

ABSTRACT

MONCEAUX, CHRISTOPHER JON. Synthesis of a Conjugated Ladder Polymer for Application in Direct Writing. (Under the Direction of Christopher B. Gorman.)

Since the discovery of electroluminescence in conjugated polymers in 1990, electro-optic devices such as light emitting diodes, flat panel all polymer displays, and lasers have received a great deal of attention. Greater conjugation in these π -electron systems leads to enhanced fluorescence and smaller band gaps. Upon this basis we have proposed exploiting these facets via a ladder polymer. A ladder polymer is an organic polymer that consists of linear molecules in which two cyclic subunits are linked together in a regular sequence, yielding a very rigid structure. Owing to their rigid structures and enhanced conjugation these materials would find many applications in nanoelectronics and high temperature environments, as well as exhibiting high laser damage thresholds.

Several synthetic routes are proposed and explored attempting to successfully synthesize an A-B or A-A type monomer. This monomer will undergo palladium catalyzed α -arylation to form a processible precursor polymer which then will be chemically converted to an all aromatic ladder polymer.

**SYNTHESIS OF A CONJUGATED LADDER POLYMER FOR APPLICATION
IN DIRECT WRITING**

by
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A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

CHEMISTRY

Raleigh

2004

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DEDICATION

I would like to dedicate this work to my loving parents, Anna and Murphy Monceaux. From my first memories as a child I can remember their constant and endless attention to my education and interests. This coupled with their relentless persistence to ensure I never settled for anything short of the best, like being a C student, has made earning a Master's Degree in Chemistry possible. Thank you both. I love you.

Results! Why, man, I have gotten a lot of results. I know several thousand things that won't work.

-Thomas A. Edison

BIOGRAPHY

Christopher Jon Monceaux was born September 6th, 1978 on George Air Force Base near Victorville, California to Lieutenant Colonel Murphy and Anna Monceaux. As a member of an U.S. Air Force family, he moved every few years and attended elementary school near or on U.S. Air Force Installations including Clovis AFB in New Mexico, Shaw AFB in South Carolina, England AFB in Louisiana, and Misawa AFB in Japan. His father was ultimately stationed at Langley AFB in Virginia, where Chris attended both Tabb Intermediate and High Schools, graduating in 1997. While in Virginia, Chris participated in several sports including soccer, football, wrestling, and namely swimming. Also during his time in High School, Chris earned the award of Eagle Scout in 1997. Upon graduation Chris attended Radford University in Virginia. Initially enrolled as a Geology major, his interest in Chemistry was instituted through his undergraduate General Chemistry professor, Dr. Preston Durrill. The enthusiasm and extraordinary teaching ability of this professor caused Chris to change his major to Chemistry and graduate *cum laude* in the spring of 2001. Further being challenged by his professors at Radford University and wanting to extend his knowledge in Chemistry, Chris attended North Carolina State University under the direction of Professor Christopher B. Gorman.

ACKNOWLEDGEMENTS

Again I would like to thank my parents Anna and Murphy Monceaux for their support and love through the years of my graduate career, as well as my brother Jonathan Monceaux. I would like to also thank my late Grandfather for teaching me the importance of a hard work ethic. Leaving my home state of Virginia and moving to North Carolina alone proved to be a difficult transition, I could not have made it with some of the following friendships. I would first like to thank Dr. Joseph Sloop for welcoming me into his home and showing me the initial hoops to jump through. He became a good friend and valuable resource. Best of luck teaching at the United States Military Academy, I am sure you are enjoying it. I met Joe Bousquet shortly after arriving in Raleigh and soon not only became great friends at school, but on the golf course and at the watering holes of Raleigh as well. In exchange for him and his roommate, Matt Stier, to eventually show me to appreciate the game of hockey (Go Canes!), I converted the native Massachusetts men into a true NASCAR fans (Do what?). I would also like to acknowledge Szymon Dembowy for not only showing the ropes in Dabney 508, my first laboratory, but having several in depth conversations about aviation, the latest consumer electronics, introducing me to Polish Vodka, and diving. Best wishes for you and your wife Aneta. Stephen McCall for helping me push those electrons around and teaching me to appreciate *some* liberal political views. Also, I would like to thank Randy Petrie and Jon Vaught for slice breaks, jam bands, seminar lunches, and their friendship through the years at NC State. I would like to add the friendships I have maintained with my friends from Virginia: Clayton Simmons, Christopher Darouse, Kristen Pudish, Nicole Reams, as well as my fellow Radford

Alumni, Chris DeNeale and Dan Kaminsky have proven to be an invaluable asset to my wellbeing. Tamara Williams, you have been an incredible inspiration both academically and emotionally down the homestretch of my graduate career, as well as making me happier than ever before, I love you and am so thankful you are a part of my life.

On a more professional note, I would like to thank my committee members, Dr. T. Brent Gunnoe and Dr. Jeffery White. I would like to give a special thanks to Dr. Shultz, also of my advisory committee, for his willingness to give suggestions and advice on my research, as well as for great conversation on Friday afternoons over a few pints. Most importantly on my advisory committee is of course my Research Advisor, Dr. Christopher Gorman. I commend him most for his approachability and keeping a positive outlook on a very trying synthetic project, especially when I would become extremely frustrated and negative. I would also like to thank him for going out of his way to keep me on a Research Assistantship as well as understanding facets of my personal life that emerged while a graduate student. As for my group members I would like to foremost thank someone who I value as an incredibly intelligent and hardworking colleague, Young-Rae Hong. Always concerned about the direction of my synthesis, he offered several suggestions and taught me several synthetic techniques, saving me an immeasurable amount of time. Also Young-Rae was a great friend, teaching me several interesting and unforgettable aspects of Korean food and culture, best of luck to you and your wife! Furthermore, I would like to acknowledge the senior members of my group Dr. Tyson Chasse and Dr. Ryan Fuierer for their willingness to always assist in any difficulties I encountered as well as being of invaluable help in preparing written documents and presentations. A special thanks to Christopher Cameron, through his

challenging me in several aspects, I learned several unforgettable lessons. Drew Wassel, without your liberal bantering I would have never become so interested in political issues of this world. Finally, I would also like to thank all other group members I have had the pleasure to work with. Brandon Walker, Namjin Kim, James Williams, Matthew Lewis, Holly Robuck, Aneta Dembowa, Angela Allen, Joshua Yohannan, Molina Sheepwash, Stephan Kraemer, Jennifer Ayers, Tiffani Bailey and Diana Stefanescu.

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1 Introduction to Interconnect Patterning

Introduction:

Over the past 40 years computing power has increased as the integral unit of its operation, the transistor, has decreased in size.¹ In 1965, Intel co-founder Gordon Moore proposed “Moore’s Law”.² After several revisions, the law is now understood to dictate computing power (transistor density) doubles every 18 months as can be seen in Figure 1.1.

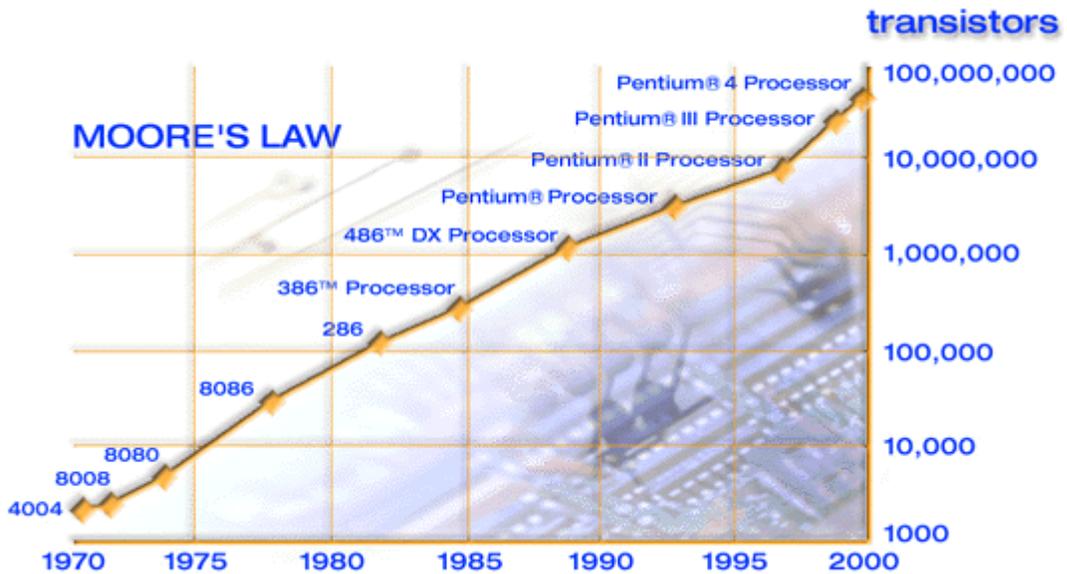


Figure 1.1 Moore’s Law^a

Clearly as society desires faster and more efficient computing power, the size of the transistor must decrease. This decrease in size will at sometime arrive at the sub-molecular scale, a point at which current fabrication technology will be surpassed.

^a Taken from Intel at: <http://www.intel.com/research/silicon/mooreslaw.htm>

Interconnect Patterning:

The paramount difficulty in miniaturization of transistors will be namely interconnects. Interconnects are the components of a transistor devoted to connecting memory elements on the chip to create a logic circuit. Conventional manufacturing trends using copper interconnects employ the technique of photolithography.³ Figure 1.2 depicts the inefficient photolithographic process for copper interconnect patterning. This process consists of at least nine industrialized steps; film cleaning and adhesion promoter deposition, photoresist deposition, prebake, mask alignment, light exposure, development, postbake, metal etch, and finally stripping.⁴

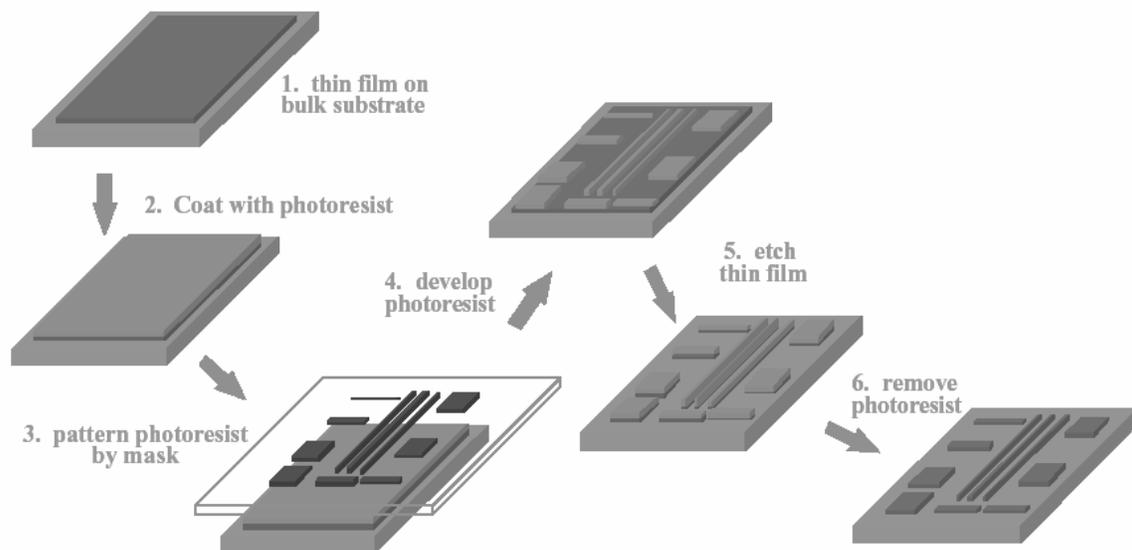


Figure 1.2 Photolithographic Patterning^b

An alternative technology being explored is a process in which a material would be directly transformed into patterns with desired properties by direct writing. One such

^b Taken from: www2.acae.cuhk.edu.hk/~ace3200/protectedfiles/Lecture/lecture-notes-01.PDF

example shown by Kordás and co-workers, is the laser assisted direct writing of copper metal on a poly(imide) substrate.⁵ In this example, assemblies of micron-resolved lines of copper showing good conductivity and substrate adhesion. Additionally the application of inkjet printing and computer aided design (CAD) has also emerged as technique to direct write copper. Copper is delivered in the form of a CVD ink precursor to a preheated substrate and decomposes on the surface of the substrate leaving a metallic copper film as seen in Figure 1.3. The print head nozzle precisely controls the ink drop size, delivery speed, and drop frequency; hence minimal waste. While the technique of ink jet printing of copper presents promise as a potential candidate to replace photolithographic methods, patterning can only be achieved at resolutions of $90\ \mu\text{m}$.⁶

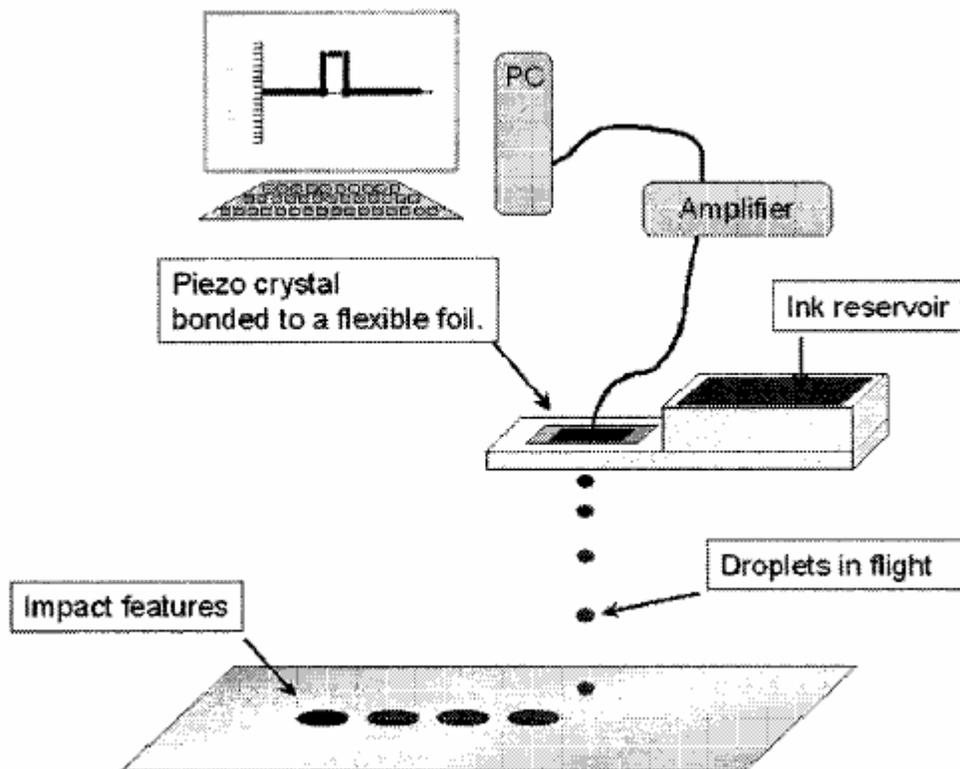


Figure 1.3 Inkjet Patterning

Alternatively research by Liu and co-workers has shown patterning of several metals such as Au, Ge, Ag, Cu, Pd, Pt, etc. on the nanometer scale using “dip pen” lithography.⁷ In an environment with an appreciable humidity, the space between the tip and the surface acts as a capillary and the surface condenses water from the surrounding air (Figure 1.4). The condensed water or meniscus is used to transport molecules (ink) from the AFM tip (pen) to the surface (paper).⁸

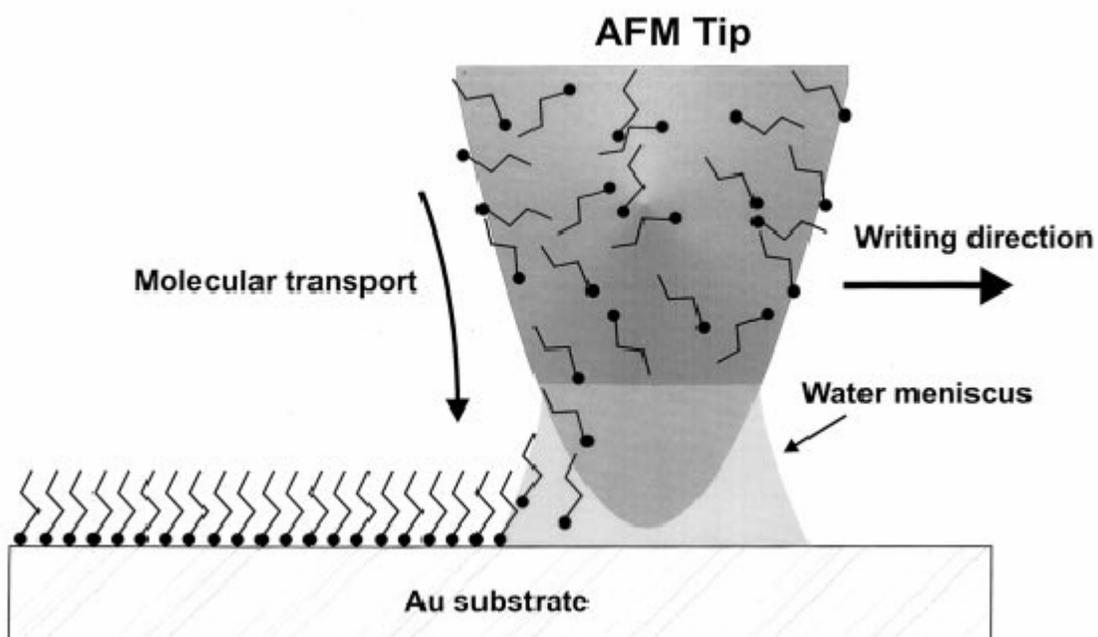


Figure 1.4 Dip Pen Lithography

The technique used by Liu and co-workers, specifically designated E-DPN (electrochemical “dip pen” lithography) utilized the meniscus as a nanoscale electrochemical cell in which the metal salts are dissolved, electrochemically reduced, and deposited onto the surface. Although a straightforward process coupled with the

ability to form patterning on the nanoscale, the miniaturization of metals as seen in the above examples will intrinsically fall victim to the phenomenon of electromigration.

At the nanoscale it follows that the interconnects are very narrow giving rise to high current densities. As current passes through an interconnect, its momentum can be transferred to the metallic atoms in the lattice. Eventually this phenomenon of electromigration will open voids within the interconnect or cause cracks in the adjacent dielectric, extruding metal atoms from the interconnect. Either of these events will cause failure.⁹

Conducting polymers, due to their covalent bonding between molecules will not suffer from electromigration. It is well known that polymers containing alternating single and multiple bonds (a conjugated sequence) can be candidates for conductive polymers. The π -conjugation gives rise to semi-conducting band structure. Upon doping of the polymer reductively (e.g. AsF_5 , SbF_5 , or I_2) or oxidatively, the polymer will facilitate charge transport, rendering it a conductive material.¹⁰ Conducting polymers have superior processing ability over metals leading to lower fabrication costs, thus giving these materials potential applications in batteries, integrated circuits, field effect transistors, optical memory storage devices, and electroluminescent devices.¹¹ For all of the potential applications to become reality, nanolithographic methods must be developed and explored.

Current industrial practices employ the use of photolithography for the patterning of metallic interconnects. This can be extended to the patterning of polymeric interconnects. An example of this would be the construction of all polymer integrated circuits via photochemical patterning.¹² In this technique, depicted in Figure 1.5, de

Leeuw and co-workers doped polyaniline with camphorsulfonic acid. The doped polyaniline was then dissolved in *m*-cresol followed by the addition of a photoinitiator. This solution is spin coated onto a polyimide foil and the resulting film was exposed to ultraviolet light through a mask, where the conducting polyaniline is reduced to its leucoemeraldine insulating form. The unexposed polyaniline films were left as conducting regions (i.e. interconnects) in an insulating matrix and the photoinitiator is removed by sublimation.

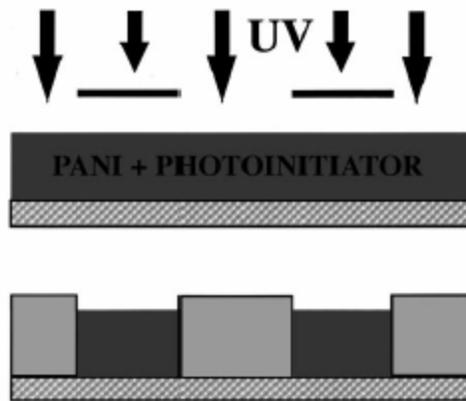
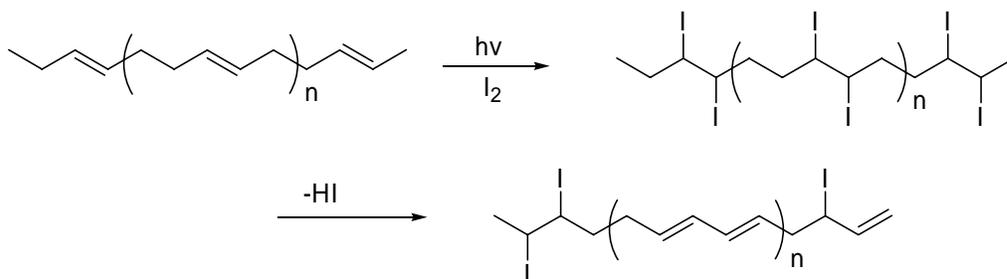


Figure 1.5 Polymeric photochemical patterning

Another method is one in which patterning from a processible precursor material is followed by mild and well defined chemistry to arrive at the less processible conductive material. One such case is the photochemical generation of conducting patterns in polybutadiene films.¹³ Dai and co-workers reported that insulating patterns of *cis*-1,4-polybutadiene can be photoisomerized via UV radiation to *trans*-1,4-isomer followed by I₂ induced conjugation and self doping with the excess I₂, resulting in

conducting patterns. Combined with microlithography, this was shown to be a straightforward method to generate conducting patterns.

Scheme 1.1 Reaction of 1,4-polybutadiene with iodine



Although the above examples are well defined and attractive methods for patterning, these techniques are limited by the photomask to spatial resolution on the microscale. Additionally, from a mass fabrication perspective, photochemical patterning may prove to be costly.¹⁴

As mentioned earlier DPN lithography is another method in which to pattern metal interconnects on the nanoscale. Research in DPN has been extended to polymeric systems in order to achieve infallible interconnects at the nanometer scale. Mirkin and co-workers have shown self-doped sulfonated polyaniline (SPAN) and doped polypyrrole (PPy) with charged backbones can be used to construct monolayers on oppositely charged surfaces via electrostatic forces.¹⁵ The researchers extended this to making DPN-generated polymer patterns with resolutions down to 130 nm. Liu and co-workers have shown that their aforementioned E-DPN technique can also be used for patterning polythiophene nanostructures on either semiconducting or insulating surfaces with resolutions in the sub-100 nm region.¹⁶ Here the AFM tip was coated in an EDOT chloroform solution and dried. A silicon (111) wafer with native oxide is used as the substrate. The applied voltage provides a pathway for the oxidative polymerization onto

the surface. Currently technology limits DPN into making patterns that AFM can visualize via lateral force microscopy (LFM) or topographic imaging. On the whole, DPN may be capable of patterning much lower than abovementioned values, but such patterns can not be visualized by current AFM imaging techniques.¹⁷

Although conducting polymers do service the need for covalent electronic materials, they do suffer from low conductivities. Copper for example has shown conductivity on the order of 10^6 Siemens/cm. Conducting polymers such as trans-polyacetylene, an unstable and non-processible material, has shown conductivities of 10^5 Siemens/cm, whereas polythiophene and polyaniline, both mentioned in previous applications, have shown conductivities on the order of 10 Siemens/cm. Clearly these materials will not supplant copper and other highly conducting metals.

Aromatic ladder polymers or graphitic ribbons containing planar conformation and high π -delocalization have great potential in the field of molecular electronics.¹⁸⁻²⁰ An aromatic ladder polymer consists of cyclic subunits fused together to form a linear structure in which each repeat unit has at least two covalent bonds to the next. The simplest example of an aromatic ladder polymer is poly(acene) (Figure 1.6). This polymer is predicted to be an intrinsic conductor (e.g. it has a very small or zero bandgap and thus a metallic band structure).²¹

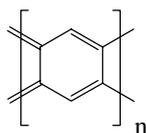
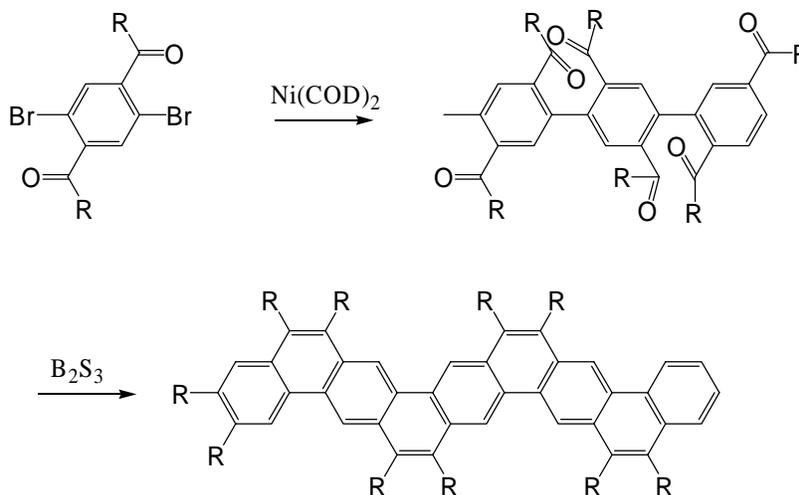


Figure 1.6 Poly(acene)

The principal impediment in the use of aromatic ladders in the aforementioned applications is poor to no solubility in organic solvents which in turn leads to difficulty in

processing. For example, the first aromatic ladder polymers were synthesized by direct condensation of their respective monomers.²² However, this approach failed due to the insoluble oligomers that precipitated out of solution, therefore no longer reacting to make larger polymeric materials. To solve this problem, most approaches turn to soluble precursor polymers which can be converted into a fused aromatic structure. Essential to an attractive route is methodology to a high molecular weight precursor and mild, well-defined chemistry to convert it to the aromatic ladder structure. One such route proposed by Scherf and co-workers is a simple two step “classical” ladder synthesis (Scheme 2).²³

Scheme 1.2 Scherf Cyclization

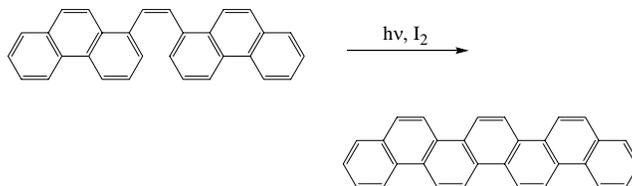


“Classical” refers to the cyclization of a substituted open chain precursor to the aromatic ladder. The first step is the formation of the precursor by an A-A monomer coupling through a Yamamoto condensation. The cyclization then proceeds by stirring the precursor in a solution of B₂S₃ to give the fused aromatic ladder. The most apparent advantage of course is the scheme entails only two steps. Another advantage is that alkoxy groups can be placed on the starting material to increase solubility, giving ladder

polymers with M_n : ca. 12,000 and M_w : ca. 22,000 and a degree of polymerization of 20. Thus, this process could not be extended to DPN due to the harsh reductive conditions of the B_2S_3 .

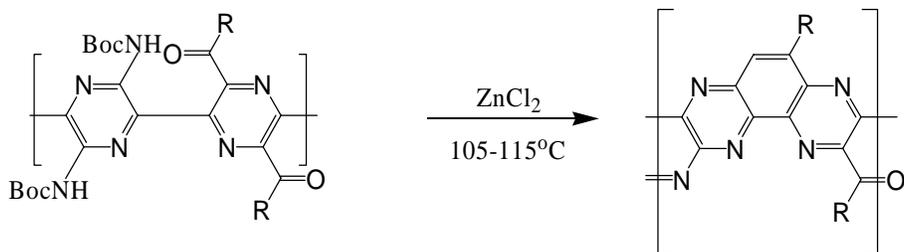
Another approach is One such route to an aromatic ladder is photochemical cyclization reported by Mallory et al., shown in Scheme 1.3. In this approach, stilbene analogues were prepared using the Wittig reaction. The resulting molecules were then photochemically cyclized in the presence of UV light and I_2 to give [n]phenacenes, where n is the number of fused benzene rings.²⁴ Although this technique could be applied to direct writing due to a mild chemical conversion to an all aromatic ladder, the limit of this approach is the insolubility of the oligomeric stilbene precursors.

Scheme 1.3. Mallory Cyclization



Alternatively, Tour and co-workers have proposed a route to electron deficient pyrazine ladder polymers.²⁵ In this case, two pyrazine monomers were polymerized to the corresponding pyrazine precursor via step growth polymerization, followed by a reductive cyclization (Scheme 3). The R groups are again solubilizing groups.

Scheme 1.4 Tour Pyrazine Ladder



Although this method does present a synthesis for a conjugated aromatic ladder, as shown in the above scheme, the synthesis required to arrive at the monomers is quite elaborate. In addition, heating in the presence of ZnCl₂ does not prove lucrative for application in direct writing. In fact there exist several other examples of making ladder polymers from well defined and known chemistry^{24,26-30} however, none have acceptable mild conditions in which to convert the insulating precursor to the all-aromatic conjugated ladder polymer.

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2 Novel Aromatic Ladder for Use in Direct Writing

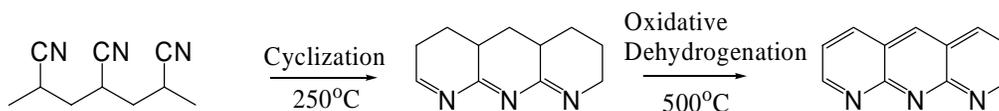
Introduction:

The previous chapter discussed the need to replace metallic interconnects if one desires to fabricate interconnects on the nanometer scale. Polymeric materials would serve as functional interconnects at the nanometer scale, but will prove unsatisfactory due to their relatively low conductivity. Here we have proposed an aromatic ladder polymer, which are theorized to be excellent conducting materials which could function as interconnects at the nanometer scale. Due to their rigidity, their solubility and therefore processibility will poor to non-existent. To alleviate this problem, we have also designed soluble and processible precursor polymer which could then be converted to an aromatic ladder structure. For these to be precursors to be adapted for use in DPN (Dip Pen Nanolithography) there is a need for mild and well defined chemistry for the conversion of the precursor to the ladder polymer in order to avoid damaging the substrate one desires on which to write. None of the examples in the previous chapter addressed this need for mild and well defined conversion chemistry. This chapter will discuss our proposed ladder system that will address these needs as well as the synthetic steps required to arrive at our polymer.

Results and Discussion:

Several resinous materials can be converted to graphitic like carbon. One example is the conversion of poly(acrylonitrile) to the graphitic structure of Black Orlon® (Scheme 2.1) via thermal oxidative dehydrogenation (typically $> 600\text{ }^{\circ}\text{C}$).¹⁻⁷

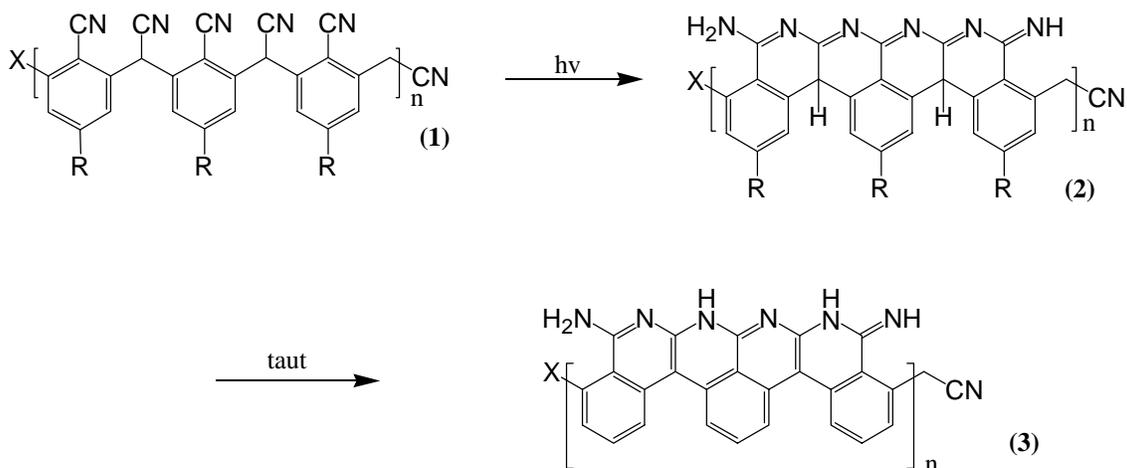
Scheme 2.1 Cyclization of poly(acrylonitrile)



Although this process involves high temperatures, the first step, cyclization of the pendant nitrile groups, occurred at relatively low temperatures and could be catalyzed by radicals or base. However, in the first step, the chemical transformation does not directly result in an aromatic ladder structure, but we think it can be adapted to synthesize a graphitic material for use in DPN.

Here is the proposed precursor polymer (1) which can be converted to the non-aromatic ladder (2) via preceded cyclization of the pendant nitrile groups.⁸⁻³⁹ The subsequent tautomerization should provide a pathway to a mild conversion into an all aromatic conjugated ladder polymer (3) (Scheme 2.2).

Scheme 2.2 Precursor polymer and cyclization



A C-H to N-H tautomerization of this kind has no known precedent. We have shown that AM1 calculations on oligomeric molecules similar to ours have shown heats of formation that preclude a stable non-aromatic structure (Figure 2.1). With these numbers, we are confident that the tautomerization will in fact occur upon cyclization of the precursor.

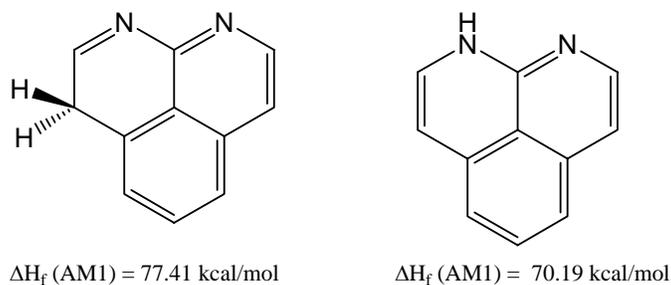
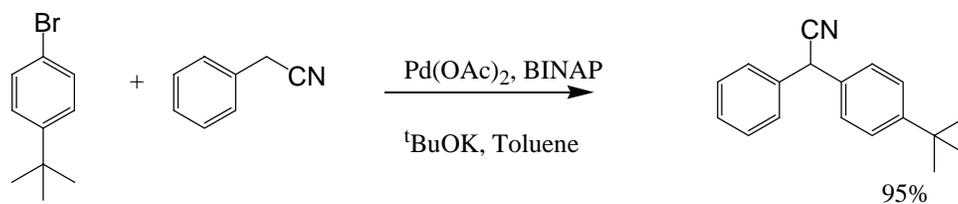


Figure 2.1 AM1 calculations for C-H to N-H hydride shift.

Initial research efforts were devoted to find a synthetic route to the precursor polymer (1). Palladium complexes are known to catalyze condensation polymerizations of halophenyl alkyl ketones.⁴⁰ Moreover, it has been shown that palladium catalyzed methods for the direct coupling of aryl bromides with a variety of nitrile enolates do exist

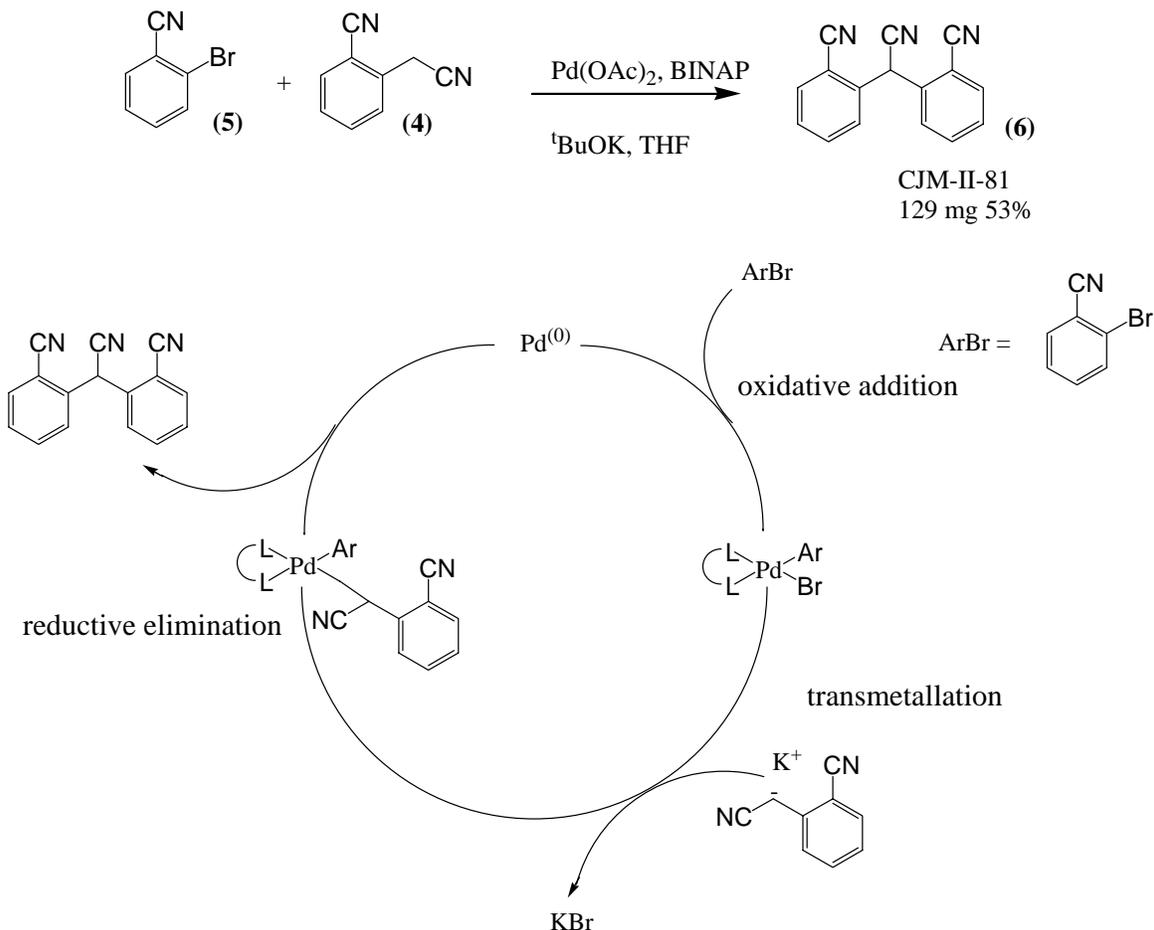
as depicted in Scheme 2.3.⁴¹

Scheme 2.3 α -Arylation of nitrile enolate



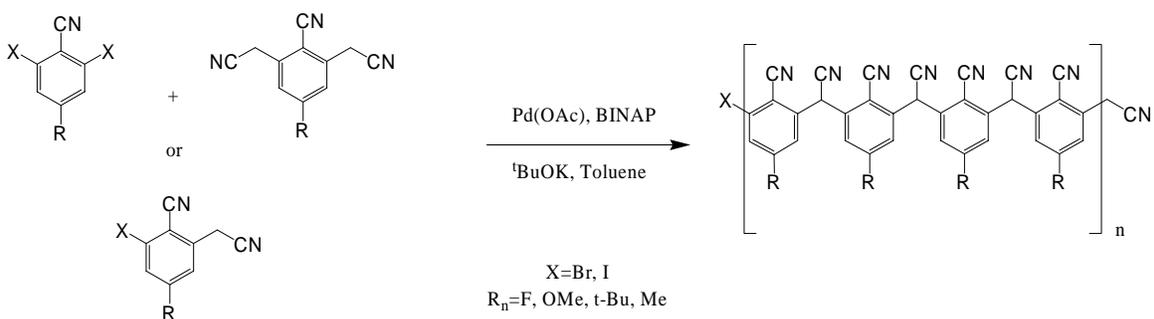
It was determined that this chemistry could be extended to α -cyano-*o*-tolunitrile (4) (A-A analog) which would couple with 2-bromobenzonitrile (5) (B-B analog) in the presence of a palladium catalyst to form the dibenzonitrile acetonitrile (6). This type of reaction is often referred to as α -arylation, and in our case works in modest yield (53%), albeit under unoptimized conditions (Scheme 2.4).

Scheme 2.4 α -Arylation model reaction and proposed mechanism



These above precedents have driven us to propose a step growth polymerization via coupling of a dibenzylic cyanide A-A monomer with a dihaloarene B-B monomer shown in Scheme 2.5.

Scheme 2.5 Step growth polymerization of proposed monomers



We believe that with precedented palladium coupling in order to form our precursor polymer along with mild chemistry, either photochemically catalyzed or using a catalytic amount of a nucleophilic base such as sodium amide, will prove to be an excellent method in which to adapt graphitic materials for use in direct writing. Methods to develop the monomers must now be developed.

Experimental:

Experiments requiring the use of microwave energy were conducted using a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC). The instrument had variable power settings of 0-300 W. Reactions were performed in 10 mL glass tubes and sealed with a septum. Instrument was also equipped with a temperature and pressure control devices. α -Cyano-*o*-tolunitrile was purified by flash chromatography. All other reagents were used as received.

Di-(2-cyanophenyl)-acetonitrile (6). Following procedure was performed in a N_2 dry box. In a vial was dissolved α -cyano-*o*-tolunitrile (1.2 mmol, 171 mg) in THF (1 mL). In a separate vial, equipped with a stir bar, was placed potassium *tert*-butoxide (KO^tBu) (1.3 mmol, 146 mg) in THF (1 mL). α -Cyano-*o*-tolunitrile solution was injected into KO^tBu suspension and was allowed to stir for 10 minutes. Solution turned dark red, indicating enolate formation. In 10 mL glass tube for use in microwave reactor containing a stir bar, was added 2-bromobenzonitrile (1.0 mmol, 182 mg), palladium acetate (0.02 mmol, 4.5 mg), and BINAP (0.02 mmol, 12.5 mg) in THF (1 mL). Dark red enolate solution was added to glass tube which was then sealed with a septum. Vessel was removed from dry box and placed in microwave reactor. Power set to 250 W,

temperature was set to 180⁰C, and reaction time was set to 10 minutes. Crude material was poured onto a plug of silica gel and washed with a 1:5 EtOAc:Hexanes (300 mL) eluent. TLC showed two spots. The lower spot was collected via flash chromatography (EtOAc:Hex 1:5). Upon removal of eluent, colorless needles formed (260 mg, 53%). ¹H NMR (CDCl₃): δ 5.90 (s, 1H), 7.54 (t, 2H), 7.62 (d, 2H), 7.68 (d, 2H), 7.74 (d, 2H).

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3 Synthesis of Step Growth Monomers

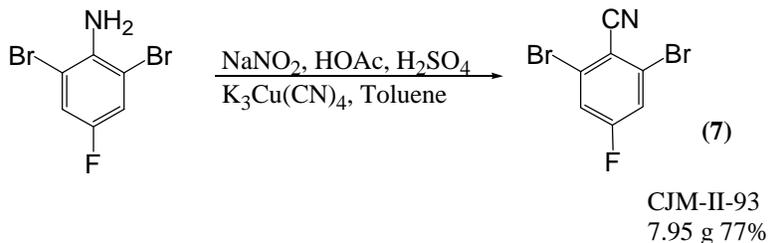
Introduction:

Having successfully demonstrated that α -arylation does in fact work for our substrates, synthetic approaches for an A-A and B-B monomer system and an A-B monomer system were developed. As depicted in Scheme 2.3, the monomers proposed will require a nitrile functionality in the 1 position. For the A-A monomer a benzylic cyanide will be required at both the 2 position and the 6 position. The B-B monomer will require an aryl bromide or iodide in both the 2 and 6 positions. The A-B monomer will have an aryl bromide or iodide in the 2 position and a benzylic cyanide in the 6 position. For each monomer system, a NMR active substituent will be in the 4 position in order to obtain a resolute solid state NMR of both the precursor and final ladder.

Results and Discussion:

The B-B monomer (7) was synthesized in one step from Sandmeyer chemistry in relatively high yield (Scheme 3.1).¹

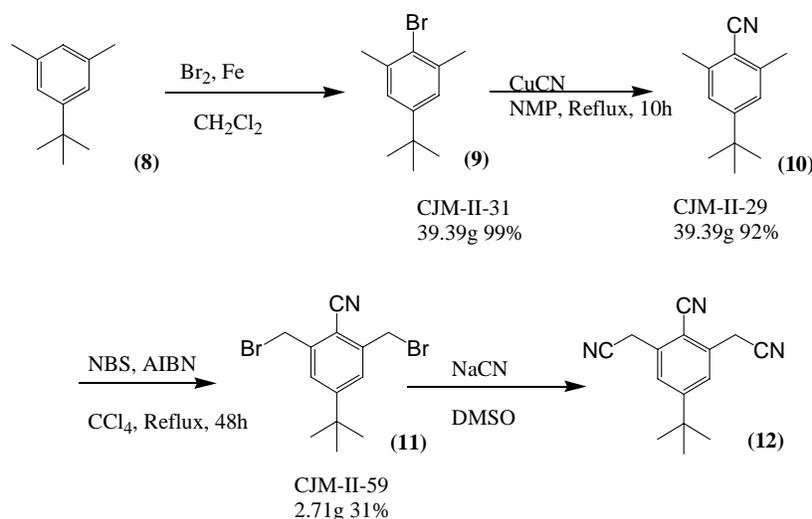
Scheme 3.1 Synthesis of B-B Monomer



In the case of the A-A monomer (12), a multi-step synthesis was proposed in Scheme 3.2. The regiospecific bromination² of 5-tert-butyl-m-xylene (8) occurred in almost

quantitative yield to form (9). The Rosenmund-von Braun cyanation occurred in high yield to form (10) followed by the Wohl-Ziegler bromination.³ This bromination occurred in modest yield under these reaction conditions to yield (11). Much difficulty was encountered on the final step, a S_N2 conversion of the benzylic bromides to benzylic cyanides, to arrive at our desired molecule (12). Unclear NMR spectra and several products as evidenced by TLC lead us to conclude that our desired molecule may not be possible to synthesize via straightforward S_N2 chemistry. This problem will be addressed in more detail later in this chapter.

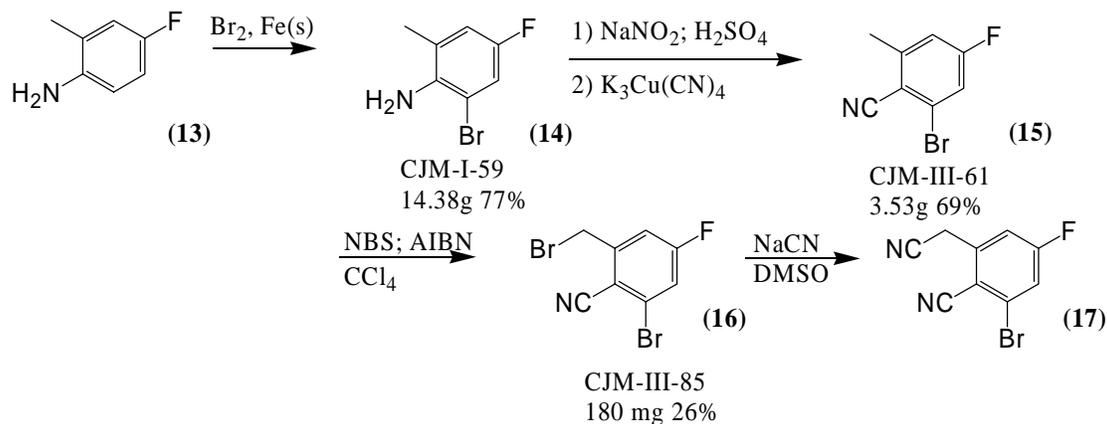
Scheme 3.2 Synthesis of A-A Monomer



It was also proposed to synthesize an A-B monomer that would also follow the desired α -arylation mechanism, to form the precursor polymer (Scheme 2.3). This monomer would also necessitate a multi-step synthesis depicted in Scheme 3.3. The direct bromination of 4-fluoro-2-methylaniline (13) occurred in moderate yield to form (14) followed by conversion to the nitrile again via Sandmeyer chemistry (15). Benzylic bromides were installed yet again via the Wohl-Ziegler bromination to give (16).

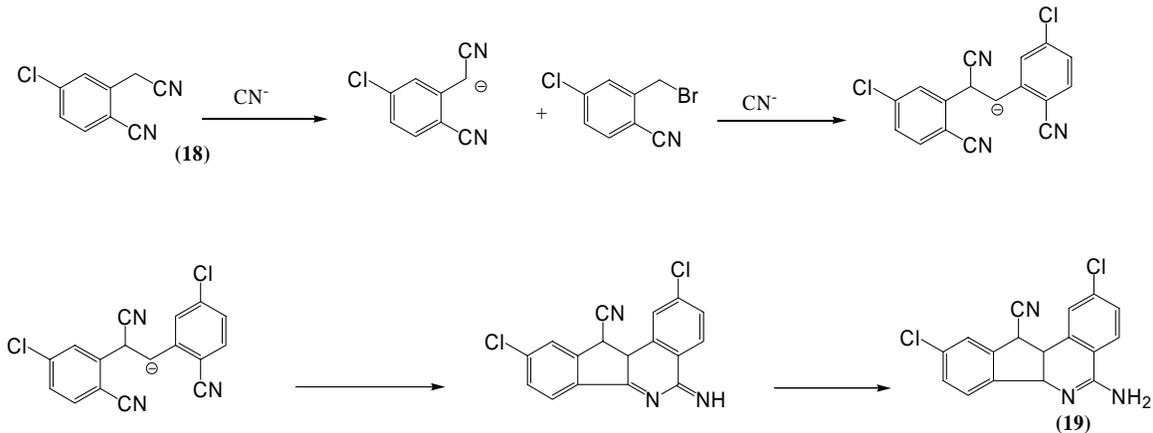
however, the S_N2 chemistry involving the benzylic bromide to be converted to the desired benzylic cyanide (17) proved to be ineffective.

Scheme 3.3 Synthesis of A-B Monomer.



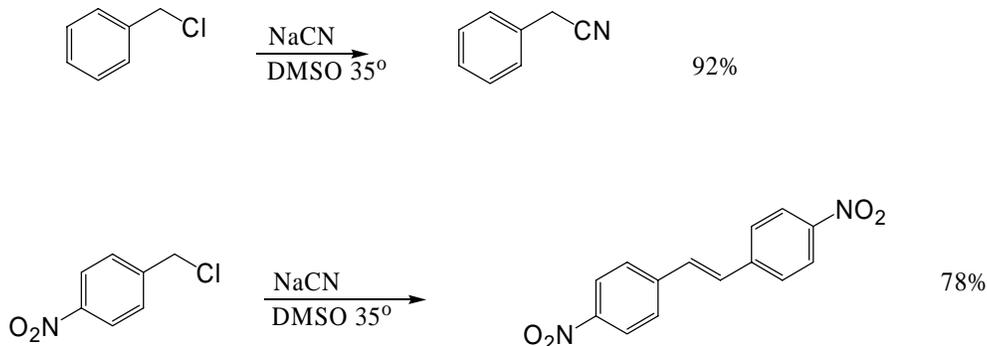
In an effort to address our difficulty with the final S_N2 step, literature concerning cyanide substitution in the presence of electron withdrawing substituents was consulted. Interestingly, Ando and co-workers found that intermediary *o*-cyanobenzyl cyanides were unusually reactive in the case when chlorosubstituents were involved.⁴ For example, the researchers found that when molecule such as (18) was subjected to NaCN and trace of NaI in acetone solvent, the undesired cyclization product (19) would form, represented in Scheme 3.4.

Scheme 3.4 Alkylation and cyclization of A-B monomer



Moreover, it was found that electron-deficient substrates in the presence of cyanide anion did undergo elimination reactions rather than the expected substitution reactions⁵ in significant yield as seen in Scheme 3.5.

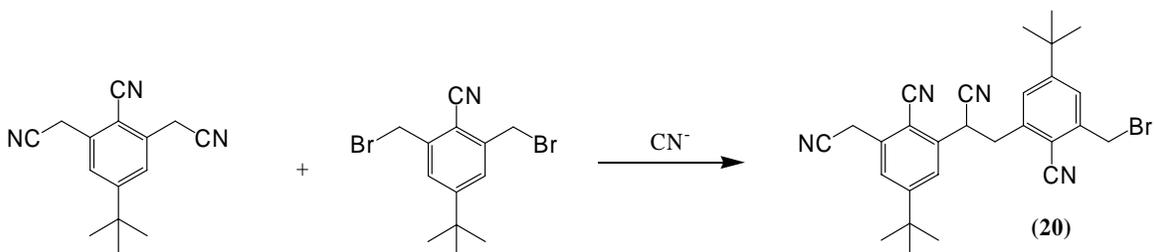
Scheme 3.5 Substitution and elimination reactions involving CN^-



In the case of the A-A monomer it was also found that multiple references concerning α -cyano-*o*-tolunitriles⁶⁻⁸, most notably findings by Buckley and co-workers, have led us to hypothesize that the first formed *o*-cyanobenzyl cyanide would undergo alkylation with the *o*-cyanobenzyl bromide under basic conditions to form the undesired molecule (20) as seen in Scheme 3.6. As for the A-B monomer, we have hypothesized

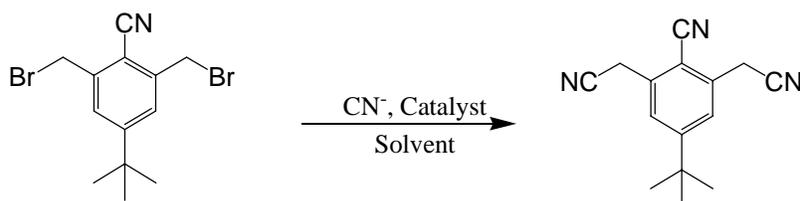
that our monomer, just as, if not more electron deficient would suffer the same fate as proposed in Scheme 3.4.

Scheme 3.6 Proposed alkylation of product (BnCN) with starting material (BnBr)



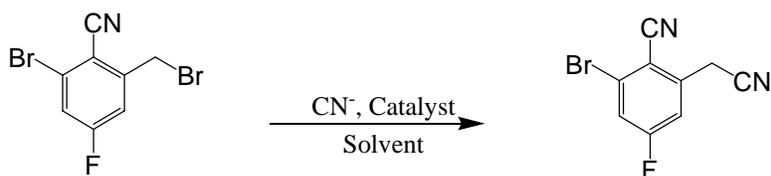
Due to the highly electron withdrawing nature of our benzylic cyanide molecules, investigation into the alteration of the $\text{S}_{\text{N}}2$ substitution of the cyanide ion was deemed necessary. Our aim would be to have the cyanide ion act as a nucleophile quickly and efficiently rather than behave as a base, causing the aforementioned complications. Several attempts by changing solvent, altering temperature conditions, varying ion exchange catalysts, examining order of addition, attempting to run the reaction under anaerobic and non-hygroscopic conditions, and purification of starting materials in order to arrive at this molecule, as dictated by Table 1 (A-A) and Table 2 (A-B), were all attempts to do so, although none did prove successful. With our findings in literature and judging from our results, it was determined that a route must be proposed that avoids sources of nucleophilic cyanide.

Table 1 Attempts to generate A-A monomer via cyanide substitution



Entry	Cyanide	Catalyst	Solvent	Temperature	Order	Result ³
CJM-II-61	KCN	18-O-6	MeCN	25	Br to CN	Failed
CJM-II-63	NaCN	None	DMSO	40	Br to CN	Failed
CJM-II-67	KCN	18-O-6	MeCN	25	Br to CN	No Reaction
CJM-II-77	KCN	18-O-6	MeCN	-20	Br to CN	No Reaction
CJM-II-89	KCN	18-O-6	THF	-78	Br to CN	No Reaction
CJM-III-1	KCN	18-O-6	THF	-78	Br to CN	No Reaction
CJM-III-19	KCN	18-O-6	THF	Add -78 to RT	Br to CN	Failed
CJM-III-29	NaCN	None	DMSO	60	Br to CN	Failed
CJM-III-31	NaCN	None	DMSO	40	Br to CN	Failed
CJM-III-37	NaCN	None	DMSO/H ₂ O	25	CN to Br	Failed
CJM-III-45	NaCN	None	DMSO	25	CN to Br	Failed
CJM-III-69	NaCN	None	DMSO-d ₆	25	CN to Br	Trace
CJM-III-79	NaCN	None	DMSO-d ₆	25	CN to Br	Trace
CJM-IV-13	KCN	18-O-6	MeOH/THF	25	CN to Br	No Reaction

³ Failed – Desired product was not formed

Table 2 Attempts to generate A-B monomer

Entry	Cyanide	Catalyst	Solvent	Temperature	Order	Result
CJM-II-43	NaCN	None	DMF	90	Br to CN	Failed
CJM-II-53	NaCN	None	DMF	90	Br to CN	Failed
CJM-II-54	NaCN	None	EtOH/H ₂ O	25	Br to CN	Failed
CJM-II-54	KCgN	None	EtOH/H ₂ O	25	Br to CN	Failed
CJM-II-54	KCN	None	MeCN	40	Br to CN	No Reaction
CJM-II-54	KCN	(<i>t</i> -Bu) ₄ NI	MeCN	25	Br to CN	No Reaction
CJM-II-69	KCN	18-O-6	MeCN	0	Br to CN	Failed
CJM-IV-1	NaCN	None	DMSO	25	CN to Br	Failed
CJM-IV-25	KCN	None	THF/MeOH	25	CN to Br	Failed

Experimental:

General Procedures. Starting materials and solvents were purchased from commercial vendors and used without further purification.

2,6-Dibromo-4-fluorobenzonitrile (7). 2,6-Dibromo-4-fluoromethylaniline (10 g, 37 mmol) was dissolved in 100 mL of a 2M HOAc solution at 60°C. Concentrated sulfuric acid (5.5 ml, 103.6 mmol) was added. Solution was then cooled to 0°C. A solution of NaNO₂ (2.80 g, 40.7 mmol in 6.00 mL dI water) was added slowly. Formation of diazonium salt was judged by appearance of deep red solution color (diazonium salt solutions extremely reactive and unstable, kept cold and prepared as

needed). In a separate flask, CuSO₄ (7.08 g, 44.4 mmol) was dissolved in 30 mL dI water. Ice was added to solution followed by addition of aqueous KCN (12.04 g, 185 mmol) in 30 mL water. The voluminous precipitate that formed initially soon dissolved, forming the copper complex. To this complex was added NaHCO₃ (25 g, 296 mmol) and toluene (200 mL). This system was heated to 55°C and was added drop wise via addition funnel the diazonium salt solution. After 1 hour of vigorous stirring, the organic phase was separated and extracted with toluene. The combined organic phases were washed with 2N NaOH solution (2X200 mL) and then with brine. Organic phase was dried over MgSO₄ and concentrated leaving brown solid. Purified by column chromatography (DCM:Hex 1:4). Collected 7.95 g (77%) as yellow fluffy solid. ¹H NMR (CDCl₃): δ 7.42 (d, 2H).

2-Bromo-5-tert-butyl-m-xylene (9). To a solution of 5-tert-Butyl-m-xylene (1.72 mL, 9.12 mmol) in dichloromethane (5 mL) was added iron powder (catalytic amount). Solution was cooled to 15°C. Bromine (10 mmol, .51mL) was added (5.1 mL;10% v/v in DCM). Solution was stirred overnight and poured into 250 mL of ice water. Extracted with ether and combined organic layers were dried over MgSO₄ and concentrated. Colorless prisms formed upon cooling. Collected 2.18 g (99%). ¹H NMR (CDCl₃): δ 1.45 (s, 9H), 2.6 (s, 6H), 7.5 (s, 2H).

2-Cyano-5-tert-butyl-m-xylene (10). A mixture of 2-Bromo-5-tert-butyl-m-xylene (2 g, 8.3 mmol), CuCN (1.3 g, 14.5 mmol), and NMP (15 mL) was stirred at 180°C overnight. Solution was cooled and poured into a 1:1 aqueous NH₄OH contained in an ice bath. This mixture was stirred for 4 hours and filtered. Filtrate was washed with water several times. Dried filtrate in oven-vacuum overnight. Dried grey filtrate

was washed through a plug of silica gel with DCM. Upon evaporation of solvent colorless needles formed. Collected 1.43 g (92%). ^1H NMR (CDCl_3): δ 1.25 (s, 9H), 2.55 (s, 6H), 7.15 (s, 2H).

2-Cyano-5-tert-butyl-m-(bis)-benzyl bromide (11). To a mixture of 2-Cyano-5-tert-butyl-m-xylene (5.0 g, 26.7 mmol), recrystallized NBS (10 g, 56.2 mmol), and benzoyl peroxide (100 mg, 15 mol%) was added 30 mL of CCl_4 . Vessel was purged with N_2 for 0.5 hours followed by heating to reflux for 72 hours. Solution was cooled and was added 2N NaOH (250 mL) and aqueous sodium thiosulfate. Extracted with CCl_4 and dried over MgSO_4 . CCl_4 was distilled for recycling. Residue was purified by column chromatography (EA:Hex 1:30) to yield colorless powder. Collected 2.86 g (31%). ^1H NMR (CDCl_3): δ 1.35 (s, 9H), 2.63 (s, 4H), 7.50 (s, 2H).

2-Bromo-4-fluoro-6-methylaniline (14). 2-Fluoro-4-methylaniline (10.3 mL, 92.5 mmol) was stirred in 50 mL dry DCM. Solution was cooled to 10°C and 10% v/v Br_2 solution in DCM (53 mL, 101.8 mmol) was added drop wise. Reaction mixture was stirred for 2 h at room temperature. Poured into 2M NaOH solution (250 mL), washed with water, and extracted with diethyl ether. Combined organic layers were dried over MgSO_4 . Upon removal of solvent brownish needles formed. Collected 14.7 g (77%). ^1H NMR (CDCl_3): δ 2.21 (s, 3H), 3.8 (s, 2H), 6.70 (d, 1H), 7.05 (d, 1H).

2-Bromo-4-fluoro-6-methylbenzotrile (15). 2-Bromo-4-Fluoro-6-methylaniline (4.85 g, 24 mmol) was dissolved in 50 mL of a 2M HOAc solution at 60°C . Concentrated sulfuric acid (3.6 mL, 67.2 mmol) was added. Solution was then cooled to 0°C . A solution of NaNO_2 (1.82 g, 26.4 mmol in 6.00 mL dI water) was added slowly. Formation of diazonium salt was judged by appearance of deep red solution color

(diazonium salt solutions extremely reactive and unstable, kept cold and prepared as needed). In a separate flask, CuSO_4 (4.6 g, 29 mmol) was dissolved in 20 mL dI water. Ice was added to solution followed by addition of aqueous KCN (7.8 g, 120 mmol) in 20 mL water. The voluminous precipitate that formed initially soon dissolved, forming the copper complex. To this complex was added NaHCO_3 (20 g) and toluene (100 mL). This system was heated to 55°C and was added drop wise via addition funnel the diazonium salt solution. After 1 hour of vigorous stirring, the organic phase was separated and extracted with toluene. The combined organic phases were washed with 2N NaOH solution (2 X 100 mL) and then with brine. Organic phase was dried over MgSO_4 and concentrated leaving brown solid. Purified by column chromatography (DCM:Hex 1:4). Collected 3.53 g (69%) as light brown needles. ^1H NMR (CDCl_3): δ 2.58 (s, 3H), 6.95 (d, 1H), 7.25 (d, 1H).

2-Bromo-6-bromomethyl-4-fluoro-benzonitrile (17). To a mixture of 2-Bromo-4-fluoro-6-methylbenzonitrile (.50 g, 2.34 mmol), recrystallized NBS (.936 g, 5.26 mmol), and benzoyl peroxide (1 mg, 15 mol%) was added 30 mL of benzene. Vessel was purged with N_2 for 0.5 hours followed by heating to reflux for 72 hours. Solution was cooled and was added 2N NaOH (100 mL) and aqueous sodium thiosulfate. Extracted with toluene and dried over MgSO_4 . Residue was purified by column chromatography (EA:Hex 1:30) to yield colorless powder. Collected 180 mg (26%). ^1H NMR (CDCl_3): δ 4.6 (s, 2H), 7.25 (d, 1H), 7.40 (d, 1H).

References:

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4 Acetonitrile as a Co-monomer

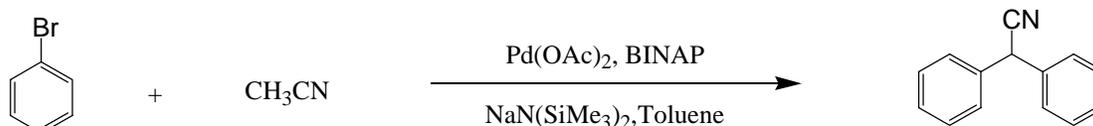
Introduction:

The preceding chapter demonstrated the unusually strong basic affect the cyanide ion has on acidic protons in the presence of electron deficient aromatic rings (Schemes 3.4 - 3.6). This precedent has caused complications in our synthesis of both the A-A monomer (Scheme 3.2) and the A-B monomer (Scheme 3.3). Having recognized this difficulty, we have sought out other methods in which to substitute benzylic cyanides onto aromatic systems.

Results and Discussion:

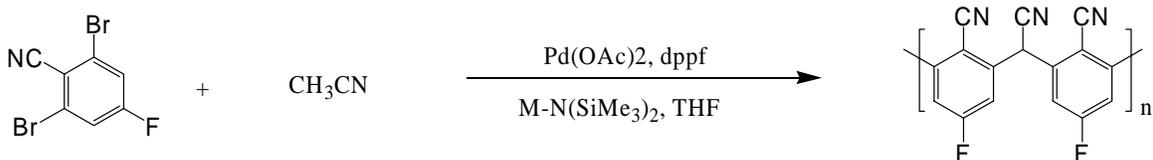
In our re-examination of Hartwig and co-workers efforts in the α -arylation of nitrile enolates (Scheme 2.3), it was noticed that acetonitrile underwent diarylation in 62 percent conversion (Scheme 4.1). It is hypothesized that the monoarylated product is easily deprotonated and is unhindered enough to undergo transmetallation onto palladium as seen in Scheme 4.1.¹

Scheme 4.1 Acetonitrile diarylation



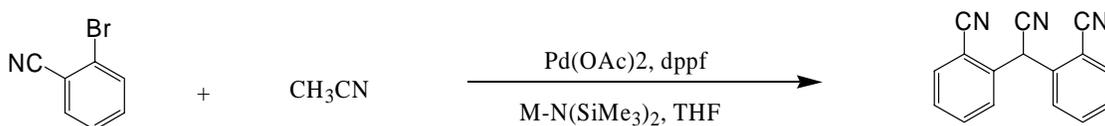
This method would prove to be an elegant fashion in which to construct our precursor polymer. Ideally we could take a dihaloarene, such as (7), acetonitrile, base, and ligated palladium catalyst yielding our precursor polymer in one step as shown in Scheme 4.2.

Scheme 4.2 Proposed precursor polymerization from polyarylation of acetonitrile



Rather than having to deal with an unfamiliar polymeric product, as seen in Scheme 4.2, we desired to ascertain the efficacy of this chemistry via a molecule that would yield a dimeric product shown in scheme 4.3.

Scheme 4.3 Proposed dimerization from diarylation of acetonitrile

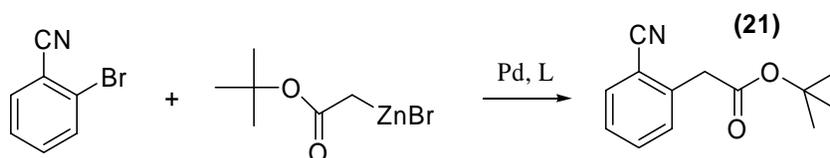


As summarized in Table 3, attempts to synthesize the dimer shown in Scheme 4.3 were unsuccessful using this approach. Having been able to synthesize the above dimer by monoarylation (Scheme 2.5) and able to reproduce the chemistry in Scheme 4.1 with similar yield, it was hypothesized that the nitrile functionality on our substrate did not tolerate the hardness of the alkali anion of acetonitrile.

It was then hypothesized that moving towards a softer base such as zinc alkyls. Zinc alkyls are known to be of the most efficient organometallic reagents for transmetalation onto palladium. This is evidenced by Negishi cross coupling where unsymmetric biaryls are formed by cross coupling an aryl halide with an organozincate in the presence of catalytic amounts of either nickel or palladium.²⁻⁴ Additionally zincates are very tolerable of a variety of functional groups⁵, an obvious concern in using our substrate. Hartwig and co-workers have shown that palladium catalysts bearing hindered

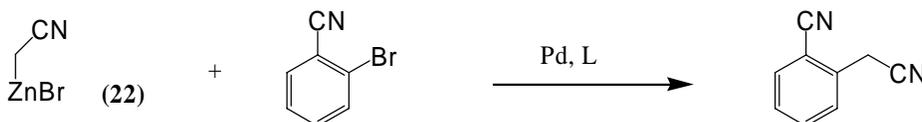
alkyl phosphine ligands (L = ligand) enhanced the coupling of a Reformatsky reagent, a bromozinc enolate of an ester⁶, with an assortment of base sensitive substrates, specifically 2-bromobenzonitrile (6) shown in Scheme 4.4.⁷

Scheme 4.4 Negishi coupling of α -bromoester



The above reaction occurs in 91 percent yield. We would like to extend this chemistry using the α -bromoacetonitrile zincate (11) to establish a one step model reaction in making of our A-A or A-B monomer shown below in Scheme 4.5.

Scheme 4.5 Proposed Negishi coupling



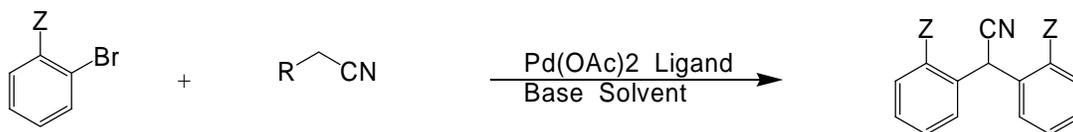
Attempts to couple α -bromoacetonitrile zincate to 2-bromobenzonitrile involving varying palladium catalyst, ligands, and zinc sources gave no productive results. In addition, having successfully synthesized (10) following this method, it was decided to further investigate the generation of the α -bromoacetonitrile zincate.

Orsini⁸ and several other researchers⁹⁻¹¹ have shown that α -bromoacetonitrile can be converted into the corresponding Reformatsky intermediate (11) and be used as a nucleophilic reagent towards halogen-containing electrophiles. The Reformatsky intermediate was prepared by adding a few drops of bromoacetonitrile to activated zinc wool (1 mol equivalent). As soon as the reaction began, the remaining bromoacetonitrile

was added in anhydrous THF (4.3 M) at -5°C . Due to the exothermic nature of the reaction, high temperatures must be avoided or brown solutions were formed. Removal of the solvent resulted in a colorless foamy compound which was directly used for elucidation and nucleophilic reactions. The zincate is identified as a 1:1 molar complex of (2) with THF and recovered in 98% yield. In our hands it has been found that brown solutions are formed quite readily when using this approach. Through ensuring our zinc was freshly activated, bromoacetonitrile freshly distilled, and closely monitoring temperature conditions, all in a nitrogen atmosphere, the NMR spectra did show promising signatures.

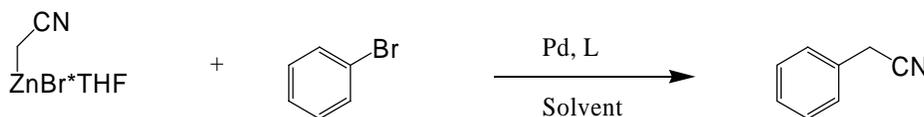
Although it was found that although our α -bromoacetonitrile zincate could be formed and isolated, it never transmetallated the benzyl cyanide to any palladium catalysts or nickel catalyst we tried as seen in Table 4.

Table 3 Attempts at diarylation of acetonitrile



Z	R	Base	Eq Base	Pd	L	Solvent	T	Result
CN(1.0)	H(1.3)	NaN(SiMe ₃) ₂	1.3	(Oac)	DPPF	Toluene	100	Alt Product
CN(1.0)	H(1.3)	KOtBu	1.3	(Oac)	DPPF	Toluene	100	Alt Product
CN(2.0)	H(1.3)	NaN(SiMe ₃) ₂	1.3	(Oac)	DPPF	Toluene	80	Trace
CN(2.0)	H(1.3)	NaN(SiMe ₃) ₂	1.3	(Oac)	DPPF	Toluene	100	Trace
CN(2.0)	H(1.3)	NaN(SiMe ₃) ₂	1.3	(Oac)	DPPF	Toluene	80	NR
CN(2.0)	H(1.3)	NaN(SiMe ₃) ₂	1.3	(Oac)	DPPF	Toluene	50	Trace-NR
CN(2.0)	H(1.3)	NaN(SiMe ₃) ₂	2.3	(Oac)	DPPF	Toluene	100	NR
H	Ph(1.3)	KOtBu	1.3	(Oac)	DPPF	Toluene		48%
CN	ArCN	KOtBu	1.3	(Oac)	DPPF	THF		53%
CN	ArCN	KOtBu	1.3	(Oac)	DPPF	Toluene/THF		48%
H	H(1.3)	NaN(SiMe ₃) ₂	1.3	(Oac)	DPPF	Toluene		64%

Table 4 Attempts to couple Reformatsky intermediate to bromobenzene



Pd Catalyst	Ligand	Solvent	Conditions	Result
Pd(dba) ₂	P ^t Bu ₃	THF	Room Temp	No Reaction
Pd(dba) ₂	P ^t Bu ₃	THF	50 ^o C	No Reaction
Pd(PPh ₃) ₄	N/A	THF	Room Temp	No Reaction
Pd(dba) ₂	dppf	THF	Room Temp	No Reaction
Ni(PPh ₃) ₄	N/A	THF	Room Temp	No Reaction

Experimental:

Bromoacetonitrile was distilled and collected via vacuum filtration. Zinc was activated following literature procedure.⁶ All other starting materials and solvents were used as prepared unless otherwise noted.

α -Bromoacetonitrile zincate (22). To activated zinc beads (5.4 mmol, 0.35 g) in a vial equipped with a stir bar was added 0.1 mL of d-DMF and bromoacetonitrile (0.45 mmol, 0.03 mL). Vial was fitted with a PTFE screw cap and removed from drybox and warmed to 50⁰C. Reaction was allowed to commence and was placed into a 20⁰C water bath. Bromoacetonitrile (1.35 mmol, 0.094 mL) in 0.8 mL d-DMF was added drop wise. Deuterated DMF was used in order observe structure directly during reaction. ¹H NMR (DMF-d₇): δ 0.82 (s, 2H, ZnCH₂).

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5 Another Synthetic Approach to Step Growth Monomers

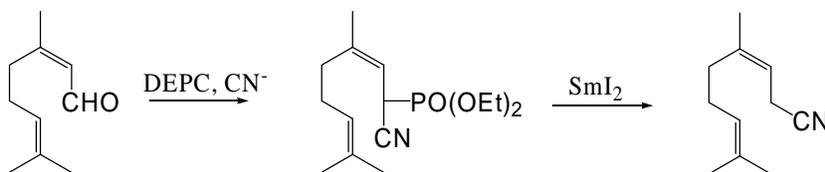
Introduction:

In the previous two chapters, it has been shown that benzylic cyanides cannot be synthesized via nucleophilic substitution with cyanide ion or efficiently as hoped with an acetonitrile co-monomer. Here we propose indirectly substituting our benzylic cyanide by way of a phenyl aldehyde in the absence of the ortho nitrile functionality.

Results and Discussion:

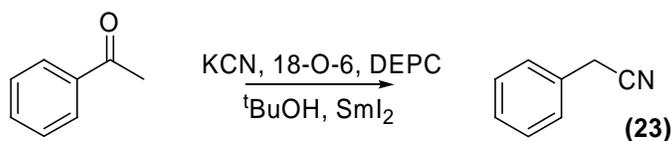
It has been shown that cyanophosphates, which are readily obtained from carbonyl compounds such as aldehydes from treatment with commercially available diethyl cyanophosphonate and cyanide ion, can be reduced with samarium diiodide¹⁻³ as shown in Scheme 5.1 to yield nitriles. Samarium diiodide has been noted for its mild reducing power as well as its solubility in organic solvents such as THF.³

Scheme 5.1 Conversion of an aldehyde to a nitrile



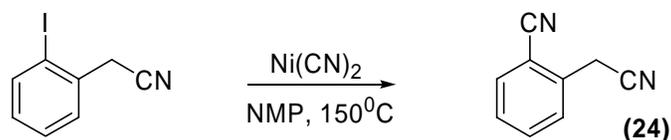
With this precedent, the next step was to extend this chemistry to aromatic systems. Naturally we adapted this chemistry to readily available benzaldehyde. In our hands we have shown that benzaldehyde can be converted to benzyl cyanide in moderate yield, depicted in Scheme 5.2.

Scheme 5.2 Conversion of benzaldehyde to benzyl cyanide



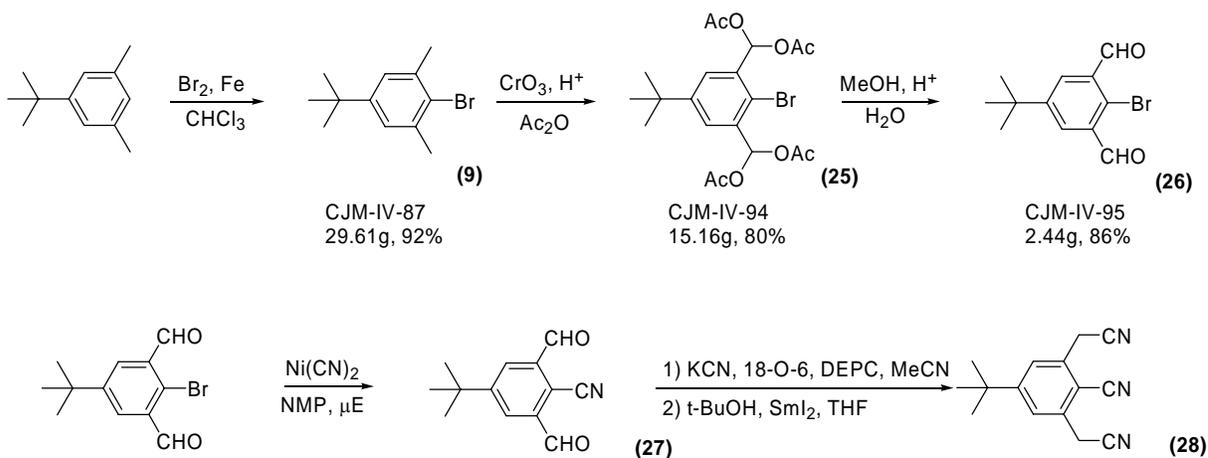
We have also shown that an aryl halide with a benzyl cyanide substituent can undergo a Rosenmund-von Braun like cyanation in quantitative yield, a critical step in forming our A-B monomer, shown in Scheme 5.3.

Scheme 5.3 Cyanation of 2-iodophenylacetonitrile



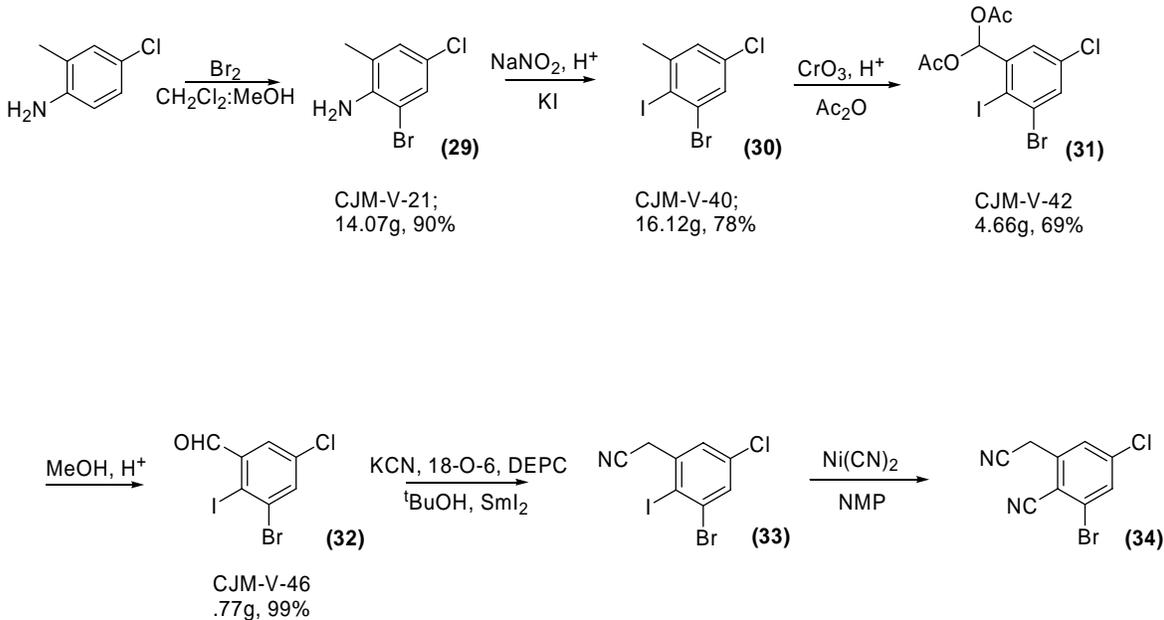
Subsequently, a synthetic scheme to make an A-A monomer involving the conversion of a carbonyl to a nitrile was then proposed, as shown in Scheme 5.4. The regiospecific bromination was performed as before giving excellent yield. The successive benzylic oxidation was carried out in acetic anhydride using sulfuric acid and chromium (VI) oxide occurred in relatively high yield. The bis-ketal groups were then hydrolyzed with sulfuric acid and water in methanol to give the bis-aldehyde in good yield.⁴ The next step was to install an aryl cyanide via a transition metal cyanide salt, nickel (II) cyanide.⁵ It was found after several attempts it was determined that steric hindrance prohibited the completion of this reaction. This was evidenced by the fact that p-bromobenzaldehyde did quantitatively undergo cyanation under the former conditions.

Scheme 5.4 Synthesis of A-A monomer



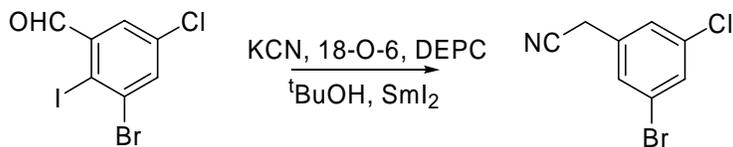
It was then determined that the efficacy of the SmI_2 reduction to be tested on an A-B monomer system, shown in Scheme 5.5. Bromination of the aniline, which occurred in high yield, was performed using elemental bromine in methanol and methylene chloride. The following halogenation was achieved by formation of a diazonium salt with sodium nitrate followed by stirring in potassium iodide.⁶ Benzylic oxidation to form the ketal and the subsequent hydrolysis were both conducted in the same manner shown above in Scheme 5.4.

Scheme 5.5 Synthesis of A-B monomer



It had appeared the aldehyde then underwent transformation to the benzylic cyanide in quantitative yield. It was not until the failure of the relatively facile step of converting the aryl iodide to an aryl cyanide that we began to re-examine our samarium iodide chemistry. Upon further investigation it was found that samarium diiodide provides a very efficient in which to form aryl radicals from aryl iodides, as seen in Scheme 5.6. These aryl radicals in the presence of a proton source, as in our case *tert*-butanol, are quenched to give a phenyl proton. A reinvestigation of our H^1 -NMR and comparison of our reaction conditions led us to conclude that the samarium iodide was going to interfere with our proposed synthesis by giving an undesired product seen in Scheme 5.6.

Scheme 5.6 Samarium diiodide reduction of aryl halide and conversion of aldehyde to nitrile



Experimental:

General Procedures. Starting materials and solvents were purchased from commercial vendors and used without further purification.

Benzyl Cyanide (23). Operations performed in N₂ dry box unless other wise noted. Diiodoethane was freshly purified before use by dissolving in diethyl ether followed by washing with sodium thiosulfate. Organic layer was extracted with diethyl ether and dried over MgSO₄. Upon removal of solvent, white powder was collected. Potassium cyanide was dried by making a fine powder with mortar and pestle, followed by drying in vacuum at 50⁰C overnight, and storing in N₂ dry box. Potassium cyanide (1.5 mmol, 98 mg), a catalytic amount of 18-crown-6, and benzaldehyde (0.5 mmol, 60.1 mg) were dissolved in 1 mL anhydrous THF. Vessel was capped with PTFE septum and removed from drybox. Diethyl cyanophosphonate (1.5 mmol, 0.3 mL) was added and allowed to stir for 1 hour. In separate vessel Samarium metal (2.3 mmol, 345 mg) and diiodoethane (1.5 mmol, 422 mg) in THF (5 mL) was stirred for approximately 1 hour. The initial colorless mixture turned deep blue, indicating formation of SmI₂. Capped with PTFE septum and removed from dry box. Phosphonate solution was cannulated into SmI₂ solution and was allowed to stir overnight. Reaction was quenched with a 10 % HCl (10 mL) solution and extracted with diethyl ether. Organic layer was washed with 5% aqueous sodium bisulfite, water, and brine. Combined organic layers were dried over MgSO₄. 41 mg of a viscous liquid was collected (70%). ¹H NMR (CDCl₃): δ 3.75 (s, 2H), 7.30-7.45 (m, 5H).

α -Cyano-o-tolunitrile (24). In a glass vessel equipped with PTFE stir bar for use in microwave reactor, described in Chapter 2, was placed 2-iodophenylacetonitrile (2.06 mmol, 0.50 g), Ni(CN)₂*4H₂O (1.23 mmol, 0.23 g) and NMP (3 mL). Vessel was sealed with septum and placed in microwave reactor. Temperature was set to 150⁰C for 10 minutes. After allowing vessel to cool to room temperature, it was taken out of the microwave reactor and septum was removed. Contents were poured in to a separatory funnel and washed with water and diethyl ether. Combined organic layers were dried over MgSO₄. Collected 286 mg of a yellowish solid (99%). ¹H NMR (CDCl₃): δ 3.98 (s, 2H), 7.43 (m, 1H), 7.60-7.80 (m, 3H).

Acetic acid acetoxy-(2-bromo-5-tert-butyl-3-diacetoxymethyl-phenyl)-methyl ester (25). To a suspension of 2-Bromo-5-tert-butyl-m-xylene (4 mmol, 0.965 g) in Ac₂O (8 mL) was added concentrated sulfuric acid (22.5 mmol, 1.2 mL) drop wise at such a rate to maintain a reaction temperature less than 10⁰C. To the resulting mixture was added chromium (VI) oxide (14 mmol, 1.4 g) in Ac₂O (7 mL) drop wise. Warning: Extremely reactive! This solution was kept cold and added drop wise to maintain reaction temperature below 10⁰C. Dark green solution was allowed to warm to room temperature while stirring for two hours. Poured solution portion wise onto ice slurry and allowed to stand for 12 hours. Precipitate was filtered and washed several times with deionized water. Dried in vacuum. White powder, collected 1.22 g (65%). ¹H NMR (DMSO-d₆): δ 1.38 (s, 9H), 2.18 (s, 12H), 7.58 (s, 2H), 7.95 (s, 1H).

2-Bromo-5-tert-butyl-benzene-1,3-dicarbaldehyde (26). To a suspension of (23) in methanol (2.5 mL) at 0⁰C was added concentrated sulfuric acid (98.7 mmol, 5.3 mL) drop wise. Resulting orange solution was stirred at room temperature for 1 hour.

Water was then added drop wise at 0°C. Resulting precipitate was collected and washed with water, dried in vacuum. Collected .28 g of yellowish powder (99%). ¹H NMR (CDCl₃): δ 1.38 (s, 9H), 8.19 (s, 2H), 10.58 (s, 1H).

2-bromo-4-chloro-6-methylaniline (29). To a solution of 4-chloro-2-methylaniline (70.6 mmol, 10 g) in a 1:1 DCM:MeOH solvent (80 mL) was added drop wise at room temperature, a solution of bromine (74.2 mmol, 3.8 mL) in 36 mL of the a 1:1 DCM:MeOH solvent. Solution was stirred overnight, followed by removal of solvent in vacuum. To the residue was added a 200 mL of 20% NaOH solution. Extracted with diethyl ether. Upon solvent removal brownish needles formed. Recovered 14.07 g (90%). ¹H NMR (CDCl₃): δ 2.1 (s, 3H), 4.0 (s, 2H), 6.85 (s, 1H), 7.2 (s, 1H).

3-Bromo-5-chloro-2-iodotoluene (30). 2-bromo-4-chloro-6-methylaniline (62.6 mmol, 13.8 g) was dissolved in a warm acetic acid solution (1:1 v/v 150 mL) followed by addition of concentrated sulfuric acid (9.4 mL). Solution was cooled to about 5°C followed by the drop wise addition of NaNO₂ (68.86 mmol, 4.75 g) in 15 mL of deionized water. Formation of diazonium salt was judged complete by appearance of deep reddish solution color. In a separate vessel was added potassium iodide (407 mmol, 67.5 g) in 300 mL of ice water. Next was added cold diazonium salt solution slowly to the iced KI solution. Poured mixture into separatory funnel; washed with sodium bisulfite, brine, and extracted with diethyl ether. Upon solvent removal white needles formed, collected 16.12 g (78%). ¹H NMR (CDCl₃): δ 2.5 (s, 3H), 7.18 (s, 1H), 7.42 (s, 1H).

Acetic acid acetoxy-(3-bromo-5-chloro-2-iodo-phenyl)-methyl ester (31). To a suspension of 2-bromo-5-chloro-1-iodotoluene (14.0 mmol, 4.64 g) in Ac₂O (45 mL) was

added concentrated sulfuric acid (78.4 mmol, 4.17 mL) drop wise at 20⁰C. To the resulting mixture was added chromium (VI) oxide (14 mmol, 1.4 g) in Ac₂O (7 mL) drop wise. Warning: Extremely reactive! Keep cold and add drop wise to maintain reaction temperature below 20⁰C. Dark green solution was allowed to warm to room temperature while stirring overnight. Poured solution portion wise onto ice slurry and allowed to stand for 12 hours. Precipitate was filtered and washed several times with deionized water. Dried in vacuum. Yellowish powder, collected 4.10 g (69%). ¹H NMR (DMSO-d₆): δ 2.18 (s, 6H), 7.45 (s, 1H), 7.55 (s, 1H), 8.00 (s, 1H).

3-Bromo-5-chloro-2-iodo-benzaldehyde (32). To a suspension of (31) (4.47 mmol, 2.00 g) in methanol (10 mL) was added drop wise sulfuric acid (425 mmol, 22.6 mL) at 0⁰C. After addition of the acid the yellowish suspension was allowed to stir at room temperature for 2 hours. Cooled mixture to 0⁰C and added water (45 mL) drop wise. Collected precipitate and washed several times with water. Dried in vacuum and collect yellowish powder, collected 1.50 g (97%). ¹H NMR (CDCl₃): δ 7.75 (s, 1H), 7.85 (s, 1H), 10.05 (s, 1H).

(3-Bromo-5-chloro-2-iodo-phenyl)-acetonitrile (33). Operations performed in N₂ dry box unless other wise noted. Diiodoethane was freshly purified before use by dissolving in diethyl ether followed by washing with sodium thiosulfate. Organic layer was extracted with diethyl ether and dried over MgSO₄. Upon removal of solvent, white powder was collected. Potassium cyanide was dried by making a fine powder with mortar and pestle, followed by drying in vacuum at 50⁰C overnight, and storing in N₂ dry box. Potassium cyanide (1.5 mmol, 98 mg), a catalytic amount of 18-crown-6, and 3-Bromo-5-chloro-2-iodo-benzaldehyde (0.5 mmol, 172 mg) were dissolved in 1 mL

anhydrous THF. Vessel was capped with PTFE septum and removed from drybox. Diethyl cyanophosphonate (1.5 mmol, 0.3 mL) was added and allowed to stir for 1 hour. In separate vessel Samarium metal (2.3 mmol, 345 mg) and diiodoethane (1.5 mmol, 422 mg) in THF (5 mL) was stirred for approximately 1 hour. The initial colorless mixture turned deep blue, indicating formation of SmI₂. Capped with PTFE septum and removed from dry box. Phosphonate solution was cannulated into SmI₂ solution and was allowed to stir overnight. Reaction was quenched with a 10 % HCl (10 mL) solution and extracted with diethyl ether. Organic layer was washed with 5% aqueous sodium bisulfite, water, and brine. Dried organic layer over MgSO₄. ¹H NMR (DMSO-d₆): δ 4.20 (s, 2H), 6.85 (s, 1H), 7.59 (s, 1H), 7.85 (s, 1H).

2-Bromo-4-chloro-6-cyanomethyl-benzonitrile (34). In a glass vessel equipped with PTFE stir bar for use in microwave reactor, described in Chapter 2, was placed suspected (3-Bromo-5-chloro-2-iodo-phenyl)-acetonitrile (0.5 mmol, 178 mg), Ni(CN)₂*4H₂O (0.3 mmol, 55 mg) and NMP (1 mL). Vessel was sealed with septum and placed in microwave reactor. Temperature was set to 150⁰C for 10 minutes. After allowing vessel to cool to room temperature, it was taken out of the microwave reactor and septum was removed. Contents were poured in to a separatory funnel and washed with water and diethyl ether. Combined organic layers were dried over MgSO₄. TLC showed starting material.

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6 Appendix A – ^1H NMR Spectra of Synthesized Molecules

