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# **The Synthesis of Ferrocene-Based Ionic Liquids**

Stephen C. Petrochko

Honors Project in Chemistry  
3150: 497-001

A Report on Undergraduate Research in Laboratory of Professor Christopher J. Ziegler to satisfy the Graduation Requirements for the Degree of Bachelor of Science in the field of Chemistry at the Williams Honors College of the University of Akron.

April 25, 2019

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## **The Synthesis of Ferrocene-Based Ionic Liquids**

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*Honors Project in Chemistry [3150:497-001]  
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*Submitted: April 25, 2019*

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### **ABSTRACT**

Ionic liquids are compounds which are held together through ionic interactions, and can be classified as salts. However, while most salts have very high melting temperatures, ionic liquids are a class of compounds that can melt at very low temperatures, often at room temperatures. Ionic liquids can have optimal electronic properties for electrochemical applications, particularly for the easy transport of charges. Some new materials are being explored for the development of ionic liquids; one of these materials is ferrocene. Varying the substituents which are attached to ferrocene may produce a material that can be used as an electrolyte in energy storage devices, particularly in redox-flow batteries (RFBs). Using an ionic liquid as an electrolyte can increase the charge density, as the charged material may be the actual liquid largely undiluted by a solvent such as water. The synthesis and characterization of a series of ferrocene based ionic compounds is discussed in this study. These compounds contain bis-ferrocene sulfonates as the anion, with 1-alkyl-3-methylimidazolium species as cations, where the alkyl groups are: methyl, pentyl, hexyl, octyl, decyl, and dodecyl. These salts have been synthesized successfully, and are characterized by methods including infrared (IR) spectroscopy,

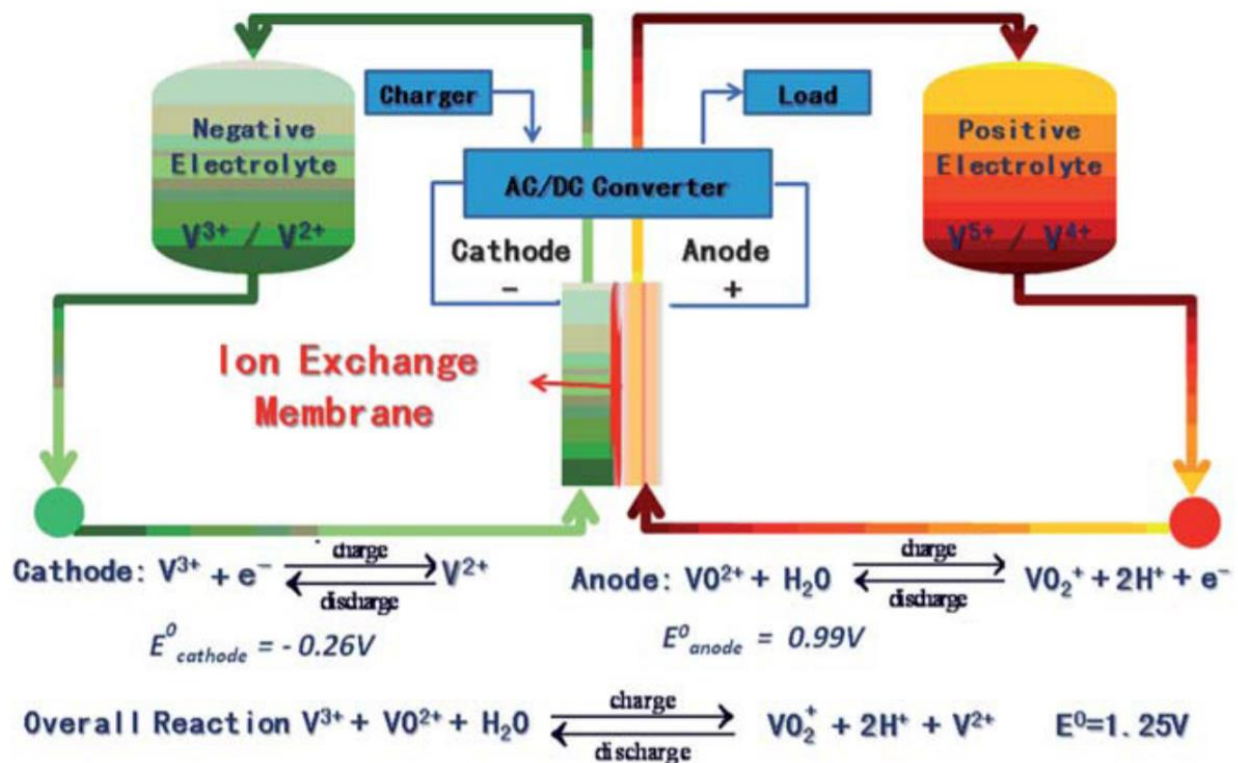
proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR), and carbon nuclear magnetic resonance spectroscopy ( $^{13}\text{C}$  NMR); additionally, some crystal structures were obtained. The electrochemical analyses were conducted by the collaborating research group of Professor Aliaksei Boika.

## **INTRODUCTION**

In recent years, demand for energy sources has been increasing, and it is desirable to use renewable sources of energy.<sup>1</sup> This demand is the product of concerns about pollution of the atmosphere that is caused by the combustion of traditional carbon-based fuels.<sup>2,3</sup> Among the competitors for energy sources that could supplement or even replace fuels such as coal and oil is solar energy.<sup>4</sup> Solar energy is an abundantly available resource; however technical obstacles prevent immediate large-scale implementation of solar energy, aside for economic considerations.<sup>5</sup> One of the foremost difficulties to incorporating solar energy is the irregularity of the power supply; night, clouds, and other variations limit the reliability of this source. Carbon-based storage of energy doesn't have this particular limitation as the energy is stored in the form of a chemical bond, thus containing the energy in a portable material. In order to overcome this limitation, some form of energy storage is necessary; the natural method to store energy from photovoltaics is to use a battery, of which redox flow batteries (RFBs) are a viable type.

Redox flow batteries are a type of wet-cell battery that were first developed by the National Aeronautics and Space Administration (NASA) in the 1970s.<sup>6</sup> RFBs, like other electrochemical cells, utilize the changing of the oxidation state of a material as a method to store voltage.<sup>7</sup> RFBs are also capable of utilizing only one material as its electrolyte, i.e. the

anolyte and catholyte can be different oxidation states of the same material.<sup>8</sup> Currently, the industry standard substance to use in a RFB are vanadium based materials.<sup>9,10</sup> However, the vanadium based systems have a low energy density.<sup>11</sup> New materials are being explored to see if the energy density can be increased. One approach is to use salts, such as ionic liquids, as the electrolyte.



**Figure 1.** A sample layout of a redox flow battery. Note that different oxidation states of the same starting material can be present on either side of a semi-permeable membrane. Image source: *Ion Exchange Membranes for Vanadium Redox Flow Battery (VRB) Applications*.<sup>12</sup>

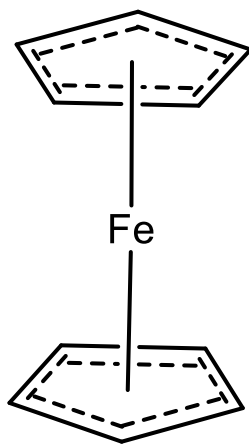
The two most common classifications of chemical bonding are covalent bonds and ionic bonds. Covalent bonding occurs when two atoms share their electron density, whereas ionic interactions result from electrostatic attraction between two or more oppositely charged species. Ionic compounds, or salts, generally have very high melting temperatures.<sup>13</sup> These high melting

temperatures reflect very strong interactions between the component species, as more energy is required to change the constituents from a tightly held lattice in the solid state, to the liquid state where the particles are capable of moving more freely. However, the high melting temperature is also due to the efficient packing; if bulky ions are used, then the packing would not be as efficient, and the melting temperature would be reduced.<sup>14</sup> Salts whose melting temperature is near room temperature are known as ionic liquids.

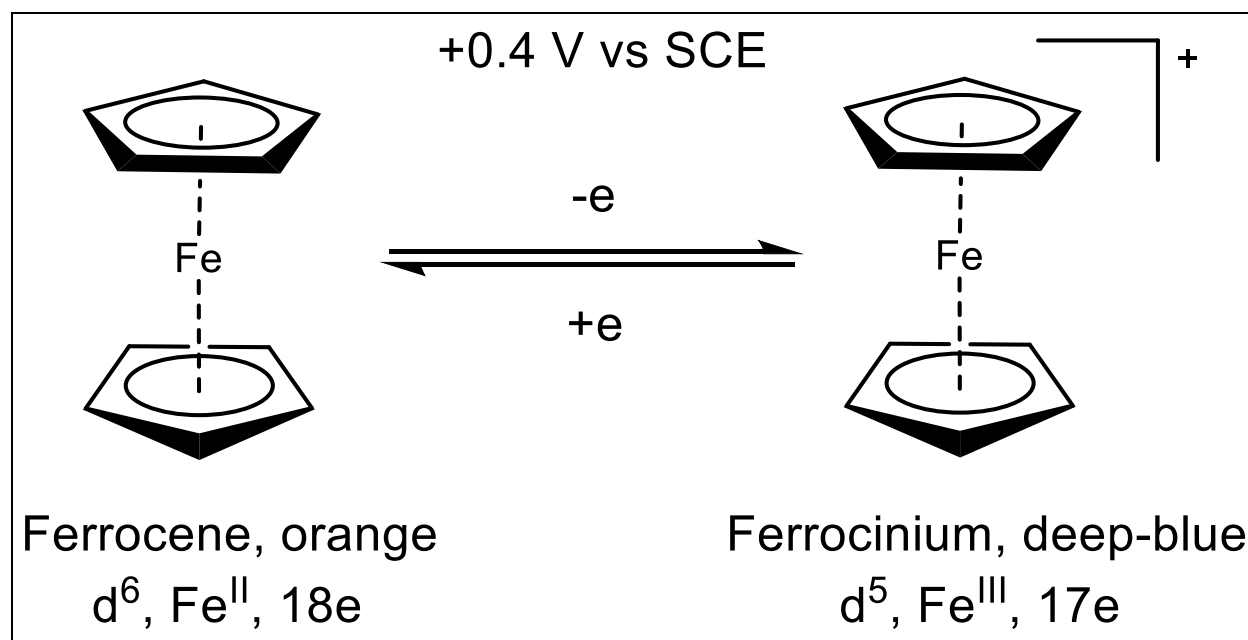
Ionic liquids (ILs) have very interesting properties. Typically, in patent and academic literature, a substance can be referred to as an ionic liquid if the melting temperature is around or below 100° C.<sup>15</sup> They are polar alternatives to aqueous solutions, and immiscible in many organic solvents, as well as having such a low vapor pressure that it is negligible; as a result, ILs are liquids that do not evaporate.<sup>16</sup> Using ILs as an electrolyte in a RFB may be possible.<sup>17,18</sup> This would increase the charge density of the electrolyte compared with dissolved species, as little or no solvent would be necessary, thus increasing the concentration of redox active species, as the presence of solvent dilutes the charges species. One substance which may yield successful redox active compounds is ferrocene; this organometallic material has already been observed to be a good material for the synthesis of ILs and specifically in Redox Active Ionic Liquids (RAILs).<sup>19,20,21</sup>

Ferrocene is both an organometallic and metallo-organic compound; organometallic compounds are substances where a metal or metal ion is directly attached to a carbon.<sup>22</sup> Ferrocene, a yellow-orange substance, is an organometallic compound where an iron (II) is bound to two aromatic cyclopentadienyl rings; it was first isolated in 1951 by Kealy and Pauson.<sup>23</sup> However, the correct structure of ferrocene was discovered about a year subsequently, by Geoffrey Wilkinson.<sup>24</sup> Ferrocene is an organometallic sandwich compound and similar

compounds include such substances as cobaltocene and chromocene.<sup>25,26,27</sup> However, these compounds are not as stable as ferrocene, which is stable in air, thus making ferrocene the more ideal material for ease of manipulation in the laboratory.<sup>28,29</sup> Additionally, if any material were developed that could be used on an industrial scale, it would be necessary that the material be stable to the atmosphere.



**Figure 2.** The structure of ferrocene. Note that the iron (II) binds via d-orbital interactions to all 10 carbons.<sup>30</sup> This image abbreviates this by showing the iron attached to the center of the aromatic cyclopentadienyl rings, with eclipsed conformation shown.



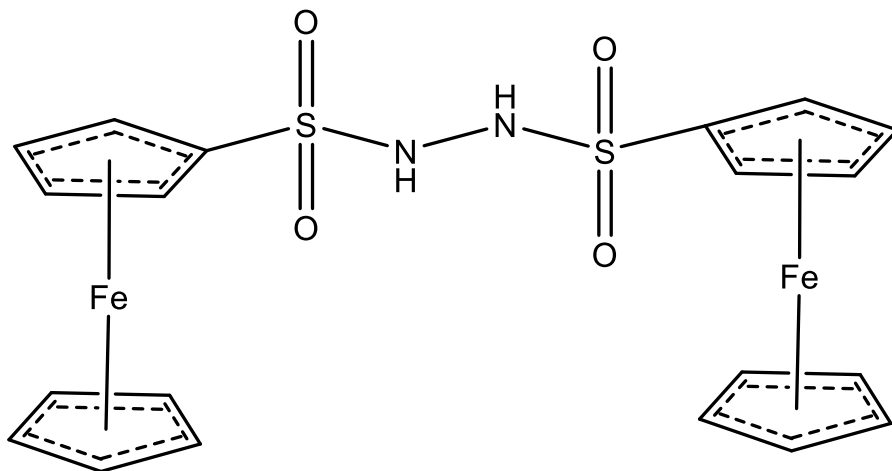
**Figure 3.** The reversible oxidation and reduction of ferrocene. Image adapted from *Why Is Ferrocene so Exceptional?*<sup>31</sup>

Ferrocene by itself can be reversibly oxidized and reduced.<sup>32</sup> Although it is possible that several oxidation states are possible to achieve, ferrous iron (II) and ferric iron (III) are by far the most common oxidation states, which yield a charge of 0 and +1, respectively.<sup>33,34,35</sup> In principle, this means that ferrocene alone could be used as an electron storage unit in a RFB. However, there are notable limitations to such a method. The tendency for a substance to be oxidized or reduced is described by the standard reduction potential for comparisons of different species.<sup>36,37,38</sup> Ferrocene, often abbreviated as Fc, has a redox potential of  $\text{Fc}^+/\text{Fc}^0$  of  $E^0 = +400$  mV with respect to the normal hydrogen electrode (NHE).<sup>39</sup> This is not incredibly large, and it would be desirable for battery applications if this redox potential could be increased, to increase the overall voltage of a RFB. Additionally, ferrocene alone is known to have low solubility in aqueous media.<sup>40</sup> Since water is a readily available, cheap, and non-toxic solvent, any new

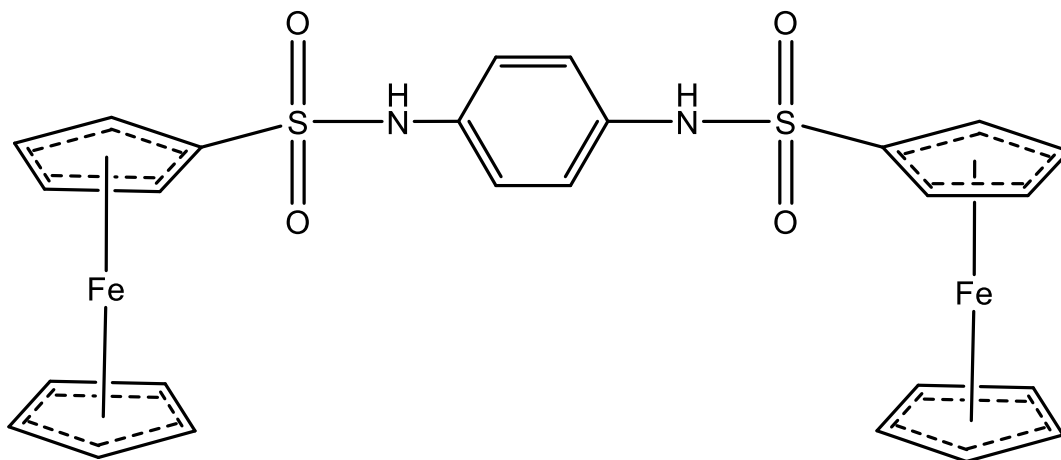


electroactive material should be water soluble. Attaching polar substituents to one or both of the cyclopentadienyl rings may increase its solubility, or have its viscosity lowered by, water; sulfonyl substituents may fit this purpose.

It may be possible to link together more than one ferrocene into one molecule.<sup>41,42</sup> An advantage of this would be that more than one iron would be present, possibly allowing for more than one oxidation per molecule. If this is successful, the number of electrons that could be contributed into an electrochemical cell would be larger, thus increasing the total energy density of a RFB. Synthetically, such a dimerization would likely require a bridge, such as a sulfonamide.<sup>43</sup> If such a synthesis were successful, then it might be possible to use electrochemical analysis, such as cyclic voltammetry, to observe a single oxidation, a double oxidation, or a mixed valence state, where the oxidation of one ferrocene alters the voltage of the second.



**Figure 4.** The hypothetical structure of a sulfonamide hydrazine bridged ferrocene dimer. If able to dimerize a ferrocene structure, then greater electron density could be achieved for a battery electrolyte.

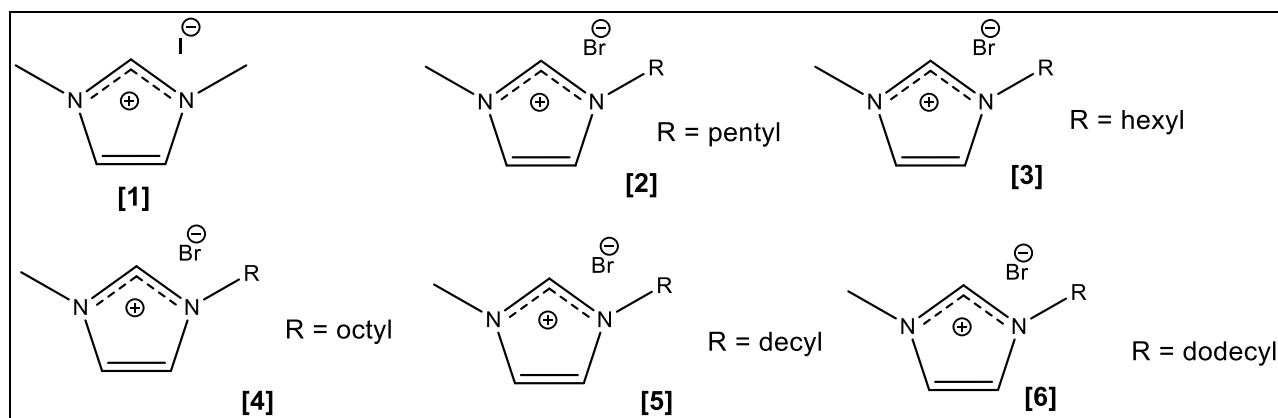


**Figure 5.** A hypothetical structure of a sulfonamide bridged ferrocene dimer with a conjugated  $\pi$  system in the bridge. If such a product can be produced, then it may be possible to observe 2 distinct oxidation events, or a mixed valence system by electrochemical analysis.

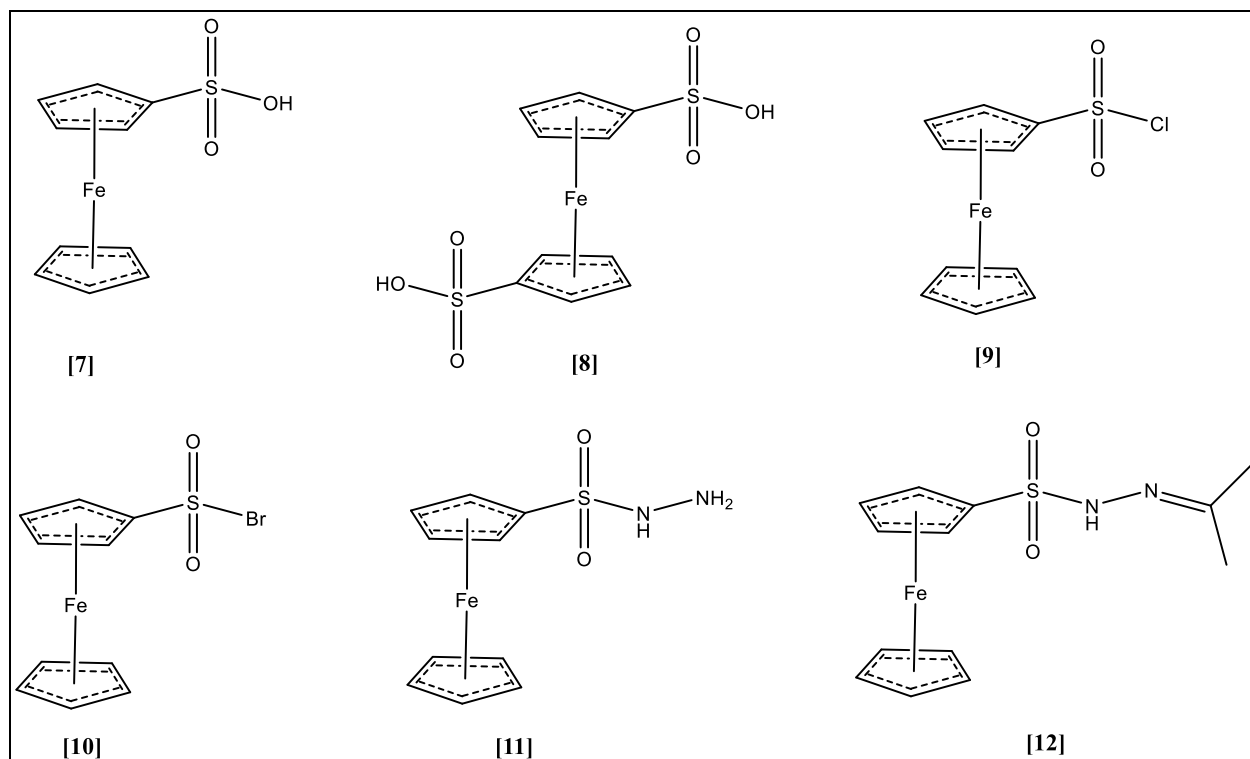
If the synthesis of a ferrocene dimer is not successful, then it is possible to use the ferrocene sulfonyl group as a component in an ionic species. The ferrocene sulfonyl group could be modified into a sulfonate group. Changing the substituents on a ferrocene is known to have an effect upon its redox potential.<sup>44</sup> It may be that preparing a ferrocene containing salt could exhibit good redox properties such as optimal potentials and good reversibility. Preparing a series of salts could be a beneficial to analyze if any alterations to the structural motif of the compound would yield a material that would have optimal electrochemical properties for a RFB.

To prepare a salt, both anionic and cationic species are necessary. Ferrocene sulfonate or bis-ferrocene sulfonates can be used as anions. For cations, imidazolium species will be considered; imidazolium cations are known to have been used successfully in the synthesis of ILs.<sup>45</sup> 1-Methylimidazolium cations can be prepared with alkyl chains of varying length. By preparing several imidazolium species, each with a different length alkyl chain, a series of salts can be synthesized, characterized, and electrochemically tested for their viability in an

electrochemical cell. This viability is determined by several factors including the overall redox potential, as well as the reversibility of the oxidation and reduction.

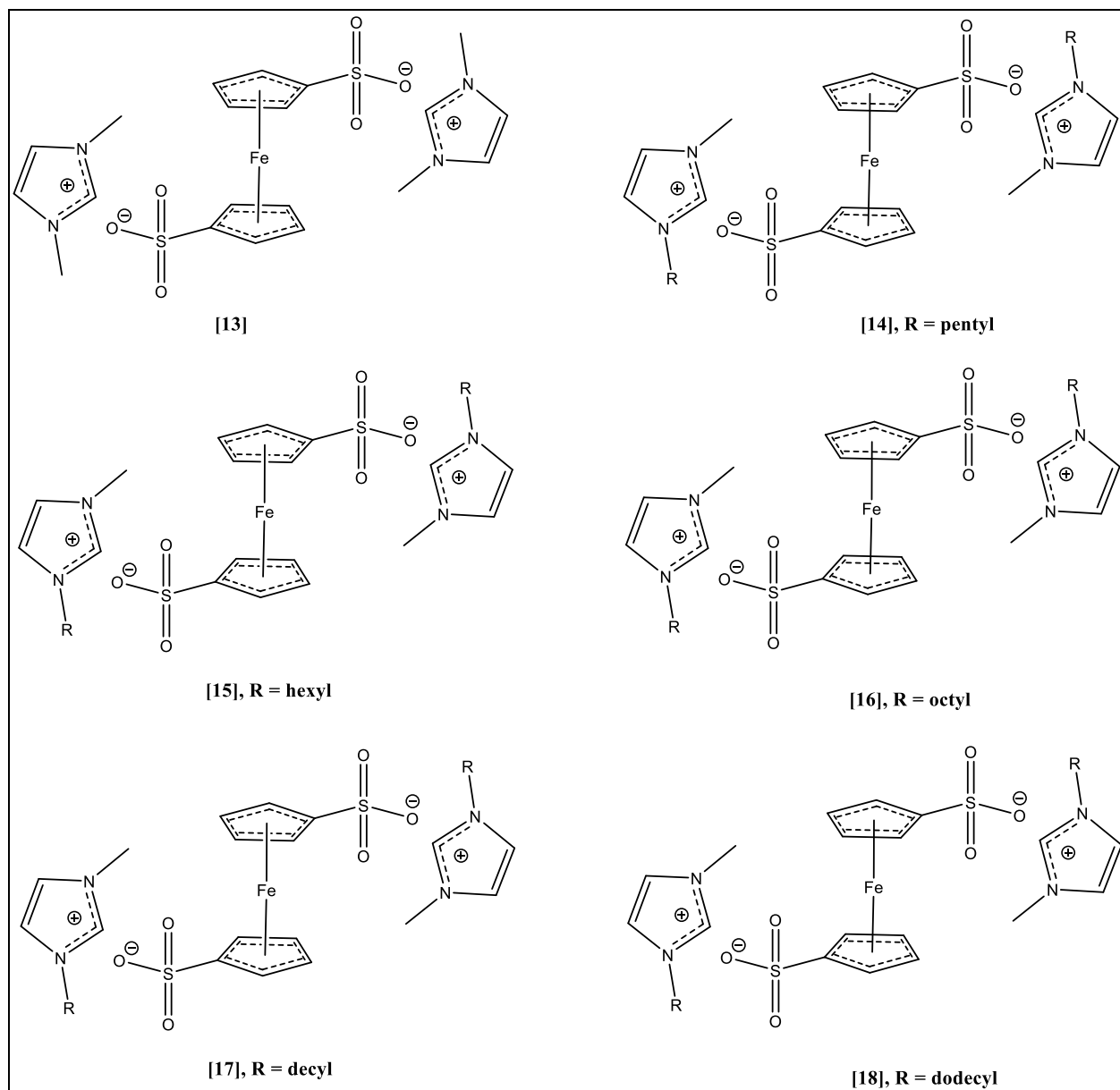


**Scheme 1.** Compounds **1-6**, which are 1-alkyl-3-methylimidazolium halides.



**Scheme 2.** Compounds **7-12**, which are the ferrocene species used. Note that the series of bis-1-alkyl-3-methylimidazolium salts are synthesized with the twice deprotonated form of compound

**8.**



**Scheme 3.** Compounds **13-18**, which are bis-1-alkyl-3-methylimidazolium ferrocene sulfonate salts.

Reversibility of oxidation and reduction is an attribute which is crucial to any material for a rechargeable battery. Reversibility can be measured easily by cyclic voltammetry.<sup>46</sup> In cyclic

voltammetry, a substance is exposed to a variable voltage scan, and the resultant current is measured.<sup>47</sup> Consequently, as graphical analysis of this process plots current with respect to electrochemical potential, or voltage, these plots are referred to as cyclic voltammograms.<sup>48</sup> If both an oxidation peak and a reduction peak are present, then this indicates that the substance being tested has reversible redox characteristics. Additionally, cyclic voltammetry can be used to detect if multiple oxidations can occur, as well as detecting the possible presence of a mixed valence state.

## **EXPERIMENTAL**

The synthesis methodologies used were based upon previous work in the Ziegler Research Group of the University of Akron, particularly on the synthesis of bis-ferrocene sulfonic acid.<sup>49,50</sup> Synthesis of mono-ferrocene sulfonic acid was derived from technique published by Slocum *et al.*<sup>51</sup> Synthesis of 1-alkyl-3-methylimidazolium bromides were derived from technique published by Bhosale *et al.*<sup>52</sup>

The following materials utilized were used as received, without additional purification. Ferrocene and chlorosulfonic acid were obtained from Acros Organics, 1-methylimidazole and PCl<sub>5</sub> were obtained from BeanTown Chemical, silver (I) oxide was obtained from Aldrich. The solvents used were stored with 4 Å molecular sieves. Borosilicate glassware was employed in all syntheses.

The spectroscopic techniques utilized included FT-IR spectroscopy, <sup>1</sup>H NMR spectroscopy, <sup>13</sup>C NMR spectroscopy, UV-visual spectroscopy, and X-ray crystallography. The infrared measurements were obtained by a ThermoScientific Nicolet iS5 FTIR Spectrophotometer. The NMR spectra were obtained from Varian 300 MHz, and 500 MHz

instruments. The UV-visual spectra were obtained from a Varian Cary 100 Bio UV-Visual Spectrophotometer. Crystal structures were obtained by single crystal X-ray diffraction using Bruker APEX X-ray diffractometer.

Samples of compounds **13-18** were provided to Dr. Aliaksei Boika for electrochemical analysis. The analyses consisted of conducting measurements utilizing a CH Instruments CHI 920d cyclic voltammetry apparatus.

**Synthesis of ferrocene sulfonyl chloride, [Compound 9].** This synthesis was based on previously published work.<sup>51</sup> Ferrocene (5.0 g, 27 mmol) was dissolved in ~100-150 mL of diethyl ether in an Erlenmeyer flask with a magnetic stir bar, which was placed in an ice water bath and allowed to cool while stirring. Chlorosulfonic acid (2.0 mL, 30 mmol) was added dropwise, covering the top of the flask with paper to prevent splattering. The flask was removed from the ice water bath, and the solution was stirred for approximately 48 hours. To this ether mixture, PCl<sub>5</sub> (3.6 g, 17.3 mmol) was added, and stirred overnight. The mixture was transferred to a large beaker and quenched of any remaining PCl<sub>5</sub> by the addition of ~100-200 mL ice water. The less dense organic layer was removed, and placed into a separation funnel. The mixture was washed thrice with water, and once with brine, the aqueous layer being removed after each washing. The organic portion was removed and dried with anhydrous MgSO<sub>4</sub> drying agent. After filtration, the excess volatiles were removed with a rotary evaporator. The resulting solid, dark orange in color, was stored in a desiccator. Yield for this product was around 1.53 g (20%). IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3113 (CH), 1375 (S=O), 1202, 1141, 1109, 1031, 1015, 1000, 832, 817, 584.

**Synthesis of ferrocene sulfonyl hydrazine, [Compound 11].** This synthesis was based on previously published work.<sup>53</sup> Ferrocene sulfonyl chloride (1.0 g, 5.4 mmol) was dissolved in methanol. Hydrazine monohydrate,  $\text{H}_2\text{NNH}_2\cdot\text{H}_2\text{O}$  (0.855 mL, 17.6 mmol) was added. The mixture was stirred for around 2 days at room temperature. Excess volatiles were removed with a rotary evaporator; the resulting dark solid was stored in a desiccator.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  7.1 (s), 4.3 (s, 2H), 4.2 (s, 5H), 4.1 (s, 2H); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3255, 3098, 3029, 2952 (CH), 1602 (C-N), 1505, 1419, 1163, 1106, 1046, 1014, 966, 818, 648.

**Synthesis of ferrocene sulfonyl bromide, [Compound 10]:** Ferrocene sulfonyl hydrazine (0.40 g, 1.4 mmol) was stirred in a round bottom flask at  $0^\circ\text{C}$  with a few milliliters of chloroform as solvent. Liquid bromine (0.37 mL, 7.1 mmol) was added in excess, approximately 5 equivalents. The mixture was stirred overnight.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  4.3-4.1 (t), 2.5 (s); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3247, 3091 (CH), 1652 (aromatic CH), 1575, 1179, 1106, 1063, 055, 1024, 1015, 961, 839, 813, 658, 647.

**Ferrocene sulfonyl hydrazine acetone, [Compound 12]:**  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  4.3 (s, 2H), 4.2 (d, 5H), 4.1 (d, 2H), 2.3 (d), 1.8 (d, 6H), 1.1 (m); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3366, 2975 (CH), 2491, 1647 (C=N), 1381, 1334 (S=O), 1225, 1172, 1063, 983, 879, 838, 664.

**Synthesis of bis-ferrocene sulfonic acid, [Compound 8].** Ferrocene (1.0 g, 5.4 mmol) was dissolved in ~100 mL of acetic anhydride in an Erlenmeyer flask with a magnetic stir bar, which was placed in an ice water bath and allowed to cool while stirring. Chlorosulfonic acid (0.80 mL, 12 mmol) was added dropwise. The flask was removed from the ice water bath, and the solution

was stirred for approximately 48 hours. The green-yellow precipitate, presumably the desired product, was removed by vacuum filtration connected with a water aspirator, allowed to dry, and stored in a desiccator in a refrigerator. The yields were high, near 100 %. The excess filtrate was safely disposed.

**Synthesis of 1,3-dimethylimidazolium iodide, [Compound 1].** Methylimidazole (0.971 mL, 12.2 mmol) was placed in a small round bottom flask with a magnetic stir bar. Iodomethane (0.84 mL, 13 mmol) was added in slight excess (about 1.1 equivalents); acetonitrile was used as reflux solvent. The mixture was connected to a water-cooled reflux condenser, and brought to ~70-80°C, and stirred for approximately 48 hours. The mixture was removed from heat, and excess volatiles were removed with a rotary evaporator. The product was stored in a desiccator in a refrigerator. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ<sub>H</sub> 9.1 (s, 1H), 7.7 (m, 2H), 3.9-3.8 (m, 6H), 3.4-3.3 (m).

**Synthesis of 1-pentyl-3-methylimidazolium bromide, [Compound 2].** Methylimidazole (0.971 mL, 12.2 mmol) was placed in a small round bottom flask with a magnetic stir bar. 1-Bromopentane (1.66 mL, 12.9 mmol) was added in slight excess (about 1.1 equivalents); acetonitrile was used as reflux solvent. The mixture was connected to a water-cooled reflux condenser, and brought to ~70-80°C, and stirred for approximately 48 hours. The mixture was removed from heat, and excess volatiles were removed with a rotary evaporator. The product was stored in a desiccator in a refrigerator. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ<sub>H</sub> 9.3 (s, 1H), 7.8-7.2 (d, 2H), 4.2 (t, 2H), 3.9 (s, 3H), 1.7 (m, 2H), 1.1 (d, 4H), 0.7-0.6 (m, 3H).



**Synthesis of 1-hexyl-3-methylimidazolium bromide, [Compound 3].** Methylimidazole (0.971 mL, 12.2 mmol) was reacted with slight excess of 1-bromohexane (2.21 g, 13.4 mmol) in identical method to the reaction with 1-pentyl-3-methylimidazolium bromide. Yield for this reaction was about 2.87 g (95 %);  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  10.0 (s, 1H), 8.4-8.3 (d, 2H), 6.2 (s), 4.7 (m, 2H), 4.3 (s, 3H), 4.1 (s), 2.1 (s, 2H), 1.5 (s, 6H), 1.1 (m, 3H).

**Synthesis of 1-octyl-3-methylimidazolium bromide, [Compound 4].** Methylimidazole (0.971 mL, 12.2 mmol) was reacted with 1-bromooctane (2.58 g, 13.4 mmol) in identical method to the reaction with 1-pentyl-3-methylimidazolium bromide.

**Synthesis of 1-decyl-3-methylimidazolium bromide, [Compound 5].** Methylimidazole (0.971 mL, 12.2 mmol) was reacted with 1-bromodecane (2.96 g, 13.4 mmol) in identical method to the reaction with 1-pentyl-3-methylimidazolium bromide.

**Synthesis of 1-dodecyl-3-methylimidazolium bromide, [Compound 6].** Methylimidazole (0.971 mL, 12.2 mmol) was reacted with 1-bromododecane (3.34 g, 13.4 mmol) in identical method to the reaction with 1-pentyl-3-methylimidazolium bromide. Yield for this reaction was around 0.929 g (23 %);  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  9.6 (s, 1H), 7.9-7.8 (m, 2H), 4.2 (m, 2H), 3.9 (s, 3H), 3.4 (s, 1H), 2.0 (s, 3H), 1.8-1.7 (t, 2H), 1.1 (s, 21H), 0.8-0.7 (t, 3H).

**Synthesis of bis-1,3-dimethylimidazolium ferrocene sulfonate, [Compound 13].** Bis-ferrocene sulfonic acid (0.50 g, 1.4 mmol) was placed into a round bottom flask that is covered with aluminum foil, along with a magnetic stir bar. Silver oxide (0.34 g, 1.4 mmol) was added to the flask, and a small quantity of methanol, ~5-10 mL (which has been stored with 4 Å molecular sieves), was added. This mixture was stirred for approximately 5-15 minutes at room temperature. 1,3-Dimethylimidazolium iodide (0.65 g, 2.9 mmol) was added to the still-covered flask. The mixture was stirred for approximately 48 hours, also at room temperature. The mixture was filtered by gravity filtration to remove the gray precipitate, which was presumably silver iodide, washing with some extra methanol if necessary to fully collect the brown colored filtrate. Excess volatiles were removed from the filtrate via a rotary evaporator. Some samples required to have additional time uncovered in the fume hood to remove all excess volatile compounds. The product, which was a low melting temperature substance, was stored in a desiccator in a refrigerator. Yield: 0.781 g, 207 %;  $^1\text{H}$  NMR (DMSO- $d_6$ , 300 MHz):  $\delta_{\text{H}}$  9.2 (s, 2H), 7.7 (s, 4H), 4.3 (s, 2H), 4.1 (s, 2H), 3.9 (s, 12H), 1.6 (s);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta_{\text{C}}$  173.5 (s), 138.0-137.8 (m), 128.5 (s), 123.6 (s), 120.6 (s), 97.2 (s), 70.5 (s), 68.1 (s), 40.0-39.2 (m), 35.8 (s), 32.9 (s), 26.2 (s); UV-vis (DMSO):  $\lambda_{\text{max}}$  410 nm; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3447, 3149, 3090, and 3041 (CH), 1786, 1700, 1652 (C=N), 1575 (aromatic CH), 1471, 1389, 1342 (S=O), 1172, 1059, 1039, 1025, 1009, 856, 832, 822, 777, 717, 647, 622, 558.

**Synthesis of bis-1-pentyl-3-methylimidazolium ferrocene sulfonate, [Compound 14].** Bis-ferrocene sulfonic acid (0.50 g, 1.4 mmol) was placed into a round bottom flask that was covered with aluminum foil, along with a magnetic stir bar. Silver oxide (0.34 g, 1.4 mmol) was added to the flask, and a small quantity of methanol, ~5-10 mL (which has been stored with 4 Å molecular sieves), was added. This mixture was stirred for approximately 5-15 minutes at room temperature. 1-Pentyl-3-methylimidazolium bromide (0.68 g, 2.9 mmol) was added to the still-covered flask. The mixture was stirred for approximately 48 hours, also at room temperature. The mixture was filtered by gravity filtration to remove the gray precipitate, which was presumably silver iodide, washing with some extra methanol if necessary to fully collect the brown colored filtrate. Excess volatiles were removed from the filtrate via a rotary evaporator. Some samples required to have additional time uncovered in the fume hood to remove all excess volatile compounds. The product, which was a low melting temperature substance, was stored in a desiccator in a refrigerator. Yield: 0.664 g, 146 %;  $^1\text{H}$  NMR (DMSO- $d_6$ , 300 MHz):  $\delta_{\text{H}}$  9.2 (s, 2H), 7.8-7.7 (d, 4H), 4.3 (s, 4H), 4.1 (m, 8H), 3.9 (s), 3.6-3.4 (m), 3.2 (s), 2.5 (s), 2.0-1.9 (m), 1.8 (s, 4H), 1.3 (s, 12H), 0.9 (s, 6H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta_{\text{C}}$  137.6 (s), 124.0-122.5 (d), 97.1 (s), 70.5 (s), 68.1 (s), 49.0 (s), 40.2-39.2 (m), 36.3 (s), 29.3 (s), 27.8 (s), 21.7 (s), 13.9 (s); UV-vis (DMSO):  $\lambda_{\text{max}}$  410 nm; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3341, 3148, 3101, 2956, 2932, 2862 (CH), 1645 (C=N), 1568, 1467, 1387 (S=O), 1173, 1039, 1013, 830, 749, 647, 622.

**Synthesis of bis-1-hexyl-3-methylimidazolium ferrocene sulfonate, [Compound 15].** Bis-ferrocene sulfonic acid (0.50 g, 1.4 mmol) was reacted with silver oxide (0.34 g, 1.4 mmol), and then 1-hexyl-3-methylimidazolium bromide (0.72 g, 2.9 mmol) in identical procedure to bis-1-pentyl-3-methylimidazolium ferrocene sulfonate. Yield: 0.786 g, 166 %;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  9.3 (s), 7.8-7.5 (m), 4.4-3.6 (m), 3.2 (s), 2.5 (s), 1.8-0.8 (m);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz):  $\delta_{\text{C}}$  137.4 (s), 124.0 (s), 122.7 (s), 97.2 (s), 70.7 (s), 68.3 (s), 49.1-48.9 (m), 40.3-39.3 (m), 31.1 (s), 30.9 (s), 25.5 (s), 22.2 (s), 14.1 (s); UV-vis (DMSO):  $\lambda_{\text{max}}$  410 nm; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3341, 3148, 3101 (CH), 2956, 2929, 2859, 1645, 1569 (C=N), 1467, 1387 (S=O), 1174, 1039, 1013, 831, 760, 647, 624, 566.

**Synthesis of bis-1-octyl-3-methylimidazolium ferrocene sulfonate, [Compound 16].** Bis-ferrocene sulfonic acid (0.50 g, 1.4 mmol) was reacted with silver oxide (0.34 g, 1.4 mmol), and then 1-octyl-3-methylimidazolium bromide (0.79 g, 2.9 mmol) in identical procedure to bis-pentylmethylimidazolium ferrocene sulfonate.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  9.2 (s, 1H), 7.7 (d, 3H), 4.4-3.8 (m, 36H), 3.2 (s), 2.9 (s), 1.7 (d, 4H), 1.2 (s, 21H), 0.8 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz):  $\delta_{\text{C}}$  136.7 (s), 123.4 (s), 122.1 (s), 96.5 (s), 70.3 (s), 67.7 (s), 48.3 (s), 39.7-38.7 (m), 35.6 (s), 30.9 (s), 28.2-28.1 (d), 21.8 (s), 13.6 (s); UV-vis (DMSO):  $\lambda_{\text{max}}$  410 nm; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3379, 3111, 2928, 2858, 2826 (CH), 1573 (C=N), 1467, 1176, 1030, 831, 649, 625, 564.

**Synthesis of bis-1-decyl-3-methylimidazolium ferrocene sulfonate, [Compound 17].** Bis-ferrocene sulfonic acid acid (0.43 g, 1.2 mmol) was reacted with silver oxide (0.29 g, 1.2 mmol), and then decylmethylimidazolium bromide (0.75 g, 2.5 mmol) in identical procedure to bis-pentylmethylimidazolium ferrocene sulfonate.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  9.1 (s), 7.7 (s), 4.3 (s), 4.1 (s), 3.2 (m), 1.2 (s), 0.9 (s);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz):  $\delta_{\text{C}}$  96.9 (s), 70.1 (s), 67.7 (s), 48.7 (s), 39.8-38.8 (m), 31.0 (s), 29.2-28.2 (m), 25.3 (s), 21.8 (s), 13.7 (s); UV-vis ( $\text{DMSO}$ ):  $\lambda_{\text{max}}$  410 nm; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3373, 2926, 2856, 2833 (CH), 1652, 1575 (C=N), 1456, 1176, 1022, 650, 566, 559.

**Synthesis of bis-1-dodecyl-3-methylimidazolium ferrocene sulfonate, [Compound 18].** Bis-ferrocene sulfonic acid acid (0.68 g, 2.0 mmol) was reacted with silver oxide (0.43 g, 1.9 mmol), and then dodecylmethylimidazolium bromide (0.93 g, 2.8 mmol) in identical procedure to bis-pentylmethylimidazolium ferrocene sulfonate.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta_{\text{H}}$  9.2 (s), 7.7 (s), 4.3 (s), 4.1 (s), 3.8 (s), 3.5 (s), 3.2 (s), 1.7 (s), 1.2 (s), 0.8 (s);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz):  $\delta_{\text{C}}$  135.9 (s), 122.9 (s), 121.5 (s), 69.6 (s), 67.3 (s), 48.0-47.8 (d), 39.5 (s), 35.1 (s), 31.5 (s), 30.5 (s), 28.2-27.6 (m), 24.7 (s), 21.3 (s), 13.1 (s); UV-vis ( $\text{DMSO}$ ):  $\lambda_{\text{max}}$  410 nm; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3402, 2923, 2853 (CH), 1652, 1574 (C=N), 1467, 1177, 1041, 833, 649, 622, 578, 553.

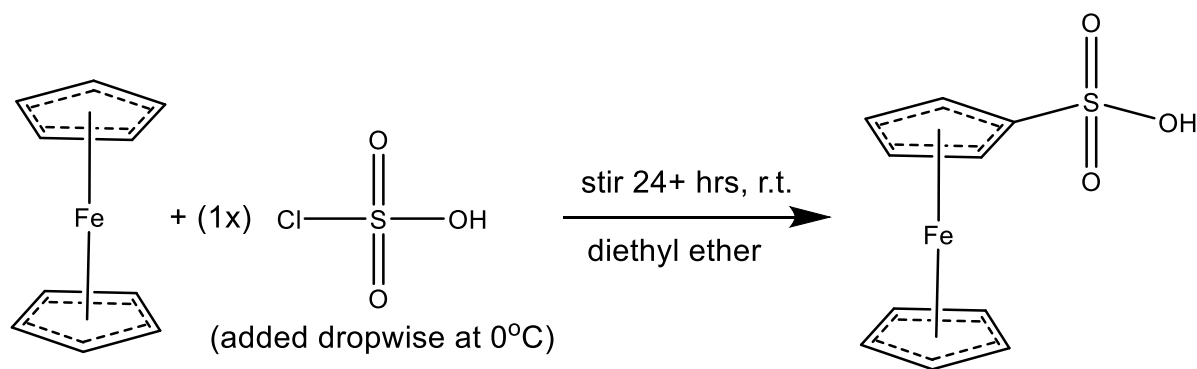
Compound	12	13	14
Emp. form	C <sub>13</sub> H <sub>16</sub> FeN <sub>2</sub> O <sub>2</sub> S	C <sub>20</sub> H <sub>26</sub> FeN <sub>4</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>42</sub> FeN <sub>4</sub> O <sub>6</sub> S <sub>2</sub>
Form. weight	320.19	538.42	650.62
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P2 <sub>1</sub> /n
a/ Å	8.2021(2)	6.0473(3)	12.6496(6)
b/ Å	8.3348(3)	7.2193(4)	8.2945(4)
c/ Å	10.4399(3)	12.9235(6)	15.1429(7)
α(°)	80.331(2)	79.742(3)	90
β(°)	78.937(2)	85.815(3)	109.691(2)
γ(°)	84.240(2)	89.305(3)	90
Volume (Å <sup>3</sup> )	688.77(4)	553.71(5)	1495.92(12)
Z	2	1	2
Dc (Mg/m <sup>3</sup> )	1.544	1.615	1.444
μ (mm <sup>-1</sup> )	1.244	0.916	0.692
F(000)	332	280	688
Reflections collected	12921	10494	14217
Data/Restraints/Parameters	3557 / 0 / 178	2784 / 0 / 153	3743 / 0 / 189
GOF on F <sup>2</sup>	1.108	1.048	1.055
R1 (on F <sub>o</sub> <sup>2</sup> , I > 2σ(I))	0.0340	0.0348	0.0374
wR2 (on F <sub>o</sub> <sup>2</sup> , I > 2σ(I))	0.0821	0.0747	0.0898
R1 (all data)	0.0436	0.0451	0.0545
wR2 (all data)	0.0858	0.0798	0.0979

**Table 1.** The X-ray data collection and structure parameters for the crystal structures. Image of crystal structures can be seen in Figures **11**, **20**, and **24**, as well as in Appendix B.

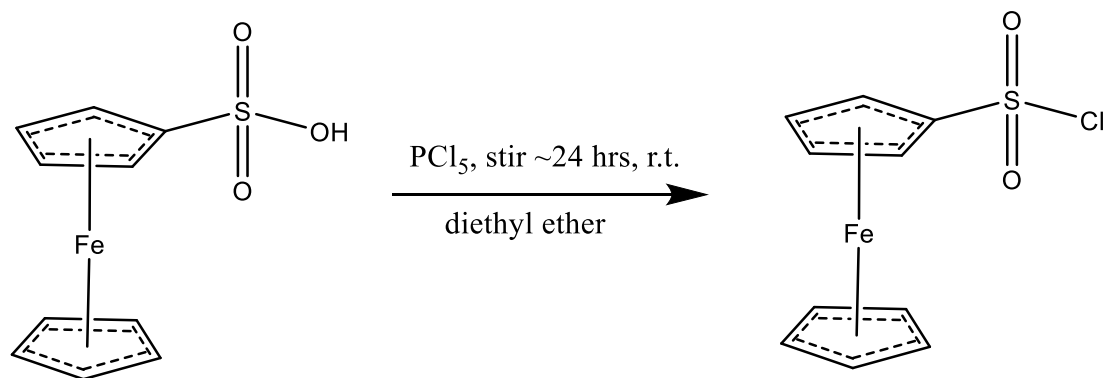
## RESULTS AND DISCUSSION

Spectroscopic analyses were used to verify the synthesis of the compounds. Spectra are listed in full in Appendix B. The IR spectra are not as useful at determining the overall structure of a molecule, but they can be useful for detecting the presence of certain functional groups. The  $^1\text{H}$  NMR spectra are possibly the most useful in synthetic verification. The integration values, when normalized, can be used to determine the number of hydrogen atoms at that particular resonance.

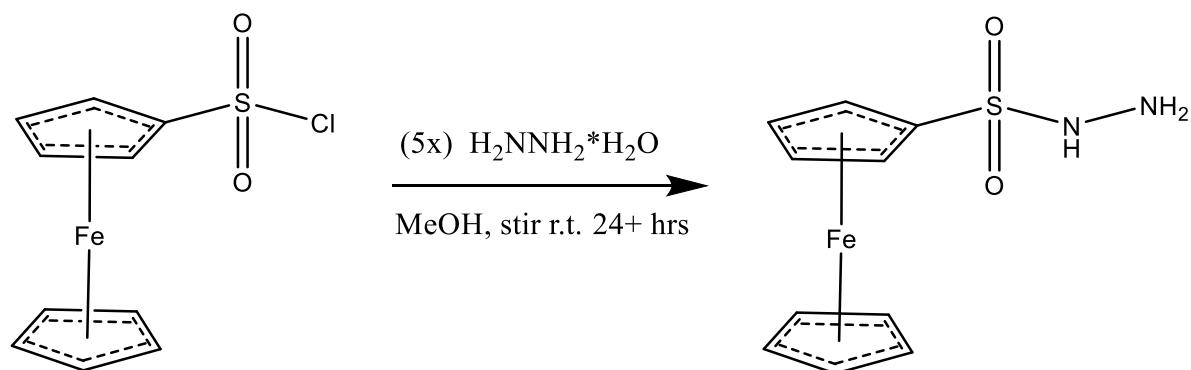
The synthesis of a sulfonamide bridged ferrocene dimer was ultimately unsuccessful. Reactions with the ferrocene sulfonyl hydrazine proved to be difficult to successfully reproduce. The bis-1-alkyl-3-methylimidazolium ferrocene sulfonate salts proved to be much more successful, synthetically. However, in the attempt to prepare a dimerized compound, one serendipitous substance was uncovered. The ferrocene sulfonyl hydrazine reacted to form a Schiff base. This species, compound 12, is believed to be previously unknown to the chemical literature. This was observed by the discovery of the crystal structure of this compound. It is possible that this substance was formed by exposure of the ferrocene sulfonyl hydrazine to acetone.



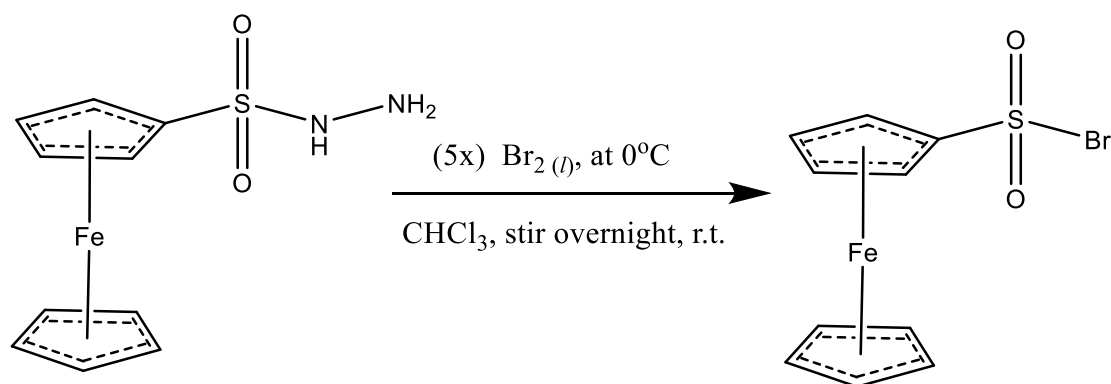
**Figure 6.** The reaction to produce ferrocene sulfonic acid [Compound 7].



**Figure 7.** The synthesis of ferrocene sulfonyl chloride [Compound **9**] from ferrocene sulfonic acid [Compound **7**].

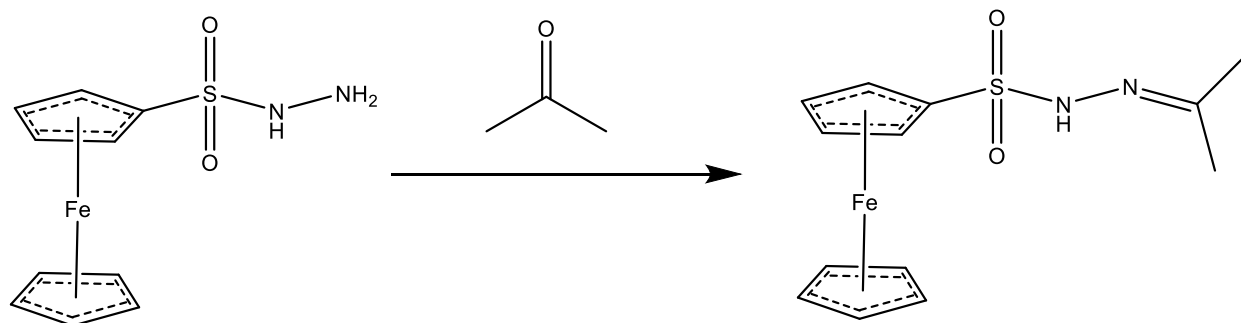


**Figure 8.** The synthesis of ferrocene sulfonyl hydrazine [Compound **11**] from [Compound **7**].

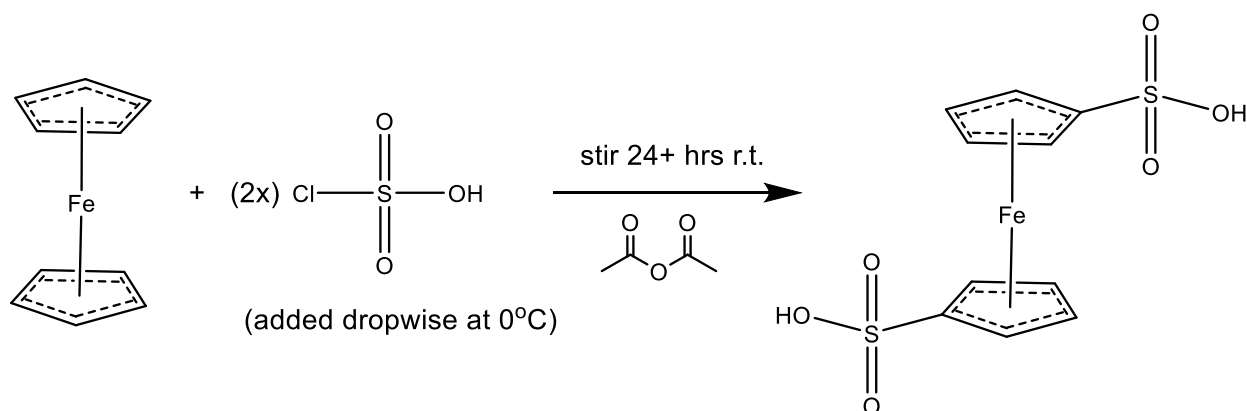


**Figure 9.** The synthesis of ferrocene sulfonyl bromide [Compound **10**] from [Compound **11**].

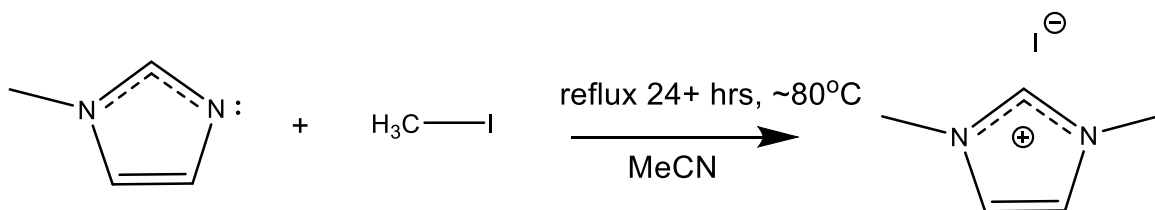




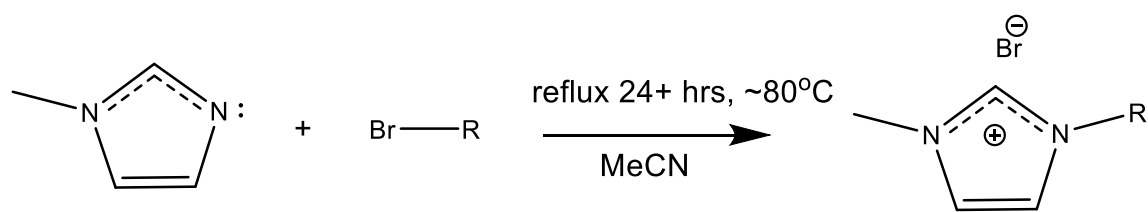
**Figure 10.** A proposed reaction of the serendipitous production of a new Schiff base [Compound 12] from the ferrocene sulfonyl hydrazine [Compound 11], likely upon exposure to acetone.



**Figure 11.** The synthetic reaction to produce bis-ferrocene sulfonic acid [Compound 8].

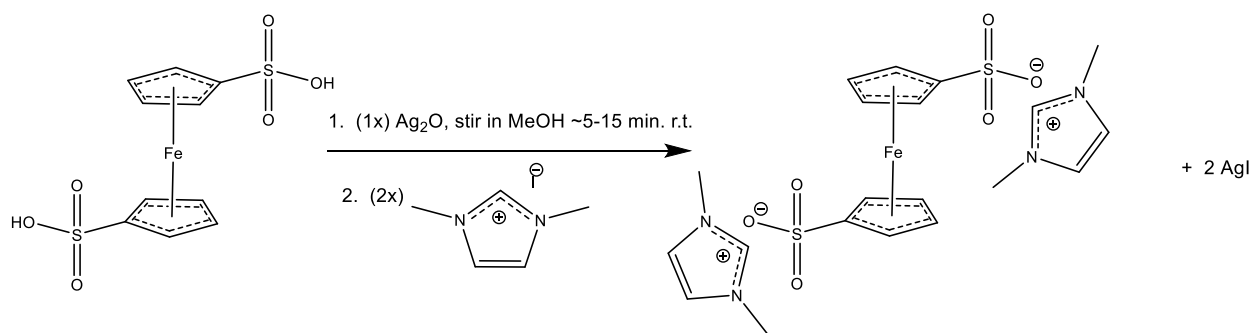


**Figure 12.** The synthetic reaction to produce 1,3-dimethylimidazolium iodide [Compound 1].

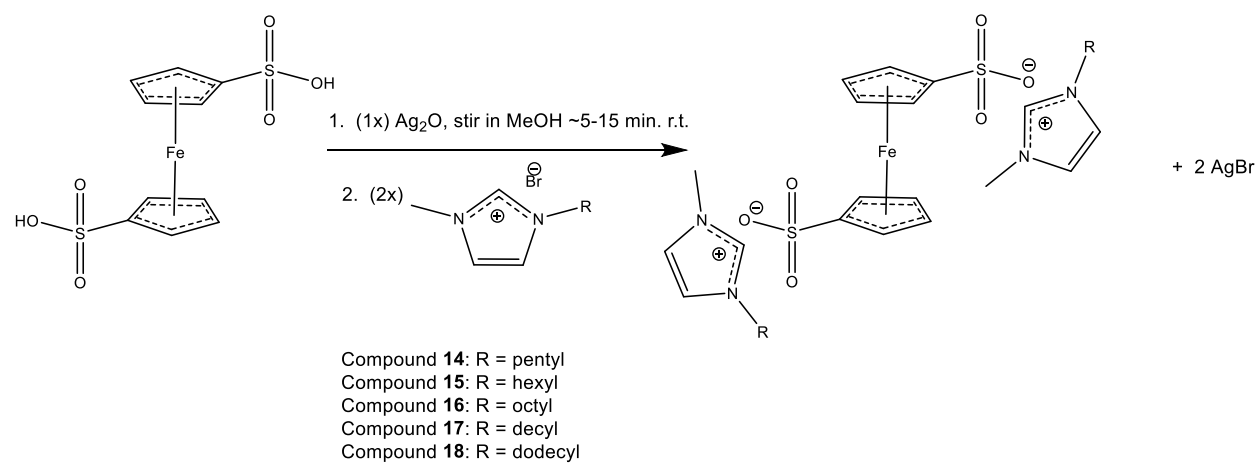


Compound **2**: R = pentyl  
 Compound **3**: R = hexyl  
 Compound **4**: R = octyl  
 Compound **5**: R = decyl  
 Compound **6**: R = dodecyl

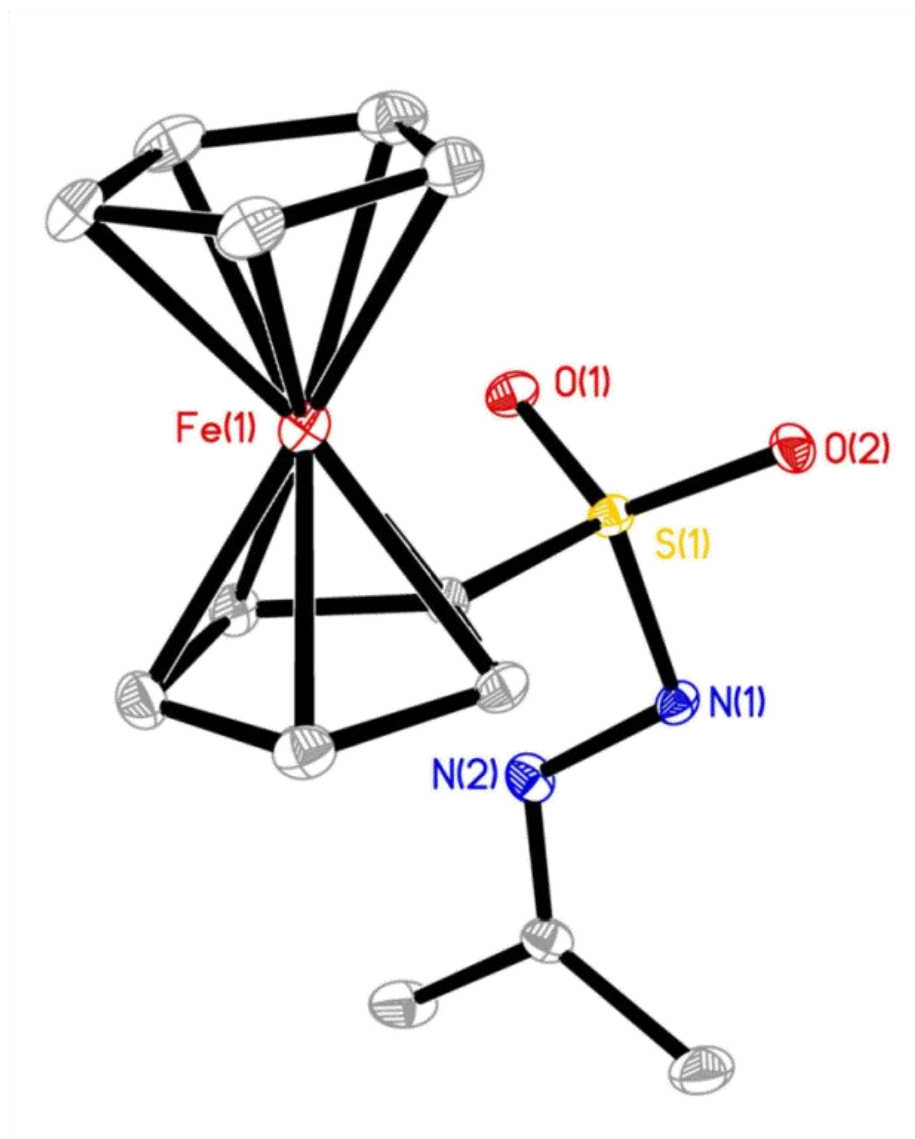
**Figure 13.** The synthetic reactions to produce 1-alkyl-3-methylimidazolium bromides, compounds **2-6**.



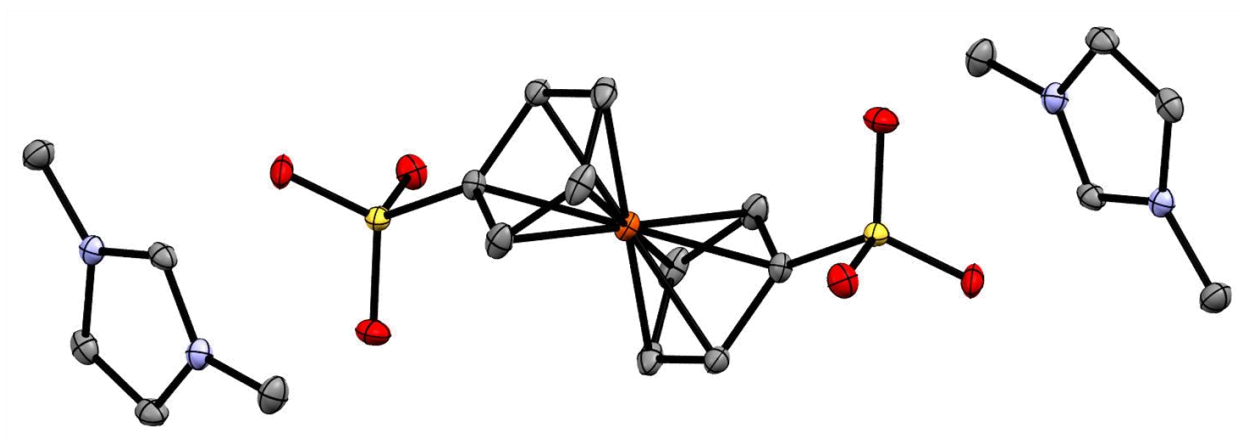
**Figure 14.** The synthetic reaction presumably producing bis-1,3-dimethylimidazolium ferrocene sulfonate, [Compound **13**], a bulky salt, along with a gray precipitate.



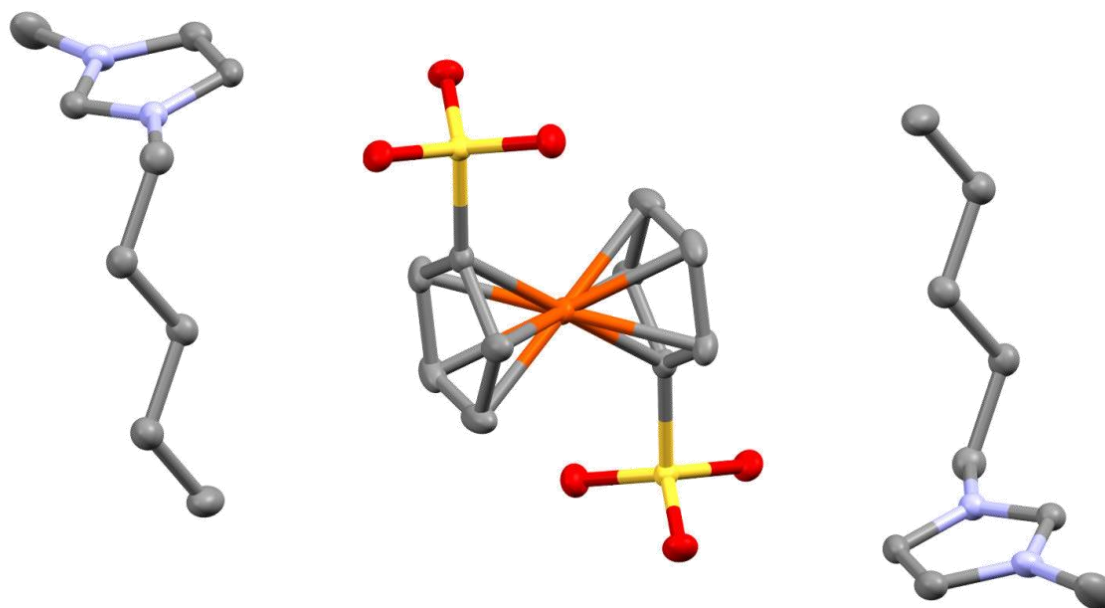
**Figure 15.** The synthetic reaction presumably producing bis-1-alkyl-3-methylimidazolium ferrocene sulfonates, [Compounds **14-18**], bulky salts, along with a gray precipitate, presumed to be silver bromide.



**Figure 16.** The crystal structure, discovered by using X-ray diffraction, of the new Schiff base, [Compound 12], ferrocene sulfonyl hydrazine acetone. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are displayed at the 35% level.



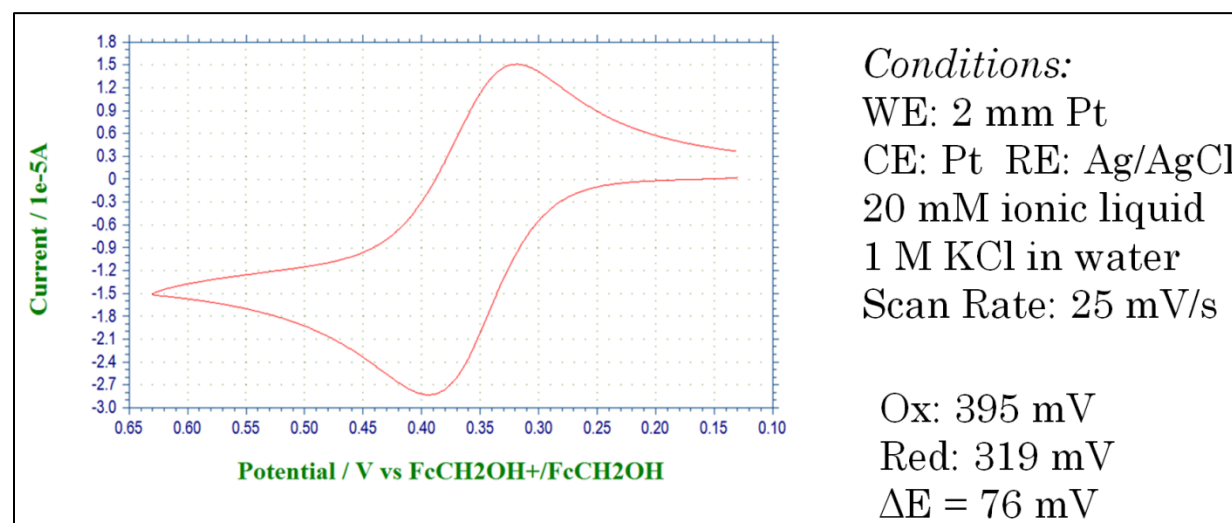
**Figure 17.** The crystal structure obtained of compound **13**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are displayed at the 35% level.



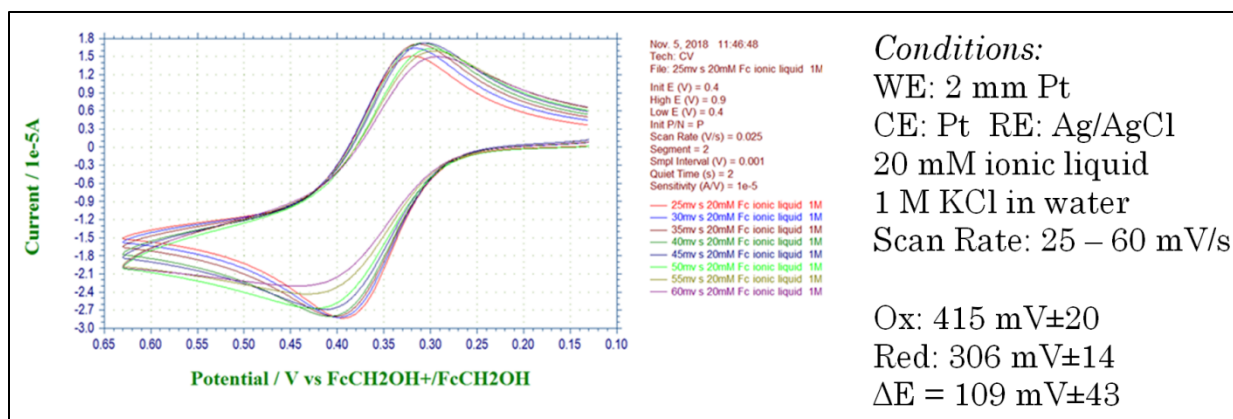
**Figure 18.** The crystal structure obtained of compound **14**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are displayed at the 35% level.

Solubilities of bis-1-alkyl-3-methylimidazolium ferrocene sulfonate salts								
Alkyl group	Water	MeOH	EtOH	Acetic Anhydride	MeCN	DCM	Diethyl Ether	DMSO
Methyl	S	S	P	P	I	I	I	S
Pentyl	S	S	S	I	I	I	I	S
Hexyl	S	S	S	I	I	S	I	S
Octyl	S	S	S	I	I	S	I	S
Decyl	P	S	S	I	P	S	I	S
Dodecyl	S	S	S	I	P	S	I	S
			S: Soluble	P: Partially Soluble	I: Insoluble			

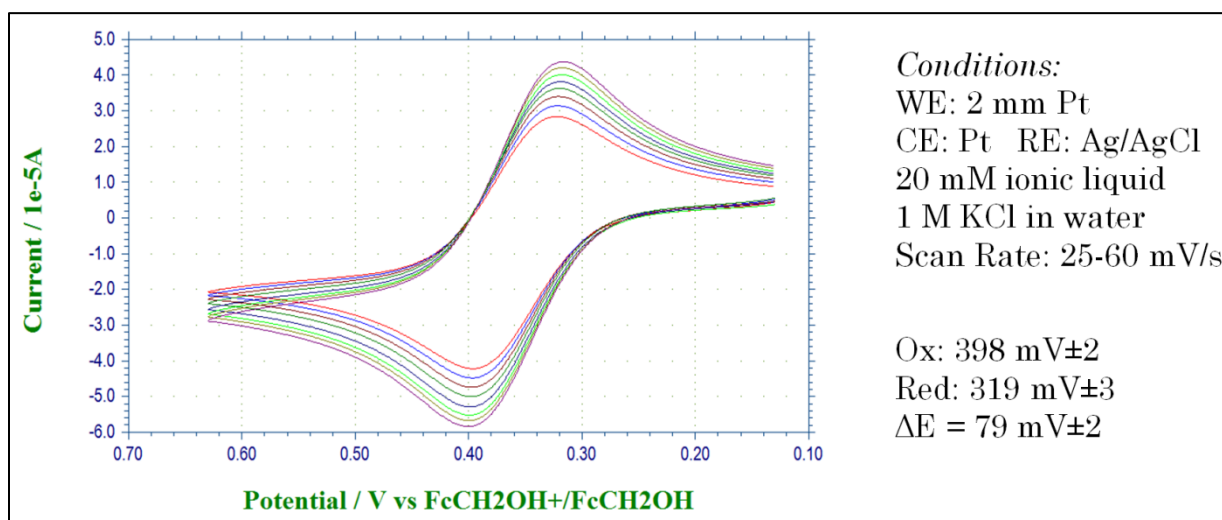
**Table 2.** The solvents in which the bis-1-alkyl-3-methylimidazolium ferrocene sulfonate salts were tested to be soluble or insoluble. Water solubility was high.



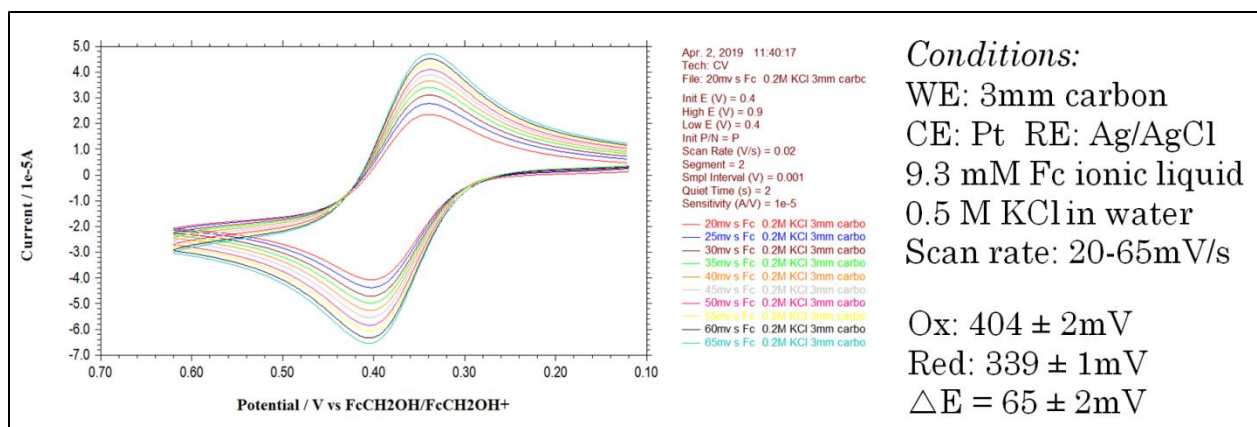
**Figure 19.** The cyclic voltammogram for the bis-1,3-dimethylimidazolium ferrocene sulfonate compound **12**. Note that the oxidation peak is present in the lower portion of the graph, and that the reduction peak is also present; this shows that the compound has reversible redox chemistry.



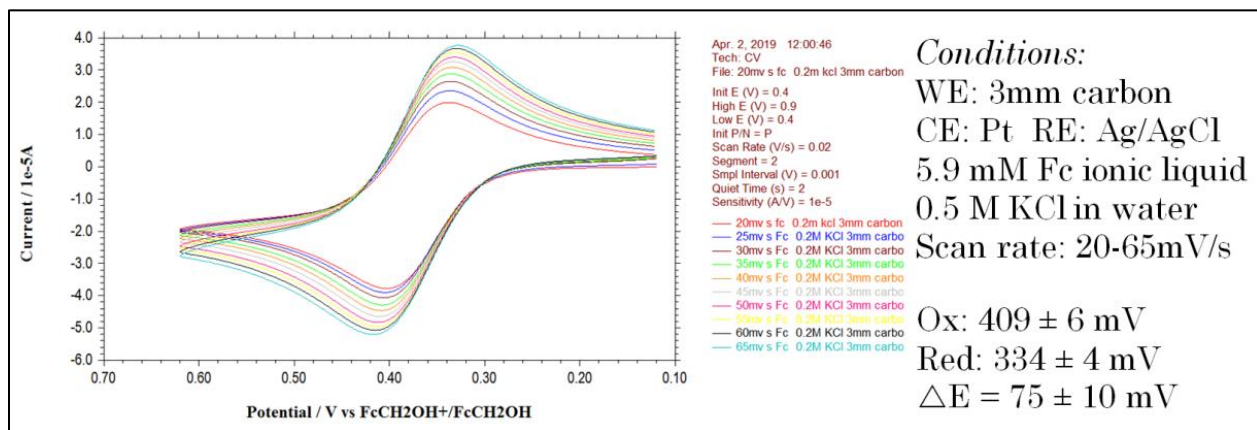
**Figure 20.** The cyclic voltammogram of the bis-1,3-dimethylimidazolium ferrocene sulfonate, with different scan rates.



**Figure 21.** The cyclic voltammogram of compound **14**. Multiple scan rates are tested.

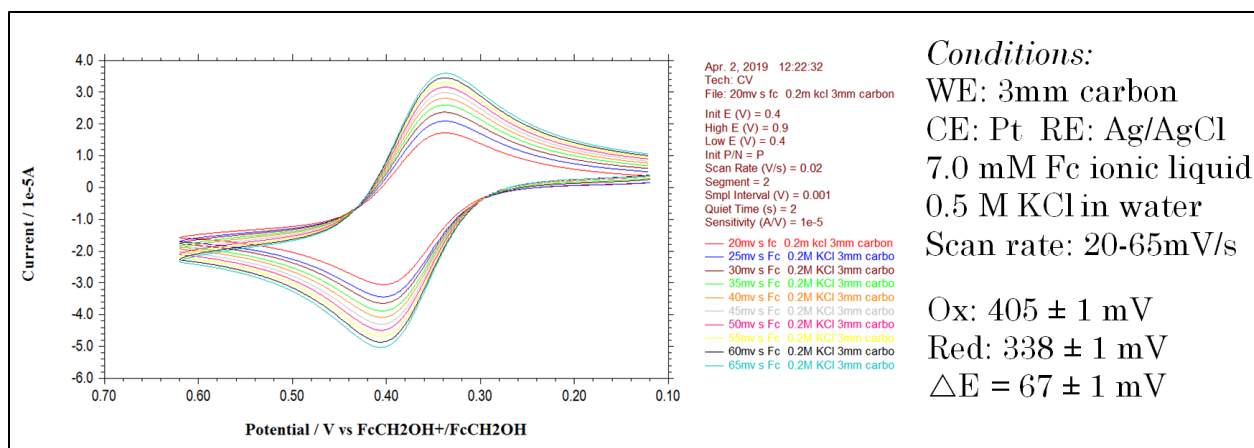


**Figure 22.** The cyclic voltammogram of compound **15**. Multiple scan rates are tested.

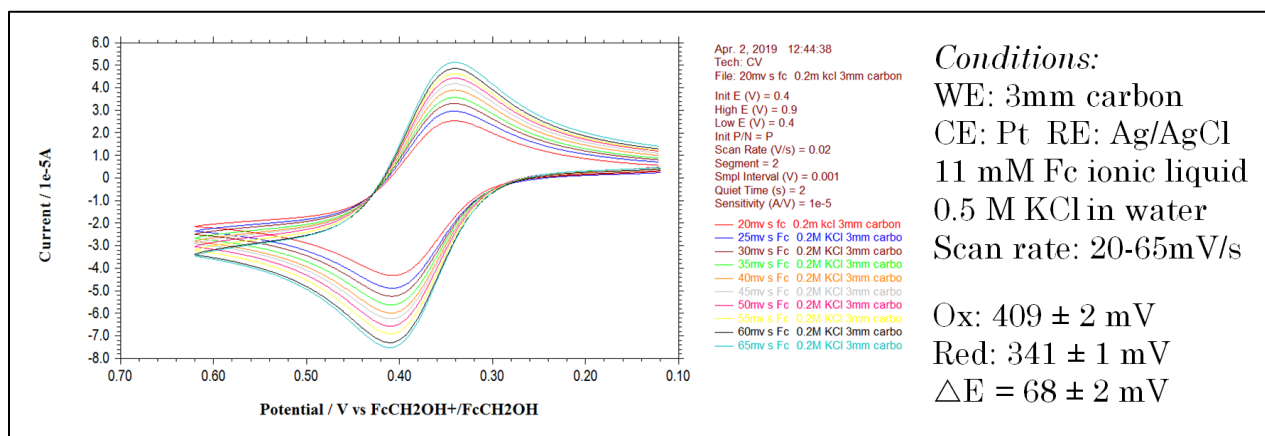


**Figure 23.** The cyclic voltammogram of compound **16**. Multiple scan rates are tested.





**Figure 24.** The cyclic voltammogram of compound **17**. Multiple scan rates are tested.



**Figure 25.** The cyclic voltammogram of compound **18**. Multiple scan rates are tested.

The cyclic voltammetry studies indicate that these bis-1-alkyl-3-methylimidazolium ferrocene sulfonates are indeed reversible. This is due to the presence of both oxidation and reduction peaks in the cyclic voltammograms. Further study would be beneficial to determine if

after charging and discharging these materials repeatedly, if they would retain their reversible redox chemistry. The redox potentials for these bis-salts were not substantially increased compared with ferrocene alone. However, Compounds **13-18** were water soluble and were seen to have reversible redox chemistry, displaying similar voltammogram appearance.

It is notable that for many of the compounds, the melting temperature range was not determined. This is due to the apparently highly hygroscopic tendency of these materials; upon exposure to air, they had the appearance of melting. However, sometimes these materials were sufficiently dry to crystallize, as is evident from the crystal structures. It would seem that the properties of these materials may be affected by their environment. Additional study on these ferrocene sulfonate salts could use differential scanning calorimetry (DSC) in order to better elucidate their melting points and other thermal properties.

The crystal structures of compounds **12-14** were determined via single crystal X-ray diffraction studies. In such studies, hydrogen atoms are typically omitted for clarity, and because the hydrogen atoms positions are determined by calculation alone due to their small mass. The football-shaped ellipsoids located at the positions of atoms are thermal ellipsoids; the direction of the ellipsoid indicates the direction of positional uncertainty due to thermal vibrations, while the size of the ellipsoids indicates the magnitude of this uncertainty.

Any errors seen in this research may stem from several sources. The yields of some of the bis-1-alkyl-3-methylimidazolium ferrocene sulfonate salts were above 100%; this should theoretically be impossible if stoichiometric quantities of reagents were used. These high yields are most likely due to the highly hygroscopic nature of these salts; additional water is the source of the extra mass. It is also possible that the products could contain some residual starting material, especially if the ratio of starting materials was off, and it is possible that the resulting

products were not entirely pure, residual solvent or products from reaction with atmospheric oxygen are some possible sources for these unusually large yields. These measurements may be improved by sequestering the products into low moisture environments.

## **CONCLUSIONS**

With the increase in demand for renewable sources of energy, storage of that energy is becoming an issue. Currently, redox flow batteries (RFBs) are a promising technology for this energy storage, yet the current vanadium based materials that are used have a low energy density. In the Ziegler laboratory, new ferrocene based materials are explored to examine if they may exhibit properties as viable components of a RFB. A series of bis-1-alkyl-3-methylimidazolium ferrocene sulfonate salts was synthesized, where the linear alkyl group included the following: methyl, pentyl, hexyl, octyl, decyl, and dodecyl groups. This synthesis was verified by standard chemical techniques, including IR spectroscopy, proton NMR spectroscopy, and carbon NMR spectroscopy; additionally, some compounds proffered a crystalline material, whose structure was elucidated by X-ray diffraction. These characterization techniques indicate that the synthesis of this series of compounds was indeed successful. The usefulness of these salts is determined by electrochemical analysis, particularly cyclic voltammetry; on such a voltammogram, if both an oxidation peak and a reduction peak are present, then the compound tested have reversible redox chemistry. These bis-1-alkyl-3-methylimidazolium ferrocene sulfonates did indeed exhibit reversible redox characteristics, which indicate that ferrocene based salts, which melt at low temperatures, are a class of compounds which are worthy of additional study for their battery applications.

## **ACKNOWLEDGEMENTS**

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## **REFERENCES**

- (1) Lewis, Nathan S.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci.* **2006**, *103* (43), 15729–15735.
- (2) Eisenberg, Richard; Nocera, D. G. Preface: Overview of the Forum on Solar and Renewable Energy. *Inorg. Chem.* **2005**, *44* (20), 6799–6801.
- (3) Sebri, Maamar; Salha, O. Ben. *On the Causal Dynamics between Economic Growth, Renewable Energy Consumption, CO2 Emissions and Trade Openness: Fresh Evidence from BRICS Countries*; 2013.
- (4) Morton, O. A New Day Dawning? *Nature* **2006**, *443*, 19–22.
- (5) Lewis, N. S. Toward Cost-Effective Solar Energy Use. *Science* (80-. ). **2007**, *315* (5813), 798–801.
- (6) Thaller, L. H. Electrically Rechargeable Redox Flow Cell. 3996064, 1976.
- (7) Skoog, Douglas A.; West, Donald M.; Holler, F. James; Crouch, S. R. *Fundamentals of Analytical Chemistry*, 2nd editio.; Brooks/Cole: Belmont, CA, 2014.
- (8) Rycheik, M.; Skyllas-Kazacos, M. Characteristics of a New All-Vanadium Redox Flow

- Battery. *J. Power Sources* **1988**, 22, 59–67.
- (9) Minke, C.; Turek, T. Materials, System Designs and Modelling Approaches in Techno-Economic Assessment of All-Vanadium Redox Flow Batteries – A Review. *J. Power Sources* **2018**, 376, 66–81.
  - (10) Li, L.; Kim, S.; Wang, W.; Vijayakumar, M.; Nie, Z.; Chen, B.; Zhang, J.; Xia, G.; Hu, J.; Graff, G.; et al. A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage. *Adv. Energy Mater.* **2011**, 1 (3), 394–400.
  - (11) Gupta, S.; Lim, T. M.; Mushrif, S. H. Insights into the Solvation of Vanadium Ions in the Vanadium Redox Flow Battery Electrolyte Using Molecular Dynamics and Metadynamics. *Electrochim. Acta* **2018**, 270, 471–479.
  - (12) Li, Xianfeng; Zhang, Huamin; Mai, Zhensheng; Zhang, Hongzhang; Vankelecom, I. Ion Exchange Membranes for Vanadium Redox Flow Battery (VRB) Applications. *Energy Environ. Sci.* **2011**, 4, 1147–1160.
  - (13) Silberberg, M. S. *Principles of General Chemistry*, 3rd editio.; Lange, M., Ed.; McGraw-Hill, 2013.
  - (14) Turner, E. A.; Pye, C. C.; Singer, R. D. Use of Ab Initio Calculations toward the Rational Design of Room Temperature Ionic Liquids. *J. Phys. Chem. A* **2003**, 107 (13), 2277–2288.
  - (15) Rogers, Robin D., Seddon, K. R. Ionic Liquids - Solvents of the Future? *Science* (80-. ). **2003**, 302, 792–793.
  - (16) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, 99 (8), 2071–2084.
  - (17) Chakrabarti, M. H.; Mjalli, F. S.; AlNashef, I. M.; Hashim, M. A.; Hussain, M. A.; Bahadori, L.; Low, C. T. J. Prospects of Applying Ionic Liquids and Deep Eutectic

- Solvents for Renewable Energy Storage by Means of Redox Flow Batteries. *Renew. Sustain. Energy Rev.* **2014**, *30*, 254–270.
- (18) Takechi, K.; Kato, Y.; Hase, Y. A Highly Concentrated Catholyte Based on a Solvate Ionic Liquid for Rechargeable Flow Batteries. *Adv. Mater.* **2015**, *27* (15), 2501–2506.
- (19) Miura, Y.; Shimizu, F.; Mochida, T. Preparation, Properties, and Crystal Structures of Organometallic Ionic Liquids Comprising 1-Ferrocenyl-3-Alkylimidazolium-Based Salts of Bis(Trifluoromethanesulfonyl)Amide and Hexafluorophosphate. *Inorg. Chem.* **2010**, *49* (21), 10032–10040.
- (20) Mochida, T.; Funasako, Y.; Azumi, H. Charge-Transfer Complexes from Decamethylferrocene and 1,4-Quinone Derivatives: Neutral–ionic Phase Diagrams for Metallocene Complexes. *Dalt. Trans.* **2011**, *40* (36), 9221.
- (21) Tahara, H.; Uranaka, K.; Hirano, M.; Ikeda, T.; Sagara, T.; Murakami, H. Electrochromism of Ferrocene- and Viologen-Based Redox-Active Ionic Liquids Composite. *ACS Appl. Mater. Interfaces* **2019**, *11* (1), 1–6.
- (22) Elschenbroich, C. *Organometallics*, 3rd Editio.; Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2006.
- (23) Kealy, T. J.; Pauson, P. L. A New Type of Organo-Iron Compound. *Nature* **1951**, *168* (4285), 1039–1040.
- (24) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. The Structure of Iron Bis-Cyclopentadienyl. *J. Am. Chem. Soc.* **1952**, *74* (8), 2125–2126.
- (25) Opitz, J. Electron Impact Ionization of Cobalt-Tricarbonyl-Nitrosyl, Cyclopentadienyl-Cobalt-Dicarbonyl and Biscyclopentadienyl-Cobalt: Appearance Energies, Bond Energies and Enthalpies of Formation. *Int. J. Mass Spectrom.* **2003**, *225*, 115–126.

- (26) Poli, R.; Cacelli, I. Orbital Splitting and Pairing Energy in Open-Shell Organometallics: A Study of Two Families of 16-Electron Complexes [Cp<sub>2</sub>M] (M = Cr, Mo, W) and [CpM(PH<sub>3</sub>)] (M = Co, Rh, Ir). *Eur. J. Inorg. Chem.* **2005**, 2005 (12), 2324–2331.
- (27) García-Suárez, V. M.; Ferrer, J.; Lambert, C. J. Strongly Correlated Electron Physics in Nanotube-Encapsulated Metallocene Chains. *Phys. Rev. B* **2006**, 74 (20), 205421.
- (28) Choi, J.; Dowben, P. A. Cobaltocene Adsorption and Dissociation on Cu(111). *Surf. Sci.* **2006**, 600 (15), 2997–3002.
- (29) Singh, A.; Lumb, I.; Mehra, V.; Kumar, V. Ferrocene-Appended Pharmacophores: An Exciting Approach for Modulating the Biological Potential of Organic Scaffolds. *Dalt. Trans.* **2019**, 48 (9), 2840–2860.
- (30) Brett, C. M.; Bursten, B. E. Theoretical Studies of 18-Electron M(C<sub>n</sub>H<sub>n</sub>)(C<sub>10–n</sub>H<sub>10–n</sub>) (M=Fe, Ru, Os; N=3, 4, 5) Sandwich Complexes. *Polyhedron* **2004**, 23 (17), 2993–3002.
- (31) Astruc, D. Why Is Ferrocene so Exceptional? *Eur. J. Inorg. Chem.* **2017**, 2017 (1), 6–29.
- (32) Torubaev, Y. V.; Pavlova, A. V.; Pasynskii, A. A.; Raghuvanshi, A.; Shaikh, M. M. Oxidation of Ferrocene and 1,1'-Ferrocene Triselenide by Bromine and Phenyltellurium Tribromide. *Russ. J. Coord. Chem.* **2015**, 41 (10), 638–643.
- (33) Heinze, K.; Hempel, K.; Beckmann, M. Multielectron Storage and Photo-Induced Electron Transfer in Oligonuclear Complexes Containing Ruthenium(II) Terpyridine and Ferrocene Building Blocks. *Eur. J. Inorg. Chem.* **2006**, 2006 (10), 2040–2050.
- (34) Brennan, M. Taking Ferrocenium up a Notch. *Nat. Chem.* **2016**, 8, 903.
- (35) Perruchas, S.; Avarvari, N.; Rondeau, D.; Levillain, E.; Batail, P. Multielectron Donors Based on TTF–Phosphine and Ferrocene–Phosphine Hybrid Complexes of a Hexarhenium(III) Octahedral Cluster Core. *Inorg. Chem.* **2005**, 44 (10), 3459–3465.

- (36) Pegis, M. L.; Roberts, J. A. S.; Wasylenko, D. J.; Mader, E. A.; Appel, A. M.; Mayer, J. M. Standard Reduction Potentials for Oxygen and Carbon Dioxide Couples in Acetonitrile and N , N -Dimethylformamide. *Inorg. Chem.* **2015**, *54* (24), 11883–11888.
- (37) Isse, A. A.; Lin, C. Y.; Coote, M. L.; Gennaro, A. Estimation of Standard Reduction Potentials of Halogen Atoms and Alkyl Halides. *J. Phys. Chem. B* **2011**, *115* (4), 678–684.
- (38) Wardman, P. Reduction Potentials of One-Electron Couples Involving Free Radicals in Aqueous Solution. *J. Phys. Chem.* **1989**, *18* (4), 1637–1755.
- (39) Gagne, Robert R.; Koval, Carl A.; Lisensky, G. C. Ferrocene as an Internal Standard for Electrochemical Measurements. *Inorg. Chem.* **1980**, *19*, 2855–2857.
- (40) Yousefinejad, S.; Honarasa, F.; Solhjoo, A. On the Solubility of Ferrocene in Nonaqueous Solvents. *J. Chem. Eng. Data* **2016**, *61* (1), 614–621.
- (41) Koide, S.; Yokoyama, K. Electrochemical Characterization of an Enzyme Electrode Based on a Ferrocene-Containing Redox Polymer. *J. Electroanal. Chem.* **1999**, *468* (2), 193–201.
- (42) Leber, R.; Wilson, L. E.; Robaschik, P.; Inkpen, M. S.; Payne, D. J.; Long, N. J.; Albrecht, T.; Hirjibehedin, C. F.; Heutz, S. High-Vacuum Deposition of Biferrocene Thin Films on Room-Temperature Substrates. *Chem. Mater.* **2017**, *29* (20), 8663–8669.
- (43) Nagahora, N.; Ogawa, S.; Kawai, Y.; Sato, R. Synthesis, Structure, and Electrochemical Properties of Biferrocenes Annulated with 1,2-Dithiin and 1,2-Dithiin 1,1-Dioxides. *Tetrahedron Lett.* **2005**, *46* (24), 4157–4160.
- (44) Schrage, B. R.; Zhao, Z.; Ziegler, C. J.; Boika, A. Cation-Anion Redox Switching in an All-Ferrocene Salt. *ChemElectroChem* **2018**, *5* (23), 3624–3627.



- (45) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. Thermal Properties of Imidazolium Ionic Liquids. *Thermochim. Acta* **2000**, 357–358, 97–102.
- (46) Mabbott, G. A. An Introduction to Cyclic Voltammetry. *J. Chem. Educ.* **1983**, 60 (9), 697.
- (47) Marken, F.; Neudeck, A.; Bond, A. M. Cyclic Voltammetry. In *Electroanalytical Methods*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2010; pp 57–106.
- (48) Heinze, J. Cyclic Voltammetry—“Electrochemical Spectroscopy”. New Analytical Methods(25). *Angew. Chemie Int. Ed. English* **1984**, 23 (11), 831–847.
- (49) Chanawanno, K.; Holstrom, C.; Crandall, L. A.; Dodge, H.; Nemykin, V. N.; Herrick, R. S.; Ziegler, C. J. The Synthesis and Structures of 1,1'-Bis(Sulfonyl)Ferrocene Derivatives. *Dalt. Trans.* **2016**, 45 (36), 14320–14326.
- (50) Chanawanno, K.; Blesener, T. S.; Schrage, B. R.; Nemykin, V. N.; Herrick, R. S.; Ziegler, C. J. Amino Acid Ferrocene Conjugates Using Sulfonamide Linkages. *J. Organomet. Chem.* **2018**, 870, 121–129.
- (51) Slocum, D. W.; Achermann, W. The Preparation of Several N-Substituted and N,N-Disubstituted Ferrocenesulfonamides. *Synth. React. Inorg. Met. Chem.* **1982**, 12 (4), 397–405.
- (52) Bhosale, V. K.; Kulkarni, P. S. Ultrafast Igniting, Imidazolium Based Hypergolic Ionic Liquids with Enhanced Hydrophobicity. *New J. Chem.* **2017**, 41 (3), 1250–1258.
- (53) Chanawanno, Kullapa; Holstrom, Cole; Nemykin, Victor N.; Herrick, Richard S.; Ziegler, C. J. New 1,1'-Ferrocene Bis(Sulfonyl) Reagents. *Chem. Sel.* **2016**, 1 (20), 6438–6441.
- (54) Council, N. R. *Prudent Practices in the Laboratory*; National Academies Press: Washington, D.C., 1995.

## **APPENDICES**

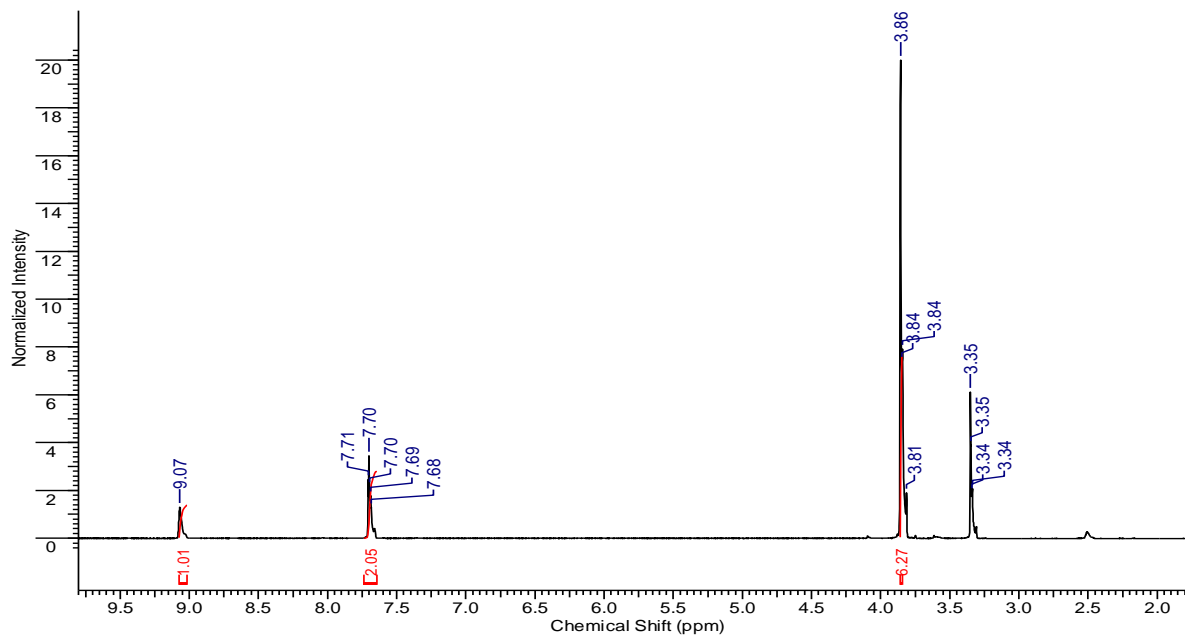
## Appendix A - Considerations for Safe Laboratory Procedures

Safe laboratory practices were observed during this study. Prior to this study, the safety overview of *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, was reviewed.<sup>54</sup> Personal Protective Equipment (PPE), such as safety goggles and nitrile gloves, were worn at all time when in the laboratory where any potential exposure to chemical could occur. Any waste products were disposed appropriately; organic wastes were placed into the appropriate halogenated or non-halogenated waste receptacle as warranted. Whenever any waste products were capable of being safely disposed in the drain, they were only done so with copious water flow to dilute them. Open flames were not used for heating any materials; the safer heating technique of having an electric hot plate warm an oil bath was used. At the conclusion of each laboratory session, care was taken that the laboratory counter-space was adequately tidy, and that hands were washed.

## Appendix B – Acquired Spectra

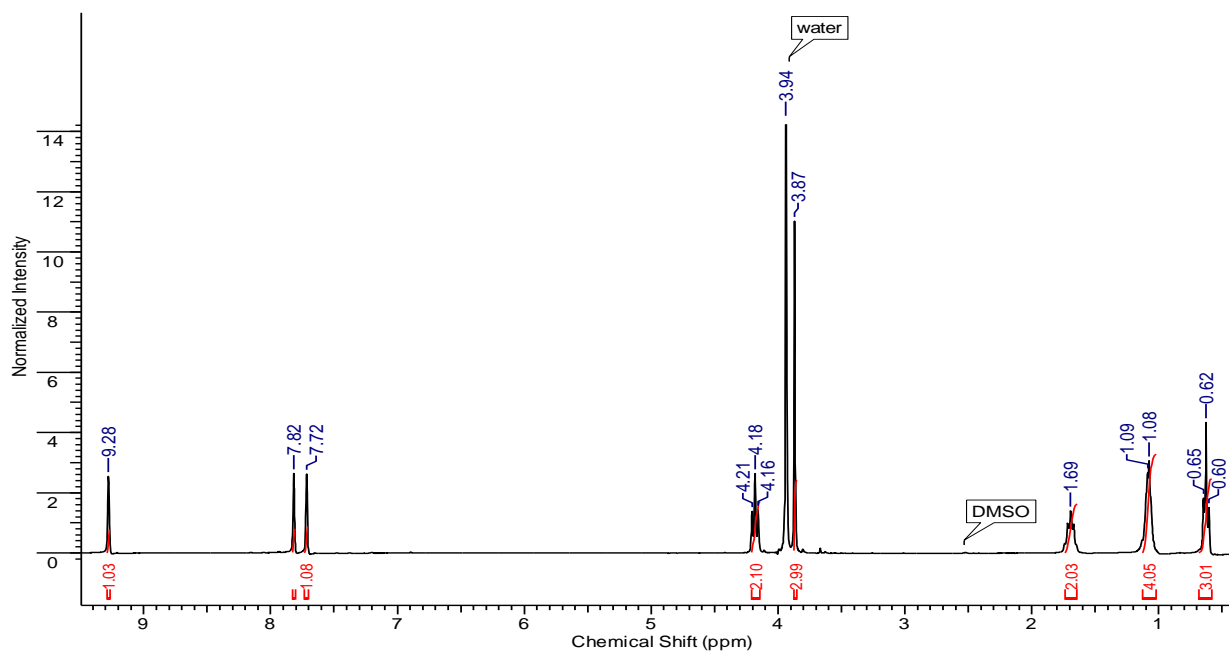
### 1,3-dimethylimidazolium iodide [Compound 1]:

$^1\text{H}$  NMR spectrum (solvent is DMSO):



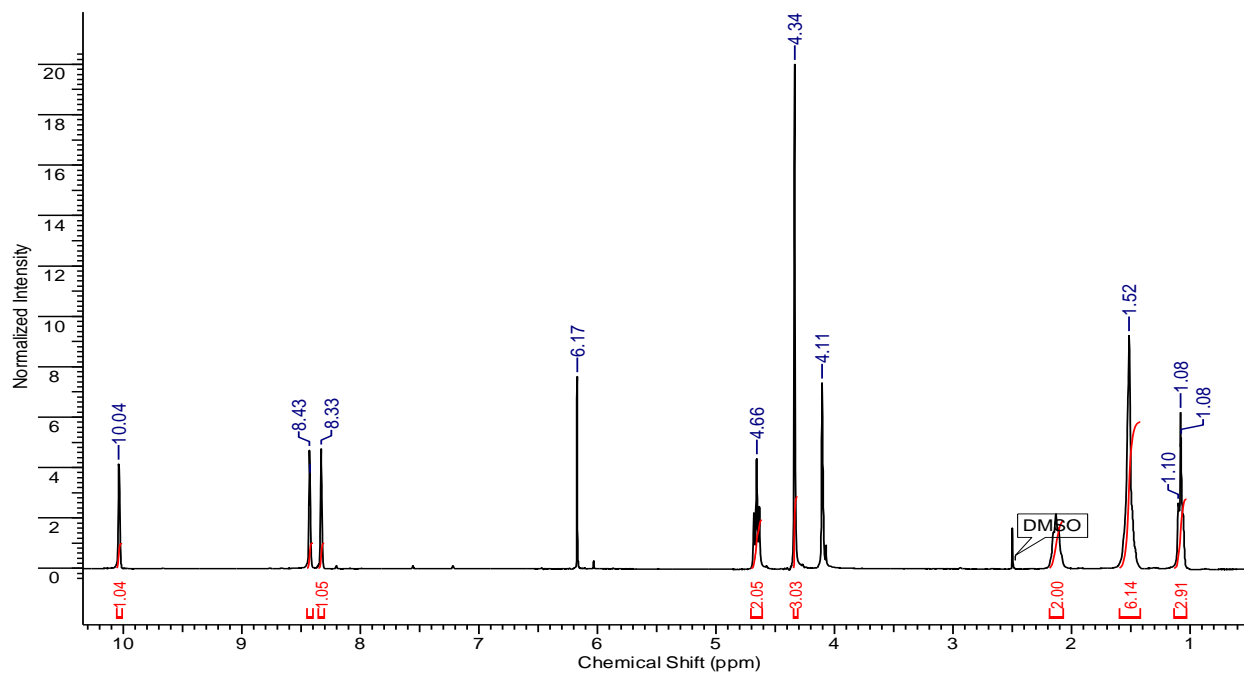
### 1-pentyl-3-methylimidazolium bromide [Compound 2]:

$^1\text{H}$  NMR spectrum (solvent is DMSO):



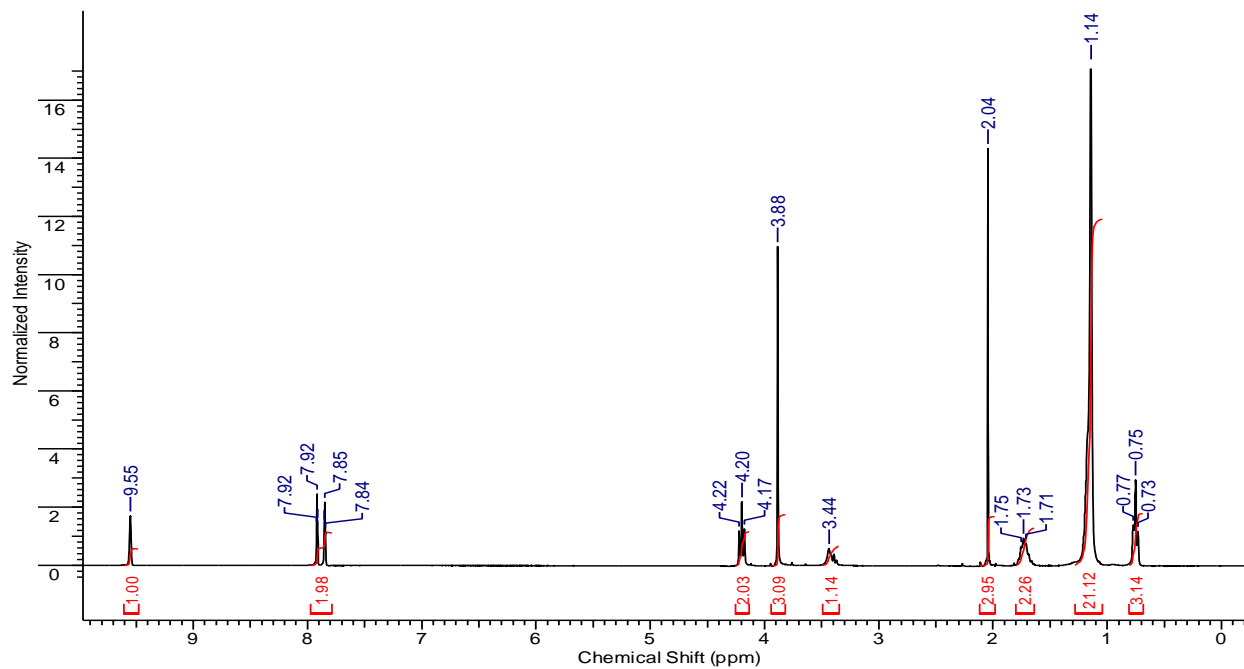
### 1-hexyl-3-methylimidazolium bromide [Compound 3]

$^1\text{H}$  NMR spectrum (solvent is DMSO):



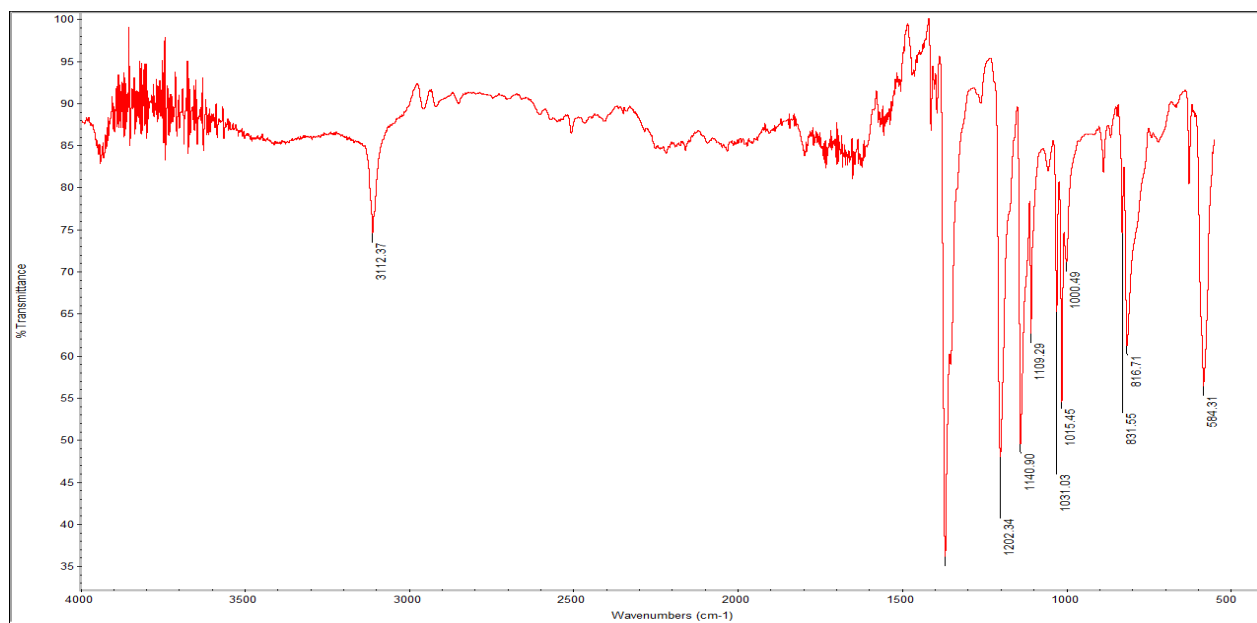
### 1-dodecyl-3-methylimidazolium bromide [Compound 6]

$^1\text{H}$  NMR spectrum (solvent is DMSO):



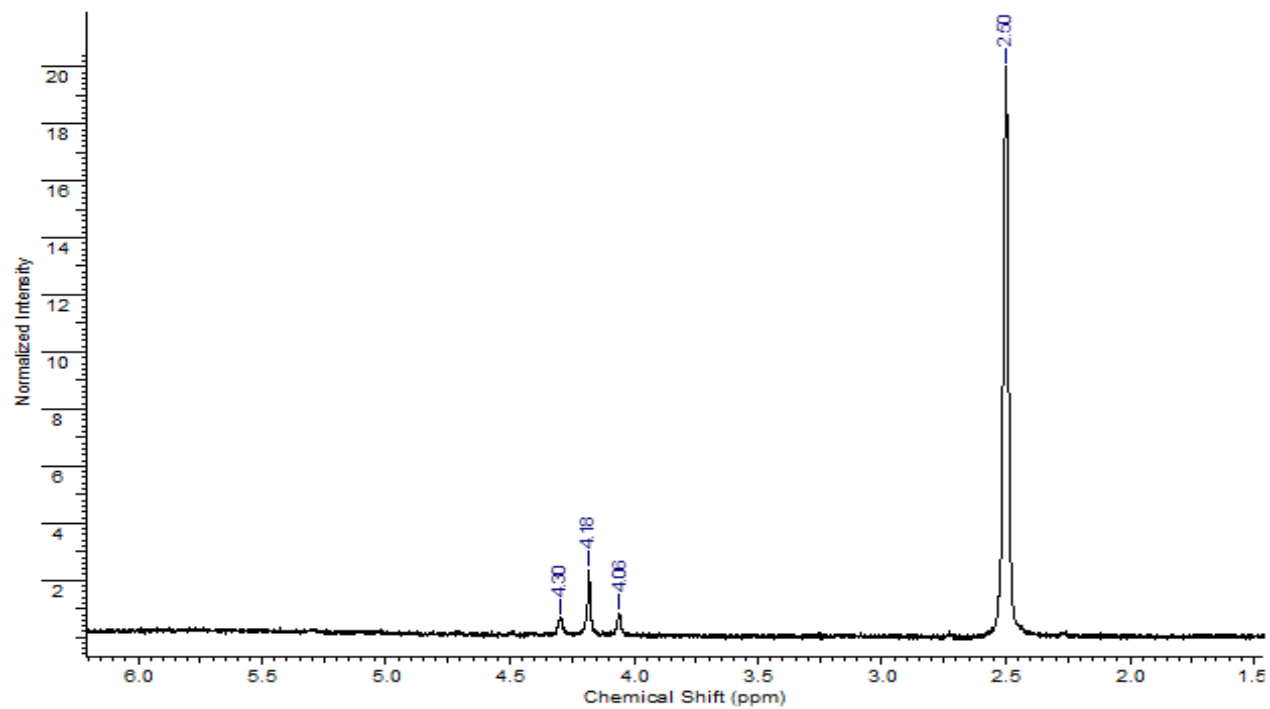
## Ferrocene sulfonyl chloride [Compound 9]:

IR spectrum:

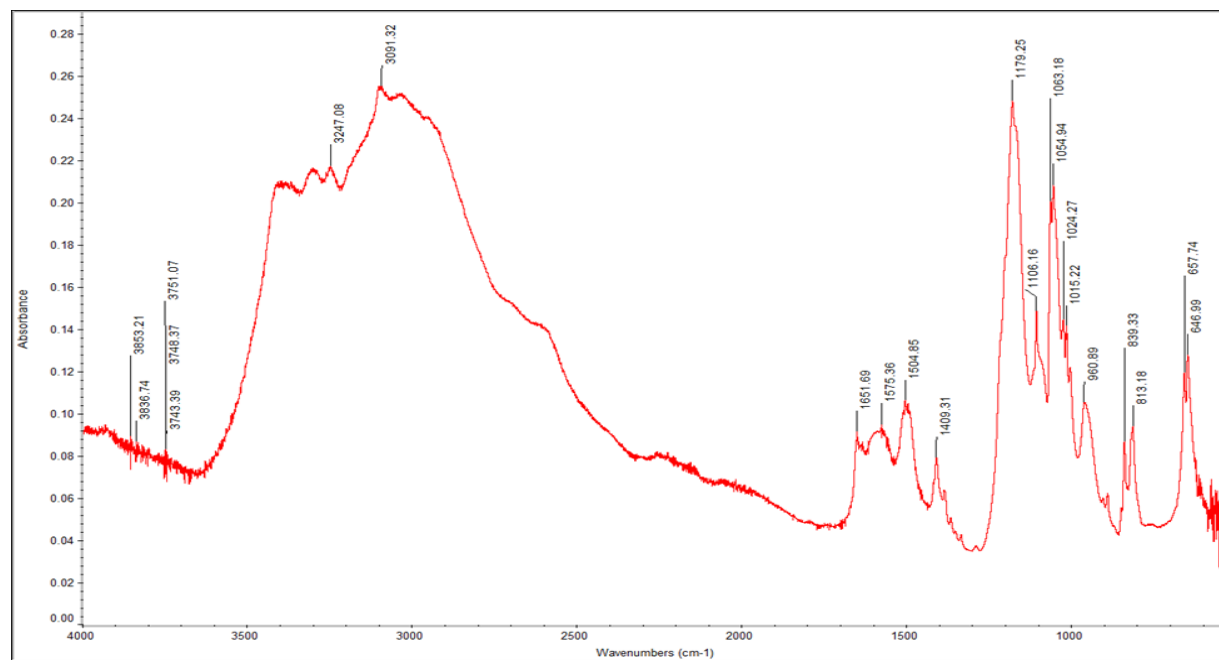


## Ferrocene sulfonyl bromide

<sup>1</sup>H NMR spectrum (solvent is DMSO):

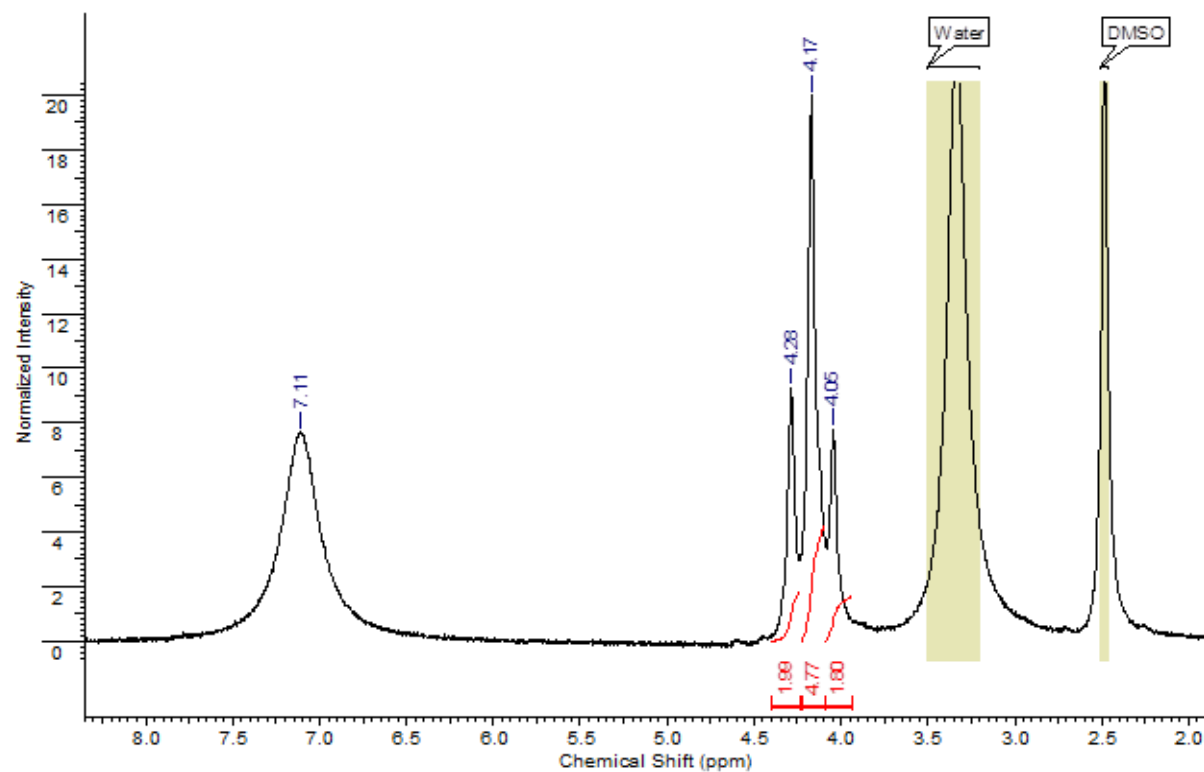


IR spectrum:

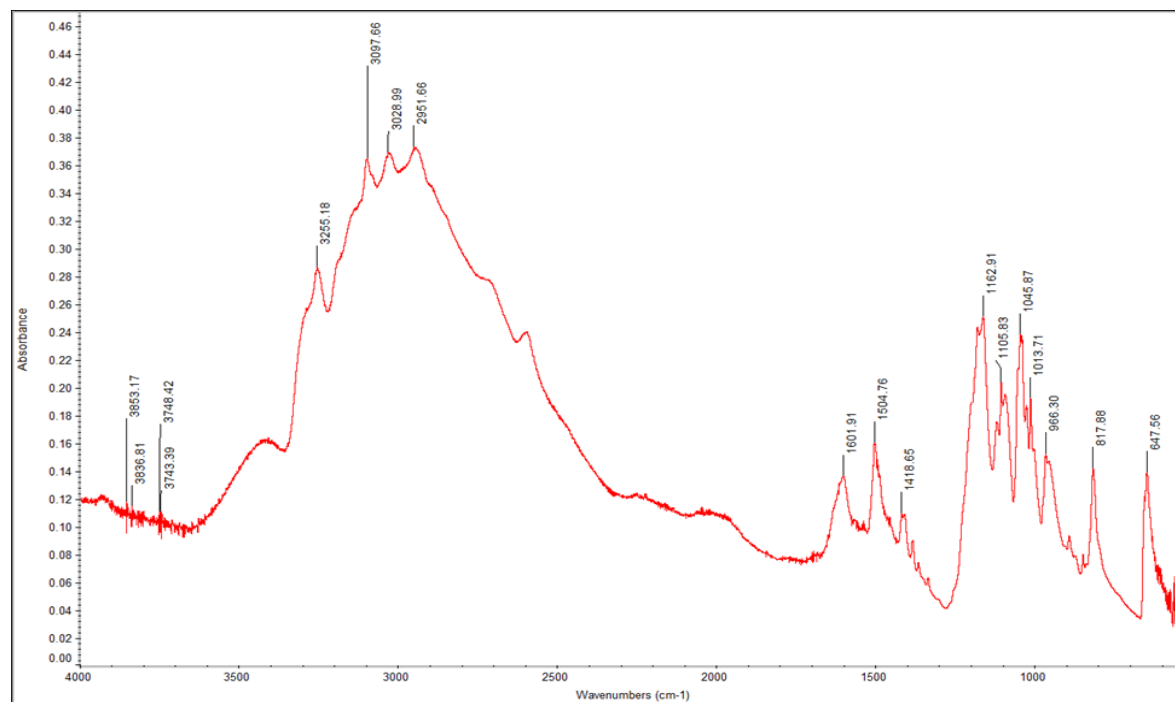


**Ferrocene sulfonyl hydrazine [Compound 11]:**

<sup>1</sup>H NMR spectrum (solvent is DMSO):

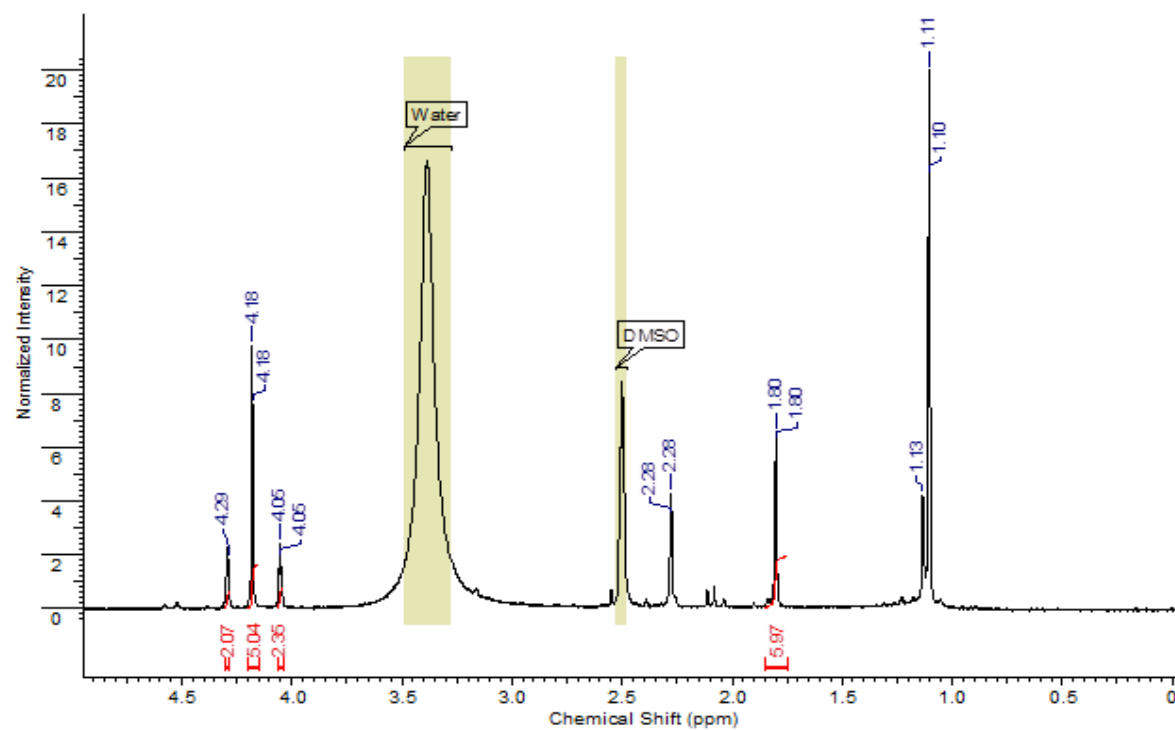


IR spectrum:



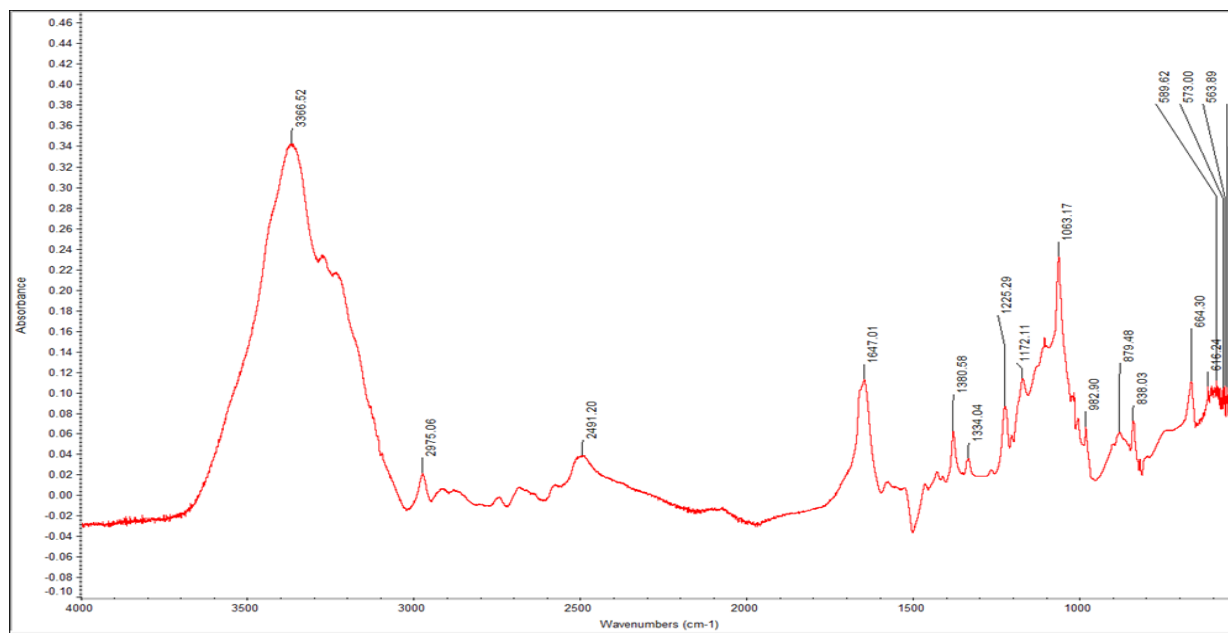
**Ferrocene sulfonyl hydrazine acetone [Compound 12]:**

<sup>1</sup>H NMR spectrum (solvent is DMSO):



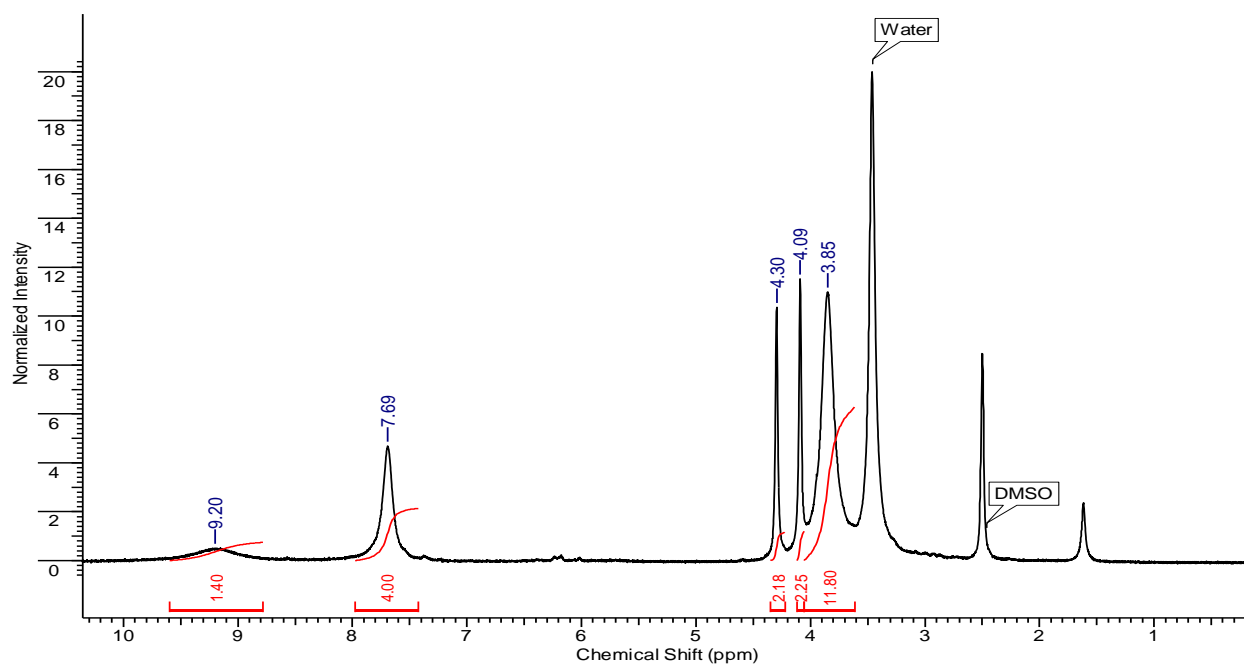


IR spectrum:

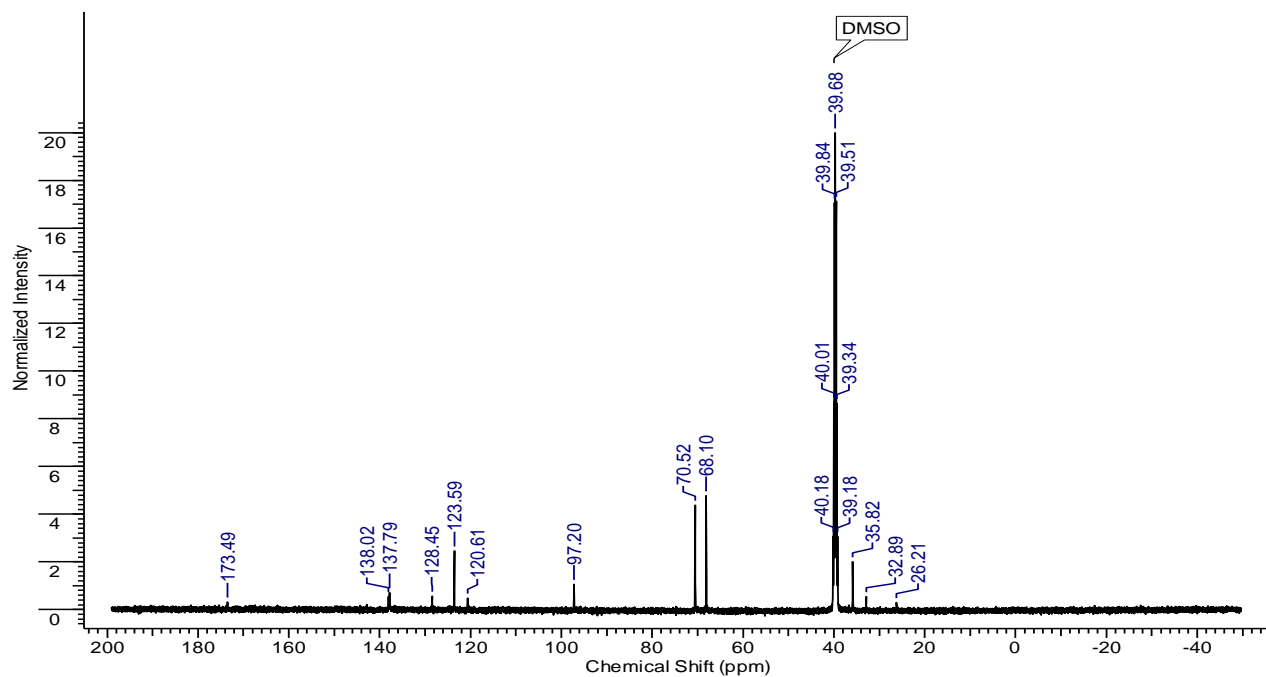


**Bis-1,3-dimethylimidazolium ferrocene sulfonate [Compound 13]:**

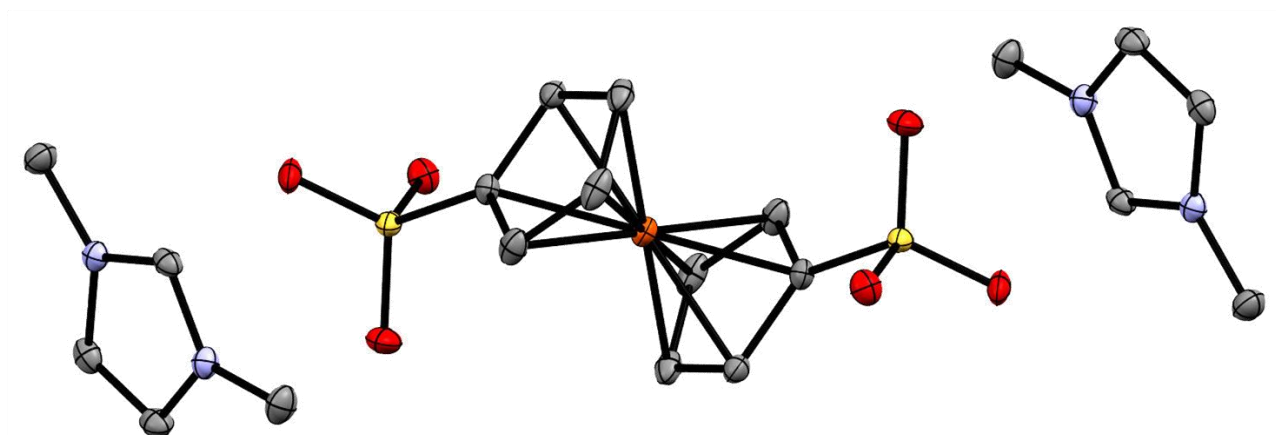
$^1\text{H}$  NMR spectrum (solvent is DMSO):



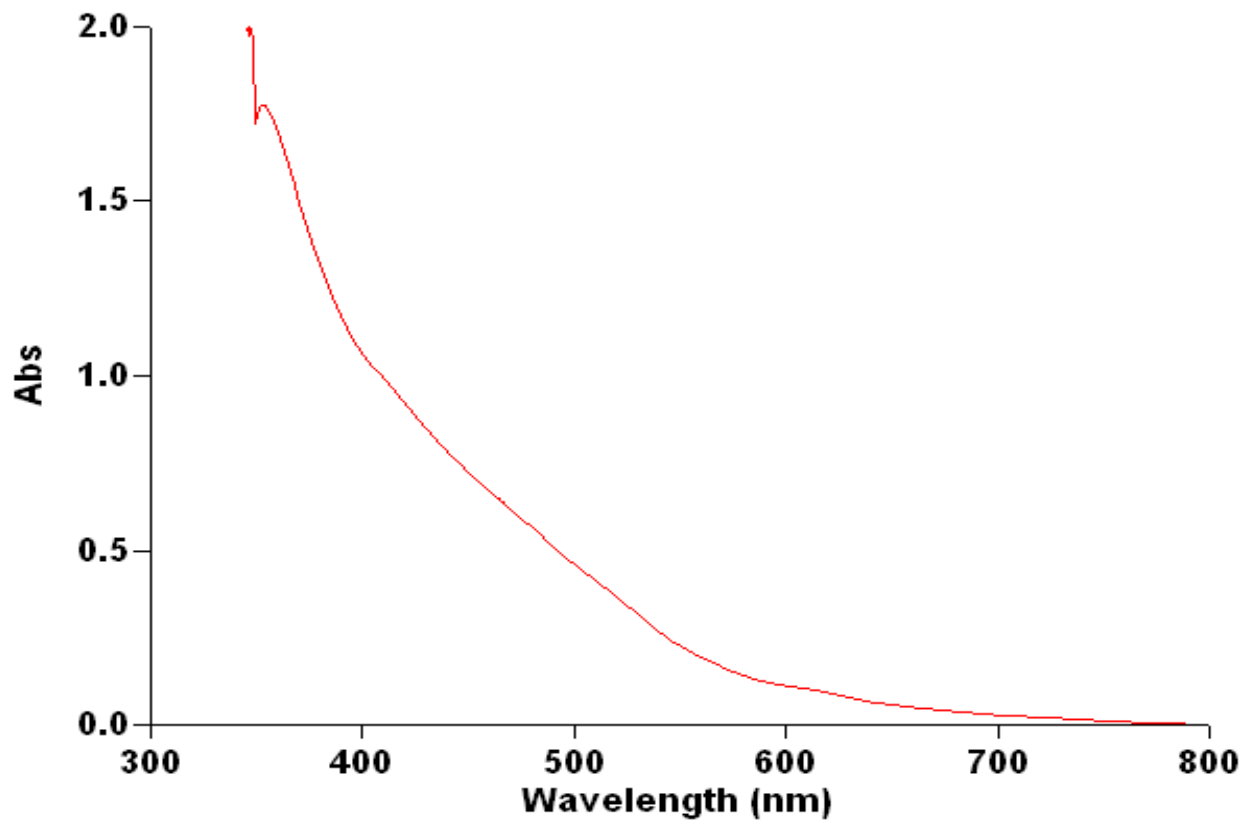
$^{13}\text{C}$  NMR spectrum (solvent is DMSO):



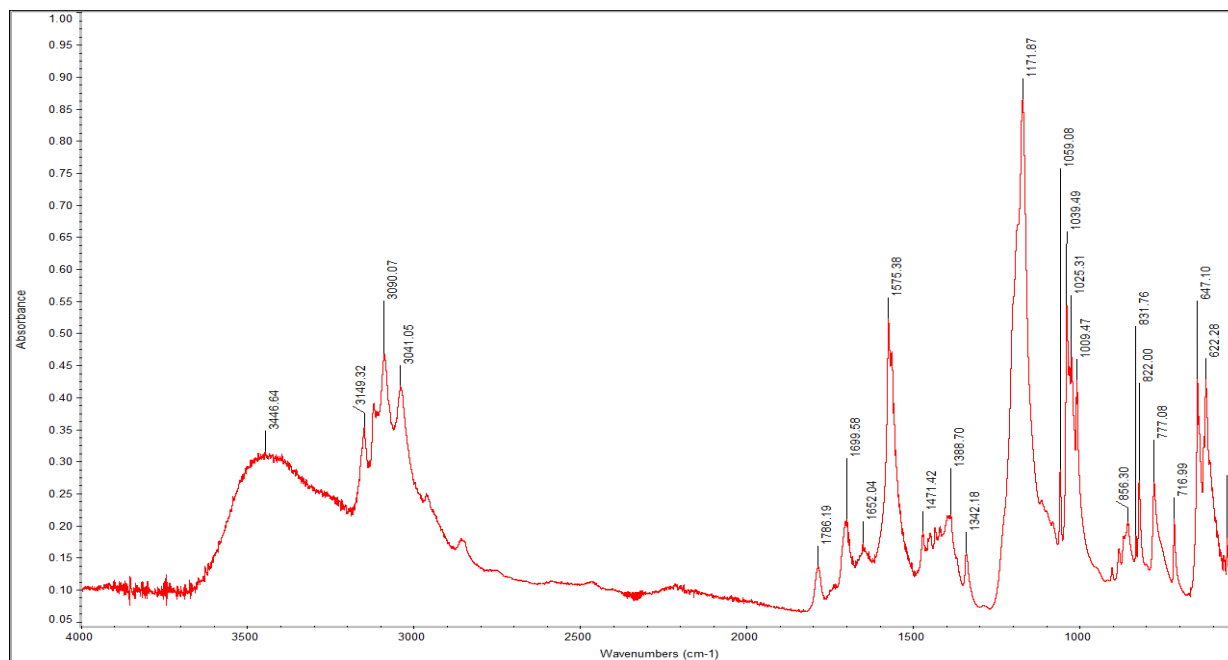
Crystal structure:



UV-visual spectrum (solvent is DMSO):

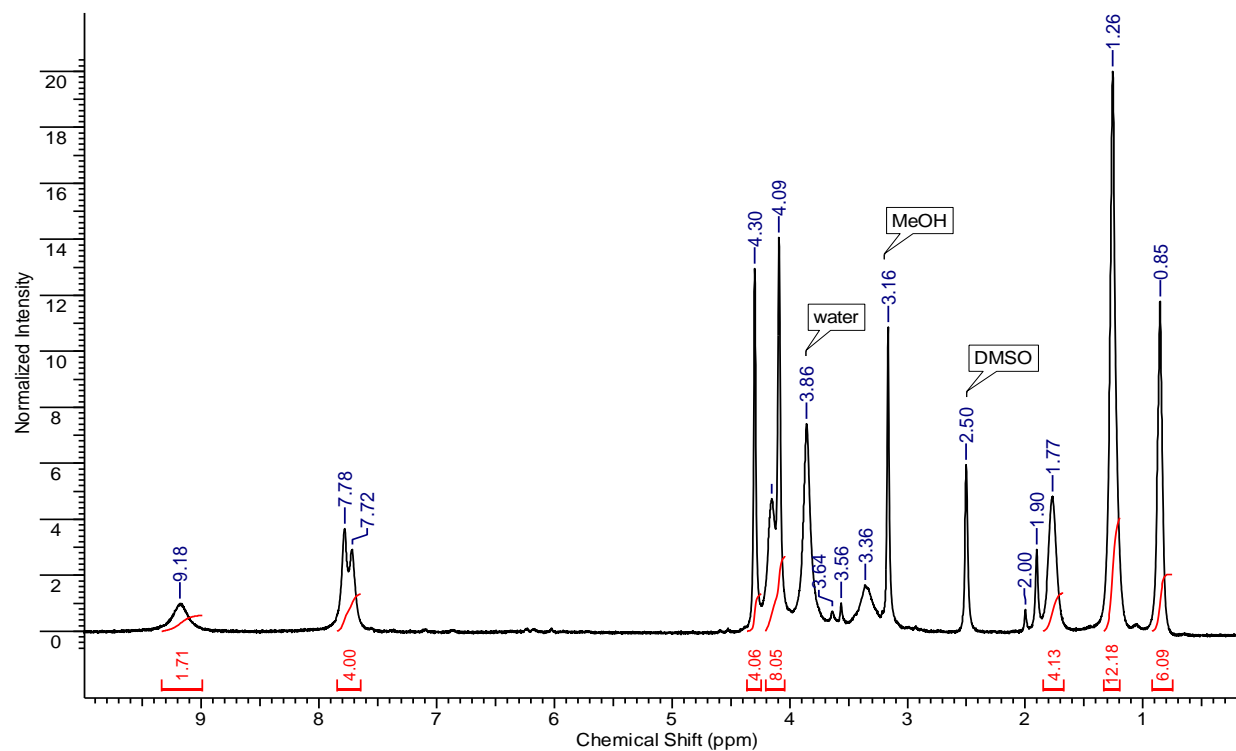


IR spectrum:

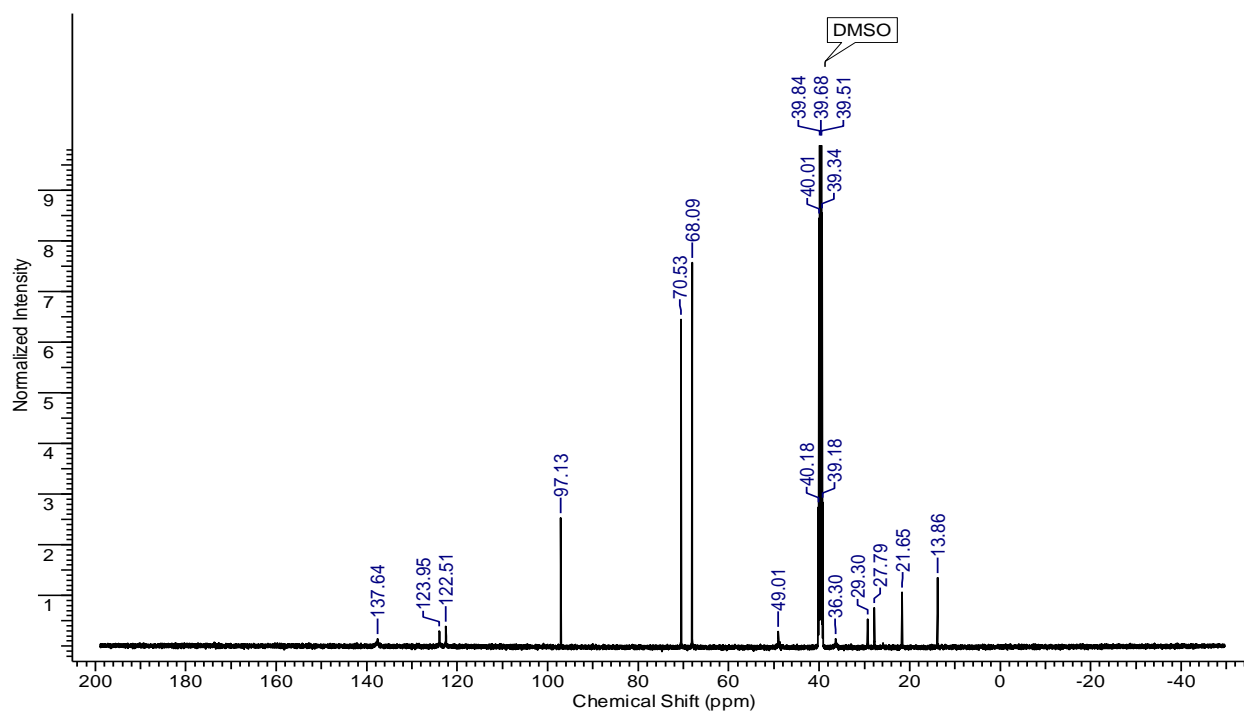


**Bis-1-pentyl-3-methylimidazolium ferrocene sulfonate [Compound 14]:**

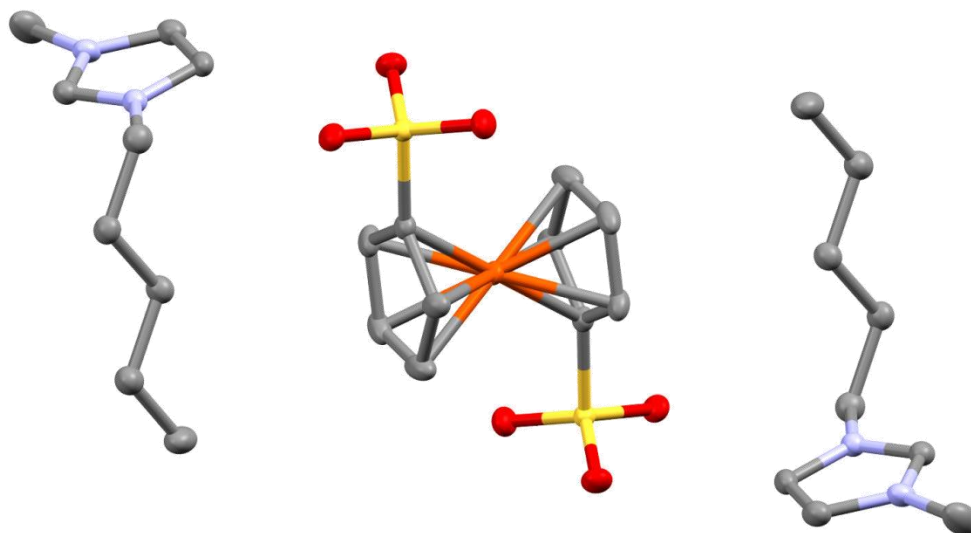
<sup>1</sup>H NMR spectrum (solvent is DMSO):



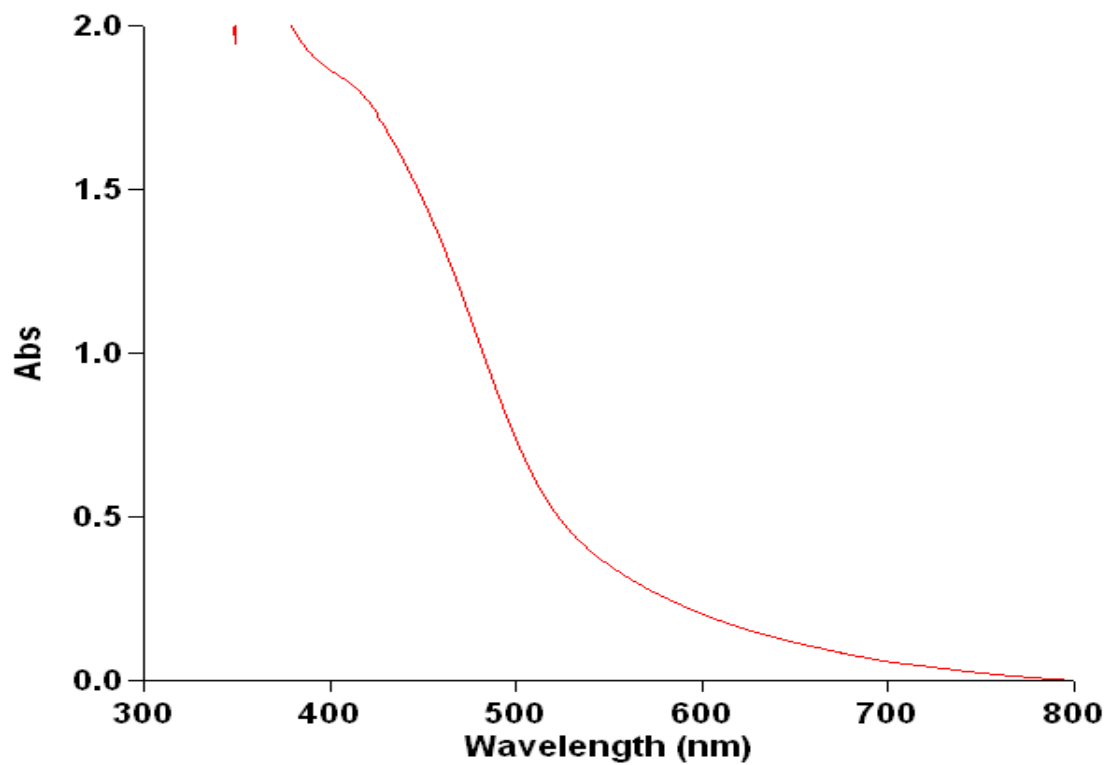
$^{13}\text{C}$  NMR spectrum (solvent is DMSO):



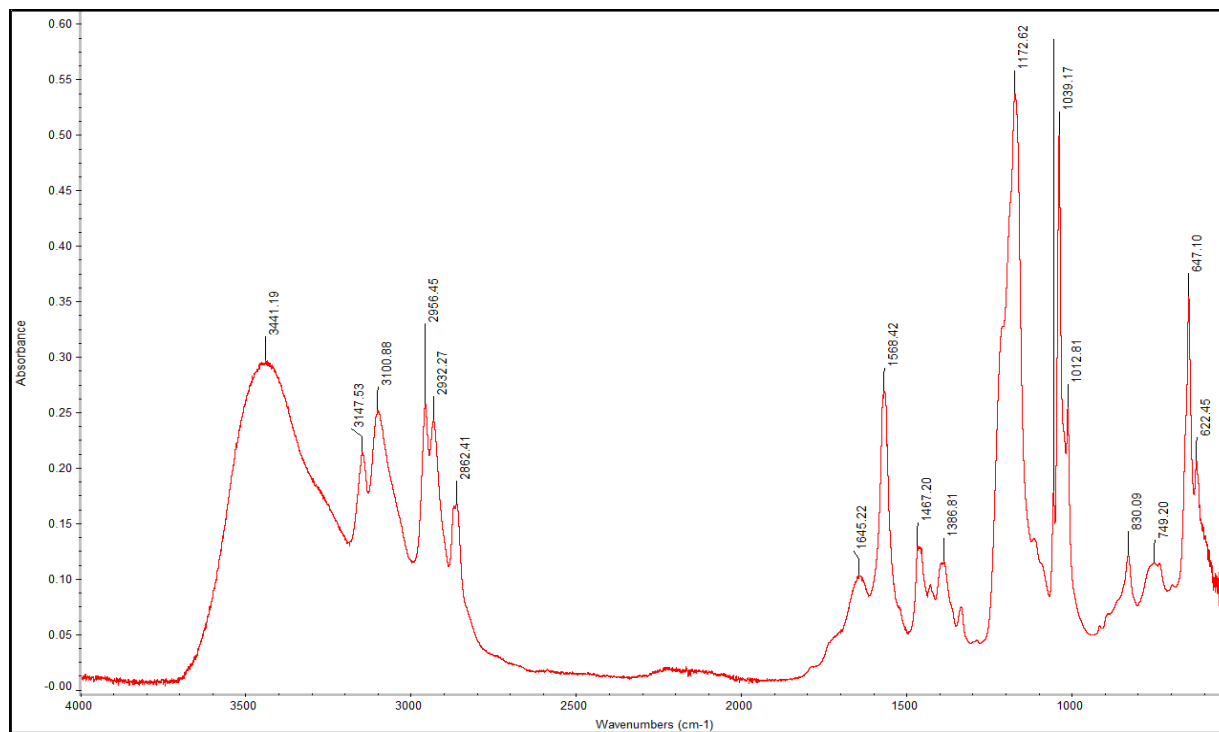
Crystal Structure:



UV-visual spectrum (solvent is DMSO):

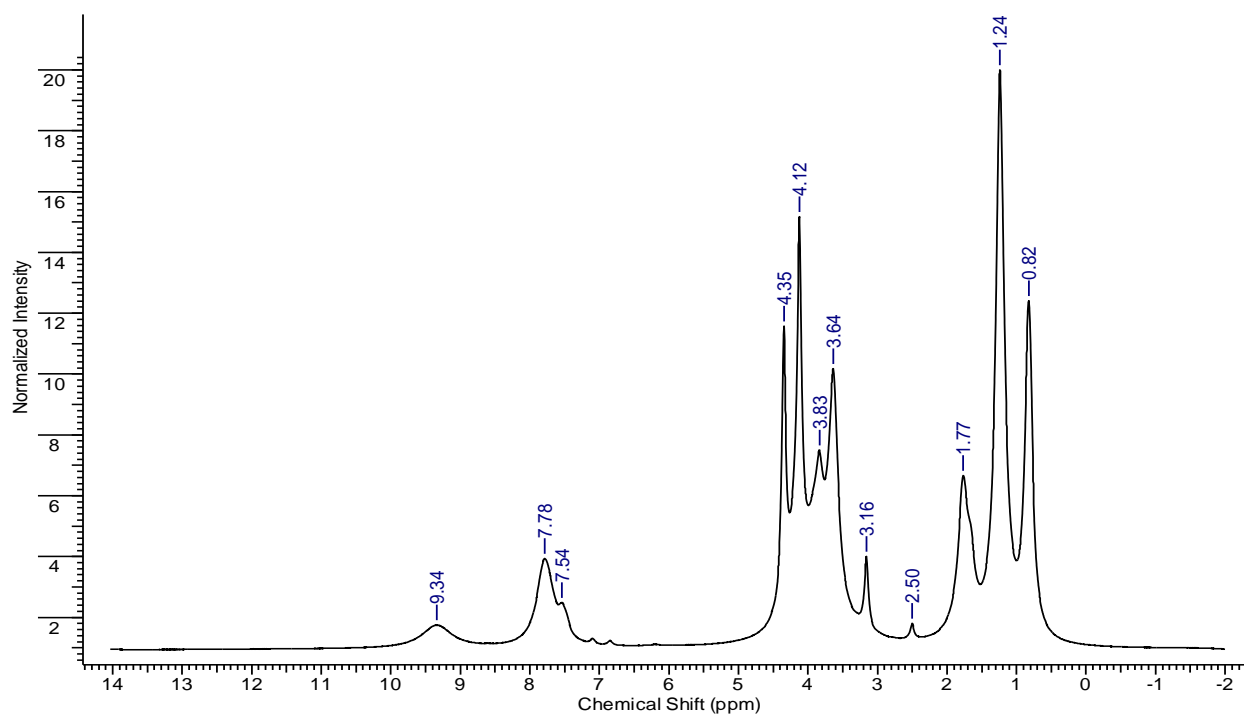


IR spectrum:

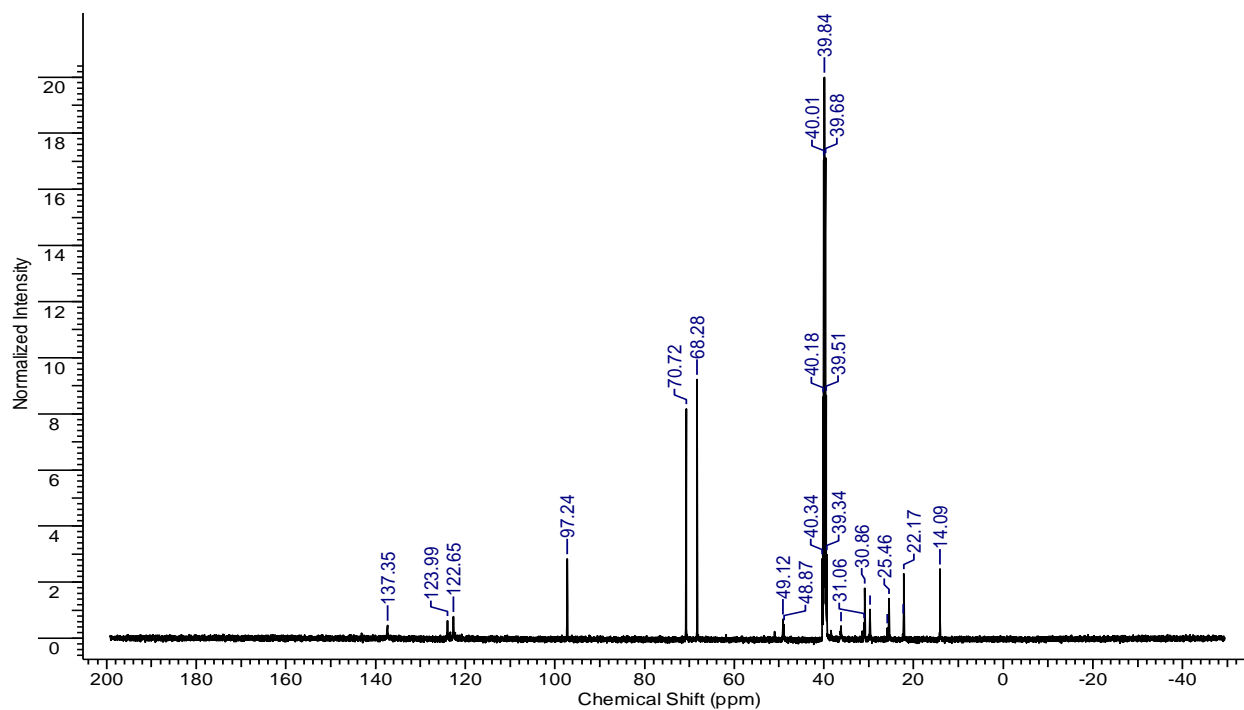


**Bis-1-hexyl-3-methylimidazolium ferrocene sulfonate [Compound 15]:**

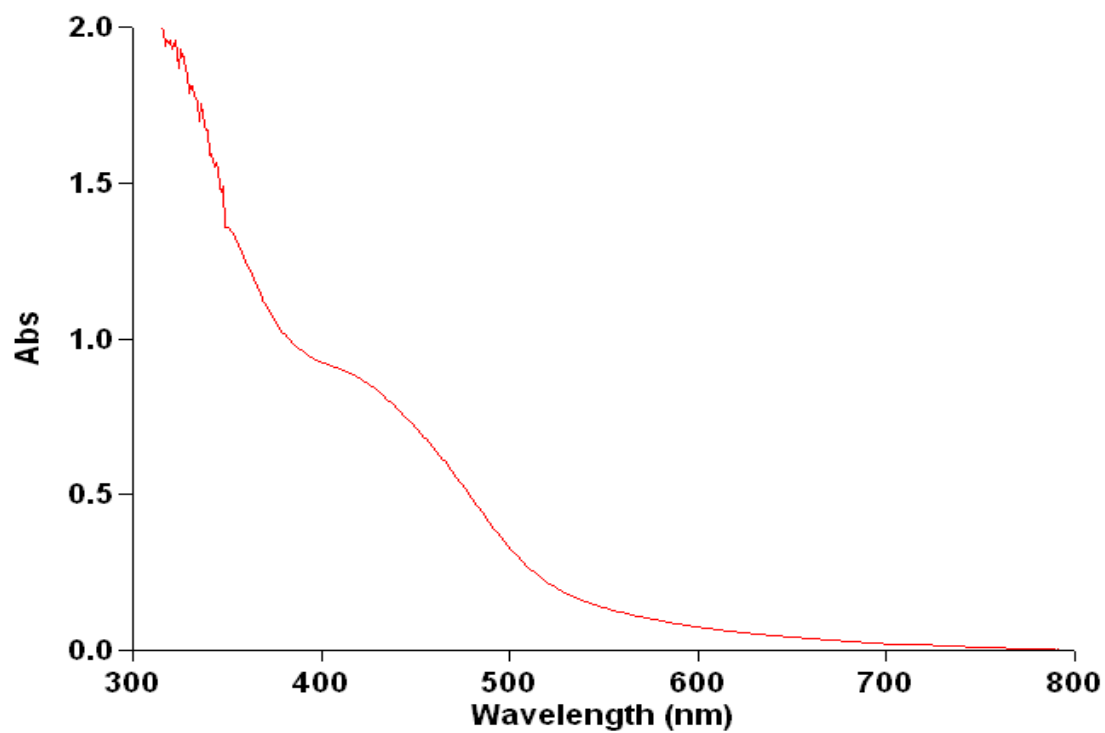
$^1\text{H}$  NMR spectrum (solvent is DMSO):



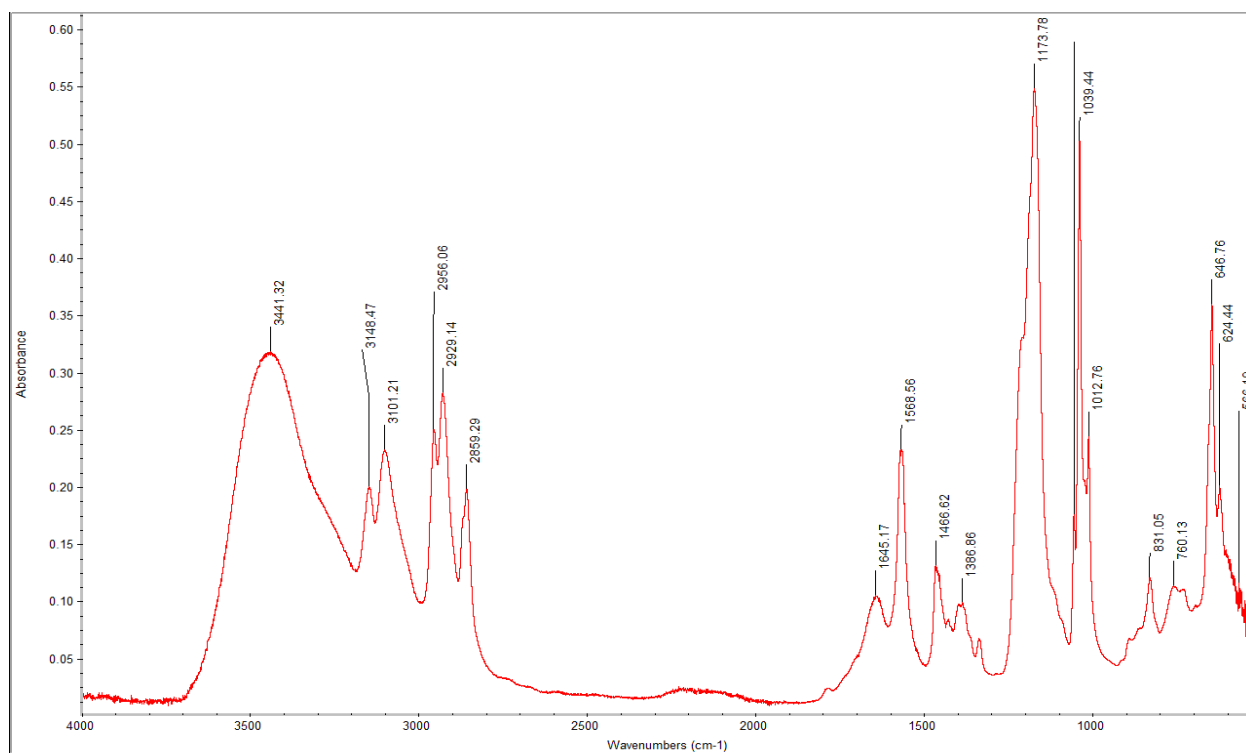
$^{13}\text{C}$  NMR spectrum (solvent is DMSO):



UV-visual spectrum (solvent is DMSO):



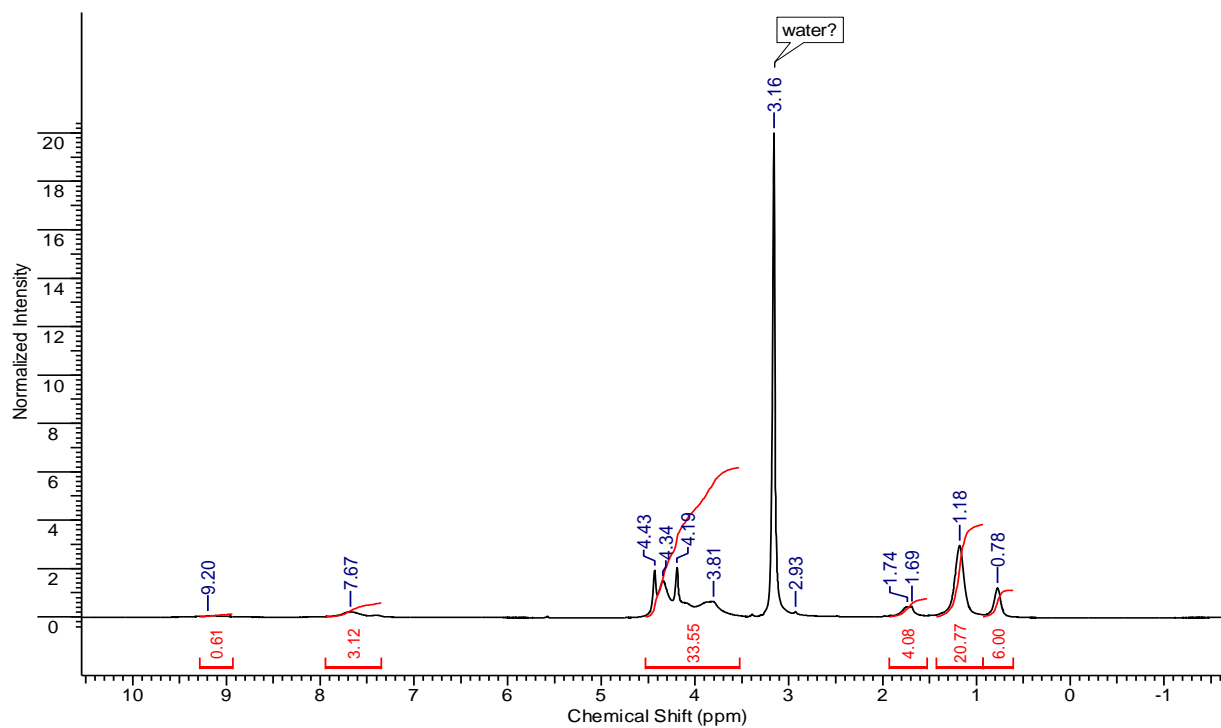
IR spectrum:



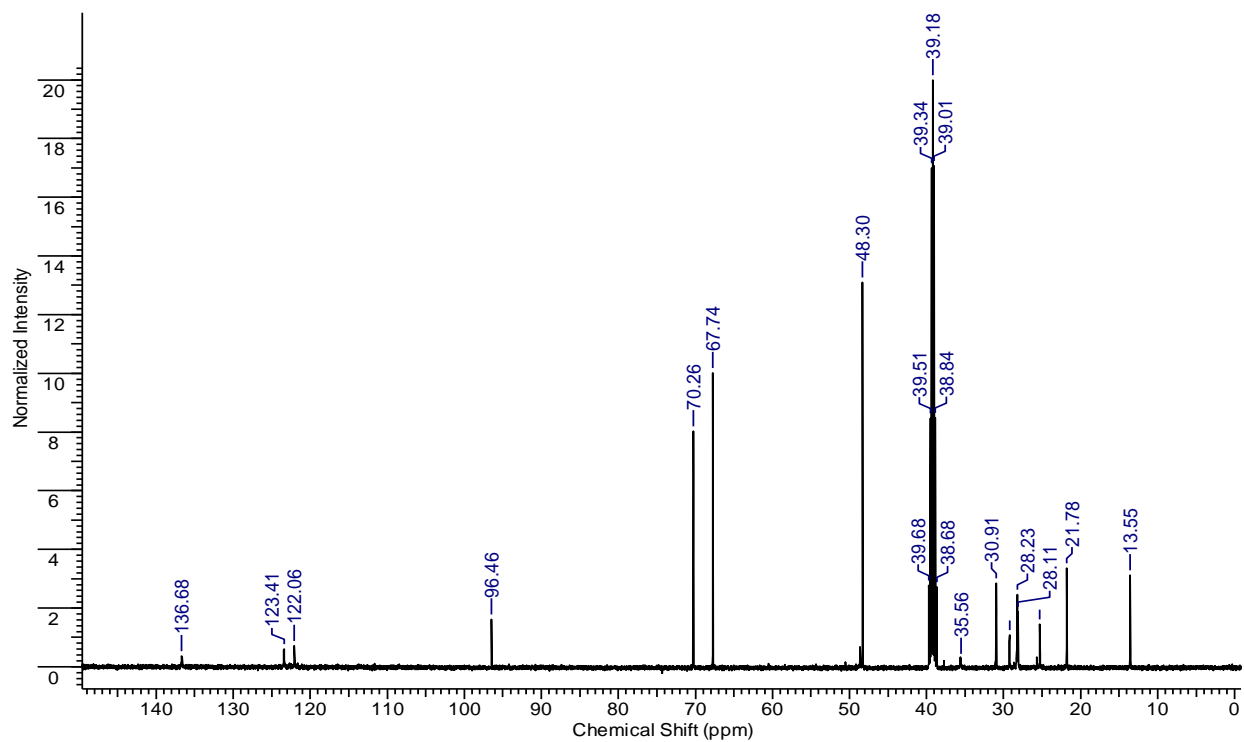


**Bis-1-octyl-3-methylimidazolium ferrocene sulfonate [Compound 16]:**

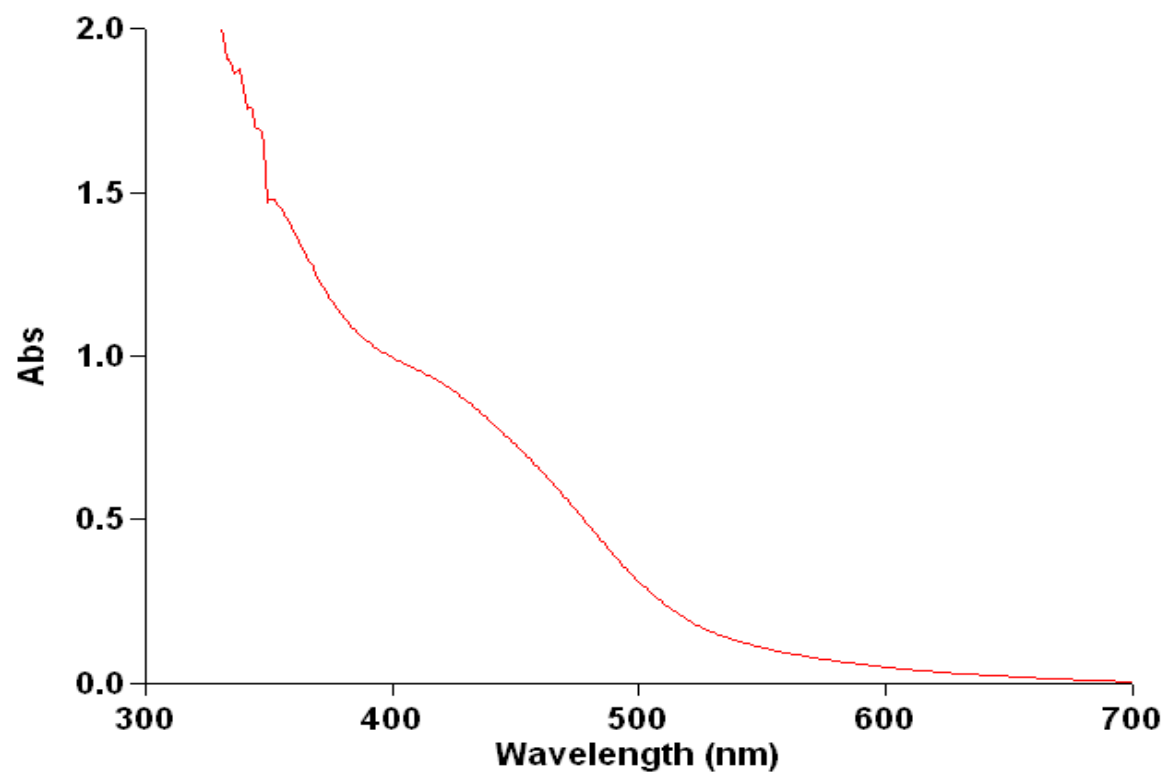
$^1\text{H}$  NMR spectrum (solvent is DMSO):



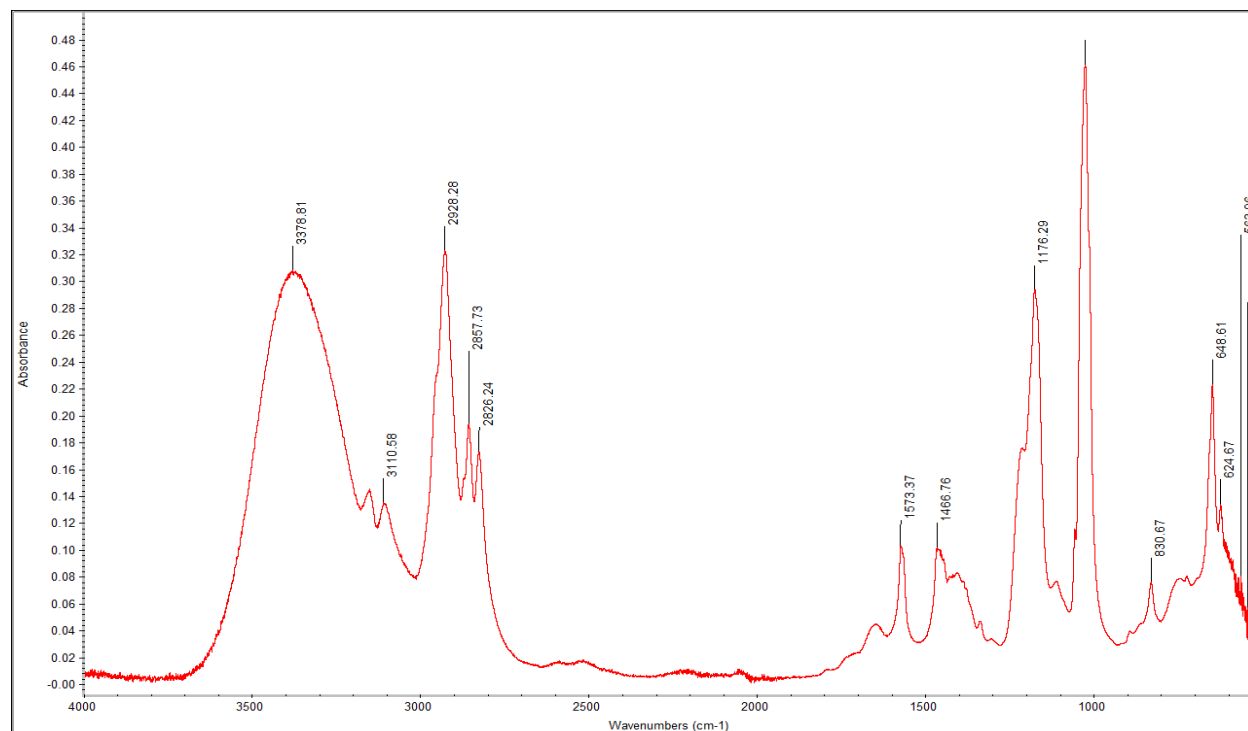
$^{13}\text{C}$  NMR spectrum (solvent is DMSO):



UV-visual spectrum (solvent is DMSO):

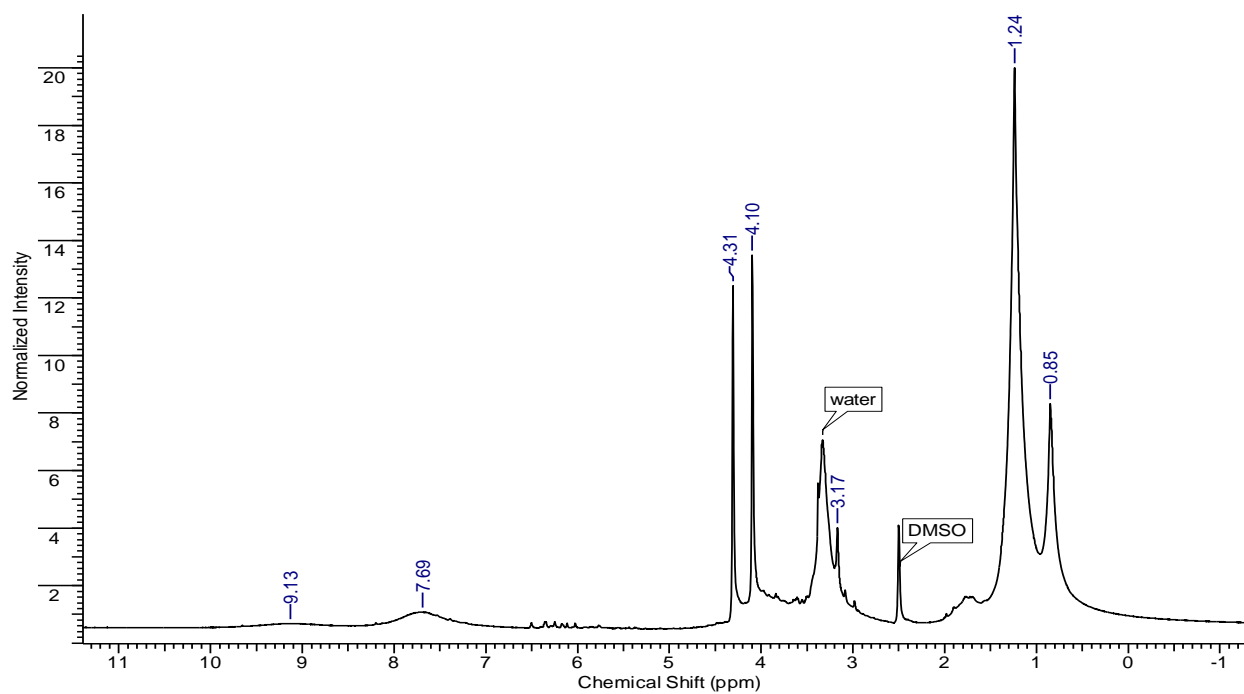


IR spectrum:

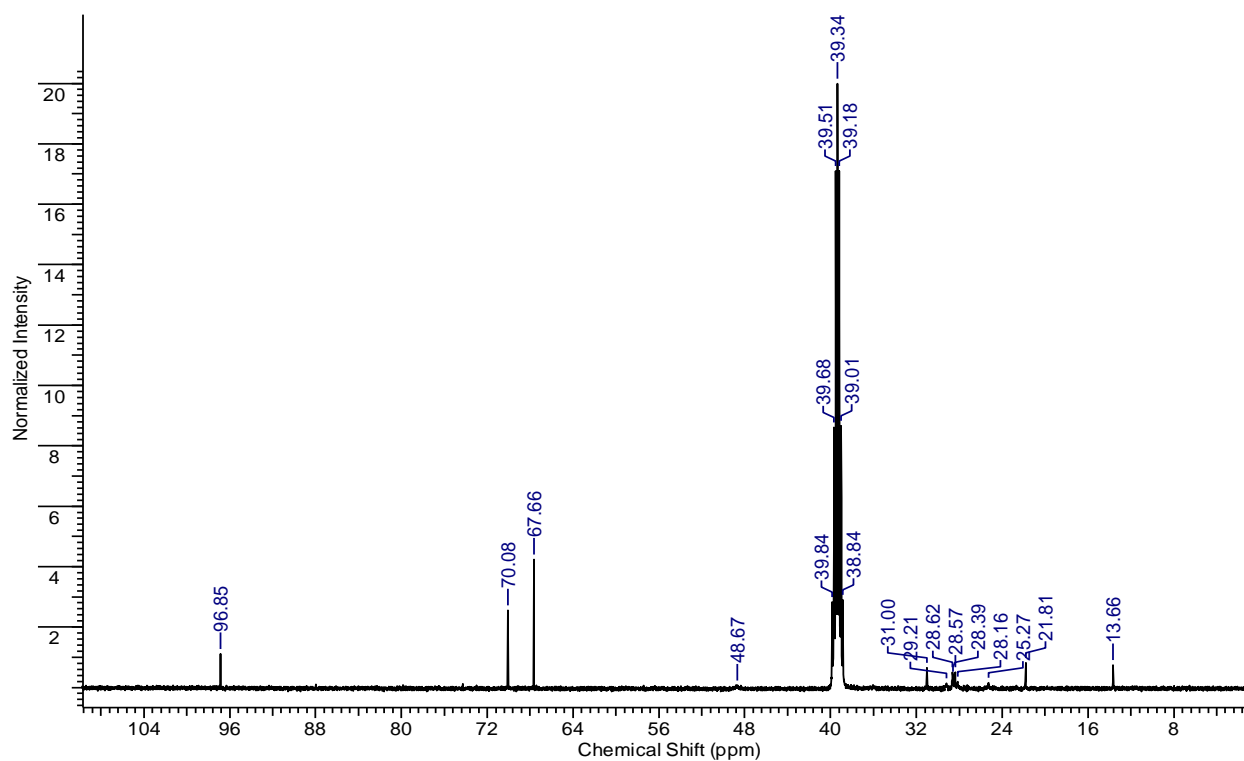


**Bis-1-decyl-3-methylimidazolium ferrocene sulfonate [Compound 17]:**

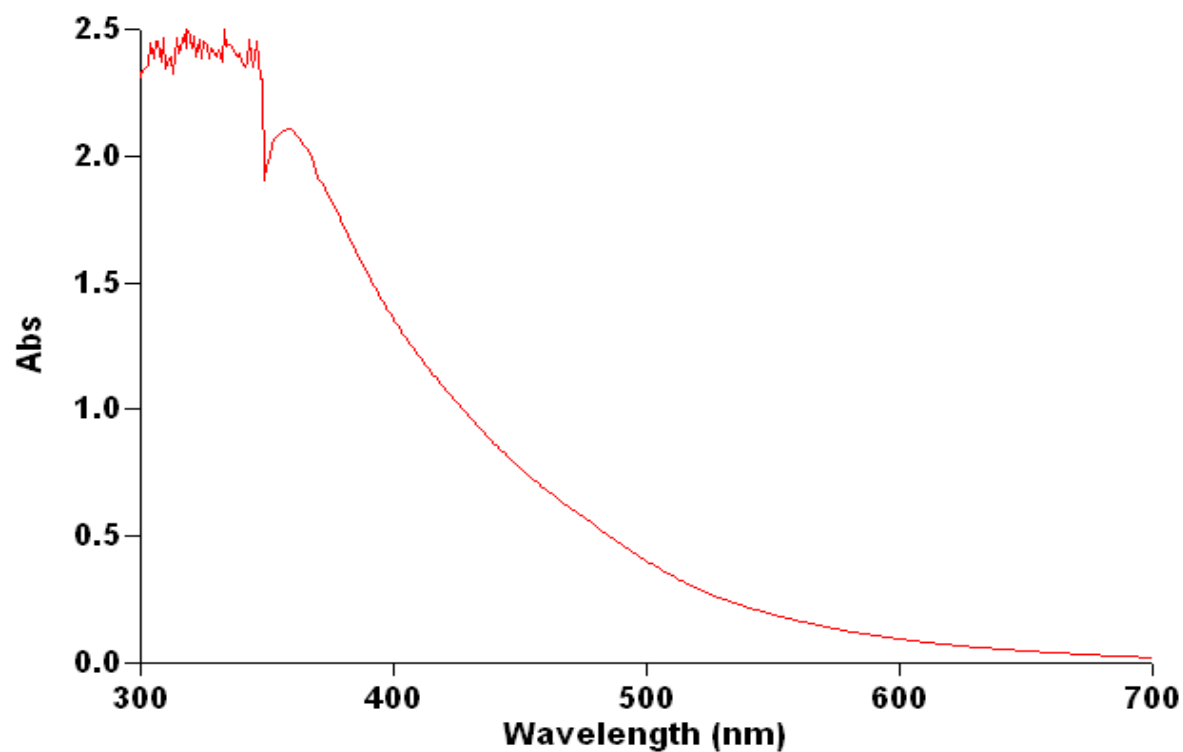
$^1\text{H}$  NMR spectrum (solvent is DMSO):



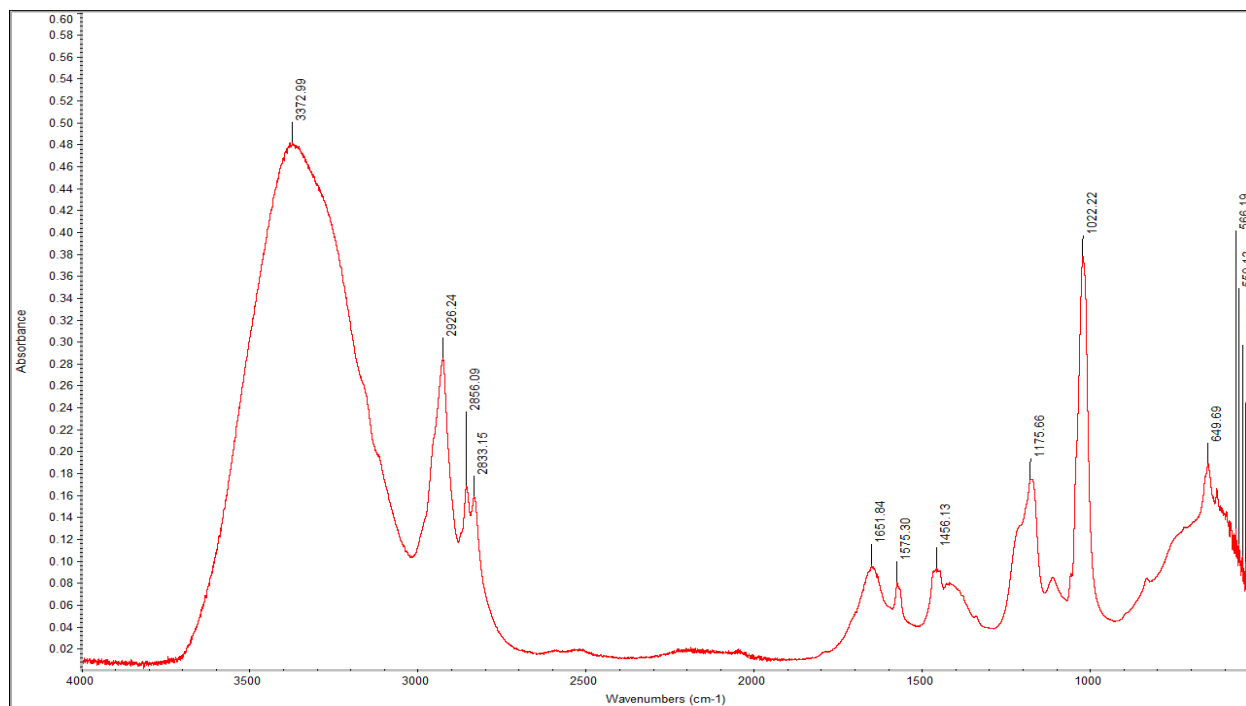
$^{13}\text{C}$  NMR spectrum (solvent is DMSO):



UV-visual spectrum (solvent is DMSO):

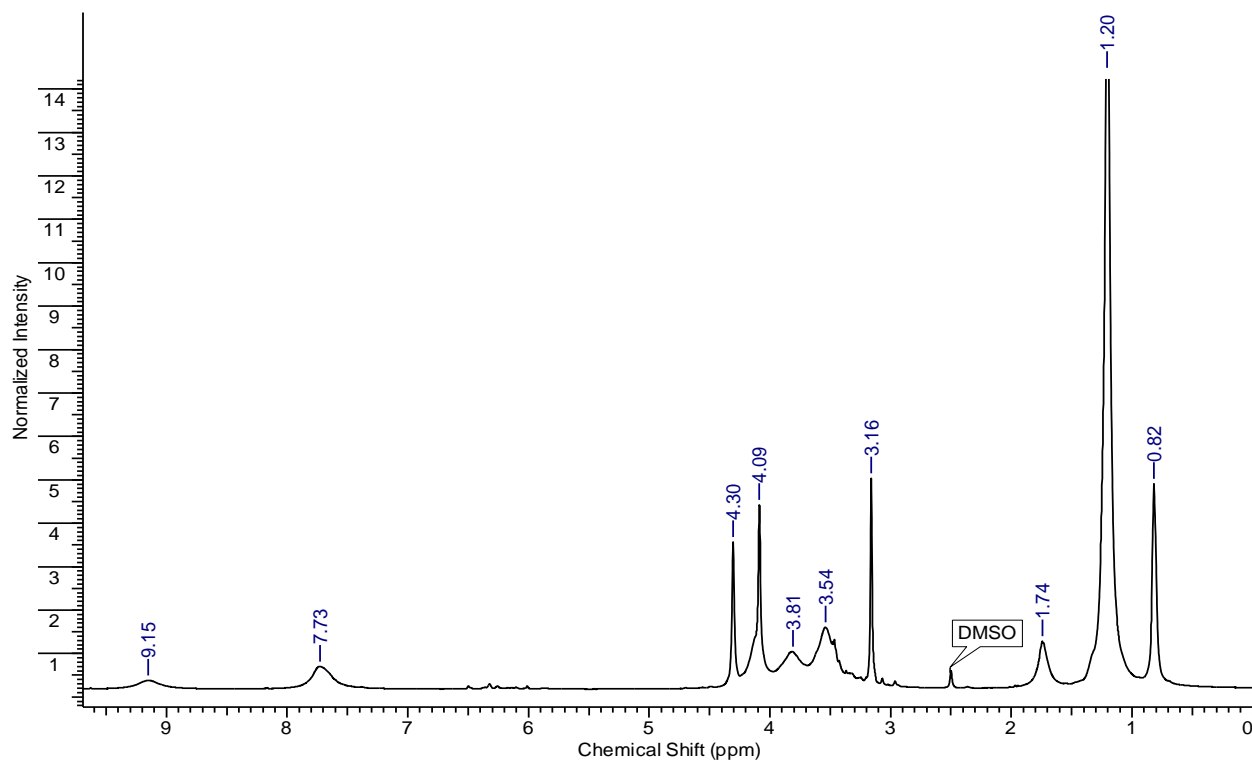


IR spectrum:

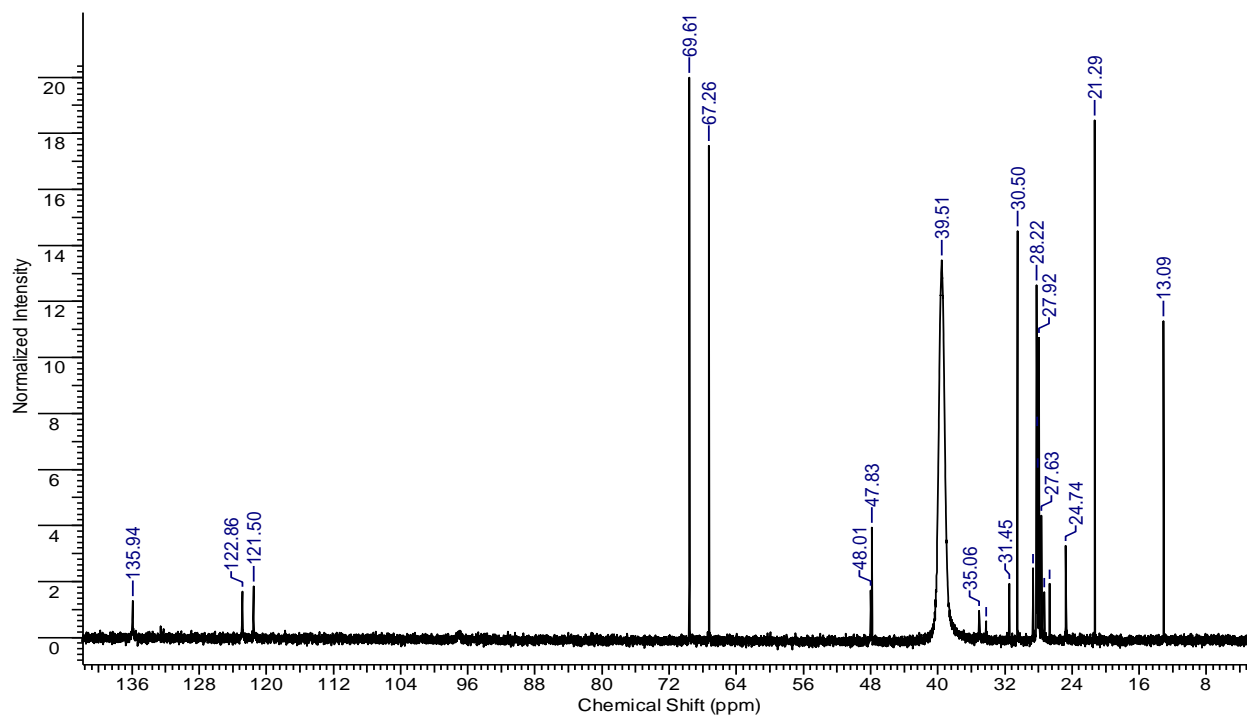


**Bis-1-dodecyl-3-methylimidazolium ferrocene sulfonate [Compound 18]:**

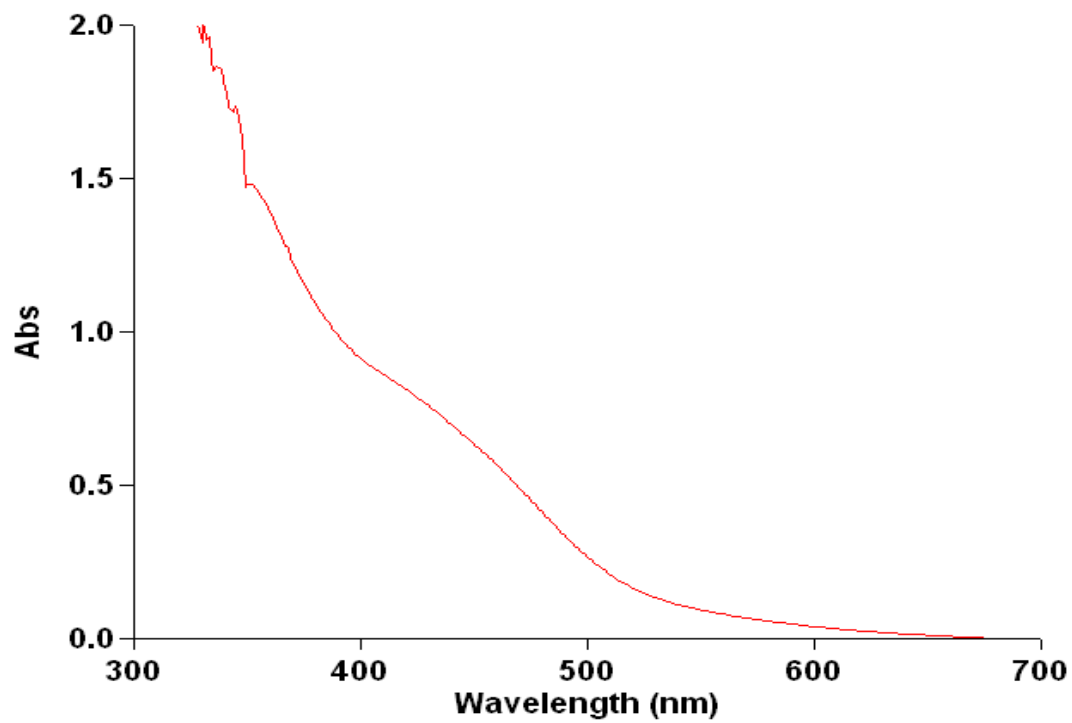
$^1\text{H}$  NMR spectrum (solvent is DMSO):



$^{13}\text{C}$  NMR spectrum (solvent is DMSO):



UV-visual spectrum (solvent is DMSO):



IR spectrum:

