ABSTRACT

SCAMMON, DAVID WILLIAM. Correlating Exchange Coupling in Semiquinone-NitronylNitroxide Donor-Bridge-Acceptor Biradicals with Current Flow through Molecules. (Under the direction of Dr. David A. Shultz).

Herein several semiquinone-bridge-nitronylnitroxide (SQ-B-NN) biradicals compounds with naphthalene bridges of various substitution are discussed. After a general introduction to donor-bridge-acceptor (D-B-A) biradical compounds and the theories used to evaluate their magnetic coupling is presented in Chapter 1, the synthesis, characterization, and evaluation of naphthyl-spaced SQ-B-NN biradicals is presented in Chapter II. Appendices A-C also present new cases of SQ-B-NN biradicals targeted in hopes of further testing the effect bridge identity plays in D-B-A exchange coupling.

Chapter I focuses on the physical organic theory behind the evaluation of SQ-B-NN biradical magnetic and electronic coupling through the valence bond configuration interaction model and application of the superexchange model. The topics discussed to elucidate the basis of this evaluations will include the Pauli Exclusion Principle, Hund’s Rules, the Heisenberg Hamiltonian, and magnetic exchange coupling. In addition, this chapter will focus on the current rectification through molecules and the application of the SQ-B-NN biradical paradigm in evaluating conductance through molecules.

Chapter II will focus on the synthesis, characterization, and evaluation of five naphthyl bridged SQ-B-NN biradicals with different bridge substitution pattern (1,5-NAP, 2,6-NAP, 1,4-NAP, 1-NN-7-SQ-NAP, and 1-SQ-7-NN-NAP). This chapter will evaluate how the identity of the bridge frontier molecular orbitals impact the magnitude of exchange coupling in D-B-A biradicals. To this end, the electronic and magnetic data presented by the five paramagnetic SQ-naphthalene-NN biradicals will be compared with one another.

Appendix A will present the current state of a new project that is in many ways a continuation of the evaluation of bridge frontier molecular orbitals presented in Chapter II. SQ-B-NN biradical compounds with bithiophene bridges of different substitution are presented to help elucidate the role of the bridge in electronic coupling. The presently completed synthesis and future directions of the project will be discussed.
Finally, appendices B and C present antiferromagnetically coupled biradical compounds of relevance. Appendix B discusses the synthesis and evaluation of an antiferromagnetically coupled naphthyl-bridged SQ-B-NN used to illustrate the differences between ferromagnetically and antiferromagnetically coupled SQ-B-NN biradicals and Appendix C presents three new SQ-B-SQ biradical compounds. These three new compounds are clones of SQ-B-NN and NN-B-NN complexes already in existence and will be used to correlate exchange coupling in biradicals with identical bridges but different spin-bearing units. The current state of this project will be discussed in Appendix C.
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Correlating Exchange Coupling in Semiquinone-NitronylNitroxide Donor-Bridge-Acceptor Biradicals with Current Flow through Molecules.

by
David William Scammon

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APPROVED BY:

David A. Shultz
Committee Chair

Felix N. Castellano

Christopher B. Gorman

Vincent Lindsay
BIOGRAPHY

David W. Scammon was born in Atlanta, Georgia where he lived with his parents Steven and Lia Scammon for four years. While in Atlanta his sister Amanda was born and a year following the family moved to Ridgefield, CT where he spent the rest of his primary school years. David found a fondness for drawing and an entrepreneurial spirit, selling commissioned drawings of his classmate’s favorite cartoon characters for cookies at lunch in grade 5. Aside from drawing he found great joy in puzzles and games, falling in love with the strategy and prediction that the activities brought. In addition to joy in puzzles, David found a deep routed love of competition, using this to fuel a high school career as a four-year varsity swimmer and diver. While not originally interested in the sciences, the guidance of a high school physics teacher from grade 12, Wes Desantis, began to gradually steer David to pursue a career of science and research. Desantis, being the first teacher that really resonated with him, sparked within David a deep interest and love for the natural sciences, putting into perspective the genuine wonderment that science offered to those who sought to better understand the fundamental workings of the universe.

After graduating High School David pursued an undergraduate degree at Elon, University in North Carolina, moving back south after putting up with the cold northern weather for long enough. When first starting his undergraduate studies, David was uncertain where to put his focus. While not having much of a passion for any given subject at first, he gravitated heavily to math and the natural sciences. After finding chemistry, physics, and applied mathematics the most interesting, engaging, and rewarding – but pursuing multiple majors too demanding – David majored in Chemistry, with a focus in applied mathematics. He participated heavily in undergraduate research, working on projects in computational chemistry under Dr. Joel Karty as well as inorganic synthesis and catalysis under Dr. Karl Sienerth at Elon University, then further studying catalysis in at the University of Bristol in Bristol, UK under Professor. Duncan Wass during his summer REU program in 2014.

David grew fond of the challenges synthetic chemistry offered, and his desire to further that passion lead him to attend graduate school at North Carolina State University following his graduation from Elon University in 2015.
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I. General Introduction, Background and Theory

I.1 Introduction to Donor-Bridge-Acceptor Molecules

This work will focus on the theory, synthesis, characterization, and evaluation of Donor-Bridge-Acceptor (D-B-A) biradicals, more specifically how manipulation of the molecular architecture between a consistent set of donor and acceptor units affects the extent of donor-acceptor electronic coupling (\textit{vide infra}). D-B-A molecules are typically comprised of an electron donating group (the donor) and an electron withdrawing group (the acceptor) covalently attached to by a functional group referred to as the bridge. These molecules have drawn interest in the scientific community due to their various applications spread across a multitude of different systems and fields.\textsuperscript{58,71,72} A few examples are outlined below.

![Diagram of solar energy conversion scheme utilizing photoinduced electron transfer within a D-B-A molecule.](image)

**Figure I-1.** Solar energy conversion scheme utilizing photoinduced electron transfer within a D-B-A molecule.

D-B-A molecules are integral components of dye-sensitized solar cells. The donor moiety of a D-B-A molecule can be photoexcited to allow for an electron transfer to the acceptor unit. This process is bridge-mediated, as the electron must “pass through” the spacing unit between the donor and acceptor moieties, resulting in a charge-separated state. Once the molecule is in its charge-separated state, the $D^+\cdot B\cdot A^-$ zwitterion can participate in reduction-oxidation processes to return to its ground state (Fig. I-1). This light-driven redox process can be utilized to create functional solar energy conversion electrochemical cells.\textsuperscript{71,72}

D-B-A systems also have applications in the emerging field of molecular electronics,\textsuperscript{1} specifically $\pi$-stacked tertiary arylurea D-B-As have been shown to display molecular wire\textsuperscript{2} behavior while other D-B-A molecules have been shown to display molecular diode activity.\textsuperscript{3,4} These and other D-B-A systems are effective because the donor and acceptor units in the D-B-A
molecules are electronically coupled to one another via the bridge. This coupling can be evaluated and correlated to specific molecular features through determination of the electronic coupling matrix element between the donor (D) and acceptor (A), $H_{DA}$.\textsuperscript{19}

I.2 The Electronic Coupling Matrix Element, $H_{DA}$

I.2.1 Introduction to $H_{DA}$

Electron Transfer (ET) is a process that is found in a striking number of relevant biological systems, as well as the primary process within solar cells. Furthermore, ET is a central focus in molecular electronics as it is the key step that propagates the electronic signal between two molecular “diodes”.\textsuperscript{5} When it comes to quantitatively observing and evaluating ET in a system the electronic coupling matrix element, $H_{DA}$, is a key parameter. In fact, the magnitude of $H_{DA}$ helps control the rate of the transfer. Unfortunately, $H_{DA}$ cannot be measured directly,\textsuperscript{19} although several methods can be used to evaluate it. One such approach involves magnetic field dependent ET kinetics of photoactive D-B-A molecules that undergo a photoinduced ET (PET). The D-B-A system is first photoexcited to generate a D*-B-A excited state which then undergoes intramolecular ET to yield the zwitterionic D+-B-A` charge-separated state which then energetically decays back to the ground D-B-A state (Fig. I-2).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_I-2.png}
\caption{Jablonski diagram of a generic D-B-A moiety that undergoes a photoinduced electron transfer event. $k_{CS}$ is the charge separation rate constant, $k_{ISC}$ is the intersystem crossing rate constant between singlet and triplet states, and $k_{CR}$ is the charge recombination rate constant.}
\end{figure}
Figure I-3. Diagram of a model MMM experiment. A thiol functionalized bridge is attached to a gold substrate and a gold tipped STM probe is brought close to the substrate allowing for an electronic current to be passed from probe to substrate. The probe tip is then varied in distance from the substrate, breaking the connection between the two and allowing for measurement of average conductance through the bridging unit.

Through ultrafast transient absorption spectroscopy, the rate of charge separation can be determined. Then, through the paired application of a tunable magnetic field with ultrafast transient absorption spectroscopy the magnetically-variable triplet yields can be determined. Application of an Anderson superexchange model then allows for analysis of $2J$ as a function of charge separation/recombination rates.\(^6\)

The magnitude of $H_{DA}$ can also be evaluated by analysis of Metal-Bridge-Metal (M-B-M) conductance experiments, where a molecular spacer acts as the bridge (Fig. I-3). Conductance ($g$) measurements have been used to study a series of molecular electronic features, and the conductance is defined as the ease with which current flows, and is the inverse of resistance ($g = 1/R$). Conductance measurements have been used to model molecular wire behavior\(^{24-26}\) as well as to model bridge contributions to electronic coupling.\(^{45}\) M-B-M devices are also very commonly used basis for the theoretical evaluation of bridge fragments to electronic coupling.\(^{21,22,27,28,29-38}\) The most typical M-B-M conductance experiments begin by layering a thiol or amine functionalized compound to a gold substrate. Then, a gold-plated probe is passed over the functionalized substrate. When the gold-plated probe is passed close enough to the substrate, the organic fragment acts as a bridging unit between the probe and substrate, allowing
for the conductance of the system to be measured when an electronic bias is applied across the electrodes. Then, to ensure that the molecular fragment is conducting the current and affecting the measurement, the probe is moved slowly away from the substrate, stretching the bridge until it ultimately breaks the connection between probe and substrate. This break is characterized by a sharp decrease in conductance and is where the “break junction” conductance experiment derives its name. The exact orientation of the bridging unit is impossible to determine in a M-B-M experiment, acknowledging this, the break-junction experiment is repeated thousands of times to generate an average conductance value for the functionalized bridge. This average conductance value is related to $H_{DA}$ through Green’s Function (a mathematical tool used to evaluate complex differential equations.), allowing for the evaluation of electronic coupling in M-B-M experiments.39-42

$H_{DA}$ can be evaluated through analysis of the exchange coupling ($J$) between two unpaired electrons in ground state D-B-A biradical molecules. Our approach uses this method of evaluation. Ground-state D-B-A biradical molecules can be considered as ground-state analogues of the charge-separated excited state generated in the PET process, as well as model systems for single molecule-mediated electron transport between biased electrodes.7-10 This approach provides a handful of unique advantages for evaluating $H_{DA}$. First and foremost, the electronic coupling between the unpaired electrons in a ground state D-B-A biradical is far stronger than that observed in the PET experiment of D-B-A molecules by orders of magnitude, allowing for more precise evaluations of $H_{DA}$. Because each of the Shultz group biradicals contain consistent semiquinone (SQ) donor and nitronylnitroxide (NN) acceptor subunits, the values of $H_{DA}$ and $J$ for SQ-bridge-NN (SQ-B-NN) biradicals with different bridging units can be directly compared to one another. This standardization of donor and acceptor units allows for the study of exclusively the bridge’s role in electronic coupling, limited only by synthetic constraints. Another advantage unique to the Shultz group biradical architecture is that the SQ-B-NN biradicals are air stable crystals, as opposed to transient excited states like in the PET experiments or molecular devices as in the M-B-M experiments. This allows for SQ-B-NN crystals to be grown and their exact structure and conformation to be determined through X-ray crystallography. With this information available, detailed structural and spectroscopic features, such as π-system torsion angles8 and exact D-A distance,9 can be related in a straightforward manner to the exchange coupling parameter, $J$ (and therefore $H_{DA}$, vide infra). These advantages
to the study of ground state biradical D-B-A molecules give us a unique vantage point in the study of structure-property relationships for electronic coupling, allowing us to probe the unique effects of each unique bridging unit. Finally, ET rate constants, conductance and $J$ are all proportional to $H_{DA}^2$, not $H_{DA}$. While $H_{DA}^2$ has no sign, $J$ does, and the sign of $J$ can provide clues to the nature of the superexchange pathway.

1.2.2 Relating $J$ and $g$ through $H_{DA}$

Since $J$, $k_{et}$, and $g$ are all proportional to $H_{DA}^2$, it has long been theorized that the three measurements of electronic coupling are also related to one another, likely through $H_{DA}$. In 2001 Abraham Nitzan theorized that the rate of electron transfer measured from an electronically active D-B-A system would be related to the conductance observed through the same bridge in a M-B-M break junction system. He predicted that these two quantities would be related through the term $H_{DA}$ by the following Eqs.:

$$k_{et} = \frac{2\pi}{\hbar} |H_{DA}|^2 F$$

$$g = \frac{e^2}{\pi \hbar} |H_{DA}|^2 \Gamma_D \Gamma_A$$

$$g \approx \frac{8e^2}{\pi^2 \Gamma_D \Gamma_A F} k_{et}$$

In Eq. 1.1, the magnitude of the electron transfer rate constant ($k_{et}$) is primarily determined by $H_{DA}$ and the Franck-Condon weighted density of nuclear states ($F$). The magnitude of $g$ is also determined by $H_{DA}$ and influenced by the energy widths of electrode orbitals due to bonding with the donor and acceptor ($\Gamma_D, \Gamma_A$) (Eq. 1.2). Through the shared term $H_{DA}$, the two parameters $g$ and $k_{et}$ are related to one another in Eq. 1.3. However, Eq. 1.3 is only proposed to hold true under strict conditions. First, the two systems must experience uniform energy shifts. The effect of binding the bridge to the donor/acceptor moieties must equal that of the binding to the two electrodes. The effect of the donor/acceptor binding to the bridge must also result in the same changes to the electronic structure of the bridge imposed by the metal-bridge interactions. This relationship can also only hold true when the M-B-M system is under zero bias and super exchange must be the dominant pathway for electronic coupling.
Nitzan’s proposed relationship between $k_{et}$ and $g$ was tested experimentally by the Ratner and Wasielewski groups in 2010. In their work the electron transfer rate constants and calculated transmission for four separate bridged systems were measured. The transport calculations were also used to study the conductance through each bridge, as when the applied bias of the system approached zero the differential conductance can be approximated as the transmission at the common Fermi energy of the two electrodes. This approach of studying conductance is known as the Landauer approach. The study showed that the identity of the bridge directly impacts the electronic coupling of a system. It was shown that the conjugated bridge facilitated electron transfer much better than the cross conjugated bridge, showing a 30-fold difference in the rate of charge transfer. A torsional dependence was also observed for the π-system bridges, suggesting that the primary pathway for electron transfer is through superexchange. It was also noted that the σ-bridges offered much weaker coupling than the π-bridged systems, also indicative of a superexchange primary pathway. The calculated transmission determined for the four bridges reflected the patterns observed in the rate of charge separation and recombination, however any quantitative agreement between the two measurements was poor.

This lack of agreement was addressed in a 2013 paper written by David Waldeck and David Beratan that compared the rate constant for the charge transfer event and the conductance through peptide nucleic acid (PNA) oligomers as well as a series of alkane bridges. In both experiments it was shown that the PNA duplexes presented the slowest charge transfer rate as well as the highest conductance. An exponential distance dependence was also observed over a limited bridge length, indicative of a superexchange pathway. Importantly, a correlation between $g$ and $k_{et}$ was found between complexes of the same bridging chemistry through a power law relation. A loss of correlation was observed when comparing the whole data, showing no overall distance dependence, rather a distance dependence only within each bridge paradigm. This was attributed to differences of energy barrier shifts, charge-mediation characteristics, and dephasing between different bridge chemistries.

The power law relation between $k_{et}$ and $g$ was reaffirmed by Waldeck and Beratan in a 2014 paper which outlined theoretical framework to compute $k_{et}$ and molecular conductances. Analysis indicates several influencing factors that would lead to a non-linear rate-conductance
relationship explained by a power law trend.\textsuperscript{81} The population relaxation and dephasing rates are expected to differ when the bridge is connected to a donor/acceptor as opposed to metal electrodes. Molecular bridges also experience a stabilization of state when connected to an electrode in response to charge injection, resulting in modified charge transfer barriers. Finally, donor electronic states differ from the work function of a metal electrode, also resulting in different CT barriers.

Recent work by Kirk, et al. has shown a power law relationship between $J$ (in SQ-B-NN biradicals complexes) and calculated $g$ (in M-S-B-S-M constructs). The exponent of the power law is the ratio of the distance damping factors for exchange and conductance ($b_g/b_J$).\textsuperscript{82} Strong bridge-bridge coupling ($H_{BB}$, vide infra) in SQ-B-NN biradicals complexes compared to M-S-B-S-M devices results in $b_g/b_J > 1$. 
I.3 Exchange Coupling in Biradicals and the Superexchange Model

I.3.1 Background

In the 1960s a physics professor at the California Institute of Technology, Dr. Harden M. McConnell, published a landmark paper describing “electronic coupling” in a molecule and referred to it as $H_{xy}$, where “x” and “y” were the two portions of the molecule that were coupled.\(^{11}\) (1.4)

$$H_{DA} = \frac{H_{DB}H_{BA}}{\Delta \epsilon_{DB}} \left( \frac{H_{BB}}{\Delta \epsilon_{DB}} \right)^{N-1}$$

Here, $H_{xy}$ is the electronic coupling between units “x” and “y” (D = donor, B = bridge, A = acceptor), $\Delta \epsilon_{DB}$ is the difference in energy between donor and bridge, and N is the number of bridging units. The adoption of McConnell’s electronic coupling model is universal, and his paper has been cited thousands of times. The utility of McConnell’s model is highlighted in the work of the Wasielewski group, who used this theory to evaluate the degree of electronic coupling displayed in D-B-A molecules with photo-accessible charge separated transient excited states.\(^{6}\) The approach makes use of a theory developed by physicist Philip Warren Anderson. McConnell’s expression lacked measurable variables but portions of Anderson’s “superexchange” model related $H_{DA}$ to measurable magnetic and spectroscopic molecular features through magnetic exchange coupling, $J$ (1.5)\(^{12}\)

$$2J = \frac{H_{DA}}{\Delta \epsilon}$$

the interaction between unpaired electrons in inorganic solids, but the results also apply to molecules and charge-separated excited states. The exchange parameter, $J$, can be determined as a fit parameter in magnetic susceptibility experiments, and sometimes from variable-temperature electronic absorption spectroscopy. With the help of these theories, Wasielewski could determine $2J$ for his complexes by measuring the triplet yield of his complex at various magnetic fields strengths.\(^{6}\) Exchange coupling of Shultz group biradicals are evaluated in a similar way as they can be treated using a superexchange model.
1.3.2 Definition of the Exchange Coupling Parameter $J$

When two spins are exchange-coupled, the spins can align in one of the quantum mechanically allowed orientations: parallel or antiparallel. The spin parallel configuration corresponds to a triplet state ($S=1$) while the spin antiparallel configuration corresponds to a singlet state ($S=0$). The mathematical description of this coupling is illustrated in the Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian (1.6).

$$\hat{H}_{ab} = -2J_{ab}\hat{S}_a\hat{S}_b$$

(1.6)

$\hat{S}_a$ and $\hat{S}_b$ represent the spin angular momentum operators and $J_{ab}$ is the isotropic exchange coupling parameter between unpaired electrons $a$ and $b$. The total spin operator is the sum of the two individual spin operators and is written: $\hat{S}_{\text{tot}} = \hat{S}_a + \hat{S}_b$. With some manipulation, $\hat{S}_a$ and $\hat{S}_b$ can be replaced with $\hat{S}^2_{\text{tot}}$ and the individual $\hat{S}^2_a$ and $\hat{S}^2_b$ operators, allowing for a straightforward evaluation of the spin state energies in terms of $J_{ab}$.

$$\hat{S}^2_{\text{tot}} = (\hat{S}_a + \hat{S}_b)^2 = \hat{S}^2_a + \hat{S}^2_b + 2\hat{S}_a\hat{S}_b$$

(1.7)

$$\hat{S}_a\hat{S}_b = \frac{\hat{S}^2_{\text{tot}} - \hat{S}^2_a - \hat{S}^2_b}{2}$$

(1.8)

$$\hat{H}_{ab} = -2J_{ab}\hat{S}_a\hat{S}_b = -J_{ab}(\hat{S}^2_{\text{tot}} - \hat{S}^2_a - \hat{S}^2_b)$$

(1.9)

Since the eigenvalue of the spin operator $\hat{S}^2$ is $S(S+1)$, the energies of both the triplet and singlet states can be solved using Eq. (1.10).

$$E = -J_{ab}[S_{\text{tot}}(S_{\text{tot}} + 1) - S_a(S_a + 1) - S_b(S_b + 1)]$$

(1.10)

The energy of the $S_{\text{tot}}=0$ singlet state ($E_s$) can be described as:

$$E_s = -J_{ab}\left[0(0 + 1) - \frac{1}{2}\left(\frac{1}{2} + 1\right) - \frac{1}{2}\left(\frac{1}{2} + 1\right)\right] = -J_{ab}\left(0 - \frac{3}{4} - \frac{3}{4}\right) = \frac{3}{2}J_{ab}$$

(1.11)

While the energy of the $S_{\text{tot}}=1$ triplet state ($E_t$) is:

$$E_t = -J_{ab}\left[1(1 + 1) - \frac{1}{2}\left(\frac{1}{2} + 1\right) - \frac{1}{2}\left(\frac{1}{2} + 1\right)\right] = -J_{ab}\left(2 - \frac{3}{4} - \frac{3}{4}\right) = -\frac{1}{2}J_{ab}$$

(1.12)
The difference in energy between the singlet and triplet states gives:

$$\Delta E_{st} = E_s - E_t = \frac{3}{2} J_{ab} - \left( -\frac{1}{2} J_{ab} \right) = 2J_{ab}$$  \hspace{1cm} (1.13)

As shown in Eqs. (1.11) and (1.12), exchange coupling favors parallel spins energetically by a magnitude of $2J_{ab}$, and therefore, if $J > 0$, the two spins are ferromagnetically coupled. A negative $J$-value indicates that the two electrons are antiferromagnetically coupled. These two scenarios are illustrated in Fig. I-4. In addition, $J$ also illustrates the degree of coupling with its magnitude. A large magnitude of $J$ suggests a strong degree of exchange coupling between the two electrons.

Figure I-4. Model energy level diagram displaying the difference in $2J$ for a two-electron system with a triplet ground state (left) and a singlet ground state (right).
I.3.3 Potential and Kinetic Exchange

The parameter, $J$ is a sum of two exchange integrals: potential exchange, also known as ferromagnetic exchange, and kinetic exchange, also known as antiferromagnetic exchange: $J = J_F + J_{AF}$.\(^\text{13}\) Eq. (1.13) shows that if ferromagnetic exchange is the dominating term in the exchange coupled system $J$ will have a positive value, and if the antiferromagnetic exchange dominates, $J$ will have a negative value. The easiest way to predict the sign of $J$, and the lowest-energy spin state of the D-B-A molecule where D, B and A have conjugated π-systems, is through application of Hund’s first rule to simple Hückel Molecular Orbitals (HMO).\(^\text{14}\) Hund’s rule states that electron spin is maximized for the lowest energy degenerate electronic configuration.\(^\text{15}\) Electrons belong to a class of subatomic particles known as fermions, which possess half-integral spins and are completely indistinguishable from one another. Both Hund’s rule and the Pauli Exclusion principle are derived from this indistinguishability.

Consider a system possessing two atomic orbitals (AOs) denoted A and B, and each of these orbitals contains an electron denoted 1 and 2. Both symmetric (1.14) and antisymmetric (1.15) spatial wavefunctions guarantee indistinguishability of the two fermions, provided that they are paired with antisymmetric and symmetric spin wavefunctions, respectively.

$$\psi_{\text{sym}} = \frac{1}{\sqrt{2}} [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \quad (1.14)$$

$$\psi_{\text{anti}} = \frac{1}{\sqrt{2}} [\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)] \quad (1.15)$$

Using the Hamiltonian operator (1.16) the energies of the states corresponding to each spatial wavefunctions can be determined; as shown in Eqs. (1.17) and (1.18), respectively.

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1.16)$$

$$E_{\text{sym}} = \frac{\langle [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] | \hat{H} | [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \rangle}{\langle [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] | [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \rangle} \quad (1.17)$$

$$E_{\text{anti}} = \frac{\langle [\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)] | \hat{H} | [\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)] \rangle}{\langle [\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)] | [\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)] \rangle} \quad (1.18)$$

A coulomb integral ($j$) can be written for each of these energies (1.19), as well as an exchange integral ($k$) between the two energies (1.20).
\[ j = \langle \Phi_A^2(1) | \hat{H} | \Phi_B^2(2) \rangle \quad \text{and} \quad j = \langle \Phi_B^2(1) | \hat{H} | \Phi_A^2(2) \rangle \] (1.19)

\[ k = 2 \langle \Phi_A(1) \Phi_B | \hat{H} | \Phi_A(2) \Phi_B(2) \rangle \] (1.20)

Substituting Eqs. (1.19) and (1.20) to Eqs. (1.17) and (1.18), the energies of the singlet (symmetric) and triplet (antisymmetric) spin states can be defined in terms of \( j \) and \( k \) (1.21).

\[ E_s = \left[ \frac{j + k}{1+0} \right] = j + k \quad \text{and} \quad E_t = \left[ \frac{j - k}{1+0} \right] = j - k \] (1.21)

These energies can be represented visually (Fig. I-5). The coulomb integral between the two singularly occupied AOs arises from the electron-electron repulsion between electrons 1 and 2 when they are isolated in their respective AOs (green and blue). The exchange integral results from the repulsion the electrons 1 and 2 experience when they occupy the overlap region (yellow) between the two AOs.

**Figure I-5.** Visual representation of two orthogonal p-orbitals, \( \Phi_A \) and \( \Phi_B \), where the yellow region is the overlap between the two orbitals. The left figure represents a diagram of Hund’s first rule, while the right figure represents the Pauli Exclusion Principle.

The Pauli Exclusion Principle generally states that two or more fermions cannot occupy the same quantum state. Since electrons are fermions they must obey this principle, therefore two electrons of identical spin are forbidden from occupying the same orbital. Due to this
principle, the triplet spin orientation is forbidden to exist within the overlap region. This conclusion is observed mathematically in Eq. (1.21); the exchange integral is subtracted from the coulomb integral in the triplet but added in the singlet. This decreased electron-electron repulsion is what causes the triplet to be lower in energy in a system displaying solely potential exchange. By simply taking the difference between the two arguments presented in (1.21) the energy difference between the singlet and triplet states can be found for a system that displays purely ferromagnetic interactions (1.22).

\[ E_s - E_t = (j + k) - (j - k) = 2k \]  

(1.22)

Since this energy difference of $2k$ is purely ferromagnetic in nature it can be described as the ferromagnetic portion ($J_{FM}$) of the total exchange integral, $J$. Another important consequence is that should a large overlap density occur (yellow area, Fig. I-5) between two orthogonal orbitals, the electrons will prefer to align parallel to avoid the large electron-electron repulsion within the overlap region. This is observed with interactions between AOs, as well as MOs.\textsuperscript{16,17}

In a biradical molecule, each unpaired electron occupies a separate MO, and the two singularly occupied molecular orbitals (SOMOs) must experience an overlap in orbital density for the two to be electronically coupled. As previously stated, the simple model of Hund’s rule (Fig. I-5) can be extended to MOs.\textsuperscript{17} The overlap between the two SOMOs is determined through comparison of the orbital coefficients of the fragment orbitals determined through simple Hückel MO theory. Should the fragment orbitals share a non-zero overlap kinetic exchange can occur. While the triplet state is stabilized by the exchange integral in potential exchange, the singlet state is stabilized through kinetic exchange. Kinetic exchange can be well illustrated by two SOMOs with a non-zero overlap density, hence allowed electron transfer. In the triplet configuration, the electrons are forbidden from interacting due to the Pauli Exclusion Principle; they have the same spin quantum number (Fig. I-6).
Figure I-6. Diagram of a supposed system with two unpaired electrons in separate orbitals that share a non-zero overlap density. The triplet case will not gain energetic stability from electron delocalization due to the parallel alignment of the two separate spins while the singlet will because the antiparallel nature of the singlet orientation allows for electron transfer.

However, the electrons in the singlet state are already aligned antiparallel and can partake in electron delocalization, lowering the energy of the singlet state proportional to the electronic coupling ($H_{DA}$). Based on previous work,\textsuperscript{13,19} it has been shown that the antiferromagnetic contribution ($J_{AF}$) to exchange parameter ($J$) includes not only an $H_{DA}$ term but also must consider the mean charge transfer energy ($U$) between the open and closed shell states (that result from electron transfer between singly-occupied AOs). Thus, the exchange parameter is a sum of the ferromagnetic and antiferromagnetic terms (1.23).

$$J = J_{FM} + J_{AF} = 2k_{AB} - \frac{2H_{AB}^2}{U}$$  \hspace{1cm} (1.23)

Here $J_{FM}$ is the purely ferromagnetic contribution to exchange coupling, $J_{AF}$ is the contribution to exchange coupling that is purely antiferromagnetic in nature, $k_{AB}$ is an electron exchange integral between two SOMOs, $U$ is the mean charge transfer energy between the open- and closed-shell states of the molecule, and $H_{AB}$ is the electronic coupling matrix element describing the extent of interaction between electrons in SOMOs $a$ and $b$. Due to the reliance upon orbital overlap present in kinetic exchange, should the two occupied orbital fragments be orthogonal to one another the overlap density will be nonexistent, antiferromagnetic exchange will not occur, and as such, $J_{AF} = 0$. Recall that ferromagnetic exchange is not entirely dependent on orbital overlap density, as interactions within the overlap region are destabilizing factors due to the Pauli exclusion principle. Because of this, even if the fragment MOs are orthogonal to one another $J_{AF}$ will maintain a nonzero value, and any exchange will be purely ferromagnetic in nature. Though this explanation is not optimal to evaluate $H_{DA}$ based on spectroscopic
parameters, it is noteworthy that a reasonable understanding of D-B-A biradical superexchange interactions can be gathered from simple HMO theory, Hund’s rule, and the Pauli exclusion principle in the form of Eq. (1.23). A more detailed model that takes advantage of spectroscopic parameters will be presented later in this document.

I.3.4 Measuring the Exchange Coupling Parameter, $J$

Exchange coupling in biradical complexes can be measured as a fit parameter in magnetometry experiments, which utilize our Superconducting Quantum Interference Device (SQUID) magnetometer. Exchange coupling can also be measured by Electron Paramagnetic Resonance (EPR) spectroscopy. A plot of magnetic susceptibility ($\chi$) as a function of temperature can be used to determine $J$ via Van Vleck’s Eq. (1.24):

$$\chi = \frac{N\sum_n E_n^{(1)} e^{-E_n^{(0)} / k_BT}}{k_BT \sum_n e^{-E_n^{(0)} / k_BT}}$$

Here $N$ is Avogadro’s Number, $k_B$ is the Boltzmann constant, $T$ is temperature, and $E_n$ is the energy of a given state as determined by the HDVV Hamiltonian (Eq. 1.6). Biradicals are two-spin systems so, as stated previously, only the triplet ($S=1$) and singlet ($S=0$) states are possible. After some unit conversion Eqs. (1.24) and (1.7) can be combined into (1.25):

$$\chi = \frac{NG^2\beta^2 \sum_S S(S+1)(2S+1)e^{E_S / k_BT} e^{-E_S / k_BT}}{\sum_S (2S+1)e^{E_S / k_BT}}$$

(1.25)

where $\beta$ is the Bohr magneton, $S$ is the total spin of a given state, $E_S$ is the energy of a given state, and $G$ is the g-factor ($g = \sim 2$ for organic radicals). For a two electrons system, $S=1$ and $S=0$ can be substituted into Eq. (1.25).

$$\chi = \frac{NG^2\beta^2 \sum_S (2S+1)(2S+1)e^{E_S / k_BT} e^{-E_S / k_BT}}{(20+1)e^{E_{S=0} / k_BT} + (2S+1)e^{-E_S / k_BT}}$$

(1.26)

$$\chi = \frac{NG^2\beta^2}{2k_BT} \left( \frac{e^{E_{S=0} / k_BT}}{1e^{-E_{S=0} / k_BT}} \right)$$

(1.27)
Eq. (1.27) can then be multiplied by the exp(E_s/k_B T) to obtain Eq. (1.28).

\[
\chi = \frac{NG^2g^2}{2k_BT} \left( \frac{E_s - E_t}{6e^{-E_s/k_BT}} \right)
\]  

(1.28)

Recall that the value \(E_s - E_t\) has already been defined in Eq. (1.13). Through substitution of this variable’s definition in Eq. (1.28), Eq. (1.29) is generated with the assumption that the singlet state is the ground state.

\[
\chi = \frac{NG^2g^2}{2k_BT} \left( \frac{2J_{ab}}{6e^{-2J_{ab}/k_B T}} \right)
\]  

(1.29)

Eq. (1.28) can also be manipulated to represent the case of a triplet ground state. By assigning the energy of the triplet state \(E_t\) from Eq. (1.13) an arbitrary value of zero Eq. (1.30) can be generated then substituted into (1.27) to generate Eq. (1.31).

\[
\Delta E_{st} = E_s - E_t = E_s - 0 = 2J_{ab}
\]  

(1.30)

\[
\chi = \frac{NG^2g^2}{2k_BT} \left( \frac{6e^0}{e^{-2J_{ab}/k_B T} + 3e^0} \right) = \frac{NG^2g^2}{2k_BT} \left( \frac{6}{e^{-2J_{ab}/k_B T} + 3} \right)
\]  

(1.31)

Eq.s (1.31) and (1.29) establish a relationship between \(J\) and \(\chi\), allowing for the analysis of radical exchange coupling through measurements of magnetic susceptibility.

Alternatively, \(J\) can be evaluated by variable-temperature EPR spectrscopy in a similar fashion. The intensity of an EPR signal is directly proportional to paramagnetic magnetic susceptibility \(\chi_{para}\) by the Curie law44 (1.32).

\[
I_{EPR} \propto \chi_{para} = \frac{C}{T}
\]  

(1.32)

Here \(T\) is temperature and \(C\) is the Curie constant (= Ng^2b^2S(S+1)/3k_B).13 If both the singlet (S=0) and a triplet (S=1), can be thermally populated, the relative triplet concentration is given by the Boltzmann distribution (1.33).

\[
\frac{n_t}{n_s + n_t} = \frac{e^{-E_t/k_B T}}{1 + e^{-E_s/k_B T} + 3e^{-E_t/k_B T}}
\]  

(1.33)
The result of combining Eqs. (1.33) and (1.32) is shown in Eq. (1.34)

\[ I_{\text{EPR}} \propto \chi_{\text{para}} = \frac{C}{T} \frac{-E_L}{3e^{k_bT} + 3e^{k_bT}} \]  

(1.34)

which can then be multiplied by $\exp(-E_S/k_bT)$ and substituted with Eq. (1.13) to generate Eq. (1.35).

\[ I_{\text{EPR}} \propto \chi_{\text{para}} = \frac{C}{T} \frac{3e^{k_bT}}{1 + 3e^{k_bT}} \frac{2J_{ab}}{3e^{k_bT}} \]  

(1.35)

Through this Eq., temperature-dependent EPR intensity can be used to determine the exchange coupling parameter, $J_{ab}$. 
I.4 The Valence Bond Configuration Interaction Model

As mentioned before, simple HMO theory can be used to evaluate ground state biradical D-B-A exchange coupling, but a model exists which more fully expresses the interactions, and provides a straightforward connection between experimentally-determined magnetic exchange parameters and $H_{AB}$-values using experimentally-determined spectroscopic features of SQ-B-NN molecules. The Valence Bond Configuration Interaction (VBCI) model utilizes fragment valence MOs or AOs to generate ground- and excited configurations. The former are superexchange-mixed via $H_{AB}$ with the latter to produce perturbed electronic states. For our biradicals, the exchange parameter measured by magnetometry is proportional to $H_{AB}^2$. Importantly, critical VBCI parameters can be determined spectroscopically. This allows for the evaluation of excited state contributions to the ground state exchange in biradical D-B-As.

![Figure I-7. Frontier Molecular Orbital diagram of SQ-NN π-interactions.](image-url)
It is important to distinguish the VBCI model from the MO model. Key interactions between SQ and NN frontier orbital fragments are shown in Fig. I-7. Notice that the SQ and NN SOMOs lack the correct orbital symmetry to mix directly (and the nodal carbon in the NN SOMO). However, the crucial mixing is that of SQ SOMO and the NN LUMO. This mixing results in the stabilization of the SQ SOMO, while the NN LUMO increases in energy. The important consequence of this mixing is that the SQ SOMO gains NN character and the resultant exchange integral is now defined by significant overlap density, and ferromagnetic SQ-NN exchange is both predicted and observed. The MO model, although useful for predicting ferromagnetic exchange, does not allow for a straightforward evaluation of the electronic coupling, \( H_{DA} \). In the VBCI model, MO fragments of the constituent donor (SQ), bridge, and acceptor (NN) are used only to generate configurations and states, overall orbital mixing is ignored. At idealized \( C_{2v} \) symmetry, the ground configuration is given by \((a_2)^1(1b_2)^1(2b_2)^0\), that is one electron in each of the NN- and SQ SOMOs. Since these orbitals are orthogonal, the resulting states are degenerate, and \( J = 0 \). Experiment clearly demonstrates that this is not the case. However, if excited configurations are mixed into the ground state, \( J \neq 0 \).

Figure I-8. SQ-NN electronic coupling with representative fragment MOs.
The lowest energy excited configurations are the singlet and triplets derived from an SQ(SOMO) $\rightarrow$ NN(LUMO) transition. Since the VBCI model is a state model, such a transition should be observed in the electronic absorption spectrum, and indeed it is. These excited singlet and triplet “charge-transfer configurations” (CTCs) are both $\langle a_2 \rangle^1(1b_2)^0(2b_2)^1$. Since the $a_2$ SQ SOMO and the $2b_2$ NN LUMO are both orthogonal and share a sizeable overlap density (Fig. I-8), the energy of the $^3$CTC $<$ $^1$CTC. Importantly, it is $H_{AB}$ that describes the transfer of an unpaired electron from the SQ SOMO to the NN LUMO. Thus, $H_{AB}$ is responsible for mixing the CTC configurations into the corresponding ground configurations. This mixing generates the observed singlet-triplet gap for the ground configurations (GCs, Fig. I-9). Based on the interactions modeled within this VBCI framework, an Eq. can be derived, which relates the exchange coupling parameter to electronic coupling (1.36).

$$2J_{AB} = \frac{2H_{AB}^2K_0}{U^2-K_0^2}$$  \hspace{1cm} (1.36)

Here $J_{AB}$ is the exchange coupling constant between two exchange coupled moieties “A” and “B”, $K_0$ is the single-site excited state exchange integral (excited singlet-triplet state energy gap), and $U$ is the mean charge transfer energy between the ground- and charge transfer configurations. An important feature of Eq. 1.36 is that the parameters $K_0$, and $U$ are obtainable through electronic absorbance spectroscopy and $2J_{AB}$ is determined through
magnetometry. With the VBCI model and Eq. (1.36) it is possible to calculate the off-diagonal electronic coupling matrix element $H_{ab}$, allowing for quantitative analysis of the radical coupling event. Eq. (1.36) is also significant because it not only relates a qualitative analysis of electronic coupling to spectroscopic features, but also illustrates a direct proportionality between the exchange coupling parameter $J$ and the square of electronic coupling element, Eq. 1.37.

$$J \propto H_{ab}^2$$

With this relation, as well as information from prior Shultz Group work, it is possible to calculate the electronic coupling displayed by any synthetically viable SQ-bridge-NN species by measuring $U$ and $K_0$ to calculate $H_{DA}$ (Eq. 1.38).

$$\frac{J_{SQ-B-NN}}{J_{SQ-NN}} = \frac{H_{SQ-B-NN}^2}{H_{SQ-NN}^2}$$

An important modification of our VBCI model involves placing a bridge fragment between SQ and NN. In this case, both the SQ(SOMO) and the NN(LUMO) take on bridge character. Consequently, the pertinent superexchange pathway involves the bridge LUMO as shown in Fig. I-10.

Figure 1-10. Left: Frontier NN(SOMO), SQ(SOMO) and NN(LUMO) orbitals fragments utilized in the VBCI model taking into account a bridge fragment, right. Note that both the SQ(SOMO) and the NN(LUMO) have bridge character, provided that the corresponding torsion angles are less than 90°. Right: VBCI model illustrating SQ $\rightarrow$ B-NN CT configurations ($^1$EC and $^3$EC; $a_2^11b_2^02b_2^0$) that mix with corresponding ground configurations ($^1$GC and $^3$GC; $a_2^11b_2^12b_2^0$) to create the experimentally-evaluated singlet-triplet gap ($2J_{SQ-B-NN}$).
I.5 Prior Work: SQ-NN Biradicals in the Shultz Group

Prior to my work in the Shultz group, several $\text{SQ-B-NN D-B-A}$ molecules had been designed and generated to test the role of specific bridge features on electronic coupling. For instance, in 2013 a paper was published by the Shultz Group that illustrated distance dependence of on electronic coupling and the validity of our superexchange-type valence bond configuration interaction (VBCI) model.$^9$ This series of structures is shown in Fig. I-11.

![Figure I-11. A Series of $\text{SQ-NN}$ biradicals generated with varying spin center distances in order to ascertain distance dependence on electronic coupling (left). A plot relating spin center distance to electronic coupling magnitude in an exponential manner (right).$^9$](image)

The parent $\text{SQ-NN}$ complex was generated to get a baseline measurement of $\text{SQ-NN}$ magnetic exchange coupling ($J$) when no bridging unit is present, minimizing distance between the two spin centers of the SQ-NN biradical. This distance was then manipulated by adding a series of bridge fragments, thereby varying the distance between $\text{SQ}$ and $\text{NN}$. Since these $\text{SQ-B-NN}$ biradicals are stable solids at room temperature crystals of each one of the complexes were grown and their exact structure were determined via X-ray crystallography. When the magnitude of $J$ was determined for each biradical and contrasted with their respective spin center distances, it was found that the distance between spin centers affects the degree of electronic coupling in an exponential manner, consistent with a superexchange model.$^9$ Another variation that has been explored to elucidate bridge-mediated electronic coupling involved torsions between donor, bridge, and acceptor fragments. In 2015, another paper was published where the bridge maintained the same basic architecture to enforce a constant bridge distance ($\text{para-phenylene}$), but the bridge was rotated out-of-plane by various degrees to probe the torsional dependence of exchange/electronic coupling.$^8$ By generating a series of phenyl-bridged biradicals with
differing numbers of methyl groups on the phenyl bridge, the torsion angles between bridge-acceptor and bridge-donor fragments was systematically altered. Since the electronic coupling is modulated by the bridge π-system, and π-system conjugation varies as the cosine of torsion angle, exchange/electronic coupling varies as \( \cos^2 \) of the torsions. Four bridge methyl substitutions render the \( \text{SQ} \) and \( \text{NN} \) π-systems nearly orthogonal to that of the bridge. In addition, a bicyclo-[2,2,2]-octane-bridged system displaying purely σ-bridge-interactions was prepared (Fig. I-12, center). A 3-D “mesh” plot displaying D-B torsion, A-B torsion, and electronic and magnetic coupling parameters was generated computationally by our collaborator Martin L. Kirk and his group at the University of New Mexico. This plot was generated prior to the analysis of physical complexes themselves and fits the experimentally determined \( J \)-values extremely well (Fig. I-12, right). Following these experiments, Eqs. (1.39) and (1.40) used to calculate \( J \) could modified to include bridge-donor and bridge-acceptor torsion angular dependence, a structurally intimate feature available through X-ray crystallography.\(^8\)

\[
H_{DA} = \frac{H_{DB}H_{BA}}{\delta_{DA}} \tag{1.39}
\]
\[
H_{ij} = H_{ij}^0 \cos(\Phi) \tag{1.40}
\]

**Figure I-12.** To test the torsional dependence of the bridge on electronic coupling between radicals a series of phenyl spaced D-B-As were generated with varying number of methyl groups at the “R” positions of the phenyl group (left). A bicyclooctane bridged D-B-A was also generated to test a full σ-character bridge (center). Mesh plots comparing \( J_{DA}/H_{DA} \) to A-B and D-B torsion angles illustrates the angular dependence (right).\(^8\)

More recently, two \( \text{SQ}-\text{B-NN} \) complexes were generated to probe the effect of bridge dipole on electronic coupling.\(^{46}\) Thus, two isomeric D-B-A molecules were synthesized both having a thiophene-pyridine bridge: one isomer with the pyridine end connected to the \( \text{SQ} \) donor
and the thiophene end connected to the NN acceptor, and a second isomer with the opposite connectivity (Fig. I-13).

![Pyridine-thiophene bridged SQ-B-NN ground state biradical D-B-As generated to test the impact of bridge dipole on electronic coupling (bottom). The LUMO of the pyridine-thiophene bridge (top).](image)

Figure I-13. Pyridine-thiophene bridged SQ-B-NN ground state biradical D-B-As generated to test the impact of bridge dipole on electronic coupling (bottom). The LUMO of the pyridine-thiophene bridge (top).

Unexpectedly, it was found that dipole moment did not display a novel degree of “recification” (the ratio of J-values is proportional to the ratio of conductance values through the thiophene-pyridine bridge). Consistent with the VBCI model, this was proposed to be due to the bridge LUMO, as per Fig. I-10. The VBCI superexchange pathway utilizes the LUMO of the bridge, and surprisingly the pyridine-thiophene LUMO is quite symmetric, having nearly identical coefficients on the pyridine and thiophene carbons that connect to SQ and NN. This similarity between atomic electron densities in the LUMO of the pyridine-thiophene bridge is considered to be the source of nearly equivalent J-values and consequently the lack of recification in pyridine-thiophene M-B-M constructs.

I.6 Naphthalene as a Molecular Bridge

Our current model for molecular recification emphasizes the importance of the bridge LUMO, and suggests that very different J-values and therefore sizable rectification ratios can be obtained using bridges with very different LUMO coefficients at the substitution sites. We have
considered several bridges to test our hypothesis. One hypothesis involves a series of naphthelene-bridged SQ-B-NN biradical complexes (Fig. I-14). Also shown in Fig I-14 the naphthalene LUMO possesses no electronic density on the two carbon atoms that fuse the rings. This means that should the LUMO be cheifly responsible for the coupling of the donor SQ and acceptor NN subunits no exchange coupling would be observed in isomers with substituents on opposing rings. As will be discussed in future chapters this is not what is observed, and the 1,5-, 2,5-, and 1,7-subsitutued isomers do exhibit exchange coupling facilitated by higher energy orbitals. This work will explore the results of naphthalene-bridged SQ-B-NN biradical complexes, including synthesis of all napthyl isomers, analysis of magnetic data, and future directions of SQ-B-NN D-B-A biradical projects.

Figure I-14. LUMO of naphthalene with proposed substitutions to create a series of ferromagnetically coupled isomers capable of displaying electron-density dependent current rectification.
II. Determining the Role of Bridge LUMO Electron Density in Electronic Coupling

II.1 Molecular Rectification

With the advent of newer and more sensitive technology, the miniaturization of technology has hit a stride. Most electronic devices that can function comparably in a smaller form have been driven to take on such a state. This economic drive towards smaller technology may hold its limits with the nanoscale, but the progression to that point will be met with a multitude of challenges. One notable difficulty faced is the atomic irreproducibility displayed by silicon-based devices: at a point of miniaturization the atomic details of a device will become a problem. Such difficulties could possibly be tackled on a molecular level by replacing components of electrical circuits with molecules. The sheer structural tunability of organic molecules offers a wide variety of possible methods to overcome the inevitable complications found in the miniaturization of devices.57

Electrical circuits vary in composition based on the purpose they are designed to fulfil. For many applications, current needs to be converted from an alternating (AC) to a direct (DC), and this requires a device that only allows for “one-way” flow of electrons. This is often achieved through the installation of a semiconductor diode. Such a component is known as a rectifier.59 The concept of a molecular rectifier is not a new one and dates back to groundbreaking theoretical work published by Aviram and Ratner in 1974.58 Their proposed organic rectifier molecule consisted of a donor and acceptor group spaced by a s-bonded bicyclooctane bridge. In their model, the donor and acceptor units were connected to the anode and cathode of a circuit respectively, and they proposed that rectification could be achieved through specific energetic tuning of the molecule’s frontier molecular orbitals (FMOs). The work proposed that the energetic alignment of the Fermi level of the electrodes and their respective molecular contact’s FMOs would be the primary deciding factor in molecular rectifying events.58,59 After years of theoretical development, great progress has been made to develop the field of molecular electronics, including specific steps that teased out general rules and parameters that define a molecular rectifier.

There are multiple possible transport mechanisms that can contribute to molecular rectification, and in each case the rectification behavior is a consequence of inherent asymmetry. Generally, molecular rectifiers display activity that can be categorized within three broad, but
different, categories, each of which is not mutually exclusive (Figure II-1). The three categories are:

1. **S-type (Schottky-type):** Molecules with asymmetric Schottky barriers at both electrode interfaces.
2. **A-type (Asymmetric-type):** Molecules displaying localized conductive states closer to one electrode or another (achieved through asymmetric functionalization).
3. **U-type (unimolecular-type):** Molecules with asymmetric MO distribution in the orbitals accessed during the charge transport process.

The asymmetry that gives rise to rectification behavior in a S-type rectifier is that of the molecule’s Schottky barriers. A Schottky barrier is the potential energy barrier present for an electron to transfer from a semiconductor to a bound electrode. The magnitude of a Schottky barrier is dependent on the chemical identity of the junction as the energy alignment of the electrode and the molecule’s binding contact determine the barrier’s height. As such, asymmetry in an S-type rectifier is achieved through differing molecule-electrode binding substrates, or having the cathode and the anode composed of different metals. This gives rise to different dipoles at each junction.

![Figure II-1](image)

**Figure II-1.** The frameworks of the three types of molecular rectifiers. Here “Mₙ” is a metal electrode, “Sₓ” is a binding substrate, “Dₓ” is the distance between organic bridge and metal electrode, and “Oₓ” is an organic fragment of the bridge.

In an A-type rectifier, asymmetry arises from inequivalent bridge-electrode distances. Differing the lengths of the electrode-linking portions on either side of the bridge often results in the two sides of the bridge having differing transport characteristics; this difference is what allows for current rectification in an A-type rectifier.
The third type of molecular rectifier is the U-type rectifier. In the U-type rectifier, the molecule-metal contact and the electrode identity are constant throughout both sides of the junction, and asymmetric current flow through the bridge is attributed to asymmetry in the FMOs of the bridge. U-type rectifiers are considered to be the mechanism for true molecular rectification as its definition does not include any metal-molecule interactions, so the rectification event is due solely to molecular features. U-type rectification is also fundamentally parallel with concepts initially proposed by Aviram and Ratner in 1974. By these credentials, any source of rectification “observed” within the SQ-B-NN framework render it a U-type rectifier.

Van Dyck and Ratner also presented three design rules for making molecular rectifiers that take advantage of the three general types of rectification in a 2015 publication. These three design rules are as follow:

1. The molecule must contain donor and acceptor anchoring moieties which are chemisorbed to the metal electrodes asymmetrically.
2. The anchoring moieties must have energy levels close to the fermi level of the electrodes they are in contact with.
3. The asymmetrically coordinated donor and acceptor moieties must be weakly coupled through a conjugated bridging fragment.

In pursuit of a D-B-A U-type rectifier these three rules can be applied to the experimental design of SQ-B-NN molecules. With the assumption that the SQ and NN units act not only as the donor and acceptor moieties but also as the electrodes, SQ-B-NN molecules can be studied as molecular rectifier analogues (Figure II-2).
Figure II-2. SQ-B-NN isomers with pyridine-thiophene bridging units. Here the SQ donor subunits serve as the anode and the NN acceptor subunit serves as the cathode. Through this paradigm the pyridine-thiophene bridge was studied as an analogue of a unimolecular rectifier.

II.2 Target Molecules and Expectations

It has been shown on multiple occasions that the magnitude of electronic coupling $H_{DA}$ relies heavily on the nature of the bridging unit between the donor and acceptor groups. Coupling in SQ-B-NN biradicals is predominantly via the bridge LUMO, and a series of methyl substituted phenyl-bridged SQ-B-NN has shown that breaking the planarity and conjugation of the D-B-A triad’s π-orbitals directly affects the magnitude of $H_{DA}$. Furthermore, installation of a bridge that displays an inherent dipole moment has shown that $H_{DA}$ is only moderately affected by the orientation of bridge polarity. The dipole-bridged SQ-B-NN complexes in which B = pyridine-thiophene were synthesized and studied in hopes that orienting the bridge dipole with-and opposed to the SQ-NN dipole would result in markedly different of electronic couplings. Success of this approach would have hinted at bridging units most likely to give current rectification. However, such an observation was not observed when measuring SQ-NN coupling in two pyridine-thiophene D-B-A isomers, due to the symmetry of the pyridine-thiophene LUMO. With the design parameters laid out by Van Dyck and Ratner in mind, a series of naphthalene-bridged SQ-B-NN species have been designed to test the effect that the pattern of atomic orbital coefficients of a nonpolar bridging unit has on electronic coupling as determined by magnetic exchange coupling.
It has been shown that in the Shultz Group SQ-B-NN biradicals, exchange coupling is predominantly modulated by through the LUMO of the bridging unit. The LUMO of naphthalene (Figure II-3) offers a unique electronic landscape for probing changes in coupling afforded by different substitution patterns. This template enables the proposal of multiple comparable SQ-naphthalene(NAP)-NN isomers, with SQ and NN substitutions on positions with differing orbital coefficients. Five ferromagnetically-coupled SQ-NAP-NN isomers have been proposed for synthesis and analysis (Figure II-4).

![Figure II-3. Hückel Molecular Orbital theory calculated LUMO electron density of naphthalene.](image)

![Figure II-4. Proposed naphthyl bridged SQ-NAP-NN D-B-A moiety substitutions shown over the LUMO of naphthalene. Isomers 1,5-NAP, 2,6-NAP, and 1,4-NAP serve to probe LUMO electronic structure dependence, while 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP are proposed analogues unimolecular rectifiers.](image)

It is important to note that the central carbons that fuse the two six-membered rings of naphthalene are nodal in the LUMO and this provides no pathway for transannular coupling. This means that using exclusively the naphthyl LUMO, the only isomer that would be predicted to exhibit non-zero coupling would be the isomer 1,4-NAP. Further evaluation of the Hückel calculated MOs shows that the LUMO+1 orbital is also unable to facilitate coupling between the two rings and that the lowest energy molecular orbital that possesses appropriate Hückel coefficients to allow for coupling between the two fused rings is the LUMO+2 (Figure II-5). This means that the other four isomers (2,6-, 1,5-, and both 1,7-substituted isomers) will have one exchange pathway through the LUMO+2 orbital while the 1,4-substituted isomer will be able to
utilize both the LUMO and LUMO+2 pathways. This is expected to be reflected in the magnitude of exchange coupling exhibited by these complexes.

Figure II-5. Hückel Molecular Orbital theory calculated LUMO through LUMO+2 energy levels for naphthalene.

Comparisons between the electronic couplings of complexes 1,5-NAP and 2,6-NAP, as well as between 1,4-NAP and 2,6-NAP will help to illustrate the coupling difference between attaching the donor and acceptor moieties to bridge positions with large and small MO coefficients. In complex 1,5-NAP and 1,4-NAP both the donor and acceptor groups are positioned on carbons with a large LUMO coefficient while 2,6-NAP has both donor and acceptor located on carbons with a smaller LUMO coefficient. Our prediction is that 1,4-NAP and 1,5-NAP will facilitate electronic coupling to a larger degree than the 2,6-NAP isomer due to the larger coefficients at the points of substitution. This prediction holds steadfast to information reported by Taniguchi and coworkers in 2011 who, in metal-molecule-metal break junction experiments measured a rectification ratio (RR) of 1.6 between their 1,5- and 2,6-napthyl derivatives, and as discussed in section I.3, \(J_{DA}\) and \(g\) are proportional to one another through \(H_{DA}\). Taniguchi and coworkers also showed that the largest degree of electronic coupling was observed through 1,4-substituted naphthalene. In accordance with these observations, 1,4-NAP is expected to have a larger \(J_{SQNN}\) than 1,5-NAP.

In order to further probe the utility of D-B-A systems in molecular electronic rectification, as well as to advance a current design understanding of single molecule rectifiers, proposed "unimolecular rectifying" isomers 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP have been prepared. Theoretically, the difference in coefficients at the points of attachment should act as a sort of electronic funnel, promoting a preferential degree of electronic coupling in one isomer over the other. The initial prediction in this model was that the 1-NN-7-SQ-NAP will have a
stronger degree of electronic coupling because the acceptor **NN** is attached to a position with a larger Hückel coefficient. This is important because the exchange in a **SQ-B-NN** biradical is between the **SQ** unit and the FOMOs of the combined **B-NN** fragment. Therefore, increasing the electronic density at the point of acceptor substitution should increase the **NN** character in the combined **B-NN** subunit.

The **SQ-B-NN** paradigm presents an ideal framework for studies focused on bridge mediation of charge transport. This is because the structural analysis of **SQ-B-NN** complexes is conducted in the solid state on X-ray quality crystal samples. Since the exact conformation (torsion angles, bond lengths, etc.) of the bridge is known from the crystal structure, specific changes in the magnitude of electronic coupling between similar isomers can be directly attributed to the identity of the bridge. This advantage is paramount for the proposed study focusing on bridge substitution and the effect of electronic orbital coefficients on the magnitude of electronic coupling. With the exact conformation known, and corrections for **SQ-B-NN** bridge length and torsion angles determined in prior studies, differences in corrected coupling between the proposed isomers is only varied as a function of bridge FMOs.
II.3 Synthetic Discussion

Synthesis of Ferromagnetically Coupled Naphthyl-Bridged SQ-NN Biradicals.

The synthesis of bridged SQ-NN biradicals is a process that can be most easily tackled when thinking about the tetrad in terms of its individual parts: the donor, the acceptor, the ancillary ligand, and the bridge. The semiquinone donor unit was installed on the bridges as 5 (MOM$_2$CatBpin), which was synthesized through the following procedures generated by past members of the Shultz group illustrated in Scheme II-1.$^{62}$

![Scheme II-1](image)

Scheme II-1. Synthetic route for 2-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5 (MOM$_2$CatBpin).

The protocol starts with the *para* bromination of 2-tert-butylphenol to make 1, which is then oxidized with 2-iodoxybenzoic acid (IBX)$^{63}$ to generate the quinone (2). The added solubility gained through the application of a CH$_2$Cl$_2$ and MeOH mixture allows the oxidation to occur over a matter of minutes as opposed to days in pure CH$_2$Cl$_2$. Quinone (2) can then be reduced to the catechol (3) with either ascorbic acid or sodium dithionite, dithionite is used with preference over ascorbic acid due to its faster rate of reduction. If left on the benchtop for any
extended duration of time, 3 will oxidize back to its quinone form. To prevent this, the hydroxyl groups are protected with methoymethyl (MOM) groups to yield 4. The MOM protection also serves to remove the phenolic protons from the molecule allowing the t-BuLi-induced lithium-halogen exchange to occur. The resulting aryllithium is then quenched with 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to generate MOM$_2$CatBpin, which is subsequently recrystallized and stored below room temperature. The route outlined in Scheme II-1 allows for multi-gram bulk syntheses of 4 and generation of MOM$_2$CatBpin on a gram scale, a bulk batch considering the intervals at which it is consumed.

The nitronylnitroxide (NN) acceptor is added to the tetrad through a reaction with a bis(hydroxylamine) (7, BHA) which was prepared in two steps.$^{53}$ Dimerization of 2-nitropropane affords dinitrobutane (6), the starting material for the amalgam reduction to produce BHA, 7. The mercury amalgam reaction proceeds well to product when compared to other known routes and gives clean product with minimal purification though the method itself requires the implementation of toxic materials. The reaction is also incredibly sensitive to solvent, failing should any peroxides be present in the THF used as the reaction solvent. With all conditions adequately addressed, the synthetic route outlined in Scheme II-2 produces BHA with reasonable yield on a multi-gram scale, allowing for bulk generation of the NN starting reagent. The cyclization that uses BHA to generate a tetramethylimidazolidinediol group in later steps of biradical synthesis is sensitive to trace metals left behind from the amalgam reaction so BHA is recrystallized from MeOH before being used in any following reactions.

![Scheme II-2. Synthetic route for N,N-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) 7 (BHA).](image)

The ancillary (ZnTp$^{\text{Cum,Me}}$)$^+$ complex ion is installed last on the tetrad, and its starting materials can be prepared in bulk and stored safely near the end of the synthetic route illustrated in Scheme II-3.$^{64}$ The protocol begins with the Friedel-Crafts acylation of cumene to form 4-isopropylacetophenone (8) which is then transformed to diketone (9) through a Claisen
condensation. Both steps can be carried out in large batches allowing for both 8 and 9 to be cleanly prepared in bulk quantities (tens of grams). In the next step, cyclization of the diketone with hydrazine yields the pyrazole (10). Compound 10 is purified either through multiple recrystallizations from petroleum ether, or through sublimation in preparation for the next reaction. The reaction used to create the tris(pyrazolyl)borate species (11) is a very sensitive melt reaction that can fail should any of its specific conditions not be met. For instance, should the sand bath temperature be too warm the result will be a charred and highly-colored glass-like solid, or, should the starting pyrazole be slightly impure the reaction will not produce the desired tris(pyrazolyl)borate. The reaction is also incredibly moisture sensitive; it is often best to run the reaction under inert gas that has been passed through a drying tube. Also, because the reaction temperature is so high, a glass stir bar must be used as opposed to a more common Teflon-coated magnetic stir bar, which decomposes ~225 °C.

Scheme II-3. Synthetic route for Zn(OH)Tp\textsuperscript{Cum,Me} (12).\textsuperscript{64}
Once the reaction has generated 11 as a colorless glass, the material is covered in hexanes and sonicated until it is a suspension of colorless solid. This solid is then filtered and washed with hexanes to recover unreacted pyrazole, which can then be resublimed and used in subsequent melt reactions. Compound 11 is then recrystallized from acetonitrile to remove left over potassium borohydride, then stored under inert atmosphere. When the zinc complex is needed, 11 is reacted with zinc(II) perchlorate hexahydrate to obtain the tris(pyrazolyl)borate zinc complex (12). Complex 12 decomposes when left open to ambient conditions and, as such, is best used immediately following isolation and drying. However, it is worth noting that 12 will not decompose rapidly in the absence of atmosphere and can be stored for close to a month in a desiccator under vacuum.

Each biradical has a unique synthetic route in compliance with the commercially available derivatives of the bridges. The goal of each synthetic route was to obtain a naphthaldehyde derivative functionalized with an appropriate functional group at the desired position for carbon-carbon bond formation. The synthetic scheme for the 2,6-NAP bridge is shown below in Scheme II-4. The most cost-efficient route to a leaving group-aldehyde derivative of 2,6-substituted naphthalene began with 6-bromo-2-naphthoic acid. With the bromine already attached to the ring, the only synthetic alteration needed to prepare the 2,6-napthyl bridge was to transform the carboxylic acid to an aldehyde; this was achieved in two steps. First the carboxylic acid was reduced with borane-tetrahydrofuran complex to give the primary alcohol47 (13), which was then oxidized with pyridinium chlorochromate (PCC)48 to form the 6-bromo-2-naphthaldehyde (14). Aldehyde 14 proved challenging to isolate in pure form at first, yielding yellow and tan solids in yields as low as 46%. Even the least colored of these solids still displayed large baseline spots on TLC. Eventually conditions were determined to isolate 14 with high yield and purity. Homogenizing PCC with four times its mass in silica and filtering the reaction solution through florisil66 gave a colorless solid in higher yields and purity than 14 isolated after even multiple pads of silica or celite.
Scheme II-4. Synthetic route for 6-bromo-2-naphthaldehyde (14).

The 1,5-bridge was generated in one step as shown in Scheme II-5. The conditions for this bromination were tricky to optimize and ultimately heavily reliant upon the concentration and temperature of the reaction solution. Only by heating CH$_2$Cl$_2$ solutions with concentrations of naphthaldehyde greater than 3M was 15 generated. Aldehyde 15 was typically isolated as a mixture of naphthaldehyde starting material and product in molar ratios ranging between 1:1 and 2:1 (starting material: product). The next step in the process is a carbon-carbon bond forming reaction, for which the starting material impurity remained inactive before being removed via flash chromatography. Once the leaving group and aldehyde substituted naphthalene derivatives had been generated the donor, acceptor, and ancillary ligand were attached to generate a complete biradical tetrad.

Scheme II-5. Synthetic route for 5-bromo-1-naphthaldehyde (15).

The 1,7-bridges were made to fit the same leaving group and aldehyde paradigm as the 2,6- and 1,5-bridges, however imagined routes to 8-bromo-2-napthaldehyde and 7-bromo-1-napthaldehyde were found to be cost inefficient. Triflate protected alcohols have been shown to work as suitable leaving groups for Suzuki-type cross coupling reactions and appropriate
starting materials for both target naphthols we readily available. For these reasons bridges 7-formynaphthalen-1-yl trifluoromethanesulfonate (20) and 8-formynaphthalen-2-yl trifluoromethanesulfonate (24) were synthesized following the steps outlines in Scheme II-6 and Scheme II-7, respectively.

Scheme II-6. Synthetic route for 7-formynaphthalen-1-yl trifluoromethanesulfonate (20)

The synthetic route to 20 began with the bromination of 7-bromo-1-tetralone. This was achieved in good yield under mild conditions using NBS as a source of bromine to afford 16. After the bromine has been installed alpha to the tetralone carbonyl, dehydrohalogenation and tautomerization yields the naphthol. This is achieved with relative ease by dissolving 16 in DMF with Li$_2$CO$_3$ and LiBr then heating the mixture to 140°C overnight. The next day the reaction is filtered, extracted with EtOAc, and washed with NH$_4$Cl, brine, and water to remove the reaction solvent, then dried over Na$_2$SO$_4$, concentrated, and purified via flash chromatography to yield naphthol 17. Both reactions implemented produce 16 and 17 are high-yielding and behave well on a large scale allowing the two to be run on multi-gram scales making the bridge of this isomer easy to produce in bulk quantities. With the primary alcohol installed and the tetralone aromatized to naphthalene the aldehyde now needs to be installed. Following protection, this is
achieved through a lithium halogen exchange at the 7-position of naphthalene which is then quenched with DMF to produce the corresponding aldehyde following an aqueous workup. As mentioned, for the lithium halogen exchange to be successful, the hydroxyl group must be protected. Initial trials involved triflate protecting the hydroxyl group on 16 and then conducting the lithium halogen exchange but this route proved unfruitful, leading to not only the desired product but also a litany of undesired side products. These were likely due to undesired reactions between the triflate group and the butyllithium reagent, and after purification the yield of 20 was remarkably low. As a result, two more steps were added to the synthesis where the alcohol of 17 was first protected with a methoxymethyl protecting group before being subjected to the lithium halogen exchange to afford the naphthaldehyde (19). Once the aldehyde was installed the MOM group was removed with catalytic acid and replaced with the triflate protecting group, affording the leaving group/aldehyde starting material for the 1-SQ-7-NN-NAP isomer (20).

\[ \text{Scheme II-7. Synthetic route for 8-formylnaphthalen-2-yl trifluoromethanesulfonate (24).} \]

The generation of the bridge starting material for the 1-NN-7-SQ-NAP isomer is outlined above in Scheme II-7. It begins with a diazonium salt reaction to replace the amine of 8-aminonaphthalen-2-ol with an iodine substituent (21). This is achieved in good yield on the gram
scale. First, the aminonapthalenol is dissolved in a 1:1 mixture of water and acetonitrile and chilled to 0°C before three equivalents of acid are added. Next, an aqueous solution of NaNO₂ is added and the reaction is stirred for 45m before KI added, also as an aqueous solution, and the mixture is stirred and warmed to room temperature overnight. The next day the mixture is diluted with Et₂O, washed with brine and NaHCO₃ and eluted through a silica pad with 20% Et₂O/hexanes for purification. From here the alcohol at the other end of the naphthalene is protected with a MOM functional group for much the same reason as in the synthesis of 20. With the alcohol protected, the iodine can be targeted selectively by reaction with i-PrMgCl and the resulting Grignard reagent can be quenched with water to afford the aldehyde 23. From this point the MOM protecting group can be removed with catalytic acid before being replaced with a triflate protecting group to afford 24.

Scheme II-8. Synthetic route for 2,6-NAP (31).

With the bridge generated and reactants in hand, biradical species can be generated in five steps according to Scheme II-8. Initially the synthetic route to make MOM$_2$CatBpin was low-yielding and produced impure product so a different route, illustrated in Scheme II-8, was tested to install the donor on the bridge. The borolane substituted phenol (25) was easily generated from the brominated phenol through a palladium-mediated reaction and isolated through flash chromatography as a colorless solid.\textsuperscript{54} The colorless solid was then used in a Suzuki coupling reaction with 14 to generate the 2,6-substituted phenol naphthaldehyde (26). Initially these couplings did produce 26 but did so with poor purity and yield while also producing a side product which was coincident with the product on thin layer chromatography (TLC) in many solvent combinations making 26 challenging to isolate. In hopes of finding optimal conditions for the coupling reaction a series of test reactions were run, their results are shown in Table II-1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Catalyst</th>
<th>Base</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>KOAc</td>
<td>48h</td>
<td>29%</td>
</tr>
<tr>
<td>THF</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>K$_2$CO$_3$</td>
<td>48h</td>
<td>24%</td>
</tr>
<tr>
<td>THF</td>
<td>PdCl$_2$(PPh$_3$)$_2$</td>
<td>K$_2$CO$_3$</td>
<td>48h</td>
<td>32%</td>
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<tr>
<td>THF</td>
<td>PdCl$_2$(DPPF)$_2$</td>
<td>K$_2$CO$_3$</td>
<td>48h</td>
<td>21%</td>
</tr>
</tbody>
</table>
After testing a handful of different coupling methodologies to prepare 26 as well as a couple duplicate reactions on different nitrogen lines, to ensure the inert gas atmosphere was not compromised, the route outlined in Scheme II-9 was attempted. At first, this route too resulted in lack-luster yields as shown in Table II-2. These initial reactions were found to proceed slower with 5 than they had with 25. In addition, at this point, the yields upon completion were not as hoped for so another route was tested which is also shown in Scheme II-10.

Table II-2. Initial reaction conditions for synthesis of 26 via Scheme II-9.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Catalyst</th>
<th>Base</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>K$_2$CO$_3$</td>
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<tr>
<td>THF</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>K$_2$CO$_3$</td>
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<td>25%</td>
</tr>
<tr>
<td>THF</td>
<td>PdCl$_2$(DPPF)$_2$</td>
<td>K$_2$CO$_3$</td>
<td>96h</td>
<td>17%</td>
</tr>
</tbody>
</table>

After testing a handful of different coupling methodologies to prepare 26 as well as a couple duplicate reactions on different nitrogen lines, to ensure the inert gas atmosphere was not compromised, the route outlined in Scheme II-9 was attempted. At first, this route too resulted in lack-luster yields as shown in Table II-2. These initial reactions were found to proceed slower with 5 than they had with 25. In addition, at this point, the yields upon completion were not as hoped for so another route was tested which is also shown in Scheme II-10.

Scheme II-10. Alternate synthetic route for 6-(3-(tert-butyl)-4,5-dihydroxyphenyl)-2-naphthaldehyde (28).

Following the initial results of donor installation on the 2,6-bridge the conclusion was reached that the most likely source of fault in the reaction would be the bridge moiety as it remained unchanged in all prior couplings. Scheme II-10 was attempted next as a first step to trouble shooting the reaction. The thought behind the route outlined in Scheme II-10 was that protecting the aldehyde$^{51}$ may result in faster coupling reactions. This route also proved
unfruitful, and the results of this scheme are shown in Table II-3. Even with the aldehyde protected, the reaction proceeded remarkably slow, but the addition of the protecting group did have a positive influence on the reaction. The resulting final reaction solution after heating to reflux did not display a spot coincident with the product on TLC, allowing for cleaner isolation of 26 and, eventually, 28. These trials also brought to light a favorable base/solvent pair for the donor-bridge coupling reaction. The combination of Na$_2$CO$_3$ and toluene allowed for faster reaction times when compared to THF and K$_2$CO$_3$ due to higher boiling point of the solvent and the smaller base cation.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Catalyst</th>
<th>Base</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
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<td>15%</td>
</tr>
<tr>
<td>PhMe</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>Na$_2$CO$_3$</td>
<td>48h</td>
<td>16%</td>
</tr>
</tbody>
</table>

The next attempt a successful coupling reaction was to swap the halogen to the donor and the boron leaving-group to the bridge, a manipulation that had proven helpful in the synthesis of past biradicals in the Shultz group. While these complexes were ultimately created this route was never tested because the root of the issue was elucidated during the synthesis of the naphthalene-borolane. A new method for the purification of 14 was found that produced the naphthaldehyde with much greater purity. Initially, purification of 14 was attempted with multiple silica and/or celite pads and the result was, at best, a tan solid that appeared pure by NMR but still displayed a dark baseline spot on TLC. Following a new work up, a single pad of florisil was used to purify the naphthaldehyde with better results than multiple pads of silica/celite resulting in a colorless solid displaying only a single spot when checked with TLC. This visually purer naphthaldehyde was put to the test and used to attempt to progress towards biradical following the coupling route outlined in Scheme II-8 as the route used to generate MOM$_2$CatBpin was still displaying poor results in both yield and purity at this point in time. The new naphthaldehyde produced a drastic increase in yield and purity as outlined in Table II-4. Not only did the pure naphthaldehyde allow the reaction to proceed with higher yields within a reasonable timeframe the complexity of the
resulting reaction mixture decreased. The coincident spot, as well as other faint spots that had been previously observed on TLC, disappeared after pure 14 was used in the reaction. The formation of these undesirable side products was attributed to the presence of chromium impurities left over from the PCC oxidation which appeared on baseline in the oxidations prior to the implementation of the florisil pad. The previously noted spot which was nearly coincident with 14 was isolated via flash chromatography and analyzed. The proton NMR of the coincident spot displayed remarkable similarities to 14, showing the same splitting and integration but with different chemical shifts for the aromatic protons as well as the aldehyde proton. This in combination with the R_ƒ difference on TLC lead to the conclusion that the coincident impurity was [2,2’-binaphthalene]-6-6’-dicarbaldehyde. Following a series of Suzuki couplings of the new naphthaldehyde to the phenol-borolane the synthetic route to obtain MOM₂CatBpin was deconvoluted, allowing for a much easier isolation of MOM₂CatBpin at higher yield and purity through the distillation of 1 before the IBX oxidation. When the purer MOM₂CatBpin was tested in a coupling reaction with the florisil purified 14 the results were incontrovertibly better, giving yields as high as 65% after heating to reflux for 48 h. Furthermore, by utilizing the phase-transfer properties of Bu₄NBr (10% loading) and a 20% H₂O in toluene solvent mixture, the naphthyl bridge Suzuki coupling reactions consistently yielded above 60% and were complete in under 24h. Through these subsequent improvements, the optimal conditions for these Suzuki couplings were found to be constant throughout all isomers when coupling MOM₂CatBpin with a bromonaphthaldehyde. These conditions only changed slightly when the leaving group was changed from a bromine to a triflate protected alcohol. When initially tested under the conditions outlined above, the triflate coupling reactions were low yielding, but when an equivalent of KBr was added the reactions produced results comparable to those observed with a bromine leaving group.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Catalyst</th>
<th>Base</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhMe</td>
<td>Pd(PPh₃)₄</td>
<td>Na₂CO₃</td>
<td>52h</td>
<td>53%</td>
</tr>
<tr>
<td>PhMe</td>
<td>Pd(PPh₃)₄</td>
<td>Na₂CO₃</td>
<td>48h</td>
<td>47%</td>
</tr>
<tr>
<td>PhMe:THF:H₂O (19:1:1)</td>
<td>Pd(PPh₃)₄</td>
<td>Na₂CO₃</td>
<td>48h</td>
<td>65%</td>
</tr>
</tbody>
</table>

Table II-4. Reaction conditions for the synthesis of 28 via Scheme II-8 with florisil purified bromonaphthaldehyde (14).
Recall from the earlier donor moiety synthesis that the catechol (3) is unstable and will readily oxidize to the quinone (2) so MOM groups were installed on 3. However, once the donor moiety has been installed on the bridging fragment, the rapid oxidation becomes much less favored, is no longer of major concern, and the catechol is deprotected with catalytic acid in MeOH with near quantitative yield. After the deprotection of the catechol-bridge species, the next step is to install the NN acceptor. This is achieved in two steps, then immediately coordinated to the (ZnTp\textsuperscript{Cum,Me}\textsuperscript{+}) complex ion (12) and then stirred under ambient conditions to allow for aerial oxidation of the catechol to the final semiquinone donor and completing the D-B-A synthesis.

In the generation of the naphthyl-bridged SQ-B-NN complexes 2,6-NAP was isolated first, and as such the steps converting donor-naphthaldehyde derivatives to their final biradical states were first optimized on the 2,6-naphthyl derivatives (Scheme II-9). With the deprotected catechol-naphthaldehyde (28) generated and BHA on hand, BHA is cyclized to generate the hydroxylamine precursor to the NN radical (29). This last step provided a synthetic hurdle due to its incredibly particular solvent requirements. Initially, the reaction was conducted in a minimal amount of dry MeOH so that the product would precipitate from solution and would be easily isolated through filtration.\textsuperscript{7,8,9} When this reaction was attempted using 28 the solvent conditions were difficult to reproduce exactly. On a 100 mg scale, a scale comparable to past group

**Scheme II-11.** Generation of the 2,6-NAP mono- and biradical complexes (30, 31).
member’s laboratory notebooks, the reaction could be run in 3 mL of dried MeOH. The product precipitated, and was isolated through filtration in 59% yield, but the yellow product proved impure by $^1$H NMR, displaying a large amount of starting material. After a series of attempts a new approach was conceived. The product catechol-bridge-hydroxylamine species (29) is soluble in Et$_2$O while the BHA reagent is not; this solubility difference led ultimately to a new procedure. By running the reaction as a slurry in MeOH with a stoichiometric excess of BHA the reaction was forced to consume all 28 present in the flask, 29 precipitating in the process. This reaction is followed via $^1$H NMR spectroscopy and once the aldehyde peak of 28 was no longer present in the reaction solution NMR spectrum, the reaction solvent was removed under reduced pressure. The residue was dissolved in Et$_2$O and passed through a silica pad, and the filtrate was then concentrated to afford 29 as a colorless solid with high yield and reproducibility. This method, while reproducible and high yielding, was incredibly slow, sometimes taking five or more days to consume all the starting materials. This reaction was modified again, and by using $p$-TsOH (1 mol%) as an acid catalyst the reaction proceeded much faster, often finishing overnight. It was also discovered that the silica pad could be avoided as the resulting catechol-bridge-bishydroxylamine product would precipitate from solution when dripped into saturated brine solution. As a result of these discoveries, the synthetic procedure was altered allowing for milder conditions. By using a 1 mol% $p$-TsOH the reaction would proceed quickly regardless of concentration, and batches of 100mg could be run in 5-10mL of dry MeOH. The solution of acid catalyst, BHA, and aldehyde would stir overnight and likely be complete the next day, showing no 2,4-dinitrophenyl-hydrazine (DNP) stain on the reaction TLC. The reaction solution could then be concentrated in vacuo down to 2-3mL of MeOH and dripped into 200mL of brine with vortex stirring. The product would crash out of solution and could be isolated via filtration and washed with Et$_2$O, leaving the remaining BHA starting material in the brine and on the filter paper. This procedure was found to produce product in greater purity while remaining just as high-yielding and reproducible as the aforementioned procedure.

The conversion of 29 to the 2,6-naphthyl monoradical (30) is heavily reliant on reaction time, stoichiometry, and pH. The reaction has a multitude of points at which failure is possible, which can be most easily addressed after the procedure has been stated. This reaction was also reimagined throughout my work with the naphthyl series, becoming much more reproducible and resolved. The initial preps used to first isolate 30 began with complex 29 being added to an oven
dried round-bottom flask that is wrapped in aluminum foil to protect it from light. 29 was then dissolved in Et₂O and pH 7 buffer then sublimed elemental iodine dissolved in Et₂O is added dropwise to the solution in the dark. The biphasic mixture was immediately transferred to a separatory funnel containing pH 7 buffer, shaken briefly with saturated Na₂S₂O₄, then the organic layer is quickly separated. The Et₂O solution was then washed with brine solution, dried over Na₂SO₄, and the reaction completion was confirmed by EPR spectroscopy.

Should the reaction be successful its spectrum will display a five-line hyperfine pattern \( (a_N = 7.5 \text{ Gauss}) \) in the room-temperature Electron Paramagnetic Resonance (EPR) spectrum consistent with the NN monoradical. The multitude of issues that arise in this reaction come from the often rapid dehydration for the cyclized hydroxylamine to undergo which, after oxidation using I₂, yields the iminonitroxide (IN) derivative as opposed to the desired NN (Figure II-6).

![Figure II-6](image)

**Figure II-6.** Two possible monoradical products when oxidizing a cyclized bishydroxylamine with elemental iodine.

To prevent the undesired reaction, the procedure features a series of conditions. A 1M pH7 buffer is implemented to slow dehydration. Using too much iodine will also result in the generation of the IN so is best to be as precise as possible with the stoichiometry of this reaction. Even though the reaction conditions can be difficult to optimize, the iodine oxidation is high yielding, highly reproducible, and easy to monitor visually. The reaction undergoes color changes following the addition of the ethereal iodine solution, and turns a dark red. Once excess iodine has been removed with saturated Na₂S₂O₄ solution, the resulting organic phase will be a deep blue or green color. The IN and NN derivatives have different characteristic colors, and a color change from one to the other can be noted if shaking the reaction with an excess of Na₂S₂O₄ solution. However, the characteristic color of each species can change based on the bridge so the only true diagnostic method to determine whether the oxidation was successful in generating the NN monoradical is observation of the 5-line N-hyperfine pattern in the EPR spectrum. The difference between IN and NN EPR spectra comes from the two nitrogen atoms:
in NN the nitrogen atoms are chemically equivalent while in the IN moiety the nitrogens are inequivalent; this difference affects the splitting patterns in their respective EPR spectra (Figure II-7). In the case of the IN, the presence of two inequivalent nitrogens results in a seven-line EPR splitting pattern, while the NN gives a five-line splitting pattern. These line spacings are determined by the magnitudes of the nitrogen hyperfine coupling constants ($a_N$). A hyperfine coupling constant, $a_N = 7.5$ Gauss is typically observed for a monoradical NN species, while IN is a triplet of triplets with $a_N = 9$ and $4.5$ Gauss.

![Figure II-7. The simulated EPR hyperfine splitting patterns of an iminonitroxide (IN, left) radical and a nitronylnitroxide (NN, right) radical.](image)

While the initial NN oxidation procedure was reproducible, a few alterations were eventually implemented that made the reaction cleaner and more reliable. The use of $\text{Na}_2\text{S}_2\text{O}_4$, while necessary if running the reaction in a stoichiometric excess of I$_2$, was eventually removed as well because after many iterations it was found that the reaction rarely required a full equivalent of I$_2$. The revised procedure for the I$_2$ oxidation of BHA kept the same solvents, starting with compound 29 (~100 mg scale) being dissolved in 7mL of Et$_2$O, combined with 9mL of pH 7 buffer mixed with vortex stirring to promote as much phase mixing as possible. Between 1 and 1.2 equivalents of I$_2$ was then dissolved in 3mL of Et$_2$O and the Et$_2$O/I$_2$ solution was added to the solution of 29 dropwise until the color of the I$_2$ began to persist for more than a few seconds; typically, only 3-5 drops. The solution would then stir until the color normalized
(5-10 m) and more I₂ would be added. Typically, catechol-bridge-BHA complexes were observed to be lightly colored so the initial solution would be either colorless or light yellow and the addition of the I₂ solution would cause the solution to turn red-brown; the color of I₂ in solution. Initially, when the I₂ color became obvious, the mixture would return to its faintly colored state quickly, but as more I₂ solution is added the reaction mixture would take longer to change from the I₂ color, sometimes taking close to 10 m. Once the color of the I₂ begins to persist for longer (~0.5 equivalents of I₂), the color that the solution returns to begins to shift away from the initial near transparent yellow to a more highly colored purple or blue (color depends on bridge chemistry and substitution). At this point it is best monitor the reaction via TLC in 100% Et₂O to determine the amount of remaining starting material (which will run with an R_f ~ 1.0 and be yellow in color) compared to the amount of product present (typically R_f ~ 0.8 and either purple or blue in color). As more I₂ is added the solution will eventually begin to relax from the I₂ color into a very opaque purple/blue color, and at this point the reaction should be checked by both TLC and EPR until IN begins to form. This will be noted visually as the solution begins to take on a faint green color, and the EPR spectrum shows signals due to IN (by the rise of small peaks outside the spectral width of NN), and on TLC by the rise of a light yellow spot just below that of the blue/purple NN. As soon as indications of IN begin to manifest, no more I₂ is added. Very typically the whole equivalent of I₂ will not be used. From this point the reaction mixture is transferred to a separatory funnel, washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford a blue/purple solid in good purity and yield.

Once the catechol-bridge-NN species has been prepared in pure form, the ancillary Zn complex (12) is attached to the catechol. In doing so, the second radical is generated, and the D-B-A biradical complex synthesis completed. The standard operating procedure for this reaction has also changed because of observations made over the course of the course of this project. The initial preparation began with combining 12 and a catechol-bridge-NN in an oven dried round-bottom flask and purge pumping it three times, then suspending the solids in a minimal amount of CH₂Cl₂:MeOH (2:3) mixture and stirring for 2 h. This initial 2 h stirring is sufficient to complex the Zn⁺ to the catechol (nominally to form the protonated catecholate complex). Following the 2 h stir under an inert gas atmosphere, the cap was removed and the reaction was stirred overnight open to air. Atmospheric oxygen is sufficient to oxidize the intermediate catechol
complex to the semiquinone radical complex. This reaction will typically lose a large amount of
CH₂Cl₂ overnight to evaporation and the next day small crystals are found lining the flask at the
MeOH solvent line due to the sparing solubility of SQ-B-NN molecules. The crystals would then
be washed into the solution with CH₂Cl₂ and the solvent removed. This initial procedure worked
well for the 2,6-NAP isomer but alterations had to be made to accommodate the reactivity
presented by the other isomers.

When initially attempted with this procedure the 1,5-NAP isomer synthesis did not work
nearly as well as the 2,6-NAP isomer. The crude EPR spectrum of the reaction mixture not as
clean as that of the crude 2,6-NAP, but purification was attempted anyway. When crystals of the
resulting reaction were finally grown and solved by X-ray diffraction, the structure was not the
desired product, but instead a molecule that certainly began as 1,5-NAP and reacted further. The
solved structure showed the framework of 1,5-NAP but instead of a NN radical at the 5-position
it seemed to show something more analogous of an IN radical. Furthermore, there was another
(ZnTp\textsuperscript{Cum,Me})\textsuperscript{+} complex ion attached to the side of bridging the naphthyl ring. This brought to
light new considerations for the generation of SQ-B-NN biradicals. For this reaction to occur a
second equivalent of ancillary ligand must be available, through either a stoichiometric excess or
discoordination of a second ligand. In addition, the NN radical unit had reacted intramolecularly.
This initial attempt at 1,5-NAP likely decomposed through the pathway presented in Figure II-8.
The SQ radical has sufficient spin density para- to its point of substitution where it would be
within Van Der Waals distance of the paramagnetic oxygen on the NN subunit. Here the two
radicals could react with one another forming a new carbon-oxygen bond. From there, another
oxygen must be introduced, followed by a second equivalent of Zn(OH)Tp\textsuperscript{Cum,Me} to produce the
final decomposition product that was isolated. After these observations on the decomposition of
1,5-NAP were noted, new procedures for SQ generation were attempted using only one
equivalent of Zn(OH)Tp\textsuperscript{Cum,Me}. In the other preparations of SQ-B-NN biradicals an equivalent of
KOH was added in an attempt to help facilitate the initial deprotonation of catechol, however
here when making 1,5-NAP this adaptation gave rise to synthetic problems. Initial trials found
that one equivalent of KOH worked well to generate the SQ unit in trials run with 2,6-NAP but
proved too harsh of a reagent to use in the generation of 1,5-NAP. Ultimately the generation of
1,5-NAP was achieved with the use of a single equivalent of Zn(OH)Tp\textsuperscript{Cum,Me} along with a
single equivalent of K₂CO₃. This procedure then became the new standard for the generation of the SQ radical, being used to generate all subsequent naphthyl bridged SQ-B-NN.

**Figure II-8.** The proposed decomposition pathway of 1,5-NAP in excess of Zn(OH)TpCum,Me (left) and the determined crystal structure for the decomposition product (right). Hydrogens and tris(cumenyl-methylpyrazolyl)borate “fingers” of the ancillary ligands are omitted for clarity.

To confirm the existence of the biradical species, an EPR is particularly useful. A biradical will display similar spectral features (hyperfine splitting pattern) to the catechol-bridge-NN species because the NN unit is still present, but the apparent hyperfine coupling constant decreases two-fold (aₙ = 3.6 Gauss in a SQ-B-NN biradical) due to the exchange coupling of the SQ and NN radicals being far greater than the hyperfine-coupling (Figure II-9).⁴⁴
Figure II-9. Electron Paramagnetic Resonance (EPR) spectrum of the 2,6-NAP monoradical (29) and biradical (30) species overlaid to illustrate spectral differences.

Figure II-10. EPR spectrum of the crude product solid resulting from the complexation of 12 and the 1,5-NAP monoradical (24 – Scheme 10).

The EPR spectrum of the crude solid isolated after biradical generation is rarely that of the pure biradical, and often displays features of both mono- and biradical species (Figure II-10),
so purification is required. The Shultz Group SQ-B-NN biradicals have been shown to display near shocking stability, remaining paramagnetic after sitting exposed to atmospheric conditions for extended periods of time and stable to prolonged recrystallizations. That being said, SQ-B-NN biradicals are labile and decompose on most stationary chromatography phases, making chromatography less straightforward. However, the biradical compounds are stable on a basic alumina stationary phase over short periods of time, allowing for small scale (<25 mg) separations via a series of pipet columns. Luckily, the monoradical species stay at baseline with this basic stationary phase, allowing for the successful elution of the biradical with no other paramagnetic impurities. Though no paramagnetic impurities exist following the basic alumina pipet column, excess 12 is still typically present in the eluted mixture. Thus, the final step in the purification of SQ-BNN biradicals is recrystallization to separate out the remaining diamagnetic impurity (12). These crystals are typically grown through liquid-liquid layering of CH₂Cl₂ and MeOH. The crude biradical solid is dissolved in a minimal amount of CH₂Cl₂ in a small vial and then MeOH is added carefully via pipette so as to minimizing mixing of the two solvents. This technique, specifically with this solvent combination, has been used to grow the large majority of Shultz group SQ-B-NN biradical complexes over the years, crystal growth using CH₂Cl₂ and MeOH is not always successful. Other solvent combinations have been used to successfully grow X-ray quality crystals of SQ-B-NN complexes. Notably, a mixture of Et₂O and hexane was used to grow the 2,6-NAP crystals via vapor diffusion with MeOH. Solvent mixtures such as CH₂Cl₂/n-hexanes, benzene/MeOH, and toluene/n-hexane have also been used to grow various Shultz Group SQ-B-NN biradical crystals. These steps have been utilized in the generation the four aforementioned naphthyl-bridged SQ-NN biradical complexes (2,6-NAP (Scheme II-9), 1,5-NAP (Scheme II-12), 1-SQ-7-NN-NAP (Scheme II-13), 1-NN-7-SQ-NAP (Scheme II-14) as well as one more naphthyl bridged isomer with 1,4-bridge substitution (1,4-NAP, Scheme II-15). The bridge synthesis for the 1,4-substituted isomer started from commercially available 4-bromo-1-naphthanoic acid and followed the same synthetic route as the 2,6-NAP isomer as shown in Scheme II-12.
Scheme II-12. Synthetic route for 1,5-NAP (36).

Scheme II-13. Synthetic route for 1-SQ-7-NN-NAP (41).

Scheme II-14. Synthetic route for 1-NN-7-SQ-NAP (46).
Scheme II-12. continued

Scheme II-13. continued

Scheme II-14. continued
Scheme II-15. Synthetic route for 1,4-NAP (51).

II.4. Results and Discussion
II.4.1 Crystallography

Full characterization and analysis of a SQ-B-NN biradical complex requires an X-ray crystal structure, as the value of \( J \) is dependent on specific features of the molecule. Namely, the distance between \( SQ \) and \( NN \) spin centers, the bridge-donor torsion angle, and the bridge-acceptor torsional angle, and the positions of connectivity of \( SQ \) and \( NN \) on the bridge are of great importance when determining the exact value of \( J \).\textsuperscript{8,9} Spectroscopic observations can be used to evaluate electronic coupling, \( H_{DA} \), but the precise examination of \( H_{DA} \) requires a
Figure II-11. Thermal ellipsoid plots determined through the X-ray diffraction of SQ-B-NN biradical crystals. The torsion angles between the bridge and its substituents are shown below each structure. Hydrogens and tris(cumanyl-methylpyrazolyl)borate “fingers” of the ancillary ligands are omitted for clarity.

crystal structure. The determined thermal ellipsoid plots of 2,6-NAP, 1,5-NAP, 1,4-NAP, 1-SQ-7-NN-NAP, and 1-NN-7-SQ-NAP are shown in Figure II-11 along with labeled B-SQ and B-NN torsion angles. The 2,6-substituted isomer is the most planar in the series, having bridge-substituent torsion angles of 4° and 43°, followed closely by the isomer 1-SQ-7-NN-NAP which exhibited torsion angles of 13° and 49°. The other isomers in this series are all exhibit more drastic SQ-bridge and bridge-NN torsion, an observation that should be reflected in the experimental $J$-values. As mentioned previously, the exchange coupling of SQ and NN units in these D-B-A biradical complexes is explained using a superexchange (VBCI) model. The
hallmark of a superexchange mechanism is not only exponential decay of the exchange/electronic coupling with increasing distance,\(^9\) but also dependence on the planarity of the conjugated \(\pi\)-pathway,\(^8\) reducing in magnitude further as a molecule strays from planarity. Each of these compounds shares near identical bond lengths within the \(\text{SQ}\) and \(\text{NN}\) moieties, all consistent with the presence of semiquinone oxidation state\(^8,9,46\) and nitronylnitroxide radical\(^8,9,46\) confirming that the attached substituents are indeed \(\text{SQ}\) and \(\text{NN}\).

**II.4.2 Electron Paramagnetic Resonance (EPR) Spectroscopy**

The EPR spectrum of a biradical is also paramount to the confirmation of its structure. The EPR spectra of \(\text{1,5-NAP}, \text{1,4-NAP}, \text{and 2,6-NAP}\) are shown below in Figure II-12.

![EPR spectra](image)

**Figure II-12.** Fluid solution EPR spectra of isomers \(\text{1,5-NAP}\) (middle), \(\text{1,4-NAP}\) (right), and \(\text{2,6-NAP}\) (left) with hyperfine splitting labeled.

Both complexes display the characteristic “biradical pattern” shown by Shultz Group \(\text{SQ-B-NN}\) biradicals: a broad, five-line hyperfine pattern with apparent \(a_N \sim 4\) Gauss. While the spectrum of \(\text{2,6-NAP}\) shows only the lines characteristic of the biradical complex, the \(\text{1,5-NAP}\) and \(\text{1,4-NAP}\) spectra also shows small signals just outside of the typical spectral width of a \(\text{SQ-B-NN}\) biradical. These features are attributed to remaining \(\text{NN}\) monoradical starting material. This small impurity can be corrected for while fitting the variable temperature magnetic susceptibility data and will manifest in the form of a lower mole fraction of biradical with an \(S = \frac{1}{2}\) paramagnetic impurity.
Figure II-13. The fluid solution EPR spectra of isomers 1-NN-7-SQ-NAP and 1-SQ-7-NN-NAP labeled with hyperfine splitting (left, right) and the EPR spectrum of 1-NN-7-SQ-NAP with “shoulder” spectral feature labeled the EPR spectra of 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP are shown in Figure II-13 and exhibit similar characteristics to the spectra of 2,6-NAP, 1,4-NAP, and 1,5-NAP but with a notable additional spectral feature which will be referred to as the “shoulder”. Both of the 1,7-substituted monoradical isomers show a routine five-line pattern with a splitting of 7 Gauss, but following the complexation the shoulder feature appeared in the spectra of both 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP. Despite this shoulder, both isomers clearly exhibit the five-line pattern with hyperfine splitting of 3.5 Gauss just like isomers 2,6-NAP, 1,4-NAP, and 1,5-NAP. This is not the first time that a Shultz Group SQ-B-NN biradical has shown this spectral feature. The m-phenyl bridged SQ-B-NN complex synthesized by Dr. Dan Stasiw also showed a similar broad spectral feature in its EPR. This shoulder was attributed to steric blocking of the NN subunit by the cumenyl “fingers” of the ancillary TpCum,Me ligand. Thus, NN rotation is inhibited at room temperature, and as such the fluid solution EPR takes on the “shouldered” pattern. This feature eventually relaxes to the predicted pattern when the sample is heated, showing the expected five-line biradical pattern with no shoulder at temperatures sufficiently high enough to force the full rotation of the NN subunit. This contention is supported by space filling models of both the 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP based on X-ray crystal structures. From these
models (Figure II-14), it is clear that the rotation of the NN subunit in both 1,7-substituted isomers is inhibited by the positioning of the ancillary ligand.

Figure II-14. The crystal structures 1-NN-7-SQ-NAP (top left) and 1-SQ-7-NN-NAP (top right) displayed as thermal ellipsoids, as well as their space filling models (bottom)

Both 1,7-substituted NN subunits are positioned within the space between two of the ancillary ligand’s three cumenyl “fingers”, resulting in slow rotation at room temperature. The anomalous EPR spectral features in the spectra of 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP are therefore attributed to this inhibited rotation.
II.4.3 Electronic Absorption Spectroscopy

Conjugated SQ-B-NN biradicals also display characteristic $\pi$-$\pi^*$ bands with SQ $\rightarrow$ Bridge-NN charge transfer character in their electronic absorption (EA) spectra that are used to confirm the presence of both SQ and NN groups in the same molecule.\textsuperscript{85}

![Electronic Absorption spectrum of purified 2,6-NAP with labeled electronic transition bands.](image)

Figure II-15. Electronic Absorption spectrum of purified 2,6-NAP with labeled electronic transition bands.

One of the most distinct characteristics of any ferromagnetically-coupled (conjugated) SQ-B-NN biradical complex is the charge transfer (CT) band characteristic of the SQ $\rightarrow$ NN interaction. This transition shows up as a strong band around 23,000 cm$^{-1}$ in an electronic absorption spectrum and is $\pi \rightarrow \pi^*$ in nature.\textsuperscript{19} Other characteristic bands can be observed in the EA spectrum of a SQ-B-NN biradical (Figure II-15) that can be attributed to individual SQ and NN EA transitions. Two NN transitions can be observed surrounding the SQ$\rightarrow$NN CT band, a band of $n \rightarrow \pi^*$ character exists at lower energies, ~20,000 cm$^{-1}$ and another NN transition of $\pi \rightarrow \pi^*$ character can be found ~ 27,000 cm$^{-1}$. The SQ unit also displays its own electronic transition with $n \rightarrow \pi^*$ character as a broad band between 10,000 – 15,000 cm$^{-1}$. The SQ$\rightarrow$NN CT band is not displayed in every SQ-B-NN complex, but instead is unique to specifically ferromagnetically-coupled, conjugated SQ-NN D-B-A complexes. Antiferromagnetically-
coupled/cross conjugated SQ-NN D-B-As will not display this characteristic band. An example of this phenomenon is shown in Figure II-16, where the electronic absorption spectra of a ferromagnetically-coupled SQ-NAP-NN isomer (2,6-NAP) and an antiferromagnetically-coupled SQ-NAP-NN isomer (2,7-NAP, Appendix B) are overlaid.

**Figure II-16.** Electronic absorption spectrum of 2,6-NAP overlain with the electronic absorption spectrum of 2,7-NAP (above). Each electronic transition is labeled with its transition type.

This spectral feature is not present in antiferromagnetic isomers because in antiferromagnetically-coupled radicals, the SQ and NN units are cross-conjugated through the bridge, while in their ferromagnetic counterparts the SQ and NN are conjugated through the bridge. Cross-conjugation results in orthogonal SQ(SOMO) and Bridge-NN(LUMO) orbitals and, as a consequence, the SQ → B-NN CT transition is absent in the electronic absorption. This allows for the SQ → B-NN CT band to be used as partial proof of existence for ferromagnetic coupling in SQ-NN D-B-A molecules.

Within the context of the VBCI model of SQ-B-NN exchange coupling, that one might anticipate that within in a series of compounds with the same bridge, or a series of compounds with a repeating bridge, the energy and intensity of the SQ → B-NN CT band could be used to evaluate the relative magnitudes of ferromagnetic $J$-values. If so, the comparison of electronic
absorption spectra could be used to anticipate a trend in the magnitude of $J$ before magnetometry measurements are taken. Figure II-17 shows the overlaid EA spectra of all five conjugated naphthyl-bridged SQ-B-NN isomers.

![Figure II-17. Electronic absorption spectra (toluene solvent) of all naphthyl-bridged SQ-B-NN isomers. The electronic absorption spectra of 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP are overlaid (a) and those of 2,6-NAP, 1,5-NAP, and 1,4-NAP are overlaid (b).](image)

There is a reasonable variation between the $\text{SQ} \rightarrow \text{B-NN}$ CT bands, all of them displaying energetic transitions near 23,000 cm$^{-1}$. When comparing the electronic absorption spectra of the two 1,7-substituted isomers there is a very notable difference between the intensity and shape of the $\text{SQ} \rightarrow \text{B-NN}$ ILCT band.

Recent work investigating the effect of bridge torsion on the electronic coupling in SQ-B-NN biradicals has revealed that bridge geometry plays a large role in the intensity, shape, and energy of the SQ and NN CT bands. Torsion about the SQ-B bond have been shown to effect the intensity and energy of the $\text{SQ} \rightarrow \text{B-NN}$ ILCT, while the twisting of the B-NN bond results in a blue-shift and merging of the ILCT with the NN $\pi-\pi^*$ band.$^{85}$ The large torsion of the SQ-B bond (49°) combined with the small torsion of the B-NN bond (13°) in 1-SQ-7-NN-NAP account for the spectra shown in Figure II-17, and this isomer’s spectrum shows clear definition of the $\text{SQ} \rightarrow \text{B-NN} \ \pi-\pi^*$ ILCT band, albeit of lower intensity (compared to those in Figure II-17B). 1-NN-7-SQ-NAP’s electronic structure in comparison shows a more intense $\text{SQ} \rightarrow \text{B-NN}$
ILCT band that is merged with the NN π-π* band as a result of a lesser SQ-B torsion (32°) combined with a much larger B-NN torsion (61°). These effects are also present in the electronic structures of the 1,4-, 1,5-, and 2,6-substituted isomers. Between the three isomers compared in the Figure II-17B, 2,6-NAP is expected to be most planar, having the smallest SQ-B torsion (43°) and a nearly planar B-NN bond (4°) in the crystal structure. Previous work has suggested that solution spectra can be analyzed using solid-state structures for qualitative analysis. As a result, the expected EA spectrum of 2,6-NAP would have the most intense SQ → B-NN ILCT of the three isomers and a well-defined NN π-π* band, exactly what is observed. The SQ-B torsions of 1,5-NAP and 1,4-NAP are nearly identical (57° and 59°) and as a result their SQ → B-NN ILCT band intensities are both low when compared to that of 2,6-NAP. Both 1,5-NAP and 1,4-NAP have large B-NN torsions as well (50° and 52°), and as a result their SQ → B-NN ILCT and NN π-π* bands are merged. Thus, the conformation-dependent EA spectral features of isomeric NAP-bridged biradical complexes mirror those of PhMeₙ-bridged isomers.

The isomer with the lowest energy CT band is the 2,6-NAP around 22,000 cm⁻¹. All other isomers show ILCT bands around 23,000 cm⁻¹ with the exception of 1-NN-7-SQ-NAP which shows the most blue-shifted ILCT at almost 24,000 cm⁻¹. Should the energy of the SQ → B-NN ILCT band be proportional to the magnitude of J_{SQNN}, these plots would indicate J_{2,6-NAP} < J_{1-SQ-7-NN-NAP} < J_{1,4-NAP} < J_{1,5-NAP} < J_{1-NN-7-SQ-NAP}. As will be discussed in the next section, this is not the observed order of J_{SQNN} couplings. Recent work analyzing the effect of bridge torsions on electronic structure in SQ-B-NN complexes also showed that these individual electronic effects alone do not predict the magnitude of J_{SQNN}, as both SQ and NN torsions relative to the bridge combine to attenuate J_{SQNN}.85

<table>
<thead>
<tr>
<th>Compound</th>
<th>SQ→B-NN ILCT (cm⁻¹)</th>
<th>ε_{max} (M⁻¹ cm⁻¹)</th>
<th>NN→NN π→π* (cm⁻¹)</th>
<th>ε_{max} (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5-NAP</td>
<td>23,300</td>
<td>5970</td>
<td>25,500</td>
<td>6,470</td>
</tr>
<tr>
<td>2,6-NAP</td>
<td>22,200</td>
<td>19,400</td>
<td>26,000</td>
<td>15,650</td>
</tr>
<tr>
<td>1,4-NAP</td>
<td>23,000</td>
<td>8830</td>
<td>25,100</td>
<td>7,350</td>
</tr>
<tr>
<td>1-SQ-7-NN-NAP</td>
<td>23,150</td>
<td>6880</td>
<td>26,100</td>
<td>12,890</td>
</tr>
<tr>
<td>1-NN-7-SQ-NAP</td>
<td>23,980</td>
<td>6080</td>
<td>26,560</td>
<td>8,050</td>
</tr>
</tbody>
</table>
II.4.4 Superconducting Quantum Interference Device (SQUID) Magnetometry

The final test of a newly generated SQ-B-NN biradical is the most important to any analysis of its electronic coupling: determine the magnitude of $J$ through nonlinear least-squares fits of variable-temperature magnetic susceptibility data. This experiment is conducted in the solid state with only X-ray-quality crystals to allow the direct comparison of exchange/electronic coupling to differences between bridge topography between compounds. The magnitude of $J$ is calculated as a fit parameter of a plot of magnetic susceptibility as a function temperature, exemplified in Figure II-18.

![Figure II-18. The $\chi_{\text{para}}$/$T$ plots of thirteen SQ-B-NN biradical complexes overlain over one another. The complexes displaying a $J$ value are antiferromagnetic in nature while those displaying a positive slope](image)

While this is arguably the most important characterization of a new SQ-B-NN biradical, it is important to also measure the saturation magnetization of each biradical first to determine the field at which to run the magnetic susceptibility experiment (making sure $\chi_{\text{para}}$ is linear with applied field, H). This is done by taking the same X-ray quality crystalline sample and subjecting it to a variable magnetic field at a constant temperature (typically 2 K).

The data collected is used to generate a saturation magnetization plot that shows at what field the sample saturates, as well as the ground-state molecular “spin” of the sample ($M_{\text{sat}} = N g m_B S$, where $N =$ Avogadro’s number, $g$ is Landé’s constant, $m_B$ is the Bohr magneton, and...
S is the spin quantum number of the ground state). Both pieces of data are important factors in the analysis of SQ-B-NN compounds. The deviation from linearity of magnetization vs. applied field determined the maximum applied field strength to be used for the variable-temperature magnetic susceptibility measurements, while the molecular spin of the sample offers insight into the purity and ground spin-state of the compound. Since SQ-B-NN compounds have two interacting unpaired electrons per molecule, the molecular spin should be no more than 2 m\(_B\), and in fact is often less than 2 m\(_B\) because (1) the Brillouin function predicts this for H/T < 2 for 3.5 Tesla/Kelvin (the maximum value of H/T for our 7 T instrument), (2) antiferromagnetic intermolecular interactions that reduce the moment, or (3) the molecule is a ground state singlet.

Figure II-19. Saturation magnetization plots of 1,5-NAP (A), 2,6-NAP (B), 1,4-NAP (C), 1-NN-7-SQ-NAP (D), and 1-SQ-7-NN-NAP (E).
Thus “spin” < 2 m_B is routinely observed in SQ-B-NN biradicals, which when pure biradicals typically saturate at ~1.8 Bohr magnetons. The saturation magnetization plots of 2,6-NAP, 1,5-NAP, 1-SQ-7-NN-NAP, and 1-NN-7-SQ-NAP are shown in Figure II-19.

All naphthyl-bridged SQ-B-NN compounds show saturation magnetization plots with limits of just below 2 m_B as expected except for the 1-NN-7-SQ-NAP isomer. This isomer also acts differently than the other isomers in its variable temperature magnetic susceptibility plot (Figure II-22) showing a x_{para}T vs T plot with a trend representative of an isomer with an antiferromagnetic exchange coupling. This result was unexpected; however, it can be explained by inspecting the crystal structure of the 1-NN-7-SQ-NAP isomer. When considering the whole crystal lattice of the 1-NN-7-SQ-NAP isomer it is notable that there are four biradical compounds in the unit cell (Figure II-20).

![Figure II-20. Crystal structure of 1-NN-7-SQ-NAP with unit cell showing (left) and zoomed in unit cell with π-stack interim distance labeled.](image)

More importantly, the naphthalene bridges of the two molecules in the unit cell are stacked in such a way that provides a moderately strong antiferromagnetic coupling (pseudo σ-bonding). This stacking separates the molecules by a value of 3.5 Å, just 0.1 Å longer than the sum of the Van Der Waal radius between two carbon atoms (Van Der Waal radius of carbon = 1.7 Å).^{119, 120} This distance is typical of a π-stacking interaction between two aromatic compounds. This π-stack interaction has its own exchange coupling that is not only antiferromagnetic in nature but also capable of dominating the ferromagnetic interaction present between the SQ and NN of the D-B-A moiety. This second exchange coupling presented a
difficult scenario where the fitting parameters used to evaluate typical SQ-B-NN biradicals are rendered moot. The system had to be evaluated using a new set of fit parameters derived from the spin functions and eigenvalues of the idealized system.

Figure II-21. Idealized spin interactions between two 1-NN-7-SQ-NAP molecules. Here $J_{\text{inter}}$ is the intermolecular exchange coupling, $J_{\text{SQ-NN}}$ is the exchange coupling between an individual donor SQ and acceptor NN, and the four spin centers are labeled 1-4.

The system was modeled as a linear tetramer of spins with three exchange couplings, two of equal value (the SQ-NN exchange coupling) and one of separate magnitude (the intermolecular interaction of the four spins), visualized in Figure II-21 where $J_{\text{SQ-NN}}$ is the exchange between donor and acceptor and $J_{\text{inter}}$ is the intermolecular exchange. This resulted in a 16x16 spin Hamiltonian matrix producing six eigenvalues: one of quintet, three of triplet, and two of singlet spin characteristics. The eigenvalues of the six energies are as follow:

Quintet: $E_{2a} = -0.5J_{\text{inter}} - J_{\text{SQ-NN}}$

Triplet: $E_{1a} = -0.5J_{\text{inter}} + J_{\text{SQ-NN}}$

Triplet: $E_{1b} = +0.5J_{\text{inter}} - \sqrt{J_{\text{inter}}^2 + J_{\text{SQ-NN}}^2}$

Triplet: $E_{1c} = +0.5J_{\text{inter}} + \sqrt{J_{\text{inter}}^2 + J_{\text{SQ-NN}}^2}$

Singlet: $E_{0a} = +0.5J_{\text{inter}} + J_{\text{SQ-NN}} - \sqrt{J_{\text{inter}}^2 - 2J_{\text{inter}} \cdot J_{\text{SQ-NN}} + 4J_{\text{SQ-NN}}^2}$
Singlet: \( E_{0b} = +0.5J_{\text{inter}} + J_{SQ-NN} + \sqrt{J_{\text{inter}}^2 - 2J_{\text{inter}} \cdot J_{SQ-NN}} + 4J_{SQ-NN}^2 \)

These quantities, along with their corresponding spin quantum numbers, can be used to solve equation (2.1) for an expression that can be used to fit the magnetitic data acquired for the 1-NN-7-SQ-NAP isomer (2.2).

\[
\chi = \frac{Ng^2 R^2 \sum S(S+1)(2S+1)e^{-\frac{E_S}{k_B T}}}{2k_B T} \sum S(S+1)e^{-\frac{E_S}{k_B T}}
\]

\[ (2.1) \]

\[
\chi = \frac{Ng^2 R^2 \text{NUM}}{3k_B T \text{DEN}}
\]

\[ (2.2) \]

NUM = 

\[
6e \frac{0.5J_{\text{inter}} - J_{SQ-N}}{k_B T} + 6e \frac{-0.5J_{\text{inter}} + \sqrt{J_{\text{inter}}^2 + J_{SQ-N}^2}}{k_B T} + 6e \frac{-0.5J_{\text{inter}} - J_{SQ-N}}{k_B T} + 30e \frac{0.5J_{\text{inter}} + J_{SQ-N}}{k_B T}
\]

DEN = 

\[
1e \frac{-0.5J_{\text{inter}} - J_{SQ-NN} + J_{\text{inter}}^2 - 2J_{\text{inter}} \cdot J_{SQ-NN} + 4J_{SQ-N}^2}{k_B T} \]

\[
+ 1e \frac{-0.5J_{\text{inter}} - J_{SQ-NN} - J_{\text{inter}}^2 - 2J_{\text{inter}} \cdot J_{SQ-NN} + 4J_{SQ-N}^2}{k_B T} + 3e \frac{0.5J_{\text{inter}} - J_{SQ-NN}}{k_B T}
\]

\[
+ 3e \frac{-0.5J_{\text{inter}} + J_{SQ-NN}}{k_B T} + 3e \frac{-0.5J_{\text{inter}} + J_{SQ-NN}}{k_B T} + 5e \frac{0.5J_{\text{inter}} + J_{SQ-NN}}{k_B T}
\]

1-NN-7-SQ-NAP was found to display \( J_{\text{inter}} = -23 \text{ cm}^{-1} \) and \( J_{SQ-NN} = +4 \text{ cm}^{-1} \) compared to its partner isomer 1-SQ-7-NN-NAP, which exhibited \( J_{SQNN} = +10 \text{ cm}^{-1} \) (Figure II-22). This result agrees well with the crystal structure of the two compounds as 1-NN-7-SQ-NAP is more twisted overall than the 1-SQ-7-NN-NAP isomer (Figure II-11) and, as such, is expected to exhibit a
lesser degree of coupling. The other naphthyl isomer’s magnetic data (including 1-SQ-7-NN-NAP) were fit using the singlet-triplet model of exchange coupling derived in Chapter I.3.4

Figure II-22. Variable temperature magnetic susceptibility data for synthesized naphthyl bridged SQ-NN biradicals 1,4-NAP (A), 2,6-NAP (B), 1,5-NAP (C), 1-NN-7-SQ-NAP (D), and 1-SQ-7-NN-NAP (E).

The 1,4-NAP, 2,6-NAP, and 1,5-NAP isomers behaved in a manner typical of previously analyzed Shultz Group SQ-B-NN biradicals, presenting exchange couplings of +211 cm\(^{-1}\), +59 cm\(^{-1}\), and +193 cm\(^{-1}\) respectively. These values, as well as those of the 1,7-substituted isomers, are the reported exchange coupling constants of the two isomers without accounting for torsion angles between the bridge and donor/acceptor units. In order to report these two values in terms of a rectification ratio, as was done with the pyridine-thiophene SQ-B-NN biradicals in the 2017 Chemical Science paper,\(^46\) the reported exchange couplings must be corrected for their determined torsion angles. This is done through Equation 2.3.
\[ \sqrt{J_{SQBNN}} \propto H_{SQNN} = \frac{\cos \theta_{SQB} H_{SQB} \cos \theta_{BNHNN}}{\Delta} \cdot \left( \frac{\cos \theta_{BBH}}{\Delta} \right) \approx c \sqrt{g} \]  \hspace{1cm} (2.3)

For example, when the determined values of \( J \) and the corresponding torsion angles of the 2,6-NAP and 1,5-NAP isomers are inserted into (2.3) the resulting rectification ratio is determined to be 14 favoring the 1,5-NAP isomer (2.4)

\[ \frac{J_{2,6}^0}{J_{1,5}^0} = J_{1,5} \times 0.73^2 \times = \frac{193 \text{ cm}^{-1}}{59 \text{ cm}^{-1}} = \frac{1.616 \text{ cm}^{-1}}{110 \text{ cm}^{-1}} = \frac{8.0}{0.5} = 14 = RR^0 \]  \hspace{1cm} (2.4)

This evaluation was performed for all five isomers with their relevant partners and the resulting corrected \( J \) values, rectification ratios are shown in Table II-6. The electronic couplings, \( H_{SQNN} \) were also estimated through a simple relationship between \( J_{DA} \) and \( H_{DA} \) in SQ-B-NN D-B-As and the parent, unbridged SQ-NN complex.\(^9\)

2,6-NAP was the least twisted of the naphthyl isomers with the NN almost completely planar with the bridge (4° torsion) and the SQ subunit rotated 43° away from planarity. As such, \( J_{\text{experimental}} \) for 2,6-NAP was not impacted greatly by the correction and the idealized planar complex was calculated to have \( J_{\text{corrected}} = +110 \text{ cm}^{-1} \). The isomers 1,4-NAP and 1,5-NAP on the other hand were greatly twisted, showing torsion angles between the bridge and the donor/acceptor units of greater than 50°. Due to these large torsions angles the calculated planar geometry exchange coupling values for 1,4-NAP and 1,5-NAP differed greatly from their experimental values, giving \( J_{\text{corrected}} \) of 2,060 cm\(^{-1}\) and 1,583 cm\(^{-1}\) for 1,4-NAP and 1,5-NAP.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( J_{\text{experimental}} ) (cm(^{-1}))</th>
<th>( J_{\text{corrected}} ) (cm(^{-1}))</th>
<th>RR</th>
<th>( H_{SQNN} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5-NAP</td>
<td>193</td>
<td>1,583</td>
<td>3.2</td>
<td>6,300</td>
</tr>
<tr>
<td>2,6-NAP</td>
<td>59</td>
<td>110</td>
<td></td>
<td>3,500</td>
</tr>
<tr>
<td>1,4-NAP</td>
<td>211</td>
<td>2,060</td>
<td>3.6</td>
<td>6,600</td>
</tr>
<tr>
<td>1-SQ-7-NN-NAP</td>
<td>10.3</td>
<td>25.1</td>
<td>2.3</td>
<td>1,500</td>
</tr>
<tr>
<td>1-NN-7-SQ-NAP</td>
<td>4.5</td>
<td>26.8</td>
<td></td>
<td>1,000</td>
</tr>
</tbody>
</table>
respectively. These magnitudes of $J_{\text{SQNN}}$ are simply unreasonable, illustrating the limits of correcting J-values using a simple cosine-squared relation.\textsuperscript{46} As such, calculations at a higher level of theory are required to access the value of $J_{\text{SQNN}}$ for the idealized planar conformations.

As discussed previously, conductance and exchange coupling are both related to the square of $\text{H}_{\text{DA}}$. Because of this relation, the determined $J_{\text{SQNN}}$ of these complexes can be compared to one another to estimate a rectification ratio (RR) between two SQ-B-NN compounds thought of as analogues of molecular rectifiers. When comparing the experimentally determined $J_{\text{SQNN}}$ values between the compounds were the donor and acceptor were attached to positions with large Hückel coefficients (1,4-NAP and 1,5-NAP) and the compound where the donor and acceptor were attached to positions with low Hückel coefficients (2,6-NAP) fairly large RRs are calculated. 1,5-NAP’s $J_{\text{SQNN}}$ ($J_{1,5-\text{NAP}} = +193 \text{ cm}^{-1}$) is over three-fold that of 2,6-NAP ($J_{2,6-\text{NAP}} = +59 \text{ cm}^{-1}$) giving a RR of 3.2 favoring 2,6-NAP. The RR calculated when comparing 1,4-NAP ($J_{1,4-\text{NAP}} = +211 \text{ cm}^{-1}$) to 2,6-NAP is 3.6 favoring 1,4-NAP. Both RRs suggest that the positioning of donor and acceptor regarding bridge electron density makes a great deal of difference in the electronic exchange between the two subunits. In both cases the isomer with the donor and acceptor attached to bridge positions with large Hückel coefficients in orbitals displayed a $J_{\text{SQNN}}$ greater than three-times that of the isomer with SQ and NN attached at positions with lower Hückel coefficients. 1,4-NAP exhibited a larger value of electronic exchange compared to 1,5-NAP even though they both had their SQ and NN subunits attached to positions with identically large Hückel coefficients and had similar bridge-subunit torsion angles. This difference of coupling can be attributed partially to a distance drop off as the SQ and NN subunits are further apart in the 1,5-substituted isomer than in the 1,4-substituted isomer and exchange coupling decreases exponentially with distance.\textsuperscript{9} This also is likely a reflection of the lower energy pathway assessable to 1,4-NAP since 1,5-NAP must utilize the LUMO+2 bridge orbital to facilitate coupling between the two fused six-member rings of naphthalene. These rectification ratios calculated from experimentally determined $J_{\text{SQNN}}$ are different than those calculated from measured single-molecule conductance measurements made by Taniguchi and coworkers in 2011 (RR = 7.9 between 1,4- and 2,6-substitutions and RR = 1.6 between 1,5- and 2,6-substitutions),\textsuperscript{65} however the trend of conductance magnitude remains consistent with that of exchange coupling (1,4- > 1,5- > 2,6-substitution). This differences in magnitude could be reminiscent of a difference in pathway dependence as the nodal carbons could impact
conductance more than it does exchange coupling. Recent work by Kirk, et al. shows that the HOMO is the dominant orbital contributing to the computed conductance values for SQ-B-NN biradical magnetic superexchange coupling. However, naphthalene’s HOMO has the same nodal pattern as its LUMO. This could explain the stark contrast exhibited between the conductance of the 1,4-subsituted bridge and other isomers in the work done by Taniguchi and coworkers, as well as explain why the RR found between 1,4-NAP and 2,6-NAP is much lower than that found from the same bridge geometries through conductance. In addition our use of experimental J-values to estimate RRs also reflects differences in molecular conformations. Thus, critical analysis of coupling with respect to orbital coefficients is obfuscated by differences in conformation.

The unimolecular rectifier analogues 1-SQ-7-NN-NAP and 1-NN-7-SQ-NAP were also greatly twisted so the idealized J_{SQNN} magnitudes for a planar conformation cannot be used to draw any conclusions. However, there was a notable RR between the experimentally determined exchange couplings of the two isomers. The isomer 1-SQ-7-NN-NAP exhibited a larger magnitude of exchange coupling than 1-NN-7-SQ-NAP by a factor of just over 2 (RR = 2.3). This finding is in agreement with the initial hypothesis of the study, suggesting attaching the donor SQ subunit to a position on the bridge with a larger Hückel coefficient facilitates coupling between it and the combined molecular fragment of the bridge connected to the NN. However, the veracity of this conclusion is clouded by differences in conformation.

**II.5 Conclusions**

Five naphthyl bridged SQ-B-NN biradicals have been synthesized, characterized, and evaluated for exchange coupling. These isomers were targeted to evaluate the effect of bridge substitution, regarding Hückel coefficients on the overall exchange coupling between the donor and acceptor. When comparing the first set of isomers (2,6-NAP, 1,4-NAP, and 1,5-NAP) it becomes appears that the points of donor and acceptor bridge substitution play a key role in the magnitude of J_{SQNN} (J_{1,4-NAP} > J_{1,5-NAP} > J_{2,6-NAP}). However, this conclusion must be viewed with some skepticism given the large differences in molecular conformation within the series. That said, even with the large SQ-B and NN-B torsion angles in the 1,4- and 1,5-substituted naphthyl isomers the experimentally-determined J_{SQNN} for 1,4-NAP and 1,5-NAP were greater
than three-fold larger than that of 2,6-NAP (RR_{1,4} = 3.6, RR_{1,5} = 3.2). These RRs are the largest calculated using ratios of $J$-values to date. This provide further support that the electronic structure of the bridge (i.e. AO coefficients of the LUMO) can greatly impact exchange coupling in D-B-A biradical complexes. This observation is consistent with the initial hypothesis that attaching donor and acceptor units to bridge positions with larger Hückel coefficients will produce compounds with a greater exchange coupling than partner compounds with donor and acceptor connected to positions with lesser coefficients. The exchange parameter $J_{1,4\text{-NAP}}$ was larger than $J_{1,5\text{-NAP}}$ even though they had approximately equivalent bond torsions and identical Hückel coefficients at points of attachment. This is likely due to the difference in exchange pathways between the two isomers as well as SQ-NN distances. 1,5-NAP has its donor and acceptor subunits on different sides of the fused ring bridge, meaning that the LUMO cannot be used in the exchange pathway due to the nodes at the central carbons while 1,4-NAP has both donor and acceptor on the same ring. As a result, 1,5-NAP must use the HOMO+2 for exchange coupling, which is the lowest energy orbital that contains electron density at both points of substitution as well as on the central fusing carbons. Since the HOMO+2 also has appropriate structure to facilitate exchange in 1,4-NAP the 1,4-substituted isomer may possess multiple exchange pathways. This, in addition to the slight increase in distance between the spin centers in 1,5-NAP compared to 1,4-NAP explains the larger magnitude of $J_{1,4\text{-NAP}}$.

The unimolecular rectifier analogue 1,7-substituted isomers showed a notable difference in $J_{SQNN}$, presenting a RR of 2.3 favoring the isomer 1-SQ-7-NN-NAP. This result is inconsistent with the initial hypothesis that attaching the acceptor unit to a position on the bridge with larger Hückel coefficients will yield a larger magnitude of exchange coupling due to an increase in mixing between the acceptor NN orbitals and the FOMOs of the bridge molecular fragment. These initial conclusions are based on the experimentally determined magnitudes of $J_{SQNN}$ and do not consider differences in bridge-subunit torsions because the torsions present in both 1,7-substituted isomers are too large to be evaluated with the simple cosine relation outlined earlier. Further calculations at a higher level of theory are required to evaluate the true difference in exchange coupling between these two isomers at an idealized planar geometry.

It is also important to note that the complicated spin system shown by the 1-NN-7-SQ-NAP isomer may need to be evaluated using high-level computations. The complexity of the
biradical dimer spin model may have more than one unique solution and more calculations are needed before making final conclusions about the magnitude of exchange coupling. That being considered, the current working model for fitting the magnetic susceptibility data gathered from 1-NN-7-SQ-NAP shows virtually no error in the fit values of $J_{\text{inter}}$ and $J_{\text{SQNN}}$ and the fit parameters alone can be used to simulate magnetic data characteristic of well-studied cases. As such, it seems reasonable that the proposed conclusions could very well be coincident with the final conclusions of the 1,7-NAP unimolecular rectification analogue study following subsequent computational investigation.
II-6 Experimental

4-bromo-2-(tert-butyl)phenol (1): 2-(tert-butyl)phenol (39.8 g, 0.270 mmol) was charged to an oven-dried 250 mL round-bottom flask with stir bar and dissolved in 120 mL of dichloromethane. The flask was fit with an addition funnel and a drying-tube then chilled to -40 °C. Liquid bromine (40.96 g, 0.29 mol) was poured into the dripping funnel, diluted with CH₂Cl₂ and added to the chilled reaction solution dropwise. Upon completion the reaction was stirred and allowed to warm to room temperature overnight. The reaction was then quenched with water and transferred to a separatory funnel, diluted with diethyl ether, and washed with brine and sodium bicarbonate. The solution was then dried over sodium sulfate then concentrated to yield 1 (55.2 g, 90%) as a dark red oil. Characterization data was consistent with ref. 76.

5-bromo-1-(tert-butyl)-2,3-bis(methoxymethoxy)benzene (4): 4-bromo-2-(tert-butyl)phenol (7.1 g, 31 mmol) was charged to an oven-dried 250 mL round-bottom flask with stir bar, chilled to 0 °C, and dissolved in 60 mL dichloromethane and 20 mL methanol. 2-Iodoxybenzoic acid (9.52g, 34 mmol) was added to the mixture at 0 °C and allowed to stir for 30 min. The solvent was removed and the oil was dissolved in hexanes, passed through a silica pad, and eluted with hexanes. The filtrate was concentrated under reduced pressure and a red-brown solid was isolated. Sodium dithionite (6.8 g, 39 mmol) was dissolved in minimal DI water and chilled to 0 °C, the isolated red-brown solid was dissolved in minimal acetone then dripped into the chilled sodium dithionite solution. The mixture was stirred at 0 °C until yellow then transferred to a separatory funnel, diluted with diethyl ether, washed with brine and the organic layer was then dried over sodium sulfate. The solution was concentrated under reduced pressure to give a yellow oil. The oil was transferred to a nitrogen-purged oven-dried 100 mL 2-neck round-bottom flask with stir bar, dissolved in 40 mL of dichloromethane and chilled to 0 °C. Chloromethyl methyl ether/methyl acetate mixture (8.0 g, 97 mmol) was added to the reaction solution at 0 °C then N,N-diisopropylethylamine (12.8 g, 100 mmol) was added to the mixture dropwise. Following the dropwise addition the solution was stirred at 0 °C for 30 min before being brought to reflux overnight. The reaction mixture was diluted and transferred to a separator funnel with diethyl ether, washed with ammonium chloride then brine, dried over Na₂SO₄, then passed through a silica pad and eluted with diethyl ether and dried over sodium sulfate. The solution
was concentrated under reduced pressure to 4 (6.6 g, 64%) as a dark red oil. Characterization data was consistent with ref. 76.

2-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5): 1.05 g (3.15 mmol) of 4 was charged to an oven-dried round-bottom flask with stir bar and purge-pumped three times. The red oil was dissolved in 4 mL of dry tetrahydrofuran and chilled to -78 °C. 4.2 mL of 1.7 M tert-butyl lithium in pentane was added to the solution dropwise then the mixture was stirred at -78 °C for 10 min then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.73 g, 3.9 mmol) was added to the solution dropwise. The solution was stirred at -78 °C for 10 minutes before being warmed to room temperature and stirred overnight. The reaction mixture was diluted with diethyl ether, passed through a silica pad and eluted with diethyl ether, concentrated under reduced pressure and purified via flash chromatography to yield 5 (0.72 g, 60%) as a light yellow solid. Characterization data was consistent with ref. 76.

2,3-dimethyl-2,3-dinitrobutane (6): 2-Nitropropane (51.69 g, 580 mmol) and 120 mL of 6 M sodium hydroxide were charged to a 1 L round-bottom flask with stir bar and chilled to 0 °C in an ice bath. Bromine (48.2 g, 302 mmol) was added dropwise to the flask, 320 mL of ethanol was added to the flask following addition and the mixture was brought to reflux overnight. The reaction was quenched with 100 mL of water and stirred for 1 h the following day then the mixture was filtered, washed with ethanol, then dried to obtain 32.2 g of 6 (63%), a colorless solid. Characterization data was consistent with ref. 78.

N,N-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) (BHA, 7): Aluminum foil (4.7 g, 170 mmol) was torn into small chunks and placed in a 500 mL round-bottom flask with stir bar and covered in water. Mercury(II) chloride (3.2 g, 12 mmol) was added to the reaction vessel with water and the mixture was stirred for 5 min then the water was decanted off. The amalgam was washed three times with ca. 50 mL water, methanol, then THF then covered with a layer of tetrahydrofuran. The vessel was chilled to 0 °C then 6 (5.0 g, 28 mmol) was added to the mixture followed by 17 mL of water. The reaction was stirred for 1 h then filtered over a pad of celite
and washed with tetrahydrofuran and methanol. The filtrate was concentrated under reduced pressure to afford a colorless solid which was then purified through recrystallization from methanol to yield BHA (2.2 g, 53%). Characterization data was consistent with ref. 53.

1-(4-isopropylphenyl)ethan-1-one (8): Aluminum(III) chloride (30.00 g, 225.0 mmol) was charged to an oven-dried 1 L round-bottom flask with stir bar and dissolved in 325 mL of carbon disulfide. The solution was chilled to 0 °C then acetyl chloride (16.1 mL, 0.226 mmol) was added dropwise with rigorous stirring, the solution was then left to stir for 1 h at 0 °C. The reaction was then poured into a solution of 300 mL of cooled D.I. water and 10 mL concentrated hydrochloric acid. 120 mL of saturated sodium bicarbonate was added and the mixture was then allowed to stir for 15 min. The aqueous layer was separated and the organic layer was washed with sodium bicarbonate and brine then dried over sodium sulfate. The reaction mixture was then filtered and concentrated under reduced pressure to give 8 (25.77 g, 85%) as an amber oil. Characterization data was consistent with ref. 74.

1-(4-isopropylphenyl)butane-1,3-dione (9): Sodium hydride (3.1 g, 75 mmol) was charged to a 250 mL round-bottom flask with stir bar then washed 3 times with hexanes, a layer of hexanes was left over the solid after the last wash. The reaction vessel was cooled to 0 °C and 50 mL of THF was added. Ethanol (4.45 mL, 76 mmol) was slowly added to the chilled solution, the mixture was then warmed to 50 °C and stirred for 2 h. Ethyl acetate (59.0 mL, 604 mmol) was added to the mixture dropwise followed by the dropwise addition of 8 (10.0 g, 60.0 mmol). The mixture was left in the ice bath overnight to stir and slowly warm to room temperature. The dark red solution was concentrated under reduced pressure and the resulting solid was washed with hexanes then dried under vacuum. The tan solid was dissolved in minimal diethyl ether, methanol, and a small amount of water and chilled in an ice bath, the mixture was then acidified with concentrated hydrochloric acid until the solution turned yellow. The acidic mixture was then transferred to a separatory funnel, diluted with diethyl ether and washed with brine. The solution was dried over sodium sulfate then filtered and concentrated under reduced pressure to yield 9 (7.96 g, 65%) as a red-orange oil. Characterization data was consistent with ref. 75.
**3-(4-isopropylphenyl)-5-methyl-1H-pyrazole (10):** 7.96 g (39 mmol) of 9 was charged to an oven-dried 250 mL round-bottom flask with stir bar and dissolved in 100 mL of dry ethanol. 7 drops of concentrated hydrochloric acid were added to the solution followed by the dropwise addition of hydrazine monohydrate (4.4 g, 78 mmol) and the mixture was brought to reflux overnight. The reaction mixture was concentrated under reduced then transferred to a separatory funnel with diethyl ether, washed with brine and dried over sodium sulfate. The solvent was removed in vacuo to 10 (5.22 g, 67%) as a colorless solid which was then recrystallized from petroleum ether. Characterization data was consistent with ref. 73.

**KBHTp^{Cum, Me} (11):** 31.3 g (6.38 mmol) of 10 was charged to an oven-dried Schlenk flask with a glass stir bar. Potassium borohydride (0.12 g, 2.22 mmol) was then added and the vessel was left under vacuum for 2 h. The reaction vessel was filled with nitrogen then placed in a sand bath preheated to 240 °C and the melted solids were stirred for 16 h. The resulting glass-like solid was covered with 40 mL of hexanes and sonicated until the glass broken up. The slurry was filtered and the recovered solid was covered with acetonitrile. The acetonitrile covering the solid was heated to dissolve the crystals. The solution was once again cooled to -41 °C until crystals formed, the acetonitrile was removed with a syringe and the KBHTp^{Cum, Me} crystals (0.460 g, 34%) were dried under vacuum and stored under inert gas. Characterization data was consistent with ref. 64.

**Zn(OH)Tp^{Cum, Me} (12):** Zinc(II) perchlorate hexahydrate (180 mg, 0.48 mmol) and KBHTp^{Cum, Me} (306 mg, 0.48 mmol) were charged to an oven-dried 100 mL Schlenk flask with stir bar and covered with 60 mL dry methanol. The slurry was stirred for 1.5 h then potassium hydroxide (132 mg, 2.36 mmol) was cannulated into the reaction vessel in minimal methanol, the mixture was stirred for 2 h. The reaction mixture was passed through an oven-dried medium frit and washed through with dichloromethane. The filtrate was concentrated under reduced pressure until about 75% of the solvent was removed until a colorless precipitate formed. To the resulting slurry 1 mL of hexanes was added and the mixture was cooled in an ice bath. The slurry was filtered to yield Zn(OH)Tp^{Cum, Me} (285 mg, 87%) as a colorless solid which was stored under inert gas. Characterization data was consistent with ref. 64.
(6-bromonaphthalen-2-yl)methanol (13): 6-Bromo-2-naphthoic acid (2.5 g, 9.8 mmol) was charged to an oven-dried 100 mL round-bottom flask with stir bar and purge-pumped three times. The naphthoic acid was dissolved in dry tetrahydrofuran then chilled to 0 °C. Boranetetrahydrofuran (2.2 g, 25 mmol) was added slowly and the reaction was warmed to room temperature and stirred overnight. The solution was diluted with a small amount of ethyl acetate then quenched slowly with water. After being quenched, 8 mL of 1 M sodium hydroxide solution was added to the reaction and the solution was then diluted with ethyl acetate and washed with brine. The organic layer was isolated and concentrated under reduced pressure to yield 13 (2.18 g, 98%) as a colorless solid. Characterization data was consistent with ref. 77.

6-bromo-2-naphthaldehyde (14): Pyridinium chlorochromate (0.606 g, 2.81 mmol) was homogenized with 4x by mass of silica and charged to an oven-dried 100 mL 2-neck round-bottom flask and purge-pumped 3 times. 30 mL of dry dichloromethane was added to the flask and the mixture was brought to reflux. 13 (0.309 g, 1.38 mmol) was added to the refluxing solution as a slurry in 15 mL of dry dichloromethane then left to reflux overnight. The reaction mixture was passed through a florisil pad and eluted with dichloromethane, the filtrate was then concentrated to yield 14 (0.29 g, 96%) as a white solid. Characterization data was consistent with ref. 48.

5-bromo-1-naphthaldehyde (15): 1-Naphthaldehyde (10.05 g, 64.36 mmol) was charged to a 100 mL oven-dried round-bottom flask with stir bar and dissolved in 20 mL chloroform and the mixture was brought to reflux. Liquid bromine (10.28 g, 64.33 mmol) was dripped into the reaction and the mixture was brought to reflux until the evolution of hydrogen bromide ceased. Once cooled the solution was added to 100 mL of chilled pH 7 buffer solution, stirred for 30 min, then filtered through a glass wool plug. The organic layer was separated, dried over sodium sulfate, then filtered through a silica pad and eluted with chloroform. The filtrate was concentrated under reduced pressure to yield 15 (6.1 g, 40%) as a tan solid in a 1.9:1 ratio of product to starting material. Characterization data was consistent with ref. 49.
**2,7-dibromo-2,4-dihydronaphthalen-1(2H)-one (16):** An oven dried 200 mL round bottom flask was charged with 2.63 g (11.7 mmol) 7-bromo-3,4-dihydronaphthalene-1(2H)-one, 2.900 g (16.4 mmol) \(n\)-bromosuccinimide, and 0.250 g (1.31 mmol) \(p\)-toluenesulfonic acid. The flask was purge-pumped three times then the solids were dissolved in 80 mL DCM and the solution was brought to reflux for 3 h in the dark then cooled to room temperature. The reaction mixture was diluted with Et\(_2\)O, washed with brine, passed through a celite pad and dried over Na\(_2\)SO\(_4\). The solution was concentrated under reduced pressure and purified via flash chromatography (20% EtOAc/Hexanes) and the resulting oil was added to a 100 mL oven dried round bottom flask with 2.640 g (30.39 mmol) lithium carbonate and 1.47 g (19.9 mmol) lithium bromide then purge-pumped three times. The solids were suspended in 50 mL of DMF and heated at 140° C for 16 h. The slurry was cooled to room temperature then filtered and the solid was washed with EtOAc. The filtrate was washed with ammonium chloride, water, and brine then dried over sodium sulphate and concentrated under reduced pressure. The reaction was then purified via flash chromatography to yield 1.958 g (89%) 17. Characterization data was consistent with ref. 70.

**7-bromo-1-(methoxymethoxy)naphthalene (18):** 17 (0.9391, 4.21 mmol) and a catalytic amount (1%) of 4-(dimethylamino)pyridine were added to an oven dried 50 mL round bottom flask and purge-pumped three times. 20 mL dry DCM was then added to the round bottom flask and the mixture was then chilled to 0 °C. 3 mL (16.82 mmol) \(n\)-ethyldiisopropylamine was then added to the reaction dropwise and the mixture was allowed to stir for 15 min before 1.71 mL (10.52 mmol) Chloromethyl methyl ether/methyl acetate solution was added and the reaction was brought to reflux for 16 h. The reaction was cooled to room temperature, diluted with Et\(_2\)O and washed with saturated ammonium chloride and brine solutions then dried over sodium sulphate and concentrated under reduced pressure. The resulting oil was purified via flash chromatography (20% EtOAc/hexanes) to yield 1.016 g (91%) 18. \(^1\)H NMR (400MHz ,CDCl\(_3\)) \(d = 8.42\) (s, 1 H), 7.66 (d, \(J = 8.4\) Hz 1 H), 7.55 (d, \(J = 8.4\), 3 H), 7.42 (d, \(J = 6.8\) Hz, 1 H), 7.38 (t, \(J = 8\) Hz, 1 H), 7.12 (d, \(J = 6.8\) Hz, 1 H), 5.38 (s, 2 H), 3.54 (s, 3H).
7-formylnaphthalen-1-yl trifluoromethanesulfonate (20): 18 (306 mg, 1.15 mmol) was charged to an oven dried 50 mL round bottom flask and purge-pumped three times. D was dissolved in 15mL dry THF and chilled to -78 °C. n-BuLi (1.38 mmol) was added to the reaction dropwise and the solution stirred for 15m before 0.27 mL (3.45 mmol) of dry DMF was added. The reaction was warmed to room temperature and stirred for 2 h, then 1 mL of water was added to the reaction and the mixture was left to stir 16 h. The solution was diluted with Et$_2$O, washed with brine, eluted through a silica pad with 20% Et$_2$O/hexanes and dried with sodium sulphate then concentrated under reduced pressure to afford 233 mg (94%) of a colorless oil. The oil was added to a 100 mL round bottom flask and dissolved in 10 mL MeOH, 1 mL of concentrated HCl was added and the solution stirred overnight. The mixture was diluted with Et$_2$O, washed with brine and dried over sodium sulphate, then the solvent was removed under reduced pressure. The flask with the resulting oil was purge-pumped three times before 20 mL dry DCM and 0.36 mL (4.63 mmol) dry pyridine were added, and the mixture was cooled to 0 °C. 0.52 mL (3.10 mmol) triflic anhydride was added to the reaction slowly in 5 mL DCM and the reaction stirred and warmed to room temperature for 2 h. The reaction was diluted with 10 mL Et$_2$O and 5 mL of 2M were added before the mixture was transferred to a separatory funnel and washed with sodium bicarbonate and brine. The organic layer was dried with sodium sulphate and the solvent was removed under reduced pressure. The resulting oil was purified via flash chromatography to yield 250 mg (53%) 20. $^1$H NMR (400MHz,CDCl$_3$) d = 10.23 (s, 1 H), 8.55 (s, 1 H), 8.10-7.94 (m, 3 H), 7.67 (d, $J$ = 3.6 Hz, 1 H), 7.59 (d, $J$ = 3.6 Hz, 1 H) $^{13}$C NMR (101MHz ,CHLOROFORM-d) d = 191.4, 171.1, 146.3, 137.3, 135.5, 129.4, 128.6, 128.5, 127.2, 124.2, 119.0, 60.4. $^{19}$F NMR (377MHz, CHLOROFORM-d) d = -73. [M+H]$^+$ calcd for: C$_{12}$H$_7$F$_3$O$_4$S 305.00899; found 305.00889.

8-Iodoaphthalen-2-ol (21): 8-aminonaphthalen-2-ol (1.002 g, 6.42 mmol) was added to a 100 mL round bottom flask and dissolved in 16 ml 1:1 ACN:Water and 2 mL (24 mmol) concentrated HCl. The mixture was chilled to 0 °C and sodium nitrite (490 mg, 7.10 mmol) was added, the solution was then stirred for 45 m at 0 °C. Potassium iodide (2.09 g, 12.59 mmol) was dissolved in minimal water and added to the reaction slowly then the solution was warmed to room temperature and stirred overnight. The mixture was diluted with Et$_2$O, washed with brine
and sodium thiosulfate, dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The oil was then loaded onto a silica pad and eluted with 60 mL 20% Et₂O/hexanes to yield 21 (1.177 g, 70%). Characterization data was consistent with ref. 69.

1-Iodo-7-(methoxymethoxy)naphthalene (22): 21 (834 g, 3.09 mmol) and a catalytic amount (1%) of 4-(dimethylamino)pyridine were charged to an oven dried 100 mL round bottom flask and dissolved in 50 mL dry DCM under an atmosphere of N₂. The solution was chilled to 0 °C and 3.10 mL (17.44 mmol) n-ethyldiisopropylamine was then added to the reaction dropwise and the mixture was allowed to stir for 15 min before 1.76 mL (10.90 mmol) Chloromethyl methyl ether/methyl acetate solution was added and the reaction was brought to reflux for 16 h. The reaction was cooled to room temperature, diluted with Et₂O and washed with saturated ammonium chloride and brine solutions then dried over sodium sulphate and concentrated under reduced pressure. The resulting oil was purified via flash chromatography (20% EtOAc/hexanes) then charged to an oven dried 50 mL round bottom flask and purge-pumped three times. The oil was dissolved in 15mL dry THF and chilled to 0 °C. 9.5 mL of 1.65 M Isopropylmagnesium chloride (15.45 mmol) was added to the reaction dropwise and the solution stirred for 1 h before 1.5 mL (18.54 mmol) of dry DMF was added. The reaction was stirred for 30 m at 0 °C, then at room temperature for 3 h before 1 mL of water was added to the reaction and the mixture was left to stir 16 h. The solution was diluted with Et₂O, washed with brine, dried with sodium sulphate then concentrated under reduced pressure and purified via flash chromatography to afford 0.553 mg (82%) 23. Characterization data was consistent with ref. 122.

8-formylnaphthalen-2-yl trifluoromethanesulfonate (24): 379 mg (1.76 mmol) 23 was added to a 100 mL round bottom flask and dissolved in 10 mL MeOH, 1 mL of concentrated HCl was added and the solution stirred overnight. The mixture was diluted with Et₂O, washed with brine and dried over sodium sulphate, the solvent was then removed under reduced pressure. The flask with the resulting oil was purge-pumped three times before 10 mL dry DCM and 0.42 mL (5.26 mmol) dry pyridine were added, and the mixture was cooled to 0 °C. 0.52 mL (3.10 mmol) triflic
anhydride was added to the reaction slowly in 5 mL DCM and the reaction stirred and warmed to room temperature for 2 h. The reaction was diluted with 10 mL Et₂O and 5 mL of 2M were added before the mixture was transferred to a separatory funnel and washed with sodium bicarbonate and brine. The organic layer was dried with sodium sulphate and the solvent was removed under reduced pressure. The resulting oil was purified via flash chromatography to yield 412 mg (77%) 24. ¹H NMR (400MHz ,CDCl₃) δ = 10.33 (s, 1 H), 9.32 (s, 1 H), 8.16 (d, J = 8.0 Hz, 1 H), 8.08 (d, J = 6.8 Hz, 1 H), 8.2 (d, J = 9.2 Hz, 1 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.53 (dd, J = 6 Hz, 1 H). ¹³C NMR (101MHz ,CHLOROFORM-d) δ = 193.0, 149.7, 138.4, 134.9, 132.7, 131.5, 130.9, 130.5, 126.3, 121.1, 117.6, 60.4. ¹⁹F NMR (377MHz, CHLOROFORM-d) δ = -73. [M+H]⁺ calcd for: C₁₂H₇F₃O₄S 305.00899; found 305.00855.

6-(3-(tert-butyl)-hydroxyphenyl)-2-naphthaldehyde (26): An oven-dried 50 mL round-bottom flask was charged with 102 mg (0.46 mmol) of 14, 130 mg (0.47 mmol) of 21, and 150 mg (0.99 mmol) of Na₂CO₃. The vessel was transferred to the glovebox and 0.026 mg (0.02 mmol) of Pd(PPh₃)₄ was added. The vessel was sealed and transferred out of the glovebox, placed under a flow of nitrogen, and the solids were dissolved in 5 mL of dried toluene and 1 mL of degassed H₂O. The mixture was brought to reflux 72 h then the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in EtOAc, run through a silica pad, washed three times with ammonium chloride, three times with brine, and dried over Na₂SO₄. The solvent was removed under reduced pressure, and the crude reaction mixture was purified via column chromatography to afford 73 mg (53%) of 26, a yellow solid. ¹H NMR (300 MHz, CHLOROFORM-d) δ =1.43 - 1.52 (m, 9 H) 4.92 (s, 1 H) 6.80 (d, J=8.06 Hz, 1 H) 7.44 (dd,
$J=8.06, 2.20 \text{ Hz, 1 H}) 7.64 (s, 1 \text{ H}) 7.81 (d, J=8.55 \text{ Hz, 1 H}) 7.95 (s, 2 \text{ H}) 8.03 (dd, J=11.23, 6.35 \text{ Hz, 1 H}) 8.33 (s, 1 \text{ H}) 10.14 (s, 1 \text{ H})$

6-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-2-naphthaldehyde (27): 14 (190 mg, 0.85 mmol), 5 (330 mg, 0.85 mmol), Pd(PPh$_3$)$_4$ (49 mg, 5 mol%) and sodium carbonate (182 mg, 1.71 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 20 mL of dry toluene and 1 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 20-48 h. The reaction solvent was removed under reduced pressure and the resulting oil was dissolved in ethyl acetate and filtered through a silica pad. The filtrate was diluted with ethyl acetate, transferred to a separatory funnel, washed with ammonium chloride and brine, then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 27 (217 mg, 62%) as a light yellow solid. $^1$H NMR (400MHz ,CDCl$_3$) $\delta = 10.18 (s, 1 \text{ H}), 8.36 (s, 1 \text{ H}), 8.09 - 8.03 (m, 2 \text{ H}), 8.02 - 7.98 (m, 2 \text{ H}), 7.83 (dd, J = 1.9, 8.5 \text{ Hz, 1 H}), 7.40 (dd, J = 2.2, 13.1 \text{ Hz, 2 H}), 5.29 (d, J = 1.9 \text{ Hz, 4 H}), 3.70 (s, 3 \text{ H}), 3.58 (s, 3 \text{ H}), 1.52 (s, 9 \text{ H})$. $^{13}$C NMR (101MHz ,CHLOROFORM-d) $\delta = 192.1, 150.6, 146.2, 143.9, 141.9, 136.8, 135.2, 134.2, 134.0, 131.6, 129.9, 129.2, 126.9, 125.5, 123.3, 119.9, 113.8, 99.2, 95.5, 57.6, 56.4, 35.4, 30.5. [M+H]$^+$ calcd for C$_{25}$H$_{28}$O$_5$: 409.20095; found 409.19996.

2-(6-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (29): 27 (105 mg, 0.26 mmol) was added to an oven-dried 50 mL round-bottom flask
with stir bar and dissolved in minimal ethyl acetate. Five drops of concentrated hydrochloric acid were added to the solution and the mixture was stirred overnight. The reaction was transferred to a separatory funnel, diluted with ethyl acetate, washed with brine then dried over sodium sulfate. The solvent was evaporated under reduced pressure and 78 mg (0.53 mmol) of BHA was added then the vessel was purge-pumped with nitrogen 3 times. The solids were suspended in 1.5 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 48-72 h. The solvent was removed under reduced pressure to give a yellow solid which was dissolved in diethyl ether, filtered through silica, and eluted with diethyl ether. The filtrate was concentrated under reduced pressure to 30 (90 mg, 72%) as a light yellow solid. 1H NMR (400MHz ,DMSO-d6) δ = 9.56 (br. s., 1 H), 8.22 (br. s., 1 H), 7.98 (s, 1 H), 7.92 (d, J = 8.4 Hz, 3 H), 7.80 (s, 2 H), 7.72 - 7.63 (m, 2 H), 7.12 - 7.04 (m, 2 H), 4.68 (s, 1 H), 1.43 (s, 9 H), 1.11 (d, J = 7.0 Hz, 12 H). 13C NMR (101MHz ,CHLOROFORM-d) δ = 150.7, 149.2, 144.3, 143.3, 141.2, 138.4, 136.5, 135.2, 133.5, 132.5, 132.1, 130.0, 128.7, 120.9, 116.7, 95.7, 71.4, 70.1, 39.7, 34.7, 29.7, 22.5, 20.4. [M+H]⁺ calcd for C27H34N2O4: 451.25913 ; found 451.25877.

2-(6-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (30): To a 50 mL oven-dried round-bottom flask with stir bar 311 mg (0.66 mmol) of 29 was added and dissolved in 10 mL of Et₂O and 3 mL pH 7 phosphate buffer. 188 mg (0.74 mmol) of I₂ was added to a 100 mL separatory funnel and dissolved in 5 mL Et₂O. The round-bottom flask was shielded from light and the I₂ ether solution was added dropwise to the shielded flask. Following addition, the separatory funnel was rinsed into the reaction solution with 5 mL of Et₂O then 30 mL of pH 7 buffer was charged to the separatory funnel and the reaction solution was transferred to the separatory funnel with Et₂O. The reaction
was quickly washed with 10 mL saturated Na$_2$S$_2$O$_3$ solution then washed three times with saturated brine and dried over Na$_2$SO$_4$. The reaction solvent was removed under reduced pressure to afford 139 mg (45%) of 30, as a blue solid. [M+H]$^+$ calcd for C$_{27}$H$_{31}$N$_2$O$_4$: 448.23566; found 448.23490.

2,6-NAP (31): To an oven-dried 25 mL round-bottom flask with stir bar, 139 mg (0.300 mmol) of 30 was added with 213 mg (0.300 mmol) of Zn(OH)Tp$^{\text{Cum, Me}}$ and purge-pumped three times. 8 mL of dried MeOH was added to the flask and the solution was stirred for 2 h under an inert atmosphere of N$_2$. The septum was then removed and the reaction was stirred vigorously overnight open to atmospheric conditions. The solvent was removed under reduced pressure and the resulting solid was purified by column chromatography (Basic alumina, 50% EtOAc in Hexanes) the recrystallized through vapor diffusion between a mixture of Et$_2$O/hexanes and MeOH to yield 20 (140 mg, 40%) a brown solid. [M+H]$^+$ calcd for C$_{66}$H$_{75}$BN$_8$O$_4$Zn: 1119.53686; found 1119.53426

5-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-1-naphthaldehyde (32): 15 (190 mg, 0.86 mmol), 5 (330 mg, 0.86 mmol), Pd(PPh$_3$)$_4$ (49 mg, 5 mol%) and sodium carbonate (211 mg, 1.99 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 20 mL of dry toluene and 1 mL of degassed water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 20-48 h. The reaction solvent was removed under reduced pressure and the resulting oil was dissolved in ethyl acetate and filtered through a silica pad. The filtrate was diluted with ethyl acetate, transferred to a separatory funnel, washed with ammonium chloride and brine, then dried
over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 32 (240 mg, 69%) as a light yellow solid. $^1$H NMR (300 MHz, CHLOROFORM-$d$) δ ppm 1.45 (s, 9 H) 3.49 (s, 3 H) 3.69 (d, $J$=0.49 Hz, 3 H) 5.19 (s, 2 H) 5.30 (s, 2 H) 7.10 (dd, $J$=14.41, 1.95 Hz, 2 H) 7.47 - 7.57 (m, 2 H) 7.67 (d, $J$=8.55 Hz, 1 H) 7.96 (d, $J$=6.35 Hz, 1 H) 8.22 (d, $J$=8.55 Hz, 1 H) 9.27 (s, 1 H) 10.40 (s, 1 H). $^{13}$C NMR (101MHz, CHLOROFORM-$d$) δ = 193.5, 149.9, 145.6, 143.3, 140.9, 136.5, 135.1, 133.5, 132.1, 131.5, 131.0, 128.5, 128.0, 124.9, 124.1, 122.6, 116.7, 99.2, 95.5, 57.6, 56.4, 35.3, 30.6. [M+H]$^+$ calcd for C$_{25}$H$_{28}$O$_5$: 409.20095; found 409.19996.

5-(6-(3-($\text{tert}$-butyl)-4,5-dihydroxyphenyl)naphthalen-1-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (34): 32 (206 mg, 0.50 mmol) was added to an oven-dried 50 mL round-bottom flask with stir bar and dissolved in minimal ethyl acetate. 5 drops of concentrated hydrochloric acid were added to the solution and the mixture was stirred overnight. The reaction was transferred to a separatory funnel, diluted with ethyl acetate, washed with brine then dried over sodium sulfate. The solvent was evaporated under reduced pressure, BHA (164 mg, 1.11 mmol) was added and the vessel was purge-pumped with nitrogen 3 times. The solids were suspended in 3 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 48-72 h. The solvent was removed under reduced pressure to give a yellow solid which was dissolved in diethyl ether, filtered through silica, and eluted with diethyl ether. The filtrate was concentrated under reduced pressure to give 34 (165 mg, 82%) as a light yellow solid. $^1$H NMR (300 MHz, CHLOROFORM-$d$) δ ppm 1.08 (s, 12 H) 1.43 (s, 9 H) 5.79 (s, 1 H) 6.79 (d, $J$=1.95 Hz, 1 H) 6.92 (d, $J$=1.71 Hz, 1 H) 7.33 - 7.40 (m, 1 H) 7.40 - 7.53 (m, 1 H) 7.90 - 7.96 (m, 2 H) 8.42 (d, $J$=8.06 Hz, 1 H). $^{13}$C NMR (101MHz, DMSO-$d_6$) δ = 145.3, 143.8, 141.2, 137.9, 135.8, 133.7,
5-(6-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (35): To a 50 mL oven-dried round-bottom flask with stir bar 110 mg (0.23 mmol) of 34 was added and dissolved in 10 mL of Et₂O and 3 mL pH 7 phosphate buffer. 75mg (0.29 mmol) of I₂ was added to a 100 mL separatory funnel and dissolved in 5 mL Et₂O. The round-bottom flask was shielded from light and the I₂ ether solution was added dropwise to the shielded flask. Following addition, the separatory funnel was rinsed into the reaction solution with 5 mL of Et₂O then 30 mL of pH 7 buffer was charged to the separatory funnel and the reaction solution was transferred to the separatory funnel with Et₂O. The reaction was quickly washed with 10 mL saturated Na₂S₂O₃ solution then washed three times with saturated brine and dried over Na₂SO₄. The reaction solvent was removed under reduced pressure to afford 70 mg (69%) of 35, as a blue solid. Insufficient material available for characterization, more is being generated. [M+H]⁺ calcd for C₂₇H₃₁N₂O₄: 448.23566; found 448.23483.

1,5-NAP (36): To an oven-dried 25 mL round-bottom flask with stir bar, 70 mg (0.15 mmol) of 35 was added with 108 mg (0.16 mmol) of Zn(OH)Tp̅Cu₅Me and purge-pumped three times. 8 mL of dried MeOH was added to the flask and the solution was stirred for 2 h under an inert atmosphere of N₂. The septum was then removed and the reaction was stirred vigorously overnight open to atmospheric conditions. The solvent was removed under reduced pressure and the resulting solid was purified by column chromatography (Basic alumina, 50% EtOAc in
Hexanes) and recrystallized through vapor diffusion between a mixture of Et₂O/hexanes and MeOH to yield 36 (94 mg, 35%), a dark green solid. [M]⁺ calcd for C₆₈H₇₅BN₈O₄Zn: 1118.53013; found 1118.53061.

8-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-2-naphthaldehyde (37): 20 (124 mg, 0.41 mmol), 5 (174 mg, 0.46 mmol), Pd(PPh₃)₄ (4 mg, 1 mol%) and sodium carbonate (92 mg, 0.87 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 37 (130 mg, 78%).¹H NMR (400MHz, CDCl₃) δ = 10.05 (s, 1 H), 8.51 (s, 1 H), 8.03 - 7.94 (m, 2 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.68 (t, J = 7.6 Hz, 1 H), 7.56 (dd, J = 1.1, 7.1 Hz, 1 H), 7.21 (d, J = 2.1 Hz, 1 H), 7.16 (d, J = 2.1 Hz, 1 H), 5.34 (s, 2 H), 5.25 - 5.22 (m, 2 H), 3.73 (s, 3 H), 3.55 - 3.51 (m, 3 H), 1.49 (s, 9 H).¹³C NMR (101MHz, CHLOROFORM-d) δ = 192.5, 149.9, 143.5, 141.7, 137.0, 134.2, 133.6, 130.9, 128.7, 128.0, 127.5, 122.5, 122.4, 116.5, 109.2, 99.1, 95.4, 60.3, 57.6, 56.4, 35.4, 30.6, 22.7, 21.1, 14.2. HRMS-HESI (m/z): [M+Na]⁺ calcd for C_{25}H_{28}O_{5} 431.18290; found 431.18250.

2-(8-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (39): 37 (81 mg, 0.199 mmol) was dissolved in 10 mL MeOH and 1 mL concentrated HCl and the mixture stirred overnight. The solution was diluted with Et₂O, washed with brine, dried over sodium sulphate, and concentrated under reduced pressure. The oil was combined
with BHA (63 mg, 0.425 mmol) and 1 mg (1 mol %) p-toluenesulfonic acid then the vessel was purge-pumped 3 times. The solids were suspended in 5 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 16 h. About 80% of the reaction solution was removed under reduced pressure then the slurry was added dropwise to 200 mL brine with stirring and filtered resulting in 39 (74 mg, 77%) as a light yellow solid. ¹H NMR (600MHz, DMSO-d₆) δ = 9.52 (s, 1 H), 8.17 (d, J = 7.1 Hz, 1 H), 7.87 (d, J = 8.5 Hz, 2 H), 7.80 (br. s., 1 H), 7.57 (dd, J = 1.5, 8.5 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 1 H), 6.78 – 6.71 (m, 2 H), 4.52 (s, 1 H), 1.42 - 1.35 (m, 9 H), 1.21 (m, 6 H), 1.09 (s, 6 H). [M+H]⁺ calcd for C₂₇H₃₄N₂O₄: 451.25913; found 451.25835.

2-(8-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (40): To a 50 mL oven-dried round-bottom flask with stir bar 64 mg (0.144 mmol) of 39 was added and dissolved in 7 mL of Et₂O and 9 mL pH 7 phosphate buffer. 40 mg (0.159 mmol) of I₂ was dissolved in 5 mL Et₂O and added to the reaction dropwise and the reaction was monitored via EPR. Once finished, the reaction was transferred to a separatory funnel, washed with brine, and dried over sodium sulphate. The reaction solvent was removed under reduced pressure to afford 62 mg (97%) of 40, as a purple solid. HRMS-HESI (m/z): [M+H]⁺ calcd for C₂₇H₃₁N₂O₄ 448.22783; found 448.22773

1-SQ-7-NN-NAP (41): 39 (62 mg, 0.14 mmol), Zn(OH)Tp⁵⁺mce (96 mg, 0.14 mmol), potassium carbonate (8mg, 0.14 mmol) were added to an oven dried 50 mL round bottom flask, then the flask was purge-pumped three times. The solids were dissolved in 6 mL dry DCM and 4 mL dry MeOH and the reaction was stirred for 2 h under inert atmosphere, then opened to air and stirred
overnight. The next day the reaction was filtered and the collected solid was washed with MeOH and set to recrystallize via liquid layering of DCM and MeOH to afford 1-SQ-7-NN-NAP (52mg, 34%) as brown crystals. HRMS-HESI (m/z): [M] calcd for C_{66}H_{75}BN_{8}O_{4}Zn: 1118.52903; found 1118.52953

7-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-1-naphthaldehyde (42): 23 (140 mg, 0.46 mmol), 5 (192 mg, 0.51 mmol), Pd(PPh_{3})_{4} (5 mg, 1 mol%) and sodium carbonate (97 mg, 0.92 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 42 (122 mg, 70%). ¹H NMR (400MHz, CHLOROFORM-d) δ = 10.43 (s, 1 H), 9.50 (d, J = 0.8 Hz, 1 H), 8.09 (d, J = 8.3 Hz, 1 H), 8.01 - 7.94 (m, 2 H), 7.84 (dd, J = 1.8, 8.5 Hz, 1 H), 7.60 (dd, J = 7.3, 8.0 Hz, 1 H), 7.48 - 7.43 (m, 2 H), 5.31 (d, J = 4.3 Hz, 4 H), 3.72 (s, 3 H), 3.59 (s, 3 H), 1.55 (s, 9 H). ¹³C NMR (101MHz, CHLOROFORM-d) δ = 193.4, 150.5, 146.1, 143.8, 141.9, 137.1, 135.8, 134.9, 132.7, 131.5, 130.9, 128.8, 126.6, 124.7, 122.7, 120.2, 114.2, 99.2, 95.6, 57.6, 56.4, 35.4, 30.6. HRMS-HESI (m/z): [M+Na]^+ calcd for C_{25}H_{28}O_{5}: 431.18290; found 431.18209

2-(7-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-1-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (44): 42 (114 mg, 0.36 mmol) was dissolved in 10 mL MeOH and 1 mL concentrated HCl and the mixture stirred overnight. The solution was diluted with Et₂O, washed with brine,
dried over sodium sulphate, and concentrated under reduced pressure. The oil was combined with BHA (107 mg, 0.72 mmol) and 7 mg (1 mol %) p-toluenesulfonic acid then the vessel was purge-pumped 3 times. The solids were suspended in 5 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 16 h. About 80% of the reaction solution was removed under reduced pressure then the slurry was added dropwise to 200 mL brine with stirring and filtered resulting in 44 (123 mg, 77%) as a light-yellow solid. \(^1\)H NMR (600MHz, DMSO-d\(_6\)) \(\delta = 8.63 (s, 1 \text{ H}), 7.96 (d, J = 7.1 \text{ Hz}, 1 \text{ H}), 7.93 (d, J = 8.5 \text{ Hz}, 2 \text{ H}), 7.82 \text{ (br. s., } 1 \text{ H}), 7.68 \text{ (dd, } J = 1.5, 8.5 \text{ Hz, 1 H}), 7.47 \text{ (t, } J = 7.6 \text{ Hz, 1 H}), 7.13 - 7.09 \text{ (m, 2 H)}, 5.47 \text{ (s, 1 H)}, 1.44 - 1.40 \text{ (m, 9 H)}, 1.21 - 1.17 \text{ (m, 6 H)}, 1.12 \text{ (s, 6 H)}. \(^{13}\)C NMR (151MHz, DMSO-d\(_6\)) \(\delta = 145.9, 144.4, 138.5, 137.6, 136.4, 133.5, 132.4, 131.1, 129.0, 127.6, 125.8, 125.3, 124.7, 121.8, 116.6, 112.2, 67.0, 65.4, 35.0, 29.9, 24.8, 18.3, 15.6. HRMS-HESI (m/z): [M+H]\(^+\) calcd for C\(_{27}\)H\(_{34}\)N\(_2\)O\(_4\): 449.24458; found 449.24380

2-(7-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (45): To a 50 mL oven-dried round-bottom flask with stir bar 71 mg (0.157 mmol) of 44 was added and dissolved in 7 mL of Et\(_2\)O and 9 mL pH 7 phosphate buffer. 45 mg (0.177 mmol) of I\(_2\) was dissolved in 5 mL Et\(_2\)O and added to the reaction dropwise and the reaction was monitored via EPR. Once finished, the reaction was transferred to a separatory funnel, washed with brine, and dried over sodium sulphate. The reaction solvent was removed under reduced pressure to afford 61 mg (87%) of 45, as a purple solid. HRMS-HESI (m/z): [M+H]\(^+\) calcd for C\(_{27}\)H\(_{31}\)N\(_2\)O\(_4\): 448.23566; found 448.23584
7-SQ-1-NN-NAP (46): 45 (61 mg, 0.14 mmol), Zn(OH)Tp${}^{\text{cum,me}}$ (107 mg, 0.15 mmol), and potassium carbonate (8 mg, 0.13 mmol) were added to an oven dried 50 mL round bottom flask, then the flask was purge-pumped three times. The solids were dissolved in 6 mL dry DCM and 4 mL dry MeOH and the reaction was stirred for 2 h under inert atmosphere, then opened to air and stirred overnight. The next day the reaction was filtered and the collected solid was washed with MeOH and set to recrystallize via liquid layering of DCM and MeOH to afford 1-SQ-7-NN-NAP (42 mg, 28%) as brown crystals. $[M]^+$ calcd for $C_{27}H_{31}N_2O_4$: 1118.52903; found 1118.53058

4-bromo-1-naphthaldehyde (47): 4-Bromo-1-naphthaldehyde (1.029 g, 4.10 mmol) was charged to an oven dried 100 mL round bottom flask and purge pumped three times. The naphthaldehyde was dissolved in 30 mL dry THF and solution was chilled to 0 °C then 12 mL of 1M borane-tetrahydrofuran (12 mmol) was added slowly and the solution stirred and warmed to room temperature overnight. The reaction was diluted with EtOAc, quenched with water, and 7 mL of 1M NaOH was added before the reaction was washed with brine, dried with sodium sulfate, filtered and concentrated under reduced pressure to afford the relevant primary alcohol (4-bromonaphthalen-1-yl)methanol. 1.84 g (8.54 mmol) of pyridinium chlorochromate was homogenized with 8 g of silica and the mixed powder was added to an oven dried 200 mL three-neck round bottom flask. The powder was placed under an inert atmosphere of N$_2$, suspended in 80 mL of DCM, and brought to reflux. The (4-bromonaphthalen-1-yl)methanol oil generated earlier was dissolved in 20 mL of DCM and added to the refluxing slurry and the reaction was left to reflux 16 h. The solution was cooled to room temperature, diluted with Et$_2$O and eluted through a florisil pad with Et$_2$O then concentrated to afford 47 (0.683 g, 75%) as a colorless
solid. $^1$H NMR (400MHz, CHLOROFORM-d) δ = 10.37 (s, 1 H), 9.32 - 9.24 (m, 1 H), 8.40 - 8.31 (m, 1 H), 7.96 (d, $J$ = 7.6 Hz, 1 H), 7.80 (d, $J$ = 7.8 Hz, 1 H), 7.77 - 7.66 (m, 2 H). $^{13}$C NMR (101MHz, CHLOROFORM-d) δ = 192.6, 136.1, 132.2, 131.5, 131.3, 131.0, 129.8, 129.4, 128.3, 127.8, 125.2. HRMS-HESI (m/z): [M+H]$^+$ calcd for C$_{11}$H$_7$BrO: 451.25913; found 431.18250

4-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-1-naphthaldehyde (48): 47 (196 mg, 0.88 mmol), 5 (374 mg, 0.98 mmol), Pd(PPh$_3$)$_4$ (52 mg, 5 mol%) and sodium carbonate (201 mg, 1.9 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 48 (335 mg, 92%). $^1$H NMR (400MHz, CHLOROFORM-d) δ = 10.41 (s, 1 H), 9.36 (d, $J$ = 8.5 Hz, 1 H), 8.08 - 7.95 (m, 2 H), 7.69 (s, 1 H), 7.61 - 7.51 (m, 2 H), 7.17 (d, $J$ = 2.1 Hz, 1 H), 7.13 (d, $J$ = 2.0 Hz, 1 H), 5.32 (s, 2 H), 5.22 - 5.19 (m, 2 H), 3.48 (s, 3 H), 3.46 (s, 3 H), 1.20 (s, 9 H). $^{13}$C NMR (101MHz, CHLOROFORM-d) δ = 193.2, 149.9, 147.5, 146.1, 143.4, 136.2, 134.5, 132.1, 131.2, 130.4, 128.7, 126.9, 126.0, 125.1, 122.3, 116.4, 99.1, 95.5, 65.8, 31.6, 30.5, 22.6, 15.2. HRMS-HESI (m/z): [M+H]$^+$ calcd for C$_{25}$H$_{28}$O$_5$: 409.20095; found 409.20108

2-(4-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-1-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (49): 48 (335 mg, 0.82 mmol) was dissolved in 10 mL MeOH and 1 mL concentrated HCl and the mixture stirred overnight. The solution was diluted
with Et₂O, washed with brine, dried over sodium sulphate, and concentrated under reduced pressure. The oil was combined with BHA·H₂SO₄ (303 mg, 1.23 mmol) and 110 mg (0.79 mmol) potassium carbonate then the vessel was purge-pumped 3 times. The solids were suspended in 5 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 16 h. About 80% of the reaction solution was removed under reduced pressure then the slurry was added dropwise to 200 mL brine with stirring and filtered resulting in 49 (275 mg, 71%) as a light yellow solid. ¹H NMR (400MHz, CHLOROFORM-d) δ = 9.55 (s., 1 H), 8.49 (d, J = 8.4 Hz, 1 H), 8.18 (br. s., 1 H), 8.03 - 7.91 (m, 2 H), 7.79 (s, 2 H), 7.56 - 7.42 (m, 2 H), 7.38 (d, J = 7.4 Hz, 1 H), 6.81 (d, J = 1.6 Hz, 1 H), 6.72 (d, J = 1.6 Hz, 1 H), 5.44 (s, 1 H), 1.39 (s, 9 H), 1.19 (s, 6 H), 1.12 (s, 6 H). ¹³C NMR (101MHz, CHLOROFORM-d) δ = 150.0, 148.6, 145.0, 141.1, 140.6, 138.3, 136.5, 135.3, 131.2, 130.5, 130.2, 129.7, 123.8, 119.7, 90.9, 71.7, 70.1, 39.6, 34.7, 29.2, 23.3, 20.4. HRMS-HESI (m/z): [M+H]⁺ calcd for C₂₇H₃₄N₂O₄: 451.25913; found 451.25915

2-(4-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-1-yl)-4,4,5,5-tetramethyl-1,3-dihydroimidazol-3-oxide-1-oxyl (50): To a 50 mL oven-dried round-bottom flask with stir bar 110 mg (0.23 mmol) of 49 was added and dissolved in 10 mL of Et₂O and 3 mL pH 7 phosphate buffer. 75mg (0.29 mmol) of I₂ was added to a 100 mL separatory funnel and dissolved in 5 mL Et₂O. The round-bottom flask was shielded from light and the I₂ ether solution was added dropwise to the shielded flask. Following addition, the separatory funnel was rinsed into the reaction solution with 5 mL of Et₂O then 30 mL of pH 7 buffer was charged to the separatory funnel and the reaction solution was transferred to the separatory funnel with Et₂O. The reaction was quickly washed with 10 mL saturated Na₂S₂O₃ solution then washed three times with
saturated brine and dried over Na$_2$SO$_4$. The reaction solvent was removed under reduced pressure to afford 50 (84 mg, 80%) as a purple solid. HRMS-HESI ($m/z$): [M+H]$^+$ calcd for C$_{27}$H$_{31}$N$_2$O$_4$: 448.23566; found 448.23533

1,4-NAP (51): 84 mg (0.19 mmol) of 50, 124 mg (0.18 mmol) ZnTp$_{\text{cum,mc}}$, and 25 mg (0.18 mmol) potassium carbonate were added to an oven dried 50 mL round bottom flask, then the flask was purge-pumped three times. The solids were dissolved in 6 mL dry DCM and 4 mL dry MeOH and the reaction was stirred for 2 h under inert atmosphere, then opened to air and stirred overnight. The next day the reaction was filtered and the collected solid was washed with MeOH and set to recrystallize via liquid layering of DCM and MeOH to afford 1,4-NAP (124 mg, 49%) as brown crystals. HRMS-HESI ($m/z$): [M]$^-$ calcd for C$_{66}$H$_{75}$BN$_8$O$_4$Zn: 1118.53013; found 1118.53090
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Appendix A.

Further Exploration of SQ-B-NN D-B-As as Analogues of Molecular Rectifiers

A.1 Molecular Rectification and Target Molecules

As discussed previously, the study of current rectification on the fundamental level of electron transport will be of utmost importance to the development of smaller and smaller electrical circuits. As the miniaturization of technology continues, the paradigms that are probed to test materials properties must also shrink, bringing to light the importance of single molecule electronics. The U-type rectifier, a single molecule with properties that display asymmetric directional current flow, is a system that provides unique framework to study properties of electron transport at the most fundamental level. In a U-type single molecule rectifier, the directional bias of current flow stems from the asymmetry of the molecule’s frontier molecular orbitals.

The effect of spin bearing subunit positioning regarding bridge LUMO electronic density was discussed a previous chapter, but there are many ways to impose possible bridge asymmetry in an electron transport event. The transport event observed in Shultz Group SQ-B-NN biradicals has been shown to be mediated by a super exchange pathway, a pathway heavily dependent on bridge conjugation. As such, theoretically current rectifying DBA systems can be imaged through adaptations of bridge conjugated pathways. It is predicted that interruptions in a radical’s conjugated pathway should hamper the degree of electronic coupling and, as a result, impact the magnitude of \( J_{\text{SQNN}} \).

This theory has already been tested in the Shultz Group by Dr. Patrick Hewitt. Hewitt devised a set of biphenyl spaced SQ-B-NN compounds wherein asymmetry is imposed through substitution patterns. Typically, in a SQ-B-NN DBA the SQ subunit can fully delocalize throughout the bridge, but the NN subunit possesses a node at the carbon that bonds to the bridge, making NN delocalization throughout the spacing unit impossible through typical kinetic exchange. Through the differential placement of the SQ unit in a phenyl bridge a similar event is observed illustrated by a simple electron delocalization arrow pushing diagram involving the lone radical of the SQ (Figure A-1).
When the SQ is substituted para to the positioning of the second phenyl ring as in \textit{p-SQ-m-NN} the SQ lone radical can be delocalized fully through the two phenyl rings. However, when the SQ subunit is positioned meta to the second phenyl ring (\textit{m-SQ-p-NN}) the lone radical of the SQ cannot delocalize into the second phenyl ring of the bridge. It was predicted that this difference in radical density between the two bridges would result in a rectification-type observation between the magnitude of exchange coupling between the two isomers. Based on this inequivalence of resonance, it was predicted that \textit{p-SQ-m-NN} would display a greater magnitude of exchange coupling than \textit{m-SQ-p-NN} due to the enhanced delocalization offered by the para-positioning of the SQ. However, when the two complexes were studied via magnetometry the data indicated that the two isomers effectively displayed the same magnitude of exchange coupling (Figure A-2).
Isomer $m$-$SQ$-$p$-$NN$ displayed an exchange coupling of $-5.45 \pm 0.07$ cm$^{-1}$ and $p$-$SQ$-$m$-$NN$ displayed an exchange coupling of $-5.56 \pm 0.09$ cm$^{-1}$; the two values were identical with error accounted for. It was noted that the magnitudes of the two $J$ values were rather low, not even $\pm 10$ cm$^{-1}$, and the question was posed whether or not this absence of difference would also be observed in isomers with stronger magnitudes of exchange coupling. Perhaps the degree of difference between these two isomers was small enough that it was lost to the error of the measurement.

In order to paint a more complete picture of this possible source of asymmetry between proposed rectifier analogues two bithiophene bridged $SQ$-$B$-$NN$ isomers were imagined and targeted for analysis based on a previous Shultz Group study published in 2013 addressing distance dependence in $SQ$-$B$-$NN$ biradicals.\textsuperscript{9} In the study, it is shown that the magnitude of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{X-ray diffraction determined crystal structures and magnetic data of proposed molecular rectifier analogues $p$-$SQ$-$m$-$NN$ and $m$-$SQ$-$p$-$NN$.}
\end{figure}
electronic coupling decreases exponentially with regards to increasing distance between the two spin centers, but it is also shown that thiophene bridges facilitate stronger coupling between the two spin centers when compared to analogous phenyl bridges. The SQ-B-NN biphenyl spaced isomer displayed exchange coupling with a magnitude of 20 cm\(^{-1}\) while the bithiophene spaced isomer showed exchange coupling of over five-fold that (Figure A-3).

**Figure A-3.** Structures and experimentally determined exchange couplings of SQ-B-NN DBA complexes SQ-(Ph)\(_2\)-NN and SQ-(T)\(_2\)-NN.\(^9\)

In an attempt to further explore this possible source of rectification, isomers 5-SQ-4’-NN-T\(_2\) and 5-NN-4’-SQ-T\(_2\) were imagined. These two isomers also show the same inequivalent delocalization of the SQ lone radical through a simple electron-pushing diagram as the \(p\)-SQ-\(m\)-NN and \(m\)-SQ-\(p\)-NN, with the SQ subunit in compound 5-SQ-4’-NN-T\(_2\) delocalizing through both thiophene bridging units and that of the 5-NN-4’-SQ-T\(_2\) isomer remaining localized within the first bridging thiophene (Figure A-4). By the same logic presented in the previous case, it is proposed that 5-SQ-4’-NN-T\(_2\) will display a larger magnitude of exchange coupling when compared to 5-NN-4’-SQ-T\(_2\) due to the greater degree of SQ lone radical delocalization.
Figure A-4. Proposed molecular rectifier analogues 5-SQ-4’-NN-T₂ and 5-NN-4’-SQ-T₂, as well as illustrations of the electron pushing delocalization possible for the SQ radical as allowed by each substitution pattern.

A.2 Discussion of Completed Work

As discussed in the previous section, the synthesis of SQ-B-NN biradical complexes is best approached when split into its constituent parts. Largely, the same routes used to approach the prior synthesis of the naphthyl series are applied here to make the bithiophene bridged SQ-B-NN biradicals, but the bridge syntheses are unique.

The route to the first thiophene subunit in the 5-SQ-4’-NN-T₂ began with the bromination of 3-formylthiophene. The route that was initial attempted hoped to use t-BuLi and dibromoethane to provide conditions that would favor product 53 heavily through the loss of biproduct gases (Scheme A-1).
Scheme A-1. Initial synthetic pathway to 5-bromo-3-thiophenecarboxaldehyde (53).

To assure that the aldehyde of 3-formylthiophene remained untouched during the \( t\)-BuLi deprotonation the functional group was first protected with ethylene glycol to produce 52. Following the purification of 52 the thiophene was deprotected at the 4-position with \( t\)-BuLi, bromine was added electrophilically through dibromoethane, and the glycol protecting group was removed with acid. This reaction turned out to produce 53 as the primary product, however it also produced a large number of impurities, resulting in challenging purification and ultimately little to no resulting pure 53. The next attempted synthetic route to 53 using NBS (Scheme A-2) proved more fruitful, producing 53 reliably on a multigram scale with simple purification via flash chromatography.

Scheme A-2. Secondary route to 5-bromo-3-thiophenecarboxaldehyde (53). This path produced 53 in better yield and purity.

From here, 53 was Stille coupled to tributyl(thiophene-2-yl)stannane, which was generated in one step through the deprotonation of thiophene with BuLi and subsequent quenching with tributyltin chloride. This Stille coupling worked well to produce 56 in good yield. To finish the aldehyde-bridge-leaving group paradigm desired bridge starting material of
5-SQ-4’-NN-T₂ the next step was the bromination of the second unsubstituted thiophene ring. This bromination proved to be very selective, producing an overwhelming majority of 57 with both HPyBr₃ and NBS reagents (Scheme A-3). However, both reactions were very slow, so other routes to 57 were considered.

Scheme A-3. Proposed routes to leaving group-bridge-aldehyde paradigm for the generation of 5-SQ-4’-NN-T₂.

It was imagined that 53 could be coupled to a thiophene ring that already possessed the MOM-protected catechol subunit, making the long bromination of the bithiophene preliminary bridge unit unnecessary. Attempts to generate the coupling partners for both a Stille-type and Suzuki-type carbon-carbon cross coupling reaction to 53 were targeted for synthesis (Scheme A-4).

Scheme A-4. Alternative routes tested in an attempt to decrease the total reaction time required to generate 5-SQ-4’-NN-T₂.
However, both theorized coupling partners proved unattainable through the imagined steps. The Stille coupling partner (Scheme A-4, top) seemed to not be attainable from starting material 54, showing near no desired product and producing an uncharacterized blue side product. The Suzuki coupling partner (Scheme A-4, bottom) initially proved more promising with the bromination of 54 to produce 55 being high yielding and clean, however, while the attempt to install the pinacol boronate subunit was successful, the resulting MOMCAT-thiophene-boropinacol molecule was unstable. Other theoretical routes were imagined, however at that point 57 had been generated and purified in quantities large enough to proceed with biradical synthesis.

![Scheme A-5](image)

**Scheme A-5.** Synthetic pathway to generate 5-SQ-4'-NN-T₂ (61) starting from leaving group-bridge-aldehyde paradigm 57.

From the aldehyde-bridge-leaving group paradigm 57 the standard SQ-B-NN synthesis was applied to generate 5-SQ-4'-NN-T₂ (Scheme A-5). The coupling of 57 to the MOM-protected catechol subunit worked well, however the deprotection of the MOM groups on 58 proved difficult. Typical conditions to deprotect the MOM groups, a drop of concentrated HCL in MeOH, did not produce the desired product (59), and instead produced a highly fluorescent product with poor solubility; likely a polymerized form of 59. A couple other methods were attempted for the deprotection of 58. In previous cases involving acid sensitive D-B-A
compound precursors with MOM-protected alcohol deprotection had been achieved in a microwave reactor with small catalytic amounts of $p$-TsOH. However, when 58 was reacted with catalytic $p$-TsOH in deoxygenated MeOH at 80 °C and 35 W for 5m in a microwave reactor the same highly fluorescent insoluble material was obtained. Eventually it was discovered that the deprotection does outpace the polymerization reaction in very dilute solutions. The most successful deprotections run on this compound were set up on a 75 mg scale in 40 mL of MeOH with 5 mL of a 2M solution of HCl left to stir under an inert gas atmosphere for 5-8 days; resulting in a solution that is 4 mM in substrate and 0.2 M in acid. The next step, the cyclization of the BHA, is typically done with catalytic $p$-TsOH to facilitate the reaction, however with the apparent acid sensitivity of the compound the old prep for the cyclization of BHA was implemented. The I$_2$ oxidation of BHA 59 to NN 60 worked well under typical conditions and attempts to generate the biradical were made also following the typical conditions outlined previously. The crude material gathered from the reaction of 60 and Zn(OH)Tp$^{cum,me}$ was filtered and collected with DCM to afford a highly colored solid with EPR shown in Figure A-5.

![Image]

**Figure A-5.** EPR spectrum of crude solid 5-SQ-4’-NN-T$_2$.

This EPR spectrum is indicative of a successful complexation and shows a “biradical” pattern with 4G hyperfine splitting, however thus far conditions for XRD quality growth have not been pinned down.
Scheme A-6. Proposed synthetic route to generate 5-NN-4'-SQ-T₂ (67).

The proposed route to isomer 5-NN-4'-SQ-T₂ (67) is outlined above in Scheme A-6. The route begins with the coupling of the MOM₂CATBPIN (5) subunit to 2-bromothiophene, followed by the deprotonation and subsequent quench with tributyltin chloride to generate a Stille coupling partner for commercially available 5-bromo-2-thiophenecarboxaldehyde. The reaction that installs the tin leaving group at the 5-position of 62 is low yielding, however the starting material is easily recovered so the reaction can be repeated until a good amount of 63 is generated. The same acid-mediated polymerization side reaction is noted in this isomer as well, and the same dilute reaction conditions are implemented to deprotect 64 and no p-TsOH is used in the cyclization of 65 to prevent any side products. The CAT-bridge-NN (66) molecule was generated in good yield, but when the complexation reaction was attempted to generate 67 only
monoradical NN splitting patterns was observed after stirring open to air overnight. Material was being bulked up for another attempt at making 67 but not enough was made in time for another attempt. It is also worth noting that another pathway to a viable bridge starting material with aldehyde-bridge-leaving group character was imagined that would theoretically reduce the throughput time required to make 64 (Scheme A-7).

![Scheme A-7. Proposed alternate synthetic route to generate the bridging unit for 5-NN-4’-SQ-T2 (67).](image)

In this route 5-bromo-2-thiophenecarboxaldehyde would be converted into a suitable cross-coupling partner for commercially available 2,4-dibromothiophene, having its 5-position bromine swapped out for a boronic ester or pinacol then coupled to the bromine at the 2-position of 2,4-dibromothiophene. There is literature precedent for the selective reaction at the 2-position of 2,4-dibromothiophene in Suzuki-type cross-coupling reactions, Sebastian Fredrick et al reported an 85% yield of 4-bromo-2-phenylthiophene when reacting 2,4-dibromothiophene with phenylboronic acid, suggesting that the 2-position of 2,4-dibromothiophene is highly favored over the 4-position. While 2,4-dibromothiophene was ordered with intention of testing this route, it did not arrive in time for this path to be tested before labs were shut down due to COVID-19.
A.3 Experimental

2-(thiophen-3-yl)-1,3-dioxolane (52): 550 mg (4.9 mmol) of 3-formylthiophene were added to a 50 mL oven-dried round bottom flask along with 0.55 ml (9.8 mmol) and 93 mg (0.48 mmol) of p-TsOH and dissolved in 20 mL of PhMe. The mixture was then brought to reflux and stirred overnight. The next day the reaction was cooled to room temperature, diluted with Et₂O and washed with brine. The organic layer was dried over Na₂SO₄ and concentrated then, the resulting oil was eluted through a silica pad with a 20% Et₂O/hexanes mixture and the eluent was concentrated to afford 52 (397 mg, 52%) as an oil.

5-bromothiophene-3-carbaldehyde (53): 2.85g (25 mmol) of 3-formylthiophene and 4.53 g (25 mmol) of n-bromosuccinimide were combined in a 100 mL round bottom flask and placed under a stream of nitrogen for 30 m. The solids were then dissolved in 15 mL of N,N-dimethylformamide, shielded from light, and left to stir for 24 h in the dark. The mixture was diluted with 50 mL of a 1:1 mixture of Et₂O/hexanes then the solution was washed with 2M NaOH, DI water, brine, and dried with MgSO₄ and concentrated. The resulting oil was purified via flash chromatography (40% EtOAc/hexanes ) to afford 53 (3.65 g, 75%) as an oil. ¹H NMR (400MHz ,DMSO-d₆) δ = 9.75 (s, 1 H), 8.58 (s, 1 H), 7.56 (s, 1 H).

2-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)thiophene (54): 2-bromothiophene (165 mg, 1.0 mmol), 5 (227 mg, 0.59 mmol), Pd(PPh₃)₄ (34 mg, 5 mol%), tetrabutylammonium bromide (32 mg, 10 mol%), and sodium carbonate (130 mg, 1.2 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 54 (167 mg, 83%) as a colorless oil. (400MHz ,DMSO-d₆) δ = 7.47 (d, J = 4.8 Hz, 1 H), 7.35 (d, J = 4.8 Hz, 1 H), 7.24 (d, J = 2.4 Hz, 1 H), 7.13 (d, J = 2.4 Hz, 1 H), 7.09 (t, J = 3.2 Hz, 1 H), 5.24 (s, 2H), 5.15 (s, 2H), 3.54 (s, 3H), 3.42 (s, 3H), 1.38 (s, 9H).
[2,2'-bithiophene]-4-carbaldehyde (56): Tributyl(thiophen-2-yl)stannane (410 mg, 1.1 mmol), 53 (204 mg, 1.1 mmol), Pd(PPh₃)₄ (12 mg, 5 mol%) and cesium fluoride (162 mg, 1.1 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. The solids were suspended in 10 mL dry THF and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 56 (185 mg, 89%) as a colorless oil. (400MHz ,DMSO-d₆) δ = 9.83 (s, 1 H), 8.53 (s, 1 H), 7.58 (s, 1 H), 7.43 (d, J = 4 Hz, 1 H), 7.11 (m, 2 H)

5'-bromo-[2,2'-bithiophene]-4-carbaldehyde (57): 56 (123 mg, 0.63 mmol) and n-bromosuccinimide (115 mg, 0.64 mmol) were dissolved in 10 mL N,N-dimethylformamide and the mixture was shielded from light and left to stir for 7 days. The reaction was then poured into 100 mL of brine and the suspension was filtered. The solid was washed with Et₂O and the eluent was dried with MgSO₄ and concentrated to afford 57 (0.140, 80%). (400MHz ,DMSO-d₆) δ = 9.82 (s, 1 H), 8.56 (s, 1 H), 7.59 (s, 1 H), 7.29 (d, J = 4 Hz, 1 H), 7.24 (d, J = 4Hz, 1 H)

5'-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-[2,2'-bithiophene]-4-carbaldehyde (58): 57 (108 mg, 0.39 mmol), 5 (157 mg, 0.41 mmol), Pd(PPh₃)₄ (22 mg, 5 mol%), tetrabutylammonium bromide (17 mg, 10 mol%) and sodium carbonate (90 mg, 0.85 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 58 (101 mg, 58%) as a colorless oil. (400MHz , ACETONE-d₆) δ = 9.91 (s, 1 H), 8.41 (s, 1 H), 7.62 (s, 1 H), 7.38-7.36 (m, 3 H), 7.30 (d, J = 2.4 Hz, 1 H), 5.31 (s, 2 H), 5.26 (s, 2 H), 3.62 (s, 3 H), 3.53 (s, 3 H), 1.47 (s, 9H).
2-(5'-(3-(tert-butyl)-4,5-dihydroxyphenyl)-[2,2'-bithiophen]-4-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (59): 58 (114 mg, 0.36 mmol) was dissolved in 40 mL MeOH and 5 mL of 2M HCl and stirred overnight. The solution was diluted with Et₂O, washed with brine, dried over sodium sulphate, and concentrated under reduced pressure. The oil was combined with BHA (107 mg, 0.72 mmol) and 7 mg (1 mol %) p-toluenesulfonic acid then the vessel was purge-pumped 3 times. The solids were suspended in 5 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 16 h. About 80% of the reaction solution was removed under reduced pressure then the slurry was added dropwise to 200 mL brine with stirring and filtered resulting in 59 (71 mg, 52%) as a light yellow solid. (400MHz, ACETONE-d₆) δ = 7.23 (s, 1 H), 7.25 (s, 1 H), 7.15-7.14 (m, 2 H), 7.10-7.08 (m, 2 H), 4.75 (s, 1 H), 1.45 (s, 9 H), 1.18 (s, 6 H), 1.09 (s, 6 H).

2-(5'-(3-(tert-butyl)-4,5-dihydroxyphenyl)-[2,2'-bithiophen]-4-yl)-4,4,5,5-tetramethyl-1,3-dihydroimidazol-3-oxide-1-oxyl (60): To a 50 mL oven-dried round-bottom flask with stir bar 71 mg (0.145 mmol) of 59 was added and dissolved in 7 mL of Et₂O and 9 mL pH 7 phosphate buffer. 40 mg (0.157 mmol) of I₂ was dissolved in 5 mL Et₂O and added to the reaction dropwise and the reaction was monitored via EPR. Once finished, the reaction was transferred to a separatory funnel, washed with brine, and dried over sodium sulphate. The reaction solvent was removed under reduced pressure to afford 55 mg (77%) of 60, as a green solid. Not enough material was generated for full characterization.

5-SQ-4’-NN-T₂ (61): 55 mg (0.11 mmol) of 60, 105 mg (0.15 mmol) ZnTp⁷cum,me, and 18 mg (0.13 mmol) potassium carbonate were added to an oven dried 50 mL round bottom flask, then the flask was purge-pumped three times. The solids were dissolved in 6 mL dry DCM and 4 mL dry MeOH and the reaction was stirred for 2 h under inert atmosphere, then opened to air and stirred overnight. The next day the reaction was filtered and the collected solid was washed with MeOH to afford 5-SQ-4’-NN-T₂ as brown crystals. Not enough material was generated for full characterization.
3-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)thiophene (62): 3-bromothiophene (161 mg, 0.98 mmol), 5 (257 mg, 0.67 mmol), Pd(PPh₃)₄ (8 mg, 5 mol%), tetrabutylammonium bromide (22 mg, 10 mol%), and sodium carbonate (141 mg, 1.3 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 62 (182 mg, 83%) as a colorless oil. ¹H NMR (400MHz, DMSO-d₆) δ = 7.72 (d, J = 6 Hz, 1 H), 7.59 (s, 1 H), 7.43 (d, J = 6 Hz, 1 H), 7.26 (d, J = 2 Hz, 1 H), 7.17 (d, J = 2 Hz, 1 H), 5.23 (s, 2 H), 5.15 (s, 2 H), 3.42 (s, 3 H), 3.32 (s, 3 H), 1.39 (s, 9 H).

tributyl(4-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)thiophen-2-yl)stannane (63): 182 mg (0.54 mmol) of 62 was charged to an oven-dried round-bottom flask with stir bar and purge-pumped three times. The oil was dissolved in 20 mL of dry tetrahydrofuran and chilled to -78 °C. 0.35 mL of 1.7 M tert-butyl lithium in pentane was added to the solution dropwise then the mixture was stirred at -78 °C for 10 min then tributyltin chloride (0.2 mL, 0.61 mmol) was added to the solution dropwise. The solution was stirred at -78 °C for 10 minutes before being warmed to room temperature and stirred overnight. The reaction mixture was diluted with diethyl ether, passed through a silica pad and eluted with diethyl ether, concentrated under reduced pressure and purified via flash chromatography to yield 5 (70 mg, 30%) as a light yellow oil.

4'-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-[2,2'-bithiophene]-5-carbaldehyde (64): 5-bromothiophene-2-carbaldehyde (150 mg, 0.78 mmol), 63 (350 mg, 0.56 mmol), Pd(PPh₃)₄ (6 mg, 5 mol%) and cesium fluoride (85 mg, 0.55 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. The solids were suspended in 15 mL dry THF and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 64 (98 mg, 64%) as a colorless
oil. (400MHz , ACETONE-d<sub>6</sub>) δ = 9.93 (s, 1 H), 7.94 (d, J = 4 Hz, 1 H), 7.89 (s, 1 H), 7.77 (s, 1 H), 7.51 (d, J = 4 Hz, 1 H), 7.41 (d, J = 2.4 Hz, 1 H), 7.30 (d, J = 2.4 Hz, 1 H), 5.30 (s, 2 H), 5.25 (s, 2 H), 3.61 (s, 3 H), 3.51 (s, 3 H), 1.47 (s , 9H).

2-(4'-((3-(tert-butyl)-4,5-dihydroxyphenyl)-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (65): 64 (55 mg, 0.12 mmol) was dissolved in 40 mL MeOH and 5 mL of 2M HCl and stirred overnight. The solution was diluted with Et<sub>2</sub>O, washed with brine, dried over sodium sulphate, and concentrated under reduced pressure. The oil was combined with BHA (25 mg, 0.17 mmol) and the vessel was purge-pumped 3 times. The solids were suspended in 5 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 16 h. About 80% of the reaction solution was removed under reduced pressure then the slurry was added dropwise to 200 mL brine with stirring and filtered resulting in 59 (39 mg, 64%) as a light yellow solid. <sup>1</sup>H NMR (400MHz ,DMSO-d<sub>6</sub>) δ = 9.46 (s, 1 H), 8.16 (s, 1 H), 7.99 (s, 1 H), 7.40 (s, 1 H), 7.17 (d, J = 3.6 Hz, 1H), 7.00 (d, J = 3.6 Hz, 1 H), 6.95 (d, J = 2.4 Hz, 1 H), 6.93 (d, J = 2.4 Hz, 1 H), 4.70 (s, 1 H), 1.39 (s, 9 H), 1.06 (s, 6 H), 1.04 (s, 6 H).

2-(5'-(3-(tert-butyl)-4,5-dihydroxyphenyl)-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethy-1,3-dihydroimidazol-3-oxide-1-oxyl (66): To a 50 mL oven-dried round-bottom flask with stir bar 102 mg (0.21 mmol) of 65 was added and dissolved in 7 mL of Et<sub>2</sub>O and 9 mL pH 7 phosphate buffer. 56 mg (0.22 mmol) of I<sub>2</sub> was dissolved in 5 mL Et<sub>2</sub>O and added to the reaction dropwise and the reaction was monitored via EPR. Once finished, the reaction was transferred to a separatory funnel, washed with brine, and dried over sodium sulphate. The reaction solvent was removed under reduced pressure to afford 81 mg (80%) of 60, as a green solid. Not enough material was generated for full characterization.
Appendix B:

Antiferromagnetically Coupled Naphthyl Bridged SQ-NN Biradicals

B.I Introduction

![2,7-NAP](image)

**Figure B-1.** Structure of 2,7-NAP.

This chapter will focus on the synthesis and characterization of the antiferromagnetically coupled SQ-NAP-NN isomer: 2,7-NAP (Fig. B-1). Antiferromagnetically coupled SQ-NN biradicals display some of the same characteristics as ferromagnetically coupled SQ-NN biradicals but the magnitude of $J$ in antiferromagnetically coupled isomers is much less, often by orders of magnitude. Many characterization techniques used to identify the ferromagnetic isomers can also be applied to the antiferromagnetic isomers. The EPR spectrum of an antiferromagnetic NN monoradical will still display a five-line hyperfine splitting pattern with an a-splitting of 7G and the biradical complex will still show a more complicated 5-line pattern with an a-splitting of 4G, but other features such as the SQ$\rightarrow$NN CT band observed in the electronic absorption spectrum of the ferromagnetic isomers will be absent (fig. B-2) as a result of this weak coupling.
Figure B-2. Overlain electronic absorption spectra of 2,6-NAP and 2,7-NAP with labeled electronic transitions. The SQ→NN CT band is highlighted by a gold oval to draw attention to its absence in the antiferromagnetically coupled isomer.

Due to the cross-conjugation weakened coupling, structure dependent analysis of antiferromagnetically coupled SQ-B-NN biradicals becomes challenging. The impact made by specific structural augmentation becomes challenging to tease out of data at low magnitudes of $J$, so most SQ-B-NN are designed to be ferromagnetic in nature. The isomer 2,7-NAP was originally generated as a part of a set of antiferromagnetic SQ-B-NN isomers designed to test the dependence of $J_{SQNN}$ on electronic orbital density in the bridge LUMO, much like 1,5-NAP and 2,6-NAP. This project was set put on the back-burner following the generation of 2,7-NAP because both the bridge orbital dependence, as well as orbital rectification events will be better illustrated in a ferromagnetically coupled set of isomers.
B.2 Synthesis of 2,7-NAP

The synthesis of ferromagnetic SQ-B-NN biradicals has been outlined in the section II.3. This procedure also applied to antiferromagnetic SQ-B-NN biradicals and was implemented to generate 2,7-NAP as well. The bridge synthesis is unique, as in all SQ-B-NN biradicals, but the generation of the mom-protected catechol borolane (MOM₂CatBpin, scheme II-1), BHA (7, scheme II-2), and the tris-pyrazole ancillary Zn ligand (12, scheme II-3) were all prepared according to the procedure outlined in section II.3.

Scheme B-1. Synthetic route for the generation of 7-bromo-2-naphthaldehyde (68).

The bridge synthesis (scheme B-1) begins a lithium-halogen exchange on 2,7-dibromonaphthalene. The lithiation reagent is used in a 1:2 stoichiometric ratio with 2,7-dibromonapthalene, then quickly quenched to reduce the chance of producing a doubly lithiated 2,7-substituted naphthalene. The reaction is quenched with DMF to yield 7-bromo-2-naphthaldehyde (68). From the bromo-naphthaldehyde the 2,7-NAP biradical complex is generated in five steps with starting materials 5, 7, and 12 on hand (scheme B-2).
Scheme B-2. Synthetic route for the generation of the biradical 2,7-NAP (73).

First, the donor moiety is install on the bridge with a palladium-mediated cross coupling Suzuki-Miyaura reaction to yield 69, which can be quickly deprotected in the presence of catalytic hydrochloric acid to produce 70. With the MOM-groups removed from the catechol 70 is then stirred in the dark for 48 h or longer with BHA to generate 71. With the NN framework installed, 71 is then oxidized with I2 to produce the monoradical species 72, which is then complexed overnight with 12 to produce the biradical 2,7-NAP compound (73).
B.3 Characterization

Since the degree of electronic coupling between the radicals in 2,7-NAP is likely to be weak the complex was not intensively studied or characterized beyond proof of its existence. As discussed in the main document, the first means of characterization for SQ-B-NN biradicals is EPR spectroscopy. The monoradical compound (39) displayed a five-line hyperfine splitting pattern with an a-value of 7 G, consistent with previously isolated NN complexes. After being complexes to the ZnTp ancillary ligand (12) and run through a pipet column of basic alumina a crude EPR was taken of the reaction solid free of paramagnetic impurities (Fig. B-3). The resulting spectrum, while not clean or concentrated, displays a signal with multiple peaks separated by an a-value of 4 G, consistent with other SQ-B-NN complexes.

Figure B-3. Crude EPR of 2,7-NAP.
B.4 Experimental

7-Bromo-2-naphthaldehyde (68): 2,7-Dibromonaphthalene (1.51 g, 5.28 mmol) was charged to an oven-dried 50 mL round-bottom flask with stir bar and purge-pumped three times. The solid was dissolved in 10 mL of dry tetrahydrofuran and chilled to -78 °C. 2.4 mL of 2.5 M \textit{n}-butyl lithium solution in hexanes was added to the solution dropwise and the mixture was stirred for 30 min at -78 °C following the addition. 0.60 mL of dry, degassed dimethylformamide was added dropwise to the cold solution and the reaction was stirred at -78 °C for 30 min after the addition before being warmed to room temperature. The solution was diluted with diethyl ether, passed through a celite pad, and eluted with diethyl ether. The reaction was washed with water and brine then dried over sodium sulfate and concentrated under reduced vacuum to yield 68 (0.59 g, 48%) as a colorless solid. Characterization data was consistent with ref. 79.

7-(3-(\textit{tert}-butyl)-4,5-bis(methoxymethoxy)phenyl)-2-naphthaldehyde (69): 68 (226 mg, 1.02 mmol), 5 (386 mg, 1.00 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (59 mg, 5 mol%) and sodium carbonate (221 mg, 2.09 mmol) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 19 mL of dry toluene, 1 mL of dry THF, and 1 mL of degassed water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 24-48 h. The reaction solvent was removed under reduced pressure and the resulting oil was dissolved in ethyl acetate and filtered through a silica pad. The filtrate was diluted with ethyl acetate, transferred to a separatory funnel, washed with ammonium chloride and brine, then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography to yield 69 (274 mg, 65%) as a light yellow solid.

1\textsuperscript{H} NMR (300 MHz, CHLOROFORM-\textit{d}) \(\delta\) ppm 1.45 (s, 9 H) 3.48 - 3.52 (m, 3 H) 3.60 - 3.65 (m, 3 H) 5.24 (s, 4 H) 7.31 (dd, \(J=11.72, 2.20\) Hz, 2 H) 7.77 - 7.83 (m, 1 H) 7.89 (d, \(J=0.98\) Hz, 3 H) 8.07 (d, \(J=1.71\) Hz, 1 H) 8.35 (s, 1 H) 10.12 (s, 1 H)

2-(7-(\textit{tert}-butyl)-4,5-dihydroxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (71): 69 (105 mg, 0.22 mmol) was added to an oven-dried 50 mL round-bottom flask with stir bar and dissolved in minimal ethyl acetate. 5 drops of concentrated hydrochloric acid
were added to the solution and the mixture was stirred overnight. The reaction was transferred to a separatory funnel, diluted with ethyl acetate, washed with brine then dried over sodium sulfate. The solvent was evaporated under reduced pressure then **BHA** (71 mg, 0.48 mmol) was and the vessel was purge-pumped with nitrogen 3 times. The solids were suspended in 2.5 mL of dry methanol, the vessel was shielded from light and the reaction was stirred for 48-72 h. The solvent was removed under reduced pressure to give a yellow solid which was dissolved in diethyl ether, filtered through silica, and eluted with diethyl ether. The filtrate was concentrated under reduced pressure to give **71** (81 mg, 75%) as a light yellow solid. $^1$H NMR (300 MHz, CHLOROFORM-$d$) δ ppm 1.17 (s, 4 H) 1.41 - 1.45 (m, 9 H) 4.91 (s, 1 H) 6.95 (s, 1 H) 7.16 (s, 1 H) 7.57 (d, $J=9.52$ Hz, 2 H) 7.74 - 7.80 (m, 2 H) 7.86 (d, $J=7.81$ Hz, 1 H) 7.92 (s, 1 H)

**2-(7-(3-(tert-butyl)-4,5-dihydroxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (72):** To a 50 mL oven-dried round-bottom flask with stir bar 75 mg (0.16 mmol) of **71** was added and dissolved in 10 mL of Et$_2$O and 3 mL pH 7 phosphate buffer. 55 mg (0.22 mmol) of I$_2$ was added to a 100 mL separatory funnel and dissolved in 5 mL Et$_2$O. The round-bottom flask was shielded from light and the I$_2$ ether solution was added dropwise to the shielded flask. Following addition, the separatory funnel was rinsed into the reaction solution with 5 mL of Et$_2$O then 30 mL of pH 7 buffer was charged to the separatory funnel and the reaction solution was transferred to the separatory funnel with Et$_2$O. The reaction was quickly washed with 10 mL saturated Na$_2$S$_2$O$_3$ solution then washed three times with saturated brine and dried over Na$_2$SO$_4$. The reaction solvent was removed under reduced pressure to afford 25 mg (34%) of **72**, a blue solid. Insufficient material available for characterization, more is being generated.

**2,7-NAP (73):** To an oven-dried 25 mL round-bottom flask with stir bar, 25 mg (0.05 mmol) of **72** was added with 39 mg (0.06 mmol) of Zn(OH)Tp$^{\text{Cum,Me}}$ and purge-pumped three times. 8 mL of dried MeOH was added to the flask and the solution was stirred for 2 h under an inert atmosphere of N$_2$. The septum was then removed and the reaction was stirred vigorously overnight open to atmospheric conditions. The solvent was removed under reduced pressure and
the resulting solid was purified by column chromatography (Basic alumina, 50% EtOAc in Hexanes) to yield a brown solid.
APPENDIX C

Antiferromagnetically-Coupled Biradicals: Correlating the Magnitudes of Ferro- and Antiferromagnetic Exchange Through Common Molecular Bridges

C.1 Introduction

Organic biradicals and polyradicals have been used to study the fundamental properties of fundamental electronic structure, molecular magnetism, molecular electronic, and electron transfer theory. Borden and Davidson divided biradicals into two classes based on overlap the overlap of the singly-occupied MO (SOMO) fragments, separating them into disjoint and nondisjoint biradicals. Disjoint biradicals are non-Kekulé structures that display zero overlap density between the two SOMOs, while nondisjoint biradicals share at least some overlap between SOMOs. Disjoint biradicals typically display either a singlet ground state or have a very small singlet-triplet gap, while nondisjoint biradicals typically exhibit a triplet ground state. As such, most organic biradical/polyradical literature uses an MO model to discuss magnetic exchange, focused on the overlap or lack thereof of SOMO density. Alternatively, we use a VBCI/McConnell superexchange model to describe the coupling between the spins of SQ-B-NN biradicals, utilizing a methodology that relates $J_{SQNN}$ to the square of the electronic coupling matrix element $H_{SQNN}^2$, according to equation (C.1).

$$J_{DA} = \frac{H_{DA}^2 K_0}{U^2 - K_0^2}$$ (C.1)

As discussed previously, the SQ-B-NN biradical paradigm has been used to study the effect of bridge identity on exchange coupling through a variety of structural modifications. Separating the donor SQ and acceptor NN units with a series of phenyl spacers showed that $J_{SQNN}$ varied exponentially with distance, resulting in a greater coupling with lesser distance between spin-bearing units. Studying the effect of bridge rotation on the magnitude of $J_{SQNN}$ showed that when the conjugated bridge linker is rotated out of plane from the donor and acceptor units the magnitude of $J_{SQNN}$ decreased. Also, as discussed in pervious chapters and primarily investigated with a series of pyridine-thiophene bridges, the identity of the bridge FOMOs plays a large role in the magnitude of $J_{SQNN}$. These D-B-A biradicals have all helped to probe the effect that the bridge plays in facilitating electronic coupling between conjugated
donor and acceptor subunits, but a wider scope of information is needed to probe true role of the bridge in broad-spoken magnetic coupling. Using the same bridge spacer between two different spin bearing units could provide a different facilitation of coupling for a variety of reasons not limited to overlap of SOMO densities. As such, the investigation of SQ-B-SQ (D-B-D) and NN-B-NN (A-B-A) complexes would serve to advance the full vision of how bridge identity impacts the coupling between two spin-bearing subunits.

Bis-NN compounds reminiscent of characterized SQ-B-NN compounds have been previously studied for exchange coupling (Figure C-1).

![Chemical structures of SQ-B-NN and NN-B-NN complexes](image)

**Figure C-1.** Previously studied SQ-B-NN biradicals with varying bridge chemistries and substitution patterns as well as their correlated NN-B-NN biradicals of identical bridge.9,20,108,109,112-117
When compared to one another, the bis-NN complexes all show opposite exchange-type (ferromagnetic vs antiferromagnetic) which is to be expected based on the difference of spin positioning between a SQ and a NN subunits, but moreover they also differ in magnitude. In a general sentence, the magnitude of exchange coupling between SQ and NN is typically greater than that between NN and NN. However, when plotting the magnitudes of $J_{SQ-B-NN}$ against that of $J_{NN-B-NN}$ for the identical bridge a definite trend is observed (Figure C-2).

![Figure C-2. A plot comparing the exchange coupling of SQ-B-NN biradicals and their corresponding NN-B-NN biradicals of identical bridge chemistry. A clear trend is present between the magnitude of $J_{SQ-B-NN}$ and $J_{NN-B-NN}$ indicated by the near linear relation ($R = 0.98$).](image)

The clear relation between the magnitude of $J_{SQ-B-NN}$ and that of the corresponding $J_{NN-B-NN}$ suggests that the effect the bridge has on the exchange coupling is ubiquitous between the D-B-A case and the A-B-A case. The next logical series of compounds to study in order to determine whether the bridge impacts exchange coupling in the same way regardless of the identity of the spin-bearing unit would be a series of SQ-B-SQ (bis-SQ) compounds of the same bridges. Herein is discussed the currently completed worked in the synthesis of three of the relevant bis-SQ compounds.
C.2 Completed Work

Three bis-SQ compounds have been targeted for synthesis and magnetic evaluation. These three bis-SQs are counterparts to thiophene and phenyl spaced SQ-B-NN and NN-B-NN compounds that have already been generated and studied (Figure C-3).

All three of these compounds were generated using the same two-step synthetic pathway from commercially available dibromo starting materials of the appropriate geometry (Scheme C-1). Reacting two equivalents of 5 with any of the dibromo starting materials results in the generation of the bridge in question substituted with two mom-protected tertbutyl catechols which deprotect.
when stirred overnight in MeOH with catalytic acid to form the bis-catechol compounds. Once deprotected, the bis-catechol compounds are stirred in a 2:3 mixture of DCM:MeOH with 1.95 stoichiometric equivalents of Zn(OH)TPc^{cum,me} and K_{2}CO_{3} under an nitrogen atmosphere for an hour. During this hour, reaction mixture changes colors, going from the colorless solution characteristic of the bis-catechol compounds to a more highly colored solution characteristic of paramagnetic final product. The p-phenyl complex presented a highly colored blue solution, while both thiophene isomers were dark green in color. Following that hour stirring under nitrogen the reaction vessels were opened to air and stirred overnight to complete the oxidation to SQ. All three isomers displayed the same single line EPR pattern in their room temperature fluid solution EPR spectra (Figure C-4), suggesting that in all three cases one, if not both catechol substituents reacted appropriately to form the SQ. The reaction was then filtered and washed with MeOH before the resulting solid was recrystallized.

![EPR Spectrum](image)

**Figure C-4.** Room temperature fluid solution EPR spectrum of \( p\text{-Ph-SQ}_{2} \)

Multiple solvent combinations were attempted in efforts to grow X-ray quality crystals of the three bis-SQ compounds, however only conditions to recrystallize \( p\text{-Ph-SQ}_{2} \) were found. \( p\text{-Ph-SQ}_{2} \) crystals for X-ray analysis were grown via the liquid-layering of DCM and EtOH and solved for the structure shown in figure C-5.
Figure C-5. Thermal ellipsoid plot determined through X-ray diffraction of $p$-Ph-$SQ_2$ crystals grown from liquid layering of DCM and EtOH. Hydrogens and tris(2-cumynyl-methylpyrazolyl)borate “fingers” of the ancillary ligands are omitted for clarity.
Scheme C-1. Synthetic route used to create the three bis-SQ biradical compounds \textit{p-Ph-SQ$_2$}, \textit{2,4-Th-SQ$_2$}, and \textit{2,5-Th-SQ$_2$}.
C.3 Experimental

5,5''-di-tert-butyl-[1,1':4',1''-terphenyl]-3,3'',4,4''-tetraol (74): 1,4-Dibromobenzene (99 mg, 0.42 mmol), 5 (307 mg, 0.81 mmol), Pd(PPh₃)₄ (45 mg, 5 mol%), sodium carbonate (171 mg, 1.6 mmol) and tetrabutylammonium bromide (13 mg, 10 mol%) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography. The MOM-protected product was then dissolved in 10 mL of MeOH and 0.5 mL of concentrated HCl then left to stir overnight. The next day the reaction was diluted with Et₂O, washed with brine, dried over sodium sulphate, and concentrated under reduced pressure to afford 74 (127 mg, 75%) as a colorless oil. ¹H NMR (400MHz, CHLOROFORM-d) δ = 7.61 (s, 4 H), 7.28 (s, 4 H), 1.49 (s, 18 H)

p-Ph-SQ₂ (75): 74 (49 mg, 0.12 mmol), Zn(OH)Tp cum,me (170 mg, 0.25 mmol), and K₂CO₃ (36 mg, 0.24 mmol) were added to an oven dried round bottom flask and purge pumped three times. The solids were suspended in 4 mL of DCM and 6 mL of MeOH then the slurry was left to stir under a nitrogen atmosphere for 24 h. The reaction was then opened to air and left to stir for another 24 h. The resulting suspension was then filtered and the solid was washed with MeOH and collected with DCM, then concentrated under reduced pressure and recrystallized via vapor diffusion of EtOH and DCM to afford 74 (220 mg, 79%) as a blue solid. Insufficient material available for characterization.

5,5'-(thiophene-2,4-diyl)bis(3-(tert-butyl)benzene-1,2-diol) (76): 2,4-Dibromothiophene (113 mg, 0.47 mmol), 5 (355 mg, 0.93 mmol), Pd(PPh₃)₄ (11 mg, 2 mol%), sodium carbonate (198 mg, 1.9 mmol) and tetrabutylammonium bromide (15 mg, 10 mol%) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a
nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography. The MOM-protected product was then dissolved in 10 mL of MeOH and 0.5 mL of concentrated HCl then left to stir overnight. The next day the reaction was diluted with Et₂O, washed with brine, dried over sodium sulphate, and concentrated under reduced pressure to afford 74 (129 mg, 68%) as a colorless oil. ¹H NMR (400MHz, ACETONE-d₆) δ = 7.70 (s, 1 H), 7.57 (s, 1 H), 7.40 (m, 2 H), 7.33 (d, J = 8.8 Hz, 2 H), 1.47 (s, 18 H)

2,4-Thio-SQ₂ (77): 76 (61 mg, 0.15 mmol), Zn(OH)Tp⁻cum,me (211 mg, 0.30 mmol), and K₂CO₃ (46 mg, 0.33 mmol) were added to an oven dried round bottom flask and purge pumped three times. The solids were suspended in 4 mL of DCM and 6 mL of MeOH then the slurry was left to stir under a nitrogen atmosphere for 24 h. The reaction was then opened to air and left to stir for another 24 h. The resulting suspension was then filtered and the solid was washed with MeOH and collected with DCM, then concentrated under reduced pressure to afford 77 (130 mg, 50%) as a purple solid. Insufficient material available for characterization.

5,5'-(thiophene-2,5-diyl)bis(3-(tert-butyl)benzene-1,2-diol)(78): 2,5-Dibromothiophene (160 mg, 0.48 mmol), 5 (367 mg, 0.97 mmol), Pd(PPh₃)₄ (11 mg, 2 mol%), sodium carbonate (211 mg, 1.9 mmol) and tetrabutylammonium bromide (15 mg, 10 mol%) were added to an oven-dried 50 mL round-bottom flask with stir bar under an inert gas atmosphere. 8 mL of dry toluene, and 2 mL of deoxygenated water were added to the vessel and the flask was then fitted with a nitrogen-purged condenser, shielded from light, and brought to reflux for 16 h. The reaction solvent was transferred to a separatory funnel, washed with brine then dried over sodium sulfate. The reaction mixture was concentrated under reduced pressure and purified via flash chromatography. The MOM-protected product was then dissolved in 10 mL of MeOH and 0.5 mL of concentrated HCl then left to stir overnight. The next day the reaction was diluted with Et₂O, washed with brine, dried over sodium sulphate, and concentrated under reduced pressure to afford 74 (141 mg, 71%) as a colorless oil. ¹H NMR (400MHz, ACETONE-d₆) δ = 7.37 (d, J = 2 Hz, 2 H), 7.35 (s, 2 H), 7.31 (d, J = 2 Hz, 2 H), 1.47 (s, 18 H)
2,5-Thio-SQ₂ (79): 78 (51 mg, 0.12 mmol), Zn(OH)Tp^{cum,mc} (173 mg, 0.25 mmol), and K₂CO₃ (34 mg, 0.25 mmol) were added to an oven dried round bottom flask and purge pumped three times. The solids were suspended in 4 mL of DCM and 6 mL of MeOH then the slurry was left to stir under a nitrogen atmosphere for 24 h. The reaction was then opened to air and left to stir for another 24 h. The resulting suspension was then filtered and the solid was washed with MeOH and collected with DCM, then concentrated under reduced pressure to afford 79 (168 mg, 77%) as a purple solid. Insufficient material available for characterization.
## Appendix D.

### Crystallographic Data

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<tr>
<td>Largest diff. peak/hole/ e Å⁻³</td>
<td>0.769 and -0.608 eÅ⁻³</td>
<td>1.334 and -1.571 eÅ⁻³</td>
</tr>
</tbody>
</table>