 1 H), 8.39 (s, 1 H), 7.81 (br s, 1 H), 7.35 (ABq, *J*=8.3 Hz, Δν=110.6 Hz, 4 H), 2.65 (t, *J*=7.6 Hz, 2 H), 2.33 (s, 3 H), 1.63 (p, *J*=7.8, 6.1, 2 H), 1.40-1.22 (m, 6 H), 0.93 (t, *J*= 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.83, 145.36, 144.28, 140.22, 132.55, 129.38, 129.03, 125.18, 120.44, 119.69, 111.21, 99.49, 84.76, 36.43, 32.08, 31.53, 29.32, 25.49, 22.99, 14.49. HRMS Calcd $C_{22}H_{23}{}^{79}BrN_2O_3$: 442.0892. Found: 442.0895.

Methyl 4-(trimethylsilylethynyl)benzoate. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were methyl 4-iodobenzoate (5.00 g, 19.1 mmol), bis(triphenylphosphine)palladium(II) chloride (0.670 g, 0.955 mmol), copper(I) iodide (0.36 g, 1.91 mmol), THF (50 mL), diisopropylethylamine (13.31 mL, 76.4 mmol) and trimethylsilylacetylene (3.51 mL, 24.8 mmol) at 60°C for 18 h. Column chromatography (silica gel, 1:1 hexanes/methylene chloride) afforded the desired product (4.34 g, 98% yield) as orange crystals. IR (KBr) 2958.6, 2159.9, 1720.7, 1603.2, 1443.2, 1404.8, 1278.3, 1243.6, 1171.1, 1110.5, 1017.0, 841.6, 771.1 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dt, *J*=8.7 Hz, 1.7 Hz, 2 H), 7.54 (dt, *J*=8.6, 1.7 Hz, 2 H), 3.94 (s, 3 H), 0.28 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 132.06, 129.89, 129.57, 127.97, 104.27, 97.88, 52.40, 0.029. HRMS calculated for $C_{13}H_{16}O_2Si$: 232.091959. Found: 232.0919

Methyl 4-ethynylbenzoate (89). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. The compounds used were methyl 4-(trimethylsilylethynyl)benzoate (0.75 g, 3.23 mmol), potassium carbonate (2.23 g, 16.15 mmol), methanol (50 mL) and methylene chloride (50 mL) for 2 h. Extraction of the product afforded 0.49 g of the desired product that was immediately reacted in the next step.



Methyl 2′-acetamido-4,4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoate. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were **88** (0.23 g, 0.52 mmol), **89** (0.11 g, 0.68 mmol), copper(I) iodide (0.01 g, 0.05 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.03 mmol), diisopropylethylamine (0.36 mL, 2.08 mmol), and THF (15 mL) at 75 °C for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of methylene chloride as the eluent. R_f: 0.20. The reaction afforded 0.26 g (96 % yield) of the desired material. IR (KBr) 3426.99, 3286.07, 2926.72, 2844.78, 2361.19, 2334.33, 2194.63, 1722.66, 1671.72, 1602.42, 1546.11, 1494.92, 1426.27, 1407.39, 1339.77, 1276.39, 1173.17, 1105.95, 760.00 cm^{-1}. ^{1}H NMR (400 MHz, $CHCl_3$) δ 8.86 (s, 1 H), 8.33 (s, 1 H), 8.06 (br s, 1 H), 7.85 (ABq, *J*=6.8 Hz, Δν=188.8 Hz, 4 H), 7.35 (ABq, *J*=8.2 Hz, Δν=170.20 Hz, 4 H), 3.98 (s, 3 H), 2.66 (t, *J*=7.6 Hz, 2 H), 2.35 (s, 3 H), 1.65 (p, *J*=7.8, 6.1 Hz, 2 H), 1.40-1.37 (m, 6 H), 0.93 (t, *J*=6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.70, 166.52, 145.43, 144.23, 142.39, 132.65, 132.03, 131.37, 130.30, 129.15, 129.03, 126.09, 123.95, 121.65, 119.74, 111.04, 100.61, 98.76, 85.46, 85.05, 52.86, 36.45, 32.08, 31.54, 29.32, 25.56, 22.99, 14.48. HRMS Calcd $C_{32}H_{30}N_2O_5$: 522.2155. Found: 522.2147.

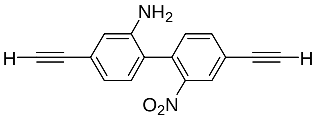
Methyl 2′-amino-4,-4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoate (90). To a 100 mL round bottom flask equipped with a magnetic stirbar was added methyl 2′-acetamido-4,4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoate (0.10 g, 0.19 mmol), potassium carbonate (0.16 g, 1.15 mmol), methanol (15 mL), and methylene chloride (15 mL). The reaction mixture was allowed to react at room temperature for 1 h. The reaction was quenched with water and extracted with methylene chloride (3×). Organic layers were combined and dried over $MgSO_4$. Volatiles were removed in vacuo. No further purification was needed. The reaction afforded 0.09 g (99 % yield) of the desired material. IR (KBr) 3475.47, 3362.54, 2914.63, 2850.15, 2205.37, 1706.79, 1629.40, 1596.36, 1543.77, 1519.70, 1426.27, 1316.01, 1290.51, 1279.59, 1173.73, 1141.49, 1114.87, 760.00, 679.40, 614.93, 469.85 cm^{-1}. ^{1}H NMR (400 MHz, $CHCl_3$) δ 8.31 (s, 1 H), 7.85 (ABq, *J*= 8.6 Hz, Δν=182.9 Hz, 4 H), 7.36 (ABq, *J*=8.2 Hz, Δν=129.83 Hz, 4 H), 6.95 (s, 1 H), 4.92 (br s, 2 H), 3.96 (s, 3 H), 2.64 (t, *J*=7.6 Hz, 2 H), 1.65 (p, *J*=7.7, 6.8 Hz, 2 H), 1.36-1.27 (m, 6 H), 0.91 (t, *J*=7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.74, 151.42, 145.13, 139.96, 132.46, 131.92, 130.77, 130.64, 130.10, 129.00, 127.11, 121.96, 120.01, 118.38, 106.80, 98.72, 96.69, 86.51, 85.81, 52.75, 36.42, 32.08, 31.56, 29.32, 22.99, 14.47. HRMS Calcd $C_{30}H_{28}N_2O_4$: 480.2049. Found: 480.2050.

2´-Amino-4,4´-diphenylethynyl-4´´-*n*-hexyl-5´-nitrobenzoic acid (91). The procedure by Corey et al. was followed.[34] To a 250 mL round bottom flask equipped with a magnetic stirbar was added **90** (0.07 g, 0.15 mmol), lithium hydroxide (0.02, 0.75 mmol), methanol (9 mL), methylene chloride (5 mL), and water (3 mL). The reaction mixture was allowed to stir at room temperature for 2.5 d. The reaction was quenched with water and extracted with methylene chloride (3×). The yellow aqueous phases were combined and acidified to pH = 3 whereupon a yellow solid precipitated. The solid material was collected on a fritted funnel. The collected solid reaction mixture was purified by gravity column chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.10. The reaction afforded 0.065 g (94 % yield) of the desired material. IR (KBr) 3460.77, 3378.60, 2957.49, 2921.54, 2844.51, 2207.7, 1580.98, 1542.74, 1428.19, 1385.56, 1307.71, 1242.23, 1108.70, 774.89, 646.51, 615.69, 456.49 cm^{-1}. ^{1}H NMR (400 MHz, MeOH) δ 8.22 (s, 1 H), 7.72 (ABq, *J*=8.5 Hz, Δν=142.14 Hz, 4 H), 7.38 (ABq, *J*=8.2 Hz, Δν=97.07 Hz, 4 H), 6.99 (s, 1 H), 2.61 (t, *J*=7.6 Hz, 2 H), 1.69-1.59 (m, 2 H), 1.42-1.28 (m, 6 H), 0.96-0.86 (m, 3 H).

4,4´-Dibromo-2,2´-dinitrobiphenyl (92).[35] In a large oven dried screw capped tube equipped with a magnetic stirbar was added 2,2´-dinitrobiphenyl (2.44 g, 10.0 mmol) and silver acetate (4.01 g, 24.0 mmol). Glacial acetic acid (20 mL), sulfuric acid (2.03 mL, 38.0 mmol), and bromine (1.54 mL, 30.0 mmol) were sequentially added and the reaction vessel was capped. The reaction vessel was heated to 80 ºC for 16 h. The reaction mixture was cooled and was poured into ice water. The solid material was then collected by filtration. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.58. The reaction afforded 1.43 (36 % yield) of the desired material as a yellow solid. IR (KBr) 3097.4, 2861.5, 1523.1, 1384.6, 1338.5, 1271.8, 1241.0, 1148.7, 1092.3, 1000.0, 892.3, 835.9, 764.1, 723.1, 697.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J*=2.0 Hz, 2 H), 7.81 (dd, *J*=2.0, 8.2 Hz, 2 H), 7.15 (d, *J*=8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.07, 136.34, 131.76, 131.69, 127.81, 122.66. HRMS Calcd $C_{12}H_6Br_2N_2O_4$: 399.8694. Found: 399.8675.

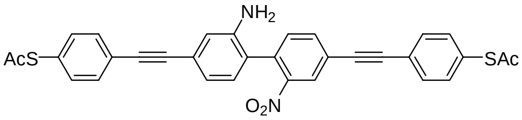
4,4´-Bis(trimethylsilylethynyl)-2,2´-dinitrobiphenyl (93). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 4,4´-dibromo-2,2´-dinitrobiphenyl (1.50 g, 3.73 mmol), trimethylsilylacetylene (1.32 mL, 9.33 mmol), copper(I) iodide (0.07 g, 0.37 mmol), bis(triphenylphosphine)palladium(II) chloride (0.13 g, 0.19 mmol), triphenylphosphine (0.20 g, 0.75 mmol), triethylamine (1.62 mL, 14.92 mmol), and THF (25 mL) at 75 ºC for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.55. The reaction afforded 1.44 g (88 % yield) of the desired compound as a very viscous yellow liquid. IR (KBr) 3743.6, 3651.3, 3076.9, 2953.8, 2892.3, 2153.8, 2061.8, 1943.6, 1876.9, 1805.1, 1610.4, 1523.3, 1477.1, 1405.3, 1338.6, 1256.6, 1215.6, 1143.8, 1092.5, 1000.2, 928.4, 851.5, 759.2, 692.5, 641.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J*=1.6 Hz, 2 H), 7.71 (dd, *J*=6.2, 0.7 Hz, 2 H), 7.20 (d, *J*=6.9 Hz, 2 H), 0.19 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.76, 136.22, 133.26, 130.71, 128.04, 124.97, 101.67, 98.74, -0.07. HRMS Calcd $C_{22}H_{24}N_2O_4Si_2$: 436.1275. Found: 436.1281.

2-Amino-4,4´-bis(trimethylsilylethynyl)-2´-nitrobiphenyl (94). **93** (0.70 g, 1.60 mmol), glacial acetic acid (15 mL), and THF (15 mL) were added to a 100 mL round bottom flask equipped with a magnetic stirbar and a West condenser. The reaction mixture was heated to reflux. Iron powder (0.20 g, 3.52 mmol) was carefully added to the refluxing reaction mixture.[36] The reaction mixture was allowed to reflux for 2 h while being monitored by TLC. The reaction mixture was cooled, quenched with water, and filtered through filter paper to remove unreacted iron. The filtrate was extracted with brine (3×) and diluted with methylene chloride. Organic layers were combined and dried over magnesium chloride. Volatiles were removed in vacuo. The crude reaction mixture was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.68. The reaction afforded 0.13 g (21 % yield, 33 % based on a recovered 0.26 g of starting material) of the desired material. IR (KBr) 3469.7, 3382.5, 2953.8, 2154.7, 1617.1, 1529.9, 1479.1, 1413.7, 1346.2, 1242.5, 848.4, 759.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J*=1.7 Hz, 1 H), 7.68 (dd, *J*=7.8, 1.6 Hz, 1 H), 7.36 (d *J*= 7.8 Hz, 1 H), 6.93-6.86 (m, 3 H), 3.49 (s, 2 H), 0.28 (s, 9 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.08, 143.25, 135.73, 132.67, 132.41, 128.92, 127.58, 124.33, 124.19, 123.13, 122.56, 118.91, 104.72, 101.77, 98.24, 94.43, 0.09, -0.12. HRMS Calcd $C_{22}H_{26}N_2O_2Si_2$: 406.1533. Found: 406.1532.



2-Amino-4,4´-diethynyl-2´-nitrobiphenyl. See the general procedure for the deprotection of trimethylsilyl-protected alkynes. The compounds used were **94** (0.13 g, 0.33 mmol), potassium carbonate (0.46 g, 3.30 mmol), methanol (10 mL) and methylene chloride

(10 mL) for 2 h. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.



95. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-amino-4,4´-diethynyl-2´-nitrobiphenyl (0.09 g, 0.33 mmol), **3** (0.22 g, 0.79 mmol), copper(I) iodide (0.02 g, 0.10 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.03 mmol), diisopropylethylamine (0.46 mL, 2.64 mmol), and THF (10 mL) at 50 ºC for 2 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.55. The reaction afforded 0.11 g (61 % yield, two steps) of the desired compound as a bright yellow solid. IR (KBr) 3128.2, 2924.8, 2859.4, 1718.8, 1348.6, 1261.1, 1108.5, 948.7, 825.2, 614.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J*=1.2 Hz, 1 H), 7.78 (dd, *J*=6.2, 1.6 Hz, 1 H), 7.58 (dd, *J*=6.6, 1.8 Hz, 2 H), 7.54 (d, *J*=8.6 Hz, 2 H), 7.46-7.36 (m, 5 H), 7.02-6.94 (m, 3 H), 3.59 (s, 2 H), 2.45 (s, 3 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.26, 192.96, 149.29, 143.50, 135.56, 134.24, 134.14, 132.74, 132.66, 132.44, 132.36, 132.26, 132.14, 129.17, 128.02, 127.35, 124.42, 124.22, 124.09, 123.21, 122.38, 118.631, 91.64, 90.84, 88.86, 88.12, 30.48, 30.42. HRMS Calcd $C_{32}H_{22}N_2O_4S_2$: 563.1099. Found: 563.1094.

3,3´-Dinitro-2,2´-bipyridyl (97).[37] To a 250 mL round bottom flask equipped with a magnetic stirbar and a West condenser was added 2-chloro-3-nitropyridine (15.0 g, 94.61 mmol) and copper bronze (15.03 g, 236.53 mmol). DMF (100 mL) was added and the reaction mixture was heated to reflux for 18 h. The reaction mixture was cooled and filtered through a pad of celite. The filter cake was washed with hot DMF. The filtrate was poured into 1 L of water and the desired material precipitated. The solid material was collected on a fritted funnel to give 3.57 g (35 % yield) of a golden brown solid. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.91 (dd, *J*=4.8, 1.5 Hz, 2 H), 8.60 (dd, *J*=8.3, 1.5 Hz, 2 H), 7.67 (dd, *J*=8.4, 4.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.52, 151.79, 144.33, 133.44, 124.65.

5,5´-Dibromo-3,3´-dinitro-2,2´-bipyridyl (98). To a 100 mL round bottom flask equipped with a magnetic stirbar was added **97** (1.00 g, 4.06 mmol). The starting material was dissolved in MeOH (50 mL) and CH_2Cl_2 (50 mL). In a separate 100 mL two necked round bottom flask was added KBr (9.66 g, 81.2 mmol), and then bromine (4.33 mL, 81.2 mmol) was slowly added.[38] The KBr/Br_2 mixture was slowly transferred via cannula over 30 min to the first flask containing the bipyridine. The desired material precipitated and was collected on a fritted funnel. The collected solid was added to an oven dried pressure tube equipped with a magnetic stirbar and capped with a septum. Bromine (0.42 mL, 8.12 mmol) was added, the septum was removed and the reaction vessel was quickly sealed with a screw cap then heated to 180 ºC for 3 d. The reaction was cooled and poured into a solution of ice water. 1 M $NaHSO_3$ (aq) was added to react with any unreacted bromine. The solution was made alkaline with NaOH (s). The resulting solution was extracted with CH_2Cl_2 (4×). The organic layers were combined and dried over $MgSO_4$. Volatiles were removed in vacuo. The reaction mixture was purified by gravity liquid chromatography using silica gel as the stationary phase and 2:3 ethyl acetate/hexanes as the eluent mixture. $R_f = 0.41$. The reaction afforded 0.52 g (45 % yield). IR (KBr) 3425.07, 3059.70, 1578.41, 1544.96, 1428.03, 1345.68, 1232.84, 1104.05, 1027.57, 897.37, 879.49, 789.60, 749.49, 649.64, 551.72, 475.22 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J*=2.0 Hz, 2 H), 8.67 (d, *J*= 2.1 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ154.26, 148.55, 143.76, 135.50, 120.86. HRMS Calcd $C_{10}H_4Br_2N_4O_4$: 401.8600. Found: 401.8603.

4-(Trimethylsilylethynyl)benzaldehyde. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 4-iodobenzaldehyde (0.5 g, 2.15 mmol), THF (2.7 mL), trimethylsilylacetylene (0.44 mL, 0.31g, 3.18 mmol), diisopropylethylamine (0.6 mL, 3.5 mmol), bis(triphenylphosphine)palladium(II) chloride (4 mg, 0.21 mmol) and copper iodide (0.0020 g, 2.1 mmol) at room temperature for 24 h. After workup, the residue was purified by silica gel column chromatography using hexane/methylene chloride (1:1) to provide 0.063 g (73%) of the title compound as a brown solid. MP: 60-66°C. IR (KBr) 2955.6, 2833.4, 2722.2, 2144.5, 1700.0, 1594.5, 1555.6, 1383.3, 1294.5, 1244.5, 1200.0, 1155.6, 861.1, 838.9, 755.6, 661.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.98 (s, 1 H), 7.81 (d, *J* = 8.37 Hz, 2 H), 7.59 (d, *J* = 8.28 Hz, 2 H), 0.13 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 191.38, 135.59, 132.47, 129.34, 103.83, 99.02, -0.21. Anal. Calcd for $C_{12}H_{14}OSi$: C, 71.00; H, 6.95. Found: C, 71.29; H, 6.96.

4-Ethynylbenzaldehyde. According to the general procedure, the compounds used were 4-(trimethylsilylethynyl)benzaldehyde (0.093 g, 0.45 mmol), methylene chloride (5 mL), methanol (5 mL) and potassium carbonate (0.47 g, 3.42 mmol) for 6 h The residue was purified by silica gel column chromatography using methylene chloride to provide 0.056 g (95%) of the title compound as a pale yellow solid. MP: 84-86°C. IR (KBr) 3210.3, 1696.9, 1682.0, 1600.0, 1550.0, 1384.6, 1205.1, 1164.1, 825.6, 738.5 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.01 (s, 1 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.25 Hz, 2 H), 3.27 (s, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.38, 137.06, 133.83, 130.62, 129.43, 83.84, 82.28. FABMS Calcd for C_9H_6O: 130. Found: 130.

4-Thioacetyldiphenylethynylcarboxaldehyde (110). See the Pd/Cu coupling protocol. The compounds used were 4-ethynylbenzaldehyde (0.049 g, 0.37 mmol), **3** (0.123 g, 0.44 mmol), bis(triphenylphosphine)palladium(II) chloride (0.013 g, 0.06 mmol), copper iodide (0.35 mg, 0.18 mmol) and THF (0.2 mL). The residue was purified by silica gel column chromatography using methylene chloride/hexane (1:1) as the eluent. The solvent was removed in vacuo to afford 0.078 g (75%) of the title product as a yellow solid. MP: 122-123°C. IR (KBr) 3138.5, 2841.0 1697.4, 1594.9, 1379.5, 1287.2, 1123.1, 959.0, 820.5, 723.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.10 (s, 1 H), 7.84 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 8.25 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.14, 192.31, 136.67, 135.34, 134.17, 133.27, 130.67, 130.26, 130.04, 124.76, 93.68, 91.18, 31.66. FABMS Calcd for $C_{17}H_{12}O_2S$: 280. Found: 280. Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.34. Found: C, 72.21; H, 4.35.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(phenyl)porphyrin (111). A solution of **110** (0.10 g, 0.35 mmol) and *meso*-phenyldipyrrromethane **(102)**[41] (0.079 g, 0.36 mmol), in $CHCl_3$ (36 mL) at room temperature was degassed under nitrogen for 15 min. This was followed by the addition of two drops of $BF_3{}^{\cdot}OEt_2$. The solution was left stirring under nitrogen for 1 h after which time DDQ (0.081 g, 0.36 mmol) was added and stirring continued for another 1 h. The solvent was removed in vacuo and the crude sample was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification with methylene chloride/hexane (1:1) to provide 0.047 g (27%) of the title compound in the first major fraction as a purple powder. MP: 200-204°C. IR (KBr) 3435.9, 3128.2, 1625.6, 1384.6, 1123.1, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (m , 8 H), 8.19 (d, *J* = 7.92 Hz, 8 H), 7.91 (d, *J* = 7.83 Hz, 4 H), 7.70-7.76 (m, 10 H), 7.45 (d, *J* = 8.19 Hz, 4 H), 2.46 (s, 6 H), -2.79 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.49, 142.47, 141.99, 134.59, 134.52, 134.32, 132.31, 130.06, 128.24, 127.79, 126.71, 124.52, 122.48, 122.43, 120.53, 120.44, 119.47, 119.37, 119.31, 119.21, 91.0, 89.81, 30.32. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 450.92 (5.52), 570.12 (3.23), 619.50 (3.91), 670.58 (4.73). FABMS Calcd for $C_{64}H_{42}N_4O_2S_2$: 962. Found: 962. Anal. Calcd for $C_{64}H_{42}N_4O_2S_2.CHCl_3$: C, 72.11; H, 4.00; N, 5.17. Found: C, 73.15; H, 4.33; N, 5.17.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(4-methylphenyl)porphyrin (112). See the preparation of **111** for the synthetic protocol. The compounds used were **110** (0.125 g, 0.45 mmol), *meso*-(4-methylphenyl)dipyrrromethane **(103)**[41] (0.1 g, 0.45 mmol), $CHCl_3$ (36.66 mL), two drops of $BF_3{}^{\cdot}OEt_2$, and DDQ (0.10 g, 0.45 mmol). The solvent was removed *in vacuo* and the sample was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification with methylene chloride/hexane (1:1) to provide 0.059 g (27%) of the title compound in the first major fraction as a purple solid. MP: 214-216°C. IR (KBr) 3433.3, 3128.2, 1704.3, 1464.5, 1384.6, 1108.5, 963.2, 796.2, 730.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89-8.84 (m, 8 H), 8.19 (d, *J* = 8.19 Hz, 4 H), 8.07 (d, *J* = 7.89 Hz, 4 H), 7.9 (d, *J* = 7.95 Hz, 4 H), 7.68 (d, *J* = 8.22 Hz, 4 H), 7.53 (d, *J* = 7.89 Hz, 4 H), 7.45 (d, *J* = 8.34 Hz, 4 H), 2.69 (s, 6 H), 2.46 (s, 6 H), -2.75 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.50, 142.58, 139.07, 137.45, 134.58, 134.48, 134.32, 132.31, 130.04, 131.00, 128.22, 127.44, 124.54, 122.37, 120.70, 120.53, 119.16, 119.00, 91.03, 89.77, 30.32, 21.52. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 456.03 (5.20), 617.80 (3.59), 679.10 (4.42). HRFABMS Calcd for $C_{66}H_{46}N_4O_2S_2$: 990.3062. Found: 990.3080. Anal. Calcd for $C_{66}H_{46}N_4O_2S_2$: C, 79.97; H, 4.67; N, 5.65. Found: C, 80.42; H, 4.98; N, 5.97.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(4-bromophenyl)porphyrin (113). See the preparation of **111** for the synthetic protocol. The compounds used were **110** (0.061 g, 0.22 mmol), *meso*-(4-bromophenyl)dipyrromethane **(104)**[41] (0.065 g, 0.22 mmol), $CHCl_3$ (21.87 mL), two drops of $BF_3{\cdot}OEt_2$and DDQ (0.049 g, 0.22 mmol). The solvent was removed in vacuo and the crude sample was purified by silica gel column chromatography using methylene chloride followed by a second column purification with methylene chloride/hexane (1:1) to provide 0.034 g (28%) of the title compound in the first major fraction as a purple solid. MP: 204-206 °C. IR (KBr) 3435.9, 3138.5, 2923.1, 1625.6, 1461.5, 1384.6, 1117.9, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (m, 8 H), 8.21 (d, *J* = 8.07 Hz, 4 H), 8.05 (d, *J* = 8.04 Hz, 4 H), 7.91 (m, 8 H), 7.68 (d, *J* = 8.22 Hz, 4 H), 7.48 (d, *J* = 8.19 Hz, 4 H), 2.46 (s, 6 H), -2.82 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.50, 142.25, 142.21, 140.86, 135.82, 134.57, 134.33, 132.43, 132.31, 130.10, 129.96, 128.27, 124.47, 122.59, 122.58, 119.69, 118.90, 90.90, 89.91, 30.34. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 458.68 (5.69), 571.82 (3.32), 675.69 (4.92), 621.20 (4.10). HRFABMS calcd for $C_{64}H_{40}Br_2N_4O_2S_2$: 1119.1038. Found: 1119.1039. Anal. Calcd for $C_{64}H_{40}Br_2N_4O_2S_2$: C, 68.57; H, 3.59; N, 4.99. Found: C, 67.81; H, 3.92; N; 4.86.

5,15-Bis(4-thioacetyldiphenylethynyl)-10,20-bis(4-iodophenyl)porphyrin (114). See the preparation of **111** for the synthetic protocol. The compounds used were **110** (0.060 g, 0.21 mmol), *meso*-(4-iodophenyl)dipyrrromethane **(105)**[41] (0.075 g, 0.21 mmol), $CHCl_3$ (43 mL), two drops of $BF_3{\cdot}OEt_2$ and DDQ (0.049 g, 0.21 mmol). The solvent was removed in vacuo and the crude sample was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification with methylene chloride/hexanes (1:1, v/v) to provide 0.034 g (28%) of the title compound in the first major fraction as a purple powder. MP = 216-218 °C. IR (KBr) 3435.9, 3128.2, 1466.7, 1384.6, 1117.9, 800 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.86-8.83 (m, 8 H), 8.17 (d, *J* = 8.13 Hz, 4 H), 8.05 (d, *J* = 8.19 Hz, 4 H), 7.89 (d, *J* = 7.95 Hz, 8 H), 7.67 (d, *J* = 8.22 Hz, 4 H), 7.45 (d, *J* = 8.19 Hz, 4 H), 2.46 (s, 6 H), -2.84 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.26, 143.26, 142.51, 137.13, 136.94, 135.59, 135.34, 133.34, 132.10, 131.14, 129.40 125.54, 123.67, 120.76, 120.07, 95.40, 92.07, 91.07, 31.61. HRFABMS Calcd for $C_{64}H_{40}I_2N_4O_2S_2$: 1214.0682. Found: 1214.0759. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 457.88 (5.44), 578.63 (3.35), 614.39 (3.85), 673.99 (4.66). Anal. Calcd for $C_{64}H_{40}I_2N_4O_2S_2.CHCl_3$: C, 58.51; H, 3.09; N; 4.19. Found: C, 57.85; H, 3.15; N, 4.54.

***Meso*-(4-thioacetyldiphenylethynyl)dipyrromethane (115).** A solution of pyrrole (6 mL, 87 mmol) and **110** (0.055 g, 0.19 mmol) in methanol (0.27 mL) was treated with acetic acid (0.82 mL) under nitrogen at room temperature for 20 h. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic phase was dried over $MgSO_4$ and the solvents were removed in vacuo. The crude sample was purified by silica gel column chromatography using methylene chloride/triethylamine (100:1, v/v) and was isolated as the second light yellow band. The solvent was removed in vacuo to provide 0.067 g (86%) of the title product as a tan viscous oil. IR (KBr) 3394.9, 3169.2, 1384.6, 1117.9, 1025.6, 769.2, 717.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (br s, 2 H), 7.53 (d, *J* = 8.13 Hz, 2 H), 7.45 (d, *J* = 8.25 Hz, 2 H), 7.37 (d, *J* = 8.04 Hz, 2 H), 7.19 (d, *J* = 8.31 Hz, 2 H), 6.7 (br s, 2 H), 6.17 (dd, *J* = 5.4, 2.6 Hz, 2 H), 5.89 (br s, 2 H), 2.41 (s, 3 H), 5.41 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.43, 142.75, 134.17, 132.12, 131.92, 128.44, 127.96, 124.485, 121.405, 117.45, 108.43, 107.39, 90.96, 88.72, 43.94, 30.43. HRFABMS Calcd for $C_{25}H_{20}N_2OS$: 396.1296. Found: 396.1303.

5,10,15,20-*tetrakis*(4-thioacetyldiphenylethynyl)porphyrin (116). To a stirred solution of **110** (0.062 g, 0.22 mmol) and pyrrole (0.015 g, 0.22 mmol) in $CHCl_3$(22 mL) that contained 0.75% EtOH was added two drops of $BF_3{\cdot}OEt_2$. The reaction mixture was allowed to stir under nitrogen for 5 h. After 5 h, *p*-chloranil (0.05 g, 0.22 mmol) was added and the reaction mixture stirred for another 1 h. The solvent was removed in vacuo and the crude residue was purified by silica gel column chromatography using methylene chloride as the eluent followed by a second column purification using methylene chloride/hexane (5:1). The solvent was removed in vacuo to provide 0.02 g (29%) of purple solid. MP: 168-170°C. IR (KBr): 3403.2, 3128.2, 1703.3, 1464.5, 1336.4, 1304.7, 11108.5, 956.0, 883.3, 796.2, 738 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 8 H), 8.19 (d, *J* = 8.13 Hz, 8 H), 7.91 (d, *J* = 8.13 Hz, 8 H), 7.62 (d, *J* = 8.67 Hz, 8 H), 7.45 (d, *J* = 8.13 Hz, 8 H), 2.46 (s, 12 H), -2.78 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.14, 142.13, 134.43, 134.17, 132.16, 129.96, 128.15, 124.37, 122.43, 119.51, 90.91, 89.85, 30.43. UV/Vis (CH_2Cl_2) λ_{max} (log ε): 464.55 (5.69), 628.01 (3.90), 685.91 (4.91). FABMS Calcd for $C_{84}H_{54}N_4O_4S_4$: 1310. Found: 1310.

4-Trimethylsilylethynylbenzonitrile. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 4-bromobenzonitrile (0.50 g, 2.75

mmol), trimethylsilylacetylene (0.59 mL, 4.13 mmol), copper(I) iodide (0.05 g, 0.28 mmol), bis(triphenylphosphine)palladium(II) chloride (0.10 g, 0.14 mmol), triphenylphosphine (0.14 g, 0.55 mmol), triethylamine (1.19 mL, 11.00 mmol), and THF (15 mL) at 65 °C for 60 h. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.60. The reaction afforded 0.52 g (93 % yield) of the desired compound as off white crystals. IR (KBr) 3128.2, 2953.8, 2225.6, 2143.6, 1600.0, 1492.3, 1384.6, 1246.2, 1174.4, 841.0, 753.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J*=8.4 Hz, 2 H), 7.52 (d, *J*=8.3 Hz, 2 H), 0.26 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ132.15, 131.63, 127.73, 118.17, 111.53, 102.74, 99.35, -0.30. HRMS calcd $C_{12}H_{13}NSi$: 199.0817. Found: 199.0816.

4-Ethynylbenzonitrile. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were 4-trimethylsilylethynylbenzonitrile (0.35 g, 1.72 mmol), potassium carbonate (1.19 g, 8.60 mmol), methanol (10 mL), and methylene chloride (10 mL) for 2 h. The material was immediately reacted in the next step without additional purification or identification.

118. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 4-ethynylbenzonitrile (0.22 g, 1.65 mmol), **3** (0.60 g, 2.15 mmol), copper(I) iodide (0.03 g, 0.17 mmol), bis(triphenylphosphine)palladium(II) chloride (0.06 g, 0.09 mmol), triphenylphosphine (0.09 g, 0.34 mmol), triethylamine (0.96 mL, 6.88 mmol) and THF (20 mL) at 65 °C for 3 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/hexanes as the eluent. $R_f = 0.49$. The compound was further purified by a hexanes wash to give 0.28 g (76 % yield over two steps) of the desired compound as yellow crystals. IR (KBr) 3117.9, 2225.6, 1692.3, 1379.5, 1266.7, 1164.1, 1112.8, 1010.3, 959.0, 825.6, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J*=8.6 Hz, 2 H), 7.59 (d, *J*=8.6 Hz, 2 H), 7.56 (d, *J*=8.62 Hz, 2 H), 7.42 (d, *J*=8.6 Hz, 2 H), 2.42 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ

192.94, 134.22, 132.25, 132.10, 132.02, 129.16, 127.78, 132.32, 118.41, 111.77, 92.88, 89.22, 30.48. HRMS calcd $C_{17}H_{11}NOS$: 277.0561. Found: 277.0573.

2-Trimethylsilylethynylbenzonitrile. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-bromobenzonitrile (0.50 g, 2.75 mmol), trimethylsilylacetylene (0.59 mL, 4.13 mmol), copper(I) iodide (0.05 g, 0.28 mmol), bis(triphenylphosphine)palladium(II) chloride (0.10 g, 0.14 mmol), triphenylphosphine (0.14 g, 0.55 mmol), triethylamine (1.19 mL, 11.00 mmol) and THF (15 mL) at 65 °C for 60 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. $R_f = 0.60$. The reaction afforded 0.52 g (93 % yield) of the desired compound as off white crystals. IR (KBr) 3066.7, 2953.8, 2902.6, 225.6, 2153.8, 1589.7, 1559.0, 1476.9, 1446.2, 1405.1, 1251.3, 1220.5, 1164.1, 1092.3, 1035.9, 953.8, 861.5, 764.1, 733.3, 697.4, 641.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J*=7.7 Hz, 1 H), 7.53 (t, *J*=13.7 Hz, 1 H), 7.52 (d, *J*=11.7 Hz, 1 H), 7.38 (t, *J*=8.8 Hz, 1 H), 0.30 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.45, 132.35, 132.08, 128.35, 126.87, 117.20, 115.73, 102.16, 100.49, -0.19. HRMS calcd $C_{12}H_{13}NSi$: 199.0817. Found: 199.0814.

2-Ethynylbenzonitrile. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were 2-trimethylsilylethynylbenzonitrile (0.35 g, 1.72 mmol), potassium carbonate (1.19 g, 8.60 mmol), methanol (10 mL) and methylene chloride (10 mL) for 2 h. The material was immediately reacted in the next step without additional purification or identification.

120. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-ethynylbenzonitrile (0.22 g, 1.72 mmol), **3** (0.61 g, 2.15 mmol) as described above using copper(I) iodide (0.03 g, 0.17 mmol), bis(triphenylphosphine)palladium(II) chloride (0.06 g, 0.09 mmol), triphenylphosphine (0.09 g, 0.34 mmol), triethylamine (0.96 mL, 6.88 mmol), and THF (20 mL) at 65 °C for 48 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:3 ethyl acetate/hexanes as the eluent. R_f = 0.38. The compound was further purified by a hexanes wash to give 0.23 g (48 % yield over two steps) of the desired compound as a yellow solid. IR (KBr) 3425.6, 3138.5, 2369.2, 2225.6, 1702.6, 1656.4, 1384.6, 1112.8, 1015.4, 943.6, 825.6, 769.2, 620.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J*=7.7 Hz, 1 H), 7.65 (d, *J*=8.4 Hz, 2 H), 7.64 (buried d, 1 H), 7.57 (t, *J*=7.6, 1 H), 7.44 (buried d, 1 H), 7.41 (d, *J*=8.7 Hz, 2 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.96, 134.20, 132.64, 132.46, 132.35, 132.14, 129.27, 128.46, 126.81, 123.14, 117.41, 115.45, 95.08, 87.06, 30.48. HRMS calcd $C_{17}H_{11}NOS$: 277.0561. Found: 277.0574.

2-Trimethylsilylethynylpyridine. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-bromopyridine **(121)** (0.45 mL, 3.16 mmol), trimethylsilylacetylene (0.68 mL, 4.74 mmol), copper(I) iodide (0.06 g, 0.32 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.16 mmol), triphenylphosphine (0.17 g, 0.63 mmol), triethylamine (1.38 mL, 12.64 mmol), and THF (15 mL) at 70 °C for 48 h. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.15. The reaction afforded 0.50 g (88 % yield) of the desired compound. IR (KBr) 3056.4, 2953.8, 2902.6, 2153.8, 1579.5, 1559.0, 1456.4, 1425.6, 1246.2, 1220.5, 1148.7, 1046.2, 984.6, 866.7, 841.0, 774.4, 759.0, 733.3, 697.4, 651.3 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J*=3.1 Hz, 1 H), 7.63 (t, *J*=6.1 Hz, 1 H), 7.43 (d, *J*=7.7 Hz, 1 H), 7.20 (t, *J*=3.6 Hz, 1 H), 0.27 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.87, 143.03, 135.97, 127.20, 122.95, 103.65, 94.76, -0.07. HRMS calcd $C_{10}H_{13}NSi$: 175.0817. Found: 175.0812.

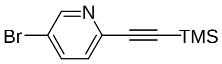
2-Ethynylpyridine. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were 2-trimethylsilylethynylpyridine (0.35 g, 1.95 mmol), potassium carbonate (1.35 g, 9.75 mmol), methanol (15 mL), and methylene chloride

(15 mL) for 2 h. The material was immediately reacted in the next step without additional purification or identification.

122. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-ethynylpyridine (0.20 g, 1.95 mmol), **3** (0.66 g, 2.34 mmol), copper(I) iodide (0.02 g, 0.12 mmol), bis(triphenylphosphine)palladium(II) chloride (0.04 g, 0.06 mmol), triphenylphosphine (0.06 g, 0.23 mmol), diisopropylethylamine (1.36 mL, 7.80 mmol), and THF (15 mL) at 50 °C for 16 h. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. R_f (product): 0.38. The reaction afforded 0.26 g (53 % yield over two steps) of the desired compound as a yellow solid. IR (KBr) 3128.2, 2215.4, 1697.4, 1574.4, 1461.5, 1384.6, 1276.9, 1117.9, 1005.1, 948.7, 830.8, 779.5, 733.3, 615.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J*=4.0 Hz, 1 H), 7.65 (t, *J*=5.8 Hz, 1 H), 7.59 (d, *J*=8.0 Hz, 2 H), 7.51 (d, *J*=4.0 Hz, 1 H), 7.38 (d, *J*=8.6 Hz, 2 H), 7.22 (t, *J*=3.7 Hz, 1 H), 2.41 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 193.01, 150.05, 143.04, 136.14, 134.12, 132.50, 128.94, 127.26, 123.39, 122.96, 90.12, 88.28, 30.46. HRMS calcd $C_{15}H_{11}NOS$: 253.0561. Found: 253.0562.

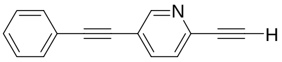
124. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 5-bromopyrimidine (0.18 g, 1.15 mmol), **9**[16] (0.24 g, 1.38 mmol), copper(I) iodide (0.02 g, 0.12 mmol), bis(triphenylphosphine)palladium(II) chloride (0.04 g, 0.06 mmol), triphenylphosphine (0.06 g, 0.23 mmol), triethylamine (0.51 mL, 4.60 mmol), and THF (15 mL) at 75 °C for 4 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. R_f (product): 0.53. The reaction afforded 0.15 g (52%) of the desired compound as bright yellow solid. IR (KBr) 3425.6, 3128.2, 2215.4, 1702.6, 1656.4, 1543.6, 1384.6, 1117.9, 1097.4, 943.6, 820.6, 717.9, 615.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1 H), 8.85 (s, 2 H), 7.76 (d, *J*=8.1 Hz, 2 H), 7.42 (d, *J*=8.0 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 192.84, 158.57, 156.79, 134.26, 132.22, 129.49, 122.82, 119.59, 95.46, 83.84, 30.50. HRMS calcd $C_{14}H_{10}N_2OS$: 254.0514. Found: 254.0513.



3-Bromo-6-(trimethylsilylethynyl)pyridine. See the general coupling procedure. The compounds used were 2,5-dibromopyridine **(125)** (2.37 g, 10.0 mmol), bis(triphenylphosphine)palladium(II) chloride (0.35 g, 0.50 mmol), copper(I) iodide (0.19 g, 1.0 mmol), triphenylphosphine (0.52 g, 2.0 mmol), triethylamine (4.35 mL, 40.0 mmol), THF (50 mL), and trimethylsilylacetylene (1.4 mL, 10 mmol) at 65 °C for 2 d. The reaction was separated via flash chromatography affording a light brown solid (2.130 g, 84% yield), R_f = 0.22 (50% hexanes/methylene chloride). IR (KBr) 3031.8, 2958.2, 2163.8, 1561.3, 1543.6, 1451.4, 1367.0, 1248.9, 1089.4, 1001.1, 844.6, 760.9, 678.6, 642.87, 534.52 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 2.4, 0.73 Hz, 1 H), 7.76 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.32 (dd, *J* = 8.2, 0.73 Hz, 1 H). ^{13}C NMR δ 151.05, 141.36, 138.72, 128.19, 120.24, 102.58, 96.40, -0.40.

3-Ethynylphenyl-6-(trimethylsilylethynyl)pyridine (126). See the general procedure for the coupling reaction. The compounds used were 5-bromo-2-(trimethylsilylethynyl)pyridine (2.00 g, 7.90 mmol), bis(triphenylphosphine)palladium(II) chloride (0.28 g, 0.40 mmol), copper(I) iodide (0.15 g, 0.8 mmol), THF (20 mL), diisopropylethylamine (5.50 mL, 31.6 mmol), and phenylacetylene (0.87 mL, 7.9 mmol) at 55 °C overnight. The reaction was separated via flash chromatography affording a light brown solid (1.37 g, 63%), R_f = 0.36 (2:1 methylene chloride to hexanes). IR (KBr) 2959.5, 2157.9, 1492.3, 1463.6, 1384.0, 1247.7, 1019.9, 844.4, 754.8, 690.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 1.3 Hz, 1 H), 7.74 (dd, *J* = 6.0, 2.6 Hz, 1 H), 7.53 (m, 2 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.36 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.32, 141.52, 138.38, 131.73, 129.02, 128.52, 126.59, 122.33, 119.76, 103.51, 96.95, 94.49, 85.93, -0.12. HRMS Calc'd for $C_{19}H_{17}NSi$: 275.1130. Found: 275.1126.



2-Ethynyl-5-ethynylphenylpyridine. See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. The compounds used were **126** (272 mg, 1.00 mmol), potassium carbonate (690 mg, 5.00 mmol), methanol (30 mL) and dichloromethane (30 mL) for 2.5 h. The product was used without purification.

127. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-ethynyl-5-ethynylphenylpyridine (0.167 g, 1.00 mmol), **3** (0.334 g, 1.20 mmol), bis(triphenylphosphine)palladium(II) chloride (0.035 g, 0.050 mmol), copper(I) iodide (0.019 g, 0.10 mmol), triphenylphosphine (0.026 g, 0.10 mmol), THF (30 mL) and diisopropylethylamine (0.70 mL, 4.0 mmol) at 50 °C for 2 d. Column chromatography eluting with 3:1 methylene chloride to hexanes yielded 199 mg (56%) of a light brown solid. IR (KBr) 3052.1, 2923.3, 2214.1, 1703.5, 1571.6, 1536.4, 1493.7, 1460.4, 1397.5, 1359.9, 1222.2, 1124.8, 1107.4, 1081.7, 1013.6, 943.1, 824.9, 754.3, 687.7, 618.5, 523.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (br s, 1 H), 7.80 (dd, J = 2.0, 8.1 Hz, 1 H), 7.62 (1/2ABq, J = 8.5 Hz, 2 H), 7.54 (m, 3 H), 7.41 (1/2ABq, J = 8.1 Hz, 2 H), 7.37 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.15, 152.51, 141.57, 138.50, 134.23, 132.61, 131.75, 129.28, 129.05, 128.53, 126.63, 123.23, 122.33, 119.73, 94.61, 90.22, 85.97, 30.37. HRMS $C_{23}H_{16}NOS$ Calc'd: 353.0870. Found: 353.0874.

129. See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-iodoaniline (**128**) (0.607 g, 2.77 mmol), bis(triphenylphosphine)palladium(II) chloride (0.098 g, 0.139 mmol), copper(I) iodide (0.053 g, 0.277 mmol), diisopropylethylamine (1.93 mL, 11.08 mmol), **89** (0.488 g, 3.05 mmol) and THF (25 mL) at 70 °C for 7 d. Column chromatography (silica gel with methylene chloride as eluent) afforded the desired product (0.40 g, 57% yield). IR (KBr) 3468.06, 3375.97, 2941.49, 2210.75, 1711.99, 1602.74, 1485.37, 1453.52, 1308.06, 1280.46, 1099.68, 770.84, 753.54, 695.52 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dt, *J*=8.5 Hz, 1.8 Hz, 2 H), 7.59 (dt, *J*=8.5, 1.7 Hz, 2 H), 7.40 (dd, *J*=7.8, 1.5 Hz, 1 H), 7.18 (td, *J*=7.6, 1.5 Hz, 1 H), 6.75 (m, 2 H), 4.33 (br s, 2 H), 3.94 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.95, 148.44, 132.74, 131.70, 130.70, 129.98, 129.76, 128.46, 118.44, 114.87, 107.64, 94.43, 89.54, 52.65. HRMS calculated for $C_{16}H_{13}NO_2$,: 251.094629. Found: 251.0940.

4-(2'-Aminoethynylphenyl)benzoic acid (130). 129 (0.300 g, 1.194 mmol), lithium hydroxide (0.250 g, 5.97 mmol), methanol (30 mL), water (10 mL), methylene chloride (20 mL) and a stir bar were added to a 100 mL round bottom flask.[34] The mixture was stirred at room temperature for 2 d. The mixture was washed with methylene chloride and the layers separated. The aqueous portion was adjusted to pH = 4 and washed with methylene chloride to afford 0.277 g of product (98% yield). IR (KBr) 3468.1, 3376.3, 3054.3, 2957.6, 2656.7, 2538.5, 2205.4, 1681.3, 1604.8, 1488.4, 1422.2, 1318.8, 1281.9, 860.4, 758.7 cm^{-1}. ^{1}H NMR (400 MHz, d-DMSO) δ 7.95 (dt, *J*=8.5, 1.8 Hz, 2 H), 7.72 (dt, *J*=8.5, 1.7 Hz, 2 H), 7.26 (dd, *J*=7.7, 1.5 Hz, 1 H), 7.11 (td, *J*=7.7, 1.6 Hz, 1 H), 6.75 (dd, *J*=8.3, 0.6 Hz, 1 H), 6.55 (td, *J*=7.6, 1.0 Hz, 1 H), 5.59 (br s, 2 H). ^{13}C NMR (100 MHz, d-DMSO) δ 167.65, 150.85, 132.88, 132.12, 131.19, 130.72, 130.24, 128.32, 116.66, 114.94, 105.64, 94.14, 90.90. HRMS calculated for $C_{15}H_{11}NO_2$,: 237.0790. Found: 237.0792.

Methyl 4-(2´-methoxyethynylphenyl)benzoate (132). See the general procedure for the Pd/Cu-catalyzed coupling reaction. The compounds used were 2-iodoanisole **(131)** (0.49 mL, 3.74 mmol), **89** (0.50 g, 3.12 mmol), copper(I) iodide (0.06 g, 0.31 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.16 mmol), diisopropylethylamine (2.17 mL, 12.48 mmol) and THF (15 mL) at 75 ºC for 2.5 d. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.59. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 diethyl ether/hexanes as the eluent. $R_f = 0.54$. The reaction afforded 0.47 g (57 % yield) of the desired compound as a white solid. IR (KBr) 3426.87, 2941.49, 2828.66, 2200.00, 1720.89, 1597.73, 1487.07, 1463.09, 1433.24, 1275.68, 1245.54, 1167.90, 1102.30, 1018.13, 853.62, 753.68, 691.05, 474.58 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (ABq, *J*=8.7 Hz, Δν=159.91 Hz, 4 H), 7.52 (dd, *J*= 7.6, 1.8, 1 H), 7.36 (td *J*=7.4, 1.7 Hz, 1 H), 6.98 (td, *J*=7.5, 1.0 Hz, 1 H), 6.94 (dd, *J*=8.4, 0.7 Hz, 2 H), 3.95 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.05, 160.50, 134.09, 132.88, 131.95, 130.73, 129.99, 129.84, 129.69, 128.76, 120.95, 112.31, 111.14, 93.06, 89.29, 56.26, 52.61. HRMS Calcd $C_{17}H_{14}O_3$: 266.0943. Found: 266.0945.

4-(2´-Methoxyphenylethynyl)benzoic acid (133). To a 100 mL round bottom flask equipped with a magnetic stirbar was added **132** (0.30 g, 1.16 mmol), LiOH (0.14, 5.82 mmol), methanol (18 mL), methylene chloride (10 mL), and water (6 mL).[34] The reaction mixture was allowed to stir at room temperature for 2 d. The reaction was quenched with water and extracted with methylene chloride (3×). The yellow aqueous phases were combined and acidified to pH = 3 whereupon a white solid precipitated. The solid material was collected on a fritted funnel. No further purification was needed. The reaction afforded 0.28 g (97 % yield) of the desired material. IR (KBr) 3445.36, 2962.62, 2829.10, 2659.63, 2536.38, 2212.84, 1681.14, 1604.93, 1488.82, 1457.92, 1425.90, 1317.19, 1297.57, 1278.77, 1244.42, 1178.84, 1098.43, 1016.26, 954.64, 858.43, 757.58, 697.86, 554.07 cm^{-1}. ^{1}H NMR (400 MHz, d-DMSO) δ 13.00 (br s, 1 H), 7.80 (ABq, *J*=8.2 Hz, Δν=135.77 Hz, 4 H), 7.52 (dd, *J*=7.5, 1.7 Hz, 1 H), 7.42 (td, *J*=7.7, 1.7 Hz, 1 H), 7.12 (d, *J*=8.4 Hz, 1 H), 7.00 (td, *J*=7.4, 0.6 Hz, 1 H), 3.33 (s, 3 H). ^{13}C NMR (100 MHz, d-DMSO) δ 167.59, 160.67, 134.09, 132.20, 131.78, 131.27, 130.43, 127.88, 121.43, 112.32, 111.60, 93.08, 89.81, 56.61. HRMS Calcd $C_{16}H_{12}O_3$: 252.0786. Found: 252.0782.