Phenylene Ethynylene Diazonium Salts as Potential Self-Assembling Molecular Devices

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Supporting Information.

General: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Acetonitrile was distilled from calcium hydride. Hexanes and dichloromethane were distilled under nitrogen. *N,N*-Diisopropylethylamine (Hünig's base) and triethylamine were distilled over calcium hydride. Sulfolane (Aldrich) was used as received. Silica gel plates were 250 μm thick, 40 F_{254} grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^{1}H, ^{13}C NMR and ^{19}F spectra were obtained at 400, 100 and 470.5 MHz, respectively. IR assignments have 2 cm^{-1} resolution.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Sonogashira Protocol). [12] To an oven-dried screw cap tube or a round bottom flask equipped with a a magnetic stir bar was added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (1-5 mol % based on aryl halide), and copper(I) iodide (1-5 mol % based on aryl halide). The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen 3X. Triethylamine or *N,N*-diisopropylethylamine (Hünig's base) was added followed by THF to serve as a co-solvent. After 5 min at room temperature, the terminal alkyne was added and the reaction mixture was stirred until complete reaction was noted by TLC. External heating up to 80 ºC was used for sluggish reactions. The reaction vessel was cooled to room temperature and quenched with water or a saturated solution of NH_4Cl. The organic layer was diluted with dichloromethane and washed with a

saturated solution of NH_4Cl until the blue color of copper complexes could not be seen in the aqueous phase. The combined aqueous layers were extracted with dichloromethane 3X. The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo*. The crude product was then purified by flash or column chromatography (silica gel). An alternative work-up procedure consisted of solvent removal *in vacuo* directly followed by chromatography.

General Procedure for the Deprotection of a Trimethylsilyl (TMS)-Protected Alkyne. To a round bottom flask equipped with a magnetic stir bar was added the TMS-protected alkyne, 5 equivalents of potassium carbonate, and equal volumes of methanol and dichloromethane. The reaction vessel was sealed with a rubber septum and then filled with nitrogen. The reaction was allowed to go to completion at which time the reaction was quenched with a saturated solution of NaCl. The resulting solution was extracted as stated in the previous section.

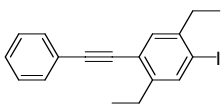
General Procedure for the Reduction of Aromatic Nitro Compounds to Anilines. A round bottom flask equipped with a reflux condenser and a magnetic stirring bar was charged with the nitro compound, THF and ethanol. Ground $SnCl_2 \cdot 2H_2O$ (7-10 redox equivalents for each nitro group) was immediately added with stirring. Vigorous exothermic reaction accompanied by a refluxing of the solvent was observed. The reaction was allowed to complete at room temperature. When starting material was no longer detected by TLC, the reaction mixture was treated with 50% aqueous KOH to dissolve tin compounds. The phases were then separated. The aqueous phase was extracted with ether 3X and discarded. The extracts were combined with the organic phase, washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*.

General Procedure for the Diazotization of Anilines with Nitrosonium Tetrafluoroborate in the Acetonitrile - Sulfolane System. $NOBF_4$[9] was weighed out in a nitrogen filled dry box and placed in a round bottom flask equipped with a magnetic stirring bar and sealed with a septum. Acetonitrile and sulfolane were injected in a 5 to 1 volume ratio and the resulting suspension was cooled in a dry ice/acetone bath to – 40 ºC. The solution of the aniline was prepared by adding warm sulfolane (45-50 ºC) to the amine under a nitrogen blanket, sonication for 1 min and subsequent addition of acetonitrile (10-20% by volume). The aniline solution was then added to the nitrosonium salt suspension over a period of 10 min. The reaction mixture was kept at – 40 ºC for 30 min and was then allowed to warm to the room temperature. At

this point, the diazonium salt was precipitated by the addition of ether or dichloromethane, collected by filtration, washed with ether or dichloromethane and dried. Additional purification of the salt was accomplished by repricipitation from DMSO by dichloromethane and/or ether.

1,4-Diethylbenzene.[1] A solution of 4-ethylacetophenone (31.26 g, 211 mmol) in ethanol (200 mL) and concentrated hydrochloric acid (50 mL) was placed in a Parr bottle, together with palladium on activated charcoal (10%, 4.00 g), and hydrogenated at 60 psi and 50 ºC until hydrogen consumption ceased. The resulting mixture was filtered through a Celite pad, diluted with water (200 mL), evaporated *in vacuo* to 250 mL, and the organic phase was separated. The aqueous phase was extracted with hexanes (30 mL) 3X and discarded. The extracts were combined with the organic phase, washed with water (50 mL) 3X and evaporated *in vacuo* to give the product as a colorless oil (22.0 g, 77 % yield). IR (KBr) 2965, 2931, 2873, 1515, 1457, 1452, 829 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 4H), 2.68 (q, *J*=7.6 Hz, 4 H), 1.29 (t, *J*=7.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 128.0, 28.5, 15.7.

1,4-Diiodo-2,5-diethylbenzene (13). 1,4-Diethylbenzene (20.10 g, 150.0 mmol), iodine (34.29 g, 135.0 mmol), periodic acid dihydrate (17.10 g, 75.0 mmol), acetic acid (125 mL), water (25 mL) and sulfuric acid (3.6 mL) were stirred in a 500 mL round bottom flask equipped with a stir bar for 22 h at 100 ºC. The resulting dark solution was poured into water (300 mL) and treated with $NaHSO_3$ (14.6 g, 140 mmol) to remove unreacted iodine. The phases were separated, and the aqueous phase was extracted with dichloromethane (50 mL) 3X. The organic phase was combined with the extracts and washed with water (100 mL, 3X), Na_2CO_3 (10%, 100 mL), water (100 mL) twice and evaporated *in vacuo*. The crude product thus obtained was recrystallized 3X from ethanol/acetone (10:1) to give heavy colorless needles (32.5 g, 56% yield): mp 68-69 ºC (lit.[12] 68-69 mp ºC). IR (KBr) 2961, 1463, 1454, 1382, 1318, 1044, 1035, 888, 713 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2 H), 2.64 (q, *J*=7.5 Hz, 4 H), 1.19 (t, *J*=7.5 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.13, 138.93, 100.53, 33.33, 14.63. HRMS found *m/z* 385.9028, $C_{10}H_{12}I_2$ requires 385.9028.



(1) Yao, Y. Ph.D. Dissertation, University of South Carolina, Columbia, SC, 1998.

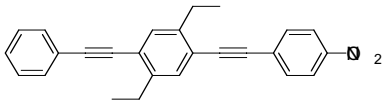
1-Iodo-4-phenylethynyl-2,5-diethylbenzene (14). 1,4-Diiodo-2,5-diethylbenzene (**2**, 1.93 g, 5.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.175 g, 0.25 mmol), copper(I) iodide (0.095 g, 0.50 mmol), Hünig's base (20.0 mL), and ethynylbenzene (0.510 g, 5.0 mmol) were used following the general procedure for couplings. The tube was capped and heated to 50 ºC in an oil bath for 24 h. Column chromatography (hexanes as eluent) afforded the desired product (0.682 g, 38% yield). IR (KBr) 3052, 2929, 2869, 1492, 1460, 1474, 1442, 1383, 889, 754, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.50-7.54 (m, 2H), 7.33-7.38 (m, 4H), 2.79 (q, *J*=7.6 Hz, 2 H), 2.69 (q, *J*=7.6 Hz, 2 H), 1.27 (t, *J*=7.6 Hz, 3 H), 1.21 (t, *J*=7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.53, 144.03, 138.93, 131.73, 131.73, 128.63, 128.53, 123.53, 122.93, 101.03, 93.83, 87.73. HRMS found *m/z* 360.0372, $C_{18}H_{17}I$ requires 360.0375.

Trimethyl-(4-nitrophenylethynyl)silane. 1-Iodo-4-nitrobenzene (1.25 g, 5.0 mmol), bis(dibenzylideneacetone)palladium (0.086 g, 0.15 mmol), triphenylphosphine (0.157 g, 0.60 mmol), copper(I) iodide (0.057 g, 0.30 mmol), Hünig's base (1.29 g, 10.0 mmol), THF (30 mL) and trimethylsilylacetylene (0.740 g, 7.50 mmol) were used following the general procedure for couplings. The tube was capped and stirred at 45 ºC temperature for 2 h. Flash column chromatography (CH_2Cl_2 as eluent) afforded the desired product as orange needles (0.937 g, 85% yield): mp 94-96 ºC (lit.[11b] mp 96-97 ºC). IR (KBr) 3102, 2953, 2896, 2159, 1592, 1519, 1348, 1248, 870, 845 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, AA' part of AA'XX' pattern, *J*=8.6, 2.5, 1.8, 0.5 Hz, 2 H), 7.60 (m, XX' part of AA'XX' pattern, *J*=8.6, 2.5, 1.8, 0.5 Hz, 2 H), 0.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 132.7, 130, 123.5, 102.7, 100.6, -0.3.

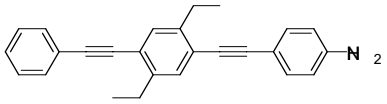
1-Ethynyl-4-nitrobenzene. Trimethyl-(4-nitrophenylethynyl)silane (0.547 g, 2.5 mmol) was dissolved in THF (3 mL) in a 25 ml round bottom flask equipped with a magnetic stirring bar and sealed with a septum under nitrogen. Tetrabutylammonium fluoride was injected as a 1.0 M solution in THF (3.0 mL, 3.0 mmol) and the reaction mixture was allowed to stir for 30 min. After stripping the solvents, the dark product mixture was separated on a short column of silica (CH_2Cl_2 as eluent) to afford light yellow crystals (0.258 g, 70% yield): mp 150-152 ºC (lit.[2] mp 153 ºC). IR (KBr) 3251, 2106, 1594, 1510, 1342, 1105, 854, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (m, AA' part of AA'XX' pattern, *J*=8.5, 2.5, 1.8, 0.5 Hz, 2 H),

(2) Eaborn, C.; Skinner, G. A.; Walton, D. R. M. *J. Chem. Soc. B* **1966**, 922

7.65 (m, XX' part of AA'XX' pattern, *J*=8.5, 2.5, 1.8, 0.5 Hz, 2 H), 3.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 133.4, 132.9, 128.9, 123.7, 123.5, 82.3, 81.6, 78.3.

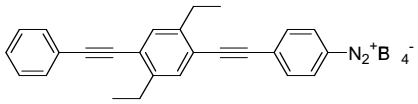


4-(2,5-diethyl-4-phenylethynylphenylethynyl)nitrobenzene (15). 1-Iodo-4-phenylethynyl-2,5-diethylbenzene (**3**, 2.88 g, 8.0 mmol), bis(dibenzylideneacetone)palladium (0.137 g, 0.24 mmol), triphenylphosphine (0.251 g, 0.96 mmol), copper(I) iodide (0.091 g, 0.48 mmol), Hünig's base (2.32 g, 18.0 mmol), THF (20 mL) and 1-ethynyl-4-nitrobenzene (**5**, 1.29 g, 8.8 mmol) were used following the general procedure for couplings. The tube was capped and heated to 60 ºC in an oil bath for 5 h. The product was isolated from the dichloromethane extracts by chromatography on a short column of silica with CH_2Cl_2 as eluent as bright yellow needles (2.995 g, 99% yield): mp 117-119 ºC. IR (KBr) 2967, 2212, 1590, 1499, 1518, 1339, 1106, 855, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, AA' part of AA'XX' pattern, *J*=8.5, 2.5, 1.8, 0.4 Hz, 2 H), 7.66 (m, XX' part of AA'XX' pattern, *J*=8.5, 2.5, 1.8, 0.4 Hz, 2 H), 7.54 (m, AA' part of AA'YY'X pattern, *J*=7.5, 7.0, 1.6, 1.4, 1.1, 0.6 Hz, 2 H), 7.42 (s, 1H), 7.41 (s, 1H), 7.37 (m, YY' part of AA'YY'X pattern, *J*=7.5, 7.0, 1.6, 1.4, 1.1, 0.6 Hz, 2 H), 7.35 (tt, *J*=7.0, 1.4 Hz, 1 H), 2.87 (q, *J*=7.7 Hz, 2 H), 2.86 (q, *J*=7.5 Hz, 2 H), 1.32 (t, *J*=7.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.13, 144.03, 143.83, 132.33, 131.93, 131.73, 131.63, 130.63, 128.63, 128.63, 128.63, 128.53, 123.93, 123.43, 121.33, 94.93, 93.93, 92.23, 88.13, 27.33, 14.93, 14.83. HRMS found *m/z* 379.1575, $C_{26}H_{21}NO_2$ requires 379.1572.



4-(2,5-Diethyl-4-phenylethynylphenylethynyl)aniline (1). According to the general reduction procedure, 4-(2,5-diethyl-4-phenylethynylphenylethynyl)nitrobenzene (**6**, 2.84 g, 8.50 mmol), $SnCl_2{\cdot}2H_2O$ (9.60 g, 42.5 mmol), THF (50 mL) and ethanol (3 mL) were used. The product was isolated as orange needles (2.54 g, 97% yield): mp 92-94 ºC. IR (KBr) 3449, 3368, 2970, 2929, 2871, 2198, 1622, 1600, 1516, 1176, 899, 828, 761, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.54 (m, 2 H), 7.30-7.37 (m, 7 H), 7.93 (m, XX' part of AA'XX' pattern, *J*=8.5, 2.6, 1.9, 0.4 Hz, 2 H), 3.81 (s, 2 H), 2.84 (q, *J*=7.6 Hz, 2 H), 2.83 (q, *J*=7.6 Hz, 2 H), 1.30 (t, *J*=7.6 Hz, 3 H), 1.29 (t, *J*=7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.93, 143.53,

143.23, 133.13, 131.73, 131.43, 128.63, 128.43, 123.83, 123.43, 121.93, 114.93, 113.03, 95.13, 93.93, 88.63, 86.43, 27.4, 14.9, 14.8. HRMS found *m/z* 349.1826, $C_{26}H_{23}N$ requires 349.1831.



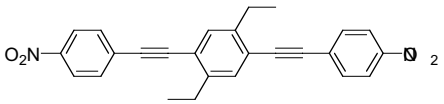
4-(2,5-Diethyl-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (7). Following the general diazotization procedure, 4-(2,5-diethyl-4-phenylethynylphenylethynyl)aniline (**7**, 1.047 g, 3.00 mmol) was treated with $NOBF_4$[9] (0.368 g, 3.15 mmol) in pure acetonitrile (20 mL). The product precipitated as orange needles in the course of the reaction. The precipitation was brought to completion with ether (20 mL). The salt was washed with ether and dried *in vacuo* (1.257 g, 93% yield). IR (KBr) 3107, 2966, 2258, 2198, 1578, 1071, 1048, 843, 755, 687, 529 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 8.90 (m, AA' part of AA'XX' pattern, *J*=8.7, 2.4, 1.7, 0.4 Hz, 2 H), 8.21 (m, XX' part of AA'XX' pattern, *J*=8.7, 2.4, 1.7, 0.4 Hz, 2 H), 7.59 (s, 1 H), 7.58-7.61 (m, 2 H), 7.52 (s, 1 H), 7.42-7.47 (m, 3 H), 2.92 (q, *J*=7.3 Hz, 2 H), 2.91 (q, *J*=7.4 Hz, 2 H), 1.316 (t, *J*=7.4 Hz, 3 H), 1.315 (t, *J*=7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 143.99, 143.08, 135.45, 132.79, 131.85, 131.24, 130.96, 130.14, 128.36, 128.13, 124.15, 122.18, 119.57, 112.65, 99.67, 94.99, 91.71, 87.18, 26.44, 14.44, 14.17.

4-(2,5-Diethyl-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (7). Following the general diazotization procedure 4-(2,5-diethyl-4-phenylethynyl)aniline (1.047 g, 3.00 mmol) was treated with $NOBF_4$[9] (0.386 g, 3.30 mmol) in acetonitrile (3 mL) and sulfolane (3 mL). The product precipitated as shiny orange needles during the course of the reaction. The precipitation was brought to completion with ether (20 mL). The salt was washed with dichloromethane dried *in vacuo* and reprecipitated from DMSO with dichloromethane/ether (1.125 g, 84% yield). The spectral data were identical to that collected from a previously obtained sample.

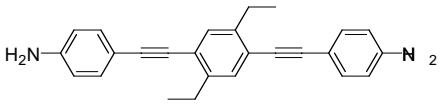
1,4-Bis(trimethylsilylethynyl)-2,5-diethylbenzene. 1,4-Diiodo-2,5-diethylbenzene (1.93 g, 5.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.351 g, 0.50 mmol), copper(I) iodide (0.190g, 1.0 mmol), Hünig's base (15 mL), and trimethylsilylacetylene (1.47 g, 15.0 mmol) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 24 h. Flash column chromatography (hexanes as eluent) afforded the desired product, which was freed from the orange impurities by recrystallization from methanol (1.43 g, 88% yield): mp 97-99 ºC. IR (KBr) 2961, 2156,

1488, 1253, 1192, 900, 866, 839, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 2.72 (q, *J*=6.7 Hz, 4 H), 1.21 (t, *J*=6.7 Hz, 6 H), 0.25 (s, 18H) ^{13}C NMR (100 MHz, CDCl3) δ 144.02, 143.08, 128.43, 125.56, 118.45, 115.09, 23.80, 22.13, 15.74, 13.28. HRMS found *m/z* 326.1887, $C_{20}H_{30}Si_2$ requires 326.1886.

1,4-Diethynyl-2,5-diethylbenzene. 1,4-Bis(trimethylsilylethynyl)-2,5-diethylbenzene (1.402 g, 4.30 mmol), potassium carbonate (5.90 g, 43.0 mmol), methanol (30 ml) and dichloromethane (30 ml) were used according the general procedure. Flash column chromatography (hexanes as eluent) afforded the product as an orange oil (0.781 g, 99.8 % yield). IR (KBr) 3295, 2967, 2933, 2873, 1489, 1457, 1249, 897, 841, 648, 608 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2H), 2.76 (q, *J*=8.0 Hz, 4 H), 3.30 (s, 2H), 1.23 (t, *J*=8.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.13, 132.43, 122.03, 82.33, 81.83, 27.13, 14.83.

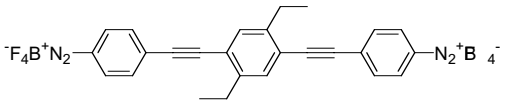


4-[2,5-diethyl-4-(4-nitrophenylethynyl)phenylethynyl]nitrobenzene. 1-Iodo-4-nitrobenzene (5.48 g, 22.0 mmol), bis(dibenzylideneacetone)palladium (0.344 g, 0.60 mmol), triphenylphosphine (0.629 g, 2.40 mmol), copper(I) iodide (0.228 g, 1.20 mmol), Hünig's base (5.68 g, 44.0 mmol), THF (60 mL) and 1,4-diethynyl-2,5-diethylbenzene (**10**, 1.820 g, 10.0 mmol) were used following the general procedure for couplings. The tube was capped and heated to 50 ºC in an oil bath for 12 h. The product was isolated from the dichloromethane extracts by a two-fold recrystallization from THF/ether (3.661 g, 86% yield): mp 218-220 ºC (dec). IR (KBr) 2961, 2930, 2868, 2211, 1592, 1513, 1340, 852, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (m, AA' part of AA'XX' pattern, *J*=8.5, 2.5, 1.8, 0.5 Hz, 2 H), 7.68 (m, XX' part of AA'XX' pattern, *J*=8.5, 2.5, 1.8, 0.5 Hz, 2 H), 2.87 (q, *J*=8.0 Hz, 4 H), 1.33 (t, *J*=8.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.33, 144.23, 132.43, 132.23, 130.43, 123.93, 122.63, 93.43, 92.83, 27.43, 14.93. HRMS found *m/z* 424.1422, $C_{26}H_{20}N_2O_4$ requires 424.1423.



4-[2,5-Diethyl-4-(4-aminophenylethynyl)phenylethynyl]aniline (2). According to the general reduction procedure, 4-[2,5-diethyl-4-(4-nitrophenylethynyl)phenylethynyl]nitrobenzene (3.392 g, 8.00 mmol), $SnCl_2{\cdot}2H_2O$ (18.08 g, 80.0 mmol), THF (50 mL) and ethanol (5 mL) were used. The product was isolated as orange needles (2.80 g, 96% yield): mp 146-148 ºC. IR (KBr) 3450, 3361, 2963, 2950, 2864, 2207,

1618, 1603, 1518, 1293, 1177, 830, 528 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, AA' part of AA'XX' pattern, *J*=8.4, 2.4, 2.2, 0.5 Hz, 4 H), 7.33 (s, 2H), 6.61 (m, XX' part of AA'XX' pattern, *J*=8.4, 2.4, 2.2, 0.5 Hz, 4 H), 3.81 (s, 4H), 2.82 (q, *J*=7.5 Hz, 4 H), 1.26 (t, *J*=7.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.83, 143.18, 133.04, 131.36, 122.67, 114.98, 113.18, 94.83, 86.55, 27.38, 14.88. HRMS found *m/z* 364.1938, $C_{26}H_{23}N$ requires 364.1939.

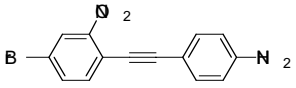


4-[2,5-diethyl-4-(4-diazoniophenylethynyl)phenylethynyl]benzenediazonium tetrafluoroborate (8). Following the general diazotization procedure 4-[2,5-diethyl-4-(4-aminophenylethynyl)phenylethynyl]aniline (**2**, 1.092 g, 3.00 mmol) was treated with $NOBF_4$[9] (0.736 g, 6.30 mmol) in pure acetonitrile (20 mL). The product precipitated as orange needles in the course of the reaction. The salt was washed with dichloromethane dried *in vacuo* and reprecipitated from DMSO with dichloromethane/ether (1.350 g, 80% yield). The solubility of **8** in acetonitrile at room temperature is about 2 mg/mL. IR (KBr) 3105, 2975, 2259, 2208, 1576, 1418, 1578, 975, 846, 533, 522 cm^{-1}. ^1H NMR (400 MHz, CD_3CN) δ 8.45 (m, AA' part of AA'XX' pattern, *J*=8.7, 2.4, 1.7, 0.4 Hz, 4 H), 8.00 (m, XX' part of AA'XX' pattern, *J*=8.7, 2.4, 1.7, 0.4 Hz, 4 H), 7.62 (s, 2H), 2.92 (q, *J*=7.6 Hz, 4 H), 1.31 (t, *J*=7.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 144.66, 134.12, 133.50, 133.13, 132.49, 121.95, 114.59, 97.57, 92.98, 26.43, 14.76.

1,4-Dibromo-2-nitrobenzene (16). 1,4-Dibromobenzene (118.0 g, 500 mmol) was suspended in concentrated sulfuric acid (200 ml) contained in a 1 L 3-neck round bottom flask equipped with a mechanical stirrer and a thermometer. A mixture of concentrated sulfuric acid (320 mL) and nitric acid (69%, 160 mL) was added at room temperature. **Caution! The temperature must be kept below 60 ºC to avoid excessive oxidation and dinitration.** A mildly exothermic reaction was observed and solid pieces of starting material converted in oil droplets. The reaction mixture was heated to 50 ºC for 30 min at which point the oily product solidified. The reaction mixture was poured over 1 Kg of ice, and a yellow product was collected by filtration. To remove phenolic impurities, crude product was dissolved in dichloromethane (250 mL), washed with water (50 mL) twice, 10% aqueous KOH (50 mL) 3X, dried over $MgSO_4$ and evaporated *in vacuo*. Finally, the product was distilled at 90 ºC (0.25 torr) and was collected as a slightly

greenish yellow crystalline mass (110.6 g, 79% yield): mp 82-84 ºC (lit.[3] mp 85 ºC). IR (KBr) 3413, 3087, 1578, 1527, 1457, 1350, 1033, 876, 827, 754, 455 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J*=2.2 Hz, 1H), 7.62 (dd, *J*=8.5, 0.3 Hz, 1H), 7.56 (dd, *J*=8.5, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.13, 136.24, 136.14, 128.51, 121.42, 113.24.

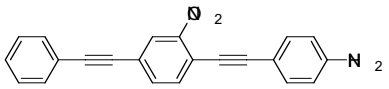
4-Ethynylaniline. 4-Iodoaniline (6.57 g, 30.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.842 g, 1.20 mmol), copper(I) iodide (0.114 g, 0.60 mmol), triethylamine (50.0 mL), and trimethylsilylacetylene (3.92 g, 40.0 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at room temperature for 4 h. After solvent removal *in vacuo*, the residue was chromatographed on a short column of silica (dichloromethane as eluent) and treated with K_2CO_3 (4.20 g, 30.0 mmol) in methanol (50 mL) for 8 h. Methanol was removed *in vacuo* and the remaining solids dissolved in warm ether/hexanes (1:1). The resulting suspension was gravity filtered through paper to remove insolubles and the filtrate was evaporated to afford an orange crystalline material that was recrystallized from ether/hexanes to give yellow crystals (3.170 g, 90% yield): mp 102-104 ºC (lit.[11b] mp 104-105 ºC). IR (KBr) 3485, 3388, 3260, 2097, 1619, 1512, 1305, 1177, 829, 672, 604, 532 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, AA' part of AA'XX' pattern, *J*=8.3, 2.7, 2.0, 0.4 Hz, 2 H), 6.57 (m, XX' part of AA'XX' pattern, *J*=8.3, 2.7, 2.0, 0.4 Hz, 2 H), 2.96 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.21, 133.62, 114.74, 111.40, 84.59, 77.55, 77.23, 76.91, 75.12.



1-Bromo-3-nitro-4-(4-aminophenylethynyl)benzene. 1,4-Dibromo-2-nitrobenzene (**16**, 5.62 g, 20.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.140 g, 0.20 mmol), copper(I) iodide (0.038 g, 0.20 mmol), triethylamine (10.0 mL), THF (10 mL) and 4-ethynylaniline (1.170 g, 10.0 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at room temperature for 4 h. After solvent removal *in vacuo*, the residue was chromatographed on a column of silica (dichloromethane as eluent) to give a mixture of the desired product along with its regioisomer as a red solid. The desired product was isolated from the mixture by a two-fold recrystallization from dichloromethane/hexanes as fine bright red needles (1.561 g, 49% yield): mp 147-149 ºC. IR (KBr) 3457,

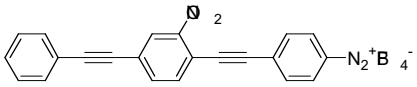
(3) Corbett, J. F.; Holt, P. F. *J. Chem. Soc*. **1963**, 2385.

3367, 2194, 1623, 1593, 1513, 1550, 1334, 1273, 1136, 834, 817, 528 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J*=2.0 Hz), 7.67 (dd, *J*=8.4, 2.0 Hz), 7.51 (d, *J*=8.4 Hz), 7.96 (m, AA' part of AA'XX' pattern, *J*=8.2, 2.7, 1.9, 0.4 Hz, 2 H), 7.93 (m, XX' part of AA'XX' pattern, *J*=8.2, 2.7, 1.9, 0.4 Hz, 2 H), 3.39 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.27, 147.85, 135.82, 135.12, 133.71, 127.73, 120.62, 118.59, 114.63, 111.09, 100.24, 82.86. HRMS found *m/z* 315.9845, $C_{14}H_9N_2BrO_2$ requires 315.9848.



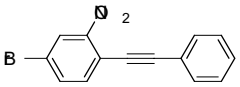
4-(2-Nitro-4-phenylethynylphenylethynyl)aniline (3). 1-Bromo-3-nitro-4-(4-aminophenylethynyl)benzene (0.697 g, 2.20 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.062 g, 0.088 mmol), copper(I) iodide (0.0084 g, 0.044 mmol), triethylamine (10.0 mL) and ethynylbenzene (0.306 g, 3.00 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at 80 ºC for 2 h. After solvent removal *in vacuo*, the residue was chromatographed on a column of silica with dichloromethane to give red needles of the desired product (0.72 g, 97% yield): mp 166-168 ºC. IR (KBr) 3454, 3381, 3360, 2177, 2197, 1594, 1623, 1539, 1520, 1299, 1342, 1133, 829, 758, 690, 527 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J*=1.6, 0.3 Hz), 7.66 (dd, *J*=8.2, 1.6, Hz), 7.61 (d, *J*=8.1 Hz), 7.52-7.57 (m, 2 H), 7.36-7.43 (m, 5 H), 3.94 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.93, 147.81, 135.12, 134.04, 133.76, 131.74, 129.04, 128.49, 127.59, 122.97, 122.18, 118.95, 114.64, 111.29, 100.75, 93.03, 87.05, 83.71. HRMS found *m/z* 338.1058, $C_{22}H_{14}N_2O_2$ requires 338.1055.

4-(2-Nitro-4-phenylethynylphenylethynyl)aniline. 1,4-Dibromo-2-nitrobenzene (**16**, 2.86 g, 10.2 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.230 g, 0.40 mmol), copper(I) iodide (0.038 g, 0.20 mmol), triethylamine (20.0 mL), THF (20.0 mL) and 4-ethynylaniline (1.17 g, 10.00 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at room temperature for 6 h and ethynylbenzene (1.22 g, 12.0 mmol) was injected. The reaction mixture was stirred at 100 ºC for 3 h and worked up as previously described. The product was isolated from the mixture with its regioisomer by two-fold crystallization from dichloromethane/hexanes as red needles (1.54 g, 46% yield). The spectroscopic properties of the product matched those of the previously obtained sample.



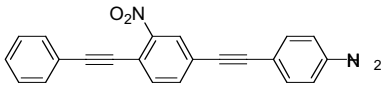
4-(2-Nitro-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (9). Following the general diazotization procedure, 4-(2-nitro-4-phenylethynyl)aniline (**3**, 0.845 g, 2.50 mmol) was treated with $NOBF_4$[9] (0.307 g, 2.63 mmol) in pure acetonitrile (20 mL). The starting amine was poorly soluble in acetonitrile and was used as a suspension. The product was precipitated with ether (50 mL) as a brown powder. The salt was washed with ether and dried *in vacuo* (0.584 g, 54% yield). ^{1}H NMR (400 MHz, CD_3CN) exhibited many extraneous peaks and other spectral information was not obtained.

4-(2-Nitro-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (9). Following the general diazotization procedure 4-(2-Nitro-4-phenylethynyl)aniline (**3**, 0.0845 g, 0.250 mmol) was treated with $NOBF_4$[9] (0.0322 g, 0.275 mmol) in acetonitrile (2 mL)/sulfolane (2 mL). The product was precipitated with ether (12 mL) as dark orange scales. The salt was washed with ether and reprecipitated from DMSO (0.5 mL) and CH_2Cl_2 (20 mL) as lustrous dark orange plates (0.0885 g, 81% yield). IR (KBr) 3103, 2279, 2209, 1576, 1345, 1540, 1084, 841, 764 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6, line width of about 1.9 Hz was observed) δ 8.78 (d, *J*=8.9 Hz, 2 H), 8.30 (s, 1 H), 8.03 (d, *J*=8.9 Hz, 2 H), 7.85-7.92 (m, 2 H), 7.57-7.60 (m, 2 H), 7.42-7.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 149.00, 135.46, 134.85, 134.15, 133.31, 132.84, 1.34, 129.13, 128.21, 127.15, 125.66, 121.06, 114.81, 114.25, 94.57, 94.42, 94.11, 86.29.

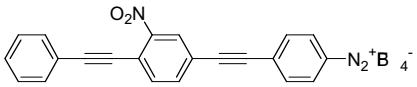


1-Bromo-3-nitro-4-phenylethynylbenzene. 1,4-Dibromo-2-nitrobenzene (2.81 g, 10.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.211 g, 0.30 mmol), copper(I) iodide (0.029 g, 0.15 mmol), triethylamine (15.0 mL), THF (15 mL) and ethynylbenzene (1.02 g, 10.0 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at room temperature for 6 h. After solvent removal *in vacuo*, the residue was chromatographed on a short column of silica (dichloromethane as eluent) to give a mixture of the desired product, together with its regioisomer as a yellow solid that was found to contain 81% of the desired isomer by ^{1}H NMR. The mixture was enriched by column chromatography on silica with dichloromethane/hexanes (1:2). The desired product was isolated as fine yellow needles after recrystallization of the enriched isomer mixture from dichloromethane/hexanes (2.377 g, 75% yield): mp 87-89 ºC. IR (KBr) 2215, 1548, 1520, 1335, 1272, 838, 750, 679, 524 cm^{-1}. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J*=2.0 Hz, 1H), 7.71 (dd, *J*=8.3, 2.0 Hz, 1H), 7.55-7.59 (m, 3H), 7.35-7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.74, 135.93, 135.48, 132.01, 129.46, 128.48, 127.81, 122.04, 121.77, 117.71, 98.45, 84.00. HRMS found *m/z* 300.9744, $C_{14}H_8BrNO$ requires 300.9738.

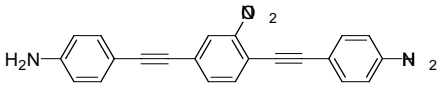


4-(3-Nitro-4-phenylethynylphenylethynyl)aniline (4). 1-Bromo-3-nitro-4-phenylethynylbenzene (1.208 g, 4.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.070 g, 0.10 mmol), copper(I) iodide (0.019 g, 0.10 mmol), triethylamine (6.0 mL), THF (6.0 mL) and 4-ethynylaniline (0.479 g, 4.10 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at room temperature for 15 h. After solvent removal *in vacuo*, the residue was chromatographed on a short column of silica with dichloromethane/hexanes (1:1) to afford the desired product as an orange solid (0.560 g, 44% yield): mp 175-177 ºC. IR (KBr) 3303, 2985, 1696, 1587, 1522, 1406, 1314, 1243, 1153, 1060, 839, 757, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, *J*=1.0 Hz, 1H), 7.64 (d, *J*=1.0 Hz, 2H), 7.58-7.61 (m, 2H), 7.34-7.40 (m, 3H), 7.35 (m, AA' part of AA'XX' pattern, *J*=8.0, 2.5, 2.0, 0.4 Hz, 2 H), 6.65 (m, XX' part of AA'XX' pattern, *J*=8.0, 2.5, 2.0, 0.4 Hz, 2 H), 3.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 149.4, 147.5, 134.9, 134.3, 133.3, 132.0, 129.3, 128.5, 127.1, 124.9, 122.3, 117.1, 114.7, 11.1, 98.4, 94.9, 85.3, 85.0. HRMS found *m/z* 338.1059, $C_{22}H_{14}N_2O_2$ requires 338.1055. Unreacted 1-bromo-3-nitro-4-phenylethynylbenzene was also recovered (0.363 g).



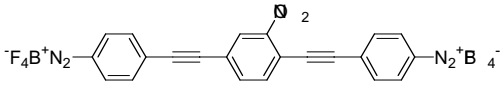
4-(3-Nitro-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (10). 4-(3-Nitro-4-phenylethynylphenylethynyl)aniline (**4**, 0.338 g, 1.00 mmol) dissolved in dichloromethane (15 mL) was added to a suspension of $NOBF_4$ (0.234 g, 2.00 mmol) in acetonitrile (15 mL). A work-up like that described in the general procedure for diazotization afforded a yellow-orange powder (0.222 g). The ^1H NMR spectrum of the salt demonstrated the presence of impurities that could not be removed by recrystallization from acetonitrile/ether or DMSO/ether. No further spectral information was collected.

4-(3-Nitro-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (10). Following the general diazotization procedure, 4-(3-nitro-4-phenylethynylphenylethynyl)aniline (**4**, 0.0676 g, 0.200 mmol) was treated with $NOBF_4$ (0.025 g, 0.210 mmol) in acetonitrile (2 mL)/sulfolane (2 mL). The product was precipitated with ether (20 mL) as fine orange-red crystals. The salt was washed with ether and reprecipitated from DMSO (0.6 mL) and CH_2Cl_2 (10 mL) as heavy lustrous red plates (0.0676 g, 77% yield). IR (KBr) 3101, 2279, 2209, 1576, 1540, 1346, 1083, 1034, 840, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 7.94 (m, AA' part of AA'XX' pattern, *J*=8.7, 2.4, 1.7, 0.4 Hz, 2 H), 7.82 (dd, *J*=1.7, 0.4 Hz, 1 H), 7.49 (m, XX' part of AA'XX' pattern, *J*=8.7, 2.4, 1.7, 0.4 Hz, 2 H), 7.62 (dd, *J*=8.1, 1.7 Hz, 1 H), 7.56 (dd, *J*=8.1, 0.4 Hz, 1 H), 7.07 (m, AA' part of AA'XX'Y pattern, *J*=7.8, 7.6, 1.8, 1.3, 1.3, 0.6 Hz, 2 H), 6.94 (tt, *J*= 7.6, 1.3 Hz, 1 H), 6.91 (m, YY' part of AA'XX'Y pattern, *J*=7.8, 7.6, 1.8, 1.3, 1.3, 0.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 137.24, 136.97, 136.23, 135.40, 133.72, 133.00, 131.08, 129.96, 129.48, 122.81, 122.75, 120.68, 114.12, 100.47, 98.81, 91.04, 85.57.



4-[2-Nitro-4-(4-aminophenylethynyl)phenylethynyl]aniline (5). 1,4-Dibromo-2-nitrobenzene (**16**, 1.124 g, 4.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.112 g, 0.16 mmol), copper(I) iodide (0.015 g, 0.08 mmol), triethylamine (8.0 mL), THF (8.0 mL) and 4-ethynylaniline (1.029 g, 8.80 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at room temperature for 13 h. After solvent removal *in vacuo*, the residue was chromatographed on a short column of silica with dichloromethane γ dichloromethane/ether (10:1) to afford the desired product as a dark red powder that was recrystallized from THF/hexanes (1.28 g, 91% yield): mp 190-192 ºC (dec). IR (KBr) 3380, 2202, 1611, 1540, 1341, 1519, 1298, 829 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 8.07 (d, *J*=1.7 Hz, 1 H), 7.63 (dd, *J*=8.1, 1.7 Hz, 1 H), 7.56 (d, *J*=8.1 Hz, 1 H), 7.30 (m, AA' part of AA'XX' pattern, *J*=8.4, 2.4, 1.9, 0.3 Hz, 2 H), 6.65 (m, XX' part of AA'XX' pattern, *J*=8.4, 2.4, 1.9, 0.3 Hz, 2 H), 7.27 (m, AA' part of AA'XX' pattern, *J*=8.4, 2.5, 2.0, 0.4 Hz, 2 H), 6.64 (m, XX' part of AA'XX' pattern, *J*=8.4, 2.5, 2.0, 0.4 Hz, 2 H), 4.97 (s, 2 H), 4.89 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) 148.48,

148.04, 147.60, 133.66, 132.77, 132.33, 131.95, 125.52, 122.58, 116.64, 113.10, 113.08, 107.96, 99.82, 94.02, 83.96, 82.39. HRMS found *m/z* 353.1164, $C_{22}H_{15}N_3O_2$ requires 353.1164.



4-[2-Nitro-4-(4-diazoniophenylethynyl)phenylethynyl]benzenediazonium tetrafluoroborate (11). Following the general diazotization procedure 4-[2-Nitro-4-(4-aminophenylethynyl)phenylethynyl]aniline (**5**, 0.654 g, 1.85 mmol) was treated with $NOBF_4$[9] (0.491 g, 4.20 mmol) in acetonitrile (10 mL)/sulfolane (10 mL). The product was precipitated with ether (20 mL). The salt was washed with ether and reprecipitated from DMSO (10.0 mL) and CH_2Cl_2 (40 mL) as orange crystals (0.754 g, 74% yield). IR (KBr) 2272, 2218, 1578, 1541, 1574, 1349, 1087, 1080, 1056, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 8.79 (m, AA' part of AA'XX' pattern, *J*=8.7, 2.2, 1.8, 0.4 Hz, 2 H), 8.77 (m, AA' part of AA'XX' pattern, *J*=8.6, 2.3, 1.7, 0.5 Hz, 2 H), 8.50 (dd, *J*=1.7, 0.4 Hz, 1 H), 8.13 (m, XX' part of AA'XX' pattern, *J*=8.7, 2.2, 1.8, 0.4 Hz, 2 H), 8.10 (m, XX' part of AA'XX' pattern, *J*=8.6, 2.3, 1.7, 0.5 Hz, 2 H), 8.08 (dd, *J*=8.0,1.7 Hz, 1 H), 8.04 (d, *J*=8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 149.10, 136.33, 135.47, 133.53, 133.39, 133.31, 133.03, 132.94, 128.20, 123.30, 116.73, 115.30, 115.05, 107.76, 95.82, 95.19, 93.53, 91.01.

2,5-Dibromoaniline. 1,4-Dibromonitrobenzene (**16**, 28.1 g, 100 mmol) was reduced with $SnCl_2 \cdot 2H_2O$ (112.8 g, 500 mmol) in THF (100 mL) and ethanol (100 mL) as described in the general procedure. The desired amine was obtained as a white solid (24.16 g, 96 % yield): mp 54-55 ºC (lit.[4] mp 54.5-55 ºC).

***N*-Acetyl-2,5-dibromoaniline.** A solution of 2,5-dibromoaniline (27.00 g, 107.6 mmol) and acetic anhydride (32.84 g, 322 mmol) in dichloromethane (50 mL) in a 250 mL round bottom flask equipped with a reflux condenser was treated dropwise with aqueous KOH (87%, 22.6 g, 350 mmol, in 20 mL of water). Because of the exothermic nature of the reaction, the reaction mixture was refluxed by itself, and abundant white needles formed. The precipitate was collected by filtration after 30 min, washed with water, cold dichloromethane (50 mL) and recrystallized from ethanol/acetone to yield colorless scales. (30.12 g, 96 % yield): mp 173-175 ºC (lit.[5] mp 172.5-173 ºC). ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 8.58 (br s, 1 H), 8.39 (d,

(4) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc*. **1994**, *116*, 11723.
(5) Doornbos, C. *Org. Prep. Proced. Int*. **1969**,*1*, 287.

J=2.5 Hz, 1 H), 7.56 (d, *J*=8.5 Hz, 1 H), 7.23 (dd, *J*=8.5, 2.5 Hz, 1 H), 2.21 (s, 3 H). ^{13}C NMR (100 MHz, CDCl3) δ 169.54, 139.04, 134.87, 129.05, 127.01, 121.78, 24.28.

***N*-Acetyl-2,5-dibromo-4-nitroaniline.** Nitric acid (69%, 50 mL), and sulfuric acid (98%, 100 mL) were added to a three neck 1 L round bottom flask equipped with a mechanical stirrer and a thermometer and cooled to -10 ºC in an ice bath. *N*-acetyl-2,5-dibromoaniline (**25**, 22.0 g, 75.1 mmol) was then added to the acid mixture and stirred at -10 ºC . **Caution! The temperature of the reaction mixture must be maintained below -10°C with dry ice to avoid the formation of thermally unstable impurities.**[14] The reaction mixture became extremely thick after all of **25** had been added. Two hours later, the mixture was poured over ice (1 Kg) and a slightly yellow crystalline product was collected by filtration, rinsed with water (100 mL, 3X), absolute ethanol (50 mL, 3X), ether (50 mL) twice and recrystallized from THF (100 mL)/ethanol (100 mL). The purified product was collected as long, silky, slightly yellow needles (18.25 g, 72% yield): mp 180-182 ºC (lit.[15] mp 181.5-182 ºC). IR 3297, 3102, 1672, 1568, 1535, 1503, 1346, 1261, 1062 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1 H), 8.17 (s, 1 H), 7.78 (s, 1 H), 2.31 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.60, 144.34, 140.12, 129.72, 125.92, 115.75, 110.59, 25.29.

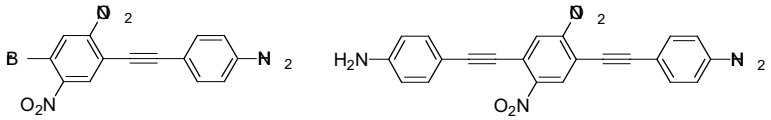
2,5-Dibromo-4-nitroaniline. *N*-Acetyl-2,5-dibromo-4-nitroaniline (13.52 g, 40.00 mmol), THF (50 mL), methanol (50 mL) and KOH (87%, 2.90 g, 45.00 mmol) were added to a 500 mL round bottom flask containing a stirring bar. The mixture was stirred at room temperature[6] for 12 h and diluted with water (500 mL). The bright yellow powder thus formed was collected by filtration, washed with water (50 mL, 2X) and recrystallized from THF/ethanol to afford bright yellow heavy crystals (10.592 g, 90% yield): mp 181-183 ºC (lit.[15] mp 180-181.5 ºC). IR (KBr) 3482, 3367, 1680, 1618, 1548, 1478, 1504, 1308, 1257, 1137, 1050 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 8.91 (s, 1 H), 7.13 (s, 1 H), 6.73 (br s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 151.28, 135.90, 131.10, 118.22, 115.48, 104.14. HRMS found *m/z* 293.8646, $C_6H_4Br_2N_2O_2$ requires 293.8640.

2,5-Dibromo-4-nitrobenzenediazonium tetrafluoroborate. Following the general diazotization procedure a warm solution of 2,5-dibromo-4-nitroaniline (8.874 g, 30.00 mmol) in acetonitrile (5 mL) and sulfolane (35 mL) was added to a suspension of $NOBF_4$ (3.861 g, 33.00 mmol) in acetonitrile (25 mL) and sulfolane (5 mL) maintained at –30 ºC in a round bottom flask equipped with a magnetic stirring bar. The

(6) Temperatures in excess of 35ºC cause significant product loss.

product was precipitated by ether (500 mL) as colorless leaflets that were then washed with ether and dried *in vacuo* (10.852 g, 91% yield). IR (KBr) 3092, 2942, 2287, 1544, 1354, 1265, 1084, 1062 cm^{-1}. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 9.49 (s, 1 H), 8.94 (s, 1 H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 157.05, 141.88, 132.25, 126.71, 123.77, 115.18.

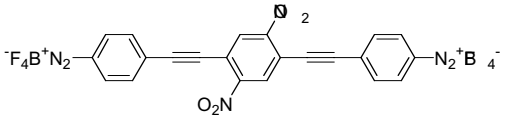
1,4-Dibromo-2,5-dinitrobenzene. A solution of 2,5-dibromo-4-nitrobenzenediazonium tetrafluoroborate (10.852 g, 27.5 mmol) in water (700 mL) was added to a solution of $NaNO_2$ (20.01 g, 290 mmol) in water (100 mL) contained in a 2 L beaker. The immediate formation of a voluminous pink foam was observed. After all of the diazonium solution had been introduced, the reaction mixture was extracted with dichloromethane (50 mL, 3X). Dark extracts were evaporated in vacuo and the residue was chromatographed on silica with dichloromethane eluent. Evaporation of the eluate afforded an orange product that was recrystallized from dichloromethane/hexanes and sublimed *in vacuo* to give heavy, slightly yellow crystals (5.510 g, 62% yield): mp 129-131 ºC (lit.[7] mp 128-129 ºC). IR (KBr) 3095, 1540, 1455, 1369, 1341, 1266, 1066, 895, 842 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.98, 130.75, 113.26.



4-(4-Bromo-2,5-dinitrophenylethynyl)aniline and 4-[2,5-dinitro-4-(4-aminophenylethynyl)phenylethynyl]aniline (6).[8] 1,4-Dibromo-2,5-dinitrobenzene (0.977 g, 3.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.042 g, 0.06 mmol), copper(I) iodide (0.011 g, 0.06 mmol), triethylamine (5.0 mL), THF (5.0 mL) and 4-ethynylaniline (0.468 g, 4.00 mmol) were used following the general procedure for couplings. The reaction mixture was stirred at room temperature for 12 h. After solvent removal *in vacuo*, the residue was sonicated with dichloromethane (10 mL) and filtered. The filter cake was washed 5X with dichloromethane (10 mL) and dried *in vacuo* to afford dark purple crystals of the diamine **6** (0.432 g, 36% yield): mp >270 ºC. IR (KBr) 3494, 3387, 2184, 1600, 1400, 1523, 1537, 1308, 1337, 1251, 1136 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 (s, 2 H), 7.27-7.29 (m, 2 H), 6.59-6.61 (m, 2 H), 5.93 (br s, 4 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.18, 149.89, 133.67, 129.43,

(7) Hammond, G. S.; Modic, F. J. *J. Amer. Chem. Soc*. **1953**, *75*, 1385.
(8) The procedure is optimized to give comparable yields of both mono and bis alkynylated products.

116.95, 113.66, 106.10, 103.45, 82.23. HRMS found *m/z* 398.1018, $C_{22}H_{14}N_4O_4$ requires 398.1015. Combined filtrates were chromatographed on a short column of silica with dichloromethane/hexanes (2:1) to afford 4-(4-bromo-2,5-dinitrophenylethynyl)aniline as a dark brown powder (0.466 g, 43% yield): mp 165-167 ºC. IR (KBr) 3501, 3397, 2186, 1625, 1592, 1522, 1258, 1146 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 8.52 (s, 1 H), 8.27 (s, 1 H), 7.26-7.28 (m, 2 H), 6.61-6.63 (m, 2 H), 5.67 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 151.33, 150.78, 148.8, 133.35, 130.4, 129.21, 119.32, 113.39, 110.67, 106.06, 103.98, 81.31. HRMS found *m/z* 360.9694, $C_{14}H_8N_3O_4Br$ requires 360.9698.



4-[2,5-Dinitro-4-(4-diazoniophenylethynyl)phenylethynyl]benzenediazonium tetrafluoroborate (12). Following the general diazotization procedure 4-[2,5-dinitro-4-(4-aminophenylethynyl)phenylethynyl]aniline (**6**, 0.199 g, 0.500 mmol) was treated with $NOBF_4$[9] (0.128 g, 1.10 mmol) in acetonitrile (5.0 mL)/sulfolane (5.0 mL). The product was precipitated with ether (20 mL). The salt was washed with ether and reprecipitated from DMSO and CH_2Cl_2 as light-sensitive yellow crystals (0.215 g, 72% yield). IR (KBr) 3107, 2291, 1579, 1546, 1342, 1078, 830 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 8.85 (s, 2H), 8.79 (d, *J*=9 Hz, 2 H), 8.20 (d, *J*=9 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 150.60, 133.93, 133.83, 133.14, 132.40, 131.75, 117.