RICE UNIVERSITY

Advances in Molecular Electronics:
Synthesis and Testing of Potential Molecular Electronic Devices

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
Doctor of Philosophy

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HOUSTON, TEXAS

OCTOBER, 2002
For Heather, Mom and Dad
OCTOBER, 2002

ABSTRACT

Advances in Molecular Electronics:

Synthesis and Testing of Potential Molecular Electronic Devices

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New potential molecular electronics devices have been synthesized based on our knowledge of previous systems that have come out of our group. Previous studies and current studies have shown that simple molecular systems demonstrate negative differential resistance (NDR) and memory characteristics. The new systems rely primarily on the redox properties of the compounds to improve upon the solid state properties already observed. Most of these new organic compounds use thiol-based “alligator clips” for attachment to metal surfaces. Some of the compounds, however, contain different “alligator clips,” primarily isonitriles, for attachment to metal substrates. It is our hope that these new “alligator clips” will offer lower conductivity barriers (higher current density). Electrochemical tests have been performed in order to evaluate those redox properties and in the hope of using those electrochemical results as a predictive tool to evaluate the usefulness of those compounds. Also, organic structures with polymerizable functionalities have been synthesized in order to cross-link the molecules once they are a part of a self-assembled monolayer (SAM). This has been shown to enable the electrochemical growth of polypyrrole from a SAM in a controllable manner.
Acknowledgements

I’ve decided to write these acknowledgements following the timeline of my existence. This is to insure that there appears to be no order of importance placed on anyone in particular and that no one’s feelings are hurt as a result thereof. Therefore, without further delay:

First, I wish to thank my parents, David Sr. and Joyce, for bringing me into this world. I thank them for all the encouragement they gave to me growing up and for not pressuring me into doing things I didn’t want to do. They allowed me to make my own decisions and follow my own paths. Along the same lines, I would like to thank my only sister, Hope, for giving me just the right balance between kindness and cruelty (as would any sibling). It was this balance that enabled me to toughen up without being grizzled.

Second, I would like to thank all my former teachers and mentors from public schools on through my undergraduate institution, Appalachian State University. In particular are Claire Olander, my undergraduate advisor, for guiding me through my time at ASU, Claudia Cartaya, my research advisor, for giving me the opportunity to play and learn some things at the same time (my undergraduate research was the beginning of “Microwave Dave”). Also, Ann Holder, for giving me the opportunity to get to know her and all the faculty and staff at ASU while also learning some things in the chemistry stockroom.

Third, I have to thank my dear wife, Heather. Without her, I would not have had the desire or endurance for graduate school. She has always encouraged and supported me in whatever decisions I needed to make. She pushed me to go to graduate school and she encouraged me to make the move from South Carolina to follow Jim Tour to Rice University. I have regretted none of the choices that I have made with her advice and
unending support. She has pushed me to do more than I thought I could ever do. She is my everything.

Next, I would like to thank my research advisor, Professor James Tour, for his encouragement and support throughout my graduate school years. I want to thank him for teaching me to understand what questions to ask and what answers to have. I also thank him for showing me what a good salesman can do. I always said he must have a little of P.T. Barnum in him. I also wish to thank Professor Robert Curl and Dr. Michael Wong for taking the time and putting forth the effort to be members of my PhD committee.

I also wish to thank all my friends, past and present, from whom I've learned much about life, love, happiness, and some useful stuff. I do not wish to list any of them by name for fear of generating an incredibly long list and of possibly forgetting someone very important. You all know who you are. If you are in doubt, then you must not have been a good friend; I hope all my friends know they are my friends and will continue to be.
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<td>Day(s); Doublet (spectral)</td>
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<td>HF</td>
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<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<td>I(V)</td>
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<td>LRMS</td>
<td>Low-Resolution Mass Spectrum</td>
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<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<tr>
<td>μ</td>
<td>Micro</td>
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<td>m</td>
<td>Multiplet (spectral), Meter(s), Milli</td>
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<tr>
<td>M</td>
<td>Moles per Liter Methyl Methanol</td>
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<td>MgSO₄</td>
<td>Magnesium sulfate</td>
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<td>MP</td>
<td>Melting Point</td>
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<td>mRAM</td>
<td>Single Molecular Random Access Memory</td>
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<td>MS</td>
<td>Mass Spectrometry</td>
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<td>MW</td>
<td>Molecular Weight</td>
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<td>NDR</td>
<td>Negative Differential Resistance</td>
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<tr>
<td>nm</td>
<td>Nanometer</td>
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<td>NMR</td>
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<td>Ohm</td>
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<td>p</td>
<td>Pico, pentet (in NMR)</td>
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<td>Acronym</td>
<td>Description</td>
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<tr>
<td>PPh₃</td>
<td>Triphenylphosphine</td>
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<td>Ppm</td>
<td>Parts per Million (in NMR)</td>
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<td>PVR</td>
<td>Peak to Valley Ratio</td>
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<td>Quartet (spectral)</td>
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<td>Q</td>
<td>Charge</td>
</tr>
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<td>RAM</td>
<td>Random Access Memory</td>
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<td>RIE</td>
<td>Reactive Ion Etching</td>
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<td>Rf</td>
<td>Retention Factor (in chromatography)</td>
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<td>Room Temperature</td>
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<tr>
<td>σ</td>
<td>Conductive State</td>
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<tr>
<td>s</td>
<td>Singlet (NMR); Second(s)</td>
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<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
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<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SET</td>
<td>Single Electron Transistor</td>
</tr>
<tr>
<td>SiCl₃</td>
<td>Trichlorosilane</td>
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<tr>
<td>SRAM</td>
<td>Static Random Access Memory</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>τ</td>
<td>Time Constant</td>
</tr>
<tr>
<td>t</td>
<td>Triplet (spectra)</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium Floride</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>TMS</td>
<td>Trimethylsilyl, Tetramethysilane</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>V</td>
<td>Volt</td>
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<tr>
<td>Vis</td>
<td>Visible</td>
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<td>w</td>
<td>Weight</td>
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Preface

(Summary of Research)

Advances in Molecular Electronics:

Synthesis and Testing of Potential Molecular Electronic Devices

By

David Wilson Price, Jr.

Chapter 1 discusses the design, purpose, and syntheses (and some testing) of conjugated organic molecules for potential use as molecular electronics devices. Since certain compounds with nitro groups have demonstrated negative differential resistance (NDR) when incorporated into a solid-state device or testbed, the quest for molecular electronics components has intensified. The compounds in this chapter were designed based on the limited knowledge we had from testing, as well as chemical intuition. All the compounds described here have thiol-based moieties ("alligator clips") incorporated for attachment to metal surfaces.

Chapter 2 discusses the syntheses of the same basic organic molecules shown in Chapter 1, except these compounds have different "alligator clips" for attachment to metal surfaces. These various moieties, such as isonitriles, are intended to be able to bond to surfaces that perhaps thiol-based structures cannot. Also, the new alligator clips may provide lower conduction barriers, therefore providing for higher current densities from solid-state devices.

Chapter 3 describes the electrochemical testing of the aforementioned organic molecules. The wet electrochemical testing was performed as part of a study and theory
formation of how these molecules behave as switches and memory elements. It has been reasoned that the molecules are being reduced in the solid state when a voltage is applied to the system, giving rise to different conductive states. Based on this, cyclic voltammetry was used as a tool to probe and understand the redox activities of these potential molecular electronics devices.

Chapter 4 describes the synthesis and application of conjugated organic compounds that contain polymerizable functionalities. The goal is to allow the compounds to self-assemble onto a surface and then polymerize the monolayer that is formed. This should enable one to make a more robust monolayer that cannot be easily removed. Also, the monolayer should have less freedom to move, part of the goal being to create a monolayer that one can evaporate metal onto without the metal penetrating the monolayer. This is something highly desirable for the testing of molecular electronics devices.

Chapter 5 shows the synthesis of a conjugated organic molecule for the purpose of modifying the Schottky barriers in organic light-emitting diodes (OLEDs). The goal is to create more efficient OLEDs by tailoring the interfaces between organic polymers and the metals used in OLEDs. The compound described could be used for that purpose.
Chapter 1

Synthesis and Testing of Functionalized Phenylene Ethynlenes for potential use as Devices in a Molecular Computer
Introduction

Molecular electronics is currently a topic of considerable interest among a diverse community of scientists and engineers. In fact, Science magazine recently declared the field of molecular electronics the “breakthrough of the year.”¹ Computers have become so much a part of everyone’s life that computer manufacturers are spending trillions of dollars to improve and further miniaturize the components of those computers to compete with each other. The problem, however, lies in the fact that the methods currently used to make the microchips can only be commercially scaled down to 0.13 microns and ultimately to only about 0.03 microns.² Experts at Intel® estimate that the silicon roadmap, the future of silicon transistors, will reach its limit in 10-15 years. If electronics and computer components are to continue decreasing in size beyond the 30 nanometer limit, new technologies must be explored or invented.

Using scanning tunneling microscopy (STM), it has been shown that an electron can tunnel from the STM tip, through a phenylene ethynylene molecule, and into a gold surface.³ Molecular scale devices seem to be a logical approach to reduce the size of current electronic devices. A typical organic “molecular wire” is only about 2 nm long (20 Å) compared to the ultimate 30 nm limit (300 Å) for current devices. Current personal computers utilize devices, such as Intel’s® Pentium 4® processors, that contain approximately $10^7$ transistors per cm². Self-assembled monolayers (SAMs) of molecular scale wires can achieve ordering of approximately $10^{14}$ molecules/cm², a full seven orders of magnitude greater than presently available. Also, one can manufacture 1 mole of these molecular wires or molecular devices in a flask, which amounts to $6 \times 10^{23}$ devices. Also, these molecular devices can be made inexpensively and self-assembled
easily onto various surfaces. These impressive facts give hope that molecular scale electronics will be the next technological step in the computer industry.

There have been other methods to test the conductivity of organic molecules as well. Reed and coworkers at Yale University devised a method in which they could test the conductivity of a single molecular scale wire. They found that they could form a self-assembled monolayer on a thin, notched gold wire with the desired molecular scale wires and then stretch the wire until it broke. When they brought the two newly formed tips back together only one molecule made contact between both gold tips and conductivity was subsequently measured. SAMs have been made with different organic compounds and have been studied extensively.

Reed and coworkers then devised an additional method to measure the conductivity of organic molecular scale wires using what they call “nanopores”. The nanopore is manufactured by subjecting a Si$_3$N$_4$-Si-Si$_3$N$_4$ layered wafer to e-beam lithography and plasma etching techniques.

This process generates a small hole in the upper surface of the wafer measuring approximately 30 nm. Gold is then vapor deposited from the bottom side to fill the pore. This gives a gold surface roughly 50 nm across. It is this controlled size gold surface that then allows a small amount of the organic molecules to form the SAM. A thin layer of gold is then deposited on top of the SAM. The two gold surfaces then make up the electrodes used for testing by applying both forward and reverse biases.

Many molecular wires have been synthesized for use as molecular devices, including switches, wires, controllers, and gates. The NDR (Negative Differential Resistance) effect was discovered when a molecular wire that was synthesized for testing
as a switch in an applied field was instead tested for its electrical conductivity in a nanopore device. Figure 1 depicts the configuration of a nanopore device as constructed in Mark Reed’s lab at Yale University. The advantage of this configuration is that it is inherently sealed and protected from atmospheric impurities. Devices constructed in this manner have been shown to have long-term stability of at least one year.

**Figure 1.** Schematic of a nanopore device. The top portion of the figure shows a silicon based wafer possessing a pore approximately 30 -50nm wide. Gold is vapor-deposited from the top of the wafer which fills the pore (middle portion of figure). A self-assembled monolayer (SAM) is formed on the upper surface of the nanopore. Finally, gold is deposited on top of the SAM. A variable potential is then applied across the SAM via electrical contacts with the two gold surfaces and the current/voltage properties are measured (bottom portion of figure).
The defining characteristic of NDR is that it will only carry significant current at one narrow range of voltage. A nitro-amino containing compound was shown to demonstrate this NDR effect as well as a mono-nitro compound (Fig. 2) and, more recently, poly-nitrated compounds.

Figure 2. I/V plots from the nanopore devices containing the nitro-amino compound (top) and the mono-nitro compound (bottom). The nitro-amino plot shows NDR at 60 K. The plot on the bottom demonstrates the NDR effect at room temperature (295 K). The plot on the bottom also shows a sharper and more pronounced NDR effect at a lower temperature (180 K).
Speculation by various members of the team brought about the idea that the mechanism of the NDR effect may involve the reduction of the molecules in the nanopore device. It was thought that the “turn-on” voltage, that is, the potential where current began to increase dramatically, was the result of a single-electron reduction of the molecules. The “turn-off” voltage, where the current essentially stopped, occurred because of a second single-electron reduction. In an effort to understand the mechanism behind the NDR effect, theoretical calculations\textsuperscript{12} and cyclic voltammetric measurements\textsuperscript{13} on the nitro-only compound were performed, both of which are generally in good agreement (Chapter 3). Therefore, it was necessary to design and synthesize a variety of compounds that would differ from the nitro-only compound only slightly in order to piece together a picture of the mechanism.

Of recent interest is the fact that both the nitro-amino compound and the mono-nitro compound demonstrate molecular dynamic random access memory (molecular DRAM) (Fig. 3).\textsuperscript{14} That is, the nanopore devices containing either of these compounds can store conductive states that differ enough from one another to be recognizable. This essentially constitutes DRAM as seen in modern computers.
Figure 3. $I(V)$ characteristics of the nanopore devices. On the left, the nitro-amino device at 200 K. "0" denotes the initial state, "1" the stored written state, and "1"-"0" the difference of the two states. On the right, $I(V)$ characteristics of stored and initial/erased states in nitro-only device at ambient temperature (300 K). Notches indicate the set-point for building a DRAM cell.

Most recently, a dinitro-biphenyl compound has demonstrated the NDR effect at room temperature as well. However, the effect is well defined at room temperature whereas the mono-nitro compound had well defined behavior only at lower temperatures. Initial reports from our collaborators at Yale (Reed) show that this device also shows memory that persists for more than two hours. The synthesis and $I/V$ plot for this compound is located in the results and discussion section. More testing is underway to confirm this and to determine exactly how long the memory effect lasts.

More work in our group and amongst collaborators is currently underway to further exploit and understand these properties as well as to test new compounds. Quick screening methods are being developed to help find compounds that demonstrate interesting and useful properties.
Results and Discussion

Scheme 1

Scheme 1 shows an improved synthesis of the traditional thioacetyl “alligator clip” (1)\(^1\)\(^5\) The starting material, 4-iodobenzene-sulfonyl chloride, commonly called pipsyl chloride, is condensed with dimethylacetamide (DMA) then reduced with Zn and dimethyl dichlorosilane to give the free thiol. The thiol is then deprotonated with potassium carbonate and acetylated with acetyl chloride, all in one pot. The advantages of this procedure include shorter reaction time, elimination of the use of organolithium reagents, higher yield, and a more facile purification. Also, this procedure can be easily scaled up without increasing the reaction time.

Scheme 2

Scheme 2 shows the complete synthesis of an unfunctionalized molecular wire. David Allara at Penn State requested this compound to do some basic experiments with molecular wires that would simply conduct; i.e. no switching or memory characteristics.
1-Bromo-4-iodobenzene was coupled to trimethylsilylacetylene (TMSA) to afford compound 2 in excellent yield.\textsuperscript{18} To this was coupled phenylacetylene to give a mixture that was inseparable. I believe there was some homocoupled phenylacetylene that could not be separated from the desired product. The mixture was taken onto the deprotection which again proved to be an inseparable mixture. Finally, coupling with the alligator clip afforded the desired product 3 in 25% yield over the 3 steps.

Scheme 3

Scheme 3 shows the synthesis of an ethyl-functionalized molecular wire. The compound has been previously synthesized in the Tour group by Leroy Jones,\textsuperscript{16} however, this is part of a new synthetic route to obtain the product. The overall synthesis is much shorter and the overall yield is higher than the previous route. 3-Nitroacetophenone was reduced to 3-ethylaniline 4 in 46% yield.\textsuperscript{6} This low yield was probably due to problems with leaks in the hydrogenation apparatus. 3-Ethylaniline (4) was then iodinated in 48%
yield using triethylbenzylammonium iodine dichloride\textsuperscript{19} to afford compound 5. Cooling the solution in an ice bath before addition of the iodinating agent increased the yield from 46% to 84%. Compound 5 was then coupled to TMSA to afford 6 in 58% yield. Diazotization and substitution with iodide provided 7 in good yield. From this point, the synthetic route closely followed the previous procedure.\textsuperscript{17} Sonogashira\textsuperscript{18} coupling of 7 with phenylacetylene provided 8 in modest yield. Deprotection of the terminal alkyne and coupling with thioacetic acid S-(4-iodo-phenyl) ester (1) provided final desired wire 10 in a modest yield of 70%. Curiously, this was exactly the same yield reported previously. This new synthesis consists of 7 steps instead of the previous 9 and proceeded in 26% overall yield from 3-ethylaniline as opposed to 15% by the previous route.

Scheme 4

Scheme 4 shows the synthesis of the "mononitro" molecular device.\textsuperscript{19} 2,5-Dibromonitrobenzene was coupled with TMSA, followed with a coupling with phenylacetylene and finally deprotection of the terminal alkyne to afford 11. A complete workup and column chromatography were performed after each step to purify the
compounds with a limited degree of success. Because each transformation does not change the acidity or polarity of the compounds, separation by chromatography has limited success. Therefore, after some purification, each mixture of compounds was taken onto the next step. After the deprotection step, purification was greatly simplified and compound 11 was isolated pure in 35% yield over 3 steps.

Sonogashira-Castro-Stephens coupling\textsuperscript{11,12} of 11 with 1 provided 12 in a moderate yield of 47% by using 20% catalyst loading compared to the usual 5% loading. There appears to be some inherent problem with the coupling of nitro compounds with thioacetate compounds.

**Scheme 5**

Scheme 5 depicts an improved synthesis of our group’s standard “mono-nitro” compound. This route is a drastic improvement over the previous route that used 2,5-dibromo-nitrobenzene because that route showed no selectivity in the initial coupling
This route alleviates this by only having one aromatic halide in each coupling reaction. The synthesis of 12 began with the iodination of 2-nitroaniline to give 13 in high yield. Coupling of 13 with phenylacetylene provided 14 in high yield. Note that this methodology allows one to generate derivatives of the "mono-nitro" device in high yield by coupling at only one available site; a route not easily available through other means. Next, the amine is replaced by an iodide via the diazonium salt to give 15, again in high yield. TMSA was coupled with 15 in high yield (89%) to provide 16 which was deprotected to 11 in 96% yield. Compound 11 was then coupled with the thioacetyl alligator clip (1) to provide 12 in a good yield of 58%. The key to obtaining the higher yield of 12 was to use 5 mol% palladium catalyst, 10 mol% copper, and 20 mol% of triphenylphosphine (dubbed the 5,10,20 method). A lower amount of triphenylphosphine (eg; 12.5 mol%) normally results in much lower coupling yields. The NDR and memory characteristics of this compound were shown in Figures 1 and 2. This compound has become a highly sought after and tested compound by many research groups because of its room temperature behavior.

Scheme 6
Scheme 6 shows the synthesis of a regioisomer of 12 designated as the “nitro-up” or “meta-nitro” compound; when assembled on a metal surface, the nitro will be pointing away from the metal of the SAM. The synthesis works analogously to the original nitro compound 12. However, the first reaction couples phenylacetylene with the more reactive bromide ortho to the nitro functionality. Then, the less reactive meta bromide was coupled with TMSA followed by removal of the TMS protective group to afford 17. After each step, limited purification via chromatography was performed and compound 17 was isolated in 32% overall yield (comparable to 11). Coupling\textsuperscript{11,12} with 4-iodo-1-benzenethioacetate (1) and 40% catalyst loading afforded 18 in a modest 52% yield. It appears that changing the catalyst loading from 20% to 40% had no significant effect on the yield of the couplings in Schemes 4 and 6. These are isolated cases and no in depth studies or repetition of the reactions has been done to verify that hypothesis. Compound 18 has been sent to Mark Reed at Yale and is awaiting testing to determine if the nitro orientation has any effect on the electronic properties.
Scheme 7

Scheme 7 shows a highly improved synthesis of the “nitro-up” or “meta-nitro” device 18. The logic of the synthesis is the same as that of Scheme 5. 4-Iodo-2-nitroaniline was coupled with TMSA to provide 19 in a high yield of 91%. The amino group of 19 was converted to an iodine through a diazotization followed by reaction with an iodine source (NaI, I₂). This iodo compound (20) was then coupled with phenylacetylene to provide 21 in an excellent yield (98%). The alkyne was then deprotected using potassium carbonate and methanol to afford compound 17. The terminal alkyne was then coupled with the thioacetyl alligator clip to provide final compound 18 in a high yield of 73%, once again using the 5,10,20 catalyst loading method.
Scheme 8

Scheme 8 shows the synthesis of the mono-nitro compound containing two alligator clips, for use in contacting two metal surfaces or crosslinking nanoparticles. 2,5-Dibromonitrobenzene was coupled with an excess of TMSA to afford compound 22 in a modest 66% yield. The yield was expected to be much higher. I believe the competing cyclization between nitro and alkyne plays an important role. Compound 22 was then deprotected to give diyne 23 in 99% yield. This was then coupled with 2 equivalents of alligator clip 1 to afford compound 24 in 50% yield. A previous route afforded only 20% of the desired product. The key again was to use the 5,10,20 catalyst method. The lower yielding example used only 10 mol% of triphenylphosphine.

Scheme 9

Scheme 9 shows the sequence for the deprotection of the mono-nitro device to give the free thiol (25). Base-promoted deprotection for this compound did not work.
well because if trace amounts of oxygen are around the thiolate dimerizes to the disulfide. This means strict exclusion of air is a must, even on workup. However, acid-catalyzed deprotection works very well because dimerization is greatly reduced or even eliminated. The relatively low yield (60%) could be due to decomposition (possibly dimerization) on the silica gel used for purification. Proton NMR revealed that there was approximately 80% thiol to 20% disulfide. David Allara at Penn State requested this compound and it was determined that the disulfide would not interfere with SAM formation; therefore, the impure compound was used as is.

Scheme 10

Scheme 10 shows the deprotection of the bis(thioacetyl) nitro compound 24 to give the bis(thiol) compound 26. The procedure remained the same as in Scheme 9. However, purification was made easier by the fact that if the thiols dimerized to the disulfide, a polymer would form. Therefore, any polymer formed in this manner precipitated from solution and thus separated from the desired product. This compound was sent to David Allara as well for testing.
Scheme 11

Scheme 11 depicts the synthesis of another protected mercaptan and its use as an alligator clip. The iodo derivative of this TMS-ethyl protected thiophenol has been used in Sonogashira couplings with great success.\textsuperscript{21} I found this procedure and decided to try it to determine if the TMS-ethyl group would increase the yield of the final Sonogashira couplings. The removal of the protecting group utilizes only a TBAF solution in THF at room temperature.\textsuperscript{21} This procedure could easily replace our current procedure because of its simplicity. 4-Bromothiophenol was converted to compound 27 using catalytic tert-butyl peroxide at 100 °C in 30% yield. Yu and coworkers report a yield for this conversion of almost 90%.\textsuperscript{21} If this alligator clip comes into standard usage, the yield will have to be increased. Attempts to couple compound 27 with terminal alkynes under Sonogashira conditions failed, probably because of the electron donating ability of the TMS ethyl group deactivating the bromide towards oxidative addition of the palladium. Compound 27 was converted to its iodide analog 28 in moderate yield through lithium-halogen exchange and iodine quench. This was coupled with a nitro-containing alkyne 11 intermediate to afford 29 in a much better yield than when using the thioacetate
alligator clip. This coupling was performed using only 5% catalyst compared to 20% catalyst needed to achieve a lower but comparable yield (when not using the 5,10,20 catalyst method) with the thioacetates.

Scheme 12

 Scheme 12 shows the complete synthesis of the dinitrobiphenyl device described earlier. This is the compound which shows a well defined room temperature NDR as well as long-term (hours) memory. This is part of the ongoing pursuit of compounds with better electron withdrawing properties that may have different and interesting electronic properties in a device.

4,4'-Biphenyl was nitrated using the conditions of Shaw and Turner\textsuperscript{15} to give the 2,3'-dinitro product 30 in 70% yield. By literature precedent and by my own \textsuperscript{1}H-NMR analysis of the crude product mixture, there was approximately 84% of the desired
product and 16% of the 2,2'-dinitro product. Recrystallization from ethanol/acetone would only allow for isolation of 70% of pure 30. Although the 2,2'-product is useful and is currently being used in making a device, it is obtained in higher yields through an alternative method and therefore not isolated here.

Coupling of 30 with 4-ethynyl-1-benzenethioacetate afforded monocoupled product (not shown) in low yield (14%). This has been a problem common to any couplings of nitro-containing compounds with thioacetate-containing compounds. Also, although it was not tried with this specific compound, any further couplings of nitro-containing compounds with thioacetate-containing compounds have afforded low yields at best. Coupling of compound 30 with TMSA afforded 31 in a modest 58% yield. It is not certain why the yield was not higher; presumably some dicoupling and some monocoupling to the opposite side of the starting material occurred. Coupling of 31 with phenylacetylene provided 32 in a higher yield of 67%. Coupling of nitro compounds can be problematic because cyclization between the nitro and alkyne can result as seen by Rosen and coworkers.24 Lower temperatures and shorter reaction times as well as the use of lower amounts of base in the reactions may help to prevent these cyclizations.

Deprotection of the alkyne using potassium carbonate and methanol afforded 33 in 98% yield. Coupling of the terminal alkyne with the alligator clip 1 afforded final product 34 in good yield. Figure 4 shows the results of solid-state testing of 34 by Mark Reed at Yale. This compound was actually tested in a “planar” configuration (Figure 5), different than the nanopore. In this configuration, gold pads are lithographically patterned onto a silicon substrate. The compound is then allowed to self-assemble onto the gold. Finally, gold is evaporated onto the top of the SAMs to form the final device.
Figure 4. I-V characteristics of 34 in a planar test-device configuration. The red arrows indicate a negative potential sweep used to “reset” the device to its initial state.
**Figure 5.** Schematic of the mesa (planar) device configuration. A silicon wafer has lithographically patterned features. The SAM is formed on the lower Au surface first, then the top Au gold contact is evaporated to cover the SAM. The initially exposed Au is approximately 1 micron in diameter.

As can be seen in Figure 4, the dinitro compound shows NDR similar to the mono-nitro and nitro-amino devices. However, 34 shows a rather well-defined peak at room temperature, whereas the mono-nitro device demonstrated a well-defined peak only at lower temperatures with an ill-defined curve at room temperature. This helps to demonstrate that the nitro groups play a key role in the NDR switching mechanism and memory effects.
Scheme 13

Scheme 13 shows the complete synthesis of the 2,3'-dinitrobiphenyl compound with two alligator clips. 2,3'-Dinitro-4,4'-dibromobiphenyl\textsuperscript{25} was coupled with an excess of TMSA at room temperature to provide 35 in good yield. If the reaction was heated to 45 °C for only a few hours, the yield was reduced (56%) possibly due to cyclization between the 3'-nitro group and the alkyne\textsuperscript{24} although no evidence for this reaction was observed or sought out. Deprotection of the terminal alkynes provided 36, which was coupled with two equivalents of alligator clip 1 to provide 37 in good yield (59%). No electronics tests have yet been done.
Scheme 14

Scheme 14 shows the complete synthesis of another dinitrobiphenyl compound. This compound, however, is the 2,2'-isomer. It is not certain what effect the position of the nitro groups will have on the electronic properties of the devices at this time until further testing is complete.

2,5-Dibromonitrobenzene was subjected to Ullman coupling conditions to give the biphenyl compound 38 in good yield. Coupling of 38 with TMSA afforded 39 in 46% yield. Subsequent coupling with phenylacetylene afforded 40 in 77% yield. Deprotection of the alkyne using potassium carbonate and methanol afforded terminal alkyne 41 in 97% yield. Coupling of 41 with the alligator clip, again using 20% palladium catalyst, afforded 42 in a surprising 72% yield. This yield is much higher than some other yields of couplings with nitro compounds and thioacetates. It is not certain
why this particular reaction proceeded better than the others. This compound is with Mark Reed awaiting testing as well.

Scheme 15

Scheme 15 shows the complete synthesis of the 2,2'-dinitro biphenyl compound containing two alligator clips for possible use in contacting two metal surfaces or crosslinking nanoparticles. Compound 43 was made by coupling two equivalents of TMSA with 2,2'-dinitro-4,4'-dibromobiphenyl. Deprotection of the terminal alkynes provided 44, which was then coupled with two equivalents of alligator clip 1 to provide 45 in a low yield of 26%. This low yield was expected since we have consistently had difficulties coupling the alligator clip with nitro containing compounds. This compound is currently with various collaborators awaiting testing.
Scheme 16

Scheme 16 shows the complete synthesis of another biphenyl core for use in a molecular device. This continues the concept of “more nitros” currently being pursued for optimization of the memory hold times in this class of devices. 4,4'-Dibromo-2,2'-dinitrobiphenyl was reduced to the corresponding diamine. The amines were then protected as acetamides to give compound 46 in 89% yield over 2 steps. Mixed acid nitration at 0 °C afforded compound 47 in 75% yield. Potassium carbonate/methanol-promoted deprotection of 47 failed to remove the acetyl groups, but acidic hydrolysis using H$_2$SO$_4$ and water easily provided 48. Coupling of 48 with 1 equivalent of phenylacetylene provided an inseparable mixture of starting material, monocoupled product and dicoupled product, which was taken onto the next step. HOF oxidation afforded tetranitro compound 49 in 11% yield over 2 steps. The use of acetone as solvent may be the cause of the low yield, although more work would need to be done to determine the cause. Final coupling of 49 with the alkynyl alligator clip afforded 50 in
a low, albeit expected, yield of 24%. No electrical tests have yet been conducted on this compound.

Scheme 17

Scheme 17 shows the unintentional synthesis of trinitro compound 51. Compound 46 was subjected to similar mixed acid nitration conditions as described for 47. However, the reaction was allowed to warm to RT and stir overnight as opposed to only for 5 hours as in Scheme 16. This change resulted in an unexpected transformation into 51. Presumably, the nitration occurred as expected to give 47 and then, possibly, an acid-catalyzed deprotection and condensation of the amines to give the dinitro benzo[c]cinnoline followed by a third nitration ortho to the azo functionality (4 position). This remains speculative at this time. Two Sonogashira couplings with 51 have been attempted with no success. It is possible that the palladium oxidatively adds to the C-Br bond that has two nitro groups ortho to it. This could give a highly stable organometallic species that would prevent the subsequent steps needed for the catalytic cycle. It is also possible that the steric of the two nitro groups do not even permit the oxidative addition of the palladium to the C-Br bond so that the catalytic cycled never even begins.
Scheme 18 shows the synthesis of 49, a regioisomer of 48 by a similar sequence to Scheme 16. This compound was synthesized so that the coupling of phenylacetylene would be more selective than the coupling of 48 with phenylacetylene. Reduction of 2,3′-dinitro-4,4′-dibromobiphenyl\(^{25}\) followed by acetyl protection of the amines afforded 52 in 100% yield over 2 steps. Mixed acid nitration afforded 53 in a modest yield of 43%. The presence of other isomers was detected by TLC and proton-NMR. Compound 53 was then deprotected using 3 N HCl in THF to afford the free amines in 96% yield. The biphenyl core (54) was then coupled with phenylacetylene to give an inseparable mixture of starting material, desired product, and dicoupled material. After some attempt to purify (column chromatography), the mixture was taken onto the oxidation step. Fluorine was used to generate HOF in situ which oxidized the amines to nitro groups to afford 49 in 45% yield (over 2 steps).\(^{27}\) This is an improvement over the prior route which afforded 49 in 11% over 2 steps from the symmetric biphenyl 48. This improvement is thought to arise from the unsymmetrical biphenyl core 53, which allows some degree of selectivity in the Sonogashira couplings.\(^{18}\)
Scheme 19

Scheme 19 shows the complete synthesis of a mononitro biphenyl compound. This compound was synthesized to compare its properties to those of the standard mononitro device and to the dinitro biphenyl device. The comparison to the mono-nitro device should reveal any differences that adding a barrier (i.e. the biphenyl twist) or length to the molecule will make. The comparison to the biphenyl dinitro device should determine what difference exists between having one or two nitro groups on a biphenyl core.

The synthesis began with the stannylation of (4-bromo-phenylethynyl)-trimethylsilane (2) to give 55 in 68% yield. This was then subjected to a Stille coupling with compound 15 to give the biphenyl product 56 in a good yield of 67%. Compound 56 was then deprotected using potassium carbonate and methanol to liberate the terminal alkyne 57 in 99% yield. The alkyne was then coupled with the thioacetyl alligator clip 1 to give the final compound 58 in a good yield of 67%. This compound has been sent to Mark Reed for testing.
Scheme 20

Scheme 20 shows the synthesis of another biphenyl potential device. However, this compound contains two amino groups and two nitro groups. The reasoning behind this design is that if each ring of the biphenyl is in a zwitterionic or pseudo-quinoidal form, the two rings may interact in an interesting, unknown manner not seen in any previous devices (Figure 6). Until some data is generated from the solid-state testing of this compound, it is difficult to speculate on how this system may behave.
**Figure 6.** Schematic depicting the alignment of the internal dipoles and interactions of 61 that may occur in a solid-state device.
The synthesis began with compound 48 shown in Scheme 16. Compound 48 was coupled with 1 equivalent of TMSA. This product could not be fully purified via column chromatography. Therefore, after limited purification, the product was coupled with phenylacetylene and purified to give 59 in a low, yet statistically expected, yield of 35% over the two steps. Deprotection of the terminal alkyne yielded 60, which was passed through a silica plug to purify, in 80% yield. This alkyne was then coupled with the thioacetyl alligator clip to afford final compound 61 in a low yield of 36%. It is not certain why this yield is lower than usual, but the coupling of nitrated compounds with thioacetyl-containing compounds rarely gives high yields. This compound has been sent to Mark Reed for testing. We are awaiting results.

**Scheme 21**

![Scheme 21](image)

Scheme 21 shows the first synthesis of a new class of potential moletronics devices: fluorene-based compounds. Because biphenyl cores create a barrier to
conduction due to biphenyl twisting (approximately 70°), conduction could be improved by forcing the biphenyl to be more planar. Fluorene is nearly planar due to its methylene bridge connecting the 2- and 2'-carbons. By being in a permanent near-planar position, a fluorene-containing device should have a more conjugated backbone and possibly be more conductive.

The synthesis began with the bromination of fluorene to give 62 in quantitative yield. Next, 62 was nitrated using mixed acid conditions to give 63 in 63% yield (only somewhat lower than the literature yield). 63 was then coupled with two equivalents of TMSA to give 64 in 65% yield. This yield could almost certainly be improved upon because the coupling was only performed once. The terminal alkynes were then deprotected to give compound 65 in 92% yield. Finally, the diyne was coupled with 2 equivalents of the thioacetyl alligator clip (1) to afford 66 in a reasonable yield of 45%. This compound has also been sent to Mark Reed for testing and results are pending.

**Scheme 22**

![Scheme 22](image)

Scheme 22 depicts the synthesis of a nitro-fluorene potential device with only one alligator clip. Compound 63 was coupled with one equivalent of TMSA to afford an inseparable mixture of products. After a limited degree of purification, the impure
product was coupled with phenylacetylene which again provided an inseparable mixture of products. Deprotection of the terminal alkyne afforded 67 which was >90% pure after column chromatography. The determination of the order of coupling was based on a prior knowledge of Sonogashira couplings. The palladium oxidatively adds to the C-Br bond that is closest and most affected by the electron-withdrawing nitro group. In this case it is the C-Br bond that is meta to the nitro group. Compound 67 was then coupled with the thioacetyl alligator clip to provide final compound 68 in an overall yield of 23% (over 4 steps). This compound has been sent to Reed and awaits testing.

Scheme 23

Scheme 23 shows the synthesis of 70, the isomer of 68, which was accomplished by simple reversal of the first two coupling steps. Compound 63 was first coupled with phenylacetylene followed by the addition of TMSA in the same pot. Again, this product could not be purified so was taken onto the next step with limited purification. Deprotection of the alkyne afforded 69 in ~38% yield (>90% purity) over the two steps. Coupling of 69 with the thioacetyl alligator clip afforded final compound 70 in 25% yield over the three steps. Again, this compound was sent to Mark Reed for testing.
Scheme 24 shows the synthesis of a potential device containing a fluorenone core. This compound was designed and synthesized based on the concept that the carbonyl functionality of the fluorenone may act as an electron sink and allow for facile reductions. If this is the case, this may be a new type of device which contains no nitro functionalities. This could also make the compounds more stable to ambient conditions, which seems to have been a problem in the past.

The synthesis began with the oxidation of 2,7-dibromofluorene using a catalytic amount of chromium(VI) oxide and t-butyl hydroperoxide to regenerate the catalyst.\(^\text{32}\) The reaction proceeded smoothly to afford 2,7-dibromo-9-oxo-fluorene (71) in 83% yield.\(^\text{33}\) Next, 71 was coupled with 2 equivalents of TMSA to afford 72 in a modest yield of 58%.\(^\text{34}\) The yield could most likely be improved upon but no attempts were made to optimize the conditions. 72 was then deprotected using potassium carbonate and methanol to liberate the free alkynes in high yield (97%).\(^\text{34}\) Dyne 73 was then coupled with two equivalents of the alligator clip 1 in a modest yield of 56%. This yield was suspiciously similar to the yield obtained in the TMSA coupling step. These results
suggest that there may be some unforeseen problem in the couplings of alkynes with fluorenones. This compound has been sent to various collaborators and is in the testing process.

Scheme 25

Scheme 25 shows the synthesis of a potential molecular device containing a nitrated fluorenone core. This concept combines the idea of using nitro groups with the use of a carbonyl functionality. This could provide new and interesting electronic properties in a solid state device in that there could be two modes of switching and memory which may lead to multiple states.

The synthesis began with the oxidation of 2,7-dibromo-4-nitrofluorene (63) using the catalytic chromium(VI) method described for the previous synthesis.\(^{32}\) The yield was lower than for the oxidation of 62. This could be due to the fact that 63 is more electron-deficient and therefore less susceptible to oxidation, similar to the oxidation of amines on nitro-substituted compounds.\(^{27}\) The final product could not be completely purified so was taken onto the next step. 75 was then coupled with two equivalents of TMSA to
afford 76 in a modest yield of 42% over the two steps. 76 was then deprotected to afford 77 in 98% yield. The liberated alkynes were then coupled with two equivalents of alligator clip 1 to afford 78 in a good yield of 60%.

Scheme 26

Scheme 26 shows the complete synthesis of a molecular device with a quinone as the central core. Quinones are commonly used by nature in biological systems as electron shuttles, including ubiquinones and Vitamin K₁. The concept behind this device is that if the nitro compounds work so well because of reduction of the compounds, the quinone should work exceptionally well since quinones are readily reduced and oxidized and both forms are generally stable. In solution, quinones are reduced to hydroquinones, picking up hydrogen atoms from solvent or reagents. However, in the solid state, such as the nanopore, there would be no sources of easily accessed hydrogen atoms. Therefore, the reduced form of the quinone should be some
sort of radical anion yet should still be stabilized by the gain of aromaticity in the pseudo-
hydroquinone core.

1,4-Dimethoxybenzene was brominated using bromine and glacial acetic acid to
give 79 in good yield.\textsuperscript{37} Compound 79 was then coupled (Sonogashira conditions) with
phenylacetylene. Compound 81 was prepared in 79\% yield by the coupling of TMSA
with compound 80. Deprotection of the alkyne afforded 82 in 79\% yield as well.
Coupling with the alligator clip afforded compound 83 in 76\% yield. The final step was
to oxidize the dimethoxy core to the quinone core. This route had to be taken because
quinones cannot be used in the palladium-catalyzed couplings. Quinones are known to
oxidize palladium(0) to palladium(II), shutting down the catalytic cycle.\textsuperscript{38} Ceric
ammonium nitrate (CAN) is a mild and neutral oxidizing agent known to generate
quinones from dimethoxybenzenes and therefore was a logical choice for this
procedure.\textsuperscript{39} The final device 84 was obtained in 74\% yield. However, yields with this
level of success were unusual. Other attempts resulted in much lower yields (\textasciitilde 20\%).
This candidate is under evaluation by Mark Reed’s research group.

It should be noted that the couplings presented here proceeded in much higher
yields than coupling with nitro compounds even though the intermediates could never be
fully purified. Also, the coupling with the alligator clip proceeded in a much higher yield
than with the nitro compounds and only a 5\% catalyst loading was used. This lends
support to the idea that the nitro-thioacetate combination is detrimental to couplings.
Scheme 27

Scheme 27 shows the synthesis of the quinone device with alligator clips on both ends.\textsuperscript{35} This compound can be used to crosslink nanoparticles for bridging connections on a chip or other devices. 2,5-Dibromo-1,4-dimethoxybenzene was coupled with an excess of TMSA to give compound 85 in 79% yield. Subsequent deprotection afforded the diyne 86 in 98%. This was then coupled with 2 equivalents of the alligator clip to give compound 87 in good yield. This dimethoxy compound could be of use itself in being an electron-rich molecular wire with, presumably, good conductivity. Compound 87 was oxidized using the CAN procedure discussed earlier to generate 88. The moderate yield of 49% is rather typical of the many attempts by this author while literature reports much higher yields for similar systems. For cases where the authors generate the quinone from dimethoxy benzene derivatives using CAN, however, there are no thioacetate or similar groups.
Scheme 28

Scheme 28 shows the synthesis of another new class of potential moletronics devices: isatogens. The isatogen, also called an indolone N-oxide, is only the central 6,5-fused ring portion of this compound. This isatogen, in particular, is only a rearranged version of the mononitro device 12. Because it has the same atomic composition as 12, a comparison of the solid-state electronic properties of isatogen 89 with 12 should be very interesting and informative. Also, isatogens are known to be efficient spin traps for radicals. 24 If isatogens can stabilize radicals better than a simple nitro group, isatogens may give longer memory lifetimes in the solid state. Another note of interest is that this compound has an orange color while the starting compound 12 is yellow. This also gives some indication as to the different properties of the new composition.

Compound 12 was dissolved in THF and a drop of TBAF was added. The solution was stirred for 15 minutes before quenching with acid. To my knowledge this is the first example of TBAF inducing this rearrangement. Most syntheses use UV light or hot pyridine. 40 This compound has been sent to Mark Reed for testing.

Summary

Many different molecular electronics device candidates have been synthesized with a few tested. These device candidates were designed based on rational thought and chemical intuition using the solid-state results we have received from Mark Reed’s group at Yale University.
Experimental Procedures

**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 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. 1H NMR spectra were observed at 400 MHz and 13C 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 by Terry Marriott at Rice University’s mass spectrometry lab. All new compounds were named using the Beilstein AutoNom feature of Beilstein Commander software.

**General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).** 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 equivalents 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 \( N,N \)-diisopropylethylamine (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 \( \text{NH}_4\text{Cl} \). The organic layer was diluted with methylene chloride and washed with a saturated solution of \( \text{NH}_4\text{Cl} \) (3×). The combined aqueous layers were extracted with methylene chloride (3×). The combined organic layers were dried over anhydrous \( \text{MgSO}_4 \) and the solvent removed \textit{in vacuo}. The crude product was then purified by flash or column chromatography (silica gel).

**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 equivalents of potassium carbonate, and equivalent amounts of methanol 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 \( \text{NaCl} \). 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.

\[
\text{Thioacetic acid } S^-\text{(4-iodo-phenyl) ester (1, DWP-4-92).}^{15} \text{ Pipsyl chloride (5.00 g, 16.5 mmol) was added to a 250 mL addition funnel, the air was removed and replaced with nitrogen (3×). Zinc (3.78 g, 57.8 mmol) was added to a 500 mL round bottom flask}
\]
(with the addition funnel attached), the air was removed and replaced with nitrogen (3×). Dichloroethane (2 ×130 mL) was then added to the flask and the funnel. Dimethylacetamide (4.64 mL, 49.5 mmol) was added to the addition funnel and dimethyldichlorosilane (7.04 mL, 57.8 mmol) was added to the round bottom flask. The contents of the addition funnel were then slowly added to the contents of the round bottom flask over a period of 35 min. The apparatus was then placed in a 75°C oil bath for 1.5 h. Potassium carbonate (1.25 g, 9.08 mmol) was then added and heating continued for an additional 30 min. After cooling to room temperature, acetyl chloride (4.71 mL, 66 mmol) was added and the mixture was stirred overnight. The mixture was then filtered, washed with brine and dichloromethane, and dried over magnesium sulfate. Column chromatography (silica gel using 1:1 dichloromethane/hexanes as eluent; Rf = 0.56) afforded the desired product (4.18 g, 91% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)) δ 7.72 (dt, \(J= 8.5, 2.1\) Hz, 2 H), 7.11 (dt, \(J= 8.5, 2.1\) Hz, 2 H), 2.41 (s, 3 H).

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\text{Br} \quad \text{TMS}
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(4-Bromo-phenylethynyl)-trimethyl-silane (2, DWP-1-243, 292, DWP-4-3).\(^{19}\)

1-Bromo-4-iodobenzene (6.21 g, 22.0 mmol), bis(dibenzylideneacetone)palladium(0) (0.253 g, 0.44 mmol), copper(I) iodide (0.084 g, 0.44 mmol), triphenylphosphine (0.289 g, 1.1 mmol), THF (20 mL), DIEA (15.3 mL, 88 mmol), and TMSA (3.2 mL, 22.6 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 1 h. Flash column chromatography (silica gel using hexanes as eluent) afforded the desired product (5.16 g, 93% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.41 (dt, \(J = 8.7, 2.0\) Hz, 2 H), 7.30 (dt, \(J = 8.7, 2.1\) Hz, 2 H), 0.23 (s, 9 H).
Thioacetic acid S-[4-(4-phenylethynyl-phenylethynyl)-phenyl] ester (3, DWP-I-290).¹⁰ (4-Bromo-phenylethynyl)-trimethyl-silane (0.500 g, 1.97 mmol), bis(dibenzyldieneacetone)palladium(0) (0.057 g, 0.099 mmol), copper(I) iodide (0.019 g, 0.099 mmol), triphenylphosphine (0.065 g, 0.247 mmol), THF (10 mL), DIEA (0.69 mL, 3.94 mmol), and phenylacetylene (0.26 mL, 2.36 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred in a 50 °C oil bath for 15 h. By ¹H NMR, only half of the material had reacted. The material was resubjected to the coupling conditions and heated in a 80 °C oil bath for 1 d. Flash column chromatography (silica gel using 3:1 hexanes/dichloromethane as eluent) afforded a mixture of products, which was taken onto the next step. The mixture (0.740 g), potassium carbonate (1.36 g, 9.85 mmol), methanol (40 mL), and dichloromethane (40 mL) were used following the general procedure for deprotection to give a mixture of products, half of which was taken onto the next step. The mixture, bis(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.05 mmol), copper(I) iodide (0.019 g, 0.10 mmol), triphenylphosphine (0.033 g, 0.125 mmol), THF (25 mL), DIEA (0.35 mL, 2.0 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (0.277 g, 0.98 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 70 °C oil bath for 2 d. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (0.086 g, 25% yield). IR (KBr) 3052.6, 2202.6, 1698.2, 1513.0, 1478.6, 1439.7, 1395.4, 1353.0, 1142.5, 1108.8, 1014.4, 940.6, 838.8, 827.6, 756.1, 691.8, 619.6, 526.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (m, 4 H), 7.50 (s, 4 H), 7.39 (dt, J = 8.5, 1.9 Hz, 2 H), 7.34 (m, 3 H), 2.42
(s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.84, 134.66, 132.59, 132.06, 131.98, 128.92, 128.81, 128.69, 124.70, 123.84, 123.39, 123.10, 91.83, 91.16, 90.83, 89.45, 30.71. HRMS calc’d for C$_{24}$H$_{15}$OS: 352.0922. Found: 352.0920 (Error = 0.62 ppm).

3-Ethyl-phenylamine (4, DWP-II-23).\textsuperscript{20} 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%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.07 (t, $J = 7.7$ Hz, 1 H), 6.61 (dd, $J = 7.5$, 0.6 Hz, 1 H), 6.52 (m, 2 H), 3.59 (br s, 2 H), 2.56 (q, $J = 7.6$ Hz, 2 H), 1.21 (m, 3 H).

3-Ethyl-4-iodo-phenylamine (5, DWP-II-29, 81).\textsuperscript{42} 3-Ethyl-phenylamine (2.86 g, 23.6 mmol), sodium bicarbonate (3.96 g, 47.2 mmol), methanol (15 mL), and dichloromethane (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 dichloromethane (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 dichloromethane, and dried over magnesium
sulfate. Flash column chromatography (silica gel using dichloromethane 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\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 8.4\) Hz, 1 H), 6.57 (d, \(J = 2.8\) Hz, 1 H), 6.26 (dd, \(J = 8.3, 2.8\) Hz, 1 H), 3.63 (br s, 2 H), 2.62 (q, \(J = 7.5\) Hz, 2 H), 1.17 (t, \(J = 7.5\) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.53, 147.31, 140.06, 115.98, 115.41, 86.23, 34.44, 15.02. HRMS calc’d for C\(_8\)H\(_{10}\)NI: 246.9860. Found: 246.9855 (Error = 0.98 ppm).

![3-Ethyl-4-trimethylsilanylethynyl-phenylamine (6, DWP-II-35)](image)

3-Ethyl-4-iodo-phenylamine (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 the solution was stirred at RT for 1.5 h. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product (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\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.22 (d, \(J = 8.2\) Hz, 1 H), 6.47 (d, \(J = 2.3\) Hz, 1 H), 6.40 (dd, \(J = 8.2, 2.4\) Hz, 1 H), 3.72 (br s, 1 H), 2.69 (q, \(J = 7.5\) Hz, 2 H), 1.20 (t, \(J = 7.5\) Hz, 3 H), 0.21 (s, 9 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.81, 147.34, 134.17, 114.68, 112.57, 112.35, 105.20, 95.47, 28.19, 14.91, 0.57.
(2-Ethyl-4-iodo-phenylethynyl)-trimethyl-silane (7, DWP-II-99, 93). To a 200 mL round bottom flask was added NOBF₄ (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-trimethylsilanyylethynyl-phenylamine (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 methylene chloride. Flash column chromatography (silica gel using hexanes as eluent) afforded the product as a white solid (3.67 g, 78% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 1.8 Hz, 1 H), 7.44 (dd, J = 8.1, 1.7 Hz, 1 H), 7.11 (d, J = 8.1 Hz, 1 H), 2.72 (q, J = 7.5 Hz, 2 H), 1.21 (t, J = 7.6 Hz, 3 H), 0.23 (s, 9 H).

(2-Ethyl-4-phenylethynyl-phenylethynyl)-trimethyl-silane (8, DWP-II-103). (2-Ethyl-4-iodo-phenylethynyl)-trimethyl-silane (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 DIPEA (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$_3$) $\delta$ 7.51 (m, 2 H), 7.39 (d, $J = 8.1$ Hz, 1 H), 7.35 (m, 1 H), 7.32 (m, 3 H), 7.27 (dd, $J = 7.9$, 1.6 Hz, 1 H), 2.79 (q, $J = 7.6$ Hz, 2 H), 1.25 (t, $J = 7.6$ Hz, 3 H), 0.25 (s, 9 H).

![Chemical Structure](image)

**2-Ethyl-1-ethyl-4-phenylethynyl-benzene (9, DWP-II-115).** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (m, 2 H), 7.43 (d, $J = 7.9$ Hz, 1 H), 7.38 (m, 1 H), 7.34 (m, 3 H), 7.29 (dd, $J = 7.9$, 1.7 Hz, 1 H), 3.32 (s, 1 H), 2.81 (q, $J = 7.6$ Hz, 2 H), 1.25 (t, $J = 7.6$ Hz, 3 H).

![Chemical Structure](image)

**Thioacetic acid S-[4-(2-ethyl-4-phenylethynyl-phenylethynyl)-phenyl] ester (10, DWP-II-116).** 2-Ethyl-1-ethynyl-4-phenylethynyl-benzene (0.897 g, 3.89 mmol) was coupled with thioacetic acid S-(4-iodo-phenyl) ester (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 dichloromethane/hexanes as eluent) followed by recrystallization from ethanol afforded the desired product as an off-white solid (1.03 g, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (m, 4 H), 7.47 (d, $J = 8.0$ Hz, 1 H), 7.42 (m, 1 H), 7.39 (dt, $J = 8.5$, 1.8 Hz, 2 H), 7.34 (m, 4 H), 2.86 (q, $J = 7.6$ Hz, 2 H), 2.43 (s, 3 H), 1.30 (t, $J = 7.6$ Hz, 3 H).

1-Ethynyl-2-nitro-4-phenylethynyl-benzene (11, DWP-II-9).$^{19}$ 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 the solution was stirred at RT for 10 h. Flash column chromatography (silica gel using 2:1 hexanes/dichloromethane as eluent) afforded a mixture of products that was taken onto the next step. The product mixture (3.09 g), bis(triphenylphosphine)palladium(II) dichloride (0.217 g, 0.31 mmol), copper(I) iodide (0.118 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/dichloromethane as eluent) afforded a mixture of products that was taken onto the next step. The product mixture (1.95 g), potassium carbonate (4.2 g, 30.4 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the
desired product as an orange solid (1.23 g, 37% yield). 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\(_3\)) \(\delta\) 8.16 (d, \(J = 1.5\) Hz, 1 H), 7.67 (dd, \(J = 8.1, 1.5\) Hz, 1 H), 7.64 (d, \(J = 7.8\) Hz, 1 H), 7.53 (m, 2 H), 7.37 (m, 3 H), 3.58 (s, 1 H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.62, 135.82, 135.65, 132.24, 129.72, 128.96, 127.80, 125.51, 122.33, 117.01, 94.35, 87.04, 86.97, 78.82. HRMS calc'd for C\(_{16}\)H\(_9\)NO\(_2\): 247.0633. Found: 247.0632 (Error = 0.68 ppm).

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\text{NO}_2 \\
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**Thioacetic acid \(S\)-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (12, DWP-I-23, II-11).**\(^{10,19}\) 1-Ethynyl-2-nitro-4-phenylethynyl-benzene (0.500 g, 2.02 mmol)) was coupled with thioacetic acid \(S\)-(4-iodo-phenyl) ester (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 dichloromethane/hexanes as eluent) afforded the desired product as an orange solid (0.381 g, 47% yield). 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\(_3\)) \(\delta\) 8.22 (dd, \(J = 1.1, 0.3\) Hz, 1 H), 7.70 (dd, \(J = 8.1, 1.5\) Hz, 1 H), 7.67 (d, \(J = 8.0\) Hz, 1 H), 7.61 (dt, \(J = 8.5, 1.9\) Hz, 2 H), 7.54 (m, 2 H), 7.42 (dt, \(J = 8.5, 1.8\) Hz, 2 H), 7.37 (m, 3 H), 2.43 (s, 3 H). \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 193.54, 149.90, 135.71, 134.96, 134.68, 132.97, 132.24, 129.93,
129.66, 128.96, 128.06, 124.87, 123.80, 122.44, 118.05, 98.24, 94.21, 87.25, 86.70, 30.77. HRMS calculated for C\textsubscript{24}H\textsubscript{15}NO\textsubscript{3}S: 397.0076. Found: 397.0773 (Error=0.8 ppm).

4-Iodo-2-nitro-phenylamine (13, DWP-III-28).\textsuperscript{43} 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 (liq\textsuperscript{21} mp: 121-123 °C) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 8.40 (d, J = 2.1 Hz, 1 H), 7.54 (dd, J = 8.8, 2.1 Hz, 1 H), 6.59 (d, J = 8.8 Hz, 1 H), 6.09 (br s, 2 H).

2-Nitro-4-phenylethynyl-phenylamine (14, DWP-III-31, DWP-4-2) 4-Iodo-2-nitro-phenylamine (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, 114 mmol), THF (35 mL) and phenylacetylene (4.60 mL, 37.9 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 2.5 h. Precipitation from dichloromethane/hexanes followed by extraction with
Et₂O and water afforded the desired product (7.93 g, 88% yield): mp 162-163°C. IR (KBr) 3470.7, 3342.1, 1641.5, 1598.7, 1552.2, 1516.3, 1411.5, 1340.5, 1234.8, 1142.8, 833.7, 756.2, 687.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, J = 2.0 Hz, 1 H), 7.52 (m, 3 H), 7.38 (m, 3 H), 6.81 (dd, J = 8.6, 0.4 Hz, 1 H), 6.24 (br s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 144.60, 138.67, 132.22, 131.91, 129.90, 128.81, 128.74, 123.38, 119.27, 112.52, 89.06, 87.97. HRMS calc’d for C₁₄H₁₀N₂O₂: 238.074228. Found: 238.074109 (Error = 0.50 ppm).

1-Iodo-2-nitro-4-phenylethynyl-benzene (15, DWP-III-34, 4-6) To a 500 mL round bottom flask (cooled to −20 to −30 °C) was added BF₃·OEt₂ followed by 2-Nitro-4-phenylethynyl-phenyamine (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 Et₂O was added to effect precipitation of the diazonium salt. The salt was filtered and washed with cold Et₂O 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 (8.40 g, 33.1 mmol). The diazonium salt was then slowly added to this solution over 15 min. The solution was washed with Na₂S₂O₃ (aq) and extracted with dichloromethane to afford the desired product which needed no further purification (9.78 g, 85% yield): mp 114-116°C. IR (KBr) 3078.2, 3047.5, 2211.9, 1522.2, 1439.3, 1351.6, 1014.3, 891.6, 824.3, 755.0, 686.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.2 Hz, 1 H), 7.96 (d, J = 1.9 Hz, 1 H), 7.52 (m, 2 H), 7.36 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ 142.28, 136.04, 132.20, 129.67, 128.96, 128.42,
125.42, 122.36, 93.70, 86.55, 85.86. HRMS calc’d for C₁₄H₈NO₂I: 348.959973. Found: 348.959869 (Error = 0.30 ppm).

Trimethyl-(2-nitro-4-phenylethynyl-phenylethynyl)-silane (16, DWP-I-20, III-79) ¹⁰ 1-Iodo-2-nitro-4-phenylethynyl-benzene (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 NH₄Cl (aq) and Et₂O. Column chromatography (silica gel using 2:1 hexanes/dichloromethane as eluent; Rf = 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, CDCl₃) δ 8.12 (d, J = 1.5 Hz, 1 H), 7.63 (dd, J = 8.1, 1.6 Hz, 1 H), 7.59 (d, J = 8.1 Hz, 1 H), 7.52 (m, 2 H), 7.36 (m, 3 H), 0.27 (s, 9 H). ¹³C NMR (75 MHz, CDCl₃) δ 150.06, 135.07, 135.02, 131.82, 129.24, 128.55, 127.33, 124.46, 122.04, 117.61, 105.70, 99.21, 93.70, 86.79, 29.73, -0.38. HRMS calc’d for C₁₀H₁₇O₂NSi: 319.1029. Found: 319.1026 (Error=0.9 ppm).

1-Ethynyl-2-nitro-4-phenylethynyl-benzene (11, DWP-III-80) ¹⁰ Trimethyl-(2-nitro-4-phenylethynyl-phenylethynyl)-silane (2.87 g, 8.98 mmol), potassium carbonate
(5.0 g, 36 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following
the general deprotection method described earlier (2.13 g, 96% yield). \(^1\)H NMR (400
MHz, CDCl\(_3\)) \(\delta\) 8.15 (m, 1 H), 7.67 (dd, \(J = 8.0\), 1.5 Hz, 1 H), 7.63 (d, \(J = 8.0\) Hz, 1 H),
7.53 (m, 2 H), 7.36 (m, 3 H), 3.58 (s, 1 H).

![Chemical structure](image)

**Thioacetic acid S-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester**
(12, DWP-III-81).\(^2\)\(^3\) 1-Ethynyl-2-nitro-4-phenylethynyl-benzene (0.500 g, 2.02 mmol)
was coupled with thioacetic acid S-(4-iodo-phenyl) ester (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\(_4\)Cl (aq) and dichloromethane. Column chromatography
(silica gel using 1:1 hexanes/dichloromethane as eluent; Rf = 0.29) followed by
recrystallization from dichloromethane/hexanes afforded the desired compound as a
yellow solid (0.468 g, 58% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.22 (d, \(J = 1.5\) Hz, 1
H), 7.70 (dd, \(J = 8.1\), 1.5 Hz, 1 H), 7.66 (d, \(J = 8.1\) Hz, 1 H), 7.60 (dt, \(J = 8.3\), 1.8 Hz, 2
H), 7.54 (m, 2 H), 7.42 (dt, \(J = 8.2\), 1.8 Hz, 2 H), 7.37 (m, 3 H), 2.43 (s, 3 H).
**4-Ethynyl-2-nitro-1-phenylethynyl-benzene (17, DWP-II-22)**

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 the solution was stirred at RT for 4 h. Flash column chromatography (silica gel using 2:1 hexanes/dichloromethane as eluent) afforded a mixture of products that was taken onto the next step. The product mixture, 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 dichloromethane/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), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection. Flash column chromatography (silica gel using 2:1 dichloromethane/hexanes as eluent) afforded the desired product as a yellow solid (1.14 g, 32% yield).

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, CDCl₃) δ 8.14 (d, J = 0.8 Hz, 1 H), 7.62 (t, J = 0.8 Hz, 2 H), 7.57 (m, 2 H), 7.36 (m, 3 H), 3.28 (s, 1 H).

¹³C NMR (100 MHz, CDCl₃) δ 149.71, 136.23, 134.89, 132.23, 129.95,
128.93, 128.61, 123.15, 122.52, 119.30, 99.62, 85.02, 81.82, 81.39. HRMS calc’d for 
C_{16}H_{9}NO_{2}: 247.0633. Found: 247.0637 (Error = 1.4 ppm).

Thioacetic acid S-[4-(3-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester

(18, DWP-II-27) 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (0.201 g, 0.815 mmol))
was coupled with thioacetic acid S-(4-iodo-phenyl) ester (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
dichloromethane/hexanes as eluent) afforded the desired product as an orange solid
(0.152 g, 52% yield). 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, CDCl₃) δ 8.21 (m, 1
H), 7.68 (m, 2 H), 7.59 (m, 2 H), 7.56 (dt, J =8.1, 1.7 Hz, 2 H), 7.42 (dt, J = 8.2, 1.7 Hz,
2 H), 7.37 (m, 3 H), 2.43 (s, 3 H). ^13C NMR (100 MHz, CDCl₃) δ 193.54, 149.89, 135.69,
134.93, 134.72, 132.73, 132.51, 129.89, 129.68, 128.92, 128.10, 124.07, 123.64, 122.62,
118.78, 99.54, 93.05, 88.76, 85.19, 30.75. HRMS calc’d for C_{24}H_{15}NO_{2}S: 397.0764.
Found: 397.0773 (Error = 2.1 ppm).
2-Nitro-4-trimethylsilanylethynyl-phenylamine (19, DWP-III-53, III-190, 4-45) 4-Iodo-2-nitro-phenylamine (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/dichloromethane as eluent; Rf = 0.43) afforded the desired product as a red-orange solid (5.07 g, 91% yield). 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, CDCl₃) δ 8.24 (d, J = 2.0 Hz, 1 H), 7.39 (dd, J = 8.6, 1.9 Hz, 1 H), 6.71 (d, J = 8.5 Hz, 1 H), 6.17 (br s, 2 H), 0.22 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 144.72, 138.90, 130.46, 119.07, 103.50, 93.95, 0.34. HRMS calc’d for C₁₁H₁₄N₂O₂Si: 234.082457. Found: 234.082512 (Error = 0.23 ppm).

(4-Iodo-3-nitro-phenylethynyl)-trimethyl-silane (20, DWP-III-57, 4-51) To a 500 mL round-bottom flask equipped with a stir bar, cooled to -20°C, was added BF₃ OEt₂ (7.5 mL, 59.16 mmol). 2-Nitro-4-trimethylsilanylethynyl-phenylamine (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 Et₂O were added to effect precipitation of
the diazonium salt. The salt was filtered and washed with cold Et₂O 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 Na₂S₂O₃ (aq) and extracted with dichloromethane. Only a silica plug (with 1:1 hexanes/dichloromethane; Rf = 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, CDCl₃) δ 7.94 (d, J = 8.1 Hz, 1 H), 7.88 (d, J = 1.9 Hz, 1 H), 7.27 (dd, J = 8.1, 1.9 Hz, 1 H), 0.24 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 153.24, 142.15, 136.33, 128.79, 125.20, 101.66, 99.70, 86.26, 0.07. HRMS calc’d for C₁₁H₁₂INO₂Si: 344.968203. Found: 344.968494 (Error = 0.84 ppm).

Trimethyl-(3-nitro-4-phenylethynyl-phenylethynyl)-silane (21, DWP-III-58)

(4-Iodo-3-nitro-phenylethynyl)-trimethyl-silane (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 the solution was stirred at ambient temperature for 1.5 h. Flash column chromatography (silica gel using 1:2 dichloromethane/hexanes as eluent; Rf: 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, CDCl₃) δ 8.13 (m, 1 H), 7.61 (s, 2 H), 7.57 (m, 2 H), 7.37 (m, 3 H), 0.26 (s, 9 H). ¹³C-NMR (100 MHz, CDCl₃) δ 149.72, 135.98, 134.77, 132.49, 129.86, 128.91, 128.42, 124.26, 122.61, 118.75, 102.40, 99.86, 99.38, 85.14, 0.12. HRMS calc’d for C₁₀H₁₇NO₂Si: 319.102858. Found: 319.102382 (Error = 1.5 ppm).

4-Ethynyl-2-nitro-1-phenylethynyl-benzene (17, DWP-III-59) Trimethyl-(3-nitro-4-phenylethynyl-phenylethynyl)-silane (3.40 g, 10.64 mmol), potassium carbonate (5.9 g, 42.56 mmol), methanol (40 mL), and dichloromethane (40 mL) were used following the general procedure for deprotection to afford the desired product (2.46 g, 94% yield) ¹H NMR (400 MHz, CDCl₃) δ 8.16 (t, J = 1.0 Hz, 1 H), 7.64 (d, J = 1.1 Hz, 2 H), 7.58 (m, 2 H), 7.36 (m, 3 H), 3.28 (s, 1 H).

Thioacetic acid S-[4-(3-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (18, DWP-III-60) 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (0.500 g, 2.02 mmol) was coupled with thioacetic acid S-(4-iodo-phenyl) ester (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 NH₄Cl (aq) and diethyl ether. Column chromatography (silica
gel using 1:1 hexanes/dichloromethane as eluent; Rf = 0.36) afforded the desired compound as a yellow solid (0.588 g, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (m, 1 H), 7.68 (m, 2 H), 7.57 (m, 4 H), 7.42 (dt, $J = 8.4$, 1.8 Hz, 2 H), 7.37 (m, 3 H), 2.43 (s, 3 H).

\[ \text{NO}_2 \]
\[ 
\begin{array}{c}
\text{TMS} \equiv \text{C} \equiv \text{C} \equiv \text{TMS}
\end{array}
\]

2-Nitro-1,4-bis-trimethylsilany lethynyl-benzene (22, DWP-II-40, 43) 2,5-Dibromonitrobenzene (3.05 g, 10.9 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 mmol), and TMSA (4.60 mL, 32.6 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/dichloromethane as eluent) afforded the desired product (2.26 g, 66% yield). 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$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (m, 1 H), 7.55 (m, 2 H), 0.25 (d, $J = 0.4$ Hz, 9 H), 0.24 (d, $J = 0.3$ Hz, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.30, 135.80, 135.30, 128.13, 124.60, 118.29, 106.20, 102.27, 99.98, 99.48, 0.09, -0.03. HRMS calc’d for C$_{16}$H$_{21}$NO$_2$Si$_2$: 315.1114. Found: 315.1111 (Error = 1.1 ppm).

\[ \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \]

1,4-Diethynyl-2-nitro-benzene (23, DWP-II-56) 2-Nitro-1,4-bis-trimethylsilany lethynyl-benzene (2.17 g, 6.88 mmol), potassium carbonate (9.5 g, 68.8
mmol), methanol (25 mL), and dichloromethane (25 mL) were used following the general procedure for deprotection to give the desired product (1.17 g, 99%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (m, 1 H), 7.63 (m, 2 H), 3.58 (s, 1 H), 3.29 (s, 1 H).

**Thioacetic acid** $S\{4-[4-(4-acetylsulfanyl-phenylethynyl)-2-nitrophenylethynyl]-phenyl\}$ ester (24, DWP-II-60, III-165) 1,4-Diethynyl-2-nitro-benzene (1.79 g, 10.48 mmol) was coupled with 2 equivalents of thioacetic acid $S\{4-iodo-phenyl\}$ ester (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$_4$Cl (aq) and dichloromethane. Column chromatography (silica gel using 1:3 hexanes/dichloromethane as eluent; $R_f = 0.49$) afforded the desired compound as a yellow solid (2.445 g, 50% yield). $\text{IR (KBr)}$ 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$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21 (d, $J = 1.3$ Hz, 1 H), 7.69 (dd, $J = 8.1$, 1.5 Hz, 1 H), 7.67 (d, $J = 8.0$ Hz, 1 H), 7.60 (dt, $J = 8.4$, 1.8 Hz, 2 H), 7.56 (dt, $J = 8.3$, 1.8 Hz, 2 H), 7.42 (d, $J = 7.9$ Hz, 4 H), 2.430 (s, 3 H), 2.427 (s, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.52, 193.49, 149.90, 135.75, 135.00, 134.72, 134.68, 132.98, 132.74, 130.00, 129.75, 128.15, 124.43, 123.74, 123.57, 118.36, 98.47, 93.28, 88.70, 86.64, 30.76. HRMS calc’d for C$_{28}$H$_{17}$NO$_4$S$_2$: 471.059903. Found: 471.060194 (Error = 0.62 ppm).
4-(2-Nitro-4-phenylethynyl-phenylethynyl)-benzenethiol (25, DWP-III-90)

Thioacetic acid S-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (0.100 g, 0.25 mmol) was added to a 10 mL round-bottom flask equipped with a stir bar. Air was removed and nitrogen backfilled (3×). Methanol (3 mL) and THF (3 mL) were added followed by concentrated H₂SO₄ (2 drops). After 3 h, 2 additional drops of H₂SO₄ were added. After an additional 2 h, the flask was placed in a 50°C oil bath for 45 min (6 h total reaction time). The mixture was washed with water and dichloromethane. Column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent; Rf = 0.72) afforded 0.066 g as a mixture of product and disulfide (~80:20 respectively). IR (KBr) 3446.4, 2914.4, 2550.8, 2207.7, 1538.8, 1504.9, 1343.0, 1101.6, 819.9, 753.3, 686.8, 512.7 cm⁻¹.

1,4-Bis-(4-sulfanyl-phenylethynyl)-2-nitrobenzene (26, DWP-II-179, III-184)

Thioacetic acid S-[4-{4-(4-acetysulfanyl-phenylethynyl)-2-nitro-phenylethynyl}-phenyl] ester (0.500 g, 1.06 mmol), dichloromethane (30 mL), methanol (30 mL) and a stir bar were placed in a 200 mL round-bottom flask. Concentrated H₂SO₄ (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 dichloromethane. ¹H NMR showed a mixture of ~2:1 product:starting material. The reaction was resubjected 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 dichloromethane/hexanes afforded the desired product (0.315 g, 77% yield). 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, CDCl₃) δ 8.18 (m, 1 H), 7.64 (m, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 7.38 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 5.6 Hz, 4 H), 3.545 (s, 1 H), 3.539 (s, 1 H). ¹³C-NMR (100 MHz, CDCl₃) δ 149.74, 135.56, 134.78, 134.19, 133.79, 133.01, 132.72, 129.28, 129.20, 127.97, 124.36, 119.64, 119.49, 118.39, 98.93, 93.56, 87.73, 85.78

![Chemical structure](image)

4-(4-Bromo-phenylsulfanyl)-ethyl]-trimethyl-silane (27, DWP-II-18, 28)²³ 4-Bromothiophenol (1.00 g, 5.29 mmol) was added to a 5 mL round bottom flask containing a stir bar. Air was removed and N₂ backfilled (3 ×). Vinyltrimethylsilane (0.936 mL, 6.06 mmol) and t-butylperoxide (0.14 mL, 0.74 mmol) were added to the flask under N₂. The mixture was then heated in a 100 °C oil bath for 7.5 h. The reaction was then cooled to RT, diluted with hexanes, washed with 10% NaOH solution, and dried over magnesium sulfate. Flash column chromatography (silica gel using hexanes as eluent) afforded the desired product (0.459 g, 30%). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (dt, J = 8.5, 1.7 Hz, 2 H), 7.14 (dt, J = 1.9 Hz, 2 H), 2.91 (m, 2 H), 0.89 (m, 2 H), 0.02 (s, 9 H).
[2-(4-Iodo-phenylsulfanyl)-ethyl]-trimethyl-silane (28, DWP-II-68)\(^{23}\) [2-(4-
Bromo-phenylsulfanyl)-ethyl]-trimethyl-silane (0.995, 3.44 mmol) was added to a 100
mL round bottom flask containing a stir bar. Air was removed and nitrogen backfilled (3
\(\times\)). Et\(_2\)O (25 mL) was added and the solution was cooled to -78 °C. Next, \(\tau\)-butyl
lithium (4.25 mL, 7.23 mmol) was slowly added to the flask and allowed to stir for 40
min. A cooled solution of iodine (1.135 g, 4.47 mmol) in Et\(_2\)O was cannulated to the
flask and stirred for 10 min before warming to 0 °C. The solution was stirred for 30 min
and washed with a sodium thiosulfate solution before drying over magnesium sulfate.
Flash column chromatography (silica gel using hexanes as eluent) afforded the desired
product (0.430 g, 37%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (dt, \(J = 8.4, 1.7\) Hz, 2 H),
6.99 (dt, \(J = 8.3, 1.7\) Hz, 2 H), 2.91 (m, 2 H), 0.89 (m, 2 H), 0.02 (d, \(J = 0.3\) Hz, 9 H).

Trimethyl-[2-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenylsulfanyl]-
ethyl]-silane (29, DWP-II-72) 1-Ethynyl-2-nitro-4-phenylethynyl-benzene (0.081 g,
0.327 mmol)) was coupled with [2-(4-Iodo-phenylsulfanyl)-ethyl]-trimethyl-silane (0.100
g, 0.297 mmol) using the Pd/Cu cross coupling method described earlier using
bis(triphenylphosphine)palladium(II) dichloride (0.011 g, 0.016 mmol), copper(I) iodide
(0.006 g, 0.032 mmol), THF (10 mL), and DIEA (0.23 mL, 1.31 mmol) in an oven dried
screw cap tube under nitrogen. The solution was stirred in a 50 °C oil bath for 1 d.
Column chromatography (silica gel using 1:1 dichloromethane/hexanes as eluent)
afforded the desired product as an orange-red solid (0.080 g, 59% yield). IR (KBr) 3414.5, 2955.3, 2919.5, 2888.8, 2203.0, 1716.1, 1587.8, 1540.7, 1502.7, 1342.1, 1268.8, 1247.2, 1087.1, 858.7, 837.6, 758.6, 691.0, 525.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 1.5 Hz, 1 H), 7.67 (dd, J = 8.1, 1.6 Hz, 1 H), 7.64 (d, J = 8.1 Hz, 1 H), 7.53 (m, 2 H), 7.48 (d, J = 8.2 Hz, 2 H), 7.37 (m, 3 H), 7.22 (m, 2 H), 2.98 (m, 2 H), 0.94 (m, 2 H), 0.05 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.73, 140.72, 135.63, 134.76, 132.74, 132.21, 129.58, 128.94, 128.04, 127.82, 124.32, 122.52, 119.12, 118.55, 99.39, 93.94, 87.33, 85.63, 29.04, 16.96, -1.34. HRMS calc’d for C₂₇H₂₅NO₂SSi: 455.1375. Found: 455.1384 (Error = 1.9 ppm).

4,4'-Dibromo-2,3'-dinitro-biphenyl (30, DWP-I-250, II-92, III-11, 4-84)¹⁵

Nitric acid (70%, 30.6 mL) was added to a 100 mL round bottom flask containing a stir bar and cooled to approximately 0 °C in an ice bath. 4,4'-Dibromobiphenyl (4.01 g, 12.85 mmol) was then slowly added to the acid and the mixture was stirred at 0 °C for 40 min. Ice water was then added to the mixture at which point a light yellow solid precipitated out of the solution. The solid was filtered and washed with water then air-dried. Recrystallization from ethanol/acetone afforded the desired product as yellow needles (3.59 g, 70% yield): mp 150-151 °C (lit. mp 152-153 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, J = 2.0 Hz, 1 H), 7.82 (dd, J = 8.3, 2.0 Hz, 1 H), 7.79 (d, J = 0.4 Hz, 1 H), 7.78 (d, J = 6.8 Hz, 1 H), 7.30 (dd, J = 8.2, 2.2 Hz, 1 H), 7.29 (d, J = 8.1 Hz, 1 H).
(4'-Bromo-3,2'-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (31, DWP-II-20) 4,4'-Dibromo-2,3'-dinitrobiphenyl (1.00 g, 2.49 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.088 g, 0.125 mmol), copper(I) iodide (0.047 g, 0.249 mmol), THF (10 mL), DIEA (1.73 mL, 9.96 mmol), and TMSA (0.39 mL, 2.7 mmol) were used for 4 h at RT following the general procedure for couplings. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product as a brown solid (0.605 g, 58% yield): mp 106-108°C. IR (KBr) 3098.7, 3068.3, 2955.3, 2852.9, 2069.4, 1597.9, 1525.5, 1462.9, 1347.1, 1250.9, 1152.4, 1099.1, 1036.9, 866.9, 840.2, 826.6, 760.3, 536.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 1.8 Hz, 1 H), 7.93 (d, J = 1.8 Hz, 1 H), 7.80 (dd, J = 8.1, 1.9 Hz, 1 H), 7.66 (d, J = 7.9 Hz, 1 H), 7.42 (dd, J = 8.0, 1.8 Hz, 1 H), 7.30 (d, J = 8.3 Hz, 1 H), 0.26 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.44, 149.04, 137.98, 136.62, 135.81, 133.45, 132.89, 132.45, 128.23, 124.42, 123.48, 118.86, 106.01, 99.30, 0.01. HRMS calc’d for C₁₇H₁₅N₂O₄BrSi: 419.9967. Found: 419.9963 (Error = 0.9 ppm).

(3,2'-Dinitro-4'-phenylethylnyl-biphenyl-4-ylethynyl)-trimethyl-silane (32, DWP-II-21) (4'-Bromo-3,2'-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (0.509 g, 1.21 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.043 g, 0.061 mmol), copper(I) iodide (0.023 g, 0.121 mmol), triphenylphosphine (0.032 g, 0.121 mmol), THF (20 mL), DIEA (0.84 mL, 4.84 mmol), and phenylacetylene (0.20 mL, 1.82 mmol) were
used following the general procedure for couplings. The tube was capped and the solution was heated in a 70 °C oil bath for 1 d. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product as a brown oil (0.355 g, 67% yield). IR (KBr) 3065.8, 2958.3, 2883.6, 2213.7, 2160.5, 1530.7, 1490.9, 1347.7, 1249.5, 1078.8, 891.0, 844.6, 756.4, 689.6, 527.2 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 1.6 Hz, 1 H), 8.00 (d, J = 1.8 Hz, 1 H), 7.78 (dd, J = 8.0, 1.6 Hz, 1 H), 7.68 (d, J = 8.0 Hz, 1 H), 7.55 (m, 2 H), 7.45 (dd, J = 8.0, 1.8 Hz, 1 H), 7.39 (m, 4 H), 0.29 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.52, 148.77, 138.46, 135.94, 135.74, 133.20, 132.47, 132.26, 132.23, 129.73, 128.98, 127.97, 125.92, 124.49, 122.34, 118.79, 105.92, 99.38, 93.76, 86.74, 0.01. HRMS calc’d for C₂₅H₂₀N₂O₄Si: 440.1192. Found: 440.1187 (Error = 1.2 ppm).

4'-Ethynyl-2,3'-dinitro-4-phenylethynyl-biphenyl (33, DWP-II-64, 4-93) (3,2'-Dinitro-4'-phenylethynyl-biphenyl-4-ylethynyl)-trimethyl-silane (0.334 g, 0.758 mmol), potassium carbonate (0.524 g, 3.79 mmol), methanol (20 mL), and dichloromethane (20 mL) were used following the general procedure for deprotection to afford the desired product as a brown oil (0.274 g, 98% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 1.5 Hz, 1 H), 8.02 (d, J = 1.7 Hz, 1 H), 7.78 (dd, J = 8.0, 1.6 Hz, 1 H), 7.71 (d, J = 8.0 Hz, 1 H), 7.55 (m, 2 H), 7.48 (dd, J = 8.0, 1.8 Hz, 1 H), 7.38 (m, 4 H), 3.58 (s, 1 H).
**Thioacetic acid S-[4-(3,2'-dinitro-4'-phenylethynyl-biphenyl-4'-ylethynyl)-phenyl] ester (34, DWP-II-66, 4-95)**

4'-Ethynyl-2,3'-dinitro-4-phenylethynyl-biphenyl (1.10 g, 2.99 mmol) was coupled with thioacetic acid S-(4-iodo-phenyl) ester (0.831 g, 2.99 mmol) using the Pd/Cu cross coupling method described earlier using bis(dibenzylideneacetone)palladium(0) (0.086 g, 0.149 mmol), copper(I) iodide (0.057 g, 0.30 mmol), triphenylphosphine (0.157 g, 0.60 mmol), THF (20 mL), and DIEA (2.1 mL, 12.0 mmol) in a screw cap tube under nitrogen. The solution was stirred in a 50 °C oil bath for 3 h. Column chromatography (silica gel using dichloromethane as eluent; Rf = 0.70) afforded the desired product as an orange solid (0.981 g, 63% yield): mp 156-158°C. IR (KBr) 3078.2, 2924.6, 2858.0, 2207.6, 1709.0, 1528.4, 1495.7, 1346.2, 1280.9, 1112.6, 846.6, 827.0, 760.8, 691.0, 618.5 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.13 (d, \(J = 1.6\) Hz, 1 H), 8.09 (d, \(J = 1.9\) Hz, 1 H), 7.79 (dd, \(J = 8.0, 1.7\) Hz, 1 H), 7.74 (d, \(J = 8.1\) Hz, 1 H), 7.62 (dt, \(J = 8.2, 1.8\) Hz, 2 H), 7.56 (m, 2 H), 7.51 (dd, \(J = 8.1, 1.8\) Hz, 1 H), 7.43 (m, 3 H), 7.38 (m, 3 H), 2.43 (s, 3 H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.51, 149.97, 148.79, 138.47, 135.99, 135.28, 134.69, 133.20, 133.02, 132.72, 132.27, 132.26, 130.00, 129.73, 128.99, 128.01, 125.97, 124.82, 123.76, 122.35, 118.84, 97.98, 93.79, 86.74, 86.43, 30.76. HRMS calc’d for C\(_{30}\)H\(_{18}\)N\(_2\)O\(_5\)S: 518.0936. Found: 518.0947 (Error = 2.0 ppm).
2,3'-Dinitro-4,4'-bis-trimethylsilylethylenebiphenyl (35, DWP-III-17, 15)

4,4'-Dibromo-2,3'-dinitro-biphenyl\textsuperscript{25} (1.50 g, 3.73 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.131 g, 0.187 mmol), copper(I) iodide (0.071 g, 0.373 mmol), THF (20 mL), DIEA (5.2 mL, 30 mmol) and TMSA (1.32 mL, 9.33 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at ambient temperature for 17 h. Flash column chromatography (silica gel using 1:1 dichloromethane/hexanes as eluent; Rf: 0.59) afforded the desired product (1.20 g, 74% yield): mp 82-90\degree C. IR (KBr) 3073.1, 2960.4, 2899.2, 2164.0, 1533.8, 1477.8, 1348.8, 1250.8, 1219.9, 1079.1, 847.5, 760.3, 643.0 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.07 (d, \( J = 1.6 \) Hz, 1 H), 8.00 (d, \( J = 1.8 \) Hz, 1 H), 7.74 (dd, \( J = 8.0, 1.6 \) Hz, 1 H), 7.70 (d, \( J = 8.0 \) Hz, 1 H), 7.46 (dd, \( J = 8.0, 1.9 \) Hz, 1 H), 7.39 (d, \( J = 7.9 \) Hz, 1 H), 0.31 (s, 9 H), 0.30 (s, 9 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 150.49, 148.61, 138.39, 136.29, 135.72, 133.47, 132.43, 132.10, 128.36, 125.70, 124.45, 118.77, 105.88, 101.84, 99.72, 99.34, 0.10, -0.01. HRMS calc’d for C\textsubscript{22}H\textsubscript{24}N\textsubscript{2}O\textsubscript{4}Si\textsubscript{2}: 436.127465. Found: 436.126508. (Error = 2.2 ppm).

4,4'-Diethynyl-2,3'-dinitro-biphenyl (36, DWP-III-19, 4-104) 2,3'-Dinitro-4,4'-bis-trimethylsilylethylenebiphenyl (0.815 g, 1.87 mmol), potassium carbonate (1.55 g, 11.2 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection to afford the desired product (0.508 g, 93% yield).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.14 (d, \(J = 1.3\) Hz, 1 H), 8.06 (d, \(J = 1.7\) Hz, 1 H), 7.79 (m, 2 H), 7.51 (dd, \(J = 7.9, 1.7\) Hz, 1 H), 7.44 (d, \(J = 8.0\) Hz, 1 H), 3.63 (s, 1 H), 3.33 (s, 1 H).

**Thioacetic acid S-\{4-\{4'-\{4-acetylsulfanyl-phenylethynyl\}-phenylethynyl\}-3,2'-dinitro-biphenyl\}-4-ylethynyl\}\-phenyl) ester (37, DWP-III-21, 4-106) 4,4'-Diethynyl-2,3'-dinitro-biphenyl (1.26 g, 4.31 mmol), bis(dibenzyldieneacetone)palladium(0) (0.124 g, 0.216 mmol), copper(I) iodide (0.082 g, 0.431 mmol), triphenylphosphine (0.226 g, 0.862 mmol), THF (20 mL), DIEA (4.5 mL, 25.9 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (2.40 g, 8.62 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at 55°C for 4.5 h. Flash column chromatography (silica gel using dichloromethane as eluent; Rf: 0.45) followed by precipitation from dichloromethane/hexanes afforded the desired product as a slightly yellow solid (1.52 g, 59% yield): mp 176-179°C (decomp.). IR (KBr) 3073.1, 2211.7, 1709.3, 1534.1, 1348.8, 1118.5, 951.2, 827.0, 623.5 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.15 (d, \(J = 1.7\) Hz, 1 H), 8.11 (d, \(J = 1.8\) Hz, 1 H), 7.82 (dd, \(J = 8.0, 1.6\) Hz, 1 H), 7.77 (d, \(J = 8.1\) Hz, 1 H), 7.64 (dt, \(J = 8.2, 1.7\) Hz, 2 H), 7.59 (dt, \(J = 8.2, 1.7\) Hz, 2 H), 7.53 (dd, \(J = 8.0, 1.8\) Hz, 1 H), 7.45 (m, 5 H), 2.452 (s, 3 H), 2.446 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.51, 149.99, 148.82, 138.38, 136.05, 135.30, 134.75, 134.69, 133.51, 133.02, 132.78, 132.69, 132.32, 130.01, 129.86, 128.11, 125.57, 124.82, 123.75, 123.46, 118.93, 98.04, 92.88, 88.17, 86.40, 30.77. MALDI-MS calc’d for C\(_{22}\)H\(_{24}\)N\(_2\)O\(_4\)Si\(_2\): 593, Found: 593.
4,4'-Dibromo-2,2'-dinitro-biphenyl (38, DWP-I-142, 212, II-90, 105, 110, III-109, 113, 205).26 2,5-Dibromonitrobenzene (18.0 g, 64.1 mmol), copper powder (9.00 g, 141 mmol), DMF (120 mL), and a stir bar were added to a 250 mL round bottom flask equipped with a West condenser. The flask was heated in a 120°C oil bath for 2 h. The solution was filtered and diluted with water to precipitate yellow-brown crystals. Flash chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded pale yellow crystals (4.8 g, 75% yield): 149-150°C (lit. mp 146-148°C).26 1H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 2.0 Hz, 2 H), 7.81 (dd, J = 8.2, 2.0 Hz, 2 H), 7.14 (d, J = 8.2 Hz, 2 H). 13C NMR (100 MHz, CDCl₃) δ147.79, 137.04, 132.45, 132.39, 128.48, 123.33.

(4'-Bromo-2,2'-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (39, DWP-II-70) 4,4'-Dibromo-2,2'-dinitrophenyl17 (4.00 g, 9.95 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.211 g, 0.300 mmol), copper(I) iodide (0.114 g, 0.597 mmol), THF (20 mL), DIEA (6.9 mL, 40 mmol), and TMSA (1.49 mL, 10.5 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 5 h. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product as a viscous brown oil (1.923 g, 46% yield). IR (KBr) 3083.4, 2958.5, 2899.0, 2868.3, 2177.0, 1530.8, 1346.2, 1249.7, 845.4, 760.2 cm⁻¹. 1H NMR (400 MHz, CDCl₃) δ 8.34
(d, J = 2.0 Hz, 1 H), 8.26 (d, J = 1.6 Hz, 1 H), 7.79 (dd, J = 8.1, 2.0 Hz, 1 H), 7.71 (dd, J = 7.9, 1.7 Hz, 1 H), 7.19 (d, J = 8.1 Hz, 1 H), 7.14 (d, J = 8.1 Hz, 1 H), 0.27 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.80, 147.21, 136.97, 136.82, 133.17, 133.00, 132.48, 131.18, 128.53, 128.36, 125.60, 123.11, 102.01, 99.35, 0.14. HRMS calc'd for C$_{17}$H$_{15}$N$_2$O$_4$BrSi: 417.9985. Found: 417.9989 (Error = 1.0 ppm).

![Chemical Structure](image)

**(2,2'-Dinitro-4'-phenylethynyl-biphenyl-4-ylyethynyl)-trimethyl-silane** (40, DWP-II-73) (4'-Bromo-2,2'-dinitro-biphenyl-4-ylyethynyl)-trimethyl-silane (1.91 g, 4.55 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.136 mmol), copper(I) iodide (0.052 g, 0.273 mmol), THF (20 mL), DIEA (3.2 mL, 18 mmol), and phenylacetylene (0.60 mL, 5.5 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 1 d, followed by heating to 50 °C for 2 h. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product as a yellow-brown solid (1.54 g, 77% yield): 143-146°C. IR (KBr) 3083.4, 2957.7, 2888.8, 2207.7, 2161.6, 1529.3, 1349.0, 1249.4, 1217.1, 1004.2, 843.8, 756.2, 689.2, 517.8 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.32 (d, J = 1.5 Hz, 1 H), 8.28 (d, J = 1.5 Hz, 1 H), 7.76 (dd, J = 7.9, 1.6 Hz, 1 H), 7.71 (dd, J = 7.9, 1.5 Hz, 1 H), 7.56 (m, 2 H), 7.37 (m, 3 H), 7.22 (d, J = 7.9 Hz, 1 H), 7.21 (d, J = 7.9 Hz, 1 H), 0.30 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.40, 147.31, 136.79, 136.42, 133.83, 133.44, 132.28, 131.37, 131.32, 129.65, 128.99, 128.47,
128.04, 125.62, 125.40, 122.50, 102.19, 99.17, 93.31, 86.97, 0.18. HRMS calc’d for 
C_{25}H_{20}N_2O_4Si: 440.1192. Found: 440.1187 (Error = 1.3 ppm).

![Chemical structure](image)

4'-Ethynyl-2,2'-dinitro-4-phenylethynyl-biphenyl (41, DWP-II-77) (2,2'-
Dinitro-4'-phenylethynyl-biphenyl-4-ylethynyl)-trimethyl-silane (1.50 g, 3.41 mmol),
potassium carbonate (1.89 g, 13.7 mmol), methanol (20 mL), and dichloromethane (20 mL) were used following the general procedure for deprotection to afford the desired product as a viscous brown oil (1.21 g, 97% yield). ^1H NMR (400 MHz, CDCl₃) δ 8.35
(d, J = 1.6 Hz, 1 H), 8.31 (d, J = 1.6 Hz, 1 H), 7.77 (m, 2 H), 7.57 (m, 2 H), 7.38 (m, 3 H),
7.25 (m, 2 H), 3.27 (s, 1 H).

![Chemical structure](image)

Thioacetic acid S-[4-(2,2'-dinitro-4'-phenylethynyl-biphenyl-4-ylethynyl)-
phenyl] ester (42, DWP-II-79) 4'-Ethynyl-2,2'-dinitro-4-phenylethynyl-biphenyl (1.21 g,
3.30 mmol)) was coupled with thioacetic acid S-(4-iodo-phenyl) ester (0.917 g, 3.30 mmol) using the Pd/Cu cross coupling method described earlier using bis(dibenzylideneacetone)palladium(0) (0.380 g, 0.660 mmol), copper(I) iodide (0.126 g, 0.660 mmol), triphenylphosphine (0.433 g, 1.65 mmol), THF (25 mL), and DIEA (1.15 mL, 6.60 mmol) in a 100 mL round bottom flask under nitrogen. The solution was
stirred in a 40 °C oil bath for 1 d. Column chromatography (silica gel using 2:1
dichloromethane/hexanes as eluent) afforded the desired product as a green-yellow solid
(1.23 g, 72% yield). IR (KBr) 3078.2, 2919.5, 2842.7, 2207.7, 1698.9, 1526.2, 1350.6, 1111.8, 1088.9, 826.4, 762.0, 691.1, 617.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 1.5 Hz, 2 H), 7.79 (dd, J = 8.0, 1.7 Hz, 2 H), 7.58 (m, 4 H), 7.43 (dt, 8.0, 1.7 Hz, 2 H), 7.39 (m, 3 H), 7.28 (d, J = 8.0 Hz, 1 H), 7.27 (d, J = 7.9 Hz, 1 H), 2.44 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 193.55, 147.48, 147.45, 136.46, 136.42, 134.74, 133.82, 133.40, 132.78, 132.27, 131.43, 131.34, 129.71, 129.63, 128.96, 128.20, 128.13, 125.70, 125.24, 126.63, 122.48, 93.30, 92.37, 88.39, 86.90, 30.77. HRMS calc’d for C₃₀H₁₈N₂O₅S: 518.0936. Found: 518.0941 (Error = 0.79 ppm).

![Chemical structure](attachment:structure.png)

**2,2'-Dinitro-4,4'-bis-trimethylsilanylethynyl-biphenyl (43, DWP-III-14)**

2,2'-Dinitro-4,4'-dibromobiphenyl²⁶ (1.50 g, 3.73 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.131 g, 0.187 mmol), copper(I) iodide (0.071 g, 0.373 mmol), THF (20 mL), DIEA (5.20 mL, 29.8 mmol) and TMSA (1.32 mL, 9.33 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 45 °C oil bath for 3 h. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (1.3 g, 80% yield): mp 82-90°C. IR (KBr) 3083.4, 2959.3, 2899.0, 2166.8, 1530.8, 1350.2, 1250.3, 1219.2, 930.2, 844.7, 753.3, 644.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, J = 1.6 Hz, 2 H), 7.75 (dd, J = 7.9, 1.7 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 0.31 (s, 18 H). ¹³C NMR (100 MHz, CDCl₃) δ 147.06, 136.51, 133.54, 130.97, 128.31, 125.23, 101.88,
98.96, -0.07. HRMS calc’d for C₂₂H₂₄N₂O₄Si₂: 436.127465. Found: 436.126915. (Error = 1.3 ppm).

4,4′-Diethynyl-2,2′-dinitro-biphenyl (44, DWP-III-18) 2,2′-Dinitro-4,4′-bis-trimethylsilany lethynyl-biphenyl (1.31 g, 3.00 mmol), potassium carbonate (2.49 g, 18.0 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection to afford the desired product (0.825 g, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 1.5 Hz, 2 H), 7.80 (dd, J = 7.9, 1.6 Hz, 2 H), 7.27 (d, J = 7.9 Hz, 2 H), 3.31 (s, 2 H).

Thioacetic acid S-{4-[4′-(4-acetylsulfanyl-phenylethynyl)-2,2′-dinitro-biphenyl-4-ylethynyl]-phenyl] ester (45, DWP-III-20) 4,4′-Diethynyl-2,2′-dinitro-biphenyl (0.825 g, 2.82 mmol), bis(dibenzylideneacetone)palladium(0) (0.324 g, 0.564 mmol), copper(I) iodide (0.107 g, 0.564 mmol), triphenylphosphine (0.370 g, 1.41 mmol), THF (20 mL), DIEA (2.0 mL, 11.3 mmol), and thioacetic acid S-(4-ido-phenyl) ester (1.65 g, 5.92 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at ambient temperature for 1 d. Flash column chromatography (silica gel using dichloromethane as eluent; Rf: 0.46) followed by precipitation from dichloromethane/hexanes afforded the desired product as slightly
yellow solid (0.434 g, 26% yield): mp 160-173°C (decomp.). IR (KBr) 3083.4, 2202.6, 1716.5, 1524.4, 1347.7, 1117.3, 828.6, 597.6 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.40 (d, \(J = 1.5\) Hz, 2 H), 7.83 (dd, \(J = 8.0, 1.7\) Hz, 2 H), 7.62 (dt, \(J = 8.5, 1.8\) Hz, 4 H), 7.47 (dt, \(J = 8.5, 1.8\) Hz, 4 H), 7.32 (d, \(J = 7.9\) Hz, 2 H), 2.47 (s, 6 H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.56, 147.43, 136.52, 134.74, 133.74, 132.79, 131.43, 129.73, 128.20, 125.26, 123.60, 92.41, 88.40, 30.78.

![Chemical structure](attachment:image.png)

\(\textit{N(-2'\text{-Acetylamino-4,4'-dibromo-biphenyl-2-yl)-acetamide}}\) (46 DWP-II-130, III-94, 95, 111, 112, 120, 121, 159, 160, 206, 207) 4,4'-Dibromo-2,2'-dinitro-biphenyl (5.75 g, 14.3 mmol), ethanol (70 mL) and concentrated HCl (25 mL) were added to a 250 mL round-bottom flask.\(^{26}\) Tin powder (6.79 g, 57.2 mmol) was then added slowly while stirring. The mixture was then heated to reflux for 30 min before being poured into ice and water. The product was extracted with ethyl acetate and washed with NaOH (aq). The crude diamine was then placed in a 250 mL round-bottom flask with glacial acetic acid (6.2 mL) and a stir bar. Acetic anhydride (5.4 mL, 57.2 mmol) was then added and the flask was heated in a 70°C oil bath for 40 min. Water was then added and the mixture neutralized with NaOH (aq). The crude product was extracted with ethyl acetate. Column chromatography (silica gel using 1:1 dichloromethane/ethyl acetate as eluent; \(Rf = 0.46\)) afforded the desired compound (5.17 g, 85% yield): mp 127-129°C. IR (KBr) 3412.0, 3277.6, 3109.0, 3047.5, 3011.7, 1675.5, 1564.9, 1510.4, 1450.2, 1397.4, 1367.8, 1278.7, 1083.9, 1003.0, 879.6, 813.2, 686.1, 602.9, 502.4 cm\(^{-1}\). \(^1\)H NMR (400 MHz,
CDCl$_3$ $\delta$ 8.28 (br s, 2 H), 7.35 (dd, $J$ = 8.2, 1.9 Hz, 2 H), 7.01 (d, $J$ = 8.1 Hz, 2 H), 6.91 (br s, 2 H), 1.96 (s, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.49, 136.95, 131.97, 128.90, 127.38, 126.94, 123.80, 24.54. HRMS calc’d for C$_{16}$H$_{14}$N$_2$O$_2$Br$_2$: 425.940305. Found: 425.940263 (Error = 0.099 ppm).

\[ \text{NHAc} \quad \text{NO}_2 \]
\[ \text{O}_2\text{N} \quad \text{AcmN} \]

$N$-$\text{(2’-Acetylamino-4,4’-dibromo-5,5’-dinitro-biphenyl-2-yl)-acetamide}$ (47, DWP-I-237, II-135 III-125, 127, 163, 4-4) To a 500 mL round-bottom flask was added conc. H$_2$SO$_4$ (85 mL) followed by the slow addition of $N$-$\text{(2’-acetylamino-4,4’-dibromo-biphenyl-2-yl)-acetamide}$ (8.90 g, 20.9 mmol). The mixture was cooled to $-10^\circ$C and a solution of conc. H$_2$SO$_4$ (50 mL) and conc. HNO$_3$ (50 mL) was added slowly over 2.25 h. The mixture was allowed to warm to 10$^\circ$C over 1 h before being poured onto ice and extracted with ethyl acetate. Column chromatography (silica gel using 2:1 dichloromethane/ethyl acetate; Rf = 0.49) afforded the desired compound (8.11 g, 75% yield): mp 252-254$^\circ$C. IR (KBr) 3385.5, 3355.1, 3114.1, 3073.1, 3037.3, 1704.7, 1599.3, 1552.2, 1533.0, 1495.2, 1329.1, 1233.8, 1049.2, 1004.6, 839.3, 666.8 cm$^{-1}$. $^1$H NMR (200 MHz, acetone-\text{d}_6) $\delta$ 9.03 (br s, 2 H), 8.70 (m, 2 H), 8.06 (s, 2 H), 1.97 (s, 6 H). $^{13}$C NMR (100 MHz, acetone-\text{d}_6) $\delta$ 169.66, 145.54, 141.55, 129.24, 128.66, 128.56, 126.86, 115.14, 23.49. HRMS calc’d for C$_{16}$H$_{12}$Br$_2$N$_4$O$_6$: 513.912380. Found: 513.912528 (Error = 0.29 ppm).
4,4'-Dibromo-5,5'-dinitro-biphenyl-2,2'-diamine (48, DWP-II-192, 188, III-128, 129, 133, 167, 4-7) To a 100 mL round-bottom flask was added conc. H₂SO₄ (30 mL) followed slowly by N-(2'-acetylamino-4,4'-dibromo-5,5'-dinitro-biphenyl-2-yl)-acetamide (1.00 g, 1.94 mmol). Water was added (20 mL) slowly over 30 min (temperature reached 90°C). The flask was placed in a 90°C oil bath for 1 h, at which point water (30 mL) was added and the reaction mixture cooled to ~50°C. The mixture was then poured onto ice and the solid was filtered to give the desired product as a yellow solid (0.805 g, 96% yield): mp >300°C. IR (KBr) 3463.3, 3375.0, 1628.5, 1586.0, 1541.8, 1500.5, 1297.9, 1250.1, 1116.9, 1060.6 cm⁻¹. ¹H NMR (400 MHz, acetone-d₆) δ 7.94 (s, 2 H), 7.23 (s, 2 H), 6.01 (br s, 4 H). ¹³C NMR (125 MHz, acetone-d₆) δ 152.10, 130.86, 120.01, 119.22, 117.05. HRMS calc’d for C₁₂H₈N₄O₄Br₂: 429.891251. Found: 429.891129 (Error = 0.28 ppm).

4-Bromo-5,5'-dinitro-4-phenylethynyl-biphenyl-2,2'-diamine (DWP-II-198)

4,4'-Dibromo-5,5'-dinitro-biphenyl-2,2'-diamine (0.900 g, 2.08 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.073 g, 0.104 mmol), copper(I) iodide (0.040 g, 0.21 mmol), THF (25 mL), DIEA (1.45 mL, 8.32 mmol), and phenylacetylene (0.25 mL, 2.3 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 1 d. Flash column chromatography
(silica gel using 1:1 hexanes/ethyl acetate as eluent; Rf: 0.51) afforded an inseparable mixture of products and starting material (0.784 g) which was taken onto the next step.

4'-Bromo-2,5,2',5'-tetranitro-4-phenylethynyl-biphenyl (49, DWP-II-200) To a small plastic bottle with a stir bar was added acetonitrile (90 mL) and water (3 mL). The solution was cooled to −25 °C and 20% F₂ in He was bubbled through at 70 cc/min for 2.5 h. The F₂ flow was turned off and He was bubbled through for 15 min at 70 cc/min to removed any excess F₂. 4-Bromo-5,5'-dinitro-4-phenylethynyl-biphenyl-2,2'-diamine (0.784 g as a mixture) in acetone (10 mL) was then added to the solution and stirred for 2.5 min before being poured into a saturated sodium bicarbonate solution. The material was washed with water and extracted with dichloromethane. Column chromatography (silica gel using 2:1 dichloromethane/hexanes as eluent) afforded the desired product as an orange solid (0.120 g, 11% yield over 2 steps). IR (KBr) 3098.7, 2202.6, 1544.6, 1341.8, 1265.4, 912.1, 835.3, 753.3, 681.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 1 H), 8.62 (s, 1 H), 8.08 (s, 1 H), 7.88 (s, 1 H), 7.69 (m, 2 H), 7.48 (m, 3 H). HRMS calc'd for C₂₀H₁₀N₄O₈Br: 511.960386. Found: 511.959830 (Error = 1.1 ppm).
Thioacetic acid \( S-[4-2,5,2',5'-\text{tetranitro-4'-phenylethynyl-biphenyl-4-ylthynyl}]-\text{phenyl} \) ester (50, DWP-II-202, III-88) 4'-Bromo-2,5,2',5'-tetranitro-4-phenylethynyl-biphenyl (0.110 g, 0.214 mmol), bis(dibenzylideneacetone)palladium(0) (0.025 g, 0.043 mmol), copper(I) iodide (0.008 g, 0.043 mmol), triphenylphosphine (0.023 g, 0.086 mmol), THF (15 mL), DIEA (0.075 mL, 0.43 mmol), and 4-thioacetyl-1-ethynylbenzene\(^{28}\) (0.049 g, 0.278 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 2 h and then at 50 °C for 1 h. Flash column chromatography (silica gel using 1:2 hexanes/dichloromethane as eluent) followed by precipitation from dichloromethane/hexanes afforded the desired product as an orange solid (0.031 g, 24% yield). IR (KBr) 3073.1, 2212.7, 1707.9, 1548.8, 1340.8, 1270.9, 1118.3, 912.1, 829.3, 759.1, 681.6, 615.1 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.63 (s, 2 H), 8.13 (s, 1 H), 8.11 (s, 1 H), 7.70 (m, 4 H), 7.49 (m, 5 H), 2.49 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 193.00, 151.13, 148.49, 134.59, 133.08, 132.68, 131.71, 131.42, 131.23, 131.14, 130.71, 128.94, 127.65, 127.55, 122.27, 121.62, 121.29, 121.17, 102.87, 101.60, 84.11, 82.88, 30.64.

3,8-Dibromo-2,4,9-trinitro-benza[c]cinnoline (51, DWP-II-203) To a 100 mL round bottom flask with a stir bar was added conc. H\(_2\)SO\(_4\) (20 mL). \( N-(2'-\text{Acetylamino-4,4'-dibromo-biphenyl-2-yl})\)-acetamide (1.96 g, 4.60 mmol) was slowly added to the flask
and the mixture was cooled to 0 °C. A mixture of conc. HNO₃ (15 mL) and conc. H₂SO₄ (15 mL) was added slowly to the cooled mixture over 40 min. The mixture was then allowed to warm to room temperature overnight before being poured into ice water. The resulting yellow solid was filtered and purified via flash column chromatography (silica gel using dichloromethane as eluent) followed by recrystallization from ethanol/acetone. (1.15 g, 53% yield). Mp: 280 °C (decomp.) IR (KBr) 3088.5, 1543.8, 1352.6, 1096.4, 927.4, 901.8, 855.8, 819.9 cm⁻¹. ¹H NMR (400 MHz, d-acetone) δ 9.90 (s, 1 H), 9.71 (s, 1 H), 9.47 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 152.94, 151.77, 146.16, 138.53, 136.71, 123.14, 122.12, 121.32, 119.51, 116.08, 107.69. HRMS calc’d for C₁₂H₅N₅O₆Br₂: 472.843068 Found: 472.842752 (Error = 0.67 ppm).

4,4’-Dibromo-biphenyl-2,3’-diamine (DWP-II-194, 207) 4,4’-Dibromo-2,3’-dinitro-biphenyl²⁵ (6.10 g, 15.2 mmol), concentrated HCl (30 mL), and EtOH (80 mL) were added to a 250 mL round bottom flask containing a stir bar. Tin powder (7.21 g, 60.7 mmol) was slowly added to the solution with stirring. The solution was heated to reflux for 30 min and then poured into ice water. The mixture was extracted with ethyl acetate and washed with 50% NaOH (aq). Removal of the solvent provided the crude product, which was taken onto the next step with no further purification (5.28 g). mp: 87-90 °C IR (KBr) 3423.0, 3408.6, 3324.0, 3304.2, 3190.9, 1616.1, 1590.3, 1559.6, 1478.1, 1402.1, 1301.3, 1241.3, 1037.4, 908.9, 799.8, 661.8, 461.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 8.1 Hz, 1 H), 6.91 (m, 2 H), 6.86 (m, 1 H), 6.75 (d, J = 2.0 Hz, 1 H), 6.64 (dd, J = 8.1, 2.0 Hz, 1 H), 4.18 (br s, 2 H), 3.84 (br s, 2 H). ¹³C NMR (100
MHz, CDCl$_3$) $\delta$ 145.28, 144.95, 139.23, 133.52, 131.84, 125.97, 122.60, 121.77, 120.28, 118.46, 116.40, 108.80. HRMS calc’d for C$_{12}$H$_{10}$N$_2$Br$_2$: 341.919157. Found: 341.918664 (Error = 1.4 ppm).

\[
\begin{array}{c}
\text{Br} \\
\text{NHAc} \quad \text{NHAc} \\
\text{Br} \\
\end{array}
\]

**N-(3'-Acetylamino-4,4'-dibromo-biphenyl-2-yl)-acetamide (52, DWP-II-208)**

4,4'-Dibromo-biphenyl-2,3'-diamine (5.28 g, 12.4 mmol) and acetic acid (6.8 mL) were added to a 100 mL round bottom flask followed by acetic anhydride (5.73 mL, 60.7 mmol). The flask was placed in a 70 °C oil bath for 40 min. The solution was neutralized with 50% NaOH (aq) and extracted with dichloromethane. Removal of the solvent gave the desired product (6.47 g, 100% over 2 steps). Mp: 168-171 °C. IR (KBr) 3386.2, 3260.8, 3022.9, 1685.9, 1575.7, 1510.2, 1449.5, 1386.2, 1275.8, 1050.3, 1025.8, 806.8 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.55 (br s, 1 H), 8.22 (br s, 1 H), 7.68 (m, 2 H), 7.50 (br s, 1 H), 7.30 (dd, $J$ = 8.2, 1.7 Hz, 1 H), 7.11 (d, $J$ = 8.2 Hz, 1 H), 6.99 (dd, $J$ = 8.2, 2.2 Hz, 1 H), 2.28 (s, 3 H), 2.13 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.19, 168.91, 137.66, 136.24, 133.65, 131.40, 129.60, 127.76, 126.53, 125.08, 123.57, 122.97, 114.04, 25.07, 25.02. HRMS calc’d for C$_{16}$H$_{14}$N$_2$O$_2$Br$_2$: 425.940266. Found: 425.939783 (Error = 1.1 ppm).

\[
\begin{array}{c}
\text{Br} \\
\text{NHAc} \quad \text{NHAc} \\
\text{O}_2\text{N} \\
\text{O}_2\text{N} \\
\text{Br} \\
\end{array}
\]

**N-(5'-Acetylamino-4,4'-dibromo-5,2'-dinitro-biphenyl-2-yl)-acetamide (53, DWP-III-5, 50)** To a 500 mL round-bottom flask was added $N$-(3-acetylamino-4,4-
dibromo-biphenyl-2-yl)-acetamide (2.45 g, 5.75 mmol), dichloromethane (20 mL) and conc. H$_2$SO$_4$ (70 mL) and the mixture was cooled to -15°C. Next, an ice cold solution of HNO$_3$ (15 mL, 70%) and conc. H$_2$SO$_4$ (15 mL) were added dropwise over 1 h. The mixture was allowed to warm to 0°C over 2 h at which point the reaction was poured onto ice and washed with water and ethyl acetate. Column chromatography (silica gel using 3:1 dichloromethane/ethyl acetate; Rf = 0.21) afforded the desired product (1.29 g, 43% yield): mp 229-232°C. IR (KBr) 3387.3, 3338.3, 1699.0, 1570.7, 1533.1, 1507.5, 1466.7, 1371.3, 1335.1, 1236.9, 1074.0, 895.0 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (br s, 2 H), 7.33 (dd, $J = 8.2$, 2.0 Hz, 2 H), 7.15 (br s, 2 H), 6.98 (d, $J = 8.2$ Hz, 2 H), 1.92 (s, 6 H). $^{13}$C-NMR (125 MHz, acetone-d$_6$) $\delta$ 169.59, 169.38, 144.85, 143.88, 142.13, 141.05, 130.94, 130.18, 129.33, 127.58, 127.08, 125.62, 114.65, 113.66, 23.99, 23.56. HRMS calc'd for C$_{16}$H$_{12}$Br$_2$N$_4$O$_6$: 515.910536. Found: 515.910650 (Error = 0.22 ppm).

4,4'-Dibromo-5,6'-dinitro-biphenyl-2,3'-diamine (54, DWP-III-62, III-65) To a 100 mL round-bottom flask was added N-(5'-acetylamino-4,4'-dibromo-5,2'-dinitrobiphenyl-2-yl)-acetamide (0.441 g, 0.854 mmol), 3 N HCl (20 mL), and THF (20 mL). The solution was heated to reflux for 3 h before being neutralized with NaOH and extracted with ethyl acetate to give the desired product as a yellow solid (0.356 g, 96% yield): mp 250-270°C (decomp.). IR (KBr) 3472.6, 3446.7, 3353.5, 3234.0, 1624.4, 1588.7, 1556.8, 1496.9, 1300.5, 1255.8, 1126.4, 1055.6, 903.1, 841.6 cm$^{-1}$. $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 8.34 (s, 1 H), 7.84 (s, 1 H), 7.17 (s, 1 H), 6.82 (s, 1 H), 6.30 (br s, 2
H), 5.90 (br s, 2 H). $^{13}$C NMR (100 MHz, acetone-$d_6$) δ 151.76, 151.73, 137.73, 137.57, 133.48, 131.24, 128.10, 123.68, 119.10, 117.21, 116.45, 106.11. HRMS calc’d for C$_{12}$H$_8$Br$_2$N$_4$O$_4$: 429.891251. Found: 429.891548 (Error = 0.69 ppm).

![Chemical Structure](image)

4'-Bromo-2,5,2',5'-tetranitro-4-phenylethylnyl-biphenyl (49, DWP-III-64, III-75, III-69, III-84, III-85) 4,4'-Dibromo-5,6'-dinitro-biphenyl-2,3'-diamine (1.04 g, 2.41 mmol) and phenylacetylene (0.29 mL, 2.6 mmol) were coupled following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.085 g, 0.12 mmol), copper(I) iodide (0.046 g, 0.24 mmol), THF (20 mL), and DIEA (1.7 mL, 9.6 mmol). The tube was capped and the solution was stirred in a 40°C oil bath for 1.5 h. The temperature was then increased to 50°C for 1 d. Flash column chromatography (silica gel using 1:1 ethyl acetate/hexanes as eluent; Rf: 0.42) followed by precipitation from acetone/hexanes afforded the desired product (0.780 g, ~72% yield) which was taken directly onto the oxidation step.$^{27}$ 0.300 g (0.662 mmol) of this compound dissolved in THF (10 mL). Acetonitrile (90 mL) and water (3 mL) were placed in a plastic bottle and cooled to -45°C. A 20% mixture of F$_2$ in He was bubbled through at 60 cc/min for 2.5 h. Helium was then bubbled through for 20 min at 60 cc/min. Added the THF solution and stirred for 2.5 min. The reaction mixture was then poured into NaHCO$_3$ (aq) and extracted with dichloromethane. Column chromatography (silica gel using 2:1 dichloromethane/hexanes as eluent; Rf = 0.46) afforded the desired tetranitro product
(0.180 g, 45% over 2 steps). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (s, 1 H), 8.58 (s, 1 H), 8.04 (s, 1 H), 7.84 (s, 1 H), 7.65 (m, 2 H), 7.43 (m, 3 H).

Trimethyl-(4-tributylstannanyl-phenylethynyl)-silane (55, DWP-4-5). To a 500 mL round-bottom flask was added (4-bromo-phenylethynyl)-trimethyl-silane (3.63 g, 14.3 mmol) and a stir bar. Air was removed and N$_2$ backfilled (3×). THF (50 mL) was added and the solution cooled to -78°C. Next, $n$-BuLi (6.22 mL of a 2.53 M solution) was added dropwise over 15 min. The solution was stirred for 10 min. Tributyltin chloride (4.46 mL, 16.4 mmol) in THF (10 mL) was then added over 15 min. The reaction was allowed to warm to room temperature overnight before washing with NaCl (aq) and dichloromethane. Column chromatography (silica gel using hexanes as eluent; Rf = 0.65) followed by Kugelrohr distillation (150°C at 1.5 mm Hg) removed the impurities and left the desired product as an oil (4.53 g, 68% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (m, 4 H), 1.50 (m, 6 H), 1.29 (m, 6 H), 1.03 (m, 6 H), 0.86 (m, 9 H), 0.22 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.93, 136.74, 136.59, 136.44, 131.60, 131.40, 131.20, 122.86, 105.85, 94.51, 29.55, 29.44, 29.34, 28.01, 27.73, 27.45, 14.07, 11.70, 11.62, 10.00, 8.38, 8.31, 0.42.

Trimethyl-(2'-nitro-4'-phenylethynyl-biphenyl-4-ylethynyl)-silane (56, DWP-4-8) 1-Iodo-2-nitro-4-phenylethynyl-benzene (3.41 g, 9.78 mmol),
bis(dibenzylideneacetone)palladium(0) (0.112 g, 0.200 mmol), and triphenylarsine (0.122 g, 0.400 mmol) were placed in a screw cap tube. Air was removed and N₂ backfilled (3×). Trimethyl-(4-tributylstannanyl-phenylethynyl)-silane (19) (3.41 g, 9.78 mmol) and THF (35 mL) were then added. The tube was capped and placed in a 80°C oil bath for 19 h. The mixture was washed with NaCl (aq) and diethyl ether. Column chromatography (silica gel using 3:1 hexanes/dichloromethane as eluent; Rf = 0.50) afforded the desired product (2.59 g, 67% yield): mp 107-110°C. IR (KBr) 3062.5, 2962.5, 2157.0, 1533.1, 1492.8, 1355.6, 1248.3, 855.1, 829.0, 762.8, 694.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, J = 1.6 Hz, 1 H), 7.71 (dd, J = 8.0, 1.6 Hz, 1 H), 7.55 (m, 2 H), 7.51 (dt, J = 8.3, 1.8 Hz, 2 H), 7.37 (m, 4 H), 7.25 (dt, J = 8.3, 1.7 Hz, 2 H), 0.26 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.37, 137.25, 135.44, 135.35, 132.73, 132.21, 129.51, 128.94, 128.17, 127.48, 124.59, 123.91, 122.60, 104.80, 96.25, 92.89, 87.09, 0.34. HRMS calc’d for C₂₅H₂₁SiNO₂: 395.134158. Found: 395.134321 (Error = 0.41 ppm).

4'-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (57, DWP-4-11) Trimethyl-(2'-nitro-4'-phenylethynyl-biphenyl-4-ylethynyl)-silane (2.52 g, 6.37 mmol), potassium carbonate (2.64 g, 19.1 mmol), methanol (25 mL), and dichloromethane (25 mL) were used following the general deprotection method to afford the product (2.03 g, 99% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 1.7 Hz, 1 H), 7.72 (dd, J = 8.0, 1.7 Hz, 1 H), 7.56-7.52 (m, 4 H), 7.40-7.36 (m, 4 H), 7.27 (dt, J = 8.5, 1.8 Hz, 2 H), 3.13 (s, 1 H).
Thioacetic acid \( S\text{-}[4\text{-}(2\text{'-nitro-4\text''-phenylethynyl-biphenyl-4-yethynyl})\text{-phenyl}]\) ester (58, DWP-4-12) 4'-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (1.00 g, 3.09 mmol), bis(dibenzylideneacetone)palladium(0) (0.089 g, 0.155 mmol), copper(I) iodide (0.059 g, 0.31 mmol), triphenylphosphine (0.162 g, 0.620 mmol), THF (15 mL), DIEA (2.15 mL, 12.4 mmol), and thioacetic acid \( S\text{-}(4\text{-iodo-phenyl})\) ester (0.859 g, 3.09 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at ambient temperature for 16 h. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent; Rf: 0.47) followed by precipitation from dichloromethane/hexanes afforded the desired product as a yellow solid (0.982 g, 67% yield): mp134-136°C. IR (KBr) 3057.4, 2202.1, 1707.2, 1527.3, 1494.8, 1350.1, 1111.0, 1085.5, 1003.7, 953.9, 829.3, 758.0, 688.8, 606.1, 545.5 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.01 (d, \( J = 1.6 \) Hz, 1 H), 7.73 (dd, \( J = 8.0, 1.6 \) Hz, 1 H), 7.55 (m, 6 H), 7.39 (m, 6 H), 7.37 (m, 4 H), 7.31 (dt, \( J = 8.3, 1.7 \) Hz, 2 H), 2.43 (s, 3 H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 193.86, 149.38, 137.34, 135.44, 134.69, 132.67, 132.49, 132.24, 129.55, 128.97, 128.73, 128.38, 127.56, 124.71, 124.65, 123.70, 122.60, 92.96, 90.88, 90.39, 87.12, 30.75. HRMS calc’d for \( C_{39}H_{19}SNO_3 \): 473.108566. Found: 473.108635 (Error = 0.15 ppm).

4-Bromo-5,5'-dinitro-4'-trimethylsilyl-phenylnyl-biphenyl-2,2'-diamine (DWP-III-150, 4-10, 4-13) 4,4'-Dibromo-5,5'-dinitro-biphenyl-2,2'-diamine (2.49 g, 5.76
mmol) was coupled with TMSA (1.06 mL, 7.49 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.202 g, 0.288 mmol), copper(I) iodide (0.110 g, 0.576 mmol), THF (75 mL), and DIEA (4.0 mL, 23.04 mmol). The tube was capped and the solution was heated in a 45 °C oil bath for 3 h. Flash column chromatography (silica gel using 1:1 hexanes/ethyl acetate as eluent; Rf = 0.65) afforded the impure desired product (1.44 g, ~80% pure) which was taken directly onto the next step. \(^1\)H NMR (400 MHz, acetone-d\(_6\)) \(\delta\) 7.98 (d, \(J = 1.1\) Hz, 1 H), 7.95 (d, \(J = 1.1\) Hz, 1 H), 7.25 (m, 1 H), 7.09 (m, 1 H), 5.98 (br s, 2 H), 5.94 (br s, 2 H), 0.20 (s, 9 H).

![Chemical Structure](image)

\textbf{5,5'-Dinitro-4-phenylethynyl-4'-trimethylsilanylethynyl-biphenyl-2,2'-diamine (59, DWP-III-152, 4-14)} Crude 4-bromo-5,5'-dinitro-4'-trimethylsilanylethynyl-biphenyl-2,2'-diamine (from the previous reaction; 1.44 g, ~2.56 mmol) was coupled with phenylacetylene (0.46 mL, 4.16 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.112g, 0.160 mmol), copper(I) iodide (0.061 g, 0.320 mmol), THF (30 mL), and DIEA (2.2 mL, 12.8 mmol). The tube was capped and the solution was heated in a 50 °C oil bath for 16 h. Flash column chromatography (silica gel using 1:1 hexanes/ethyl acetate as eluent; Rf = 0.59) afforded the desired product (0.937 g, 35% yield over 2 steps). IR (KBr) 3457.2, 3366.9, 1621.2, 1541.7, 1504.0, 1311.1, 1252.7, 845.6, 755.8 cm\(^{-1}\). \(^1\)H NMR (200 MHz, acetone-d\(_6\)) \(\delta\) 8.04 (s, 1 H), 8.00 (s, 1 H), 7.61 (m, 2 H), 7.47 (m, 3 H), 7.16 (s, 1 H), 7.09 (s, 1 H), 5.96 (br s, 2 H), 5.94 (br s, 2 H), 0.27 (s, 9 H). \(^{13}\)C NMR (100 MHz, acetone-d\(_6\))...
δ 151.58, 151.50, 139.02, 138.68, 132.13, 129.68, 129.59, 129.52, 129.10, 123.22, 120.88, 120.58, 120.42, 120.25, 119.64, 101.71, 101.41, 95.47, 86.58, -0.72. HRMS calc’d for C_{25}H_{22}N_{4}O_{4}Si: 470.141034. Found: 470.141303 (Error = 0.57 ppm).

4′-Ethynyl-5,5′-dinitro-4-phenylethynyl-biphenyl-2,2′-diamine (60, DWP-III-156, 4-17) 5,5′-Dinitro-4-phenylethynyl-4′-trimethylsilanylethynyl-biphenyl-2,2′-diamine (1.38 g, 2.93 mmol), potassium carbonate (1.62 g, 11.7 mmol), methanol (100 mL), dichloromethane (50 mL), and THF (50 mL) were used following the general deprotection method described earlier. A short silica plug (using 1:1 hexanes/ethyl acetate; Rf = 0.42) afforded the desired product (0.934 g, 80% yield). 1H NMR (200 MHz, acetone-d_{6}) δ 8.05 (s, 1 H), 8.01 (s, 1 H), 7.61 (m, 2 H), 7.47 (m, 3 H), 7.16 (s, 1 H), 7.13 (s, 1 H), 5.98 (br s, 4 H), 4.08 (s, 1 H).

Thioacetic acid S-[4-(2,2-diamino-5,5-dinitro-4-phenylethynyl-biphenyl-4-yloxy)-phenyl]-phenyl ester (61, DWP-4-20) 4′-Ethynyl-5,5′-dinitro-4-phenylethynyl-biphenyl-2,2′-diamine (0.934 g, 2.34 mmol), bis(dibenzylideneacetone)palladium(0) (0.067 g, 0.117 mmol), copper(I) iodide (0.045 g, 0.234 mmol), triphenylphosphine (0.123 g, 0.468 mmol), THF (20 mL), DIEA (1.63 mL, 9.36 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (0.716 g, 2.57 mmol) were used following the general procedure.
for couplings. The tube was placed in a 50°C oil bath for 15 h. Column chromatography (silica gel using 1:1 hexanes/ethyl acetate; Rf = 0.45) followed by precipitation from acetone/hexanes and dichloromethane/hexanes afforded the desired product as a yellow-green solid (0.460 g, 36% yield): mp 200-208°C (decomp.). IR (KBr) 3463.1, 3360.6, 3237.0, 3047.5, 2207.7, 1690.5, 1622.6, 1602.0, 1538.1, 1504.7, 1302.8, 1254.8, 1096.4, 819.9, 743.1 cm⁻¹. ¹H NMR (400 MHz, acetone-d₆) δ 8.08 (s, 1 H), 8.07 (s, 1 H), 7.68 (dt, J= 8.3, 1.8 Hz, 2 H), 7.62 (m, 2 H), 7.53 (dt, J= 8.4, 1.8 Hz, 2 H), 7.47 (m, 3 H), 7.19 (s, 1 H), 7.18 (s, 1 H), 5.98 (br d, J= 8.8 Hz, 4 H), 2.46 (s, 3 H). ¹³C NMR (100 MHz, acetone-d₆) δ 192.49, 151.68, 151.61, 138.70, 138.66, 134.93, 132.63, 132.14, 130.07, 129.81, 129.74, 129.60, 129.11, 124.16, 123.22, 120.91, 120.54, 120.50, 120.25, 119.78, 119.69, 95.50, 94.51, 88.14, 86.61, 29.84.

2,7-Dibromo-9H-fluorene (62, DWP-III-158). To a 1 L round-bottom flask, wrapped in aluminum foil, was added fluorene (50.0 g, 301 mmol) and CHCl₃ (450 mL). The solution was cooled to 0°C and ferric chloride (0.716 g, 4.50 mmol) was added. Bromine (32.6 mL, 632 mmol) was added slowly over 15 min at which point the ice bath was removed and the solution allowed to warm slowly over 3 h. The mixture was washed with Na₂S₂O₃ (aq) and extracted with CHCl₃ followed by drying with MgSO₄ to afford the desired product (98.1 g, 100% yield): mp 161-164°C (lit mp 163.5-165.5°C). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (m, 2 H), 7.55 (d, J= 8.1 Hz, 2 H), 7.47 (m, 2 H), 3.81 (s, 2 H).
**2,7-Dibromo-4-nitro-9H-fluorene (63, DWP-III-200, 202, 4-83).** To a 250 mL round-bottom flask was added 2,7-Dibromo-9H-fluorene (10.0 g, 30.7 mmol) and glacial acetic acid (125 mL). The solution was heated to 35°C and a solution of HNO₃ (7 mL) and H₂SO₄ (7 mL) was added slowly over 20 min. The mixture was stirred for 5 min and then heated to 70°C for 15 min. After cooling to room temperature, a yellow solid was filtered and washed with water. Recrystallization from ethanol/toluene afforded the desired product as yellow crystals (7.15 g, 63% yield): mp 192-193°C (lit²¹ mp 194.5-195.5°C). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J= 1.4 Hz, 1 H), 7.92 (d, J= 8.6 Hz, 1 H), 7.87 (br s, 1 H), 7.71 (br s, 1 H), 7.53 (m, 1 H), 3.96 (s, 2 H).

**4-Nitro-2,7-bis-trimethylsilylazylethynyl-9H-fluorene (64, DWP-4-16)** 2,7-Dibromo-4-nitro-9H-fluorene (1.00 g, 2.70 mmol) was coupled with TMSA (0.42 mL, 3.0 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.135 mmol), copper(I) iodide (0.051 g, 0.270 mmol), THF (20 mL), and DIEA (1.9 mL, 10.8 mmol). The tube was capped and the solution was stirred at room temperature for 1 d. More TMSA was added (0.76 mL, 5.4 mmol) and the tube was placed in a 55°C oil bath for 15 h. Flash column chromatography (silica gel using 3:1 hexanes/dichloromethane as eluent; Rf = 0.51) afforded the desired product (0.709 g, 65% yield): mp 221-224°C. IR (KBr) 3077.9, 3052.3, 2959.7, 2898.7, 2150.8, 1517.0, 1449.8, 1356.2, 1248.3, 980.3, 938.1, 842.2, 759.3, 701.1, 655.4, 424.8 cm⁻¹. ¹H NMR
(400 MHz, CDCl₃) δ 7.96 (m, 2 H), 7.77 (d, J= 1.4 Hz, 1 H), 7.64 (m, 1 H), 7.47 (m, 1 H), 3.90 (s, 2 H), 0.262 (s, 9 H), 0.258 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 147.02, 145.19, 144.82, 137.28, 134.13, 132.55, 131.70, 128.58, 127.21, 125.14, 124.11, 122.66, 105.26, 103.02, 98.10, 96.68, 36.96, 0.34, 0.21. HRMS calc’d for C₂₃H₂₅NO₂Si₂: 403.142387. Found: 403.142344 (Error = 0.11 ppm).

![Chemical structure](image)

**2,7-Diethynyl-4-nitro-9H-fluorene (65, DWP-4-21)** 4-Nitro-2,7-bis-trimethylsilylancylethylnl-9H-fluorene (0.700 g, 1.73 mmol), potassium carbonate (0.954 g, 6.90 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general deprotection method described earlier to afford the desired product (0.418 g, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (m, 2 H), 7.82 (m, 1 H), 7.69 (m, 1 H), 7.52 (m, 1 H), 3.96 (s, 2 H), 3.22 (s, 1 H), 3.17 (s, 1 H).

![Chemical structure](image)

**Thioacetic acid S-[4-[7-(4-acetyl)sulfanyl-phenylethylnyl]-5-nitro-9H-fluoren-2-ylythynyl]-phenyl] ester (66, DWP-4-22)** 2,7-Diethynyl-4-nitro-9H-fluorene (0.418 g, 1.60 mmol), bis(dibenzylideneacetone)palladium(0) (0.046 g, 0.080 mmol), copper(I) iodide (0.030 g, 0.160 mmol), triphenylphosphine (0.084 g, 0.320 mmol), THF (65 mL), DIEA (1.1 mL, 6.4 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (0.934 g, 3.36 mmol) were used following the general procedure for couplings. The tube was placed in
a 55°C oil bath for 17 h. Column chromatography (silica gel using 5:1 dichloromethane/hexanes; Rf = 0.61) followed by precipitation from dichloromethane/hexanes afforded the desired product as a yellow solid (0.402 g, 45% yield): mp 197-200°C. IR (KBr) 1708.2, 1526.7, 1488.8, 1354.1, 1287.8, 1119.0, 946.4, 829.2, 608.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (m, 2 H), 7.83 (d, J= 1.4 Hz, 1 H), 7.69 (m, 1 H), 7.54 (m, 5 H), 7.39 (m, 4 H), 3.95 (s, 2 H), 2.43 (s, 3 H), 2.42 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 193.76, 193.60, 147.22, 145.30, 145.03, 137.34, 134.70, 134.65, 134.15, 132.68, 132.63, 132.25, 131.46, 129.38, 128.81, 128.27, 126.93, 125.32, 124.62, 123.94, 123.93, 122.48, 91.69, 91.44, 90.86, 89.34, 37.06, 30.75, 30.72. HRMS calc’d for C₃₃H₂₁NO₄S₂: 559.091203. Found: 559.091932 (Error = 1.3 ppm).

2-Ethynyl-4-nitro-7-phenylethynyl-9H-fluorene (67, DWP-4-35) 2,7-Dibromo-4-nitro-9H-fluorene (1.00 g, 2.70 mmol) was coupled with TMSA (0.42 mL, 3.0 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.135 mmol), copper(I) iodide (0.051 g, 0.270 mmol), THF (30 mL), and DIEA (1.90 mL, 10.8 mmol) (the tube was cooled to 0°C before addition of TMSA). The reaction was allowed to warm to room temperature and stirred for 1 d. Flash column chromatography (silica gel using 3:1 hexanes/dichloromethane as eluent; Rf = 0.45) afforded the impure intermediate (0.849 g, ~57% by NMR) which was taken onto the next coupling following the Pd/Cu protocol. Bis(triphenylphosphine)palladium(II) dichloride (0.077 g, 0.110 mmol), copper(I) iodide (0.042 g, 0.219 mmol), THF (30 mL),
and DIEA (1.53 mL, 8.76 mmol) and phenylacetylene (0.48 mL, 4.4 mL) were used with the crude material. The reaction was placed in a 55°C oil bath and stirred for 1 d. Flash column chromatography (silica gel using 3:1 hexanes/dichloromethane as eluent; Rf = 0.40) afforded the impure intermediate (0.453 g, ~90% by NMR) which was taken onto the step. Potassium carbonate (0.611 g, 4.42 mmol), methanol (50 mL), and dichloromethane (50 mL) were added following the general deprotection method described earlier to afford the slightly impure (~95 % purity by NMR) product (0.373 g, ~41% yield over 3 steps). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) δ 7.99 (m, 2 H), 7.77 (d, J= 1.0 Hz, 1 H), 7.67 (m, 1 H), 7.52 (m, 4 H), 7.34 (m, 4 H), 3.91 (s, 2 H), 3.21 (s, 1 H).

Thioacetic acid \(S\)-[4-(4-nitro-7-phenylethynyl-9H-fluoren-2-ylyethynyl)]phenyl] ester (68, DWP-4-38) 2-Ethynyl-4-nitro-7-phenylethynyl-9H-fluorene (0.373 g, 1.11 mmol), bis(dibenzylideneacetone)palladium(0) (0.032 g, 0.055 mmol), copper(I) iodide (0.021 g, 0.111 mmol), triphenylphosphine (0.058 g, 0.220 mmol), THF (20 mL), DIEA (0.77 mL, 4.42 mmol), and thioacetic acid \(S\)-(4-iodo-phenyl) ester (0.338 g, 1.22 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 3 h. Column chromatography (silica gel using 1:1 dichloromethane/hexanes) followed by precipitation from dichloromethane/hexanes afforded the desired product as a yellow solid [0.297 g, ~55% yield (23% over 4 steps)]: mp 180-183°C. IR (KBr) 1713.9, 1544.6, 1516.6, 1490.7, 1346.4, 1289.3, 1117.0, 944.8, 824.0, 752.5, 689.8, 609.1, 537.5 cm\(^{-1}\). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) δ 8.05 (m, 2 H),
7.87 (d, J= 0.90 Hz, 1 H), 7.73 (s, 1 H), 7.56 (m, 5 H), 7.42 (m, 2 H), 7.37 (m, 3 H), 4.00 (s, 2 H), 2.43 (s, 3 H).  
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.63, 147.21, 145.31, 145.03, 137.09, 134.71, 134.28, 132.69, 132.25, 132.11, 131.41, 129.36, 128.96, 128.84, 128.20, 126.94, 125.31, 124.41, 123.96, 123.40, 122.39, 91.69, 91.62, 89.80, 89.37, 37.08, 30.75. HRMS calc'd for C$_{31}$H$_{19}$NO$_3$S: 485.108566. Found: 485.108900 (Error = 0.69 ppm).

7-Ethynyl-4-nitro-2-phenylethynyl-9H-fluorene (69, DWP-4-36, 4-52) 2,7-Dibromo-4-nitro-9H-fluorene (5.00 g, 13.5 mmol) was coupled with phenylacetylene (1.56 mL, 14.2 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.190 g, 0.27 mmol), copper(I) iodide (0.103 g, 0.54 mmol), THF (70 mL), and DIEA (9.4 mL, 54 mmol). The reaction was allowed stirred at room temperature for 14 h at which point TMSA (2.86 mL, 20.2 mmol) was added. The tube was placed in a 55°C oil bath for 6 h. After workup, the reaction was found not to be complete. Therefore, the crude material was reacted with bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.135 mmol), copper(I) iodide (0.051 g, 0.27 mmol), THF (70 mL), and DIEA (9.4 mL, 54 mmol). The tube was placed in a 60°C oil bath for 1 d. Flash column chromatography (silica gel using 3:1 hexanes/dichloromethane as eluent; Rf = 0.43) afforded the impure intermediate (2.25 g, ~94% by NMR) which was taken onto the next step. Potassium carbonate (3.04 g, 22 mmol), methanol (100 mL), and dichloromethane (100 mL) were added following the general deprotection method described earlier to afford the slightly impure (~93 % purity
by NMR) product (1.75 g, ~41% yield over 2 steps). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)
8.04 (m, 1 H), 8.02 (d, \(J = 8.3\) Hz, 1 H), 7.87 (m, 1 H), 7.69 (m, 1 H), 7.54 (m, 3 H), 7.37 (m, 3 H), 3.98 (s, 2 H), 3.18 (s, 1 H).

\[
\text{Thioacetic acid } S\text{-}[4-(5\text{-nitro-7-phenylethynyl-9H-fluoren-2-ylethynyl})\text{-phenyl} \text{ester (70, DWP-4-53)}}
\]

7-Ethynyl-4-nitro-2-phenylethynyl-9H-fluorene (0.875 g, 2.59 mmol), bis(dibenzylideneacetone)palladium(0) (0.074 g, 0.13 mmol), copper(I) iodide (0.049 g, 0.26 mmol), triphenylphosphine (0.136 g, 0.520 mmol), THF (35 mL), DIEA (1.80 mL, 10.4 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (0.792 g, 2.85 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 3 h. Column chromatography (silica gel using 2:1 dichloromethane/hexanes as eluent; \(R_f = 0.60\)) followed by precipitation from dichloromethane/hexanes afforded the desired product as a yellow solid (0.841 g, ~67% yield (25% over 4 steps)): mp 192-195°C. IR (KBr) 3042.1, 2202.1, 1705.1, 1520.1, 1491.6, 1350.2, 1287.1, 1111.7, 944.4, 827.4, 757.8, 691.6, 614.6 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (m, 2 H), 7.86 (m, 1 H), 7.72 (m, 1 H), 7.55 (m, 5 H), 7.37 (m, 5 H), 3.98 (s, 2 H), 2.43 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.80, 147.18, 145.35, 145.00, 137.45, 134.67, 133.91, 132.64, 132.23, 132.18, 131.48, 129.39, 128.93, 128.71, 128.29, 126.87, 125.30, 124.66, 123.86, 122.94, 122.78, 92.56, 91.46, 90.79, 87.80, 37.08, 30.73. HRMS calc’d for C\(_{31}\)H\(_{19}\)NO\(_3\)S: 485.108566. Found: 485.108470 (Error = 0.20 ppm).
2,7-Dibromo-fluoren-9-one (71, DWP-4-32,90).\textsuperscript{33} 2,7-Dibromo-fluorene (10.0 g, 30.7 mmol) was added to a 500 mL round bottom flask equipped with a stir bar along with dichloromethane (400 mL). \textit{t}-Butyl hydroperoxide (20.6 mL, 215 mmol) and catalytic chromium(III) oxide (0.153 g, 1.53 mmol) were then added. The solution was stirred at ambient temperature for 1 d, at which point starting material remained. The solution was then heated to reflux for 19 h. After cooling to ambient temperature, the solution was filtered through alumina. \textsuperscript{1}H-NMR showed approximately 50\% conversion. The mixture was resubjected to the reaction conditions with 0.306 g (3.07 mmol) of chromium(III) oxide and heated to reflux for 20 h. The material was filtered through alumina \textsuperscript{1}H-NMR showed approximately 90\% product). The product was then recrystallized from ethanol/toluene to afford the pure product (8.65 g, 83\% yield): mp 205-209°C (lit. mp 205-207°C).\textsuperscript{46} \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \textdelta 7.75 (d, J = 1.8 Hz, 2 H), 7.61 (dd, J = 7.9, 1.9 Hz, 2 H), 7.37 (d, J = 7.9 Hz, 2 H).

2,7-Bis-trimethylsilylanychyl-fluoren-9-one (72, DWP-4-81).\textsuperscript{34} 2,7-Dibromo-9-oxo-fluorene (0.753 g, 2.21 mmol) was coupled with TMSA (0.69 mL, 4.9 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.078 g, 0.110 mmol), copper(I) iodide (0.042 g, 0.22 mmol), THF (20 mL), and DIEA (2.30 mL, 13.3 mmol). The tube was capped and stirred at 50°C for 15 h. Flash column chromatography (silica gel using 2:1 hexanes/dichloromethane as eluent; Rf = 0.47)
afforded the desired product (0.480 g, 58% yield): mp 164-168°C. IR (KBr) 2958.4, 2898.7, 2154.6, 1715.0, 1603.5, 1463.6, 1249.5, 859.1, 758.7, 644.7, 535.7 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, J = 1.5, 0.7 Hz, 2 H), 7.56 (dd, J = 7.7, 1.5 Hz, 2 H), 7.43 (dd, J = 7.7, 0.7 Hz, 2 H), 0.24 (s, 18 H). ¹³C NMR (100 MHz, CDCl₃) δ 192.49, 143.75, 138.57, 134.71, 128.25, 124.79, 120.87, 104.30, 97.12, 0.27.

2,7-Diethynyl-fluoren-9-one (73, DWP-4-87).³⁴ 2,7-Bis-trimethylsilylanylylethynyl-fluoren-9-one (0.480 g, 1.28 mmol), potassium carbonate (0.709 g, 5.13 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general deprotection method described earlier to afford the desired product (0.285 g, 97% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (m, 2 H), 7.61 (dd, J = 7.7, 1.5 Hz, 2 H), 7.48 (d, J = 7.8 Hz, 2 H), 3.17 (s, 2 H).

Thioacetic acid S-{4-[7-(4-acytylsulfanyl-phenylethynyl)-9-oxo-9H-fluoren-2-ylethynyl]-phenyl} ester (74, DWP-4-88) 2,7-Diethynyl-fluorenone (0.285 g, 1.24 mmol), bis(dibenzylideneacetone)palladium(0) (0.036 g, 0.062 mmol), copper(I) iodide (0.024 g, 0.124 mmol), triphenylphosphine (0.065 g, 0.248 mmol), THF (25 mL), DIEA (1.30 mL, 7.44 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (0.690 g, 2.48 mmol) were used following the general procedure for couplings. The tube was placed in a 50°C oil bath for 4 h. Column chromatography (silica gel using dichloromethane as eluent; Rf
= 0.47) afforded the desired product as a yellow solid (0.370 g, 56% yield): mp 239-
241°C. IR (KBr) 1725.8, 1702.5, 1600.3, 1490.4, 1101.9, 957.3, 829.8, 785.3, 618.8,
526.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 0.8 Hz, 2 H), 7.65 (dd, J = 7.9,
1.4 Hz, 2 H), 7.53 (m, 6 H), 7.40 (d, J = 8.4 Hz, 2 H), 2.43 (s, 6 H). ¹³C NMR (100 MHz,
CDCl₃) δ 193.74, 192.48, 143.81, 138.34, 134.88, 134.68, 132.64, 128.99, 127.94,
124.63, 124.36, 121.09, 91.10, 90.54, 30.73. HRMS calc’d for C₃₃H₂₀O₃S₂: 528.085390.
Found: 528.085952 (Error = 1.1 ppm).

![2,7-Dibromo-4-nitro-fluoren-9-one](image)

2,7-Dibromo-4-nitro-fluoren-9H-fluorene (1.00 g, 2.70 mmol) and dichloromethane (60 mL) were added to a 100 mL round bottom flask equipped with a stir bar. Chromium(III) oxide (0.013 g, 0.135 mmol) and tert-butyl hydroperoxide (1.80 mL, 18.9 mmol) were then added and the solution was stirred at ambient temperature for 1 d (red solution). The solution was then heated to reflux for 19 h (yellow solution). After cooling to ambient temperature, the mixture was filtered through alumina. Column chromatography (silica gel using 1:1 dichloromethane/hexanes as eluent; Rf = 0.51) afforded the desired product as a yellow solid (0.637 g, ~ 95% pure). ¹H-NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 1.8 Hz, 1 H),
8.02 (d, J = 1.9 Hz, 1 H), 7.91 (d, J = 8.3 Hz, 1 H), 7.88 (d, J = 2.0 Hz, 1 H), 7.71 (dd, J = 8.3, 2.0 Hz, 1 H).
4-Nitro-2,7-bis-trimethylsilyl ethynyl-fluoren-9-one (76, DWP-4-148) 2,7-Dibromo-4-nitro-fluorenone (0.637 g, 1.65 mmol) was coupled with TMSA (0.51 mL, 3.6 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.058 g, 0.083 mmol), copper(I) iodide (0.031 g, 0.165 mmol), THF (25 mL), and triethylamine (5 mL). The tube was capped and stirred at ambient temperature for 5 h. Flash column chromatography (silica gel using 2:1 hexanes/dichloromethane as eluent; Rf = 0.61) afforded the desired product (0.475 g, 42% yield over 2 steps): 234-235°C. IR (KBr) 2958.1, 2903.8, 2156.0, 1732.1, 1557.9, 1531.4, 1453.2, 1356.3, 1249.2, 845.2, 767.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 1.5 Hz, 1 H), 7.93 (m, 2 H), 7.81 (d, J = 1.6 Hz, 1 H), 7.62 (dd, J = 8.1, 1.7 Hz, 1 H), 0.26 (s, 9 H), 0.25 (s, 9 H). ¹³C-NMR (100 MHz, CDCl₃) δ 190.02, 144.84, 139.63, 139.16, 137.06, 136.02, 134.92, 133.30, 131.55, 128.41, 126.75, 126.40, 126.04, 103.57, 101.62, 100.84, 99.20, 0.18, 0.06. HRMS calc’d for C₂₃H₂₅NO₃Si₂: 417.121651. Found: 417.121826 (Error = 0.42 ppm).

2,7-Diethynyl-4-nitro-fluoren-9-one (77, DWP-4-149) 4-Nitro-2,7-bis-trimethylsilyl ethynyl-fluoren-9-one (0.450 g, 1.07 mmol), potassium carbonate (0.887 g, 6.42 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the
general deprotection method described earlier to afford the desired product (0.290 g) which was taken directly onto the next step with no further purification.

Thioacetic acid S-[4-\{7-(4-acetylsulfanyl-phenylethynyl)-5-nitro-9-oxo-9H-fluoren-2ylethynyl]-phenyl] ester (78, DWP-4-150) 2,7-Diethynyl-4-nitro-fluorenone (0.290 g, 1.05 mmol), bis(dibenzylideneacetone)palladium(0) (0.030 g, 0.053 mmol), copper(I) iodide (0.020 g, 0.105 mmol), triphenylphosphine (0.055 g, 0.21 mmol), THF (25 mL), DIEA (1.1 mL, 6.3 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (0.613 g, 2.21 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 18 h. Column chromatography (silica gel using dichloromethane as eluent; Rf = 0.63), followed by precipitation form dichloromethane/hexanes (to remove dba) afforded the desired product as an orange solid (0.372 g, 60% yield over 2 steps): mp 234-236°C.  IR (KBr) 2202.1, 1724.8, 1557.4, 1528.2, 1492.1, 1454.4, 1354.4, 1235.5, 1113.1, 1090.7, 937.0, 822.0, 602.8 cm\(^{-1}\).  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.13 (d, \(J = 1.5\) Hz, 1 H), 7.97 (m, 2 H), 7.84 (d, \(J = 1.2\) Hz, 1 H), 7.67 (dd, \(J = 8.1, 1.6\) Hz, 1 H), 7.55-7.52 (m, 4 H), 7.42-7.38 (m, 4 H), 2.43 (s, 3 H), 2.42 (s, 3 H).  \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.57, 193.43, 189.94, 144.93, 139.62, 138.87, 137.17, 135.05, 134.72, 134.67, 133.00, 132.80, 132.73, 131.18, 130.02, 129.45, 128.03, 126.60, 126.56, 125.83, 123.90, 123.25, 93.80, 92.75, 89.91, 88.13, 30.78, 30.75. HRMS calc’d for C\(_{33}\)H\(_{19}\)NO\(_3\)S\(_2\): 573.070468. Found: 573.071403 (Error = 1.6 ppm).
1,4-Dibromo-2,5-dimethoxy-benzene (79, DWP-I-127, II-34).\textsuperscript{37} In a 100 mL round bottom flask, 1,4-dimethoxybenzene (10.0 g, 72.4 mmol) was dissolved in glacial acetic acid (20 mL). A solution of bromine (7.42 mL, 145 mmol) in glacial acetic acid (7.5 mL) was then added dropwise to the first solution at room temperature over 40 min. The resulting mixture was stirred for 2 h. The crude product was washed with ice-cold water and ice-cold methanol to afford fine white crystals. The mother liquor was concentrated and cooled to afford more white crystals (15.9 g, 74\% yield): mp 136-138 °C (lit\textsuperscript{37} mp 144-145°C). IR (KBr) 3091.9, 3022.1, 2968.8, 2944.4, 2842.8, 1694.9, 1494.2, 1475.6, 1436.5, 1358.2, 1275.0, 1211.8, 1185.0, 1065.4, 1021.9, 860.5, 760.4, 441.8 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.13 (s, 2 H), 3.87 (s, 6 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 150.93, 117.53, 110.90, 57.43.

1-Bromo-2,5-dimethoxy-4-phenylethynyl-benzene (80, DWP-I-140, 170).\textsuperscript{35} 1,4-Dibromo-2,5-dimethoxy-benzene (2.96 g, 10.0 mmol), bis(dibenzylideneacetone)palladium(0) (0.115 g, 0.20 mmol), copper(I) iodide (0.038 g, 0.20 mmol), triphenylphosphine (0.131 g, 0.50 mmol), THF (15 mL), DIEA (6.97 mL, 40.0 mmol) and phenylacetylene (1.21 mL, 11.0 mmol) were used following the general procedure for coupling. The tube was heated in a 50°C oil bath for 18 h. Column chromatography (silica gel using 19:1 hexanes/diethyl ether as eluent) afforded the
desired product, slightly impure (approximately 15% by NMR) in moderate yield (1.02 g, 32% yield). This was taken onto the next step in this impure form. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (m, 2 H), 7.33 (m, 3 H), 7.09 (s, 1 H), 7.02 (s, 1 H), 3.86 (s, 6 H).

(2,5-Dimethoxy-4-phenylethynyl-phenylethynyl)-trimethyl-silane (81, DWP-I-193).$^{35}$ 1-Bromo-2,5-dimethoxy-4-phenylethynyl-benzene (1.0 g, 3.15 mmol), bis(dibenzylideneacetone)palladium(0) (0.036 g, 0.063 mmol), copper(I) iodide (0.012 g, 0.063 mmol), triphenylphosphine (0.042 g, 0.16 mmol), THF (20 mL), DIEA (2.2 mL, 12.6 mmol), and TMSA (0.89 mL, 6.3 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 60 °C oil bath for 1 d. Flash column chromatography (silica gel using 24:1 hexanes/ethyl acetate as eluent) afforded the desired product slightly impure (0.830 g, 79% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (m, 2 H), 7.32 (m, 3 H), 6.98 (s, 1 H), 6.95 (s, 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 0.27 (s, 9 H).

1-Ethynyl-2,5-dimethoxy-4-phenylethynyl-benzene (82, DWP-I-200).$^{35}$ (2,5-Dimethoxy-4-phenylethynyl-phenylethynyl)-trimethyl-silane (0.830 g, 2.48 mmol), potassium carbonate (1.71 g, 12.4 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection to afford the desired
product (0.513 g, 79% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (m, 2 H), 7.33 (m, 3 H), 7.00 (s, 1 H), 6.98 (s, 1 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 3.39 (s, 1 H).

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**Thioacetic acid \(S\)-[4-(2,5-dimethoxy-4-phenylethynyl-phenylethynyl)-phenyl] ester (83, DWP-I-201).**\(^{35}\) 1-Ethynyl-2,5-dimethoxy-4-phenylethynyl-benzene (0.513 g, 1.96 mmol), bis(dibenzylideneacetone)palladium(0) (0.058 g, 0.10 mmol), copper(I) iodide (0.019 g, 0.10 mmol), triphenylphosphine (0.066 g, 0.25 mmol), THF (20 mL), DIEA (1.37 mL, 7.84 mmol), and thioacetic acid \(S\)-(4-iodo-phenyl) ester (0.608 g, 2.16 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 55 °C oil bath for 3 d. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product slightly impure (0.621 g, 76% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (m, 4 H), 7.38 (d, \(J = 8.1\) Hz, 2 H), 7.33 (m, 3 H), 7.03 (s, 1 H), 7.02 (s, 1 H), 3.874 (s, 3 H), 3.870 (s, 3 H), 2.40 (s, 3 H).

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**Thioacetic acid \(S\)-[4-(3,6-dioxo-4-phenylethynyl-cyclohexa-1,4-dienylethynyl)-phenyl] ester (84, DWP-I-211, 216).**\(^{35}\) Thioacetic acid \(S\)-[4-(2,5-dimethoxy-4-phenylethynyl-phenylethynyl)-phenyl] ester (0.050 g, 0.12 mmol), acetonitrile (5 mL), and THF (5 mL) were added to a 25 mL round bottom flask containing a stir bar. A solution of ceric ammonium nitrate (0.132 g, 0.240 mmol) in
water (1 mL) was added in one portion. After stirring at RT for 30 min, another equivalent solution of ceric ammonium nitrate was added. After 20 additional min, the reaction was quenched by adding water (30 mL) to effect precipitation of an orange solid. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product (0.034 g, 74% yield). IR (KBr) 3053.0, 2924.3, 2852.6, 2205.4, 1703.4, 1652.7, 1568.8, 1483.7, 1442.2, 1354.8, 1221.3, 1105.4, 1089.4, 949.6, 920.1, 830.9, 758.2, 688.2, 620.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (m, 4 H), 7.42 (m, 2 H), 7.38 (m, 3 H), 6.98 (s, 1 H), 6.97 (s, 1 H), 2.42 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 193.22, 182.74, 182.67, 136.88, 136.51, 134.63, 133.34, 133.24, 132.99, 132.84, 130.94, 103.63, 128.99, 122.81, 121.80, 105.38, 103.99, 84.17, 82.92, 30.80. HRMS calc’d for C₂₄H₁₄O₃S: 382.0664. Found: 382.0663 (Error = 0.08 ppm).

![Chemical Structure](image)

**1,4-Dimethoxy-2,5-bis-trimethylsilanylethynyl-benzene (85, DWP-II-33).**

1,4-Dibromo-2,5-dimethoxy-benzene (1.75 g, 5.91 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.207 g, 0.296 mmol), copper(I) iodide (0.113 g, 0.591 mmol), triphenylphosphine (0.155 g, 0.591 mmol), THF (20 mL), DIEA (4.10 mL, 23.6 mmol), and TMSA (2.51 mL, 17.7 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 55 °C oil bath for 2 d. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (1.54 g, 79% yield). IR (KBr) 2957.0, 2898.2, 2851.2, 2829.0, 2149.1, 1496.8, 1464.1, 1449.1, 1388.2, 1283.7, 1249.0, 1223.6, 1203.1,
117.24, 1039.6, 883.2, 841.3, 757.4, 626.4 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.89 (s, 2 H), 3.81 (s, 6 H), 0.25 (s, 18 H) \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.56, 116.59, 113.81, 101.22, 100.84, 56.83, 0.40. HRMS calc’d for C\(_{18}\)H\(_{26}\)O\(_2\)Si\(_2\): 330.1471. Found: 330.1468 (Error = 1.1 ppm).

![Chemical structure](image)

**1,4-Diethyl-2,5-dimethoxy-benzene (86, DWP-II-38)**.\(^{35}\) 1,4-Dimethoxy-2,5-bis-trimethylsilanylethynyl-benzene (1.50 g, 4.54 mmol), potassium carbonate (6.27 g, 45.4 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general procedure for deprotection to give the desired product (0.829 g, 98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.96 (s, 2 H), 3.84 (s, 6 H), 3.37 (s, 2 H).

![Chemical structure](image)

**Thioacetic acid S-[4-[4-(4-acetylsulfanyl-phenylethynyl)-2,5-dimethoxy-phenylethynyl]-phenyl] ester (87, DWP-II-39)**.\(^{35}\) 1,4-Diethyl-2,5-dimethoxy-benzene (0.810 g, 4.35 mmol), bis(dibenzyldieneacetone)palladium(0) (0.253 g, 0.44 mmol), copper(I) iodide (0.084 g, 0.44 mmol), triphenylphosphine (0.115 g, 0.440 mmol), THF (30 mL), DIEA (4.50 mL, 26.1 mmol), and thioacetic acid S-(4-iodo-phenyl) ester (2.54 g, 9.14 mmol) were used following the general procedure for couplings. The solution was then stirred in a 60°C oil bath for 16 h. Crystallization from dichloromethane/hexanes afforded the desired product (1.81 g, 85%). IR (KBr) 3129.1,
3057.4, 3006.2, 2975.5, 2847.4, 2207.2, 1697.7, 1506.8, 1483.1, 1463.1, 1396.2, 1279.2, 1223.5, 1122.2, 1034.2, 949.5, 898.8, 825.5, 765.6, 616.8 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (dt, \(J = 8.5, 1.9\) Hz, 4 H), 7.39 (dt, \(J = 8.5, 2.0\) Hz, 4 H), 7.01 (s, 2 H), 3.89 (s, 6 H), 2.42 (s, 6 H). \(^\text{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.85, 154.43, 134.58, 132.65, 128.64, 124.84, 116.08, 113.75, 94.76, 87.73, 56.91, 30.70. HRMS calc’d for C\(_{28}\)H\(_{22}\)O\(_4\)S\(_2\): 486.0960. Found: 486.0956 (Error = 0.76 ppm).

![Thioacetic acid S-\[4-(4-acetylsulfanyl-phenylethynyl)-3,6-dioxo-cyclohexa-1,4-dienylethynyl]-phenyl\] ester (88, DWPII-41, 42, 46, 48, 51, 52, 55).\(^{35}\) Thioacetic acid S-\[4-(4-acetylsulfanyl-phenylethynyl)-2,5-dimethoxy-phenylethynyl]-phenyl\] ester (0.050 g, 0.103 mmol), acetonitrile (5 mL), and THF (3 mL) were added to a 25 mL round bottom flask containing a stir bar. A solution of ceric ammonium nitrate (0.339 g, 0.618 mmol) in water (2 mL) was added in two portions, one half was added initially and after 30 min, the second half was added. After stirring at RT for 3 h the reaction was quenched by adding water to effect precipitation of an orange solid. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product (0.023 g, 49% yield). IR (KBr) 2922.2, 2847.4, 2203.4, 1694.9, 1660.1, 1569.9, 1351.8, 1212.3, 1119.7, 1084.6, 1013.2, 960.3, 826.8, 620.6 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (dt, \(J = 8.3, 1.6\) Hz, 4 H), 7.42 (dt, \(J = 8.3, 1.6\) Hz, 4 H), 7.00 (s, 2 H), 2.43 (s, 6H). \(^\text{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.23, 182.61, 136.86, 134.64, 133.25, 133.07,
130.97, 122.78, 104.14, 84.08, 30.79. HRMS calc’d for C_{26}H_{16}O_{4}S_{2}: 456.0500. Found: 456.0490 (Error = 2.2 ppm).

Thioacetic acid \(S\)-[4-(3-oxo-1-oxy-6-phenylethynyl-3H-indol-2-yl)-phenyl] ester (89, DWP-III-89, III-103, 4-80) To a 10 mL round bottom flask was added thioacetic acid \(S\)-[4-(2-nitro-4-phenylethynyl-phenylethynyl)-phenyl] ester (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 3 N HCl (~1 mL) was added. The product was extracted with dichloromethane. Column chromatography (silica gel using 2:1 dichloromethane/hexanes; Rf = 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\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.73 (dt, \(J= 8.8, 1.9\) Hz, 2 H), 7.80 (m, 1 H), 7.67 (dd, \(J= 7.5, 1.2\) Hz, 1 H), 7.61 (m, 1 H), 7.55 (m, 4 H), 7.38 (m, 3 H), 2.44 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.42, 186.17, 148.26, 134.83, 134.59, 132.33, 131.47, 130.95, 129.79, 128.98, 128.58, 126.98, 122.42, 122.19, 122.09, 117.51, 95.28, 88.41, 53.83, 30.84. HRMS calc’d for C\(_{24}\)H\(_{15}\)NO\(_3\)S: 397.077266. Found: 397.076587 (Error = 1.7 ppm).
References


Chapter 2

Synthesis of Alternative Systems to use as Alligator Clips for Attachment to Metal Substrates.
Introduction

If devices made using molecular electronics are going to succeed in becoming an integral part of our technology and everyday lives, they must be made comparable, if not better, in performance to current electronic devices. One problem is that our present organic devices do not allow for sufficient current output at normal operating voltages. They only demonstrate picoamps or nanoamps of current over 250 nm² in the 1-5 volt operating range. This pales in comparison to the microamps of current that are commonly achieved in present solid-state devices.

The barrier to conduction seems to be the attachment to the metal surface; i.e. the “alligator clip.” It is not certain why the sulfur-gold connection causes such impedance to electron flow. It is possible that the distance between the aromatic ring and metal surface on which the SAM is formed is too great. This could, perhaps, break or bottleneck the path of electrons and cause the current flow to be reduced. In essence, the wire has been “broken” and the electrons are forced to jump from the aromatic ring to the gold surface. It is also possible the angle of the molecule relative to surface is not in proper alignment for maximum current. The π orbitals may not be in the proper placement relative to the conduction band of the gold surface. Or it may be simply that the sulfur atom itself does not allow for current to easily flow. Sulfur, although it contains unpaired electrons, may act as a small resistor in the device and be the limiting factor in current output. Selenium and tellurium have been shown to be comparable to sulfur for use as alligator clips.¹ ² Selenium appears to allow for slightly better conduction than sulfur while tellurium is much worse. Whatever the reason, it is clear that this problem must be overcome.
A possible solution to this problem is to change the alligator clip entirely. One avenue that has been explored is the use of isonitriles to attach the compounds to metal surfaces.\textsuperscript{3} Isonitriles form weaker bonds to gold and other metal substrates and weaker chemisorption might make for a better alligator clip; i.e. better conduction. Also, the SAMs that are formed using isonitriles may be more perpendicular to the surface, which might allow for better conduction as well.

Part of the reason that isonitriles have not been studied or used extensively in our group is that they can be problematic to synthesize. There are only a few known methods to make aryl isonitriles, the primary way being to dehydrate a formamide.\textsuperscript{4} This can be problematic in that the formamides can be rather insoluble and difficult to characterize. However, we now seem to have an excellent method for dehydrating these systems by using triphosgene.\textsuperscript{5,6}

Still thinking in the realm of organometallic chemistry, we came upon the idea of metal insertion into organic compounds. Aryl halides, particularly aryl iodides, allow facile insertion of many metals including palladium(0).\textsuperscript{7} This, and consequent transformations, are the basis for metal-catalyzed organic reactions. We hope to take this idea to a metal surface, such as a Pd(0) surface, to generate SAMs of molecular devices utilizing the aryl-halide functionality as an alligator clip (Figure 1).
**Figure 1.** Diagram showing how a molecular wire with an aryl-halide moiety could function as an alligator clip to anchor the device to the metal.

One advantage of using this method would be that the pi system of electrons in the aromatic ring would be much closer to the metal surface than with other alligator clips such as the sulfur clip or isonitrile clip. One possible disadvantage of the system is that the halogen atoms must still be present on the metal. This may interfere with quality SAM formation and create defects that could result in electrical shorts in the final device. One molecular device, containing a nitro-amino core, with this potential alligator clip has been synthesized and is awaiting testing at Penn State.

**Results and Discussion**

**Scheme 1**
Scheme 1 shows the synthetic route to a simple two-ring system containing an isonitrile alligator clip. 4-Iodoaniline was converted to the formamide using formic acid and acetic anhydride in 81% yield. Approximately 7% of the aniline was converted to the acetamides as determined by $^1$H-NMR of the crude material. N-(4-Iodo-phenyl)-formamide (1) was then coupled with phenylacetylene to provide 2 in a high yield of 89%. This compound was then reacted with triphosgene (a less hazardous phosgene substitute) to provide isonitrile 3 in high yield (87%).$^5, 6$ This compound was made as a simple system for assembly tests and as a reaction comparison to other reactions making isonitriles and nitro groups on the same compound.

Scheme 2

Scheme 2 shows the complete synthesis of an unfunctionalized wire with two isonitrile alligator clips. 1,4-Diiodobenzene was coupled with 2 equivalents of trimethylsilylacetylene (TMSA) to provide 4 in high yield. Next, the alkynes were deprotected to afford diyne 5 in quantitative yield. Compound 5 was then coupled with 2 equivalents of formamide 1 to provide the poorly soluble 6. This compound was then doubly dehydrated using the triphosgene method with poor success to provide
bis(isonitrile) 7. Part of the reason for the low yield could be due to the poor solubility of 6 in dichloromethane. The bis-formamide probably forms a hydrogen-bonded polymer through intermolecular interactions between formamide moieties. It may be possible that in future endeavors to synthesize this compound, one may wish to try different solvents. However, in this case, more than ample quantities of 7 were obtained so no further efforts were attempted. This compound was sent to Dave Allara at Penn State for testing.

Scheme 3

Scheme 3 shows the complete synthesis of the mononitro device with an isonitrile alligator clip. Formamide 1 was coupled with TMSA to provide 8 in quantitative yield. The terminal alkyne was then deprotected to afford 9 in high yield. Next, the alkyne was coupled with 1-iodo-2-nitro-4-phenylethynyl-benzene (described in Chapter 1) to give penultimate compound 10 in 67% yield. In the past, the dehydration of a formamide to generate an isonitrile has been difficult, particularly in the presence of a nitro group. However, by generating phosgene in situ from triphosgene, the dehydration was accomplished in 86% yield to give isonitrile 11, which was sent to various collaborators.
for testing. 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 4**

Scheme 4 shows the synthesis of the "nitro-up" or "meta-nitro" compound containing an isonitrile alligator clip. 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (discussed in Chapter 1) was coupled with N-(4-iodo-phenyl)-formamide (1) to provide 12 as an impure solid. This product was taken onto the next reaction with triphosgene with no further purification. This dehydration reaction afforded the isonitrile 13 in 58% yield over the 2 steps. 13 has been sent to Mark Reed for testing. We are awaiting results.

**Scheme 5**
The complete synthesis of the mononitro device containing two isonitriles is shown in scheme 5. 1,4-Diethynyl-2-nitro-benzene (discussed in Chapter 1) was coupled with 2 equivalents of formamide 1 to afford 14 in 79% yield. This compound was then dehydrated using triphosgene to afford 15 in a moderate yield of 42%. This depressed yield, as before, could be due to the extremely poor solubility of the bis-formamide precursor.

Scheme 6

Scheme 6 shows the synthesis of a mononitro biphenyl compound with an isonitrile alligator clip. 4'-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (described in Chapter 1) was coupled with formamide 1 to give 16 in high yield. Formamide 16 was then dehydrated using triphosgene to afford isonitrile 17 in a good yield of 73%. This compound has been sent to Mark Reed for testing.
Scheme 7

Scheme 7 shows the synthesis of the 2,3'-dinitrobiphenyl device constructed with an isonitrile alligator clip in lieu of the standard thioacetyl alligator clip. 4'-Ethynyl-2,3'-dinitro-4-phenylethynyl-biphenyl (shown in Chapter 1) was coupled with formamide 1 to provide 18 in an approximate yield of 93%. The exact yield was not determined due to some apparent impurities as shown by $^1$H-NMR as well as the difficulty in peak assignment in $^1$H-NMR due to the tautomerizing nature of the formamide groups. Compound 18 was then dehydrated using triphosgene to provide 19 in a yield of 91% over the two steps. This compound has been sent to various collaborators for testing.
Scheme 8

Scheme 8 depicts the synthesis of the 2,3'-dinitro device with two isonitrile alligator clips. 4,4'-Diethynyl-2,3'-dinitro-biphenyl (shown in Chapter 1) was coupled with 2 equivalents of formamide 1 to provide 20 in an approximate yield of 94%. The precise yield could not be ascertained due to the same reasons described earlier. Therefore, compound 20 was taken onto the dehydration step to afford final product 21 in a moderate yield of 51%. This is actually an encouraging yield considering the poor solubility of the bis-formamide precursor. This compound has been sent to various collaborators for testing.
Scheme 9

Scheme 9 shows the synthesis of a nitro-fluorene compound containing an isonitrile alligator clip. The synthesis began with the coupling of formamide 1 with 7-ethynyl-4-nitro-2-phenylethynyl-9H-fluorene (discussed in Chapter 1) to provide 22 in approximately 90% yield (the starting alkyne was not pure). This compound could not be fully purified by column chromatography. Therefore, the slightly impure 22 was dehydrated to give the isonitrile 23 in an overall yield of 31% over two steps. This compound has been sent to various collaborators for testing.
Scheme 10

Scheme 10 shows the complete synthesis of the nitro-amino compound with an aryl-iodide as an alligator clip for surface attachment. \textit{N}(2,5-Dibromo-4-nitro-phenyl)-acetamide\textsuperscript{9} was coupled with phenylacetylene to afford 24 in 43\% yield. This coupling has been problematic for other members of the group as well similar yields were obtained. Compound 24 was then coupled with TMSA to afford 25 in a modest 64\% yield. Compound 25 was deprotected to the terminal alkyne and free amine in quantitative yield in 2 hours to afford 26. It is interesting to note that the nitro group being present in a para position relative to the amide facilitates the deprotection of the amine under such mild conditions. The electron-withdrawing power of the nitro group seems the pull enough electron density away from the amide, thereby making the carbonyl of the acetyl group more susceptible to nucleophilic attack. Compound 26 was then coupled with 3 equivalents of 1,4-diiodobenzene to afford 27 in 73\% yield. Three equivalents of the diiodo compound were used to prevent the alkyne from coupling on both reactive sites of the diiodobenzene. This compound was sent to David Allara at
Penn State to determine if they could form a good quality SAM on a metal surface. We are still awaiting results.

**Scheme 11**

Scheme 11 shows the synthesis of the mono-nitro compound with a carboxylic acid terminus in lieu of the standard thioacetate. This compound was made en route to an isonitrile terminus; however, as shown in the alternative synthesis of Scheme 3, the isonitrile was instead made via the formamide in high yield. Compound 29 has value since the acid terminus can assemble onto some surfaces such as aluminum oxides.\(^\text{10,11}\) 1-Iodo-2-nitro-4-phenylethynyl-benzene (described in Chapter 1) was coupled with 4-ethynyl-benzoic acid methyl ester\(^\text{12}\) in quantitative yield to give 28. Finally, the ester was saponified\(^\text{13}\) to give acid terminated molecular wire 29. Little effort was made to convert the acid to the isonitriles (acid to isocyanate via Curtius rearrangement, and reduction of isocyanate to isonitrile) due to the success of Scheme 3.

**Summary**

The molecular electronic device candidates that were described in Chapter 1 are described here with alternative alligator clips such as isonitriles, aryl iodides, and
terminal alkynes. These device candidates could form SAMs on metal substrates other than gold. Also, these candidates could provide for higher current carrying moletronics devices.

**Experimental Procedures**

**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 F254 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 by Terry Marriott at Rice University’s mass spectrometry lab. All new compounds were named using the Beilstein Autonom feature of Beilstein Commander software.

**General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).**

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 equivalents per palladium) were used. The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen (3x). 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 NH₄Cl. The organic layer was diluted with methylene chloride and washed with a saturated solution of NH₄Cl (3x). The combined aqueous layers were extracted with methylene chloride (3x). The combined organic layers were dried over anhydrous MgSO₄ and the solvent removed in vacuo. The crude product was then purified by flash or column chromatography (silica gel).

**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 equivalents of potassium carbonate, and equivalent amounts of methanol 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.
\textbf{N-(4-Iodo-phenyl)-formamide (1, DWP-4-107).} 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 dichloromethane/hexanes to afford the desired product (19.9 g, 81\% yield): mp 111-112°C (lit mp = 108-109°C).\textsuperscript{17} \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.65 (d, \(J = 11.3\) Hz, 0.44 H), 8.40 (br s, 0.25 H), 8.36 (d, \(J = 1.4\) Hz, 0.71 H), 7.62 (dd, \(J = 11.8, 8.6\) Hz, 2 H), 7.44 (br s, 0.55 H), 7.30 (d, \(J = 8.7\) Hz, 1.16 H), 6.84 (d, \(J = 8.6\) Hz, 0.85 H).

\begin{center}
\begin{tikzpicture}

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\textbf{N-(4-Phenylethynyl-phenyl)-formamide (2, DWP-III-63).} \textsuperscript{N-(4-Iodo-phenyl)-formamide} (1.00 g, 4.05 mmol) was coupled with phenylacetylene (0.49 mL, 4.4 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.057 g, 0.081 mmol), copper(I) iodide (0.031 g, 0.16 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\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.73 (d, \(J = 11.3\) Hz, 0.41 H), 8.38 (d, \(J = 1.7\) Hz, 0.52 H), 7.80 (br d, \(J = 12.4\) Hz, 0.44 H), 7.51 (m, 5 H),
7.32 (m, 4 H), 7.22 (br s, 0.42 H), 7.04 (d, J= 8.6 Hz, 0.81 H). HRMS calc’d for C_{15}H_{11}NO: 221.084064. Found: 221.084352 (Error = 1.3 ppm).

\[ \text{NC} \]

1-Isocyano-4-phenylethynyl-benzene (3, DWP-III-70). To a large test tube was added N-(4-phenylethynyl-phenyl)-formamide (0.400 g, 1.81 mmol) and triphosgene (0.198 g, 0.670 mmol). Air was removed and N\textsubscript{2} backfilled (3×). The tube was cooled to 0°C and dichloromethane (20 mL) and triethylamine (10 mL) was added. A solution of tetrabutylammonium chloride (0.050 g, 0.181 mmol) in dichloromethane (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 (0.237 mmol) of triphosgene was added. After 1 h, an additional 0.053 g (0.179 mmol) of triphosgene was added. After 1 h (5 h total time), the reaction was complete by TLC. The mixture was washed with water and dichloromethane. Column chromatography (silica gel using 1:1 hexanes/ethyl acetate as eluent; Rf = 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\(^{-1}\). \(^1\text{H}\) NMR (400 MHz, CD\textsubscript{3}Cl\textsubscript{3}) \(\delta\) 7.52 (m, 4 H), 7.35 (m, 5 H). \(^{13}\text{C}\) NMR (100 MHz, CD\textsubscript{3}Cl\textsubscript{3}) \(\delta\) 166.09, 132.97, 132.11, 129.30, 128.88, 126.87, 125.21, 122.88, 92.60, 88.13. HRMS calc’d for C_{15}H_{9}N: 203.073499. Found: 203.073127 (Error = 1.8 ppm).
1,4-Bis-trimethylsilylalkynyl-benzene (4, DWP-5-45).\textsuperscript{18,19} 1,4-Diiodobenzene (7.97 g, 24.2 mmol) was coupled with TMSA (7.20 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\textsuperscript{20} mp 122°C). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (s, 4 H), 0.22 (s, 18 H).

1,4-Diethynyl-benzene (5, DWP-5-47).\textsuperscript{18,19} 1,4-Bis-trimethylsilylalkynyl-benzene (3.00 g, 11.1 mmol), potassium carbonate (9.20 g, 66.5 mmol), methanol (100 mL) and dichloromethane (100 mL) were used following the procedure for deprotection. After stirring for 1 h at RT, the solution was filtered and worked up in the usual manner to afford the desired product (1.40 g, 100%). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (s, 4 H), 3.15 (s, 2 H).

$N$-{4-[4-(4-Formylamino-phenylethynyl)-phenylethynyl]-phenyl}-formamide (6, DWP-5-48). 1,4-Diethynyl-benzene (1.40 g, 11.1 mmol) was coupled with 4-iodoformanilide (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 (7.70 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 dichloromethane 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. ¹H NMR (400 MHz, DMSO-d₆) δ 10.43 (d, J = 1.5 Hz, 1.52 H), 10.35 (d, J = 10.8 Hz, 0.45 H), 8.91 (d, J = 10.8 Hz, 0.47 H), 8.32 (d, J = 1.8 Hz, 1.55 H), 7.67 (d, J = 8.7 Hz, 3.29 H), 7.57-7.52 (m, 8 H), 7.27 (d, J = 8.6 Hz, 0.88 H).

1.4-Bis-(4-isocyano-phenylethynyl)-benzene (7, DWP-5-50). To a 500 mL round bottom flask was added N-{4-[4-(4-formylamino-phenylethynyl)-phenylethynyl]-phenyl}-formamide (2.00 g, 5.49 mmol). Air was removed and N₂ backfilled (3×). Dichloromethane (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 (2.73 mmol) of triphosgene was added. After 60 min an additional 0.81 g (2.73 mmol) of triphosgene was added. After 40 min an additional amount of triphosgene (0.81 g, 2.73 mmol) was added. After 2.25 h (total time), the reaction was warmed to ambient temperature. An additional 0.25 equivalents of triphosgene (0.405 g, 1.36 mmol) was added and stirred for 1.5 h. The solvents were then removed under reduced pressure. Column chromatography (silica gel using dichloromethane as eluent; Rf = 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. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (dt, J = 8.8,
2.0 Hz, 4 H), 7.50 (s, 4 H), 7.35 (dt, J = 8.7, 2.0 Hz, 4 H). ¹³C NMR (125 MHz, CDCl₃)
δ 166.39, 133.02, 132.13, 126.94, 124.82, 123.32, 92.02, 90.24. HRMS calc’d for
C₂₄H₁₂N₂: 328.100048. Found: 328.100238 (Error = 0.58 ppm).

\[
\text{TMS} \equiv \quad \text{NHCHO}
\]

\textit{N-(4-Trimethylsilanylethynyl-phenyl)-formamide (8, DWP-III-36).} ⁸ \textit{N-(4-}
Iodo-phenyl)-formamide (6.00 g, 24.3 mmol), bis(triphenylphosphine)palladium(II)
dichloride (0.168 g, 0.240 mmol), copper(I) iodide (0.091 g, 0.48 mmol), DIEA (8.5 mL,
49 mmol), THF (20 mL) and trimethylsilylacetylene (3.6 mL, 25 mmol) were used
following the general procedure for couplings. The tube was capped and the solution was
stirred at RT for 2 h. Normal workup using diethyl ether instead of dichloromethane
afforded the desired product (5.28 g, 100% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.75
(br d, J = 10.8 Hz, 0.42 H), 8.57 (br d, J = 9.2 Hz, 0.43 H), 8.39 (d, 1.7 Hz, 0.51 H), 7.56
(br s, 0.44 H), 7.54-7.53 (m, 3.13 H), 7.04 (dt, J = 8.7, 2.1 Hz, 0.93 H), 0.27 (d, J = 1.8
Hz, 9 H).

\[
\text{H} \equiv \quad \text{NHCHO}
\]

\textit{N-(4-Ethynyl-phenyl)-formamide (9, DWP-III-41).} ⁸ \textit{N-(4-
Trimethylsilanylethynyl-phenyl)-formamide (5.28 g, 24.3 mmol), potassium carbonate
(13.4 g, 97.2 mmol), methanol (100 mL), and dichloromethane (100 mL) were used
following the general procedure for deprotection to afford the desired product (3.29 g,
93% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J = 11.3$ Hz, 0.43 H), 8.36 (d, 1.6 Hz, 0.56 H), 8.29 (br d, $J = 10.5$ Hz, 0.40 H), 7.46 (m, 3.74 H), 7.02 (dt, $J = 8.6$, 2.1 Hz, 0.95 H), 3.06 (d, $J = 12.5$ Hz, 1 H).

\[
\text{N-[4-(2-Nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide (10, DWP-III-44).} \quad 4$-$\text{Ethynylphenyl}-2$-$\text{nitro-1-iodobenzene (1.92 g, 5.50 mmol), N-(4-ethynyl-phenyl)-formamide (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 RT for 1 d followed by heating at 50°C for 1 h. Flash column chromatography (silica gel using ethyl acetate as eluent; Rf: 0.75 ) afforded the desired product as a yellow solid (1.36 g, 67% yield): mp 180-183°C. 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$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.76 (d, $J = 1.3$ Hz, 0.43 H), 8.40 (d, $J = 1.7$ Hz, 0.66 H), 8.21 (m, 1 H), 7.69 (m, 1 H), 7.65 (d, $J = 8.0$ Hz, 1 H), 7.59 (s, 0.57 H), 7.57 (s, 2.63 H), 7.52 (m, 2 H), 7.37 (m, 3 H), 7.19 (br s, 0.55 H), 7.07 (d, $J = 8.7$ Hz, 0.76 H). HRMS calc’d for C$_{23}$H$_{14}$N$_2$O$_3$: 366.100442. Found: 366.100191 (Error = 0.69 ppm).}
1-(4-Isocyano-phenylethynyl)-2-nitro-4-phenylethynyl-benzene (11, DWP-III-46, 49). N-[4-(2-Nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide (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 N₂ backfilled. Dichloromethane (50 mL) and triethylamine (15 mL) were then added followed by tetrabutylammonium chloride (0.076 g, 0.273 mmol) in dichloromethane (20 mL). After 3 h, starting material remained so an additional 0.162 g (0.545 mmol) of triphosgene was added. The reaction was complete after an additional 1 h (4 h total). The solution was washed with water and dichloromethane and dried over MgSO₄. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent; Rf: 0.55) afforded the desired product as a yellow solid. Recrystallization from hexanes/dichloromethane 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, CDCl₃) δ 8.22 (d, J = 1.5 Hz, 1 H), 7.71 (dd, J = 8.1, 1.6 Hz, 1 H), 7.66 (d, J = 8.1 Hz, 1 H), 7.60 (dt, J = 8.6, 2.0 Hz, 2 H), 7.54 (m, 2 H), 7.38 (m, 5 H).

¹³C NMR (100 MHz, CDCl₃) δ 166.80, 149.92, 135.79, 134.91, 133.47, 132.24, 129.74, 128.98, 128.10, 127.03, 125.31, 124.10, 122.35, 117.52, 96.94, 94.52, 87.71, 87.13.

HRMS calc’d for C₂₃H₁₂N₂O₂: 348.089878. Found: 348.090186 (Error = 0.88 ppm).
**N-[4-(3-Nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide (12, DWP-III-61)**. 4-Ethynyl-2-nitro-1-phenylethynyl-benzene (0.675 g, 2.73 mmol) was coupled with **N-(4-iodo-phenyl)-formamide** (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, 11 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; Rf = 0.73) afforded the desired product (0.890 g, 89% yield): mp 174-177°C (decomp.). 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, CDCl₃) δ 9.48 (s, 0.38 H), 8.95 (m, 0.18 H), 8.42 (s, 0.87 H), 8.25 (d, J = 0.9 Hz, 1 H), 7.92-7.85 (m, 2 H), 7.77 (d, J = 8.7 Hz, 1.8 H), 7.68-7.59 (m, 4.3 H), 7.55-7.45 (m, 3.15 H), 7.36 (d, J = 8.3 Hz, 0.45 H). HRMS calc’d for C₂₃H₁₄N₂O₃: 366.09982. Found: 366.099982 (Error = 1.3 ppm).

**4-(4-Isocyano-phenylethynyl)-2-nitro-1-phenylethynyl-benzene (13, DWP-III-66, 68)**. To a large test tube was added **N-[4-(3-Nitro-4-phenylethynyl-phenylethynyl)-phenyl]-formamide** (0.400 g, 1.09 mmol) and triphosgene (0.120 g, 0.404 mmol). Air was removed and N₂ backfilled (3×). The tube was cooled to 0°C and dichloromethane (20 mL) and triethylamine (7 mL) was added. A solution of tetrabutylammonium chloride (0.030 g, 0.109 mmol) in dichloromethane (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 (0.14 mmol) 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 dichloromethane. Column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent; RF = 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, CDCl₃) δ 8.21 (t, J= 1.0 Hz, 1 H), 7.69 (d, J= 1.1 Hz, 2 H), 7.57 (m, 4 H), 7.38 (m, 5 H). ¹³C NMR (100 MHz, CDCl₃) δ 166.80, 149.88, 135.66, 135.02, 133.23, 132.53, 129.98, 128.95, 128.16, 127.07, 123.94, 123.54, 122.52, 119.17, 99.86, 91.93, 89.78, 85.10. HRMS calc’d for C₂₃H₁₂N₂O₂: 348.089878. Found: 348.089919 (Error = 0.12 ppm).

\[ \text{N-\{4-[4-(4-Formylamino-phenylethynyl)-2-nitro-phenylethynyl]-phenyl\}-formamide (14, DWP-III-78).} \]

1,4-Diethyl-2-nitro-benzene (1.09 g, 6.39 mmol) was coupled with 2 equivalents of N-(4-iodo-phenyl)-formamide (3.47 g, 14.0 mmol) following the Pd/Cu protocol using bis(dibenzyldieneacetone) 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, 26 mmol), and THF (30 mL). After stirring at 50°C for 3 h, the reaction mixture was washed with NH₄Cl (aq) and dichloromethane. The insoluble product was filtered to afford the desired compound as a red-orange powder (2.08 g, 79% yield): mp 200-230°C. IR (KBr) 2202.6, 1681.8, 1604.2, 1521.8, 1299.9, 831.2 cm⁻¹. ¹H
NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.92 (m, 0.4 H), 8.29 (m, 2.5 H), 7.86 (m, 2 H), 7.70 (m, 3.3 H), 7.57 (m, 4.3 H), 7.30 (m, 1 H), 7.22 (br s, 1.7 H).

1,4-Bis-(4-isocyano-phenylethynyl)-2-nitro-benzene (15, DWP-4-174). To a 500 mL round bottom flask was added $N$-{4-[4-(4-formylamino-phenylethynyl)-2-nitrophénylethynyl]-phenyl}-formamide (37) (0.500 g, 1.22 mmol). Air was removed and $N_2$ backfilled (3×). Dichloromethane (150 mL) and triethylamine (40 mL) was 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 (1.83 mmol) of triphosgene was added. After 3 h an additional 0.494 g (1.83 mmol) 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 dichloromethane as eluent; $R_f = 0.84$) followed by precipitation from dichloromethane/hexanes and a second silica column (dichloromethane 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$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (d, $J = 1.1$ Hz, 1 H), 7.71 (dd, $J = 8.1, 1.5$ Hz, 1 H), 7.68 (dd, $J = 8.0, 0.3$ Hz, 1 H), 7.60 (dt, $J = 8.7, 2.0$ Hz, 2 H), 7.56 (dt, $J = 8.6, 2.0$ Hz, 2 H), 7.38 (d, $J = 8.4$ Hz, 4 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.00, 149.95, 135.80, 135.03, 133.51, 133.26, 128.26, 127.09, 127.06, 124.35, 123.95, 123.79, 118.25, 97.45, 92.41, 89.57, 87.51. HRMS calc'd for $C_{24}H_{11}N_3O_2$: 373.085127. Found: 373.085373 (Error = 0.66 ppm).
N-[4-(2'-Nitro-4'-phenylethynyl-biphenyl-4-ylethynyl)-phenyl]-formamide
(16, DWP-4-15). 4'-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (1.01 g, 3.12 mmol) was
coupled with N-(4-iodo-phenyl)-formamide (0.771 g, 3.12 mmol) following the Pd/Cu
protocol using bis(dibenzylideneacetone)palladium(0) (0.090 g, 0.156 mmol), copper(I)
iodide (0.059 g, 0.31 mmol), triphenylphosphine (0.162 g, 0.62 mmol), DIEA (2.2 mL,
12 mmol), and THF (15 mL). After stirring at room temperature for 18 h, the reaction
mixture was washed with NH₄Cl (aq) and dichloromethane. Column chromatography
(silica gel using dichloromethane followed by 1:1 dichloromethane/ethyl acetate as
eluent; Rf = 0.66) afforded the desired compound (1.28 g, 93% yield): mp 190-200°C
decomp.). IR (KBr) 1687.6, 1603.4, 1522.4, 1352.5, 1298.0, 838.4, 756.6, 691.9 cm⁻¹.
¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, J = 11.4 Hz, 0.4 H), 8.39 (d, J = 1.6 Hz, 0.6 H),
8.00 (m, 1 H), 7.72 (m, 1 H), 7.54 (m, 7 H), 7.48 (br s, 0.22 H), 7.45 (br s, 0.22 H), 7.42
(d, J = 7.9 Hz, 1 H), 7.38 (m, 3 H), 7.30 (m, 2 H), 7.15 (br s, 0.6 H), 7.05 (m, 0.82 H).
HRMS calc'd for C₂₉H₁₈N₂O₅: 442.131742. Found: 442.132230 (Error = 1.1 ppm).

4'-(4-Isocyano-phenylethynyl)-2-nitro-4-phenylethynyl-biphenyl (17, DWP-4-18). To a 50 mL round bottom flask was added N-[4-(2'-Nitro-4'-phenylethynyl-
biphenyl-4-ylethynyl)-phenyl]-formamide (0.500 g, 1.13 mmol). Air was removed and
N₂ backfilled (3×). Dichloromethane (25 mL) and triethylamine (5 mL) were added and
the tube was cooled to 0°C. Triphosgene (0.152 g, 0.570 mmol) was then added. After
30 min starting material remained by TLC. An additional 0.076 g (0.285 mmol) of triphosgene was added. After 30 min (1 h total time), the reaction was complete by TLC. The mixture was washed with water and dichloromethane. Column chromatography (silica gel using dichloromethane as eluent; RF = 0.84) afforded the product (0.348 g, 73% yield): 180-190°C (decomp.). IR (KBr) 3052.6, 2121.2, 1540.9, 1523.3, 1501.1, 1348.1, 999.2, 834.2, 760.2, 692.7, 538.3 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J= 1.4 Hz, 1 H), 7.73 (dd, J= 8.0, 1.8 Hz, 1 H), 7.56 (m, 6 H), 7.41 (d, J= 8.2 Hz, 1 H), 7.37 (m, 5 H), 7.31 (dt, J= 8.5, 1.9 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 166.26, 149.35, 137.71, 135.44, 135.29, 133.06, 132.47, 132.22, 129.55, 128.95, 128.44, 127.55, 126.92, 126.39, 124.95, 124.77, 123.23, 122.56, 93.02, 91.97, 89.40, 87.03. HRMS calc’d for C₂₉H₁₈N₂O₂: 424.121178. Found: 424.121021 (Error = 0.37 ppm).

\[
\text{\textit{N-}[4-(3',2'-Dinitro-4'-phenylethynyl-biphenyl-4'-ylethynyl)-phenyl]-formamide (18, DWP-4-113).} \quad \text{4'-Ethynyl-3,2'-dinitro-4-phenylethynyl-biphenyl (1.10 g, 2.99 mmol) was coupled with \textit{N}-\text{(4-iodo-phenyl)-formamide (0.739 g, 2.99 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone)palladium(0) (0.086 g, 0.150 mmol), copper(I) iodide (0.057 g, 0.30 mmol), triphenylphosphine (0.157 g, 0.60 mmol), DIEA (2.1 mL, 12.0 mmol), and THF (20 mL). After stirring at 55°C for 4 h, the reaction mixture was washed with NH₄Cl (aq) and dichloromethane. The resulting solution was diluted with hexanes to precipitate the desired compound (1.48 g) which was taken onto the next step with no further purification: mp 236-240°C (decomp.). IR (KBr) 3361.9, 3073.1, 2202.5, 1692.6, 1600.5, 1520.1, 1405.4, 1337.3, 1282.2, 1238.6,}
\]
1144.5, 834.0, 753.7, 685.6 cm⁻¹. ¹H NMR (400 MHz, acetone-d₆) δ 8.43 (s, 0.73 H), 8.26 (d, J = 1.7 Hz, 1 H), 8.22 (d, J = 1.6 Hz, 1 H), 8.00 (dd, J = 8.1, 1.7 Hz, 1 H), 7.94 (d, J = 8.1 Hz, 1 H), 7.82-7.76 (m, 4.1 H), 7.67-7.60 (m, 4.63 H), 7.49 (m, 3.43 H).

![Chemical Structure](image)

4'-Isoeeyano-phenylethynyl)-2,3'-dinitro-4-phenylethynyl-biphenyl (19, DWP-4198). To a large test tube was added N-[4-(3,2'-dinitro-4'-phenylethynyl-biphenyl-4-ylethynyl)-phenyl]-formamide (0.500 g, 1.03 mmol). Air was removed and N₂ backfilled (3×). Dichloromethane (40 mL) and triethylamine (10 mL) was added and the solution was cooled to 0°C. Triphosgene (0.278 g, 1.03 mmol) was then added. After 2 h starting material remained by TLC. An additional 0.139 g (0.51 mmol) of triphosgene was added. After 45 min, an additional 0.139 g (0.51 mmol) of triphosgene was added. After 15 additional min, 0.278 g (1.03 mmol) of triphosgene was added (total of 3 equivalents). After 4.5 h (total time), the reaction was complete by TLC. The mixture was washed with NaCl (aq) and dichloromethane. Column chromatography (silica gel using dichloromethane as eluent; Rf = 0.84) afforded the product as a yellow solid (0.438 g, 91% yield): mp 160°C (decomp.). IR (KBr) 2119.7, 1525.6, 1341.3, 840.4, 761.6, 691.6, 543.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, J = 1.4 Hz, 1 H), 8.10 (d, J = 1.6 Hz, 1 H), 7.80 (dd, J = 8.0, 1.3 Hz, 1 H), 7.75 (d, J = 8.1 Hz, 1 H), 7.62 (d, J = 8.3 Hz, 2 H), 7.57-7.52 (m, 3 H), 7.43 (d, J = 7.9 Hz, 1 H), 7.40-7.38 (m, 5 H). ¹³C NMR (100 MHz, CDCl₃) δ 166.88, 150.01, 148.77, 138.92, 136.02, 135.22, 133.53, 133.08, 132.82, 132.28, 132.22, 129.77, 129.00, 128.04, 127.18, 127.04, 126.10,
124.90, 124.08, 122.32, 118.37, 96.71, 93.90, 87.43, 86.68. HRMS calc'd for C$_{29}$H$_{15}$N$_{3}$O$_{3}$: 469.106256. Found: 469.107078 (Error = 1.8 ppm).

\[
\text{\textit{N}-[4-[4-(4-Formylamino-phenylethynyl)-3,2'-dinitro-biphenylethynyl]-phenyl}-formamide (20, DWP-4-114).}
\]

4,4'-Diethyl-2,3'-dinitro-biphenyl (1.25 g, 4.28 mmol) was coupled with \textit{N}-(4-iodo-phenyl)-formamide (2.22 g, 8.99 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone)palladium(0) (0.123 g, 0.214 mmol), copper(I) iodide (0.082 g, 0.43 mmol), triphenylphosphine (0.226 g, 0.86 mmol), THF (25 mL), and DIEA (4.5 mL, 26 mmol). The reaction was stirred at 55°C for 4 h. The tube was filled with solid that was filtered and washed with dichloromethane to remove salts and starting materials to afford the desired product (2.13 g, 94% yield): mp 240°C (decomp.). IR (KBr) 3362.2, 3231.9, 3073.1, 2883.6, 2204.7, 1690.4, 1601.0, 1521.3, 1406.2, 1336.6, 1285.9, 1245.0, 1144.1, 836.9, 691.9, 533.1 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 10.47 (d, $J$ = 9.1 Hz, 1.4 H), 10.40 (t, $J$ = 9.4 Hz, 0.49 H), 8.93 (d, $J$ = 10.4 Hz, 0.44 H), 8.33 (s, 1.5 H), 8.26 (d, $J$ = 17.1 Hz, 2 H), 7.97 (d, $J$ = 7.8 Hz, 1 H), 7.92 (d, $J$ = 8.1 Hz, 1 H), 7.79 (d, $J$ = 8.0 Hz, 1.16 H), 7.72-7.68 (m, 4 H), 7.61-7.55 (m, 4 H), 7.32 (m, 1 H).

\[
\text{4,4'-Bis-(4-isocynano-phenylethynyl)-2,3'-dinitro-biphenyl (21, DWP-5-51).}
\]

To a 500 mL round bottom flask was added \textit{N}-[4-[4-(4-Formylamino-phenylethynyl)-}
3,2′-dinitro-biphenylethynyl]-phenyl}-formamide (1.0 g, 1.89 mmol). Air was removed and N₂ backfilled (3×). Dichloromethane (200 mL) and triethylamine (20 mL) was added and the solution was cooled to 0°C. Triphosgene (0.560 g, 1.89 mmol) was then added. After 30 min starting material remained by TLC. An additional 0.280 g (0.95 mmol) of triphosgene was added. After 60 min an additional 0.280 g (0.95 mmol) of triphosgene was added. After 40 min an additional amount of triphosgene (0.280 g, 0.95 mmol) was added. After 2.25 h (total time), the reaction was warmed to ambient temperature. An additional 0.25 equivalents of triphosgene (0.140 g, 0.48 mmol) was added and stirred for 1.5 h. The solvents were then removed under reduced pressure. Column chromatography (silica gel using dichloromethane as eluent; Rf = 0.84) afforded the product (0.478 g, 51% yield): 140-150°C (decomp.). IR (KBr) 2122.8, 1531.5, 1505.5, 1338.1, 841.9, 528.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, J = 1.6 Hz, 1 H), 8.10 (d, J = 1.8 Hz, 1 H), 7.81 (dd, J = 7.9, 1.6 Hz, 1 H), 7.76 (d, J = 8.1 Hz, 1 H), 7.62 (dt, J = 8.4, 1.9 Hz, 2 H), 7.58 (dt, J = 8.4, 1.9 Hz, 2 H), 7.53 (dd, J = 7.9, 1.8 Hz, 1 H), 7.46 (d, J = 8.0 Hz, 1 H), 7.41-7.38 (m, 4 H). ¹³C NMR (125 MHz, CDCl₃) δ 167.03, 166.94, 150.04, 148.82, 138.65, 136.06, 135.27, 133.74, 133.54, 133.30, 132.76, 132.38, 128.19, 127.11, 127.05, 125.21, 124.89, 124.02, 123.74, 118.55, 96.85, 91.85, 89.12, 87.34. LRMS calc’d for C₃₀H₁₄N₄O₄: 494.1 Found: 494.0.

\[ \text{N-[4-(5-Nitro-7-phenylethynyl-9H-fluoren-2-ythynyl)-phenyl]-formamide} \]

(22, DWP-4-55). 7-Ethynyl-4-nitro-2-phenylethynyl-9H-fluorene (0.875 g, ~2.59 mmol)
was coupled with N-(4-iodo-phenyl)-formamide (0.704 g, 2.85 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone) palladium(0) (0.074 g, 0.129 mmol), copper(I) iodide (0.049 g, 0.26 mmol), triphenylphosphine (0.136 g, 0.518 mmol), DIEA (1.8 mL, 10 mmol), and THF (35 mL). The tube was placed in a 55°C oil bath for 3 h. Column chromatography (silica gel using 3:1 dichloromethane/ethyl acetate; Rf = 0.35) afforded the impure product (1.07 g) which was taken directly onto the next step. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.42 (s, 0.9 H), 10.35 (d, $J = 10.7$ Hz, 0.3 H), 8.90 (d, $J = 10.8$ Hz, 0.3 H), 8.32 (d, $J = 1.5$ Hz, 1 H), 8.11 (s, 1 H), 8.07 (s, 1 H), 7.86-7.81 (m, 2.3 H), 7.73-7.45 (m, 13 H), 7.26 (d, $J = 8.4$ Hz, 0.7 H).

![Chemical Structure](image)

**7-(4-Isocyano-phenylethynyl)-4-nitro-2-phenylethynyl-9H-fluorene (23, DWP-4-74).** To a 500 mL round bottom flask was added N-[4-(5-nitro-7-phenylethynyl-9H-fluoren-2-ylethynyl)-phenyl]-formamide (1.07 g, ~2.3 mmol). Air was removed and N$_2$ backfilled (3×). Dichloromethane (250 mL) and triethylamine (50 mL) was added and the flask was cooled to 0°C. Triphosgene (0.434 g, 1.61 mmol) was then added. After 3 h the solution was at room temperature and starting material remained by TLC. An additional 0.124 g (0.46 mmol) of triphosgene was added. After 15 min (3.25 h total time), the reaction was complete by TLC. The mixture was washed with water and dichloromethane. Column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent; Rf = 0.39) followed by precipitation from dichloromethane/hexanes afforded the product (0.356 g, 31% yield over 2 steps): 210-
225°C (decomp.). IR (KBr) 3068.0, 2119.2, 1519.9, 1504.2, 1360.8, 1287.6, 838.3, 752.8, 686.8 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (m, 2 H), 7.83 (s, 1 H), 7.68 (s, 1 H), 7.53 (m, 5 H), 7.36 (m, 5 H), 3.96 (s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 166.36, 147.15, 145.36, 145.00, 137.74, 133.72, 133.04, 132.22, 132.17, 131.46, 129.42, 128.94, 128.25, 126.93, 126.87, 125.31, 124.92, 123.31, 123.11, 122.73, 92.67, 92.56, 89.79, 87.74, 37.07. HRMS calc’d for C₃₀H₁₆N₂O₂: 436.121178. Found: 436.121833 (Error = 1.5 ppm).

\[
\begin{array}{c}
\text{N-(2-Bromo-4-nitro-5-phenylethynyl-phenyl)-acetamide (24, DWP-I-209).}^{19}
\end{array}
\]

\text{N-(2,5-Dibromo-4-nitro-phenyl)-acetamide}^{9} \quad (5.00 \text{ g, 14.8 mmol),}

bis(dibenzylideneacetone)palladium(0) (0.173 g, 0.300 mmol), copper(I) iodide (0.057 g, 0.300 mmol), triphenylphosphine (0.194 g, 0.740 mmol), DIEA (10.3 mL, 59.2 mmol), THF (80 mL) and phenylacetylene (1.63 mL, 14.8 mmol) were used following the general procedure for couplings. The solution was stirred at RT for 1 d. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product (2.28 g, 43%). ¹H NMR (400 MHz, CDCl₃) δ 8.83 (s, 1 H), 8.37 (s, 1 H), 7.77 (br s, 1 H), 7.60 (m, 2 H), 7.37 (m, 3 H), 2.30 (s, 3 H).
\[ \text{N-(4-Nitro-5-phenylethynyl-2-trimethylsilanylethynyl-phenyl)-acetamide (25, DWP-I-215).} \]

\[ N-(2-Bromo-4-nitro-5-phenylethynyl-phenyl)-acetamide (1.70 \text{ g, 4.73 mmol}), \text{bis(dibenzylideneacetone)palladium(0) (0.055 g, 0.095 mmol), copper(I) iodide (0.018 g, 0.095 mmol), triphenylphosphine (0.062 g, 0.237 mmol), DIEA (3.29 mL, 18.9 mmol), THF (10 mL) and TMSA (0.87 mL, 6.1 mmol) were used following the general procedure for couplings. The solution was heated in a 60 °C for 5 d. Flash column chromatography (silica gel using dichloromethane as eluent) afforded the desired product (1.13 g, 64%).} \]

\[
\begin{align*}
\text{H} & \text{NMR (400 MHz, CDCl}_3\text{) } \delta \ 8.80 \text{ (s, 1 H), 8.19 (s, 1 H), 8.10 (br s, 1 H), 7.60 (m, 2 H), 7.36 (m, 3 H), 2.26 (s, 3 H), 0.31 (s, 9 H).}
\end{align*}
\]

\[ \text{2-Ethynyl-4-nitro-5-phenylethynyl-phenylamine (26, DWP-I-219).} \]

\[ N-(4-Nitro-5-phenylethynyl-2-trimethylsilanylethynyl-phenyl)-acetamide (1.00 g, 2.66 mmol), potassium carbonate (1.84 g, 13.3 mmol), methanol (50 mL) and dichloromethane (50 mL) were used following the procedure for deprotection. After stirring for 2 h at RT, the solution was filtered and worked up in the usual manner to afford the desired product (0.698 g, 100%).} \]

\[
\begin{align*}
\text{H} & \text{NMR (400 MHz, CDCl}_3\text{) } \delta \ 8.18 \text{ (s, 1 H), 7.54 (m, 2 H), 7.32 (m, 3 H), 6.84 (s, 1 H), 4.97 (br s, 2 H), 3.48 (s, 1 H).}
\end{align*}
\]
2-(4-Iodo-phenylethynyl)-4-nitro-5-phenylethynyl-phenylamine (27, DWP-I-220). 2-Ethynyl-4-nitro-5-phenylethynyl-phenylamine (0.698 g, 2.67 mmol), bis(dibenzylideneacetone)palladium(0) (0.046 g, 0.080 mmol), copper(I) iodide (0.015 g, 0.080 mmol), triphenylphosphine (0.052 g, 0.20 mmol), DIEA (1.86 mL, 10.7 mmol), THF (20 mL) and 1,4-diiodobenzene (2.64 g, 8.01 mmol) were used following the general procedure for couplings. The solution was heated in a 50 °C oil bath for 16 h. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (0.909 g, 73%). IR (KBr) 3463.2, 3360.3, 3221.6, 2207.7, 1628.0, 1602.5, 1539.4, 1514.9, 1470.4, 1284.3, 1248.7, 1005.4, 820.5, 754.9, 685.7, 623.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1 H), 7.71 (dt, J = 8.5, 1.9 Hz, 2 H), 7.58 (m, 2 H), 7.36 (m, 3 H), 7.24 (dt, J = 8.5, 1.9 Hz, 2 H), 6.92 (s, 1 H), 4.84 (br s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 151.35, 139.97, 138.20, 133.41, 132.50, 130.62, 129.67, 128.87, 122.93, 121.96, 121.44, 118.42, 107.30, 98.04, 96.76, 95.65, 86.31, 85.03. HRMS calc’d for C₂₂H₁₃N₂O₂I: 464.00217. Found: 464.00216 (Error = 0.034 ppm).

4-(2-Nitro-4-phenylethynyl-phenylethynyl)-benzoic acid methyl ester (28, DWP-III-37) 4-Ethynylphenyl-2-nitro-1-iodobenzene (4.0 g, 11.46 mmol), 4-ethynyl-benzoic acid methyl ester¹² (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 RT for 1 h. Normal workup using Et2O instead of dichloromethane 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, CDCl₃) δ 8.21 (dd, J = 1.5, 0.4 Hz, 1 H), 8.03 (dt, J = 8.6, 1.7 Hz, 2 H), 7.70 (dd, J = 8.1, 1.5 Hz, 1 H), 7.66 (d, J = 7.9 Hz, 1 H), 7.63 (dt, J = 8.6, 1.7 Hz, 2 H), 7.54 (m, 2 H), 7.37 (m, 3 H), 3.91 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 166.77, 149.92, 135.75, 134.99, 132.37, 132.24, 130.89, 130.02, 129.69, 128.97, 128.07, 127.21, 125.14, 122.39, 117.78, 97.96, 94.39, 87.76, 87.19, 52.74. HRMS calc’d for C₂₄H₁₅NO₄: 381.100108. Found: 381.099938 (Error = 0.45 ppm).

4-(2-Nitro-4-phenylethynyl-phenylethynyl)-benzoic acid (29, DWP-III-39) 4-(2-Nitro-4-phenylethynyl-phenylethynyl)-benzoic acid methyl ester (2.0 g, 5.24 mmol), lithium hydroxide monohydrate (1.1 g, 26.2 mmol), MeOH (130 mL), water (45 mL), dichloromethane (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 3 N 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, 1 H), 8.02 (m, 2 H), 7.96 (dd, J = 8.1, 1.5 Hz, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.71 (m, 2 H), 7.64 (m, 2 H), 7.48 (m, 3 H).
$^{13}$C NMR (125 MHz, DMSO) δ 167.46, 150.24, 136.70, 135.86, 132.75, 132.58, 132.43, 130.58, 129.77, 128.25, 126.37, 124.74, 122.13, 117.12, 97.76, 94.45, 87.83, 87.74. HRMS calc'd for $C_{23}H_{13}NO_4$: 367.084458. Found: 367.084044 (Error = 1.1 ppm).
References


Chapter 3

Electrochemical Testing of Potential Molecular Devices
Introduction

The molecular Negative Differential Resistance (mNDR) effect was discovered when a molecular wire (1) that was synthesized for testing as a switch in an externally applied electric field was simply tested for its electrical conductivity. The defining characteristic of NDR is that it will only carry current at one narrow range of voltages. 1 showed an intense NDR when tested in the nanopore configuration. The I/V curve is shown in Figure 1.

![Chemical structure of molecule 1](image)

**Figure 1.** I/V curve from nanopore testing of 1 at 60 K.

Speculation by various members of the team brought about the idea that the mechanism may involve the reduction of the molecules in the nanopore device. It was thought that the "turn-on" voltage, that is, the potential where current began to increase...
dramatically, was the result of a single-electron reduction of the molecules. The "turn-off" voltage, where the current essentially stopped, occurred because of a second single-electron reduction. In an effort to understand the mechanism behind the NDR effect, calculations (by Jorge Seminario at the University of South Carolina) and cyclic voltammetric measurements on derivatives of 1 were performed. Also, it was necessary to design, synthesize, and test a variety of compounds that would differ from compound 1 only slightly in order to piece together a picture of the mechanism.

The theoretical studies by Seminario suggest that this switching is based on changes in the lowest unoccupied molecular orbital (LUMO) upon charging. For the ground state unperturbed molecule (Q = 0), there is minor LUMO contribution from the lower ring (Figure 2). This would result in little current flow through the LUMO orbitals. For the singly reduced molecule (Q = -1), the LUMO is completely delocalized, suggesting little resistance to electron flow. For the doubly reduced molecule (Q = -2), there is little LUMO contribution on the lowest ring. This would indicate a rapid turn off of the current flow through the molecule.
**Figure 2.** Nitroaniline compound (analogous to 1) and LUMOs of each state (Q = 0, neutral ground state, Q = -1, first reduction, Q = -2, second reduction).

**Results and Discussions**

Electrochemical testing began with 1a. Because of potential problems using the thioacetate moiety (possible reduction of carbonyl group) and the fact that the acetyl portion was absent in the nanopore device itself, a methyl sulfide group was used in its place. This was used to more accurately mimic the S-Au bond, as well as to determine if the sulfur had any effect on the mechanism. This was tested in conjunction with the nitroaniline compound with no alligator clip moiety (1b) and the compound with the thioacetyl alligator clip (1). The results of the tests are shown in Figure 3.
Figure 3. Cyclic voltammetry results for 1, 1a, and 1b.
1a and the nitroaniline compound with no alligator clip (1b) showed almost identical reduction potentials suggesting that the sulfur plays little if any role in the CV effects. All three derivatives showed first reduction potentials of -1.7 V and second reduction potentials of -2.3 V. This gives a potential difference of 0.6 V, which corresponds nicely with a potential difference of approximately 0.6-0.7 V from the I/V plot of the nanopore (Figure 1). It should be noted here that changing the solvent to acetonitrile and the electrolyte to tetrabutylammonium hexafluorophosphate had no significant effect on the peak potentials. It should also be noted that this research is not focused on in depth electrochemical studies. These cyclic voltammetry experiments are intended to be used as a simple tool to help predict and understand the solid state properties of these potential moletronics devices.

**Scheme 1**

![Scheme 1](attachment:image.png)

Scheme 1 shows the synthesis of the unfunctionalized compound 2. 1,4-Diiodobenzene was coupled with an excess of phenylacetylene to afford 2 in a low yield of 21%. Although the yield could most certainly be improved upon, there was enough material obtained from this one reaction so that no further reactions were attempted. The CV for compound 2 is shown in Figure 4.
**Figure 4.** Cyclic voltamogram of unfunctionalized compound 2.

As Figure 4 shows, there are no reductions in the usual desired range of 0 to -2.3 V as in the case of the nitro-amino compound. An unfunctionalized compound similar to 2 but with a thiol alligator clip, shows no switching behavior in a solid-state testing device. This data helps suggest that the switching mechanism is based on reduction of the organic compound.

Figure 5 shows the CV of an ethyl-functionalized molecular wire 3 which has been tested in the nanopore also. In the nanopore this compound shows no switching behavior either. However, the CV does show a reduction at -2.2 V. This could be due to the reduction of the carbonyl of the thioacetyl functionality since it is still present on this test compound. Also, it can be seen that there are no other reductions, particularly around -1.0 V to -2.0 V as there is with the nitroaniline compound.
Figure 5. Cyclic voltammogram of ethyl functionalized compound 3.

Compound 4 showed the NDR effect as well as the nitroaniline device, and it persisted to room temperature (Figure 6) unlike the nitroaniline device which operated only at low temperature.
Figure 6. I/V plots at three different temperatures (K) from the nanopore device containing the mononitro compound 4.

As can be seen in the well-defined low-temperature curve of Figure 6 (180 K), the mono-nitro device seems to switch on at approximately 1.3 V and switches off at 1.9 V. This gives a difference in switching voltages of 0.6 V. Scheme 2 shows the synthesis of 4a, the mono-nitro compound with no alligator clip. Once it was determined that the sulfur moiety played no significant role in the electrochemistry, we decided to use compounds with no end groups at all. The CVs are generally cleaner and the compounds are much easier to synthesize.

Scheme 2
2,5-Dibromonitrobenzene was coupled with an excess of phenylacetylene to give final product 4a in a modest yield of 64%. As noted in Chapter 1, the cyclization reaction between the nitro group and the alkyne ortho to it may be a problem here leading to reduced yields.

Figure 7 shows the CV of compound 4a. As can be seen from the figure, there are two clear reduction peaks at -1.4 V and -2.1 V. These peaks are quasi-reversible, indicating 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. Also, these reduction peaks are shifted approximately +0.3 V from those of the nitroaniline device. This may give some insight into the differences in the switching behavior of the two compounds.

![Cyclic voltammogram of mono-nitro compound 4a.](image)

Figure 7. Cyclic voltammogram of mono-nitro compound 4a.

Figure 8 shows the I/V curve of the 2,3'-dinitro biphenyl device (5) described in Chapter 1. This device behaves even better than both the nitro-amino devices and mono-
nitro devices. This can be seen from the fact that even at room temperature, 5 shows a well-defined switching behavior, whereas the mono-nitro device 4, showed well-defined behavior only at lower temperatures.

![Compound 5](image)

**Figure 8.** I/V plots of compound 5 tested in the mesa configuration with Au chemisorbed contact and Ti/Au physisorbed contact at room temperature (300 K). The arrows indicate a negative potential sweep necessary to "reset" the switch.

**Scheme 3**

![Scheme 3](image)
Scheme 3 shows the synthesis of the 2,3'-dinitrobiphenyl compound with no alligator clips (5a). This compound was synthesized for the purposes of this electrochemical testing. 4,4'-Dibromo-2,3'-dinitrobiphenyl was coupled with an excess of phenylacetylene to afford compound 5a in a good yield of 80%. The CV for this compound can be seen in Figure 9. There appear to be three distinct reduction peaks, although they seem to be only quasi-reversible. The 1st and 3rd potentials are approximately the same in relation to the mononitro compound 4a discussed previously. Interestingly, 5a has a third reduction not seen in any of the previous devices. It is likely that the new reduction is due to the presence of two nitro groups instead of just one as in the previous compounds. This new reduction potential is -1.60 V, which is approximately 0.2 V difference from the first potential.

![Graph](image)

**Figure 9.** Cyclic voltammogram of the 2,3'-dinitro-biphenyl compound with no alligator clips (5a). The reduction potentials were found to be -1.37 V, -1.60 V and -2.26 V.

From this data, it seemed that this system should have better electronic properties than previous systems, and this is precisely what has been observed. As can be seen in Figure 8, the switching “on” potential of the 2,3'-dinitro biphenyl device is approximately
2.7 V and the switching “off” potential is approximately 2.9 V. The difference here is approximately 0.2 V, closely corresponding to the difference in the CV reduction potentials. This data lends more support to the proposed theory of switching operation.

**Scheme 4**

Scheme 4 shows the synthesis of the 2,2'-dinitro-biphenyl compound with no alligator clips. This compound was made for the purpose of these CV experiments. 4,4'-Dibromo-2,2'-dinitrobiphenyl was coupled with an excess of phenylacetylene to afford compound 6 in a yield of 86%. CV measurements were performed as usual and can be seen in Figure 10.

**Figure 10.** Cyclic voltammagram of the 2,2'-dinitro biphenyl compound 6. There are two clear and quasi-reversible reductions observed at −1.32 V and −1.61 V.
The reduction potentials are almost identical to the first two reductions of the 2,3'-dinitro-biphenyl compound. However, both of these reductions appear to be reversible in this system. Also, there is no observation of a third reduction at approximately -2.0 to -2.2 V, as was seen with the 2,3'-dinitro system. One could reason that the third reduction could be due to some reaction between a nitro group and an alkyne of 5a located in an ortho position relative to the nitro. This may be reasonable because the 2,2'-dinitro device is the first of these compounds that does not have this nitro-alkyne relationship. This may also be reasonable because nitro groups and alkynes in this relationship are known to react and form a new cyclic structure, such as an isatogen (Chapter 1).

Figure 11 shows the CV results of the mono-nitro biphenyl device 7 described in Chapter 1. As can be seen in the plot, there are again two reductions, one at -1.47 V and another at -2.19 V. These potentials are close to those of the mono-nitro device described earlier, however, the second reduction here is much less pronounced than for the mono-nitro device. Also, the second reduction does not seem to be reversible. As was seen with the 2,2'-dinitro biphenyl device, there is no “nitro-ortho alkyne” relationship with compound 7. This could be the reason that the second reduction is a weak reduction.
Figure 11. Cyclic voltammogram of mono-nitro biphenyl compound 7.

Figure 12 shows the cyclic voltammogram of the tetra-nitro device 8 described in Chapter 1. The two voltammagrams represent the same compound from different synthetic batches. As can be seen, the CVs look similar but are not exactly the same. I believe that this is because the tetra-nitro device is very redox reactive and may not be very stable. Upon close examination, there appear to be several reductions in both CVs between -0.7 V and -1.4 V. Because there are four nitro groups located in this system, several reductions could be possible and may overlap, thereby making the voltammagrams difficult to interpret.
Figure 12. Cyclic voltammograms of tetrinitro biphenyl compound 8.

Figure 13 shows a CV for teta-nitro compound 8a. This compound was isolated as a byproduct from an intermediate reaction on the way to device 8. This CV shows more clearly the many reductions present between -0.7 V and -1.4 V. Upon close inspection, there appear to be four reductions present with three of them being quasi-reversible. From this data, it seems that this device (8) may be an excellent redox center
for use in molecular electronics; however, it also seems that there could be some stability problems associated with the compound.

![Compound 8a](image)

**Figure 13.** Cyclic voltammogram of tetra-nitro compound 8a.

The cyclic voltammogram for dinitro-diamino device 9 is shown in Figure 14. Although this compound was not designed to rely on its redox properties to behave as a functional device (it should rely on the ability of dipole moments of the internal rings to align with an applied electric field; Chapter 1), the electrochemical properties were measured to compare with the other devices.
Figure 14. Cyclic voltammogram of dinitro-diamino biphenyl compound 9.

At close examination, one can see what appears to be two peaks overlapping. It is estimated that there are two reductions at -1.71 V and -1.80 V. This may be due to the presence of two nitro groups on the system.

Figure 15 shows the CV of nitro-fluorene compound 10. There is a clearly visible reduction peak at -1.40 V and another reduction, which is not so clear, at -2.0 V. These are similar to the results for the mono-nitro biphenyl compound 7 which showed reductions at -1.47 V and -2.19 V. The second reduction of the mono-nitro biphenyl 7 device was likewise not well-defined. These results show the similar behavior of the two devices with only a minor shift in reduction potentials.
Figure 15. Cyclic voltammogram of nitro-fluorene compound 10.

Figure 16 shows the CV for fluorenone device 11. The graph shows a single reduction at -1.45 V which appears to be quasi-reversible. This is almost the same value for the reduction potential for the nitro-fluorene 55. One could argue that there is a second reduction at -2.1 V but it is not clear. This data suggests that this device may give similar results to previously tested compounds when tested in a solid-state testbed such as the nanopore device.
Figure 16. Cyclic voltammogram of fluorenone compound 11.

Figure 17 shows the cyclic voltammogram for the nitro-fluorenone device 12. This compound shows two clear reduction peaks. The reduction potentials are -1.26 V and -1.66 V. Other than the tetra-nitro device, this is the lowest reduction potential observed for any biphenyl or fluorenyl-based compounds. Upon close inspection, it appears that the first reduction peak may be two close, overlapping peaks, with the first reduction being approximately -1.16 V. In my opinion, due to the interesting CV properties and the brilliant orange color of this compound, this could be one of the most interesting compounds synthesized to date for the moletronics project.
Figure 17. Cyclic voltammogram of nitro-fluorenone compound 12.

In addition to examining devices containing nitro groups, our group is also examining the possibility of using other electroactive cores for devices. Perhaps an obvious choice is nature’s electron carrier, the quinone. Scheme 5 depicts the synthesis of a quinone compound with no alligator clips. 2,5-Dibromo-1,4-dimethoxybenzene was coupled with an excess of phenylacetylene to afford compound 13 in 92% yield. This compound was subjected to the CAN oxidation conditions to afford the desired quinone compound 14 in 47% yield. As stated previously in Chapter 1, the optimum conditions for the oxidation have not yet been obtained for these systems.
Scheme 5

CV measurements were performed on this compound following our standard method (Figure 18). The reduction potential was found to be $-0.64 \text{ V}$, which is typical of quinones. The reduction potential should be a 2-electron reduction, again typical of quinones. This is the lowest reduction potential of any potential devices synthesized in our group. According to our current hypothesis of how these molecular electronic devices work, the quinone should be able to store two electrons easily in the solid state.

Figure 18. Cyclic voltammogram of quinone compound 14.
Scheme 6 shows the formation of an isatogen 15 from the unfunctionalized mononitro compound 4a. TBAF was used to attempt the transformation but failed. As shown in Scheme 6, heating the compound to reflux in pyridine promoted the cyclization and rearrangement in good yield. This compound was synthesized for CV testing and to determine the reaction conditions required.

CV testing revealed two reductions: one at -0.62 V and the second at -1.39 V (Figure 19). This is markedly different from the mononitro compound which shows two reductions: one at -1.39 V and the second at -2.09 V. In addition, the quinone compound reported shows only one reduction at -0.64 V. It seems intuitively obvious that for isatogen 15, the first reduction is of the carbonyl group (similar to the quinone) and the second belongs to the "pseudo-nitro" (nitron) group. This gives rise to the idea that carbonyl-containing systems may be effective moletronics devices. Due to its brilliant orange color and interesting CV properties, I believe that this is another very important and potentially useful compound for the moletronics project.
Figure 19. Cyclic voltammogram of isatogen 15.

Summary

Although absolute values of the reduction potentials cannot be compared between the nanopore (pseudo solid state) and solution experiments, solution CV helps to support the proposed mechanism wherein reduction of the system occurs to open or close a transport channel. Also, it is hoped that CV testing may prove itself to be a method of quick-screening compounds for solid state testing as well as a way to predict solid-state electronic properties. However, more data needs to be obtained before this can be firmly established.

Experimental Procedures

General: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. \(N,N\text{-dimethylformamide (DMF)}\) was distilled over calcium hydride and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexanes were distilled. \(N,N\text{-Diisopropylethylamine (DIEA)}\) was
distilled over calcium hydride. Silica gel plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. 1H NMR spectra were observed at 400 MHz and 13C NMR spectra were observed at 100 MHz on a Bruker 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 by Terry Marriott at Rice University’s mass spectrometry lab. 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/AgNO3 reference electrode. The solutions were 1 mM in DMF + 0.1 M n-Bu4NBF4. The scan rate was 0.1 V/s at 25°C. All new compounds were named using the Beilstein Autonom feature of Beilstein Commander software.

**General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).** 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 equivalents 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 NH₄Cl. The organic layer was diluted with methylene chloride and washed with a saturated solution of NH₄Cl (3×). The combined aqueous layers were extracted with methylene chloride (3×). The combined organic layers were dried over anhydrous MgSO₄ and the solvent removed in vacuo. The crude product was then purified by flash or column chromatography (silica gel).

**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 equivalents of potassium carbonate, and equivalent amounts of methanol 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.

**General Procedure for Electrochemical Testing of Potential Moletronics 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/AgNO₃ non-aqueous reference electrode. The solutions were 1 mM in DMF and 0.1 M n-Bu₄NBF₄. The scan rate was 0.1 V/s at 25°C.
1,4-Bis-phenylethynyl-benzene (2, DWP-I-67).\textsuperscript{9} 1,4-Diodobenzene (0.200 g, 0.606 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.021 g, 0.030 mmol), copper(I) iodide (0.012 g, 0.061 mmol), THF (20 mL), DIEA (0.84 mL, 4.85 mmol), and phenylacetylene (0.17 mL, 1.52 mmol) were used following the general procedure for couplings. The solution was heated in a 70 °C oil bath for 17 h. After workup, the solid was washed with cold hexanes. A silica plug (using dichloromethane as eluent) afforded the desired product as a white solid (0.035 g, 21%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.58-7.55 (m, 4 H), 7.54 (s, 4 H), 7.40-7.37 (m, 6 H).

2-Nitro-1,4-bis-phenylethynyl-benzene (4a, DWP-I-184, II-63). 2,5-Dibromonitrobenzene (8.69 g, 30.9 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.434 g, 0.619 mmol), copper(I) iodide (0.236 g, 1.24 mmol), THF (40 mL), DIEA (21.5 mL, 124 mmol), and phenylacetylene (7.47 mL, 68.0 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/dichloromethane as eluent) followed by recrystallization from 95% ethanol afforded the desired product as yellow needles (6.17 g, 62%): 96-98°C. 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\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.21 (m, 1 H), 7.69 (dd, \(J = 8.1, 1.5\) Hz, 1 H), 7.66 (dd, \(J = 8.1, 0.4\) Hz, 1 H), 7.59 (m, 2 H), 7.54 (m, 2 H), 7.37 (m, 6 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 149.69, 135.44, 134.68, 132.30, 132.02, 129.63,
129.40, 128.75, 128.71, 127.80, 124.31, 122.47, 122.30, 118.26, 99.09, 93.78, 87.10, 85.04. HRMS calc’d for C_{22}H_{13}NO_{2}: 323.0946. Found: 323.0943 (Error = 1.2 ppm).

2,3'-Dinitro-4,4'-bis-phenylethynyl-benzene (5a, DWP-I-298, II-4). 4,4'-Dibromo-2,3'-dinitro biphenyl (0.402 g, 1.00 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.050 mmol), copper(I) iodide (0.019 g, 0.10 mmol), triphenylphosphine (0.033 g, 0.125 mmol), THF (10 mL), DIEA (0.70 mL, 4.0 mmol), and phenylacetylene (0.33 mL, 3.0 mmol) were used following the general procedure for couplings. The tube was capped and the solution was heated in a 70 °C oil bath for 1 d. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (0.355 g, 80% yield): mp 144-147°C. IR (KBr) 3080.9, 2847.8, 2213.0, 1542.0, 1521.4, 1440.9, 1341.0, 1279.1, 1140.0, 1071.9, 889.7, 837.0, 761.6, 689.9, 529.4 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 8.12 (d, \(J = 1.6\) Hz, 1 H), 8.07 (d, \(J = 1.8\) Hz, 1 H), 7.79 (dd, \(J = 8.0, 1.6\) Hz, 1 H), 7.74 (d, \(J = 8.0\) Hz, 1 H), 7.60 (m, 2 H), 7.55 (m, 2 H), 7.50 (dd, \(J = 8.0, 1.9\) Hz, 1 H), 7.44 (d, \(J = 7.9\) Hz, 1 H), 7.38 (m, 6 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 149.95, 148.81, 138.10, 135.97, 135.22, 133.26, 132.65, 132.54, 132.27, 129.88, 129.73, 128.99, 128.93, 127.99, 125.89, 124.75, 122.65, 122.37, 119.24, 99.05, 93.75, 86.77, 84.99. HRMS calc’d for C_{28}H_{16}N_{2}O_{4}: 444.1110. Found: 444.1110 (Error = 0.03 ppm).
**2,2′-Dinitro-4,4′-bis-phenylethynyl-benzene (6, DWP-I-217).** 4,4′-Dibromo-2,2′-dinitrobiphenyl (1.00 g, 2.49 mmol), bis(dibenzylideneacetone)palladium(0) (0.043 g, 0.075 mmol), copper(I) iodide (0.014 g, 0.075 mmol), triphenylphosphine (0.050 g, 0.19 mmol), THF (15 mL), DIEA (1.73 mL, 9.96 mmol), and phenylacetylene (0.68 mL, 6.2 mmol) were used following the general procedure for couplings. The tube was capped and the solution was heated in a 50 °C oil bath for 2 d. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (0.955 g, 86% yield): mp 234-236°C. IR (KBr) 3078.2, 2212.5, 1595.1, 1546.5, 1531.6, 1490.2, 1441.7, 1350.1, 1070.8, 898.7, 839.6, 827.4, 765.1, 692.8, 530.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 1.6 Hz, 2 H), 7.79 (dd, J = 7.9, 1.7 Hz, 2 H), 7.56 (m, 4 H), 7.38 (m, 6 H), 7.27 (d, J = 7.9 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 147.48, 136.39, 133.48, 132.26, 131.35, 129.61, 128.96, 128.13, 125.66, 122.49, 93.25, 86.90. HRMS calc’d for C₂₈H₁₆N₂O₄: 444.1110. Found: 444.1113 (Error = 0.73 ppm).

**1,4-Dimethoxy-2,5-bis-phenylethynyl-benzene (13, DWP-I-185).**¹⁰ 2,5-Dibromo-1,4-dimethoxybenzene (8.74 g, 29.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.415 g, 0.591 mmol), copper(I) iodide (0.225 g, 1.18 mmol), triphenylphosphine (0.310 g, 1.18 mmol), THF (35 mL), DIEA (20.5 mL, 118 mmol), and phenylacetylene (7.8 mL, 70.9 mmol) were used following the
general procedure for couplings. The solution was heated in a 65 °C oil bath for 3 d. Recrystallization from benzene afforded the desired product (9.22 g, 92%): mp 175-177°C (lit. 176-176.5°C).\(^{10}\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (m, 4 H), 7.34 (m, 6H), 7.03 (s, 2H), 3.89 (s, 6 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.10, 131.89, 128.60, 128.50, 123.39, 115.86, 113.57, 95.23, 85.86, 56.66.

![Structural formula of 2,5-Bis-phenylethynyl-[1,4]benzoquinone](image)

**2,5-Bis-phenylethynyl-[1,4]benzoquinone (14, DWP-I-177, 189, 199, II-74).**\(^{10}\) 2,5-Di(ethynylphenyl)-1,4-dimethoxybenzene (0.300 g, 0.886 mmol) and THF (6 mL) were added to a 25 mL round bottom flask containing a stir bar. A solution of ceric ammonium nitrate (1.46 g, 2.66 mmol) in water (3 mL) was slowly added to the flask and allowed to stir for 15 min. Water was added and the organic materials were extracted with dichloromethane. Flash column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent) afforded the desired product (0.129 g, 47%). IR (KBr) 3047.5, 2203.0, 1706.2, 1655.3, 1568.3, 1215.4, 1100.6, 902.1, 757.6, 686.4 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (dd, \(J = 7.9, 1.5\) Hz, 4 H), 7.38 (m, 6 H), 6.99 (s, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 182.87, 136.55, 133.34, 132.83, 130.57, 128.97, 121.83, 105.26, 82.90. HRMS calc’d for C\(_{22}\)H\(_{12}\)O\(_2\): 308.0837. Found: 308.0834 (Error = 1.2 ppm).
1-Oxy-2-phenyl-6-phenylethynyl-indol-3-one (15, DWP-III-135). 2-Nitro-1,4-bis-phenylethynyl-benzene (0.100 g, 0.310 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 dichloromethane as eluent; Rf = 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. $^1$H NMR (500 MHz, CDCl₃) δ 8.64 (m, 2 H), 7.79 (m, 1 H), 7.66 (dd, $J$= 7.5, 1.2 Hz, 1 H), 7.60 (d, $J$= 7.6 Hz, 1 H), 7.56 (m, 2 H), 7.49 (m, 3 H), 7.38 (m, 3 H). $^{13}$C NMR (100 MHz, CDCl₃) δ 186.44, 148.30, 134.61, 133.29, 132.32, 131.36, 130.79, 129.75, 129.01, 128.97, 128.33, 126.15, 122.46, 122.15, 122.04, 117.41, 95.10, 88.48. HRMS calc'd for C$_{22}$H$_{13}$NO$_2$: 323.094629. Found: 323.094450 (Error = 0.55 ppm).
References


Chapter 4

Synthesis of Molecular Systems with Polymerizable Functionalities
Introduction

An issue that faces those of us interested in molecular electronics is how we can evaluate the potential usefulness of compounds in a quick and efficient way. Up to this time, most compound testing has been performed in nanopores.\textsuperscript{1-3} This can be a long and arduous process because the nanopores themselves can be difficult to prepare. Also, because it is still not certain why particular compounds show NDR and memory, to test new compounds in this way can be a waste of time and valuable nanopore assemblies. Therefore, it is imperative that we find a method of quick-screening compounds to determine their usefulness before those compounds are assembled into nanopores.

The chief reason that the nanopore device\textsuperscript{2} must be used is that it confines the molecules to a small (30-50 nm) area that is essentially defect-free. This ensures high-quality SAM formation so that when a metal is vapor-deposited on top of the molecules, no leakage of the top contact to the bottom contact occurs; i.e. no short circuits. If we can find some way to deposit a metal onto a larger area SAM, it should prove easier to more quickly test these compounds.

One possible way of doing this is to covalently connect each molecule of the SAM after monolayer formation. This would essentially be a polymerization process. By connecting all the molecules together, it should be more difficult for metal atoms or clusters to penetrate the SAM thereby causing shorts. I have devised two possible ways of achieving this. One method of achieving the surface polymerization is through the use of conjugated diyne functionalities (Figure 1). Similar work has already been done by Crooks.\textsuperscript{4,5} He and coworkers used long aliphatic chains containing diynes to form monolayers and then, through UV irradiation of the monolayers, to polymerize those
compounds. Then they showed, using electrochemical techniques, that the polymerized SAMs passivated the metal substrates; no electrolytes could penetrate the polymers.

Figure 1. Schematic representation of how a SAM of diyne compound 5 may be polymerized via UV radiation.

It is our hope that this approach can be applied similarly to quick-screening for molecular electronics. By placing conjugated diynes on the end of the molecules opposite the alligator clips, it should be possible to force those diynes to polymerize once in a monolayer structure. As can be seen in Schemes 1 and 2 below, two compounds have already been synthesized to do this, although little collaborative testing has been done.

The other method involves the use of dipyrrromethane functionalities located on the end of the molecule opposite the alligator clip used for SAM formation. Once a part of the monolayer, the pyrrole functionalities could be polymerized to form a polymer network along the top of the SAM. This could be done in one of two general ways. The pyrrole moieties could either be connected electrochemically or chemically to adjacent pyrrole moieties (Figure 2).
Figure 2. Representation of how polypyrrole (Ppy) could be formed on top of a pyrrole-containing SAM.

The other method would involve a "porphyrin-like" approach. The dipyrrromethanes, once a part of a SAM, could be reacted with an aldehyde and Lewis acid to create a "porphyrin-like" network across the top of the SAM. If this does not appear to completely seal the top of the SAM, we can use an aldehyde, Lewis acid, and additional pyrrole (Figure 3). In either case, if the new polymerized surface is insulating, DDQ can be added to oxidize and increase conjugation through the network, just as in porphyrin chemistry.
**Figure 3.** Representation of how a polymer network may be formed on top of a SAM using pyrrole and an aldehyde. ($R =$ continuing polymer network)

**Results and Discussions**

**Scheme 1**

Scheme 1 depicts the synthesis of an “unfunctionalized-core” wire with the diyne functionality and a butyl “cap.” The butyl portion was used for two reasons. First, the starting material, hex-1-yne, was readily available and a liquid, which is easier to work
with than a gas. Second, the butyl group, if the polymerization on the SAM is achieved, should provide some "cushioning" for the top metal contact deposition while also allowing the metal to contact the conjugated portion of the system (necessary for conduction of electrons). Iodination of hex-1-yne\textsuperscript{8} provided \textbf{1} in good yield. Coupling of the iodoalkyne with 4-ethynylbromobenzene using copper iodide in pyrrolidine\textsuperscript{9} afforded \textbf{2} in good yield. Sonogashira coupling of \textbf{2} with TMSA provided \textbf{3}, again, in good yield. Deprotection of the terminal alkyne afforded \textbf{4} which was then taken onto another coupling with the standard thioacetate alligator clip to give \textbf{5} in a low yield of 31\%. I cannot speculate on why the coupling did not proceed more smoothly than observed. It's highly probable that if the reaction were repeated with more care to keeping oxygen out of the system, the yield would be higher. This compound was sent to Paul Weiss at Penn State for evaluation in the polymerization on a SAM.
Scheme 2

Scheme 2 shows the synthesis of a nitro-containing diyne compound similar to an unfunctionalized diyne which I synthesized earlier. Paul Weiss has performed some preliminary experiments which show that he can use an STM tip to induce polymerization of small domains of these diyne functionalities after they are part of a SAM. Ultimately, we would like to be able to induce polymerization of the entire SAM to seal up defect sites in the SAM.

The synthesis began with terminal alkyne 4 being coupled with 4-iodo-2-nitroaniline to give 6 in a good yield of 74%. 6 was then diazotized and converted to the iodide to afford 7 in 59% yield. 7 was then coupled with TMSA in high yield followed by a high yielding potassium carbonate deprotection to give terminal alkyne 9. This alkyne was then coupled with the thioacetyl alligator clip to provide final compound 10.
in a good yield of 64%. This compound has been sent to Paul Weiss for testing. We are waiting for more results.

**Scheme 3**

The synthesis of a dipyrrromethane compound is shown in Scheme 3. The reason for making this compound was to see that if once in a SAM, these molecules could be polymerized to seal the surface and high defect sites, as described earlier. These dipyrrromethanes could be polymerized in either of the two ways discussed previously.

The synthesis began with the coupling of 4-bromobenzaldehyde with TMSA to provide **11** in high yield.\textsuperscript{10} Deprotection of the terminal alkyne gave **12** in almost quantitative yield. **12** was then coupled with the thioacetyl alligator clip to afford **13** in a good yield of 86%.\textsuperscript{10} Finally, pyrrole was allowed to react overnight with **13** in the presence of acetic acid to afford dipyrrromethane **14** in high yield.\textsuperscript{10}

Initial attempts to polymerize pyrrole on top of a SAM of **14** were unsuccessful. The SAMs were formed in the usual manner with basic conditions\textsuperscript{11} on a gold substrate. The polymerization conditions used consisted of a 0.1 M solution of \( n- \)
tetrabutylammonium tetrafluoroborate in acetonitrile. The pyrrole concentrations varied from 0.01 mM to 0.01 M. At high concentrations, a visible amount of polypyrrole was deposited (a black film could be seen depositing onto the substrate). The thickness of these films could not be determined by ellipsometry. At lower concentrations, however, the gold was actually observed to disappear from the substrate leaving behind the titanium or chromium adhesion layer. It was later determined that the electrolyte itself was the culprit behind the disappearing gold. It is reasoned that the tetrafluoroborate counterion of the electrolyte was possibly decomposing to BF$_3$ and F$^-$. It could be that the fluoride ion, at high potentials, could be reacting with the gold and pulling it from the surface. It was seen that at potentials above +1.0 V, the gold disappeared while using this electrolyte. When the electrolyte was switched to $p$-toluene sulfonic acid (pTSA), the gold remained intact at potentials greater than 2.0 V. As can be seen in Figure 4, the electrochemical polymerization of pyrrole, using pTSA as electrolyte, on top of the SAM was a success.
Figure 4. Plot of thickness of polypyrrole layer vs number of electrochemical cycles used to grow polypyrrole.

Figure 4 shows two different polypyrrole growth experiments. The thickness of a polypyrrole layer grown using a pyrrole concentration of 0.1 mM, was found to increase at a rate of approximately 1.0 nm per cycle. The CV cycle used was 0 V to 1.2 V and back to 0 V at 0.1 V/s. This was found to be the optimal conditions for polypyrrole growth. At 0.5 mM pyrrole concentration, the thickness rate increase was found to be approximately 2-3 nm per cycle. From this data, it can be seen that polypyrrole can be electrochemically grown from a pyrrole-functionalized SAM in a controlled manner with the rate of growth controlled by pyrrole concentration.
Scheme 4

Scheme 4 shows the partial synthesis of a nitro-containing dipyrrromethane system for the same purpose as described previously. Compound 12 was coupled with (4-ido-3-nitro-phenylethynyl)-trimethyl-silane to provide 15 as an impure solid (~90% yield). 15 was then deprotected to liberate the terminal alkyne 16 in an overall yield of 76% over the 2 steps. 16 was then coupled with the thioacetyl alligator clip to provide 17 in 80% yield. Although not the final target compound, 17 could be a potential moletronics device. 17 was then reacted with pyrrole and acetic acid in methanol to afford final compound 18 in 75% yield. No attempts were made to polymerize the pyrrole functionalities or to deposit polypyrrole on a SAM of this compound.
Scheme 5

Scheme 5 shows the synthesis of bipyrrrole 20 which was used to form the polypyrrole deposits in some experiments. The synthesis starts with reacting pyrrole with 2-pyrrolidinone and phosphorous oxychloride to yield intermediate 19 in a moderate yield of 41%. Next, 19 was dehydrogenated using palladium on charcoal in boiling xylenes in a low yield of 16%. However, the yield was 41% based on recovered starting material. Enough bipyrrrole 20 was obtained from this sequence, so no further attempts were made to optimize conditions.

This bipyrrrole was used to circumvent the problem of loss of gold from the substrates described earlier. As described earlier, the gold was only removed from the surface at potentials above 1.0 V while pyrrole needs a potential of approximately 1.2 V to polymerize. Therefore, I decided to try to polymerize bipyrrrole to obtain polypyrrole on the SAM. Bipyrrrole polymerizes at much lower potentials (0.55 V) than pyrrole. As seen in Figure 5, the bipyrrrole polymerization worked even while using tetrafluoroborate as an electrolyte.
Figure 5. Plot of thickness of polypyrrole layer vs number of electrochemical cycles used to grow polypyrrole from a bipyrrrole solution.

Figure 5 shows two different polypyrrole growth experiments. The thickness of a polypyrrole layer grown using a bipyrrrole concentration of 0.01 mM, was found to increase at a rate of approximately 1.0 nm per cycle. The CV cycle used was 0V to 0.7 V and back to 0 V at 0.1 V/s. This was found to be the optimal conditions for polypyrrole growth from bipyrrrole. At 0.05 mM pyrrole concentration, the thickness rate increase was found to be approximately 1.5 to 2 nm per cycle. From this data, it can be seen that polypyrrole also can be electrochemically grown from a pyrrole-functionalized SAM in a controlled manner with the rate of growth controlled by bipyrrrole concentration.
Summary

The synthesis of a number of compounds with polymerizable moieties has been shown. The compounds containing diyne structures have undergone limited testing. It has been shown that polypyrrole can be electrochemically grown in a controlled fashion from a SAM containing pyrrole functionalities. In the future, this work could be used for growth of conducting polymers or as ways to make SAMs more robust and less prone to penetration by top-metal evaporation.

Experimental Procedures

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 by Terry Marriott at Rice University’s mass spectrometry lab. All new compounds were named using the Beilstein Autonom feature of Beilstein Commander software.
General Procedure for Electrochemical Polymerization of Pyrrole or Bipyrrrole. The CVs were performed on a BAS CV-50W using a SAM on Au as working electrode, platinum wire as auxiliary electrode, with a Ag/AgNO₃ non-aqueous reference electrode. The solutions were 0.1 M n-Bu₄NBF₄ or p-toluene sulfonic acid in acetonitrile. The scan rate was 0.1 V/s at 25°C.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol). 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 equivalents 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 NH₄Cl. The organic layer was diluted with methylene chloride and washed with a saturated solution of NH₄Cl (3×). The combined aqueous layers were extracted with methylene chloride (3×). The combined organic layers were dried over anhydrous MgSO₄ and the solvent removed in vacuo. The crude product was then purified by flash or column chromatography (silica gel).
**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 equivalents of potassium carbonate, and equivalent amounts of methanol 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.

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**1-Iodo-hex-1-yne (I, DWP-II-170).** 1-Hexyne (2.55 mL, 22.2 mmol) and THF (50 mL) were added to a 100 mL round bottom flask wrapped in aluminum foil with a stir bar under N₂. Silver nitrate (0.377 g, 2.22 mmol) and N-iodosuccinimide (5.00 g, 22.2 mmol) were then added and the mixture was allowed to stir for 2.5 h. The solution was washed with water and diethyl ether and dried over MgSO₄. Flash column chromatography (silica gel using hexanes as eluent) afforded the desired product (3.18 g, 69% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.39 (t, J = 7.0 Hz, 2 H), 1.51 (m, 2 H), 1.43 (m, 2 H), 0.93 (t, J = 7.2 Hz, 3 H).

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**1-Bromo-4-octa-1,3-diynyl-benzene (2, DWP-II-171).** 1-Iodo-hex-1-yne (0.181 g, 1.00 mmol) and 1-bromo-4-ethynylbenzene¹⁷ (0.208 g, 1.00 mmol) were added to a 10 mL round bottom flask with a stir bar under N₂. Pyrrolidine (5 mL) was then added
followed by copper(I) iodide (0.019 g, 0.10 mmol) and the mixture was allowed to stir for 30 min. The solution was washed with NH₄Cl (aq) and diethyl ether and dried over MgSO₄. Flash column chromatography (silica gel using hexanes as eluent; Rf: 0.44) afforded the desired product (0.169 g, 65% yield): mp 67-68°C. IR (KBr) 2951.2, 2863.2, 2238.4, 1483.5, 1467.0, 1390.2, 1066.4, 1007.6, 822.2, 521.3 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dt, J = 8.8, 2.1 Hz, 2 H), 7.35 (dt, J = 8.7, 2.1 Hz, 2 H), 2.39 (t, J = 7.0 Hz, 2 H), 1.58 (m, 2 H), 1.48 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 134.06, 131.86, 123.38, 121.30, 85.81, 75.75, 73.72, 65.08, 30.41, 22.16, 19.50, 13.75. HRMS calc’d for C₁₄H₁₃Br: 260.020073. Found: 260.019621 (Error = 1.7 ppm).

Trimethyl-(4-octa-1,3-diyynyl-phenylethynyl)-silane (3, DWP-II-173). 1-Bromo-4-octa-1,3-diyynyl-benzene (0.148 g, 0.567 mmol), TMSA (0.14 mL, 0.98 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.023 g, 0.033 mmol), copper(I) iodide (0.012 g, 0.066 mmol), triphenylphosphine (0.021 g, 0.081 mmol), DIEA (10 mL), and THF (10 mL) were used following the general procedure for couplings. The tube was capped and the solution was stirred at 85 °C for 15 h. Flash column chromatography (silica gel using hexanes as eluent; Rf: 0.34) afforded the desired product as a white solid (0.120 g, 76% yield): mp 67-68°C. IR (KBr) 2956.3, 2868.3, 2238.4, 2156.7, 1496.2, 1248.9, 866.0, 842.8, 757.9, 549.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (m, 4 H), 2.39 (t, J = 7.0 Hz, 2 H), 1.58 (m, 2 H), 1.48 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H), 0.27 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 132.67, 132.24, 123.87, 122.57, 104.82, 97.27,
86.35, 76.71, 74.59, 65.38, 30.65, 22.37, 19.73, 13.96, 0.29. HRMS calc’d for C_{19}H_{22}Si: 278.149080. Found: 278.149051 (Error = 0.10 ppm).

1-Ethynyl-4-octa-1,3-diynyl-benzene (4, DWP-II-175). Trimethyl-(4-octa-1,3-diynyl-phenylethynyl)-silane (0.110 g, 0.395 mmol), potassium carbonate (0.218 g, 1.58 mmol), methanol (10 mL), and dichloromethane (10 mL) were used following the general procedure for deprotection to afford the desired product (0.073 g, 90% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.44 (s, 4 H), 3.21 (s, 1 H), 2.40 (t, J = 7.0 Hz, 2 H), 1.59 (m, 2 H), 1.48 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H).

Thioacetic acid S-[4-(4-octa-1,3-diynyl-phenylethynyl)-phenyl] ester (5, DWP-II-176. III-154). 1-Ethynyl-4-octa-1,3-diynyl-benzene (0.073 g, 0.35 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.007 g, 0.011 mmol), copper(I) iodide (0.004 g, 0.021 mmol), THF (8 mL), DIEA (0.25 mL, 1.42 mmol), and 4-(thioacetyl)iodobenzene (0.098 g, 0.35 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at ambient temperature for 3.5 h then heated in a 45 °C oil bath for 12 h. Flash column chromatography (silica gel using 1:1 hexaenes/dichloromethane as eluent; Rf: 0.55) afforded the desired product (0.039 g, 31% yield): mp 116-118°C. IR (KBr) 2960.5, 2934.2, 2852.9, 1699.8, 1509.1, 1394.7, 1103.4, 1012.0, 957.4, 826.0, 616.9, 536.7 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta
7.57 (d, J = 8.4 Hz, 2 H), 7.48 (s, 4 H), 7.42 (d, J = 8.4 Hz, 2 H), 2.46 (s, 3 H), 2.41 (t, J = 7.0 Hz, 2 H), 1.59 (m, 2 H), 1.49 (m, 2 H), 0.96 (t, J = 7.2 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.81, 134.66, 132.86, 132.60, 131.99, 128.78, 124.57, 123.68, 122.65, 91.36, 90.97, 86.51, 76.84, 74.63, 65.41, 30.73, 30.65, 22.39, 19.76, 13.99. HRMS calc’d for C$_{24}$H$_{20}$OS: 356.123488. Found: 356.123163 (Error = 0.91 ppm).

2-Nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-phenylamine (6, DWP-III-155, III-182). 1-Ethynyl-4-octa-1,3-diynyl-benzene (0.859 g, 4.16 mmol) was coupled with 4-iodo-2-nitro-aniline (0.999 g, 3.79 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.080 g, 0.114 mmol), copper(I) iodide (0.043 g, 0.228 mmol), THF (20 mL), and DIEA (2.64 mL, 15.2 mmol). The reaction was stirred in a 50°C oil bath for 2 h. Column chromatography (silica gel using dichloromethane as eluent; Rf = 0.84) afforded the desired product (0.967 g, 74% yield): mp 177-178°C. IR (KBr) 3462.3, 3345.9, 2965.6, 2934.8, 1632.6, 1553.0, 1516.4, 1352.1, 1250.6, 825.0, 533.1 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, J= 1.9 Hz, 1 H), 7.46 (dd, J= 8.6, 2.0 Hz, 1 H), 7.41 (m, 4 H), 6.77 (d, J= 8.6 Hz, 1 H), 6.21 (br s, 2 H), 2.36 (t, J= 7.0 Hz, 2 H), 1.54 (m, 2 H), 1.44 (m, 2 H), 0.92 (t, J= 7.3 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.57, 138.41, 132.67, 132.05, 131.58, 129.87, 123.60, 122.21, 119.13, 111.95, 90.22, 88.51, 86.25, 65.22, 30.47, 22.19, 19.56, 13.76. HRMS calc’d for C$_{22}$H$_{18}$N$_2$O$_2$: 342.136828. Found: 342.136566 (Error = 0.77 ppm).
1-Iodo-2-nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-benzene (7, DWP-III-168, III-186). To a 100 mL round bottom flask (cooled to -20°C) was added BF$_3$OEt$_2$ (1.43 mL, 11.3 mmol). 2-Nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-phenylamine (0.967 g, 2.82 mmol) in THF (50 mL) was then added dropwise over 15 min. Next, t-BuONO (1.17 mL, 9.87 mmol) in THF (15 mL) was added dropwise over 5 min. The reaction was allowed to warm to 0°C over 40 min before 200 mL of ice-cold Et$_2$O was added. The precipitate was filtered to give 0.781 g of the diazonium salt. To a 200 mL round bottom flask was added acetonitrile (70 mL), sodium iodide (0.845 g, 5.64 mmol) and iodine (0.716 g, 2.82 mmol). The diazonium salt was added to this solution slowly and stirred for 30 min at room temperature. This afforded the desired product which required no further purification (0.761 g, 59% yield): mp 137-140°C. IR (KBr) 2950.2, 2931.2, 2858.0, 2238.4, 2197.4, 1920.9, 1525.7, 1353.0, 1016.6, 887.1, 836.6, 822.9, 543.9 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J$= 8.2 Hz, 1 H), 7.94 (d, $J$= 1.9 Hz, 1 H), 7.44 (s, 4 H), 7.33 (dd, $J$= 8.2 Hz, 1 H), 2.36 (t, $J$= 7.0 Hz, 2 H), 1.56 (m, 2 H), 1.44 (m, 2 H), 0.92 (t, $J$= 7.3 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.36, 135.98, 132.95, 132.07, 128.39, 125.03, 123.51, 122.59, 93.10, 88.70, 86.82, 86.24, 65.33, 30.62, 22.37, 19.75, 13.94. HRMS calc’d for C$_{22}$H$_{16}$INO$_2$: 453.022574. Found: 453.023040 (Error = 1.0 ppm).
Trimethyl-[2-nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-phenylethynyl]-silane (8, DWP-III-188). 1-Iodo-2-nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-benzene (0.868 g, 1.91 mmol) was coupled with TMSA (0.32 mL, 2.3 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.067 g, 0.096 mmol), copper(I) iodide (0.036 g, 0.191 mmol), THF (30 mL), and DIEA (1.33 mL, 7.64 mmol). The reaction was stirred at ambient temperature for 2.5 h. Column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent; Rf = 0.77) afforded the desired product (0.741 g, 92% yield): mp 99-101°C. IR (KBr) 2965.6, 2929.7, 2852.9, 2238.4, 2207.7, 2156.5, 1542.6, 1347.0, 1250.8, 836.6, 753.3, 538.3 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J= 1.5 Hz, 1 H), 7.63 (dd, J= 8.1, 1.5 Hz, 1 H), 7.59 (d, J= 8.1 Hz, 1 H), 7.44 (s, 4 H), 2.36 (t, J= 7.0 Hz, 2 H), 1.55 (m, 2 H), 1.44 (m, 2 H), 0.92 (t, J= 7.3 Hz, 3 H), 0.26 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.28, 135.28, 135.26, 132.76, 131.89, 127.56, 124.26, 123.28, 122.50, 118.10, 106.22, 99.33, 93.28, 89.14, 86.60, 76.92, 74.19, 65.15, 30.44, 22.18, 19.56, 13.75, -0.20. HRMS calc’d for C₂₇H₂₅NO₂Si: 423.165458. Found: 423.165551 (Error = 0.22 ppm).

1-Ethynyl-2-nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-benzene (9, DWP-III-193). Trimethyl-[2-nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-phenylethynyl]-silane (0.718 g, 1.70 mmol), potassium carbonate (0.703 g, 5.09 mmol), methanol (25 mL), and dichloromethane (25 mL) were used following the general deprotection procedure to
afford the product (0.570 g, 96% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (m, 1 H), 7.66 (m, 2 H), 7.45 (s, 4 H), 3.59 (s, 1 H), 2.36 (t, $J$= 7.0 Hz, 2 H), 1.56 (m, 2 H), 1.44 (m, 2 H), 0.92 (t, $J$= 7.3 Hz, 3 H).

**Thioacetic acid S-{4-[2-nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-phenylethynyl]-phenyl} ester (10, DWP-III-194).** 1-Ethynyl-2-nitro-4-(4-octa-1,3-diynyl-phenylethynyl)-benzene (0.550 g, 1.57 mmol), bis(dibenzylideneacetone)palladium(0) (0.045 g, 0.78 mmol), copper(I) iodide (0.030 g, 0.16 mmol), triphenylphosphine (0.082 g, 0.31 mmol), THF (20 mL), DIEA (1.1 mL, 6.3 mmol), and 4-(thioacetyl)iodobenzene (0.479 g, 1.72 mmol) were used following the general procedure for couplings. The tube was placed in a 50°C oil bath for 2 h. Column chromatography (silica gel using 1:1 hexanes/dichloromethane as eluent; Rf = 0.48) afforded the desired product as a yellow solid (0.504 g, 64% yield): mp 148-150°C (decomp.). IR (KBr) 2960.5, 2928.9, 2863.2, 2214.8, 1712.4, 1541.0, 1345.1, 836.6, 616.7 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (m, 1 H), 7.67 (m, 2 H), 7.60 (dt, $J$= 8.5, 1.9 Hz, 2 H), 7.46 (s, 4 H), 7.42 (dt, $J$= 8.5, 1.9 Hz, 2 H), 2.43 (s, 3 H), 2.37 (t, $J$= 7.0 Hz, 2 H), 1.55 (m, 2 H), 1.44 (m, 2 H), 0.92 (t, $J$= 7.3 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.48, 149.90, 135.67, 134.99, 134.67, 132.97, 132.96, 132.10, 130.01, 128.08, 124.46, 123.74, 123.48, 122.69, 118.32, 98.48, 93.60, 89.40, 86.81, 86.64, 77.29, 74.38, 65.34, 30.76, 30.63, 22.37, 19.75, 13.94. HRMS calc’d for C$_{32}$H$_{23}$NO$_5$S: 501.139866. Found: 501.140327 (Error = 0.92 ppm).
4-Trimethylsilanylethynyl-benzaldehyde (11, DWP-4-39, 4-46).\textsuperscript{10} 4-Bromo-benzaldehyde (10.0 g, 54.0 mmol) was coupled with TMSA (8.4 mL, 59 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.379 g, 0.540 mmol), copper(I) iodide (0.206 g, 1.08 mmol), THF (50 mL), and DIEA (28.2 mL, 162 mmol). The reaction was placed in a 50°C oil bath for 1.5 h. Kugelrohr distillation (95°C at 1.5 mm Hg) afforded the desired product (10.0 g, 91% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.97 (s, 1 H), 7.78 (m, 2 H), 7.57 (m, 2 H), 0.24 (s, 9 H).

4-Ethynyl-benzaldehyde (12, DWP-4-60, 4-64).\textsuperscript{10} 4-Trimethylsilanylethynyl-benzaldehyde (5.00 g, 24.7 mmol), potassium carbonate (10.2 g, 74.1 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general deprotection procedure to afford the desired product (3.12 g, 97% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.99 (s, 1 H), 7.82 (dt, \(J=\) 8.5, 1.7 Hz, 2 H), 7.61 (dt, \(J=\) 8.4, 1.8 Hz, 2 H), 3.27 (s, 1 H).

Thioacetic acid S-[4-(4-formyl-phenylethynyl)-phenyl] ester (13, DWP-4-73).\textsuperscript{10} 4-Ethynyl-benzaldehyde (1.03 g, 7.91 mmol) was coupled with 4-(thioacetyl)iodobenzene (2.20 g, 7.91 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.111 g, 0.158 mmol), copper(I) iodide (0.060 g, 0.316 mmol), THF (30 mL), and DIEA (5.5 mL, 32 mmol). The reaction was
placed in a 55°C oil bath for 3 h. Column chromatography (silica gel using 3:1
dichloromethane/hexanes as eluent; Rf = 0.49) afforded the product (1.90 g, 86% yield):
mp 123-126°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.01 (s, 1 H), 7.86 (dt, $J$= 8.5, 1.7 Hz, 2
H), 7.66 (dt, $J$= 8.2, 1.6 Hz, 2 H), 7.56 (dt, $J$= 8.5, 1.7 Hz, 2 H), 7.41 (dt, $J$= 8.5, 1.9 Hz,
2 H), 2.43 (s, 3 H).

Thioacetic acid $S$-(4-{4-[bis-(1H-pyrrol-2-yl)-methyl]-phenylethynyl}-phenyl)
ester (14, DWP-4-75, 109). To a 50 mL round bottom flask was added thioacetic acid
$S$-[4-(4-formyl-phenylethynyl)-phenyl] ester (0.200 g, 0.710 mmol), pyrrole (22.4 mL)
and methanol (1.0 mL). Glacial acetic acid (3.1 mL) was added and the solution was
placed under a blanket of N$_2$. The reaction was stirred at ambient temperature for 20 h.
The solution was then washed with water and dichloromethane. Column chromatography
(silica gel using dichloromethane as eluent; Rf = 0.47) afforded the desired product
(0.233 g, 83% yield): mp 160-168°C (decomp.). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (s,
2 H), 7.55 (dt, $J$= 8.4, 1.9 Hz, 2 H), 7.48 (dt, $J$= 8.3, 1.7 Hz, 2 H), 7.40 (dt, $J$= 8.4, 1.9
Hz, 2 H), 7.18 (d, $J$= 8.2 Hz, 2 H), 6.67 (m, 2 H), 6.17 (m, 2 H), 5.90 (m, 2 H), 5.44 (s, 1
H), 2.42 (s, 3 H).
4-(2-Nitro-4-trimethylsilylhexynyl-phenylethynyl)-benzaldehyde (15, DWP-4-65). (4-Iodo-3-nitro-phenylethynyl)-trimethyl-silane (2.00 g, 5.79 mmol) was coupled with 4-ethynyl-benzaldehyde (0.807 g, 6.20 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.122 g, 0.174 mmol), copper(I) iodide (0.066 g, 0.347 mmol), THF (30 mL), and DIEA (4.0 mL, 23 mmol). The reaction was stirred at ambient temperature for 2.5 h. Column chromatography (silica gel using 1:1 dichloromethane/hexanes as eluent; Rf = 0.39) afforded the slightly impure product (2.0 g, ~90% yield). IR (KBr) 2970.7, 2161.6, 1695.3, 1597.0, 1540.7, 1344.8, 1245.6, 1202.6, 859.0, 759.7, 684.0 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.00 (s, 1 H), 8.13 (m, 1 H), 7.86 (m, 2 H), 7.69 (m, 2 H), 7.63 (d, \(J=1.0\) Hz, 2 H), 0.25 (s, 9 H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 191.69, 149.78, 136.58, 136.14, 134.92, 132.96, 130.00, 128.67, 128.50, 125.12, 117.83, 102.19, 100.58, 97.69, 88.56, 0.10. HRMS calc’d for C\(_{20}\)H\(_{17}\)NO\(_3\)Si: 347.097772. Found: 347.097349 (Error = 1.2 ppm).

4-(4-Ethynyl-2-nitro-phenylethynyl)-benzaldehyde (16, DWP-4-68). 4-(2-Nitro-4-trimethylsilylhexynyl-phenylethynyl)-benzaldehyde (1.95 g, ~5.61 mmol), potassium carbonate (3.10 g, 22.4 mmol), methanol (50 mL), and dichloromethane (50 mL) were used following the general deprotection method. Column chromatography (silica gel using 2:1 dichloromethane/hexanes as eluent; Rf = 0.47) afforded the product (1.16 g, 76% yield over 2 steps): mp 165-166°C. IR (KBr) 3240.0, 1689.3, 1600.9,
1538.5, 1519.4, 1344.3, 1204.0, 841.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 1 H), 8.19 (m, 1 H), 7.88 (dt, J= 8.5, 1.8 Hz, 2 H), 7.72 (dt, J= 8.2, 1.6 Hz, 2 H), 7.68 (d, J= 1.1 Hz, 2 H), 3.32 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 191.71, 136.66, 136.38, 135.02, 133.00, 130.02, 128.74, 128.60, 124.05, 118.45, 97.90, 88.28, 82.28, 81.21.

![Thioacetic acid](image)

**Thioacetic acid S-{4-[4-(4-formyl-phenylethynyl)-3-nitro-phenylethynyl]-phenyl} ester (17, DWP-4-71).** 4-(4-Ethynyl-2-nitro-phenylethynyl)-benzaldehyde (1.13 g, 4.10 mmol), bis(dibenzylideneacetone)palladium(0) (0.118 g, 0.205 mmol), copper(I) iodide (0.078 g, 0.410 mmol), triphenylphosphine (0.215 g, 0.82 mmol), THF (40 mL), DIEA (2.8 mL, 16 mmol), and 4-(thioacetyl)iodobenzene (1.20 g, 4.31 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 2.5 h. Column chromatography (silica gel using dichloromethane as eluent; Rf = 0.63) followed by precipitation from dichloromethane/hexanes afforded the desired product as a yellow solid (1.39 g, 80% yield): mp 166-168°C. IR (KBr) 2217.9, 1693.8, 1608.5, 1538.2, 1344.5, 1198.9, 823.8, 630.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 1 H), 8.23 (m, 1 H), 7.88 (dt, J= 8.4, 1.6 Hz, 2 H), 7.71 (m, 4 H), 7.56 (dt, J= 8.5, 1.9 Hz, 2 H), 7.42 (dt, J= 8.5, 1.8 Hz, 2 H), 2.43 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 193.48, 191.72, 149.99, 136.62, 135.84, 135.06, 134.73, 133.00, 132.75, 130.03, 129.88, 128.70, 128.20, 124.97, 123.47, 117.87, 97.84, 93.62, 88.58, 77.62, 30.76. HRMS calc'd for C₂₅H₁₅NO₄S: 425.072181. Found: 425.072339 (Error = 0.37 ppm).
Thioacetic acid $S$-[4-(4-[bis-(1H-pyrrol-2-yl)-methyl]-phenylethynyl]-3-nitro-phenylethynyl]-phenyl] ester (18, DWP-4-154). To a 25 mL round bottom flask was added thioacetic acid $S$-[4-(4-formyl-phenylethynyl)-3-nitro-phenylethynyl]-phenyl] ester (0.200 g, 0.470 mmol), pyrrole (15 mL) and methanol (0.7 mL). Added glacial acetic acid (2.0 mL) and placed under a blanket of $N_2$. The reaction was stirred at ambient temperature for 22 h. The solution was then washed with water and dichloromethane. Column chromatography (silica gel using dichloromethane as eluent; Rf = 0.45) afforded the desired product as a yellow solid (0.191 g, 75% yield): mp 157-159°C (decomp.). IR (KBr) 3411.3, 3365.0, 2202.6, 1695.1, 1539.9, 1519.6, 1345.1, 1115.1, 1096.4, 827.4, 724.8, 542.3 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (m, 1 H), 7.93 (br s, 2 H), 7.69 (dd, $J = 8.1$, 1.5 Hz, 1 H), 7.66 (dd, $J = 8.1$, 0.6 Hz, 1 H), 7.57-7.52 (m, 4 H), 7.43-7.40 (m, 2 H), 7.22 (d, $J = 8.1$ Hz, 2 H), 6.71 (m, 2 H), 6.15 (dd, $J = 3.3$, 2.7 Hz, 2 H), 5.91-5.89 (m, 2 H), 5.49 (s, 1 H), 2.43 (s, 3 H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 193.59, 149.84, 144.15, 135.71, 134.92, 134.73, 132.78, 132.73, 132.13, 129.68, 129.03, 128.12, 124.05, 123.64, 121.26, 118.76, 117.93, 109.00, 107.90, 99.36, 93.08, 88.78, 85.32, 44.36, 30.77. HRMS calc’d for C$_{33}$H$_{23}$N$_3$O$_5$S: 541.146014. Found: 541.145296 (Error = 1.3 ppm).
4,5-Dihydro-3H, 1'H-[2,2']bipyrrrolyl (19, DWP-4-152). To a 500 mL round bottom flask was added pyrrole (25.0 mL, 358 mmol), 2-pyrrolidinone (13.7 mL, 178 mmol), and dichloroethane (100 mL). The mixture was cooled to 0°C and POCl₃ (25.2 mL, 270 mmol) was added dropwise over 1 h. The solution was stirred for 1 h before removing the ice bath and allowing to warm to ambient temperature over the next 2 h. The solution was diluted with chloroform (60 mL) and poured into an ice-cold solution of NaOAc (100 g in 250 mL H₂O). Next, 500 mL of 10 M KOH was added to adjust the pH to ~11. The solution turned from dark-red to light-orange. The mixture was extracted with chloroform and dried over potassium carbonate. The product was then recrystallized from chloroform to afford 9.88 g (41% yield) of pure product: mp 164-165°C. ¹H-NMR (400 MHz, CDCl₃) 6.91 (s, 1 H), 6.50 (d, J = 2.5 Hz, 1 H), 6.22 (t, J = 3.0 Hz, 1 H), 3.98 (t, J = 7.2 Hz, 2 H), 2.87 (t, J = 8.2 Hz, 2 H), 1.99 (quintet, J = 7.7 Hz, 2 H).

1H, 1'H-[2,2']Bipyrrrolyl (20, DWP-4-155). 4,5-Dihydro-3H, 1'H-[2,2']bipyrrrolyl (1.00 g, 7.45 mmol), palladium on carbon (5%, 0.50 g) and xylenes (20 mL) were placed in a 50 mL round bottom flask. N₂ was bubbled into mixture with hollow glass tube. The solution was heated to reflux for 3.5 h and then filtered through a bed of celite. The solvents were removed and the product purified via column chromatography (silica gel using dichloromethane as eluent; Rf = 0.48) to provide
product (0.158 g, 16% yield, 41% based on recovered starting material) and starting material (61% recovered): mp 165-180°C (decomp.). $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.20 (br s, 2 H), 6.76 (s, 2 H), 6.24-6.20 (m, 4 H).
References


Chapter 5

Synthesis of Phenylene-Ethylenes for use in Light Emitting Diodes (LEDs) to Control the Schottky Barrier and Charge Injection
Introduction

Light emitting diodes (LEDs) have found their way into many uses in today's society. From wristwatches to flat panel displays, the LED is a common sight that many people take for granted. Because of the many uses of LEDs, industry and academia are constantly searching for better and cheaper ways to make them more efficient and improve stability of the metal/organic interfaces. One way to achieve this is to control the Schottky energy barrier. The hole Schottky energy barrier is the energy difference between the metal Fermi energy and the highest occupied single electron state (HOMO) of the organic layer.\textsuperscript{1} This barrier can be controlled to a certain extent by using a metal with a different work function. Calcium has a low work function (2.9 eV) but there are certain difficulties in working with calcium metal due to its reactivity toward oxygen. Aluminum is much easier to work with and more stable. However, aluminum has a higher work function (4.4 eV), which can affect the properties of the device.\textsuperscript{2} The barrier can also be controlled by using a self-assembled monolayer (SAM) of organic molecules in between the metal and the organic polymer. Campbell and coworkers used alkanethiolates to form the SAMs on a silver electrode.\textsuperscript{1} This resulted in changing the Schottky energy barriers predictably as desired. However, the alkanes served as insulators and blocked charge injection at the metal/polymer interface. Later, Campbell and coworkers used conjugated phenylene-ethynlenes with thiol end groups to form the SAMs on a copper surface.\textsuperscript{3} The molecules they used are shown in Figure 1.

![Figure 1](image)

**Figure 1.** Conjugated thiols used to form SAMs on copper to control Schottky barrier.
The fluorinated molecule resulted in decreasing the Schottky barrier, while the nonfluorinated molecule increased the Schottky barrier. When a diode was made using these thiols, copper as the anode, poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (also known as MEH-PPV), and calcium for the cathode, a lower bias was required to generate current when the fluorinated SAM was used than when no SAM was used. The use of the nonfluorinated SAM caused the need for a higher bias for current to flow.

The phenylene-ethynylene 3 was synthesized as part of a continuation of this project. This compound was made with a carboxylic end group so that a SAM can be formed on an aluminum surface.\textsuperscript{4,5} We are currently waiting for results from Dr. Ian Campbell on the testing of this compound.

\textbf{Results and Discussion}

\textbf{Scheme 1}
Scheme 1 displays the total synthesis of one of the compounds to be tested in an LED. Methyl-4-iodobenzoate was coupled with trimethylsilylacetylene using Sonogashira conditions to give 1 in excellent yield. The ester was used because the carboxylic acid could interfere with the palladium-catalyzed cross coupling. Also, carboxylic acids tend to be somewhat insoluble in organic solvents. An ester is easier to work with and can be easily converted to the acid in the final step of the synthesis. Compound 1 was then deprotected using the typical potassium carbonate/methanol protocol and subsequently coupled (Sonogashira conditions) with 2-idoaniline to give 2 in good yield. Finally, 2 was saponified using lithium hydroxide and a methanol/water solution of 3:1 to give 3 in excellent yield.6 Final product 3 was then shipped to Campbell for testing in an LED. We are still waiting for word on those results.

**Summary**

A phenylene-ethynylene compound has been synthesized for potential use as an interfacial layer in organic light-emitting diodes. This layer could possibly help modify the Schottky barrier and alter the charge injection from metal to the bulk organic layer.

**Experimental Procedures**

**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 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. 1H 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 by Terry Marriott at Rice University’s mass spectrometry lab. All new compounds were named using the Beilstein Autonom feature of Beilstein Commander software.

**General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).**\(^7,8\) 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 equivalents 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$_4$Cl. The organic layer was diluted with methylene chloride and washed with a saturated solution of NH$_4$Cl (3×). The combined aqueous layers were extracted with methylene chloride (3×). The combined organic layers were dried over
anhydrous MgSO₄ and the solvent removed in vacuo. The crude product was then purified by flash or column chromatography (silica gel).

**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 equivalents of potassium carbonate, and equivalent amounts of methanol 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.

\[ \text{TMS} \equiv \text{C} \equiv \text{CO}_2\text{Me} \]

4-Trimethylsilanylethynyl-benzoic acid methyl ester (1, DWP-I-26, 70).⁹ Methyl-4-iodobenzoate (5.00 g, 19.1 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.670 g, 0.955 mmol), copper(I) iodide (0.364 g, 1.91 mmol), THF (50 mL), DIEA (13.3 mL, 76.4 mmol) and trimethylsilylacetylene (3.51 mL, 24.8 mmol) were used following the general procedure for coupling. The tube was capped and the solution was heated to 60 °C in an oil bath for 18 h. Column chromatography (silica gel with 1:1 hexanes/ methylene chloride as eluent) afforded the desired product (4.34 g, 98% yield) as orange crystals. IR (KBr) 2958.6, 2159.9, 1720.7, 1603.2, 1443.2, 1404.8, 1278.3, 1243.6, 1171.1, 1110.5, 1017.0, 841.6, 771.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (dt, J=8.7 Hz, 1.7 Hz, 2 H), 7.54 (dt, J=8.6, 1.7 Hz, 2 H), 3.94 (s, 3 H), 0.28 (s, 9 H). ¹³C
NMR (100 MHz, CDCl₃) δ 166.68, 132.06, 129.89, 129.57, 127.97, 104.27, 97.88, 52.40, 0.029.

4-Ethynyl-benzoic acid methyl ester (DWP-I-28, 43, 52). Methyl-4-(trimethylsilylethynyl)benzoate (0.750 g, 3.23 mmol) was deprotected to the terminal alkyne via the procedure described above using potassium carbonate (2.23 g, 16.2 mmol), methanol (50 mL), and methylene chloride (50 mL). The mixture, in a round bottom flask, was stirred at room temperature for 2 h. Extraction of the product following the procedure described previously yielded 0.488 g of the desired product (as determined by TLC), which was immediately reacted in the next step.

4-(2-Amino-phenylethynyl)-benzoic acid methyl ester (2, DWP-I-44). 2-Iodoaniline (0.607g, 2.77 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.098 g, 0.139 mmol), copper(I) iodide (0.053g, 0.277 mmol), THF (25 mL), DIEA(1.93 mL, 11.08 mmol) and 4-ethynyl-benzoic acid methyl ester (0.488 g, 3.05 mmol) were used following the general procedure for coupling. The tube was capped and the solution was heated to 70 °C in an oil bath for 7 d. Column chromatography (silica gel with methylene chloride as eluent) afforded the desired product (0.40 g, 57% yield). IR (KBr) 3468.1, 3376.0, 2941.5, 2210.8, 1712.0, 1602.7, 1485.4, 1453.5, 1280.5, 1099.7, 770.8 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dt, J=8.5 Hz, 1.8 Hz, 2 H), 7.59 (dt, J=8.5, 1.7 Hz, 2
H), 7.40 (dd, \( J=7.8 \), 1.5 Hz, 1 H), 7.18 (td, \( J=7.6 \), 1.5 Hz, 1 H), 6.75 (m, 2 H), 4.33 (bs, 2 H), 3.94 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 166.95, 148.44, 132.74, 131.70, 130.70, 129.98, 129.76, 128.46, 118.44, 114.87, 107.64, 94.43, 89.54, 52.65. HRMS calculated for \( \text{C}_{16}\text{H}_{13}\text{NO}_2\): 251.0946. Found: 251.0940 (Error=2.5 ppm).

4-(2-Amino-phenylethynyl)-benzoic acid (3, DWP-I-95). 4-(2-Amino-phenylethynyl)-benzoic acid methyl ester (0.300 g, 1.19 mmol), lithium hydroxide (0.250 g, 5.97 mmol), methanol (30 mL), water (10 mL), methylene chloride (20 mL) and a stir bar were added to a 100 mL round bottom flask. The mixture was stirred at room temperature for 2 days. The mixture was washed with methylene chloride and the layers separated. The pH of the aqueous portion was adjusted to 4 and washed with methylene chloride to afford 0.277 g of product (98% yield). IR (KBr) 3468.1, 3376.3, 3054.3, 2957.6, 2656.7, 2538.5, 2205.4, 1681.3, 1604.8, 1488.4, 1422.2, 1318.8, 1281.9, 860.4, 758.7 cm\(^{-1}\). \(^1\)H NMR (400 MHz, d-DMSO) \( \delta \) 7.95 (dt, \( J=8.5 \), 1.8 Hz, 2 H), 7.72 (dt, \( J=8.5 \), 1.7 Hz, 2 H), 7.26 (dd, \( J=7.7 \), 1.5 Hz, 1 H), 7.11 (td, \( J=7.7 \), 1.6 Hz, 1 H), 6.75 (dd, \( J=8.3 \), 0.6 Hz, 1 H), 6.55 (td, \( J=7.6 \), 1.0 Hz, 1 H), 5.59 (bs, 2 H). \(^{13}\)C NMR (100 MHz, d-DMSO) \( \delta \) 167.65, 150.85, 132.88, 132.12, 131.19, 130.72, 130.24, 128.32, 116.66, 114.94, 105.64, 94.14, 90.90. HRMS calculated for \( \text{C}_{15}\text{H}_{11}\text{NO}_2\): 237.0790. Found: 237.0792 (Error=0.93 ppm).
References


RICE UNIVERSITY

Advances in Molecular Electronics:
Synthesis and Testing of Potential Molecular Electronic Devices

Volume II:
Spectral Data for Chapter 1

by

David Wilson Price, Jr.

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

HOUSTON, TEXAS

OCTOBER, 2002
Chapter 1

Synthesis and Testing of Functionalized Phenylene Ethynylenes for
Potential use as Devices in a Molecular Computer:

Spectral Data
DWP-III-53

\[ \text{N}_2\text{H}_4 \]
DWP-II-21

Chemical structure with labels for nitro groups and a TMS group.
DWP-II-70

\[
\begin{align*}
\text{Br} & \quad \text{NO}_2 \\
\text{O}_2\text{N} & \quad \equiv - \text{TMS}
\end{align*}
\]
DWP-II-73
DWP-45

NO₂

H
DWP-II-33
The diagram shows a chemical structure labeled as DWP-II-55, with specific wavenumbers noted at various points. The wavenumbers range from 4000 to 100 cm⁻¹. Key wavenumbers include 1694.90, 1660.12, 1596.86, 1483.73, 1396.85, 1351.85, 1212.28, 1119.71, 1084.60, 960.29, 895.29, 826.78, 620.99, and 552.03 cm⁻¹. The structure includes benzene rings and a quinone group, indicated by the labels AcS and Sac.
RICE UNIVERSITY

Advances in Molecular Electronics:
Synthesis and Testing of Potential Molecular Electronic Devices

Volume III:
Spectral Data for Chapters 2,3,4,5

by

David Wilson Price, Jr.

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

Houston, Texas
October, 2002
Chapter 2

Synthesis of Alternative Systems to use as Alligator Clips for Attachment to Metal Substrates:

Spectral Data
Chapter 3

Electrochemical Testing of Potential Molecular Devices:

Spectral Data
Chapter 4

Synthesis of Molecular Systems with Polymerizable Functionalities:

Spectral Data
DWP-4-154
Chapter 5

Synthesis of Phenylene-Ethynlenes for use in Light Emitting Diodes (LEDs) to Control the Schottky Barrier and Charge Injection:

Spectral Data