

Synthesis of nitrile-terminated potential molecular electronic devices

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Abstract—Several potential molecular devices have been synthesized consisting of oligo(phenylene ethynylene) (OPE) backbones containing a terminal nitrile group alligator clip as a means of attachment to a metal surface. The synthesis of four new nitrile-containing OPEs is discussed, including an improved synthesis of an intermediate used in our prior production of OPEs containing acetate-protected thiol alligator clips. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The quest to find a highly conductive method of attachment to the ‘outside’ world has become paramount to success of molecular electronics. Several studies have been made using thiols,^{1,2} isocyanides,^{2–4} pyridines,^{5,6} fatty acids,¹ and diazonium salts⁷ (carbon attachment via loss of N₂) as the

attachment point of the molecules to the metal surface in the formation of self-assembled monolayers (SAMs). The functionality that allows the molecules to bond with the metal surface is called an ‘alligator clip’ in reference to the macroscopic world’s method of using alligator clips to form connections of wires to metallic contacts. The nanoscopic alligator clips facilitate the flow of electricity from the metal through the wire. While all of these functionalities confer reasonable conductivity according to the limited amount of testing done so far, the search is far from complete.

The nitrile group offers two modes of binding to a metal surface.⁸ The bonding mode that is of interest to molecular electricians is the eta-one mode in which the lone pair of nitrogen is involved in a sigma bond normal to the metal surface. Previous work has shown this to be the case with acetonitrile and nickel.⁹ For this reason the synthesis of four new nitrile-terminated oligo(phenylene ethynylenes) (OPEs) **1–4** (Fig. 1) was undertaken.

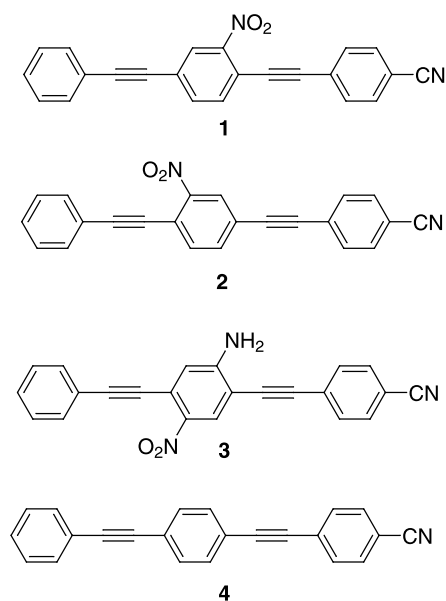
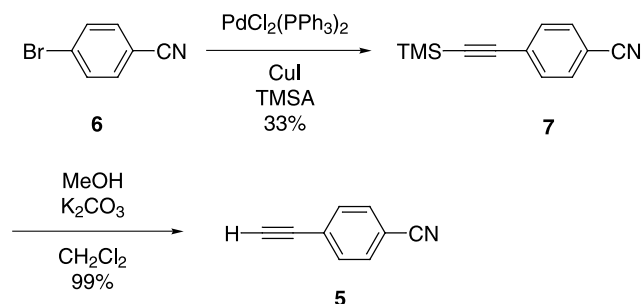


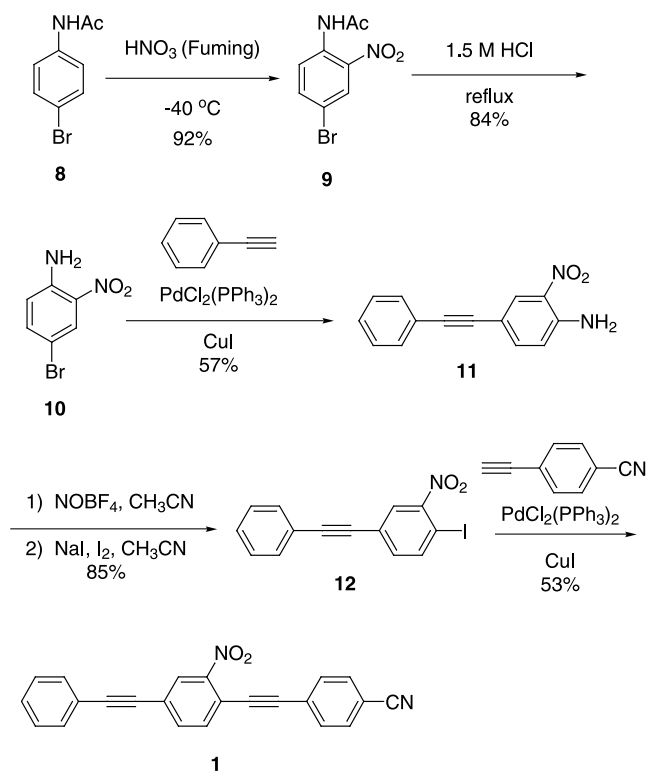
Figure 1. Nitrile-terminated compounds **1–4**.

Keywords: alligator clip; nitroaniline; oligo(phenylene ethynylene).

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Scheme 1. Synthesis of alligator clip **5**.



Scheme 2. Synthesis of mono-nitro compound 1.

2. Results and discussion

In order to expedite the synthesis of the molecular wires, a semi-convergent approach was undertaken in which most of the compound was assembled and in the last step coupled with the moiety containing the alligator clip. The alkynyl

clip **5** was synthesized starting from commercially available 4-bromobenzonitrile (**6**) (Scheme 1).

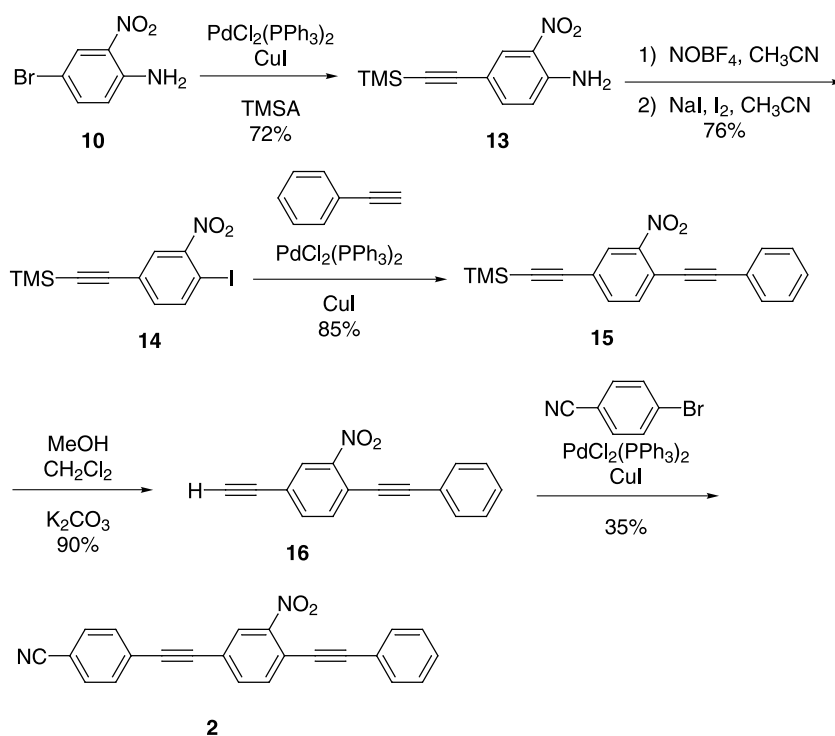
Trimethylsilylacetylene (TMSA) was coupled to **6** in a rather low yield via a Sonogashira¹⁰ coupling. Deprotection of the alkyne-protecting group afforded **5** in nearly quantitative yield.

The synthesis of **1** began with the nitration of 4-bromoacetanilide (**8**) carried out at -40°C using fuming nitric acid to produce 4-bromo-2-nitroacetanilide (**9**), as shown in Scheme 2. Deprotection of the acetamide with refluxing 1.5 M hydrochloric acid produced 4-bromo-2-nitroaniline (**10**) that was then coupled to phenylacetylene in 57% yield. Diazotization of the amine followed by replacement with iodide resulted in the formation of **12** in high yield. A final coupling with nitrile **5** afforded desired product **1** in fair yield.

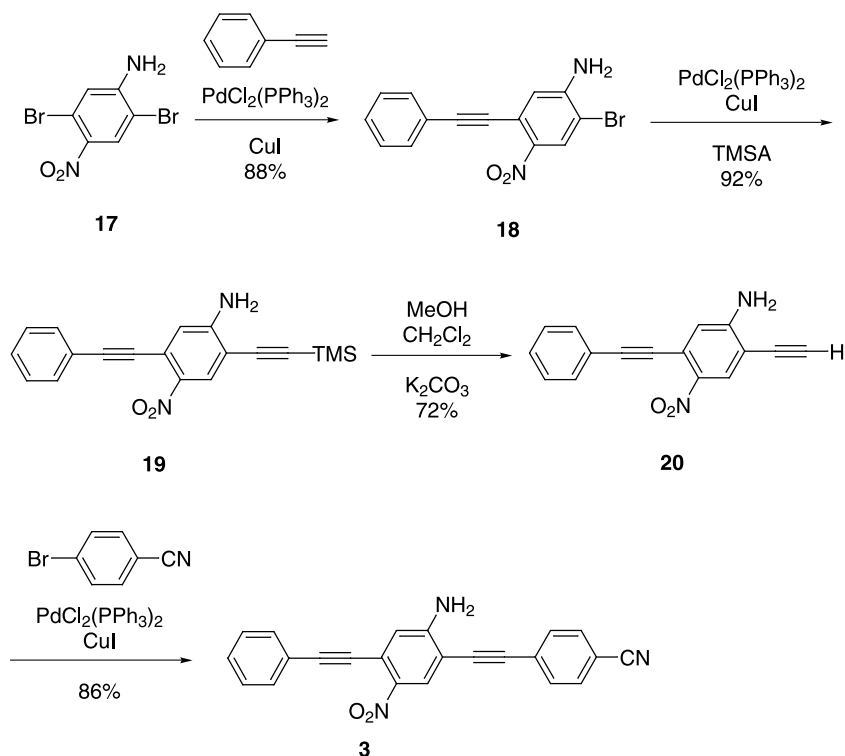
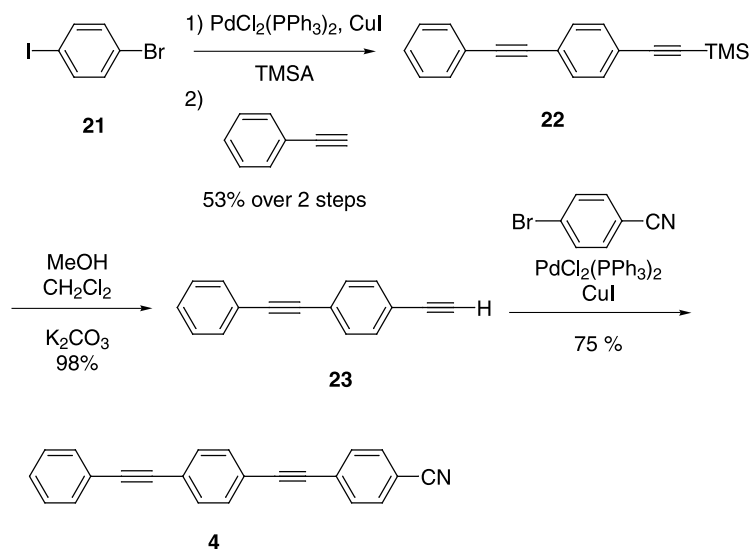
Compound **2** is a regioisomer of compound **1** and was synthesized according to Scheme 3. Aniline **10** was coupled to TMSA to give alkyne **13**. Diazotization followed by replacement with iodide produced compound **14** in good yield. **14** was then coupled to phenylacetylene in 85% yield to produce **15**.

Removal of the trimethylsilyl group afforded the terminal alkyne (**16**) in an excellent yield. The final coupling produced desired compound **2** in a low yield. This final coupling might improve if 4-iodobenzonitrile were used as the source of the nitrile group, a reaction that will be attempted in future optimization work.

Nitroaniline **3** was synthesized according to Scheme 4. This is the nitrile analog of the low temperature negative



Scheme 3. Synthesis of mono-nitro compound 2.

Scheme 4. Synthesis of nitroaniline **3**.Scheme 5. Synthesis of unfunctionalized wire **4**.

differential resistance (NDR) compound that was reported previously.^{11,12}

The synthesis of **3** began with the selective coupling of phenylacetylene to 2,5-dibromo-4-nitroaniline (**17**) at room temperature to give **18**.¹² This is an improvement over the reported procedure in which phenylacetylene was coupled with the acetamide of compound **17**. Coupling with TMSA afforded **19** in very good yield. Deprotection to unmask the terminal alkyne afforded **20**, which was then coupled with **6** to produce the desired compound **3**.

The unfunctionalized wire **4** was synthesized according to

Scheme 5. The synthesis began with a one pot coupling of TMSA with iodobromide **21** followed by the coupling with phenylacetylene to produce **22** in 53%. Deprotection of the trimethylsilyl group afforded **23**, that was then coupled to **6** in good yield producing desired nitrile **4**.

3. Conclusion

Four nitrile-terminated OPEs have been synthesized for molecular electronics-related studies, including the formation of SAMs in test-beds and subsequent electrical measurements. An improved synthesis of **18**, an

intermediate in syntheses of related OPEs, is reported. The SAM formation and electrical measurement work is on going in both our labs and those of our collaborators. The results will be reported when they are available.

4. Experimental

4.1. General procedure

All reactions were carried out under a dry nitrogen atmosphere unless noted. ^1H NMR was carried out on a 400 MHz Bruker model Avance 400. Proton chemical shifts (δ) are reported as shifts from the internal standard tetramethylsilane (TMS). ^{13}C NMR was carried out on a 100 MHz Bruker model Avance 400. All peaks are reported relative to the 77.0 ppm peaks of deuterio chloroform (CDCl_3). IR was carried out on a Nicolet Avatar 360 FTIR. Reagent grade diethyl ether, and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane (CH_2Cl_2) was distilled from calcium hydride (CaH_2) under nitrogen. Triethylamine and *N,N*-diisopropylamine were distilled over CaH_2 under a nitrogen atmosphere. Bulk hexanes were distilled prior to use. Gravity column chromatography and flash chromatography were carried out using 230–400 mesh silica gel from EM Science. Thin layer chromatography (TLC) was performed using Merck 40 F₂₅₄ on a thickness of 0.25 mm. Mass Spectrometry was obtained from the Rice University Mass Spectrometry Laboratory.

4.2. General Pd/Cu-coupling reaction procedures¹⁰

To an oven dried glass sealed tube all solids including the aryl halide (bromide or iodide), alkyne, copper iodide, triphenylphosphine and palladium catalyst were added. The atmosphere was removed via vacuum and replaced with dry nitrogen (3 \times). THF, remaining liquids, and Hünig's base or triethylamine were added and the reaction was heated in an oil bath while stirring. Upon cooling the reaction mixture was filtered via gravity filtration to remove solids and diluted with CH_2Cl_2 . The reaction mixture was extracted with an aqueous solution of ammonium chloride (NH_4Cl) (3 \times). The organic layer was dried with magnesium sulfate and filtered. The solvent was then removed in vacuo.

4.3. General procedure for the deprotection of trimethylsilyl protected alkynes¹³

To a round bottom flask equipped with a stir bar were added the protected alkyne, potassium carbonate (5 equiv. per protected alkyne), methanol, and CH_2Cl_2 . The reaction was stirred, and upon completion the reaction mixture was diluted with CH_2Cl_2 and washed with brine (3 \times). The organic layer was dried over MgSO_4 , and the solvent removed in vacuo.

4.4. General procedure for the diazotization of anilines with nitrosonium tetrafluoroborate in the acetonitrile–sulfolane system¹⁴

NOBF_4 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°C . The solution of the aniline was prepared by adding warm sulfolane ($45\text{--}50^\circ\text{C}$) 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°C 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 CH_2Cl_2 , collected by filtration, washed with ether or CH_2Cl_2 and dried. Additional purification of the salt was accomplished by re-precipitation from DMSO by CH_2Cl_2 and/or ether.

4.4.1. 4-Trimethylsilylethynylbenzonitrile (7). Compound **6** (3.64 g, 20 mmol), bis(triphenylphosphine)palladium(II) chloride (0.42 g, 0.6 mmol), copper(I) iodide (0.11 g, 0.6 mmol), TMSA (3.40 mL, 24 mmol), Hünig's base (7.70 mL, 50 mmol), and THF (20 mL) were reacted according to the general coupling procedure above. The reaction was heated at 45°C overnight. Crude product was recrystallized from ethanol yielding 1.31 g (33%) of a white solid. Mp $99\text{--}101^\circ\text{C}$. IR (KBr) 3061.8, 2959.0, 2232.7, 2155.8, 1601.5, 1497.5, 1407.8, 1268.9, 1248.5, 1216.9, 1177.3, 862.3, 841.0, 758.5, 724.6, 697.6, 628.6, 555.4 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dt, $J=8.7$ Hz, 2H), 7.51 (dt, $J=8.7$ Hz, 2H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 132.9, 132.3, 128.4, 118.9, 112.2, 103.4, 100.0, 0.2. HRMS calcd for $\text{C}_{12}\text{H}_{13}\text{NSi}$: 199.08172. Found: 199.0820.

4.4.2. 4-Ethynylbenzonitrile (5). Compound **7** (1.00 g, 5.02 mmol), potassium carbonate (3.46 g, 25.00 mmol), methanol (50 mL) and CH_2Cl_2 (30 mL) were reacted according to the general deprotection procedure above to yield 624 mg (99%) of a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J=8.7$ Hz, 2H), 7.55 (d, $J=8.5$ Hz, 2H), 3.28 (s, 1H).

4.4.3. 4-Bromo-2-nitroacetamide (9). To a 500 mL round bottom flask was added fuming nitric acid (30 mL) and cooled to -40°C . Compound **8** (3.00 g, 14.15 mmol) was added and allowed to stir for 10 min. The reaction mixture was then poured over ice and the precipitate that formed was collected yielding 3.33 g (92%) of a yellow solid. Mp $106\text{--}108^\circ\text{C}$. IR (KBr) 3364.1, 3122.6, 3096.5, 1711.9, 1603.5, 1572.7, 1484.4, 1445.8, 1337.0, 1257.9, 1220.3, 1143.2, 1074.1, 998.3, 872.1, 843.8, 759.4, 722.5, 665.4, 588.1, 529.0 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.24 (br s, 1H), 8.70 (d, $J=9.1$ Hz, 1H), 8.35 (d, $J=2.4$ Hz, 1H), 7.03 (dd, $J=9.1$, 2.3 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 139.1, 136.9, 134.4, 128.6, 124.0, 115.7, 26.0.

4.4.4. 4-Bromo-2-nitroaniline (10). To a 250 mL round bottom flask was added **9** (12.12 g, 47.16 mmol), THF (40 mL) and 2 M hydrochloric acid (200 mL) and heated to reflux over night. The next day the solid was collected and recrystallized from ethanol yielding 7.98 g (77%) of a bright orange solid. Mp $113\text{--}115^\circ\text{C}$. IR (KBr) 3472.5, 3351.6, 3174.3, 3092.6, 1636.7, 1591.5, 1558.9, 1499.6, 1455.1,

1402.1, 1364.6, 1337.1, 1248.0, 1161.4, 1102.1, 881.2, 815.7, 762.9, 703.6, 626.8, 521.0, 451.9 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J=2.4$ Hz, 1H), 7.41 (dd, $J=8.9, 2.3$ Hz, 1H), 6.70 (d, $J=8.9$ Hz, 1H) 6.06 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 138.9, 132.9, 128.7, 120.8, 108.2. HRMS calcd for $\text{C}_6\text{H}_5\text{N}_2\text{O}_2\text{Br}$: 215.9535. Found: 215.9537.

4.4.5. 4-Ethynylphenyl-2-nitroaniline (11). Compound **10** (2.17 g, 10 mmol), bis(triphenylphosphine)palladium(II) chloride (140 mg, 0.2 mmol), copper(I) iodide (38 mg, 0.2 mmol), phenylacetylene (1.32 mL, 12 mmol), triphenylphosphine (131 mg, 0.5 mmol) triethylamine (10 mL), and THF (20 mL) were reacted according to the general coupling procedure above. The reaction was heated at 65°C for 2 days. The crude product was passed through a column (silica, 5:2 petroleum ether/ethyl acetate) and precipitated from CH_2Cl_2 with hexanes to yield 1.34 g (57%) of a bright red solid. Mp $160\text{--}163^\circ\text{C}$. IR (KBr) 3471.5, 3344.1, 3175.2, 1640.3, 1598.6, 1551.7, 1515.2, 1463.1, 1410.6, 1371.4, 1343.0, 1234.2, 1175.1, 1143.3, 831.4, 756.6, 687.4 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J=1.9$ Hz, 1H), 7.51–7.45 (m, 3H), 7.36–7.31 (m, 3H), 6.77 (d, $J=8.6$ Hz, 1H), 6.19 (br s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 138.7, 132.2, 131.9, 129.9, 128.8, 128.7, 123.4, 119.3, 112.5, 89.1, 88.0. HRMS calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$: 238.0742. Found: 238.0744.

4.4.6. 5-Ethynylphenyl-2-iodonitrobenzene (12). In a 50 mL round bottom flask **11** (500 mg, 2.13 mmol), NOBF_4 (273 mg, 2.34 mmol), and acetonitrile (25 mL) were diazotized according to the procedure above. The contents of the 50 mL round bottom were then transferred via cannula into a solution of sodium iodide (639 mg, 4.26 mmol) and iodine (541 mg, 2.13 mmol) in acetonitrile (15 mL). The solution was allowed to stir for 30 min. The crude mixture was diluted with CH_2Cl_2 and washed with a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$. The organics were dried over MgSO_4 and the solvents removed in vacuo to yield 708 mg (85%) of a yellow brown solid. Mp $110\text{--}112^\circ\text{C}$. IR (KBr) 3052.8, 2210.8, 1597.0, 1521.6, 1490.8, 1462.4, 1438.4, 1350.5, 1274.3, 1248.9, 1157.5, 1132.0, 1067.9, 1012.6, 915.4, 889.6, 825.7, 753.0, 685.1, 557.0, 525.4, 504.0 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J=8.2$ Hz, 1H), 7.95 (d, $J=1.9$ Hz, 1H), 7.53–7.51 (m, 2H), 7.38–7.33 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 142.3, 136.0, 132.2, 129.7, 129.0, 128.4, 125.4, 122.4, 93.7, 86.6, 85.9.

4.4.7. 2'-Nitro-4,4'-diethynylphenyl-1-cyanobenzene (1). Compound **12** (603 mg, 1.74 mmol), **5** (242 mg, 1.92 mmol), bis(triphenylphosphine)palladium(II) chloride (63 mg, 0.09 mmol), copper(I) iodide (34 mg, 0.18 mmol), triphenylphosphine (60 mg, 0.23 mmol) Hünig's base (0.76 mL, 4.35 mmol), and THF (20 mL) were coupled according to the general coupling procedure above. The reaction was heated at 45°C for 3 days. The crude product was purified via flash chromatography (silica, 5:2 petroleum ether/ethyl acetate) to yield 316 mg (53%) of a light yellow solid. Mp $155\text{--}156^\circ\text{C}$ dec. IR (KBr) 3081.5, 3054.2, 2222.1, 1597.8, 1537.4, 1517.0, 1442.4, 1400.7, 1348.9, 1305.7, 1269.2, 1184.7, 1139.1, 1070.2, 1023.6, 893.4, 837.8, 758.7, 695.8, 552.0, 533.8 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J=1.5$ Hz, 1H), 7.72 (dd,

$J=8.0, 1.6$ Hz, 1H) 7.68 (d, $J=8.1$ Hz, 1H), 7.66 (s, 4H), 7.55–7.53 (m, 2H), 7.39–7.37 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 135.9, 135.1, 132.9, 132.6, 132.3, 129.8, 129.0, 128.2, 127.5, 125.6, 122.3, 118.7, 117.2, 113.1, 96.7, 94.7, 89.1, 87.1. HRMS calcd for $\text{C}_{23}\text{H}_{12}\text{N}_2\text{O}_2$: 348.0899. Found: 348.0893.

4.4.8. 2-Nitro-4-trimethylsilylethynylaniline (13). Compound **10** (2.17 g, 10 mmol), TMSA (1.70 mL, 12 mmol), bis(triphenylphosphine)palladium(II) chloride (351 mg, 0.50 mmol), copper(I) iodide (190 mg, 1.0 mmol), triphenylphosphine (328 mg, 1.25 mmol) Hünig's base (4.35 mL, 25.0 mmol), and THF (20 mL) were reacted according to the general coupling procedure above. The reaction was heated overnight at 45°C . The crude product was purified via flash column chromatography (silica, 5:2 petroleum ether/ethyl acetate) followed by precipitation from CH_2Cl_2 with hexane to yield 1.24 g (53%) of a bright yellow solid. 0.576 g of starting material was recovered (72% yield based on recovered starting material). Mp $102\text{--}105^\circ\text{C}$ dec. IR (KBr) 3441.9, 3345.4, 2959.4, 2161.0, 2142.4, 1629.8, 1589.5, 1550.6, 1515.0, 1477.1, 1413.1, 1353.7, 1332.1, 1285.8, 1247.4, 1215.9, 1165.3, 1081.6, 935.8, 839.1, 758.2, 695.1, 636.7, 567.4 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J=1.9$ Hz, 1H), 7.39 (dd, $J=8.7, 1.9$ Hz, 1H), 6.71 (d, $J=8.8$ Hz, 1H), 6.18 (br s, 1H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 144.7, 138.9, 130.5, 119.1, 112.4, 103.5, 94.0, 0.3. HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{Si}$: 234.025. Found: 234.025.

4.4.9. 2-Iodo-5-trimethylsilylethynynitrobenzene (14). In a 100 mL round bottom flask **13** (500 mg, 2.13 mmol), NOBF_4 (274 mg, 2.35 mmol), acetonitrile (7 mL) and sulfolane (7 mL) were diazotized according to the above procedure. The contents of the 100 mL round bottom flask were then transferred to a solution of iodine (541 mg, 2.13 mmol), sodium iodide (639 mg, 4.36 mmol) in acetonitrile (20 mL). After initial evolution of gas subsided the mixture was allowed to stir for 30 min. The crude mixture was diluted with CH_2Cl_2 and washed with a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$. The organics were dried over MgSO_4 and the solvents removed in vacuo to yield 735 mg (76%) of a light brown solid. IR (KBr) 3088.6, 2959.8, 2898.3, 2166.4, 2142.1, 1590.9, 1530.6, 1464.4, 1357.7, 1252.2, 1218.1, 1143.6, 1019.1, 930.3, 847.9, 760.1, 690.4, 652.6, 470.1, 447.9 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J=8.1$ Hz, 1H), 7.88 (d, $J=1.9$ Hz, 1H), 7.27 (dd, $J=8.1, 1.9$ Hz, 1H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 142.2, 136.4, 128.8, 125.2, 101.7, 99.7, 86.3, 0.1. HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{INO}_2\text{Si}$: 344.9682. Found: 344.9678.

4.4.10. 2-Ethynylphenyl-5-trimethylsilylethynynitrobenzene (15). Compound **14** (494 mg, 1.43 mmol), phenylacetylene (0.18 mL, 1.72 mmol), bis(triphenylphosphine)palladium(II) chloride (50 mg, 0.07 mmol), copper(I) iodide (27 mg, 0.14 mmol), triethylamine (5 mL), and THF (10 mL) were coupled according to the general coupling procedure above. The reaction was stirred at room temperature for 45 min. The crude product was purified via flash column chromatography (silica, 5:1 hexanes/ CH_2Cl_2) to yield 388 mg (85%) of a yellow solid. IR (KBr) 3061.3, 2960.1, 2899.3, 2215.3, 2164.2, 1611.4,

1542.8, 1500.4, 1443.1, 1400.3, 1348.1, 1252.3, 1217.0, 1139.3, 1069.6, 1025.2, 935.6, 904.6, 856.5, 810.5, 758.4, 734.9, 691.4, 632.8 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.13 (t, $J=1.0$ Hz, 1H), 7.61 (m, 2H), 7.58–7.56 (m, 2H), 7.37–7.36 (m, 3H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.7, 136.0, 134.8, 132.5, 129.8, 128.9, 128.4, 124.2, 122.6, 118.8, 102.4, 99.8, 99.4, 85.2, 0.2. HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2\text{NSi}$: 319.1029. Found: 319.1028.

4.4.11. 5-Ethynyl-2-ethynylphenyl-nitrobenzene (16).

Compound **15** (388 mg, 1.21 mmol), potassium carbonate (839 mg, 6.07 mmol), methanol (20 mL), and CH_2Cl_2 (20 mL) were reacted according to the general deprotection procedure above yielding 268 mg (90%) of the desired compound. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (t, $J=0.9$ Hz, 1H), 7.64 (d, $J=1.0$ Hz, 2H), 7.64–7.56 (m, 2H), 7.39–7.34 (m, 3H), 3.28 (s, 1H).

4.4.12. 3'-Nitro-4,4'-diethynylphenyl-1-cyanobenzene (2).

Compound **16** (268 mg, 1.08 mmol), bis(triphenylphosphine)palladium(II) chloride (23 mg, 0.03 mmol), copper(I) iodide (11 mg, 0.06 mmol), triphenylphosphine (16 mg, 0.06 mmol), **6** (236 mg, 1.3 mmol), triethylamine (5 mL), and THF (10 mL) were reacted according to the general coupling procedure above. The reaction mixture was heated at 70°C overnight. Upon cooling to room temperature the crude product was purified via flash column chromatography (silica, 1:1 hexanes/ CH_2Cl_2) to yield 131 mg (35%) of a yellow solid. Mp 140°C dec. IR (KBr) 3082.1, 3053.1, 2224.5, 2209.2, 1601.2, 1539.6, 1442.3, 1402.1, 1342.2, 1308.5, 1271.5, 1139.8, 912.9, 836.1, 757.3, 689.3, 554.9, 529.4 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.23 (t, $J=1.1$ Hz, 1H), 7.70 (d, $J=0.9$ Hz, 2H), 7.68–7.58 (m, 6H), 7.40–7.36 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 135.8, 135.1, 132.7, 132.6, 132.6, 130.1, 129.0, 128.3, 127.3, 123.2, 122.5, 119.4, 118.7, 112.8, 100.1, 91.8, 91.2, 85.1. HRMS calcd for $\text{C}_{23}\text{H}_{12}\text{N}_2\text{O}_2$: 348.0899. Found: 348.0891.

4.4.13. 2-Bromo-5-ethynylphenyl-4-nitroaniline (18).¹²

Compound **17** (1.622 g, 5.48 mmol), phenylacetylene (0.66 mL, 6.03 mmol), bis(triphenylphosphine)palladium(II) chloride (115 mg, 0.16 mmol), copper(I) iodide (61 mg, 0.32 mmol), triphenylphosphine (84 mg, 0.32 mmol), triethylamine (5 mL), and THF (10 mL) were reacted according to the general coupling procedure above. The reaction was stirred at room temperature for 3 h. The crude product was purified via flash column chromatography (silica, 3:1 CH_2Cl_2 /hexanes) to yield 1.522 g (88%) of a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 7.58–7.56 (m, 2H), 7.38–7.34 (m, 3H), 6.94 (s, 1H).

4.4.14. 5-Ethynylphenyl-4-nitro-2-trimethylsilylethynylaniline (19).¹²

Compound **18** (500 mg, 1.58 mmol), TMSA (0.27 mL, 1.90 mmol), bis(triphenylphosphine)palladium(II) chloride (56 mg, 0.08 mmol), copper(I) iodide (30 mg, 0.16 mmol), triphenylphosphine (52 mg, 0.20 mmol), triethylamine (5 mL), and THF (10 mL) were coupled according to the general coupling procedure above. The reaction mixture was heated at 65°C overnight. The crude product was purified via flash column chromatography to yield 528 mg (92%) of desired product. ^1H NMR (400 MHz,

CDCl_3) δ 8.20 (s, 1H), 7.58–7.56 (m, 2H), 7.37–7.34 (m, 3H), 6.88 (s, 1H), 4.83 (br s, 2H), 0.27 (s, 9H).

4.4.15. 2-Ethynyl-5-ethynylphenyl-4-nitroaniline (20).¹²

Compound **19** (487 mg, 1.46 mmol), potassium carbonate (1.01 g, 7.28 mmol), CH_2Cl_2 (20 mL), and methanol (20 mL) were reacted according to the general deprotection procedure listed above yielding 274 mg (72%) of desired product. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (s, 1H), 7.58–7.56 (m, 2H), 7.37–7.33 (m, 3H), 6.88 (s, 1H), 4.88 (br s, 2H), 3.50 (s, 1H).

4.4.16. 4-(2-Amino-5-nitro-4-phenylethynyl-phenylethynyl)-benzonitrile (3).

Compound **20** (383 mg, 1.46 mmol), **6** (293 mg, 1.61 mmol), bis(triphenylphosphine)palladium(II) chloride (49 mg, 0.07 mmol), copper(I) iodide (27 mg, 0.14 mmol), triphenylphosphine (47 mg, 0.18 mmol), triethylamine (5 mL), and THF (10 mL) were reacted according to the general coupling procedure above. The reaction was heated at 65°C overnight. Upon cooling to room temperature the crude product was purified via flash column chromatography to yield 326 mg (86%) of the desired yellow solid. Mp 180°C dec. IR (KBr) 3452.0, 3356.9, 3239.8, 2922.1, 2221.9, 2204.8, 1625.9, 1594.9, 1542.9, 1514.0, 1476.4, 1312.2, 1245.5, 1143.2, 905.2, 844.2, 756.8, 690.2, 559.7 cm^{-1} . ^1H NMR (400 MHz, DMSO) δ 8.25 (s, 1H), 7.92 (q, $J=3.3$ Hz, 4H), 7.60–7.57 (m, 2H), 7.49–7.47 (m, 3H), 7.14 (br s, 2H), 7.02 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.8, 137.2, 133.3, 133.2, 132.5, 131.8, 130.5, 129.8, 127.8, 122.7, 121.1, 119.4, 118.9, 111.8, 105.1, 96.9, 95.5, 89.3, 87.2.

4.4.17. 4-Ethynylphenyl(trimethylsilyl)ethynylbenzene (22).¹⁵

Compound **21** (2.829 g, 10.00 mmol), (trimethylsilyl)acetylene (1.48 mL, 10.5 mmol), bis(triphenylphosphine)palladium(II) chloride (140 mg, 0.20 mmol), copper(I) iodide (76 mg, 0.40 mmol), triphenylphosphine (131 mg, 0.50 mmol), Hünig's base (6.97 mL, 40 mmol), and THF (20 mL) were reacted according to the general coupling procedure above. The reaction was allowed to stir at room temperature overnight. The liquid was then cannulated into a second screw cap tube under nitrogen, containing bistriphenylphosphinepalladium(II) chloride (140 mg, 0.20 mmol) and copper(I) iodide (76 mg, 0.40 mmol). Phenylacetylene (1.32 mL, 12.00 mmol) was added and the tube capped and heat at 80°C overnight. The crude product was purified via flash column chromatography (silica, petroleum ether) to yield 1.467 g (53%) of a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.50 (m, 2H), 7.46–7.41 (m, 4H), 7.35–7.32 (m, 3H), 0.24 (s, 9H).

4.4.18. 4-Ethynylphenylethynylbenzene (23).¹⁵

Compound **22** (549 mg, 2 mmol), potassium carbonate (1.382 g, 10 mmol), methanol (30 mL), and CH_2Cl_2 (30 mL) were reacted according to the general deprotection procedure above yielding 405 mg (98%) of the desired white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.49 (m, 2H), 7.47–7.43 (m, 4H), 7.35–7.32 (m, 3H), 3.15 (s, 1H).

4.4.19. 4-(4-Phenylethynyl-phenylethynyl)-benzonitrile (4).

Compound **23** (396 mg, 1.95 mmol), **6** (426 mg, 2.34 mmol), bis(triphenylphosphine)palladium(II) chloride (70 mg, 0.10 mmol), copper(I) iodide (38 mg, 0.20 mmol),

triphenylphosphine (66 mg, 0.25 mmol), triethylamine (10 mL), and THF (20 mL) were coupled according to the general coupling procedure above. The mixture was heated at 60°C overnight. Upon cooling to room temperature the crude product was subjected to flash column chromatography yielding 445 mg (75%) of desired white solid. Mp 228–230°C dec. IR (KBr) 3083.1, 2225.4, 2210.0, 1925.4, 1681.0, 1597.8, 1511.4, 1482.4, 1440.9, 1403.5, 1307.7, 1271.6, 1178.4, 1124.6, 1103.5, 1068.9, 839.2, 760.0, 691.7, 551.6, 526.5, 440.9 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.65–7.62 (m, 2H), 7.60–7.58 (m, 2H), 7.53–7.49 (m, 6H), 7.37–7.33 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 132.1, 132.1, 132.1, 129.0, 128.8, 128.4, 124.5, 123.3, 122.3, 118.9, 112.1, 93.8, 92.2, 89.8.

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