RICE UNIVERSITY

Synthesis of Conjugated Molecules: From Electronics to MoleculART

by

Stéphanie Hina Chanteau

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HOUSTON, TEXAS

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Volume I of III
A mes parents
Abstract

Synthesis of Conjugated Molecules: From Electronics to MoleculART

By

Stéphanie Hina Chanteau

Chapter 1 discusses the purpose, the design, and the syntheses of new potential electronic devices. Based on previous and current studies, new oligo(phenylene ethynylene)s containing pyridyl alligator clips have been synthesized for molecular electronics using a series a palladium-catalyzed couplings. Although the testing of these devices is still pending, these devices are expected to show negative differential resistance and molecular memory properties due to their electron-withdrawing nature.

Chapter 2 describes the thermal analysis testings of several molecular electronics candidates to gain insight about their suitability for a new hybrid molecular/solid-state approach using chemical vapor deposition process.

Chapter 3 depicts the synthesis of new amphiphilic molecules containing a free radical and a carboxylic group as potential devices for quantum computing. These candidates have been tested on silver surface to assess their chemical integrity when self-assembled as a monolayer.

Chapter 4 discusses the synthesis of an array of 2 nm-tall anthropomorphic conjugated molecules, the NanoKids, in the monomeric, dimeric and polymeric forms and the use of them in an educational outreach project as 3D animated models to teach science in selected schools. These molecules are called, as a class, NanoPutians.

Finally, chapter 5 discusses the synthesis and the challenges of devising an army of NanoKids moving on a surface.
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First, I would like to thank my parents. Merci d’avoir toujours été là pour moi, de m’avoir réconfortée quand je n’allais pas bien. Vous m’avez apporté non seulement un soutien financier, mais aussi moral pendant toutes ces années, en m’encourageant à aller jusqu’au bout de moi-même, à continuer malgré tous les obstacles à franchir. Je n’aurais jamais pu y arriver sans vous. Merci du plus profond de mon cœur.

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Third, I would like to thank Michael Stewart, one of the most creative guy I know. Thanks for your insightful advices and your time.

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Special thanks to Dustin James, for proofing all the reports and for his wise advices.

Then, I would like to thank all my friends from the past and present. I don’t need to cite you, you know who you are. Even if our paths have separated, I still keep a space for you in my life. Merci. Thank you.

Finally, I would like to thank you, Reader, for reading this thesis (and dusting it). Hopefully you find something inspiring. Enjoy!
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<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>Ac</td>
<td>Acetyl</td>
</tr>
<tr>
<td>AIBN</td>
<td>Azoisobutylnitrile</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>Aq</td>
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<td>Ar</td>
<td>Aryl</td>
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<td>Bp</td>
<td>Boiling Point</td>
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<td>Bu</td>
<td>Butyl</td>
</tr>
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<td>t-Bu</td>
<td>tert-Butyl</td>
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<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>calc’d</td>
<td>Calculated</td>
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<tr>
<td>CH$_2$Cl$_2$</td>
<td>Methylene Chloride</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter(s)</td>
</tr>
<tr>
<td>cm$^{-1}$</td>
<td>Inverse Centimeter(s)</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary Metal Oxide Semiconductor</td>
</tr>
<tr>
<td>CuI</td>
<td>Copper Iodide</td>
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<tr>
<td>CV</td>
<td>Cyclic Voltamgram</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical Shift in Part per Million Downfield from Tetramethylsilane</td>
</tr>
<tr>
<td>d</td>
<td>Day(s); Doublet (spectral)</td>
</tr>
<tr>
<td>DCC</td>
<td>Dicyclohexylcarbodiimide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>DIEA</td>
<td>Diisopropylethylamine</td>
</tr>
<tr>
<td>DMAP</td>
<td>$N,N$-Dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>$N, N$-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<tr>
<td>EDCI</td>
<td>1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride</td>
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<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>Et$_2$O</td>
<td>Diethyl ether</td>
</tr>
<tr>
<td>eV</td>
<td>electronvolt</td>
</tr>
<tr>
<td>FITC</td>
<td>Fluorescein isothiocyanate</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>Hex</td>
<td>Hexanes</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>High-Resolution Mass Spectrum</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>I(V)</td>
<td>Function of Current versus Voltage</td>
</tr>
<tr>
<td>$J$</td>
<td>Coupling Constant (in NMR)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>K</td>
<td>Degrees Kelvin</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>L</td>
<td>Liter(s)</td>
</tr>
<tr>
<td>LDI</td>
<td>Laser Desorption Ionization</td>
</tr>
<tr>
<td>LRMS</td>
<td>Low-Resolution Mass Spectrum</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>μ</td>
<td>Micro</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet (spectral); Meter(s); Milli</td>
</tr>
<tr>
<td>M</td>
<td>Moles per Liter</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix Assisted Laser Desorption Ionization</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>min</td>
<td>Minute(s)</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>mol</td>
<td>Mole(s)</td>
</tr>
<tr>
<td>Mp</td>
<td>Melting Point</td>
</tr>
<tr>
<td>MRFM</td>
<td>Magnetic Resonance Force Microscope</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Wavenumber for IR</td>
</tr>
<tr>
<td>NDR</td>
<td>Negative Differential Resistance</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>Ammonium Chloride</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>OPE</td>
<td>Oligo(phenylene ethynylene)</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>PPh₃</td>
<td>Triphenylphosphine</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per Million (in NMR)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSU</td>
<td>Pennsylvania State University</td>
</tr>
<tr>
<td>PVR</td>
<td>Peak to Valley Ratio</td>
</tr>
<tr>
<td>Py</td>
<td>Pyridine</td>
</tr>
<tr>
<td>q</td>
<td>Quartet (spectral)</td>
</tr>
<tr>
<td>Q</td>
<td>Charge</td>
</tr>
<tr>
<td>RAM</td>
<td>Random Access Memory</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>RTD</td>
<td>Resonant Tunneling Diode</td>
</tr>
<tr>
<td>σ</td>
<td>Conductive State</td>
</tr>
<tr>
<td>s</td>
<td>Singlet (NMR); Second(s)</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
</tr>
<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>t</td>
<td>Triplet (spectral)</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium Fluoride</td>
</tr>
<tr>
<td>TBS</td>
<td>Tert-butyldimethylsilyl; tert-butyldimethylsilane</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethylpiperidinyloxy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilylacetylene</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl, Tetramethysilane</td>
</tr>
<tr>
<td>TMSA</td>
<td>Trimethylsilylacetylene</td>
</tr>
<tr>
<td>US</td>
<td>United States</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
PART I: ELECTRONICS

The important thing is to create. Nothing else matters; creation is all.

Pablo Picasso
CHAPTER 1

SYNTHESIS OF POTENTIAL MOLECULAR DEVICES CONTAINING
PYRIDYL ALLIGATOR CLIPS FOR MOLECULAR ELECTRONICS
1. Introduction

Computers play a big part of our everyday life. According to the US census bureau, in August 2000, 54 million households (51% of the households) had one or more computers. Semiconductor manufacturers are building with faster speeds, containing chips with smaller features, each year. Nowadays, about 77 million transistors, with sizes as small as 90 nanometers, can fit on a chip. However, the limit of transistor miniaturization, which is thought to be 30 nm, is close to being reached. This 30 nm limit, is thought to be fixed by fundamental physical laws. Another emerging problem is that using conventional lithography methods, the smaller one makes a feature, the more expensive and difficult the process becomes. Many experts predict that by the year 2015, a top-end fabrication facility will cost over 100 billion dollars. With the traditional silicon technology limits to be reached in 10 to 15 years, alternate technologies have to be considered.

2. Background

The use of organic molecules such as conjugated oligomers and aromatic molecules as single electron conductors has attracted considerable attention due to their exciting potential in future electronic devices. Molecular electronics involves the complement of transistors with molecules in devices capable of electronic logic and memory. Molecular-based systems may afford the most attractive route towards allowing the continuous scaling down of the size of computers. The main advantage of molecular electronics is that chemical syntheses allow one to tailor a library of molecules in just a few steps and at very low cost. With molecules only a couple of nanometers in size,
devising chips containing billions of switches and components becomes a possibility. If devices were to be based upon single molecules, using routine chemical syntheses, one could prepare $6 \times 10^{23}$ (Avogadro's number) devices in a single reaction flask, hence, more devices than are presently in use by all the computational systems combined, worldwide. Equally attractive is the fact that self-assembled monolayers can permit ordering of ca. $10^{14}$ molecules/cm$^2$ as opposed to $10^8$ transistors on a 1 cm$^2$ chip. In 2001, molecular electronics was named "Breakthrough of The Year" by Science.$^3$

It all began when Aviram and Ratner$^4$ presented over three decades ago the theoretical underpinnings for the design of organic molecules bearing donor and acceptor groups that were calculated to present the properties of a $p$-$n$ junction and thus function as molecular rectifiers. Across the years, several solid-state testbeds have been engineered to demonstrate this theory.

Our work focused mainly on a class of molecular electronic devices based on a string of three benzene rings separated by ethynyl groups. These molecules are typically referred to as oligo(phenylene ethynylene)s (OPEs). OPEs are assembled on metallic surfaces, usually gold, via functional groups called "alligator clips" —typically a benzenethiol unit—located at one of the termini. Organo-sulfur compounds, such as alkyl or aromatic thiols are well-known to form close-packed and well-ordered monolayers,$^5,6$ so-called "self-assembled monolayers" (SAMs) on a metal surface.$^7,8$

In 1996, the conductance of OPEs was measured by Paul Weiss and David Allara from Pennsylvania State University using STM (Scanning Tunneling Microscopy) (Figure 1).$^9,11$
In this report, OPEs were inserted into a SAM of dodecanethiols. Using an atomically sharp tip of metal held over the surface, the topography of the surface was monitored by the minute current of tunneling electrons between the surface and the tip. With this method, single OPE molecules could be isolated and showed conductance.

In 1997, Reed et al.\textsuperscript{12} from Yale University measured for the first time the conductance of a single molecule by using a mechanically controllable break junction method (Figure 2).
Benzene-1,4-dithiol (HS-C₆H₆-SH) was self-assembled onto two adjacent Au electrodes, which were then moved together in picometer increments by the use of a piezo element until one molecule of benzenedithiol bridged the gap. By the application of a difference of potential between the two electrodes, the current through a single molecule was measured. This study provided a direct, quantitative measurement of the molecular conductance of a junction containing a single molecule, a fundamental step in the emerging field of molecular scale electronics.

However being conductive is not a sufficient property for having molecular devices. To behave as computer switches, molecular devices have to execute 2 major
tasks: open or close to process information, and stay open or closed for long enough periods to act as short-term memory devices.

The first requirement was met by Reed and Tour when an electrically conductive molecule was tailored. A new solid-state testbed was designed using the nanopore approach\textsuperscript{13,14} (Figure 3).

**Figure 3**

![Nanopore Diagram](image)

The nanopore test was simple: a 30 nm hole was made through a silicon nitride layer containing a resist. The pore was then filled with gold metal and a SAM was formed on the gold surface (about 1000 molecules assembled). Finally, gold was evaporated on the top of the SAM. The application of a difference of potential between the two electrodes created a current that could be measured (Figure 4).
Figure 4 shows a typical I(V) characteristic of a nitroamino OPE at 60 K. The positive bias corresponds to the hole injection from the chemisorbed thiol-Au contact and the electron injection from the evaporated contact. At about 1.7 V, the molecules start to conduct and at about 2.2 V, the molecules suddenly stop conducting. This behavior is similar to those of switches with a peak to valley ratio of 1030:1. This effect where there is a sudden spike in the current as the voltage is scanned is called negative differential resistance (NDR). The I(V) curve is fully reversible upon change in bias direction. The NDR effect has also been observed at room temperature$^{15}$ with the compounds containing the nitro group although the peak to valley ratio was only 1.5:1. It is believed that the nitro group is responsible for the NDR effect as no such phenomena was observed with amine-only compounds. To support the suggested mechanism of the NDR effect, a cyclic voltammogram curve is presented in Figure 5.
The diagram shows a two-step electron reduction: as the voltage increases, the molecule undergoes a one electron reduction at -1.70 V, thereby supplying a charge carrier for the electron transport. A further increase in the voltage causes the second electron reduction at -2.33 V, thus blocking the current. The width of the I(V) peak in Figure 4 correlates well with the difference in the two electron reduction potentials. The cyclic voltamogram curve of a mononitro also exhibited two reduction potentials at -1.39 V and -2.09 V. The fact that the mononitro device is more readily reduced than the nitroamino device indicates that the nitro group could be responsible for the room temperature NDR.

The mechanism of the NDR effect is unclear and the subject of quite some controversy between several groups. Seminario et al.\textsuperscript{16,17} have theorized that the switching originates from an internal conformational twist that is induced by charge transfer to the molecule. To support their theory, an \textit{ab initio} molecular study was carried out (Figure 6) to explain the electrical behavior of a \(\pi\)-conjugated amino-nitro(OPE) resembling a resonant tunneling diode (RTD) when an external voltage is applied between two ends.
Under the assumption that conduction occurred through the LUMO and that the HOMO-LUMO gap determined the conduction barrier, the simulation results demonstrated that when the molecule carried a negative charge, the LUMO was delocalized, yielding to maximum transport of the electrons. When the charge was 0 or −2, the LUMO was localized bringing the molecular admittance to zero. Weiss and Allara\textsuperscript{18} on the other hand have developed by STM data that supports the theory that the conductance switching in mononitro and nitroamino single molecules was the result of conformational changes (tilting relative to the surface normal) in the molecule rather than electrostatic effects of charge transfer.

Aside from the NDR effect, Mark Reed \textit{et al.}\textsuperscript{19,20} have recently met the second goal in building a molecular computer, that molecular devices can behave as memory devices. A memory device operates by the storage of a high- or low-conductivity state (Figure 7).
Figure 7 shows the I(V) characteristics of a nitroamino device. "0" represents the initial state and "1" the state after a write pulse. The device initially probed with a positive voltage sweep (write pulse) exhibits a low-conductivity state. Subsequent positive sweeps (read pulses) show a high conductivity. Bias in the negative direction causes the I(V) to be identically reset to the initial "0".

Figure 8
Figure 8 shows a measured memory diagram of a molecular device. An initially low-conductivity state (low σ) was changed (written) into a high-conductivity state (high σ) upon application of a voltage pulse. The high σ state persisted as a stored “bit”, which was unaffected by successive read pulses. Only a negative bias could change the conductivity back to its initial state. This current storage persisted for as long as 10 min and was reminiscent of a random access memory cell (RAM cell). It is interesting to note that mononitro devices had the reverse conductivity: they were initially highly conductive and became weakly conductive after a positive bias. Unfunctionalized or amine-only OPEs did not exhibit storage. In light of these results, it could be concluded that the nitro group could be responsible for the memory effect whereas the presence of an amine group changed the initial conductivity states of the molecule (most likely caused by the different dipole distribution it introduced to the molecule). These results demonstrated an erasable molecular memory cell at room temperature.
Even though thiolate SAMs on gold surface have been the most extensively studied systems, a problem persists with the use of the sulfur atom, its resistance to charge conduction. One possible explanation for such effect could be that the distance between the aromatic ring and the metal surface is too great and therefore “bottlenecks” the path of electrons and causes the electron flow to be reduced, called impedance. Another possibility is that the angle of the molecule relative to the surface is not in proper alignment for allowing the current to be maximum. Or, it could be inherent to the electronic properties of the sulfur atom itself. To investigate the impedance problem, several alligator clips such as organo-selenium, organo-tellurium, diazonium salts, nitriles and isonitriles have been studied in order to minimize the impedance mismatches between molecular structures and metal surfaces and to have a better energy match between the LUMO of the molecule and the Fermi level of the metal.\textsuperscript{21}

The work presented here mainly focuses on OPEs containing pyridines, which offer several advantages due to the inherent properties of the pyridine moiety. Pyridine-containing OPEs have been reported to show NDR and memory effects,\textsuperscript{22,23} which can be attributed to their redox ability. Moreover, several studies have indicated that they are candidates for alligator clips.\textsuperscript{24,25} One of the reasons is that due to their electron deficient ring, they present a better conduction due to a better match of their molecular orbital with the Fermi level of the metal. Indeed, the calculated LUMO of a thiophenol is at 0.210 eV whereas the calculated LUMO of a pyridine is at 0.138 eV (calculated by Spartan), the energy of the Fermi level of Au being at -5.31 eV.\textsuperscript{26} In addition, several reports have studied the assembly of pyridines on gold,\textsuperscript{27} and other metals as well. Pyridines have been observed to assemble on the surface both through the delocalized $\pi$-
electron system and the lone pair electrons associated with the nitrogen atom. The relative contributions from the lone pair and the $\pi$-electron bonding determine the orientation of the ring. When the $\pi$-electrons are involved in the bonding, the ring will be predominantly parallel to the surface whereas when pyridine is nitrogen bonded, a more perpendicular orientation is expected. The way pyridines assemble on surfaces is dependent on the metal, the coverage and the temperature. Observed Raman spectra and infrared spectra have indicated that the chemisorption of a pyridine molecule on coinage metal surfaces has the upright or slightly tilted configuration through the $N$-end adsorbed on these metal surfaces when the coverage is high or reaches the monolayer coverage.$^{28,29}$ Wu et al.$^{30}$ have investigated the binding interactions between the pyridine and small coinage metal clusters such as copper, silver and gold. They found that the order in the binding energies between pyridine and metals clusters is Cu=Ag > Au. The donation of the lone-pair electrons on the nitrogen atom of the pyridine molecule is the major contribution to the binding interaction. The back donation interaction from the metal atoms to the $\pi$-type anti-bonding orbital is very weak in all the complexes. For gold in particular, the binding is dispersive in nature, with significant contributions from charge polarization effects but minimal contributions from charge transfer and covalent bonding. This weaker binding energy between pyridines and other metals (e.g. 4.7 kcal/mol for Py-Ag, 22.4 kcal/mol for Py-Cu$^{31}$ and 8.4 kcal/mol for Py-Au$^{32}$) compared to the binding energy between S-Au (40 kcal/mol$^{33}$) could reduce the resistance to the charge conduction.

This chapter focuses mainly on the synthesis of a new class of pyridyl-based OPEs as potential switching and memory devices.
3. Results and Discussion

3.1 Synthesis

3.1.1. Synthesis of alligator clips

Scheme 1

The most commonly used alligator clip is the 4-thioacetyliodobenzene $^1$ (Scheme 1). To prepare 1, para-diiodobenzene was lithiated, and the generated anion was quenched with sulfur and acetyl chloride.

Scheme 2

A pyridyl alligator clip was then synthesized. Compound 3 (Scheme 2) was easily obtained via a Sonogashira$^{35}$ coupling of 4-iodopyridine 2 with trimethylsilylacetylene (TMSA). Compound 2 was itself obtained by the formation of the diazonium salt of 4-aminopyridine followed by iodination.$^{36}$ The deprotection of the trimethylsilyl (TMS) group with potassium carbonate in methanol has to be followed immediately by the coupling of the free alkyne$^{37-40}$ 4 as it decomposes after a couple of hours.

3.1.2. Synthesis of the core
Since molecular-scale devices containing nitro and nitroamine redox center on the internal phenyl ring have exhibited NDR behavior, several mononitro and nitroamino devices have been synthesized.

Scheme 3 depicts the synthesis of the core of the OPEs

Scheme 3

Compounds 5 through 10 were synthesized according to the literature\textsuperscript{41} but some modifications were made to improve the yield. To start, para-dibromobenzene was nitrated using concentrated sulfuric acid and nitric acid in order to get 2,5-dibromonitrobenzene 5. Reduction of the nitro was accomplished with tin chloride in good yield. The aniline 6 was then protected using acetyl chloride in order to furnish the acetamide 7. After a second nitration, followed by a deprotection, 2,5-dibromo-4-nitroaniline 9 was oxidized using the HOF oxidation.\textsuperscript{42} This afforded the dinitrodibromide 10 in excellent yield.

3.1.3. Synthesis of one-terminal molecular devices
Scheme 4

Molecular device 13 (Scheme 4) was synthesized as a model study for self-assembly. *P*-Bromoiodobenzene was coupled to TMSA and phenyl acetylene to give 11. The TMS protecting group was removed with potassium carbonate and methanol to give 12 in excellent yield and finally a last coupling step to 4-iodopyridine afforded 13 in a moderate yield.

Since it has been reported that the nitro group was responsible for the NDR and the memory effects, 15 and 17 were synthesized to study the importance of the position of the nitro group relative to the “alligator clip” on these effects.

Scheme 5

15 (Scheme 5), which has the nitro group oriented toward the pyridyl group (2' site), was synthesized by first coupling 3 with 2,5-dibromonitrobenzene. Since the free
alkyne 4 was not very stable, the TMS protecting group was removed in situ in order to
give 14 in good yield. Coupling of 14 with phenylacetylene afforded the device 15.

**Scheme 6**

![Scheme 6](image)

The synthesis of 17 (Scheme 6), which has the nitro group pointing away from the
pyridyl group (3' site), resembles the approach used for 15 except that the steps are
reversed. In this case, the phenylacetylene was first coupled to 2,5-dibromonitrobenzene
5 to give 16 in moderate yield. The TMS protected pyridyl clip was then coupled to 16 to
furnish 17 in good yield.

**Scheme 7**

![Scheme 7](image)

Scheme 7 depicts the synthesis of a nitroamino device which was synthesized by
coupling of the acetamide 8 to phenylacetylene to afford 18 in 55% yield. A last
coupling step with the protected pyridyl clip furnished the molecular device 19.
Since theoretical studies have shown that dinitro-containing OPEs can act as molecular memories, a molecule containing a dinitro core and a pyridyl alligator clip was synthesized. The synthesis of the dinitro 23 started with the coupling of 9 to phenylacetylene to give 21, which was then oxidized using HOF to furnish the dinitro molecule 22. Attempt to couple 22 with TMSA using Sonogashira palladium-catalyzed coupling conditions was very low yielding (9%). Instead an alternative route was chosen using Stille coupling. The organostannane 20, made from 4 in a reasonable yield, was coupled to 22 using Pd(dba)$_2$ and triphenylarsine, this affording 23 in 30% yield.

In order to conduct current through the molecular orbitals with minimal inhibition, these organic oligomers must have all their phenyl rings in the same plane. By replacing the terminal phenylethynyl group by a phenyl group, a barrier to conduction is introduced as the molecule becomes slightly twisted due to steric hindrance. To study the effect of this rotational barrier, 25 was synthesized (Scheme 9).
Scheme 9

The Suzuki coupling\(^{47,48}\) of 2,5-dibromo-4-nitroacetanilide 8 with phenyl boronic acid was used to synthesize compound 24 (Scheme 9), which was then coupled to 4-(trimethylsilylethynyl)pyridine 3 to afford 25.

The biphenyl 25 could also be obtained by another route (Scheme 10).

Scheme 10

This route uses a Stille\(^{45}\) coupling instead of Suzuki’s. The organostannane 26 was synthesized by lithium-bromide exchange on bromobenzene followed by quenching with tributyltin chloride. The Stille\(^{45}\) coupling of 26 with 9 furnished 27 in good yield. It
was followed by a Sonogashira\textsuperscript{35} coupling with TMSA which afforded 28, which was deprotected to the free alkyne 29 in excellent yield. The last step of the synthesis was the coupling to 4-iodopyridine to give the device 25 in good yield. This route gave slightly higher yield than the route using the Suzuki coupling.\textsuperscript{47,48}

For conjugated linear molecules, it has been demonstrated that better control and improvement of electronic charge and hole injection is possible when utilizing fluorinated OPEs.\textsuperscript{49} Because of the lower intermolecular interaction, OPEs with fluorine substituents also show tighter molecular packing in SAMs\textsuperscript{8} and behavior as $n$-type organic semiconductors.\textsuperscript{50} With that in mind, the synthesis of pentafluoroarene OPEs was undertaken.

**Scheme 11**

![Scheme 11](image)

Scheme 11 depicts the synthesis of a pentafluoro mononitro device. The synthesis started with $\alpha$-nitroaniline, which was iodinated\textsuperscript{51} to give 30 in reasonable yield. Coupling with TMSA afforded 31 in excellent yield, followed by removal of the TMS
protecting group to yield 32. The next step was the coupling with bromopentafluorobenzene, which was low yielding in our hands, this furnishing 33. Iodination was performed with trifluoroborane and isoamyl nitrite to form the diazonium salt first, followed by quenching with sodium iodide and iodine to give 34. The last step was the coupling with the freshly deprotected ethynylpyridine which afforded the final device 35.

3.1.4. Synthesis of two-terminal molecular devices

In our work with pyridyl alligator clips, two-terminal molecular devices were synthesized as they can serve as cross-linkers between metallic nanoparticles for bridging connections in future electronic devices.

Scheme 12

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
N & \quad \equiv \\
\text{O}_2\text{N} & \quad \text{TMS}
\end{align*}
\]

\[
\xrightarrow{\text{K}_2\text{CO}_3, \text{MeOH}, \text{Pd}(\text{PPh}_3)_2\text{Cl}_2, \text{PPh}_3, \text{CuI, THF}, 64^\circ \text{C}, \text{24\%}}
\]

\[
\begin{align*}
N & \quad \equiv \\
\text{O}_2\text{N}
\end{align*}
\]

Scheme 12 outlines the synthesis of 36 from 2,5-dibromonitrobenzene 5. Once again, potassium carbonate was used as a base for the in situ removal of the TMS protecting group and for the coupling, as the free alkyne was unstable. Attempts to perform the reaction at room temperature gave mostly the homocoupled bis(ethynylpyridine) and coupling at one side of the aryl dibromide.
Compound 38 resembles 36, but has a nitroaniline core instead of a nitro core. Unlike the potential molecular device 36, the synthesis of 38 (Scheme 13) commenced with the coupling of 2,5-dibromo-4-nitroacetanilide 8 with TMSA to give 37, which was then coupled with 4-iodopyridine in low yield. The low yield of the coupling reactions could be due to the cyclization between the nitro and the alkyne unit, a process reported by Rosen et al.\textsuperscript{52}

Figure 9

The molecular device 39 (Figure 9) was synthesized in an effort to form a SAM via the protected benzenethiol terminal group enabling the pyridyl end of the molecule to serve as a better top contact linker with the evaporated metal (when compared to an unfunctionalized phenyl group) when incorporated into a device.

The route to synthesize 39 was designed so that the coupling of the 4-thioacetylidoiodobenzene 1 to the nitro core is the last step because the coupling of the alligator clip 1 with an aryl halide bearing a nitro group is generally very low yielding.
The synthesis started with the coupling of triisopropylsilylacetylene (TIPSA) to 2,5-dibromonitrobenzene 5 to furnish 40, which was then coupled to TMSA in good yield (Scheme 14). Selective deprotection of the TMS protecting group was accomplished with potassium carbonate. 42 was then submitted to a Sonagashira coupling with 4-iodopyridine. Unfortunately, deprotection of the TIPS protecting group of 43 by tetrabutylammonium fluoride lead to the immediate decomposition of the product.
The second attempt (Scheme 15) was performed with a different protecting group than TIPS. Melissaris\textsuperscript{53} reported the use of 2-methyl-3-butyn-2-ol (MEBYNOL) as an inexpensive and fast way to protect a free alkyne. 5 was coupled to 2-methyl-3-butyn-2-ol to give 44 which was then coupled to TMSA. The TMS protecting group of 45 was then selectively removed with potassium carbonate the furnish 46. Coupling of 46 with 4-iodopyridine afforded 47 in 68\% yield. Unfortunately, attempts to remove the alcohol protecting group with sodium hydroxide failed.
Scheme 16

The last route (Scheme 16) comprised the use of p-iodo-2-nitroaniline 30, which was coupled with the freshly deprotected 4-ethynylpyridine in order to furnish 48. The Sandmeyer reaction was then used to iodinate at the terminal position in a very good yield. 49 was then coupled to TMSA to afford 50 which was deprotected to give the free alkyne 51. Finally, the last coupling with 4-thioacetyliodobenzene 1 afforded the final device 39 in low yield as expected.

Scheme 17
The synthesis of a nitro-amino device resembling 39 is shown in Scheme 17. 55 was synthesized by coupling 2,5-dibromo-4-nitroacetonilide 8 with 3 in moderate yield to afford the bromide 52. 52 was then coupled with TMSA to afford 53 in 49% yield, which was deprotected with potassium carbonate to give 54. The last step of this synthesis was the coupling with 4-thioacetylthiobenzene (1), which afforded the potential device 55 in good yield (75%).

3.2. Self-assembly

Self-assembly test were performed on some pyridine OPEs (Table 1). Typically, a gold substrate was placed into a solution of 1 mg of the test molecule in 20 mL of THF. The sample was removed after 24 h and washed with acetone, THF and ethanol. After drying with nitrogen, the thickness was measured by ellipsometry. All the thicknesses were calculated based on the refractive index \( n_f = 1.55 \) of the OPEs.

Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Structure</th>
<th>Time</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td><img src="https://via.placeholder.com/150" alt="Structure 1" /></td>
<td>24 h</td>
<td>2.0 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>45 h</td>
<td>1.7 nm</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
<td><img src="https://via.placeholder.com/150" alt="Structure 2" /></td>
<td>24 h</td>
<td>1.1 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>45 h</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>3</td>
<td>19</td>
<td><img src="https://via.placeholder.com/150" alt="Structure 3" /></td>
<td>24 h</td>
<td>1.4 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48 h</td>
<td>1.7 nm</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td><img src="https://via.placeholder.com/150" alt="Structure 4" /></td>
<td>72 h</td>
<td>1.9 nm</td>
</tr>
</tbody>
</table>

\(^a\) Thanks to Lijing Yang for performing these experiments.
\(^b\) Calculated by Molecular Mechanics including Au-N bond.
The results showed that pyridines OPEs where the nitro groups points towards the pyridine ring (Entry 1) are easier to assemble than the OPEs with the nitro group pointing away from the pyridyl unit (Entry 2). Nitroamino devices seemed to assemble fairly well on gold, although the value for the biphenyl nitroamino (Entry 3) is slightly higher than the theoretical value, therefore the formation of a multilayer might be possible.

4. Summary

The synthesis of OPEs containing pyridines units as potential electronic devices has been accomplished using a series of palladium-catalyzed couplings. Some preliminary assembly testings were performed and conductance tests are currently under way.
5. Experimental Procedures

General. All reactions were performed in an oven-dried flask and under an atmosphere of nitrogen unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Toluene, triethylamine, methylene chloride were distilled over calcium hydride before use. Silica gel plates were 250 μm thick, 40 F₂₅₄ grade from EM science. Silica gel was grade 60 (230-400 mesh) from EM Science. Melting points were taken on a Mel-Temp (Laboratory Devices) apparatus. FT-IR spectra were taken on a Nicolet Avatar 360 spectrometer. ¹H NMR spectra were observed at 400 MHz and ¹³C NMR spectra were observed at 100 MHz on a Bruker AVANCE 400 spectrometer. Mass spectrometry was performed by Terry Marriott and Yunxuan Xiao 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 testing of compounds. The CVs were performed on a BAS CV-50W using a glassy carbon electrode as the working electrode, platinum wire as the auxiliary electrode, and a Ag/AgNO₃ non-aqueous reference electrode. The solutions were 1 mM in DMF and 0.1M in n-Bu₄NBF₄. the scan rate was 0.1 V/s at 25 °C. Oxygen and water were not rigorously excluded from the measurements.

Ellipsometry measurements. Monolayer thickness was determined using a Rudolph series 431A ellipsometer. The He-Ne laser (632.8 nm) light was incident at 70° on the sample. Measurements were carried out before and immediately after
monolayer adsorption. All the thicknesses were calculated based on the refractive index of \( n_r = 1.55, k_r = 0 \).

**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 all solids including the aryl halide, bis(triphenylphosphine) palladium(II) chloride (4-5 mol % based on the aryl halide) and copper(I) iodide (8-10 mol % based on the aryl halide). Alternately, bis(dibenzylideneacetone)palladium(0) (2 mol % based on the aryl halide), copper(I) iodide (2 mol % based on aryl halide) and triphenylphosphine (4 equivalents per palladium) were used. The vessel was sealed with a rubber septum, evacuated and backfilled with dry nitrogen (3 x). THF and remaining liquids were added followed by \( N,N\)-diisopropylamine or triethylamine. The reaction was heated, if necessary, until complete. The reaction vessel was cooled to room temperature, quenched with water or a saturated solution of \( \text{NH}_4\text{Cl} \) and extracted with \( \text{Et}_2\text{O} \). The combined organic layers were dried over anhydrous \( \text{MgSO}_4 \), filtered and the solvent removed *in vacuo*.

**General procedure for the in-situ removal of the TMS protecting group and conducting the Sonogashira Coupling.** To a solution of the aryl halide (1.0 mmol), \( \text{K}_2\text{CO}_3 \) (5.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.05 mmol), copper iodide (0.05 mmol) and triphenylphosphine (0.20 mmol) in THF (2 mL) under nitrogen were added via a cannula the TMS-protected alkyne (1.20 mmol) in THF (2 mL) and
MeOH (1 mL). The reaction was heated, if necessary, until complete. The solvent was removed by rotary evaporation and the brown residue was diluted with water and extracted with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered and the solvent evaporated in vacuo.

**General Procedure for the Deprotection of Trimethylsilyl-Protected Alkynes.**

To a round bottom flask equipped with a stir bar were added the protected alkyne, potassium carbonate (10 equiv per protected alkyne), methanol, and methylene chloride. The reaction was heated, and upon completion the reaction mixture was diluted with methylene chloride and washed with brine (3×). The organic layer was dried over MgSO₄, and the solvent removed in vacuo.

![AcS-](image)

**Thioacetic acid S-(4-iodo-phenyl) ester**<sup>34</sup>(l). To a three-neck flask 500 mL equipped with an addition funnel was added <i>p</i>-diiodobenzene (17.12 g, 51.90 mmol) in THF (250 mL). The mixture was cooled to −78 °C. To this solution was added drop wise (1 drop/3 sec) via the addition funnel t-BuLi (1.68 M, 61.8 mL). After complete addition, the mixture was allowed to stir at −78 °C for another 45 min. Sulfur (1.75 g, 54.46 mmol) was added, the reaction was stirred for 10 min at −78 °C (dry ice acetone bath), 10 min at 0 °C (ice water bath) and then cooled back down to −78 °C. Acetyl chloride (4.4 mL, 62.21 mmol) was added. The reaction was allowed to warm to RT overnight. Water (100 mL) and CH₂Cl₂ (50 mL) were added. The combined organic phases were washed with brine, dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by
flash chromatography (silica gel, hexane/CH₂Cl₂ 1/1) afforded 10.25 g (71% yield) of the title compound as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J=8.5 Hz, 2 H), 7.14 (d, J=8.5 Hz, 2 H), 2.43 (s, 3 H).

4-Iodopyridine³⁶ (2). A solution of 4-aminopyridine (6.0 g, 63.8 mmol) and fluoboric acid 51% (51 mL, 41.8 mmol) was made and cooled down to −25 °C under air. Sodium nitrite (4.8 g, 70 mmol) was then added slowly. The mixture was stirred at −10 °C for 30 min. A solution of sodium iodide (34.5 g, 230 mmol) and iodine (8.1 g, 31.9 mmol) in water (100 mL) was then added portionwise to the pyridine solution. The excess iodine was neutralized by adding dropwise a saturated solution of sodium bisulfite until the black solution turned yellow-brown. The pH was carefully adjusted to 10 with a saturated solution of K₂CO₃. The aqueous phase was separated and extracted with Et₂O. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was eliminated in vacuo. The resulting yellow solid was purified by sublimation to afford 9.5 g (73% yield) of a colorless solid. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J=6 Hz, 2 H), 7.70 (d, J=6 Hz, 2 H).

4-(Trimethylsilyleneethyl)pyridine³⁷-⁴⁰ (3). See the general Pd/Cu procedure. To a solution of 4-iodopyridine (2) (3.27 g, 15.98 mmol), bis(dibenzylideneacetone)palladium(0) (0.45 g, 0.78 mmol), copper(I) iodide (0.148 g, 0.78 mmol) and triphenylphosphine (0.82 g, 3.1 mmol) in THF (25 mL) were added Et₃N
(2.4 mL, 17.2 mmol) and trimethylsilylacetylene (3.2 mL, 22.5 mmol). The mixture was heated to 65 °C for 21 h. Purification by flash chromatography (silica gel, CH₂Cl₂, Et₂O/CH₂Cl₂ 20/80) afforded 3.00 g (99% yield) of the title compound as a yellow oil. 

\(^1\)H NMR (400 MHz, CDCl₃) δ 8.57 (dd, J=4.5, 1.6 Hz, 2 H), 7.31 (dd, J=4.5, 1.7 Hz, 2 H), 0.27 (s, 9 H).

\[
\begin{align*}
\text{4-Ethynylpyridine}^{37-40} (4). \text{ See the general TMS-protected alkyne deprotection procedure. To a solution of 4-(trimethylsilyl-ethylene)pyridine (3) (1.086 g, 6.20 mmol) in MeOH (20 mL) and CH₂Cl₂ (20 mL) in the dark was added K₂CO₃ (8.58 g, 62.08 mmol) under air. The solution was stirred at 23 °C for 1 h. The reaction afforded 0.56 g (87% yield) of the title compound as a yellow solid. The compound was stored under nitrogen, in the dark and in the freezer.} 
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl₃) δ 8.61 (dd, J=4.6, 1.6 Hz, 2 H), 7.39 (dd, J=4.5, 1.6 Hz, 2 H), 3.33 (s, 1 H).

\[
\begin{align*}
\text{2,5-Dibromonitrobenzene}^{41} (5). \text{ A mixture of nitric acid 69.8% (40 mL, 62.9 mmol) and concentrated sulfuric acid (25 mL, 45.1 mmol) was added dropwise to a solution of 1,4-dibromobenzene (29.88 g, 126.6 mmol) in sulfuric acid (50 mL, 90.2 mmol) at 0 °C under air. While continuing agitation, the ice bath was allowed to melt and the reaction mixture warmed to RT. The suspension was stirred overnight. The mixture was poured over ice and the solid precipitate was collected and washed with}
\end{align*}
\]
large amounts of water. After a brief air dry, it afforded 35.6 g (100% yield) of the title compound as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, $J$=2.2 Hz, 1 H), 7.60 (1/2 AB$_q$, $J$=8.5 Hz, $\Delta v$=22.6, 1 H), 7.54 (1/2 AB$_q$ d, $J$=8.6, 2.2 Hz, $\Delta v$=22.6, 1 H).

\[ \text{2,5-Dibromoaniline}^{41} (6). \] To a slurry of 2,5-dibromonitrobenzene (5) (19.33 g, 68.8 mmol) in ethanol (36 mL) under air was added tin(II) chloride dihydrate (73.1 g, 324.0 mmol). After 10 min, an exotherm occurred which rapidly warmed the reaction mixture to reflux. Once the exotherm subsided, the mixture was cooled in an ice bath and then poured over ice water. The pH was adjusted to 10 with a saturated solution of NaOH. The precipitate was filtered then suspended in ethanol (100 mL). A solution of 50% NaOH (100 mL, 1.25 mmol) was then added to the slurry and the mixture was stirred for several minutes and then poured over 400 mL of water. The precipitate was filtered and the filter cake was washed with 2 M NaOH and water. After drying, it afforded 12.2 g (71% yield) of the title compound. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, $J$=8.4 Hz, 1 H), 6.91 (d, $J$=2.2 Hz, 1 H), 6.74 (dd, $J$=8.5, 2.2 Hz, 1 H), 4.14 (brs, 2 H).

\[ \text{2,5-Dibromoacetanilide}^{41} (7). \] To a solution of 2,5-dibromoaniline (6) (14.35 g, 57.2 mmol) in acetone (200 mL) under air were added K$_2$CO$_3$ (47.2 g, 341.5 mmol) and acetyl chloride (16.3 mL, 229.0 mmol). The mixture was heated to reflux for 3 h. After
cooling, K₂CO₃ was filtered and the solvent was evaporated in vacuo. The solid was washed with hexane and the filtration afforded 13.8 g (82% yield) of the title compound as an off-white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.59 (br s, 1 H), 7.58 (br s, 1 H), 7.39 (d, J=8.5 Hz, 1 H), 7.12 (dd, J= 8.5, 2.4 Hz, 1 H), 2.25 (s, 3 H).

2,5-Dibromo-4-nitroacetanilide[^11] (8). To a mixture of 69.8% nitric acid (12 mL, 18.9 mmol) and 96.1% sulfuric acid (12 mL, 21.6 mmol) was added 2,5-dibromoacetanilide (7) (5.02 g, 17.1 mmol) at 0 °C under air. The mixture was stirred for 3 h at 0 °C, then poured over ice water. The precipitate was filtered and the filter cake was washed with water. After purification by flash chromatography (silica gel, CH₂Cl₂), the reaction afforded 3.64 g (63% yield) of the title compound as an off-white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1 H), 8.21 (s, 1 H), 7.77 (brs, 1 H), 7.28 (s, 1 H), 2.32 (s, 3 H).

2,5-Dibromo-4-nitroaniline[^56] (9). To a solution of 2,5-dibromo-4-nitroacetanilide (8) (1.75 g, 5.18 mmol) in MeOH (30 mL) and CH₂Cl₂ (30 mL) under air was added K₂CO₃ (7.15 g, 51.74 mmol). The solution was stirred at 23 °C for 3 h. The reaction mixture was diluted with water and extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. The
reaction afforded 1.52 g (99% yield) of the title compound as a yellow solid. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.23 (d, $J=0.5$ Hz, 1 H), 7.11 (d, $J=0.5$ Hz, 1 H), 6.87 (br s, 2 H).

1,4-Dibromo-2,5-dinitrobenzene$^{42}$ (10). To a 250 mL polyethylene bottle were added H$_2$O (6 mL) and CH$_3$CN (180 mL) and the mixture was cooled to $-20$ °C. F$_2$ (20% in He) was then bubbled through the solution at a rate of 50 sccm for 6 h. The resulting HOF/CH$_3$CN solution was then purged with He for 15 min. The 2,5-dibromo-4-nitroaniline (9) (1.76 g, 5.96 mmol) was then added in EtOAc (20 mL) and mixed at $-20$ °C for 5 min before being neutralized by pouring into a saturated NaHCO$_3$ solution. The reaction afforded 1.93 g (99% yield) of the title compound as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (s, 2 H).

Trimethyl-(4-phenylethynyl-phenylethynyl)-silane$^{57}$ (11). See the general Pd/Cu procedure. To a solution of 1-bromo-4-iodobenzene (2.802 g, 9.904 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.147 g, 0.210 mmol), copper(I) iodide (0.077 g, 0.404 mmol) in THF (10 mL) were added diisopropylamine (6 mL, 34.35 mmol) and trimethylsilylacetylene (1.44 mL, 10.13 mmol). The mixture was stirred at 23 °C for 1 d. This reaction was transferred via cannula into another screw cap tube filled with bis(triphenylphosphine)palladium(II) dichloride (0.147 g, 0.210 mmol), copper(I) iodide (0.077 g, 0.404 mmol) and THF (10 mL). To this new mixture was added phenyl
acetylene (1.2 mL, 10.89 mmol). The mixture was stirred at 83 °C for 1 d. Purification by flash chromatography (silica gel, petroleum ether) afforded 1.35 g (50% yield) of the title compound as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53 (m, 2 H), 7.46 (d, \(J=2.5\) Hz, 4 H), 7.35 (m, 3 H), 0.27 (s, 9 H).

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4-Ethynyl-1-phenylethynylbenzene\(^5\) (12). See the general TMS-protected alkyne deprotection procedure. To a solution of trimethyl-(4-phenylethynyl-phenylethynyl)-silane (11) (0.889 g, 3.244 mmol) in MeOH (30 mL) and CH\(_2\)Cl\(_2\) (30 mL) under air was added K\(_2\)CO\(_3\) (4.48 g, 32.44 mmol). The solution was stirred at 23 °C for 2 h. The reaction afforded 0.65 g (99% yield) of the title compound as a yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (m, 2 H), 7.49 (s, 4 H), 7.36 (m, 3 H), 3.19 (s, 1 H).

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4-(4-Phenylethynyl-phenylethynyl)-pyridine (13). See the general Pd/Cu procedure. To a solution of 4-ethynyl-1-phenylethynylbenzene (12) (0.65 g, 3.22 mmol), 4-iodopyridine (0.726 g, 3.54 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.113 g, 0.161 mmol), copper(I) iodide (0.033 g, 0.161 mmol) in THF (20 mL) was added Et\(_3\)N (5 mL). The mixture was stirred at 55 °C for 2 d. Purification by flash chromatography (silica gel, EtOAc/hexane 1/1) afforded 0.290 g (32% yield) of the title compound as a white solid. Mp: 216-220 °C. IR (KBr) 3438.8, 3036.3, 2213.7, 1586.7, 1511.6, 1407.6 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.63 (d, \(J=5.5\) Hz, 2 H), 7.55 (m, 6 H), 7.43 (d, \(J=5.5\) Hz, 2 H), 7.38 (m, 3 H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.5, 131.8,
131.7, 131.6, 128.6, 128.4, 125.6, 124.3, 122.8, 121.7, 93.9, 91.9, 88.8, 88.2. HRMS calc'd for C_{21}H_{13}N: 279.1048, found: 279.1049. Anal. Calc'd for C_{21}H_{13}N: C, 90.29; H, 4.69; N, 5.01; Found: C, 89.61; H, 4.68; N, 4.98.

4-(4-Bromo-2-nitro-phenylethynyl)-pyridine (14). See the general Pd/Cu procedure. To a solution of 2,5-dibromonitrobenzene 5 (0.43 g, 1.53 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.052 g, 0.074 mmol), copper(I) iodide (0.015 g, 0.078 mmol), triphenylphosphine (0.079 g, 0.30 mmol) and K_{2}CO_{3} (0.83 g, 6.0 mmol) in THF (2 mL) were added via cannula 3 (0.342 g, 1.95 mmol) in THF (4 mL) and MeOH (1.5 mL). The mixture was heated at 23 °C for 2 d. Purification by flash chromatography (silica gel, EtOAc/hexane 90/10, 70/30, 50/50) afforded 330 mg (71% yield) of the title compound as an off-white solid. Mp: 166-171 °C. IR (KBr) 3424.4, 3093.3, 1592.3, 1521.4, 1409.3, 1341.4, 1272.6 cm^{-1}. ^{1}H NMR (400 MHz, CDCl_{3}) δ 8.68 (br s, 2 H), 8.29 (d, J=1.9 Hz, 1 H), 7.79 (dd, J=8.3, 2.0 Hz, 1 H), 7.62 (d, J=8.3 Hz, 1 H), 7.44 (d, J=4.7 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_{3}) δ 145.0, 136.2, 135.7, 130.1, 128.1, 126.7, 125.7, 123.2, 116.5, 94.8, 87.8. HRMS calc'd for C_{13}H_{7}BrN_{2}O_{2}: 303.9672, found: 303.9682.
4-(2-Nitro-4-phenylethynyl-phenylethynyl)-pyridine (15). See the general Pd/Cu procedure. To a solution of 14 (88.8 mg, 0.293 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.011 g, 0.016 mmol), copper(I) iodide (0.004 g, 0.021 mmol) and triphenylphosphine (0.008 g, 0.029 mmol) in THF (4 mL) were added Et₃N (0.25 mL, 1.76 mmol) and phenylacetylene (0.1 mL, 9.1 mmol). The mixture was stirred at 56 °C for 36 h. Purification by flash chromatography (silica gel, EtOAc/hexane 20/80) afforded 65 mg (69% yield) of the title compound as a yellow solid. Mp: 132-134 °C. IR (KBr) 3445.3, 3046.3, 2203.5, 1548.5, 1529.1, 1399.9, 1341.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (br d, J=4.9 Hz, 2 H), 8.27 (d, J=1.5 Hz, 1 H), 7.76 (1/2 ABqd, J=8.0, 1.6 Hz, 1 H), 7.72 (1/2 ABqd, J=8.0, 0.5 Hz, 1 H), 7.56 (m, 2 H), 7.45 (dd, J=5.9, 1.7 Hz, 2 H), 7.40 (m, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.6, 135.4, 134.7, 131.8, 129.3, 128.5, 127.7, 125.3, 121.9, 116.7, 95.3, 94.3, 88.5, 86.6. HRMS calc’d for C₂₁H₁₂N₂O₂: 324.0899, found: 324.0895. Anal. Calc’d for C₂₁H₁₂N₂O₂: C, 77.77; H, 3.73; N, 8.64; Found: C, 77.47; H, 3.72; N, 8.59.

1-Bromo-4-ethynylphenyl-3-nitrobenzene (16). See the general Pd/Cu procedure. To a solution of 2,5-dibromonitrobenzene (5) (0.937 g, 3.34 mmol), bis(dibenzylideneacetone)palladium(0) (0.095 g, 0.166 mmol), copper(I) iodide (0.032 g, 0.168 mmol) and triphenylphosphine (0.173 g, 0.66 mmol) in THF (4 mL) were added Et₃N (1 mL, 7.2 mmol) and phenylacetylene (0.50 mL, 4.56 mmol). The mixture was stirred at 23 °C for 48 h. Purification by flash chromatography (silica gel, CH₂Cl₂/
hexane 1/8) afforded 0.48 g (47% yield) of the title compound as a yellow solid. Mp: 58-74 °C. IR (KBr) 3421.9, 3085.5, 2213.4, 1595.7, 1545.9, 1521.3, 1336.5, 1269.2 cm⁻¹.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, J=1.9 Hz, 1 H), 7.72 (dd, J=8.3 Hz, 2.0, 1 H), 7.59 (m, 3 H), 7.40 (m, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 135.9, 135.5, 132.0, 129.4, 128.5, 127.8, 122.0, 121.8, 117.7, 98.4, 84.0. HRMS calc’d for C₁₄H₈NO₂Br: 302.9720, found: 302.9725.

2-Ethynylphenyl-5-(4'-ethynylpyridyl)-1-nitrobenzene (17). See the general in-situ deprotection and coupling procedure. To a solution of 16 (0.306 g, 1.01 mmol), K₂CO₃ (0.713 g, 5.16 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.050 mmol), copper(I) iodide (0.009 g, 0.047 mmol) and triphenylphosphine (0.052 g, 0.198 mmol) in THF (2 mL) were added via cannula 3 (0.217 g, 1.24 mmol) in THF (2 mL) and MeOH (1 mL). The mixture was heated at 60 °C for 18 h. Purification by flash chromatography (silica gel, EtOAc/hexane 20/80, 40/60) afforded 260 mg (79% yield) of the title compound as a yellow solid. Mp: 144-146 °C. IR (KBr) 3442.3, 3053.0, 2209.4, 1631.3, 1584.8, 1524.7, 1404.3, 1344.7, 1269.0, 826.4, 755.2, 686.6 cm⁻¹.

¹H NMR (400 MHz, CDCl₃) δ 8.67 (dd, J=4.4, 1.6 Hz, 2 H), 8.27 (br s, 1 H), 7.74 (m, 2 H), 7.63 (d, J=1.8 Hz, 1 H), 7.60 (m, 1 H), 7.42 (m, 5 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.0, 135.4, 134.7, 132.1, 130.2, 129.6, 128.5, 128.0, 125.5, 122.7, 122.1, 119.2, 99.7, 90.8, 90.3, 84.6. HRMS calc’d for C₂₁H₁₂N₂O₂: 324.0899, found: 324.0897.
\[ \text{N-(2-Bromo-4-nitro-5-phenylethynyl-phenyl)-acetamide}^{59} \] (18). See the general Pd/Cu coupling procedure. To a solution of 2,5-dibromo-4-nitroacetanilide (8) (1.49 g, 4.416 mmol), bis(triphenylphosphine)palladium(II) (0.16 g, 0.226 mmol) dichloride, copper(I) iodide (43 mg, 0.226 mmol) in THF (11 mL) were added phenyl acetylene (0.53 mL, 4.858 mmol) and triethylamine (5.5 mL). The mixture was stirred at RT overnight then at 40 °C for 1 h. Purification by flash chromatography (silica gel, CH₂Cl₂) afforded 0.86 g (55% yield) of the title compound as a yellow solid. \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 8.86 (s, 1 H), 8.40 (s, 1 H), 7.80 (br s, 1 H), 7.63 (m, 2 H), 7.40 (m, 3 H), 2.31 (s, 3 H).

4-Nitro-5-phenylethynyl-2-pyridin-4-ylythynyl-phenylamine (19). See the general in-situ deprotection and coupling procedure. To a solution of \( N-(2\)-bromo-4-nitro-5-phenylethynyl-phenyl)-acetamide \ (18) (0.84 g, 2.34 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.083 g, 0.117 mmol), copper(I) iodide (0.022 g, 0.117 mmol), K₂CO₃ (1.94 g, 14.04 mmol) in THF (4 mL) were added 4-trimethylsilanylethynylpyridine (3) (0.451 g, 2.57 mmol) in THF (12 mL) via a cannula and MeOH (4 mL). The mixture was heated to 55 °C for 14 h. Purification by flash chromatography (silica gel, AcOEt) afforded 271 mg (34% yield) of the title compound as a yellow solid. Mp: 224-229 °C. IR (KBr) 3451.7, 3351.1, 3202.6, 2206.4, 1622.9,
1588.4, 1539.0, 1474.4, 1306.7, 1249.8 cm\(^{-1}\). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.64 (d, \(J=5.7\) Hz, 2 H), 8.25 (s, 1 H), 7.67 (dd, \(J=4.5, 1.5\) Hz, 2 H), 7.59 (m, 2 H), 7.47 (m, 3 H), 7.15 (br s, 1 H), 7.03 (s, 1 H). \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 154.0, 149.8, 136.3, 131.7, 131.2, 130.0, 129.7, 129.0, 125.5, 121.8, 120.4, 118.1, 103.9, 96.1, 93.4, 88.4, 86.3. HRMS \(m/z\) calc'd for C\(_{21}\)H\(_{13}\)N\(_3\)O\(_2\) 339.1008, found 339.1004.

4-Tributylstannanylylethynyl-pyridine\(^6\) (20). In a 100 mL round bottom flask was added 4-ethynylpyridine (4) (0.440 g, 4.272 mmol) in THF (40 mL). The reaction was cooled to \(-78^\circ\)C and n-BuLi (2.0 mL, 4.96 mmol) was added. The mixture was stirred at \(-78^\circ\)C for 1 h. Tributyltin chloride (1.26 mL, 4.65 mmol) was added and the reaction mixture was allowed to warm up to RT overnight. The solution was diluted with water and extracted with Et\(_2\)O. The combined organic phases were dried over MgSO\(_4\), filtered, and the solvent evaporated \textit{in vacuo}. Purification by flash chromatography (silica gel, Et\(_2\)O/CH\(_2\)Cl\(_2\) 1/9) afforded 0.867 g (51% yield) of the title compound as a clear liquid. The compound was not pure enough to perform its full characterization data. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.53 (dd, \(J=4.4, 1.6\) Hz, 2 H), 7.28 (dd, \(J=4.4, 1.6\) Hz, 2 H), 1.63 (m, 6 H), 1.38 (sex, \(J=7.3\) Hz, 6 H), 1.09 (m, 6 H), 0.92 (t, \(J=7.3\) Hz, 9 H).

2-Bromo-4-nitro-5-(phenylethynyl)aniline\(^5\) (21). See the general Pd/Cu procedure. To a solution of 2,5-dibromo-4-nitroaniline (9) (2.69 g, 9.093 mmol),
bis(triphenylphosphine)palladium(II) dichloride (0.320 g, 0.456 mmol), copper(I) iodide (0.088 g, 0.463 mmol) in THF (20 mL) were added Et₃N (10 mL) and phenylacetylene (1.1 mL, 10.03 mmol). The mixture was stirred at 23 °C for 1 d. Purification by flash chromatography (silica gel, CH₂Cl₂) afforded 2.39 g (83% yield) of the title compound as a brown solid. ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1 H), 7.59 (m, 2 H), 7.37 (m, 3 H), 6.96 (s, 1 H).

![Chemical structure of the compound](image)

4-(Phenylethynyl)-2,5-dinitrobromobenzene⁴² (22). To a 250 mL polyethylene bottle were added H₂O (3 mL) and CH₃CN (90 mL) and the mixture was cooled to −20 °C. F₂ (20% in He) was then bubbled through the solution at a rate of 50 cc/s for 3 h. The resulting HOF/CH₃CN solution was then purged with He for 15 min. The 2-bromo-4-nitro-5-ethynylphenylaniline (21) (0.90 g, 2.86 mmol) was then added in EtOAc (20 mL) and mixed at −20 °C for 2 min before being neutralized by pouring into a saturated NaHCO₃ solution. The reaction afforded 0.81 g (81% yield) of the title compound as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1 H), 8.13 (s, 1 H), 7.61 (m, 2 H), 7.44 (m, 3 H).

![Chemical structure of the compound](image)

4-(2,5-Dinitro-4-phenylethynyl-phenylethynyl)-pyridine (23). To a solution of 4-(phenylethynyl)-2,5-dinitrobromobenzene (22) (0.297 g, 0.856 mmol),
bis(dibenzylideneacetone)palladium(0) (0.017 g, 0.030 mmol), triphenylarsine (0.021 g, 0.069 mmol) in THF (10 mL) was added 4-tributylstannylthienyl-pyridine (20) (0.353 g, 0.901 mmol) via a cannula. The mixture was stirred at 65 °C for 2 d. The solvent was evaporated in vacuo. The residue was diluted with a saturated solution of NH₂Cl and extracted with EtOAc. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/hexane 1/1) afforded 95 mg (30% yield) of the title compound as a yellow solid. Mp: 300 °C (browning). IR (KBr) 3421.4, 2203.6, 1590.6, 1547.9, 1340.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.71 (br s, 2 H), 8.41 (s, 1 H), 8.41 (s, 1 H), 7.64 (m, 2 H), 7.49 (d, J= 5.8 Hz, 2 H), 7.43 (m, 5 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.9, 150.0, 132.4, 130.9, 130.7, 129.4, 128.7, 125.7, 121.1, 120.0, 117.1, 102.8, 97.4, 86.5, 83.1. HRMS calc’d for C₂₁H₁₁N₃O₄: 369.0750, found: 369.0751.

**2-Bromo-4-nitro-5-phenyl-1-acetanilide (24).** To a mixture of 2,5-dibromo-4-nitroacetanilide (8) (0.79 g, 2.34 mmol), phenyl boronic acid (0.402 g, 3.3 mmol), bis(dibenzylideneacetone)palladium(0) (0.068 g, 0.12 mmol), cesium carbonate (1.16 g, 3.55 mmol) and triphenylphosphine (0.062 g, 0.24 mmol) was added toluene (7 mL). The mixture was stirred at 67 °C for 3 d. The toluene was removed by distillation (bp: 110 °C). The residue was diluted with water and extracted with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered, and the solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexane/CH₂Cl₂ 1/1) afforded 400 mg
(51% yield) of the title compound as a white solid. IR (KBr) 3373.6, 3322.4, 3086.5, 1774.0, 1681.7, 1568.9, 1528.8, 1445.8, 1389.4, 1358.6, 1245.8, 1179.1, 1112.5, 1056.1, 1030.4, 999.6, 872.0, 850.9, 768.9, 697.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1 H), 8.15 (s, 1 H), 7.80 (br s, 1 H), 7.40-7.38 (m, 3 H), 7.29-7.27 (m, 2 H) 2.26 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 143.8, 139.3, 137.7, 136.8, 128.7, 128.5, 128.5, 127.9, 123.3, 110.6, 25.1. HRMS calc’d for C₁₄H₁₁BrN₂O₃: 333.9953, found: 333.9952.

![Chemical structure image]

6-Nitro-4-pyridin-4-ylethynyl-biphenyl-3-ylamine (25). See the general in-situ deprotection and coupling procedure. To a solution of 24 (80.5 mg, 0.241 mmol), K₂CO₃ (0.151 g, 1.09 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.009 g, 0.014 mmol), copper(I) iodide (0.003 g, 0.014 mmol) and triphenylphosphine (0.014 g, 0.053 mmol) in THF (2 mL) were added via cannula 3 (0.053 g, 0.3 mmol) in THF (2 mL) and MeOH (1 mL). The mixture was heated to 70 °C for 3 d. Purification by flash chromatography (silica gel, EtOAc/hexane 30/70) afforded 60 mg (79% yield) of the title compound as a yellow solid. Mp: 187-190 °C. IR (KBr) 3410.2, 3323.4, 3212.1, 2215.1, 1627.6, 1592.4, 1548.4, 1511.7, 1410.5, 1331.9 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.64 (br d, J=4.8, 2 H), 8.16 (s, 1 H), 7.39 (m, 5 H), 7.27 (m, 2 H), 6.62 (s, 1 H), 5.03 (br s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 149.8, 140.6, 138.8, 138.2, 130.5, 128.4, 128.1, 127.5, 125.3, 116.4, 104.9, 93.2, 87.9. HRMS calc’d for C₁₉H₁₃N₃O₂: 315.1008, found: 315.1011. Anal. Calc’d for C₁₉H₁₃N₃O₂: C, 72.37; H, 4.16; N, 13.33; Found: C, 71.69; H, 4.13; N, 13.08.
Tributyl-phenyl-stannane\(^{61}\) (26). In a 100 mL round bottom flask was added bromobenzene (1.329 g, 8.465 mmol) in THF (15 mL). The reaction was cooled to \(-78^\circ\)C and \(n\)-BuLi (5.9 mL, 8.97 mmol) was slowly added. The mixture was stirred at \(-78^\circ\)C for 30 min. Tributyltin chloride (1.26 mL, 4.65 mmol) was added and the reaction mixture was allowed to warm up to RT. The solution was diluted with water and extracted with Et\(_2\)O. The combined organic phases were dried over MgSO\(_4\), filtered, and the solvent evaporated \textit{in vacuo}. Purification by flash chromatography (silica gel, hexane) afforded 2.01 g (65% yield) of the title compound as a clear liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \delta 7.47 (m, 2 H), 7.32 (m, 3 H), 1.55 (m, 6 H), 1.33 (sex, \(J=7.3\) Hz, 6 H), 1.04 (m, 6 H), 0.89 (t, \(J=7.3\) Hz, 9 H).

4-Bromo-6-nitro-biphenyl-3-ylamine\(^{62}\) (27). To a solution of 2,5-dibromo-4-nitroaniline (9) (1.73 g, 5.848 mmol), bis(dibenzylideneacetone)palladium(0) (0.124 g, 0.215 mmol), triphenylarsine (0.131 g, 0.428 mmol) in THF (20 mL) was added tributylphenyl-stannane (26) (1.96 g, 5.35 mmol) via a cannula. The mixture was stirred at 80 \(^\circ\)C for 20 h. The solvent was evaporated \textit{in vacuo}. The residue was diluted with a saturated solution of NH\(_4\)Cl and extracted with Et\(_2\)O. The combined organic phases were dried over MgSO\(_4\), filtered, and the solvent evaporated \textit{in vacuo}. Purification by flash chromatography (silica gel, CH\(_2\)Cl\(_2\)) afforded 1.40 g (89% yield) of the title compound as
a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (s, 1 H), 7.39 (m, 3 H), 7.26 (m, 2 H), 6.63 (s, 1 H), 4.72 (br s, 2 H).

**6-Nitro-4-trimethylsilylethynyl-biphenyl-3-ylamine (28).** See the general Pd/Cu procedure. To a solution of 2-bromo-4-nitro-5-phenyl-1-aniline (27) (1.40 g, 4.780 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.168 g, 0.239 mmol), copper(I) iodide (0.046 g, 0.239 mmol) in THF (15 mL) were added Et$_3$N (4 mL) and trimethylsilylacetylene (0.72 mL, 5.06 mmol). The mixture was stirred at 60 °C for 36 h. Purification by flash chromatography (silica gel, hexane/CH$_2$Cl$_2$ 20/80) afforded 1.05 g (71% yield) of the title compound as a yellow solid. Mp: 184-193 °C. IR (KBr) 3491.1, 3390.6, 2955.5, 2152.0, 1622.1, 1541.6, 1497.2, 1308.6, 1256.5 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (s, 1 H), 7.39 (m, 3 H), 7.27 (m, 2 H), 6.57 (s, 1 H), 4.83 (br s, 2 H), 0.30 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.2, 140.0, 138.6, 138.4, 130.3 128.4, 128.0, 127.6, 116.0, 106.3, 102.4, 98.8, -0.1. HRMS calc’d for C$_{17}$H$_{18}$N$_2$O$_2$Si: 310.1138, found: 310.1144.

**4-Ethynyl-6-nitro-biphenyl-3-ylamine (29).** See the general TMS-protected alkyne deprotection procedure. To a solution of 6-nitro-4-trimethylsilylethynyl-biphenyl-3-ylamine (28) (1.05 g, 3.386 mmol) in MeOH (30 mL) and CH$_2$Cl$_2$ (30 mL)
was added \( \text{K}_2\text{CO}_3 \) (4.68 g, 33.86 mmol). The solution was stirred at 23 °C for 4 h. The reaction afforded 0.77 g (96% yield) of the title compound as a yellow solid, which was too unstable to attain its complete characterization data. \(^1\text{H NMR (400 MHz, CDCl}_3\) \( \delta \)

\[
8.13 \text{ (s, 1 H), 7.40 (m, 3 H), 7.26 (m, 2 H), 6.58 (s, 1 H), 5.31 (br s, 2 H), 3.49 (s, 1 H).}
\]

6-Nitro-4-pyridin-4-ylethylnyl-biphenyl-3-ylamine (25). See the general Pd/Cu procedure. To a solution of 4-ethynyl-6-nitro-biphenyl-3-ylamine (29) (0.77 g, 3.235 mmol), 4-iodopyridine (0.695 g, 3.392 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.115 g, 0.165 mmol), copper(I) iodide (0.036 g, 0.189 mmol) in THF (10 mL) was added \( \text{Et}_3\text{N} \) (5 mL). The mixture was stirred at 55 °C for 2 d. Purification by flash chromatography (silica gel, EtOAc) afforded 0.77 g (76% yield) of the title compound as a yellow solid. \(^1\text{H NMR (400 MHz, DMSO-\text{d}_6) \delta}\)

\[
8.64 \text{ (br s, 2 H), 8.13 (s, 1 H), 7.67 (d, } J=5.8 \text{ Hz, 2 H), 7.40 (m, 3 H), 7.28 (m, 2 H), 7.02 \text{ (br s, 2 H), 6.65 (s, 1 H).}
\]

4-Iodo-2-nitroaniline\(^{51}\) (30). To a stirred solution of \( \alpha \)-nitroaniline (13.85 g, 100.4 mmol) in glacial acetic acid (50 mL) containing anhydrous sodium acetate (9.31 g, 0.113 mmol), iodine monochloride (6.4 mL, 0.125 mmol) in acetic acid (30 mL) was added over 30 min under air. The reaction mixture was heated on the water bath (80 °C) for 30 min, stirred for another 30 min at RT, then diluted slowly with water (100 mL)
which caused the separation of the red-brown crystalline product. Stirring was continued for 1 h and after 16 h the product was washed free of acetic acid and dried in air. Upon crystallization from ethanol (120 mL) and water (25 mL), 4-iodo-2-nitroaniline (15 g, 56% yield) was obtained as small cinnamon colored crystals. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$=2.0 Hz, 1 H), 7.58 (dd, $J$=2.1, 8.8 Hz, 1 H), 6.61 (d, $J$=8.8 Hz, 1 H), 6.10 (br s, 2 H).

![2-Nitro-4-trimethylsilanylethynyl-phenylamine](image)

**2-Nitro-4-trimethylsilanylethynyl-phenylamine**$^{58}$ (31). See the general Pd/Cu procedure. To a solution of 4-iodo-2-nitroaniline (30) (19.57 g, 74.16 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.04 g, 1.483 mmol), copper(I) iodide (1.13 g, 5.93 mmol) in THF (200 mL) were added Et$_3$N (50 mL) and trimethylsilylacetylene (12.1 mL, 85.28 mmol). The mixture was stirred at RT for 48 h. Purification by flash chromatography (silica gel, hexane/EtOAc 80/20) afforded 16.75 g (96% yield) of the title compound as a yellow crystals. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (d, $J$=1.9 Hz, 1 H), 7.42 (dd, $J$=8.6 Hz, 1.9 Hz, 1 H), 6.74 (d, $J$=8.6 Hz, 1 H), 6.20 (br s, 2 H), 0.24 (s, 9 H).

![4-Ethynyl-2-nitro-phenylamine](image)

**4-Ethynyl-2-nitro-phenylamine** (32). See the general TMS-protected alkyne deprotection procedure. To a solution of 2-nitro-4-trimethylsilanylethynyl-phenylamine (31) (8.17 g, 34.86 mmol) in MeOH (100 mL) and CH$_2$Cl$_2$ (100 mL) was added K$_2$CO$_3$ (24.09 g, 174.3 mmol). The solution was stirred at 23 °C for 20 h. The procedure
afforded 3.64 g (64% yield) of the title compound as bright orange crystals. Mp: 115-120 °C. IR (KBr) 3495.3, 3378.6, 3259.8, 1630.4, 1584.4, 1551.0, 1515.1, 1464.4, 1413.1, 1362.7, 1281.4, 1256.3, 1199.6, 1163.3 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J=1.9 Hz, 1 H), 7.42 (dd, J=8.6 Hz, 1.9 Hz, 1 H), 6.77 (d, J=8.6 Hz, 1 H), 6.25 (br s, 2 H), 3.01 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 138.7, 131.7, 130.4, 119.1, 110.9, 82.0, 76.7. HRMS calc’d for C₈H₆N₂O₂: 162.0429, found: 162.0427.

2-Nitro-4-pentafluorophenylethynyl-phenylamine (33). See the general Pd/Cu procedure. To a solution of 4-ethyl-2-nitro-phenylamine (32) (3.64 g, 22.49 mmol), bis(triphenylphosphine)palladium(II) dichloride (631 mg, 0.900 mmol), copper(I) iodide (343 mg, 1.80 mmol) in THF (55 mL) were added Et₃N (15 mL) and pentafluorobenzene (2.94 mL, 23.57 mmol). The mixture was stirred at 80 °C for 20 h. The hot reaction mixture was diluted with EtOAc, then filtered over a plug a silica and all the solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc) afforded 8.42 mg (11% yield) of the title compound as an orange solid. Mp: 196-200 °C. IR (KBr) 3582.7, 3472.6, 3347.2, 3092.1, 2262.1, 1630.7, 1555.7, 1523.9, 1501.4, 1416.3, 1348.9, 1283.9, 1255.4 cm⁻¹. ¹H NMR (400 MHz, CD₂CN) δ 8.25 (d, J=2.0 Hz, 1 H), 7.49 (dd, J=8.8, 2.0 Hz, 1 H), 6.98 (d, J=8.8 Hz, 1 H), 6.85 (br s, 2 H) ¹³C NMR (100 MHz, CD₂CN) δ 147.8, 139.0, 132.4, 131.2, 121.0, 120.9, 109.5, 101.4. HRMS calc’d for C₁₄H₇F₅N₂O₂: 328.0271, found: 328.0272.
(34). To BF₃·Et₂O (1.52 mL, 12.09 mmol), cooled to -30 °C was added a solution of 33 (0.992 g, 3.022 mmol) in THF (20 mL). The yellow suspension was stirred for 20 min after which a solution of isoamyl nitrite (1.42 mL, 10.58 mmol) in THF (10 mL) was added. The reaction mixture was stirred for 20 min at -30 °C then warmed to -5 °C. The diazonium salt was precipitated by ether and filtered. The precipitate was washed with ether. The solid was then dissolved in a minimum amount of dry acetonitrile (20 mL) and NaI (766 mg, 6.044 mmol) and iodine (453 mg, 3.022 mmol) were added. After stirring for a 5 min, a sat. solution of sodium thiosulfate was added and the mixture extracted with Et₂O. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. The reaction afforded 100 mg (7% yield) of the title compound as a yellow solid. Mp: 130-135 °C. IR (KBr) 3440.8, 3092.7, 1543.6, 1530.1, 1518.4, 1501.3, 1442.9, 1356.9, 1262.6, 1113.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J=8.1 Hz, 1 H), 8.03 (d, J=1.9 Hz, 1 H), 7.43 (dd, J=8.1, 1.9 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 142.5, 139.2, 135.9, 128.4, 123.2, 97.8, 87.8. HRMS calc’d for C₁₄H₃F₃INO₂: 438.9129, found: 438.9120.

4-(2-Nitro-4-pentafluorophenylethynyl-phenylethynyl)-pyridine (35). See the general Pd/Cu procedure. To a solution in the dark of 34 (230 mg, 0.525 mmol), bis(triphenylphosphine)palladium(II) dichloride (25 mg, 0.036 mmol), copper(I) iodide
(18 mg, 0.095 mmol) and 4-ethynylpyridine (4) (70 mg, 0.680 mmol) in THF (30 mL) was added Et$_3$N (15 mL). The mixture was stirred at 65 °C for 16 h. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (silica gel, CH$_2$Cl$_2$/Et$_2$O 80/20). The reaction afforded 120 mg (55% yield) of the title compound as a yellow fluffy solid. Mp: 176-178 °C. IR (KBr) 3431.3, 3089.4, 2227.4, 1588.8, 1546.5, 1520.9, 1498.3, 1443.7, 1408.1, 1346.4, 1260.3, 1214.8, 1120.2 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (br s, 2 H), 8.31 (d, J=1.5 Hz, 1 H), 7.81 (dd, J=8.1, 1.5 Hz, 1 H), 7.76 (d, J=8.1 Hz, 1 H), 7.45 (d, J=5.7 Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.2, 149.9, 135.8, 135.2, 130.3, 128.2, 125.8, 123.4, 118.5, 97.1, 96.3, 88.4. HRMS calc’d for C$_{21}$H$_7$F$_5$N$_2$O$_2$: 414.0423, found: 414.0467. Anal. Calc’d for C$_{21}$H$_7$F$_5$N$_2$O$_2$: C, 60.88; H, 1.70; N, 6.76; Found: C, 60.81; H, 1.59; N, 6.72.

![Chemical structure](image)

2,5-Bis(4'-ethynylpyridyl)-1-nitrobenzene (36). See the general in-situ deprotection and coupling procedure. To a solution of 2,5-dibromonitrobenzene 5 (0.28 g, 0.997 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.07 g, 0.098 mmol), copper(I) iodide (0.019 g, 0.098 mmol), triphenylphosphine (0.106 g, 0.40 mmol) and K$_2$CO$_3$ (1.1 g, 7.96 mmol) in THF (4 mL) were added via a cannula 3 (0.377 g, 2.15 mmol) in THF (4 mL) and MeOH (2 mL). The mixture was heated at 64 °C for 20 h. Purification by flash chromatography (silica gel, EtOAc) afforded 60 mg (24% yield) of the title compound as a yellow fluffy solid. Mp: 184-186 °C. IR (KBr) 3414.0, 3036.7, 1616.0, 1589.4, 1538.1, 1519.9, 1407.9, 1345.7, 1271.1, 1214.1, 828.3 cm$^{-1}$. $^1$H NMR
(400 MHz, CDCl₃) δ 8.67 (m, 4 H), 8.30 (d, J=1.3 Hz, 1 H), 7.79 (1/2 ABqd, J=8.0, 1.4 Hz, 1 H), 7.76 (1/2 ABq, J=8.0 Hz, 1 H), 7.46 (m, 2 H), 7.42 (m, 2 H). ¹³C NMR (100 MHz, DMSO-d₆) δ 150.2, 150.1, 149.4, 136.3, 135.4, 129.2, 129.1, 128.0, 125.5, 125.4, 123.3, 116.6, 95.0, 90.6, 90.6, 88.1. HRMS calc’d for C₂₀H₁₁N₃O₂: 325.0851, found: 325.0847.

[N-(4-Nitro-2,5-bis-trimethylsilanylylnylethynyl-phenyl)-acetamide (37)] See the general Pd/Cu procedure. To a solution of 2,5-dibromo-4-nitroacetanilide (8) (0.78 g, 2.3 mmol), bis(dibenzylideneacetone)palladium(0) (0.068 g, 0.118 mmol), copper(I) iodide (0.023 g, 0.012 mmol), triphenylphosphine (0.123 g, 0.47 mmol) in THF (8 mL) were added Et₃N (1 mL, 7.2 mmol) and trimethylsilylacetylene (1 mL, 7.0 mmol). The mixture was heated at 67 °C for 48 h. Purification by flash chromatography (silica gel, CH₂Cl₂/hexane 35/65) afforded 410 mg (47% yield) of the title compound as an off-white solid. Mp: 162-164 °C. IR (KBr) 3372.9, 2962.9, 2146.0, 1727.2, 1611.2, 1544.9, 1501.5, 1457.1, 1404.3, 1338.2, 1250.6, 1222.3, 881.9 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 1 H), 8.15 (s, 1 H), 8.10 (br s, 1 H), 2.27 (s, 3 H), 0.33 (s, 9 H), 0.28 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 144.2, 142.4, 128.1, 123.8, 120.2, 111.5, 106.7, 106.2, 99.5, 97.4, 24.9, -0.3, -0.5. HRMS calc’d for C₁₈H₂₄N₂O₃Si₂: 372.1326, found: 372.1326.
4-Nitro-2,5-bis-pyridin-4-ylethynyl-phenylamine (38) See the general in-situ deprotection and coupling procedure. To a solution of 37 (0.056 g, 0.15 mmol), 4-iodopyridine (0.08 g, 0.39 mmol), K$_2$CO$_3$ (0.17 g, 1.2 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.01 g, 0.015 mmol), copper(I) iodide (0.004 g, 0.021 mmol) and triphenylphosphine (0.016 g, 0.061 mmol) in THF (4 mL) was added MeOH (1 mL). The mixture was heated at 60 °C for 50 h. Purification by flash chromatography (silica gel, EtOAc) afforded 8 mg (16% yield) of the title compound as a yellow solid. Mp: 154-160 °C. IR (KBr) 3730.2, 3438.6, 2204.8, 1592.4, 1541.1, 1409.8, 1308.5, 1249.9, 818.8 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.67 (dd, $J$=4.4, 1.7 Hz, 2 H), 8.65 (dd, $J$= 4.5, 1.7 Hz, 2 H), 8.34 (s, 1 H), 7.44 (dd, $J$=4.5, 1.7 Hz, 2 H), 7.40 (dd, $J$=4.4, 1.6 Hz, 2 H), 6.99 (s, 1 H), 5.03 (br s, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.3, 150.0, 149.9, 139.6, 130.7, 130.5, 130.0, 125.7, 125.3, 120.3, 118.5, 106.5, 94.7, 94.2, 89.6, 87.3. HRMS calc’d for C$_{20}$H$_{12}$N$_4$O$_2$: 340.0960, found: 340.0958.

(4-Bromo-2-nitro-phenylethynyl)-triisopropyl-silane (40). See the general Pd/Cu procedure. To a solution of 2,5-dibromonitrobenzene (5) (3.012 g, 10.72 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.377 g, 0.537 mmol), copper(I) iodide (0.103 g, 0.541 mmol) in THF (5 mL) were added Et$_3$N (15 mL) and triisopropylsilylacetylene (2.6 mL, 11.59 mmol). The mixture was stirred at 50 °C for 1
d. Purification by flash chromatography (silica gel, hexane/Et$_2$O 95/5) afforded 2.05 g (50% yield) of the title compound as a yellow oil. Mp: 39-48 °C. IR (NaCl) 3091.5, 2942.3, 2863.7, 2161.8, 1530.2, 1466.3, 1342.8, 1252.3, 1216.1, 1091.9 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, J=2.0 Hz, 1 H), 7.68 (dd, J=8.3, 2.0 Hz, 1 H), 7.53 (d, J=8.3 Hz, 1 H), 1.15 (s, 21 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.3, 136.4, 135.7, 127.6, 122.0, 117.6, 102.7, 100.1, 18.6, 11.2 ppm. HRMS calc'd for C$_{17}$H$_{25}$BrNO$_2$Si: 384.0820, found: 384.0821.

![2-Nitro-1-[(triisopropylsilanyl)-ethynyl]-4-trimethylsilanylethynyl-benzene](image)

2-Nitro-1-[(triisopropylsilanyl)-ethynyl]-4-trimethylsilanylethynyl-benzene (41). See the general Pd/Cu procedure. To a solution of (4-bromo-2-nitrophenylethynyl)-triisopropyl-silane 40 (2.43 g, 6.36 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.225 g, 0.321 mmol), copper(I) iodide (0.063 g, 0.329 mmol) in THF (10 mL) were added Et$_3$N (5.3 mL, 38.10 mmol) and trimethylsilylacetylene (1.0 mL, 7.03 mmol). The mixture was stirred at 50 °C overnight. Purification by flash chromatography (silica gel, hexane/Et$_2$O 98/2) afforded 1.98 g (78% yield) of the title compound as a yellow oil. IR (NaCl) 2944.0, 2892.0, 2865.8, 2163.7, 1544.5, 1526.7, 1488.1, 1463.3, 1348.9, 1250.8, 1213.1 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 (t, J=1 Hz, 1 H), 7.58 (d, J=1 Hz, 2 H), 1.15 (s, 21 H), 0.27 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.8, 135.3, 135.2, 127.7, 124.0, 118.2, 103.0, 101.9, 100.8, 99.4 ppm. HRMS calc'd for C$_{22}$H$_{33}$NO$_2$Si$_2$: 399.2050, found: 399.2046.
(4-Ethynyl-2-nitro-phenylethynyl)-triisopropyl-silane (42). See the general TMS-protected alkyne deprotection procedure. To a solution of 2-nitro-1-[(triisopropylsilanyl)-ethynyl]-4-trimethylsilylethynyl-benzene 41 (1.73 g, 4.33 mmol) in MeOH (20 mL) and CH₂Cl₂ (20 mL) was added K₂CO₃ (5.99 g, 43.33 mmol). The solution was stirred at 23 °C for 20 min. The reaction afforded 1.37 g (97% yield) of the title compound as a light black oil that was too unstable to attain its complete characterization data. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1 H), 7.62 (d, J=0.9 Hz, 2 H), 3.29 (s, 1 H), 1.15 (s, 21 H).

4-{3-Nitro-4-[triisopropylsilanyl]-ethyl}-phenylethynyl]-pyridine (43). See the general Pd/Cu procedure. To a solution of (4-ethynyl-2-nitro-phenylethynyl)-triisopropyl-silane (42) (1.37 g, 4.189 mmol), 4-iodopyridine (0.914 g, 4.46 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.147 g, 0.210 mmol), copper(I) iodide (0.044 g, 0.228 mmol) in THF (15 mL) was added Et₃N (3.5 mL, 25.13 mmol). The mixture was stirred at 46 °C for 36 h. Purification by flash chromatography (silica gel, hexane/EtOAc 1/1) afforded 1.26 g (74% yield) of the title compound as a white solid. The compound was not pure enough to perform its full characterization. ¹H NMR (400 MHz, CDCl₃) δ 8.66 (dd, J=4.4, 1.6 Hz, 2 H), 8.20 (s, 1 H), 7.68 (m, 2 H), 7.43 (dd, J=4.4, 1.6 Hz, 2 H), 1.16 (s, 21 H).
4-(4-Bromo-2-nitro-phenyl)-2-methyl-but-3-yn-2-ol (44). See the general Pd/Cu procedure. To a solution of 2,5-dibromonitrobenzene (5) (3.395 g, 12.085 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.347 g, 0.495 mmol), copper(I) iodide (0.095 g, 0.499 mmol) in THF (20 mL) were added Et₃N (20 mL) and 2-methyl-3-butyln-2-ol (1.4 mL, 14.31 mmol). The mixture was stirred at 23 °C for 2 d. Purification by flash chromatography (silica gel, CH₂Cl₂) afforded 1.85 g (54% yield) of the title compound as a brown oil. Mp: 49-52 °C. IR (KBr) 3324.2, 3087.2, 2978.1, 2931.8, 2233.5, 1550.1, 1524.0, 1474.1, 1338.1, 1262.0, 1154.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J=2.0 Hz, 1 H), 7.69 (1/2 ABqdd, J=8.3, 2.0, 0.4, 1 H), 7.46 (d, J=8.3 Hz, 1 H), 1.64 (s, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 135.9, 135.5, 127.7, 123.0, 122.1, 117.9, 117.1, 102.9, 91.1, 65.8, 31.0. HRMS calc’d for C₁₁H₁₀BrNO₃:292.9844, found: 282.9846.

2-Methyl-4-(2-nitro-4-trimethylsilyl-ethynyl-phenyl)-but-3-yn-2-ol (45). See the general Pd/Cu procedure. To a solution of 4-(4-bromo-2-nitro-phenyl)-2-methyl-but-3-yn-2-ol (44) (4.02 g, 14.159 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.337 g, 0.481 mmol), copper(I) iodide (0.108 g, 0.567 mmol) in THF (35 mL) were added Et₃N (14 mL) and trimethylsilylacetylene (2.42 mL, 17.02 mmol). The mixture was stirred at 55 °C for 2 d. Purification by flash chromatography (silica gel, CH₂Cl₂/Et₂O 90/10) afforded 1.91 g (45% yield) of the title compound as a brown solid. Mp: 80-82 °C. IR (KBr) 3536.4, 3084.8, 2978.3, 2930.2, 2231.8, 2168.21, 1541.6,
1519.6, 1345.7, 1263.7, 1249.0, 1166.8 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J=1.4 Hz, 1 H), 7.60 (1/2 ABq, J=4.1, 1.7 Hz, 1 H), 7.52 (d, J=8.1 Hz, 1 H), 1.65 (s, 6 H), 0.27 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 135.5, 134.4, 127.8, 124.1, 117.6, 103.3, 101.8, 99.5, 31.0, -0.3 ppm. HRMS calc’d for C₁₁H₁₉NO₃Si: 303.1134, found: 301.1135.

4-(4-Ethynyl-2-nitro-phenyl)-2-methyl-but-3-yn-2-ol (46). See the general TMS-protected deprotection procedure. To a solution of 2-methyl-4-(2-nitro-4-trimethylsilanylethynyl-phenyl)-but-3-yn-2-ol (45) (1.91 g, 6.34 mmol) in MeOH (40 mL) and CH₂Cl₂ (40 mL) was added K₂CO₃ (8.77 g, 63.4 mmol). The solution was stirred at 23 °C for 2 h. The reaction afforded 1.41 g (97% yield) of the title compound as a dark brown solid. That was too unstable to attain its complete characterization data. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J=1.6 Hz, 1 H), 7.63 (1/2 ABq, J=8.1, 1.7 Hz, 1 H), 7.55 (1/2 ABq, J=8.1 Hz, 1 H), 3.29 (s, 1 H), 1.65 (s, 6 H).

2-Methyl-4-(2-nitro-4-pyridin-4-yethynyl-phenyl)-but-3-yn-2-ol (47). See the general Pd/Cu procedure. To a solution of 4-(4-ethynyl-2-nitro-phenyl)-2-methyl-but-3-yn-2-ol (46) (1.38 g, 6.026 mmol), 4-iodopyridine (1.381 g, 6.736 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.127 g, 0.181 mmol), copper(I) iodide (0.035 g, 0.184 mmol) in THF (25 mL) was added Et₃N (10 mL). The mixture was stirred
at 60 °C for 4 h. Purification by flash chromatography (silica gel, EtOAc) afforded 1.26 g (68% yield) of the title compound as a brown solid. Mp: 140-146 °C. IR (KBr)
3170.1, 2977.9, 2929.2, 2855.8, 2216.7, 1595.2, 1541.4, 1406.4, 1342.4, 1262.2, 1171.2
\text{cm}^{-1}. \text{^1H NMR (400 MHz, CDCl}_3) \delta 8.66 \text{ (dd, } J=4.5, 1.4 \text{ Hz, } 2 \text{ H)}, 8.20 \text{ (d, } J=1.6 \text{ Hz, } 1 \text{ H)}, 7.70 \text{ (1/2 ABqd, } J=8.1, 1.7 \text{ Hz, } 1 \text{ H)}, 7.60 \text{ (1/2 ABd, } J=8.1 \text{ Hz, } 1 \text{ H)}, 7.40 \text{ (dd, } J=4.4, 1.6 \text{ Hz, } 2 \text{ H)}, 1.66 \text{ (s, } 6 \text{ H}). \text{^13C NMR (100 MHz, CDCl}_3) \delta 149.7, 135.3, 134.7, 130.3, 127.7, 125.5, 122.8, 118.6, 104.4, 90.8, 90.1, 65.5, 31.0 \text{ ppm. HRMS calc'd for}
C_{13}H_{14}N_2O_3: 306.1004, \text{ found: } 306.1007.

2-Nitro-4-pyridin-4-ylyethyl-phenylamine (48). See the general Pd/Cu
procedure. To a solution of 4-iodo-2-nitroaniline (30) (1.422 g, 5.388 mmol), 4-
eynlypyridine (4) (0.56 g, 5.437 mmol), bis(triphenylphosphine)palladium(II)
dichloride (0.114 g, 0.163 mmol), copper(I) iodide (0.035 g, 0.184 mmol) in THF (20
mL) was added Et\textsubscript{3}N (8 mL). The mixture was stirred at 23 °C overnight and then at 45
°C for 20 h. The solvent was evaporated \textit{in vacuo}. The residue was diluted with a
saturated solution of NH\textsubscript{4}Cl and extracted with EtOAc. The combined organic phases
were dried over MgSO\textsubscript{4}, filtered, and the solvent evaporated \textit{in vacuo}. Purification by
flash chromatography (silica gel, hexane/AcOEt 1/1) afforded 0.84 g (65% yield) of the
title compound as a red-orange solid. Mp: 216-220 °C. IR (KBr) 3395.3, 3299.7,
3201.9, 2208.6, 1640.7, 1590.9, 1553.9, 1349.3 \text{ cm}^{-1}. \text{^1H NMR (400 MHz, CDCl}_3) \delta
8.61 \text{ (d, } J=6.0 \text{ Hz, } 2 \text{ H)}, 8.38 \text{ (d, } J=1.9 \text{ Hz, } 1 \text{ H)}, 7.51 \text{ (dd, } J=8.6, 2.0 \text{ Hz, } 1 \text{ H)}, 7.39 \text{ (dd,
$J$=4.5, 1.6 Hz, 2 H), 6.83 (d, $J$=8.7, 1 H), 6.33 (br s, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
149.6, 144.8, 138.2, 131.7, 131.4, 130.3, 125.4, 119.0, 110.6, 92.5, 86.0. HRMS calc’d for C$_{13}$H$_9$N$_3$O$_2$: 239.0695, found: 239.0695.

![4-(4-Iodo-3-nitro-phenylethynyl)-pyridine](image)

4-(4-Iodo-3-nitro-phenylethynyl)-pyridine (49). A solution of 2-nitro-4-pyridin-4-ylethynyl-phenylamine (48) (0.742 g, 3.105 mmol) and fluoboric acid 51% (11 mL, 88.32 mmol) was cooled down to −40 °C in an atmosphere of air. Sodium nitrite (0.262 g, 3.798 mmol) was then added slowly. The mixture was stirred at −30 °C for 30 min. A solution of sodium iodide (1.41 g, 9.4 mmol) and iodine (0.79 g, 3.11 mmol) in water (30 mL) was then added portionwise to the pyridine solution. The excess iodine was neutralized by adding dropwise a saturated solution of sodium bisulfite until the black solution turned yellow-brown. The pH was carefully adjusted to 10 with a saturated solution of K$_2$CO$_3$. The aqueous phase was separated and extracted with AcOEt. The combined organic phases were dried over MgSO$_4$, filtered and the solvent was removed in vacuo. The procedure afforded 1.02 g (94% yield) of the title compound as a red solid. Mp: 194-196 °C. IR (KBr) 3437.9, 2209.4, 1588.9, 1524.0, 1461.5, 1354.3 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (br s, 2 H), 8.05 (d, $J$=8.2 Hz, 1 H), 8.0 (s, 1 H), 7.40 (m, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.0, 149.8, 142.1, 135.7, 130.1, 128.2, 125.6, 123.6, 90.2, 90.0, 87.0. HRMS calc’d for C$_{13}$H$_7$IN$_2$O$_2$: 349.9552, found: 349.9549.
4-(3-Nitro-4-trimethylsilanylethynyl-phenylethynyl)-pyridine (50). See the general Pd/Cu procedure. To a solution of 4-(4-iodo-3-nitro-phenylethynyl)-pyridine (49) (1.00 g, 2.86 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.100 g, 0.143 mmol), copper(I) iodide (0.030 g, 0.158 mmol) in THF (20 mL) were added Et<sub>3</sub>N (10 mL) and trimethylsilylacetylene (0.49 mL, 3.447 mmol). The mixture was stirred at 23 °C overnight then at 45 °C for 2 h. Purification by flash chromatography (silica gel, hexane/EtOAc 1/1) afforded 0.609 g (67% yield) of the title compound as a brown solid. Mp: 80-83 °C. IR (KBr) 3434.9, 3078.5, 2958.5, 2151.5, 1590.2, 1543.6, 1522.7, 1350.5, 1248.1 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CdCl<sub>3</sub>) δ 8.67 (br s, 2 H), 8.17 (d, J=1.1 Hz, 1 H), 7.69 (1/2 AB<sub>qt</sub>, J=8.1, 0.8 Hz, 1 H), 7.65 (1/2 AB<sub>q</sub>, J= 8.1 Hz, 1 H), 7.40 (d, J=4.3 Hz, 2 H), 0.29 (s, 9 H). <sup>13</sup>C NMR (100 MHz, CdCl<sub>3</sub>) δ 150.0, 149.8, 135.2, 135.2, 130.2, 127.6, 125.5, 123.0, 118.6, 106.6, 98.8, 90.7, 90.3, -0.5. HRMS calc’d for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Si: 320.0981, found: 320.0985.

4-(4-Ethynyl-3-nitro-phenylethynyl)-pyridine (51). See the general TMS-protected alkyne deprotection procedure. To a solution of 4-(3-nitro-4-trimethylsilanylethynyl-phenylethynyl)-pyridine (50) (0.609 g, 1.903 mmol) in MeOH (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added K<sub>2</sub>CO<sub>3</sub> (2.63 g, 19.03 mmol). The solution was stirred at 23 °C for 2.5 h. The reaction afforded 0.47 g (100% yield) of the title compound as a light brown solid, that was too unstable to attain its complete
characterization data. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.68 (d, J=4.3 Hz, 2 H), 8.23 (d, J=0.9 Hz, 1 H), 7.73 (m, 2 H), 7.46 (d, J=4.6 Hz, 2 H), 3.67 (s, 1 H).

\[
\begin{align*}
\text{Thioacetic acid S-[4-(2-nitro-4-pyridin-4-ylethynyl-phenylethynyl)-phenyl] ester (39). See the general Pd/Cu procedure. To a solution of 4-(4-ethynyl-3-nitro-phenylethynyl)-pyridine (51) (0.47 g, 1.895 mmol), 4-thioacetyliodobenzene (0.580 g, 2.087 mmol), bis(dibenzylideneacetone)palladium(0) (0.218 g, 0.379 mmol), copper(I) iodide (0.072 g, 0.379 mmol) in THF (20 mL) was added diisopropylethylamine (1.32 mL, 7.58 mmol). The mixture was stirred at 48 °C for 2 d. Two purifications by flash chromatography were done first with EtOAc, then with EtOAc/hexane 1/1. The residue was dissolved in CH$_2$Cl$_2$ (5 mL) and MeOH (8 mL), and CH$_2$Cl$_2$ was evaporated. After The solid precipitated and was filtered, affording 50 mg (7% yield) of the title compound as a yellow solid. Mp: 156-160 °C. IR (KBr) 3444.0, 2207.9, 1694.6, 1633.0, 1590.2, 1522.8, 1347.9 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (d, J= 4.3 Hz, 2 H), 8.7 (d, J=1.5 Hz, 1 H), 7.75 (1/2 AB$q$ d, J=8.1, 1.5 Hz, 1 H), 7.72 (1/2 AB$q$, J= 8.1 Hz, 1 H), 7.63 (dd, J=6.6, 1.8 Hz, 2 H), 7.44 (dd, J=6.6, 1.8 Hz, 2 H), 7.41 (dd, J=4.3 Hz, 1.5 Hz, 2 H), 2.46 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) 193.0, 150.0, 149.5, 135.5, 134.7, 134.3, 132.6, 130.1, 129.8, 128.0, 125.5, 123.2, 123.0, 118.7, 98.6, 90.7, 90.5, 86.0, 30.3. HRMS calc’d for C$_{23}$H$_{14}$N$_2$O$_3$S: 398.0725, found: 398.0724.
2-Bromo-4-nitro-5-pyridin-4-yethynyl-phenylamine (52). See the general in-situ deprotection and coupling procedure. To a solution of 2,5-dibromo-4-nitroacetanilide (8) (0.877 g, 8.84 mmol), K$_2$CO$_3$ (1.08 g, 7.81 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.054 g, 0.077 mmol), copper(I) iodide (0.025 g, 0.13 mmol) and triphenylphosphine (0.068 g, 0.26 mmol) in THF (4 mL) were added via a cannula 3 (0.404 g, 2.30 mmol) in THF (8 mL) and MeOH (3 mL). The mixture was stirred at 23 °C for 1 d. Purification by flash chromatography (silica gel, EtOAc/hexane 40/60 50/50) afforded 290 mg (39% yield) of the title compound as a yellow solid. Mp: 226-228 °C. IR (KBr) 3385.4, 3297.7, 3171.3, 1646.8, 1591.7, 1556.9, 1471.3, 1297.8 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.66 (br d, J=3.8 Hz, 2 H), 8.32 (d, J=1.3 Hz, 1 H), 7.53 (br d, J=4.5 Hz, 2 H), 7.06 (d, J=1.3 Hz, 1 H), 6.94 (br s, 2 H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 151.3, 150.1, 136.4, 130.7, 129.6, 125.3, 118.1, 117.7, 106.0, 91.9, 89.7. HRMS calc’d for C$_{13}$H$_8$BrN$_3$O$_2$: 316.9800, found: 316.9801.

4-Nitro-5-pyridin-4-yethynyl-2-trimethylsilylethynyl-phenylamine (53). See the general Pd/Cu procedure. To a solution of 47 (0.310 g, 0.975 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.05 mmol), copper(I) iodide (0.011 g, 0.05 mmol) and triphenylphosphine (0.026 g, 0.10 mmol) in THF (10 mL) were
added Et₃N (0.9 mL, 6.5 mmol) and trimethylsilylacetylene (0.2 mL, 1.4 mmol). The mixture was stirred at 60 °C for 2 d. Purification by flash chromatography (silica gel, Et₂O) afforded 160 mg (49% yield) of the title compound as a yellow solid. Mp: 145-150 °C. IR (KBr) 3451.9, 3379.1, 2960.5, 2149.5, 1620.4, 1597.9, 1545.5, 1512.2, 1317.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.65 (dd, J=4.6, 1.5 Hz, 2 H), 8.25 (s, 1 H), 7.44 (dd, J=4.3, 1.5 Hz, 2 H), 6.93 (s, 1 H), 4.90 (s, 2 H), 0.30 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 149.9, 139.4, 130.7, 130.4, 125.7, 119.6, 118.1, 107.9, 104.3, 98.4, 93.7, 89.8, -0.2. HRMS calc'd for C₁₈H₁₇N₃O₂Si: 335.1090, found: 335.1089.

2-Ethynyl-4-nitro-5-pyridin-4-ylyethynyl-phenylamine (54). See the general TMS-protected alkyne deprotection procedure. To a solution of 53 (160 mg, 0.477 mmol) in MeOH (15 mL) and CH₂Cl₂ (15 mL) was added K₂CO₃ (0.66 g, 4.77 mmol). The solution was stirred at 23 °C for 2 h. The reaction afforded 0.11 g (88% yield) of the title compound as a yellow solid that was too unstable to attain its complete characterization data. ¹H NMR (400 MHz, DMSO-d) δ 8.67 (dd, J=4.5, 1.6 Hz, 2 H), 8.12 (s, 1 H), 7.53 (dd, J=4.5, 1.6 Hz, 2 H), 7.03 (s, 1 H), 6.97 (br s, 2 H), 4.70 (s, 1 H).

Thioacetic acid S-[4-(2-amino-5-nitro-4-pyridin-4-ylyethynyl-phenylethynyl)-phenyl] ester (55). See the general Pd/Cu procedure. To a solution of 54 (0.110 g,
0.418 mmol, 4-thioacetyliodobenzene (1) (0.124 g, 0.446 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.015 g, 0.021 mmol), copper(I) iodide (0.004 g, 0.021 mmol) and triphenylphosphine (0.014 g, 0.053 mmol) in THF (13 mL) was added Et₃N (0.4 mL, 2.9 mmol). The mixture was stirred at 50 °C for 2 d. The reaction was checked by TLC (EtOAc/hexane 75/25). More bis(triphenylphosphine)palladium(II) dichloride (0.014 g, 0.020 mmol), copper(I) iodide (0.035 g, 0.018 mmol) and triphenylphosphine (0.085 g, 0.324 mmol) were added and the reaction was stirred at 60 °C for 1 d. Purification by flash chromatography (silica gel, EtOAc/hexane 66/33) afforded 130 mg (75% yield) of the title compound as a yellow solid. Mp: 185-188 °C. IR (KBr) 3438.2, 3195.9, 2922.4, 1695.4, 1627.7, 1596.5, 1545.1, 1514.8, 1477.2, 1402.8, 1316.4, 1249.9 cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆) δ 8.68 (br d, J=4.0 Hz, 2 H), 8.23 (s, 1 H), 7.79 (d, J=8.1 Hz, 2 H), 7.54 (d, J=5.0 Hz, 2 H), 7.49 (d, J= 8.0 Hz, 2 H), 7.13 (br s, 2 H), 7.06 (s, 1 H), 2.46 (s, 3 H). ¹³C NMR (100 MHz, DMSO-d₆) δ 193.0, 153.8, 150.2, 136.3, 134.3, 132.3, 130.7, 129.7, 128.7, 125.3, 123.1, 118.7, 118.3, 105.4, 95.7, 92.5, 90.1, 85.5, 30.3. HRMS calc'd for C₂₃H₁₅N₃O₃S: 413.0834, found: 413.0940.
6. References


(54) Sandmeyer, T. Ber. 1884, 17, 1633, 2650.


CHAPTER 2

THERMAL ANALYSIS OF MOLECULAR DEVICES FOR VAPOR PHASE ASSEMBLY
1. Introduction

Over the past years, it has become obvious that molecular scale electronics$^{1,2}$ constitutes a possible alternative to typical semiconductor manufacturing processes in the future of electronics. Current work on molecular electronics relies on liquid phase processing, which is inexpensive and builds upon a large body of experience with self-assembled monolayers (SAM).$^{3-6}$ A new approach is being developed by building a hybrid molecular/solid-state circuit configuration which will be fabricated by a more scaleable and production-worthy vapor phase fabrication process. This hybrid approach couples the current developing molecular electronics technology and the existing solid-state circuitry. It is planned that molecular devices, namely oligo(phenylene ethynylene)s (OPEs), presenting negative differential resistance$^{7,8}$ (NDR) will be used in combination with conventional solid state (CMOS) circuits.

Gas phase processing is used for this approach. This involves vapor phase deposition of molecules instead of self-assembly as well as inert gas mediated evaporation of the metal to reduce the molecular mean free path and thus reduce the risk of the molecule monolayer destruction by dissipation of the metal’s excess energy. The core advantages of the gas phase processing approach are the built-in ability to purify molecular stocks and the ability to use metal layers other than gold. It also offers a superior uniformity and reproducibility as gases allow for very precise and shallow etching. This, in turn, will allow for a more scalable and extensible technology. The deposition of the molecules will be performed at University of Virginia in the John Bean group using a growth chamber molecular beam epitaxy.
(MBE) system which can obtain vacuum as low as $10^{-10}$ torr, which should allow molecular devices to evaporate at moderate temperature.

The first step in this process is to demonstrate the ability to vapor phase deposit molecular oligomer devices on surfaces like Cu and Al without destroying the integrity of the molecules. Several studies on chemical vapor deposition of oligomers and polymers have been reported in the literature. Chiang et al.\textsuperscript{9} have reported the remarkable thermal stability of quinoline oligomers and their vaporization at 200-250 °C under a nitrogen flow with an overall pressure of 0.5 torr. In 2000, Seoul\textsuperscript{10} reported the CVD of poly(phenylene)s ($n = 8-9$) at 500 °C at $2 \times 10^{-6}$ torrs. This temperature is quite high, but we would not need such a high temperature since we would be using a higher vacuum.

To assess the thermal behavior of molecular devices, differential scanning calorimetry (DSC) analyses and thermogravimetric analyses (TGA) were performed on several OPE compounds.

2. Results and discussion

Several OPEs containing different alligator clips, mainly pyridines, anilines, nitriles and isonitriles were tested. Our hope was that these alligator clips will be of sufficient low bonding energy to the coinage metals that they will migrate around to fall into a low energy monolayer. Pyridines, in particular, seem to adsorb well on copper through the nitrogen atom and exhibit a small tilt facewise with respect to the surface normal.\textsuperscript{11-13}
The results of the DSCs indicated that the molecules had a common behavior. In most of the DSC analyses, two peaks appeared (Figure 1): a sharp endothermic peak which corresponds to the melting point of the oligomers, and an exotherm, which indicates the crosslinking of the oligomers due to the acetylene units. \textsuperscript{14,15}

**Figure 1**

![Graph showing DSC and TGA results for molecule 35.](image)

DSC (top) and TGA (bottom) of molecule 35.

Polymeric carbon or glassy carbon resulted from the thermal polymerization and crosslinking (via a radical mechanism (Scheme 1)) of the acetylene units.
Scheme 1

The exothermic peak is critical to identify, since it represents the crosslinking temperature below which the CVD process must be conducted in order to prevent molecular degradation. These maximum stability temperature values were acquired and corroborated by TGA on selected compounds. These results helped to determine the temperature at which the molecules start to vaporize or decompose. When the compound shows a weight loss by TGA and at the same time the DSC analysis shows no exotherm or change in the heat capacity at the same temperature, then it is a good indication that the molecule has reached the temperature of vaporization and that decomposition does not occur. Going to temperatures above the melting point of the molecule should not be a problem to the CVD, as long as the molecule as a liquid has a low volatility, to allow the control of the deposition of the molecules. In other words, liquids with high volatility do not allow a good control of the deposition rate because all the molecules vaporize at a narrow temperature range, therefore it is very difficult to achieve a monolayer. The ideal system would be to have a molecule that can sublime in a controllable way.
Table 1 summarizes the obtained results from the DSC and TGA analyses. It is important to note that few TGA analyses were obtained as the presence of the nitro group caused the platinum pan to corrode at temperatures approaching 800°C. Therefore, TGA analyses were performed with an aluminum pan using a maximum temperature of 400 °C.

Table 1

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<th>Compound</th>
<th>Reference #</th>
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<th>TGA 5% weight loss (°C)</th>
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*The temperature was determined by taking the temperature at which the decomposition of the OPE starts and subtracting 5 °C as a precaution.

Several conclusions can be drawn from the table. As shown above, the most stable molecules are the unfunctionalized nitrile (SMD-II-86) and pyridine (SC2-110) OPEs. As one might expect, the nitro moiety lowers the stability of the molecules. For
example, the mononitro isonitrile DWP-III-49 is more stable to heat than the dinitro isonitrile SMD-II-171. The same is observed for the nitriles SMD-II-86 and SMD-II-63.

OPEs containing the pentafluoro moiety were tested because fluorinated molecules have interesting properties, namely volatility, electronegativity and high thermal stability.\textsuperscript{16,17} As a comparison, pentafluoropyridine has a boiling point of 84 °C whereas pyridine boils at 115 °C; the same happens for pentafluorobenzaldehyde (164 °C) and benzaldehyde (179 °C). A number of fluorinated polymers have been reported to exhibit high thermal stability. For example an extensive investigation has recently been made into the stability of classes of organic compounds and it was found that hexafluorobenzene was much more stable (above 650 °C) than any other compound tested. The mode of decomposition of fluorocarbons and hydrocarbons differ; dehydrogenation is one of the most important ways for a hydrocarbon to decompose whereas fluorocarbons usually cleave at higher temperature at the weaker C-C bond leaving the strong C-F bond intact.\textsuperscript{18} In our study case, the same behavior has been observed as that the pentafluoro compound FM-iv-120 exhibits much higher thermal stability than its hydrogenated counterpart SMD-II-70, as shown by DSC and TGA. In the same manner, SC5-78 starts to loose weight at the same temperature as its hydrogenated counterpart SC5-70 but is more stable to heat, as shown by the DSC. The same can be noted for the nitrile SMD-II-63 and its counterpart FM-iv-119. If this reveals to be a general tendency of the pentafluoroaryl moiety, then it is an interesting feature that will need to be exploited for CVD applications and other surface chemistry techniques suitable for molecular electronics.
3. Summary

The thermal analyses of several potential molecular devices were obtained in order to determine their thermal stability for chemical vapor phase deposition process.
4. Experimental procedures

Thermogravimetric analysis (TGA) was performed with a TA Q50 instrument at temperature ranges from 30 - 400 °C or 30 - 800 °C at a rate of 10 °C/min under nitrogen. For experiments heating to 400 °C, an aluminum pan was used, whereas for experiments heating to 800 °C, a platinum pan was used. Differential scanning calorimetry (DSC) was performed with a TA Q10 instrument using a 30 - 450 °C scanning window at a rate of 10 °C/min under nitrogen.
5. References


CHAPTER 3

SYNTHESIS OF MOLECULAR DEVICES FOR QUANTUM COMPUTING
1. Introduction

It has become common knowledge that silicon technology, grounded in classical physics, is close to reaching its physical and economic limits (see chapter 1). For several years now, numbers of teams have been working on complementing the transistors with molecular electronic devices made of oligo(phenylene-ethynylene)s.\(^1\)

The idea of a quantum computer has been developed theoretically over several decades to elucidate fundamental questions concerning the capabilities and limitations of machines in which information is treated quantum mechanically.\(^2,3\) Unlike molecular electronics which uses an electrical field to manipulate a flow of electrons with their charge as a handle, the idea of quantum computing relies on the vision of fully exploiting the quantum mechanical nature of spin. Electrons can be described by a quantum number characteristic of its intrinsic angular momentum, the spin which arises from Paul Dirac’s relativistic wave equation, derived in the late 1920’s.\(^4,5\) In spin electronics or “spintronics”, it is the electron spin that carries the information and not the electron charge. The ones and the zeros of classical digital computers are replaced by the quantum state of a two-level system (a quantum bit or “qubit”). Logical operations carried out on the qubits and their measurement to determine the result of computation must obey quantum-mechanical laws. This offers the prospect of massively powerful information processing by manipulating quantum objects in a superposition of states. Adding the spin degree of freedom to conventional semiconductor charge-based electronics or using the spin degree of freedom alone will add substantially more capability and performance to electronic products. The potential advantages of these new devices include the nonvolatility of the memory, increased data processing speed (which
could dramatically speed up the solution of certain mathematical problems), decreased electric power consumption, and increased integration densities compared to conventional devices. With quantum computing, the ideas of artificial intelligence and quantum communication become tangible.

Using the language of classical physics, a spin is either up or down, but quantum mechanics means that it can also be held in a superposition that is simultaneously up and down. Whereas the binary-encoded bits of classical computing have two available states, 1 and 0, qubits have more. In quantum computing, the boolean states 0 and 1 are represented by a fixed pair of reliably distinguishable states of the qubit, for example horizontal and vertical photon polarizations: $|0\rangle = \leftrightarrow$, $|1\rangle = \updownarrow$. But a qubit can also exist in a continuum of intermediate states or superpositions, represented mathematically as complex linear combinations of the basis states $|0\rangle$ and $|1\rangle$. So for example, two qubits can simultaneously represent $|00\rangle$, $|01\rangle$, $|10\rangle$ and $|11\rangle$. As a comparison, an $n$-bit memory can exist in any of $2^n$ logical states, labeled 000...0 to 111...1 whereas a string of $n$ qubits can exist in any state of the form $\Psi = \sum c_x |x\rangle$ where $\Psi$ is a complex vector, $x = 00...0$ to 11...1 and $c_x$ are complex numbers.$^6$

Electron$^{7,8}$ and nuclear$^{9,10}$ spins have been identified as promising candidates for qubits because they are natural two state systems and decoherence times for the spin degree of freedom are unusually large.$^{11}$ Nuclear spins in particular have been proposed as candidates for storing both classical and quantum information$^{12,13}$ because their spin lifetimes exceed those of electrons by at least several orders of magnitude and because conventional nuclear magnetic resonance techniques allow their control. Moreover, they are also extremely well isolated from their environment so operations on nuclear spin
qubits could have low error rates. The primary challenge in using nuclear spins in quantum computers lies in measuring the spins. However this can be solved by coupling electron and nuclear spins using their hyperfine interaction\textsuperscript{14} and measuring the nuclear spin polarization by its effect on the electronic properties of a sample.\textsuperscript{15,16} Another major challenge is that processing information with qubits requires that they are all maintained in a coherent superposition, an interweaving in which none of the qubits is allowed to collapse into its up or down state. This is very difficult to accomplish since any interactions of the qubits with their environment tend to induce this “decoherence”, losing information. In principle, quantum computation can only occur in systems that are almost completely isolated from their environment and which consequently must dissipate no energy during the process of computation, conditions that are extraordinarily difficult to fulfill in practice. However, Awschalom \textit{et al.} have recently reported that one can coherently control spins in semiconductors on femtosecond time scales.\textsuperscript{17}

In order to create a more robust approach to meet the difficult challenge of creating physical structures that will be capable of quantum computing operations, a new platform was proposed. Specifically, the fabrication of a new material structure based on self-assembling molecular arrays with constituent organic molecules containing embedded spins, in which the spins act as qubits, and for which each qubit environment in the molecules is identical for every single molecule. Spins will be manipulated and detected using highly localized magnetic interactions from the state-of-the art scanning probe magnetic resonance force microscopes (MRFM) which will be used to detect electron spin resonance (ESR) signals and nuclear magnetic resonance (NMR) signals.
The molecules designed for this project have a stable spin $\frac{1}{2}$ electron (a stable free radical) and contain an atom with a strong nuclear spin $\frac{1}{2}$ magnetic moment, e.g. $^{125}$Te. In addition, these molecules have been designed with hydrophilic groups such as COOH at one end for their attachment on surfaces like silver or alumina using self-assembly methods. Figure 1 illustrates the type of molecules to be synthesized. Ultimately, the molecules will be modified so that the nuclear spin and the electron spins are close to each other in order to achieve hyperfine coupling interaction.

Figure 1

2. Results and discussion

2.1. TEMPO radical terminated devices

In order to conduct preliminary self-assembly tests with radicals, the syntheses of amphiphilic molecules with 2,2,6,6-tetramethylpiperidinyloxyl moiety (TEMPO) was accomplished. The first set of target molecules was designed with a nitroxyll free radical contained in the TEMPO moiety along with a long alkyl chain terminated by COOH for the attachment of the molecules to metallic surfaces. The long chains were necessary to give enough freedom to the molecule to rearrange its hydrocarbon chain in order to form a close packed SAM. These targets were synthesized as test molecules to assess how free radicals assemble on a silver and alumina surfaces.
2.1.1. Devices with an amine linkage

Scheme 1 outlines the synthetic route toward the first target.

Scheme 1

The synthesis of a long chain terminated device is illustrated in Scheme 1. The first attempts began with 6-bromohexanoic acid, which was esterified in a Fisher-type fashion with MeOH and catalytic amount of sulfuric acid to afford 1. Endeavors to nucleophilically displace the bromide by a primary amine were unsuccessful. 16-Bromohexadecanoic acid was esterified to furnish 2 in good yield. The reaction of 2 with 4-amino-TEMPO in DMF at 90 °C gave traces of the methyl ester 3. A better yield could be obtained when lithium iodide was added. The next step, which was the deprotection of the acid using lithium hydroxide, did not yield the intended product.
2.1.2. Devices with an ester linkage

Since the reaction of 4-amino-TEMPO with an organobromide was fruitless, another route was taken using 4-hydroxy-TEMPO. The advantage of 4-hydroxy-TEMPO is that esterifications are much easier than nucleophilic displacement of a halogen by an amine, a reaction that usually requires high temperature. Moreover 4-hydroxy-TEMPO is considerably less expensive than its amino counterpart. So, a new target molecule with an ester linkage was designed.

Scheme 2 depicts the attempts towards the synthesis of a long chain COOH-terminated device with an ester linkage.

Scheme 2

The synthesis of a long chain molecule with an ester linkage began with the esterification of hexadecanedioic acid with 4-hydroxy-TEMPO (Scheme 2). When the reaction was run in dicyclohexylcarbodiimide (DCC) and N,N-dimethylaminopyridine (DMAP), the product was obtained but its separation from the formed urea was not possible. To solve this problem, DCC was replaced by 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), which was water soluble. This second reaction condition\textsuperscript{18} provided 4 in 12% yield. The compound was sent for self-assembly testing to the Allara group at Pennsylvania State University.
Scheme 3

In order to distinguish the signals coming from the TEMPO part and the signals coming from the aliphatic chain, the device 5 with deuterated TEMPO was synthesized using the same procedure as for 4 (Scheme 3). The low yield on both reactions can be explained by the obtention of the diester but mostly by unreacted starting material.

2.1.3. Devices with an ether linkage

Since the esterification procedures were still very low yielding, the synthesis of devices with ether linkages was attempted. By doing so, the importance of the linkage moiety for the self-assembly could be assessed.

Scheme 4

Scheme 4 shows the synthesis of a long chain device with an ether linkage. The first two attempts to treat methyl-16-bromohexadecanoate with 4-hydroxy-TEMPO in presence of sodium hydride failed. The third condition using NaH and DMF gave a low
yield of 6. Compound 6 could also be obtained under potassium hydroxide and DMSO conditions. Oddly and luckily enough, the methyl ester was removed at the same time avoiding the deprotection step. This compound was also sent for testing.

Scheme 5

As for compound 4, a deuterated TEMPO device was also synthesized using the sodium hydride procedure (Scheme 5). 7 was obtained in 27%.

2.1.4. Devices with a urea linkage

Scheme 6

In order to determine the importance of the linkage moiety in the self-assembly process, the synthesis of a molecule with a urea linkage was attempted (Scheme 6). 4-Amino-TEMPO was transformed to an isocyanate via a procedure by Sigurdsson\textsuperscript{19} to furnish 8 in low yield. After esterification of 12-aminododecanoic acid with MeOH and
thionyl chloride,²⁰ 9 was treated with the isocyanate 8. Unfortunately, neither methylene chloride nor DMF solvent conditions yielded any product. The synthesis of that device was therefore abandoned.

2.2. Galvinoxyl radical terminated devices

One known stable free radical moiety is the galvinoxyl group. Therefore, the synthesis of galvinoxyl containing devices was attempted.

Scheme 7
Scheme 7 outlines the synthesis of a galvinoxyl molecule following known procedures. 4-Bromo-2,6-di-tert-butylphenol was treated with butyllithium and then quenched with trimethylsilyl chloride to provide 10 in excellent yield. After protection of the alcohol of 11-bromoundecanol with TBSCI, 11 was coupled to methyl-4-hydroxybenzoate in excellent yield to afford 12. After a lithium-bromide exchange on 10, two equivalents of the resulting anion were used to attack the methyl ester of 12. After acidic hydrolysis, 13 was furnished in 87% yield. The TBS protecting group was removed by 1% HCl ethanol in 97% yield. The alcohol 14 was then oxidized to the aldehyde 15 using the Dess-Martin periodinane reagent. Finally 15 was oxidized to the acid 16 using sodium chlorite and potassium dihydrogenphosphate. Attempts to generate the radical using potassium ferricyanide gave an impure product.

2.3. Tellurium devices

Finally, the synthesis of tellurium devices was attempted.
As shown in Scheme 8, a procedure by Knapp\textsuperscript{25} was followed to make the organotellurium derivative. Tellurium metal was treated with sodium hydride to make the sodium ditelluride Na\textsubscript{2}Te\textsubscript{2} which was quenched with methyl-5-bromovalerate 17 to give 18 in low yield. The reaction has to be performed in the dark and the tellurium compounds stored under N\textsubscript{2} and in the freezer as they decompose easily to give Te metal as a black deposition at the bottom of the flask. Reduction of the ditelluride was accomplished by sodium borohydride to give the sodium tellurol NaTeR which was quenched with methyl-5-bromovalerate 17 to give the telluride 19 in 73\% yield. An alternative route is to treat Te metal with sodium hydride and to add methyl-5-bromovalerate as well as sodium borohydride in one pot. This afforded 19 in 33\% yield. Saponification of the esters with sodium hydroxide gave the diacid 20. Attempts to esterify with 4-hydroxy-TEMPO in the Mitsunobu\textsuperscript{26} condition failed.
Scheme 9

An alternative route was taken towards the synthesis of a tellurium-TEMPO containing device (Scheme 9). 5-Bromovaleric acid was esterified using DCC and DMAP to give 21 in good yield. The next step which was the reaction with the ditelluride 18 failed. This approach coupled with some of the others outlined in this chapter, should be successful. Due to allergic reaction that I experienced, I had to cease working with Te compounds.

3. Self-Assembly Testing

All the self-assembly, reflectance Fourier transformed infra-red (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements were carried out by the Allara group at Pennsylvania State University. The Electron Spin Resonance (ESR) measurements were done at Cornell University in the John Marohn’s group. The focus of their work has been to assemble and characterize TEMPO containing molecules. The first experiments were designed to see how well-ordered these molecules assemble on silver oxide.

All experiments were performed on compounds 4 through 7. The molecules (0.3-0.5 mM) in dry CH₂Cl₂ under N₂ were allowed to assemble on the gold substrate (Si/Cr/Au) for 18-24 h after which the substrate was rinsed with CH₂Cl₂.

The following report has been written by Josh Stapleton from the Allara group.
3.1. IR results

The first IR results on SAMs made of 4 and 6 showed that the $\nu$(C-H) stretching region (2800-3000 cm$^{-1}$) was too complex to be able to discern anything about the relative degree of ordering present within the monolayer. This was due to the fact that the $\nu$(C-H) stretching region contained information about both that alkyl chain and the TEMPO group. To resolve this issue, analogs of 4 and 6 were synthesized with a completely deuterated-TEMPO group, 5 and 7 respectively. By deuterating the TEMPO group, it was possible to draw some general conclusions about the degree of ordering present in the alkyl chain by looking at the $\nu$(CH$_2$) asymmetric stretching ($d^-$) mode and the $\nu$(CH$_2$) symmetric stretching ($d^+$) modes and by comparing their frequencies to those of SAMs that are known to be ordered.

Bulk (KBr dispersion) and monolayer infrared spectra are shown for compounds 5 and 7 in Figures 2 and 3, respectively.
Figure 2: IR of deuterated-TEMPO-Ester 5

Figure 3: IR of deuterated-TEMPO-Ether 7
While a rigorous interpretation of the infrared data is pending because of the need for more conclusive experiments, a few qualitative conclusions can be drawn. Evidence for the molecules assembling onto the AgO surface through a carboxylate group is seen in both Figures 2 and 3. The KBr spectra of both compounds shows the $\nu$(C=O) stretching mode indicative of a carboxylic acid group at $\sim$ 1715 cm$^{-1}$. The analogous monolayer spectrum indicates that this functional group is no longer present in the monolayer structure and a new mode has grown in at $\sim$ 1400 cm$^{-1}$. These two pieces of data, the loss of the $\nu$(C=O) mode and the appearance of a $\nu$(CO$_2$) mode indicate that the molecule is anchored to the AgO surface via a carboxylate group. The $\sim$ 1730 cm$^{-1}$ mode present in the monolayer spectra of 5 is due to the carbonyl group of the ester group. The $\nu$(C-H) stretching region (2800-3000 cm$^{-1}$) in the monolayer spectra of 5 indicate d$^+$ and d$^-$ modes at 2851 cm$^{-1}$ and 2920 cm$^{-1}$, respectively, while the equivalent modes are at 2850 cm$^{-1}$ and 2916 cm$^{-1}$ for 7. It should be noted that a well-ordered palmitic acid/AgO SAM exhibits d$^+$ and d$^-$ modes at 2849 cm$^{-1}$ and 2915-1919 cm$^{-1}$. The greater the degree of conformational disorder present in a film, the higher the observed frequency will be for the d$^+$ and d$^-$ vibrations. In light of these results, it is implied that the TEMPO monolayers form fairly well-ordered SAMs. However, in the monolayer spectra of 5 and 7 higher frequency shoulders can be seen on both the d$^+$ and d$^-$ modes. This is indicative of a certain degree of disorder in the film; quantitative peak fitting will be required to completely interpret this data.

3.2. XPS results

XPS spectra of the C 1s for SAMs of 5 and 7 are shown below in Figures 4 and 5, respectively. Both spectra were acquired with a take off angle of 45° and a pass energy
of 40 eV. The non-charge corrected peak fits can be seen in the figure insets. The areas under the curves are integrated and expressed in %. A simple way to interpret these percentages is that 1 C from carbonyl group represents about 5% of the areas in Figure 4. Following that rationale, the spectrum shows 1 C from COO⁻ (4.85%), 2 C's alpha to the ester, 2 C's alpha to the nitroxyl group, 1 C alpha to the carbonyl, 1 C alpha to the COO⁻ and 12 C's from the rest of the molecule. The same kind of interpretation can be drawn from Figure 5 except that 1 C is represented by 4.4% of the areas. This data corroborates well the chemical integrity of the SAMs. The N 1s (not shown) indicates a peak at ~ 401 eV which agrees with the literature values for the binding energy of an N-O radical. The N 1s and O 1s spectra are not included because they need to be reacquired using modified parameters to obtain better spectra.

Figure 4. d-TEMPO-Ester 5 on AgO₃
3.3. ESR Results

Figure 6 shows the ESR spectrum of 5-SAM on AgO. This spectrum shows the main transition at ~ 3600 G and the half field transition at ~ 1800 G. The initial interpretation by the Cornell group indicates that the radicals are free to approach each other within 0.15-0.2 nm, which is feasible in a monolayer structure. More ESR work is currently being done with a group at PSU in an effort to obtain better quantitative information.
4. Summary

The first step toward the synthesis of molecular devices for quantum computing has been undertaken. Amphiphilic molecules bearing an electron spin have been synthesized. Their testing on silver surfaces has shown that they form a well-packed self-assembled monolayer, as proven by surface analyses.
5. Experimental Procedures

General. All reactions were performed in an oven-dried flask and under an atmosphere of nitrogen unless stated otherwise. 4-Hydroxy-TEMPO and Te powder (-200 mesh) were purchased from Aldrich. 4-Amino-TEMPO was purchased from Acros and the deuterated analog 4-hydroxy-TEMPO-d_{17} was purchased from C/D/N isotopes (www.cdniso.com). N,N-Dimethylformamide (DMF) was distilled over anhydrous magnesium sulfate. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Toluene, triethylamine, methylene chloride and methanol were distilled over calcium hydride before use. 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. Melting points were taken on a Mel-Temp (Laboratory Devices) apparatus. FT-IR spectra were taken on a Nicolet Avatar 360 spectrometer. \textsuperscript{1}H NMR spectra were observed at 400 MHz and \textsuperscript{13}C NMR spectra were observed at 100 MHz on a Bruker AVANCE 400 spectrometer. Mass spectrometry was performed by Terry Marriott and Yunxuan Xiao at Rice University’s mass spectrometry lab. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. The presence of the TEMPO side chain make \textsuperscript{13}C NMR analysis impossible for 3, 4, 5, 6, 7, 21. All new compounds were named using the Beilstein AutoNom feature of Beilstein Commander software when possible.

Surface measurements. All reflectance FTIR and X-ray photoelectron spectroscopy (XPS) measurements were performed at Penn State by the Allara group. The electron spin resonance measurements (ESR) were carried out at Cornell University in the John Marhon’s group.
Methyl-6-bromohexanoate\(^{27}\) (1). 6-Bromohexanoic acid (174 mg, 0.892 mmol), sulfuric acid (3 drops) and MeOH (5 mL) were stirred under air at reflux for 1 d after which the reaction mixture was diluted with sat. aq. NaHCO\(_3\) until pH=8 and extracted with Et\(_2\)O. The combined organic phases were washed with brine, dried over MgSO\(_4\), filtered and evaporated. The reaction afforded 0.184 g (98% yield) of the product as a clear liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.67 (s, 3 H), 3.41 (t, \(J=6.9\) Hz, 2 H), 2.32 (t, \(J=6.9\) Hz, 2 H), 1.88 (quintet, \(J=7\) Hz, 2 H), 1.66 (quintet, \(J=7\) Hz, 2 H), 1.46 (m, 2 H).

Methyl-16-bromohexadecanoate (2). 6-Bromohexadecanoic acid (474 mg, 1.413 mmol), sulfuric acid (3 drops) and MeOH (12 mL) were stirred under air at reflux for 1 d after which the reaction mixture was diluted with sat. aq. NaHCO\(_3\) until pH=8 and extracted with Et\(_2\)O. The combined organic phases were dried over MgSO\(_4\), filtered and evaporated. The reaction afforded 0.460 g (93% yield) of the product as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.67 (s, 3 H), 3.41 (t, \(J=6.9\) Hz, 2 H), 2.30 (t, \(J=6.9\) Hz, 2 H), 1.85 (quintet, \(J=7\) Hz, 2 H), 1.62 (m, 2 H), 1.43 (m, 2 H), 1.26 (s, 20 H).

(3). A solution of methyl-16-bromohexadecanoate (2) (243 mg, 0.696 mmol), 4-amino-TEMPO (238 mg, 1.391 mmol) and LiI (93 mg, 0.696 mmol) in DMF was heated to 90 °C for 12 h then 115 °C for 6 h. The reaction mixture was diluted with brine and extracted with ether. The combined organic phases were dried over MgSO\(_4\), filtered, and
the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/MeOH 90/10) afforded 86 mg (28% yield) of the title compound as an orange oil. IR (KBr) 3459.9, 2972.5, 2925.6, 2853.0, 1738.9, 1462.5, 1359.3, 1244.0, 1176.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 4.12 (br s, 3 H), 2.74 (br s, 4 H), 2.08 (br s, 4 H), 1.73 (br s, 21 H). HRMS calc'd for C₂₆H₅₁N₂O₃ 439.3900, found 439.3896.

(4). A solution of hexadecanedioic acid (600 mg, 2.095 mmol), hydroxy-TEMPO (361 mg, 2.095 mmol) and DMAP (128 mg, 1.045 mmol) in dry CH₂Cl₂ (25 mL) was cooled to 0 °C. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (442 mg, 2.304 mmol) was added and the reaction mixture stirred at 0 °C for 5 h. The reaction mixture was diluted with water and extracted with CH₂Cl₂. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/hexane 50/50) followed by two recrystallizations from hexanes afforded 115 mg (12% yield) of the title compound as pink crystals. Mp: 64-65 °C. IR (KBr) 2970.9, 2920.8, 2853.2, 1729.6, 1714.4, 1471.0, 1421.4, 1401.9, 1328.2, 1285.4, 1246.3, 1205.4, 1170.2 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 2.46 (br s, 2 H), 2.40 (br s, 2 H), 1.73 (br s, 4 H), 1.35 (br s, 20 H). HRMS calc'd for C₂₅H₄₆NO₅ 440.3376, found 440.3375. Anal. Calc’d for C₂₅H₄₆NO₅: C, 68.14; H, 10.52; N, 3.18; Found: C, 68.42; H, 10.63; N, 3.15.
(5). A solution of hexadecanedioic acid (302 mg, 1.056 mmol), hydroxy-TEMPO-\textit{d}_{17} (200 mg, 1.056 mmol) and DMAP (65 mg, 0.528 mmol) in dry CH\textsubscript{2}Cl\textsubscript{2} (40 mL) was cooled to 0 °C. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (223 mg, 1.162 mmol) was added and the reaction mixture stirred at 0 °C for 5 h. The reaction mixture was diluted with water and extracted with CH\textsubscript{2}Cl\textsubscript{2}. The combined organic phases were dried over MgSO\textsubscript{4}, filtered, and the solvent evaporated \textit{in vacuo}. Purification by flash chromatography (silica gel, EtOAc/hexane 50/50) followed by two recrystallizations from hexanes afforded 132 mg (27% yield, 40% based on recovered starting material) of the title compound as pink crystals. Mp: 62-66 °C. IR (KBr) 3444.0, 2920.4, 2853.2, 2225.3, 2122.1, 1728.7, 1715.2, 1471.9, 1424.0, 1410.0, 1332.6, 1290.8, 1246.9, 1206.3, 1174.1 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textdelta 2.53 (br s, 2 H), 1.83 (br s, 2 H), 1.47 (br, s, 10 H). HRMS calc’d for C\textsubscript{25}H\textsubscript{29}D\textsubscript{17}NO\textsubscript{5} 457.4443, found 457.4443. Anal. Calc’d for C\textsubscript{25}H\textsubscript{29}D\textsubscript{17}NO\textsubscript{5}: C, 65.60; H, 13.87; N, 3.06; Found: C, 65.68; H+D, 10.15; N, 3.00.

(6). A solution of methyl-16-bromohexadecanoate (2) (1.037 g, 2.969 mmol), 4-hydroxy-TEMPO (614 mg, 3.56 mmol) and NaH (60% in mineral oil) (712 mg, 17.81 mmol) in DMF was stirred at RT for 3 d. The reaction mixture was diluted with brine and extracted with ether. The organic phase was discarded and the aqueous phase was
acidified with aq. HCl (1 M). The mixture was extracted with ether. The combined organic phases were dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/hexane 50/50) followed by three recrystallizations from hexanes afforded 172 mg (14% yield) of the title compound as light pink solid. Mp: 49-50 °C. IR (KBr) 3442.4, 2974.1, 2920.5, 2852.3, 1713.6, 1471.0, 1426.9, 1409.6, 1364.3, 1242.6, 1203.2, 1178.2, 1098.3 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.40 (br m, 2 H), 2.40 (br s, 2 H), 1.78 (br s, 2 H), 1.68 (br s, 2 H), 1.30 (br s, 22 H). HRMS calc’d for C$_{25}$H$_{48}$NO$_4$: 426.3583, found 426.3581. Anal. Calc’d for C$_{25}$H$_{48}$NO$_4$: C, 70.38; H, 11.34; N, 3.28; Found: C, 70.41; H, 11.41; N, 3.25.

6 was also obtained by mixing methyl-16-bromohexadecanoate (2) (258 mg, 0.739 mmol), 4-hydroxy-TEMPO (126 mg, 0.733 mmol), KOH (206 mg, 3.665 mmol) in DMSO (10 mL) and stirring at RT for 18 h. The reaction mixture was diluted with water and extracted with EtOAc. The organic phase was discarded and the aqueous phase was acidified with aq. HCl (1 M) until pH=5. The mixture was extracted with EtOAc. The combined organic phases were dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/hexane 25/75) afforded 48 mg (15% yield) of the title compound as light pink solid.

(7). A solution of methyl-16-bromohexadecanoate (2) (369 mg, 1.056 mmol), 4-hydroxy-TEMPO–d$_{17}$ (200 mg, 1.056 mmol) and NaH (60% in mineral oil) (253 mg, 6.336 mmol) in DMF (10 mL) was stirred at RT for 3 d. The reaction mixture was diluted with brine and extracted with ether. The organic phase was discarded and the aqueous
phase was acidified with aq. HCl (1 M). The mixture was extracted with ether. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/hexane 50/50) followed by three recrystallizations from hexanes afforded 129 mg (27% yield, 49% based on recovered starting material) of the title compound as light pink solid. Mp: 52-55 ºC. IR (KBr) 2924.8, 2853.3, 2227.0, 1709.3, 1464.5, 1180.9, 1096.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 3.39 (m, 2 H), 2.41 (br s, 2 H), 2.01 (br s, 2 H), 1.92 (br s, 2 H), 1.30 (br s, 18 H). HRMS calc’d for C₂₅H₃₁D₁₇NO₄: 443.4650, found: 443.4656. Anal. Calc’d: C 67.67; H, 4.76; N, 3.16; Found: C, 67.91; H+D, 11.05; N, 2.96.

(8).¹⁹ To a cold (-8 °C) solution of 4-amino-TEMPO (627 mg, 3.66 mmol) in CH₂Cl₂ (4.8 mL) was added quickly diphosgene (0.48 mL, 4.026 mmol) in CH₂Cl₂ (4.8 mL). The cooling bath was removed and the mixture stirred at RT for 5 min. The reaction mixture was diluted with CH₂Cl₂ (50 mL) and washed with 1 M HCl (5 X) then 1 M NaOH (4 X). The organic phase was dried with MgSO₄, filtered and the solvent removed in vacuo to afford 184 mg (25% yield) of the title compound as a pink solid. The compound was stored in CH₂Cl₂ and in the freezer. IR (KBr) 2295.3, 2979.4, 2940.4, 2259.1, 1749.2, 1668.5, 1465.6, 1381.2, 1364.2, 1242.2, 1217.5, 1178.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.73 (br m).
Methyl-12-aminododecanoate\textsuperscript{20} (9). To a suspension of 12-aminododecanoic acid (1.50 g, 6.965 mmol) in MeOH (15 mL) was added thionyl chloride (0.81 mL, 11.14 mmol). The suspension was stirred at RT for 40 min. The solvent was evaporated and the solid resuspended in dry ether. The white solid was filtered off and washed with ether. After drying in air, the reaction afforded 1.70 g (100\% yield) of the compound. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \delta 7.86 (br s, 2 H), 3.34 (s, 3 H), 2.73 (sext, \textit{J}=6.1 Hz, 2 H), 2.28 (t, \textit{J}=7.4 Hz, 2 H), 1.52 (m, 4 H), 1.24 (s, 14 H).

(4-Bromo-2,6-di-\textit{tert}-butyl-phenoxo)-trimethyl-silane\textsuperscript{28} (10). To a solution of 4-bromo-2,6-di-\textit{tert}-butylphenol (purchased from Aldrich) (8.29 g, 29.06 mmol) in THF (45 mL) at -78 °C was added dropwise \textit{n}-BuLi (13.81 mL, 30.52 mmol). After stirring at -78 °C for 30 min, TMSCl (5.53 mL, 43.59 mmol) was added and the reaction mixture was allowed to warm to RT. The reaction mixture was diluted with water and extracted with ether. The combined organic phases were dried over MgSO\textsubscript{4}, filtered, and the solvent evaporated \textit{in vacuo}. The reaction afforded 10.05 g (97\% yield) of the title compound as white crystals. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.33 (s, 2 H), 1.40 (s, 18 H), 0.41 (s, 9 H).
tert-Butyldimethyl-11-bromo-undecanoyloxy-silane\textsuperscript{29} (11). A solution of imidazole (3.25 g, 47.77 mmol), tert-butyldimethylsilyl chloride (5.76 g, 38.22 mmol) and 11-bromoundecanol (8.0 g, 31.85 mmol) in distilled CH\(_2\)Cl\(_2\) (70 mL) was stirred at RT for 1 d. The white suspension was diluted with water and extracted with CH\(_2\)Cl\(_2\). The combined organic phases were dried over MgSO\(_4\), filtered, and the solvent evaporated \textit{in vacuo}. It afforded 11.64 g (100\% yield) of the title compound as a clear liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.60 (t, \(J=6.7\) Hz, 2 H), 3.41 (t, \(J=6.9\) Hz, 2 H), 1.87 (quint, \(J=6.9\) Hz, 2 H), 1.51 (t, \(J=6.8\) Hz, 2 H), 1.42 (t, \(J=7.2\) Hz, 2 H), 1.29 (s, 12 H), 0.90 (s, 9 H), 0.05 (s, 6 H).

4-[11-(tert-Butyl-dimethyl-silanyloxy)-undecyloxy]-benzoic acid methyl ester (12). To a solution of methyl-4-hydroxybenzoate (1.73 g, 11.40 mmol), K\(_2\)CO\(_3\) (4.73 g, 34.20 mmol) in DMF (30 mL) was added tert-butyldimethyl-11-bromo-undecanoyloxy-silane 11 (5.00 g, 13.68 mmol). The solution was stirred at 90 °C for 18 h. The reaction mixture was diluted with brine and extracted with ether. The combined organic phases were washed with water, dried over MgSO\(_4\), filtered, and the solvent evaporated \textit{in vacuo}. Purification by flash chromatography (silica gel, CH\(_2\)Cl\(_2\)) afforded 4.57 g (92\% yield) of the title compound as a clear liquid. IR (KBr) 2928.5, 2855.5, 2254.6, 1719.6, 1606.4, 1511.3, 1470.7, 1435.1, 1281.0, 1255.2, 1168.6, 1103.0 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (m, 2 H), 6.90 (m, 2 H), 4.00 (t, \(J=6.7\) Hz, 2 H), 3.89 (s, 3 H), 3.60 (t, \(J=6.7\) Hz, 2 H), 1.80 (quint., \(J=6.7\) Hz, 2 H), 1.48 (m, 4 H), 1.29 (s, 12 H), 0.90 (s, 9
H), 0.05 (s, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.1, 163.2, 131.8, 122.5, 114.3, 68.3, 63.5, 33.1, 29.8, 29.7, 29.63, 29.56, 29.3, 26.2, 26.0, 18.6. HRMS calc’d for C$_{35}$H$_{44}$O$_4$Si: 436.3009, found 436.3019.

2,6-Di-tert-butyl-4-[(4-[11-(tert-butyl-dimethyl-silyloxy)-undecyloxy]-phenyl)-(3,5-di-tert-butyl-4-hydroxy-phenyl)-methylene]-cyclohexa-2,5-dienone (13).

To a solution of (4-bromo-2,6-di-tert-butyl-phenoxy)-trimethyl-silane (10) (2.21 g, 6.18 mmol) in THF (35 mL) at -78 °C was slowly added t-BuLi (9.50 mL, 13.28 mmol) over 10 min. After 50 min at -78 °C, a cold solution of 4-[11-(tert-butyl-dimethyl-silyloxy)-undecyloxy]-benzoic acid methyl ester (12) (1.0 g, 2.29 mmol) in THF (10 mL) was added. The yellow reaction mixture was allowed to warm to 15 °C over 4 h. Water was added (4 mL) and the green solution was allowed to stir at RT overnight. The dark blue solution was then acidified with dilute HCl (1 M) until the color changed to bright orange then it was extracted with ether. The combined organic phases were washed with water, dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexane/CH$_2$Cl$_2$ 40/60 then 3/1) afforded 1.60 g (87% yield) of the title compound as a bright orange sticky solid. IR (KBr) 3633.3, 3582.6, 2928.0, 2856.2, 1597.6, 1495.1, 1435.0, 1386.5, 1359.6, 1335.2, 1252.6, 1173.7 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.21 (m, 4 H), 7.05 (s, 2 H), 6.92 (m, 2 H), 5.52 (s, 1 H), 4.04 (t, J=6.7 Hz, 2 H), 3.61 (t, J=6.7 Hz, 2 H), 1.84 (quint, J=6.7 Hz, 2 H), 1.50 (m, 4 H), 1.42
(s, 18 H), 1.30 (s, 12 H), 1.29 (s, 18 H), 0.90 (s, 9 H), 0.05 (s, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 186.2, 160.5, 158.9, 155.8, 146.4, 135.4, 134.6, 133.4, 133.2, 133.1, 132.3, 130.5, 128.3, 113.9, 68.4, 63.6, 35.5, 35.4, 34.6, 33.1, 30.6, 29.9, 29.85, 29.82, 29.79, 29.77, 29.68, 29.5, 26.3, 26.2, 26.0, 18.6. HRMS calc'd for C$_{52}$H$_{82}$O$_4$Si: 798.5982, found 798.5989.

![Chemical Structure](image)

**2,6-Di-tert-butyl-4-[(3,5-di-tert-butyl-4-hydroxy-phenyl)-[4-(11-hydroxyundecyloxy)-phenyl]-methylene]-cyclohexa-2,5-dienone (14).** In a 500 mL flask was mixed 13 (2.40 g, 3.00 mmol) in 100 mL of HCl (1%) in ethanol. After 30 min at RT, the red solution was diluted with water and extracted with ether. The combined organic phases were washed with water, dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. After a passage through a plug of silica gel (hexane/EtOAc 66/33), 1.99 g (97% yield) of the title compound was afforded as a bright orange sticky solid. IR (KBr) 3630.6, 3450.8, 2929.0, 2857.2, 1597.5, 1493.9, 1455.1, 1435.5, 1359.9, 1335.0, 1295.0, 1252.6, 1174.0, 1117.8 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (m, 4 H), 7.04 (s, 2 H), 6.92 (m, 2 H), 5.52 (s, 1 H), 4.04 (t, $J$=6.7 Hz, 2 H), 3.64 (t, $J$=6.7 Hz, 2 H), 1.84 (quint., $J$=6.7 Hz, 2 H), 1.57 (m, 2 H), 1.50 (m, 2 H), 1.42 (s, 18 H), 1.32 (s, 12 H), 1.29 (s, 18 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 186.2, 160.5, 159.0, 155.7, 146.3, 135.4, 134.5, 133.4, 133.2, 133.1, 132.3, 130.5, 128.3, 113.9, 68.4, 63.2, 60.6, 35.43, 35.39, 34.6, 33.0,
30.5, 29.9, 29.8, 29.74, 29.70, 29.6, 29.5, 26.3, 25.9, 21.2, 14.4. HRMS calc’d for C_{46}H_{68}O_{4}+: 684.5118, found 684.5112.

11-{(4-[(3,5-Di-tert-butyl-4-hydroxy-phenyl)-(3,5-di-tert-butyl-4-oxo-cyclohexa-2,5-dienylidene)-methyl]-phenoxy)-undecanal (15). To a solution of the alcohol 14 (215 mg, 0.314 mmol) and pyridine (0.14 mL, 1.73 mmol) in CH_2Cl_2 (12 mL) was added Dess-Martin reagent (466 mg, 1.098 mmol). The reaction mixture was allowed to stir at RT for 2 h after which the orange solution turned brown. The mixture was diluted with CuSO_4.5H_2O and extracted with CH_2Cl_2. The combined organic phases were dried over MgSO_4, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH_2Cl_2) afforded 91 mg (42% yield) of the title compound as a red-orange sticky solid. IR (KBr) 3627.8, 2953.1, 2858.4, 2717.5, 2249.8, 1724.6, 1596.8, 1495.1, 1455.3, 1435.5, 1359.7, 1335.1, 1295.0, 1252.6, 1174.1 cm^{-1}. ^1H NMR (400 MHz, CDCl_3) δ 9.76 (s, 1 H), 7.21 (m, 4 H), 7.04 (s, 2 H), 6.92 (m, 2 H), 5.53 (s, 1 H), 4.04 (t, J=6.5 Hz, 2 H), 2.42 (dt, J=7.3, 1.8 Hz, 2 H), 1.84 (m, 2 H), 1.63 (m, 2 H), 1.47 (m, 2 H), 1.42 (s, 18 H), 1.32 (s, 10 H), 1.28 (s, 18 H). ^13C NMR (100 MHz, CDCl_3) δ 203.0, 186.1, 160.5, 158.9, 155.7, 146.3, 135.3, 134.5, 133.4, 133.2, 133.0, 132.2, 130.5, 128.2, 113.9, 68.3, 44.1, 35.40, 35.37, 34.5, 30.5, 29.86, 29.77, 29.63, 29.56, 29.50, 29.45, 29.3, 26.2, 22.2. HRMS calc’d for C_{46}H_{66}O_{4}: 682.4961, found: 682.4961.
11-{4-[(3,5-Di-tert-butyl-4-hydroxy-phenyl)-(3,5-di-tert-butyl-4-oxo-cyclohexa-2,5-dienylidene)-methyl]-phenoxy}-undecanoic acid (16). To a solution of the aldehyde 15 (91 mg, 0.133 mmol), KH$_2$PO$_4$ (145 mg, 1.064 mmol), 2-methylbut-2-ene (0.57 mL, 5.32 mmol) and t-BuOH (2.3 mL) was added dropwise a solution of sodium chlorite (120 mg, 1.33 mmol) in water (0.8 mL). The orange solution was stirred at RT for 40 min then diluted with brine and extracted with EtOAc. The combined organic phases were dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexane/EtOAc 66/33) afforded 57 mg (61% yield) of the title compound as a red-orange sticky solid. IR (KBr) 3631.0, 2954.6, 2858.7, 2250.5, 1708.7, 1596.9, 1494.5, 1455.4, 1435.7, 1360.2, 1335.2, 1293.7, 1252.5, 1174.5 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (m, 4 H), 7.04 (s, 2 H), 6.92 (m, 2 H), 5.53 (s, 1 H), 4.04 (t, $J=6.5$ Hz, 2 H), 2.36 (t, $J=7.4$ Hz, 2 H), 1.84 (m, 2 H), 1.65 (m, 2 H), 1.49 (m, 2 H), 1.42 (s, 18 H), 1.32 (s, 10 H), 1.28 (s, 18 H).$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 180.2, 160.5, 159.0, 146.3, 135.3, 134.6, 133.4, 130.5, 113.9, 68.3, 66.1, 41.9, 35.4, 35.2, 34.6, 34.3, 30.8, 30.4, 29.9, 29.7, 29.6, 29.55, 29.48, 29.4, 29.2, 26.3, 24.9, 15.4. HRMS calc'd for C$_{46}$H$_{66}$O$_5$ 698.4910, found 698.4910.

5-Bromo-pentanoic acid methyl ester$^{30}$ (17). 5-Bromovaleric acid (10.5 g, 58.0 mmol), sulfuric acid (4 drops) and MeOH (40 mL) were stirred at reflux for 1 d after
which the reaction mixture was diluted with sat. aq. NaHCO₃ until pH=8 and extracted with Et₂O. The combined organic phases were washed with brine, dried over MgSO₄, filtered and evaporated. The reaction afforded 11.3 g (100% yield) of the product as a clear liquid. ¹H NMR (400 MHz, CDCl₃) δ 3.69 (s, 3 H), 3.42 (t, J=6.9 Hz, 2 H), 2.36 (t, J=7.3 Hz, 2 H), 1.90 (m, 2 H), 1.80 (m, 2 H).

Dimethyl-6,7-ditelluradecanedioate²⁵ (18). A solution of Te (1.27 g, 10 mmol) and sodium hydride (0.44 g, 11 mmol) in DMF (50 mL) was stirred in the dark at 70 °C for 3 h. The purple solution was cooled to RT then a solution of methyl-5-bromopentanoate (2.15 g, 11 mmol) in DMF (10 mL) was added. After 1 h at RT, 200 mL of water was added. The reaction mixture was extracted with ether. The combined organic phases were washed with water (3 x), dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography in the dark (silica gel, CHCl₃) afforded 0.66 g (14% yield) of the title compound as a dark orange oil. The ditelluride was light sensitive and was stored in the freezer under N₂. ¹H NMR (400 MHz, CDCl₃) δ 3.68 (s, 6 H), 3.09 (t, J=7.2 Hz, 4 H), 2.36 (t, J=7.4 Hz, 4 H), 1.74 (m, 8 H).

5-(4-Methoxycarbonylbutyltellanyl)-pentanoic acid methyl ester (19). A solution of the ditelluride dimethyl-6,7-ditelluradecanedioate (18) (0.60 g, 1.24 mmol) and NaBH₄ (374 mg, 9.88 mmol) in ethanol (40 ml) was stirred in the dark at RT for 5
min. To the colorless solution was added methyl-5-bromopentanoate. The reaction mixture was stir at RT for 1 h, after which water was added, and the mixture was extracted with ether. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography in the dark (silica gel, CH₂Cl₂) afforded 0.65 g (73% yield) of the title compound as a clear liquid. IR (KBr) 3454.9, 2928.8, 2847.8, 1737.2, 1629.0, 1435.7, 1261.5, 1196.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 3.66 (s, 6 H), 2.62 (t, J=7.0 Hz, 4 H), 2.31 (t, J=7.3 Hz, 4 H), 1.72 (m, 8 H). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 51.7, 33.8, 33.5, 31.9, 27.4, 2.1. HRMS calc'd for C₁₂H₂₂TeO₄ 360.0586, found 360.0586.

That compound could also be synthesized by another method: A solution of Te (0.60 g, 4.70 mmol) and sodium hydride (0.226 g, 5.643 mmol) in DMF (25 mL) was stirred in the dark at 70 °C for 3 h. The reaction mixture was allowed to cool to RT for 30 min after which methyl-5-bromopentanoate (2.75 g, 14.11 mmol), NaBH₄ (1.42 mg, 37.62 mmol) and ethanol (30 ml) were added. The reaction was stirred at RT for 2 h, after which water was added and the pH adjusted between 3-5 withaq. HCl (1 M). The mixture was extracted with ether and the ether phase washed with water. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography in the dark (silica gel, CH₂Cl₂) afforded 0.55 g (33% yield) of the title compound as a clear liquid.

\[ \text{HOOC} \quad \text{Te} \quad \text{COOH} \]

5-(4-Carboxy-butyltellanyl)-pentanoic acid (20). In a flask were heated 5-(4-methoxycarbonyl-butyltellanyl)-pentanoic acid methyl ester (19) (0.645 g, 1.802 mmol),
NaOH (2 N, 18 mL) and ethanol (35 mL) to reflux for 30 min. Water was added and the mixture extracted with ether. The ether phase was discarded and the aqueous phase was acidified with dilute HCl. The aqueous phase was extracted with ether and the combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography in the dark (silica gel, EtOAc) afforded 0.110 g (19% yield) of the title compound as a yellow powder. IR (KBr) 3410.8, 3021.6, 2927.6, 2857.7, 1693.7, 1429.7, 1403.1, 1331.4, 1278.5, 1211.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 2.63 (t, J=7.0 Hz, 4 H), 2.40 (t, J=7.3 Hz, 4 H), 1.78 (m, 8 H). ¹³C NMR (100 MHz, CDCl₃) δ 33.3, 31.7, 27.2, 1.6. HRMS calc’d for C₁₀H₁₈TeO₄ 332.0273, found 332.0268.

(21). To a solution of 5-bromovaleric acid (0.771 g, 4.259 mmol), para-toluenesulfonic acid (0.810 g, 4.259 mmol) and DMAP (0.520 g, 4.259 mmol) in CH₂Cl₂ (30 mL) were added DCC (1.142 g, 5.537 mmol) and 4-hydroxy-TEMPO (0.734 g, 4.259 mmol). The solution was stirred at RT for 4 d. The solvent was removed. Purification by flash chromatography (silica gel, EtOAc/hexane 25/75) afforded 1.079 g (76% yield) of the title compound as a red-orange oil. IR (KBr) 3453.5, 2973.6, 1732.6, 1462.6, 1364.0, 1241.9, 1171.7 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 3.60 (br s, 2 H), 2.52 (br s, 2 H), 2.10 (br s, 2 H), 2.00 (br s, 2 H). HRMS calc’d for C₁₆H₂₅NO₃Br 334.1018, found 334.1015.
6. References


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PART II - MOLECULAR ART

When it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly as concerned with describing facts as with creating images.

Niels Bohr
CHAPTER 4

SYNTHESIS OF ANTHROPOMORPHIC MOLECULES. THE NANOPUTIANS
1. Introduction

It seems that there has been a slow divergence in the way chemists, as scientists, and non-scientific people perceive and envision material objects that constitute this world. Many people think that chemists live in their own world, a world of atoms and molecules, that chemistry is a foreign language and that chemical equations are complex algorithms. Chemists conceive an object as the final desired product obtained after a series of logical chemical procedures designed especially to give it its final structure. They have this ability to observe an entity at the macroscopic level and imagine the same entity at the nanoscopic scale. By doing so, they can rationally explain its physical characteristics. For chemists, chemical structures can generate as much beauty, inspiration and impact in their attributes as an aesthetic piece of art. $C_{60}$, which is commonly identified as a soccer ball shaped molecule, has captivated chemists for 18 years now by its electronic, physical, chemical and biological properties. “The most beautiful molecule” as it is frequently called, owes its title not only for the perfect symmetry it holds under the artistic eye but also for its intrinsic chemical “beauty”. However the full appreciation of its molecular entity by the non-chemist usually fails.

The first reason for such divergent points of view resides in the difficulty to imagine something a million times smaller than a pin head. Indeed, it is hard to appreciate the splendor within a field that builds entities that cannot be seen by the naked eye. The second reason is inherent in the fact that the structural drawings that chemists use hold little attraction to those uneducated in chemistry. The learning process of the physical and chemical concepts of this world and the matter of which it is constituted would be best accomplished through a point of view that is at the junction between the
points of view of the chemist and the layperson. Pursuing this enterprise is one step towards enriching human cognition of this world. It is to illustrate these words that this chapter stands for.

An artistic side lays within each one of us; everybody has this innate ability for beauty appreciation, even if taste and color are personal matters. The first thing that an infant learns at school, before even reading and writing, is drawing, designing, creating. Graphic expression is a very ancient way to communicate. Prehistoric men used to draw on the walls of their caverns and today those drawings are priceless. We have learned so much about the way they were living at that time by analyzing the wall paintings.

However if beauty appreciation is universal, science appreciation is not. But the former can be exploited in order to benefit the latter. The association of science with art is a concept that could already be found in primeval cultures. Centuries ago, ancient civilizations engineered sophisticated buildings decorated with delicate drawings. Stonehenge and the great cities of the Maya, Toltec and Incas were all aligned to astronomical meridians and the position of the sun and moon at the solstice and equinox days. One remarkable example in North America is the Chaco Canyon in New Mexico, where evidence of construction dating to the 800's AD has been found. Astronomy played an important role in the Chacoan culture. Chacoans designed, oriented and located their major buildings in relationship to the sun and moon. They marked the solstices, the equinoxes, solar noon and the standstill positions of the moon in thirteen light markings on petroglyphs on the Sun Dagger on the Fajada Butte.²⁴ The Sun Dagger is the only known site in the world that marks the extreme positions of both the moon and the sun (Figure 1).
Figure 1


Even more impressive is that eleven of the major Chacoan buildings are oriented to the sun and moon; and that each of the major buildings also has an internal geometry that corresponds to the relationships of the solar and lunar cycles.
More recently, Leonardo da Vinci mastered both art and science. This genius was a Florentine artist of the XV\textsuperscript{th} century, one of the great masters of the High Renaissance, who was also celebrated as a painter, sculptor, architect, engineer, and scientist. His profound love of knowledge and research was the keynote of both his artistic and scientific endeavors. His innovations in the field of painting influenced the course of Italian art for more than a century after his death, and his scientific studies—particularly in the fields of anatomy, optics, and hydraulics—anticipated many of the developments of modern science. A creator in all branches of art, a discoverer in most branches of science, and an inventor in branches of technology, da Vinci deserves, perhaps more than anyone, the title of *Homo Universalis*, Universal Man.\textsuperscript{7,8} His polyvalence is so far unrivaled.

At a very small level like the nanometer scale, there is an infinite world that has yet to be explored and shared. The beauty of chemistry is that chemical reactions are the most precise operation possible since they occur on a single atom or sets of atoms at the nanometer scale level. In order to share the beauty of the nanoscale, it is important to convey the art, form and precision of its science in a venue that can be valued by the chemist and the layperson alike. Graphical representations play a key role in this mission. Hoffmann and Laszlo\textsuperscript{9} have reflected in their writing about chemical representations. Chemical drawings are not realistic representations because they are symbols, signs of 3-D objects and atoms too tiny to see. The letters that are commonly used by chemists to represent elements are just established conventions; they are drawings, abstractions of reality. For a really accurate representation, one should take in account that atoms are not nailed down in space but moving in near harmonic motion
around those sites. Rather than stationary objects, atoms are made of a nucleus and electrons that should be represented by their probability to be at a certain place in space. With this rationale, the way a molecule is drawn is a mere representation of how the molecule actually is. So really, chemical representations are artistic representations. Chemistry and art are quite similar in the way that as long as one has imagination and knowledge, one can basically create almost anything one wants. Both rely in assembling small pieces together to create a somewhat perfect whole.

People already make use of art to communicate their chemistry. For example, Kawata et al. have designed microbulls made of polyurethane acrylate (Figure 2). These 10-μm-long, 7-μm-high bulls are the smallest model animals ever made artificially, and are about the size of a red blood cell.

**Figure 2**

![Microbulls](image)

We want to take the challenge even further than the micrometer scale, we are talking about molecules, we are dealing with the nanometer scale. Molecular Art is all
over the web.\textsuperscript{11,12} People have transformed proteins into beautiful and attractive structures by "dressing" them with fancy shapes and lively colors. The aim is to try to help the layperson relate to the nanoworld by attributing common object names to their molecules, for example rotaxanes make "molecular necklaces",\textsuperscript{13} rhodium pyridyl complexes make "molecular rectangles".\textsuperscript{14} Recently some images of microfilaments and polymers taken by scientists at University of Massachusetts, Amherst were viewed as art and displayed in an exhibit on campus.\textsuperscript{15}

In our work, we are using this process by taking everyday life objects and transposing them into the nanoscopic world. Our aim is to communicate science through object recognition, to get through to people by helping them correlate concepts in chemistry to what they already know. The synthesis of anthropomorphic molecules finds its \textit{raison d'être} in this motive. Apart from the fundamental phenomenon that objects can be recognized, we often recognize an object visually on the basis of its characteristic shape. Most objects are recognized by their shape properties. Color, texture and motion play only a secondary role.\textsuperscript{16} Objects are segmented, typically at regions of sharp concavity and the resultant parts matched against the best fitting primitive geometric shape such as cylinders, blocks, wedges and cones.\textsuperscript{17} Humans, even young infants, show a remarkable ability to rapidly recognize objects even tough they may appear at an infinite number of sizes, orientations in depth, and positions in the visual field.\textsuperscript{18} One of the most widely recognized shapes is the human body, especially the human face. Studies have demonstrated that a 3-day-old baby can recognize the face of its mother.\textsuperscript{19,20} Exploiting this phenomenon, 2-nm tall figures resembling humans have been synthesized
(Figure 3). Indeed, what better way to touch people and generate interest in chemistry than to achieve the ultimate in human miniaturization by chemical means?

Figure 3

These anthropomorphic molecules are dubbed, as a class, NanoPutians, following the lead of the Lilliputians in Jonathan Swift’s classic, *Gulliver’s Travels*. We implore the reader’s indulgence for this chapter as we are trying to emphasize the aesthetic side of chemistry. We took the liberty to employ terms like “head”, “waist”, “arms” as well as having drawn certain molecules in non-equilibrium conformations in order to enhance their rapid cognitive classification.

2. Results and discussion

2.1. Synthesis of NanoKid

NanoKid was prepared via separate syntheses of the top and bottom body-portions followed by joining at the “waist”, thereby constituting a convergent synthetic approach. The result is an example of classical synthetic chemical protocols and underscores the facility with which structures can be attained at the nanoscale using the tools of molecular synthesis.

The top-half was made as follows (Scheme 1).
1,4-Dibromobenzene was iodinated in good yield.\(^{21}\) 3,3-Dimethylbutyne was then coupled to 1 to give 2. Formylation\(^{22}\) of 2 was accomplished by lithium-halogen exchange followed by quenching with DMF to afford the aldehyde 3. The aldehyde was protected as the acetal using 1,2-ethanediol in the presence of a catalytic amount of para-toluenesulfonic acid with azeotropic removal of water via a Dean-Stark trap. Attempts to couple 4 to the bottom-half (vide infra) gave a low yield (9\%) of the desired product due to the poor reactivity of the bromoarene in the presence of the sterically encumbering ortho-moiety. The bromide was therefore exchanged with an iodide by lithium-halogen exchange and quenching with 1,2-diiodoethane to afford 5 as the top-body portion.
For the preparation of the lower-body segment, nitroaniline was brominated to afford 6 that was further converted to the diazonium salt and reduced to remove the diazo moiety (Scheme 2). Conversion of the nitro group to the amine afforded 8. Sandmeyer reaction was then used to make the diazonium salt followed by iodination to afford the dibromoiodobenzene 9. This latter compound was coupled to trimethylsilylacetylene via a Pd/Cu mixed catalyst to give 10. Analogous coupling of the dibromoarene 10 to two equivalents of 1-pentyne afforded 11. 11 was then desilylated in alkaline methanol to yield the lower half, 12, of NanoKid.
Scheme 3

The last step in the NanoKid synthesis involves the coupling of the top and bottom portions. This was accomplished by once again using the Pd/Cu-catalyzed protocol\textsuperscript{26} to afford 4.6 billion trillion NanoKids (13), each with the structure shown in Scheme 3.

2.2. Synthesis of NanoPutians

NanoKid (13) can now serve as the progenitor of the NanoPutians.
A facile procedure using microwave irradiation\textsuperscript{27-30} was used for the head-conversion reactions. NanoKid (13) with an excess of a 1,2- or 1,3-diol, in the presence of a catalytic amount of \textit{para}-toluenesulfonic acid, was irradiated for a few minutes, after which a new NanoPutian was “born” (Figure 4). Table 1 shows the obtained yields of the conversion of NanoKid (13) into NanoPutians \textbf{14-22} using microwave irradiation in the presence of selected diols.
Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Diol&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Equiv. of Diol</th>
<th>Irradiation (min)</th>
<th>NanoPutian</th>
<th>Yield (%)</th>
<th>Diastereomeric ratio&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="#" alt="Diol1" /></td>
<td>20</td>
<td>7</td>
<td>14</td>
<td>91</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td><img src="#" alt="Diol2" /></td>
<td>11</td>
<td>13</td>
<td>15</td>
<td>25&lt;sup&gt;d&lt;/sup&gt;</td>
<td>55 : 45</td>
</tr>
<tr>
<td>3</td>
<td><img src="#" alt="Diol3" /></td>
<td>100</td>
<td>1</td>
<td>16</td>
<td>85</td>
<td>1 : 1</td>
</tr>
<tr>
<td>4</td>
<td><img src="#" alt="Diol4" /></td>
<td>20</td>
<td>7</td>
<td>17</td>
<td>94</td>
<td>10 : 3</td>
</tr>
<tr>
<td>5</td>
<td><img src="#" alt="Diol5" /></td>
<td>5</td>
<td>10</td>
<td>18</td>
<td>87</td>
<td>10 : 3</td>
</tr>
<tr>
<td>6</td>
<td><img src="#" alt="Diol6" /></td>
<td>9</td>
<td>9</td>
<td>19</td>
<td>24&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.2 : 1</td>
</tr>
<tr>
<td>7</td>
<td><img src="#" alt="Diol7" /></td>
<td>20</td>
<td>16</td>
<td>20</td>
<td>90</td>
<td>17 : 12 : 12 : 9</td>
</tr>
<tr>
<td>8</td>
<td><img src="#" alt="Diol8" /></td>
<td>15</td>
<td>10</td>
<td>21</td>
<td>84</td>
<td>1.6 : 1</td>
</tr>
<tr>
<td>9&lt;sup&gt;c&lt;/sup&gt;</td>
<td><img src="#" alt="Diol9" /></td>
<td>22</td>
<td>---</td>
<td>22</td>
<td>9&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
</tbody>
</table>

<sup>a</sup>The cyclic diols for entries 5 and 7 were prepared by catalytic OsO<sub>4</sub> dihydroxylation of the corresponding alkenes. The diols for entries 2 and 6 were prepared by reductive pinacol coupling of the 1,4- and 1,5-diketones with SmI<sub>2</sub> and Mg/TiCl<sub>4</sub>, respectively.

<sup>b</sup>Ratios determined by <sup>1</sup>H NMR using the diastereotopic acetal protons that were consistently well separated.

<sup>c</sup>NanoChef (22) was synthesized using chlorotrimethylsilane (5 equiv) in dichloromethane.

<sup>d</sup>Yields based on recovered NanoKid (13) for entries 2, 6 and 9 were 33%, 58% and 20%, respectively.

This includes NanoAthlete (14), NanoPilgrim (15), NanoGreenBeret (16), NanoJester (17), NanoMonarch (18), NanoTexan (19) NanoScholar (20) and NanoBaker (21). By using this microwave irradiation method, conventional solvents such as benzene and long reaction times are obviated. Decomposition resulted when the NanoChef (22) synthesis was attempted under the microwave conditions (Table I, entry 9). This was probably due
to polymerization involving the electron rich catechol and the aldehyde-based oxonium intermediate. Rather, a procedure employing catechol and chlorotrimethylsilane was efficacious,\textsuperscript{31} albeit low yielding; only 23 billion billion NanoChefs were formed. Although there are no microscopy tools, including scanning probe microscopy, currently available that could assess chemical structure at these dimensions, the NanoPutians were unequivocally characterized using routine spectroscopic (NMR and FTIR) and mass spectrometric analysis.

In a separate combinatorial experiment, we sought to make the entire NanoPutian population at once by starting with NanoKid (13) and adding all the appropriate diols (except catechol) in a single flask to generate 14-21 in one microwave oven reaction. Indeed, the conversion proceeded as planned in 4 min and the formation of 14-21 was confirmed by mass spectrometric analysis of the reaction mixture where the mass of each Nanoputian was detected. However, since a few of the figures have the same molecular weight, further confirmation was obtained using $^1$H NMR peak matching of the mixture against the individual NanoPutian spectra that had previously been obtained.

Figure 5 shows the electron cloud-based space-filling model of the Nanoputians in which the colors of the atoms were modified to enhance the visual recognition properties of the NanoPutians, although chemists routinely use these types of features with rigorous uniformity for each atom type. Artistic liberty has been taken to promote the rapid recognition of the NanoPutians.
Figure 5

NanoKid (13)   NanoAthlete (14)   NanoPilgrim (15)

NanoGreenBeret (16)   NanoJester (17)   NanoMonarch (18)

NanoTexan (19)   NanoScholar (20)   NanoBaker (21)   NanoChef (22)
Figure 6, entitled "Keep on truckin'" shows NanoKid (13) in its energy-minimized conformation that was determined using molecular mechanics (Spartan). The hydrogen atoms and multiple bonds are not shown, merely the carbon and oxygen atomic placement in the most stable energy conformation as would exist in a vacuum where 13 is the only molecule present. Note the comparison of the stick figure drawn for 13 in Scheme 3 to the molecular mechanics energy-minimized form of 13. Interestingly, the rigidity of the backbone molecular structure causes the conformation in Figure 6 to be quite similar to the visually recognizable form drawn for 13 in Scheme 3, although the minimized structure gives the appearance of walking or "strutting" to NanoKid.

Figure 6

2.3. Synthesis of the NanoToddler

Following the same route as for NanoKid, NanoToddler was synthesized (Scheme 4).
1-Butyne was coupled to 10 to give 23 in good yield, followed by deprotection with potassium carbonate and methanol. The upper body 5 and the lower part 24 were then coupled to afford the NanoToddler 25 in 78% yield. Figure 7 shows the electron cloud-based space filling model of the NanoToddler.

Figure 7

2.4. Synthesis of NanoBalletDancers
Scheme 5

Scheme 5 outlines the synthesis of the NanoBalletDancers. 2,5-dibromoaniline was diiodinated using a procedure by Wilson. The resulting aniline 26 was then deaminated via diazotization and nitrogen expulsion using isoamyl nitrite and DMF. 27 was coupled to 3,3-dimethylbutyne in order to put on the arms to furnish 28, which was then treated with tert-butyl lithium and DMF in order to get the aldehyde. This reaction is not selective as it yields equal amounts of the 2 aldehyde products 29 and 30. After separation, compound 29 was protected with ethylene glycol to give 31.
Scheme 6

The bottom part was obtained by formylation of dibromoiodobenzene 9 in moderate yield to give 32 (Scheme 6). Activation of the bromides by the aldehyde for the Sonogashira coupling of the feet 1-pentyne afforded excellent yield of 33.
Compound 31 was lithiated with butyllithium and the formed anion was quenched with the aldehyde 33 to give the alcohol 34 (Scheme 7). Then, following a procedure by Hart\textsuperscript{33} the alcohol was converted to the xanthate 35 in good yield by treatment with NaH, CS\textsubscript{2} and methyl iodide. The reduction of the “waist” with tri-n-butyltin hydride in presence of a catalytic amount of AIBN afforded the
NanoBalletDancer 36 in fair yield. And finally to complete the synthesis, the microwave head exchange procedure proceeded in excellent yield to furnish the NanoBalletDancer 37. Figure 8 shows the electron cloud-based space-filling model of the NanoBalletDancers 36 and 37.

Figure 8

![Electron Cloud-Based Space-Filling Model](image)

2.5. Synthesis of a NanoPutian Chain

In an effort to unite the NanoPutians into an extended "hand-holding" chain, an AB-polymer target was sought (Figure 9).

Figure 9

![AB-Polymer Target](image)
Scheme 8

The synthesis of the NanoPutian’s with “hand” moieties for the chain starts with the coupling of dibromodiodobenzene 1 with the protected alkyne 38 (Scheme 8), which was obtained by treatment of 3-butyn-1-ol with tert-butyldimethylsilyl chloride, to afford 39 in excellent yield. The precursor to the acetal that serves as a head was then obtained by forming an aldehyde by lithiation followed by quenching with DMF. This furnishes 40.
The Sonogashira\textsuperscript{26} coupling of the aldehyde 40 with the bottom part alkyne 12 was accomplished in excellent yield to afford the headless NanoKid 41 (Scheme 9). Acetal protection using the conventional method using the Dean-Stark trap gave very poor yield (6\%). Rather a procedure using chlorotrimethylsilane\textsuperscript{31} followed by the deprotection of the alcohols furnished 42 in 36\% over 2 steps. After the first step, a fraction of the TBS protected alcohols was deprotected. Compound 42 seems to be
sensitive to moisture and possibly light. It was used in the next few hours or kept under nitrogen in the dark and the in freezer. Using the same procedure, the aldehyde 41 was also converted to the hydroxyl-tipped NanoAthlete 43 in good yield over 2 steps. Here again, after the first step, most of the TBS protected alcohols were deprotected. Compound 43 seems to be more stable to hydrolysis than its homologous 42.

In order to have an ester linkage between 42 and 43, the terminal alcohols of one of the two compounds needed to be oxidized. However, several attempts to oxidize the alcohols failed to cleanly afford the diacid. To circumvent the oxidation problem, the structure of the target polymer was modified; the ester linkage was replaced by a carbonate moiety (Scheme 10).
Following a procedure by Konakahara, the $p$-nitrophenylchloroformate 44 was synthesized using diphosgene and Hünigs’ base. This chloroformate was then attacked by the alcohol 43 to give 45 in very good yield. Finally, by repeating the same reaction with the NanoKid 42, 3 compounds were obtained. The dimers 46 and 47 were afforded in 21\% and 23\%, respectively, although they could not be conclusively distinguished between each other by NMR. The third compound was the polymer 48. The regioisomeric pairs of hetero-dimers have differing arm directions. If we let a hyphen, "−", be the arrangement of arms within a single NanoPutian while the double headed arrow, "↔", is the bonding pattern between any two NanoPutians, then the arm directions in these products are as follows: 46 is down→up↔up→down, 47 is up→down↔up→down, and AB-polymer 48 consisting of three regioisomeric bonding patterns, namely down→up↔up→down; up→down↔up→down; up→down↔down→up (Scheme 10). In 46 there is a mirror plane between the two parts of the dimer (except the heads). In 47, there is an axis of symmetry down the middle of the dimer (except for the heads). 46 (less polar) and 47 were the only two non-baseline spots by TLC using 1:1
EtOAc/hexane. 46 and 47, after flash chromatography, had $M_n = 775$ and 745 with $M_w = 800$ and 765, respectively, by size exclusion chromatography (SEC) relative to polystyrene. Their actual molecular weights of 1130.5 were confirmed by mass spectrometry (MALDI) for each. The silica gel chromatographic baseline material consisted of higher oligomers and polymers which were then flushed from the chromatography column using EtOAc. LDI-MS showed a range of peaks centered around 47,500 which corresponds to the 42-mer, while the SEC showed 48 to have $M_n = 23,500$ and a $M_w = 36,600$, relative to polystyrene. Figure 10 shows the electron cloud-based space filling model of the dimers 46 and 47.

Figure 10

3. The NanoKids™ Educational Outreach Project

The synthesis of these anthropomorphic molecules inspired us to use them for an educational outreach project. The next generation of research professionals is sitting on middle school benches right now. Children of that age are an easy demographic target because their minds are being shaped, their personalities start to develop and their attention is easy to captivate. The resources to motivate, enthrall their interest and attract them to science have to be found. Scientists are often viewed as nerds or even “mad
scientists”. They are usually unpopular among the youngsters, almost as much as members in the chess club. People generally label chemists as reclusive and unconcerned about their personal appearance. One stereotype often seen in movies is the old, skinny scientist with glasses, long white hair, and slumped shoulders. Most often, the character is anti-social and has neglected his children. This lack of interest by young people in being a chemist is also due in part to the concern about the dangers of chemistry, like getting hurt by an explosion or developing a cancer because of handling dangerous chemicals. Another commonplace belief is that chemistry is difficult to learn. Many people think that one have to be really smart to be a chemist. Chemistry is no more difficult than any other field. It is these stereotypes and concerns that we have to address in order to keep our profession alive.

For all these reasons, we decided to give our profession a hand. The NanoKids™ Educational Outreach Project has been created for this aim. The project is directed by Suzanne Lamminen. Its mission is to increase the students’ comprehension of chemistry, physics, biology, and materials science at the molecular level, to provide teachers with conceptual tools to teach nanoscale science and the emerging molecular technology. The project is intended to demonstrate that art and science can combine to facilitate learning for students with diverse learning styles and interests. To accomplish this mission, 24 DVD-videos starring the NanoKids™ themselves will be created. Each DVD will be comprised of a 10-minute 3-D animated video lesson/adventures. The first two lessons are finished and are currently being introduced in selected HISD (Houston Independent School District) schools throughout Houston. Eight public and 3 independent schools are participating this year. To complement the DVD lessons, an interactive digital student
workbook with information, encompassing exercises, games, and sound-bites is available to help students digest and integrate the lessons. For teachers, a guide is available containing a step-by-step explanation of the DVDs as well as a walk through workbook and exercises. A website will also be in place so that students can go online and learn and teachers can receive help if they have questions. And finally, last but not the least, a parents' guide with a brief introduction to the subject matter will be available so that parents can help their children in their homework and maybe at the same time learn about science.

Figure 11 contains some still pictures of the first DVD.

**Figure 11**

Atkis and Marski, the NanoKids™  
NanoKids™ size comparison

DNA explanation  
Dr Tour reading the NMR spectrum
4. Summary

The synthesis of anthropomorphic molecules has been accomplished in monomeric, dimeric and polymeric forms. This new class of molecules, called NanoPutians, has inspired an educational outreach project to educate and entertain children in middle school.
5. Experimental Procedures

General. All reactions were performed in an oven-dried flask and under an atmosphere of nitrogen unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Toluene, triethylamine, methylene chloride were distilled over calcium hydride before use. Silica gel plates were 250 μm thick, 40 F₂₅₄ grade from EM science. Silica gel was grade 60 (230-400 mesh) from EM Science. Melting points were taken on a Mel-Temp (Laboratory Devices) apparatus. FT-IR spectra were taken on a Nicolet Avatar 360 spectrometer. ¹H NMR spectra were observed at 400 MHz and ¹³C NMR spectra were observed at 100 MHz on a Brüker AVANCE 400 spectrometer. Mass spectrometry was performed by Terry Marriott at Rice University’s mass spectrometry lab. Combustion analyses were obtained from Altantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. The microwave model is Sharp Carousel R-510C, used on high setting.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).²⁶,²⁹ 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 all solids including the aryl halide, bis(triphenylphosphine) palladium(II) chloride (2-5 mol % based on the aryl halide) and copper(I) iodide (4-10 mol % based on the aryl halide). The vessel was sealed with a rubber septum, evacuated and backfilled with dry nitrogen (3×). THF and remaining liquids were added followed by N,N-diisopropylamine or triethylamine. The reaction heated, if necessary, until complete. The reaction vessel was cooled to room
temperature, quenched with water or a saturated solution of NH₄Cl and extracted with Et₂O. The combined organic layers were dried over anhydrous MgSO₄, filtered and the solvent removed in vacuo.

**General Procedure for the Deprotection of Trimethylsilyl-Protected Alkynes.**

To a round bottom flask equipped with a stir bar were added the protected alkyne, potassium carbonate (10 equiv per protected alkyne), methanol, and methylene chloride. The reaction was heated, and upon completion the reaction mixture was diluted with methylene chloride and washed with brine (3×). The organic layer was dried over MgSO₄, and the solvent removed in vacuo.

![Structural formula](image)

**2,5-Dibromo-1,4-diodobenzene**¹¹ (1). A solution of p-dibromobenzene (19.50 g, 82.69 mmol) in concentrated sulfuric acid (250 mL) under air was heated to 125-135 °C. Iodine (80.87 g, 318.63 mmol) was added portion-wise as the reaction mixture is heated. The mixture was allowed for 1 d and cooled to RT. It was then poured into ice water. The solid was filtered and washed with a saturated solution of sodium bisulfite and a saturated solution of sodium bicarbonate. Recrystallization from benzene and purification by flash chromatography (silica gel, CH₂Cl₂) afforded 32.88 g (81% yield) of the title compound as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 2 H).
2,5-Bis(3,3-dimethylbutynyl)-1,4-dibromobenzene (2). See the general Pd/Cu procedure. To a solution of 2,5-dibromo-1,4-diiodobenzene (4.288 g, 8.79 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.379 g, 0.541 mmol), copper(I) iodide (0.206 g, 1.08 mmol) in THF (40 mL) were added Et₃N (20 mL) and cold (0 °C) 3,3-dimethyl-1-butyne (2.22 mL, 18.03 mmol). The mixture was stirred at RT for 20 h. Purification by flash chromatography (silica gel, hexanes) afforded 2.43 g (70% yield) of the title compound as a white solid. Mp: 154-158 °C. IR (KBr) 2968.9, 2922.4, 2895.6, 2863.5, 2242.6, 2207.6, 1463.2, 1358.6, 1263.8, 1199.5, 1061.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (s, 2 H), 1.34 (s, 18 H). ¹³C NMR (100 MHz, CDCl₃) δ 135.8, 126.3, 123.7, 106.0, 30.7, 28.4. HRMS calc’d for C₁₈H₂₀Br₂: 393.9932, found: 393.9917.

2,5-Bis(3,3-dimethylbutynyl)-4-bromobenzaldehyde (3). To a solution of 2,5-bis(3,3-dimethylbutynyl)-1,4-dibromobenzene (2.43 g, 6.135 mmol) in THF (30 mL) cooled to −78 °C under nitrogen was added dropwise n-BuLi (2.48 M, 2.72 mL). The reaction mixture was allowed to stir at −78 °C for 1 h. To this mixture was added DMF (0.48 mL, 6.135 mmol) pre-dried over molecular sieves. The reaction mixture was allowed to stir for another 1 h and then warmed to RT for 4 h. It was then diluted with water and extracted with Et₂O. The combined organic phases were washed with brine,
dried over MgSO₄, filtered and evaporated. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 1/1) afforded 1.77 g (83% yield) of the title compound as a white solid. Mp: 98-102 °C. IR (KBr) 2967.4, 2925.7, 2897.2, 2864.5, 2837.4, 2734.6, 2238.6, 2213.4, 1699.4, 1586.4, 1519.9, 1466.2, 1379.7, 1362.2, 1010.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.31 (s, 1 H), 7.76 (s, 1 H), 7.58 (s, 1 H), 1.28 (s, 9 H), 1.27 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 190.0, 136.2, 134.1, 131.1, 130.7, 126.6, 125.9, 107.8, 105.7, 77.1, 73.6, 30.5, 28.2, 28.1. HRMS calc’d for C₁₉H₂₁OBr: 344.0776, found: 344.0772.

2,5-Bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)bromobenzene (4). To a round bottom flask equipped with a Dean-Stark trap for azeotropic removal of the water were added 2,5-(3',3'-dimethylbutynyl)-4-bromobenzenaldehyde (16.14 g, 46.75 mmol), ethylene glycol (5.20 mL, 93.49 mmol), para-toluenesulfonic acid (0.133 g, 0.701 mmol) and toluene (50 mL). The reaction mixture was heated to reflux for 3 d. It was then diluted with water. The pH was adjusted to 10 with 50% NaOH and the solution was extracted with ether. The combined organic phases were dried over MgSO₄, filtered and evaporated. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 60/40) afforded 13.98 g (77% yield) of the title compound as a white solid. Mp: 128-134 °C. IR (KBr) 2967.5, 2926.9, 2897.6, 2866.2, 2239.9, 1594.3, 1532.7, 1470.1, 1398.1, 1362.5, 1268.3, 1075.3 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 1 H), 7.56 (s, 1 H), 6.06 (s, 1 H),
4.17 (m, 2 H), 4.03 (m, 2 H), 1.34 (s, 9 H), 1.32 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.6, 135.4, 130.4, 125.6, 125.2, 123.6, 105.7, 104.7, 101.3, 77.9, 75.1, 65.4, 30.7, 28.3, 28.2. HRMS calc’d for C$_{21}$H$_{25}$O$_2$Br: 388.1038, found 388.1032. Anal. Calc’d: C, 64.78; H, 6.47; Found: C, 64.91; H, 6.57.

2,5-Bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene (5). To a solution of 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)bromobenzene (0.51 g, 1.310 mmol) in THF (25 mL) cooled to –78 °C under nitrogen was added dropwise n-BuLi (2.48 M, 0.57 mL). The reaction mixture was allowed to stir at –78 °C for 30 min. To this solution was added a solution of 1,2-diiodoethane (0.554 g, 1.965 mmol) in THF (10 mL). The reaction mixture was allowed to warm to RT overnight. It was diluted with a saturated solution of sodium bicarbonate and extracted with ether. The combined organic phases were washed with brine, dried over MgSO$_4$, filtered and evaporated in vacuo. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$/hex 1/1) afforded 0.49 g (86%) of the title product as a white solid. Mp: 172-178 °C. IR (KBr) 2967.3, 2926.0, 2896.1, 2866.1, 2235.8, 1531.1, 1465.2, 1396.7, 1362.1, 1266.8, 1074.3 cm$^{-1}$. $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (s, 1 H), 7.51 (s, 1 H), 6.05 (s, 1 H), 4.16 (m, 2 H), 4.03 (m, 2 H), 1.35 (s, 9 H), 1.32 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.7, 138.5, 129.6, 129.2, 123.5, 105.6, 103.9, 101.4, 101.3, 81.7, 74.8, 65.4, 30.8, 30.7, 28.3, 28.3. HRMS calc’d for C$_{21}$H$_{25}$IO$_2$: 436.0899, found: 436.0895.
2,6-Dibromo-4-nitroaniline$^{22}$ (6). A solution of $p$-nitroaniline (20.08 g, 145.37 mmol) in glacial acetic acid (179 mL) at 65 °C was vigorously stirred during the addition of bromine (14.93 mL, 290.51 mmol) in glacial acetic acid (110 mL) under air within 4 hours. A very heavy precipitate formed after about one-third of the bromine had been added and the precipitate was re-dissolved by the addition of hot water (20 ml), and then the remaining two thirds of the bromine solution was added. After complete addition, the reaction mixture was poured with stirring into a slurry of water and ice. After thorough washing with water and air-drying the reaction afforded 41.90 g (97%) of the title compound as a yellow-green solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.36 (s, 1 H), 5.30 (br s, 2 H).

3,5-Dibromonitrobenzene$^{22}$ (7). To a stirred, boiling (90 °C) mixture of 2,6-dibromo-4-nitroaniline (19.23 g, 65.01 mmol), ethanol (220 mL) and concentrated sulfuric acid (22 mL), sodium nitrite (14.46 g, 209.60 mmol) under air was added in portions as rapidly as foaming would permit. The reaction mixture was stirred at 90°C for 36 h. The mixture was allowed to cool, poured into ice water and the solids were collected by filtration and washed with water. The 3,5-dibromobenzene was separated from the remaining inorganic salts by dissolving it in boiling ethanol and filtering the hot
solution, from which 14.56 g (80% yield) of the orange product crystallized on cooling.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.33 (d, \(J=1.7\) Hz, 2 H), 8.01 (t, \(J=1.7\) Hz, 1 H).

![3,5-Dibromoaniline](image)

**3,5-Dibromoaniline**\(^{22}\) (8). To a solution of 3,5-dibromonitrobenzene (4.84 g, 17.24 mmol) in ethanol (40 mL) and THF (40 mL) stirred under air was added slowly tin(II) chloride dihydrate (19.22 g, 85.29 mmol). The mixture was allowed to stir at RT for 20 h. The solvent was then evaporated in vacuo, and an aqueous solution of sodium hydroxide was added. After 2 h of stirring, the reaction was extracted with Et\(_2\)O. The combined organic phases were dried over MgSO\(_4\), filtered, and the solvent removed in vacuo. The reaction afforded 3.80 g (89% yield) of the title compound as a brown solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.02 (t, \(J=1.5\) Hz, 1 H), 6.75 (d, \(J=1.5\) Hz, 2 H), 3.78 (br s, 2 H).

![3,5-Dibromoiodobenzene](image)

**3,5-Dibromoiodobenzene** (9). 3,5-Dibromoaniline (13.0 g, 51.81 mmol) was dissolved in concentrated sulfuric acid (100 mL) at 50 °C under air. After the solution was cooled to 0 °C, sodium nitrite (7.15 g, 103.62 mmol) was added portion-wise with continuous stirring, maintaining the temperature below 5 °C. The reaction was allowed to stir at 0 °C for 2 h. The solution was poured onto ice and KI (25.80, 155.43 mmol) in 125 mL of water was added. The mixture was then heated to 80 °C for 15 min. The solid was removed by filtration and washed with cold water. Recrystallization from ethanol gave an
orange solid (13.20 g, 70% yield). Mp: 120–126 °C. IR (KBr) 3095.3, 3060.8, 1546.9, 1398.4, 1095.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J=1.7 Hz, 2 H), 7.65 (t, J=1.7 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 138.5, 133.6, 123.4, 94.4 ppm. HRMS calc’d for C₆H₃Br₂I: 359.7646, found: 359.7652.

3,5-Dibromo(trimethylsilylethynyl)benzene (10). See the general Pd/Cu procedure. To a solution of 3,5-dibromoiodobenzene (13.20 g, 36.484 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.023 g, 1.46 mmol), copper(I) iodide (0.694 g, 3.644 mmol) in THF (130 mL) were added Et₃N (40 mL) and trimethylsilylacetylene (5.20 mL, 36.48 mmol). The mixture was stirred at RT for 2 d. Purification by flash chromatography (silica gel, hexanes) afforded 11.0 g (91% yield) of the title compound as a clear liquid. IR (NaCl) 3073.9, 2959.6, 2898.0, 2167.4, 1578.0, 1540.0, 1418.8, 1401.5, 1249.9, 1103.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (t, J=1.8 Hz, 1 H), 7.59 (d, J=1.8 Hz, 2 H), 0.25 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 134.2, 133.3, 126.5, 122.5, 101.6, 97.6, -0.3. HRMS calc’d for C₁₁H₁₂Br₂Si: 331.9056, found: 331.9053.
3,5-(1-Pentynyl)-1-(trimethylsilylethynyl)benzene (11). See the general Pd/Cu procedure. To a solution of bis(triphenylphosphine)palladium(II) dichloride (0.926 g, 1.32 mmol), copper(I) iodide (0.628 g, 3.30 mmol) in THF (100 mL) and Et₃N (70 mL) were added 3,5-dibromo(trimethylsilylethynyl)benzene (11.0 g, 33.12 mmol) via a cannula and 1-pentyne (6.86 mL, 69.56 mmol). The mixture was heated to 75 °C for 3 d. After checking by TLC, additional bis(triphenylphosphine)palladium(II) dichloride (0.502 g, 0.716 mmol), copper(I) iodide (0.304 g, 1.59 mmol), THF (40 mL), Et₃N (20 mL) and 1-pentyne (3.26 mL, 33.12 mmol) were added. The reaction was allowed to stir for another 20 h at 80 °C. Purification by flash chromatography (silica gel, hexanes) afforded 6.89 g of the title compound as a clear liquid and 2.86 g of the mono coupled product. This monocoupled product was taken to a reaction flask with bis(triphenylphosphine)palladium(II) dichloride (0.188 g, 0.269 mmol), copper(I) iodide (0.102 g, 0.538 mmol), 1-pentyne (1.2 mL, 12.17 mmol) and Et₃N (30 mL) in THF (40 mL). The mixture was stirred at 70 °C for 3 d. After the same work-up and purification method as above, it afforded 0.84 g of the product. The overall yield for this reaction is 76%. IR (NaCl) 2962.7, 2933.7, 2902.1, 2872.2, 2836.0, 2233.64, 2155.3, 1581.1, 1460.4, 1413.4, 1250.2, 1170.7 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J=1.5 Hz, 2 H), 7.36 (t, J=1.5 Hz, 1 H), 2.36 (t, J=7.0 Hz, 4 H), 1.63 (sext, J=7.2 Hz, 4 H), 1.04 (t, J=7.3 Hz, 6 H), 0.25 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 134.4, 133.8, 124.4, 123.3,
103.7, 94.9, 91.2, 79.4, 22.1, 21.3, 13.5, -0.2. HRMS calc'd for C\textsubscript{21}H\textsubscript{26}Si: 306.1804, found: 306.1806.

![Molecular structure](image)

3,5-(1-Pentynyl)-1-ethynylbenzene (12). See the general TMS-protected alkyne deprotection procedure. To a solution of 3,5-(1-pentynyl)-1-(trimethylsilylethynyl)benzene (1.729 g, 5.649 mmol) in MeOH (40 mL) and CH\textsubscript{2}Cl\textsubscript{2} (40 mL) was added K\textsubscript{2}CO\textsubscript{3} (7.80 g, 56.49 mmol). The solution was stirred at RT for 2 h. The reaction afforded 1.32 g (100% yield) of the title compound as a yellow oil. IR (NaCl) 3294.9, 2963.2, 2933.1, 2871.6, 2835.2, 2233.5, 1581.9, 1460.8, 1415.1, 1380.0, 1339.5. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.41 (s, 3 H), 3.06 (s, 1 H), 2.37 (t, J=7.0 Hz, 4 H), 1.62 (sext, J=7.2 Hz, 4 H), 1.05 (t, J=7.4 Hz, 6 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 134.8, 133.9, 124.6, 122.3, 91.5, 82.3, 79.2, 77.7, 22.0, 21.3, 13.5. HRMS calc'd for C\textsubscript{18}H\textsubscript{18}: 234.1408, found: 234.1406.
"NanoKid" (13). To a solution of 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene (3.93 g, 9.017 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.253 g, 0.361 mmol), copper(I) iodide (0.137 g, 0.721 mmol) in THF (40 mL) were added Et₃N (20 mL) and 3,5-(1-pentynyl)-1-ethynylbenzene (2.07 g, 8.846 mmol) in THF (20 mL) via a cannula. The mixture was stirred at RT for 16 h and at 34 °C for 1 h. The solvent was evaporated in vacuo. The residue was diluted with water and extracted with Et₂O. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH₂Cl₂ 60/40) afforded 4.31 g of the title compound as a yellow oil but was contaminated with 12% of 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene. This contaminated material was re-subjected to the reaction by adding 3,5-(1-pentynyl)-1-ethynylbenzene (0.299 g, 1.278 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.034 g, 0.048 mmol), copper(I) iodide (0.020 g, 0.105 mmol), TEA (10 mL) and THF (60 mL). The mixture was allowed to stir at 50 °C for another 2 d. The solvent was evaporated in vacuo. The residue was diluted with water and extracted with Et₂O. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH₂Cl₂ 60/40) afforded 4.17 g (85% yield) of the title compound as a yellow sticky solid. IR
(NaCl, CHCl₃) 2966.0, 2930.6, 2897.2, 2869.0, 2230.0, 1580.8, 1473.5, 1454.3, 1397.7 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (s, 1 H), 7.53 (s, 1 H), 7.46 (d, J=1.5 Hz, 2 H), 7.38 (t, J=1.5 Hz, 1 H), 6.11 (s, 1 H), 4.19 (m, 2 H), 4.05 (m, 2 H), 2.38 (t, J=7.0 Hz, 4 H), 1.60 (sext, J=7.2 Hz, 4 H), 1.37 (s, 9 H), 1.34 (s, 9 H), 1.05 (t, J=7.2 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 135.4, 134.2, 133.6, 129.5, 125.7, 125.5, 124.5, 123.5, 122.3, 105.0, 104.2, 101.4, 92.0, 91.3, 88.4, 79.4, 77.8, 75.5, 65.5, 31.0, 30.8, 28.3, 22.1, 21.3, 13.5. HRMS calc'd for C₃₉H₄₂O₂: 542.3185, found: 542.3183. Anal. Calc'd: C, 86.30; H, 7.80; Found: C, 86.27; H, 7.82.

“NanoAthlete” (14). In a small vial, NanoKid (0.243 g, 0.448 mmol), paratoluene sulfonic acid monohydrate (0.003 g, 0.014 mmol), 2,2-dimethyl-1,3-propanediol (0.932 g, 8.956 mmol) and MgSO₄ (0.113 g, 0.939 mmol) were subjected to microwave irradiation for 7 min (heating 2 min at a time). The reaction mixture was then diluted with a saturated solution of NaHCO₃ and extracted with ether. The combined organic phases were dried over MgSO₄, filtered and evaporated in vacuo. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 60/40) afforded 239 mg (91% yield) of the title compound as a yellow sticky solid. IR (NaCl, CHCl₃) 2965.4, 2929.8, 2899.5, 2866.9, 2228.3, 1579.8, 1455.0, 1401.4, 1384.1, 1362.4, 1266.7, 1108.0 cm⁻¹. ¹H NMR (400
MHz, CDCl$_3$) $\delta$ 7.72 (s, 1 H), 7.53 (s, 1 H), 7.47 (d, $J=1.5$ Hz, 2 H), 7.38 (t, $J=1.5$ Hz, 1 H), 5.69 (s, 1 H), 3.80 (d, $J=11$ Hz, 2 H), 3.64 (d, $J=11$ Hz, 2 H), 2.38 (t, $J=7.0$ Hz, 4 H), 1.62 (sext, $J=7.2$ Hz, 4 H), 1.37 (s, 9 H), 1.36 (s, 9 H), 1.34 (s, 3 H), 1.05 (t, $J=7.2$ Hz, 6 H), 0.81 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.9, 135.0, 134.1, 133.5, 129.3, 125.9, 125.3, 124.5, 123.5, 121.5, 104.4, 104.1, 99.7, 91.8, 91.2, 88.5, 79.4, 78.0, 77.9, 75.6, 31.0, 30.9, 30.2, 28.23, 28.19, 23.15, 22.0, 21.8, 21.3, 13.4. HRMS calc’d for C$_{42}$H$_{48}$O$_2$: 584.3654, found: 584.3648. Anal. Calc’d: C, 86.26; H, 8.27; Found: C, 86.19; H, 8.25.

1,2-Dimethylocyclobutandediol. In a 500 mL three neck flask equipped with a condenser, a solution of Sml$_2$ (1.4 M in THF, 350 mL) was heated to reflux. To this solution acetonilacetone (3.43 mL, 29.17 mmol) was added slowly over 2 h. The dark blue solution turned yellow and was allowed to stir at reflux for 24 h. The reaction mixture was then quenched with 1 N HCl (100 mL), the aqueous layer saturated with NaCl and extracted with ether. The combined organic phases were dried over MgSO$_4$, filtered and evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/hex 60/40) afforded 464 mg (14% yield) of the title compound. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.50 (br s, 2 H), 1.95 (m, 2 H), 1.79 (m, 2 H), 1.26 (s, 6 H).
"NanoPilgrim"(15). In a small vial, NanoKid (136 mg, 0.251 mmol), para-toluenesulfonic acid monohydrate (3 mg, 0.013 mmol), 1,2-dimethyl-1,2-cyclobutanediol (320 mg, 2.759 mmol) and MgSO₄ (60 mg, 0.501 mmol) were subjected to microwave irradiation for 13 min (heating 2 min at a time). The reaction mixture was purified flash chromatography (silica gel, hex/CH₂Cl₂ 60/40) to afford 38 mg (25% yield, 33% yield based on recovered starting material) of the title compound as a yellow sticky oil. The product was inseparable from the aldehyde which complicated charaterization. The product was obtained as an inseparable 45:55 mixture of diastereoisomers. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 0.45 H), 7.60 (s, 0.55 H), 7.53 (s, 0.55 H), 7.52 (s, 0.45 H), 7.46 (d, J=1.4 Hz, 4 H), 7.37 (t, J=1.4 Hz, 2 H), 6.47 (s, 0.55 H), 6.21 (s, 0.45 H), 2.38 (t, J=7.0 Hz, 8 H), 2.21 (pseudo pent, J=5.4 Hz, 4 H), 2.00 (pseudo q, J=5.4 Hz, 2 H), 1.85 (pseudo q, J=5.4 Hz, 2 H), 1.61 (sext, J=7.2 Hz, 8 H), 1.39-1.35 (m, 36 H), 1.05 (m, 24 H). HRMS calc’d for C₄₃H₄₆O₂: 596.3654, found: 596.3649.
"NanoGreenBeret" (16). In a small vial, NanoKid (0.206 g, 0.380 mmol), para-
toluenesulfonic acid monohydrate (0.014 g, 0.075 mmol), 1,2-propanediol (2.78 mL, 37.69 mmol) and MgSO₄ (0.500 g, 4.15 mmol) were subjected to microwave irradiation for 1 min. The reaction mixture was then diluted with a saturated solution of NaHCO₃ and extracted with ether. The combined organic phases were dried over MgSO₄, filtered and evaporated in vacuo. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 60/40) afforded 179 mg (85% yield) of the title compound as a yellow sticky solid. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2966.0, 2231.2, 1584.7, 1531.6, 1451.4, 1379.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 0.5 H), 7.60 (s, 0.5 H), 7.53 (s, 2 H), 7.47 (t, J=1.2 Hz, 4 H), 7.38 (t, J=1.2 Hz, 2 H), 6.23 (s, 0.5 H), 6.13 (s, 0.5 H), 4.45 (pseudo sext, J=6.1 Hz, 0.5 H), 4.35 (m, 1 H), 4.13 (dd, J=6.5, 7.4 Hz, 0.5 H), 3.63 (t, J=7.4 Hz, 0.5 H), 3.58 (dd, J=6.5, 7.4 Hz, 0.5 H), 2.38 (t, J=7.0 Hz, 8 H), 1.60 (sext, J=7.3 Hz, 8 H), 1.42 (d, J=6.1 Hz, 3 H), 1.372 (s, 4.5 H), 1.366 (s, 4.5 H), 1.36 (s, 3 H), 1.34 (s, 4.5 H), 1.33 (s, 4.5 H), 1.05 (t, J=7.3 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 138.3, 135.3, 134.2, 133.5, 129.6, 129.4, 125.74, 125.68, 125.65, 125.5, 124.5, 123.5, 122.4, 122.2, 105.0, 104.9, 104.1, 101.4, 100.6, 92.0, 91.3, 88.41, 88.39, 79.4, 77.8, 75.6, 75.5, 73.7, 72.5, 72.1, 71.3, 31.0, 30.8, 28.2, 22.0,
21.3, 18.4, 18.2, 13.4. HRMS calc'd for C_{40}H_{44}O_2: 556.3341, found: 556.3341. Anal. Calc'd: C, 86.29; H, 7.97; Found: C, 86.16; H, 8.03.

"NanoJester" (17). In a small vial, NanoKid (0.254 g, 0.468 mmol), para-toluenesulfonic acid monohydrate (0.003 g, 0.014 mmol), cis-cyclopentanediol (0.974 g, 9.54 mmol) and MgSO_4 (0.113 g, 0.936 mmol) were subjected to microwave irradiation for 6.5 min (heating 1 min at a time). The reaction mixture was then diluted with a saturated solution of NaHCO_3 and extracted with ether. The combined organic phases were dried over MgSO_4, filtered and evaporated in vacuo. Purification by flash chromatography (silica gel, hex/CH_2Cl_2 60/40) afforded 257 mg (94% yield) of the title compound as a yellow sticky oil. The product was obtained as an inseparable 10:3 mixture of diastereoisomers. IR (NaCl, CHCl_3) 2964.9, 2868.5, 2230.5, 1581.1, 1491.0, 1456.6, 1403.2, 1361.8 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl_3) (major) \(\delta\) 7.69 (s, 1 H), 7.52 (s, 1 H), 7.43 (d, \(J=1.5\) Hz, 2 H), 7.39 (t, \(J=1.5\) Hz, 1 H), 5.94 (s, 1 H), 4.65 (d, \(J=3.5\) Hz, 2 H), 2.38 (t, \(J=7.0\) Hz, 4 H), 2.10 (m, 2 H), 2.07 (m, 2 H), 1.62 (sext, \(J=7.2\) Hz, 4 H), 1.49 (m, 2 H), 1.39 (s, 9 H), 1.34 (s, 9 H), 1.05 (t, \(J=7.4\) Hz, 6 H). \(^13\)C NMR (100 MHz, CDCl_3) (major) \(\delta\) 137.2, 134.9, 134.1, 133.4, 129.3, 125.7, 125.7, 124.5, 123.4, 122.4, 104.7, 104.0, 101.6, 100.0, 91.2, 88.4, 81.9, 79.3, 77.8, 75.3, 33.0, 30.9, 30.69, 30.66,
28.14, 28.10, 22.0, 21.2, 13.3. HRMS calc'd for C_{42}H_{40}O_{2} 582.3498, found: 582.3491. Anal. Calc'd: C, 86.55; H, 7.96; Found: C, 86.74; H, 7.88.

Cis-1,2-cycloheptanediol.\textsuperscript{41} To a 50 mL round bottom flask under nitrogen were added N-methylmorpholine-N-oxide (3.61 g, 30.84 mmol), cycloheptene (3 mL, 25.70 mmol), acetone (5 mL), H_{2}O (12.6 mL) and osmium tetroxide (0.077 mmol). The flask was equipped with a glass stopper and the reaction was shaken (automated) vigorously at RT for 3 d. The acetone was evaporated \textit{in vacuo} and the residue was diluted with brine and extracted with CH_{2}Cl_{2}. The combined organic phases were dried over MgSO_{4}, filtered and the solvent evaporated \textit{in vacuo}. Purification by flash chromatography (silica gel, EtOAc/hex 70/30) afforded 371 mg (11\% yield) of the title product as a white solid.

\textsuperscript{1}H NMR (400 MHz, CDCl_{3}) \delta 3.88 (m, 2 H), 2.08 (d, J=4.0 Hz, 2 H), 1.82-1.39 (m, 10 H).

"NanoMonarch" (18). In a small vial, NanoKid (99 mg, 0.182 mmol), para-toluenesulfonic acid monohydrate (0.004 g, 0.021 mmol), \textit{cis}-1,2-cycloheptanediol (0.109 g, 0.838 mmol) and MgSO_{4} (0.044 g, 0.365 mmol) were subjected to microwave
irradiation for 10 min (heating 1 min at a time). The reaction mixture was then diluted with a saturated solution of NaHCO₃ and extracted with ether. The combined organic phases were dried over MgSO₄, filtered and evaporated in vacuo. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 60/40) afforded 97 mg (87% yield) of the title compound as a yellow sticky oil. The product was obtained as a 10:3 ratio of diastereoisomers. IR (NaCl, CHCl₃) 2966.7, 2931.7, 2867.4, 2230.5, 1581.1, 1453.5, 1411.1, 1361.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) (major) δ 7.67 (s, 1 H), 7.51 (s, 1 H), 7.47 (d, J=1.5 Hz, 2 H), 7.38 (t, J=1.5 Hz, 1 H), 6.08 (s, 1 H), 4.31 (m, 2 H), 2.38 (t, J=7.0 Hz, 4 H), 2.04-1.64 (m, 8 H), 1.60 (sext, J=7.2 Hz, 4 H), 1.37 (s, 9 H), 1.34 (s, 9 H), 1.32 (m, 2 H), 1.05 (t, J=7.2 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 137.7, 135.1, 134.2, 133.5, 129.7, 125.8, 125.7, 124.5, 123.5, 122.5, 104.7, 104.0, 99.8, 91.2, 88.5, 80.2, 79.9, 79.4, 77.9, 75.5, 31.0, 30.8, 30.4, 28.23, 28.20, 24.2, 22.0, 21.3, 13.4. HRMS calc’d for C₄₄H₅₀O₂ 610.3811, found: 610.3811. Anal. Calc’d: C, 86.51; H, 8.25; Found: C, 86.50; H, 8.29.

**Heptan-2,6-dione.**⁴² In a 500 mL round bottom flask, a suspension of MnCl₂ (12.28 g, 97.63 mmol) in THF was cooled to 0 °C. MeLi (58.6 mL, 82 mmol) was added slowly. The reaction mixture was stirred at 0 °C for 30 min then at RT for 30 min. It was then cooled to −10 °C, and CuCl (0.386 g, 3.91 mmol) and glutaryl dichloride (5 mL, 39.05 mmol) were added. The reaction was allowed to warm to RT overnight. It was then diluted with a saturated solution of NH₄Cl and extracted with ether. The combined organic phases were dried over MgSO₄, filtered and evaporated in vacuo. Purification by
flash chromatography (silica gel, EtOAc/hex 50/50) afforded 2.63 g (52% yield) of the desired dione. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.47 (t, $J$=7.0 Hz, 4 H), 2.13 (s, 6 H), 1.83 (pent, $J$=7 Hz, 2 H).

![Chemical structure](image)

**Cis-1,2-Dimethyl-1,2-cyclopentanediol.** In a 250 round bottom flask, a suspension of magnesium turnings (1.06 g, 43.60 mmol) (prewashed with 5% HCl, water, acetone and ether) in THF (80 mL) was cooled to −78 °C. TiCl$_4$ (4.4 mL, 40 mmol) was added to this suspension and the yellow solution was allowed to warm to room temperature where it turned black. After 2 h, the reaction mixture was cooled to −40 °C and a solution of heptan-2,6-dione (0.512 g, 4.0 mmol) in THF (5 mL) was slowly added. The reaction mixture was allowed to stir at −40 °C for 2 h. The black solution was quenched with water, the solvent evaporated and filtered over celite. The black filtrate was extracted with ether. The combined organic phases were dried over MgSO$_4$, filtered and evaporated in vacuo. Purification by flash chromatography (silica gel, EtOAc/hex 60/40) afforded 130 mg (25% yield) of the desired diol. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.29 (s, 2 H), 1.96-1.89 (m, 2 H), 1.81-1.67 (m, 4 H), 1.20 (s, 6 H).
"NanoTexan" (19). In a small vial, NanoKid (59 mg, 0.109 mmol), para-toluenesulfonic acid monohydrate (few crystals), 1,2-dimethyl-1,2-cyclopentanediol (130 mg, 1.0 mmol) and MgSO₄ (50 mg, 0.748 mmol) were subjected to microwave irradiation for 9 min (heating 1 min at a time). The reaction mixture was purified flash chromatography (silica gel, hex/CH₂Cl₂ 60/40) to afford 34 mg (24% yield, 58% yield based on recovered starting material) of the title compound as a yellow sticky oil. The desired product was inseparable from the deprotected NanoBoy (aldehyde), which made the full characterization difficult. The product was obtained as an inseparable 1:3.2 mixture of diastereoisomers. $^1$H NMR (400 MHz, CDCl₃) δ (major) 7.70 (s, 1 H), 7.51 (s, 1 H), 7.46 (d, $J$=1.5 Hz, 2 H), 7.37 (t, $J$=1.5 Hz, 1 H), 6.06 (s, 1 H), 2.38 (t, $J$=7.0 Hz, 4 H), 2.16 (m, 2 H), 1.64 (sext, $J$=7.0 Hz, 4 H), 1.39-1.34 (m, 28 H), 1.06 (t, $J$=7.3 Hz, 6 H). HMRS calc’d for C₄₄H₅₀O₂: 610.3811, found: 610.3811.

4-Methyl-cis-1,2-cyclohexanediol.⁴⁴ To a 100 mL round bottom flask under nitrogen were added $N$-methylmorpholine-$N$-oxide (5.77 g, 49.28 mmol), 4-methylcyclohexene (5 mL, 41.07 mmol), acetone (8 mL), H₂O (20.1 mL) and osmium
tetraoxide (0.123 mmol). The flask was equipped with a glass stopper and the reaction was automatically shaken vigorously at RT for 3 d. The acetone was evaporated *in vacuo* and the residue was diluted with brine and extracted with Et₂O. The combined organic phases were dried over MgSO₄, filtered and the solvent evaporated *in vacuo*. Purification by flash chromatography (silica gel, EtOAc/hex 60/40) afforded 1.31 g (24% yield) of the title product as a white liquid. The product was obtained as an inseparable mixture of diastereoisomers in a 1:1 ratio. ¹H NMR (400 MHz, CDCl₃) (both isomers) δ 3.95 (m, 2 H), 3.61 (m, 2 H), 2.20 (br s, 4 H), 1.90 (m, 2 H), 1.82-1.63 (m, 6 H), 1.45-1.14 (m, 6 H), 0.93 (d, J=6.3 Hz, 3 H), 0.88 (d, J=6.3 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) (both isomers) δ 72.0, 71.9, 69.8, 68.9, 39.5, 37.5, 32.6, 31.2, 30.6, 28.7, 27.6, 25.3, 22.3, 21.7.

"NanoScholar" (20). In a small vial, NanoKid (92 mg, 0.170 mmol), para-toluenesulfonic acid monohydrate (few crystals), 4-methyl-*cis*-1,2-cyclohexanediol (443 mg, 3.408 mmol) and MgSO₄ (41 mg, 0.341 mmol) were subjected to microwave irradiation for 16 min (heating 2 min at a time). The reaction mixture was purified flash chromatography (silica gel, hex/CH₂Cl₂ 60/40) to afford 93 mg (90% yield) of the title compound as a yellow sticky oil. The product was obtained as an inseparable 17:12:12:9 mixture of diastereoisomers. IR(NaCl, CHCl₃) 2966.62, 2869.1, 2231.7, 1581.6, 1455.6,
1361.8, 1265.2, 1103.3 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) (four isomers) \(\delta\) 7.67 (s, 1 H), 7.66 (s, 1 H), 7.56 (s, 1 H), 7.55 (s, 1 H), 7.52 (m, 4 H), 7.47 (m, 8 H), 7.38 (m, 4 H), 6.43 (s, 1 H), 6.42 (s, 1 H), 6.16 (s, 1 H), 6.15 (s, 1 H), 4.30 (m, 8 H), 2.38 (t, \(J=7.0\) Hz, 16 H), 2.28 (m, 4 H), 2.0-1.7 (m, 12 H), 1.63 (sext, \(J=7.0\) Hz, 16 H), 1.55-1.45 (m, 4 H), 1.37-1.32 (m, 72 H), 1.30-1.15 (m, 8 H), 1.05 (t, \(J=7.3\) Hz, 24 H), 0.95 (m, 12 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (four isomers) \(\delta\) 140.9, 140.8, 139.2, 139.1, 135.41, 135.37, 134.4, 133.8, 129.6, 129.4, 129.2, 125.9, 125.82, 125.79, 125.73, 125.4, 124.8, 123.7, 122.8, 122.2, 105.5, 105.4, 105.3, 104.3, 104.2, 101.1, 99.9, 99.8, 92.1, 92.0, 91.5, 88.7, 79.6, 78.2, 77.4, 76.7, 76.1, 76.0, 75.8, 75.8, 75.5, 74.8, 74.6, 74.3, 73.4, 39.0, 36.0, 35.8, 35.5, 34.9, 31.3, 31.2, 31.1, 31.0, 30.6, 29.9, 29.4, 29.3, 29.1, 28.6, 28.5, 27.0, 26.9, 26.7, 26.5, 26.4, 25.5, 22.9, 22.44, 22.39, 22.3, 22.0, 21.8, 21.5, 14.3, 13.7. HMRS calc’d for C\(_{44}\)H\(_{50}\)O\(_2\): 610.3811, found: 610.3812. Anal. Calc’d: C, 86.51; H, 8.25; Found: C, 86.36; H, 8.27.

“NanoBaker” (21). In a small vial, NanoKid (128 mg, 0.236 mmol), para-toluenesulfonic acid monohydrate (few crystals), \textit{cis}-1,2-cyclohexanediol (411 mg, 3.54 mmol) and MgSO\(_4\) (116 mg, 0.964 mmol) were subjected to microwave irradiation for 10 min (heating 2 min at a time). The reaction mixture was purified flash chromatography
(silica gel, hex/CH₂Cl₂ 60/40) to afford 118 mg (84% yield) of the title compound as a yellow sticky oil. The product was obtained as an inseparable 1:1.63 mixture of diastereoisomers. IR(NaCl, CHCl₃) 2969.4, 2869.4, 2252.8, 1581.9, 1455.5, 1362.6, 1265.5, 1153.3 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ (major) 7.68 (s, 1 H), 7.52 (s, 1 H), 7.46 (m, 2 H), 7.37 (m, 1 H), 6.15 (s, 1 H), 4.30 (m, 1 H), 4.20 (m, 1 H), 2.38 (t, J=6.9 Hz, 4 H), 1.87-1.70 (m, 4 H), 1.69-1.58 (m, 8 H), 1.37 (s, 9 H), 1.36 (s, 9 H), 1.05 (t, J=7.3 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) (two isomers) δ 140.7, 138.9, 135.2, 135.2, 134.2, 133.6, 129.2, 128.9, 125.7, 125.6, 125.6, 125.2, 124.5, 123.5, 122.6, 122.0, 105.3, 105.1, 104.1, 104.0, 100.7, 99.6, 91.9, 91.8, 91.2, 88.5, 79.4, 78.0, 77.2, 75.7, 75.6, 75.1, 74.6, 31.0, 30.8, 28.33, 28.27, 28.26, 27.6, 27.1, 22.1, 21.3, 21.1, 20.7, 13.5. HMRS calc'd for C₄₃H₄₆O₂: 596.3654, found: 596.3654.

"NanoChef" (22). To 100 mL round bottom flask equipped with a condenser, NanoKid (223 mg, 0.411 mmol), catechol (0.998 g, 9.063 mmol) and MgSO₄ (0.498 g, 4.137 mmol) were added. The atmosphere was removed and replaced with nitrogen. To the flask were added trimethylsilyl chloride (0.26 mL, 2.05 mmol) and freshly distilled CH₂Cl₂. The mixture was allowed to stir at reflux for 42 h. A 5% solution of NaHCO₃ was added and the reaction was extracted with CH₂Cl₂. The combined organic phases
were dried over MgSO\textsubscript{4}, filtered and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hex/ CH\textsubscript{2}Cl\textsubscript{2} 60/40) afforded 23 mg (9% yield, 20% recovered) of the title product as a white solid. Mp: 117-124 °C. IR (KBr) 2965.8, 2929.0, 2899.5, 2867.0, 2224.6, 1580.0, 1481.1, 1350.4, 1229.5 1022.2 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDC\textsubscript{3}) \textdelta 7.63 (s, 1 H), 7.60 (s, 1 H), 7.47 (d, J=1.5 Hz, 2 H), 7.40 (t, J=1.5 Hz, 1 H), 7.22 (s, 1 H), 6.89 (m, 4 H), 2.39 (t, J=7.0 Hz, 4 H), 1.62 (sext, J=7.2 Hz, 4 H), 1.35 (s, 9 H), 1.29 (s, 9 H), 1.05 (t, J=7.2 Hz, 6 H). \textsuperscript{13}C NMR (100 MHz, CDC\textsubscript{3}) \textdelta 147.6, 136.2, 135.7, 134.4, 133.6, 129.8, 126.8, 125.9, 124.6, 123.3, 122.2, 121.7, 108.6, 108.0, 106.0, 104.9, 92.7, 91.4, 88.1, 79.4, 75.0, 30.9, 30.7, 28.3, 22.1, 21.3, 13.5. HRMS calc’d for C\textsubscript{43}H\textsubscript{42}O\textsubscript{2}: 590.3185, found: 590.3178.

**Mixture of NanoPutians.** In a small vial, NanoKid (163 mg, 0.30 mmol) was mixed with cis-1,2-dimethyl-1,2-cyclopentanediol (78 mg, 0.60 mmol), cis-cyclopentane-1,2-diol (61 mg, 0.60 mmol), cis-1,2-dimethylcyclobutane-1,2-diol (69 mg, 0.60 mmol), cis-cycloheptane-1,2-diol (78 mg, 0.60 mmol), 4-methyl-cis-1,2-cyclohexanediol (78 mg, 0.60 mmol), cis-1,2-cyclohexanediol (69 mg, 0.60 mmol), 1,2-propanediol (0.044 mL, 0.60 mmol), 2,2-dimethyl-1,3-propanediol (62 mg, 0.60 mmol), para-toluenesulfonic acid monohydrate (few crystals) and MgSO\textsubscript{4} (130 mg, 1.08 mmol). The reaction mixture was subjected to microwave irradiation for 4 min. The crude reaction was purified by flash chromatography (silica gel, hex/CH\textsubscript{2}Cl\textsubscript{2} 66/33), which afforded 161 mg of a mixture of all the NanoFigures.
3,5-(1-butynyl)-1-(trimethylsilylethylnyl)benzene (23). See the general Pd/Cu procedure. A solution of 3,5-dibromo(trimethylsilylethylnyl)benzene 10 (1.91 g, 5.75 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.202 g, 0.288 mmol), copper(I) iodide (0.109 g, 0.575 mmol) in THF (30 mL) and Et₃N (15 mL) was cooled to −70 °C. To this solution was added cold (-70 °C) 1-butyne (3 mL, 37.63 mmol). The mixture was allowed to warm to room temperature and heated to 74 °C for 2 d. After checking by TLC, more of the cold 1-butyne (2.4 mL, 30.10 mmol) was added. The reaction was allowed to stir for another 2 d. Purification by flash chromatography (silica gel, hexanes) afforded 1.34 g (84% yield) of the title compound as a clear liquid. IR (NaCl) 2976.2, 2938.1, 2241.0, 2160.8, 1580.7, 1454.5, 1413.5, 1316.1, 1249.9 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J=1.5 Hz, 2 H), 7.35 (t, J=1.5 Hz, 1 H), 2.40 (q, J=7.5 Hz, 4 H), 1.22 (t, J=7.5 Hz, 6 H), 0.24 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 134.4, 133.8, 124.4, 123.4, 103.7, 94.9, 92.6, 78.5, 13.8, 13.0, -0.2. HRMS calc'd for C₁₉H₂₂Si: 278.1491, found: 278.1486.

3,5-butynyl-1-ethenylbenzene (24). See the general TMS-protected alkyne deprotection procedure. To a solution of 3,5-butynyl-1-(trimethylsilylethylnyl)benzene 23 (0.450 g, 1.616 mmol) in MeOH (20 mL) and CH₂Cl₂ (20 mL) under air was added
K₂CO₃ (2.21 g, 15.98 mmol). The solution was stirred at RT for 2 h. The reaction afforded 0.65 g (99% yield) of the title compound as a yellow oil. That was too unstable to attain its complete characterization data. IR (KBr) 3301.2, 2977.6, 2937.4, 2239.7, 1582.3, 1453.8, 1316.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (m, 3 H), 3.05 (s, 1 H), 2.40 (q, J=7.5 Hz, 4 H), 1.22 (t, J=7.5 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 135.0, 134.2, 124.7, 122.6, 93.1, 82.5, 14.0, 13.3. HRMS calc’d for C₁₆H₁₄: 206.1095, found: 206.1094.

"NanoToddler"(25). See the general Pd/Cu procedure. To a solution of 2-(2,5-bis(3,3-dimethylbutynyl)-4-iodo-phenyl)-[1,3]-dioxolane 5 (0.49 g, 1.123 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.039 g, 0.056 mmol), copper(I) iodide (0.021 g, 0.112 mmol) in THF (20 mL) were added Et₃N (20 mL) and 3,5-butynyl-1-ethynylbenzene 24 (0.253 g, 1.228 mmol) in THF (20 mL) via a cannula. The mixture was stirred at 80 °C for 42 h. Purification by flash chromatography (silica gel, hexanes/CH₂Cl₂ 60/40) afforded 0.45 g (78% yield) of the title compound as a yellow oil. IR (KBr) 2970.4, 2895.4, 2235.5, 1580.8, 1473.9, 1454.9, 1396.7, 1316.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (s, 1 H), 7.53 (s, 1 H)7.46 (d, J=1.4Hz, 2 H), 7.38 (t, J=1.4Hz, 1 H), 6.11 (s, 1 H), 4.18 (m, 2 H), 4.05 (m, 2 H), 2.40 (q, J=7.5 Hz, 4 H), 1.37 (s, 9 H), 1.34 (s, 9 H), 1.23 (t, J=7.5 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 135.4, 134.2,
3,6-dibromo-2,4-diiodoaniline (26). In 500 mL round bottom flask equipped with an addition funnel, 2,5-dibromoaniline (9.52 g, 37.96 mmol), sodium acetate (6.85 g, 83.50 mmol) and acetic acid (60 mL) were stirred at RT under air. To this suspension was added slowly ICl (4.26 mL, 83.50 mmol) in acetic acid (15 mL). The mixture was heated to 80 °C for 5 h, diluted with water and stirred for 1 more hour after which it was stood overnight. The suspension was filtered, washed with a saturated solution of sodium bisulfite and water. After drying, it afforded a brown solid. NMR shows a mixture of product and monoiiodinated byproduct in a 1:0.3 ratio. The mixture was mixed with sodium acetate (6.85 g, 83.50 mmol) and acetic acid (80 mL). To this suspension was added slowly ICl (2.9 mL, 56.94 mmol) in acetic acid (20 mL). The mixture was heated to 80 °C for 18 h, diluted with water and stirred for 1 more hour after which it was stood overnight. The suspension was filtered, washed with a saturated solution of sodium bisulfite and water. After drying, it afforded a brown solid (16.80 g, 88% yield). Mp: 136-148 °C. IR (KBr) 3488.6, 2925.0, 2854.4, 1597.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1 H), 75.65 (br s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 141.1, 135.6, 105.3, 90.2, 82.9 ppm. HRMS calc'd for C₁₂H₅Br₂I₂N: 500.6722, found: 500.6721.
2,5-dibromo-1,3,diiodobenzene (27). Isoamyl nitrite (5.4 mL, 40.11 mmol) and DMF (20 mL) were heated to 65 °C under air. To this mixture was slowly added 3,6-dibromo-2,4-diiodoaniline 31 (16.80 g, 33.42 mmol) in DMF (80 mL). The reaction mixture was stirred for 24 h, diluted with HCl (1 M, 60 mL), extracted with CHCl₃. The combined organic phases were dried over MgSO₄, filtered and evaporated in vacuo. The NMR of the crude shows a mixture of starting material and product. The crude was subjected to the same reaction for 2 d at 70 °C. The reaction mixture was diluted with HCl (1 M, 60 mL), and water. The light brown solid was filtered, recrystallized from ethanol and after purification by flash chromatography (silica gel, hex) it afforded 7.07 g (43% yield) of the title compound as a white solid. Mp: 126–130 °C. IR (KBr) 3071.3, 1530.7, 1517.1, 1370.0, 1350.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 142.3, 135.5, 121.8, 100.4 ppm. HRMS calc’d for C₆H₂Br₂I₂: 485.6613, found: 485.6612.

2,6-Bis(3,3-dimethylbutynyl)-1,4-dibromobenzene (28). See the general Pd/Cu procedure. To a solution of 2,5-dibromo-1,3,diiodobenzene (1.78 g, 3.650 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.256 g, 0.365 mmol), copper(I) iodide (0.139 g, 0.730 mmol) in THF (50 mL) were added Et₃N (15 mL) and 3,3-dimethyl-1-
butyne (0.99 mL, 8.03 mmol). The mixture was stirred at RT for 1 d. Purification by flash chromatography (silica gel, hexanes) afforded 1.08 g (75% yield) of the title compound as a white solid. Mp: 124–138 °C. IR (KBr) 2968.8, 2927.2, 2899.0, 2866.3, 2225.6, 1558.4, 1544.0, 1393.2 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (s, 2 H), 1.34 (s, 18 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 134.3, 128.4, 127.8, 119.8, 105.1, 86.5, 30.9, 28.5 ppm. HRMS calc’d for C\(_{18}\)H\(_{20}\)Br\(_2\): 393.9932, found: 393.9938.

![Chemical structures](image)

**4-bromo-2,6-(3,3-dimethylbutynyl)benzaldehyde (29) and 4-bromo-3,5-(3,3-dimethylbutynyl)benzaldehyde (30).** To 2,6-bis(3,3-dimethylbutynyl)-1,4-dibromobenzene (4.47 g, 11.28 mmol) in THF (50 mL) cooled to −78 °C under nitrogen was added dropwise t-BuLi (1.7 M, 13.94 mL). The reaction mixture was allowed to stir at −78 °C for 30 min. To this mixture was added DMF (1.75 mL, 22.56 mmol) pre-dried over molecular sieves. The reaction mixture was allowed to warm to RT overnight. It was then diluted with water and extracted with Et\(_2\)O. The combined organic phases were washed with brine, dried over MgSO\(_4\), filtered and evaporated. Purification by flash chromatography (silica gel, hex/CH\(_2\)Cl\(_2\) 75/25) afforded 1.47 g (38% yield) of the first compound and 1.45 g (37% yield) of the second compound as white solids. 1\(^{st}\) product 29: Mp: 97-100 °C. IR (KBr) 2967.9, 2923.6, 2898.2, 2863.6, 2757.6, 2229.5, 1705.5, 1553.6, 1475.2, 1453.6, 1390.2, 1263.9 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.54 (s, 1 H), 7.54 (s, 2 H), 1.35 (s, 18 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 190.5, 135.7, 135.2, 127.7, 126.8, 107.2, 75.5, 30.8, 28.6 ppm. HRMS calc’d for C\(_{19}\)H\(_{21}\)BrO: 344.0776,
found: 344.0779. 2\textsuperscript{d} product 30: Mp: 102-114 °C. IR (KBr) 2968.5, 2928.3, 2900.8, 2866.9, 2704.2, 2230.6, 1706.9, 1568.6, 1455.7, 1426.3, 1378.9, 1361.1, 1263.0 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.90 (s, 1 H), 7.76 (s, 2 H), 1.36 (s, 18 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 190.6, 135.7, 135.8, 132.0, 128.2, 105.5, 77.7, 30.9, 28.6 ppm. HRMS calc’d for C\textsubscript{19}H\textsubscript{21}BrO: 344.0776, found: 344.0774.

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\begin{align*}
\text{3,5-Bis(3,3-dimethylbut-1-ynyl)-4-(1,3-dioxolane)bromobenzene (31). To a} \\
\text{round bottom flask equipped with a Dean-Stark trap for azeotropic removal of the water} \\
\text{were added 4-bromo-2,6-bis(3,3-dimethylbutynyl)benzaldehyde 29 (1.52 g, 4.40 mmol),} \\
\text{ethylene glycol (1.47 mL, 26.41 mmol), \textit{para}-toluenesulfonic acid (0.042 g, 0.22 mmol) } \\
\text{and toluene (100 mL). The reaction mixture was heated to reflux for 1 d. It was then} \\
\text{diluted with aq. K}_2\text{CO}_3. The solution was extracted with ether. The combined organic} \\
\text{phases were dried over MgSO}_4, \text{filtered and evaporated. Purification by flash} \\
\text{chromatography (silica gel, hex/CH}_2\text{Cl}_2 \text{60/40) afforded 1.22 g (71\% yield) of the title} \\
\text{compound as a white solid.}) \text{. Mp: 96-98 °C. IR (KBr) 2966.8, 2926.1, 2890.8, 2221.3,} \\
1560.1, 1383.2, 1256.7, 1101.9, 1080.3 \text{ cm}\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.47 (s, 2 H), 6.31 (s, 1 H), 4.29 (m, 2 H), 4.06 (m, 4 H), 1.32 9s, 18 H). \textsuperscript{13}C NMR (100 MHz,} \\
\text{CDCl}_3 \(\delta\) 137.4, 135.8, 126.1, 122.2, 104.7, 102.2, 76.1, 66.4, 31.1, 28.4 ppm. HRMS} \\
calc’d for C\textsubscript{21}H\textsubscript{25}BrO\textsubscript{2}: 388.1038, found: 388.1030.
3,5-dibromobenzaldehyde (32). To 3,5-dibromobenzaldehyde (6.037 g, 16.686 mmol) in THF (50 mL) cooled to -78 °C under nitrogen was added dropwise n-BuLi (2.39 M, 7.68 mL). The reaction mixture was allowed to stir at -78 °C for 30 min. To this mixture was added DMF (1.55 mL, 20.023 mmol) pre-dried over molecular sieves. The reaction mixture was allowed to warm to RT overnight. It was then diluted with water and extracted with Et₂O. The combined organic phases were washed with brine, dried over MgSO₄, filtered and evaporated. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 50/50) afforded 1.25 g (28% yield) of the title compound as a white solid. Mp: 86-90 °C. IR (KBr) 3079.1, 1704.1, 1281.7 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1 H), 7.95 (d, J=1.6 Hz, 2 H), 7.92 (t, J=1.6 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 189.4, 139.8, 139.1, 131.4, 124.2 ppm. HRMS calc’d for C₇H₄Br₂O: 263.8609, found: 263.8602.

3,5-Bis(pentynyl)benzaldehyde (33). See the general Pd/Cu procedure. To a solution of 3,5-dibromobenzaldehyde 32 (2.60 g, 9.855 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.691 g, 0.985 mmol), copper(I) iodide (0.375 g, 1.971 mmol) in THF (50 mL) were added Et₃N (20 mL) and 1-pentyne (5.83 mL, 59.13 mmol). The mixture was stirred at 80 °C for 2 d. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 50/50) afforded 2.19 g (93% yield) of the title
compound as a yellow liquid. IR (KBr) 2964.5, 2933.9, 2872.9, 2233.9, 1702.4, 1591.4, 1448.2, 1384.0, 1339.3, 1152.9 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.93 (s, 1 H), 7.77 (d, $J$=1.5 Hz, 2 H), 7.64 (s, 1 H), 2.40 (t, $J$=4.3 Hz, 4 H), 1.64 (sext, $J$=2.8 Hz, 4 h), 1.06 (t, $J$=7.4 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 191.4, 140.0, 136.6, 131.6, 125.6, 92.7, 79.2, 22.2, 21.6, 13.7 ppm. HRMS calc'd for C$_{17}$H$_{18}$O: 238.1358, found: 238.1359.

[3,5-Bis-(3,3-dimethyl-but-1-ynyl)-4-[1,3]dioxolan-2-yl-phenyl]-3,5-di-pent-1-ynyl-phenyl]methanol (34). To a solution of 3,5-bis(3,3-dimethylbut-1-ynyl)-4-(1,3-dioxolane)bromobenzene 31 (1.747 g, 4.487 mmol) in THF (25 mL) at -78 °C was added n-Buli (2.39 M, 2.44 mL) dropwise. The reaction mixture was stirred for 30 min. Then 3,5-Bis(pentynyl)benzaldehyde 33 (1.176 g, 4.936 mmol) was added. The reaction mixture was allowed to warm to RT. It was then diluted with aq. NaOH and extracted with Et$_2$O. The combined organic phases were dried over MgSO$_4$, filtered and evaporated. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$) afforded 1.97 g (78% yield) of the title compound as a white sticky solid. Mp: 64-80 °C. IR (KBr) 3446.2, 2966.3, 2930.9, 2898.9, 2870.4, 2228.0, 1589.4, 1455.7, 1389.6, 1361.8, 1259.1, 1202.1, 1088.2 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (t, $J$=1.5 Hz, 1 H), 7.30 (s, 2 H), 7.24 (d, $J$=1.3 Hz, 2 H), 6.36 (s, 1 H), 5.62 (d, $J$=2.7 Hz, 1 H), 4.31 (m, 2 H), 4.07 (m,
2 H), 2.37 (t, J=7.0 Hz, 4 H), 2.18 (d, J=2.7 Hz, 1 H), 1.62 (sext, J=7.3 Hz, 4 H), 1.32 (s, 18 H), 1.04 (t, J=7.3 Hz, 6 H) $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.8, 143.4, 137.5, 134.2, 131.2, 129.2, 124.6, 103.5, 102.4, 91.2, 80.2, 74.8, 66.3, 31.2, 28.4, 22.3, 21.6, 13.8 ppm. HRMS calc’d for C$_{38}$H$_{44}$O$_3$: 548.3290, found: 548.3290.

![Chemical structure](image)

Dithiocarbonic acid O-[[3,5-bis-(3,3-dimethyl-but-1-ynyl)-4-[1,3]dioxolan-2-yl-phenyl]-[3,5-di-pent-1-ynyl-phenyl]-methyl] ester S-methyl ester (35). Using a 3-neck round bottom flask, a solution of the alcohol 34 (0.195 g, 0.346 mmol) in THF (10 mL) was made. To this solution were added NaH (71 mg, 1.778 mmol) and a pinch of imidazole. After warming up to 60 °C for 30 min, the solution turns milky yellow-orange. CS$_2$ (0.13 mL, 2.13 mmol) was added. After 30 min at 60 °C, MeI (0.13 mL, 2.13 mmol) was added. The milky yellow solution was stirred for another 30 min after which is was quenched with brine and extracted with CH$_2$Cl$_2$. The combined organic phases were dried over MgSO$_4$, filtered and evaporated. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$/hex 33/66 then CH$_2$Cl$_2$) afforded 0.188 g (83% yield) of the title compound as a white sticky solid. IR (KBr) 2966.8, 2929.9, 2899.7, 2870.5, 2225.4, 1589.8, 1451.7, 1428.3, 1361.7, 1198.0, 1088.8, 1058.8 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (s, 1 H), 7.38 (t, J=1.4 Hz, 1 H), 7.29 (s, 2 H), 7.22 (d, J=1.3 Hz, 2 H), 6.36 (s, 1 H), 4.30 (m, 2 H), 4.06 (m, 2 H), 2.60 (s, 3 H), 2.37 (t, J=7.0 Hz, 4 H), 1.62 (sext, J=7.3 Hz, 4 H),
1.32 (s, 18 H), 1.04 (t, J=7.3 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 214.7, 139.2, 138.9, 138.4, 134.8, 132.0, 129.7, 124.8, 124.8, 103.9, 102.3, 91.6, 83.3, 79.9, 66.3, 31.1, 28.4, 22.3, 21.6, 13.8. HRMS calc'd for C$_{46}$H$_{46}$O$_3$S$_2$: 638.2888, found: 638.2887.

**NanoBalletDancer (36).** To a solution of the xanthate 35 (1.86 mg, 0.2849 mmol), 2,2'-azabis(2-methylpropionitrile) (pinch) in toluene (7 mL) was added tri-$n$-butyltin hydride (0.196 mL, 0.728 mmol). This solution was heated to 80 °C for 3 h. The solvent was evaporated in vacuo and the residue was diluted with water and extracted with ether. The combined organic phases were dried over MgSO$_4$, filtered and evaporated. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$/hex 50/50) afforded 0.103 g of the product mixed with some starting material. The mixture is resubmitted to the same amount of reagents for 7 h instead of 3 h. The solvent is evaporated *in vacuo* and the residue is diluted with water and extracted with ether. The combined organic phases were dried over MgSO$_4$, filtered and evaporated. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$/hex 50/50) afforded 67 mg (43% yield) of the title compound as a white sticky solid. IR (KBr) 2968.7, 2900.7, 2871.4, 2252.1, 1586.6, 1457.1, 1391.2, 1088.0 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (s, 1 H), 7.15 (s, 2 H), 7.07 (s, 2 H), 6.36 (s, 1 H), 4.31 (m, 2 H), 4.06 (m, 2 H), 3.79 (s, 2 H), 2.37 (t, J=7.0 Hz, 4 H), 1.62 (sext, J=7.3 Hz, 4 H), 1.32 (s, 18 H), 1.04 (t, J=7.3 Hz, 6 H). $^{13}$C NMR (100
MHz, CDCl$_3$) $\delta$ 140.8, 140.5, 136.5, 134.1, 132.8, 131.3, 124.5, 124.4, 103.2, 102.5, 90.9, 80.3, 66.3, 40.7, 31.2, 28.4, 22.3, 21.6, 13.8. HRMS calc’d for C$_{38}$H$_{44}$O$_2$: 532.3341, found: 532.3331.

NanoBalletDancer (37). In a small vial, 36 (59 mg, 0.108 mmol), para-toluenesulfonic acid monohydrate (few crystals), 2,2-dimethyl-1,3-propanediol (0.225 mg, 2.158 mmol) and MgSO$_4$ (0.58 mg, 0.482 mmol) were subjected to microwave irradiation for 8 min (heating 2 min at a time). The reaction mixture was then diluted with a saturated solution of NaHCO$_3$ and all solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hex/CH$_2$Cl$_2$ 66/33) afforded 59 mg (93% yield) of the title compound as a white solid. Mp: 146-150 °C. IR (KBr) 2963.1, 2929.0, 2866.8, 2837.6, 2219.8, 1586.5, 1457.2, 1422.6, 1392.0, 1363.5, 1266.0, 1098.8 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (s, 1 H), 7.15 (s, 2 H), 7.05 (s, 2 H), 6.00 (s, 1 H), 3.81 (d, J=11.1 Hz, 2 H), 3.77 (s, 2 H), 3.61 (d, J=11.1 Hz, 2 H), 2.37 (t, J=7.0 Hz, 4 H), 1.62 (sext, J=7.3 Hz, 4 H), 1.49 (s, 3 H), 1.34 (s, 18 H), 1.04 (t, J=7.3 Hz, 6 H), 0.80 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.6, 140.1, 136.4, 134.2, 132.7, 131.3, 124.4, 123.7, 102.7, 102.1, 90.8, 80.3, 78.7, 77.8, 40.7, 31.1, 30.7, 28.4, 24.6, 22.3, 22.2, 21.6, 13.8.
HRMS calc'd for C_{41}H_{50}O_{2}: 574.3811, found: 574.3813. Anal. Calc'd: C, 85.67; H, 8.77; Found: C, 85.56; H, 8.78.

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\begin{array}{c}
\text{OTBS} \\
\end{array}
\]

**Tert-butyldimethyl-but-3-ynyloxy-silane**\(^{45}\) (38). To a mixture of imidazole (13.49 g, 198.17 mmol) and tert-butyldimethylsilylchloride (23.49 g, 158.54 mmol) were added 3-Butyn-1-ol (10 mL, 132.12 mmol) and distilled (130 mL) The white suspension was stirred at RT for 1 d, diluted with water and extracted with CH\(_2\)Cl\(_2\). The combined organic phases were dried over MgSO\(_4\), filtered, and the solvent evaporated in vacuo. After a plug (silica gel, hexanes/CH\(_2\)Cl\(_2\) 75/25), it afforded 24.09 g (99% yield) of the title compound as a clear liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 3.75\) (t, \(J=7.1\) Hz, 2 H), 2.40 (dt, \(J=7.1, 2.6\) Hz, 2 H), 1.96 (t, \(J=2.6\) Hz, 1 H), 0.90 (s, 9 H), 0.09 (s, 6 H).

\[
\begin{array}{c}
\text{TBSO} \\
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**2,5-Bis(tert-butyldimethylsiloxy)-1,4-dibromobenzene** (39). See the general Pd/Cu procedure. To a solution of 2,5-dibromo-1,4-diodobenzene (19.84 g, 40.687 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.856 g, 1.22 mmol), copper(I) iodide (0.620 g, 3.25 mmol) in THF (50 mL) were added Et\(_3\)N (50 mL) and tert-butyldimethyl-but-3-ynyloxy-silane \(^{38}\) (17.98 g, 97.65 mmol) in THF (50 mL) via a cannula. The mixture was stirred at RT for 1 d. Purification by flash chromatography
(silica gel, hexanes/CH\textsubscript{2}Cl\textsubscript{2} 60/40) afforded 23.36 g (96% yield) of the title compound as a white low boiling solid. IR (KBr in CHCl\textsubscript{3}) 3308.8, 3017.6, 2955.0, 2930.5, 2883.5, 2857.4, 2233.8, 1469.6, 1386.5, 1355.2, 1255.7, 1215.8, 1106.6 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{\textdelta} 7.60 (s, 2 H), 3.84 (t, \textit{J}=7.1 Hz, 4 H), 2.69 (t, \textit{J}=7.1 Hz, 4 H), 0.92 (s, 18 H), 0.10 (s, 12 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \textsuperscript{\textdelta} 136.4, 126.6, 123.6, 95.2, 79.3, 61.8, 26.1, 24.3, 18.5, -5.0 ppm. HRMS calc'd for C\textsubscript{26}H\textsubscript{40}Br\textsubscript{2}O\textsubscript{2}Si\textsubscript{2}: 583.0699, found: 583.0704.

![Chemical Structure]

**2,5-Bis(4-tertbutyldimethylsiloxy)-4-bromobenzaldehyde** (40). To a solution of 2,5-bis(4-tertbutyldimethylsiloxy)-1,4-dibromobenzene \textbf{39} (10.14 g, 16.895 mmol) in THF (80 mL) cooled to \textdegree78 \textdegree C under nitrogen was added dropwise \textit{n}-BuLi (2.53 M, 6.67 mL). The reaction mixture was allowed to stir at \textdegree78 \textdegree C for 30 min. To this mixture was added DMF (1.37 mL, 17.74 mmol) pre-dried over molecular sieves. The reaction mixture was allowed to warm to RT overnight. It was then diluted with water and extracted with Et\textsubscript{2}O. The combined organic phases were washed with brine, dried over MgSO\textsubscript{4}, filtered and evaporated. Purification by flash chromatography (silica gel, hex/CHCl\textsubscript{3} 20/80) afforded 5.94 g (64% yield) of the title compound as a white solid. Mp: 78-82 \textdegree C. IR (KBr) 2953.0, 2929.4, 2885.6, 2856.4, 2230.0, 1694.8, 1588.2, 1524.6, 1470.7, 1254.9, 1107.3 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{\textdelta} 10.41 (s, 1 H), 7.90 (s, 1 H), 7.73 (s, 1 H), 3.85 (m, 4 H), 2.70 (m, 4 H), 0.92 (s, 18 H), 0.10 (s, 12 H). \textsuperscript{13}C NMR (100
MHz, CDCl$_3$) δ 190.7, 136.9, 134.8, 131.7, 127.1, 126.3, 97.7, 95.3, 79.5, 61.8, 61.6, 26.1, 26.0, 24.3, 18.5, -5.04, -5.08 ppm. HRMS calc’d for C$_{27}$H$_{41}$BrO$_3$Si$_2$: 548.1778, found: 548.1776.

2,5-Bis-[4-(tert-butyl-dimethyl-silanyloxy)-but-1-ynyl]-4-(3,5-di-pent-1-ynyl-phenylethynyl)-benzaldehyde (41). See the general Pd/Cu procedure. To a solution of 2,5-bis(4-tertbutyldimethylsilox)-4-bromobenzaldehyde 40 (2.04 g, 3.718 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.261 g, 0.372 mmol), copper(I) iodide (0.142 g, 0.744 mmol) in THF (15 mL) were added Et$_3$N (20 mL) and 3,5-(1-pentynyl)-1-ethynylbenzene 12 (1.479 g, 6.32 mmol) in THF (25 mL) via a cannula. The mixture was stirred at 70 °C for 1 d. Purification by flash chromatography (silica gel, hexanes/CHCl$_3$ 25/75) afforded 2.46 g (94% yield) of the title compound as a yellow oil. IR (KBr) 2957.7, 2930.8, 2857.3, 2232.8, 1696.2, 1585.3, 1466.6, 1385.6, 1334.4, 1255.0, 1105.3 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 10.45 (s, 1 H), 7.93 (s, 1 H), 7.61 (s, 1 H), 7.45 (d, J=1.5 Hz, 2 H), 7.43 (t, J=1.5 Hz, 1 H), 3.87 (t, J=7.1 Hz, 4 H), 2.74 (m, 4 H), 2.39 (t, J=7.0 Hz, 4 H), 1.62 (sext, J=7.2 Hz, 4 H), 1.05 (t, J=7.3 Hz, 6 H), 0.92 (s, 9 H), 0.88 (s, 9 H), 0.10 (s, 6 H), 0.07 (s, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 191.0, 136.6, 135.3, 135.0, 133.8, 130.7, 130.6, 126.2, 125.0, 123.1, 96.9, 95.8, 94.4, 91.9, 87.9, 79.6, 79.5,
62.0, 61.7, 26.1, 24.3, 22.3, 21.6, 18.6, 18.5, 13.8, -5.05, -5.09. HRMS calc’d for C_{45}H_{50}O_{2}Si_{2}: 702.3924, found: not able to obtain.

4-\{5-[1,3]Dioxolan-2-yl-2-(3,5-di-pent-1-ynyl-phenylethynyl)-4-(4-hydroxy-but-1-ynyl)-phenyl\}-but-3-yn-1-ol (42). In a flask equipped with a condenser, a solution of the aldehyde 41 (1.58 g, 2.247 mmol), ethylene glycol (1 mL, 17.98 mmol), TMSCl (1.75 mL, 13.678 mmol) (distilled over CaH\textsubscript{2}) in CH\textsubscript{2}Cl\textsubscript{2} (100 mL) was made. This solution was refluxed for 20 h after which aq. NaOH was added. The mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2}. The combined organic phases were dried over MgSO\textsubscript{4}, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 40/60) afforded a mixture of the product as well as the TBS protected boy. The mixture was submitted to a TBS deprotection with TBAF (4.0 mL, 4.0 mmol) in THF (40 mL) for 25 min. The reaction is diluted with water and extracted with Et\textsubscript{2}O. The combined organic phases were dried over MgSO\textsubscript{4}, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 25/75) afforded 417 mg (36% yield) of the title compound as a white solid. This compound was light and moisture sensitive. One has to use it next the next hours or keep it under N\textsubscript{2} in the freezer. Mp: 115-116 °C. IR (KBr) 3372.3, 2960.6, 2931.4, 2872.5, 2230.3, 1580.9, 1485.2, 1461.1, 1387.6, 1341.3, 1167.1, 1078.0, 1043.6 cm\textsuperscript{-1}. \textsuperscript{1}H NMR
(400 MHz, CDCl₃) δ 7.63 (s, 1 H), 7.54 (s, 1 H), 7.45 (d, J=1.5 Hz, 2 H), 7.39 (t, J=1.5 Hz, 1 H), 6.17 (s, 1 H), 4.14-4.04 (m, 4 H), 3.83 (m, 4 H), 2.81 (t, J=6.2 Hz, 2 H), 2.70 (t, J=6.2 Hz, 2 H), 2.38 (t, J=7.0 Hz, 4 H), 2.04 (m, 1 H), 1.62 (sext, J=7.2 Hz, 4 H), 1.05 (t, J=7.3 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 139.6, 135.5, 134.9, 133.7, 129.4, 126.2, 125.4, 124.9, 123.3, 122.2, 101.6, 94.9, 92.9, 92.8, 91.7, 88.1, 81.3, 79.6, 65.6, 61.3, 61.2, 79.6, 24.5, 24.3, 22.3, 21.6, 13.7. HRMS calc’d for C₃₅H₃₄O₄: 518.2457, found: 518.2460.

4-{5-(5,5-Dimethyl-[1,3]dioxan-2-yl)-2-(3,5-di-pent-1-ynyl-phenylethynyl)-4-(4-hydroxy-but-1-ynyl)-phenyl]-but-3-yn-1-ol (43). In a flask equipped with a condenser, a solution of the aldehyde 41 (1.97 g, 2.802 mmol), 2,2-dimethyl-1,3-propanediol (2.33 g, 22.42 mmol), TMSCl (1.79 mL, 134.01 mmol) (distilled over CaH₂) in CH₂Cl₂ (150 mL) was made. This solution was refluxed for 18 h after which aq NaOH was added. The mixture was extracted with CH₂Cl₂. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded a mixture of the product as well as the TBS protected girl. The mixture was submitted to a TBS deprotection with TBAF (3.25 mL, 3.25 mmol) in THF (60 mL) for 20 min. The reaction was diluted with
water and extracted with Et₂O. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded 1.17 g (75% yield) of the title compound as a white solid. Mp: 110-111 °C. IR (KBr) 3435.7, 2963.0, 2935.5, 2873.2, 2251.0, 1581.7, 1465.9, 1386.4, 1097.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1 H), 7.54 (s, 1 H), 7.45 (d, J=1.5 Hz, 2 H), 7.39 (t, J=1.5 Hz, 1 H), 5.67 (s, 1 H), 3.84-3.76 (m, 6 H), 3.66 (d, J=10.9 Hz, 2 H), 2.78 (t, J=6.2 Hz, 2 H), 2.73 (t, J=6.2 Hz, 2 H), 2.38 (t, J=7.0 Hz, 4 H), 1.62 (sext, J=7.2 Hz, 4 H), 1.31 (s, 3 H), 1.05 (t, J=7.3 Hz, 6 H), 0.80 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 135.6, 134.8, 133.7, 130.0, 125.9, 125.7, 124.8, 123.3, 121.5, 99.5, 93.1, 92.7, 92.6, 91.7, 81.3, 79.6, 79.2, 78.0, 61.2, 30.5, 24.34, 24.28, 23.3, 22.3, 22.0, 21.5, 14.4. HRMS calc'd for C₃₈H₄₀O₄: 560.2927, found: 560.2979.

\[ \text{Cl} \quad \begin{array}{c} O \\ \text{NO}_2 \end{array} \]

*p-Nitrophenylchloroformate*[^34] (44). In a flask under N₂ equipped with a condenser, a solution of nitrophenol (4.0 g, 28.75 mmol) in CH₂Cl₂ was made. After cooling to -30 °C, diphosgene (4.85 mL, 40.26 mmol) and diisopropylethylamine (5.1 mL, 28.75 mmol) were added. This solution was stirred for 2 h at 0 °C, then at reflux for 2 h. The solvent was evaporated in vacuo (no heat). The crystalline solid was suspended in THF (80 mL), stirred for 5 min after which a white powder of iPr₂EtN.HCl crashes out. This solid was filtered off, and the supernatant collected and evaporated to give a liquid residue. This residue was rediluted in hexanes, stirred for a few min. The hexanes supernatant solution which contained the product was evaporated. This step was repeated
several times to obtain 2.09 g (36% yield) of the white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (m, 2 H), 7.45 (m, 2 H).

![Chemical structure](image)

(45). To a solution of the alcohol 43 (1.17 g, 2.087 mmol), DMAP (40 mg, 0.334 mmol) in CH$_2$Cl$_2$ (20 mL) cooled to 0 °C were added pyridine (0.85 mL, 10.435 mmol) and a solution of $p$-nitrophenylchloroformate (1.656 g, 8.220 mmol) in CH$_2$Cl$_2$ (10 mL) cooled at 0 °C. This yellow milky solution was stirred at 0 °C for 1h 15 min after which a solution of NaHCO$_3$ was added to quench the reaction. The mixture was extracted with CH$_2$Cl$_2$. The combined organic phases were dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded 1.614 g (87% yield) of the title compound as a white sticky solid. Mp:23-58 °C. IR (KBr) 2966.8, 2253.3, 1766.6, 1595.4, 1528.1, 1468.8, 1384.5, 1349.7, 1218.1 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.29 (m, 2 H), 8.25 (M, 2 H), 7.80 (s, 1 H), 7.57 (s, 1 H), 7.43 (d, $J$=1.5 Hz, 2 H), 7.39 (m, 2 H), 7.37 (t, $J$=1.5 Hz, 1 H), 7.35 (m, 2 H), 5.72 (s, 1 H), 4.51 (dt, $J$=6.6, 2.0 Hz, 4 H), 3.76 (d, $J$=11.1 Hz, 2 H), 3.68 (d, $J$=10.9 Hz, 2 H), 2.99 (m, 4 H), 2.35 (t, $J$=7.0 Hz, 4 H), 1.60 (sext, $J$=7.2 Hz, 4 H), 1.31 (s, 3 H), 1.04 (t, $J$=7.3 Hz, 6 H), 0.78 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.6, 155.5, 152.6, 152.4, 145.7, 145.5, 139.5, 135.8, 134.8, 133.7, 130.3, 126.0, 125.7, 125.6, 125.4, 124.8, 123.3,
122.0, 121.9, 121.4, 99.5, 92.8, 91.7, 90.9, 90.6, 87.9, 81.2, 79.5, 79.2, 78.0, 66.90, 30.5, 23.3, 22.2, 22.0, 21.5, 20.5, 20.4, 13.7. LRMS calc'd for C_{52}H_{46}N_{2}O_{12}: 890.3, found: 890.5. MALDI (Dithranol) calc'd for C_{52}H_{46}N_{2}O_{12}: 890, found: 890.

**Synthesis of the dimers 46 and 47, and the polymer 48.** 42 (113.9 mg, 0.2196 mmol) and 45 (195.7 mg, 0.2196 mmol) were carefully weighed into a round bottom flask and DMAP (67 mg, 0.549 mmol) was added. After removal of the oxygen, CH_{2}Cl_{2} (5 mL) was added and the solution was stirred at RT for 21 h after which a solution of NaHCO_{3} was added to quench the reaction. The mixture was extracted with CH_{2}Cl_{2}. The combined organic phases were dried over MgSO_{4}, filtered, and the solvent evaporated *in vacuo*. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50 then EtOAc) afforded 46 and 47, 56 mg (23%) and 52 mg (21%) (the two isomers could not be clearly distinguished between each other although they were separable) and 42 mg of 48. 46 or 47 (the less polar of the two, blue spot on TLC under UV irradiation): IR (KBr) 2962.2, 2933.4, 2904.5, 2871.6, 2234.1, 1747.8, 1580.6, 1463.6, 1401.1, 1336.5, 1266.8, 1096.6 cm^{−1}. \(^1\)H NMR (400 MHz, CDCl_{3}) \( \delta \) 7.68 (s, 1 H), 7.51 (s, 1 H), 7.43 (s, 1 H), 7.42 (d, \( J=1.5 \) Hz, 2 H), 7.39 (s, 1 H), 7.37 (t, \( J=1.5 \) Hz, 2 H), 7.35 (d, \( J=1.5 \) Hz, 2 H), 5.96 (s, 1 H), 5.55 (s, 1 H), 4.33 (m, 8 H), 3.93 (m, 4 H), 3.64 (s, 2 H), 3.55 (d, \( J=10.2 \) Hz, 1 H), 3.38 (d, \( J=10.2 \) Hz, 1 H), 2.88 (m, 8 H), 2.36 (m, 8 H), 1.60 (m, 8 H), 1.17 (s, 3 H), 1.04 (m, 12 H), 0.72 (s, 3 H). \(^1\)C NMR (100 MHz, CDCl_{3}) \( \delta \) 155.5, 155.1, 139.8, 139.2, 135.9, 135.2, 134.6, 134.5, 134.0, 133.9, 133.7, 129.8, 129.7, 126.1, 125.5, 125.3, 125.1, 124.8, 124.6, 124.5, 123.8, 123.6, 122.3, 121.7, 101.4, 99.3, 92.5, 92.2, 91.8, 91.4, 91.2, 91.1, 88.7, 81.0, 79.8, 79.7, 78.8, 78.0, 66.2, 66.1, 66.0, 65.5, 65.4, 30.2, 23.2,
22.31, 22.29, 22.26, 22.0, 21.5, 20.5, 20.4, 20.2, 13.7. MALDI (dithranol, Ag) calc’d for C\textsubscript{75}H\textsubscript{70}O\textsubscript{10}: 1130.5, found: 1130.4. GPC (THF, PS) \( M_n = 775, M_w = 800 \). 46 or 47 (the more polar of the two, gray-black spot on TLC under UV irradiation): IR (KBr) 2963.0, 2932.7, 2872.1, 2250.2, 1745.9, 1580.9, 1463.9, 1401.3, 1269.2, 1096.2 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.64 (s, 1 H), 7.48 (s, 1 H), 7.43 (d, \( J=1.3 \) Hz, 2 H), 7.39 (t, \( J=1.4 \) Hz, 4 H), 7.35 (t, \( J=1.5 \) Hz, 1 H), 7.32 (t, \( J=1.5 \) Hz, 1 H), 6.01 (s, 1 H), 5.61 (s, 1 H), 4.39-4.30 (m, 8 H), 3.98-3.90 (m, 4 H), 3.68 (s, 2 H), 3.57 (d, \( J=10.2 \) Hz, 1 H), 3.52 (d, \( J=10.2 \) Hz, 1 H), 2.95-2.81 (m, 8 H), 2.38 (m, 8 H), 1.60 (m, 8 H), 1.21 (s, 3 H), 1.07 (m, 12 H), 0.76 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 155.2, 155.0, 139.6, 139.1, 135.9, 135.4, 134.7, 134.5, 133.94, 133.91, 133.7, 130.0, 129.9, 126.1, 125.7, 125.6, 125.5, 124.5, 123.6, 121.6, 121.1, 101.5, 99.4, 92.7, 92.3, 92.1, 91.5, 91.4, 91.2, 88.4, 88.1, 80.8, 80.7, 79.9, 79.8, 79.3, 79.2, 78.0, 66.3, 66.2, 66.0, 65.9, 65.5, 30.3, 29.9, 23.3, 22.3, 22.2, 22.0, 21.6, 21.2, 20.5, 20.4, 14.4, 13.7. MALDI (dithranol, Ag) calc’d for C\textsubscript{75}H\textsubscript{70}O\textsubscript{10}: 1130.5, found: 1130.5. GPC (THF, PS): \( M_n = 745, M_w = 765 \). 48 (blue tailing spot on TLC under UV irradiation): IR (KBr) 2964.5, 2933.9, 2873.0, 2253.0, 1746.3, 1581.0, 1463.2, 1402.0, 1255.9 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.75 (br s, 1 H), 7.62 (br s, 1 H), 7.54 (t, \( J=1.5 \) Hz, 1 H), 7.52 (t, \( J=1.4 \) Hz, 1 H), 7.44 (m, 4 H), 7.39 (br t, 2 H), 6.10 (s, 0.5 H), 6.08 (s, 0.5 H), 5.67 (br t, 1 H), 4.39-4.30 (m, 8 H), 4.15-4.03 (m, 4 H), 3.76 (dd, \( J=10.9, 3.67 \) Hz, 2 H), 3.66 (d, \( J=10.7 \) Hz, 1 H), 2.93-2.82 (m, 8 H), 2.38 (m, 8 H), 1.60 (m, 8 H), 1.21 (d, \( J=4.0 \) Hz, 3 H), 1.07 (m, 12 H), 0.80 (d, \( J=4.0 \) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 154.9, 154.8, 154.8, 139.5, 139.1, 136.0, 135.6, 134.7, 133.7, 130.3, 130.1, 126.1, 125.8, 125.7, 125.5, 124.83, 124.81, 123.4, 122.2, 121.5, 101.4, 99.5, 92.9, 92.7, 91.7, 90.7, 88.1, 87.9, 81.0, 79.6, 78.9, 78.0, 65.9, 65.8, 65.7,
30.4, 29.9, 23.3, 22.3, 22.0, 21.5, 21.2, 20.4, 13.7. LDI MS: a broad peak centered at 47,536. GPC (THF, PS): $M_n = 23,500$, $M_w = 36,600$. 
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CHAPTER 5

SYNTHERESIS OF A MARCHING NANOARMY
1. Introduction

In 1959, physicist Richard Feynman gave a talk entitled "there is plenty of room at the bottom" in which he opens the idea of building machines atom by atom. This talk became the beginning of nanotechnology. But it was not until the 1980's that the idea of tiny robots, "nanobots", repairing our bodies started to emerge and bloom. Over the past few years, the construction of motors and machines of nanosize dimensions has offered a great challenge to scientists. The increasing interest in nanomachines can be explained by the fact that researchers have always been amazed by the way nature works. Every enzyme, bacteria or cell performs its own tasks, with few or no errors. For example, macrophages which are present in all tissues of the body carry out several tasks. Among those errands, macrophages engulf large particles such as bacteria, yeast and dying cells by a process called phagocytosis. They secrete signaling molecules called cytokines and chemokines which orchestrate the immune response. They also secrete and respond to a wide range of inflammatory mediators and play a central role in acute and chronic inflammation. Macrophages also present processed foreign antigens to already primed T-lymphocytes allowing the enhancement or inhibition of a specific immune response. They behave like tiny cleaning machines in our body. Still in the biological system, myosin V has captivated the attention of many researchers by the complexity of its movement. Myosin V is a dimeric molecular motor that moves progressively down on an actin chain, with the center of mass moving about 37 nm for each adenosine triphosphate hydrolyzed. The debate resides within the fact that scientists argue on whether the myosin "walks" in a "hand-over-hand" model in which the two heads alternate in the lead
whether the myosin follows a “inchworm” model in which one head always leads.\(^2\) These microscopic walking robots have inspired researchers in devising a similar system.

The desire to reproduce such sophisticated systems drives the quest for constructing nanomachines capable of exceptional specificity and precision. A molecular shuttle with a translational motion has recently been synthesized.\(^3\) It consists of a macrocycle in a rotaxane able to slide reversibly between two hydrogen-bonding stations after a nanosecond electrical pulse. For rotary motions, light-driven\(^4\) and field-driven motors have been designed. An example of field-driven nanomachines are caltrop-shaped molecules which have been created with molecular arms having a strong net dipole moment and legs with sulfur-tipped bonding units capable of binding to a gold surface.\(^5\) The strong dipole moment of the arms was designed to allow the control of the rotating motion by an electric field.

The idea of tiny machines performing tasks inspired us to use the NanoKids and trying to transform them into NanoBots by making them walk on a surface.

Figure 1 depicts the strategy (designed by Michael Casavant) that will be used to detect their movement.

**Figure 1**

After self-assembly of the NanoKids on a metal surface, a potential will be applied across the surface. The rationale behind this design is that the NanoKids' self-
assembled monolayer (SAM) will reorganize into a more highly packed structure and therefore reveal a strip of bare metal surface on one side.

2. Results and discussion

2.1. NanoKids with thiol-terminated feet

The most widely studied systems for self-assembly are thiols. For this reason, the synthesis of NanoKids with thiol feet was carried out, as a test to study their self-assembly.

2.1.1. Synthesis

Scheme 1
As described in Scheme 1, 3-butyn-1-ol was mesylated to afford 1 in excellent yield and then converted to the but-1-yn-4-yl thioacetate 2 via a procedure by Kellogg using the cesium thioacetate salts. The yield was not very high due to the relative volatility of 2. The free alkyne 2 was then coupled to the aryl dibromide via a palladium catalyzed coupling to furnish 3 in low yield. The trimethylsilyl (TMS) group was removed using tetrabutylammonium fluoride (TBAF) and the resulting free alkyne 4 was coupled to the top part previously synthesized (Chapter 4). The NanoKid with “sticky” feet 5 was obtained in 31% yield.

2.1.2. Self-assembly tests

Compound 5 was then permitted to self-assemble on a gold surface (Figure 2).

Figure 2
The acetyl protecting groups were removed by a solution of ammonium hydroxide in THF to give the free thiols or thiolate. A gold plated substrate (Si/Cr/Au) was then dipped into this solution, and after incubating for 4 days, the resultant surface was rinsed and the thickness measured by ellipsometry. This compound formed a SAM with an ellipsometrically measured thickness of 1.97 nm compared to a calculated thickness of 2.11 nm along the surface normal; the difference being indicative of the routinely observed sp³-sulfur hybridization and intermolecular interaction-induced tilt angle from the surface normal.

2.2. NanoKids with COOH-terminated feet

Once we were assured that the NanoKids formed a SAM, the next step was to try to make them move on the surface. For that, assembly on gold via the thiols was not adequate since the S-Au bond was too strong (~ 1.8 eV) and would not allow any movement. It seemed that a better approach would be to assemble the molecules on silver via a carboxylic acid group since carboxylic acids are immediately deprotonated into carboxylate anions which are mobile on AgO. Moreover, the literature suggested that performing the self-assembly in a humid environment could be beneficial to make the COOH layer even more labile, since water is necessarily present for the equilibrium reaction \( \text{COO}^- \rightleftharpoons \text{COOH} \) to take place. For that, Houston is an appropriate city with its humid atmosphere.
2.2.1. Synthesis

Scheme 2

The synthesis of the Walking NanoKid started with the synthesis of the bottom part. 3,5-Dibromo(trimethylsilylethynyl)benzene was coupled to the tert-butylidimethylsilyl (TBS) alcohol protected free alkyne via a Sonogashira coupling in excellent yield to give 6 (Scheme 2). The two TBS protecting groups were removed as well as the TMS protecting group after treatment with 3 equivalents of TBAF in THF to give the diol 7. Attempts to oxidize the homopropargylic alcohols by Jones oxidation failed probably due to the formation of an allene.
Scheme 3

To circumvent the problem of the oxidation of homopropargylic alcohols, a longer chain for the feet was synthesized (Scheme 3). For that synthesis, pentyn-1-ol was protected with TBSCI to furnish 8 in excellent yield. The free alkyne was then coupled to 3,5-dibromo(trimethylsilyl)ethynylbenzene to give 9, which was deprotected to afford 10 in an excellent overall yield. The diol was then oxidized with the Jones reagent to
give the diacid 11 as a white solid. Endeavors to purify the diacid by flash chromatography failed since the compound remained inside the column, even after flushing with several polar solvents. Instead, purification was accomplished by dissolving the crude in a minimum amount of THF followed by precipitation in hexanes. The diacid was then esterified in a Fisher type esterification to protect the acids as they might affect the palladium-catalyzed coupling by serving as ligands. This gave the bottom part 12 which was ready for the coupling with the aryl iodide top part to furnish 13. Finally, 13 was saponified using lithium hydroxide to give the Walking NanoKid 14. The acidification of the carboxylate ion has to be done carefully since the deprotection of the aldehyde can occur if the pH is too low and the separation of the aldehyde from the product can be problematic since purification by flash chromatography is excluded. In this case, acidification with a CH₃COOH/CH₃COONa buffer at pH 4.5 worked very well as the pure diacid precipitated from the aqueous solution.

2.2.2. Self-assembly tests

In order to run some self-assembly tests, the Walking Nanokid 14 was self-assembled on Si/Cr/Ag. After evaporation of the silver, the substrate was immediately placed in an ethanolic solution of the NanoKid 14 (0.5 mM) for several days. Ellipsometry showed a thickness of about 1.3 nm (theory being 1.6 nm) which corresponds to a monolayer. As a reference, 16-bromohexadecanoic acid was also assembled in the same way. The ellipsometry results also showed a monolayer.

In order to observe these SAMs, atomic force microscopy (AFM) images were also taken. They showed a very rough surface with small hills of about 50 nm long at a height of 15 nm above the valleys. The Root Mean Square (RMS) value was around 3
nm, which for our purpose is very rough. There were no plates large enough to conduct the NanoKids motion. In order to observe any changes, plates had to be large and flat enough so that the displacement of the molecules would not be on the same order as the resolution of the AFM (about 8 nm), and also so that the displacement of the molecules or the contraction of the SAM would be significant enough so that the packing of the monolayer would change and therefore reveal a naked AgO surface. Moreover, the presence of these high plates could be a disadvantage to our experiment, since the NanoKids, in order to walk, would have to overcome or “climb” these hills. This was very disappointing to us. In order to smooth the silver surfaces, we tried to anneal them using a hydrogen flame. The silver substrate was placed in front of the flame for a few seconds at a distance of about 10 cm from the source. After a few seconds, we observed that the formation of a white dull film on the silver surface. Changing the distance to the flame or the amount of time of flame exposure did not improve the annealation.

We decided to change the Si/Cr/Ag substrate to a mica/Ag substrate. 50 nm of silver were evaporated on freshly cleaved mica at a rate of 1.3 Å/s at 3.4 Amps. At this thickness, ellipsometry measurements could not be done as the laser goes through the silver layer. Both high quality and regular quality micas were used with almost no difference in the RMS by AFM. After self-assembly of the NanoKid 14 for 4 d, the RMS was 1.1 nm which was still an improvement compared to the Si/Cr/Ag substrate (Figure 3).
With plates like these, it would be very difficult to observe any motion of the NanoKids. Apart from the fact that the plates were not big enough (50-90 nm) compared to the resolution of the AFM tip (9 nm), one of the difficulties was that we had to observe one specific plate among this multitude, before and after applying the electric field. Another challenge was that we needed to see an edge of the plate in order to see if the SAM has been contracted. For all these reasons, it seemed to us that observing the NanoKids motion by AFM was not feasible.

2.3. NanoKid with a Fluorescein Head

To replace the AFM as a tool to image the movement of the NanoKids, we decided to use a confocal microscope. We were confident that if we could attach a fluorophore on the NanoKids’ head and insert them, very diluted, into a SAM of non-fluorescent molecules, we would be able to observe a change in the fluorescence pattern.
The confocal microscope available at Rice which has a resolution of about 1 μm would permit us to do some preliminary fluorescence testing. Later on, for more precise experiments we could use potentially open a collaboration with groups that have microscopes with better resolution, e.g. Paul Barbara at UT, Austin.

2.3.1. Synthesis

The synthesis of a NanoKid with a fluorescent head was undertaken. Fluorescein isothiocyanate (FITC) was chosen as a fluorophore as it is small and commonly use for protein labeling.

**Scheme 4**

![Scheme 4](image)

In order to run some test reactions, the thiol 16 was synthesized (Scheme 4). para-Bromobenzaldehyde was condensed with 3-bromo-1,2-propanediol using a Dean-Stark trap following a procedure by Heathcock to give the acetal 15 in excellent yield. The bromide was then treated with thiourea to afford 16 in 42% yield. Having the thiol in hand, we proceeded to the reaction with FITC, which unfortunately gave only starting material.

Since the route using the condensation of a thiol and an isothiocyanate failed, a new strategy was adopted which consisted of synthesizing the primary amine, also known to easily condense with FITC.
Scheme 5

The previously synthesized aryl iodide NanoKid top part was submitted to a transacetalization with 3-bromo-1,2-propanediol to give 17 in excellent yield (Scheme 5). Further displacement of the bromide by an azide using sodium azide in DMF gave 18 in 82% yield. The reaction was very slow at RT and had to be heated to 65 °C in order to speed it up. Since attempts to reduce the azide to an amine using the Staudinger\textsuperscript{10} reaction were very messy, we modified our route towards the synthesis of the final tagged NanoKid.
The aryl iodide 17 was coupled to the diester 12 in a Sonogashira\textsuperscript{7} coupling in good yield (Scheme 6). The bromide 19 was then displaced by an azide at 65 °C in DMF to furnish 20. Although again messy, the Staudinger\textsuperscript{10} reaction on 20 afforded the amine 21 in 42% yield. Finally, the methyl esters were removed by treatment with lithium hydroxide to afford the diacid 22.
Scheme 7 depicts another set of test reactions in order to seek the ideal reaction conditions for the condensation of the amine to the isothiocyanate. Commercially available 12-aminododecanoic acid was allowed to stir at RT with FITC and 5 equiv. of NaHCO₃ in DMF. After a couple of days, the reaction gave a mixture of the desired product along with byproducts. Not satisfied by this result, the same reaction was run in a NaHCO₃/Na₂CO₃ buffer pH 9. Once again, a mixture of desired product and impurities
was obtained. Finally, a procedure using NaHCO$_3$ and THF/H$_2$O on methyl-12-aminododecanoate afforded success. After a couple of days, the pure desired product 23 was obtained in 100% yield. The deprotection of the methyl ester unfortunately afforded a mixture of products. Therefore the same procedure was attempted directly on the 12-aminododecanoic acid. This last process furnished the desired product 24 in excellent yield.

Scheme 8

The same reaction conditions were applied to the NanoKid 22 (Scheme 8). This afforded 25 in excellent yield.
2.3.2. Self-Assembly Tests

In order to run the first set of experiments, Ag was evaporated on freshly cleaved high quality mica. A SAM was made by first dipping the Ag substrate into an ethanolic solution of lauric acid (4 mg, 20 mL) for 39 h then into a solution of 24 (4 mg, 20 mL) in water for 4 min. Hoping that 4 min was enough time for 24 to insert into the SAM of lauric acid, the first image of the SAM was obtained with the confocal microscope. However, that image was very disappointing due to the weak fluorescence. Four possible reasons could explain the weak fluorescence: the first is that since no special care was taken to avoid light during the reaction and handling of the fluorophore molecule, it was possible that the fluorescein was already quenched when observed by the confocal microscope. The second reason is that maybe 4 min of assembly in the solution of 24 was not enough. The third reason is that the maximum fluorescence of the fluorescein occurs at about pH 9 but the assembly was done in neutral water, pH 7. Finally the fourth reason is that maybe the metal surface quenched the fluorescence.

A self-assembly test was run on Mica/Ag (thickness 140 nm). A solution of 12-aminododecanoic acid and 0.2% of 24 in NaHCO₃/Na₂CO₃ buffer pH 9 was made. The substrate was left for 40 h in the solution. The ellipsometry readings showed that the thickness was 2.47 nm (theo 2.47 nm). Since the SAM should mostly be composed of 12-aminododecanoic acid, such thickness readings meant that probably a multilayer was obtained.

Some self-assembly tests were also run on Si/Cr/Ag. In order to see the effect of the solvent and the pH on the assembly of 24, a SAM of 24 was assembled in water, in EtOH and in a NaHCO₃/Na₂CO₃ buffer pH 9. The thicknesses obtained were 1.60 nm,
3.64 nm and 1.25 nm, respectively, after 24 h, theoretical thickness being 2.47 nm. However, this varies since another test in water gave a thickness of 2.12 nm. These discrepancies can possibly be explained by the change in the configuration of the fluorescein due to the pH (Figure 4).

Figure 4

![Chemical Structures]

Looking at this figure, several potential problems become more obvious. The optimum pH for the fluorescence of the fluorescein is above 7. However at that pH the lactone no longer exists and the carboxylate is free and therefore ready to assemble on Ag. This makes the NanoKid attach to the surface not only by the feet but also by the head. Moreover, when the assembly was done in water, the compound was not very soluble and the Ag layer got destroyed. Finally, the presence of the thiocarbonyl group might be a potential problem since thiocarbonyls also have an affinity for Ag.

2.4. NanoKids with Lissamine Rhodamine Head

The obvious solution to the above mentioned problems was to change the fluorophore. We needed a fluorophore with no affinity for Ag which meant that it could not contain any carboxylic acid (which excluded all the fluorescein derivatives, the Alexa Fluor dyes, most of the rhodamines and the oregon green dyes), amines, alcohols or
thiocarbonyls. Moreover, we needed a fluorophore that excited at 488 nm and 568 nm (required by our confocal microscope), that was not too sensitive to pH (so that it can be assembled in EtOH which was the best solvent for self-assembly and for solubility reasons) and that was not too expensive. A thorough search leaded us to Lissamine Rhodamine B sulfonyl chloride. This fluorophore has a maximum excitation at 568 nm, was insensitive to pH and was photostable, did not contain any group that had an affinity for Ag and was relatively inexpensive (5 g for $40) compared to other fluorophores.

Scheme 9
Scheme 9 depicts several attempts to couple the amine to the sulfonyl chloride. Each time only a few mg of crude impure material (15% yield) was obtained. This material was quite insoluble, except in DMSO and MeOH, although MeOH was not a good solvent since it was too nucleophilic and esterified with the $\text{SO}_3^-$ moiety. Attempts to purify products by flash chromatography failed, as well as preparative TLC, recrystallization or Sohxlet extraction. The same problem was encountered with the
NanoKid 22 as the starting material. After several unsuccessful attempts to get 27 pure, the synthesis of that compound was abandoned.

2.5. Challenges

After some more in-depth literature searching, we found that Ag might not be the best surface after all. Fluorescence quenching by metals is well known. The effect of the dye-molecule-metal surface distance has been studied by several groups. The Langmuir-Blodgett technique or the evaporation method has permitted the preparation of a wide variety of molecule-metal systems, in which dye molecules have been separated from a metal surface by a spacer with a known fixed thickness.\textsuperscript{11-13} It has been found that at small distances (< 20 nm), the quantum yield falls rapidly toward zero due to nonradiative energy transfer from the excited molecules to the metal.\textsuperscript{14,15} Despite the plethora of studies, very few focused on distances smaller than 5 nm. Among them, a report by Brillante\textsuperscript{11} actually shows that a fluorophore at a distance of 2.68 nm assembled on AgO by Langmuir-Blodgett techniques was almost totally quenched. This finding was very disappointing to us.

From there, our strategy was to try to find an alternative surface to Ag even if we needed to change the carboxylic acid feet. We could not use Au, Al\textsubscript{2}O\textsubscript{3} or other metals as they were also known to quench the fluorescence. We thought about using SiO\textsubscript{2} but the molecule binds too strongly to the surface as a covalent bond forms between O and Si or C atoms when alkyltrichlorosilanes or aryl diazonium salt are self-assembled (3-3.5 eV).\textsuperscript{16} We thought about using glass as an alternative. Carboxylic acids are known to assemble on glass, but SAMs of carboxylic acids are not stable to solvent rinsing.\textsuperscript{17,18} We also thought about mica, but SAMs on mica have been the subject of very little research.
One way to put molecules on mica was to spin coat but the formed film would not be a SAM. The molecules would just lay flat on the mica, in a disordered manner. Granick\textsuperscript{19} has assembled organotrichlorosilanes on mica but the molecule was covalently bonded to the mica.

3. Summary

After all these obstacles, we came to the conclusion that this project presented a lot of challenges and needed to be rethought. We will leave this work to be continued by subsequent workers in the group.
4. Experimental Procedures

**General.** All reactions were performed in an oven-dried flask under an atmosphere of nitrogen unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Toluene, triethylamine and methylene chloride were distilled over calcium hydride before use. Silica gel plates were 250 µm thick, 40 F₂₅₄ grade from EM science. Silica gel was grade 60 (230-400 mesh) from EM Science. Melting points were taken on a Mel-Temp (Laboratory Devices) apparatus. FT-IR spectra were taken on a Nicolet Avatar 360 spectrometer. ¹H NMR spectra were observed at 400 MHz and ¹³C NMR spectra were observed at 100 MHz on a Brüker AVANCE 400 spectrometer. Mass spectrometry was performed by Terry Marriott and Yunxuan Xiao at Rice University's mass spectrometry lab. All new compounds were named using the Beilstein AutoNom feature of Beilstein Commander software when possible.

**Ellipsometric measurements:** Thicknesses were determined immediately before and immediately after monolayer formation. Measurements of surface optical constants and molecular layer thicknesses were taken with a single wavelength (632.8 nm laser) Gaertner Stokes Ellipsometer. Thicknesses were calculated based on the refractive index $n_f = 1.55$, $k_f = 0$.

**Atomic Force Microscopy (AFM) measurements:** All measurements were performed with a Digital Instruments Nanoscope IIIa tapping mode instrument and TESP tips.

**General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira
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 all solids including the aryl halide, bis(triphenylphosphine) palladium(II) chloride (2-5 mol % based on the aryl halide) and copper(I) iodide (4-10 mol % based on the aryl halide). The vessel was sealed with a rubber septum, evacuated and backfilled with dry nitrogen (3x). THF and remaining liquids were added followed by N,N-diisopropylamine or triethylamine. The reaction heated, if necessary, until complete. The reaction vessel was cooled to room temperature, quenched with water or a saturated solution of NH₄Cl and extracted with Et₂O. The combined organic layers were dried over anhydrous MgSO₄, filtered and the solvent removed in vacuo.

**General Procedure for the Deprotection of Trimethylsilyl-Protected Alkynes.**

To a round bottom flask equipped with a stir bar were added the protected alkyne, potassium carbonate (10 equiv per protected alkyne), methanol, and methylene chloride. The reaction was heated, and upon completion the reaction mixture was diluted with methylene chloride and washed with brine (3x). The organic layer was dried over MgSO₄, and the solvent removed in vacuo.

![3-Butyn-1-yl-mesylate](image)

**3-Butyn-1-yl-mesylate**

Using a 3-neck round bottom flask equipped with an addition funnel, a solution of 3-butyn-1-ol (3.78 mL, 50 mmol), TEA (20 mL, 144 mmol) and dry ether (100 mL) was cooled to -20 °C. To this ethereal solution was added a solution of CH₃SO₂Cl (7.74 mL, 100 mmol) in ether (50 mL). After being stirred for
another 15 min at -20 °C, the reaction was worked up by adding a solution of 1 N HCl until the mixture was acidic. The ether layer was extracted with cold water and brine. The organic phase was dried over MgSO₄, filtered, and the solvent evaporated in vacuo. This reaction afforded 7.07 g (95% yield) of a clear liquid. ¹H NMR (400 MHz, CDCl₃) δ 4.33 (t, J=6.8 Hz, 2 H), 3.08 (s, 3 H), 2.68 (dt, J=6.6, 2.7 Hz, 2 H), 2.08 (t, J=2.7 Hz, 1 H).

\[ \text{But-1-yn-4-yl thioacetate}^{22} (2) \] To a solution of thiolacetic acid distilled over P₂O₅ (6.06 g, 79.63 mmol) in dry MeOH (50 mL) was added cesium carbonate (23.59 g, 72.39 mmol). The light yellowish solution was stirred at RT for 1 h. The MeOH was evaporated and acetone was added to crystallize the cesium salt. The acetone was removed by decantating. The white salt was washed with acetone (2×), then dried. To this salt were added distilled CH₃CN and a solution of 3-butyn-1-yl-mesylate (1) (10.56 g, 71.28 mmol) in CH₃CN. This solution was stirred at RT for 1 d. The reaction was diluted with water and extracted with Et₂O. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH₂Cl₂ 60/40) afforded 4.58 g (50% yield) of the title compound as a light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 3.05 (t, J=7.0 Hz, 2 H), 2.48 (dt, J=7.0, 2.7 Hz, 2 H), 2.36 (s, 3 H), 2.02 (t, J=2.7 Hz, 1 H).
3,5-(4-Thioacetylbutynyl)-1-(trimethylsilylethynyl)benzene (3). See the general Pd/Cu procedure. To a solution of bis(triphenylphosphine)palladium(II) dichloride (0.438 g, 0.625 mmol), copper(I) iodide (0.238 g, 1.25 mmol) in THF (15 mL) were added via cannula Et$_3$N (20 mL), a solution of 3,5-dibromo(trimethylsilylethynyl)benzene (2.07 g, 6.25 mmol) in THF (15 mL) and a solution of but-1-yn-4-yl thioacetate (2) (1.68 g, 13.12 mmol) in THF (20 mL). The mixture was stirred at 75 °C for 4 d. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$) afforded a mixture of starting material, mono product and decoupled product. This mixture was resubmitted to the same reaction conditions with the same reagents and the mixture was heated at 80° C for 4 d. Purification by flash chromatography (silica gel, hex/CH$_2$Cl$_2$ 50/50) afforded 0.531 g (20% yield) of the title compound as a yellow sticky liquid. IR (KBr) 2959.3, 2248.7, 2155.9, 1692.8, 1581.0, 1413.5, 1354.1, 1249.8, 1132.5 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J$=1.5 Hz, 2 H), 7.35 (t, $J$=1.5 Hz, 1 H), 3.09 (t, $J$=7.0 Hz, 4 H), 2.68 (t, $J$=7.0 Hz, 4 H), 2.34 (s, 3 H), 0.24 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.5, 134.6, 134.4, 124.0, 123.7, 103.6, 95.6, 88.9, 80.5, 30.8, 28.5, 20.6, 0.0. HRMS calc’d for C$_{23}$H$_{26}$O$_2$S$_2$Si: 426.1144, found: 426.1146.
3,5-(4-Thioacetylbutynyl)-1-(ethynyl)benzene (4). To a solution of 3,5-(4-thioacetylbutynyl)-1-(trimethylsilylethynyl)benzene (3) (0.531 g, 1.246 mmol) in THF (5 mL) were added a mixture of acetic anhydride (0.47 mL, 4.984 mmol) and acetic acid (0.286 mL, 4.984 mmol) and TBAF (1 M, 2.990 mmol). This solution was stirred at RT for 35 min. The reaction is diluted with water and extracted with ether. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hex/CH₂Cl₂ 30/70) afforded 0.379 g (86% yield) of the title compound as a yellow oil. IR (KBr) 3303.6, 2253.1, 1689.7, 1582.6, 1433.7, 1355.0, 1133.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J=1.5 Hz, 2 H), 7.40 (t, J=1.5 Hz, 1 H), 3.11 (t, J=7.0 Hz, 4 H), 3.07 (s, 1 H), 2.68 (t, J=7.0 Hz, 4 H), 2.37 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 135.1, 134.6, 124.2, 122.8, 89.2, 82.3, 80.4, 78.3, 30.9, 28.5, 20.7. HRMS calc’d for C₂₀H₁₈O₂S₂: 354.0748, found: 354.0748.
(5). See the general Pd/Cu procedure. To a solution of the free alkyne 4 (0.379 g, 1.070 mmol), 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene (0.467 g, 1.0170 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.038 g, 0.0535 mmol), copper(I) iodide (0.020 g, 0.107 mmol) in THF (20 mL) was added Et₃N (10 mL). This solution was stirred at RT for 20 h. Purification by flash chromatography (silica gel, CH₂Cl₂) afforded 0.224 g (31% yield) of the title compound as a yellow sticky oil. IR (KBr, CDCl₃) 2970.8, 28.97.9, 2252.7, 1689.8, 1581.6, 1273.8, 1455.7, 1399.5, 1359.3, 1133.7, 1107.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (s, 1 H), 7.52 (s, 1 H), 7.47 (d, J=1.5 Hz, 2 H), 7.38 (t, J=1.5 Hz, 1 H), 6.11 (s, 1 H), 4.19 (m, 2 H), 4.05 (m, 2 H), 3.11 (t, J=7.0 Hz, 4 H), 2.69 (t, J=7.0 Hz, 4 H), 2.37 (s, 6 H), 1.36 (s, 9 H), 1.33 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 138.7, 135.7, 134.6, 134.2, 129.7, 125.9, 125.7, 124.2, 123.9, 122.6, 105.3, 104.5, 101.6, 91.9, 89.0, 88.9, 80.5, 78.0, 75.7, 65.7, 53.6, 31.2, 31.0, 30.83, 28.51, 28.49, 28.47, 20.6. HRMS calc’d for C₄₁H₄₂O₄S₂: 662.2525, found: 662.2525.
1,3-Bis-[4-(tert-butyl-dimethyl-silanyloxy)-but-1-ynyl]-5-
trimethylsilanylethynyl-benzene (6). See the general Pd/Cu procedure. To a solution of
bis(triphenylphosphine)palladium(II) dichloride (0.173 g, 0.247 mmol), copper(I) iodide
(0.094 g, 0.494 mmol) in THF (80 mL) and Et,N (20 mL) were added 3,5-
dibromo(trimethylsilylethynyl)benzene (4.1 g, 12.34 mmol) and tert-butyldimethyl-but-
3-ynyloxy-silane (6.36 g, 34.55 mmol). The mixture was heated at 80 °C for 24 h.
Purification by flash chromatography (silica gel, hexanes/CH2Cl2 60/40) afforded 6.29 g
(95% yield) of the title compound as a clear oil. IR (KBr) 2955.5, 2929.3, 2857.1, 2245.1,
2159.5, 1581.3, 1471.5, 1414.4, 1385.3, 1361.1, 1251.4, 1107.8 cm⁻¹. ¹H NMR (400
MHz, CDCl₃) δ 7.39 (d, J=1.2 Hz, 2 H), 7.34 (br t, 1 H), 3.79 (t, J=7.1 Hz, 4 H), 2.61 (t,
J=7.1 Hz, 4 H), 0.90 (s, 18 H), 0.23 (s, 9 H), 0.08 (s, 6 H). ¹³C NMR (100 MHz, CDCl₃)
δ 134.6, 134.3, 124.4, 123.6, 103.8, 95.3, 88.5, 80.4, 69.5, 62.0, 26.1, 24.0, 18.6, 0.1.
HRMS calc’d for C₃₁H₅₀O₂Si₃: 538.3119, found: 538.3114.

4-[3-Ethynyl-5-(4-hydroxy-but-1-ynyl)-phenyl]-but-3-yn-1-ol (7). To a
solution of 1,3-bis-[4-(tert-butyl-dimethyl-silanyloxy)-but-1-ynyl]-5-
trimethylsilanylethynyl-benzene (3.4 g, 6.308 mmol) in THF (210 mL) was added rapidly
TBAF (25.23 mL, 25.23 mmol). The solution was allowed to stir at RT for 10 min while it turned blue. After addition of water, the orange solution was extracted with ether, and the organic layer was dried over MgSO₄ and filtered. The solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded 0.96 g (64% yield) of the title compound as a yellow solid. Mp: 82-90 °C. IR (KBr) 3290.7, 2886.0, 2240.7, 1581.9, 1416.9, 1043.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J=1.5 Hz, 2 H), 7.42 (t, J=1.5 Hz, 1 H), 3.80 (t, J=7.0 Hz, 4 H), 3.08 (s, 1 H), 2.67 (t, J=7.0 Hz, 4 H), 2.05 (br s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 135.1, 134.6, 124.2, 122.8, 88.1, 81.2, 80.9, 78.4, 61.2, 23.9. HRMS calc’d for C₁₆H₁₄O₂: 238.0994, 238.0991.

tert-Butyldimethyl-pent-4-ynyloxy-silane²³(8). To a mixture of imidazole (3.80 g, 55.89 mmol) and tert-butyldimethylsilyl chloride (7.13 g, 46.28 mmol) were added 4-pentyn-1-ol (4 mL, 42.99 mmol) and distilled CH₂Cl₂ (50 mL). The white suspension was stirred at RT for 2 h, diluted with water and extracted with CH₂Cl₂. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. It afforded 7.73 g (91% yield) of the title compound as a clear liquid. ¹H NMR (400 MHz, CDCl₃) δ 3.71 (t, J=6 Hz, 2 H), 2.27 (dt, J=7.1, 2.7 Hz, 2 H), 1.93 (t, J=2.6 Hz, 1 H), 1.75 (quint, J=6 Hz, 2 H), 0.90 (s, 9 H), 0.06 (s, 6 H).
1,3-Bis-[5-(tert-butyl-dimethyl-silyloxy)-pent-1-ynyl]-5-
trimethylsilanylethynyl-benzene (9). See the general Pd/Cu procedure. To a solution of
bis(triphenylphosphine)palladium(II) dichloride (0.328 g, 0.467 mmol), copper(I) iodide
(0.178 g, 0.934 mmol) in THF (40 mL) and Et$_3$N (20 mL) were added 3,5-
dibromo(trimethylsilylethynyl)benzene (3.88 g, 11.68 mmol) and tert-butyl(dimethyl-
pent-4-ynoxy)silane (8) (5.79 g, 29.20 mmol). The mixture was heated at 65 °C for 30
h. Purification by flash chromatography (silica gel, hexanes/CH$_2$Cl$_2$ 60/40) afforded 6.16
g (93% yield) of the title compound as a clear oil. IR (KBr) 2954.3, 2929.1, 2896.6,
2857.0, 2233.0, 2158.0, 1580.7, 1471.3, 1413.4, 1387.9, 1360.6, 1251.2, 1106.0 cm$^{-1}$. $^1$H
NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (d, $J$=1.5 Hz, 2 H), 7.33 (t, $J$=1.4 Hz, 1 H), 3.72 (t, $J$=7.0
Hz, 4 H), 2.47 (t, $J$=7.0 Hz, 4 H), 1.80 (quint, $J$=6.1 Hz, 4 H), 0.90 (s, 18 H), 0.24 (s, 9
H), 0.09 (s, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.6, 134.1, 124.6, 123.6, 103.9, 95.2,
91.2, 79.5, 61.8, 31.9, 26.2, 18.6, 16.0, 0.1, -5.1. HRMS calc’d for C$_{33}$H$_{54}$Si$_3$O$_2$ calc’d
566.3432, found 566.3437.

5-[3-Ethynyl-5-(5-hydroxy-pent-1-ynyl)-phenyl]-pent-4-yn-1-ol (10). To a
solution of 1,3-bis-[5-(tert-butyl-dimethyl-silyloxy)-pent-1-ynyl]-5-
trimethylsilanyleneethylbenzene (9) (6.16 g, 10.86 mmol) in THF (350 mL) was added TBAF quickly (34.75 mL, 34.75 mmol). The solution was allowed to stir at RT for 8 min while it turned green, purple then green again. After addition of water, the orange solution was extracted with ether, and the ether extracts dried over MgSO₄ and filtered. The solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded 2.64 g (91% yield) of the title compound as a clear oil. IR (KBr) 3291.0, 2948.8, 2866.0, 2235.2, 1581.9, 1417.1, 1349.6, 1051.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J=1.5 Hz, 2 H), 7.37 (t, J=1.4 Hz, 1 H), 3.79 (t, J=7.0 Hz, 4 H), 3.06 (s, 1 H), 2.51 (t, J=7.0 Hz, 4 H), 1.83 (quint, J=7.1 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ 135.0, 134.3, 124.5, 122.7, 90.9, 82.4, 79.7, 78.2, 61.8, 31.4, 16.1. HRMS calc’d for C₁₉H₁₈O₂: 266.1307, found: 266.1305.

5-[3-(4-Carboxy-but-1-ynyl)-5-ethynyl-phenyl]-pent-4-ynoic acid (11). In a 1 L flask was dissolved CrO₃ (12.13 g, 121.35 mmol) in H₂SO₄ (202 mL, 1.5 M). The solution was cooled to 0 °C. The diol 10 (4.04 g, 15.17 mmol) was added dropwise with an addition funnel over 1 h. A brown precipitate formed. After stirring at 0 °C for 30 min, the reaction mixture was allowed to stir at RT for 4.5 h after which it was diluted with ether and filtered over Florisil. The cake was washed with ether. Aqueous NaOH was added and extracted with ether (3 X). The organic phase was discarded and the aqueous phase was acidified with diluted HCl until the pH was around 4. Extraction with ether, drying over MgSO₄ and filtration afforded a yellow solid. The solid was dissolved
in a minimal amount of THF. Hexanes was quickly added to form a white suspension that was quickly isolated via filtration. The yellow impurity remained at the bottom of the flask. After repeating this step several times, the white suspension in hexanes was evaporated to give 1.22 g (27% yield) of the white product as a solid. Mp: 127-132 °C. IR (KBr) 3304.7, 2924.7, 2621.0, 2238.9, 1714.2, 1583.4, 1426.3, 1408.8, 1291.4, 1211.4 cm⁻¹. ¹H NMR (400 MHz, CD₂COCD₂) δ 7.39 (s, 2 H), 7.36 (s, 1 H), 3.75 (s, 1 H), 2.71-2.60 (m, 8 H). ¹³C NMR (100 MHz, CD₂COCD₂) δ 206.7, 173.4, 135.6, 134.9, 126.0, 124.3, 91.9, 82.8, 80.9, 80.0, 33.8, 16.1. HRMS calc’d for C₁₈H₁₄O₄: 294.0892, found: 294.0891.

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\begin{align*}
\text{MeOOC} & \quad \text{COOMe} \\
\text{MeOOC} & \quad \text{COOMe}
\end{align*}
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5-[3-Ethynyl-5-(4-methoxycarbonyl-but-1-ynyl)-phenyl]-pent-4-ynoic acid methyl ester (12). The diacid 11 (0.520 g, 1.766 mmol) was dissolved in MeOH (40 mL) containing 5 drops of H₂SO₄. The reaction mixture was stirred at reflux for 1.5 d after which the MeOH was removed. Purification by flash chromatography (silica gel, hexanes/EtOAc 60/40) afforded 0.363 g (64% yield) of the title compound as a white solid. Mp: 54-57 °C. IR (KBr) 3289.6, 2952.0, 2240.8, 1737.8, 1581.4, 1436.9, 1366.7, 1198.1, 1169.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J=1.5 Hz, 2 H), 7.35 (t, J=1.5 Hz, 1 H), 3.71 (s, 6 H), 3.06 (s, 1 H), 2.73-2.59 (m, 8 H). ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 135.0, 134.5, 124.2, 122.7, 89.5, 82.3, 79.8, 78.2, 52.1, 33.4, 15.5. HRMS calc’d for C₂₀H₁₈O₄: 322.1205, found: 322.1206.
NanoKid with methyl ester feet (13). See the general Pd/Cu procedure. To 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene (0.474 g, 1.086 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.038 g, 0.054 mmol), copper(I) iodide (0.021 g, 0.109 mmol) and 5-[3-ethynyl-5-(4-methoxycarbonyl-but-1-ynyl)-phenyl]-pent-4-ynoic acid methyl ester (12) (0.350 g, 1.086 mmol) were added THF (30 mL) and Et₃N (10 mL). The mixture was stirred at 60 °C for 24 h. Purification by flash chromatography (silica gel, CH₂Cl₂) afforded 0.493 g (72% yield) of the title compound as a yellow oil. IR (KBr) 2968.4, 2924.3, 2893.2, 2862.1, 2221.6, 1741.2, 1581.5, 1474.4, 1436.9, 1362.3, 1265.0, 1200.4, 1166.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (s, 1 H), 7.52 (s, 1 H), 7.45 (d, J=1.5 Hz, 2 H), 7.35 (t, J=1.5 Hz, 1 H), 6.10 (s, 1 H), 4.20-4.17 (m, 2 H), 4.06-4.01 (m, 2 H), 3.73 (s, 6 H), 2.74-2.54 (m, 8 H), 1.34 (s, 9 H), 1.32 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 138.7, 135.7, 134.6, 134.1, 129.7, 125.9, 125.8, 124.2, 123.8, 122.6, 105.3, 104.4, 101.6, 92.0, 89.3, 88.8, 79.9, 78.0, 75.7, 65.7, 33.5, 31.2, 31.0, 28.5, 15.5. HRMS calc'd for C₄₁H₄₂O₆: 630.2981, found: 630.2978.
Nanokid with carboxylic feet (14). A solution of the NanoKid 13 with methyl ester feet (0.210 mg, 0.333 mmol), LiOH.6H2O (0.14 mg, 3.33 mmol) in MeOH (15 mL), water (5 mL) and CH2Cl2 (10 mL) was stirred at RT for 3 d. The MeOH and CH2Cl2 were removed in vacuo. The resulting residue was diluted with EtOAc and brine. Some white solid precipitated between the two phases. The solid was filtered, and a 1 M CH3COOH/CH3COONa buffer was prepared (in a 100 mL volumetric flask, 61.31 mL of CH3COOH (1 M) and 3.15 g CH3COONa were mixed and filled to 100 mL with water. 30 mL of the buffer was added to the carboxylate salt. The suspension was stirred at RT for 20 min or until the carboxylate salt was dissolved and a white suspension of the acid formed. The white product was filtered (121 mg, 60% yield). Mp: 140-150 °C. IR (KBr) 2970.2, 2925.9, 2898.3, 2858.2, 2251.3, 2213.6, 1712.8, 1582.1, 1491.0, 1474.2, 1454.1, 1415.1, 1265.7, 1214.6, 1107.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (s, 1 H), 7.53 (s, 1 H), 7.46 (d, J=1.5 Hz, 2 H), 7.36 (t, J=1.5 Hz, 1 H), 6.12 (s, 1 H), 4.20-4.17 (m, 2 H), 4.06-4.01 (m, 2 H), 2.76-2.67 (m, 8 H), 1.34 (s, 9 H), 1.32 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ 178.1, 138.1, 135.6, 134.6, 134.1, 129.7, 125.9, 125.8, 124.2, 123.8, 122.6, 105.3, 104.5, 101.6, 92.0, 89.0, 88.9, 80.1, 78.0, 75.7, 65.7, 34.9, 33.5, 31.2, 31.0, 28.5, 15.2. HRMS calc’d for C₃₉H₃₈O₆: 602.2668, found: 602.2661.
4-Bromomethyl-2-(4-bromo-phenyl)-[1,3]dioxolane (15). In a round bottom flask equipped with a Dean-Stark trap and a condenser were added 3-bromopropanediol (2.84 mL, 32.43 mmol), para-toluenesulfonic acid (103 mg, 0.540 mmol), 4-bromobenzaldehyde (1.0 g, 5.4 mmol) and benzene (80 mL). The reaction was stirred at reflux for 24 h allowing azeotropic removal of the water. After 24 h, dilute aqueous NaOH was added and the mixture was extracted with ether. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH₂Cl₂/hex 40/60) afforded 1.73 g (99% yield) of the title compound as a clear liquid. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2934.9, 2880.2, 1588.1, 1490.8, 1421.75, 1373.0, 1209.1, 1071.1 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (m, 2 H), 7.36 (m, 2 H), 5.97 (s, 0.5 H), 5.82 (s, 0.5 H), 4.52-4.48 (m, 1 H), 4.33 (dd, J=8.7, 6.3 Hz, 0.5 H), 4.18-4.10 (m, 1 H), 3.89 (dd, J=8.8, 6.2 Hz, 0.5 H), 3.59-3.51 (dd, J=10.2, 4.6 Hz, 0.5 H), 3.49-3.37 (m, 1.5 H). ¹³C NMR (100 MHz, CDCl₃) δ 136.7, 136.2, 131.82, 131.78, 128.5, 128.3, 123.9, 123.7, 104.4, 103.8, 75.9, 75.4, 70.0, 69.6, 32.7, 32.3. HRMS calc'd for C₁₀H₁₀Br₂O₂: 319.9048, found: 319.9041.
[2-(4-Bromo-phenyl)-[1,3]dioxolan-4-yl]-methanethiol (16). To thiourea (0.429 g, 5.64 mmol) under N₂, was added 4-bromomethyl-2-(4-bromo-phenyl)-[1,3]dioxolane (15) (1.73 g, 5.37 mmol) in EtOH (11 mL). The reaction was allowed to stir at reflux overnight, then cooled down to RT. An aqueous solution of NaOH (2.5 N, 3.2 mL) was added and the mixture allowed to stir at reflux for another 2 h. After cooling down to RT, water was added to quench the reaction. The mixture was extracted with ether. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH₂Cl₂) afforded 626 mg (42% yield) of the title compound as a light yellow oil. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2880.2, 2251.0, 1596.1, 1488.2, 1421.2, 1384.2, 1297.7, 1216.8, 1072.4, 1012.0 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (m, 2 H), 7.36 (m, 2 H), 5.93 (d, J=1.8 Hz, 0.25 H), 5.90 (d, J=1.8 Hz, 0.25 H), 5.77 (s, 0.25 H), 5.75 (s, 0.25 H), 4.42-4.36 (m, 1 H), 4.28-4.22 (m, 0.5 H), 4.12-4.09 (m, 0.5 H), 3.90 (m, 0.5 H), 3.80-3.73 (m, 0.5 H), 3.00-2.75 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 137.0, 136.4, 131.5, 128.4, 128.1, 123.5, 123.3, 103.7, 103.0, 102.99, 76.6, 76.53, 76.48, 75.9, 75.85, 70.0, 69.9, 69.6, 69.5, 53.6, 35.8, 35.6, 35.5, 35.32, 35.30, 35.0. MS calc'd for C₂₀H₂₀Br₂O₄S₂ calc'd 274.0, found 273.9.
2-[2,5-Bis-(3,3-dimethyl-but-1-ynyl)-4-ido-phenyl]-4-bromomethyl-[1,3]dioxolane (17). In a round bottom flask equipped with a Dean-Stark trap and a condenser were added 3-bromopropanediol (4.0 mL, 45.83 mmol), para-toluenesulfonic acid (44 mg, 0.229 mmol), 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene (2.00 g, 4.583 mmol) and benzene (100 mL). The reaction was stirred at reflux for 20 h allowing azeotropic removal of the water. After 20 h, dilute aqueous NaOH was added and the reaction was extracted with ether. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH₂Cl₂/hex 40/60) afforded 2.00 g (83% yield) of the title compound as a white sticky solid. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2968.1, 2926.5, 2896.7, 2866.1, 2237.0, 1588.8, 1529.5, 1466.5, 1381.5, 1362.1, 1264.9, 1202.7, 1185.7, 1153.0, 1070.7 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1 H), 7.55 (s, 0.5 H), 7.50 (s, 0.5 H), 6.22 (s, 0.5 H), 6.09 (s, 0.5 H), 4.57-4.53 (m, 0.5 H), 4.49-4.46 (m, 0.5 H), 4.38 (m, 0.5 H), 4.15 (s, 0.5 H), 4.13 (s, 0.5 H), 3.91 (d, J=6.3 Hz, 0.5 H), 3.88 (d, J=6.3 Hz, 0.5 H), 3.59-3.52 (m, 1 H), 3.47-3.39 (m, 1 H), 1.365 (s, 4.5 H), 1.357 (s, 4.5 H), 1.33 (s, 4.5 H), 1.32 (s, 4.5 H). ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 141.9, 138.0, 137.5, 130.0, 129.9, 129.3, 129.2, 123.8, 123.6, 106.1, 106.0, 104.3, 104.2, 102.5, 102.2, 102.1, 101.9, 81.83, 81.79, 76.0, 75.4, 74.9, 74.8, 70.1, 69.7, 32.5, 32.4, 31.8, 31.0, 30.9, 28.52, 28.48. HRMS calc’d for C₂₂H₂₆BrI₂O₂: 528.0161, found: 530.0169.
4-Azidomethyl-2-[2,5-bis-(3,3-dimethyl-but-1-ynyl)-4-iodo-phenyl]-1,3]dioxolane (18). A solution of 2-[2,5-bis-(3,3-dimethyl-but-1-ynyl)-4-iodo-phenyl]-4-bromomethyl-[1,3]dioxolane (17) (355 mg, 0.671 mmol) and sodium azide (436 mg, 6.708 mmol) in DMF (15 mL) was stirred at RT for 20 h then at 45 °C for 18 h. The reaction mixture was diluted with water and extracted with ether. The combined organic phases were dried over MgSO₄, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH₂Cl₂/hex 40/60) afforded 270 mg (82% yield) of the title compound as a white sticky solid. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2969.1, 2927.0, 2897.4, 2866.9, 2236.0, 2102.1, 1588.9, 1530.0, 1466.7, 1401.1, 1380.9, 1362.5, 1265.4, 1083.5 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 0.5 H), 7.86 (s, 0.5 H), 7.59 (s, 0.5 H), 7.50 (s, 0.5 H), 6.23 (s, 0.5 H), 6.06 (s, 0.5 H), 4.57-4.53 (m, 0.5 H), 4.47-4.43 (m, 0.5 H), 4.38-4.35 (m, 0.5 H), 4.26 (dd, J=8.5, 6.5 Hz, 0.5 H), 4.08 (dd, J=8.5, 6.5 Hz, 0.5 H), 3.97 (dd, J=8.4, 5.5 Hz, 0.5 H), 3.84 (dd, J=8.4, 5.5 Hz, 0.5 H), 3.54-3.50 (m, 1.5 H), 3.47-3.39 (m, 0.5 H), 1.36 (s, 9 H), 1.33 (s, 4.5 H), 1.32 (s, 4.5 H). ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 141.8, 138.3, 137.4, 130.0, 129.8, 129.4, 129.2, 123.8, 123.6, 106.1, 105.9, 104.2, 104.2, 102.1, 101.92, 101.88, 101.8, 81.8, 81.7, 75.2, 75.1, 74.9, 74.8, 68.0, 53.0, 52.4, 30.9, 28.5, 28.4, 28.4. HRMS calc'd for C₂₂H₂₆IN₃O₂: 491.1070, found: 491.1066.
5-[3-[4-(4-Bromomethyl-[1,3]dioxolan-2-yl)-2,5-bis-(3,3-dimethyl-but-1-ylnyl)-phenylethynyl]-5-(4-methoxycarbonyl-but-1-ylnyl)-phenyl]-pent-4-ynoic acid methyl ester (19). To 2-[2,5-bis-(3,3-dimethyl-but-1-ylnyl)-4-iodo-phenyl]-4-bromomethyl-[1,3]dioxolane (17) (0.751 g, 1.42 mmol), bis(triphenylphosphine)palladium(II) dichloride (43 mg, 0.062 mmol), copper(I) iodide (0.024 g, 0.123 mmol) and the diester halide 12 (0.398 g, 1.235 mmol) were added THF (30 mL) and Et$_3$N (12 mL). The mixture was stirred at 65 °C for 18 h. The solvent was evaporated in vacuo. The residue was diluted with NH$_4$Cl and extracted with Et$_2$O. The combined organic phases were dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$) afforded 0.681 g (76% yield) of the title compound as a yellow sticky solid. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2969.1, 2926.9, 2898.7, 2867.4, 2249.9, 1739.6, 1581.7, 1491.4, 1474.3, 1437.5, 1362.8, 1260.3, 1201.1, 1167.6, 1107.3, 1063.5 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (s, 0.5 H), 7.55 (s, 0.5 H), 7.51 (s, 0.5 H), 7.50 (s, 0.5 H), 7.43 (d, $J$=1.5 Hz, 2 H), 7.33 (s, 1 H), 6.24 (s, 0.5 H), 6.11 (s, 0.5 H), 4.57-4.53 (m, 0.5 H), 4.50-4.46 (m, 0.5 H), 4.36 (m, 0.5 H), 4.12 (d, $J$=5.3 Hz, 1 H), 3.88 (m, 0.5 H), 3.69 (s, 6 H), 3.56-3.52 (m, 1 H), 3.46-3.38 (m, 1 H), 2.71-2.67 (m, 4 H), 2.60-2.50 (m, 4 H), 1.35 (s, 4.5 H), 1.34 (s, 4.5 H), 1.30 (s, 4.5 H), 1.29 (s, 4.5 H). $^{13}$C
NMR (100 MHz, CDCl$_3$) δ 172.2, 137.9, 137.4, 135.5, 135.4, 134.5, 133.9, 129.5, 129.5, 126.0, 125.9, 125.8, 125.77, 124.2, 123.6, 122.6, 122.3, 105.4, 105.4, 104.52, 104.48, 102.4, 102.0, 92.0, 89.3, 88.6, 79.7, 77.8, 75.9, 75.5, 75.4, 75.3, 70.0, 69.6, 51.9, 33.3, 32.4, 31.1, 30.9, 30.8, 28.3, 15.4. HRMS calc'd for C$_{42}$H$_{43}$BrO$_6$: 722.2243, found: 722.2240.

5-[3-[4-(4-Azidomethyl-[1,3]dioxolan-2-yl)-2,5-bis-(3,3-dimethyl-but-1-ynyl)-phenylethynyl]-5-(4-methoxycarbonyl-but-1-ynyl)-phenyl]-pent-4-ynoic acid methyl ester (20). A solution of the bromide 19 (0.675 g, 0.933 mmol) and sodium azide (0.606 g, 9.33 mmol) in DMF (20 mL) was stirred at 60 °C for 19 h. The reaction mixture was diluted with brine and extracted with ether. The combined organic phases were dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH$_2$Cl$_2$) afforded 0.580 g (91% yield) of the title compound as a clear sticky oil. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2969.1, 2926.9, 2867.7, 2219.0, 2102.7, 1740.3, 1581.7, 1491.7, 1474.5, 1437.5, 1416.7, 1362.8, 1266.0, 1200.8, 1167.7, 1107.6 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (s, 0.5 H), 7.55 (s, 0.5 H), 7.52 (s, 0.5 H), 7.51 (s, 0.5 H), 7.44 (d, J=1.5 Hz, 2 H), 7.35 (s, 1 H), 6.27 (s, 0.5 H), 6.10 (s, 0.5 H), 4.50-4.46 (m, 0.5 H),
4.38 (m, 0.5 H), 4.28 (m, 0.5 H), 4.08 (m, 0.5 H), 3.97 (m, 0.5 H), 3.88 (m, 0.5 H), 3.69 (s, 6 H), 3.56-3.39 (m, 2 H), 2.71-2.67 (m, 4 H), 2.60-2.52 (m, 4 H), 1.35 (s, 4.5 H), 1.34 (s, 4.5 H), 1.30 (s, 4.5 H), 1.29 (s, 4.5 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.3, 138.2, 137.4, 135.6, 135.4, 134.5, 134.0, 129.7, 129.6, 126.0, 125.97, 125.9, 125.8, 124.2, 124.7, 122.66, 122.5, 105.5, 105.3, 104.6, 104.5, 102.1, 101.9, 92.1, 89.4, 88.7, 79.8, 77.8, 75.53, 75.46, 75.2, 75.1, 68.0, 53.6, 53.0, 52.4, 52.0, 33.4, 31.12, 13.11, 30.9, 28.4, 15.4. HRMS calc'd for C$_{42}$H$_{43}$N$_3$O$_6$: 685.3152, found: 685.3155.

5-[3-[4-(4-Aminomethyl-[1,3]dioxolan-2-yl)-2,5-bis-(3,3-dimethyl-but-1-ynyl)phenylethynyl]-5-(4-methoxycarbonyl-but-1-ynyl)-phenyl]-pent-4-ynoic acid methyl ester (21). To a solution of the azide 20 (580 mg, 0.846 mmol) in anhydrous THF (10 mL) was slowly added a solution of triphenylphosphine (333 mg, 1.269 mmol) in THF (10 mL). The reaction mixture was allowed to stir at RT overnight. The solvent was evaporated, and water was added. After extraction with ether, the combined organic phases were dried over MgSO$_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CHCl$_3$/MeOH/TEA 20/1/0.1) afforded 235 mg (42% yield) of the title compound as a yellow sticky oil. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 2968.6, 2920.4,
2897.1, 2867.3, 2221.7, 1740.6, 1581.7, 1491.4, 1474.6, 1437.4, 1416.7, 1362.5, 1265.2, 1200.7, 1168.2, 1107.1 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (s, 0.5 H), 7.57 (s, 0.5 H), 7.50 (s, 1 H), 7.43 (d, \(J=1.5\) Hz, 2 H), 7.33 (s, 1 H), 6.17 (s, 0.5 H), 6.09 (s, 0.5 H), 4.25 (m, 1.5 H), 4.07 (t, \(J=7.8\) Hz, 0.5 H), 3.87 (dd, \(J=7.8, 6.2\) Hz, 0.5 H), 3.74 (dd, \(J=7.8, 6.2\) Hz, 0.5 H), 3.69 (s, 6 H), 2.94 (m, 2 H), 2.71-2.67 (m, 4 H), 2.60-2.52 (m, 4 H), 1.43 (br s, 2 H), 1.35 (s, 4.5 H), 1.34 (s, 4.5 H), 1.30 (s, 4.5 H), 1.29 (s, 4.5 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.3, 138.6, 137.9, 135.5, 135.4, 134.5, 133.9, 132.2, 132.1, 129.60, 129.56, 128.7, 128.6, 125.9, 125.8, 125.7, 124.2, 123.7, 122.6, 122.3, 105.2, 104.4, 101.6, 101.1, 91.9, 89.3, 88.7, 79.8, 78.6, 78.3, 77.9, 77.4, 75.6, 75.5, 68.4, 68.0, 52.0, 44.7, 44.4, 33.4, 31.1, 30.92, 30.90, 28.4, 15.4. HRMS calc’d for C\(_{42}\)H\(_{45}\)NO\(_6\): 659.3247, found: 659.3253.

![Structure](image)

5-[3-[4-(4-Aminomethyl-[1,3]dioxolan-2-yl)-2,5-bis-(3,3-dimethyl-but-1-ynyl)-phenylethynyl]-5-(4-carboxy-but-1-ynyl)-phenyl]-pent-4-ynoic acid (22). In a round bottom flask, under air were added the diester 21 (225 mg, 0.341 mmol), LiOH.H\(_2\)O (143 mg, 3.41 mmol), MeOH (15 mL), H\(_2\)O (5 mL) and CH\(_2\)Cl\(_2\) (10 mL). The reaction mixture was stirred at RT for 1 d. MeOH and CH\(_2\)Cl\(_2\) were evaporated under reduced pressure. A CH\(_3\)COOH/CH\(_3\)COONa buffer (pH=4.8) was added until a white solid
precipitated. The solid was filtered and dried. The reaction afforded 215 mg (100% yield) of the title compound as a white solid, an inseparable 1:1 mixture of diastereoisomers. Mp: decomp. IR (KBr) 3434.8, 2967.8, 2924.6, 2862.1, 2226.2, 1711.1, 1580.4, 1405.8, 1386.9, 1265.5, 1202.1, 1156.1, 1108.7, 1068.6 cm⁻¹. ¹H NMR (400 MHz, CD₃OD) δ 7.63 (s, 0.5 H), 7.50 (s, 0.5 H), 7.42 (m, 3 H), 7.33 (s, 1 H), 6.26 (s, 0.5 H), 6.10 (s, 0.5 H), 4.56 (m, 0.5 H), 4.45 (m, 0.5 H), 4.30 (t, J=7.8 Hz, 0.5 H), 4.15 (t, J=7.8 Hz, 0.5 H) 3.98 (dd, J=7.8, 6.2 Hz, 0.5 H), 3.77 (dd, J=7.8, 6.2 Hz, 0.5 H), 3.26-3.08 (m, 2 H), 2.67 (t, J=7.3 Hz, 4 H), 2.51 (t, J=7.3 Hz, 4 H), 1.33 (s, 18 H). ¹³C NMR (100 MHz, CD₃OD) δ 179.2, 178.5, 139.7, 138.7, 136.4, 136.1, 135.5, 134.6, 133.2, 133.1, 130.9, 130.7, 130.2, 127.3, 127.1, 126.2, 124.8, 124.2, 123.8, 106.6, 106.55, 105.54, 105.5, 103.3, 102.8, 93.2, 92.33, 92.30, 89.3, 80.1, 78.9, 76.7, 76.56, 74.83, 74.7, 69.2, 43.6, 42.7, 37.0, 31.7, 31.39, 31.36, 29.5, 23.0, 17.2. MALDI (dithranol) calc'd for C₄⁶H₄₁NO₆: 631, found: 632.

![Chemical structure](image)

(23). In a reaction flask were mixed, methyl-12-aminododecanoate (31 mg, 0.135 mmol), fluorescein isothiocyanate (53 mg, 0.135 mmol), NaHCO₃ (57 mg, 0.675 mmol), THF (5.5 mL), and water (1 mL). After stirring for 2 d, THF was evaporated and a CH₃COOH/CH₃COONa buffer pH=4.5 was added until an orange precipitate formed and was filtered. After drying in the vacuum oven, 83 mg (100% yield) of a red-orange solid was obtained. IR (KBr) 3353.1, 2925.1, 2852.6, 1732.3, 1606.9, 1539.7, 1504.5, 1456.2,
1384.3, 1301.0, 1257.5, 1207.1, 1175.6, 1111.9 cm$^{-1}$. $^1$H NMR (400 MHz, CD$_3$OD) δ 8.13 (br s, 1 H), 7.73 (d, $J$=7.9 Hz, 1 H), 7.14 (d, $J$=8.2 Hz, 1 H), 6.71 (d, $J$=8.8 Hz, 2 H), 6.66 (d, $J$=2.4 Hz, 2 H), 6.55 (dd, $J$=8.7, 2.4 Hz, 2 H). 3.62 (s, 3 H), 3.57 (br s, 2 H), 2.27 (t, $J$=7.5 Hz, 2 H), 1.64-1.55 (m, 4 H), 1.34 (m, 16 H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.2, 154.7, 130.7, 126.3, 114.5, 112.1, 103.7, 52.1, 50.0, 45.9, 35.0, 31.0, 30.8, 30.7, 30.6, 30.5, 30.3, 30.1, 28.2, 26.2. MALDI (dithranol) calc'd for C$_{34}$H$_{38}$N$_2$O$_7$S: 618, found: 619.

(24). In a reaction flask were mixed 12-aminododecanoic acid (29 mg, 0.135 mmol), fluorescein isothiocyanate (53 mg, 0.135 mmol), NaHCO$_3$ (57 mg, 0.675 mmol), THF (14.5 mL), and water (3 mL). After stirring at RT for 3 d, THF was evaporated and a CH$_3$COOH/CH$_3$COONa buffer pH=4.8 was added until an orange precipitate formed and was filtered. After drying in the vacuum oven, 75 mg (92% yield) of a red-orange solid is obtained. IR (KBr) 3432.0, 2925.3, 2852.9, 1715.0, 1634.1, 1604.5, 1538.6, 1504.9, 1455.8, 1384.4, 1305.5, 1259.4, 1207.1, 1176.0, 1113.9 cm$^{-1}$. $^1$H NMR (400 MHz, CD$_3$OD) δ 8.11 (br s, 1 H), 7.75 (d, $J$=7.9 Hz, 1 H), 7.15 (d, $J$=8.2 Hz, 1 H), 6.72 (d, $J$=8.8 Hz, 2 H), 6.67 (d, $J$=2.4 Hz, 2 H), 6.56 (dd, $J$=8.7, 2.4 Hz, 2 H), 3.59 (br s, 2 H), 2.25 (t, $J$=7.5 Hz, 2 H), 1.64-1.52 (m, 4 H), 1.34 (m, 16 H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 178.6, 171.5, 162.7, 154.7, 142.6, 131.5, 130.7, 130.1, 126.2, 120.3, 114.4,
112.0, 103.7, 69.0, 45.9, 40.9, 35.6, 30.8, 30.76, 30.72, 30.59, 30.57, 30.4, 30.3, 30.1, 28.2, 27.2, 26.7, 26.5. MALDI (dithranol) calc'd for C_{33}H_{36}N_{2}O_{7}S: 604. found: 605.

(25). In a reaction flask were mixed 22 (36 mg, 0.057 mmol), fluorescein isothiocyanate (22 mg, 0.057 mmol), NaHCO₃ (24 mg, 0.286 mmol), THF (5.5 mL), and water (1 mL). After stirring at RT for 3 d, THF was evaporated and a CH₃COOH/CH₃COONa buffer pH=4.8 was added until an orange precipitate formed and was filtered. After drying in the vacuum oven, 58 mg (99% yield) of a red-orange solid is obtained. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr) 3430.2, 2968.7, 2920.4, 2862.1, 2233.0, 1712.8, 1698.7, 1631.1, 1581.9, 1504.4, 1470.1, 1409.9, 1304.9, 1264.4, 1208.2, 1110.9 cm⁻¹. ¹H NMR (500 MHz, CD₃OD) δ 8.24 (d, J=1.5 Hz, 0.5 H), 8.09 (br s, 0.5 H), 7.80 (d, J=8.1 Hz, 0.5 H), 7.69 (br s, 0.5 H), 7.61 (s, 0.5 H), 7.53 (s, 0.5 H), 7.43 (s, 0.5 H), 7.40 (d, J=1.5 Hz, 1 H), 7.33 (m, 2 H), 7.11 (d, J=8.2 Hz, 1 H), 6.76 (dd, J=7.8, 1.9 Hz, 2 H), 6.71 (m, 0.5 H), 6.67 (d, J=2.4 Hz, 1 H), 6.64 (m, 1 H), 6.56 (m, 2 H), 6.22 (s, 0.5 H), 6.06 (s, 0.5 H), 4.61 (m, 0.5 H), 4.53 (m, 0.5 H), 4.31 (m, 0.5 H), 4.13 (m, 0.5 H), 4.03-3.85 (m, 3 H), 2.29 (m, 4 H).
2.54 (m, 4 H), 1.34 (s, 4.5 H), 1.32 (s, 13.5 H). \(^{13}\)C NMR (125 MHz, CD\(_3\)OD) δ 183.6, 183.5, 178.5, 178.2, 177.5, 171.8, 164.3, 155.2, 142.6, 140.2, 136.2, 135.5, 134.63, 134.60, 131.1, 130.9, 130.85, 130.5, 127.2, 127.1, 126.9, 126.7, 126.3, 126.2, 126.1, 124.9, 124.8, 124.0, 123.9, 115.3, 112.8, 112.5, 106.6, 105.7, 105.6, 103.9, 103.8, 103.6, 102.7, 102.4, 93.2, 93.1, 92.0, 89.3, 89.2, 80.2, 80.1, 79.0, 78.9, 76.8, 76.8, 76.6, 69.6, 69.0, 47.4, 36.34, 36.29, 35.5, 31.6, 31.6, 31.42, 31.36, 31.0, 29.5, 29.4, 22.3, 16.92, 16.88. MALDI (Dithranol) calc'd for C\(_{61}\)H\(_{52}\)N\(_2\)O\(_{11}\)S: 1021, found: 1021.
5. References

(1) Yildiz, A.; Forkey, J. N.; McKinney, S. A.; Ha, T.; Goldman, Y. E.; Selvin, P. R. 
    *Science* 2003, 300, 2061-2065.


(3) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; 


    1986, 90, 4474.


Synthesis of Conjugated Molecules: From Electronics to MolecuLART

Volume II of III: Spectral Data

by

Stéphanie Hina Chanteau

HOUSTON, TEXAS

NOVEMBER 2003
PART I: ELECTRONICS
CHAPTER 1

SYNTHESIS OF POTENTIAL MOLECULAR DEVICES CONTAINING PYRIDYL ALLIGATOR CLIPS FOR MOLECULAR ELECTRONICS
<table>
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<td>89.61</td>
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<tr>
<td>H</td>
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<td>N</td>
<td>5.01</td>
<td>4.98</td>
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**Single Components:** C, H, N

**Analyse for:** C, H, N

**Hygroscopic:** No

**To be dried:** Yes

**Temp.:** 20°C

**Vac.:** 101.3 kPa

**FAX Service:** Yes

**Fax Phone #:** 713-348-6150

**Rush Service:** No

**Phone Service:** Price List

---

**Sample No.:** 802-110

**P.O. Box 2288 Norcross, Georgia 30091**

**(770) 242-0102**

**Sample Received:** OCT 27 2005

**Date Completed:** OCT 27 2008
SPEC: sc2-110 (19-Feb-01 18:07:10)
Samp: SC2-110 C21 H13 N MW=279.104799
Oper: TDM
Base: 279.07
Masses: 50.00 > 400.00
Peak: 1000.0 mmu
Intensity: 1037526

RES #9 0 12.04 min {SI +VE +LMR RSCAN (EXP) UP HR NRM} (+82-10)

Scans: 1 > 119
Client: SC/TMT
Peaks: 94
RIC: 1760969

1.0E+06

279.1

---

The diagram shows a mass spectrum with peaks at various masses, including 279.1. The spectrum is labeled with mass numbers and intensities, indicating the molecular weight and composition of the sample.
SPEC: sc1186 (06-Sep-00 15:58:38)
Samp: SC1-186 C21 H12 N2 O2 MW=324
Oper: TIM Study: EI + HR
Base: 324.08 Masses: 50.00 > 900.00
Peak: 1000.0 amu Intensity: 371742
REG #9 0 10.95 min (EI +VE +LMR SCAN (EXP) UP HR NRM) (+52-12)

Scan: 1 > 92
Client: SC/JMP
#Peaks: 223
RIC: 2754072

3.7E+05
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<tr>
<td>H</td>
<td>3.73%</td>
<td>3.72%</td>
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<tr>
<td>N</td>
<td>8.64%</td>
<td>8.59%</td>
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</table>

**Elements Present:** C, H, N, O

**Analyzed for:** C, H, N

**Hygroscopic:** No  
**Explosive:** No

**M.P.:**  
**B.P.:**

**To be dried:** Yes  
**Yes:**

**Temp.:**  
**Time:**

**FAX Service:** Yes  
**No:**  
**Fax Phone #:** 713-346-6750

**Rush Service:** (SEE CURRENT)

**Phone Services:**  
**PRICE LIST**

**Phone No.:**

---

**Sample No.:** ac5-70  
**SUBMITTER:**  
**Company / School:** Rice University  
**Address:** 1800 Rice Blvd  
**Location:** Houston, TX 77005

**PROFESSOR/SUPERVISOR:**  
**NAME:**  
**DATE:** 10/21/03

**Remarks:**

---

**Date Received:** OCT 27 2003  
**Date Completed:** OCT 27 2003
SPEC: sc2-41 (21-Nov-00 15:39:09)
Samp: SC2-41 C51 H13 N3 O2 MW=339.100777
Oper: TDM Study: EI + HR
Base: 339.09 Masses: 45.00 > 600.00
Peak: 1000.0 mpu Intensity: 63102

RNC $9 @ 12.06 min (EI +VE +LMR BSCAN (EXP) UF HR NRM) {+$9-17 (+62-40)}

339.09

105.03

77.04

sc2-41

322.09

6.3E+04
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<tr>
<td>H</td>
<td>4.46</td>
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<td>4.13</td>
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<tr>
<td>N</td>
<td>13.33</td>
<td>13.03</td>
<td>13.08</td>
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NO CHARGE FOR DUPLICATES

Date Received: OCT 27 2003
Date Completed: OCT 27 2003
SPEBC: sc5-74 (14-Aug-03 16:25:43)
Samp: SC5-74 C8 H6 N2 O2 mm=162.042927
Oper: Xian Study: DEI + HR
Base: 162.01 Masses: 50.00 > 200.00
Peak: 10000.0 mnu Intensity: 5449904
REG #9 @ 5.35 min (EI +VE +LMR BSCAN (EXP) UP HR NRM) (+50-9)

162.01

sc5-74

NO2

NH2

5.4E+06
SPEC: sc5-75 (14-Aug-03 11:44:53)
Samp: sc5-75 Cl4 H5 P5 N2 O2  mw=328.0271
Oper: Xiao  Study: DHE + HR
Base: 328.03  Masses: 200.00 > 450.00
Peak: 1000.0 mnu  Intensity: 2382083
FKG #9 @ 9.69 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM) (+155-24)

Scans: 1 > 160  Client: SC/JMT
#Peaks: 143  RIC: 7082319

F  F
|   |   |
F  F
\-\-\-\-\-\-\-
F  F
\-\-\-\-\-\-\-
NO₂

sc5-75
## ATLANTIC MICROLAB, INC.

Sample No. A65 - 78

100 Box 2208
Lorcrass, Georgia 30031
770) 242-0082

Professor/Supervisor: Prof. Tour

<table>
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<tr>
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<td>H</td>
<td>1.70</td>
<td>1.59</td>
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<tr>
<td>N</td>
<td>6.76</td>
<td>6.72</td>
</tr>
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</table>

**Single**  
**Duplicate**

- Elements Present: C, H, N, O, F
- Analysis for: C, H, N
- Hygroscopic:  
- Explosive:  
- M.P.:  
- B.P.:  
- To be dried: Yes  
- No  
- Temp.:  
- Vuc.:  
- Time:  
- FAX Service  
- Fax. Phone #: 313-348-6350  
- Rush Service: (SEE CURRENT)  
- Phone Service: PRICE LIST  
- Phone No.:  

Date Received: OCT 27 2003  
Date Completed: OCT 27 2003
SPBC: sc2-233 (24-Oct-00 15:52:27)  
Samp: SC2-23-3 Cl7 H24 Br N O2 S1 MW=381.0759  
Oper: TDM  
Base: 340.00  
Peak: 1000.0 ppm  
TMS  
Scan: 1 > 131  
Client: SC/JMF  
#Peaks: 259  
RIC: 2342476  

REG #9 @ 14.35 min {EI + VE + LMR BSCAN (EXP) UP HR NRX} {+80-65}  

4.0E+05
SPEC: sc2-148 (15-Aug-01 11:28:56)
Sample: SC2-148 C23 H14 N2 O2 S Mn=398.072515
Spectra: TEM Study: EI + HR
Mass: 356.04 Masses: 50.00 > 500.00
Peak: 1000.0 m/z Intensity: 533675
REG #9 @ 12.86 min [EI +VE +LR MS + EX + UP HR NRM] (70-10)

Scans: 1 x 112
Client: SC/JHF
#Peaks: 109
RTC: 3169560
5.38 x 05

[Diagram of molecule labeled sc2-148]
SPEC: sc1193-1 (27-Sep-00 17:36:27)
Semp: SCI-193-1 C18 H17 N3 O2 Si MW=335.10900
Oper: TDM Study: EI + HR
Base: 69.00 Masses: 50.00 > 600.00
Peak: 1000.0 ppm Intensity: 2729599

RNC #9 8 10.03 min (EI +VE +LMK BSCAN (EXP) UP HR NRM) {+53-10} 2.7E+05
<table>
<thead>
<tr>
<th>Element</th>
<th>Theory</th>
<th>Found</th>
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</thead>
<tbody>
<tr>
<td>C</td>
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<td>64.63</td>
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<tr>
<td>O</td>
<td>11.61</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>7.76</td>
<td></td>
</tr>
</tbody>
</table>

Sample No. sc2-202-10
R.O. Box 2288 C23 H15 N3 O3 S
Norcross, Georgia 30091
(770) 242-0082
www.atlanticmicrolab.com
PROFESSOR/SUPERVISOR: Dr. J.M. Tour

SUBMITTER
Company/School Rice University
Address 6100 Main Street
Ctr for Nanoscale Sci & Te
Houston, TX 77005
NAME Stephanie Chante
DATE 10/25/00

Single [x] Duplicates [ ]

Elements: CHNOS
Present: CHN
Analyze for: CHN
Hygroscopic [x] Explosive [ ]
M.P. [ ] B.P. [ ]
To be dried: Yes [x] No [ ]
Temp. [ ] Vac. [ ] Time [ ]
FAX Service [x] FAX Phone #: 713-346-6250
Rush Service [ ] (SEE CURRENT
Phone Service [ ] PRICE LIST)
Phone No. [ ]

Date Received OCT 30 2000
Remarks:
Date Completed OCT 31 2000
CHAPTER 2

THERMAL ANALYSIS OF MOLECULAR DEVICES FOR VAPOR PHASE ASSEMBLY
Sample: yao-III-114
Size: 5.0000 mg
Method: Ramp
Comment: thioacetate thiol

File: C:\TAIData\DSC\Staphyao-III-114.001
Operator: steph
Run Date: 14-Jul-03 08:33
Instrument: DSC Q10 V6.21 Build 233

DSC

Heat Flow (W/g)

Temperature (°C)

Exo Up

206.40°C
1.747 W/g

160.23°C

397.82°C

Universal V3.6C TA Instruments
Sample: yao-III-114
Size: 3.2240 mg
Method: Ramp
Comment: thioacetate thiol

File: C:\TAI\DATA\TGA\stepholyste-II-114.003
Operator: SC
Run Date: 14-Jul-03 12:30
Instrument: TGA Q50 V4.10 Build 157

![Graph of weight percentage vs. temperature](image)

- 370.95°C 5.000% Loss
- 25.59% weight loss (0.9540 mg)
Sample: yao-4-62
Size: 5.2000 mg
Method: Ramp
Comment: phenyl mononitro thiol

File: C:\TA\Data\DSC\Stephiyao-4-62.001
Operator: steph
Run Date: 14-Jul-03 10:22
Instrument: DSC Q10 V6.21 Build 233

Heat Flow (W/g)

131.42°C
6.325 W/g

99.14°C

214.02°C

Temperature (°C)
Sample: yao-4-62
Size: 5.1820 mg
Method: Ramp
Comment: phenyl nitro thiol

Temperature (°C)

Weight (%)

80.13°C

375.70°C 5.000% Loss

27.52% weight loss (1.426mg)

Universal V3.8C TA Instruments
Sample: yao-1-162
Size: 4.2000 mg
Method: Ramp
Comment: phenyl phenyl thiol

File: C:\TA\Data\DSC\Stephiyao-1-162.001
Operator: steph
Run Date: 14-Jul-03 13:59
Instrument: DSC Q10 V6.21 Build 233

![DSC Thermogram](image)

**DSC Thermogram**

- Heat Flow (W/g)
- Temperature (°C)

- Peaks:
  - 166.79°C (1.882 W/g)
  - 238.72°C
  - 152.60°C

**Chemical Structure**:

![Chemical Structure](image)

**Structure**: YAO-4-59

**Explanation**: The thermogram shows the heat flow against temperature, highlighting key peaks and transitions in the sample's properties.

**Temperature**: The temperature range spans from 0 to 500°C, capturing the thermal behavior of the sample.

**Heat Flow**: The heat flow ranges from -0.5 to 2.0 W/g, indicating the sample's thermal response.

**Sample Details**: The sample is a phenyl phenyl thiol, with a size of 4.2000 mg, measured by DSC with specific details noted in the operator and file entries.
Sample: DWP-II-39
Size: 7.0120 mg
Method: Ramp
Comment: phenyl nitro carboxylic

File: CATA\Data\TGA\steph\DWP-II-39.001
Operator: steph
Run Date: 11-Aug-03 10:00
Instrument: TGA Q50 V4.10 Build 157

![Graph showing weight percentage versus temperature](attachment:image.png)

- 139.47°C
- 273.05°C 5.000% Loss
- 22.09% weight loss (1.548mg)
Sample: SMD-III-93
Size: 3.1000 mg
Method: Ramp
Comment: phenyl phenyl aniline OPV

File: C:\TA\Data\DSC\Steph\SMD-III-93.001
Operator: Steph
Run Date: 23-Jul-03 15:38
Instrument: DSC Q10 V6.21 Build 233

1.0
0.5
0.0
-0.5
-1.0
-1.5

Heat Flow (W/g)

135.44°C
161.51°C
271.65°C

Exo Up

Temperature (°C)

Universal V3.6C TA Instruments
Sample: SMD-3-36
Size: 4.6000 mg
Method: Ramp
Comment: phenyl mononitro aniline OPV

File: C:\TAI\Data\DSC\StephSMD-3-36.001
Operator: Steph
Run Date: 24-Jul-03 13:07
Instrument: DSC Q10 V6.21 Build 233

![DSC Diagram]

- Heat Flow (W/g)
- Temperature (°C)

Key Temperatures:
- 134.06°C
- 187.96°C
- 206.72°C
- 340.37°C
Sample: sc5-65
Size: 5.3000 mg
Method: Ramp
Comment: pyridine nitro pyridine

File: C:\Data\DSC\Steph-sc5-65.001
Operator: steph
Run Date: 15-Jul-03 08:07
Instrument: DSC Q10 V6.21 Build 233

![DSC graph showing peak at 191.74°C with a heat flow of 12.18 W/g and other temperature points: 157.87°C, 228.90°C, and 252.22°C.](image-url)
Sample: sc5-85
Size: 3.8140 mg
Method: Ramp
Comment: pyridine nitro pyridina

TGA

File: C:\TAD ata\TGAstephc sc5-65.001
Operator: steph
Run Date: 06-Aug-03 15:45
Instrument: TGA Q50 V4.10 Build 157

Temperature (°C)

Weight (%) 105

153.98°C

341.02°C 5.000% Loss

14.75% weight loss (0.5625mg)
Sample: sc5-78
Size: 8.3150 mg
Method: Ramp
Comment: pentafluoro nitro pyridine

TGA

File: C:\TAIData\TGA\steph\sc5-78.001
Operator: steph
Run Date: 07-Aug-03 08:12
Instrument: TGA Q50 V4.10 Build 157

![Graph showing weight loss as a function of temperature. Peaks at 94.23°C and 219.73°C with 5.00% loss and 17.77% weight loss respectively.]
Sample: sc5-73
Size: 6.2000 mg
Method: Ramp
Comment: pentafluoro nitroup pyridine

DSC
File: C:\TAData\DSC\steph\sc5-73.001
Operator: steph
Run Date: 30-Jul-03 15:24
Instrument: DSC Q10 V6.21 Build 233

Heat Flow (W/g)

Temperature (°C)

149.99°C
182.81°C
176.06°C
225.94°C

Exo Up

Universal V3.6C TA Instruments
Sample: sc5-97
Size: 3,3000 mg
Method: Ramp
Comment: pentfluoro nitroamino pyridine

DSC

File: C:\TAM\Data\DSC\Steph\sc5-97.001
Operator: steph
Run Date: 28-Aug-03 10:27
Instrument: DSC Q10 V6.21 Build 233

Heat Flow (W/g)

201.97°C

257.71°C

Temperature (°C)

Exo Up
Sample: DWP-Ill-49b
Size: 5.7000 mg
Method: Ramp
Comment: phenyl mononitro isonitrile

File: C:\TA\Data\DSC\Stepph\DWP-Ill-49b.001
Operator: stepp
Run Date: 24-Jul-03 14:41
Instrument: DSC Q10 V6.21 Build 233

[Graph showing a sharp peak at 157.45°C with a chemical structure labeled DWP-9-49]
Sample: DWP-III-49
Size: 7.5140 mg
Method: Ramp
Comment: phenyl nitro isonitrile
Sample: SMD-II-171
Size: 3.7000 mg
Method: Ramp
Comment: phenyl dinitro isonitrile

25
20
15
10
5
0
-5
0 100 200 300 400 500
Temperature (°C)

Heat Flow (W/g)

172.64°C
111.59°C
278.21°C

SMD-II-171

File: C:\TA\Data\DSC\steph\SMD-II-171.002
Operator: steph
Run Date: 23-Jul-03 13:23
Instrument: DSC Q10 V6.21 Build 233
Sample: DWP-5-50
Size: 4.3000 mg
Method: Ramp
Comment: isonitrile phenyl isonitrile

File: C:\TAT\Data\DSC\StephDWP-5-50.001
Operator: steph
Run Date: 06-Aug-03 11:24
Instrument: DSC Q10 V6.21 Build 233

---

**Graph:**

- **Temperature (°C):**
  - 163.46°C
  - 238.08°C

- **Heat Flow (W/g):**
  - Exo Up

---

**Chemical Structure:**

```
CN-CH3
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**Sample Name:** DWP-5-50
Sample: DWP-5-50
Size: 4.4310 mg
Method: Ramp
Comment: isonitrile phenyl isonitrile

TGA

File: C:\TGAData\TGA\steph\DWP-5-50.001
Operator: steph
Run Date: 07-Aug-03 09:45
Instrument: TGA Q50 V4.10 Build 157

Temperature (°C)

Weight (%)

149.24°C

5.279% weight loss (0.2339 mg)

415.56°C 5.000% Loss

Universal V3.6C TA Instruments
Sample: SMD-II-86
Size: 4.1370 mg
Method: Ramp
Comment: phenyl phenyl nitrile

TGA

File: \TA\Data\TGA\steph\SMD-II-86.001
Operator: steph
Run Date: 06-Aug-93 10:57
Instrument: TGA Q50 V4.10 Build 157

Temperature (°C)

Weight (%)
Sample: fmiv119
Size: 3,5000 mg
Method: Ramp
Comment: pentfluoro nitro nitrile ope

174.80°C
148.06°C
208.71°C

Heat Flow (W/g)

Temperature (°C)

DSC
File: C:TA\Data\DSC\pancho\fmiv119.001
Operator: pancho
Run Date: 30-Jul-03 13:33
Instrument: DSC Q10 V6.21 Build 233

fmiv-119

Universal V4.6C TA Instruments
Sample: SMD-II-70
Size: 2.5000 mg
Method: Ramp
Comment: phenyl nitroup nitrile

File: C:\TA\Data\DSC\Steph\SMD-II-70.001
Operator: steph
Run Date: 22-Sep-03 11:39
Instrument: DSC Q10 V6.21 Build 233

DSC

![Graph with temperature and heat flow data](image)

- **SMD-II-70**
- Heat Flow (W/g)
- Temperature (°C)
- Points:
  - 72.71°C
  - 136.82°C
  - 159.91°C
  - 296.17°C

Universal V3.8C TA Instruments
Sample: SMD-II-70
Size: 2.6900 mg
Method: Ramp
Comment: phenyl nitroup nitrile

File: C:\TDA\Data\TGA\steph\SMD-II-70.001
Operator: steph
Run Date: 22-Sep-03 11:48
Instrument: TGA Q50 V4.10 Build 157

![Temperature vs. Weight Graph](image)

**Temperature (°C)**
0 50 100 150 200 250 300 350 400

**Weight (%)**
75 80 85 90 95 100 105

- 103.53°C
- 264.12°C 5.000% Loss
- 24.36% weight loss (0.6554mg)

**Chemical Structure**

![Chemical Structure Diagram](image)
Sample: fm-iv-120
Size: 3.2000 mg
Method: Ramp
Comment: pentafluoro nitroup nitrile

DSC

File: C:\TA\Data\DSC\Steph\fm-iv-120.001
Operator: steph
Run Date: 22-Sep-03 13:10
Instrument: DSC Q10 V6.21 Build 233

![Graph showing heat flow vs. temperature with key points: 196.04°C, 205.73°C, and 314.82°C.]

Universal V3.8C TA Instruments
Sample: fm-iv-120
Size: 3.7290 mg
Method: Ramp
Comment: pentafluoro nitrophen nitrile

File: C:\TA\Data\TGA\Stepr\fm-iv-120.001
Operator: steph
Run Date: 22-Sep-03 13:15
Instrument: TGA Q50 V4.10 Build 157

TGA

```
178.95°C
260.40°C 5.00% Loss
36.18% weight loss (1.349 mg)
```

```
0 50 100 150 200 250 300 350 400
Flourine
```

```
Weight (%)
```

```
0 60 70 80 90 100
```

```
Temperature (°C)
```

```
fm-iv-120
```

Universal V3.8C TA Instruments
CHAPTER 3

SYNTHESIS OF MOLECULAR DEVICES FOR QUANTUM COMPUTING
SPEC: sc4-194 (07-Mar-03 11:41:22)
Samp: SC4-194 C25 H46 N O S, mw=440.3376
Oper: TDM
Base: 124.07
Peak: 1000.0 mpm
REG #9 @ 12.39 min (EI +VE +LMR PSCAN (EXP) UP HR NRM) (+#9-12 (+71-9))

Scan: 1 > 80
Client: 3C/JMT
#Peaks: 165
RIR: 4391055

7.8E+04
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<th>Found 2</th>
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<td>68.41</td>
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<tr>
<td>H</td>
<td>10.52</td>
<td>10.63</td>
<td>10.68</td>
</tr>
<tr>
<td>N</td>
<td>3.18</td>
<td>3.15</td>
<td>3.17</td>
</tr>
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</table>

**Single** ☐  **Duplicate** ☐

- **Elements Present:** C, H, N
- **Hygroscopic:** ☐  **Explosive:** ☐
- **M.P.:** 64-65°C  **B.P.:**
- **To be dried:** Yes ☐  No ☐
- **Temp.:**  Vac.  **Time:**

**FAX Service** ☐  **FAX Phone #** 713-748-6740
- **Rush Service:** ☐  **(See Current)**  **Phone Service:** ☐  **PRICE LIST**  **Phone No.:**

---

**Date Received:** MAR 11 2003  **Date Completed:** MAR 11 2003

**Remarks:**

![Chemical structure](image_url)
### ATLANTIC MICROLAB, INC.

**Sample No.:** sc5-59  
**Company/School:** Rice University  
**Address:** 1000 Rice Blvd, Houston, TX 77005

**PROFESSOR/SUPERVISOR:** PROF TOUR  
**NAME:** Stephanie CHANTER

**DATE:** 7/11/03

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<td>65.60</td>
<td>65.64</td>
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<td>H</td>
<td>13.87</td>
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<tr>
<td>N</td>
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**H + D as H:**

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<td></td>
<td></td>
<td>10.15</td>
<td></td>
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**Elements Present:** C, H, O, N, D

**Hygroscopic:** No  
**Explosive:** No

**M.P.** B.P.  
**Temp.**

**To be dried:** Yes  
**Vac. Time**

**FAX Service**

**Fax Phone #** 713-348-6250

**Rush Service** (SEE CURRENT)

**Phone Service** PRICE LIST

**Phone No.:**

---

**Date Received:** JUL 09 2003  
**Date Completed:** JUL 09 2003

**Remarks:**

![Chemical Structure](image-url)

HOOC

sc5-59
Sample No. DC 4-177

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0082

www.atlanticmicrolab.com

SUBMITTER
Company/School Rice University/Chemistry
Address 1500 Rice Blvd
Houston, TX 77005

NAME Stephanie CHANTERL DATE 2/7/03

P.O. #: CC

PROFESSOR/SUPERVISOR: PROF. TOU

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<tr>
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<td>70.38</td>
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<td>H</td>
<td>11.34</td>
<td>11.40</td>
</tr>
<tr>
<td>O</td>
<td>15.00</td>
<td>3.22</td>
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<tr>
<td>N</td>
<td>3.28</td>
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Date Completed 16/2/03

Single □ Duplicate □

Elements Present: C, H, O, N

Analyze for: C, H, N

Hygroscopic □ Explosive □

M. P. 72-73°C B. P.

To be dried: Yes □ No □
Temp. Vac. Time

FAX Service □ FAX Phone #: 713 348 6250

Rush Service □ (SEE CURRENT Phone Service □ PRICE LIST)
Phone No. 305-857-5000
**ATLANTIC MICROLAB, INC.**

Sample No. 5-61

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0082

PROFESSOR/SUPERVISOR: PROF TOUR

NAME: Stephen CHERDUB

Date: 7/9/03

---

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<td>67.89</td>
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<td>H</td>
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<td></td>
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<td>N</td>
<td>3.16</td>
<td>2.90</td>
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<td>H + D as H:</td>
<td>11.05</td>
<td>11.03</td>
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Single ☐ Duplicate ☑

Elements: C, H, O, N, D

Present: C, H, O, N, D

Analyze for: C, H, N

Hygroscopic ☐ Explosive ☐

M.P. _______ B.P. _______

To be dried: Yes ☐ No ☑

Temp. _______ Time _______

FAX Service ☑ Fax Phone # 713-348-6250

Rush Service ☐ (SEE CURRENT

Phone Service ☐ PRICE LIST)

Phone No.

---

Date Received: JUL 9 9 2003 Date Completed: JUL 9 9 2003

Remarks:

![Chemical Structure](image-url)
SPRC: se4-116 (12-Aug-03 15:15:13)
Samp: SC4-116 C52 H82 04 Si 798.598239861
Oper: Xiong Study: DRI + HR
Base: 798.81 Masses: 400.00 > 850.00
Peak: 1000.0 mV Intensity: 145710
RAG #9 @ 0.16 min (R1 +VE +IMR RSCAN (EXP) UP HR NRM) (+139-10)

1.5E+05

799

504-116
SPEC: sc4-139 (20-Dec-02 16:07:39)
Samp: SC4-139 C46 H66 O5 mw=698.4910
Oper: TDM     Study: DRE + HR
Base: 177.02   Masses: 50.00 > 750.00
Peak: 1000.0 mnu  Intensity: 3206004

REG #9 at 35.66 min (EI +VE +LHR NSCAN (EXP) UP LR NB) (+35-14) 3.2E+06
SPEC: sc4-90 (07-Oct-02 17:51:45)
Samp: SC4-90 C10 H18 O4 Te mw=332.02727
Oper: TDM Study: DEI + HR
Base: 83.91 Masses: 50.00 > 450.00
Peak: 1000.0 m/z Intensity: 4350218

REG #9 @ 15.71 min {EI +VE +LNR BSCAN (EXP) UP HR NRM} (+95-10) 3.8E+05

HOOC-Te-CONH
sc4-90
Synthesis of Conjugated Molecules: From Electronics to MoleculART

Volume III of III: Spectral Data

by

Stéphanie Hina Chateau

HOUSTON, TEXAS

NOVEMBER 2003
PART II- MOLECULAR ART
CHAPTER 4

SYNTHESIS OF ANTHROPOMORPHIC MOLECULES. THE NANOPUTIANS
SPRC: ec2-155 (17-May-01 16:30:24)
Samp: SC2-155 C18 H20 Br2 MW=393.993197
Oper: TQM
Study: EI + HR
Base: 395.93
Masses: 45.00 > 495.00
Peak: 1000.0 mnu
Intensity: 485376
REG #9 @ 10.17 min (EI +VE +LRN IRSCAN (EXP) UP HR HRM) (+57-15)

Scans: 1 > 88
Client: SC/JMT
#Peaks: 425
RJC: 5120387

4.9E+05
SPEC: sc2-161 (17-May-01 15:50:19)
Samp: SC2-161 C19 H21 O Br MW=344.077588
Oper: TDM  Study: EI + HR
Base: 328.99  Masses: 45.00 > 550.00
Peak: 1000.0 mmu  Intensity: 613053

REG #9 @ 10.27 min (EI +VE +1MR BSCAN (EXP) UR HR NRW) (+52-10)

329.0
346.0
314.0
267.0
265.1
235.1
207.1
192.1
189.0
178.0
152.0
152.0
115.0
100.0
78.1
53.4
89.0
128.0
0
50 100 150 200 250 300 350

Client: SC/JMT
#Peaks: 165
RTC: 4349655
Scan: 1 > 80

6.1EB+05
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<td>64.91</td>
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<tr>
<td>H</td>
<td>6.47</td>
<td>6.57</td>
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**Elements Present:** C H Br O

**Analyze for:** C H

**Hygroscopic:** No  
**Explosive:** No  
**M.P.:**  
**B.P.:**

**To be dried:** Yes  
**Vac. Temp.:**  
**Vac. Time:**

**FAX Service:** Yes  
**Fax Phone #:** 313246 6250

**Rush Service:** (See Current Price List)

**Date Received:** AUG 15 2003  
**Date Completed:** AUG 15 2003
SPEC: sc2-194 (15-Aug-01 14:52:33)
Sample: SC2-194 C21 H26 S1 MM=306.180380
Operator: TDM
Study: EI + HR
Base: 291.1
Masses: 50.00 -> 400.00
Intensity: 4867926
Scan #: 1
Peaks: 179
Client: SC/JMT
RNC: 12273019

REG #9 @ 7.67 min (EI +VE +LMR BSCAN (EXP) UP HR NRM) (+42-65)
Molecular structure:

*Chemical structure diagram*

100
90
80
70
60
50
40
30
20
10
0
291.1
306.1
73.0
117.0
131.0
189.0
230.0
233.0
262.1
277.1
308.1
50
100
150
200
250
300
350
400

4.9E+06
# ATLANTIC MICROLAB, INC.

Sample No. 4c3-5 Naookil

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0082

PROFESSOR/SUPERVISOR: PROF TORE
NAME: Stephanie Oakenfull
DATE: 8/2/03

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<tr>
<td>C</td>
<td>86.30</td>
<td>86.27</td>
</tr>
<tr>
<td>H</td>
<td>7.80</td>
<td>7.82</td>
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<tbody>
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<td></td>
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<tr>
<td>Analyze for: C H</td>
<td></td>
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Hygroscopic: Explosive: |
M.P.: R.P. |
To be dried: Yes: No: |
Temp: Vac. Time |
FAX Service: Fax Phone #: 313 348 6250 |
Rush Service: (SEE CURRENT PHONE SERVICE: PRICE LIST) |
Phone No. |

Date Received: AUG 15 2003 Date Completed: AUG 15 2003

Remarks:
SPEC: sc2-200 (15-Aug-01 15:43:01)
Samp: SC2-200 C42 H48 O2 MW=584.368431
Oper: TDM  Study: EI + HR
Base: 584.30  Masses: 50.00 > 620.00
Peak: 100.0 mmu  Intensity: 847247

Scan: 1 > 93
Client: SC/JMT
#Peaks: 531
RIC: 3710393

REG #9 @ 10.98 min (EI +VE +LMR BSCAN (EXP) UP HR NRM) {+58-10}
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<tr>
<td>C</td>
<td>86.26</td>
<td>86.19</td>
</tr>
<tr>
<td>H</td>
<td>8.23</td>
<td>8.25</td>
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</table>

Elements: CHO

Hygroscopic: □ Explosive: □

M.P.: B.P.:

To be dried: Yes □ No □

Temp. Vac. Time

FAX Service: □ Phone #: 713.348.6250

Rush Service: □ Phone Service: □ PRICE LIST

Sample No. D63-15

DATE 8/15/03

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0082

PROFessor/supervisor: PROF TOUR

NAME Stephanie Charbon

Date Received AUG 15 2003

Remarks:

Date Completed AUG 15 2003
### ATLANTIC MICROLAB, INC.

**Sample No.:** NC 3 - 11 NandreeBeak  
**SUBMITTER**  
Company / School: Rice University  
Address: 1900 Rice Blvd  
Houston, TX 77005

**PROFESSOR/SUPERVISOR:** PROF  
**NAME:** Stephanie Chantran

<table>
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<tr>
<td>C</td>
<td>96.20</td>
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<tr>
<td>H</td>
<td>7.97</td>
<td>8.03</td>
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- **Elements Present:** C\(\text{CHO}\)
- Analyze for: C\(\text{H}\)
- Hygroscopic:  
- Explosive:  
- M.P.:  
- B.P.:  
- To be dried: Yes  
- No:  
- Temp.  
- Vac.  
- Time  

**FAX Service:**  
**Fax Phone #:**  
**Rush Service:** (SEE CURRENT

**Phone Service:** PRICE LIST  
**Phone No.:**

**Date Received:** AUG 15 2003  
**Date Completed:** AUG 15 2003

**Remarks:**
### ATLANTIC MICROLAB, INC.

**Sample No.** 3-20 Nano-Testa

**Company / School** Rice University

**Address** 1400 Rice Blvd

**Institution** TX 77005

**PROFESSOR/SUPERVISOR** PROF TOURO

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<td>H</td>
<td>7.36</td>
<td>7.38</td>
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**NAME** S. CHANDRA

**DATE** 8/15/03

**Analysis**

- **Single Box**
- **Duplicate Box**

- **Elements Present:** CHO
- **Analyzed for:** CH

- **Hygroscopic Box**
- **Explosive Box**
- **M.P.**
- **B.P.**

- **To be dried:** Yes
- **Temp.**
- **Vac.**
- **Time**

- **FAX Service**
- **Fax Phone #** 713-348-6250

- **Rush Service**
- **Phone Service**
- **Phone Service**
- **Phone No.**

**Received** AUG 15 2003

**Date Completed** AUG 15 2003

[Chemical structure diagram]

[Additional notes or comments]

---

**Markings:**

- [ ]

---

**Remarks:**

[Additional remarks or notes]
SPEC: sc3-31 (25-Jul-01 17:40:57)
Samp: SC3-31 C44 H50 O2 MW=610.381081
Oper: TDM
Hasc: 610.38
Masses: 50.00 > 650.00
Peak: 1000.0 mpp
Intensity: 26622

REG #9 @ 33.01 min (EI +VE +IMR BSCAN (EXP) UP HR HRM) (+168-10)

2.75+04
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<td>H</td>
<td>8.25</td>
<td>8.23</td>
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**Elements Present:** C, H, O

**Analyze for:** CH

**To be dried:** Yes

**Temp.**

**Vac.**

**Time**

**FAX Service**

**Fax:** 12345678

**Phone #**

**Rush Service** (SEE CURRENT)

**Phone Service** (PRICE LIST)

**Phone No.**

---

**Sample No.:** sc3-31

**Company/School:** Rice University

**Address:** 1000 Rice Blvd, Houston, TX 77005

**Professor/Supervisor:** Prof. Tom

**NAME:** Stephanie Chandras

**DATE:** 8/18/03

**Date Received:** AUG 15 2003

**Date Completed:** AUG 15 2003

**Remarks:**
SPEC: sc2-63 (15-Aug-01 18:39:37)
Stump: SC3-63 C44 H50 O2 MW=610.381081
Oper: TDM Study: EI + HR
Base: 610.34 Masses: 50.00 > 650.00
Peak: 1000.0 ppm Intensity: 543619

Scan: 1 > 113
Client: SC/TNT
Peaks: 280
Ric: 3434339

REG #9 @ 11.51 min (EI +VE +LMR ESCAN (EXP) UP HR NRM) (+46-7)

83.9
100.0
119.0 150.0 183.0 254.9 256.9 321.1 378.2 441.2 499.2 504.1 554.3 595.3 613.3

610.3
# ATLANTIC MICROLAB, INC.

Sample No. 3-63

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0082

PROFESSOR/SUPERVISOR: PROF TOU
P.O. #: 

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<td>8.27</td>
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Single □ Duplicate □

Elements Present: CHO

Analyze for: CH

Hygroscopic □ Explosive □
M.P.: □ B.P.:
To be dried: Yes □ No □
Temp. _____ Vac. _____ Time _____

FAX Service: □ Fax Phone #: 413-348-6250
Rush Service: □ (SEE CURRENT PHONE SERVICE: □ PRICE LIST)
Phone No. 

Date Received: AUG 15 2003
Remarks:

Date Completed: AUG 15 2003
SPEC: sc3-57 (15-Aug-01 18:01:33)
Samp: SC3-57 C43 H48 O2 MW=596.365431
Oper: TPN
Study: EI + HR
Base: 586.31
Masses: 50.00 > 650.00
Peak: 1000.0 ppm
Intensity: 171310

REG #9 @ 16.74 min (EI +VE +LIMR BSCAN (EXP) UP HR NRM) (+#9-60 (+75-20))

1.7E+05
SPEC: sc3-30 (10-Jul-01 13:13:11)
Samp: S83-30 C43 H42 O2 Mn=590.318480
Oper: TTM Study: EI + HR
Base: 542.36 Masses: 50.00 > 900.00
Peak: 1000.0 m/z Intensity: 1893738
RPG 89 @ 16.67 min (EI +VE +LHR BSCAN (EXP) UP HR NRM) (+78-10)

| Scans: | 1 > 105 |
| Client: | SC/JNR |
| #Peaks: | 503 |
| RIC: | 11423573 |

1.9E+06
Nanofigure mixture
sc3-65
SPEC: sc3-65.dat (20-Aug-01 16:40:42)
Samp: SC3-65 mix 542,556,582,584,596,610
Oper: TDM Study: EI + HR
Base: 582.44 M asses: 50.00 > 750.00
Peak: 1000.0 mnu Intensity: 1058935
Scan 98 @ 6.19 min (EI +VE +LMR BSCAN (EXP) UPH HR NRM)

Nanofigure mixture
sc3-65
SPEC: sc3-65.dat (20-Aug-01 16:40:43)
Samp: SC3-65 mix (542,556,592,594,596,610
Oper: TDN
Base: 582.44
Peak: 1000.0 amu
Scans: 1 > 211
Client: SC/TMT
#Peaks: 1064
RNC: 15982178

Scan 98 @ 6.19 min (EI +VE +LMR ESCAN (EXP) UP HR NRM)

Nanofigure mixture
sc3-65
### ATLANTIC MICROLAB, INC.

**Sample No.** SC2-171  
**Submitter**  
**Company/School** Rice University  
**Address** 1000 Rice Blvd  
**Location** Houston, TX 77005  

**PROFESSOR/SUPERVISOR:** PROF TOUR  
**P.O. #:**  

**NAME:** Stephanie Chang  
**DATE:** 2/18/03

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<td>86.34</td>
</tr>
<tr>
<td>H</td>
<td>7.44</td>
<td>7.58</td>
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**Elements Present:** C H O  
**Analyze for:** C H  
**M.P.**  
**B.P.**  
**Hygroscopic:** ☑  
**Explosive:** ☑  
**To be dried:** Yes ☑ No ☑  
**Temp.**  
**Vac.**  
**Time**  
**FAX Service:** ☑  
**Fax:** 713 348 6250  
**Rush Service:** ☑ (SEE CURRENT)  
**Phone Service:** ☑ (PRICE LIST)  
**Phone No.**

**Date Received:** AUG 15 2003  
**Date Completed:** AUG 15 2003

**Remarks:**
SPE6: sc3-131 (15-Aug-02 19:41:37)
Sample: SC3-131 C17 H18 O 238.135765
Operator: TIM
Base: 238.11
Masses: 50.00 > 450.00
Peak: 1000.0 mmm
Intensity: 8799716
RSG #9 @ 10.17 min (EI +VE +LMR ESCAN (EXP) UP LR NRM) (+62-10)

Client: SC/JWT
#Peaks: 377
RTR: 51816244

8.8E+06

238.1

100

80

60

40

20

0

20

40

60

80

100

120

140

160

180

200

220

240

260

CHO

sc3-131
SPRC: sc3-148-2 (27-Nov-02 11:49:34)
Sample: SC3-148-2 C38 H44 O3 548.329045
Optx: TDM        Study: ET + HR
Base: 180.98     Masses: 50.00 > 610.00
Peak: 1000.0 ppm  Intensity: 3194360

REG #9 @ 15.18 min (ET +VE +LMR ESCAN (EXP) UP HR NRM) (+81-15)

3.2E-06
SPEC: sc3-152 (27-Nov-02 11:26:24)
Samp: SC3-152 C30 H44 O2 532.334131
Oper: TDM  
Base: 473.28  
Masses: 50.00 > 610.00
Peak: 1000.0 mmu  
Intensity: 2007798
REG #9 @ 15.28 min (EI +VE +LIMR BSCAN (EXP) UP HR NRM) (+#9-7 (+81-20))

-client: SC/JMP
#Peaks: 460
RIC: 24157662

2.0E+06
### ATLANTIC MICROLAB, INC.

**Sample No.:** ac3-154

**SUBMITTER**
- **Company/School:** Rice University
- **Address:** 1600 Rice Blvd
  - Houston, TX 77005

**PROFESSOR/SUPERVISOR:** PROF TOOR

**P.O. #:**

**NAME:** Apohanic Shankar

**DATE:** 9/18/03

---

<table>
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<th>Theory</th>
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<tr>
<td>C</td>
<td>85.67</td>
<td>85.56</td>
</tr>
<tr>
<td>H</td>
<td>8.77</td>
<td>8.78</td>
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</tbody>
</table>

---

**Single**

- **Elements Present:** C, H, O
- **Analyze for:** C, H
- **Hygroscopic:** No
- **Explosive:** No
- **M.P.:**
- **B.P.:**
- **To be dried:** Yes
- **Temp.:**
- **Vac.:**
- **Time:**

**FAX Service:** Yes
- **Fax Phone #:** 913-318-6750

**Rush Service:** (SEE CURRENT PHONE SERVICE PRICE LIST)

---

**Date Received:** AUG 15 2003

**Remarks:**

**Date Completed:** AUG 15 2003

---

**sc3-154**
SPEC: sc3-161 (18-Nov-02 13:28:58)
Samp: SC3-161 C30 H40 O4 560.292660
Oper: TDM Study: EI + HR
Base: 83.96 Masses: 50.00 > 650.00
Peak: 1000.0 mmm Intensity: 669211

REG #9 @ 18.39 min (EI +VE +LMR BSCAN (EXP) UP HR NRM) (+96-13)

Scans: 1 x 101
Client: SC/JMF
#Peaks: 725
RIC: 10980332

6.7E-05

[Diagram of molecular structure]

179
dimer 46 or 47
SC4-34-7 in Dithranol + Ag

dimer 46 or 47
dimer 46 or 47
dimer 46 or 47
SC4-34-6 in Dithranol + Ag

dimer 46 or 47
dimer 46 or 47
SC4-34-5 Neat

Polymer 48
CHAPTER 5

SYNTHESIS OF A MARCHING NANOARMY
SPEC: sc3-179 (09-Sep-02 12:50:59)
Samp: SC3-179 C20 H18 O2 S2 354.074825
Oper: TDM
Base: 277.05
Peak: 1000.0 zmu

HRMS #5 @ 11.17 min (EI +VR +LMR BSCAN (EXP) UP HR NRM) (+72-56)

Scan: 1 > 97
Client: SC/NMT
#Peaks: 310
RIC: 36428293

9.4E+05
SPEB: sc5-11 (13-Aug-03 17:36:08)
Samp: SC5-11 C22 H26 I F3 O2  mw=491.106972
Oper: Xiao     Study: D81 + HR
Base: 491.11   Masses: 200.00 - 550.00
Peak: 1000.0 mmu  Intensity: 137880
REG 69 @ 7.76 min (EI +VE +LR) NSCAN (EXP) UP HR NRM (+100-16)  

Client: SC/SCP
#Peaks: 171
RIC: 939750

Scans: 1 > 109

1.4E+05
SC5-37 in Dithranol Matrix from MeOH
SC5-43 in Dithranol Matrix from MeOH
Molecular Ion is [M+H]+ and [M+Na]+