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Improved and new syntheses of potential molecular electronics devices

David W. Price, Jr., Shawn M. Dirk, Francisco Maya and James M. Tour*

Department of Chemistry and Center for Nanoscale Science and Technology, MS 222, Rice University, 6100 Main St., Houston, TX 77005, USA

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Abstract—New syntheses of ethyl and nitro substituted oligo(phenylene ethynylene)s (OPEs) have been developed. To further explore whether the presence of nitro functionality in OPEs leads to switching and memory capabilities, new nitro substituted OPEs have been designed and synthesized. An isatogen-based system, a structure that is isomeric to the nitro OPE, has been synthesized. Additionally, pyridine-based and chromium-based compounds have been synthesized. We surmise that redox reactions of these candidates may impart switching capabilities and electrochemical studies are shown. U-shaped OPEs were synthesized to inhibit leakage of metals deposited during formation of top contacts on self-assembled monolayers (SAMs). The OPEs contain either thiol-based moieties or isonitrile groups to enable formation of SAMs on metal substrates.

1. Introduction

The growing field of molecular electronics has demonstrated that simple oligo(phenylene ethynylene)s (OPEs) are conductive and can be used as molecular wires.[1–3] It has also been shown that functionalizing OPEs with nitro groups causes them to demonstrate electronic switching and memory behavior.[4–6] The mechanism behind these effects in solid-state hybrid systems seems to be the result of a redox center (nitro group) in these compounds.[7,8] It is this redox center that accepts electrons, leading to changes in the conformation and conductivity of the molecules, resulting in the switching characteristics. As a result, we have designed and synthesized new OPEs for use in potential molecular electronics devices. These OPEs contain cores that may be reduced or oxidized (depending on functionality), yielding a variety of potential nanoscale computing components. We have incorporated functional groups different from our group's standard monothioacetate 'alligator clip' for formation of attachments to metal surfaces or metal nanoparticles. It is our hope that these alternative molecular junctions will enable the use of different metals, providing better conductivity in the final solid-state devices. We anticipate that the U-shaped (US) OPEs we have synthesized will act to prevent leakage of evaporated top-contact metal atoms through a self-assembled monolayer (SAM).

Keywords: molecular electronics; cyclization reaction; alligator clip.

* Corresponding author. Tel.: +1-713-348-6246; fax: +1-713-348-6250; e-mail: tour@rice.edu

2. Molecular wires

Scheme 1 shows the synthesis of an ethyl-functionalized OPE, **8**, previously synthesized in our group.[9] This is part of a new synthetic route that is shorter with a higher overall yield. The synthesis starts with 3-nitroacetophenone, which was reduced to 3-ethylaniline **1** and iodinated using triethylbenzylammonium iodide dichloride[10] to afford the aniline **2**. Cooling the solution in an ice bath before addition of the iodinating reagent was critical to ensure a high yield. Compound **2** was then coupled to trimethylsilylacetylene (TMSA) to afford **3** in acceptable yield. Diazotization and substitution with iodide provided **4** in good yield. From this point, the synthetic route closely followed the previous procedure.[9] Sonogashira[11] coupling of **4** with phenylacetylene provided **5** in modest yield. Deprotection of the terminal alkyne and coupling with 4-(thioacetyl)iodobenzene (**7**) provided the final desired wire **8** in good yield. This new route shortens the synthesis by two steps and doubles the overall yield of the previous route.[9]

Scheme 2 shows the synthetic route to a simple two-ring OPE containing an isonitrile alligator clip that we intend to use as a model in developing our synthetic and self-assembly chemistry. 4-Iodoaniline was converted to the formamide **9** using formic acid and acetic anhydride in high yield. Approximately 7% of the aniline was converted to the acetamide as determined by ^{1}H NMR of the crude material. Formamide **9** was then coupled with phenylacetylene to provide the extended formamide **10** in very good yield. Triphosgene, which is a less hazardous phosgene substitute, was employed to provide isonitrile **11** in high yield.[12,13]

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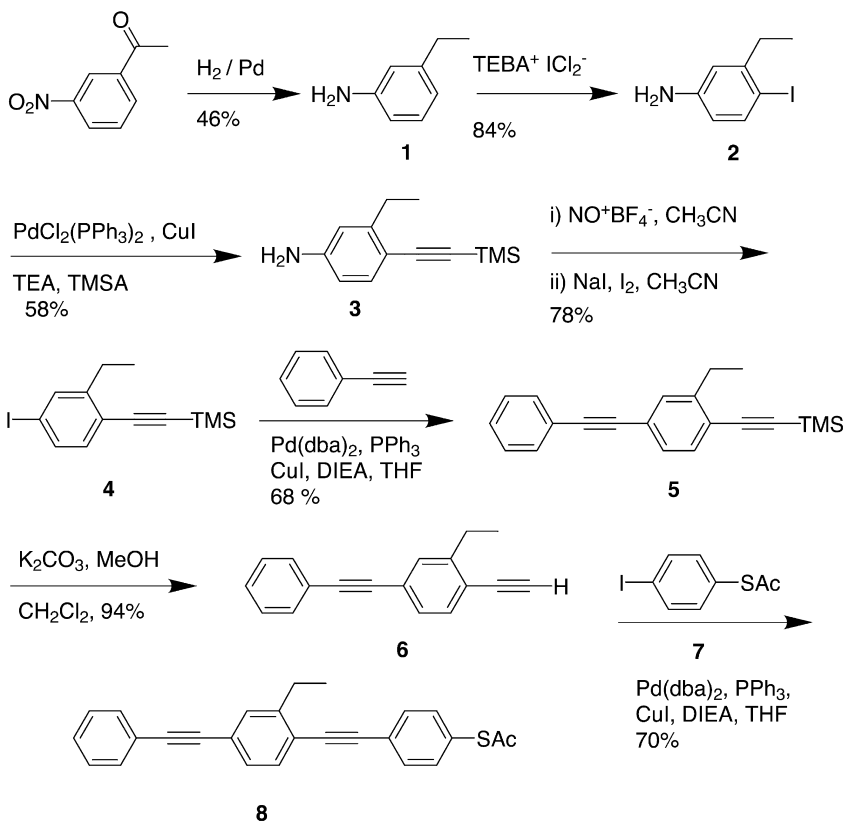


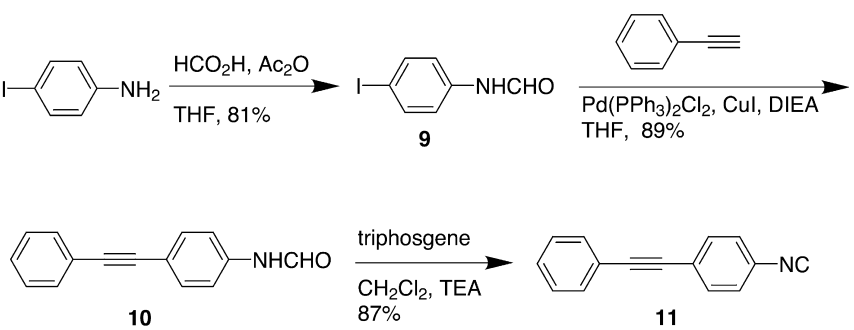
Scheme 1.

Scheme 3 shows the complete synthesis of an unfunctionalized OPE with two isonitrile alligator clips. 1,4-Diiodobenzene was coupled with 2 equiv. of TMSA to provide **12** in high yield. Next, the alkynes were deprotected to afford the diyne **13** in quantitative yield. Compound **13** was coupled with 2 equiv. of formamide **9** to provide the poorly soluble **14**. This compound was then doubly dehydrated using the triphosgene method with poor success to provide bis(isonitrile) **15**. Part of the reason for the low yield could be due to the poor solubility of **14** in CH_2Cl_2.

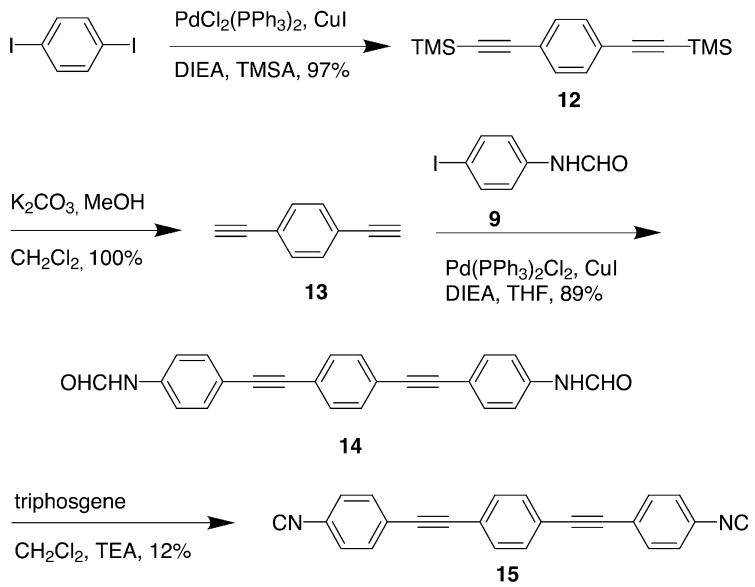
3. Molecular switches and memory components containing nitro groups

Scheme 4 shows the synthesis of a mononitro OPE **17**, which has become a standard, of sorts, for electrical studies by many research groups.[5] In this paper we report some small synthetic modifications that permit a significant yield enhancement.[14] 2,5-Dibromonitrobenzene was coupled with TMSA, followed by coupling with phenylacetylene and deprotection of the terminal alkyne, to afford the intermediate **16**. After the deprotection step, purification was greatly simplified compared to previous work and **16** was isolated in pure form. Subsequent Sonogashira–Castro–Stephens coupling[11,12] with the alligator clip **7** provided the final target **17** in low yield, similar to results from coupling related nitro-containing molecules to **7**. We subsequently found that using higher percentages of triphenylphosphine as ligand can generally increase the yields of such couplings.

Scheme 5 depicts another synthesis of the mononitro compound. This route is an improvement over the previous route that used 2,5-dibromonitrobenzene because that route showed no selectivity in the initial coupling step. The



Scheme 2.

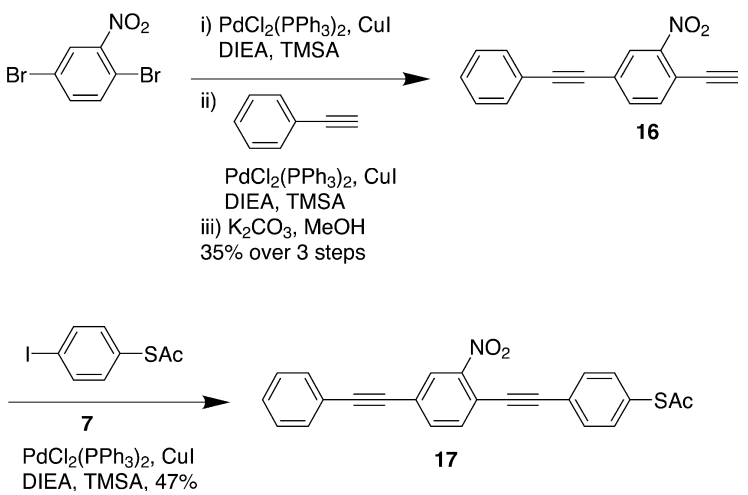


Scheme 3.

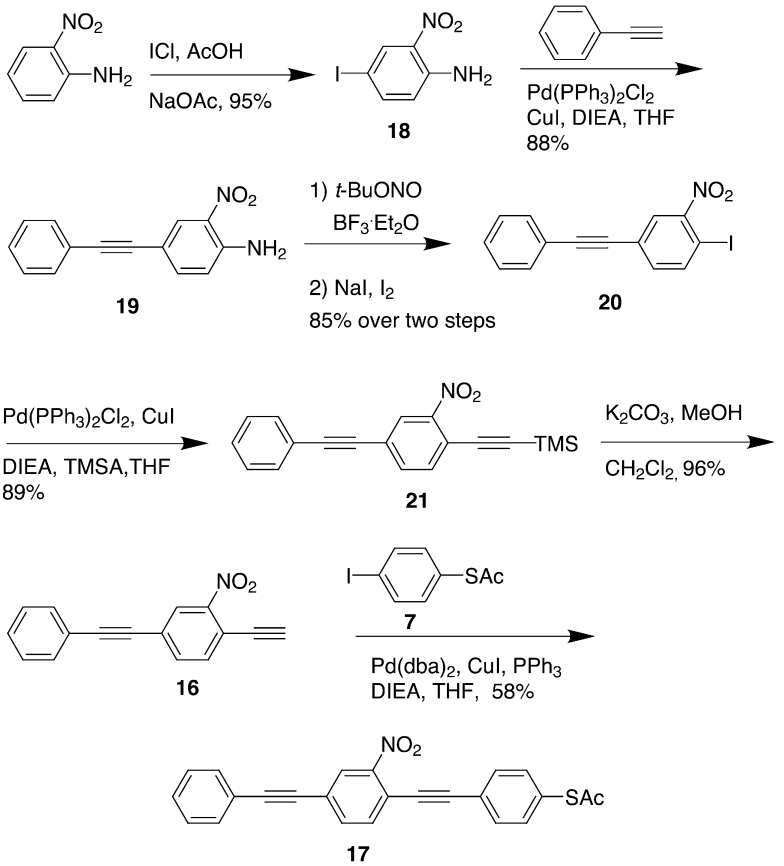
synthesis of **17** began with the iodination of 2-nitroaniline to give **18** in high yield.[15] Coupling of **18** with phenylacetylene provided the aniline **19**, which was transformed to the iodide via the diazonium salt to furnish the intermediate **20**, again in very good yield. Subsequent coupling with TMSA furnished the protected alkyne **21**, and a basic deprotection provided **16** in excellent yield. A final coupling of this intermediate with the alligator clip **7** afforded the desired device **17** in reasonable yield. The use of 5 mol% palladium catalyst, 10 mol% copper co-catalyst, and 20 mol% of triphenylphosphine ligand was found to be the optimal ratio (dubbed the '5,10,20' ratio). This route provides intermediate **16** in 61% yield over five steps, compared to 35% over three steps in the previous route. Also, the purification of each of the intermediates in this route is simpler and less time-consuming. The negative differential resistance (NDR) and memory characteristics of this compound were reported elsewhere.[3,4] This compound has become a highly tested OPE by many research groups due its room temperature NDR behavior.

Scheme 6 shows the complete synthesis of the mononitro device with an isonitrile alligator clip. Formamide **9** was coupled with TMSA to provide the protected alkyne **22** in quantitative yield.[16] The terminal alkyne was deprotected to afford **23**. Next, the free alkyne was coupled with 1-iodo-2-nitro-4-phenylethynylbeznene (**20**) to give penultimate compound **24** in good yield. In the past, the dehydration of a formamide to generate an isonitrile has been difficult, particularly in the presence of a nitro group due to its electron-withdrawing nature deactivating the reactivity of the formamide. However, by generating phosgene in situ from triphosgene,[13] the dehydration was accomplished in high yield to give the final isonitrile **25**. The use of tetrabutyl ammonium chloride was intended to help promote the decomposition of triphosgene to phosgene; however, it was later determined in subsequent reactions that the chloride ion was not necessary.

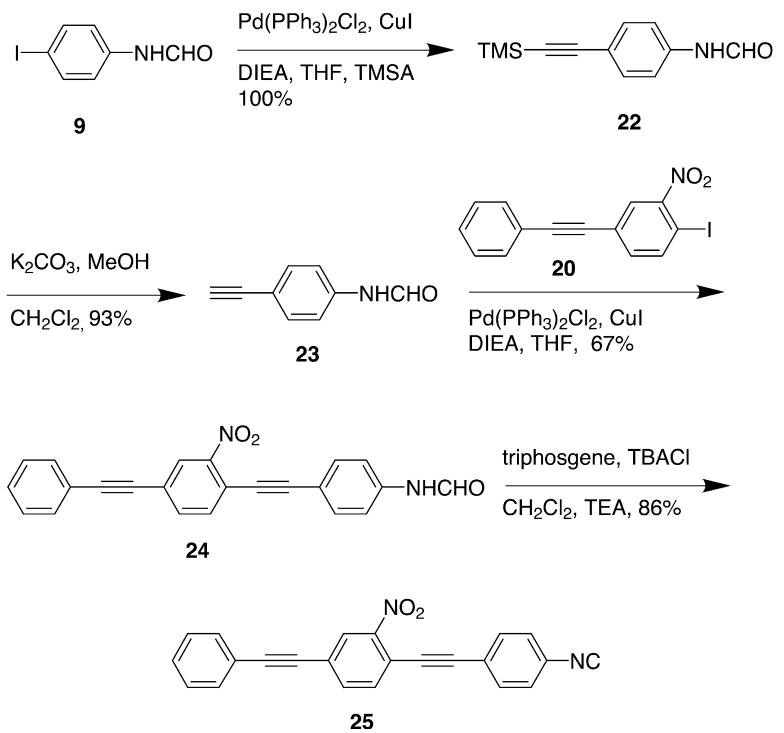
Scheme 7 shows the synthesis of **26**, the mono-nitro



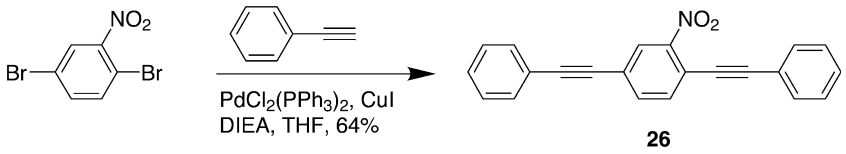
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

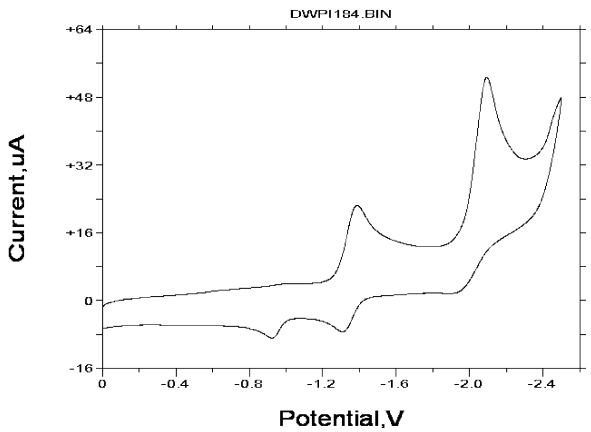


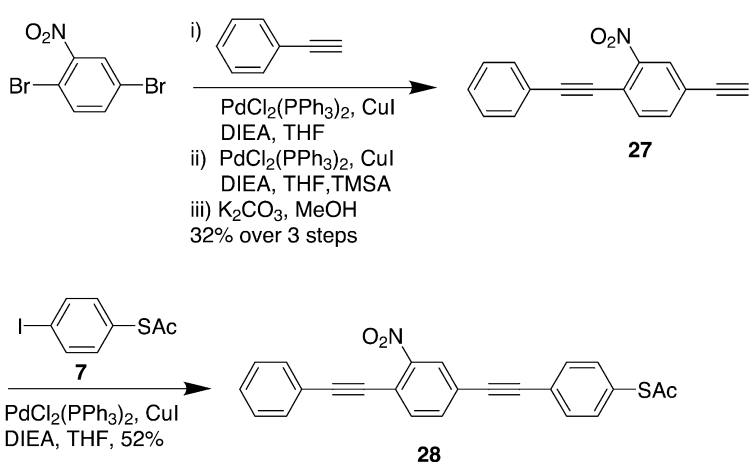
Figure 1. Cyclic voltammagram of simple device **26**.

compound with no alligator clips. This compound was made for the purposes of cyclic voltammagram (CV) testing as reported elsewhere.[8] The CVs for compounds lacking the alligator clip are generally cleaner and the compounds are much easier to synthesize. In a one-step synthesis, 2,5-dibromonitrobenzene was coupled with an excess of phenylacetylene to give final product **26** in a moderate yield. As noted elsewhere,[17] the cyclization reaction between the nitro group and the alkyne *ortho* to it may be the reason for the reduced yields.

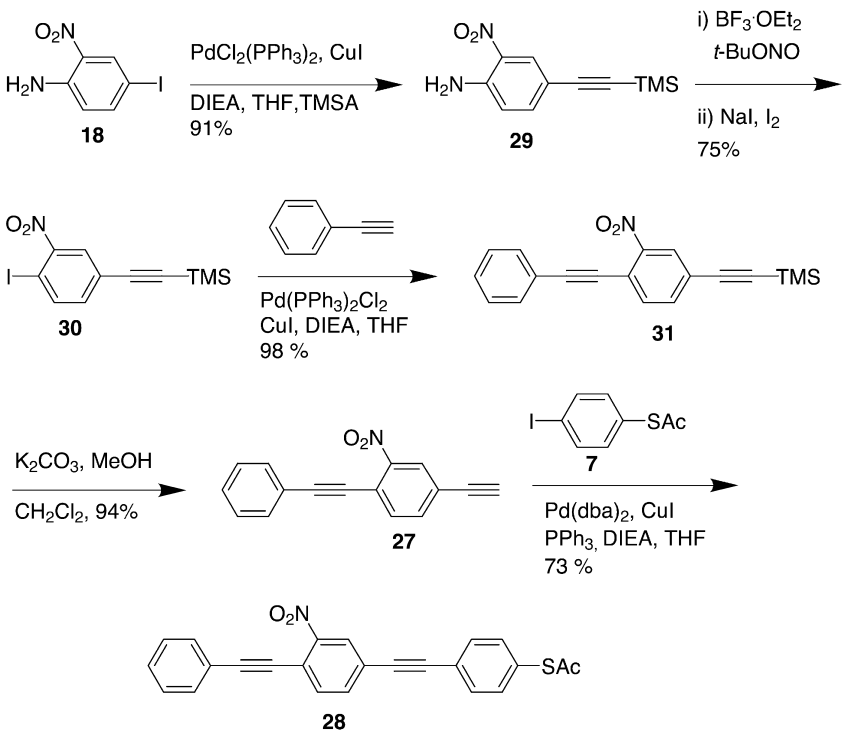
Figure 1 shows the CV of compound **26**. The electrochemical testing was performed in an attempt to understand why some functionalized OPEs behave as molecular switches. From the figure, there are at least two clear reduction peaks at −1.4 and −2.1 V. These peaks are quasi-reversible with the third oxidation peak indicating that the reduction at −1.4 V is comprised of two separate events. The reductions are of limited reversibility in solution. In the solid-state, however, the reductions may well be completely reversible as long as there is no water or oxygen present.

Scheme 8 shows the synthesis of a regioisomer of **17** with the nitro group at the 3′-position rather than the 2′-position. Its synthesis was pursued in order to study the effects from the subtle position change of the nitro group on the device chemistry of the system. The synthesis works analogously to the original nitro compound **17**. However, the first reaction couples phenylacetylene with the more reactive bromide at the 2-position of 2,5-dibromonitrobenzene. The subsequent coupling with TMSA occurs at the less reactive bromine position. After each step, limited purification via chromatography was needed, and removal of the TMS protective group afforded the free alkyne **27**. A final coupling with the alligator clip **7** afforded the desired device **28** in a moderate yield. This OPE is currently being evaluated to determine the effect of the orientation of the nitro group.

Scheme 9 shows a highly improved synthesis of the device **28**. The logic of the synthesis is the same as that of Scheme 5. 4-Iodo-2-nitroaniline (**18**) was coupled with TMSA to provide the aniline **29** in high yield. The amino group of **29** was converted to an iodide through a diazotization followed by reaction with an iodine source. The iodo compound **30** was then coupled with phenylacetylene to provide **31** in excellent yield. The alkyne **31** was deprotected using potassium carbonate and MeOH to afford **27** in good yield over four easy steps where the previous route afforded **27** in only 32% yield over three steps where purification was more difficult. Coupling of **27** with the alligator clip **7** under the 5,10,20 catalyst loading method proceeded to provide final OPE **28** in good yield.



Scheme 8.

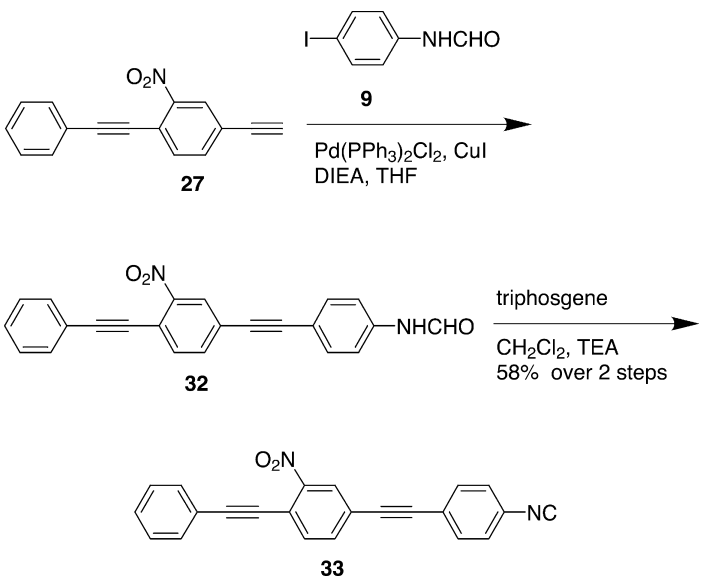


Scheme 9.

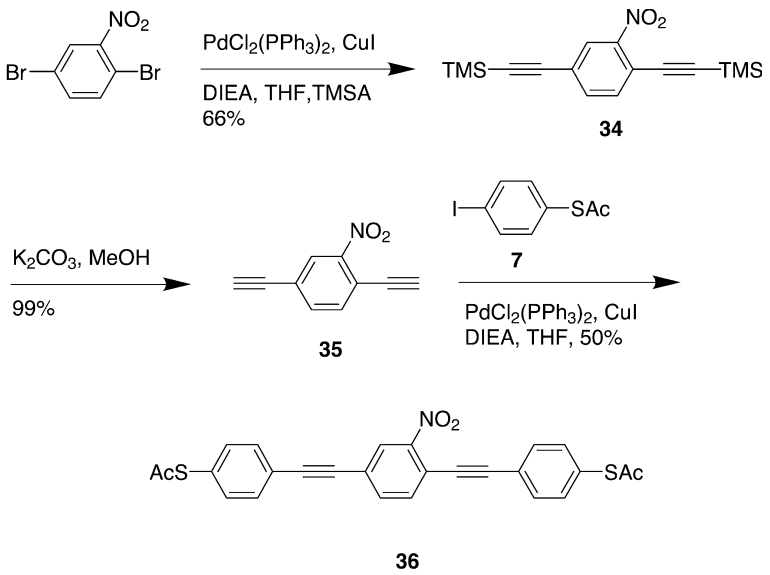
Scheme 10 shows the synthesis of the regioisomeric nitro compound relative to **25**, with the nitro group at the 3′ rather than the 2′-position and containing an isonitrile alligator clip. The free alkyne **27** was coupled with the formamide **9** to provide the precursor **32** as an impure and difficult to dissolve solid. This product was taken into the next dehydration with triphosgene with no further purification. Triethylamine (TEA) was used as a co-solvent with CH_2Cl_2 in order to afford the isonitrile **33** as the desired OPE.

Scheme 11 shows the synthesis of the mono-nitro compound functionalized with two alligator clips, for use contacting two metal surfaces or as a crosslinker between nanoparticles. 2,5-Dibromonitrobenzene was coupled with an excess of TMSA to afford the intermediate **34** in good yield. The competing cyclization between nitro and alkyne might be responsible for the modest yield. Deprotection of the alkyne **34** in excellent yield was followed by coupling under the 5,10,20 catalyst method with 2 equiv. of alligator clip **7** to afford final OPE **36** in moderate yield. A previous route afforded only 20% of the desired product. The lower yielding example used only 10 mol% of triphenylphosphine instead of 20 mol%.

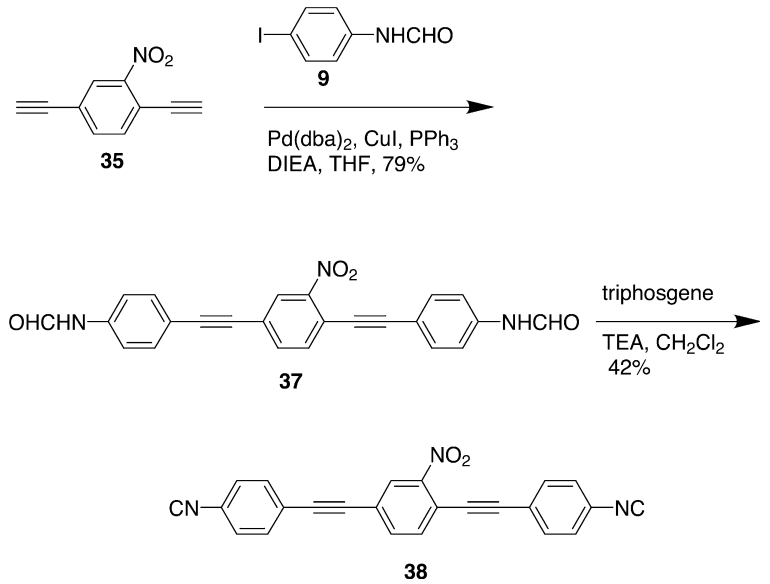
The complete synthesis of the mononitro system containing two isonitriles is shown in Scheme 12.



Scheme 10.



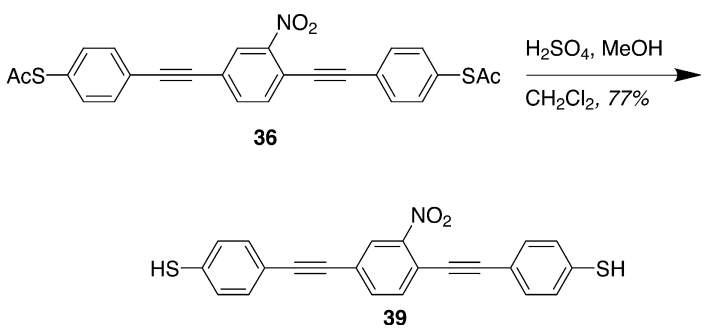
Scheme 11.



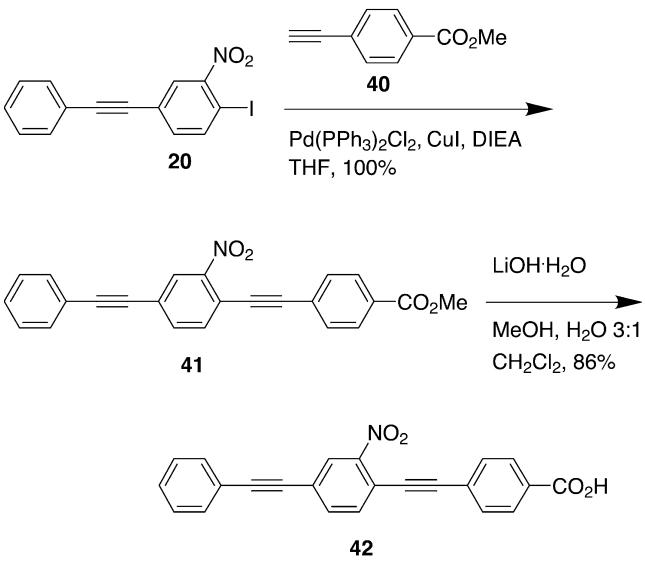
Scheme 12.

1,4-Diethynyl-2-nitrobenzene (**35**) was coupled with 2 equiv. of the formamide **9** to afford **37** as the desired bis(formamide), with quite low solubility. This intermediate was then dehydrated using triphosgene to afford the final target **38** in a modest yield that was depressed due to the solubility problems.

Scheme 13 shows the deprotection of the bis(thioacetyl) nitro compound **36** to give the bis(thiol) compound **39**. This compound is desirable in that there is no in situ deprotection of the thiols needed when assembling onto metal surfaces or nanoparticles. This makes the assembly process much simpler and more successful. Base-promoted deprotection



Scheme 13.

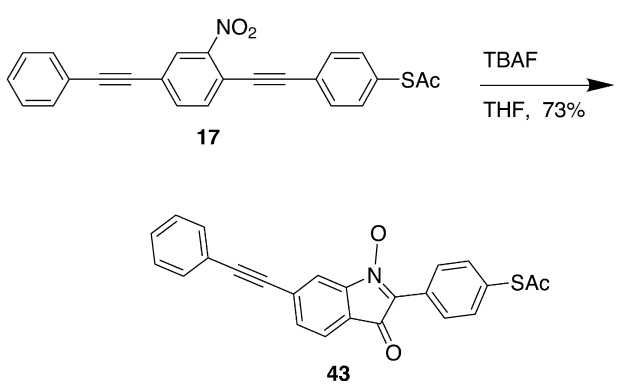


Scheme 14.

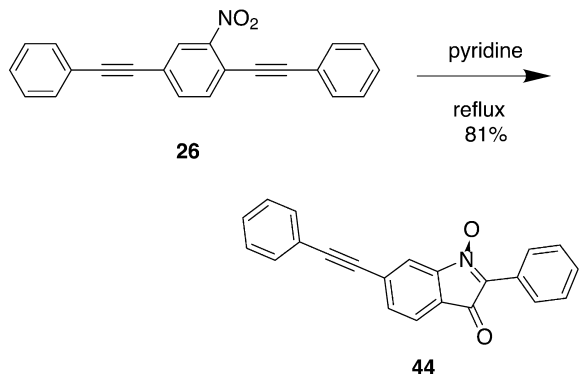
of this compound did not work well because if trace amounts of oxygen are present, the thiloate dimerizes to the disulfide, affording a polymer.[18] Of course, strict exclusion of air must be maintained, even on workup. However, acid-catalyzed deprotection works well because polymerization is greatly reduced.[19] Purification was made easier by the fact that any polymer formed precipitated from solution and separated from the desired soluble product.

Scheme 14 shows the synthesis of the mononitro compound with a carboxylic acid terminus in lieu of the standard thioacetate. Compound **42** has value because the acid terminus can assemble onto some surfaces such as aluminum oxides.[20,21] For this, **20** was coupled with 4-ethynylbenzoic acid methyl ester (**40**)[22] in quantitative yield to give **41**. Finally, the ester was saponified[23] to give the desired acid terminated molecular device **42** in very good yield.

Scheme 15 shows the synthesis of a new class of potential molecular electronic devices. The isatogen, also called an indolone *N*-oxide, is the central 6,5-fused ring portion of this compound. Because it has the same atomic composition as **17**, a comparison of the solid-state electronic properties of isatogen **43** with **17** should be very interesting and informative. Also, isatogens are known to be efficient spin traps for radicals.[17] If isatogens can stabilize radicals better



Scheme 15.



Scheme 16.

than a simple nitro group, isatogens may give longer memory lifetimes in the solid state.

Compound **17** was dissolved in THF and one drop of TBAF in THF was added. The solution was stirred for 15 min before quenching with acid. To our knowledge, this is the first example of TBAF inducing this rearrangement. Most syntheses use UV light or hot pyridine.[24]

Scheme 16 shows the formation of isatogen **44** from the simple mononitro compound **26**. TBAF was initially employed to attempt the transformation as in Scheme 15, with no success. However, heating the compound to reflux in pyridine indeed promoted the cyclization and rearrangement in good yield.[24]

The CV testing of **44** revealed at least two clear reductions: one at −0.62 V and the second at −1.39 V (Fig. 2). This is markedly different from the mononitro OPE **26** that shows two reductions, one at −1.39 V and the second at −2.09 V.[8]

4. Heteroatom-containing OPEs

Potential molecular electronic devices may have novel properties when heteroatoms or metals are part of their structural core. We became interested in the synthesis of candidates containing pyridine moieties and aryl chromium tricarbonyl complexes. Based on the facility of pyridine-based compounds to undergo reduction, we pursued the synthesis of molecule **49**, outlined in Scheme 17.

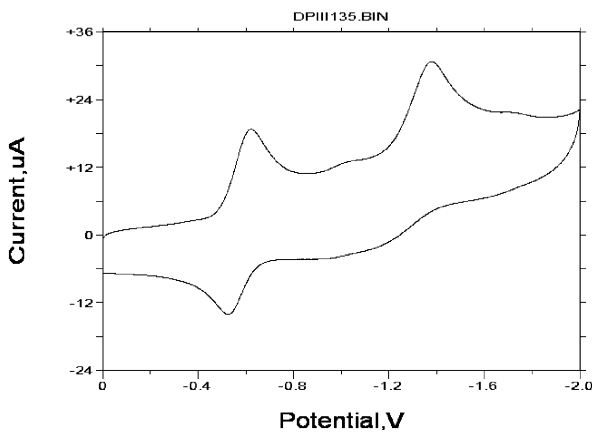
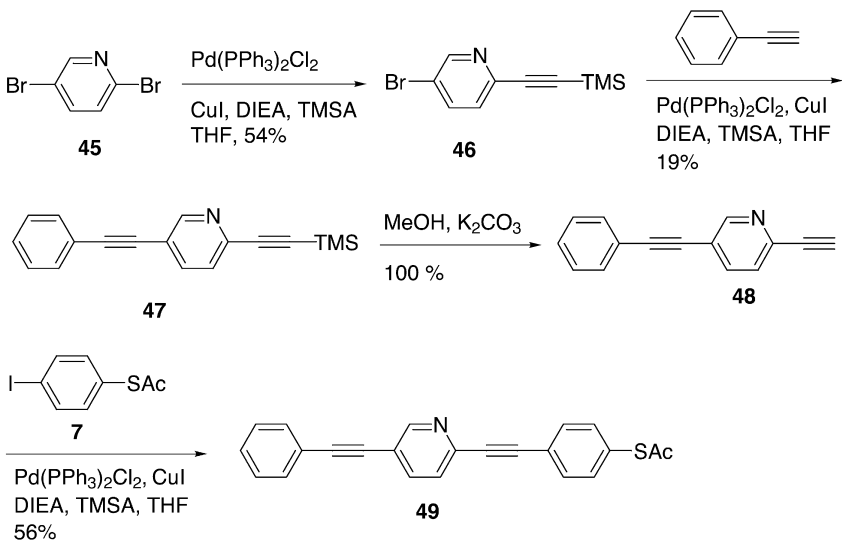


Figure 2. Cyclic voltammagram of isatogen **44**.



Scheme 17.

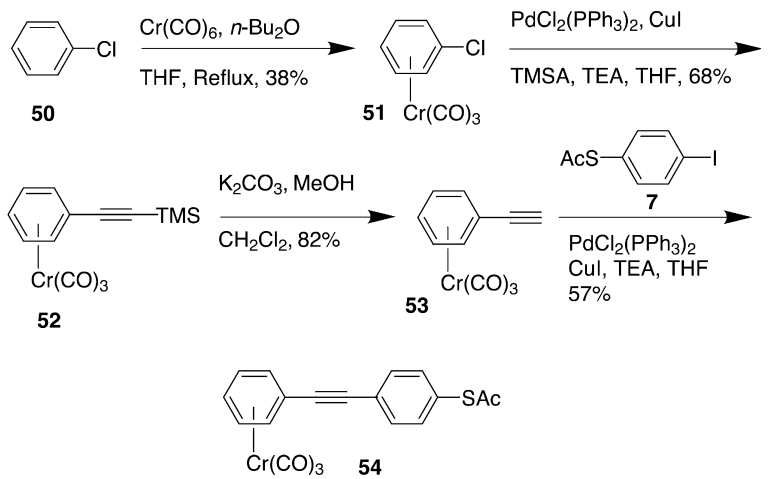
The synthesis of OPE **49** starts with 2,5-dibromopyridine (**45**), which undergoes Sonogashira coupling with TMSA selectively at the 2-position, in order to provide the intermediate **46**. The semi-crude reaction mixture was carried on directly to the next step, where **46** was coupled via a second Sonogashira reaction with phenylacetylene to yield the protected alkyne **47**. OPE **47** was subsequently deprotected and coupled to **7** via a palladium–copper reaction to yield desired molecule **49** in moderate yield.

Continuing to pursue novel compounds that may switch due to oxidation or reduction, attention was turned to the synthesis of aryl-chromium complexes. Knowing that it has been previously reported that chromium tricarbonyl groups act in an electron-withdrawing mode,[25] the synthesis of compound **54** was pursued as outlined in Scheme 18.

Starting with chlorobenzene (**50**), the aryl chromium tricarbonyl compound **51** was synthesized according to Mahaffy and Pauson's procedure.[26] In retrospect, the yield may have been improved if we had used Wright's procedure, in which the chromium hexacarbonyl is first complexed with acetonitrile and then reacted with the desired arene to displace the acetonitrile ligands.[27] The aryl chromium tricarbonyl compound easily underwent Sonogashira coupling with TMSA to afford the intermediate **52** in good yield. Deprotection unmasked the terminal alkynyl hydrogen of compound **53** in good yield. Final compound **54** was obtained in good yield via a Sonogashira coupling with **7**.

5. 'U-shaped' molecular wires

We have also made efforts in the construction of a molecule dubbed a U-shaped (US) molecular wire. We have demonstrated that the 'on–off' behavior observed with nitro-functionalized OPEs could be due to conformation changes of the molecules in a SAM.[28] On the other hand, Seminario and co-workers have theorized that this switching behavior has origins in a one-electron reduction of the molecules, producing changes in the molecular orbitals that result in alterations in orbital overlap and the degree of delocalization.[8] Based on these hypotheses, we thought that a US OPE should limit the conformational changes since it would be anchored to the surface through two thiol–Au



Scheme 18.

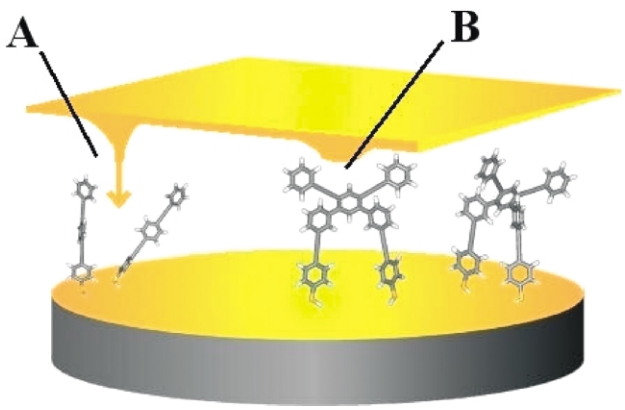
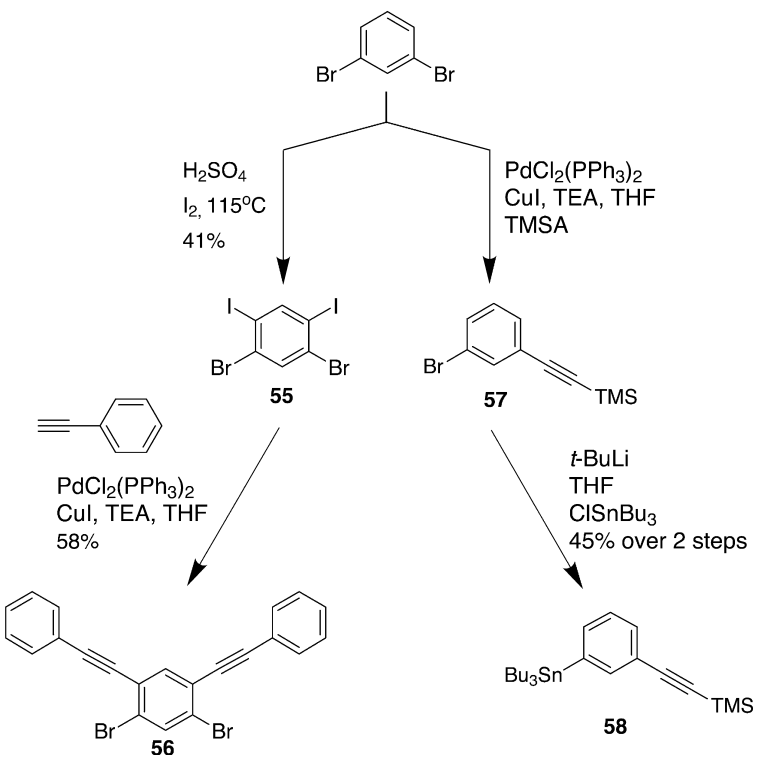


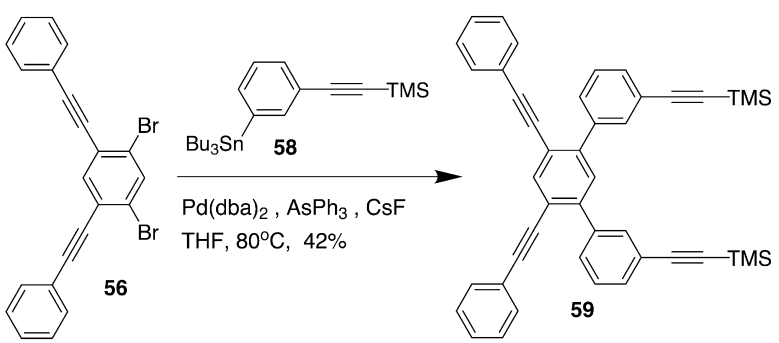
Figure 3. Schematic of linear OPEs and US OPE molecules on a metal surface indicating the top-contact metal-leakage problem. **A** points to a site where metal leakage between linear OPEs has occurred while **B** indicates blockage of such a leak by the aromatic bridging in the US OPE molecules.

bonds. Moreover, we theorized that these top-bridged linear OPEs (Fig. 3) may reduce the top contact metal leakage problem by closing up the free space between molecules where the leak can occur ('A' in Figure 3), instead producing a SAM where metal leakage is blocked by the tetra-substituted aromatic core ('B' in Figure 3).

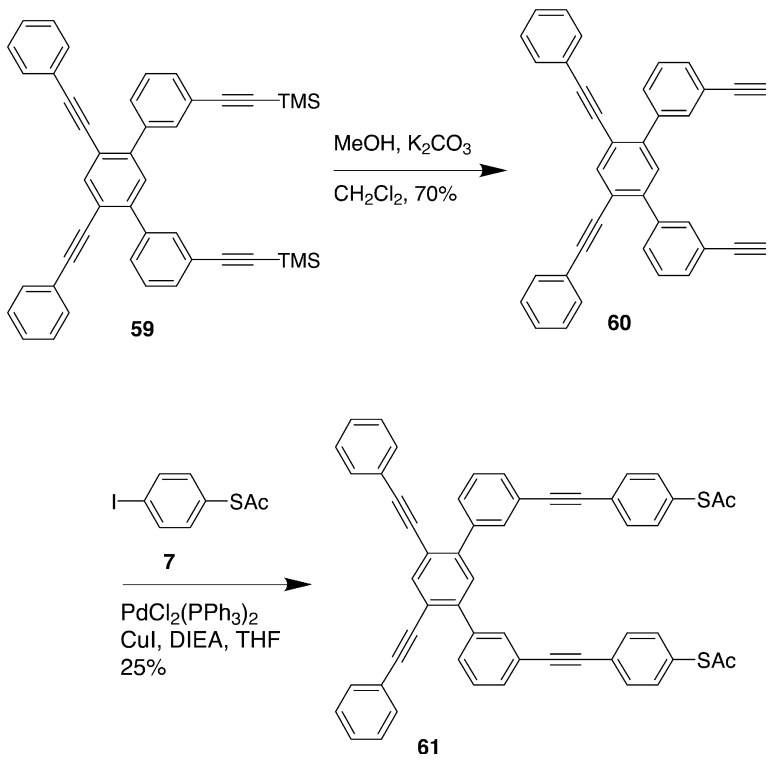
The synthesis began with an initially divergent route, as shown in Scheme 19. 1,3-Dibromobenzene was iodinated, where an excess of iodine in refluxing sulfuric acid yielded the desired diiododibromobenzene **55**. It was found on further attempts that the optimal reaction time was 10 h. Extending this time caused the yield to decrease. Selectively coupling the iodides with phenylacetylene afforded the dibromobis(phenylethynyl)benzene **56**, needed for further Stille couplings. The addition of excess phenylacetylene promoted the loss of the halide selectivity in the couplings, yielding small amounts of the tetracoupled product. This



Scheme 19.



Scheme 20.



Scheme 21.

byproduct was difficult to separate from the desired product. Stannane **58** was prepared via Sonogashira coupling between 1,3-dibromobenzene and TMSA, followed by a stannylation via a lithium–halogen exchange of the remaining bromine and quenching with tributyltin chloride.

Disappointedly, the aryl–aryl bond formation was again difficult when the double Stille coupling was employed. Reaction conditions were changed in several ways, searching for better yields of the desired product. Equimolar addition per bromide of cesium fluoride[29] as shown in Scheme 20 allowed for the isolation of the desired intermediate **59**.

Scheme 21 shows the final steps in the synthesis of US OPE **61**. Basic deprotection of the alkynes afforded **60** in modest yields. Final coupling with the thioacetyl alligator clip **7** furnished the desired US OPE **61**.

6. Conclusions

In this work, we have improved the yields of previously synthesized devices, and have introduced several new molecular electronics candidates, based on a strategy of synthesizing different regioisomers and cores.

Many of the new OPEs are functionalized with electron-withdrawing groups and metals that are either incorporated into their core or that are aryl-complexed. They also contain either thiol-based or isonitrile alligator clips for attachment to metal surfaces and formation of SAMs. The alligator clip functionality allows the investigation of potential solid-state behavior as switches and memory elements. Isatogens, compounds isomeric to the nitro-functionalized OPEs, were synthesized for comparison in our testbed devices. Finally, we synthesized a novel US OPE containing two alligator clip moieties that could lead to formation of a conformationally-locked SAM on the metal surface. This novel structure might provide insights to discern the relation between conformation and electronic properties of molecular electronic devices. Work is currently underway to evaluate these compounds for their effectiveness as nanoscale devices. Self-assembly and testing of **61** will be reported elsewhere.

7. Experimental

7.1. General

All reactions were performed under an atmosphere of nitrogen unless stated otherwise. *N*,*N*-dimethylformamide (DMF) was distilled over calcium hydride and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexanes were distilled. *N*,*N*-Diisopropylethylamine (DIEA) was distilled over calcium hydride. 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 NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Brüker Avance 400 spectrometer. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett–Packard GC model 5890A. Melting points were determined on a Büchi melting point apparatus. Mass spectrometry was performed at Rice University's mass spectrometry lab. All new compounds were named using the Beilstein Autonom feature of Beilstein Commander software.

7.2. General procedure for the coupling of a terminal alkyne with an aryl halide utilizing a palladium–copper cross-coupling (Castro–Stephens/Sonogashira protocol)[11,30]

To an oven-dried screw cap tube or a round bottom flask equipped with a water cooled West condenser and a magnetic stir bar were added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (5 mol% based on aryl halide), and copper(I) iodide (10 mol% based on aryl halide). Alternately, bis(dibenzylideneacetone)palladium(0) (2 mol% based on aryl halide), copper(I) iodide (2 mol% based on aryl halide) and triphenylphosphine (2.5 equiv. per palladium) were used. The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). A co-solvent of THF was added followed by *N*,*N*-diisopropylamine (DIEA). The terminal alkyne was then added and the reaction heated, if necessary, until complete. 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 CH_2Cl_2 and washed with a saturated solution of NH_4Cl (3×). The combined aqueous layers were extracted with CH_2Cl_2 (3×). 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).

7.3. General procedure for the coupling of an aryl stannane with an aryl halide utilizing a palladium-catalyzed cross-coupling (Stille coupling)[31]

To an oven dried large screw-cap tube were added all the solids, along with a stirring bar. The vessel was capped with at least one septa and wired down. The stannane was kept in a round bottom flask; both vessels were purged with dry nitrogen (3×). Solvent was added to the stannane and the solution was transferred to the remaining vessel via syringe before heating in an oil bath while stirring. The reaction mixture was kept at no less than 75°C for no less than 12 h. When the reaction was complete, the reaction was quenched and the solvent removed in vacuo.

7.4. General procedure for the deprotection of a trimethylsilyl (TMS) protected alkyne

To a round bottom flask equipped with a magnetic stir bar were added the TMS-protected alkyne, 5 equiv. of potassium carbonate, and equivalent amounts of MeOH and methylene chloride. 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 with the resulting terminal alkyne quickly employed in the next palladium copper cross-coupling step.

7.5. General procedure for electrochemical testing of potential molecular electronics devices

The CVs were performed on a BAS CV-50W using a glassy carbon electrode as working electrode, platinum wire as auxiliary electrode, with a $Ag/AgNO_3$ non-aqueous reference electrode. The solutions were 1 mM in DMF and 0.1 M *n*-Bu_4NBF_4. The scan rate was 0.1 V/s at 25°C.

7.5.1. 3-Ethyl-phenylamine (1).[9] 3-Nitroacetophenone (16.52 g, 100 mmol), 10% palladium on charcoal (2 g), anhydrous ethanol (100 mL), and conc. hydrochloric acid (20 mL) were added to a screw cap Parr hydrogenation flask. The mixture was kept at approximately 70°C and under 60 psi of hydrogen for 1 d. The charcoal was filtered from the solution and the solvents were removed in vacuo. The crude product was distilled (75°C/1.1 mm Hg) to give the desired product as an oil (5.62 g, 46%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J=7.7 Hz, 1H), 6.61 (dd, J=7.5, 0.6 Hz, 1H), 6.52 (m, 2H), 3.59 (br s, 2H), 2.56 (q, J=7.6 Hz, 2H), 1.21 (m, 3H).

7.5.2. 3-Ethyl-4-iodo-phenylamine (2).[10] 3-Ethyl-phenylamine (**1**) (2.86 g, 23.60 mmol), sodium bicarbonate (3.96 g, 47.2 mmol), MeOH (15 mL), and CH_2Cl_2 (15 mL) were added to a 100 mL round bottom flask containing a stir bar and cooled to 0°C. A solution of triethylbenzylammonium dichloroiodide (9.20 g, 23.60 mmol) in CH_2Cl_2 (15 mL) was slowly added to the flask under N_2 over 15 min. The ice bath was then removed and the solution stirred for 25 min. The solution was poured into water, extracted with CH_2Cl_2, and dried over magnesium sulfate. Flash column chromatography (silica gel using CH_2Cl_2 as eluent) afforded the desired product as a dark oil (4.90 g, 84%). IR (KBr) 3453.9, 3364.8, 2963.8, 2928.7, 2870.2, 1610.5, 1460.5, 1422.0, 1311.5, 1250.1, 1007.9, 860.8, 803.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J=8.4 Hz, 1H), 6.57 (d, J=2.8 Hz, 1H), 6.26 (dd, J=8.3, 2.8 Hz, 1H), 3.63 (br s, 2H), 2.62 (q, J=7.5 Hz, 2H), 1.17 (t, J=7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.3, 140.1, 116.0, 115.4, 86.2, 34.4, 15.0. HRMS calcd for $C_8H_{10}NI$: 246.9860. Found: 246.9855 (error=0.98 ppm).

7.5.3. 3-Ethyl-4-trimethylsilanylethynyl-phenylamine (3). 3-Ethyl-4-iodo-phenylamine (**2**) (1.9 g, 7.69 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.216 g, 0.307 mmol), copper(I) iodide (0.029 g, 0.154 mmol), triethylamine (15 mL), and TMSA (1.41 mL, 10.0 mmol) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 1.5 h. Flash column chromatography (silica gel using CH_2Cl_2 as eluent) afforded the desired product as an oil (0.972 g, 58% yield). IR (KBr) 3469.0, 3377.9, 3218.1, 2962.4, 2932.5, 2888.8, 2863.2, 2144.3, 1621.8, 1493.7, 1455.7, 1316.6, 1249.3, 1220.5, 840.2, 758.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J=8.2 Hz, 1H), 6.47 (d, J=2.3 Hz, 1H), 6.40 (dd, J=8.2, 2.4 Hz, 1H), 3.72 (br s, 1H), 2.69 (q, J=7.5 Hz, 2H), 1.20 (t, J=7.5 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 147.3, 134.2, 114.68, 112.6, 112.4, 105.2, 95.5, 28.2, 14.9, 0.6.

7.5.4. (2-Ethyl-4-iodo-phenylethynyl)-trimethyl-silane (4).[9] To a 200 mL round bottom flask was added $NOBF_4$ (1.83 g, 15.69 mmol) and acetonitrile (60 mL) under nitrogen. The flask was cooled to −40°C and a solution of 3-ethyl-4-trimethylsilanylethynyl-phenylamine (**3**) (3.10 g, 14.26 mmol) in acetonitrile (30 mL) was added slowly. The resulting solution was stirred for 30 min while warming to

−10°C. The solution was then cannulated into a solution of sodium iodide (4.27 g, 28.52 mmol) and iodine (3.62 g, 14.26 mmol) in acetonitrile (30 mL) at ambient temperature. The reaction was stirred for 20 min before washing with aqueous sodium thiosulfate and CH_2Cl_2. Flash column chromatography (silica gel using hexanes as eluent) afforded the product as an orange oil (3.67 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J=1.8 Hz, 1H), 7.44 (dd, J=8.1, 1.7 Hz, 1H), 7.11 (d, J=8.1 Hz, 1H), 2.72 (q, J=7.5 Hz, 2H), 1.21 (t, J=7.6 Hz, 3H), 0.23 (s, 9H).

7.5.5. (2-Ethyl-4-phenylethynyl-phenylethynyl)-trimethyl-silane (5).[9] (2-Ethyl-4-iodo-phenylethynyl)-trimethyl-silane (**4**) (2.0 g, 6.09 mmol)) was coupled with phenylacetylene (0.74 mL, 6.7 mmol) using the Pd/Cu cross-coupling method described earlier using bis(dibenzylideneacetone)palladium(0) (0.173 g, 0.30 mmol), copper(I) iodide (0.116 g, 0.61 mmol), triphenylphosphine (0.176 g, 0.67 mmol), THF (10 mL), and DIEA (4.3 mL, 24.4 mmol) in an oven dried screw cap tube under nitrogen. The reaction mixture was stirred at ambient temperature for 3 h. Column chromatography (silica gel using hexanes as eluent) afforded the desired product (1.26 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.39 (d, J=8.1 Hz, 1H), 7.35 (m, 1H), 7.32 (m, 3H), 7.27 (dd, J=7.9, 1.6 Hz, 1H), 2.79 (q, J=7.6 Hz, 2H), 1.25 (t, J=7.6 Hz, 3H), 0.25 (s, 9H).

7.5.6. 2-Ethyl-1-ethynyl-4-phenylethynyl-benzene (6).[9] (2-Ethyl-4-phenylethynyl-phenylethynyl)-trimethyl-silane (**5**) (1.26 g, 4.15 mmol), potassium carbonate (2.87 g, 20.76 mmol), MeOH (20 mL), and CH_2Cl_2 (20 mL) were used following the general procedure for deprotection (0.897 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.43 (d, J=7.9 Hz, 1H), 7.38 (m, 1H), 7.34 (m, 3H), 7.29 (dd, J=7.9, 1.7 Hz, 1H), 3.32 (s, 1H), 2.81 (q, J=7.6 Hz, 2H), 1.25 (t, J=7.6 Hz, 3H).

7.5.7. Thioacetic acid *S*-[4-(2-ethyl-4-phenylethynyl-phenylethynyl)-phenyl] ester (8).[9] 2-Ethyl-1-ethynyl-4-phenylethynyl-benzene (**6**) (0.897 g, 3.89 mmol)) was coupled with 4-thioacetyl-1-iodobenzene (**7**) (1.083 g, 3.89 mmol) using the Pd/Cu cross-coupling method described earlier using bis(dibenzylideneacetone)palladium(0) (0.067 g, 0.117 mmol), copper(I) iodide (0.044 g, 0.233 mmol), triphenylphosphine (0.077 g, 0.293 mmol), THF (10 mL), and DIEA (2.7 mL, 15.6 mmol) in an oven dried screw cap tube under nitrogen. The tube was heated in a 45°C oil bath for 15 h. Column chromatography (silica gel using 1:1 CH_2Cl_2/hexanes as eluent) followed by recrystallization from ethanol afforded the desired product as an off-white solid (1.03 g, 70% yield): mp 106–107°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 4H), 7.47 (d, J=8.0 Hz, 1H), 7.42 (m, 1H), 7.39 (dt, J=8.5, 1.8 Hz, 2H), 7.34 (m, 4H), 2.86 (q, J=7.6 Hz, 2H), 2.43 (s, 3H), 1.30 (t, J=7.6 Hz, 3H).

7.5.8. *N*-(4-Iodo-phenyl)-formamide (9).[32] Formic acid (88%, 13.7 mL, 320 mmol) and acetic anhydride (18.8 mL, 200 mmol) were mixed in a 500 mL round bottom flask and heated to 60°C for 30 min. The mixture was then cooled to 10°C. 4-Iodoaniline (21.9 g, 100 mmol) in THF (50 mL) was then added to the mixture slowly. Stirring was continued overnight at ambient temperature. The THF was removed under reduced pressure and water was added to cause precipitation. The solid formed was filtered and washed with water. The material was recrystallized from CH_2Cl_2/hexanes to afford the desired product (19.9 g, 81% yield): mp 111–112°C (lit. mp 108–109°C).[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J=11.3 Hz, 0.44H), 8.40 (br s, 0.25H), 8.36 (d, J=1.4 Hz, 0.71H), 7.62 (dd, J=11.8, 8.6 Hz, 2H), 7.44 (br s, 0.55H), 7.30 (d, J=8.7 Hz, 1.16H), 6.84 (d, J=8.6 Hz, 0.85H).

7.5.9. *N*-(4-Phenylethynyl-phenyl)-formamide (10). *N*-(4-Iodo-phenyl)-formamide (1.0 g, 4.05 mmol) was coupled with phenylacetylene (0.49 mL, 4.45 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.057 g, 0.081 mmol), copper(I) iodide (0.031 g, 0.162 mmol), THF (15 mL), and DIEA (1.4 mL, 8.1 mmol). The reaction was stirred at room temperature for 2 h. Column chromatography (silica gel using ethyl acetate as eluent) afforded the desired product (0.798 g, 89% yield): mp 192–195°C. IR (KBr) 3234.7, 2909.2, 1682.6, 1606.4, 1518.4, 1286.4, 842.1, 755.2, 693.8, 482.7 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J=11.3 Hz, 0.41H), 8.38 (d, J=1.7 Hz, 0.52H), 7.80 (br d, J=12.4 Hz, 0.44H), 7.51 (m, 5H), 7.32 (m, 4H), 7.22 (br s, 0.42H), 7.04 (d, J=8.6 Hz, 0.81H). HRMS calcd for $C_{15}H_{11}NO$: 221.084064. Found: 221.084352 (error=1.3 ppm).

7.5.10. 1-Isocyano-4-phenylethynyl-benzene (11). To a large test tube was added *N*-(4-phenylethynyl-phenyl)-formamide (0.400 g, 1.81 mmol) and triphosgene (0.198 g, 0.67 mmol). Air was removed and N_2 backfilled (3×). The tube was cooled to 0°C and CH_2Cl_2 (20 mL) and triethylamine (10 mL) was added. A solution of tetrabutylammonium chloride (0.050 g, 0.181 mmol) in CH_2Cl_2 (10 mL) was then added. The reaction was allowed to slowly warm to room temperature over 3 h. Because starting material remained (by TLC), an additional 0.070 g of triphosgene was added. After 1 h, an additional 0.053 g of triphosgene was added. After 1 h (5 h total time), the reaction was complete (by TLC). The mixture was washed with water and CH_2Cl_2. Column chromatography (silica gel using 1:1 hexanes/ethyl acetate as eluent; R_f=0.86) afforded the product (0.320 g, 87% yield): mp 101–102°C (decomp.). IR (KBr) 3416.1, 3083.4, 2217.9, 2126.1, 1505.3, 1442.8, 1403.7, 1194.5, 1103.2, 842.5, 761.1, 692.5, 525.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 4H), 7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 133.0, 132.1, 129.3, 128.9, 126.9, 125.2, 122.9, 92.6, 88.1. HRMS calcd for $C_{15}H_9N$: 203.073499. Found: 203.073127 (error=1.8 ppm).

7.5.11. 1,4-Bis-trimethylsilanylethynyl-benzene (12).[14,34] 1,4-Diiodobenzene (7.97 g, 24.2 mmol) was coupled with TMSA (7.2 mL, 50.8 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.170 g, 0.242 mmol), copper(I) iodide (0.092 g, 0.484 mmol), THF (50 mL), and DIEA (16.9 mL, 96.8 mmol). The reaction was stirred at room temperature for 1.5 h. Column chromatography (silica gel using hexanes as eluent) afforded the desired product (6.33 g, 97% yield): mp 122–125°C (lit.[35] mp 122°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 4H), 0.22 (s, 18H).

7.5.12. 1,4-Diethynyl-benzene (13).[14,34] 1,4-Bis-trimethylsilanylethynyl-benzene (**12**) (3.0 g, 11.1 mmol), potassium carbonate (9.2 g, 66.5 mmol), MeOH (100 mL) and CH_2Cl_2 (100 mL) were used following the procedure for deprotection. After stirring for 1 h at room temperature, the solution was filtered and worked up in the usual manner to afford the desired product (1.40 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 4H), 3.15 (s, 2H).

7.5.13. *N*-{4-[4-(4-Formylamino-phenylethynyl)-phenylethynyl]-phenyl}-formamide (14). 1,4-Diethynyl-benzene (**13**) (1.40 g, 11.1 mmol) was coupled with 4-iodo-formanilide (**9**) (5.48 g, 22.2 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.156 g, 0.222 mmol), copper(I) iodide (0.085 g, 0.444 mmol), THF (20 mL), and DIEA (7.7 mL, 44.4 mmol). The reaction was stirred at 50°C for 14 h. The tube was filled with solid that was filtered and washed with CH_2Cl_2 to remove salts and starting materials to afford the desired product (3.78 g, ~94% yield): mp 218–225°C. IR (KBr) 3180.6, 3043.3, 1705.1, 1604.3, 1522.6, 1406.4, 1294.4, 838.0, 541.6, 484.9 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.43 (d, J=1.5 Hz, 1.52H), 10.35 (d, J=10.8 Hz, 0.45H), 8.91 (d, J=10.8 Hz, 0.47H), 8.32 (d, J=1.8 Hz, 1.55H), 7.67 (d, J=8.7 Hz, 3.29H), 7.57–7.52 (m, 8H), 7.27 (d, J=8.6 Hz, 0.88H).

7.5.14. 1,4-Bis-(4-isocyano-phenylethynyl)-benzene (15). To a 500 mL round bottom flask was added *N*-{4-[4-(4-formylamino-phenylethynyl)-phenylethynyl]-phenyl}-formamide (**14**) (2.0 g, 5.49 mmol). Air was removed and N_2 backfilled (3×). CH_2Cl_2 (250 mL) and triethylamine (50 mL) was added and the tube was cooled to 0°C. Triphosgene (1.63 g, 5.49 mmol) was then added. After 30 min starting material remained (by TLC). An additional 0.81 g of triphosgene was added. After 60 min an additional 0.81 g of triphosgene was added. After 40 min an additional amount of triphosgene (0.81 g) was added. After 2.25 h (total time), the reaction was warmed to ambient temperature. An additional 0.25 equiv. of triphosgene (0.405 g) was added and stirred for 1.5 h. The solvents were then removed under reduced pressure. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.84) afforded the product (0.220 g, 12% yield) and starting materials (39% recovered): mp 230–250°C. IR (KBr) 3047.5, 2128.8, 1518.2, 1419.1, 1275.7, 841.8, 531.5, 435.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dt, J=8.8, 2.0 Hz, 4H), 7.50 (s, 4H), 7.35 (dt, J=8.7, 2.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 133.0, 132.1, 126.9, 124.8, 123.3, 92.0, 90.2. HRMS calcd for $C_{24}H_{12}N_2$: 328.100048. Found: 328.100238 (error=0.58 ppm).

7.5.15. 1-Ethynyl-2-nitro-4-phenylethynyl-benzene (16).[14] 2,5-Dibromonitrobenzene (4.0 g, 14.24 mmol), bis-(triphenylphosphine)palladium(II) dichloride (0.300 g, 0.427 mmol), copper(I) iodide (0.163 g, 0.854 mmol), THF (30 mL), DIEA (9.9 mL, 57.0 mmol), and TMSA (2.21 mL, 15.66 mmol) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 10 h. Flash column chromatography (silica gel using 2:1 hexanes/CH_2Cl_2 as eluent) afforded a mixture of products that was taken onto the next step. The product mixture (3.09 g), bis(triphenylphosphine)-palladium(II) dichloride (0.217 g, 0.31 mmol), copper(I) iodide (0.118 g, 0.62 mmol), THF (30 mL), DIEA (7.2 mL, 41.44 mmol), and phenylacetylene (1.7 mL, 15.54 mmol) were used following the general procedure for couplings. The tube was heated in a 50°C oil bath for 15 h. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded a mixture of products that was taken onto the next step. The product mixture (1.95 g), potassium carbonate (4.2 g, 30.4 mmol), MeOH (50 mL), and CH_2Cl_2 (50 mL) were used following the general procedure for deprotection. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product as an orange solid (1.23 g, 37% yield). IR (KBr) 3267.2, 3250.1, 3079.6, 2208.4, 2102.6, 1541.6, 1522.5, 1496.0, 1347.1, 1275.2, 900.9, 840.5, 825.0, 759.0, 688.0, 528.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J=1.5 Hz, 1H), 7.67 (dd, J=8.1, 1.5 Hz, 1H), 7.64 (d, J=7.8 Hz, 1H), 7.53 (m, 2H), 7.37 (m, 3H), 3.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 135.8, 135.7, 132.2, 129.7, 129.0, 127.8, 125.5, 122.3, 117.0, 94.4, 87.0, 87.0, 78.8. HRMS calcd for $C_{16}H_9NO_2$: 247.0633. Found: 247.0632 (error=0.68 ppm).

7.5.16. Thioacetic acid *S*-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (17).[14] 1-Ethynyl-2-nitro-4-phenylethynyl-benzene (**16**) (0.500 g, 2.02 mmol)) was coupled with 4-thioacetyl-1-iodobenzene (**7**) (0.675 g, 2.43 mmol) using the Pd/Cu cross-coupling method described earlier using bis(dibenzylideneacetone)palladium(0) (0.232 g, 0.404 mmol), copper(I) iodide (0.077 g, 0.404 mmol), triphenylphosphine (0.212 g, 0.808 mmol), THF (10 mL), and DIEA (0.7 mL, 4.04 mmol) in an oven dried screw cap tube under nitrogen. The tube was stirred in a 50°C oil bath for 2 d. Column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent) afforded the desired product as an orange solid (0.381 g, 47% yield): mp 110–112°C. IR (KBr) 2217.9, 1697.6, 1541.6, 1346.8, 1128.2, 954.9, 824.1, 755.9, 685.5, 618.7, 526.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J=1.1, 0.3 Hz, 1H), 7.70 (dd, J=8.1, 1.5 Hz, 1H), 7.67 (d, J=8.0 Hz, 1H), 7.61 (dt, J=8.5, 1.9 Hz, 2H), 7.54 (m, 2H), 7.42 (dt, J=8.5, 1.8 Hz, 2H), 7.37 (m, 3H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 149.9, 135.7, 135.0, 134.7, 133.0, 132.2, 129.9, 129.7, 129.0, 128.1, 124.9, 123.8, 122.4, 118.1, 98.2, 94.2, 87.3, 86.7, 30.8. HRMS calculated for $C_{24}H_{15}NO_3S$: 397.0076. Found: 397.0773 (error=0.8 ppm).

7.5.17. 4-Iodo-2-nitro-phenylamine (18).[36] 2-Nitroaniline (30.0 g, 217 mmol), sodium acetate (18.7 g, 228 mmol) and acetic acid (150 mL) were added to a 500 mL round bottom flask with a stir bar. To this flask was added a solution of iodine monochloride (37.0 g, 228 mmol) in acetic acid (100 mL) and the resulting solution was heated at 80°C for 30 min. The solution was immediately poured into water (600 mL) and allowed to stand for 3 h. The orange solid was filtered to give the desired product (54.5 g, 95%): mp 121–124°C (lit.[15] mp 121–123°C) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J=2.1 Hz, 1H), 7.54 (dd, J=8.8, 2.1 Hz, 1H), 6.59 (d, J=8.8 Hz, 1H), 6.09 (br s, 2H).

7.5.18. 2-Nitro-4-phenylethynyl-phenyamine (19). 4-Iodo-2-nitro-phenylamine (**18**) (10.0 g, 37.9 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.266 g, 0.379 mmol), copper(I) iodide (0.144 g, 0.758 mmol), DIEA (19.8 mL,

113.7 mmol), THF (35 mL) and phenylacetylene (4.6 mL, 37.9 mmol) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 2.5 h. Precipitation from CH_2Cl_2/hexanes followed by extraction with Et_2O and water afforded the desired product (7.93 g, 88% yield). IR (KBr) 3470.7, 3342.1, 1641.5, 1598.7, 1552.2, 1516.2, 1411.5, 1340.5, 1234.8, 1142.8, 833.7, 756.2, 687.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J=2.0 Hz, 1H), 7.52 (m, 3H), 7.38 (m, 3H), 6.81 (dd, J=8.6, 0.4 Hz, 1H), 6.24 (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 $C_{14}H_{10}N_2O_2$: 238.074228. Found: 238.074109 (error=0.50 ppm).

7.5.19. 1-Iodo-2-nitro-4-phenylethynyl-benzene (20). To a 500 mL round bottom flask (cooled to −20 to −30°C) was added $BF_3{\cdot}OEt_2$ followed by 2-nitro-4-phenylethynyl-phenylamine (**19**) (7.89 g, 33.1 mmol) in THF (55 mL) over 15 min. Next, *t*-BuONO (13.8 mL, 115.9 mmol) in THF (45 mL) was added over 20 min. The solution was allowed to warm to 0°C over 25 min and Et_2O was added to effect precipitation of the diazonium salt. The salt was filtered and washed with cold Et_2O to afford 10.92 g of solid. To a 500 mL round bottom flask was added acetonitrile (125 mL), sodium iodide (9.92 g, 66.2 mmol) and iodine (8.4 g, 33.1 mmol). The diazonium salt was then slowly added to this solution over 15 min. The solution was washed with $Na_2S_2O_3$ (aq) and extracted with CH_2Cl_2 to afford the desired product that needed no further purification (9.78 g, 85% yield). IR (KBr) 3078.2, 3047.5, 2211.9, 1522.2, 1439.3, 1351.6, 1014.3, 891.5, 824.3, 755.0, 686.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J=8.2 Hz, 1H), 7.96 (d, J=1.9 Hz, 1H), 7.52 (m, 2H), 7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 136.0, 132.2, 129.7, 129.0, 128.4, 125.2, 122.4, 93.7, 86.6, 85.9. HRMS calcd for $C_{14}H_8NO_2I$: 348.959973. Found: 348.959869 (error=0.30 ppm).

7.5.20. Trimethyl-(2-nitro-4-phenylethynyl-phenylethynyl)-silane (21).[14] 1-Iodo-2-nitro-4-phenylethynyl-benzene (**20**) (3.56 g, 10.2 mmol) was coupled with TMSA (1.5 mL, 10.6 mmol) following the Pd/Cu protocol described earlier using bis(triphenylphosphine)-palladium(II) dichloride (0.072 g, 0.102 mmol), copper (I) iodide (0.039 g, 0.204 mmol), DIEA (3.5 mL, 20.4 mmol), and THF (20 mL). After stirring at ambient temperature for 5.5 h, the reaction was washed with NH_4Cl (aq) and Et_2O. Column chromatography (silica gel using 2:1 hexanes/CH_2Cl_2 as eluent; R_f=0.58) afforded the desired product (2.89 g, 89% yield). IR (KBr) 3093.3, 2919.1, 2847.4, 2202.1, 1704.7, 1526.4, 1348.0, 1113.6, 1080.4, 827.4, 756.8, 689.8, 615.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J=1.5 Hz, 1H), 7.63 (dd, J=8.1, 1.6 Hz, 1H), 7.59 (d, J=8.1 Hz, 1H), 7.52 (m, 2H), 7.36 (m, 3H), 0.27 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 135.1, 135.0, 131.8, 129.2, 128.6, 127.3, 124.5, 122.0, 117.6, 105.7, 99.2, 93.7, 86.8, 29.7, −0.4. HRMS calcd for $C_{19}H_{17}O_2NSi$: 319.1029. Found: 319.1026 (error=0.9 ppm).

7.5.21. 1-Ethynyl-2-nitro-4-phenylethynyl-benzene (16).[14] Trimethyl-(2-nitro-4-phenylethynyl-phenylethynyl)-silane (**21**) (2.87 g, 8.98 mmol), potassium carbonate (5.0 g, 36 mmol), MeOH (50 mL), and CH_2Cl_2 (50 mL) were used following the general deprotection method described earlier (2.13 g, 96% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 1H), 7.67 (dd, J=8.0, 1.5 Hz, 1H), 7.63 (d, J=8.0 Hz, 1H), 7.53 (m, 2H), 7.36 (m, 3H), 3.58 (s, 1H).

7.5.22. Thioacetic acid *S*-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (17).[14] 1-Ethynyl-2-nitro-4-phenylethynyl-benzene (**16**) (0.500 g, 2.02 mmol) was coupled with thioacetic acid *S*-(4-iodo-phenyl) ester (**7**) (0.562 g, 2.02 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone) palladium(0) (0.058 g, 0.101 mmol), copper(I) iodide (0.038 g, 0.202 mmol), triphenylphosphine (0.106 g, 0.404 g), DIEA (1.4 mL, 8.08 mmol), and THF (20 mL). After stirring at 45°C for 3 h, the reaction mixture was washed with NH_4Cl (aq) and CH_2Cl_2. Column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent; R_f=0.29) followed by recrystallization from CH_2Cl_2/hexanes afforded the desired compound as a yellow solid (0.468 g, 58% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J=1.5 Hz, 1H), 7.70 (dd, J=8.1, 1.5 Hz, 1H), 7.66 (d, J=8.1 Hz, 1H), 7.60 (dt, J=8.3, 1.8 Hz, 2H), 7.54 (m, 2H), 7.42 (dt, J=8.2, 1.8 Hz, 2H), 7.37 (m, 3H), 2.43 (s, 3H).

7.5.23. *N*-(4-Trimethylsilanylethynyl-phenyl)-formamide (22).[16] *N*-(4-Iodo-phenyl)-formamide (**9**) (6.0 g, 24.3 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.168 g, 0.24 mmol), copper(I) iodide (0.091 g, 0.48 mmol), DIEA (8.5 mL, 48.6 mmol), THF (20 mL) and TMSA (3.6 mL, 25.5 mmol) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 2 h. Normal workup using diethyl ether instead of CH_2Cl_2 afforded the desired product (5.28 g, 100% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (br d, J=10.8 Hz, 0.42H), 8.57 (br d, J=9.2 Hz, 0.43H), 8.39 (d, J=1.7 Hz, 0.51H), 7.56 (br s, 0.44H), 7.54–7.53 (m, 3.13H), 7.04 (dt, J=8.7, 2.1 Hz, 0.93H), 0.27 (d, J=1.8 Hz, 9H).

7.5.24. *N*-(4-Ethynyl-phenyl)-formamide (23).[16] *N*-(4-Trimethylsilanylethynyl-phenyl)-formamide (**22**) (5.28 g, 24.3 mmol), potassium carbonate (13.4 g, 97.2 mmol), MeOH (100 mL), and CH_2Cl_2 (100 mL) were used following the general procedure for deprotection to afford the desired product (3.29 g, 93% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J=11.3 Hz, 0.43H), 8.36 (d, J=1.6 Hz, 0.56H), 8.29 (br d, J=10.5 Hz, 0.40H), 7.46 (m, 3.74H), 7.02 (dt, J=8.6, 2.1 Hz, 0.95H), 3.06 (d, J=12.5 Hz, 1H).

7.5.25. *N*-[4-(2-Nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide (24). 4-Ethynylphenyl-2-nitro-1-iodo-benzene (**20**) (1.92 g, 5.5 mmol), *N*-(4-ethynyl-phenyl)-formamide (**23**) (0.798 g, 5.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.039 g, 0.055 mmol), copper(I) iodide (0.021 g, 0.11 mmol), DIEA (1.9 mL, 11 mmol), and THF (30 mL) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 1 d followed by heating at 50°C for 1 h. Flash column chromatography (silica gel using ethyl acetate as eluent; R_f: 0.75) afforded the desired product as a yellow solid (1.36 g, 67% yield): mp 180–183°C

(decomp.). IR (KBr) 3364.1, 3057.8, 2873.4, 2210.2, 1687.0, 1602.3, 1541.8, 1520.9, 1406.8, 1344.9, 1301.2, 1274.1, 1145.2, 831.4, 758.0, 689.8, 528.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J=1.3 Hz, 0.43H), 8.40 (d, J=1.7 Hz, 0.66H), 8.21 (m, 1H), 7.69 (m, 1H), 7.65 (d, J=8.0 Hz, 1H), 7.59 (s, 0.57H), 7.57 (s, 2.63H), 7.52 (m, 2H), 7.37 (m, 3H), 7.19 (br s, 0.55H), 7.07 (d, J=8.7 Hz, 0.76H). HRMS calcd for $C_{23}H_{14}N_2O_3$: 366.100442. Found: 366.100191 (error=0.69 ppm).

7.5.26. 1-(4-Isocyano-phenylethynyl)-2-nitro-4-phenylethynyl-benzene (25). *N*-[4-(2-Nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide (**24**) (1.00 g, 2.73 mmol) and triphosgene (0.300 g, 1.01 mmol) were added to a 500 mL round bottom flask with a stir bar. Air was removed and N_2 backfilled. CH_2Cl_2 (50 mL) and triethylamine (15 mL) were then added followed by tetrabutylammonium chloride (0.076 g, 0.273 mmol) in CH_2Cl_2 (20 mL). After 3 h, starting material remained so an additional 0.162 g of triphosgene was added. The reaction was complete after an additional 1 h (4 h total). The solution was washed with water and CH_2Cl_2 and dried over $MgSO_4$. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent; R_f: 0.55) afforded the desired product as a yellow solid. Recrystallization from hexanes/CH_2Cl_2 provided the product as yellow needles (0.814 g, 86% yield), mp 168°C (decomp.). IR (KBr) 3078.2, 3052.6, 2217.9, 2119.6, 1539.0, 1510.6, 1349.6, 1265.4, 896.7, 838.0, 761.9, 696.8, 536.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J=1.5 Hz, 1H), 7.71 (dd, J=8.1, 1.6 Hz, 1H), 7.66 (d, J=8.1 Hz, 1H), 7.60 (dt, J=8.6, 2.0 Hz, 2H), 7.54 (m, 2H), 7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 149.9, 135.8, 134.9, 133.5, 132.2, 129.7, 129.0, 128.1, 127.0, 125.3, 124.1, 122.4, 117.5, 96.9, 94.5, 87.7, 87.1. HRMS calcd for $C_{23}H_{12}N_2O_2$: 348.089878. Found: 348.090186 (error=0.88 ppm).

7.5.27. 2-Nitro-1,4-bis-phenylethynyl-benzene (26). 2,5-Dibromonitrobenzene (8.69 g, 30.93 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.434 g, 0.619 mmol), copper(I) iodide (0.236 g, 1.238 mmol), THF (40 mL), DIEA (21.5 mL, 123.72 mmol), and phenylacetylene (7.47 mL, 68.05 mmol) were used following the general procedure for couplings. The solution was heated in a 45°C oil bath for 1 h. A silica plug (using 2:1 hexanes/CH_2Cl_2 as eluent) followed by recrystallization from 95% ethanol afforded the desired product as yellow needles mp 96–98°C (6.17 g, 62%). IR (KBr) 2211.9, 1543.8, 1449.8, 1344.0, 1260.3, 1076.0, 910.9, 841.7, 761.5, 690.6, 526.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (m, 1H), 7.69 (dd, J=8.1, 1.5 Hz, 1H), 7.66 (dd, J=8.1, 0.4 Hz, 1H), 7.59 (m, 2H), 7.54 (m, 2H), 7.37 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 135.4, 134.7, 132.3, 132.0, 129.6, 129.4, 128.8, 128.7, 127.8, 124.3, 122.5, 122.3, 118.3, 99.1, 93.8, 87.1, 85.0. HRMS calcd for $C_{22}H_{13}NO_2$: 323.0946. Found: 323.0943 (error=1.2 ppm).

7.5.28. 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (27). 2,5-Dibromonitrobenzene (4.0 g, 14.24 mmol), bis-(triphenylphosphine)palladium(II) dichloride (0.300 g, 0.427 mmol), copper(I) iodide (0.163 g, 0.854 mmol), THF (30 mL), DIEA (9.9 mL, 57.0 mmol), and phenylacetylene (1.72 mL, 15.66 mmol) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 4 h. Flash column chromatography (silica gel using 2:1 hexanes/CH_2Cl_2 as eluent) afforded a mixture of products that was taken onto the next step. The product mixture, bis(triphenylphosphine)-palladium(II) dichloride (0.262 g, 0.373 mmol), copper(I) iodide (0.142 g, 0.747 mmol), triphenylphosphine (0.196 g, 0.746 mmol), THF (30 mL), DIEA (8.7 mL, 49.8 mmol), and TMSA (3.5 mL, 24.88 mmol) were used following the general procedure for couplings. The tube was heated in a 60°C oil bath for 18 h. Flash column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent) afforded a mixture of products that was taken onto the next step. The product mixture (2.70 g), potassium carbonate (5.5 g, 39.8 mmol), MeOH (50 mL), and CH_2Cl_2 (50 mL) were used following the general procedure for deprotection. Flash column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent) afforded the desired product as a yellow solid (1.14 g, 32% yield): mp 67–69°C. IR (KBr) 3268.6, 2202.7, 1612.2, 1544.2, 1516.4, 1439.5, 1345.4, 1270.9, 1135.5, 899.8, 832.1, 786.1, 760.1, 683.5, 529.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J=0.8 Hz, 1H), 7.62 (t, J=0.8 Hz, 2H), 7.57 (m, 2H), 7.36 (m, 3H), 3.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 136.2, 134.9, 132.2, 130.0, 128.9, 128.6, 123.2, 122.5, 119.3, 99.6, 85.0, 81.8, 81.4. HRMS calcd for $C_{16}H_9NO_2$: 247.0633. Found: 247.0637 (error=1.4 ppm).

7.5.29. Thioacetic acid *S*-[4-(3-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (28). 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (**27**) (0.201 g, 0.815 mmol)) was coupled with 4-thioacetyl-1-iodobenzene (**7**) (0.206 g, 0.741 mmol) using the Pd/Cu cross-coupling method described earlier using bis(dibenzylideneacetone)-palladium(0) (0.170 g, 0.296 mmol), copper(I) iodide (0.056 g, 0.296 mmol), triphenylphosphine (0.155 g, 0.592 mmol), THF (10 mL), and DIEA (0.51 mL, 2.96 mmol) in an oven dried screw cap tube under nitrogen. The tube was stirred in a 60°C oil bath for 1 d. Column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent) afforded the desired product as an orange solid (0.152 g, 52% yield): mp 165–168°C. IR (KBr) 3062.6, 2215.1, 1695.7, 1536.8, 1522.5, 1504.6, 1348.3, 1132.8, 955.6, 828.2, 752.9, 685.0, 624.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (m, 1H), 7.68 (m, 2H), 7.59 (m, 2H), 7.56 (dt, J=8.1, 1.7 Hz, 2H), 7.42 (dt, J=8.2, 1.7 Hz, 2H), 7.37 (m, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 149.9, 135.7, 134.9, 134.7, 132.7, 132.5, 129.9, 129.7, 128.9, 128.1, 124.1, 123.6, 122.6, 118.8, 99.5, 93.1, 88.8, 85.2, 30.8. HRMS calcd for $C_{24}H_{15}NO_3S$: 397.0764. Found: 397.0773 (error=2.1 ppm).

7.5.30. 2-Nitro-4-trimethylsilanylethynyl-phenylamine (29). 4-Iodo-2-nitro-phenylamine (**18**) (6.26 g, 23.7 mmol) was coupled with TMSA (3.68 mL, 26.07 mmol) following the Pd/Cu protocol using bis(triphenylphosphine-palladium(II) dichloride (0.168 g, 0.24 mmol), copper(I) iodide (0.091 g, 0.48 mmol), THF (30 mL), and DIEA (12.4 mL, 71.1 mmol). The reaction mixture was stirred at ambient temperature for 3 h. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent; R_f=0.43) afforded the desired product as a red–orange solid (5.07 g, 91% yield): mp 106–107°C. IR (KBr) 3441.7, 3346.5,

2958.9, 2161.1, 2142.4, 1629.7, 1551.7, 1517.4, 1477.6, 1414.2, 1332.0, 1285.4, 1247.1, 1166.4, 936.8, 838.7, 757.2, 695.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J=2.0 Hz, 1H), 7.39 (dd, J=8.6, 1.9 Hz, 1H), 6.71 (d, J=8.5 Hz, 1H), 6.17 (br s, 2H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 138.9, 130.5, 119.1, 103.5, 94.0, 0.3. HRMS calcd for $C_{11}H_{14}N_2O_2Si$: 234.082457. Found: 234.082512 (error=0.23 ppm).

7.5.31. (4-Iodo-3-nitro-phenylethynyl)-trimethyl-silane (30). To a 500 mL round-bottom flask equipped with a stir bar, cooled to −20°C, was added $BF_3{\cdot}OEt_2$ (7.5 mL, 59.16 mmol). 2-Nitro-4-trimethylsilanylethynyl-phenylamine (**29**) (3.46 g, 14.79 mmol) in THF (70 mL) was then added over 25 min. Next, *t*-BuONO (6.16 mL, 51.77 mmol) in THF (25 mL) was added over 10 min. The mixture was allowed to warm to 0°C over 30 min. Next, 150 mL of ice-cold Et_2O were added to effect precipitation of the diazonium salt. The salt was filtered and washed with cold Et_2O to afford 4.25 g of solid. To a 500 mL round bottom flask was added acetonitrile (40 mL), sodium iodide (2.44 g, 16.27 mmol) and iodine (0.375 g, 1.48 mmol). The diazonium salt was then slowly added to this solution and stirred for 60 min. The solution was washed with $Na_2S_2O_3$ (aq) and extracted with CH_2Cl_2. Only a silica plug (with 1:1 hexanes/CH_2Cl_2; R_f=0.71) was required to obtain the desired compound as a red oil (3.84 g, 75% yield). IR (KBr) 3088.8, 2959.3, 2893.5, 2166.7, 1530.2, 1464.4, 1358.6, 1250.0, 1217.2, 1143.6, 1019.2, 930.8, 844.9, 760.6, 687.6, 652.3 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, 136.3, 128.8, 125.2, 101.7, 99.7, 86.3, 0.1. HRMS calcd for $C_{11}H_{12}INO_2Si$: 344.968203. Found: 344.968494 (error=0.84 ppm).

7.5.32. Trimethyl-(3-nitro-4-phenylethynyl-phenylethynyl)-silane (31). (4-Iodo-3-nitro-phenylethynyl)-trimethyl-silane (**30**) (3.80 g, 11.01 mmol) was coupled with phenylacetylene (1.26 mL, 11.45 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.155 g, 0.22 mmol), copper(I) iodide (0.084 g, 0.44 mmol), THF (20 mL), and DIEA (3.8 mL, 22 mmol). The tube was capped and stirred at ambient temperature for 1.5 h. Flash column chromatography (silica gel using 1:2 CH_2Cl_2/hexanes as eluent; R_f: 0.66) afforded the desired product (3.44 g, 98% yield). IR (KBr) 2958.1, 2904.1, 2210.7, 2156.5, 2141.0, 1607.6, 1524.2, 1499.4, 1353.2, 1248.3, 935.2, 847.4, 758.6, 688.6, 635.6, 528.7 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 1H), 7.61 (s, 2H), 7.57 (m, 2H), 7.37 (m, 3H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 136.0, 134.8, 132.5, 129.9, 128.9, 128.4, 124.3, 122.6, 118.8, 102.4, 99.9, 99.4, 85.1, 0.1. HRMS calcd for $C_{19}H_{17}NO_2Si$: 319.102858. Found: 319.102382 (error=1.5 ppm).

7.5.33. 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (27). Trimethyl-(3-nitro-4-phenylethynyl-phenylethynyl)-silane (**31**) (3.40 g, 10.64 mmol), potassium carbonate (5.9 g, 42.56 mmol), MeOH (40 mL), and CH_2Cl_2 (40 mL) were used following the general procedure for deprotection to afford the desired product (2.46 g, 94% yield) ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, J=1.0 Hz, 1H), 7.64 (d, J=1.1 Hz, 2H), 7.58 (m, 2H), 7.36 (m, 3H), 3.28 (s, 1H).

7.5.34. Thioacetic acid *S*-[4-(3-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (28). 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (**27**) (0.500 g, 2.02 mmol) was coupled with thioacetic acid *S*-(4-iodo-phenyl) ester (**7**) (0.562 g, 2.02 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone) palladium(0) (0.058 g, 0.101 mmol), copper(I) iodide (0.038 g, 0.202 mmol), triphenylphosphine (0.106 g, 0.404 g), DIEA (1.4 mL, 8.08 mmol), and THF (20 mL). After stirring at 45°C for 2 h, the reaction mixture was washed with NH_4Cl (aq) and diethyl ether. Column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent; R_f=0.36) afforded the desired compound as a yellow solid (0.588 g, 73% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (m, 1H), 7.68 (m, 2H), 7.57 (m, 4H), 7.42 (dt, J=8.4, 1.8 Hz, 2H), 7.37 (m, 3H), 2.43 (s, 3H).

7.5.35. *N*-[4-(3-Nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide (32). 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (**27**) (0.675 g, 2.73 mmol) was coupled with *N*-(4-iodo-phenyl)-formamide (**9**) (0.674 g, 2.73 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.038 g, 0.055 mmol), copper(I) iodide (0.021 g, 0.11 mmol), THF (20 mL), and DIEA (1.9 mL, 10.9 mmol). The reaction was stirred at room temperature for 1 h then placed in a 45°C oil bath for 2.5 h. Column chromatography (silica gel using ethyl acetate as eluent; R_f=0.73) afforded the desired product (0.890 g, 89% yield): mp 174–177°C. IR (KBr) 3242.1, 3155.0, 3091.5, 3057.8, 2212.0, 1685.4, 1664.9, 1590.1, 1532.9, 1410.2, 1343.2, 1306.8, 842.0, 754.4, 691.0, 529.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 0.38H), 8.95 (m, 0.18H), 8.42 (s, 0.87H), 8.25 (d, J=0.9 Hz, 1H), 7.92–7.85 (m, 2H), 7.77 (d, J=8.7 Hz, 1.8H), 7.68–7.59 (m, 4.3H), 7.55–7.45 (m, 3.15H), 7.36 (d, J=8.3 Hz, 0.45H). HRMS calcd for $C_{23}H_{14}N_2O_3$: 366.100442. Found: 366.099982 (error=1.3 ppm).

7.5.36. 4-(4-Isocyano-phenylethynyl)-2-nitro-1-phenylethynyl-benzene (33). To a large test tube was added *N*-[4-(3-nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide (**32**) (0.400 g, 1.09 mmol) and triphosgene (0.120 g, 0.404 mmol). Air was removed and N_2 backfilled (3×). The tube was cooled to 0°C and CH_2Cl_2 (20 mL) and triethylamine (7 mL) was added. A solution of tetrabutylammonium chloride (0.030 g, 0.109 mmol) in CH_2Cl_2 (10 mL) was then added. The reaction was allowed to slowly warm to room temperature over 4.5 h. Because starting material remained (by TLC), an additional 0.042 g of triphosgene was added. After 1 h (5.5 h total time), the reaction was complete (by TLC). The mixture was washed with water and CH_2Cl_2. Column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent; R_f=0.40) afforded the product (0.247 g, 65% yield): mp 164–166°C. IR (KBr) 3415.1, 3078.2, 2212.8, 2123.0, 1538.2, 1524.3, 1346.6, 839.8, 757.1, 686.7, 526.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (t, J=1.0 Hz, 1H), 7.69 (d, J=1.1 Hz, 2H), 7.57 (m, 4H), 7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 149.9, 135.7, 135.0, 133.2, 132.5, 130.0, 129.0, 128.2, 127.1, 123.9, 123.5, 122.5, 119.2, 99.9, 91.9, 89.8,

85.1. HRMS calcd for $C_{23}H_{12}N_2O_2$: 348.089878. Found: 348.089919 (error=0.12 ppm).

7.5.37. 2-Nitro-1,4-bis-trimethylsilanylethynyl-benzene (34). 2,5-Dibromonitrobenzene (3.05 g, 10.86 mmol), bis-(triphenylphosphine)palladium(II) dichloride (0.229 g, 0.326 mmol), copper(I) iodide (0.124 g, 0.651 mmol), THF (20 mL), triethylamine (9.1 mL, 65.16 mmol), and TMSA (4.6 mL, 32.58 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 40°C oil bath for 2 d. Flash column chromatography (silica gel using 2:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product (2.26 g, 66% yield): mp 78–80°C. IR (KBr) 3078.2, 2958.6, 2898.4, 2164.4, 1540.2, 1525.2, 1487.5, 1352.1, 1246.6, 1213.4, 1141.6, 845.7, 760.7, 702.4, 629.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 1H), 7.55 (m, 2H), 0.25 (d, J=0.4 Hz, 9H), 0.24 (d, J=0.3 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 135.8, 135.3, 128.1, 124.6, 118.3, 106.2, 102.3, 100.0, 99.5, 0.1, −0.1. HRMS calcd for C_{16},H_{21},N,O_2,Si_2: 315.1114. Found: 315.1111 (error=1.1 ppm).

7.5.38. 1,4-Diethynyl-2-nitro-benzene (35). 2-Nitro-1,4-bis-trimethylsilanylethynyl-benzene (**34**) (2.17 g, 6.88 mmol), potassium carbonate (9.5 g, 68.8 mmol), MeOH (25 mL), and CH_2Cl_2 (25 mL) were used following the general procedure for deprotection to give the desired product (1.17 g, 99%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (m, 1H), 7.63 (m, 2H), 3.58 (s, 1H), 3.29 (s, 1H).

7.5.39. Thioacetic acid *S*-{4-[4-(4-acetylsulfanyl-phenylethynyl)-2-nitro-phenylethynyl]-phenyl} ester (36). 1,4-Diethynyl-2-nitro-benzene (**35**) (1.79 g, 10.48 mmol) was coupled with 2 equiv. of thioacetic acid *S*-(4-iodo-phenyl) ester (**7**) (5.83 g, 20.96 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone) palladium(0) (0.301 g, 0.524 mmol), copper(I) iodide (0.199 g, 1.05 mmol), triphenylphosphine (0.551 g, 2.1 mmol), DIEA (10.9 mL, 62.88 mmol), and THF (20 mL). After stirring at 45°C for 1.5 h, the reaction mixture was washed with NH_4Cl (aq) and CH_2Cl_2. Column chromatography (silica gel using 1:3 hexanes/CH_2Cl_2 as eluent; R_f=0.49) afforded the desired compound as a yellow solid (2.445 g, 50% yield): mp 159–162°C (decomp.). IR (KBr) 3068.0, 2960.5, 2924.6, 2842.7, 2212.1, 1695.8, 1538.1, 1521.3, 1503.0, 1396.2, 1346.3, 1267.5, 1116.2, 1091.9, 1013.6, 956.2, 825.1, 759.8, 620.0, 549.7 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J=1.3 Hz, 1H), 7.69 (dd, J=8.1, 1.5 Hz, 1H), 7.67 (d, J=8.0 Hz, 1H), 7.60 (dt, J=8.4, 1.8 Hz, 2H), 7.56 (dt, J=8.3, 1.8 Hz, 2H), 7.42 (d, J=7.9 Hz, 4H), 2.430 (s, 3H), 2.427 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 193.5, 149.9, 135.8, 135.0, 134.7, 134.7, 133.0, 132.7, 130.0, 129.8, 128.2, 124.4, 123.7, 123.6, 118.4, 98.5, 93.3, 88.7, 86.6, 30.8. HRMS calcd for $C_{26}H_{17}NO_4S_2$: 471.059903. Found: 471.060194 (error=0.62 ppm).

7.5.40. *N*-{4-[4-(4-Formylamino-phenylethynyl)-2-nitro-phenylethynyl]-phenyl}-formamide (37). 1,4-Diethynyl-2-nitro-benzene (**35**) (1.09 g, 6.39 mmol) was coupled with 2 equiv. of *N*-(4-iodo-phenyl)-formamide (**9**) (3.47 g, 14.05 mmol) following the Pd/Cu protocol using bis-(dibenzylideneacetone) palladium(0) (0.073 g, 0.128 mmol), copper(I) iodide (0.049 g, 0.256 mmol), triphenylphosphine (0.084 g, 0.32 mmol), DIEA (4.5 mL, 25.6 mmol), and THF (30 mL). After stirring at 50°C for 3 h, the reaction mixture was washed with NH_4Cl (aq) and CH_2Cl_2. The insoluble product was filtered to afford the desired compound as a red–orange powder (2.08 g, 79% yield): mp 200–230°C (decomp.). IR (KBr) 2202.6, 1681.8, 1604.2, 1521.8, 1299.9, 831.2 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 8.92 (m, 0.4H), 8.29 (m, 2.5H), 7.86 (m, 2H), 7.70 (m, 3.3H), 7.57 (m, 4.3H), 7.30 (m, 1H), 7.22 (br s, 1.7H).

7.5.41. 1,4-Bis-(4-isocyano-phenylethynyl)-2-nitro-benzene (38). To a 500 mL round bottom flask was added *N*-{4-[4-(4-formylamino-phenylethynyl)-2-nitro-phenylethynyl]-phenyl}-formamide (**37**) (0.500 g, 1.22 mmol). Air was removed and N_2 backfilled (3×). CH_2Cl_2 (150 mL) and triethylamine (40 mL) were added and the tube was cooled to 0°C. Triphosgene (0.494 g, 1.83 mmol) was then added. After 2 h starting material remained (by TLC). An additional 0.494 g of triphosgene was added. After 3 h an additional 0.494 g of triphosgene was added. After 6 h (total time), the reaction was filtered to remove any starting material remaining. The solvents were then removed under reduced pressure. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.84) followed by precipitation from CH_2Cl_2/hexanes and a second silica column (CH_2Cl_2 as eluent) afforded the product as a yellow solid (0.193 g, 42% yield): mp 174–184°C (decomp.). IR (KBr) 2129.6, 1512.0, 1342.2, 841.3, 533.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J=1.1 Hz, 1H), 7.71 (dd, J=8.1, 1.5 Hz, 1H), 7.68 (dd, J=8.0, 0.3 Hz, 1H), 7.60 (dt, J=8.7, 2.0 Hz, 2H), 7.56 (dt, J=8.6, 2.0 Hz, 2H), 7.38 (d, J=8.4 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 150.0, 135.8, 135.0, 133.5, 133.3, 128.3, 127.1, 127.1, 124.4, 124.0, 123.8, 118.3, 97.5, 92.4, 89.6, 87.5. HRMS calcd for $C_{24}H_{11}N_3O_2$: 373.085127. Found: 373.085373 (error=0.66 ppm).

7.5.42. 1,4-Bis-(4-sulfanyl-phenylethynyl)-2-nitro-benzene (39). Thioacetic acid *S*-{4-[4-(4-acetylsulfanyl-phenylethynyl)-2-nitro-phenylethynyl]-phenyl} ester (**36**) (0.500 g, 1.06 mmol), CH_2Cl_2 (30 mL), MeOH (30 mL) and a stir bar were placed in a 200 mL round-bottom flask. Concentrated H_2SO_4 (5 drops) was then added and the flask was placed in a 50°C oil bath for 7 h. The reaction mixture was then washed with water and CH_2Cl_2. ^1H NMR showed a mixture of ~2:1 product to starting material. The reaction was re-subjected to the above conditions except 25 drops of acid were used. The reaction was again heated in a 50°C oil bath for 4.5 h. The workup was the same as before. Precipitation from CH_2Cl_2/hexanes afforded the desired product (0.315 g, 77% yield): mp 140–155°C (decomp.). IR (KBr) 2545.2, 2355.7, 2208.9, 1582.3, 1537.1, 1500.8, 1398.7, 1340.5, 1264.8, 1092.6, 820.4, 521.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (m, 1H), 7.64 (m, 2H), 7.43 (d, J=8.1 Hz, 2H), 7.38 (d, J=8.1 Hz, 2H), 7.24 (d, J=5.6 Hz, 4H), 3.545 (s, 1H), 3.539 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 135.6, 134.8, 134.2, 133.8, 133.0, 132.7, 129.3, 129.2, 128.0, 124.4, 119.6, 119.5, 118.4, 98.9, 93.6, 87.7, 85.8.

7.5.43. 4-(2-Nitro-4-phenylethynyl-phenylethynyl)-benzoic acid methyl ester (41). 4-Ethynylphenyl-2-nitro-1-iodobenzene (**20**) (4.0 g, 11.46 mmol), 4-ethynyl-benzoic

acid methyl ester (**40**)[22] (1.93 g, 12.03 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.160 g, 0.229 mmol), copper(I) iodide (0.087 g, 0.46 mmol), DIEA (4.0 mL, 22.9 mmol), and THF (15 mL) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 1 h. Normal workup using Et_2O instead of CH_2Cl_2 afforded the desired product with no need for further purification (4.37 g, 100% yield): mp 152–154°C (decomp.). IR (KBr) 3078.2, 2955.3, 2217.9, 1716.5, 1602.4, 1540.2, 1434.0, 1357.7, 1278.5, 1105.5, 1015.5, 833.8, 757.3, 688.4, 517.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J=1.5, 0.4 Hz, 1H), 8.03 (dt, J=8.6, 1.7 Hz, 2H), 7.70 (dd, J=8.1, 1.5 Hz, 1H), 7.66 (d, J=7.9 Hz, 1H), 7.63 (dt, J=8.6, 1.7 Hz, 2H), 7.54 (m, 2H), 7.37 (m, 3H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 149.9, 135.8, 135.0, 132.4, 132.2, 130.9, 130.0, 129.7, 129.0, 128.1, 127.2, 125.1, 122.4, 117.8, 98.0, 94.4, 87.8, 87.2, 52.7. HRMS calcd for $C_{24}H_{15}NO_4$: 381.100108. Found: 381.099938 (error=0.45 ppm).

7.5.44. 4-(2-Nitro-4-phenylethynyl-phenylethynyl)-benzoic acid (42). 4-(2-Nitro-4-phenylethynyl-phenylethynyl)-benzoic acid methyl ester (**41**) (2.0 g, 5.24 mmol), lithium hydroxide monohydrate (1.1 g, 26.2 mmol), MeOH (130 mL), water (45 mL), CH_2Cl_2 (100 mL), and THF (60 mL) were added to a 500 mL round bottom flask and stirred at ambient temperature for 2 d. The suspension was poured into water and the pH adjusted to 4 with 3N HCl. Hexanes were added to ensure precipitation of all organic components and the solid was filtered to afford the desired product as a yellow solid (1.66 g, 86% yield): mp 234–250°C (decomp.). IR (KBr) 2817.1, 2653.2, 2530.3, 2207.7, 1683.5, 1601.5, 1541.6, 1521.9, 1421.3, 1340.6, 1314.0, 1293.0, 840.4, 758.6, 692.0 cm^{-1}. ^1H NMR (400 MHz, DMSO) δ 8.34 (m, 1H), 8.02 (m, 2H), 7.96 (dd, J=8.1, 1.5 Hz, 1H), 7.93 (d, J=8.0 Hz, 1H), 7.71 (m, 2H), 7.64 (m, 2H), 7.48 (m, 3H). ^{13}C NMR (125 MHz, DMSO) δ 167.5, 150.2, 136.7, 135.9, 132.8, 132.6, 132.4, 130.6, 129.8, 128.3, 126.4, 124.7, 122.1, 117.1, 97.8, 94.5, 87.8, 87.7. HRMS calcd for $C_{23}H_{13}NO_4$: 367.084458. Found: 367.084044 (error=1.1 ppm).

7.5.45. Thioacetic acid *S*-[4-(3-oxo-1-oxy-6-phenylethynyl-3*H*-indol-2-yl)-phenyl] ester (43). To a 10 mL round bottom flask was added thioacetic acid *S*-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (**17**) (0.100 g, 0.25 mmol). Air was removed and N_2 backfilled (3×). THF (5 mL) was added followed by TBAF (1 drop of a 1.0 M solution). The solution was stirred for 15 min at room temperature before 3N HCl (~1 mL) was added. The product was extracted with CH_2Cl_2. Column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes; R_f=0.48) afforded the product as a bright orange solid (0.073 g, 73% yield): mp 202–205°C. IR (KBr) 3093.6, 3047.5, 2212.8, 1714.3, 1699.8, 1634.1, 1588.9, 1517.0, 1380.5, 1181.0, 1126.0, 835.6, 743.1, 692.0, 630.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (dt, J=8.8, 1.9 Hz, 2H), 7.80 (m, 1H), 7.67 (dd, J=7.5, 1.2 Hz, 1H), 7.61 (m, 1H), 7.55 (m, 4H), 7.38 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 186.2, 148.3, 134.8, 134.6, 132.3, 131.5, 131.0, 129.8, 129.0, 128.6, 127.0, 122.4, 122.2, 122.1, 117.5, 95.3, 88.4, 53.8, 30.8. HRMS calcd for $C_{24}H_{15}NO_3S$: 397.077266. Found: 397.076587 (error=1.7 ppm).

7.5.46. 1-Oxy-2-phenyl-6-phenylethynyl-indol-3-one (44). 2-Nitro-1,4-bis-phenylethynyl-benzene (**26**) (0.100 g, 0.31 mmol) and pyridine (6 mL) were placed in a 25 mL round bottom flask. The solution was heated to reflux for 24 h. Hexanes were added and the solvents removed. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.84) afforded the product as an orange solid (0.081 g, 81% yield): mp 159–170°C. IR (KBr) 3057.8, 2212.8, 1717.2, 1525.3, 1384.2, 1314.0, 887.1, 838.8, 779.5, 751.8, 686.2, 500.6 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (m, 2H), 7.79 (m, 1H), 7.66 (dd, J=7.5, 1.2 Hz, 1H), 7.60 (d, J=7.6 Hz, 1H), 7.56 (m, 2H), 7.49 (m, 3H), 7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 148.3, 134.6, 133.3, 132.3, 131.4, 130.8, 129.8, 129.0, 129.0, 128.3, 126.2, 122.5, 122.2, 122.0, 117.4, 95.1, 88.5. HRMS calcd for $C_{22}H_{13}NO_2$: 323.094629. Found: 323.094450 (error=0.55 ppm).

7.5.47. 5-Bromo-2-(trimethylsilylethynyl)pyridine (46). To a large screw cap tube equipped with a stir bar was added 2,5-dibromopyridine (**45**) (2.37 g, 10.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.35 g, 0.50 mmol), copper(I) iodide (0.19 g, 1.0 mmol) and triphenylphosphine (0.52 g, 2.0 mmol). The atmosphere was replaced with nitrogen and THF (40 mL), triethylamine (4.35 mL, 40.0 mmol), THF (10 mL), and TMSA (1.4 mL, 10 mmol) were added. The reaction mixture turned dark brown in color as the reaction was heated at 65°C for 2 d. The reaction was subjected to the aqueous work up procedure listed above. The reaction afforded 2.25 g of an inseparable mixture of product and starting material. NMR showed the mixture to be 54% product. ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, J=2.4, 0.73 Hz, 1H), 7.76 (dd, J=8.4, 2.4 Hz, 1H), 7.32 (dd, J=8.2, 0.73 Hz, 1H).

7.5.48. 2-(Phenylethynyl)-5-(trimethylsilylethynyl)pyridine (47). To a 250 mL round bottom flask equipped with a stir bar were added **46** (2.25 g, 9.50 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.53 g, 0.76 mmol), copper(I) iodide (0.29 g, 1.5 mmol) and triphenylphosphine (0.80 g, 3.0 mmol). The atmosphere was evacuated and replaced with nitrogen and THF (50 mL), triethylamine (4.13 mL, 38.0 mmol), and phenylacetylene (3.13 mL, 28.5 mmol) were added. The reaction was heated to reflux and maintained for 2 d. The triethylamine salts that formed during the reaction were filtered off and the reaction was washed with aqueous ammonium chloride (3×). The remaining solvent was removed in vacuo to yield 272 mg (19%) of desired product over 2 steps: mp 98–100°C. IR (KBr) 2959.5, 2157.9, 1492.3, 1463.6, 1384.0, 1247.7, 1019.9, 844.4, 754.8, 690.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J=1.3 Hz, 1H), 7.74 (dd, J=6.0, 2.6 Hz, 1H), 7.53 (m, 2H), 7.43 (d, J=8.0 Hz, 1H), 7.36 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 141.5, 138.4, 131.7, 131.6, 131.5, 129.4, 129.3, 129.0, 128.5, 128.3, 128.2, 128.1, 127.9, 126.6, 122.3, 119.8, 103.5, 97.0, 94.5, 85.9, −0.1. HRMS calcd for $C_{19}H_{17}NSi$: 275.1130. Found: 275.1126.

7.5.49. 2-(Phenylethynyl)-5-(ethynyl)pyridine (48). To a 100 mL round bottom flask equipped with a magnetic stir

bar was added solid 2-(phenylethynyl)-5-(trimethylsilylethynyl)pyridine (**47**) (272 mg, 1.00 mmol), and potassium carbonate (690 mg, 5.00 mmol). The atmosphere was removed and replaced with nitrogen (3×) and MeOH (30 mL), and CH_2Cl_2 (30 mL) were added. The reaction was allowed to heat for 2.5 h at which time the reaction was diluted with CH_2Cl_2 and extracted with deionized water (3×) and dried over magnesium sulfate, filtered and the solvent removed in vacuo to produce desired product in quantitative yield. The product was used as soon as it was isolated without identification or purification.

7.5.50. 2-(Phenylethynyl)-5-(1-thioacetyl(phenylethynyl))pyridine (49). To a small screw cap tube equipped with a stir bar was added 2-(phenylethynyl)-5-(ethynyl)-pyridine (**48**) (0.167 g, 1.00 mmol), 1-thioacetyliodobenzene (**7**) (0.334 g, 1.20 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.050 mmol), copper(I) iodide (0.019 g, 0.10 mmol) and triphenylphosphine (0.026 g, 0.10 mmol). The atmosphere was replaced with nitrogen and THF (30 mL), and DIEA (0.70 mL, 4.0 mmol) were added. The reaction was heated at 50°C for 2 d. The reaction was subjected to the aqueous work up procedure listed above. Column chromatography eluting with 3:1 CH_2Cl_2/hexanes to yield 199 mg (56%) of a brown solid: mp 140–150°C (decomp.). IR (KBr) 3050.6, 2924.3, 2213.8, 1703.1, 1571.6, 1536.1, 1512.3, 1493.2, 1460.2, 1397.5, 1359.4, 1221.8, 1156.0, 1124.5, 1107.1, 1081.3, 1013.3, 942.6, 846.8, 824.6, 753.9, 687.5, 618.3, 523.1, 449.7 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (br s, 1H), 7.80 (dd, J=2.0, 8.1 Hz, 1H), 7.62 (1/2ABq, J=8.5 Hz, 2H), 7.54 (m, 3H), 7.41 (1/2ABq, J=8.1 Hz, 2H), 7.37 (m, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 193.1, 152.5, 141.6, 138.4, 134.2, 132.6, 131.7, 129.2, 129.0, 128.5, 126.6, 123.2, 122.3, 119.7, 94.5, 90.2, 90.0, 85.9, 30.3. HRMS $C_{23}H_{16}NOS$ calcd: 353.0870. Found: 353.0874.

7.5.51. Chlorobenzenetricarbonylchromium(0) (51).[26] Chlorobenzene (**50**) (10.0 mL, 97.7 mmol), chromium(0) hexacarbonyl (2.00 g, 9.09 mmol), and *n*-butyl ether (45 mL) were added to a round bottom flask equipped with a condenser and a stir bar and the contents of the flask were frozen with liquid nitrogen and the atmosphere was removed and replaced with nitrogen (3×). THF (5 mL) was added and the reaction mixture was allowed to reflux for 22 h. The reaction was then poured onto ice (~200 mL) and filtered through a pad of SiO_2. The SiO_2 was washed with hexanes (50 mL). The solvents were removed in vacuo to yield 0.854 g of a bright yellow solid (38%). IR (KBr) 3100.6, 1960.1, 1872.8, 1530.7, 1497.9, 1470.4, 1442.6, 1405.2, 1252.8, 1146.7, 1083.0, 1012.9, 992.3, 815.0, 703.3, 661.7, 627.0, 541.3, 479.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.41 (br s, 4H), 5.04 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 231.9, 93.4, 91.4, 88.3.

7.5.52. Trimethylsilylethynylbenzenetricarbonylchromium(0) (52). Chlorobenzenetricarbonylchromium(0) (**51**) (294 mg, 1.18 mmol), trimethylsilyl acetylene (0.22 mL, 1.54 mmol), bis(triphenylphosphine)palladium dichloride (42 mg, 0.06 mmol), copper(I) iodide (11 mg, 0.06 mmol), Triethylamine (5 mL), and THF (10 mL) were coupled according to the general coupling procedure. The reaction was heated to 50°C while stirring overnight and worked up as above. The crude product was purified via flash column chromatography (1:1 CH_2Cl_2/hexanes) to yield 250 mg of desired product (68%). IR (KBr) 3446.3, 3077.8, 2959.2, 2170.4, 1959.9, 1889.2, 1521.2, 1455.3, 1406.8, 1287.7, 1250.1, 1213.6, 1150.2, 995.11, 844.8, 817.9, 760.0, 701.7, 675.3, 655.1, 619.4, 538.4, 523.8, 473.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 (d, J=6.4 Hz, 2H), 5.29 (t, J=6.4 Hz, 2H), 5.19 (t, J=6.4 Hz, 1H), 0.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.4, 100.9, 96.1, 95.2, 91.9, 90.7, 90.6, 0.1.

7.5.53. Ethynylbenzenetricarbonylchromium(0) (53). Trimethylsilylethynylbenzenetricarbonylchromium(0) (**52**) (0.24 g, 0.77 mmol), potassium carbonate (621 mg, 4.50 mmol), MeOH (20 mL) and CH_2Cl_2 (20 mL) were reacted and worked up according to the general deprotection procedure to yield 0.15 g of desired product (82%) The product was used directly in the next synthetic step. ^1H NMR (400 MHz, $CDCl_3$) δ 5.45 (br s, 2H), 5.28 (br d, J=5.6 Hz, 3H), 2.92 (s, 1H).

7.5.54. 4′-Thioacetylphenylethynlbenzenetricarbonylchromium(0) (54). Ethynylbenzenetricarbonylchromium(0) (**53**) (0.15 g, 0.63 mmol), 4-iodo(thioacetyl)benzene (**7**) (0.21 g, 0.77 mmol), bis(triphenylphosphine)palladium dichloride (0.03 g, 0.04 mmol), copper(I) iodide (8 mg, 0.04 mmol), triethylamine (5 mL) and THF (10 mL) were coupled according to the general procedure. The reaction mixture was heated at 50°C overnight and worked up according to the general procedure. The crude product was purified via flash column chromatography to yield 0.14 g of a yellow solid (57%): mp 102–110°C (decomp.). IR (KBr) 3422.0, 3085.4, 1962.5, 1881.3, 1701.5, 1525.1, 1486.7, 1453.0, 1397.6, 1353.4, 1114.0, 1089.4, 1014.7, 951.3, 833.4, 654.7, 622.7, 533.8, 478.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J=8.4 Hz, 2H), 7.38 (d, J=8.4 Hz, 2H), 5.51 (d, J=6.4 Hz, 2H), 5.34 (t, J=6.4 Hz, 2H), 5.25 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.4, 193.6, 134.6, 132.9, 129.5, 123.4, 95.2, 91.8, 91.1, 90.2, 30.7.

7.5.55. 1,5-Dibromo-2,4-diiodo-benzene (55).[37] Into a 500 mL round bottom flask, was added a solution of 1-3-dibromobenzene (5 g, 21.2 mmol) in conc. sulfuric acid (150 mL). The solution was heated to 90°C and iodine (22 g, 85 mmol) was added in small portions over 30 min. The dark solution was left under reaction at 115°C for 12 h. The reaction mixture was then poured into ice water, and the dark precipitate filtered and dissolved in hot benzene. The dark purple solution was washed with aq. $NaHSO_3$ (800 mL), water (500 mL) and brine (300 mL) before being dried over $MgSO_4$ and solvent removed in vacuo. The light yellow solid was recrystallized from benzene to afford a white solid (4.5 g, 47%) as the desired product. ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.84 (m, 1H).

7.5.56. 1,5-Dibromo-2,4-bis-phenylethynyl-benzene (56). Following the general Pd/Cu procedure, **55** (5.85 g, 9.95 mmol) was dissolved in THF (40 mL), adding $PdCl_2((C_6H_5)_3P)_2$ (280 mg, 4 mol%). CuI (152 mg, 8 mol%) was then added, followed by addition of TEA (11 mL, 8 equiv.) and phenylacetylene (2.24 mL, 2.05 equiv.). After 14 h, the reaction was quenched with ether and, after aqueous work up, a white solid was isolated

(3.23 g, 75%) as the desired product: mp 112°C. IR (KBr) 2957.62, 2924.73, 2214.18, 2157.51, 1947.95, 1634.64, 1487.54, 1487.54, 1445.51, 1374.28, 1278.71, 1248.09, 1124.85, 1057.01 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.74 (s, 1H), 7.59 (m, 4H), 7.38 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 135.9, 132.0, 129.2, 128.7, 125.5, 125.0, 122.6, 95.5, 86.8 ppm. HRMS calcd for $C_{22}H_{12}Br_2$: 433.930596. Found: 433.930331 (error=0.21 ppm).

7.5.57. (3-Bromo-phenylethynyl)-trimethyl-silane (57). Following the general Pd/Cu procedure, 1,3-dibromobenzene (5 g, 21.2 mmol) was dissolved in THF (40 mL), adding $PdCl_2((C_6H_5)_3P)_2$ (298 mg, 2 mol%), CuI (161 mg, 4 mol%), followed by addition of TEA (11.8 mL, 85 mmol) and TMSA (3.14 mL, 22.25 mmol). After stirring for 12 h at 75°C, the reaction was quenched with ether and followed by standard work up. Flash chromatography purification (hexanes as eluent), gave a clear liquid (4.61 g, 47%) as the desired product. IR (KBr) 3058.99, 2959.08, 2897.58, 2160.51, 1582.07, 1551.74, 1466.60, 1400.62, 1296.03, 1251.05, 1218.74, 1061.82 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dt, J=1.6, 0.4 Hz, 1H), 7.44 (dm, J=1.6 Hz, 1H), 7.38 (dq, J=1.6, 0.4 Hz, 1H), 7.17 (dt, J=8.0, 0.4 Hz, 1H), 0.26 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 131.8, 130.6, 129.8, 125.3, 122.2, 103.5, 96.0, 0.1 ppm. HRMS calcd for $C_{11}H_{13}BrSi$: 251.997301. Found: 251.997002 (error=1.2 ppm).

7.5.58. Trimethyl-(3-tributylstannanyl-phenylethynyl)-silane (58). Into a 500 mL N_2 purged round bottom flask equipped with an addition funnel was added **57** (18.85 g, 75 mmol) and THF (100 mL), followed by cooling to −78°C. *t*-BuLi (92 mL, 153 mmol) was added dropwise and left to react for 1 h. To the dark purple solution was added Bu_3SnCl (21.2 mL, 78 mmol) dropwise, and stirred for another 1 h before letting it warm to room temperature. The reaction mixture was quenched with water and washed with brine, followed by extractions with ether and drying over $MgSO_4$. After filtration and removal of solvent, a clear light liquid remained, which was distilled and flashed twice (silica gel using hexanes as eluent) in order to afford a clear liquid (22 g, 76%) as the desired product. IR (KBr) 2957.85, 2925.14, 2850.88, 2158.34, 1462.18, 1379.89, 1250.79, 1072.66 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 1H), 7.43 (m, 2H), 7.28 (m, 1H), 1.57 (m, J=8 Hz, 6H), 1.10 (m, J=8 Hz, 6H), 0.93 (t, J=8 Hz, 9H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.8, 136.6, 131.8, 127.7, 122.9, 106.0, 94.1, 29.3, 27.6, 13.9, 9.8, 0.3. HRMS calcd for $C_{23}H_{40}SiSn$: 464.193257. Found: 464.192494 (error=1.6 ppm).

7.5.59. 1,3-Bis-[(3′-trimethylsilyl-ethynyl)phenyl]-4,6-bis-phenylethynyl-benzene (59). Following the general Stille coupling procedure, CsF (35 mg, 2 equiv.), **56** (100 mg, 2.3 mmol), $Pd(dba)_2$ (27 mg, 20 mol%) and $AsPh_3$ (28 mg, 40 mol%) were submitted to reaction after **58** (218 mg, 0.6 mmol) was dissolved in THF (2 mL) and transferred via cannula. After the reaction mixture was stirred at 75°C for 20 h, it was allowed to cool to room temperature and diluted with CH_2Cl_2 before removing the solvents in vacuo. The crude material was purified via flash chromatography twice (7:1 hexanes/CH_2Cl_2 eluent), yielding a light brown oil (60 mg) as the desired product: mp 95°C. IR (KBr) 3057.71, 2956.99, 2924.55, 2157.05, 1596.42, 1491.05, 1467.25, 1444.81, 1382.30, 1249.20, 1071.21 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, 1H), 7.92 (m, 1H), 7.68 (m, 1H), 7.66 (m, 1H), 7.52 (m, 2H), 7.43 (m, 5H), 7.33 (m, 6H), 0.27 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 139.9, 137.3, 133.1, 131.7, 131.5, 130.4, 129.7, 128.6, 128.5, 128.2, 123.3, 123.2, 121.1, 105.2, 94.7, 93.8, 88.3, 0.2. HRMS calcd for $C_{44}H_{38}Si_2$: 622.251209. Found: 622.250499 (error=1.1 ppm).

7.5.60. 1,3-Bis-(3′-ethynyl)phenyl-4,6-bis-phenylethynyl-benzene (60). Into a 50 mL round bottom flask was added **59** (270 mg, 0.4 mmol), which was dissolved in CH_2Cl_2 (3 mL). K_2CO_3 (180 mg, 1.3 mmol) was added, followed by MeOH (3 mL). After 30 min, a white solid began precipitating from the dark solution. After 1 h TLC showed no more starting material. After quenching with water and extracting with CH_2Cl_2, the organic layer was dried over $MgSO_4$ and solvents removed. The brown solid was dissolved in THF and precipitated with hexanes to isolate a light yellow solid (125 mg, 70%) as the desired product: mp decomposed at 170°C. IR (KBr) 3282.81, 2850.91, 2094.55, 1905.45, 1607.27, 1522.06, 1479.38, 1274.20, 1105.45 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.93 (m, 2H), 7.72 (m, 2H), 7.56 (m, 2H), 7.51 (s, 1H), 7.47 (1H), 7.44 (m, 5H), 7.33 (m, 6H), 3.13 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.0, 137.4, 133.2, 131.7, 131.7, 130.5, 130.0, 128.7, 128.5, 128.3, 123.2, 122.2, 121.2, 93.9, 88.2, 83.7, 77.3. HRMS calcd for $C_{38}H_{22}$: 478.172667. Found: 478.172151 (error=1.1 ppm).

7.5.61. 1,3-Bis-[(3′-(4″-thioacetyl)phenylethynyl)phenyl]-4,6-bis-phenylethynyl-benzene (61). Following the general Pd/Cu procedure, **60** (125 mg, 0.26 mmol) was dissolved in THF (2 mL), adding $PdCl_2((C_6H_5)_3P)_2$ (37 mg, 20 mol%), CuI (20 mg, 40 mol%), followed by addition of Hünig's base (0.31 mL, 2.1 mmol) and 4-iodo-thioacetylbenzene (**7**) (152 mg, 2.1 equiv.). After stirring for 12 h at 75°C, the reaction was quenched with EtOAc and normal work-up to afford a light yellow solid (50 mg, 25%) as the desired product: mp decomposed at 162°C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 2H), 7.99 (s, 1H), 7.73 (m, 2H), 7.58 (m, 7H), 7.47 (m, 6H), 7.42 (m, 4H), 7.30 (m, 6H), 2.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 142.7, 140.0, 137.4, 134.4, 132.8, 132.4, 132.4, 131.7, 131.2, 130.5, 129.7, 128.7, 128.6, 128.4, 128.3, 124.6, 123.2, 122.9, 121.2, 93.9, 91.2, 89.2, 88.3, 30.5. HRMS calcd for $C_{54}H_{34}O_2S_2$: 778.200495. Found: 778.200026 (error=0.60 ppm).

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