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Accoutrements of a molecular computer: switches, memory components and alligator clips

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Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday

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Abstract—Several second generation memory components consisting of oligo(phenylene ethynylene)s containing easily reducible functionalities consisting of either nitro or quinone cores have been synthesized for incorporation into molecular electronic devices. Additionally, two new types of contacts between organic compounds and a metal surface based on diazonium salts or pyridine have been synthesized and integrated into molecules for use in molecular electronic devices. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Recent advances in the field of molecular electronics have shown that oligo(phenylene ethynylene)s containing nitro groups are good candidates for electronic switching and storage devices.[1] Since the mechanism of switching and electron storage involves a reduction upon applying a potential,[2] the search continues for a second generation of storage and switching devices containing reversibly reducible functional groups. To this end, two polynitro compounds as well as several quinone derivatives have been synthesized. Quinones are frequently found in nature as electron acceptors and can be easily reduced and re-oxidized, thus making them ideal for study in molecular electronic devices.[3,4]

In order to make molecular electronic components an alternative to the presently utilized silicon analogs will demand reliable low energy contacts between molecules and conductive leads. Typically, this is accomplished via a thiol group, which connects the active molecule to a metal contact forming a well-ordered self-assembled monolayer (SAM).[5] In an attempt to improve on the presently used thiol alligator clip, we utilized the well-established reactivity of aromatic diazonium salts toward transition metals[6] to produce a direct connection of the organic molecules to metal surfaces through a carbon–metal bond.[7] We have also built on early work showing that pyridine can assemble on a metal surface[8] by synthesizing molecules containing pyridine alligator clips.[9]

Keywords: diazonium; self-assembled monolayer; molecular computer; quinones; memory components; switches.

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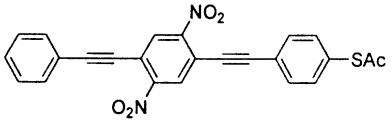
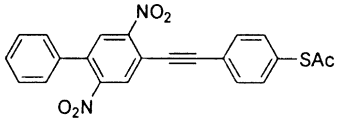
2. Switches and memory components

In an effort to improve the electron storage time by adding more nitro groups, synthetic targets **1** and **2** were chosen. The synthesis of compound **1** is outlined in Scheme 1.



1



2

The synthesis of **1** began by Sonogashira coupling[10] 2,5-dibromo-4-nitroaniline[11] (**3**) to phenylacetylene affording **4**, which was subjected to an HOF oxidation[12] forming **5**. A final coupling produced desired compound **1** in 24% yield. The low yield in this coupling may be indicative of the easily deprotected thiol or a stable palladacycle intermediate that formed during coupling.

In order to conduct electrons all the phenyl rings in the conjugated molecule should be preferentially planar to each other.[13] If a phenyl group replaces the terminal phenylethynyl group, the system cannot attain planarity. In an effort to determine the effect of a rotational barrier (i.e. conduction barrier), the synthesis of compound **2** was initiated via a Suzuki[14] coupling of 2,5-dibromo-4-nitro-

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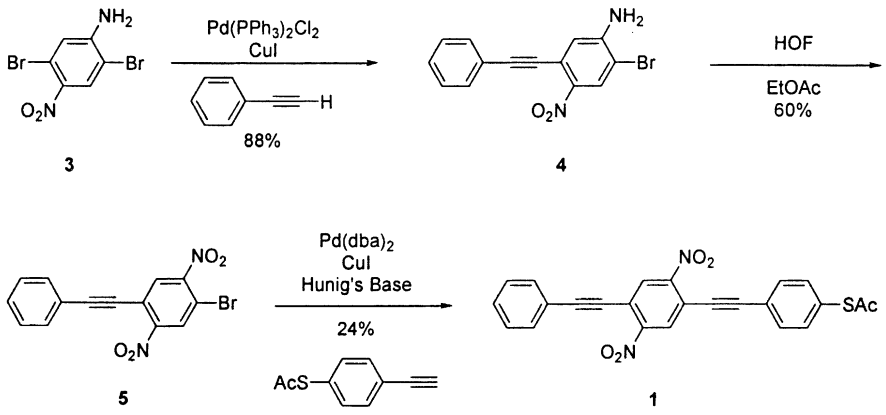
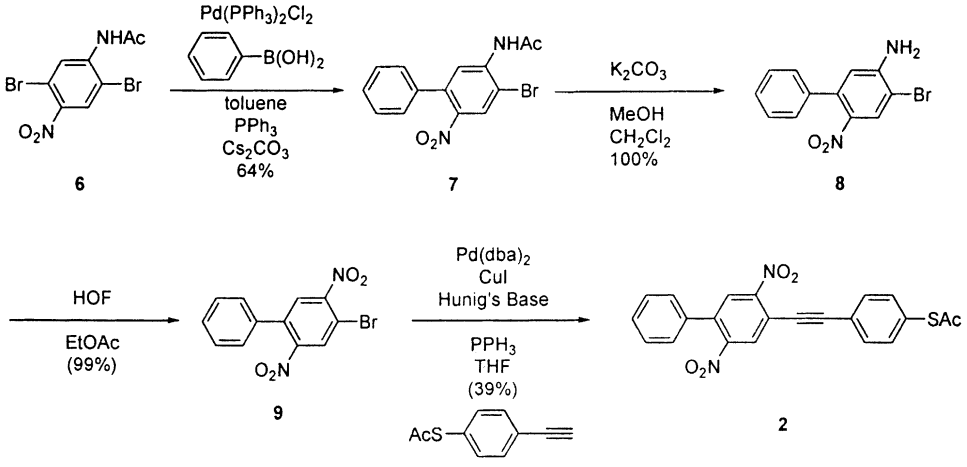


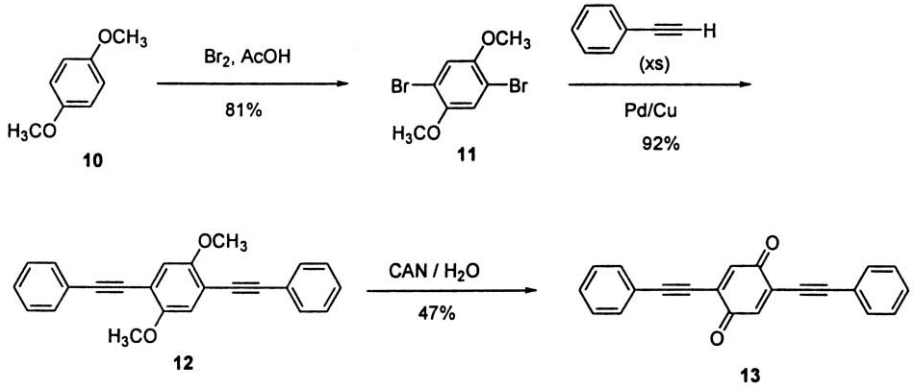
Scheme 1.

acetanilide (**6**)[11] to phenylboronic acid to form compound **7**. The acetyl group was removed to provide the aniline (**8**) functionality that would subsequently undergo an HOF oxidation to afford **9** in nearly quantitative yield. A final Sonogashira coupling provided **2** (Scheme 2).

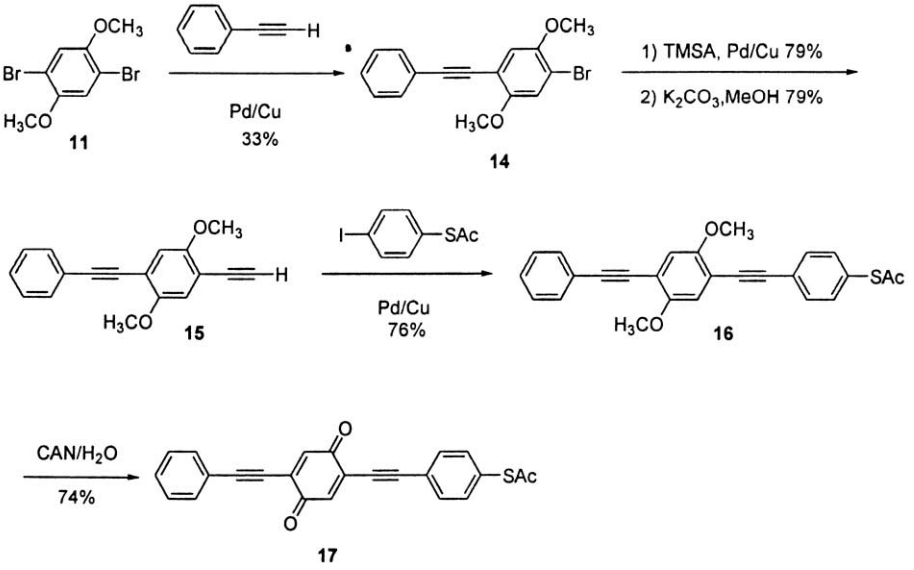
13 was synthesized for the purpose of studying the electrochemical properties of the quinone-containing molecular system.[15] Scheme 3 shows the synthesis of **13** from 1,4-dimethoxybenzene (**10**). **10** was converted to **11** using bromine and glacial acetic acid in good yield.[16] Compound **11** was then cross-coupled with an excess of phenylacetylene to afford compound **12**, which was then oxidized to the quinone affording desired compound **13**. This synthetic route had to be used because quinones generally cannot be used in the palladium-catalyzed couplings since quinones are known to oxidize palladium(0) to palladium(II), terminating the catalytic cycle.[17] Ceric



Scheme 2.



Scheme 3.

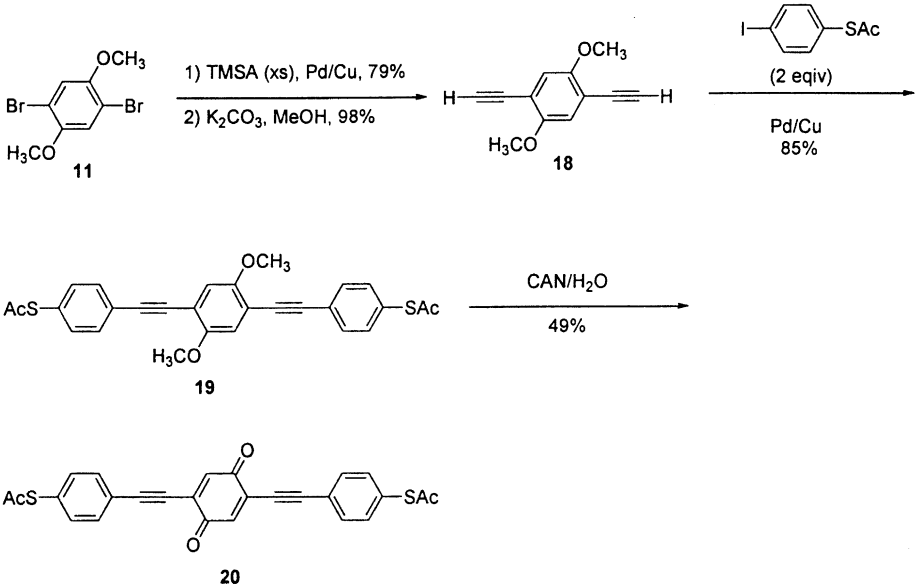


Scheme 4.

ammonium nitrate (CAN) is a mild and neutral oxidizing agent known to generate quinones from dimethoxybenzenes and therefore was a logical choice for this procedure.[18] This oxidation afforded the desired quinone compound in 47% yield. The optimum conditions for the oxidation have not yet been obtained for these systems.

Scheme 4 shows the synthesis of the quinone-containing molecular system with one thioacetate group serving as a protected alligator clip. Cross-coupling of **11** with phenylacetylene afforded **14** in a modest yet statistically expected yield of 33% due to the equal reactivity of both aryl bromides of **11** under Sonogashira coupling conditions. **15** was prepared by the cross-coupling[10] of trimethylsilylacetylene with **14** followed by deprotection of the alkyne to afford **15**. Further palladium-catalyzed cross-coupling with 4-iodobenzenethioacetate afforded compound **16**. The final compound **17** was obtained in 74% yield via the CAN oxidation.[18] However, this yield was an isolated incident. Other attempts resulted in much lower yields (~20%). More work is underway to optimize the conditions of this CAN oxidation.

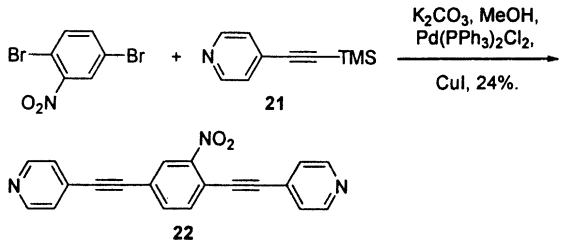
Scheme 5 shows the synthesis of the quinone-containing molecular system with alligator clips on both ends (**5**). This compound can be used to crosslink metallic nanoparticles for bridging connections in future molecular electronic devices. **11** was cross-coupled with an excess of trimethylsilylacetylene followed by a subsequent deprotection to cleanly afforded the diyne **18**. This was subsequently cross-coupled with 2 equiv. of 4-iodobenzenethioacetate to afford compound **19**. Finally, **19** was oxidized using the CAN procedure to generate **20** in modest yield.



Scheme 5.

3. Alligator clips

The synthesis of several compounds containing a pyridine alligator clip for incorporation into a molecular electronic device began with compound **21**. The synthesis of **22** was accomplished by coupling pyridine **21**[19] with 2,5-dibromonitrobenzene as shown in Eq. (1). The low yield may be due to a stable copper acetylide formed after the TMS group is cleaved. If an in situ deprotection was not used, the pyridine alkyne proved to be unstable.

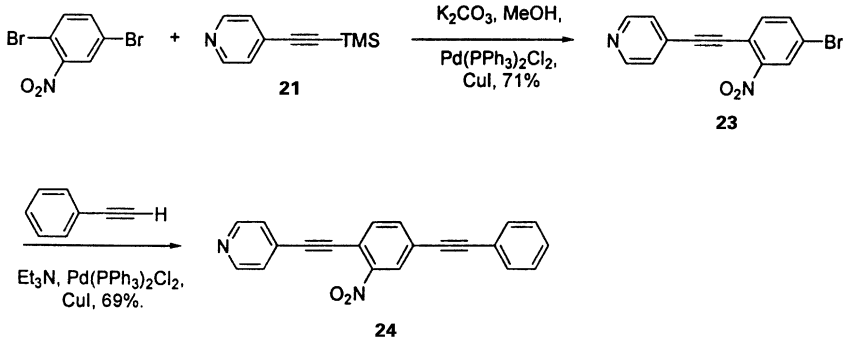


(1)

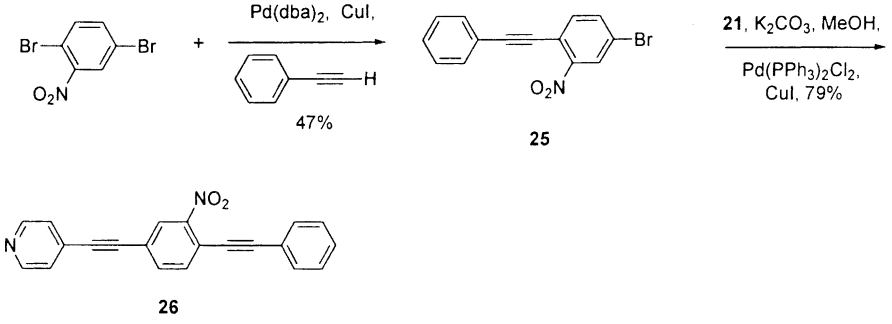
24 was synthesized according to Scheme 6. The synthesis began by coupling one equivalent of **21** to 2,5-dibromonitrobenzene selectively to the position *ortho* to the nitro group affording **23**. Coupling **23** to phenylacetylene to produce **24** completed the synthesis.

The synthesis of compound **26** was initiated to study the effect of the nitro group in relation to the chemisorbed pyridine alligator clip. To this end, compound **24** was synthesized in a manor analogous to the synthesis of **23**, as shown in Scheme 7. Coupling one equivalent of phenylacetylene selectively to 2,5-dibromonitrobenzene to produce **25** then coupling to **21** to afford **26** in good yield completed the synthesis.

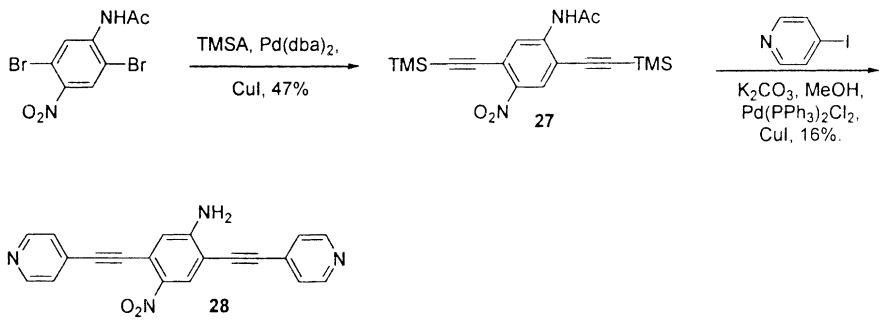
Linker **28** was synthesized according to Scheme 8. The synthesis commenced with the coupling of 2,5-dibromo-4-nitroacetanilide[11] with excess trimethylsilylacetylene to give **27**, which was then deprotected in situ and coupled with 4-iodopyridine to produce **28** in poor yield. The low yield of the coupling reactions could be due to the cyclization process reported by Rosen et al.[20] between the nitro and the alkyne unit.



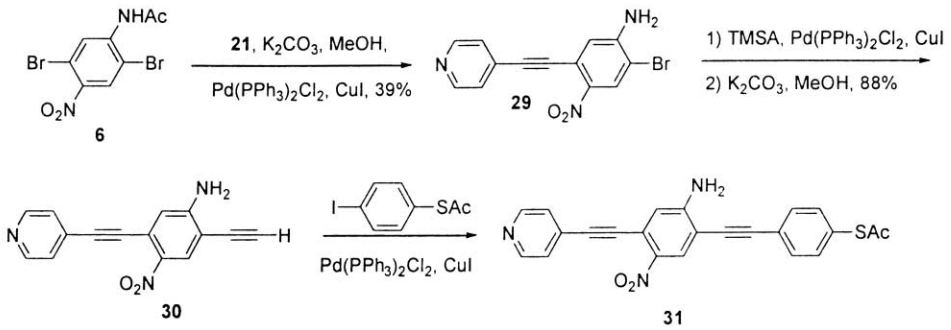
Scheme 6.



Scheme 7.



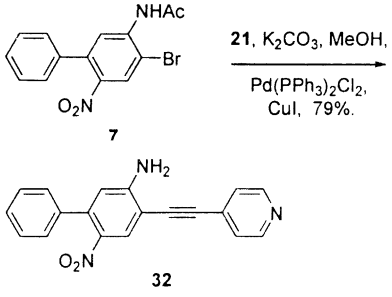
Scheme 8.



Scheme 9.

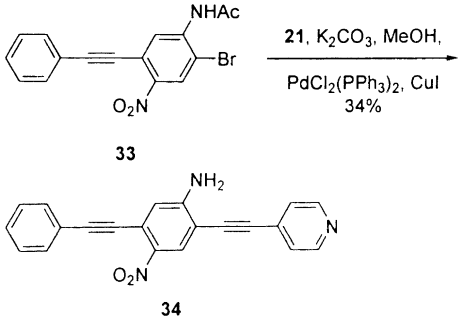
Compound **31** was synthesized in an effort to form an SAM via the protected benzenethiol terminal group enabling the pyridyl end of the molecule to serve as a better top contact with metal than a phenyl when incorporated into a device. **31** was synthesized by coupling the 2,5-dibromo-4-nitroacetanilide[11] with **21** in a low yield to afford compound **29**. **29** was then coupled with trimethylsilylacetylene, followed by deprotection with potassium carbonate to yield **30**. Finally, **30** was coupled with 4-iodobenzenethioacetate, which afforded the molecular device **31** in good yield (75%) (Scheme 9).

32 was synthesized to study the effect of a rotational barrier analogous to that described for **2**. The synthesis of **32** began with previously synthesized **7** and coupling to **21** in good yield, as shown in Eq. (2).



(2)

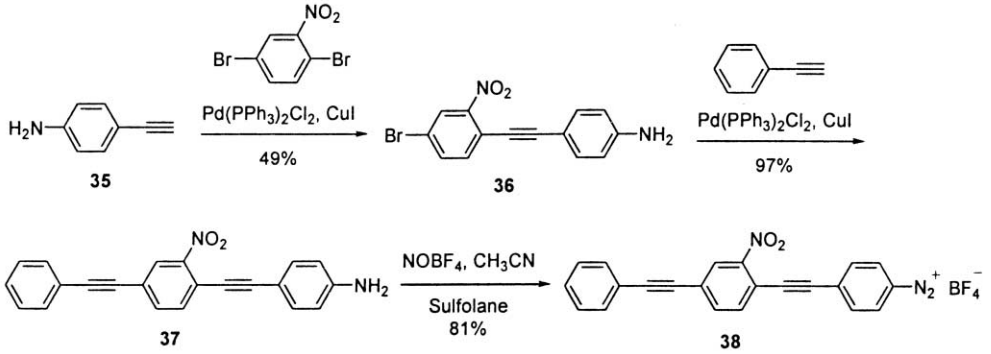
Compound **34** was synthesized according to Eq. (3) using the previously described **33**. Compound **34** is analogous to a thiol terminated nitroaniline that previously exhibited negative differential resistance (NDR) in a device embodiment.[1]



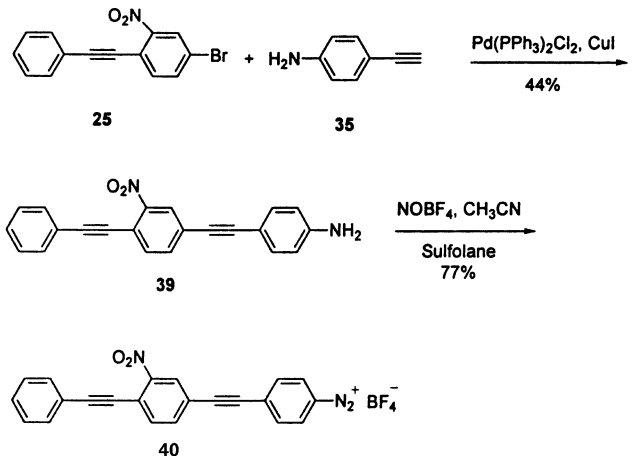
(3)

In addition to the pyridine-containing systems, three potential memory and switching components terminated by diazonium salts were synthesized. **38** is analogous to the thioacetyl terminated NDR and memory component[1] and the pyridyl terminated **24**. The synthesis of **38** began by coupling **35**[7] to 2,5-dibromonitrobenzene in moderate yield to afford **36**, which was then coupled to phenylacetylene to produce compound **37**. Diazotization of **37** produced the completed molecule **38** in good yield (Scheme 10).

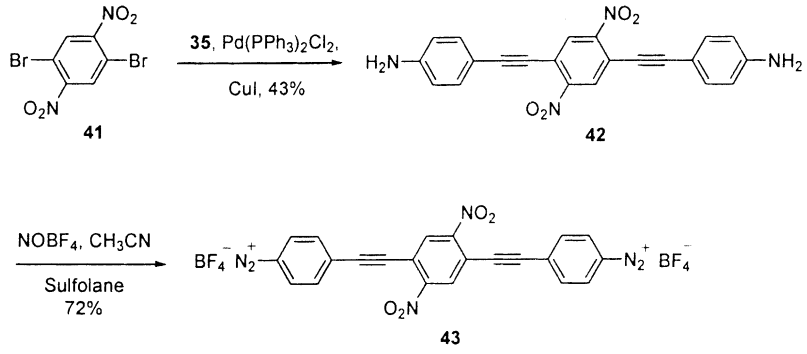
40 is similar in structure to **26** except the pyridyl group has been replaced with the aryl diazonium salt. The synthesis of **40** is shown is Scheme 11. Coupling aniline **35** to nitrocompound **25** produced diazonium precursor **39** in moderate yield. Diazotization of aniline **42** afforded desired product **37**.



Scheme 10.



Scheme 11.



Scheme 12.

Nanoparticle linker **43** was synthesized according to Scheme 12. Starting from dinitro **41**[12] and coupling aniline **35** afforded dinitrodianiline **42**, which was subsequently diazotized to produce **43** in good yield.

4. Conclusions

Many oligo(phenylene ethynylene)s containing reversibly reducible functionalities based on quinone and nitro cores have been synthesized. These molecules have methods of attachment to a metal surface ranging from the standard protected thiol groups to the novel diazonium and pyridyl linkages. Work is currently underway to examine the assembly of these various compounds on metal surfaces as well as their efficiency as switches and memory devices.

5. Experimental

5.1. General procedure

All reactions were carried out under a dry nitrogen atmosphere unless noted. 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*-diisopropylethylamine (Hünig's base) 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 F_{254} on a thickness of 0.25 mm.

5.2. General Pd/Cu coupling reaction procedures[10]

To an oven dried glass screw capped tube were added all solids including the aryl halide (bromide or iodide), alkyne, copper iodide, triphenylphosphine and palladium catalyst. The atmosphere was removed via vacuum and replaced with dry nitrogen (3×). 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×). The organic layer was dried with magnesium sulfate and filtered. The solvent was then removed in vacuo.

5.3. General procedure for the deprotection of trimethylsilyl-protected alkynes

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

5.4. General HOF oxidation procedure[12]

To a 125 mL polyethylene bottle were added H_2O (2 mL) and CH_3CN (60 mL) and cooled to −20°C. F_2 (20% in He) was then bubbled through the solution at a rate of 50 sccm for 2 h. The resulting HOF/CH_3CN solution was purged with He for 15 min. The species to be oxidized was added in acetone or ethyl acetate (10 mL) and mixed at −20°C for 5 min before being neutralized by pouring into a saturated $NaHCO_3$ solution. The organic phase was then separated, dried over $MgSO_4$ and the solvents were removed in vacuo.

5.5. General procedure for the diazotization of anilines with nitrosonium tetrafluoroborate in the acetonitrile–sulfolane system[7]

$NOBF_4$ 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 5:1 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 (45–50°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 dichloromethane, collected by filtration, washed with ether or dichloromethane and dried. Additional purification of the salt was accomplished by re-precipitation from DMSO by dichloromethane and/or ether.

5.5.1. 4-Ethynlphenyl-2,4-dinitrobromobenzene (5).[12] 2-Bromo-4-nitro-5-ethynlphenylaniline (490 mg, 1.48 mmol) in ethyl acetate (10 mL) was oxidized according to the general HOF oxidation procedure to yield 320 mg (60%) of a yellow solid. IR (KBr) 3442.7, 3101.4, 2216.8, 1610.6, 1540.9, 1461.3, 1384.8, 1358.7, 1337.1, 1264.4, 906.2, 849.6, 824.4, 760.2, 689.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.09 (s, 1H), 7.60–7.58 (m, 2H), 7.41–7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 150.4, 132.7, 131.7, 131.0, 130.7, 129.1, 121.5, 119.8, 113.9, 102.0. HRMS calcd: 345.9589; found: 345.9585.

5.5.2. 2′,5′-Dinitro-4,4′-diethynylphenyl-1-thioacetylbenzene (1). 4 (300 mg, 0.86 mmol), 4-ethynyl(thioacetyl)-benzene (183 mg, 1.04 mmol), bis(dibenzylideneacetone)-palladium (12 mg, 0.02 mmol), copper(I) iodide (4 mg, 0.02 mmol), triphenylphosphine (13 mg, 0.05 mmol), Hunig's base (0.60 mL) and THF (20 mL) were reacted according to the general coupling procedure. The reaction mixture was heated at 60°C overnight and worked up according to the procedure above. The crude compound was purified via flash chromatography (silica, 3:1 dichloromethane/hexane) to yield 90 mg (24%) of a bright yellow solid. IR (KBr) 2220.2, 1705.2, 1545.5, 1499.81, 1396.8, 1337.5, 1286.1, 1252.1, 1108.6, 1087.2, 953.2, 926.0, 868.3, 827.2, 756.7, 684.1, 618.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J=0.4 Hz, 1H), 8.35 (d, J=0.4 Hz, 1H), 7.63–7.59 (m, 4H), 7.46–7.40 (m, 5H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 151.1, 134.7, 133.1, 132.7, 131.0, 130.7, 129.1, 122.8, 121.7, 119.4, 118.6, 102.4, 100.9, 84.8, 83.5, 30.8. HRMS calcd: 442.0623; found: 442.0634.

5.5.3. 2-Bromo-4-nitro-5-phenylacetanilide (7). 6 (676 mg, 2 mmol), triphenylphosphine (52 mg, 0.2 mmol), phenylboronic acid (293 mg, 2.4 mmol), bis(triphenylphosphine)-palladium dichloride (70 mg, 0.1 mmol), and cesium carbonate (977 mg, 3 mmol) were placed in a 100 mL round bottom flask and the atmosphere was removed and replaced with nitrogen. Toluene (30 mL) was added and the reaction was heated at 60°C for 2 d. The reaction was worked up by diluting with ether, washing with aqueous ammonium chloride (2×), drying over $MgSO_4$, and removing the solvents in vacuo. The crude product was purified via flash chromatography (CH_2Cl_2) to yield 430 mg (64%) of a white solid. IR (KBr) 3373.6, 3322.4, 3086.5, 1774.0, 1681.7, 1568.9, 1528.8, 1445.8, 1389.4, 1358.6, 1245.8, 1179.1, 1112.5, 1056.1, 1030.4, 999.6, 872.0, 850.9, 768.9, 697.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.15 (s, 1H), 7.80 (br s, 1H), 7.40–7.38 (m, 3H), 7.29–7.27 (m, 2H) 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.44, 143.77, 139.34, 137.74, 136.81, 128.67, 128.51, 128.47, 127.85, 123.31, 110.59, 25.05. HRMS calcd for $C_{14}H_{11}BrN_2O_3$: 333.9953; found: 333.9952.

5.5.4. 2-Bromo-4-nitro-5-phenylaniline (8). 7 (500 mg, 1.49 mmol), potassium carbonate (1.031 g, 7.46 mmol), methanol (30 mL), and methylene chloride (30 mL) were added to a 100 mL round bottom flask and stirred at room temperature under a nitrogen blanket for 2 h. The reaction was worked up by filtering off the K_2CO_3 and washing with CH_2Cl_2 to yield 437 mg (100%) of the title compound. IR (KBr) 3463.7, 3349.2, 3221.3, 1623.9, 1584.6, 1555.4, 1495.5, 1443.6, 1406.9, 1305.6, 1259.4, 1123.9, 1051.7, 896.7, 846.5, 760.1, 701.3, 632.1, 563.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.39–7.36 (m, 3H), 7.23–7.21 (m (overlapping), 2H), 6.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 139.4, 138.5, 130.7, 128.8, 128.4, 128.2, 128.1, 117.2, 106.3. HRMS calcd: 291.9848; found: 291.9846.

5.5.5. 2,5-Dinitro-4-phenylbromobenzene (9).[12] **8** (373 mg, 1.28 mmol) in ethyl acetate (10 mL) was oxidized according to the general HOF oxidation procedure to yield 407 mg (99%) of an orange solid. IR (KBr) 3446.7, 3090.4, 1542.8, 1461.1, 1443.1, 1347.3, 1257.7, 1114.6, 1076.2, 1051.8, 1021.0, 904.5, 842.5, 768.8, 743.7, 699.9, 551.0, 485.16 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.89 (s, 1H), 7.47–7.45 (m, 3H), 7.31–7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 150.6, 137.2, 134.4, 130.8, 130.1, 129.7, 128.9, 128.1, 114.1. HRMS calcd: 321.9589; found: 321.9592.

5.5.6. 2′,4′-Dinitro-5′-phenyl-4-ethynylphenyl-1-thioacetylbenzene (2). 9 (147 mg, 0.46 mmol), 4-ethynyl(thioacetyl)-benzene (106 mg, 0.60 mmol), bis(dibenzylideneacetone)-palladium (26 mg, 0.05 mmol), copper(I) iodide (9 mg, 0.05 mmol), triphenylphosphine (12 mg, 0.05 mmol), Hünig's base (0.16 mL) and THF (20 mL) were coupled according to the general coupling procedure. The reaction mixture was stirred and heated overnight at 45°C. Crude product was purified via column chromatography (silica, 3:1 dichloromethane/hexanes) to yield 75 mg of an orange solid (39%). IR (KBr) 2922.7, 2214.3, 1702.7, 1542.8, 1488.1, 1357.1, 1271.1, 1115.1, 1088.6, 956.0, 908.6, 829.9, 770.5, 707.0, 623.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.10 (s, 1H), 7.63 (d, J=8.4 Hz, 2H), 7.48–7.44 (m, 5H), 7.36–7.33 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 151.2, 150.6, 136.8, 134.8, 134.7, 133.1, 130.8, 130.2, 130.1, 129.6, 128.6, 128.1, 122.9, 119.0, 99.8, 84.5, 30.8. HRMS calcd: 418.0623; found: 418.0619.

5.5.7. 2,5-Dibromo-1,4-dimethoxybenzene[16] **(11).** In a

100 mL round bottom flask, 1,4-dimethoxybenzene (10.0 g, 72.4 mmol) was dissolved in glacial acetic acid (20 mL). A solution of bromine (7.42 mL, 145.0 mmol) in glacial acetic acid (7.5 mL) was added dropwise to the first solution at room temperature over 40 min. The resulting mixture was allowed to stir for 2 h. The crude product was washed with ice-cold water and ice-cold methanol to afford fine white crystals. The mother liquor was concentrated and cooled to afford more white crystals (15.9 g, 74% yield). Mp 136–138°C (lit[21] mp 144–145°C). IR (KBr) 3091.9, 3022.1, 2968.8, 2944.4, 2842.8, 1694.9, 1494.2, 1475.6, 1436.5, 1358.2, 1275.0, 1211.8, 1185.0, 1065.4, 1021.9, 860.5, 760.4, 441.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 2H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.93, 117.53, 110.90, 57.43.

5.5.8. 2,5-Di(ethynylphenyl)-1,4-dimethoxybenzene (12). 11 (8.745 g, 29.55 mmol), bis(triphenylphosphine)palladium dichloride (0.415 g, 0.591 mmol), copper(I) iodide (0.225 g, 1.182 mmol), triphenylphosphine (0.310 g, 1.182 mmol), THF (35 mL), Hünig's base (20.5 mL, 118 mmol), and phenylacetylene (7.8 mL, 70.92 mmol) were used following the general procedure for couplings. The solution was heated in a 65°C oil bath for 3 d. Recrystallization from benzene afforded the desired product, mp 175–177°C (lit.[16] 176–177°C) (9.22 g, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 4H), 7.34 (m, 6H), 7.03 (s, 2H), 3.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.10, 131.89, 128.60, 128.50, 123.39, 115.86, 113.57, 95.23, 85.86, 56.66.

5.5.9. 2,5-Di(ethynylphenyl)benzoquinone (13). 12 (0.300 g, 0.886 mmol) and THF (6 mL) were added to a 25 mL round bottom flask containing a stir bar. A solution of ceric ammonium nitrate (1.46 g, 2.658 mmol) in water (3 mL) was slowly added to the flask and allowed to stir for 15 min. Water was added and the organic materials were extracted with dichloromethane. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (0.129 g, 47%). IR (KBr) 3047.5, 2203.0, 1716.2, 1655.3, 1568.3, 1215.4, 1100.6, 902.1, 757.6, 686.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J=7.9, 1.5 Hz, 4H), 7.38 (m, 6H), 6.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.87, 136.55, 133.34, 132.83, 130.57,128.97, 121.83, 105.26, 82.90. HRMS calcd for $C_{22}H_{12}O_2$: 308.0837; found: 308.0834.

5.5.10. 2-Bromo-5-ethynylphenyl-1,4-dimethoxybenzene (14). 11 (2.96 g, 10.0 mmol), bis(dibenzylideneacetone)-palladium (0.115 g, 0.20 mmol), copper(I) iodide (0.038 g, 0.20 mmol), triphenylphosphine (0.131 g, 0.50 mmol), THF (15 mL), Hünig's base (6.97 mL, 40.0 mmol) and phenylacetylene (1.21 mL, 11.0 mmol) were used following the general procedure for coupling. The tube was heated in a 50°C oil bath for 18 h. Column chromatography (silica gel using 19:1 hexanes/diethyl ether as eluent) afforded the desired product, somewhat impure (approximately 15% impurities by NMR) in moderate yield (1.02 g, 32% yield). This was taken onto the next step in this impure form. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.33 (m, 3H), 7.09 (s, 1H), 7.02 (s, 1H), 3.86 (s, 6H).

5.5.11. 1,4-Dimethoxy-2-ethynylphenyl-5-(trimethylsilylethynyl)benzene. 14 (1.0 g, 3.15 mmol), bis(dibenzylideneacetone)palladium (0.036 g, 0.063 mmol), copper(I) iodide (0.012 g, 0.063 mmol), triphenylphosphine (0.042 g, 0.16 mmol), THF (20 mL), Hünig's base (2.2 mL, 12.6 mmol), and trimethylsilylacetylene (0.89 mL, 6.3 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 60°C oil bath for 1 d. Flash column chromatography (silica gel using 24:1 hexanes/ethyl acetate as eluent) afforded the desired product slightly impure (0.83 g, 79% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.32 (m, 3H), 6.98 (s, 1H), 6.95 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 0.27 (s, 9H).

5.5.12. 1,4-Dimethoxy-2-ethynyl-5-(ethynylphenyl)benzene (15). 1,4-Dimethoxy-2-ethynylphenyl-5-(trimethylsilylethynyl)benzene (0.830 g, 2.48 mmol), potassium carbonate (1.71 g, 12.4 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection to afford the desired product (0.513 g, 79% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.33 (m, 3H), 7.00 (s, 1H), 6.98 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.39 (s, 1H).

5.5.13. 4,4′-Di(ethynylphenyl)-2′,5′-dimethoxy-1-benzenethioacetate (16). 15 (0.513 g, 1.96 mmol), bis(dibenzylideneacetone)palladium(0) (0.058 g, 0.10 mmol), copper(I) iodide (0.019 g, 0.10 mmol), triphenylphosphine (0.066 g, 0.25 mmol), THF (20 mL), Hünig's base (1.37 mL, 7.84 mmol), and 4-(thioacetyl)iodobenzene (0.608 g, 2.16 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 55°C oil bath for 3 d. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product slightly impure (0.621 g, 76% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 4H), 7.38 (d, J=8.1 Hz, 2H), 7.33 (m, 3H), 7.03 (s, 1H), 7.02 (s, 1H), 3.874 (s, 3H), 3.870 (s, 3H), 2.40 (s, 3H).

5.5.14. 2-Ethynylphenyl-5-((4′-thioacetyl)ethynylphenyl)-benzoquinone (17). 16 (0.050 g, 0.12 mmol), acetonitrile (5 mL), and THF (5 mL) were added to a 25 mL round bottom flask containing a stir bar. A solution of ceric ammonium nitrate (0.13 g, 0.24 mmol) in water (1 mL) was added in one portion. After stirring at room temperature for 30 min, another equivalent solution of ceric ammonium nitrate (0.13 g, 0.24 mmol) was added. After 20 additional minutes, the reaction was quenched by adding water (30 mL) to effect precipitation of an orange solid. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product (0.034 g, 74% yield). IR (KBr) 3053.0, 2924.3, 2852.6, 2205.4, 1703.4, 1652.7, 1568.8, 1483.7, 1442.2, 1354.8, 1221.3, 1105.4, 1089.4, 949.6, 920.1, 830.9, 758.2, 688.2, 620.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 4H), 7.42 (m, 2H), 7.38 (m, 3H), 6.98 (s, 1H), 6.97 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.22, 182.74, 182.67, 136.88, 136.51, 134.63, 133.34, 133.24, 132.99, 132.84, 130.94, 130.63, 128.99, 122.81, 121.80, 105.38, 103.99, 84.17, 82.92, 30.80. HRMS calcd for $C_{24}H_{14}O_3S$: 382.0664; found: 382.0663.

5.5.15. 1,4-Dimethoxy-2,5-bis(trimethylsilylethynyl)-benzene. 11 (1.75 g, 5.91 mmol), bis(triphenylphosphine)-palladium dichloride (0.207 g, 0.296 mmol), copper(I)

iodide (0.113 g, 0.591 mmol), triphenylphosphine (0.155 g, 0.591 mmol), THF (20 mL), Hünig's base (4.1 mL, 23.64 mmol), and trimethylsilylacetylene (2.51 mL, 17.73 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 55°C oil bath for 2 d. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (1.54 g, 79% yield). IR (KBr) 2957.0, 2898.2, 2851.2, 2829.0, 2149.1, 1496.8, 1464.1, 1449.1, 1388.2, 1283.7, 1249.0, 1223.6, 1203.1, 1172.4, 1039.6, 883.2, 841.3, 757.4, 714.9, 696.2, 626.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 3.81 (s, 6H), 0.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.56, 116.59, 113.81, 101.22, 100.84, 56.83, 0.40. HRMS calcd for $C_{18}H_{26}O_2Si_2$: 330.1471; found: 330.1468.

5.5.16. 1,4-Dimethoxy-2,5-diethynylbenzene (18). 1,4-Dimethoxy-2,5-bis(trimethylsilylethynyl)benzene (1.50 g, 4.54 mmol), potassium carbonate (6.27 g, 45.4 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection to give the desired product (0.829 g, 98%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 3.84 (s, 6H), 3.37 (s, 2H).

5.5.17. 2,5-Bis(4′-(thioacetyl)ethynylphenyl)-1,4-dimethoxybenzene (19). 18 (0.810 g, 4.35 mmol), bis(dibenzylideneacetone)palladium (0.253 g, 0.44 mmol), copper(I) iodide (0.084 g, 0.44 mmol), triphenylphosphine (0.115 g, 0.44 mmol), THF (30 mL), Hünig's base (4.5 mL, 26.1 mmol), and 4-(thioacetyl)iodobenzene[22] (2.54 g, 9.14 mmol) were used following the general procedure for couplings. The solution was stirred in a 60°C oil bath for 16 h. Crystallization from dichloromethane/hexanes afforded the desired product (1.81 g, 85%). IR (KBr) 3129.1, 3057.4, 3006.2, 2975.5, 2940.0, 2847.4, 2207.2, 1697.7, 1506.8, 1483.1, 1463.1, 1396.2, 1279.2, 1223.5, 1122.2, 1034.2, 949.5, 898.8, 825.5, 765.6, 616.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (dt, J=8.5, 1.9 Hz, 4H), 7.39 (dt, J=8.5, 2.0 Hz, 4H), 7.01 (s, 2H), 3.89 (s, 6H), 2.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.85, 154.43, 134.58, 132.65, 128.64, 124.84, 116.08, 113.75, 94.76, 87.73, 56.91, 30.70. HRMS calcd for $C_{28}H_{22}O_4S_2$: 486.0960; found: 486.0956.

5.5.18. 2,5-Bis(4′-(thioacetyl)ethynylphenyl)benzoquinone (20). 19 (0.050 g, 0.103 mmol), acetonitrile (5 mL), and THF (3 mL) were added to a 25 mL round bottom flask containing a stir bar. A solution of ceric ammonium nitrate (0.339 g, 0.618 mmol) in water (2 mL) was added in two portions at 30 min intervals. After stirring at room temperature for 3 h, the reaction was quenched by adding water to effect precipitation of an orange solid. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product (0.023 g, 49% yield). IR (KBr) 2922.2, 2847.4, 2203.4, 1694.9, 1660.1, 1569.9, 1351.8, 1212.3, 1119.7, 1084.6, 1013.2, 960.3, 826.8, 620.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, J=8.3, 1.6 Hz, 4H), 7.42 (dt, J=8.3, 1.6 Hz, 4H), 7.00 (s, 2H), 2.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.23, 182.61, 136.86, 134.64, 133.25, 133.07, 130.97, 122.78, 104.14, 84.08, 30.79. HRMS calcd for $C_{26}H_{16}O_4S_2$: 456.0500; found: 456.0490.

5.5.19. 2,5-Bis(4′-ethynylpyridyl)-1-nitrobenzene (22). To a solution of 2,5-dibromonitrobenzene (0.28 g, 0.997 mmol), bis(triphenylphosphine)palladium dichloride (0.07 g, 0.098 mmol), copper(I) iodide (0.019 g, 0.098 mmol), triphenylphosphine (0.106 g, 0.40 mmol) and K_2CO_3 (1.1 g, 7.96 mmol) in THF (4 mL) were added via a cannula **21** (0.377 g, 2.15 mmol) in THF (4 mL) and MeOH (2 mL). The mixture was heated at 64°C for 20 h. The solvent was removed by rotary evaporation and the black residue was washed with aqueous K_2CO_3 and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexane/AcOEt 70:30, 50:50, 20:80, 0:100) afforded 60 mg (24% yield) of the title compound as a yellow solid. Mp 178–180°C. IR (KBr) 3414.0, 3036.7, 1616.0, 1589.4, 1538.1, 1519.9, 1407.9, 1345.7, 1271.1, 1214.1, 828.3 cm^{-1}. ^1H NMR (400 MHz, DMSO-d) δ 8.69 (br s, 4H), 8.44 (d, J=1.4 Hz, 1H), 8.04 (1/2 ABqd, J=8.0, 1.4 Hz, 1H), 7.99 (1/2 ABq, J=8.0 Hz, 1H), 7.60 (d, J=5.8 Hz, 2H), 7.57 (d, J=5.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d) δ 150.21, 150.13, 149.42, 136.27, 135.36, 129.16, 129.11, 127.96, 125.50, 125.39, 123.25, 116.55, 94.98, 90.63, 90.59, 88.13. HRMS calcd for $C_{20}H_{11}N_3O_2$: 325.0851; found: 325.0847.

5.5.20. 1-Bromo-4-(4′-ethynylpyridyl)-3-nitrobenzene (23). To a solution of 2,5-dibromonitrobenzene (0.43 g, 1.53 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.052 g, 0.074 mmol), copper(I) iodide (0.015 g, 0.078 mmol), triphenylphosphine (0.079 g, 0.30 mmol) and K_2CO_3 (0.83 g, 6.0 mmol) in THF (2 mL) were added via a cannula **21** (0.342 g, 1.95 mmol) in THF (4 mL) and MeOH (1.5 mL). The mixture was heated at 23°C for 2 d. The solvent was removed by rotary evaporation and the residue was diluted with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexane/AcOEt 90:10, 70:30, 50:50) afforded 330 mg (71% yield) of the title compound as an off-white solid. Mp 166–171°C. IR (KBr) 3424.4, 3093.3, 1592.3, 1521.4, 1409.3, 1341.4, 1272.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (br s, 2H), 8.29 (d, J=1.9 Hz, 1H), 7.79 (dd, J=8.3, 2.0 Hz, 1H), 7.62 (d, J=8.3 Hz, 1H), 7.44 (d, J=4.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.96, 136.22, 135.69, 130.14, 128.08, 126.67, 125.65, 123.19, 116.48, 94.80, 87.81. HRMS calcd for $C_{13}H_7BrN_2O_2$: 303.9672; found: 303.9682.

5.5.21. 5-Ethynylphenyl-2-(4′-ethynylpyridyl)-1-nitrobenzene (24). To a solution of **23** (88.8 mg, 0.293 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.011 g, 0.016 mmol), copper(I) iodide (0.004 g, 0.021 mmol) and triphenylphosphine (0.008 g, 0.029 mmol) in THF (4 mL) were added Et_3N (0.25 mL, 1.76 mmol) and phenylacetylene (0.1 mL, 9.1 mmol). The mixture was stirred at 56°C for 36 h. The solvent was evaporated in vacuo. The residue was diluted with water and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, AcOEt/hexane 20:80) afforded 65 mg (69% yield) of the title compound as a yellow solid. Mp 130–132°C. IR (KBr) 3445.3, 3046.3, 2203.5, 1548.5, 1529.1, 1399.9, 1341.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (br d, J=4.9 Hz, 2H), 8.27 (d,

J=1.5 Hz, 1H), 7.76 (1/2 ABqd, J=8.0, 1.6 Hz, 1H), 7.72 (1/2 ABqd, J=8.0, 0.5 Hz, 1H), 7.56 (m, 2H), 7.45 (dd, J=5.9, 1.7 Hz, 2H), 7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.58, 135.39, 134.65, 131.81, 129.34, 128.54, 127.67, 125.32, 121.85, 116.66, 95.30, 94.30, 88.52, 86.63. HRMS calcd for $C_{21}H_{12}N_2O_2$: 324.0899; found: 324.0895.

5.5.22. 1-Bromo-4-ethynylphenyl-3-nitrobenzene (25). To a solution of 2,5-dibromonitrobenzene (0.937 g, 3.34 mmol), bis(dibenzylideneacetone)palladium (0.095 g, 0.166 mmol), copper(I) iodide (0.032 g, 0.168 mmol) and triphenylphosphine (0.173 g, 0.66 mmol) in THF (4 mL) were added Et_3N (1 mL, 7.2 mmol) and phenylacetylene (0.5 mL, 4.56 mmol). The mixture was stirred at 23°C for 48 h. The mixture was washed with a saturated solution of NH_4Cl and then extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH_2Cl_2/hexane 1:8) afforded 0.48 g (47% yield) of the title compound as a yellow solid. Mp 58–74°C. IR (KBr) 3421.9, 3085.5, 2213.4, 1595.7, 1545.9, 1521.3, 1336.5, 1269.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J=1.9 Hz, 1H), 7.72 (dd, J=8.3 Hz, 2.0, 1H), 7.59 (m, 3H), 7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.71, 135.91, 135.45, 131.99, 129.44, 128.46, 127.78, 122.03, 121.75, 117.69, 98.43, 84.00. HRMS calcd for $C_{14}H_8NO_2Br$: 302.9720; found: 302.9725.

5.5.23. 2-Ethynylphenyl-5-(4′-ethynylpyridyl)-1-nitrobenzene (26). To a solution of **25** (0.306 g, 1.01 mmol), K_2CO_3 (0.713 g, 5.16 mmol), bis(triphenylphosphine)-palladium dichloride (0.035 g, 0.05 mmol), copper(I) iodide (0.009 g, 0.047 mmol) and triphenylphosphine (0.052 g, 0.198 mmol) in THF (2 mL) were added via a cannula **21** (0.217 g, 1.24 mmol) in THF (2 mL) and MeOH (1 mL). The mixture was heated at 60°C for 18 h. The solvent was removed by rotary evaporation and the brown residue was diluted with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, AcOEt/hexane 20:80, 40:60) afforded 260 mg (79% yield) of the title compound as a yellow solid. Mp 144–146°C. IR (KBr) 3442.3, 3053.0, 2209.4, 1631.3, 1584.8, 1524.7, 1404.3, 1344.7, 1269.0, 826.4, 755.2, 686.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, J=4.4, 1.6 Hz, 2H), 8.27 (br s, 1H), 7.74 (m, 2H), 7.63 (d, J=1.8 Hz, 1H), 7.60 (m, 1H), 7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.99, 135.41, 134.65, 132.14, 130.19, 129.61, 128.54, 127.95, 125.50, 122.68, 122.06, 119.15, 99.67, 90.83, 90.27, 84.62. HRMS calcd for $C_{21}H_{12}N_2O_2$: 324.0899; found: 324.0897.

5.5.24. 2,5-Bis(trimethylsilylethynyl)-4-nitroacetanilide (27). To a solution of **6** (0.78 g, 2.3 mmol), bis(dibenzylideneacetone)palladium (0.068 g, 0.118 mmol), copper(I) iodide (0.023 g, 0.012 mmol), and triphenylphosphine (0.123 g, 0.47 mmol) in THF (8 mL) were added Et_3N (1 mL, 7.2 mmol) and trimethylsilylacetylene (1 mL, 7.0 mmol). The mixture was heated at 67°C for 48 h. The solvent was removed by rotary evaporation and the brown residue was diluted with water and extracted with Et_2O. The combined organic phases were dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH_2Cl_2/hexane 35:65) afforded 410 mg (47% yield) of the title compound as an off-white solid. Mp 162–164°C. IR (KBr) 3372.9, 2962.9, 2146.0, 1727.2, 1611.2, 1544.9, 1501.5, 1457.1, 1404.3, 1338.2, 1250.6, 1222.3, 881.9 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.15 (s, 1H), 8.10 (br s, 1H), 2.27 (s, 3H), 0.33 (s, 9H), 0.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.21, 144.19, 142.41, 128.11, 123.82, 120.18, 111.52, 106.66, 106.16, 99.50, 97.44, 24.90, −0.31, −0.46. HRMS calcd for $C_{18}H_{24}N_2O_3Si_2$: 372.1326; found: 372.1326.

5.5.25. 2,5-Bis(4′-ethynylpyridyl)-4-nitroaniline (28). To a solution of **27** (0.056 g, 0.15 mmol), 4-iodopyridine (0.08 g, 0.39 mmol), K_2CO_3 (0.17 g, 1.2 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.01 g, 0.015 mmol), copper(I) iodide (0.004 g, 0.021 mmol) and triphenylphosphine (0.016 g, 0.061 mmol) in THF (4 mL) was added MeOH (1 mL). The mixture was heated at 60°C for 50 h. The solvent was removed by rotary evaporation and the brown residue was diluted with water and extracted with AcOEt. The combined organic phases were dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, AcOEt) afforded 8 mg (16% yield) of the title compound as a yellow solid. Mp 154–160°C. IR (KBr) 3730.2, 3438.6, 2204.8, 1592.4, 1541.1, 1409.8, 1308.5, 1249.9, 818.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, J=4.4, 1.7 Hz, 2H), 8.65 (dd, J=4.5, 1.7 Hz, 2H), 8.34 (s, 1H), 7.44 (dd, J=4.5, 1.7 Hz, 2H), 7.40 (dd, J=4.4, 1.6 Hz, 2H), 6.99 (s, 1H), 5.03 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.26, 150.03, 149.90, 139.56, 130.71, 130.52, 130.00, 125.65, 125.33, 120.33, 118.52, 106.57, 94.67, 94.19, 89.55, 87.27. HRMS calcd for $C_{20}H_{12}N_4O_2$: 340.0960; found: 340.0958.

5.5.26. 2-Amino-4-(4′-ethynylpyridyl)-5-nitrobromobenzene (29). To a solution of **6** (0.877 g, 8.84 mmol), K_2CO_3 (1.08 g, 7.81 mmol), bis(triphenylphosphine)palladium dichloride (0.054 g, 0.077 mmol), copper(I) iodide (0.025 g, 0.13 mmol) and triphenylphosphine (0.068 g, 0.26 mmol) in THF (4 mL) were added via a cannula **21** (0.404 g, 2.30 mmol) in THF (8 mL) and MeOH (3 mL). The mixture was stirred at 23°C for 1 d. The solvent was evaporated in vacuo. The residue was diluted with water and extracted with AcOEt. The combined organic phases were dried over $MgSO_4$, filtered and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, AcOEt/hexane 40:60, 50:50) afforded 290 mg (39% yield) of the title compound as a yellow solid. Mp 226–228°C. IR (KBr) 3385.4, 3297.7, 3171.3, 1646.8, 1591.7, 1556.9, 1471.3, 1297.8 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d) δ 8.66 (br d, J=3.8 Hz, 2H), 8.32 (d, J=1.3 Hz, 1H), 7.53 (br d, J=4.5 Hz, 2H), 7.06 (d, J=1.3 Hz, 1H), 6.94 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d) δ 151.33, 150.12, 136.44, 130.70, 129.64, 125.32, 118.13, 117.73, 106.02, 91.85, 89.72. HRMS calcd for $C_{13}H_8BrN_3O_2$: 316.9800; found: 316.9801.

5.5.27. 4-Amino-2-(4′-ethynylpyridyl)-1-nitro-5-(trimethylsilylethynyl)benzene. To a solution of **29** (0.310 g, 0.975 mmol), bis(triphenylphosphine)palladium dichloride (0.035 g, 0.05 mmol), copper(I) iodide (0.011 g,

0.05 mmol) and triphenylphosphine (0.026 g, 0.10 mmol) in THF (10 mL) were added Et_3N (0.9 mL, 6.5 mmol) and trimethylsilylacetylene (0.2 mL, 1.4 mmol). The mixture was stirred at 60°C for 2 d. The solvent was evaporated in vacuo. The residue was diluted with water and extracted with AcOEt. The combined organic phases were dried over $MgSO_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, Et_2O) afforded 160 mg (49% yield) of the title compound as a yellow solid. Mp 145–150°C. IR (KBr) 3451.9, 3379.1, 2960.5, 2149.5, 1620.4, 1597.9, 1545.5, 1512.2, 1317.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J=4.6, 1.5 Hz, 2H), 8.25 (s, 1H), 7.44 (dd, J=4.3, 1.5 Hz, 2H), 6.93 (s, 1H), 4.90 (s, 2H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.44, 149.90, 139.35, 130.65, 130.43, 125.65, 119.56, 118.06, 107.93, 104.28, 98.37, 93.70, 89.79, −0.15. HRMS calcd for $C_{18}H_{17}N_3O_2Si$: 335.1090; found: 335.1089.

5.5.28. 4-Amino-5-ethynyl-2-(4′-ethynylpyridyl)-1-nitrobenzene (30). To a solution of 4-amino-2-(4′-ethynylpyridyl)-1-nitro-5-(trimethylsilylethynyl)benzene (160 mg, 0.477 mmol) in MeOH (15 mL) and CH_2Cl_2 (15 mL) was added K_2CO_3 (0.66 g, 4.77 mmol). The solution was stirred at 23°C for 2 h. The reaction mixture was diluted with water and extracted with AcOEt. The combined organic layers were dried over $MgSO_4$, filtered, and the solvent evaporated in vacuo. The reaction afforded 0.11 g (88% yield) of the title compound as a yellow solid. The product was too unstable to attain its complete characterization data. ^1H NMR (400 MHz, DMSO-d) δ 8.67 (dd, J=4.5, 1.6 Hz, 2H), 8.12 (s, 1H), 7.53 (dd, J=4.5, 1.6 Hz, 2H), 7.03 (s, 1H), 6.97 (br s, 2H), 4.70 (s, 1H).

5.5.29. 4-Amino-2-(4′-ethynylpyridyl)-5-(4′-thioacetylphenylethynyl)-1-nitrobenzene (31). To a solution of **30** (0.110 g, 0.418 mmol), 4-thioacetyliodobenzene[10] (0.124 g, 0.446 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.015 g, 0.021 mmol), copper(I) iodide (0.004 g, 0.021 mmol) and triphenylphosphine (0.014 g, 0.053 mmol) in THF (13 mL) was added Et_3N (0.4 mL, 2.9 mmol). The mixture was stirred at 50°C for 2 d. The reaction was checked by TLC (AcOEt/hexane 75:25). More bis(triphenylphosphine)palladium dichloride (0.014 g, 0.020 mmol), copper(I) iodide (0.035 g, 0.018 mmol) and triphenylphosphine (0.085 g, 0.324 mmol) were added and the reaction was stirred at 60°C for 1 d. The solvent was evaporated in vacuo. The residue was diluted with water and extracted with AcOEt. The combined organic layers were dried over $MgSO_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, AcOEt/hexane 66:33) afforded 130 mg (75% yield) of the title compound as a yellow solid. Mp 185–188°C. IR (KBr) 3438.2, 3195.9, 2922.4, 1695.4, 1627.7, 1596.5, 1545.1, 1514.8, 1477.2, 1402.8, 1316.4, 1249.9 cm^{-1}. ^1H NMR (400 MHz, DMSO-d) δ 8.68 (br d, J=4.0 Hz, 2H), 8.23 (s, 1H), 7.79 (d, J=8.1 Hz, 2H), 7.54 (d, J=5.0 Hz, 2H), 7.49 (d, J=8.0 Hz, 2H), 7.13 (br s, 2H), 7.06 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d) δ 192.98, 153.79, 150.13, 136.28, 134.31, 132.32, 130.69, 129.67, 128.66, 125.34, 123.05, 118.70, 118.26, 105.43, 95.72, 92.51, 90.12, 85.54, 30.32. HRMS calcd for $C_{23}H_{15}N_3O_3S$: 413.0834; found: 413.0940.

5.5.30. 2-(4′-Ethynylpyridyl)-4-nitro-5-phenylaniline (32). To a solution of **7** (80.5 mg, 0.241 mmol), K_2CO_3 (0.151 g, 1.09 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.009 g, 0.014 mmol), copper(I) iodide (0.003 g, 0.014 mmol) and triphenylphosphine (0.014 g, 0.053 mmol) in THF (2 mL) were added via a cannula **1** (0.053 g, 0.3 mmol) in THF (2 mL) and MeOH (1 mL). The mixture was heated to 70°C for 3 d. The solvent was removed by rotary evaporation and the brown residue was diluted with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, AcOEt/hexane 30:70) afforded 60 mg (79% yield) of the title compound as a yellow solid. Mp 187–190°C. IR (KBr) 3410.2, 3323.4, 3212.1, 2215.1, 1627.6, 1592.4, 1548.4, 1511.7, 1410.5, 1331.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (br d, J=4.8 Hz, 2H), 8.16 (s, 1H), 7.39 (m, 5H), 7.27 (m, 2H), 6.62 (s, 1H), 5.03 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.23, 149.82, 140.65, 138.82, 138.19, 130.49, 128.36, 128.06, 127.52, 125.34, 116.41, 104.85, 93.24, 87.89. HRMS calcd for $C_{19}H_{13}N_3O_2$: 315.1008; found: 315.1011.

5.5.31. 1-Bromo-4-(4′-ethynyl)pyridine-3-nitrobenzene (34). To a solution of **33**[1] (0.84 g, 2.34 mmol), bis(triphenylphosphine)palladium dichloride (0.083 g, 0.117 mmol), copper(I) iodide (0.022 g, 0.117 mmol), and K_2CO_3 (1.94 g, 14.04 mmol) in THF (4 mL) were added **21** (0.451 g, 2.57 mmol) in THF 12 mL) via a cannula and MeOH (4 mL). The mixture was heated to 55°C for 14 h. The solvent was removed by rotary evaporation and the residue was diluted with water, washed with brine and extracted with AcOEt. The combined organic phases were dried over $MgSO_4$, filtered and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, AcOEt) afforded 271 mg (34% yield) of the title compound as a yellow solid. Mp 224–229°C. IR (KBr) 3451.7, 3351.1, 3202.6, 2206.4, 1622.9, 1588.4, 1539.0, 1474.4, 1306.7, 1249.8 cm^{-1}. ^1H NMR (400 MHz, DMSO-d) δ 8.64 (d, J=5.7 Hz, 2H), 8.25 (s, 1H), 7.67 (dd, J=4.5, 1.5 Hz, 2H), 7.59 (m, 2H), 7.47 (m, 3H), 7.15 (br s, 1H), 7.03 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d) δ 153.97, 149.83, 136.31, 131.67, 131.17, 130.01, 129.69, 128.99, 125.45, 121.78, 120.40, 118.06, 103.92, 96.13, 93.41, 88.37, 86.25. HRMS calcd for $C_{21}H_{13}N_3O_2$: 339.1008; found: 339.1004.

5.5.32. 1-Bromo-3-nitro-4-(4-aminophenylethynyl)benzene (36). 1,4-Dibromo-2-nitrobenzene (5.62 g, 20.0 mmol), bis(triphenylphosphine)palladium dichloride (0.140 g, 0.20 mmol), copper(I) iodide (0.038 g, 0.20 mmol), triethylamine (10.0 mL), THF (10 mL) and **35** (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 twofold recrystallization from dichloromethane/hexanes as fine bright red needles (1.561 g, 49% yield). Mp 147–149°C. IR (KBr) 3457, 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, 2H), 7.93 (m, XX′ part of AA′XX′ pattern, J=8.2, 2.7, 1.9, 0.4 Hz, 2H), 3.39 (s, 2H). ^{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 calcd for $C_{14}H_9N_2BrO_2$: 315.9848; found: 315.9845.

5.5.33. 4-(2-Nitro-4-phenylethynylphenylethynyl)aniline (37). 36 (0.697 g, 2.20 mmol), bis(triphenylphosphine)-palladium 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°C 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°C. IR (KBr) 3454, 3381, 3360, 2177, 2197, 1594, 1623, 1539, 1520, 1299, 1342, 1133, 829, 758, 690, 527 cm^{-1}. ^{1}H 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, 2H), 7.36–7.43 (m, 5H), 3.94 (s, 2H). ^{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 calcd for $C_{22}H_{14}N_2O_2$: 338.1055; found: 338.1058.

5.5.34. 4-(2-Nitro-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (38). Following the general diazotization procedure **37** (0.0845 g, 0.250 mmol) was treated with $NOBF_4$ (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, 2H), 8.30 (s, 1H), 8.03 (d, J=8.9 Hz, 2H), 7.85–7.92 (m, 2H), 7.57–7.60 (m, 2H), 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.

5.5.35. 4-(3-Nitro-4-phenylethynylphenylethynyl)aniline (39). 25 (1.208 g, 4.0 mmol), bis(triphenylphosphine)palladium 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 **35** (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°C. IR (KBr) 3303, 2985, 1696, 1587, 1522, 1406, 1314, 1243, 1153, 1060, 839, 757, 692 cm^{-1}. ^{1}H 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, 2H), 6.65 (m, XX′ part of AA′XX′ pattern, J=8.0, 2.5, 2.0, 0.4 Hz, 2H), 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 calcd for $C_{22}H_{14}N_2O_2$: 338.1055; found: 338.1059.

5.5.36. 4-(3-Nitro-4-phenylethynylphenylethynyl)benzenediazonium tetrafluoroborate (40). Following the general diazotization procedure, **39** (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}. ^{1}H 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, 2H), 7.82 (dd, J=1.7, 0.4 Hz, 1H), 7.49 (m, XX′ part of AA′XX′ pattern, J=8.7, 2.4, 1.7, 0.4 Hz, 2H), 7.62 (dd, J=8.1, 1.7 Hz, 1H), 7.56 (dd, J=8.1, 0.4 Hz, 1H), 7.07 (m, AA′ part of AA′XX′Y pattern, J=7.8, 7.6, 1.8, 1.3, 1.3, 0.6 Hz, 2H), 6.94 (tt, J=7.6, 1.3 Hz, 1H), 6.91 (m, YY′ part of AA′XX′Y pattern, J=7.8, 7.6, 1.8, 1.3, 1.3, 0.6 Hz, 2H). ^{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.

5.5.37. 4-(2,5-Dinitro-4-(4-aminophenylethynyl)phenylethynyl)aniline (42). 1,4-Dibromo-2,5-dinitrobenzene[12] (0.977 g, 3.0 mmol), bis(triphenylphosphine)palladium 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 5× with dichloromethane (10 mL) and dried in vacuo to afford dark purple crystals of the diamine **42** (0.432 g, 36% yield). Mp >270°C. 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, 2H), 7.27–7.29 (m, 2H), 6.59–6.61 (m, 2H), 5.93 (br s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.18, 149.89, 133.67, 129.43, 116.95, 113.66, 106.10, 103.45, 82.23. HRMS calcd for $C_{22}H_{14}N_4O_4$: 398.1015; found 398.1018.

5.5.38. 4-(2,5-Dinitro-4-(4-diazoniophenylethynyl)phenylethynyl)benzenediazonium tetrafluoroborate (43). Following the general diazotization procedure **42** (0.199 g, 0.500 mmol) was treated with $NOBF_4$ (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}. ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 8.85 (s, 2H), 8.79 (d, J=9 Hz, 2H), 8.20 (d, J=9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 150.60, 133.93, 133.83, 133.14, 132.40, 131.75, 117.62, 116.32, 96.91, 91.51.

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