Abstract

OGALLO, LINDA AJUANG. Synthesis of Ligands For Electronic and Magnetic Structure-Property Relationship Studies. (Under the direction of David Shultz.)

The next generation of molecules will take advantage of electronic spin as well as electronic charge. The success of making these materials will be contingent upon two things; one is having a building block available and the second is having information on the structure-property relationships of the organic compounds carrying the unpaired electrons. Different ligands were synthesized for the purpose of exploring these relationships. This paper discusses the different methods and problems encountered during the synthesis of these ligands.

Synthesis of Ligands For Electronic and Magnetic Structure-Property Relationship Studies

By

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David A. Shultz
Chair of Advisory Committee

Christopher B. Gorman

Christian Melander

Dedication

To my dearest mom and dad, a tree is only as strong as its roots. You have believed in me sometimes more than I believe in myself. You have counseled and supported me through every decision I've made. You gave me the chance to be anything I want, and accepted a lot of my decisions even when you didn't fully agree with them. I wouldn't have the freedom to be who I am if it wasn't for you, thank you.

Biography

I was born on the 19th of November 1981 to Laban and Joan Ogallo in Nairobi, Kenya. I attended Ngara girl's high school where I was first introduced to chemistry. I was drawn to the subject because it was the one subject that everyone said was hard but came easy for me. I had my heart set on becoming a literature professor then, I was going to write novels and teach at a small collage. Then come high school graduation and my plans had changed I had decided to stick to the thing I was good at, which at the time was chemistry. That was how I ended up at North Carolina Central University in the chemistry department in August 2001. After a lot of guidance from the very supportive faculty at North Carolina Central University I decided to continue in the area of chemistry. I was admitted to North Carolina State University in August of 2004 and completed my requirements for Masters in May 2007.

Acknowledgements

To my family for their constant support, for keeping me grounded and encouraging me every step of the way, thank you. I'd like to thank God because without him I wouldn't be who I am today. I would also like to thank my friends for encouraging me to keep going, being my support and letting me vent out my frustrations on you. To my group members past, Sofi, you taught me to wipe on and wipe off. Candice your determination is amazing, you were a huge help and I wouldn't be an expert at separating stuck glassware without you, Nick, Chuck, knowing you was definitely an experience. To my present group members, Rob, you've been a great help. You're smarter than most people I know and you seem to know everything about everything, thanks for all your help and support. To Tashni-Ann Coote, I could write a book thanking you for everything you have done for me. You took me under your wing and showed me the ropes, left no stone unturned. You encourage me and always kept me laughing, made coming to lab fun for me, you've kept me going when I didn't feel like it and you never let me give up. You are more than a co-worker, you're my sister and my friend.

To my advisor Dave, for always expecting much from me, for being very encouraging and making chemistry interesting, thank you. Lastly, I'd like to acknowledge the NCSU chemistry department for giving me the opportunity to become a better chemist.

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CHAPTER 1

Introduction

The next generation of molecules will take advantage of electronic spin as well as electronic charge.[1] The success of making these materials will be contingent upon two things; one is having a building block available and the second is having information on the structure-property relationships of the organic compounds carrying the unpaired electrons. Different ligands were synthesized for the purpose of exploring these relationships.

Magnetism

1.1 Importance of magnetism

In order to fully appreciate and understand the magnetic properties exhibited by organic species, one should at least have a basic understanding of the types of magnetism and their origin. Magnetism has played a crucial role in the development of our society throughout history. It has been speculated that the magnetic phenomena has been around since before 800 B.C.[2] The first magnetic technology invention is believed to have been the compass. Though the concept has been around for ages, it was only with the development of Quantum Mechanics in the twentieth century that the understanding of magnetism really began.[3]

1.2 Types of magnetism

All materials respond to an external magnetic field (H). 4 Magnetism can be measured by a material's response (repulsion or attraction) to an applied field (H). Any type of magnetism is typically a bulk property and not an isolated molecular

phenomenon. There are five major types of magnetic behavior: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. Diamagnetism involves closed-shell systems in which all electrons are paired into bonds and perhaps lone pairs. This pairing results in no magnetic moment. Diamagnetic materials become weakly magnetized in the opposite direction to that of an applied magnetic field as shown in **Figure 1.1a**. Paramagnetism involves an open-shell system where electron spins are randomly and rapidly orienting and reorienting giving no net magnetic moment as shown in **Figure 1.1b.** If exposed to an external magnetic field, all the electrons in the paramagnet will align with the magnetic field, but reorient randomly when the field is removed.[4]

The latter three are a result of the response of a paramagnetic material to an external applied field. Above their ordering temperatures, i.e. the temperature below which spontaneous alignment occurs, these materials behave as paramagnets.[5] Ferromagnetism as shown in **Figure 1.1c** is the parallel alignment of the electrons in three dimensions, resulting in a permanent magnetic moment. Antiferromagnetism occurs when the electron spins align themselves in an antiparallel fashion resulting in no permanent magnetic moment as shown in **Figure 1.1d.** Ferrimagnetism is similar to antiferromagnetism in that the electron spins are paired antiparallel, but magnitude of the dipole moments of the electrons are different so that a net magnetic moment is observed as shown in **Figure 1.1e.**

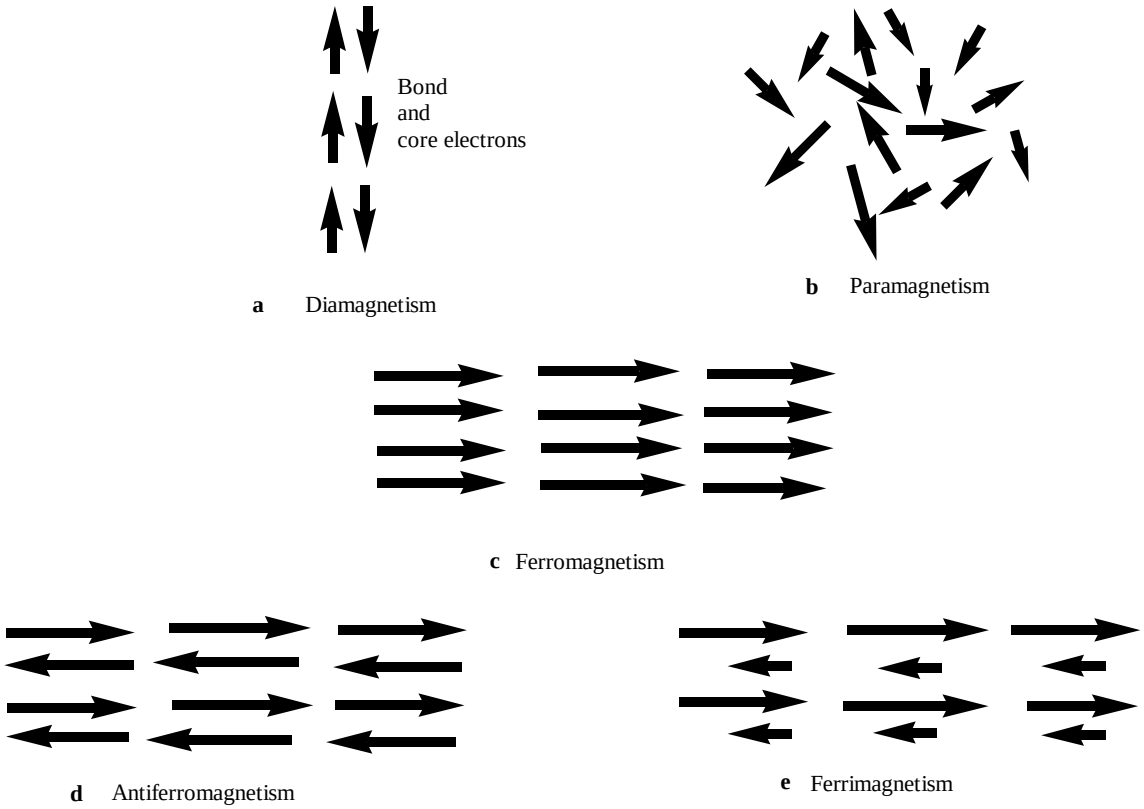


Figure 1.1: The "Big Five" magnetic behavior

1.3. Biradicals

An interesting class of paramagnetic molecules that show an electron spin alignment that resembles ferro- and antiferromagnets are bi- and polyradicals. Molecules with two or more unpaired electrons can be defined as bi- and polyradicals respectively. The unpaired electrons are placed in non-bonding molecular orbitals that are degenerate or nearly so. In biradicals, the two electrons could be placed in two different ways, one with both electrons facing opposite direction i.e. singlet state (antiferromagnetic coupling) or with both electrons facing the same direction i.e. triplet state (ferromagnetic coupling), as shown in **Figure 1.2.**

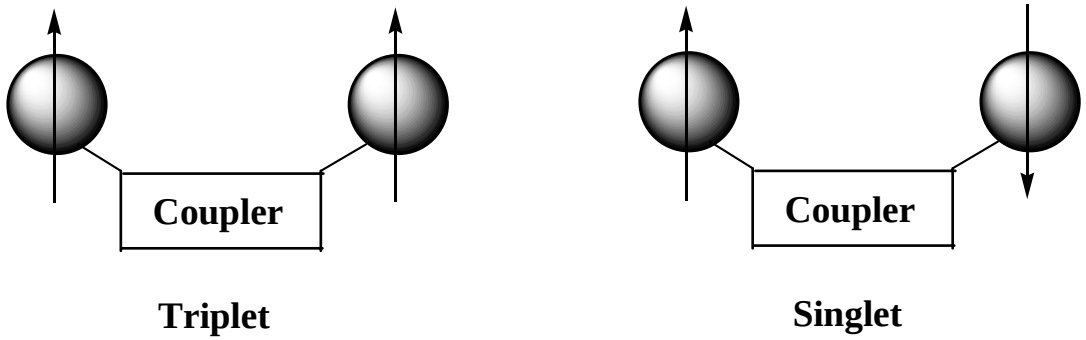
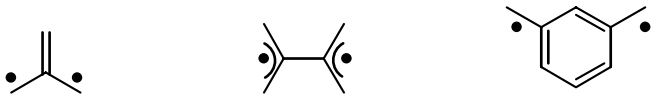


Figure 1.2 Cartoon of ferromagnetic coupling (right) antiferromagnetic coupling (left)

Biradicals are usually described as non- Kekulè hydrocarbons, meaning that they have no resonance structure that pairs the two electrons into a π-bond. These biradicals have either a singlet or a triplet ground state.[6] Some examples of non- Kekulè hydrocarbons include trimethylmethane (TMM) (**Figure 1.3a**) tetramethyleneethane (TME)(**1.3b**), *m*-benzoquinodimethane (MBQDM)(**1.3c**).

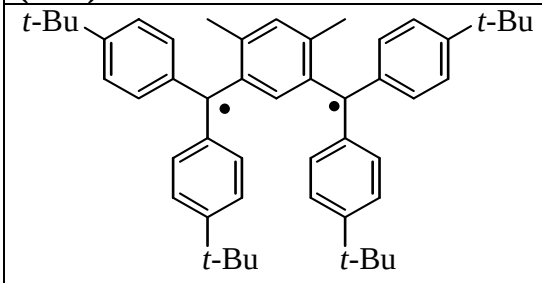
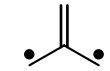


TMM **a** TME **b** MBQDM **c**

Figure 1.3 Biradicals with neither singlet or triplet ground state

Biradicals studied by the Shultz group can be divided into two groups, homospin biradicals and heterospin biradicals.[7] Homospin biradicals are those in which there are two spin carriers that are the same, while heterospin biradicals are those that have two different spin carriers. Heterospin biradicals can be further broken down into donor-donor spin carriers and donor-acceptor spin carriers. The following is a list of biradicals and list of coupling constants that have been studied over the years.[7-16] **Table 1.1** is a compilation of many biradicals that have been studied over the past 10 years with their corresponding J-values both measured and calculated.

Table 1.1. Table of biradicals with measured and calculated J-values.

Biradical **Measured J (cm^{-1})**	**Biradical** **Calculated J (cm^{-1})**
 >0	 +6143.80 [a14]
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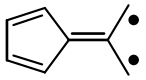
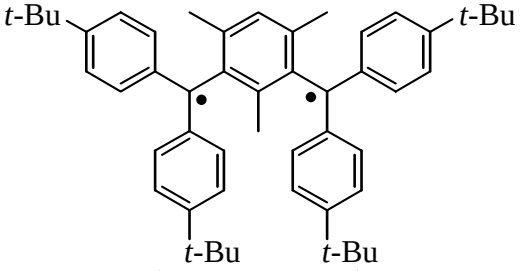
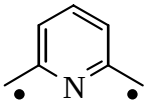
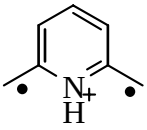
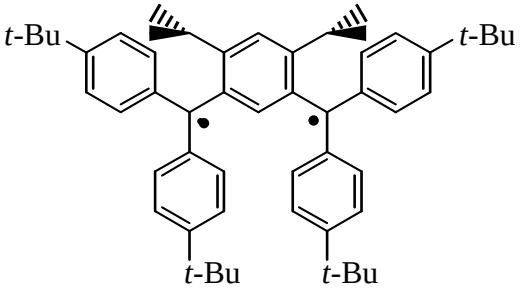
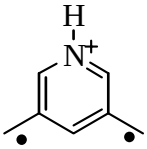
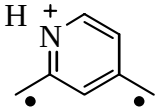
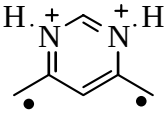
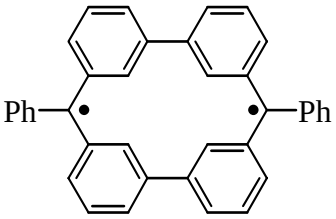
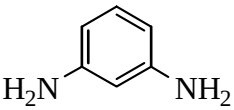
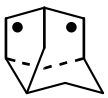
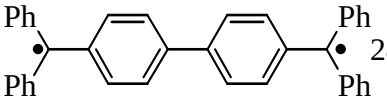
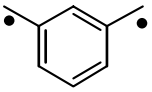
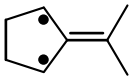
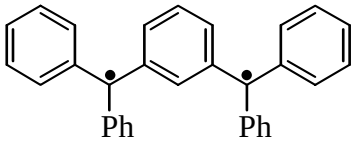
	 +2769[b41]
 >0	 +3000[a42]
	 -643[a42]
 <0	 +2286[a42]
	 -250[a42]
	 -7787[a42]
 -71.44< J <85.17[18]	 -3822[a42]
	 -232.20[a16]
 28.60< J <32.10[18]	 +3572[a16]
	 +2679[a16]
 >0	 +607.20[a16]
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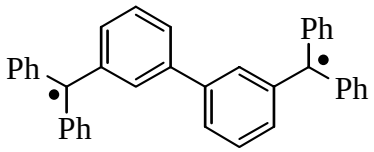
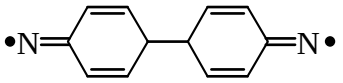
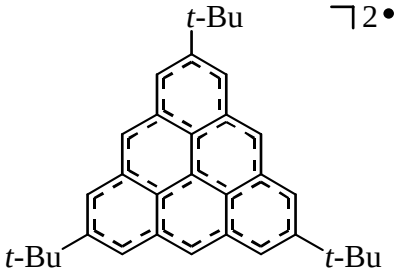
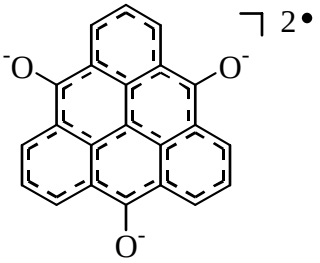
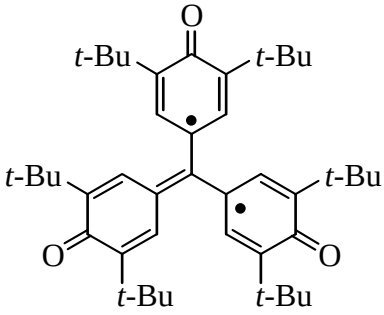
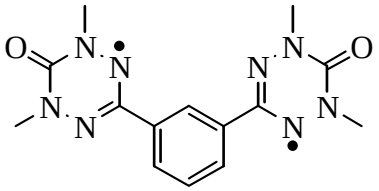
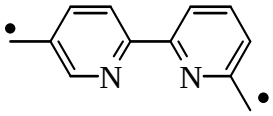
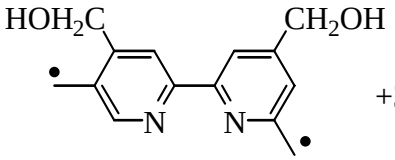
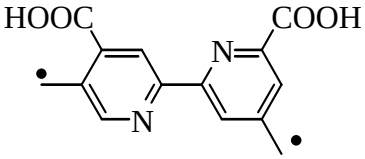
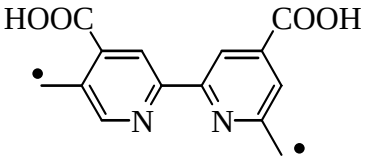
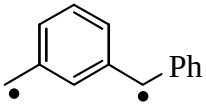
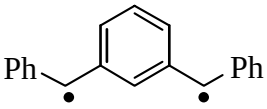
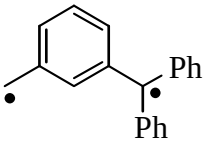
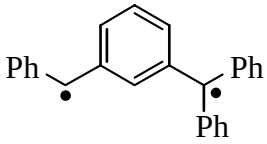
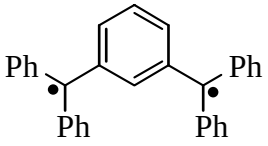
	>0
	-214.3[20]
	>0
	>0
	+245.0[22]
	>0
	+3277.32[c43]
	+3277.32[c43]
	+3219.81[c43]
	+3176.06[c43]
	+0.13[c34]
	+0.93[c35]
	+1114[c37]
	+0.66[c33]
	+0.44[c35]

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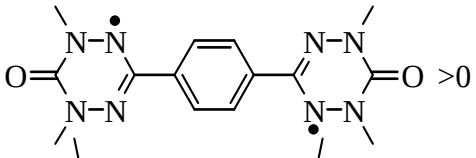
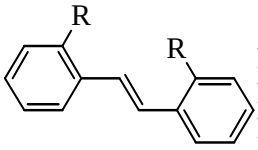
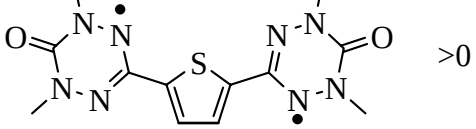
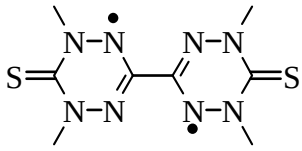
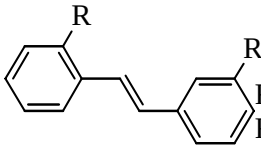
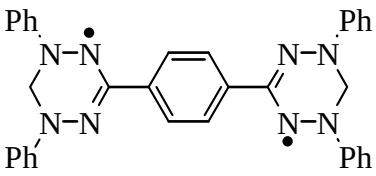
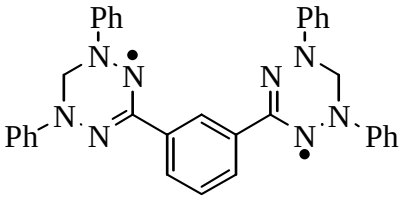
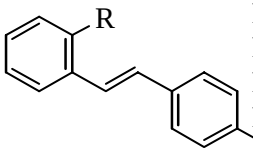
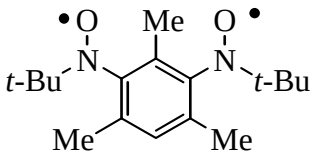
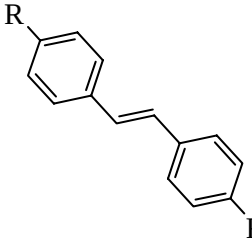
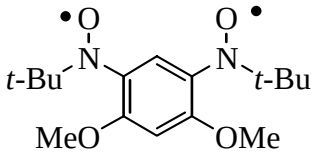
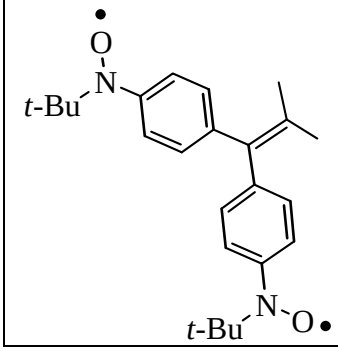
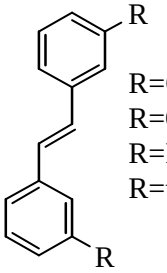
 >0	 R=CH$_2$ • -964.40^{d28} R=O • -2500^{d28} R=HNO • -428.60^{d28} R=t-Bu-NO • -71.40^{d28}
 >0	
 +560^{23}	 R=CH$_2$ • +821.60^{d28} R=O • +17860^{d28} R=HNO • +428.60^{d28} R=t-Bu-NO • +214.30^{d28}
 >0	
 >0	 R=CH$_2$ • -1321.60^{d28} R=O • -4465^{d28} R=HNO • -500^{d28} R=t-Bu-NO • -214.30^{d28}
 >0	 R=CH$_2$ • -285.80^{d28} R=O • -321.50^{d28} R=HNO • -214.30^{d28} R=t-Bu-NO • -178.60^{d28}
 >0	
 >0	 R=CH$_2$ • -1607.40^{c28} R=O • -2857.60^{c28} R=HNO • -643^{c28} R=t-Bu-NO • -428.60^{c28}

Table 1.1 cont

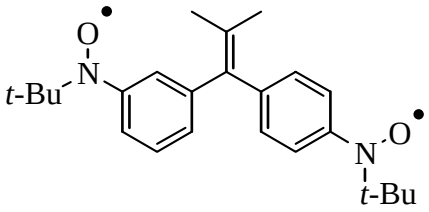
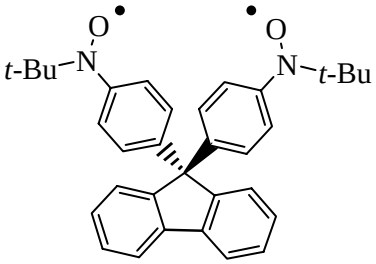
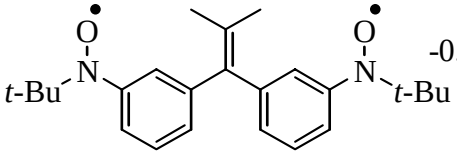
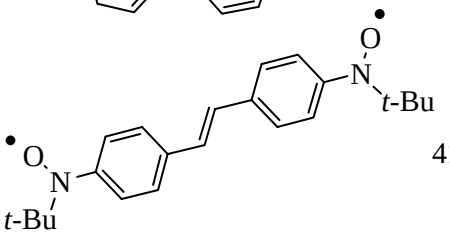
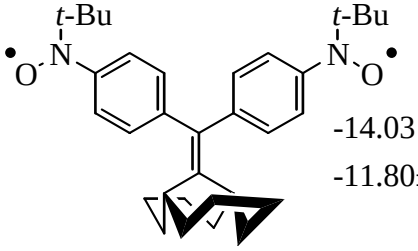
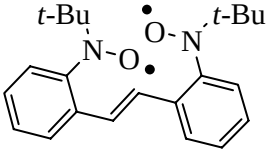
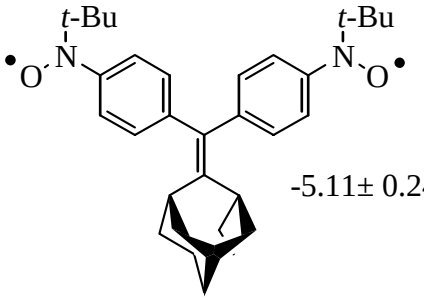
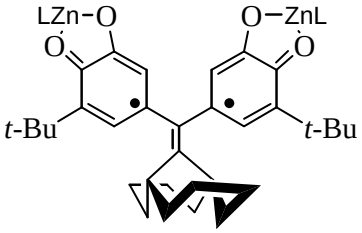
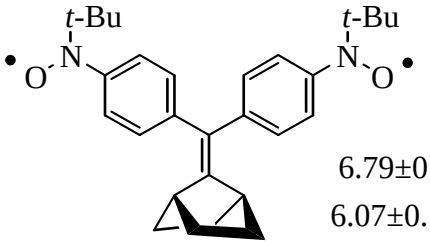
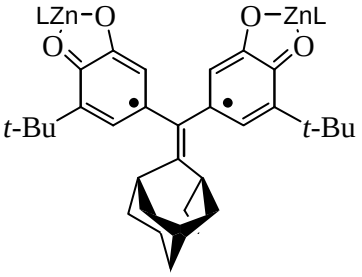
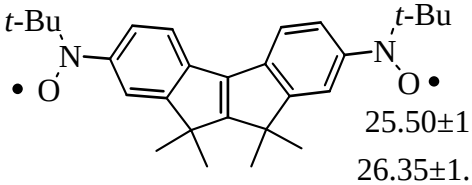
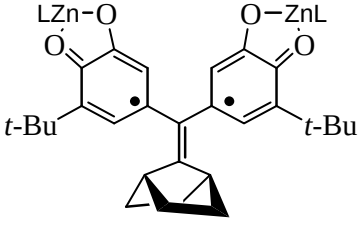
Biradical	Measured J (cm^{-1})	Biradical	Measured J (cm^{-1})
	-1.70[26]		-2.61±0.01[27] 2.85±0.13[a27]
	-0.90[26]		41.80±1[28]
	-14.03 ±0.12[27] -11.80±1.20[a27]		-9.60< J <0
	-5.11± 0.24[a27]		-30.30±0.80
	6.79±0.18[27] 6.07±0.15[e27]		24.40± 0.60[29]
	25.50±1.60[27] 26.35±1.73[a27]		87.00± 3.00[29]

Table 1.1 cont

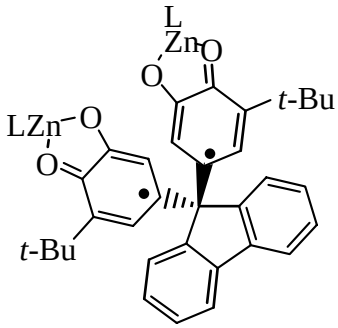
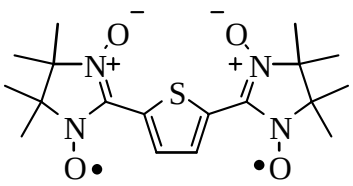
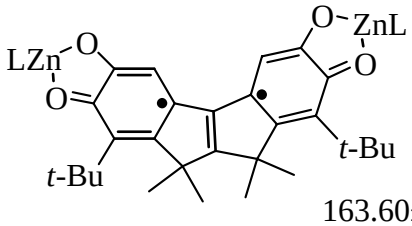
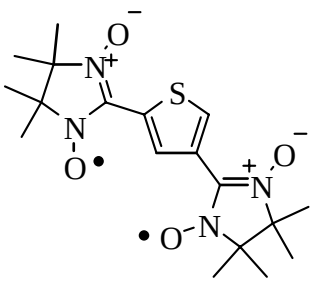
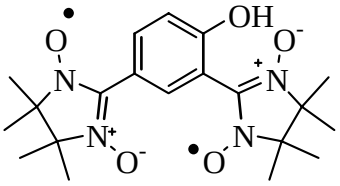
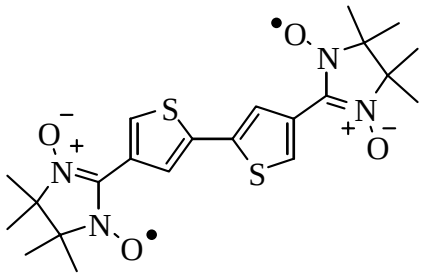
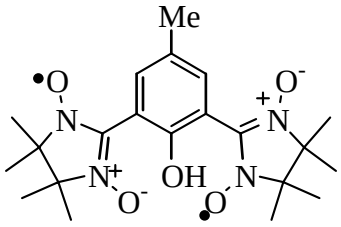
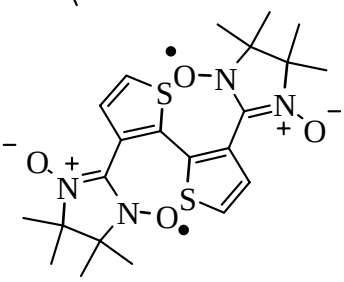
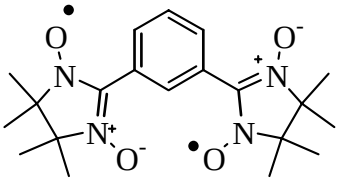
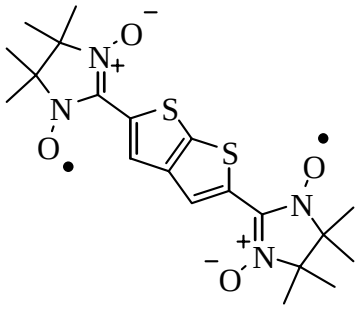
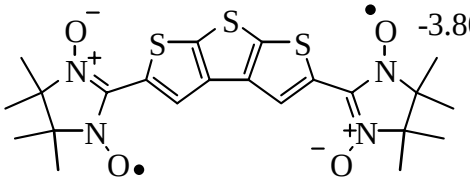
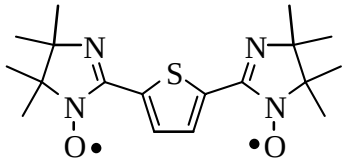
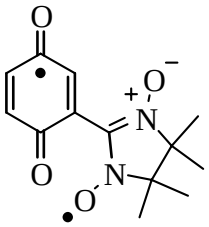
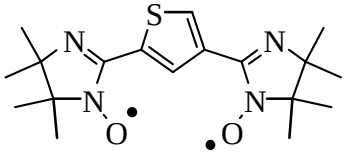
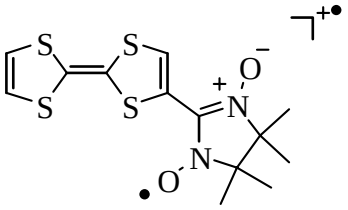
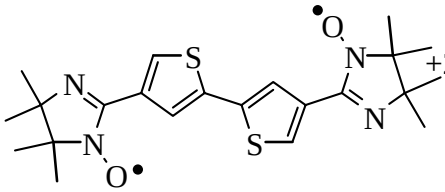
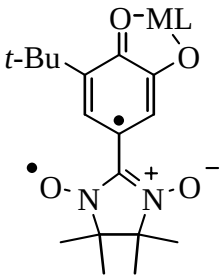
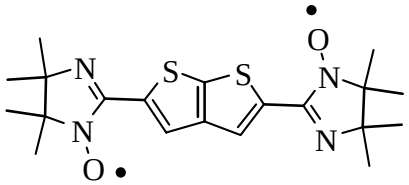
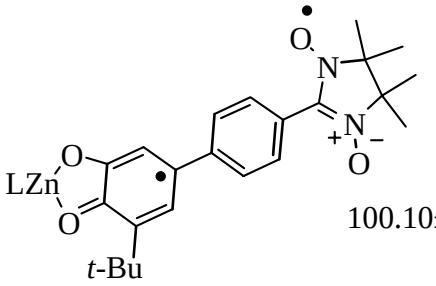
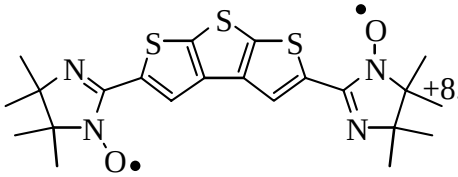
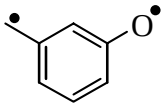
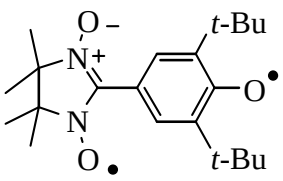
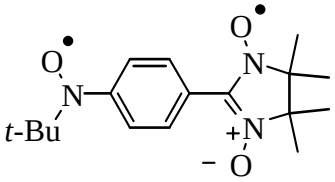
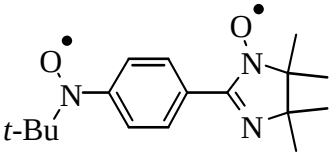
 0.99± 0.06[29]	 -79.90[32]
 163.60±1.60[29]	 -20.90[32]
 9.04±20[31]	 ~0
 4.20±0.30[31]	 -4.17[32]
 ~13.93	 -9.73[33]
	 -3.80[33]

Table 1.1 cont

 -20.90[32]	 >0
 +11.10[32]	 +69.50[37]
 +2.10[32]	 M=Mn -41.3±0.5[6] M=Ni -87.8±4.0[6] M=(OMe)Cu 75.6±1.0[6] M=Zn >300[6]
 -5.20[32]	 100.10±3.20[6]
 +8.00[33]	 >0
 >0	 >300[39]
	 +75[40]

[a]ab initio calculations. [b]UHF calculations. [c]UB3LYP method. [d]PVC film sample analysis. Measured values of J-values by SQUID magnetometry.

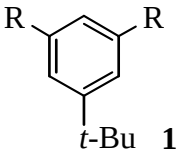
CHAPTER 2

Synthesis Of Ligands for electronic and magnetic property studies in dinuclear valence tautomers

2.1. Background

Compounds with the same molecular formula but different electronic structure are sometimes called valence tautomers. Valence tautomerism is defined as a reversible intramolecular metal-ligand electron transfer coupled with a spin-crossover at the metal center.[17-22] The ligands synthesized for this study were used to determine the impact of bridging ligand geometry on electronic and magnetic properties of the dinuclear valence tautomers. $[Cp_2Yb]_2$(μ-1,3(2,2′-bipyridyl)-5-*t*-Bu-C_6H_3) (**1**) and $[Cp_2Yb]_2$(μ-1,4(2,2′-bipyridyl)- C_6H_4) (**2**) and their two-electron oxidation products $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ were synthesized with the aim of determining the impact of the bridging ligand geometry on the electronic and magnetic properties of these materials. It was predicted on the basis of established spin coupling considerations, that having a 1,3 geometry would promote ferromagnetic coupling, while 1,4 geometry would promote antiferromagnetic coupling. However, the magnetic susceptibility measurements on **1** and **2** indicate that, in both cases, the exchange coupling mediated by the bis-2,2′-bipyridyl ligand was found to be small. The results also showed an unexpected similarity in electronic and magnetic

behavior of **1** and **2.** [23]

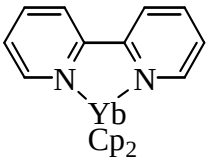


1

2

1,3-geometry 1,4 - geometry

R =



2.2. Synthesis of 1,3-(2,2'-bypirydyl)-5-*t*-Butyl-benzene (*m*-bpy)

1,3-(2,2'-bypirydyl)-5-*t*-Butyl-benzene is not a new compound to the Shultz group and its synthesis has recently been published. [18] There have been a lot of problems with the purification of the compound because of a colored impurity that would prevent the compound from crystallizing. This impurity had same retention factor (RF) by thin layer chromatography (TLC) as the *m*-bpy (3) in most of the solvent systems that had been tried. The main objective of this project was to synthesize and optimize purification of the *m*-bpy compound (3). Figure 2.1 shows the molecules that need to be synthesized in order to get 1,3-(2,2'-bypirydyl)-5-*t*-Butyl-benzene (3).

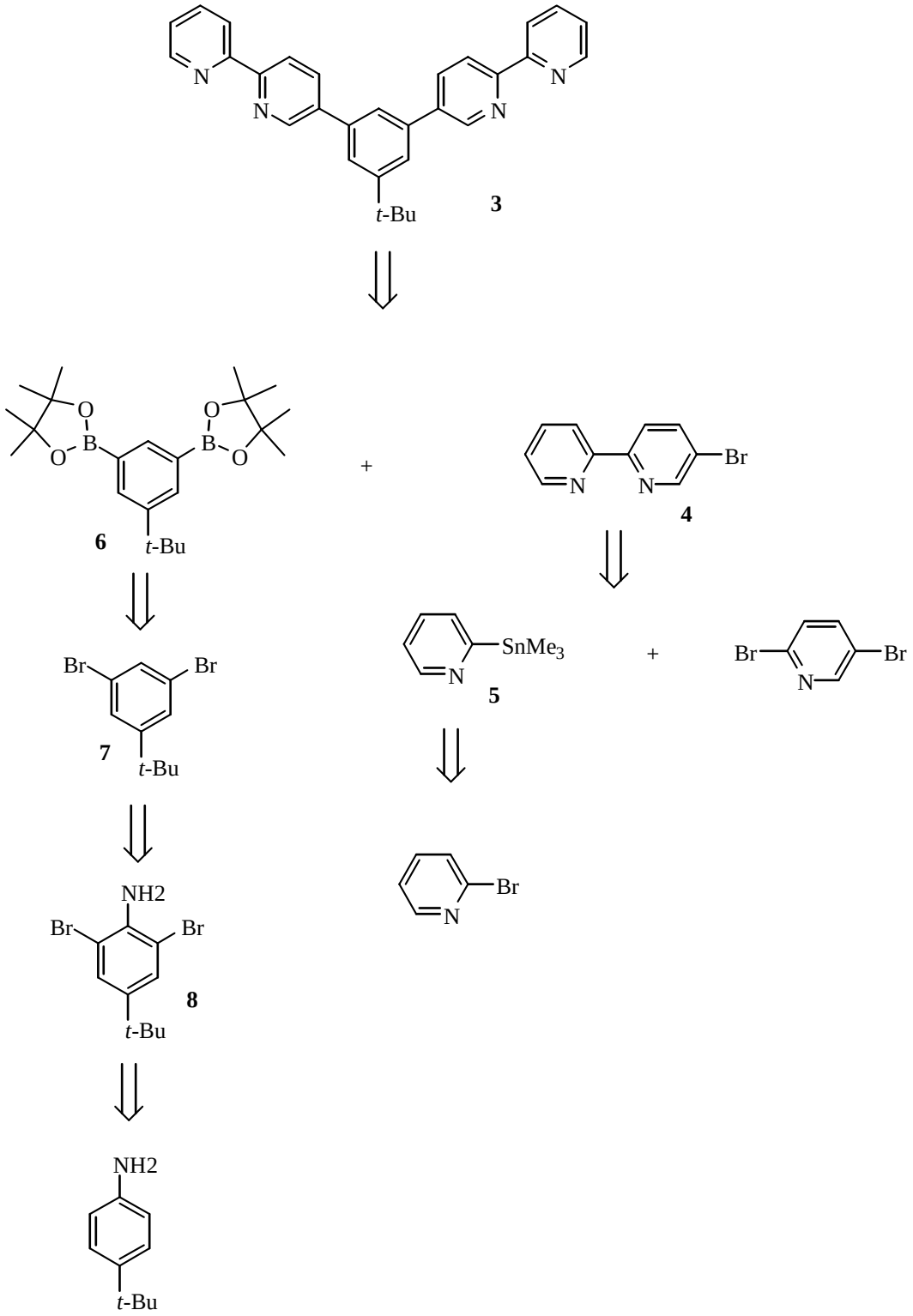


Figure 2. 1 Retrosynthesis of 1,3-(2,2'-bipyridyl)-5-t-Butyl-benzene

The first step towards the synthesis is the lithiation of 2-bromopyridine. The mechanism is a metal halogen exchange, which is very exothermic and is therefore

carried out at very low temperature. Two equivalents of the very basic *t*-butyllithium was used to prevent the competing side reaction between the aryl lithium salt and the *tert*-butyl bromide formed.

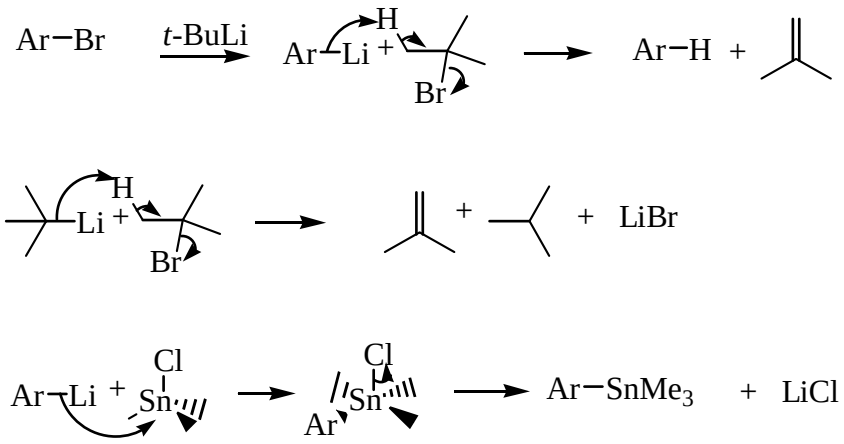


Figure 2. 2 Mechanism for preparation of **5**.

The aryl lithium salt was then quenched with trimethyltin chloride. Trimethyltin chloride is highly toxic. To avoid overexposure to the tin reagent, a quantitative yield of the product was taken. This subsequently affects the stoichiometric ratio of the next step, resulting in a low overall yield. Excess trimethyltin chloride was removed via bulb to bulb distillation. The solvent used in the reaction was ether, which is very volatile. As a result, any product that was distilled over with the trimethyltin waste during the distillation process was discarded.

5-bromo-2-2'-bipyridine (4) was prepared in situ, by coupling the trimethyltin product (5) with 2,5-dibromopyridine through a Stille reaction. The mechanism involves an oxidative addition of the bromopyridine to form a Pd(II) intermediate, followed by a transmetalation and finally a reductive elimination that results in the aryl-aryl coupling.

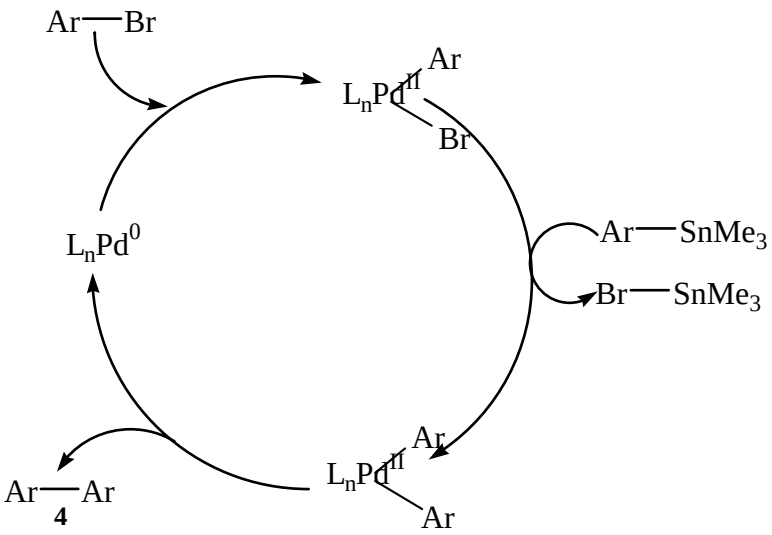


Figure 2. 3 Stille reaction mechanism.

Tert-butyl aniline was brominated and reductively deaminated to give 1,3-dibromo-5-*tert*-butylbezene (**7**). The bisboronate ester (**6**) was prepared via a cross-coupling reaction of the halide (**7**) with the (alkoxy)diboron. Treatment of phenylpalladium (II) bromide with KOAc is said to give a *trans*-ArPdOAc(PPh_3)$_2$ which exhibits high reactivity toward (alkoxy)diboron derivatives selectively giving the phenylboronate at room temperature. The transmetalation forming the Ar-Pd-OAc intermediate and its reaction with the (alkoxy)diboron has been proposed as a key step.[24]

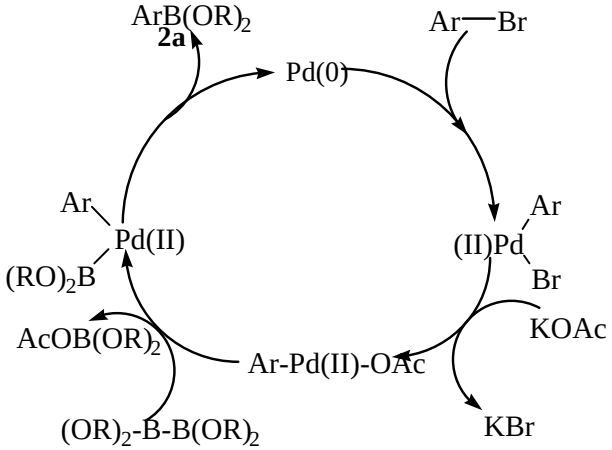


Figure 2.4 Reaction mechanism for (alkoxy) diboron.

Organoboron compounds are highly electophilic but the organic groups on the boron are weakly nucleophilic. The use of a negatively charged base, which coordinates to the boron, allows for a 1,2-migration of the organic group on the boron to an adjacent positive center.[24] Therefore we propose an alternative mechanism for the formation of (**6**) involving the coordination of the acetate group to one of the boron centers of the (alkoxy) diboron allowing a 1,2 migration of the transmetalation of the uncoordinated boronic center as shown in **Figure 2.5**.

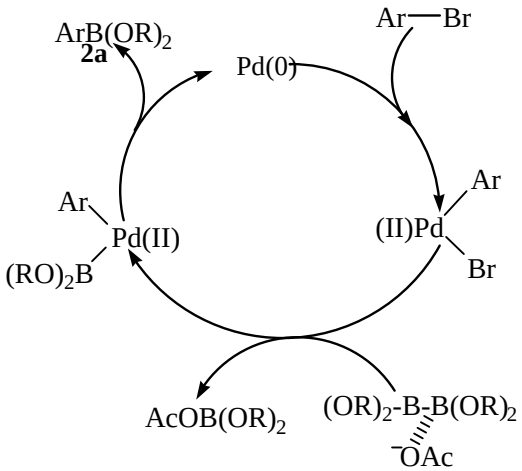


Figure 2. 5 Alternative reaction mechanism for (alkoxy) diboron

The *m*-bpy (**3**) was synthesized via a Suzuki reaction between the bromobipyridine and the boronic ester (**6**). The mechanism is much like most cross coupling reactions which involves oxidative addition, transmetalation and reductive elimination. The oxidative addition step which involves the reaction of bromobipyridine and the Pd(0) catalyst is believed to be the rate determining step as is often the case in a catalytic cycle.[24] The final product, 1,3-(2,2'-bypirydyl)-5-*t*-butyl-benzene(**3**), was formed through a reductive elimination as shown in the **Figure 2.6**. The elimination is speculated to take place after a reaction from the *cis*-Pd complex. The *trans* compounds isomerize to the *cis* complex before the elimination takes place.[24] It is suggested that

during the reductive elimination, the pi-bond of the aryl groups participate in the bond formation.

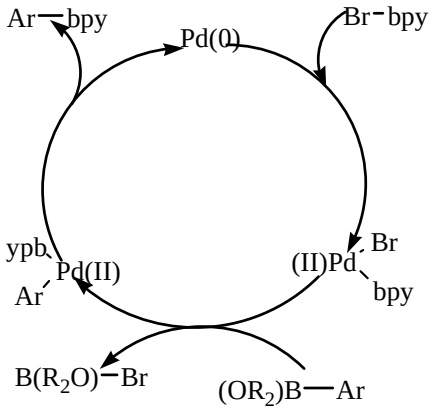


Figure 2. 6 Suzuki reaction mechanism.

2.3. Synthesis of 1,4-(2,2'-bipyridyl)-benzene (*p*-bpy)

Synthesis of the *para* substituted 1,4-(2,2'-bipyridyl)-benzene (*p*-bpy) (**9**) ligand followed the same procedure as the *meta*-substituted bipyridine ligand. The *p*-diiodobenzene was commercially available, which reduces the number of synthetic steps required when compared to the *m*-bpy (**3**) synthesis.

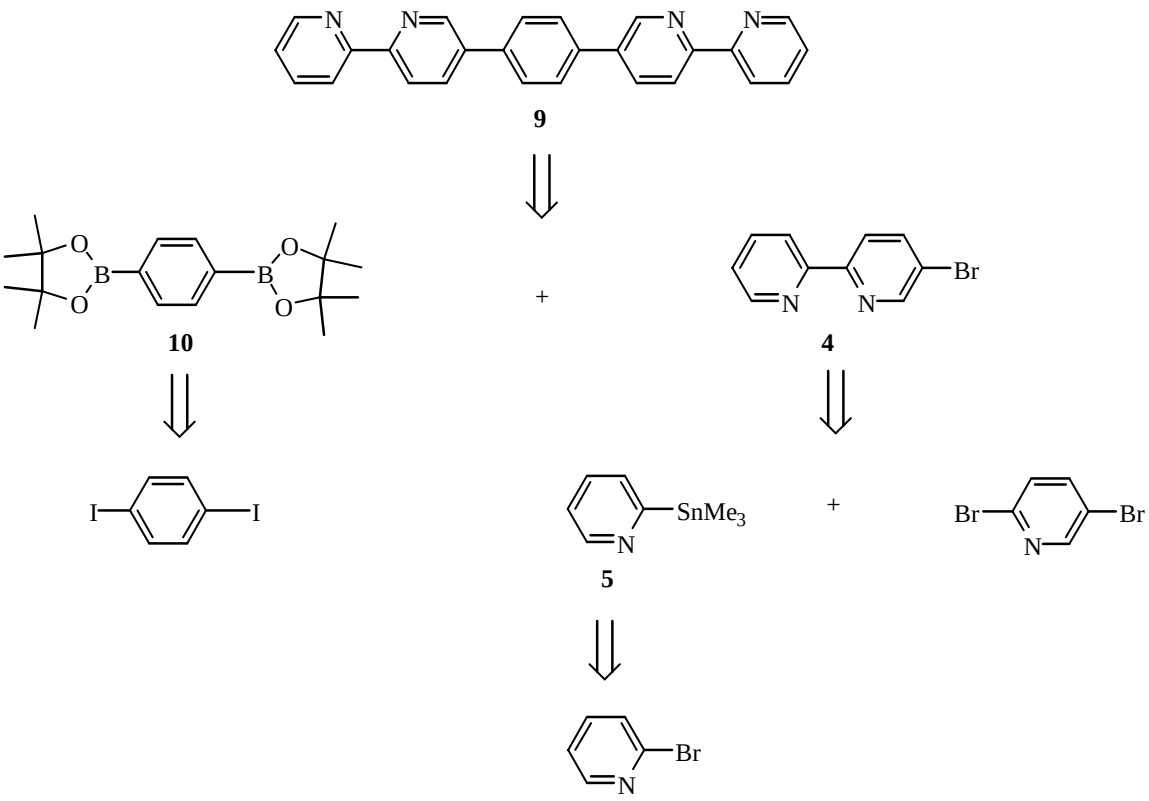


Figure 2. 7 Retrosynthesis of 1,4-(2,2'-bipyridyl)-benzene (p-bpy).

Reaction time for the Suzuki coupling of the *para* compound (**9**) was much faster than the *meta* compound (**3**). The *para* substituted compound took two days to reach completion while the *meta* substituted compound took up to a week under the same conditions. An NMR of the crude yield of the *para* substituted compound showed about 80% conversion of the starting material to the product. The *meta* compound showed less than 50% conversion even after a week.

The *para* substituted compound crystallized on formation making it easier to purify while the *meta* compound formed an impurity that prevented the it from crystallizing. The impurity formed did not show on the NMR and had roughly the same Rf by TLC as the starting material. The compound was finally purified by running the crude *m*-bpy (**3**) through a series of silica gel columns using 5:1 petroleum ether:ethyl acetate mixture. The first few aliquots that looked pure on the TLC plate were discarded because they

contained traces of the impurity and caused the product not to crystallize. The overall yield of the *para* compound was far greater than that of the *meta* compound. The reason for this could be due to steric hindrance of the *tert*-butyl group but a detailed study on this issue has not been done.

CHAPTER 3

Synthesis of ligands for electronic and magnetic property studies in biradicals

3.1. Homospin biradicals

Biradicals can sometimes be looked at as two monoradicals linked by a coupler. Each spin carrier has its own properties, but when multiple spin carriers are brought together within one species, their individual properties can combine in interesting ways. These combinations can lead to novel electronic properties and in turn, these new molecules can be used as components for molecular electronics or molecular magnets.[32] Through altering the substituents on the coupler, the Shultz group have demonstrated the first experimental evidence of polar substituent effects on exchange coupling in triplet ground-state biradicals. [25]

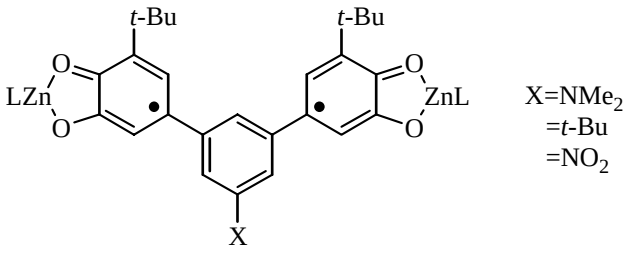


Figure 3.0 a Bis(semiquinone) complex with variable couplers**.**

The electronic and magnetic effects of changing the substituent group on the spin carriers are also being examined.[31] Further studies on the properties of these homospin biradicals are still been carried out by the Shultz group. The ligand synthesized in this project was towards a contribution to this study.

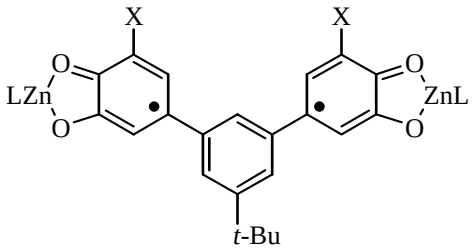


Figure 3.0b Bis(semiquinone) complex with variable spin carriers.

3.2 Synthesis of 5-bromo-3-chlorocatechol

5-bromo-3-chlorocatechol was synthesized to study the effect of the chlorine group as a substituent on the spin carrier. **Figure 3.1** shows the compounds that needed to be synthesized to make the ligand (**11**).

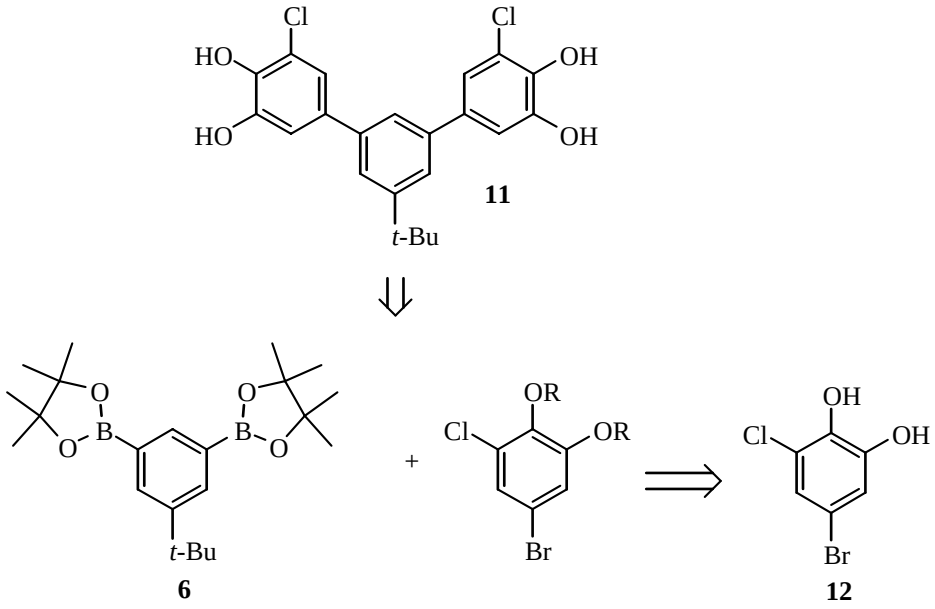


Figure 3. 1 Retrosynthesis of bis(chloro catechol) **11**.

Synthesis of **6** has been shown in **Section 2.1** and therefore only the synthesis of **12** will be discussed. The journey towards this synthesis was very fascinating because even though there were many theoretical ways proposed to make this compound most of them turned out to be fruitless. The complexity of the synthesis of such a simple looking molecule brings to light the difference between theoretical and experimental chemistry.

The different ways previously attempted to make compound **12** are shown in **Figure 3.2**[31]. The attempts shown either failed or gave multiple side products making the analysis and purification difficult.

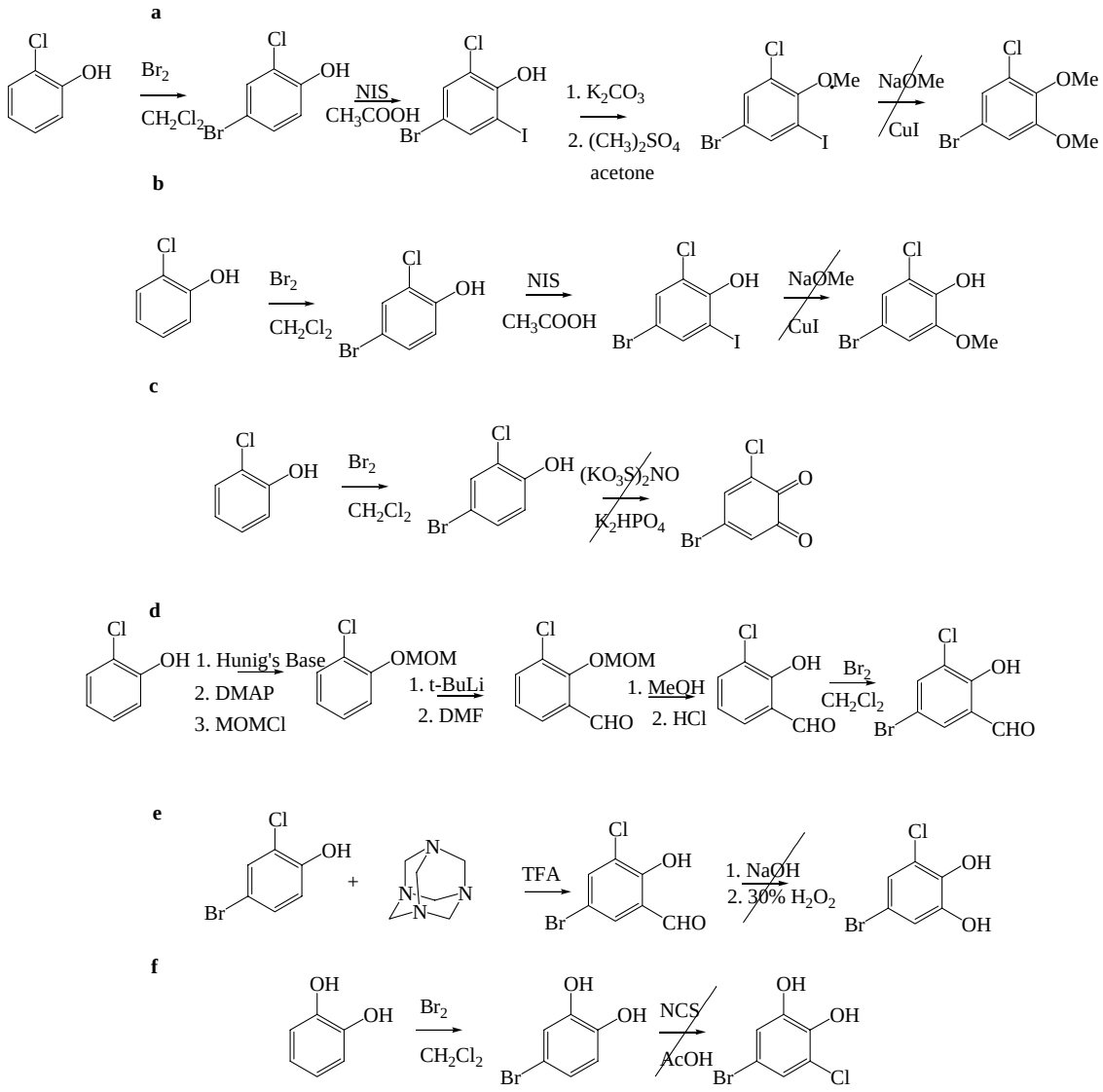
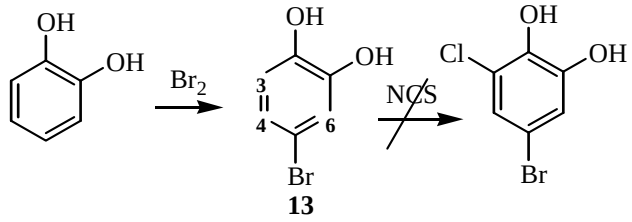


Figure 3. 2 Synthesis attempts for compound **12**.

Of all the reactions previously attempted, reaction step **f** in **Figure 3.2** seemed be the most promising, even though an NMR of the final product was complicated and showed multiple products. This would be a two-step synthesis and the first step yields

approximately 90%. The focus was placed on increasing the purity and yield of the chlorination to provide a viable solution to this synthesis.



13

Figure 3. 3 Synthesis proposed of compound **12**.

Theoretically, the hydroxyl group is primarily *para* directing. At lower temperature we would be able to get exclusively the *para* product during bromination, especially if we kept the bromine:catechol ratio at 1:1 to yield **13**. It was anticipated that the chlorination step would yield multiple products but would mainly chlorinate at positions 3 and 4 because position 6 was more hindered. We would then separate the compound using column chromatography.

Bromination of the catechol yielded a product that looked pure by TLC. The 1H NMR data showed the desired product and an impurity having a singlet multiplicity in the aromatic region. C^{13} NMR data led to the conclusion that both the singly and the doubly brominated and product were formed, with the singly brominated being the major product. Unfortunately an attempt to control the reaction conditions to yield only one product were unsuccessful. Under-bromination yielded both products and starting material and both products have the same Rf value by TLC so separating them was impossible. A second bromination probably occurs immediately after **12** is formed as shown in **Figure 3.4**.

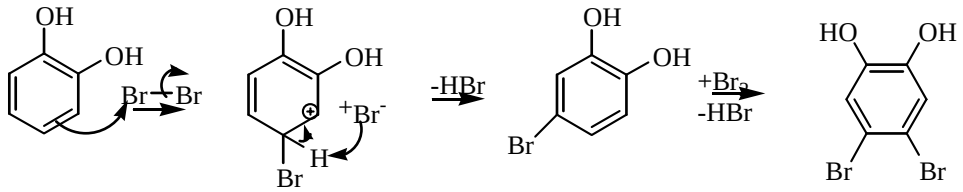


Figure 3.4 Bromination of catechol.

No literature was found for the separation of similar compounds. Chlorination of both the single and the doubly brominated product would lead to multiple side products, thus explaining the variety of aromatic signals on the NMR.

Having a hydroxyl and a methoxy group on the ring should enhance selectivity compared to having two hydroxyl groups. The hydroxyl group is a stronger electron donor and should therefore dictate the position where halogenation takes place. With this in mind, the second approach proposed was to start with 2-chlorophenol, MOM(methoxy methyl) protect the hydroxyl group then ortho lithiate and add an OH group. The OH group would then be methyl protected and the MOM group deprotected to give 3-chloro guiacol. The purpose of methyl protecting the alcohol is to help direct the bromination to the *para* position. Hydroxyl groups are mainly *ortho*- and *para*-directing and both *ortho* positions were occupied, so this led to the conclusion that the bromination would occur exclusively *para* to the OH group.

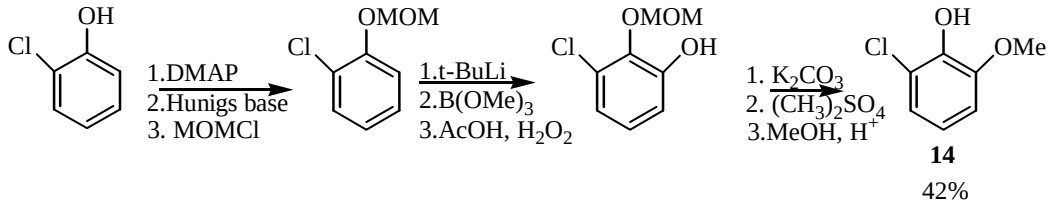


Figure 3.5 Synthesis of 3-chloroguiacol.

Another route used to make the 3-chloro guiacol (**14**) was to first MOM protect guiacol, then ortho lithiate and quench with hexachloroethane as the nucleophile. This would be followed by a deprotection of the MOM group to give chloroguaiacol.

This method involved one less step and also gave a better overall yield. The product was analyzed by 1Hand 13C NMR, mass spectrometry and proved to be the right compound.

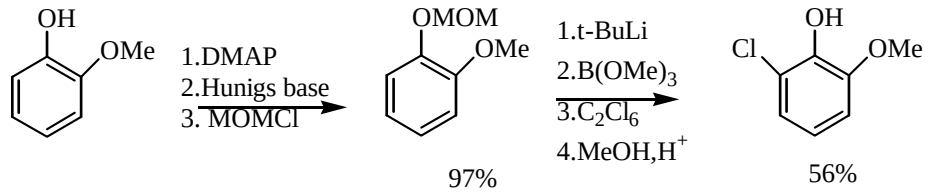


Figure 3. 6 Alternate synthesis of 3-chloroguiacol

Bromination of 3-chloroguaiacol gave a different result than was expected. The 1H NMR of the product showed the major compound having a two doublets with a *J* coupling of 9Hz which is typical of two hydrogen's *ortho* to each other. This indicates that the compound was brominated at the position either *ortho* to the methoxy group, or *ortho* to the chlorine group as shown in **Figure 3.7**. It could be argued that since the methoxy group is directing the bromination primarily to the *para* position, and the chlorine is also an ortho directing group, the most plausible product would be 4-bromo3-chloroguaiacol. The experimental data also accounts for 3-chloro-6-bromoguaiacol and there is therefore no way of distinguishing between the two products by NMR. *J* values indicative *meta*-coupling on the NMR indicated the formation of our desired product but in a lower ratio to the *para* product. Unfortunately isolation of the desired product would be difficult since all products had approximately the same Rf (retention factor) value by TLC in various solvent concentrations.

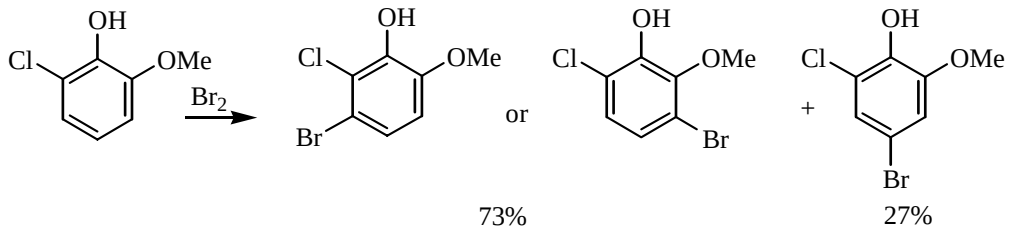


Figure 3. 7 Bromination of 3-chloroguiacol

The next approach taken was the bromination of guaiacol followed by the chlorination of the resulting product. Bromination of guaiacol yields exclusively 5-bromo-guaiacol with over 90% yield. Chlorination of the bromoguaiacol was first attempted using sodium hypochlorite. This yielded the desired 4-bromo-2-methoxy-phenol but also returned our starting material. Attempts to re-subject the product mixture to the reaction conditions did not change the result.

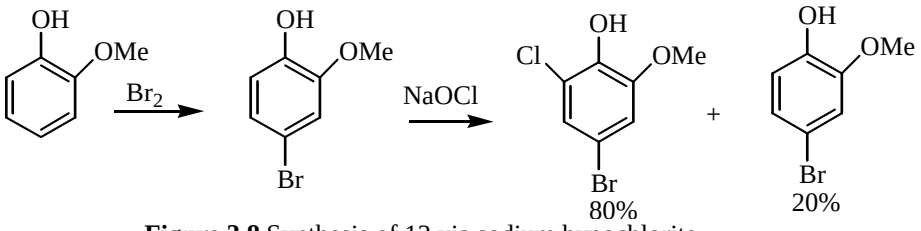


Figure 3.8 Synthesis of 12 via sodium hypochlorite

Tert-butyl hypochlorite, which is made by reacting *tert*-butylalcohol with sodium hypochlorite, is more reactive than sodium hypochlorite. When *tert*-butyl hypochlorite was used as the chlorinating agent in the reaction with 5-bromoguaiacol, the reaction went to completion forming the desired 5-bromo-3-chloroguaiacol.

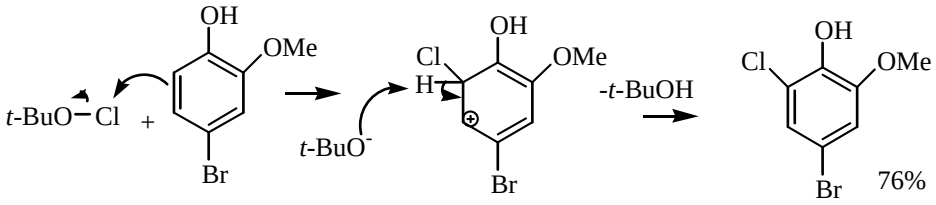
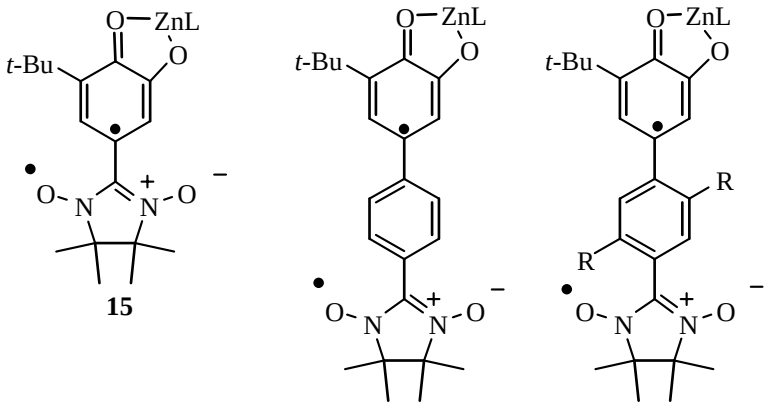


Figure 3.9 Synthesis of 12 via t-butyl hypochlorite.

3.3. Heterospin biradicals

Heterospin biradicals as previously discussed in **Section 1.3** have different spin carriers in the same molecule. The Shultz group has characterized and studied the nitronyl nitroxide semiquinone zinc complex (**15**) extensively. [13,26, 27] The phenyl-spaced nitronyl nitroxide semiquinone zinc complex (**16**) has also been studied and fully characterized. EPR studies have been performed on the complex to complete the

characterization of this biradicals. The Shultz group is interested in studying how changing the torsion angle of the bridge in this nitronyl nitroxide-bridge-semiquinone zinc complex affects the magnetic and electronic properties of this compound. The objective of this project was to synthesize the *para*-xylene bridge nitronyl nitroxide semiquinone zinc complex (**18**).



15 **16**

Figure 3. 10 Nitronyl nitroxide-bridge-semiquinone zinc complex

3.4. Synthesis of SQ-*p*-xylene-N

Synthesis of the SQ-*para*-xylene-NN (**17**) was similar to the SQ-Phenyl-NN (**16**) previously published. The *para*-xylene bridge unlike the phenyl bridge was not commercially available and had to be synthesized.[28] **Figure 3.11** shows the compounds necessary towards the synthesis of the biradical (**17**).

5-bromo-3-*t*-butylcatechol (**22**) is the primary building block of many compounds in the Shultz group and it has been synthesized in a number of ways.[28] I utilized a synthetic scheme that involved MOM protection of 2-*tert*-butyl phenol. The mechanism proposed for this reaction was an S_N2 substitution with a nucleophilic attack of the deprotonated alcohol on MOM chloride.

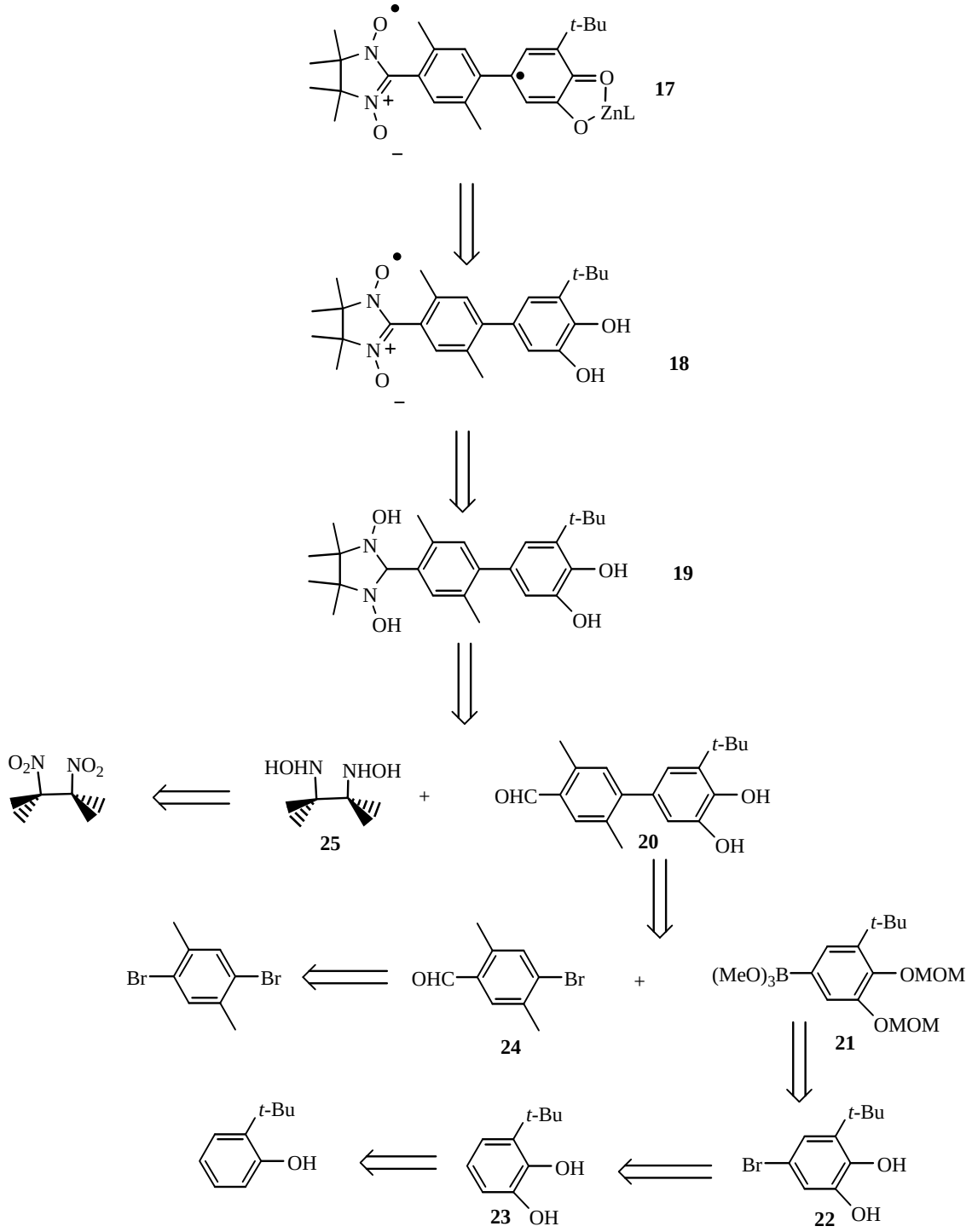


Figure 3. 11 Retrosynthesis of nitronyl nitroxide-p-xylene-semiquinone zinc complex.

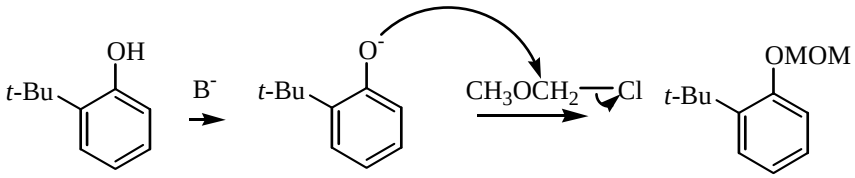


Figure 3.12 MOM protection of t-butyl chloride.

A hydroxyl group was placed at a position ortho to the MOM protected alcohol by a lithiation using *tert*-butyl lithium. The methoxymethoxy (MOM) group does more than protect the alcohol, it also provides selective lithiation by coordinating to the lithium.[29-31] The lithium salt formed was then quenched with trimethyl borate to give the boronate ester. This was then reacted with hydrogen peroxide to form the alcohol as shown in **Figure 3.13**.

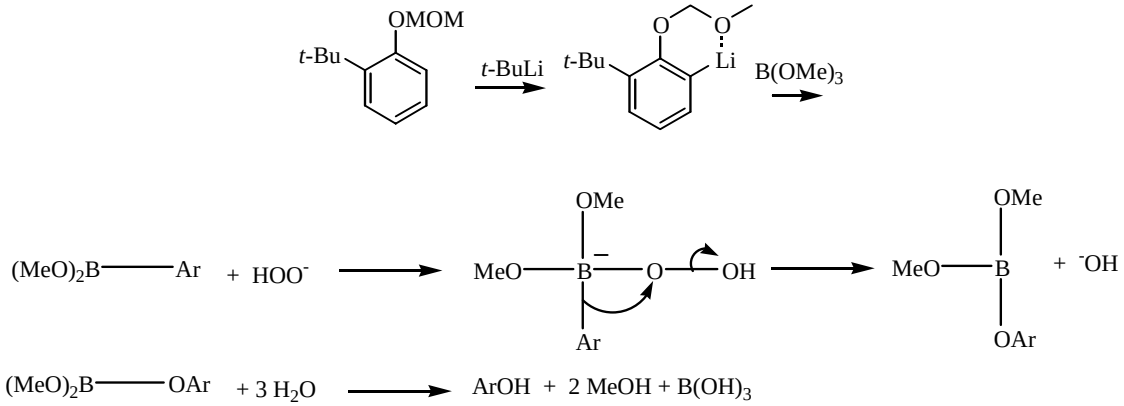


Figure 3.13. Preparation of 3-tert-Butyl-2-methoxymethoxy-phenol.

Deprotection of the resulting product was done with methanol and a catalytic amount of acid gave t*ert*-butyl catechol (**23**) as shown in **Figure 3.14**. The mechanism suggested for this reaction was the same as most ether cleavages.[32]

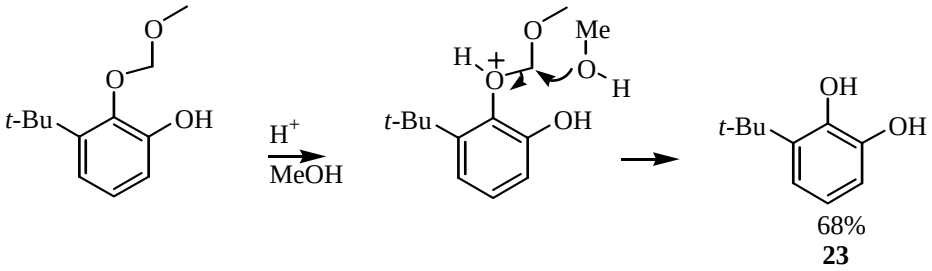


Figure 3. 14 MOM deprotection of 3-tert-Butyl-2-methoxymethoxy-phenol.

t-Butyl catechol (**23**) was then brominated to give 5-bromo-3-tert-butyl-benzene-1,2-diol (**22**). The mechanism followed was the same as that of an electrophilic addition on a benzene ring and is directed by the hydroxyl group. An 1H NMR of the crude product showed that the main product had the bromination occurring at position 5, *meta* to the *tert*-butyl group. A probable explanation given for the preference for position 5 as opposed to position 4, which is also para to a hydroxyl group, was steric hindrance caused by the presence of the *tert*-butyl group *ortho* to position 4. The catechol (**22**) was then methyl protected as shown in **Figure 3.15** and then purified by sublimation.

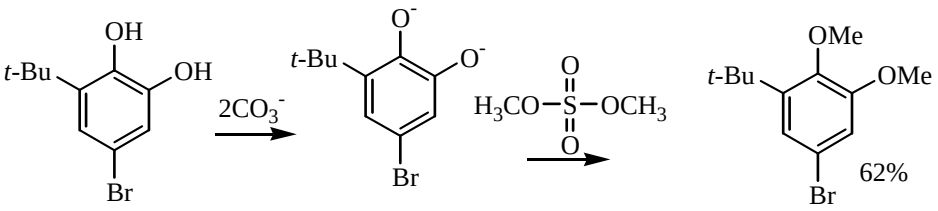
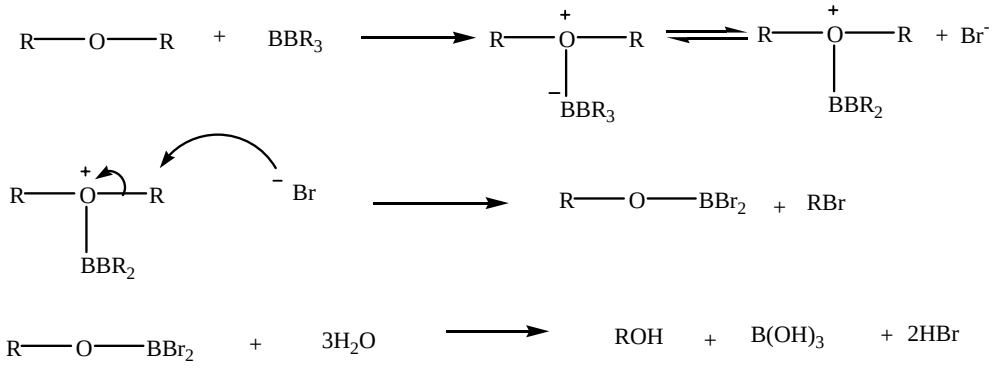


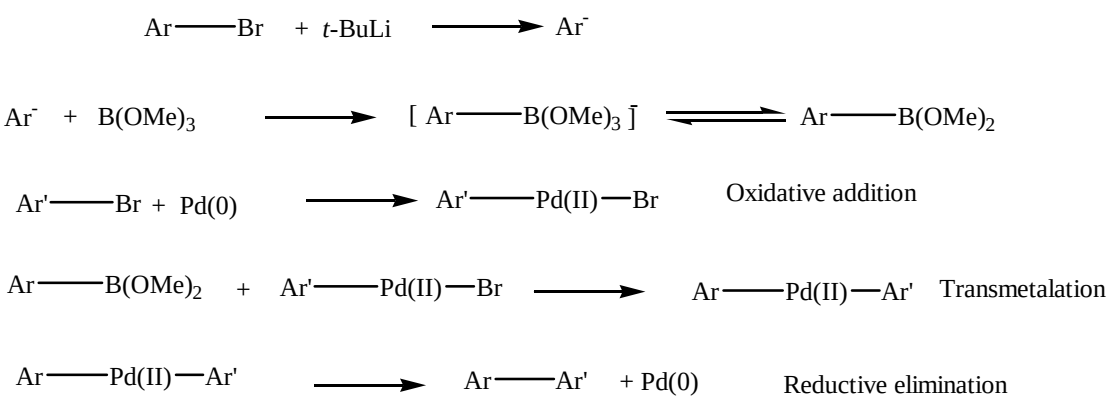
Figure 3.15 Methyl protection of **22**

The catechol (**22**) was recovered by de-methylation using boron tribromide. The mechanism is shown in **Scheme 3.1** and involves an attack of the bromine ion on an adduct formed from the ether and the electrophilic boron reagent. This was then followed by a cleavage step to give the alcohol.[33]



Scheme 1 Mechanism for ether cleavage with boron tribromide.[33]

5-Bromo-3-tert-butyl-benzene-1,2-diol (**22**) was then MOM protected because proceeding with the methylated product caused problems in the synthesis of (**16**). The MOM-protected product was lithiated and quenched with trimethyl borate to make its boronate ester (**21**). This was then coupled to 4-bromo-2,5-dimethylbenzaldehyde (**24**) through a Suzuki reaction to give the catechol-aldehyde (**20**).



Scheme 3.2. Suzuki mechanism.[34]

4-bromo-2,5-dimethylbenzaldehyde (**24**) was synthesized from 2,5-dibromo-*p*-xylene by lithiation and quenching with DMF. The mechanism involved a lithium halogen exchange with one of the bromines and the resulting anion adds to the carbonyl group on the dimethylformamide. The aldehyde was then formed after an acid work up as shown in **Figure 3.16**.

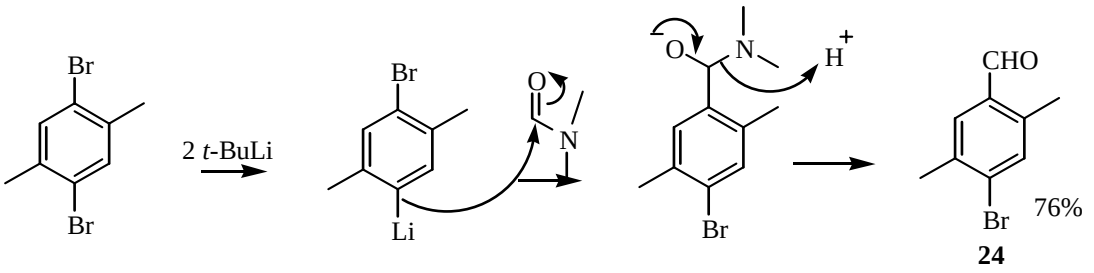


Figure 3. 16 Synthesis of aldehyde **24**.

The catechol-aldehyde was made by deprotection of the MOM groups. Synthesis of the bis(hydroxyamine) compound (**25**) had been a problem in the Shultz group. The current procedure gave very low yield and irreproducible results. The reaction required activated zinc and optimal temperatures, which had to be between 4-8°or the reaction would not work.[35] Bis(hydroxyamine) is unstable in solution and can therefore not be purified using the standard purification methods. The use of Al/Hg in place of the zinc reduced the 2,3-dimethyl-2,3-dinitrobutane to the bis(hydroxylamine) (**25**) with high yields and great reproducibility.[36]

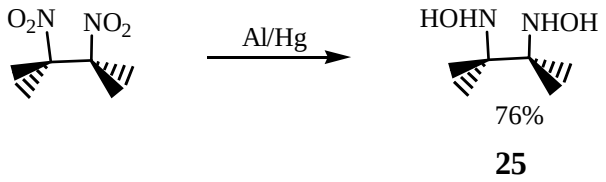


Figure 3. 17 Reduction of 2,3-Dimethyl-2,3-dinitro-butane.

The imidazolidine (**19**) was prepared by the condensation of the catechol-aldehyde(**20**) with bis(hydroxyamine) (**25**) in dry methanol at room temperature. The mechanism is shown in **Figure 3.18** and involves the formation of an enamine, which is then followed by the formation of the imidazolidine.

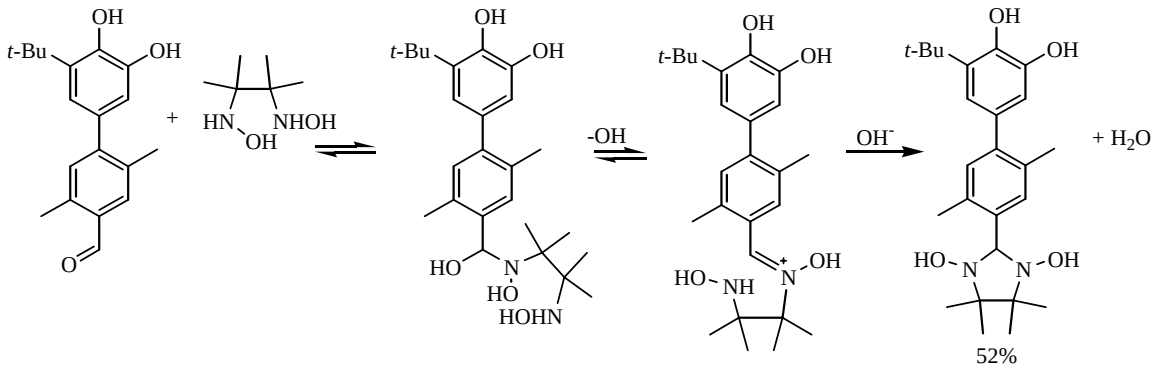
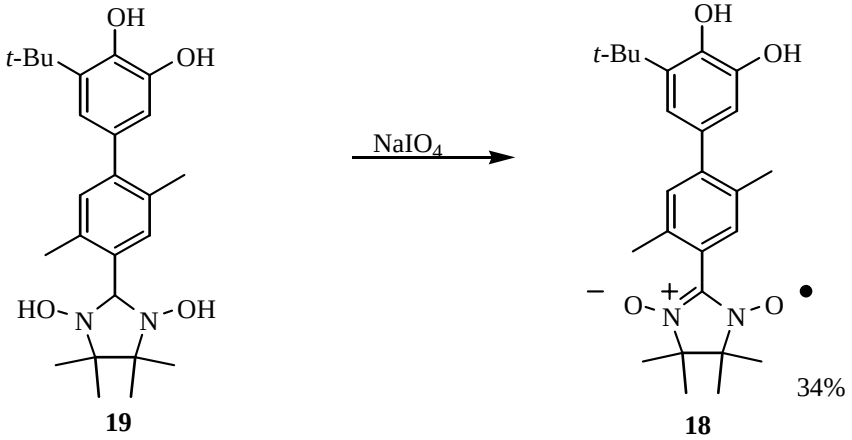


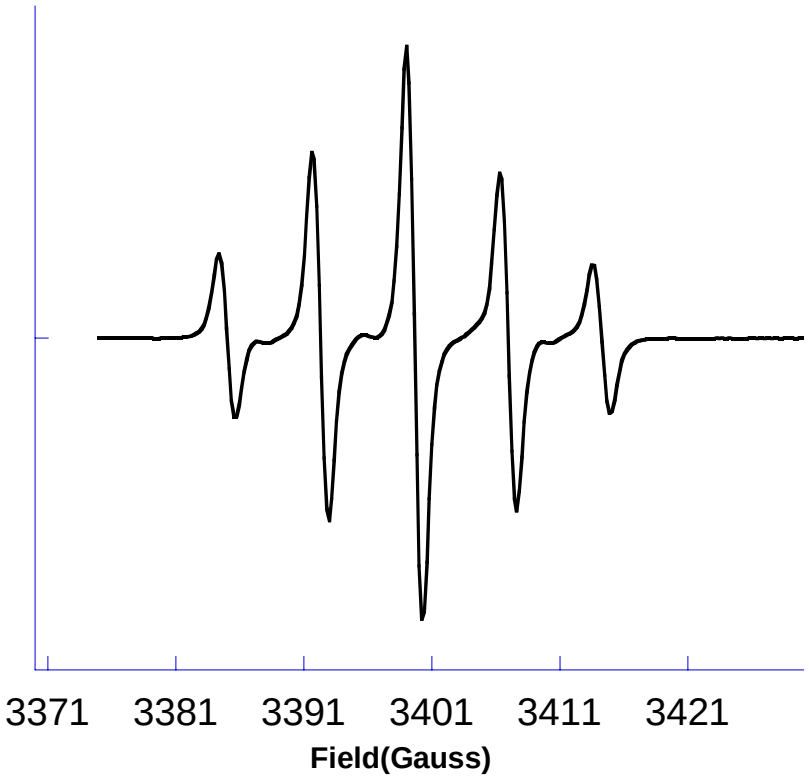
Figure 3. 18. Condensation of catechol aldehyde with bis(hydroxyamine).

The imidazolidine was oxidized with sodium periodate to give the nitronyl nitroxide monoradical (**18**). Fluid solution EPR of the Cat-*p*-xylene-NN (**18**) showed a five-line splitting pattern, which confirms the formation of the monoradical and is shown in **Graph 4.1**.



19 **18**

Figure 3.19 Oxidation of imidazolidine **19**



Graph 4.1.Experimental data from EPR spectra for NN-p-xylene-Cat.

The splitting of the EPR signal is defined as the hyperfine splitting and is caused by the interaction of ^{14}N nucleus with the unpaired electron. The number of lines and the intensities describe the number of nuclei along with their spins to which the electron is interacting. In the case of the **NN**, there are two equivalent ^{14}N nuclei with nuclear spin quantum number I=1. The number of possible orientations for the angular momentum is $2nI+1$, where n is the number of identical nuclei. In our case n = 2 giving five orientations for the $2nI+1$. The overall splitting pattern should therefore have a five line pattern with intensities in the ratio of approximately 1:2:3:2:1 ratio as shown in **Figure 3.20**.

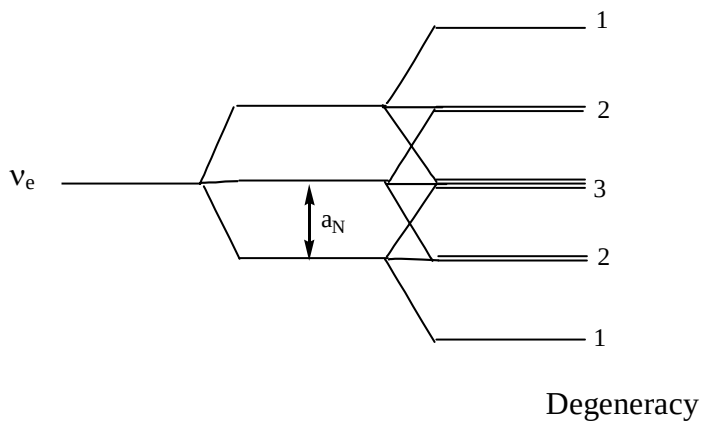


Figure 3.20. Hyperfine splitting of NN.

The EPR spectrum shown in **Graph 4.1**. matches the splitting pattern predicted by **Figure 3.20**. The IR spectrum showed a broad OH peak around 3300 cm^{-1}, confirming that the monoradical was the NN-*p*-xylene-catechol and not the NN- *p*-xylene-semiquinone monoradical. The IR spectrum also showed the traces of the NN- *p*-xylene-semiquinone monoradical.

3.5. Conclusion and Future work

We have synthesized different ligands for the purpose of studying structure related magnetic and electronic properties between different molecules. A better understanding on the electronic and magnetic properties of dinuclear valence tautomers was accomplished due to the synthesis of the *meta* and the *para* bipyridine ligands **3** and **9**.[23]

Shultz group studies the magnetic and electronic effects of changing the substituent group on the spin carried in homospin biradicals. We have synthesized a new compound 5-bromo-3-chlorocatechol (**12**) towards this study. The study of the torsion effect of the bridge on electronic and magnetic properties of nitronyl nitroxide-semiquinone bridged zinc complex has also been of interest. The *para*-xylene bridge nitronyl nitroxide-catechol ligand (**18**) was synthesized for this study. A new more

efficient procedure for making the bis(hydroxyamino) compound was also adopted. To fully complete the torsion effect of the bridge on nitronyl nitroxide-semiquinone bridged zinc complex study, the tetramethylphenyl bridge will have to be synthesized.

The Shultz group is also interested in studying how changing the polarity of the bridge affects the singlet-triplet gap of the nitronyl nitroxide-semiquinone bridged zinc complex. In order to achieve this the *para*-dimethoxy phenyl bridge nitronyl nitroxide-semiquinone zinc complex will have to be synthesized.

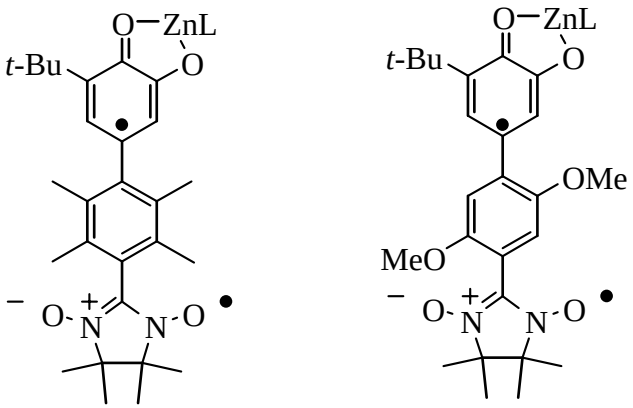


Figure 3.21. Proposed complexes**.**

The study of different SQ-bridge-NN donor acceptor biradicals has been a topic of interest in the Shultz group. One of the recurring problems is the oxidation of the catechol to the semiquinone as a bi-product during the oxidation of the imidazolidine. We are therefore working on a catechol-protecting group, whose deprotection conditions can be done in the presence of the nitronyl nitroxide monoradical. This means that the deprotection reaction conditions would have to be either basic or neutral. We are proposing the synthesis of the carbonate-protecting group because the conditions of its removal are neutral and mild, which should not affect the nitronyl nitroxide.[37]

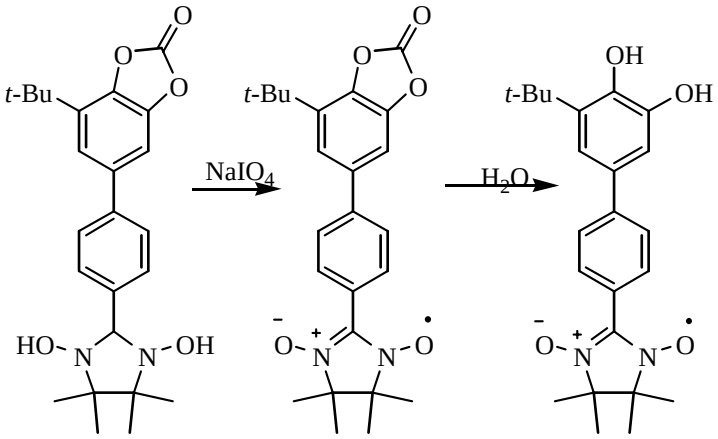


Figure 3.22 Future work on protecting group.

The synthesis would require the formation of 6-bromo-4-*tert*-butyl-benzo[1,3]dioxole (**27**). This would then be coupled to benzaldehyde to give the acetal-aldehyde (**28**). The carbonate would be formed from the acetal (**28**) by reacting it with phosphorous pentachloride and hydrolyzing the resulting product with water to give (**29**).

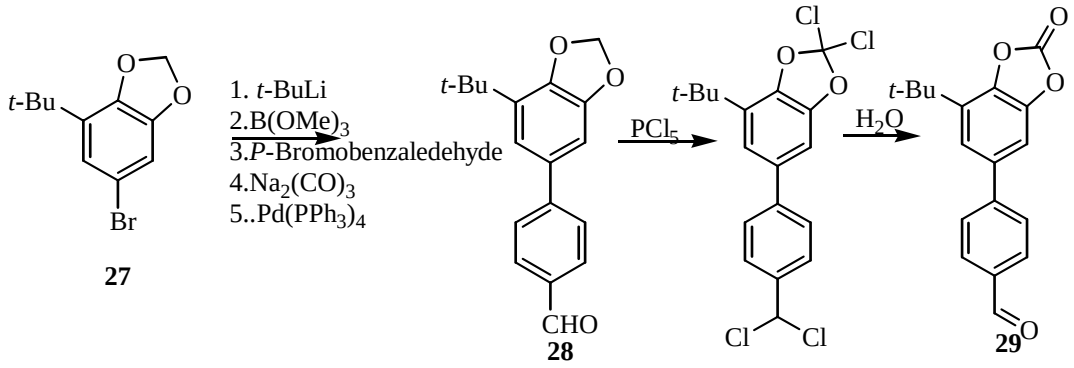


Figure 3.23 Future work on protecting group synthesis.

The carbonate protecting group also provides a solution to another problem in the synthesis of the olefin bridge SQ-Bridge-NN complexes. Once the MOM protected alcohol is deprotected to give the catechol aldehyde (**30**), tautomerisation seems to be taking place as shown in **Figure 3.24**, preventing any further synthesis involving this molecule. The carbonate-protected catechol does not have to be deprotected before the

condensation to form the imidazolidine and therefore allows the synthesis of the SQ-vinyl-NN biradical.

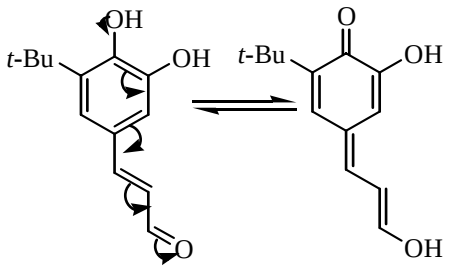


Figure 3.24 Proposed tautomerization of the vinyl bridge.

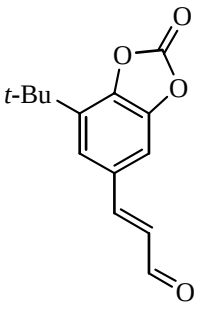
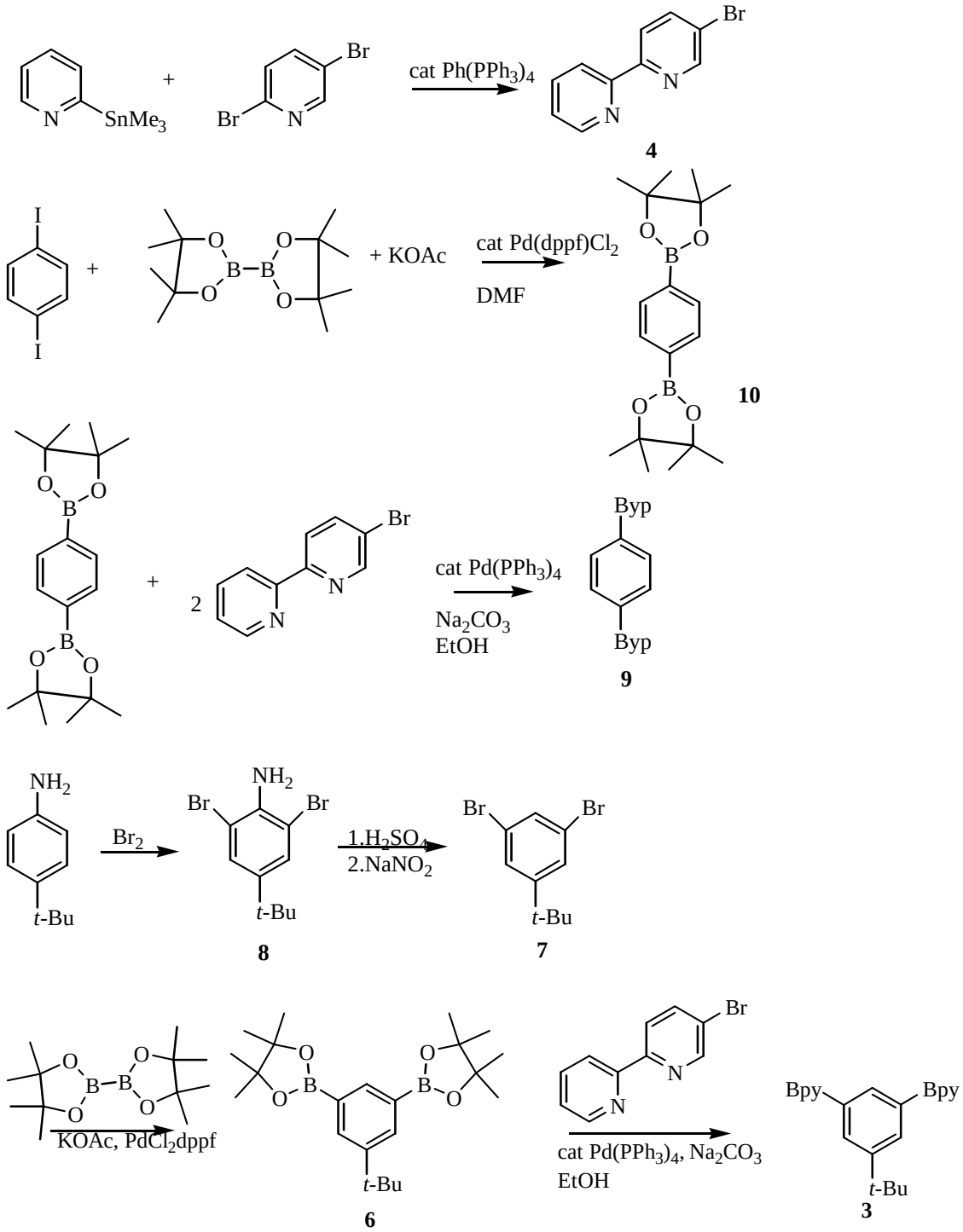


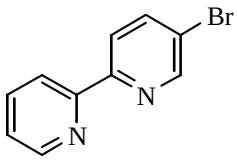
Figure 3.25 No tautomerization with the carbonate protecting group.

Experimental

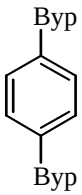
All reactions were done in oven dried glassware and under nitrogen unless otherwise stated. THF and toluene were distilled under argon from sodium/ benzophenone ketyl, and acetonitrile, methylene chloride, and methanol were distilled from CaH_2 under argon. *tert*-Butyllithium (1.5 M in pentane) was used as received from Acros Chemical. Other chemicals were purchased from Aldrich Chemical Co. Column and radial chromatography were carried out using silica gel (230-400 mesh for column). Fluid solution EPR spectra were simulated using WinSim.[38] NMR spectra were recorded at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR in CDC_{l3} solution if not otherwise specified. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Scheme 2 Synthesis of bis-bpy ligand



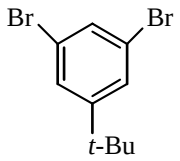


5-bromo-2,2'-bipyridine(4). (1.25 mmol) 2-bromopyrydine was placed in a schlenk flask in ether and cooled to -78°. *N*-BuLi (1.375 mmol) was added drop wise and the reaction stirred for 2hrs. Trimethyltin chloride ($SnMe_3Cl$) (1.375mmol) was added drop wise and reaction stirred overnight. Solvent and excess trimethyltin chloride was removed by bulb to bulb distillation under vacuum. *M*-xylene, 2,5-dibromopyridine (1.375 mmol), and 1mole % $Pd(PPh_3)_4$ was added under positive nitrogen pressure and the reaction refluxed at 120° overnight. The cooled solution was poured into sodium hydroxide (NaOH) in a separation funnel. Aqueous layer was back washed with toluene. Organic layers were combined and dried over sodium sulphate (Na_2SO_4), then solvent removed by bulb to bulb distillation. Product was purified by column chromatography to yield 28% of **4** as an off white solid. Physical properties were identical to those previously reported.[33]

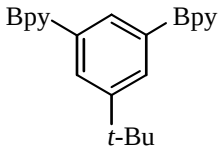


1,4-Bis(4'-2',2"-bipyridyl)benzene (9). *Para*-diiodobenzene (6.07mmol), *bis*-pinacolatodiboron (13.37mmol), dry potassium acetate (KOAc) (36.47mmol) and 40ml dimethylformamide (DMF)(dry) were placed in a Schlenk flask. The reaction was refluxed at 80° overnight under nitrogen. The resulting solution was worked up with dichloromethane (DCM) and water, passed through a celite-silica gel plug using 1:1

petroleum ether (PE): Ether (Et_2O) as a solvent. The resulting solid product was re-crystallized with methanol (MeOH) to yield 83% of **10** as a white solid. ^1H NMR ($CDCl_3$ 300 MHz) δ(ppm): 7.80 (s 4H), 1.35 (s 32H). **10** (0.847mmol), **4** (2.12mmol), Sodium carbonate (Na_2CO_3) (4.2mmol), Cat Palladium tetrakis $(Pd(PPh))_4$, 5ml ethanol (EtOH) and 10ml tetrahydrofuran (THF) were placed in a Schlenk flask. The reaction was refluxed at 70° for 2 days while being monitored by thin layer chromatography (TLC). Product was worked up with sodium chloride (NaCl) and DCM and resulting solid purified by re-crystallization with MeOH to yield **9** in 80% yield as a white solid. Physical properties were identical to those previously reported.[27]

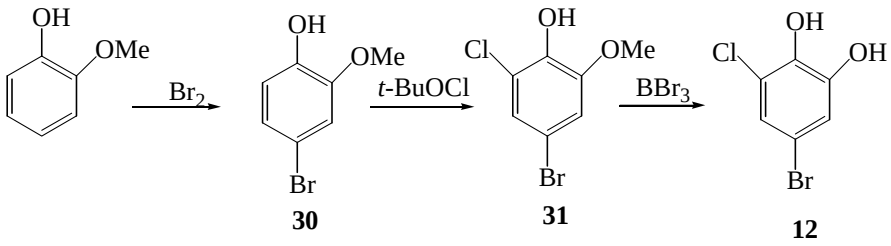


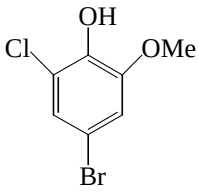
3,5-Dibrmo-*tert*-butylbenzene (7). A mixture of 1:1 DCM: MeOH and 4-*t*-butylanaline (63.42 mmol) were cooled to -15°. A solution of bromine in DCM was added drop wise and the reaction left to warm up to room temperature overnight. Solvent was taken off and a whitish brown solid was left. The solid was dissolved in ether and washed with water. The organic layer was removed *in vacuo* to yield **(8)** a brown oil in 95% yield. **8** (60.0mmol) was dissolved in 60ml EtOH and sulfuric acid in a dry 2-neck flask. Reaction was brought to a boil. $NaNO_2$ was added slowly and stirred till all the nitrogen came off (about 10 min). The round bottom flask was then placed in an ice bath for 20 min and then in the refrigerator overnight. The solvent was taken off and the product dissolved in Et_2O and washed with water. Product was then purified by column chromatography using 100% petroleum ether to yield a clear oil. Physical properties were identical to those previously reported.[39]



1,3-Bis(4'-2',2"-bipyridine)-5-*tert*-butylbenzene(3). 1e (17.0 mmol), bispinacolatodiboron (37.6mmol), dry KOAc (102.6mmol), 80ml DMF and Pd(dppf)Cl_2 (2.5mmol) were placed in a Schlenk flask and refluxed under nitrogen and stirred overnight. DMF was taken off by bulb-bulb distillation then product dissolved in DCM. The resulting solution was worked up with DCM and water, then passed through a celite-silica gel plug using 1:1 PE: Et2O as a solvent. The resulting solid product was re-crystallized with MeOH to yield 83% of **6** as a white solid. **6** (2.54mmol), **4** (6.55mmol), Na_2CO_3 (4.2mmol), Cat $Pd(PPh_3)_4$, 5ml EtOH and 10ml THF were placed in a schlenk flask. The reaction was refluxed at 70° for 2 days while being monitored by TLC. Product was worked up with NaCl and DCM and resulting solid purified by re-crystallization with MeOH to yield **3** in 80% yield as a white solid. Physical properties were identical to those previously reported.[18]

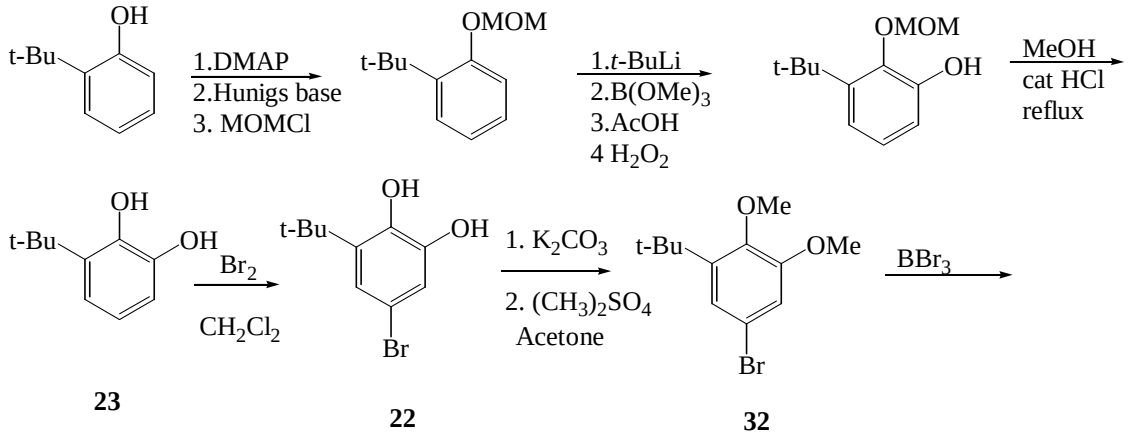
Scheme 3 Synthesis of 3-chloro-5-bromo-catechol



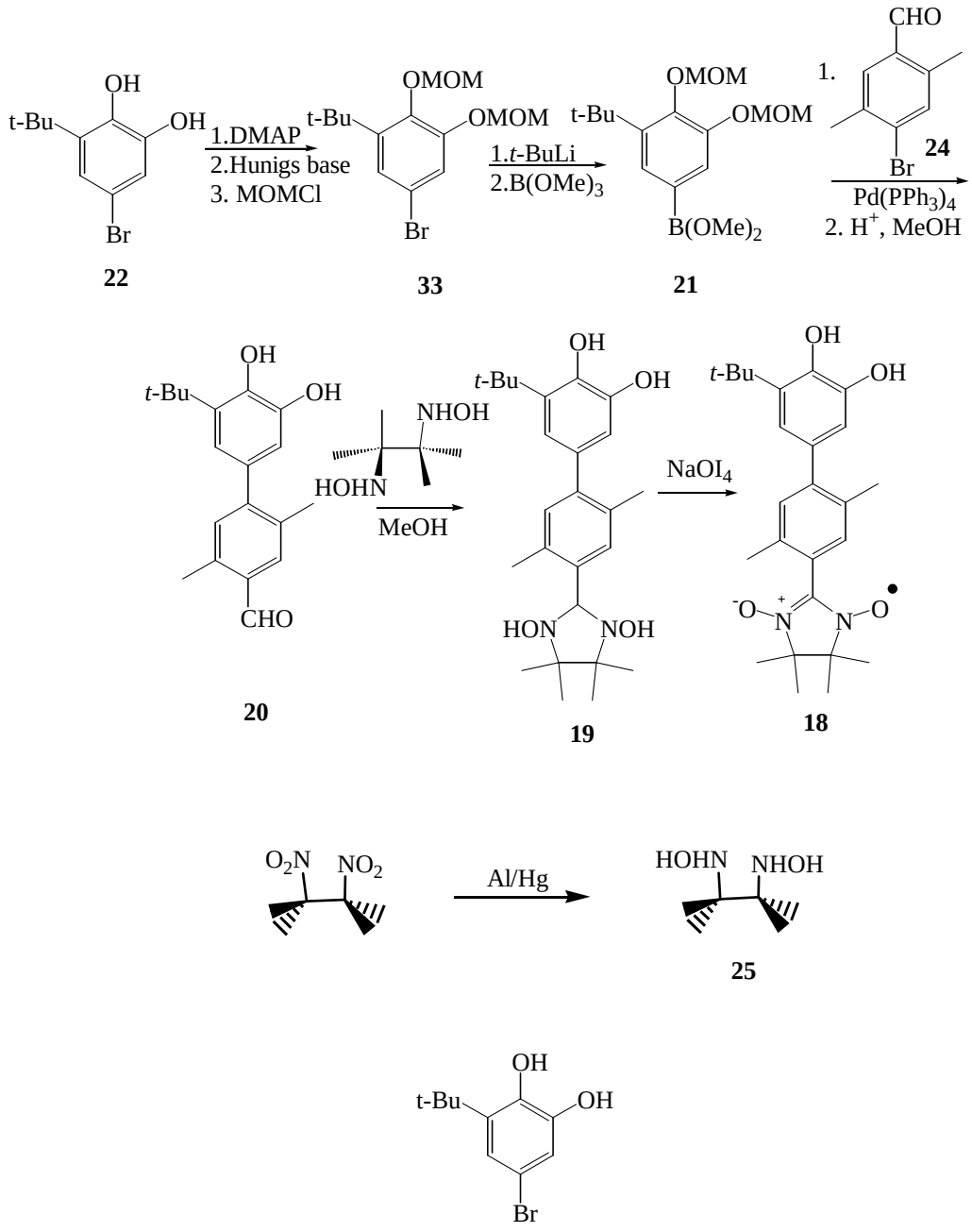


4-Bromo-2-chloro-6-methoxyphenol (31). Guaiacol (80.5mmol) and 150ml DCM were cooled to -15° and a dilute solution of bromine in DCM was added drop wise. The reaction was stirred overnight and then worked up with brine and DCM and the organic layer concentrated to give **30** 98% yield**.** (41.9mmol) 4-bromoguaiacol (**30)** was dissolved in ethyl ether and cooled to 0°. *Tert*-butylhypochlorite was added drop wise and the reaction stirred for an hour. The solvent was taken off and the product purified column chromatography using 3:1 petroleum ether: ether to yield **31**. Yield: 73%. H^1 NMR ($CDCl_3$): δ 7.12 (d, J= 2.1Hz, 1H), δ 6.90 (d, J= 2.1Hz, 1H), 5.77 (s, 1H), 3.90 (s, 3H). MS and elemental analysis data are yet to be determined.

Scheme 4.3. Synthesis of SQ-bridge-NN

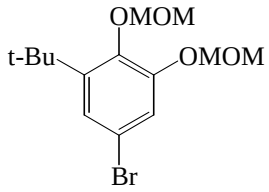


23 **22** **32**

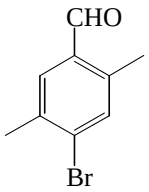


5-Bromo-3-*tert*-butyl-benzene-1,2-diol (22). To a dry 3 neck flask fitted with a condenser and dropper was added *tert*-butylphenol, Hunigs base, and dichloromethane. The reaction was cooled to 0° in ice-water bath under nitrogen. Dimethylaminopyridine was added slowly. The reaction was stirred for half and hour then chloromethoxymethane was added drop wise and the reaction stirred for a further hour at 0°, then refluxed

overnight. The reaction solution was washed with saturated sodium bicarbonate and the aqueous layer back extracted with dichloromethane. The organic layers were combined and washed with sodium chloride and the aqueous layer back extracted with dichloromethane. The organic layer was then concentrated and passed through a basified (triethylamine) silica gel plug using petroleum ether as a solvent. The resulting solution was then concentrated in vacuo to yield a pale yellow oil. 1-*tert*-Butyl-2-methoxymethoxy-benzene was then placed in an schlenk flask and dry pentane was added. The solution cooled to -78° under nitrogen. *Tert*-butyllithium was added drop wise and reaction stirred for an hour at -78° then at room temperature for 2hrs. Tetrahydrofuran was added to quench excess *tert*-butyllithium and reaction cooled to -78°. Trimethylborate was added drop wise and reaction stirred for an hour. The reaction was then brought up to 0° and acetic acid was added drop wise. Hydrogen peroxide was then added and reaction was then stirred overnight. Work up was done with water and petroleum ether to give 3-*tert*-Butyl-2-methoxymethoxy-phenol. This was deprotected by refluxing in methanol and catalytic amount of hydrochloric acid to yield 3-*tert*-Butyl-benzene-1,2-diol (**23**). The reaction was refluxed overnight. The catechol **(23)** was placed in a round bottom flask and dichloromethane added, a solution of bromine in dichloromethane was then added drop wise via a dropper and stirred overnight. Resulting solution was washed with sodium chloride and organic layer dried in anhydrous sodium sulphate and concentrated in vacuo. Physical properties were identical to those previously reported.[28]

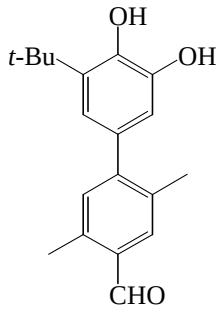


5-Bromo-1-*tert*-butyl-2,3-bis-methoxymethoxy-benzene (33). Bromo-*tert*-butyl catechol (**22**) was then placed in a dry 3-neck flask fitted with a condenser and dropper. Dimethylaminopyridine, and dichloromethane were added and the reaction cooled to 0° under nitrogen. NN-ethyl-diisopropylamine was slowly added. The reaction was stirred for half and hour then cloromethoxymethane was added drop wise and the reaction stirred for a further hour at 0°, then refluxed overnight. The reaction solution was washed with saturated sodium bicarbonate and the aqueous layer back extracted with dichloromethane. The organic layers were combined and washed with sodium chloride and the aqueous layer back extracted with dichloromethane. The organic layer was then concentrated and passed through a basified (triethylamine) silica gel plug using 3:1 petroleum ether: Ethyl ether as a solvent. The resulting solution was then concentrated *in vacuo*. Physical properties were identical to those previously reported.[28]



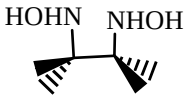
4-Bromo-2,5-dimethyl-benzaldehyde (24). 2,5-dibromo-para-xylene (12.4g, 46.9mmol) and tetrahydrofuran were placed in a dry schlenk flask and cooled to -78° under nitrogen. *Tert*-butyllithium (52.1ml, 93.9mmol) was added drop wise and reaction stirred for an hour. Dimethylformamide (3.8ml, 51.6 mmol) was added and reaction left

to warm to room temperature and stirred overnight. The reaction mixture was poured into 10% hydrogen chloride and shaken vigorously. The organic layer was separated, washed with water, dried in sodium sulphate then concentrated *in vacuo* to produce a pale yellow solid. The solid was recrystallized in hexanes to produce colorless needles. Yield: 7.8g (78%) ^{1}H NMR ($CDCl_3$): δ10.19 (s, 1H), 7.63 (s, 1H), 7.45 (s, 1H), 2.62 (s, 3H), 2.43 (s, 3H). MS and elemental analysis data are yet to be determined.

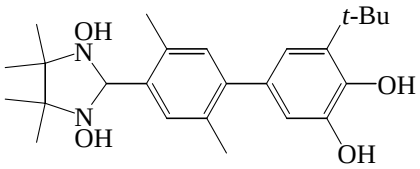


5'-*tert*-Butyl-3',4'-dihydroxy-2,5-dimethyl-biphenyl-4-carbaldehyde (20). 5-Bromo-1-*tert*-butyl-2,3-bis-methoxymethoxy-benzene (**33**) (2.3g, 6.90 mmol) and tetrahydrofuran where placed in a schlenk flask and cooled to -78°. *Tert*-butyllithium was added drop wise and reaction stirred for an hour at -78°. Trimethylborate was added drop wise and reaction stirred to room overnight. The aldehyde (**24**), sodium carbonate and palladium tetrakis were added under positive pressure and the reaction refluxed for 3 days. The resulting solution was washed with sodium chloride and organic layer concentrated. The product was purified by silica gel column chromatography using 5:1 petroleum ether: ethyl acetate and further purified my recrystallization from methanol to yield white solid. ^{1}H NMR (DMSO): δ10.26 (s, 1H), 7.68 (s, 1H), 7.13 (s, 1H), 7.00 (s, 1H), 6.94 (s, 1H), 5.26(s, 2H), 5.19 (s, 2H), 3.68 (s, 3H), 3.51 (s, 3H), 2.65 (s, 3H), 2.32 (s, 3H), 2.04 (s, 3H), 1.44 (s, 9H). The methoxymethyl groups were removed by refluxing

in methanol with a catalytic amount of hydrochloric acid. Work up is done by taking off methanol and re-dissolving product in dichloromethane and washing with water. Product is then purified by re-crystallizing in hexanes to yield a while solid. Yield (47%) ^{1}H NMR (DMSO-d_6) δ10.20 (s, 1H), 9.54 (s, 1H), 8.25 (s, 1H), 7.69 (s, 1H), 7.14 (s, 1H), 6.70 (s, 1H), 6.14 (s, 1H), 2.59 (s, 3H), 2.29 (s, 3H), 1.36 (s, 9H). MS and elemental analysis data are yet to be determined.

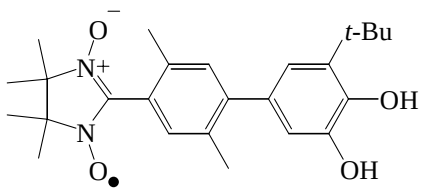


2,3-bis(hydroxylamino)-2,3-dimethylbutane (25). 5g of 2,3-dinitro-2,3-dimethylbutane was placed in a round bottom flask and tetrahydrofuran added to it. The reaction was cooled to 0° in an ice bath and 10ml water added. To 2.9g of aluminum foil was added 3% aqueous solution of mercury chloride. This was stirred for 2 min at room temperature then the solution discarded. The aluminum was then washed with water then tetrahydrofuran each 3 times. It was then added to the cooled dinitro solution and the mixture stirred for 20min. This was then passed through a celite plug. The resulting solution was concentrated and dried to give **25** in 76% yield. Physical properties were identical to those previously reported.[35]



2-(5'-*tert*-Butyl-3',4'-dihydroxy-2,5-dimethyl-biphenyl-4-yl)-4,4,5,5-tetramethyl-imidazolidine-1,3-diol (19). Methanol was placed in a round bottom flask and degassed for an hour. **20** and the bishydroxylamine were added and reaction purged for half an hour and stirred. The reaction was followed my thin layer chromatography to make sure all starting material was gone. Reaction rate depended on amount of reagents went for 2-

4 days. Solution was passed through a silica plug and the plug washed with ether. The resulting solution was concentrated to yield **19** as an off white solid. Yield: 52% ^{1}H NMR (DMSO-d_6) δ9.39 (s, 1H), 8.04 (s, 1H), 7.62 (s, 1H), 6.87 (s, 1H), 6.63 (s, 1H), 6.54 (s, 1H), 4.86 (s, 1H), 2.34 (s, 3H), 2.19 (s, 3H), 1.35 (s, 9H), 1.09 (s, 1H). MS and elemental analysis data are yet to be determined.



Catechol-*m*-xylene-nitronyl nitroxide (18). The imidazolidine **19** was placed in a round bottom flask, tetrahydrofuran added and cooled to 0°. A solution of sodium periodate in water was added and the reaction stirred in air for about 3 hours, while monitoring by thin layer chromatography. The reaction was then filtered and the product was crashed out of the solution using 98%hexanes dichloromethane and filtered to give a purple solid. Product was analyzed by EPR (Graph 4.1) and IR. Yield: 32 mg (34%), IR film ν (cm^{-1}): 3503, 3197, 2956, 2869, 2361, 1493, 1435, 1386, 1164, 1132, 1070, 1018, 954, 868, 834, 801, 738, 647, 542. EPR(298K): pentet, a_N = 7.3 G. MS and elemental analysis data are yet to be determined.

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