

Synthesis of New Molecule-Based Magnets Using Bridging Organic Radicals

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Abstract

Several new families of organic acceptors that are candidates as building blocks of molecule-based ferrimagnets were synthesized and characterized. These families include fluorodicyanostilbenes, a tetrachlorodicyanostilbene, naphthyltricyanoethylenes, bromophenyltricyanoethylenes, and an anthryltricyanoethylene. The magnetic networks were synthesized by reacting each acceptor with $\text{V}(\text{CO})_6$. The magnets synthesized in this study were characterized using a SQUID magnetometer, elemental analysis, and infrared spectroscopy. Although some combinations failed to yield magnetically ordered materials, others exhibited ordering temperatures in the range of 95 K – 260 K. The ordering temperatures and saturation magnetizations were compared among families of acceptors and correlated with individual properties of the acceptors such as reduction potential and structure.

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General Audience Abstract

Several new families of organic molecules have been created and examined for use as building blocks of molecule-based magnets. These families include fluorodicyanostilbenes, a tetrachlorodicyanostilbene, naphthyltricyanoethylenes, bromophenyltricyanoethylenes, and an anthryltricyanoethylene. The 3-D magnetic scaffoldings were created by combining an individual organic molecule in one of the families listed above with vanadium. The magnets created in this study were examined using a SQUID magnetometer, elemental analysis, and infrared spectroscopy. Some of the combinations of the organic molecules with vanadium failed to result in a 3-D magnetic scaffolding and showed no magnetic properties. Others showed magnetic properties in the below certain temperatures in the range of 95 K – 260 K. The magnetic properties were compared among families of molecules and correlated with individual properties of each molecule such as electronic effects and structure.

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Chapter 1: Magnetism Background

1.1 Introduction

Scientists have studied many phenomena throughout the ages, including light, sound, and motion, but one of the least understood is magnetism. The ancient Greeks found that magnetite can attract other pieces of magnetite (Fe_3O_4). Scientists such as Gauss, Coulomb, Faraday, and Maxwell conducted quantitative experiments and developed theories of magnetism.^{1,2} What started as a curiosity has evolved into technologies that have many applications in everyday electronics such as in speakers and receivers for cell phones and the hard drives of computers.³

With the evolution of electronics, especially in the field of renewable energy, comes the need for new materials that can replace rare earth magnets. For example, wind turbine generators are often composed of neodymium-iron-boron magnets and often use other rare earth metals such as praseodymium (Pr), dysprosium (Dy) and terbium (Tb). The element content of these magnets can be up to 32% by weight, which means that a wind farm would require large amounts of rare earth metals.⁴ Previously identified atom-based magnets are synthesized incurring high metallurgical costs. The metals for these magnets are located in countries like Russia and China and are often difficult to obtain because of the instability of alliances and because of the cost.^{5,6}

In the 21st century, there has been a shift in using organic and polymeric materials as replacements for metal and ceramic materials. Research in the area of magnetism has yielded new molecule-based magnetic materials that have ordering temperatures at or above room temperature,⁷ high saturation magnetizations,⁸ and large coercive fields.⁹ Molecule-based magnets are interesting because the magnets are derived from organic molecules whose steric and electronic properties can, in principle, be fine-tuned using the tools of ordinary organic synthesis. This

chapter presents a brief discussion of some fundamentals of magnetism followed by a review of literature on networks of organic radicals bridging metal ions in Chapter 2.

1.2 Spin States and Orbital Splitting

The fundamental building block of magnetism is the unpaired electron. In the absence of an applied field, the two spin states, $S = +\frac{1}{2}$ and $S = -\frac{1}{2}$, are degenerate. However, in an applied magnetic field the energies of these two orientations are split. For polyelectronic species, Hund's rule dictates that the ground state of a given electron configuration is the one with maximum total spin. The total spin of the molecule or ion will then be $\frac{1}{2} \times$ (total number of unpaired electrons). To determine the spin state, one must consider the influence of orbital splitting as well as the electron configuration of the molecule or ion according to the application of the Aufbau Principle.

The spin states for first row transition metal ions are determined by the degree of d orbital splitting which may be understood using ligand field theory. The metal ion with no ligands bound to it has five degenerate d orbitals. In an octahedral geometry, symmetry dictates that the six symmetry-adapted linear combinations of orbitals capable of sigma bonding that surround the metal transform as the irreducible representations a_{1g} , e_g , and t_{1u} . Mixing these orbitals with the atomic orbitals on the metal results in the d orbitals being split into different energy levels. For an octahedral field, the $d_{x^2-y^2}$ and d_{z^2} orbitals are degenerate and have e_g symmetry with lobes along the coordinate axes. The d_{xy} , d_{yz} , and d_{xz} orbitals are separately degenerate and have t_{2g} symmetry with lobes between the coordinate axes. The d_{xy} , d_{yz} , and d_{xz} do not have the correct symmetry for σ interactions with the ligands and remain non-bonding. However, the $d_{x^2-y^2}$ and d_{z^2} orbitals have the correct symmetry for σ interactions with the ligands and form bonding and anti-bonding

orbitals. As the strength of the M-L σ bonds increase, the splitting of the octahedral field increases.

Figure 1-1.

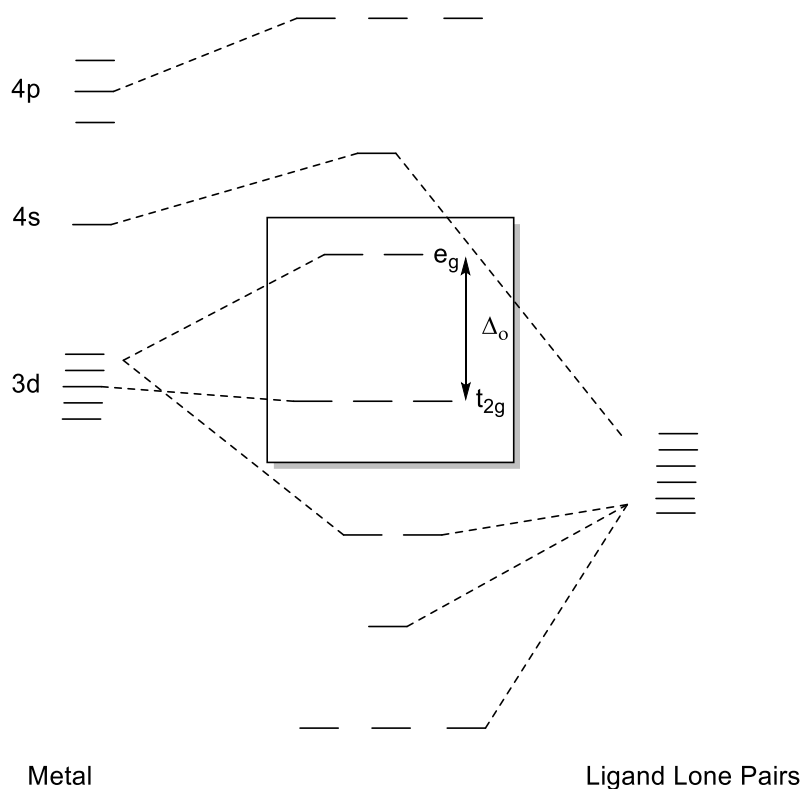


Figure 1-1: A ligand field theory picture of metal ligand bonding in an octahedral complex. The solid box contains the d orbitals

Ligand field theory provides a model for explaining why different ligands give rise to larger or smaller values of Δ_o , the splitting between the metal e_g and t_{2g} set. The interaction described above would result from a ligand, such as ammonia, in the middle of the spectrochemical series that ranks ligands by how they affect Δ_o . Ligands can be arranged along a continuum of high field to low field. The high field (large Δ_o) ligands form σ bonds and can also accept π electrons from the metal. An example of a high field ligand is carbon monoxide (CO). CO can accept π electrons from the metal into the CO π^* orbital. Since the π^* orbitals are higher in energy than the metal t_{2g} orbitals, the interaction between the ligand and the metal lowers the energy of the metal orbitals.

Low field ligands engage in sigma donation, but also donate π electrons to the metal. An example of a weak field ligand is chloride. Chloride is a good π donor because the Cl p orbitals are lower in energy than the metal t_{2g} orbitals. The orbital overlap between the ligands and the metal d orbitals results in raising these orbitals in energy but lowers the energy of the ligand p orbitals.¹⁰ A large Δ_o between the e_g and t_{2g} sets of d orbitals favors a complex with more paired electrons known as a low spin complex, whereas a small Δ_o favors a complex with more unpaired electrons known as a high spin complex, Figure 1-2. The entire discussion above applies to a situation referred to as “spin only,” because the magnetic properties of many compounds can be explained with a model that only considers electron spin. The spin-only model applies to all the compounds discussed in this dissertation. There is additionally the possibility of an orbital contribution of which a further discussion can be found in Kahn.¹¹

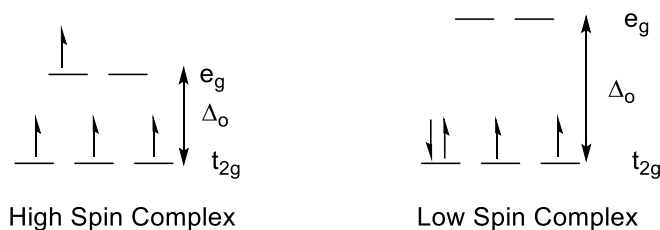


Figure 1-2: A d^4 high spin complex on the left and a d^4 low spin complex on the right.

1.3 Changes in Magnetization with Temperature

1.3.1 Paramagnetism and Magnetic Susceptibility

Unpaired electrons give rise to a magnetic dipole moment. A magnetic dipole moment is the magnetic moment of an electron caused by its intrinsic properties of spin and charge.¹² The value that expresses the density of permanent or induced magnetic dipole moments in a magnetic material is known as magnetization.¹³ In a solid, when those magnetic dipole moments act independently of one another and respond only to the applied magnetic field, this behavior is

paramagnetism. Each set of unpaired electrons is randomly oriented with respect to each other and create no net magnetization. When an external magnetic field is applied, these electrons tend to lower their energy by aligning with the field, producing non-zero magnetization. Once the field is removed, the magnetization dissipates, Figure 1-3. Because thermal motion always tends to randomize the orientation of the magnetic dipoles, magnetization varies with temperature following the Curie Law, which will be discussed in the next section.

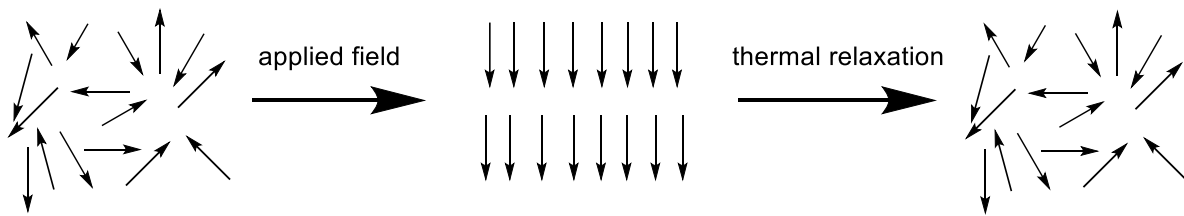


Figure 1-3: The representation of magnetic dipole moments in a state of paramagnetism, applying a magnetic field to align the magnetic dipole moments, and then thermal relaxation back to paramagnetism.

Magnetic susceptibility (χ) is defined as the degree of magnetization (M) that a material acquires in response to an applied magnetic field (H).¹⁴ The equation for magnetic susceptibility is $\chi = \frac{M}{H}$. Magnetic susceptibility can be measured in a variety of ways. The most common way is using a Superconducting Quantum Interference Device magnetometer (SQUID).¹⁵

1.3.2 Curie Law

The Curie Law states that the magnetic susceptibility of a paramagnetic material is inversely proportional to the absolute temperature.¹¹ The equation for the Curie Law is $\chi = \frac{C}{T}$.

Combining it with the above gives $\frac{M}{H} = \frac{C}{T}$ which is analogous to an “ideal gas law” for magnetism.

The relationship between temperature and magnetic susceptibility when graphing χT vs. T for a paramagnetic material is equivalent to the Curie constant, $C = \frac{N_A g^2 \mu_B^2 S(S+1)}{3kT}$, where N_A is

Avogadro's number with a value of $6.0220 \times 10^{23} \text{ mol}^{-1}$; g is the Landè constant with a value of around 2.0, μ_b is the Bohr magneton with a value of $9.274 \times 10^{-24} \text{ J T}^{-1}$, k is Planck's constant with a value of $1.3807 \times 10^{-23} \text{ J K}^{-1}$, and S is the total spin of the molecule. N_A , μ_b , and k can be lumped together to equal 0.375 emu K/mol , where emu stands for electromotive units.

Magnetic susceptibility can be plotted in terms of $1/\chi$ vs T or in terms of χT vs. T to examine Curie Law, Figure 1-4. It is usually plotted in terms of χT vs. T because any deviation in χT from paramagnetism is easily noticed. When the χT vs. T curve increases, it indicates ferromagnetic coupling. However, when the curve decreases there could be a variety of reasons for deviation, one of which is antiferromagnetic coupling.

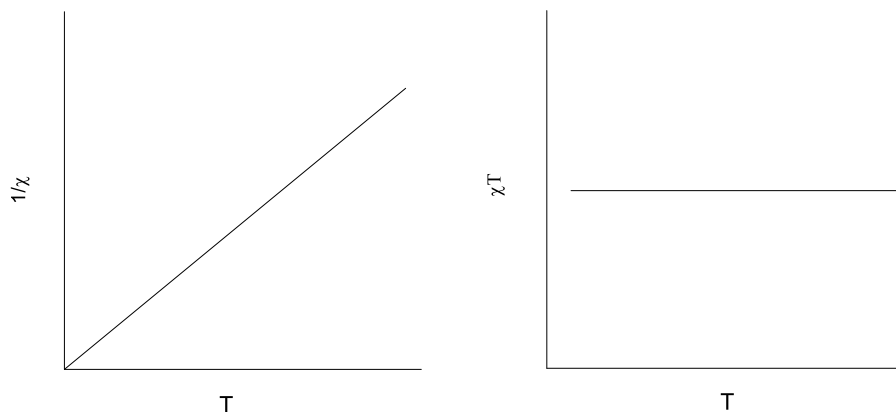


Figure 1-4: Curie Law magnetic behavior of paramagnetic substances.

1.3.3 Deviations from Curie Behavior: The Curie-Weiss Law

Molecule-based magnets follow the Curie law when interactions between magnetic dipoles can be neglected.¹⁶ However, when there are interactions between magnetic dipoles, molecule-based magnets exhibit significant deviations from the Curie Law. One source of deviations relevant to this dissertation is non-negligible magnetic interactions between the spin centers that

are coordinated to each other. These interactions can be of two general forms, one that favors parallel alignment of neighboring spins (ferromagnetic coupling) and one that favors antiparallel alignment (antiferromagnetic coupling).

To model the deviations from Curie Law, a mean-field model¹¹ can be used to derive the Curie Weiss Law, $C = \frac{\chi}{T-\theta}$. The θ term can be determined empirically from the inverse magnetic susceptibility versus temperature plot, Figure 1-5.

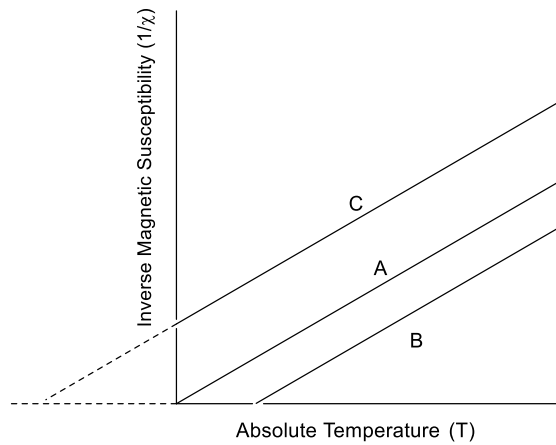


Figure 1-5: A graph of inverse magnetic susceptibility versus temperature with Curie Law (A), ferromagnetic coupling (B) and antiferromagnetic coupling (C) represented.¹⁷

When there is antiferromagnetic coupling between spins, θ is negative and the x-intercept of the graph is negative. When there is ferromagnetic coupling between spins, θ is positive and the x-intercepts of the graph is positive. The Curie Weiss law accounts for deviations from Curie law behavior, however it does not address the specific reason for deviation.

1.3.4 Magnetic Ordering

The phenomena we are most interested in are those that result in long-range magnetic order. Long-range order is defined as when unpaired electrons on adjacent magnetic lattice sites are aligned either parallel or antiparallel over macroscopic distances. The three basic types of magnetic ordering that solids display are ferromagnetism, antiferromagnetism, and ferrimagnetism. At

sufficiently high temperatures, all spin-containing solids are paramagnets. However, at sufficiently low temperature, the sample can become long-range ordered.

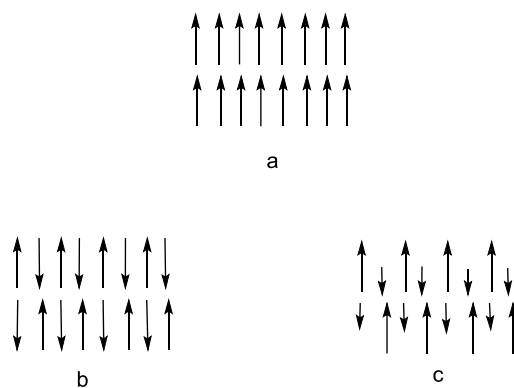


Figure 1-6: Representation of the magnetic dipole orientation for a) ferromagnetism, b) antiferromagnetism, and c) ferrimagnetism.

1.3.4.1 Ferromagnetism

Coupling is the interaction between molecules that can produce magnetic ordering. If a material has spin interactions between neighboring molecules that align the spins in the same direction, the material is displaying ferromagnetic coupling, which leads to ferromagnetic ordering. However, coupling is not synonymous with ordering: just as intermolecular interactions can cause condensation of a gas into a liquid or a solid, coupling can lead to magnetic ordering or deviation from Curie Law and incomplete ordering.¹⁸ In ferromagnetic ordering, a large domain of magnetic dipoles in the material become oriented in the same direction, Figure 1-6a, and can remain ordered even in the absence of the applied magnetic field. The temperature at which a material's intrinsic magnetic properties change from paramagnetism to ferromagnetism is called the Curie temperature, T_C . An example of a ferromagnet is $\gamma\text{-Fe}_2\text{O}_3$.¹⁹

1.3.4.2 Antiferromagnetism

If the material has strong spin interactions between neighboring molecules that align the spins in opposing directions, the material is displaying antiferromagnetic coupling. Just like

ferromagnetic coupling leads to ferromagnetic ordering, antiferromagnetic coupling can lead to antiferromagnetic ordering. The opposing spins have the same magnitude and cancel any internal net magnetic field, Figure 1-6b. The temperature at which a material's intrinsic magnetic properties change from paramagnetism to antiferromagnetism is called the Néel temperature, T_N .²⁰ An example of an antiferromagnet is FeBO_3 .²¹

1.3.4.3 Ferrimagnetism

If the magnetic dipoles of the material antiferromagnetically couple but magnetic dipoles on one lattice site are different in magnitude from those on the adjacent site, the result is ferrimagnetism, Figure 1-6c. Ferrimagnetism can be seen almost as a combination of antiferromagnetism and ferromagnetism. The nearest neighbor interactions are similar to antiferromagnetism except that one set of magnetic dipoles is larger than the opposing set of magnetic dipoles. The incomplete cancellation causes a net magnetization analogous to ferromagnets.¹⁶ For ferromagnetic materials, researchers often use the term critical temperature (T_c) at which the materials intrinsic magnetic properties change from paramagnetism to ferrimagnetism. An example of a mineral that is ferrimagnetic is magnetite (Fe_3O_4) which contains alternating Fe^{3+} (5 unpaired electrons) and Fe^{2+} (4 unpaired electrons) centers spaced between oxygen atoms in the crystal lattice.²²

The molecule-based magnets described in this dissertation are ferrimagnetic. There are two sources of unpaired electrons in a molecule-based magnetic material, those from a metal and those from an organic radical, which tend to align their spins antiferromagnetically because of a direct exchange interaction.

1.4 Magnetic Measurements

1.4.1 SQUID Magnetometer

The most sensitive technique for making magnetic measurements uses a Superconducting Quantum Interference Device Magnetometer. The SQUID allows for the direct determination of magnetic moment for a sample with sensitivities down to 5×10^{-18} T. Several types of measurements can be made including magnetization (M) versus applied magnetic field (H) at a constant temperature, magnetization versus temperature at a constant applied field, and AC susceptibility measurements. The SQUID comprises of two niobium-lead superconductors that are separated by thin insulating layers that create two parallel Josephson Junctions. These materials are kept at liquid helium temperatures (4 K) to maintain superconductivity. Because of the temperature being controlled by liquid helium the SQUID can make measurements on materials in temperatures as low as 1.8 K and as high as 300 K.

1.4.2 M vs T Measurements

In order to find the ordering temperature of a material, one must use the SQUID to measure magnetization versus temperature at a constant applied magnetic field. Most materials that are measured using M vs. T are first cooled from room temperature down to 5 K in a small field (field cooling) or absent a field (zero field cooling). Once the temperature is stable, the magnetization is measured every 5 K from 5 K to 300 K in a very small applied magnetic field. The plot generated is typically a plateau that has a steep drop in magnetization as the material reaches its ordering temperature. The steepest part of the curve can be extrapolated to estimate the ordering temperature, Figure 1-7.

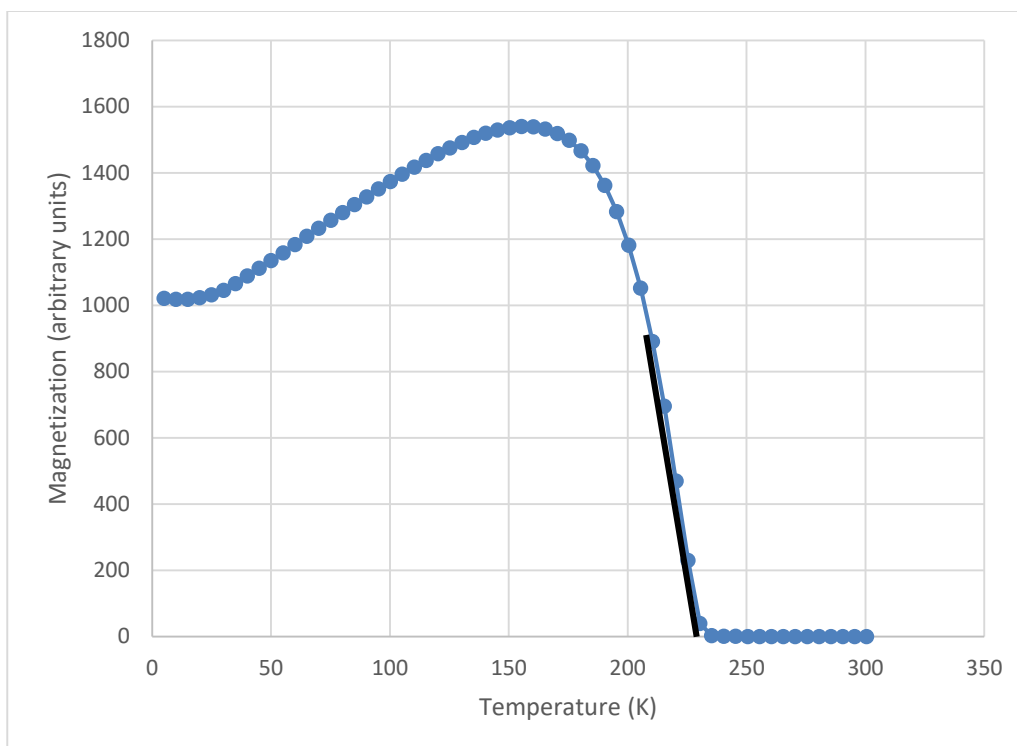


Figure 1-7: A magnetization versus temperature plot at a constant applied magnetic field of 5 G for $V(3\text{-BrPTCE})_2$. The ordering temperature is determined by extrapolating the steepest part of the curve to the x axis as displayed by the black line.

1.4.3 M vs H Measurements

Using the SQUID, the magnetization of a material can also be measured versus an applied magnetic field at a constant temperature, Figure 1-8). Starting at zero field, the applied magnetic field is increased until the sample reaches a desired magnetic field or saturation magnetization. Then the field is decreased past zero in the opposite direction to the opposite desired magnetic field or until saturation magnetization in the opposite direction. The field is then returned to zero. M vs. H plots show if a sample exhibits hysteresis, which is characteristic of permanent magnets and reflects the fact that the material possesses the knowledge of its recent history. This phenomenon manifests in non-zero coercivity and remanence magnetization of the sample. Coercivity is the ability of the magnetized material

to withstand an external magnetic field without becoming demagnetized. This value can be found on the M vs. H plot where the hysteresis loop crosses the x-axis. Remanence is the magnetization that remains after a sample is saturated and then the applied magnetic field is removed. This value can be found on the M vs. H plot where the hysteresis loop crosses the y-axis. The term “soft” is used to describe a magnet in which the coercivity is small.

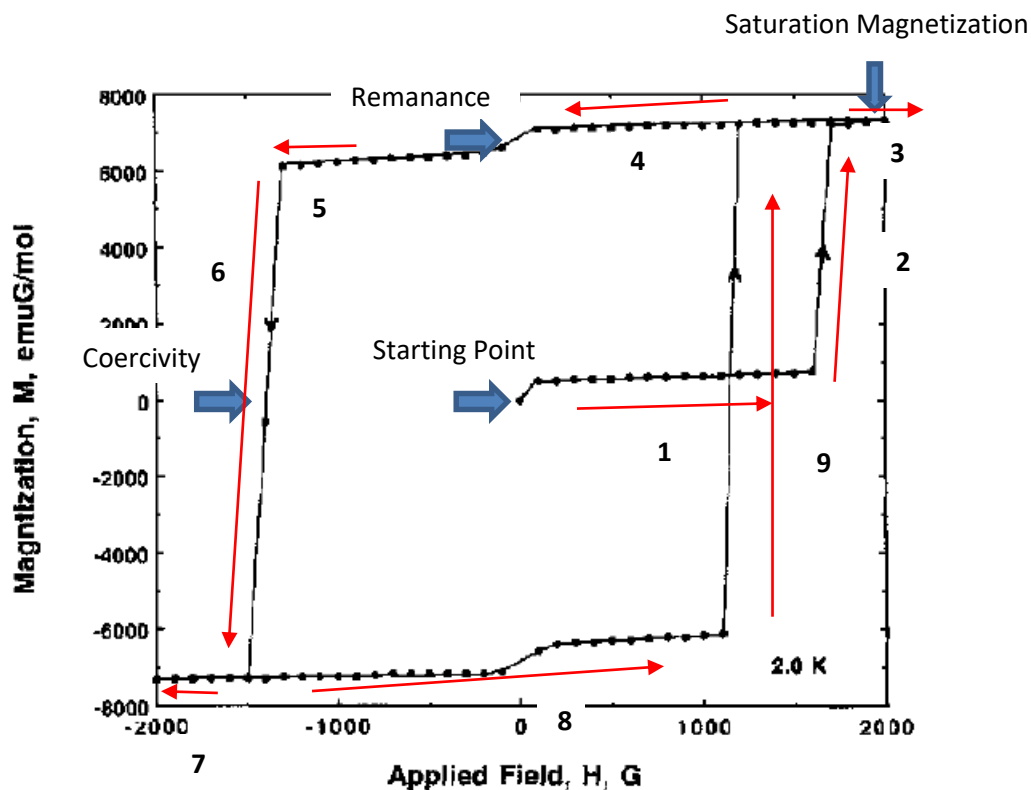


Figure 1-8: Shows the hysteresis loop for $[\text{MnCp}^*_2][\text{TCNE}]$.²³ The loop begins at the starting point and following the red arrows and numbers to form the hysteresis loop.

1.4.4 AC Susceptibility Measurements

In order to measure ac susceptibility, the magnetic flux of a sample is measured in the pickup coil when the sample is placed in an ac magnetic field. If the sample is paramagnetic, the sample will continue to follow the alternating magnetic field at low frequencies and at high frequencies, which produces an in-phase signal (χ') and give zero signal for the out-of-phase

signal (χ'') that lags 90° behind the applied magnetic field. For a sample that is beginning to exhibit long-range order, the signals show a temperature dependence. When the frequency is very low, the magnetic moment of the sample can follow the alternating applied magnetic field. When the frequency is higher, the magnetic moment of the sample will no longer be able to follow the alternating applied magnetic field. This results in a decrease in the in-phase, or real, component (χ') and the development of an out-of-phase, or imaginary, component (χ'') below a certain temperature. Both χ' and χ'' are sensitive to thermodynamic phase changes and can be used to measure ordering temperatures, Figure 1-9.²⁴

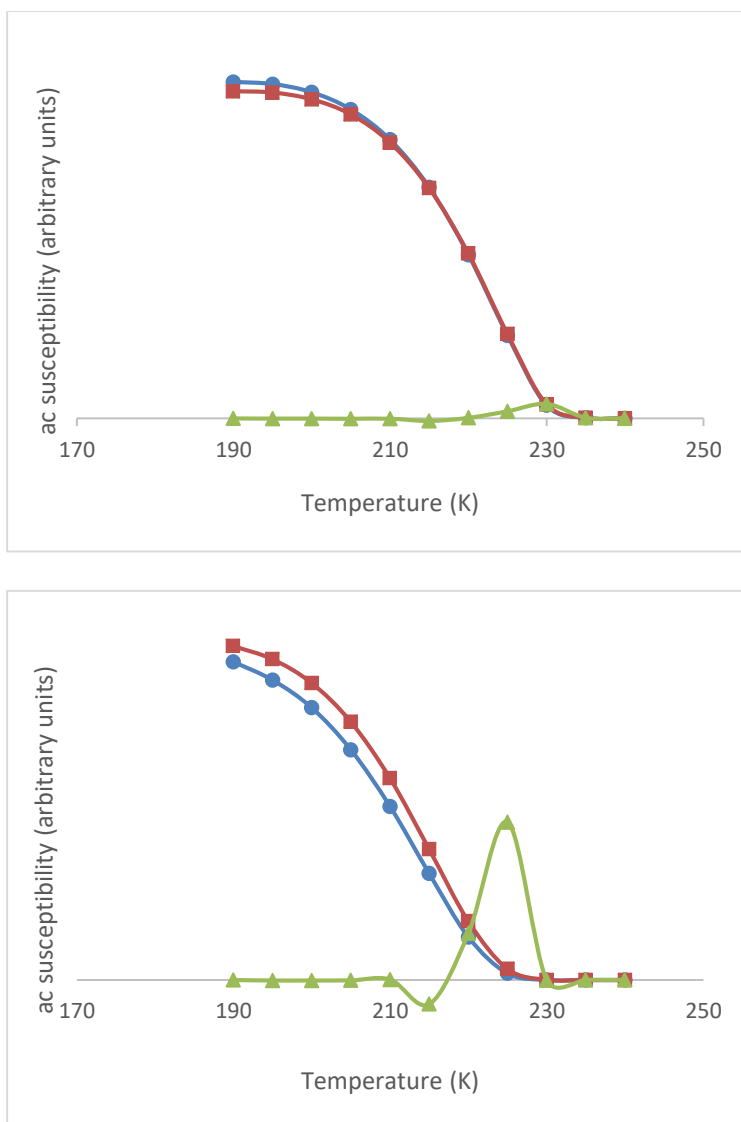


Figure 1-9: Plot of the real (top) and imaginary (bottom) parts of the ac susceptibility for $V(3\text{-BrPTCE})_2$ measured at 10 Hz (●), 100 Hz (■) and 1000 Hz (▲).

The discussion above is limited to the topics that are immediately relevant to this dissertation. For additional information on other fundamentals of magnetism, books by Carlin, Kahn, or Coey should be consulted.^{3,11,25}

Chapter 2 Molecule-Based Magnetism Based on Bridging Radical Anions

2.1 Introduction

Molecule-based magnets are defined as materials where molecular orbitals play a main role, whether by housing one or more unpaired electrons and/or by mediating magnetic coupling between spin centers.¹⁸ One goal in this field is to produce substances that exhibit long-range magnetic order at room temperature, ideally mimicking the behavior of a permanent magnet. In this dissertation, the key building block will mediate coupling between a metal containing cation with unpaired spins and an organic radical anion. However, the inherent reactivity of organic free radicals, molecules that contain at least one unpaired electron,²⁶ presents a problem: they tend to want to dimerize to pair up their electrons.

One way to stabilize an organic radical is through delocalization of the unpaired electron. To do this, molecules must be designed so that the unpaired electron resides in a π -type orbital, which allows for the delocalization of the spin onto several atoms. For example, a benzyl radical is less reactive than a phenyl radical.²⁷ The benzyl radical can delocalize through various resonance structures without creating formal charges, while the phenyl radical is localized in a sp^2 hybrid orbital.

A radical with a long lifetime is said to be persistent. Persistence can be improved by using substituents to sterically hinder access to the radical. As an example, if the *tert*-butyl radical is compared to the methyl radical, the *tert*-butyl radical has a longer lifetime than the methyl radical²⁸ because the methyl substituents on the *tert*-butyl radical provide more steric hindrance than the hydrogen atoms on the methyl radical. This increased steric hindrance keeps potential reactants from accessing the radical. An excellent example of persistence and stability is butylated hydroxytoluene (BHT). Once the OH bond is homolyzed, the BHT radical has increased stability

because of the steric hindrance by the *tert*-butyl groups on the 2 and 6 positions of the phenyl ring. These groups do not allow any dimerization to occur between BHT molecules but leave enough room for BHT to react with oxygen. BHT is electronically stabilized because of the electron density in the phenyl ring. This density stabilizes the radical on the oxygen through resonance, Figure 2-1.

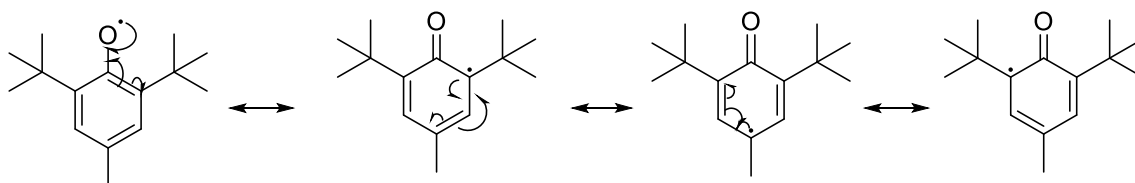


Figure 2-1: Resonance stabilization of the BHT radical.

In the field of molecule-based magnets there are a variety of different types of magnets. Initially, purely organic radical molecules such as nitronyl nitroxides and verdazyl radicals were studied in an attempt to obtain organic materials with characteristics similar to inorganic materials. However, bridging organic radicals in conjunction with paramagnetic transition metal ions are currently of interest. The advantages of the latter approach is that it is easier to produce strong magnetic coupling and to take advantage of the versatility and degeneracy of the metal *d* orbitals for magnetic interactions.²⁹

2.2 Tetracyanoethylene Radical Anions as Bridging Ligands

Bridging organic radical anions differ from the previously discussed neutral organic radicals because of their ability to form 3-D networks with transition metal ions. The precursor to the radical anion is a closed shell molecule with a delocalized π^* molecular orbital. It accepts an electron from the metal and then coordinates to it. By design, it can then coordinate to at least one other transition metal ion and serve as a bridging ligand to mediate spin communication between the transition metal centers. There are examples of molecule-based magnets ordering

antiferromagnetically, ferromagnetically, and ferrimagnetically with ordering temperatures anywhere from 5 K to above room temperature with high saturation magnetizations and hysteresis. Because the focus of this dissertation is on synthesizing molecule-based magnets using TCNE derivatives, this chapter will be to review pertinent cyanide and cyanocarbon materials with an emphasis on bridging radical anions.

2.2.1 Metalloporphyrin TCNE

An important bridging organic radical used in synthesizing molecule-based magnets is derived from tetracyanoethylene (TCNE) by one-electron reduction. TCNE is a closed-shell neutral molecule that easily undergoes a one-electron reduction (0.302 V vs. Ag/AgCl)³⁰ to form a resonance-stabilized radical anion. Some of the radical spin density and negative charge density reside in the nitrogen atom of each nitrile, creating a favorable site for interaction with the cationic metal centers.

One class of compounds with TCNE bridging radical anions are the metalloporphyrin TCNE linear chains. Miller and coworkers synthesized $[\text{MnTTP}]^{\cdot+} [\text{TCNE}]^{\cdot-}$, where TTP is *meso*-tetraphenylporphinato and $\cdot$ represents four unpaired electrons on Mn(III). This complex was the first TCNE metalloporphyrin and was found to be a 1-D chain structure with Mn(III) porphyrin cations coordinated to the TCNE radical anions in a donor-acceptor-donor-acceptor fashion ($\text{D}^+ \text{A}^{\cdot-} \text{D}^+ \text{A}^{\cdot-}$), Figure 2-2.

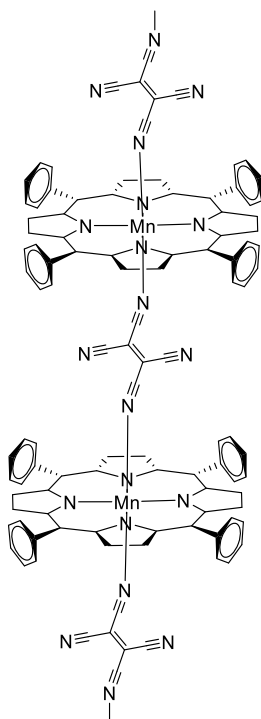


Figure 2-2: The $[\text{MnTPP}]^{3+} [\text{TCNE}]^{-}$ linear chain showing the two Mn TPP rings interconnected by a TCNE radical anion with exterior TCNE radical anions continuing the chain.

The crystal structure of the complex exhibited almost planar TCNE molecules with a slight twist between the uncoordinated $\text{N}\equiv\text{C}-\text{C}=\text{C}-\text{C}\equiv\text{N}$ atoms of 1.9° .³¹ The Mn TPP molecules were essentially planar, similar to other metallo-*meso*-tetraphenylporphyrinato complexes.^{8,32,33}

The temperature-dependent magnetic susceptibility was measured for $[\text{MnTPP}]^{3+} [\text{TCNE}]^{-}$ from 1.4-360 K. The susceptibility fit the Curie-Weiss expression only from 115 to 250 K. A minimum was found around 250 K, which is characteristic of 1-D ferrimagnetic behavior. 1-D ferrimagnetic behavior has this initial minimum in the magnetic susceptibility because of short-range antiferromagnetic interactions. The four spins on the Mn(III) are coupled antiferromagnetically to the one spin on TCNE radical anion. Additional interchain interactions give rise to long-range order ferromagnetic order at lower temperatures. Modeling the data as a one-dimensional material was unsuccessful, suggesting additional couplings among different chains (3-D effects).³¹

2.2.2 $V(TCNE)_2$

The first room temperature magnet, $V[TCNE]_2 \cdot y(\text{solvent})$, was synthesized by Manriquez and co-workers via reaction of TCNE with $V(C_6H_6)_2$. The complex exhibited an ordering temperature above 350 K but showed signs of degradation before the final ordering temperature could be reached.³⁴ The morphology was examined by PXRD and TEM to show that it is amorphous. However, examinations by XANES, EXAFS, XPS, and IR suggest that there is a local structure to the material with the vanadium existing in the 2+ oxidation state in a pseudo-octahedral geometry, assumed to be mostly nitrogen-bound TCNE radical anions.³⁵ These bridging TCNE radical anions create a 3-D network.

The $V[TCNE]_2 \cdot y(\text{solvent})$ system was tested by Morin and coworkers for solvent dependence by synthesizing the compound in tetrahydrofuran (THF), acetonitrile, and dichloromethane (DCM). The complex synthesized in DCM was measured up to 350 K before sample degradation but was estimated to have an ordering temperature of around 400 K.³⁶ The complex synthesized in acetonitrile exhibited the lowest magnetic ordering temperature at 60-150 K, and the complex synthesized in THF exhibited a magnetic ordering temperature of 205 K, falling between DCM and acetonitrile.^{37,38} The data shows that the magnetic properties of $V(TCNE)_2$ are solvent dependent.

This solvent dependence also plays a role in the amorphous structure of the material. It is speculated that this behavior stems from DCM being the least coordinating solvent, THF being a weakly-coordinating solvent, and acetonitrile being the most coordinating solvent. The acetonitrile and THF compete with the TCNE radical anion for coordination sites on the vanadium metal. When either solvent coordinates to the metal, it displaces a TCNE radical anion and disrupts the 3-D network. The three dimensionality of a magnetic material is suspected to increase the magnetic

ordering temperature because of the increasing number of near-neighbor interactions. DCM is the solvent of choice because it cannot compete with TCNE and does not disrupt the 3-D network which results in the highest magnetic ordering temperature and magnetic susceptibility.³⁷

2.2.3 $M(\text{TCNE})_2$

After the discovery of $\text{V}(\text{TCNE})_2$, other transition metals were examined to replace vanadium. Miller and coworkers synthesized the $M(\text{TCNE})_2$ complexes (where $M = \text{Fe}$ (**1**), Mn (**2**), Co (**3**), and Ni (**4**)) by reacting TCNE with MI_2 in dichloromethane. The oxidation state of 2+ for the $\text{Fe}(\text{TCNE})_2$ was determined by ^{57}Fe Mossbauer spectroscopy. Because of the similarity of the Mn , Co , and Ni derivatives to $\text{V}(\text{TCNE})_2$, their oxidation states were assigned as 2+ as well. Thermogravimetric analysis indicated that CH_2Cl_2 was present in each network ranging from 0.4 to 1.1 molecules.

The temperature-dependent magnetization was examined for each compound and compounds **1** and **2** exhibited ordering temperatures of 121 and 107 K respectively, while both compounds **3** and **4** exhibited an ordering temperature of 44 K. Hysteresis was observed for all of the compounds at 2 K except compound **2** and the coercive fields ranged from 300 G to 6500 G. The result of this research showed that the vanadium metal is significant in the high ordering temperature of $\text{V}(\text{TCNE})_2$.³⁹

2.3 Tetracyanoquinodimethane Radical Anion as a Bridging Ligand

2.3.1 $M(\text{TCNQ})_2$

Another important bridging organic radical is that derived from 7,7,8,8-tetracyanoquinodimethane (TCNQ). This molecule is valued because of its bridging capabilities, its ability to be easily reduced, and its ease of coordination with metal ions. TCNQ, much like TCNE, is a closed-shell molecule that becomes a radical anion by accepting an electron from a

metal. TCNQ has a large conjugated system, which helps to delocalize the radical which grants the radical a longer lifetime. The radical spin tends to reside in the nitrogen atoms of the coordinating nitrile groups, similar to TCNE, and can interact with unpaired electrons in metal centers.

Zhao and coworkers synthesized four networks with the molecular formula $M(\text{TCNQ})_2(\text{MeOH})_x$, where $M = \text{Mn, Fe, Co, and Ni}$. These solids were found to have crystal structures of a pseudo octahedral configuration with a $\mu_4\text{-(TCNQ-TCNQ)}^{2-}$ and two MeOH bound to the metal centers,⁴⁰ Figure 2-3.

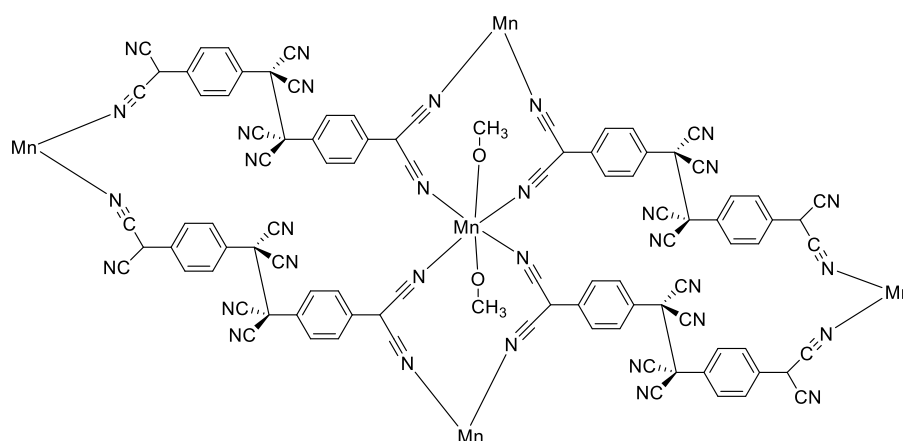


Figure 2-3: The $\text{Mn}(\text{TCNQ})_2(\text{MeOH})_x$ complex showing the $\mu_4\text{-(TCNQ-TCNQ)}^{2-}$ and 2-D network to other octahedral Mn centers.

Temperature-dependent magnetic measurements found that the Ni and Mn derivatives exhibited small antiferromagnetic coupling behavior below 50 K, while the Fe and Co derivatives were found to have isolated spin centers, where there is no mediated magnetic coupling between one metal center and another. The overarching conclusion is that the paramagnetism was from the metal centers and was not affected by the TCNQ molecules. The TCNQ-TCNQ interactions created paired organic radicals, which appear to create a closed shell species.⁴¹ A closed-shell

species is a species that has no unpaired electrons, which in this case, cannot facilitate magnetic coupling.

2.3.2 $V(TCNQR_2)_2$

Subsequently, TCNQ was studied with different substituents on the phenyl ring. Vickers and coworkers sought to synthesize the first vanadium TCNQ compound⁴² in hopes of obtaining a complex with magnetic ordering at room temperature similar to the $V(TCNE)_2$ complex.³⁴ The vanadium compounds were synthesized by using a substituted $TCNQR_2$ where $R = H, Br, Me, Et, i\text{-}Pr, OMe, OEt, \text{ and } OPh$, Figure 2-4.

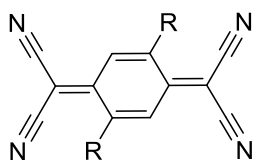


Figure 2-4: The $TCNQR_2$ molecule indicating where the R substituents are located.

All of the $V(TCNQR_2)_2$ compounds exhibited ferrimagnetism except for when R was bromine. The bromine derivative showed no magnetic ordering at low temperatures. The OEt substituent on the TCNQ exhibited the highest Curie temperature at 106 K, while the Me substituent exhibited the lowest Curie temperature at 7.5 K. A suspected interaction between the oxygen of the alkyloxy group enhances the magnetic coupling of the $V(TCNQ(OEt_2))_2$; however, the OPh group makes the oxygen too sterically hindered to have this $V\text{-}O$ interaction, which is the proposed reason why the OPh derivative only has a Curie temperature of 20 K.

2.3.3 $Ru_2(TCNQ)$

Miyasaka and coworkers have synthesized a $Ru_2(TCNQF_4)$ compound for its charge transfer properties as well as its unique magnetic properties. In the case of this compound, an electron is transferred from one Ru center to the $TCNQF_4$ ligand. The compound was synthesized

by using two $\text{Ru}_2^{\text{II,II}}(\text{O}_2\text{CCF}_3)_4$ for every one TCNQF_4 ultimately resulting in a molecular formula of $\{\text{Ru}_2^{\text{II,II}}(\text{O}_2\text{CCF}_3)_4\}[\text{TCNQF}_4]$, Figure 2-5.

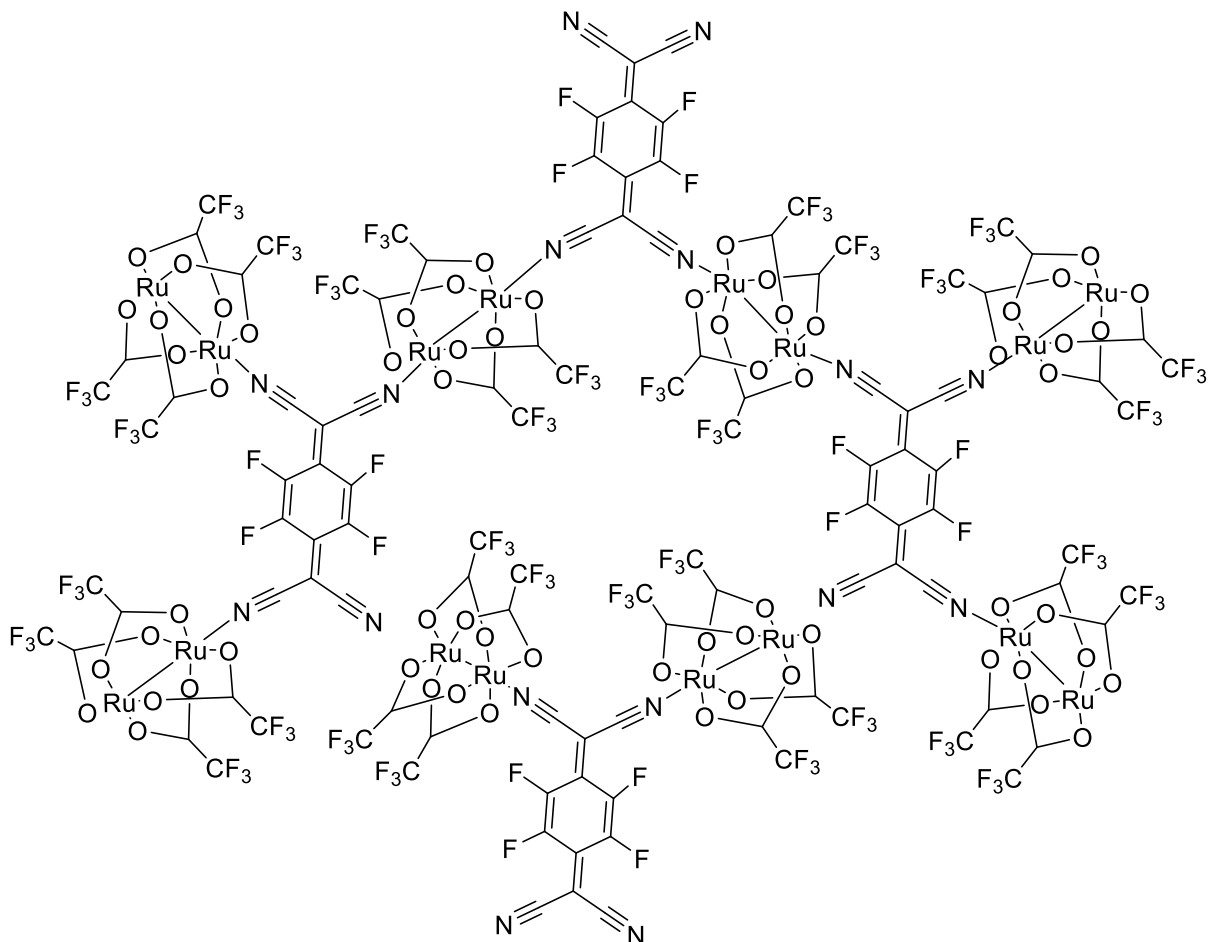


Figure 2-5: The structure of the $\{\text{Ru}_2^{\text{II,II}}(\text{O}_2\text{CCF}_3)_4\}[\text{TCNQF}_4]$ compound.

The compound exhibited antiferromagnetic long-range coupling and a Néel temperature of 95 K and the Ru centers have magnetic exchange interactions via the $\text{TCNQF}_4^{\cdot-}$.

$\{\text{Ru}_2^{\text{II,II}}(\text{O}_2\text{CCF}_3)_4\}[\text{TCNQF}_4]$ exhibits a large hysteresis reaching a saturation magnetization only in a 7 T field. This compound was the first example of a magnet for a Ru_2 -TCNQ system.⁴³

Similarly, a $[\{\text{Ru}_2(\text{O}_2\text{CPh-}m\text{-F})_4\}_2(\text{BDTA-TCNQ})]$ network was synthesized, where BDTA-TCNQ is (bis(1,2,5-thia-diazolo)tetracyanoquinodimethane) and $\text{O}_2\text{CPh-}m\text{-F}$ is *m*-fluorobenzoate, which was also examined for charge transfer and magnetic properties, Figure 2-6.

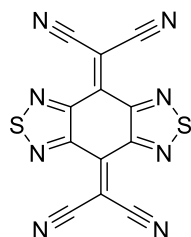


Figure 2-6: The BDTA-TCNQ molecule, which bridges between Ru centers through the CN functional groups.

This compound exhibited ferromagnetic ordering and a Curie temperature of 107 K. The χ measurements indicated long-range ferromagnetic order because of a sudden increase in χ around 110 K, which peaked at 1.8 K in the χ vs T plot. The $1/\chi$ vs T plot is nearly linear in the paramagnetic region and follows the Curie-Weiss law. The Weiss value is 99 K. Such a large Weiss constant indicates relatively strong coupling between the Ru and the BDTA-TCNQ of the compound.⁴⁴

2.4 Other Conjugated Cyanocarbon Acceptors

2.4.1 $\text{V}(\text{TCNP})_2$

Aside from TCNE and TCNQ, other related cyanocarbon molecules have been used in molecule-based magnetism. A goal was set to find other cyano-based acceptors to stabilize magnetically ordered materials. Vickers and coworkers synthesized tetracyanopyrazine (TCNP), Figure 2-7, and combined it with hexacarbonylvandadium(0) in dichloromethane.

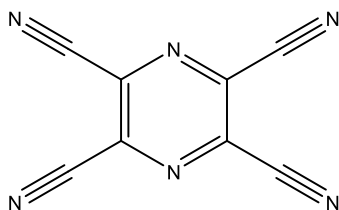


Figure 2-7: Structure of TCNP.

Elemental analysis was used to determine the formula for the magnetic material, which was $V(\text{TCNP})_2 \cdot 0.83\text{CH}_2\text{Cl}_2$. The compound was found to be air-sensitive and powder diffraction data indicated an amorphous structure similar to $V(\text{TCNE})_2$. Because the IR spectra of the magnetic material was similar to that of $V(\text{TCNE})_2$, $V(\text{TCNP})_2$ was proposed to have a similar structure.

The temperature-dependent magnetic susceptibility was measured at 5 G for $V(\text{TCNP})_2$ which exhibited a critical temperature of 200 K. Long-range antiferromagnetic coupling was exhibited as indicated in the decrease of the χ^{-1} of the χ^{-1} vs T plot above 270 K. Field dependent magnetization was measured at 2 K and the remanant magnetization and coercivity were found to be 1860 emu G/mol and 8 G respectively. These small values indicate that $V(\text{TCNP})_2$ is a soft ferrimagnet. The saturation magnetization was found to be 5200 emu G/mol which is very close to the theoretical value, 5585 emu G/mol, for antiferromagnetically coupled $S = 3/2 V^{\text{II}}$ and two $S = 1/2 [\text{TCNP}]^{\cdot-}$.⁴⁵ Overall this work exhibited that extending the distance between nitriles and vanadium spin sites compared to TCNE is more effective for TCNP ($T_c = 200$ K) than for TCNQ ($T_c = 56$ K).⁴²

2.4.2 $V(\text{TCNB})_2$

Tetracyanobenzene (TCNB) was synthesized by Taliaferro and coworkers. TCNB was synthesized because it is structurally similar to TCNP but substituents could be potentially

substituted on the 3- and 6- positions of the benzene ring, Figure 2-8. Multiple sources of vanadium were used to synthesize $V(\text{TCNB})_2$ but for the purpose of this discussion we will focus on $V(\text{CO})_6$ in dichloromethane.⁴⁶

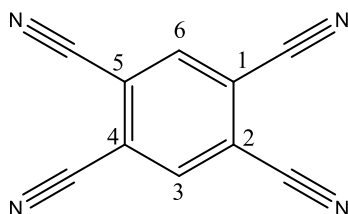


Figure 2-8: Structure of TCNB with spots to put substituents in the 3 and 6 positions of the benzene ring.

It was determined through elemental analysis that the formula for this material was $V(\text{TCNB})_2 \cdot 0.7\text{CH}_2\text{Cl}_2$. The material was found to degrade in air and powder diffraction experiments indicated that the $V(\text{TCNB})_2$ was amorphous, similar to the other $V(\text{TCNE})_2$ -like materials and was therefore proposed to be structurally similar.

The 2 K to 400 K temperature-dependent magnetic susceptibility measurements were taken in a 5 G field and it was determined that $V(\text{TCNB})_2$ had an ordering temperature of 325 K. In the magnetic susceptibility versus applied magnetic field measurements at 10 K, the magnetic material exhibited a saturation magnetization of 4700 emu G/mol which is only 84 % of the expected value, 5585 emu G/mol. The remanant magnetization and coercivity were 990 emu G/mol and 7 G respectively. These results are indicative of $V(\text{TCNB})_2$ being a soft ferrimagnet.⁴⁶

2.4.3 $V(\text{MeTCEC})_2$ and $V(\text{ETCEC})_{1.3}$

The above cyanocarbon molecules are similar to TCNE and TCNQ because of their ability to coordinate through any of the four nitrile substituents as well as being completely symmetrical. The methyl- and ethyltricyanoethylenecarboxylate, Figure 2-9, were synthesized in order to identify the advantages and disadvantages of a reduced symmetry of a cyanocarbon acceptor.^{47,48}

The carbonyl oxygen was also of interest to determine whether it could become an additional exchange pathway for mediating magnetic coupling. These molecules were synthesized via a Michael addition with methyl or ethylcyanoacetate and TCNE with pyridine as the catalyst.

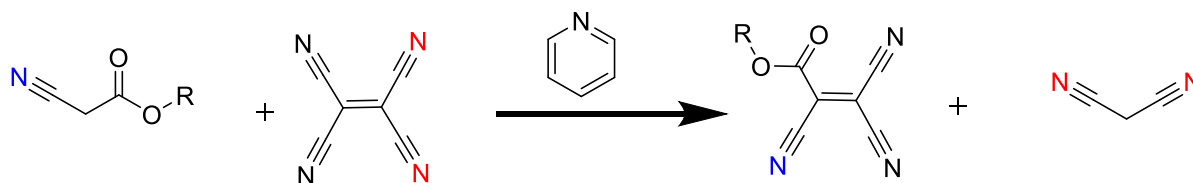


Figure 2-9: Synthesis of methyltricyanoethylenecarboxylate (MeTCEC) and ethyltricyanoethylenecarboxylate (ETCEC).

Each acceptor was combined with $\text{V}(\text{CO})_6$ in dichloromethane which resulted in an air-sensitive black precipitate. Elemental analysis determined that the molecular formula for each vanadium magnet was $\text{V}(\text{MeTCEC})_2 \cdot 0.6\text{CH}_2\text{Cl}_2$ and $\text{V}(\text{ETCEC})_{1.3} \cdot 0.3\text{CH}_2\text{Cl}_2$. The IR spectra were taken for neutral MeTCEC and ETCEC which exhibited carbonyl stretches at 1752 cm^{-1} and 1748 cm^{-1} respectively. The reduced acceptors, $[\text{MeTCEC}]^{\cdot-}$ and $[\text{ETCEC}]^{\cdot-}$, exhibited carbonyl stretches at 1657 cm^{-1} and 1679 cm^{-1} respectively. However, $\text{V}(\text{MeTCEC})_2$ and $\text{V}(\text{ETCEC})_2$ exhibited carbonyl stretches at 1754 cm^{-1} and 1751 cm^{-1} , respectively, which indicates $\text{V}-\text{O}=\text{C}$ bonding in the materials.

The temperature-dependent magnetic susceptibility in a 5 G field was measured for each vanadium magnet. $\text{V}(\text{MeTCEC})_2$ exhibited a critical temperature of 300 K while $\text{V}(\text{ETCEC})_2$ exhibited a critical temperature of 150 K.^{47,48} A structure-property relationship was determined for these magnetic materials including a comparison of TCNE. Because the energy of the acceptor π^* orbital is important in determining the bulk magnetic properties,⁴⁹ there should be a strong correlation between reduction potential and ordering temperature. The most difficult acceptor to

reduce was ETCEC (-0.05 V vs SCE, -0.008V vs Ag/AgCl) and the easiest to reduce acceptor is TCNE (0.260 V vs SCE, 0.302 V vs Ag/AgCl). As expected, the ordering temperature decreased from $V(TCNE)_2$ to $V(ETCEC)_2$.⁴⁷

2.5 Tunable Analogs of TCNE

2.5.1 $V(H_5PTCE)_2$

The Yee group has pursued a strategy of synthesizing TCNE analogs that can be systematically modified. One of the first derivatives that was synthesized replaced one nitrile substituent on the ethylene backbone of TCNE with a phenyl ring. The reason behind this synthesis was to determine how changing the substituents on the phenyl ring would correlate to ordering temperature. Phenyltricyanoethylene (H_5PTCE) can be easily synthesized from benzaldehyde and malononitrile.⁵⁰ The first two acceptors synthesized using this approach were H_5PTCE and pentafluorophenyltricyanoethylene (F_5PTCE), Figure 2-9.

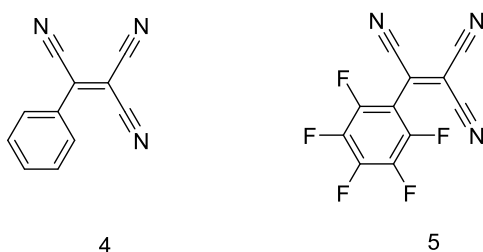


Figure 2-9: Structures of TCNE analogues.

Each of the acceptors was combined with $V(CO)_6$ in DCM to yield magnetic materials. While the network derived from compound 5 exhibited magnetic ordering at room temperature, around 307 K, the network derived from compound 4 exhibited magnetic ordering only around 215 K. Both of these compounds were classified as ferrimagnets, and this research shows that

phenyltricyanoethylene exhibits a high ordering temperature and that the fluorine substituents increase the magnetic ordering temperature.⁵⁰

2.5.2 F_xPTCE

Harvey and coworkers undertook a systematic examination of the role of fluorine substitution on the resultant magnetic properties beginning with the mono- and difluoro substituted derivatives to determine the optimum positions. The derivatives that were synthesized are shown in Figure 2-10.

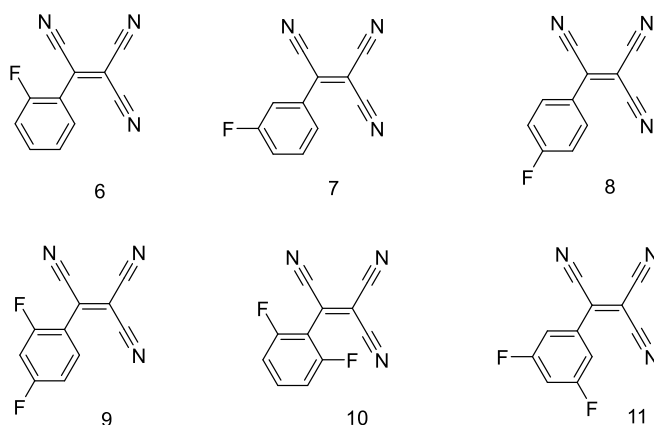


Figure 2-10: Structures of TCNE analogues.

For the mono-substituted derivatives, molecule **6** was found to be the most favorable building block for high magnetic ordering temperatures at 257 K, followed by molecule **7** at 233 K and lastly was molecule **8** at 160 K. For the disubstituted derivatives, the magnet derived from molecule **10** had the highest ordering temperature at 300 K, followed by **11** at 263 K, and lastly by **9** at 242 K, Table 2-1.⁴⁹

Table 2-1: Ordering temperatures of the mono- and difluorinated PTCE acceptors combined with V(CO)₆.

Magnet	T _c , K
V(2-F ₁ PTCE) ₂ (6)	257

$V(3-F_1PTCE)_2$ (7)	233
$V(4-F_1PTCE)_2$ (8)	160
$V(2,6-F_2PTCE)_2$ (9)	300
$V(2,4-F_2PTCE)_2$ (10)	263
$V(3,5-F_2PTCE)_2$ (11)	242

Following upon Harvey's research, Amshumali and coworkers conducted further research to establish how the tri- and tetrafluorinated phenyl group would affect the ordering temperature, derivatives **12-15** were synthesized, Figure 2-11.

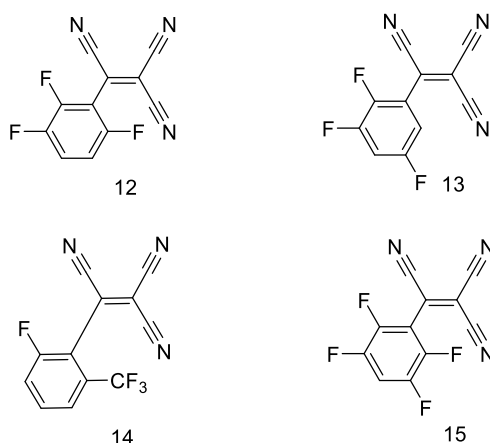


Figure 2-11: Structures of TCNE analogues.

Based on the results from the mono- and difluorinated acceptors, it was predicted that acceptor **15**, which does not have a fluorine at the 4- position, should be optimized and give a magnet with the highest magnetic ordering temperatures and this was observed at 315 K. The magnets derived from acceptors **12** and **13** displayed ordering temperatures of 310 K and 279 K respectively. These results provided more evidence that the 2- and 6- position of the phenyl ring are more favorable for synthesizing magnets with high ordering temperatures. The magnet derived

from acceptor **14** resulted in an ordering temperature of 282 K, which is a lower ordering temperature than the magnet synthesized with the 2,6-difluorophenyltricyanoethylene acceptor, Table 2-2. This result shows that the trifluoromethyl substituent in the 2- or 6- position is not as beneficial as a fluorine substituent for synthesizing a magnet with a high ordering temperature. This is likely because the fluorine substituent is more electron withdrawing and creates less steric interactions between the substituent on the ring and the ethylene backbone.⁷

Table 2-2: Ordering temperatures of the tri- and tetrafluorinated PTCE acceptors combined with V(CO)₆.

Magnet	T _c , K
V(2,3,6-F ₃ PTCE) ₂ (12)	310
V(2,3,5-F ₃ PTCE) ₂ (13)	279
V(2-F ₁ ,6-CF ₃ PTCE) ₂ (14)	282
V(2,3,5,6-F ₄ PTCE) ₂ (15)	315

To summarize these results, the substituent on the 4- position of the phenyl ring is detrimental to magnetic ordering. It is hypothesized that the fluorine substitution in the 4- position is susceptible to nucleophilic aromatic substitution by the vanadium metal or some other nucleophile. The substituents on the 2- and/or 6- positions on the phenyl ring had the greatest positive impact for magnetic ordering, while the substituents on the 3- and 5- position had the second greatest positive impact.⁷ It was also found that the CF₃ substituent placed in the 6- position on the phenyl ring had a smaller positive impact on magnetic ordering temperature than fluorine in the 6- position.

2.6 Conclusion

Molecule-based magnets continue to be an interesting and growing class of magnetic materials that can exhibit an extensive range of magnetic ordering and magnetic behaviors as shown by this short review of history. A successful strategy for producing a variety of new

materials uses a building block approach in which one block is an organic radical anion and the other is a transition metal cation possessing more than one unpaired electron. In the reaction flask, electrostatic attractions cause them to self-assemble to form a neutral ferrimagnetic network. The properties exhibited by some of these magnets are ordering temperatures at or above room temperature,⁷ high saturation magnetizations,⁸ and large coercive fields.⁹ However, most of them are magnetically soft, with low coercivities, and small remanant magnetizations.

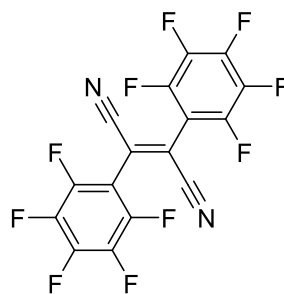
Although there are now many examples of magnetically ordered solids, a question that remains is how they work and what effects their magnetic properties. The discovery of new tunable TCNE derivatives opens up a method of systematic synthesis of more materials like $V(\text{TCNE})_2$ to try to discover the inner workings of how structure of the organic acceptors affects the magnetic properties of these magnets.

Chapter 3 Synthesis of α -Fluorodicyanostilbenes(α -F_nDCS) (where α indicates the positions of substituents) and Magnetic Measurements of V(α -F_nDCS)₂

3.1 Introduction

The fluorinated phenyltricyanoethylene ligands described in the previous chapter provided key insights into the importance of the number and position of fluorine substitution on the phenyl ring of the acceptor molecule on the magnetic properties of corresponding V(F_nPTCE)₂ magnets.^{7,49,51} To summarize, the most important positions for fluorine substitutions on the phenyl ring are *ortho*- to the olefin and greater fluorine substitution is generally better except in the position *para*- to the olefin.

This part of the dissertation will focus on the analogous fluorinated dicyanostilbene derivatives of TCNE, in which instead of one phenyl ring replacing a nitrile, two *trans* nitriles have been replaced with phenyl rings substituted with fluorine atoms, Figure 3-1. Kaul and coworkers were the first to react dicyanoperfluorostilbene (DCPFS) with V(CO)₆ in THF. A black precipitate formed and was found to be very air-sensitive. Powder diffraction was conducted on the isolated compound indicating that it was structurally amorphous. Upon measuring the magnetization of V(DCPFS)₂ as a function of temperature, the material ordered ferrimagnetically with a $T_C \approx 205 \pm 5$ K.⁵² V(DCPFS)₂ was found to be a soft ferrimagnet with a very small amount of hysteresis and a very small coercive field of less than 20 G.



DCPFS

Figure 3-1: Structure of dicyanoperfluorostilbene.

There are a number of differences between $V(DCPFS)_2$ and the vanadium phenyltricyanoethylene family of magnets, starting with their different sensitivity to solvent used in their preparation. For instance, synthesizing $V(DCPFS)_2$ in dichloromethane (DCM) instead of THF yields a material with a much lower ordering temperature of 100 K. This result is in sharp contrast with the reaction of all of the F_nPTCE acceptors with $V(CO)_6$ where DCM is the solvent of choice and coordinating solvents lower the ordering temperature of the resulting vanadium magnet. A plausible explanation for this observation is that additional coordinating ligands are required to prepare $V(DCPFS)_2$ because dicyanoperfluorostilbene possesses only two nitrile coordination sites, so that based on the stoichiometry, without solvent, each $V(II)$ would only be four-coordinate.

One consequence of this requirement is that the connectivity of the network is lower because each stilbene can only bridge two metals, whereas each phenyltricyanoethylene can bridge three metals. However, there are at least three good reasons for exploring the dicyanostilbene family of magnets. DFT calculations have shown that there is greater spin density on the nitrogen atoms of the nitrile functional groups for dicyanoperfluorostilbene as compared to F_5PTCE potentially yielding stronger coupling between the unpaired electrons on the metal and organic ligand.⁵³ Furthermore, because the nitrile nitrogen atoms are symmetry related, the prospects of a crystalline product might be improved. Finally, though this has not yet been explored, the apparently necessity of a coordinating ligand provides another variable that can be tuned to improve the properties of the resulting magnet.

In this chapter, we investigate the effects of acceptor structure on the magnetic ordering temperature of the resulting $V[\text{acceptor}]_2$ materials by systematically varying the number and

positions of fluorine substitution on the phenyl rings of dicyanostilbene. This is analogous to what has previously been explored for the tricyanoethylene family of compounds. As a first goal, we sought to prepare the 2,2',3,3',5,5',6,6'-octafluorodicyanostilbene because, as stated previously, examination of the F_nPTCE family of compounds had revealed that substitution in the 4-position was detrimental to T_c. Our hope was to observe an increase in T_c by removing analogous fluorine atoms from perfluorodicyanostilbene.

Including octafluorostilbene, eight new acceptors were synthesized and their reactions with hexacarbonylvanadium(0) were investigated. The eight acceptors that have been synthesized are 2,2'-difluoro- (2,2'-F₂DCS), 3,3'-difluoro- (3,3'-F₂DCS), 4,4'-difluoro- (4,4'-F₂DCS), 2,2',6,6'-tetrafluoro- (2,2',6,6'-F₄DCS), 2,2',4,4'-tetrafluoro- (2,2',4,4'-F₄DCS), 3,3',5,5'-tetrafluoro- (3,3',5,5'-F₄DCS), 3,3',4,4',5,5'-hexafluoro- (F₆DCS), and 2,2',3,3',5,5',6,6'-octafluorodicyanostilbene (F₈DCS), Figure 3-2.

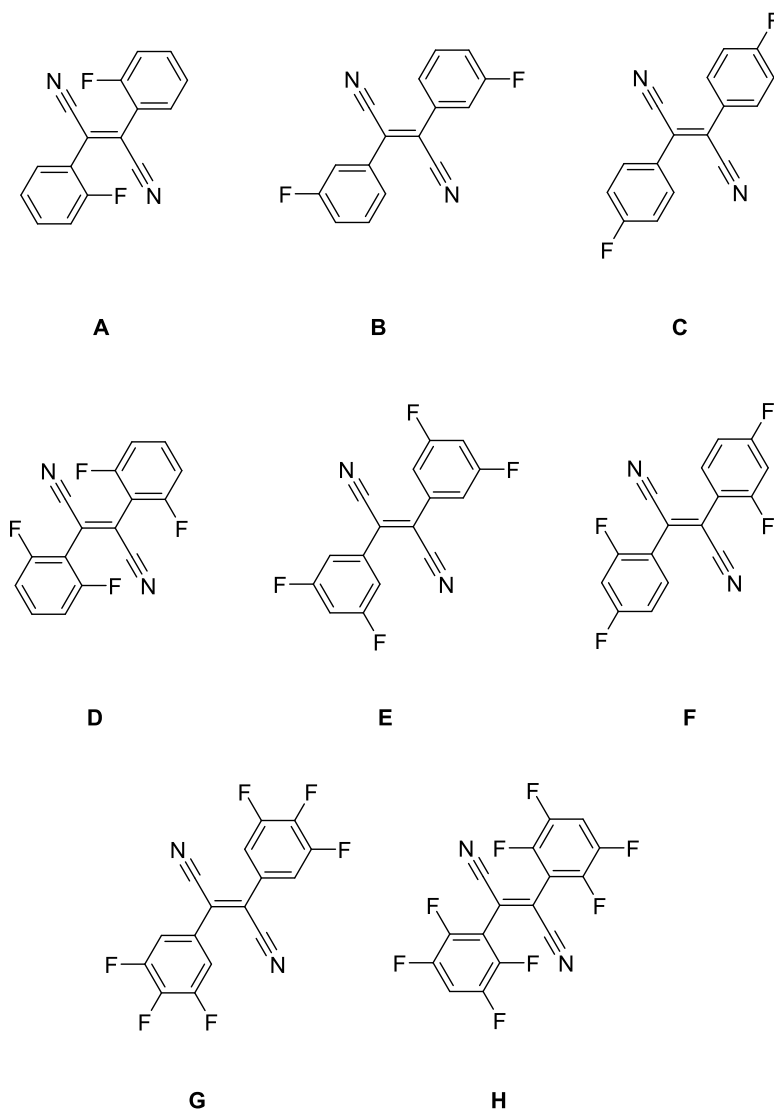


Figure 3-2: All the synthesized analogs of dicyanostilbene from left to right and then top to bottom: 2,2'-difluoro- (A), 3,3'-difluoro- (B), 4,4'-difluoro- (C), 2,2',6,6'-tetrafluoro- (D), 2,2',4,4'-tetrafluoro- (E), 3,3',5,5'-tetrafluoro- (F), 3,3',4,4',5,5'-hexafluoro- (G), and 2,2',3,3',5,5',6,6'- octafluorodicyanostilbene- (H).

3.2 Synthesis and Characterization of the acceptors

Synthesis of the acceptors, Figure 3-3, can be achieved either in one step using commercially available appropriately substituted phenylacetonitrile starting materials or by two-step synthesis from commercially available appropriately substituted benzyl bromide starting materials. Purification was conducted via column chromatography on silica gel using a mixture of

hexanes and dichloromethane as well as mixtures of hexanes and ethyl acetate as eluents. The identity and purity of these acceptors was verified by ^1H and ^{19}F NMR, high resolution mass spectrometry, IR, and by measuring melting points. Each of the acceptors was also characterized by cyclic voltammetry. The acceptor redox potentials were measured in acetonitrile with $[\text{Bu}_4\text{N}]^+ [\text{ClO}_4]^-$ as the backing electrolyte, and potentials are reported relative to Ag/AgCl.

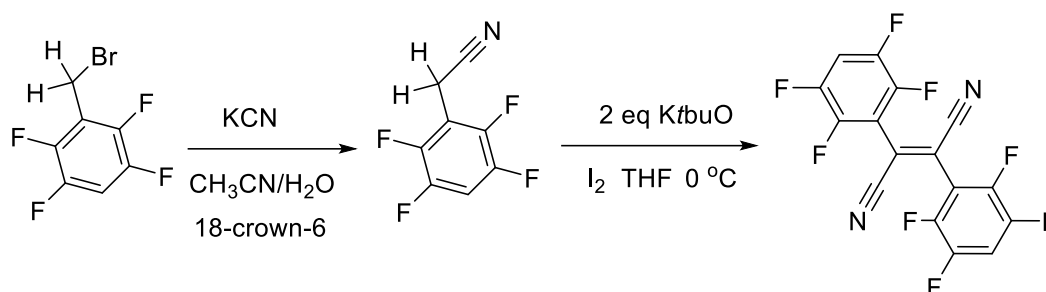


Figure 3-3: Synthesis of F_6DCS from tetrafluorobenzylbromide.

A summary of the reduction potentials for the acceptors is presented in Table 3-2. As expected, the acceptors are all more difficult to reduce than their phenyltricyanoethylene analogs. This reflects the stronger electron withdrawing nature of $-\text{CN}$ over that of a (poly)fluorinated phenyl group. All of these new compounds are reduced at potentials that are more negative than -0.787 V with respect to Ag/AgCl, which was the reduction potential of DCPFS. Somewhat surprisingly, several examples exhibit irreversible electrochemistry including all of the difluoro-compounds and the 2, 2', 4, 4' tetrafluoro- species.

3.3 Reaction of acceptors with $\text{V}(\text{CO})_6$ and characterization of the products

Despite the somewhat disappointing electrochemistry results, each acceptor was reacted with $\text{V}(\text{CO})_6$ in dichloromethane with two equivalents of THF in an attempt to synthesize a vanadium[acceptor] $_2$ magnet. For the acceptors that yielded magnets when combined with hexacarbonylvanadium(0) in THF, the reaction was usually very fast. The color changes from

yellow to reddish-purple and the final product is a nearly black insoluble solid that decomposes quickly upon exposure to air. For the acceptors that did not yield magnets, the reaction mixture changed colors from yellow straight to black with no intermediate color change and no formation of a precipitate. With the exception of the 3,3',5,5'-F₄DCS, only the acceptors with 6 or more fluorine atoms formed ordered magnetic materials.

On the basis of elemental analysis and the experiment of using up to three times excess acceptor, the suggested formulas for the vanadium magnets give a 2:1 ratio for the acceptor-to-vanadium with small amounts of solvents to agree with the elemental analysis. Previously, it was shown that for tricyanoethylene-based magnets, coordinating solvents were detrimental to the magnitude of the ordering temperature. However, for dicyanostilbene molecules THF was confirmed to be important for getting the highest ordering temperature.⁵² Because the reaction was run in dichloromethane with two equivalents of THF, it was assumed that there would be two THF molecules per formula unit, similar to V(DCPFS)₂. However, best fit to the elemental analysis data suggested only one THF and varying amounts of dichloromethane. Other amounts of THF and dichloromethane were tested to determine which formula was most accurate for the vanadium magnets. Generally, the formula unit that contained only one THF molecule and less than two dichloromethane molecules per formula unit agreed closest with the elemental analysis.

For the acceptors that apparently did not form networks, the irreversible electrochemistry exhibited by those acceptors most likely played a role. It is most probably the case that these acceptors exhibited decomposition following the reduction step before coordination to the vanadium ion can occur. Dicyanostilbene and the 2,2',6,6'-F₄DCS both have very negative reduction potentials and are most likely not reduced by the vanadium(0) which results in a

paramagnetic material. Evidence of this is given through the lack of a precipitate in the reaction mixture as well as no $\nu_{\text{C}\equiv\text{N}}$ stretches in the IR of the resulting solid.

Infrared spectrometry was used to characterize the products of the reaction with $\text{V}(\text{CO})_6$ with each acceptor. The IR spectrum of each magnetic phase exhibited a $\nu_{\text{C}\equiv\text{N}}$ shift to a lower wavenumber when compared to the neutral acceptors, which is consistent of the one electron reduction of the coordinated radical anion, Table 3-1. A red shift was exhibited which is consistent with the expected decrease in the CN bond order. The IR spectra exhibit broad $\nu_{\text{C}\equiv\text{N}}$ stretches for the magnet as opposed to the sharp $\nu_{\text{C}\equiv\text{N}}$ stretches shown in the neutral acceptors. The broad stretches indicate a variety of different bonding environments for the radical anionic acceptor. Because the material is amorphous, several different bonding environments are plausible such as vanadium bound nitrile groups, uncoordinated nitrile groups, and nitrile groups bound to vanadium where the vanadium has variable numbers of radicals coordinated.

Table 3-1: Summary of CN stretching frequencies for neutral acceptors and resulting solids after reaction with $\text{V}(\text{CO})_6$.

Acceptor	Acceptor $\nu_{\text{C}\equiv\text{N}}$, cm^{-1}	Solid $\nu_{\text{C}\equiv\text{N}}$, cm^{-1}
2,2'-F ₂ DCS	2221	Not Observed
3,3'-F ₂ DCS	2220	Not Observed
4,4'-F ₂ DCS	2222	Not Observed
2,2',6,6'-F ₄ DCS	2233	Not Observed
2,2',4,4'-F ₄ DCS	2235	Not Observed
3,3',5,5'-F ₄ DCS	2231	2112
F ₆ DCS	2227	2108
F ₈ DCS	2237	2119
DCPFS ^a	2230, 2228	2117

^a Previous work⁵⁴

The field cooled (5 G) temperature-dependent magnetization data (M vs T) was collected in a 5 G applied field promptly after synthesizing each magnetic phase. The ordering temperatures

were estimated by extrapolating the steep linear portion of the M vs. T curve and are summarized in table 3-2. Ordering temperatures were also determined by the onset of a non-zero out of phase (χ'') component of ac susceptibility at 1 Hz, 10 Hz, and 100 Hz (appendix A, section 7.4). The M vs T data is plotted in Figure 3-4. The reported ordering temperatures are a result of an average of at least two experiments. The previously reported V(DCS)₂ and V(DCPFS)₂ systems were used as reproducibility standards. As with the previous studies, the DCS did not react to give a magnetically ordered phase, and the V(DCPFS)₂ ordering temperature was 205 K.

Table 3-2: Summary of the properties of the fluoro-substituted dicyanostilbenes.

Acceptor	T _c ^a (K)	E _{1/2} ^b (V)	M _s , emu G/mol
Dicyanostilbene	No Ordering	-1.222	N/A
2,2'-F ₂ DCS	No Ordering	Irreversible	N/A
3,3'-F ₂ DCS	No Ordering	Irreversible	N/A
4,4'-F ₂ DCS	No Ordering	Irreversible	N/A
2,2',6,6'-F ₄ DCS	No Ordering	-1.012	N/A
2,2',4,4'-F ₄ DCS	No Ordering	Irreversible	N/A
3,3',5,5'-F ₄ DCS	170	-0.877	4082
F ₆ DCS	190	-0.882	3863
F ₈ DCS	150	-0.847	7320
DCPFS ^c	205	-0.787	7000

^a All vanadium magnets were measured in a 5G field. ^b Acceptor redox potentials, relative to Ag/AgCl were

measured in acetonitrile with [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte. ^c Previous work referenced to Ag/AgCl.⁵⁴ Each magnetic measurement was conducted twice.

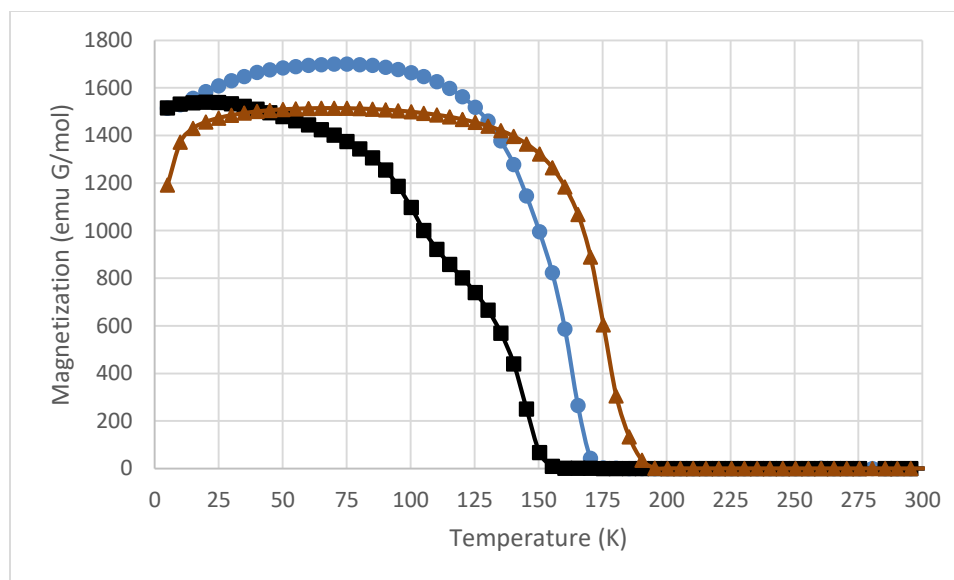


Figure 3-4: A plot of M vs T for $V(3,3',5,5'\text{-F}_4\text{DCS})_2$ (●), $V(\text{F}_6\text{DCS})_2$ (▲), and $V(\text{F}_8\text{DCS})_2$ (■) in a 5 G field.

For the $V(3,3',5,5'\text{-F}_4\text{DCS})_2$ the magnetization initially increases to a max at 75 K, and then a slow decrease before it sharply starts to decrease as the sample is warmed to 300 K. The sample reaches almost zero magnetization at its ordering temperature of 170 K. For $V(\text{F}_6\text{DCS})_2$ the magnetization increases sharply from 5-15 K and maintains constant up to 80 K before starting to decrease. The magnetization starts to sharply decrease at 145 K until the magnetization is almost zero at its ordering temperature of 190 K. For the $V(\text{F}_8\text{DCS})_2$ the magnetization steadily decreases from 5 K to its ordering temperature of 150 K. However, there is a small feature at around 110 K, which is similar to that of $V(\text{DCPFS})_2$.⁵⁴ This may indicate the presence of a second magnetic phase. For the $V(3,3',5,5'\text{-F}_4\text{DCS})_2$ and $V(\text{F}_6\text{DCS})_2$ have sharp transitions around T_C which suggests greater structural and magnetic uniformity.

Measurements of magnetization versus applied magnetic field was conducted on the magnetic materials at 5 K. A sample M vs H curve is plotted in Figure 3-5 and complete data is

shown in appendix A, section 7.5. The coercivity for each of the magnetic materials was found to be around 2.5 G, which is to be expected for soft ferrimagnets.⁵⁴ The remanent magnetization ranges from 1456 emu-G/mol for the F₈DCS to 501 emu-G/mol for the F₆DCS vanadium magnets. Saturation magnetization was reached at 100 G for each of the magnetic materials. The theoretical saturation magnetization for a (assuming $g=2$) $S = 3/2$ V^{II} antiferromagnetically coupled to two $S = 1/2$ acceptors per formula unit is 5585 emu-G/mol. The saturation magnetization for the V(3,3',5,5'-F₄DCS)₂ up to the V(DCPFS)₂ were found to be 4082, 3863, 7320, and 7000⁵² emu-G/mol respectively. The 3,3',5,5'-F₄DCS and F₆DCS magnets were slightly lower than what was expected for the ideal saturation magnetization while the F₈DCS and DCPFS were slightly higher than expected.

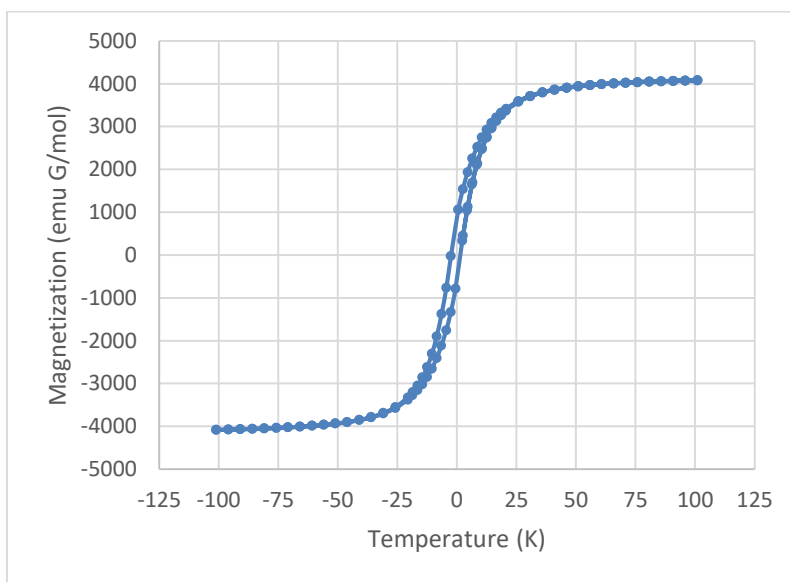


Figure 3-5: Plot for M vs H for V[3,3',5,5'-F₄DCS]₂ at 5 K.

3.4 Conclusion

We have synthesized eight new acceptors constructed on the dicyanostilbene scaffold. Three of these molecules yield new molecule-based ferrimagnets from the reaction with hexacarbonylvanadium(0) with ordering temperatures ranging from 150 K to 190 K. The main

determining factors for whether or not a magnet forms appears to be redox potential, because of the remaining five acceptors, four show irreversible electrochemistry. The fifth acceptor has a very negative redox potential and perhaps cannot be reduced.

The magnetic behavior of these magnets is similar to that of the $V(F_xPTCE)_2$ in that there is low coercivity and remanent magnetization which is characteristic of soft ferrimagnets. The structure-property relationships for the family of fluorodicyanostilbene acceptors have been examined and have been shown to be different from the fluorophenyltricyanoethylene family of compounds. One observation is that the substitution in the 4- (4'-) positions of the phenyl ring in the DCS family of compounds enhances the ordering temperature of the vanadium dicyanostilbene magnets, whereas for the tricyanoethylene magnets, it was detrimental. This may be because the tricyanoethylene acceptors are more susceptible to nucleophilic aromatic substitution by the vanadium metal or some other nucleophile than the dicyanostilbene acceptors due to the extra nitrile substituent being much more electron withdrawing than the perfluorinated phenyl substituent.^{49,50,55} Thus the magnet derived from DCPFS has a higher ordering temperature than the F_8DCS and the F_6DCS has a higher ordering temperature than the $3,3',5,5'-F_4DCS$.

In M vs T plots, the $V(3,3',5,5'-F_4DCS)_2$ and $V(F_6DCS)_2$ seem to have very sharp transitions at their ordering temperatures while the $V(F_8DCS)_2$ has a stepped transition. This suggests that the absences of fluorine substituents in the 2 and 6 position of the phenyl rings contributes to a more structurally uniform material. Most likely this because the fluorine atoms substituted in the 2 and 6 position makes the acceptors non-planar. In future research it may be beneficial to test this hypothesis by conducting crystal growing experiments on $V(3,3',5,5'-F_4DCS)_2$ and/or $V(F_6DCS)_2$.

3.5 Experimental

3.5.1 General Methods

The difluorodicyanostilbene and tetrafluorodicyanostilbene syntheses were conducted following the procedures in Braiek.⁵⁶ The synthesis of the vanadium magnets using dicyanostilbene loosely followed the literature procedure in Fitzgerald.⁵² All reagents were used as received except for the synthesis of the final magnets, the tetrahydrofuran and diethyl ether were dried over sodium benzophenone ketyl under nitrogen, distilled into Schlenk flasks and degassed by successive freeze-pump-thaw cycles remove oxygen. The dry tetrahydrofuran used in the dicyanostilbene synthesis was also dried over sodium benzophenone ketyl under nitrogen and distilled. The $V(CO)_6$ was prepared from $[Na(diglyme)_2][V(CO)_6]$ using a literature procedure,⁵⁷ and the synthesis of the tetrafluorophenylacetonitrile was done loosely following the literature procedure in Iranpoor.⁵⁸ The trifluorophenyl acetonitrile followed a patent.⁵⁹

3.5.2 Synthesis of Molecules

2,3,5,6-tetrafluorophenylacetonitrile

In a 100 mL RBF, potassium cyanide (6.83 g, 0.105 mol) was dissolved with stirring in 15.3 mL of deionized water. In a separate flask, 2,3,5,6-tetrafluorobenzylbromide (5.10 g, 0.0210 mol) was dissolved in 35 mL of ethanol. The 2,3,5,6-tetrafluorobenzylbromide solution was added dropwise to the KCN solution. The reaction was stirred for 1 h and then was transferred to a separatory funnel. Deionized water (10 mL) was added to the solution and the aqueous layer was extracted with diethyl ether (3 x 15 mL). The combined organic layer was dried with magnesium sulfate, filtered, and evaporated to leave a light yellow liquid. Yield: 2.93 g (0.0155 mol, 74.0 %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.14 (dt, J = 2.1, 0.4 Hz, 1H), 3.80 (td, J = 1.3, 0.4 Hz, 2H), ^{19}F NMR (400 MHz, $CDCl_3$): δ (ppm vs C_6F_6) 24.46 (m, 2F), 20.04 (m, 2F).

3,4,5-trifluorophenylacetonitrile

In a 50 mL RBF, 3,4,5-trifluorobenzylbromide (7.00 g, 0.0311 mol) was dissolved in 18.5 mL of acetonitrile. In a separate vial, potassium cyanide (2.43 g, 0.0373 mol) was dissolved with stirring in 4.5 mL of deionized water and 18-crown-6 (0.27 g, 0.0103 mol) was added. The KCN solution was added dropwise to the organic mixture at room temperature. The reaction was stirred at 50 °C for 3 h, cooled and transferred to a separatory funnel. Deionized water (10 mL) and brine (10 mL) was added to the solution and the aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic layer was dried with magnesium sulfate, filtered, and evaporated to leave a clear liquid. Yield: 5.04 g (0.0295 mol, 95.0 %). ^1H NMR (400 MHz, CDCl_3): δ 7.00 (m, 1H), 3.73 (s, 2H), ^{19}F NMR (400 MHz, CDCl_3): δ (ppm vs C_6F_6) 29.59 (m, 2F), 1.68 (m, 1F).

2,2'-difluorodicyanostilbene (2,2'-F₂DCS)

A mixture of 2-fluorophenylacetonitrile (2.5 g, 0.0185 mol) and iodine (4.69 g, 0.0185 mol) was dissolved in 80 mL of dry diethyl ether in a Schlenk flask under N_2 . The solution was cooled to -78 °C and sodium methoxide (1.99 g, 0.0370 mol) dissolved separately in 10 mL of dry methanol was added via addition funnel over a period of 30 min. The flask was then stirred for another 30 min and the solution was then placed in an ice bath for another 5 h at 0 °C with vigorous stirring. Then 5 % HCl was added dropwise to the flask while keeping the temperature below 10 °C. The resulting precipitate was collected on a filter, dried briefly under air, and purified by silica gel chromatography (9:1 hexane: ethyl acetate). Evaporation of the product-containing fraction afforded a white powder. Yield: 0.541 g (0.00179 mol, 21.9 %). Melting point: 173 °C, ^1H NMR (400 MHz, CDCl_3): δ 7.41 (m, 2H), 7.21 (td, 2H), 7.14 (td, 2H), 7.04 (m, 2H), ^{19}F NMR (400

MHz, CDCl₃): δ (ppm vs C₆F₆) 52.21 (m, 2F) HRMS (ESI) calcd for [M]⁺: 266.0656; found: 266.06555, FT-IR: (cm⁻¹) 2221.

3,3'-difluorodicyanostilbene (3,3'-F₂DCS)

3,3'-F₂DCS was synthesized using a similar procedure to 2,2'-F₂DCS but using 3-fluorophenylacetonitrile as the starting material. Yield: 0.609 g (0.00202 mol, 24.7 %). Melting point: 122 °C, ¹H NMR (400 MHz, CDCl₃): δ 7.63 (m, 2H), 7.56 (m, 2H), 7.54 (m, 2H), 7.29 (m, 2H), ¹⁹F NMR (400 MHz, CDCl₃): δ (ppm vs C₆F₆) 51.86 (m, 2F) HRMS (ESI) calcd for [M]⁺: 266.0656; found: 266.0655, FT-IR: (cm⁻¹) 2220.

4,4'-difluorodicyanostilbene (4,4'-F₂DCS)

4,4'-F₂DCS was synthesized using a similar procedure to 3,3'-F₂DCS but using 4-fluorophenylacetonitrile as the starting material. Yield: 0.767 g (0.00254 mol, 31.1 %). Melting point: 189-190 °C, ¹H NMR (400 MHz, CDCl₃): δ 7.85 (m, 4H), 7.24 (m, 4H), ¹⁹F NMR (400 MHz, CDCl₃): δ (ppm vs C₆F₆) 55.70 (m, 2F) HRMS (ESI) calcd for [M]⁺: 266.0656; found: 266.0657, FT-IR: (cm⁻¹) 2222.

2,2',6,6'-tetrafluorodicyanostilbene (2,2',6,6'-F₄DCS)

2,2',6,6'-F₄DCS was synthesized using a similar procedure to 2,2'-F₂DCS but using 2,6-difluorophenylacetonitrile as the starting material. Yield: 0.658 g (0.00176 mol, 32.4 %). Melting point: 201-203 °C, ¹H NMR (400 MHz, CDCl₃): δ 7.58 (m, 2H), 7.13 (m, 4H), ¹⁹F NMR (400 MHz, CDCl₃): δ (ppm vs C₆F₆) 53.20 (m, 4F) HRMS (ESI) calcd for [M]⁺: 302.0467; found: 302.0464, FT-IR: (cm⁻¹) 2233.

2,2',4,4'-tetrafluorodicyanostilbene (2,2',4,4'-F₄DCS)

2,2',4,4'-F₄DCS was synthesized using a similar procedure to 3,3'-F₂DCS but using 2,4-difluorophenylacetonitrile as the starting material and purification by washing the solid with ether. Yield: 0.987 g (0.00264 mol, 48.7 %). Melting point: 178 °C, ¹H NMR (400 MHz, CDCl₃): δ 7.64 (m, 2H), 7.07 (m, 4H), ¹⁹F NMR (400 MHz, CDCl₃): δ (ppm vs C₆F₆) 60.18 (m, 2F), 57.27 (q, 2F) HRMS (ESI) calcd for [M]⁺: 302.0467; found: 302.0469, FT-IR: (cm⁻¹) 2235.

3,3',5,5'-tetrafluorodicyanostilbene (3,3',5,5'-F₄DCS)

3,3',5,5'-F₄DCS was synthesized using a similar procedure to 3,3'-F₂DCS but using 3,5-difluorophenylacetonitrile as the starting material and purification by washing the solid with ether. Yield: 1.005 g (0.00267 mol, 49.6 %). Melting point: 176 °C, ¹H NMR (400 MHz, CDCl₃): δ 7.39 (m, 4H), 7.06 (tt, 2H), ¹⁹F NMR (400 MHz, CDCl₃): δ (ppm vs C₆F₆) 56.13 (m, 4F) HRMS (ESI) calcd for [M]⁺: 302.0467; found: 302.0468, FT-IR: (cm⁻¹) 2231.

3,3',4,4',5,5'-hexafluorodicyanostilbene (F₆DCS)

In a 100 mL round bottom flask, 3,4,5-trifluorophenyl acetonitrile (5.00 g, 0.0292 mol) and iodine (7.42 g, 0.0292 mol) were stirred together in 45 mL of THF. The flask was then placed in an ice bath and allowed to cool to 0 °C. In a small beaker, potassium hydroxide (3.28 g, 0.0584 mol) was dissolved in 10 mL of water. The water solution was added via addition funnel over a period of 40 min. The reaction was left to stir overnight. The majority of the solvent was removed by rotary evaporator and a saturated solution of sodium thiosulfate (20 mL) was added. The solution was extracted with diethyl ether (3 x 50 mL). The ether was dried with magnesium sulfate, filtered, and rotary evaporated to dryness. A gradient silica gel column was run to purify the product with the eluent starting with hexanes, to 4:1 hexanes to dichloromethane, and ending with 2:1 hexanes to dichloromethane which resulted in white powder. Yield: 1.186 g (0.00351 mol,

24.0 %). Melting point: 146 °C, ^1H NMR (400 MHz, CDCl_3): δ 7.52 (m, 4H), ^{19}F NMR (400 MHz, CDCl_3): δ (ppm vs C_6F_6) 32.12 (m, 4F), 10.29 (m, 2F) HRMS (ESI) calcd for $[\text{M}]^+$: 338.0278; found: 338.0277, FT-IR: (cm^{-1}) 2227.

2,2',3,3',5,5',6,6'-octafluorodicyanostilbene ($F_8\text{DCS}$)

In a 250 mL round bottom flask, 2,3,5,6-tetrafluorophenylacetonitrile (1.50 g, 0.00793 mol) and iodine (2.03 g, 0.00793 mol) were stirred together in a solution of 15 mL of THF and 30 mL of deionized water. The reaction flask was put into an ice bath and was cooled to 0 °C. Then, potassium hydroxide (0.95 g, 0.0167 mol) was dissolved separately in 20 mL of deionized water to which 10 mL of THF was added. The potassium hydroxide solution was added to the reaction flask via addition funnel over a period of 40 min. The reaction was stirred overnight. A solid formed in the bottom of the flask and was collected by filtration. The solid was purified by dry loading the product onto a silica gel column for column chromatography using a 2:1 hexane to dichloromethane mixture as the eluent. The product was obtained as a white powder. Yield: 0.342 g (0.000914 mol, 23.0 %). Melting point: 211-212 °C, ^1H NMR (400 MHz, CDCl_3): δ 7.40 (tt, J = 9.3, 7.4 Hz, 2H), ^{19}F NMR (400 MHz, CDCl_3): δ (ppm vs C_6F_6) 27.07 (m, 4F), 25.94 (m, 4F) HRMS (ESI) calcd for $[\text{M}]^+$: 374.0090; found: 374.0092, FT-IR: (cm^{-1}) 2237.

3.5.3 Synthesis of Vanadium Based Magnets $\text{V}(3,3',5,5'\text{-F}_4\text{DCS})_2$:

Under a nitrogen atmosphere, 3,3',5,5'- F_4DCS (63.7 mg, 0.211 mmol) dissolved in 2 mL of DCM was added dropwise to a solution of 2 equivalents of THF and hexacarbonylvandium(0) (15 mg, 0.068 mmol) dissolved in 2 mL of DCM with stirring. After 1 h, the solvent was evaporated off and the black precipitate was triturated with 10 mL of ether for 15 min. The

precipitate was then collected on a medium frit, rinsed with ether (3×2 mL), and dried in vacuo for 1 h. Yield: 30.0 mg (67.0 %), FT-IR: (cm^{-1}) 2112, Anal. Calcd for $\text{C}_{32}\text{H}_{12}\text{F}_8\text{N}_4\text{V} \cdot (\text{THF})(0.7\text{CH}_2\text{Cl}_2)$: C, 56.06; H, 2.73; N, 7.13. Found: C, 55.91; H, 2.25; N, 7.60.

V(F₆DCS)₂

$\text{V}(\text{F}_6\text{DCS})_2$ was prepared using a similar procedure to that of $\text{V}(3,3',5,5'\text{-F}_4\text{DCS})_2$. Yield: 33.3 mg (60.8 %), FT-IR: (cm^{-1}) 2108, Anal. Calcd for $\text{C}_{30}\text{H}_8\text{F}_{12}\text{N}_6\text{V} \cdot (\text{THF})(1.1\text{CH}_2\text{Cl}_2)$: C, 49.97; H, 2.05; N, 6.28. Found: C, 49.87; H, 1.84; N, 6.77.

V(F₈DCS)₂

$\text{V}(\text{F}_8\text{DCS})_2$ was prepared using a similar procedure to that of $\text{V}(3,3',5,5'\text{-F}_4\text{DCS})_2$. Yield: 30.1 mg (54.0 %), FT-IR: (cm^{-1}) 2119, Anal. Calcd for $\text{C}_{32}\text{H}_4\text{F}_{16}\text{N}_4\text{V} \cdot (\text{THF})(1.5\text{CH}_2\text{Cl}_2)$: C, 45.16; H, 1.51; N, 5.62. Found: C, 45.20; H, 1.86; N, 5.54.

Chapter 4 Synthesis and Characterization of 2,2',6,6'-Tetrachlorodicyanostilbene and Its Reaction with Hexacarbonylvanadium(0)

4.1 Introduction

Knowledge about $V(TCNE)_2$ has greatly expanded since its discovery in 1991. Elemental analysis, infrared spectrometry, and analysis of the magnetic properties of the compound suggests that the oxidation state of the vanadium is 2+ and that there are two TCNE acceptors per formula unit.^{34,60} An improved synthesis for $V(TCNE)_2$ was discovered that was more facile and enhanced the saturation magnetization of the magnet nearly twofold.⁶¹ EXAFS determined that the vanadium metal center is coordinated in an octahedral geometry by six nitrogen atoms.⁶⁰ $V(TCNE)_2$ has unfortunately eluded single-crystal X-ray analysis.

Despite this progress, there are relatively few examples of structurally characterized bridging TCNE radical anions bound to paramagnetic metal ions. Wang and coworkers attempted to synthesize a molecular square where organic radical anions would act as edges and the corners would be spin-bearing metal ions to model the coordination of TCNE radical anion.⁶² In theory these squares could offer structural and magnetic information which could be compared to ab initio calculations.

In that work, $Mn(ClO_4)_2$ was reacted with tris(pyrazol-1-ylmethyl)amine (TPA) in acetonitrile and subsequently with $K(TCNE)$. The TPA ligand was used because it is tridentate and leaves two *cis* coordination sites open for TCNE molecules to bind. Unfortunately, the crystal structure shows a dinuclear Mn species with the dimer dianion $(TCNE_2)^{2-}$ with the formula $[Mn(TPA)CH_3CN(\mu-TCNE)]_2$. As shown in Figure 4-1, the TCNE is coordinated to Mn as a dimer in which the TCNE molecules are not orthogonal to each other, but are instead π -stacked. This

dimerization of TCNE has been previously reported in uncoordinated $(\text{TCNE}_2)^{2-}$ as well as other non-transition metal TCNE complexes.^{12,63}

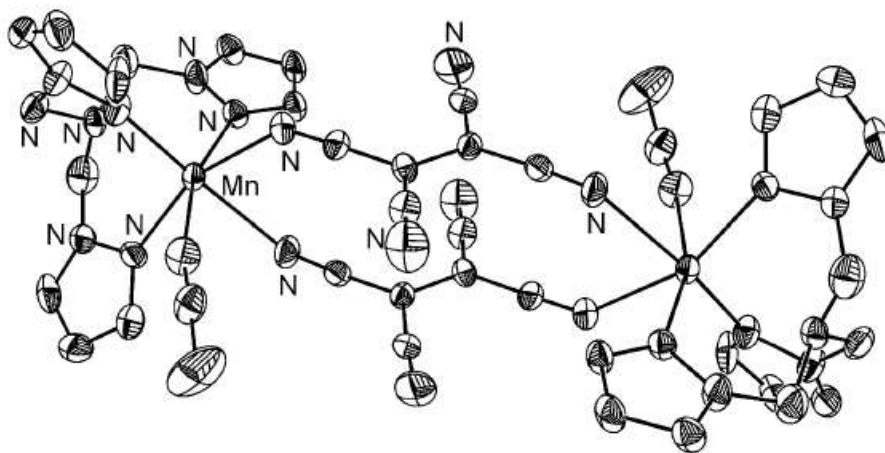


Figure 4-1: 30 % thermal ellipsoid plot of the dinuclear complex showing the π -stacked TCNE molecules.

Hydrogens omitted for clarity.⁶⁴

The temperature-dependent magnetic susceptibility was determined for $[\text{Mn}(\text{TPA})\text{CH}_3\text{CN}(\mu\text{-TCNE})]_2$. The dimer dianion $(\text{TCNE}_2)^{2-}$ that is bridging the two metal centers was confirmed to be a diamagnetic species based upon the magnetic susceptibility of the complex being characteristic of high spin d^5 , spin-only Mn^{II} . Diamagnetism refers to a species that has paired electrons and is not magnetically active.

The dimerization of the TCNE radical anions in the manganese compound resulted because TCNE is planar. The double bonds in the ethylene backbone can π -stack to form a four-center two-electron bond.⁶² Thus we sought to design and synthesize an acceptor that can serve as a bridging ligand but cannot dimerize due to sterics.

Previously, the Yee group has synthesized a family of fluorinated phenyltricyanoethylenes where one of the nitrile substituents is replaced with a phenyl ring. Because tricyanoethylene has

three potential coordinating points, if bulky substituents were placed in the 2 and 6 position of the phenyl ring, the molecules could still stack in a staggered manner to create a diamagnetic species via the a two-center, two-electron bond. An example of this is the π -stacking of TCNQ radical anions in Cu(TCNQ), Figure 4-2.⁶⁵

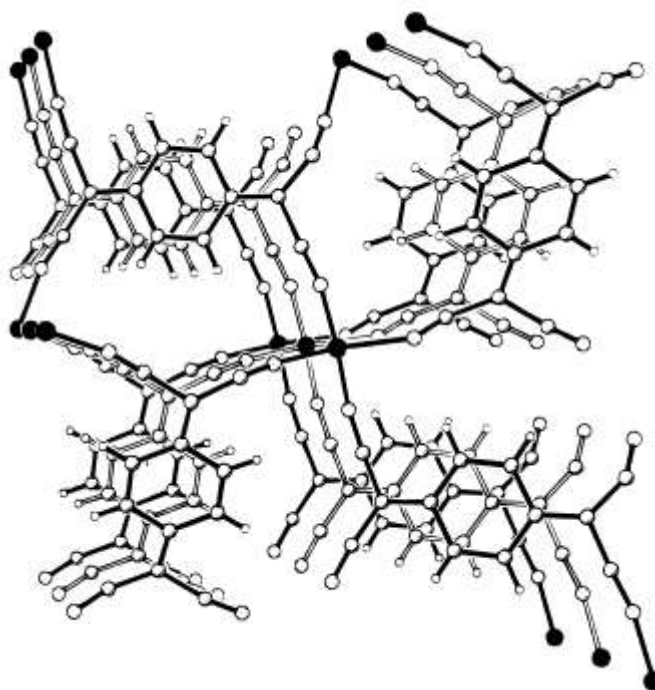


Figure 4-2: Crystal structure of the diamagnetic phase I of Cu(TCNQ) complex showing μ_4 -(TCNQ-TCNQ)²⁻.⁶⁵

In contrast, it should be possible to prepare a non-planar substituted dicyanostilbene that could not dimerize in any way to create a diamagnetic species. This concept would require substitution in all of the positions *ortho*- to the olefin central C=C bond. In this chapter, we report the synthesis of just such a molecule, 2,2',6,6'-tetrachlorodicyanostilbene (TCDCS), and its reaction with hexacarbonylvanadium(0).

4.2 Synthesis and characterization of TCDCS

TCDCS was a synthetic challenge because the substituent chlorines in the 2- and 6-position of the starting material make the oxidative dimerization difficult, Figure 4-3. The steric

bulk of the chlorine substituents prevent the deprotonation step that leads to oxidation of bis(dichlorophenyl)succinonitrile into the final product. The first synthetic method attempted was an oxidative dimerization which resulted in isolation of a monocyanated stilbene side product, Figure 4-3A. This product was hydrocyanated and then oxidized to get a small sample of the TCDCS. The side product for the oxidative dimerization occurs because tert-butoxide deprotonates the benzyl carbon of a dichlorophenylacetonitrile, which then attacks the iodine substituted benzyl carbon of a second dichlorophenylacetonitrile in which the iodine acts as a leaving group. This forms the succinonitrile which then gets deprotonated and a nitrile substituent is the leaving group forming the product of Figure 4-3A. The more successful method to obtain the desired product was stepwise formation of the carbon-carbon bond followed by further oxidation, Figure 4-3B.

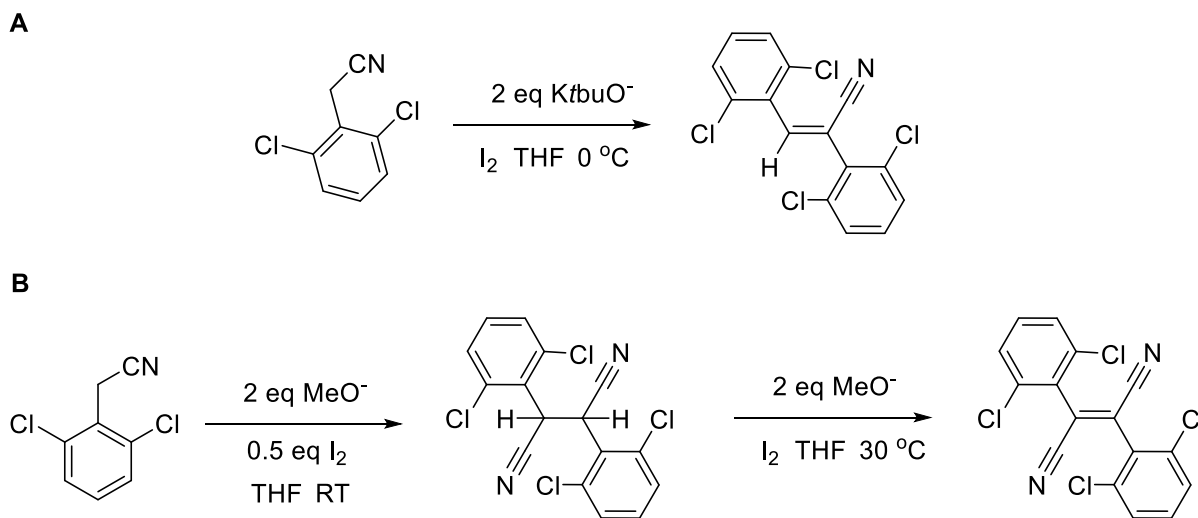


Figure 4-3: A) The oxidative dimerization leading to a side product. B) The two-step synthesis of TCDCS.

The desired stilbene derivative was characterized by melting point, IR, mass spectrometry, and ¹H NMR spectrometry. Cyclic voltammetry revealed a one-electron reduction at -1.259 V vs Ag/AgCl in acetonitrile with [Bu₄N]⁺[ClO₄]⁻ as the supporting electrolyte. The reduction potential is more negative than that of dicyanoperfluorostilbene (DCPFS) which has a reduction potential

of -0.787 V vs. Ag/AgCl. This is unfavorable because TCDCS will be difficult for the hexacarbonylvanadium(0) to reduce.

The reason for the very negative reduction potential is because of the broken conjugation between the phenyl rings and the olefin caused by the steric bulk of the chlorine atoms in the 2- and 6- positions. Two crystal structures (*cif* file in Appendix A, section 7.6) were determined using X-ray diffraction, Figure 4-4. As can be seen from each crystal structure, the phenyl rings are non-planar with the ethylene backbone. The dihedral angle between the phenyl ring and the ethylene backbone is 66.9°.

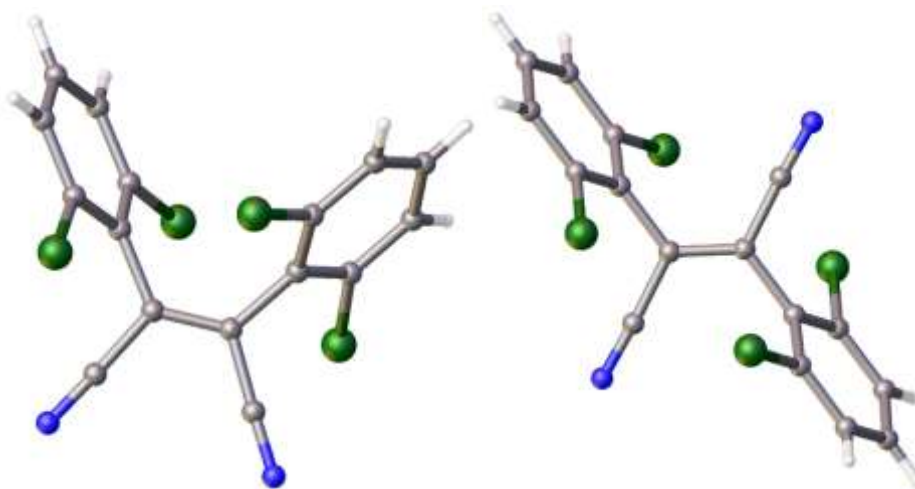


Figure 4-4: Crystal structures for TCDCS showing the *cis* and *trans* molecules where white is H, grey is C, blue is N, and green is Cl.

4.3 Reaction of acceptors with V(CO)₆ and characterization of the products

Several reactions of TCDCS with V(CO)₆ were attempted to synthesize a V[TCDCS]₂. The first attempt used dichloromethane as a solvent, resulting in a paramagnetic material. The second

attempt used 3 mL of THF to dissolve the $\text{V}(\text{CO})_6$ and 7 mL of THF to dissolve the TCDCS, which also resulted in paramagnetic material. For the attempts that did not form magnetically ordered phases, it is most probably the case that solubility of the acceptor was an issue. Without proper solubility the acceptor cannot form the 3-D network with the vanadium to exhibit magnetic ordering. The final attempt used 3 mL of THF for the $\text{V}(\text{CO})_6$ and 15 mL of THF for the TCDCS, which resulted in an ordered sample. The reaction very quickly changed to yellow and then to a grey insoluble product.

Infrared spectra of the neutral acceptor and of the paramagnetic material were obtained. The neutral acceptor exhibited a $\nu_{\text{C}\equiv\text{N}}$ stretch around 2218 cm^{-1} . The product of the reaction of the acceptor and the $\text{V}(\text{CO})_6$ exhibited no $\nu_{\text{C}\equiv\text{N}}$ stretch, however, a new peak was observed in the IR spectrum at 1832 cm^{-1} . The peak at 1832 cm^{-1} falls in the range of $\nu_{\text{C}=\text{O}}$ stretches in the IR spectrum and is most likely a type of carbonyl coordinated to the vanadium metal. It cannot be $\text{V}(\text{CO})_6$ because the $\nu_{\text{C}=\text{O}}$ stretch for this compound is at 1976 cm^{-1} . However, a previously reported reaction of $\text{V}(\text{CO})_6$ and tetracyanobenzene has shown a $\nu_{\text{C}=\text{O}}$ stretch in the IR at 1845 cm^{-1} which is indicative of $[\text{V}(\text{CO})_6]^-$.⁴⁶ This vanadium species is known to originate from the disproportionation of $\text{V}(\text{CO})_6$.⁶⁶

The field cooled temperature-dependent magnetization data (M vs T), Figure 4-5, was collected in a 5 G applied field promptly after synthesizing $\text{V}(\text{TCDCS})_2$. The data shows the magnetization gradually decreases until it is almost zero at around 125 K, Figure 4-5. The magnitude of the magnetization is very small, which indicates that only a small portion of the bulk sample is magnetically ordered.

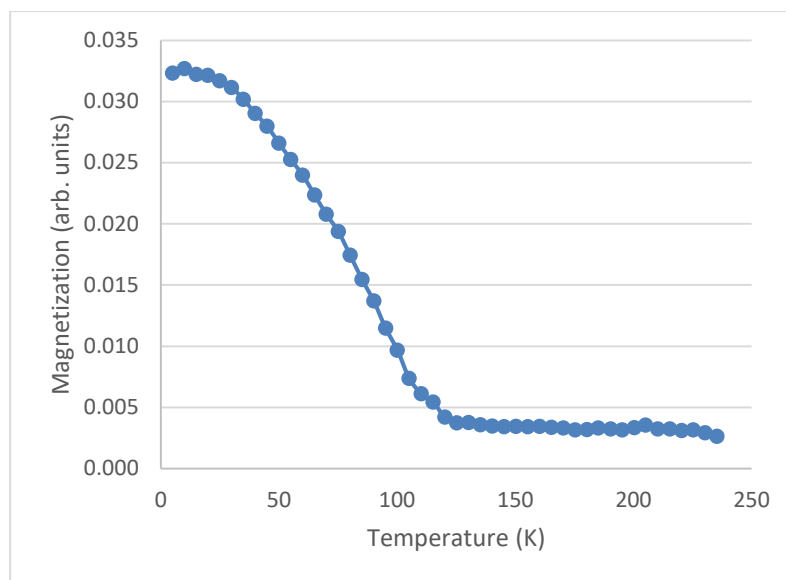


Figure 4-5: A plot of M vs T for $V(TCDCS)_2$. Magnetization units are multiplied by 1000.

Measurements of magnetization versus applied magnetic field was also conducted on the magnetic material at 5 K. The M vs H curve is plotted in Figure 4-6. The curve is indicative of a small portion of the bulk sample being magnetically ordered. If the material was not magnetically ordered, the M vs H graph would be a straight line going from the bottom left corner to the top right corner of the graph and passing through zero.

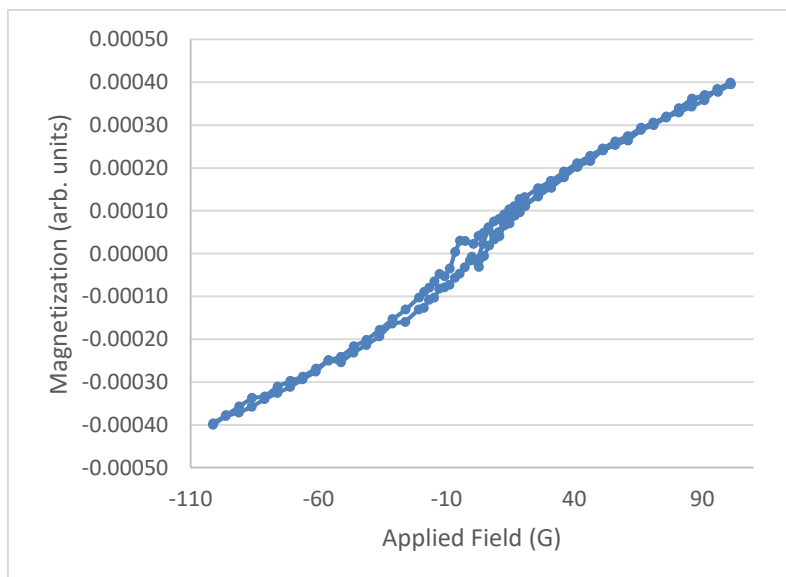


Figure 4-6: Plot of M vs H for V(TCDCS)₂ at 5K.

As mentioned above, solubility of the acceptor was an issue. The synthesis that yielded magnetic material used almost twice the amount of solvent of the literature procedure.⁵² This being the case, the vanadium cations may have been completely coordinated by THF molecules and resulted in a very small amount of the acceptor coordinating to each vanadium.

4.4 Conclusion

A stepwise synthetic method was developed for 2,2',6,6'-tetrachlorodicyanostilbene. The crystal structure of the acceptor has been obtained and shows that the chlorines substituents in the 2 and 6 positions of the phenyl rings make the molecule non-planar, as desired. However, this makes the molecule very difficult to reduce by one electron and extremely insoluble, which proves problematic for use in synthesizing a vanadium magnet. Nevertheless, we have evidence that it does form a (probably ferri) magnetically ordered phase with an ordering temperature of 125 K. In the future we will attempt to synthesize the TCDCS radical anion and coordinate it to manganese tris(pyrazol-1-ylmethyl)amine to synthesize a magnetic square and as well try to find conditions to prepare a useful sample of the magnet.

4.5 Experimental

4.5.1 General Methods

The following is a procedure describing the synthesis of the TCDCS and its reaction with hexacarbonylvanadium(0). All reagents were used as received except the tetrahydrofuran and diethyl ether, which were dried over sodium benzophenone under nitrogen, distilled into Schlenk flasks and freeze, pump, thawed to remove oxygen. The dry tetrahydrofuran used in the TCDCS synthesis was also dried over sodium benzophenone under nitrogen and distilled. The V(CO)₆ was prepared from [Na(diglyme)₂][V(CO)₆] using a literature procedure.⁵⁷

4.5.2 Synthesis of Molecules

2,3-Bis(2,6-dichlorophenyl)succinonitrile

In a 250 mL Schlenk flask, 2,6-dichlorophenylacetonitrile (1.00 g, 0.00538 mol) and iodine (0.68 g, 0.00269 mol) were stirred together in a solution of 50 mL of dry THF. The reaction flask was put into an ice bath and was allowed to cool to 0 °C. Then, sodium tert-butoxide (0.52 g, 0.00538 mol) was dissolved separately in 10 mL of dry THF. The sodium tert-butoxide solution was added to the reaction flask via addition funnel over a period of 20 min. The reaction was stirred overnight. The solvent was evaporated and the solid was washed with cold EtOH until white. Yield: 0.511 g (0.00138 mol, 51.0 %). ^1H NMR (400MHz, CDCl_3): δ 7.50 (td, 4H), 7.39 (t, 2H), 6.01 (s, 2H).

2,2',6,6'-Tetrachlorodicyanostilbene

In a 250 mL Schlenk flask, 2,3-bis(2,6-dichlorophenyl)succinonitrile (0.50 g, 0.00135 mol) and iodine (0.34 g, 0.00135 mol) were stirred together in a solution of 100 mL of dry THF. The reaction flask was heated at 30 °C. Then, sodium methoxide (0.52 g, 0.00538 mol) was dissolved separately in 10 mL of dry THF. The sodium methoxide solution was added to the reaction flask via addition funnel over a period of 20 min. The reaction was stirred for 1 hr. The solvent was evaporated and the solid was washed with cold EtOH until white. Melting point: 276.5-278 °C, Yield: 0.258 g (0.000701 mol, 52 %). ^1H NMR (400MHz, CDCl_3): δ 7.52 (dd, 4H), 7.46 (dd, 2H), HRMS (ESI) calcd for $[\text{M}]^+$: 368.0380; found: 368.0369, FT-IR: (cm^{-1}) 2218.

4.5.3 Attempts of Synthesis of the Vanadium Based Magnet $\text{V}(\text{TCDCS})_2$

Attempts 1 and 2 found in appendix A, section 7.6.

Attempt 3:

Under a nitrogen atmosphere, 2,2',6,6'-TCDCS (50.1 mg, 0.136 mmol) dissolved in 15 mL of THF was added dropwise to vanadium hexacarbonyl (15 mg, 0.068 mmol) dissolved in 3 mL of THF with stirring. After 1 hour, the solvent was evaporated and the grey precipitate was tritrated with 10 mL of ether for 15 min. The precipitate was then collected on a medium frit, rinsed with ether (3×2 mL), and dried in vacuo for 1 h. Yield: 0.0311 g

Chapter 5 Synthesis and Magnetic Properties of Vanadium (1-Naphthyltricyanoethylene)₂ and Vanadium (2-Naphthyltricyanoethylene)₂

5.1 Introduction

The synthesis of the family of fluorophenyltricyanoethylene acceptors was a key first step in creating a library of TCNE derivatives.⁵⁰ There are several ways that these acceptors can affect the magnetic ordering temperature of the resulting magnet. For example, the reduction potential has been shown to be correlated with T_c . Also, steric interactions with substituents in the 2, and 6 positions of the phenyl ring cause nonplanarity. This can affect a change in the magnetic properties in a number of ways. For instance, disruption of the extended conjugated system in turn, affects the spin density distribution and the charge density distribution in the radical anion. Furthermore, the twist about the phenyl/olefin dihedral affects how well the material packs in the solid. Finally, as has been previously suggested, undesired dimerization of the acceptor radical anions is probably impeded by steric bulk that disrupts planarity. In this chapter, the scaffold has been used to design three acceptors with similar electronic properties but different steric properties in an attempt to discern the relative importance of each.

One way to start to determine whether steric bulk to prevent dimerization of radical anionic acceptors or an extended conjugated system in the radical anionic acceptor is more impactful is to examine TCNE derivatives with extended conjugated systems against derivatives with abbreviated conjugated systems. For example, comparisons of a phenyl substituent against a naphthyl substituent to examine the effects of extended conjugation on magnetic ordering temperature, or comparisons of a phenyl substituent against a cyclohexyl substituent to examine the effects of abbreviated conjugation on magnetic ordering temperature.

In previous studies, reaction of phenyltricyanoethylene (H₅PTCE) with hexacarbonylvanadium(0) gave a black, amorphous, air-sensitive precipitate. It is assumed that the structure is a disordered network of V²⁺ cations bridged through the three nitrile nitrogen atoms of H₅PTCE. Temperature-dependent magnetization was measured at 5 G for V(H₅PTCE)₂, which exhibited an ordering temperature of 215 K. Saturation magnetization near 5585 emu G/mol and a near zero coercivity shows that V(H₅PTCE)₂ is a soft ferrimagnet.⁵⁰

To assess the importance of extended structural conjugation, phenylcyanoethylene derivatives were investigated. Three new acceptors, 1-naphthyltricyanoethylene (1-NTCE), 2-naphthyltricyanoethylene (2-NTCE) and 1-anthryltricyanoethylene (1-ATCE) were synthesized. All three acceptors extend the conjugation of the phenyl ring, but the 2-naphthyl should not exhibit as much steric hindrance that renders the radical anion non-planar. The 1-NTCE is akin to having a methyl group in the 2 position on the H₅PTCE, which would break the conjugation between the naphthyl ring and the TCE moiety.

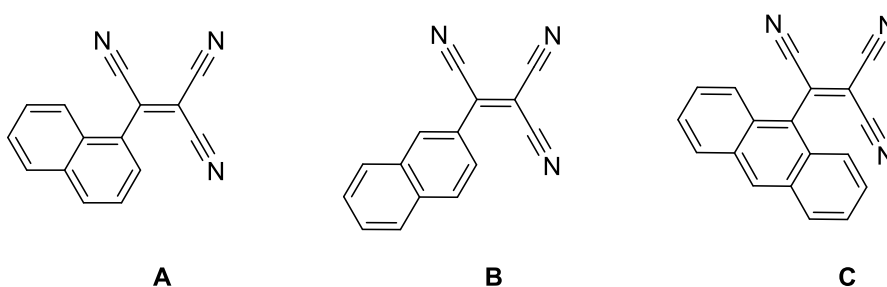


Figure 5-1: Structure of 1-naphthyltricyanoethylene (**A**), 2-naphthyltricyanoethylene (**B**), and 1-anthryltricyanoethylene (**C**).

5.2 Synthesis and characterization of the acceptors

The synthesis of the desired acceptors is achieved in three steps starting from the commercially available aldehydes.⁵⁰ Figure 5-2 illustrates the scheme for preparing the 1-

naphthyltricyanoethylene. Note that the 1-naphthyltricyanoethylene was synthesized by Ericka Bruske under my supervision. The 2-naphthyltricyanoethylene and 1-anthryltricyanoethylene are made analogously. The purity of the acceptors was determined by ^1H NMR, IR, mass spectrometry, and melting point.

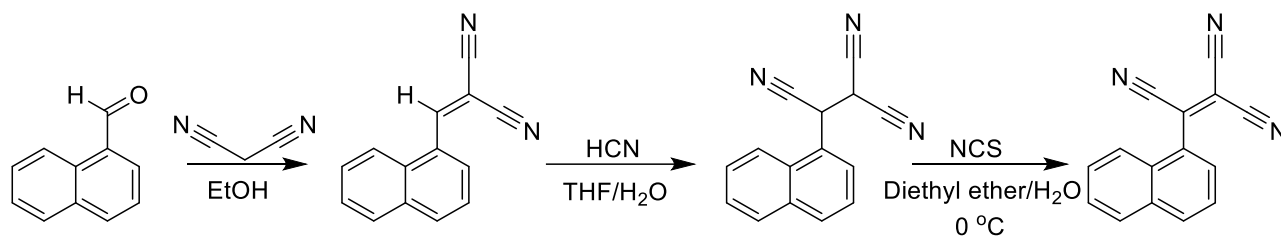


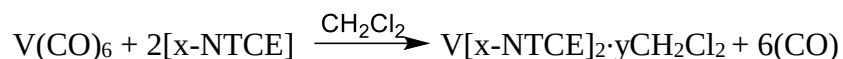
Figure 5-2: Synthesis of 1-naphthyltricyanoethylene. Yields for each step of the synthesis were 56 %, 72 %, and 87 % respectively.

The reversibility of the one-electron reduction of each acceptor was verified by cyclic voltammetry. The acceptor redox potentials were measured in acetonitrile with $[\text{Bu}_4\text{N}]^+ [\text{ClO}_4]^-$ as the electrolyte and are reported relative to Ag/AgCl. The reduction potentials vs Ag/AgCl for the 1-NTCE, 2-NTCE, and 1-ATCE acceptors were -0.62 V, -0.57 V, and -0.64 V respectively. These compounds are more difficult to reduce than the H_5PTCE which had a reduction potential of -0.40 V vs Ag/AgCl. Most likely the difficulty in reduction is a result of the steric bulk of the 1-naphthalene and anthracene making the substituent twist out of the plane of the ethylene backbone. This twist would limit the conjugation of the system from extending completely into the anthryl and naphthyl rings. The 2-naphthyl substituent must exhibit more twist than the phenyl substituent but not as much as the 1-naphthyl substituent.

5.3 Reaction of 1-NTCE, 2-NTCE, and 1-ATCE with $\text{V}(\text{CO})_6$ and characterization of the products

The synthesis of the magnets was performed by combining hexacarbonylvandadium(0) with the desired acceptor in dichloromethane in a nitrogen glovebox. The reaction of the naphthyl

acceptors with $\text{V}(\text{CO})_6$ is very fast and the solution changes from a yellow color to a dark green color. The final product precipitates as a black insoluble material that cannot be redissolved and is extremely air-sensitive. Elemental analysis has determined that the molecular formula for the magnetic material is a 1:2 vanadium-to-acceptor ratio with a small amount of solvent in the crystallization lattice. This formula agrees with the formula found for the other similarly synthesized vanadium magnets.^{49,50} The general scheme to make the magnetic compounds is shown below where the x can represent connectivity in the 1 or 2 position for the naphthyl group, Scheme 5-1.



Scheme 5-1: Chemical reaction for preparation of $\text{V}[\text{x-NTCE}]_2$.

When 1-ATCE was combined with hexacarbonylvanadium(0) in dichloromethane under a nitrogen atmosphere there was a color change from purple to black which resulted in a black insoluble material similar to both $\text{V}(\text{x-NTCE})_2$ magnets. However, when the solid was measured for magnetic susceptibility, the result indicated that it was a paramagnet. This is an interesting result as 1-ATCE has a sufficiently low reduction potential and has a reversible one electron reduction which is generally what is needed to synthesize these molecule-based magnets. It seems likely that the anthryl group on the ethylene backbone makes the acceptor too sterically hindered to bridge between two vanadium cations.

The IR spectrum of each magnetically ordered phase exhibited a $\nu_{\text{C}\equiv\text{N}}$ red shift when compared to the neutral acceptors, which is consistent of the one electron reduction of the coordinated radical anionic acceptors as shown in Table 5-1. The IR spectra also exhibit broad $\nu_{\text{C}\equiv\text{N}}$ stretches for the magnet as opposed to the sharp $\nu_{\text{C}\equiv\text{N}}$ stretches shown in the neutral acceptors.

The broad stretches indicate a variety of different bonding environments for the radical anionic acceptor. The reaction of 1-ATCE with $V(CO)_6$ exhibited $\nu_{C\equiv N}$ stretches that were red shifted from the neutral acceptor. This result indicates that 1-ATCE was reduced by one electron even though magnetometry showed that the compound did not form a 3-D coordination network.

Table 5-1: Summary of CN stretching frequencies for neutral acceptors and resulting solids.

Acceptor	Acceptor $\nu_{C\equiv N}$, cm^{-1}	Solid $\nu_{C\equiv N}$, cm^{-1}
1- NTCE	2235	2192, 2130
2- NTCE	2231	2190, 2132
1-ATCE	2238	2191, 2133

The field cooled (5 G) magnetization data (M vs T) was collected in a 5 G applied field promptly after synthesizing each $V[acceptor]_2$ magnet. The ordering temperatures were estimated by extrapolating the steep linear portion of the M vs. T curve. Ordering temperatures were also determined by the onset of a non-zero out of phase (χ'') component of ac susceptibility at 10 Hz, 100 Hz, and 1000 Hz (see Appendix A, section 7.4). The M vs T data is plotted in Figure 5-3. The results are summarized in, Table 5-2.

Table 5-2: Summary of the magnetic properties of the vanadium naphthyltricyanoethylenes versus the vanadium phenyltricyanoethyle magnets^a

Magnet	T_c , K	Deviation in T_c , K	M_s , emu G/mol	$E_{1/2}$, V
$V(H_5PTCE)_2$ ^b	215	± 2.5	5060	-0.40
$V(1-NTCE)_2$	130	± 5	3813	-0.62
$V(2-NTCE)_2$	185	± 5	5680	-0.57
$V(1-ATCE)_2$	Not observed	N/A	N/A	-0.64

^a M(H) measurements were taken at 5K. Acceptor redox potentials, relative to Ag/AgCl, were measured in acetonitrile with $[Bu_4N]^+ [PF_6]^-$ as the electrolyte. ^b previous work.⁴⁹ Each magnetic measurement was conducted twice.

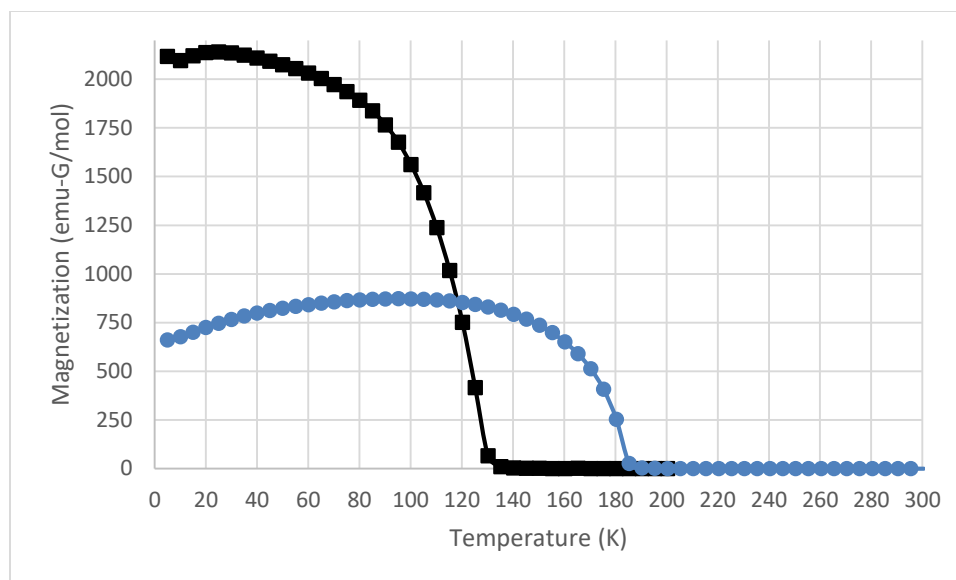


Figure 5-3: Plot of M vs T in a 5 G field for $V(1\text{-NTCE})_2$ (■) and $V(2\text{-NTCE})_2$ (●).

For the $V(1\text{-NTCE})_2$ the magnetization first decreases and then increases for about 10 K until finally slowly starting to decrease as the sample is warmed to 300 K. The sample reaches almost zero magnetization at its ordering temperature of 130 K. For $V(2\text{-NTCE})_2$, the magnetization increased up until about 120 K and then quickly decreases as the material approaches its ordering temperature, 185 K. The ordering temperatures are reproducible for both compounds and show that the connectivity of the naphthyl group has an influence on the ordering temperature of the magnetic material.

For $V(1\text{-ATCE})_2$ the temperature-dependent magnetization was measured at 5 G, but the sample had no ordering temperature and exhibited paramagnetism. Although the IR spectrum and the color change during the reaction indicates that a reaction occurred between the hexacarbonylvanadium(0) and 1-ATCE, the final product was a paramagnetic material and not the desired magnetically ordered material.

Measurements of magnetization versus applied magnetic field were conducted on both magnetic materials at 5 K. A representative plot is shown in Figure 5-4. The coercivities were around 2 G for both the 1 and the 2-NTCE vanadium magnets. The remanant magnetizations were small and were around 1107 emu-G/mol and 1947 emu-G/mol respectively. These small coercivities and remanant magnetizations are common for soft ferrimagnets.^{49,50,53} Saturation magnetization was reached at 100 G for both magnetic materials. For a vanadium (II) system with a spin of $S = 3/2$ antiferromagnetically coupling to two radical anionic acceptors with spins of $S = 1/2$, the theoretical saturation magnetization would be 5585 emu-G/mol (assuming $g = 2$). For the 1-NTCE the saturation magnetization was 3813 emu-G/mol, which is much lower than the theoretical value. For the 2-NTCE the saturation magnetization was 5680 emu-G/mol, very close to the ideal value. It is hypothesized that the reason for $V(1\text{-NTCE})_2$ having such a low saturation magnetization is because the steric bulk of the 1-naphthyl substituent on the acceptor prevents a good 3-D network from forming which results in lower mediation of coupling between the vanadium metal centers. For 1-ATCE, the steric bulk appears to be significant enough to prevent formation of $V(1\text{-ATCE})_2$, instead producing an unknown paramagnetic material.

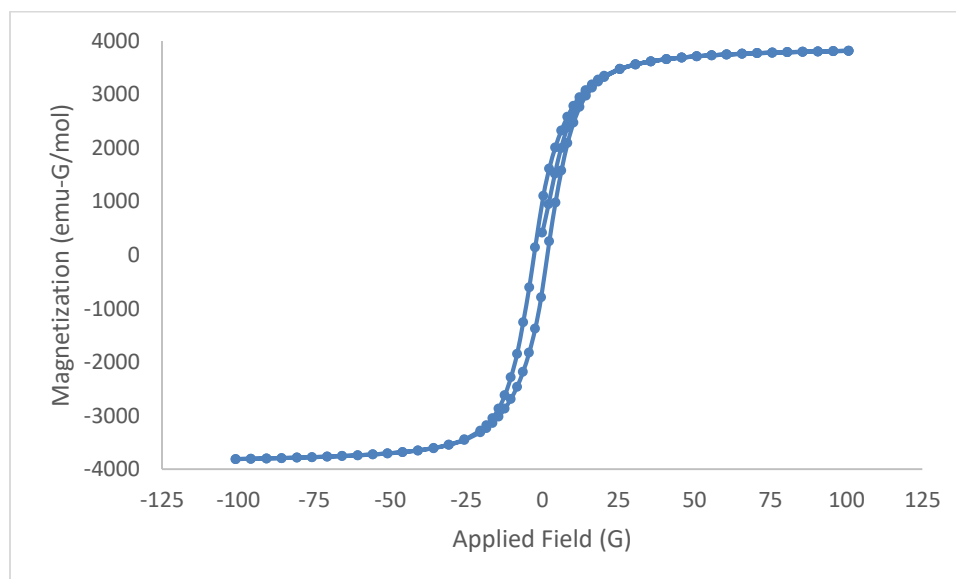


Figure 5-4: Plot of M vs H for V(1-NTCE)₂ at 5 K.

Comparing the magnets derived from naphthyl vs the phenyl tricyanoethylenes, the H₅PTCE has the highest ordering temperature followed by the 2-NTCE and the 1-NTCE. This result is a bit surprising considering the NTCE's have an extended conjugated system, which should help to promote a higher ordering temperature. The 2-NTCE is not as sterically encumbered as the 1-NTCE because of its connectivity.

5.4 Conclusion

Two new H₅PTCE derivatives were synthesized that extended the conjugation of the the acceptor by ring annulation. V(2-NTCE)₂ has a higher ordering temperature at 185 K compared to V(1-NTCE)₂ with an ordering temperature of 130 K. Neither of these magnetic materials had a higher ordering temperature than the V(H₅PTCE)₂ which suggests that extending the conjugated system through the phenyl ring does not contribute to a higher ordering temperature. The saturation magnetization was lower for V(1-NTCE)₂ than for V(2-NTCE)₂ which suggests that steric bulk plays a significant role in how well the 3-D network forms and that the lack of a good network reduces the coupling between magnetic centers.

The next step for this research is to synthesize H₅PTCE derivatives that have a less conjugated system to determine the effects on ordering temperature. A few acceptors that we would like to investigate would be cyclohexyltricyanoethylene, 1-(5,6,7,8-tetrahydronaphthyl)tricyanoethylene, and 2-(5,6,7,8-tetrahydronaphthyl)tricyanoethylene because they are analogous to the acceptors studied in this chapter but with abbreviated conjugated systems.

5.5 Experimental

5.5.1 General Methods

The synthesis of the 1- and 2-naphthyltricyanoethylenes and 1-anthryltricyanoethylene are based on literature procedures.⁴⁹ All reagents were used as received except for the following: the dichloromethane used in the magnet synthesis was distilled from calcium hydride and the $\text{V}(\text{CO})_6$ was prepared from $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ using a literature procedure.⁵⁷

5.5.2 Synthesis of Molecules and Vanadium Based Magnets

2-(1-Naphthyl)-1,1,2-tricyanoethylene

2-(1-Naphthyl)-1,1-dicyanoethylene

In a 100 mL round bottom flask, 1-naphthaldehyde (3.00 g, 0.019 mol) and malononitrile (1.26 g, 0.019 mol) were stirred together and dissolved in 40 mL of 100% ethanol. While stirring, ten drops of triethylamine were added. The solution was allowed to stir for 1 h. A yellow solid precipitated. The solid was collected and washed with water (3 x 20 mL). The yellow powder was dried in an oven overnight. Yield: 2.19 g (0.011 mol, 56 %). Melting point: 141-142 °C, ^1H NMR (400 MHz, CDCl_3): δ 8.67 (s, 1H), 8.28 (d, 1H), 8.11 (d, 1H), 7.95 (m, 2H), 7.64 (m, 3H); HRMS (ESI) calcd for $[\text{M}]^+$: 204.0687; found: 204.0701.

2-(1-Naphthyl)-1,1,2-tricyanoethane

In a 100 mL round bottom flask, (1.00 g, 0.0049 mol) 1-(naphthyl-1,1-dicyanoethylene was dissolved in 25 mL of THF. Separately, potassium cyanide (0.33 g, 0.0051 mol) was dissolved in 25 mL of DI water and cooled in an ice bath. In quick succession, the cold potassium cyanide solution was added to the ethanol solution followed by 100 mL of ice cold DI water. After stirring for 45 min, 1 mL of conc. HCl was added to yield an off white precipitate. After stirring the solution another 15 min, the off white precipitate was collected on a filter, rinsed thoroughly with

water, and dried in an oven overnight. Yield: 0.82 g (0.0035 mol, 72 %). Melting point: 134 °C, ^1H NMR (400 MHz, CDCl_3): δ 8.02 (t, 2H), 7.94 (d, 1H), 7.76 (d, 1H), 7.71 (t, 1H), 7.64 (q, 2H), 5.30 (d, 1H), 4.39 (d, 1H); HRMS (ESI) calcd for $[\text{M}]^+$: 231.0796; found: 231.0775.

2-(1-Naphthyl)-1,1,2-tricyanoethylene (1-NTCE)

In a 100 mL round bottom flask equipped with a magnetic stirbar, 1-(naphthyl)1,1,2-tricyanoethane (0.50 g, 0.0022 mol) was dissolved in 15 mL of diethyl ether and cooled to 0 °C. N-Chlorosuccinimide (0.30 g, 0.0023 mol) was then added with rapid stirring. Over the course of 20 min, 15 mL of ice cold DI water was also added with vigorous stirring. A precipitate formed and was collected on a filter, washed with cold DI water (3 x 20 mL), and then dried in an oven overnight. Yield: 0.43 g (0.0019 mol, 87 %). Melting point: 131.5-132.5 °C, ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, 1H), 8.00 (d, 1H), 7.95 (d, 1H), 7.75 (m, 2H), 7.70 (m, 1H), 7.63 (m, 1H); HRMS (ESI) calcd for $[\text{M}]^+$: 229.0640; found: 229.0641, FT-IR: (cm^{-1}) 2230.

2-(2-Naphthyl)-1,1,2-tricyanoethylene

2-NTCE was synthesized using a similar procedure using 2-naphthaldehyde as the starting material.

2-(2-Naphthyl)-1,1-dicyanoethylene

Yield: 2.00 g (0.0098 mol, 51 %). Melting point: 141-142 °C, ^1H NMR (400 MHz, CDCl_3): δ 8.28 (s, 1H), 8.09 (dd, 1H), 7.93 (m, 4H), 7.68 (m, 2H), 7.61 (m, 2H); HRMS (ESI) calcd for $[\text{M}]^+$: 204.0687; found: 204.0701.

2-(2-Naphthyl)-1,1,2-tricyanoethane:

Yield: 0.84 g (0.0036 mol, 74 %). Melting point: 144-145 °C, ^1H NMR (400 MHz, CDCl_3): δ 8.01 (m, 2H), 7.92 (m, 2H), 7.63 (m, 2H), 7.51 (dd, 1H), 4.62 (d, 1H), 4.43 (d, 1H); HRMS (ESI) calcd for $[\text{M}]^+$: 231.0796; found: 231.0808.

2-(2-Naphthyl)-1,1,2-tricyanoethylene (2-NTCE)

Yield: 0.40 g (0.0017 mol, 80 %). Melting point: 183-184 °C, ^1H NMR (400 MHz, CDCl_3): δ 8.56 (s, 1H), 8.07 (dd, 1H), 8.03 (d, 2H), 7.95 (d, 1H), 7.76 (m, 1H), 7.68 (m, 1H); HRMS (ESI) calcd for $[\text{M}]^+$: 229.0640; found: 229.0629, FT-IR: (cm^{-1}) 2231

$\text{V}(\text{1-NTCE})_2$

Under a nitrogen atmosphere, vanadium hexacarbonyl (15 mg, 0.068 mmol) dissolved in 2 mL of dichloromethane was added dropwise to a solution containing 1-NTCE (48.3 mg, 0.211 mmol) in 2 mL of dichloromethane with stirring. After 15 min, the black precipitate was collected on a medium frit, rinsed with dichloromethane (3×2 mL), and dried in vacuo for 1 h. Yield: 35 mg (84 %). Anal. Calcd for $\text{C}_{30}\text{H}_{14}\text{N}_6\text{V} \cdot 0.45\text{CH}_2\text{Cl}_2$: C, 66.83; H, 2.74; N, 15.36. Found: C, 66.87; H, 2.97; N, 15.40.

$\text{V}[\text{2-NTCE}]_2$

$\text{V}(\text{2-NTCE})_2$ was prepared using a similar procedure to that of $\text{V}(\text{1-NTCE})_2$. Yield: 34 mg (81 %). Anal. Calcd for $\text{C}_{30}\text{H}_{14}\text{N}_6\text{V} \cdot 1.4\text{CH}_2\text{Cl}_2$: C, 60.15; H, 2.70; N, 13.40. Found: C, 59.65; H, 2.50; N, 13.63.

Chapter 6: Synthesis and Magnetic Properties of $V(x-Br_nPTCE)_2$

6.1 Introduction

The fluorophenyltricyanoethylene family was an interesting starting point for exploring the features that give rise to the magnetic properties of $V(TCNE)_2$. This research showed that the position of the fluorine substitution on the phenyl ring affects the magnetic ordering temperature of the vanadium magnets. Tatum and coworkers conducted experiments on the chlorophenyltricyanoethylene family of acceptors by synthesizing 10 new acceptors to combine with hexacarbonylvanadium (0) in DCM, Figure 6-1. The chloro- family of acceptors was of interest because the chlorine atom is larger than the fluorine atom. The structure-property relationships of these magnetic materials were compared to those of the fluorophenyltricyanoethylene family of acceptors.

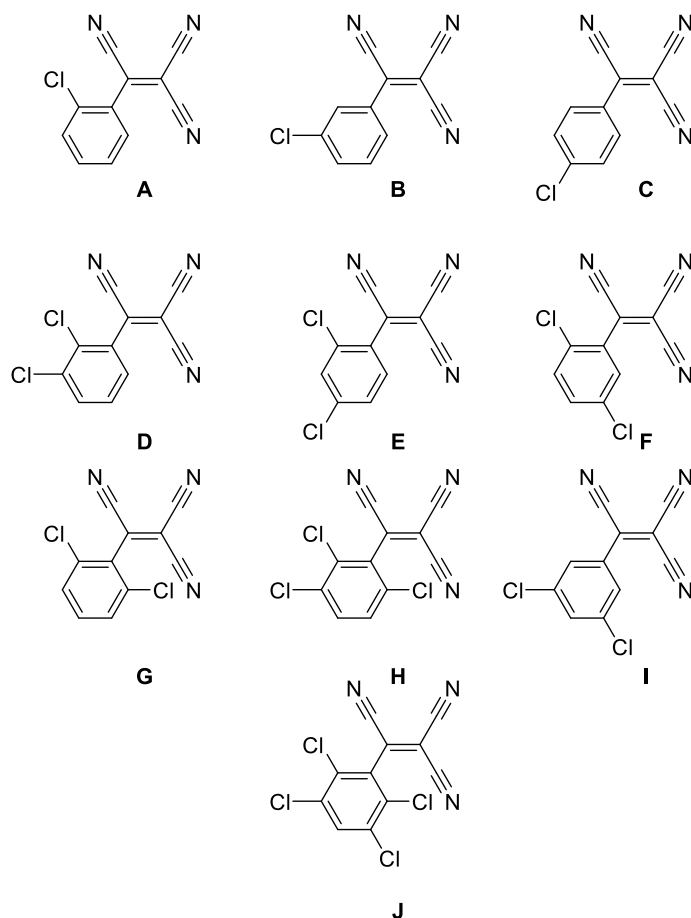


Figure 6-1: All the synthesized chlorophenyltricyanoethylene acceptors from left to right and then top to bottom: 2-chloro (**A**), 3-chloro (**B**), 4-chloro (**C**), 2,3-dichloro (**D**), 2,4-dichloro (**E**), 2,5-dichloro (**F**), 2,6-dichloro (**G**), 2,3,6-trichloro (**H**), 3,5-dichloro (**I**), 2,3,5,6-tetrachlorophenyltricyanoethylene (**J**).

For analogous acceptors **A**, **B**, and **C**, the structure-property relationships were similar to the fluorinated acceptors in that the substitutions *ortho*- and *meta*- to the olefin on the phenyl ring increased the ordering temperature of the material while the substitution *para*- to the TCE unit on the phenyl ring sharply decreased the ordering temperature. When looking at acceptors **D-G**, acceptor **G** has the highest ordering temperature at 285 K. Acceptors **D**, **E**, and **F** have lower ordering temperatures, all around 256 K. Acceptor **G** was thought to have the highest ordering because of the steric hindrance of the chlorines substituents in the 2- and 6- positions of the phenyl

rings making the ring non-planar and causing the spin density to be pushed to the three nitrogen atoms on the nitrile substituents connected to the ethylene backbone. It is unclear if the reason for the decrease in ordering temperature when adding more chlorine substituents on the phenyl ring is due to a secondary steric interaction, electronic effects or both. The results for the chlorinated acceptors were vastly different from those of the fluorinated acceptor in the multisubstituent acceptors.

In order to understand if steric or electronic effects lower the ordering temperature of the chlorinated acceptors, four analogous brominated derivatives were synthesized, Figure 6-2, and their reaction with hexacarbonylvanadium(0) were investigated. The bromine substituents are larger and much less electronegative than the fluorine and chlorine substituents. The four acceptors that have been synthesized are the 2-, 3-, and 4-bromo and the 2,6-dibromophenyltricyanoethylenes.

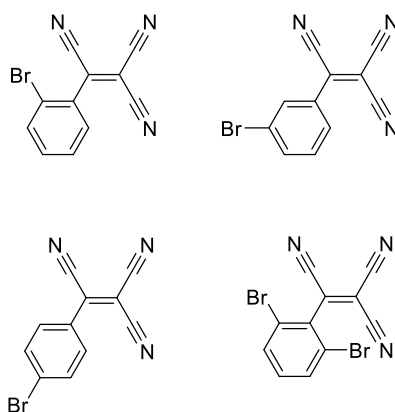


Figure 6-2: Structures of the bromine substituted phenyltricyanoethylenes.

6.2 Synthesis and characterization of the acceptors

Synthesis of the acceptors was achieved from commercially available substituted benzaldehydes in a three-step synthesis analogous to the synthesis for the naphthyltricyanoethylenes. Note that all of the acceptors in this chapter were synthesized by

undergraduates under my supervision. The identity and purity of these acceptors was determined by ^1H NMR, mass spectrometry, IR, and measuring melting points. The reversibility of the one-electron reduction of each acceptor was verified by cyclic voltammetry. The acceptor redox potentials were measured in acetonitrile with $[\text{Bu}_4\text{N}]^+ [\text{ClO}_4]^-$ as the electrolyte and were reported relative to Ag/AgCl. A summary of the reduction potentials for the acceptors can be seen in Table 6-2. The bromo- family of acceptors has reductions potentials more negative than -0.58V vs Ag/AgCl as compared to the H_5PTCE which had a reduction potential of -0.40 V vs Ag/AgCl.⁴⁹ The brominated acceptors are more difficult to reduce which we expected because bromine is less electronegative compared to chlorine and fluorine.

6.3 Reaction of acceptors with $\text{V}(\text{CO})_6$ and characterization of the products

The synthesis of the vanadium magnets was conducted by combining the desired acceptor with hexacarbonylvandium(0) in DCM under an inert atmosphere. The reaction proceeds quickly with a color change from yellow to a dark-bluish purple. The product precipitates as an insoluble black material that is air-sensitive and assumed to be amorphous based on previous studies of vanadium magnet materials.^{7,49,50} The ratio of acceptor to vanadium is 2:1 with small amounts of solvents trapped in the proposed three dimensional network as confirmed by elemental analysis. These results agree with previously synthesized vanadium TCNE derivative magnets.^{7,49,50}

Infrared spectrometry was conducted for each of the neutral acceptors as well as for each of the magnetic materials. The IR of the magnetic materials exhibited a red shifted $\nu_{\text{C}\equiv\text{N}}$ stretch, which is consistent with the one electron reduction of the coordinated radical anions, Table 6-1. The magnetic material exhibited broad $\nu_{\text{C}\equiv\text{N}}$ stretches as opposed to the sharp stretches displayed by the neutral acceptors. These broad stretches indicate a variety of different bonding

environments such a nitrile substituent bound to a vanadium having variable numbers of radical anions coordinated.

Table 6-1: Summary of CN stretching frequencies for neutral bromo- acceptors and resulting magnets

Acceptor	Acceptor $\nu_{\text{C}\equiv\text{N}}$, cm^{-1}	Magnet $\nu_{\text{C}\equiv\text{N}}$, cm^{-1}
2-BrPTCE	2244	2196, 2123
3-BrPTCE	2238	2196, 2123
4-BrPTCE	2238, 2231	2197, 2119
2,6-Br ₂ PTCE	2231	2194, 2119

The field cooled (5G) temperature-dependent magnetization data was collected in a 5 G applied field promptly after synthesizing each magnetic material. The ordering temperatures were estimated by extrapolating the steep linear portion of the M vs T curve. Ordering temperatures were also determined by the onset of non-zero out of phase (χ'') component of ac susceptibility at 10 Hz, 100 Hz, and 1000 Hz (see Appendix A, section 7.4). The M vs T is plotted in Figure 6-3. The summarized results can be found in Table 6-2.

Table 6-2: Summary of the magnetic properties of the bromotricyanoethylenes

Acceptor	^a T _c , K	^b E _{1/2} , V	M _s , emu G/mol
2-BrPTCE	220	-0.56	3837
3-BrPTCE	230	^c	^c
4-BrPTCE	95	-0.53	^c
2,6-Br ₂ PTCE	260	-0.50	2986

^a All vanadium magnets were measured in a 5G field. ^b Acceptor redox potentials, relative to Ag/AgCl were measured in acetonitrile with [Bu₄N]⁺[ClO₄]⁻ as the electrolyte. ^c Data has not yet been collected. Each magnetic measurement was conducted twice.

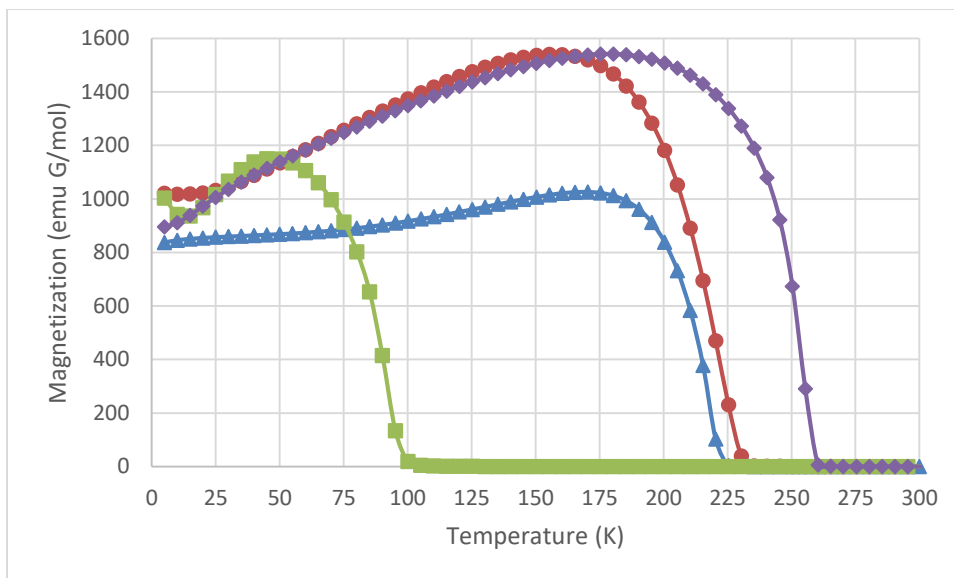


Figure 6-3: A plot of M vs T for $V(2\text{-BrPTCE})_2$ ($\blacktriangle$), $V(3\text{-BrPTCE})_2$ ($\bullet$), $V(4\text{-BrPTCE})_2$ ($\blacksquare$), and $V(2,6\text{-Br}_2\text{PTCE})_2$ ($\blacklozenge$) in a 5 G field.

For the $V(2\text{-BrPTCE})_2$ the magnetization remains relatively constant with a slight increase just before a sharp decrease as the sample is warmed to 300 K. The sample reaches almost zero magnetization at its ordering temperature of 220 K. For $V(3\text{-BrPTCE})_2$ the magnetization steadily increases up to around 150 K, where it starts to decrease sharply and almost reaches zero at its ordering temperature of 230 K. For $V(4\text{-BrPTCE})_2$ the magnetization decreases until 10 K and then quickly increases up to 50 K. The magnetization then sharply decreases to reach its ordering temperature of 95 K. For $V(2,6\text{-Br}_2\text{PTCE})_2$ the magnetization steadily increases up to 180 K and then sharply decreases to reach its ordering temperature of 260 K.

For the monobrominated acceptors, the bromine substituent in the 3- position results in a magnet with the highest ordering temperature, followed by the bromine substituent in the 2- position, and lastly the bromine substituent in the 4- position, Table 6-3.

Table 6-3: A comparison of ordering temperature vs position on the phenyl ring for the fluoro-, chloro-, and bromo-acceptors.

Position	F	Cl	Br
V(2-XPTCE) ₂	257	271	220
V(3-XPTCE) ₂	233	243	230
V(4-XPTCE) ₂	160	146	95
V(2,6-X ₂ PTCE) ₂	300	285	260

This trend is slightly different than the trend found for the chlorinated and fluorinated families of acceptors where the 2- position results in a magnet with the highest ordering temperature and the 4- position results in a magnet with the lowest ordering temperature. Of the three family of acceptors, the chlorine substituent in the 2- position results in a magnet with the overall highest ordering temperature, whereas the bromine substituent in the 4- position results in a magnet with the overall lowest ordering temperature. This may be because the steric hindrance is optimum for a chlorine substituent as opposed to too little steric hindrance for the fluorine substituent and too much steric hindrance for the bromine substituent. Substitution in the 3- position of the phenyl ring seems to be the most closely related for the acceptors as the resulting magnet has an ordering temperature of 230 K for 3-bromo-, 233 K for the 3-fluoro- and 243 K of 3-chloro-substituted acceptors. Substitution in the 4- position results in a magnet with lower ordering temperatures where the highest is the fluoro-substituted acceptor at 160 K and the lowest is the bromo-substituted acceptor at 95 K. This trend is as expected because the bromine in the 4- position is the most favorable leaving group for nucleophilic aromatic substitution, which is the hypothesized reason behind the low ordering temperature for magnets synthesized with an acceptor with a substitution in the 4- position. Overall, the disubstituted acceptors result in magnets with high ordering temperatures, with 2,6 difluoro- acceptor having the highest ordering temperature, followed by the dichloro-, and dibromo- respectively.

6.4 Conclusion

We have expanded the list of acceptors that support magnetic ordering when combined with $\text{V}(\text{CO})_6$ to include a family of bromine-substituted phenyltricyanoethylenes. The pattern for ordering temperatures of the resulting magnets was different for the bromo- family of acceptors than for the fluoro- and chloro- family of acceptors in that the 3- position for the bromo-family of acceptors resulting in the highest ordering temperature while the 2- position resulted in a higher ordering temperature in the other two families. The resulting magnet from substitution in the 4- position exhibited lower ordering temperatures as the halogen substitution became less electronegative and became a better leaving group for nucleophilic aromatic substitution. The resulting magnet from substitution in the 2- and 6- position resulted in the fluoro-family of acceptors having the highest ordering temperature at 300 K, followed by the chloro-family of acceptors at 285 K, and finally the bromo-family of acceptors at 260 K. For future work more bromo- family acceptors need to be synthesized to obtain an idea of how multiple bromine substituents affect ordering temperature. Then, theoretical calculations of electron affinity, dihedral angle, and spin density need to be calculated for the bromo- family of acceptors and compared with the ordering temperatures of the resulting magnets.

6.5 Experimental

6.5.1 General Methods

The synthesis of the bromotricyanoethylene family of compounds are based on literature procedures.⁴⁹ All reagents were used as received except for the following: the dichloromethane used in the magnet synthesis was distilled from calcium hydride and the $\text{V}(\text{CO})_6$ was prepared from $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ using a literature procedure.⁵⁷

6.5.2 Synthesis of Molecules and Vanadium Based Magnets

2-(2-Bromophenyl)-1,1,2-tricyanoethylene

2-(2-Bromophenyl)-1,1-dicyanoethylene

In a 100 mL round bottom flask, 2-bromobenzaldehyde (2.5 g, 0.013 mol) and malononitrile (1.16 g, 0.018 mol) were stirred together in 40 mL of 100% ethanol. While stirring, ten drops of triethylamine were added. The solution was allowed to stir for 1 h. A white solid precipitated out of solution. The solid was collected on a filter and washed with water (3 x 20 mL). The white powder was dried in an oven overnight. Melting point: °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 8.22 (s, 1H), 8.12 (m, 1H), 7.74 (m, 1H), 7.48 (m, 2H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(2-Bromophenyl)-1,1,2-tricyanoethane

In a 250 mL round bottom flask, (2.00 g, 0.009 mol) 1-(2-dibromophenyl)-1,1-dicyanoethylene was dissolved in 100 mL of EtOH. Separately, potassium cyanide (1.17 g, 0.018 mol) was dissolved in 300 mL of DI water and cooled in an ice bath. In quick succession, the cold potassium cyanide solution was added to the ethanol solution. After stirring for 1 h, 1 mL of conc. HCl was added to yield an off white precipitate. After stirring the solution another 15 min, the off white precipitate was collected on a filter, rinsed thoroughly with water, and dried in an oven overnight. Melting point: °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 7.81 (dd, 1H), 7.69 (dd, 1H), 7.55 (td, 1H), 7.42 (td, 1H), 4.99 (d, 1H), 4.34 (d, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(2-Bromophenyl)-1,1,2-tricyanoethylene (2-BrPTCE)

In a 100 mL round bottom flask equipped with a magnetic stirbar, 1-(2-bromophenyl)1,1,2-tricyanoethane (1.50 g, 0.006 mol) was dissolved in 40 mL of diethyl ether and cooled to 0 °C. N-Chlorosuccinimide (1.54 g, 0.012 mol) was then added with rapid stirring. Over the course of 20 min, 80 mL of ice cold DI water was also added with vigorous stirring. A precipitate formed and

was collected on a filter. The precipitate was washed with cold DI water (3x 20 mL) and then dried in an oven overnight. Melting point: 148.5 °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 7.80 (m, 1H), 7.54 (m, 2H), 7.47 (m, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:, FT-IR: (cm^{-1}) 2244.

2-(3-Bromophenyl)-1,1,2-tricyanoethylene

3-BrPTCE was synthesized using a similar procedure, using 3-bromobenzaldehyde as the starting material.

2-(3-Bromophenyl)-1,1-dicyanoethylene

Melting point: °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 7.97 (m, 1H), 7.89 (m, 1H), 7.75 (m, 1H), 7.71 (s, 1H), 7.43 (t, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(3-Bromophenyl)-1,1,2-tricyanoethane

Melting point: °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 7.67 (m, 2H), 7.44 (m, 2H) 4.43 (d, 1H), 4.25 (d, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(3-Bromophenyl)-1,1,2-tricyanoethylene (3-BrPTCE)

Melting point: 70.0-70.9 °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 8.09 (t, 1H), 7.93 (m, 1H), 7.85 (m, 1H), 7.51 (t, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:, FT-IR: (cm^{-1}) 2238.

2-(4-Bromophenyl)-1,1,2-tricyanoethylene

4-BrPTCE was synthesized using a similar procedure, using 4-bromobenzaldehyde as the starting material.

2-(4-Bromophenyl)-1,1-dicyanoethylene

Melting point: °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 7.76 (m, 2H), 7.72 (s, 1H), 7.70 (m, 2H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(4-Bromophenyl)-1,1,2-tricyanoethane

Melting point: °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 7.67 (m, 2H), 7.39 (m, 2H), 4.42 (d, 1H), 4.24 (d, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(4-Bromophenyl)-1,1,2-tricyanoethylene (4-BrPTCE)

Melting point: 173.4-174.1 °C Yield: g (mol, %) ^1H NMR (400 MHz, CDCl_3): δ 7.87 (m, 2H), 7.79 (m, 2H); HRMS (ESI) calcd for $[\text{M}]^+$; found:, FT-IR: (cm^{-1}) 2238, 2231.

2-(2,6-Bromophenyl)-1,1,2-tricyanoethylene

2,6-diBrPTCE was synthesized using a similar procedure, using 2, 6 dibromobenzaldehyde as the starting material.

2-(2,6-dibromophenyl)-1,1-dicyanoethylene

Melting point: 108.5-112 °C Yield: 2.19 g (0.007 mol, 74%) ^1H NMR (400 MHz, CDCl_3): δ 7.88 (s, 1H), 7.66 (d, 2H), 7.24 (t, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(2,6-dibromophenyl)-1,1,2-tricyanoethane

Melting point: 174.8-175.8 °C Yield: 1.89 g (0.006 mol, 87%) ^1H NMR (400 MHz, CDCl_3): δ 7.71 (d, 2H), 7.27 (t, 1H), 5.63 (d, 1H), 5.13 (d, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:.

2-(2,6-dibromophenyl)-1,1,2-tricyanoethylene (2,6-Br₂PTCE)

Melting point: 160.3-161 °C Yield: 0.58 g (0.002 mol, 39%) ^1H NMR (400 MHz, CDCl_3): δ 7.74 (d, 2H), 7.37 (t, 1H); HRMS (ESI) calcd for $[\text{M}]^+$; found:; FT-IR: (cm^{-1}) 2231.

V(2-BrPTCE)₂

Under a nitrogen atmosphere, vanadium hexacarbonyl (15 mg , 0.068 mmol) dissolved in 2 mL of dichloromethane was added dropwise to a solution containing 2-BrPTCE (54.4 mg, 0.211 mmol) in 2 mL of dichloromethane with stirring. After 15 min, the black precipitate was collected on a medium frit, rinsed with dichloromethane (3×2 mL), and dried in vacuo for 1 h. Yield: 25 mg (64 %). Anal. Calcd for $\text{C}_{22}\text{H}_8\text{N}_6\text{Br}_2\text{V} \cdot 0.4\text{CH}_2\text{Cl}_2$: C, 44.79; H, 1.48; N, 13.99. Found: C, 44.82; H, 1.56; N, 13.80, FT-IR: (cm^{-1}) 2196, 2123.

V(3-BrPTCE)₂

$\text{V}(3\text{-BrPTCE})_2$ was prepared using a similar procedure to that of $\text{V}(2\text{-BrPTCE})_2$. Yield: mg (%). Anal. Calcd for $\text{C}_{22}\text{H}_8\text{N}_6\text{Br}_2\text{V} \cdot 0.55\text{CH}_2\text{Cl}_2$: C, ; H, ; N, . Found: C, ; H, ; N, , FT-IR: (cm^{-1}) 2196, 2123.

V(4-BrPTCE)₂

$\text{V}(4\text{-BrPTCE})_2$ was prepared using a similar procedure to that of $\text{V}(2\text{-BrPTCE})_2$. Yield: 42 mg (81 %). Anal. Calcd for $\text{C}_{22}\text{H}_8\text{N}_6\text{Br}_2\text{V} \cdot 0.55\text{CH}_2\text{Cl}_2$: C, 44.16; H, 1.50; N, 13.70. Found: C, 44.09; H, 1.45; N, 13.75, FT-IR: (cm^{-1}) 2197, 2119.

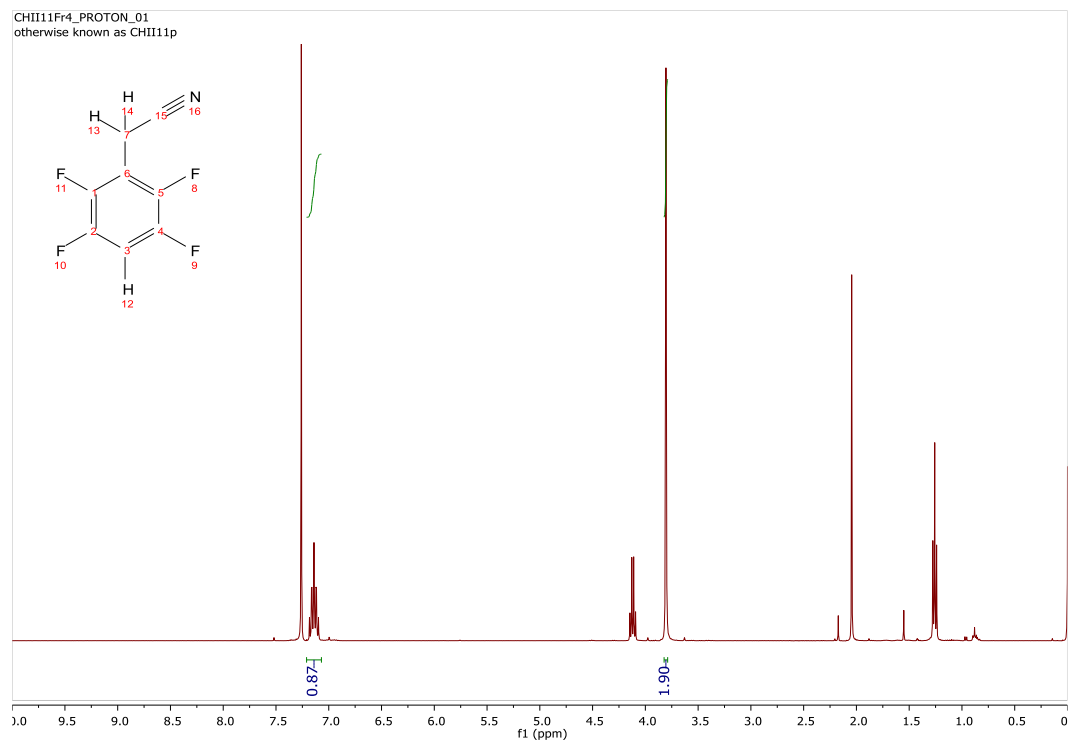
V(2,6-Br₂PTCE)₂

$\text{V}(2,6\text{-diBrPTCE})_2$ was prepared using a similar procedure to that of $\text{V}(2\text{-BrPTCE})_2$. Yield: 44 mg (89 %). Anal. Calcd for $\text{C}_{22}\text{H}_6\text{N}_6\text{Br}_4\text{V} \cdot 0.55\text{CH}_2\text{Cl}_2$: C, 35.13; H, 0.93; N, 10.90. Found: C, 35.09; H, 1.05; N, 10.84, FT-IR: (cm^{-1}) 2194, 2119.

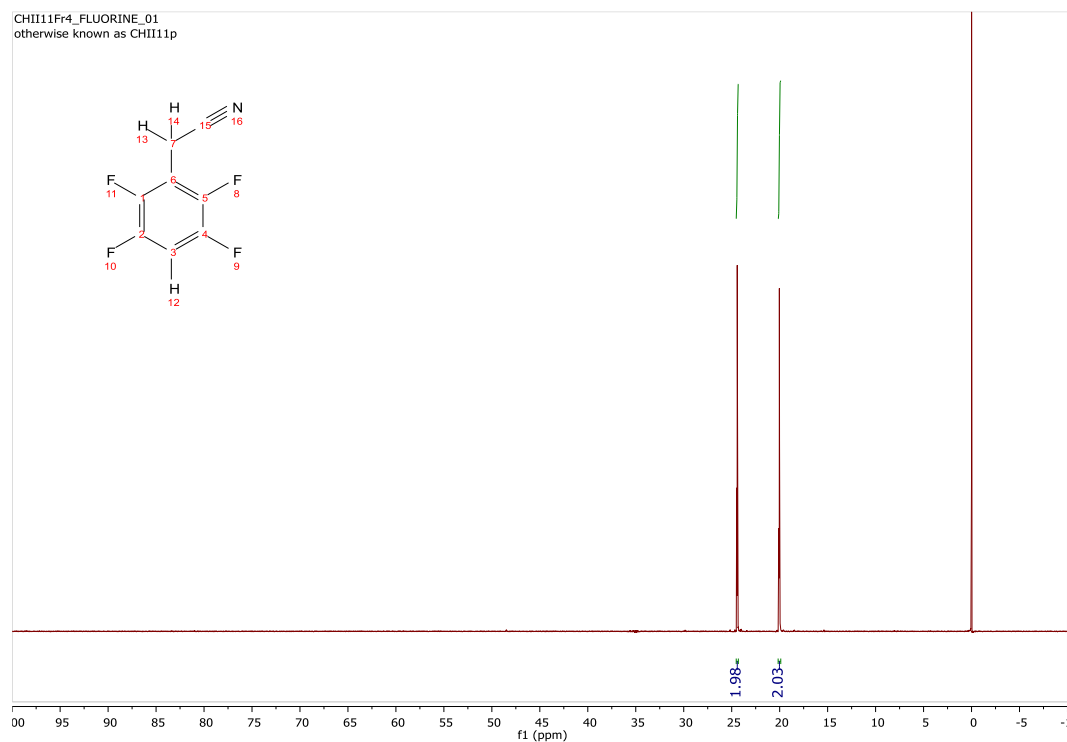
Appendix A

A.1 NMR:

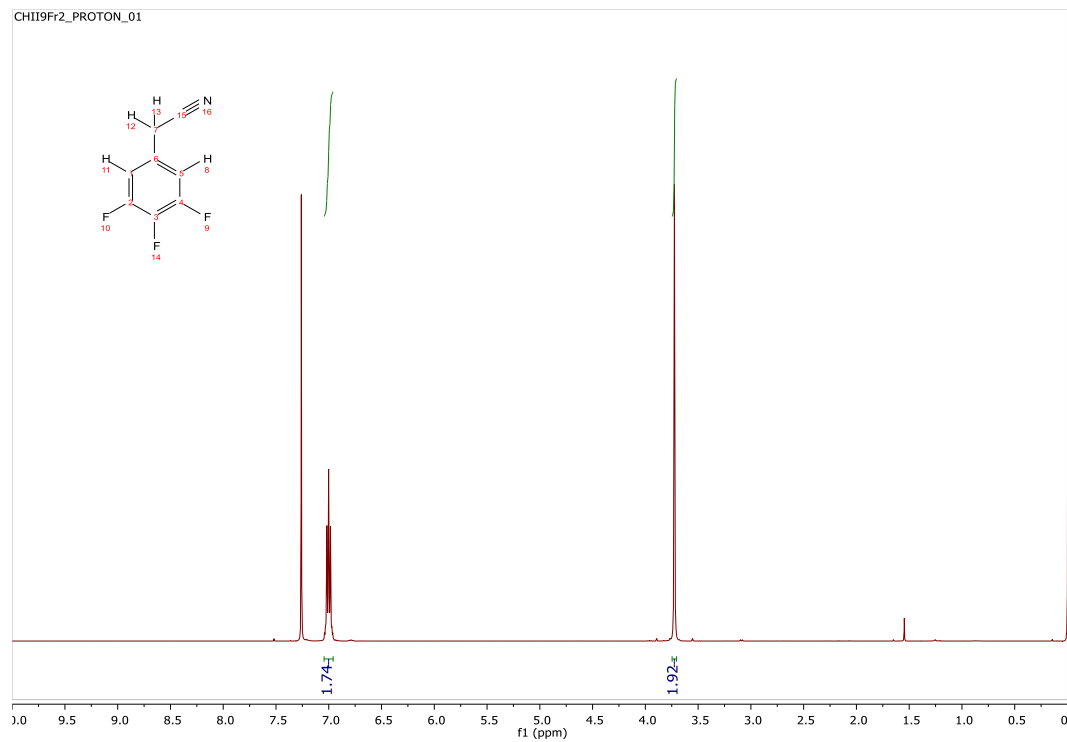
2, 3, 5, 6 Tetrafluorophenyl Acetonitrile 400 MHz ^1H NMR in CDCl_3 presence of ethyl acetate, acetone, and water peaks



2, 3, 5, 6 Tetrafluorophenyl Acetonitrile 376 MHz ^{19}F NMR (ppm vs C_6F_6)



3, 4, 5 Trifluorophenyl Acetonitrile 400 MHz ^1H NMR in CDCl_3 presence of water peak



CH119F2_FLUORINE_01

Chemical structure of 2,4-difluorophenylacetylene is shown. The structure is labeled with proton numbers: H-13 and H-12 for the alkyne, H-11 and H-10 for the ortho protons, H-8 and H-9 for the meta protons, and H-14 for the para proton.

The ^1H NMR spectrum displays two main signals:

- A sharp peak at approximately 3.0 ppm, integrated as 2.01H.
- A multiplet at approximately 7.2 ppm, integrated as 0.99H.

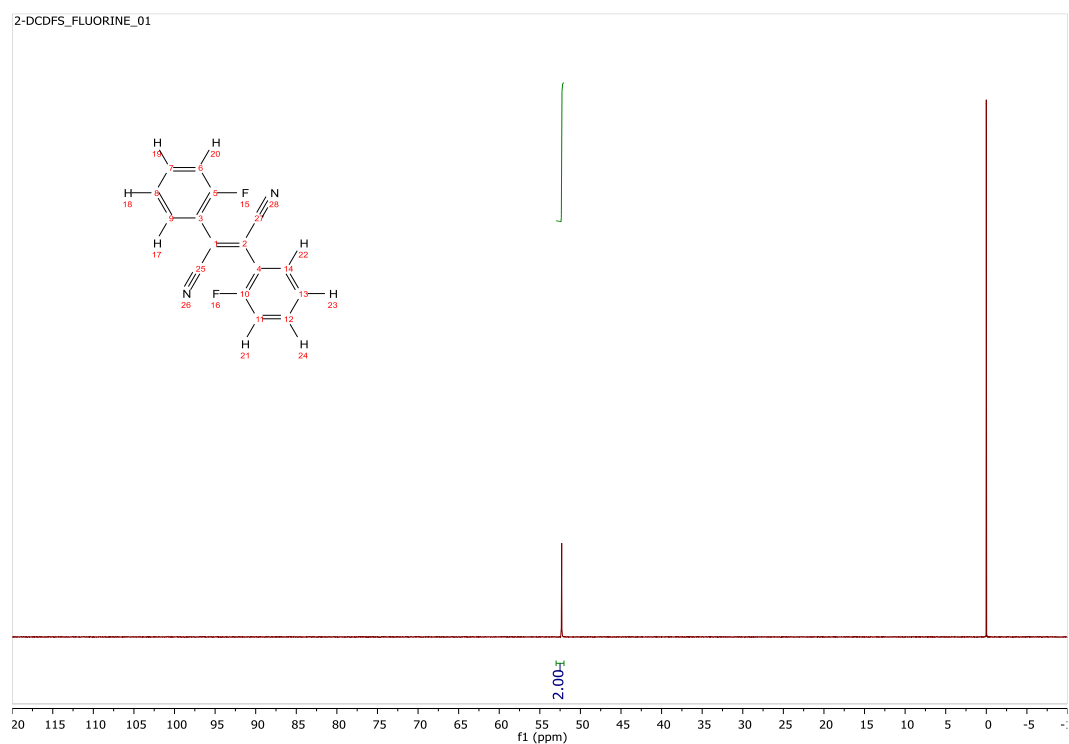
2-DCDFS_PROTON_01

Chemical structure of 2,6-difluoro-4,4'-dicyanobiphenyl-3,3'-diol is shown above the spectrum. The structure is labeled with protons 1 through 26.

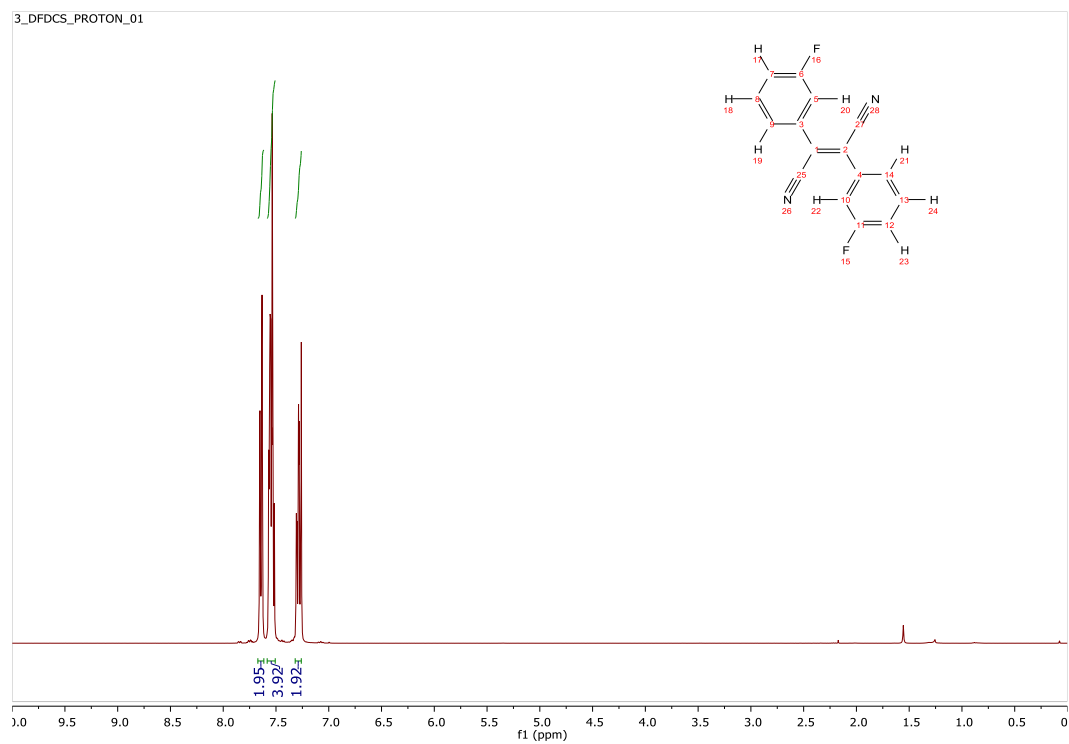
Peak list (ppm):

Chemical Shift (ppm)	Integration
7.75	1.96
7.65	1.88
7.55	1.97
7.45	1.92
5.10	0.00
2.20	0.00
1.50	0.00

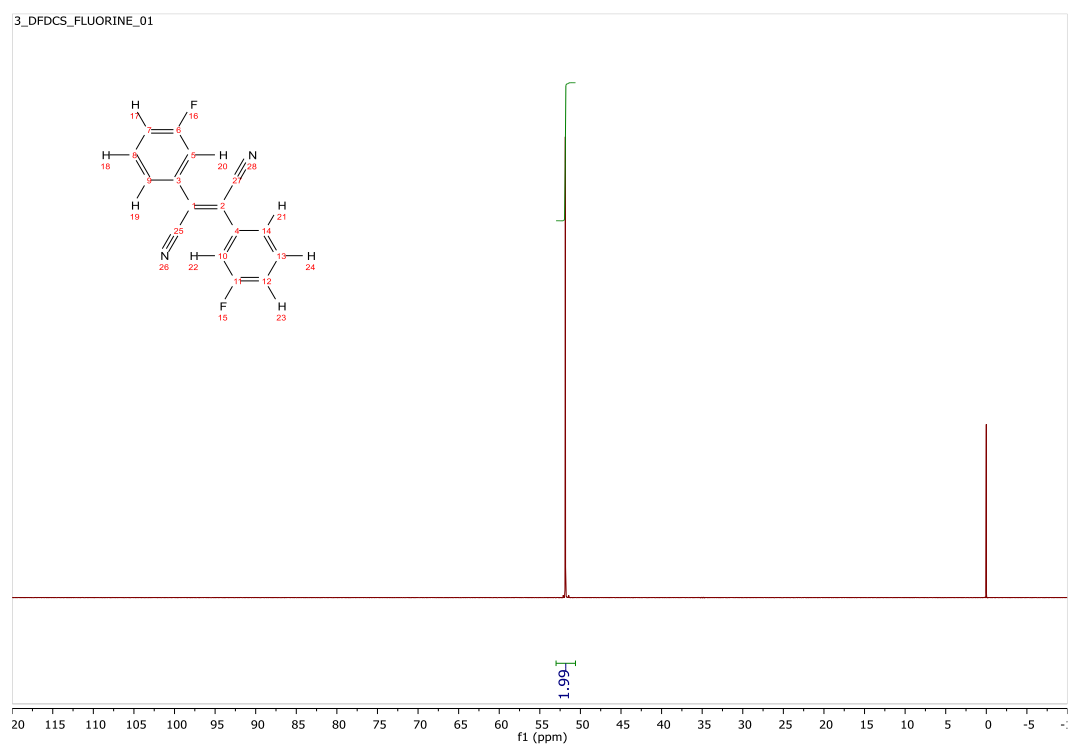
2, 2' difluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



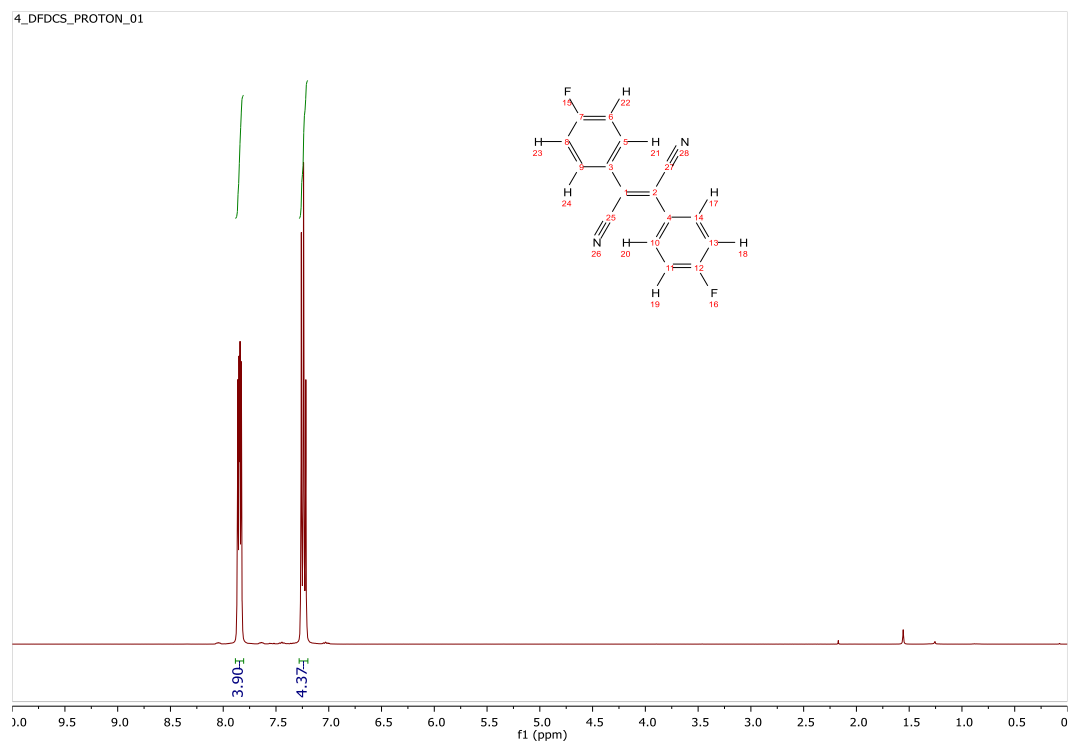
3, 3' difluorodicyanostilbene 400 MHz ^1H NMR in CDCl_3 presence of water peak



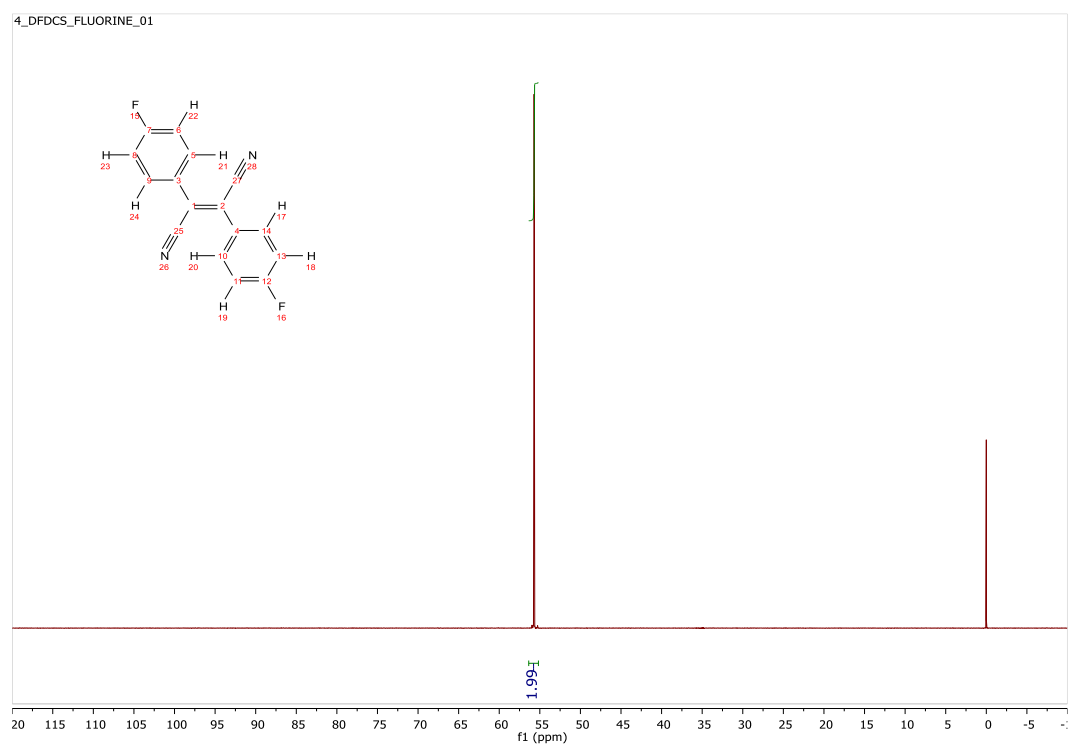
3, 3' difluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



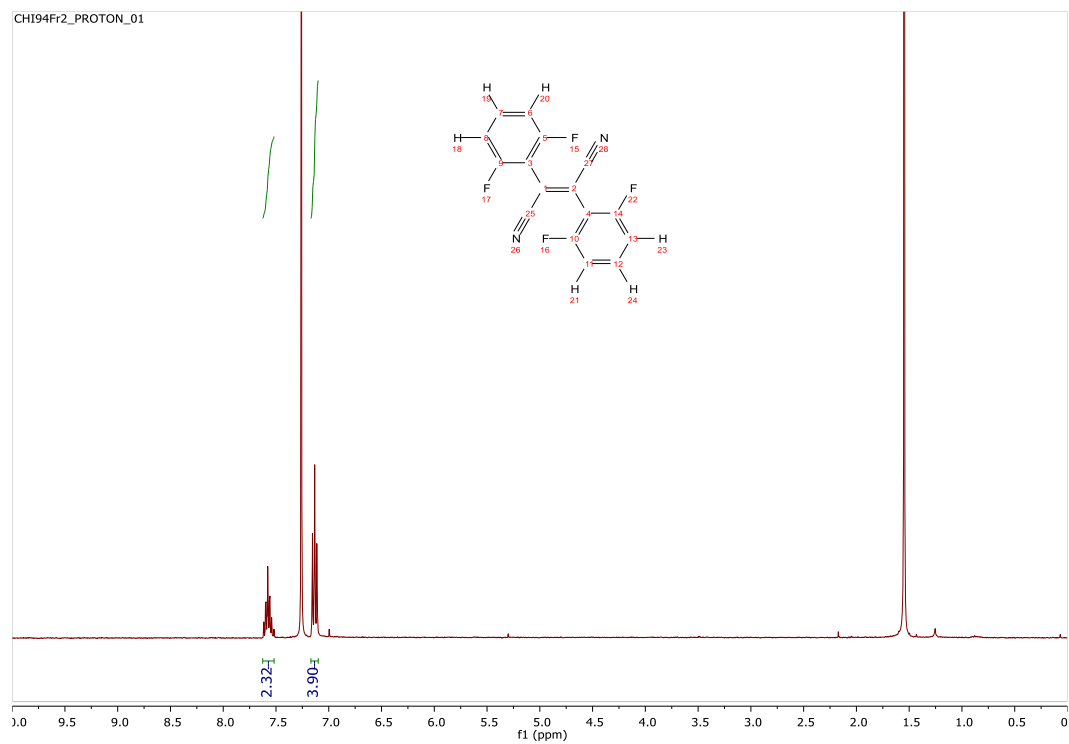
4, 4' difluorodicyanostilbene 400 MHz ^1H NMR in CDCl_3 presence of acetone and water peaks



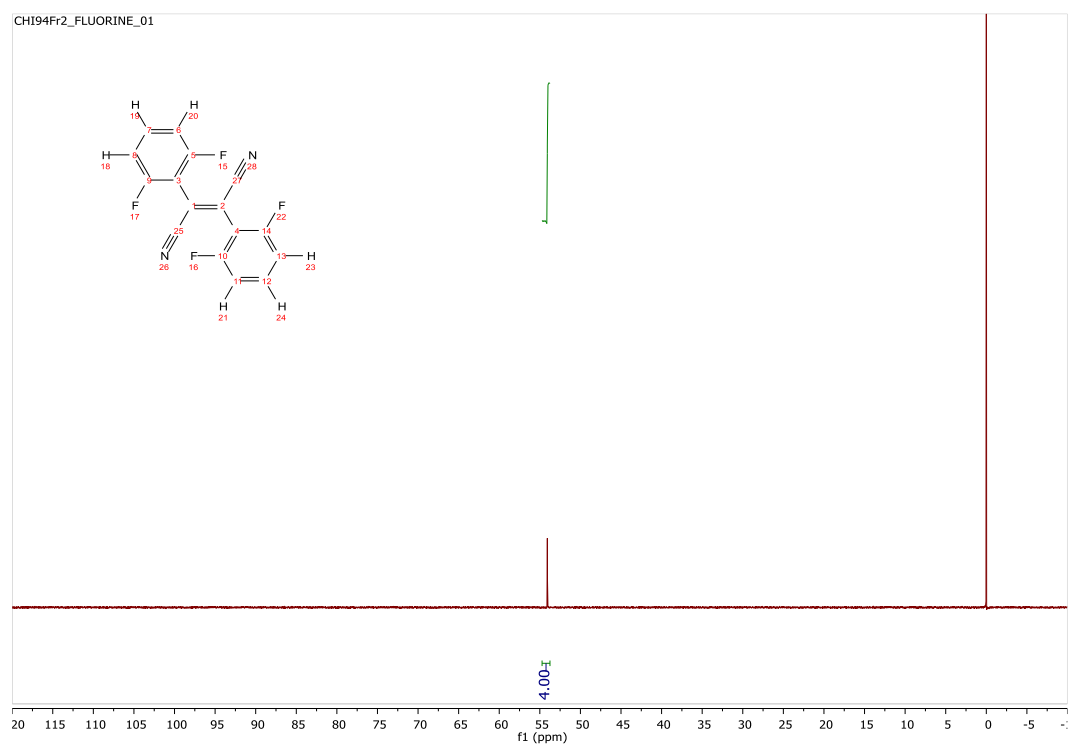
4, 4' difluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



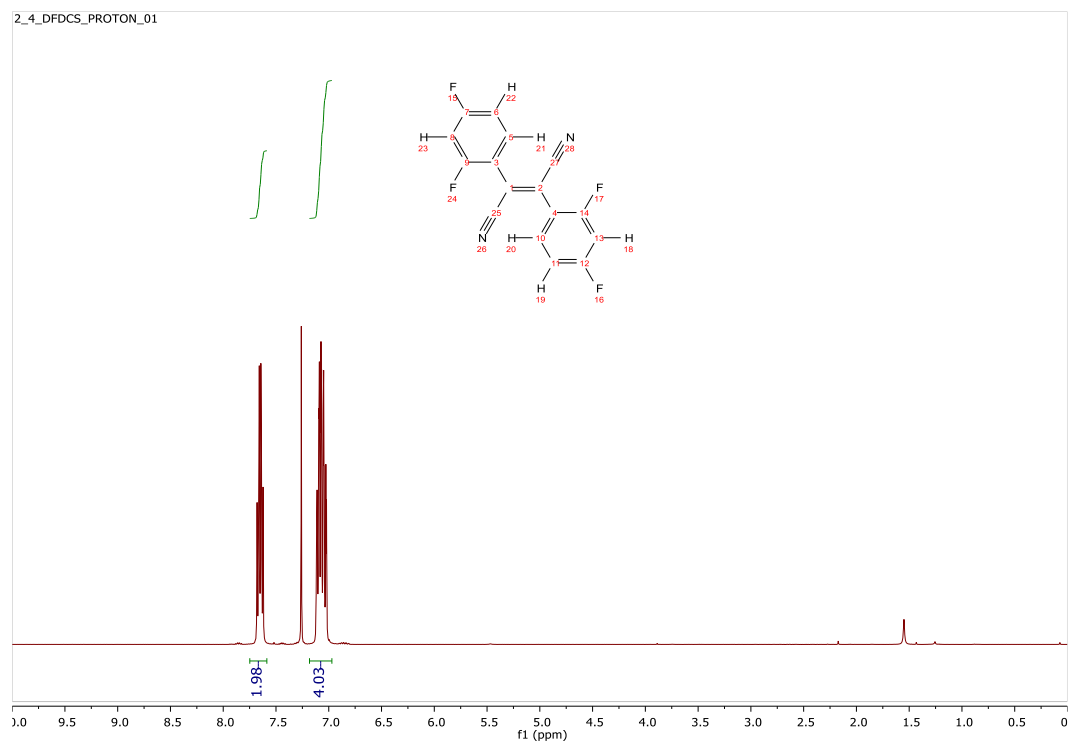
2, 2', 6, 6'-tetrafluorodicyanostilbene 400 MHz ^1H NMR in CDCl_3 presence of water peak



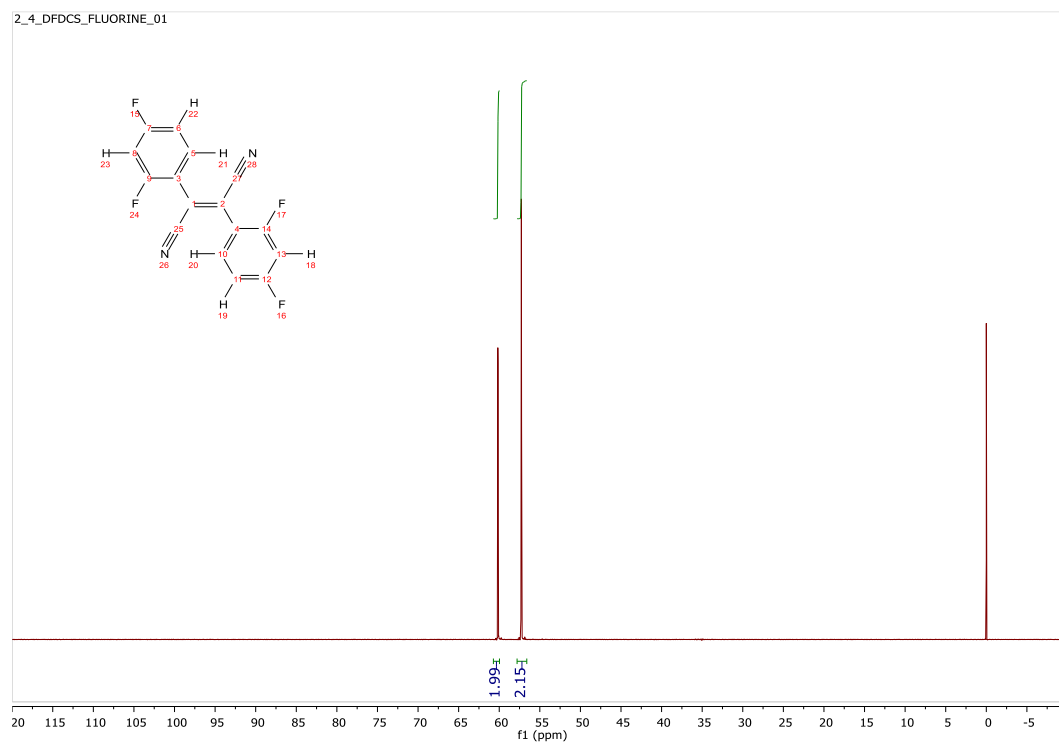
2, 2', 6, 6'tetrafluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



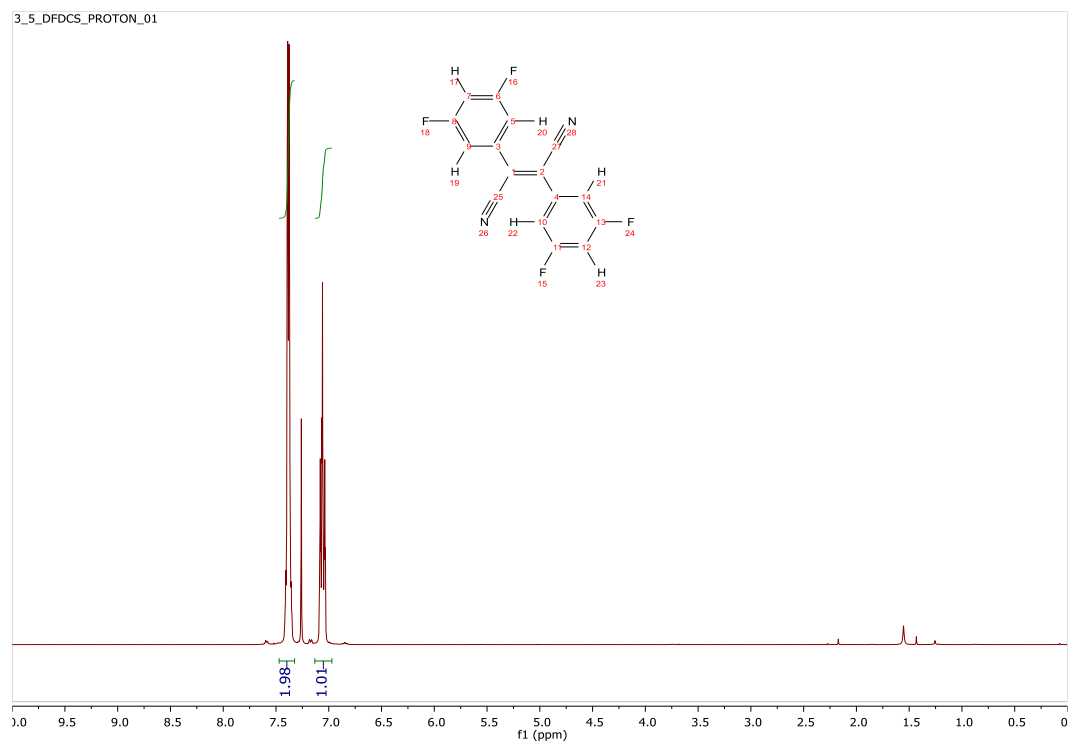
2, 2', 4, 4'tetrafluorodicyanostilbene 400 MHz ^1H NMR in CDCl_3 presence of water peak



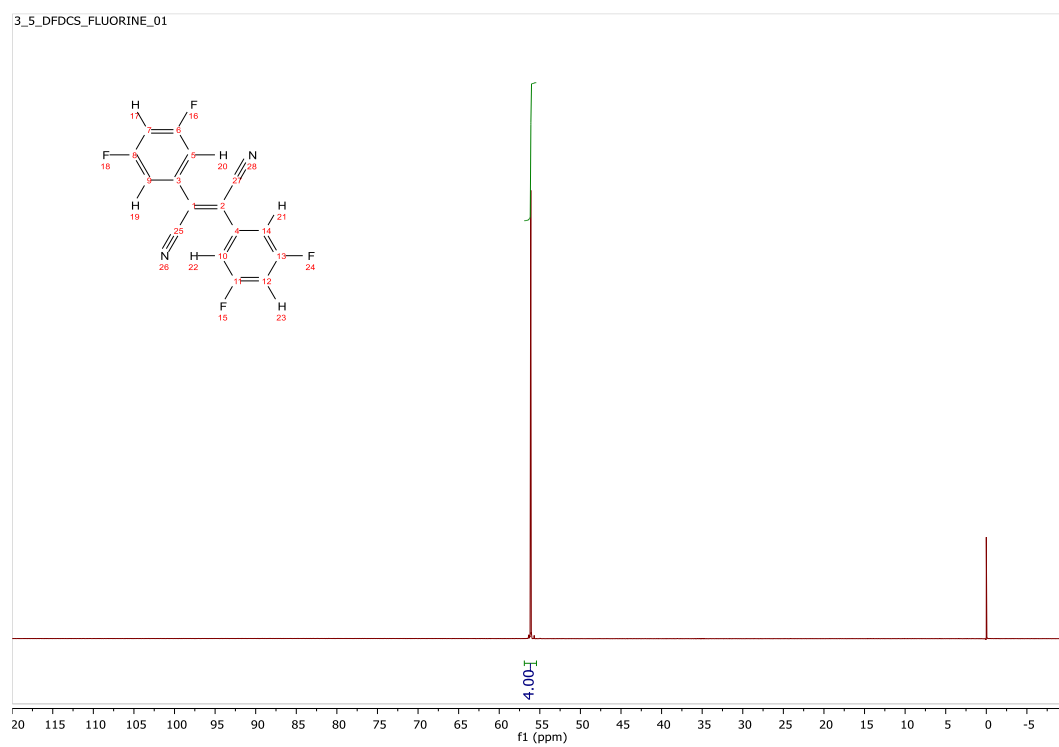
2, 2', 4, 4'tetrafluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



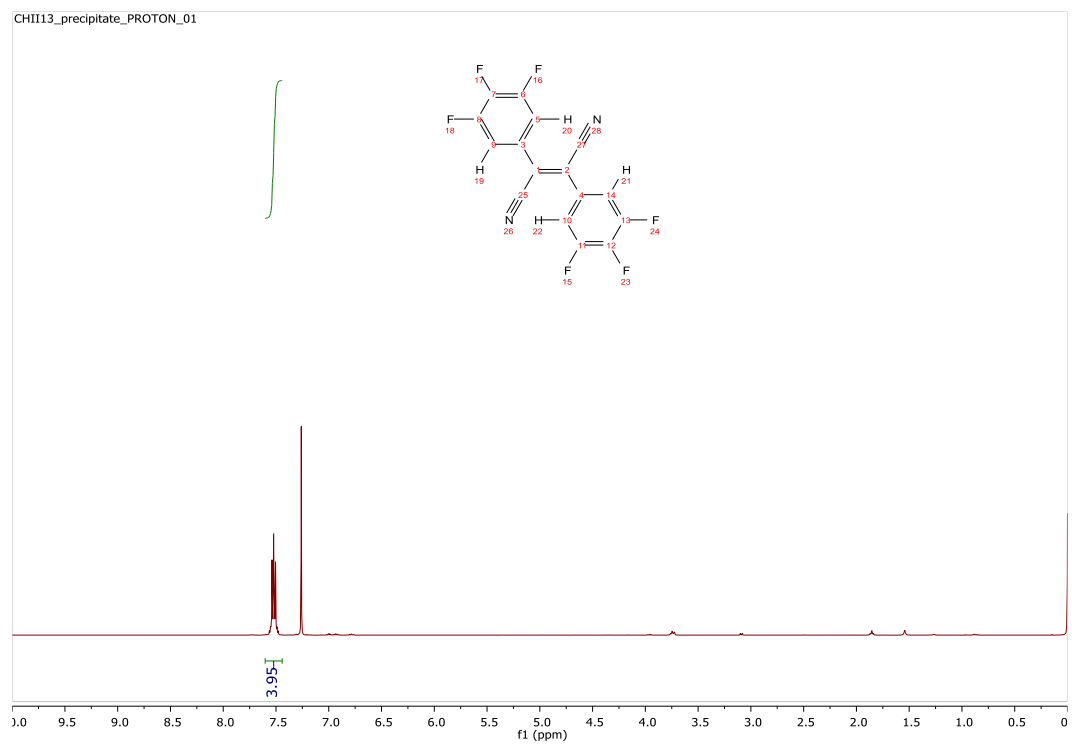
3, 3', 5, 5'tetrafluorodicyanostilbene 400 MHz ^1H NMR in CDCl_3 presence of water peak



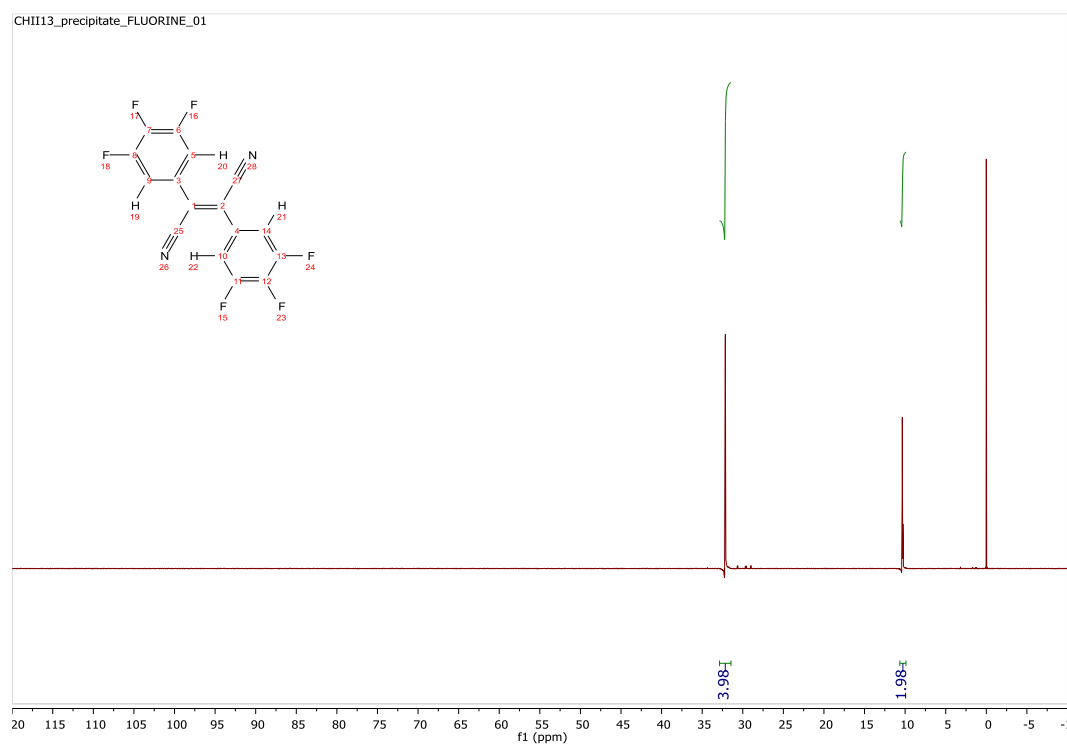
3, 3', 5, 5'tetrafluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



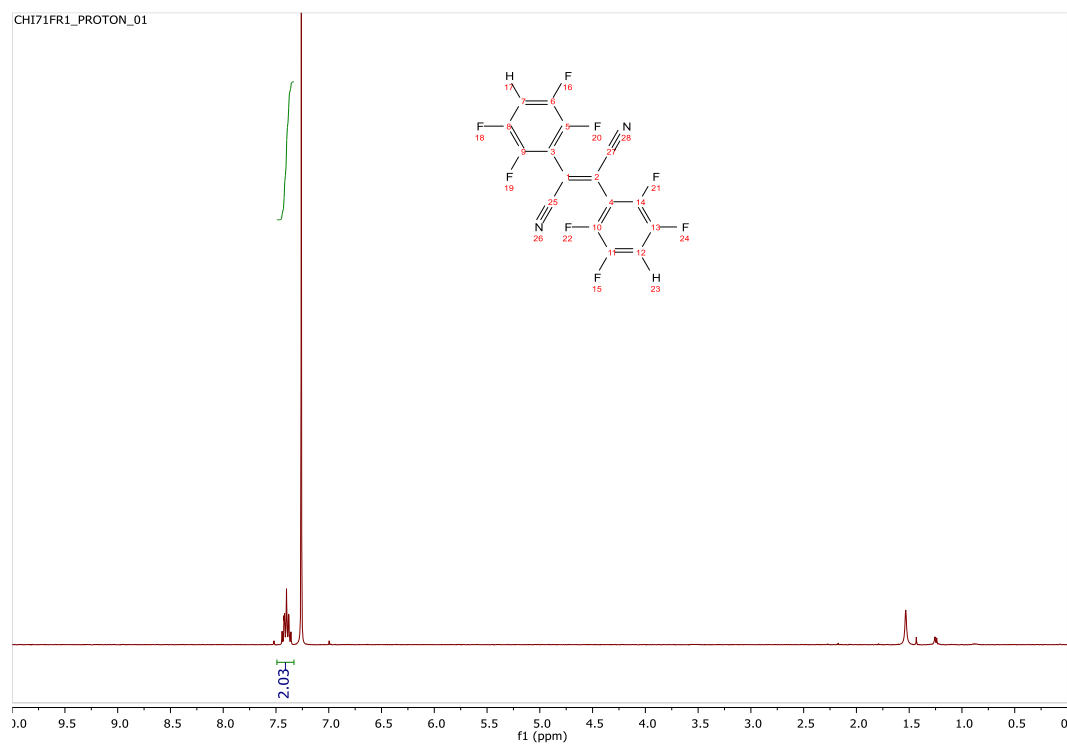
3, 3', 4, 4', 5, 5' hexafluorodicyanostilbene 400 MHz ^1H NMR in CDCl_3



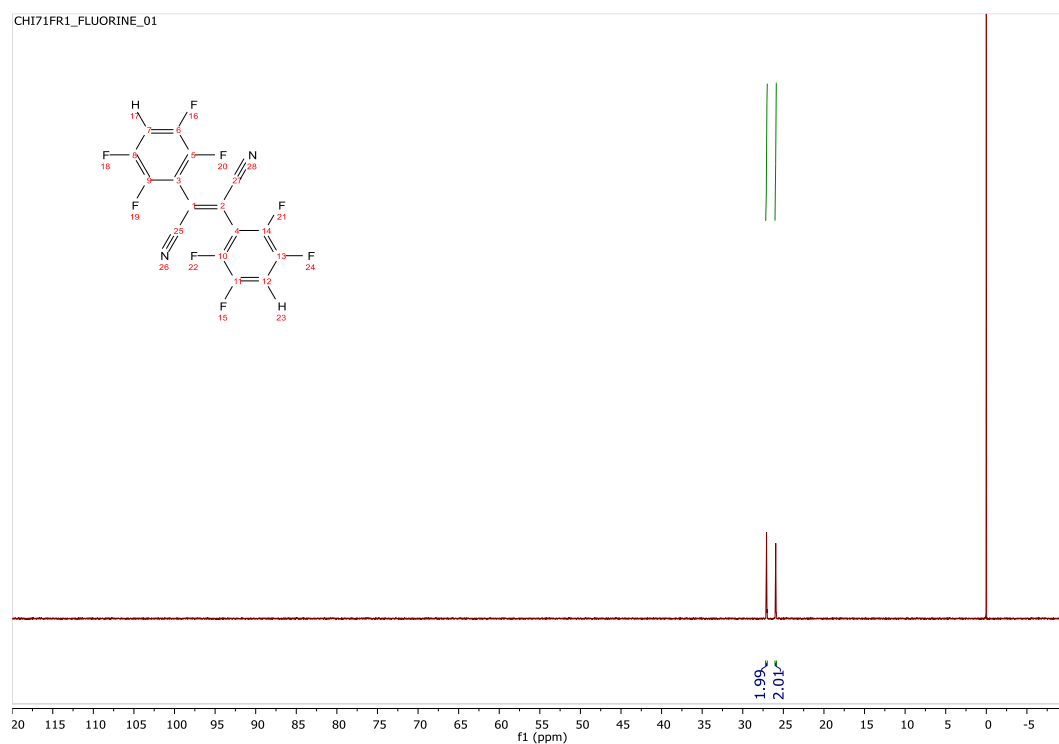
3, 3', 4, 4', 5, 5' hexafluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



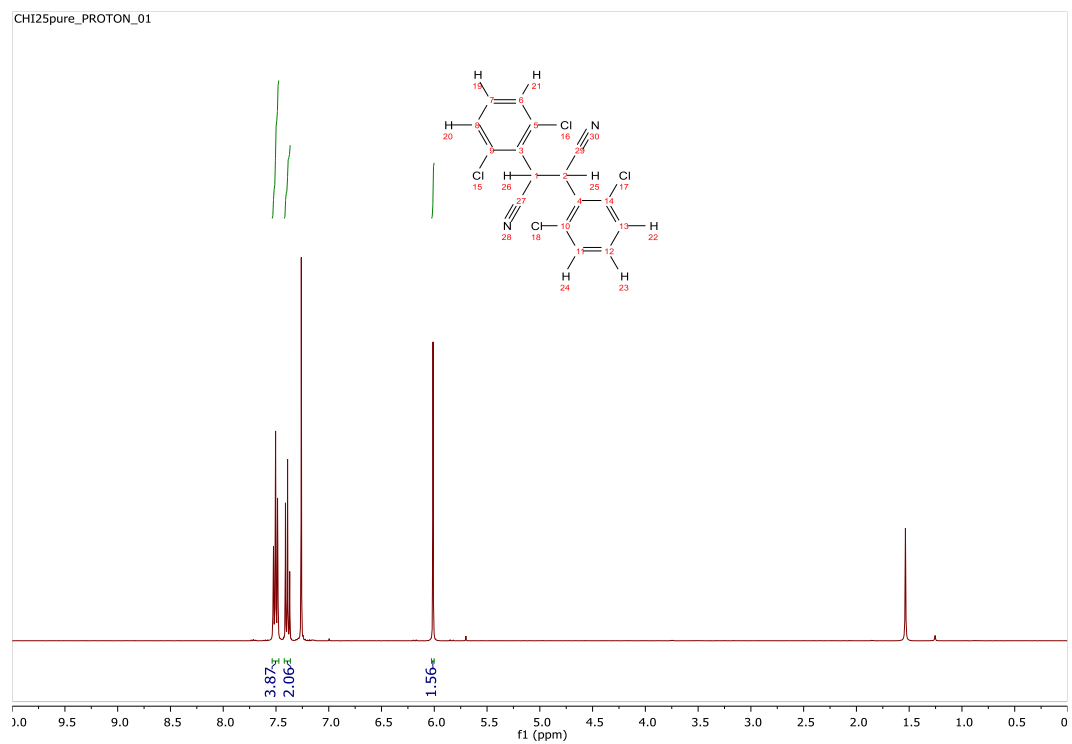
2, 2', 3, 3', 5, 5', 6, 6'-octafluorodicyanostilbene 400 MHz ^1H NMR in CDCl_3 presence of water and hexanes peak



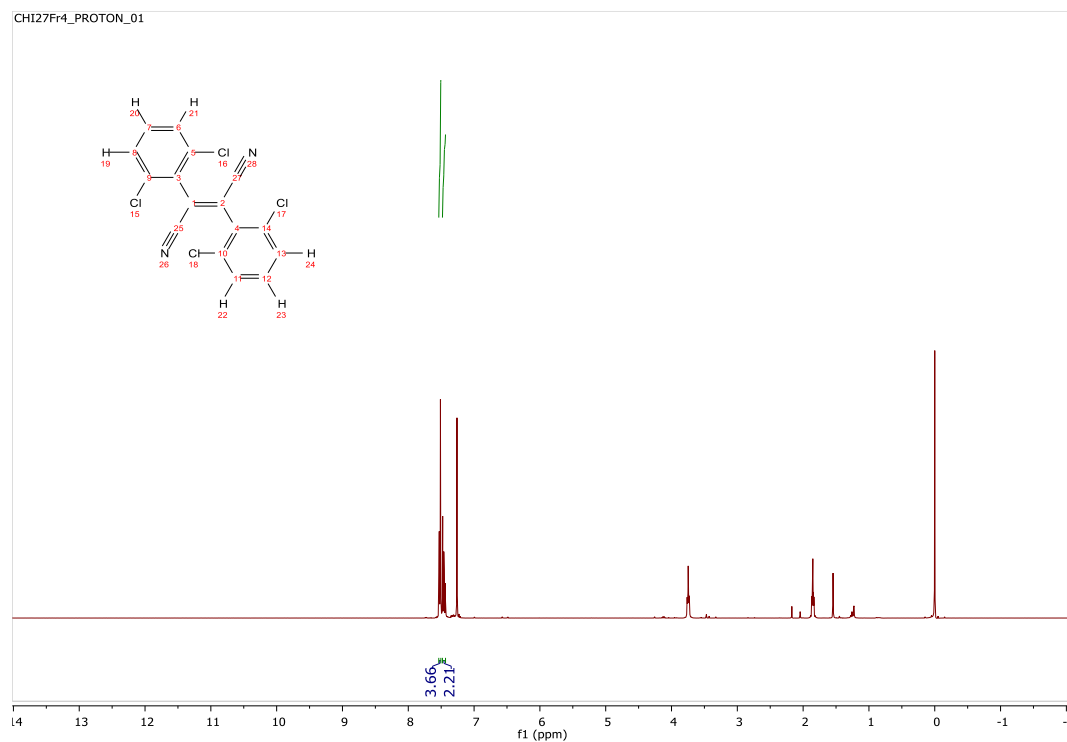
2, 2', 3, 3', 5, 5', 6, 6'octafluorodicyanostilbene 376 MHz ^{19}F NMR (ppm vs C_6F_6)



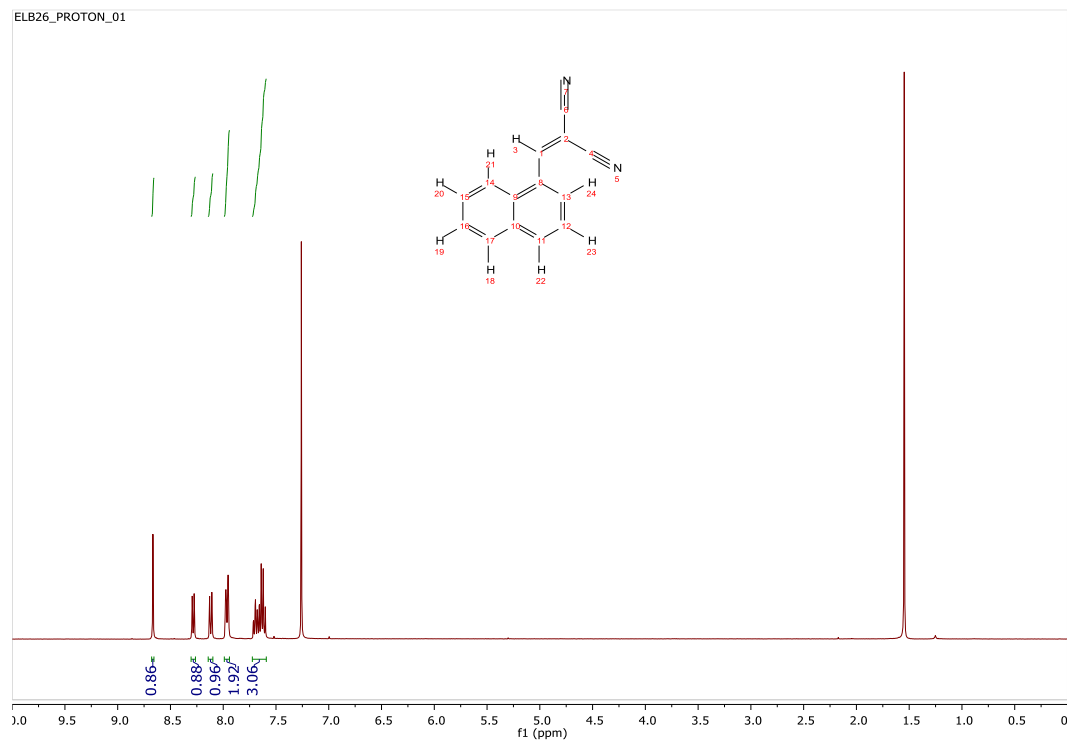
2,3-bis(2,6-dichlorophenyl)succinonitrile 400 MHz ^1H NMR in CDCl_3 presence of water peak



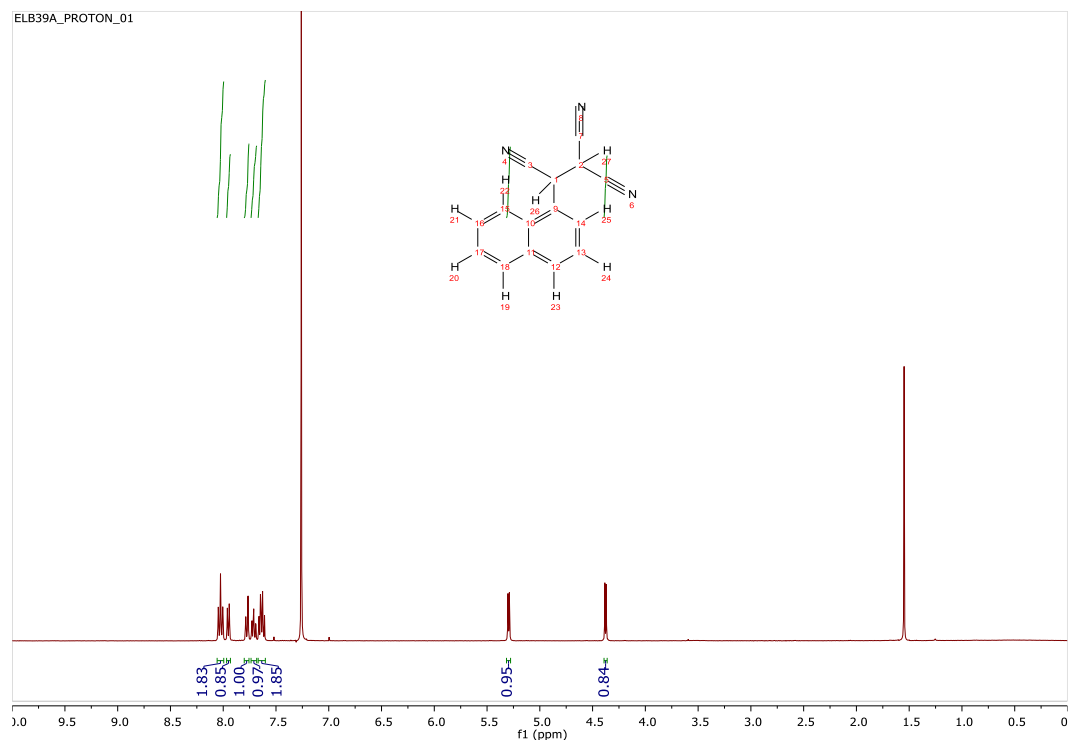
2, 2',6, 6' tetrachlorodicyanostilbene 400 MHz ^1H NMR in CDCl_3 presence of ethyl acetate and water peak



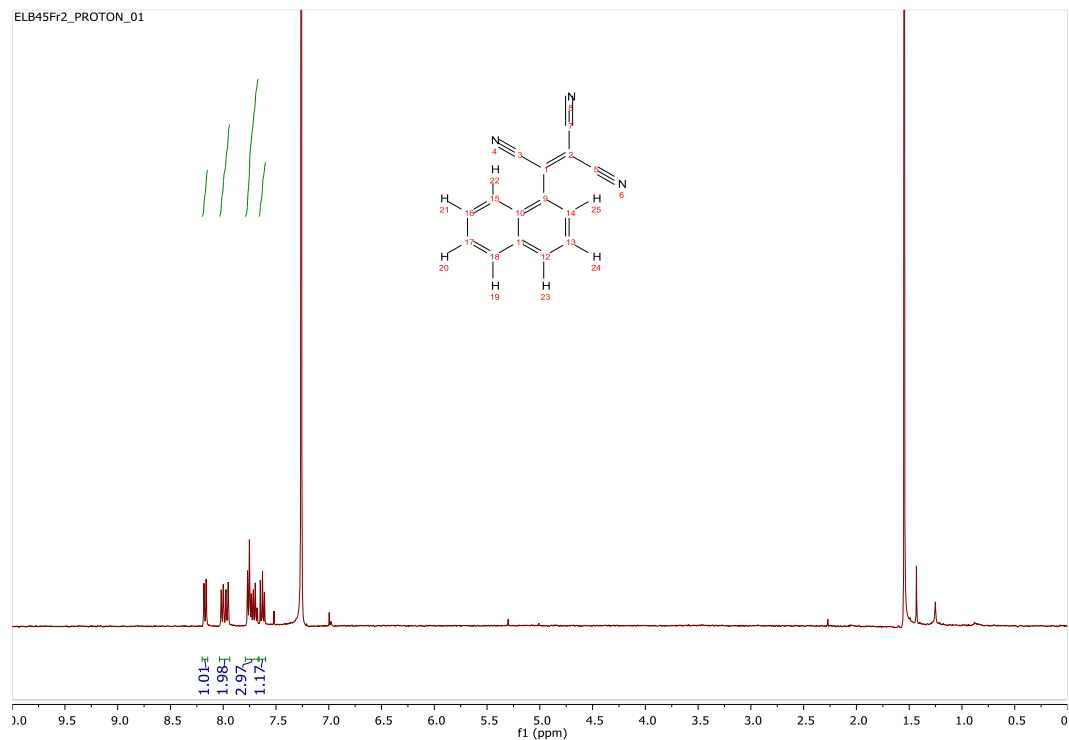
2-(1-naphthyl)-1,1-dicyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Ericka Burske presence of water peak



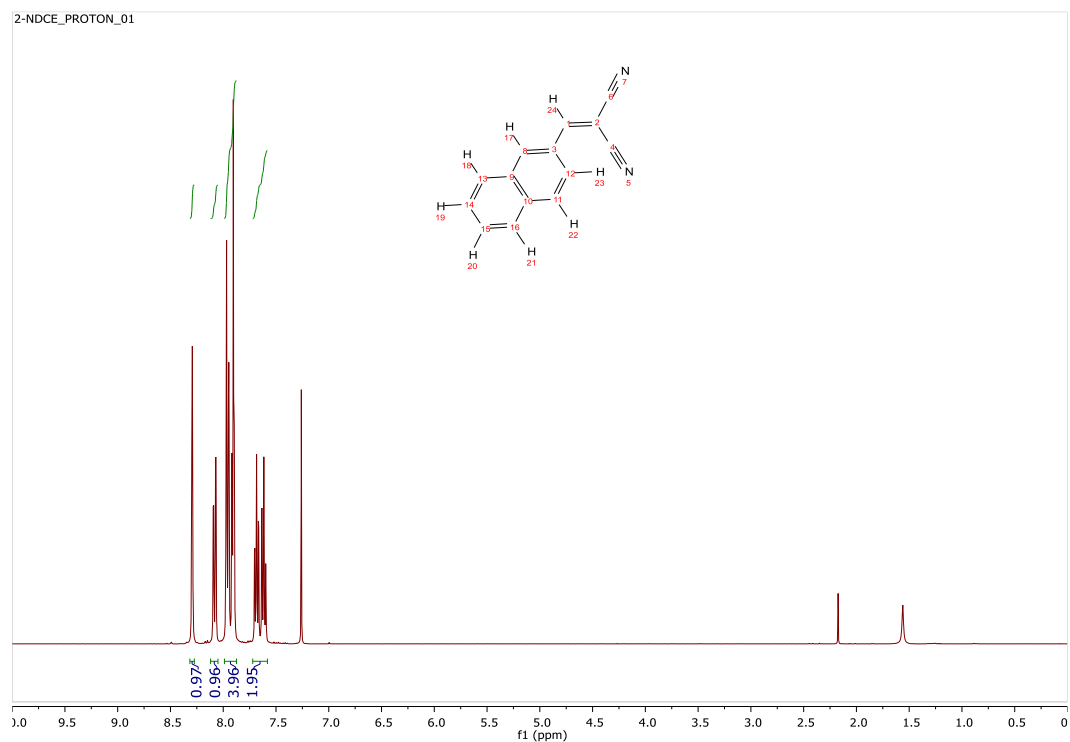
2-(1-naphthyl)-1,1,2-tricyanoethane 400 MHz ^1H NMR in CDCl_3 courtesy of Ericka Burske presence of water peak



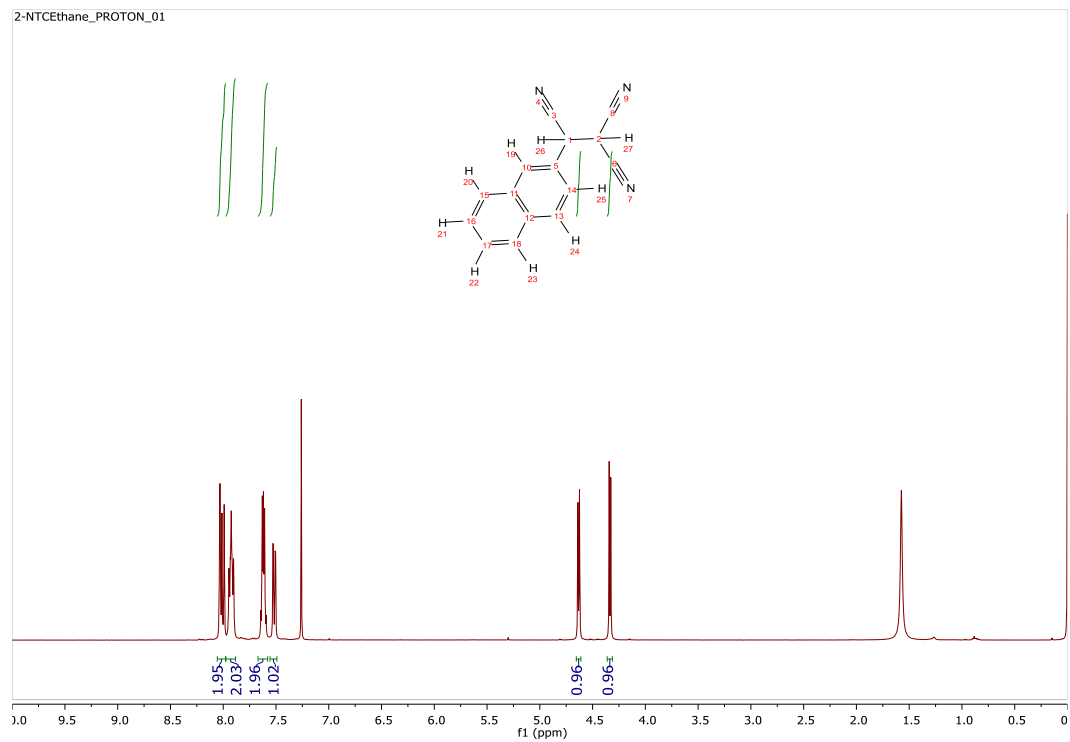
2-(1-naphthyl)-1,1,2-tricyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Ericka Burske presence of water and hexanes peak



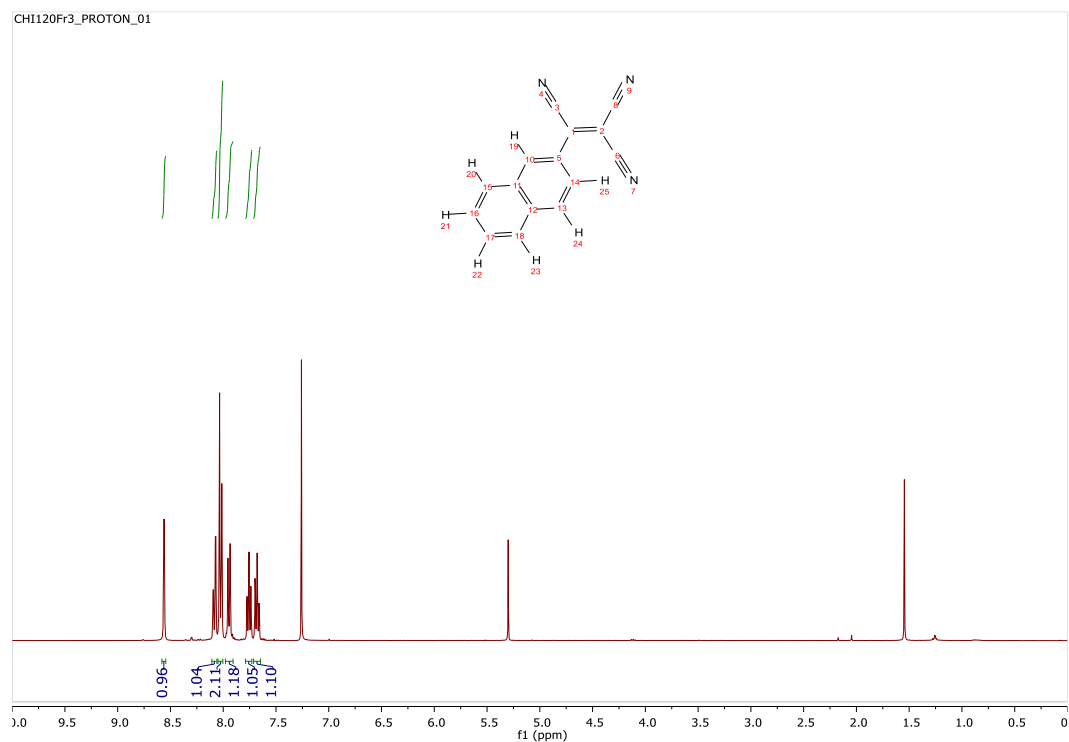
2-(2-naphthyl)-1,1-dicyanoethylene 400 MHz ^1H NMR in CDCl_3 presence of acetone and water peaks



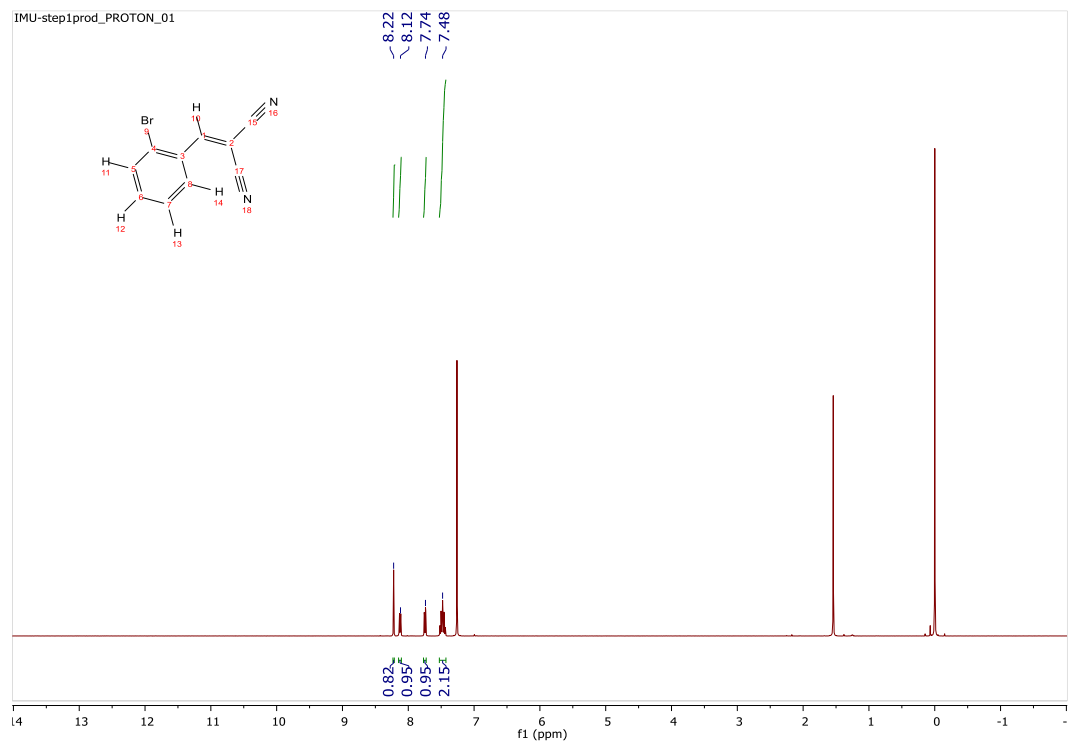
2-(2-naphthyl)-1,1,2-tricyanoethane 400 MHz ^1H NMR in CDCl_3 presence of water peak



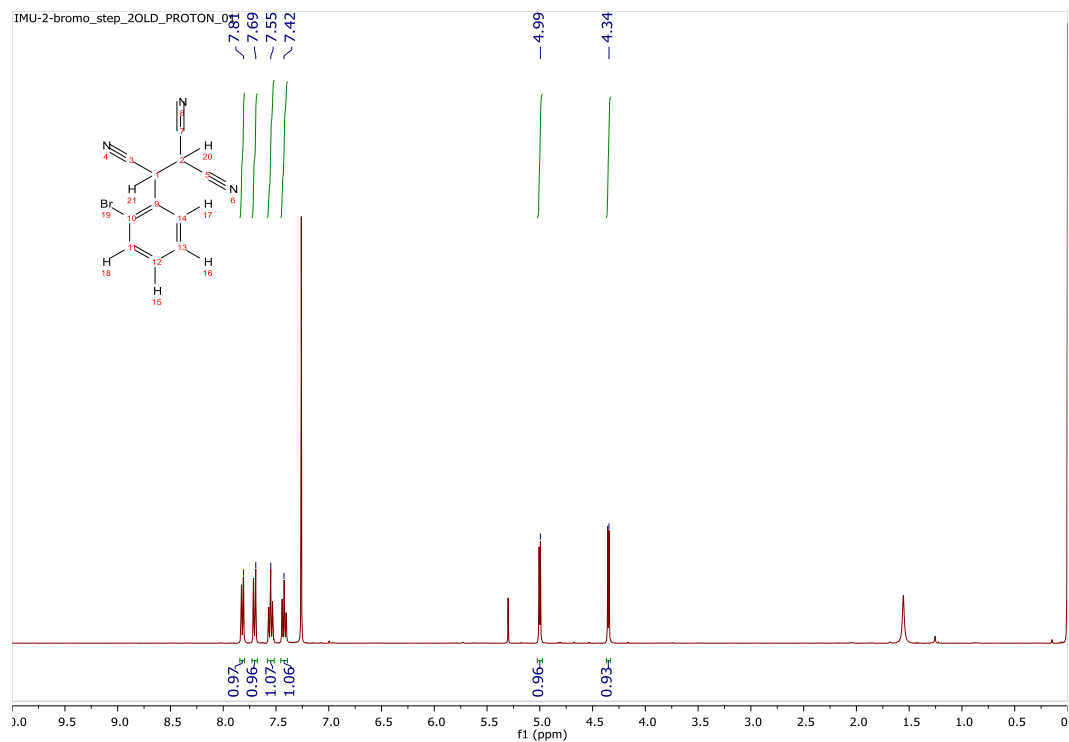
2-(2-naphthyl)-1,1,2-tricyanoethylene 400 MHz ^1H NMR in CDCl_3 presence of water peak



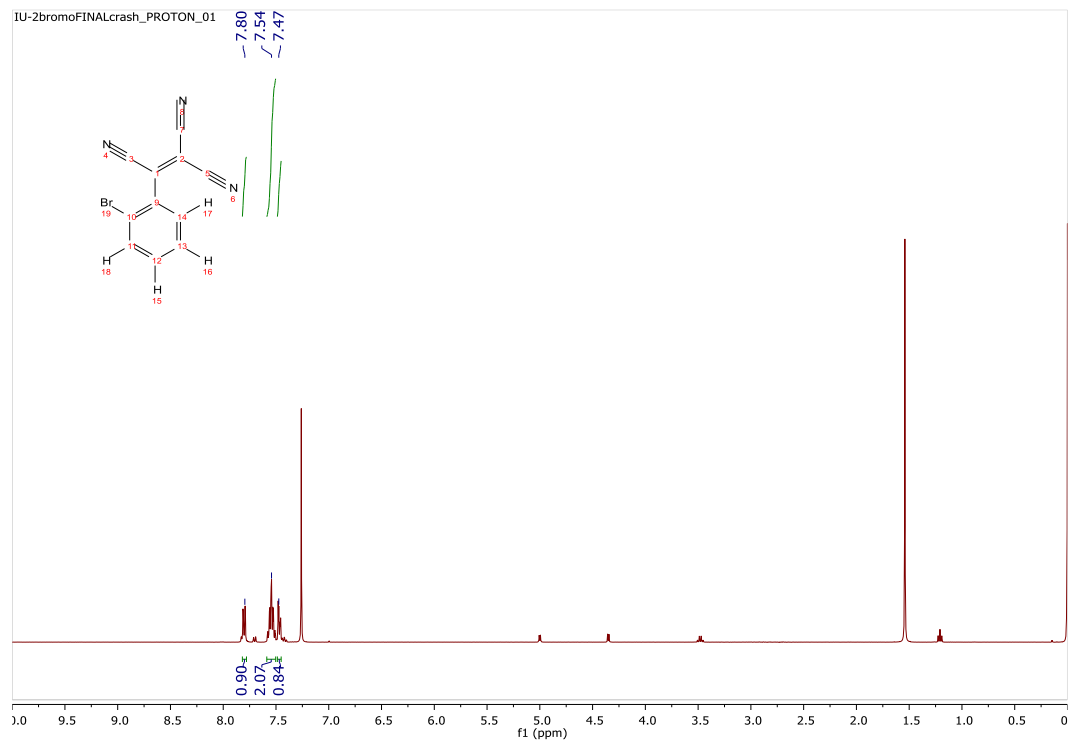
2-(2-bromophenyl)-1,1-dicyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate presence of water peak



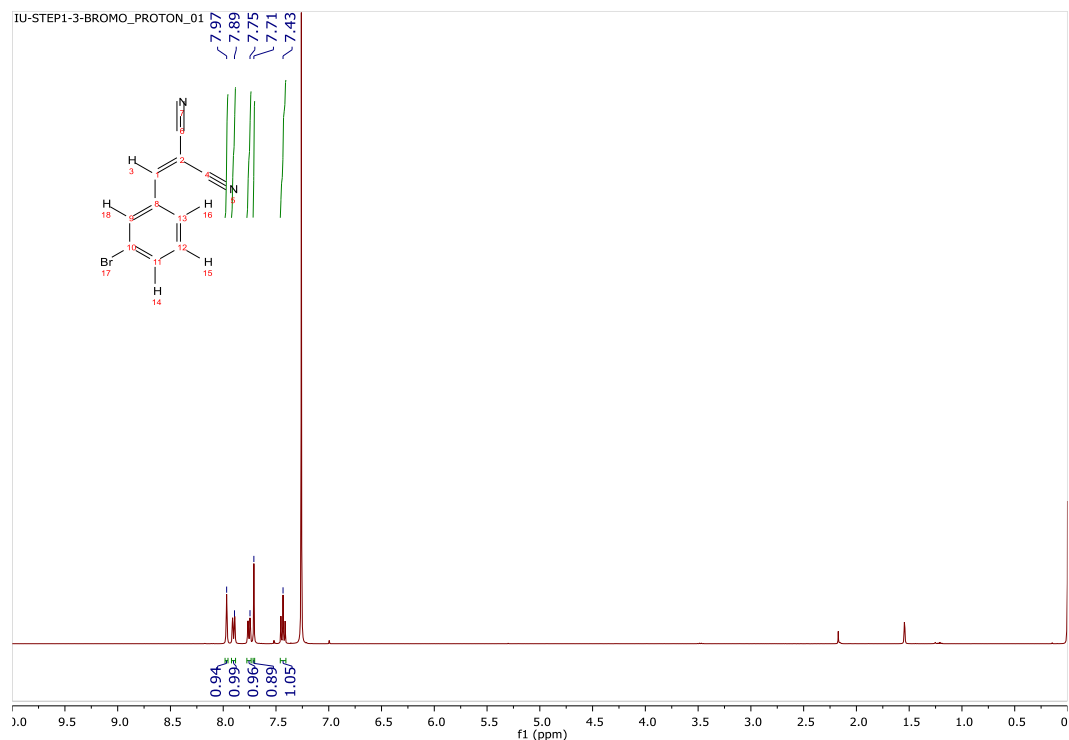
2-(2-bromophenyl)-1,1,2-tricyanoethane 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate presence of water peak



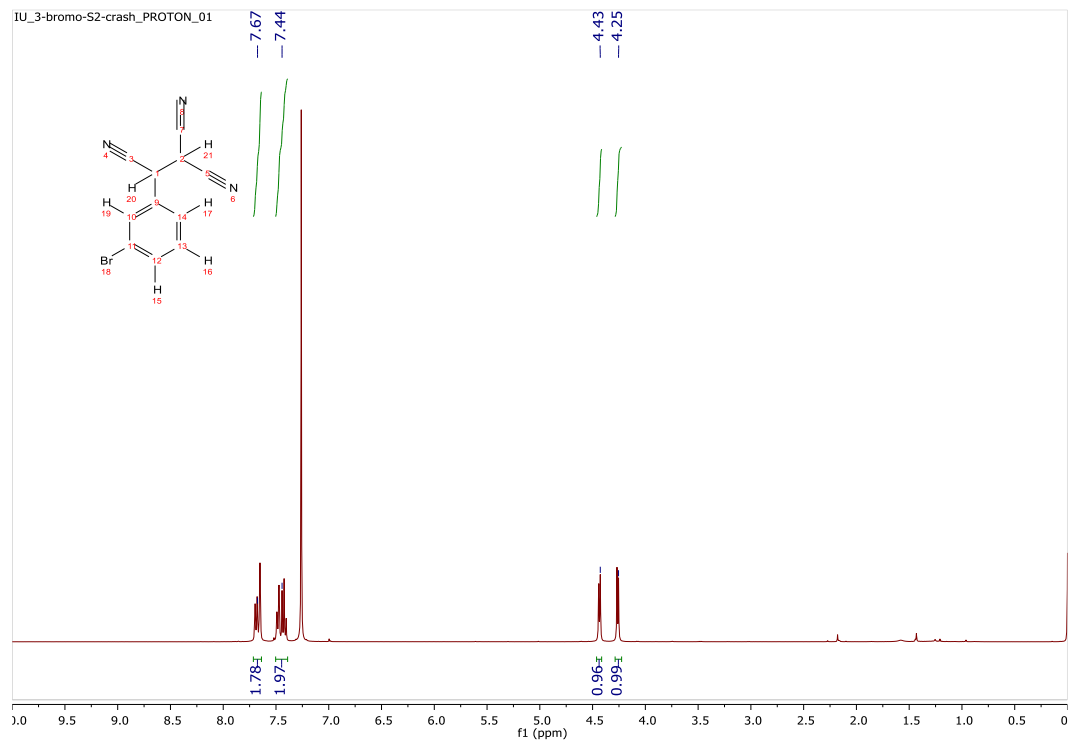
2-(2-bromophenyl)-1,1,2-tricyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate presence of water peak and incomplete reduction



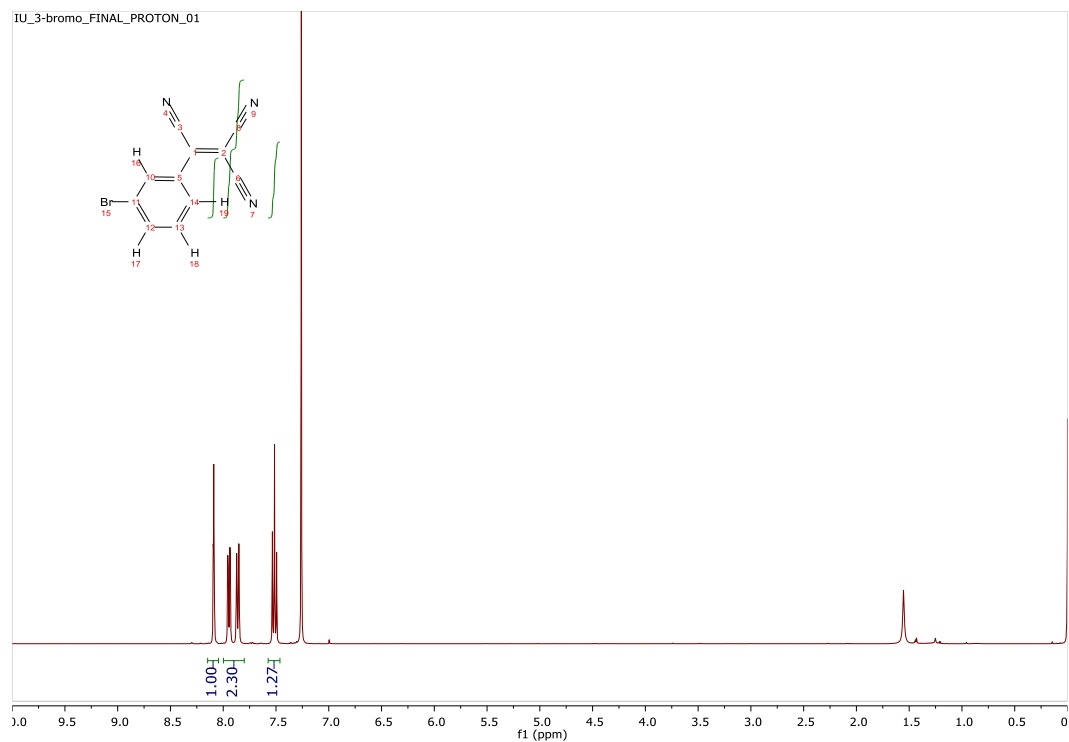
2-(3-bromophenyl)-1,1-dicyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate presence of acetone and water peaks



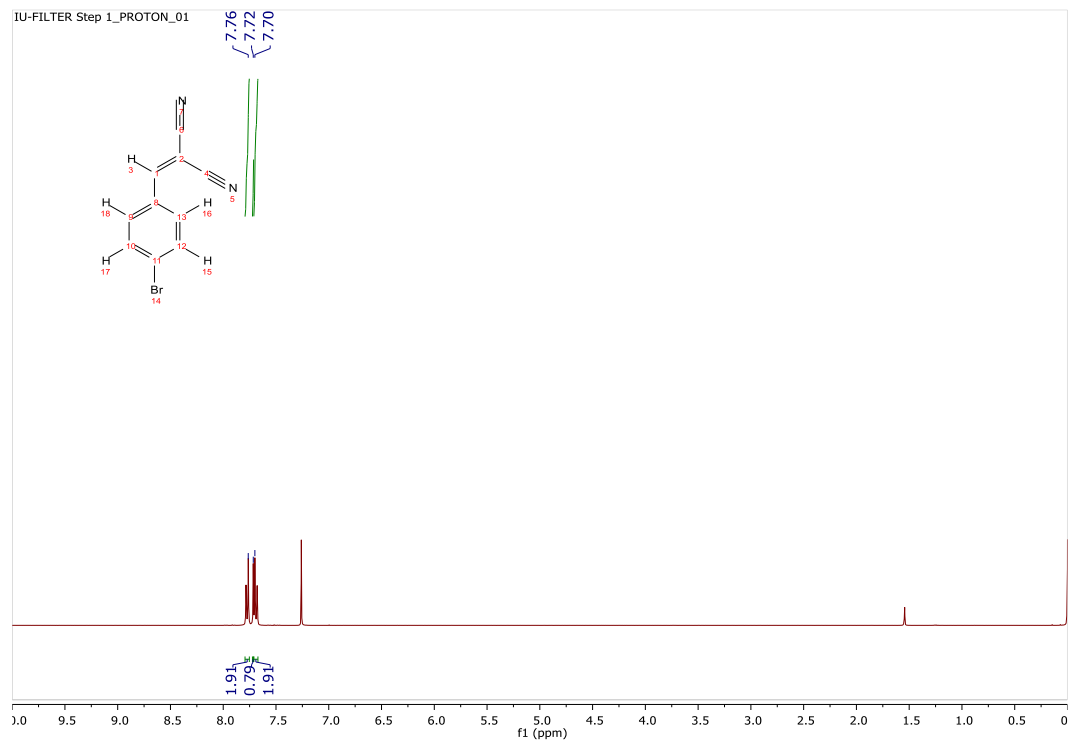
2-(3-bromophenyl)-1,1,2-tricyanoethane 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate presence of acetone and water peaks



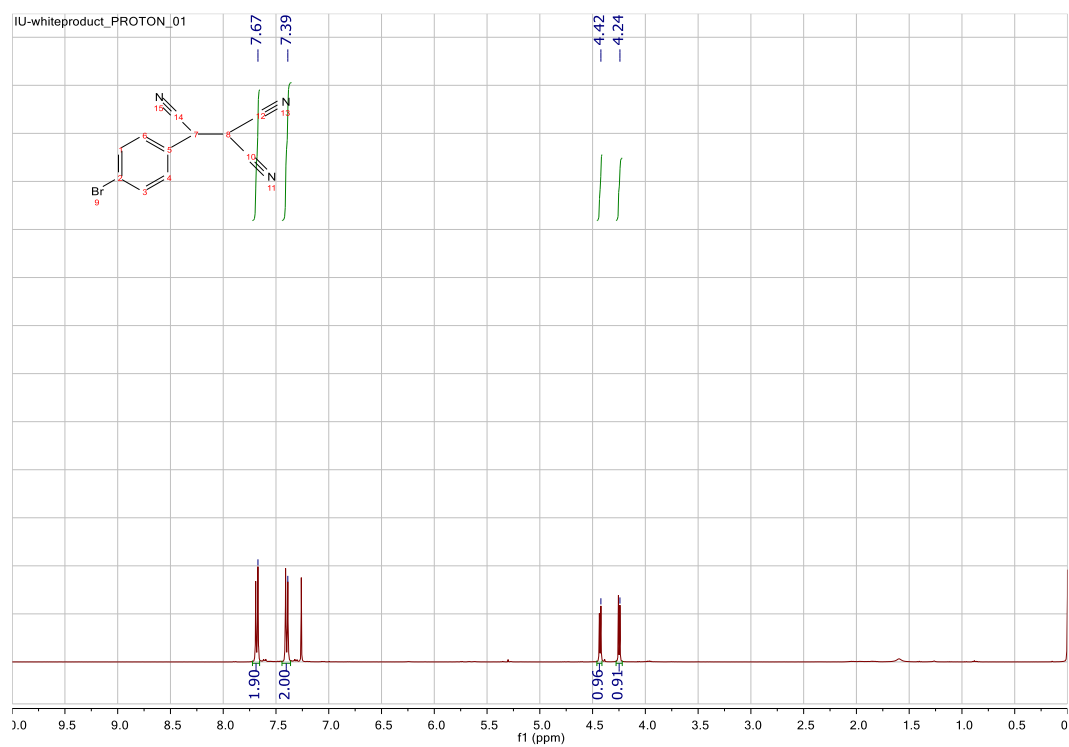
2-(3-bromophenyl)-1,1,2-tricyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate presence of water peak



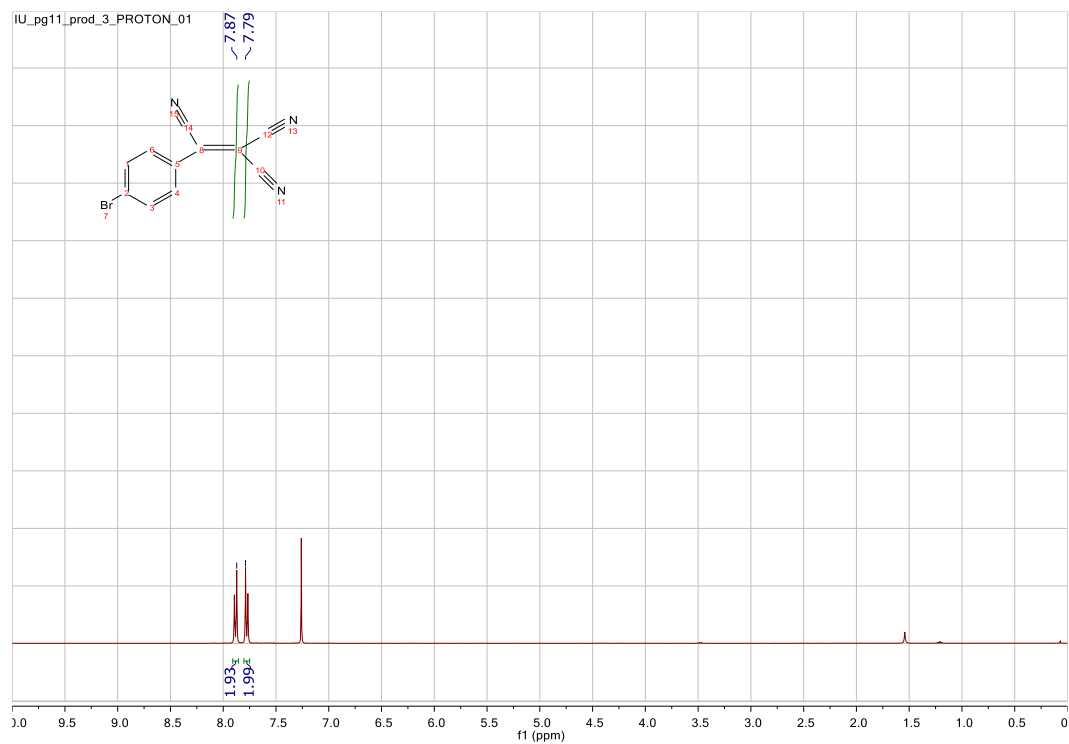
2-(4-bromophenyl)-1,1-dicyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate presence of water peak



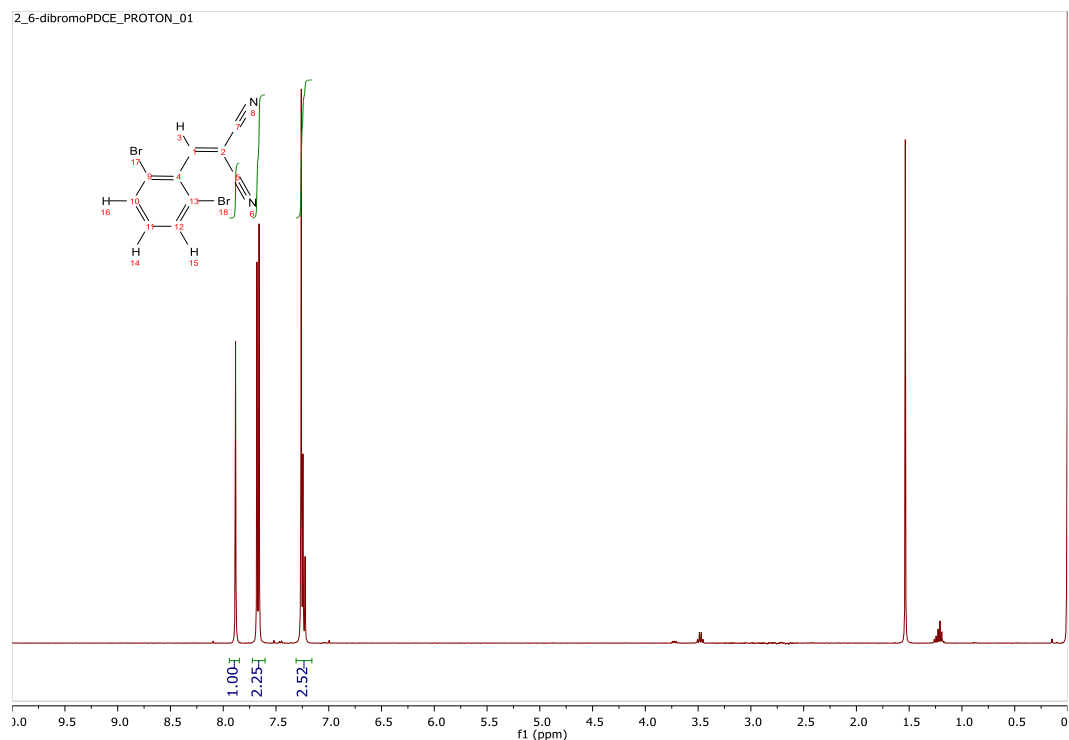
2-(4-bromophenyl)-1,1,2-tricyanoethane 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate



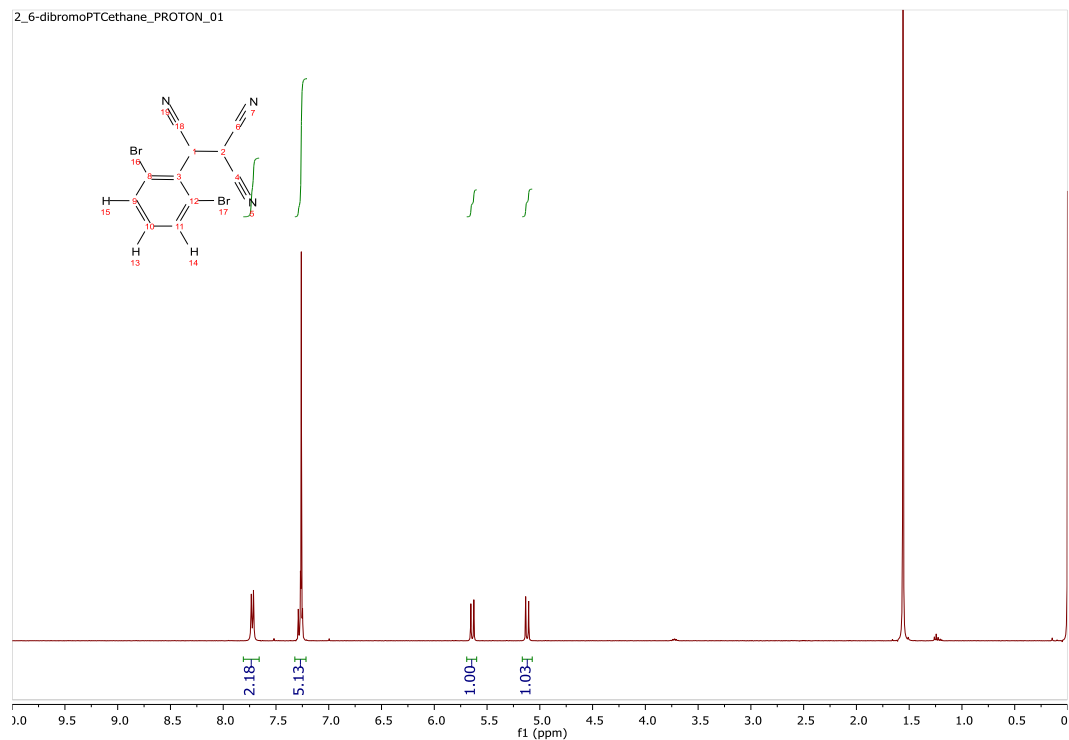
2-(4-bromophenyl)-1,1,2-tricyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Isabella Ulate



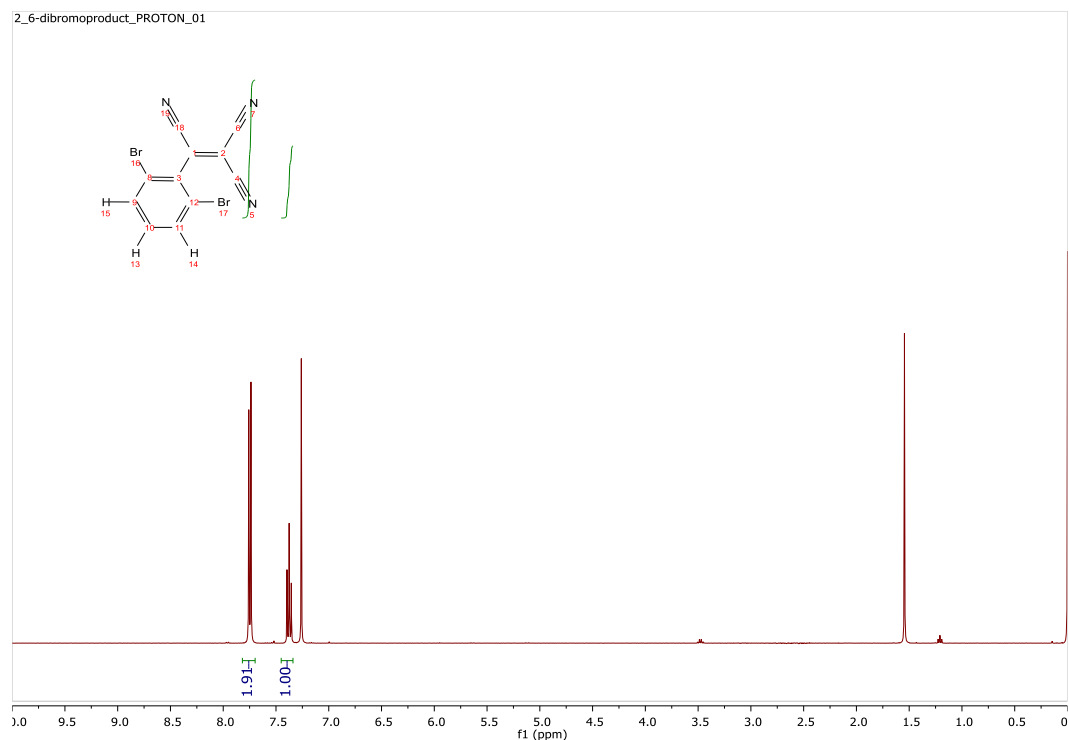
2-(2,6-bromophenyl)-1,1-dicyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Steven Miller presence of ethyl acetate and water peaks



2-(2,6-bromophenyl)-1,1,2-tricyanoethane ^1H NMR in CDCl_3 courtesy of Steven Miller presence of ethyl acetate and water peaks

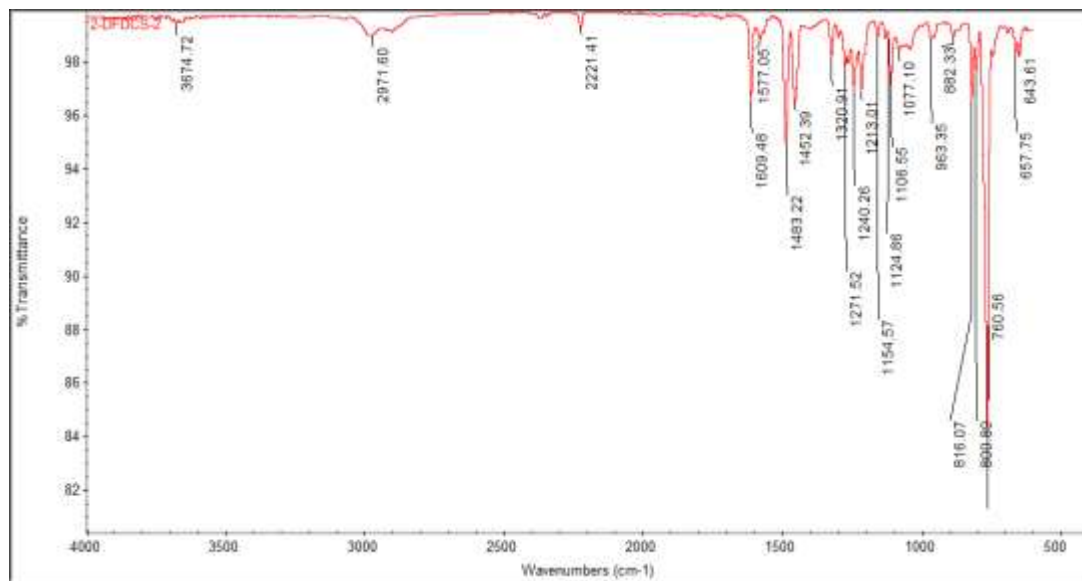


2-(2,6-bromophenyl)-1,1,2-tricyanoethylene 400 MHz ^1H NMR in CDCl_3 courtesy of Steven Miller
 presence of water peak

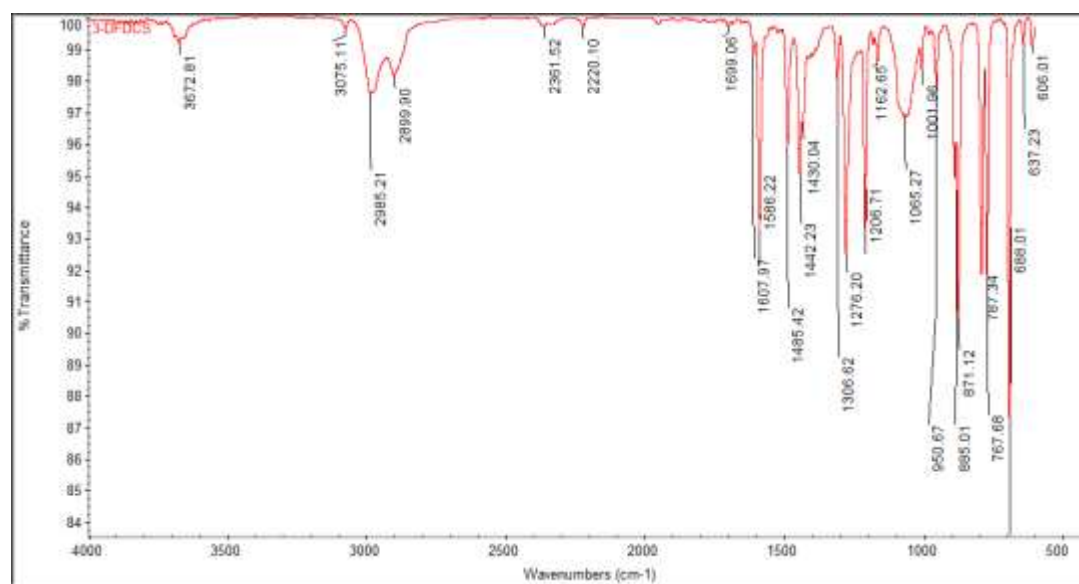


A.2 IR:

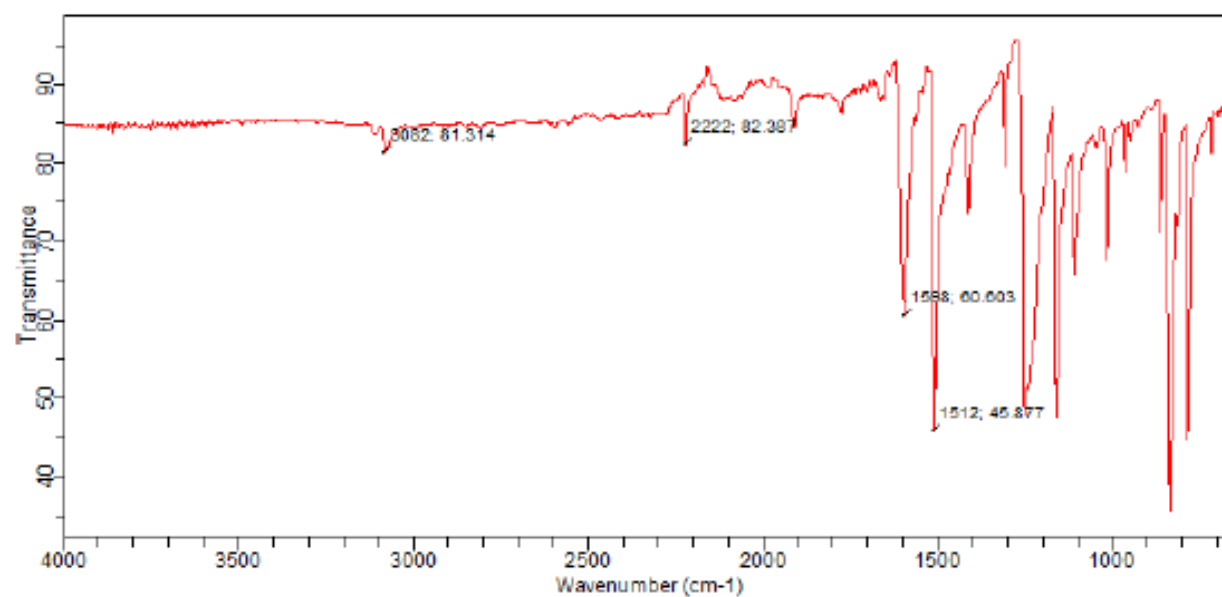
IR spectrum of 2, 2' difluorodicyanostilbene as mull



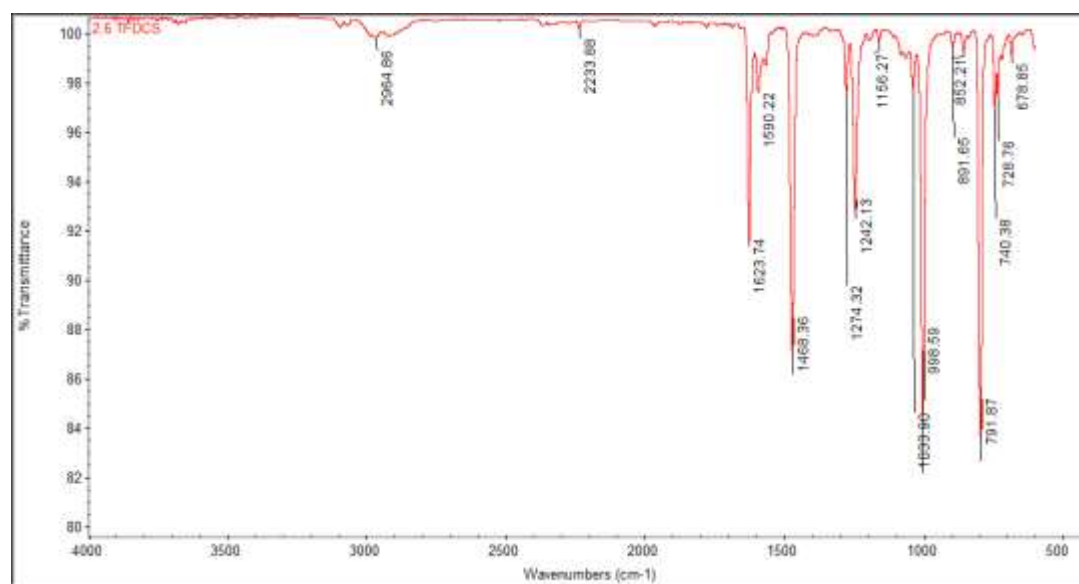
IR spectrum of 3, 3' difluorodicyanostilbene as mull



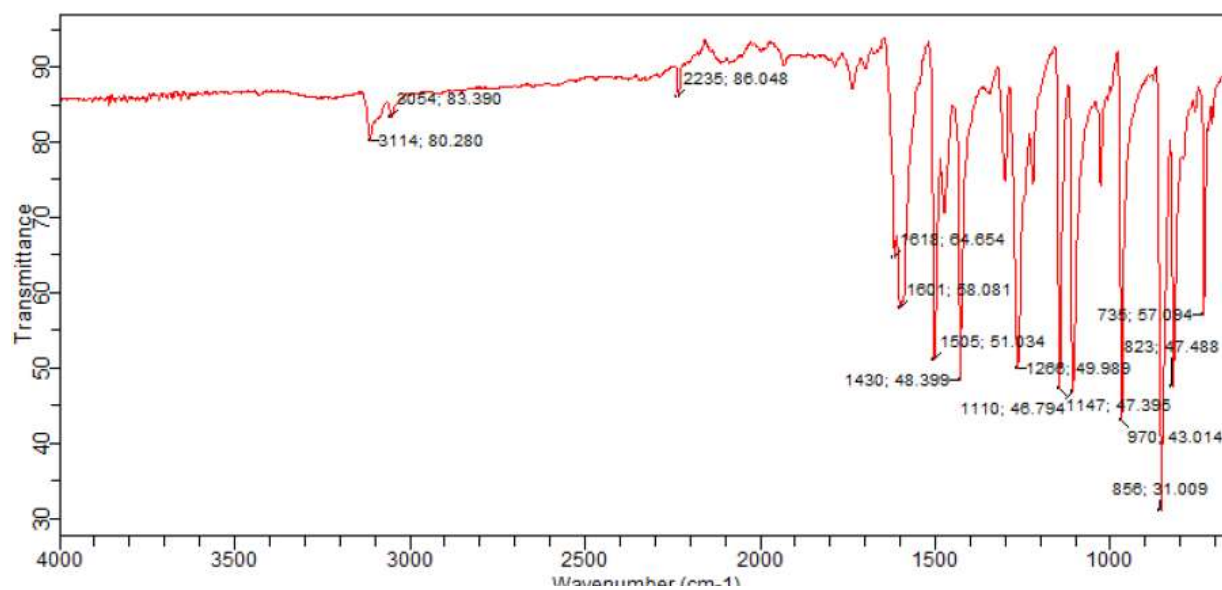
IR spectrum of 4, 4' difluorodicyanostilbene as mull



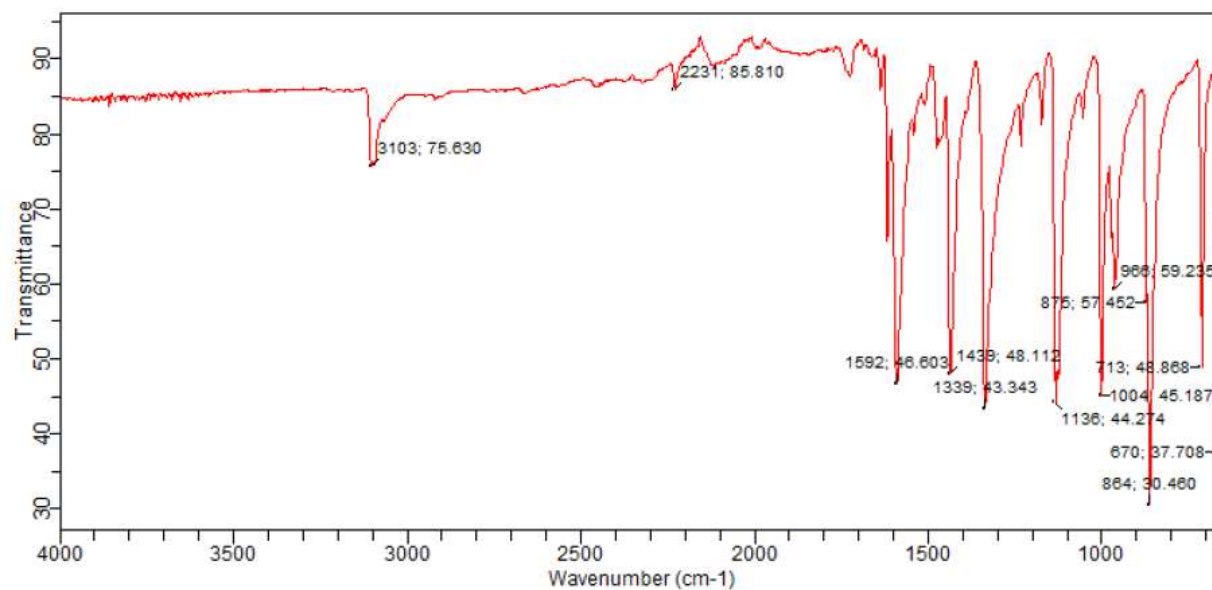
IR spectrum of 2, 2', 6, 6'tetrafluorodicyanostilbene as mull



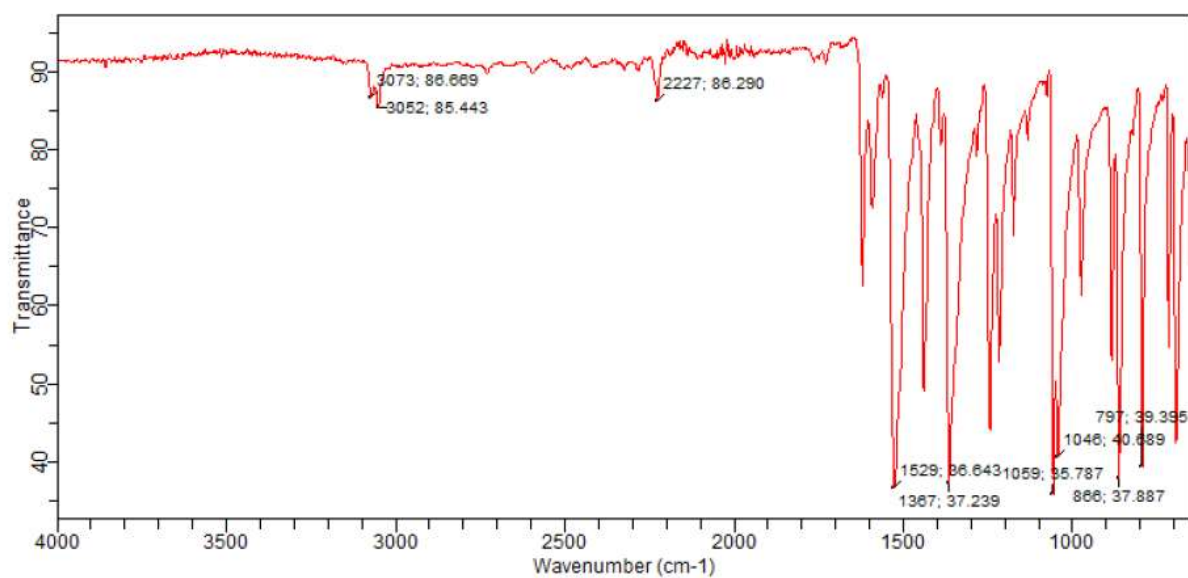
IR spectrum of 2, 2', 4, 4'tetrafluorodicyanostilbene as mull



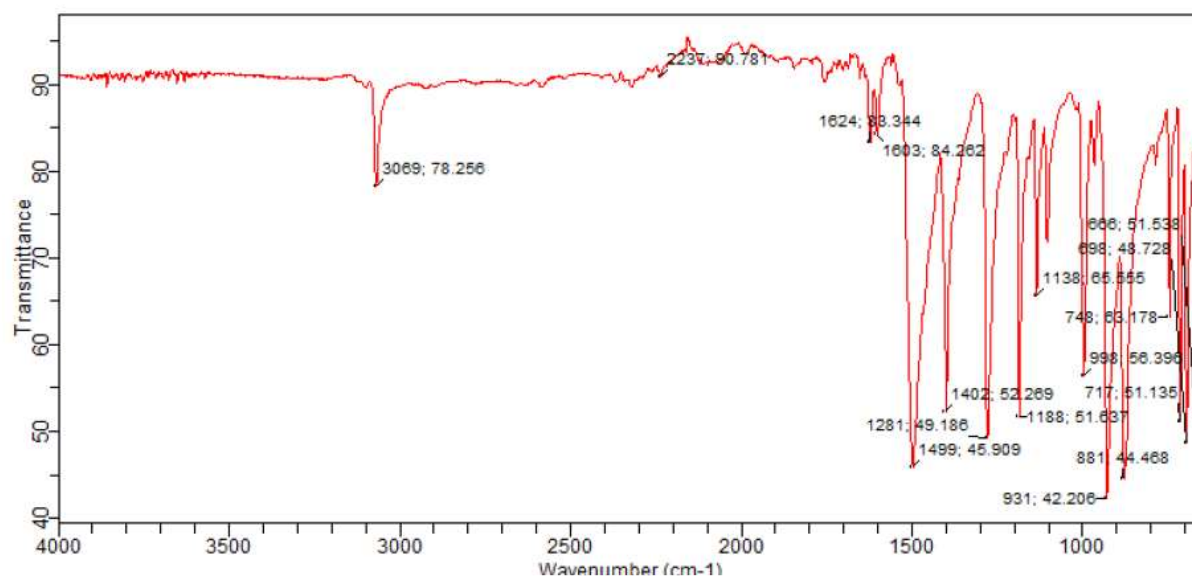
IR spectrum of 3, 3', 5, 5'tetrafluorodicyanostilbene as mull



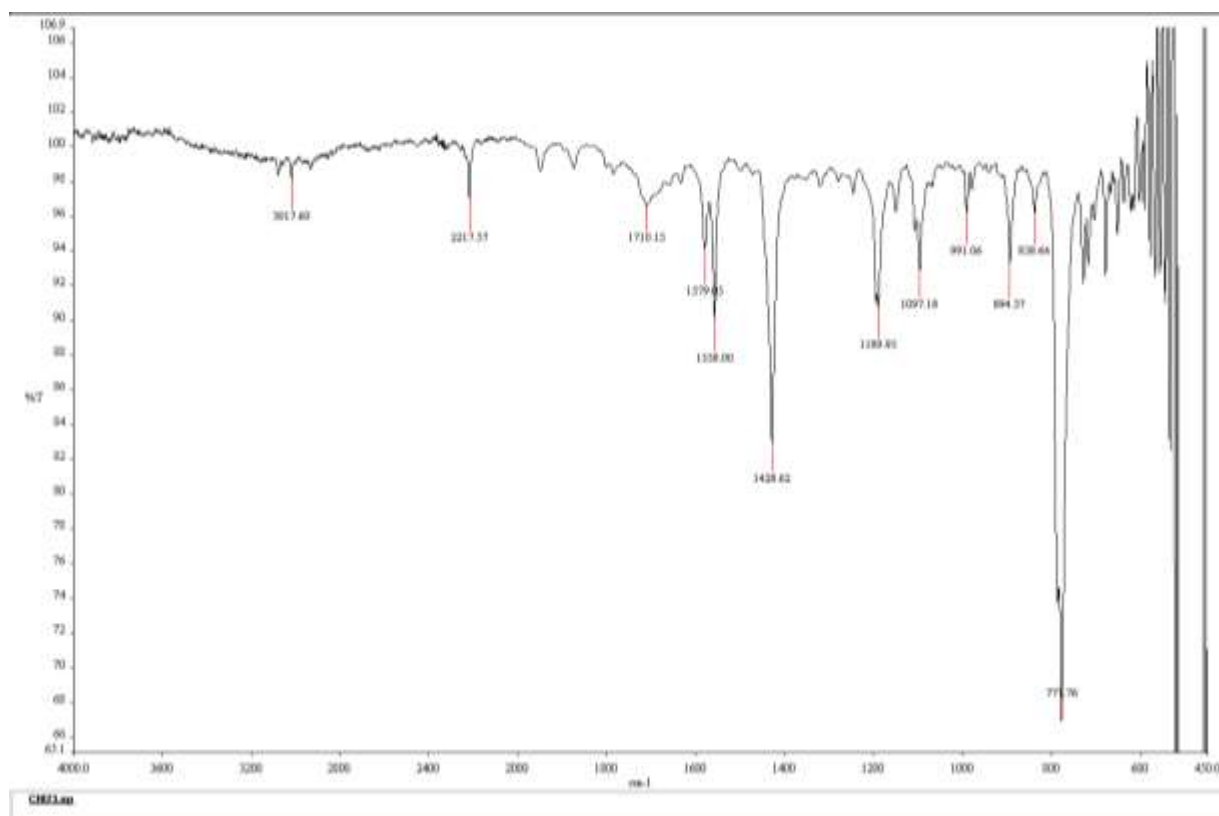
IR spectrum of 3, 3', 4, 4', 5, 5' hexafluorodicyanostilbene as mull



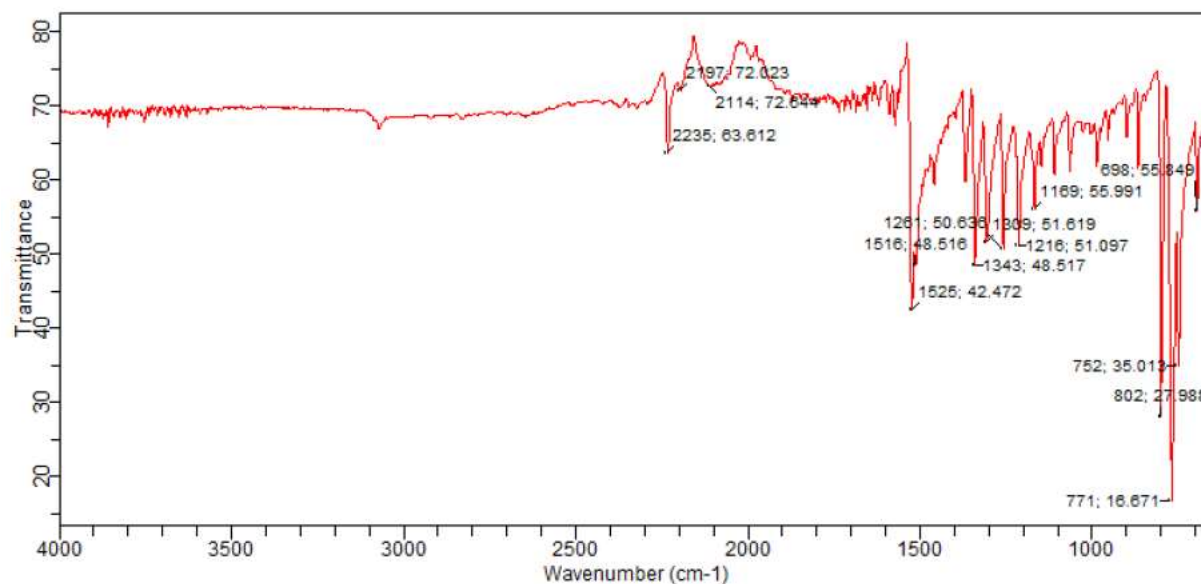
IR spectrum of 2, 2', 3, 3', 5, 5', 6, 6'-octafluorodicyanostilbene as mull



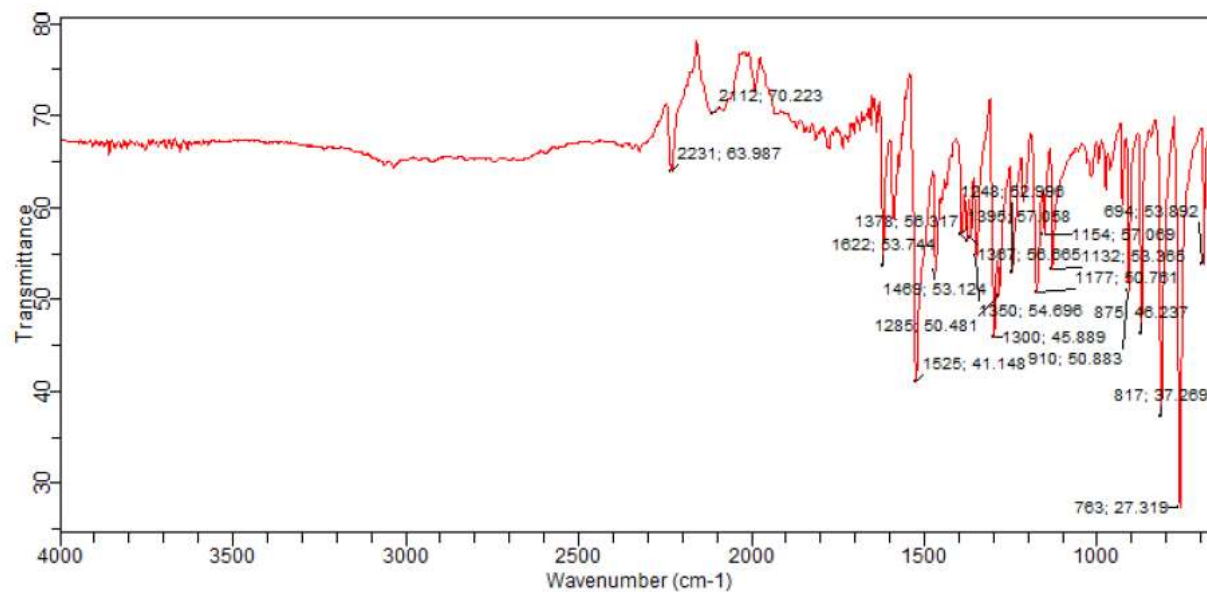
IR spectrum of 2, 2', 6, 6'-tetrachlorodicyanostilbene as mull



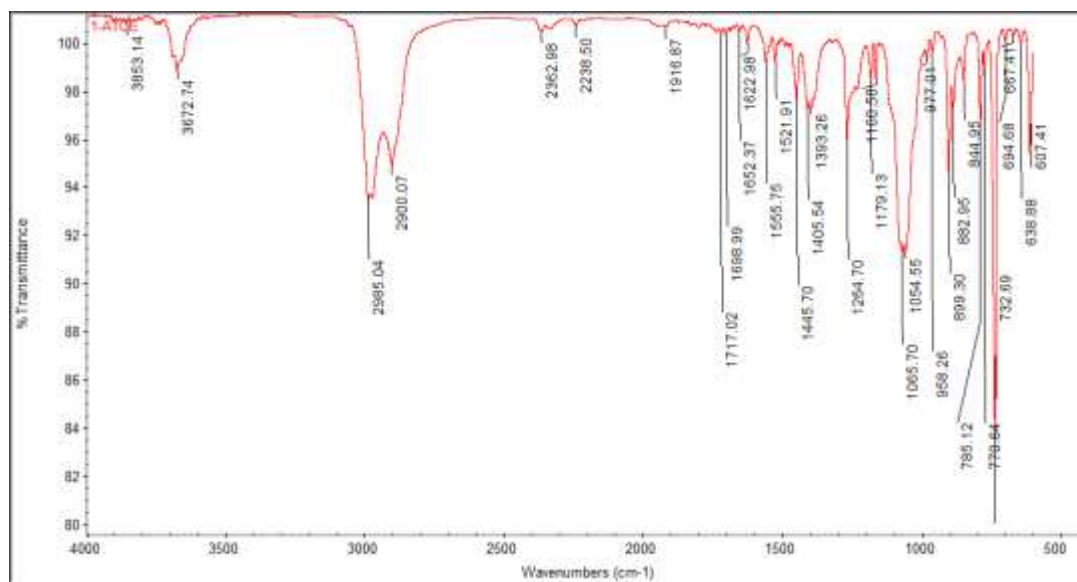
IR spectrum of 2-(1-naphthyl)-1,1,2-tricyanoethylene as mull



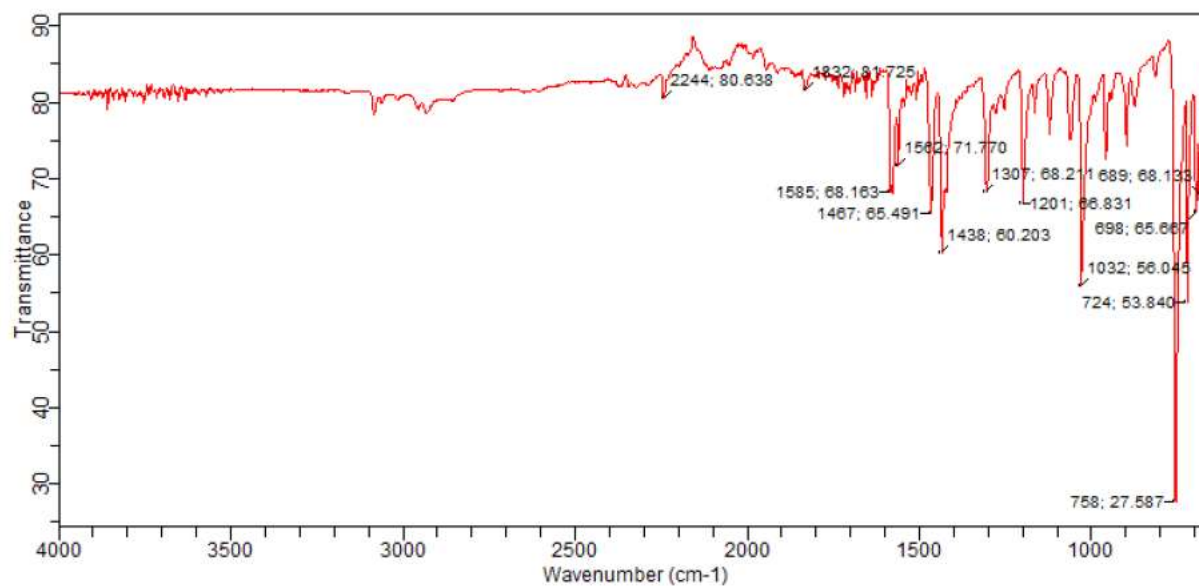
IR spectrum of 2-(2-naphthyl)-1,1,2-tricyanoethylene as mull



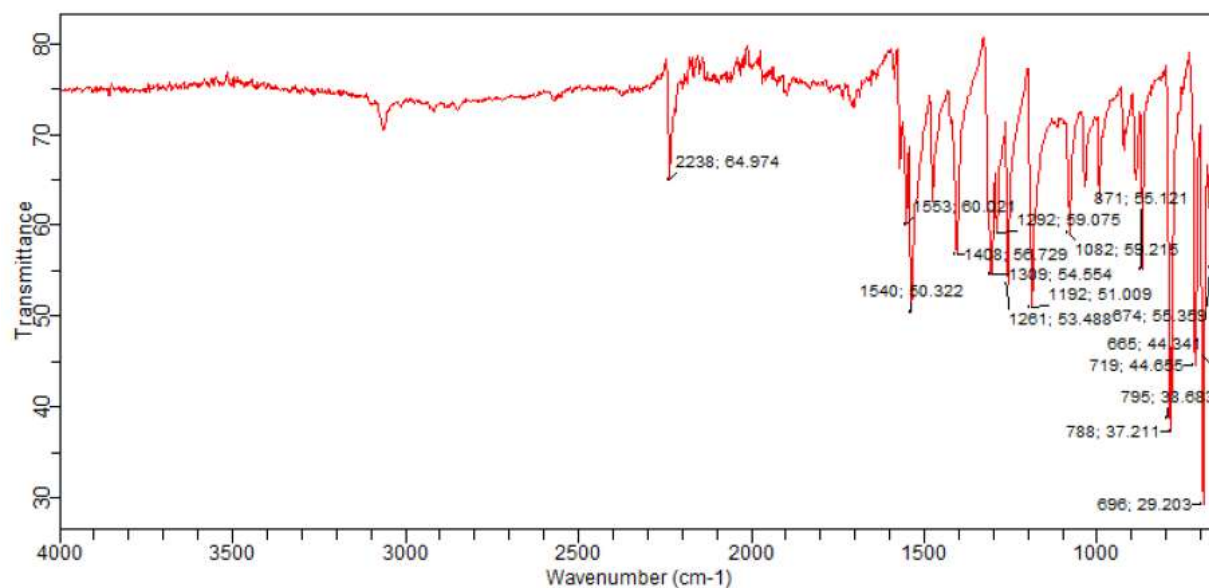
IR spectrum of 2-(1-anthryl)-1,1,2-tricyanoethylene as mull



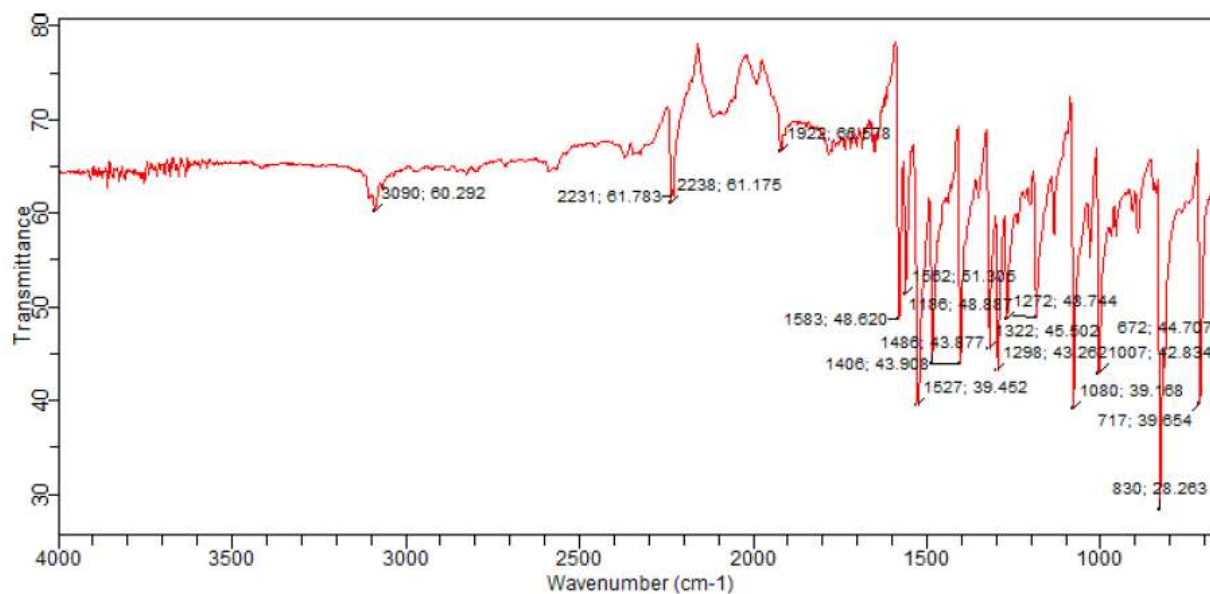
IR spectrum of 2-(2-bromophenyl)-1,1,2-tricyanoethylene as mull courtesy of Isabella Ulate



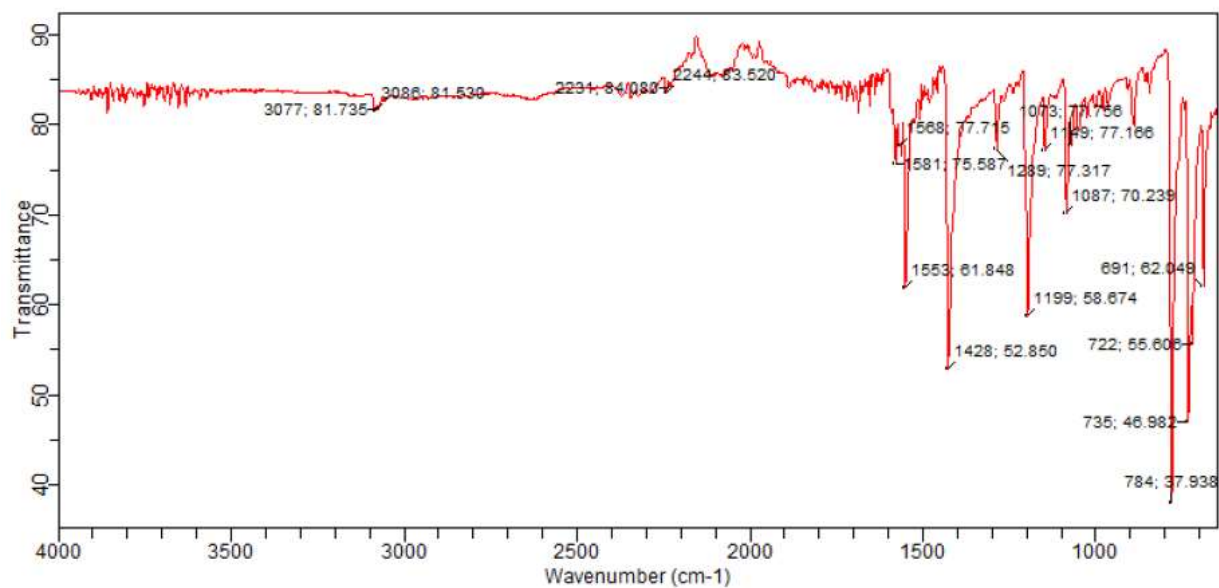
IR spectrum of 2-(3-bromophenyl)-1,1,2-tricyanoethylene as mull courtesy of Isabella Ulate



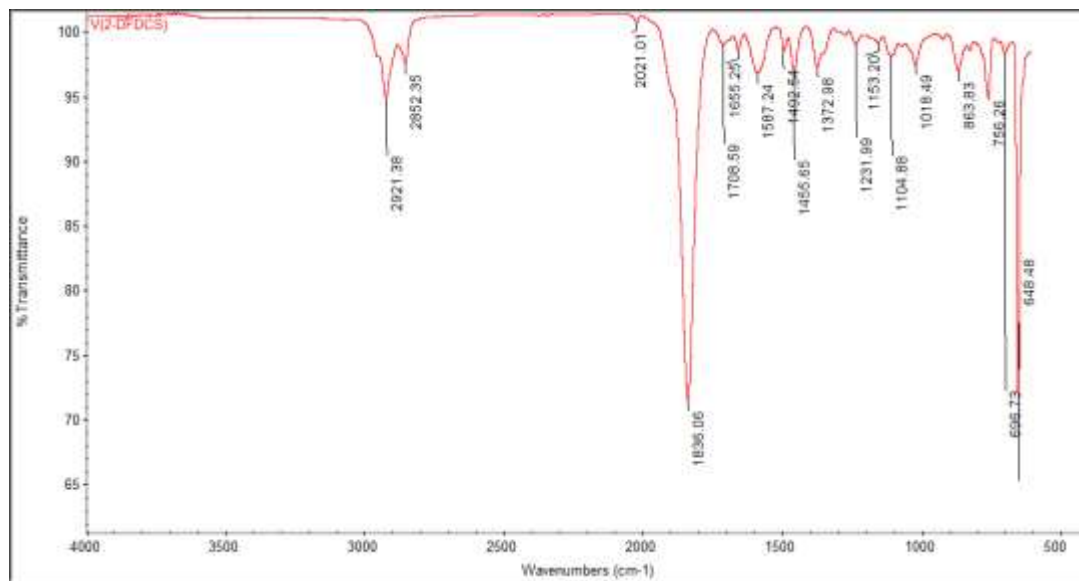
IR spectrum of 2-(4-bromophenyl)-1,1,2-tricyanoethylene as mull courtesy of Isabella Ulate



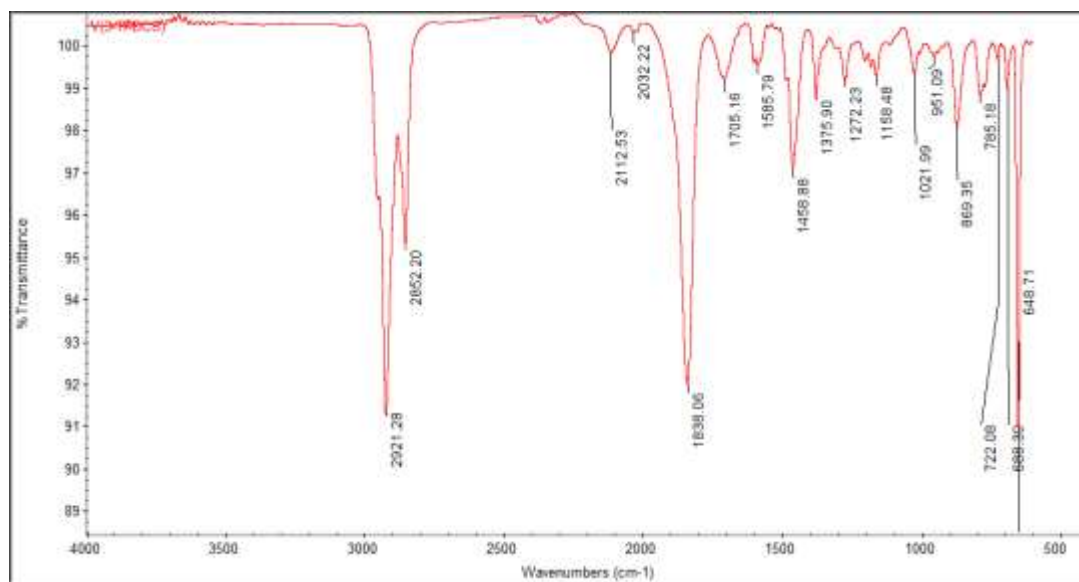
IR spectrum of 2-(2,6-bromophenyl)-1,1,2-tricyanoethylene as mull courtesy of Steven Miller



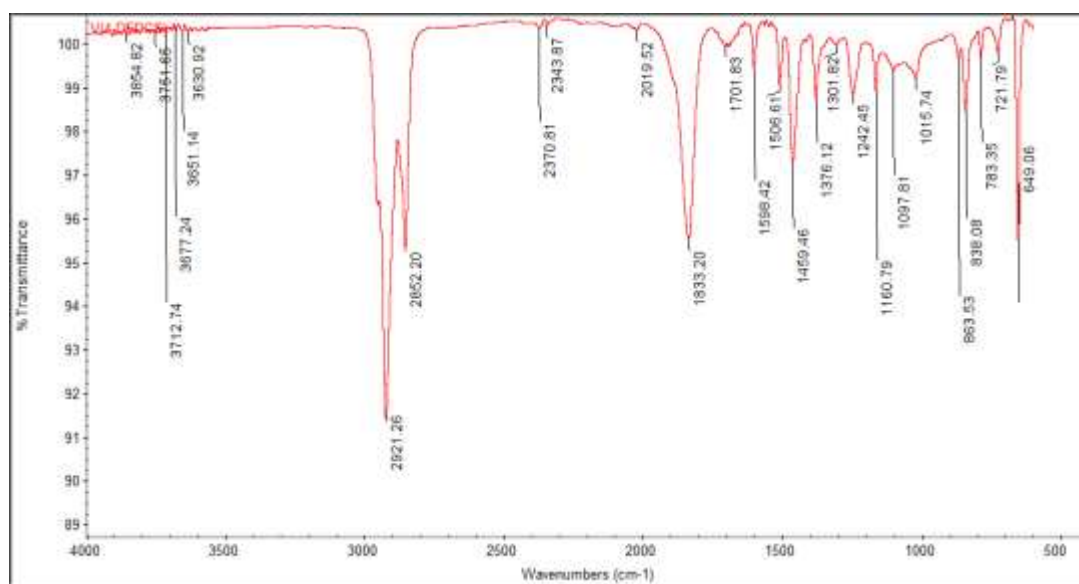
IR spectrum of V (2, 2' difluorodicyanostilbene) as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



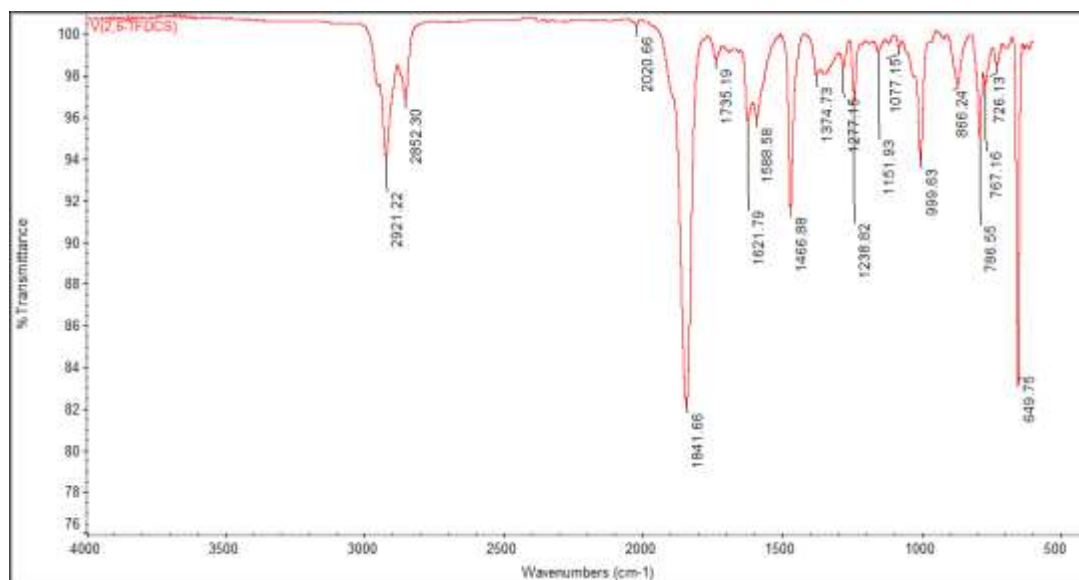
IR spectrum of V (3, 3' difluorodicyanostilbene) as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



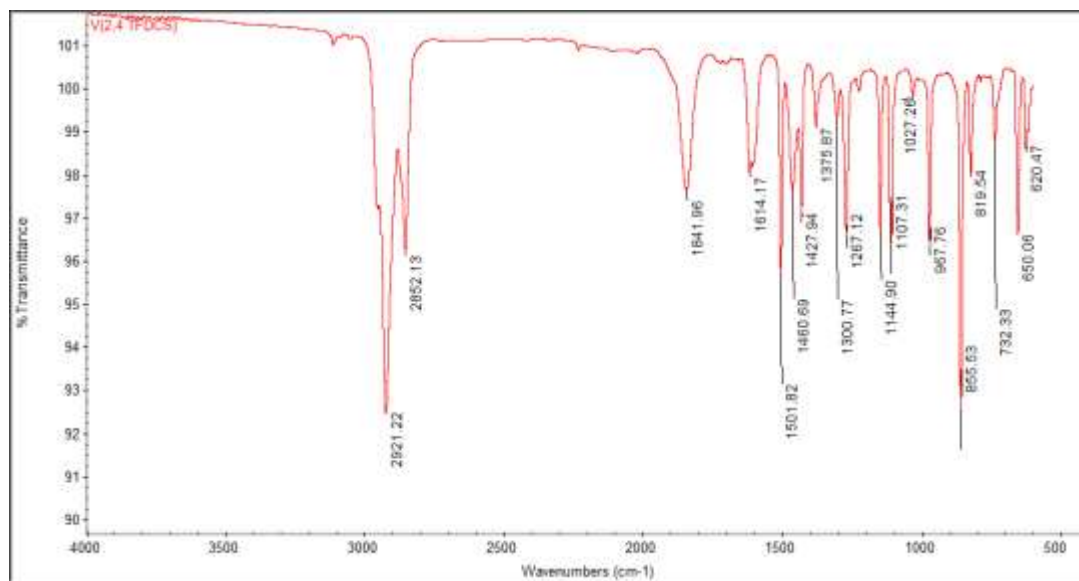
IR spectrum of V (4, 4' difluorodicyanostilbene) as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



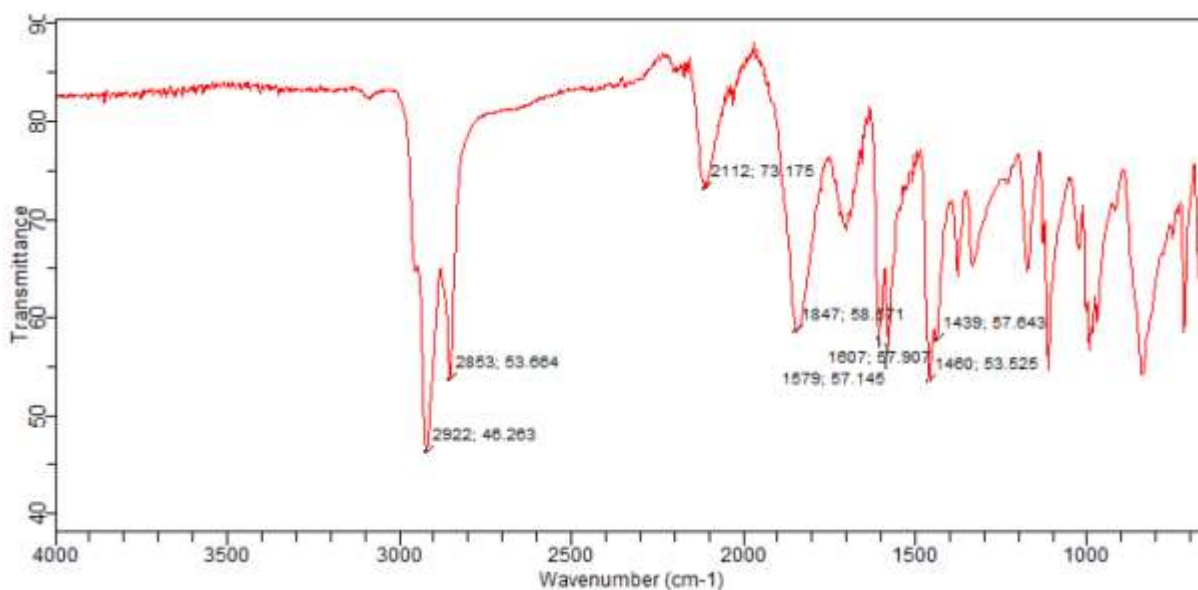
IR spectrum of V (2, 2', 6, 6'-tetrafluorodicyanostilbene) as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



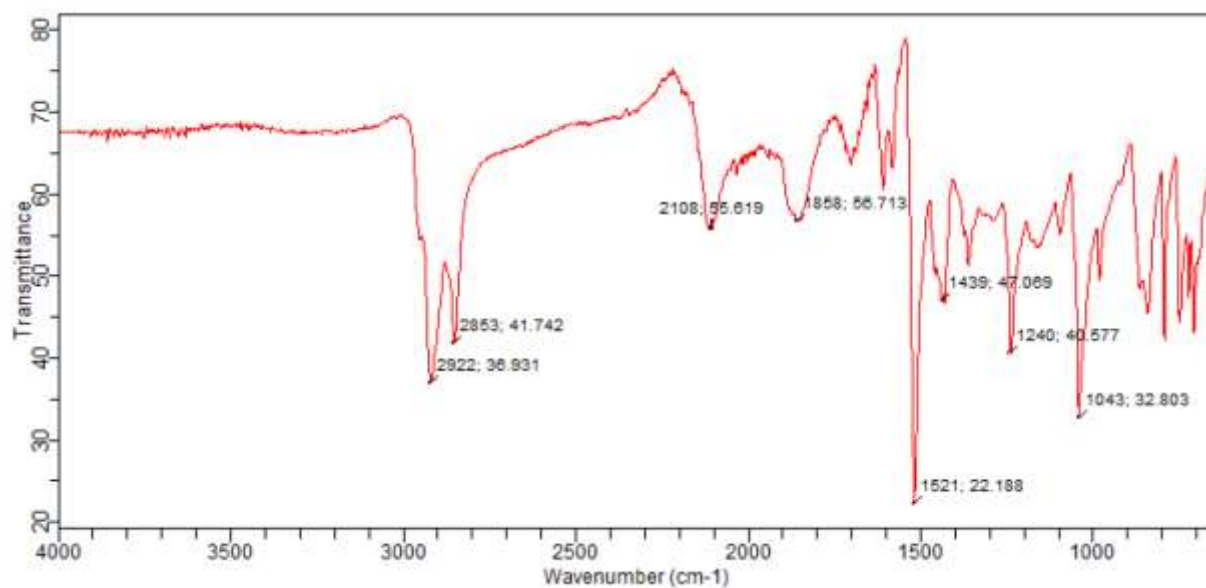
IR spectrum of V (2, 2', 4, 4'-tetrafluorodicyanostilbene) as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



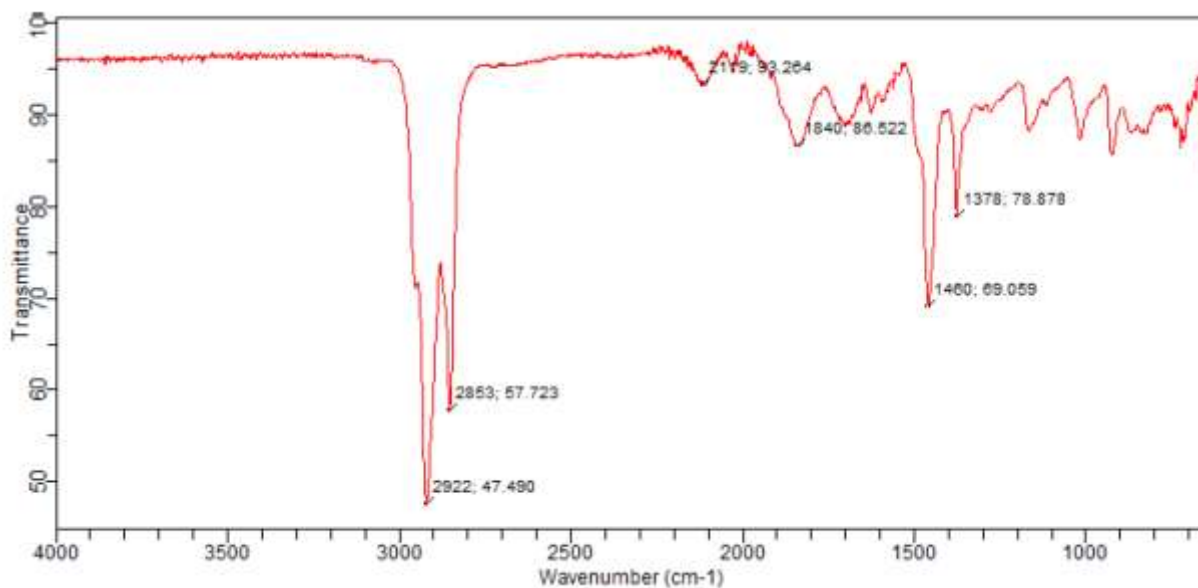
IR spectrum of $V(3,5-F_4DCS)_2 (THF)(0.7CH_2Cl)$ as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



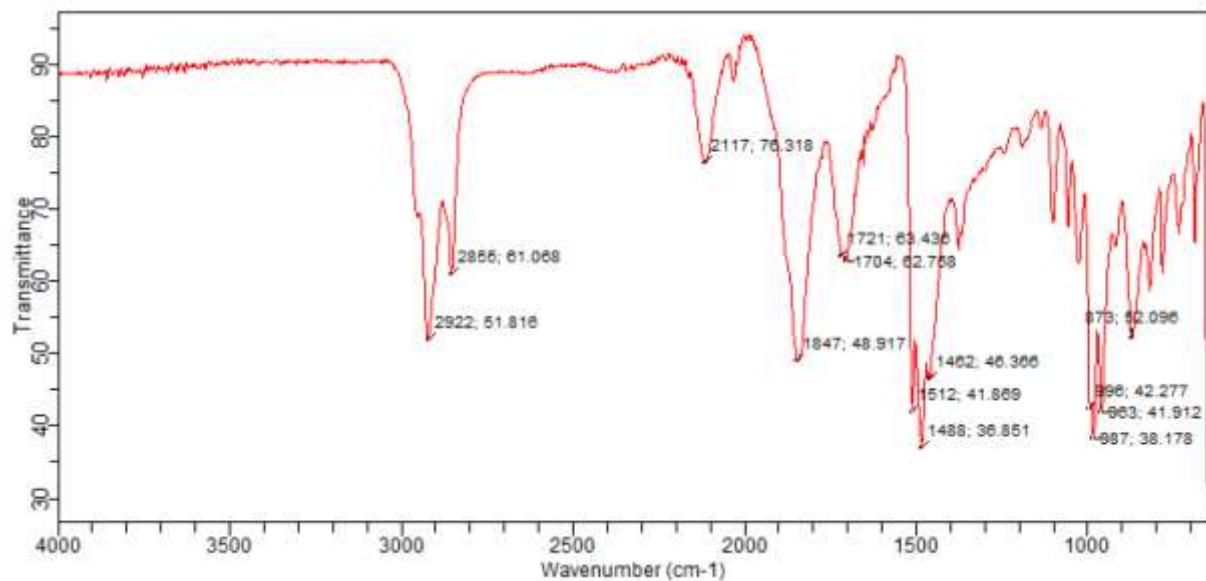
IR spectrum of $V(F_6DCS)_2 (THF)(1.1(CH_2Cl))$ as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



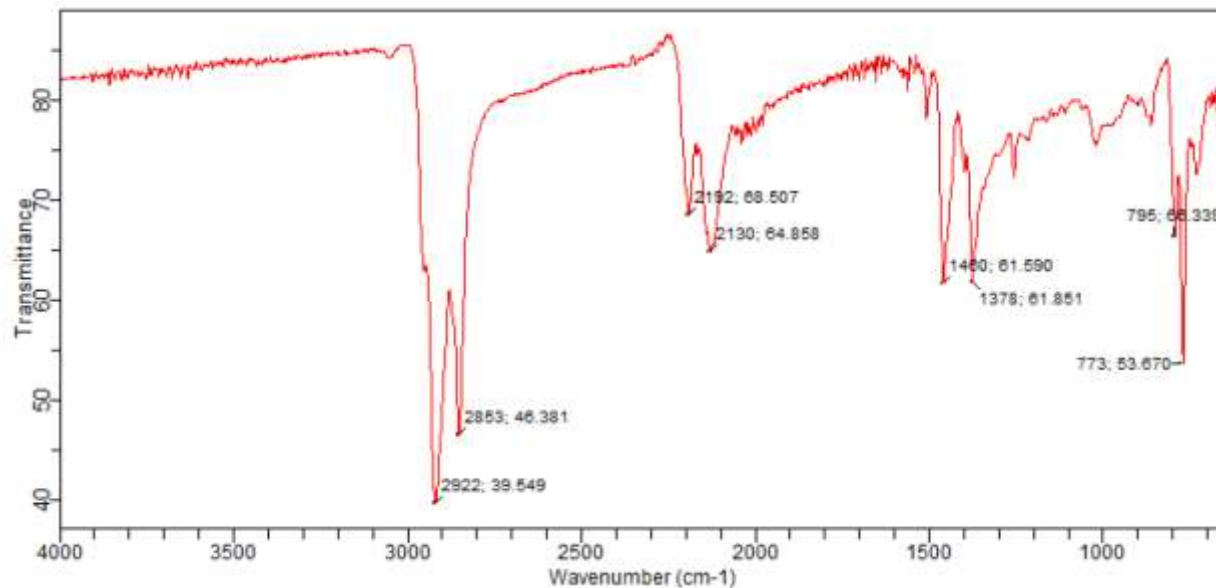
IR spectrum of $V(F_8DCS)_2 (THF)(1.3CH_2Cl)$ as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



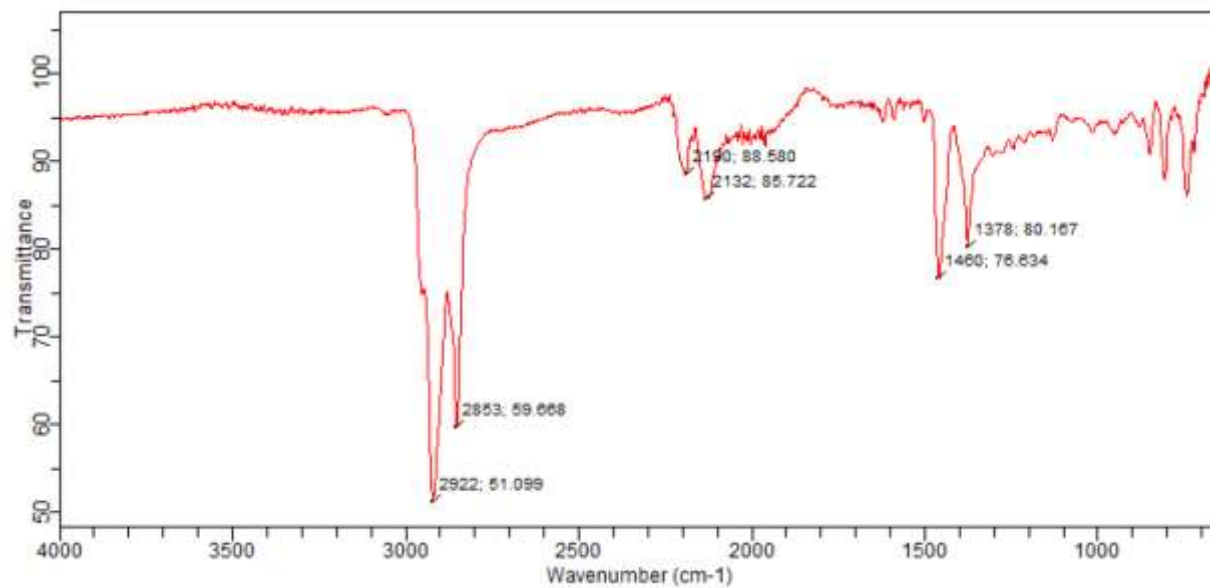
IR spectrum of $V(DCPFS)_2 \cdot 2.00THF$ as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



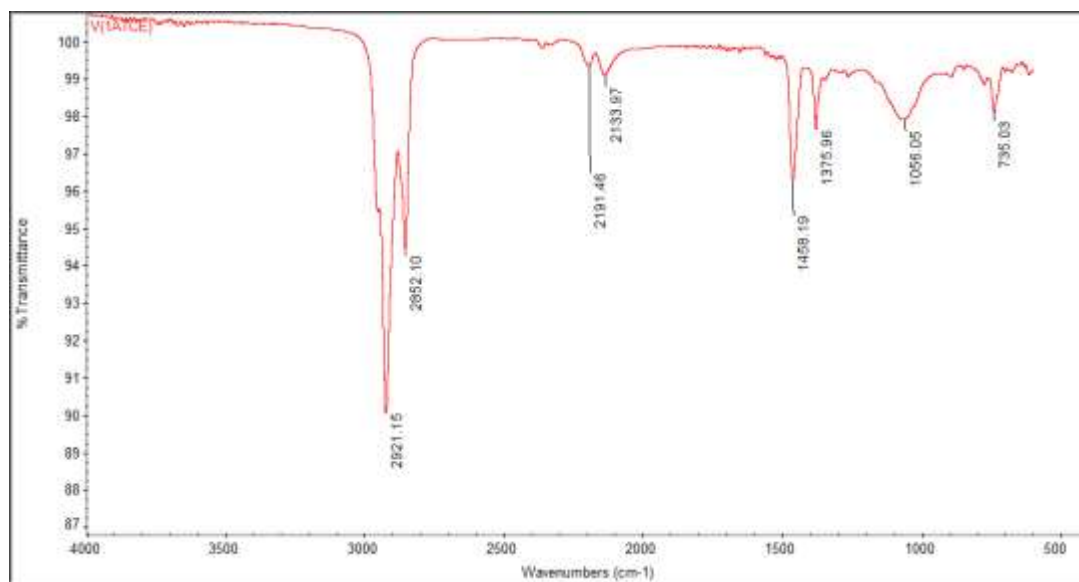
IR spectrum of V (1-NTCE)₂ 0.45CH₂Cl as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



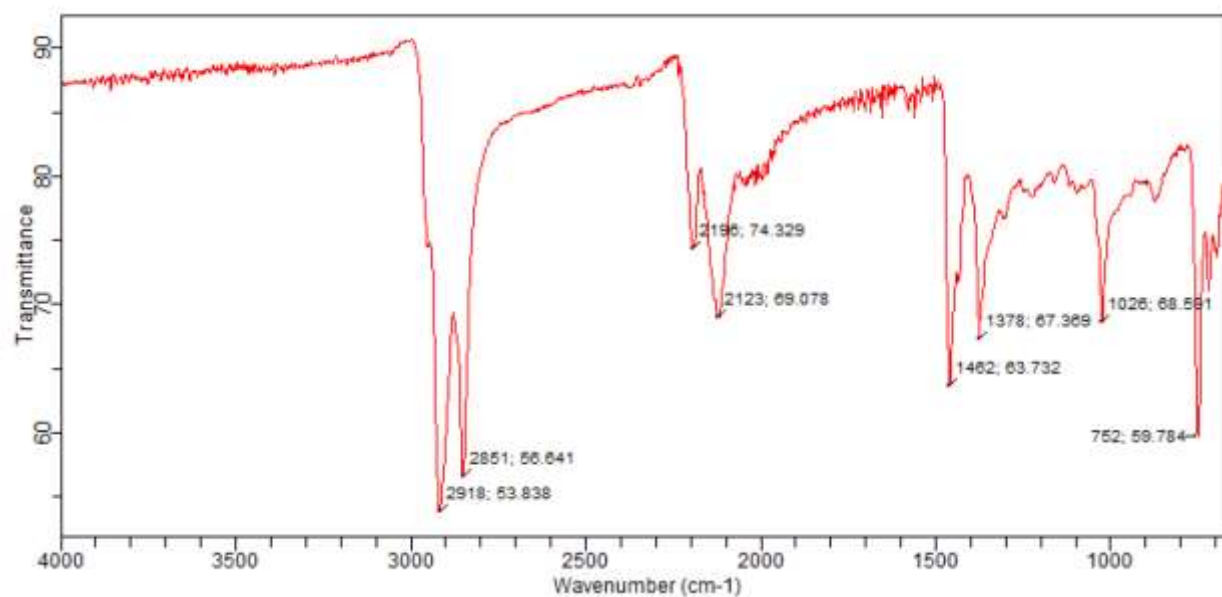
IR spectrum of V (2-NTCE)₂ 1.40CH₂Cl as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



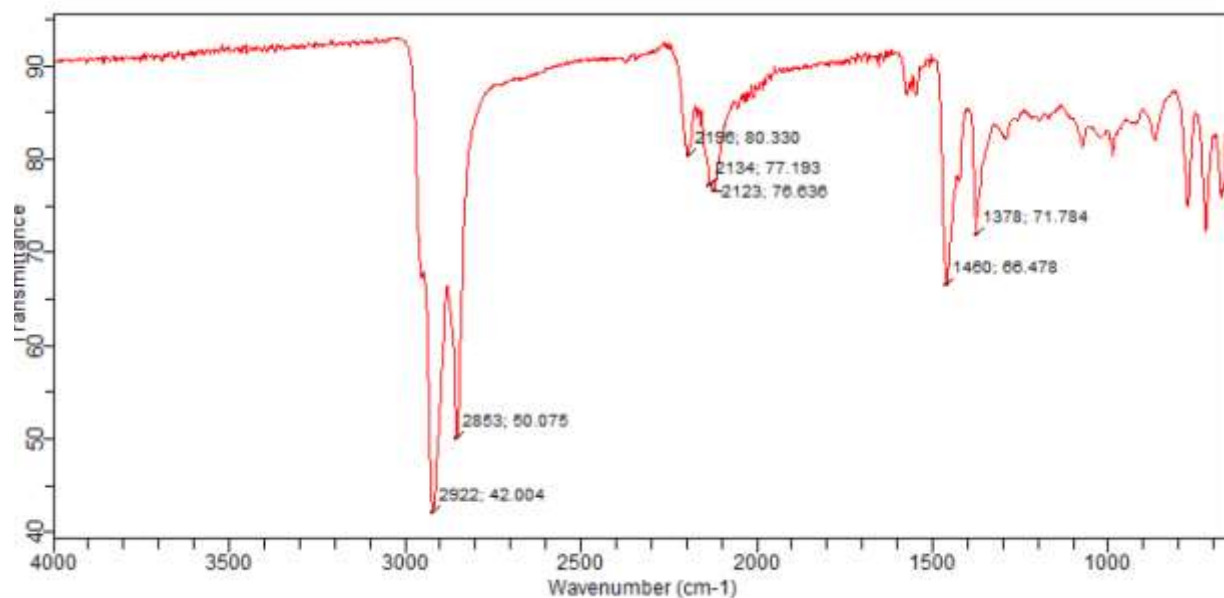
IR spectrum of V (1-ATCE)₂ as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



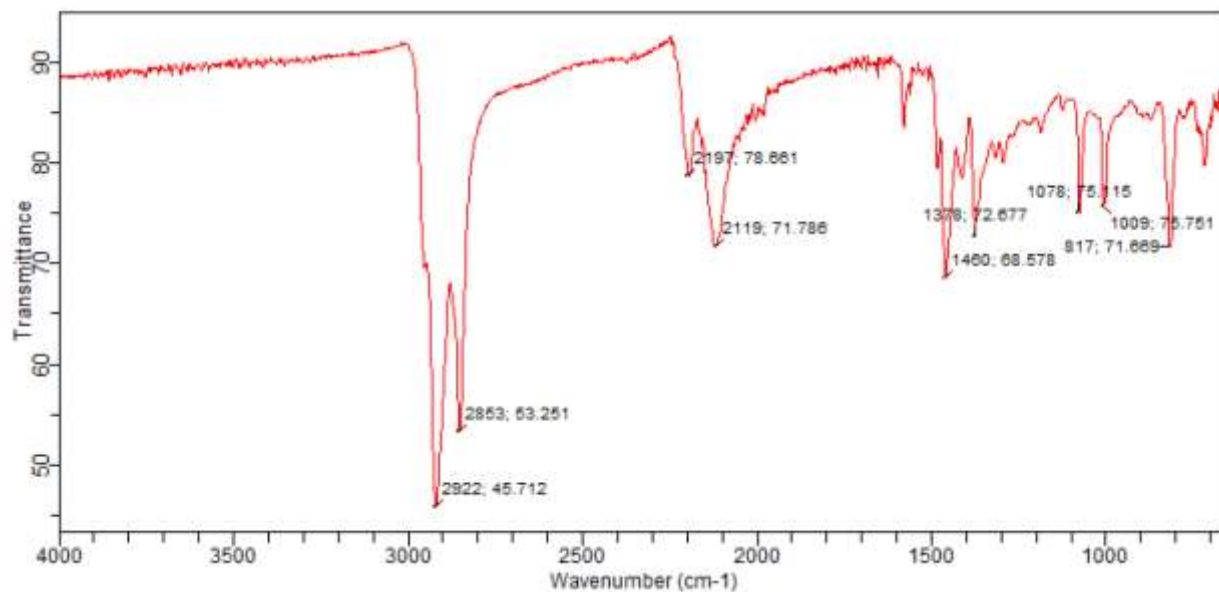
IR spectrum of V (2-BrPTCE)₂ 0.40CH₂Cl as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



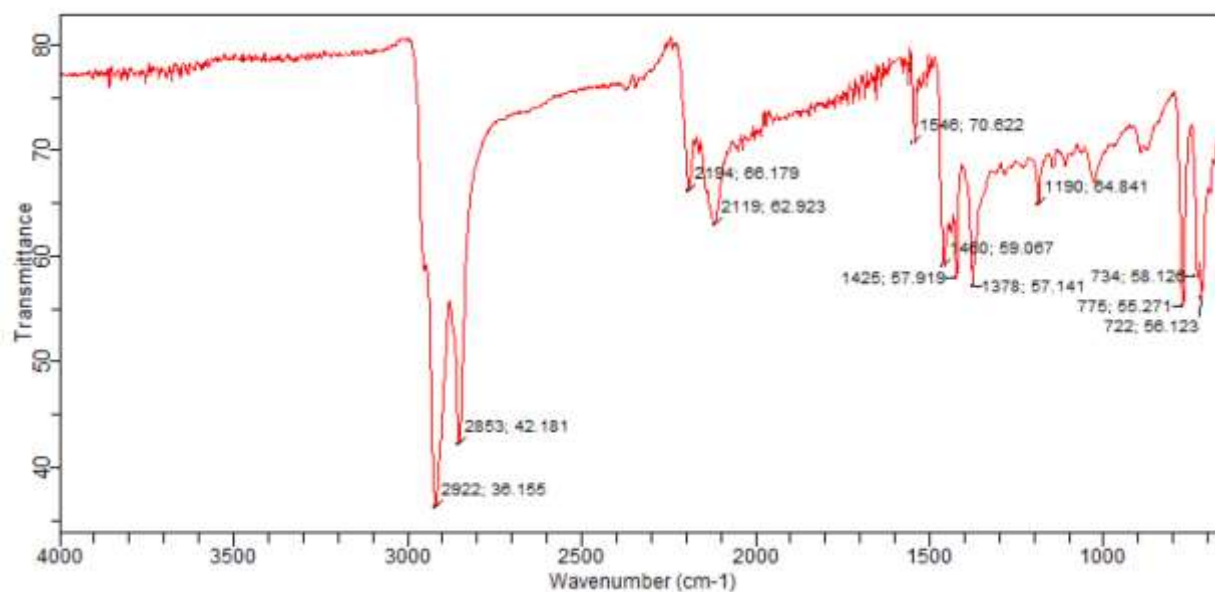
IR spectrum of V (3-BrPTCE)₂ yCH₂Cl as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



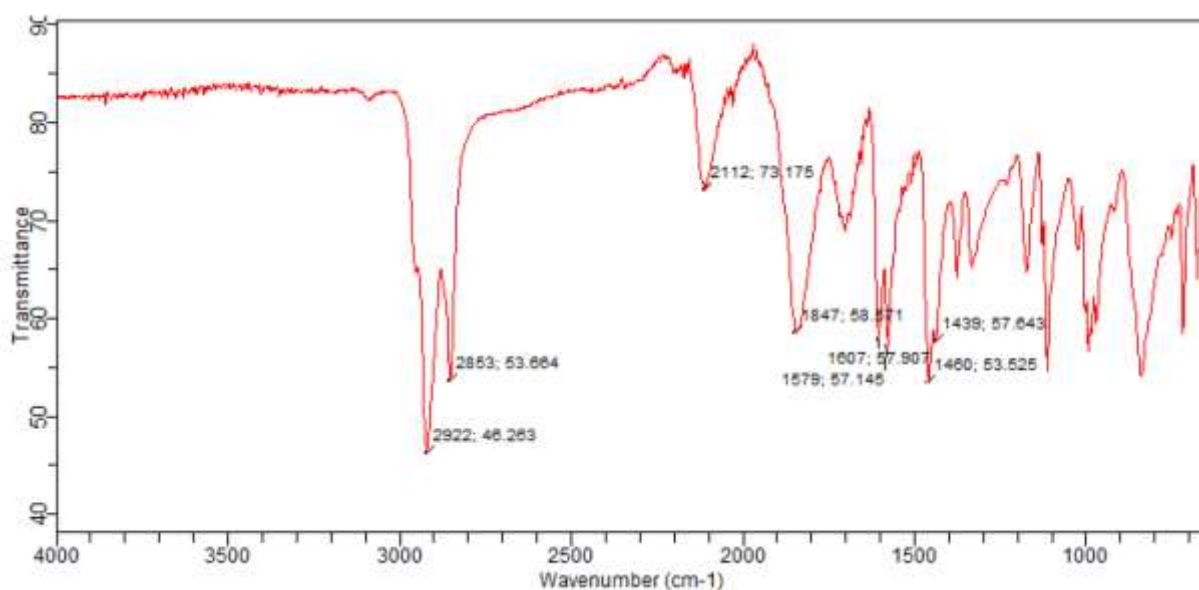
IR spectrum of V (4-BrPTCE)₂ 0.55CH₂Cl as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)



IR spectrum of V (2, 6-Br₂PTCE)₂ 0.55CH₂Cl as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)

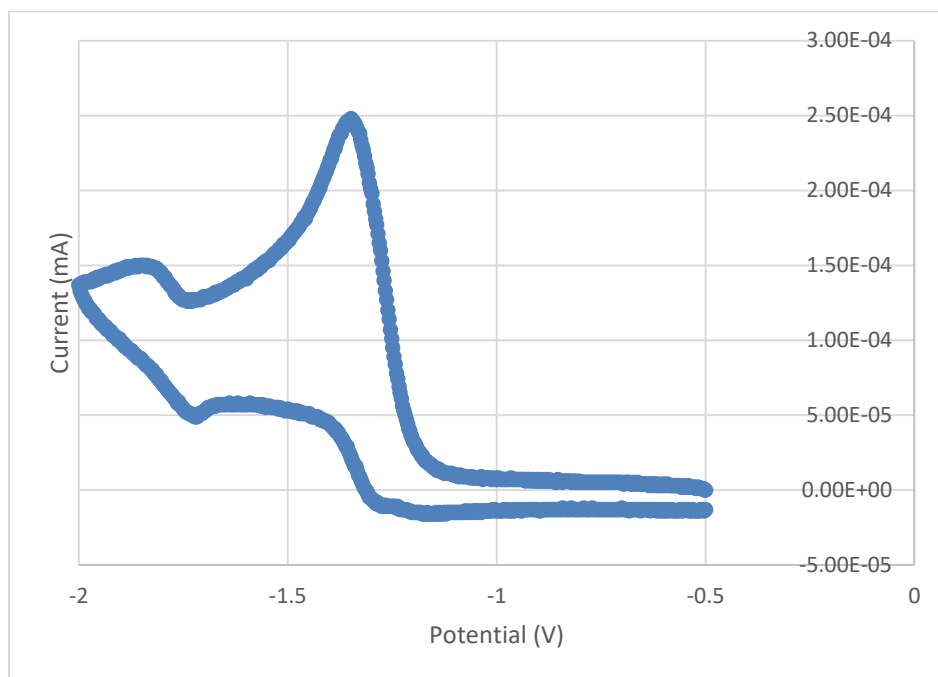


IR spectrum of V (3, 5-Br₂PTCE)₂ γCH₂Cl as Nujol mull (peaks at 2922 and 2853 are Nujol peaks)

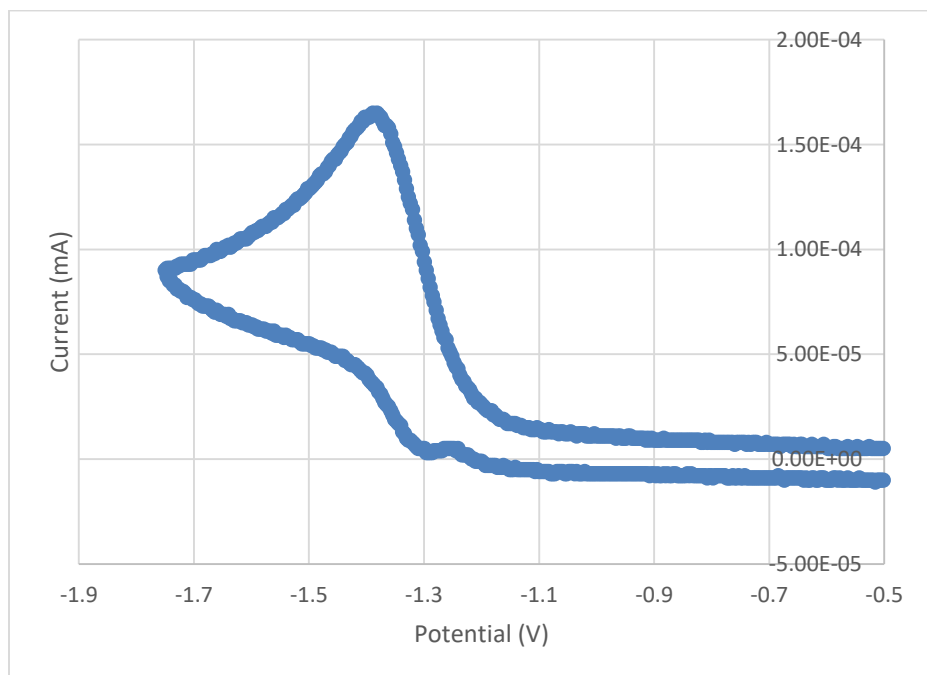


A.3 Cyclic Voltammetry:

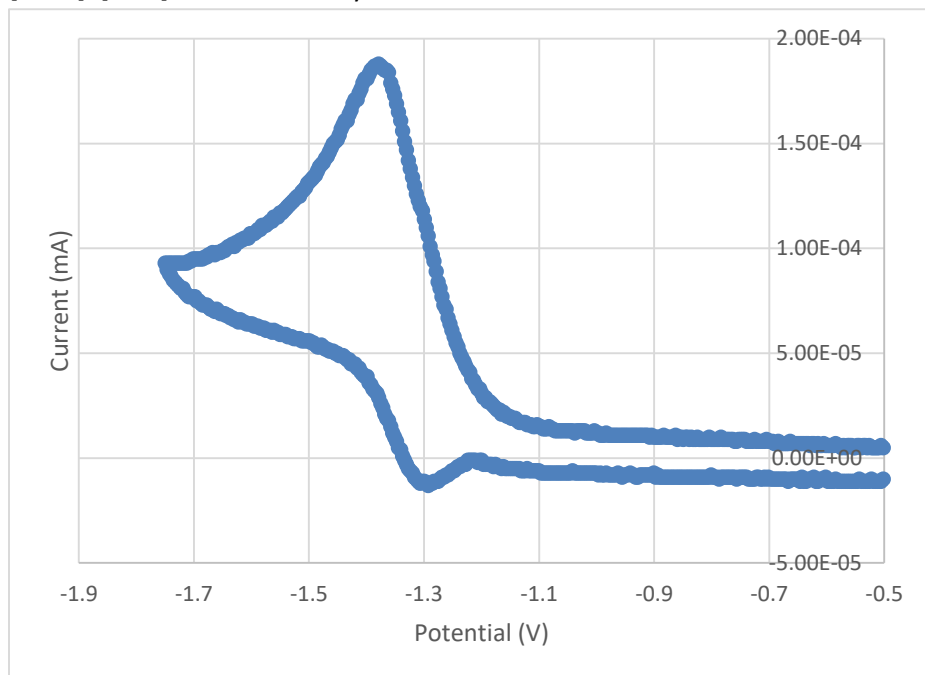
2, 2' difluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



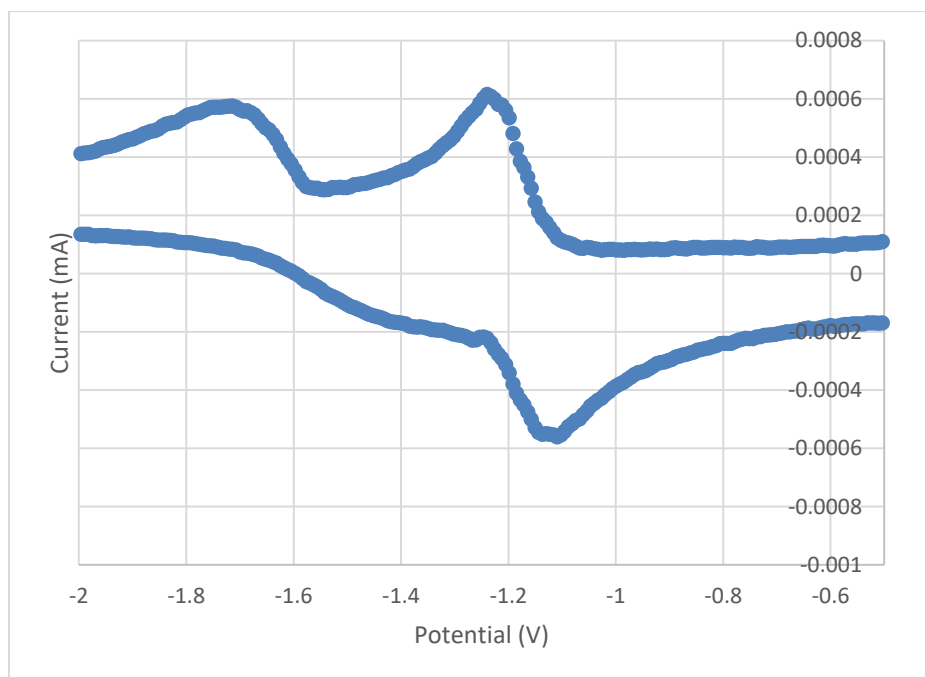
3, 3' difluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



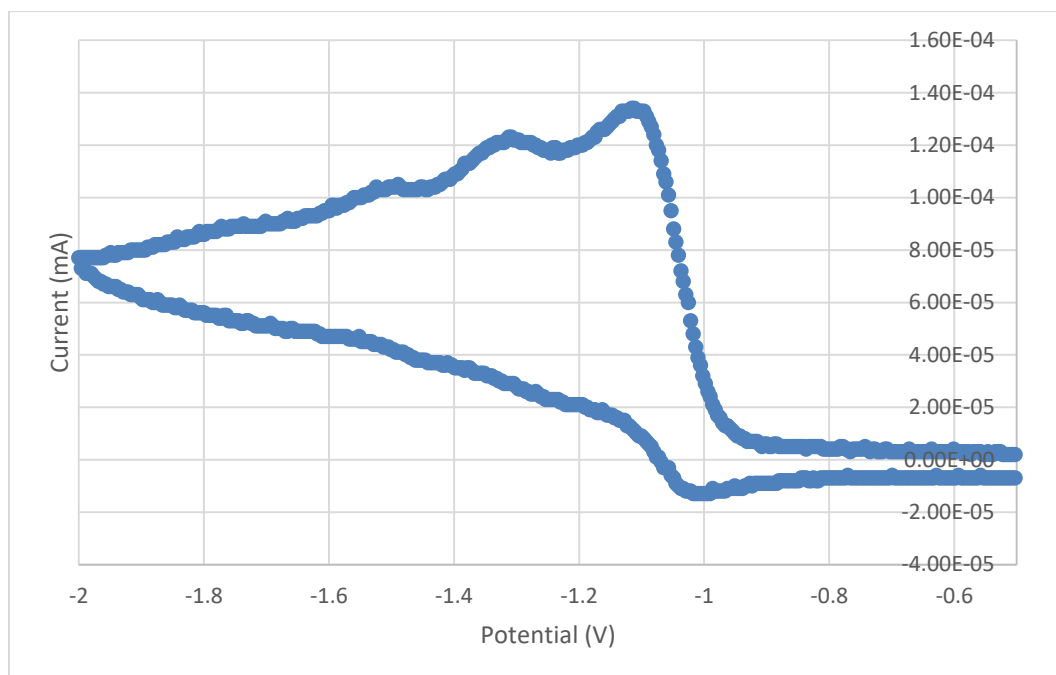
4, 4' difluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



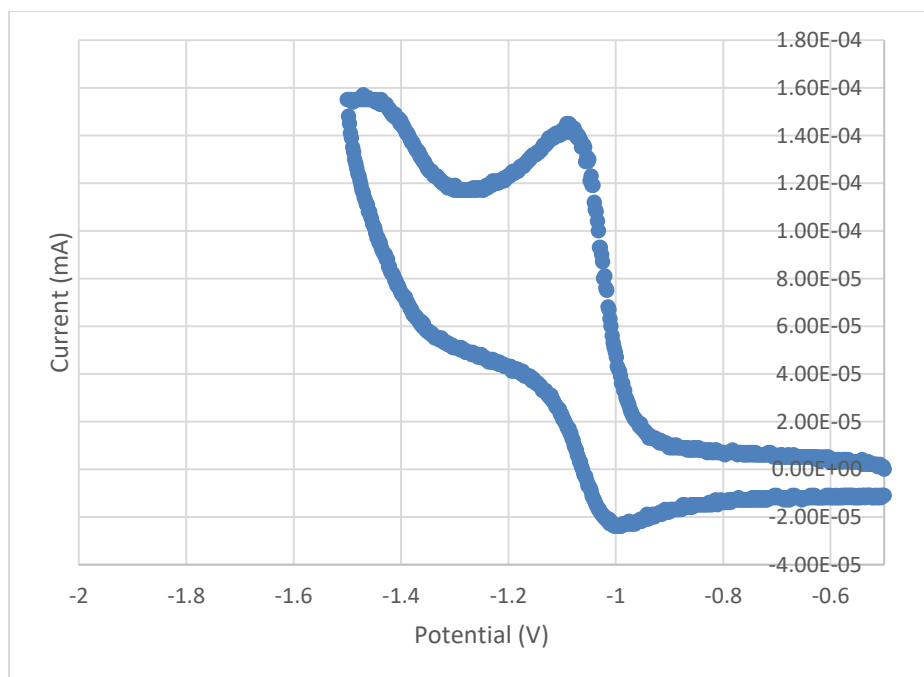
2, 2', 6, 6' tetrafluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



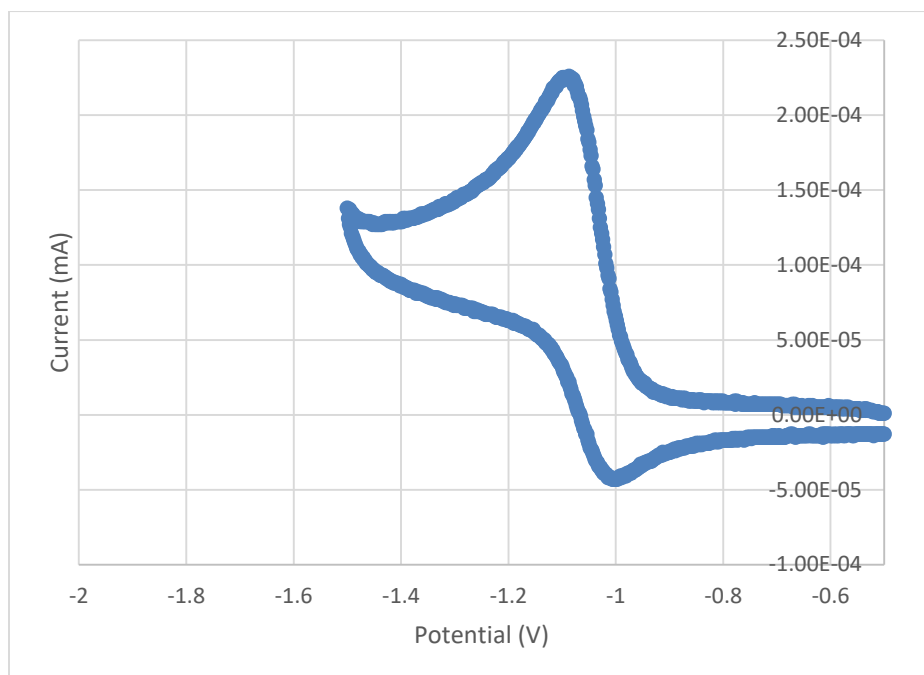
2, 2', 4, 4'tetrafluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



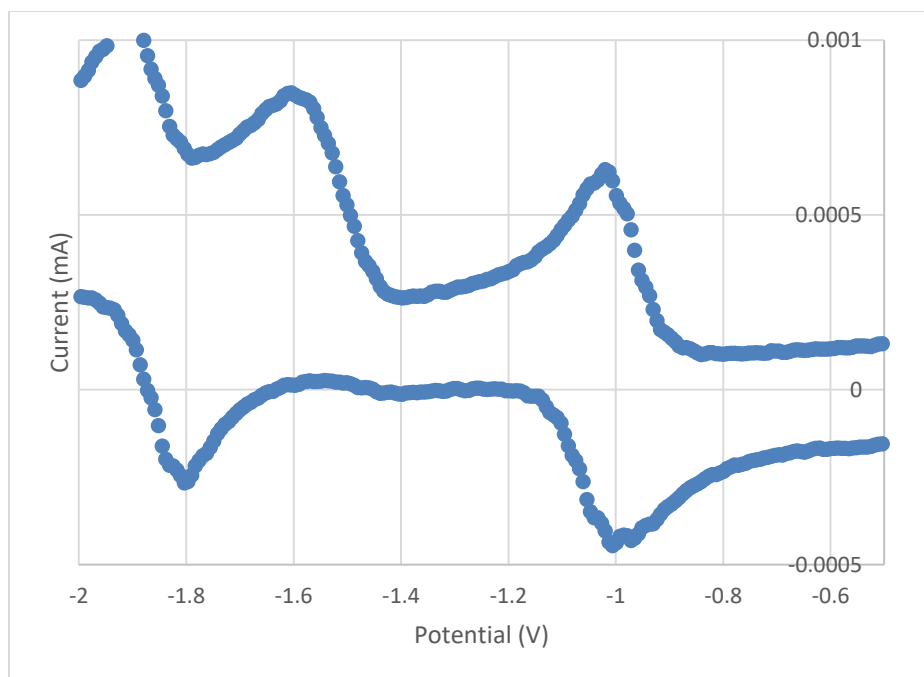
3, 3', 5, 5'tetrafluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



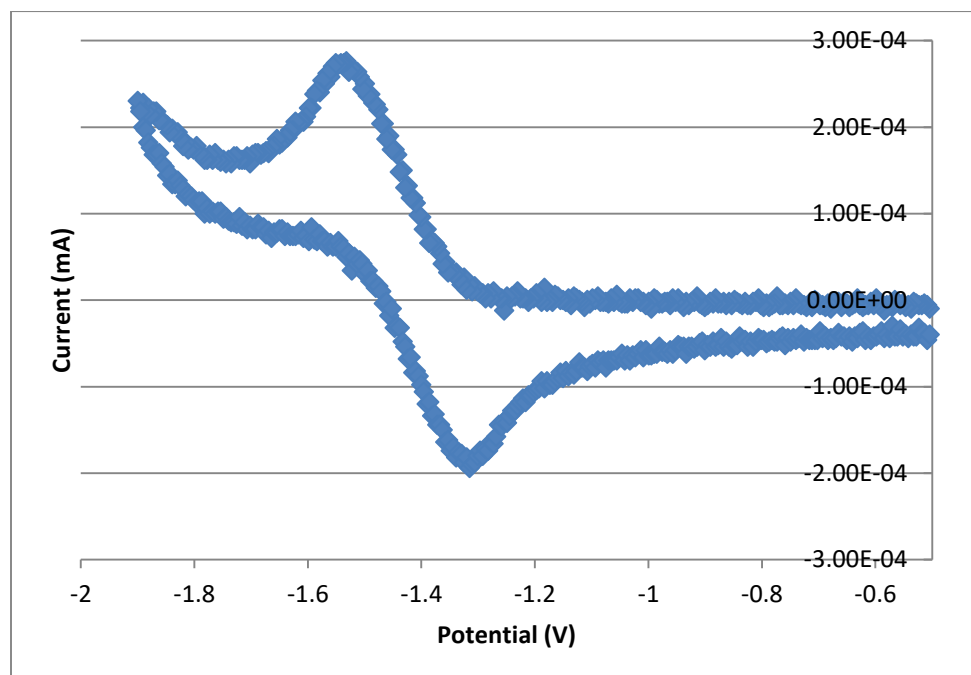
3, 3', 4, 4', 5, 5' hexafluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



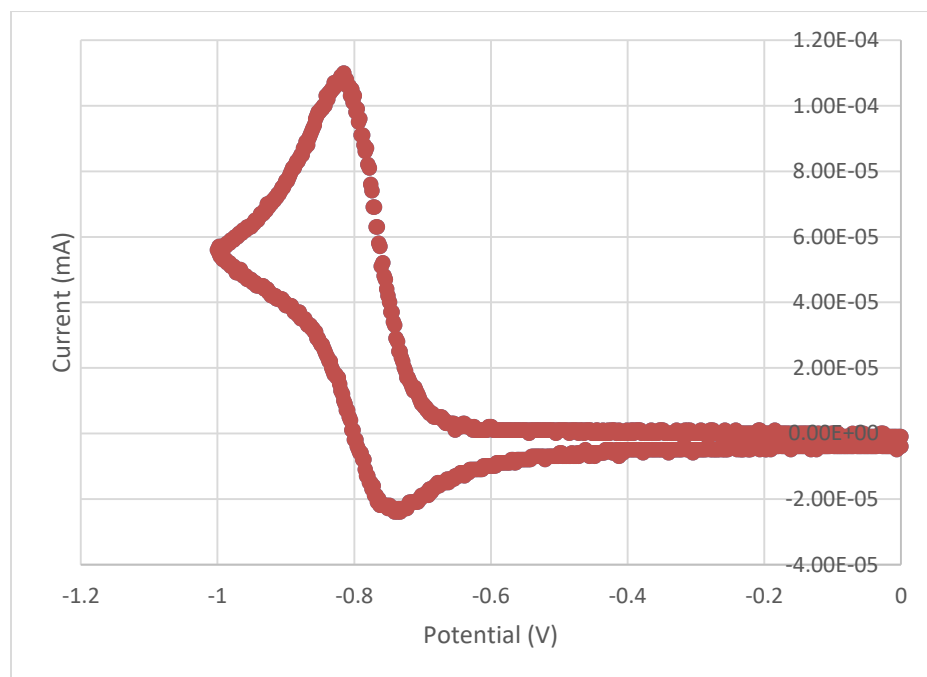
2, 2', 3, 3', 5, 5', 6, 6' octafluorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



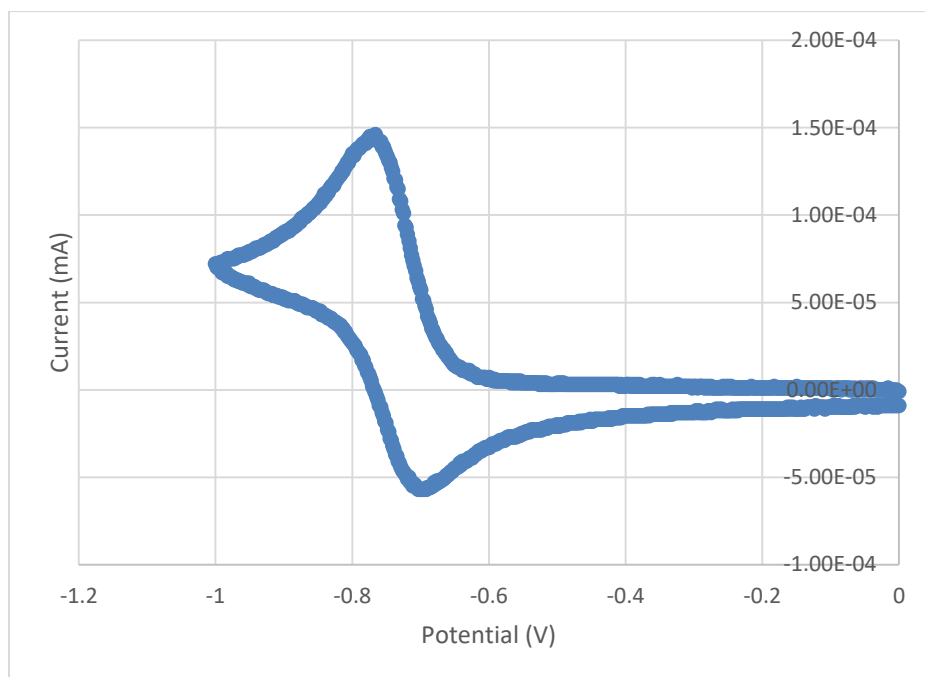
2, 2',6, 6' tetrachlorodicyanostilbene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



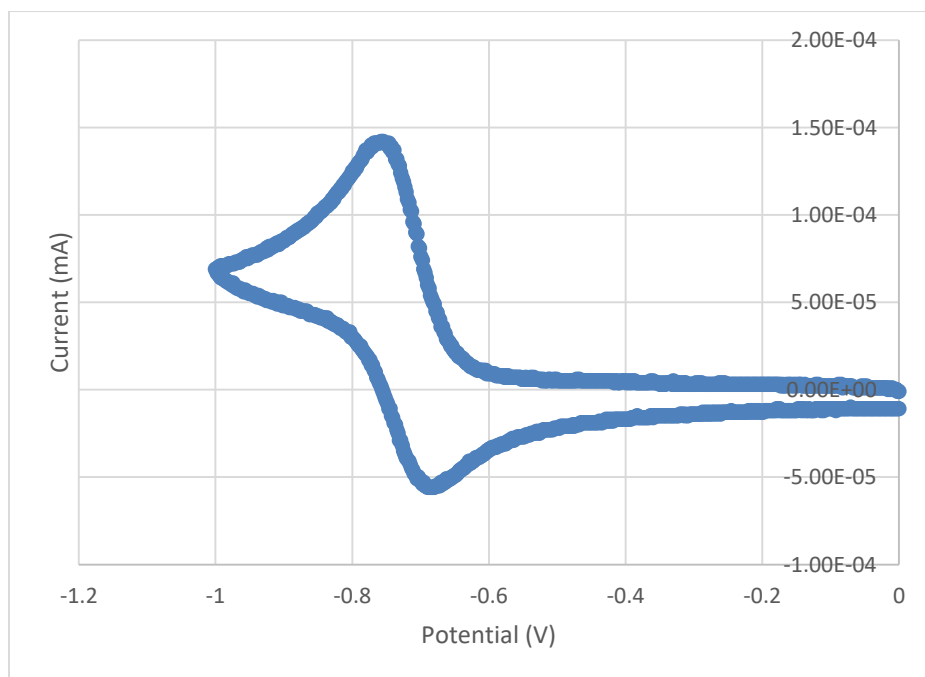
1-(naphthyl)-1,1,2-tricyanoethylene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



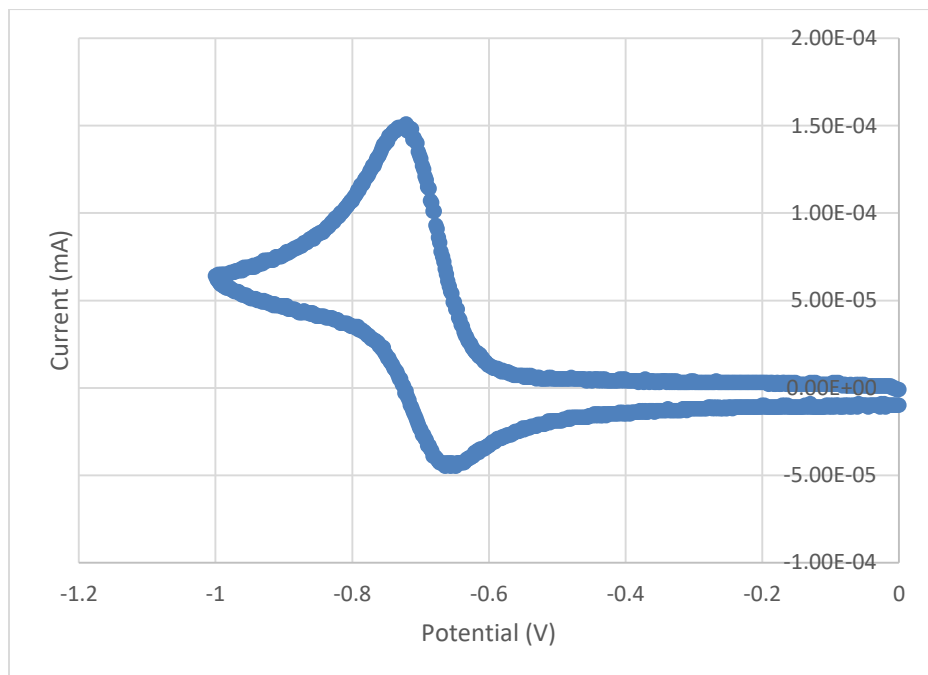
2-(naphthyl)-1,1,2-tricyanoethylene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



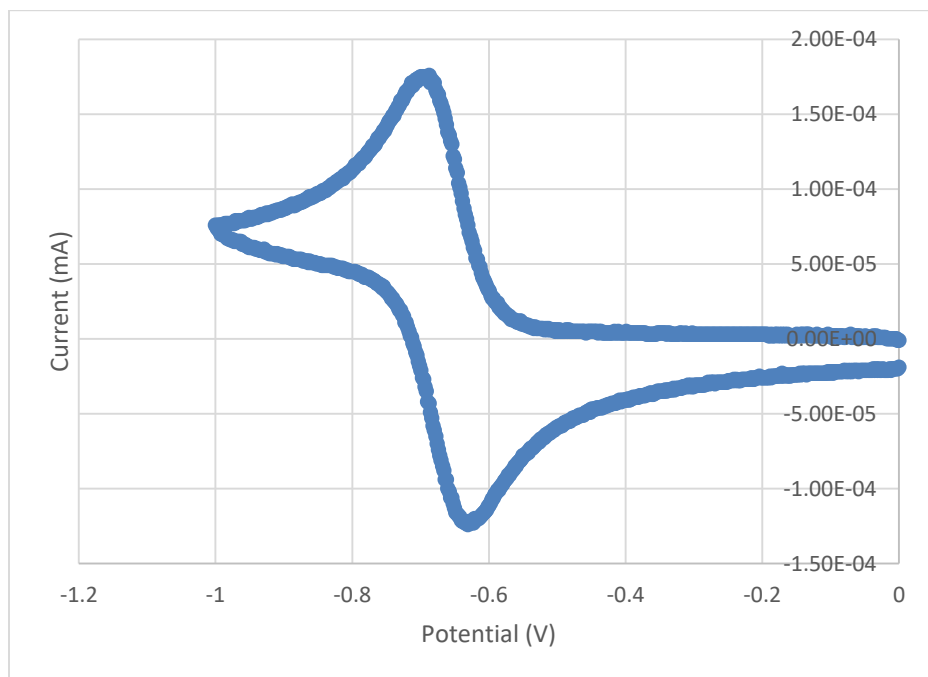
2-(2-bromophenyl)-1,1,2-tricyanoethylene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.



2-(4-bromophenyl)-1,1,2-tricyanoethylene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.

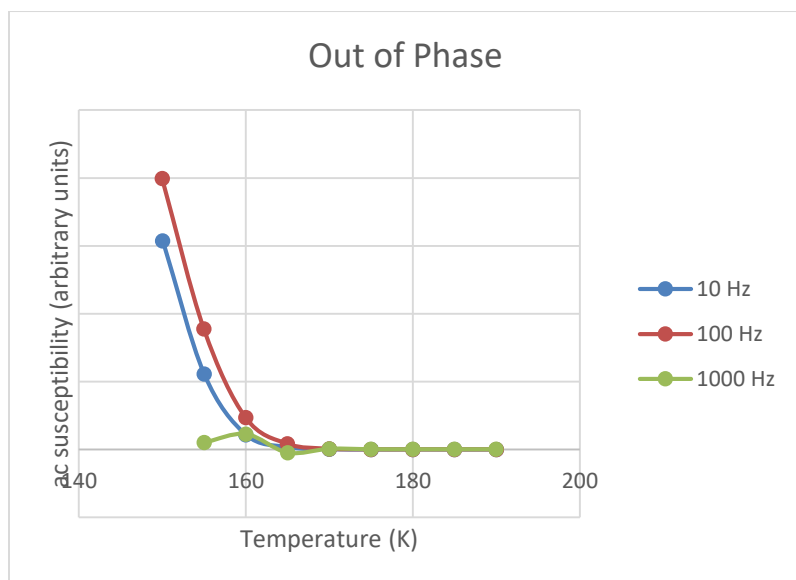
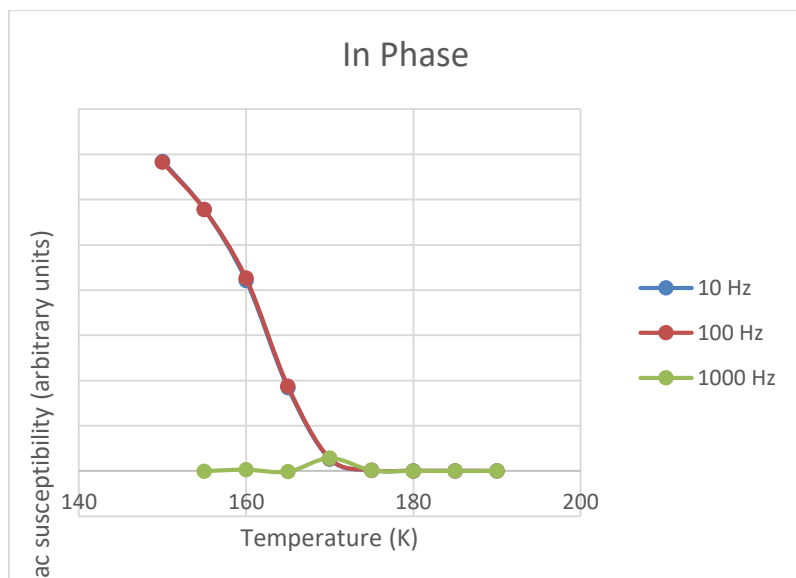


2-(2,6-bromophenyl)-1,1,2-tricyanoethylene: 500 mV scan rate, Ag/AgNO₃ reference electrode, run in acetonitrile, [Bu₄N]⁺ [ClO₄]⁻ as the electrolyte.

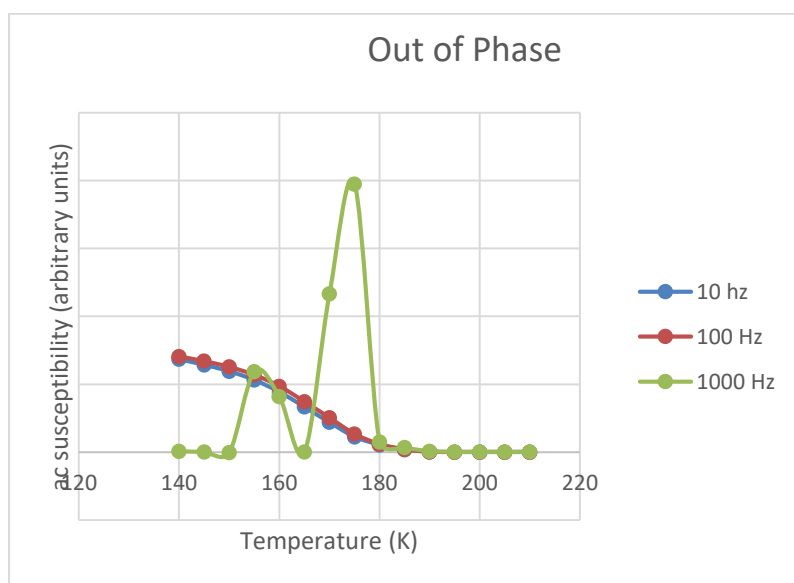
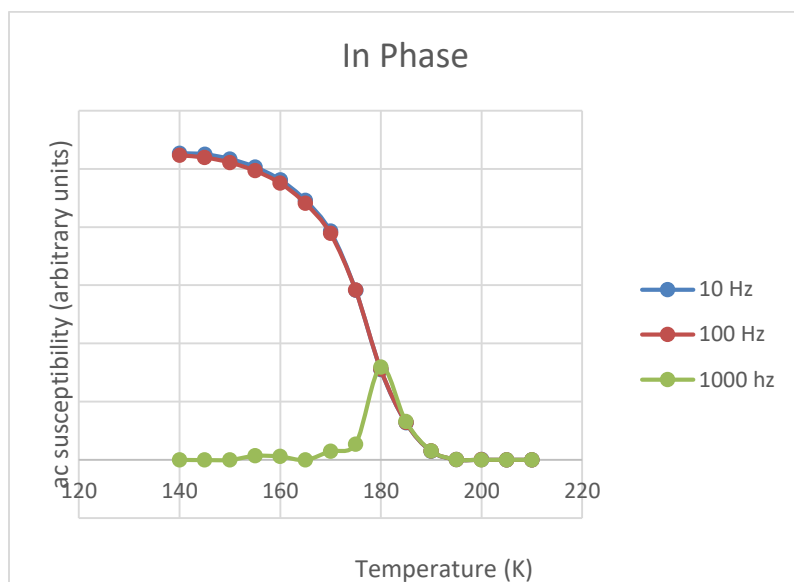


A.4 Ac Susceptibility:

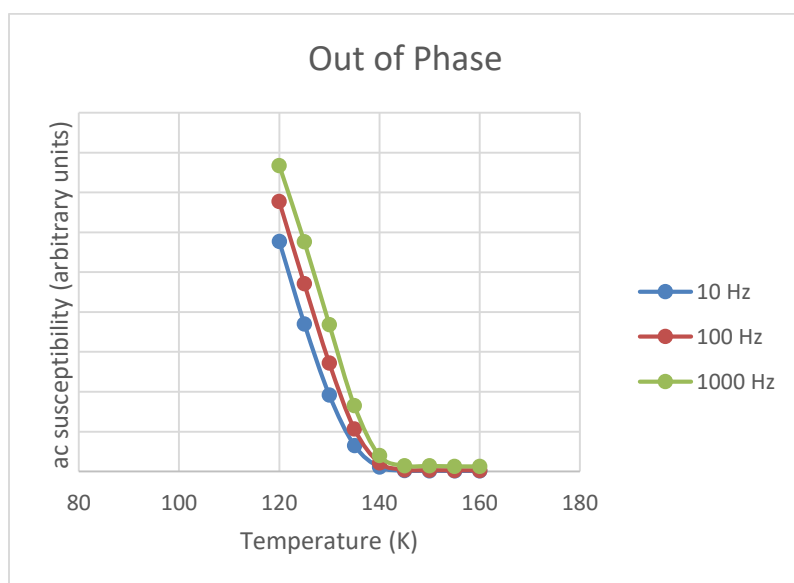
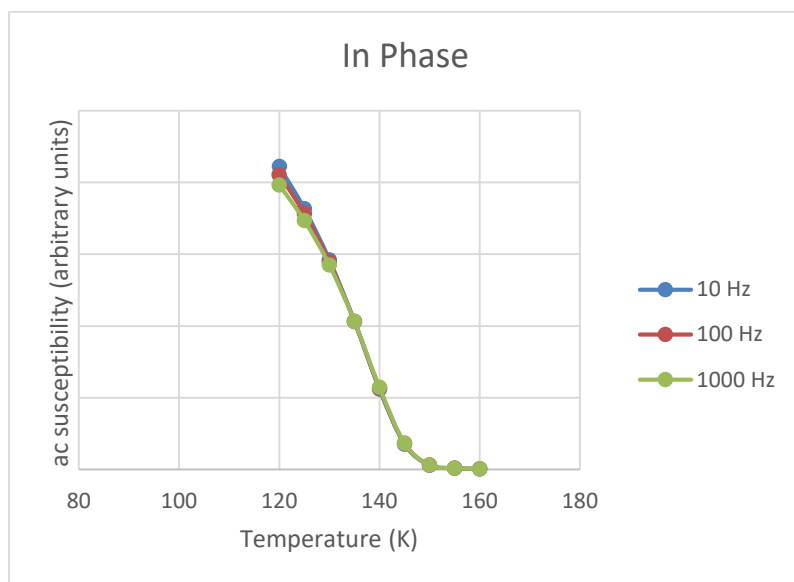
$V(3,5-F_4DCS)_2$



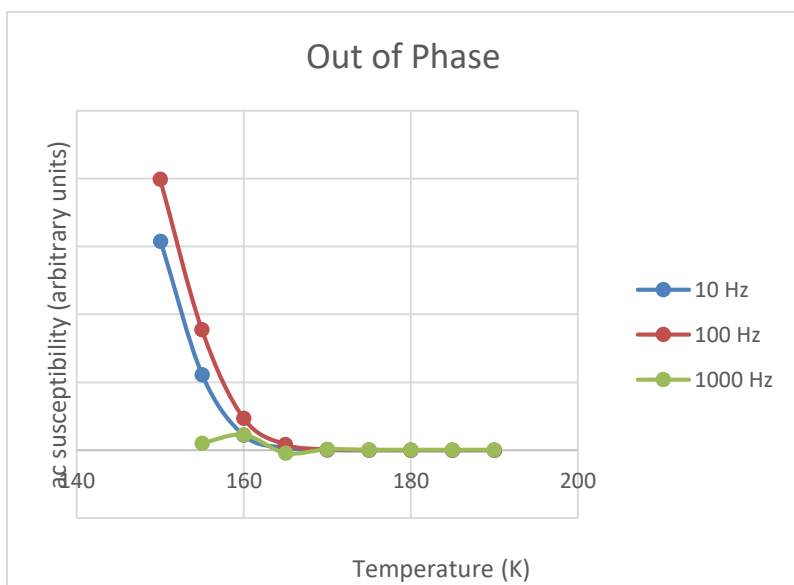
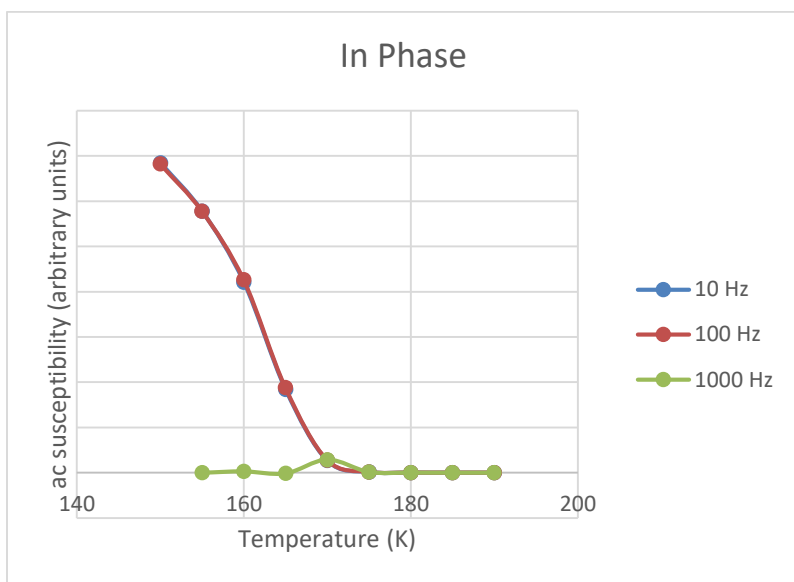
$V(F_6DCS)_2$



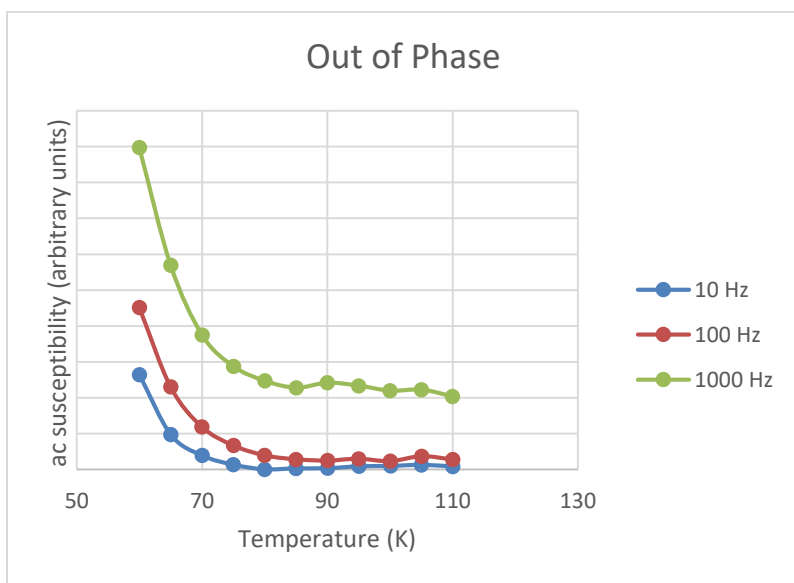
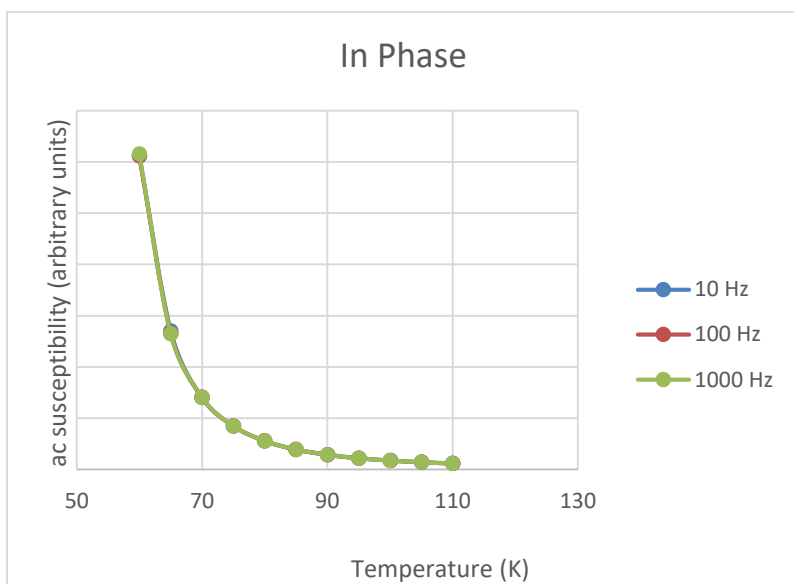
$V(F_8DCS)_2$



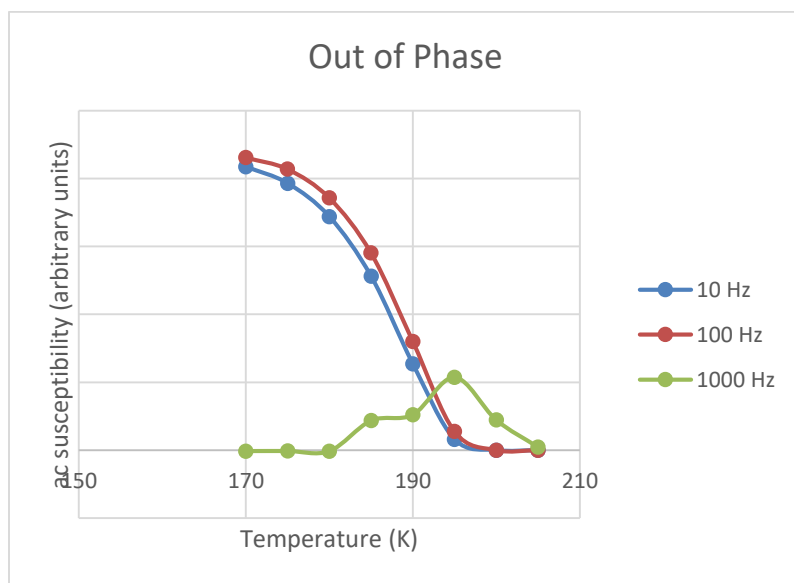
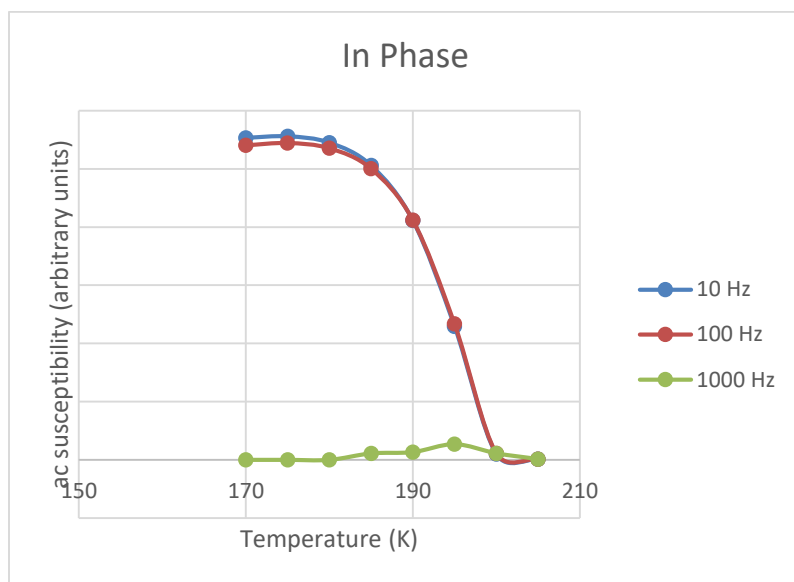
V(1-NTCE)₂



V(2-NTCE)₂

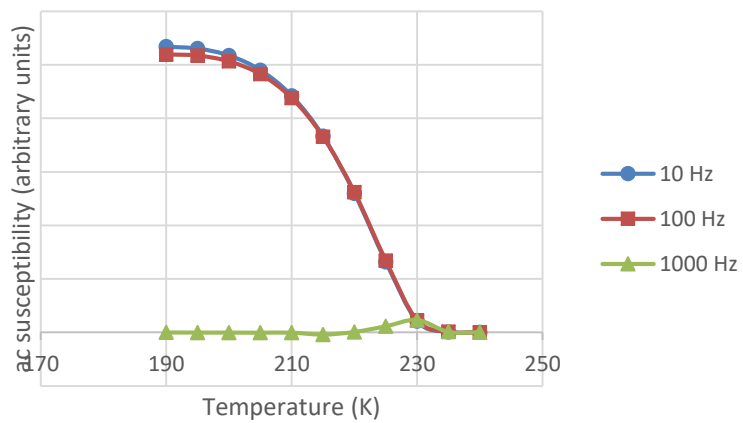


$V(2\text{-BrPTCE})_2$

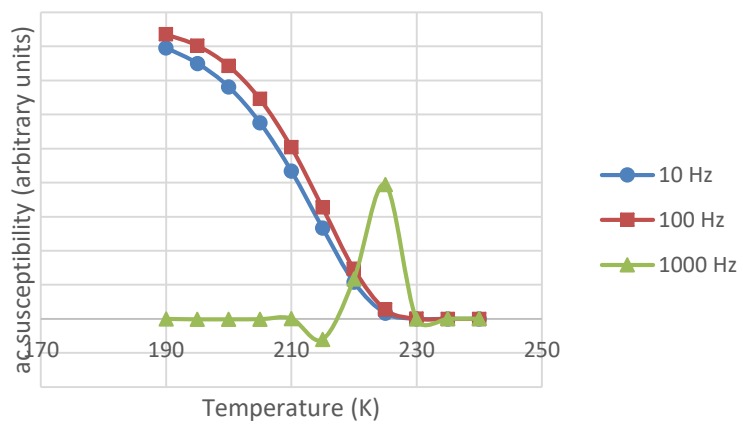


$V(3\text{-BrPTCE})_2$

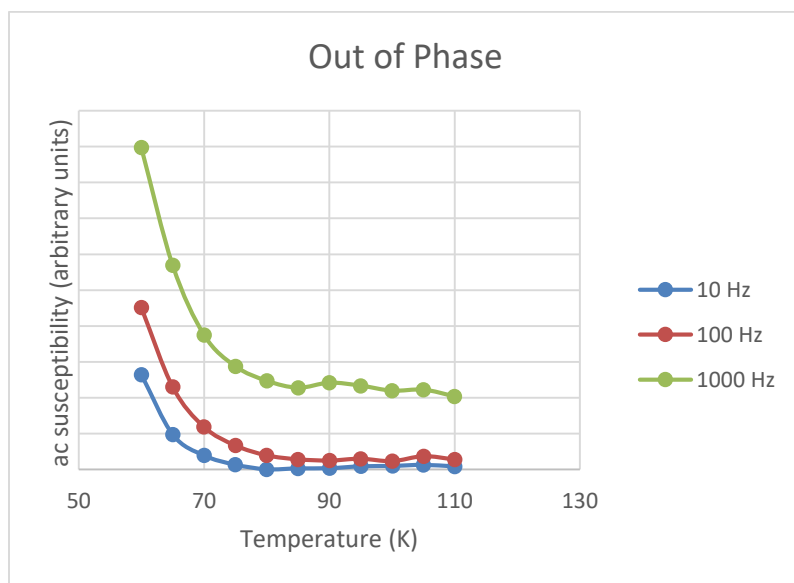
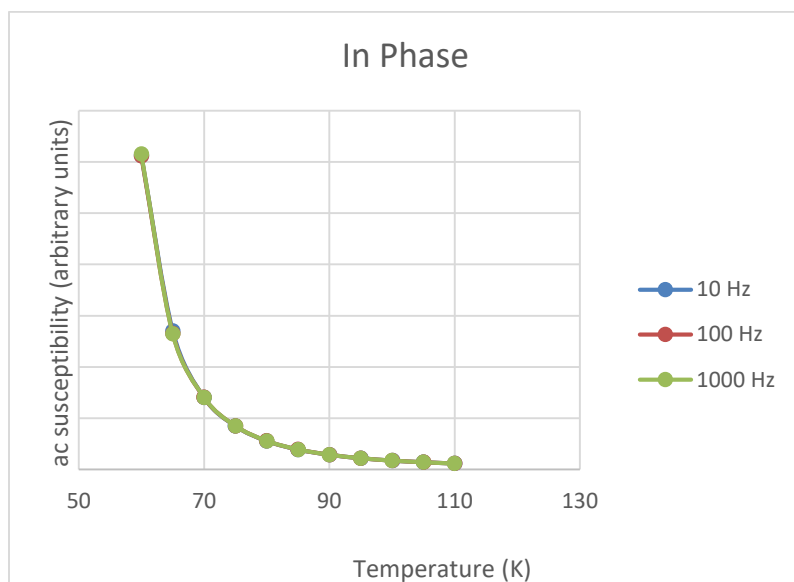
In Phase



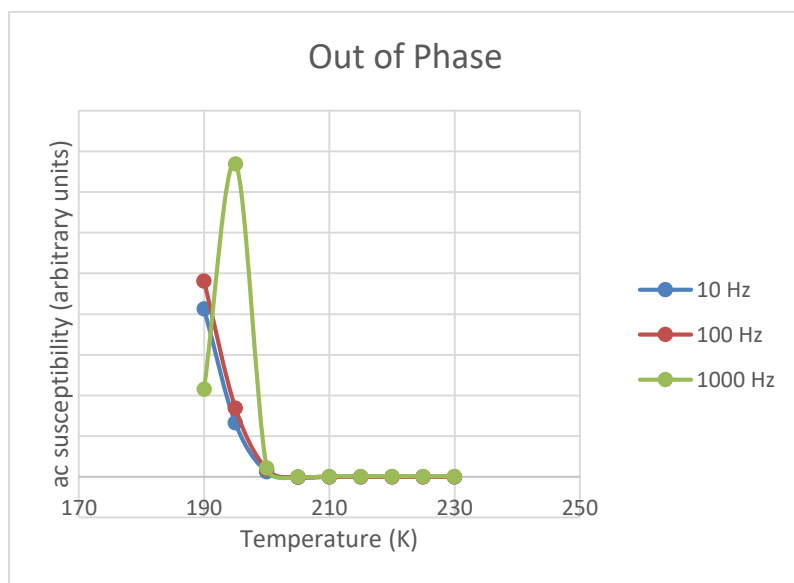
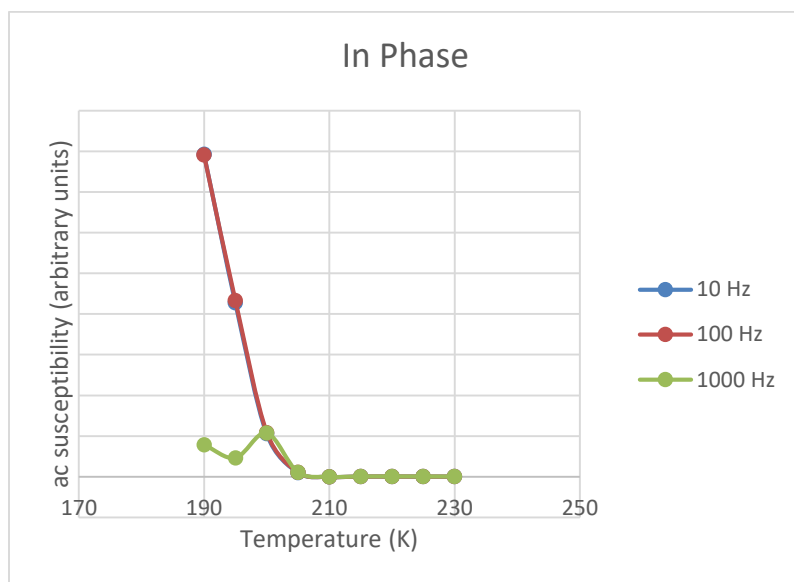
Out of Phase



V(4-BrPTCE)₂

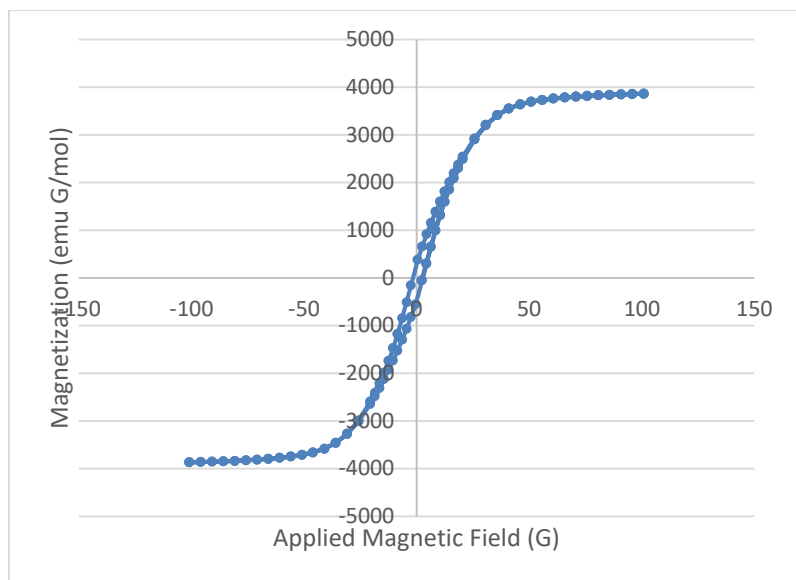


$V(2,6\text{-Br}_2\text{PTCE})_2$

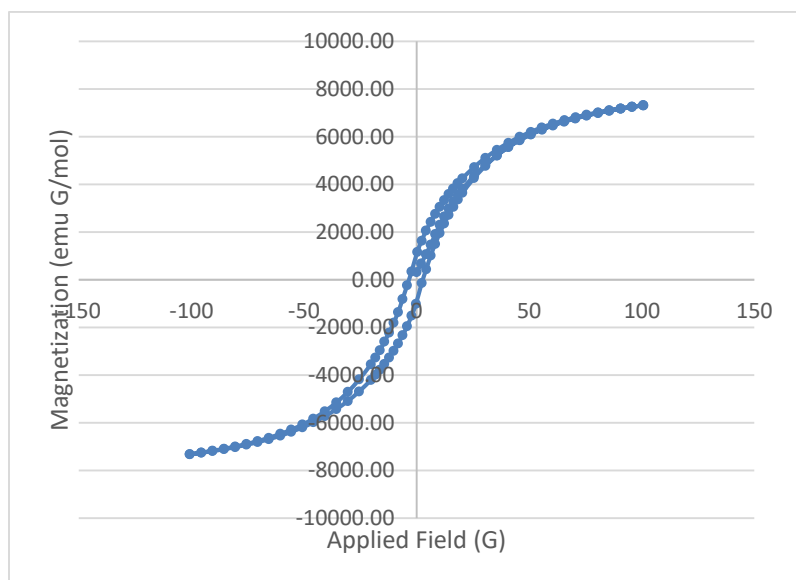


A.5 M vs H:

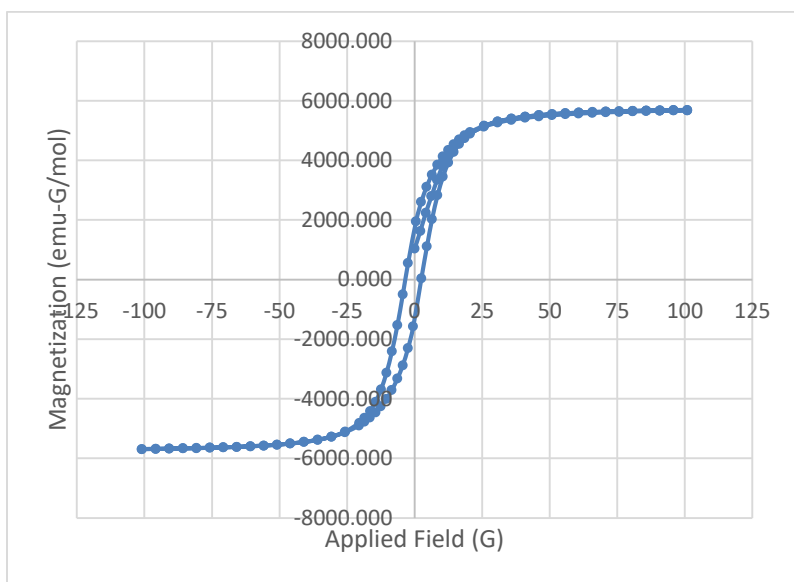
$V(F_6DCS)_2$



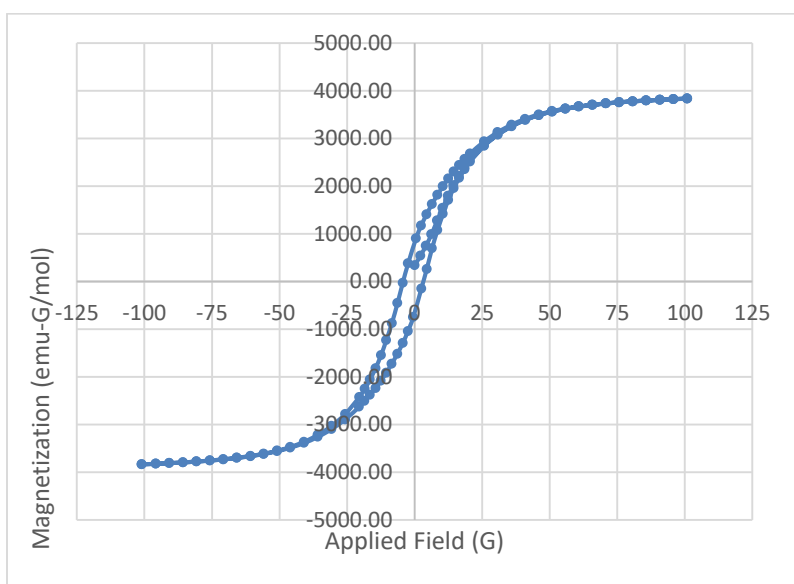
$V(F_8DCS)_2$



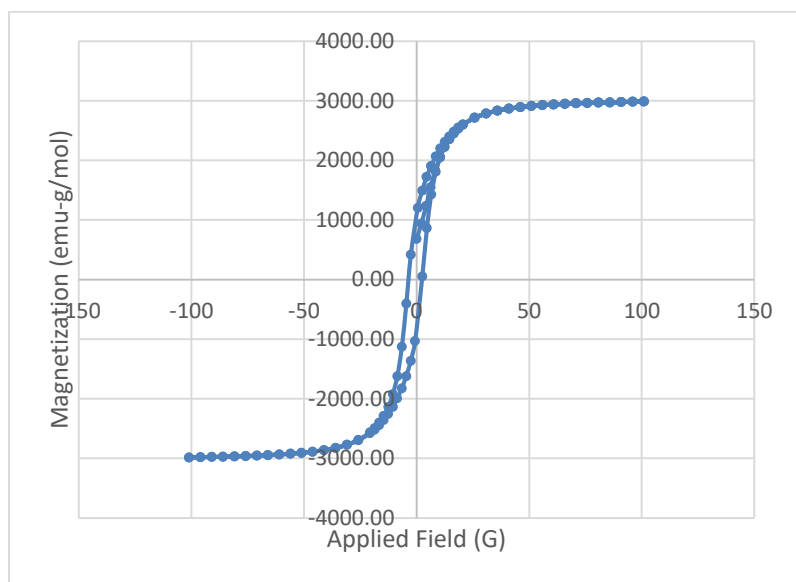
V(2-NTCE)₂



V(2-BrPTCE)₂



V(2,6-BrPTCE)₂



A.6 Extra Information for DCTCS:

A.6.1 Procedures:

Attempt 1:

Under a nitrogen atmosphere, 2,2',6,6'-TCDCS (50.1 mg, 0.136 mmol) dissolved in 2 mL of DCM was added dropwise to vanadium hexacarbonyl (15 mg, 0.068 mmol) dissolved in 2 mL of DCM with stirring. After 1 hour, the solvent was evaporated off and the grey/white precipitate was titrated with 10 mL of ether for 15 min. The precipitate was then collected on a medium frit, rinsed with ether (3 × 2 mL), and dried in vacuo for 1 h. Reaction did not yield magnetic material.

Attempt 2:

Under a nitrogen atmosphere, 2,2',6,6'-TCDCS (50.1 mg, 0.136 mmol) dissolved in 7 mL of THF was added dropwise to vanadium hexacarbonyl (15 mg, 0.068 mmol) dissolved in 3 mL of THF with stirring. After 1 hour, the solvent was evaporated off and the grey/white precipitate was titrated with 10 mL of ether for 15 min. The precipitate was then collected on a medium frit, rinsed with ether (3 × 2 mL), and dried in vacuo for 1 h. Reaction did not yield magnetic material.

A.6.2 Cif file:



CHX6abs_final.cif

A.6.3 Crystal Experimental:

A colorless plate (0.11 x 0.22 x 0.32 mm³) was centered on the goniometer of a Rigaku Oxford Diffraction Gemini E Ultra diffractometer operating with MoK α radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.⁶⁷ The Laue symmetry and systematic absences were consistent with the monoclinic space groups *Cc* and *C2/c*. The

centric space group C2/c was chosen. The structure was solved using SHELXT-2014⁶⁸ and refined using SHELXL-2014⁶⁹ via Olex2.⁷⁰ The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. Olex2 was used for molecular graphics generation.⁷⁰

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